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

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A ring-opening diphosphination of methylene- and vinylcyclopropanes with tetraaryldiphosphines ($Ar_2P–PAr_2$) 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_3-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[1] as well as invaluable synthetic reagents and intermediates, as exemplified by Wittig reaction, Horner-Wadsworth-Emmons reaction,[2] and Appel reaction.[3] 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 θ of supporting ligands,[4] 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.[5] On the other hand, given the recent progress of phosphinative difunctionalization reactions of alkenes such as carbophosphination, aminophospination, and cyanophosphination,[6] 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.[7,8] In 2005, Oshima and Yorimitsu reported the V-40-initiated radical diphosphinaion of terminal alkynes with diphosphines.[9] Ogawa also developed the same radical diphosphination under UV irradiation.[10] Additionally, some noncatalyzed and Brønsted base-mediated reactions were also reported to date.[11] 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.[12] 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).[13a] Subsequently, the same research group improved the reaction efficiency and scope by using further modified diphosphine monosulfides $R_2P–P(S)R_2$[13b] and disulfides $R_2(S)P–P(S)R_2$.[13c] 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[14a] and 1,3-dienes[14b] 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).[15] 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_3 groups.

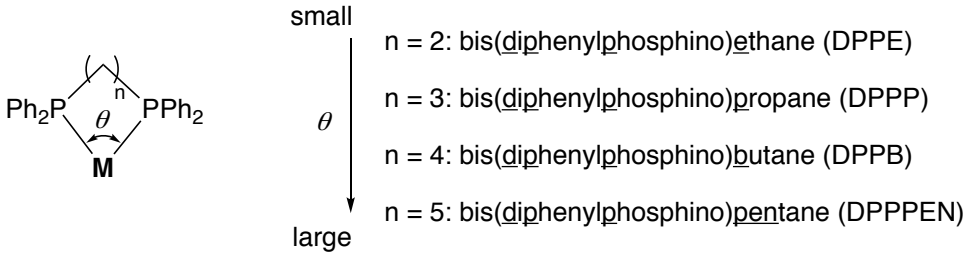
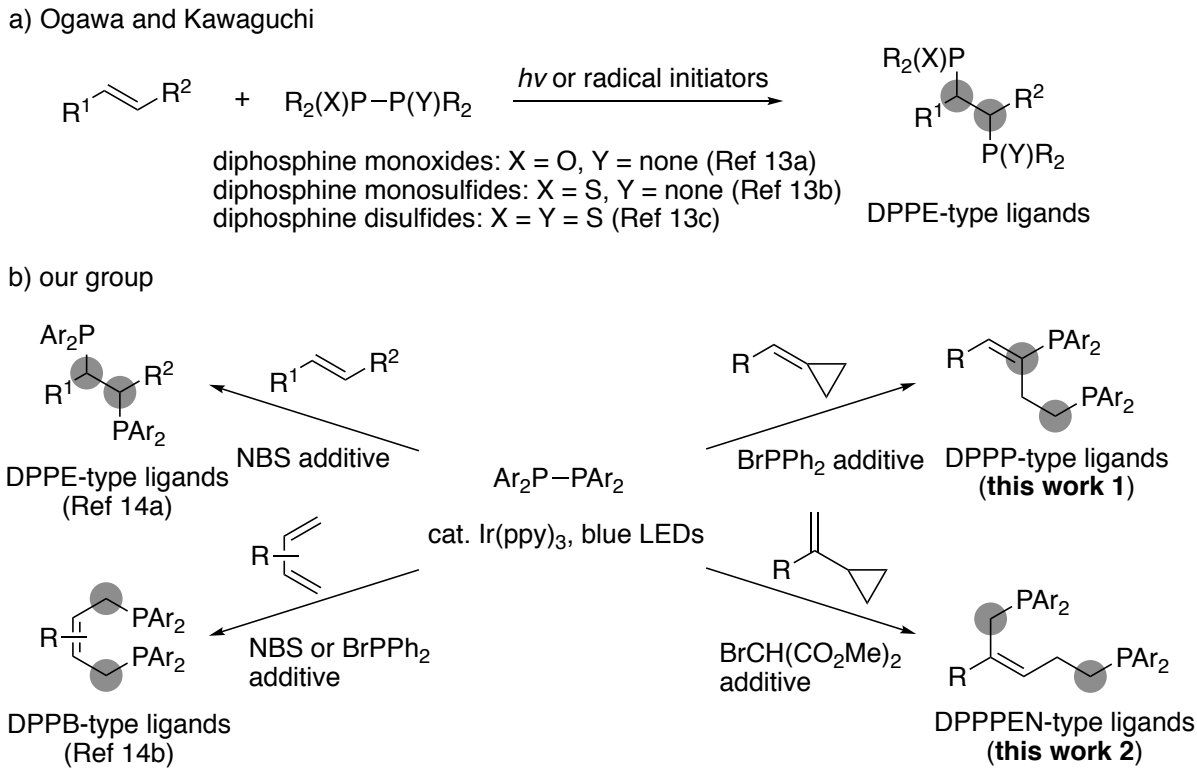


Figure 1. Commonly used 1,n-bis(diphenylphosphino)alkanes. M = transition metals.

