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Indium Catalyzed Hydrofunctionalization of Styrene Derivatives Bearing Hydroxy Group with Organosilicon Nucleophiles

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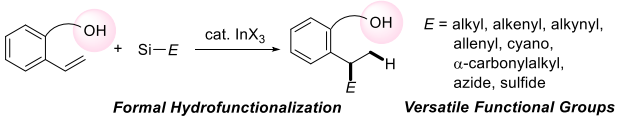
Supporting Information Placeholder

ABSTRACT

Hydrofunctionalization is one of the most important transformation reactions of alkenes. Herein, we described the development of an indium-triiodide-catalyzed hydrofunctionalization of alkenes bearing a hydroxy group using various types of organosilicon nucleophiles. Indium triiodide was the most effective catalyst, whereas typical Lewis acids such as $TiCl_4$, $AlCl_3$, $BF_3{\cdot}OEt_2$ were ineffective. Many functional groups were successfully introduced, and these resulted in yields of 31 to 86%. Various styrene derivatives were also applicable to this reaction. Mechanistic investigation revealed that the present hydrofunctionalization proceeded through Brønsted acid-catalyzed intramolecular hydroalkoxylaiton of alkenes followed by InI_3-catalyzed substitution reaction of cyclic ether intermediates.



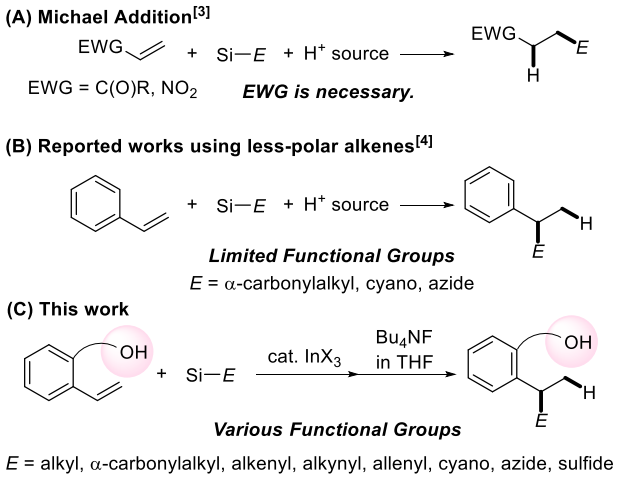
Main Text

INTRODUCTION

Alkenes are important fundamental materials in organic synthesis and industrial chemistry, and many useful transformations of alkenes have been established.[1] Therefore, the direct addition reaction of alkenes with various reagents such as electrophilic, nucleophilic, and radical ones to give functionalized alkanes with high selectivity and high step economy is highly desired even now. In this context, many examples for hydrofunctionalization of alkenes through the addition of E-H (E = C, O, N, P, and S) to alkenes have already been reported.[2] One example involves the hydrofunctionalization of Michael acceptors such as α,β-unsaturated carbonyl compounds or nitriles with a variety of organosilicon nucleophiles, which is a well-developed method[3] (Scheme 1-A). However, the application of less-polar alkenes to the process of hydrofunctionalization has been insufficiently developed, and available organosilicon nucleophiles are limited to silyl enolates, silyl cyanides and silyl azides[4] (Scheme 1-B). Our group also reported the regioselective hydrofunctionalization of simple alkenes with silyl ketene acetals and a stoichiometric amount of indium[4g] or bismuth salts[4f] through carboindation or carbobismuthination, respectively. Herein, the regioselective hydrofunctionalization of less-polar alkenes bearing a hydroxy group with organosilicon nucleophiles was accomplished in the presence of catalytic amount of indium trihalide (Scheme 1-C). The present reaction proceeded through a unique reaction mechanism including Brønsted acid-catalyzed hydroalkoxylaiton of alkenes followed by InI_3-catalyzed substitution reaction of cyclic ether intermediates, which is quite different from our previously reported method

through carbometalation. In the present hydrofunctionalization, various organosilicon nucleophiles as well as silyl ketene acetals were allowed to use. Moreover, not only mono-substituted alkenes but also di- and tri-substituted alkenes, which often showed low reactivity for previously developed hydrofunctionalization,[4c,4f,4g,4j] were applicable. It is noted that a wide range of functional groups could be introduced into alkenes via a single synthetic operation.[5]

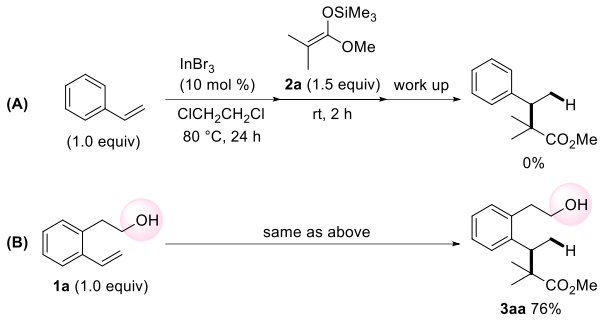
Scheme 1. (A) Michael Addition; (B) Hydrofunctionalization by Organosilicon Nucleophiles with Less-polar Alkenes; (C) This Work Allows the Introduction of Versatile Functional Groups to Alkenes



RESULTS AND DISCUSSION

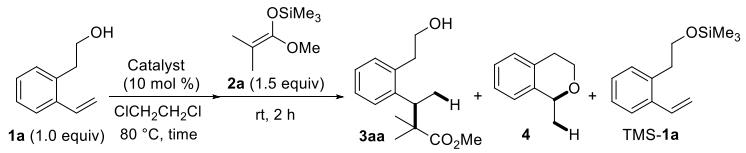
Optimization of Reaction Conditions. The reaction of styrene with silyl ketene acetal **2a** was attempted in the presence of a catalytic amount of indium tribromide, but instead of obtaining the hydrofunctionalization product, the polymerization of styrene occurred (Scheme 2-A). Interestingly, we found that *o*-(2-hydroxyethyl)styrene (**1a**) afforded the target product **3aa** in a high yield (Scheme 2-B).

Scheme 2. Investigation of Indium Bromide Catalyzed Reaction of Silyl Ketene Acetal with Styrene (A) or Styrene Derivative 1a (B)



That result prompted us to investigate the effect of acid catalysts on the hydrofunctionalization of **1a** with **2a** (Table 1). As shown in Scheme 2-(B), $InBr_3$ gave **3aa** in a 76% yield (entry 1). $GaBr_3$ also afforded **3aa** in approximately the same yield (entry 2). On the other hand, the desired product **3aa** was not obtained, and starting alkene **1a** and TMS-**1a** were recovered in the cases of the reaction using $InCl_3$, $In(OTf)_3$ or BiI_3 (entries 3-5). The reaction catalyzed by InI_3 raised the yield of **3aa** to 92% (entry 6). Without the addition of **2a**, only cyclic ether **4** was produced in a high yield (entry 7). Thus, the hydrofunctionalization product could be obtained via **4**. Typical Lewis acids such as $ZnCl_2$, $AlCl_3$, and $TiCl_4$ were ineffective for the desired hydrofunctionalization and either gave the cyclic ether **4** or recovered the starting material (entries 8-10). The reaction using $BF_3{\cdot}OEt_2$ resulted in complicated mixture (entry 11). A cationic gold catalyst, which is often used to functionalize alkenes,[6] was ineffective (entry 12). The reaction catalyzed by HI aq. would not afford the product **3aa**, but did produce cyclic ether **4** in a high yield (entry 13).

Table 1. The Effect of Acid Catalysts on the Hydrofunctionalization of Styrene Derivative 1a with Organosilicon Nucleophile 2a[a]



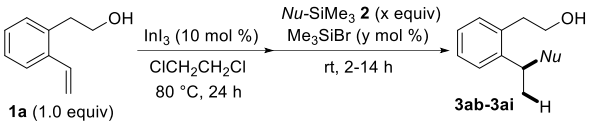
			yield (%)[b]			recovery of **1a** (%)
entry	catalyst	time (h)	**3aa**	4	TMS-**1a**	
1	$InBr_3$	24	76	0	0	0
2	$GaBr_3$	24	72	0	0	0
3	$InCl_3$	96	0	16	33	15
4	$In(OTf)_3$	24	0	40	3	5
5	BiI_3	72	0	0	91	0
6	InI_3	24	92 (71)[c]	0	0	0
7[d]	InI_3	24	0	90	0	0
8	$ZnCl_2$	96	0	0	45	8
9	$AlCl_3$	24	1	56	0	0
10	$TiCl_4$	48	0	57	0	0
11	$BF_3{\cdot}OEt_2$	24	0	0	0	0
12	$AuCl_3$/AgOTf	24	0	52	0	0
13	HI aq.	24	0	77	0	0

[a]1st step: **1a** (0.5 mmol), catalyst (0.05 mmol), $ClCH_2CH_2Cl$ (1 mL), 80 ˚C, 24 h. 2nd step: **2a** (0.75 mmol),

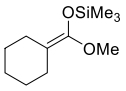
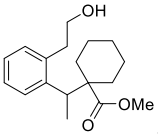
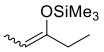
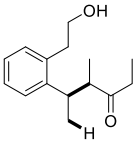
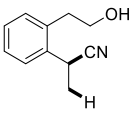
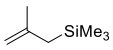
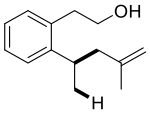
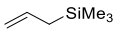
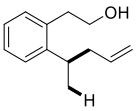
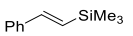
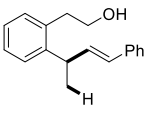
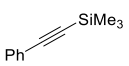
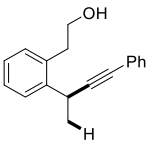
rt, 2 h. The reaction was quenched with Bu_4NF (1 M in THF). [b]Yields were determined by ^1H NMR using internal standards (bromoform). [c]Isolated yield. [d]The 2nd step was not carried out.

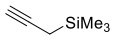
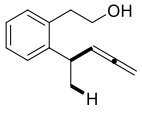
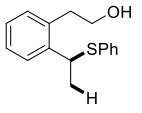
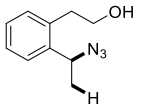
Substrate Scope of Organosilicon Nucleophiles. Reactions of **1a** with various organosilicon nucleophiles **2** catalyzed by InI_3 were carried out (Table 2). The bulky silyl ketene acetal **2b** was suitable for this reaction system to provide the cyclohexane derivative **3ab** in high yield (entry 1). The silyl enol ether **2c** afforded the target product **3ac** (entry 2). Hydrofunctionalization with the silyl cyanide **2d** occurred (entry 3), but the reported method[4b] that uses a Brønsted acid for hydrocyanation of styrene gave only cyclic ether **4** (see Scheme S1 in Supporting Information for detail). Methallylsilane **2e** also provided the hydrofunctionalization product in moderate yield (entry 4).[7] Reactions using allylsilane **2f**, alkenylsilane **2g**, alkynylsilane **2h**, and propargylsilane **2i** proceeded efficiently in the presence of a catalytic amount of InI_3/Me_3SiBr (entries 5-8). The addition of Me_3SiBr was necessary for the reactions using nucleophiles **2f-2i**, which have a relatively low level of nucleophilicity. In these cases, the combination of InX_3 with Me_3SiX showed high Lewis acidity.[8] To the best of our knowledge, the reaction using **2i** is the first example of an intermolecular Markovnikov hydroallenylation toward less-polar alkenes.[9] Heteroatom nucleophiles such as silyl sulfide **2j** and silyl azide **2k** were applicable to this reaction system (entries 9 and 10).[10]

Table 2. Scope of Hydrofunctionalization Using Various Organosilicon Nucleophiles[a]



1a (1.0 equiv) 3ab-3ai

entry	*Nu*-SiMe$_3$ (x equiv)	Me$_3$SiBr (y mol %)	yield of **3** (%)[b]
1[c]	 **2b** (3.0 equiv)	none	 **3ab** 74
2	 **2c** (3.0 equiv)	none	 **3ac** 69
3[d]	Me$_3$SiCN **2d** (5.0 equiv)	none	 **3ad** 31
4	 **2e** (1.5 equiv)	none	 **3ae** 55
5	 **2f** (1.5 equiv)	10	 **3af** 86
6	 **2g** (3.0 equiv)	20	 **3ag** 59
7	 **2h** (3.0 equiv)	20	 **3ah** 54

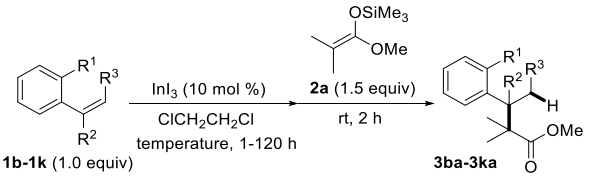
8[e]		20		**3ai** 68
	2i (3.0 equiv)			
9	Me_3SiSPh	none		**3aj** 59
	2j (3.0 equiv)			
10[f]	Me_3SiN_3	none		**3ak** 54
	2k (3.0 equiv)			

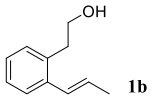
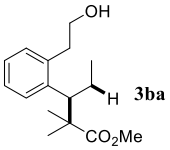
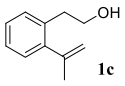
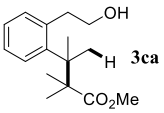
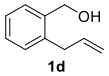
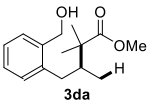
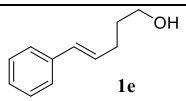
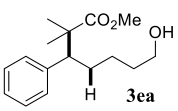
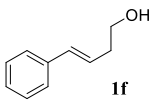
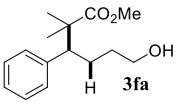
[a]1st step: **1a** (0.5 mmol), InI_3 (0.05 mmol), $ClCH_2CH_2Cl$ (1 mL), 80 ˚C, 24 h. 2nd step: **2** (0.75-2.5 mmol), Me_3SiBr (0-0.1 mmol), rt, 2-14 h (See Experimental Section for detail). The reaction was quenched with Bu_4NF (1 M in THF). [b]Isolated yield. [c]InI_3 (20 mol %). [d]InI_3 (20 mol %), 70 ˚C at the 2nd step. [e]35 ˚C at the 2nd step. [f]50 ˚C at the 2nd step.

