



# Regio- and stereoselective synthesis of 1-aryl-1-thio-2-thiophosphinyethene derivatives via a radical process

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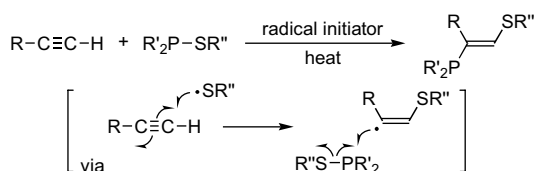
## ABSTRACT

Radical additions of *S*-thiophosphinyl dithiocarbonate to terminal aromatic alkynes afford (*E*)-1-aryl-1-thio-2-thiophosphinyethene derivatives regio- and stereoselectively in high yields. The transformations of the products are also described.

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## 1. Introduction

Radical additions of heteroatom–heteroatom bonds to alkenes and alkynes are fundamental methods to introduce two heteroatoms to organic molecules in one operation. Among them, radical additions of dichalcogenides to carbon–carbon multiple bonds have been widely investigated.<sup>1</sup> However, in spite of the increasing utilities of organophosphorus compounds in organic chemistry,<sup>2</sup> examples of radical additions of phosphorus–heteroatom bonds are limited.<sup>3,4</sup> Our group recently reported a radical thiophosphination of alkynes with thiophosphines (Scheme 1).<sup>4b</sup> The reaction proceeds through the addition of sulfur-centered radical to the terminal carbon of alkyne followed by the efficient reaction of the resulting vinyl radical with the phosphino group of thiophosphine.



Scheme 1. Our previous work.<sup>4b</sup>

After reporting the reaction shown in Scheme 1,<sup>4b</sup> we explored another intermolecular radical addition reaction to introduce both phosphorus and sulfur atoms to alkynes with the regioselectivity opposite to the previous reaction. Here we report the synthesis of (*E*)-1-aryl-1-thio-2-thiophosphinyethene derivatives via a radical process using a thiophosphinylated dithiocarbonate.<sup>5</sup> Stereoselective syntheses of (*E*)-1-aryl-1-thio-2-thiophosphinyethenes are scarcely reported.<sup>6</sup>

## 2. Result and discussion

A mixture of phenylacetylene (**1a**), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**), and a catalytic amount of dilauroyl peroxide (DLP, (C<sub>11</sub>H<sub>23</sub>CO<sub>2</sub>)<sub>2</sub>)<sup>7</sup> was heated in benzene at reflux temperature for 4 h (Table 1, entry 1). NMR analysis of the crude mixture indicated the formation of the corresponding adduct, *S*-2-diphenylthiophosphinyl-1-phenylethenyl *O*-ethyl dithiocarbonate (91%, a single isomer). Silica gel column chromatography followed by gel permeation chromatography (GPC)<sup>8</sup> afforded **3a** in 76% yield. We confirmed by X-ray analysis that the *E* isomer was exclusively formed.

This reaction would proceed as follows (Scheme 2). Initially, an undecyl radical, thermally generated from DLP, would attack the sulfur atom of the thiocarbonyl moiety of **2** to generate diphenylthiophosphinoyl radical (**A**) with the formation of *O*-ethyl *S*-undecyl dithiocarbonate.<sup>5</sup> The phosphorus-centered radical **A** would react with the triple bond of **1a** to furnish vinyl radical **B**.<sup>9</sup> An equilibrium would exist between radicals **B** and **B'**. However, only radical **B** would react with **2** to furnish radical **C** (vide infra). Finally,

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**Table 1**  
Addition of **2** to various terminal alkynes

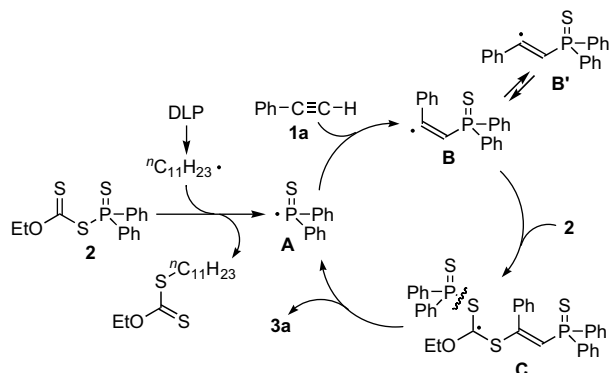
Entry	Ar	Products	Isolated yield (%)
1	Ph ( <b>1a</b> )	<b>3a</b>	76 <sup>a</sup> (91) <sup>c</sup>
2	4-Me-C <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	<b>3b</b>	71 <sup>b</sup> (89) <sup>c</sup>
3	2,4,6-Me <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> ( <b>1c</b> )	<b>3c</b>	83 <sup>a</sup>
4	1-Naphthyl ( <b>1d</b> )	<b>3d</b>	73
5	4-MeO-C <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )	<b>3e</b>	88
6	4-Ac-C <sub>6</sub> H <sub>4</sub> ( <b>1f</b> )	<b>3f</b>	92
7	4-NC-C <sub>6</sub> H <sub>4</sub> ( <b>1g</b> )	<b>3g</b>	85
8	4-MeO <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> ( <b>1h</b> )	<b>3h</b>	79
9	4-OHC-C <sub>6</sub> H <sub>4</sub> ( <b>1i</b> )	<b>3i</b>	88
10	4-Br-C <sub>6</sub> H <sub>4</sub> ( <b>1j</b> )	<b>3j</b>	87 <sup>b</sup>
11	4-HOCH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> ( <b>1k</b> )	<b>3k</b>	88

<sup>a</sup> Yield after purification by GPC.

