

Title	Synthesis of DPPP- And DPPPEN-Type Bidentate Ligands by Ring-Opening Diphosphination of Methylene- And Vinylcyclopropanes under Visible-Light-Promoted Photoredox Catalysis
Author(s)	Kato, Yugo; Otomura, Nobutaka; Hirano, Koji et al.
Citation	Journal of Organic Chemistry. 2020, 85(9), p. 5981-5994
Version Type	AM
URL	<a href="https://hdl.handle.net/11094/92702">https://hdl.handle.net/11094/92702</a>
rights	© 2020 American Chemical Society.
Note	

*Osaka University Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

Osaka University

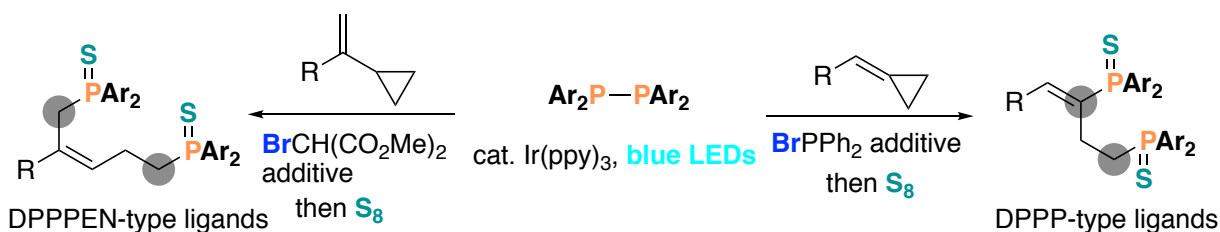
# Synthesis of DPPP- and DPPPEN-Type Bidentate Ligands by Ring-Opening Diphosphination of Methylene- and Vinylcyclopropanes under Visible-Light-Promoted Photoredox Catalysis

Yugo Kato, Nobutaka Otomura, Koji Hirano,\* and Masahiro Miura\*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

*k\_hirano@chem.eng.osaka-u.ac.jp; miura@chem.eng.osaka-u.ac.jp*



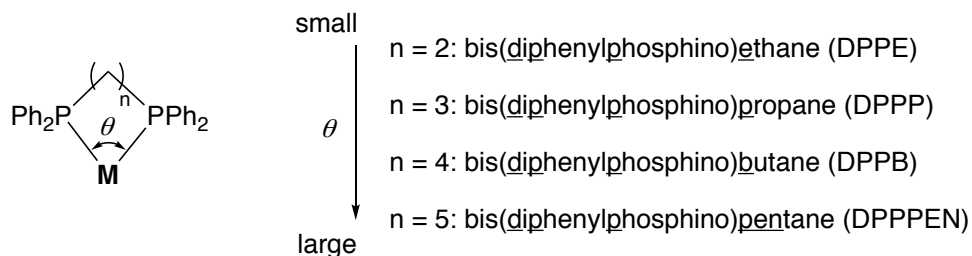
A ring-opening diphosphination of methylene- and vinylcyclopropanes with tetraaryldiphosphines ( $\text{Ar}_2\text{P}-\text{PAr}_2$ ) has been developed to afford the corresponding 1,3-diphenylphosphinopropane- and 1,3-diphenylphosphinopentane-type bidentate ligands, respectively. The reaction proceeds under bromine cation-initiated, visible-light-promoted photoredox catalysis at ambient temperature. Owing to the

ready availability of functionalized diphosphines, the electronically diverse MeO- and CF<sub>3</sub>-substituted bidentate ligands are also easily prepared.

## Introduction

The tertiary phosphines are now one of the indispensable chemical entities in organic synthetic chemistry because they are ancillary ligands for transition-metal catalysts<sup>1</sup> as well as invaluable synthetic reagents and intermediates, as exemplified by Wittig reaction, Horner-Wadsworth-Emmons reaction,<sup>2</sup> and Appel reaction.<sup>3</sup> In particular, 1,n-bis(diphenylphosphino)alkanes ( $n = 2-5$ ) are the most commonly used bidentate ligands because of their uniquely rigid chelating nature (Figure 1). The activity and selectivity of transition-metal complexes are highly dependent on the electronic/steric nature and bite angle  $\theta$  of supporting ligands,<sup>4</sup> and rapid and concise synthesis of various 1,n-bis(diphenylphosphino)alkane-type ligands is thus an important task in synthetic community. The nucleophilic substitution reaction of 1,n-dihalogenated alkanes with highly reactive metal phosphides is the classical but reliable synthetic approach to the aforementioned compounds.<sup>5</sup> On the other hand, given the recent progress of phosphinative difunctionalization reactions of alkenes such as carbophosphination, aminophosphination, and cyanophosphination,<sup>6</sup> the diphosphination reaction of alkynes and/or alkenes with diphosphines ( $R_2P-PR_2$ ) is also considered to be more attractive owing to its potentially better efficiency.<sup>7,8</sup> In 2005, Oshima and Yorimitsu reported the V-40-initiated radical diphosphination of terminal alkynes with diphosphines.<sup>9</sup> Ogawa also developed the same radical diphosphination under UV irradiation.<sup>10</sup> Additionally, some noncatalyzed and Brønsted base-mediated reactions were also reported to date.<sup>11</sup> However, the diphosphination of less reactive alkenes had been a long-standing challenging issue in this research field, except for some specially designed and highly reactive diphosphines.<sup>12</sup> In 2016, Ogawa and Kawaguchi reported the breakthrough and successful reaction of simple alkenes with diphosphine monoxides  $R_2P-P(O)R_2$  instead of the parent diphosphines  $R_2P-PR_2$ , giving the corresponding DPPE-type bidentate ligands ( $n = 2$  in Figure 1) (Scheme 1a).<sup>13a</sup> Subsequently, the same research group improved the reaction efficiency and scope by using further modified diphosphine monosulfides  $R_2P-P(S)R_2$ <sup>13b</sup> and disulfides  $R_2(S)P-P(S)R_2$ .<sup>13c</sup> Our group also focused on the unique reactivity of diphosphines  $R_2P-PR_2$  under  $Ir(ppy)_3$  photoredox catalysis and

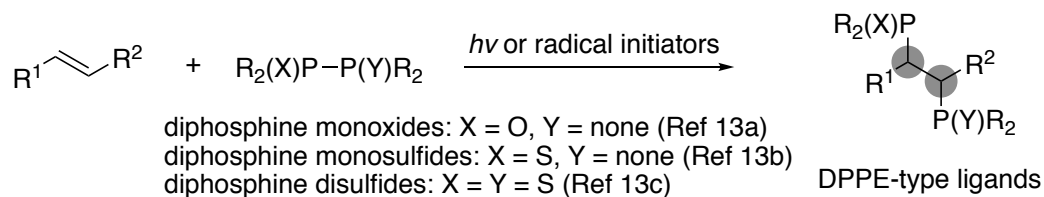
succeeded in the development of diphosphination of alkenes<sup>14a</sup> and 1,3-dienes<sup>14b</sup> with the assistance of bromine cation additives to provide the corresponding DPPE- and DPPB-type bidentate ligands ( $n = 2, 4$  in Figure 1), respectively (Scheme 1b, left).<sup>15</sup> However, the synthesis of 1, $n$ -bis(diphenylphosphino)alkanes with the odd-numbered methylene tethers, namely, DPPP- and DPPPEN-type ligands ( $n = 3, 5$  in Figure 1) still remains unexplored. Given the large impact of ligand bite angles on the catalytic activity/selectivity of transition metal catalysis, development of potentially more efficient access to such bidentate ligands is greatly appealing. Herein, we report a ring-opening diphosphination of methylene- and vinylcyclopropanes with diphosphines under bromine cation initiated, visible-light-promoted photoredox catalysis to deliver the corresponding DPPP- and DPPPEN-type ligands, respectively (Scheme 1b, right). Functionalized tetraaryldiphosphines are readily prepared, and the present protocol thus can provide the electronically tuned bisphosphinoalkanes with electron-donating Me and MeO as well as electron-withdrawing CF<sub>3</sub> groups.



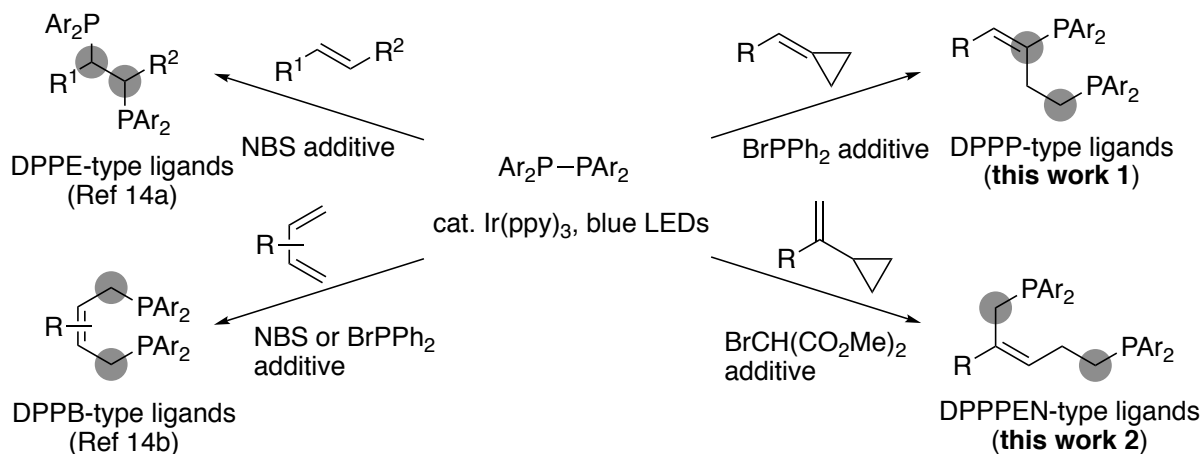
**Figure 1.** Commonly used 1, $n$ -bis(diphenylphosphino)alkanes. M = transition metals.

## Scheme 1. Approaches to 1,*n*-Bis(diphenylphosphino)alkane-Type Bidentate Ligands via Diphosphination of Alkenes with Diphosphine Derivatives

a) Ogawa and Kawaguchi



b) our group



## Results and Discussion

Our optimization studies commenced with benzylidencyclopropane (**1a**) and tetraphenyldiphosphine (**2a**; Table 1). Based on the previous work,<sup>14a,b</sup> treatment of **1a** with **2a** (2.0 equiv) in the presence of 0.50 mol % Ir(ppy)<sub>3</sub> photocatalyst (PC) and 20 mol % NBS additive in DCE solvent under blue light-emitting diode (LED) irradiation (2.4 W) followed by addition of S<sub>8</sub> afforded the desired ring-opening diphosphinated product **3aa-S** in 36% <sup>31</sup>P NMR yield with 88:12 *E/Z* ratio (entry 1). We next screened some representative bromine cation sources as the additive (entries 2–7), with BrPPh<sub>2</sub> proving to be optimal (entry 2). Subsequent investigations of other PCs revealed that [Ir{dFCF<sub>3</sub>ppy}<sub>2</sub>(bpy)]PF<sub>6</sub> showed a good performance comparable to Ir(ppy)<sub>3</sub> (entry 9) while Ir(ppy)<sub>2</sub>(dtbpy)PF<sub>6</sub>, Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, and organic dye eosin Y (Na) gave much lower or no reactivity (entries 8, 10, and 11). After additional fine tuning, with increased amounts of Ir(ppy)<sub>3</sub> (2.0 mol %) and **2a** (2.5 equiv) the DPPP-type **3aa-S** was

finally obtained in 74%  $^{31}\text{P}$  NMR yield with 93:7 *E/Z* ratio (56% yield and *E/Z* = 86:14 after purification; entry 12). The control experiments confirmed that the photocatalyst and visible light were necessary for satisfying conversion of **1a** (entries 13 and 14). On the other hand, even without  $\text{BrPPh}_2$  the reaction proceeded albeit with a much lower yield (entry 15).

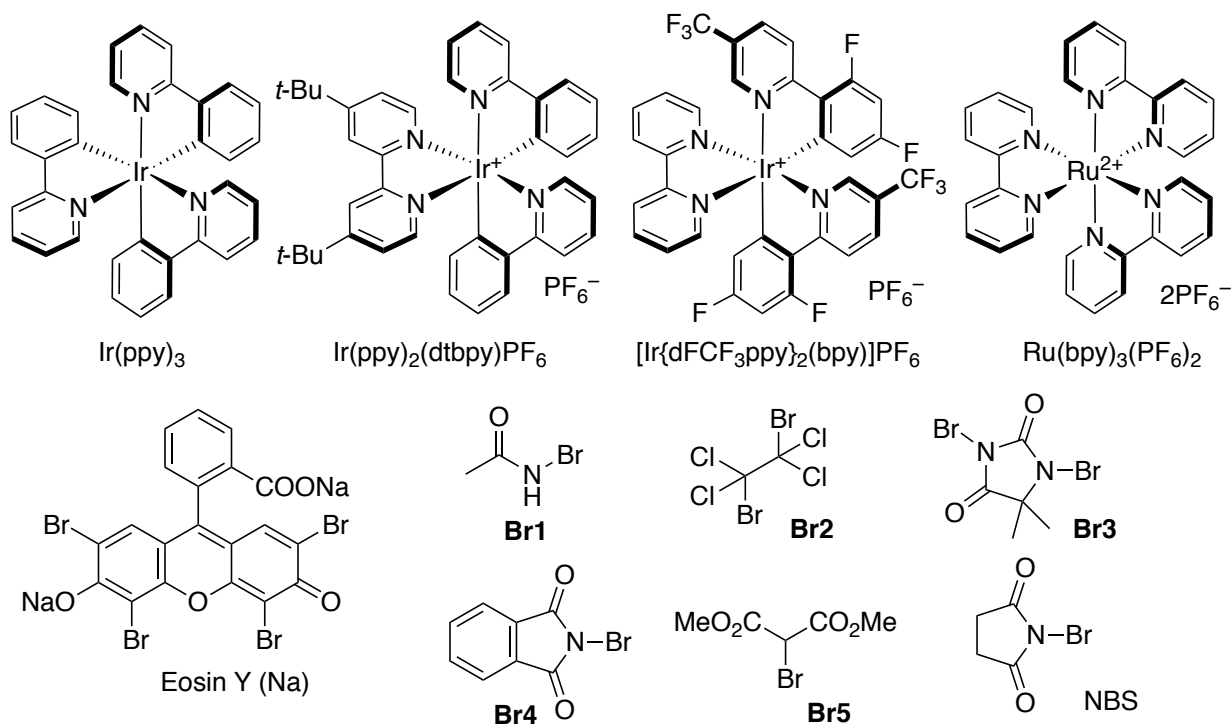
**Table 1. Optimization for Ring-Opening Diphosphination of Benzyldenecyclopropane (**1a**) with Tetraphenyldiphosphine (**2a**) under Visible-Light-Promoted Photoredox Catalysis<sup>a</sup>**

Reaction scheme: **1a** + **2a**  $\xrightarrow[\text{DCE, blue LEDs, 4 h then } \text{S}_8, \text{ rt, 30 min}]{\text{PC (0.50 mol \%), additive (20 mol \%)}$  **3aa-S**

entry	PC	additive	yield (%) <sup>b</sup> , <i>E/Z</i> <sup>c</sup>	
1	$\text{Ir}(\text{ppy})_3$	NBS	36	88:12
2	$\text{Ir}(\text{ppy})_3$	$\text{BrPPh}_2$	56	86:14
3	$\text{Ir}(\text{ppy})_3$	<b>Br1</b>	24	79:21
4	$\text{Ir}(\text{ppy})_3$	<b>Br2</b>	45	87:13
5 <sup>d</sup>	$\text{Ir}(\text{ppy})_3$	<b>Br3</b>	24	86:14
6	$\text{Ir}(\text{ppy})_3$	<b>Br4</b>	11	88:12
7	$\text{Ir}(\text{ppy})_3$	<b>Br5</b>	44	84:16
8	$\text{Ir}(\text{ppy})_2(\text{dtbpy})\text{PF}_6$	$\text{BrPPh}_2$	13	89:11
9	$[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$	$\text{BrPPh}_2$	51	84:16
10	$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$	$\text{BrPPh}_2$	0	–
11 <sup>e</sup>	Eosin Y (Na)	$\text{BrPPh}_2$	0	–
12 <sup>f</sup>	$\text{Ir}(\text{ppy})_3$	$\text{BrPPh}_2$	75 (56)	93:7 (86:14)

13 <sup>f</sup>	None	BrPPh <sub>2</sub>	0	–
14 <sup>f,g</sup>	Ir(ppy) <sub>3</sub>	BrPPh <sub>2</sub>	0	–
15 <sup>f</sup>	Ir(ppy) <sub>3</sub>	none	38	77:23

<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), PC (0.0013 mmol), additive (0.050 mmol), DCE (1.5 mL), blue LED irradiation (2.4 W), 4 h, ambient temp, N<sub>2</sub> then S<sub>8</sub> (1.3 mmol based on S atom), rt, 30 min, N<sub>2</sub>. <sup>b</sup> <sup>31</sup>P NMR yield with O=P(OEt)<sub>3</sub> internal standard. Isolated yield is in parentheses. <sup>c</sup> Determined by <sup>31</sup>P NMR of the crude mixture. The ratio of the isolated product in parentheses. <sup>d</sup> With **Br3** (0.025 mmol). <sup>e</sup> With green LEDs (2.4 W). <sup>f</sup> With Ir(ppy)<sub>3</sub> (0.0050 mmol), **2a** (0.63 mmol), DCE (1.0 mL), and S<sub>8</sub> (1.5 mmol). <sup>g</sup> In dark.

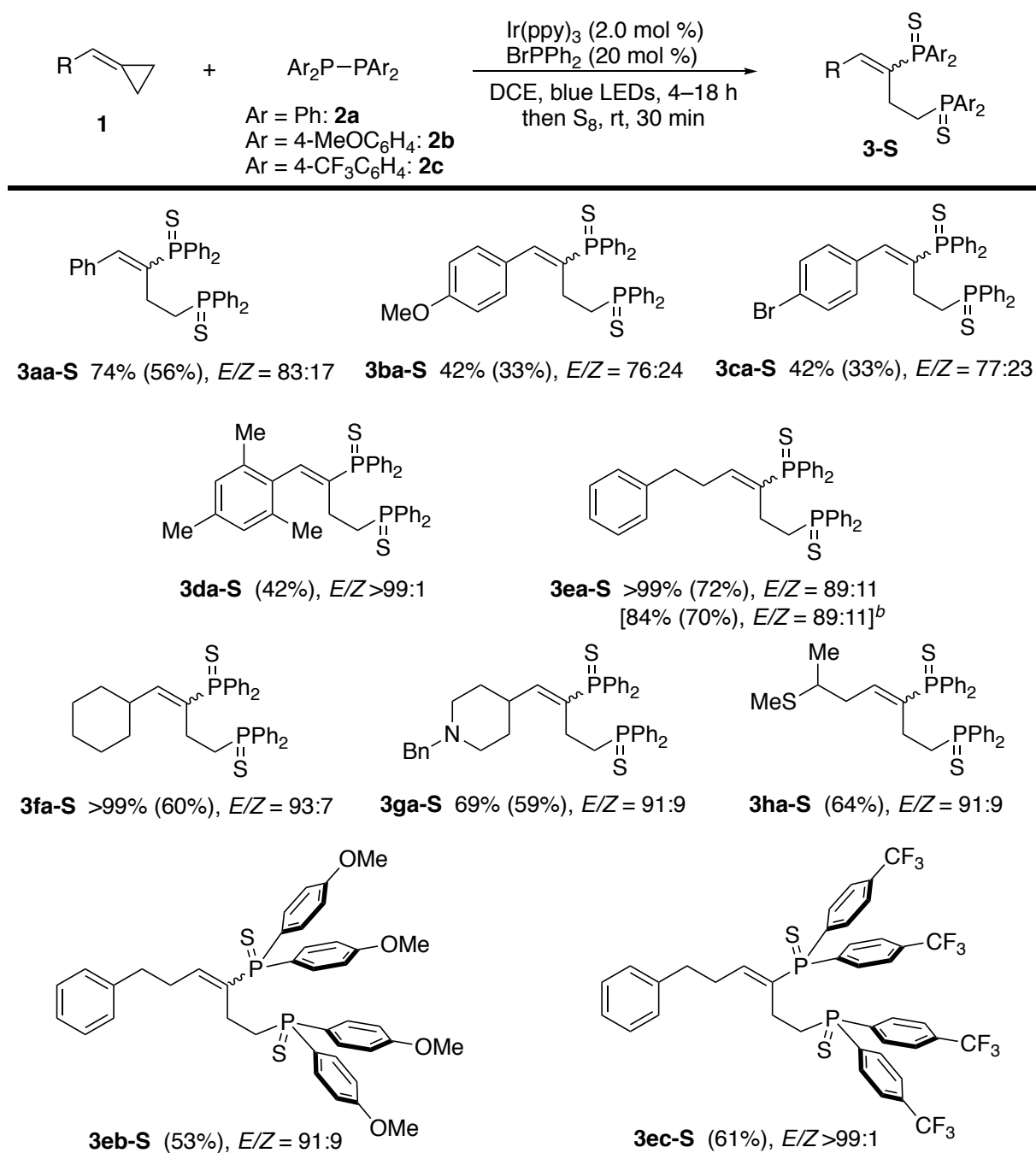


With conditions of entry 12 in Table 1, we investigated the scope of methylenecyclopropanes **1** (Scheme 2). The introduction of both electron-donating (MeO) and electron-withdrawing (Br) groups on the benzene of **1a** gave somewhat negative impact to deliver the corresponding diphosphinated products **3ba-S** and **3ca-S** in moderate yields. The bulky mesityl-substituted substrate produced **3da-S** with high *E*-



selectivity ( $E/Z >99:1$ ). On the other hand, the aliphatic substrates showed better reactivity: the phenethyl- and cyclohexyl-substituted methylenecyclopropanes underwent the ring-opening diphosphination smoothly to furnish **3ea-S** and **3fa-S** in 72 and 60% yields, respectively. The structure of **3ea-S** was confirmed by X-ray analysis, and the stereochemistry of the major isomer was also determined to be *E* (see the Supporting Information for details). Additionally, the photoredox catalysis was compatible with the amine and sulfur functional groups, and the DPPP-type ligands **3ga-S** and **3ha-S** with additional coordinating heteroatoms were obtained in synthetically acceptable yields. Additionally notable is the successful application of electronically modified tetraaryldiphosphines: the readily prepared MeO- and CF<sub>3</sub>-substituted diphosphines **2b** and **2c** could also be coupled with **1e** to form the electronically tuned **3eb-S** and **3ec-S** in good yields with high stereoselectivity.

