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Rhodium(III)-Catalyzed Regioselective C−H Alkenylation of Phenylphosphine Sulfides

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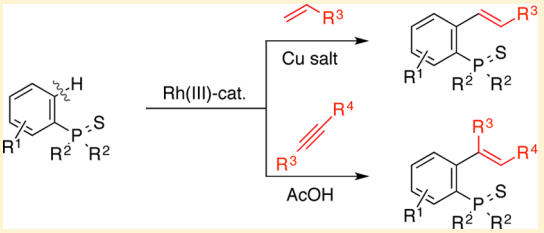
Supporting Information

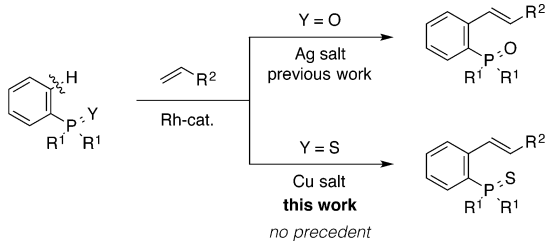
ABSTRACT: The regioselective alkenylation at the *ortho* position of phenylphosphine sulfides using alkenes proceeds efficiently in the presence of a cationic Cp*-rhodium(III) catalyst and an appropriate oxidant. A similar rhodium catalyst also promotes the redox-neutral coupling of the phosphine sulfides with alkynes to afford *ortho*-alkenylated products.



INTRODUCTION

The direct C−H functionalization reactions of arenes and heteroarenes under transition-metal catalysis have attracted much attention as powerful synthetic tools because they provide atom- and step-economical routes to target molecules from readily available substrates without preactivation by halogenation or metalation.[1] Among such useful transformations, catalytic dehydrogenative alkenylation using alkenes in the presence of a palladium catalyst and an oxidant, known as the Fujiwara−Moritani reaction,[2] has been developed and utilized in the synthesis of π-conjugated alkenylarene molecules. However, in this reaction there is a substantial problem of forming mixtures of regioisomers of alkenylarenes. This can be overcome by utilizing a directing group, which is capable of inducing regioselective C−H alkenylation at the proximate positions. As such directing groups, oxygen- and nitrogen-containing substituents including carboxyl, hydroxy, amide, and pyridyl functions have been widely employed.[1] In addition, phosphorus-containing groups such as phosphinoxy and phosphine oxide groups have been recently shown to be applicable. As leading examples, Kim and Lee's and Moon's groups (using palladium catalyst)[3] and we (using rhodium or ruthenium catalyst)[4,5] reported P−OH or P═O group-directed regioselective functionalization. In the context of our continuous studies on rhodium catalysis,[1t] we succeeded in finding that phenylphosphine sulfides also undergo catalytic alkenylation through C−H bond cleavage directed by their P═S group to produce *ortho*-alkenylated phenylphosphine sulfides (Scheme 1). Such *ortho*-substituted phenylphosphine sulfides have recently attracted attention because of their applicability as soft and flexible ligands for transition metals.[6] In addition, a relevant *ortho*-alkenylation using internal alkynes in the presence of a similar catalyst system is also disclosed herein.

Scheme 1. Rhodium-Catalyzed Regioselective Alkenylation



RESULTS AND DISCUSSION

In an initial attempt, dicyclohexyl(phenyl)phosphine sulfide (**1a**) (0.25 mmol) was treated with butyl acrylate (**2a**) (2 mmol) under conditions similar to those for the reaction of phenylphosphine oxides,[4a] in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol) and AgOAc (1 mmol) in *o*-dichlorobenzene (3 mL) at 120 °C for 6 h under N_2. In contrast to the oxides, sulfide **1a** did not undergo alkenylation smoothly. Thus, only a trace amount of desired product, butyl (*E*)-3-[2-(dicyclohexylphosphorothioyl)phenyl]acrylate (**3a**), was formed (entry 1 in Table 1). One of reasons for the failure is likely due to the thiophilicity of silver. Expectedly, the use of $Cu(OAc)_2{\cdot}H_2O$ (0.5 mmol) in place of AgOAc significantly improved the reaction efficiency to give **3a** in 50% yield (entry 2). It was confirmed that the reaction did not proceed at all in the absence of the rhodium catalyst (entry 3). The use of cationic $[Cp^*Rh(MeCN)_3][SbF_6]_2$ is essential for the reaction: electrically neutral $[Cp^*RhCl_2]_2$ did not promote the reaction effectively (entry 4). The yield of **3a** was enhanced to 60% in chlorobenzene (entry 5). The addition of 1,2,3,4-tetraphenyl- and 1,2,3,4,5-pentaphenyl-1,3-cyclopentadienes

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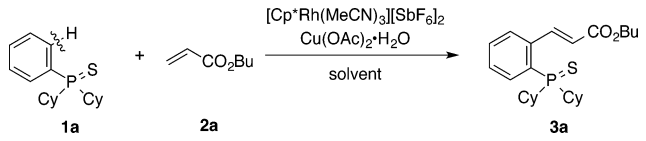
Table 1. Reaction of Dicyclohexyl(phenyl)phosphine Sulfide (1a) with Butyl Acrylate (2a)[a]



1a 2a 3a

entry	additive	solvent	yield of 3a (%)[b]
1[c]		*o*-$C_6H_4Cl_2$	tr
2		*o*-$C_6H_4Cl_2$	50
3[d]		*o*-$C_6H_4Cl_2$	0
4[e]		*o*-$C_6H_4Cl_2$	tr
5		C_6H_5Cl	60
6	$C_5H_2Ph_4$[f]	C_6H_5Cl	62
7	C_5HPh_5[g]	C_6H_5Cl	69
8	C_5HPh_5[g]	diglyme	74 (61)
9[h]	C_5HPh_5[g]	diglyme	69 (58)

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (2 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), additive (0.01 mmol), $Cu(OAc)_2\cdot H_2O$ (0.5 mmol), in solvent (3 mL) at 120 °C for 8 h under N_2, unless otherwise noted. [b]GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c]Using AgOAc (1 mmol) in place of $Cu(OAc)_2\cdot H_2O$. [d]Without $[Cp^*Rh(MeCN)_3][SbF_6]_2$. [e]Using $[(Cp^*RhCl_2)_2]$ (0.005 mmol) in place of $[Cp^*Rh(MeCN)_3][SbF_6]_2$. [f]$C_5H_2Ph_4$ = 1,2,3,4-tetraphenyl-1,3-cyclopentadiene. [g]C_5HPh_5 = 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene. [h]With **2a** (1 mmol).

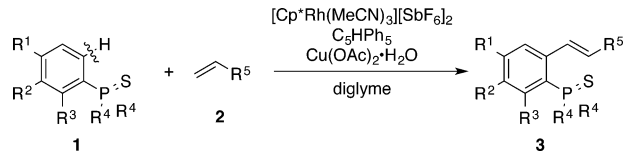
(0.01 mmol) ($C_5H_2Ph_4$ and C_5HPh_5, respectively) slightly improved the **3a** yield (entries 6 and 7). This kind of Cp-ligand was previously employed for promoting rhodium-catalyzed oxidative coupling,[7] although its exact role was not clear. With C_5HPh_5 in diglyme, the best yield of **3a** (74%) was obtained (entry 8). Under these conditions, a comparable yield was still achieved even when the amount of **2a** was reduced to 1 mmol (entry 9).