<sup>b</sup> Yield after recrystallization.

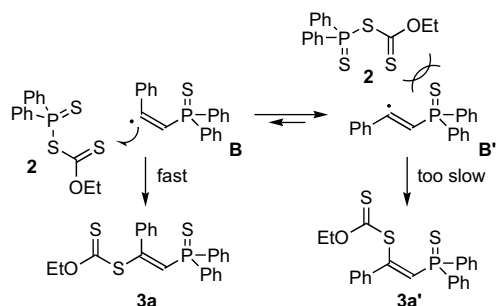
<sup>c</sup> Yield in parentheses was determined by <sup>31</sup>P NMR.

fragmentation of radical **C** would produce **3a** and regenerate the phosphorus-centered radical **A** to complete the radical chain.



**Scheme 2.**

The *E* selectivity of the reaction can be explained as outlined in **Scheme 3**. Vinyl radical **B'** would reside in larger population than radical **B** in the equilibrium because radical **B** has a favorable *E* configuration. However, the diphenylthiophosphinyl moiety and reagent **2** are so large that the steric repulsion between **B'** and **2** would prevent the reaction. Hence, only **B** can react with **2** to form product **3a** exclusively.

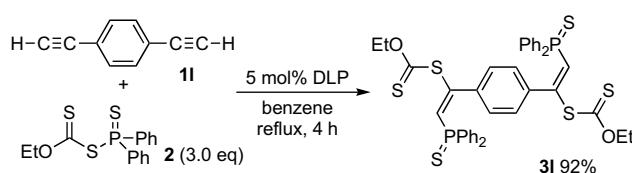


**Scheme 3.**

A variety of aryl-substituted terminal alkynes underwent the radical addition reaction with complete regio- and stereoselectivity (**Table 1**). The *E* configurations of **3** were deduced from comparing

the <sup>1</sup>H NMR spectra of **3b–3k** with the spectrum of **3a**. Both electron-rich and electron-deficient aryl-substituted acetylenes reacted with **2** to afford **3** in high yields. The addition of **2** to sterically hindered alkynes like **1c** and **1d** proceeded smoothly (entries 3 and 4). Functional groups such as alkoxy (entry 5), keto (entry 6), cyano (entry 7), ester (entry 8), formyl (entry 9), and bromo (entry 10) moieties remained unchanged under the reaction conditions. It is worth noting that a hydroxy group did not affect the reactivity (entry 11). However, attempts to perform addition reactions of **2** across 1-dodecyne, trimethylsilylacetylene, methyl propiolate, and 1-phenylpropyne resulted in failure, suffering from low conversion.

The reaction of thiophosphinyl dithiocarbonate **2** with *p*-diethynylbenzene (**1l**) efficiently afforded *p*-bis(1-thio-2-thio-phosphinylethenyl)benzene **3l**. The double addition proceeded with perfect regio- and stereoselectivity in a very high yield (**Scheme 4**).



**Scheme 4.**

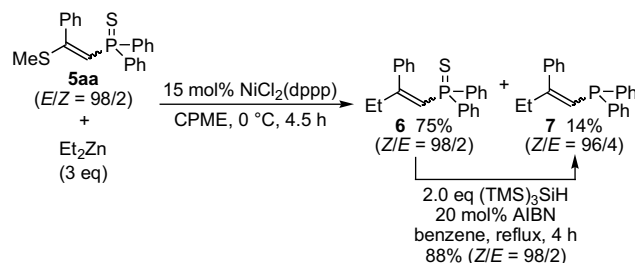
We next attempted to carry out stereospecific transformations of product **3**. It was found that hydrolysis of the dithiocarbonate moieties of **3** followed by *S*-alkylation proceeded<sup>10</sup> in the presence of excess potassium hydroxide and reactive alkyl halides **4** to provide thiophosphinylated vinyl sulfides **5** in excellent yields with retention of configuration (**Table 2**).<sup>11</sup>

**Table 2**  
Hydrolysis of **3** followed by alkylation with **4**

Entry	<b>3</b>	R-X ( <b>4</b> )	Products	Isolated yield (%)	<i>E/Z</i>
1	<b>3a</b>	Me-I ( <b>4a</b> )	<b>5aa</b>	98	98:2
2	<b>3a</b>	Allyl-Br ( <b>4b</b> )	<b>5ab</b>	98	98:2
3	<b>3a</b>	Bn-Br ( <b>4c</b> )	<b>5ac</b>	88	99:1
4	<b>3b</b>	Me-I ( <b>4a</b> ) <sup>a</sup>	<b>5ba</b>	93	98:2

<sup>a</sup> KOH and **4a** (3.2 equiv) were used.

