Supplementary Information (SI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2025

Supplementary Information

An Improved and Convenient New Synthesis of the Pheromone Components of the Tomato Leafminer *Tuta absoluta*

Shuai Yang, [a] Yan Cai, [a] and Zhiwei Miao [*a,b]

[a] State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Weijin Road 94, Tianjin 300071, P. R. China.

[b] Department of Ecological and Resources Engineering, Fujian Key laboratory of Eco-Industrial Green Technology, Wuyi University, Wuyishan, Fujian 354300, P. R. China.

E-mail: miaozhiwei@nankai.edu.cn

Table of Contents

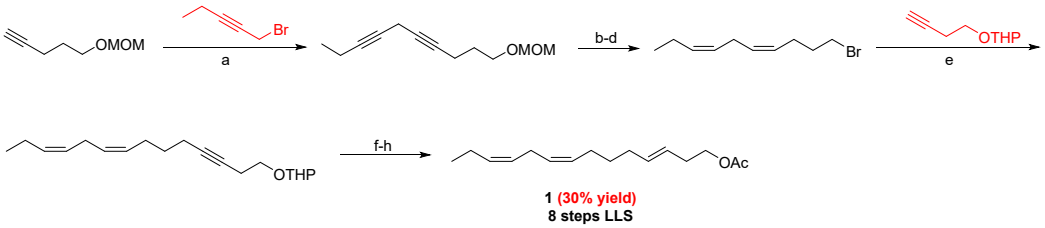
I. Supplementary Methods

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Leyan silica gel plates silica gel plates (GF254) using UV light as visualizing agent, and an water solution of K_2CO_3 and $KMnO_4$. Leyan silica gel (60, particle size 300-400 mesh) was used for flash column chromatography. NMR spectra were recorded on Bruker 400 MHz instrument. Gas chromatography (GC) using Agilent 8860 series with HP-5 column (30 m × 320 μm × 0,25 μm).

II. Summaries of Previous Syntheses

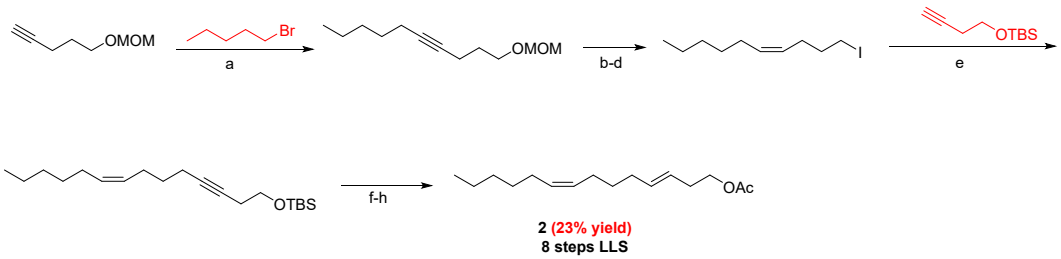
a). M. Puigmartí, M. P. Bosch and A. Guerrero. *Synthesis,* **2015**, 47, 961–968. (C5+C5+C4 strategy).

Pheromone 1



Key: (a) *i*-PrMgCl, CuBr· Me_2S, 0 ℃; (b) H_2, Lindlar catalyst, quinoline, r.t; (c) 6 M HCl aq, reflux; (d) NBS, Ph_3P, 0 ℃ to r.t; (e) *n*-BuLi, HMPA, -65 ℃ to r.t; (f) $NaNH_3$, -35 ℃; (g) PTSA, r.t; (h) Ac_2O, Et_3N, DMAP, r.t.

Pheromone 2

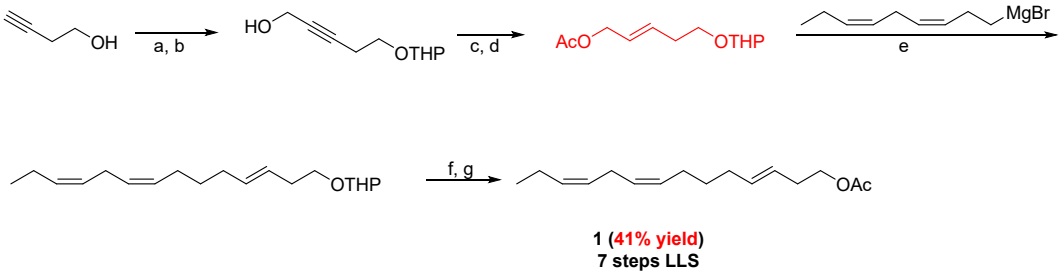


Key: (a) *n*-BuLi, HMPA, -70 ℃ to r.t; (b) 6 M HCl aq, reflux; (c) H_2, Lindlar catalyst, quinoline, r.t; (d) I_2, Ph_3P, imidazole, 0 ℃; (e) *n*-BuLi, HMPA, -65 ℃ to r.t; (f) $NaNH_3$, -35 ℃; (g) TBAF, r.t; (h) Ac_2O, Et_3N, DMAP, r.t.

b) J. A. Cabezas. *Tetrahedron Letters*, **2019**, 60, 407–410. (C4+C1+C9 strategy)

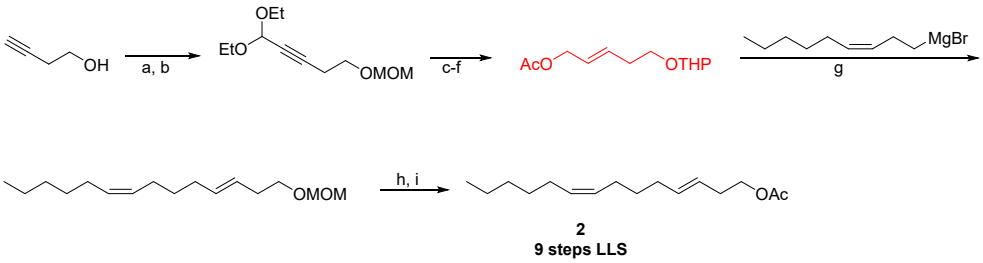
G. Eric, G. Loic and G. Olivier, PCT. Pat., WO2022171965, 2022.

Method A



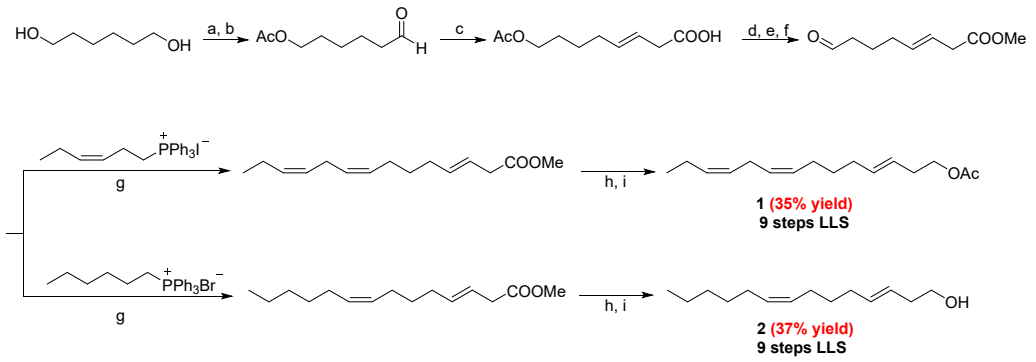
Key: (a) DHP, *p*-TSA, r.t; (b) *n*-BuLi, $(CH_2O)n$, -78 ℃ to r.t; (c) $LiAlH_4$, diglyme, 140 ℃; (d) Ac_2O, pyridine, r.t; (e) Li_2CuCl_4, -78 ℃ to r.t; (f) PTSA/EtOH, 60 ℃; (g) Ac_2O, Et_3N, DMAP, r.t.

Method B



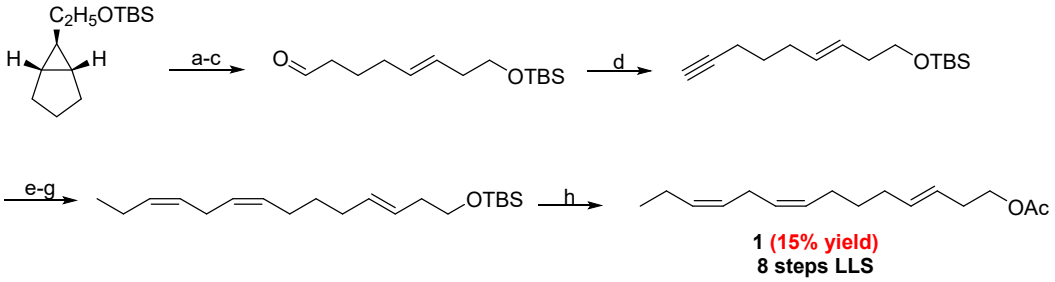
Key: (a) $CH_2(CH_3)_2$, *p*-TSA, LiBr, r.t; (b) CH_3MgCl, $CH(OEt)_3$, 50 ℃ to 90 ℃; (c) H_2, Lindlar catalyst, quinoline, r.t; (d) 1 M HCl aq, r.t; (e) $NaBH_4$, 0 ℃to r.t; (f) Ac_2O, pyridine, r.t; (g) Li_2CuCl_4, -78 ℃ to r.t; (h) HCl aq, reflux;; (i) Ac_2O, pyridine, r.t.

c) K. Dong et al, *Tetrahedron Letters,* **2022,** *107*, 153928. (C6+C2+C6 strategy)



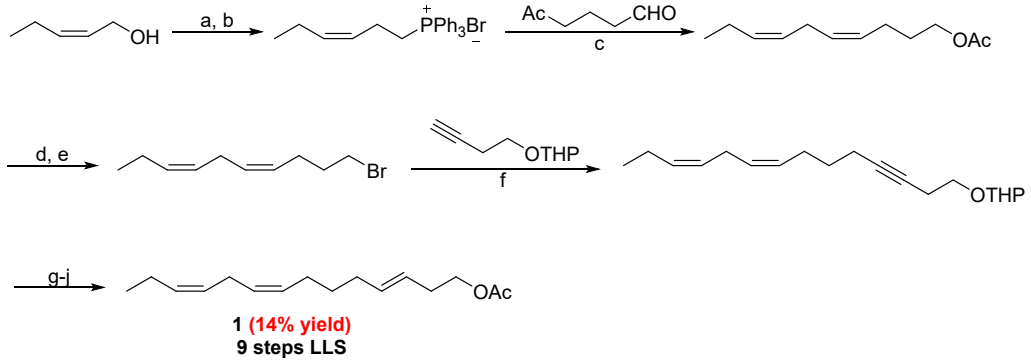
Key: (a) EtOAc, ion-exchange resins, 80 °C; (b) $[Cu(MeCN)_4]OTf$, bpy, TEMPO, N-methyl imidazole, O_2, rt; (c) $CH_2(COOH)_2$, piperidinium acetate, DMSO, 85 °C; (d) NaOH, 50 °C; (e) H_2SO_4, MeOH, reflux; (f) $[Cu(MeCN)_4]OTf$, bpy, TEMPO, N-methyl imidazole, O_2, rt; (g) $KN[Si(Me)_3]_2$, 78 °C; (h) $LiAlH_4$, rt; (i) Ac_2O, DMAP, Et_3N, rt.

d) D. M. Zubrytski et al, *Russ J Org Chem*., 2017, **53**, 6, 813-823. (C8 + C1 + C5 strategy)



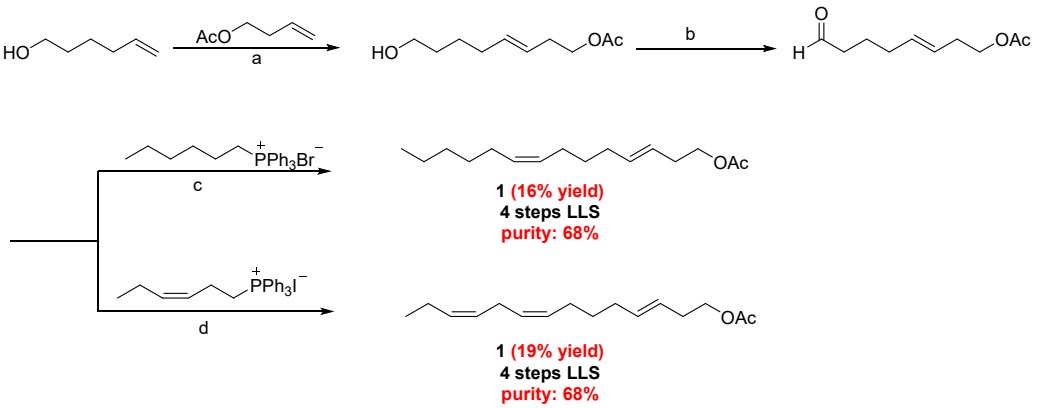
Key: (a) $PhI(OAc)_2$, MeOH, rt; (b) *t*-$BuMe_2SiCl$, ImH, DMF, 0 °C to rt; (c) DIBAl, toulene, -78 °C; (d) CBr_4, Et_3N, PPh_3, -78 °C then *n*-BuLi, THF, -78 °C; (e) $EtC{\equiv}CCH_2Br$, CuI, NaI, K_2CO_3, DMF, rt; (f) $Ti[OPr\text{-}i]_4$, *i*-PrMgCl, Et_2O, -78 °C to -41 °C; (g) 10% HCl; PPTS, EtOH, reflux. (h) AcCl, Et_3N, Et_2O, rt.

e) Y. Du, Y. Li, H. Guo, Y. Dong, Q. Shi and Z. Du, CN. Pat., CN119552076A, 2025. (C6 + C4 + C4 strategy)



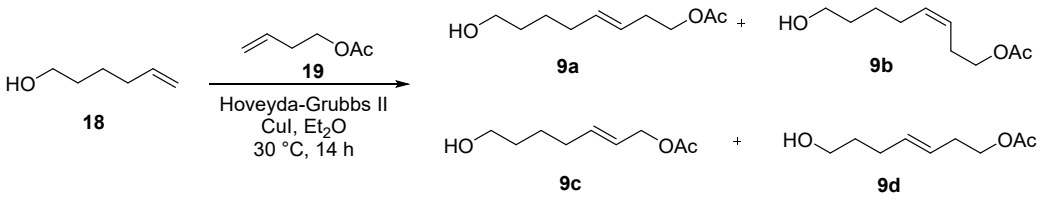
Key: (a) NBS, DCM, PPh_3, -30 °C; (b) PPh_3, toulene, 90 °C; (c) NaH, THF, -20 °C; (d) LiOH, MeOH, rt; (e) NBS, DCM, PPh_3, -30 °C; (f) *n*-BuLi, THF, -20 °C to 0 °C; (g) $LiAlH_4$, Et_2O, rt; (h) *p*-TsOH, MeOH. rt; (i) Ac_2O, pyridine, 0 °C.

f) Indian Institute of Science Education and Research (Iiser) Tirupati, IN Pat, IN202541011805A. 2025.
(C6 + C5 + C3 strategy)



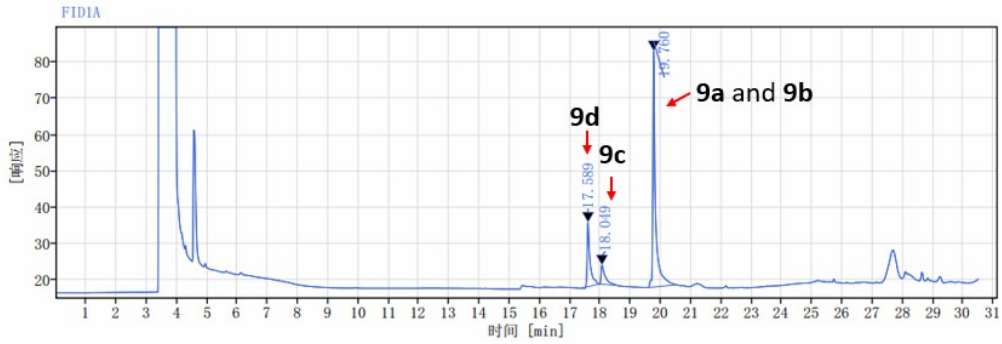
Key: (a) Grubbs II, DCM, rt; (b) DMP, DCM, 0 °C; (c) LiHMDS, THF, -78 °C to rt; (d) LiHMDS, THF, -78 °C to rt.

