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Acid/Phosphide-Induced Radical Route to Alkyl and Alkenyl Sulfides and Phosphonothioates from Sodium Arylsulfinates in Water

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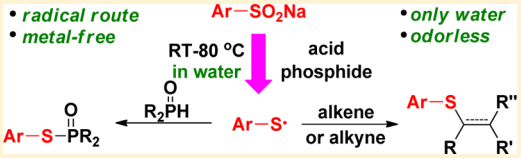
Supporting Information

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 and 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 thiol odors, 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, and (3) thermolysis.[2] Nevertheless, most of these approaches suffer from limitations including bad odor, air-sensitive thiols or their derivatives preprepared from them, and the need for metal catalysts, excess oxidants and toxic organic solvents, and high temperature (in the cases of thermolysis). Thus, 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 within the concept of green chemistry and an appealing task in sulfur chemistry.[4]

Furthermore, radicals in the ecofriendly 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 stable, odorless, and easy-to-handle sulfur compounds that have been widely applied as sulfonating agents[2] or coupling partners via 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 aryl sulfide cations. Thus, sodium arylsulfinates also have great potential for deriving the corresponding arylsulfenyl radicals under the designated reduction conditions.

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

RESULTS AND DISCUSSION

During the investigation of the synthesis of *β*-iodoalkenyl sulfides,[9] a trace of alkenyl sulfide **3a** was found in the presence of base (Table 1, entry 1). Encouraged by this result, 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 (entries 9 and 15). The amounts of H_2SO_4 and sodium *p*-toluenesulfinate and reaction temperature were also optimized (entries 10−18). The best option was to use 2.0 equiv of sodium *p*-toluenesulfinate and 0.5 equiv of H_2SO_4 at 80 °C (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 diethyl 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).

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 and 15−20).

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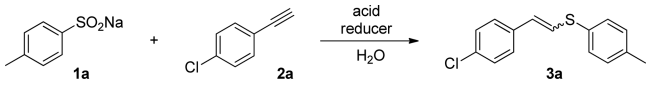
Table 1. Optimization of Reaction Conditions[a]



entry	additive (x equiv)	reducer	temp (°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 °C, 10 h. [b]The yield of **3a** and the 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.

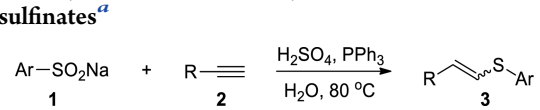
Aliphatic alkynes could also provide the corresponding products, but the stereoselectivity was poor (entries 8−11). Heteroaryl acetylenes were also applied in the reaction successfully with satisfactory results (entries 12−14).

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−f,m,n**), and alkylalkenes can also provide the desired adducts (**4h−l**). 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 when that *N*-benzyl-1*H*-pyrrole-2,5-dione was used. 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,b,f−h**). The formation of products was also observed in the cases of diaryl chlorophosphines without acid (**5a,c−e**). 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.

To further probe the mechanism, radical-trapping experiments were designed and investigated (see Table S1). All of the

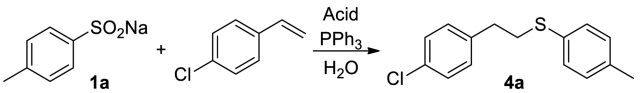
Table 2. Hydrothiolation of Alkynes with Sodium Arylsulfinates[a]



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. Optimization of Reaction Conditions[a]



entry	x	temp (°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.