Under the optimized reaction conditions, the coupling reactions of a number of substituted phenyl- and naphthylphosphine sulfides with alkenes were next examined (Table 2). Treatment of **1a** with various acrylate esters **2b**–**e** gave the corresponding *ortho*-alkenylated phenylphosphine sulfides in moderate to good yields (entries 1–5). In some cases, contamination by trace amounts of 2*Z*-isomers was observed. In contrast, the reaction with an acrylamide **2g** afforded **3g** as a mixture of 2*E*- and 2*Z*-isomers (entry 6). It was found that styrene (**2h**) is less reactive than acrylic acid derivatives. However, the reaction of **1a** with **2h** proceeded by increasing the amount of Rh catalyst and extending the reaction time to 30 h to give the stilbene derivative **3h** (entry 7).

A series of *para*- and *meta*-substituted phenylphosphine sulfides **1b**–**h** underwent the coupling with **2a** to produce **3i**–**o** in 35–74% yields (entries 8–14). In the reaction of dicyclohexyl(2-naphthyl)phosphine sulfide (**1l**), alkenylation took place at the sterically less hindered position to afford a 3-alkenylated product **3p** selectively (entry 15). In addition to these aryldicyclohexylphosphine sulfides, diisopropyl(phenyl)-phosphine sulfide (**1j**) also reacted with **2a** to give **3q** (entry 16).

A plausible mechanism for the reaction of phenylphosphine sulfide **1** with alkene **2** is illustrated in Scheme 2. Coordination of the P═S group[6d] of **1** to a cationic Rh^{III} center and subsequent *ortho*-rhodation would occur to form a five-membered rhodacycle intermediate **A**. Then, alkene insertion to form **B** and *β*-hydrogen elimination may take place to

Table 2. Reaction of Phenylphosphine Sulfides 1 with Alkenes 2[a]



1 2 3

entry	1	2	product, % yield (*E*:*Z*)[b]
1	**1a**	**2b**: R = CO_2Bu^i	**3b**: R = CO_2Bu^i, 60 (>99:1)
2		**2c**: R = CO_2Bu^t	**3c**: R = CO_2Bu^t, 73 (96:4)
3		**2d**: R = CO_2Cy	**3d**: R = CO_2Cy, 65 (>99:1)
4		**2e**: R = CO_2Et	**3e**: R = CO_2Et, 42 (98:2)
5		**2f**: R = CO_2Ph	**3f**: R = CO_2Ph, 30 (93:7)
6		**2g**: R = $CONMe_2$	**3g**: R = $CONMe_2$, 30 (74:26)
7[c]		**2h**: R = Ph	**3h**: R = Ph, 32 (96:4)
8	**1b**: R = Me	**2a**	**3i**: R = Me, 48 (98:2)
9	**1c**: R = OMe		**3j**: R = OMe, 35 (93:7)
10	**1d**: R = Cl		**3k**: R = Cl, 38 (97:3)
11	**1e**: R = Me	**2a**	**3l**: R = Me, 74 (>99:1)
12	**1f**: R = OMe		**3m**: R = OMe, 57 (97:3)
13	**1g**: R = Ph		**3n**: R = Ph, 74 (98:2)
14	**1h**: R = CF_3		**3o**: R = CF_3, 41 (93:7)
15	**1i**	**2a**	**3p**, 49 (97:3)
16	**1j**	**2a**	**3q**, 61 (97:3)

[a]Reaction conditions: **1** (0.25 mmol), **2** (1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), C_5HPh_5 (0.01 mmol), $Cu(OAc)_2\cdot H_2O$ (0.5 mmol), in diglyme (3 mL) at 120 °C for 8 h under N_2, unless otherwise noted. [b]Determined by ^1H NMR. [c]The reaction was conducted with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol) in the absence of C_5HPh_5 for 30 h.

produce **3** involving H^+ release. The resulting Rh^I species would be oxidized by Cu^{II} to regenerate Rh^{III}.

To obtain mechanistic insight, a deuterated substrate, dicyclohexyl(d_5-phenyl)phosphine sulfide (**1a**-d_5), was treated with **2a** under standard conditions (Scheme 3a). In the early stage, considerable contamination by protons at the *ortho* positions of recovered **1a**-d_n as well as at the 6-position of produced **3a**-d_n was observed. This result indicates that the initial C–H(D) bond cleavage step to form **A** is likely reversible. This is supported by the observed H–D exchange at the *ortho* positions of **1a** upon treatment with CD_3CO_2D in chlorobenzene in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (Scheme 3b). Interestingly, the H–D exchange did not take

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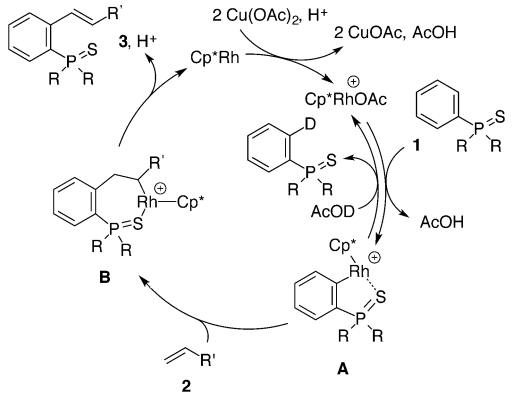
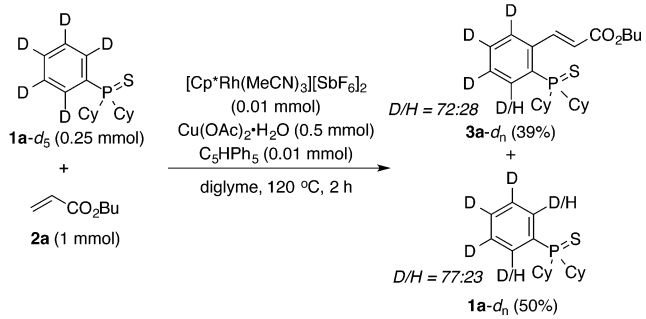
Scheme 2. Plausible Mechanism for the Reaction of 1 with 2

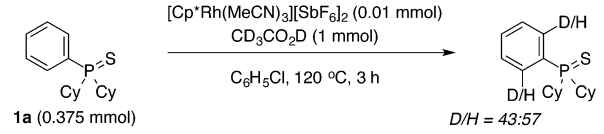


Scheme 3. Investigation for Mechanistic Insights

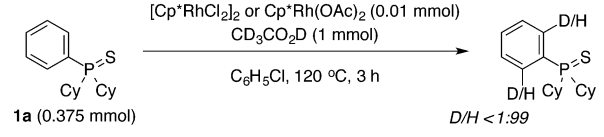
a. Reaction Using Deuterium-Labeled Substrate



b. Treatment Using CD_3CO_2D with Cationic Rh Species



c. Treatment Using CD_3CO_2D with Neutral Rh Species



place at all in the presence of neutral Rh^{III} species such as $[Cp^*RhCl_2]_2$ and $Cp^*Rh(OAc)_2$ (Scheme 3c). Therefore, the use of a cationic Rh catalyst is essential to facilitate the C–H(D) bond cleavage step, while it is likely that other steps including alkene insertion can also be promoted by it.

It was found that alkenylation on an alkenyl C–H bond can be performed by utilizing the P═S directing group. Thus, treatment of dicyclohexyl(1-phenylethen-1-suppyl)phosphine sulfide (**4**) (0.25 mmol) with **2a** (1 mmol) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), C_5HPh_5 (0.01 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (0.5 mmol) in diglyme (3 mL) at 120 °C for 8 h under N_2 gave butyl (2*E*,4*Z*)-5-(dicyclohexylphosphorothioyl)-5-phenylpenta-2,4-dienoate (**5**) in a moderate yield (Scheme 4).