**Scheme 2. Synthesis of DPPP-Type Ligands 3 from Various Methylene-cyclopropanes 1 and Tetraaryldiphosphines 2 under Visible-Light-Promoted Photoredox Catalysis<sup>a</sup>**



<sup>a</sup> <sup>31</sup>P NMR yields with O=P(OEt)<sub>3</sub> internal standard are shown. Isolated yields are in parentheses. <sup>b</sup>

On a 1.0 mmol scale.

Prompted by the aforementioned successful synthesis of DPPP-type ligands via ring-opening diphosphination of methylene-cyclopropanes, we then moved our attention to vinylcyclopropane **4a** for

the synthesis of DPPPEN-type ligand **5aa-S** (Table 2). Under the almost same conditions as in the BrPPh<sub>2</sub>-promoted reaction of methylenecyclopropane **1a** with **2a**, **4a** was converted to the targeted **5aa-S** in 61% <sup>1</sup>H NMR yield with 27:73 *E/Z* ratio (entry 1). Among other bromine cation sources tested (entries 2–7), dimethyl bromomalonate (**Br5**) was the best choice from the viewpoints of reactivity and practicality to afford **5aa-S** in 77% <sup>1</sup>H NMR yield (60% yield after purification; entry 7). Evaluation of other PCs proved a slightly better performance of Ir(ppy)<sub>3</sub> (entries 8–10). On the other hand, the control experiments revealed that the reaction occurred even in the absence of a photocatalyst and light (entries 11–13), thus suggesting the background reaction probably via a phosphonium cation species (*vide infra*).

**Table 2. Optimization for Ring-Opening Diphosphination of Vinylcyclopropane **4a** with Tetraphenyldiphosphine (**2a**) under Visible-Light-Promoted Photoredox Catalysis<sup>a</sup>**

Reaction scheme: Vinylcyclopropane **4a** + Tetraphenyldiphosphine **2a** (Ph<sub>2</sub>P–PPh<sub>2</sub>) → **5aa-S**. Conditions: PC (0.50 mol %), additive (20 mol %), DCE, blue LEDs, 4 h, then S<sub>8</sub>, rt, 30 min.

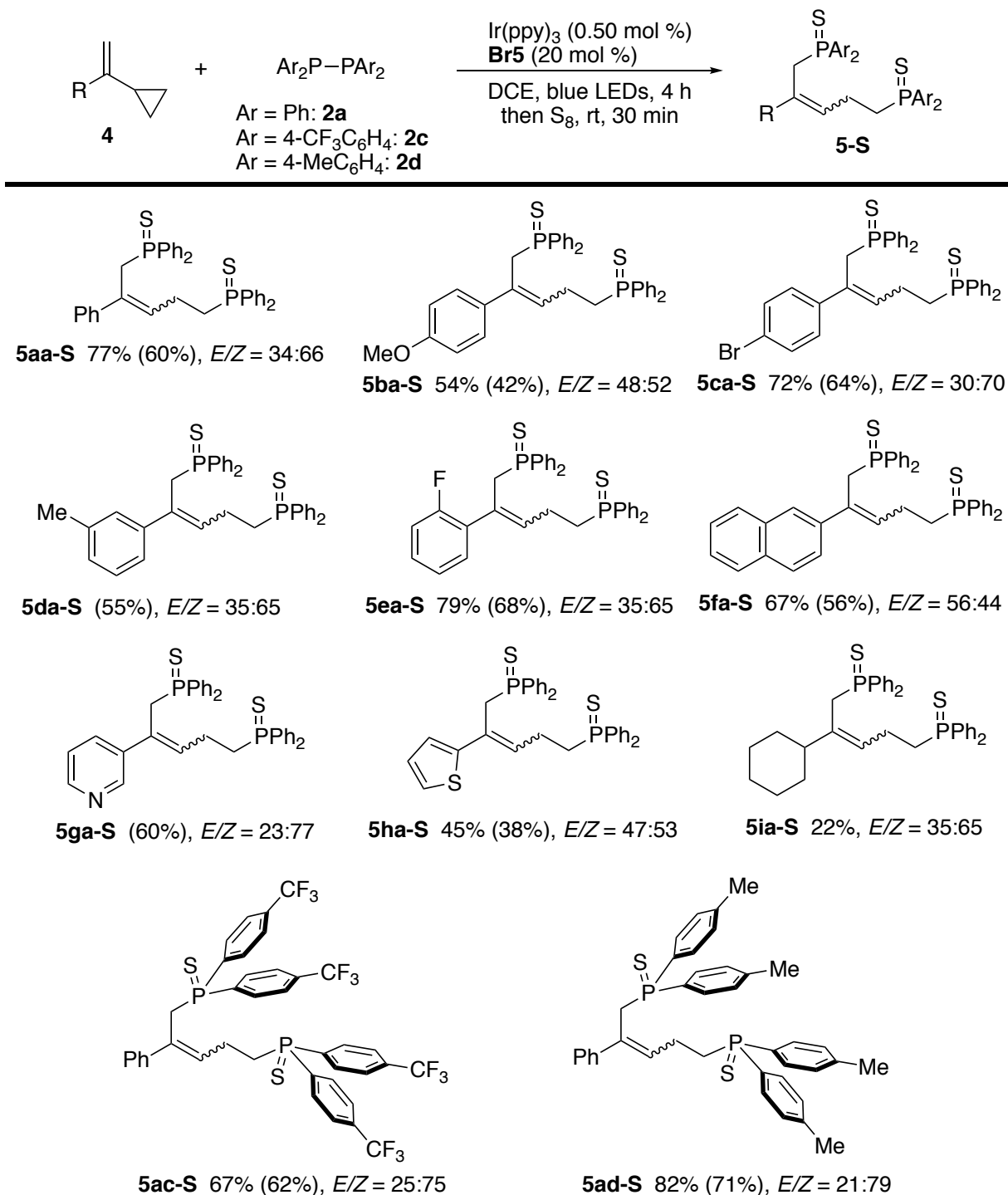
entry	PC	additive	yield (%) <sup>b</sup> , <i>E/Z</i> <sup>c</sup>	
1	Ir(ppy) <sub>3</sub>	BrPPh <sub>2</sub>	61	27:73
2	Ir(ppy) <sub>3</sub>	NBS	66	28:72
3	Ir(ppy) <sub>3</sub>	<b>Br1</b>	80 <sup>d</sup>	25:75
4	Ir(ppy) <sub>3</sub>	<b>Br2</b>	46	18:82
5 <sup>e</sup>	Ir(ppy) <sub>3</sub>	<b>Br3</b>	65	25:75
6	Ir(ppy) <sub>3</sub>	<b>Br4</b>	26	15:85
7	Ir(ppy) <sub>3</sub>	<b>Br5</b>	77 (60)	(34:66)
8	Ir(ppy) <sub>2</sub> (dtbpy)PF <sub>6</sub>	<b>Br1</b>	73	20:80
9	[Ir{dFCF <sub>3</sub> ppy} <sub>2</sub> (bpy)]PF <sub>6</sub>	<b>Br1</b>	74	24:76

10 <sup>f</sup>	eosin Y (Na)	<b>Br1</b>	39	20:80
11	None	<b>Br5</b>	29	23:77
12 <sup>g</sup>	Ir(ppy) <sub>3</sub>	<b>Br5</b>	20	33:67
13 <sup>g</sup>	None	<b>Br5</b>	29	22:78

<sup>a</sup> Reaction conditions: **4a** (0.25 mmol), **2a** (0.50 mmol), PC (0.0013 mmol), additive (0.050 mmol), DCE (1.5 mL), blue LED irradiation (2.4 W), 4 h, ambient temp, N<sub>2</sub> then S<sub>8</sub> (1.3 mmol based on S atom), rt, 30 min, N<sub>2</sub>. <sup>b</sup> <sup>1</sup>H NMR yield with O=P(OEt)<sub>3</sub> internal standard. Isolated yield is in parentheses. <sup>c</sup> Determined by <sup>31</sup>P NMR of the crude mixture. The ratio of the isolated product in parentheses. <sup>d</sup> The purification was difficult because of the formation of unidentified byproducts. <sup>e</sup> With **Br3** (0.025 mmol). <sup>f</sup> With green LEDs (2.4 W). <sup>g</sup> In dark.

The Ir(ppy)<sub>3</sub>/**Br5** system was also applicable to several aryl-substituted vinylcyclopropanes **4** that bear MeO, Br, Me, and F substituents at the para, meta, and ortho positions on the benzene ring (**5ba-S–5ea-S**; Scheme 3). The naphthalene ring was also tolerated under the standard conditions (**5fa-S**). Moreover, the heteroaromatic substrates could also participate in the reaction to form the pyridine- and thiophene-containing DPPPEN-type ligands **5ga-S** and **5ha-S** in acceptable yields. However, different from the methylenecyclopropane derivatives **1**, the aliphatic system showed much lower reactivity (**5ia-S**). Again, the salient feature of the photoredox catalysis was the ready introduction of functionalized diarylphosphino groups: the electron-withdrawing and -donating DPPPEN-type ligands **5ac-S** and **5ad-S** were successfully obtained in good yields. On the other hand, our attempts to apply tetracyclohexyldiphosphine remained unsuccessful (data not shown).

**Scheme 3. Synthesis of DPPPEN-Type Ligands 5 from Various Vinylcyclopropanes 4 and Tetraaryldiphosphines 2 under Visible-Light-Promoted Photoredox Catalysis<sup>a</sup>**



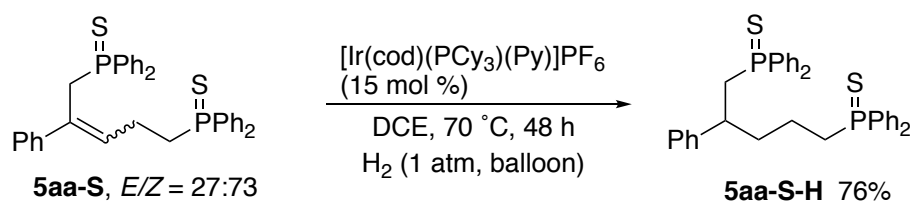
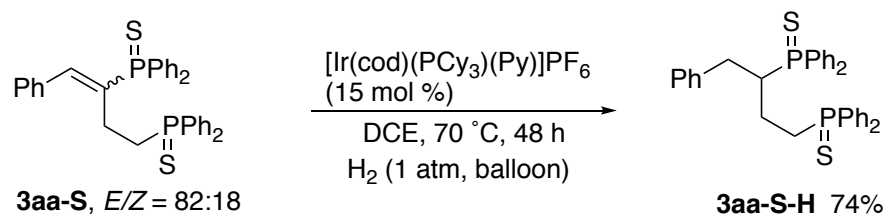
<sup>a</sup> <sup>1</sup>H NMR yields with O=P(OEt)<sub>3</sub> internal standard are shown. Isolated yields are in parentheses.

Both DPPP-(**3aa-S**) and DPPPEN-type (**5aa-S**) ligands obtained above were readily hydrogenated by Crabtree's catalyst [Ir(cod)(PCy<sub>3</sub>)(Py)]PF<sub>6</sub><sup>16</sup> to form the corresponding saturated derivatives **3aa-S-H** and **5aa-S-H** in 74 and 76% yields, respectively (Scheme 4a). Moreover, the desulfidation was possible with

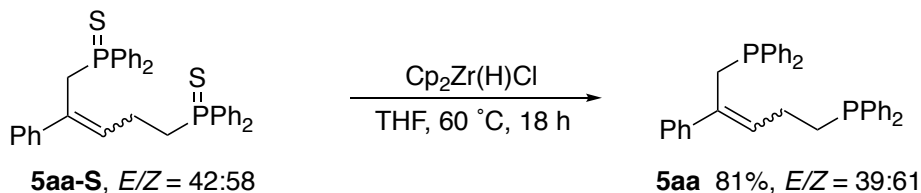
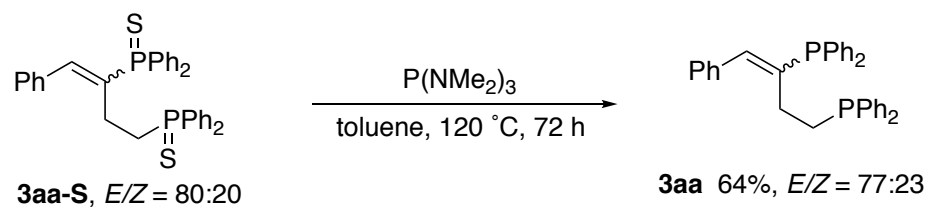
$P(NMe_2)_3$ <sup>17</sup> or Schwartz reagent  $Cp_2Zr(H)Cl$ ,<sup>18</sup> and the coordinating P(III) bisphosphines **3aa** and **5aa** were isolated in good yields (Scheme 4b).

**Scheme 4. Hydrogenation and Desulfidation of DPPP- and DPPPEN-Type Ligands 3aa-S and 5aa-S**

a) Hydrogenation



b) Desulfidation



On the basis of the literature information,<sup>19</sup> the proposed reaction mechanisms of methylenecyclopropane **1a** and vinylcyclopropane **4a** are indicated in Scheme 5a,b, respectively. In the case of **1a** (Scheme 5a), the excited Ir(III)\* undergoes a single electron transfer to the  $BrPPh_2$  additive to generate the phosphinyl radical **6**; this step was supported by the luminescence quench of  $Ir(ppy)_3$  with  $BrPPh_2$ .<sup>14a</sup> Subsequent radical addition to **1a** followed by the ring-opening affords the primary radical

7', and the back electron transfer to Ir(IV) forms cation 8' along with the regeneration of Ir(III) in the ground state to complete the Ir photocatalytic cycle. However, given the rate constant of the ring-opening process of radical 7<sup>20</sup> and somewhat lower oxidation potential of Ir(IV)/(III) of Ir(ppy)<sub>3</sub>,<sup>21</sup> the reverse order, back electron transfer and then ring-opening, is also plausible. The cation species is trapped with 2a at the most sterically accessible terminal position regioselectively to generate the ring-opening phosphonium species 9, which finally participates in the single electron transfer reduction,<sup>22</sup> en route to the DPPP-type 3aa and the starting phosphinyl radical 6. Given that additive-free conditions also provides 3aa (entry 15 in Table 1), the direct generation of 6 from 2a via an energy transfer mechanism<sup>23</sup> might be competitive. Additionally, the possibility of the radical chain mechanism cannot be completely excluded, although the light ON/OFF experiment of 1e with 2a can support the Ir photoredox mechanism (Figure 2).

The reaction mechanism of 4a is principally the same as that of 1a (Scheme 5b), which includes i) phosphinyl radical 6 generation via BrPPh<sub>2</sub>, ii) radical addition of 6 to 4a, iii) ring-opening/one electron oxidation via back electron transfer (10/10' to 11/11'), iv) regioselective addition of diphosphine 2a (11/11' to 12/12'), and v) formation of DPPPEN-type ligand 5aa and regeneration of phosphinyl radical 6. The bromine cation source Br5 initially reacted with diphosphine 2a to generate BrPPh<sub>2</sub> in situ.<sup>24</sup> The reaction of 4a with 2a was promoted, to some extent, only by Br5 (entries 11 and 12 in Table 2), thus suggesting additional pathway via a phosphonium cation-like species generated in situ (Scheme 5c): the driving force of this background process might be attributed to the formation of a highly stable tertiary benzyl cation intermediate.

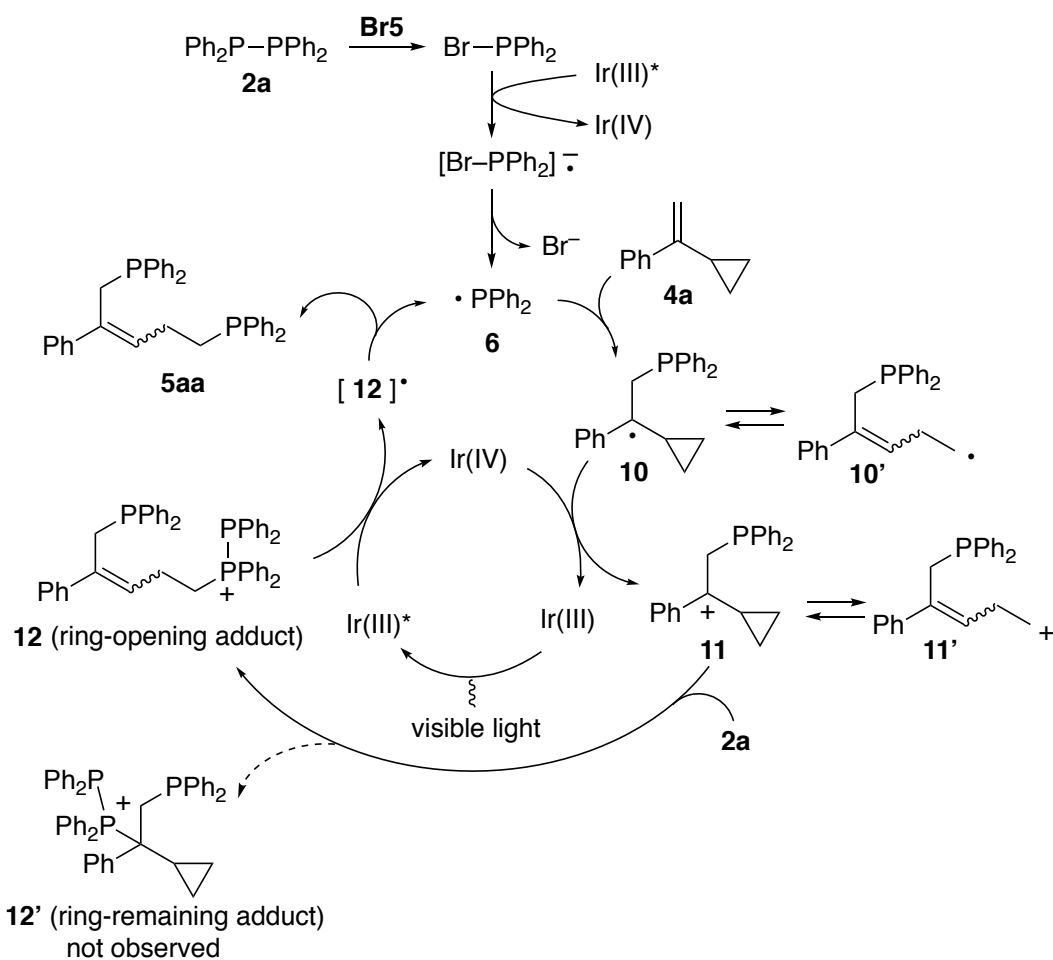
In both reactions, the energy transfer from excited Ir(III)\* to BrPPh<sub>2</sub> can be an alternative pathway to form the phosphinyl radical 6. However, the reactivity trend of Ir(ppy)<sub>3</sub>, Ir(ppy)<sub>2</sub>(dtbpy)PF<sub>6</sub>, and [Ir{dFCF<sub>3</sub>ppy}<sub>2</sub>(bpy)]PF<sub>6</sub> was not fully correlated with each T<sub>1</sub> energy (57.8, 49.2, and 60.4 kcal/mol, respectively).<sup>23</sup>

In both catalytic cycles, the stereochemistry (*E* or *Z*) is kinetically determined in the ring-opening step to form the more sterically and thermodynamically favored (*E*)-3aa and (*Z*)-5aa preferably, but in the