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

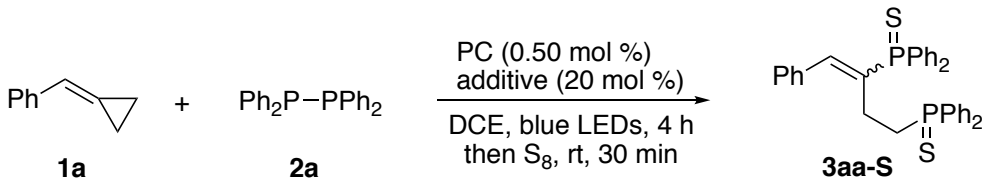


Results and Discussion

Our optimization studies commenced with benzylidenecyclopropane (**1a**) and tetraphenyldiphosphine (**2a**; Table 1). Based on the previous work,[14a,b] treatment of **1a** with **2a** (2.0 equiv) in the presence of 0.50 mol % $Ir(ppy)_3$ 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_8 afforded the desired ring-opening diphosphinated product **3aa-S** in 36% ^{31}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 $BrPPh_2$ proving to be optimal (entry 2). Subsequent investigations of other PCs revealed that $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ showed a good performance comparable to $Ir(ppy)_3$ (entry 9) while $Ir(ppy)_2(dtbpy)PF_6$, $Ru(bpy)_3(PF_6)_2$, 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 $Ir(ppy)_3$ (2.0 mol %) and **2a** (2.5 equiv) the DPPP-type **3aa-S** was

finally obtained in 74% ^{31}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 $BrPPh_2$ the reaction proceeded albeit with a much lower yield (entry 15).

Table 1. Optimization for Ring-Opening Diphosphination of Benzylidenecyclopropane (1a) with Tetraphenyldiphosphine (2a) under Visible-Light-Promoted Photoredox Catalysis[a]

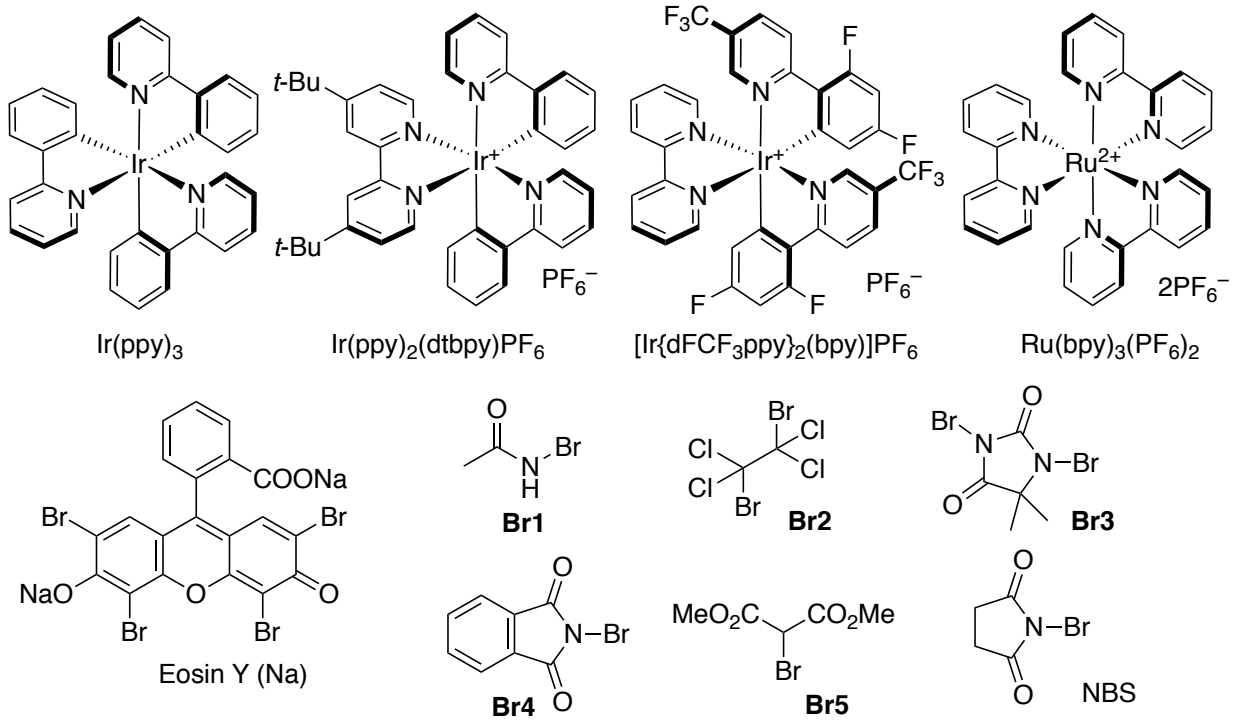


1a **2a** **3aa-S**

entry	PC	additive	yield (%)[b], *E/Z*[c]	
1	$Ir(ppy)_3$	NBS	36	88:12
2	$Ir(ppy)_3$	$BrPPh_2$	56	86:14
3	$Ir(ppy)_3$	**Br1**	24	79:21
4	$Ir(ppy)_3$	**Br2**	45	87:13
5[d]	$Ir(ppy)_3$	**Br3**	24	86:14
6	$Ir(ppy)_3$	**Br4**	11	88:12
7	$Ir(ppy)_3$	**Br5**	44	84:16
8	$Ir(ppy)_2(dtbpy)PF_6$	$BrPPh_2$	13	89:11
9	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	$BrPPh_2$	51	84:16
10	$Ru(bpy)_3(PF_6)_2$	$BrPPh_2$	0	–
11[e]	Eosin Y (Na)	$BrPPh_2$	0	–
12[f]	$Ir(ppy)_3$	$BrPPh_2$	75 (56)	93:7 (86:14)

13[f]	None	$BrPPh_2$	0	–
14[f,g]	$Ir(ppy)_3$	$BrPPh_2$	0	–
15[f]	$Ir(ppy)_3$	none	38	77:23

