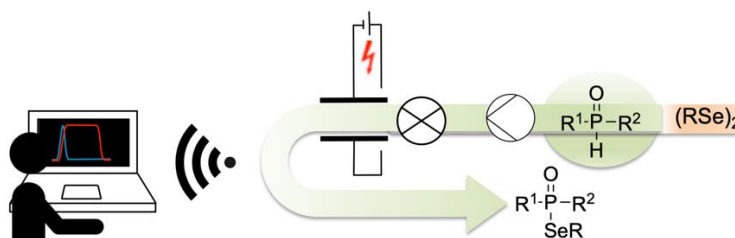# Accelerating Electrochemical Synthesis through Automated Flow: Efficient Synthesis of Chalcogenophosphites

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Abstract Integrated electrochemical reactors in automated flow systems have been utilised for chalcogenophosphite formations. Multiple electrochemical reactions can be performed using a programmed sequence in a fully autonomous way. Differently functionalised chalcogenophosphites have been efficiently synthesised in short reaction times.

Heteroatom bond formation to phosphorous moieties, especially with chalcogens such as selenium and sulfur, are important chemical transformations in organic synthesis.[1] Many bioactive molecules contain selenium- or sulfur–phosphorous bonds (Figure 1).[2]
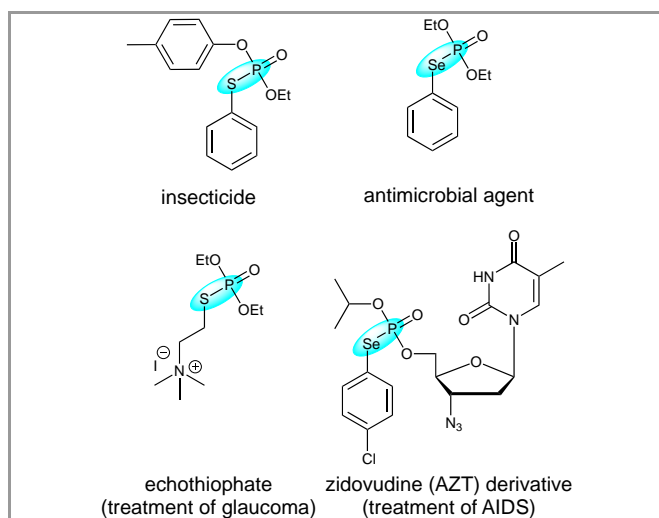

Figure 1. Bioactive molecules with P–Se and P–S bonds.

The synthesis of selenium- or sulfur–phosphorous bonds has been studied with different chemical methods but often expensive metals or toxic reagents are used.[3] Phosphorous can form bonds with various nucleophiles in electrochemical batch reactions using supporting electrolytes such as Bu$_4$NI,[4,5] Bu$_4$NBr,[6] KI,[7] and DMMI[8] as halogen-containing mediators with electrodes such as platinum and metal catalyst such as Cu[9] with typically long reaction times. Very recently, such electrochemical methods have been applied in the selective formation of phosphorous–sulfur[4] and phosphorous–selenium[6] bonds. Lee, Cai and co-authors used stoichiometric amounts of Bu$_4$NI and Bu$_4$NBr electrolytes and Pt electrodes with reaction times of 6 to 7 hours. While batch electrochemical methods are standard protocols, continuous flow syntheses[10] and flow electrochemical reactions[11] have recently emerged as highly beneficial additions to the portfolio of organic chemists in academia and industry. Electrochemistry integrated in flow reactions has not yet been explored to obtain phosphorous functionalised chalcogen derivatives. In continuation of our efforts towards the development of tools and techniques to carry out flow transformations, we have recently disclosed the first use of an integrated flow electrochemical reactor in an automated way.[12] In this work we apply the same methodology for the efficient synthesis of phosphorous–sulfur and phosphorous–selenium bonds.

