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Palladium-catalyzed synthesis of indane and cyclobuta[*a*]indenes from homoallylic alcohols derived from Baylis–Hillman adducts: base-dependent stereoselectivity for the benzylidene group in cyclobuta[*a*]indene

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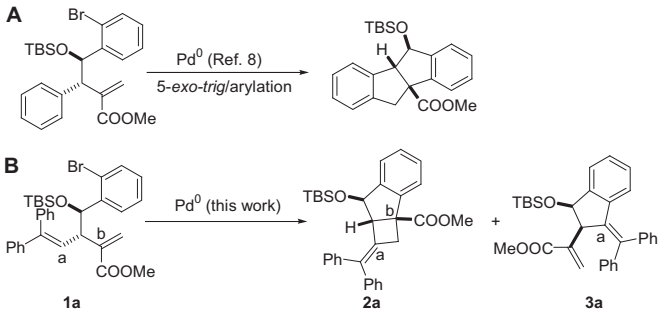
ABSTRACT

Various indane and cyclobuta[*a*]indene derivatives were synthesized by palladium-catalyzed cyclization of homoallylic alcohol derivatives prepared from Baylis–Hillman adducts. Especially, cyclobuta[*a*]indene derivative was synthesized stereoselectively by palladium-catalyzed 5-*exo*-*trig*/4-*exo*-*trig* cascade cyclization, albeit in moderate yield. The *Z* isomer was formed exclusively in the presence of Et_3N by usual Heck-type carbopalladation process while *E* isomer with Cs_2CO_3 most likely by a concerted metalation/deprotonation (CMD) process.

1. Introduction

The palladium-catalyzed domino reactions coupled with suitably designed starting materials allow for rapid establishment of complex molecules.[1–3] In particular, a palladium-catalyzed consecutive carbon–carbon bond-formation through a Heck-type cascade cyclization has become one of the most popular methods for the synthesis of multiple ring system.[2] The formation of a σ-alkylpalladium(II) intermediate lacking a suitable β-hydrogen *syn* with respect to the palladium center is highly required for the effective cascade bond formations.[3] The formation of a cyclobutane ring through a Heck-type cascade cyclization, however, has been scarcely observed.[4,5] In addition, most of the reported examples suffer from low yield, and the structures of cyclobutane derivatives were so limited.[4,5]

Recently, Baylis–Hillman adducts have been used extensively for the synthesis of various important compounds.[6,7] Among the numerous chemical transformations of the Baylis–Hillman adducts Pd-catalyzed reactions have received a special attention,[7,8] including inter- and intramolecular Heck-type reactions. Very recently, we reported an intramolecular Heck/arylation cascade to make the indeno[2,1-*a*]indene scaffold from a TBS-protected homoallylic alcohol, prepared from Baylis–Hillman adduct, as shown in Scheme 1A.[8] During the studies, we were interested in the Pd-catalyzed reaction of 2-phenylstyryl derivative **1a**. The formations of **2a** and **3a** were expected. Heck-type cyclization reaction to the 2-phenylstyryl moiety (position-a) would produce an indane derivative **3a**, while a cyclization reaction to the acrylate moiety (position-b) would produce **2a** via a Heck-type cascade cyclization (5-*exo*-*trig*/4-*exo*-*trig*),[5] as shown in Scheme 1B.



Scheme 1. Synthetic rationale of cyclobuta[*a*]indane and/or indane.

2. Results discussion

The starting material **1a** was prepared in four steps from 3-phenylcinnamaldehyde via the Baylis–Hillman reaction with methyl acrylate, bromination, indium-mediated Barbier-type reaction with

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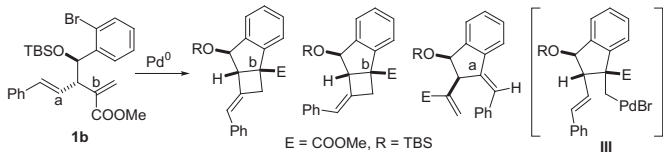
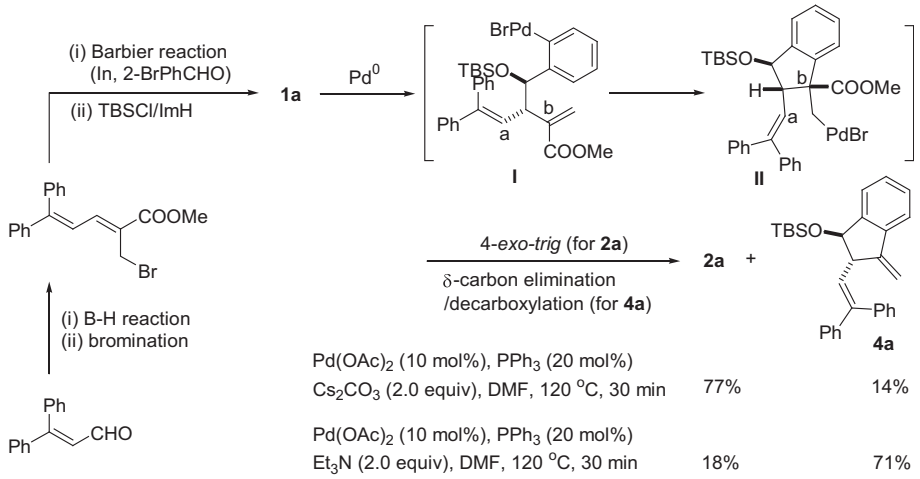
2-bromobenzaldehyde, and protection of the hydroxyl group with TBSCl in good overall yield, according to our previous paper (Scheme 2).[8] When we carried out the reaction of **1a** under the influence of Pd(OAc)$_2$/PPh$_3$/Cs$_2$CO$_3$ in DMF (120 °C, 30 min), cyclobuta[*a*]indene **2a**[9] was isolated in good yield (77%) along with a methyleneindane **4a** (14%),[10] as shown in Scheme 2.[11] Cyclobuta[*a*]indene derivative **2a** might be formed via an initial 5-*exo*-*trig* cyclization of an arylpalladium bromide **I** to acrylate moiety, and subsequent 4-*exo*-*trig* cyclization of the reactive σ-alkylpalladium complex **II**[4a,12] to the 2-phenylstyryl moiety and β-H elimination. Methyleneindane derivative **4a** might be formed via a δ-carbon elimination/decarboxylation of intermediate **II**.[7c,8,13] Interestingly, the formation of indane **3a** was not observed at all. Heck reaction of arylpalladium complex to sterically hindered alkene is known to be difficult,[14] thus the formation of an indane derivative **3a** via a 5-*exo*-*trig* cyclization to the 2-phenylstyryl moiety (position-a) would be difficult, while 4-*exo*-*trig* cyclization of a reactive σ-alkylpalladium complex **II** could be conducted even to the sterically congested 2-phenylstyryl moiety to give **2a**.

syn β-H elimination could explain the formation of **2b**-*Z*. The quite different stereochemical results and the formation of unusual **2b**-*E* were very interesting, although the regioselectivities for the first 5-*exo*-*trig* carbopalladation of arylpalladium complex (positions b:a) were moderate (31–36:51–56).



	2b-*E*	2b-*Z*	3b
Cs_2CO_3/DMF, 110 °C, 10 min (entry 1 in Table 1)	34	2	51
Et_3N/DMF, 110 °C, 30 min (entry 14 in Table 1)	0	31	56

Scheme 3. Stereoselective synthesis of **2b**-*E* (under Cs_2CO_3) and **2b**-*Z* (under Et_3N).



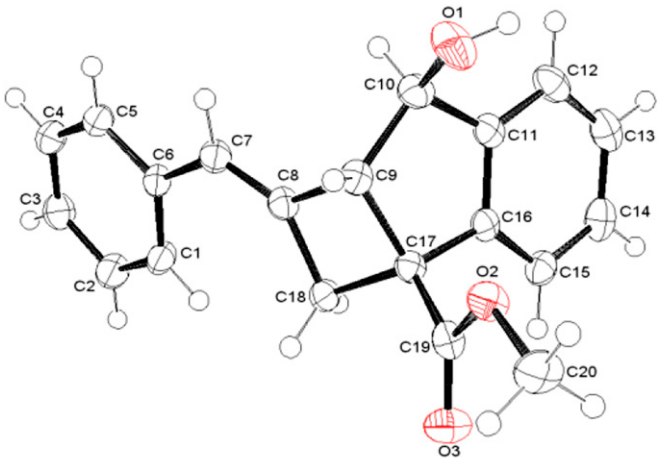
Scheme 2. Regioselective formation of cyclobuta[*a*]indene **2a** (under Cs_2CO_3) and methyleneindane **4a** (under Et_3N).