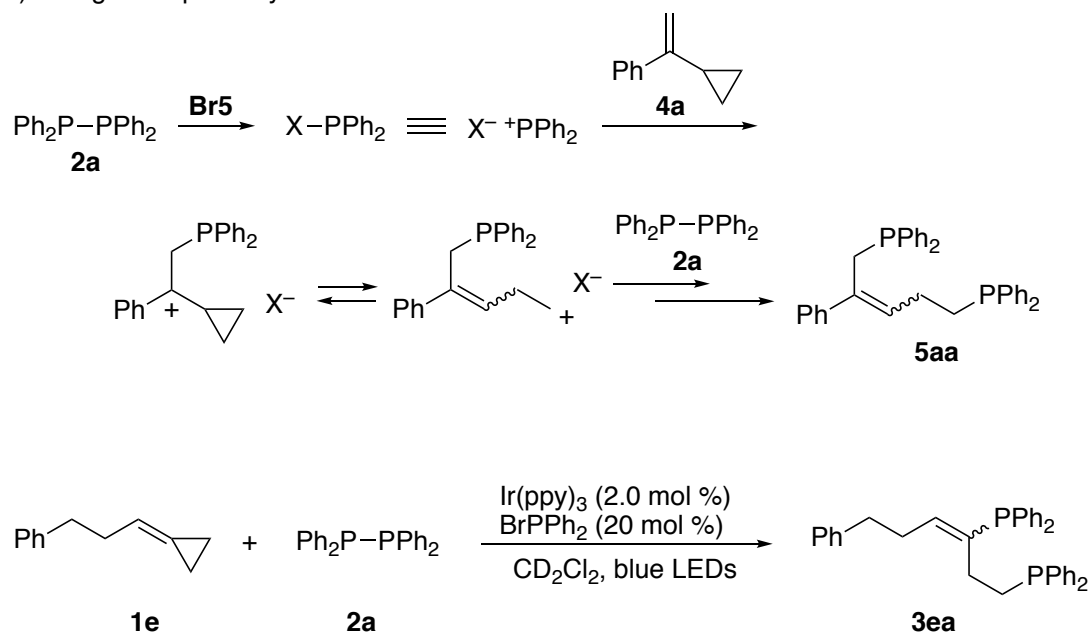


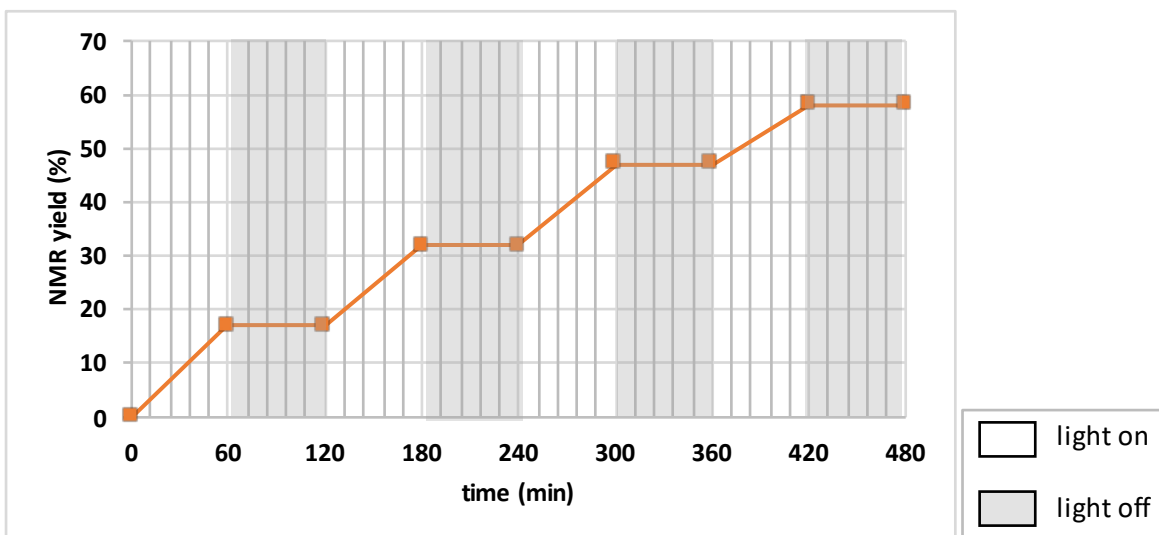


b) plausible mechanism with **4a**



c) background pathway with **4a**





**Figure 2.** ON/OFF experiment of **1e** with **2a**.

## Conclusions

We have developed bromine cation-initiated, visible-light-promoted photoredox catalysis for ring-opening diphosphination of methylene- and vinylcyclopropanes with tetraaryldiphosphines to form the corresponding 1,3-bis(diphenylphosphino)propane (DPPP) and 1,5-bis(diphenylphosphino)pentane (DPPPEN) derivatives. Combined with the previous work on the synthesis of 1,2-bis(diphenylphosphino)ethane (DPPE)<sup>14a</sup> and 1,4-bis(diphenylphosphino)butane (DPPB) derivatives,<sup>14b</sup> the Br<sup>+</sup>/photoredox system can provide concise access to all commonly used 1,n-bis(diphenylphosphino)alkane (n = 2–5) bidentate ligands from relatively simple unsaturated hydrocarbon materials. Thus, the present protocols can supply sterically and electronically diverse bidentate ligands to accelerate further development of homogeneous transition-metal catalysis. Application of newly synthesized bisphosphine ligands in catalysis are now under investigation.

## Experimental Section

**Instrumentation and Chemicals** <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were generally recorded at 400, 100, 376, and 162 MHz (Ascend 400, Bruker; analyzed by Bruker Top Spin 4.0.5), respectively, for CDCl<sub>3</sub> solutions. HRMS data were obtained by APCI using TOF. TLC analyses were

performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel 60F<sub>254</sub>. Silica gel (Wakosil C-200) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-20AR (pump, SHIMADZU, 7.5 mL/min chloroform) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line YMC-GPC T2000 (20 × 600 mm, particle size: 10 μm) (preparative columns, YMC). Unless otherwise noted, materials obtained from commercial suppliers were used as received. DCE was freshly distilled from CaH<sub>2</sub>. Methylene cyclopropanes **1**<sup>28</sup> and vinylcyclopropanes **4**<sup>29</sup> were prepared from the corresponding aldehydes and ketones according to the literature. Tetraaryldiphosphines **2** were synthesized via the condensation of chloro- and hydrophosphines.<sup>9,11a,15a</sup> Blue LED irradiation was conducted with 1.0 m blue LED tape (2.4 W, 3 cm distance from the reaction vessel) without any special temperature control (see the Supporting Information for the picture of the reaction setup). All reactions were carried out under nitrogen atmosphere unless otherwise noted.

The stereochemistry of DPPP-type ligand **3ea-S** was determined by X-ray analysis (CCDC 1983992), and that of others **3** was assigned by analogy. The stereochemistry of DPPPEN-type ligands **5** was assigned according to the reported NOESY analysis of **5aa-S**.<sup>15a</sup>

**Typical Procedure for Ring-Opening Diphosphination of Methylene cyclopropanes 1 with Diphosphines 2.** The synthesis of **3aa-S** is representative (Scheme 2). Ir(ppy)<sub>3</sub> (3.2 mg, 0.005 mmol) and tetraphenyldiphosphine (**2a**; 231 mg, 0.63 mmol) were placed in a 10-mL Schlenk flask, which was filled with N<sub>2</sub>. DCE (1.5 mL) and BrPPh<sub>2</sub> (13 mg, 0.050 mmol) were added, and the solution was stirred for 3 min. Benzylidenecyclopropane (**1a**; 36 mg, 0.25 mmol) was added into the mixture, and the resulting solution was irradiated with blue LEDs at ambient temperature for 4 h (2.4 W with LED tapes, no special temperature control, 3 cm distance from the LEDs, see Figure S1). Elemental sulfur (S<sub>8</sub>; 48 mg, 1.5 mmol of S atom) was then added. After the mixture was stirred for further 30 min at room temperature, the solution was filtered through a short pad of Celite, silica gel, alumina, anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residual solid was dissolved in CDCl<sub>3</sub>, and the yield was calculated by

<sup>1</sup>H NMR with triethyl phosphate as an internal standard (18 mg, 0.10 mmol). After the NMR analysis, concentration in vacuo and purification by column chromatography on silica gel with hexane-ethyl acetate (5:1, v/v) gave 2,4-bis(diphenylthiophosphinyl)-1-phenylbut-1-ene (**3aa-S**, 79 mg, 0.14 mmol, *E/Z* = 83:17) in 56% yield.

**1.0 mmol Scale Synthesis of 3ea-S.** Ir(ppy)<sub>3</sub> (13 mg, 0.020 mmol) and tetraphenyldiphosphine (**2a**; 930 mg, 2.5 mmol) were placed in a 10-mL Schlenk flask, which was filled with N<sub>2</sub>. DCE (4.0 mL) and BrPPh<sub>2</sub> (53 mg, 0.20 mmol) were added, and the solution was stirred for 3 min. 3-Phenylpropylidenecyclopropane (**1e**; 160 mg, 1.0 mmol) was added into the mixture, and the resulting solution was irradiated with blue LEDs at ambient temperature for 18 h (2.4 W with LED tapes, no special temperature control, 3 cm distance from the LEDs, see Figure S1). Elemental sulfur (S<sub>8</sub>; 240 mg, 7.5 mmol of S atom) was then added. After the mixture was stirred for further 30 min at room temperature, the solution was directly purified by column chromatography on silica gel with hexane-ethylacetate (5:1, v/v) gave 1,3-bis(diphenylthiophosphinyl)-6-phenylhex-3-ene (**3ea-S**, 420 mg, 0.71 mmol, *E/Z* = 89:11) in 70% yield.

**(*E*)-2,4-Bis(diphenylthiophosphinyl)-1-phenylbut-1-ene ((*E*)-3aa-S).** Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v) and then by GPC (chloroform); white solid; m.p. 116.5-118.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.73-2.80 (m, 2H), 2.94-3.03 (m, 2H), 6.86 (d, *J* = 24.2 Hz, 1H), 7.29-7.53 (m, 17H), 7.70-7.75 (m, 4H), 7.80-7.86 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 22.5 (d, *J* = 12.3 Hz, 1C), 31.6 (d, *J* = 52.7 Hz, 1C), 128.6 (d, *J* = 12.1 Hz, 4C), 128.7 (2C), 128.9 (d, *J* = 10.1 Hz, 4C), 129.1 (1C), 129.6 (2C), 131.1 (d, *J* = 10.3 Hz, 4C), 131.2 (d, *J* = 83.0 Hz, 2C), 131.4 (d, *J* = 2.8 Hz, 2C), 131.8 (d, *J* = 2.8 Hz, 2C), 132.3 (d, *J* = 79.5 Hz, 2C), 132.4 (d, *J* = 10.3 Hz, 4C), 133.4 (dd, *J* = 17.2 Hz, 76.6 Hz, 1C), 134.7 (d, *J* = 19.5 Hz, 1C), 143.3 (d, *J* = 12.0 Hz, 1C); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ 42.38, 50.15; HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>34</sub>H<sub>31</sub>P<sub>2</sub>S<sub>2</sub>, 565.1337; found, 565.1335.

**(Z)-2,4-Bis(diphenylthiophosphinyl)-1-phenylbut-1-ene ((Z)-3aa-S)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v) and then by GPC (chloroform); white solid; m.p. 174.5-176.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.63-2.74 (m, 2H), 2.97-3.04 (m, 2H), 6.84-6.90 (m, 3H), 7.13-7.17 (m, 4H), 7.20-7.27 (m, 4H), 7.34-7.40 (m, 4H), 7.40-7.51 (m, 3H), 7.70-7.80 (m, 8H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 30.9 (d, *J* = 12.8 Hz, 1C), 35.4 (d, *J* = 52.8 Hz, 1C), 127.4 (2C), 128.0 (1C), 128.2 (d, *J* = 12.4 Hz, 4C), 128.7 (d, *J* = 12.0 Hz, 4C), 130.0 (2C), 131.08-131.10 (m, 2C), 131.14 (d, *J* = 10.3 Hz, 4C), 131.5 (d, *J* = 3.0 Hz, 2C), 131.58 (d, *J* = 10.4 Hz, 4C), 131.61 (d, *J* = 76.0 Hz, 2C), 132.4 (d, *J* = 73.3 Hz, 2C), 133.0 (dd, *J* = 15.6 Hz, 74.5 Hz, 1C), 135.3 (d, *J* = 5.5 Hz, 1C), 144.8 (d, *J* = 6.3 Hz, 1C); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ 37.23, 42.22; HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>34</sub>H<sub>31</sub>P<sub>2</sub>S<sub>2</sub>, 565.1337; found, 565.1318.

**2,4-Bis(diphenylthiophosphinyl)-1-(4-methoxyphenyl)but-1-ene (3ba-S, E/Z = 76:24)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v); 50.4 mg (33%); white solid; m.p. 94.9-96.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), for mixture, δ 2.60-2.70 (m, 0.24 x 2H for **(Z)-3ba-S**), 2.80-2.91 (m, 0.76 x 2H for **(E)-3ba-S**), 2.94-3.02 (m, 0.76 x 2H for **(E)-3ba-S**), 2.94-3.02 (m, 0.24 x 2H for **(Z)-3ba-S**), 3.63 (s, 0.24 x 3H for **(Z)-3ba-S**), 3.83 (s, 0.76 x 3H for **(E)-3ba-S**), 6.39-6.42 (m, 0.24 x 2H for **(Z)-3ba-S**), 6.74 (d, *J* = 24.5 Hz, 0.76 x 1H for **(E)-3ba-S**), 6.87-6.90 (m, 0.76 x 2H for **(E)-3ba-S**), 7.15-7.19 (m, 0.76 x 1H for **(E)-3ba-S**), 7.22-7.26 (m, 0.24 x 3H for **(Z)-3ba-S**), 7.35-7.53 (m, 0.76 x 13H for **(E)-3ba-S**), 7.35-7.53 (m, 0.24 x 12H for **(Z)-3ba-S**), 7.74-7.84 (m, 0.76 x 8H for **(E)-3ba-S**), 7.69-7.84 (m, 0.24 x 8H for **(Z)-3ba-S**); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), for mixture, δ 22.6 (d, *J* = 12.4 Hz, 1C for **(E)-3ba-S**), 30.9 (d, *J* = 12.4 Hz, 1C for **(Z)-3ba-S**), 31.3 (d, *J* = 52.0 Hz, 1C for **(E)-3ba-S**), 35.4 (d, *J* = 51.9 Hz, 1C for **(Z)-3ba-S**), 55.2 (1C for **(Z)-3ba-S**), 55.5 (1C for **(E)-3ba-S**), 112.8 (2C for **(Z)-3ba-S**), 114.4 (2C for **(E)-3ba-S**), 127.4 (d, *J* = 19.9 Hz, 1C for **(E)-3ba-S**), 128.0 (d, *J* = 5.7 Hz, 1C for **(Z)-3ba-S**), 128.2 (d, *J* = 12.3 Hz, 4C for **(Z)-3ba-S**), 128.69 (d, *J* = 11.9 Hz, 4C for **(E)-3ba-S**), 128.69 (d, *J* = 11.9 Hz, 4C for **(Z)-3ba-S**), 128.8 (d, *J* = 12.2 Hz, 4C for **(E)-3ba-S**), 130.0 (dd, *J* =

17.2 Hz, 78.8 Hz, 1C for (*E*)-**3ba-S**), 131.0 (d,  $J = 2.9$  Hz, 2C for (*Z*)-**3ba-S**), 131.1 (d,  $J = 10.1$  Hz, 4C for (*Z*)-**3ba-S**), 131.2 (d,  $J = 10.1$  Hz, 4C for (*E*)-**3ba-S**), 131.4 (d,  $J = 2.9$  Hz, 2C for (*Z*)-**3ba-S**), 131.51 (d,  $J = 2.9$  Hz, 2C for (*E*)-**3ba-S**), 131.52 (2C for (*Z*)-**3ba-S**), 131.55-132.41 (m, 1C for (*Z*)-**3ba-S**), 131.55 (d,  $J = 83.5$  Hz, 2C for (*E*)-**3ba-S**), 131.60 (d,  $J = 10.2$  Hz, 4C for (*Z*)-**3ba-S**), 131.78 (d,  $J = 81.6$  Hz, 2C for (*Z*)-**3ba-S**), 131.78 (d,  $J = 2.9$  Hz, 2C for (*E*)-**3ba-S**), 131.9 (2C for (*E*)-**3ba-S**), 132.36 (d,  $J = 79.4$  Hz, 2C for (*E*)-**3ba-S**), 132.42 (d,  $J = 79.5$  Hz, 2C for (*Z*)-**3ba-S**), 132.5 (d,  $J = 10.2$  Hz, 4C for (*E*)-**3ba-S**), 142.6 (d,  $J = 12.6$  Hz, 1C for (*E*)-**3ba-S**), 144.7 (d,  $J = 6.5$  Hz, 1C for (*Z*)-**3ba-S**), 159.4 (1C, for (*Z*)-**3ba-S**), 160.4 (1C, for (*E*)-**3ba-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  37.12 (1P for (*Z*)-**3ba-S**), 42.17 (1P for (*E*)-**3ba-S**), 42.51 (1P for (*Z*)-**3ba-S**), 50.88 (1P for (*E*)-**3ba-S**); HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{35}\text{H}_{33}\text{OP}_2\text{S}_2$ , 595.1443; found, 595.1442.

**2,4-Bis(diphenylthiophosphinyl)-1-(4-bromophenyl)but-1-ene (3ca-S, *E/Z* = 77:23)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v); 52.9 mg (33%); white solid; m.p. 95.3-97.3 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.64-2.75 (m, 0.77 x 2H for (*E*)-**3ca-S**), 2.64-2.75 (m, 0.23 x 2H for (*Z*)-**3ca-S**), 2.90-3.02 (m, 0.77 x 2H for (*E*)-**3ca-S**), 2.90-3.02 (m, 0.23 x 2H for (*Z*)-**3ca-S**), 6.79 (d,  $J = 23.9$  Hz, 0.77 x 1H for (*E*)-**3ca-S**), 6.95-6.98 (m, 0.23 x 2H for (*Z*)-**3ca-S**), 7.09-7.11 (m, 0.23 x 2H for (*Z*)-**3ca-S**), 7.16-7.21 (m, 0.77 x 1H for (*E*)-**3ca-S**), 7.26-7.31 (m, 0.77 x 2H for (*E*)-**3ca-S**), 7.26-7.31 (m, 0.23 x 3H for (*Z*)-**3ca-S**), 7.35-7.54 (m, 0.77 x 13H for (*E*)-**3ca-S**), 7.35-7.54 (m, 0.23 x 10H for (*Z*)-**3ca-S**), 7.68-7.84 (m, 0.77 x 8H for (*E*)-**3ca-S**), 7.68-7.84 (m, 0.23 x 8H for (*Z*)-**3ca-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.6 (d,  $J = 12.4$  Hz, 1C for (*E*)-**3ca-S**), 31.0 (d,  $J = 13.2$  Hz, 1C for (*Z*)-**3ca-S**), 31.6 (d,  $J = 53.6$  Hz, 1C for (*E*)-**3ca-S**), 35.3 (d,  $J = 53.0$  Hz, 1C for (*Z*)-**3ca-S**), 122.3 (1C for (*Z*)-**3ca-S**), 123.5 (1C for (*E*)-**3ca-S**), 128.3 (d,  $J = 12.4$  Hz, 4C for (*Z*)-**3ca-S**), 128.70 (d,  $J = 11.7$  Hz, 4C for (*E*)-**3ca-S**), 128.70 (d,  $J = 11.7$  Hz, 4C for (*Z*)-**3ca-S**), 128.9 (d,  $J = 12.4$  Hz, 4C for (*E*)-**3ca-S**), 130.4 (2C for (*Z*)-**3ca-S**), 131.08 (d,  $J = 83.1$  Hz, 2C for (*E*)-**3ca-S**), 131.09 (d,  $J = 10.3$  Hz, 4C for (*E*)-**3ca-S**), 131.10 (d,  $J = 10.4$  Hz, 4C for (*Z*)-**3ca-S**), 131.15 (2C for (*Z*)-**3ca-S**), 131.21 (d,  $J = 4.0$  Hz, 2C for (*Z*)-**3ca-S**), 131.25 (2C for (*E*)-**3ca-S**), 131.3 (d,  $J = 83.0$  Hz, 2C for (*Z*)-

**3ca-S**), 131.5 (d,  $J = 3.8$  Hz, 2C for **(Z)-3ca-S**), 131.56 (d,  $J = 2.7$  Hz, 2C for **(E)-3ca-S**), 131.62 (d,  $J = 9.7$  Hz, 4C for **(Z)-3ca-S**), 132.0 (d,  $J = 3.0$  Hz, 2C for **(E)-3ca-S**), 132.1 (2C for **(E)-3ca-S**), 132.2 (d,  $J = 79.4$  Hz, 2C for **(E)-3ca-S**), 132.3 (d,  $J = 80.0$  Hz, 2C for **(Z)-3ca-S**), 132.4 (d,  $J = 10.5$  Hz, 4C for **(E)-3ca-S**), 133.6 (d,  $J = 19.8$  Hz, 1C for **(E)-3ca-S**), 134.2 (d,  $J = 13.3$  Hz, 1C for **(Z)-3ca-S**), 134.5 (dd,  $J = 14.5$  Hz, 74.3 Hz, 1C for **(Z)-3ca-S**), 134.6 (dd,  $J = 16.9$  Hz, 75.9 Hz, 1C for **(E)-3ca-S**), 141.9 (d,  $J = 12.4$  Hz, 1C for **(E)-3ca-S**), 143.2 (d,  $J = 5.7$  Hz, 1C for **(Z)-3ca-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  37.08 (1P for **(Z)-3ca-S**), 42.22 (1P for **(Z)-3ca-S**), 42.35 (1P for **(E)-3ca-S**), 50.12 (1P for **(E)-3ca-S**); HRMS (APCI)  $m/z$ :  $(\text{M} + \text{H})^+$  calcd for  $\text{C}_{34}\text{H}_{30}\text{BrP}_2\text{S}_2$ , 643.0442; found, 643.0452.

**(E)-2,4-Bis(diphenylthiophosphinyl)-1-(2,4,6-trimethylphenyl)but-1-ene ((E)-3da-S)**. Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v); 62.9 mg (42%); white solid; m.p. 175.5-177.5 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.10 (s, 6H), 2.18-2.25 (m, 2H), 2.32 (s, 3H), 2.46-2.56 (m, 2H), 6.86 (s, 2H), 7.10 (d,  $J = 22.6$  Hz, 1H), 7.25-7.29 (m, 4H), 7.36-7.42 (m, 6H), 7.45-7.54 (m, 6H), 7.85-7.91 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.4 (2C), 21.2 (1C), 22.8 (d,  $J = 13.7$  Hz, 1C), 30.9 (d,  $J = 53.4$  Hz, 1C), 128.5 (d,  $J = 11.9$  Hz, 4C), 128.7 (2C), 128.9 (d,  $J = 12.3$  Hz, 4C), 130.8 (d,  $J = 10.2$  Hz, 4C), 131.2 (d,  $J = 2.8$  Hz, 2C), 131.5 (d,  $J = 83.0$  Hz, 2C), 131.8 (d,  $J = 2.8$  Hz, 2C), 132.1 (d,  $J = 17.3$  Hz, 1C), 132.28 (d,  $J = 10.6$  Hz, 4C), 132.34 (d,  $J = 79.4$  Hz, 2C), 134.5 (2C), 135.7 (dd,  $J = 17.3$  Hz, 73.3 Hz, 1C), 137.3 (1C), 145.7 (d,  $J = 11.6$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  41.87 (1P), 46.79 (1P); HRMS (APCI)  $m/z$ :  $(\text{M} + \text{H})^+$  calcd for  $\text{C}_{37}\text{H}_{37}\text{P}_2\text{S}_2$ , 607.1806; found, 607.1803.

