

## Research Article

# Practical Synthesis and Field Application of the Synthetic Sex Pheromone of Rice Stem Borer, *Chilo suppressalis* (Lepidoptera: Pyralidae)

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Rice stem borer, *Chilo suppressalis*, is a common and major serious pest of rice, maize, and wheat crops across Asia, Europe, and Oceania countries. Its sex pheromone consists of three analogously compounds, i.e., (Z)-hexadec-11-enal (1), (Z)-octadec-13-enal (2), and (Z)-hexadec-9-enal (3), as long-chain aliphatic internal *cis*-alkenyl aldehydes. In order to perform an economic and widespread pest control management of rice stem borer, a versatile and efficient synthetic strategy is required. A versatile and efficient synthesis using a common synthetic route for *cis*-alkenals with high overall yields is described. Commercially available inexpensive aliphatic diols were chosen as starting materials. Two key steps were employed to synthesize the long-chain aliphatic internal *cis*-alkenes in excellent yields, including the alkylation of terminal alkynes without the utilization of a highly polar aprotic cosolvent and the versatile *cis*-selective semihydrogenation for the reduction of internal alkynes with excellent stereoselectivity. The results of field tests showed that the synthetic sex pheromone blend was highly effective for the capture of rice stem borer.

## 1. Introduction

Rice, maize, and wheat are three of the most important food crops in the world and are the primary staple foods for most of world population [1]. According to Food and Agricultural Organization of the United Nations, rice, maize, and wheat are three of the top four world's most produced crops, with Asia and Americas constituting the largest consuming and producing regions and India and China being the top two largest countries for rice cultivation in the world [2, 3]. However, the infestation by agricultural pests, especially by rice stem borer, is a major concern for farmers of rice, maize, and wheat crops worldwide [4]. The rice stem borer, *Chilo suppressalis*, is a common and major serious pest of rice, maize, and wheat crops that causes extensive crop damage and yield loss and is widely distributed in Asia, Europe, and Oceania countries. It attacks the stems, leaves, and panicles

of the target drops to form dead hearts and white heads during the vegetative and reproductive stages [5, 6].

Introduction of improved rice varieties in the 1960s embraced chemical insecticides and pesticides as a prominent technology of agricultural revolution [7]. Thereafter, four different methods have been employed to control the pest population since 1970, i.e., agricultural control, biological control, chemical control, and breeding and growing of resistant varieties [8, 9]. Regarding the efficiency and effectiveness of the pest control method, chemical control is still the main strategy for insect pest control. However, the sporadically abuse of chemical pesticides has resulted in serious environmental pollution, increased pesticide resistance, and severe threat to human health due to pesticide residue [10, 11]. In order to achieve a green and sustained agricultural environment and to reduce the utilization frequency and dosage of chemical pesticides, as well as to

ensure environmental and crop safety while controlling the pest population, the application of biological pheromone-based pest control methods serves as powerful alternative pest management strategies with safer and environmentally friendly concerns, thereby grabbing attention of organic chemists, entomologists, and ecologists [12]. Moreover, the development of convenient and highly effective formulation of pheromone-based pest control products is currently a very important task for integrated pest management and biological pesticides. Pheromone-based pest control methods exhibit several fascinating advantages; for example, insect sex pheromones are species-specific and effective in very small dosages, do not develop chemical resistance, and are nontoxic and applicable without spreading. However, regarding to their drawbacks, pheromone-based pest managements should be applied to large areas in order to achieve the acceptable economic and effective level of pest controls.

The sex pheromone of rice stem borer, *Chilo suppressalis*, was first independently identified as a mixture of two aldehyde components (Z)-hexadec-11-enal (**1**, abbreviated as Z11-16:Ald) and (Z)-octadec-13-enal (**2**, abbreviated as Z13-18:Ald) by Nesbitt et al. [13] and Ohta et al. [14] in 1975 and 1976, respectively. It was later found that the attractiveness of the blend of **1** and **2** was less efficient as compared to the attractiveness by virgin females. Subsequently in 1983, Tatsuki and coworkers reported the identification of (Z)-hexadec-9-enal (**3**, abbreviated as Z9-16:Ald), as the third aldehyde component of the sex pheromone of rice stem borer [15]. The mixture of all three aldehyde components **1**, **2**, and **3**, as shown in Figure 1, in an approximate ratio of 48:6:5 [16], or an alternative very similar ratio of 41:5:4 [17] was found to be the most effective in attracting male counterparts of *Chilo suppressalis*. However, the chemical compositions of the sex pheromone of rice stem borer are all chemically unstable aldehyde compounds, and aldehydes are known to be unstable upon the exposure of air under sunlight for a long period of time, which might lead to further oxidation into the corresponding carboxylic acid derivatives. Therefore, in order to ensure the effectiveness of the pheromone lure of rice stem borer, a proper formulation including the utilization of appropriate antioxidants to protect this aldehyde blend from decomposition should be performed.

