Synthesis of 1-Stannylated and 1-Iodinated 1-Chloroalkenes as Versatile Synthetic Intermediates

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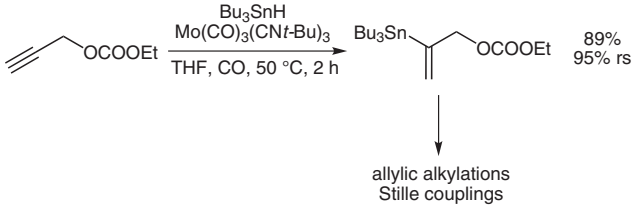
Abstract: An efficient and convenient synthesis of 1-stannylated and iodinated 1-chloroalkenes is described based on $MoBI_3$-catalyzed hydrostannations of 1-chloroalkynes, followed by a tin–iodine exchange. The 1-chloro-1-iodoalkenes are suitable substrates for further modification, for example, via cross-coupling reactions.

Key words: chloroalkynes, cross-coupling, hydrostannation, molybdenum, vinyl halides

For synthetic chemists vinylstannanes are very attractive synthetic building blocks, especially because they are easily accessible, for example, via hydrostannations of alkynes. Generally, these hydrostannations can be performed under radical or transition-metal-catalyzed conditions.[1] Most of these methods are suffering from difficulties in controlling the regioselectivity of the tin hydride addition to unsymmetrical alkynes, though transition-metal-catalyzed reactions provide clean *cis* addition, based on the reaction mechanism.[2] Hydrometallations of terminal alkynes generally give rise to the terminal (*E*)-vinylstannanes, also accessible via stannylcupration.[3] Yamamoto et al. reported the synthesis of the corresponding *Z*-isomers in the presence of Lewis acids,[4] and Williams et al. described a *Z*-selective hydrotelluration–transmetallation approach.[5] In addition, Hale et al.[6] as well as the group of Miura and Hosomi[7] reported the regioselective, radical hydrostannation of propargyl alcohol derivatives. Our group has developed a new molybdenum-based catalyst $Mo(CO)_3(CN\textit{t}\text{-}Bu)_3$ ($MoBI_3$), which is especially suitable for highly regio- and stereoselective hydrostannations of functionalized alkynes.[8] Best results are obtained with terminal, electron-poor alkynes, to which the tin moiety is transferred towards the sterically more hindered position, close to the electron-withdrawing group.[9] For example, propargyl acetate or carbonates give excellent yields of the stannylated derivatives, which are ideal substrates for further modifications, such as allylic alkylations and Stille couplings (Scheme 1).[10]

Vinyl iodides are also interesting synthetic precursors due to their versatility in organic synthesis[11] and photochemistry.[12] The iodide can be transformed selectively in the presence of other, less reactive, leaving groups.[11a,13] For example, chloroiodoalkenes can be used for the stereoselective synthesis of highly functionalized alkenes.[14] Unfortunately, procedures for the synthesis of these interesting building blocks are rather limited. They can be obtained by addition of hydrogen chloride to iodopropiolic acid, providing the two stereoisomers in almost equal amounts.[15] In principle, hydrogen iodide can also be added towards chloroalkynes, but these reactions usually end up with diaddition products.[16] Although the halogen exchange between dichlorovinylethyl sulfone and sodium iodide also yields the desired product,[17] in general vinylchlorides are unsatisfactory substrates because of their reluctance towards exchange.[18] Barluenga et al. described the formation of chloroiodoalkenes by reaction of 1-chloroalkynes with bis(pyridine)iodine(I) tetrafluoroborate.[19]

Herein, we describe our investigations of Mo-catalyzed regio- and stereoselective hydrostannations of 1-chloroalkynes **1**, and the conversion of the chlorinated vinylstannanes **2** obtained into the corresponding 1,1-chloroiodoalkenes **4** (Table 1). The required chloroalkynes can easily be obtained from terminal alkynes via deprotonation and halogenation with *N*-chlorosuccinimide (NCS).[20] Although in these substrates the triple bond is not terminal, we hoped that the electron-withdrawing effect of the halogen might cause a regioselective tin hydride addition. And indeed, in the presence of 3 mol% $Mo(CO)_3(CN\textit{t}\text{-}Bu)_3$ ($MoBI_3$) 1-chloropentyne (**1a**) was hydrostannated regio- and stereoselectively towards chlorostannane **2a**. The crude product was carefully investigated by NMR, and only one set of signals was observed in the ^1H, ^{13}C, and ^{119}Sn spectra. By far the best results were obtained in the presence of a slight excess of Bu_3SnH (1.5 equiv)[21] and with THF as solvent at 60 °C (Table 1, entry 1). Hydroquinone was added to suppress competitive radical hydrostannations. Interestingly, a CO atmosphere had no influence on the outcome of the reaction, as observed previously with terminal alkynes.[22]