**1,3-Bis(diphenylthiophosphinyl)-6-phenylhex-3-ene (3ea-S, E/Z = 89:11)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v); 108.6 mg (72%); white solid; m.p. 177.9-179.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.21-2.27 (m, 0.11 x 2H for **(Z)-3ea-S**), 2.44-2.63 (m, 0.89 x 6H for **(E)-3ea-S**), 2.44-2.63 (m, 0.11 x 6H for **(Z)-3ea-S**), 2.67-2.71 (m, 0.89 x 2H for **(E)-3ea-S**), 6.40 (td,  $J = 7.3$ , 21.8 Hz, 0.89 x 1H for **(E)-3ea-S**), 6.40 (td,  $J = 7.7$ , 38.9 Hz, 0.11 x 1H for **(Z)-3ea-S**), 6.86-6.88 (m, 0.11 x 2H for **(Z)-3ea-S**), 7.06-7.08 (m, 0.89 x 2H for **(E)-3ea-S**), 7.12-7.25 (m,

0.89 x 3H for (*E*)-**3ea-S**), 7.12-7.25 (m, 0.11 x 3H for (*Z*)-**3ea-S**), 7.35-7.49 (m, 0.89 x 12H for (*E*)-**3ea-S**), 7.35-7.49 (m, 0.11 x 12H for (*Z*)-**3ea-S**), 7.52-7.57 (m, 0.89 x 4H for (*E*)-**3ea-S**), 7.60-7.65 (m, 0.11 x 4H for (*Z*)-**3ea-S**), 7.74-7.82 (m, 0.89 x 4H for (*E*)-**3ea-S**), 7.74-7.82 (m, 0.11 x 4H for (*Z*)-**3ea-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  21.68 (d,  $J = 13.1$  Hz, 1C for (*E*)-**3ea-S**), 21.68 (d,  $J = 13.1$  Hz, 1C for (*Z*)-**3ea-S**), 30.3 (d,  $J = 14.1$  Hz, 1C for (*Z*)-**3ea-S**), 30.7 (d,  $J = 15.0$  Hz, 1C for (*E*)-**3ea-S**), 33.2 (d,  $J = 52.6$  Hz, 1C for (*E*)-**3ea-S**), 33.3 (d,  $J = 59.4$  Hz, 1C for (*Z*)-**3ea-S**), 34.4 (1C for (*Z*)-**3ea-S**), 34.6 (1C for (*E*)-**3ea-S**), 126.0 (1C for (*Z*)-**3ea-S**), 126.2 (1C for (*E*)-**3ea-S**), 128.3-128.7 (m, 12C for (*Z*)-**3ea-S**), 128.52 (d,  $J = 11.7$  Hz, 4C for (*E*)-**3ea-S**), 128.53 (2C for (*E*)-**3ea-S**), 128.54 (d,  $J = 11.7$  Hz, 4C for (*E*)-**3ea-S**), 128.7 (2C for (*E*)-**3ea-S**), 130.7-133.6 (m, 1C for (*Z*)-**3ea-S**), 131.0 (d,  $J = 10.1$  Hz, 4C for (*E*)-**3ea-S**), 128.7 (2C for (*E*)-**3ea-S**), 130.7-133.6 (m, 1C for (*Z*)-**3ea-S**), 131.0 (d,  $J = 10.1$  Hz, 4C for (*E*)-**3ea-S**), 131.07 (d,  $J = 10.9$  Hz, 4C for (*E*)-**3ea-S**), 131.07 (d,  $J = 83.1$  Hz, 2C for (*E*)-**3ea-S**), 131.41 (d,  $J = 2.9$  Hz, 2C for (*E*)-**3ea-S**), 131.41 (d,  $J = 2.9$  Hz, 2C for (*Z*)-**3ea-S**), 131.56 (d,  $J = 2.8$  Hz, 2C for (*E*)-**3ea-S**), 131.56 (d,  $J = 2.8$  Hz, 2C for (*Z*)-**3ea-S**), 131.7 (d,  $J = 10.8$  Hz, 4C for (*Z*)-**3ea-S**), 132.2 (d,  $J = 10.0$  Hz, 4C for (*E*)-**3ea-S**), 132.25 (d,  $J = 78.9$  Hz, 2C for (*Z*)-**3ea-S**), 132.30 (d,  $J = 79.5$  Hz, 2C for (*E*)-**3ea-S**), 132.9 (d,  $J = 80.7$  Hz, 2C for (*Z*)-**3ea-S**), 133.1 (dd,  $J = 16.8$  Hz, 78.0 Hz, 1C for (*E*)-**3ea-S**), 140.5 (1C for (*E*)-**3ea-S**), 140.7 (1C for (*Z*)-**3ea-S**), 146.2 (d,  $J = 9.7$  Hz, 1C for (*E*)-**3ea-S**), 147.6 (d,  $J = 8.6$  Hz, 1C for (*Z*)-**3ea-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  37.55 (1P for (*Z*)-**3ea-S**), 42.36 (1P for (*Z*)-**3ea-S**), 42.53 (1P for (*E*)-**3ea-S**), 47.26 (1P for (*E*)-**3ea-S**); HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{36}\text{H}_{35}\text{P}_2\text{S}_2$ , 593.1650; found, 593.1642.

**2,4-Bis(diphenylthiophosphinyl)-1-cyclohexylbut-1-ene (3fa-S, *E/Z* = 93:7)**. Purified by silica gel column chromatography with hexane/ethyl acetate (50/1, v/v) and then by GPC (chloroform); 84.5 mg (60%); white solid; m.p. 108.6-110.6 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  0.64-0.73 (m, 0.07 x 2H for (*Z*)-**3fa-S**), 0.81-0.91 (m, 0.07 x 2H for (*Z*)-**3fa-S**), 0.96-1.15 (m, 0.93 x 3H for (*E*)-**3fa-S**), 1.26-1.48 (m, 0.07 x 6H for (*Z*)-**3fa-S**), 1.26-1.38 (m, 0.93 x 2H for (*E*)-**3fa-S**), 1.57-1.66 (m, 0.93 x 5H for (*E*)-**3fa-S**), 1.95-2.02 (m, 0.07 x 1H for (*Z*)-**3fa-S**), 2.46-2.72 (m, 0.07 x 4H for (*Z*)-**3fa-S**), 2.46-2.55 (m, 0.93 x 1H for (*E*)-**3fa-S**), 2.60-2.72 (m, 0.93 x 4H for (*E*)-**3fa-S**), 5.77 (dd,  $J = 9.8, 22.8$  Hz, 0.93 x 1H



for (**E**)-**3fa-S**), 5.77 (dd,  $J = 11.2, 39.5$  Hz, 0.07 x 1H for (**Z**)-**3fa-S**), 7.36-7.50 (m, 0.93 x 12H for (**E**)-**3fa-S**), 7.36-7.50 (m, 0.07 x 12H for (**Z**)-**3fa-S**), 6.63-7.87 (m, 0.93 x 8H for (**E**)-**3fa-S**), 6.63-7.87 (m, 0.07 x 8H for (**Z**)-**3fa-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for (**E**)-**3fa-S**,  $\delta$  21.8 (d,  $J = 13.3$  Hz, 1C), 25.3 (2C), 25.7 (1C), 32.2 (d,  $J = 1.0$  Hz, 2C), 34.1 (d,  $J = 52.7$  Hz, 1C), 38.2 (d,  $J = 14.3$  Hz, 1C), 128.59 (d,  $J = 12.3$  Hz, 4C), 128.64 (d,  $J = 11.9$  Hz, 4C), 130.3 (dd,  $J = 16.7$  Hz, 77.4 Hz, 1C), 131.1 (d,  $J = 10.4$  Hz, 4C), 131.5 (d,  $J = 2.8$  Hz, 2C), 131.57 (d,  $J = 83.5$  Hz, 2C), 131.60 (d,  $J = 2.8$  Hz, 2C), 132.2 (d,  $J = 10.3$  Hz, 4C), 132.3 (d,  $J = 79.3$  Hz, 2C), 152.8 (d,  $J = 8.0$  Hz, 1C) (the signals for (**Z**)-**3fa-S** cannot be assigned because of its lower intensity);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  38.56 (1P for (**Z**)-**3fa-S**), 42.41 (1P for (**E**)-**3fa-S**), 42.48 (1P for (**Z**)-**3fa-S**), 46.77 (1P for (**E**)-**3fa-S**); HRMS (APCI)  $m/z$ : (M+H) $^+$  calcd for  $\text{C}_{34}\text{H}_{37}\text{P}_2\text{S}_2$ , 571.1806; found, 571.1803.

**2,4-Bis(diphenylthiophosphinyl)-(1-(1-benzylpiperidin-4-yl)but-1-ene (3ga-S, E/Z = 95:5).**

Purified by silica gel column chromatography with hexane/ethyl acetate/triethylamine (5/5/1, v/v/v); 97.8 mg (59%); white solid; m.p. 178.2-180.2 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  1.26-1.37 (m, 0.95 x 2H for (**E**)-**3ga-S**), 1.26-1.37 (m, 0.05 x 8H for (**Z**)-**3ga-S**), 1.53-1.56 (m, 0.95 x 2H for (**E**)-**3ga-S**), 1.98-2.05 (m, 0.95 x 2H for (**E**)-**3ga-S**), 2.54-2.82 (m, 0.95 x 7H for (**E**)-**3ga-S**), 2.54-2.82 (m, 0.05 x 5H for (**Z**)-**3ga-S**), 3.30 (s, 0.05 x 2H for (**Z**)-**3ga-S**), 3.46 (s, 0.95 x 2H for (**E**)-**3ga-S**), 5.67 (dd,  $J = 9.8, 22.5$  Hz, 0.95 x 1H for (**E**)-**3ga-S**), 6.12 (dd,  $J = 11.0, 38.9$  Hz, 0.05 x 1H for (**Z**)-**3ga-S**), 7.21-7.32 (m, 0.95 x 5H for (**E**)-**3ga-S**), 7.21-7.32 (m, 0.05 x 5H for (**Z**)-**3ga-S**), 7.36-7.50 (m, 0.95 x 12H for (**E**)-**3ga-S**), 7.36-7.50 (m, 0.05 x 12H for (**Z**)-**3ga-S**), 7.60-7.85 (m, 0.95 x 8H for (**E**)-**3ga-S**), 7.60-7.85 (m, 0.05 x 8H for (**Z**)-**3ga-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for (**E**)-**3ga-S**,  $\delta$  21.8 (d,  $J = 13.2$  Hz, 1C), 31.4 (2C), 34.3 (d,  $J = 52.7$  Hz, 1C), 36.1 (d,  $J = 14.6$  Hz, 1C), 52.8 (2C), 63.5 (1C), 127.0 (1C), 128.2 (2C), 128.6 (d,  $J = 12.1$  Hz, 4C), 128.7 (d,  $J = 11.9$  Hz, 4C), 129.3 (2C), 131.1 (d,  $J = 10.3$  Hz, 4C), 131.3 (d,  $J = 82.5$  Hz, 2C), 131.5 (d,  $J = 2.8$  Hz, 2C), 131.6 (dd,  $J = 17.7$  Hz, 77.5 Hz, 1C), 131.7 (d,  $J = 2.9$  Hz, 2C), 132.2 (d,  $J = 10.4$  Hz, 4C), 132.3 (d,  $J = 79.4$  Hz, 2C), 138.4 (1C), 151.4 (d,  $J = 8.1$  Hz, 1C) (the signals for (**Z**)-**3ga-S** cannot be assigned because of its lower intensity);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ),

for mixture,  $\delta$  38.20 (1P for **(Z)**-3ga-S), 42.37 (1P for **(Z)**-3ga-S), 42.53 (1P for **(E)**-3ga-S), 46.82 (1P for **(E)**-3ga-S); HRMS (APCI)  $m/z$ : (M + H)<sup>+</sup> calcd for C<sub>40</sub>H<sub>42</sub>NP<sub>2</sub>S<sub>2</sub>, 662.2228; found, 662.2245.

**1,3-Bis(diphenylthiophosphinyl)-6-(thiomethyl)-hept-3-ene (3ha-S, E/Z = 91:9)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v); 89.6 mg (64%); white solid; m.p. 87.2-89.2 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  1.04 (d,  $J$  = 6.8 Hz, 0.09 x 3H for **(Z)**-3ha-S), 1.21 (d,  $J$  = 6.8 Hz, 0.91 x 3H for **(E)**-3ha-S), 1.88 (s, 0.09 x 3H for **(Z)**-3ha-S), 2.03 (s, 0.91 x 3H for **(E)**-3ha-S), 2.46-2.57 (m, 0.91 x 2H for **(E)**-3ha-S), 2.63-2.84 (m, 0.91 x 5H for **(E)**-3ha-S), 2.46-2.84 (m, 0.09 x 7H for **(Z)**-3ha-S), 5.90-6.00 (m, 0.91 x 1H for **(E)**-3ha-S), 6.51 (m, 0.09 x 1H for **(Z)**-3ha-S), 7.35-7.50 (m, 0.91 x 12H for **(E)**-3ha-S), 7.35-7.50 (m, 0.09 x 12H for **(Z)**-3ha-S), 7.60-7.66 (m, 0.09 x 4H for **(Z)**-3ha-S), 7.76-7.86 (m, 0.91 x 8H for **(E)**-3ha-S), 7.76-7.86 (m, 0.09 x 4H for **(Z)**-3ha-S); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  12.96 (1C for **(Z)**-3ha-S), 13.30 (1C for **(E)**-3ha-S), 20.6 (1C for **(Z)**-3ha-S), 20.8 (1C for **(E)**-3ha-S), 21.9 (d,  $J$  = 13.1 Hz, 1C for **(E)**-3ha-S), 30.5 (d,  $J$  = 13.1 Hz, 1C for **(Z)**-3ha-S), 33.5 (d,  $J$  = 52.8 Hz, 1C for **(E)**-3ha-S), 33.7 (d,  $J$  = 54.0 Hz, 1C for **(Z)**-3ha-S), 35.5 (d,  $J$  = 14.8 Hz, 1C for **(E)**-3ha-S), 36.9 (d,  $J$  = 7.6 Hz, 1C for **(Z)**-3ha-S), 40.5 (1C for **(Z)**-3ha-S), 40.7 (1C for **(E)**-3ha-S), 128.58 (d,  $J$  = 12.3 Hz, 4C for **(E)**-3ha-S), 128.63 (d,  $J$  = 12.1 Hz, 4C for **(E)**-3ha-S), 128.7-128.8 (m, 8C for **(Z)**-3ha-S), 131.0-133.2 (m, 2C for **(Z)**-3ha-S), 131.0 (d,  $J$  = 10.0 Hz, 4C for **(Z)**-3ha-S), 131.06 (d,  $J$  = 10.4 Hz, 2C for **(E)**-3ha-S), 131.08 (d,  $J$  = 10.4 Hz, 2C for **(E)**-3ha-S), 131.2 (d,  $J$  = 82.8 Hz, 2C for **(E)**-3ha-S), 131.4-131.4 (m, 2C for **(Z)**-3ha-S), 131.55 (d,  $J$  = 2.8 Hz, 2C for **(E)**-3ha-S), 131.58 (d,  $J$  = 2.5 Hz, 2C for **(E)**-3ha-S), 131.8 (d,  $J$  = 4.1 Hz, 2C for **(Z)**-3ha-S), 132.17 (d,  $J$  = 79.4 Hz, 1C for **(E)**-3ha-S), 132.22-132.34 (m, 4C for **(Z)**-3ha-S), 132.22-133.13 (m, 2C for **(Z)**-3ha-S), 132.27 (d,  $J$  = 10.3 Hz, 2C for **(E)**-3ha-S), 132.27 (d,  $J$  = 79.2 Hz, 1C for **(E)**-3ha-S), 132.29 (d,  $J$  = 10.4 Hz, 2C for **(E)**-3ha-S), 133.5 (dd,  $J$  = 15.8 Hz, 73.5 Hz, 1C for **(Z)**-3ha-S), 134.1 (dd,  $J$  = 16.6 Hz, 78.0 Hz, 1C for **(E)**-3ha-S), 144.1 (d,  $J$  = 10.1 Hz, 1C for **(E)**-3ha-S), 145.6 (d,  $J$  = 7.8 Hz, 1C for **(Z)**-3ha-S); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  37.31 (1P for **(Z)**-3ha-S), 42.27 (1P for **(Z)**-

**3ha-S**), 42.56 (1P for (*E*)-**3ha-S**), 47.24 (1P for (*E*)-**3ha-S**); HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>32</sub>H<sub>35</sub>P<sub>2</sub>S<sub>3</sub>, 577.1371; found, 577.1391.

**1,3-Bis[bis(4-methoxyphenyl)thiophosphinyl]-6-phenylhex-3-ene (3eb-S, *E/Z* = 91:9)**. Purified by silica gel column chromatography with hexane/ethyl acetate (3/1, v/v) and then by GPC (chloroform); 38.3 mg (53%); white solid; m.p. 92.9-94.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), for mixture, δ 2.45-2.70 (m, 0.91 x 8H for (*E*)-**3bc-S**), 2.45-2.70 (m, 0.09 x 8H for (*Z*)-**3eb-S**), 3.79 (s, 0.91 x 6H for (*E*)-**3eb-S**), 3.81 (s, 0.09 x 12H for (*Z*)-**3eb-S**), 3.82 (s, 0.91 x 6H for (*E*)-**3eb-S**), 5.76 (td, *J* = 7.3, 22.2 Hz, 0.91 x 1H for (*E*)-**3eb-S**), 6.37 (td, *J* = 7.6, 38.6 Hz, 0.09 x 1H for (*Z*)-**3eb-S**), 6.85-6.90 (m, 0.91 x 8H for (*E*)-**3eb-S**), 6.85-6.90 (m, 0.09 x 13H for (*Z*)-**3eb-S**), 7.08-7.10 (m, 0.91 x 2H for (*E*)-**3eb-S**), 7.17-7.19 (m, 0.91 x 1H for (*E*)-**3eb-S**), 7.22-7.26 (m, 0.91 x 2H for (*E*)-**3eb-S**), 7.42-7.48 (m, 0.91 x 4H for (*E*)-**3eb-S**), 7.50-7.57 (m, 0.09 x 4H for (*Z*)-**3eb-S**), 7.65-7.72 (m, 0.91 x 4H for (*E*)-**3eb-S**), 7.65-7.72 (m, 0.09 x 4H for (*Z*)-**3eb-S**); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), for (*E*)-**3eb-S**, δ 21.83 (d, *J* = 13.3 Hz, 1C), 21.83 (d, *J* = 15.1 Hz, 1C), 33.9 (d, *J* = 53.6 Hz, 1C), 34.7 (1C), 55.5 (4C), 114.06 (d, *J* = 13.5 Hz, 4C), 114.13 (d, *J* = 13.1 Hz, 4C), 122.4 (d, *J* = 89.3 Hz, 2C), 123.9 (d, *J* = 85.3 Hz, 2C), 126.2 (1C), 128.6 (2C), 128.8 (2C), 133.0 (d, *J* = 11.8 Hz, 4C), 134.05 (d, *J* = 12.0 Hz, 4C), 134.06 (dd, *J* = 16.4 Hz, 79.0 Hz, 1C), 140.8 (1C), 145.4 (d, *J* = 9.7 Hz, 1C), 162.1 (d, *J* = 2.8 Hz, 2C), 162.2 (d, *J* = 2.8 Hz, 2C) (the signals for (*Z*)-**3eb-S** cannot be assigned because of its lower intensity); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>), for mixture, δ 35.90 (1P for (*Z*)-**3eb-S**), 40.89 (1P for (*Z*)-**3eb-S**), 41.12 (1P for (*E*)-**3eb-S**), 45.61 (1P for (*E*)-**3eb-S**); HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>40</sub>H<sub>43</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>, 713.2073; found, 713.2065.

**(*E*)-1,3-Bis[bis(4-trifluoromethylphenyl)thiophosphinyl]-6-phenylhex-3-ene ((*E*)-**3ec-S**)**. Purified by silica gel column chromatography with hexane/ethyl acetate (15/1, v/v); 55.0 mg (61%); white solid; m.p. 114.6-116.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.42-2.53 (m, 2H), 2.66-2.77 (m, 6H), 5.66-5.76 (m, 1H), 7.07-7.09 (m, 2H), 7.18-7.22 (m, 1H), 7.25-7.29 (m, 2H), 7.60-7.69 (m, 12H), 7.93-7.98 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 21.7 (d, *J* = 13.9 Hz, 1C), 30.8 (d, *J* = 15.3 Hz, 1C), 33.1 (d, *J* =

52.8 Hz, 1C), 34.4 (1C), 123.48 (q,  $J = 271.2$  Hz, 2C), 123.52 (q,  $J = 271.2$  Hz, 2C), 125.7 (dq,  $J = 3.8$  Hz, 12.6 Hz, 4C), 125.8 (dq,  $J = 4.1$  Hz, 11.0 Hz, 4C), 126.6 (1C), 128.78 (2C), 128.81 (2C), 131.6 (dd,  $J = 16.8$  Hz, 79.9 Hz, 1C), 131.7 (d,  $J = 10.9$  Hz, 4C), 132.7 (d,  $J = 11.0$  Hz, 4C), 133.8 (dq,  $J = 3.1$  Hz, 32.9 Hz, 2C), 134.0 (dq,  $J = 2.6$  Hz, 32.9 Hz, 2C), 134.8 (d,  $J = 80.9$  Hz, 2C), 136.0 (d,  $J = 77.2$  Hz, 2C), 140.3 (1C), 147.4 (d,  $J = 9.1$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  41.63 (1P), 46.32 (1P);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.23 (12F); HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{40}\text{H}_{31}\text{F}_{12}\text{P}_2\text{S}_2$ , 865.1145; found, 865.1123.

