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# Synthesis of the sex pheromones of *Spodoptera frugiperda* (J. E, Smith)

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**Abstract:** The sex pheromone of *Spodoptera frugiperda* (J. E, Smith), has the advantages of the safety to the environment and the natural enemies, and without insecticides resistance. Its active components included (*Z*)-dodec-7-en-1-yl acetate, (*Z*)-dodec-9-en-1-yl acetate, (*Z*)-tetradec-9-en-1-yl acetate, (*Z*)-hexadec-11-en-1-yl acetate, (*E*)-dodec-7-en-1-yl acetate and (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate. The novel, efficient and concise synthesis of *S. frugiperda* (J. E, Smith) sex pheromones has been achieved. The key steps of this synthetic approach involved Wittig coupling of aldehyde with functionalized phosphomium salt, the alkylation of alkynes, and Knoevenagel condensation reaction of malonic acid with propionic aldehyde. Furthermore, the Wittig reaction of hydroxy-bearing phosphomium salt and Knoevenagel condensation reaction were firstly applied to the synthesis of *S. frugiperda* (J. E, Smith) sex pheromones.

**Keywords:** *Spodoptera frugiperda* (J. E, Smith); synthesis of pheromones; functionalized phosphomium salt; Knoevenagel condensation reaction

# 草地贪夜蛾性信息素的合成

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**摘 要：**草地贪夜蛾性信息素具有不伤害天敌、不产生抗药性、对环境安全等优点。其主要活性成分为：(*Z*)-7-十二碳烯-1-醇乙酸酯、(*Z*)-9-十二碳烯-1-醇乙酸酯、(*Z*)-9-十四碳烯-1-醇乙酸酯、(*Z*)-11-十六碳烯-1-醇乙酸酯、(*E*)-7-十二碳烯-1-醇乙酸酯和 (9*Z*, 12*E*)- 9,12-十四碳二烯-1-醇乙酸酯。本文研究了一种高效、简捷的合成草地贪夜蛾性信息素的新方法，其关键步骤包括：醛与官能团化鏻盐的 Wittig 偶联、炔的烷基化以及丙二酸与丙醛的 Knoevenagel 缩合等反应。其中醛与羟基鏻盐的 Wittig 反应及 Knoevenagel 缩合反应首次用于草地贪夜蛾性信息素的合成。

**关键词:** 草地贪夜蛾；信息素合成；官能团化鏻盐；Knoevenagel 缩合反应

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## 0 Introduction

*Spodoptera frugiperda* (J. E, Smith), has caused substantial damage to various grain and forage crops throughout the Americans and has recently invaded into Africa and Asia[1]. This pest becomes very difficult to control because of its resistance to many insecticides including *Bacillus thuringiensis* (Bt) corns[2-3]. The sex pheromone technology is one of the most promising and environment-friendly strategies which can be used for monitoring, mating disruption, attracting and mass trapping of *S. frugiperda* (J. E, Smith)[4].

The main active components of *S. frugiperda* (J. E, Smith) sex pheromone have been isolated and identified as *Z* enol acetates (**1**-**4**), (*E*)-dodec-7-en-1-yl acetate (**5**) and (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (**6**) (Fig. 1)[5]. The key to prepare these unsaturated esters is to construct *Z*- and *E*- double C-C bonds. The main strategies for the *Z*-olefins involve the Lindlar hydrogenation of alkynes[6a-6b], olefin metathesis[7], deriving from methyl (*Z*)-hexadec-11-enoate or (*Z*)-2-butene-1,4-diol[8a], protonolysis or deiodoboronation of vinylic organoboranes[9] and the catalytic Shapiro reaction[10]. As for the *E*-olefins, the current methods are based on cyclopropane cleavage reaction[11], Grignard coupling of alkenyl halides[12], and *E*-materials such as methyl (*E*)-pent-3-enoate or (*E*)-pent-3-enenitrile[13-14a]. However, these reported approaches suffered from some limitations, such as expensive *Z* or *E* olefins, tedious synthetic sequences, or toxicity to environment.

To develop a more concise and efficient synthetic route of *S. frugiperda* (J. E, Smith) sex pheromones, herein, we have disclosed the preparation of the unsaturated esters **1**-**6** based on the following key strategies: Wittig coupling of the aldehyde with functionalized phosphomium salt, the alkylation of alkynes, and Knoevenagel condensation reaction of malonic acid with propionic aldehyde (**Schemes 1-4**).