Finally, cross-coupling reactions of vinyl sulfide **5aa** with organometallic reagents were examined.<sup>12</sup> Coupling reactions with Grignard reagents resulted in failure. However, treatment of **5aa** with diethylzinc in the presence of a catalytic amount of NiCl<sub>2</sub>(dppp) in cyclopentyl methyl ether (CPME) at 0 °C afforded ethylated compound **6** effectively (**Scheme 5**). This cross-coupling reaction proceeded without loss of stereochemistry, albeit



**Scheme 5.**

partial desulfidation at the thiophosphinyl moiety was observed. Phosphine sulfide **6** could be converted to **7** by the action of tris(trimethylsilyl)silane via a radical pathway.<sup>13</sup> The overall reaction can be regarded as a *trans*-carbophosphination of the starting alkyne to prepare a  $\beta$ -disubstituted alkenylphosphine stereoselectively.<sup>14</sup>

### 3. Conclusion

We have developed an intermolecular addition of *S*-thiophosphinyl dithiocarbonate to arylacetylenes to produce (*E*)-1-aryl-1-thio-2-thiophosphinylethene derivatives, which were difficult to be prepared. Taking advantage of mild radical conditions, the reactions proceed without loss of various functional groups. Further transformation of the products enabled us to synthesize stereocontrolled, multisubstituted alkenyl phosphines.

In light of the importance of organophosphorus and organosulfur compounds, the products or their derivatives can be useful for diverse purposes such as a new type of ligands, building blocks for organic synthesis, and components of supramolecular structures.

## 4. Experimental

### 4.1. General

#### 4.1.1. Instrumentation

<sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. <sup>31</sup>P NMR (121.5 MHz) spectra were taken on a Varian MERCURY 300 spectrometer and were obtained in CDCl<sub>3</sub> with 85% H<sub>3</sub>PO<sub>4</sub> solution as an external standard. Chemical shifts ( $\delta$ ) are in parts per million relative to tetramethylsilane at 0.0 ppm for <sup>1</sup>H, relative to CDCl<sub>3</sub> at 77.0 ppm for <sup>13</sup>C, and relative to H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm for <sup>31</sup>P. DEPT, H–H COSY, H–C COSY, and NOE analyses allowed the assignments of the signals of each compound. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Melting points were determined on Yanaco micro melting point apparatus. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F<sub>254</sub>. Silica gel (Wakogel 200 mesh) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 10 mL/min, UV and RI detectors). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

#### 4.1.2. Materials

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzene, methanol, CPME, diphenylthiophosphinyl chloride, and potassium hydroxide were purchased from Wako Pure Chemicals. Potassium *O*-ethyl dithiocarbonate and NiCl<sub>2</sub>(dppp) were available from TCI. DLP and iodomethane were obtained from Nacalai Tesque. Neat diethylzinc was purchased from Aldrich and was diluted with degassed dry hexane to prepare a 1.0 M solution, which was stored under argon. Benzene was dried over slices of sodium. Alkynes were commercially available or readily prepared by the conventional Sonogashira reactions. *S*-Diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**) was synthesized from potassium *O*-ethyl dithiocarbonate and diphenylthiophosphinyl chloride (vide infra).

### 4.2. Experimental procedures

#### 4.2.1. Preparation of *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**)

Under argon, diphenylthiophosphinyl chloride (3.08 mL, 15.0 mmol) was added to a suspension of potassium *O*-ethyl dithiocarbonate (2.64 g, 16.5 mmol) in THF (20.0 mL) at ambient temperature. After 4 h, a diluted NaCl solution was poured into the suspension and the mixture was extracted twice with hexane/EtOAc=2:1. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc=20:1 to 10:1) afforded *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**) as a yellow solid in 84% yield (4.25 g, 12.6 mmol).

#### 4.2.2. General procedure for additions of thiophosphinyl dithiocarbonate **2** to alkynes **1**

Under argon, a mixture of alkyne **1** (0.50 mmol), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**, 0.20 g, 0.60 mmol), and DLP (0.010 g, 0.025 mmol) was heated in boiling benzene (2.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Silica gel column chromatography (hexane/EtOAc) followed by GPC or recrystallization (if needed) afforded a 1-aryl-1-thio-2-thiophosphinylethene derivative **3** as a white or yellow solid (*E/Z*>99:1). The *E* configuration was assigned by X-ray analysis (See 4.2.7.2).

#### 4.2.3. Double addition of thiophosphinyl dithiocarbonate **2** to **11**

Under argon, a mixture of *p*-diethynylbenzene (**11**, 0.063 g, 0.50 mmol), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**, 0.51 g, 1.5 mmol), and DLP (0.010 g, 0.025 mmol) was heated in boiling benzene (3.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Filtration with EtOAc followed by short column chromatography on silica gel (CHCl<sub>3</sub>) afforded 1,4-bis{[(*E*)-2-diphenylthiophosphinyl-1-(ethoxythiocarbonylsulfanyl)ethenyl]benzene (**31**) as a pale yellow solid in 92% yield (0.37 g, 0.46 mmol).

#### 4.2.4. General procedure for transformation of dithiocarbonates **3** to sulfides **5**

Transformation of **3a** to **5aa** is representative. Under argon, ground potassium hydroxide (0.056 g, 1.0 mmol) was added to a suspension of dithiocarbonate **3a** (0.088 g, 0.20 mmol) and iodomethane (**4a**, 0.062 mL, 1.0 mmol) in methanol (3.0 mL) at ambient temperature. After stirring for 30 min, the mixture was quenched with a diluted NaCl/NH<sub>4</sub>Cl solution and extracted three times with hexane/EtOAc=1:1. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc=10:1) afforded {2-diphenylthiophosphinyl-1-(methylthio)ethenyl}benzene (**5aa**) as a white solid in 98% yield (0.072 g, 0.20 mmol, *E/Z*=98:2).

