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Article

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Acid/phosphide-induced radical route to alkyl, alkenyl sulfides and phosphonothioates from sodium arylsulfinates in water

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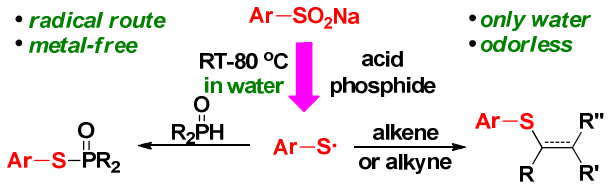


Abstract: A newly developed aqueous system with acid and phosphide was introduced in which odorless and stable sodium arylsulfinates can *in situ* generate arylsulfenyl radicals. These radicals have high reactivity to react with alkynes, alkenes and *H*-phosphine oxides for the synthesis of alkyl, alkenyl sulfides and phosphonothioates. The control experiments and quantum calculations are also performed to gain insights into the generation mechanism of arylsulfenyl radicals. Notably, the chemistry is free of smell thiols, organic solvents and metals.

Introduction

Thiyl radicals especially arylsulfenyl radicals, which are at the center of some extremely efficient radical reactions for the synthesis of organosulfur compounds, have also attracted the interest of synthetic chemists.[1] Typically, arylsulfenyl radicals are generated through three main strategies: (1) the use of radical initiators; (2) photolysis; (3) thermolysis.[2] Nevertheless, most of these

approaches suffer from limitations including the use of smell, air sensitive thiols or their derivatives pre-prepared from them, the demand of metal catalysts, excess oxidants and toxic organic solvents, and high temperature (in the cases of thermolysis). Thus, the further exploration of metal-free protocols for the formation of arylsulfenyl radicals using odorless and easy-to-handle precursors[3] in green solvents under mild conditions is still desirable guided by the concept of green chemistry and an appealing task in sulfur chemistry.[4]

Furthermore, the radicals in the eco-friendly systems may have unique reactivity compared with thiyl radicals formed *via* traditional routes, which may result in new viable accesses to important organosulfur derivatives. On the one hand, sodium aryl sulfinates are a kind of stable, odorless and easy-to-handle sulfur compounds that have been widely applied as sulfonating agents[2] or coupling partners *via* the desulfonation.[5] More recently, much attention has been paid to the construction of C-S bonds with these compounds[6] and analogues[7] as the sulfur sources under reduction conditions, in which they are utilized as the precursors of arylsulfide cations. Thus, sodium arylsulfinates also have great potential to derive the corresponding arylsulfenyl radicals under designated reduction conditions.

One the other hand, water is an ideal choice as the reaction medium.[8] Our group has reported a strategy for the *in situ* generation of arylsulfenyl radicals from sodium arylsulfinates in aqueous reduction systems using I_2 and PPh_3 to achieve the iodothiolation of alkynes.[9] Along this line, we develop a new

aqueous system (acid/phosphide) for the synthesis of alkyl, alkenyl sulfides and phosphonothioates under relatively mild conditions, in which arylsulfenyl radicals can be derived from sodium arylsulfinates. To the best of our knowledge, there is the first example on the formation of arylsulfenyl radicals under acidic and reductive conditions. Furthermore, the generation mechanism of arylthiyl radicals in the system is also investigated by performing the control experiments and quantum chemical calculations.

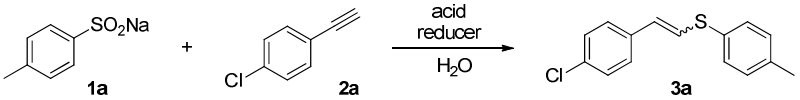
Results and discussion

During the investigations of the synthesis of *β*-iodoalkenyl sulfides,[9] trace of alkenyl sulfide **3a** was found in the presence of base (Table 1, entry 1). Encouraged by these results, we further optimized the reaction conditions. The results indicate that I_2 is not necessary for the reaction and the use of strong acid (H_2SO_4) in place of base can afford the best yield in the model reaction (entries 2-8). Both acid and reducer are necessary for the reaction (entry 9, 15). The amounts of H_2SO_4, sodium *p*-toluenesulfinate and reaction temperature were also optimized (entries 10-18). The best option was using 2.0 equiv of sodium *p*-toluenesulfinate and 0.5 equiv of H_2SO_4 in 80 ^oC (entry 15).

Potassium *p*-toluenesulfinate could also provide a satisfactory yield (entry 15), but sodium *p*-toluenesulfinate is cheaper. Various reducing agents such as hydrazine hydrate, Zn powder, HCOOH, iodotrimethylsilane (TMSI) and dietyl phosphite were also screened (entries 19-23). Only phosphide could afford the

desired product, and PPh_3 emerged as the best choice. The desired product **3a** was also afforded with moderate yield (55%) in the case of toluenesulfinic acid even without H_2SO_4, indicating that acid may be used to form toluenesulfinic acid *in situ* and promote the reaction (entry 24).

Table 1. The optimization of reaction conditions[a]



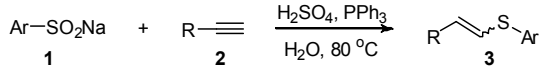
entry	additive (x equiv)	reducer	t (^{o}C)	yield (%)[b]	*Z*/*E*[b]
1	$NaOH/I_2$ (1.2/1.5)	PPh_3	120	25	91/9
2	NaOH (1.2)	PPh_3	120	trace	/
3	TsOH (1.2)	PPh_3	120	33	82/18
4	$HOCH_2COOH$ (1.2)	PPh_3	120	42	83/17
5	AcOH (1.2)	PPh_3	120	54	64/36
6	CF_3COOH (1.2)	PPh_3	120	31	77/23
7	HCl (1.2)	PPh_3	120	68	56/44
8	H_2SO_4 (1.2)	PPh_3	120	86	14/86
9	/	PPh_3	120	nr	/
10	H_2SO_4 (1.5)	PPh_3	120	94	19/81
11	H_2SO_4 (1.5)	PPh_3	80	98	17/83
12	H_2SO_4 (1.5)	PPh_3	80	88[c]	32/68
13	H_2SO_4 (1.5)	PPh_3	50	90	66/34
14	H_2SO_4 (1.5)	PPh_3	25	44	77/23
15	H_2SO_4 (0.5)	PPh_3	80	96, 94[d], nr[e]	17/83
16	H_2SO_4 (0.3)	PPh_3	80	84	16/84
17	H_2SO_4 (1.0)	PPh_3	80	95	17/83
18	H_2SO_4 (2.0)	PPh_3	80	99	17/83
19	H_2SO_4 (0.5)	$(EtO)_2P(O)H$	80	69	16/84
20	H_2SO_4 (0.5)	$N_2H_4{\cdot}H_2O$	80	nr	/
21	H_2SO_4 (0.5)	Zn	80	nr	/
22	H_2SO_4 (0.5)	HCOOH	80	nr	/
23	H_2SO_4 (0.5)	TMSI	80	nr	/
24	/	PPh_3	80	55[f]	13/87

[a] Reaction conditions: 4-chlorophenylacetylene 0.250 mmol, sodium *p*-toluenesulfinate 0.500 mmol, PPh_3 0.750 mmol, additive x equiv, H_2O 1.0 mL, t ^{o}C, 10 h. [b] The yield of 3a and *Z*/*E* ratio were determined by GC-MS and ^1H NMR on crude products. [c] 1.5 equiv of sodium *p*-toluenesulfinate was used. [d] 2 equiv of potassium *p*-toluenesulfinate was used. [e] Without PPh_3. [f] 2 equiv of toluenesulfinic acid instead of sodium *p*-toluenesulfinate was used.

With the optimized conditions in hands, the scope of the reaction was studied (Table 2). Generally, *E*-isomer adducts were the main products because they are the thermodynamic products, and the stereoselectivity was more than 80%. A

range of terminal arylethynes containing electron-donating and -withdrawing groups reacted with **1** to give the corresponding adducts in moderate to excellent yields (entries 1-7, 15-20). Aliphatic alkynes could also provide the corresponding products but the stereoselectivity was poor (entries 8-11). Heteroaryl acetylenes were also applied in the reaction successfully with satisfactory results (entries 12-14).