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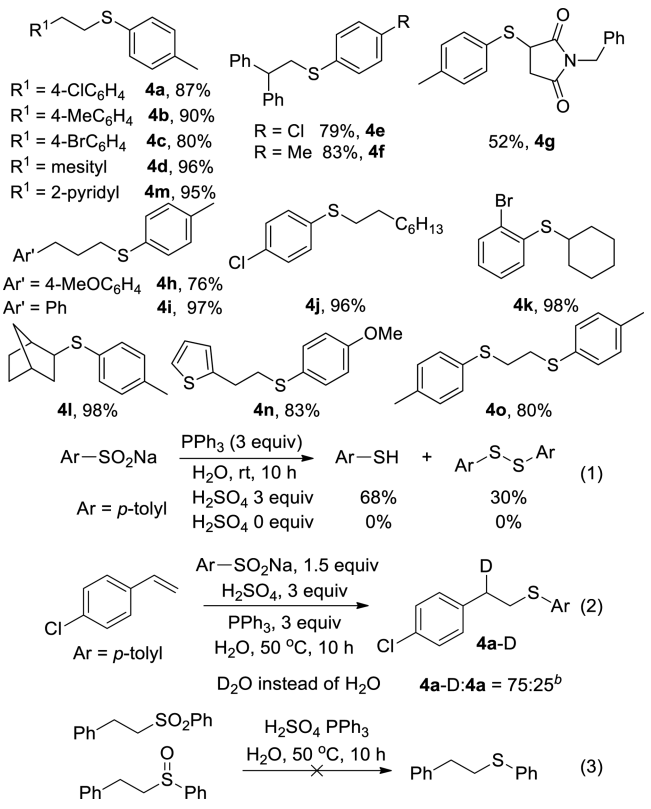
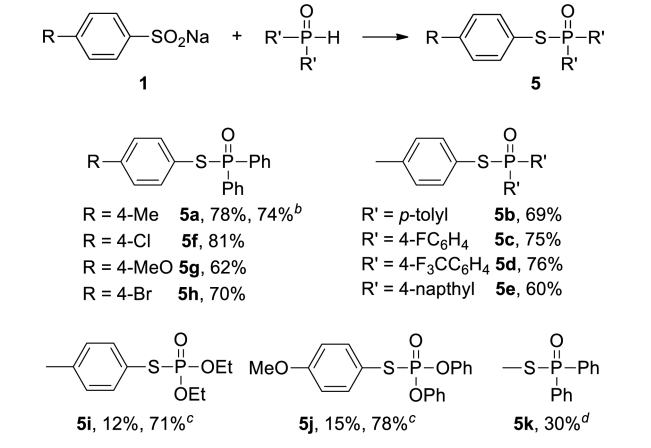
Scheme 1. Hydrothiolations of Alkenes with Sodium Arylsulfinates[a]



[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.

Scheme 2. Reactions of Sodium Arylsulfinates and *H*-Phosphine Oxides[a]

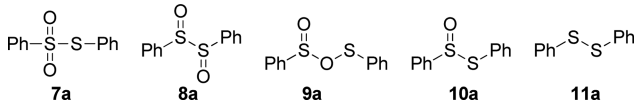


[a]Conditions: sodium arylsulfinates (0.250 mmol), *H*-phosphine oxides (0.500 mmol), H_2SO_4 (0.125 mmol), H_2O (1.0 mL), rt, 6 h. Isolated yields. [b]Use of diaryl phosphate chloride instead of *H*-phosphine oxides in the absence of H_2SO_4. [c]The reaction was performed in DMF without H_2SO_4 at 100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

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** and **C** were separated and further identified by ^1H 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 the H_2SO_4/PPh_3 system (Figure S1).

Control experiments were also performed to confirm whether *S*-phenyl benzenesulfonothioate, 1,2-di-*p*-tolyldisulfane, or 4-methylbenzenethiol were the intermediates in the system (Table S2). Although the desired products could be obtained with satisfactory yields in some cases, these reactions did not contain a radical route. Thus, none of them are the intermediates in these reactions. According to the calculation results of the bond dissociation energies (BDEs) (Table 4), it can be concluded that **8a** and **10a** have a higher probability of yielding a radical by homolysis than other intermediates.[12]

Table 4. Calculated Values of Some Possible Intermediates' BDEs Based on Quantum Calculations



		BDE (kJ/mol)	
compd	dissociation bond	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.