The Vapourtec automated flow system with the integrated Ion electrochemical microflow reactor has unique features which accelerate the reaction process and minimise the required manpower. The system is able to self-load the required chemicals, collect the reaction output, auto-clean the system while allowing exact temperature, flow rate and current control in each reaction. Furthermore, it can be operated remotely from the office or other locations with internet connection. The only limitation faced in this system is the number of accessible loading and collection vials. A schematic representation of the system is shown in Figure 2.
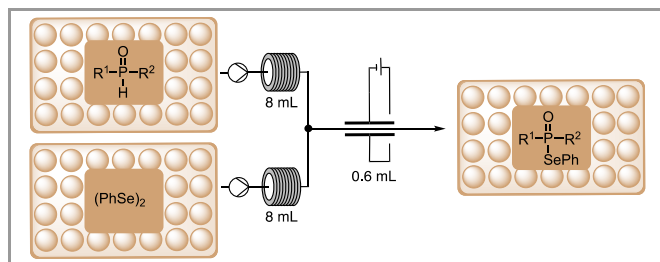
Figure 2. Automated flow electrochemical synthesis of chalcogeno-phosphites.

Initially the reaction between diethylphosphite **1** and diphenyl diselenide **2** in acetonitrile was investigated using different reaction conditions, electrode materials and electrolytes. Interestingly, the reaction does not proceed without electrolyte despite the close distance of the electrodes in the flow reactor (0.5 mm) indicating a participation of the electrolyte as a mediator in this transformation.

Table 1 Reaction of **1** and **2** to *O,O*-diethyl *Se*-phenyl phosphoroselenoate **3a** using a flow electrochemical reactor.[a]

Entry	Electrolyte	Flow [ml/min]	Current [mA]	**3a** Yield [%][b]
1	Bu$_4$NI	1.0	80	90
2	Et$_4$NBr	1.0	80	94
3	Et$_4$NCl	1.0	80	97
4	Bu$_4$NBF$_4$	1.0	80	52
5	Bu$_4$NClO$_4$	1.0	80	44
6	**Et$_4$NCl**	**1.2**	**96**	**97**
7	Et$_4$NCl	1.4	112	94
8	Et$_4$NCl	1.8	144	90
9[c]	Et$_4$NCl	1.2	96	68
10[d]	Et$_4$NCl	1.2	96	56
11[e]	Et$_4$NCl	1.2	96	50

[a] Reaction conditions: Graphite anode, Pt cathode, **1** (0.2 M), electrolyte (0.01 M), acetonitrile used as solvent. [b] Determined using ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. [c] Dichloromethane used as solvent. [d] Methanol used as solvent. [e] Dimethylformamide used as solvent.

In this reaction, initially different electrolytes such as Et$_4$NI, Et$_4$NBr, Et$_4$NCl, Bu$_4$NBF$_4$ and Bu$_4$NClO$_4$ were screened and among these Et$_4$NCl showed the highest yield of 97% (Table 1, entries 1–5). To reduce the time of reaction, the flow rate was increased from 1.0 mL/min up to 1.8 mL/min. At 1.2 mL/min still 97% yield was obtained but at higher flow rates lower yields were observed (Table 1, entries 6–8). Acetonitrile was already the solvent of choice, other solvents such as dichloromethane, methanol or dimethylformamide resulted in decreased yields (Table 1, entries 9–11). Different electrode combinations were screened but these

were all less encouraging. A decrease in the phosphite concentration led to reduced yields of the product (see supporting information). The optimal reaction conditions with the highest space-time yield are shown in entry 6 of Table 1. These conditions have now been applied to the automated synthesis of a large variety of products in order to investigate the scope and general applicability of this electrochemical methodology (Figure 3).[13]