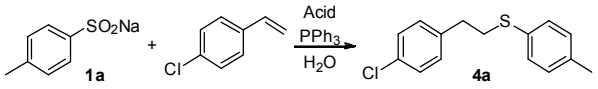
Table 2. The hydrothiolation of alkynes with sodium arylsulfinates[a]



entry	Ar	R	**3**	yield (%)[b]	*E*/*Z*[c]
1	4-$CH_3C_6H_4$	4-ClC_6H_4	*E*-**3a**	74[d]	83/17
2	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**3b**	92	86/14
3	4-$CH_3C_6H_4$	4-$MeOC_6H_4$	**3c**	83	85/15
4	4-$CH_3C_6H_4$	4-*n*-BuC_6H_4	**3d**	90	85/15
5	4-$CH_3C_6H_4$	4-BrC_6H_4	**3e**	89	88/12
6	4-$MeOC_6H_4$	4-ClC_6H_4	**3f**	89	80/20
7	4-$MeOC_6H_4$	4-$CF_3C_6H_4$	**3g**	96	87/13
8	4-$CH_3C_6H_4$	*n*-C_4H_9	**3h**	79	53/47
9	4-$CH_3C_6H_4$	*n*-C_8H_{17}	**3i**	78	46/54
10	4-$MeOC_6H_4$	cyclopentyl	**3j**	90	60/40
11	4-$MeOC_6H_4$	cyclohexyl	**3k**	92	64/36
12	4-$MeOC_6H_4$	2-pyridyl	*E*-**3l**	72[d]	81/19
13	4-$MeOC_6H_4$	3-pyridyl	*E*-**3m**	90[d]	99/1
14	4-ClC_6H_4	2-thienyl	**3n**	89	15/85
15	Ph	Ph	**3o**	72	88/12
16	Mesityl	Ph	**3p**	92	90/10
17	2-$CH_3C_6H_4$	Ph	**3q**	90	90/10
18	4-ClC_6H_4	Ph	**3r**	96	82/18
19	2-BrC_6H_4	Ph	**3s**	82	50/50
20	4-$MeOC_6H_4$	Ph	**3t**	91	89/11

[a] Reaction conditions: sodium arenesulfinate 1 0.500 mmol, alkynes 2 0.250 mmol, PPh_3 0.750 mmol, H_2SO_4 0.125 mmol, H_2O 1.0 mL, 80 °C, 10 h. [b] Isolated yields, a mixture of *E* and *Z* stereoisomers. [c] *E*/*Z* ratio was determined by GC-MS and ^1H NMR on crude products. [d] The isolated yields of *E* isomers.

Table 3. The optimization of reaction conditions[a]



entry	x	tempreture (°C)	yield (%)[b]
1	1.5	130	87
2	1.5	100	63
3	1.5	80	68
4	1.5	50	34
5	1.5	25	14
6	/	50	nr
7	2.0	50	70
8	**3.0**	**50**	**91 (87)**[c]

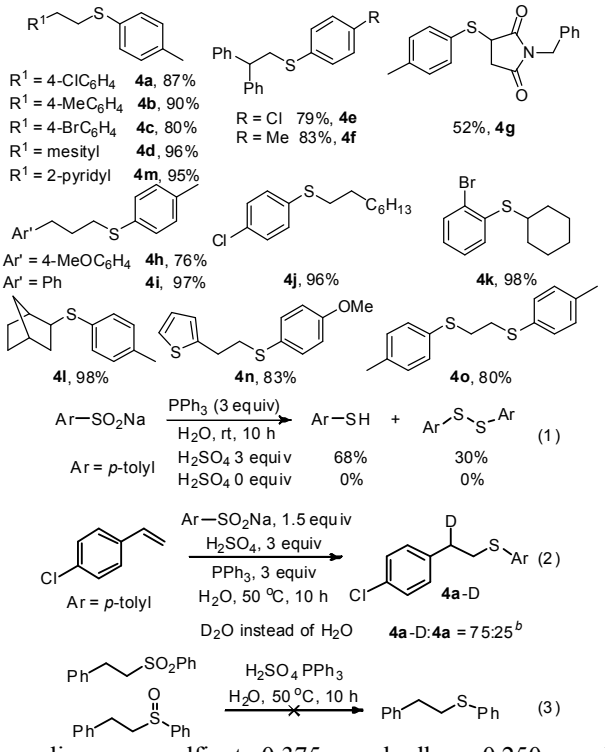
[a] Reaction conditions: 4-chlorostyrene 0.250 mmol, sodium *p*-toluenesulfinate 0.375 mmol, PPh_3 0.750 mmol, acid x equiv, H_2O 1.0 mL, t °C, 10 h. [b] GC yields. [c] Isolated yield.

Likewise, the approach was also applied in the hydrothiolation of alkenes by just increasing the amount of acid to 3.0 equiv at 50 °C (Table 3). Further investigations indicated that sodium arylsulfinates could react with a series of arylalkenes to yield the final products (Scheme 1, **4a**-**4f**, **4m**, **4n**), and alkylalkenes can also provide the desire adducts (**4h**-**4l**). Nevertheless, most electron-deficient alkenes failed to be employed in the reaction (such as 4-nitrostyrene and chalcone), and only 52% yield of **4g** was produced using *N*-benzyl-1*H*-pyrrole-2,5-dione. The product **4o** was afforded from trimethylvinylsilane *via* addition and substitution reactions. The results of control experiments indicate that H_2SO_4 can enhance the reduction of sodium arylsulfinates (Scheme 1, eq. 1), and the hydrogen source is mainly from water (eq. 2). In addition, PPh_3 could not reduce $PhS(O)CH_2CH_2Ph$ or $PhS(O_2)CH_2CH_2Ph$ to sulfur product $PhSCH_2CH_2Ph$ (eq. 3).

It should be noted that phosphonothioates which have promising bioactivities and pest-control applications,[10] could also be generated using *H*-phosphine oxides instead of PPh_3 as the reducing agent at room temperature. Compared

with other approaches for the synthesis of these compounds,[11] the protocol is free of metal catalysts and organic solvents and no heating is required. The acid (H_2SO_4) proved to be necessary for the reaction. Reactions of *H*-phosphine oxides occurred in moderate to good yields (Scheme 2, **5a**, **5b**, **5f**-**5h**). The formation of products was also observed in the cases of diaryl chlorophosphines without acid (**5a**, **5c**-**5e**). A solvent switch to DMF along with an increase in reaction temperature to 100 °C was found to improve the poor yields of **5i** and **5j**. A poor yield of **5k** was obtained using sodium methanesulfinate instead of sodium arylsulfinates.

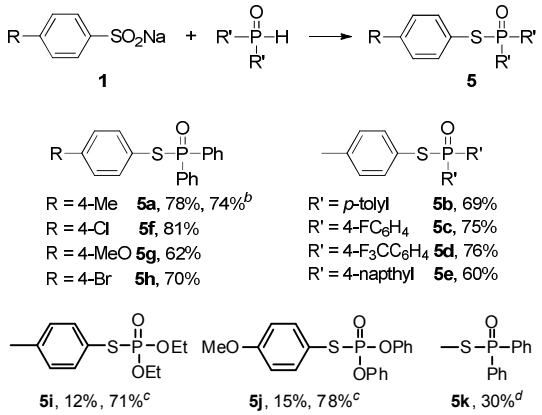
Scheme 1. The hydrothiolations of alkenes with sodium arylsulfinates[a]



[a] Reaction conditions: sodium arenesulfinate 0.375 mmol, alkene 0.250 mmol, PPh_3 0.750 mmol, H_2SO_4 0.750 mmol, H_2O 1.0 mL, 50 °C, 10 h. Isolated yields. [b] Based on ^1H NMR results.

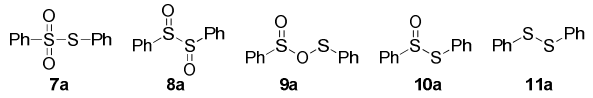
To further probe the mechanism, radical trapping experiments were designed and investigated (see Table S1, SI). All the reactions were inhibited in the presence of radical traps (TEMPO, BHT, 1,1-diphenylethylene). All three radical trapping products (**A**-**C**) were observed by GC-MS, and **A, C** were separated and further identified by ^{1}H and ^{13}C NMR suggesting these transformations may include radical processes. The further electron paramagnetic resonance (EPR) experiments also indicate that free radicals are generated in H_2SO_4/PPh_3 system (Figure S1, SI).

