Tetrahedron 66 (2010) 9021–9031

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Cationic iridium complex is a new and efficient Lewis acid catalyst for aldol and Mannich reactions

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ARTICLE INFO

Article history:
Received 28 July 2010
Received in revised form 3 September 2010
Accepted 3 September 2010
Available online 15 September 2010

Keywords:
Iridium
Mukaiyama aldol reaction
Chemoselectivity
Mannich reaction
β-Lactam
Tetrahydroquinoline

ABSTRACT

A cationic iridium complex $[Ir(cod)_2]SbF_6$ was found to be a new and efficient Lewis acid catalyst for Mukaiyama aldol and Mannich reactions. Aldehydes react smoothly with silyl enol ethers to give β-siloxy ketones in the presence of 0.5 mol % of $[Ir(cod)_2]SbF_6$. The reaction of *N*-alkyl arylaldimines with ketene silyl acetals in the presence of 5 mol % $[Ir(cod)_2]SbF_6/P(OPh)_3$ gave β-amino esters. After Mannich reaction was complete, stirring of the reaction mixture for 24 h led to cyclization to give β-lactam. The reaction of *N*-aryl benzaldimine with silyl enol ether derived from acetophenone gave a tetrahydroquinoline derivative as a single diastereomer.

1. Introduction

The aldol reaction is the most important carbon–carbon bond-forming reaction in organic synthesis.[1] Due to its advantages over the classical aldol reaction, Mukaiyama aldol reaction has been studied extensively as a modern synthetic method since it was first reported in 1973.[2] This reaction provides numerous opportunities for chemo-, regio-, and stereoselective carbon–carbon bond formation. Initially, a stoichiometric amount of $TiCl_4$ was used to promote Mukaiyama aldol reaction.[2] Recently, it has become common to use catalytic amounts of Lewis acids in Mukaiyama aldol reaction. Much effort has been devoted to the development of chiral Lewis acid catalysts for the enantioselective aldol reaction. Chiral Lewis acids, such as titanium,[3] tin,[4] boron,[5] copper,[6] and silver[7] have been successfully used. In contrast to the success with these metals, group VIII–X metal Lewis acids have been used far less often for Mukaiyama aldol reaction. Most of the catalytic carbon–carbon bond-forming reactions with group VIII–X transition metal complexes are based on a redox process of the metal due to the ability of such transition metals to exist in several different oxidation states.[8] The catalytic cycle begins with oxidative addition and ends with reductive elimination to give a product and regenerate a catalytic active species. On the other hand, the catalytic reaction using the high electrophilicity of group VIII–X metals without a change in the oxidation state of the metal has been relatively unexplored. A limited number of aldol reactions catalyzed by group VIII–X transition metal Lewis acids have been reported.[9–12] New catalysts are needed to further expand the scope and selectivity of the aldol reaction. In the course of our study on iridium-catalyzed carbon–carbon bond-forming reactions,[13] we first found that a cationic iridium complex is an efficient catalyst for Mukaiyama aldol reaction. We report here the full details of the cationic iridium complex-catalyzed aldol reaction. Furthermore, we extend this chemistry to Mannich reaction.

2. Results and discussion

Catalyst screening was performed by the reaction of benzaldehyde (**1a**) with 1.5 equiv of silyl enol ether **2a**. The results are summarized in Table 1. The reaction proceeded at room temperature to give β-siloxy ketone **3aa**. Neutral iridium complex $[Ir(cod)Cl]_2$ did not give the product (entry 1), and the starting material was recovered after 24 h. Iridium triflate $[Ir(cod)_2]OTf$ gave **3aa** in 95% yield (entry 2). A catalyst loading of 0.5 mol % led to the product in nearly quantitative yield. The counter anion of the cationic iridium complex had a profound effect on the reaction. $[Ir(cod)_2]BF_4$ gave no product (entry 3). $[Ir(cod)_2]PF_6$ gave **3aa** in moderate yield (entry 4). $[Ir(cod)_2]SbF_6$ gave the best result (entry 5). The reaction was completed in 30 min. The product was obtained in quantitative yield. When $P(OPh)_3$ was used as a ligand, the product **3aa** and the

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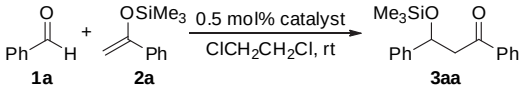
doi:10.1016/j.tet.2010.09.015

Table 1
Reaction of benzaldehyde (**1a**) with silyl enol ether **2a**[a]



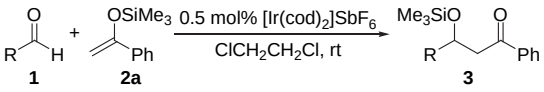
Entry	Catalyst	Time (h)	Yield[b] (%)
1[c]	$[Ir(cod)Cl]_2$	24	0
2	$[Ir(cod)_2]OTf$	6	95
3	$[Ir(cod)_2]BF_4$	24	0
4	$[Ir(cod)_2]PF_6$	24	46
5	$[Ir(cod)_2]SbF_6$	0.5	>99
6[d]	$[Ir(cod)_2]SbF_6/P(OPh)_3$	0.5	60 (38)[e]
7[f]	$[Ir(cod)_2]SbF_6/PPh_3$	24	66
8[g]	$[Ir(cod)_2]SbF_6$/DPPE	24	0
9	$[Rh(cod)_2]SbF_6$	0.5	97
10	$NaSbF_6$	24	0
11[h]	$NaSbF_6$	24	2

[a] Reaction condition: **1a** (2 mmol) and **2a** (3 mmol) in the presence of a catalyst (0.01 mmol) in 1,2-dichloroethane (10 mL).
[b] Isolated yield.
[c] Catalyst (0.005 mmol) was used.
[d] $P(OPh)_3$ (0.02 mmol) was used as a ligand.
[e] The number in parenthesis represents the yield of desilylated alcohol **3′aa**.
[f] PPh_3 (0.02 mmol) was used as a ligand.
[g] DPPE (0.01 mmol) was used as a ligand.
[h] At reflux temperature.

desilylated alcohol **3′aa** were obtained in 60% and 38% yield, respectively (entry 6). The use of PPh_3 as a ligand decreased the yield to 66% (entry 7). When DPPE was used, the starting material was recovered (entry 8). Cationic rhodium complex gave slightly decreased yield of **3aa** compared to that given by cationic iridium complex (entry 9). It is well known that F^- is an efficient catalyst for the aldol reaction.[14] To determine whether F^- may be a catalytically active species for this reaction, we examined the reaction using 0.5 mol % of $NaSbF_6$ as a catalyst (entries 10 and 11). The starting material was recovered after the reaction for 24 h at room temperature. $NaSbF_6$ was soluble in 1,2-dichloroethane to give a homogeneous reaction mixture. Hence, this result strongly suggests that the catalytically active species is a cationic iridium species.

By using the optimized reaction conditions described above, we explored the scope of the reaction with a variety of aldehydes (Table 2). Good functional-group compatibility was observed under the reaction conditions. The reaction of fluoro-, chloro-, and methyl-substituted aldehydes gave the corresponding products in high yields (entries 1–3). Dehalogenation did not occur under the reaction conditions. Sterically hindered *ortho*-substituted aldehydes (**1e** and **1f**) required heating to give the product (entries 4 and 5). Although methoxy and ester groups are Lewis basic sites, these substrates reacted smoothly with **2a** at room temperature to give the respective products in 90% and 96% yield (entries 6 and 8). The reaction of *p*-acetylbenzaldehyde **1h** with **2a** gave the product in 60% yield (entry 7). Silyl enol ether **2a** reacted exclusively at the formyl group in **1h**. Notably, the reaction of cyano-, nitro-, and dimethylamino-substituted aldehydes gave the respective products in yields of 83–95% (entries 9–11). These functional groups have strong coordinating ability to deactivate the Lewis acid catalyst. However, these aldehydes reacted smoothly with **2a** under refluxing 1,2-dichloroethane. These reactions required more demanding conditions than the reaction of benzaldehyde. 1-Naphthylaldehyde as well as 2-naphthylaldehyde reacted with **2a** at room temperature within 30 min to give the products in quantitative yield (entries 12 and 13). Heteroaromatic aldehydes could be used for the reaction. While oxygenated heterocycle 2-furylaldehyde reacted with **2a** to give the product in 80% yield at room temperature (entry 15), sulfur-containing heterocycle 2-thiophenecarbaldehyde required refluxing 1,2-dichloroethane to give the product in 89% yield (entry 16). Although sulfur-containing compounds can act as catalyst poisons due to their strong coordinating properties, the product was obtained in high yield. 2-Pyridinecarbaldehyde did not give the product even under refluxing conditions (entry 14). The reaction of aliphatic unsaturated aldehydes gave the products in decreased yield compared to those with aromatic aldehydes (entries 17 and 18). Cinnamyl aldehyde **1r** reacted with **2a** to give the product in 72% yield. Dienyl aldehyde **1s** also reacted with **2a** to give the product in 65% yield. Michael addition of **2a** to these unsaturated aldehydes was not observed at all.[15] Aliphatic aldehydes **1t**–**w** reacted smoothly with **2a** at room temperature to give the product in yields of 85–92%. The substituent at the α-position gave a somewhat decreased yield of the product. Pivaloyl aldehyde **1x** gave the product in 72% yield (entry 23).