Phosphite derivatives such as ethoxy (**3a**), methoxy (**3b**), *n*-butoxy (**3c**), isopropoxy (**3d**), 2-ethylhexyl (**3e**) and benzyl (**3f**) provided the products in good yields. A cyclic phosphite was investigated and formed the product **3g** with 84% isolated yield. Similarly, the phenoxy substituted product **3h** was formed in an excellent yield of 95%. Among different phosphine oxide derivatives, the phenyl (**3i**), tolyl (**3j**), 3,5-dimethyl benzene (**3k**) and 2-naphthyl (**3l**) substituted products were isolated in good yields. Also unsymmetrical compounds bearing ethoxy and phenyl substituents provided the product **3m** in 80% yield. Cyclic derivative **3n** was formed in 86% yield. Similar to diphenyl diselenide, other dichalcogenides such as dibenzyl diselenide and diphenyl disulfide could be employed to give phosphoroseleno-ates **3o–3r** and phosphorosulfonates **3s–3u**, but the yields of the phosphorosulfonates were found to be slightly lower than the yields of the corresponding phosphoroselenoates.[14]
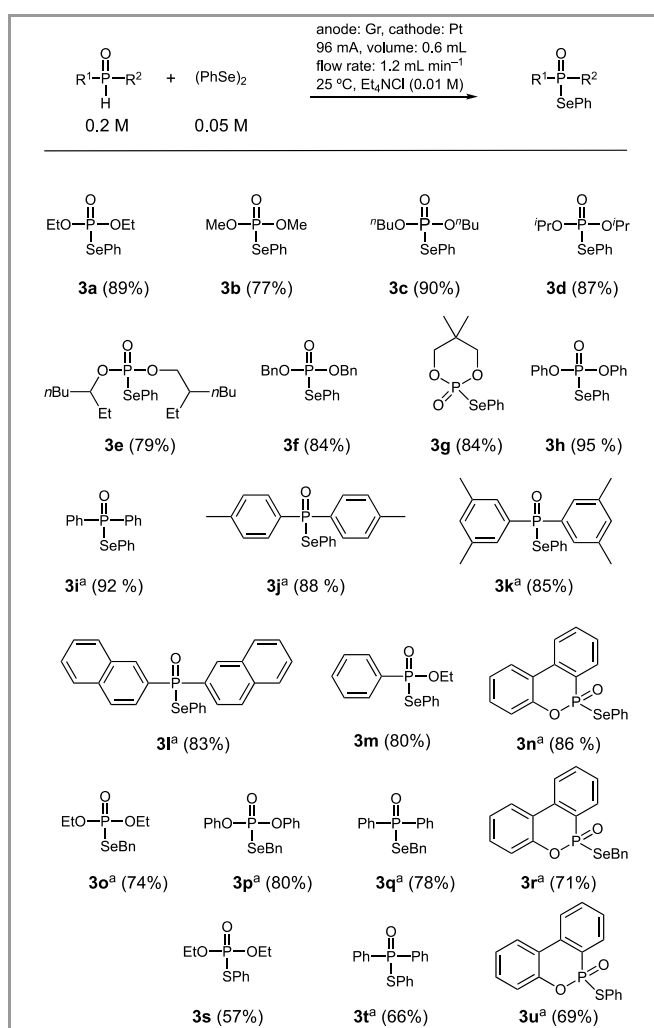

Figure 3. Substrate scope for the electrochemical selenenylation and thiolation of phosphites. [a] A mixture of CH$_3$CN / THF (1:1) was used.

In order to get some insight into the mechanism, we studied the electrooxidation properties of each compound. From cyclic voltammogram (CV) experiments, diethyl phosphite shows no oxidation peak and diphenyl diselenide shows two oxidation peaks at 1.46 V and 1.8 V (vs Ag/AgCl) while Et$_4$NCl showed an obvious oxidation peak at 1.41 V (vs Ag/AgCl) indicating that Et$_4$NCl is earlier oxidised (see Figure S3, supporting information).

Based on previous literature reports[4-6,8,15] and our initial studies, the proposed mechanism involved in the selenenylation of phosphites is shown in Figure 4. The diselenide **2** is reduced at the cathode to generate the radical anion **I**, which then reacts the the phosphite to generate the selenophosphite **3** and the radical anion **II**. This intermediate **II** is then oxidised to the selenyl radical **III** which dimerises to **2** and a proton, which will be finally reduced to hydrogen at the cathode. Other mechanisms in the literature suggest the involvement of elemental halides[4,6] or halide radicals[8] generated from the electrolyte. This cannot be excluded here, but the fact that the reaction proceeds also without halide anions (Table 1, entries 4 and 5) suggest that a different mechanism must also be operating here.
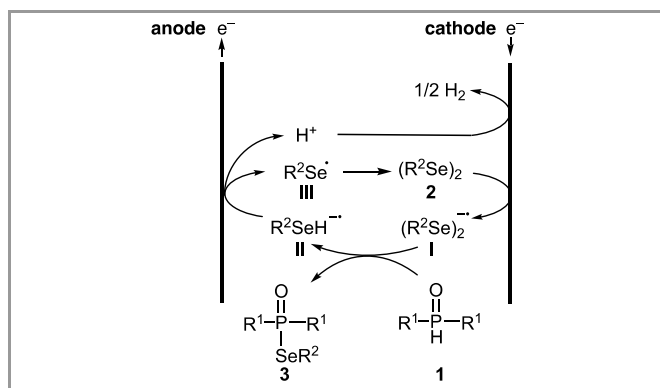