Scheme 1 Molybdenum-catalyzed hydrostannations

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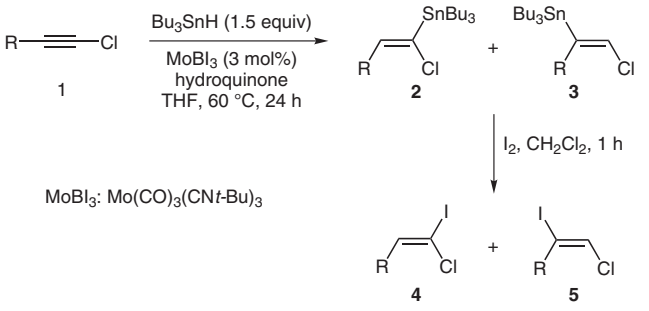
Therefore, we investigated the hydrostannation of several other chloroalkynes (entries 2–5) under these optimized reaction conditions.[23] While all alkyl-substituted alkynes gave comparable results, the corresponding phenyl derivate **1e** provided a mixture of the two regioisomeric products **2e** and **3e** in a 7:3 ratio. In this case, the reaction does not go to completion, even though the amount of catalyst was increased to 5 mol%. But the different reaction behavior of the arylalkynes is not surprising and was previously also observed by various other investigators.[2]

Table 1 Synthesis of Chlorinated Vinylstannanes and Vinyliodides

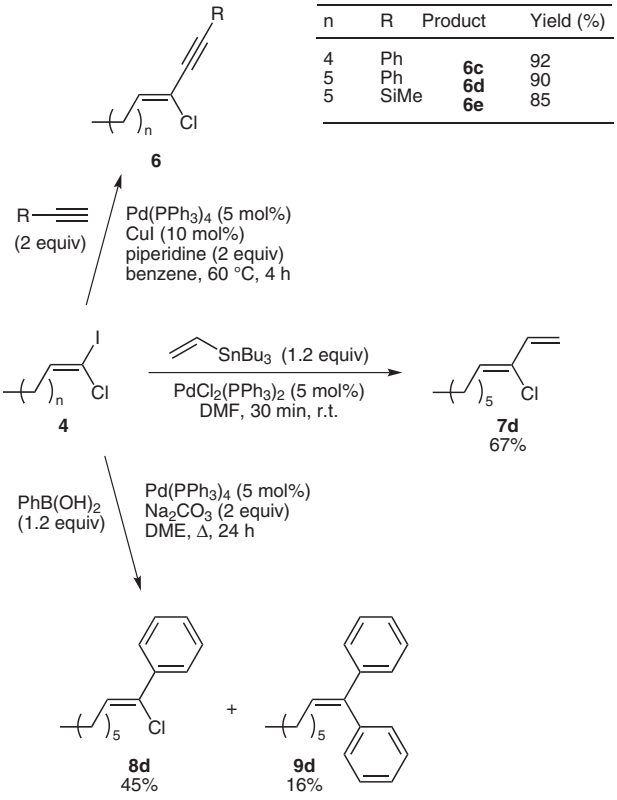


Entry	Substrate	R	Product	Yield (%)	Product	Yield (%)
1	**1a**	*n*-Pr	**2a**	69	**4a**	77
2	**1b**	*n*-Bu	**2b**	75	**4b**	86
3	**1c**	*n*-Pen	**2c**	76	**4c**	79
4	**1d**	*n*-Hex	**2d**	78	**4d**	85
5	**1e**	Ph	**2e/3e**	42/19	**4e/5e**	48/21

The stannylated chlorostannanes obtained were subjected to a subsequent tin–iodide exchange.[24] This clean reaction provided the requested mixed dihalogenated alkenes in good yield and with retention of the olefin geometry. Because the stannylated phenylsubstituted alkenes were difficult to separate by chromatography, the regioisomeric mixture was subjected to the halogen exchange. Therefore, a mixture of the alkenes **4e** and **5e** was obtained.