#### 4.2.5. Cross-coupling reaction of **5aa** with diethylzinc

Under argon, diethylzinc (1.0 M hexane solution, 0.60 mL, 0.60 mmol) was added to a suspension of (*E*)-{2-diphenylthiophosphinyl-1-(methylthio)ethenyl}benzene (**5aa**, 0.073 g, 0.20 mmol) and NiCl<sub>2</sub>(dppp) (0.016 g, 0.030 mmol) in CPME (3.0 mL) at 0 °C. The reaction was monitored by TLC. After 4.5 h, the mixture was quenched with diluted NaCl solution and extracted three times with EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through a pad of Florisil®, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc=20:1 to 10:1) afforded 1-diphenylthiophosphinyl-2-phenyl-1-butene (**6**) as a white solid in 75% yield (0.052 g, 0.15 mmol, *Z/E*=98:2) and 1-diphenylphosphino-2-phenyl-1-butene (**7**) in 14% yield (8.7 mg, 0.027 mmol, *Z/E*=96:4).

#### 4.2.6. Desulfidation of vinylphosphine sulfide **6**

Under argon, a mixture of vinylphosphine sulfide **6** (0.035 g, 0.10 mmol), tris(trimethylsilyl)silane (0.062 mL, 0.20 mmol), and AIBN (3.2 mg, 0.020 mmol) was heated in boiling benzene (2.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Silica gel column chromatography (hexane/EtOAc=50:1 to 20:1) afforded 1-diphenylphosphino-2-phenyl-1-butene (**7**) as a colorless oil in 88% yield (0.028 g, 0.088 mmol, *Z/E*=98:2).

#### 4.2.7. Characterization data

**4.2.7.1. S-Diphenylthiophosphinyl O-ethyl dithiocarbonate (2).** IR (neat) 1436, 1366, 1254, 1096, 1033, 722, 689, 653 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.00 (t, *J*=7.0 Hz, 3H), 4.40 (q, *J*=7.0 Hz, 2H), 7.47–7.52 (m, 4H), 7.53–7.58 (m, 2H), 7.95–8.02 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 12.65, 71.12, 128.67 (d, *J*=13.4 Hz), 131.62 (d, *J*=11.4 Hz), 132.23 (d, *J*=2.9 Hz), 132.67 (d, *J*=84.5 Hz), 204.27 (d, *J*=4.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 59.46. Found: C, 53.36; H, 4.43%. Calcd for C<sub>15</sub>H<sub>15</sub>OPS<sub>3</sub>: C, 53.23; H, 4.47%. Mp: 58–59 °C.

**4.2.7.2. (E)-S-2-Diphenylthiophosphinyl-1-phenylethenyl O-ethyl dithiocarbonate (3a).** IR (Nujol) 1438, 1240, 1103, 1041, 715, 693, 635 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.07 (t, *J*=7.0 Hz, 3H), 4.42 (q, *J*=7.0 Hz, 2H), 6.96–7.01 (m, 2H), 7.02 (d, *J*=15.5 Hz, 1H), 7.01–7.05 (m, 1H), 7.25–7.30 (m, 4H), 7.31–7.36 (m, 2H), 7.48–7.52 (m, 2H), 7.75–7.82 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.14, 70.53, 127.42, 128.27 (d, *J*=12.9 Hz), 129.28, 129.65, 130.13 (d, *J*=73.1 Hz), 131.27 (d, *J*=3.4 Hz), 131.30 (d, *J*=10.5 Hz), 132.03 (d, *J*=86.0 Hz), 136.44 (d, *J*=4.8 Hz), 149.15, 209.24 (d, *J*=1.5 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 28.97. Found: C, 62.74; H, 5.04%. Calcd for C<sub>23</sub>H<sub>21</sub>OPS<sub>3</sub>: C, 62.70; H, 4.80%. Mp: 106–107 °C. The *E* configuration was determined by X-ray analysis. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC 710609). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: 44 1223 336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**4.2.7.3. (E)-S-2-Diphenylthiophosphinyl-1-(4-methylphenyl)ethenyl O-ethyl dithiocarbonate (3b).** IR (Nujol) 1559, 1506, 1438, 1244, 1102, 1043, 827, 715, 631 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.10 (t, *J*=7.0 Hz, 3H), 2.16 (s, 3H), 4.43 (q, *J*=7.0 Hz, 2H), 6.75–6.79 (m, 2H), 6.97 (d, *J*=16.0 Hz, 1H), 7.25–7.30 (m, 4H), 7.32–7.38 (m, 4H), 7.75–7.82 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.20, 21.19, 70.50, 128.03, 128.22 (d, *J*=12.9 Hz), 129.55 (d, *J*=74.0 Hz), 129.63, 131.11 (d, *J*=2.9 Hz), 131.35 (d, *J*=11.0 Hz), 132.22 (d, *J*=85.9 Hz), 133.61 (d, *J*=4.9 Hz), 139.49, 149.27, 209.53; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 29.11. Found: C, 63.27; H, 5.07%. Calcd for C<sub>24</sub>H<sub>23</sub>OPS<sub>3</sub>: C, 63.41; H, 5.10%. Mp: 123–124 °C.