Interestingly, methyleneindane **4a** was obtained as a major product (71%) when the reaction was carried out in the presence of Et_3N, along with a low yield of **2a** (18%). The results stated that 4-*exo*-*trig* cyclization of an alkylpalladium intermediate **II** was facilitated with Cs_2CO_3 while Et_3N made the δ-carbon elimination/decarboxylation process more facile. Although complete regiocontrol (**2a**+**4a**:**3a**=89–91:0) was achieved very nicely in the first carbopalladation of arylpalladium intermediate **I**; however the highly dependent nature of products distribution (**2a**:**4a**) on the reaction conditions made us suspect the mechanism for the 4-*exo*-*trig* carbopalladation step to **2a**.

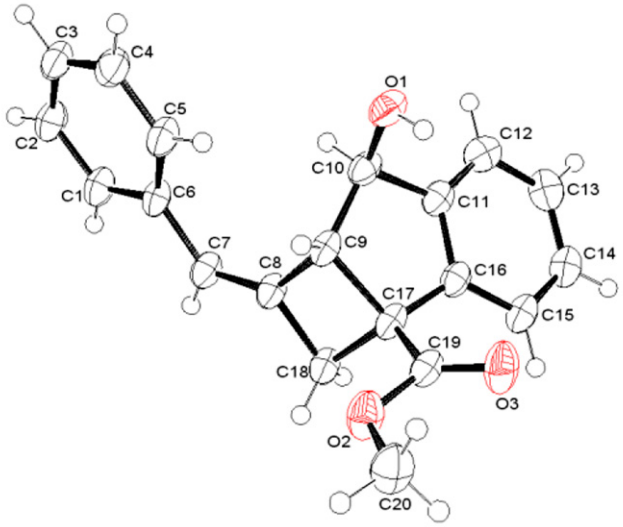
Thus we decided to examine the reaction of cinnamyl derivative **1b** in order to obtain more insights on the mechanism of 4-*exo*-*trig* cyclization. The reaction of **1b** under the influence of Cs_2CO_3 afforded three compounds, **2b**-*E* (34%),[15] **2b**-*Z* (2%),[15] and an indane derivative **3b** (51%), as shown in Scheme 3. The structures of **2b**-*E* and **2b**-*Z* were confirmed unequivocally by their X-ray crystal structures (Fig. 1). In this entry, a 5-*exo*-*trig* cyclization to the styryl moiety (position-a) occurred to produce **3b** as a major product, in sharply contrast to the reaction of **1a**, which did not produce **3a** at all. In contrast, the reaction of **1b** under Et_3N conditions gave **2b**-*Z* (31%) and **3b** (56%). Compound **2b**-*Z* is a generally expected compound that could be formed via a 5-*exo*-*trig*/4-*exo*-*trig* cascade cyclization. The usual *syn*-carbopalladation of an alkylpalladium intermediate **III**, rotation around the C–C bond, and the following

We then performed the reactions of **1b** under different conditions in order to get more insights on the regio- and stereoselectivities, as summarized in Table 1. The regioselectivity for the first carbopalladation (**2b** vs **3b**) was not high in most entries, especially in DMF. Interestingly, a highly selective carbopalladation to styryl moiety forming **3b** was observed in toluene (entries 3, 17 and 18), and the yield reached to 92%. The highest yield of **2b**-*E* reached to 44% (entries 11 and 12) while that of **2b**-*Z* to maximum 31% (entry 14). As noted above, the most interesting point was the stereochemistry of **2b**. Generally, **2b**-*E* was the major product under the influence of Cs_2CO_3 (entries 1–7 and 11–13) while **2b**-*Z* in the presence of an organic base (entries 14–21). The best result for **2b**-*E* was obtained when Cs_2CO_3 and pivalic acid were used together (entry 11).[16a,c,e] In addition, a similar result was obtained without pivalic acid by reducing the amounts of Pd(OAc)$_2$ and PPh$_3$ (entries 12 and 13). The relatively high yield of **2b**-*E* (39%) under the Jeffery conditions (entry 7) is noteworthy.

As noted above, the formation of **2b**-*Z* is usually expected while the formation of **2b**-*E* is quite unusual. Several mechanistic scenarios could account for the formation of **2b**-*E* from the alkylpalladium intermediate **III** (Scheme 4). The first mechanism is an electrophilic metalation/deprotonation (EMD),[12a,17] a stepwise metalation process similar to S_EAr, which involves the ionization of the Pd–Br σ-bond to form an electrophilic cationic palladium species,[17a,b] subsequent formation of a carbocationic intermediate,



2b-*E* in its OH form



2b-*Z* in its OH form

Fig. 1. ORTEP drawings of compounds **2b**-*E* and **2b**-*Z* in their OH forms.

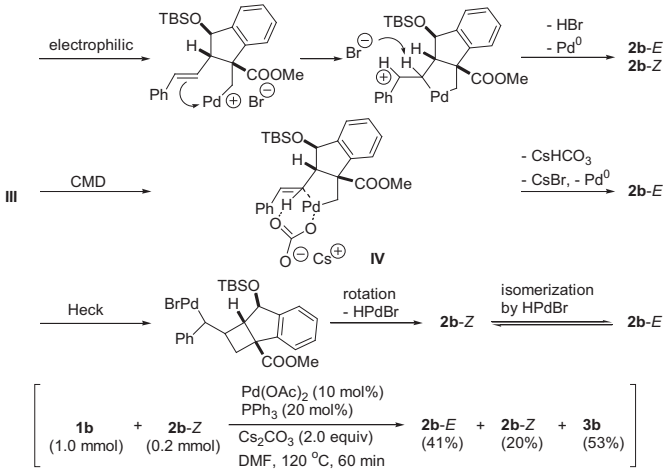
a base (or bromide)-assisted proton abstraction, and reductive elimination of Pd^0. The expected product might be a mixture of **2b**-*Z* and **2b**-*E*. The second possibility is a concerted metalation/deprotonation (CMD) process that suggested by many research groups including Fagnou,[16] Sames,[18a] Charette,[18b] DeBoef,[18c] and Chang,[18d] and the stereochemical outcome of our experiment could be explained nicely with this mechanism. In addition, the reaction conditions that produce **2b**-*E* in high yield (entries 11–13 in Table 1) are very similar to those of the reactions that proceed by a CMD mechanism involving the intermediate **IV**.[16a,c,e] The third possibility could be a formation of **2b**-*Z* as an initial product via the usual Heck reaction and a subsequent double bond isomerization catalyzed by HPdBr species.[5b,14b,19] However, the first and third mechanisms are insufficient to explain the high *E*-selectivity (>44/1) when we consider the small energy difference[20] between **2b**-*E* and **2b**-*Z* although both mechanisms cannot be ruled out completely. In addition, the possibility for HPdBr-catalyzed isomerization of **2b**-*Z* to **2b**-*E* was found to be very low based on the following experiment, shown in Scheme 4. Compound **2b**-*Z* was recovered completely intact under the reaction conditions, and compounds **2b**-*E* and **3b** must be produced from the reaction of **1b**. Thus, we

Table 1
Pd-catalyzed cyclizations of **1b**

Entry	Conditions[a,b]	**2b**-*E*[c]	**2b**-*Z*[c]	**3b**[c]
1	Cs_2CO_3, DMF, 110 °C, 10 min	**34**	2	51
2	Cs_2CO_3, CH_3CN, reflux, 10 min	13	4	68
3	Cs_2CO_3, toluene, reflux, 10 min	5	5	**82**
4	Cs_2CO_3, DMF, 140 °C, 10 min	31	4	56
5	Cs_2CO_3, DMF, 80 °C, 20 min	25	3	63
6[d]	Cs_2CO_3, DMF, 110 °C, 3 h	30	2	49
7[e]	Cs_2CO_3, DMF, 120 °C, 20 min	**39**	4	33
8	Na_2CO_3, DMF, 120 °C, 30 min	20	18	54
9	$NaHCO_3$, DMF, 120 °C, 30 min	25	19	54
10	KOAc, DMF, 110 °C, 20 min	24	20	51
11[f]	Cs_2CO_3, DMF, 120 °C, 30 min	**44**	<1	53
12[g]	Cs_2CO_3, DMF, 120 °C, 10 min	**44**	<1	51
13[h]	Cs_2CO_3, DMF, 120 °C, 2 h	**41**	<1	50
14	Et_3N, DMF, 110 °C, 30 min	0	**31**	**56**
15	Et_3N, DMF, 80 °C, 30 h	0	26	53
16	Et_3N, CH_3CN, reflux, 1 h	0	17	77
17	Et_3N, toluene, reflux, 3 h	0	7	**87**
18	Et_3N, toluene, 70 °C, 12 h	0	3	**92**
19	DIEA, DMF, 110 °C, 10 min	0	23	69
20	DBU, DMF, 120 °C, 20 min	11	19	35
21	DABCO, DMF, 110 °C, 2 h	0	13	64

[a] $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %) is common unless otherwise stated.
[b] Base was used in 2.0 equiv unless otherwise stated.
[c] Isolated yield (%).
[d] $(t\text{-}Bu)_3P$ was used instead of PPh_3.
[e] TBAC (3.0 equiv) was used instead of PPh_3.
[f] PivOH (30 mol %) was added.
[g] $Pd(OAc)_2$ (10 mol %) and PPh_3 (5 mol %) were used.
[h] $Pd(OAc)_2$ (3 mol %) and PPh_3 (1 mol %) were used.

