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Synthesis of Cyclopropane-Containing Phosphorus Compounds by Radical Coupling of Butenylindium with Iodo Phosphorus Compounds

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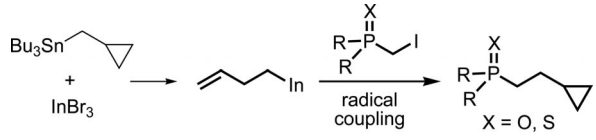
Keywords: Tin / Indium / Phosphorus / Radical reactions / C–C coupling / Cyclopropylmethylation

The radical coupling of α- or β-iodo phosphorus compounds such as iodo phosphonate, iodo phosphane oxide, and iodo phosphonothioate with butenylindium species, prepared by transmetalation between a (cyclopropylmethyl)stannane and $InBr_3$, afforded the corresponding cyclopropylmethylated products. The radical reaction was initiated by the radical species generated from butenylindium assisted by a small amount of oxygen. Butenylindium works not only as a cyclopropylmethylating reagent, but also as a radical initiator. For successful coupling, a tin/indium transmetalation was used, where it was important for the tin halide by-product to be inert to the reaction system. In addition, the transmetalation of a (cyclopropylmethyl)stannane and $InBr_3$ provided the dibutenylindium bromide as a single product, which smoothly coupled with the unstable phosphonyl radical species from the iodo phosphorus compound. A photochemical method (UV irradiation) was also applied and accelerated the coupling reaction. The cyclopropylmethylated phosphonate produced was a good intermediate in the Horner–Wadsworth–Emmons reaction and gave functionalized olefins bearing the cyclopropane moiety.

Introduction

Phosphonates have been recognized as highly valuable compounds in medicinal chemistry because of their potential biological activities.[1] Moreover, in the field of organic synthesis, they are widely used as important intermediates in the Horner–Wadsworth–Emmons (HWE) reaction.[2–4] Therefore, development of a synthetic method for more functionalized phosphonates is an important subject. An α-iodo phosphonate is a good functionalized candidate for radical coupling with an organometallic species.[5] However, its synthetic applications have been restricted to radical addition to alkenes or alkynes,[6] and no example of radical coupling reactions for α-iodo phosphonates with organometallic reagents has been reported, as far as we know. To develop this type of reaction, a new type of organometallic species is required. Recently, we found that a butenylindium species generated from the transmetalation between a (cyclopropylmethyl)stannane[7] and an indium halide was a useful reagent for radical coupling with α-iodocarbonyl compounds to afford cyclopropylmethylated carbonyl compounds.[8] Herein, we report the unprecedented radical coupling of the butenylindium species with iodo phosphorus compounds such as iodo phosphonate, iodo phosphane oxide, or iodo phosphonothioate (Scheme 1). This is also a useful route to produce phosphorus compounds bearing a cyclopropyl ring,[9,10] which has the potential for pharmacological utility.[11]



Scheme 1. Radical coupling of iodo phosphorus compounds with butenylindium generated by tin/indium transmetalation.

Results and Discussion

To optimize the reaction conditions, the effects of additives and solvents were investigated by performing the reaction of (cyclopropylmethyl)stannane **1** and diethyl (iodomethyl)phosphonate (**2a**) in a nitrogen-flushed flask (Table 1). First, we examined the coupling reaction using $InBr_3$ in toluene at room temperature. Although these conditions are considered optimal for radical coupling with α-iodo carbonyl compounds,[8] the reaction yield was low (Entry 1). Raising of the reaction temperature improved the yield to 48% (Entry 2). When hexane was used instead of toluene, the best results were obtained, furnishing **3a** in 74% yield (Entry 3).[12,13] Unfortunately, decreasing of the $InBr_3$ amount to a catalytic one afforded only traces of **3a** (Entry 4). Changing of the reaction solvent to 1,2-dichloroethane or acetonitrile resulted in decreased yields (Entries 5

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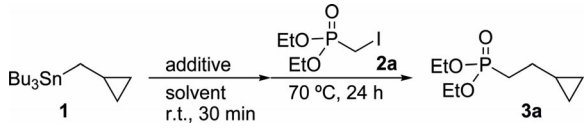
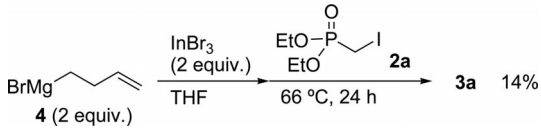
Table 1. Reaction of (cyclopropylmethyl)stannane **1** with diethyl (iodomethyl)phosphonate (**2a**).[a]



Entry	Additive	Solvent	Yield [%][b]
1[c]	$InBr_3$	toluene	18
2[d]	$InBr_3$	toluene	48
3	$InBr_3$	hexane	74
4[e]	$InBr_3$	hexane	<5
5	$InBr_3$	$ClCH_2CH_2Cl$	57
6	$InBr_3$	MeCN	15
7	InI_3	hexane	57
8	$GaCl_3$	hexane	28
9	$BF_3{\cdot}OEt_2$	hexane	0
10	$AlCl_3$	hexane	0
11[f]	$InBr_3$	hexane	0
12[g]	$InBr_3$	hexane	8

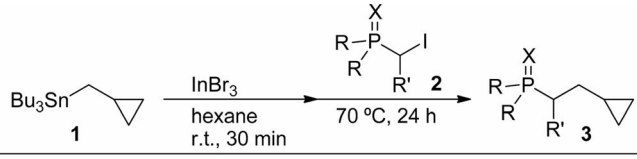
[a] Unless otherwise noted, reactions were carried out in a nitrogen-flushed flask by using 1.6 mmol of **1**, 0.8 mmol of **2a**, and 0.8 mmol of additive. [b] Determined by ^1H NMR spectroscopy. [c] At room temperature. [d] At 80 °C. [e] $InBr_3$ (0.08 mmol) was used. [f] TEMPO (0.08 mmol) was added. [g] In a nitrogen-filled glovebox ($O_2 < 0.1$ ppm).

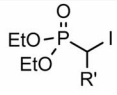
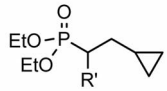
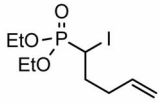
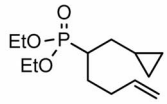
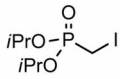
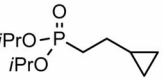
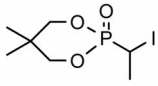
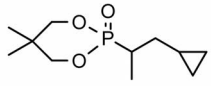
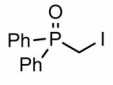
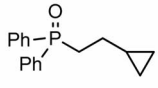
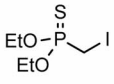
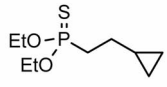
and 6). The use of InI_3 instead of $InBr_3$ gave a lower yield (Entry 7). In the reaction with alkyl chlorides, gallium trichloride was a good catalyst,[14] but it was less effective for this coupling (Entry 8). Other group 13 Lewis acids ($BF_3{\cdot}OEt_2$ and $AlCl_3$) were not effective at all (Entries 9 and 10). The loading of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a radical inhibitor completely suppressed the coupling (Entry 11). When the reaction was carried out under severely restricted conditions – free of oxygen – in a nitrogen-filled glove box ($O_2 < 0.1$ ppm), the coupling was significantly depressed (Entry 12). These results indicate that this reaction follows a radical mechanism and is promoted by a considerably small amount of O_2. It is assumed that the in situ generated butenylindium species acts as a radical initiator as well as an alkylating reagent.