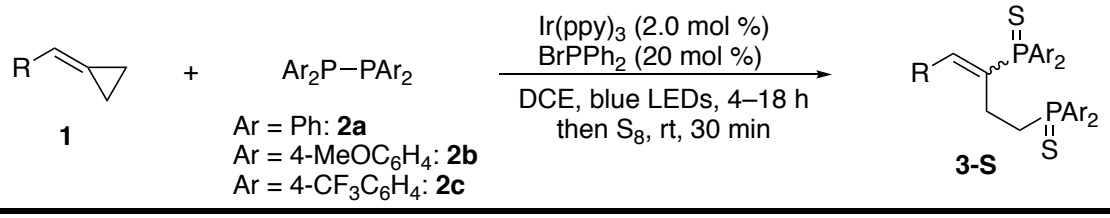
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), PC (0.0013 mmol), additive (0.050 mmol), DCE (1.5 mL), blue LED irradiation (2.4 W), 4 h, ambient temp, N_2 then S_8 (1.3 mmol based on S atom), rt, 30 min, N_2. [b] ^{31}P NMR yield with $O{=}P(OEt)_3$ internal standard. Isolated yield is in parentheses. [c] Determined by ^{31}P NMR of the crude mixture. The ratio of the isolated product in parentheses. [d] With **Br3** (0.025 mmol). [e] With green LEDs (2.4 W). [f] With $Ir(ppy)_3$ (0.0050 mmol), **2a** (0.63 mmol), DCE (1.0 mL), and S_8 (1.5 mmol). [g] In dark.

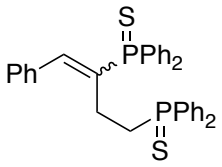


With conditions of entry 12 in Table 1, we investigated the scope of methylenecyclopropanes **1** (Scheme 2). The introduction of both electron-donating (MeO) and electron-withdrawing (Br) groups on the benzene of **1a** gave somewhat negative impact to deliver the corresponding diphosphinated products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

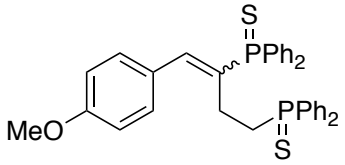
selectivity (*E*/*Z* >99:1). On the other hand, the aliphatic substrates showed better reactivity: the phenethyl- and cyclohexyl-substituted methylenecyclopropanes underwent the ring-opening diphosphination smoothly to furnish **3ea-S** and **3fa-S** in 72 and 60% yields, respectively. The structure 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_3-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 Methylenecyclopropanes 1 and Tetraaryldiphosphines 2 under Visible-Light-Promoted Photoredox Catalysis[a]

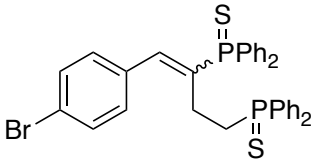




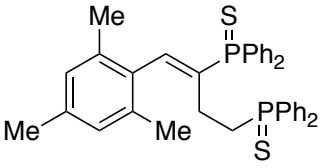
3aa-S 74% (56%), *E*/*Z* = 83:17



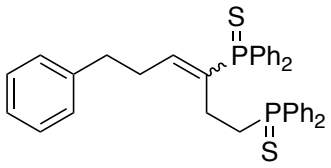
3ba-S 42% (33%), *E*/*Z* = 76:24



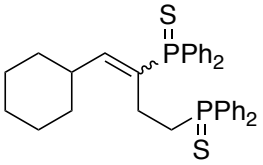
3ca-S 42% (33%), *E*/*Z* = 77:23



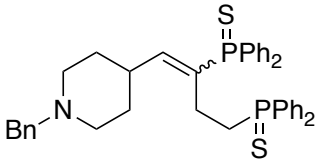
3da-S (42%), *E*/*Z* >99:1



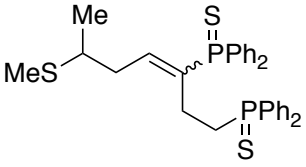
3ea-S >99% (72%), *E*/*Z* = 89:11
[84% (70%), *E*/*Z* = 89:11][b]



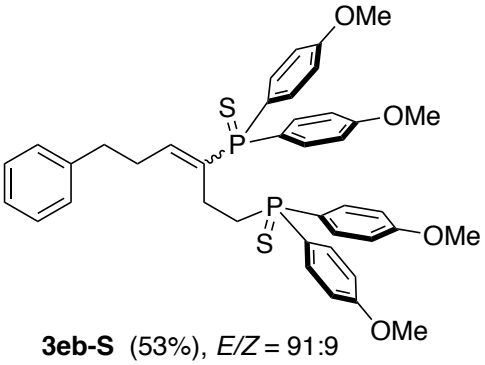
3fa-S >99% (60%), *E*/*Z* = 93:7



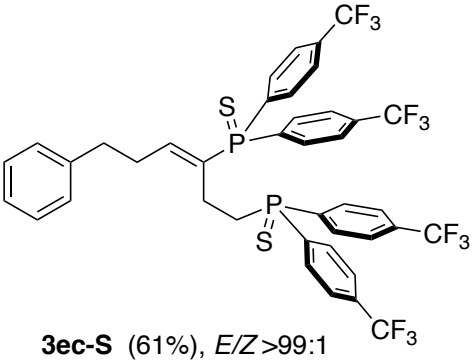
3ga-S 69% (59%), *E*/*Z* = 91:9



3ha-S (64%), *E*/*Z* = 91:9



3eb-S (53%), *E*/*Z* = 91:9



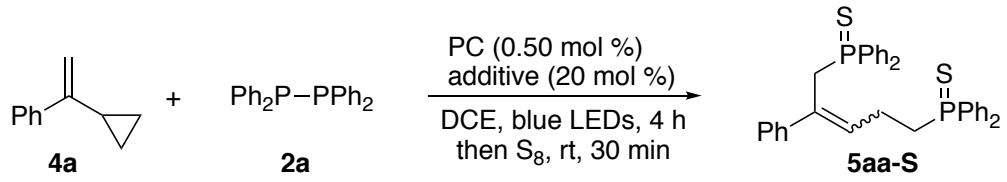
3ec-S (61%), *E*/*Z* >99:1

[a] ^{31}P NMR yields with $O=P(OEt)_3$ internal standard are shown. Isolated yields are in parentheses. [b] On a 1.0 mmol scale.

