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Aqueous $ZnCl_2$ Complex Catalyzed Prins Reaction of Silyl Glyoxylates: Access to Functionalized Tertiary α-Silyl Alcohols

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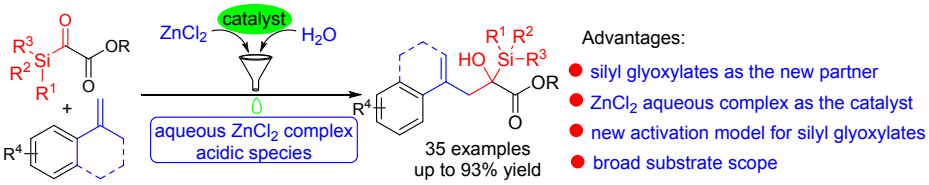


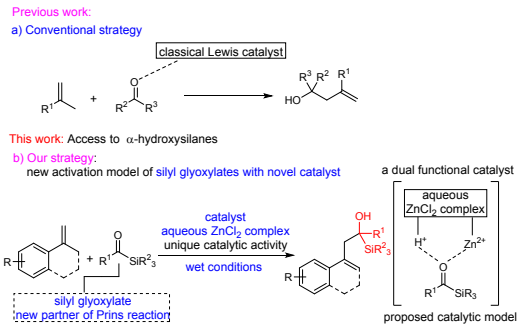
Abstract: An efficient Prins reaction of silyl glyoxylates in the presence of an aqueous $ZnCl_2$ complex as a catalyst was developed, providing functionalized tertiary α-silyl alcohols in high yields under mild conditions. A preliminary investigation indicated that the aqueous $ZnCl_2$ complex acted as a dual functional catalyst of Brønsted and Lewis acid to activate the carbonyl groups of silyl glyoxylates via a dual-activation model.

■INTRODUCTION

Because of their unique properties, organosilicon compounds are famous in pharmaceutical chemistry and synthetic chemistry and materials science.[1] Among them, functionalized tertiary α-silyl alcohols are useful intermediates in carbon−carbon bond formation and rearrangement reactions.[2] Consequently, several catalytic methods have been developed and the nucleophilic addition to acylsilanes is the most used strategy for their preparation. For example, with alkynes and Grignard reagents as the nucleophiles, the addition reaction of acylsilanes were well developed by the group of Marek[3] and Chan[4] and Harutyunyan,[5] affording the tertiary α-silyl alcohols in high yields. Moreover, with aldehydes[6] and sulphur[7] or other nucleophiles,[8] tertiary α-silyl alcohols were obtained under mild conditions. More recently, Oestreich group[9] reported a new approach to the synthesis of functionalized tertiary α-silyl alcohols via an copper-catalyzed addition of acylsilanes with an in-situ-formed boron nucleophile across 1,3-diene.

Silyl glyoxylates are useful organosilicon reagents in the Brook rearrangement.[2,10] Due to the poor reactivity of the carbonyl group in silyl glyoxylates, the high nucleophilicity of metal-based reagents is used in the transformations.[2,10] Generally, Lewis-acid activated aldehydes or acetals are typically used in Prins reactions,[11] but silyl glyoxylate as electronphile in Prins reaction is still limitation, and the undeveloped Prins reaction of silyl glyoxylates is highly desirable owing to the low reactivities of the unusual carbonyl groups in silyl glyoxylates, although an electron-withdrawing group is directly bonded to the sp^2-carbon atoms.[2e] It is well known that Lewis acid catalysts lower the activation barriers of

Scheme 1. Aqueous $ZnCl_2$ Complex Catalyzed Prins Reaction of Silyl Glyoxylates



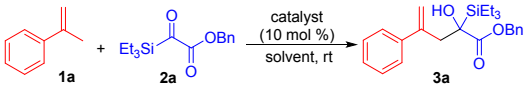
enophiles,[11] and our previous work indicated that the carbonyl groups in silyl glyoxylates could also be activated by Brønsted acids,[6] hydrogen bonding,[8b] and water[7,8a]. The classic Lewis acids, such as $TiCl_4$, $FeCl_3$, and $AlCl_3$, have been used in the Prins reaction (Scheme 1a).[11] However, they exhibited poor reactivities in the Prins reaction of silyl glyoxylates (Table 1 for details). Meanwhile, our preliminary studies[6,7,8a,b] indicated that the proposed activation models via hydrogen bonding failed in the Prins reaction of silyl glyoxylates (Table 2 for details). It is essential to develop a highly efficient catalyst to activate the carbonyl groups in silyl glyoxylates. In our continuous efforts to explore the new reaction model of silyl glyoxylates, herein we report an aqueous solution of $ZnCl_2$[12] for the Prins reaction of silyl glyoxylates (Scheme 1b). Compared to traditional Lewis and Brønsted acids, the unique catalytic activity of the aqueous $ZnCl_2$ complex was explored, and it acted as a dual functional catalyst of Brønsted and Lewis acids to activate the carbonyl groups of silyl glyoxylates in the Prins reaction via a

dual-activation model. It is important to note that this catalyst can be generated in-situ from the reaction of $ZnCl_2$ with water in an appropriate molar ratio.

■RESULTS AND DISCUSSION

Our investigation was initiated with α-methyl styrene (**1a**) and silyl glyoxylate (**2a**) as the model substrates in the presence of traditional metal Lewis acid catalyst in dry conditions. As shown in Table 1, the desired product **3a** was obtained with a 38% yield using $TiCl_4$ catalyst. The reaction was monitored by TLC (thin layer chromatography) and a certain amount of silyl glyoxylate (**2a**) was still left when the reaction was quenched after 72 h (Table 1, entry 1). To further improve the product yield, other catalysts, including Fe salts, Al salts, Cu salts, Zn salts and Sc salts, were examined (Table 1, entries 2–10). The yield of desired product **3a** is increased up to 48% by using an absolutely anhydrous commercially available $ZnCl_2$ (10 mol %)[13] as a catalyst (Table 1, entry 11). To further improve the product yield, other solvents, including THF, EtOAc, DMF, CH_3CN, DMSO, and toluene, were examined. They all produced a negative effect on the reaction, and no desired product was observed (Table 1, entries 12–17). Considering the effect of H-bonding for activating the carbonyl group, a series of organocatalyst was examined (Table 2). However, no reaction was observed when thioureas and Brønsted acid catalysts were applied to the reaction (Table 2, entries 1–6). To our delight, the relatively strong Brønsted acids, HCl (aq.) and *p*-toluenesulfonic acid (PTSA), provided product **3a** with 19% and 16% yield, respectively (Table 2, entries 7 and 8). However, no product was detected using the sterically hindered camphorsulfonic acid (CSA) as a catalyst (Table 2, entry 9).

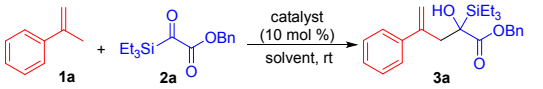
Table 1. Optimization of Reaction Conditions with Lewis Acid Catalyst[a]



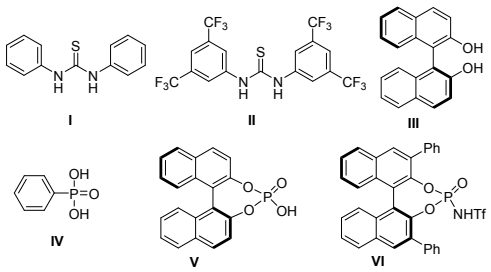
entry	catalyst	solvent	time (h)	yield (%)[b]
1	$TiCl_4$	CH_2Cl_2	72	38
2	$FeCl_3$	CH_2Cl_2	72	46
3	$FeCl_2$	CH_2Cl_2	72	44
4	$Fe(OAc)_2$	CH_2Cl_2	48	NR
5	$AlCl_3$	CH_2Cl_2	48	NR
6	$Al(OH)_3$	CH_2Cl_2	48	NR
7	Al_2O_3	CH_2Cl_2	48	NR
8	$Zn(OTf)_2$	CH_2Cl_2	48	NR
9	$Cu(OTf)_2$	CH_2Cl_2	48	NR
10	$Sc(OTf)_3$	CH_2Cl_2	72	21
11	$ZnCl_2$	CH_2Cl_2	72	48
12	$ZnCl_2$	THF	72	NR
13	$ZnCl_2$	EtOAc	72	NR
14	$ZnCl_2$	DMF	72	NR
15	$ZnCl_2$	CH_3CN	72	NR
16	$ZnCl_2$	DMSO	72	NR
17	$ZnCl_2$	toluene	72	NR

[a]Reactions were performed with 0.40 mmol of **1a**, 0.10 mmol of **2a**, and 10 mol % of catalyst in 1.0 mL CH_2Cl_2 and stirred for the indicated time at room temperature. [b]Isolated yield after purification by column chromatography and the reaction was monitored by TLC. NR = no reaction. TES = triethylsilyl.

Table 2. Optimization of Reaction Conditions with Thioureas and BrønstedAcid Catalysts[a]



entry	catalyst	time (h)	yield (%)[b]
1	**I**	24	NR
2	**II**	24	NR
3	**III**	48	NR
4	**IV**	24	NR
5	**V**	48	NR
6	**VI**	48	NR
7	HCl[c]	120	19
8	PTSA	120	16
9	CSA	120	NR

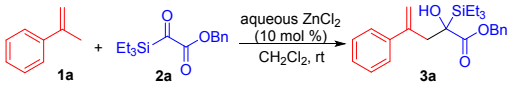


[a]Reactions were performed with 0.40 mmol of **1a**, 0.10 mmol of **2a**, and 10 mol % of catalyst in 1.0 mL CH_2Cl_2 and stirred for the indicate time at room temperature. [b]Isolated yield after purification by column chromatography. [c]HCl (aq.) = 12 mol/L. NR = no reaction.

The preliminary results showed that carbonyl groups of silyl glyoxylates could be activated by Lewis acid (48% yield for dry $ZnCl_2$ in Table 1, entry 11) and Brønsted acid (19% yield for HCl (12 mol/L) in Table 2, entry 7) albeit with low efficiency, for examples. We questioned whether carbonyl groups of silyl glyoxylates could be activated by one catalyst with dual-activation functions. In this regard, the water-compatible Lewis acid showed superior reactivity in aqueous solutions compared with anhydrous environments, and protons could be generated from the hydrolysis of the Lewis acid.

Indeed, the powerful Brønsted acidity was observed at a high concentration of the aqueous $ZnCl_2$ solution in the 1970's and further applications in organic synthesis have been ignored in the past decades.[12] To explore the catalytic activities of aqueous $ZnCl_2$ solutions in the model reaction, the effect of product yield on the different ratio of H_2O to $ZnCl_2$ in CH_2Cl_2 was examined, as shown in Table 3 and Figure 1. The product yield increased with the decrease of water content, and a 90% yield of **3a** was obtained (Table 3, entry 13) when the molar ratio of H_2O to $ZnCl_2$ was around at 2:1 to 1:6. It should be noted that the yield decreased rapidly as the $ZnCl_2$ content increased, and a 48% yield of **3a** was obtained in the absence of water.