Scheme 2. Reaction of the butenylindium species prepared by Grignard reagent and $InBr_3$.

Table 2. Cyclopropylmethylation of iodo phosphorus compounds.[a]



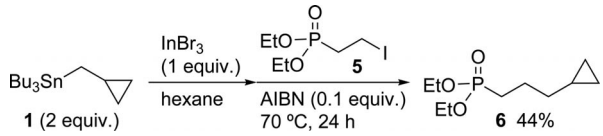
Entry	Iodophosphorus compound		Product		Yield [%][b]
1		R' = H **2a**		**3a**	74 (60)
2		R' = Me **2b**		**3b**	68 (50)
3		R' = Et **2c**		**3c**	57 (32)
4		**2d**		**3d**	35 (22)
5		**2e**		**3e**	78 (68)
6		**2f**		**3f**	67 (58)
7		**2g**		**3g**	75 (52)
8		**2h**		**3h**	31 (21)

[a] All reactions were carried out in a nitrogen-flushed flask by using 1.6 mmol of **1**, 0.8 mmol of **2**, and 0.8 mmol of $InBr_3$. [b] Determined by ^1H NMR spectroscopy. Values in parentheses indicate isolated yields after column chromatography.

Oshima et al. have reported a radical reaction of α-halo carbonyl compounds with the butenylindium species prepared by transmetalation between 3-butenylmagnesium bromide (**4**) and indium halide.[15] However, application to the coupling with **2a** failed, and most of the unreacted **2a** was recovered (Scheme 2). The low yield was probably caused by the magnesium salt ($MgBr_2$) generated in situ. In fact, the addition of $MgBr_2$ to the optimized tin/indium system (Table 1, Entry 3) decreased the yield from 74 to 8%.[16] The preparation of a butenylindium species by tin/indium transmetalation, where the by-product Bu_3SnBr is inert to the reaction system due to its low Lewis acidity, is essential for successful coupling with α-iodo phosphonates.

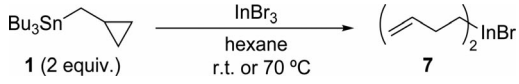
With the optimized system in hand, couplings with various types of iodo phosphorus compounds succeeded (Table 2).[17] Methyl- and ethyl-substituted secondary iodo phosphonates **2b** and **2c** effectively gave the corresponding products **3b** and **3c**, respectively (Entries 2 and 3). In the case of iodo phosphonate **2d**, which contains an olefin moiety, the coupling reaction selectively proceeded at the iodo site to afford the desired product **3d** (Entry 4). The coupling with butenylindium overcame the difficulty of the selective synthesis of **3d**, for instance, by a sequential allylation/cyclopropanation route to **2d**. This coupling reaction was hardly affected by the alkoxy groups on the phosphorus atom. For example, sterically demanding isopropyl-substituted phosphonate **2e** furnished the product **3e** in high yield (Entry 5). In addition, phosphonate **3f**, bearing a cyclic alkoxy moiety, was also obtained (Entry 6). Iodo phosphane oxide **2g** and iodo phosphonothioate **2h** were both viable reagents (Entries 7 and 8).

Interestingly, cyclopropylmethylation occurred even with β-iodo phosphonate **5** to give the corresponding product **6**, although a radical initiator was required as shown in Scheme 3.[18,19] This result expands the scope of the synthesis of cyclopropane-containing phosphorus compounds. When 1-iodoundecane was used instead of **5**, no product was obtained. This result indicates that the phosphonate moiety of **5** is involved in the stabilization of the β-radical.



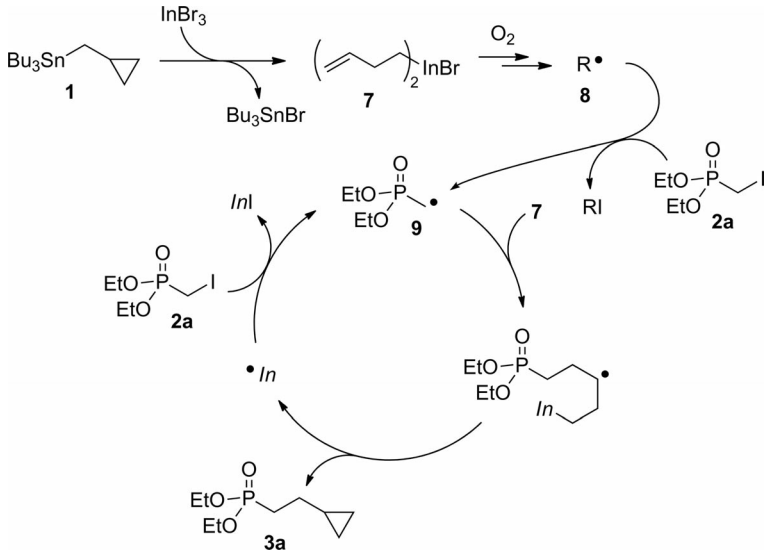
Scheme 3. Cyclopropylmethylation of β-iodo phosphonate **5**.

In order to investigate the transmetalation step under optimal conditions, a mixture of **1** and $InBr_3$ (**1**/$InBr_3$, 2:1) in hexane was monitored by NMR spectroscopy (Scheme 4, see the Supporting Information for details). When the transmetalation was carried out at room temperature for 30 min, small signals corresponding to dibutenylindium bromide (**7**) appeared as a single product, and most of **1** did not react.[20] This result strongly indicates a predominant formation of the dibutenylindium species over the monobutenylindium species. Meanwhile, transmetalation at 70 °C was completed within 30 min to give **7** quantitatively. Dibutenylindium **7** was stable enough under the reaction conditions (70 °C), and with no decomposition it should contribute to the radical coupling.



Scheme 4. Transmetalation between **1** and $InBr_3$.

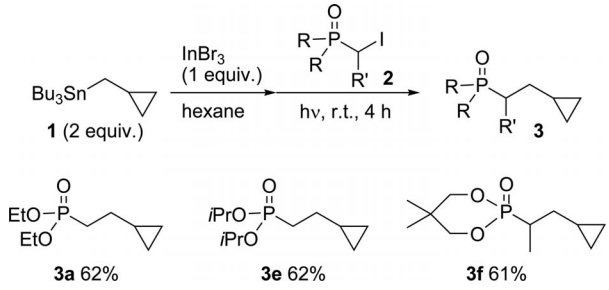
A plausible reaction mechanism is shown in Scheme 5. Transmetalation between (cyclopropylmethyl)stannane **1** and $InBr_3$ affords dibutenylindium bromide (**7**). In the radical initiation step, a small amount of radical species **8** (structure not fully determined) generated from **7** with O_2 abstracts an iodo radical from iodo phosphonate **2a** to pro-



Scheme 5. Plausible reaction mechanism.

