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Addition of diphenylphosphinodithioic acid and thioacetic acid with vinylidenecyclopropanes: reversed regioselectivities

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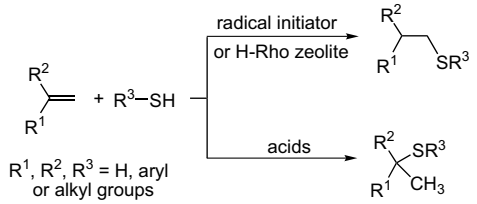
ABSTRACT

The reaction of vinylidenecyclopropanes **1** with diphenylphosphinodithioic acid produces the adducts **3** in good to high yields in toluene upon heating at 100 °C within 1 h, whereas adducts **5** are obtained in excellent yields in reversed regioselectivity from the reaction of **1** with thioacetic acid under identical conditions. The radical reaction processes have been discussed on the basis of deuterium labeling experiment and the control experiments in the presence of radical inhibitors (TEMPO and BHT) or a proton scavenger (DTBMP).

1. Introduction

Thiocarbonyl or thiophosphoryl groups containing compounds are very useful building blocks in the synthesis of various sulfur-containing organic compounds[1] which play important roles in biological and chemical processes.[2] Thus far, the synthesis of thiocarbonyl or thiophosphoryl groups containing compounds is very similar as the preparation of thioethers and their analogues from the addition of alkenes with thiols achieved by radical initiators[3] or Brønsted acid such as sulfuric and perchloric acids.[3a,4] Generally, the free radical process produces anti-Markovnikov-type adducts, while the acid-catalyzed/promoted[5,6] process leads to Markovnikov-type adducts (Scheme 1).



Scheme 1. Two types of addition of thiols to double bonds.

Vinylidenecyclopropanes (VDCPs) **1** are one of the most remarkable organic compounds in the area of highly strained small rings, which have an allene moiety connected by a cyclopropane ring and yet they are thermally stable and reactive substances in organic synthesis. Much pioneering work has been done for this kind of particular organic compounds.[7,8] However, few reports on the intermolecular radical reactions of VDCPs to form thiocarbonyl or thiophosphoryl groups containing compounds or thioethers have been reported so far. For example, Pasto and co-workers have reported the radical addition reactions of vinylidenecyclopropane with 1,1-dichloro-2,2-difluoroethylene or thiophenol to provide the corresponding addition products in good yields (Scheme 2).[9,10] In the radical addition of vinylidenecyclopropane with thiophenol, the corresponding 1,2-addition product was obtained in good yield. In this paper, we wish to disclose that in the reactions of VDCPs **1** with diphenylphosphinodithioic acid or thioacetic acid upon heating in toluene, the corresponding thiophosphoryl or thiocarbonyl groups adducts were obtained in good yields in different regioselectivities.

2. Results and discussion

Initial examinations were performed by using diphenylvinylidenecyclopropane **1a** as substrate to react with diphenylphosphinodithioic acid **2** in various solvents at different temperatures [from room temperature (25 °C) to 100 °C] and the results of these experiments are summarized in Table 1. In the presence of radical initiator such as azobis(isbutyronitrile) (AIBN), we found that the

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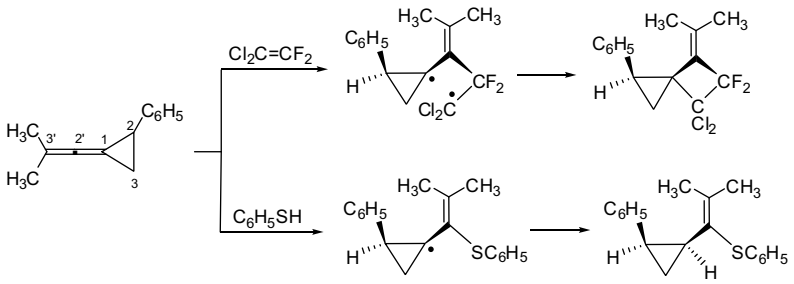
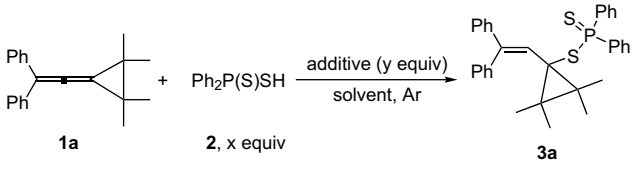


Scheme 2. Radical reactions of VDCP with multi-halo-substituted alkene and thiophenol.

Table 1
Optimization of the reaction conditions of **1a** with **2**



Entry[a]	Solvent	Additive	*x*	*y*	Temp (°C)	Time (h)	Yield [b] (%) **3a**
1	Toluene	AIBN	1.1	1.1	100	3	54
2	*Toluene*		*1.1*		*100*	*1*	*94*
3	Toluene	TEMPO	1.0	1.0	100	4	—[c]
4	Toluene	BHT	1.0	1.0	100	4	90
5	Toluene		1.0		25	1	Complex
6	MeCN		1.1		80	1	22
7	DCE		1.1		80	1	53
8	Benzene		1.1		70	1	71
9[d]	DMF		1.1		100	24	4

[a] Reaction conditions: VDCP **1a** (0.18 mmol), **2** (*x* equiv) and additive (*y* equiv) were dissolved in toluene (3 mL), then the mixtures were stirred for different time at various temperatures.
[b] Isolated yield.
[c] 76% of **1a** was recovered.
[d] 92% of **1a** was recovered.

corresponding 1,2-addition product **3a** was produced in 54% yield in toluene at 100 °C within 3 h (Table 1, entry 1). Interestingly, in the absence of any additive, **3a** was given in 94% yield under otherwise identical conditions within 1 h (Table 1, entry 2). It was not surprised that there was nearly none of product **3a** obtained in the presence of radical inhibitor such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) along with the recovery of the starting materials **1a** in 76% yield (Table 1, entry 3). However, another radical inhibitor 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) has no influence on the reaction outcome, giving adduct **3a** in 90% yield (Table 1, entry 4). If the reaction was carried out at room temperature (25 °C), many unidentified products including **3a** were produced within 1 h (Table 1, entry 5). In some other solvents, such as acetonitrile, 1,2-dichloroethane (DCE), benzene and *N*,*N*-dimethylformamide (DMF), **3a** was produced in lower yields than that in toluene (Table 1, entries 6–9). The structure of **3a** has been determined by IR, NMR, MS spectroscopic data and elemental analysis as well as the X-ray diffraction. The ORTEP drawing is shown in Figure 1 and its CIF data have been presented in Supplementary data.[11]