Table 3. Optimization of Reaction Conditions with Aqueous $ZnCl_2$ Catalyst[a]



entry	catalyst (molar ratio of H_2O:$ZnCl_2$)	time (h)	yield (%)[b]
1	H_2O	72	0
2	9:1	72	17
3	8:1	72	36
4	7:1	72	59
5	6:1	72	72
6	5:1	72	78
7	4:1	72	81
8	3:1	72	84
9	2:1	72	88
10	1.3:1	72	84
11	1:1	72	87
12	1:2	72	88
13	1:3	18[c]	90
14	1:4	24[c]	87
15	1:5	24[c]	88
16	1:6	20[c]	88
17	1:7	24[c]	82
18	1:8	72	70
19	$ZnCl_2$	72	48

[a]Reactions were performed with 0.40 mmol of **1a**, 0.10 mmol of **2a**, and 10 mol % of aqueous $ZnCl_2$ in 1.0 mL CH_2Cl_2 and stirred for the indicated time at rt. [b]Isolated yield after purification by column chromatography. [c]Reactions were finished for the indicate time at rt.

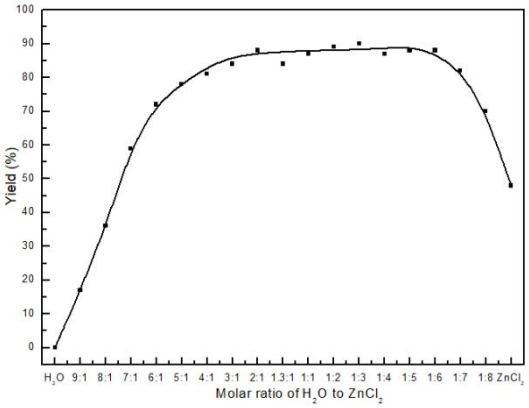
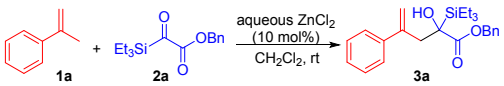


Figure 1. The Relationship between the Product Yield and Ratio of H_2O to $ZnCl_2$ from the Data in Table 3.

Considering the polymerization of double bonds in Lewis acid catalyzed Prins reaction, the loading of α-methyl styrene (**1a**) was further optimized. As shown in Table 4, when 1 equiv. of α-methyl styrene (**1a**) was used, the reaction was sluggish with 57% yield. In this transformation, the starting material of α-methyl styrene (**1a**) was consumed after 48 h and silyl glyoxylate (**2a**) was still not exhausted. And the similar results were also observed when 2 equiv. or 3 equiv. of **1a** was used (Table 4, entries 2 and 3). Further investigation showed that the high yield of 90% was obtained when 4 equiv. of α-methyl styrene (**1a**) was used and starting material of silyl glyoxylate (**2a**) was utterly consumed (Table 4, entry 4). To our delight, the yield was slightly increased to 91% when the reaction was performed with 5 equiv. of **1a** (Table 4, entry 5). Considering almost the same yield of **3a** between 4 and 5 equiv. of **1a** used in the reaction, we chose 4 equiv. of α-methyl styrene (**1a**) as the best condition.

Table 4. Optimization of the Loading of α-Methyl Styrene (1a) with Aqueous $ZnCl_2$Catalyst[a]



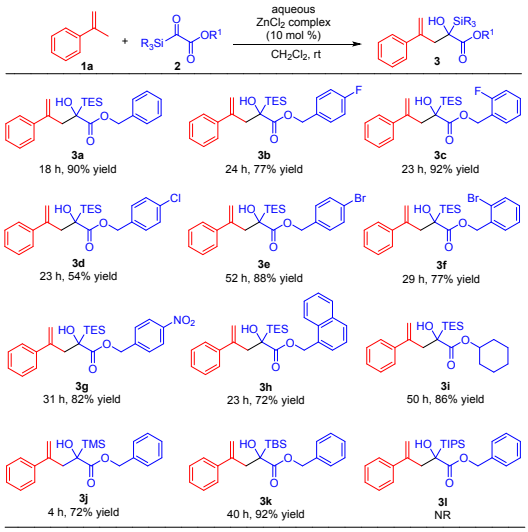
entry	**1a** (equiv.)	time (h)	yield (%)[b]
1	1	48	57
2	2	36	79
3	3	24	81
4	4	18	90
5	5	18	91

[a]Reactions were performed with indicated mmol of **1a**, 0.10 mmol of **2a**, and 10 mol % of aqueous $ZnCl_2$ complex (H_2O:$ZnCl_2$ = 1:3 in molar ratio) in 1.0 mL CH_2Cl_2 and stirred for the indicated time at rt. [b]Isolated yield after purification by column chromatography.

With the optimal reaction conditions in hand, the generality of silyl glyoxylates in the Prins reaction was firstly investigated. As shown in Scheme 2, a

series of silyl glyoxylates bearing different ester groups successfully reacted with **1a**. All the halogen-substituted substrates were suitable in the reaction, affording the corresponding products (**3b**–**f**) with good yields. When a silyl glyoxylate with a strong electron-withdrawing group was subjected to the reaction, an 82% yield of the corresponding product **3g** was obtained. Silyl glyoxylates containing a bulky 2-naphthyl ester group or a cyclohexyl-based ester group were well tolerated, giving the corresponding products (**3h** and **3i**) in high yields. The reaction rate was accelerated when the silyl glyoxylate with less steric hindrance (TMS) was used as substrate, generating 72% yield of product **3j** in 2 h. In contrast, when silyl glyoxylate with a bulky TBS group was employed, an obvious slow reaction was observed (**3k** *vs* **3j**). However, no product **3l** was detected when large-sized group (TIPS) attached to the silyl glyoxylate was used as the substrate under the same conditions.

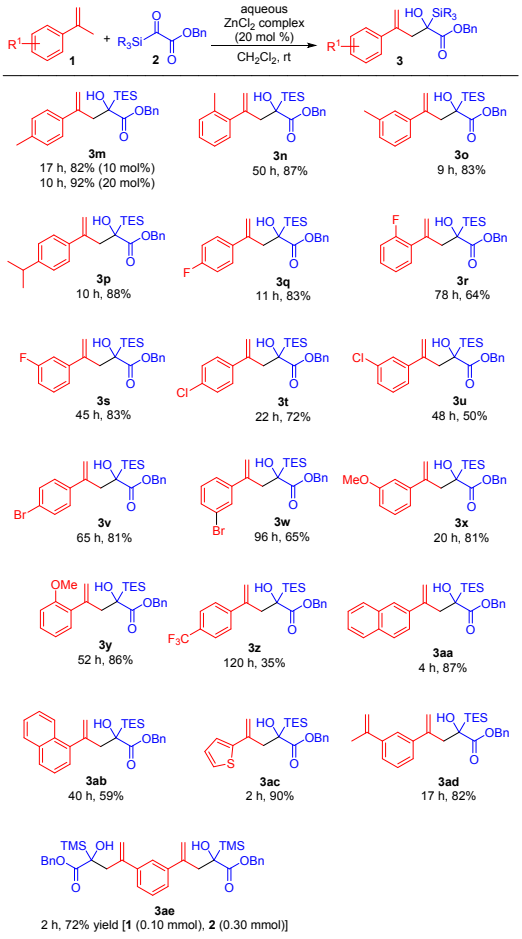
Scheme 2. The Scope of Silyl Glyoxylates[a]



[a]Reactions were performed with **1a** (0.40 mmol), **2a** (0.10 mmol), aqueous $ZnCl_2$ complex (10 mol %, H_2O:$ZnCl_2$ = 1:3 in molar ratio) in 1.0 mL of CH_2Cl_2 at room temperature. TMS = trimethylsilyl, TES = triethylsilyl, TBS = *tert*-butyldimethylsilyl, TIPS = tri(isopropyl)silyl.

To further survey the reaction scope, we explored the Prins reaction of silyl glyoxylates **2** with different styrenes **1**, and the results are presented in Scheme 3. When a reaction of 4-methyl-α-methyl styrene with **2a** was performed with 20 mol % catalyst, a 92% yield of **3m** was obtained. α-Methyl styrenes with alkyl substituents, such as *o*-Me, *m*-Me, and *p*-^{i}Pr on the benzene rings underwent reactions smoothly, affording the corresponding products (**3n**–**p**) with good yields. Generally, α-methyl styrenes containing halogen substituent were also tolerated in the reactions, providing the anticipated products (**3r**–**w**) with 64–83% yields. Compared to electron-donating groups, the reactions were influenced unfavorably by the substrates bearing electron-withdrawing groups (**3x**–**3y** *vs* **3z**). The effects other substituent on α-methyl styrene were also evaluated and the reactions afforded the corresponding products (**3aa**–**ae**) with high yields. The mono Prins reaction product **3ad** was isolated with the use of silyl glyoxylate (TES derivative). Notably, even the molar ratio of **1** to **2** was also fixed at 1:4, no double Prins reaction product was observed. Interestingly, the double Prins reaction product **3ae** was isolated with a 72% yield when 1,3-di(*iso*-propenyl)benzene reacted with smaller-sized silyl glyoxylate (TMS derivative). To our surprise, this reaction rate (**3ae**) is faster than the reaction of silyl glyoxylate with TES substituent (**3ad**) and the reaction was completely finished in 2 h. No mono Prins reaction product was obtained even when the molar ratio of **1** to **2** was fixed at 4:1.

Scheme 3.The Scope of Styrenes[a]

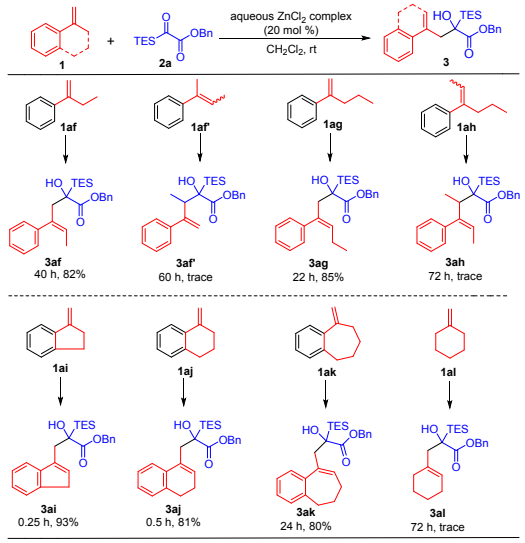


[a]Reactions were performed with **1** (0.40 mmol), **2** (0.10 mmol), aqueous $ZnCl_2$ complex (20 mol %, H_2O:$ZnCl_2$ = 1:3 in molar ratio) in CH_2Cl_2 (1.0 mL) at room temperature.