III. Synthesis of (*E*)-8-hydroxyoct-3-en-1-yl acetate(9b) by olefin cross-metathesis.



A dried flask under an N_2 atmosphere was charged with compound **18** (100 mg, 1.0 mmol, 1 equiv), compound **19** (570 mg, 5.0 mmol, 5 equiv) and CuI (10 mg, 0.05 mmol, 0.05 equiv) was added freshly distilled Et_2O (5 mL, 0.2 M). The Hoveyda-Grubbs' second generation catalyst (63 mg, 0.1 mmol, 0.1 equiv) was added in one portion. The reaction mixture was allowed to stir at 30 ℃ for 14 h. The reaction mixture was allowed to cool ambient temperature, at which point it was concentrated in vacuo. The residue was subjected to flash column chromatography (SiO_2: petroleum ether/ethyl acetate, 1:1) to furnish the mixture of **9a**、**9b**、**9c** and **9d**.

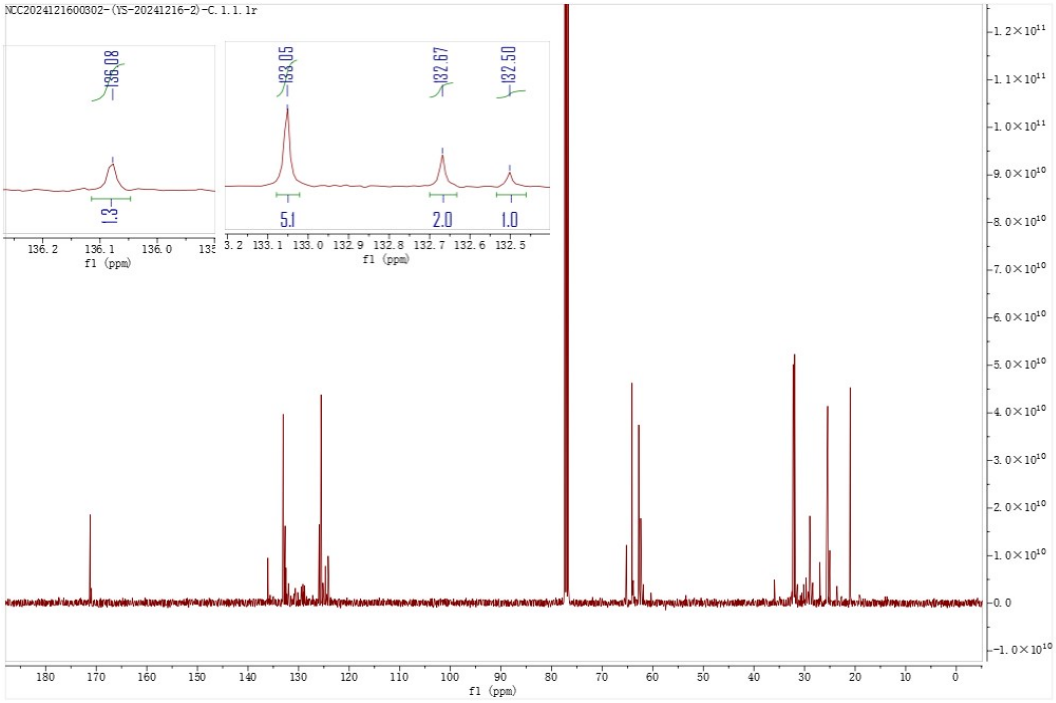
Gas chromatography (GC) of mixture of **9a**、**9b**、**9c** and **9d**.



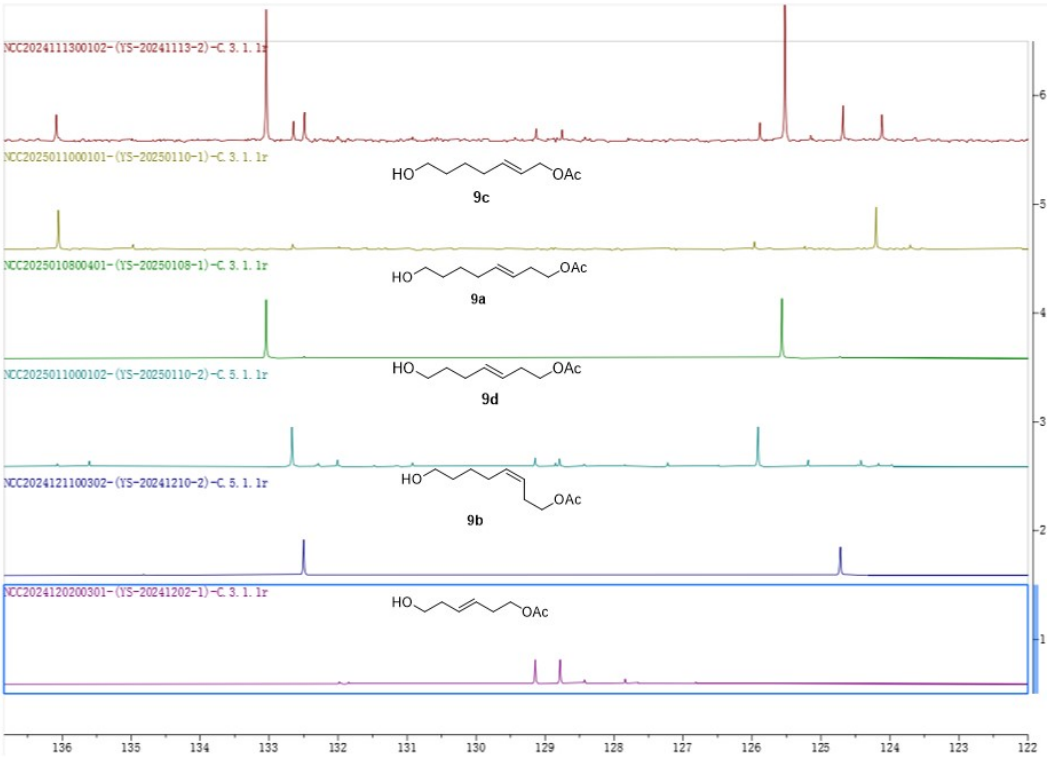
信号: FID1A

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
17.589	MM m	0.57	114.78	17.72	20.35	
18.049	MM m	0.62	50.30	5.26	8.92	
19.760	BB	0.93	398.89	65.10	70.73	
		总和	563.97			

^{13}C NMR integration (120-140 ppm range) established the product ratio as 5a:5b:5c:5d = 5:1:1.3:2.

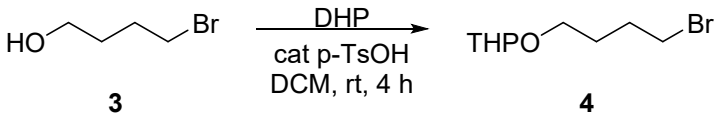


Quantitative analysis of a mixture of **9a**, **9b**, **9c**, and **9d** by ^{13}C NMR (120-140 ppm range).



IV. Experimental Procedures.

2-(4-bromobutoxy)tetrahydro-2H-pyran (4)



3 **4**

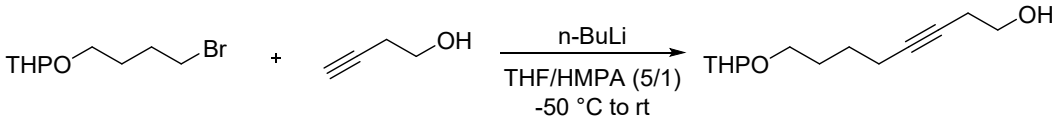
A solution of 4-bromo-1-butanol **3** (1 g, 6.5 mmol, 1 equiv) and *p*-toluenesulfonic acid (22 mg, 0.13 mmol, 0.02 equiv) in CH_2Cl_2 (5 mL) being cooled to 0 °C was added the 3,4-dihydro-2H-pyran (820 mg, 9.75 mmol, 1.5 equiv). The mixture was warmed to room temperature and stirring was continued for 4 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure to give the compound **4** (960 mg, 4.1

mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 (dd, *J* = 4.5, 2.7 Hz, 1H), 3.86 (ddd, *J* = 11.1, 7.6, 3.4 Hz, 1H), 3.79 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.56 – 3.50 (m, 1H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.45 – 3.40 (m, 1H), 2.09 – 1.92 (m, 2H), 1.89 – 1.80 (m, 1H), 1.80 – 1.68 (m, 3H), 1.56 (tdd, *J* = 12.2, 6.8, 3.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 98.87, 66.48, 62.37, 33.75, 30.72, 29.84, 28.39, 25.46, 19.62.

8-((tetrahydro-2H-pyran-2-yl)oxy)oct-3-yn-1-ol (6)



4 **5** **6**

To a stirred -50 ℃ solution of 3-butyn-1-ol **5** (590 mg, 8.4 mmol, 2 equiv) in THF (20 mL) under N_2 atmosphere was added dropwise n-butylithium (2.5 M in hexane, 6.7 mL, 4 equiv). The mixture was warmed to -30 ℃ and stirring was continued for 2 h. A solution of compound **4** (1 g, 4.2 mmol, 1 equiv) in HMPA (5 mL) was added to the reaction. The mixture was warmed to room temperature and stirring was continued for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (40 mL) and extracted with ethyl acetate (2×40 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 10:1 to 4:1) gave **6** (402 mg, 1.8 mmol, 42%) as a light-yellow

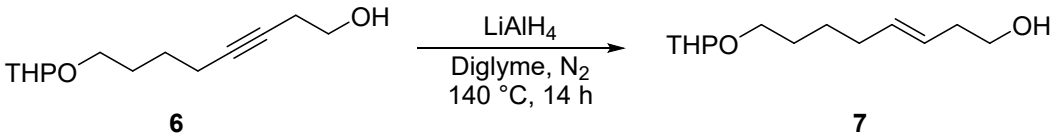
oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 (dd, *J* = 4.5, 2.8 Hz, 1H), 3.88 (ddd, *J* = 11.1, 7.5, 3.3 Hz, 1H), 3.78 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.69 (t, *J* = 6.2 Hz, 2H), 3.56 – 3.48 (m, 1H), 3.43 (dt, *J* = 9.7, 6.3 Hz, 1H), 2.44 (tt, *J* = 6.2, 2.4 Hz, 2H), 2.23 (tt, *J* = 6.9, 2.4 Hz, 2H), 1.93 – 1.80 (m, 2H), 1.78 – 1.67 (m, 3H), 1.64 – 1.51 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 98.87, 82.35, 67.05, 62.36, 61.37, 30.74, 28.94, 25.75, 25.48, 23.20, 19.64, 18.60.

HRMS (ESI) Calcd. for $C_{13}H_{22}NaO_3^+$[M+Na]$^+$:249.1461, Found: 249.1469.

(*E*)-8-((tetrahydro-2H-pyran-2-yl)oxy)oct-3-en-1-ol (7)



6 **7**

A solution of compound **6** (350 mg, 1.5 mmol, 1 equiv) in diglyme (10 mL) being cooled to 0 ℃ was added the $LiAlH_4$ (176 mg, 4.6 mmol, 3 equiv) under N_2 atmosphere. The mixture was warmed to 140 ℃ and stirring was continued for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (40 mL) and extracted with ethyl acetate (2×40 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 4:1) gave **7** (267 mg, 1.2 mmol, 76%) as a light-yellow oil.

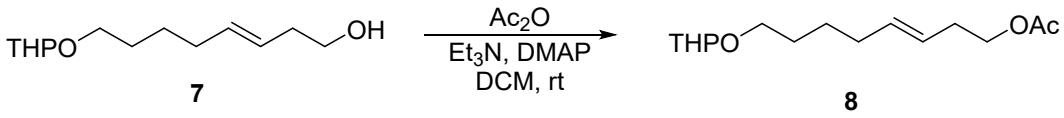
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 – 5.53 (m, 1H), 5.48 – 5.35 (m, 1H), 4.59 (dd,

J = 4.5, 2.8 Hz, 1H), 3.88 (ddd, *J* = 11.0, 7.4, 3.3 Hz, 1H), 3.76 (dt, *J* = 9.7, 6.8 Hz, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.59 – 3.49 (m, 1H), 3.41 (dt, *J* = 9.8, 6.6 Hz, 1H), 2.36 – 2.23 (m, 2H), 2.08 (q, *J* = 7.0, 6.5 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.78 – 1.69 (m, 1H), 1.65 – 1.52 (m, 7H), 1.50 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.91, 126.16, 98.88, 67.45, 62.36, 62.05, 36.00, 32.45, 30.77, 29.24, 26.07, 25.50, 19.68.

HRMS (ESI) Calcd. for $C_{13}H_{24}NaO_3^+$[M+Na]$^+$:251.1618, Found: 251.1614.

(*E*)-8-((tetrahydro-2H-pyran-2-yl)oxy)oct-3-en-1-yl acetate (8)



A solution of compound **7** (267 mg, 1.2 mmol, 1 equiv) and 4-(dimethylamino)pyridine (3 mg, 0.024 mmol, 0.02 equiv) in CH_2Cl_2 (5 mL) being cooled to 0 ℃ was added the Et_3N (359 mg, 3.5 mmol, 3 equiv) and the acetic anhydride (239 mg, 2.3 mmol, 2 equiv). The mixture was warmed to room temperature and stirring was continued for 2 h. The reaction was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 10:1) gave **8** (303 mg, 1.1 mmol, 95%) as a light-yellow oil.