Under these optimized conditions, we next examined the generality of this transformation using a variety of vinylidenecyclopropanes **1**. The results are summarized in Table 2. We found that the corresponding adducts **3** were obtained in good to high yields within 1 h whether R^1 group of **1** was an aryl or alkyl group or the electron-donating or -withdrawing groups were introduced on the aromatic rings (Table 2). As for symmetrical diarylvinylidenecyclopropanes **1b–e**, the corresponding adducts **3b–e** were obtained in good to excellent yields as the corresponding sole

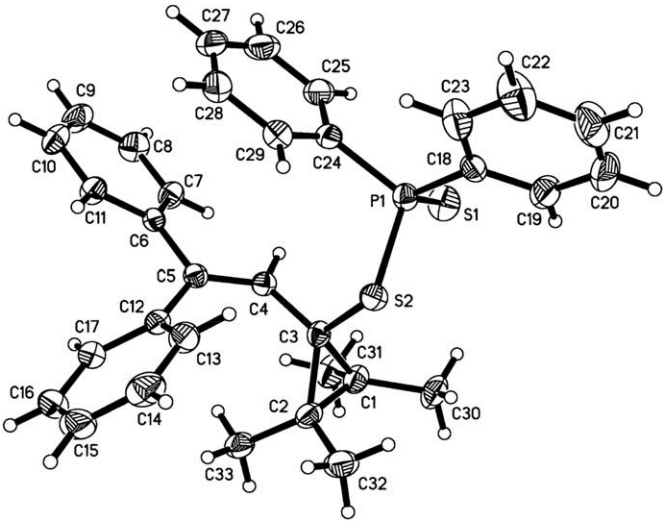
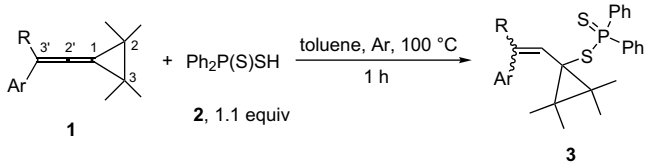


Figure 1. The ORTEP drawing of compound **3a**.

products (Table 2, entries 1–4). As for the unsymmetrical vinylidenecyclopropanes **1f–k** bearing different aryl or alkyl groups at the C3′ position, the corresponding adducts were obtained as mixtures of *E*- and *Z*-isomers in good yields (Table 2, entries 5–10).

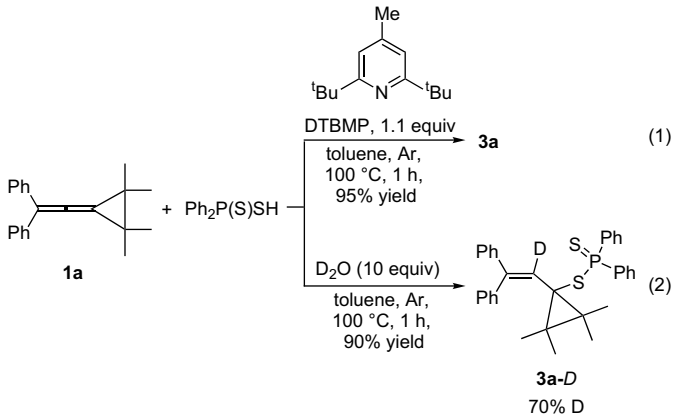
Table 2
Radical addition reactions of **1** with **2** under the optimal conditions



Entry[a]	R/Ar	Yield[b] (%) **3**
1	*p*-$CH_3C_6H_4$/*p*-$CH_3C_6H_4$, **1b**	**3b**, 90
2	*p*-$CH_3OC_6H_4$/*p*-$CH_3OC_6H_4$, **1C**	**3c**, 99
3	*p*-ClC_6H_4/*p*-ClC_6H_4, **1d**	**3d**, 79
4	*p*-FC_6H_4/*p*-FC_6H_4, **1e**	**3e**, 84
5	*p*-$CH_3OC_6H_4$/C_6H_4, **1f**	**3f**, 83[c]
6	*p*-ClC_6H_4/C_6H_4, **1g**	**3g**, 83[d]
7	*p*-FC_6H_4/C_6H_4, **1h**	**3h**, 82[e]
8	*m*,*p*-di-FC_6H_4/C_6H_4, **1i**	**3i**, 72[f]
9	*o*-$CH_3C_6H_4$/C_6H_4, **1j**	**3j**, 76[g]
10	CH_3/C_6H_4, **1k**	**3k**, 78[h]

[a] Reaction conditions: VDCP **1** (0.18 mmol) and **2** (1.1 equiv) were dissolved in toluene (3.0 mL), and then the mixtures were stirred for 1 h at 100 °C.
[b] Isolated yield.
[c] *E*- or *Z*-isomeric mixture=3:2.
[d] *E*- or *Z*-isomeric mixtures=1:1.
[e] *E*- or *Z*-isomeric mixtures=1:1.
[f] *E*- or *Z*-isomeric mixtures=1:1.
[g] *E*- or *Z*-isomeric mixtures=2:1.
[h] *E*- or *Z*-isomeric mixtures=4:1.

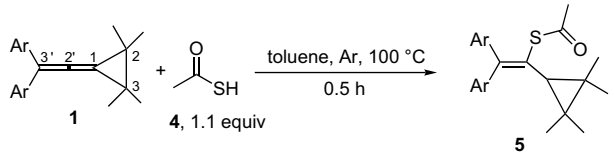
In order to have a clear understanding of the mechanism for this process, we also examined the reaction of diphenylvinylidenecyclopropane **1a** with diphenylphosphinodithioic acid **2** under these optimized reaction conditions in the presence of 1.1 equiv of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), which has weak nucleophilicity and is often used as a scavenger of proton or protic acid.[12] We found that the yield of the product **3a** was not affected in this situation, which can exclude the carbocationic process (run 1, Scheme 3). On the other hand, when the reaction was carried out in the presence of D_2O (10.0 equiv), the corresponding addition product was formed in 90% yield along with 70% of D content, suggesting that there is a rapid deuterium–proton exchange between diphenylphosphinodithioic acid and D_2O and subsequently a radical reaction takes place to give the deuterium-containing adduct (run 2, Scheme 3).