To further investigate the generality of alkenes, other substituted alkenes were examined, as shown in Scheme 4. The 1,1-disubstituted alkenes with a long alkyl chain (**1af** and **1ag**) were well tolerated,

providing the corresponding products **3af** and **3ag** with high yields. However, when the trisubstituted alkenes (**1af'** and **1ah**) were used in the reaction, only trace amounts of products were observed, event with long reaction times. The rigid cyclic alkenes proceeded smoothly with different reactivity. For examples, the substrates **1ai** and **1aj** exhibited high reactivity, and the reactions were completed within 0.5 h. The reaction was sluggish when substrate **1ak** was used as an enophile. When a cyclic alkene, 1-methylenecyclohexane (**1al**) was subjected to the reaction, no desired product (**3al**) was detected.

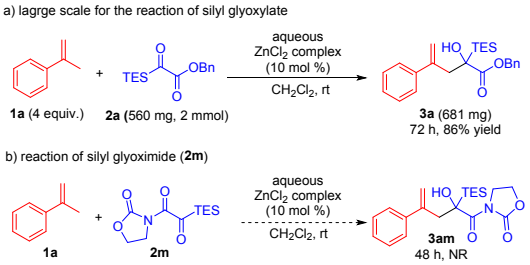
Scheme 4. The Extended Scope of Substituted Alkenes[a]



[a]Reactions were performed with **1** (0.40 mmol), **2a** (0.10 mmol), aqueous $ZnCl_2$ complex (20 mol %, H_2O:$ZnCl_2$ = 1:3 in molar ratio) in CH_2Cl_2 (1.0 mL) at room temperature.

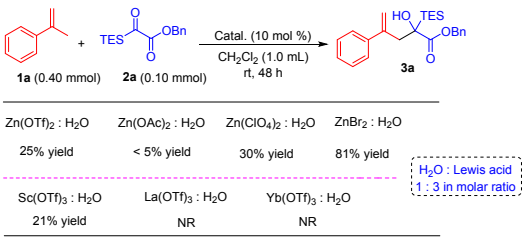
The reaction can be easily scaled up to 2 mmol of silyl glyoxylate (**2a**), generating the corresponding product **3a** in the yield of 86% under standard condition (Scheme 5a). To further assess the feasibility of introducing the amide into silyl glyoxylate, the reaction of silyl glyoximide (**2m**) with styrene **1a** was carried out under the standard conditions. However, no addition product (**3am**) was observed (Scheme 5b).

Scheme 5. Scale-up Reaction and the Reactivity of Silyl Glyoximide



Since the highly efficient catalytic activities of rare-earth salts in aqueous media were disclosed by Kobayashi,[14] the unique catalytic activities of water-compatible Lewis acids were ascribed to the hydrolysis constant (K_h) and water exchange rate constant (WERC).[15] We attempted to understand the difference in activity between the aqueous $ZnCl_2$ complex and other water compatible Lewis acids. Representative rare-earth salts, such as $Sc(OTf)_3$, $La(OTf)_3$, and $Yb(OTf)_3$ were investigated, and the poor reactivity was observed. Meanwhile, other Zn salts, including $Zn(OTf)_2$, $Zn(OAc)_2$, $Zn(ClO_4)_2$, and $ZnBr_2$ also exhibited low catalytic activity (Scheme 6). These results suggested that the catalytic activity of the aqueous $ZnCl_2$ solution exhibited a superior catalytic reactivity and complementary selectivity to the traditional water-compatible Lewis acids. Early investigation[12] showed that a hyper-concentrated aqueous $ZnCl_2$ solution would be regarded as a strong protonic acid. In this regard, the molar ratio of H_2O:$ZnCl_2$ was sufficiently low to minimize outer-sphere hydration, and polarization of water molecules coordinated to Zn^{2+} weakened the O–H bond to enhance the acidity (Scheme 7, **TS-I**). Considering that $ZnCl_2$ was also effective in this reaction, a Brønsted acid/Lewis acid co-catalytic model was proposed (Scheme 7, **TS-II**). To further understand the catalytic model, the crystal structure of a zinc chloride hydrate is beneficial to explore the possible reaction process. Fortunately, the single-crystal structure of $ZnCl_2 \cdot 1.3H_2O$, which is in the optimal range of molar ratio of H_2O to $ZnCl_2$ (1:2 to 1:6), was confirmed by Foliner and Brehler.[16] The crystal structure clearly showed that the polymeric structure with bridging chlorides was formed and the two-thirds of the zinc atoms are tetrahedrally coordinated with four chlorine atoms and other one-third is octahedrally coordinated with four water molecules and two chlorine atoms. This unique structure indicated water is only partially coordinated with zinc chloride and a Brønsted/Lewis acid co-catalytic model was reasonably proposed (**TS-II**).

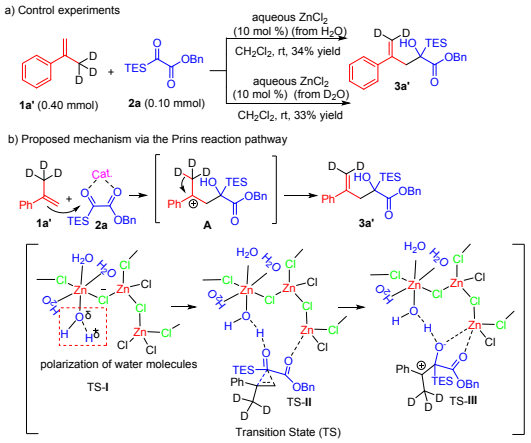
Scheme 6. The Catalytic Reactivity of Other Lewis Acids[a]



[a]Reactions were performed with **1** (0.40 mmol), **2a** (0.10 mmol), aqueous metal complex (20 mol %, H_2O:metal salts = 1:3 in molar ratio) in CH_2Cl_2 (1.0 mL) at room temperature.

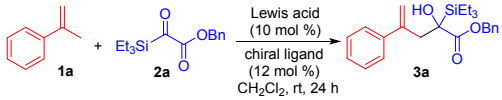
To further investigate the reaction mechanism, the control experiments were conducted. As shown in Scheme 7a, when deuterated α-methyl styrene (**1a'**)[17] was used as the starting material under the standard conditions, deuterated product (**3a'**) was obtained in 34% yield. Compared to the catalyst prepared from the H_2O, the same deuterated product (**3a'**) was achieved when the reaction was performed with the aqueous $ZnCl_2$ catalyst prepared from the D_2O. Generally, the ene reaction proceeded through a cyclic transition state to form a new bond and the corresponding product with deuterated hydroxyl group (-OD) could be generated by 1,5-hydrogen shift process in the control experiment. However, no product with deuterated hydroxyl group (-OD) was observed. The control experiment indicated that the reaction proceed through stepwise mechanism involving carbocation intermediates, which can be considered as Prins reaction.[11] Accordingly, the reaction pathway via a stepwise mechanism was proposed. As shown in Scheme 7b, the carbonyl group of silyl glyoxylate **2a** could be efficiently activated by acidic catalyst. Next, the geometrically non-rigid π-complex (**Ts-II**) was formed and non-classical three-membered ring opened to form the carbocation intermediate (**TS-III**). Followed by the elimination of deuterium to regenerate the double bond in transition state **A** and **TS-III**, product **3a'** was generated, and the catalyst was regenerated for the next run.

Scheme 7. The Control Experiments and Proposed Reaction Mechanism

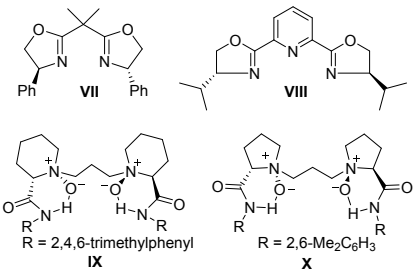


The asymmetric Prins reaction of silyl glyoxylates will be great value for preparation of chiral functionalized tertiary α-silyl alcohols. The straightforward method is directly application of chiral ligand to this reaction. As shown in Table 5, chiral ligands of bis(oxazoline) were firstly investigated. Surprisingly, the reaction cannot be carried out in the presence of complexes of aqueous $ZnCl_2$ with chiral ligands **VII** and **VIII** (Table 5, entries 1 and 2). Subsequently, chiral *N*,*N*'-dioxides **IX** and **X** were further selected as the chiral ligands in the reaction, and no reaction was observed (Table 5, entries 3 and 4).

Table 5. Asymmetric Prins Reaction[a]



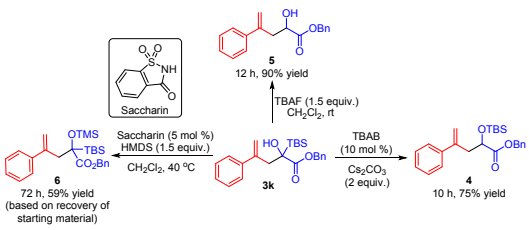
entry	catalyst	yield (%)[b]
1	aqueous $ZnCl_2$/**VII**	NR
2	aqueous $ZnCl_2$/**VIII**	NR
3	aqueous $ZnCl_2$/**IX**	NR
4	aqueous $ZnCl_2$/**X**	NR



[a]Reactions were performed with 0.40 mmol of **1a**, 0.10 mmol of **2a**, and 10 mol % of chiral complex in 1.0 mL CH_2Cl_2 and stirred for 24 h at rt. [b]Isolated yield after purification by column chromatography.

To verify the transformations of Prins reaction products (Scheme 8), [1,2]-Brook rearrangement of **3k** was first carried out under PTC conditions,[6] generating the corresponding product **4** in 75% yield. Moreover, the TBS group in **3k** was efficiently removed on treatment with TBAF,[18] and the corresponding product **5** was obtained in 90% yield. A more powerful transformation has been showed that the alcohol of **3k** was protected as TMS ether (**6**) under mild conditions.[19]

Scheme 8. Further Transformations of Product 3k



■CONCLUSIONS

In summary, we developed a novel example of the catalytic Prins reaction with silyl glyoxylates as the enophiles. Compared to the classical catalysts, this reaction was realized by the high concentration of an aqueous $ZnCl_2$ solution. In this process, the unique catalytic activity of the aqueous $ZnCl_2$ complex was first discovered in the Prins reaction and a Brønsted/Lewis acid co-catalytic model was proposed for the activation of silyl glyoxylates. Significant

progress has been achieved with a broad substrate scope, providing an array of functionalized tertiary α-silyl alcohols in good yields. Further studies of new reactions with aqueous $ZnCl_2$ complex are currently underway.

■EXPERIMENTAL SECTION

General information. Chemicals and analytical grade solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. Flash column chromatography was performed on silica gels (200–300 mesh). All ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or a 600 MHz NMR spectrometer. Chemical shifts were reported in ppm and the coupling constants *J* are given in Hz. Tetramethylsilane (TMS, δ = 0.00 ppm) or $CHCl_3$ (δ = 7.26 ppm) served as an internal standard for ^1H NMR; while $CDCl_3$ was used as an internal standard (δ = 77.0 ppm) for ^{13}C NMR. HRMS data were obtained on a Bruker Apex II mass instrument (ESI) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

Alkenes compounds were prepared according to the literature.[20] General procedure for the preparation of alkenes and their NMR data were provided. 1-Methylenecyclohexane (**1al**) was purchased from commercial sources and directly used without further purification. Silyl glyoxylates **2a**, **2e** and **2i–l** have been prepared in our previous work,[6] and silyl glyoxylates **2b–d** and **2f–h** were newly prepared according to the reported method.[6] The NMR data of **2b–d** and **2f–h** were provided. Silyl glyoximide (**2m**) was prepared according to the reported method.[21]

General experimental procedure

Typical procedure for the preparation of aqueous $ZnCl_2$ complex (H_2O:$ZnCl_2$ = 1:3 in molar ratio)

After standard cycles of evacuation and back-filling with dry and pure nitrogen three times, an oven-dried Schlenk tube by a heat gun to ≈ 200 °C equipped with a magnetic stirring bar was charged with $ZnCl_2$ (100 mmol, 13.6 g). H_2O (33.33 mmol, 0.60 g) was added to the tube by syringe. After stirring at room temperature for 6 h, the mixture was stored under nitrogen atmosphere.