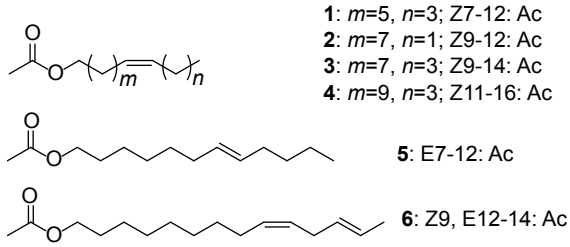



**Fig. 1 The main active components of *S. frugiperda* (J. E, Smith) sex pheromones**

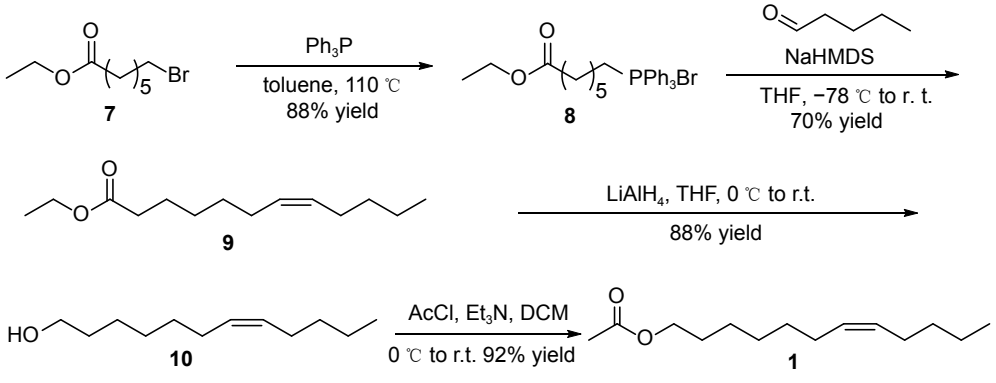
## 1 Experimental section

### 1.1 Instruments and reagents

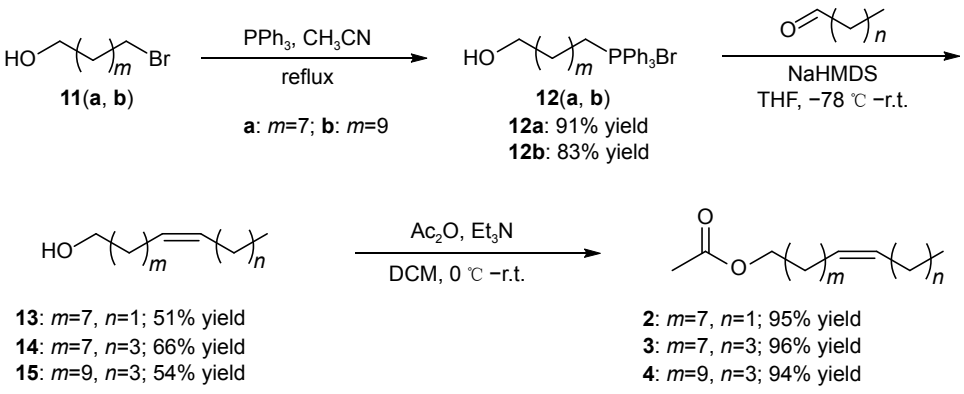
All reactions were conducted under an argon atmosphere with Schlenk techniques unless indicated. Solvents were purified following the standard strategies, and other commercial reagents were used directly. $^1$H and $^{13}$C NMR spectra were collected on a Bruker DP-X300 MHz spectrometer with internal tetramethylsilane (TMS) for $^1$H NMR and $CDCl_3$ for $^{13}$C NMR. High resolution mass spectrometry (HMRS) data were recorded on an Agilent instrument with the TOF MS technique.

### 1.2 Experimental procedure

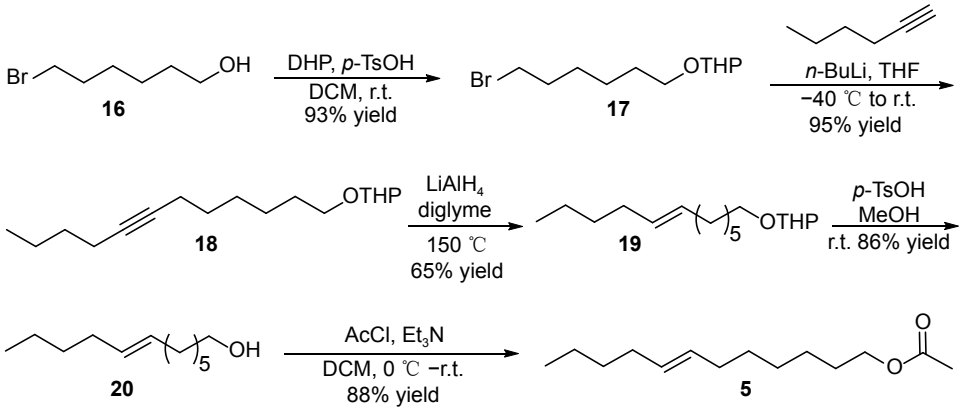
1.2.1 (7-Ethoxy-7-oxoheptyl)triphenylphosphonium bromide (**8**) In a three-neck 100-mL Schlenk flask, ethyl 7-bromoheptanoate (**7**) (2.371 g, 10.0 mmol),



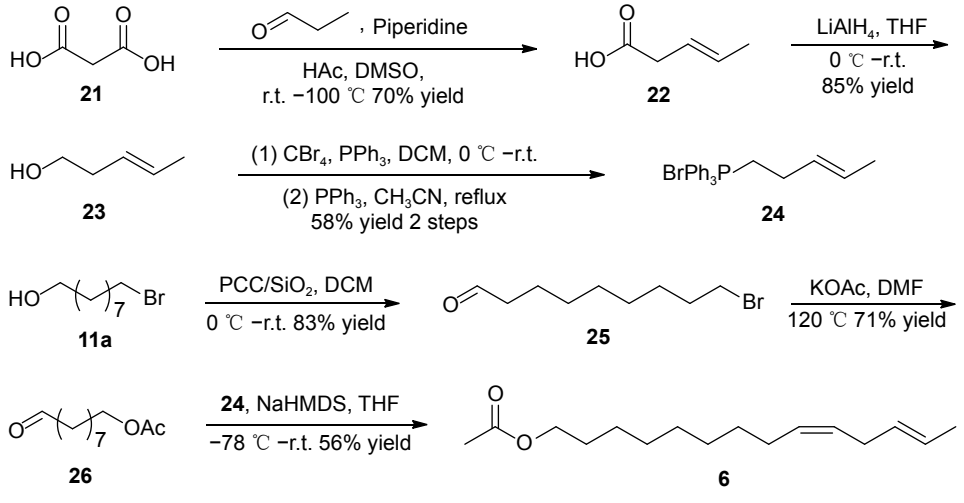

**Scheme 1 The synthesis of the sex pheromone 1**




**Scheme 2 The synthesis of the sex pheromones 2-4**




**Scheme 3 The synthesis of the sex pheromone 5**




**Scheme 4 The synthesis of the sex pheromone 6**

$Ph_3P$ (3.934 g, 15.0 mmol) and anhydrous toluene (30 mL) were added under an argon atmosphere at room temperature. The reaction mixture was heated to 110 °C and stirring for 24 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography ($V$(dichloromethane) : $V$(methanol) = 20 : 1) to provide (7-ethoxy-7-oxoheptyl)triphenylphosphonium bromide (**8**) (4.395 g, 88% yield) as a colorless oil. NMR characterization data for compound **8** were consistent with the literature data[15].