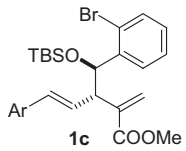
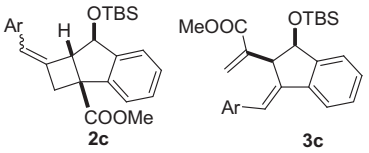
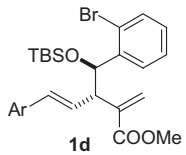
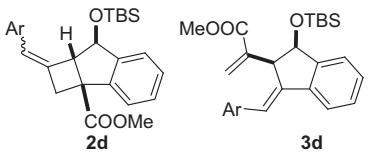
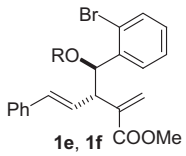
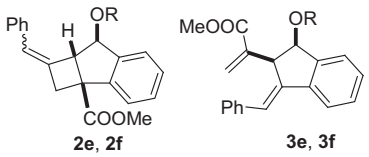
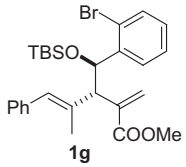
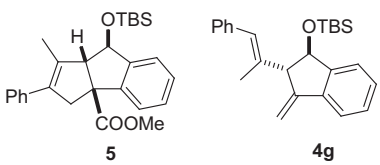
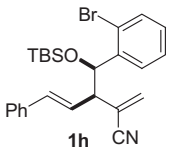
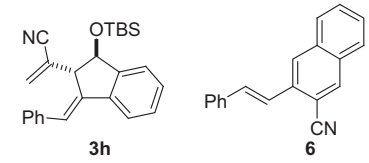
assumed that the most likely mechanism would be a CMD process, which could produce **2b**-*E* as the sole product. Although the base-mediated CMD process has been suggested mostly in palladium-catalyzed aryl C–H activation by arylpalladium intermediate[16,18] the mechanism might be acting in the case of alkenyl C–H activation by alkylpalladium species.[4a,21] However, there was no example involving an alkenyl C–H activation, most likely by a CMD process, by alkylpalladium species, to the best of our knowledge.



Scheme 4. Plausible mechanisms for the formation of **2b**-*E*.

In order to check the contribution of EMD mechanism, we examined the reactions of *p*-fluoro derivative **1c** and *p*-methoxy derivative **1d**. If an EMD mechanism contributes to some extent, then even a subtle change could be observed in the reaction rate or on the ratios of **2**/**3** and *E*/*Z*. However, the results were very similar with that of **1b**, as shown in Table 2 (entries 1 and 2). Corresponding *E*-isomers were obtained in 37–39% under the influence

Table 2
Palladium-catalyzed domino reactions of **1c**–**h**

Entry	Substrate	Product (%)[a]
1[b]	 **1c**	 **2c** **3c** Condition A: **2c**-*E* (37), **2c**-*Z* (0), **3c** (55) Condition B: **2c**-*E* (0), **2c**-*Z* (30), **3c** (59)
2[c]	 **1d**	 **2d** **3d** Condition A: **2d**-*E* (39), **2d**-*Z* (0), **3d** (52) Condition B: **2d**-*E* (0), **2d**-*Z* (23),[d] **3d** (62)[d]
3	 **1e**, **1f** **1e**: RO = AcO **1f**: RO = TBDPSO	 **2e**, **2f** **3e**, **3f** Condition A: **2e**-*E* (23), **2e**-*Z* (0), **3e** (29) Condition B: **2e**-*E* (0), **2e**-*Z* (15), **3e** (57) Condition A: **2f**-*E* (40), **2f**-*Z* (0), **3f** (55)
4	 **1g**	 **5** **4g** Condition A: **5** (85), **4g** (12) Condition B: **5** (22), **4g** (57)
5	 **1h**	 **3h** **6** Condition A: **3h** (73), **6** (17)

[a]Condition A: $Pd(OAc)_2$ (10 mol %), PPh_3 (5 mol %), Cs_2CO_3 (2.0 equiv), DMF, 120 °C, 30 min. Condition B: $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), Et_3N (2.0 equiv), DMF, 120 °C, 30 min.
[b]Ar is 4-fluorophenyl.
[c]Ar is 4-methoxyphenyl.
[d]Compounds **2d**-*Z* and **3d** were isolated together in 85%, and the ratio was determined based on ^1H NMR.

of Cs_2CO_3 (condition A), while *Z*-isomers 23–30% in the presence of Et_3N (condition B) along with indane derivatives **3c** and **3d** in 52–62%. Thus, the EMD mechanism would not be the major process for the formation of *E*-isomers, **2c**-*E* and **2d**-*E*. The reaction of the acetate **1e** showed a similar reactivity (entry 3) although the combined yield of **2e** and **3e** was somewhat lower in both conditions. However, the *E*/*Z* selectivity was strictly obeyed; **2e**-*E* was formed under the influence of Cs_2CO_3 while **2e**-*Z* with Et_3N. TBDPS derivative **1f** showed the same reactivity (entry 3). Based on the experimental results, we tentatively concluded that the formation of *E*-isomers of **2a**–**f** would involve an alkenyl C–H activation process most likely via a CMD mechanism. When we block the α-position of the styryl moiety with a methyl group as in **1g** (entry 4) in order to prevent 4-*exo*-*trig* cyclization, the reaction proceeded in a 5-*exo*/5-*endo* cascade cyclization to produce cyclopenta[*a*]indene derivative **5**[22,23] as the major product (85%), along with a low yield of **4g** under the influence of Cs_2CO_3.[11] Under the conditions of Et_3N, the first cyclization also occurred to the acrylate moiety; however, δ-carbon elimination/decarboxylation process proceeded predominantly to produce methyleneindane **4g** as the major product (57%). The structure of **5** was confirmed unequivocally by its X-ray crystal structure (Fig. 2).[22] The reaction of nitrile derivative **1h** (entry 5) produced **3h** as the major product (73%) along with a naphthalene **6** (17%) via a 6-*endo* cyclization/aromatization process, as observed in our previous paper.[8]

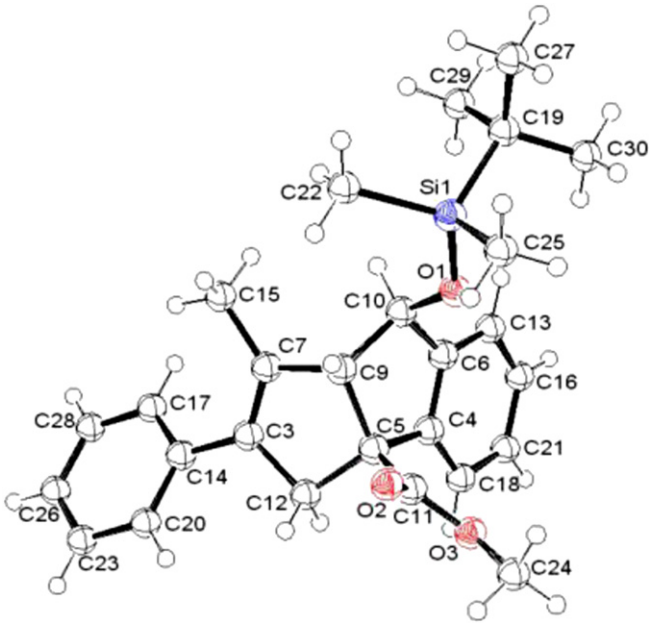
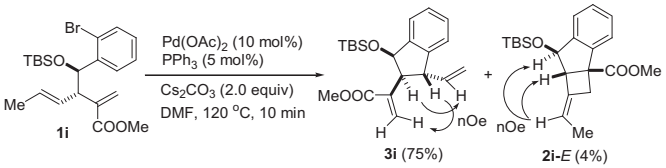


Fig. 2. ORTEP drawing of compound **5**.