General procedure for the Prins reaction

An oven-dried Schlenk tube by a heat gun to ≈ 200 °C equipped with a magnetic stirring bar was charged with aqueous $ZnCl_2$ complex (10 mol %, H_2O:$ZnCl_2$ = 1:3 in molar ratio), alkene (**1**, 0.40 mmol), silylglyoxylate (**2**, 0.10 mmol) and CH_2Cl_2 (1.0 mL) at room temperature. After stirring for the indicated time, the residue was purified via flash chromatography to give the desired product **3**.

Benzyl 2-hydroxy-4-phenyl-2-(triethylsilyl)pent -4-enoate (3a): Isolated by column chromatography (EtOAc/petroleum ether = 1:100); pale yellow oil (35.6 mg, 90% yield); R_f 0.31 (EtOAc/petroleum ether, 1:100); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.31 (m, 5H), 7.29–7.20 (m, 5H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.08 (s, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 14.0 Hz, 1H), 2.81 (s, 1H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.69–0.63 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 144.0, 142.1, 135.1, 128.7, 128.4, 128.3, 128.0, 127.3, 126.9, 117.0, 72.8, 66.9, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{32}O_3SiNa$ 419.2018; found 419.2020.

4-Fluorobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3b): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (31.9 mg, 77% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.16 (m, 7H), 7.03–6.98 (m, 2H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.08 (s, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.79 (s, 1H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.68–0.61 (m, 6H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 177.0, 162.7 (d, *J* = 246.0 Hz), 143.9 142.1, 130.8 (d, *J* = 2.0 Hz), 128.0, 127.3, 126.9, 117.1, 115.3 (d, *J* = 21.0 Hz), 72.7, 66.1, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}FO_3SiNa$ 437.1924; found 437.1918.

2-Fluorobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3c): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (38.1 mg, 92% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 7H), 7.12–7.02 (m, 2H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.08 (s,1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.4Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.77 (s, 1H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.68–0.62 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.9, 161.2 (d, *J* = 247.0 Hz), 144.1, 142.1, 131.3 (d, *J* = 4.0 Hz), 130.5 (d, *J* = 8.0 Hz), 128.0, 127.3, 126.9, 124.0 (d, *J* = 3.0 Hz), 122.4 (d, *J* = 15.0 Hz), 117.0, 115.4 (d, *J* = 21.0 Hz), 72.9, 60.6 (d, *J* = 4.0 Hz), 40.8, 7.4, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}FO_3SiNa$ 437.1924; found 437.1920.

4-Chlorobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3d): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (23.2 mg, 54% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.24 (m, 7H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 0.4 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.91(d, *J* = 14.0 Hz, 1H), 2.81 (s, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.70–0.64 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.9, 143.1, 142.1, 134.3, 133.6, 130.1, 128.6, 128.1, 127.3, 126.9,

117.2, 72.7, 66.0, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}ClO_3SiNa$ 453.1624; found 453.1627.

4-Bromobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3e): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); pale yellow oil (41.47 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.24–7.33 (m, 5H), 7.08(d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 1.6 Hz, 1H), 5.11 (s, 1H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.28 (d, *J* = 12.4 Hz, 1H), 3.19 (d, *J* = 14.0 Hz, 1H), 2.92 (d, *J* = 14.0 Hz, 1H), 2.81 (s, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.65–0.71 (m, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 176.9, 143.9, 142.1, 134.1, 131.6, 130.3,128.1, 127.3, 126.9, 122.4, 117.2, 72.7, 66.0, 40.8, 7.5, 2.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}BrO_3SiNa$ 497.1124; found 497.1111; and calcd for $C_{24}H_{31}BrO_3SiNa$ 499.1103; found 499.1105;

2-Bromobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3f): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); colorless oil (36.5 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.33–7.16 (m, 8H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.09 (s, 1H), 4.98 (d, *J* = 12.4 Hz, 1H), 4.58 (d, *J* = 12.8 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.78 (s, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.77–0.67 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.9, 144.1, 142.1, 134.7, 132.8, 130.7, 129.9, 128.0, 127.4, 127.3, 126.9, 123.9, 116.9, 73.0, 66.3, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}BrO_3SiNa$ 497.1124; found 497.1124.

4-Nitrobenzyl 2-hydroxy-4-phenyl-2-(triethyl silyl)pent-4-enoate (3g): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); colorless oil (36.2 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 9H), 5.26 (d, *J* = 1.6 Hz, 1H), 5.10 (s, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 3.19 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H), 2.82 (s, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.71–0.65 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 144.0, 142.1, 135.1, 128.7, 128.4, 128.3, 128.0, 127.3, 126.9, 117.0, 72.8, 66.9, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{24}H_{32}NO_5Si$ 442.2050; found 442.2049.

Naphthalen-1-ylmethyl 2-hydroxy-4-phenyl-2-(triethylsilyl)pent-4-enoate (3h): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (32.1 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.81 (m, 3H) , 7.53–7.47 (m, 2H), 7.44–7.39 (m, 2H),7.32–7.19 (m, 5H), 5.41 (d, *J* = 12.0 Hz, 1H), 5.20 (d, *J* = 1.6 Hz, 1H), 5.04 (s, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.80 (s, 1H), 0.85 (t, *J* = 8.0 Hz, 9H), 0.64–0.52 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.1, 144.1, 142.3, 133.7, 131.6, 130.9, 129.3, 128.6, 128.1, 127.9, 127.3, 126.9, 126.4, 125.9, 125.1, 123.6, 116.9, 73.1, 64.7, 40.8, 7.4, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{28}H_{34}O_3SiNa$ 469.2175; found 469.2162.

Cyclohexyl 2-hydroxy-4-phenyl-2-(triethylsilyl) pent-4-enoate (3i): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); pale yellow oil (33.4 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 2H), 7.29–7.20 (m, 3H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.12 (s, 1H), 4.45–4.42 (m, 1H), 3.09 (d, *J* = 14.4 Hz,1H), 2.97 (d, *J* = 14.4 Hz, 1H), 2.80 (s, 1H), 1.89–1.79 (m, 1H), 1.68–1.50 (m, 4H), 1.35–1.14 (m, 5H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.76–0.70 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7, 144.4, 142.6, 128.0, 127.2, 126.7, 116.3, 74.5, 73.2, 40.4, 31.8, 31.52, 25.3, 23.9, 7.6,2.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{23}H_{36}O_3SiNa$ 411.2331; found 411.2336.

Benzyl 2-hydroxy-4-phenyl-2-(trimethylsilyl)pent -4-enoate (3j): Isolated by column chromatography (EtOAc/petroleum ether = 1:100); colorless oil (25.5 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.15 (m, 10H), 5.21 (d, *J* = 1.6 Hz, 1H), 5.06 (s, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.78 (d, *J* = 14.0 Hz, 2H), 0.00 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.9, 144.1, 142.1, 135.3, 128.6, 128.3, 128.1, 127.4, 127.0, 116.9, 72.2, 66.9, 39.9, -4.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{26}O_3SiNa$ 377.1549; found 377.1552.

Benzyl 2-(*tert*-butyldimethylsilyl)-2-hydroxy-4-phenylpent-4-enoate (3k): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); pale yellow oil (36.4 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.03 (m, 10H), 5.09 (d, *J* = 1.6 Hz, 1H), 4.92 (t, *J* = 0.8 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.78(d, *J* = 14.0 Hz, 1H), 2.65 (s, 1H), 0.73 (s, 9H), 0.00 (s, 3H), -0.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.2, 143.8, 142.1, 134.9, 128.7, 128.4, 128.3, 128.1, 127.3, 126.9, 117.4, 72.6, 67.0, 41.3, 27.3, 18.3, -6.7, -7.3; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{32}O_3SiNa$ 419.2018; found 419.2020.

Benzyl 2-hydroxy-4-(*p*-tolyl)-2-(triethylsilyl)pent-4-enoate (3m): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (37.7 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.3 (m, 3H), 7.25–7.20 (m, 4H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.21 (d, *J* = 1.6 Hz, 1H), 5.21 (s, 1H), 4.89 (d, *J* = 12.4 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.79 (s,

1H), 2.31 (s, 3H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.69–0.63 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 143.9, 139.2, 137.0, 135.2, 128.8, 128.7, 128.4, 128.3, 126.8, 116.2, 72.9, 66.9, 40.8, 21.1, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{34}O_3SiNa$ 433.2175; found 433.2165.

Benzyl 2-hydroxy-4-(*o*-tolyl)-2-(triethylsilyl)pent-4-enoate (3n): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (35.7 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 3H), 7.18–7.04 (m, 6H), 5.24 (t, *J* = 0.8 Hz, 1H), 4.99 (d, *J* = 2.0 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 3.08 (d, *J* = 14.0 Hz, 1H), 2.85–2.81 (m, 2H), 2.27 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.64–0.58 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 144.7, 142.1, 135.1, 135.1, 130.1, 129.1, 128.7, 128.3, 128.3, 127.0, 125.4, 118.9, 72.7, 67.0, 42.4, 20.1, 7.5, 1.8; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{34}O_3SiNa$ 433.2175; found 433.2166.

Benzyl 2-hydroxy-4-(*m*-tolyl)-2-(triethylsilyl)pent-4-enoate (3o): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (34.0 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 3H), 7.25–7.03 (m, 6H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.06 (d, *J* = 0.8Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.37 (d, *J* = 12.4 Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.80 (s, 1H), 2.28 (s, 3H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.71–0.63 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 144.1, 142.2, 137.5, 135.2, 128.6, 128.4, 128.3, 128.1, 127.9, 127.6, 124.0, 116.8, 72.8, 66.9, 40.9, 21.4, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{34}O_3SiNa$ 433.2175; found 433.2166.

Benzyl 2-hydroxy-4-(4-(*iso*-propyl)phenyl)-2-(triethylsilyl)pent-4-enoate (3p): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); pale yellow oil (38.5 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 3H), 7.28–7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.06 (s, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.4 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.92–2.83 (m, 3H), 1.22 (d, *J* = 6.8 Hz, 6H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.71–0.64 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 148.0, 143.7, 139.5, 135.2, 128.6, 128.4, 128.3, 126.9, 126.1, 116.4, 72.7, 66.8, 40.9, 33.7, 24.0, 23.9, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{27}H_{38}O_3SiNa$ 461.2488; found 461.2487.