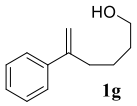
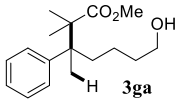
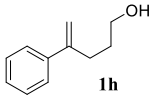
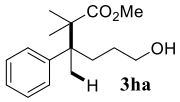
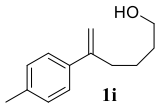
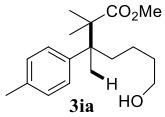
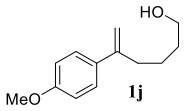
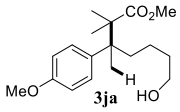
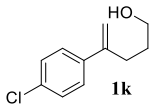
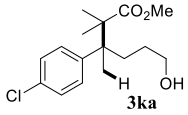
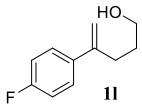
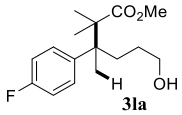
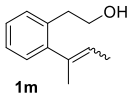
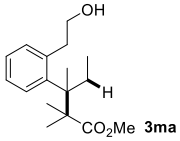
Substrate Scope and Limitation of Styrene Derivatives. The scope of styrene derivatives with a hydroxy moiety is shown in Table 3. In all cases, the nucleophilic attack of **2a** took place at a benzylic position exclusively and other regioisomers were not formed. The β-methylstyrene derivative **1b** gave the product **3ba**, and the reaction of the α-methylstyrene derivative **1c** formed vicinal quaternary carbon atoms efficiently (entries 1 and 2). The reaction using the alkene **1d**, which is not a styrene derivative, provided no hydrofunctionalized product **3da** and complicated mixture was obtained (entry 3). The result suggested that the present reaction system was limited to styrene derivatives. The styrene derivatives **1e**-**1l**, which have different carbon frameworks, were also suitable to this reaction system. The reaction of β-(hydroxyalkyl)-substituted styrenes **1e** and **1f** afforded the target products in modest yields (entries 4 and 5) while α-(hydroxyalkyl)-substituted substrates **1g** and **1h** gave higher yields (entries 6 and 7). A variety of α-(hydroxyalkyl)-substituted styrenes were applicable to this

reaction system. The reaction of styrene derivatives bearing electron donating groups **1i** and **1j**, as well as electron withdrawing groups **1k** and **1l**, proceeded smoothly to give target products **3ia-3la** in moderate to high yields (entries 8-11). The trisubstituted alkene **1m** was suitable for this reaction system (entry 12). The intermolecular addition of silyl enolates to trisubstituted alkenes without electron-withdrawing group has not been reported and the use of disubstituted alkenes usually resulted in low yields due to their steric hindrance.[4f,4g] Therefore, it is advantage of this work that trisubstituted substrate was applicable and disubstituted alkenes gave moderate to high yield.

Table 3. Scope of Hydrofunctionalization Using Various Styrene Derivatives[a,b]



entry	1	3	temp. (˚C)	yield[c] (%)
1[d]	 **1b**	 **3ba**	80	52
2	 **1c**	 **3ca**	80	53
3	 **1d**	 **3da**	80	0
4	 **1e**	 **3ea**	80	28
5	 **1f**	 **3fa**	80	30

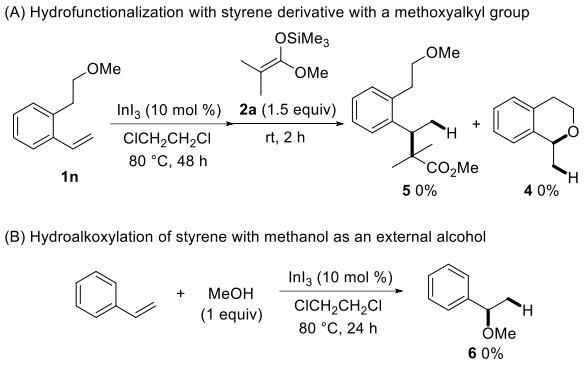
6[d]	 1g	 3ga	rt	59
7	 1h	 3ha	rt	66
8	 1i	 3ia	rt	70
9	 1j	 3ja	rt	57
10	 1k	 3ka	rt	45
11	 1l	 3la	rt	77
12[e]	 1m	 3ma	70	56

[a]1st step: **1** (0.5 mmol), InI_3 (0.05 mmol), $ClCH_2CH_2Cl$ (1 mL), rt-80 ˚C, 1-120 h (See Experimental Section for detail). 2nd step: **2a** (0.75 mmol), rt, 2 h. The reaction was quenched with Bu_4NF (1 M in THF). [b]Corresponding cyclic ethers were obtained without addition of **2a** (see Table S1 in Supporting Information for detail). [c]Isolated yield. [d]**2a** (3 equiv). [e]**2a** (4 equiv).

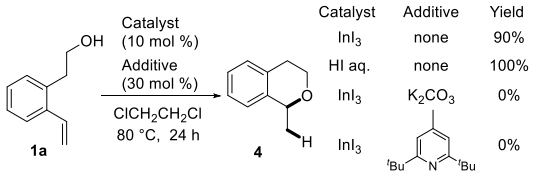
Mechanistic Investigation. Hydrofunctionalization with styrene derivative **1n**, including a methoxyalkyl group, was attempted, but gave neither the target product **5** nor the cyclic ether **4** (Scheme 3-A). Moreover, the hydroalkoxylation of styrene with methanol as an external alcohol in the presence of a catalytic amount of InI_3 afforded no benzyl ether **6** (Scheme 3-B). These control experiments suggested that the intramolecular hydroxy group is necessary for this type of hydrofunctionalization. Taking into account the result of entry 13 in Table 1, the hydroalkoxylation of **1a** can be catalyzed by a Brønsted acid, which can be generated via the alcoholysis of InI_3 with **1a**

in situ.[11] Thus, control experiments were carried out as shown in Scheme 4 to identify the active catalyst species for hydroalkoxylation. InI_3 or HI aq. efficiently catalyzed the hydroalkoxylation while the addition of K_2CO_3, or 2,6-di(*tert*-butyl)-4-methylpyridine[12] as a proton scavenger, entirely prevented the InI_3-catalyzed hydroalkoxylation of **1a**. Therefore, these results indicated that *in situ*-generated Brønsted acid promoted the formation of the cyclic ether **4**.

Scheme 3. Investigation of Styrene Derivatives without OH Group.



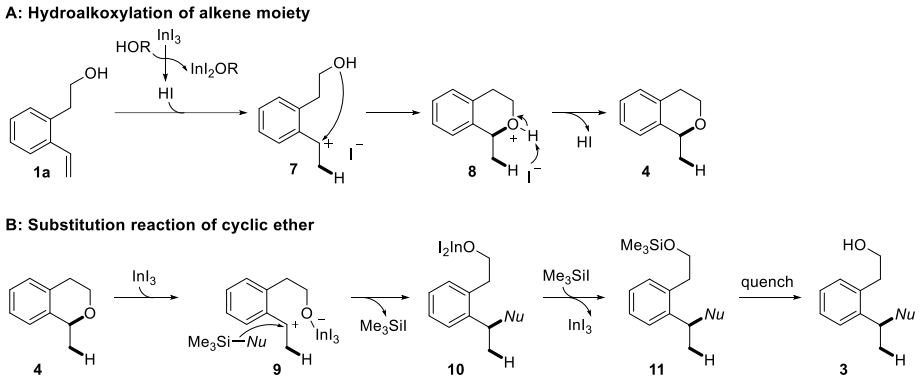
Scheme 4. Hydroalkoxylation in the Presence of a Proton Scavenger



Proposed Mechanism. A proposed mechanism for the InI_3-catalyzed hydrofunctionalization of **1a** with an organosilicon nucleophile (Me_3SiNu) is shown in Scheme 5. A trace amount of InI_3 undergoes alcoholysis with **1a** to give HI. The alkene moiety of **1a** is protonated and then alkoxylation occurs to afford cyclic ether **4**. The interaction between InI_3 and the ethereal oxygen of **4** cleaves the oxygen-carbon bond to generate carbocation **9**. A nucleophilic attack of the organosilicon compound to **9** occurs to produce the hydrofunctionalization product **10**. Transmetalation of the alkoxyindium moiety of **10** with Me_3SiI regenerates the InI_3 catalyst. The indium trihalide catalyzed substitution reaction

of ethers by an organosilicon nucleophile (Me_3SiNu) has been previously reported by our group.[13] Target alcohol product **3** is obtained after quenching by Bu_4NF.[14] In our previous reports[4f,4g], an indium trihalide coordinated to a carbon-carbon double bond and acted as a π Lewis acid to activate alkenes. Contrastively, in the present reaction, InI_3 mainly contributes to the generation of a Brønsted acid to transform an alkene into a cyclic ether intermediate and the substitution reaction of the intermediate with nucleophiles.

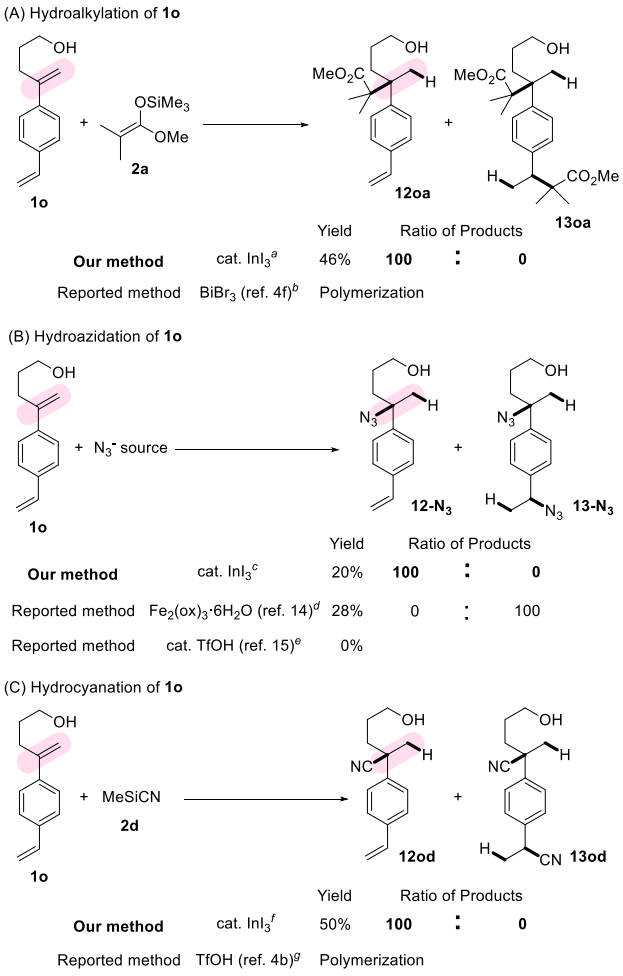
Scheme 5. Proposed Mechanism



Selective Functionalization of Alkenes. We demonstrated the selective functionalization of substrate **1o** with two types of alkene moieties (Scheme 6).[15] When **1o** underwent our developed hydrofunctionalization using silyl ketene acetal **2a**, hydroalkylation took place selectively at the alkene moiety with a hydroxyalkyl group to afford product **12oa** (Scheme 6-A). By contrast, when utilizing the $BiBr_3$-mediated hydrofunctionalization conditions,[4f] polymerization of **1o** just occurred. Moreover, the selective hydroazidation proceeded in the InI_3-mediated reaction of **1o** with silyl azide **2k** to give **12-N$_3$** (Scheme 6-B). On the other hand, the reported iron-mediated hydroazidation[16] using NaN_3 occurred at both alkene moieties of **1o** to give product **13-N$_3$**. The other reported system using

Brønsted acid catalyst and Me_3SiN_3 as an azide source[17] was employed to afford no hydroazidation product but a hydroalkoxylation intermediate and starting material **1o**. The selective hydrocyanation of **1o** with silyl cyanide **2d** was also observed under InI_3-catalyzed conditions to give **12od** exclusively, while the reported method[4b] resulted in polymerization of **1o** (Scheme 6-C). These results showed the advantage of the InI_3-catalyzed system for selective functionalization of the complex molecules.

Scheme 6. Selective Hydrofunctionalization of the Substrate 1o with Two Types of Alkene Moieties.



[a]1) **1o** (0.5 mmol), InI_3 (10 mol %), $ClCH_2CH_2Cl$ (10 mL), 5 ˚C, 17 h. 2) **2a** (1.5 mmol), rt, 12 h. [b]**1o** (0.2 mmol), $BiBr_3$ (0.3 mmol), **2a** (0.3 mmol) and CH_2Cl_2 (0.2 mL), rt, 8 h. [c]1) **1o** (0.5 mmol), InI_3 (10 mol %), $ClCH_2CH_2Cl$ (10 mL), 5 ˚C, 5 h. 2) Me_3SiN_3 (**2k**, 1.5 mmol), rt, 17 h. [d]**1o** (0.5 mmol), NaN_3 (4.0 mmol), $Fe_2(ox)_3 \cdot 6H_2O$ (2.5 mmol), $NaBH_4$ (3.2 mmol), THF (20 mL) and H_2O (20 mL), 0 ˚C, 0.5 h. [e]**1o** (0.5 mmol), TfOH (25 mol %), Me_3SiN_3 (**2k**, 1.5 mmol), SiO_2 (1.25 g), CH_2Cl_2 (2.5 mL), rt, 1 h. [f]1) **1o** (0.5 mmol), InI_3 (10 mol %), $ClCH_2CH_2Cl$ (10 mL), 5 ˚C, 19 h. 2) Me_3SiCN (**2d**, 2.5 mmol), rt, 35 h. [g]**1o** (0.5 mmol), TfOH (2.2 mmol), Me_3SiCN (**2d**, 2.1 mmol), $PhCF_3$ (4.5 mL), -5 ˚C, 1 h.

CONCLUSION

We have developed an InI_3 catalyzed hydrofunctionalization of alkenes with a hydroxyalkyl group using organosilicon nucleophiles such as silyl enolate, allylsilane, alkenylsilane, alkynylsilane, propargylsilane, silyl cyanide, silyl sulfide and silyl azide. Many functional groups that would be used for further elaboration were added to the alkene moiety in a single step. Various styrene derivatives were suitable for this reaction. It is noted that addition reaction of silyl enolate proceeded efficiently for not only monosubstituted alkenes but also multi-substituted ones compared with previously reported hydrofunctionalization. The selective functionalization of styrene derivatives with two alkene moieties was accomplished to show the preference of an alkene moiety with a hydroxyalkyl group. Mechanistic investigation showed that this hydrofunctionalization is composed of two steps: the hydroalkoxylation of an alkene catalyzed by a Brønsted acid and a sequential

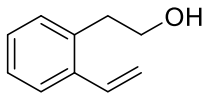
substitution reaction of cyclic ether catalyzed by InI_3. This transformation of alkene to ether allowed us to synthesize alkenes with many types of functional groups, which cannot be introduced into alkenes in our previous works. Therefore, this work provides a novel method for functionalization of alkenes.