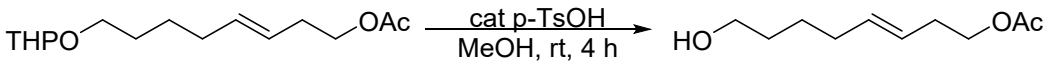
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dtt, *J* = 14.7, 6.6, 1.3 Hz, 1H), 5.39 (dtt, *J* =

15.1, 6.8, 1.3 Hz, 1H), 4.59 (dd, *J* = 4.5, 2.7 Hz, 1H), 4.08 (t, *J* = 6.9 Hz, 2H), 3.89 (td, *J* = 7.5, 3.6 Hz, 1H), 3.75 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.40 (dt, *J* = 9.6, 6.6 Hz, 1H), 2.33 (qd, *J* = 6.8, 1.2 Hz, 2H), 2.06 (s, 5H), 1.84 (qt, *J* = 8.4, 3.6 Hz, 1H), 1.73 (ddd, *J* = 12.0, 7.7, 4.3 Hz, 1H), 1.65 – 1.50 (m, 6H), 1.45 (dtd, *J* = 10.1, 7.2, 4.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.13, 133.21, 125.39, 98.86, 67.44, 64.11, 62.33, 32.39, 31.94, 30.77, 29.20, 26.02, 25.50, 20.98, 19.67.

HRMS (ESI) Calcd. for $C_{15}H_{26}NaO_4^+$[M+Na]$^+$:293.1723, Found: 293.1723.

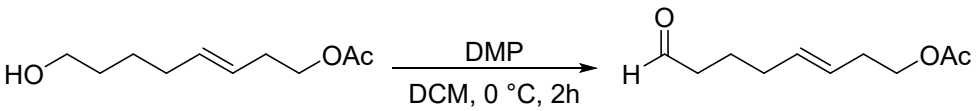
(*E*)-8-hydroxyoct-3-en-1-yl acetate (9a)



8 **9a**

A solution of compound **8** (290 mg, 1.1 mmol, 1 equiv) in MeOH (8 mL) was added the *p*-toluenesulfonic acid (4 mg, 0.02 mmol, 0.02 equiv) at room temperature. After 13 h, TLC analysis (petroleum ether/ethyl acetate, 2:1) showed the complete consumption of compound **8**. The solvent was evaporated and diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 3:1) gave **9b** (163 mg, 0.87 mmol, 82%) as a colorless oil.

(*E*)-8-oxooct-3-en-1-yl acetate (10)



9a **10**

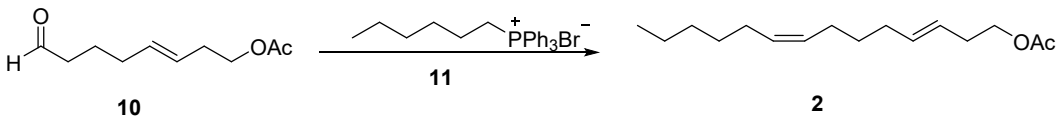
A solution of compound **9a** (145 mg, 0.78 mmol, 1 equiv) in CH_2Cl_2(10 mL) being cooled to 0 ℃ was added the Desse-Martin periodinane (661 mg, 1.6 mmol, 2 equiv) under N_2 atmosphere. The mixture was warmed to room temperture and stirring was continued for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL)、 aqueous $Na_2S_2O_3$ (5 mL) and extracted with ethyl acetate (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 4:1) gave **10** (123 mg, 0.67 mmol, 86%) as a light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 5.60 – 5.38 (m, 2H), 4.08 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 2H), 2.31 (s, 2H), 2.06 (d, *J* = 13.8 Hz, 5H), 1.69 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.47, 171.07, 131.97, 126.64, 63.93, 43.11, 31.90, 31.83, 21.65, 20.95.

HRMS (ESI) Calcd. for $C_{10}H_{16}NaO_3^+$[M+Na]$^+$:207.0992, Found: 207.0985.

(3*E*,8*Z*)-tetradeca-3,8-dien-1-yl acetate (2)



10 **2**

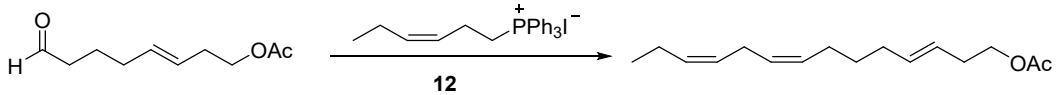
To a stirred 0 ℃ solution of compound **11** (307 mg, 0.72 mmol, 2 equiv) in THF (20 mL) under N_2 atmosphere was added dropwise Potassium bis(trimethylsiyl) amide (1 M in THF, 0.72 mL, 2 equiv). The stirring was continued for 2 h and the mixture was cooled to -78 ℃. A solution of compound **10** (67 mg, 0.36 mmol, 1 equiv) in THF (2 mL) was added to the reaction. The mixture was warmed to -50 ℃ for 2 h and 25 ℃ for another 2 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with ethyl acetate (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 20:1) gave **2** (72 mg, 0.29 mmol, 80%) as a light-yellow oil. GC purity：97%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dtt, *J* = 14.6, 6.6, 1.3 Hz, 1H), 5.46 – 5.30 (m, 3H), 4.08 (t, *J* = 6.9 Hz, 2H), 2.33 (qd, *J* = 6.8, 1.2 Hz, 2H), 2.06 (s, 3H), 2.03 (q, *J* = 7.1, 6.6 Hz, 6H), 1.43 (q, *J* = 7.5 Hz, 2H), 1.32 (tdd, *J* = 10.6, 6.9, 3.1 Hz, 6H), 0.91 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.11, 133.29, 130.31, 129.38, 125.31, 64.13, 32.16, 31.97, 31.52, 29.43(2C), 27.20, 26.63, 22.54, 20.97, 14.06.

HRMS (ESI) Calcd. for $C_{16}H_{28}NaO_2^+$[M+Na]$^+$:275.1982, Found: 275.1975.

(3*E*,8*Z*,11*Z*)-tetradeca-3,8,11-trien-1-yl acetate (1)



10 1

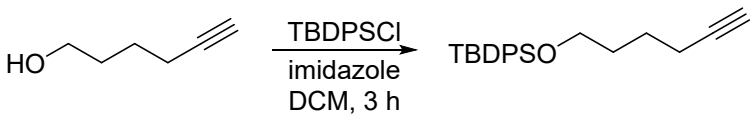
To a stirred 0 ℃ solution of compound **12** (253 mg, 0.53 mmol, 2 equiv) in THF (20 mL) under N_2 atmosphere was added dropwise Potassium bis(trimethylsiyl) amide (1 M in THF, 0.53 mL, 2 equiv). The stirring was continued for 2 h and the mixture was cooled to -78 ℃. A solution of compound **10** (50 mg, 0.27 mmol, 1 equiv) in THF (2 mL) was added to the reaction. The mixture was warmed to -50 ℃ for 2 h and 25 ℃ for another 2 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with ethyl acetate (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 20:1) gave **1** (52 mg, 0.21 mmol, 78%) as a light-yellow oil. GC purity：98%。

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (dtt, *J* = 14.5, 6.5, 1.3 Hz, 1H), 5.43 – 5.08 (m, 5H), 4.02 (t, *J* = 6.9 Hz, 2H), 2.72 (t, *J* = 6.1 Hz, 2H), 2.27 (qd, *J* = 6.9, 1.2 Hz, 2H), 2.06 – 1.91 (m, 9H), 1.38 (p, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 133.15, 131.77, 129.66, 128.34, 127.31, 125.39, 64.07, 32.12, 31.94, 29.28, 26.59, 25.51, 20.92, 20.51, 14.24.

HRMS (ESI) Calcd. for $C_{16}H_{26}NaO_2^+$[M+Na]$^+$:273.1825, Found: 273.1831.

tert-butyl(hex-5-yn-1-yloxy)diphenylsilane (14)



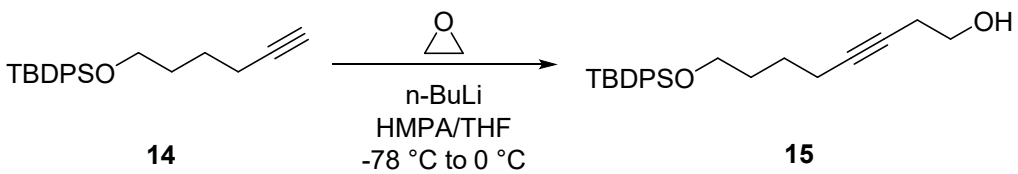
13 **14**

To a solution of 5-hexyn-1-ol (**13**) (2.0 g, 20.4 mmol, 1 equiv) and imidazole (2.1 g, 30.6 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) being cooled to 0 ℃ was added the tert-butyldiphenylsilyl chloride (5.6 g, 20.4 mmol, 1 equiv). The reaction mixture was allowed to stirred at room temperature. After 3 h, TLC analysis (petroleum ether/ethyl acetate, 3:1) showed the complete consumption of compound **13**. The reaction was quenched with H_2O (30 mL) and extracted with CH_2Cl_2 (2×30 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 50:1) gave **14** (6 g, 17.8 mmol, 87%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.52 – 7.36 (m, 6H), 3.72 (t, *J* = 5.8 Hz, 2H), 2.23 (dt, *J* = 6.7, 3.4 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.70 (qd, *J* = 6.4, 2.9 Hz, 4H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.60, 134.02, 129.58, 127.65, 84.56, 68.30, 63.34, 31.58, 26.88, 24.97, 19.24, 18.21.

8-((tert-butyldiphenylsilyl)oxy)oct-3-yn-1-ol (15)



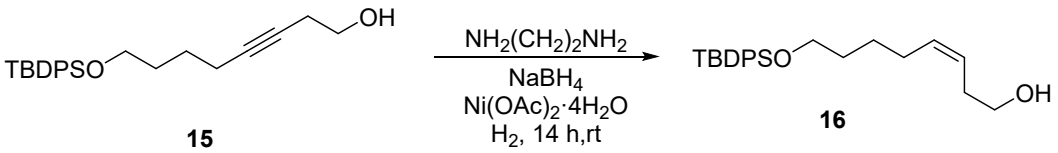
14 **15**

To a stirred -78 ℃ solution of compound **14** (1 g, 3.0 mmol, 1 equiv) in THF (20 mL) under N_2 atmosphere was added dropwise n-butylithium (2.5 M in hexane, 1.4 mL,1.2 equiv) followed by the addition of HMPA (5 mL). Ethylene oxide (3 M in THF, 10 mL,10 equiv) was added after being stirred for 30 min at –78 ℃.The mixture was warmed to 0 ℃ and stirring was continued for 5 h. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with ethyl acetate (2×50 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 50:1 to 4:1) gave **15** (500 mg, 1.3 mmol, 44%) as a light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.2, 2.3 Hz, 4H), 7.55 – 7.33 (m, 6H), 3.78 – 3.67 (m, 4H), 2.45 (ddd, *J* = 8.6, 6.2, 2.4 Hz, 2H), 2.20 (ddt, *J* = 6.7, 4.8, 2.4 Hz, 2H), 1.75 (s, 1H), 1.72 – 1.56 (m, 4H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.59, 134.05, 129.57, 127.63, 82.56, 76.52, 63.45, 61.39, 31.74, 26.88, 25.43, 23.21, 19.23, 18.55.

(*Z*)-8-((tert-butyldiphenylsilyl)oxy)oct-3-en-1-ol (16)



15 **16**

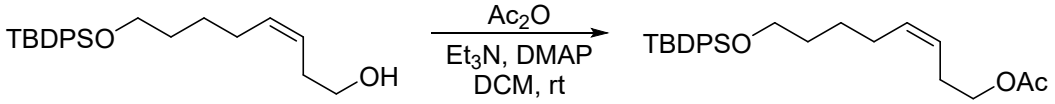
A solution of $NaBH_4$ (11 mg, 0.3 mmol, 0.38 equiv) in ethanol (10 mL) was added to a suspension of $Ni(OAc)_2{\cdot}4H_2O$ (31 mg, 0.13 mmol, 0.16 equiv) in ethanol (1.0

mL) in a H_2 atmosphere. After 30 min ethylenediamine (85 mg, 1.42 mmol, 1.8 equiv) was added to the suspension. After 30 min compound **15** (300 mg, 0.79 mmol, 1.0 equiv) in ethanol (10 mL) was also added. The reaction was then stirred for 16 h under H_2. The mixture was filtered through a Celite pad, and the filtrate was concentrated to give the crude product. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 4:1) gave **16** (250 mg, 0.65 mmol, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.58 (m, 4H), 7.49 – 7.33 (m, 6H), 5.66 – 5.52 (m, 1H), 5.43 – 5.28 (m, 1H), 3.67 (dt, *J* = 14.3, 6.4 Hz, 4H), 2.40 – 2.28 (m, 2H), 2.09 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.52 – 1.44 (m, 3H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.61, 134.13, 133.28, 129.54, 127.61, 125.24, 63.76, 62.36, 32.17, 30.83, 27.09, 26.89, 25.91, 19.24.

(*Z*)-8-((tert-butyldiphenylsilyl)oxy)oct-3-en-1-yl acetate (17)



16 **17**

A solution of compound **16** (250 mg, 0.65 mmol, 1 equiv) and 4-(dimethylamino)pyridine (1.6 mg, 0.013 mmol, 0.02 equiv) in CH_2Cl_2 (5 mL) being cooled to 0 ℃ was added the Et_3N (197 mg, 1.9 mmol, 3 equiv) and the acetic anhydride (132 mg, 1.3 mmol, 2 equiv). The mixture was warmed to room

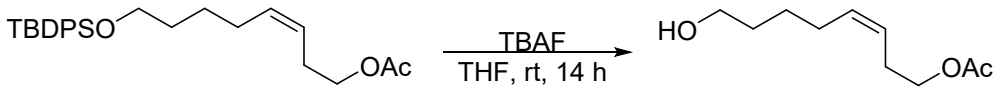
temperature and stirring was continued for 2 h. The reaction was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 5:1) gave **17** (220 mg, 0.52 mmol, 80%) as a light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.67 (m, 4H), 7.52 – 7.36 (m, 6H), 5.59 – 5.48 (m, 1H), 5.38 (dtd, *J* = 10.8, 7.2, 1.4 Hz, 1H), 4.08 (t, *J* = 6.9 Hz, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.17 – 1.90 (m, 5H), 1.69 – 1.56 (m, 2H), 1.48 (qd, *J* = 9.5, 8.6, 6.1 Hz, 2H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.86, 135.60, 134.12, 132.77, 129.54, 127.61, 124.56, 63.97, 63.77, 32.16, 27.03, 26.89, 26.84, 25.81, 20.99, 19.24.

HRMS (ESI) Calcd. for $C_{26}H_{36}NaO_3Si^+$[M+Na]$^+$: 447.2326, Found: 447.2325.

(*Z*)-8-hydroxyoct-3-en-1-yl acetate (9b)



17 **9b**

A solution of compound **17** (200 mg, 0.47 mmol, 1 equiv) in THF (5 mL) was added the tetra-n-butylammonium fluoride (1 M solution in THF, 1.4 mL, 3 equiv) at room temperature. After 13 h, TLC analysis (petroleum ether/ethyl acetate, 2:1) showed the complete consumption of compound **17**. The reaction was quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The combined organic extracts were

washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (SiO_2: petroleum ether/ethyl acetate, 3:1) gave **9b** (76 mg, 0.41 mmol, 86%) as a colorless oil.

