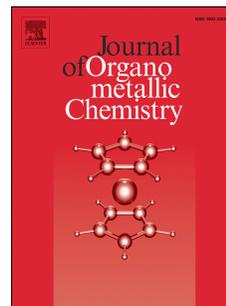


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Sihai Chen, Jinyang Chen, Xinhua Xu, Yunhua He, Rongnan Yi, Renhua Qiu



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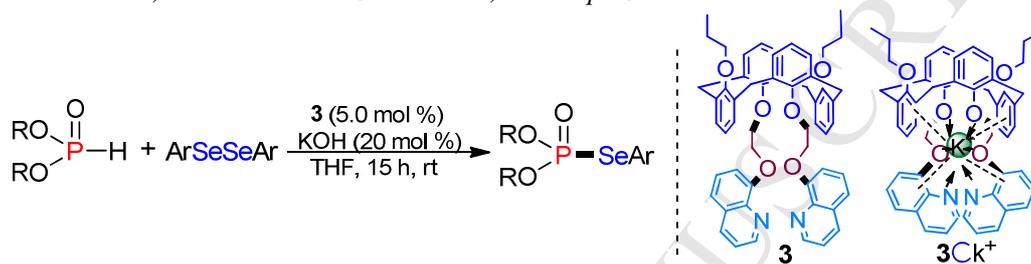
**Calix[4]arene-Assisted KOH-Catalyzed Synthesis of
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A convenient and efficient method for the synthesis of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates is described *via* a one pot reaction of diaryl diselenide and *O,O*-dialkylphosphonate catalyzed by KOH assisted by a co-catalyst of calix[4]arene **3**. The calix[4]arene **3** can be recycled for five times with good yields of the desired products for the reaction. This protocol provides a simple and efficient method for the synthesis of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates, avoiding the use of toxic reagents and expensive catalysts.

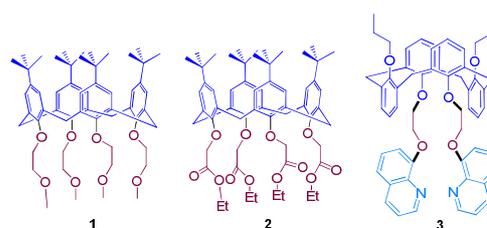
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1. Introduction

Due to the chemo-, regio- and stereoselective reactions and the useful biological activities, organoselenium compounds have become attractive synthetic targets in organic synthesis^[1]. Among these organoselenium compounds, *O,O*-dialkyl-*Se*-aryl phosphoroselenoates are important intermediates in synthesis of natural products and complex compounds.^[2] As important functional compounds and attractive synthetic intermediates in organic synthesis, the synthesis and application of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates have received considerable attentions^[3]. In 1996, Han et al. reported the reaction of phenyl lithium with *O,O*-diaryl phosphoryl chloride to prepare a series of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates in good yields^[4]. However, hard conditions were needed and toxic reagents were used in this procedure. Various methods using diaryl diselenides as starting materials were reported later^[5]. However, these procedures are dangerous because of the use of explosive reagents (such as AIBN or $\text{NaN}_3/\text{PhI}(\text{OAc})_2$) as radical initiators. A new method for the synthesis of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates catalyzed by CuI was reported by Gao and co-workers^[6]. However, at least one equivalent of organic base was used during this procedure. Therefore, a method that is efficient for the synthesis of these *O,O*-dialkyl-*Se*-aryl phosphoroselenoates is on demand. In our previous work^[7], we reported a convenient method for the synthesis of these useful compounds using diaryl diselenides and *O,O*-dialkylphosphonates as starting materials catalyzed by cesium hydroxide monohydrate. However, compared to other common alkali metal hydroxides (such as NaOH and KOH), the high cost of the use of CsOH in this procedure hinders the development of this method in industrial application.

Compare to crown ethers^[8] and cyclodextrins^[9], calixarenes with the moderate cavity show stronger complexing ability to metal cations, which enhance the nucleophilicity of the nucleophilic reagents and promote the reaction efficiently.^[10] Calixarenes (such as **1**^[11] and **2**^[12]) (Scheme 1) have been used

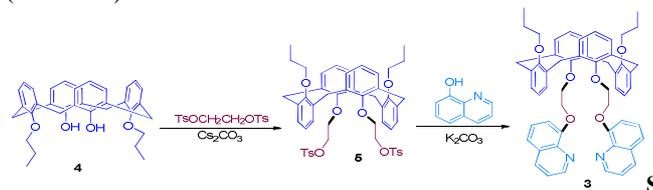
as phase transfer catalyst in organic synthesis for preparation of many useful products.^[13] Here, we report, in the first part, our results on the synthesis of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates catalyzed by Calix[4]arene-assisted KOH, which is KOH combined with an assisted co-catalyst of calix[4]arene **3**. This procedure provides a convenient and economic method for the synthesis of *O,O*-dialkyl-*Se*-aryl phosphoroselenoates by using readily available reagents as the starting materials.