Scheme 2. The reactions of sodium arylsulfinates and *H*-phosphine oxides[a]



[a] Conditions: sodium arylsulfinates 0.250 mmol, *H*-phosphine oxides 0.500 mmol, H_2SO_4 0.125 mmol, H_2O 1.0 mL, rt, 6 h. Isolated yields. [b] Use of diaryl phosphate chloride instead of *H*-phosphine oxides in the absence of H_2SO_4. [c] The reaction was performed in DMF without H_2SO_4 at 100 °C for 6 h. [d] Sodium methanesulfinate was used in place of sodium arylsulfinate.

Table 4. The calculated values of some possible intermediates' BDEs based on quantum calculations



7a **8a** **9a** **10a** **11a**

Compounds	Dissociation bond	BDE (kJ/mol)	
		B3LYP/6-31G*	B3LYP/6-311G*
7a	S-S	165.25	167.12
8a	S-S	1.75	4.33
9a	O=S-O	37.14	32.76
	S-O	134.29	133.09
10a	S-S	119.49	121.43
11a	S-S	230.40	228.14
Br_2	Br-Br	221.94 (192)[a]	190.09

[a] Actual measured value.

Control experiments were also performed to confirm whether *S*-phenyl benzene sulfonothioate, 1,2-di-*p*-tolyl disulfane or 4-methylbenzenethiol were the intermediates in the system (Table S2, SI). Although the desired products could be obtained with satisfactory yields in some cases, these reactions did not contain a radical route. Thus, all of them prove to be not the intermediates in these reactions. According to the calculation results of the bond dissociation energies (BDEs) (Table 4), it can be concluded that **8a**, **10a** have more probability to yield radical by homolysis than other intermediates.[12]

Based on these results, a proposed mechanism of the formation of aryl sulfenyl radicals in H_2SO_4/PPh_3 system was illustrated in Figure 1. **8** and **10** that are generated from sodium arylsulfinates in H_2SO_4/PPh_3 system,[12a] can form arylthiyl radicals **13** and arylsulfinyl radicals **12** (paths **I** and **II**) by homolysis. Radicals **12** can further yield radicals **13** through reduction or disproportionation (paths **III** or **IV**). Relative free energy profiles for paths **I-IV** (Figure 2) were also provided based on the studies of density functional theory

(DFT) (see Table S3, SI). The free energy barriers of path **I** and **II** are close, while the free energy barrier of path **III** is much lower than path **IV**. Thus, radicals **13** are more likely to be afforded from path **I** to **III** or path **II** to **III**.[13] Further control experiments indicated that **10a** can be observed in the reaction of phenylsulfanol itself while **7a** instead of **8a** was detected in the reaction of phenylsulfanol with benezenesulfinic acid.[12,14] These results also supported the proposed mechanism in Figure 1.

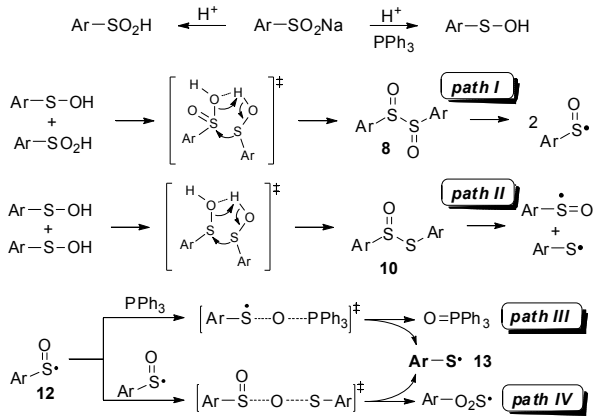


Figure 1. The proposed mechanism of the sulfenyl radical generation from sodium arylsulfinates in H_2SO_4/PPh_3 system.

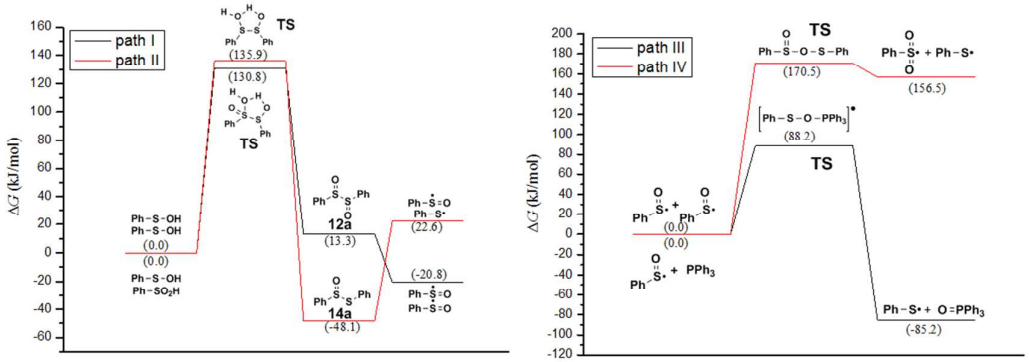


Figure 2. Relative free energy profiles (kJ/mol) for paths **I-IV.**

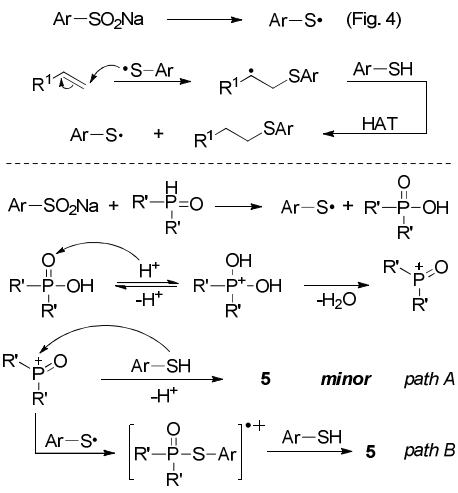


Figure 3. Tentative mechanisms.

Although the detailed mechanisms of these reactions remained to be elucidated, a tentative pathway for the hydrothiolations of alkenes was proposed (Figure 3). Arylsulfenyl radical *in situ* generated form sodium arylsulfinite based on the processes in Figure 2, adds to alkene to afford carbon radical intermediate, following hydrogen atom transfer (HAT) process with aryl thiol to form the final product.[15] The mechanism of the formation of S-P bonds was also proposed (Figure 3). There are two pathways for the transformation. The reaction can be inhibited by TEMPO, in which the radical trapping product is separated and further identified by ^{1}H, ^{13}C NMR and GC-MS (Table S1, SI), so the radical process may be the major path (path B) of the reaction.

Conclusions

In conclusion, we have reported a stable and odorless arylsulfenyl radical precursor, sodium arylsulfinate, which can be applied to several transformations for the construction of organosulfur compounds in

H_2SO_4/phosphide aqueous system. The radical trap experiments and EPR results indicate that these transformations contain radical processes. The formation mechanism of arylthiyl radicals in the system is also investigated by performing the control experiments and quantum chemical calculations. Acid promote the reduction of sodium arenesulfonates and the phosphide as a reducing agent may be enhance the generation of arylsulfenyl radicals. Although low atom economy and potential water pollution exist in the chemistry, it is free of thiols, organic solvents and metal catalysts, and provides a new application of sodium arylsulfinates in organic synthesis, which may promote the discovery of other new types of radical sulfuration reactions for the construction of *sulfur*-containing compounds.

Experimental Section

General procedures for the synthesis of alkenyl sulfides 3: A mixture of sodium arylsulfinate **1** 0.500 mmol, alkyne **2** 0.250 mmol, PPh_3 0.750 mmol and 0.125 mmol H_2SO_4 in water (1.0 mL) was stirred at 80 ^oC for 10 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed in *vacuo* to afford the crude product. Further column chromatography on silica gel (EtOAc/petroleum ether, v/v = 1/20) was needed to afford the pure desired products **3**. In the cases of *E*-**3l** and *E*-**3m**, the eluent composition is 1/10 (EtOAc/petroleum ether, v/v).