Prompted by the aforementioned successful synthesis of DPPP-type ligands via ring-opening diphopshination of methylenecyclopropanes, 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 $BrPPh_2$-promoted reaction of methylenecyclopropane **1a** with **2a**, **4a** was converted to the targeted **5aa-S** in 61% ^1H 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% ^1H NMR yield (60% yield after purification; entry 7). Evaluation of other PCs proved a slightly better performance of $Ir(ppy)_3$ (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 phosphenium cation species (vide infra).

Table 2. Optimization for Ring-Opening Diphosphination of Vinylcyclopropane 4a with Tetraphenyldiphosphine (2a) under Visible-Light-Promoted Photoredox Catalysis[a]



4a **2a** **5aa-S**

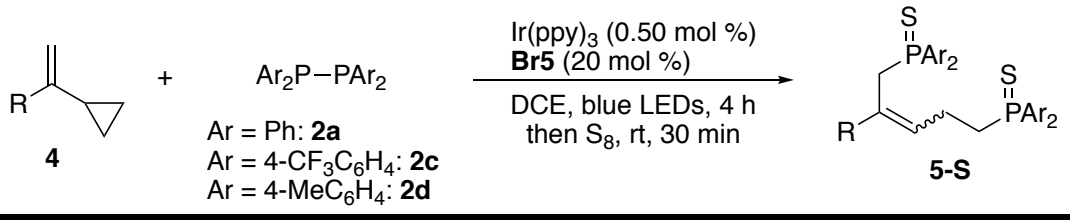
entry	PC	additive	yield (%)[b], *E/Z*[c]	
1	$Ir(ppy)_3$	$BrPPh_2$	61	27:73
2	$Ir(ppy)_3$	NBS	66	28:72
3	$Ir(ppy)_3$	**Br1**	80[d]	25:75
4	$Ir(ppy)_3$	**Br2**	46	18:82
5[e]	$Ir(ppy)_3$	**Br3**	65	25:75
6	$Ir(ppy)_3$	**Br4**	26	15:85
7	$Ir(ppy)_3$	**Br5**	77 (60)	(34:66)
8	$Ir(ppy)_2(dtbpy)PF_6$	**Br1**	73	20:80
9	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	**Br1**	74	24:76

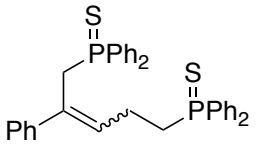
10[f]	eosin Y (Na)	**Br1**	39	20:80
11	None	**Br5**	29	23:77
12[g]	$Ir(ppy)_3$	**Br5**	20	33:67
13[g]	None	**Br5**	29	22:78

[a] 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_2 then S_8 (1.3 mmol based on S atom), rt, 30 min, N_2. [b] ^1H NMR yield with $O=P(OEt)_3$ internal standard. Isolated yield is in parentheses. [c] Determined by ^{31}P NMR of the crude mixture. The ratio of the isolated product in parentheses. [d] The purification was difficult because of the formation of unidentified byproducts. [e] With **Br3** (0.025 mmol). [f] With green LEDs (2.4 W). [g] In dark.

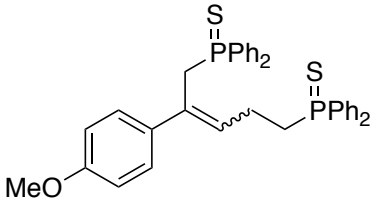
The $Ir(ppy)_3$/**Br5** system was also applicable to several aryl-substituted vinylcyclopropanes **4** that bear MeO, Br, Me, and F substituents at the para, meta, and ortho positions on the benzene ring (**5ba-S**–**5ea-S**; Scheme 3). The naphthalene ring was also tolerated under the standard conditions (**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[a]