EXPERIMENTAL SECTION

General Information. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, COSY, HMQC, HMBC, IR, MS, HRMS. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. IR spectra were recorded as thin films. Bulb-to-bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. High-resolution mass spectra were obtained by magnetic sector type mass spectrometer. All reactions were carried out under nitrogen. All products were obtained as racemic mixtures.

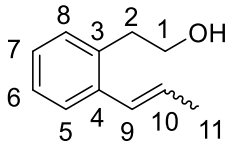
Material. Dehydrated $ClCH_2CH_2Cl$ was purchased and used without further purification. Organosilicon nucleophiles **2a**, **2d**, **2e**, **2f, 2h** and **2k** are commercially available. Styrene derivatives **1a**, **1d**, **1e**, **1f**, **1g**, **1h**, **1l** and organosilicon nucleophiles **2b**, **2c**, **2g**, **2i** and **2j** were synthesized by literature procedures and spectral data of these compounds were shown below. Styrene derivatives **1b**, **1c**, **1i**, **1j**, **1k**, **1m**, **1n** and **1o** are new compounds, and synthetic method and spectral data of these compounds were shown below. All metal salt and Me_3SiBr are commercially available.

(**1a**) 2-(2-vinylphenyl)ethan-1-ol[18]



To a three necked flask, THF (56 mL) and 1-bromo-2-vinylbenzene (4.15 g, 20 mmol) were added. This solution was cooled at -78 °C and *n*-BuLi (1.6 M hexane solution, 14 mL, 22 mmol) was dropped over 15 minutes. After stirring for 1.5 h at -78 °C, to the reaction mixture was dropped ethylene oxide (1.1 M in THF, 25 mL, 30 mmol) and the reaction mixture was stirred for 0.5 h at -78 °C. The mixture was warm to room temperature and quenched by sat. NH_4Cl aq. (25 mL). This solution was extracted with diethyl ether (20 mL x 3) and the collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (1.36 g, 45%). This is known compound and spectroscopic data were identical with those from literature.

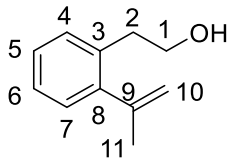
(**1b**) 2-(2-(prop-1-en-1-yl)phenyl)ethan-1-ol



To a three necked flask, THF (56 mL) and 1-bromo-2-(prop-1-en-1-yl)benzene (4.15 g, 20 mmol) were added. This solution was cooled at -78 °C and n-BuLi (1.6 M hexane solution, 14 mL, 22 mmol) was dropped over 15 minutes. After stirring for 1.5 h at -78 °C, to the reaction mixture was dropped ethylene oxide (1.1 M in THF, 25 mL, 30 mmol) and the reaction mixture was stirred for 0.5 h at -78 °C. The mixture was warm to room temperature and quenched by sat. NH_4Cl aq. (25 mL). This solution was extracted with diethyl ether (20 mL x 3) and the collected organic layer was dried

($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (*E*/*Z* = 99: 1, 1.67 g, 51%). IR: (neat) 3359 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.43 (d, *J* = 5.5 Hz, 1H, 5-H), 7.23-7.11 (m, 3H, 6-H, 7-H and 8-H), 6.65 (dq, *J* = 15.6, 1.4 Hz, 1H, 9-H), 6.11 (dq, *J* = 15.6, 6.9 Hz, 1H, 10-H), 3.80 (t, *J* = 6.9 Hz, 2H, 1-H_2), 2.94 (t, *J* = 6.9 Hz, 2H, 2-H_2), 1.90 (dd, *J* = 6.9, 1.4 Hz, 3H, 11-H_3), 1.41 (s, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 137.3 (s, C-3), 134.9 (s, C-4), 130.2 (d, C-8), 128.3 (d, C-9), 127.9 (d, C-10), 126.9 (d), 126.8 (d), 126.2 (d, C-5), 63.1 (t, C-1), 36.4 (t, C-2), 18.9 (q, C-11); MS: (CI, 70 eV) *m*/*z* 163 ($[M + 1]^+$, 43); HRMS: (EI, 70 eV); Calculated ($C_{11}H_{14}O$) 162.1045 (M); Found: 162.1046.

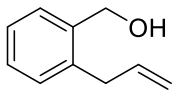
(**1c**) 2-(2-(prop-1-en-2-yl)phenyl)ethan-1-ol



To a three necked flask, THF (56 mL) and 1-bromo-2-(prop-1-en-2-yl)benzene (3,49 g, 20 mmol) were added. This solution was cooled at -78 °C and n-BuLi (1.6 M hexane solution, 14 mL, 22 mmol) was dropped over 15 minutes. After stirring for 1.5 h at -78 °C, to the reaction mixture was dropped ethylene oxide (1.1 M in THF, 25 mL, 30 mmol) and the mixture was stirred for 0.5 h at -78 °C. The reaction mixture was warm to room temperature and quenched by sat. NH_4Cl aq. (25 mL). This solution was extracted with diethyl ether (20 mL x 3) and the collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography

(hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (1.53 g, 47%). IR: (neat) 3359 (OH) cm^{-1}, 1639 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.29-7.15 (m, 3H), 7.15-7.09 (m, 1H, 7-H), 5.23-5.17 (m, 1H, 10-H^A), 4.89-4.82 (m, 1H, 10-H^B), 3.81 (t, J = 7.2 Hz, 2H, 1-H_2), 2.92 (t, J = 7.2 Hz, 2H, 2-H_2), 2.05 (s, 3H, 11-H_3), 1.39 (s, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.4 (s, C-9), 144.3 (s, C-8), 134.6 (s, C-3), 129.6 (d, C-4), 128.4 (d, C-7), 126.9 (d), 126.3 (d), 115.2 (t, C-10), 63.7 (t, C-1), 36.1 (t, C-2), 25.3 (q, C-11); MS: (CI, 70 eV) m/z 163 ($[M + 1]^+$, 100); HRMS: (EI, 70 eV) Calculated ($C_{11}H_{14}O$) 162.1045 (M) Found: 162.1043.

(**1d**) (2-allylphenyl)methanol[19]



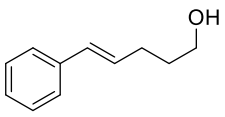
To a three necked flask, (2-bromophenyl)methanol (9.45 g, 50 mmol), hexane (50 mL), Et2O (5 mL), 3,4-dihydro-*2H*-pyran (5.12 g, 60 mmol) and Amberlyst15 (6.3 g) were added. After stirring for 45 minutes, the reaction mixture was purified by column chromatography (hexane, column length 11 cm, diameter 26 mm, silica 75 g and Amberlyst15 6.2 g) to give 2-((2-bromobenzyl)oxy)tetrahydro-2H-pyran (7.2 g, 53%).

To a three necked flask, magnesium turning (0.73 g, 30 mmol) and THF (10 mL) were added. Three drops of a solution of 2-((2-bromobenzyl)oxy)tetrahydro-2H-pyran (7.2 g, 27 mmol) in THF (12 mL) was dropped into the vessel, and then ten drops of 1,2-dibromoethane was added to the reaction mixture. The reminding THF solution of 2-((2-bromobenzyl)oxy)tetrahydro-2H-pyran was dropped into the reaction mixture over 10 minutes. After stirring for 15 minutes, the mixture was refluxed for

1 hour, and then cooled at 30 °C. A solution of allyl bromide (4.4 g, 36 mmol) in THF (10 mL) was dropped over 5 minutes. After stirring for 17 hours, the reaction mixture was quenched by sat. NH_4Cl aq. (30 mL) under ice bath. The solution was extracted by ethyl acetate (30 mL x 4). The collected organic layer was dried ($MgSO_4$) and the solvent was evaporated to give 2-((2-allylbenzyl)oxy)tetrahydro-2H-pyran (6.35 g, 100%).

To a three necked flask, 2-((2-allylbenzyl)oxy)tetrahydro-2H-pyran (6.27 g, 27 mmol), MeOH (38 mL) and 1N HCl aq. (38 mL) were added. After stirring for 20 hours at 50 °C, the reaction mixture was quenched by Et_2O (100 mL). The mixture was extracted by Et_2O (50 mL x 3) and the collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 60:40, column length 11 cm, diameter 26 mm, spherical silica gel) to give (2-allylphenyl)methanol as the target product (4.0 g, 100%). This is known compound and spectroscopic data were identical with those from literature.

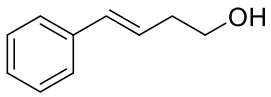
(**1e**) (*E*)-5-phenylpent-4-en-1-ol[20]



To a three necked flask, THF (250 mL) and $LiAlH_4$ (5.1 g, 130 mmol) were added. This solution was cooled at 0 °C and 5-phenylpent-4-yn-1-ol (4.28 g, 26 mmol) was added to the mixture and the reaction mixture was stirred for 1 h at 0 °C. After refluxing for 2 day, to the reaction mixture was dropped sat. potassium sodium tartrate aq. (100 mL) at 0 °C. This solution was extracted with diethyl ether (100 mL x 3) and the collected organic layer was washed by sat. NaCl aq. (100 mL). The organic

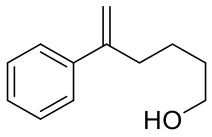
layer was dried ($MgSO_4$) and the solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (3,24 g, 77%). This is known compound and spectroscopic data were identical with those from literature.

(**1f**) (*E*)-4-phenylbut-3-en-1-ol [21]



To a three necked flask, THF (21 mL) and $LiAlH_4$ (1.78 g, 47 mmol) were added. This solution was cooled at 0 °C and 4-phenylbut-3-yn-1-ol (2.34 g, 16 mmol) in THF (21 mL) was dropped to the mixture over 10 minutes. After refluxing for 15 h, the reaction mixture was quenched by $Na_2SO_4 \cdot 10H_2O$ at 0 °C. This mixture was filtered and the filtrate was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (2.21 g, 93%). This is known compound and spectroscopic data were identical with those from literature.

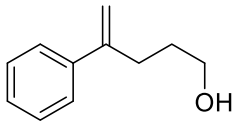
(**1g**) 5-phenylhex-5-en-1-ol[22]



To a two necked flask, $Pd(PPh_3)_4$ (0.695 g, 0.6 mmol), 1,4-dioxane (40 mL), phenyl boronic acid (3.05 g, 24 mmol), 5-hexyne-1-ol (2.10 g, 20 mmol) and acetic acid (0.13 g, 2.0 mmol) were added. After stirring for 10 minutes at rt, the reaction mixture was stirred for 16 h at 80 °C. The reaction

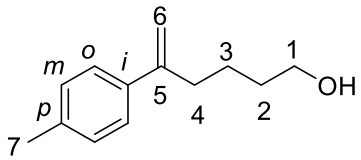
mixture was filtered and the solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (3.17 g, 90%). This is known compound and spectroscopic data were identical with those from literature.

(**1h**) 4-phenylpent-4-en-1-ol[22]



To a two necked flask, $Pd(PPh_3)_4$ (0.692 g, 0.6 mmol), 1,4-dioxane (60 mL), phenyl boronic acid (3.04 g, 24 mmol), 4-pentyne-1-ol (1.65 g, 20 mmol) and acetic acid (0.22 mL, 4.0 mmol) were added. The reaction mixture was stirred for 16 h at 80 °C. The mixture was filtered and the solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (2.60 g, 80%). This is known compound and spectroscopic data were identical with those from literature.

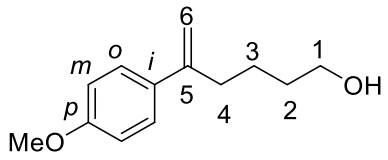
(**1i**) 5-(p-tolyl)hex-5-en-1-ol



To a two necked flask, $Pd(PPh_3)_4$ (0.343 g, 0.297 mmol), 1,4-dioxane (20 mL), *p*-tolyl boronic acid (1.70 g, 12.5 mmol), 5-hexyn-1-ol (0.981 g, 0.999 mmol) and acetic acid (0.101 g, 1.68 mmol) were added. After stirring for 24 h at 80 °C, the reaction mixture was filtered through a short pad of celite and the filtrate was evaporated. The residue was purified by column chromatography (hexane/ethyl

acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (1.17 g, 61%). IR: (neat) 3444 (OH) cm^{-1}, 1624 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.29 (d, J = 8.2 Hz, 2H, *o*), 7.13 (d, J = 8.2 Hz, 2H, *m*), 5.24 (d, J = 1.4 Hz, 1H, 6-H^A), 5.01 (d, J = 1.4 Hz, 1H, 6-H^B), 3.62 (t, J = 6.3 Hz, 2H, 1-H_2), 2.51 (t, J = 7.7 Hz, 2H, 4-H_2), 2.34 (s, 3H, 7-H_3), 1.67-1.54 (m, 2H, 2-H_2), 1.54-1.41 (m, 2H, 3-H_2), 1.67-1.41 (br, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 148.0 (s, C-5), 138.1 (s, *p*), 137.0 (s, *i*), 128.9 (d, *m*), 125.9 (d, *o*), 111.6 (t, C-6), 62.7 (t, C-1), 35.0 (t, C-4), 32.3 (t, C-2), 24.3 (t, C-3), 21.0 (q, C-7); MS: (EI, 70 eV) *m*/*z* 190 (M, 28); HRMS: (EI, 70 eV) Calculated ($C_{13}H_{18}O$) 190.1358 (M) Found: 190.1355.

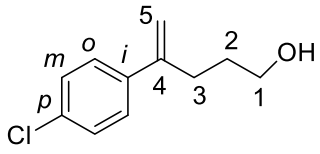
(**1j**) 5-(4-methoxyphenyl)hex-5-en-1-ol



To a two necked flask, $Pd(PPh_3)_4$ (0.352 g, 0.305 mmol), 1,4-dioxane (20 mL), *p*-methoxy phenyl boronic acid (1.85 g, 12.2 mmol), 5-hexyn-1-ol (0.977 g, 9.95 mmol) and acetic acid (0.117 g, 1.95 mmol) were added. After stirring for 24 h at 80 °C, the reaction mixture was filtered through a short pad of celite and the filtrate was evaporated. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (0.993 g, 48%). IR: (neat) 3400 (OH) cm^{-1}, 1608 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.35 (d, J = 8.9 Hz, 2H, *o*), 6.86 (d, J = 8.9 Hz, 2H, *m*), 5.21 (s, 1H, 6-H^A), 4.98 (s, 1H, 6-H^B), 3.81 (s, 3H, OMe), 3.65 (t, J = 6.0 Hz, 2H, 1-H_2), 2.51 (t, J = 7.5 Hz, 2H, 4-H_2), 1.66-1.46 (m, 4H, 2-H_2

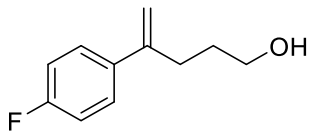
and 3-H_2), 1.39 (s, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 158.9 (s, *p*), 147.5 (s, C-5), 133.5 (s, *i*), 127.1 (d, *o*), 113.6 (d, *m*), 110.9 (t, C-6), 62.8 (t, C-1), 55.2 (q, OMe), 35.0 (t, C-4), 32.3 (t, C-3), 24.3 (t, C-2); MS: (EI, 70 eV) *m*/*z* 206 (M, 24); HRMS: (EI, 70 eV) Calculated ($C_{13}H_{18}O_2$) 206.1307 (M) Found: 206.1308.