General procedures for the synthesis of alkyl sulfides 4: A mixture of sodium arylsulfinate **1** 0.375 mmol, alkene 0.250 mmol, PPh_3 0.750 mmol and 0.75 mmol H_2SO_4 in water (1.0 mL) was stirred at 50 ^oC for 10 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed in *vacuo* to afford the crude product. Further column chromatography on silica gel (EtOAc/petroleum ether, v/v = 1/20) was needed to afford the pure desired products **4**. In the case of **4g**, the eluent composition is 1/5 (EtOAc/petroleum ether, v/v).

General procedures for the synthesis of phosphonothioates 5: A mixture of sodium arylsulfinate **1** 0.250 mmol, *H*-phosphine oxide 0.500 mmol and H_2SO_4 0.125 mmol in water (1.0 mL) was stirred at room temperature for 6 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed in *vacuo* to afford the crude product. Further column chromatography on silica gel (EtOAc/petroleum ether, v/v = 1/4) was needed to afford the pure desired products **5**.

Characterization data of all products

(*E*)-(4-Chlorostyryl)(*p*-tolyl)sulfane.[16] *E*-**3a**, yellow oil (74%, 48.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H), 6.54 (d, *J* = 15.5 Hz, 1H), 6.84 (d, *J* = 15.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 7.23-7.27 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.1, 124.7, 126.0, 127.5, 127.8, 129.0, 129.6, 130.0, 131.9, 134.2, 136.6. GC-MS (EI) *m/z*: 260.

(4-Methylstyryl)(*p*-tolyl)sulfane.[17,18] **3b**, yellow oil, was obtained as a mixture of stereoisomers in 86:14 (*E*/*Z*) ratio (92%, 55.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 3H, *Z*-**3b**), 2.27 (s, 3H, *E*-**3b**), 2.29 (s, 3H, *E*-**3b**), 2.31 (s, 3H, *Z*-**3b**), 8.34 (d, *J* = 10.5 Hz, 1H, *Z*-**3b**), 8.47 (d, *J* = 10.5 Hz, 1H, *Z*-**3b**), 6.60 (d, *J* = 15.5 Hz, 1H, *E*-**3b**), 6.74 (d, *J* = 15.5 Hz, 1H, *E*-**3b**), 7.05 (d, *J* = 8.0 Hz, 2H (*E*-**3b**)), 7.09 (d, *J* = 8.0 Hz, 2H (*E*-**3b**), 2H (*Z*-**3b**)), 7.14 (d, *J* = 8.5 Hz, 2H (*Z*-**3b**)), 7.16 (d, *J* = 8.0 Hz, 2H (*E*-**3b**)), 7.26 (d, *J* = 8.0 Hz, 2H (*E*-**3b**)), 7.30 (d, *J* = 8.0 Hz, 2H (*Z*-**3b**)), 7.37 (d, *J* = 8.0 Hz, 2H (*Z*-**3b**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 21.3, 123.1, 126.0, 126.8 (*Z*), 128.8, 129.1, 129.5, 130.1, 130.5, 131.2, 131.7 (*Z*), 134.1 (*Z*), 137.2, 137.5. GC-MS (EI) *m/z*: 240.

(4-Methoxystyryl)(p-tolyl)sulfane.[17,18] **3c**, yellow oil, was obtained as a mixture of stereoisomers in 85:15 (*E*/*Z*) ratio (83%, 59.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H (*Z*-**3c**), 3H (*E*-**3c**)), 3.83 (s, 3H, *E*-**3c**), 3.85 (s, 3H, *Z*-**3c**), 6.37 (d, *J* = 11.0 Hz, 1H (*Z*-**3c**)), 6.54 (d, *J* = 10.5 Hz, 1H (*Z*-**3c**)), 6.70 (d, *J* = 15.5 Hz, 1H (*E*-**3c**)), 6.74 (d, *J* = 15.5 Hz, 1H (*E*-**3c**)), 6.88 (d, *J* = 8.5 Hz, 2H (*E*-**3c**)), 6.96 (d, *J* = 8.5 Hz, 2H (*Z*-**3c**)), 7.17 (d, *J* = 8.0 Hz, 2H (*E*-**3c**), 2H (*Z*-**3c**)), 7.30 (d, *J* = 8.5 Hz, 2H (*E*-**3c**)), 7.34 (d, *J* = 8.0 Hz, 2H (*E*-**3c**)), 7.39 (d, *J* = 8.0 Hz, 2H (*Z*-**3c**)), 7.52 (d, *J* = 9.0 Hz, 2H (*Z*-**3c**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 55.5, 113.9 (*Z*), 114.3, 121.4, 124.4 (*Z*), 126.6 (*Z*), 127.4, 129.7 (*Z*), 130.1, 130.2, 130.5, 131.5, 132.0, 137.0, 159.4. GC-MS (EI) *m/z*: 256.

(4-Butylstyryl)(p-tolyl)sulfane. **3d**, yellow oil, was obtained as a mixture of stereoisomers in 85:15 (*E*/*Z*) ratio (90%, 63.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 8.0 Hz, 3H (*E*-**3d**), 3H (*Z*-**3d**)), 1.27-1.35 (m, 2H (*E*-**3d**), 2H (*Z*-**3d**)), 1.49-1.60 (m, 2H (*E*-**3d**), 2H (*Z*-**3d**)), 2.30 (s, 3H (*E*-**3d**), 3H (*Z*-**3d**)), 2.54 (t, *J* = 8.0 Hz, 2H (*E*-**3d**), 2H (*Z*-**3d**)), 6.35 (d, *J* = 10.5 Hz, 1H (*Z*-**3d**)), 6.48 (d, *J* = 11.0 Hz, 1H (*Z*-**3d**)), 6.63 (d, *J* = 15.5 Hz, 1H (*E*-**3d**)), 6.76 (d, *J* = 15.5 Hz, 1H (*E*-**3d**)), 7.07 (d, *J* = 8.0 Hz, 2H (*E*-**3d**)), 7.10 (d, *J* = 8.0 Hz, 2H (*E*-**3d**), 2H (*Z*-**3d**)), 7.16 (d, *J* = 7.5 Hz, 2H (*Z*-**3d**)), 7.20 (d, *J* = 7.5 Hz, 2H (*E*-**3d**)), 7.27 (d, *J* = 8.0 Hz, 2H (*E*-**3d**)), 7.31 (d, *J* = 8.0 Hz, 2H (*Z*-**3d**)), 7.40 (d, *J* = 8.0 Hz, 2H (*Z*-**3d**)), ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 21.1, 22.5, 33.7, 35.5, 123.1, 126.1, 126.8 (*Z*), 128.5 (*Z*), 128.9, 130.1, 130.4, 130.6 (*Z*), 131.4, 131.8, 134.3, 137.2, 142.6. HRMS (EI) Calcd. for $C_{19}H_{22}S$ 282.1442, found 282.1443.

(4-Bromostyryl)(p-tolyl)sulfane.[19] **3e**, yellow oil, was obtained as a mixture of stereoisomers in 88:12 (*E*/*Z*) ratio (89%, 67.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H, *Z*-**3e**), 2.29 (s, 3H, *E*-**3e**), 6.38 (d, *J* = 11.0 Hz, 1H (*Z*-**3e**)), 6.42-6.47 (m, 1H (*Z*-**3e**), 1H (*E*-**3e**)), 6.79 (d, *J* = 15.5 Hz, 1H (*E*-**3e**)), 7.03 (d, *J* = 8.0Hz, 2H (*Z*-**3e**)), 7.09-7.11 (m, 4H (*E*-**3e**), 2H (*Z*-**3e**)), 7.26-7.31 (m, 2H (*E*-**3e**), 2H (*Z*-**3e**)), 7.34 (d, *J* = 8.5 Hz, 2H (*E*-**3e**)), 7.43 (d, *J* = 8.5 Hz, 2H (*Z*-**3e**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 121.1, 125.3 (*Z*), 126.1, 127.5, 128.4 (*Z*), 128.5, 128.7 (*Z*), 130.0 (*Z*), 130.2 130.4 (*Z*), 130.7 (*Z*), 130.8 (*Z*), 131.2, 131.5, 131.9, 135.8, 137.8. GC-MS (EI) *m/z*: 304.