Scheme 3. Control and deuterium labeling experiments in the reaction of **1a** with $Ph_2P(S)SH$.

More interestingly, when using 1.1 equiv of thioacetic acid instead of $Ph_2P(S)SH$ to react with diphenylvinylidenecyclopropane **1a** under identical conditions, we found that the adduct **5a** was produced in 94% yield (Table 3, entry 1). In order to confirm this unexpected regioselectivity, a variety of vinylidenecyclopropanes **1** were examined in this reaction and the results are shown in Table 3. As for symmetrical vinylidenecyclopropanes having either electron-donating or -withdrawing groups on the benzene rings, the corresponding adducts **5** were obtained in excellent yields within 0.5 h (Table 2, entries 2–5).

Table 3
Addition reactions of **1** with thiocarboxylic acid



Entry[a]	Ar	Yield[b] (%) **5**
1	C_6H_5, **1a**	**5a**, 94
2	*p*-$CH_3C_6H_4$, **1b**	**5b**, 99
3	*p*-$CH_3OC_6H_4$, **1c**	**5c**, 96
4	*p*-ClC_6H_4, **1d**	**5d**, 96
5	*p*-FC_6H_4, **1e**	**5e**, 99

[a] Reaction conditions: VDCP **1** (0.18 mmol) and **4** (1.1 equiv) were dissolved in toluene (3.0 mL), and then the mixtures were stirred for 0.5 h at 100 °C.
[b] Isolated yield.

When radical inhibitors, such as TEMPO and BHT, were added in this reaction system, it was found that the yields of addition product **5a** dropped to 21% and 19%, along with the recovery of 68% and 64% of the substrate **1a**, respectively. When the reaction was carried out in the presence of DTBMP, the adduct **5a** was formed in 65% yield along with the recovery of 10% of **1a** (Scheme 4). These results suggest that the radical process should be the main pathway in this addition reaction.

On the other hand, we also examined the reaction of diphenylvinylidenecyclopropane **1a** with thiophenol **6** (1.1 equiv) in toluene at 100 °C and found that the adduct **8** was given in 95% yield after 1 h (Scheme 5, Eq. 1). It should be noted that using *O*,*O*-diethyl S-hydrogen phosphorodithioate **7** to replace **2** in the reaction with **1a** under identical conditions, the corresponding adduct **9** was produced in 93% yield as a variety of isomeric mixtures on the basis of ^{31}P NMR spectrum, presumably attributed to the intramolecular exchange of sulfur–oxygen atom in product **9** (Scheme 5, Eq. 2).

The reversed regioselectivity could be explained by the steric effect of the racial intermediates. Generally, the radical intermediate **B** is more stable than the vinyl radical intermediate **A**,[13] but the former is difficult to abstract the hydrogen atom of **2** to give another sulfur-containing radical species for the next cycle due to the steric repulsion between the sterically large diphenylphosphinodithioic acidic radical and the tetramethyl substituted cyclopropane in intermediate **B**. Therefore, the abstraction of a hydrogen atom from **2** by radical intermediate **A** is sterically favored. However, in the case of the addition of **1a** with **4**, the more stable radical intermediate **D** can abstract the hydrogen atom from **4** since the thiocarboxylic acid radical is sterically planar species. Consequently, the additions of **2** to vinylidenecyclopropanes and **4** to vinylidenecyclopropanes have reversed regioselectivities by undergoing different radical intermediates **A** and **D**, respectively (Fig. 2).[13a]

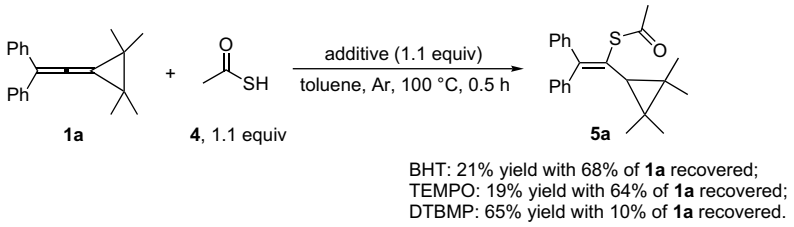
3. Conclusion

We have disclosed here a previously unknown radical addition reaction of vinylidenecyclopropanes **1** with diphenylphosphinodithioic acid **2** and thioacetic acid **4** in toluene upon heating at 100 °C within short reaction time to give the corresponding adducts smoothly. In the case of **1** with diphenylphosphinodithioic acid **2**, the corresponding adducts **3** were obtained in good to high yields. However, in the case of **1** with thioacetic acid **4** or thiophenol **6**, the corresponding adducts **5** or **8** could be formed in excellent yields in a reversed regioselectivities. A wide range of vinylidenecyclopropanes **1** have been examined in these reactions and the plausible radical reaction processes have been discussed on the basis of deuterium labeling and the control experiments in the presence of radical inhibitors such as TEMPO and BHT or proton scavenger such as DTBMP. These processes provide novel and efficient synthetic routes for the preparation of useful thiophosphoryl or thiocarbonyl groups containing compounds under mild conditions which are remarkably useful compounds serving as building blocks in the synthesis of various organosulfur containing compounds. Efforts are in progress to further elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

4. Experimental section

4.1. General methods

^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded at 300 or 400, 75 or 100, 282, and 121.45 MHz respectively. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), Bruker FT mass spectrometer (ESI), and IonSpec 4.7 Tesla FTMS (MALDI). Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Yinlong GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.



Scheme 4. Reactions of **1a** with thiocarboxylic acid in the presence of additives.

4.2. General procedure for the cycloaddition of vinylidenecyclopropanes 1 with diphenylphosphinodithioic acid 2 or thioacetic acid 4

Under argon atmosphere, vinylidenecyclopropanes (VDCPs) **1** (0.18 mmol) and diphenylphosphinodithioic acid **2** or thioacetic acid **4** (0.20 mmol, 1.1 equiv) were dissolved in toluene (3.0 mL), and then the resulting mixtures were stirred for 0.5 to 1.0 h at 100 °C. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel column with petroleum ether–EtOAc (40:1) as an eluent.