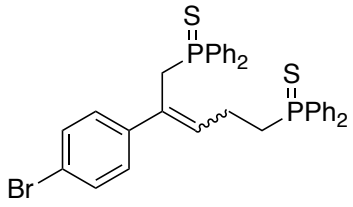




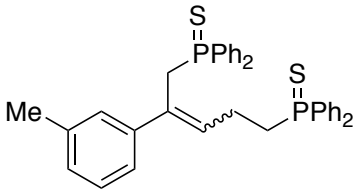
5aa-S 77% (60%), *E/Z* = 34:66



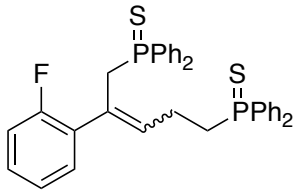
5ba-S 54% (42%), *E/Z* = 48:52



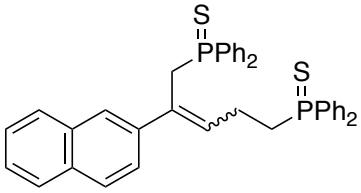
5ca-S 72% (64%), *E/Z* = 30:70



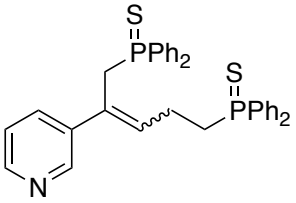
5da-S (55%), *E/Z* = 35:65



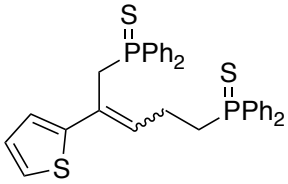
5ea-S 79% (68%), *E/Z* = 35:65



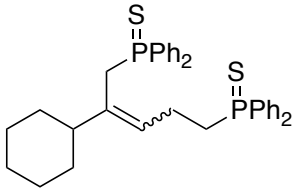
5fa-S 67% (56%), *E/Z* = 56:44



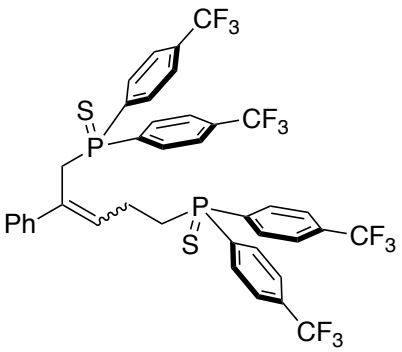
5ga-S (60%), *E/Z* = 23:77



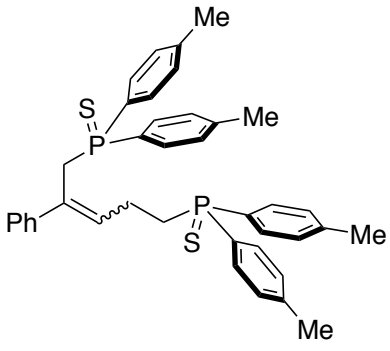
5ha-S 45% (38%), *E/Z* = 47:53



5ia-S 22%, *E/Z* = 35:65



5ac-S 67% (62%), *E/Z* = 25:75



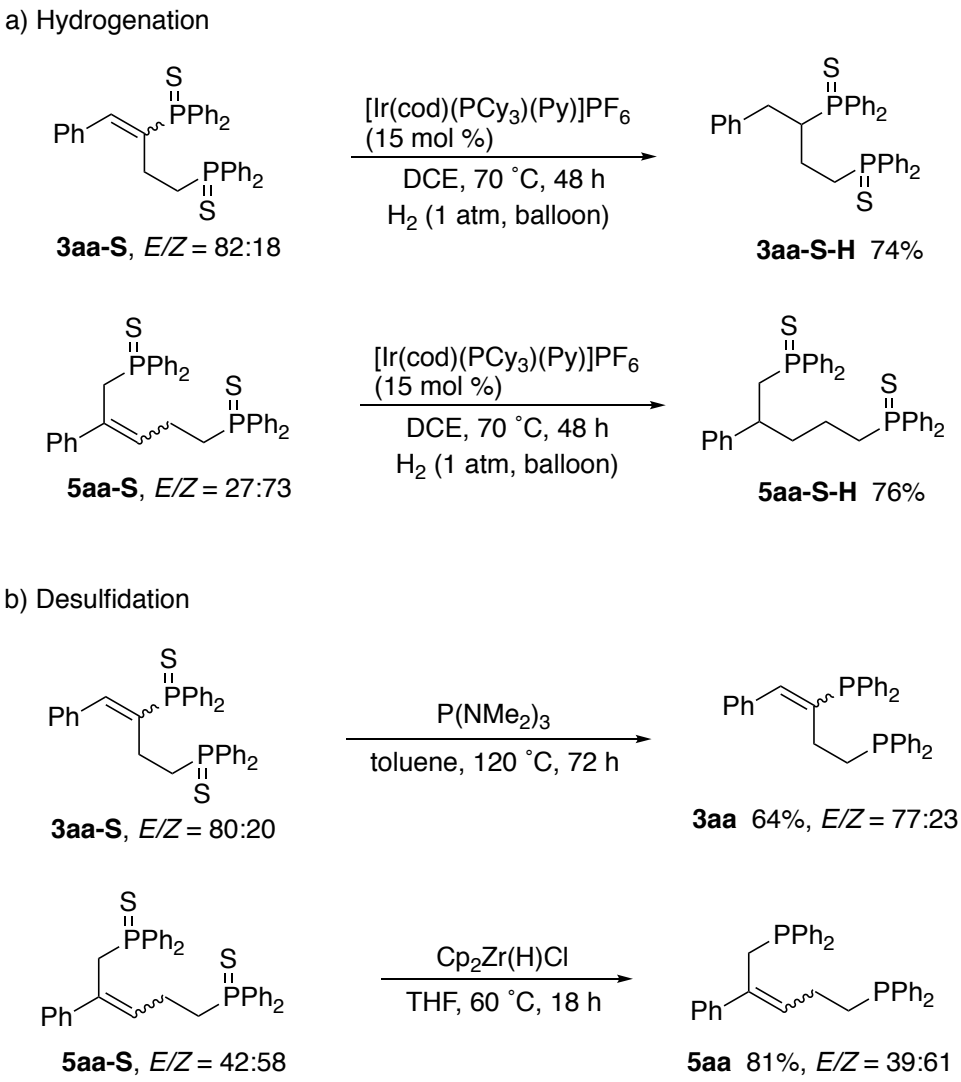
5ad-S 82% (71%), *E/Z* = 21:79

[a] ^{1}H NMR yields with O=P(OEt)$_3$ 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$_3$)(Py)]PF$_6$[16] 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

$P(NMe_2)_3$[17] or Schwartz reagent $Cp_2Zr(H)Cl$,[18] 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



On the basis of the literature information,[19] 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 $BrPPh_2$.[14a] 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**[20] and somewhat lower oxidation potential of Ir(IV)/(III) of $Ir(ppy)_3$,[21] 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,[22] 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[23] 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).