The costs for the chemical substances of insect sex pheromones are usually very expensive or some chemical substances are not commercially available, especially those with complicated chemical structures or specific stereochemistry. In order to control the population of rice stem borer ecofriendly and to reduce the cost for the manufacture of pheromone-based biocontrol products, the development of the practical synthesis of all three aldehyde components of its sex pheromone is quite essential. Mestres and coworkers had previously reported the synthesis of the dioxolane derivatives of aldehydes **1**, **2**, and **3**, which can serve as the corresponding precursors of the final sex pheromone components [18]. Aldehyde **1** and/or **2** has previously been synthesized by several groups, mainly using Wittig reaction for the formation of *cis*-fashioned alkene double bond [19–24]. In addition, **3** was synthesized by few other groups

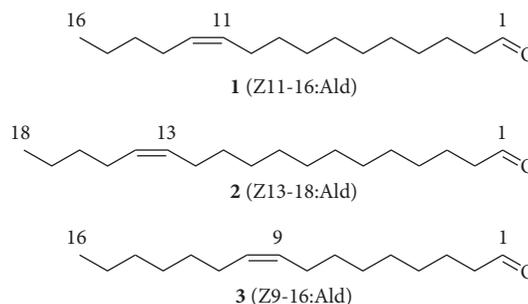


FIGURE 1: Sex pheromone components of rice stem borer, *Chilo suppressalis*.

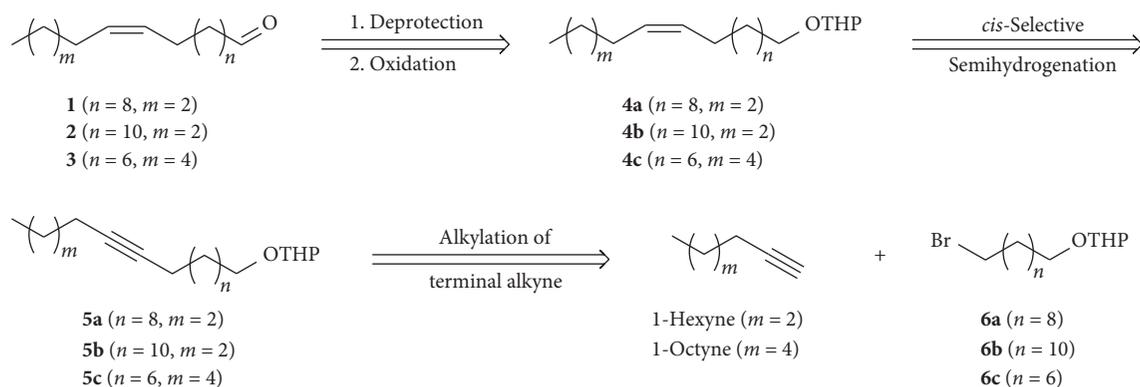
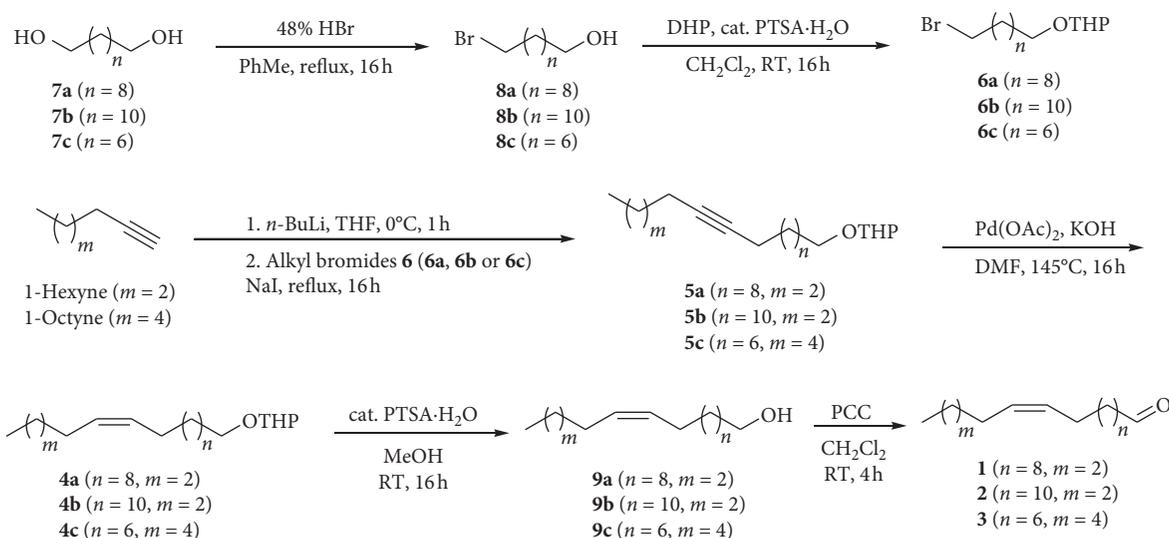
[25, 26], while **2** and **3** were also synthesized via the ozonolysis of 1,5-cyclooctadiene [27].