Table 2
Reaction of aldehydes (**1**) with silyl enol ether **2a**[a]



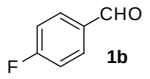
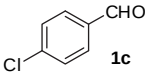
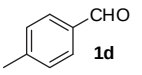
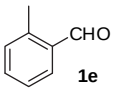
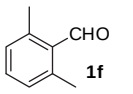
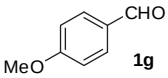
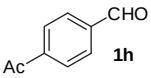
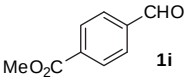
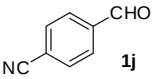
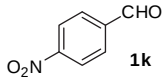
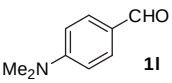
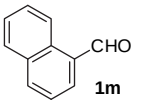
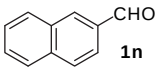
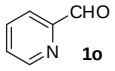
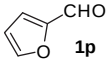
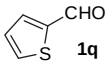
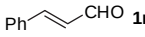
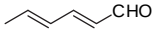
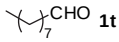
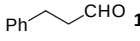
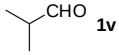
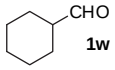
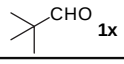
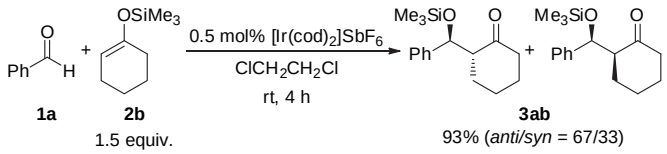
Entry	Aldehyde **1**	Product	Temperature	Time (h)	Yield[b] (%)
1	 **1b**	**3ba**	rt	1.5	87
2	 **1c**	**3ca**	rt	0.5	>99
3	 **1d**	**3da**	rt	0.5	97
4	 **1e**	**3ea**	Reflux	24 (24)[c]	55 (2)[c]
5	 **1f**	**3fa**	Reflux	24 (24)[c]	68 (1)[c]
6	 **1g**	**3ga**	rt	0.5	90
7	 **1h**	**3ha**	Reflux	24 (24)[c]	60 (17)[c]
8	 **1i**	**3ia**	rt	3	96
9	 **1j**	**3ja**	Reflux	4 (4)[c]	83 (3)[c]
10	 **1k**	**3ka**	Reflux	2 (2)[c]	94 (3)[c]
11	 **1l**	**3la**	Reflux	0.5 (0.5)[c]	95 (0)[c]
12	 **1m**	**3ma**	rt	0.5	>99

Table 2 (*continued*)

Entry	Aldehyde **1**	Product	Temperature	Time (h)	Yield[b] (%)
13	 **1n**	**3na**	rt	1	>99
14	 **1o**	**3oa**	Reflux	24	0
15	 **1p**	**3pa**	rt	0.5	80
16	 **1q**	**3qa**	Reflux	1 (1)[c]	89 (0)[c]
17	 **1r**	**3ra**	rt	0.5	72
18	 **1s**	**3sa**	rt	0.5	65
19	 **1t**	**3ta**	rt	3	90
20	 **1u**	**3ua**	rt	1	90
21	 **1v**	**3va**	rt	1	85
22	 **1w**	**3wa**	rt	0.5	92
23	 **1x**	**3xa**	rt	24	72

[a] Reaction condition: **1** (2 mmol) and **2a** (3 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.01 mmol) in 1,2-dichloroethane (10 mL).
[b] Isolated yield.
[c] $NaSbF_6$ was used as catalyst.

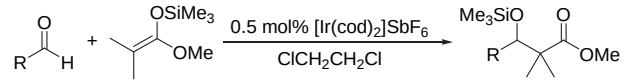
The diastereoselectivity of the reaction was examined by using the reaction of **1a** with **2b** (Scheme 1). Moderate diastereoselectivity was observed. *anti*-Selectivity was 67%. With diastereoselectivity of the reaction of **1a** with **2b**, cationic iridium catalyst was less diastereoselective than borane catalyst and gallium catalyst.[16]

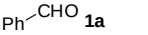
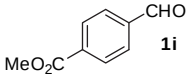
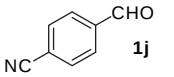
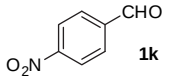
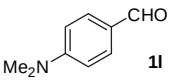
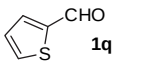
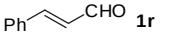
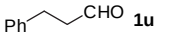


Scheme 1. The reaction of benzaldehyde (**1a**) with **2b**.

Ketene silyl acetal was a good substrate for the cationic iridium complex-catalyzed aldol reaction. The results are summarized in Table 3. Benzaldehyde reacted with **2c** at room temperature in the presence of 0.5 mol % of $[Ir(cod)_2]SbF_6$ to give the product in 99% yield (entry 1). Good functional-group compatibility was observed, as in the aldol reaction. Ester-substituted aldehyde **1i** reacted with **2c** at room temperature to give the product in 91% yield, whereas cyano-, nitro-, and dimethylamino-substituted aldehydes (**1j**, **1k**, **1l**) required heating to give the products. The yields were 91–96% (entries 2–5). Heteroaromatic aldehyde **1q** reacted with **2c** to give the product in 95% yield (entry 6). The reaction of unsaturated aldehyde **1r** gave the product in 44% yield (entry 7). The Michael reaction was not observed. The reaction of aldehyde having α-hydrogens gave the product in 92% yield at room temperature (entry 8).

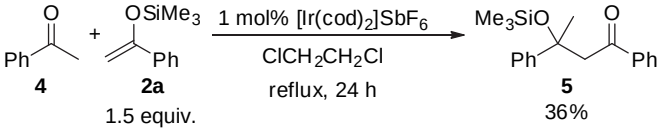
Table 3
Reaction of aldehydes (**1**) with ketene silyl acetal **2c**[a]



Entry	Aldehyde **1**	Product	Temperature	Time (h)	Yield[b] (%)
1	 **1a**	**3ac**	rt	1	99
2	 **1i**	**3ic**	rt	4	91
3	 **1j**	**3jc**	Reflux	0.5	94
4	 **1k**	**3kc**	Reflux	0.5	95
5	 **1l**	**3lc**	Reflux	0.5	96
6	 **1q**	**3qc**	Reflux	0.5	95
7	 **1r**	**3rc**	rt	0.5	44
8	 **1u**	**3uc**	rt	2	92

[a] Reaction condition: **1** (2 mmol) and **2c** (3 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.01 mmol) in 1,2-dichloroethane (10 mL).
[b] Isolated yield.

Cationic iridium catalyst was less efficient for the aldol reaction of ketone with silyl enol ether. The reaction of acetophenone (**4**) with **2a** gave the corresponding product **5** in 36% yield (Scheme 2).[17]



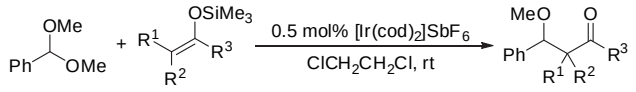
Scheme 2. The reaction of ketone (**4**) with **2a**.

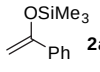
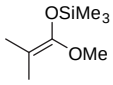
Acetal reacted smoothly with silyl enol ether and ketene silyl acetal at room temperature to give β-alkoxy ketones and β-alkoxy ester in high yields. The results are summarized in Table 4.

Cationic iridium complex acts as a Lewis acid catalyst for Mukaiyama aldol reaction. Therefore, we attempted to extend this chemistry to Mannich reaction. Mannich reaction provides a powerful and direct access to β-amino carbonyl compounds, which are extremely important as biologically active target molecules in the pharmaceutical and agrochemical industries.[18] It is important that a new catalytic synthesis of β-amino carbonyl compounds is developed. Therefore, a new catalyst for Mannich reaction has been desired.

The catalytic activity of cationic iridium complex was examined by the reaction of aldimine **8a** with ketene silyl acetal **2c** at room temperature (Table 5). A catalyst loading of 5 mol % was required for the reaction to run to completion. Due to the strong coordination ability of nitrogen atom compared to oxygen atom, Mannich reaction required a much higher catalyst loading. $[Ir(cod)_2]SbF_6$ alone gave the product in 82% yield (entry 1). The use of $P(OPh)_3$ as a ligand improved the

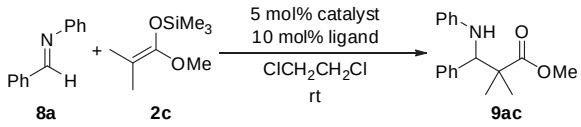
Table 4
Reaction of acetal **6a** with silyl enol ether (**2a** and **2b**) and ketene silyl acetal **2c**[a]



Entry	2	Product	Temperature	Time (h)	Yield[b] (%)
1	 **2a**	**7aa**	rt	3	98
2	 **2b**	**7ab**	rt	4	98[c]
3	 **2c**	**7ac**	rt	4	91

[a] Reaction condition: **6a** (2 mmol) and **2** (3 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.01 mmol) in 1,2-dichloroethane (10 mL).
[b] Isolated yield.
[c] *anti*/*syn*=35/65.

Table 5
Reaction of imine (**8a**) with ketene silyl acetal **2c**[a]



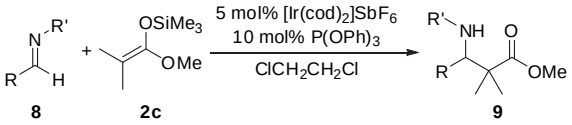
Entry	Catalyst	Ligand	Time (h)	Yield[b] (%)
1	$[Ir(cod)_2]SbF_6$	None	24	82
2	$[Ir(cod)_2]SbF_6$	$P(OPh)_3$	0.5	98
3	$[Ir(cod)_2]SbF_6$	PPh_3	24	30
4[c]	$[Ir(cod)_2]SbF_6$	DPPE	24	22
5	$[Ir(cod)_2]BF_4$	$P(OPh)_3$	24	21
6	$[Ir(cod)_2]PF_6$	$P(OPh)_3$	24	56
7	$[Ir(cod)_2]OTf$	$P(OPh)_3$	2	>99
8	$[Ir(cod)Cl]_2$	$P(OPh)_3$	24	17
9	$NaSbF_6$	$P(OPh)_3$	24	37

[a] Reaction condition: **8a** (1 mmol) and **2c** (1.5 mmol) in the presence of a catalyst (0.05 mmol) and ligand (0.1 mmol) in 1,2-dichloroethane (5 mL).
[b] Isolated yield.
[c] DPPE (0.05 mmol) was used as a ligand.

yield. $[Ir(cod)_2]SbF_6/P(OPh)_3$ and $[Ir(cod)_2]OTf/P(OPh)_3$ gave the product in quantitative yield (entries 2 and 7). When PPh_3 and DPPE were used as a ligand, the product **9ac** was obtained in low yield (entries 3 and 4). $[Ir(cod)_2]BF_4/P(OPh)_3$, $[Ir(cod)_2]PF_6/P(OPh)_3$, and $[Ir(cod)Cl]_2/P(OPh)_3$ were less effective than $[Ir(cod)_2]SbF_6/P(OPh)_3$ (entries 5, 6, and 8).

The reaction of various aldimines with ketene silyl acetal was examined under the optimized reaction conditions described above. The results are summarized in Table 6. Aromatic aldimines **8b**–**e**,**h**,**i** reacted smoothly with ketene silyl acetal **2c** at room temperature to give the products in nearly quantitative yield (entries 1–4, 7, and 8). The reaction of cyano- and nitro-group-substituted aromatic aldimines gave the products in somewhat lower yield (entries 5 and 6). Aldimines substituted with a primary alkyl group on the nitrogen atom (**8j**–**l**) exhibited good reactivity for the reaction. The products were obtained in yields of 78–99% (entries 9–11). Secondary and tertiary alkyl groups on the nitrogen atom decreased the yield. The reaction of aldimines **8m**,**n** gave the products in moderate yield (entries 12 and 13). Aldimines substituted with an electron-withdrawing group on the nitrogen atom reacted with ketene silyl acetal **2c** at room temperature to give the products in high yields (entries 14–16).