As a last entry, we examined the propenyl derivative **1i** under the influence of Cs_2CO_3, as shown in Scheme 5. Vinylindane **3i** was produced as a major product (75%) via 5-*exo*-*trig* cyclization to the propenyl moiety and the following β-H elimination, which occurred regioselectively at the methyl group to form the vinylindane **3i**.[11] The stereochemistry of **3i** was deduced by NOE experiments, and the results stated that the 5-*exo*-*trig* cyclization of arylpalladium intermediate occurred selectively to a *Si* face of the propenyl moiety. Although cyclobuta[*a*]indene **2i** was formed in a trace amount (4%) the stereochemistry was again *E* that produced most likely by a CMD process.



Scheme 5. Regio- and stereoselective synthesis of vinylindane **3i**.

In conclusion, various cyclobuta[*a*]indenes were synthesized stereoselectively along with cyclopenta[*a*]indene, methylene- and arylideneindane derivatives by palladium-catalyzed reactions from modified Baylis–Hillman adducts of cinnamaldehydes. Reaction conditions affected much on the regioselectivity as well as stereochemistry of products. During the formation of a cyclobutane ring, the first example of alkenyl C–H activation, most likely via a CMD process, was observed in the presence of Cs_2CO_3. In contrast, usual *syn*-carbopalladation, a kind of π-bond activation of C]C double

bond, worked in the presence of Et_3N. As far as we are aware this is the first example where alkene is activated stereoselectively by adopting different Heck protocols. The result implies that, whereas olefin coordination (Heck reaction) is favored in the presence of Et_3N, the alkenyl C–H activation (most likely by CMD process) occurs preferentially in the presence of Cs_2CO_3. A few examples have been reported that could not be explained by a *syn* β-H elimination process during the Heck reaction,[21] and our observation strongly suggests the involvement of a direct C–H activation process, most likely via a CMD process. Further studies are underway in this regard.

3. Experimental

3.1. General procedure

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen unless otherwise noted. Thin layer chromatography (TLC) was performed with pre-coated silica gel plates (Kieselgel $60F_{254}$, Merck). Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with *p*-anisaldehyde stain followed by heating. The separations were carried out by flash column chromatography over silica gel 60 (230–400 mesh ASTM). Organic extracts were dried over anhydrous $MgSO_4$ and the solvents were removed on a rotary evaporator under water aspirator pressure. All reagents were purchased from commercial sources and used without further treatment.

Melting points were measured with a Thomas–Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz) spectra were measured on a Varian Unity Plus 300. The signal positions are reported in parts per million relative to TMS (δ scale) used as an internal standard. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Chemical shifts of the ^{13}C NMR (75 MHz) spectra were measured relative to $CDCl_3$ (77.23 ppm). IR spectra were recorded on a Jasco FT-IR 410 spectrometer and are reported in cm^{-1}. Mass spectra were obtained from the Korea Basic Science Institute (Gwangju branch) using ESI^+ method. Elemental analyses (C, H, and N) were performed with a Fisons EA-1108 Elemental Analyzer machine at Korea Research Institute of Chemical Technology, Daejeon, Korea.

3.2. Typical procedure for the synthesis of starting material 1a

A solution of β-phenylcinnamaldehyde (625 mg, 3.0 mmol), DABCO (168 mg, 1.5 mmol), and phenol (85 mg, 0.9 mmol) in methyl acrylate (1291 mg, 15.0 mmol) was stirred at room temperature for 4 days under nitrogen atmosphere, quenched with water (10 mL), and extracted with diethyl ether (30 mL×3). The combined organic layers were washed with dilute HCl solution, brine, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatographic purification process (hexanes/ethyl acetate 20:1) to afford a Baylis–Hillman alcohol (582 mg, 66%) as colorless oil. Its selected spectroscopic data are as follows: IR (film) 3474, 3024, 1719, 1275 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.09 (d, J=6.0 Hz, 1H), 3.77 (s, 3H), 4.95 (dd, J=9.3 and 6.0 Hz, 1H), 5.75 (s, 1H), 6.23 (s, 1H), 6.24 (d, J=9.3 Hz, 1H), 7.19–7.23 (m, 2H), 7.25–7.27 (m, 5H), 7.30–7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.96, 69.77, 126.14, 127.49, 127.58, 127.62, 127.76, 128.14, 128.23, 129.59, 138.92, 141.38, 141.50, 144.79, 166.94; ESIMS m/z 317 $[M+Na]^+$. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.72; H, 6.20.

To a stirred solution of the prepared Baylis–Hillman alcohol (441 mg, 1.5 mmol) in dry dichloromethane (5 mL) was added dropwise a solution of PBr_3 (405 mg, 1.5 mmol, in 2.5 mL dry CH_2Cl_2) at 0 °C over 10 min. The reaction mixture was stirred for 1 h at the same temperature. The reaction mixture was poured into ice water and extracted with dichloromethane. The organic layers were washed with water, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatographic purification process (hexanes/ethyl acetate 30:1) to afford Baylis–Hillman bromide (503 mg, 94%) as a pale yellow solid. Its selected spectroscopic data are as follows: mp 136–139 °C; IR (KBr) 3054, 1709, 1604, 1278 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.74 (s, 3H), 4.50 (s, 2H), 7.02 (d, J=12.0 Hz, 1H), 7.19–7.24 (m, 2H), 7.31–7.38 (m, 5H), 7.40–7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.16, 52.12, 121.56, 127.62, 128.27, 128.43, 128.51, 128.68, 129.13, 130.58, 138.29, 140.10, 141.45, 153.26, 166.47; ESIMS m/z 357 $[M+H]^+$, 359 $[M+H+2]^+$. Anal. Calcd for $C_{19}H_{17}BrO_2$: C, 63.88; H, 4.80. Found: C, 63.92; H, 4.97.

To a stirred solution of the prepared Baylis–Hillman bromide (536 mg, 1.5 mmol) and 2-bromobenzaldehyde (306 mg, 1.7 mmol) in aqueous THF (1:1, 5 mL) was added indium powder (188 mg, 1.7 mmol) and stirred at room temperature for 1 h. The reaction mixture was poured into water (10 mL), extracted with diethyl ether (30 mL×3). The combined organic layers were washed with brine and dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography (hexanes/EtOAc, 10:1) to afford homoallyl alcohol (*syn*) as colorless oil, 534 mg (77%). Its selected spectroscopic data are as follows: IR (film) 3435, 3056, 1716, 1441, 1266 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.73–3.78 (m, 1H), 3.79 (s, 3H), 4.25 (d, J=2.1 Hz, 1H), 5.19 (t, J=2.1 Hz, 1H), 5.64 (t, J=1.2 Hz, 1H), 6.20 (d, J=0.9 Hz, 1H), 6.47–6.52 (m, 3H), 7.07 (ddd, J=7.5, 7.5 and 1.8 Hz, 1H), 7.14–7.31 (m, 9H), 7.38 (dd, J=8.1 and 1.2 Hz, 1H), 7.62 (dd, J=7.8 and 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.49, 52.35, 75.17, 122.04, 132.02, 126.93, 127.12, 127.28, 127.89, 128.04 (2C), 128.49, 128.76, 129.03, 132.41, 139.07, 141.21, 141.23, 141.72, 145.34, 168.75 (one carbon is overlapped); ESIMS m/z 463 $[M+H]^+$, 465 $[M+H+2]^+$. Anal. Calcd for $C_{26}H_{23}BrO_3$: C, 67.39; H, 5.00. Found: C, 67.52; H, 5.24.

A solution of the prepared homoallyl alcohol (463 mg, 1.0 mmol), TBSCl (300 mg, 2.0 mmol), and imidazole (204 mg, 3.0 mmol) in DMF (3 mL) was stirred at room temperature for 12 h under nitrogen atmosphere. The reaction mixture was poured into water (10 mL), extracted with diethyl ether (30 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatographic purification process (hexanes/ether, 50:1) to afford compound **1a**, 487 mg (83%) as colorless oil. Other compounds **1b**–**i** were prepared similarly and the spectroscopic data are as follows. Preparation of starting materials for the synthesis of **1a**–**i** is noted in detail in Supplementary data with their spectroscopic data.