With these chloroiodoalkenes in hand we carried out a series of cross coupling reactions (Scheme 2). The Sonogashira coupling of **4** with various alkynes yielded enynes **6** in excellent yield and with complete retention of olefin geometry[25] and the Stille coupling of **4d** with vinyl tributyltin at room temperature provided the chlorinated diene **7d** in 67% yields.[26] Interestingly, the Suzuki coupling with phenylboronic acid gave rise to a mixture of mono- and diarylated products.[27]

To evaluate the scope and limitations of this protocol we also investigated the hydrostannation of chlorinated propargyl alcohol derivatives **1f** and **1g** (Table 2). Terminal propargyl alcohols are excellent substrates for highly regioselective hydrostannations, and the regioselectivity correlates with the electron-withdrawing effect of the oxy substituent. In our case, the alkynes have two electron-



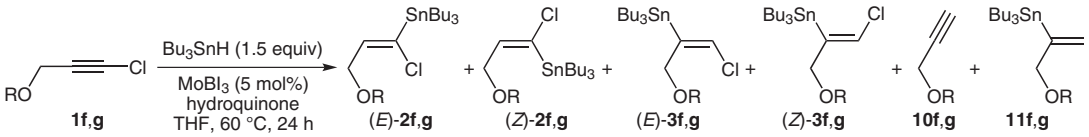
n	R	Product	Yield (%)
4	Ph	**6c**	92
5	Ph	**6d**	90
5	SiMe	**6e**	85

Scheme 2 Cross-coupling reactions of chloroiodoalkenes

withdrawing substituents on both sides. Therefore, we expected, that the substrates should react under the usual reaction conditions (what is not the case with alkylsubstituted propargyl alcohol derivatives), but that the regioselectivity should be moderate based on the opposite directing effects of the substituents. When we run the experiments we expected to obtain two products as before, but were surprised to find up to six compounds in the crude reaction mixture (determined by NMR). In the case of the THP-protected alkyne **1f** the expected regioisomeric products (*E*)-**2f** and (*E*)-**3f** were only the minor stereoisomers, while the *Z*-isomers (*Z*)-**2f** and (*Z*)-**3f** were the major components in the product mixture. In addition, the dehalogenated product **10f** and the hydrostannation product **11f** thereof were obtained (entry 1).

In the first instance we assumed that **10f** might be formed via reduction of the chloroalkyne **1f** under the reaction conditions, a process which might also explain the 'less than perfect yield' with the other alkynes **1a–e**, because the nonchlorinated alkynes are volatile and do not undergo hydrostannation. But during workup we made an interesting observation: After column chromatography (*E*)-**3f** had disappeared completely, while the product ratio of the other components was nearly unchanged (entry 2). Only the amount of **10f** was significantly increased. Obviously, this *E*-isomer is not very stable and undergoes elimination towards **10** easily, at least in the presence of silica gel. To prove this hypothesis, we added silica gel to the crude reaction mixture and analyzed this after stirring for 24 hours (entry 3). Again, the *E*-isomer was completely gone, and

Table 2 Hydrostannation of Chlorinated Propargylalcohol Derivatives



1f,g (*E*)-2f,g (*Z*)-2f,g (*E*)-3f,g (*Z*)-3f,g 10f,g 11f,g

Entry	Substrate	R	Workup	Product ratio (%)					
				(*E*)-**2**	(*Z*)-**2**	(*E*)-**3**	(*Z*)-**3**	**10**	**11**
1	**1f**	THP	crude product	16	49	9	11	9	6
2	**1f**	THP	after chromatography	20	46	–	13	15	6
3	**1f**	THP	stirring with SiO_2 for 24 h	19	49	–	14	12	6
4	**1g**	Me	crude product	35	35	17	–	4	9
5	**1g**	Me	after chromatography	47	45	–	–	1	7
6	**1g**	Me	stirring with SiO_2 for 24 h	46	44	–	–	1	9

the product ratio was comparable to the result after flash chromatography. As a second substrate we subjected the corresponding methylether **1g** towards the same protocol. In this case, the elimination product **10g** is volatile (bp 61 °C) and should disappear. Although traces of **10g** could be determined in the crude reaction mixture, after SiO_2 treatment the expected 1-chloro-1-stannylalkene **2g** was obtained as a 1:1 isomeric mixture, accompanied by 9% of the simple hydrostannation product **11g**. Probably, the instability of the 2-stannylated 1-chloralkenes **3** can also explain the perfect regioselectivity observed in the reactions of substrates **1a**–**d** (Table 1).