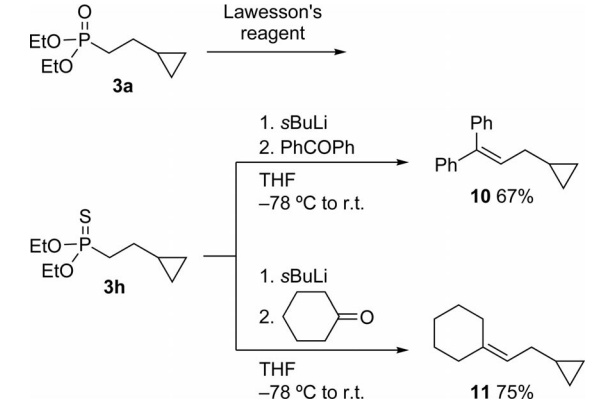
duce the α-phosphonyl radical **9**.[21,22] The fast trapping of **9** by dibutenylindium compound **7** is followed by intramolecular cyclization to give cyclopropylmethylated product **3a** along with the eliminated indium radical. This indium radical reacts with **2a** to regenerate the phosphonyl radical **9**, which completes the radical chain reaction. Decomposition of the indium species generated in the final step may be the reason for the catalytic cycle not being achieved (see Table 1, Entry 4).[23] In addition, the effective trapping of the unstable radical **9** requires the participation of the reactive dibutenylindium species, but not of the monobutenyl species.[21,24]

For this radical coupling reaction, we successfully applied a photochemical method (Scheme 6). UV irradiation of **1** with iodo phosphonate **2a** at room temperature afforded **3a** in a 62% yield, and the coupling reaction was completed within 4 h. Isopropyl-substituted **3e** and cyclic phosphonate **3f** were also obtained in satisfactory yields in a shorter reaction period compared with reactions under heating conditions.



Scheme 6. Photochemical cyclopropylmethylation.

Finally, the synthetic use of cyclopropylmethylated phosphonate **3a** as a precursor of functionalized olefins is demonstrated in Scheme 7. Phosphonate **3a** was treated with Lawesson's reagent, and the resulting phosphonothioate **3h** underwent Horner–Wadsworth–Emmons-type reactions.[25,26] The deprotonation of **3h** with *s*BuLi was followed by a reaction with benzophenone to produce trisubstituted alkene **10** without cleavage of the cyclopropyl ring. The aliphatic ketone cyclohexanone was also converted into the corresponding alkene **11** in 75% yield. This is a useful



Scheme 7. Synthesis of alkenes by an HWE-type reaction.

and reliable method for the synthesis of alkenes bearing a cyclopropane moiety, which can be easily transformed to further functionalized compounds.

Conclusions

We have developed a radical coupling reaction of the butenylindium species with α- or β-iodo phosphorus compounds to give the corresponding cyclopropylmethylated products, which are an important class of functionalized compounds for pharmaceutics, biological chemistry, and organic synthesis. To promote this radical coupling, tin/indium transmetalation is indispensable for the preparation of the butenylindium species.

Experimental Section

General: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{13}C off-resonance techniques, HMQC (heteronuclear multiple quantum correlation), HMBC (heteronuclear multiple bond correlation), and IR spectroscopy; MS and HRMS analyses; and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS (tetramethylsilane) as an internal standard. ^{119}Sn (150 MHz) spectra were obtained with Me_4Sn as an external standard. ^{31}P (160 MHz) spectra were obtained with 85 wt.-% D_3PO_4 in D_2O as an external standard. IR spectra were recorded as thin films or solids in KBr pellets. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (Merck C60 or Fuji Silysia FL100DX). Bulb-to-bulb distillation (Kugelrohr) was accomplished at the indicated oven temperature and pressure. Yields were determined by ^{1}H NMR spectroscopy using an internal standard.

Materials: Dehydrated hexane, toluene, acetonitrile, and tetrahydrofuran (THF) were purchased and used as obtained. Prior to use, 1,2-dichloroethane was distilled from P_2O_5. The additives examined in Table 1 were also purchased from commercial sources. (Cyclopropylmethyl)stannane **1**[8,14] was prepared according to a known method, and this compound is reported. Iodo phosphorus compounds **2b**,[27] **2e**,[6b] **2g**,[6b] and **5**[6b] were prepared according to known methods, and these compounds are reported. Iodo phosphorus compounds **2c**,[27] **2d**,[27] **2f**,[27] and **2h**[28] were prepared according to known methods. Diethyl (iodomethyl)phosphonate (**2a**), benzophenone, and cyclohexanone are commercially available. All other reagents are commercially available.

Preparation of Tributyl(cyclopropylmethyl)stannane (1):[8] To a flask containing magnesium (230 mmol) in THF (150 mL) was added Bu_3SnCl (200 mmol). The mixture was cooled to 0 °C, and allyl chloride (230 mmol) was added. The mixture was stirred and irradiated with ultrasound at 0 °C for 1 h. After 2 h, the reaction was quenched with water (200 mL), and the organic layer was separated. Hexane (200 mL) was added, and the organic layer was washed with water (100 mL), NaCl (saturated aqueous, 100 mL), and NH_4F (10% aqueous, 100 mL). After drying with $MgSO_4$, the solvent was evaporated, and the residue was purified by column chromatography (hexane) on silica gel to give allyltributylstannane (57.2 g, 86%). To a solution of allyltributylstannane (30 mmol) in diethyl ether (40 mL), diethylzinc (1.0 M in hexane, 43 mL) was added. To the mixture was added dropwise a solution of diiodomethane (90 mmol) in diethyl ether (30 mL) within 1 h. The reaction mixture was stirred at room temperature for 4 h and then

quenched with NH_4Cl (saturated aqueous, 100 mL). Hexane (200 mL) was added, and the organic layer was washed with NH_4Cl (saturated aqueous, 100 mL), NaCl (saturated aqueous, 100 mL), and NH_4F (10% aqueous, 100 mL). After drying with $MgSO_4$, the solvent was evaporated, and the residue was purified by column chromatography (hexane) on silica gel to give **1** (9.63 g, 85%, 84% purity, a small portion was analyzed by ^1H NMR using an internal standard). The product was used in the cyclopropylmethylation reaction without further purification. The analytical data for this compound match that reported previously.

Diethyl (1-Iodoethyl)phosphonate (2b):[27] To a mixture of diisopropylamine (2.56 g, 25.2 mmol) and THF (40 mL) at –78 °C was slowly added *n*BuLi (1.6 M in hexane, 15.2 mL). After stirring for 5 min, diethyl ethylphosphonate (1.67 g, 10.0 mmol) in THF (20 mL) was added over 15 min, and Me_3SiCl (1.19 g, 11 mmol) in THF (20 mL) was rapidly added. The mixture was warmed slowly to room temperature, stirred for 15 min, and cooled again to –78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly, and the mixture was warmed to 0 °C. After stirring for 15 min, EtOLi (1.0 M in ethanol, 20 mL) was added, and the reaction mixture was quenched by the addition of an aqueous solution of HCl (1.0 M, 20 mL). After extraction with ethyl acetate (3 × 30 mL), the collected organic layers were washed with brine (2 × 30 mL) and water (2 × 30 mL) and then dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate, 70:30) to give pure **2b** as a yellow liquid (1.60 g, 54%). The analytical data for this compound match that previously reported.