*4.2.1. 1-(2,2-Diphenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2a***

A white solid, Mp: 202–204 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.38 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 6.19 (s, 1H, CH), 6.86 (d, J=6.3 Hz, 2H, Ar), 7.07–7.15 (m, 6H, Ar), 7.23–7.41 (m, 8H, Ar), 7.73 (dd, J=7.5, 13.5 Hz, 2H, Ar), 7.91 (dd, J=6.9, 13.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.3, 19.6 (d, J_{C-P}=13.6 Hz), 21.3, 27.9, 30.5 (d, J_{C-P}=6.4 Hz), 41.4 (d, J_{C-P}=3.8 Hz), 126.8, 127.1, 127.3, 127.4, 127.7 (d, J_{C-P}=13.5 Hz), 128.2, 128.3 (d, J_{C-P}=17.3 Hz), 129.7 (d, J_{C-P}=2.1 Hz), 130.4, 130.7 (d, J_{C-P}=7.7 Hz), 130.9, 131.3, 131.9 (d, J_{C-P}=11.3 Hz), 134.1 (d, J_{C-P}=84.4 Hz), 136.3 (d, J_{C-P}=85.5 Hz), 140.6, 143.3, 143.4. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 59.5. IR (CH_2Cl_2) ν 3055, 2919, 2866, 1714, 1634, 1436, 1375, 1096, 1027, 768, 718, 697, 651 cm^{-1}. MS (%) *m*/*e* 524 (M^+, 5), 307 (100), 291 (19), 275 (25), 259 (29), 233 (49), 223 (83), 121 (27), 91 (25). Anal. Calcd for $C_{33}H_{33}S_2$: C, 75.54%; H, 6.34%. Found: C, 75.56%; H, 6.20%.

*4.2.2. 1-(2,2-Di-p-tolylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2b***

A white solid, Mp: 184–186 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.41 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.10 (s, 1H, CH), 6.74 (d, J=8.4 Hz, 2H, Ar), 6.91 (d, J=8.4 Hz, 2H, Ar), 7.06–7.08 (m, 5H, Ar), 7.24–7.37 (m, 5H, Ar), 7.72 (dd, J=7.2, 13.5 Hz, 2H, Ar), 7.89 (dd, J=6.9, 14.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.3, 19.7 (d, J_{C-P}=11.5 Hz), 21.0, 21.3, 27.9, 30.5 (d, J_{C-P}=6.5 Hz), 41.6 (d, J_{C-P}=3.5 Hz), 127.7 (d, J_{C-P}=13.4 Hz), 128.0, 128.2, 128.4, 128.5 (d, J_{C-P}=2.0 Hz), 130.3, 130.7 (d, J_{C-P}=10.7 Hz), 131.3, 131.9 (d, J_{C-P}=11.3 Hz), 134.2 (d, J_{C-P}=84.1 Hz), 136.3, 136.4 (d, J_{C-P}=85.8 Hz), 136.7, 136.9, 137.7, 140.8, 143.2. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.3. IR (CH_2Cl_2) ν 3054, 2999, 2918, 2866, 1510, 1436, 1374, 1096, 823, 718, 689, 655,

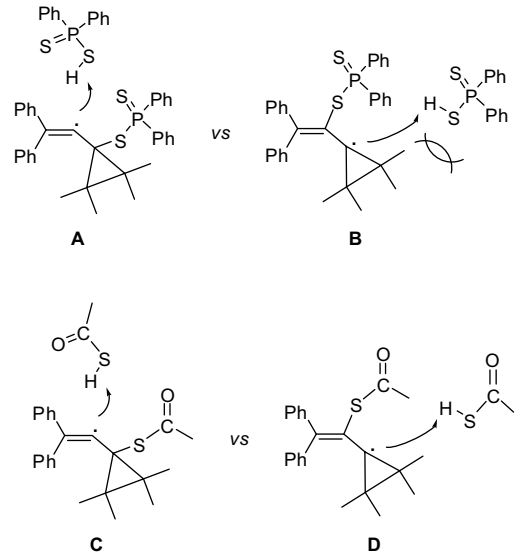
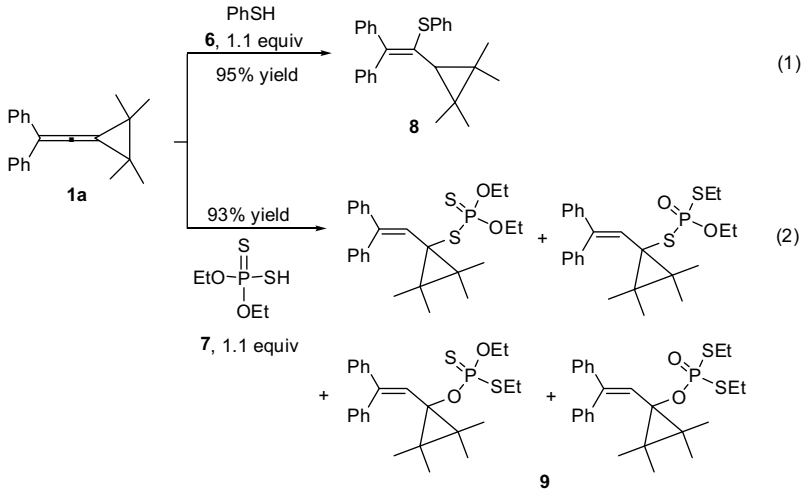


Figure 2. The two types of radical species of the addition reaction.



Scheme 5. Reactions of **1a** with two other sulfur-containing compounds.

525 cm^{-1}. MS (%) *m*/*e* 552 (M^+, 0.3), 383 (0.3), 335 (100), 302 (2.0), 287 (2.4), 261 (1.4), 251 (1.9), 216 (0.9), 210 (1.6). HRMS (EI) for $C_{35}H_{37}S_2P$: 552.2074. Found: 552.2076.