1.2.2 Ethyl (*Z*)-dodec-7-enoate (**9**) In a two-neck 50-mL Schlenk flask, the phosphomium salt **8** (1.498 g, 3.0 mmol) and anhydrous tetrahydrofuran (THF) (10 mL) was added under an argon atmosphere at

room temperature. The mixture was cooled to −78 °C, and sodium bis (trimethylsilyl) amide (1.75 mL, 2 mol/L in THF, 3.5 mmol) was then added over 25 min via syringe. The resulting mixture was stirred for 1 h at −78 °C. After valeraldehyde (0.086 1 g, 1.0 mmol) was added, the reaction mixture was allowed to warm slowly to room temperature and stirring overnight. The reaction was quenched with saturated $NH_4Cl$ aqueous solution (5 mL), and organic layer was separated. The aqueous phase was extracted with $Et_2O$ (3 × 10 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 120 : 1) to provide ethyl (*Z*)-dodec-7-enoate (**9**) (0.158 g, 70% yield) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.37−5.32 (m, 2H), 4.12 (q, $J$ = 7.1 Hz, 2H), 2.29 (t, $J$ = 7.2 Hz, 2H), 2.02−2.00 (m, 4H), 1.65−1.59 (m, 2H), 1.33−1.28 (m, 8H), 1.25 (t, $J$ = 7.2 Hz, 3H), 0.88 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 173.8, 130.1, 129.5, 60.1, 34.4, 31.9, 29.4, 28.8, 27.0, 26.9, 24.9, 22.3, 14.2, 14.0. HRMS (APCI-TOF): calcd for $C_{14}H_{27}O_2$ $[M+H]^+$ 227.201 1, found 227.200 6.

1.2.3 (*Z*)-Dodec-7-en-1-ol (**10**) In a two-neck 25-mL Schlenk flask, $LiAlH_4$ (0.114 g, 3.0 mmol) was placed under an argon atmosphere at room temperature. Anhydrous THF (5 mL) was added, and the resulting mixture was cooled to 0 °C. (*Z*)-Dodec-7-enoate (**9**) (0.226 g, 1.0 mmol) in THF (3 mL) was then added via syringe. The reaction mixture was allowed to warm slowly to room temperature and stirring overnight. The reaction was quenched with saturated $NH_4Cl$ aqueous solution (5 mL), and organic layer was separated. The aqueous phase was extracted with $Et_2O$ (3 × 5 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 120 : 1) to provide (*Z*)-dodec-7-en-1-ol (**10**) (0.162 g, 88% yield, 93% *Z* as determined by $^{13}$C NMR) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.37−5.33 (m, 2H), 3.64 (t, $J$ = 6.6 Hz, 2H), 2.03−2.01 (m, 4H), 1.61−1.53 (m, 2H), 1.34−1.33 (m, 11H), 0.89 (t, $J$ = 7.0, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 130.0, 129.7, 63.0, 32.8, 31.9, 29.7, 29.0, 27.1, 26.9, 25.6, 22.3, 14.0. HRMS (APCI-TOF): calcd for $C_{12}H_{25}O$ $[M+H]^+$ 185.190 5, found 185.190 0. NMR characterization data for compound **10** were consistent with the literature data[16].

1.2.4 (*Z*)-Dodec-7-en-1-yl acetate (**1**) In a two-neck 50-mL Schlenk flask, anhydrous dichloromethane (DCM) (3 mL) and (*Z*)-dodec-7-en-1-ol (**10**) (0.184 g, 1.0 mmol) and triethylamine ($Et_3N$) (0.607 g, 6.0 mmol) were added sequentially under an argon atmosphere at room temperature. The resulting mixture was cooled to 0 °C, acetyl chloride (0.236 g, 3.0 mmol) in DCM (2 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for additional 8 h. The reaction was quenched with water (5 mL), and organic layer was separated. The aqueous phase was extracted with $Et_2O$ (3 × 5 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 80 : 1) to provide (*Z*)-dodec-7-en-1-yl acetate (**1**) (0.208 g, 92% yield, 93% *Z* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.37−5.33 (m, 2H), 4.02 (t, $J$ = 6.7 Hz, 2H), 2.04−2.01 (m, 7H), 1.62−1.57 (m, 2H), 1.34−1.30 (m, 10H), 0.88 (t, $J$ = 6.9, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 171.0, 129.9, 129.5, 64.5, 31.9, 29.5, 28.8, 28.5, 27.0, 26.8, 25.7, 22.2, 20.8, 13.9. HRMS (APCI-TOF): calcd for $C_{14}H_{27}O_2$ $[M+H]^+$ 227.201 2, found 227.200 6. NMR characterization data for compound **1** were consistent with the literature data[9b].