Since we are in need of large quantity of the sex pheromone of rice stem borer and the corresponding long-term effective pheromone lure for its application and development to the effective pest control of rice stem borer, we have designed an efficient retrosynthetic plan to afford the desired long-chain aliphatic internal *cis*-alkenyl aldehydes **1**, **2**, and **3**, as shown in 1. Herewith, we report the practical synthesis of the aldehydes **1**, **2**, and **3** using a simple six-step synthetic strategy that is applicable to all three components, as shown in 2. The readily available starting materials, i.e., decane-1,8-diol (**7a**), dodecane-1,10-diol (**7b**), and octane-1,12-diol (**7c**), were chosen to make the overall synthesis practical and inexpensive. In addition, we also report the field application of the synthetic sex pheromone blend of rice stem borer for the evaluation of effective duration and attractiveness of the sex pheromone lure of rice stem borer.

## 2. Results and Discussion

**2.1. Synthesis.** The chemical structures of the sex pheromone components **1**, **2**, and **3** are analogously long-chain aliphatic internal *cis*-alkenyl aldehydes, as shown in Figure 1, and can be synthesized via a common and efficient synthetic plan, as shown in 3. The aldehyde moieties of the *cis*-alkenyl aldehydes **1**, **2**, and **3** can be generated simply by the deprotection of the corresponding THP-protected alkenols **4**, followed by the oxidation of primary alcohol into the aldehyde group. The key steps for the synthesis of THP-protected alkenols **4** involve the alkylation of terminal alkynes and *cis*-selective semihydrogenation to furnish pure *cis*-fashioned internal alkenes. The counterparts for the alkylation of terminal alkynes, i.e., 1-hexyne and 1-octyne, were the THP-protected bromoalcohols **6**, which can be obtained from the corresponding symmetrical diols **7** (Schemes 1 and 2).

The synthesis of THP-protected bromoalcohols **6** was started with the monobromination of the symmetrical diols **7**. Treatment of diols **7** with 48% HBr in refluxing toluene afforded the mono-brominated alcohols **8**. The isolated yields of alcohols **8a**, **8b**, and **8c** were 90%, 85%, and 91%, respectively. The hydroxyl groups of the mono-brominated alcohols **8** were protected with DHP in the presence of catalytic amount of PTSA to yield the THP-protected

SCHEME 1: Retrosynthetic analysis for internal *cis*-alkenyl aldehydes **1**, **2**, and **3**.SCHEME 2: Efficient synthesis of sex pheromone components **1**, **2**, and **3**.

bromoacetals **6**. The isolated yields of THP-protected bromoacetals **6a**, **6b**, and **6c** were 92%, 90%, and 88%, respectively. It is noteworthy that THP-protected bromoacetals **6** were stable in further steps and were easy to undergo deprotection in acidic conditions.

Thereafter, in the further stage of the synthesis, crucial modifications consist of two key steps were required to generate stereoselectively the long-chain aliphatic internal *cis*-alkenes **4**. In the first crucial step, by employing the method reported by Buck and Chong [28] or our modified procedure [29], terminal alkynes, i.e., 1-hexyne and 1-octyne, were treated with *n*-BuLi at 0°C in anhydrous THF, which resulted in the formation of the corresponding acetylide intermediates. After anhydrous solid NaI was added to the acetylide intermediates, the solution of the correlated THP-protected bromoacetals **6** in THF was injected followed by refluxing overnight to afford the corresponding internal alkynes **5**. The isolated yields of internal alkynes **5a**, **5b**, and **5c** were 88%, 80%, and 85%, respectively. It is well known that  $S_N2$  nucleophilic substitution can be significantly facilitated upon the utilization of highly polar aprotic cosolvents, e.g., hexamethylphosphoramide (HMPA) or *N,N'*-dimethylpropylene urea (DMPU); however, the amount of these polar aprotic

cosolvents is usually required in stoichiometric or excess quantities. As a result, the cost for the synthesis of sex pheromone substances and for the pest control management is significantly increased and unaffordable. In addition, the iodide anion plays an important bifunctional role, since iodide can serve as a good nucleophile to replace the bromo substituent of bromoacetals **6** and thus also serve as a good leaving group for the further alkylation reactions.

The second crucial step involves the pure *cis*-selective semihydrogenation of the internal alkynes **5**. Since Wittig olefination has been a prominent organic reaction for the construction of internal *cis*-double bond [30, 31], the practical utilization of Wittig olefination usually suffer with some difficulties; e.g., the stereoselectivity of Wittig reaction to obtain the pure long-chain *cis*-alkene isomer is practically not easy to control, the phosphonium salt precursor is gummy and usually leads to the remaining of undesired solvent residue and the low yield of product isolation, and equivalent phosphine oxide byproducts produced often limits the practical application of this method. Therefore, catalytic transfer semihydrogenation of internal alkynes **5a**, **5b**, and **5c** was performed to obtain *cis*-selective internal

TABLE 1: Comparison of the attractiveness of different sex pheromone lures for capturing male rice stem borer in Changhua in 2015.