(4-chlorostyryl)(4-methoxyphenyl)sulfane.[20] **3f**, yellow oil, was obtained as a mixture of stereoisomers in 80:20 (*E*/*Z*) ratio (89%, 61.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H, *Z*-**3f**), 3.76 (s, 3H, *E*-**3f**), 6.32-6.35 (d, *J* = 16.0Hz, 1H (*E*-**3f**)), 6.32-6.35 (m, 2H, *Z*-**3f**), 6.73-6.76 (d, *J* = 15.5Hz, 1H (*E*-**3f**)), 6.82-6.86 (m, 2H (*E*-**3f**), 2H (*Z*-**3f**)), 7.11-7.13 (d, *J* = 8.5Hz, 2H (*E*-**3f**)), 7.16-7.19 (m, 2H, *E*-**3f**), 7.27-7.29 (d, *J* = 8.5Hz, 2H (*Z*-**3f**)), 7.33-7.36 (m, 2H (*E*-**3f**), 2H (*Z*-**3f**)), 7.37-7.39 (m, 2H, *Z*-**3f**). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 115.1, 124.1, 124.6(Z), 127.1, 127.2, 128.6, 128.9, 129.4(*Z*), 130.0(*Z*), 132.8, 133.2(*Z*), 134.0, 135.4, 160.0. GC-MS (EI) *m/z*: 276.

(4-Methoxyphenyl)(4-(trifluoromethyl)styryl)sulfane. **3g**, white solid, m.p. 72-74 ^{o}C, was obtained as a mixture of stereoisomers in 87:13 (*E*/*Z*) ratio (96%, 74.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H, *Z*-**3g**), 3.76 (s, 3H, *E*-**3g**), 8.33 (d, *J* = 15.5Hz, 1H (*E*-**3g**)), 8.40 (d, *J* = 11.0 Hz, 1H (*Z*-**3g**)), 8.47 (d, *J* = 11.0 Hz, 1H (*Z*-**3g**)), 6.82-6.90 (m, 3H (*E*-**3g**), 2H (*Z*-**3g**)), 7.26 (d, *J* = 8.0Hz, 2H (*E*-**3g**)), 7.35 (d, *J* = 8.0 Hz, 2H (*E*-**3g**), 2H (*Z*-**3g**)), 7.44 (d, *J* = 8.5 Hz, 2H (*E*-**3g**)), 7.53 (d, *J* = 8.5 Hz, 2H (*Z*-**3g**)), 7.55 (d, *J* = 8.5 Hz, 2H (*Z*-**3g**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.4, 113.9 (Z), 114.1, 123.2 (q, *J* = 275.0 Hz, 1C), 122.2 (*Z*), 123.0 (*Z*), 124.6, 124.7, 124.9, 127.6 (q, *J* = 31.3 Hz, 1C), 127.7, 128.8, 130.8 (*Z*), 132.2 (*Z*), 133.3, 139.2, 160.0. HRMS (EI) Calcd. for

$C_{16}H_{13}F_3OS$ 310.0639, found 310.0634.

Hex-1-en-1-yl(p-tolyl)sulfane.[21] **3h**, yellow oil, was obtained as a mixture of stereoisomers in 53:47 (*E*/*Z*) ratio (79%, 40.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91-0.96 (m, 3H (*Z*-**3h**), 3H (*E*-**3h**)), 1.33-1.46 (m, 3h (*Z*-**3h**), 3h (E-**3h**)), 2.14-2.34 (m, 5H (*Z*-**3h**), 5H (*E*-**3h**)), 5.76-5.78 (m, 1H, *Z*-**3h**), 5.92-5.95 (m, 1H, *Z*-**3h**), 6.10-6.18 (m, 2H, *E*-**3h**), 7.12 (d, *J* = 8.0 Hz, 2H (*E*-**3h**), 2H (*Z*-**3h**)), 7.23-7.27 (m, 2H (*E*-**3h**), 2H (*Z*-**3h**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 21.1, 22.3, 22.4 (*Z*), 28.9 (*Z*), 31.3, 32.9, 121.7 (*Z*), 123.7, 129.3 (*Z*, 2C), 129.4 (2C), 129.8 (4C), 132.7 (*Z*), 136.4. GC-MS (EI) *m/z*: 206.

Dec-1-en-1-yl(p-tolyl)sulfane. **3i**, yellow oil, was obtained as a mixture of stereoisomers in 46:54 (*E*/*Z*) ratio (78%, 51.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82-0.84 (m, 3H (*Z*-**3i**), 3H (*E*-**3i**)), 1.23-1.28 (m, 10H (*Z*-**3i**), 10H (*E*-**3i**)), 1.34-1.39 (m, 2H (*Z*-**3i**), 2H (*E*-**3i**)), 2.06-2.10 (m, 1H (*Z*-**3i**), 1H (*E*-**3i**)), 2.16-2.20 (m, 1H (*Z*-**3i**), 1H (*E*-**3i**)), 2.26 (m, 3H (*Z*-**3i**), 3H (*E*-**3i**)), 5.68-5.73 (m, 1H, *E*-**3i**), 5.84-5.89 (m, 1H, *Z*-**3i**), 6.03-6.10 (m, 1H (*Z*-**3i**), 1H (*E*-**3i**)), 7.04-7.06 (m, 2H (*Z*-**3i**), 2H (*E*-**3i**)), 7.16-7.20 (m, 2H (*Z*-**3i**), 2H (*E*-**3i**)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 21.1, 22.8, 29.2 (2C), 29.4, 29.5, 32.0, 33.2, 121.7, 123.6, 129.4 (*E*), 129.8 (2C (*Z*-**3i**), 2C (*E*-**3i**)), 132.8, 136.3 (*E*), 136.5. HRMS (EI) Calcd. for $C_{17}H_{26}S$ 262.1755, found 262.1750.

(2-Cyclopentylvinyl)(4-methoxyphenyl)sulfane. **3j**, yellow oil, was obtained as a mixture of stereoisomers in 60:40 (*E*/*Z*) ratio (90%, 52.7mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19-1.27 (m, 2H (*E*-**3j**), 2H (*Z*-**3j**)), 1.48-2.59 (m, 7H (*E*-**3j**), 7H (*Z*-**3j**)), 3.73 (s, 3H (*E*-**3j**), 3H (*Z*-**3j**)), 5.58-5.59 (m, 1H, *Z*-**3j**), 5.72-5.76 (m, 1H, *E*-**3j**), 5.95-6.00 (m, 1H (*E*-**3j**), 1H (*Z*-**3j**)), 6.77-6.80 (m, 2H (*E*-**3j**), 2H (*Z*-**3j**)), 7.22-7.26 (m, 2H (*E*-**3j**), 2H (*Z*-**3j**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.2, 25.5, 33.1, 33.3, 40.2 (*Z*), 43.8, 55.5, 114.8, 121.2, 123.5(*Z*), 125.9(*Z*), 126.5(*Z*), 127.1(*Z*), 128.8(*Z*), 131.8, 132.0, 133.6(*Z*), 136.9, 139.0, 159.0. HRMS (EI) Calcd. for $C_{14}H_{18}OS$ 234.1078, found 234.1082.

(2-Cyclohexylvinyl)(4-methoxyphenyl)sulfane. **3k**, yellow oil, was obtained as a mixture of stereoisomers in 64:36 (*E*/*Z*) ratio (92%, 57.1mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02-1.65 (m, 6H (*E*-**3k**), 6H (*Z*-**3k**)), 1.66-1.68 (m, 4H (*E*-**3k**), 4H (*Z*-**3k**)), 1.97-1.99 (m, 1H, *E*-**3k**), 2.38-2.40 (m, 1H, *Z*-**3k**), 3.73 (s, 3H (*E*-**3k**), 3H (*Z*-**3k**)), 5.46-5.50 (m, 1H, *Z*-**3k**), 5.69-5.73 (m, 1H, *E*-**3k**), 5.92-5.97 (m, 1H (*E*-**3k**), 1H (*Z*-**3k**)), 6.77-6.80 (m, 2H (*E*-**3k**), 2H (*Z*-**3k**)), 7.15-7.25 (m, 2H (*E*-**3k**), 2H (*Z*-**3k**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 26.0, 26.2, 32.6, 32.9, 38.4 (*Z*), 41.4, 55.48, 114.8, 121.0, 123.1 (*Z*), 126.5(*Z*), 131.9, 132.0, 137.2 (*Z*), 140.1, 159.0. HRMS (EI) Calcd. for $C_{15}H_{20}OS$ 248.1235, found 248.1234.