Scheme 1. Structures of calix[4]arene **1**, **2** and **3**

2. Results and discussion

2.1 Synthesis of calix[4]arene **3**^[14]

The sulfonation of 25,27-di(*n*-propyl)-26,28-dihydroxy calix[4]arene (**4**)^[15] with sulphonate yields compound **5**, which then converted to calix[4]arene **3** by treatment with 8-hydroxyquinoline catalyzed by K_2CO_3 in the total yield of 54.2% (Scheme 2).

Scheme 2. The synthesis of calix[4]arene **3**

2.2 Optimization of the reaction conditions for the selenation

The reaction of *O,O*-dimethyl phosphonate (**6a**) with diphenyl diselenide (**7a**) was run at room temperature (rt) by using 10 mol% TBAB and 20 mol% KOH as co-catalyst, the desired product **8a** was obtained in 19% GC yield within 8 h (Table 1, entry 1). Then we examined a various of phase transfer catalysts to optimize the reaction conditions (Table 1, entries 1-6), and the results shown that calix[4]arene **3** was the best PTC for this reaction giving the desired product in the yield of 80% within 8 h (Table 1, entry6). To promote the reaction, a series of solvents (such as CH₂Cl₂, EtOH, DMF and THF) were explored (Table 1, entries 6-11), THF was turned out to be the best solvent, affording the desired product in 86% yield (Table 1, entry 10). On the base of above results, we examined the amount of calix[4]arene **3** and KOH necessarily to promote the reaction efficiently (Table 1, entries 11-16), and found that 5.0 mol% of calix[4]arene **3** and 20 mol% KOH was enough to afford the desired product in the yield of 90%, when the reaction time was extended to 15 h (Table 1, entry 15) in open air, while the desired product was obtained in trace under the nitrogen atmosphere (Table 1, entries 17), implying the air is involved in the reaction. Thus, the optimized conditions are as follows: 5.0 mol% of calix[4]arene **3** and 20 mol% of KOH as co-catalyst, 1.0 equiv. of **7a** and 2.2 equiv. of **6a** in THF at rt for 15 h in air.

Table 1. Optimization of the reaction conditions for the selenation.^a

Entry	PTC	KOH	Solvent	T(h)	Yield (%) ^b
1	TBAB (10)	20	CH ₃ CN	8	19
2	TBAI (10)	20	CH ₃ CN	8	22
3	18-crown-6 (10)	20	CH ₃ CN	8	62
4	1 (10)	20	CH ₃ CN	8	70
5	2 (10)	20	CH ₃ CN	8	75
6	3 (10)	20	CH ₃ CN	8	80
7	3 (10)	20	CH ₂ Cl ₂	8	73
8	3 (10)	20	Toluene	8	67
9	3 (10)	20	EtOH	8	52
10	3 (10)	20	THF	8	86
11	3 (10)	20	DMF	8	85
12	3 (5.0)	20	THF	8	86
13	3 (2.5)	20	THF	8	42
14	3 (5.0)	10	THF	8	67
15	3 (5.0)	20	THF	15	90
16	3 (5.0)	20	THF	20	90
17 ^c	3 (5.0)	20	THF	15	trace

^a Reaction conditions: **6a** (2.2 mmol), **7a** (1.0 mmol), solvent (1.0 mL), rt, in air. ^b GC yields. ^c The reaction was performed under a nitrogen atmosphere.

2.3 The scope of the selenation

With an efficient protocol for the selenation in hand, we next investigated its scope with different *O,O*-dialkylphosphonate (**6**) and diaryl diselenide (**7**). As shown in Table 2, we can find that the reaction of a variety of *O,O*-dialkylphosphonate (**6**) and diaryl diselenide (**7**) could undergo efficiently to desired products in good to excellent yields. A closer inspection of the results revealed that the functional groups (Me, Et, *i*-Pr and *n*-Bu) presenting in *O,O*-dialkylphosphonates effect the reaction slightly, and all the desired products were obtained in excellent yields (85%-92%, **8a-8d**). In addition, the reaction is not sensitive to the nature of functional groups (Me, Cl) presenting

in the benzene rings of the diaryl diselenides, and all the reactions afford the desired products in good yields (83%-89%, **8e-8j**).