Diethyl (1-Iodopropyl)phosphonate (2c): To a mixture of diisopropylamine (2.62 g, 26 mmol) and THF (40 mL) at –78 °C was slowly added *n*BuLi (1.6 M in hexane, 15 mL). After stirring for 5 min, diethyl propylphosphonate (1.79 g, 9.6 mmol) in THF (20 mL) was added over 15 min, and Me_3SiCl (1.40 g, 12.8 mmol) in THF (20 mL) was rapidly added. The mixture was warmed slowly to room temperature, stirred for 15 min, and cooled again to –78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly, and the mixture was warmed to 0 °C. After stirring for 15 min, EtOLi (1.0 M in ethanol, 20 mL) was added, and the reaction mixture was quenched by the addition of an aqueous solution of HCl (1.0 M, 20 mL). The reaction mixture was extracted with ethyl acetate (3 × 30 mL), and the collected organic layers were washed with brine (2 × 30 mL) and water (2 × 30 mL) and then dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate, 70:30) to give pure **2c** as a yellow liquid (2.5 g, 82%). IR (neat): $\tilde{\nu}$ = 1254 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.25–4.17 (m, 4 H, 2 CH_2OP), 3.72 (ddd, $^2J_{P,H}$ = 10.5 Hz, J = 10.5, 4.0 Hz, 1 H, PCH), 2.06–1.92 (m, 1 H, PCHICH^A), 1.90–1.78 (m, 1 H, PCHICH^B), 1.36 (t, J = 7.0 Hz, 6 H, 2 CH_3CH$_2$O), 1.10 (t, J = 7.0 Hz, 3 H, PCHCH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.5, 63.4, 26.9, 20.3, 16.3, 15.0 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 36.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 306 (15) $[M]^+$, 179 (65) $[M – I]^+$, 151 (27), 123 (100), 109 (52), 81 (31). HRMS (EI, 70 eV): calcd. for $C_7H_{16}IO_3P$ $[M]^+$ 303.9882; found 303.9885.

Preparation of Diethyl (1-Iodopent-4-enyl)phosphonate (2d): A mixture of 5-bromo-1-pentene (4.32 g, 29 mmol) and $P(OEt)_3$ (5.17 g, 31 mmol) was heated to 150 °C and stirred for 21 h. The volatile compounds were evaporated, and the residue was purified by distillation under reduced pressure to give diethyl pent-4-enylphosphonate (2.86 g, 48%); b.p. 120 °C/0.20 Torr. The analytical data for this compound match that previously reported.[29] To a mixture of diisopropylamine (2.75 g, 27 mmol) and THF (40 mL) at –78 °C was slowly added *n*BuLi (1.6 M in hexane, 16 mL). After stirring for 5 min, the diethyl pent-4-enylphosphonate (2.16 g, 10.4 mmol) in THF (20 mL) was added over 15 min, and Me_3SiCl (1.40 g, 12.8 mmol) in THF (20 mL) was rapidly added. The mixture was slowly warmed to room temperature, stirred for 30 min, and cooled again to –78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was added slowly to the mixture, and the reaction mixture was warmed to 0 °C. After stirring for 1 h, EtOLi (1.0 M in ethanol, 20 mL) was added, and the reaction mixture was quenched with an aqueous solution of sodium thiosulfate (20 mL). The reaction mixture was extracted with ethyl acetate (3 × 30 mL), and the collected organic layers were washed with brine (2 × 30 mL) and water (2 × 30 mL) and then dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate, 50:50). Further purification by distillation under reduced pressure gave **2d** as a yellow liquid (2.09 g, 63%); b.p. 110 °C/0.20 Torr. IR (neat): $\tilde{\nu}$ = 1245 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.73 (m, 1 H, *H*C=CH$_2$), 5.13–5.05 (d, J = 17 Hz, 1 H, HC=CH*H*), 5.02–5.00 (d, J = 10 Hz, 1 H, HC=C*H*H), 4.24–4.16 (m, 4 H, 2 CH_2OP), 3.77 (ddd, J = 10, 5 Hz, $^2J_{P,H}$ = 5 Hz, 1 H, PCH), 2.45–2.37 (m, 1 H, PCHCH$_2$C*H*H), 2.20–2.11 (m, 1 H, PCHCH$_2$CH*H*), 2.05–1.88 (m, 2 H, PCHCH_2), 1.36 (t, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 116.6, 63.6, 63.5, 33.5, 32.0, 17.1, 16.3 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 36.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 332 (9) $[M]^+$, 205 (100) $[M – I]^+$, 177 (22), 165 (21), 149 (81), 109 (40), 81 (20), 67 (44). HRMS (EI, 70 eV): calcd. for $C_9H_{18}IO_3P$ $[M]^+$ 332.0038; found 332.0036.

Preparation of Diisopropyl (1-Iodoethyl)phosphonate (2e):[30] To a mixture of diisopropyl phosphite (3.32 g, 20.0 mmol) and paraformaldehyde (0.65 g, 22 mmol) was added triethylamine (0.23 g, 2.3 mmol). The mixture was heated to 110 °C for 4 h and concentrated to give diisopropyl (hydroxymethyl)phosphonate (3.68 g, 94%).[31] The analytical data for this compound match that previously reported.[30] To a solution of the diisopropyl (hydroxymethyl)phosphonate (3.68 g, 18.8 mmol) in pyridine (10 mL) was added *p*-toluenesulfonyl chloride (4.13 g, 20.0 mmol) at 0 °C over 1 h. The mixture was warmed to room temperature. After stirring for 10 h, the reaction mixture was quenched with an aqueous solution of HCl (1 M, 50 mL) and extracted with ethyl acetate (3 × 30 mL). The collected organic layers were dried with $MgSO_4$, and the solvent was evaporated to give diisopropyl {[(*p*-tolylsulfonyl)oxy]methyl}phosphonate (4.99 g, 76%). The analytical data for this compound match that previously reported.[30] To a solution of the diisopropyl {[(*p*-tolylsulfonyl)oxy]methyl}phosphonate (4.99 g, 14.2 mmol) in acetone (60 mL) was added sodium iodide (8.65 g, 57.7 mmol). The mixture was heated to 75 °C for 24 h, quenched with sodium thiosulfate (saturated aqueous, 100 mL), and extracted with ethyl acetate (3 × 100 mL). The collected organic layers were dried with $MgSO_4$, and the solvents were evaporated. The crude product was purified by distillation under reduced pressure to give pure **2e** as a colorless liquid (2.6 g, 59%). The analytical data for this compound match that previously reported.

Preparation of 2-(1-Iodoethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (2f): A mixture of ethylphosphonic dichloride (2.93 g, 19.9 mmol) and 2,2-dimethyl-1,3-propanediol (2.12 g, 20.4 mmol) was stirred at room temperature for 15 min and heated at 50 °C for 1 h. Then $NaHCO_3$ (saturated aqueous, 100 mL) was added, and the mixture was extracted with dichloromethane (3 × 100 mL). The collected organic layers were dried with $MgSO_4$, and the solvent was evaporated to give 2-ethyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one as a white solid (2.95 g, 83%).[32] The analytical data for this compound matched that previously reported.[33] To a solution of *s*BuLi (1.0 M in hexane, 10 mL) in THF (60 mL) was slowly

added the 2-ethyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (1.76 g, 10 mmol) in THF (30 mL). After 30 min, Me_3SiCl (2.72 g, 11.3 mmol) in THF (20 mL) was rapidly added. The mixture was slowly warmed to room temperature, stirred for 30 min, and cooled again to –78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was slowly added, and the mixture was warmed to 0 °C. After stirring for 1 h, EtOLi (1.0 M in ethanol, 20 mL) was added, and the reaction mixture was quenched with sodium thiosulfate (saturated aqueous, 20 mL). The reaction mixture was extracted with ethyl acetate (3 × 30 mL), and the collected organic layers were washed with brine (2 × 30 mL) and water (2 × 30 mL) and then dried with $MgSO_4$. The solvent was evaporated, and the residue was washed with diethyl ether to give pure **2f** as a white solid (0.59 g, 20%); m.p. 200–202 °C. IR (KBr): $\tilde{\nu}$ = 1265 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.28–4.22 (m, 2 H, two protons of 4-H and/or 6-H), 4.03–3.94 (m, 3 H, two protons of 4-H and/or 6-H and PC*H*), 2.06 (dd, J = 7.7 Hz, $^3J_{P,H}$ = 17 Hz, 3 H, PCHCH_3), 1.15 (s, 3 H, 5-Me^B), 1.07 (s, 3 H, 5-Me^A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.9, 76.8, 33.1, 22.0, 21.8, 21.7, 4.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 304 (39) $[M]^+$, 177 (100) $[M - I]^+$, 149 (48) $[M - CHICH_3]^+$, 109 (52), 69 (91), 56 (26), 41 (38). HRMS (EI, 70 eV): calcd. for $C_7H_{14}IO_3P$ $[M]^+$ 303.9725; found 303.9712. $C_7H_{14}O_3PI$ (304.06): calcd. C 27.65, H 4.64, I 41.74, O 15.79, P 10.19; found C 27.82, H 4.35, I 41.46.