(*E*)-2-(2-((4-methoxyphenyl)thio)vinyl)pyridine. *E*-**3l**, yellow solid, m.p. 95-97 ^{o}C (72%, 43.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.83 (s, 3H), 6.36 (d, *J* = 15.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 7.03-7.08 (m, 2H), 7.44-7.50 (m, 3H), 7.56 (t, *J* = 8.0Hz, 1H), 8.47 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.5, 115.2, 121.2, 121.5, 123.1, 125.8, 132.9, 134.8, 136.6, 149.6, 155.0, 160.2. HRMS (EI) Calcd. for $C_{14}H_{13}NOS$ 243.0718, found 243.0724.

(*E*)-3-(2-((4-methoxyphenyl)thio)vinyl)pyridine. *E*-**3m**, yellow solid, m.p. 116-118 ^{o}C (90%, 54.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.84 (s, 3H), 6.35 (d, *J* = 15.5 Hz, 1H), 6.90-6.94 (m, 3H), 7.19-7.21 (m, 1H), 7.42-7.44 (m, 2H), 7.57-7.59 (m, 1H), 8.40-8.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.5, 115.2, 123.3, 123.6, 123.9, 129.3, 132.2, 132.7, 134.4, 147.6, 148.0, 160.1. HRMS (EI) Calcd. for $C_{14}H_{13}NOS$ 243.0718, found 243.0714.

2-(2-((4-Chlorophenyl)thio)vinyl)thiophene.[22] **3n**, yellow oil, was obtained as a mixture of stereoisomers in 15:85 (*E*/*Z*) ratio (89%, 56.1mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 10.0 Hz, 1H (*Z*-**3n**)), 6.65 (d, *J* = 15.0 Hz, 1H (*E*-**3n**)), 6.87-6.90 (m, 1H (*Z*-**3n**), 1H (*E*-**3n**)), 6.95-7.00 (m, 2H, *E*-**3n**), 7.07-7.08 (m, 1H, *Z*-**3n**), 7.19 (d, *J* = 4.0 Hz, 1H (*Z*-**3n**), 1H (*E*-**3n**)), 7.32-7.34 (m, 3H (*E*-**3n**), 2H (*Z*-**3n**)), 7.36 (d, *J* = 5.0 Hz, 1H (*Z*-**3n**)), 7.40-7.41 (m, 2H (*Z*-**3n**), 1H (*E*-**3n**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.0, 122.6, 124.8 (*E*), 125.7 (*E*), 126.6, 127.1, 127.7 (*E*), 128.5, 129.5, 131.1, 133.4, 134.4, 139.8. GC-MS (EI) *m/z*: 252.

Phenyl(styryl)sulfane.[23] **3o**, yellow oil, was obtained as a mixture of stereoisomers in 88:12 (*E*/*Z*) ratio (72%, 38.2mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.53 (d, *J* = 11.0 Hz, 1H (*Z*-**3o**)), 6.62 (d, *J* = 11.0 Hz, 1H (*Z*-**3o**)), 6.76 (d, *J* = 15.5 Hz, 1H (*E*-**3o**)), 6.91 (d, *J* = 15.5 Hz, 1H (*E*-**3o**)), 7.24-7.27 (m, 2H (*Z*-**3o**), 1H (*E*-**3o**)), 7.29 (d, *J* = 7.5 Hz, 1H (*E*-**3o**)), 7.32-7.38 (m, 6H, *E*-**3o**), 7.41 (d, *J* =

8.0 Hz, 2H (*Z*-**3o**)), 7.44 (d, *J* = 7.0 Hz, 2H (*E*-**3o**)), 7.49 (d, *J* = 7.5 Hz, 2H (*Z*-**3o**)), 7.52 (d, *J* = 7.0 Hz, 2H (*Z*-**3o**)), 7.56 (d, *J* = 7.5 Hz, 2H (*Z*-**3o**)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 123.6, 126.2, 127.1, 127.3 (*Z*), 127.7, 128.5 (*Z*), 128.8, 129.3, 130.0, 130.2 (*Z*), 132.0, 135.4, 136.7. GC-MS (EI) *m/z*: 212.

Mesityl(styryl)sulfane. **3p**, light yellow oil, was obtained as a mixture of stereoisomers in 90:10 (*E*/*Z*) ratio (92%, 58.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35 (s, 3H, *Z*-**3p**), 2.37 (s, 3H, *E*-**3p**), 2.52 (s, 6H (*E*-**3p**), 6H (*Z*-**3p**)), 6.01-6.05 (m, 1H (*E*-**3p**), 1H (*Z*-**3p**)), 6.48 (d, *J* = 10.5 Hz, 1H (*Z*-**3p**)), 6.71 (d, *J* = 15.5 Hz, 1H (*E*-**3p**)), 7.02-7.05 (m, 2H (*E*-**3p**), 2H (*Z*-**3p**)), 7.17-7.20 (m, 1H, *E*-**3p**), 7.24 (d, *J* = 7.0 Hz, 2H (*E*-**3p**)), 7.27-7.30 (m, 2H (*E*-**3p**), 1H (*Z*-**3p**)), 7.44-7.47 (m, 2H, *Z*-**3p**), 7.66 (d, *J* = 7.5 Hz, 2H (*Z*-**3p**)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 21.8 (2C), 22.2 (*Z*), 125.1, 125.2, 125.4 (*Z*), 125.6, 126.6 (*Z*), 126.7, 128.5 (*Z*), 128.7, 128.9, 129.4 (*Z*), 129.5, 137.3, 139.0 (*Z*), 139.4, 142.4 (*Z*), 143.3 (2C). HRMS (EI) Calcd. for $C_{17}H_{18}S$ 254.1129, found 254.1130.

Styryl(*o*-tolyl)sulfane.[24] **3q**, light yellow oil, was obtained as a mixture of stereoisomers in 90:10 (*E*/*Z*) ratio (90%, 50.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H, *E*-**3q**), 2.39 (s, 3H, *Z*-**3q**), 6.32 (d, *J* = 11.0 Hz, 1H (*Z*-**3q**)), 6.52-6.55 (m, 1H (*E*-**3q**), 1H (*Z*-**3q**)), 6.76 (d, *J* = 15.5 Hz, 1H (*E*-**3q**)), 7.13-7.19 (m, 4H (*E*-**3q**), 4H (*Z*-**3q**)), 7.22-7.27 (m, 4H (*E*-**3q**), 2H (*Z*-**3q**)), 7.32-7.36 (m, 1H (*E*-**3q**), 1H (*Z*-**3q**)), 7.52 (d, *J* = 7.5 Hz, 2H (*Z*-**3q**)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.5, 123.5, 126.1 (2C), 126.5 (*Z*), 126.9, 127.6 (2C), 128.4 (*Z*), 128.8 (2C), 130.6, 131.1 (2C), 133.9, 136.8, 138.9. GC-MS (EI) *m/z*: 226.

(4-Chlorophenyl)(styryl)sulfane.[25] **3r**, light yellow oil, was obtained as a mixture of stereoisomers in 82:18 (*E*/*Z*) ratio (96%, 59.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.44 (d, *J* = 11.0 Hz, 1H (*Z*-**3r**)), 6.64 (d, *J* = 10.5 Hz, 1H (*Z*-**3r**)), 6.76 (d, *J* = 15.0 Hz, 1H (*E*-**3r**)), 6.84 (d, *J* = 15.5 Hz, 1H (*E*-**3r**)), 7.26-7.43 (m, 9H (*E*-**3r**), 7H (*Z*-**3r**)), 7.53-7.54 (m, 2H, *Z*-**3r**). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 122.7, 125.3 (*Z*), 126.3, 127.5 (*Z*), 128.0, 128.2 (*Z*), 128.5, 128.9, 129.4, 131.1, 131.4, 132.9, 133.2 (*Z*), 134.0 (*Z*), 136.4. GC-MS (EI) *m/z*: 246.