Table 2. The selenation of *O,O*-dialkylphosphonate (**4**) catalyzed by calix[4]arene **3** (5 mol%)/KOH (20 mol%) in THF.^a

Entry	R	Ar	Product	Yield (%)
1	Me	Ph	MeO-P(=O)(OMe)-Se-Ph (8a)	92%
2	Et	Ph	EtO-P(=O)(OEt)-Se-Ph (8b)	90%
3	<i>i</i> -Pr	Ph	(<i>i</i> -Pr)O-P(=O)(O(<i>i</i> -Pr))-Se-Ph (8c)	87%
4	<i>n</i> -Bu	Ph	(<i>n</i> -Bu)O-P(=O)(O(<i>n</i> -Bu))-Se-Ph (8d)	85%
5	Et	4-MeC ₄ H ₆	EtO-P(=O)(OEt)-Se-4-MeC ₄ H ₆ (8e)	86%
6	<i>i</i> -Pr	4-MeC ₄ H ₆	(<i>i</i> -Pr)O-P(=O)(O(<i>i</i> -Pr))-Se-4-MeC ₄ H ₆ (8f)	83%
7	<i>n</i> -Bu	4-MeC ₄ H ₆	(<i>n</i> -Bu)O-P(=O)(O(<i>n</i> -Bu))-Se-4-MeC ₄ H ₆ (8g)	84%
8	Et	4-ClC ₄ H ₆	EtO-P(=O)(OEt)-Se-4-ClC ₄ H ₆ (8h)	89%
9	<i>i</i> -Pr	4-ClC ₄ H ₆	(<i>i</i> -Pr)O-P(=O)(O(<i>i</i> -Pr))-Se-4-ClC ₄ H ₆ (8i)	87%
10	<i>n</i> -Bu	4-ClC ₄ H ₆	(<i>n</i> -Bu)O-P(=O)(O(<i>n</i> -Bu))-Se-4-ClC ₄ H ₆ (8j)	88%

^a Reaction conditions: **6** (2.2 mmol), **7** (1.0 mmol), KOH (20 mol%), **3** (5.0 mol%), THF (2 mL), 25 °C, in air for 15 h. ^b Isolated yields.

2.4 Cycles of calix[4]arene **3**

To test the reusability and reproducibility, the calix[4]arene **3** is subjected to cycles of selenation of *O,O*-diethyl phosphonate (**6a**) as the model reaction. After completion of the reaction, calix[4]arene **3** were obtained by flash chromatography. After separating, the calix[4]arene **3** is used for next cycle of the reaction. The decline in product yield is minimal in a run of 5 cycles (90% to 85%), indicating that the calix[4]arene **3** is stable and suitable for reuse (Table 3).

Table 3. Yields of selenation of *O,O*-dialkylphosphonate by recover catalyst^a

Cycle	Yield (%) ^b
1	90
2	90
3	88
4	86
5	85

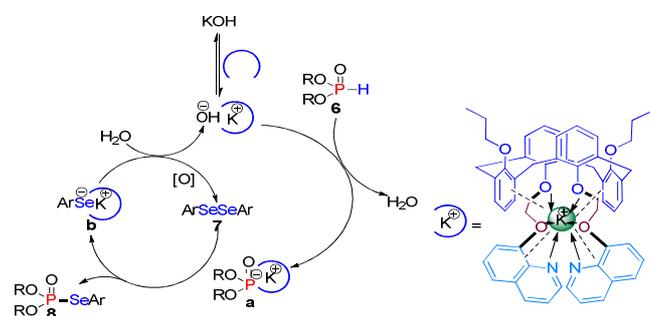
^a Reaction conditions: **6a** (2.2 mmol), **7a** (1.0 mmol), solvent (1.0 mL), rt, in air. ^b Isolated yield.

2.5 The possible mechanism

To shed light on the mechanism of the reaction, we compared the ¹H NMR spectrum of the calix[4]arene **3** and its complex

with potassium picrate (see spectrums in supplementary material). The area under a picrate anion peak at δ 8.44 was found, implying that the calix[4]arene **3**-potassium ion complex was formed in chloroform. The changes in chemical shift and peak collapsing also indicated the strong complexation between calix[4]arene **3** with K^+ ,^[16] which enhances the nucleophilicity of the KOH, and consequently promote the reaction efficiently. The desired product was obtained in poor yield when the reaction was performed under the optimized conditions except for a nitrogen atmosphere, which indicated that oxygen is needed during the selenation (Table 1, entries 16-17).

Base on the results described above and previous reports^[17], a mechanism for this reaction is proposed in Scheme 2. The complexation of calix[4]arene **3** with K^+ enhances the nucleophilicity of KOH and reacted with *O,O*-dialkylphosphonate to give intermediate **a**, which reacted with diaryl diselenides to yield *O,O*-dialkyl-Se-aryl phosphoroselenoates and organoselenium anion **b**. The organoselenium anion **b** can be converted to diaryl diselenides after the oxidation in air^[18].