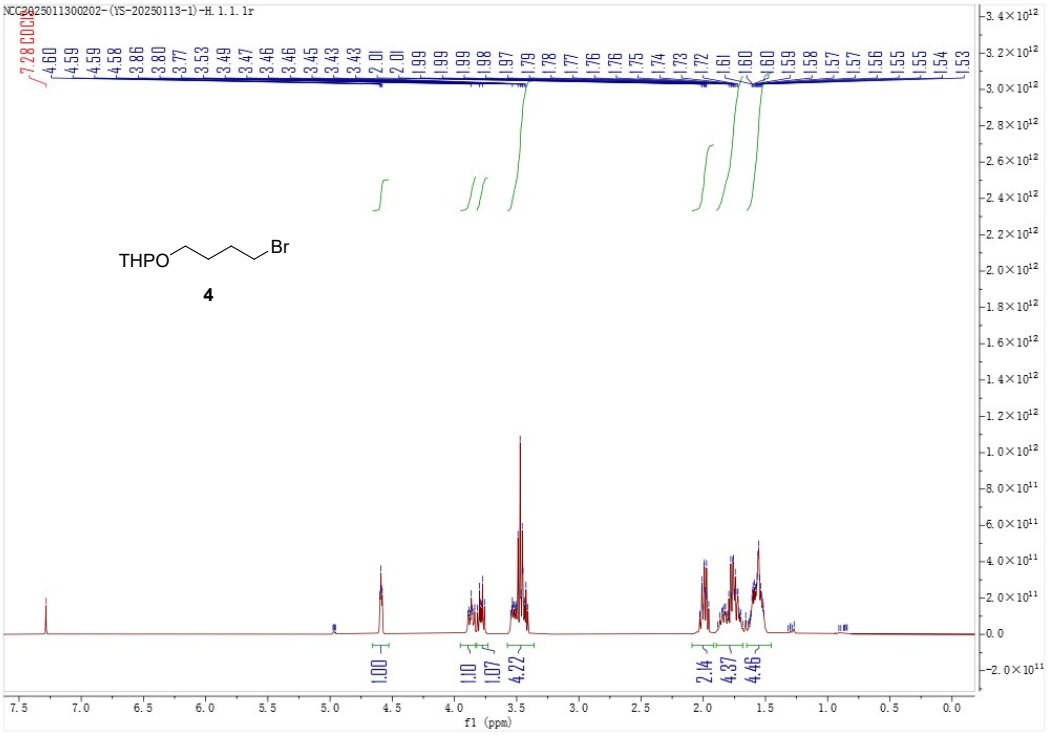
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (dtt, *J* = 10.4, 7.3, 1.5 Hz, 1H), 5.42 – 5.30 (m, 1H), 4.07 (t, *J* = 7.0 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.39 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.14 – 2.07 (m, 2H), 2.05 (s, 3H), 1.65 (s, 1H), 1.63 – 1.54 (m, 2H), 1.45 (qd, *J* = 9.8, 8.8, 5.8 Hz, 2H), 1.28 (d, *J* = 11.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.21, 132.50, 124.72, 63.95, 62.74, 32.26, 26.98, 26.83, 25.69, 20.98.

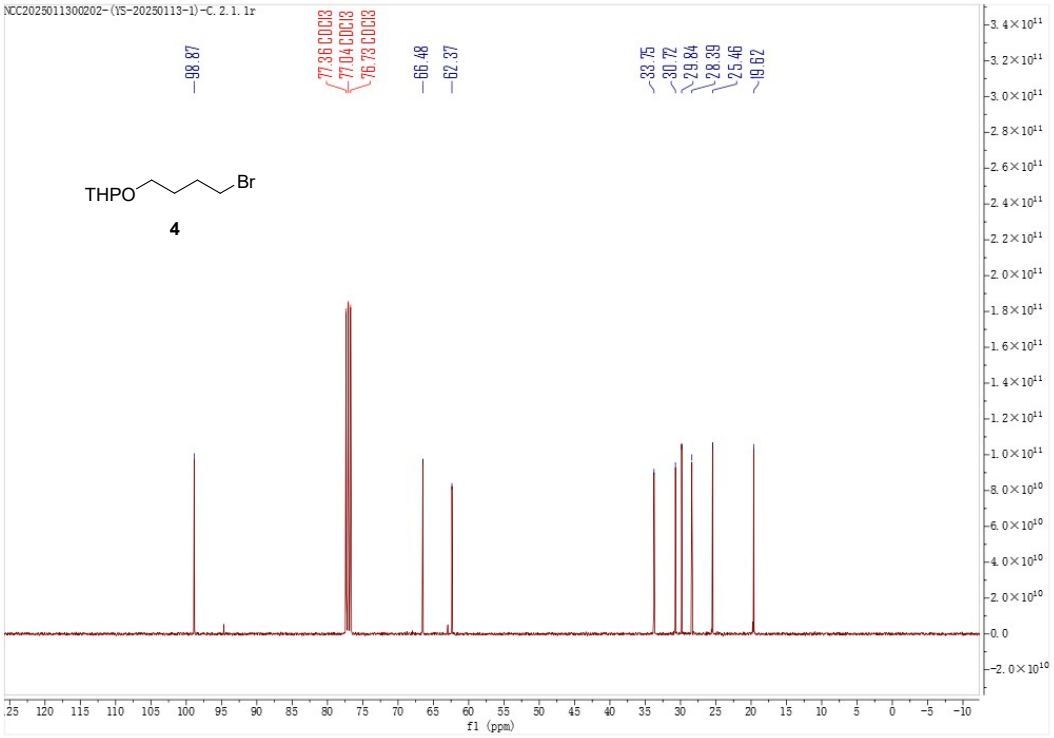
HRMS (ESI) Calcd. for $C_{10}H_{18}NaO_3^+$[M+Na]$^+$:209.1148, Found: 209.1148.

V. ^{1}H and ^{13}C NMR spectra for compounds

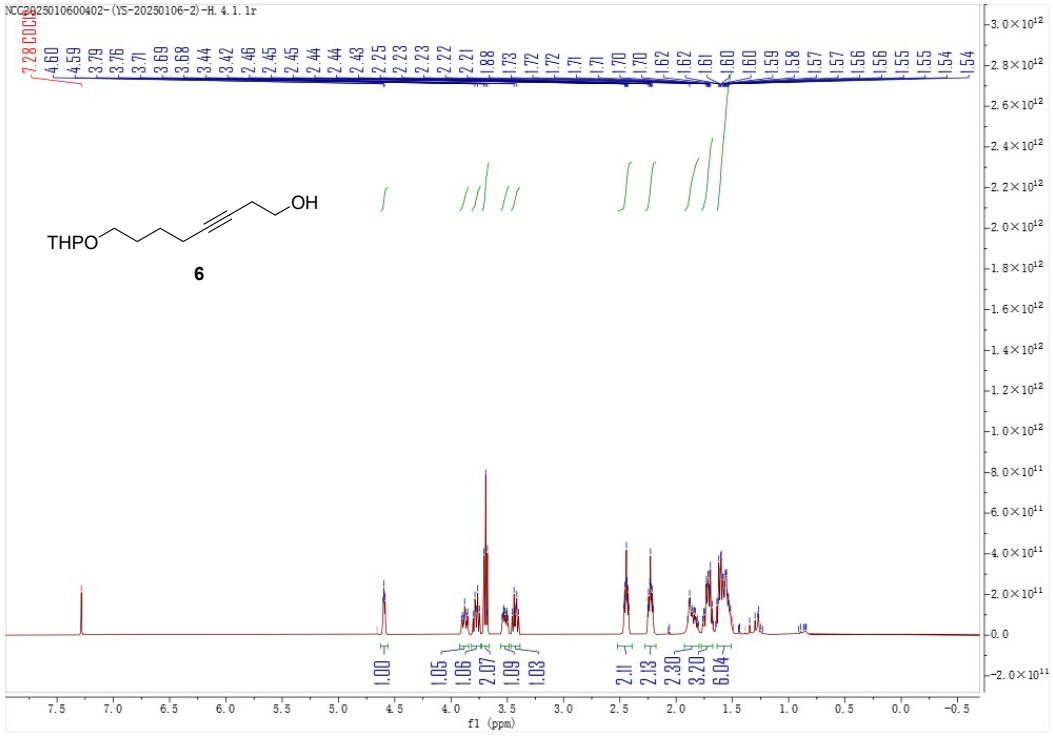
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **4**



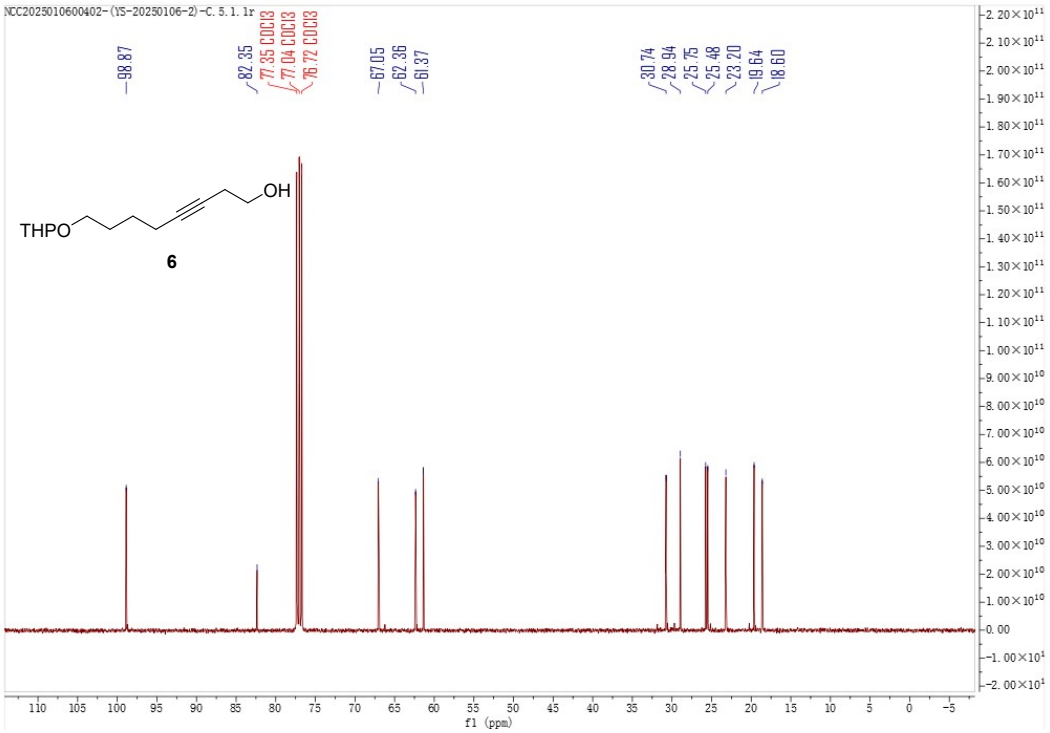
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4**



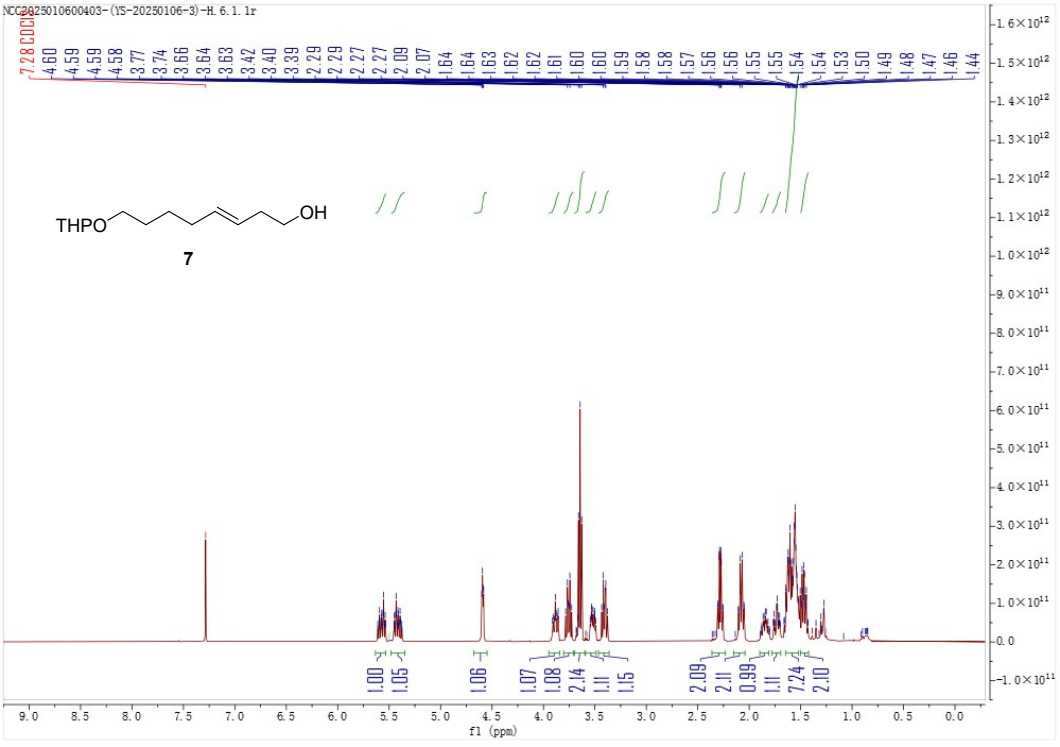
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **6**



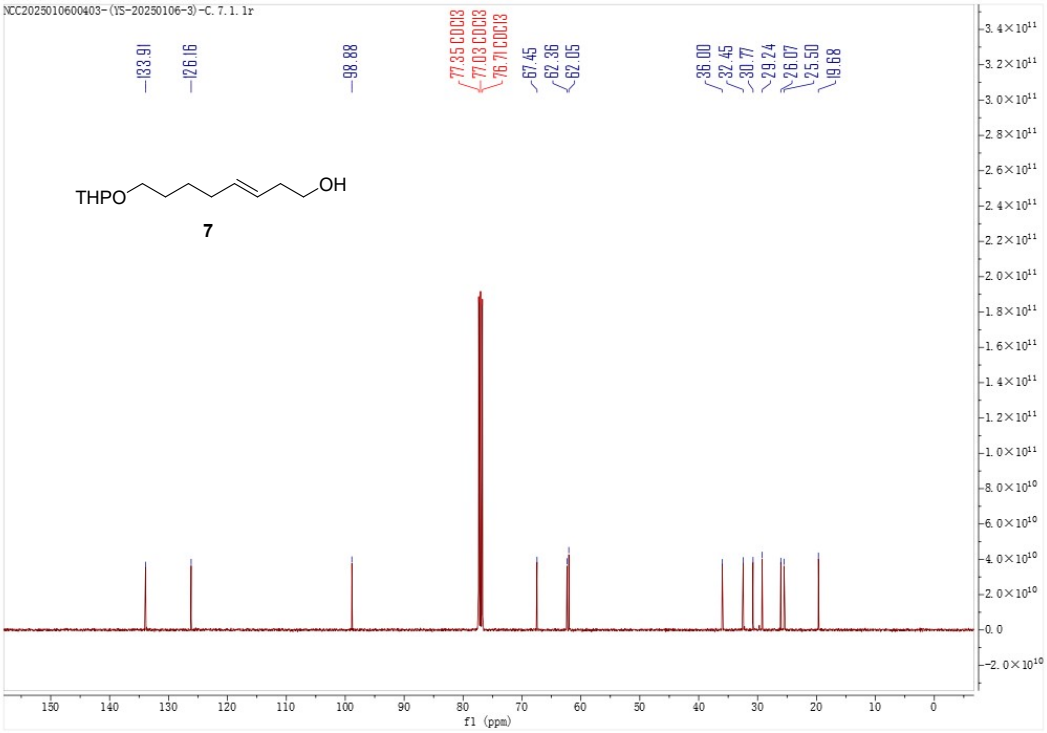
^{13}C NMR (101 MHz, $CDCl_3$) of compound **6**