Recently, we[7a,8] and other groups[5c,9] reported the Cp^*Rh^{III}-catalyzed *ortho*-alkenylation using alkynes as alkenyl source under redox-neutral conditions. Therefore, we applied the procedure to phenylphosphine sulfides. Expectedly, **1a** (0.25 mmol) reacted with 1-phenyl-1-propyne (**6a**) (0.25 mmol) in

Scheme 4. Reaction of 4 with 2a

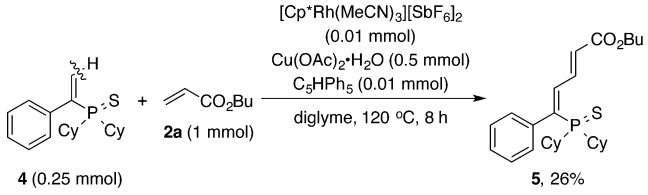
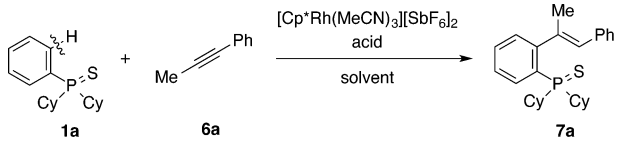


Table 3. Reaction of Dicyclohexyl(phenyl)phosphine Sulfide (1a) with 1-Phenyl-1-propyne (6a)[a]



entry	additive	solvent	yield of **3a** (%)[b]
1	AcOH	diglyme	32
2	AcOH	C_6H_5Cl	41
3	AcOH	*o*-$C_6H_4Cl_2$	37
4	AcOH	DMF	14
5	AcOH	*o*-xylene	19
6	$EtCO_2H$	C_6H_5Cl	41
7	1-$AdCO_2H$	C_6H_5Cl	35
8	PivOH	C_6H_5Cl	32
9	2,6-$Me_2C_6H_3CO_2H$	C_6H_5Cl	25
10	CF_3CO_2H	C_6H_5Cl	8
11[c]	AcOH	C_6H_5Cl	43
12[d]	AcOH	C_6H_5Cl	53 (47)

[a]Reaction conditions: **1a** (0.25 mmol), **6a** (0.25 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), acid (1 mmol), in solvent (3 mL) at 120 °C for 3 h under N_2, unless otherwise noted. [b]GC yield based on the amount of **6a** used. Value in parentheses indicates yield after purification. [c]At 100 °C. [d]With **1a** (0.38 mmol).

the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol) and AcOH (1 mmol) in diglyme (3 mL) at 120 °C under N_2 to produce dicyclohexyl(2-(1-phenylprop-1-en-2-yl)phenyl)-phosphine sulfide (**7a**) in 32% yield (entry 1 in Table 3). Chlorobenzene was found to be the solvent of choice among those examined (entries 1–5). The selection of acid was also important. $EtCO_2H$ was as effective as AcOH (entry 6), although 1-adamantanecarboxylic acid, pivalic acid, 2,6-dimethylbenzoic acid, and trifluoroacetic acid were less effective (entries 7–10). At 100 °C, a similar result was obtained (entry 11). Finally, the use of a slightly excess amount of **1a** (1.5 equiv) increased the yield of **7a** to 53% (entry 12). The NMR spectra for **7a** isolated in entry 12 showed that the alkenyl moiety of the product has *E* geometry (*E*/*Z* = >99:1).

The *ortho*-alkenylations of **1a** with other alkynes **6** were next examined. Unsubstituted and substituted diphenylacetylene **6b–e** reacted with **1a** under similar conditions to afford products **7b–e** (entries 1–4 in Table 4). In the cases with **6b** and **6c**, only the *E*-isomer of **7** was obtained selectively. The reactions of unsymmetrical alkynes **6f** and **6g** proceeded regioselectively to produce **7f** and **7g** in moderate yields (entries 5 and 6).

The *ortho*-alkenylation of **1a** with alkynes **6** seems to proceed through a common rhodacycle intermediate **A** in Scheme 2. Alkyne insertion into the C–Rh bond in **A** and subsequent protonolysis by AcOH may occur to produce **7** accompanied by regeneration of an active Rh^{III} species (Scheme 5).

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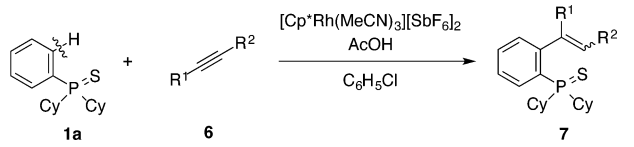
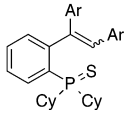
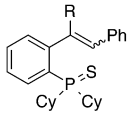
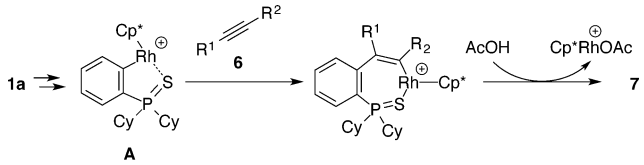
Table 4. Reaction of 1a with Alkynes 7[a]



entry	6	product, % yield (*E*:*Z*)[b]
		
1	**6b**: Ar = Ph	**7b**: Ar = Ph, 37 (>99:1)
2	**6c**: Ar = 4-ClC_6H_4	**7c**: Ar = 4-ClC_6H_4, 27 (>99:1)
3	**6d**: Ar = 4-$MeOC_6H_4$	**7d**: Ar = 4-$MeOC_6H_4$, 13 (85:15)
4	**6e**: Ar = 4-MeC_6H_4	**7e**: Ar = 4-MeC_6H_4, 13 (76:24)
		
5	**6f**: R = Bu	**7f**: R = Bu, 29 (97:3)
6	**6g**: R = $(CH_2)_4Cl$	**7g**: R = $(CH_2)_4Cl$, 23 (93:7)

[a]Reaction conditions: **1a** (0.38 mmol), **6** (0.25 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.01 mmol), AcOH (1 mmol), in chlorobenzene (3 mL) at 120 °C for 3 h under N_2. [b]Determined by ^{1}H NMR.

Scheme 5. Possible Pathway for the Reaction of 1a with 6



CONCLUSIONS

We have demonstrated that the rhodium-catalyzed *ortho*-alkenylation of phenylphosphine sulfides takes place through P═S group-directed C−H bond cleavage. The *ortho*-alkenylated phenylphosphine sulfides can also be prepared via the redox-neutral coupling with alkynes.

EXPERIMENTAL SECTION

General. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by EI using a double focusing mass spectrometer, unless noted otherwise. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC−MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Phosphine sulfides **1a−j** and **4**[10,11] and alkynes **6b−e**[12] and **6g**[13] were prepared according to published procedures. All starting materials and reagents were commercially available.

General Procedure for the Reaction of Phenylphosphine Sulfides with Alkenes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added phenylphosphine sulfide **1** (0.25 mmol), alkene **2** (1 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.01 mmol, 8 mg), C_5HPh_5 (0.01 mmol, 5 mg), $Cu(OAc)_2·H_2O$ (0.5 mmol, 100 mg), dibenzyl (ca. 30 mg) as internal standard, and diglyme (3 mL). Then, the resulting mixture was stirred under nitrogen at 120 °C for 8 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **3** was isolated by column chromatography on silica gel using hexane/ethyl acetate (20:1, v/v) as eluent.