In conclusion, we have shown that molybdenum-catalyzed hydrostannations of 1-chloroalkynes give rise to stannylated chloroalkenes, which undergo tin–iodide exchange towards the corresponding chloroiodoalkenes, suitable precursors for subsequent palladium-catalyzed cross coupling reactions.

Best results were obtained with alkyl-substituted alkynes, which form the *E*-configured 1-stannylated 1-chloro alkenes as a single regio- and stereoisomer. Further mechanistic studies, as well as synthetic applications are currently under investigation.

Acknowledgment

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(23) **General Procedure for $MoBI_3$-Catalyzed Hydrostannations**

In an oven-dried Schlenk tube the corresponding chloroalkyne (1 mmol) and $Mo(CO)_3(CN\textit{t}\text{-}Bu)_3$ ($MoBI_3$, 12.9 mg, 30 μmol) were dissolved together with hydroquinone (10 mg, 91 μmol) in dry THF (2 mL) under argon. The solution was heated to 60 °C for 10 min before Bu_3SnH (435 mg, 1.5 mmol) was added. The reaction mixture was stirred for 16–24 h. After completion, the reaction mixture was cooled to r.t., and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel (neutralized with Et_3N) using pentane or hexane as an eluent.

Tributyl(1-chloro-1-pentenyl)stannane (2a)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.0 Hz, 12 H, CH_3), 1.01–1.05 (m, 6 H, CH_2), 1.28–1.37 (m, 8 H, CH_2), 1.52–1.58 (m, 6 H, CH_2), 2.30 (dt, *J* = 6.9 Hz, J_{Sn-H} = 14.2 Hz, 2 H, CHCH_2), 5.79 (t, *J* = 6.9 Hz, J_{Sn-H} = 32.4 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (J_{Sn-C} = 342.6 Hz), 13.6, 13.7, 21.8, 27.2 (J_{Sn-C} = 60.2 Hz), 28.7 (J_{Sn-C} = 22.7 Hz), 30.8, 136.8, 142.0 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –31.9 ppm. HRMS: *m/z* calcd for $C_{13}H_{26}ClSn$ [M – C_4H_9]$^+$: 337.0740; found: 337.0729.

Tributyl(1-chloro-1-octenyl)stannane (2d)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 12 H, CH_3), 1.01–1.05 (m, 6 H, CH_2), 1.31–1.38 (m, 14 H, CH_2), 1.50–1.56 (m, 6 H, CH_2), 2.32 (dt, *J* = 6.9 Hz, J_{Sn-H} = 14.5 Hz, 2 H, CHCH_2), 5.80 (t, *J* = 6.4 Hz, J_{Sn-H} = 32.1 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (J_{Sn-C} = 341.8 Hz), 13.6, 14.1, 22.6, 27.2, (J_{Sn-C} = 57.2 Hz), 28.6, 28.8, 28.9, 31.7, 136.6, 142.3 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –32.0 ppm. HRMS: *m/z* calcd for $C_{16}H_{32}ClSn$ [M – C_4H_9]$^+$: 365.1053; found: 365.1033.

(*E*)-Tributyl(1-chloro-3-methoxypropenyl)stannane [(*E*)-2g]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 9 H, CH_3), 1.06–1.11 (m, 6 H, CH_2), 1.31–1.40 (m, 6 H, CH_2), 1.52–1.60 (m, 6 H, CH_2), 3.38 (s, 3 H, OCH_3), 4.23 (d, *J* = 5.3 Hz, J_{Sn-H} = 14.5 Hz, 2 H, CHCH_2), 5.27 (t, *J* = 5.3 Hz, J_{Sn-H} = 31.1 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.4, 13.6, 27.2, 28.7, 58.1, 69.4, 138.6, 142.2 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –28.3 ppm. HRMS: *m/z* calcd for $C_{12}H_{24}OClSn$ [M – C_4H_9]$^+$: 339.0533; found: 339.0525.