**4.2.7.4. (E)-S-2-Diphenylthiophosphinyl-1-mesitylenyl O-ethyl dithiocarbonate (3c).** IR (Nujol) 1436, 1245, 1104, 1031, 852, 712, 691, 633 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.35 (t, *J*=7.0 Hz, 3H), 2.13 (s, 3H), 2.16 (s, 6H), 4.68 (q, *J*=7.0 Hz, 2H), 6.46 (d, *J*=0.5 Hz, 2H), 7.24 (d, *J*=15.5 Hz, 1H), 7.26–7.31 (m, 4H), 7.36–7.41 (m, 2H), 7.65–7.71 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.54, 20.27, 20.92, 70.48, 125.14 (d, *J*=78.3 Hz), 128.05, 128.06 (d, *J*=12.9 Hz), 129.97 (d, *J*=6.3 Hz), 131.04 (d, *J*=2.9 Hz), 131.40 (d, *J*=11.0 Hz), 132.41 (d, *J*=86.4 Hz), 136.33, 138.72, 148.99 (d, *J*=2.9 Hz), 208.48; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 29.83. Found: C, 64.65; H, 5.64%. Calcd for C<sub>26</sub>H<sub>27</sub>OPS<sub>3</sub>: C, 64.70; H, 5.64%. Mp: 93–94 °C.

**4.2.7.5. (E)-S-2-Diphenylthiophosphinyl-1-(1-naphthyl)ethenyl O-ethyl dithiocarbonate (3d).** IR (Nujol) 1559, 1507, 1436, 1231, 1049, 1036, 798, 714, 633 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.20 (dd, *J*=7.0, 7.0 Hz, 3H), 4.48 (dq, *J*=11.0, 7.0 Hz, 1H), 4.53 (dq, *J*=11.0, 7.0 Hz, 1H), 6.75–6.80 (m, 2H), 6.85–6.90 (m, 1H), 7.20 (dd, *J*=8.0, 7.0 Hz, 1H), 7.26–7.32 (m, 2H), 7.32–7.40 (m, 3H), 7.37 (d, *J*=16.5 Hz, 1H), 7.41–7.47

(m, 2H), 7.50–7.54 (m, 1H), 7.54–7.58 (m, 1H), 7.67 (dd, *J*=7.0, 1.0 Hz, 1H), 7.73–7.80 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.36, 70.56, 124.26, 125.40, 125.84, 126.11, 127.15 (d, *J*=12.9 Hz), 128.08, 128.24 (d, *J*=12.5 Hz), 129.30 (d, *J*=1.4 Hz), 129.38 (d, *J*=85.4 Hz), 129.89, 129.93 (d, *J*=1.0 Hz), 130.21 (d, *J*=2.9 Hz), 130.99 (d, *J*=11.0 Hz), 131.10 (d, *J*=10.0 Hz), 131.27 (d, *J*=2.9 Hz), 132.53 (d, *J*=5.8 Hz), 132.96, 133.07 (d, *J*=86.9 Hz), 133.48 (d, *J*=75.0 Hz), 147.43 (d, *J*=1.5 Hz), 208.82 (d, *J*=1.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 29.31. Found: C, 66.25; H, 4.82%. Calcd for C<sub>27</sub>H<sub>23</sub>OPS<sub>3</sub>: C, 66.10; H, 4.73%. Mp: 115–116 °C.

**4.2.7.6. (E)-S-2-Diphenylthiophosphinyl-1-(4-methoxyphenyl)ethenyl O-ethyl dithiocarbonate (3e).** IR (Nujol) 1609, 1504, 1437, 1253, 1241, 1041, 834, 747, 712, 629 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.12 (t, *J*=7.0 Hz, 3H), 3.68 (s, 3H), 4.44 (q, *J*=7.0 Hz, 2H), 6.48–6.52 (m, 2H), 6.91 (d, *J*=16.0 Hz, 1H), 7.26–7.32 (m, 4H), 7.32–7.37 (m, 2H), 7.45–7.49 (m, 2H), 7.77–7.84 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.28, 55.23, 70.49, 112.81, 128.26 (d, *J*=12.9 Hz), 128.72 (d, *J*=74.0 Hz), 129.01 (d, *J*=4.8 Hz), 131.21 (d, *J*=3.3 Hz), 131.35 (d, *J*=10.5 Hz), 131.39, 132.22 (d, *J*=85.5 Hz), 148.88, 160.41, 209.71; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 29.09. Found: C, 61.25; H, 4.98%. Calcd for C<sub>24</sub>H<sub>23</sub>O<sub>2</sub>PS<sub>3</sub>: C, 61.25; H, 4.93%. Mp: 105–106 °C.

**4.2.7.7. (E)-S-1-(4-Acetylphenyl)-2-(diphenylthiophosphinyl)ethenyl O-ethyl dithiocarbonate (3f).** IR (Nujol) 1681, 1436, 1247, 1099, 1037, 819, 708, 627 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.12 (t, *J*=7.0 Hz, 3H), 2.49 (s, 3H), 4.43 (q, *J*=7.0 Hz, 2H), 7.13 (d, *J*=15.5 Hz, 1H), 7.26–7.31 (m, 4H), 7.32–7.37 (m, 2H), 7.54–7.60 (m, 4H), 7.75–7.81 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.25, 26.62, 70.70, 127.28, 128.38 (d, *J*=12.9 Hz), 129.94, 131.33 (d, *J*=11.0 Hz), 131.45 (d, *J*=2.9 Hz), 131.81 (d, *J*=86.9 Hz), 132.67 (d, *J*=71.6 Hz), 137.01, 141.05 (d, *J*=4.8 Hz), 147.53, 197.26, 208.53; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 28.73. Found: C, 62.35; H, 4.77%. Calcd for C<sub>25</sub>H<sub>23</sub>O<sub>2</sub>PS<sub>3</sub>: C, 62.22; H, 4.80%. Mp: 102–103 °C.