4.2.3. 1-(2,2-Bis(4-methoxyphenyl)vinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2c**

A white solid, Mp: 138–140 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.41 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.02 (s, 1H, CH), 6.64 (d, *J*=6.9 Hz, 2H, Ar), 6.76–6.83 (m, 4H, Ar), 7.06–7.10 (m, 3H, Ar), 7.34–7.37 (m, 5H, Ar), 7.73 (dd, *J*=6.6, 13.8 Hz, 2H, Ar), 7.92 (dd, *J*=6.6, 14.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.2, 19.6 (d, J_{C-P}=12.8 Hz), 21.3, 27.8, 30.3 (d, J_{C-P}=6.2 Hz), 41.7 (d, J_{C-P}=3.1 Hz), 55.1, 55.2, 112.6, 112.7, 127.3, 127.5 (d, J_{C-P}=13.1 Hz), 128.3 (d, J_{C-P}=12.8 Hz), 129.3, 130.6, 130.7, 131.3, 131.6, 131.9 (d, J_{C-P}=10.7 Hz), 133.2, 134.1 (d, J_{C-P}=83.7 Hz), 136.26, 136.30 (d, J_{C-P}=84.8 Hz), 142.4, 158.6, 158.7. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 59.9. IR (CH_2Cl_2) ν 3055, 2998, 2916, 2835, 1606, 1510, 1437, 1289, 1246, 1174, 1096, 1035, 834, 717, 690, 655, 526 cm^{-1}. MS (%) *m*/*e* 367 (M^+-Ph_2PS, 58), 334 (84), 319 (100), 293 (21), 278 (28), 250 (27), 217 (49), 121 (48), 43 (45). HRMS (EI) for $C_{35}H_{37}S_2O_2P$: 584.1973. Found: 584.1984.

4.2.4. 1-(2,2-Bis(4-chlorophenyl)vinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2d**

A white solid, Mp: 191–193 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.45 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 6.21 (s, 1H, CH), 6.76 (d, *J*=8.7 Hz, 2H, Ar), 7.07–7.10 (m, 5H, Ar), 7.22–7.30 (m, 4H, Ar), 7.36–7.38 (m, 3H, Ar), 7.71 (dd, *J*=6.9, 13.2 Hz, 2H, Ar), 7.88 (dd, *J*=6.9, 13.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.3, 19.7 (d, J_{C-P}=19.7 Hz), 21.2, 28.0, 30.6 (d, J_{C-P}=5.7 Hz), 41.0 (d, J_{C-P}=3.2 Hz), 127.70, 127.74, 127.9, 128.4 (d, J_{C-P}=13.2 Hz), 129.3, 130.7 (d, J_{C-P}=10.4 Hz), 130.9, 131.0, 131.1, 131.6, 131.9 (d, J_{C-P}=10.9 Hz), 133.0 (d, J_{C-P}=20.6 Hz), 134.1 (d, J_{C-P}=84.7 Hz), 136.1 (d, J_{C-P}=85.4 Hz), 138.5, 141.0, 141.4. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 60.0. IR (CH_2Cl_2) ν 3055, 2998, 2918, 2859, 1716, 1491, 1436, 1375, 1217, 1093, 1014, 833, 719, 689, 653, 518 cm^{-1}. MS (%) *m*/*e* 592 (M^+, 7), 518 (6), 375 (100), 327 (31), 291 (80), 217 (60), 155 (33), 139 (66), 125 (27). HRMS (EI) for $C_{33}H_{31}S_2PCl_2$: 592.0982. Found: 592.0980.

4.2.5. 1-(2,2-Bis(4-fluorophenyl)vinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2e**

A white solid, Mp: 165–167 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.40 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 6.14 (s, 1H, CH), 6.80 (d, *J*=6.6 Hz, 4H, Ar), 6.94–7.00 (m, 2H, Ar), 7.12 (br s, 3H, Ar), 7.33–7.38 (m, 5H, Ar), 7.71 (dd, *J*=7.2, 13.8 Hz, 2H, Ar), 7.91 (dd, *J*=7.2, 13.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.2, 19.7 (d, J_{C-P}=17.3 Hz), 21.2, 27.9, 30.4 (d, J_{C-P}=6.0 Hz), 41.2 (d, J_{C-P}=3.5 Hz), 114.3 (d, J_{C-F}=21.2 Hz), 114.4 (d, J_{C-F}=21.4 Hz), 127.7 (d, J_{C-P}=13.2 Hz), 128.4 (d, J_{C-P}=13.5 Hz), 129.6 (d, J_{C-F}=8.3 Hz), 129.8, 130.7 (d, J_{C-P}=11.0 Hz), 131.0, 131.5, 131.8, 131.9 (d, J_{C-P}=7.2 Hz), 134.1 (d, J_{C-P}=84.5 Hz), 136.1 (d, J_{C-P}=85.6 Hz), 136.3 (d, J_{C-F}=3.1 Hz), 139.2 (d, J_{C-F}=2.9 Hz), 141.2, 161.9 (d, J_{C-F}=246.3 Hz), 162.1 (d, J_{C-F}=244.2 Hz). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.1. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ −119.7, −121.2. IR (CH_2Cl_2) ν 3055, 2999, 2919, 2868, 1600, 1508, 1437, 1375, 1229, 1157, 1096, 1015, 910, 840, 718, 690, 656, 525 cm^{-1}. MS (%) *m*/*e* 560 (M^+, 3), 486 (3), 343 (100), 269 (49), 259 (100), 217 (39), 183 (25), 139 (86), 109 (30). HRMS (EI) for $C_{33}H_{31}S_2PF_2$: 560.1573. Found: 560.1571.

4.2.6. (E or Z)-1-(2-(4-Methoxyphenyl)-2-phenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2f**

A white solid, Mp: 111–1113 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.41 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.08 (s, 1H, CH), 6.81–6.85 (m, 4H, Ar), 7.05–7.15 (m, 6H, Ar), 7.34–7.38 (m, 5H, Ar), 7.72 (dd, *J*=7.5, 13.5 Hz, 2H, Ar), 7.91 (dd, *J*=7.2, 14.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 19.6 (d, J_{C-P}=14.4 Hz), 21.3, 22.6, 27.9, 30.4 (d, J_{C-P}=7.2 Hz), 31.6, 41.6 (d, J_{C-P}=4.1 Hz), 55.2, 112.7, 126.8, 127.4, 127.7 (d, J_{C-P}=13.3 Hz), 128.3, 128.4, 128.7 (d, J_{C-P}=1.9 Hz), 130.7 (d, J_{C-P}=11.1 Hz), 131.0, 131.3, 131.6, 131.9 (d, J_{C-P}=11.1 Hz), 133.0, 134.1 (d, J_{C-P}=84.0 Hz), 136.3 (d, J_{C-P}=85.6 Hz), 143.1, 143.6, 158.6. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.2. IR (CH_2Cl_2) ν 3056, 2999, 2917, 2867, 2835, 1606, 1510, 1437, 1374, 1295, 1248, 1178, 1096, 1034, 908, 839, 718, 690, 655, 641, 606, 526 cm^{-1}. MS (%) *m*/*e* 554 (M^+, 2), 337 (100), 304 (36), 289 (52), 263 (41), 253 (57), 217 (31), 165 (17), 139 (20). HRMS (EI) for $C_{34}H_{35}S_2OP$: 554.1867. Found: 554.1864.