(2-Bromophenyl)(styryl)sulfane.[26] **3s**, light yellow oil, was obtained as a mixture of stereoisomers in 50:50 (*E*/*Z*) ratio (82%, 59.4mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (d, *J* = 10.5 Hz, 1H (*Z*-**3s**)), 6.78 (d, *J* = 10.5 Hz, 1H (*Z*-**3s**)), 6.85 (d, *J* = 15.5 Hz, 1H (*E*-**3s**)), 6.94 (d, *J* = 15.5 Hz, 1H (*E*-**3s**)), 7.09-7.29 (m, 1H (*Z*-**3s**), 1H (*E*-**3s**)), 7.30-7.62 (m, 8H (*E*-**3s**), 8H (*Z*-**3s**)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.0 (*Z*), 123.1 (*Z*), 123.8, 124.3, 126.5 (*Z*), 127.6, 127.7 (*Z*), 128.2, 128.3, 128.5, 128.9, 129.1 (*Z*), 130.1, 130.5, 133.2, 135.6 (*Z*), 136.2, 136.4 (*Z*), 137.7. GC-MS (EI) *m/z*: 290.

(*E*)-(4-methoxyphenyl)(styryl)sulfane.[27] **3t**, light yellow oil, was obtained as a mixture of stereoisomers in 89:11 (*E*/*Z*) ratio (91%, 55.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.75 (s, 3H, *Z*-**3t**), 3.76 (s, 3H, *E*-**3t**), 6.34 (d, *J* = 11.0 Hz, 1H (*Z*-**3t**)), 6.42-6.47 (m, 1H (*E*-**3t**), 1H (*Z*-**3t**)), 6.76 (d, *J* = 15.5Hz, 1H (*E*-**3t**)), 6.82-6.86 (m, 2H (*E*-**3t**), 2H (*Z*-**3t**)), 7.12-7.16 (m, 1H, *E*-**3t**), 7.19-7.23 (m, 4H (*E*-**3t**), 2H (*Z*-**3t**)), 7.31-7.37 (m, 2H (*E*-**3t**), 3H (*Z*-**3t**)), 7.46 (d, *J* = 7.5Hz, 2H (*Z*-**3t**)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.5, 115.1, 124.7, 125.9, 126.0, 127.1 (*Z*), 127.3, 128.4 (*Z*), 128.8, 129.2, 133.1 (*Z*), 133.6, 136.9, 159.7. GC-MS (EI) *m/z*: 242.

(4-Chlorophenethyl)(*p*-tolyl)sulfane.[28] **4a**, yellow oil (87%, 57.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (s, 3H), 2.87 (t, *J* = 8.0 Hz, 2H), 3.09-3.12 (m, 2H), 7.11-7.14 (m, 4H), 7.25-7.29 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2 (2C), 35.5, 36.1, 128.6, 129.3, 129.9, 130.2, 132.8, 136.1, 136.3, 137.5. GC-MS (EI) *m/z*: 262.

(4-Methylphenethyl)(*p*-tolyl)sulfane.[29] **4b**, light yellow oil (90%, 54.5 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.41 (s, 6H), 2.96 (t, *J* = 8.0 Hz, 2H), 3.20 (t, *J* = 8.0 Hz, 2H), 7.15-7.21 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2 (2C), 35.5, 36.1, 128.6, 129.3, 129.9, 130.2, 132.8, 136.1, 136.3, 137.5. GC-MS (EI) *m/z*: 242.

(4-Bromophenethyl)(*p*-tolyl)sulfane.[30] **4c**, light yellow oil (80%, 61.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.33 (s, 3H), 2.85 (t, *J* = 7.5 Hz, 2H), 3.08-3.11 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 35.2, 35.9, 120.3, 129.9, 130.4, 130.5, 131.7, 132.3, 136.6, 139.3. GC-MS (EI) *m/z*: 306.

p-Tolyl(2,4,6-trimethylphenethyl)sulfane. **4d**, yellow oil (96%, 64.8 mg). ^{1}H NMR ($CDCl_3$, 500

MHz) δ 2.29-2.32 (m, 9H), 2.41 (s, 3H), 2.93-3.02 (m, 4H), 6.90 (s, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.8, 21.0, 21.2, 30.0, 33.6, 129.2, 129.9, 130.8, 132.7, 134.2, 135.9, 136.3, 136.6. HRMS (EI) Calcd. for $C_{18}H_{22}S$ 270.1442, found 270.1440.

(4-Chlorophenyl)(2,2-diphenylethyl)sulfane. **4e**, yellow solid, m.p. 84-86 °C (lit. 85-87 °C, 79%, 64.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.60 (d, *J* = 8.0 Hz, 2H), 4.21 (t, *J* = 8.0 Hz, 1H), 7.23-7.26 (m, 10H), 7.27-7.34 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.1, 50.8, 127.0, 128.1 (4C), 128.8 (4C), 129.2, 131.0, 132.2, 135.2, 143.0. HRMS (EI) Calcd. for $C_{20}H_{17}ClS$ 324.0739, found 324.0741.

(2,2-Diphenylethyl)(*p*-tolyl)sulfane.[30] **4f** (radical trapping product **C**)**,** yellow oil (83%, 63.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 3H), 3.55 (d, *J* = 7.5 Hz, 2H), 4.17 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.20-7.25 (m, 8H), 7.28-7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 40.5, 50.7, 126.8 (2C), 128.1 (4C), 128.7 (4C), 129.9 (2C), 130.5 (2C), 132.8, 136.4, 143.3 (2C). GC-MS (EI) *m/z*: 304.

1-Benzyl-3-(*p*-tolylthio)pyrrolidine-2,5-dione.[31] **4g**, yellow oil (52%, 40.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 3.00-3.05 (m, 1H), 3.22-3.26 (m, 1H), 4.30-4.33 (m, 1H), 4.56 (s, 2H), 7.25-7.29 (m, 7H), 7.68 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.9, 30.2, 43.1, 63.5, 128.2, 128.8 (4C), 129.4, 130.2, 133.3, 134.9, 146.3, 168.6, 172.9. MS (ESI) *m/z*: 311.

(3-(4-Methoxyphenyl)propyl)(p-tolyl)sulfane. **4h**, yellow oil (76%, 51.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.90-1.95 (m, 2H), 2.33 (s, 3H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 3.80 (s, 3H), 6.83-6.85 (m, 2H), 7.09-7.11 (m, 4H), 7.24-7.26 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 31.1, 33.8, 33.9, 55.4, 114.0, 129.5, 129.8, 130.1, 132.9, 133.6, 136.1, 158.0. HRMS (EI) Calcd. for $C_{17}H_{20}OS$ 272.1235, found 272.1241.

(3-Phenylpropyl)(p-tolyl)sulfane.[29] **4i**, yellow oil (97%, 58.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.84-1.89 (m, 2H), 2.25 (s, 3H), 2.68 (d, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 7.09-7.13 (m, 3H), 7.16-7.22 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 30.8, 33.8, 34.8, 126.1, 128.5, 128.6, 129.8, 130.2, 132.8, 136.2, 141.5. GC-MS (EI) *m/z*: 242.

(4-Chlorophenyl)(octyl)sulfane.[32] **4j**, colorless oil (96%, 53.8 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.26-1.30 (m, 8H), 1.37-1.41 (m, 2H), 1.59-1.65 (m, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 7.23 (s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.3, 22.8, 28.9, 29.2, 29.3, 29.3, 31.9, 34.0, 129.1, 130.3, 131.7, 135.7. GC-MS (EI) *m/z*: 256.

(2-bromophenyl)(cyclohexyl)sulfane.[33] **4k**, yellow oil (98%, 66.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.78-1.87 (m, 3H), 2.21-2.26 (m, 2H), 2.40-2.52 (m, 4H), 2.74-2.78 (m, 1H), 3.58-3.68 (m, 1H), 7.16-7.19 (m, 1H), 7.31-7.34 (m, 1H), 7.47-7.49 (m, 1H), 7.65-7.67 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.4, 31.1, 41.0, 45.3, 47.6, 127.6, 128.0, 128.9, 133.4, 134.8, 208.4. GC-MS (EI) *m/z*: 270.

bicyclo[2.2.1]heptan-2-yl(p-tolyl)sulfane.[34] **4l**, yellow oil (98%, 53.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17-1.22 (m, 3H), 1.39-1.43 (m, 1H), 1.51-1.80 (m, 4H), 2.24-2.29 (m, 2H), 2.32 (s, 3H), 3.12-3.15 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.0, 27.7, 27.9, 34.5, 35.5, 37.6, 41.2, 48.0, 128.5, 129.0, 132.8, 134.7. GC-MS (EI) *m/z*: 218.