First day of date range (end date 02/07)	Interval days (days)	Cumulative days (days)	Cumulative rainfall (mm)	Pest captured (heads)		Total pest count (heads)
				Plastic capillary lure (TG-A)	Paste lure (TG-B)	
23/04–	7	7	0.0	82	65	147
30/04–	7	14	24.5	192	188	380
07/05–	7	21	61.0	184 <sup>†</sup>	81	265
14/05–	14	35	398.5	117	115 <sup>†</sup>	232
28/05–	7	42	52.5	38	132 <sup>†</sup>	170
04/06–	7	49	30.0	55 <sup>†</sup>	192	247
11/06–	7	56	8.0	36 <sup>†</sup>	135 <sup>†</sup>	171
18/06–	7	63	21.5	17	96	113
25/06–	7	70	2.5	8	160	168
Total	70	70	598.5	729	1164	1,893

<sup>†</sup>Bird captured inside the wing sticky trap.

alkenes **4a**, **4b**, and **4c**, respectively, thereby eliminating the use of Wittig reaction [32–37, 38].

The semihydrogenation using molecular hydrogen in the presence of the Lindlar catalyst for the *cis*-selective reduction of internal alkynes into *cis*-alkenes is an important traditional organic transformation [38], and the reduction is often results in overreduced byproducts. Therefore, the *cis*-selective semihydrogenation of alkynes **5** was performed using 2 mol% of Pd(OAc)<sub>2</sub> in the presence of 1.5 equiv of KOH in DMF at 145 °C in a thick-walled sealed tube, which is considered to be a more versatile and safe hydrogenation process with excellent stereoselectivity [32]. It was found that the freshly distilled DMF gave better yields, compared with the undistilled DMF, and the *cis*-alkenes **4a**, **4b**, and **4c** were obtained in 81%, 76%, and 87% yields, respectively.

The resulting alkenes **4** were then subjected to the deprotection conditions in the presence of catalytic amount of PTSA in MeOH to afford the corresponding enols **9**. The isolated yields of enols **9a**, **9b**, and **9c** were 92%, 80%, and 86%, respectively. These alcohols were then subjected to PCC oxidation in presence of Celite in CH<sub>2</sub>Cl<sub>2</sub> as the solvent, and the desired aldehyde components **1**, **2**, and **3** were obtained in 89%, 84%, and 93% crude yields, respectively. The purpose for the utilization of Celite was to prevent the formation of inorganic lumps and to serve as an inorganic carrier for the PCC reagent. The final sex pheromone components **1**, **2**, and **3** were further purified using Kugelrohr distillation to afford colorless oils in approximately 60%–80% recovery yields.

## 2.2. Field Tests

**2.2.1. Field Test in Taiwan in 2015.** Since the damage and the crop loss caused by rice stem borer was more severe during the first rice harvest period in Taiwan, the attractiveness activity of the synthetic sex pheromone blend was first evaluated in the paddy field in Changhua County during the period of 23rd April to 2nd July in 2015. The insect pest count of rice stem borer for this field test in Taiwan is shown in Table 1.

During the date range between 23rd April and 2nd July, the total amount of male rice stem borer captured by the plastic

capillary lures (TG-A) was 729 heads, whereas that of the long-term releasing paste lures (TG-B) was 1164 heads. No insect pest was captured by the blank control trap. The results suggested that the synthetic sex pheromone blend was effective with no repellent chemical contained. After the application in paddy field for two months, the attractiveness of long-term releasing paste lure was still of satisfactory to attract the male rice stem borer effectively without the decrease of attractiveness. However, during the last few weeks of field test, the attractiveness of plastic capillary lure appeared to undergo a descending trend. In addition, since the sex pheromone blend in the plastic capillary lure was not encapsulated, the plastic capillary lure was indeed to exhibit slightly better attractiveness in the first few weeks as compared with the long-term releasing paste lure. It is noteworthy that there were several “bird-captured situations” happened during the field test period, as shown in Table 1. The reasonable explanation for this situation might be that the captured insect pest was treated as bird feed by those bird victims.

**2.2.2. Field Test in Jilin in 2018.** In order to test the attractiveness activity of the synthetic sex pheromone blend, synthesized at Chaoyang University of Technology in Taiwan, that can be utilized as the attractant for the male rice stem borer distributed in Jilin, the treatment group A, Trap 1–10, was conducted first from 27th June to 11th July. The total amount of male rice stem borer captured by these traps baited with the synthetic sex pheromone blend reached 407 heads in 15 days, and the results showed that the synthetic pheromone blend exhibited biological activity to attract the male rice stem borer.