Preparation of (Iodomethyl)diphenylphosphane Oxide (2g):[34] To a mixture of HCl (37.8 mL) and formaldehyde (37 wt.-% in water, 37.8 mL) was added chlorodiphenylphosphane (4.61 g, 21.0 mmol). The reaction mixture was heated to 100 °C for 18 h and neutralized with aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), and the collected organic layers were dried with $MgSO_4$. The solvent was evaporated, and the resulting crude product was washed with hexane to obtain pure (hydroxymethyl)-diphenylphosphane oxide as a white solid (3.50 g, 71%).[35] The analytical data for this compound match that previously reported.[35] To a solution of the (hydroxymethyl)diphenylphosphane oxide (3.35 g, 14.4 mmol) in CH_2Cl_2 (50 mL) was slowly added triethylamine (1.68 g, 16.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and cooled again to 0 °C. Then, *p*-tosyl chloride (3.30 g, 16.0 mmol) was added. The reaction mixture was kept at 0 °C for 30 min and stirred at room temperature for 4 h. After quenching with water (50 mL), the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL). The collected organic layers were dried with $MgSO_4$, and the solvent was evaporated. The crude product was recrystallized (CH_2Cl_2/Et_2O, 1:9) to give pure diphenyl{[(*p*-tolylsulfonyl)oxy]methyl}phosphane oxide as a white solid (3.93 g, 71%).[36] The analytical data for this compound match that previously reported.[36] To a solution of the diphenyl{[(*p*-tolylsulfonyl)oxy]methyl}phosphane oxide (3.86 g, 10.0 mmol) in acetone (200 mL) was added sodium iodide (5.99 g, 40.0 mmol). The mixture was heated to 75 °C for 24 h, quenched with sodium thiosulfate (saturated aqueous, 100 mL), and extracted with ethyl acetate (3 × 100 mL). The collected organic layers were dried with $MgSO_4$, and the solvent was evaporated. The crude product was washed with hexane to give pure **2g** as a white solid (3.0 g, 88%). The analytical data for this compound match that previously reported.

***O*,*O*′-Diethyl (Iodomethyl)phosphonothioate (2h):** To a mixture of diethyl (iodomethyl)phosphonate (0.832 g, 2.99 mmol) and toluene (15 mL) was added Lawesson's reagent (0.707 g, 1.75 mmol). The reaction mixture was stirred at 120 °C for 8 h, and the solvent was evaporated to give the crude product. Purification by distillation under reduced pressure gave **2h** as a colorless liquid (0.70 g, 80%); b.p. 100 °C/0.14 Torr. IR (neat): $\tilde{\nu}$ = 1022 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.25–4.09 (m, 4 H, 2 CH_2OP), 3.34 (d, $^2J_{P,H}$ = 7.5 Hz, 2 H, PCH_2), 1.35 (t, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.9, 16.0, –3.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 99.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 294 (17) $[M]^+$, 167 (100) $[(CH_3CH_2O)_2PSCH_2]^+$, 111 (41). HRMS (EI, 70 eV): calcd. for $C_5H_{11}IO_2PS$ $[M]^+$ 293.9340; found 293.9337. $C_5H_{12}IO_2PS$ (294.09): calcd. C 20.42, H 4.11; found C 20.48. H 3.93.

Diethyl (2-Iodoethyl)phosphonate (5):[6b] To a solution of diethyl (2-bromoethyl)phosphonate (2.45 g, 10.0 mmol) in acetone (160 mL) was added sodium iodide (6.01 g, 40.1 mmol). The mixture was heated to 75 °C for 24 h, quenched with sodium thiosulfate (saturated aqueous, 100 mL), and extracted with ethyl acetate (3 × 100 mL). The collected organic layers were dried with $MgSO_4$ and concentrated to give **5** as a colorless liquid (2.86 g, 98%). The analytical data for this compound match that previously reported.

Typical Procedure for the Reaction of (Cyclopropylmethyl)stannane 1 and Diethyl (Iodomethyl)phosphonate (2a): Table 1, Entry 3. To a suspension of $InBr_3$ (0.8 mmol) and hexane (1 mL) was added (cyclopropylmethyl)stannane **1** (1.6 mmol). The mixture was stirred at room temperature for 30 min, and iodo phosphonate **2a** (0.8 mmol) was added with heating at 70 °C. After stirring for 24 h, NH_4F (10% aqueous, 20 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 20 mL). The collected organic layers were dried with $MgSO_4$. Concentration of the diethyl ether solution gave crude **2a**, which was analyzed by NMR spectroscopy. Details for further purification are described under Product Data below.

Experimental Procedure for the Reaction of (Cyclopropylmethyl)-stannane 1 and Diethyl (Iodomethyl)phosphonate (2a) Under Oxygen-Free Conditions: Table 1, Entry 12. A side-necked sealable tube and screw-cap were placed in a nitrogen-filled glove box. In the glove box, (cyclopropylmethyl)stannane **1** (1.6 mmol) was added to a suspension of $InBr_3$ (0.8 mmol) in hexane (1 mL). The mixture was stirred at room temperature for 30 min, and iodo phosphonate **2a** (0.8 mmol) was added. The reaction tube was sealed with the screw-cap. Outside the glove box, the sealed reaction tube was heated to 70 °C. After stirring for 24 h, NH_4F (10% aqueous, 20 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 20 mL). The collected organic layers were dried with $MgSO_4$. Concentration of the diethyl ether solution gave the crude product, which was analyzed by NMR spectroscopy.

Experimental Procedure for the Reaction of Tributyl[(1-methyl-cyclopropyl)methyl]stannane and Diethyl (Iodomethyl)phosphonate (2a):[13] According to the typical procedure, $InBr_3$ (0.284 g, 0.8 mmol), (1-methylcyclopropyl)methyltributylstannane[14] (0.630 g, 1.6 mmol, 91% purity), and diethyl iodomethylphosphonate (**2a**, 0.228 g, 0.8 mmol) gave the crude product which was analyzed by NMR spectroscopy.

Experimental Procedure for the Reaction of the Butenylindium Species Prepared by Grignard Reagent and $InBr_3$: Scheme 2. 3-Butenylmagnesium bromide (**4**, 1.0 M in THF) was prepared by mixing magnesium (4 mmol) and 4-bromo-1-butene (4 mmol) in THF (4 mL) at room temperature for 30 min. To a solution of $InBr_3$ (1.6 mmol) in THF (1 mL) was added 3-butenylmagnesium bromide (**4**, 1.6 mmol). The mixture was stirred at room temperature for 30 min, and iodo phosphonate **2a** (0.8 mmol) was added with heating at 66 °C. After stirring for 24 h, water was added, and the reaction mixture was extracted with diethyl ether (3 × 20 mL). The collected organic layers were dried with $MgSO_4$. Concentration of the diethyl ether solution gave the crude product, which was analyzed by NMR spectroscopy.