Figure 4. Proposed mechanism for the electrochemical synthesis of selenophosphites.

We have demonstrated that phosphites can be efficiently selenenylated in flow electrochemical reactors in moderate to good yields. The use of an automated flow system integrated with the electrochemical microreactor enabled a fast synthesis of different derivatives in a straightforward way. The scope and limitation of the method are illustrated with a broad range of substrates. Compared to previous procedures, this method is fast, inexpensive, metal-free, and environmentally friendly and automated. Future research in synthesising organic compounds in an automated electrochemical way is currently ongoing in our laboratory.

Acknowledgment

Supporting Information

Yes

Primary Data

No

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(13) Experimental conditions: The electrolysis was performed in an

undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a Graphite (Gr) anode and a platinum (Pt) cathode (surface area: A = 12 cm^2). A solution of phosphite (0.2 M in CH$_3$CN) is placed in vial A and a mixture of diphenyl diselenide (0.05 M) and Et$_4$NCl (0.01 M) in CH$_3$CN placed in vial B. Each solution was injected to 8 mL sample loop. The reactor temperature was set at 25 °C with a flow rate of 1.2 mL min^{-1} and the current was set to 96 mA which switched on automatically. Then, both solutions were pumped into a PTFE coil (1 mm internal diameter) and mixed *via* a T-piece connected to a 30 cm PTFE coil before the inlet of the electrochemical rector. After reaching a steady state, the solution (12 mL) was collected at the reactor outlet automatically into a collection glass vial. The solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc/cyclohexane).

(14) Characterisation data (all NMR values given in ppm):

O,O-Diethyl Se-phenyl phosphoroselenoate (3a): 56 mg (89% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.69 – 7.60 (m, 2H), 7.38 – 7.29 (m, 3H), 4.25 – 4.11 (m, 4H), 1.30 (td, J = 7.1, 0.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.7 (d, J = 3.7 Hz), 129.6 (d, J = 1.3 Hz), 128.9 (d, J = 2.5 Hz), 123.9 (d, J = 8.7 Hz), 64.0 (d, J = 6.2 Hz), 16.05 (d, J = 7.5 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 17.9.

O,O-Dimethyl Se-phenyl phosphoroselenoate (3b): 123 mg (77% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 – 7.58 (m, 2H), 7.39 – 7.29 (m, 3H), 3.81 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.7 (d, J = 3.7 Hz), 129.7 (d, J = 2.5 Hz), 129.1 (d, J = 2.5 Hz), 123.4 (d, J = 8.7 Hz), 54.2 (d, J = 6.2 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.9.

O,O-Dibutyl Se-phenyl phosphoroselenoate (3c): 188 mg (90% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 – 7.62 (m, 2H), 7.37 – 7.27 (m, 3H), 4.18 – 4.02 (m, 4H), 1.66 – 1.59 (m, 4H), 1.42 – 1.34 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.6 (d, J = 4.7 Hz), 129.5 (d, J = 2.0 Hz), 128.8 (d, J = 2.5 Hz), 124.0 (d, J = 8.4 Hz), 67.7 (d, J = 6.4 Hz), 32.2 (d, J = 7.3 Hz), 18.8, 13.7. ^{31}P NMR (202 MHz, CDCl$_3$) δ 18.0.

O,O-Diisopropyl Se-phenyl phosphoroselenoate (3d): 168 mg (87% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 – 7.62 (m, 2H), 7.35 – 7.27 (m, 3H), 4.84 – 4.73 (m, 2H), 1.33 (d, J = 6.2 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.3 (d, J = 4.9 Hz), 129.4 (d, J = 1.8 Hz), 128.6 (d, J = 2.3 Hz), 124.7 (d, J = 8.3 Hz), 73.2 (d, J = 6.6 Hz), 24.0 (d, J = 3.8 Hz), 23.6 (d, J = 6.0 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 14.6.