Table 6
Reaction of imines (**8**) with ketene silyl acetal **2c**[a]



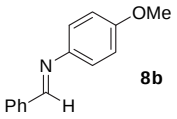
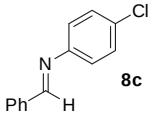
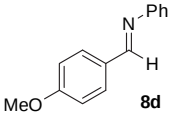
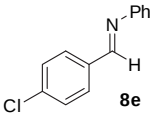
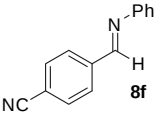
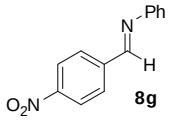
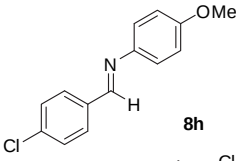
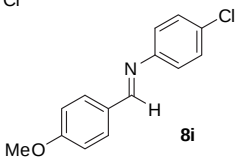
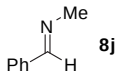
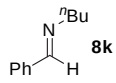
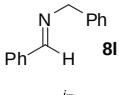
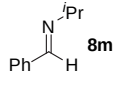
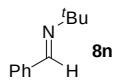
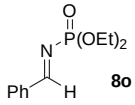
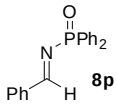
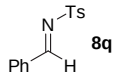
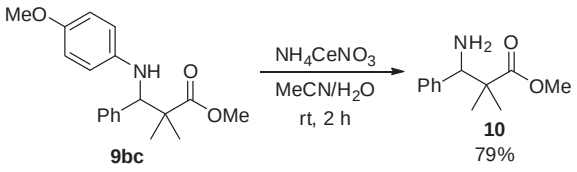
Entry	Imine	Product	Temperature	Time (h)	Yield[b] (%)
1	 **8b**	**9bc**	rt	2	95
2	 **8c**	**9 cc**	rt	0.5	96
3	 **8d**	**9dc**	rt	0.5	96
4	 **8e**	**9ec**	rt	0.5	97
5	 **8f**	**9fc**	rt	24	76
6	 **8g**	**9gc**	rt	24	79
7	 **8h**	**9hc**	rt	0.5	94
8	 **8i**	**9ic**	rt	0.5	96
9	 **8j**	**9jc**	rt	0.5	92
10	 **8k**	**9kc**	rt	0.5	>99
11	 **8l**	**9lc**	rt	0.5	78
12	 **8m**	**9mc**	rt	24	43
13	 **8n**	**9nc**	rt	24	41

Table 6 (*continued*)

Entry	Imine	Product	Temperature	Time (h)	Yield[b] (%)
14	 **8o**	**9oc**	rt	1	80
15	 **8p**	**9pc**	rt	1	89
16	 **8q**	**9qc**	rt	1	>99

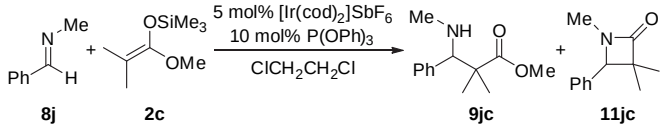
[a] Reaction condition: **8** (1 mmol) and **2c** (1.5 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.05 mmol) and $P(OPh)_3$ (0.1 mmol) in 1,2-dichloroethane (5 mL).
[b] Isolated yield.

The *N*-aryl substituent was readily removed to give free β-amino ester by oxidative cleavage.[19] A *p*-methoxyphenyl group was smoothly deprotected. Treatment of **9bc** with CAN in acetonitrile/water (9:1) at room temperature for 2 h gave **10** in 79% yield (Scheme 3). Various free β-amino esters can be obtained by Mannich reaction with ketene silyl acetals followed by deprotection.



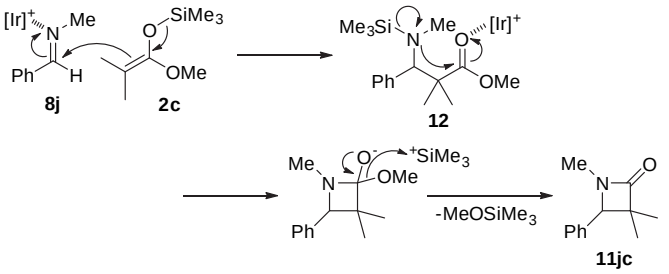
Scheme 3. Deprotection of **9bc**.

β-Lactam was obtained by this catalytic reaction (Scheme 4).[20] Aldimine **8j** reacted with ketene silyl acetal **2c** for 0.5 h to give β-amino ester **9jc** in 92% yield. The same reaction after the reaction mixture was stirred for 12 h gave β-lactam **11jc** in 78% yield. β-Amino ester **9jc** was transformed to β-lactam **11jc**. The reaction of **9jc** in the presence of 5 mol % $[Ir(cod)_2]SbF_6$ and 10 mol % $P(OPh)_3$ for 24 h did not give **11jc**. The starting material **9jc** was recovered. The result suggests that *N*-silyl β-amino ester **12** cyclizes to β-lactam **11jc** via intramolecular nucleophilic attack of a nitrogen atom to a carbonyl carbon activated by cationic iridium species (Scheme 5). The substituent on the nitrogen atom is important for cyclization. *N*-Arylaldimine **8a** did not cyclize to give β-lactam under the same reaction conditions. An alkyl substituent on the imine nitrogen is essential to cyclization to give β-lactam. An alkyl substituent increases the electron density of the nitrogen atom to promote nucleophilic attack to the carbonyl carbon.

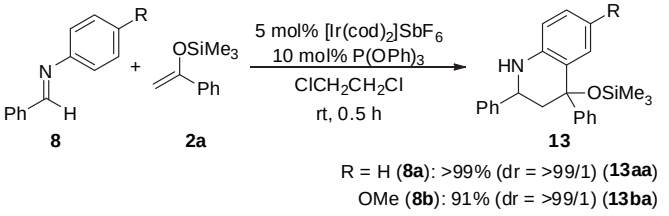


Scheme 4. The reaction of *N*-alkylaldimine **8j** with **2c**.

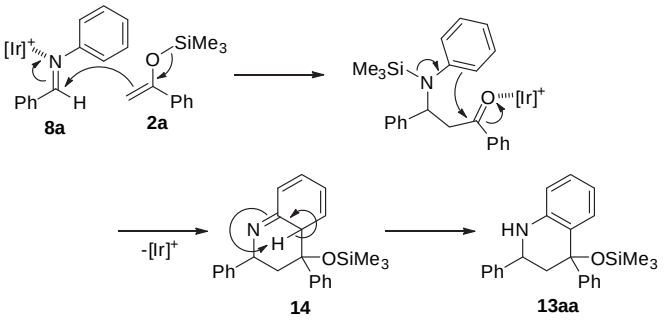
The reaction of aldimine **8a** with silyl enol ether **2a** did not give β-amino ketone. The reaction of *N*-arylaldimine **8a** with silyl enol ether **2a** gave tetrahydroquinoline derivative **13aa** in quantitative yield as a single diastereomer (Scheme 6). The $Yb(OTf)_3$-catalyzed reaction of aldimine with silyl enol ether gave a similar cyclization product.[21] However, the reaction was reported to be less diastereoselective (dr=83/17). The aldimine **8b** reacted similarly with **2a** to give **13ba** in 91% yield with complete diastereoselectivity. The formation of **13** can be explained as shown in Scheme 7. Intramolecular attack of an aromatic ring on an imine nitrogen atom to a carbonyl carbon activated by cationic iridium species gives intermediate **14**. Re-aromatization of intermediate **14** gives aromatic compound **13**.



Scheme 5. The proposed reaction pathway for the formation of β-lactam **11jc**.

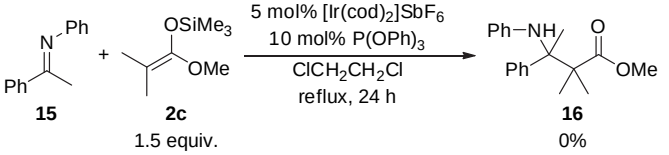


Scheme 6. The reaction of aldimine **8** with silyl enol ether **2a**.



Scheme 7. The proposed reaction pathway for the formation of tetrahydroquinoline **13aa**.

Based on the results described above, we examined Mannich reaction of ketimine. The reaction of ketimine **15** with ketene silyl acetal **2c** did not give β-amino ester **16** and starting material was recovered (Scheme 8).



Scheme 8. The reaction of ketimine **15** with ketene silyl acetal **2c**.

3. Conclusion

In conclusion, we found that cationic iridium complex is an efficient Lewis acid catalyst for Mukaiyama aldol reaction and Mannich reaction. Cationic iridium complex selectively activates an aldehyde or aldimine functionality even in the presence of a Lewis basic site, such as a nitro, ester, or cyano group. Therefore, good functional compatibility of the reaction was observed. Further development of the Lewis acid catalysis of cationic iridium complex is underway in our laboratory.

4. Experimental

4.1. General

4.1.1. Instrumentation. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL JNM-ECP 500A spectrometer using TMS, $CHCl_3$, $CDCl_3$, and H_3PO_4 as internal or external standards. Samples were dissolved in $CDCl_3$. GC analyses were performed on a Shimadzu GC-14B using 3.2 mm×2 m glass columns packed with 5% OV-17 on 60/80 mesh Chromosorb WAW-DMCS. The products were purified by column chromatography on 63–210 mesh silica gel (Kanto Kagaku; Silica Gel 60 N). High-resolution mass spectra were obtained with a JEOL Mstation JMS-700.

4.1.2. Materials. All reagents and solvents were dried and purified before use by the usual procedures. $[Ir(cod)_2]SbF_6$ was prepared as described in the literature.[13j] Aldehydes **1a**–**x**, acetophenone **4**, acetal **6a**, and imines **8a** and **8j** were purchased. Imines **8b**–**i** and **8k**–**n** were prepared by stirring equimolar amounts of the corresponding aldehydes and primary amines in CH_2Cl_2 with MS 4Å. They were then purified by either recrystallization or vacuum distillation. Imines **8o**,[22] **8p**,[23] **8q**,[24] and **15**[25] were prepared as described in the literature. Silyl enol ether **2a** was prepared as described in the literature.[26] Silyl enol ether **2b** and ketene silyl acetal **2c** were purchased.