1.2.5 (9-Hydroxnonyl)triphenylphosphonium bromide (**12a**) In a three-neck 100-mL Schlenk flask, 9-bromononan-1-ol (**11a**) (1.000 g, 4.5 mmol) and $Ph_3P$ (1.760 g, 6.7 mmol), and MeCN (40 mL)

were added under an argon atmosphere at room temperature. The reaction mixture was heated to reflux and stirring for 48 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 10 : 1) to afford (9-hydroxnonyl)triphenyl- phosphonium bromide (**12a**) as a pale yellow oil (1.980 g, 91% yield). HRMS (APCI-TOF): calcd for $C_{27}H_{35}OBrNaP$ $[M+Na]^+$ 508.150 1, found 508.120 2. NMR characterization data for compound **12a** were consistent with the literature data[15].

1.2.6 (*Z*)-Dodec-9-en-1-ol (**13**) In a 250-mL Schlenk flask, phosphonium salt **12a** (8.000 g, 16.5 mmol) and anhydrous THF (100 mL) were added under an argon atmosphere at room temperature. The mixture was cooled to −78 °C, and sodium bis (trimethylsilyl) amide (16.5 mL, 2.0 mol/L in THF, 33.0 mmol) was then added dropwise via syringe. The resulting mixture was stirred for 1 h at −78 °C. After propanal (1.920 g, 33.0 mmol) was added, the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with saturated $NH_4Cl$ aqueous solution (40 mL), and organic layer was separated. The aqueous phase was extracted with $Et_2O$ (3 × 50 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 5 : 1) to provide (*Z*)-dodec-9-en-1-ol (**13**) (1.550 g, 51% yield, 97% *Z* as determined by $^{13}$C-NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.40−5.27 (m, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.06−1.98 (m, 5H), 1.58−1.30 (m, 12H), 0.95 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 131.5, 129.2, 62.8, 32.7, 29.7, 29.4, 29.4, 29.1, 27.0, 25.7, 20.4, 14.3. HRMS (APCI-TOF): calcd for $C_{12}H_{25}O$ $[M+H]^+$ 185.190 0, found 185.190 1. NMR characterization data for compound **13** were consistent with the literature data[17a].

1.2.7 (*Z*)-Dodec-9-en-1-yl acetate (**2**) In a 100-mL Schlenk flask, anhydrous DCM (40 mL) and (*Z*)-dodec-9-en-1-ol (**13**) (1.471 g, 8.0 mmol) and $Et_3N$ (4.790 g, 47.3 mmol) were added sequentially under an argon atmosphere at room temperature. The resulting mixture was cooled to 0 °C, and acetic anhydride (2.420 g, 23.7 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for additional 8 h. The reaction was quenched with water (20 mL), and organic layer was separated. The aqueous phase was extracted with DCM (3 × 30 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 80 : 1) to provide (*Z*)-dodec-9-en-1-yl acetate (**2**) (1.715 g, 95% yield, 97% Z as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.56−5.10 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 3H), 2.04−1.90 (m, 4H), 1.64−1.30 (m, 12H), 0.96 (t, *J* = 6.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 171.1, 131.5, 129.2, 64.6, 29.7, 29.3, 29.2, 29.1, 28.6, 27.0, 25.9, 20.9, 20.5, 14.3. HRMS (APCI-TOF): calcd for $C_{14}H_{27}O_2$ $[M+H]^+$ 227.200 6, found 227.200 8. $^1$H NMR characterization data for compound **2** were consistent with the literature data[18a].

1.2.8 (*Z*)-Tetradec-9-en-1-ol (**14**) According to the similar procedure for the enol **13**, the Wittig coupling of phosphonium salt **12a** (8.000 g, 16.5 mmol) with pentanal (2.840 g, 33.0 mmol) provided (*Z*)-tetradec-9-en-1-ol (**14**) (2.327 g, 66% yield, 97% *Z* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.36−5.33 (m, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.02−1.99 (m, 5H), 1.56−1.53 (m, 2H), 1.35−1.30 (m, 14H), 0.90 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 129.8, 129.7, 62.8, 32.7, 31.9, 29.7, 29.4, 29.3, 29.16, 27.1, 26.8, 25.7, 22.8, 13.9. HRMS (APCI-TOF): calcd for $C_{14}H_{28}ONa$ $[M+Na]^+$ 235.203 2, found 235.204 0. NMR characterization data for compound **14** were consistent with the literature data[17a].

1.2.9 (*Z*)-Tetradec-9-en-1-yl acetate (**3**) According

to the similar procedure for the sex pheromones **2**, the esterification of (*Z*)-tetradec-9-en-1-ol (**14**) (2.228 g, 10.5 mmol) with acetic anhydride (3.216 g, 31.5 mmol) gave (*Z*)-tetradec-9-en-1-yl acetate (**3**) (2.557 g, 96% yield, 96% *Z* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.36−5.32 (m, 2H), 4.05 (t, $J$ = 6.8 Hz, 2H), 2.04 (s, 3H), 2.03−1.99 (m, 4H), 1.64−1.59 (m, 2H), 1.34−1.30 (m, 14H), 0.90 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 171.0, 129.8, 129.7, 64.5, 31.9, 29.7, 29.3, 29.2, 29.1, 28.6, 27.1, 26.8, 25.8, 22.3, 20.9, 13.9. HRMS (APCI-TOF): calcd for $C_{16}H_{30}O_2Na$ $[M+Na]^+$ 277.213 8, found 277.214 2. NMR characterization data for compound **3** is consistent with the literature data[6b-6c].