O,O-Bis(2-ethylhexyl) Se-phenyl phosphoroselenoate (3e): 218 mg (79% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 – 7.60 (m, 2H), 7.37 – 7.26 (m, 3H), 4.08 – 3.92 (m, 4H), 1.59 – 1.47 (m, 2H), 1.36 – 1.19 (m, 16H), 0.91 – 0.81 (m, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.6 (dt, J = 4.7, 1.8 Hz), 129.5 (d, J = 1.9 Hz), 128.7 (d, J = 2.3 Hz), 124.0 (d, J = 8.4 Hz), 70.0 (dd, J = 7.6, 2.1 Hz), 40.1 (d, J = 1.2 Hz), 30.0 (d, J = 6.9 Hz), 28.9 (d, J = 2.2 Hz), 23.4 (d, J = 5.6 Hz), 23.0, 14.1, 11.0. ^{31}P NMR (202 MHz, CDCl$_3$) δ 17.8.

O,O-Dibenzyl Se-phenyl phosphoroselenoate (3f): 211 mg (84% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 – 7.53 (m, 2H), 7.36 – 7.30 (m, 7H), 7.29 – 7.22 (m, 6H), 5.12 (qd, J = 11.7, 8.7 Hz, 4H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.0 (d, J = 4.7 Hz), 135.5 (d, J = 7.9 Hz), 129.7 (d, J = 2.2 Hz), 129.1 (d, J = 2.6 Hz), 128.7, 128.6, 128.3, 123.5 (d, J = 8.6 Hz), 69.3 (d, J = 6.1 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 18.5.

5,5-Dimethyl-2-(phenylselanyl)-1,3,2-dioxaphosphinane 2-oxide (3g): 154 mg (84% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 – 7.72 (m, 2H), 7.39 – 7.30 (m, 3H), 4.15 (dd, J = 10.6, 4.3 Hz, 2H), 3.87 (ddt, J = 24.7, 11.4, 1.6 Hz, 2H), 1.28 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.0 (d, J = 4.7 Hz), 129.8 (d, J = 2.0 Hz), 129.2 (d, J = 2.5 Hz), 122.0 (d, J = 8.0 Hz), 78.2 (d, J = 7.3 Hz), 32.7 (d, J = 7.0 Hz), 22.3, 20.6 (d, J = 1.0 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 9.7.

O,O,Se-Triphenyl phosphoroselenoate (3h): 154 mg (95% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 – 7.40 (m, 2H), 7.35 – 7.25 (m, 7H), 7.20 – 7.16 (m, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.3 (d, J = 8.6 Hz), 136.3 (d, J = 4.8 Hz), 129.8 (d, J = 1.0 Hz), 129.6 (d, J = 2.5 Hz), 129.4 (d, J = 3.0 Hz), 125.7 (d, J = 1.5 Hz), 122.7 (d, J = 9.1 Hz), 120.7 (d, J = 5.1 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 9.4.

Se-Phenyl diphenylphosphinoselenoate (3i): 198 mg (92% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.87 – 7.77 (m, 4H), 7.53 – 7.46 (m, 4H), 7.46 – 7.41 (m, 4H), 7.26 – 7.23 (m, 1H), 7.19 – 7.12 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.4 (d, J = 3.3 Hz), 134.0 (s), 133.3 (s), 132.4 (d, J = 3.1 Hz), 131.5 (d, J = 10.6 Hz), 129.4 (d, J = 1.6 Hz), 128.8 (d, J = 2.0 Hz), 128.6 (d, J = 13.2 Hz), 123.9 (d, J = 5.7 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 20.2.