*3.2.1. Compound **1a**.* Yield 83%; colorless oil; IR (film) 2949, 2855, 1722, 1257, 1081 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 3H), 0.22 (s, 3H), 1.13 (s, 9H), 3.96 (s, 3H), 4.04 (dd, J=10.8 and 3.6 Hz, 1H), 5.55 (d, J=3.6 Hz, 1H), 5.94 (s, 1H), 6.58 (s, 1H), 6.66 (d, J=10.8 Hz, 1H), 6.81–6.84 (m, 2H), 7.29 (ddd, J=7.5, 7.5 and 1.5 Hz, 1H), 7.38–7.52 (m, 9H), 7.63 (dd, J=8.1 and 1.2 Hz, 1H), 7.77 (d, J=6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.88, −4.59, 18.42, 26.16, 46.86, 51.98, 74.28, 121.94, 126.04, 126.69, 127.15, 127.27, 127.39, 128.13, 128.31, 128.55, 128.71, 129.39, 130.01, 132.56, 139.76, 140.76, 142.58, 142.75, 143.86, 167.34; ESIMS m/z 577 $[M+H]^+$, 579 $[M+H+2]^+$. Anal. Calcd for $C_{32}H_{37}BrO_3Si$: C, 66.54; H, 6.46. Found: C, 66.39; H, 6.65.

*3.2.2. Compound **1b**.* Yield 95%; colorless oil; IR (film) 2951, 2857, 1723, 1464, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 3H), 0.24 (s, 3H), 1.08 (s, 9H), 3.97 (s, 3H), 4.02 (dd, J=9.3 and 5.1 Hz, 1H), 5.61 (d, J=5.1 Hz, 1H), 5.92 (s, 1H), 6.44 (d, J=15.9 Hz, 1H), 6.53 (s, 1H), 6.71 (dd, J=15.9 and 9.3 Hz, 1H), 7.26 (ddd, J=7.5, 7.5 and 1.8 Hz, 1H), 7.41–7.52 (m, 6H), 7.68–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.03, −4.85, 18.05, 25.79, 51.41, 51.82, 74.30, 121.87, 126.14, 126.71, 127.09, 127.71, 127.76, 128.39, 128.63, 129.88, 132.19, 132.66, 137.47, 140.04, 142.30, 167.09; ESIMS m/z 501 $[M+H]^+$, 503

$[M+H+2]^+$. Anal. Calcd for $C_{26}H_{33}BrO_3Si$: C, 62.27; H, 6.63. Found: C, 62.46; H, 6.59.

3.2.3. Compound ***1c***. Yield 85%; colorless oil; IR (film) 2952, 2856, 1722, 1509, 1233 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.23 (s, 3H), 0.02 (s, 3H), 0.85 (s, 9H), 3.75 (s, 3H), 3.79 (dd, *J*=9.3 and 5.4 Hz, 1H), 5.38 (d, *J*=5.4 Hz, 1H), 5.68 (s, 1H), 6.18 (d, *J*=15.9 Hz, 1H), 6.30 (s, 1H), 6.40 (dd, *J*=15.9 and 9.3 Hz, 1H), 6.94–7.08 (m, 3H), 7.20–7.28 (m, 3H), 7.46–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.74, −4.56, 18.34, 26.06, 51.83, 52.14, 115.58 (d, *J*=21.2 Hz), 122.21, 127.01, 127.80, 127.90, 128.04, 128.97, 130.12, 131.75, 132.52, 133.90 (d, *J*=3.4 Hz), 140.22, 142.57, 162.34 (d, *J*=245.0 Hz), 167.36; ESIMS *m/z* 519 $[M+H]^+$, 521 $[M+H+2]^+$. Anal. Calcd for $C_{26}H_{32}BrFO_3Si$: C, 60.11; H, 6.21. Found: C, 60.15; H, 6.44.

3.2.4. Compound ***1d***. Yield 78%; colorless oil; IR (film) 2951, 2855, 1721, 1511, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.32 (s, 3H), −0.08 (s, 3H), 0.76 (s, 9H), 3.64 (s, 3H), 3.69 (s, 3H), 3.65–3.70 (m, 1H), 5.28 (d, *J*=5.1 Hz, 1H), 5.91 (s, 1H), 6.06 (d, *J*=15.9 Hz, 1H), 6.19 (s, 1H), 6.24 (dd, *J*=15.9 and 9.0 Hz, 1H), 6.71–6.76 (m, 2H), 6.91–6.96 (m, 1H), 7.09–7.15 (m, 3H), 7.35–7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.04, −4.87, 18.03, 25.77, 51.43, 51.76, 55.15, 74.34, 113.80, 121.86, 125.44, 126.65, 127.22, 127.61, 128.56, 129.91, 130.29, 132.03, 132.13, 140.18, 142.36, 158.83, 167.11; ESIMS *m/z* 531 $[M+H]^+$, 533 $[M+H+2]^+$. Anal. Calcd for $C_{27}H_{35}BrO_4Si$: C, 61.01; H, 6.64. Found: C, 61.23; H, 6.55.

3.2.5. Compound ***1e***. Yield 99%; colorless oil; IR (film) 3026, 1743, 1722, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.04 (s, 3H), 3.72 (s, 3H), 4.10 (m, 1H), 5.75 (s, 1H), 6.28–6.38 (m, 3H), 6.49 (d, *J*=6.3 Hz, 1H), 7.09 (ddd, *J*=7.8, 7.8 and 1.5 Hz, 1H), 7.19–7.31 (m, 6H), 7.37 (dd, *J*=8.1 and 1.8 Hz, 1H), 7.52 (dd, *J*=8.1 and 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.91, 48.73, 52.00, 75.12, 122.85, 126.28, 126.69, 127.10, 127.45, 127.47, 128.46, 129.01, 129.37, 132.92, 133.43, 136.96, 137.94, 139.28, 166.58, 169.55; ESIMS *m/z* 429 $[M+H]^+$, 431 $[M+H+2]^+$. Anal. Calcd for $C_{22}H_{21}BrO_4$: C, 61.55; H, 4.93. Found: C, 61.83; H, 5.07.

3.2.6. Compound ***1f***. Yield 88%; colorless oil; IR (film) 3057, 2951, 2857, 1721, 1434, 1076 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 9H), 3.54 (s, 3H), 3.83–3.88 (m, 1H), 5.46–5.48 (m, 2H), 6.11 (s, 1H), 6.23–6.35 (m, 2H), 6.97 (ddd, *J*=7.5, 7.5 and 1.5 Hz, 1H), 7.11–7.42 (m, 15H), 7.61–7.65 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.31, 26.98, 51.67, 52.63, 75.26, 122.87, 126.27, 126.77, 127.12, 127.36, 128.01, 128.30, 128.63, 129.29, 129.42, 130.14, 132.01, 132.57, 133.15, 133.52, 136.02, 136.14, 137.31, 139.12, 141.76, 166.79 (two carbons are overlapped); ESIMS *m/z* 625 $[M+H]^+$, 627 $[M+H+2]^+$. Anal. Calcd for $C_{36}H_{37}BrO_3Si$: C, 69.11; H, 5.96. Found: C, 69.44; H, 6.14.

3.2.7. Compound ***1g***. Yield 90%; colorless oil; IR (film) 2951, 2893, 2857, 1723, 1440, 1251, 1086 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.36 (s, 3H), −0.06 (s, 3H), 0.82 (s, 9H), 1.84 (d, *J*=1.2 Hz, 3H), 3.63 (s, 3H), 4.00 (d, *J*=7.8 Hz, 1H), 5.49 (d, *J*=7.8 Hz, 1H), 5.98 (s, 1H), 6.23 (s, 1H), 6.56 (s, 1H), 7.05–7.10 (m, 1H), 7.16–7.33 (m, 6H), 7.45 (dd, *J*=8.1 and 1.5 Hz, 1H), 7.56 (d, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.05, −4.61, 17.08, 17.93, 25.72, 51.85, 55.73, 73.53, 122.98, 126.04, 126.36, 127.25, 127.95, 128.88, 128.94, 129.28, 129.99, 132.23, 135.87, 138.37, 138.95, 142.23, 167.43; ESIMS *m/z* 515 $[M+H]^+$, 517 $[M+H+2]^+$. Anal. Calcd for $C_{27}H_{35}BrO_3Si$: C, 62.90; H, 6.84. Found: C, 63.11; H, 6.59.