1.2.10 (11-Hydroxundecyl)triphenylphosphonium bromide (**12b**) According to the similar procedure for the phosphonium salt **12a**, the reaction of 11-bromoundecan-1-ol (**11b**) (0.502 g, 2.0 mmol) with $Ph_3P$ (0.787 g, 3.0 mmol) afforded (11-hydroxundecyl) triphenyl-phosphonium bromide (**12b**) as a pale yellow oil (0.849 g, 83% yield). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 7.86−7.71 (m, 15H), 3.60−3.55 (m, 4H), 3.04 (brs, 1H), 1.62−1.47 (m, 6H), 1.27−1.19 (m, 12H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$:134.6, 134.5, 133.0, 132.9, 130.1, 129.9, 118.1, 117.0, 61.7, 32.1, 29.8, 29.6, 28.8, 28.7, 28.6, 28.4, 25.2, 22.5, 21.8. HRMS (APCI-TOF): calcd for $C_{29}H_{39}OBrP$ $[M+H]^+$ 513.191 6, found 513.178 8. $^1$H NMR characterization data for compound **12b** were consistent with the literature data[19].

1.2.11 (*Z*)-Hexadec-11-en-1-ol (**15**) According to the similar procedure for the enol **13**, the Wittig coupling of phosphonium salt **12b** (1.026 g, 2.0 mmol) with pentanal (0.120 g, 1.3 mmol) provided (*Z*)-hexadec-11-en-1-ol (**15**) (0.168 g, 54% yield, 97% *Z* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.36−5.33 (m, 2H), 3.62 (t, $J$ = 6.7 Hz, 2H), 2.17 (brs, 1H), 2.04−2.00 (m, 4H), 1.60−1.50 (m, 2H), 1.35−1.28 (m, 18H), 0.90 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 129.8, 129.8, 62.9, 32.7, 31.9, 29.7, 29.6, 29.52, 29.48, 29.4, 29.2, 27.1, 26.9, 25.7, 22.3, 13.9. HRMS (APCI-TOF): calcd for $C_{16}H_{32}ONa$ $[M+Na]^+$ 263.234 5, found 263.235 5. $^1$H NMR characterization data for compound **15** were consistent with the literature data[20].

1.2.12 (*Z*)-Hexadec-11-en-1-yl acetate (**4**) According to the similar procedure for the sex pheromones **2**, the esterification of (*Z*)-hexadec-11-en-1-ol (**15**) (0.103 g, 0.43 mmol) with acetic anhydride (0.133 g, 1.3 mmol) afforded (*Z*)-hexadec-11-en-1-yl acetate (**4**) (0.114 g, 94% yield, 96% *Z* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.35 (t, $J$ = 4.6 Hz, 2H), 4.05 (t, $J$ = 6.8 Hz, 2H), 2.04 (s, 3H), 2.01−1.99 (m, 3H), 1.64−1.57 (m, 2H), 1.35−1.28 (m, 18H), 0.88 (t, $J$ = 4.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 171.0, 129.8, 129.7, 64.6, 31.9, 29.7, 29.49, 29.47, 29.46, 29.23, 29.21, 28.6, 27.1, 26.9, 25.9, 22.3, 20.9, 13.9. HRMS (APCI-TOF): calcd for $C_{18}H_{34}O_2Na$ $[M+Na]^+$ 305.245 1, found 305.246 5. NMR characterization data for compound **4** were consistent with the literature data[20].

1.2.13 2-((6-Bromohexyl)oxy)tetrahydro-2*H*-pyran (**17**) In a 20-mL Schlenk tube, 6-bromohexan-1-ol (**16**) (0.996 g, 5.5 mmol), dihydropyrane (0.950 g, 11.0 mmol) and anhydrous DCM (10 mL) were added sequentially at room temperature. *p*-Toluenesulfonic acid (0.133 g, 1.3 mmol) was added dropwise, and the reaction mixture was stirred for 8 h at the same temperature. After the reaction was completed, it was washed with saturated $Na_2CO_3$ aqueous solution (20 mL) and organic layer was separated. The aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography ($V$(petroleum ether) : $V$(ethyl acetate) = 80 : 1) to provide 2-((6-bromohexyl)oxy)tetrahydro-2*H*-pyran (**17**) (1.360 g, 93% yield) as a pale yellow oil. HRMS (APCI-TOF): calcd for $C_{11}H_{22}O_2Br$ $[M+H]^+$ 265.079 8, found 265.079 8. NMR characterization data for compound **17** were consistent with the literature data[17c].

1.2.14 2-(Dodec-7-yn-1-yloxy)tetrahydro-2*H*-pyran (**18**) In a 50-mL Schlenk tube, hex-1-yne (0.790 g,

9.6 mmol) and anhydrous THF (20 mL) were added under an argon atmosphere at room temperature. The mixture solution was cooled to −48 °C, *n*-butyllithium (4 mL, 2.5 mol/L in *n*-hexane, 9.6 mmol) was added slowly and stirred for 2 h. 2-((6-bromohexyl)oxy) tetrahydro-2*H*-pyran (**17**) (1.270 g, 4.8 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stirred for 24 h. After the reaction was completed, it was cooled to 0 °C and quenched with water (2 mL). Organic layer was separated, and the aqueous phase was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(ethyl acetate) = 100 : 1) to generate 2-(dodec-7-yn-1-yloxy)tetrahydro-2*H*-pyran (**18**) (1.210 g, 95% yield) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.39−5.37 (m, 2H), 4.58 (t, *J* = 3.5 Hz, 1H), 3.87−3.72 (m, 2H), 3.52−3.37 (m, 2H), 2.14−2.09 (m, 4H), 1.83−1.38 (m, 18H), 0.91 (*t*, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 98.8, 80.1, 80.0, 67.5, 62.2, 31.2, 30.7, 29.6, 29.1, 28.6, 25.8, 25.5, 21.9, 19.6, 18.6, 18.4, 13.5. HRMS (APCI-TOF): calcd for $C_{17}H_{31}O_2$ $[M+H]^+$ 267.2316, found 267.2319.