**Typical Procedure for Ring-Opening Diphosphination of Vinylcyclopropanes 4 with Diphosphines 2.** The synthesis of **5aa-S** is representative (Scheme 3).  $\text{Ir}(\text{ppy})_3$  (0.80 mg, 0.0013 mmol) and tetraphenyldiphosphine (**2a**; 190 mg, 0.50 mmol) were placed in a 10-mL Schlenk flask, which was filled with  $\text{N}_2$ . DCE (1.5 mL) and dimethyl bromomalonate (**Br5**; 11 mg, 0.050 mmol) were added, and the solution was stirred for 3 min. (1-Cyclopropylvinyl)benzene (**4a**; 36 mg, 0.25 mmol) was then added into the mixture, and the resulting solution was irradiated with blue LEDs at ambient temperature for 4 h (2.4 W with LED tapes, no special temperature control, 3 cm distance from the LEDs, see Figure S1). Elemental sulfur ( $\text{S}_8$ ; 40 mg, 1.3 mmol of S atom) was then added. After the mixture was stirred for further 30 min at room temperature, the solution was filtered through a short pad of Celite, silica gel, alumina, and anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residual solid was dissolved in  $\text{CDCl}_3$ , and the yield was calculated by  $^1\text{H}$  NMR with triethyl phosphate as an internal standard (18 mg, 0.10 mmol). After the NMR analysis, concentration in vacuo and purification by GPC (chloroform) gave 1,5-bis(diphenylthiophosphinyl)-2-phenylpent-2-ene (**5aa-S**, 85 mg, 0.15 mmol,  $E/Z = 34:66$ ) in 60% yield.

**(Z)-1,5-Bis(diphenylthiophosphinyl)-2-phenylpent-2-ene ((Z)-5aa-S).** Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v) and then by GPC (chloroform); white solid; m.p. 72.9-74.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.46-2.51 (m, 2H), 2.73-2.80 (m, 2H), 3.75 (d,  $J = 13.9$  Hz, 2H), 5.74 (td,  $J = 7.7, 10.5$  Hz, 1H), 6.85-6.88 (m, 2H), 6.91-6.97 (m, 3H), 7.23-7.28 (m, 4H), 7.32-7.37

(m, 6H), 7.39-7.44 (m, 2H), 7.61-7.67 (m, 4H), 7.87-7.94 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.7 (1C), 32.7 (dd,  $J = 3.6, 54.4$  Hz, 1C), 35.6 (d,  $J = 51.4$  Hz, 1C), 126.8 (1C), 127.2 (2C), 127.8 (2C), 128.3 (d,  $J = 12.0$  Hz, 4C), 128.7 (d,  $J = 12.1$  Hz, 4C), 131.2 (d,  $J = 2.6$  Hz, 2C), 131.3 (d,  $J = 9.9$  Hz, 4C), 131.36 (d,  $J = 10.0$  Hz, 4C), 131.39 (d,  $J = 3.4$  Hz, 2C), 132.3 (d,  $J = 8.8$  Hz, 1C), 132.8 (d,  $J = 79.0$  Hz, 4C), 133.6 (dd,  $J = 11.0, 16.0$  Hz, 1C), 141.9 (d,  $J = 1.9$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  39.39, 42.65; HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{35}\text{H}_{33}\text{P}_2\text{S}_2$ , 579.1493; found, 579.1466.

**(E)-1,5-Bis(diphenylthiophosphinyl)-2-phenylpent-2-ene ((E)-5aa-S)**. Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v) and then by GPC (chloroform); white solid; m.p. 146.9-148.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.19-2.28 (m, 2H), 2.37-2.44 (m, 2H), 3.58 (d,  $J = 13.4$  Hz, 2H), 5.71 (td,  $J = 7.4, 10.2$  Hz, 1H), 6.76-6.79 (m, 2H), 6.95-7.04 (m, 3H), 7.26-7.31 (m, 4H), 7.35-7.40 (m, 6H), 7.42-7.46 (m, 2H), 7.62-7.70 (m, 8H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.3 (1C), 32.6 (dd,  $J = 4.6, 54.1$  Hz, 1C), 42.8 (d,  $J = 50.6$  Hz, 1C), 126.8 (1C), 127.9 (2C), 128.3 (d,  $J = 11.9$  Hz, 4C), 128.4 (d,  $J = 1.7$  Hz, 2C), 128.6 (d,  $J = 11.9$  Hz, 4C), 131.0 (d,  $J = 10.0$  Hz, 4C), 131.17 (d,  $J = 3.6$  Hz, 2C), 131.24 (d,  $J = 10.2$  Hz, 4C), 131.4 (d,  $J = 2.8$  Hz, 2C), 131.7 (d,  $J = 9.3$  Hz, 1C), 132.6 (d,  $J = 79.3$  Hz, 4C), 133.0 (dd,  $J = 10.2, 18.2$  Hz, 1C), 139.1 (d,  $J = 2.9$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  41.19, 41.82; HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{35}\text{H}_{33}\text{P}_2\text{S}_2$ , 579.1493; found, 579.1494.

**1,5-Bis(diphenylthiophosphinyl)-2-(4-methoxyphenyl)pent-2-ene (5ba-S, E/Z = 48:52)**. Purified by GPC (chloroform); 63.6 mg (42%); yellow solid; m.p. 99.3-101.3 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.20-2.31 (m, 0.48 x 2H for (E)-5ba-S), 2.36-2.50 (m, 0.48 x 2H for (E)-5ba-S), 2.36-2.50 (m, 0.52 x 2H for (Z)-5ba-S), 2.72-2.79 (m, 0.52 x 2H for (Z)-5ba-S), 3.55 (d,  $J = 13.4$  Hz, 0.48 x 2H for (E)-5ba-S), 3.70 (s, 0.48 x 3H for (E)-5ba-S), 3.72 (s, 0.52 x 3H for (Z)-5ba-S), 3.72 (d,  $J = 13.7$  Hz, 0.52 x 2H for (Z)-5ba-S), 6.69 (td,  $J = 9.1, 11.1$  Hz, 0.48 x 1H for (E)-5ba-S), 6.80 (td,  $J = 7.7, 10.7$  Hz, 0.52 x 1H for (Z)-5ba-S), 6.45-6.52 (m, 0.48 x 2H for (E)-5ba-S), 6.45-6.52 (m, 0.52 x 2H for (Z)-5ba-S), 6.68-6.71 (m, 0.48 x 2H for (E)-5ba-S), 6.78-6.81 (m, 0.52 x 2H for (Z)-5ba-S), 7.27-7.47 (m, 0.48 x

12H for (**E**)-**5ba-S**), 7.27-7.47 (m, 0.52 x 12H for (**Z**)-**5ba-S**), 7.61-7.71 (m, 0.48 x 8H for (**E**)-**5ba-S**), 7.61-7.71 (m, 0.52 x 4H for (**Z**)-**5ba-S**), 7.87-7.93 (m, 0.52 x 4H for (**Z**)-**5ba-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.4 (1C), 22.6 (1C), 32.7 (dd,  $J = 4.9, 53.9$  Hz, 1C), 32.8 (dd,  $J = 4.3, 54.3$  Hz, 1C), 36.1 (d,  $J = 50.9$  Hz, 1C), 43.2 (d,  $J = 51.5$  Hz, 1C), 55.3 (1C), 55.4 (1C), 113.3 (2C), 113.5 (2C), 128.3 (d,  $J = 11.7$  Hz, 4C), 128.36 (d,  $J = 11.7$  Hz, 4C), 128.38 (d,  $J = 1.3$  Hz, 2C), 128.67 (d,  $J = 12.4$  Hz, 4C), 128.70 (d,  $J = 11.7$  Hz, 4C), 129.7 (d,  $J = 1.7$  Hz, 2C), 131.1 (d,  $J = 10.3$  Hz, 4C), 131.20 (d,  $J = 2.9$  Hz, 2C), 131.23 (d,  $J = 2.9$  Hz, 2C), 131.35 (d,  $J = 9.5$  Hz, 4C), 131.41 (d,  $J = 10.3$  Hz, 4C), 131.44 (d,  $J = 9.5$  Hz, 4C), 131.36-131.49 (overlapped, 6C), 132.4 (dd,  $J = 11.6, 15.3$  Hz, 1C), 132.77 (d,  $J = 79.4$  Hz, 2C), 132.80 (d,  $J = 78.2$  Hz, 2C), 132.81 (dd,  $J = 10.9, 17.7$  Hz, 1C), 132.9 (d,  $J = 78.6$  Hz, 2C), 133.0 (d,  $J = 78.8$  Hz, 2C), 134.4 (d,  $J = 1.8$  Hz, 2C), 158.4 (1C), 158.6 (1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  39.37 (1P for (**Z**)-**5ba-S**), 41.19 (1P for (**E**)-**5ba-S**), 41.80 (1P for (**E**)-**5ba-S**), 42.62 (1P for (**Z**)-**5ba-S**); HRMS (APCI)  $m/z$ : ( $\text{M} + \text{H}$ ) $^+$  calcd for  $\text{C}_{36}\text{H}_{35}\text{OP}_2\text{S}_2$ , 609.1599; found, 609.1604.

**1,5-Bis(diphenylthiophosphinyl)-2-(4-bromophenyl)pent-2-ene (5ca-S, E/Z = 30:70)**. Purified by GPC (chloroform); 108 mg (64%); white solid; m.p. 71.6-73.6 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.15-2.24 (m, 0.30 x 2H for (**E**)-**5ca-S**), 2.35-2.42 (m, 0.30 x 2H for (**E**)-**5ca-S**), 2.44-2.54 (m, 0.70 x 2H for (**Z**)-**5ca-S**), 2.74-2.80 (m, 0.70 x 2H for (**Z**)-**5ca-S**), 3.53 (d,  $J = 13.2$  Hz, 0.30 x 2H for (**E**)-**5ca-S**), 3.71 (d,  $J = 13.5$  Hz, 0.70 x 2H for (**Z**)-**5ca-S**), 5.68-5.76 (m, 0.30 x 1H for (**E**)-**5ca-S**), 5.68-5.76 (m, 0.70 x 1H for (**Z**)-**5ca-S**), 6.60-6.63 (m, 0.30 x 2H for (**E**)-**5ca-S**), 6.67-6.70 (m, 0.70 x 2H for (**Z**)-**5ca-S**), 6.99-7.04 (m, 0.30 x 2H for (**E**)-**5ca-S**), 6.99-7.04 (m, 0.70 x 2H for (**Z**)-**5ca-S**), 7.27-7.48 (m, 0.30 x 12H for (**E**)-**5ca-S**), 7.27-7.48 (m, 0.70 x 12H for (**Z**)-**5ca-S**), 7.60-7.69 (m, 0.30 x 8H for (**E**)-**5ca-S**), 7.60-7.69 (m, 0.70 x 4H for (**Z**)-**5ca-S**), 7.87-7.92 (m, 0.70 x 4H for (**Z**)-**5ca-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.3 (1C for (**E**)-**5ca-S**), 22.7 (1C for (**Z**)-**5ca-S**), 32.55 (dd,  $J = 4.3, 53.9$  Hz, 1C for (**E**)-**5ca-S**), 32.62 (dd,  $J = 3.7, 54.7$  Hz, 1C for (**Z**)-**5ca-S**), 36.0 (d,  $J = 51.6$  Hz, 1C for (**Z**)-**5ca-S**), 42.9 (d,  $J = 50.9$  Hz, 1C for (**E**)-**5ca-S**), 120.8 (1C for (**Z**)-**5ca-S**), 121.0 (1C for (**E**)-**5ca-S**),

128.44 (d,  $J = 12.3$  Hz, 4C for (**E**)-**5ca-S**), 128.44 (d,  $J = 12.3$  Hz, 4C for (**Z**)-**5ca-S**), 128.70 (d,  $J = 12.3$  Hz, 4C for (**E**)-**5ca-S**), 128.70 (d,  $J = 12.3$  Hz, 4C for (**Z**)-**5ca-S**), 129.0 (d,  $J = 1.4$  Hz, 2C for (**Z**)-**5ca-S**), 130.3 (d,  $J = 1.8$  Hz, 2C for (**E**)-**5ca-S**), 130.8 (2C for (**Z**)-**5ca-S**), 131.05 (2C for (**E**)-**5ca-S**), 131.06 (d,  $J = 9.5$  Hz, 4C for (**E**)-**5ca-S**), 131.24-131.37 (m, 1C for (**E**)-**5ca-S**), 131.24-131.37 (m, 1C for (**Z**)-**5ca-S**), 131.28 (d,  $J = 2.2$  Hz, 2C for (**Z**)-**5ca-S**), 131.31 (d,  $J = 8.4$  Hz, 4C for (**Z**)-**5ca-S**), 131.36 (d,  $J = 2.2$  Hz, 2C for (**E**)-**5ca-S**), 131.37 (d,  $J = 10.3$  Hz, 4C for (**E**)-**5ca-S**), 131.37 (d,  $J = 10.3$  Hz, 4C for (**Z**)-**5ca-S**), 131.44 (d,  $J = 3.0$  Hz, 2C for (**Z**)-**5ca-S**), 131.5 (d,  $J = 3.0$  Hz, 2C for (**E**)-**5ca-S**), 132.50 (d,  $J = 78.8$  Hz, 2C for (**E**)-**5ca-S**), 132.6 (d,  $J = 79.5$  Hz, 2C for (**E**)-**5ca-S**), 132.7 (d,  $J = 79.5$  Hz, 2C for (**Z**)-**5ca-S**), 132.8 (d,  $J = 79.5$  Hz, 2C for (**Z**)-**5ca-S**), 133.8 (dd,  $J = 10.2, 17.5$  Hz, 1C for (**E**)-**5ca-S**), 134.1 (dd,  $J = 10.2, 15.3$  Hz, 1C for (**Z**)-**5ca-S**), 138.0 (d,  $J = 2.9$  Hz, 1C for (**E**)-**5ca-S**), 140.8 (d,  $J = 2.1$  Hz, 1C for (**Z**)-**5ca-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  39.11 (1P for (**Z**)-**5ca-S**), 40.73 (1P for (**E**)-**5ca-S**), 41.76 (1P for (**E**)-**5ca-S**), 42.57 (1P for (**Z**)-**5ca-S**); HRMS (APCI)  $m/z$ : ( $\text{M} + \text{H}$ ) $^+$  calcd for  $\text{C}_{35}\text{H}_{32}\text{BrP}_2\text{S}_2$ , 657.0599; found, 657.0614.

**1,5-Bis(diphenylthiophosphinyl)-2-(3-methylphenyl)pent-2-ene (5da-S,  $E/Z = 35:65$ ).** Purified by GPC (chloroform); 80.4 mg (55%); pale yellow solid; m.p. 105.6-107.6 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.06 (s, 0.65 x 3H for (**Z**)-**5da-S**), 2.07 (s, 0.35 x 3H for (**E**)-**5da-S**), 2.21-2.29 (m, 0.35 x 2H for (**E**)-**5da-S**), 2.38-2.44 (m, 0.35 x 2H for (**E**)-**5da-S**), 2.46-2.55 (m, 0.65 x 2H for (**Z**)-**5da-S**), 2.76-2.83 (m, 0.65 x 2H for (**Z**)-**5da-S**), 3.56 (d,  $J = 13.5$  Hz, 0.35 x 2H for (**E**)-**5da-S**), 3.73 (d,  $J = 13.6$  Hz, 0.65 x 2H for (**Z**)-**5da-S**), 5.69-5.78 (m, 0.35 x 1H for (**E**)-**5da-S**), 5.69-5.78 (m, 0.65 x 1H for (**Z**)-**5da-S**), 6.48 (s, 0.35 x 1H for (**E**)-**5da-S**), 6.57 (s, 0.65 x 1H for (**Z**)-**5da-S**), 6.61-6.82 (m, 0.35 x 2H for (**E**)-**5da-S**), 6.61-6.82 (m, 0.65 x 2H for (**Z**)-**5da-S**), 6.84-6.92 (m, 0.35 x 1H for (**E**)-**5da-S**), 6.84-6.92 (m, 0.65 x 1H for (**Z**)-**5da-S**), 7.25-7.30 (m, 0.35 x 4H for (**E**)-**5da-S**), 7.25-7.30 (m, 0.65 x 4H for (**Z**)-**5da-S**), 7.33-7.45 (m, 0.35 x 8H for (**E**)-**5da-S**), 7.33-7.45 (m, 0.65 x 8H for (**Z**)-**5da-S**), 7.61-7.69 (m, 0.35 x 8H for (**E**)-**5da-S**), 7.61-7.69 (m, 0.65 x 4H for (**Z**)-**5da-S**), 7.89-7.94 (m, 0.65 x 4H for (**Z**)-**5da-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  21.3 (1C for (**Z**)-**5da-S**), 21.4 (1C for (**E**)-**5da-S**), 22.4

(1C for (*E*)-**5da-S**), 22.7 (1C for (*Z*)-**5da-S**), 32.7 (dd,  $J = 4.4, 53.9$  Hz, 1C for (*E*)-**5da-S**), 32.8 (dd,  $J = 3.6, 53.9$  Hz, 1C for (*Z*)-**5da-S**), 36.0 (d,  $J = 51.7$  Hz, 1C for (*Z*)-**5da-S**), 43.0 (d,  $J = 50.5$  Hz, 1C for (*E*)-**5da-S**), 124.4 (d,  $J = 1.4$  Hz, 1C for (*Z*)-**5da-S**), 125.5 (d,  $J = 2.2$  Hz, 1C for (*E*)-**5da-S**), 127.6 (1C for (*Z*)-**5da-S**), 127.7 (1C for (*E*)-**5da-S**), 127.79 (1C for (*Z*)-**5da-S**), 127.97 (1C for (*E*)-**5da-S**), 127.96-127.97 (m, 1C for (*Z*)-**5da-S**), 128.2 (d,  $J = 11.7$  Hz, 4C for (*Z*)-**5da-S**), 128.3 (d,  $J = 12.4$  Hz, 4C for (*E*)-**5da-S**), 128.65 (d,  $J = 11.7$  Hz, 4C for (*E*)-**5da-S**), 128.70 (d,  $J = 12.4$  Hz, 4C for (*Z*)-**5da-S**), 129.2 (d,  $J = 1.6$  Hz, 1C for (*E*)-**5da-S**), 131.1 (d,  $J = 10.2$  Hz, 4C for (*E*)-**5da-S**), 131.2 (d,  $J = 2.9$  Hz, 4C for (*Z*)-**5da-S**), 131.36 (d,  $J = 10.2$  Hz, 4C for (*Z*)-**5da-S**), 131.39 (d,  $J = 10.2$  Hz, 4C for (*E*)-**5da-S**), 131.41 (d,  $J = 10.2$  Hz, 4C for (*Z*)-**5da-S**), 131.43 (d,  $J = 3.7$  Hz, 4C for (*E*)-**5da-S**), 131.9 (d,  $J = 9.2$  Hz, 1C for (*E*)-**5da-S**), 132.4 (d,  $J = 8.8$  Hz, 1C for (*Z*)-**5da-S**), 132.7 (d,  $J = 78.7$  Hz, 2C for (*E*)-**5da-S**), 132.8 (d,  $J = 79.4$  Hz, 2C for (*E*)-**5da-S**), 132.87 (d,  $J = 79.5$  Hz, 2C for (*Z*)-**5da-S**), 132.93 (d,  $J = 79.5$  Hz, 2C for (*Z*)-**5da-S**), 133.0 (dd,  $J = 11.1, 17.5$  Hz, 1C for (*E*)-**5da-S**), 133.4 (dd,  $J = 10.7, 16.6$  Hz, 1C for (*Z*)-**5da-S**), 137.2 (1C for (*Z*)-**5da-S**), 137.4 (1C for (*E*)-**5da-S**), 139.2 (d,  $J = 2.2$  Hz, 1C for (*E*)-**5da-S**), 141.9 (d,  $J = 1.4$  Hz, 1C for (*Z*)-**5da-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  39.35 (1P for (*Z*)-**5da-S**), 41.18 (1P for (*E*)-**5da-S**), 41.92 (1P for (*E*)-**5da-S**), 42.69 (1P for (*Z*)-**5da-S**); HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{36}\text{H}_{35}\text{P}_2\text{S}_2$ , 593.1650; found, 593.1668.