NMR Study of Transmetalation Between (Cyclopropylmethyl)-stannane 1 and $InBr_3$: Scheme 4. A mixture of (cyclopropylmethyl)-stannane **1** and $InBr_3$ (**1**/$InBr_3$, 2:1) in hexane was prepared in a nitrogen-flushed flask. After mixing at room temperature or 70 °C, the mixture was transferred into an NMR tube ([D_6]benzene as an external standard); the resulting spectrum can be found in the Supporting Information.

Experimental Procedure for the Reaction of (Cyclopropylmethyl)-stannane 1 and Diethyl (Iodomethyl)phosphonate (2a) Under UV Irradiation Conditions: Scheme 6. To a suspension of $InBr_3$ (0.8 mmol) and hexane (1 mL) was added (cyclopropylmethyl)-stannane **1** (1.6 mmol). The mixture was stirred at room temperature for 2 h, and diethyl (iodomethyl)phosphonate (**2a**, 0.8 mmol) was added. The mixture was placed at a distance of approximately 10 cm from a 300 W high-pressure mercury lamp for 4 h. NH_4F (10% aqueous, 20 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 20 mL). The collected organic layers were dried with $MgSO_4$ and concentrated to give the crude product, which was analyzed by NMR spectroscopy. Purification by column chromatography (hexane/ethyl acetate, 70:30) gave product **3a**.

Typical Procedure for the Synthesis of Alkenes by Horner–Wadsworth–Emmons (HWE) Type Reaction: Scheme 7. To a solution of *O*,*O*′-diethyl (2-cyclopropylethyl)phosphonothioate (**3h**, 0.23 mmol) in THF (2 mL) was slowly added *s*BuLi (1.0 M in hexane, 0.30 mL) at –78 °C, and the mixture was stirred for 15 min. Benzophenone (0.24 mmol) in THF (2 mL) was slowly added, and the mixture was warmed to room temperature and stirred for 18 h. Then, NH_4Cl (saturated aqueous, 10 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 10 mL). The collected organic layers were dried with $MgSO_4$, and the solvent was evaporated to give the crude product. Purification by column chromatography (hexane, 200 mL) gave product **10**.

Preparation of *O*,*O*′-Diethyl (2-Cyclopropylethyl)phosphonothioate (3h) with Lawesson's Reagent: Scheme 7. To a mixture of diethyl (2-cyclopropylethyl)phosphonate (**3a**, 0.136 g, 0.66 mmol) and toluene (3 mL) was added Lawesson's reagent (0.157 g, 0.39 mmol). The reaction mixture was stirred at 125 °C for 4 h, and the solvent was evaporated to give the crude product. Purification by distillation under reduced pressure gave product **3h** as a colorless liquid (0.077 g, 53%).

Product Data: Spectral data for the products are shown in the Supporting Information.

Diethyl (2-Cyclopropylethyl)phosphonate (3a): According to the typical procedure, $InBr_3$ (0.283 g, 0.80 mmol), **1** (0.637 g, 1.55 mmol, 84% purity), and **2a** (0.224 g, 0.80 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded product **3a** (0.100 g, 60%). Compound **3a** was further purified by distillation under reduced pressure; b.p. 90 °C/0.2 Torr. IR (neat): $\tilde{\nu}$ = 1250 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.16–4.02 (m, 4 H, 2 CH_2OP), 1.89–1.80 (m, including $^2J_{P,H}$ = 18 Hz, 2 H, PCH_2), 1.54–1.45 (m, 2 H, PCH_2CH_2), 1.32 (t, J = 7.2 Hz, 6 H, 2 CH_3), 0.81–0.71 (m, 1 H, PCH_2CH_2CH), 0.47–0.42 (m, 2 H), 0.08–0.05 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.2, 27.5, 25.5, 16.3, 11.6, 4.4 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 46.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 206 (10) $[M]^+$, 191 (60) $[M - CH_3]^+$, 179 (32), 178 (52) $[M - C_2H_4]^+$, 165 (24) $[M - C_3H_5]^+$, 163 (40), 152 (69), 151 (42) $[M - CH_2C_3H_5]^+$, 150 (41), 149 (34), 138 (67), 137 (31) $[M - CH_2CH_2C_3H_5]^+$, 135 (79), 134 (32), 133 (48), 125 (95), 124 (38), 123 (21), 111 (52), 110 (23), 109 (100), 108 (26), 97 (99), 96 (53), 93 (21), 82 (39), 81 (61), 80 (21), 69 (26) $[CH_2CH_2C_3H_5]^+$, 68 (38), 67 (40), 65 (28), 41 (41) $[C_3H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_9H_{19}O_3P$ 206.1072; found 206.1067.

Diethyl [1-(Cyclopropylmethyl)ethyl]phosphonate (3b): According to the typical procedure, $InBr_3$ (0.282 g, 0.80 mmol), **1** (0.555 g, 1.59 mmol, 99% purity), and **2b** (0.216 g, 0.74 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 50:50) afforded product **3b** (0.082 g, 50%). Further purification by distillation under reduced pressure gave **3b** as a colorless liquid (0.050 g, 31%); b.p. 75 °C/0.22 Torr. IR (neat): $\tilde{\nu}$ = 1238 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.14–4.05 (m, 4 H, 2 CH_2OP), 2.04–1.88 (m, 2 H, PCH_2), 1.62–1.52 (m, 1 H, PCH_2CH), 1.47–1.35 (m, 1 H, PCHCH*H*), 1.32 (t, 6 H, 2 CH_3CH_2OP), 1.25 (dd, J = 18 Hz, J = 7.0 Hz, 3 H, $PCHCH_3$), 0.85–0.75 (m, 1 H, $PCHCH_2CH$), 0.55–0.38 (m, 2 H), 0.15 to –0.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.4, 61.3, 35.1, 31.6, 16.5, 13.3, 9.2, 5.7, 3.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 49.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 220 (47) $[M]^+$, 205 (43) $[M - CH_3]^+$, 192 (25) $[M - CH_3CH]^+$, 179 (30) $[M - C_3H_5]^+$, 177 (27), 166 (68), 165 (35) $[M - CH_2C_3H_5]^+$, 152 (28), 149 (46), 147 (25), 139 (50), 138 (96) $[(CH_3CH_2O)_2PO]^+$, 123 (29), 111 (100), 110 (37), 109 (60), 82 (54) $[M - (CH_3CH_2O)_2PO]^+$, 81 (36), 67 (31), 65 (24), 55 (40) $[CH_2C_3H_5]^+$, 41 (24) $[C_3H_5]$. HRMS (EI, 70 eV): calcd. for $C_{10}H_{21}O_3P$ $[M]^+$ 220.1228; found 220.1217.