1.2.15 (*E*)-2-(Dodec-7-en-1-yloxy)tetrahydro-2*H*-pyran (**19**) In a two-neck 100-mL Schlenk flask, $LiAlH_4$ (0.114 g, 3.0 mmol) and anhydrous diglyme (40 mL) were added under an argon atmosphere at room temperature. 2-(Dodec-7-yn-1-yloxy)tetrahydro-2*H*-pyran (**18**) (0.226 g, 1.0 mmol) was then added, and the reaction mixture was heated to reflux and stirring for 24 h. After the reaction was compledted, it was cooled to 0 °C. The reaction was quenched with saturated $NH_4Cl$ aqueous solution (3 mL) and MeOH (2 mL). The resulting mixture was filtered and rinsed with diethyl ether (30 mL). The combined filtrates were dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(ethyl acetate) = 110 : 1) to provide (*E*)-2-(dodec-7-en-1-yloxy)tetrahydro-2*H*-pyran (**19**) (0.174 g, 65% yield, 88% *E* as determined by $^{13}$C NMR) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.40−5.37 (m, 2H), 4.58 (t, *J* = 3.5 Hz, 1H), 3.87−3.72 (m, 2H), 3.52−3.36 (m, 2H), 1.98−1.95 (m, 4H), 1.59−1.53 (m, 8H), 1.33−1.29 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 130.4, 130.2, 98.8, 67.6, 62.3, 32.5, 32.3, 31.8, 30.8, 29.7, 29.6, 29.0, 26.1, 25.5, 22.2, 19.7, 13.9. HRMS (APCI-TOF): calcd for $C_{17}H_{33}O_2$ $[M+H]^+$ 269.2465, found 269.2475.

1.2.16 (*E*)-Dodec-7-en-1-ol (**20**) In a 20-mL Schlenk tube, (*E*)-2-(dodec-7-en-1-yloxy)tetrahydro-2*H*-pyran (**19**) (0.268 g, 1.0 mmol) and MeOH (10 mL) were added at room temperature. *p*-Toluenesulfonic acid (0.180 g, 0.1 mmol) was then added, and the reaction mixture was stirred for 30 min at the same temperature. After the reaction was completed, it was quenched with saturated $Na_2CO_3$ aqueous solution (3 mL) and organic layer was separated. The aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography ((*V*(petroleum ether) : *V*(ethyl acetate) = 50 : 1) to provide (*E*)-dodec-7-en-1-ol (**20**) (0.158 g, 86% yield, 88% *E* as determined by $^{13}$C NMR) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), *δ*: 5.39−5.33 (m, 2H), 3.64 (t, *J* = 6.1 Hz, 2H), 2.03−1.98 (m, 4H), 1.56−1.29 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$), *δ*: 130.4, 130.1, 63.0, 32.7, 32.5, 32.2, 31.8, 29.5, 28.9, 25.6, 22.2, 13.9. HRMS (APCI-TOF): calcd for $C_{12}H_{25}O$ $[M+H]^+$ 185.1897, found 185.1900. NMR characterization data for compound **20** were consistent with the literature data[9b].

1.2.17 (*E*)-Dodec-7-en-1-yl acetate (**5**) In a 20-mL Schlenk tube, anhydrous DCM (10 mL), (*E*)-dodec-7-en-1-ol (**20**) (0.184 g, 1.0 mmol) and $Et_3N$ (0.607 g, 6.0 mmol) were added sequentially under an argon atmosphere at room temperature. The resulting mixture was cooled to 0 °C, acetyl chloride (0.236 g, 3.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred

for additional 8 h. The reaction was quenched with water (5 mL), and organic layer was separated. The aqueous phase was extracted with DCM (3 × 10 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(ethyl acetate) = 80 : 1) to provide (*E*)-dodec-7-en-1-yl acetate (**5**) (0.199 g, 88% yield, 88% *E* as determined by $^{13}$C NMR) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.40−5.37 (m, 2H), 4.05 (t, $J$ = 6.8 Hz, 2H), 2.05 (s, 3H), 2.03−1.96 (m, 4H), 1.63 –1.29 (m, 12H), 0.89 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 171.2, 130.5, 130.1, 64.6, 32.5, 32.2, 31.8, 29.5, 28.7, 28.6, 25.8, 22.2, 21.0, 13.9. HRMS (APCI-TOF): calcd for $C_{14}H_{27}O_2$ $[M+H]^+$ 227.201 1, found 227.200 6. NMR characterization data for compound **5** were consistent with the literature data[9b].

1.2.18 (*E*)-Pent-3-enoic acid (**22**) In a 100-mL Schlenk flask, malonic acid (**21**) (10.406 g, 100.0 mmol), propionic aldehyde (2.904 g, 50.0 mmol) and dimethyl sulfoxide (DMSO) (40 mL) were added under an argon atmosphere at room temperature. Piperidine (0.042 6 g, 0.5 mmol) and acetic acid (0.030 0 g, 0.5 mmol) were added and the reaction mixture was stirred for 20 min at the same temperature. The reaction mixture was maintained for 2 h at 40 °C, and then was heated to 100 °C and stirred for additional 8 h. After the reaction mixture was cooled to room temperature, water (120 mL) was added. The resulting mixture was extracted with diethyl ether (3 × 100 mL), and the combined organic phases were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(ethyl acetate) = 2 : 1) to provide (*E*)-pent-3-enoic acid (**22**) (3.495 g, 70% yield, 97% *E* as determined by $^{13}$C NMR) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 10.61 (s, 1H), 5.68−5.47 (m, 2H), 3.07 (ddd, $J$ = 4.5, 2.3, 1.3 Hz, 2H), 1.72−1.69 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 178.8, 130.0, 121.9, 37.7, 17.8. HRMS (APCI-TOF): calcd for $C_5H_8O_2Na$ $[M+Na]^+$ 123.041 7, found 123.0416. NMR characterization data for compound **22** were consistent with the literature data[21a].