**1,5-Bis(diphenylthiophosphinyl)-2-(2-fluorophenyl)pent-2-ene (5ea-S, *E/Z* = 35:65).** Purified by GPC (chloroform); 100.0 mg (68%); white solid; m.p. 96.2-98.2 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.15-2.24 (m, 0.35 x 2H for (*E*)-**5ea-S**), 2.39-2.46 (m, 0.35 x 2H for (*E*)-**5ea-S**), 2.50-2.59 (m, 0.65 x 2H for (*Z*)-**5ea-S**), 2.88-2.81 (m, 0.65 x 2H for (*Z*)-**5ea-S**), 3.60 (d,  $J = 13.0$  Hz, 0.35 x 2H for (*E*)-**5ea-S**), 3.78 (d,  $J = 13.8$  Hz, 0.65 x 2H for (*Z*)-**5ea-S**), 5.75-5.80 (m, 0.35 x 1H for (*E*)-**5ea-S**), 5.75-5.80 (m, 0.65 x 1H for (*Z*)-**5ea-S**), 6.49-6.54 (m, 0.65 x 1H for (*Z*)-**5ea-S**), 6.66-6.77 (m, 0.35 x 1H for (*E*)-**5ea-S**), 6.66-6.77 (m, 0.65 x 2H for (*Z*)-**5ea-S**), 6.86-6.94 (m, 0.35 x 2H for (*E*)-**5ea-S**), 6.86-6.94 (m, 0.65 x 1H for (*Z*)-**5ea-S**), 6.95-7.01 (m, 0.35 x 1H for (*E*)-**5ea-S**), 7.24-7.47 (m, 0.35 x 12H for (*E*)-**5ea-S**), 7.24-7.47 (m, 0.65 x 12H for (*Z*)-**5ea-S**), 7.62-7.73 (m, 0.35 x 8H for (*E*)-**5ea-S**), 7.62-7.73 (m, 0.65



x 4H for (**Z**)-**5ea-S**), 7.90-7.96 (m, 0.65 x 4H for (**Z**)-**5ea-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.2 (1C, for (**Z**)-**5ea-S**), 22.7 (1C, for (**E**)-**5ea-S**), 32.3 (dd,  $J = 5.1, 55.0$  Hz, 1C, for (**E**)-**5ea-S**), 32.8 (dd,  $J = 3.8, 54.5$  Hz, 1C, for (**Z**)-**5ea-S**), 35.2 (dd,  $J = 4.4, 52.6$  Hz, 1C, for (**Z**)-**5ea-S**), 42.0 (d,  $J = 51.3$  Hz, 1C, for (**E**)-**5ea-S**), 114.7 (d,  $J = 22.1$  Hz, 1C, for (**Z**)-**5ea-S**), 115.2 (d,  $J = 21.8$  Hz, 1C, for (**E**)-**5ea-S**), 123.7 (d,  $J = 3.1$  Hz, 1C, for (**E**)-**5ea-S**), 123.9 (d,  $J = 3.1$  Hz, 1C, for (**Z**)-**5ea-S**), 126.2 (dd,  $J = 0.8, 8.9$  Hz, 1C, for (**E**)-**5ea-S**), 128.2-128.3 (m, 1C, for (**Z**)-**5ea-S**), 128.3 (d,  $J = 12.0$  Hz, 4C, for (**Z**)-**5ea-S**), 128.4 (d,  $J = 11.9$  Hz, 4C, for (**E**)-**5ea-S**), 128.67 (d,  $J = 12.0$  Hz, 4C, for (**E**)-**5ea-S**), 128.72 (d,  $J = 11.9$  Hz, 4C, for (**Z**)-**5ea-S**), 128.9 (d,  $J = 8.5$  Hz, 1C, for (**Z**)-**5ea-S**), 129.1 (d,  $J = 8.0$  Hz, 1C, for (**E**)-**5ea-S**), 129.5 (dd,  $J = 2.3, 13.7$  Hz, 1C, for (**Z**)-**5ea-S**), 131.1 (d,  $J = 10.2$  Hz, 4C, for (**E**)-**5ea-S**), 131.20 (d,  $J = 10.1$  Hz, 4C, for (**Z**)-**5ea-S**), 131.23-131.48 (m, 1C, for (**E**)-**5ea-S**), 131.24 (d,  $J = 2.8$  Hz, 2C, for (**Z**)-**5ea-S**), 131.28 (d,  $J = 9.8$  Hz, 4C, for (**E**)-**5ea-S**), 131.30 (d,  $J = 3.5$  Hz, 2C, for (**E**)-**5ea-S**), 131.37 (d,  $J = 10.2$  Hz, 4C, for (**Z**)-**5ea-S**), 131.44 (d,  $J = 2.9$  Hz, 2C, for (**Z**)-**5ea-S**), 131.46 (d,  $J = 3.5$  Hz, 2C, for (**E**)-**5ea-S**), 131.54 (d,  $J = 4.0$  Hz, 1C, for (**E**)-**5ea-S**), 131.54 (d,  $J = 4.0$  Hz, 1C, for (**Z**)-**5ea-S**), 132.6 (d,  $J = 79.3$  Hz, 2C, for (**E**)-**5ea-S**), 132.7 (d,  $J = 79.4$  Hz, 2C, for (**E**)-**5ea-S**), 132.76 (d,  $J = 79.0$  Hz, 2C, for (**Z**)-**5ea-S**), 132.83 (d,  $J = 79.2$  Hz, 2C, for (**Z**)-**5ea-S**), 135.8 (dd,  $J = 10.7, 17.8$  Hz, 1C, for (**E**)-**5ea-S**), 136.3 (dd,  $J = 10.9, 16.8$  Hz, 1C, for (**Z**)-**5ea-S**), 159.36 (d,  $J = 243.6$  Hz, 1C, for (**E**)-**5ea-S**), 159.44 (d,  $J = 244.2$  Hz, 1C, for (**Z**)-**5ea-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  38.83 (1P for (**Z**)-**5ea-S**), 40.42 (1P for (**E**)-**5ea-S**), 41.88 (1P for (**E**)-**5ea-S**), 42.56 (1P for (**Z**)-**5ea-S**);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  -114.95 (1F for (**Z**)-**5ea-S**), -114.21 (1F for (**E**)-**5ea-S**); HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{35}\text{H}_{32}\text{FP}_2\text{S}_2$ , 597.1399; found, 597.1415.

**1,5-Bis(diphenylthiophosphinyl)-2-(2-naphthyl)pent-2-ene (5fa-S, E/Z = 56:44)**. Purified by GPC (chloroform); 88.4 mg (56%); pale yellow solid; m.p. 97.5-99.5 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  2.25-2.31 (m, 0.56 x 2H for (**E**)-**5fa-S**), 2.40-2.44 (m, 0.56 x 2H for (**E**)-**5fa-S**), 2.54-2.61 (m, 0.44 x 2H for (**Z**)-**5fa-S**), 2.81-2.85 (m, 0.44 x 2H for (**Z**)-**5fa-S**), 3.50 (d,  $J = 13.5$  Hz, 0.56 x 2H for (**E**)-**5fa-S**), 3.85 (d,  $J = 13.8$  Hz, 0.44 x 2H for (**Z**)-**5fa-S**), 5.83 (td,  $J = 8.3, 10.4$  Hz, 0.56 x 1H for (**E**)-**5fa-**

S), 5.89 (td,  $J = 7.6, 10.4$  Hz, 0.44 x 1H for **(Z)-5fa-S**), 6.92 (dd,  $J = 1.6, 8.2$  Hz, 0.56 x 1H for **(E)-5fa-S**), 7.02 (dd,  $J = 1.8, 8.5$  Hz, 0.44 x 1H for **(Z)-5fa-S**), 7.12-7.24 (m, 0.56 x 9H for **(E)-5fa-S**), 7.12-7.24 (m, 0.44 x 9H for **(Z)-5fa-S**), 7.29-7.52 (m, 0.56 x 8H for **(E)-5fa-S**), 7.29-7.52 (m, 0.44 x 8H for **(Z)-5fa-S**), 7.56-7.69 (m, 0.56 x 9H for **(E)-5fa-S**), 7.56-7.69 (m, 0.44 x 5H for **(Z)-5fa-S**), 7.91-7.94 (m, 0.44 x 4H for **(Z)-5fa-S**);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.4 (1C for **(E)-5fa-S**), 22.8 (1C for **(Z)-5fa-S**), 32.77 (dd,  $J = 4.7, 53.9$  Hz, 1C for **(E)-5fa-S**), 32.81 (dd,  $J = 4.0, 54.2$  Hz, 1C for **(Z)-5fa-S**), 36.2 (d,  $J = 51.6$  Hz, 1C for **(Z)-5fa-S**), 43.0 (d,  $J = 50.8$  Hz, 1C for **(E)-5fa-S**), 125.4 (d,  $J = 1.1$  Hz, 1C for **(Z)-5fa-S**), 125.6 (1C for **(Z)-5fa-S**), 125.8 (1C for **(E)-5fa-S**), 125.87 (1C for **(E)-5fa-S**), 125.89 (1C for **(Z)-5fa-S**), 126.3 (d,  $J = 1.5$  Hz, 1C for **(Z)-5fa-S**), 126.5 (d,  $J = 1.7$  Hz, 1C for **(E)-5fa-S**), 127.3 (1C for **(Z)-5fa-S**), 127.4 (1C for **(Z)-5fa-S**), 127.5 (1C for **(E)-5fa-S**), 127.6 (d,  $J = 1.9$  Hz, 1C for **(E)-5fa-S**), 127.7 (1C for **(E)-5fa-S**), 128.0 (1C for **(Z)-5fa-S**), 128.1 (1C for **(E)-5fa-S**), 128.18 (d,  $J = 12.0$  Hz, 4C for **(Z)-5fa-S**), 128.24 (d,  $J = 11.9$  Hz, 4C for **(E)-5fa-S**), 128.5 (d,  $J = 12.0$  Hz, 4C for **(E)-5fa-S**), 128.7 (d,  $J = 10.2$  Hz, 4C for **(Z)-5fa-S**), 131.0 (d,  $J = 10.1$  Hz, 4C for **(E)-5fa-S**), 131.1 (d,  $J = 2.9$  Hz, 2C for **(Z)-5fa-S**), 131.2 (d,  $J = 2.9$  Hz, 2C for **(E)-5fa-S**), 131.33 (d,  $J = 9.9$  Hz, 4C for **(E)-5fa-S**), 131.34 (d,  $J = 3.5$  Hz, 2C for **(E)-5fa-S**), 131.35 (d,  $J = 10.2$  Hz, 4C for **(Z)-5fa-S**), 131.36 (d,  $J = 9.6$  Hz, 4C for **(Z)-5fa-S**), 131.43 (d,  $J = 3.0$  Hz, 2C for **(Z)-5fa-S**), 132.0 (d,  $J = 7.9$  Hz, 1C for **(E)-5fa-S**), 132.3 (1C for **(E)-5fa-S**), 132.35 (1C for **(E)-5fa-S**), 132.35 (d,  $J = 7.7$  Hz, 1C for **(Z)-5fa-S**), 132.58 (d,  $J = 79.6$  Hz, 2C for **(E)-5fa-S**), 132.60 (d,  $J = 79.1$  Hz, 2C for **(E)-5fa-S**), 132.8 (d,  $J = 79.2$  Hz, 2C for **(Z)-5fa-S**), 132.9 (d,  $J = 79.2$  Hz, 2C for **(Z)-5fa-S**), 132.96 (1C for **(Z)-5fa-S**), 132.96 (1C for **(Z)-5fa-S**), 133.5 (dd,  $J = 10.6, 17.6$  Hz, 1C for **(E)-5fa-S**), 134.0 (dd,  $J = 10.7, 16.0$  Hz, 1C for **(Z)-5fa-S**), 136.7 (d,  $J = 2.6$  Hz, 1C for **(E)-5fa-S**), 139.2 (d,  $J = 1.9$  Hz, 1C for **(Z)-5fa-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  39.40 (1P for **(Z)-5fa-S**), 41.02 (1P for **(E)-5fa-S**), 41.82 (1P for **(E)-5fa-S**), 42.70 (1P for **(Z)-5fa-S**); HRMS (APCI)  $m/z$ :  $(\text{M} + \text{H})^+$  calcd for  $\text{C}_{39}\text{H}_{35}\text{P}_2\text{S}_2$ , 629.1650; found, 629.1644.

**1,5-Bis(diphenylthiophosphinyl)-2-(3-pyridyl)pent-2-ene (5ga-S, E/Z = 23:77)**. Purified by GPC (chloroform); 90.7 mg (60%); pale yellow solid; m.p. 82.5-84.5 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), for

mixture,  $\delta$  2.17-2.26 (m, 0.23 x 2H for (*E*)-5ga-S), 2.39-2.46 (m, 0.23 x 2H for (*E*)-5ga-S), 2.51-2.58 (m, 0.77 x 2H for (*Z*)-5ga-S), 2.73-2.80 (m, 0.77 x 2H for (*Z*)-5ga-S), 3.57 (d,  $J = 13.4$  Hz, 0.23 x 2H for (*E*)-5ga-S), 3.78 (d,  $J = 13.4$  Hz, 0.77 x 2H for (*Z*)-5ga-S), 5.73 (td,  $J = 7.7, 10.4$  Hz, 0.77 x 1H for (*Z*)-5ga-S), 5.79 (td,  $J = 7.6, 10.5$  Hz, 0.23 x 1H for (*E*)-5ga-S), 6.83-6.86 (m, 0.23 x 1H for (*E*)-5ga-S), 6.83-6.86 (m, 0.77 x 1H for (*Z*)-5ga-S), 7.04-7.06 (m, 0.23 x 1H for (*E*)-5ga-S), 7.14-7.17 (m, 0.77 x 1H for (*Z*)-5ga-S), 7.28-7.33 (m, 0.23 x 4H for (*E*)-5ga-S), 7.28-7.33 (m, 0.77 x 4H for (*Z*)-5ga-S), 7.35-7.46 (m, 0.23 x 8H for (*E*)-5ga-S), 7.35-7.45 (m, 0.77 x 8H for (*Z*)-5ga-S), 7.64-7.72 (m, 0.23 x 8H for (*E*)-5ga-S), 7.64-7.72 (m, 0.77 x 4H for (*Z*)-5ga-S), 7.87-7.92 (m, 0.77 x 4H for (*Z*)-5ga-S), 8.11 (d,  $J = 2.0$  Hz, 0.23 x 1H for (*E*)-5ga-S), 8.13 (d,  $J = 2.0$  Hz, 0.77 x 1H for (*Z*)-5ga-S), 8.20 (dd,  $J = 1.1, 4.7$  Hz, 0.77 x 1H for (*Z*)-5ga-S), 8.24 (dd,  $J = 1.4, 4.6$  Hz, 0.23 x 1H for (*E*)-5ga-S);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  22.4 (1C for (*E*)-5ga-S), 22.8 (1C for (*Z*)-5ga-S), 32.5 (dd,  $J = 3.6, 54.7$  Hz, 1C for (*Z*)-5ga-S), 32.6 (dd,  $J = 4.6, 54.7$  Hz, 1C for (*E*)-5ga-S), 35.7 (d,  $J = 51.4$  Hz, 1C for (*Z*)-5ga-S), 42.7 (d,  $J = 50.7$  Hz, 1C for (*E*)-5ga-S), 122.7 (1C for (*Z*)-5ga-S), 122.8 (1C for (*E*)-5ga-S), 128.4 (d,  $J = 9.2$  Hz, 1C for (*E*)-5ga-S), 128.54 (d,  $J = 12.0$  Hz, 4C for (*E*)-5ga-S), 128.54 (d,  $J = 12.0$  Hz, 4C for (*Z*)-5ga-S), 128.73 (d,  $J = 12.0$  Hz, 4C for (*E*)-5ga-S), 128.73 (d,  $J = 12.0$  Hz, 4C for (*Z*)-5ga-S), 129.2 (d,  $J = 8.4$  Hz, 1C for (*Z*)-5ga-S), 131.1 (d,  $J = 9.9$  Hz, 4C for (*E*)-5ga-S), 131.29 (d,  $J = 10.1$  Hz, 4C for (*Z*)-5ga-S), 131.31 (d,  $J = 10.2$  Hz, 4C for (*E*)-5ga-S), 131.4 (d,  $J = 10.1$  Hz, 4C for (*Z*)-5ga-S), 131.51 (d,  $J = 3.1$  Hz, 2C for (*E*)-5ga-S), 131.51 (d,  $J = 3.1$  Hz, 2C for (*Z*)-5ga-S), 131.55 (d,  $J = 2.8$  Hz, 2C for (*E*)-5ga-S), 131.55 (d,  $J = 2.8$  Hz, 2C for (*Z*)-5ga-S), 132.4 (d,  $J = 79.3$  Hz, 2C for (*E*)-5ga-S), 132.57 (d,  $J = 79.3$  Hz, 2C for (*E*)-5ga-S), 132.57 (d,  $J = 79.3$  Hz, 2C for (*Z*)-5ga-S), 132.8 (d,  $J = 79.5$  Hz, 2C for (*Z*)-5ga-S), 134.9 (1C for (*Z*)-5ga-S), 135.1 (d,  $J = 1.5$  Hz, 1C for (*E*)-5ga-S), 135.5 (dd,  $J = 10.7, 17.1$  Hz, 1C for (*E*)-5ga-S), 135.8 (dd,  $J = 10.7, 14.5$  Hz, 1C for (*Z*)-5ga-S), 136.6 (1C for (*E*)-5ga-S), 137.9 (d,  $J = 1.5$  Hz, 1C for (*Z*)-5ga-S), 147.3 (1C for (*Z*)-5ga-S), 147.7 (1C for (*E*)-5ga-S), 147.8 (1C for (*Z*)-5ga-S), 148.9 (1C for (*E*)-5ga-S);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  38.86 (1P for (*Z*)-5ga-S), 40.41 (1P for (*E*)-5ga-S), 41.74 (1P for (*E*)-5ga-S), 42.56 (1P for (*Z*)-5ga-S); HRMS (APCI)  $m/z$ : (M + H)<sup>+</sup> calcd for  $\text{C}_{34}\text{H}_{32}\text{NP}_2\text{S}_2$ , 580.1446; found, 580.1449.

**1,5-Bis(diphenylthiophosphinyl)-2-(2-thiophenyl)pent-2-ene (5ha-S, E/Z = 47:53).** Purified by GPC (chloroform); 54.3 mg (38%); pale yellow solid; m.p. 125.2-127.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), for mixture, δ 2.33-2.39 (m, 0.47 x 2H for (**E**)-5ha-S), 2.41-2.48 (m, 0.47 x 2H for (**E**)-5ha-S), 2.41-2.48 (m, 0.53 x 2H for (**Z**)-5ha-S), 2.63-2.67 (m, 0.53 x 2H for (**Z**)-5ha-S), 3.68 (d, *J* = 13.3 Hz, 0.47 x 2H for (**E**)-5ha-S), 3.74 (d, *J* = 13.4 Hz, 0.53 x 2H for (**Z**)-5ha-S), 5.74 (td, *J* = 7.3, 9.8 Hz, 0.53 x 1H for (**Z**)-5ha-S), 5.74 (td, *J* = 7.7, 10.4 Hz, 0.47 x 1H for (**E**)-5ha-S), 6.43 (dd, *J* = 1.1, 3.5 Hz, 0.47 x 1H for (**E**)-5ha-S), 6.46 (dd, *J* = 0.8, 3.6 Hz, 0.53 x 1H for (**Z**)-5ha-S), 6.58 (dd, *J* = 3.6, 5.1 Hz, 0.53 x 1H for (**Z**)-5ha-S), 6.63 (dd, *J* = 3.5, 5.1 Hz, 0.47 x 1H for (**E**)-5ha-S), 6.90 (dd, *J* = 1.0 Hz, 5.1 Hz, 0.53 x 1H for (**Z**)-5ha-S), 7.01 (dd, *J* = 1.1, 5.1 Hz, 0.47 x 1H for (**E**)-5ha-S), 7.32-7.48 (m, 0.47 x 12H for (**E**)-5ha-S), 7.32-7.48 (m, 0.53 x 12H for (**Z**)-5ha-S), 7.69-7.77 (m, 0.47 x 8H for (**E**)-5ha-S), 7.69-7.77 (m, 0.53 x 4H for (**Z**)-5ha-S), 7.83-7.87 (m, 0.53 x 4H for (**Z**)-5ha-S); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>), for mixture, δ 22.67 (1C), 22.72 (1C), 32.5 (dd, *J* = 3.6, 54.6 Hz, 1C), 32.6 (dd, *J* = 4.8, 54.4 Hz, 1C), 36.9 (d, *J* = 51.1 Hz, 1C), 43.7 (d, *J* = 50.2 Hz, 1C), 123.9 (1C), 124.38 (d, *J* = 1.4 Hz, 1C), 124.44 (d, *J* = 9.5 Hz, 1C), 125.1 (1C), 125.7 (d, *J* = 9.4 Hz, 1C), 126.8 (1C), 126.9 (1C), 127.0 (d, *J* = 1.5 Hz, 1C), 128.4 (d, *J* = 11.9 Hz, 4C), 128.5 (d, *J* = 11.9 Hz, 4C), 128.70 (d, *J* = 12.0 Hz, 4C), 128.72 (d, *J* = 12.0 Hz, 4C), 131.2 (d, *J* = 10.2 Hz, 4C), 131.3 (d, *J* = 10.1 Hz, 4C), 131.4 (d, *J* = 3.0 Hz, 2C), 131.46 (d, *J* = 2.8 Hz, 2C), 131.47 (d, *J* = 9.9 Hz, 4C), 131.47 (d, *J* = 2.8 Hz, 2C), 131.54 (d, *J* = 2.9 Hz, 2C), 131.6 (d, *J* = 10.2 Hz, 4C), 132.3 (dd, *J* = 10.2, 15.3 Hz, 1C), 132.6 (d, *J* = 79.5 Hz, 2C), 132.75 (d, *J* = 79.5 Hz, 2C), 132.76 (d, *J* = 79.2 Hz, 2C), 132.9 (d, *J* = 79.5 Hz, 2C), 135.1 (dd, *J* = 10.1, 17.8 Hz, 1C), 140.7 (d, *J* = 3.2 Hz, 1C), 145.3 (d, *J* = 2.5 Hz, 1C); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>), for mixture, δ 39.46 (1P for (**Z**)-5ha-S), 41.61 (1P for (**E**)-5ha-S), 41.90 (1P for (**E**)-5ha-S), 42.66 (1P for (**Z**)-5ha-S); HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>33</sub>H<sub>31</sub>P<sub>2</sub>S<sub>3</sub>, 585.1058; found, 585.1080.