The captured insect pest count of rice stem borer for the field test in Jilin is shown in Table 2. The total number of the male rice stem borer captured by sex pheromone traps 1–10 and 11–20 from 11th July to 20th September reached 2566 and 2774 heads, respectively. The duration with large amount of trapped male rice stem borers were almost coincided with the mass occurrence period of rice stem borer in Jilin. It is noteworthy that synthetic sex pheromone blend not only can be used for mass trapping of rice stem borer, but also can serve as an excellent tool for the forecasting of the population of rice stem borer.

TABLE 2: The pest count of male rice stem borer captured using the paste lure of the synthetic sex pheromone blend in Jilin in 2018.

First day of date range (end date 20/09)	Interval days (days)	Cumulative days (days)	Pest captured (heads)		Total pest count (heads)
			Trap 1–10	Trap 10–20	
11/07–	15	15	97	125	222
26/07–	15	30	372	507	879
11/08–	8	38	1112	1089	2201
19/08–	12	50	896	957	1853
31/08–	21	71	89	96	185
Total	71	71	2566	2774	5340

### 3. Conclusion

In summary, we have developed a versatile and common synthetic strategy for the synthesis of three analogously long-chain aliphatic internal *cis*-alkenyl aldehydes **1**, **2**, and **3**, as the sex pheromone components of rice stem borer, *Chilo suppressalis*. The modified synthesis of three *cis*-alkenyl aldehydes was accomplished in six steps, involving monobromination of diols, THP-protection, alkylation of terminal alkyne, *cis*-semihydrogenation, THP-deprotection, and oxidation, with the overall yield of 48%, 31%, and 47% for the sex pheromone components **1**, **2**, and **3**, respectively. The synthesis started with the monobromination of diols **7**, followed by the THP-protection of the remaining hydroxyl group to yield the corresponding THP-protected bromoacetals **6**. Two key steps were required to generate the long-chain aliphatic internal *cis*-alkenes **4** in excellent *cis*-stereoselectivity, including the alkylation of the terminal alkyne under greener conditions without the utilization of highly polar aprotic cosolvents, and the versatile pure *cis*-selective semihydrogenation process with excellent stereoselectivity for the reduction of long-chain aliphatic internal alkynes **5**. Using this synthetic strategy, the sex pheromone components **1**, **2**, and **3** can be obtained more practically in large quantities and can be subjected to the practical pest control of rice stem borer. The field tests performed in Changhua, Taiwan, suggested that the synthetic sex pheromone blend was effective. Since the sex pheromone blend in the long-term releasing paste lure was encapsulated, the attractiveness was competitive in the first few weeks as compared with the plastic capillary lure. The attractiveness of long-term releasing paste lure can last for at least two months to attract the male rice stem borer effectively without the decrease of attractiveness, whereas that of the plastic capillary lure appeared to undergo a descending trend after one month of field application. The field test results obtained in Jilin showed the coincided match with the mass occurrence period of rice stem borer in northern east of China. The synthetic sex pheromone blend of rice stem borer not only can be used for mass trapping but also can serve as an excellent tool for the monitoring of the pest distribution.

## 4. Experimental Section

### 4.1. Synthesis

**4.1.1. General Techniques and Materials.** All substrates and reagents were purchased as reagent grade from commercial suppliers and used as received. Substrates and reagents

including octane-1,8-diol (**4**), decane-1,10-diol (**5**), dodecane-1,12-diol (**6**), 1-hexyne, 1-octyne, hydrobromic acid, sodium iodide, potassium hydroxide, 3,4-dihydropyran (DHP), *p*-toluenesulfonic acid monohydrate (PTSA·H<sub>2</sub>O), and pyridinium chlorochromate (PCC) were purchased from Alfa Aesar. Palladium acetate and Lindlar catalyst were purchased from Strem Chemicals. *n*-BuLi was purchased as a 2.5 M solution in *n*-hexane from Sigma-Aldrich or Chemetall. Organic solvents including toluene, dichloromethane, and methanol were purchased from DUKSAN Chemicals and used without prior drying procedure. Tetrahydrofuran and *N,N*-dimethylformamide were purchased from Avantor and were dried by distillation using sodium-benzophenone ketyl and calcium hydride, respectively.

The proton and carbon-13 nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 200 MHz NMR spectrometer at ambient temperature. Chemical shift ( $\delta$ ) and coupling constant ( $J$ ) were expressed in unit of ppm and Hz, respectively. Samples for NMR measurements were dissolved in CDCl<sub>3</sub>, and the CHCl<sub>3</sub> residue in the corresponding deuterated solvent was used as the internal standard. The chemical shift of CHCl<sub>3</sub> was calibrated at  $\delta$  7.26 ppm in <sup>1</sup>H NMR spectra and  $\delta$  77.0 ppm in <sup>13</sup>C NMR spectra.