General Procedure for the Reaction of Phenylphosphine Sulfides with Alkynes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added phenylphosphine sulfide **1** (0.38 mmol), alkyne **6** (0.25 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.01 mmol, 8 mg), AcOH (1 mmol, 57 μL), dibenzyl (ca. 30 mg) as internal standard, and chlorobenzene (3 mL). Then, the resulting mixture was stirred under nitrogen at 120 °C for 3 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **7** was isolated by column chromatography on silica gel using hexane/ethyl acetate (20:1, v/v) as eluent. Further purification by gel permeation chromatography (GPC) was performed, if needed.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3a). Colorless oil, 66 mg (61%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.08−2.43 (m, 26H), 4.27 (t, *J* = 6.5 Hz, 2H), 6.29 (d, *J* = 15.5 Hz, 1H), 7.47−7.60 (m, 3H), 8.36 (d, *J* = 15.5 Hz, 1H), 8.39−8.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 25.5 (d, *J* = 1.5 Hz), 26.32 (d, *J* = 1.5 Hz), 26.33 (d, *J* = 2.3 Hz), 26.5 (d, *J* = 13.3 Hz), 27.4 (d, *J* = 2.2 Hz), 30.7, 39.7 (d, *J* = 48.6 Hz), 64.3, 121.6, 127.8 (d, *J* = 8.7 Hz), 128.5 (d, *J* = 62.2 Hz), 129.4 (d, *J* = 11.3 Hz), 131.3 (d, *J* = 11.2 Hz), 136.4 (d, *J* = 9.8 Hz), 137.1 (d, *J* = 5.9 Hz), 143.5 (d, *J* = 2.2 Hz), 166.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.7; HRMS *m*/*z* calcd for $C_{25}H_{38}O_2PS$ (M + H$^+$) 433.2325, found 433.2331.

Isobutyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3b). Colorless oil, 65 mg (60%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, *J* = 6.7 Hz, 6H), 1.09−2.43 (m, 23H), 4.06 (d, *J* = 6.5 Hz, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 7.47−7.63 (m, 3H), 8.33−8.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 25.6 (d, *J* = 1.2 Hz), 26.36 (d, *J* = 13.5 Hz), 26.37 (d, *J* = 2.7 Hz), 26.5 (d, *J* = 13.8 Hz), 27.4 (d, *J* = 2.1 Hz), 27.9, 39.8 (d, *J* = 48.5 Hz), 71.0, 121.6, 127.9 (d, *J* = 8.5 Hz), 128.6 (d, *J* = 60.3 Hz), 129.4 (d, *J* = 11.2 Hz), 131.5 (d, *J* = 2.7 Hz), 136.4 (d, *J* = 9.5 Hz), 137.2 (d, *J* = 6.1 Hz), 143.5 (d, *J* = 2.3 Hz), 166.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.5; HRMS *m*/*z* calcd for $C_{25}H_{38}O_2PS$ (M + H$^+$) 433.2325, found 433.2351.

***tert*-Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3c).** (*E*:*Z* = 96:4) Yellow oil, 79 mg (73%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09−1.41 (m, 10H), 1.58 (s, 9H), 1.61−2.43 (m, 12H), 6.02 (d, *J* = 12.0 Hz, 1H, *Z*), 6.19 (d, *J* = 15.5 Hz, 1H), 7.40−7.63 (m, 3H), 8.23 (d, *J* = 15.5 Hz, 1H), 8.38−8.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6 (d, *J* = 1.5 Hz), 26.4 (d, *J* = 3.0 Hz), 26.5 (d, *J* = 13.2 Hz), 26.6 (d, *J* = 13.9 Hz), 27.5 (d, *J* = 2.5 Hz), 28.2, 39.8 (d, *J* = 48.4 Hz), 81.0, 123.8, 127.7 (d, *J* = 8.6 Hz), 128.4 (d, *J* = 60.5 Hz), 129.2 (d, *J* = 11.3 Hz), 131.4 (d, *J* = 2.5 Hz), 136.7 (d, *J* = 10.0 Hz), 137.2 (d, *J* = 5.8 Hz), 142.7 (d, *J* = 2.5 Hz), 165.3; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 63.5 (*Z*), 64.8 (*E*); HRMS *m*/*z* calcd for $C_{25}H_{38}O_2PS$ (M + H$^+$) 433.2325, found 433.2328.

Cyclohexyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3d). Pale yellow oil, 65 mg (65%); hexane/ethyl acetate 95 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07−2.45 (m, 32H), 4.98 (tt, *J* = 3.5, 8.6 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 7.47−7.63 (m, 3H), 8.36 (d, *J* = 15.5 Hz, 1H), 8.40−8.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 25.4, 25.6 (d, *J* = 1.0 Hz), 26.38 (d, *J* = 2.5 Hz), 26.39 (d, *J* = 13.0 Hz), 26.5 (d, *J* = 13.0 Hz), 27.5 (d, *J* = 2.0 Hz), 31.6, 39.8 (d, *J* = 48.5 Hz), 72.9, 122.2, 127.7 (d, *J* = 8.5 Hz), 128.5 (d, *J* = 60.5 Hz), 129.4 (d, *J* = 11.1 Hz), 131.5 (d, *J* = 2.7 Hz), 136.5 (d, *J* = 9.5 Hz), 137.1 (d, *J* = 6.5 Hz), 143.2 (d, *J* = 2.8 Hz), 165.6; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.7; HRMS *m*/*z* calcd for $C_{27}H_{40}O_2PS$ (M + H$^+$) 459.2481, found 459.2495.

Ethyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3e). (*E*:*Z* = 98:2) Yellow oil, 42 mg (42%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09−2.44 (m, 25H), 4.32 (q, *J* = 7.1 Hz, 2H), 6.11 (d, *J* = 12.0 Hz, 1H, *Z*), 6.29 (d, *J* = 15.5 Hz, 1H), 7.48−7.63 (m, 3H), 8.370 (d, *J* = 15.6 Hz, 1H),

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8.371−8.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 25.6 (d, J = 1.4 Hz), 26.3 (d, J = 11.7 Hz), 26.4 (d, J = 2.9 Hz), 26.5 (d, J = 11.6 Hz), 27.4 (d, J = 2.8 Hz), 39.8 (d, J = 48.6 Hz), 60.8, 121.6, 127.9 (d, J = 8.5 Hz), 128.6 (d, J = 60.2 Hz), 129.4 (d, J = 11.0 Hz), 131.5 (d, J = 2.5 Hz), 136.5 (d, J = 9.7 Hz), 137.2 (d, J = 6.6 Hz), 143.7 (d, J = 2.8 Hz), 166.3; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.7; HRMS m/z calcd for $C_{23}H_{34}O_2PS$ (M + H$^+$) 405.2012, found 405.2024.

Phenyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-acrylate (3f). (*E*:*Z* = 96:4) Yellow oil, 33 mg (30%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08−1.42 (m, 10H), 1.58−1.78 (m, 6H), 1.80−1.91 (m, 2H), 2.00−2.11 (m, 2H), 2.23−2.42 (m, 2H), 6.30 (d, J = 11.9 Hz, 1H, *Z*), 6.49 (d, J = 15.5 Hz, 1H), 7.18−7.24 (m, 2H), 7.28−7.31 (m, 1H), 7.40−7.48 (m, 2H), 7.52−7.61 (m, 2H), 7.62−7.72 (m, 2H), 8.32−8.45 (m, 1H), 8.65 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6 (d, J = 1.0 Hz), 26.39 (d, J = 13.5 Hz), 26.41 (d, J = 2.7 Hz), 26.5 (d, J = 13.9 Hz), 27.2 (d, J = 2.6 Hz), 39.8 (d, J = 48.6 Hz), 120.3, 121.5, 126.0, 128.1 (d, J = 8.7 Hz), 128.8 (d, J = 59.4 Hz), 129.5, 129.8 (d, J = 11.1 Hz), 131.5 (d, J = 2.4 Hz), 136.3 (br), 137.1 (br), 145.8 (d, J = 2.8 Hz), 150.7, 164.9; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 61.7 (*Z*), 64.2 (*E*); HRMS m/z calcd for $C_{27}H_{34}O_2PS$ (M + H$^+$) 453.2012, found 453.2011.