3.2.8. Compound ***1h***. Yield 85%; white solid, mp 81–83 °C; IR (KBr) 2932, 2856, 2222, 1256, 1088 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.21 (s, 3H), 0.11 (s, 3H), 0.91 (s, 9H), 3.35 (t, *J*=6.0 Hz, 1H), 5.32 (d, *J*=6.0 Hz, 1H), 5.50 (s, 1H), 5.88 (s, 1H), 6.32–6.40 (m, 2H), 7.11 (ddd, *J*=7.8, 7.8 and 1.8 Hz, 1H), 7.23–7.34 (m, 6H), 7.48 (dd, *J*=7.8 and 1.2 Hz, 1H), 7.52 (d, *J*=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.16, −4.80, 18.14, 25.72, 56.36, 75.82, 118.20, 122.02, 122.50, 125.72, 126.41, 127.28, 127.75, 128.55, 129.16, 132.32, 132.74, 133.14, 136.57, 141.02 (one carbon is overlapped); ESIMS *m/z* 468 $[M+H]^+$, 470 $[M+H+2]^+$. Anal. Calcd for $C_{25}H_{30}BrNOSi$: C, 64.09; H, 6.45; N, 2.99. Found: C, 64.28; H, 6.53; N, 2.77.

3.2.9. Compound ***1i***. Yield 90%; colorless oil; IR (film) 2952, 2857, 1723, 1256, 1084 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.25 (s, 3H), 0.00 (s, 3H), 0.85 (s, 9H), 1.60 (dd, *J*=6.6 and 1.5 Hz, 3H), 3.57 (dd, *J*=9.3 and 5.4 Hz, 1H), 3.72 (s, 3H), 5.20–5.32 (m, 2H), 5.62 (s, 1H), 5.65–5.74 (m, 1H), 6.24 (s, 1H), 7.06 (ddd, *J*=7.8, 7.8 and 1.5 Hz, 1H), 7.23 (d, *J*=7.5 Hz, 1H), 7.43–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.09, −4.87, 17.91, 18.06, 25.76, 51.05, 51.73, 74.21, 121.89, 126.46, 127.35, 128.33 (2C), 128.43, 130.12, 132.06, 140.40, 142.56, 167.31; ESIMS *m/z* 439 $[M+H]^+$, 441 $[M+H+2]^+$. Anal. Calcd for $C_{21}H_{31}BrO_3Si$: C, 57.39; H, 7.11. Found: C, 57.58; H, 7.02.

3.3. Typical procedure for the Pd-catalyzed reaction of 1a

A solution of **1a** (173 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 10 mol %), PPh_3 (16 mg, 20 mol %), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2 mL) was stirred at 120 °C for 30 min under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, quenched with water (10 mL), and extracted with diethyl ether (30 mL×3). The combined organic layers were washed with dilute HCl solution, brine, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatographic purification process (hexanes/ether 50:1) to afford compounds **2a** (115 mg, 77%) as a white solid and **4a** (18 mg, 14%) as colorless oil.

3.3.1. Compound ***2a***. Yield 77%; white solid, mp 127–129 °C; IR (KBr) 2951, 2856, 1729, 1252, 1077 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.22 (s, 3H), −0.20 (s, 3H), 0.75 (s, 9H), 2.94 (dd, *J*=16.2 and 3.3 Hz, 1H), 3.57 (d, *J*=16.2 Hz, 1H), 3.72 (s, 3H), 4.18 (d, *J*=3.3 Hz, 1H), 4.8 (s, 1H), 6.94–6.98 (m, 2H), 7.10–7.43 (m, 11H), 7.45–7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.87, −4.56, 17.85, 25.59, 42.65, 52.14, 54.28, 61.49, 77.28, 125.06, 125.82, 126.69, 127.10, 127.94, 128.04, 128.38, 128.65, 129.07, 129.15, 132.99, 138.99, 140.04, 140.32, 143.76, 146.22, 174.03; ESIMS *m/z* 519 $[M+Na]^+$. Anal. Calcd for $C_{32}H_{36}O_3Si$: C, 77.38; H, 7.31. Found: C, 77.64; H, 7.49.

3.3.2. Compound ***4a***. Yield 71%; colorless oil; IR (film) 2958, 2855, 1259, 1083 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 3H), 0.22 (s, 3H), 0.92 (s, 9H), 3.74–3.81 (m, 1H), 5.08 (d, *J*=2.7 Hz, 1H), 5.13 (d, *J*=6.3 Hz, 1H), 5.52 (d, *J*=3.0 Hz, 1H), 6.08 (d, *J*=10.2 Hz, 1H), 7.24–7.32 (m, 13H), 7.44–7.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −4.33, −4.01, 18.01, 25.81, 56.49, 79.97, 104.72, 120.60, 124.15, 127.21, 127.27, 127.55, 128.06, 128.09, 128.17, 128.81, 128.82, 129.73, 138.86, 139.39, 142.69, 145.37, 146.17, 149.30; ESIMS *m/z* 461 $[M+Na]^+$. Anal. Calcd for $C_{30}H_{34}OSi$: C, 82.14; H, 7.81. Found: C, 82.39; H, 7.67.

3.3.3. Compound ***2b****-E*. Yield 44%; white solid, mp 116–118 °C; IR (KBr) 2951, 2889, 2855, 1731, 1233, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.21 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 2.98 (ddd, *J*=16.5, 2.7 and 2.7 Hz, 1H), 3.74 (s, 3H), 3.79 (dd, *J*=16.5 and 2.7 Hz, 1H), 4.01 (t, *J*=2.7 Hz, 1H), 5.20 (s, 1H), 6.39 (q, *J*=2.7 Hz, 1H), 7.12–7.16 (m, 3H), 7.22–7.40 (m, 5H), 7.44–7.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.34, −4.32, 18.27, 25.86, 42.62, 52.30, 55.92, 61.64, 80.02, 124.97, 125.45, 126.15, 126.67, 127.21, 128.35, 128.40, 129.35, 136.74, 137.78, 143.14, 146.00, 173.87; ESIMS *m/z* 443 $[M+Na]^+$. Anal. Calcd for $C_{26}H_{32}O_3Si$: C, 74.24; H, 7.67. Found: C, 74.46; H, 7.69.

3.3.4. Compound ***2b****-Z*. Yield 31%; colorless oil; IR (film) 2951, 2855, 1730, 1235, 1082 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 3H),

0.13 (s, 3H), 0.91 (s, 9H), 2.75 (ddd, J=15.9, 3.3 and 2.1 Hz, 1H), 3.65 (dd, J=15.9 and 2.1 Hz, 1H), 3.81 (s, 3H), 4.35 (t, J=3.3 Hz, 1H), 5.17 (s, 1H), 6.22 (q, J=2.1 Hz, 1H), 7.26–7.33 (m, 3H), 7.34–7.44 (m, 5H), 7.54 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.32, −3.91, 17.98, 25.61, 42.70, 52.20, 54.89, 61.72, 76.90, 125.03, 125.92, 126.59, 126.67, 127.71, 127.94, 128.54, 129.22, 136.16, 136.78, 143.40, 145.96, 174.00; ESIMS m/z 443 $[M+Na]^+$. Anal. Calcd for $C_{26}H_{32}O_3Si$: C, 74.24; H, 7.67. Found: C, 74.31; H, 7.86.

3.3.5. Compound ***3b****.* Yield 92%; colorless oil; IR (film) 2952, 2891, 2857, 1719, 1251, 1131 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.14 (s, 3H), 0.22 (s, 3H), 0.93 (s, 9H), 3.79 (s, 3H), 4.90 (d, J=7.2 Hz, 1H), 5.33 (t, J=1.2 Hz, 1H), 5.42 (d, J=7.2 Hz, 1H), 6.12 (d, J=0.9 Hz, 1H), 7.01 (d, J=1.2 Hz, 1H), 7.21–7.24 (m, 1H), 7.29–7.38 (m, 7H), 7.59–7.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.83, −4.72, 18.19, 25.78, 50.13, 51.84, 77.10, 119.52, 121.50, 124.86, 126.62, 127.01, 128.26, 128.46 (2C), 128.66, 136.71, 138.22, 141.20, 144.87, 167.70 (one carbon is overlapped); ESIMS m/z 443 $[M+Na]^+$. Anal. Calcd for $C_{26}H_{32}O_3Si$: C, 74.24; H, 7.67. Found: C, 74.47; H, 7.69.