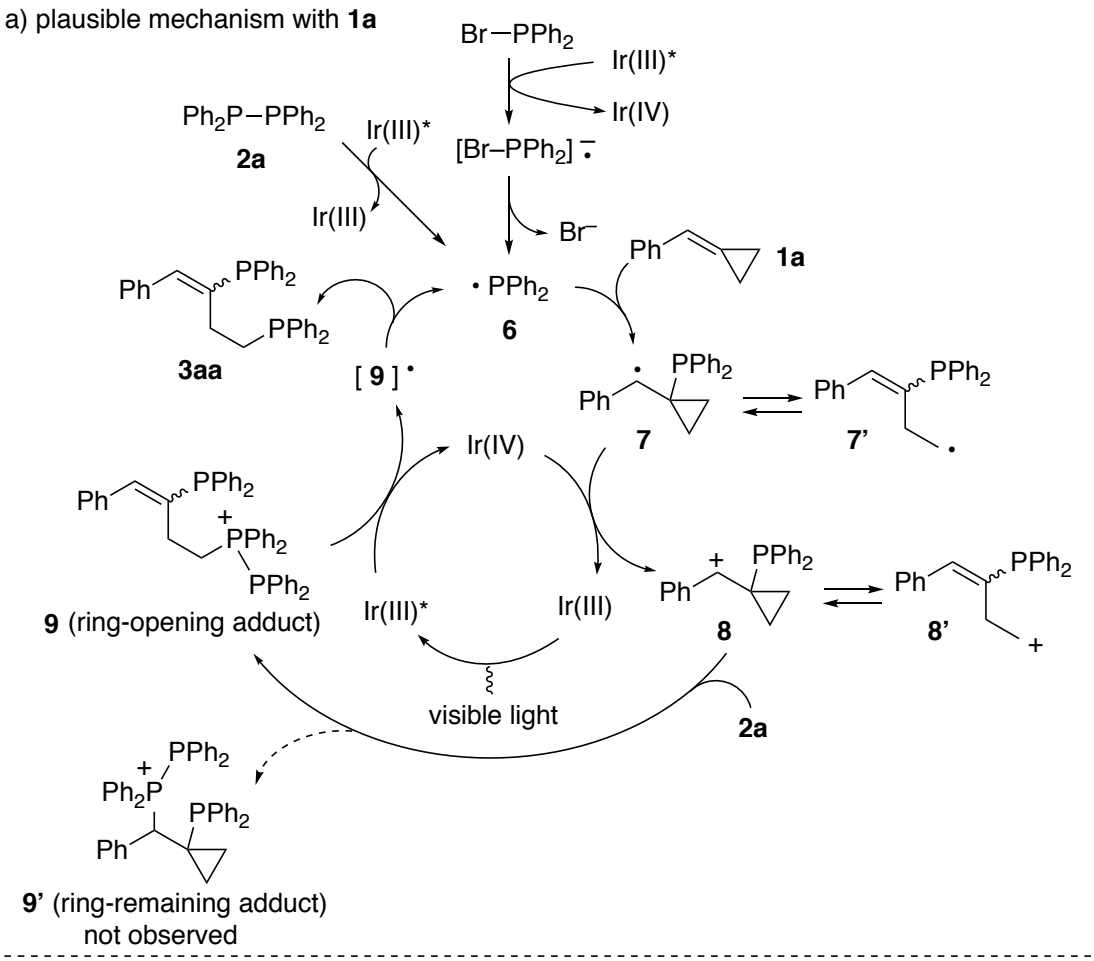
The reaction mechanism of **4a** is principally the same as that of **1a** (Scheme 5b), which includes i) phosphinyl radical **6** generation via $BrPPh_2$, ii) radical addition of **6** to **4a**, iii) ring-opening/one electron oxidation via back electron transfer (**10**/**10'** to **11**/**11'**), 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 $BrPPh_2$ in situ.[24] 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 phosphenium 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 $BrPPh_2$ can be an alternative pathway to form the phosphinyl radical **6**. However, the reactivity trend of $Ir(ppy)_3$, $Ir(ppy)_2(dtbpy)PF_6$, and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ was not fully correlated with each T_1 energy (57.8, 49.2, and 60.4 kcal/mol, respectively).[23]

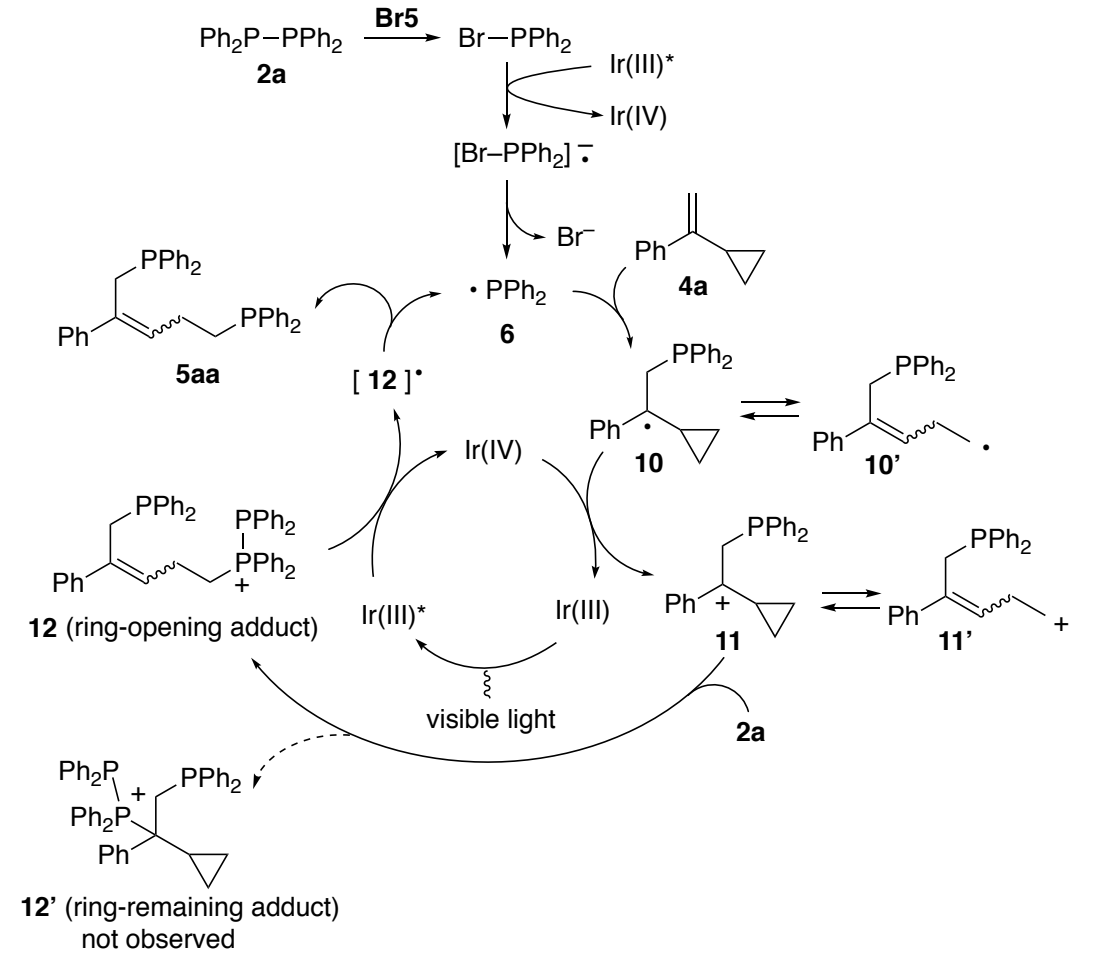
In both catalytic cycles, the stereochemistry (*E* or *Z*) is kinetically determined in the ring-opening step to form the more sterically and thermodynamically favored (*E*)-**3aa** and (*Z*)-**5aa** preferably, but in the