**1,5-Bis[bis(4-trifluoromethylphenyl)thiophosphinyl]-2-phenylpent-2-ene (5ac-S, E/Z = 25:75).** Purified by GPC (chloroform); 138.9 mg (62%); white solid; m.p. 111.6-113.6 °C; <sup>1</sup>H NMR (600 MHz,

CDCl<sub>3</sub>), for mixture,  $\delta$  2.25-2.31 (m, 0.25 x 2H for (*E*)-5ac-S), 2.48-2.53 (m, 0.25 x 2H for (*E*)-5ac-S), 2.61-2.68 (m, 0.75 x 2H for (*Z*)-5ac-S), 2.92-2.96 (m, 0.75 x 2H for (*Z*)-5ac-S), 3.61 (d,  $J = 13.2$  Hz, 0.25 x 2H for (*E*)-5ac-S), 3.83 (d,  $J = 13.5$  Hz, 0.75 x 2H for (*Z*)-5ac-S), 5.75 (td,  $J = 7.8, 10.7$  Hz, 0.75 x 1H for (*Z*)-5ac-S), 5.79 (td,  $J = 7.3, 11.1$  Hz, 0.25 x 1H for (*E*)-5ac-S), 6.68 (d,  $J = 7.5$  Hz, 0.25 x 2H for (*E*)-5ac-S), 6.71 (d,  $J = 6.7$  Hz, 0.75 x 2H for (*Z*)-5ac-S), 6.87-6.89 (m, 0.75 x 2H for (*Z*)-5ac-S), 6.89-6.92 (m, 0.25 x 2H for (*E*)-5ac-S), 6.95-6.97 (m, 0.75 x 1H for (*Z*)-5ac-S), 6.99-7.02 (m, 0.25 x 1H for (*E*)-5ac-S), 7.52-7.53 (m, 0.25 x 4H for (*E*)-5ac-S), 7.52-7.53 (m, 0.75 x 4H for (*Z*)-5ac-S), 7.62-7.65 (m, 0.25 x 4H for (*E*)-5ac-S), 7.62-7.65 (m, 0.75 x 4H for (*Z*)-5ac-S), 7.71-7.76 (m, 0.25 x 4H for (*E*)-5ac-S), 7.71-7.76 (m, 0.75 x 4H for (*Z*)-5ac-S), 7.78-7.82 (m, 0.25 x 4H for (*E*)-5ac-S), 8.05-8.09 (m, 0.75 x 4H for (*Z*)-5ac-S); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  22.2 (1C for (*E*)-5ac-S), 22.8 (1C for (*Z*)-5ac-S), 32.3 (dd,  $J = 5.1, 54.5$  Hz, 1C for (*E*)-5ac-S), 32.5 (dd,  $J = 4.1, 54.7$  Hz, 1C for (*Z*)-5ac-S), 36.0 (d,  $J = 51.7$  Hz, 1C for (*Z*)-5ac-S), 42.9 (d,  $J = 51.0$  Hz, 1C for (*E*)-5ac-S), 123.45 (q,  $J = 271.8$  Hz, 2C for (*Z*)-5ac-S), 123.48 (q,  $J = 273.1$  Hz, 2C for (*E*)-5ac-S), 123.52 (q,  $J = 270.8$  Hz, 2C for (*E*)-5ac-S), 123.52 (q,  $J = 270.8$  Hz, 2C for (*Z*)-5ac-S), 125.30-125.82 (m, 8C for (*E*)-5ac-S), 125.30-125.82 (m, 8C for (*Z*)-5ac-S), 127.08 (1C for (*Z*)-5ac-S), 127.09 (1C for (*Z*)-5ac-S), 127.38 (1C for (*Z*)-5ac-S), 127.38 (1C for (*Z*)-5ac-S), 127.5 (1C for (*E*)-5ac-S), 128.08 (1C for (*E*)-5ac-S), 128.08 (1C for (*E*)-5ac-S), 128.2 (1C for (*Z*)-5ac-S), 128.33 (1C for (*E*)-5ac-S), 128.34 (1C for (*E*)-5ac-S), 131.3 (d,  $J = 10.7$  Hz, 4C for (*Z*)-5ac-S), 131.35-131.89 (m, 1C for (*E*)-5ac-S), 131.35-131.89 (m, 1C for (*Z*)-5ac-S), 131.6 (d,  $J = 10.6$  Hz, 4C for (*E*)-5ac-S), 131.7 (d,  $J = 10.5$  Hz, 4C for (*E*)-5ac-S), 131.8 (d,  $J = 11.0$  Hz, 4C for (*Z*)-5ac-S), 133.24-134.04 (m, 4C for (*E*)-5ac-S), 133.24-134.04 (m, 4C for (*Z*)-5ac-S), 133.5 (dd,  $J = 11.1, 17.1$  Hz, 1C for (*E*)-5ac-S), 133.8 (dd,  $J = 12.1, 15.5$  Hz, 1C for (*Z*)-5ac-S), 136.41 (d,  $J = 76.4$  Hz, 2C for (*E*)-5ac-S), 136.44 (d,  $J = 77.1$  Hz, 2C for (*Z*)-5ac-S), 136.5 (d,  $J = 77.2$  Hz, 2C for (*E*)-5ac-S), 136.7 (d,  $J = 77.2$  Hz, 2C for (*Z*)-5ac-S), 138.3 (d,  $J = 2.5$  Hz, 1C for (*E*)-5ac-S), 141.3 (d,  $J = 2.0$  Hz, 1C for (*Z*)-5ac-S); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  38.51 (1P for (*Z*)-5ac-S), 39.87 (1P for (*E*)-5ac-S), 41.06 (1P for (*E*)-5ac-S), 41.89 (1P for (*Z*)-5ac-S); <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>), for

mixture,  $\delta$  -63.41 (6F for **(Z)**-5ac-S), -63.33 (6F for **(E)**-5ac-S), -63.23 (6F for **(E)**-5ac-S), -63.20 (6F for **(Z)**-5ac-S); HRMS (APCI)  $m/z$ : (M + H)<sup>+</sup> calcd for C<sub>39</sub>H<sub>29</sub>F<sub>12</sub>P<sub>2</sub>S<sub>2</sub>, 851.0989; found, 851.0994.

**1,5-Bis[bis(4-methylphenyl)thiophosphinyl]-2-phenylpent-2-ene (5ad-S, E/Z = 21:79)**. Purified by GPC (chloroform); 111.5 mg (71%); white solid; m.p. 114.2-116.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  2.19-2.23 (m, 0.21 x 2H for **(E)**-5ad-S), 2.29-2.35 (m, 0.21 x 2H for **(E)**-5ad-S), 2.29 (s, 0.21 x 6H for **(E)**-5ad-S), 2.30 (s, 0.79 x 6H for **(Z)**-5ad-S), 2.31 (s, 0.79 x 6H for **(Z)**-5ad-S), 2.34 (s, 0.21 x 6H for **(E)**-5ad-S), 2.40-2.47 (m, 0.79 x 2H for **(Z)**-5ad-S), 2.68-2.72 (m, 0.79 x 2H for **(Z)**-5ad-S), 3.52 (d,  $J$  = 13.5 Hz, 0.21 x 2H for **(E)**-5ad-S), 3.71 (d,  $J$  = 13.7 Hz, 0.79 x 2H for **(Z)**-5ad-S), 5.65 (td,  $J$  = 7.4, 10.2 Hz, 0.21 x 1H for **(E)**-5ad-S), 5.70 (td,  $J$  = 7.6, 10.5 Hz, 0.79 x 1H for **(Z)**-5ad-S), 6.76-6.77 (m, 0.21 x 2H for **(E)**-5ad-S), 6.84-6.86 (m, 0.79 x 2H for **(Z)**-5ad-S), 6.91-6.94 (m, 0.79 x 2H for **(Z)**-5ad-S), 6.95-6.99 (m, 0.21 x 2H for **(E)**-5ad-S), 6.95-6.99 (m, 0.79 x 1H for **(Z)**-5ad-S), 7.01-7.02 (m, 0.21 x 1H for **(E)**-5ad-S), 7.04-7.07 (m, 0.21 x 4H for **(E)**-5ad-S), 7.04-7.07 (m, 0.79 x 4H for **(Z)**-5ad-S), 7.12-7.16 (m, 0.21 x 4H for **(E)**-5ad-S), 7.12-7.16 (m, 0.79 x 4H for **(Z)**-5ad-S), 7.50-7.54 (m, 0.21 x 4H for **(E)**-5ad-S), 7.50-7.54 (m, 0.79 x 4H for **(Z)**-5ad-S), 7.52-7.55 (m, 0.21 x 4H for **(E)**-5ad-S), 7.75-7.79 (m, 0.79 x 4H for **(Z)**-5ad-S); <sup>13</sup>C {<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>), for mixture,  $\delta$  21.40 (2C for **(E)**-5ad-S), 21.40 (2C for **(Z)**-5ad-S), 21.44 (1C for **(E)**-5ad-S), 21.44 (1C for **(Z)**-5ad-S), 21.45 (1C for **(E)**-5ad-S), 21.45 (1C for **(Z)**-5ad-S), 22.3 (1C for **(E)**-5ad-S), 22.7 (1C for **(Z)**-5ad-S), 32.8 (dd,  $J$  = 4.3, 54.8 Hz, 1C for **(E)**-5ad-S), 32.9 (dd,  $J$  = 3.8, 54.8 Hz, 1C for **(Z)**-5ad-S), 36.2 (d,  $J$  = 51.9 Hz, 1C for **(Z)**-5ad-S), 43.1 (d,  $J$  = 50.7 Hz, 1C for **(E)**-5ad-S), 126.4 (1C for **(Z)**-5ad-S), 126.5 (1C for **(E)**-5ad-S), 127.1 (1C for **(Z)**-5ad-S), 127.2 (1C for **(Z)**-5ad-S), 127.65 (1C for **(Z)**-5ad-S), 127.65 (1C for **(Z)**-5ad-S), 127.83 (1C for **(E)**-5ad-S), 127.83 (1C for **(E)**-5ad-S), 128.47 (1C for **(E)**-5ad-S), 128.48 (1C for **(E)**-5ad-S), 128.9 (d,  $J$  = 12.5 Hz, 4C for **(Z)**-5ad-S), 129.0 (d,  $J$  = 12.6 Hz, 4C for **(E)**-5ad-S), 129.28 (d,  $J$  = 12.4 Hz, 4C for **(E)**-5ad-S), 129.32 (d,  $J$  = 12.1 Hz, 4C for **(Z)**-5ad-S), 129.5 (d,  $J$  = 78.5 Hz, 2C for **(E)**-5ad-S), 129.6 (d,  $J$  = 79.7 Hz, 2C for **(E)**-5ad-S), 129.7 (d,  $J$  = 81.3 Hz, 2C for **(Z)**-5ad-S), 129.8 (d,  $J$  = 81.5 Hz, 2C for **(Z)**-5ad-S), 131.0 (d,  $J$  = 10.5 Hz, 4C for **(E)**-5ad-S), 131.2 (d,  $J$  = 10.6 Hz, 4C

for (**Z**)-**5ad-S**), 131.3 (d,  $J = 10.2$  Hz, 4C for (**E**)-**5ad-S**), 131.4 (d,  $J = 10.3$  Hz, 4C for (**Z**)-**5ad-S**), 131.8 (d,  $J = 7.7$  Hz, 1C for (**E**)-**5ad-S**), 132.4 (d,  $J = 8.8$  Hz, 1C for (**Z**)-**5ad-S**), 133.0 (dd,  $J = 10.3, 17.5$  Hz, 1C for (**E**)-**5ad-S**), 133.5 (dd,  $J = 11.1, 16.0$  Hz, 1C for (**Z**)-**5ad-S**), 139.4 (d,  $J = 2.8$  Hz, 1C for (**E**)-**5ad-S**), 141.48 (d,  $J = 2.9$  Hz, 2C for (**Z**)-**5ad-S**), 141.54 (d,  $J = 2.9$  Hz, 2C for (**E**)-**5ad-S**), 141.6 (d,  $J = 3.0$  Hz, 2C for (**Z**)-**5ad-S**), 141.7 (d,  $J = 2.9$  Hz, 2C for (**E**)-**5ad-S**), 142.1 (d,  $J = 1.8$  Hz, 1C for (**Z**)-**5ad-S**);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ), for mixture,  $\delta$  38.81 (1P for (**Z**)-**5ad-S**), 40.65 (1P for (**E**)-**5ad-S**), 41.23 (1P for (**E**)-**5ad-S**), 41.99 (1P for (**Z**)-**5ad-S**); HRMS (APCI)  $m/z$ :  $(\text{M} + \text{H})^+$  calcd for  $\text{C}_{39}\text{H}_{41}\text{P}_2\text{S}_2$ , 635.2119; found, 635.2106.

**Typical Procedure for Hydrogenation.** The synthesis of **3aa-S-H** is representative (Scheme 4). 2,4-Bis(diphenylthiophosphinyl)-1-phenylbut-1-ene (**3aa-S**; 28.2 mg, 0.050 mmol) and Crabtree's catalyst ( $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ , 6.0 mg, 0.0075 mmol) were placed in a 20-mL two necked reaction flask. DCE (2.0 mL) was added, and the flask was evacuated and refilled with  $\text{H}_2$ . The resulting solution was stirred at  $70^\circ\text{C}$  for 48 h under  $\text{H}_2$  (1 atm, balloon). The mixture was then filtered through a pad of Celite. The filtrate was evaporated in vacuo and purified by silica gel column chromatography with hexane/ethyl acetate (3/1, v/v) to afford 1,3-bis(diphenylthiophosphinyl)-4-phenylbutane (**3aa-S-H**; 21.4 mg, 0.037 mmol) in 74% yield.

**1,3-Bis(diphenylthiophosphinyl)-4-phenylbutane (3aa-S-H).** Purified by hexane/ethyl acetate (3/1, v/v); 21.4 mg (74%); yellow solid; m.p.  $57.5\text{-}59.5^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.76-1.93 (m, 1H), 1.97-2.15 (m, 1H), 2.15-2.29 (m, 1H), 2.54-2.68 (m, 1H), 2.78-2.88 (m, 1H), 2.89-2.99 (m, 1H), 3.18-3.29 (m, 1H), 7.04-7.09 (m, 2H), 7.15-7.25 (m, 3H), 7.25-7.31 (m, 2H), 7.32-7.52 (m, 12H), 7.53-7.60 (m, 2H), 7.94-8.04 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.24 (1C), 29.69 (dd,  $J = 5.7, 55.9$  Hz, 1C), 34.19 (1C), 40.05 (dd,  $J = 14.0, 53.0$  Hz, 1C), 126.61 (1C), 128.44 (d,  $J = 11.8$  Hz, 2C), 128.56 (d,  $J = 11.7$  Hz, 2C), 128.68 (2C), 128.69 (d,  $J = 11.7$  Hz, 2C), 128.74 (d,  $J = 12.2$  Hz, 2C), 129.07 (2C), 130.89 (d,  $J = 10.1$  Hz, 2C), 130.91 (d,  $J = 10.2$  Hz, 2C), 131.19 (d,  $J = 2.6$  Hz, 1C), 131.30 (d,  $J = 9.4$

Hz, 2C), 131.31 (d,  $J = 3.1$  Hz, 1C), 131.52 (d,  $J = 76.2$  Hz, 1C), 131.52 (d,  $J = 9.4$  Hz, 2C), 131.52 (d,  $J = 2.7$  Hz, 2C), 131.56 (d,  $J = 76.6$  Hz, 1C), 132.15 (d,  $J = 79.1$  Hz, 1C), 132.73 (d,  $J = 79.7$  Hz, 1C), 138.87 (d,  $J = 14.7$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  42.08, 49.61; HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{34}\text{H}_{33}\text{P}_2\text{S}_2$ , 567.1493; found, 567.1501.

**1,5-Bis(diphenylthiophosphinyl)-2-phenylpentane (5aa-S-H).** Purified by hexane/ethyl acetate (2/1, v/v); 22.1 mg (76%); yellow solid; m.p. 52.4-54.4 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33-1.47 (m, 1H), 1.47-1.56 (m, 1H), 1.69-1.80 (m, 1H), 1.85-1.95 (m, 1H), 2.25-2.47 (m, 2H), 2.62 (ddd,  $J = 5.8, 12.4, 18.2$  Hz, 1H), 2.83 (ddd,  $J = 7.0, 10.2, 17.3$  Hz, 1H), 3.32-3.44 (m, 1H), 6.91-6.98 (m, 2H), 6.98-7.07 (m, 3H), 7.17-7.24 (m, 2H), 7.27-7.34 (m, 1H), 7.34-7.50 (m, 9H), 7.52-7.58 (m, 2H), 7.64-7.82 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.61 (d,  $J = 2.1$  Hz, 1C), 31.63 (d,  $J = 56.3$  Hz, 1C), 37.78 (dd,  $J = 9.9, 16.9$  Hz, 1C), 38.55 (1C), 39.09 (1C), 126.54 (1C), 127.75 (2C), 128.13 (d,  $J = 12.2$  Hz, 2C), 128.39 (2C), 128.54 (d,  $J = 11.9$  Hz, 2C), 128.59 (d,  $J = 11.9$  Hz, 2C), 128.66 (d,  $J = 12.2$  Hz, 2C), 130.72 (d,  $J = 10.0$  Hz, 2C), 130.96 (d,  $J = 4.3$  Hz, 1C), 130.99 (d,  $J = 9.9$  Hz, 2C), 131.07 (d,  $J = 10.1$  Hz, 2C), 131.22 (d,  $J = 10.2$  Hz, 2C), 131.26 (d,  $J = 2.3$  Hz, 1C), 131.29 (d,  $J = 2.5$  Hz, 1C), 131.37 (d,  $J = 2.9$  Hz, 1C), 131.63 (d,  $J = 83.0$  Hz, 1C), 132.51 (d,  $J = 79.5$  Hz, 1C), 133.05 (d,  $J = 79.4$  Hz, 1C), 134.41 (d,  $J = 80.1$  Hz, 1C), 143.23 (d,  $J = 6.9$  Hz, 1C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  41.26, 42.64; HRMS (APCI)  $m/z$ : (M + H) $^+$  calcd for  $\text{C}_{35}\text{H}_{35}\text{P}_2\text{S}_2$ , 581.1650; found, 581.1644.

**Procedure for Desulfidation of 3aa-S (Scheme 4).** 2,4-Bis(diphenylthiophosphinyl)-1-phenylbut-1-ene (**3aa-S**; 56 mg, 0.10 mmol,  $E/Z = 80:20$ ) was placed in a 2 mL microwave vessel, which was flushed with  $\text{N}_2$ . After toluene (3.0 mL) and  $\text{P}(\text{NMe}_2)_3$  (0.33 g, 2.0 mmol) were added, the mixture was stirred for 72 h at 120 °C (oil bath). The reaction vessel was then taken into the glovebox. The solution was filtered through a short pad of Celite, silica gel, alumina, and anhydrous  $\text{Na}_2\text{SO}_4$ , washed with  $\text{CH}_2\text{Cl}_2$ , and concentrated in vacuo. The residue was dissolved in a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  (14 and 1 mL,



respectively, degassed). The supernatant was passed through a silica, long-body Sep-Pak cartridge (waters), which was filled with hexane in advance. The filtrate was then concentrated to afford 1,4-bis(diphenylphosphino)-2-methyl-2-butene (**3aa**; 32 mg, 0.064 mmol, *E/Z* = 77:23) in 64% yield in an analytically pure form.

**2,4-Bis(diphenylphosphino)-1-phenylbut-1-ene (3aa, *E/Z* = 83:17).** Purified by a silica, long-body Sep-Pak cartridge (waters) with hexane/dichloromethane (14/1, 15/0, then 7.5/7.5 mL); 32.1 mg (64%); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), for mixture, δ 1.91-1.95 (m, 0.17 x 2H for (**Z**)-**3aa**), 2.15-2.19 (m, 0.83 x 2H for (**E**)-**3aa**), 2.23-2.25 (m, 0.17 x 2H for (**Z**)-**3aa**), 2.49-2.57 (m, 0.83 x 2H for (**E**)-**3aa**), 6.40 (d, *J* = 2.6 Hz, 0.83 x 1H for (**E**)-**3aa**), 7.04-7.07 (m, 0.83 x 2H for (**E**)-**3aa**), 7.16-7.37 (m, 0.83 x 19H for (**E**)-**3aa**), 7.16-7.37 (m, 0.17 x 26H for (**Z**)-**3aa**), 7.41-7.46 (m, 0.83 x 4H for (**E**)-**3aa**); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), for mixture, δ 28.10 (d, *J* = 20.3 Hz, 1C for (**E**)-**3aa**), 28.10 (d, *J* = 7.9 Hz, 1C for (**Z**)-**3aa**), 28.3 (d, *J* = 20.4 Hz, 1C for (**E**)-**3aa**), 28.5 (d, *J* = 12.9 Hz, 1C for (**Z**)-**3aa**), 127.1 (1C for (**E**)-**3aa**), 127.6 (1C for (**Z**)-**3aa**), 127.9 (2C for (**Z**)-**3aa**), 128.44-128.57 (m, 7C for (**E**)-**3aa**), 128.44-128.57 (m, 13C for (**Z**)-**3aa**), 128.5 (d, *J* = 7.3 Hz, 4C for (**E**)-**3aa**), 128.7 (d, *J* = 7.3 Hz, 4C for (**E**)-**3aa**), 129.1 (2C for (**E**)-**3aa**), 129.56 (1C for (**Z**)-**3aa**), 129.63 (1C for (**Z**)-**3aa**), 132.75 (d, *J* = 18.2 Hz, 4C for (**Z**)-**3aa**), 132.81 (d, *J* = 18.2 Hz, 4C for (**E**)-**3aa**), 133.4 (d, *J* = 18.6 Hz, 4C for (**Z**)-**3aa**), 134.3 (d, *J* = 19.5 Hz, 4C for (**E**)-**3aa**), 135.75 (d, *J* = 11.1 Hz, 2C for (**E**)-**3aa**), 135.75 (d, *J* = 11.1 Hz, 2C for (**Z**)-**3aa**), 136.7 (d, *J* = 12.5 Hz, 2C for (**Z**)-**3aa**), 137.4 (d, *J* = 8.1 Hz, 2C for (**E**)-**3aa**), 138.1 (d, *J* = 17.3 Hz, 1C for (**E**)-**3aa**), 138.3 (dd, *J* = 14.2, 14.2 Hz, 1C for (**Z**)-**3aa**), 142.2 (dd, *J* = 14.5, 16.7 Hz, 1C for (**E**)-**3aa**), 142.7 (d, *J* = 28.9 Hz, 1C for (**Z**)-**3aa**); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>), for mixture; δ -15.04 (1P for (**Z**)-**3aa**), -14.46 (1P for (**E**)-**3aa**), -11.93 (1P for (**Z**)-**3aa**), 1.41 (1P for (**E**)-**3aa**); HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>34</sub>H<sub>31</sub>P<sub>2</sub>, 501.1896; found, 501.1881.