Se-Phenyl di-p-tolylphosphinoselenoate (3j): 204 mg (88% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 – 7.66 (m, 4H), 7.52 – 7.46 (m, 2H), 7.25 – 7.19 (m, 5H), 7.18 – 7.13 (m, 2H), 2.37 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.9 (d, J = 3.1 Hz), 136.4 (d, J = 3.3 Hz), 131.5 (d, J = 11.0 Hz), 131.1, 130.3, 129.42 (d, J = 13.6 Hz), 129.40 (d, J = 1.5 Hz), 128.7 (d, J = 1.9 Hz), 124.5 (d, J = 5.6 Hz), 21.8. ^{31}P NMR (202 MHz, CDCl$_3$) δ 40.2.

Se-Phenyl bis(3,5-dimethylphenyl)phosphinoselenoate (3k): 212 mg (85% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.48 (m, 2H), 7.45 – 7.37 (m, 4H), 7.26 – 7.22 (m, 1H), 7.19 – 7.14 (m, 2H), 7.12 – 7.07 (m, 2H), 2.30 (s, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.2 (d, J = 13.9 Hz), 136.4 (d, J = 3.2 Hz), 134.0 (d, J = 3.2 Hz), 133.0, 129.2 (d, J = 1.5 Hz), 128.9 (d, J = 10.5 Hz), 128.7 (d, J = 1.9 Hz), 124.3 (d, J = 5.7 Hz), 21.3. ^{31}P NMR (202 MHz, CDCl$_3$) δ 41.2.

Se-Phenyl di(naphthalen-2-yl)phosphinoselenoate(3l): 228 mg (83% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.45 (d, J = 15.0 Hz, 2H), 7.93 – 7.82 (m, 8H), 7.61 – 7.51 (m, 6H), 7.22 – 7.15 (m, 1H), 7.14 – 7.06 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.4 (d, J = 3.2 Hz), 134.9 (d, J = 2.6 Hz), 133.7 (d, J = 9.6 Hz), 132.5 (d, J = 14.4 Hz), 131.0, 130.25, 129.4 (d, J = 1.5 Hz), 129.2, 128.8 (d, J = 1.9 Hz), 128.5 (d, J = 13.3 Hz), 127.9, 127.1, 126.1 (d, J = 12.1 Hz), 123.9 (d, J = 5.7 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 39.8.

O-Ethyl Se-phenyl phenylphosphonoselenoate (3m): 156 mg (80% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.47 (m, 2H), 7.40 – 7.35 (m, 1H), 7.28 – 7.16 (m, 5H), 7.10 – 7.04 (m, 2H), 4.32 – 4.18 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.5 (d, J = 3.6 Hz), 133.4, 132.5 (d, J = 3.3 Hz), 132.3, 131.1 (d, J = 11.0 Hz), 129.3 (d, J = 2.1 Hz), 128.8 (d, J = 2.5 Hz), 128.2 (d, J = 14.9 Hz), 124.3 (d, J = 6.6 Hz), 62.7, 16.3. ^{31}P NMR (202 MHz, CDCl$_3$) δ 38.4.

6-(Phenylselenyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3n): 192 mg (86% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 – 7.83 (m, 1H), 7.77 – 7.73 (m, 1H), 7.66 – 7.60 (m, 2H), 7.46 (tdd, J = 7.5, 3.6, 1.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 7.01 – 6.97 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.5 (d, J = 9.9 Hz), 137.1 (d, J = 3.6 Hz), 136.0 (d, J = 7.5 Hz), 133.8 (d, J = 2.8 Hz), 130.6 (d, J = 11.0 Hz), 129.19 (d, J = 2.5 Hz), 129.13 (d, J = 2.9 Hz), 128.5 (d, J = 14.9 Hz), 126.6, 125.73, 125.0 (d, J = 1.0 Hz), 124.8, 123.3 (d, J = 11.2 Hz), 122.1 (d, J = 7.2 Hz), 122.0 (d, J = 11.7 Hz), 120.2 (d, J = 7.0 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 31.2.

Se-Benzyl O,O-diethyl phosphoroselenoate (3o): 136 mg (74% yield). The ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 4.16 – 3.98 (m, 6H), 1.30 (td, J = 7.1, 0.7 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.5 (d, J = 4.7 Hz), 129.0, 128.7, 127.5, 63.5 (d, J = 5.5 Hz), 29.5 (d, J = 4.6 Hz), 16.0 (d, J = 7.5 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 20.2.