On the basis of these results, a proposed mechanism of the formation of aryl sulfenyl radicals in the H_2SO_4/PPh_3 system is illustrated in Figure 1. Compounds **8** and **10** are generated from

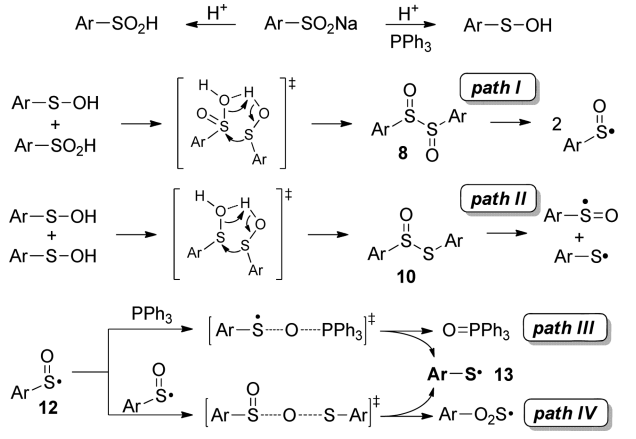


Figure 1. Proposed mechanism of the sulfenyl radical generation from sodium arylsulfinates in the H_2SO_4/PPh_3 system.

sodium arylsulfinates in the H_2SO_4/PPh_3 system[12a] and 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 on the basis of the studies of density functional theory (DFT) (see Table S3). The free energy barriers of path **I** and **II** are close,

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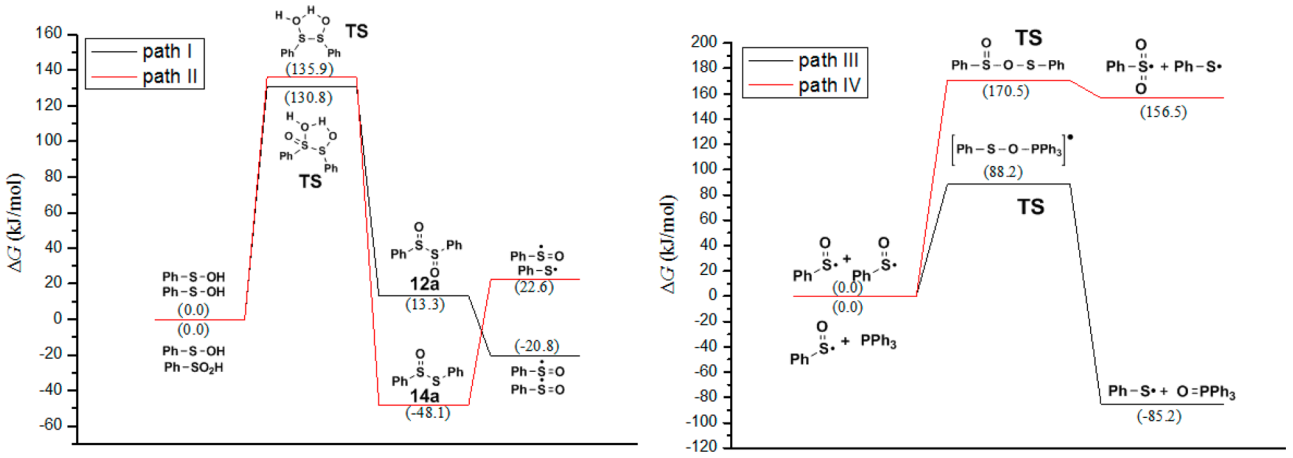

Figure 2. Relative free energy profiles (kJ/mol) for paths **I**–**IV**.

while the free energy barrier of path **III** is much lower than that of 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.

Although the detailed mechanisms of these reactions remain to be elucidated, a tentative pathway for the hydrothiolations of alkenes is proposed (Figure 3). Arylsulfenyl radical in situ

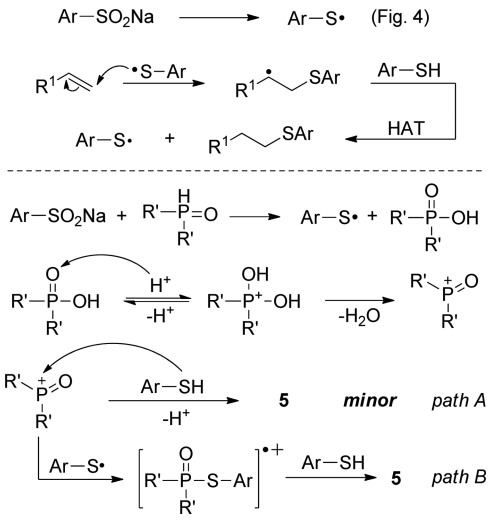

Figure 3. Tentative mechanisms.