4.2.7. (Z or E)-5-(4-Methoxyphenyl)-2-methyl-5-phenyl-3-(propan-2-ylidene)pent-4-en-2-yl diphenylphosphinodithioate **2f**

A white solid, Mp: 105–107 °C; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.36 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 6.12 (s, 1H, CH), 6.66 (d, *J*=9.2 Hz, 2H, Ar), 6.80 (d, *J*=9.2 Hz, 2H, Ar), 7.07–7.11 (m, 3H, Ar), 7.25–7.27 (m, 3H, Ar), 7.38–7.43 (m, 5H, Ar), 7.73 (dd, *J*=7.5, 13.5 Hz, 2H, Ar), 7.92 (dd, *J*=7.2, 13.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.3, 19.7 (d, J_{C-P}=20.9 Hz), 21.3, 27.8, 30.4 (d, J_{C-P}=7.2 Hz), 41.6 (d, J_{C-P}=3.3 Hz), 55.2, 112.8, 127.0, 127.3, 127.8 (d, J_{C-P}=13.5 Hz), 128.3, 128.4, 129.3, 130.4, 130.7 (d, J_{C-P}=12.0 Hz), 131.3, 131.9 (d, J_{C-P}=10.3 Hz), 134.2 (d, J_{C-P}=84.8 Hz), 136.0, 136.3 (d, J_{C-P}=84.7 Hz), 140.8, 142.8, 158.8. ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 59.9. IR (CH_2Cl_2) ν 3056, 2999, 2918, 2867, 2835, 1714, 1605, 1509, 1437, 1246, 1096, 1035, 826, 718, 690, 647, 615 cm^{-1}. MS (%) *m*/*e* 554 (M^+, 2), 337 (100), 304 (14), 289 (19), 263 (35), 253 (51), 217 (24), 165 (9), 121 (12). HRMS (EI) for $C_{34}H_{35}S_2OP$: 554.1867. Found: 554.1863.

4.2.8. 1-(2-(4-Chlorophenyl)-2-phenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2g**

The ratio of *E*/*Z*=1:1. A light yellow solid, Mp: 98–100 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.36 (s, 1.6H, CH_3), 0.45 (s, 1.4H, CH_3), 1.06–1.09 (m, 3H, CH_3), 1.21–1.25 (m, 3H, CH_3), 1.48 (s, 3H, CH_3), 6.18 (s, 0.5H, CH), 6.21 (s, 0.5H, CH), 6.77–6.85 (m, 2H, Ar), 7.06–7.17 (m, 4H, Ar), 7.23–7.40 (m, 9H, Ar), 7.68–7.75 (m, 2H, Ar), 7.84–7.95 (m, 2H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.15, 55.21. IR (CH_2Cl_2) ν 3056, 2998, 2945, 2918, 2867, 1980, 1592, 1487, 1437, 1375, 1306, 1185, 1095, 1014, 908, 822, 733, 719, 690, 654, 525 cm^{-1}. MS (%) *m*/*e* 558 (M^+, 4), 356 (8), 341 (100), 308 (45), 293 (60), 257 (87), 217 (57), 165 (34), 139 (39). HRMS (EI) for $C_{33}H_{32}S_2PCl$: 558.1372. Found: 558.1366.

4.2.9. 1-(2-(4-Fluorophenyl)-2-phenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2h**

The ratio of *E*/*Z*=1:1. A light yellow solid, Mp: 88–90 °C; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.35 (s, 1.5H, CH_3), 0.43 (s, 1.5H, CH_3), 1.06–1.08 (m, 3H, CH_3), 1.22–1.26 (m, 3H, CH_3), 1.49 (s, 3H, CH_3), 6.14 (s, 0.5H, CH), 6.19 (s, 0.5H, CH), 6.79–6.85 (m, 3H, Ar), 6.94–6.98 (m, 1H, Ar), 7.09–7.16 (m, 4H, Ar), 7.26–7.28 (m, 2H, Ar), 7.34–7.41 (m, 5H, Ar), 7.70–7.75 (m, 2H, Ar), 7.86–7.96 (m, 2H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.31, 55.34. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ −121.6, −120.1. IR (CH_2Cl_2) ν 3055, 2999, 2918, 2867, 1715, 1600, 1507, 1437, 1375, 1224, 1158, 1096, 845, 718, 690, 656, 525 cm^{-1}. MS (%) *m*/*e* 542 (M^+, 5), 468 (2), 325 (100), 309 (18), 277 (29), 251 (49), 241 (81), 217 (26), 139 (32). HRMS (EI) for $C_{33}H_{32}S_2PF$: 542.1667. Found: 542.1674.

4.2.10. 1-(2-(3,4-Difluorophenyl)-2-phenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2i**

The ratio of *E*/*Z*=1:1. A light yellow solid, Mp: 109–111 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.33 (s, 1.5H, CH_3), 0.53 (s, 1.5H, CH_3), 1.06–1.14 (m, 3H, CH_3), 1.21–1.25 (m, 3H, CH_3), 1.49 (s, 3H, CH_3), 6.16

(s, 0.5H, CH), 6.23 (s, 0.5H, CH), 6.48–6.55 (m, 0.5H, Ar), 6.64–6.69 (m, 0.5H, Ar), 6.84–6.87 (m, 1H, Ar), 7.01–7.06 (m, 1H, Ar), 7.11–7.30 (m, 5H, Ar), 7.36–7.41 (m, 6H, Ar), 7.68–7.75 (m, 2H, Ar), 7.82–7.99 (m, 2H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 55.0, 55.4. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ −146.1, −144.73, −144.68, −144.4. IR (CH_2Cl_2) ν 3056, 2998, 2918, 2868, 1805, 1714, 1513, 1436, 1278, 1096, 777, 747, 718, 690, 652, 615 cm^{-1}. MS (%) *m*/*e* 560 (M^+, 5), 343 (52), 295 (18), 259 (31), 217 (32), 139 (23), 86 (63), 84 (100), 49 (100). HRMS (EI) for $C_{33}H_3S_2PF_2$: 560.1573. Found: 560.1577.