3.3.6. Compound ***2c****-E.* Yield 37%; colorless oil; IR (film) 2952, 2891, 2857, 1731, 1509, 1234, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.21 (s, 3H), 0.22 (s, 3H), 0.94 (s, 9H), 3.94 (ddd, J=16.2, 3.0 and 3.0 Hz, 1H), 3.74 (s, 3H), 3.75 (dd, J=16.2 and 3.0 Hz, 1H), 3.99 (t, J=3.0 Hz, 1H), 5.19 (s, 1H), 6.36 (q, J=2.4 Hz, 1H), 6.90–6.97 (m, 2H), 7.07–7.12 (m, 2H), 7.29–7.40 (m, 3H), 7.42–7.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.32 (2C), 18.26, 25.85, 42.39, 52.29, 55.91, 61.63, 80.05, 115.32 (d, J=21.2 Hz), 124.38, 124.97, 126.18, 128.40, 128.73 (d, J=8.0 Hz), 129.40, 132.95 (d, J=2.9 Hz), 137.25, 143.15, 146.02, 161.15 (d, J=246.0 Hz), 173.81; ESIMS m/z 461 $[M+Na]^+$, 307 $[M+1-TBSOH]^+$. Anal. Calcd for $C_{26}H_{31}FO_3Si$: C, 71.20; H, 7.12. Found: C, 71.42; H, 7.30.

3.3.7. Compound ***2c****-Z.* Yield 30%; colorless oil; IR (film) 2951, 2856, 1732, 1509, 1233, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.56 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 2.69 (ddd, J=15.9, 3.0 and 2.1 Hz, 1H), 3.58 (dd, J=15.9 and 2.1 Hz, 1H), 3.76 (s, 3H), 4.25 (t, J=3.0 Hz, 1H), 5.09 (s, 1H), 6.12 (q, J=2.1 Hz, 1H), 7.00–7.07 (m, 2H), 7.24–7.39 (m, 5H), 7.49 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.30, −3.86, 17.97, 25.59, 42.67, 52.22, 54.87, 61.49, 76.95, 115.45 (d, J=21.1 Hz), 125.05 (d, J=1.1 Hz), 125.40, 125.93, 128.00, 129.22 (d, J=7.4 Hz), 129.30, 132.95 (d, J=2.8 Hz), 135.80, 143.34, 145.81, 161.53 (d, J=245.0 Hz), 173.91; ESIMS m/z 461 $[M+Na]^+$, 307 $[M+1-TBSOH]^+$. Anal. Calcd for $C_{26}H_{31}FO_3Si$: C, 71.20; H, 7.12. Found: C, 71.02; H, 7.31.

3.3.8. Compound ***3c****.* Yield 59%; colorless oil; IR (film) 2952, 2857, 1718, 1509, 1245, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 3H), 0.22 (s, 3H), 0.93 (s, 9H), 3.79 (s, 3H), 4.84 (d, J=7.2 Hz, 1H), 5.31 (d, J=0.9 Hz, 1H), 5.42 (d, J=7.2 Hz, 1H), 6.11 (d, J=0.9 Hz, 1H), 6.96 (d, J=0.9 Hz, 1H), 6.98–7.05 (m, 2H), 7.25–7.36 (m, 5H), 7.57–7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.82, −4.71, 18.17, 25.77, 49.93, 51.87, 77.00, 115.39 (d, J=21.1 Hz), 119.44, 120.24, 124.91, 126.63, 128.29, 128.71, 130.04 (d, J=8.0 Hz), 132.94 (d, J=3.4 Hz), 138.09, 140.92, 141.05, 144.85, 161.68 (d, J=246.0 Hz), 167.69; ESIMS m/z 461 $[M+Na]^+$. Anal. Calcd for $C_{26}H_{31}FO_3Si$: C, 71.20; H, 7.12. Found: C, 71.43; H, 7.19.

3.3.9. Compound ***2d****-E.* Yield 39%; colorless oil; IR (film) 2951, 2856, 1730, 1512, 1251, 1074 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.21 (s, 3H), 0.22 (s, 3H), 0.94 (s, 9H), 2.4 (ddd, J=16.2, 2.7 and 2.7 Hz, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 3.72–3.80 (m, 1H), 3.98 (t, J=2.7 Hz, 1H), 5.18 (s, 1H), 6.33 (q, J=2.7 Hz, 1H), 6.77–6.80 (m, 2H), 7.06–7.09 (m, 2H), 7.30–7.39 (m, 3H), 7.43–7.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.30, −4.32, 18.27, 25.87, 42.46, 52.24, 55.23, 55.97, 61.62, 80.11, 113.87, 124.85, 124.96, 126.18, 128.30, 128.42, 129.30, 129.73, 134.98, 143.32, 146.12, 158.35, 173.96; ESIMS m/z 473 $[M+Na]^+$. Anal. Calcd for $C_{27}H_{34}O_4Si$: C, 71.96; H, 7.60. Found: C, 72.21; H, 7.39.

3.3.10. Compound ***2d****-Z.* Yield 23% (based on ^{1}H NMR); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.04 (s, 3H), 0.09 (s, 3H), 0.87 (s, 9H), 2.67 (ddd, J=15.9, 3.0 and 2.1 Hz, 1H), 3.57 (dd, J=15.9 and 2.1 Hz, 1H), 3.75 (s, 3H), 3.81 (s, 3H), 4.26 (t, J=3.0 Hz, 1H), 5.14 (s, 1H), 6.11 (q, J=2.1 Hz, 1H), 7.23–7.35 (m, 7H), 7.47–7.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.24, −3.86, 17.96, 25.61, 42.63, 52.13, 53.38, 54.87, 61.53, 76.89, 113.93, 125.01, 125.91, 127.88, 128.88, 129.17, 129.63, 133.46, 143.49, 145.92, 158.31, 174.00 (one carbon is overlapped).

3.3.11. Compound ***3d****.* Yield 62%; colorless oil; IR (film) 2952, 2895, 2856, 1719, 1512, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.38 (s, 3H), 0.47 (s, 3H), 1.18 (s, 9H), 4.04 (s, 3H), 4.05 (s, 3H), 5.11 (d, J=7.2 Hz, 1H), 5.58 (t, J=0.9 Hz, 1H), 5.66 (d, J=7.2 Hz, 1H), 6.35 (d, J=0.9 Hz, 1H), 7.08–7.13 (m, 2H), 7.20 (d, J=1.2 Hz, 1H), 7.49–7.58 (m, 5H), 7.80–7.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.81, −4.71, 18.21, 25.80, 50.06, 51.83, 55.26, 77.22, 113.95, 119.26, 121.02, 124.81, 126.53, 128.20, 128.26, 129.55, 129.81, 138.19, 138.97, 141.49, 144.55, 158.65, 167.85; ESIMS m/z 473 $[M+Na]^+$, 319 $[M+1-TBSOH]^+$.

3.3.12. Compound ***2e****-E.* Yield 23%; colorless oil; IR (film) 3027, 2952, 1732, 1232 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 3H), 3.03 (ddd, J=16.5, 2.7 and 2.7 Hz, 1H), 3.87 (s, 3H), 3.84 (dd, J=16.5 and 2.7 Hz, 1H), 4.11 (t, J=2.7 Hz, 1H), 6.16 (s, 1H), 6.60 (q, J=2.7 Hz, 1H), 7.12–7.17 (m, 3H), 7.21–7.30 (m, 2H), 7.31–7.43 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.33, 42.71, 52.49, 55.93, 58.29, 80.32, 125.04, 126.79, 126.86, 127.04, 127.33, 128.43, 128.69, 130.37, 135.54, 136.60, 141.73, 144.51, 170.92, 173.39; ESIMS m/z 371 $[M+Na]^+$. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 76.03; H, 5.89.

3.3.13. Compound ***2e****-Z.* Yield 15%; colorless oil; IR (film) 3027, 2953, 1734, 1231 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H), 2.77 (ddd, 15.9, 3.3 and 2.4 Hz, 1H), 3.63 (dd, J=15.9 and 2.4 Hz, 1H), 3.80 (s, 3H), 4.56 (t, J=3.0 Hz, 1H), 6.14 (s, 1H), 6.22 (q, J=2.4 Hz, 1H), 7.21–7.28 (m, 2H), 7.30–7.34 (m, 4H), 7.39–7.44 (m, 2H), 7.51–7.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.26, 42.74, 52.50, 55.00, 57.71, 77.42, 124.95, 127.10 (2C), 127.71, 127.83, 128.49, 128.59, 130.28, 133.70, 135.87, 142.11, 144.34, 170.31, 173.46; ESIMS m/z 371 $[M+Na]^+$. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.86; H, 6.07.