4.2. Experimental procedures

*4.2.1. Representative procedure for aldol reaction of aldehyde (**1**) with silyl enol ether (**2a** and **2b**) and ketene silyl acetal (**2c**).* A flask was charged with $[Ir(cod)_2]SbF_6$ (6.2 mg, 0.01 mmol), and then evacuated and filled with argon. To the flask were added 1,2-dichloroethane (10 mL) and benzaldehyde (**1a**) (208 mg, 1.96 mmol). Silyl enol ether **2a** (573 mg, 2.98 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 0.5 h. The progress of the reaction was monitored by GLC. After the reaction was completed, the solvent was evaporated in vacuo. Column chromatography of the residue gave **3aa** (*n*-hexane/AcOEt=95/5, 584 mg, 1.96 mmol, >99% yield).

*4.2.2. Representative procedure for Mannich reaction of imine (**8**) with ketene silyl acetal (**2c**) and silyl enol ether (**2a**).* A flask was charged with $[Ir(cod)_2]SbF_6$ (32.0 mg, 0.05 mmol), and the flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (5 mL) and triphenylphosphite (30.5 mg, 0.10 mmol). *N*-Benzylideneaniline (**8a**) (183 mg, 1.01 mmol) and ketene silyl acetal **2c** (267 mg, 1.54 mmol) were added to the reaction mixture. The mixture was stirred at room temperature for 0.5 h. The progress of the reaction was monitored by GLC. After the reaction was completed, the solvent was evaporated in vacuo. Column chromatography of the residue gave **9ac** (*n*-hexane/AcOEt=90/10, 282 mg, 0.99 mmol, 98% yield).

*4.2.3. Procedure for cleavage of the amino moiety on N-(4-methoxyphenl)-substituted β-amino ester **9bc**[19b].* A flask was charged with *N*-(4-methoxyphenyl)-substituted β-amino ester **9bc** (313 mg, 1.00 mmol) and then evacuated and filled with argon. To the flask was added acetonitrile (22 mL). A solution of ammonium cerium nitrate (2750 mg, 5.02 mmol) in water (17 mL) was added slowly (25 min) to the stirred reaction mixture at room temperature. After 2 h, a saturated aqueous solution of $NaHCO_3$ was added until pH 6 was reached. Sodium sulfite was then added until the mixture became a brown suspension. The reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo. Column chromatography of the residue gave **10** (eluent: AcOEt, 163 mg, 0.79 mmol, 79% yield).

4.3. Spectroscopic data

*4.3.1. 1,3-Diphenyl-3-trimethylsilyloxy-1-propanone (**3aa**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.01 (s, 9H), 3.04 (dd, *J*=15.6 and 3.9 Hz, 1H), 3.59 (dd, *J*=15.6 and 8.7 Hz, 1H), 5.41 (dd, *J*=8.7 and 3.9 Hz, 1H), 7.27 (t, *J*=7.3 Hz, 1H), 7.36 (t, *J*=7.3 Hz, 2H), 7.44–7.47 (m, 4H), 7.56 (t, *J*=7.3 Hz, 1H), 7.98 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.6, 71.6, 125.7 (2C), 127.3, 128.27 (2C), 128.34 (2C), 128.4 (2C), 132.9, 137.5, 144.7, 198.4. HRMS: calcd for $C_{18}H_{22}O_2Si$ ($[M]^+$), 298.1389. Found: *m*/*z* 298.1378.

*4.3.2. 1,3-Diphenyl-3-hydroxy-1-propanone (**3′aa**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.36–3.38 (m, 2H), 3.61 (dd, *J*=3.2 and 7.3 Hz, 1H), 5.35 (ddd, *J*=3.2, 5.0, and 7.3 Hz, 1H), 7.30 (t, *J*=7.3 Hz, 1H), 7.38 (t, *J*=7.3 Hz, 2H), 7.43–7.47 (m, 4H), 7.58 (t, *J*=7.3 Hz, 1H), 7.95 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.4, 70.0, 125.7 (2C), 127.6, 128.1 (2C), 128.5 (2C), 128.7 (2C), 133.6, 136.6, 143.0, 200.1. HRMS: calcd for $C_{15}H_{15}O_2$ ($[M+H]^+$), 227.1072. Found: *m*/*z* 227.1068.

*4.3.3. 3-(4′-Fluorophenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ba**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.03 (s, 9H), 3.02 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.54 (dd, *J*=15.6 and 8.2 Hz, 1H), 5.37 (dd, *J*=8.2 and 4.1 Hz, 1H), 7.02 (t, *J*=8.7 Hz, 2H), 7.38–7.40 (m, 2H), 7.45 (t, *J*=7.3 Hz, 2H), 7.55 (t, *J*=7.3 Hz, 1H), 7.95 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.6, 71.0, 115.1 (d, $^{2}J_{CF}$=21.5 Hz, 2C), 127.3 (d, $^{3}J_{CF}$=8.1 Hz, 2C), 128.3 (2C), 128.5 (2C), 133.0, 137.4, 140.5 (d, $^{4}J_{CF}$=3.2 Hz), 162.0 (d, $^{1}J_{CF}$=243.7 Hz), 198.2. HRMS: calcd for $C_{18}H_{21}FO_2Si$ ($[M]^+$), 316.1295. Found: *m*/*z* 316.1295.

*4.3.4. 3-(4′-Chlorophenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ca**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.02 (s, 9H), 3.01 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.54 (dd, *J*=15.6 and 8.2 Hz, 1H), 5.38 (dd, *J*=8.2 and 4.1 Hz, 1H), 7.31 (d, *J*=8.7, Hz, 2H), 7.37 (d, *J*=8.7, Hz, 2H), 7.45 (t, *J*=7.3 Hz, 2H), 7.55 (t, *J*=7.3 Hz, 1H), 7.95 (t, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.5, 70.9, 127.1 (2C), 128.3 (2C), 128.43 (2C), 128.44 (2C), 132.9, 133.0, 137.3, 143.3, 198.0. HRMS: calcd for $C_{18}H_{21}ClO_2Si$ ($[M]^+$), 332.0999. Found: *m*/*z* 332.0986.

*4.3.5. 3-(4′-Methylphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3da**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.02 (s, 9H), 2.34 (s, 3H), 3.01 (dd, *J*=15.6 and 3.7 Hz, 1H), 3.57 (dd, *J*=15.6 and 8.7 Hz, 1H), 5.37 (dd, *J*=8.7 and 3.7 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 2H), 7.32 (d, *J*=8.0 Hz, 2H), 7.44 (t, *J*=7.3 Hz, 2H), 7.53 (t, *J*=7.3 Hz, 1H), 7.97 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 21.0, 49.6, 71.5, 125.6 (2C), 128.31 (2C), 128.34 (2C), 128.9 (2C), 132.8, 136.8, 137.5, 141.7, 198.4. HRMS: calcd for $C_{19}H_{24}O_2Si$ ($[M]^+$), 312.1546. Found: *m*/*z* 312.1546.

*4.3.6. 3-(2′-Methylphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ea**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.04 (s, 9H), 2.40 (s, 3H), 2.89 (dd, *J*=15.6 and 2.7 Hz, 1H), 3.54 (dd, *J*=15.6 and 9.2 Hz, 1H), 5.59 (dd, *J*=9.2 and 2.7 Hz, 1H), 7.13 (d, *J*=7.3 Hz, 1H), 7.18 (t,

J=7.3 Hz, 1H), 7.25 (t, *J*=7.3 Hz, 1H), 7.47 (t, *J*=7.8 Hz, 2H), 7.56 (t, *J*=7.8 Hz, 1H), 7.60 (d, *J*=7.3 Hz, 1H), 7.99 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 19.0, 48.2, 68.4, 125.9, 126.1, 127.0, 128.39 (2C), 128.43 (2C), 130.2, 132.9, 133.3, 137.6, 142.8, 198.5. HRMS: calcd for $C_{19}H_{24}O_2Si$ ($[M]^+$), 312.1546. Found: *m*/*z* 312.1555.

*4.3.7. 3-(2′,6′-Dimethylphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3fa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.08 (s, 9H), 2.44 (br s, 3H), 2.62 (br s, 3H), 2.88 (dd, *J*=15.4 and 3.2 Hz, 1H), 3.91 (dd, *J*=15.4 and 9.6 Hz, 1H), 5.83 (dd, *J*=9.6 and 3.2 Hz, 1H), 7.01 (br s, 2H), 7.07 (t, *J*=7.3 Hz, 1H), 7.48 (t, *J*=7.3 Hz, 2H), 7.57 (t, *J*=7.3 Hz, 1H), 8.00 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.4 (3C), 20.8 (br, 2C), 45.3, 68.6, 126.9, 128.2 (br), 128.3 (2C), 128.4 (2C), 130.3 (br), 132.8, 134.1 (br), 137.1 (br), 137.7, 139.6, 198.7. HRMS: calcd for $C_{20}H_{25}O_2Si$ ($[M-H]^+$), 325.1624. Found: *m*/*z* 325.1617.

*4.3.8. 3-(4′-Methoxyphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ga**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.0 (s, 9H), 3.03 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.55 (dd, *J*=15.6 and 8.5 Hz, 1H), 3.78 (s, 3H), 5.34 (dd, *J*=8.5 and 4.1 Hz, 1H), 6.88 (d, *J*=8.7 Hz, 2H), 7.34 (d, *J*=8.7 Hz, 2H), 7.44 (t, *J*=7.3 Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.96 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.6, 55.1, 71.3, 113.6 (2C), 126.9 (2C), 128.3 (2C), 128.4 (2C), 132.9, 136.8, 137.5, 158.8, 198.5. HRMS: calcd for $C_{19}H_{23}O_3Si$ ($[M-H]^+$), 327.1416. Found: *m*/*z* 327.1422.

*4.3.9. 3-(4′-Acetylphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ha**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.03 (s, 9H), 2.57 (s, 3H), 3.01 (dd, *J*=16.0 and 4.1 Hz, 1H), 3.54 (dd, *J*=16.0 and 8.7 Hz, 1H), 5.44 (dd, *J*=8.7 and 4.1 Hz, 1H), 7.43 (t, *J*=7.8 Hz, 2H), 7.50–7.54 (m, 3H), 7.93 (d, *J*=8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 26.5, 49.2, 71.0, 125.8 (2C), 128.3 (2C), 128.4 (2C), 128.5 (2C), 133.1, 136.2, 137.2, 150.1, 197.6, 197.8. HRMS: calcd for $C_{20}H_{24}O_3Si$ ($[M]^+$), 340.1495. Found: *m*/*z* 340.1487.