(*E*)-3-(2-(Dicyclohexylphosphorothioyl)phenyl)-*N*,*N*-dimethylacrylamide (3g). (*E*:*Z* = 74:26) Yellow oil, 30 mg (30%); hexane/ethyl acetate 50:50 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.63 (m, 13H), 1.65−2.13 (m, 7H), 2.23−2.39 (m, 2H, *Z*), 2.39−2.51 (m, 2H, *E*), 2.88 (s, 3H, *Z*), 2.90 (s, 3H, *Z*), 3.12 (s, 3H, *E*), 3.20 (s, 3H, *E*), 6.20 (d, J = 12.3 Hz, 1H, *Z*), 6.72 (d, J = 14.9 Hz, 1H, *E*), 7.36−7.43 (m, 3H, *Z*), 7.47−7.55 (m, 3H, *E*), 7.50 (d, J = 11.5 Hz, 1H, *Z*), 7.83−7.97 (m, 1H, *Z*), 8.16 (d, J = 15.0 Hz, 1H, *E*), 8.48−8.70 (m, 1H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.59 (d, J = 1.3 Hz, *E*), 25.64 (d, J = 1.3 Hz, *Z*), 26.1 (br, *Z*), 26.2 (d, J = 13.6 Hz, *E*), 26.41 (d, J = 13.1 Hz, overlapped, *Z*), 26.43 (d, J = 2.6 Hz, *E*), 26.5 (d, J = 13.6 Hz, overlapped), 27.7 (d, J = 2.3 Hz, *E*), 34.5 (*Z*), 36.0 (*E*), 37.4 (*E*), 37.7 (*Z*), 39.4 (d, J = 48.2 Hz, *E*), 39.9 (d, J = 49.1 Hz, *Z*), 121.5 (*E*), 124.1 (*Z*), 125.8 (d, J = 62.7 Hz, *Z*), 127.7 (d, J = 5.7 Hz, *E*), 127.8 (d, J = 10.6 Hz, *Z*), 128.5 (d, J = 60.7 Hz, *E*), 128.9 (d, J = 11.3 Hz, *E*), 130.1 (d, J = 9.1 Hz, *Z*), 131.1 (d, J = 2.6 Hz, *Z*), 131.3 (d, J = 2.6 Hz, *E*), 133.5 (br, *Z*), 134.8 (d, J = 2.9 Hz, *Z*), 137.1 (d, J = 10.3 Hz, *E*), 137.9 (d, J = 6.5 Hz, *E*), 140.5 (br, *Z*), 141.6 (d, J = 2.0 Hz, *E*), 165.8 (*E*), 168.1 (*Z*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 60.8 (*Z*), 66.3 (*E*); HRMS m/z calcd for $C_{23}H_{35}NOPS$ (M + H$^+$) 404.2171, found 404.2175.

(*E*)-Dicyclohexyl(2-styrylphenyl)phosphine Sulfide (3h). (*E*:*Z* = 93:7) Yellow oil, 33 mg (32%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06−1.51 (m, 10H), 1.58−2.46 (m, 12H), 6.73 (d, J = 12.3 Hz, 1H, *Z*), 6.90 (d, J = 15.9 Hz, 1H), 7.29−7.66 (m, 8H), 7.94 (d, J = 15.6 Hz, 1H), 8.22 (dd, J = 7.8, 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6 (br), 26.4 (d, J = 2.7 Hz), 26.5 (d, J = 6.5 Hz), 26.6 (d, J = 6.5 Hz), 27.0 (d, J = 2.0 Hz), 39.4 (d, J = 48.9 Hz), 126.4 (d, J = 63.0 Hz), 127.0, 127.2 (d, J = 11.2 Hz), 127.9 (d, J = 9.0 Hz), 128.0 (d, J = 3.9 Hz), 128.2, 129.0, 131.4 (d, J = 2.7 Hz), 132.2, 135.3, 137.1, 141.2 (d, J = 5.8 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 63.2 (*E*), 65.7 (*Z*); HRMS m/z calcd for $C_{26}H_{34}PS$ (M + H$^+$) 409.2113, found 409.2137.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)-5-methylphenyl)acrylate (3i). (*E*:*Z* = 98:2) Colorless oil, 54 mg (48%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H), 1.07−2.38 (m, 26H), 2.41 (s, 3H), 4.26 (t, J = 6.5 Hz, 2H), 6.09 (d, J = 12.0 Hz, 1H, *Z*), 6.28 (d, J = 15.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 5.0 Hz, 1H), 8.29 (dd, J = 8.0, 14.1 Hz, 1H), 8.34 (d, J = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 21.2, 25.6 (d, J = 1.2 Hz), 26.39 (d, J = 2.6 Hz), 26.40 (d, J = 13.8 Hz), 26.5 (d, J = 13.8 Hz), 27.4 (d, J = 2.1 Hz), 30.8, 40.5 (d, J = 48.8 Hz), 64.6, 121.4, 125.6 (d, J = 62.3 Hz), 128.7 (d, J = 8.9 Hz), 130.3 (d, J = 11.5 Hz), 136.7 (d, J = 9.5 Hz), 137.0 (d, J = 6.4 Hz), 141.9 (d, J = 2.6 Hz), 143.8 (d, J = 2.5 Hz), 166.4; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.1; HRMS m/z calcd for $C_{26}H_{40}O_2PS$ (M + H$^+$) 447.2481, found 447.2485.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)-5-methoxyphenyl)acrylate (3j). (*E*:*Z* = 93:7) Pale yellow oil, 41 mg (35%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H), 1.09−2.37 (m, 26H), 3.87 (s, 3H), 4.27 (t, J = 6.5 Hz, 2H), 6.10 (d, J = 12.0 Hz, 1H, *Z*), 6.27 (d, J = 15.5 Hz, 1H), 7.01 (dd, J = 2.5, 8.7 Hz, 1H), 7.06 (dd, J = 3.0, 3.1 Hz, 1H), 8.32 (d, J = 14.4 Hz, 1H), 8.35 (d, J = 13.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.7, 25.6 (br), 26.37 (d, J = 2.5 Hz), 26.39 (d, J = 14.1 Hz), 26.5 (d, J = 14.2 Hz), 27.4 (d, J = 2.1 Hz), 30.8, 39.8 (d, J = 49.3 Hz), 55.4, 64.7, 113.8 (d, J = 9.5 Hz), 114.2 (d, J = 12.2 Hz), 119.5 (d, J = 65.8 Hz), 121.8, 138.6 (br), 138.7, 143.6 (d, J = 2.0 Hz), 161.9 (d, J = 2.7 Hz), 166.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 61.8 (*Z*), 63.4 (*E*); HRMS m/z calcd for $C_{26}H_{40}O_3PS$ (M + H$^+$) 463.2430, found 463.2438.