course of reaction the *E/Z* isomerization occurred via the energy transfer[25] to increase the ratio of thermodynamically unfavored (*Z*)-**3aa** and (*E)*-**5aa** (see the Supporting Information for a detailed profile of the *E/Z* ratio along the reaction time).[26,27]

Scheme 5. Plausible Mechanisms of Reactions of Methylenecyclopropane 1a and Vinylcyclopropane 4a



b) plausible mechanism with **4a**



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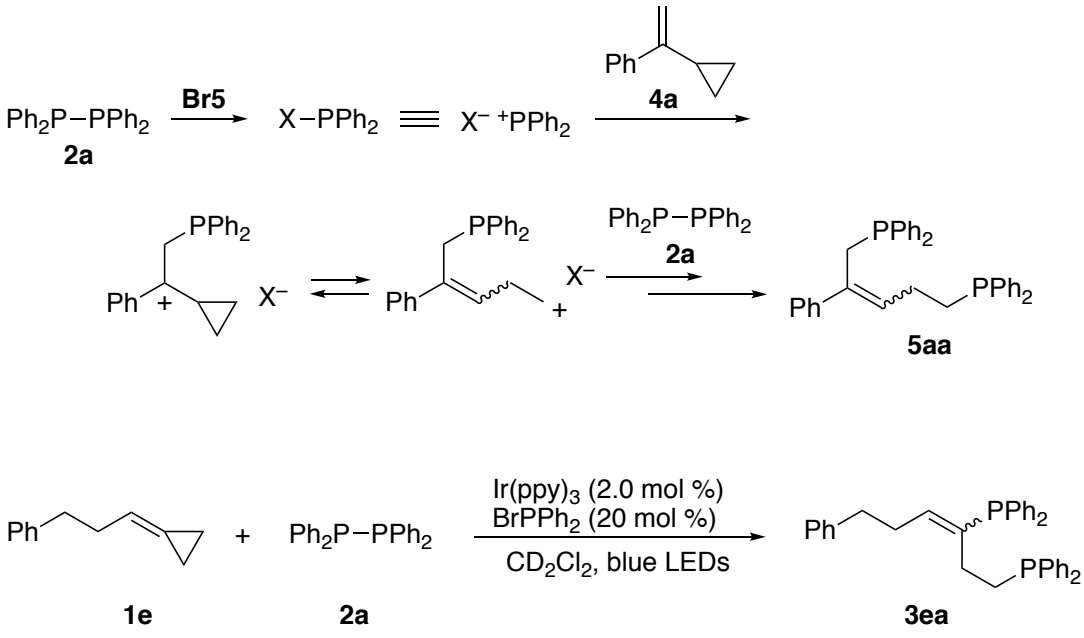
c) background pathway with **4a**



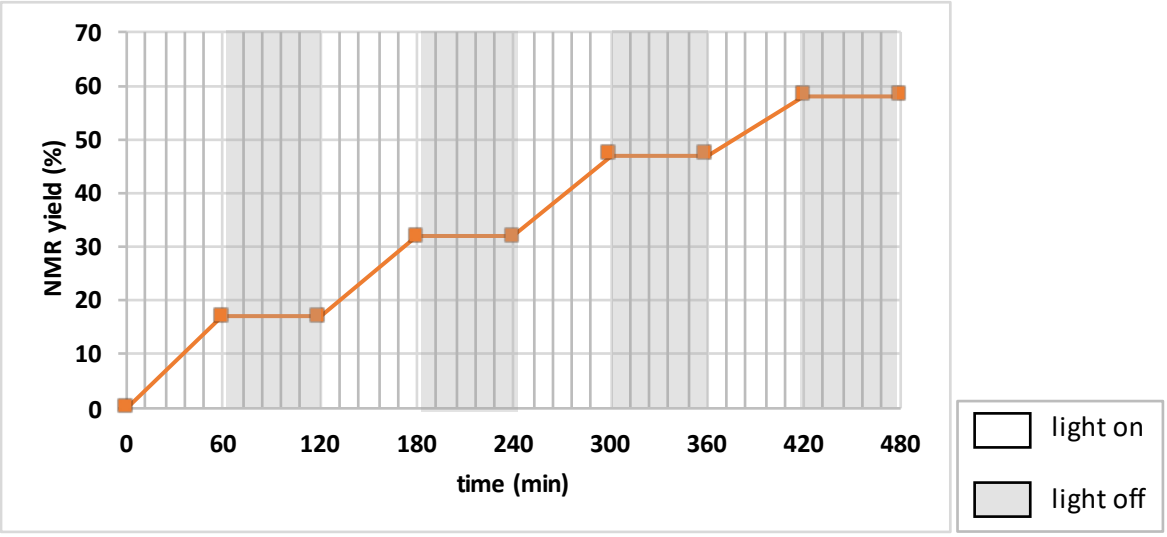


Figure 2. ON/OFF experiment of **1e** with **2a**.