(**1k**) 4-(4-chlorophenyl)pent-4-en-1-ol



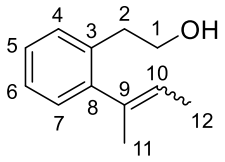
To a two necked flask, $Pd(PPh_3)_4$ (0.352 g, 0.305 mmol), 1,4-dioxane (20 mL), *p*-chloro phenyl boronic acid (1.81 g, 11.6 mmol), 4-pentyn-1-ol (0.811 g, 9.64 mmol) and acetic acid (0.125 g, 2.08 mmol) were added. After stirring for 24 h at 80 °C, the reaction mixture was filtered through a short pad of celite and the filtrate was evaporated. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (0.715 g, 36%). IR: (neat) 3433 (OH) cm^{-1}, 1716 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.34 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 8.9 Hz, 2H), 5.28 (d, J = 0.92 Hz, 1H, 5-H^A), 5.10 (d, J = 0.92 Hz, 1H, 5-H^B), 3.65 (t, J = 6.4 Hz, 2H, 1-H_2), 2.57 (t, J = 7.8 Hz, 2H, 3-H_2), 1.70 (tt, J = 7.8, 6.4 Hz, 2H, 2-H_2), 1.29 (s, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 146.8 (s, C-4), 139.4 (s, *i*), 133.2 (s, *p*), 128.4 (d), 127.4 (d), 113.0 (t, C-5), 62.2 (t, C-1), 31.4 (t, C-3), 30.9 (t, C-2); MS: (EI, 70 eV) *m*/*z* 196 (M, 2); HRMS: (EI, 70 eV) Calculated ($C_{11}H_{13}ClO$) 196.0655 (M) Found: 196.0654.

(**1l**) 4-(4-fluorophenyl)pent-4-en-1-ol[22]



To a two necked flask, $Pd(PPh_3)_4$ (0.328 g, 0.3 mmol), 1,4-dioxane (20 mL), *p*-fluorophenyl boronic acid (1.69 g, 12 mmol), 4-pentyne-1-ol (0.839 g, 10 mmol) and acetic acid (0.13 g, 2.0 mmol) were added. The reaction mixture was stirred for 24 h at 80 °C. The mixture was filtered and the solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (0.341 g, 19%). This is known compound and spectroscopic data were identical with those from literature.

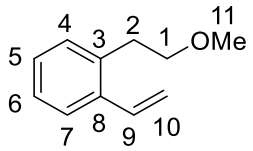
(**1m**) 2-(2-(but-2-en-2-yl)phenyl)ethan-1-ol



To a three necked flask, THF (35 mL) and 1-bromo-2-(but-2-en-2-yl)benzene (2.55 g, 12 mmol) were added. This solution was cooled at -78 °C and n-BuLi (1.6 M hexane solution, 9 mL, 13 mmol) was dropped over 15 minutes. After stirring for 1.5 h at -78 °C, to the reaction mixture was dropped ethylene oxide (1.1 M in THF, 16 mL,18 mmol) and the mixture was stirred for 0.5 h at -78 °C. The reaction mixture was warm to room temperature and quenched by sat. NH_4Cl aq. (15 mL). This solution was extracted with diethyl ether (20 mL x 3) and the collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (0.368 g, 17%, ratio of stereoisomer = 85:15). IR: (neat) 3352 (OH) cm^{-1}; ^1H NMR: (400

MHz, $CDCl_3$) major stereoisomer 7.30-7.19 (m, 3H, 4-H, 5-H and 6-H), 7.03 (dd, J = 5.6, 3.6 Hz, 1H, 7-H), 5.58 (qq, J = 6.5, 1.7 Hz, 1H, 10-H), 3.80 (dd, J = 7.0, 12.8 Hz, 2H, 1-H_2), 2.91-2.76 (m, 2H, 2-H_2), 1.96 (m, 3H, 11-H_3), 1.41-1.33 (br, 1H, OH), 1.37 (d, J = 6.5 Hz, 3H, 12-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) major stereoisomer 142.3 (s, C-8), 136.7 (s, C-9), 135.3 (s, C-3), 129.5 (d, C-4), 128.8 (d, C-7), 126.8 (d), 126.6 (d), 122.4 (d, C-10), 63.4 (t, C-1), 36.1 (t, C-2), 26.0 (q, C-11), 14.8 (q, C-12); MS: (CI, 70 eV) *m*/*z* 176 (M, 5); HRMS: (EI, 70 eV) Calculated ($C_{12}H_{16}O$) 176.1201 (M) Found: 176.1205.

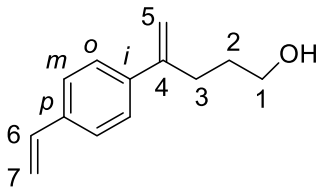
(**1n**) 1-(2-methoxyethyl)-2-vinylbenzene



To a branched reactor vessel, NaOH aq. (50 wt%, 1g), benzene (2 mL), 2-(2-vinylphenyl)ethan-1-ol (0.737 g, 5 mmol), tributylamine (0.0492 g, 0.27 mmol) and dimethyl sulfate (0.962 g, 8 mmol) were added. After stirring for 3 h at 40 °C, the reaction mixture was quenched by diethyl ether (4 mL) and H_2O (4 mL). This solution was extracted with diethyl ether (5 mL x 3), and washed by H_2O (4 mL) and sat. NaCl aq. (5 mL). The collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane) column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (0.649 g, 81%). IR: (neat) 1115 (OMe) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.49 (dd, J = 3.6, 5.3 Hz, 1H), 7.24-7.15 (m, 3H), 7.01 (dd, J = 17.4, 11.1 Hz, 1H, 9-H), 5.64 (dd, J = 17.4, 1.4 Hz, 1H, 10-H^A), 5.30 (dd, J = 11.1, 1.4 Hz, 1H, 10-H^B),

3.53 (t, J = 7.7 Hz, 2H, 1-H_2), 3.34 (s, 3H, 11-H_3), 2.97 (t, J = 7.7 Hz, 2H, 2-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 136.9 (s, C-8), 135.9 (s, C-3), 134.4 (d, C-9), 130.0 (d, C-4), 127.7 (d), 126.7 (d), 125.8 (d), 115.7 (t, C-10), 73.0 (t, C-1), 58.6 (q, C-11), 33.5 (t, C-2); MS: (CI, 70 eV) m/z 163 ([M + 1]$^+$, 100), 131 (52); HRMS: (EI, 70 eV) Calculated ($C_{11}H_{14}O$) 162.1045 (M^+) Found: 162.1046; Analysis: $C_{11}H_{14}O$ (162.10) Calculated: C, 81.44; H, 8.70 Found: C, 81.16; H, 8.52.

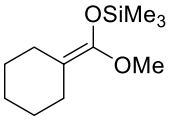
(**1o**) 2-(2-(prop-1-en-2-yl)phenyl)ethan-1-ol



To a two necked flask, $Pd(PPh_3)_4$ (0.420 g, 0.363 mmol), 1,4-dioxane (20 mL), *p*-vinyl boronic acid (2.20 g, 14.9 mmol), 4-pentyn-1-ol (1.05 g, 12.5 mmol) and acetic acid (0.13 mL, 2.40 mmol) were added. After stirring for 29 h at 80 ℃, the reaction mixture was filtered through a short pad of celite and the filtrate was evaporated. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (1.77 g, 75%). IR: (neat) 3359 (OH) cm^{-1}, 1628 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.42-7.36 (m, 4H), 6.71 (dd, J = 18.4, 10.6 Hz, 1H, 6-H), 5.76 (d, J = 18.4 Hz, 1H, 7-H^A), 5.33 (s, 1H, 5-H^A), 5.25 (d, J = 10.6 Hz, 1H, 7-H^B), 5.10 (s, 1H, 5-H^B), 3.66 (t, J = 6.3 Hz, 2H, 1-H_2), 2.61 (t, J = 7.7 Hz, 2H, 3-H_2), 1.73 (tt, J = 6.3, 7.7 Hz, 2H, 2-H_2), 1.51 (br, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 147.4 (s, C-4), 140.2 (s, *i*), 136.7 (s, *p*), 136.3 (d, C-6), 126.2 (d), 126.1 (d), 113.7 (t, C-7), 112.5 (t, C-5), 62.4 (t, C-1), 31.4 (t, C-3), 31.1 (t, C-2); MS: (CI, 70 eV) m/z 189 ([M + 1]$^+$, 100); HRMS: (EI, 70 eV)

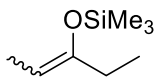
Calculated ($C_{13}H_{16}O$) 188.1201 (M) Found: 188.1199.

(**2b**) (cyclohexylidene(methoxy)methoxy)trimethylsilane[4g]



To a solution of diisopropylamine (11.5 g, 110 mmol) in THF (80 mL) was added n-BuLi (63 mL, 1.6 M in hexane) at 0 ºC. The resulted solution was stirred for 10 min at room temperature. Then, a solution of methyl cyclohexanecarboxyrate (11.4 g, 80 mmol) in THF (30 mL) was slowly added to the LDA solution at -78 ºC. After the solution was stirred for 2h at -78 ºC, trimethylsilylchloride (10.8 g, 100 mmol) was added to the reaction mixture, and the reaction mixture was stirred for 20 h at room temperature. The reaction mixture was poured into ice water and hexane, which was extracted with hexane. The organic phase was washed with brine, dried ($MgSO_4$) and concentrated. The obtained crude oil was purified by distillation (bp. 100-102 ºC, 20 mmHg) to give the desired product (14.3 g, 83%). This is known compound and spectroscopic data were identical with those from literature.

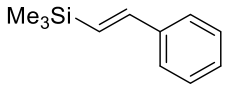
(**2c**) 3-trimetylsilyloxy-2-pentene[23]



To a solution of diisopropylamine (10.1 g, 100 mmol) in THF (100 mL) was added *n*-BuLi (1.6 M in hexane, 63 mL, 100 mmol) at 0 °C. After stirring at 0 °C for 15 min, then to reaction mixture was added 3-pentanone (6.89 g, 80 mmol) dropwise at -78 °C. After stirred for 30 min at -78 °C, Me_3SiCl

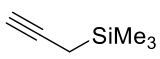
(10.9 g, 100 mmol) was added dropwise at -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 30 min. Then, sat. $NaHCO_3$ aq. (50 mL) was added and the solution was extracted with pentane (50 mL x 3). The organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure (76 °C, 85 mmHg) to give the product (12.0 g, 76% yield, E/Z = 5:1). This is known compound and spectroscopic data were identical with those from literature.

(**2g**) (*E*)-trimethyl(styryl)silane[24,25]



To a three necked flask, trimethyl(phenylethynyl)silane (3.63 g, 20.8 mmol) and dry hexane (5 mL) were added. To the reaction mixture was dropped DIBAL-H (1.0 M in hexane, 24 mL, 24 mmol). After stirring for 13 h at rt, the reaction mixture was quenched by 4 N HCl aq. (17 mL) at 0 °C. The mixture was extracted by Et_2O (20 mL x 3) and the collected organic layer was washed with sat. NaCl aq. (60 mL x 3). The organic layer was dried ($MgSO_4$) and the solvent was evaporated and the residue was purified by distillation under reduced pressure (112 °C, 23 mmHg) to give the product (2.23 g, 60%). This is known compound and spectroscopic data were identical with those from literature.

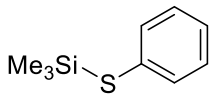
(**2i**) trimethyl(prop-2-yn-1-yl)silane[26]



To a three necked flask, Mg (1.82 g, 75 mmol), Et_2O (16 mL) and $HgCl_2$ (0.255 g, 0.94 mmol) were

added. After vigolously stirring for 30 minutes at rt, propargyl bromide (1.1 M in Et_2O, 2 mL, 2.2 mmol) was dropped to the mixture. The reaction mixture was cooled into 0 °C and propargyl bromide (1.1 M in Et_2O, 31 mL, 34.1 mmol) was dropped to the reaction mixture. After stirring for 30 minutes at rt, the reaction mixture was cooled into 0 °C and Me_3SiCl (3.34 g, 30.7 mmol) was dropped to the reaction mixture. After vigolously stirring for 9 h at rt, the reaction mixture was filtered through a celite pad and the filtrate was purified by column chromatography (Et_2O, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product (51wt% in Et_2O, 2.91 g, 36%). This is known compound and spectroscopic data were identical with those from literature.

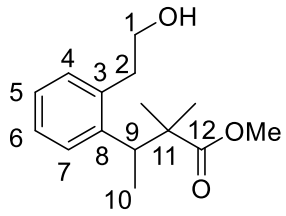
(**2j**) trimethyl(phenylthio)silane[27,28]



To a three necked flask, Et_2O (32 mL) and benzenethiol (3.60 g, 33 mmol) were added. This solution was cooled at -78 °C and *n*-BuLi (1.6 M hexane solution, 52 mL, 82.5 mmol) was dropped to the mixture over 15 minutes, followed by Me_3SiCl was dropped over 4 minutes. After stirring for 2 hours, the reaction mixture was quenched by dry hexane (18 mL). The solvent was evaporated and the residue was filtered and the residue was washed by hexane. The solvent was evaporated and the residue was purified by distillation under reduced pressure (110 °C, 20 mmHg) to give the product (4.82 g, 81%). This is known compound and spectroscopic data were identical with those from literature.