Diethyl [1-(Cyclopropylmethyl)propyl]phosphonate (3c): According to the typical procedure, $InBr_3$ (0.285 g, 0.80 mmol), **1** (0.645 g, 1.64 mmol, 88% purity), and **2c** (0.245 g, 0.80 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded product **3c** (0.060 g, 32%). Further purification by distillation under reduced pressure gave **3c** as a colorless liquid (0.040 g, 21%); b.p. 85 °C/0.2 Torr. IR (neat): $\tilde{\nu}$ = 1238 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.16–4.03 (m, 4 H, 2 CH_2OP), 1.89–1.72 (m, 1 H, 1-H), 1.89–1.61 (m, 2 H, 2-H_2), 1.61–1.36 (m, 2 H, $PCHCH_2$), 1.31 (t, J = 7.3 Hz, 6 H, 2 CH_3CH_2OP), 1.03 (t, J = 7.2 Hz, 3 H, 3-H_3), 0.92–0.82 (m, 1 H, $PCHCH_2CH$), 0.52–0.41 (m, 2 H), 0.12–0.030 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.3, 61.2, 38.2, 32.9, 21.2, 16.4, 12.2, 9.5, 5.3, 4.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 49.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 234 (20) $[M]^+$, 219 (100) $[M - CH_3]^+$, 205 (28) $[M - CH_2CH_3]^+$, 193 (12) $[M - C_3H_5]^+$, 191 (35), 180 (22), 179 (75) $[M - CH_2C_3H_5]^+$, 177 (26), 165 (44), 163 (36), 138 (47), 137 (32) $[(CH_3CH_2O)_2PO]^+$, 111 (36), 109 (36), 81 (22), 55 (32) $[CH_2C_3H_5]^+$, 41 (16) $[C_3H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_{11}H_{23}O_3P$ $[M]^+$ 234.1385; found 234.1382.

Diethyl [1-(Cyclopropylmethyl)pent-4-enyl]phosphonate (3d): According to the typical procedure, $InBr_3$ (0.283 g, 0.80 mmol), **1** (0.623 g, 1.59 mmol, 88% purity), and **2d** (0.282 g, 0.85 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded product **3d** (0.061 g, 22%). Further purification by distillation under reduced pressure gave **3d** as a colorless liquid (0.022 g, 8%); b.p. 100 °C/0.30 Torr. IR (neat): $\tilde{\nu}$ = 1261 (P=O), 1643 (C=C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.79 (ddt, J = 17.0, 10.0, 7.0 Hz, 1 H, 4-H), 5.08–5.01 (m, including $^3J_{H,H}$ = 17.0 Hz, 1 H, 5-H^B), 5.01–4.97 (m, including $^3J_{H,H}$ = 10.0 Hz, 1 H, 5-H^A), 4.14–4.05 (m, 2 H, 3-H_2), 1.95–1.76 (m, 2 H, 1-H and PCHCH*H*), 1.72–1.54 (m, 2 H, 2-H^A and PCHC*H*H), 1.48–1.34 (m, 1 H, 2-H^B), 1.32 (t, J = 7.0 Hz, 6 H, 2 CH_3), 0.95–0.82 (m, 1 H, $PCHCH_2CH$), 0.53–0.42 (m, 2 H), 0.12–0.033 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 115.0, 61.3, 35.9, 33.5, 31.7, 27.5, 16.5, 9.4, 5.41, 4.67 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 49.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 260 (5) $[M]^+$, 219 (100) $[M - C_3H_5]^+$, 206 (33), 205 (30) $[M - CH_2C_3H_5]^+$, 191 (27), 165 (39), 163 (38), 149 (20), 109 (36), 81 (22).

HRMS (EI, 70 eV): calcd. for $C_{13}H_{25}O_3P$ $[M]^+$ 260.1541; found 260.1539.

Diisopropyl (2-Cyclopropylethyl)phosphonate (3e): According to the typical procedure, $InBr_3$ (0.287 g, 0.81 mmol), **1** (0.632 g, 1.54 mmol, 84% purity), and **2e** (0.251 g, 0.81 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded product **3e** (0.130 g, 68%). Further purification by distillation under reduced pressure gave **3e** as a colorless liquid; b.p. 85 °C/0.25 Torr. IR (neat): $\tilde{\nu}$ = 1250 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.69–4.58 (m, 2 H, 2 Me_2CH), 1.83–1.74 (m, including $^2J_{P,H}$ = 18 Hz, 2 H, PCH_2), 1.50–1.42 (m, PCH_2CH_2), 1.32 (dd, J = 8.2 Hz, $^4J_{P,H}$ = 1.9 Hz, 12 H, 2 Me_2CH), 0.81–0.71 (m, 1 H, PCH_2CH_2CH), 0.46–0.42 (m, 2 H), 0.08–0.04 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.6, 27.7, 26.9, 23.9, 11.6, 4.5 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 44.8 ppm. MS (CI, 200 eV): m/z (%) = 235 (100) $[M + 1]^+$, 193 (6) $[M - 41]^+$, 191 (1) $[M - 43]^+$. HRMS (CI, 200 eV): calcd. for $C_{11}H_{24}O_3P$ 235.1463; found 235.1456. $C_{11}H_{23}O_3P$ (234.27): calcd. C 56.39, H 9.90, O 20.49, P 13.22; found C 56.12, H 9.61.

2-(1-Methyl-2-cyclopropylethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (3f): According to the typical procedure, $InBr_3$ (0.283 g, 0.80 mmol), **1** (0.748 g, 1.62 mmol, 75% purity), and **2f** (0.243 g, 0.80 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded product **3f** (0.130 g, 58%). Further purification by distillation under reduced pressure gave **3f** as a colorless liquid (0.070 g, 38%); b.p. 130 °C/0.47 Torr. IR (neat): $\tilde{\nu}$ = 1268 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.21 (dd, J = 11, $^3J_{P,H}$ = 6 Hz, 2 H, two protons of 4-H and/or 6-H), 3.67 (dd, $^3J_{P,H}$ = 17 Hz, J = 11 Hz, 2 H, two protons of 4-H and/or 6-H), 2.08–1.95 (m, 1 H, PC*H*), 1.64–1.54 (m, 1 H, PCHCH*H*), 1.43–1.33 (m, 1 H, PCHC*H*H), 1.25 (dd, $^3J_{P,H}$ = 19 Hz, J = 7.5 Hz, 3 H, $PCHCH_3$), 1.11 (s, 5-Me), 0.87 (s, 5-Me), 0.82–0.71 (m, 1 H, $PCHCH_2CH$), 0.50–0.33 (m, 2 H), 0.11 to –0.06 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.9, 73.8, 34.5, 32.6, 30.3, 21.8, 21.2, 12.8, 9.0, 5.4, 3.7 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 110.5 ppm. MS (EI, 70 eV): m/z (%) = 232 (55) $[M]^+$, 217 (51) $[M - CH_3]^+$, 191 (48) $[M - C_3H_5]^+$, 178 (59), 177 (37) $[M - CH_2C_3H_5]^+$, 164 (31), 163 (36), 150 (39), 149 (67) $[M - CH_3CHCH_2C_3H_5]^+$, 147 (46), 136 (23), 123 (51), 111 (82), 110 (36), 109 (28), 97 (21), 83 (34) $[CH_3CHCH_2C_3H_5]^+$, 82 (99), 81 (50), 71 (27), 69 (98), 68 (71), 67 (56), 57 (40), 56 (52), 55 (78) $[CH_2C_3H_5]^+$, 43 (20), 41 (100) $[C_3H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_{11}H_{21}O_3P$ $[M]^+$ 232.1228; found 232.1225.