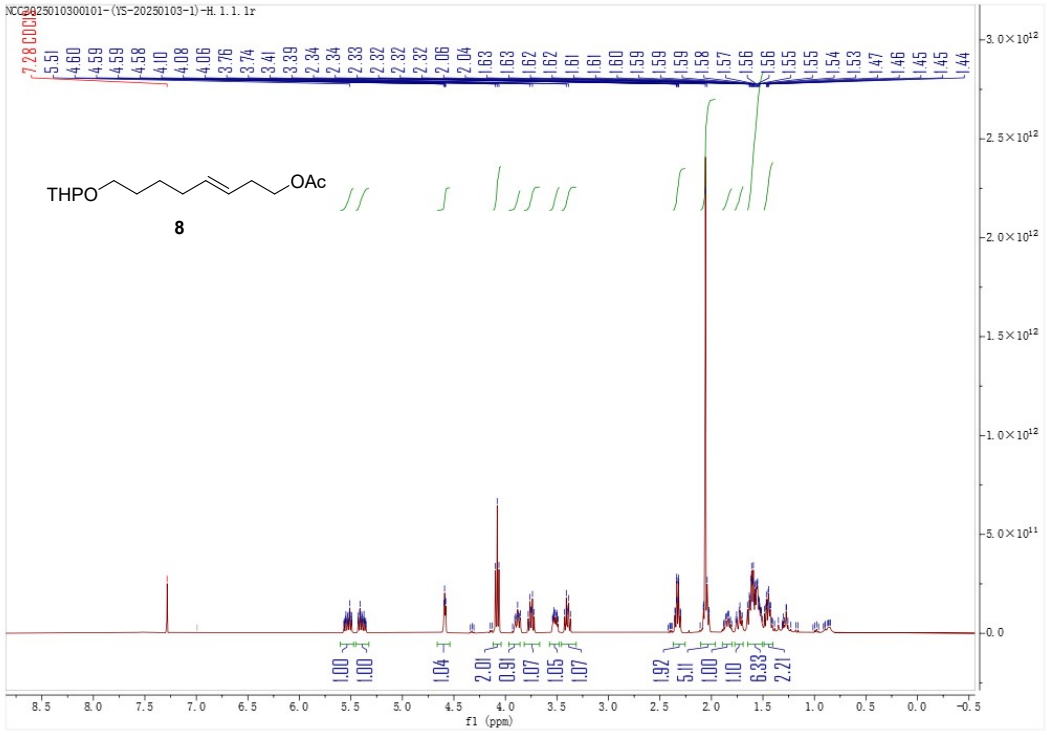
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **7**



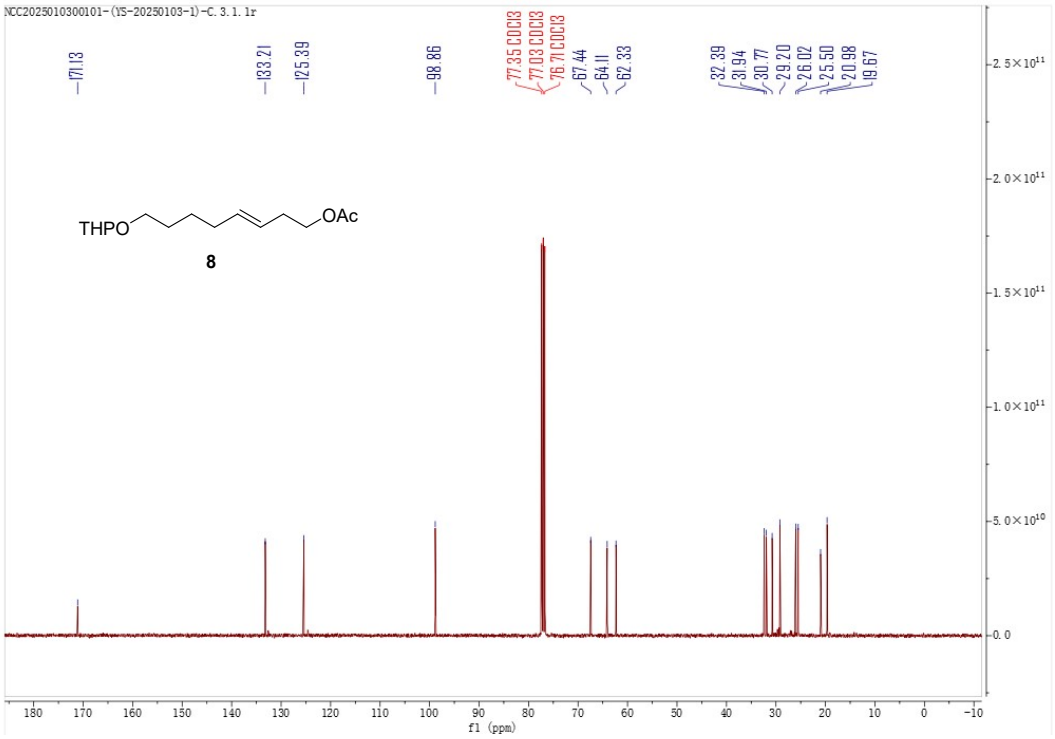
^{13}C NMR (101 MHz, $CDCl_3$) of compound **7**



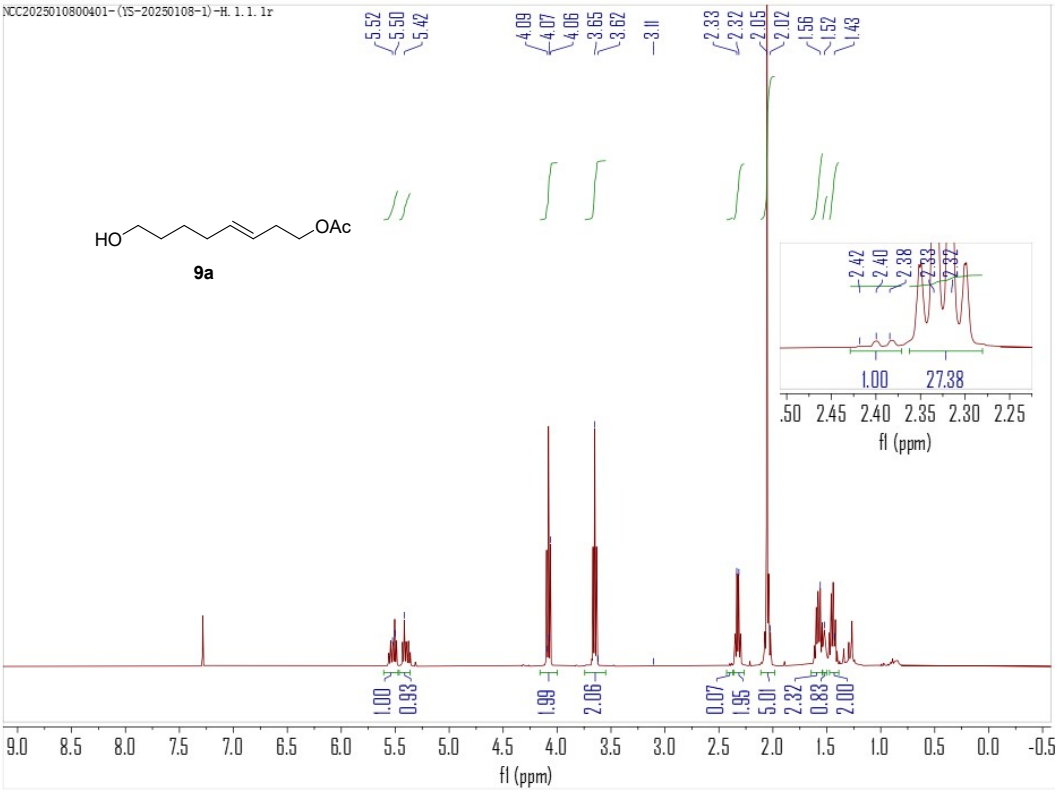
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **8**



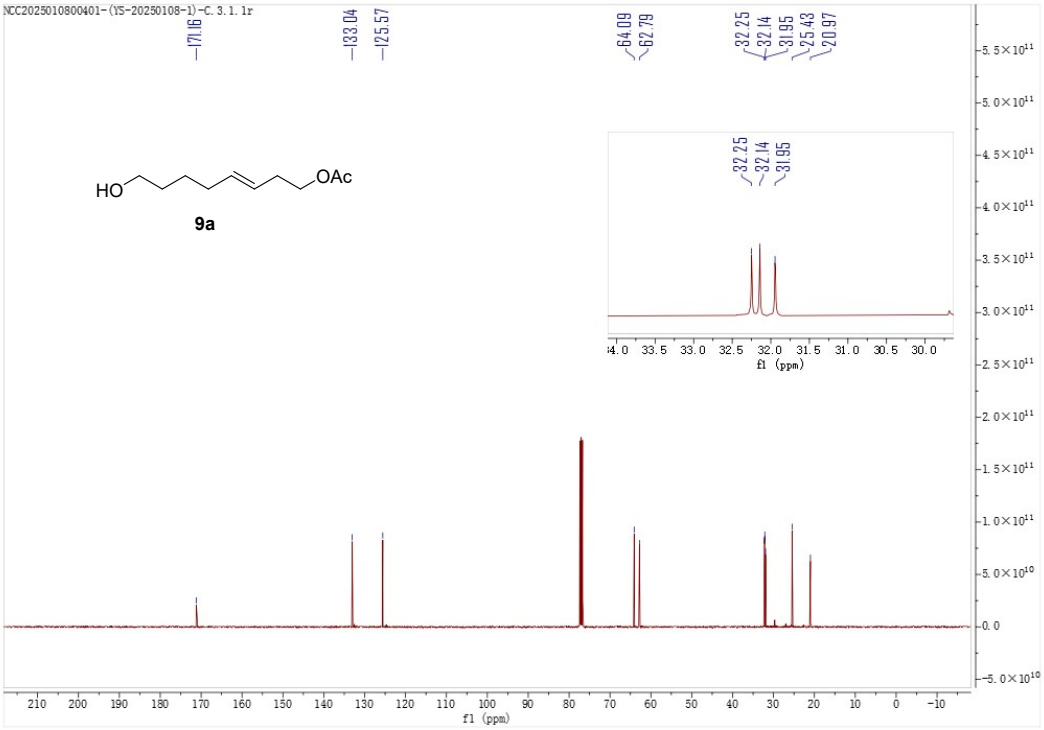
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8**



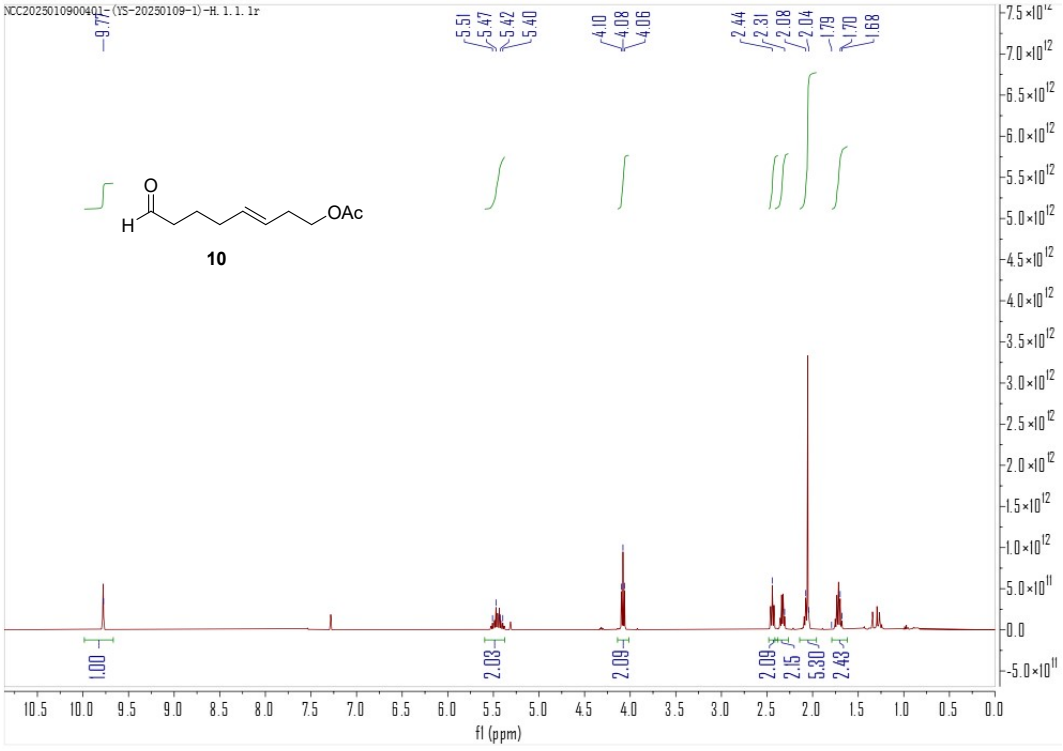
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **9a**