InI_3 catalyzed hydrofunctionalization of styrene derivatives 1 using organosilicon nucleophiles 2 (Table 1-3, Scheme 3A and Scheme 6), General Procedure. To a solution of acid catalyst (10 mol %) in 1,2-dichloroethane (1 mL) was added styrene derivatives **1** (0.5 mmol). The mixture was stirred at 80 ℃ for 24 h and then cooled to rt. Organosilicon nucleophiles **2** (0.75 mmol) was added to the reaction mixture. After stirring at rt for 2 h, the mixture was quenched by diethyl ether (2 mL), Bu_4NF (1 M in THF, 1 mL) and sat. Na_2CO_3 aq. (2 mL) and then extracted with diethyl ether (2 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (column length 11 cm, diameter 26 mm, spherical silica gel).

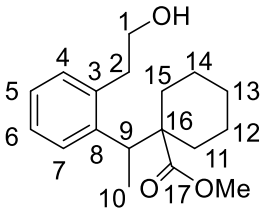
*Methyl 3-[2-(2-hydroxyethyl)phenyl]-2,2-dimethylbutanoate (**3aa**)*



From InI_3 (0.0254 g, 0.0513 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0740 g, 0.499 mmol), and dimethylketene methyl trimethylsilylacetal (0.141 g, 0.809 mmol) following general procedure, **3aa** (0.089 g, 71%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3440 (OH) cm^{-1}, 1728 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.25-7.10 (m, 4H, 4-H, 5-H, 6-H and 7-H), 3.87-3.69 (m, 2H, 1-H_2), 3.63 (s, 3H, OMe), 3.54 (q, J = 7.2 Hz, 1H, 9-H), 3.27 (ddd, J = 13.5, 7.2, 6.8 Hz, 1H, 2-H^A), 2.79 (ddd, J = 13.5, 7.7, 7.2 Hz, 1H, 2-H^B), 1.47 (s, 1H, OH), 1.23 (d, J = 7.2 Hz, 3H, 10-H_3), 1.18 (s, 3H, 11-Me^A), 1.11 (s, 3H, 11-Me^B);^{13}C NMR: (100 MHz, $CDCl_3$) 178.3 (s, C-12), 141.5 (s, C-8), 136.8 (s, C-3), 130.1 (d, C-4), 128.0 (d), 126.3 (d), 126.2 (d), 63.6 (t, C-1), 51.7 (q, C-13), 47.0 (s, C-11), 39.9 (d, C-9), 36.6 (t, C-2), 24.0 (q, 11-Me^B), 21.2 (q, 11-Me^A), 17.5

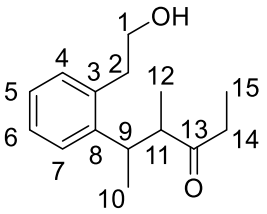
(q, C-10); MS: (CI, 70 eV) *m*/*z* 251 ([M + 1]$^+$, 100); HRMS: (EI, 70 eV) Calculated ($C_{15}H_{22}O_3$) 250.1569 (M^+) Found: 250.1571.

*Methyl 1-(1-(2-(2-hydroxyethyl)phenyl)ethyl)cyclohexane-1-carboxylate (**3ab**)*



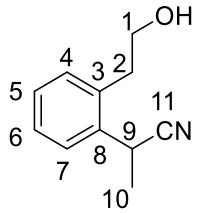
From InI_3 (0.0495 g, 0.10 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0755 g, 0.509 mmol), and (cyclohexylidene(methoxy)methoxy)trimethylsilane (0.327 g, 1.53 mmol) following general procedure (rt, 3 h at 2nd step), **3ab** (0.109 g, 74%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3440 (OH) cm^{-1}, 1716 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.19-7.11 (m, 4H, Ar), 3.78-3.67 (m, 2H, 1-H_2), 3.60 (s, 3H, OMe), 3.32-3.19 (m, 2H, 9-H and 2-H^A), 2.75 (dt, *J* = 14.0, 6.8 Hz, 1H, 2-H^B), 2.34-2.28 (br, 1H), 2.21 (s, 1H, OH), 2.08-2.00 (br, 1H), 1.65-1.51 (br, 3H), 1.33-1.21 (m, 2H), 1.24 (d, *J* = 7.2 Hz, 3H, 10-H_3), 1.21-0.95 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) 176.4 (s, C-17), 141.6 (s, C-8), 136.6 (s, C-3), 129.9 (d, C-4), 128.2 (d, C-7), 126.2 (d), 125.9 (d), 63.5 (t, C-1), 52.2 (s, C-11), 51.2 (q, OMe), 41.9 (d, C-9), 36.6 (t, C-2), 32.7 (t), 30.7 (t), 25.5 (t), 23.8 (t), 23.6 (t), 17.0 (q, C-10); MS: (EI, 70 eV) *m*/*z* 290 (M, 1); HRMS: (CI, 70 eV) Calculated ($C_{18}H_{27}O_3$) 291.1960 ([M + 1]$^+$) Found: 291.1957.

*5-[2-(2-Hydroxyethyl)phenyl]-4-methylhexan-3-one (**3ac**)*



From InI_3 (0.0226 g, 0.0456 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0765 g, 0.516 mmol), and (*Z*)-trimethyl(pent-2-en-3-yloxy)silane (0.216 g, 1.36 mmol) following general procedure (rt, 5 h at 2nd step), **3ac** (0.0837 g, 69%, d.r. = 54:46) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3433 (OH) cm^{-1}, 1709 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) diastereo mixture: 7.26-7.07 (m, 4H), 3.97-3.88 (m, 0.46H), 3.88-3.75 (m, 1.54H), 3.39-3.25 (m, 1H), 3.07 (dt, *J* = 13.5, 6.8 Hz, 0.46H), 3.02-2.78 (m, 2.54H), 2.61 (dq, J = 18.4, 7.2 Hz, 0.54H), 2.53-2.32 (m, 1H), 2.03 (dq, *J* = 17.8, 7.2 Hz, 0.46H), 1.82 (s, 0.54H), 1.20 (t, *J* = 6.8 Hz, 3H), 1.11 (t, *J* = 6.8 Hz, 1.62H), 1.10 (t, *J* = 7.2 Hz, 1.38H), 0.806 (t, *J* = 7.2 Hz, 1.62H), 0.788 (t, *J* = 6.8 Hz, 1.38H); ^{13}C NMR: (100 MHz, $CDCl_3$) diastereo mixture: 215.9 (s), 215.7 (s), 144.7 (s), 143.4 (s), 136.2 (s), 136.1 (s), 130.6 (d), 130.4 (d), 127.1 (d), 126.7 (d), 126.1 (d), 126.0 (d), 125.5 (d), 63.8 (t), 63.4 (t), 52.7 (d), 52.0 (d), 36.6 (d), 36.5 (d), 36.4 (t), 36.3 (t), 36.2 (t), 36.0 (t), 21.4 (q), 19.8 (q), 16.2 (q), 15.6 (q), 7.64 (q), 7.41 (q); MS: (CI, 70 eV) m/z 235 ($[M + 1]^+$, 100); HRMS: (CI, 70 eV) Calculated ($C_{15}H_{23}O_2$) 235.1698 ($[M + 1]^+$) Found: 235.1698.

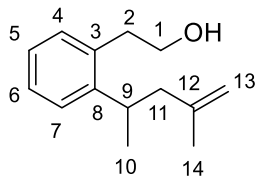
*5-[2-(2-Hydroxyethyl)phenyl]-4-methylhexan-3-one (**3ad**)*



From InI_3 (0.0565 g, 0.114 mmol, 20 mol %), 2-(2-vinylphenyl)ethan-1-ol (0.0765 g, 0.516 mmol), and trimethylsilyl cyanide (0.3 mL, 2.5 mmol) following general procedure (70 °C, 14 h at 2nd step), **3ad** (0.0284 g, 31%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3429 (OH) cm^{-1}, 2241 (CN) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.54-7.47 (m, 1H), 7.34-7.20

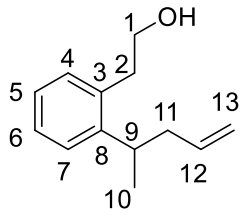
(m, 3H, 4-H, 5-H and 6-H), 4.24 (q, J = 6.8 Hz, 1H, 9-H), 3.92-3.81 (m, 2H, 1-H_2), 2.89 (t, J = 6.8 Hz, 2H, 2-H_2), 1.71 (s, 1H, OH), 1.62 (d, J = 6.8 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 136.0 (s), 135.6 (s), 130.5 (d, C-4), 128.3 (d), 127.6 (d), 127.3 (d), 122.2 (s, C-11), 63.2 (t, C-1), 35.2 (t, C-2), 27.7 (d, C-9), 21.0 (d, C-10); MS: (CI, 70 eV) *m*/*z* 176 ($[M + 1]^+$, 25), 158 (M – OH, 100); HRMS: (EI, 70 eV) Calculated ($C_{11}H_{13}NO$) 175.0997 (M^+) Found: 175.0998.

*2-(2-(4-Methylpent-4-en-2-yl)phenyl)ethan-1-ol (**3ae**)*



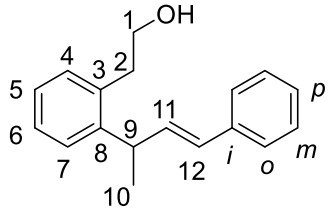
From InI_3 (0.0244 g, 0.0492 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0744 g, 0.502 mmol) and trimethyl(2-methylallyl)silane (0.115 g, 0.896 mmol) following general procedure (rt, 4 h at 2nd step), **3ae** (0.056 g, 55%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3410 (OH) cm^{-1}, 1647 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.27 (d, J = 7.2 Hz, 1H, 7-H), 7.22 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H, 4-H), 7.13 (t, J = 7.2 Hz, 1H), 4.74 (s, 1H, 13-H^A), 4.68 (s, 1H, 13-H^B), 3.83 (t, J = 6.8 Hz, 2H, 1-H_2), 3.27-3.16 (m, 1H, 9-H), 3.03-2.88 (m, 2H, 2-H_2), 2.32 (dd, J = 13.5, 6.3 Hz, 11-H^A), 2.23 (dd, J = 13.5, 8.7 Hz, 11-H^B), 1.70 (s, 3H, 14-H_3), 1.50 (s, 1H, OH), 1.20 (d, J = 6.8 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 146.0 (s, C-8), 144.0 (s, C-12), 135.0 (s, C-3), 130.1 (d, C-4), 126.9 (d), 126.1 (d, C-7), 125.8 (d), 112.2 (t, C-13), 63.5 (t, C-1), 46.6 (t, C-11), 35.9 (t, C-2), 32.1 (d, C-9), 22.4 (q, C-14), 21.6 (q, C-10); MS: (EI, 70 eV) *m*/*z* 204 (M, 2); HRMS: (CI, 70 eV) Calculated ($C_{14}H_{21}O$) 205.1592 ($[M + 1]^+$) Found: 205.1589.

*2-[2-(Pent-4-en-2-yl)phenyl]ethan-1-ol (**3af**)*



From InI_3 (0.0303 g, 0.0611 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0745 g, 0.503 mmol), allyltrimethylsilane (0.0834 g, 0.730 mmol) and Me_3SiBr (0.0097 g, 0.0634 mmol) following general procedure (rt, 3 h at 2nd step), **3af** (0.082 g, 86%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3344 (OH) cm^{-1}, 1666 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.29-7.10 (m, 4H, 4-H, 5-H, 6-H and 7-H), 5.77-5.64 (m, 1H, 12-H), 5.01 (d, J = 14.0 Hz, 1H, 13-H^A), 4.95 (d, J = 10.1 Hz, 1H, 13-H^B), 3.80 (t, J = 7.2 Hz, 2H, 1-H_2), 3.09 (sextet, J = 7.0 Hz, 1H, 9-H), 3.00-2.85 (m, 2H, 2-H_2), 2.43-2.24 (m, 2H, 11-H_2), 1.59 (s, 1H, OH), 1.23 (d, J = 7.0 Hz, 3H, 10-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 145.4 (s, C-8), 137.0 (d, C-12), 135.1 (s, C-3), 130.1 (d, C-4), 126.9 (d), 126.0 (d), 125.8 (d), 116.1 (t, C-13), 63.5 (t, C-1), 42.4 (t, C-11), 36.0 (t, C-2), 34.1 (d, C-9), 21.8 (q, C-10); MS: (CI, 70 eV) *m/z* 191 ($[M + 1]^+$, 30), 173 (M - OH, 100), 149 (M – CH_2CHCH_2, 35); HRMS: (EI, 70 eV) Calculated ($C_{13}H_{18}O$) 190.1358 (M^+) Found: 190.1357.

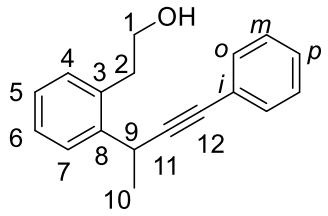
*(E)-2-[2-(4-Phenylbut-3-en-2-yl)phenyl]ethan-1-ol (**3ag**)*



From InI_3 (0.0229 g, 0.0462 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0743 g, 0.501 mmol), (*E*)-trimethyl(styryl)silane (0.2687 g, 1.52 mmol) and Me_3SiBr (0.016 g, 0.105 mmol) following general

procedure (rt, 10 h at 2nd step), **3ag** (0.0742 g, 59%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3402 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.35-7.14 (m, 9H, Ar), 6.37 (dd, *J* = 4.3, 15.9 Hz, 1H, 11-H), 6.35 (d, *J* = 15.9 Hz, 1H, 12-H), 3.94 (dq, *J* = 4.3, 6.8 Hz, 1H, 9-H), 3.85 (t, *J* = 6.8 Hz, 2H, 1-H_2), 2.98 (t, *J* = 6.8 Hz, 2H, 2-H_2), 1.58 (s, 1H, OH), 1.45 (d, *J* = 6.8 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 143.9 (s, C-8), 137.4 (s, *i*), 135.4 (s, C-3), 135.2 (d, C-11), 130.2 (d, C-4), 128.5 (d), 127.2 (d), 127.04 (d), 127.01, 126.2 (d), 126.1 (d), 63.5 (t, C-1), 37.4 (d, C-9), 35.9 (t, C-2), 21.4 (q, C-10); MS: (CI, 70 eV) *m/z* 253 ($[M + 1]^+$, 5), 235 (M – OH, 100); HRMS: (EI, 70 eV) Calculated ($C_{18}H_{20}O$) 252.1514 (M^+) Found: 252.1514.