*4.3.10. 3-(4′-Methoxycarbonylphenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ia**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.04 (s, 9H), 3.00 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.55 (dd, *J*=15.6 and 8.7 Hz, 1H), 3.88 (s, 3H), 5.44 (dd, *J*=8.7 and 4.1 Hz, 1H), 7.43 (t, *J*=7.3 Hz, 2H), 7.49 (d, *J*=8.2 Hz, 2H), 7.53 (t, *J*=7.3 Hz, 1H), 7.94 (d, *J*=7.3 Hz, 2H), 8.01 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 49.2, 51.9, 71.1, 125.7 (2C), 128.3 (2C), 128.4 (2C), 129.2, 129.7 (2C), 133.0, 137.3, 149.9, 166.8, 197.8. HRMS: calcd for $C_{20}H_{24}O_4Si$ ($[M]^+$), 356.1444. Found: *m*/*z* 356.1452.

*4.3.11. 3-(4′-Cyanophenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ja**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.01 (s, 9H), 3.02 (dd, *J*=16.0 and 4.1 Hz, 1H), 3.53 (dd, *J*=16.0 and 8.2 Hz, 1H), 5.44 (dd, *J*=8.2 and 4.1 Hz, 1H), 7.45 (t, *J*=7.3 Hz, 2H), 7.54 (d, *J*=8.5 Hz, 2H), 7.56 (t, *J*=7.3 Hz, 1H), 7.63 (d, *J*=8.5 Hz, 2H), 7.93 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 49.2, 70.8, 111.2, 118.8, 126.5 (2C), 128.3 (2C), 128.5 (2C), 132.2 (2C), 133.3, 137.1, 150.2, 197.5. HRMS: calcd for $C_{19}H_{21}NO_2Si$ ($[M]^+$), 323.1342. Found: *m*/*z* 323.1348.

*4.3.12. 3-(4′-Nitrophenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ka**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.0 (s, 9H), 3.05 (dd, *J*=16.0 and 4.4 Hz, 1H), 3.56 (dd, *J*=16.0 and 8.2 Hz, 1H), 5.50 (dd, *J*=8.2 and 4.4 Hz, 1H), 7.46 (t, *J*=7.3 Hz, 2H), 7.57 (t, *J*=Hz, 1H), 7.60 (d, *J*=8.7 Hz, 2H), 7.94 (d, *J*=7.3 Hz, 2H), 8.20 (d, *J*=8.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.2, 70.6, 123.7 (2C), 126.6 (2C), 128.3 (2C), 128.6 (2C), 133.3, 137.1, 147.2, 152.3, 197.4. HRMS: calcd for $C_{18}H_{21}NO_4Si$ ($[M]^+$), 343.1240. Found: *m*/*z* 343.1244.

*4.3.13. 3-(4′-N,N-Dimethylaminophenyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3la**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.04 (s, 9H), 2.95 (s, 6H), 3.03 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.58 (dd, *J*=15.6 and 8.7 Hz, 1H), 5.31 (dd, *J*=8.7 and 4.1 Hz, 1H), 6.72 (d, *J*=8.7, Hz, 2H), 7.30 (d, *J*=8.7 Hz, 2H), 7.45 (t, *J*=7.8 Hz, 2H), 7.55 (t, *J*=7.8 Hz, 1H), 7.98 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 40.6 (2C), 49.7, 71.5, 112.3 (2C), 126.6 (2C), 128.36 (2C), 128.38 (2C), 132.5, 132.8, 137.7, 149.9, 198.8. HRMS: calcd for $C_{20}H_{28}NO_2Si$ ($[M+H]^+$), 342.1889. Found: *m*/*z* 342.1900.

*4.3.14. 3-(1-Naphthyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3ma**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.09 (s, 9H), 3.19 (dd, *J*=16.0 and 2.3 Hz, 1H), 3.76 (dd, *J*=16.0 and 9.2 Hz, 1H), 6.29 (dd, *J*=9.2 and 2.3 Hz, 1H), 7.48 (t, *J*=7.8 Hz, 2H), 7.53–7.62 (m, 4H), 7.84 (d, *J*=7.8 Hz, 1H), 7.88 (d, *J*=7.3 Hz, 1H), 7.94 (d, *J*=8.2 Hz, 1H), 8.05 (d, *J*=7.3 Hz, 2H), 8.28 (d, *J*=8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 48.7, 68.8, 122.8, 123.3, 125.39, 125.43, 126.1, 127.7, 128.3 (2C), 128.4 (2C), 128.9, 129.6, 132.9, 133.7, 137.5, 140.3, 198.5. HRMS: calcd for $C_{22}H_{25}O_2Si$ ($[M+H]^+$), 349.1624. Found: *m*/*z* 349.1629.

*4.3.15. 3-(2-Naphthyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3na**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.02 (s, 9H), 3.13 (dd, *J*=15.6 and 3.7 Hz, 1H), 3.67 (dd, *J*=15.6 and 9.0 Hz, 1H), 5.59 (dd, *J*=9.0 and 3.7 Hz, 1H), 7.45–7.61 (m, 6H), 7.85–7.89 (m, 4H), 8.01 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 49.6, 71.8, 124.0, 124.3, 125.7, 126.1, 127.7, 127.9, 128.1, 128.37 (2C), 128.44 (2C), 132.9, 133.0, 133.2, 137.5, 142.1, 198.4. HRMS: calcd for $C_{22}H_{24}O_2Si$ ($[M]^+$), 348.1546. Found: *m*/*z* 348.1539.

*4.3.16. 3-(2-Furyl)-1-phenyl-3-trimethylsilyloxy-1-propanone (**3pa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.03 (s, 9H), 3.29 (dd, *J*=16.0 and 4.6 Hz, 1H), 3.64 (dd, *J*=16.0 and 8.2 Hz, 1H), 5.41 (dd, *J*=8.2 and 4.6 Hz, 1H), 6.24 (d, *J*=3.2 Hz, 1H), 6.31 (dd, *J*=3.2 and 1.8 Hz, 1H), 7.36 (d, *J*=1.8 Hz, 1H), 7.46 (t, *J*=7.3, Hz, 2H), 7.56 (t, *J*=7.3 Hz, 1H), 7.98 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 45.4, 64.9, 106.1, 110.1, 128.3 (2C), 128.5 (2C), 133.1, 137.3, 141.8, 156.0, 197.8. HRMS: calcd for $C_{16}H_{20}O_3Si$ ($[M]^+$), 288.1182. Found: *m*/*z* 288.1178.

*4.3.17. 1-Phenyl-3-(2-thienyl)-3-trimethylsilyloxy-1-propanone (**3qa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.05 (s, 9H), 3.20 (dd, *J*=16.0 and 4.1 Hz, 1H), 3.67 (dd, *J*=16.0 and 8.2 Hz, 1H), 5.70 (dd, *J*=8.2 and 4.1 Hz, 1H), 6.94 (dd, *J*=5.0 and 3.7, Hz, 1H), 6.98 (dd, *J*=3.7 and 0.9 Hz, 1H), 7.22 (dd, *J*=5.0 and 0.9 Hz, 1H), 7.46 (t, *J*=7.3 Hz, 2H), 7.56 (t, *J*=7.3 Hz, 1H), 7.98 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 49.6, 67.6, 123.0, 124.1, 126.4, 128.3 (2C), 128.4 (2C), 133.0, 137.3, 149.1, 197.7. HRMS: calcd for $C_{16}H_{19}O_2SSi$ ($[M-H]^+$), 303.0875. Found: *m*/*z* 303.0877.

*4.3.18. (4E)-1,5-Diphenyl-3-trimethylsilyloxy-4-penten-1-one (**3ra**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.17 (s, 9H), 3.13 (dd, *J*=15.6 and 4.8 Hz, 1H), 3.51 (dd, *J*=15.6 and 7.8 Hz, 1H), 5.07–5.11 (m, 1H), 6.39 (dd, *J*=15.6 and 6.0 Hz, 1H), 6.72 (d, *J*=15.6 Hz, 1H), 7.32 (t, *J*=7.3 Hz, 1H), 7.41 (t, *J*=7.3 Hz, 2H), 7.47 (d, *J*=7.3 Hz, 2H), 7.55 (t, *J*=7.3 Hz, 2H), 7.65 (t, *J*=7.3 Hz, 1H), 8.07 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.1 (3C), 47.1, 70.3, 126.5 (2C), 127.5, 128.4 (2C), 128.48 (2C), 128.53 (2C), 129.5, 132.0, 133.0, 136.7, 137.5, 198.4. HRMS: calcd for $C_{20}H_{23}O_2Si$ ($[M-H]^+$), 323.1467. Found: *m*/*z* 323.1458.

*4.3.19. (4E,6E)-1-Phenyl-3-trimethylsilyloxy-4,6-octadien-1-one (**3sa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.03 (s, 9H), 1.74 (d, *J*=6.4 Hz, 3H), 2.92 (dd, *J*=15.6 and 5.0 Hz, 1H), 3.33 (dd, *J*=15.6 and 7.8 Hz, 1H), 4.80–4.84 (m, 1H), 5.62 (dd, *J*=15.1 and 6.0 Hz, 1H), 5.70 (dq, *J*=15.1 and 6.4 Hz, 1H), 6.02 (dd, *J*=15.1 and 10.5 Hz, 1H), 6.20 (dd, *J*=15.1 and 10.5 Hz, 1H), 7.44 (t, *J*=7.3 Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.95 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 18.1, 47.1, 70.0, 128.3 (2C), 128.4 (2C), 129.7, 130.0, 130.7, 132.7, 132.9,

137.6, 198.5. HRMS: calcd for $C_{17}H_{23}O_2Si$ ([M−H]$^+$), 287.1467. Found: *m*/*z* 287.1471.

*4.3.20. 1-Phenyl-3-trimethylsilyloxy-1-undecanone (**3ta**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.03 (s, 9H), 0.87 (t, *J*=6.9 Hz, 3H), 1.28–1.53 (m, 14H), 2.91 (dd, *J*=15.6 and 5.0 Hz, 1H), 3.22 (dd, *J*=15.6 and 7.3 Hz, 1H), 4.30–4.35 (m, 1H), 7.44 (t, *J*=7.3, Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.96 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3C), 14.0, 22.6, 25.5, 29.2, 29.5, 29.6, 31.8, 38.1, 46.5, 69.7, 128.3 (2C), 128.4 (2C), 132.9, 137.6, 199.3. HRMS: calcd for $C_{20}H_{34}O_2Si$ ([M]$^+$), 334.2328. Found: *m*/*z* 334.2333.