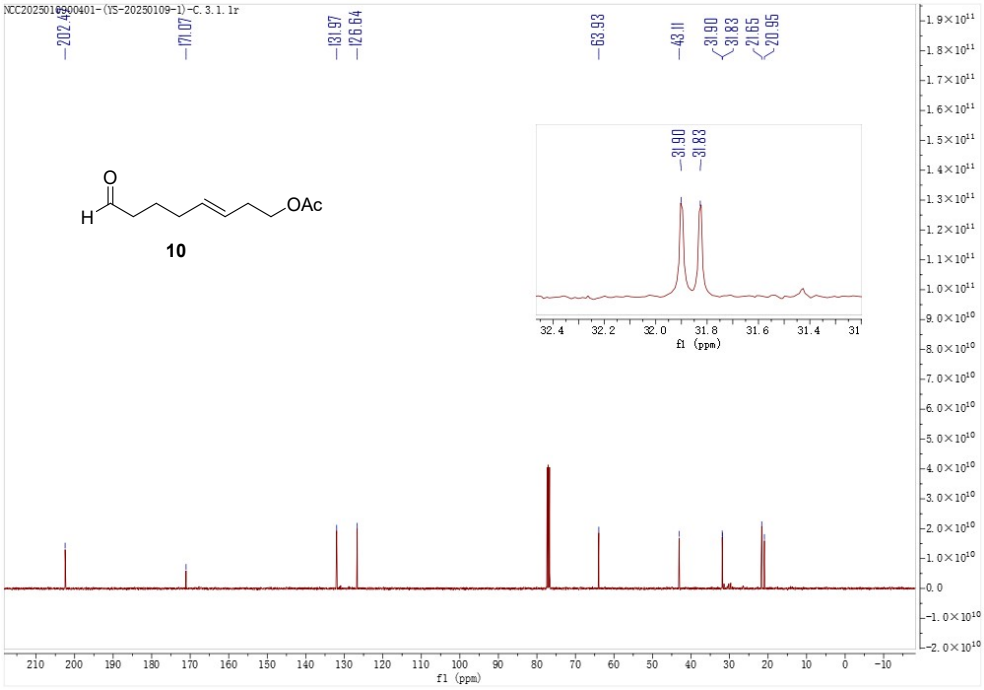
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9a**



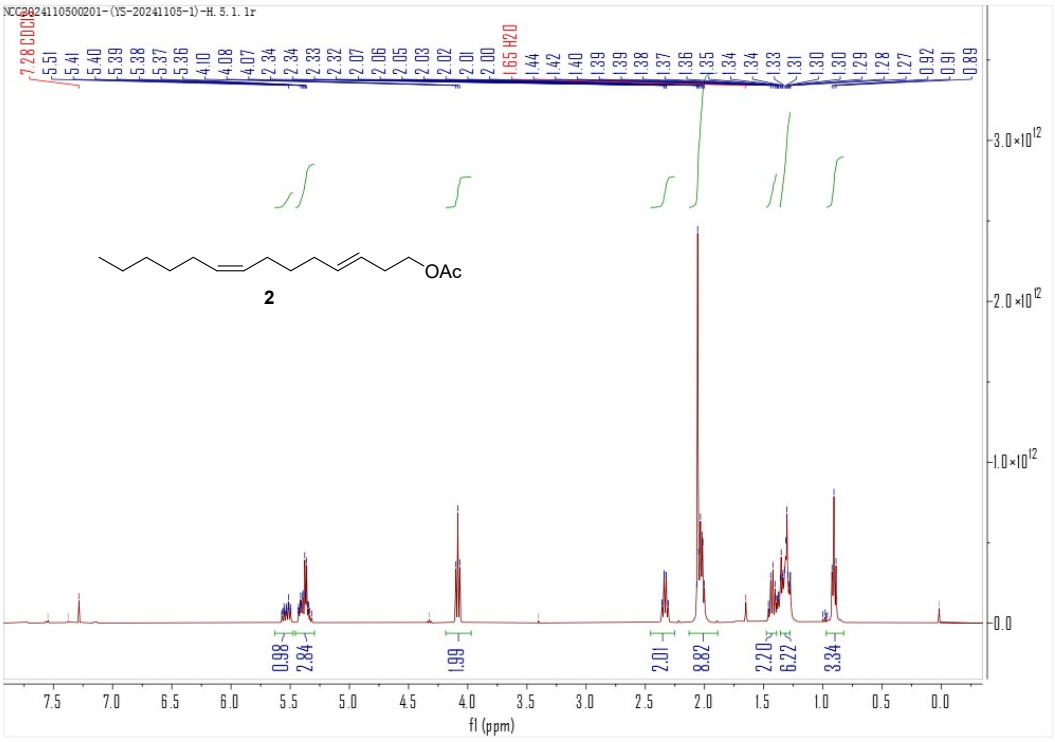
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **10**



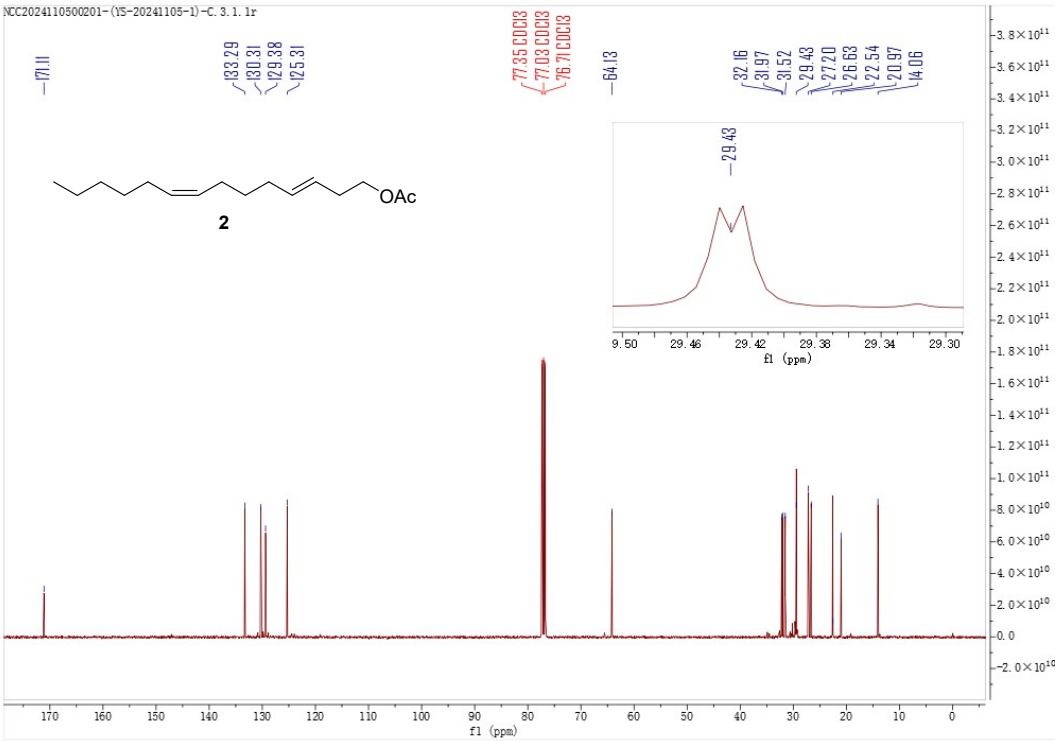
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10**



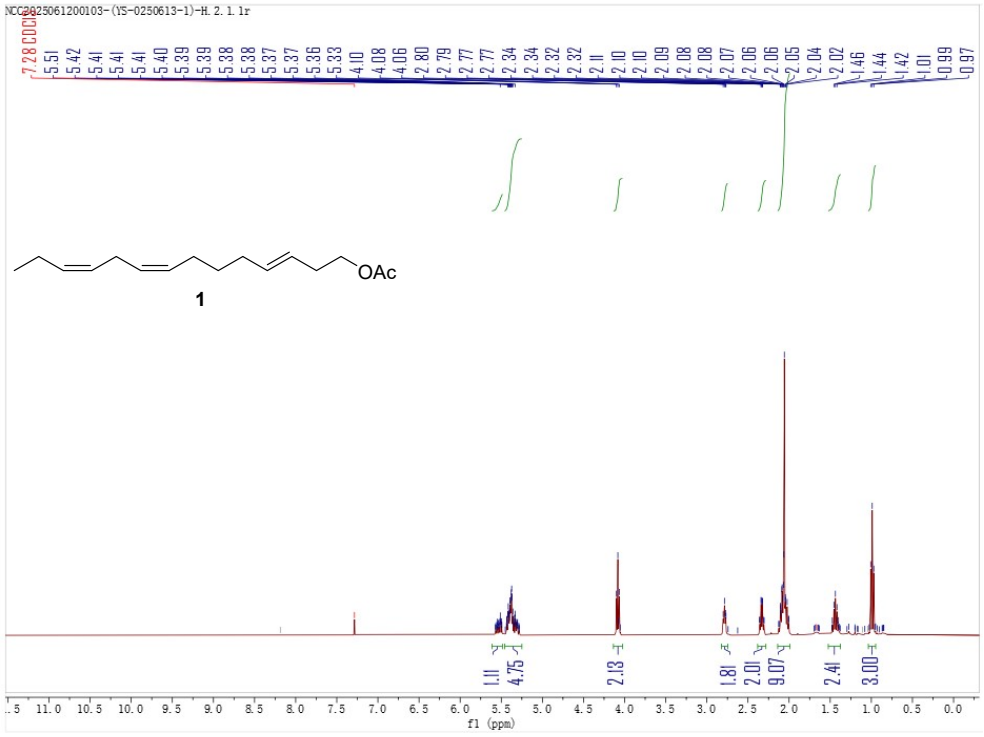
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **2**



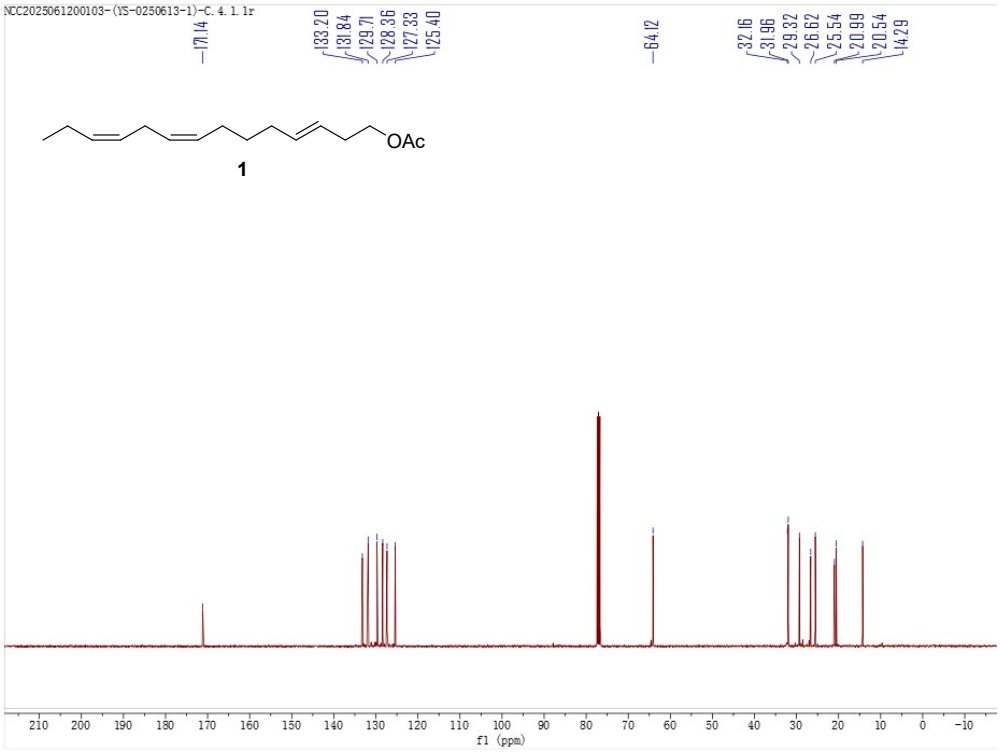
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2**



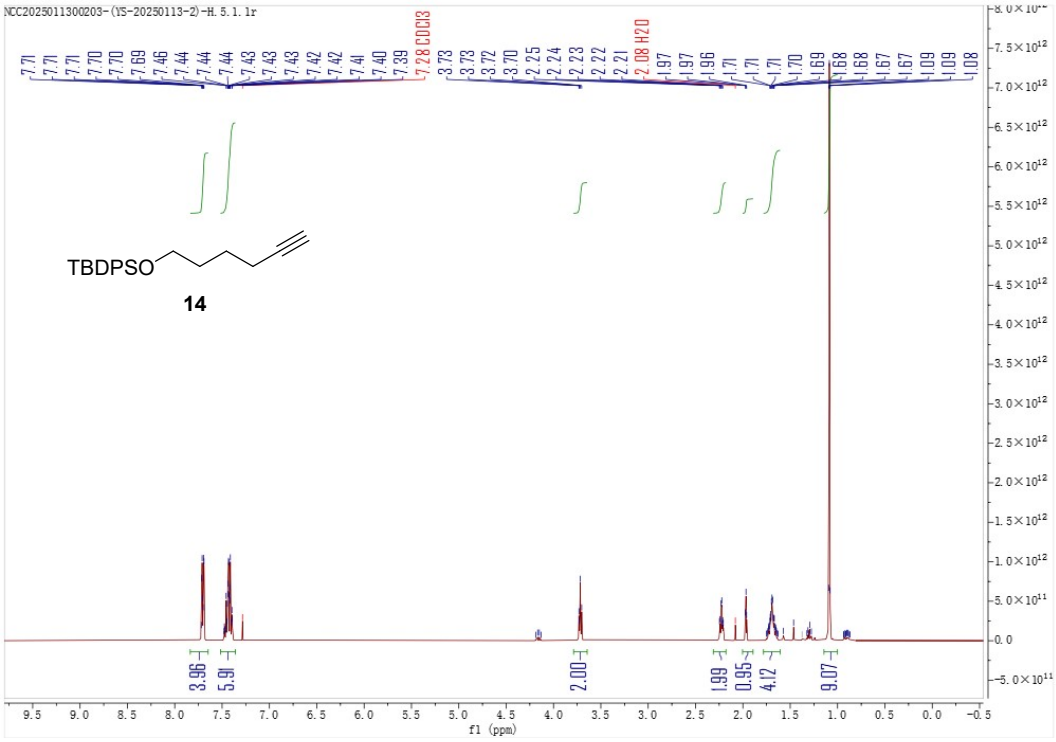
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **1**