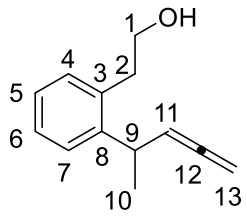
*2-(2-(4-Phenylbut-3-yn-2-yl)phenyl)ethan-1-ol (**3ah**)*



From InI_3 (0.0257 g, 0.0519 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0751 g, 0.507 mmol), trimethyl(phenylethynyl)silane (0.270 g, 1.55 mmol) and Me_3SiBr (0.0143 g, 0.0934 mmol) following general procedure (rt, 1 h at 2nd step), **3ah** (0.0684 g, 54%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3301 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.64 (d, *J* = 7.2 Hz, 1H, Ar), 7.43-7.38 (m, 2H, Ar), 7.30-7.22 (m, 4H, Ar), 7.22-7.17 (m, 2H, Ar), 4.24 (q, *J* = 6.8 Hz, 1H, 9-H), 3.88 (t, *J* = 7.2 Hz, 2H, 1-H_2), 3.04-2.92 (m, 2H, 2-H_2), 1.72 (s, 1H, OH), 1.56 (d, *J* = 6.8 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 141.8 (s, C-8), 134.9 (s, C-3), 131.5 (d), 130.1 (d, C-4), 128.2 (d), 127.7 (d), 127.5 (d), 127.2 (d), 126.9 (d), 123.6 (s, *i*), 93.1 (s, C-11), 81.7 (s, C-12), 63.4 (t, C-1), 35.6 (t, C-2), 28.5 (d, C-9), 23.8 (q, C-10); MS: (CI, 70 eV) *m/z*

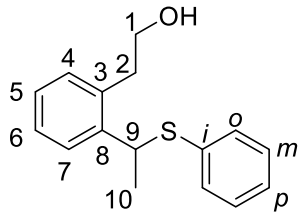
251 ([M + 1]$^+$, 20), 233 (M - OH, 100); HRMS: (CI, 70 eV) Calculated ($C_{18}H_{19}O$) 251.1436 ([M + 1]$^+$) Found: 251.1436.

*2-[2-(Penta-3,4-dien-2-yl)phenyl]ethan-1-ol (**3ai**)*



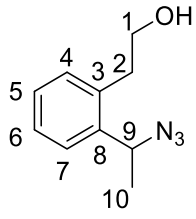
From InI_3 (0.0274 g, 0.0553 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0745 g, 0.503 mmol), trimethyl(prop-2-yn-1-yl)silane (51 wt % in Et_2O, 0.1653 g, 1.50 mmol) and Me_3SiBr (0.0170 g, 0.111 mmol) following general procedure (35 °C, 2 h at 2nd step), **3ai** (0.07 g, 68%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3394 (OH) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.31 (d, J = 7.7 Hz, 1H, 7-H), 7.25-7.21 (m, 1H), 7.20-7.14 (m, 2H), 5.30 (dt, J = 6.8, 6.5 Hz, 1H, 11-H), 4.83-4.74 (m, 2H, 13-H_2), 3.85 (dt, J = 6.3, 6.8 Hz, 2H, 1-H_2), 3.82-3.74 (m, 1H, 9-H), 2.972 (t, J = 6.8 Hz, 1H, 2-H^A), 2.966 (t, J = 6.8 Hz, 1H, 2-H^B), 1.41 (t, J = 6.3 Hz, 1H, OH), 1.34 (d, J = 7.0 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 207.8 (s, C-12), 144.3 (s, C-8), 135.2 (s, C-3), 130.1 (d, C-4), 127.1 (d), 127.0 (d), 126.2 (d), 96.0 (d, C-11), 76.7 (t, C-13), 63.5 (t, C-1), 35.9 (t, C-2), 33.6 (d, C-9), 21.5 (q, C-10); MS: (CI, 70 eV) *m*/*z* 189 ([M + 1]$^+$, 10); HRMS: (EI, 70 eV) Calculated ($C_{13}H_{16}O$) 188.1201 (M$^+$) Found: 188.1199.

*2-[2-(1-(Phenylthio)ethyl)phenyl]ethan-1-ol (**3aj**)*



From InI_3 (0.0245 g, 0.0494 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0739 g, 0.499 mmol) and trimethyl(phenylthio)silane (0.278 g, 1.52 mmol) following general procedure (rt, 13 h at 2nd step), **3aj** (0.0758 g, 59%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3394 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.51 (d, J = 7.7 Hz, 1H, 7-H), 7.42-7.36 (m, 2H), 7.32-7.15 (m, 6H), 4.66 (q, 1H, 9-H), 3.88-3.73 (m, 2H, 1-H_2), 3.03-2.82 (m, 2H, 2-H_2), 1.77 (s, 1H, OH), 1.63 (d, J = 7.2 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 141.1 (s, C-8), 135.7 (s), 134.7 (s), 133.2 (d), 130.1 (d, C-4), 128.8 (d), 127.6 (d), 127.2 (d), 127.1 (d), 127.0 (d), 63.4 (t, C-1), 43.3 (d, C-9), 35.7 (t, C-2), 22.3 (q, C-10); MS: (CI, 70 eV) *m/z* 259 ($[M + 1]^+$, 1), 149 (M – SPh, 100); HRMS: (EI, 70 eV) Calculated ($C_{16}H_{18}OS$) 258.1078 (M^+) Found: 258.1081.

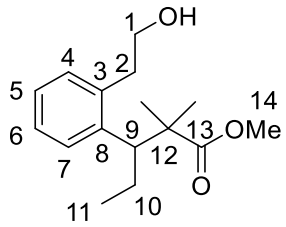
*2-[2-(1-Azidoethyl)phenyl]ethan-1-ol (**3ak**)*



From InI_3 (0.0288 g, 0.0581 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0776 g, 0.524 mmol) and azidotrimethylsilane (0.2 mL, 1.5 mmol) following general procedure (50 °C, 4 h at 2nd step), **3ak** (0.0612 g, 54%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3437 (OH) cm^{-1}, 2102 (N=N=N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.35 (d, J = 7.2 Hz, 1H, 7-H),

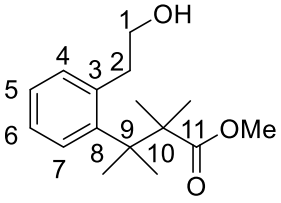
7.26-7.12 (m, 3H, 4-H, 5-H and 6-H), 4.89 (q, J = 6.8 Hz, 1H, 9-H), 3.77 (t, J = 6.8 Hz, 2H, 1-H_2), 2.87 (t, J = 6.8 Hz, 2H, 2-H_2), 1.65 (s, 1H, OH), 1.47 (d, J = 6.8 Hz, 3H, 10-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 139.2 (s, C-8), 135.7 (s, C-3), 130.3 (d, C-4), 128.1 (d), 127.2 (d), 126.1 (d, C-7), 63.5 (t, C-1), 56.7 (d, C-9), 35.4 (t, C-2), 21.1 (q, C-10); MS: (CI, 70 eV) m/z 164 ([M + 1]$^+$ – N_2 , 30); HRMS: (CI, 70 eV) Calculated ($C_{10}H_{14}N_3O$) 192.1137 ([M + 1]$^+$) Found: 192.1134.

*Methyl 3-[2-(2-hydroxyethyl)phenyl)]-2,2-dimethylpentanoate (**3ba**)*



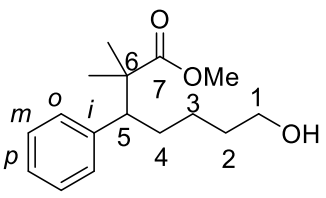
From InI_3 (0.0286 g, 0.0577 mmol), (*E*)-2-(2-(prop-1-en-1-yl)phenyl)ethan-1-ol (0.0799 g, 0.493 mmol) and dimethylketene methyl trimethylsilylacetal (0.2819 g, 1.62 mmol) following general procedure (80 °C, 15 h at 1st step), **3ba** (0.068 g, 52%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3452 (OH) cm^{-1}, 1728 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.24-7.14 (m, 4H, 4-H, 5-H, 6-H and 7-H), 3.93-3.93 (m, 1H, 1-H^A), 3.83-3.73 (m, 1H, 1-H^B), 3.65 (s, 3H, 14-H_3), 3.34 (dd, J = 11.8, 3.4 Hz, 1H, 9-H), 3.25 (dt, J = 14.0, 7.2 Hz, 1H, 2-H^A), 2.83 (ddd, J = 14.0, 7.7, 7.5 Hz, 1H, 2-H^B), 1.84-1.73 (m, 1H, 10-H^A), 1.66-1.58 (m, 1H, 10-H^B), 1.49-1.41 (m, 1H, OH), 1.16 (s, 3H, 12-Me^A), 1.03 (s, 3H, 12-Me^B), 0.677 (t, J = 7.2 Hz, 3H, 11-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 178.6 (s, C-13), 138.7 (s, C-8), 138.4 (s, C-3), 130.0 (d), 127.7 (d), 126.3 (d), 126.1 (d), 63.5 (t, C-1), 51.8 (q, C-14), 47.3 (s, C-12), 47.2 (d, C-9), 36.3 (t, C-2), 24.5 (q, 12-Me^B), 24.1 (t, C-10), 20.7 (q, 12-Me^A), 12.8 (q, C-11); MS: (CI, 70 eV) m/z 265 ([M + 1]$^+$, 100); HRMS: (CI, 70 eV) Calculated ($C_{16}H_{25}O_3$) 265.1804 ([M + 1]$^+$) Found: 265.1803.

*Methyl 3-[2-(2-hydroxyethyl)phenyl)]-2,2-dimethylpentanoate (**3ca**)*



From InI_3 (0.0264 g, 0.0533 mmol), 2-(2-(prop-1-en-2-yl)phenyl)ethan-1-ol (0.0822 g, 0.507 mmol) and dimethylketene methyl trimethylsilylacetal (0.135 g, 0.774 mmol) following general procedure (80 °C, 6 h at 1st step), **3ca** (0.1047 g, 72%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3425 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.39-7.30 (m, 1H, 7-H), 7.21-7.08 (m, 3H, 4-H, 5-H and 6-H), 3.87 (t, J = 7.2 Hz, 2H, 1-H_2), 3.56 (s, 3H, OMe), 3.11 (t, J = 7.2 Hz, 2H, 2-H_2), 1.59 (s, 4H, 9-Me and OH), 1.16 (s, 3H, 10-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.3 (s, C-11), 144.1 (s, C-8), 137.3 (s, C-3), 132.4 (d, C-4), 130.9 (d, C-7), 126.3 (d), 125.4 (d), 64.8 (t, C-1), 51.4 (q, OMe), 49.9 (s, C-10), 45.4 (s, C-9), 39.6 (t, C-2), 28.2 (q, 9-Me), 22.5 (q, 10-Me); MS: (EI, 70 eV) *m/z* 232 (M - MeOH, 5); HRMS: (CI, 70 eV) Calculated ($C_{16}H_{25}O_3$) 265.1804 ($[M + 1]^+$) Found: 265.1801.

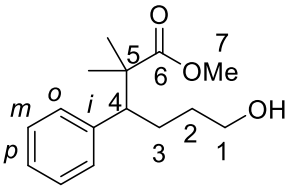
*Methyl 7-hydroxy-2,2-dimethyl-3-phenylheptanoate (**3ea**)*



From InI_3 (0.0278 g, 0.0561 mmol), (*E*)-5-phenylpent-4-en-1-ol (0.0864 g, 0.532 mmol) and dimethylketene methyl trimethylsilylacetal (0.149 g, 0.855 mmol) following general procedure (80 °C, 65 h at 1st step), **3ea** (0.040 g, 28%) was obtained after column chromatography (hexane/ethyl

acetate = 80:20). IR: (neat) 3444 (OH) cm^{-1}, 1728 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.25 (t, 2H, *m*), 7.22 (d, 1H, *p*), 7.15 (d, 2H, *o*), 3.64 (s, 3H, OMe), 3.51 (t, *J* = 6.8 Hz, 2H, 1-H_2), 2.96 (dd, *J* = 12.6, 3.4 Hz, 1H, 5-H), 1.89-1.77 (m, 1H, 4-H^A), 1.59-1.39 (m, 3H, 4-H^B and 2-H_2), 1.34 (s, 1H, OH), 1.18-1.05 (m, 2H, 3-H_2), 1.14 (s, 3H, 6-Me^A), 1.01 (s, 3H, 6-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 178.3 (s, C-7), 140.1 (s, *i*), 129.7 (d, *m*), 127.8 (d, *o*), 126.6 (d, *p*), 62.7 (t, C-1), 52.8 (d, C-5), 51.7 (q, OMe), 46.7 (s, C-6), 32.5 (t, C-2), 29.7 (t, C-4), 24.5 (q, 6-Me^A), 24.2 (t, C-3), 20.7 (q, 6-Me^B); MS: (CI, 70 eV) *m*/*z* 265 ($[M + 1]^+$, 74); HRMS: (CI, 70 eV) Calculated ($C_{16}H_{25}O_3$) 265.1804 ($[M + 1]^+$) Found: 265.1805.

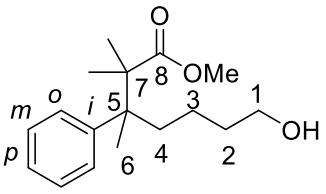
*Methyl 6-hydroxy-2,2-dimethyl-3-phenylhexanoate (**3fa**)*



From InI_3 (0.0338 g, 0.068 mmol), (*E*)-4-phenylbut-3-en-1-ol (0.0762 g, 0.514 mmol) and dimethylketene methyl trimethylsilylacetal (0.120 g, 0.688 mmol) following general procedure (80 °C, 120 h at 1st step), **3fa** (0.038 g, 30%) was obtained after column chromatography (hexane/ethyl acetate = 80:20). IR: (neat) 3437 (OH) cm^{-1}, 1728 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.38 (t, *J* = 7.2 Hz, 2H, *m*), 7.23 (t, *J* = 7.2 Hz, 1H, *p*), 7.16 (d, *J* = 7.2 Hz, 2H, *o*), 3.64 (s, 3H, 7-H_3), 3.55 (t, *J* = 6.8 Hz, 2H, 1-H_2), 2.99 (dd, *J* = 12.6, 2.9 Hz, 1H, 4-H), 1.92-1.79 (m, 1H, 3-H^A), 1.66-1.47 (m, 2H, 3-H^B and OH), 1.37-1.24 (m, 2H, 2-H_2), 1.16 (s, 3H, 5-Me^A), 1.02 (s, 3H, 5-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 178.4 (s, C-6), 139.9 (s, *i*), 129.7 (d, *o*), 127.9 (d, *m*), 126.7 (d, *p*), 62.5 (t, C-1), 52.4 (d, C-4), 51.7 (q, C-7), 46.7 (s, C-5), 31.1 (t, C-2), 26.2 (t, C-3), 24.6 (q, 5-

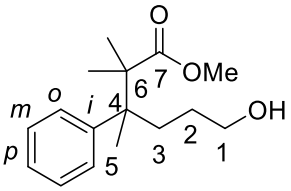
Me^B), 20.6 (q, 5-Me^A); MS: (CI, 70 eV) *m/z* 251 ($[M + 1]^+$, 100); HRMS: (CI, 70 eV) Calculated ($C_{15}H_{23}O_3$) 251.1647 ($[M + 1]^+$) Found: 251.1649.