*4.3.21. 1,5-Diphenyl-3-trimethylsilyloxy-1-pentanone (**3ua**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.09 (s, 9H), 1.84–1.97 (m, 2H), 2.70 (ddd, *J*=13.5, 11.0, and 5.5 Hz, 1H), 2.81 (ddd, *J*=13.5, 11.0, and 5.5 Hz, 1H), 3.02 (dd, *J*=15.6 and 5.0 Hz, 1H), 3.31 (dd, *J*=15.6 and 7.3 Hz, 1H), 4.43–4.48 (m, 1H), 7.19–7.24 (m, 3H), 7.31 (t, *J*=7.8 Hz, 2H), 7.48 (t, *J*=7.8 Hz, 2H), 7.58 (t, *J*=7.8 Hz, 1H), 7.98 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3C), 31.9, 39.7, 46.3, 69.2, 125.8, 128.26 (2C), 128.28 (2C), 128.34 (2C), 128.5 (2C), 133.0, 137.5, 142.0, 199.0. HRMS: calcd for $C_{20}H_{26}O_2Si$ ([M]$^+$), 326.1702. Found: *m*/*z* 326.1708.

*4.3.22. 4-Methyl-1-phenyl-3-trimethylsilyloxy-1-pentanone (**3va**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.01 (s, 9H), 0.93 (d, *J*=6.9 Hz, 3H), 0.95 (d, *J*=6.9 Hz, 3H), 1.76 (dseptet, *J*=4.1 and 6.9 Hz, 1H), 2.84 (dd, *J*=15.6 and 4.1 Hz, 1H), 3.22 (dd, *J*=15.6 and 8.2 Hz, 1H), 4.20 (dt, *J*=8.2 and 4.1 Hz, 1H), 7.45 (t, *J*=7.3 Hz, 2H), 7.55 (t, *J*=7.3 Hz, 1H), 7.96 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3C), 17.7, 18.3, 34.2, 43.0, 74.0, 128.3 (2C), 128.4 (2C), 132.9, 137.8, 199.8. HRMS: calcd for $C_{15}H_{25}O_2Si$ ([M+H]$^+$), 265.1624. Found: *m*/*z* 265.1628.

*4.3.23. 3-Cyclohexyl-1-phenyl-3-trimethylsilyloxy-1-propanone (**3wa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.0 (s, 9H), 0.99–1.27 (m, 5H), 1.37–1.44 (m, 1H), 1.66–1.82 (m, 5H), 2.91 (dd, *J*=15.6 and 3.9 Hz, 1H), 3.22 (dd, *J*=15.6 and 8.2 Hz, 1H), 4.18 (dt, *J*=8.2 and 3.9 Hz, 1H), 7.45 (t, *J*=7.3 Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.96 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3C), 26.3, 26.4, 26.5, 28.3, 29.1, 43.6, 44.4, 73.5, 128.3 (2C), 128.4 (2C), 132.8, 137.7, 199.7. HRMS: calcd for $C_{18}H_{29}O_2Si$ ([M+H]$^+$), 305.1937. Found: *m*/*z* 305.1940.

*4.3.24. 4,4-Dimethyl-1-phenyl-3-trimethylsilyloxy-1-pentanone (**3xa**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.01 (s, 9H), 0.93 (s, 9H), 2.89 (dd, *J*=16.0 and 2.5 Hz, 1H), 3.22 (dd, *J*=16.0 and 8.7 Hz, 1H), 4.12 (dd, *J*=8.7 and 2.5 Hz, 1H), 7.45 (t, *J*=7.8 Hz, 2H), 7.55 (t, *J*=7.8 Hz, 1H), 7.96 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.4 (3C), 26.1 (3C), 35.4, 41.9, 76.7, 128.2 (2C), 128.5 (2C), 132.9, 137.8, 199.8. HRMS: calcd for $C_{16}H_{27}O_2Si$ ([M+H]$^+$), 279.1780. Found: *m*/*z* 279.1785.

*4.3.25. 2-(1-Trimethylsilyloxybenzyl)-1-cyclohexanone (**3ab**)[27] (anti/syn=67/33).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) *anti*-isomer: δ −0.01 (s, 9H), 1.17–2.73 (m, 9H), 5.07 (d, *J*=7.8 Hz, 1H), 7.20–7.33 (m, 5H); *syn*-isomer: δ 0.05 (s, 9H), 1.17–2.73 (m, 9H), 5.34 (d, *J*=4.6 Hz, 1H), 7.20–7.33 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) *anti*-isomer: δ 0.1 (3C), 24.2, 28.4, 30.4, 42.1, 59.3, 73.4, 127.0 (2C), 127.4, 128.0 (2C), 142.7, 211.5; *syn*-isomer: δ 0.1 (3C), 24.4, 26.3, 26.9, 42.3, 58.4, 71.6, 126.2 (2C), 126.8, 127.8 (2C), 144.2, 211.0. HRMS: calcd for $C_{16}H_{24}O_2Si$ ([M]$^+$), 276.1546. Found: *m*/*z* 276.1545.

*4.3.26. Methyl 2,2-dimethyl-3-phenyl-3-trimethylsilyloxypropanoate (**3ac**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.03 (s, 9H), 1.01 (s, 3H), 1.14 (s, 3H), 3.69 (s, 3H), 4.99 (s, 1H), 7.24–7.31 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 19.1, 21.7, 49.0, 51.6, 79.2, 127.3, 127.4 (2C), 127.8 (2C), 140.8, 177.3. HRMS: calcd for $C_{15}H_{23}O_3Si$ ([M−H]$^+$), 279.1416. Found: *m*/*z* 279.1409.

*4.3.27. Methyl 2,2-dimethyl-3-(4′-methoxycarbonylphenyl)-3-trimethylsilyloxypropanoate (**3ic**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.05 (s, 9H), 0.98 (s, 3H), 1.11 (s, 3H), 2.27 (s, 3H), 3.66 (s, 3H), 4.97 (s, 1H), 7.02 (d, *J*=8.5 Hz, 2H), 7.27 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3C), 18.9, 21.1, 21.6, 48.9, 51.6, 78.5, 120.4 (2C), 128.6 (2C), 138.2, 149.9, 169.1, 177.0. HRMS: calcd for $C_{17}H_{26}O_5Si$ ([M]$^+$), 338.1550. Found: *m*/*z* 338.1552.

*4.3.28. Methyl 3-(4′-cyanophenyl)-2,2-dimethyl-3-trimethylsilyloxypropanoate (**3jc**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.06 (s, 9H), 0.96 (s, 3H), 1.10 (s, 3H), 3.65 (s, 3H), 4.99 (s, 1H), 7.38 (d, *J*=8.2 Hz, 2H), 7.57 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 19.6, 21.1, 48.9, 51.8, 78.4, 111.3, 118.7, 128.3 (2C), 131.3 (2C), 146.5, 176.5. HRMS: calcd for $C_{16}H_{23}NO_3Si$ ([M]$^+$), 305.1447. Found: *m*/*z* 305.1445.

*4.3.29. Methyl 2,2-dimethyl-3-(4′-nitrophenyl)-3-trimethylsilyloxypropanoate (**3kc**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.04 (s, 9H), 0.98 (s, 3H), 1.12 (s, 3H), 3.66 (s, 3H), 5.06 (s, 1H), 7.45 (d, *J*=8.5 Hz, 2H), 8.15 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 19.7, 21.0, 48.9, 51.8, 78.2, 122.7 (2C), 128.4 (2C), 147.3, 148.6, 176.4. HRMS: calcd for $C_{15}H_{23}NO_5Si$ ([M]$^+$), 325.1346. Found: *m*/*z* 325.1355.

*4.3.30. Methyl 2,2-dimethyl-3-(4′-N,N-dimethylaminophenyl)-3-trimethylsilyloxypropanoate (**3lc**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.05 (s, 9H), 0.98 (s, 3H), 1.11 (s, 3H), 2.93 (s, 6H), 3.67 (s, 3H), 4.89 (s, 1H), 6.65 (d, *J*=8.5 Hz, 2H), 7.12 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.0 (3C), 18.8, 21.9, 40.4 (2C), 49.2, 51.5, 79.0, 111.3 (2C), 128.4, 128.5 (2C), 149.8, 177.6. HRMS: calcd for $C_{17}H_{29}NO_3Si$ ([M]$^+$), 323.1917. Found: *m*/*z* 323.1912.

*4.3.31. Methyl 2,2-dimethyl-3-(2-thienyl)-3-trimethylsilyloxypropanoate (**3qc**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.00 (s, 9H), 1.05 (s, 3H), 1.21 (s, 3H), 3.67 (s, 3H), 5.24 (s, 1H), 6.86 (d, *J*=3.7 Hz, 1H), 6.92 (dd, *J*=5.0 and 3.7 Hz, 1H), 7.19 (d, *J*=5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3C), 19.9, 21.0, 49.2, 51.7, 75.7, 124.3, 124.8, 125.9, 145.0, 176.9. HRMS: calcd for $C_{13}H_{23}O_3SSi$ ([M+H]$^+$), 287.1137. Found: *m*/*z* 287.1140.

*4.3.32. Methyl (4E)-2,2-dimethyl-5-phenyl-3-trimethylsilyloxy-4-pentenoate (**3rc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.09 (s, 9H), 1.11 (s, 3H), 1.19 (s, 3H), 3.67 (s, 3H), 4.49 (d, *J*=7.3 Hz, 1H), 6.13 (dd, *J*=16.0 and 7.3 Hz, 1H), 6.51 (d, *J*=16.0 Hz, 1H), 7.24 (t, *J*=7.3 Hz, 1H), 7.32 (t, *J*=7.3 Hz, 2H), 7.37 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.3 (3C), 19.9, 21.3, 48.5, 51.7, 78.4, 126.5 (2C), 127.6, 128.6 (2C), 128.8, 132.0, 136.8, 177.1. HRMS: calcd for $C_{17}H_{26}O_3Si$ ([M]$^+$), 306.1651. Found: *m*/*z* 306.1650.