Scheme 3. The possible mechanism of the selenation.

3. Conclusions

In summary, we have developed a convenient and low-cost method for the synthesis of *O,O*-dialkyl-Se-aryl phosphoroselenoates catalyzed by calix[4]arene-assisted KOH by using easily available and cheap reagents as starting materials. The other advantages of this procedure include mild conditions, high yields and wide functional group tolerance as well as recyclable calix[4]arene co-catalyst.

4. Experimental

4.1 General

Reactions were monitored by thin layer chromatography (TLC) using gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. Silica gel 300-400 mesh size was used for column chromatography using the combination of ethyl acetate and petroleum ether as an eluent. 1H NMR and ^{13}C NMR spectra were recorded on 400 MHz and NMR plus spectrometer using residue solvent peaks as internal standards respectively. Mass spectra (MS) were obtained using EI mass spectrometer. High-resolution mass spectra (HRMS) were measured on an electron ionization (EI) mass spectrometer.

4.2 Synthesis of calix[4]arene **3**

To a solution of 25,27-di(*n*-propyl)-26,28-dihydroxy calix[4]arene (**4**)^[15] (1.0 g, 2.0 mmol) in 50 mL of dry CH_3CN was added 1,2-di(4-methyl acyloxy) ethane (1.55 g, 4.2 mmol) and Cs_2CO_3 (3.26 g, 10 mmol). The mixture solution was refluxed under a nitrogen atmosphere for 24 hours. Then the reaction solution was treated with H_2O (30 mL) and extracted with CH_2Cl_2 . The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The desired products compound **5** was

obtained by flash chromatography using ethyl acetate/hexane as an eluent. Then, 8-hydroxyquinoline (0.69 g, 4.2 mmol) was added to the solution of compound **5** and K_2CO_3 (1.38 g, 10 mmol). The reaction mixture was refluxed for 24 hours under a nitrogen atmosphere. Then the reaction solution was treated with H_2O (30 mL) and extracted with CH_2Cl_2 . The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The calix[4]arene **3** was obtained in the total yield of 54.2% by flash chromatography using ethyl acetate/hexane as an eluent. 1H NMR(400 MHz, $CDCl_3$) δ 0.84 (t, J = 8.2 Hz, 3H), 1.51-1.55 (m, 2H), 3.48 (t, J = 8.2 Hz, 2H), 3.68-3.80 (m, 4H), 4.22 (t, J = 6.4 Hz, 2H), 4.28 (t, J = 4.3 Hz, 2H), 6.46 (t, J = 6.3 Hz, 1H), 6.76 (t, J = 8.4 Hz, 1H), 7.04 (d, J = 8.5 Hz, 2H), 7.07 (t, J = 4.2 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 4.4 Hz, 2H), 7.42-7.45 (m, 1H), 8.14 (dd, J_1 = 1.3 Hz, J_2 = 1.4 Hz, 1H), 8.96 (dd, J_1 = 1.2 Hz, J_2 = 1.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 8.61, 12.50, 21.07, 21.13, 21.55, 27.70, 27.96, 28.08, 35.48, 66.23, 67.73, 71.26, 108.24, 118.41, 120.11, 120.66, 125.42, 127.95, 132.13, 134.50, 147.70, 154.28, 155.06; Ms (m/z): 851.4.

3.3 Typical procedure for the synthesis of *O,O*-dialkyl-Se-aryl phosphoroselenoate

In a round bottomed flask, calix[4]arene **3** (0.05 mmol) and KOH (0.2 mmol) was added to a solution of *O,O*-dialkylphosphonates (2.2 mmol) and diaryl diselenides (1.0 mmol) in THF (2.0 mL). The reaction mixture was stirred at rt in air for 15 hours. After finish, the reaction solution was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The desired products **8** and calix[4]arene **3** were obtained by flash chromatography using ethyl acetate/hexane as an eluent.

O,O-dimethyl-Se-phenyl phosphoroselenoate (**8a**): 1H NMR ($CDCl_3$, 400 MHz): 7.64 (d, J = 8.0 Hz, 2H), 7.37-7.30 (m, 3H), 3.81 (s, 3H), 3.78 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): 134.6 (d, J_{C-P} = 4.8 Hz, 1C), 129.5 (d, J_{C-P} = 2.1 Hz, 2C), 129.2 (d, J_{C-P} = 2.6 Hz, 2C), 126.0 (d, J_{C-P} = 8.4 Hz, 1C), 54.0 (d, J_{C-P} = 5.7 Hz, 2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): 21.97 ppm; MS (EI): m/z = 266.0. HRMS calc. for $C_8H_{11}O_3PSe$ 265.9606, found 265.9612.