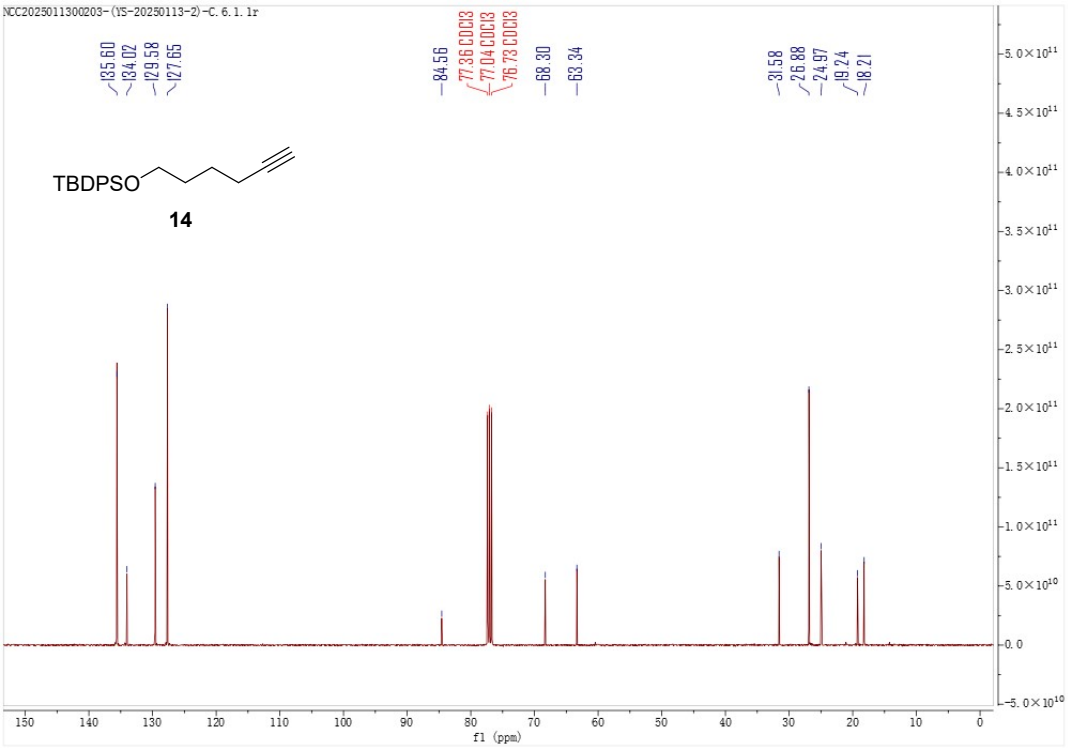
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1**



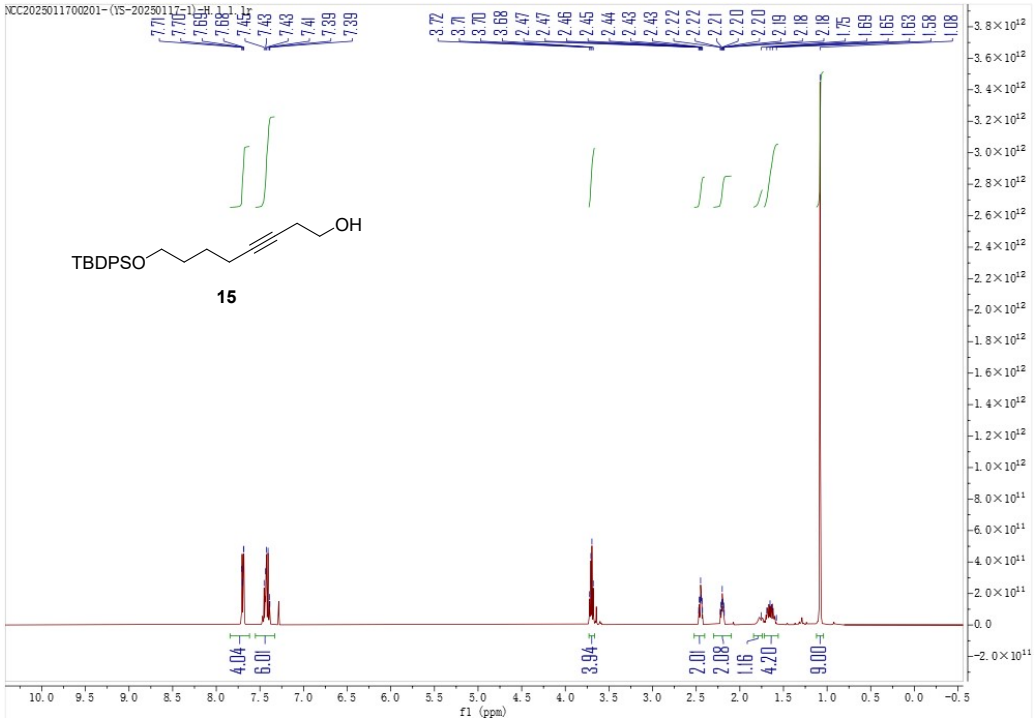
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **14**



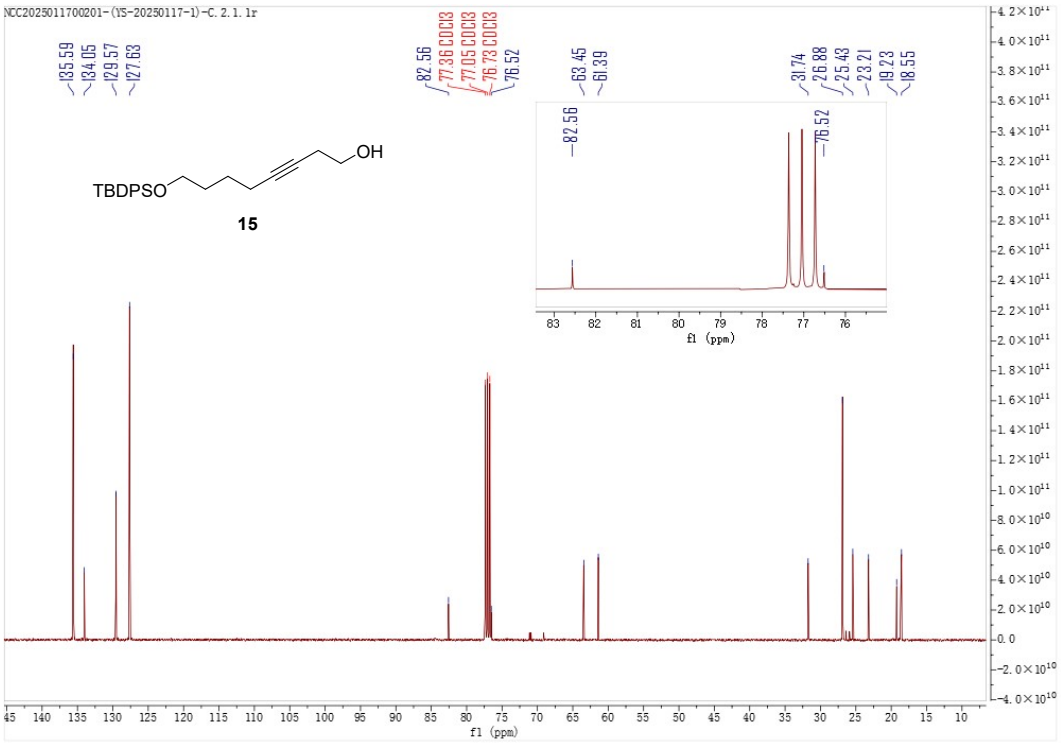
^{13}C NMR (101 MHz, $CDCl_3$) of compound **14**



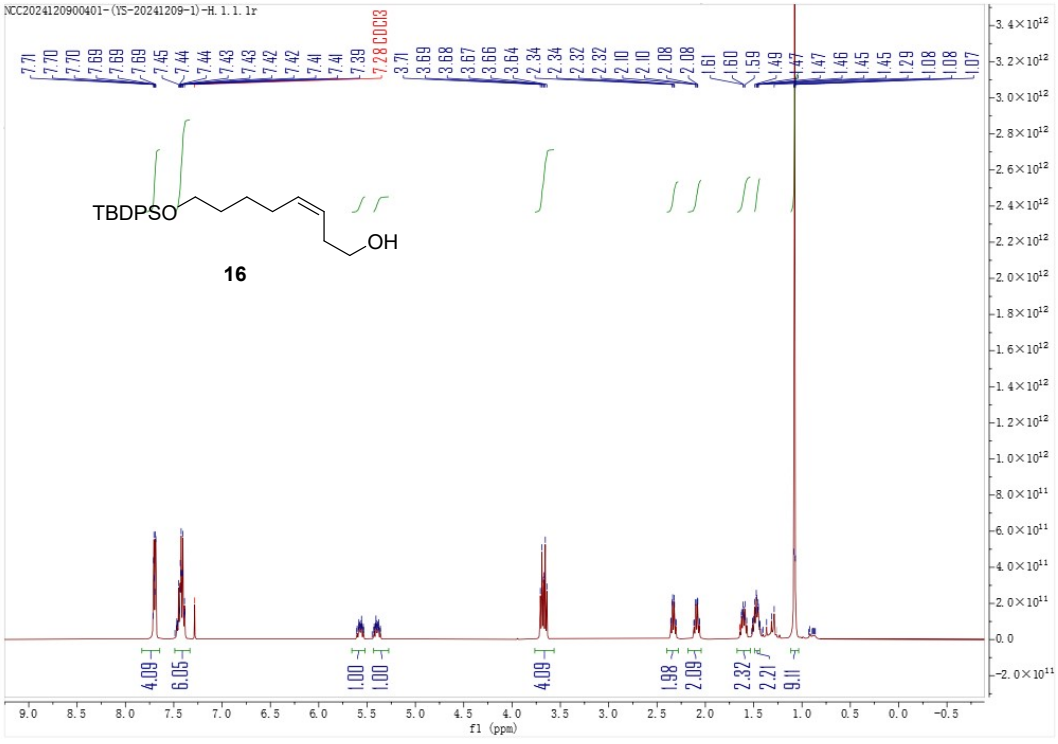
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **15**



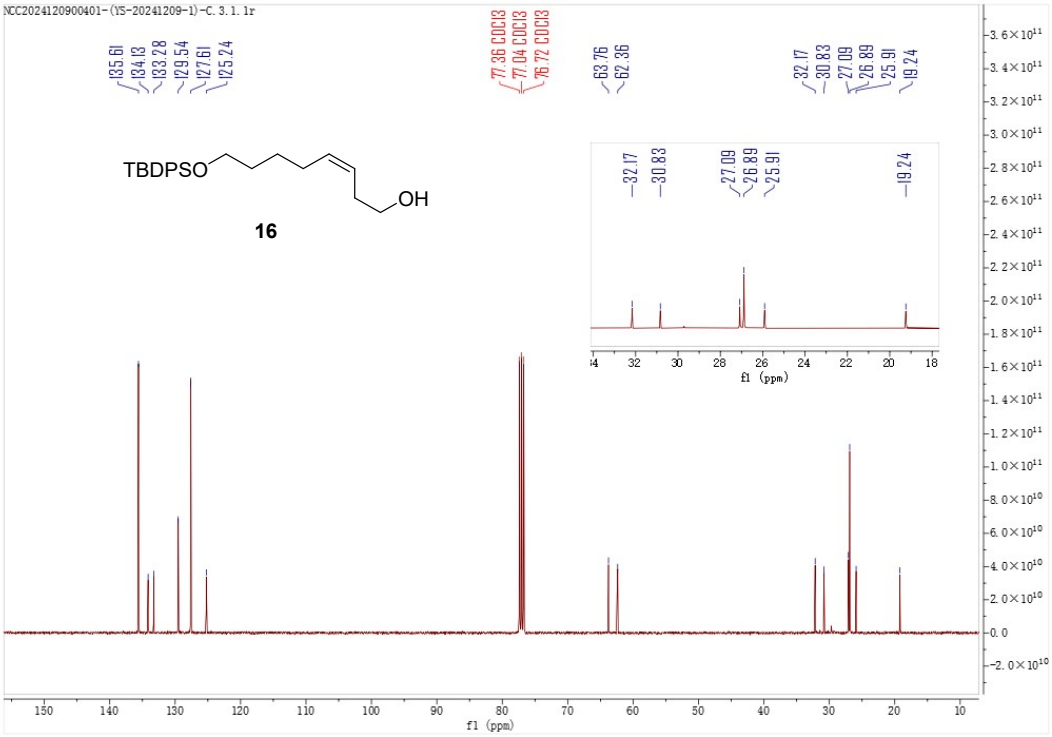
^{13}C NMR (101 MHz, $CDCl_3$) of compound **15**



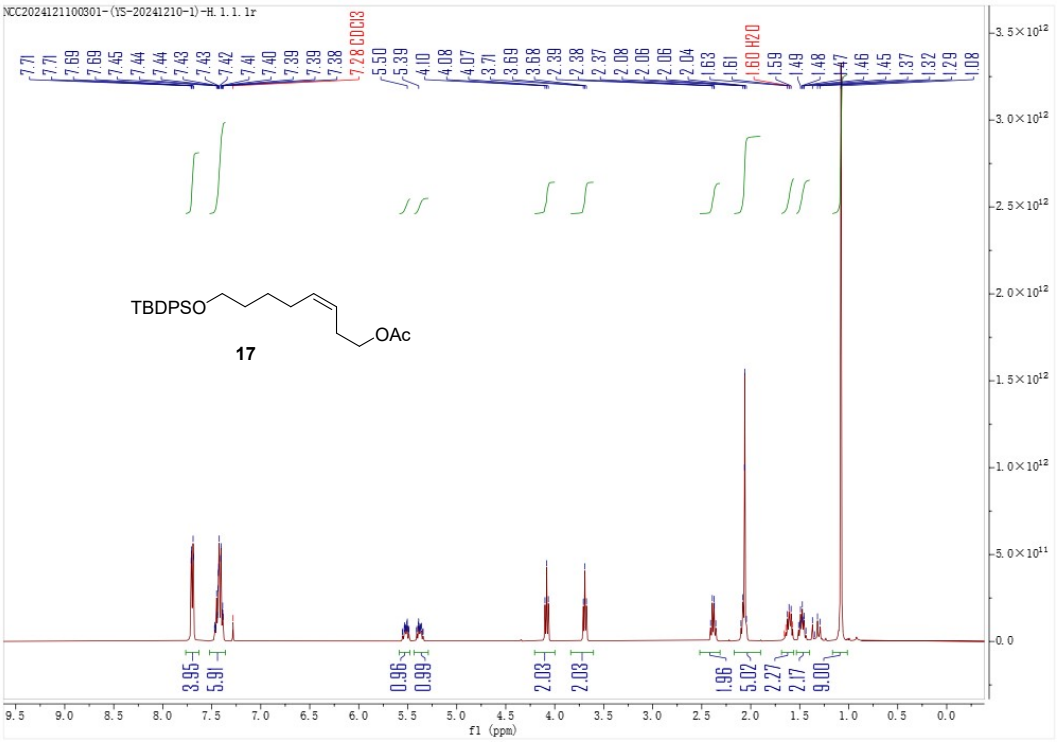
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **16**