*4.3.33. Methyl 2,2-dimethyl-5-phenyl-3-trimethylsilyloxypentanoate (**3uc**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ 0.18 (s, 9H), 1.12 (s, 3H), 1.19 (s, 3H), 1.66–1.71 (m, 2H), 2.48–2.54 (m, 1H), 2.81–2.87 (m, 1H), 3.67 (s, 3H), 4.00–4.02 (m, 1H), 7.19–7.22 (m, 3H), 7.29–7.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.8 (3C), 20.3, 21.4, 33.5, 35.1, 48.2, 51.6, 77.5, 125.8, 128.27 (2C), 128.35 (2C), 142.2, 177.5. HRMS: calcd for $C_{17}H_{28}O_3Si$ ([M]$^+$), 308.1808. Found: *m*/*z* 308.1811.

*4.3.34. 1,3-Diphenyl-3-trimethylsilyloxybutanone (**5**).* ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$) δ −0.09 (s, 9H), 1.85 (s, 3H), 3.04 (d, *J*=13.3 Hz, 1H), 3.57 (d, *J*=13.3 Hz, 1H), 7.23 (tt, *J*=1.4 and 7.8 Hz, 1H), 7.32 (t, *J*=7.8 Hz, 2H), 7.40 (t, *J*=7.8 Hz, 2H), 7.48 (dd, *J*=1.4 and 7.8 Hz, 2H), 7.51 (tt, *J*=1.4 and 7.8 Hz, 1H), 7.94 (dd, *J*=1.4 and 7.8 Hz, 2H). ^{13}C

NMR (125 MHz, $CDCl_3$) δ 2.0 (3C), 27.5, 54.2, 76.8, 125.0 (2C), 126.8, 128.0 (2C), 128.1 (2C), 129.0 (2C), 132.6, 138.4, 148.3, 199.1. HRMS: calcd for $C_{19}H_{23}O_2Si$ ($[M-H]^+$), 311.1467. Found: *m*/*z* 311.1460.

*4.3.35. 1,3-Diphenyl-3-methoxy-1-propanone (**7aa**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 3.07 (dd, *J*=16.5 and 4.6 Hz, 1H), 3.23 (s, 3H), 3.59 (dd, *J*=16.5 and 8.7 Hz, 1H), 4.88 (dd, *J*=8.7 and 4.6 Hz, 1H), 7.29 (t, *J*=7.3 Hz, 1H), 7.35–7.44 (m, 6H), 7.53 (t, *J*=7.3 Hz, 1H), 7.94 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.1, 56.8, 79.5, 126.6 (2C), 127.8, 128.2 (2C), 128.48 (2C), 128.53 (2C), 133.0, 137.2, 141.4, 197.6. HRMS: calcd for $C_{16}H_{17}O_2$ ($[M+H]^+$), 241.1229. Found: *m*/*z* 241.1230.

*4.3.36. anti-2-(1-Methoxybenzyl)-1-cyclohexanone (anti-**7ab**)[28].* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.17–1.24 (m, 1H), 1.49–1.61 (m, 2H), 1.68–1.79 (m, 2H), 1.93–2.00 (m, 1H), 2.37–2.42 (m, 1H), 2.45–2.50 (m, 1H), 2.70–2.75 (m, 1H), 3.20 (s, 3H), 4.55 (d, *J*=8.7 Hz, 1H), 7.27–7.37 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.1, 28.4, 30.5, 42.0, 56.7, 57.2, 81.8, 127.6 (2C), 127.8, 128.3 (2C), 139.4, 211.5. HRMS: calcd for $C_{14}H_{17}O_2$ ($[M-H]^+$), 217.1229. Found: *m*/*z* 217.1236.

*4.3.37. syn-2-(1-Methoxybenzyl)-1-cyclohexanone (syn-**7ab**)[28].* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.45–1.54 (m, 1H), 1.67–1.79 (m, 2H), 1.85–1.91 (m, 1H), 1.96–2.04 (m, 2H), 2.20–2.27 (m, 1H), 2.40–2.49 (m, 2H), 3.26 (s, 3H), 4.79 (d, *J*=4.1 Hz, 1H), 7.24–7.35 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 26.3, 27.0, 42.2, 57.2, 57.3, 79.9, 126.8 (2C), 127.2, 128.1 (2C), 140.8, 210.5. HRMS: calcd for $C_{14}H_{18}O_2$ ($[M]^+$), 218.1307. Found: *m*/*z* 218.1306.

*4.3.38. Methyl 2,2-dimethyl-3-methoxy-3-phenylpropanoate (**7ac**).* ^1H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ 1.01 (s, 3H), 1.12 (s, 3H), 3.19 (s, 3H), 3.71 (s, 3H), 4.49 (s, 1H), 7.26–7.35 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.7, 22.6, 47.9, 51.8, 57.3, 87.8, 126.6, 127.7 (2C), 128.3 (2C), 137.3, 177.2. HRMS: calcd for $C_{13}H_{19}O_3$ ($[M+H]^+$), 223.1334. Found: *m*/*z* 223.1340.

*4.3.39. Methyl 2,2-dimethyl-3-phenyl-3-(N-phenylamino)propanoate (**9ac**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.16 (s, 3H), 1.27 (s, 3H), 3.63 (s, 3H), 4.49 (d, *J*=6.7 Hz, 1H), 4.80 (d, *J*=6.7 Hz, 1H), 6.49 (d, *J*=8.2 Hz, 2H), 6.59 (t, *J*=7.3 Hz, 1H), 7.03 (dd, *J*=8.2 and 7.3 Hz, 2H), 7.19–7.31 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 24.5, 47.0, 52.0, 64.3, 113.4 (2C), 117.2, 127.4, 128.0 (2C), 128.2 (2C), 129.0 (2C), 139.2, 146.9, 177.0. HRMS: calcd for $C_{18}H_{22}NO_2$ ($[M+H]^+$), 284.1651. Found: *m*/*z* 284.1647.

*4.3.40. Methyl 2,2-dimethyl-3-[N-(4-methoxyphenyl)amino]-3-phenylpropanoate (**9bc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.16 (s, 3H), 1.24 (s, 3H), 3.65 (s, 6H), 4.46 (s, 2H), 6.45 (d, *J*=8.7 Hz, 2H), 6.64 (d, *J*=8.7 Hz, 2H), 7.20–7.29 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 24.5, 47.1, 52.0, 55.6, 65.2, 114.6 (2C), 114.7 (2C), 127.4, 127.9 (2C), 128.3 (2C), 139.3, 141.2, 151.9, 177.1. HRMS: calcd for $C_{19}H_{24}NO_3$ ($[M+H]^+$), 314.1756. Found: *m*/*z* 314.1758.

*4.3.41. Methyl 2,2-dimethyl-3-[N-(4-chlorophenyl)amino]-3-phenylpropanoate (**9cc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.15 (s, 3H), 1.27 (s, 3H), 3.64 (s, 3H), 4.42 (d, *J*=7.8 Hz, 1H), 4.88 (d, *J*=7.8 Hz, 1H), 6.41 (d, *J*=9.2 Hz, 2H), 6.97 (d, *J*=9.2 Hz, 2H), 7.21–7.29 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 24.6, 46.9, 52.1, 64.6, 114.4 (2C), 121.8, 127.6, 128.1 (2C), 128.2 (2C), 128.8 (2C), 138.7, 145.5, 176.9. HRMS: calcd for $C_{18}H_{21}ClNO_2$ ($[M+H]^+$), 318.1261. Found: *m*/*z* 318.1271.

*4.3.42. Methyl 2,2-dimethyl-3-(4-methoxyphenyl)-3-(N-phenylamino) propanoate (**9dc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.15 (s, 3H), 1.25 (s, 3H), 3.64 (s, 3H), 3.75 (s, 3H), 4.44 (br s, 1H), 4.75 (br s, 1H), 6.49 (d, *J*=7.8 Hz, 2H), 6.59 (t, *J*=7.8 Hz, 1H), 6.81 (d, *J*=8.5 Hz, 2H), 7.04 (t, *J*=7.8 Hz, 2H), 7.18 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 24.4, 52.0, 55.1, 63.8, 113.38 (2C), 113.39 (2C), 117.2, 129.0 (2C), 129.2 (2C), 131.1, 147.0, 158.8, 177.1. HRMS: calcd for $C_{19}H_{23}NO_3$ ($[M]^+$), 313.1678. Found: *m*/*z* 313.1685.

*4.3.43. Methyl 2,2-dimethyl-3-(4-chlorophenyl)-3-(N-phenylamino) propanoate (**9ec**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.15 (s, 3H), 1.27 (s, 3H), 3.64 (s, 3H), 4.45 (d, *J*=6.7 Hz, 1H), 4.79 (d, *J*=6.7 Hz, 1H), 6.46 (d, *J*=8.2 Hz, 2H), 6.61 (t, *J*=7.3 Hz, 1H), 7.05 (dd, *J*=8.2 and 7.3 Hz, 2H), 7.22 (d, *J*=8.5 Hz, 2H), 7.25 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 24.4, 46.8, 52.1, 63.8, 113.3 (2C), 117.5, 128.2 (2C), 129.0 (2C), 129.6 (2C), 133.2, 137.9, 146.6, 176.7. HRMS: calcd for $C_{18}H_{20}ClNO_2$ ($[M]^+$), 317.1183. Found: *m*/*z* 317.1181.

*4.3.44. Methyl 2,2-dimethyl-3-(4-cyanophenyl)-3-(N-phenylamino) propanoate (**9fc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.16 (s, 3H), 1.30 (s, 3H), 3.66 (s, 3H), 4.52 (d, *J*=7.3 Hz, 1H), 4.86 (d, *J*=7.3 Hz, 1H), 6.44 (d, *J*=7.3 Hz, 2H), 6.64 (t, *J*=7.3 Hz, 1H), 7.06 (t, *J*=7.3 Hz, 2H), 7.42 (d, *J*=8.5 Hz, 2H), 7.59 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 24.4, 46.8, 52.3, 64.3, 111.4, 113.3 (2C), 117.9, 118.6, 129.0 (2C), 129.1 (2C), 131.9 (2C), 145.3, 146.2, 176.3. HRMS: calcd for $C_{19}H_{20}N_2O_2$ ($[M]^+$), 308.1525. Found: *m*/*z* 308.1527.

*4.3.45. Methyl 2,2-dimethyl-3-(4-nitrophenyl)-3-(N-phenylamino) propanoate (**9gc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.19 (s, 3H), 1.32 (s, 3H), 3.67 (s, 3H), 4.58 (d, *J*=7.3 Hz, 1H), 4.90 (d, *J*=7.3 Hz, 1H), 6.45 (d, *J*=7.3 Hz, 2H), 6.64 (t, *J*=7.3 Hz, 1H), 7.06 (t, *J*=7.3 Hz, 2H), 7.49 (d, *J*=8.5 Hz, 2H), 8.16 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 24.5, 46.8, 52.3, 64.1, 113.3 (2C), 118.0, 123.3 (2C), 129.1 (2C), 129.2 (2C), 146.1, 147.4, 147.5, 176.2. HRMS: calcd for $C_{18}H_{21}N_2O_4$ ($[M+H]^+$), 329.1501. Found: *m*/*z* 329.1497.