Thin-layer chromatography (TLC) was performed on Merck 25 TLC aluminum sheets (silica gel 60 F<sub>254</sub>). The developed TLC sheets were visualized under UV light (254 nm) or by using appropriate TLC stains, e.g., ethanolic phosphomolybdic acid solution or potassium permanganate solution. Column chromatography was performed on Merck silica gel 60 (70–230 mesh), and Merck silica gel 60 (230–400 mesh) was used for flash column chromatography.

**4.1.2. General Synthesis Procedure for Bromoalcohols **8a**, **8b**, and **8c**.** To a stirred solution of diol **7** (300 mmol, 1.0 equiv) in toluene (600 mL) was added slowly 48% HBr (360 mmol, 1.2 equiv) at RT. The reaction mixture was refluxed at 120°C for 16 h. After cooling to 0°C for 30 min, the organic layer was separated and washed with saturated NaHCO<sub>3</sub> solution. The resulting aqueous layer was extracted with hexane (120 mL × 3). The combined organic layer was washed with brine (300 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated in vacuo to obtain the corresponding bromoalcohol **8** as a light yellow oil. The crude bromoalcohol **8** was employed in the next step without further purification. Bromoalcohols **8a**, **8b**, and **8c** were synthesized independently according to the general procedure with 90%, 85%, and 91% yields, respectively. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,

ppm) for **8a**:  $\delta$  3.63 (t,  $J$  = 6.5 Hz, 2H), 3.40 (t,  $J$  = 6.8 Hz, 2H), 1.90–1.75 (m, 2H), 1.55–1.40 (m, 3H), 1.40–1.20 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) for **8a**:  $\delta$  62.54, 33.76, 32.66, 32.53, 29.33, 29.24, 29.21, 28.58, 27.99, 25.59.

**4.1.3. General Synthesis Procedure for THP-Protected Bromoacetals 6a, 6b, and 6c.** To a stirred solution of bromoalcohol **8** (200 mmol, 1.0 equiv) and PTSA· $\text{H}_2\text{O}$  (2 mmol, 1.0 mol%) in  $\text{CH}_2\text{Cl}_2$  (250 mL) was added DHP (240 mmol, 1.2 equiv) dropwise at 0 °C. After the addition of DHP was complete, the reaction mixture was stirred at 0 °C for 30 min and then stirred at RT for 16 hr. Saturated  $\text{NaHCO}_3$  solution (100 mL) was added to the reaction mixture and stirred for 10 min to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with *n*-hexane (50 mL  $\times$  3). The combined organic layer was washed with brine (250 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo to obtain the corresponding THP-protected bromoacetal **6** as a light yellow oil. The crude bromoacetal **6** was purified by Kugelrohr distillation. Bromoacetals **6a**, **6b**, and **6c** were synthesized independently according to the general procedure with 92%, 90%, and 88% yields, respectively.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm) for **6a**:  $\delta$  4.60–4.52 (m, 1H), 3.92–3.60 (m, 2H), 3.55–3.30 (m, 4H), 1.90–1.70 (m, 4H), 1.65–1.20 (m, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) for **6a**:  $\delta$  98.62, 67.44, 62.10, 33.77, 32.66, 30.61, 29.57, 29.29, 29.26, 29.21, 28.58, 27.99, 26.06, 25.36, 19.53.

**4.1.4. General Synthesis Procedure [28] for Internal Alkynes 5a, 5b, and 5c.** The appropriate terminal alkyne substrate 1-hexyne was used for the preparation of internal alkynes **5a** and **5b**, whereas the synthesis of internal alkyne **5c** required the utilization of 1-octyne as the terminal alkyne source.

Under  $\text{N}_2$  atmosphere, a solution of 2.5 M *n*-BuLi in hexane (360 mmol, 1.2 equiv) was introduced dropwise to a stirred solution of the terminal alkyne (1-hexyne or 1-octyne, 315 mmol, 1.05 equiv) in THF (150 mL) at –30 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h. To this reaction mixture was added anhydrous solid NaI (45 mmol, 0.15 equiv) and freshly distilled bromoacetal **6** (300 mmol, 1.0 equiv) at RT. The resulting mixture was refluxed for 16 h. After cooling to RT, the reaction was quenched with saturated  $\text{NaHCO}_3$  solution (300 mL). The organic layer was separated, and the aqueous layer was extracted with *n*-hexane (200 mL  $\times$  3). The combined organic layer was washed with brine (300 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo to afford the corresponding internal alkyne **5** as a light yellow oil. The crude product was used directly for next reaction without further purification. Alkynes **5a**, **5b**, and **5c** were synthesized independently according to the general procedure with 88%, 80%, and 85% yields, respectively.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm) for **5a**:  $\delta$  4.60–4.52 (m, 1H), 3.92–3.62 (m, 2H), 3.55–3.30 (m, 2H), 2.20–2.08 (m, 2H), 1.90–1.20 (m, 28H), 0.90 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) for **5a**:  $\delta$  98.68, 80.05, 80.01, 67.56, 62.15, 31.18, 30.68, 29.67, 29.62, 29.46, 29.40, 29.29, 29.08, 28.75, 26.16, 25.43, 21.83, 19.57, 18.66, 18.34, 13.54.