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)[14a] and 1,4-bis(diphenylphosphino)butane (DPPB) derivatives,[14b] the Br^+/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 ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{1H\}$ 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 $CDCl_3$ 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 $60F_{254}$. 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_2. Methylenecyclopropanes **1**[28] and vinylcyclopropanes **4**[29] were prepared from the corresponding aldehydes and ketones according to the literature. Tetraaryldiphosphines **2** were synthesized via the condensation of chloro- and hydrophosphines.[9,11a,15a] 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**.[15a]

Typical Procedure for Ring-Opening Diphosphination of Methylenecyclopropanes 1 with Diphosphines 2. The synthesis of **3aa-S** is representative (Scheme 2). $Ir(ppy)_3$ (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_2. DCE (1.5 mL) and $BrPPh_2$ (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_8; 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_2SO_4, and concentrated in vacuo. The residual solid was dissolved in $CDCl_3$, and the yield was calculated by

^{1}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)$_3$ (13 mg, 0.020 mmol) and tetraphenyldiphophine (**2a**; 930 mg, 2.5 mmol) were placed in a 10-mL Schlenk flask, which was filled with N_2. DCE (4.0 mL) and $BrPPh_2$ (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_8; 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 42.38, 50.15; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{34}H_{31}P_2S_2$, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 37.23, 42.22; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{34}H_{31}P_2S_2$, 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; ^{1}H NMR (400 MHz, $CDCl_3$), 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**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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 $C_{35}H_{33}OP_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{34}H_{30}BrP_2S_2$, 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}H NMR (400 MHz, $CDCl_3$): δ 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); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 41.87 (1P), 46.79 (1P); HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{37}H_{37}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for mixture, δ 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 **(*Z*)-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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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 $C_{36}H_{35}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for **(*E*)-3fa-S**, δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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 $C_{34}H_{37}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for **(*E*)-3ga-S**, δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$),

for mixture, δ 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*: $(M + H)^+$ calcd for $C_{40}H_{42}NP_2S_2$, 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; ^{1}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), for mixture, δ 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**); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{32}H_{35}P_2S_3$, 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; ^{1}H NMR (400 MHz, $CDCl_3$), 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**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), 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); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), 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*: $(M + H)^+$ calcd for $C_{40}H_{43}O_4P_2S_2$, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 41.63 (1P), 46.32 (1P); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ -63.23 (12F); HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{40}H_{31}F_{12}P_2S_2$, 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). $Ir(ppy)_3$ (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 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 (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 Na_2SO_4 and concentrated in vacuo. The residual solid was dissolved in $CDCl_3$, and the yield was calculated by ^{1}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}H NMR (400 MHz, $CDCl_3$): δ 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); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 39.39, 42.65; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{35}H_{33}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$): δ 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); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 41.19, 41.82; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{35}H_{33}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for mixture, δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{36}H_{35}OP_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{35}H_{32}BrP_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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 $C_{36}H_{35}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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**); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$), for mixture, δ -114.95 (1F for **(*Z*)-5ea-S**), -114.21 (1F for **(*E*)-5ea-S**); HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{35}H_{32}FP_2S_2$, 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}H NMR (600 MHz, $CDCl_3$), for mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{39}H_{35}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$), for

mixture, δ 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**); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{34}H_{32}NP_2S_2$, 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; ^{1}H NMR (600 MHz, $CDCl_3$), 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**); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), 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); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), 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*: $(M + H)^+$ calcd for $C_{33}H_{31}P_2S_3$, 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; ^{1}H NMR (600 MHz,

$CDCl_3$), for mixture, δ 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**); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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**); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$), for

mixture, δ -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*: $(M + H)^+$ calcd for $C_{39}H_{29}F_{12}P_2S_2$, 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; ^{1}H NMR (600 MHz, $CDCl_3$), for mixture, δ 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**); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), for mixture, δ 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**); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$), for mixture, δ 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*: $(M + H)^+$ calcd for $C_{39}H_{41}P_2S_2$, 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 ($[Ir(cod)(PCy_3)(Py)]PF_6$, 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 H_2. The resulting solution was stirred at 70 ˚C for 48 h under 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. 57.5-59.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 42.08, 49.61; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{34}H_{33}P_2S_2$, 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}H NMR (400 MHz, $CDCl_3$) δ 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); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 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); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 41.26, 42.64; HRMS (APCI) *m/z*: $(M + H)^+$ calcd for $C_{35}H_{35}P_2S_2$, 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 N_2. After toluene (3.0 mL) and $P(NMe_2)_3$ (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 Na_2SO_4, washed with CH_2Cl_2, and concentrated in vacuo. The residue was dissolved in a mixture of hexane and CH_2Cl_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; ^{1}H NMR (400 MHz, $CDCl_3$), 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**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), 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**); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), 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*: $(M + H)^+$ calcd for $C_{34}H_{31}P_2$, 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_2. 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_2SO_4, washed with CH_2Cl_2, 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; ^{1}H NMR (400 MHz, $CDCl_3$), 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**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), 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**); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): 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*: $(M + H)^+$ calcd for $C_{35}H_{33}P_2$, 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), $Ir(ppy)_3$ (2.5 mg, 0.0038 mmol), and $BrPPh_2$ (9.9 mg, 0.038 mmol) in CD_2Cl_2 (0.75 mL) was set up with a NMR tube in the glovebox filled with nitrogen. The reaction progress was monitored by ^1H and $^{31}P\{^1H\}$ 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.xxxx.

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

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

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Notes

The authors declare no competing financial interest.

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