*Methyl 7-hydroxy-2,2,3-trimethyl-3-phenylheptanoate (**3ga**)*



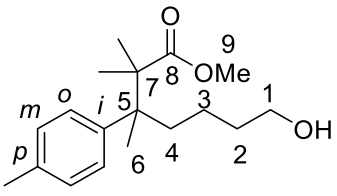
From InI_3 (0.0253 g, 0.0511 mmol), 2-(2-vinylphenyl)ethan-1-ol (0.0911 g, 0.615 mmol) and dimethylketene methyl trimethylsilylacetal (0.125 g, 0.717 mmol) following general procedure (rt, 3 h at 1st step), **3ga** (0.084 g, 59%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3444 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.32-7.15 (m, 5H, Ar), 3.55 (t, *J* = 7.0 Hz, 2H, 1-H_2), 3.50 (s, 3H, OMe), 2.24 (td, *J* = 13.0, 4.8 Hz, 1H, 4-H^A), 1.77 (s, 1H, OH), 1.63 (td, *J* = 13.0, 4.8 Hz, 1H, 4-H^B), 1.54 (tt, *J* = 7.7, 7.0 Hz, 2H, 2-H_2), 1.39 (s, 3H, 6-H_3), 1.28-1.15 (m, 1H, 3-H^A), 1.12 (s, 3H, 7-Me^A), 1.02 (s, 3H, 7-Me^B), 0.993-0.836 (m, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.2 (s, C-8), 143.0 (s, *i*), 128.2 (d), 127.3 (d), 125.9 (d, *p*), 62.7 (t, C-1), 51.2 (q, OMe), 49.7 (s, C-7), 45.9 (s, C-5), 34.8 (t, C-4), 33.5 (t, C-2), 22.1 (q, 7-Me^A), 21.7 (q, 7-Me^B), 21.2 (q, C-6), 20.8 (t, C-3); MS: (CI, 70 eV) *m/z* 279 ($[M + 1]^+$, 1), 247 (M - OMe, 3); HRMS: (CI, 70 eV) Calculated ($C_{17}H_{27}O_3$) 279.1960 ($[M + 1]^+$) Found: 279.1958.

*Methyl 6-hydroxy-2,2,3-trimethyl-3-phenylhexanoate (**3ha**)*



From InI_3 (0.0213 g, 0.0430 mmol), 4-phenylpent-4-en-1-ol (0.0862 g, 0.531 mmol) and dimethylketene methyl trimethylsilylacetal (0.139 g, 0.797 mmol) following general procedure (rt, 8 h at 1st step), **3ha** (0.092 g, 66%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3448 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.32-7.22 (m, 4H, *o* and *m*), 7.22-7.16 (m, 1H, *p*), 3.59 (td, J = 6.8, 1.9 Hz, 2H, 1-H_2), 3.50 (s, 3H, OMe), 2.31 (ddd, J = 14.0, 13.0, 3.38 Hz, 1H, 3-H^A), 1.73-1.59 (m, 2H, 3-H^B and OH), 1.48-1.34 (m, 1H, 2-H^A), 1.40 (s, 3H, 5-H_3) 1.22-1.09 (m, 1H, 2-H^B), 1.13 (s, 3H, 6-Me^A), 1.03 (s, 3H, 6-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.2 (s, C-7), 142.8 (s, *i*), 128.2 (d), 127.3 (d), 126.0 (d, *p*), 63.4 (t, C-1), 51.2 (q, OMe), 49.7 (s, C-6), 45.6 (s, C-4), 31.0 (t, C-3), 28.0 (t, C-2), 22.1 (q, 6-Me^B), 21.7 (q, 6-Me^A), 21.3 (q, C-5); MS: (CI, 70 eV) *m*/*z* 265 ($[M + 1]^+$, 100); HRMS: (EI, 70 eV) Calculated ($C_{16}H_{24}O_3$) 264.1725 (M^+) Found: 264.1724.

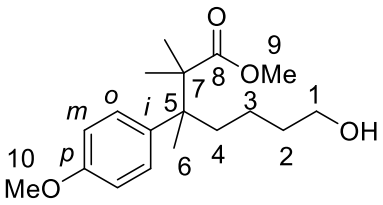
*Methyl 7-hydroxy-2,2,3-trimethyl-3-(p-tolyl)heptanoate (**3ia**)*



From InI_3 (0.0253 g, 0.0511 mmol), 5-phenylhex-5-en-1-ol (0.0908 g, 0.477 mmol) and dimethylketene methyl trimethylsilylacetal (0.123 g, 0.706 mmol) following general procedure (rt, 4 h at 1st step), **3ia** (0.097 g, 70%) was obtained after column chromatography (hexane/ethyl acetate =

70:30). IR: (neat) 3444 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.11 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 3.56 (t, J = 6.8 Hz, 2H, 1-H_2), 3.52 (s, 3H, 9-H_3), 2.31 (s, 3H, *p*-Me), 2.22 (td, J = 13.0, 3.9 Hz, 1H, 4-H^A), 1.61 (td, J = 12.6, 4.8 Hz, 1H, 4-H^B), 1.54 (tt, J = 6.8, 7.3 Hz, 2H, 2-H_2), 1.37 (s, 3H, 6-H_3), 1.30 (s, 1H, OH), 1.27-1.15 (m, 1H, 3-H^A), 1.10 (s, 3H, 7-Me^A), 1.01 (s, 3H, 7-Me^B), 0.99-0.87 (m, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.3 (s, C-8), 139.9 (s, *i*), 135.4 (s, *p*), 128.1 (d), 128.0 (d), 62.8 (t, C-1), 51.2 (q, C-9), 49.7 (s, C-7), 45.6 (s, C-5), 34.8 (t, C-4), 33.6 (t, C-2), 22.2 (q, 7-Me^A), 21.8 (q, 7-Me^B), 21.3 (q, C-6), 20.9 (t, C-3), 20.8 (q, *p*-Me); MS: (CI, 70 eV) *m/z* 293 ($[M + 1]^+$, 24); HRMS: (CI, 70 eV) Calculated ($C_{18}H_{29}O_3$) 293.2117 ($[M + 1]^+$) Found: 293.2114.

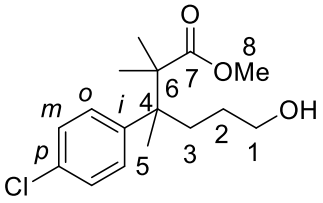
*Methyl 7-hydroxy-3-(4-methoxyphenyl)-2,2,3-trimethylheptanoate (**3ja**)*



From InI_3 (0.0266 g, 0.0537 mmol), 5-(4-methoxyphenyl)hex-5-en-1-ol (0.1075 g, 0.521 mmol) and dimethylketene methyl trimethylsilylacetal (0.121 g, 0.692 mmol) following general procedure (rt, 1 h at 1st step), **3ja** (0.092 g, 57%) was obtained after column chromatography (hexane/ethyl acetate = 60:40). IR: (neat) 3440 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.14 (d, J = 8.7 Hz, 2H, *o*), 6.81 (d, J = 8.7 Hz, 2H, *m*), 3.79 (s, 3H, 10-H_3), 3.55 (t, J = 7.2 Hz, 2H, 1-H_2), 3.52 (s, 3H, 9-H_3), 2.19 (ddd, J = 14.5, 13.5, 3.4 Hz, 1H, 4-H^A), 1.66-1.50 (m, 3H, 4-H^B and 2-H_2), 1.36 (s, 3H, 6-H_3), 1.27-1.13 (m, 2H, 3-H^A and OH), 1.10 (s, 3H, 7-Me^A), 1.01 (s, 3H, 7-Me^B), 0.98-0.87 (m, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.3 (s, C-8), 157.5 (s, *p*), 134.9 (s, *i*), 129.2 (d, *o*), 112.5

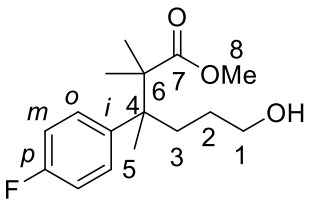
(d, *m*), 62.7 (t, C-1), 55.0 (q, C-10), 51.2 (q, C-9), 49.7 (s, C-7), 45.3 (s, C-5), 34.9 (t, C-4), 33.5 (t, C-2), 22.0 (q, 7-Me^B), 21.7 (q, 7-Me^A), 21.3 (q, C-6), 20.8 (t, C-3); MS: (EI, 70 eV) *m*/*z* 277 (M - OMe, 0.5), 207 (M - Me_2CHCO_2Me, 100); HRMS: (CI, 70 eV) Calculated ($C_{18}H_{29}O_4$) 309.2066 ([M + 1]$^+$) Found: 309.2064.

*Methyl 3-(4-chlorophenyl)-6-hydroxy-2,2,3-trimethylhexanoate (**3ka**)*



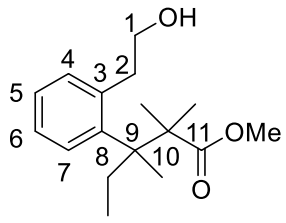
From InI_3 (0.0267 g, 0.0539 mmol), 4-(4-chlorophenyl)pent-4-en-1-ol (0.1014 g, 0.481 mmol) and dimethylketene methyl trimethylsilylacetal (0.137 g, 0.786 mmol) following general procedure (rt, 12 h at 1st step), **3ka** (0.064 g, 45%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3444 (OH) cm^{-1}, 1724 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.25 (d, *J* = 8.7 Hz, 2H, *m*), 7.17 (d, *J* = 8.7 Hz, 2H, *o*), 3.64-3.56 (m, 2H, 1-H_2), 3.52 (s, 3H, 8-H_3), 2.27 (ddd, *J* = 14.5, 13.0, 3.4 Hz, 1H, 3-H^A), 1.54 (ddd, *J* = 13.5, 13.0, 5.3 Hz, 1H, 3-H^B), 1.45-1.34 (m, 1H, 2-H^A), 1.38 (s, 3H, 5-H_3), 1.32 (s, 1H, OH), 1.19-1.06 (m, 1H, 2-H^B), 1.12 (s, 3H, 6-Me^A), 1.04 (s, 3H, 6-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.0 (s, C-7), 141.5 (s, *i*), 132.0 (s, *p*), 129.7 (d, *o*), 127.5 (d, *m*), 63.4 (t, C-1), 51.3 (q, C-8), 49.7 (s, C-6), 45.5 (s, C-4), 31.1 (t, C-3), 28.0 (t, C-2), 22.1 (q, 6-Me^B), 21.8 (q, 6-Me^A), 21.3 (q, C-5); MS: (CI, 70 eV) *m*/*z* 301 ([M + 1]$^+$ + 2, 34), 299 ([M + 1]$^+$, 100); HRMS: (CI, 70 eV) Calculated ($C_{16}H_{24}ClO_3$) 299.1414 ([M + 1]$^+$) Found: 299.1410.

*Methyl 3-(4-fluorophenyl)-6-hydroxy-2,2,3-trimethylhexanoate (**3la**)*



From InI_3 (0.0229 g, 0.046 mmol), 4-(4-fluorophenyl)pent-4-en-1-ol (0.0905 g, 0.481 mmol) and dimethylketene methyl trimethylsilylacetal (0.139 g, 0.797 mmol) following general procedure (rt, 22 h at 1st step), **3la** (0.101 g, 77%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3456 (OH) cm^{-1}, 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.21 (dd, J^4_{HF} = 5.3 Hz, J^3_{HH} = 8.7 Hz, 2H, *o*), 6.98 (dd, J^3_{HF} = 9.2 Hz, J^3_{HH} = 8.7 Hz, 2H, *m*), 3.65-3.53 (m, 2H, 1-H_2), 3.51 (s, 3H, 8-H_3), 2.27 (ddd, *J* = 14.5, 13.5, 3.4 Hz, 1H, 3-H^A), 1.67 (ddd, *J* = 13.5, 13.5, 5.3 Hz, 1H, 3-H^B), 1.52 (s, 1H, OH), 1.46-1.34 (m, 1H, 2-H^A), 1.39 (s, 3H, 5-H_3), 1.22-1.13 (m, 1H, 2-H^B), 1.12 (s, 3H, 6-Me^A), 1.03 (s, 3H, 6-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.1 (s, C-7), 161.2 (d, *J* = 255 Hz, *p*), 138.6 (d, *J* = 3.3 Hz, *i*), 129.8 (d, *J* = 7.4 Hz, *o*), 114.0 (d, *J* = 20.5 Hz, *m*), 63.3 (t, C-1), 51.3 (q, C-8), 49.8 (s, C-6), 45.3 (s, C-4), 31.1 (t, C-3), 27.9 (t, C-2), 22.0 (q, 6-Me^B), 21.7 (q, 6-Me^A), 21.4 (q, C-5); MS: (CI, 70 eV) *m/z* 283 ($[M + 1]^+$, 100); HRMS: (CI, 70 eV) Calculated ($C_{16}H_{24}FO_3$) 283.1709 ($[M + 1]^+$) Found: 283.1708.