O,O-dimethyl-Se-phenyl phosphoroselenoate (**8b**): 1H NMR ($CDCl_3$, 400 MHz): 7.65-7.63 (m, 2H), 7.385-7.29 (m, 3H), 4.24-4.12 (m, 4H), 1.30 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): 134.5 (d, J_{C-P} = 4.6 Hz, 1C), 129.5 (d, J_{C-P} = 2.0 Hz, 2C), 128.8 (d, J_{C-P} = 2.5 Hz, 2C), 123.8 (d, J_{C-P} = 8.4 Hz, 1C), 63.9 (d, J_{C-P} = 5.8 Hz, 2C), 15.9 (d, J_{C-P} = 7.4 Hz, 2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): 17.97 ppm; MS (EI): m/z = 294.0. HRMS calc. for $C_{10}H_{15}O_3PSe$ 293.9919, found 193.9930.

O,O-di(*i*-propyl)-Se-phenyl phosphoroselenoate (**8c**): 1H NMR ($CDCl_3$, 400 MHz): 7.66 (d, J = 7.6 Hz, 2H), 7.35-7.28 (m, 3H), 4.84-4.72 (m, 2H), 1.33 (d, J = 6.4 Hz, 6H), 1.25 (d, J = 6.4 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): 135.1 (d, J_{C-P} = 4.9 Hz, 1C), 129.3 (d, J_{C-P} = 1.8 Hz, 2C), 128.5 (d, J_{C-P} = 2.3 Hz, 2C), 124.6 (d, J_{C-P} = 8.2 Hz, 1C), 73.1 (d, J_{C-P} = 6.6 Hz, 2C), 23.8 (d, J_{C-P} = 3.7 Hz, 2C), 23.5 (d, J_{C-P} = 6.0 Hz, 2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): 14.69 ppm; MS (EI): m/z = 322.1. HRMS calc. for $C_{12}H_{19}O_3PSe$ 322.0232, found 322.0228.

O,O-di(*n*-butyl)-Se-phenyl phosphoroselenoate (**8d**): 1H NMR ($CDCl_3$, 400 MHz): 7.65-7.63 (m, 2H), 7.37-7.27 (m, 3H), 4.17-4.03 (m, 4H), 1.66-1.58 (m, 4H), 1.39-1.29 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 135.5 (d, J_{C-P} = 4.7 Hz, 1C), 129.4 (d, J_{C-P} = 2.0 Hz, 2C), 128.7 (d, J_{C-P} = 2.5 Hz, 2C), 123.8 (d, J_{C-P} = 8.3 Hz, 1C), 67.6 (d, J_{C-P} = 6.3 Hz, 2C), 32.0 (d, J_{C-P} = 7.2 Hz, 2C), 18.6 (s, 2C), 13.5 (s, 2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): 18.07 ppm; MS (EI): m/z = 350.0. HRMS calc. for $C_{14}H_{23}O_3PSe$ 350.0545, found 350.0541.

O,O-dimethyl-Se-(4-methylphenyl) phosphoroselenoate (**8e**): 1H NMR ($CDCl_3$, 400 MHz): 7.44 (d, J = 6.8 Hz, 2H), 7.05 (d, J = 7.6 Hz, 2H), 4.18-4.03 (m, 4H), 2.27 (s, 3H), 1.24 (t, J = 7.0 Hz, 6H)

ppm; ^{13}C NMR (CDCl_3 , 100 MHz): 138.0 (d, $J_{\text{C-P}} = 3.5$ Hz, 1C), 134.6 (d, $J_{\text{C-P}} = 4.4$ Hz, 2C), 129.3 (d, $J_{\text{C-P}} = 2.1$ Hz, 2C), 119.0 (d, $J_{\text{C-P}} = 7.5$ Hz, 1C), 62.7 (d, $J_{\text{C-P}} = 5.8$ Hz, 2C), 14.9 (d, $J_{\text{C-P}} = 7.4$ Hz, 2C) ppm; ^{31}P NMR (162 MHz, CDCl_3): 18.37 ppm; MS (EI): $m/z = 308.0$. HRMS calc. for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{PSe}$ 308.0075, found 308.0084.