(*Z*)-Tributyl(1-chloro-3-methoxypropenyl)stannane [(*Z*)-2g]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 9 H, CH_3), 1.06–1.11 (m, 6 H, CH_2), 1.31–1.40 (m, 6 H, CH_2), 1.52–1.60 (m, 6 H, CH_2), 3.34 (s, 3 H, OCH_3), 3.87 (d, *J* = 6.5 Hz, J_{Sn-H} = 14.5 Hz, 2 H, CHCH_2), 6.64 (t, *J* = 6.5 Hz, J_{Sn-H} = 75.3 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6 (J_{Sn-C} = 348.0 Hz), 13.6, 27.2 (J_{Sn-C} = 60.8 Hz), 28.7 (J_{Sn-C} = 19.8 Hz), 57.9, 71.6 (J_{Sn-C} = 14.7 Hz), 139.7, 142.1 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –32.21 ppm. HRMS: *m/z* calcd for $C_{12}H_{24}OClSn$ [M – C_4H_9]$^+$: 339.0533; found: 339.0525.

(*E*)-Tributyl(1-methoxymethylvinyl)stannane (11g)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.95 (m, 15 H, CH_2 and CH_3), 1.31–1.36 (m, 6 H, CH_2), 1.48–1.56 (m, 6 H, CH_2), 3.32 (s, 3 H, OCH_3), 4.05 (d, *J* = 1.5 Hz, J_{Sn-H} = 34.6 Hz, 2 H, CH_2), 5.28 (dt, *J* = 2.7, 1.7 Hz, J_{Sn-H} = 62.2 Hz, 1 H, CH), 5.88 (dt, *J* = 2.7, 1.7 Hz, J_{Sn-H} = 131.0 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5, 13.7, 27.3, 29.1, 57.7, 79.7, 124.6, 153.0 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –45.4 ppm. HRMS: *m/z* calcd for $C_{12}H_{25}OSn$ [M – C_4H_9]$^+$ 305.0922; found: 305.0920.

(24) **Representative Procedure for the Synthesis of 1-Chloro-1-iodoalkenes**

A solution of iodine (280 mg, 1.1 mmol) in CH_2Cl_2 (8.0 mL) was added dropwise (up to 1 h) to the solution of tributyl(1-chlorohex-1-enyl)stannane (**2b**, 408 mg, 1 mmol) in CH_2Cl_2 (7.0 mL) at 0 °C. After addition of the iodine solution the cooling bath was removed, and the reaction mixture was stirred at r.t. for 1 h, before the reaction mixture was stirred with sat. KF solution (15 mL) for 2 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash chromatography using hexane as eluent to yield 1-chloro-1-iodo-1-hexene (**4b**) as colorless oil.

1-Chloro-1-iodo-1-hexene (4b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.8 Hz, 3 H, CH_3), 1.34–1.42 (m, 4 H, CH_2), 2.18 (q, *J* = 7.5 Hz, 2 H, CH_2), 6.45 (t, *J* = 7.5 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.1, 30.0, 31.4, 66.3, 144.4 ppm. HRMS (CI): *m/z* calcd for $C_6H_{10}ClI$ [M]$^+$: 243.9516; found: 243.9556.

(25) **Representative Procedure for Sonogashira Couplings**

In an oven-dried Schlenk tube CuI (17.0 mg, 10 mol%) was added to a solution of $Pd(PPh_3)_4$ (44.0 mg, 5 mol%) in benzene (2 mL) under Ar. To this mixture 1-chloro-1-iodo-1-heptene (**4c**, 223 mg, 0.87 mmol) and piperidine (178 μL, 1.74 mmol) were added before it was warmed up to 60 °C. Phenyl acetylene was added dropwise (over 1 h), and the reaction mixture was heated at this temperature for additional 4 h. After the reaction was complete (TLC), the mixture was cooled to r.t. and diluted with Et_2O (20 mL). The organic layer was washed with sat. NH_4Cl solution and

H_2O (20 mL each). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The crude product obtained was purified by flash chromatography using hexane as eluent.