1.2.19 (*E*)-Pent-3-en-1-ol (**23**) In a 100-mL Schlenk flask, $LiAlH_4$ (1.389 g, 36.6 mmol) and anhydrous THF (60 mL) were added at 0 °C under an argon atmosphere, a solution of (*E*)-pent-3-enoic acid (**22**) (2.823 g, 28.2 mmol) in THF (10 mL) was added. The reaction mixture was allowed to warm to room temperature over 10 min and then stirred for 8 h. The reaction was quenched with water (3 mL) at 0 °C, followed by the addition of 15% NaOH aqueous solution (3 mL) and water (5 mL). The resuting mixture was stirred for 1 h and filtered. The filtrate was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to afford (*E*)-pent-3-en-1-ol (**23**) (2.060 g, 85% yield, 97% *E* as determined by $^{13}$C NMR) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.60−5.38 (m, 2H), 3.61 (t, $J$ = 6.4 Hz, 2H), 2.28−2.21 (m, 2H), 2.17 (brs, 1H), 1.69−1.66 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 128.1, 127.1, 61.9, 35.8, 17.9. HRMS (APCI-TOF): calcd for $C_5H_{10}ONa$ $[M+Na]^+$ 109.062 4, found 109.0648. NMR characterization data for compound **23** were consistent with the literature data[14a].

1.2.20 (*E*)-Bromo(pent-3-en-1-yl)triphenyl phosphane (**24**) In a 250-mL Schlenk flask, (*E*)-pent-3-en-1-ol (**23**) (1.998 g, 23.2 mmol), $CBr_4$ (11.540 g, 34.8 mmol) and anhydrous DCM (60 mL) were added under an argon atmosphere at room temperature. After cooling to 0 °C, triphenylphosphine (18.255 g, 69.6 mmol) in dry DCM (100 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for additional 5 h. After the reaction mixture was concentrated under reduced pressure, the residue was filtered and rinsed with diethyl ether (500 mL). The combined filtrates were concentrated under reduced pressure to give the crude product (*E*)-5-bromopent-2-ene (3.000 g).

In a 100-mL Schlenk flask, the crude (*E*)-5-bromopent-2-ene (0.999 g, 6.7 mmol) and dry

acetonitrile (60 mL) were added at room temperature under an argon atomosphere. Triphenylphosphine (2.649 g, 10.1 mmol) was then added, and the resulting mixture was refluxed for 48 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(chloromethane) : *V*(methanol) = 10 : 1) to provide (*E*)-bromo(pent-3-en-1-yl) triphenyl phosphane (**24**) (1.748 g, 58% yield over two steps) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 7.87−7.69 (m, 15H), 5.58−5.41 (m, 2H), 3.82−3.73 (m, 2H), 2.47−2.36 (m, 2H), 1.55−1.52 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 134.9, 134.9, 133.5, 133.4, 130.4, 130.3, 127.4, 127.2, 118.5, 117.4, 25.4, 23.1, 17.4. HRMS (APCI-TOF): calcd for $C_{23}H_{25}BrP$ $[M+H]^+$ 411.087 2, found 411.088 3. NMR characterization data for compound **24** were consistent with the literature data[14a].

1.2.21 9-Bromononanal (**25**) In a 250-mL Schlenk flask, pyridinium chlorochromate (8.687 g, 40.3 mmol), silica gel (8.690 g) and anhydrous DCM (70 mL) were added under an argon atmosphere at room temperature. The resulting mixture was cooled to 0 °C and 9-bromononan-1-ol (**11a**) (2.990 g, 13.4 mmol) in anhydrous DCM (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stired for 4 h. After the reaction was completed, DCM was removed under reduced pressure. The residue was filtered and rinsed with diethyl ether (500 mL). The filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(ethyl acetate) = 40 : 1) to provide 9-bromononanal (**25**) (2.448 g, 83% yield) as a pale yellow oil. HRMS (APCI-TOF): calcd for $C_9H_{18}OBr$ $[M+H]^+$ 221.053 6, found 221.054 4. NMR characterization data for compound **25** were consistent with the literature data[22a].

1.2.22 9-Oxononyl acetate (**26**) In a 50-mL Schlenk flask, KOAc (2.081 g, 21.2 mmol) and dimethyl formamide (DMF) (20 mL) were added at room temperature. 9-Bromononanal (**25**) (2.344 g, 10.6 mmol) was then added, and the resulting mixture was heated to 120 °C and stirred for 2 h. After the reaction was completed, it was poured into water (100 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (3 × 100 mL), and dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give 9-oxononyl acetate (**26**) (1.514 g, 71% yield) as a colorless oil. HRMS (APCI-TOF): calcd for $C_{11}H_{21}O_3$ $[M+H]^+$ 201.148 5, found 201.148 5. NMR characterization data for compound **26** were consistent with the literature data[22a].