(2-Cyclopropylethyl)diphenylphosphane Oxide (3g): According to the typical procedure, $InBr_3$ (0.285 g, 0.80 mmol), **1** (0.660 g, 1.61 mmol, 84% purity), and **2g** (0.272 g, 0.80 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 60:40) afforded product **3g** as a white solid (0.140 g, 52%); m.p. 95 °C. IR (KBr): $\tilde{\nu}$ = 1438, 1172, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 4 H, *o*), 7.53–7.43 (m, 6 H, *m* and *p*), 2.42–2.35 (m, including $^2J_{P,H}$ = 11 Hz, 2 H, PCH_2), 1.56–1.48 (m, 2 H, PCH_2CH_2), 0.79–0.69 (m, 1 H, PCH_2CH_2CH), 0.43–0.38 (m, 2 H), 0.049–0.012 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.05, 131.5, 130.6, 128.4, 29.6, 26.5, 11.9, 4.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 46.7 ppm. MS (EI, 70 eV): m/z (%) = 270 (34) $[M]^+$, 269 (28), 215 (33) $[M - CH_2C_3H_5]^+$, 255 (32), 201 (100) $[M - CH_2CH_2C_3H_5]^+$, 186 (34), 77 (23) $[C_6H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_{17}H_{19}OP$ 270.1174; found 270.1169. $C_{17}H_{19}OP$ (270.30): calcd. C 75.54, H 7.08, O 5.92, P 11.46; found: C 75.70, H 6.89.

***O,O′*-Diethyl (2-Cyclopropylethyl)phosphonothioate (3h):** According to the typical procedure, $InBr_3$ (0.286 g, 0.81 mmol), **1** (0.675 g, 1.64 mmol, 84% purity), and **2h** (0.250 g, 0.85 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 50:50) afforded product **3h** (0.040 g, 21%). Further purification by distillation under reduced pressure gave **3h** as a colorless liquid (0.020, 11%); b.p. 130 °C/0.2 Torr. IR (neat): $\tilde{\nu}$ = 1033 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.18–4.02 (m, 4 H, 2 CH_3CH_2), 2.10–2.02 (m, $^2J_{P,H}$ = 7.5 Hz, 2 H, PCH_2), 1.57–1.48 (m, 2 H, 2 PCH_2CH_2), 1.29 (td, J = 7.0 Hz, $^4J_{P,H}$ = 1.0 Hz, 6 H, 2 CH_3), 0.80–0.70 (m, 1 H, PCH_2CH_2CH), 0.47–0.42 (m, 2 H), 0.10–0.06 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.1, 34.6, 28.0, 16.1, 11.4, 4.5 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 113.9 ppm. MS (EI, 70 eV): m/z (%) = 222 (51) $[M]^+$, 194 (41) $[M - CH_3CH_2]^+$, 154 (29) $[(CH_3CH_2O)_2PS]^+$, 150 (25), 125 (23), 121 (100), 97 (45), 93 (50), 69 (21) $[M - (CH_3CH_2O)_2P(S)]^+$, 65 (33). HRMS (EI, 70 eV): calcd. for $C_9H_{19}O_2PS$ $[M]^+$ 222.0843; found 222.0842. $C_9H_{19}O_2PS$ (222.28): calcd. C 48.63, H 8.62, O 14.40, P 13.93, S 14.43; found C 48.40, H 8.33.

Diethyl (3-Cyclopropylpropyl)phosphonate (6): According to the typical procedure, $InBr_3$ (0.283 g, 0.80 mmol), **1** (0.644 g, 1.60 mmol, 86% purity), **5** (0.232 g, 0.79 mmol), and AIBN (0.013 g, 0.08 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate, 70:30) afforded the product **6** (0.032 g, 18%). Further purification was performed by distillation under reduced pressure; b.p. 80 °C/0.26 Torr. IR (neat): $\tilde{\nu}$ = 1246 (P=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.17–4.03 (m, 4 H, 2 CH_2OP), 1.82–1.65 (m, 4 H, PCH_2 and PCH_2CH_2), 1.42–1.26 (m, 2 H, $PCH_2CH_2CH_2$), 1.33 (t, J = 7.0 Hz, 6 H, 2 CH_3), 0.69–0.60 (m, 1 H, $PCH_2CH_2CH_2CH$), 0.44–0.40 (m, 2 H), 0.07–0.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.3, 35.4, 25.4, 22.4, 16.4, 10.3, 4.3 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 47.3 ppm. MS (EI, 70 eV): m/z (%) = 220 (14) $[M]^+$, 191 (23) $[M - CH_2CH_3]^+$, 165 (53) $[M - CH_2C_3H_5]^+$, 152 (100) $[M - CH_2CH_2C_3H_5]^+$, 147 (31), 138 (71) $[(CH_3CH_2O)_2PO]^+$, 125 (65), 124 (23), 111 (64), 110 (23), 109 (31), 108 (21), 97 (52), 96 (26), 82 (31) $[CH_2CH_2CH_2C_3H_5]^+$, 81 (38), 41 (23) $[C_3H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_{10}H_{21}O_3P$ 220.1228; found 220.1221.

1,1-Diphenyl-3-cyclopropyl-1-propene (10): According to the typical procedure, **3h** (0.050 g, 0.23 mmol), *s*BuLi (1.0 M in hexane, 0.30 mL), and benzophenone (0.043 g, 0.24 mmol) gave the crude product. Purification by flash column chromatography (hexane, 200 mL) gave the product **10** as a colorless liquid (0.030 g, 57%). IR (neat): $\tilde{\nu}$ = 1493, 1442, 822, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.16 (m, 10 H, 2 Ar), 6.19 (t, J = 7.0 Hz, 1 H, 2-H), 2.02 (dd, J = 7.0, 7.0 Hz, 2 H, 3-H_2), 0.83–0.73 (m, 1 H, $C{=}CHCH_2CH$), 0.46–0.41 (m, 2 H), 0.088–0.050 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 141.4, 140.2, 129.9, 129.1, 128.1, 128.0, 127.2, 126.8, 126.7, 34.5, 11.1, 4.2 ppm. MS (EI, 70 eV): m/z (%) = 234 (46) $[M]^+$, 205 (100), 193 (37) $[M - C_3H_5]^+$, 191 (22), 180 (35), 178 (25) $[M - CH_2C_3H_5]^+$, 165 (24), 115 (48), 91 (42). HRMS (EI, 70 eV): calcd. for $C_{18}H_{18}$ $[M]^+$ 234.1409; found 234.1404. $C_{18}H_{18}$ (234.34): calcd. C 7.74, H 92.26; found C 7.66, H 92.12.

(2-Cyclopropylethylidene)cyclohexane (11): According to the typical procedure, **3h** (0.038 g, 0.17 mmol), *s*BuLi (1.0 M in hexane, 0.20 mL), and cyclohexanone (0.023 g, 0.23 mmol) gave the crude product. Purification by flash column chromatography (hexane, 200 mL) afforded product **11** as a colorless liquid (0.012 g, 51%). IR (neat): $\tilde{\nu}$ = 1666 (C=C), 1446, 1014, 849, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.16 (t, J = 7.0 Hz, 1 H, C=C*H*), 2.12–2.07 (m, 4 H), 1.92 (dd, J = 7.0, 7.0 Hz, 2 H, 2-H_2), 1.55–1.43 (m, 6 H), 0.74–0.64 [m, 1 H, 2-$CH(CH_2)_2$], 0.41–0.37 (m, 2 H), 0.07–0.03 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 120.1,

37.2, 31.6, 28.8, 28.7, 27.9, 27.0, 11.3, 3.95 ppm. MS (EI, 70 eV): *m/z* (%) = 150 (38) $[M]^+$, 121 (31), 109 (53) $[M - C_3H_5]^+$, 107 (46), 94 (27), 93 (31), 81 (52), 79 (56), 68 (50), 67 (100), 55 (29), 41 (21) $[C_3H_5]^+$. HRMS (EI, 70 eV): calcd. for $C_{11}H_{18}$ $[M]^+$ 150.1409; found 150.1406.

Supporting Information (see footnote on the first page of this article): Experimental details, characterization data, and copies of NMR spectra.

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