Benzyl 4-(4-fluorophenyl)-2-hydroxy-2-(triethylsilyl)pent-4-enoate (3q): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (34.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 3H), 7.28–7.22 (m, 4H), 6.95–6.98 (m, 2H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.05(s, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 4.51 (d, *J* = 12.4 Hz, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.4 Hz, 1H), 2.79 (s, 1H), 0.97–0.93 (m, 9H), 0.69–0.63 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 162.2 (d, *J* = 245.0 Hz), 143.1, 138.2 (d, *J* = 3.0 Hz), 135.0, 128.7 (d, *J* = 25.0 Hz), 128.5, 128.43, 128.42, 116.9, 114.8 (d, *J* = 22.0 Hz), 73.0, 67.1, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}FO_3SiNa$ 437.1924; found 437.1930.

Benzyl 4-(2-fluorophenyl)-2-hydroxy-2-(triethylsilyl)pent-4-enoate (3r): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (26.5 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.36 (m, 3H), 7.15–7.23 (m, 4H), 7.04–6.08 (m, 1H), 6.92–6.97 (m, 1H), 5.23 (s, 1H), 5.20 (d, *J* = 1.6 Hz, 1H), 4.88 (d, *J* = 16.4 Hz, 1H), 4.32 (d, *J* = 12.4 Hz, 1H), 3.22 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H), 2.81 (s, 1H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.60–0.66 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.1, 159.8 (d, *J* = 245.0 Hz), 140.0, 135.0, 130.6 (d, *J* = 5.0 Hz), 130.2 (d, *J* = 15.0 Hz), 128.9 (d, *J* = 8.0 Hz), 128.7, 128.6, 128.4, 128.3, 123.8 (d, *J* = 3.0 Hz), 120.4, 115.3 (d, *J* = 23.0 Hz), 72.7, 66.9, 41.6 (d, *J* = 4.0 Hz), 7.4, 1.8; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}FO_3SiNa$ 437.1924; found 437.1914.

Benzyl 4-(3-fluorophenyl)-2-hydroxy-2-(triethylsilyl)pent-4-enoate (3s): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (34.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 3H), 7.27–7.19 (m, 3H), 7.10–7.09 (m, 1H), 7.04–7.00 (m, 1H), 6.95–6.90 (m, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.09 (s, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 2.90 (d, *J* = 14.4 Hz, 1H), 2.81 (s, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.69–0.63 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 163.8, 161.4, 144.5 (d, *J* = 8.0 Hz), 143.1 (d, *J* = 2.0 Hz), 134.9, 129.5 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 35.0 Hz), 122.5 (d, *J* = 3.0 Hz), 117.7, 114.2, 114.0, 113.9, 113.6, 73.0, 67.1, 40.5, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}FO_3SiNa$ 437.1923; found 437.1925.

Benzyl 4-(4-chlorophenyl)-2-hydroxy-2-(triethylsilyl)pent-4-enoate (3t): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (31.0 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 3H), 7.25–7.18 (m, 6H), 5.21 (d, *J* = 1.6 Hz, 1H), 5.07 (s, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.79 (s, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.70–0.63 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 143.1, 140.6, 135.0, 133.1, 128.7, 128.7, 128.5, 128.4, 128.2, 117.4, 73.0, 67.1, 40.6, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}ClO_3SiNa$ 453.1624; found 453.1632.

Benzyl 4-(3-chlorophenyl)-2-hydroxy-2-(triethyl silyl)pent-4-enoate (3u): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); pale yellow oil (21.5 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 4H), 7.26–7.18 (m, 5H), 5.24 (d, *J* = 1.2 Hz, 1H), 5.10 (s, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.80 (s, 1H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.68–0.62 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 144.1, 143.0, 134.9, 133.9, 129.3, 128.8, 128.48, 128.45, 127.3, 126.9, 125.1, 118.0, 73.0, 67.2, 40.5, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}ClO_3SiNa$ 453.1624; found 453.1624.

Benzyl 4-(4-bromophenyl)-2-hydroxy-2-(triethyl silyl)pent-4-enoate (3v): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); yellow solid (38.4 mg, 81% yield); mp 48.9 -50.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 5H), 7.26–7.22 (m, 2H), 7.19–7.16 (m, 2H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.08 (s, 1H), 4.93 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.80 (s, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.70–0.64 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 143.1, 141.1, 134.9, 131.1, 128.7, 128.51, 128.47, 128.45, 121.3, 117.5, 73.0, 67.2, 40.5, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}BrO_3SiNa$ 497.1124; found 497.1115.

Benzyl 4-(3-bromophenyl)-2-hydroxy-2-(triethyl silyl)pent-4-enoate (3w): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (30.8 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 2.0 Hz, 1H), 7.37–7.31 (m, 4H), 7.26–7.22 (m, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.23(d, *J* = 1.2 Hz, 1H), 5.09 (s, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.80 (s, 1H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.68–0.62 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 144.4, 142.9, 134.9, 130.3, 129.8, 129.6, 128.8, 128.48, 128.45, 125.6, 122.2, 118.0, 72.9, 67.2, 40.5, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{31}BrO_3SiNa$ 497.1124; found 497.1115.

Benzyl 2-hydroxy-4-(3-methoxyphenyl)-2-(triethyl silyl)pent-4-enoate (3x): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); colorless oil (34.5 mg, 81% yield); R_f 0.12 [EtOAc/petroleum ether, 1:50]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 3H), 7.25–7.16 (m, 3H), 6.92–6.86 (m, 2H), 6.79–6.77 (m, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.07 (s, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.76 (s, 3H), 3.15 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.82 (s, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.71–0.63 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 159.3, 143.9, 143.7, 135.1, 129.0, 128.7, 128.4, 128.3, 119.4, 117.0, 112.8, 112.7,72.8, 67.0, 55.1, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{25}H_{34}O_4SiNa$ 449.2124; found 449.2120.

Benzyl 2-hydroxy-4-(2-methoxyphenyl)-2-(triethyl silyl)pent-4-enoate (3y): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); colorless oil (36.6 mg, 86% yield); R_f 0.11 (EtOAc/petroleum ether, 1:50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.16 (m, 6H), 7.08–7.05 (dd, *J* = 2.0, 1.6 Hz, 1H), 6.88 (t, *J* = 6.8 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.18 (d, *J* = 2.0 Hz, 1H), 5.09 (d, *J* = 2.0 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.15 (d, *J* = 12.4 Hz, 1H), 3.71 (s, 3H), 3.32 (d, *J* = 13.6 Hz, 1H), 2.90–2.87 (m, 2H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.66–0.60 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 156.5, 143.0, 135.4, 131,5, 130.4, 128.5, 128.4, 128.3, 128.1, 120.4, 119.4, 110.5, 72.5, 66.7, 55.2, 41.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{25}H_{34}O_4SiNa$ 449.2124; found 449.2114.

Benzyl 2-hydroxy-2-(triethylsilyl)-4-(4-(trifluoro methyl)phenyl)pent-4-enoate (3z): Isolated by column chromatography (EtOAc/petroleum ether = 1:50); yellow oil (16.2 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.33–7.41 (m, 5H), 7.20–7.22 (m, 2H), 5.28 (s, 1H), 5.15 (s, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.81 (s, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.63–0.72 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 145.9, 143.2, 134.8, 128.7, 128.5, 127.1, 125.0, 125.0, 125.0, 124.9, 118.6, 73.2, 67.2, 40.4, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{25}H_{31}F_3O_3SiNa$ 487.1892; found 487.1886.

Benzyl 2-hydroxy-4-(naphthalen-2-yl)-2-(triethyl silyl)pent-4-enoate (3aa): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); colorless oil (38.8 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.71 (m, 4H), 7.47–7.41 (m, 3H), 7.27–7.22 (m, 3H), 7.04–7.02 (m, 2H), 5.37 (d, *J* = 1.6 Hz, 1H), 5.18 (s, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 3.28 (d, *J* = 14.0 Hz, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.85 (s, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.74–0.64 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.1, 143.9, 139.4, 134.9, 133.2, 132.7, 128.6, 128.3, 128.2, 128.2, 127.6, 127.5, 126.1, 125.8, 125.5, 125.4, 117.5, 72.9, 67.0, 40.8, 7.5, 2.0; HRMS (ESI-TOF)*m*/*z*: [M + Na]$^+$ calcd for $C_{28}H_{34}O_3SiNa$ 469.2175; found 469.2162.

Benzyl 2-hydroxy-4-(naphthalen-1-yl)-2-(triethyl silyl)pent-4-enoate (3ab): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); colorless oil (26.3 mg, 59% yield); ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.00–7.97 (m, 1H), 7.83–7.79 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.47–7.43 (m, 2H), 7.40–7.36 (m, 1H), 7.25–7.17 (m, 4H), 6.84 (d, *J* = 6.8 Hz, 2H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.22 (d, *J* = 2.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.29 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 2.93 (s, 1H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.65–0.51 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 143.8, 140.7, 134.78, 133.6, 131.1, 128.4, 128.4, 128.2, 128.1, 127.5, 126.0, 125.8, 125.7, 125.6, 125.2, 120.0, 72.8, 66.9, 43.0, 7.4, 1.8; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{28}H_{34}O_3SiNa$ 469.2175; found 469.2167.

Benzyl 2-hydroxy-4-(thiophen-2-yl)-2-(triethylsilyl) pent-4-enoate (3ac): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (36.2 mg, 90% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 7.16–7.10 (m, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.95–6.90 (m, 1H), 5.40 (s, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.93 (s, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 3.09 (d, *J* = 14.4 Hz, 1H), 2.92 (d, *J* = 14.4 Hz, 1H), 2.89 (s, 1H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.73–0.63 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 145.8, 137.0, 135.1, 128.9, 128.5, 128.5, 127.1, 124.6, 124.7, 114.7, 73.4, 67.2, 40.7, 7.5, 2.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{22}H_{30}O_3SSiNa$ 425.1583; found 425.1578.

Benzyl 2-hydroxy-4-(3-(prop-1-en-2-yl)phenyl)-2-(triethylsilyl)pent-4-enoate (3ad): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); pale yellow oil (35.8 mg, 82% yield); R_f 0.13 (EtOAc/petroleum ether, 1:80). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.35–7.28 (m, 4H), 7.25–7.17 (m, 4H), 5.36 (s, 1H), 5.25 (d, *J* = 1.6 Hz, 1H), 5.08 (t, *J* = 0.8 Hz, 2H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.92 (d, *J* = 14.4 Hz, 1H), 2.83 (s, 1H), 2.12 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.71–0.63(m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 144.2, 143.2, 142.2, 141.0, 135.1, 128.7, 128.4, 128.3, 127.9, 126.0, 124.5, 124.2, 116.9, 112.6, 72.9, 67.0, 40.9, 21.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{27}H_{36}O_3SiNa$ 459.2331; found 459.2329.