Butyl (*E*)-3-(5-Chloro-2-(dicyclohexylphosphorothioyl)-phenyl)acrylate (3k). (*E*:*Z* = 97:3) Colorless oil, 45 mg (38%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.08−2.40 (m, 26H), 4.27 (t, J = 6.5 Hz, 2H), 6.15 (d, J = 12.0 Hz, 1H, *Z*), 6.31 (d, J = 15.6 Hz, 1H), 7.44−7.56 (m, 2H), 8.26 (d, J = 15.6 Hz, 1H), 8.39 (dd, J = 8.4, 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 25.5 (d, J = 1.1 Hz), 26.3 (d, J = 14.5 Hz), 26.4 (overlapped), 26.5 (d, J = 13.9 Hz), 27.4 (d, J = 2.1 Hz), 30.8, 39.8 (d, J = 48.7 Hz), 64.9, 122.9, 127.2 (d, J = 60.5 Hz), 127.7 (d, J = 9.0 Hz), 129.3 (d, J = 11.8 Hz), 138.1 (d, J = 3.4 Hz), 138.3 (d, J = 10.9 Hz), 138.6 (d, J = 7.0 Hz), 142.2 (d, J = 2.0 Hz), 165.9; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.7; HRMS m/z calcd for $C_{25}H_{37}O_2ClPS$ (M + H$^+$) 467.1935, found 467.1944.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)-4-methylphenyl)acrylate (3l). Colorless oil, 82 mg (74%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.09−2.40 (m, 26H), 2.43 (s, 3H), 4.26 (t, J = 6.5 Hz, 2H), 6.28 (d, J = 15.5 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.48 (dd, J = 4.5, 7.8 Hz, 1H), 8.25 (d, J = 16.0 Hz, 1H), 8.29 (d, J = 16.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 21.5, 25.6 (d, J = 1.1 Hz), 26.4 (d, J = 13.9 Hz), 26.46 (d, J = 2.7 Hz), 26.54 (d, J = 13.8 Hz), 27.7 (d, J = 2.4 Hz), 30.8, 39.9 (d, J = 48.5 Hz), 64.6, 120.8, 127.7 (d, J = 8.9 Hz), 128.5 (d, J = 60.1 Hz), 132.2 (d, J = 2.6 Hz), 133.8 (d, J = 6.1 Hz), 137.4 (d, J = 10.0 Hz), 140.0 (d, J = 48.9 Hz), 143.3 (d, J = 42.2 Hz), 166.4; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.5; HRMS m/z calcd for $C_{26}H_{40}O_2PS$ (M + H$^+$) 447.2481, found 447.2510.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)-4-methoxyphenyl)acrylate (3m). (*E*:*Z* = 97:3) Purple oil, 66 mg (57%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.08−1.78 (m, 20H), 1.80−1.92 (m, 2H), 1.99−2.11 (m, 2H), 2.23−2.45 (m, 2H), 3.90 (s, 3H), 4.25 (t, J = 6.5 Hz, 2H), 6.07 (d, J = 11.9 Hz, 1H, *Z*), 6.24 (d, J = 15.4 Hz, 1H), 7.00 (dd, J = 2.0, 8.5 Hz, 1H), 7.56 (dd, J = 3.6, 5.0 Hz, 1H), 8.13 (dd, J = 2.6, 15.8 Hz, 1H), 8.19 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 25.6 (d, J = 1.2 Hz), 26.36 (d, J = 13.6 Hz), 26.40 (d, J = 3.1 Hz), 26.5 (d, J = 13.7 Hz), 27.8 (d, J = 2.3 Hz), 30.8, 40.1 (d, J = 48.2 Hz), 55.6, 64.6, 117.6 (d, J = 5.0 Hz), 119.3, 121.7 (d, J = 11.6 Hz), 128.7 (d, J = 6.3 Hz), 129.2 (d, J = 10.1 Hz), 131.1 (d, J = 58.8 Hz), 142.6 (d, J = 2.1 Hz), 160.6 (d, J = 13.3 Hz), 166.6; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 64.5 (*Z*), 66.4 (*E*); HRMS m/z calcd for $C_{26}H_{40}O_3PS$ (M + H$^+$) 463.2430, found 463.2442.

Butyl (*E*)-3-(3-(Dicyclohexylphosphorothioyl)-[1,1′-biphenyl]-4-yl)acrylate (3n). (*E*:*Z* = 98:2) Pale yellow oil, 95 mg (74%); hexane/ethyl acetate 95:5 (v/v, eluent);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, J = 7.4 Hz, 3H), 1.11−2.48 (m, 26H), 4.28 (t, J = 6.5 Hz, 2H), 6.15 (d, J = 12.0 Hz, 1H, *Z*), 6.36 (d, J = 15.6 Hz, 1H), 7.36−7.80 (m, 7H), 8.35 (d, J = 15.6 Hz, 1H), 8.75 (d, J = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 25.6 (br), 26.4 (d, J = 13.3 Hz), 26.5 (br), 26.6 (d, J = 13.3 Hz), 27.6 (d, J = 2.1 Hz), 30.8, 39.9 (d, J = 48.3 Hz), 64.7, 121.3, 127.1, 128.2, 128.3 (d, J = 9.0 Hz), 129.0, 129.3 (d, J = 58.9 Hz), 129.6 (d, J = 2.7 Hz), 135.3 (d, J = 11.1 Hz), 135.5 (d, J = 5.7 Hz), 139.2, 142.0 (d, J = 11.0 Hz), 143.0 (d, J = 2.3 Hz), 166.4; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 65.4; HRMS m/z calcd for $C_{31}H_{42}O_2PS$ (M + H$^+$) 509.2638, found 509.2640.

Butyl (*E*)-3-(2-(Dicyclohexylphosphorothioyl)-4-(trifluoromethyl)phenyl)acrylate (3o). (*E*:*Z* = 93:7) Colorless oil, 52 mg

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(41%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.09−2.44 (m, 26H), 4.29 (t, J = 6.6 Hz, 2H), 6.20 (d, J = 12.0 Hz, 1H, Z), 6.36 (d, J = 15.6 Hz, 1H), 7.67 (dd, J = 3.6, 8.0 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 15.6 Hz, 1H), 8.75 (d, J = 13.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 25.5 (d, J = 1.4 Hz), 26.3 (d, J = 13.3 Hz), 26.4 (d, J = 3.0 Hz), 26.5 (d, J = 13.9 Hz), 27.5 (d, J = 2.1 Hz), 30.8, 39.8 (d, J = 48.3 Hz), 65.0, 123.5 (q, J = 271.1 Hz), 123.7, 128.1−128.27 (m), 128.33 (d, J = 8.2 Hz), 130.5 (d, J = 58.1 Hz), 131.3 (dq, J = 11.2, 33.1 Hz), 133.3−133.6 (m), 140.5 (d, J = 3.6 Hz), 142.2 (d, J = 1.4 Hz), 165.8; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 63.7 (Z), 65.4 (E); HRMS m/z calcd for $C_{26}H_{37}O_2F_3PS$ (M + H$^+$) 501.2198, found 501.2211.