**4.1.5. General Synthesis Procedure [29, 32] for cis-Alkenes 4a, 4b, and 4c.** To a mixture of internal alkyne **5** (100 mmol, 1.0 equiv), ground KOH powder (150 mmol, 1.5 equiv), and catalytic amount of  $\text{Pd}(\text{OAc})_2$  (2 mmol, 2 mol%) in a thick-walled Pyrex seal tube was added degassed DMF (70 mL). The tube was sealed, and the mixture was stirred vigorously at 145 °C for 16 h. After the reaction mixture was cooled to RT, the seal tube was opened carefully inside a hood with good ventilation. The resulting reaction suspension was filtered through a Celite bed (3 cm), and the cake was washed repeatedly with *n*-hexane (300 mL). The combined filtrate was washed with water (150 mL  $\times$  5) in order to remove DMF. The combined aqueous layer was extracted with *n*-hexane (200 mL  $\times$  3). The combined organic layer was washed with brine (300 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo to afford *cis*-alkene **4** as a dark brown oil. The crude *cis*-alkene product was purified by column chromatography over silica gel with 10% *n*-hexane/ethyl acetate as a eluent to give pure *cis*-alkene **4** as a yellow oil. Alkenes **4a**, **4b**, and **4c** were synthesized independently according to the general procedure with 81%, 76%, and 87% yields, respectively.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm) for **4a**:  $\delta$  5.40–5.30 (m, 2H), 4.59–4.52 (m, 1H), 3.92–3.62 (m, 2H), 3.52–3.30 (m, 2H), 2.05–1.90 (m, 4H), 1.80–1.42 (m, 2H), 1.40–1.16 (m, 24H), 0.94–0.80 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) for **4a**:  $\delta$  129.80, 129.75, 98.38, 67.60, 62.21, 31.90, 30.72, 29.70, 29.64, 29.60, 29.54, 29.52, 29.48, 29.23, 27.12, 26.84, 26.18, 25.46, 22.75, 19.62, 13.93.

**4.1.6. General Synthesis Procedure for Alkenols 9a, 9b, and 9c.** A mixture of alkene **4** (160 mmol, 1.0 equiv) and PTSA· $\text{H}_2\text{O}$  (8 mmol, 5 mol%) in MeOH (300 mL) was stirred at RT for 16 h. After the evaporation of MeOH, the residue was treated with 1 M HCl solution (300 mL) and extracted with *n*-hexane (250 mL  $\times$  3). The combined organic layer was washed with brine (300 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo to afford alkenol **9** as a pale yellow oil. The crude product was used directly for the next reaction without further purification. Alkenols **9a**, **9b**, and **9c** were synthesized independently according to the general procedure with 92%, 80%, and 86% yields, respectively.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm) for **9a**:  $\delta$  5.35 (t,  $J$  = 4.5 Hz, 2H), 3.64 (t,  $J$  = 6.5 Hz, 2H), 2.08–1.88 (m, 4H), 1.68–1.40 (m, 4H), 1.40–1.16 (m, 16H), 0.92–0.80 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) for **9a**:  $\delta$  29.89, 129.86, 63.01, 32.87, 31.66, 29.78, 29.60, 29.52, 29.44, 29.36, 29.22, 27.24, 26.96, 25.82, 22.71, 14.15.

**4.1.7. General Synthesis Procedure for the Desired Alkenals 1, 2, and 3.** To a mixture of PCC (104 mmol, 1.3 equiv) and Celite (25 g) in  $\text{CH}_2\text{Cl}_2$  (400 mL) was added dropwise alkenols **9** (80 mmol, 1.0 equiv). The reaction mixture was stirred vigorously for 16 h at RT. The resulting reaction suspension was filtered through a silica gel plug (10 cm), and the cake was washed repeatedly with  $\text{Et}_2\text{O}$  (300 mL). The combined solution was concentrated in vacuo to afford the crude product which was subjected to Kugelrohr distillation to give pure alkenal as a colorless oil. The desired alkenals **1**,