Dibenzyl 4,4'-(1,3-phenylene)bis(2-hydroxy-2-(tri methylsilyl)pent-4-enoate) (3ae): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (45.4 mg, 72% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 6H), 7.20–7.11 (m, 8H), 5.21–5.19 (dd, *J* = 1.2, 4.4 Hz, 2H), 5.04 (d, *J* = 2.8 Hz, 2H), 4.95–4.90 (dd, *J* = 6.0, 12.0 Hz, 2H), 4.48–4.39 (dd, *J* = 12.4, 23.2 Hz, 2H), 3.09 (d, *J* = 14.0 Hz, 2H), 2.82–2.77 (m, 4H), 0.00 (d, *J* = 2.4 Hz, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.9, 144.3 (d, *J* = 4.0 Hz), 142.0, 135.3 (d, *J* = 3.0 Hz), 128.7 (d, *J* = 2.0 Hz), 128.4, 128.3 (d, *J* = 2.0 Hz), 127.7 (d, *J* = 3.0 Hz), 125.9, 125.8, 125.8, 125.6, 116.7 (d, *J* = 18.0 Hz), 72.5 (d, *J* = 21.0 Hz), 66.9 (d, *J* = 3.0 Hz), 39.9 (d, *J* = 13.0 Hz), -4.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{36}H_{46}O_6Si_2Na$ 653.2731; found 653.2722.

Benzyl (Z)-2-hydroxy-4-phenyl-2-(triethylsilyl)hex -4-enoate (3af): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); yellow oil (33.6 mg, 82% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 3H), 7.25–7.20 (m, 4H), 7.19–7.15 (m, 3H), 5.80–5.75 (dd, *J* = 6.8, 13.6 Hz, 1H), 4.73 (d, *J* = 12.4 Hz, 1H), 3.88 (d, *J* = 12.4 Hz, 1H), 3.15 (d, *J* = 13.6, Hz, 1H), 3.06 (d, *J* = 14.0 Hz, 1H), 2.76 (s, 1H), 1.80 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.73–0.60 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.2, 143.4, 135.9, 135.2, 129.0, 128.6, 128.3, 128.2, 127.9, 127.4, 126.5, 72.9, 66.7, 35.4, 15.0, 7.5, 2.0; HRMS (ESI-TOF)*m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{34}O_3SiNa$ 433.2175; found 433.2174.

Benzyl (Z)-2-hydroxy-4-phenyl-2-(triethylsilyl)hept -4-enoate (3ag): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); yellow oil (36.0 mg, 85% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 3H), 7.25–7.23 (m, 4H), 7.20–7.14 (m, 3H), 5.66 (t, *J* = 7.2 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 3.84 (d, *J* = 12.0 Hz, 1H), 3.12 (d, *J* =14.0 Hz, 1H), 3.06 (d, *J* =14.0Hz, 1H), 2.76 (s, 1H), 2.27–2.19 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.70–0.60 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.2, 143.9, 137.0, 135.2, 134.0, 128.57, 128.59, 128.2, 127.9, 127.5, 126.5, 72.4, 66.7 35.6, 22.5, 14.3 7.5, 2.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{26}H_{36}O_3SiNa$ 447.2331; found 447.2323.

Benzyl 2-hydroxy-3-(1H-inden-3-yl)-2-(triethyl silyl)propanoate (3ai): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); colorless oil (37.9 mg, 93% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.34–7.31 (m, 3H), 7.30–7.26 (m, 2H), 7.24–7.14 (m, 2H), 6.13 (s, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 3.22 (s, 2H), 3.17 (d, *J* = 18.8 Hz, 1H), 3.01 (d, *J* = 14.8 Hz, 1H), 2.88 (s, 1H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.78–0.72 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.4, 145.8, 143.9, 139.4, 135.2, 131.2, 128.9, 128.5, 125.8, 124.4, 123.5, 119.7, 74.1, 67.2, 38.0, 32.9, 7.6, 2.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{32}O_3SiNa$ 431.2018; found 431.2019.

Benzyl 3-(3,4-dihydronaphthalen-1-yl)-2-hydroxy-2-(triethylsilyl)propanoate (3aj): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); colorless oil (34.2 mg, 81% yield); R_f 0.15 (EtOAc/petroleum ether, 1:60). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 6H), 7.13–7.08 (m, 3H), 5.80 (t, *J* = 4.4 Hz, 1H), 4.97 (d, *J* = 12.0Hz, 1H), 4.78 (d,

J = 12.0Hz, 1H), 3.09 (d, *J* = 14.4 Hz, 1H), 2.90 (d, *J* = 14.4 Hz, 1H), 2.78 (s, 1H), 2.63 (t, *J* = 8.4 Hz, 2H), 2.12–2.05 (m, 2H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.78–0.70 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 144.0, 142.1, 135.1, 128.7, 128.4, 128.3, 128.0, 127.3, 126.9, 117.0, 72.8, 66.9, 40.8, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{26}H_{34}O_3SiNa$ 445.2175; found 445.2166.

Benzyl 3-(6,7-dihydro-5H-benzo[7]annulen-9-yl)-2-hydroxy-2-(triethylsilyl)propanoate (3ak): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); yellow oil (34.9 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 3H), 7.25–7.10 (m, 6H), 5.95 (t, *J* = 7.2 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 2.83 (d, *J* = 14.0 Hz, 1H), 2.79 (s, 1H), 2.64–2.47 (m, 2H), 2.12–1.95 (m, 2H), 1.88–1.80 (m, 1H), 1.68–1.58 (m, 1H), 0.94 (t, J = 8.0 Hz, 9H), 0.71–0.58 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 177.3, 141.6, 140.3, 135.8, 135.2, 130.6, 128.8, 128.7, 128.3, 128.2, 126.8, 126.6, 125.6, 72.7, 66.8, 42.2, 34.5, 32.1, 24.6, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{27}H_{36}O_3SiNa$ 459.2331; found 459.2329.

General procedure for deuteration reaction

The mixture of α-methylstyrene-methyl-d_3 (48.4 mg, 0.40 mmol), silylglyoxylate (27.8 mg, 0.10 mmol) and aqueous $ZnCl_2$ complex (10 mol%, H_2O:$ZnCl_2$ = 1:3 in molar ratio) in CH_2Cl_2 (1.0 mL) were stirred at room temperature. After stirring for the indicated time, the residue was purified via flash chromatography to give the desired product **3a'**.

Benzyl 2-hydroxy-4-phenyl-2-(triethylsilyl)pent-4-enoate-5,5-d_2 (3a'): Isolated by column chromatography (EtOAc/petroleum ether = 1:100); pale yellow oil (13.5 mg, 34% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.31 (m, 5H), 7.28–7.26 (m, 2H), 7.24–7.22 (m, 3H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 3.17 (d, *J* = 14.4 Hz, 1H), 2.90 (d, *J* = 14.4 Hz, 1H), 2.81 (s, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.68–0.64 (m, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 177.1, 143.0, 142.1, 135.1, 128.7, 128.4, 128.3, 128.1, 127.3, 126.9, 72.8, 66.9, 40.7, 7.5, 1.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{30}D_2O_3SiNa$ 421.2138; found 421.2139.

The procedure for transformations of the corresponding adduct 3k

The mixture of **3k** (396.0 mg, 1.0 mmol), TBAB (32.2 mg, 10 mol %) and Cs_2CO_3 (651.6 mg, 2.0 equiv.) in CH_2Cl_2 (20 mL) were stirred at room temperature. After stirring for 10 hours, the residue was purified via flash chromatography to give the desired product **4**.

Benzyl 2-((*tert*-butyldimethylsilyl)oxy)-4-phenylpent-4-enoate (4): Isolated by column chromatography (EtOAc/petroleum ether = 1:80); colorless oil (297.0 mg, 75% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.37–7.34 (m, 5H), 7.32–7.29 (m, 2H), 7.27–7.24 (m, 1H), 5.37 (d, *J* = 0.8 Hz, 1H), 5.14–5.07 (m, 3H), 4.29–4.26 (m, 1H), 3.07–3.04 (m, 1H), 2.83–2.79 (m, 1H), 0.81 (s, 9H), -0.10 (s, 3H), -0.15 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 173.2, 143.4, 140.0, 135.6, 128.5, 128.5, 128.3, 128.3, 127.5, 126.3, 116.0, 71.4, 66.5, 41.3, 25.6, 18.1, -5.2, -5.4; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{32}O_3SiNa$ 419.2018; found 419.2033.

To a solution of **3k** (99.0 mg, 0.25 mmol) in CH_2Cl_2 (2.0 mL) was added tetra-*n*-butylammonium fluoride (1 M in THF, 0.25 mL) at room temperature. The mixture was stirred for 12 h and then purified by flash chromatography to give the desired product **5**.

Benzyl 2-hydroxy-4-phenylpent-4-enoate (5): Isolated by column chromatography (EtOAc/petroleum ether = 1:60); colorless oil (63.5 mg, 90% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.35 (m, 5H), 7.32–7.30 (m, 4H), 7.28–7.24 (m, 1H), 5.36 (s, 1H), 5.17 (s, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 4.8 Hz, 1H), 3.06 (d, *J* = 13.8 Hz, 1H), 2.87–2.84 (m, 1H), 2.75 (d, *J* = 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 174.2, 143.4, 140.3, 135.1, 128.6, 128.5, 128.4, 128.3, 127.7, 126.4, 116.3, 69.2, 67.2, 40.5. The data are consistent with previous report.[22]

To a solution of **3k** (396.0 mg, 1 mmol) in CH_2Cl_2 (30 mL) was added saccharin (9.1 mg, 0.05 mmol). The mixture was heated to reflux in an oil bath (about 60 °C), and HMDS (241.5 mg, 1.5 mmol) was added dropwise. The mixture was maintained at reflux for 24 h, and then it was allowed to cool to ambient temperature. The mixture was diluted with CH_2Cl_2 and washed three times with brine. The combined aqueous phases were extracted twice with CH_2Cl_2, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford the product **6**.

Benzyl 2-(*tert*-butyldimethylsilyl)-4-phenyl-2-((trimethylsilyl)oxy)pent-4-enoate (6): Isolated by column chromatography (EtOAc/petroleum ether = 1:100); white solid (82.85 mg, 59% yield); mp 46.8–47.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.44–7.40 (m, 3H), 7.37–7.30 (m, 5H), 5.44 (s, 1H), 5.17 (s, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.15 (d, *J* = 14.4 Hz, 1H), 1.10 (s, 9H), 0.17 (d, *J* = 4.2 Hz, 15H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 175.2, 143.9, 141.7, 135.2, 128.9, 128.4, 128.3, 128.0,

127.1, 126.8, 117.4, 79.1, 66.4, 41.0, 27.9, 19.0, 3.6,-5.8, -7.1; HRMS (ESI-TOF)*m/z*: $[M + Na]^+$ calcd for $C_{27}H_{40}O_3Si_2Na$ 491.2424; found 491.2410.