3.3.14. Compound ***3e****.* Yield 57%; colorless oil; IR (film) 3026, 2951, 1733, 1237 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 3H), 3.81 (s, 3H), 4.95 (d, J=7.8 Hz, 1H), 5.50 (t, J=1.2 Hz, 1H), 6.18 (s, 1H), 6.61 (d, J=7.8 Hz, 1H), 7.12 (d, J=1.8 Hz, 1H), 7.19–7.41 (m, 8H), 7.67 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.07, 47.84, 52.33, 76.41, 120.11, 122.92, 125.69, 127.48, 127.53, 128.75, 128.97, 129.31, 129.53, 136.52, 136.79, 140.07, 140.92, 142.02, 167.88, 170.61; ESIMS m/z 371 $[M+Na]^+$. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.97; H, 5.51.

3.3.15. Compound ***2f****-E.* Yield 40%; white solid, mp 173–175 °C; IR (KBr) 3067, 2951, 2895, 2858, 1731, 1232 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (s, 9H), 2.84 (ddd, J=16.2, 2.7 and 2.7 Hz, 1H), 3.68 (dd, J=16.2 and 2.7 Hz, 1H), 3.80 (s, 3H), 3.93 (t, J=2.7 Hz, 1H), 5.11 (s, 1H), 5.28 (q, J=2.7 Hz, 1H), 6.89–6.92 (m, 2H), 7.04–7.09 (m, 1H), 7.14–7.19 (m, 2H), 7.24–7.37 (m, 3H), 7.40–7.51 (m, 7H), 7.78–7.83 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.29, 26.96, 42.19, 52.25, 55.92, 61.49, 80.89, 124.76, 125.49, 126.48, 126.55, 127.01, 127.75, 127.84, 128.26, 129.44, 129.81, 129.86, 133.85, 134.03, 136.14, 136.22, 136.82, 143.74, 145.72, 173.93 (two carbons are overlapped); ESIMS

m/*z* 567 $[M+Na]^+$. Anal. Calcd for $C_{36}H_{36}O_3Si$: C, 79.37; H, 6.66. Found: C, 79.71; H, 6.81.

*3.3.16. Compound **3f**.* Yield 55%; colorless oil; IR (film) 3058, 2951, 2859, 1716, 1243, 1121 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06 (s, 9H), 3.71 (s, 3H), 5.02 (dd, *J*=7.2 and 1.2 Hz, 1H), 5.37 (s, 1H), 5.70 (d, *J*=7.2 Hz, 1H), 6.20 (d, *J*=0.9 Hz, 1H), 6.49 (dd, *J*=7.8 and 0.9 Hz, 1H), 6.88 (ddd, *J*=7.5, 7.5 and 0.9 Hz, 1H), 6.96 (d, *J*=1.5 Hz, 1H), 7.14–7.24 (m, 2H), 7.30–7.45 (m, 10H), 7.51 (d, *J*=7.5 Hz, 1H), 7.65–7.69 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.40, 26.95, 49.83, 51.85, 78.12, 119.26, 121.04, 125.58, 126.93, 127.17, 127.61, 127.73, 128.01, 128.09, 128.37, 128.58, 129.64, 129.77, 133.41, 134.48, 135.96, 136.03, 136.78, 138.35, 141.37, 141.44, 144.19, 167.85; ESIMS *m*/*z* 567 $[M+Na]^+$. Anal. Calcd for $C_{36}H_{36}O_3Si$: C, 79.37; H, 6.66. Found: C, 79.44; H, 6.49.

*3.3.17. Compound **5**.* Yield 85%; white solid, mp 104–106 °C; IR (KBr) 3028, 2933, 2856, 1731, 1442, 1248, 1077 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 3H), 0.22 (s, 3H), 0.90 (s, 9H), 1.92–1.93 (m, 3H), 3.00 (ddd, *J*=16.2, 2.7 and 2.7 Hz, 1H), 3.66 (ddd, *J*=16.2, 2.7 and 2.7 Hz, 1H), 3.70 (s, 3H), 3.87 (t, *J*=0.9 Hz, 1H), 5.21 (s, 1H), 7.15–7.21 (m, 3H), 7.24–7.35 (m, 5H), 7.45–7.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.25, −4.02, 14.41, 18.04, 25.76, 48.35, 52.32, 60.75, 70.54, 77.79, 125.33, 125.36, 126.70, 127.83, 128.01, 128.20, 128.79, 132.58, 133.32, 137.09, 143.97, 145.36, 175.58; ESIMS *m*/*z* 457 $[M+Na]^+$, 303 [M+1−TBSOH]. Anal. Calcd for $C_{27}H_{34}O_3Si$: C, 74.61; H, 7.88. Found: C, 74.93; H, 7.96.

*3.3.18. Compound **4g**.* Yield 57%; white solid, mp 58–60 °C; IR (KBr) 2928, 2857, 1465, 1076 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.14 (s, 3H), 0.21 (s, 3H), 0.96 (s, 9H), 1.79 (d, *J*=1.2 Hz, 3H), 3.57–3.60 (m, 1H), 4.94 (d, *J*=2.7 Hz, 1H), 5.26 (d, *J*=5.7 Hz, 1H), 5.57 (d, *J*=3.0 Hz, 1H), 6.56 (s, 1H), 7.22–7.41 (m, 8H), 7.51–7.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.29, −3.99, 14.70, 18.12, 25.87, 66.32, 77.26, 104.11, 120.63, 124.88, 126.27, 128.11, 128.25, 128.93, 130.39, 136.57, 138.09, 139.25, 146.20, 148.26 (one carbon is overlapped); ESIMS *m*/*z* 399 $[M+Na]^+$. Anal. Calcd for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 79.98; H, 8.41.

*3.3.19. Compound **3h**.* Yield 73%; colorless oil; IR (film) 3027, 2952, 2892, 2857, 2222, 1466, 1255, 1077 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.09 (s, 3H), 0.12 (s, 3H), 0.82 (s, 9H), 3.90 (s, 1H), 5.15 (d, *J*=2.1 Hz, 1H), 5.56 (s, 1H), 5.65 (s, 1H), 7.14–7.31 (m, 9H), 7.52–7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.19, −4.01, 17.94, 25.77, 57.53, 79.81, 118.02, 120.35, 121.82, 124.27, 125.59, 127.45, 128.36, 128.85, 129.17, 129.20, 131.88, 135.96, 138.49, 140.75, 143.47; ESIMS *m*/*z* 410 $[M+Na]^+$. Anal. Calcd for $C_{25}H_{29}NOSi$: C, 77.47; H, 7.54; N, 3.61. Found: C, 77.29; H, 7.61; N, 3.39.

*3.3.20. Compound **6**.* Yield 17%; pale yellow oil; IR (film) 3053, 2927, 2856, 2221, 1494 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.33–7.44 (m, 4H), 7.51–7.65 (m, 5H), 7.83–7.90 (m, 2H), 8.19 (s, 1H), 8.24 (s, 1H); ESIMS *m*/*z* 278 $[M+Na]^+$.

*3.3.21. Compound **2i**-E.* Yield 4%; colorless oil; IR (film) 2952, 2857, 1734, 1228, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 6H), 0.94 (s, 9H), 1.43–1.47 (m, 3H), 2.62 (d, *J*=15.3 Hz, 1H), 3.34 (ddd, *J*=15.3, 2.1 and 2.1 Hz, 1H), 3.73 (s, 3H), 3.78–3.80 (m, 1H), 5.08 (s, 1H), 5.47–5.55 (m, 1H), 7.31–7.45 (m, 3H), 7.46–7.49 (m, 1H); ESIMS *m*/*z* 381 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.51; H, 8.54.

*3.3.22. Compound **3i**.* Yield 75%; colorless oil; IR (film) 2952, 2893, 2857, 1721, 1466, 1073 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 3H), 0.03 (s, 3H), 0.80 (s, 9H), 3.30 (dd, *J*=9.6 and 4.8 Hz, 1H), 3.81 (s, 3H), 4.10 (t, *J*=9.6 Hz, 1H), 5.24–5.32 (m, 3H), 5.66–5.78 (m, 1H), 5.85 (s, 1H), 6.53 (s, 1H), 7.20–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.75, −4.17, 18.07, 25.74, 49.93, 51.77, 54.00, 75.32, 117.74, 124.39, 124.90, 126.90, 127.65, 128.21, 136.76, 138.50, 143.70, 145.27, 167.72; ESIMS *m*/*z* 381 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.59; H, 8.57.

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Supplementary data

These data include experimental details, DFT calculations, X-ray structures, and copies of ^1H and ^{13}C NMR spectra. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.03.070.

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