generated from sodium arylsulfinite based on the processes in Figure 2 adds to alkene to afford carbon radical intermediate following a 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 and ^{13}C NMR and GC–MS (Table S1), 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 the 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 promotes the reduction of sodium arenesulfonates, and use of the phosphide as a reducing agent may enhance 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 and 0.125 mmol), and H_2SO_4 in water (1.0 mL) was stirred at 80 °C for 10 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL) and 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 and 0.75 mmol), and H_2SO_4 in water (1.0 mL) was stirred at 50 °C for 10 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL) and 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) and 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 (E-3a):*[16] 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,

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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 (**3b**):*.[17,18] yellow oil 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 (**3c**):*.[17,18] yellow oil 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 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 (**3e**):*[19] yellow oil 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 = 8.0 Hz, 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 (**3f**):*[20] yellow oil 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 = 16.0 Hz, 1H (*E*-**3f**)), 6.32−6.35 (m, 2H, *Z*-**3f**), 6.73−6.76 (d, J = 15.5 Hz, 1H (*E*-**3f**)), 6.82−6.86 (m, 2H (*E*-**3f**), 2H (*Z*-**3f**)), 7.11−7.13 (d, J = 8.5 Hz, 2H (*E*-**3f**)), 7.16−7.19 (m, 2H, *E*-**3f**), 7.27−7.29 (d, J = 8.5 Hz, 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 (mp 72−74 °C) 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 = 15.5 Hz, 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 = 8.0 Hz, 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 (**3h**):*[21] yellow oil 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 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 obtained as a mixture of stereoisomers in 60:40 (E/Z) ratio (90%, 52.7 mg); ^{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 obtained as a mixture of stereoisomers in 64:36 (E/Z) ratio (92%, 57.1 mg); ^{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; mp 95−97 °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 = 8.0 Hz, 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; mp 116−118 °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 (**3n**):*[22] yellow oil obtained as a mixture of stereoisomers in 15:85 (E/Z) ratio (89%, 56.1 mg); ^{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 (**3o**):*[23] yellow oil obtained as a mixture of stereoisomers in 88:12 (E/Z) ratio (72%, 38.2 mg); ^{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

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(*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 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 (***3q***)*:*[24] light yellow oil 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 (***3r***)*:*[25] light yellow oil 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 (***3s***)*:*[26] light yellow oil obtained as a mixture of stereoisomers in 50:50 (*E*/*Z*) ratio (82%, 59.4 mg); ^{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 (***3t***)*:*[27] light yellow oil 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* = 15.5 Hz, 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* = 7.5 Hz, 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 (***4a***)*:*[28] 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 (***4b***)*:*[29] 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 (***4c***)*:*[30] 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; mp 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 (***4f***) *(radical trapping product* ***C***)*:*[30] 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 (***4g***)*:*[31] 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 (***4i***)*:*[29] 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 (***4j***)*:*[32] 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 (***4k***)*:*[33] 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 (***4l***)*:*[34] 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 (***4m***)*:*[35] 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 (***4o***)*:*[36] 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

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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 (**5a**):*[37] white solid; mp 110−112 °C (lit.[37] mp 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; mp 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; mp 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; mp 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 (**5f**):*[1e] white solid; mp 99−101 °C (lit.[1e] mp 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-Nethoxyphenyl)diphenylphosphinothioate (**5g**):*[1e] white solid; mp 141−143 °C (lit.[1e] mp 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 (**5h**):*[38] white solid; mp 148−150 °C (lit.[38] mp 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 (**5i**):*[39] 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 (**5j**):*[40] 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 (**A**):*[41] white solid; mp 62−64 °C; ^{1}H 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 $[M + H]^+$.

■ ASSOCIATED CONTENT

Supporting Information

Mechanism experiments, quantum chemical calculations, and copies of NMR spectra of all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02459.

Mechanism experiments, quantum chemical calculations, and copies of NMR spectra of all products (PDF)

Tables of atom coordinates and absolute energies to document the theoretical calculations (PDF)

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Notes

The authors declare no competing financial interest.

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