General procedure for the synthesis of alkenes

To a stirred suspension of methyltriphenylphosphonium (18 mmol) or ethyltriphenylphosphonium bromide (18 mmol) in dry THF under argon and *n*-BuLi (2.5 M, 18 mmol) was added slowly at 0 °C. After stirring for 1 h, the corresponding ketone (15 mmol) was added and then the mixture was gradually warmed to rt and stirred until full conversion. The solution was poured into water at 0 °C and extracted with ethyl acetate, washed with aqueous NaCl solutions. The combined organic layers were dried over Na_2SO_4 and the solvent were removed under reduced pressure. The residue was purified by flash chromatography to afford the product **1.**

Prop-1-en-2-ylbenzene (1a). Isolated by column chromatography (petroleum ether); colorless oil (1.097 g, 62%); R_f 0.76 [petroleum ether]. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 3.9 Hz, 2H), 7.35–7.38 (m, 2H), 7.28–7.31 (m, 1H), 5.40 (s, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.3, 141.2, 128.2, 127.4, 125.5, 112.4, 21.8.

1-Methyl-4-(prop-1-en-2-yl)benzene (1b). Isolated by column chromatography (petroleum ether); colorless oil (0.832 g, 42%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.42 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 5.38 (s, 1H), 5.07 (d, *J* = 1.2 Hz, 1H), 2.39 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.1, 138.3, 137.1, 128.9, 125.4, 111.5, 21.8, 21.1.

1-Methyl-2-(prop-1-en-2-yl)benzene (1c). Isolated by column chromatography (petroleum ether); colorless oil (1.03 g, 52%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15–7.19 (m, 4H), 5.22 (s, 1H), 4.87 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.8, 143.8, 134.5, 130.1, 127.8, 126.8, 125.5, 114.7, 24.3, 19.8.

1-Methyl-3-(prop-1-en-2-yl)benzene (1d). Isolated by column chromatography (petroleum ether); colorless oil (0.851 g, 43% over two steps); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.31 (m, 2H), 7.24–7.25 (m, 1H), 7.12 (d, *J* = 6.6 Hz, 1H), 5.38 (s, 1H), 5.09 (d, *J* = 1.2 Hz, 1H), 2.39 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.4, 141.2, 137.7, 128.13, 128.11, 126.3, 122.6, 112.2, 21.9, 21.5.

1-Isopropyl-4-(prop-1-en-2-yl)benzene (1e). Isolated by column chromatography (petroleum ether); colorless oil (1.152 g, 48%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.45 (m, 2H), 7.22–7.26 (m, 2H), 5.38 (d, *J* = 0.6 Hz, 1H), 5.07 (t, *J* = 1.2 Hz, 1H), 2.90–2.97 (m, 1H), 2.17 (q, *J* = 0.6 Hz, 3H), 1.28 (d, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.1, 143.0, 138.7, 126.2, 125.4, 111.6, 33.8, 24.0, 21.8.

1-Fluoro-4-(prop-1-en-2-yl)benzene (1f). Isolated by column chromatography (petroleum ether); colorless oil (1.591 g, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.45 (m, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 5.31 (s, 1H), 5.07 (s, 1H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.3 (d, *J* = 244.5 Hz), 142.2, 137.3 (d, *J* = 3.0 Hz), 127.1 (d, *J* = 7.5 Hz), 115.0 (d, *J* = 21.0 Hz), 112.3, 21.9.

1-Fluoro-2-(prop-1-en-2-yl)benzene (1g). Isolated by column chromatography (petroleum ether); colorless oil (1.204 g, 59%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.32 (m, 1H), 7.21–7.24 (m, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.02–7.06 (m, 1H), 5.24 (s, 2H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.0 (d, *J* = 247.5 Hz), 140.2, 130.3 (d, *J* = 13.5 Hz), 128.6 (d, *J* = 7.5 Hz), 123.9 (d, *J* = 4.5 Hz), 116.5 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 24.0 Hz), 23.0 (d, *J* = 3.0 Hz).

1-Fluoro-3-(prop-1-en-2-yl)benzene (1h). Isolated by column chromatography (petroleum ether); colorless oil (0.673 g, 33%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25–7.31 (m, 2H), 7.15–7.18 (m, 1H), 6.96–6.99 (m, 1H), 5.41 (s, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 2.15 (d, *J* = 0.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.8 (*J* = 243.0 Hz), 143.5 (*J* = 9.0 Hz), 142.1 (*J* = 3.0 Hz), 129.6 (*J* = 7.5 Hz), 121.1 (*J* = 3.0 Hz), 114.1 (*J* = 21.0 Hz), 113.5, 112.4 (*J* = 21.0 Hz).

1-Chloro-4-(prop-1-en-2-yl)benzene (1i). Isolated by column chromatography (petroleum ether); colorless oil (1.687 g, 74%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 5.36 (s, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.1, 139.6, 133.1, 128.3, 126.8, 112.9, 21.7.

1-Chloro-3-(prop-1-en-2-yl)benzene (1j). Isolated by column chromatography (petroleum ether); colorless oil (1.733 g, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.33–7.39 (m, 1H), 7.22–7.26 (m, 2H), 5.37 (s, 1H), 5.12 (s, 1H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.1, 142.1, 134.2, 129.4, 125.7, 123.6, 113.6, 21.7.

1-Bromo-4-(prop-1-en-2-yl)benzene (1k). Isolated by column chromatography (petroleum ether); colorless oil (1.359 g, 46%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 14.4 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H), 5.39 (s, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.1, 140.0,

131.2, 127.1, 121.3, 113.0, 21.6.

1-Bromo-3-(prop-1-en-2-yl)benzene (1l). Isolated by column chromatography (petroleum ether); colorless oil (1.891 g, 64%); R_f 0.76 (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (t, J = 1.8 Hz, 1H), 7.38–7.40 (m, 2H), 7.20 (t, J = 7.8 Hz, 1H), 5.37 (s, 1H), 5.12 (t, J = 1.2 Hz, 1H), 2.13 (q, J = 0.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.4, 142.0, 130.3, 129.7, 128.7, 124.1, 122.5, 113.7, 21.7.

1-Methoxy-3-(prop-1-en-2-yl)benzene (1m). Isolated by column chromatography (petroleum ether); colorless oil (1.51 g, 68%); R_f 0.83 (EtOAc/petroleum ether, 1:100). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, J = 7.8 Hz, 1H), 7.08 (dd, J = 0.6, 7.2 Hz, 1H), 6.83–6.85 (m, 1H), 5.38 (s, 1H), 5.10 (d, J = 1.2 Hz, 1H), 3.84 (s, 3H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 159.5, 143.2, 142.8, 129.1, 118.1, 112.7, 112.6, 111.5, 55.2, 21.8.

1-Methoxy-2-(prop-1-en-2-yl)benzene (1n). Isolated by column chromatography (petroleum ether); colorless oil (1.199 g, 54%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.27 (m, 1H), 7.21 (d, J = 7.2 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.17 (s, 1H), 5.08 (s, 1H), 3.85 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.6, 144.3, 132.8, 129.3, 128.3, 120.5, 115.0, 110.8, 55.4, 23.2.

1-(Prop-1-en-2-yl)-4-(trifluoromethyl)benzene (1o). Isolated by column chromatography (petroleum ether); colorless oil (1.06 g, 38%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.4, 18.4 Hz, 4H), 5.45 (s, 1H), 5.21 (t, J = 1.2 Hz, 1H), 2.18 (t, J = 0.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.7, 142.2, 129.3 (q, J = 31.5 Hz), 128.0 (d, J = 9.0 Hz), 127.5 (d, J = 180.0 Hz), 125.8, 125.2 (q, J = 3.0 Hz), 122.4 (q, J = 270.0 Hz), 114.5, 21.6.

2-(Prop-1-en-2-yl)naphthalene (1aa). Isolated by column chromatography (petroleum ether); colorless oil (1.764 g, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80–7.87 (m, 4H), 7.69 (d, J = 8.4 Hz, 1H), 7.45–7.50 (m, 2H), 5.55 (s, 1H), 5.22 (d, J = 1.2 Hz, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.0, 138.3, 133.4, 132.8, 128.2, 127.7, 127.5, 126.1, 125.8, 124.2, 123.9, 113.0, 21.9.

1-(Prop-1-en-2-yl)naphthalene (1ab). Isolated by column chromatography (petroleum ether); colorless oil (1.688 g, 67%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11–8.13 (m, 1H), 7.88–7.90 (m, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.50–7.54 (m, 2H), 7.48 (t, J = 7.8 Hz, 1H), 3.36 (dd, J = 1.2, 7.2 Hz, 1H), 5.46 (t, J = 1.2 Hz, 1H), 5.12 (t, J = 1.2 Hz, 1H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.6, 142.2, 133.7, 130.8, 128.3, 127.1, 125.73, 125.71, 125.6, 125.3, 124.5, 116.1, 25.2.

2-(Prop-1-en-2-yl)thiophene (1ac). Isolated by column chromatography (petroleum ether); colorless oil (0.707 g, 38%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, J = 4.8 Hz, 1H), 7.04–7.05 (m, 1H), 6.99–7.00 (m, 1H), 5.40 (s, 1H), 4.97 (s, 1H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.8, 137.2, 127.3, 124.2, 123.5, 111.2, 21.8.

1,3-Di(prop-1-en-2-yl)benzene (1ad). Isolated by column chromatography (petroleum ether); colorless oil (1.612 g, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39–7.40 (m, 2H), 7.30–7.33 (m, 1H), 5.40 (s, 2H), 5.12 (d, J = 1.2 Hz, 2H), 2.20 (s, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.5, 141.3, 128.1, 124.7, 122.8, 112.6, 21.9.

But-1-en-2-ylbenzene (1af). Isolated by column chromatography (petroleum ether); colorless oil (1.584 g, 80%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.45 (m, 2H), 7.33–7.36 (m, 2H), 7.27–7.30 (m, 1H), 5.30 (t, J = 0.6 Hz, 1H), 5.08 (q, J = 1.2 Hz, 1H), 2.52–2.56 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.0, 141.4, 128.2, 127.2, 126.0, 110.9, 28.0, 12.9.

But-2-en-2-ylbenzene (1af'). Isolated by column chromatography (petroleum ether); colorless oil (1.03 g, 52%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–8.39 (m, 3H), 7.19–7.24 (m, 2H), 5.84–5.88 (m, 0.5H), 5.54–5.58 (m, 0.5H), 2.02 (t, J = 1.2 Hz, 3H), 1.79 (dd, J = 1.2, 6.6 Hz, 1.5H), 5.60 (dd, J = 1.8, 7.2 Hz, 1.5H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.0, 141.9, 136.8, 135.5, 128.1, 128.0, 127.9, 126.4, 126.3, 125.5, 122.4, 121.6, 25.4, 15.5, 14.8, 14.3.

Pent-1-en-2-ylbenzene (1ag). Isolated by column chromatography (petroleum ether); colorless oil (1.402 g, 64%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.24–7.61 (m, 1H), 5.26 (s, 1H), 5.05 (d, J = 1.2 Hz, 1H), 2.48 (t, J = 7.2 Hz, 2H), 1.44–1.51 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.5, 141.5, 128.2, 127.2, 126.1, 112.2, 37.4, 21.3, 13.7.