(*Z*)-1-Phenyl-3-chloro-3-nonen-1-yne (6c)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.34–1.39 (m, 4 H, CH_2), 1.47–1.51 (m, 2 H, CH_2), 2.33 (q, *J* = 7.5 Hz, 2 H, CH_2), 6.22 (t, *J* = 7.5 Hz, 1 H, CH), 7.33–7.37 (m, 3 H, ArH), 7.47–7.50 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 27.8, 29.3, 31.4, 86.5, 88.2, 113.7, 122.2, 128.3, 128.8, 131.7, 137.9 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –28.96 ppm. HRMS: *m/z* calcd for $C_{15}H_{17}$ $[M - Cl]^+$: 197.1325; found: 197.1296.

(26) **Representative Procedure for Stille Couplings**

In an oven-dried Schlenk tube $PdCl_2(PhCN)_2$ (3.8 mg, 5 mol%) was dissolved in DMF (2.0 mL) under Ar. To this solution 1-chloro-1-iodo-1-octene (**4d**, 54.0 mg, 0.2 mmol) was added, followed by the dropwise addition of vinyl tributyltin (70 μL, 0.22 mmol) at r.t. After 30 min the reaction was complete (TLC), and the reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl solution and H_2O. The organic layer was separated and dried over Na_2SO_4 and the crude product obtained after evaporation of the solvent was purified by silica gel column chromatography using hexane as eluent.

(*Z*)-3-Chloro-1,3-decadiene (7d)[28]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.3 Hz, 3 H, CH_3), 1.29–1.37 (m, 6 H, CH_2), 1.40–1.46 (m, 2 H, CH_2), 2.33 (q, *J* = 7.3 Hz, 2 H, CH_2), 5.16 (d, *J* = 11.8 Hz, 1 H, CH), 5.57 (d, *J* = 15.8 Hz, 1 H, CH), 5.79 (t, *J* = 7.3 Hz, 1 H, CH), 6.39 (dd, *J* = 11.8, 15.8 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.4, 28.8, 28.9, 31.6, 115.0, 131.9, 132.4, 134.6 ppm.

(27) **Representative Procedure for Suzuki Couplings**

A solution of phenylboronic acid (26.4 mg, 0.22 mmol) in EtOH (0.2 mL) was added to a Schlenk tube containing a solution of $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) and 1-chloro-1-iodo-1-octene (**4d**, 54.0 mg, 0.2 mmol) in DME (1.0 mL) under argon. A solution of Na_2CO_3 (64 mg, 0.6 mmol) in degassed H_2O (0.5 mL) was added to the reaction mixture, and the mixture was heated under reflux for 24 h. The reaction mixture was then cooled to r.t., diluted with H_2O (10 mL) and Et_2O (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (10 mL). The combined organic layers were washed with H_2O and dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product obtained was purified by flash chromatography on silica gel using hexanes to yield 19.0 mg (45%) of monoarylated product **8d** and 9.6 mg (16%) of diarylated product **9d**.

(*Z*)-1-Chloro-1-phenyl-1-octene (8d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.29–1.42 (m, 6 H, CH_2), 1.50–1.56 (m, 2 H, CH_2), 2.41 (q, *J* = 7.1 Hz, 2 H, CH_2), 6.16 (t, *J* = 6.6 Hz, 1 H, CH), 7.31–7.38 (m, 3 H, ArH), 7.57–7.60 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.5, 29.0, 29.6, 31.7, 126.3, 128.1, 128.2, 128.8, 132.6, 138.4 ppm. HRMS: *m/z* calcd for $C_{14}H_{19}$ $[M - Cl]^+$: 187.1481; found: 187.1482.

1,1-Diphenyl-1-octene (9d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.23–1.44 (m, 6 H, CH_2), 1.46–1.48 (m, 2 H, CH_2), 2.14 (q, *J* = 7.3 Hz, 2 H, CH_2), 6.11 (t, *J* = 7.5 Hz, 1 H, CH), 7.19–7.41 (m, 6 H, ArH), 7.45–7.49 (m, 2 H, ArH), 7.61–7.64 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.9, 29.7, 29.9, 31.7, 126.7, 126.8, 127.2, 127.3, 128.0, 128.1, 128.8, 129.9, 130.4, 140.3, 141.2, 141.4, 142.9 ppm. HRMS: *m/z* calcd for $C_{20}H_{24}$ $[M]^+$: 264.1873; found: 264.1843.

(28) Mitani, M.; Kobayashi, Y.; Koyama, K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 653.