O,O-di(i-propyl)-Se-(4-methylphenyl) phosphoroselenoate (8f): ^1H NMR (CDCl_3 , 400 MHz): 7.55-7.52 (m, 2H), 7.11 (d, $J = 7.6$ Hz, 2H), 4.82-4.73 (m, 2H), 2.33 (s, 3H), 1.34 (d, $J = 6.4$ Hz, 6H), 1.26 (d, $J = 6.4$ Hz, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): 138.6 (d, $J_{\text{C-P}} = 2.7$ Hz, 1C), 135.3 (d, $J_{\text{C-P}} = 4.7$ Hz, 2C), 130.1 (d, $J_{\text{C-P}} = 1.9$ Hz, 2C), 120.7 (d, $J_{\text{C-P}} = 8.4$ Hz, 1C), 73.0 (d, $J_{\text{C-P}} = 6.6$ Hz, 2C), 23.9 (d, $J_{\text{C-P}} = 3.7$ Hz, 2C), 23.5 (d, $J_{\text{C-P}} = 5.9$ Hz, 2C), 21.1 (s, 1C) ppm; ^{31}P NMR (162 MHz, CDCl_3): 15.06 ppm; MS (EI): $m/z = 336.0$. HRMS calc. for $\text{C}_{13}\text{H}_{21}\text{O}_3\text{PSe}$ 336.0388, found 336.0379.

O,O-di(n-butyl)-Se-(4-methylphenyl) phosphoroselenoate (8g): ^1H NMR (CDCl_3 , 400 MHz): 7.52 (d, $J = 6.8$ Hz, 2H), 7.114 (d, $J = 8.0$ Hz, 2H), 4.16-4.03 (m, 4H), 2.33 (s, 3H), 1.66-1.59 (m, 4H), 1.39-1.30 (m, 4H), 0.90 (t, $J = 7.4$ Hz, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): 138.9 (d, $J_{\text{C-P}} = 2.9$ Hz, 1C), 135.6 (d, $J_{\text{C-P}} = 4.4$ Hz, 2C), 130.2 (d, $J_{\text{C-P}} = 2.2$ Hz, 2C), 120.0 (d, $J_{\text{C-P}} = 8.5$ Hz, 1C), 67.5 (d, $J_{\text{C-P}} = 6.3$ Hz, 2C), 32.0 (d, $J_{\text{C-P}} = 7.3$ Hz, 2C), 21.2 (s, 1C), 18.7 (s, 2C), 13.5 (s, 2C) ppm; ^{31}P NMR (162 MHz, CDCl_3): 18.41 ppm; MS (EI): $m/z = 364.1$. HRMS calc. for $\text{C}_{15}\text{H}_{25}\text{O}_3\text{PSe}$ 364.0701, found 364.0695.

O,O-diethyl-Se-(4-chlorophenyl) phosphoroselenoate (8h): ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 7.2$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.22-4.15 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 136.78 (d, $J_{\text{C-P}} = 4.7$ Hz, 1C), 135.33 (d, $J_{\text{C-P}} = 3.0$ Hz, 1C), 129.67 (d, $J_{\text{C-P}} = 2.1$ Hz, 1C), 121.95 (d, $J_{\text{C-P}} = 8.6$ Hz, 1C), 64.01 (d, $J_{\text{C-P}} = 6.0$ Hz, 1C), 15.94 (d, $J_{\text{C-P}} = 7.2$ Hz, 1C) ppm; ^{31}P NMR (162 MHz, CDCl_3): 19.52 ppm; MS (EI): $m/z = 327.9$. HRMS calc. for $\text{C}_{10}\text{H}_{14}\text{ClO}_3\text{PSe}$ 327.9342, found 327.9338.

O,O-di(i-propyl)-Se-(4-chlorophenyl) phosphoroselenoate (8i): ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.59$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 4.76-4.650 (m, 2H), 1.27 (d, $J = 6.0$ Hz, 6H), 1.20 (d, $J = 6.4$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 136.45 (d, $J_{\text{C-P}} = 4.9$ Hz, 1C), 135.02 (d, $J_{\text{C-P}} = 3.2$ Hz, 1C), 129.54 (d, $J_{\text{C-P}} = 1.8$ Hz, 1C), 122.77 (d, $J_{\text{C-P}} = 8.4$ Hz, 1C), 73.38 (d, $J_{\text{C-P}} = 6.8$ Hz, 1C), 23.86 (d, $J_{\text{C-P}} = 3.9$ Hz, 1C), 23.52 (d, $J_{\text{C-P}} = 5.8$ Hz, 1C) ppm; ^{31}P NMR (162 MHz, CDCl_3): 20.12 ppm; MS (EI): $m/z = 356.4$. HRMS calc. for $\text{C}_{12}\text{H}_{18}\text{ClO}_3\text{PSe}$ 356.4138, found 356.4142.