2-(2-(p-tolylthio)ethyl)pyridine.[35] **4m**, yellow oil (95%, 54.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 7.09-7.14 (m, 4H), 7.26-7.29 (m, 2H), 7.57-7.60 (m, 1H), 8.53-8.54 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 34.5, 38.0, 121.6, 123.4, 129.8, 130.4, 132.5, 136.4, 136.5, 149.5, 160.0. GC-MS (EI) *m/z*: 229.

2-(2-((4-Methoxyphenyl)thio)ethyl)thiophene. **4n**, yellow oil (83%, 51.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.07-3.15 (m, 4H), 3.84 (s, 3H), 6.84-6.96 (m, 4H), 7.16-7.17 (m, 1H), 7.40-7.43 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.2, 37.6, 55.5, 114.8, 123.7, 125.0, 125.9, 126.9, 133.8, 143.0, 159.3. HRMS (EI) Calcd. for $C_{13}H_{14}OS_2$ 250.0486, found 250.0484.

1,2-Bis(*p*-tolylthio)ethane.[36] **4o**, yellow oil (80%, 54.8 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 6H), 3.07 (s, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.27 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 34.1, 129.9, 130.9, 131.4, 136.9. GC-MS (EI) *m/z*: 274.

S-(*p*-tolyl)diphenylphosphinothioate.[37] **5a**, white solid, m.p. 110-112 °C (lit. 112-113 °C, 72%, 58.3 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.23 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.36-7.38 (m, 2H), 7.41-7.45 (m, 4H), 7.48-7.51 (m, 2H), 7.87-7.90 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 122.3, 128.6, 128.7, 130.1, 131.7, 131.8, 132.2, 132.5, 133.1, 135.5, 139.4. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 42.0. GC-MS (EI) *m/z*: 324.

S-(*p*-tolyl)di-*p*-tolylphosphinothioate. **5b**, white solid, m.p. 145-147 °C (69%, 60.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (s, 3H), 2.41 (s, 6H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.27-7.29 (m, 4H), 7.36-7.38 (m, 2H), 7.75-7.79 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 21.8, 122.8, 129.3, 129.4, 130.1, 131.7, 131.8, 135.4, 139.1, 142.9. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 42.2. HRMS (ESI) Calcd. for $C_{21}H_{21}OPSH^+$ 353.1129, found $[M+H]^+$ 353.1139.

S-(*p*-tolyl)bis(4-fluorophenyl)phosphinothioate. **5c**, white solid, m.p. 127-129 °C (75%, 67.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.26 (s, 3H), 7.01-7.03 (d, *J* = 8.0 Hz, 2H), 7.11-7.15 (m, 4H), 7.29-7.30 (d, *J* = 6.5 Hz, 2H), 7.81-7.85 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 116.0-116.3 (d, J = 4C), 121.9, 128.1, 129.0, 130.2, 134.0-134.4 (4C), 135.4, 139.6, 164.4-166.4 (d, *J* = 254.8 Hz, 2C). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 39.4. HRMS (ESI) Calcd. for $C_{19}H_{15}F_2OPSNa^+$ 383.0447, found $[M+Na]^+$ 383.0457.

S-(*p*-tolyl)bis(4-(trifluoromethyl)phenyl)phosphinothioate. **5d**, white solid, m.p. 132-134 °C (76%, 87.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.31-7.33 (m, 2H), 7.71-7.73 (m, 4H), 7.96-8.00 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 120.3-126.8 (q, *J* = 271.3 Hz, 2C) 120.7, 122.4, 124.6, 125.7, 125.8, 130.4, 132.1, 132.3, 134.1-134.9 (q, *J* = 32.5 Hz, 2C), 135.6, 136.1, 136.9, 140.1. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 37.9. HRMS (ESI) Calcd. for $C_{21}H_{15}F_6OPSNa^+$ 483.0383, found $[M+Na]^+$ 483.0394.

S-(*p*-tolyl)di(naphthalen-2-yl)phosphinothioate. **5e**, white solid, 159-161 °C (60%, 63.3 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.22 (s, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.40-7.43 (m, 4H), 7.48-7.52 (m, 4H), 7.85-7.87 (m, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 8.06-8.11 (m, 2H), 8.91-8.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 123.3, 124.5, 124.6, 126.7, 127.4, 127.5, 128.8, 129.0, 129.7, 130.0, 133.4, 133.5, 133.6, 133.7, 133.9, 134.0, 134.1, 135.5, 139.2. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 45.5. HRMS (ESI) Calcd. for $C_{27}H_{21}OPSNa^+$ 447.0948, found $[M+Na]^+$ 447.0960.

S-(4-chlorophenyl)diphenylphosphinothioate.[1e] **5f**, white solid, m.p. 99-101 °C (lit. 103-104 °C, 81%, 69.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.16 (d, *J* = 8.5 Hz, 2H), 7.35-7.44 (m, 2H), 7.44-7.46 (m, 4H), 7.50-7.53 (m, 2H), 7.81-7.85 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 124.9, 128.7, 128.8, 129.5, 131.7, 131.8, 131.9, 132.6, 132.8, 135.7, 136.7. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 41.7. GC-MS (EI) *m/z*: 344.

S-(4-methoxyphenyl)diphenylphosphinothioate.[1e] **5g**, white solid, m.p. 141-143 °C, (lit. 140-142 °C, 62%, 52.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3H), 6.73 (d, *J* = 7.5 Hz, 2H), 7.32-7.34 (m, 2H), 7.44-7.46 (m, 4H), 7.50-7.53 (m, 2H), 7.82-7.86 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.4, 114.9, 116.1, 128.6, 128.7, 131.7, 131.8, 132.4, 133.2, 137.2, 160.0. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 41.6. GC-MS (EI) *m/z*: 340.

S-(4-bromophenyl) diphenylphosphinothioate.[38] **5h**, white solid, m.p. 148-150 °C (lit. 151-153 °C, 70%, 67.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (s, 4H), 7.42-7.46 (m, 4H), 7.50-7.53 (m, 2H), 7.82-7.86 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 123.9, 125.5, 128.7, 128.9, 131.7, 131.8 (3C), 132.4 (3C), 132.7, 136.9 (2C). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 41.7. GC-MS (EI) *m/z*: 388.

O,O-diethyl-*S*-(*p*-tolyl)phosphorothioate.[39] **5i**, colorless oil (71%, 46.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (t, *J* = 7.0 Hz, 6H), 2.33 (s, 3H), 4.11-4.23 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.42-7.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.2 (2C), 21.3, 64.1 (2C), 123.0, 130.3, 134.7, 139.4. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 23.5. GC-MS (EI) *m/z*: 260.

S-(4-methoxyphenyl)-*O*,*O*-diphenyl phosphorothioate.[40] **5j**, colorless oil (78%, 72.5 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.80 (s, 3H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.19-7.22 (m, 6H), 7.33-7.39 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6, 115.2 (2C), 120.6 (4C), 125.6 (2C), 129.9 (5C), 137.2 (2C), 150.5, 150.6, 161.1. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.6. GC-MS (EI) *m/z*: 372.

S-methyl diphenylphosphinothioate. **5k**, colorless oil (30%, 18.6 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (d, *J* = 12.0 Hz, 3H), 7.41-7.44 (m, 4H), 7.47-7.50 (m, 2H), 7.79-7.84 (m, 4H). ^{13}C NMR

($CDCl_3$, 125 MHz) δ 9.57, 127.7, 127.8, 130.5, 130.6, 131.3 (2C), 132.2 (2C). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 44.5. HRMS (EI) Calcd. for $C_{13}H_{13}OPS$ 248.0425, found 248.0418.

2,2,6,6-Tetramethyl-1-((*p*-tolylthio)oxy)piperidine.[41] **A,** white solid, m.p. 62-64 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 12H), 1.59 (s, 6H), 2.32 (s, 3H), 7.15-7.17 (d, J = 8.0 Hz. 2H), 7.66-7.67 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.9, 22.5, 32.2, 45.0, 61.8, 127.3, 130.2, 142.8, 145.7. MS (ESI) *m/z*: 280 $[M+H]^+$.

Supporting Information

Mechanism experiments, quantum chemical calculations and copies of NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgements

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