**4.2.7.8. (E)-S-1-(4-Cyanophenyl)-2-(diphenylthiophosphinyl)ethenyl O-ethyl dithiocarbonate (3g).** IR (Nujol) 2233, 1436, 1248, 1105, 1028, 901, 841, 716, 694, 636 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.14 (t, *J*=7.0 Hz, 3H), 4.44 (q, *J*=7.0 Hz, 2H), 7.18 (d, *J*=15.0 Hz, 1H), 7.26–7.30 (m, 2H), 7.30–7.35 (m, 4H), 7.37–7.42 (m, 2H), 7.58–7.62 (m, 2H), 7.74–7.80 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.26, 70.82, 112.43, 118.16, 128.48 (d, *J*=12.9 Hz), 130.30, 131.03, 131.28 (d, *J*=10.9 Hz), 131.48 (d, *J*=86.0 Hz), 131.67 (d, *J*=2.8 Hz), 134.08 (d, *J*=70.6 Hz), 141.09 (d, *J*=4.8 Hz), 146.31, 208.10 (d, *J*=1.5 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 28.41. Found: C, 61.97; H, 4.14%. Calcd for C<sub>24</sub>H<sub>20</sub>NOPS<sub>3</sub>: C, 61.91; H, 4.33%. Mp: 132–133 °C.

**4.2.7.9. (E)-S-2-Diphenylthiophosphinyl-1-(4-methoxycarbonylphenyl)ethenyl O-ethyl dithiocarbonate (3h).** IR (Nujol) 1722, 1717, 1436, 1283, 1244, 1111, 1036, 707, 629 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.09 (t, *J*=7.0 Hz, 3H), 3.88 (s, 3H), 4.41 (q, *J*=7.0 Hz, 2H), 7.12 (d, *J*=15.5 Hz, 1H), 7.26–7.32 (m, 4H), 7.33–7.38 (m, 2H), 7.52–7.56 (m, 2H), 7.63–7.67 (m, 2H), 7.74–7.80 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.22, 52.17, 70.67, 128.38 (d, *J*=12.9 Hz), 128.57, 129.69, 130.30, 131.31 (d, *J*=10.5 Hz), 131.47 (d, *J*=2.9 Hz), 131.80 (d, *J*=84.5 Hz), 132.31 (d, *J*=71.6 Hz), 140.94 (d, *J*=5.3 Hz), 147.77, 166.27, 208.49; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 28.65. Found: C, 60.16; H, 4.75%. Calcd for C<sub>25</sub>H<sub>23</sub>O<sub>3</sub>PS<sub>3</sub>: C, 60.22; H, 4.65%. Mp: 132–133 °C.

**4.2.7.10. (E)-S-2-Diphenylthiophosphinyl-1-(4-formylphenyl)ethenyl O-ethyl dithiocarbonate (3i).** IR (Nujol) 1699, 1684, 1558, 1439, 1243, 1100, 1041, 825, 715 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.11 (t, *J*=7.0 Hz, 3H), 4.43 (q, *J*=7.0 Hz, 2H), 7.17 (d, *J*=15.5 Hz, 1H), 7.26–7.32 (m, 4H), 7.33–7.38 (m, 2H), 7.49–7.52 (m, 2H), 7.64–7.67 (m, 2H), 7.75–7.81 (m, 4H), 9.85 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.23, 70.74, 128.42 (d, *J*=12.9 Hz), 128.60, 130.35 (d, *J*=1.0 Hz), 131.31 (d, *J*=10.5 Hz), 131.54 (d, *J*=3.3 Hz), 131.69 (d, *J*=86.0 Hz), 133.20 (d, *J*=71.1 Hz), 136.11,



142.44 (d,  $J=4.8$  Hz), 147.23, 191.39 (d,  $J=1.4$  Hz), 208.34 (d,  $J=1.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.61. Found: C, 61.35; H, 4.62%. Calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{PS}_3$ : C, 61.52; H, 4.52%. Mp: 110–111 °C.

4.2.7.11. (*E*)-*S*-1-(4-Bromophenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (**3j**). IR (Nujol) 1480, 1436, 1264, 1248, 1107, 1030, 819, 707  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.13 (t,  $J=7.0$  Hz, 3H), 4.44 (q,  $J=7.0$  Hz, 2H), 7.06 (d,  $J=15.5$  Hz, 1H), 7.07–7.12 (m, 2H), 7.28–7.36 (m, 6H), 7.36–7.41 (m, 2H), 7.74–7.81 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.24, 70.67, 123.61, 128.36 (d,  $J=12.4$  Hz), 130.50, 131.18, 131.34 (d,  $J=10.5$  Hz), 131.41 (d,  $J=2.9$  Hz), 131.59 (d,  $J=74.0$  Hz), 131.75 (d,  $J=87.4$  Hz), 135.44 (d,  $J=4.8$  Hz), 147.60, 208.72;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.76. Found: C, 53.04; H, 3.74%. Calcd for  $\text{C}_{23}\text{H}_{20}\text{BrOPS}_3$ : C, 53.18; H, 3.88%. Mp: 118–119 °C.