O,O-di(n-butyl)-Se-(4-chlorophenyl) phosphoroselenoate (8j): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.65-7.63 (m, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 4.09-4.01 (m, 4H), 1.59-1.52 (m, 4H), 1.32-1.23 (m, 4H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 137.42 (d, $J = 4.59$ Hz), 134.64 (d, $J = 2.89$ Hz), 130.08 (d, $J = 1.8$ Hz), 122.54 (d, $J = 8.29$ Hz), 67.79 (d, $J = 6.49$ Hz), 31.89 (d, $J = 6.89$ Hz), 18.61, 13.77; ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$): 20.23. MS (EI): $m/z = 384.0$. HRMS calc. for $\text{C}_{14}\text{H}_{22}\text{ClO}_3\text{PSe}$ 384.0842, found 384.0839.

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Appendix A. Supplementary material

All compounds are known from the literature, the copies of ^1H NMR and ^{13}C NMR spectra can be found via the "Supplementary Content" section of this article's webpage.

References and notes

[1] (a) G. Zeni, M. P. Stracke, C. W. Nogueira, A. L. Braga, P. H. Menezes, H. A. Stefani, *Org. Lett.* 6 (2004) 1135; (b) S. Liang, J. Chen, D. T. Pierce, J. X. Zhao, *ACS Appl. Mater. Interfaces* 5 (2013) 5165; (c) A. L. Eastwood, A. P. Blum, N. M. Zacharias, D. A. Dougherty, *J. Org. Chem.* 74 (2009) 9241; (d) C. W. Nogueira, G. Zeni, J. B. T. Rocha, *Chem. Rev.* 104 (2004) 6255; (e) G. Zeni, O. S.

D. Barros, A. V. Moro, A. L. Braga, C. Peppe, *Chem. Commun.* (2003) 1258; (e) J. P. Marino, H. N. Nguyen, *J. Org. Chem.* (67) 2002 6291; (f) A. V. Moro, C. W. Nogueira, N. B. V. Barbosa, P. H. Menezes, J. B. T. da Rocha, G. Zeni, *J. Org. Chem.* 70 (2005) 5257; (g) E. F. Lopes, L. C. Goncalves, J. C. G. Vinuesa, R. G. Jacob, G. Perin, C. Santi, E. J. Lenardao, *Tetrahedron Lett.* 56 (2015) 6890; (h) B. Mohan, S. Hwang, H. Woo, K. H. Park, *Tetrahedron* 70 (2014) 2699; (i) A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K. Yokoyama, N. Sonada, *J. Org. Chem.* 57 (1992) 111.

[2] (a) V. J. Blazis, K. J. Koeller, C. D. Spilling, *J. Org. Chem.* 60 (1995) 931; (b) A. Gautier, G. Garipova, O. Dubert, H. Oulyadi, S. R. Piettre, *Tetrahedron Lett.* 42 (2001) 5673; (c) T. F. Herpin, J. S. Houlton, W. B. Motherwell, B. P. Roberts, J. M. Weibel, *Chem. Commun.* (1996) 613; (d) C.-P. Chuang, S.-F. Wang, *Synth. Commun.* 25 (1995) 3459; (e) C. Lopin, G. Gouhier, A. Gautier, S. R. Piettre, *J. Org. Chem.* 68 (2003) 9916; (f) X. Huang, Q. Xu, C.-G. Liang, Q.-W. He, *Synth. Commun.* 32 (2002) 1243; (g) C. Lopin, A. Gautier, G. Gouhier, S. R. Piettre, *Tetrahedron Lett.* 41 (2000) 10195; (h) M. Marinuzzi, M. C. Fulco, R. Rizzo, R. Pellicciari, *Synlett* (2004) 1027.

[3] (a) S. Mitra, S. Mukherjee, S. K. Sen, A. Hajra, *Bioorg. Med. Chem. Lett.* 24 (2014) 2198; (b) C. Lopin, G. Gouhier, A. Gautier, S. R. Piettre, *J. Org. Chem.* 68 (2003) 9916.

[4] L.-B. Han, N. Choi, M. Tanaka, *J. Am. Chem. Soc.* 118 (1996) 7000.

[5] (a) Q. Xu, C.-G. Liang, X. Huang, *Synth. Commun.* 33 (2003) 2777; (b) J.-M. Chen, X. Huang, *Synth. Commun.* 34 (2004) 1745.

[6] Y.-X. Gao, G. Tang, Y. Cao, Y.-F. Zhao, *Synthesis* (2009) 1081.

[7] Y. Y. Li, S. H. Chen, L. Su, J. H. Li, X. H. Xu, *Chin. J. Org. Chem.* 33 (2013) 1999.