Se-Benzyl O,O-diphenyl phosphoroselenoate (3p): 193 mg (80% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.24 (m, 4H), 7.16 – 7.12 (m, 11H), 4.08 (d, J = 12.6 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.2 (d, J = 6.0 Hz), 129.9 (d, J = 1.3 Hz), 129.2, 128.8, 127.7, 125.8 (d, J = 1.7 Hz), 121.0 (d, J = 4.9 Hz), 120.4, 30.9 (d, J = 4.8 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 13.7.

Se-Benzyl diphenylphosphinoselenoate (3q): 174 mg (78% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.94 – 7.78 (m, 4H), 7.55 – 7.49

(m, 2H), 7.48 – 7.35 (m, 4H), 7.20 – 7.10 (m, 5H), 4.07 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.7 (d, J = 4.4 Hz), 134.6, 133.8, 132.4 (d, J = 3.1 Hz), 131.4 (d, J = 10.9 Hz), 129.2, 128.8, 128.7 (d, J = 5.2 Hz), 127.3, 28.4 (d, J = 2.5 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 40.0.

6-(Benzylselanyl)dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide (3r): 165 mg (71% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.84 (m, 3H), 7.70 – 7.65 (m, 1H), 7.49 (tdd, J = 7.6, 3.6, 0.9 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.29 – 7.19 (m, 6H), 7.11 – 7.05 (m, 1H), 4.24 – 4.09 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 149.4 (d, J = 9.8 Hz), 137.7 (d, J = 4.4 Hz), 135.6 (d, J = 7.6 Hz), 133.8 (d, J = 2.7 Hz), 130.8, 130.4 (d, J = 11.9 Hz), 129.2, 128.7 (t, J = 7.5 Hz), 127.8, 127.5, 126.8, 125.2 (d, J = 1.1 Hz), 125.1 (d, J = 0.6 Hz), 123.8 (d, J = 10.9 Hz), 122.3 (d, J = 12.3 Hz), 120.6 (d, J = 6.6 Hz), 29.2 (d, J = 3.7 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 33.6.

O,O-Diethyl *S*-phenyl phosphorothioate (3s): 84 mg (57% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 – 7.52 (m, 2H), 7.37 – 7.31 (m, 3H), 4.25 – 4.12 (m, 4H), 1.30 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.6 (d, J = 5.2 Hz), 129.5 (d, J = 2.2 Hz), 129.1 (d, J = 2.8 Hz), 126.7 (d, J = 7.2 Hz), 64.2 (d, J = 6.2 Hz), 16.1 (d, J = 7.2 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 22.9.

S-Phenyl diphenylphosphinothioate (3t): 124 mg (66% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 – 7.81 (m, 4H), 7.53 – 7.48 (m, 2H), 7.47 – 7.41 (m, 6H), 7.26 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.5 (d, J = 3.9 Hz), 133.1, 132.4 (d, J = 3.0 Hz), 131.7 (d, J = 10.2 Hz), 129.2 (d, J = 1.7 Hz), 129.0 (d, J = 2.2 Hz), 128.6 (d, J = 13.1 Hz), 126.3 (d, J = 5.2 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 41.3.

6-(Phenylthio)dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide (3u): 135 mg (69% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 – 7.89 (m, 1H), 7.86 – 7.81 (m, 1H), 7.75 (dd, J = 7.8, 1.6 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.50 (tdd, J = 7.5, 3.6, 1.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.28 – 7.16 (m, 5H), 7.12 – 7.06 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.6 (d, J = 9.6 Hz), 136.4 (d, J = 7.3 Hz), 136.1 (d, J = 4.3 Hz), 133.8 (d, J = 2.6 Hz), 130.9 (d, J = 10.2 Hz), 130.6, 129.4 (d, J = 3.1 Hz), 129.1 (d, J = 2.6 Hz), 128.5 (d, J = 14.9 Hz), 125.4, 124.7, 124.3 (d, J = 4.9 Hz), 123.3 (d, J = 11.5 Hz), 121.9 (d, J = 11.6 Hz), 120.1 (d, J = 7.1 Hz). ^{31}P NMR (202 MHz, CDCl$_3$) δ 34.2.

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