Hex-2-ene-3-ylbenzene (1ah). Isolated by column chromatography (petroleum ether); colorless oil (0.431 g, 18%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 7.23–7.19 (m, 1H), 7.15–7.14 (m, 1H), 5.76 and 5.53 (both dd, J = 12.0, 7.2 Hz, 1H), 2.48 and 2.31 (both t, J = 7.8, 7.2 Hz, 2H), 1.79 and 1.55 (both d, J = 6.6, 7.2 Hz, 3H), 1.40–1.26 (m, 2H), 0.90–0.84 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.5, 141.7, 141.2, 140.8, 128.5, 128.1, 127.9, 126.3, 126.2, 122.9, 121.07, 41.3, 31.3, 21.6, 21.2, 14.6, 14.2, 13.9, 123.6.

1-Methylene-2,3-dihydro-1*H*-indene (1ai). Isolated by column chromatography (petroleum ether); colorless oil (1.268 g, 65%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.20–7.24 (m, 2H), 5.46 (d, *J* = 1.2 Hz, 1H), 5.05 (s, 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.80–2.82 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6, 146.7, 141.1, 128.2, 126.4, 125.3, 120.6, 102.4, 31.2, 30.1.

1-Methylene-1,2,3,4-tetrahydronaphthalene (1aj). Isolated by column chromatography (petroleum ether); pale yellow oil (1.814 g, 84%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 1H), 7.16–7.18 (m, 2H), 7.12 (d, *J* = 6.6 Hz, 1H), 5.50 (s, 1H), 4.98 (s, 1H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.56–2.58 (m, 2H), 1.89–1.93 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.4, 137.3, 134.7, 129.2, 127.6, 125.9, 124.2, 107.8, 33.2, 30.4, 23.8.

5-Methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (1ak). Isolated by column chromatography (petroleum ether); colorless oil (1.943 g, 82%); R_f 0.83 (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.22 (m, 1H), 7.17–7.18 (m, 2H), 7.10–7.12 (m, 1H), 5.12 (d, *J* = 0.6 Hz, 1H), 5.00 (s, 1H), 2.78–2.80 (m, 2H), 2.42 (t, *J* = 5.4 Hz, 2H), 1.85–1.86 (m, 2H), 1.76–1.77 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 152.8, 144.2, 140.2, 128.9, 128.1, 127.1, 126.1, 113.7, 36.5, 36.3, 31.5, 27.3.

General procedure for the synthesis of silyl glyoxylates

Silyl glyoxylates **2a**, **2e**, **2i**–**l**, have been prepared in our previous work,[6] and silyl glyoxylate **2b**–**d** and **2f**–**h**, were newly prepared according to the reported methods.[6]

Representative procedure: A flame-dried 50-mL round-bottom flask was charged with 4-fluorophenyl 2-diazoacetate (1.176 g, 4.0 mmol, 1.0 equiv.) and dry diethyl ether (15 mL). The solution was cooled to -20 °C and *N*,*N*-diisopropylethylamine (0.91 mL, 5.2 mmol, 1.3 equiv.) was added. Triethylsilyl trifluoromethanesulfonate (1.17 mL, 5.2 mmol, 1.3 equiv.) was added dropwise via syringe over 30 min. When the addition of TESOTf was complete, the resulting suspension was stirred at -20 °C. When the reaction was complete (approximately 12 h) as judgedby TLC analysis, the suspension was allowed to warm to room temperature, hexane was added to fully precipitate the ammoniumtriflate salt, and solids were removed by filtration through a fritted funnel. The filtrate was concentrated in vacuo to give the yellow oil that was used without further purification. The yellow oil material from the previous step was dissolved in methylene chloride (15 mL). A 250-mL round bottomed flask was charged with sodium bicarbonate (9.1 g, 108 mmol, 27.0 equiv.). Water (42 mL) and acetone (28 mL) were added, and the resulting suspension was cooled to 0 °C. Oxone® (14.8 g, 24 mmol, 6.0 equiv.) was added in small portions. When the addition of Oxone® was complete, the solution of diazoacetate was added all at once. When the reaction was judged to be complete by TLC analysis, all solids were removed by filtration through a fritted funnel. Water was added to the filtrate, and the layers were separated. The organic layer was washed with water (3x50 mL) and brine, dried with sodium sulphate, and concentrated in vacuo. The residue was purified via flash chromatography (silica: 200−300; 60:1 petroleum ether: ethyl acetate) to give the desired product **2f** as a bright yellow oil (0.641 g, 45% over two steps).

4-Fluorophenyl 2-oxo-2-(triethylsilyl)acetate (2b). Isolated by column chromatography (EtOAc/petroleum ether = 1:100); yellow oil (0.480 g, 50% over two steps); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.434–7.407 (m, 1H), 7.375–7.337 (m, 1H), 7.168–7.143 (m, 1H), 7.110–7.079 (m, 1H), 5.333 (s, 2H), 0.945 (t, *J* = 7.8 Hz, 9H), 0.829–0.788 (m, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 232.0, 162.1, 161.2 (d, *J* = 247.5 Hz), 131.1 (d, *J* = 4.5 Hz), 130.8 (d, *J* = 9.0 Hz), 124.3 (d, *J* = 4.5 Hz), 122.0 (d, *J* = 13.5 Hz), 115.6 (d, *J* = 21.0 Hz), 61.1 (d, *J* = 4.5 Hz), 7.0, 2.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{21}FO_3SiNa$ 319.1136; found 319.1128.

2-Fluorophenyl 2-oxo-2-(triethylsilyl)acetate (2c). Isolated by column chromatography (EtOAc/petroleum ether = 1:100); yellow oil (0.691 g, 72% over two steps); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.399–7.376 (m, 2H), 7.060 (t, *J* = 9.0 Hz, 2H), 5.223 (s, 2H), 0.942 (t, *J* = 7.8 Hz, 9H), 0.822–0.782 (m, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 231.9, 162.9 (d, *J* = 246.0 Hz), 162.2, 130.8 (d, *J* = 7.5 Hz), 130.6 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.5 Hz), 66.5, 7.0, 2.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{21}FO_3SiNa$ 319.1136; found 319.1127.

4-Chlorobenzyl 2-oxo-2-(triethylsilyl)acetate (2d). Isolated by column chromatography (EtOAc/petroleum ether = 1:100); yellow oil (0.429 g, 43% over two steps); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.360-7.327 (m, 4H), 5.219 (s, 2H), 0.948 (t, *J* = 7.8 Hz, 9H), 0.829–0.788 (m, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 231.8, 162.1, 134.7, 133.2, 130.1, 128.9, 66.4, 7.0, 2.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{21}ClO_3SiNa$ 335.0841; found 335.0844.

2-Bromobenzyl 2-oxo-2-(triethylsilyl)acetate (2f). Isolated by column chromatography (EtOAc/petroleum ether = 1:80); yellow oil (0.570 g, 50% over two steps); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.404-7.345 (m, 4H), 5.261 (s, 2H), 0.944 (t, *J* = 7.8 Hz, 9H), 0.826–0.785 (m, 6H); ^{13}C{^{1}H} NMR (150

MHz, $CDCl_3$) δ 232.0, 162.4, 134.7, 128.7, 128.6, 67.3, 7.0, 2.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{21}BrO_3SiNa$ 379.0336; found 379.0335.

4-Nitrobenzyl 2-oxo-2-(triethylsilyl)acetate (**2g**). Isolated by column chromatography (EtOAc/petroleum ether = 1:80); yellow oil (0.827 g, 80% over two steps); ^1H NMR (600 MHz, $CDCl_3$) δ 7.597 (d, *J* = 8.4 Hz, 1H), 7.450 (d, *J* = 7.2 Hz, 1H), 7.332 (t, *J* = 7.2 Hz, 1H), 7.240–7.212 (m, 1H) 5.357 (s, 2H), 0.957 (t, *J* = 7.8 Hz, 9H), 0.847–0.808 (m, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 231.9, 162.0, 134.1, 132.9, 130.5, 130.2, 127.6, 123.8, 66.6, 7.1, 2.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{21}NO_5SiNa$ 346.1087; found 346.1085.

Naphthalen-1-ylmethyl2-oxo-2-(triethylsilyl)acetate (**2h**). Isolated by column chromatography (EtOAc/petroleum ether = 1:90); yellow oil (0.346 g, 33% over two steps); R_f 0.29 (EtOAc/petroleum ether, 1:60). ^1H NMR (600 MHz, $CDCl_3$) δ 8.026 (d, *J* = 8.4 Hz, 1H), 7.881 (t, *J* = 9.4 Hz, 2H), 7.598–7.510 (m, 3H), 7.470–7.445 (m, 1H), 5.736 (s, 2H), 0.879 (t, *J* = 8.4 Hz, 9H), 0.759–0.719 (m, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 232.1, 162.4, 133.7, 131.6, 130.2, 129.8, 128.7, 128.2, 126.7, 126.0, 125.2, 123.4, 65.4, 7.0, 2.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{19}H_{24}O_3SiNa$ 379.0336; found 379.0335.

Procedure for the synthesis of silyl glyoximide 2m

Oxazolidin-2-one (485.4 mg, 5.58 mmol), sodium carbonate (237.4 mg, 2.24 mmol) and $CuCl_2$ (30.0 mg, 0.224 mmol) were added to an oven-dried round-bottom flask. The reaction flask was purged with O_2 three times prior to the addition of toluene (6 mL) and pyridine (0.18 mL, 2.24 mmol). A balloon of O_2 was attached, and the reaction mixture was heated at 70 °C in an oil bath. (Triethylsilyl)acetylene (0.21 mL, 1.12 mmol) in toluene (6 mL) was added dropwise over 8 h via syringe pump. After stirring for 20 h and the mixture was then cooled to room temperature. The crude mixture was concentrated in vacuo and then purified by flash chromatography (EtOAc/petroleum ether = 1:4) to afford the crude ynamide (116 mg). The ynamide (116.0 mg, 0.384 mmol) was then treated with $NaIO_4$ (246.9 mg, 1.154 mmol) and RuO_2 hydrate (0.5 mg, 0.004 mmol) in a dichloromethane/acetonitrile/water (4 mL, 2/2/3 v/v) solution. The reaction was vigorously stirred for 2 h at room temperature, filtered through Celite, and concentrated in vacuo. The crude mixture was purified via silica gel flash column chromatography to afford silyl glyoximide **2m**.

1-(2-Oxooxazolidin-3-yl)-2-(triethylsilyl)ethane-1,2-dione (2m). Isolated by column chromatography (EtOAc/petroleum ether = 1:6); yellow oil (77.1 mg, 36% over two steps); R_f 0.36 (EtOAc/petroleum ether, 1:4). ^1H NMR (600 MHz, $CDCl_3$) δ 4.564-4.561 (m, 2H), 3.985-4.011 (m, 2H), 0.955 (t, *J* = 7.8 Hz, 9H), 0.784–0.825 (m, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 232.8, 171.2, 154.0, 64.6, 40.8, 6.9, 2.0.

■ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on theACS Publications website at DOI: XX

Copies of ^1H and ^{13}C NMR spectra of all newcompounds (PDF)

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Notes

The authors declare no competing financial interest.

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