Butyl (*E*)-3-(3-(Dicyclohexylphosphorothioyl)naphthalen-2-yl)acrylate (3p). (E:Z = 97:3) Mp 135−136 °C (pale yellow solid), 60 mg (49%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 3H), 1.07−2.51 (m, 26H), 4.30 (t, J = 6.5 Hz, 2H), 6.23 (d, J = 11.9 Hz, 1H, Z), 6.43 (d, J = 15.4 Hz, 1H), 7.50−7.70 (m, 2H), 7.78−8.10 (m, 3H), 8.32 (d, J = 15.4 Hz, 1H), 9.06 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 25.6 (d, J = 1.3 Hz), 26.4 (d, J = 14.3 Hz), 26.5 (d, J = 14.1 Hz), 26.6 (d, J = 2.5 Hz), 28.0 (d, J = 2.2 Hz), 30.8, 39.9 (d, J = 48.5 Hz), 64.7, 121.7, 126.8 (d, J = 61.1 Hz), 127.69 (d, J = 8.7 Hz), 127.74, 127.9, 128.7, 129.1, 132.7 (d, J = 12.3 Hz), 132.8 (d, J = 6.2 Hz), 134.0 (d, J = 2.2 Hz), 139.5 (d, J = 9.5 Hz), 143.9, 166.3; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 65.2 (Z), 65.8 (E); HRMS m/z calcd for $C_{29}H_{40}O_2PS$ (M + H$^+$) 483.2481, found 483.2497.

Butyl (*E*)-3-(2-(Diisopropylphosphorothioyl)phenyl)acrylate (3q). (E:Z = 97:3) Pale yellow oil, 53 mg (61%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (dd, J = 7.0, 18.1 Hz, 6H), 0.99 (t, J = 7.4 Hz, 3H), 1.35 (dd, J = 6.7, 17.5 Hz, 6H), 1.47 (sext, J = 7.3 Hz, 2H), 1.72 (quin, J = 6.6 Hz, 2H), 2.55−2.72 (m, 2H), 4.25 (t, J = 6.5 Hz, 2H), 6.09 (d, J = 12.0 Hz, 1H, Z), 6.33 (d, J = 15.5 Hz, 1H), 7.49−7.64 (m, 3H), 8.40 (d, J = 15.6 Hz, 1H), 8.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 17.3 (d, J = 1.9 Hz), 17.7 (d, J = 1.3 Hz), 19.2, 29.8 (d, J = 49.1 Hz), 30.7, 64.8, 121.6, 127.9 (d, J = 8.7 Hz), 129.2 (d, J = 60.9 Hz), 129.5 (d, J = 11.2 Hz), 131.6 (d, J = 2.4 Hz), 136.3 (d, J = 2.5 Hz), 136.9 (d, J = 7.1 Hz), 143.1 (d, J = 2.6 Hz), 166.4; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 72.6; HRMS m/z calcd for $C_{19}H_{30}O_2PS$ (M + H$^+$) 353.1699, found 353.1706.

Butyl (2*E*,4*Z*)-5-(Dicyclohexylphosphorothioyl)-5-phenylpenta-2,4-dienoate (5). Mp 143−144 °C (white solid), 30 mg (26%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3H), 1.08−2.12 (m, 27H), 4.09 (t, J = 6.6 Hz, 2H), 6.22 (d, J = 15.4 Hz, 1H), 7.04 (ddd, J = 1.7, 11.5, 15.4 Hz, 3H), 7.06−7.11 (m, 2H), 7.67 (dd, J = 11.5, 19.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.1, 25.8 (br), 26.1 (d, J = 2.3 Hz), 26.3 (d, J = 3.1 Hz), 26.48 (d, J = 13.5 Hz), 26.52 (d, J = 13.3 Hz), 30.6, 37.3 (d, J = 49.7 Hz), 64.5, 127.3, 128.6 (d, J = 1.2 Hz), 129.0, 129.2 (d, J = 3.6 Hz), 136.0 (d, J = 7.4 Hz), 138.4 (d, J = 15.8 Hz), 140.7 (d, J = 55.6 Hz), 144.4 (d, J = 11.2 Hz), 166.5; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 63.5; HRMS m/z calcd for $C_{27}H_{40}O_2PS$ (M + H$^+$) 459.2481, found 459.2508.

(*E*)-Dicyclohexyl(2-(1-phenylprop-1-en-2-yl)phenyl)-phosphine Sulfide (7a). Mp 160−161 °C (white solid), 49 mg (47%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09−2.00 (m, 20H), 2.29 (d, J = 1.4 Hz, 3H), 2.34−2.48 (m, 2H), 6.32 (s, 1H), 7.20−7.25 (m, 1H), 7.30−7.54 (m, 7H), 8.53 (ddd, J = 1.4, 7.7, 14.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 25.5 (br), 26.3 (d, J = 12.9 Hz), 26.5 (d, J = 13.4 Hz), 26.7 (br), 28.1 (br), 40.0 (d, J = 48.6 Hz), 126.90 (d, J = 11.4 Hz), 126.93 (d, J = 63.6 Hz), 127.2, 128.6, 128.7, 129.7 (d, J = 9.3 Hz), 130.1, 130.9 (d, J = 2.7 Hz), 136.5 (d, J = 10.8 Hz), 136.9, 138.5 (d, J = 1.4 Hz), 147.3 (d, J = 7.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 68.1; HRMS m/z calcd for $C_{27}H_{36}PS$ (M + H$^+$) 423.2270, found 423.2287.

(*E*)-Dicyclohexyl(2-(1,2-diphenylvinyl)phenyl)phosphine Sulfide (7b). Mp 196−197 °C (gray solid), 45 mg (37%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22−1.53 (m, 15H), 1.57−2.13 (m, 7H), 6.63 (s, 1H), 7.14−7.26 (m, 8H), 7.26−7.33 (m, 2H), 7.36−7.42 (m, 1H), 7.47−7.56 (m, 2H), 8.65 (ddd, J = 1.9, 8.5, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 26.2 (br, overlapped), 26.4, 27.6 (d, J = 2.6 Hz), 37.8 (d, J = 47.5 Hz), 127.4, 127.6 (d, J = 11.4 Hz), 128.1 (d, J = 61.4 Hz), 128.2, 128.4, 128.7, 129.4, 130.2, 130.8 (d, J = 2.7 Hz), 131.5, 133.5 (d, J = 9.4 Hz), 136.7, 137.7 (d, J = 11.6 Hz), 138.7, 142.9 (d, J = 2.6 Hz), 144.4 (d, J = 7.0 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 69.7; HRMS m/z calcd for $C_{32}H_{38}PS$ (M + H$^+$) 485.2426, found 485.2433.

(*E*)-(2-(1,2-Bis(4-chlorophenyl)vinyl)phenyl)dicyclohexyl-phosphine Sulfide (7c). Mp 192−193 °C (yellow solid), 37 mg (27%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.42−1.54 (m, 13H), 1.57−2.16 (m, 9H), 6.57 (s, 1H), 7.05−7.14 (m, 4H), 7.20−7.26 (m, 4H), 7.29−7.35 (m, 1H), 7.46−7.57 (m, 2H), 8.49−8.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 26.4 (br, overlapped), 27.5 (d, J = 2.1 Hz), 38.3 (d, J = 49.9 Hz), 127.8 (d, J = 11.2 Hz), 128.2 (d, J = 61.3 Hz), 128.8, 129.0, 130.56, 130.61, 130.9 (d, J = 2.7 Hz), 131.6, 133.3, 133.4 (d, J = 3.3 Hz), 134.4, 134.8, 137.1, 137.3 (d, J = 11.0 Hz), 142.2 (d, J = 1.4 Hz), 144.4 (d, J = 6.5 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 68.2; HRMS m/z calcd for $C_{32}H_{36}Cl_2PS$ (M + H$^+$) 553.1647, found 553.1646.