[8] (a) L. Li, S. Shi, L. Song, L. Guo, Y. Wang, H. Ma, J. Hou, H. Wang, *J. Organomet. Chem.* 794 (2015) 231; (b) P. Bako, Z. Rapi, G. Keglevich, T. Szabo, P. L. Soti, T. Vigh, A. Grun, T. Holczbauer, *Tetrahedron Lett.* 52 (2011) 14736; (c) N. H. Khan, A. Sadhukhan, N. C. Maity, R. I. Kureshy, S. H. R. Abdi, S. Saravanan, H. C. Bajaj, *Tetrahedron* 67 (2011) 7073; (d) S. Nagayama, S. Kobayashi, *J. Am. Chem. Soc.* 122 (2000) 11531.

[9] (a) S. Kumar, N. K. Konduru, N. Verma, N. Ahmed, *Synth. Commun.* 45 (2015) 2555; (b) S. Kumar, N. Verma, N. Ahmed, *RSC Adv.* 5 (2015) 85128; (c) J. Shankar, G. Satish, B. S. P. A. Kumar, Y. V. D. Nageswar, *Eur. J. Chem.* 5 (2014) 668; (d) K. Ramesh, M. S. Narayana, K. Karnakar, Y. V. D. Nageswar, *Tetrahedron Lett.* 52 (2011) 4734; (e) R. Sridhar, B. Srinivas, V. P. Kumar, M. Narendar, K. R. Rao, *Adv. Synth. Catal.* 349 (2007) 1873; (f) K. Surendra, N. S. Krishnaveni, R. Sridhar, K. R. Rao, *J. Org. Chem.* 71 (2006) 5819; (g) N. S. Krishnaveni, K. Surendra, K. R. Rao, *Adv. Synth. Catal.* 346 (2004) 346; (h) M. Komiyama, *J. Am. Chem. Soc.* 111 (1989) 3046.

[10] (a) K. Iwamoto, K. Araki, S. Shinkai, *Tetrahedron* 47 (1991) 4325; (b) W. Verboom, S. Datta, Z. Asfari, *J. Org. Chem.* 57 (1992) 5394; (c) V. Rawat, K. Press, I. Goldberg, A. Vigalok, *Org. Biomol. Chem.* 13 (2015) 11189; (d) S. Meninno, A. Parrella, G. Brancatelli, S. Geremia, C. Gaeta, C. Talotta, P. Neri, A. Lattanzi, *Org. Lett.* 17 (2015) 5100; (e) P. Sarkar, C. Mukhopadhyay, *Green Chem.* 17 (2015) 3452; (f) J. Gao, Z.-G. Ren, J.-P. Lang, *J. Organomet. Chem.* 792 (2015) 88.

[11] H. Taniguchi, Y. Otsuji, E. Nomura, *Bull. Chem. Soc. Jpn.* 68 (1995) 3563.

[12] R. Perrin, R. Lamartine, M. Perrin, *Pure and Appl. Chem.* 65 (1993) 1549.

[13] (a) E. Nomura, H. Taniguchi, K. Kawaguchi, *J. Org. Chem.* 58 (1993) 4709; (b) S. Shinkai, S. Mori, H. Koreishi, *J. Am. Chem. Soc.* 108 (1986) 2409; (c) R. Cacciapaglia, A. Casnati, L. Mandolini, *J. Am. Chem. Soc.* (114) 1992 10956; (d) M. Ziolkowski, S. J. Grabowski, J. J. Leszczynski, *Chem. Phys.* 355 (2009) 169; (e) B. P. Hay, T. K. Firman, B. A. Moyer, *J. Am. Chem. Soc.* 127 (2005) 1810.

[14] Ouyang, Y. J.; Qiu, R. H.; Chen, S. H.; Chen, J. Y.; Xu, X. H. *Chin. J. Org. Chem.* 2015, 35, 2636-2641.

[15] V. Percec, T. K. Bera, B. B. De, *J. Org. Chem.* 66 (2001) 2104.

[16] J. S. Kim, O. J. Shon, J. W. Ko, M. H. Cho, I. Y. Yu, J. Vicens, *J. Org. Chem.* 65 (2000) 2386.

[17] W. L. Dong, G. Y. Huang, Z. M. Li, W. G. Zhao, *Phosphorus, Sulfur, and Silicon and the other related Elements* 184 (2009) 2058.

[18] (a) Y. He, D. Huang, M. Lu, *Phosphorus, Sulfur, and Silicon and the other related Elements* 187 (2012) 1118; (b) Y. J. Ouyang, Y. Y. Li, N. B. Li, X. H. Xu, *Chin. Chem. Lett.* 24 (2013) 1103.

Mild reaction conditions

Operational simplicity

High yields

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Inexpensive catalysts

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