4.2.7.12. (*E*)-*S*-2-Diphenylthiophosphinyl-1-(4-hydroxymethylphenyl)ethenyl *O*-ethyl dithiocarbonate (**3k**). IR (Nujol) 3600–3300 (br), 1654, 1506, 1436, 1242, 1041, 826, 710, 692, 626  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.12 (t,  $J=7.0$  Hz, 3H), 1.50 (br s, 1H), 4.44 (q,  $J=7.0$  Hz, 2H), 4.51 (s, 2H), 6.96–7.00 (m, 2H), 7.03 (d,  $J=16.0$  Hz, 1H), 7.26–7.31 (m, 4H), 7.32–7.37 (m, 2H), 7.46–7.51 (m, 2H), 7.75–7.82 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.24, 64.70, 70.56, 125.73, 128.28 (d,  $J=12.4$  Hz), 129.94 (d,  $J=1.0$  Hz), 130.62 (d,  $J=73.0$  Hz), 131.21 (d,  $J=3.4$  Hz), 131.33 (d,  $J=10.5$  Hz), 132.14 (d,  $J=85.9$  Hz), 135.78 (d,  $J=4.8$  Hz), 142.05, 148.73, 209.20 (d,  $J=1.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.97. Found: C, 61.05; H, 4.90%. Calcd for  $\text{C}_{24}\text{H}_{23}\text{O}_2\text{PS}_3$ : C, 61.25; H, 4.93%. Mp: 111–112 °C.

4.2.7.13. *p*-Bis{(*E*)-2-diphenylthiophosphinyl-1-(ethoxythiocarbonylsulfonyl)ethenyl}benzene (**3l**). IR (Nujol) 1577, 1559, 1436, 1246, 1098, 1041, 846, 752, 715, 632  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.39 (t,  $J=7.0$  Hz, 6H), 4.62 (q,  $J=7.0$  Hz, 4H), 7.06 (s, 4H), 7.10 (d,  $J=15.5$  Hz, 2H), 7.24–7.29 (m, 8H), 7.31–7.36 (m, 4H), 7.71–7.78 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.70, 70.96, 128.34 (d,  $J=12.9$  Hz), 128.77, 131.29 (d,  $J=10.5$  Hz), 131.54 (d,  $J=3.4$  Hz), 131.86 (d,  $J=85.9$  Hz), 134.41 (d,  $J=71.6$  Hz), 136.99 (d,  $J=4.8$  Hz), 146.75, 209.85 (d,  $J=1.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.41. Found: C, 59.56; H, 4.47%. Calcd for  $\text{C}_{40}\text{H}_{36}\text{O}_2\text{P}_2\text{S}_6$ : C, 59.83; H, 4.52%. Mp: 158–159 °C.

4.2.7.14. (*E*)-{2-Diphenylthiophosphinyl-1-(methylthio)ethenyl}benzene (**5aa**). IR (Nujol) 1684, 1653, 1558, 1540, 1507, 1437, 1095, 715, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H), 6.05 (d,  $J=15.0$  Hz, 1H), 6.97–7.01 (m, 2H), 7.03–7.08 (m, 1H), 7.24–7.29 (m, 6H), 7.29–7.34 (m, 2H), 7.73–7.80 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.40 (d,  $J=1.5$  Hz), 112.09 (d,  $J=88.3$  Hz), 127.59, 128.08 (d,  $J=12.4$  Hz), 128.91, 128.99 (d,  $J=1.0$  Hz), 130.78 (d,  $J=2.9$  Hz), 131.31 (d,  $J=10.5$  Hz), 133.72 (d,  $J=85.9$  Hz), 135.95 (d,  $J=6.3$  Hz), 159.89 (d,  $J=2.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.83. Found: C, 68.55; H, 5.25%. Calcd for  $\text{C}_{21}\text{H}_{19}\text{PS}_2$ : C, 68.82; H, 5.23%. Mp: 106–107 °C. The *E* configuration of the major isomer was determined by NOE experiments.

4.2.7.15. (*E*)-{1-Allylthio-2-(diphenylthiophosphinyl)ethenyl}benzene (**5ab**). IR (Nujol) 1558, 1539, 1507, 1437, 1096, 906, 719, 632  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.43 (ddd,  $J=6.5, 1.0, 1.0$  Hz, 2H), 5.19–5.26 (m, 2H), 5.87 (ddt,  $J=17.0, 10.0, 6.5$  Hz, 1H), 6.25 (d,  $J=15.5$  Hz, 1H), 6.97–7.03 (m, 2H), 7.03–7.08 (m, 1H), 7.23–7.35 (m, 8H), 7.71–7.79 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  35.97, 114.35 (d,  $J=86.0$  Hz), 119.04, 127.59, 128.06 (d,  $J=12.5$  Hz), 128.97, 129.23 (d,  $J=0.9$  Hz), 130.80 (d,  $J=2.9$  Hz), 131.31 (d,  $J=10.5$  Hz), 131.76, 133.65 (d,  $J=85.9$  Hz), 135.70 (d,  $J=6.3$  Hz), 157.91 (d,  $J=2.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.77. Found: C, 70.37; H, 5.37%. Calcd for  $\text{C}_{23}\text{H}_{21}\text{PS}_2$ : C, 70.38; H, 5.39%. Mp: 81–82 °C.