2, and 3 were synthesized independently according to the general procedure with 89%, 84%, and 93% yields, respectively. **1**:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  9.76 (t,  $J=1.9$  Hz, 1H), 5.35 (t,  $J=4.8$  Hz, 2H), 2.42 (dt,  $J=1.8$ , 7.6 Hz, 2H), 2.06–1.90 (m, 4H), 1.72–1.52 (m, 2H), 1.42–1.20 (m, 16H), 0.96–0.82 (m, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  202.73, 129.76, 129.70, 43.98, 32.06, 29.83, 29.55, 29.49, 29.44, 29.35, 29.26, 27.28, 27.02, 22.46, 22.20, 14.13. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{30}\text{O}$   $[\text{M}+\text{H}]^+$ : 238.2297; found: 238.2294. **2**:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  9.75 (t,  $J=1.9$  Hz, 1H), 5.35 (t,  $J=4.5$  Hz, 2H), 2.42 (dt,  $J=1.9$ , 7.3 Hz, 2H), 2.08–1.90 (m, 4H), 1.72–1.52 (m, 2H), 1.42–1.20 (m, 20H), 0.96–0.82 (m, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  202.75, 129.72(2), 43.98, 32.06, 29.86, 29.67(3), 29.52, 29.44, 29.39, 29.26, 27.30, 27.02, 22.46, 22.21, 14.12. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{30}\text{O}$   $[\text{M}+\text{H}]^+$ : 266.2610; found: 266.2614. **3**:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  9.76 (t,  $J=1.8$  Hz, 1H), 5.42–5.24 (m, 2H), 2.42 (dt,  $J=1.6$ , 7.4 Hz, 2H), 2.06–1.88 (m, 4H), 1.76–1.50 (m, 2H), 1.46–1.18 (m, 16H), 0.96–0.82 (m, 3H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  202.76, 130.18, 129.83, 44.28, 32.18, 30.14(2), 30.06, 29.65, 29.54, 29.45, 29.40, 27.64, 23.08, 22.50, 14.55. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{30}\text{O}$   $[\text{M}+\text{H}]^+$ : 238.2297; found: 238.2299.

#### 4.2. Field Tests

**4.2.1. Pheromone Lures.** The sex pheromone blend of rice stem borer was prepared by mixing the aldehyde components **1**, **2**, and **3** in an exact ratio of 48:6:5 by weight [16] and was used for the preparation of sex pheromone lures, e.g., conventional plastic capillary lure and long-term releasing paste lure. The quantities of the sex pheromone blend of rice stem borer contained in each plastic capillary lure and long-term releasing paste lure were controlled to be 0.85 mg.

The preparation procedure of the plastic capillary is described below, whereas the long-term releasing formulation was obtained by sending the pheromone blend to Pheromone Center, Chaoyang University of Technology, and was performed according to the well-known micro-encapsulation process using modified interfacial polycondensation strategy [39, 40]. The long-term releasing lure provided by Pheromone Center was packaged into a 4 g weight ointment tube and appeared as a brown paste. For each of the pheromone trap for rice stem borer, the required amount of the pheromone paste lure was approximately 0.1 g with an applied length of ca. 1.0 cm of the very paste, which as described earlier has 0.85 mg of the sex pheromone blend of rice stem borer.

The conventional plastic capillary lure using the synthetic sex pheromone blend was also prepared by Pheromone Center, Chaoyang University of Technology, according to the following procedure. The freshly prepared sex pheromone blend of rice stem borer was diluted with hexane to an appropriate concentration. To the center of a 6 cm long plastic capillary was injected 5  $\mu\text{L}$  of the hexane solution of the sex pheromone blend, and then both ends of the corresponding plastic capillary were sealed.

**4.2.2. Pheromone Traps.** The commercial available wing sticky trap with sticky pad was employed for the capture of rice stem borer and was purchased from Zhen-Yong Enterprise Ltd., Taiwan. The wing sticky traps were fixed on a bamboo stick and were placed close to the edge of the paddy field with 30 m distance apart from each other. The elevation of the pheromone trap was set 20 cm above the top leaves of rice crops and was adjusted while necessary as the rice crop grew. Once the pheromone lure was applied to the center of the wing-type trap cover, no replacement of the cover and no additional pheromone lure were applied, where the bottom sticky pad was examined and pest count was recorded every week. The bottom sticky pad should be replaced to a new one when the pad is full of insect pests.

**4.2.3. Field Test in Taiwan in 2015.** In order to prove the attractiveness of the synthetic sex pheromone components, the field test was performed during the first rice harvest period in Taiwan, starting from 23rd April to 2nd July in 2015. The rice cultivation area was located in Dacun Township, Changhua County, Taiwan. This field test area was approximately 0.26 ha (96 m  $\times$  27 m). The north, the east, and the south sides were surrounded by paddy fields, and the west was close to an 8 meter wide road next to other paddy fields. Two different treatment groups and one blank control group were applied to the field test. The number of the plastic capillary lure group (Treatment Group A, TG-A), the paste lure group (Treatment Group B, TG-B), and blank control group (CK) were set to be 3:3:1, due to the limitation of the rice cultivation area in Taiwan. The position of all wing sticky traps was switch clockwise every two weeks.

**4.2.4. Field Test in Jilin in 2018.** A collaborated field test was carried out in a rice cultivation area from 11th July to 20th September in 2018 in Jilin, the northeastern province in China, where rice stem borer is the most significant insect pest of rice crops. The field test area was approximately 3.3 ha (300 m  $\times$  110 m), of which 1.8 ha was treated with sex pheromone traps and 0.9 ha was left untreated. The north and the west were surrounded by paddy fields, the south was next to a soybean field, and the east was close to a road. The number of the paste lure group and blank control group was set to be 20:10.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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