(*E*)-(2-(1,2-Bis(4-methoxyphenyl)vinyl)phenyl)dicyclohexyl-phosphine Sulfide (7d). (E:Z = 85:15) White solid, 18 mg (13%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21−1.52 (m, 16H), 1.60−2.10 (m, 6H), 3.72 (s, 3H, Z), 3.81 (s, 6H, E), 3.83 (s, 3H, Z), 6.46 (s, 1H, E), 6.58−6.65 (m, 2H, Z), 6.74−6.84 (m, 4H, E), 6.88−6.94 (m, 2H, Z), 7.04−7.17 (m, 4H, E), 7.31−7.35 (m, 1H, E), 7.32−7.40 (m, 2H, Z), 7.44−7.53 (m, 2H, E), 7.53−7.60 (m, 2H, Z), 7.66−7.75 (m, 1H, Z), 8.56−8.69 (m, 1H, E), 8.69−8.79 (m, 1H, Z); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5 (br), 25.4 (br, overlapped), 26.7 (d, J = 2.6 Hz), 36.6 (br), 54.2 (overlapped), 54.3 (E), 54.5 (Z), 112.6 (Z), 112.8 (E), 113.1 (E), 113.3 (Z), 126.3 (d, J = 11.3 Hz, E), 126.6 (d, J = 11.2 Hz, Z), 126.9 (Z), 127.1 (d, J = 61.8 Hz, E), 127.2 (d, J = 60.1 Hz, Z), 127.8 (Z), 127.9 (Z), 128.4 (E), 128.8 (E), 129.5 (Z), 129.6 (E), 129.7 (d, J = 2.6 Hz, E), 129.9 (E), 130.38 (E), 130.42 (Z), 130.6 (d, J = 2.7 Hz, Z), 132.2 (d, J = 9.5 Hz, Z), 132.4 (d, J = 9.4 Hz, E), 136.6 (d, J = 10.8 Hz, E), 137.1 (d, J = 10.7 Hz, Z), 137.9 (Z), 139.6 (E), 140.3 (d, J = 6.5 Hz, Z), 144.1 (d, J = 7.1 Hz, E), 157.7 (E), 158.0 (Z), 158.28 (Z), 158.33 (E); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 67.9 (Z), 69.7 (E); HRMS m/z calcd for $C_{34}H_{42}O_2PS$ (M + H$^+$) 545.2638, found 545.2636.

(*E*)-Dicyclohexyl(2-(1,2-di-p-tolylvinyl)phenyl)phosphine Sulfide (7e). (E:Z = 76:24) White solid, 17 mg (13%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26−1.53 (m, 16H), 1.59−1.91 (m, 6H), 2.23 (s, 3H, Z), 2.33 (s, 3H, E), 2.35 (s, 3H, E), 2.38 (s, 3H, Z), 6.54 (s, 1H, E), 6.73−6.82 (m, 2H, Z), 6.82−6.94 (m, 1H, E), 7.00−7.12 (m, 6H), 7.15−7.23 (m, 1H), 7.31−7.40 (m, 1H), 7.44−7.59 (m, 2H), 8.59−8.68 (m, 1H, E), 8.68−8.79 (m, 1H, Z); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2 (d, J = 2.9 Hz, Z), 21.4 (d, J = 2.6 Hz, E), 25.5 (br), 25.6 (br), 26.4 (br), 26.6 (br), 27.8 (br), 37.9 (br), 127.0 (Z), 127.5 (d, J = 11.4 Hz, E), 127.8 (d, J = 11.3 Hz, Z), 128.26 (d, J = 61.6 Hz, E), 128.31 (d, J = 61.1 Hz, Z), 129.1 (Z), 129.2 (E), 129.5 (E), 129.6 (E), 129.7 (Z), 129.8 (Z), 130.2 (E), 130.86 (d, J = 2.7 Hz, E), 130.93 (E), 131.0 (Z), 131.7 (d, J = 2.7 Hz, Z), 131.8 (Z), 133.27 (Z), 133.34 (d, J = 3.4 Hz, Z), 133.6 (d, J = 9.4 Hz, E), 134.1 (E), 136.2 (E), 137.4 (E), 137.75 (Z), 137.83 (d, J = 10.7 Hz, E), 138.15 (E), 138.24 (d, J = 11.2 Hz, Z), 140.7 (Z), 140.9 (d, J = 1.6 Hz, Z), 141.3 (d, J = 6.8 Hz, Z), 142.1 (d, J = 1.4 Hz, E), 145.1 (d, J = 7.0 Hz, E); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 69.9 (E), 68.0 (Z); HRMS m/z calcd for $C_{34}H_{42}PS$ (M + H$^+$) 513.2739, found 513.2737.

(*E*)-Dicyclohexyl(2-(1-phenylhex-1-en-2-yl)phenyl)phosphine Sulfide (7f). (E:Z = 97:3) Colorless oil, 34 mg (29%); hexane/ethyl acetate 95:5 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3H), 1.05−1.35 (m, 10H), 1.36−1.53 (m, 4H), 1.58−1.89 (m, 8H), 1.91−2.04 (m, 2H), 2.10−2.70 (m, 3H), 2.70−3.32 (br, 1H), 6.33 (s, 1H), 6.46 (s, 1H, Z), 7.15−7.22 (m, 1H), 7.28−7.34 (m, 1H), 7.37−7.49 (m, 6H), 8.45 (ddd, J = 1.9, 7.3, 14.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 23.0, 25.6 (d, J = 1.2 Hz), 26.3 (d, J = 13.9 Hz), 26.5 (d, J = 13.6 Hz), 26.7 (d, J = 1.9 Hz), 27.8(br), 30.8, 34.1, 39.4 (d, J = 48.7 Hz), 126.8 (d, J = 11.3 Hz), 126.9 (d, J = 63.5 Hz), 127.0, 128.57, 128.60, 130.1, 130.5 (d, J = 2.6 Hz), 131.1 (d, J =

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9.5 Hz), 136.0 (d, J = 11.0 Hz), 137.1, 143.8 (d, J = 1.8 Hz), 146.5 (d, J = 7.6 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 67.3 (E), 69.6 (Z); HRMS m/z calcd for $C_{30}H_{42}PS$ ($M + H^+$) 465.2739, found 465.2754.

(*E*)-(2-(6-Chloro-1-phenylhex-1-en-2-yl)phenyl)dicyclohexylphosphine Sulfide (7g). (E:Z = 93:7) Pale yellow oil, 28 mg (23%); hexane/ethyl acetate 90:10 (v/v, eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07−1.36 (m, 9H), 1.38−1.50 (m, 2H), 1.50−1.55 (m, 1H), 1.59−1.76 (m, 8H), 1.79−1.87 (m, 2H), 1.92−2.07 (m, 2H), 2.18−2.61 (m, 3H), 2.75−3.19 (m, 1H), 3.34−3.48 (m, 2H), 6.36 (s, 1H), 6.44 (s, 1H, Z), 7.17−7.23 (m, 1H), 7.27−7.33 (m, 1H), 7.38−7.51 (m, 6H), 8.28 (ddd, J = 1.4, 7.6, 13.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6 (br), 25.7, 26.4 (d, J = 13.4 Hz), 26.5 (d, J = 13.4 Hz), 26.6 (br), 27.5 (br), 32.6, 33.7, 39.6 (d, J = 48.4 Hz), 44.5, 126.8 (d, J = 11.3 Hz), 126.9 (d, J = 63.7 Hz), 127.0, 128.57, 128.59, 130.4, 130.5 (d, J = 2.7 Hz), 131.4 (d, J = 9.3 Hz), 135.1 (d, J = 10.4 Hz), 137.1, 143.1 (d, J = 2.2 Hz), 147.0 (d, J = 7.3 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 60.7 (Z), 65.3 (E); HRMS m/z calcd for $C_{30}H_{41}ClPS$ ($M + H^+$) 499.2350, found 499.2360.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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