4.2.11. 2,2,3,3-Tetramethyl-1-(2-phenyl-2-o-tolylvinyl)cyclopropyl diphenylphosphinodithioate **2j**

The ratio of *E*/*Z*=2:1. A white solid, Mp: 83–85 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.33 (s, 3H, CH_3), 0.70 (s, 1.5H, CH_3), 0.94–0.98 (m, 3H, CH_3), 1.23–1.25 (m, 6H, $2CH_3$), 1.48 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.78 (s, 1.5H, CH_3), 6.09 (s, 0.5H, CH), 6.33 (s, 1H, CH), 6.50 (d, *J*=7.8 Hz, 0.5H, Ar), 6.78 (d, *J*=6.9 Hz, 2H, Ar), 6.94–7.09 (m, 8H, Ar), 7.19–7.38 (m, 12H, Ar), 7.64–8.00 (m, 7H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 54.6, 55.8. IR (CH_2Cl_2) ν 3056, 3003, 2918, 2866, 1598, 1492, 1436, 1374, 1306, 1096, 908, 767, 731, 718, 690, 649, 525 cm^{-1}. MS (%) *m*/*e* 538 (M^+, 9), 336 (9), 321 (100), 289 (46), 273 (52), 237 (84), 217 (45), 205 (33), 91 (26). HRMS (EI) for $C_{34}H_{35}S_2P$: 538.1918. Found: 538.1919.

4.2.12. 2,2,3,3-Tetramethyl-1-(2-phenylprop-1-enyl)cyclopropyl diphenylphosphinodithioate **2k**

The ratio of *E*/*Z*=4:1. A white solid, Mp: 79–81 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.09–1.10 (m, 7H, CH_3), 1.43 (s, 7H, CH_3), 2.00 (s, 3H, CH_3), 5.73 (s, 0.24H, CH), 6.08 (s, 0.96H, CH), 6.86–6.89 (m, 2H, Ar), 7.08–7.11 (m, 3H, Ar), 7.26–7.49 (m, 9H, Ar), 7.77–8.24 (m, 5H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 60.5, 60.0. IR (CH_2Cl_2) ν 3055, 2987, 2917, 2868, 1436, 1375, 1303, 1097, 1027, 903, 748, 718, 690, 650 cm^{-1}. MS (%) *m*/*e* 462 (M^+, 2), 245 (100), 217 (20), 197 (38), 171 (32), 161 (54), 128 (47), 115 (18), 91 (24). HRMS (EI) for $C_{28}H_{31}S_2P$: 462.1605. Found: 462.1608.

4.2.13. (Deuterium labeling)-1-(2,2-diphenylvinyl)-2,2,3,3-tetramethylcyclopropyl diphenylphosphinodithioate **2a**-*D*

A white solid, Mp: 124–126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.38 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 6.20 (s, 0.3H, CH), 6.85–6.87 (m, 2H, Ar), 7.06–7.14 (m, 6H, Ar), 7.25–7.28 (m, 3H, Ar), 7.33–7.42 (m, 5H, Ar), 7.73 (dd, *J*=7.2, 12.8 Hz, 2H, Ar), 7.91 (dd, *J*=6.8, 13.2 Hz, 2H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 59.3. MS (%) *m*/*e* 525 (M^+, 6.1), 524 (2.6), 308 (100), 292 (18), 275 (26), 260 (19), 234 (45), 224 (78), 217 (31).

4.2.14. S-2,2-Diphenyl-1-(2,2,3,3-tetramethylcyclopropyl)vinyl ethanethioate **5a**

A white solid, Mp: 92–94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.63 (s, 6H, $2CH_3$), 0.93 (s, 6H, $2CH_3$), 1.80 (s, 1H, CH), 2.10 (s, 3H, CH_3), 7.06–7.09 (m, 2H, Ar), 7.24–7.27 (m, 6H, Ar), 7.31–7.34 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.3, 22.9, 25.0, 30.1, 39.8, 127.19, 127.23, 127.28, 127.6, 127.8, 129.6, 130.7, 141.8, 143.0, 154.6, 193.5. IR (CH_2Cl_2) ν 3056, 2975, 2919, 2867, 1942, 1697, 1492, 1443, 1376, 1350, 1114, 1075, 947, 757, 698, 619 cm^{-1}. MS (%) *m*/*e* 350 (M^+, 6), 307 (100), 277 (6), 223 (21), 191 (15), 165 (23), 97 (33), 57 (30), 43 (31). HRMS (EI) for $C_{23}H_{26}SO$: 350.1704. Found: 350.1704.

4.2.15. S-1-(2,2,3,3-Tetramethylcyclopropyl)-2,2-dip-tolylvinyl ethanethioate **5b**

A white solid, Mp: 101–103 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.63 (s, 6H, $2CH_3$), 0.93 (s, 6H, $2CH_3$), 1.81 (s, 1H, CH), 2.11 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.95 (d, *J*=8.0 Hz, 2H, Ar), 7.05 (d, *J*=8.0 Hz, 2H, Ar), 7.06 (d, *J*=8.0 Hz, 2H, Ar), 7.20 (d, *J*=8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.3, 21.27, 21.30, 22.9, 25.0, 30.1, 39.9, 126.2, 127.9, 128.3, 129.5, 130.7, 136.9, 137.6, 139.2, 140.3, 154.5, 193.8. IR (CH_2Cl_2) ν 3022, 2976, 2919, 2867, 1696, 1509, 1450, 1376, 1350, 1113, 945, 819, 620 cm^{-1}. MS (%) *m*/*e* 378 (M^+, 2), 335 (100), 261 (12), 219 (10), 189 (7), 165 (5), 105 (8), 97 (25), 57 (11). HRMS (EI) for $C_{25}H_{30}SO$: 378.2017. Found: 378.2023.