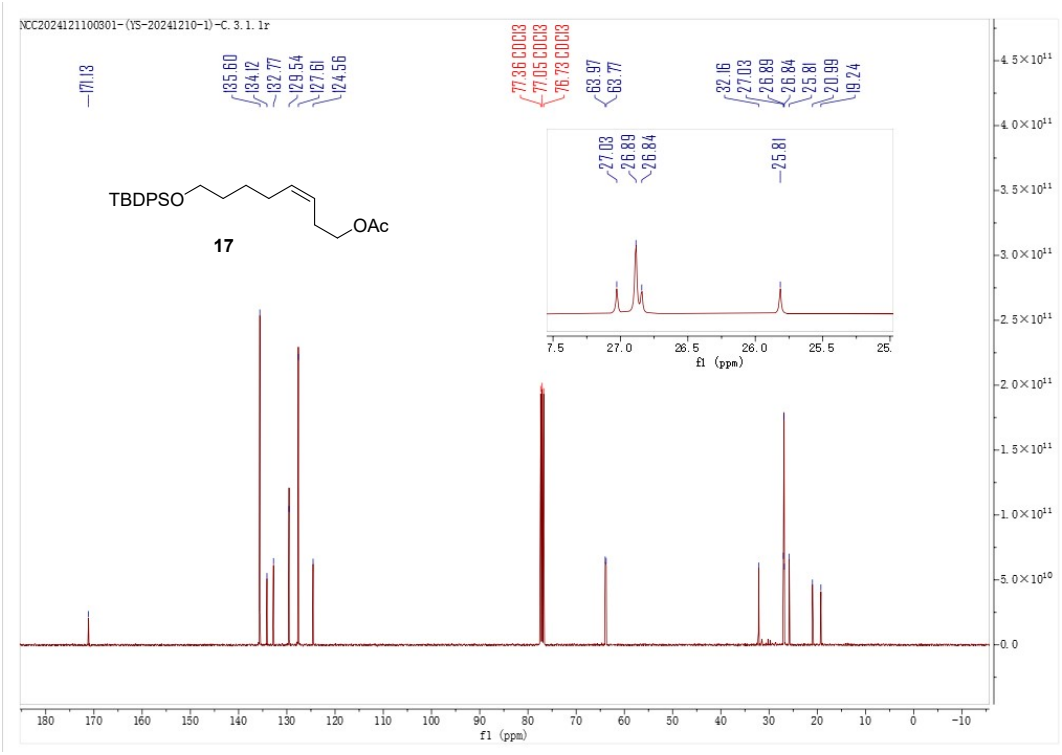
^{13}C NMR (101 MHz, $CDCl_3$) of compound **16**



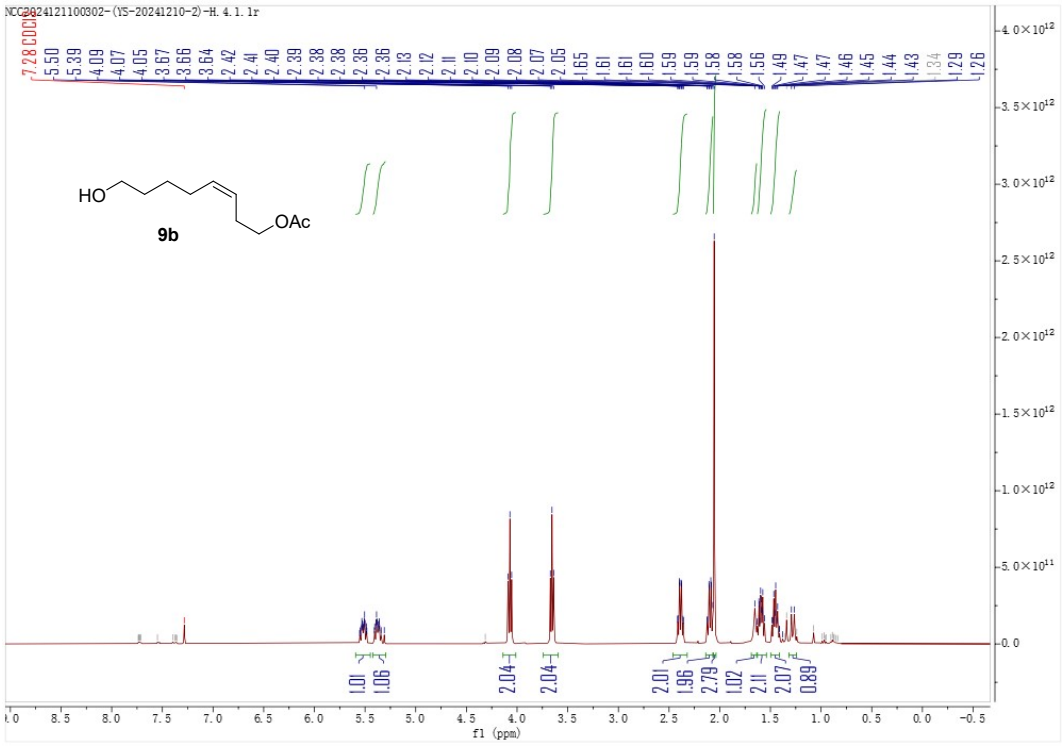
^{1}H NMR (400 MHz, $CDCl_3$)) of compound **17**



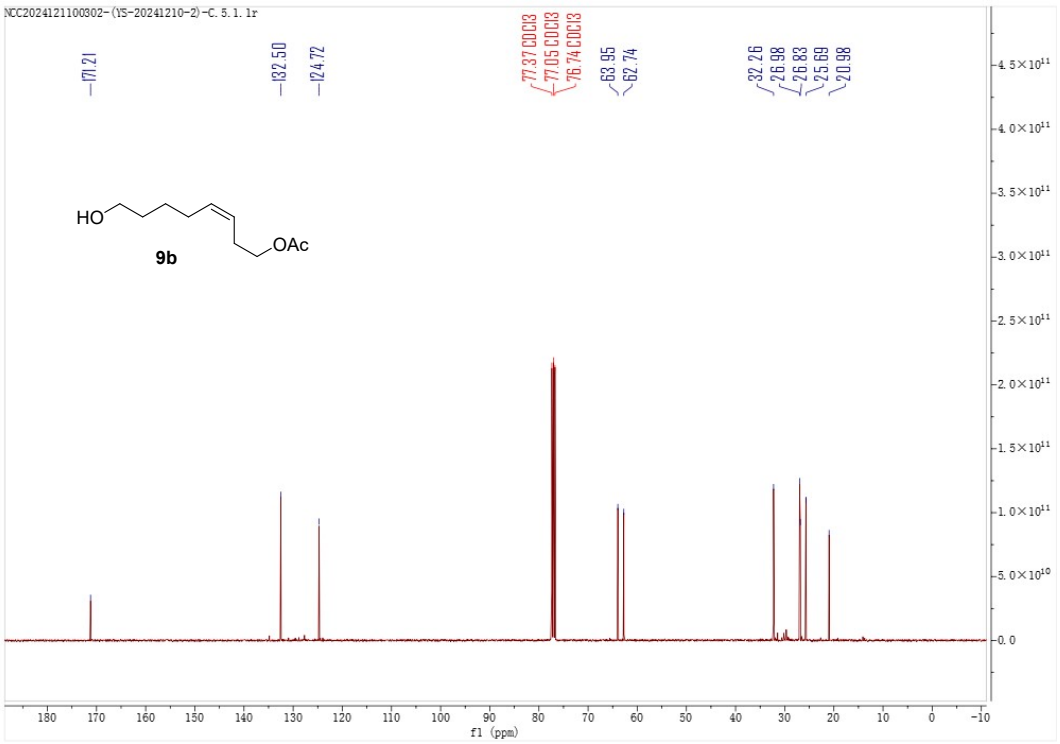
^{13}C NMR (101 MHz, $CDCl_3$) of compound **17**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **9b**

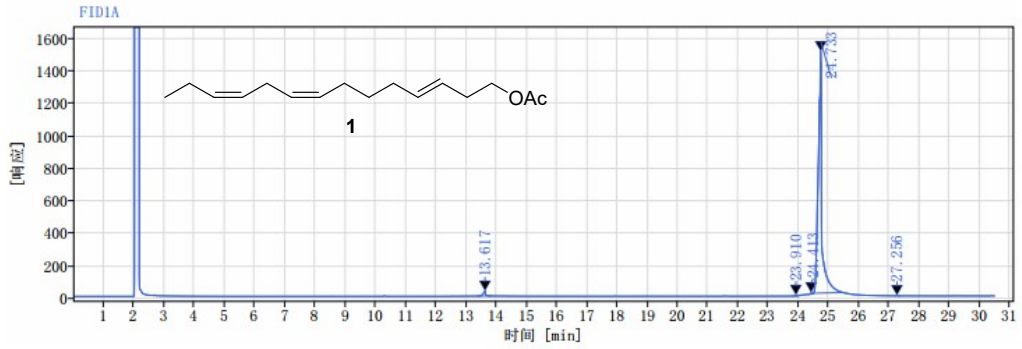


^{13}C NMR (101 MHz, $CDCl_3$) of compound **9b**



VI. Gas chromatography and HRMS of compounds 1 and 2

Gas chromatography of compounds **1** (Agilent 8860, HP-5: 30 m x 320 µm x 0,25 um)

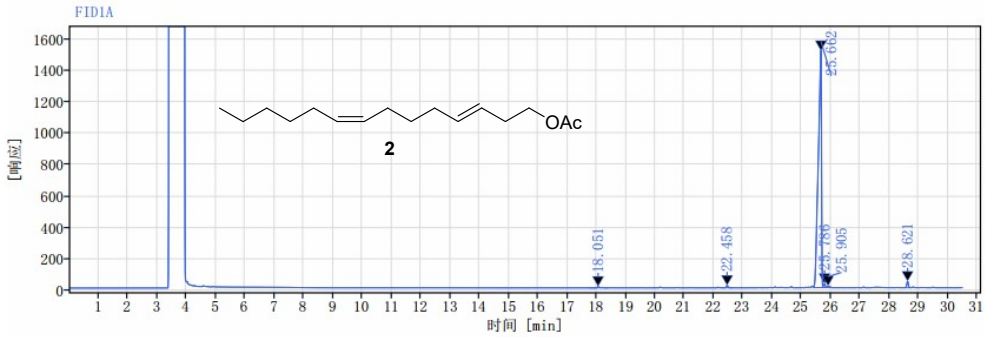


信号: FID1A

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
13.617	BB	0.49	169.21	30.20	1.35	
23.910	MM m	0.20	7.65	3.78	0.06	
24.413	MM m	0.15	5.93	7.55	0.05	
24.733	MM m	0.97	12363.22	1485.50	98.50	
27.256	MM m	0.16	6.03	1.82	0.05	
		总和	12552.05			

Gas chromatography of compounds **2** (Agilent 8860, HP-5: 30 m x 320 µm x 0,25

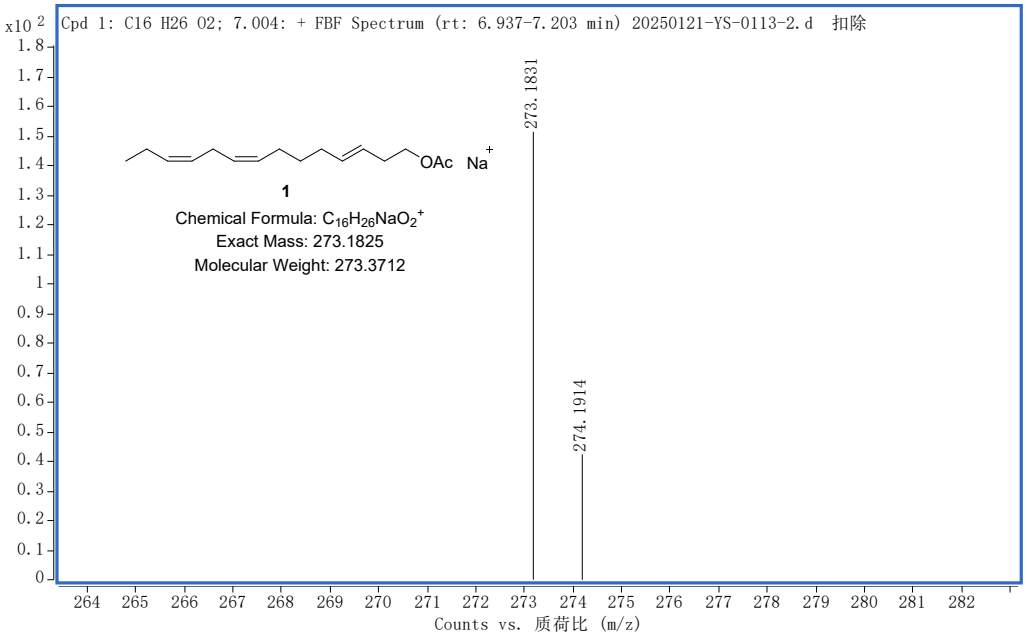
um)



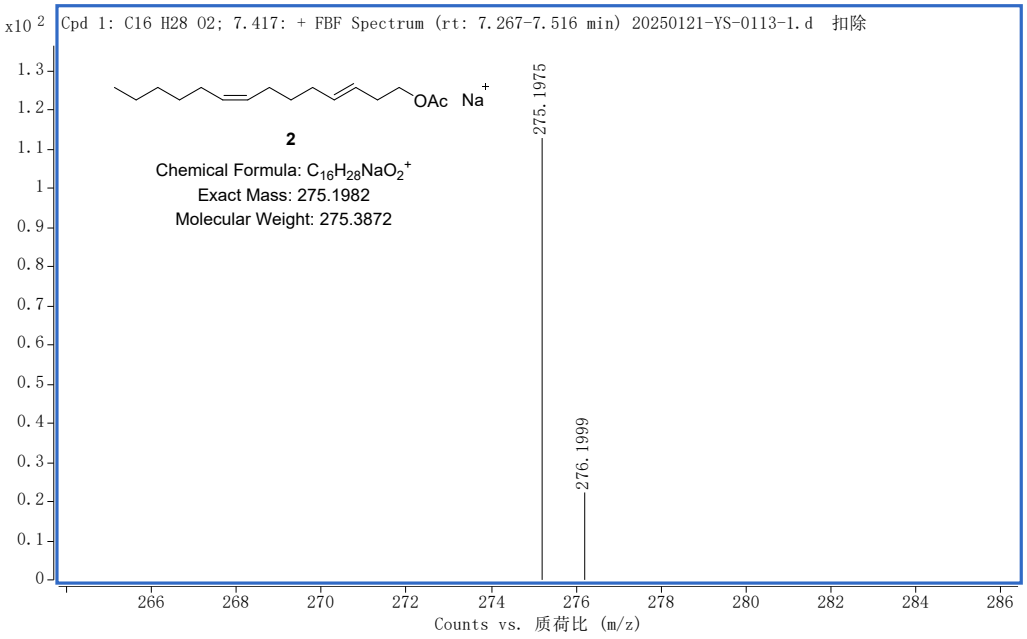
信号: FID1A

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
18.051	MM m	0.65	44.43	8.26	0.38	
22.458	MM m	0.55	58.22	14.10	0.50	
25.662	VV	0.33	11350.53	1511.08	96.72	
25.786	VB	0.13	96.30	24.29	0.82	
25.905	MM m	0.33	33.18	8.79	0.28	
28.621	BV	0.22	153.09	39.94	1.30	
		总和	11735.74			

HRMS of compounds **1**



HRMS of compounds **1**


Cpd 1: C16 H28 O2; 7.417: + FBF Spectrum (rt: 7.267-7.516 min) 20250121-YS-0113-1.d 扣除
x10 2
OAc Na+
2
Chemical Formula: C16H28NaO2+
Exact Mass: 275.1982
Molecular Weight: 275.3872
275.1975
276.1999
Counts vs. 质荷比 (m/z)