**Procedure for Desulfidation of 5aa-S (Scheme 4).** Zirconocene chloride hydride (0.19 g, 0.75 mmol) and 1,5-bis(diphenylthiophosphinyl)-2-phenylpent-2-ene (**5aa-S**; 58 mg, 0.10 mmol, *E/Z* = 42:58)

were placed in a 2 mL microwave vessel, which was flushed with N<sub>2</sub>. After THF (2.0 mL) was added, the mixture was stirred for 18 h at 60 °C (oil bath). The reaction vessel was then taken into the glovebox. The solution was filtered through a short pad of Celite, silica gel, alumina, and anhydrous Na<sub>2</sub>SO<sub>4</sub>, washed with CH<sub>2</sub>Cl<sub>2</sub>, and concentrated in vacuo to afford 1,5-bis(diphenylphosphino)-2-phenylpent-2-ene (**5aa**; 41 mg, 0.081 mmol, *E/Z* = 39:61) in 81% yield in an analytically pure form.

**1,5-Bis(diphenylphosphino)-2-phenylpent-2-ene (5aa, *E/Z* = 39:61).** Purified by simple filtration with Celite; 41.2 mg (81%); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), for mixture, δ 1.73-1.88 (m, 0.39 x 2H for (*E*)-**5aa**), 1.73-1.88 (m, 0.61 x 4H for (*Z*)-**5aa**), 1.91-1.97 (m, 0.39 x 2H for (*E*)-**5aa**), 3.12 (s, 0.39 x 2H for (*E*)-**5aa**), 3.16 (s, 0.61 x 2H for (*Z*)-**5aa**), 5.28-5.32 (m, 0.39 x 1H for (*E*)-**5aa**), 5.68-5.71 (m, 0.61 x 1H for (*Z*)-**5aa**), 7.07-7.08 (m, 0.39 x 2H for (*E*)-**5aa**), 7.19-7.49 (m, 0.39 x 23H for (*E*)-**5aa**), 7.19-7.49 (m, 0.61 x 25H for (*Z*)-**5aa**); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), for mixture, δ 25.1 (d, *J* = 17.0 Hz, 1C for (*Z*)-**5aa**), 25.5 (d, *J* = 17.2 Hz, 1C for (*E*)-**5aa**), 28.0 (dd, *J* = 1.5, 12.9 Hz, 1C for (*Z*)-**5aa**), 28.5 (dd, *J* = 2.1, 12.7 Hz, 1C for (*E*)-**5aa**), 31.0 (d, *J* = 15.7 Hz, 1C for (*Z*)-**5aa**), 40.0 (d, *J* = 14.7 Hz, 1C for (*E*)-**5aa**), 126.83 (1C for (*E*)-**5aa**), 126.83 (1C for (*Z*)-**5aa**), 126.9 (1C for (*E*)-**5aa**), 127.0 (1C for (*Z*)-**5aa**), 128.24-128.71 (m, 7C for (*E*)-**5aa**), 128.24-128.71 (m, 7C for (*Z*)-**5aa**), 128.30 (d, *J* = 6.4 Hz, 4C for (*E*)-**5aa**), 128.30 (d, *J* = 6.4 Hz, 4C for (*Z*)-**5aa**), 128.5 (d, *J* = 5.7 Hz, 4C for (*E*)-**5aa**), 128.7 (d, *J* = 5.9 Hz, 4C for (*Z*)-**5aa**), 130.3 (dd, *J* = 11.4, 13.9 Hz, 1C for (*Z*)-**5aa**), 131.2 (dd, *J* = 6.5, 13.1 Hz, 1C for (*E*)-**5aa**), 132.7 (d, *J* = 17.7 Hz, 4C for (*E*)-**5aa**), 132.9 (d, *J* = 18.1 Hz, 4C for (*Z*)-**5aa**), 133.20 (d, *J* = 18.8 Hz, 4C for (*E*)-**5aa**), 133.20 (d, *J* = 18.8 Hz, 4C for (*Z*)-**5aa**), 135.2 (d, *J* = 6.7 Hz, 1C for (*Z*)-**5aa**), 136.2 (d, *J* = 7.0 Hz, 1C for (*E*)-**5aa**), 138.3 (d, *J* = 15.6 Hz, 2C for (*Z*)-**5aa**), 138.7 (d, *J* = 13.0 Hz, 2C for (*E*)-**5aa**), 138.78 (d, *J* = 13.1 Hz, 2C for (*Z*)-**5aa**), 138.83 (d, *J* = 14.7 Hz, 2C for (*E*)-**5aa**), 140.9 (d, *J* = 2.5 Hz, 1C for (*E*)-**5aa**), 143.0 (d, *J* = 2.3 Hz, 1C for (*Z*)-**5aa**); <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ -19.36 (1P for (*E*)-**5aa**), -17.85 (1P for (*Z*)-**5aa**), -16.57 (1P for (*E*)-**5aa**), -15.81 (1P for (*Z*)-**5aa**); HRMS (APCI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>35</sub>H<sub>33</sub>P<sub>2</sub>, 515.2057; found, 515.2081.

**Procedure for an ON/OFF Experiment (Figure 2).** The reaction of (3-cyclopropylidenepropyl)benzene (**1e**; 30 mg, 0.19 mmol) with tetraphenyldiphosphine (**2a**; 174 mg, 0.48 mmol), Ir(ppy)<sub>3</sub> (2.5 mg, 0.0038 mmol), and BrPPh<sub>2</sub> (9.9 mg, 0.038 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.75 mL) was set up with a NMR tube in the glovebox filled with nitrogen. The reaction progress was monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR with a 60 min time interval of light ON and light OFF. The yield of diphosphinated product **3ea** was calculated with the internal standard, triethyl phosphate (20 mg).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/acs.joc.xxxxx.

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra for products, ORTEP drawing (**3ea-S**), pictures of reaction set-up, profile of *E/Z* ratio along the reaction time, <sup>31</sup>P NMR studies, and radical trapping experiments (PDF)

Crystallographic Data of (**3ea-S**) (CIF)

## AUTHOR INFORMATION

### Corresponding Authors

**Koji Hirano** – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan; orcid.org/0000-0001-9752-1985;*

Email: k\_hirano@chem.eng.osaka-u.ac.jp.

**Masahiro Miura** – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan; orcid.org/0000-0001-8288-6439;*

Email: miura@chem.eng.osaka-u.ac.jp.

### Authors

**Yugo Kato** – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

**Nobutaka Otomura** – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI grant nos. JP 18K19078 [Grant-in-Aid for Challenging Research (Exploratory)] to K.H. and JP 17H06092 (Grant-in-Aid for Specially Promoted Research) to M.M. We thank Dr. Yuji Nishii (Osaka University) for his assistance with X-ray analysis.

## References

- (1) (a) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004. (b) Knowles, W. S. Asymmetric Hydrogenations (Nobel Lecture) Copyright The Nobel Foundation 2002. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998. (c) Noyori, R. Asymmetric Catalysis: Science and Opportunities (Nobel Lecture) Copyright The Nobel Foundation 2002. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008.
- (2) (a) Boutagy, J.; Thomas, R. Olefin synthesis with organic phosphonate carbanions. *Chem. Rev.* **1974**, *74*, 87. (b) Maryanoff, B. E.; Reiz, A. B. The Wittig olefination reaction and modifications involving phosphoryl-stabilized carbanions. Stereochemistry, mechanism, and selected synthetic aspects. *Chem. Rev.* **1989**, *89*, 863.
- (3) Appel, R. Tertiary Phosphane/Tetrachloromethane, a Versatile Reagent for Chlorination, Dehydration, and P–N Linkage. *Angew. Chem., Int. Ed.* **1975**, *14*, 801.

- (4) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. Ligand Bite Angle Effects in Metal-catalyzed C–C Bond Formation. *Chem. Rev.* **2000**, *100*, 2741.
- (5) Selected examples: (a) Aguiar, A. M.; Daigle, D. A Stereospecific Route to trans- and cis-1,2-Vinylenebis(diphenylphosphine). *J. Am. Chem. Soc.* **1964**, *86*, 2299. (b) Zhang, J.; Wang, X.; Zhang, X.; Wu, W.; Zhang, G.; Xu, S.; Shi, M. Switchable Ethylene Tri-/Tetramerization with High Activity: Subtle Effect Presented by Backbone-Substituent of Carbon-Bridged Diphosphine Ligands. *ACS Catal.* **2013**, *3*, 2311.
- (6) (a) Li, Y.-M.; Sun, M.; Wang, H.-L.; Tian, Q.-P.; Yang, S.-D. Direct Annulations toward Phosphorylated Oxindoles: Silver-Catalyzed Carbon-Phosphorus Functionalization of Alkenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 3972. (b) Kong, W.; Merino, E.; Nevado, C. Arylphosphonylation and Arylazidation of Activated Alkenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 5078. (c) Zhou, S.-F.; Li, D.-P.; Liu, K.; Zou, J.-P.; Asekun, O. T. Direct Radical Acetoxyphosphorylation of Styrenes Mediated by Manganese(III). *J. Org. Chem.* **2015**, *80*, 1214. (d) Gao, Y.; Li, X.; Chen, W.; Tang, G.; Zhao, Y. Copper-Catalyzed Phosphonation-Annulation Approaches to the Synthesis of  $\beta$ -Phosphonotetrahydrofurans Involving C-P and C-O Bonds Formation. *J. Org. Chem.* **2015**, *80*, 11398. (e) Gao, Y.; Li, Q.; Xu, J.; Wu, Y.; Chen, W.; Tang, G.; Zhao, Y. Mn(OAc)<sub>3</sub>-mediated phosphonation-lactonization of alkenoic acids: synthesis of phosphono- $\gamma$ -butyrolactones. *Chem. Commun.* **2015**, *51*, 1605. (f) Zhang, H.-Y.; Mao, L.-L.; Yang, B.; Yang, S.-D. Copper-catalyzed radical cascade cyclization for the synthesis of phosphorated indolines. *Chem. Commun.* **2015**, *51*, 4101. (g) Li, J.-A.; Zhang, P.-Z.; Liu, K.; Shoberu, A.; Zou, J.-P.; Zhang, W. Phosphinoyl Radical-Initiated  $\alpha,\beta$ -Aminophosphinylation of Alkenes. *Org. Lett.* **2017**, *19*, 4704. (h) Zhang, P.-Z.; Zhang, L.; Li, J.-A.; Shoberu, A.; Zou, J.-P.; Zhang, W. Phosphinoyl Radical Initiated Vicinal Cyanophosphinylation of Alkenes. *Org. Lett.* **2017**, *19*, 5537. (i) Li, Y.-H.; Wang, C.-H.; Gao, S.-Q.; Qi, F.-M.; Yang, S.-D. Visible photocatalysis of novel oxime phosphonates: synthesis of  $\beta$ -aminophosphonates. *Chem. Commun.* **2019**, *55*, 11888.

- (7) (a) Hirano, K.; Miura, M. Recent advances in diphosphination of alkynes and alkenes. *Tetrahedron Lett.* **2017**, *58*, 4317. (b) Kawaguchi, S.-i.; Ogawa, A. Applications of Diphosphines in Radical Reactions. *Asian J. Org. Chem.* **2019**, 1164.
- (8) The catalytic double hydrophosphination of alkynes with hydrophosphines is also a good alternative: (a) Kamitani, M.; Itazaki, M.; Tamiya, C.; Nakazawa, H. Regioselective Double Hydrophosphination of Terminal Arylacetylenes Catalyzed by an Iron Complex. *J. Am. Chem. Soc.* **2012**, *134*, 11932. (b) Di Giuseppe, A.; De Luca, R.; Castarlenas, R.; Pérez-Torrente, J. J.; Crucianelli, M.; Oro, L. A. Double hydrophosphination of alkynes promoted by rhodium: the key role of an N-heterocyclic carbene ligand. *Chem. Commun.* **2016**, *52*, 5554. (c) Yuan, J.; Zhu, L.; Zhang, J.; Li, J.; Cui, C. Sequential Addition of Phosphine to Alkynes for the Selective Synthesis of 1,2-Diphosphinoethanes under Catalysis. Well-Defined NHC-Copper Phosphides vs in Situ CuCl<sub>2</sub>/NHC Catalyst. *Organometallics* **2017**, *36*, 455. (d) Bookham, J. L.; McFarlane, W.; Thornton-Pett, M.; Jones, S. Stereoselective addition reactions of diphenylphosphine: meso- and rac-1,2-diphenyl-1,2-bis(diphenylphosphino)ethane and their Group 6 metal tetracarbonyl complexes. Crystal structures of the molybdenum derivatives. *J. Chem. Soc., Dalton Trans.* **1990**, 3621. (e) Bookham, J. L.; Smithies, D. M.; Wright, A.; Thornton-Pett, M.; McFarlane, W. Stereoselective addition of diphenylphosphine to substituted diphenylethyne: synthetic, NMR and X-ray crystallographic studies. *J. Chem. Soc., Dalton Trans.* **1998**, 811.
- (9) Sato, A.; Yorimitsu, H.; Oshima, K. Synthesis of (*E*)-1,2-Diphosphanylene Derivatives from Alkynes by Radical Addition of Tetraorganodiphosphane Generated In Situ. *Angew. Chem., Int. Ed.* **2005**, *44*, 1694.
- (10) Kawaguchi, S.-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. Photochemical behaviors of tetraphenyldiphosphine in the presence of alkynes. *Tetrahedron Lett.* **2006**, *47*, 3919.
- (11) (a) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. Stereospecific Diphosphination of Activated Acetylenes: A General Route to Backbone-Functionalized, Chelating 1,2-Diphosphinoethenes. *Organometallics* **2006**, *25*, 5937. (b) Burck, S.; Gudat, D.; Nieger, M. Metal-Assisted, Reversible Phosphinyl Phosphination of the Carbon-Nitrogen Triple Bond in a Nitrile. *Angew.*

- Chem., Int. Ed.* **2007**, *46*, 2919. (c) Okugawa, Y.; Hirano, K.; Miura, M. Brønsted Base Mediated Stereoselective Diphosphination of Terminal Alkynes with Diphosphanes. *Org. Lett.* **2017**, *19*, 2973.
- (12) (a) Burg, A. B. Tetramethylbiphosphine: Synthesis, Thermal Condensation, Ethylene Addition, Borine Adducts and Conversion to Phosphinoborane Polymers. *J. Am. Chem. Soc.* **1961**, *83*, 2226. (b) Morse, K. W.; Morse, J. G. Free radical reactions of tetrafluorodiphosphine. Preparation of 1,2-bis(difluorophosphino)ethane. *J. Am. Chem. Soc.* **1973**, *95*, 8469. (c) Chatt, J.; Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. The preparation and properties of some diphosphines  $R_2PCH_2CH_2PR_2$  (R = alkyl or aryl) and of their rhenium(I) dinitrogen derivatives. *J. Chem. Soc., Dalton Trans.* **1985**, 1131. (d) Hajdók, I.; Lissner, F.; Nieger, M.; Strobel, S.; Gudat, D. Diphosphination of Electron Poor Alkenes. *Organometallics* **2009**, *28*, 1644.
- (13) (a) Sato, Y.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. Highly Selective Phosphinylphosphination of Alkenes with Tetraphenyldiphosphine Monoxide. *Angew. Chem., Int. Ed.* **2016**, *55*, 9700. (b) Sato, Y.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. Synthesis of Bis(phosphanyl)alkane Monosulfides by the Addition of Diphosphane Monosulfides to Alkenes under Light. *Chem.–Eur. J.* **2019**, *25*, 2295. (c) Sato, Y.; Nishimura, M.; Kawaguchi, S. i.; Nomoto, A.; Ogawa, A. Reductive Rearrangement of Tetraphenyldiphosphine Disulfide To Trigger the Bisthiophosphinylation of Alkenes and Alkynes. *Chem.–Eur. J.* **2019**, *25*, 6797.
- (14) (a) Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. Bromine Cation Initiated *vic*-Diphosphination of Styrenes with Diphosphines under Photoredox Catalysis. *Synthesis* **2018**, *50*, 3402. (b) Otomura, N.; Hirano, K.; Miura, M. Diphosphination of 1,3-Dienes with Diphosphines under Visible-Light-Promoted Photoredox Catalysis. *Org. Lett.* **2018**, *20*, 7965.
- (15) For related diphosphination of alkenes with silylphosphines, see: (a) Okugawa, Y.; Hirano, K.; Miura, M. Copper-Catalyzed Vicinal Diphosphination of Styrenes: Access to 1,2-Bis(diphenylphosphino)ethane-Type Bidentate Ligands from Olefins. *Angew. Chem., Int. Ed.* **2016**, *55*, 13558. (b) Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. *vic*-Diphosphination of Alkenes with Silylphosphine under Visible-Light-Promoted Photoredox Catalysis. *Org. Lett.* **2017**, *19*, 4802.

- (16) Crabtree, R. Iridium compounds in catalysis. *Acc. Chem. Res.* **1979**, *12*, 331.
- (17) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Imahori, H.; Ochi, N.; Sakaki, S. Phosphorus-Containing Hybrid Calixpyrins: Promising Mixed-Donor Ligands for Visible and Efficient Palladium Catalysts. *J. Am. Chem. Soc.* **2006**, *128*, 11760.
- (18) (a) Zablocka, M.; Delest, B.; Igau, A.; Skowronska, A.; Majoral, J.-P.  $[\text{Cp}_2\text{ZrHCl}]_n$  a useful reducing agent in phosphorus chemistry. *Tetrahedron Lett.* **1997**, *38*, 5997. (b) Saito, M.; Nishibayashi, Y.; Uemura, S. Synthesis of Dinuclear Complexes Bearing Metalloporphyrin–Phosphine Hybrid Ligands and Their Catalytic Activity toward Hydrosilylation of Ketones. *Organometallics* **2004**, *23*, 4012.
- (19) Selected reviews on visible-light-promoted photoredox catalysis: (a) Yoon, T. P.; Ischay, M. A.; Du, J. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527. (b) Narayanam, J. M. R.; Stephenson, C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102. (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322. (d) Ravelli, D.; Protti, S.; Fagnoni, M. Carbon–Carbon Bond Forming Reactions via Photogenerated Intermediates. *Chem. Rev.* **2016**, *116*, 9850. (e) Koike, T.; Akita, M. Fine Design of Photoredox Systems for Catalytic Fluoromethylation of Carbon–Carbon Multiple Bonds. *Acc. Chem. Res.* **2016**, *49*, 1937. Recent advances in organophosphorus chemistry under photoredox catalysis: (f) Luo, K.; Yang, W.; Wu, L. Photoredox Catalysis in Organophosphorus Chemistry. *Asian J. Org. Chem.* **2017**, *6*, 350.
- (20) (a) Hollis, R.; Hughes, L.; Bowry, V. W.; Ingold, K. U. Calibration of a Fast Benzylic Radical “Clock” Reaction. *J. Org. Chem.* **1992**, *57*, 4284. (b) Halgren, T. A.; Roberts, J. D.; Horner, J. H.; Martinez, F. N.; Tronche, C.; Newcomb, M. Kinetics and Equilibrium Constants for Reactions of  $\alpha$ -Phenyl-Substituted Cyclopropylcarbinyl Radicals. *J. Am. Chem. Soc.* **2000**, *122*, 2988.



(21) Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J. Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **2016**, *20*, 1156.

(22) For recent examples of radical generation from phosphoniums under visible-light-promoted photoredox catalysis, see: (a) Lin, Q.-Y.; Xu, X.-H.; Zhang, K.; Qing, F.-L. Visible-Light-Induced Hydrodifluoromethylation of Alkenes with a Bromodifluoromethylphosphonium Bromide. *Angew. Chem., Int. Ed.* **2016**, *55*, 1479. (b) Miura, T.; Funakoshi, Y.; Nakahashi, J.; Moriyama, D.; Murakami, M. Synthesis of Elongated Esters from Alkenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 15455.

(23) For reviews on the energy transfer mechanism, see: (a) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways. *Angew. Chem., Int. Ed.* **2019**, *58*, 1586. (b) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy transfer catalysis mediated by visible light: principles, applications, directions. *Chem. Soc. Rev.* **2018**, *47*, 7190.

(24) See the Supporting Information for details.

(25) Singh, K.; Staig, S. J.; Weaver, J. D. Facile Synthesis of *Z*-Alkenes via Uphill Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 5275.

(26) The other possibility is that an in-situ generated bromide ion works as a redox mediator. Thus, we tested KBr and Bu<sub>4</sub>NBr as additives instead of BrPPh<sub>2</sub> and dimethyl bromomalonate (**Br5**). Whereas the reaction of vinylcyclopropane **4a** resulted in no formation of the diphosphinated product **5aa-S**, the product **3aa-S** was formed from the methylenecyclopropane **1a** albeit with lower <sup>31</sup>P NMR yields of 55 and 16% (vs. 75% with BrPPh<sub>2</sub>). This result suggests the operation of a totally different reaction mechanism, which is unique to the methylenecyclopropane substrate **1a**. Actually, the control reaction of **1a** with KBr in CD<sub>2</sub>Cl<sub>2</sub> formed several unidentified products while no reaction occurred with the diphosphine **2a** and KBr. Additional studies are essential for clarification of this phenomena and will be reported in due course.

- (27) We also performed several radical trapping experiments with TEMPO, BHT, and DPE. See the Supporting Information for details.
- (28) Ai, W.; Liu, Y.; Wang, Q.; Lu, Z.; Liu, Q. Cu-Catalyzed Redox-Neutral Ring Cleavage of Cycloketone O-Acyl Oximes: Chemodivergent Access to Distal Oxygenated Nitriles. *Org. Lett.* **2018**, *20*, 409.
- (29) Klauck, F. J. R.; Yoon, H.; James, M. J.; Lautens, M.; Glorius, F. Visible-Light-Mediated Deaminative Three-Component Dicarbonylation of Styrenes with Benzylic Radicals. *ACS Catal.* **2019**, *9*, 236.