4.2.16. S-2,2-Bis(4-methoxyphenyl)-1-(2,2,3,3-tetramethylcyclopropyl)vinyl ethanethioate **5c**

A white solid, Mp: 78–80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.63 (s, 6H, $2CH_3$), 0.95 (s, 6H, $2CH_3$), 1.77 (s, 1H, CH), 2.12 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.78 (d, *J*=8.8 Hz, 2H, Ar), 6.79 (d, *J*=8.8 Hz, 2H, Ar), 6.99 (d, *J*=8.8 Hz, 2H, Ar), 7.24 (d, *J*=8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.3, 23.0, 25.1, 30.1, 40.0, 55.1, 55.2, 112.6, 112.9, 125.2, 131.0, 132.1, 134.8, 135.8, 153.8, 158.8, 159.3, 193.9. IR (CH_2Cl_2) ν 3033, 2947, 2868, 2836, 1693, 1605, 1509, 1463, 1376, 1299, 1247, 1173, 1111, 1035, 945, 833, 817, 618, 561 cm^{-1}. MS (%) *m*/*e* 367 (M^+−CH_3CO, 100), 337 (7), 283 (10), 251 (10), 212 (8), 117 (12), 105 (12), 97 (15), 57 (9). HRMS (EI) for $C_{25}H_{30}SO_3$: 410.1916. Found: 410.1912.

4.2.17. S-2,2-Bis(4-chlorophenyl)-1-(2,2,3,3-tetramethylcyclopropyl)vinyl ethanethioate **5d**

A white solid, Mp: 125–127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.63 (s, 6H, $2CH_3$), 0.95 (s, 6H, $2CH_3$), 1.70 (s, 1H, CH), 2.12 (s, 3H, CH_3), 6.99 (d, *J*=11.2 Hz, 2H, Ar), 7.24 (d, *J*=11.2 Hz, 6H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.3, 22.9, 25.1, 30.1, 39.9, 127.7, 128.0, 128.4, 131.0, 132.0, 133.4, 133.9, 140.0, 141.0, 152.3, 192.7. IR (CH_2Cl_2) ν 2919, 2869, 1698, 1488, 1111, 1090, 1016, 945, 829, 802, 614 cm^{-1}. MS (%) *m*/*e* 418 (M^+, 4), 375 (100), 340 (23), 256 (13), 215 (14), 189 (22), 97 (27), 57 (39), 43 (39). HRMS (EI) for $C_{23}H_{24}SOCl_2$: 418.0925. Found: 418.0926.

4.2.18. S-2,2-Bis(4-fluorophenyl)-1-(2,2,3,3-tetramethylcyclopropyl)vinyl ethanethioate **5e**

A white solid, Mp: 112–1114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.63 (s, 6H, $2CH_3$), 0.95 (s, 6H, $2CH_3$), 1.71 (s, 1H, CH), 2.11 (s, 3H, CH_3), 6.93–6.99 (m, 4H, Ar), 7.02–7.05 (m, 2H, Ar), 7.26–7.31 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.3, 22.9, 25.1, 30.1, 39.9, 114.4 (d, J_{C-F}=17.0 Hz), 114.7 (d, J_{C-F}=21.0 Hz), 127.5, 131.3 (d, J_{C-F}=8.6 Hz), 132.4 (d, J_{C-F}=7.8 Hz), 137.8 (d, J_{C-F}=3.0 Hz), 138.8 (d, J_{C-F}=4.1 Hz), 152.6, 162.1 (d, J_{C-F}=245.2 Hz), 162.4 (d, J_{C-F}=247.3 Hz), 192.9. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ −113.2, −114.4. IR (CH_2Cl_2) ν 3043, 2976, 2947, 2920, 2869, 1698, 1601, 1505, 1451, 1377, 1226, 1156, 1112, 1015, 946, 837, 616, 541 cm^{-1}. MS (%) *m*/*e* 386 (M^+, 3), 343 (100), 313 (7), 259 (18), 246 (19), 201 (16), 141 (11), 109 (16), 91 (4). HRMS (EI) for $C_{23}H_{24}SOF_2$: 386.1516. Found: 386.1512.

4.2.19. (2,2-Diphenyl-1-(2,2,3,3-tetramethylcyclopropyl)vinyl)(phenyl)sulfane **8**

A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.71 (s, 6H, $2CH_3$), 0.77 (s, 6H, $2CH_3$), 1.64 (s, 1H, CH), 7.19–7.44 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.5, 22.7, 25.5, 39.8, 126.3, 127.0, 127.2, 127.3, 127.8, 128.3, 130.1, 130.8, 131.6, 133.9, 136.0, 142.6, 143.0, 146.8. IR (CH_2Cl_2) ν 3056, 3019, 2978, 2918, 2867, 2729, 1944, 1874, 1802, 1581, 1491, 1475, 1442, 1376, 1119, 1025, 734, 697 cm^{-1}. MS (%) *m*/*e* 384 (M^+, 100), 259 (34), 218 (22), 191 (80), 167 (45), 151 (61), 105 (14), 91 (22), 57 (22). HRMS (EI) for $C_{27}H_{28}S$: 384.1912. Found: 384.1919.

4.2.20. The product mixtures from the reaction of vinylidenecyclopropane 1a and O,O-diethyl S-hydrogen phosphorodithioate **9**

A colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.01–1.06 (m, 6H), 3.99–4.09 (m, 4H), 6.38 (s, 1H, CH), 7.24–7.34 (m, 8H, Ar), 7.53–7.55 (m, 2H, Ar). ^{31}P NMR ($CDCl_3$, 121.45 MHz, 85% H_3PO_4) δ 93.84, 93.85, 95.69, 96.12. IR (CH_2Cl_2) ν 3058, 2983, 2921, 1494, 1443, 1373, 1158, 1099, 1016, 956, 768, 699, 651, 610 cm^{-1}. MS (%) *m*/*e* 460 (M^+,

5), 433 (5), 307 (85), 259 (31), 223 (47), 186 (60), 121 (100), 97 (96), 93 (64). HRMS (EI) for $C_{25}H_{33}O_2S_2P$: C: 460.1660. Found: 460.1654.

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Supplementary data

^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra for the corresponding addition products **3**, **5**, **8** and **9**. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.090.

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