1.2.23 (9*Z*,12*E*)-Tetradeca-9,12-dien-1-yl acetate (**6**) In a 100-mL Schlenk flask, phosphonium salt **24** (1.686 g, 4.1 mmol) and anhydrous THF (40 mL) were added under an argon atmosphere at room temperature. The mixture was cooled to −78 °C, and sodium bis(trimethylsilyl)amide (2.1 mL, 2 mol/L in THF, 4.2 mmol) was then added dropwise via syringe. The resulting mixture was stirred for 1 h at −78 °C. After aldehyde **26** (0.821 g, 4.1 mmol) was added, the reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. The reaction was quenched with saturated $NH_4Cl$ aqueous solution (20 mL), and organic layer was separated. The aqueous phase was extracted with $Et_2O$ (3 × 30 mL), and the combined organic layers were dried over anhydrous $Na_2SO_4$. After filtering, the filtrate was concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (*V*(petroleum ether) : *V*(dichloromethane) = 80 : 1) to provide (9*Z*,12*E*)-tetradeca-9, 12-dien-1-yl acetate (**6**) (0.578 g, 56% yield) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$), $\delta$: 5.46−5.30 (m, 4H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.73−2.69 (m, 2H), 2.04 (s, 3H), 2.02−1.99 (m, 2H), 1.66−1.64 (m, 5H), 1.36−1.30 (m, 10H). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$: 171.1, 130.3, 129.6, 127.6, 125.0, 64.5, 30.4, 29.6, 29.3, 29.2, 29.1, 28.6, 27.0, 25.8, 20.9, 17.8. HRMS (APCI-TOF): calcd for $C_{16}H_{29}O_2$ $[M+H]^+$ 253.216 2, found 253.216 1. NMR characterization data for compound **6** were consistent

with the literature data[14a].

## 2 Results and discussion

Our research started from the preparation of the sex pheromone **1** (Scheme 1). The initial step was the synthesis of ester-bearing phosphomium salt **8** from ethyl 7-bromoheptanoate (**7**) with 88% yield[14]. Subsequent Wittig coupling with valeraldehyde in the presence of sodium bis(trimethylsilyl)amide afforded ethyl (*Z*)-dodec-7-enoate (**9**)[15]. Its configuration of the double bond was assigned as *Z*, according to the intense resonances at $\delta$ 27.0 and 26.9, which matched the expected chemical shifts of the allylic carbons of a *Z*-double bond[17b]. Furthermore, the NMR characterization data of the reduced product of **9** were consistent with the literature data[16] for (*Z*)-dodec-7-en-1-ol (**10**), and it supported the confirmation to *Z* double configuration of **9**. The following esterification with acetyl chloride generated the sex pheromone **1** in 92% yield[9b].

We next investigated the preparations of three sex pheromones **2**-**4** (Scheme 2). To optimize the synthesis of these *Z* enol acetates, we tried hydroxy-bearing phosphomium salt in Wittig couplings of aldehydes because this method save the protection and the subsequent deprotection[18b]. Fortunately, the desired *Z* enols **13**-**15** were obtained from phosphomium salts **12a** and **12b**[15], which were synthesized by the reaction of bromo alcohol **11** and $Ph_3P$[19]. There were two evidences to support the confirmation to *Z* double configuration of enols **13**-**15**. NMR characterization data for these *Z* enols matched the literature data[20]. Meanwhile, their chemical shifts of the allylic carbons were consist with the expected ones[17b]. The final esterification with acetic anhydride afforded the target sex pheromones **2**-**4** almost quantitatively[21b].

Next, the sex pheromones **5** were synthesized (Scheme 3). In the presence of *n*-BuLi, the alkylation of hex-1-yne with tetrohydropyran(THP)-protected bromo alcohol **17** derived from 6-bromohexan-1-ol (**16**) afforded 2-(dodec-7-yn-1-yloxy)tetrahydro-2*H*-pyran (**18**) in 95% yield[22b]. The THP-protected alkynol **18** was then reduced to (*E*)-2-(dodec-7-en-1-yloxy)tetrahydro-2*H*-pyran (**19**) with $LiAlH_4$ in diglyme[23], and the assignment of its *E* double bond according to the consistence of its NMR spectra with the literature one[24] and the expected chemical shifts[17b]. After the deprotection with *p*-toluenesulfonic acid[8b], *Z* enol **20** was esterified to the desired sex pheromone **5** with acetyl chloride in $CH_2Cl_2$[9b].

Finally, we prepared the sex pheromone **6** (Scheme 4). The *E* double bond was constructed by Knoevenagel condensation reaction of malonic acid (**21**) with propionic aldehyde, and (*E*)-pent-3-enoic acid (**22**) was obtained in 70% yield[25]. Acid **22** was reduced to (*E*)-pent-3-en-1-ol (**23**) with $LiAlH_4$ in THF[26], and its NMR spectra was consistent with the literature data[14a]. Subsequent bromination and the reaction with $PPh_3$ generated phosphomium salt **24** in 58% yield in two steps[14a]. The other key intermediate **26** was then prepared. The oxidation of bromo alcohol **11a** with pyridinium chlorochromate furnished 9-bromononanal (**25**) in 83% yield[27]. Treating aldehyde **25** with KOAc resulted in the formation of 9-oxononyl acetate (**26**) in 71% yield[13]. *Z* Double bond was formed via the Wittig coupling of aldehyde **26** with phosphomium salt **24**, and the target sex pheromones **6** was obtained[15]. Its NMR spectra were identical to the reported one[13].

## 3 Conclusions

In summary, we have developed a novel, efficient and concise synthesis of *S. frugiperda* (J. E, Smith) sex pheromones. The synthetic approaches mainly include Wittig coupling of aldehyde with functionalized phosphomium salt, the alkylation of alkynes, and Knoevenagel condensation reaction of malonic acid with propionic aldehyde. It is noteworthy that this work is the first synthesis of *S. frugiperda* (J. E, Smith) sex pheromones via Knoevenagel condensation reaction and the Wittig reaction of hydroxy-bearing phosphomium salt, which could save the protection and the subsequent deprotection.

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