4.2.7.16. (*E*)-{1-Benzylthio-2-(diphenylthiophosphinyl)ethenyl}benzene (**5ac**). IR (Nujol) 1653, 1558, 1540, 1507, 1437, 1097, 906, 772, 719  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.05 (s, 2H), 6.17 (d,  $J=15.0$  Hz, 1H),

6.97–7.02 (m, 2H), 7.03–7.08 (m, 1H), 7.18–7.23 (m, 4H), 7.26–7.31 (m, 4H), 7.31–7.40 (m, 5H), 7.54–7.60 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  35.57, 114.31 (d,  $J=86.0$  Hz), 127.60 (two signals are overlapped), 128.03 (d,  $J=12.4$  Hz), 128.71, 128.82, 128.98, 129.23 (d,  $J=0.9$  Hz), 130.71 (d,  $J=2.8$  Hz), 131.21 (d,  $J=11.0$  Hz), 133.63 (d,  $J=85.9$  Hz), 135.18, 135.64 (d,  $J=6.3$  Hz), 157.86 (d,  $J=2.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.55. Found: C, 72.97; H, 5.54%. Calcd for  $\text{C}_{27}\text{H}_{23}\text{PS}_2$ : C, 73.27; H, 5.24%. Mp: 153–154 °C.

4.2.7.17. 4-{(*E*)-2-Diphenylthiophosphinyl-1-(methylthio)ethenyl}toluene (**5ba**). IR (Nujol) 1558, 1503, 1437, 1098, 914, 825, 752, 709, 629  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.17 (s, 3H), 2.36 (s, 3H), 6.01 (d,  $J=15.5$  Hz, 1H), 6.75–6.79 (m, 2H), 7.12–7.16 (m, 2H), 7.23–7.28 (m, 4H), 7.29–7.34 (m, 2H), 7.73–7.79 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.40 (d,  $J=1.5$  Hz), 21.14, 111.77 (d,  $J=88.3$  Hz), 127.99 (d,  $J=12.4$  Hz), 128.22, 128.89 (d,  $J=1.0$  Hz), 130.63 (d,  $J=2.9$  Hz), 131.34 (d,  $J=10.5$  Hz), 133.11 (d,  $J=6.6$  Hz), 133.81 (d,  $J=86.0$  Hz), 138.88, 160.03 (d,  $J=2.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.03. Found: C, 69.37; H, 5.56%. Calcd for  $\text{C}_{22}\text{H}_{21}\text{PS}_2$ : C, 69.44; H, 5.56%. Mp: 106–107 °C.

4.2.7.18. (*Z*)-1-Diphenylthiophosphinyl-2-phenylbutene (**6**). IR (Nujol) 1559, 1436, 1098, 725, 712, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.10 (t,  $J=7.5$  Hz, 3H), 2.57 (qdd,  $J=7.5, 1.5, 0.5$  Hz, 2H), 6.35 (d,  $J=19.0, 1.5$  Hz, 1H), 6.94–7.02 (m, 3H), 7.12–7.16 (m, 2H), 7.22–7.27 (m, 4H), 7.28–7.33 (m, 2H), 7.71–7.77 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  12.35, 35.14 (d,  $J=15.8$  Hz), 118.82 (d,  $J=86.8$  Hz), 127.47, 127.67, 128.01 (d,  $J=12.4$  Hz), 128.02 (d,  $J=1.5$  Hz), 130.66 (d,  $J=2.8$  Hz), 131.26 (d,  $J=10.5$  Hz), 133.48 (d,  $J=85.4$  Hz), 138.57 (d,  $J=6.8$  Hz), 162.87;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.44. Found: C, 75.96; H, 6.09%. Calcd for  $\text{C}_{22}\text{H}_{21}\text{PS}$ : C, 75.83; H, 6.08%. Mp: 79–80 °C. The *Z* configuration of the major isomer was determined by NOE experiments.

4.2.7.19. (*Z*)-1-Diphenylphosphino-2-phenylbutene (**7**). IR (neat) 2966, 1585, 1478, 1433, 1095, 1026, 837, 742, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.09 (t,  $J=7.5$  Hz, 3H), 2.60 (qdd,  $J=7.5, 1.5, 0.5$  Hz, 2H), 6.25 (d,  $J=3.5, 1.5$  Hz, 1H), 7.17–7.20 (m, 2H), 7.26–7.33 (m, 9H), 7.36–7.41 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.00, 33.98 (d,  $J=6.3$  Hz), 123.41 (d,  $J=7.6$  Hz), 127.56, 127.80, 128.11, 128.21 (d,  $J=3.8$  Hz), 128.32 (d,  $J=6.3$  Hz), 132.56 (d,  $J=18.1$  Hz), 140.38 (d,  $J=10.1$  Hz), 141.11 (d,  $J=7.6$  Hz), 160.86 (d,  $J=24.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –28.20. Calcd for  $\text{C}_{22}\text{H}_{21}\text{PS}$ : C, 83.52; H, 6.69%. HRMS found: 316.1382 ( $\Delta=+0.2$  ppm); calcd for  $\text{C}_{22}\text{H}_{21}\text{P}$ : 316.1381  $[\text{M}]^+$ . The *Z* configuration of the major isomer was determined by NOE experiments.

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## Supplementary data

NOE spectra of **5aa**, **6**, and **7**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.071.

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