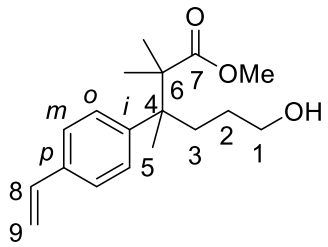
*Methyl 3-(2-(2-hydroxyethyl)phenyl)-2,2,3-trimethylpentanoate (**3ma**)*



From InI_3 (0.0298 g, 0.0601 mmol), 2-(2-(but-2-en-2-yl)phenyl)ethan-1-ol (0.0482 g, 0.273 mmol) and dimethylketene methyl trimethylsilylacetal (0.203 g, 1.16 mmol) following general procedure

(70 °C, 4 h at 1st step), **3ma** (0.043 g, 56%) was obtained after column chromatography (hexane/ethyl acetate = 50:50). IR: (neat) 3417 (OH) cm^{-1}, 1716 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.23 (dd, J = 7.3, 1.8 Hz, 1H, 7-H), 7.19 (dd, J = 6.9, 2.3 Hz, 1H, 4-H), 7.17-7.10 (m, 2H, 5-H and 6-H), 3.94-3.83 (m, 2H, 1-H_2), 3.55 (s, 3H, OMe), 3.28 (dt, J = 13.7, 6.0 Hz, 1H, 2-H^A), 2.91 (dt, J = 13.7, 6.8 Hz, 1H, 2-H^B), 2.51 (dq, J = 14.7, 7.3 Hz, 1H, 10-H^A), 1.60 (s, 3H, 9-Me), 1.60-1.51 (m, 1H, 10-H^B), 1.25 (s, 1H, OH), 1.15 (s, 3H, 12-Me^A), 1.13 (s, 3H, 12-Me^B), 0.719 (t, J = 7.3 Hz, 3H, 11-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.4 (s, C-13), 140.6 (s, C-8), 138.6 (s, C-3), 132.2 (d, C-4), 131.6 (d, C-7), 126.2 (d), 125.1 (d), 64.6 (t, C-1), 51.4 (q, OMe), 50.8 (s, C-12), 49.2 (s, C-9), 39.1 (t, C-2), 31.3 (t, C-10), 24.4 (q, 9-Me), 22.5 (q, 12-Me^A), 22.2 (q, 12-Me^B), 9.3 (q, C-11); MS: (EI, 70 eV) *m*/*z* 249 (M – CH_2CH_3, 12); HRMS: (CI, 70 eV) Calculated ($C_{17}H_{27}O_3$) 279.1960 ($[M + 1]^+$) Found: 279.1958.

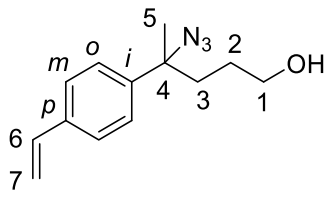
*Methyl 6-hydroxy-2,2,3-trimethyl-3-(4-vinylphenyl)hexanoate (**12oa**)*



From InI_3 (0.0251 g, 0.0507 mmol) in 1,2-dichloroethane (10 mL), 4-(4-vinylphenyl)pent-4-en-1-ol (0.080 g, 0.425 mmol) and dimethylketene methyl trimethylsilylacetal (0.302 g, 1.73 mmol) following general procedure (5 °C, 17 h at 1st step and rt, 12 h at 2nd step), **12oa** (0.0568 g, 46%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3487 (OH) cm^{-1}, 1716 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.33 (d, J = 8.6 Hz, 2H, *m*), 7.20 (d, J = 8.6 Hz, 2H,

o), 6.69 (dd, *J* = 17.7, 10.9 Hz, 1H, 8-H), 5.73 (d, *J* = 17.7 Hz, 1H, 9-H^A), 5.22 (d, *J* = 10.9 Hz, 1H, 9-H^B), 3.62-3.55 (m, 2H, 1-H_2), 3.52 (s, 3H, OMe), 2.30 (ddd, *J* = 14.0, 12.7, 3.2 Hz, 1H, 3-H^A), 1.76-1.60 (br, 1H, OH), 1.66 (ddd, *J* = 13.1, 12.7, 5.0 Hz, 1H, 3-H^B), 1.45-1.35 (m, 1H, 2-H^A), 1.39 (s, 3H, 5-H_3), 1.21-1.10 (m, 1H, 2-H^B), 1.13 (s, 3H, 6-Me^A), 1.04 (s, 3H, 6-Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 177.2 (s, C-7), 142.6 (s, *i*), 136.3 (d, C-8), 135.1 (s, *p*), 128.4 (d, *o*), 125.1 (d, *m*), 113.4 (t, C-9), 63.4 (t, C-1), 51.2 (q, OMe), 49.7 (s, C-6), 45.6 (s, C-4), 31.0 (t, C-3), 28.0 (t, C-2), 22.1 (q, 6-Me^B), 21.7 (q, 6-Me^A), 21.2 (q, C-5); MS: (EI, 70 eV) *m*/*z* 290 (M, 2); HRMS: (CI, 70 eV) Calculated ($C_{18}H_{27}O_3$) 291.1960 ($[M + 1]^+$) Found: 291.1958.

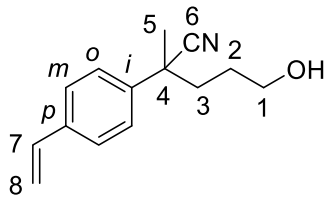
*4-Azido-4-(4-vinylphenyl)pentan-1-ol (**12-N$_3$**)*



From InI_3 (0.0261 g, 0.0527 mmol) in 1,2-dichloroethane (10 mL), 4-(4-vinylphenyl)pent-4-en-1-ol (0.0964 g, 0.512 mmol) and trimethylsilyl azide (0.167 g, 1.45 mmol) following general procedure (5 °C, 5 h at 1st step and rt, 17 h at 2nd step), **12-N$_3$** (0.0228 g, 20%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3398 (OH) cm^{-1}, 2106 (N_3) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.41 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.71 (dd, *J* = 17.9, 10.6 Hz, 1H, 6-H), 5.76 (d, *J* = 17.9 Hz, 1H, 7-H^A), 5.26 (d, *J* = 10.6 Hz, 1H, 7-H^B), 3.53 (t, *J* = 6.3 Hz, 2H, 1-H_2), 1.96-1.85 (m, 2H, 3-H_2), 1.69 (s, 3H, 5-H_3), 1.57-1.32 (m, 3H, 2-H_2 and OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 142.8 (s, *i*), 136.6 (s, *p*), 136.0 (d, C-6), 126.3 (d), 125.7 (d), 114.2 (t, C-7), 66.6 (s, C-4),

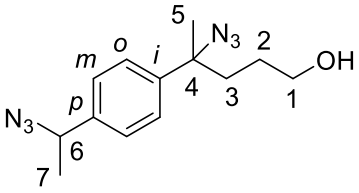
62.6 (t, C-1), 38.5 (t, C-3), 27.5 (t, C-2), 25.7 (q, C-5); MS: (EI, 70 eV) *m*/*z* 171 (M – N_3 – H_2O, 69); HRMS: (CI, 70 eV) Calculated ($C_{13}H_{18}N_3O$) 232.1450 ($[M + 1]^+$) Found: 232.1455.

*5-Hydroxy-2-methyl-2-(4-vinylphenyl)pentanenitrile (**12od**)*



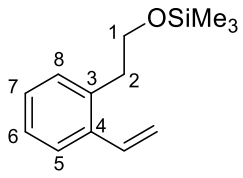
From InI_3 (0.0256 g, 0.0517 mmol) in 1,2-dichloroethane (10 mL), 4-(4-vinylphenyl)pent-4-en-1-ol (0.0949 g, 0.504 mmol) and trimethylsilyl cyanide (0.3 mL, 2.5 mmol) following general procedure (5 °C, 19 h at 1st step and rt, 35 h at 2nd step), **12od** (0.055 g, 50%) was obtained after column chromatography (hexane/ethyl acetate = 70:30). IR: (neat) 3433 (OH) cm^{-1}, 2237 (CN) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.42 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 17.4, 10.6 Hz, 1H, 7-H), 5.76 (d, *J* = 17.4 Hz, 1H, 8-H^A), 5.28 (d, *J* = 10.6 Hz, 1H, 8-H^B), 3.61 (t, *J* = 6.3 Hz, 2H, 1-H_2), 2.08-1.94 (m, 2H, 3-H_2), 1.78-1.65 (m, 1H, 2-H^A), 1.73 (s, 3H, 5-H_3), 1.57-1.38 (m, 2H, 2-H^B and OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 139.3 (s, *i*), 137.1 (s, *p*), 135.8 (d, C-7), 126.7 (d), 125.6 (d), 123.3 (s, C-6), 114.6 (t, C-8), 62.0 (t, C-1), 42.1 (s, C-4), 38.3 (t, C-3), 28.6 (t, C-2), 27.8 (q, C-5); MS: (EI, 70 eV) *m*/*z* 215 (M, 21); HRMS: (CI, 70 eV) Calculated ($C_{14}H_{18}NO$) 216.1388 ($[M + 1]^+$) Found: 216.1391.

*4-Azido-4-(4-(1-azidoethyl)phenyl)butan-1-ol (**13-N_3**)*



To a branched reaction vessel, $Fe_2(ox)_3 \cdot 6H_2O$ (1.19 g, 2.46 mmol) and H_2O (20 mL) was added. After stirring for 1 h, the solution was cooled to 0 ℃ and degassed for 10 minutes. NaN_3 (0.26 g, 4.0 mmol) and THF (10 mL) were added and the vessel was purged by N_2. To the mixture, 2-(2-(prop-1-en-2-yl)phenyl)ethan-1-ol (0.0987 g, 0.524 mmol) in THF (10 mL) was slowly added at 0 ℃, and then $NaBH_4$ (0.06 g, 1,60 mmol) was added at 0 ℃. The reaction mixture was stirred at 0 ℃ for 5 minutes and $NaBH_4$ (0.06 g, 1,60 mmol) was added. After stirring for 50 minutes at 0 ℃, the mixture was quenched by sat. NH_4Cl aq. (8 mL) and then extracted with MeOH (10 wt % in CH_2Cl_2 x 2). The collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate = 60:40, column length 11 cm, diameter 26 mm, spherical silica gel) to give the product **13-N_3** (0.035 g, 28%). IR: (neat) 3401 (OH) cm^{-1}, 2106 (N_3) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40 (d, J = 7.7 Hz, 2H, *o*), 7.32 (d, J = 7.7 Hz, 2H, *m*), 4.62 (q, J = 7.0 Hz, 1H, 6-H), 3.58 (t, J = 6.0 Hz, 2H, 1-H_2), 1.91 (t, J = 7.7 Hz, 2H, 3-H_2), 1.70 (s, 3H, 5-H_3), 1.60-1.46 (m, 1H, 2-H^A), 1.54 (d, J = 7.0 Hz, 3H, 7-H_3), 1.46-1.31 (m, 1H, 2-H^B), 1.31-1.18 (br, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 143.2 (s, *i*), 139.9 (s, *p*), 126.5 (d, *m*), 125.9 (d, *o*), 66.5 (s, C-4), 62.6 (t, C-1), 60.6 (d, C-6), 38.5 (t, C-3), 27.5 (t, C-2), 25.7 (q, C-5), 21.5 (q, C-7); MS: (EI, 70 eV) m/z 232 (M – N_3, 15); HRMS: (EI, 70 eV) Calculated ($C_{13}H_{18}N_6O$) 274.1542 (M) Found: 274.1546.

*Trimethyl(2-vinylphenethoxy)silane (TMS-**1a**)*



TMS-**1a** in a crude product was identified by ^{1}H NMR of an authentic sample of TMS-**1a** (Table 1). The authentic sample was prepared by the following procedure.[7b] The solution of $HN(SiMe_3)_2$ (0.80 mmol, 0.129 g) in CH_2Cl_2 (0.5 mL) was slowly added to the solution of **1a** (0.99 mmol, 0.147 g) and I_2 (0.010 mmol, 0.0025 g) at room temperature. After stirring for 1 hour at room temperature, $Na_2S_2O_3$ (1 g) was added to the reaction mixture and the resulting precipitation was stirred for 30 min. The supernatant liquid was directly purified by silica gel column chromatography (only CH_2Cl_2 was used as a mobile-phase) to obtain trimethyl(2-vinylphenethoxy)silane TMS-**1a** (0.88 mmol, 0.194 g, 89%). IR: (neat) 3087, 3062, 3027, 1627, 1484, 1450, 1412, 1383 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.49 (dd, J = 5.6, 4.1 Hz, 1H), 7.23-7.15 (m, 3H), 7.02 (dd, J = 17.4, 10.9 Hz, 1H), 5.65 (dd, J = 17.4, 1.2 Hz, 1 H), 5.30 (dd, J = 10.9, 1.2 Hz, 1H), 3.72 (t, J = 7.3 Hz, 2H), 2.93 (t, J = 7.3 Hz, 2H), 0.06 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) 137.0 (s), 136.0 (s), 134.5 (d), 130.4 (d), 127.7 (d), 126.7 (d), 125.7 (d), 115.7 (t), 63.2 (t), 36.7 (t), -0.61 (q); MS: (EI, 70 eV) m/z; HRMS: (EI, 70 eV) 220.1283 (M) Calculated Found: 220.1285.

InI_3 catalyzed hydroalkoxylation of styrene derivative 1a (Entry 7 in Table 1). To a solution of InI_3 (0.0250 g, 0.0504 mmol) in 1,2-dichloroethane (1 mL) was added 2-(2-vinylphenyl)ethan-1-ol **1a** (0.0777 g, 0.524 mmol). After stirring at 80 ℃ for 24 h, the mixture was quenched by diethyl ether (2 mL) and sat. Na_2CO_3 aq. (2 mL), and then extracted with diethyl ether (2 mL x 3). The collected

organic layer was dried ($MgSO_4$). The solvent was evaporated and the yield of cyclic ether **4** was determined by ^{1}H-NMR.

InI_3 catalyzed hydroalkoxylation of styrene with methanol (Scheme 3-B). To a solution of InI_3 (0.0241 g, 0.050 mmol) in 1,2-dichloroethane (1.0 mL) and methanol (20 μL, 0.50 mmol) was added styrene (56 μL, 0.50 mmol). After stirring at 80 ℃ for 24 h, the mixture was quenched by diethyl ether (2 mL) and sat. Na_2CO_3 aq. (2 mL), and then extracted with diethyl ether (2 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the yield of benzyl ether **6** was determined by ^{1}H-NMR.

InI_3 catalyzed hydroalkoxylation of styrene derivative 1a in the presence of proton scavenger (Scheme 4). To a solution of InI_3 (0.05 mmol) and proton scavenger (0.15 mmol) in 1,2-dichloroethane (1 mL) was added 2-(2-vinylphenyl)ethan-1-ol **1a** (0.50 mmol). After stirring at 80 ℃ for 24 h, the mixture was quenched by diethyl ether (2 mL) and sat. Na_2CO_3 aq. (2 mL), and then extracted with diethyl ether (2 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent was evaporated and the yield of the cyclic ether **4** was determined by ^{1}H-NMR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of ^{1}H and ^{13}C NMR spectra of materials and products (PDF)

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Notes

The authors declare no competing financial interest.

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