*4.3.46. Methyl 3-(4-chlorophenyl)-2,2-dimethyl-3-[N-(4-methoxyphenyl)amino]propanoate (**9hc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.14 (s, 3H), 1.24 (s, 3H), 3.65 (s, 3H), 3.66 (s, 3H), 4.42 (s, 1H), 4.45 (s, 1H), 6.42 (d, *J*=8.7 Hz, 2H), 6.64 (d, *J*=8.7 Hz, 2H), 7.21 (d, *J*=8.2 Hz, 2H), 7.25 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 24.4, 46.9, 52.1, 55.6, 64.7, 114.7 (4C), 128.2 (2C), 129.6 (2C), 133.1, 138.0, 140.8, 152.0, 176.8. HRMS: calcd for $C_{19}H_{22}ClNO_3$ ($[M]^+$), 347.1288. Found: *m*/*z* 347.1285.

*4.3.47. Methyl 2,2-dimethyl-3-(4-methoxyphenyl)-3-[N-(4-chlorophenyl)amino]propanoate (**9ic**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.14 (s, 3H), 1.26 (s, 3H), 3.65 (s, 3H), 3.76 (s, 3H), 4.37 (d, *J*=7.3 Hz, 1H), 4.83 (d, *J*=7.3 Hz, 1H), 6.41 (d, *J*=9.2 Hz, 2H), 6.81 (d, *J*=8.7 Hz, 2H), 6.98 (d, *J*=9.2 Hz, 2H), 7.16 (d, *J*=8.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 24.6, 47.0, 52.1, 55.1, 64.0, 113.5 (2C), 114.5 (2C), 121.8, 128.8 (2C), 129.2 (2C), 130.6, 145.5, 158.9, 177.0. HRMS: calcd for $C_{19}H_{22}ClNO_3$ ($[M]^+$), 347.1288. Found: *m*/*z* 347.1286.

*4.3.48. Methyl 2,2-dimethyl-3-phenyl-3-(N-methylamino)propanoate (**9jc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.05 (s, 3H), 1.12 (s, 3H), 1.67 (s, 1H), 2.20 (s, 3H), 3.69 (s, 3H), 3.78 (s, 1H), 7.23–7.28 (m, 3H), 7.30–7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 24.1, 34.9, 47.4, 51.8, 71.0, 127.2, 127.8 (2C), 128.8 (2C), 139.0, 177.8. HRMS: calcd for $C_{13}H_{19}NO_2$ ($[M]^+$), 221.1416. Found: *m*/*z* 221.1415.

*4.3.49. Methyl 2,2-dimethyl-3-phenyl-3-(N-n-butylamino)propanoate (**9kc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 0.84 (t, *J*=7.1 Hz, 3H), 1.04 (s, 3H), 1.10 (s, 3H), 1.22–1.39 (m, 4H), 1.55 (br s, 1H), 2.29 (ddd, *J*=11.5, 6.9, and 6.4 Hz, 1H), 2.39 (ddd, *J*=11.5, 6.9, and 6.4 Hz, 1H), 3.68 (s, 3H), 3.88 (s, 1H), 7.23–7.33 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.4, 20.3, 24.0, 32.1, 47.4, 47.5, 51.7, 68.6, 127.1, 127.7 (2C), 128.8 (2C), 139.7, 177.9. HRMS: calcd for $C_{16}H_{26}NO_2$ ($[M+H]^+$), 264.1964. Found: *m*/*z* 264.1961.

*4.3.50. Methyl 2,2-dimethyl-3-phenyl-3-(N-benzylamino)propanoate (**9lc**).* ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.03 (s, 3H), 1.12 (s, 3H), 1.87

(br s, 1H), 3.40 (d, J=13.7 Hz, 1H), 3.64 (s, 3H), 3.65 (d, J=13.7 Hz, 1H), 3.89 (s, 1H), 7.21–7.35 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 24.1, 47.4, 51.4, 51.7, 67.7, 126.8, 127.3, 127.9 (2C), 128.1 (2C), 128.2 (2C), 129.0 (2C), 139.1, 140.5, 177.7. HRMS: calcd for $C_{19}H_{24}NO_2$ ($[M+H]^+$), 298.1807. Found: m/z 298.1803.

*4.3.51. Methyl 2,2-dimethyl-3-phenyl-3-(N-i-propylamino)propanoate (**9mc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.91 (d, J=6.2 Hz, 3H), 0.92 (d, J=6.2 Hz, 3H), 1.03 (s, 3H), 1.07 (s, 3H), 1.52 (br s, 1H), 2.46 (septet, J=6.2 Hz, 1H), 3.68 (s, 3H), 3.98 (s, 1H), 7.22–7.32 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 21.6, 24.0, 24.4, 45.7, 47.6, 51.6, 65.8, 127.1, 127.7 (2C), 128.8 (2C), 140.0, 177.8. HRMS: calcd for $C_{15}H_{24}NO_2$ ($[M+H]^+$), 250.1807. Found: m/z 250.1811.

*4.3.52. Methyl 2,2-dimethyl-3-phenyl-3-(N-tert-butylamino)propanoate (**9nc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.88 (s, 9H), 0.98 (s, 3H), 1.08 (s, 3H), 1.49 (br s, 1H), 3.66 (s, 3H), 4.03 (s, 1H), 7.16–7.34 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 23.7, 30.3 (3C), 48.3, 51.0, 51.6, 62.6, 126.7, 127.4 (2C), 128.7 (2C), 143.1, 177.9. HRMS: calcd for $C_{16}H_{24}NO_2$ ($[M-H]^+$), 262.1807. Found: m/z 262.1807.

*4.3.53. Methyl 2,2-dimethyl-3-phenyl-3-(N-diethylphosphonoamino) propanoate (**9oc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.96 (t, J=6.9 Hz, 3H), 1.11 (s, 3H), 1.22 (t, J=6.9 Hz, 3H), 1.30 (s, 3H), 3.44–3.52 (m, 1H), 3.66 (s, 3H), 3.79–3.97 (m, 3H), 4.17 (s, 1H), 4.19 (s, 1H), 7.19–7.20 (m, 2H), 7.22–7.30 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.7 (d, J_{C-P}=7.6 Hz), 16.1 (d, J_{C-P}=7.1 Hz), 22.2, 24.3, 47.2 (d, J_{C-P}=7.6 Hz), 51.8, 62.0 (d, J_{C-P}=5.2 Hz), 62.2 (d, J_{C-P}=5.2 Hz), 62.8, 127.4, 127.77 (2C), 127.84 (2C), 140.6 (d, J_{C-P}=0.9 Hz), 176.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ 7.3. HRMS: calcd for $C_{16}H_{27}NO_5P$ ($[M+H]^+$), 344.1627. Found: m/z 344.1629.

*4.3.54. Methyl 2,2-dimethyl-3-phenyl-3-(N-diphenylphosphinylamino) propanoate (**9pc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.08 (s, 3H), 1.43 (s, 3H), 3.65 (s, 3H), 4.11 (dd, J=10.6 Hz, J_{H-P}=10.6 Hz, 1H), 4.74 (dd, J=10.6 Hz, J_{H-P}=10.6 Hz, 1H), 7.01–7.02 (m, 2H), 7.17–7.22 (m, 5H), 7.33–7.36 (m, 1H), 7.40–7.44 (m, 2H), 7.47–7.50 (m, 1H), 7.53–7.57 (m, 2H), 7.78–7.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 25.3, 47.18, 47.21, 52.0, 62.4, 127.3, 127.7, 127.86, 127.94, 128.4, 128.5, 131.39, 131.41, 131.5, 131.6, 131.7, 131.8, 132.6, 132.7, 177.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.4. HRMS: calcd for $C_{24}H_{27}NO_3P$ ($[M+H]^+$), 408.1729. Found: m/z 408.1738.

*4.3.55. Methyl 2,2-dimethyl-3-phenyl-3-(N-tosylamino)propanoate (**9qc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.09 (s, 3H), 1.30 (s, 3H), 2.26 (s, 3H), 3.61 (s, 3H), 4.38 (d, J=9.9 Hz, 1H), 6.23 (d, J=9.9 Hz, 1H), 6.91 (d, J=6.9 Hz, 2H), 6.95 (d, J=8.3 Hz, 2H), 7.02–7.10 (m, 3H), 7.40 (d, J=8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 22.3, 24.5, 47.1, 52.0, 64.7, 126.9 (2C), 127.3, 127.8 (2C), 127.9 (2C), 128.9 (2C), 137.1, 137.6, 142.5, 176.4. HRMS: calcd for $C_{19}H_{24}NO_4S$ ($[M+H]^+$), 362.1426. Found: m/z 362.1425.

*4.3.56. 4-Phenyl-1,3,3-trimethyl-2-azetidinone (**11jc**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.77 (s, 3H), 1.43 (s, 3H), 2.87 (s, 3H), 4.31 (s, 1H), 7.17–7.18 (m, 2H), 7.31–7.35 (m, 1H), 7.38–7.41 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 22.4, 27.0, 56.4, 68.6, 126.6 (2C), 127.9, 128.6 (2C), 136.2, 174.3. HRMS: calcd for $C_{12}H_{16}NO$ ($[M+H]^+$), 190.1232. Found: m/z 190.1232.

*4.3.57. 2,4-Diphenyl-4-trimethylsilyloxy-1,2,3,4-tetrahydroquinoline (**13aa**) (single diastereomer).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.06 (s, 9H), 2.07–2.13 (m, 2H), 4.30 (s, 1H), 4.75 (dd, J=9.4 and 5.8 Hz, 1H), 6.53–6.58 (m, 2H), 6.80 (d, J=7.8 Hz, 1H), 7.09 (dt, J=7.3 and 1.6 Hz, 1H), 7.20–7.35 (m, 6H), 7.45 (d, J=8.7 Hz, 2H), 7.46 (d, J=7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.7 (3C), 50.3, 53.3, 76.4, 114.4, 116.4, 123.8, 126.4, 126.6 (2C), 126.8 (2C), 127.56 (2C), 127.61, 128.6 (2C), 129.3, 131.2, 143.6, 146.0, 147.6. HRMS: calcd for $C_{24}H_{27}NOSi$ ($[M]^+$), 373.1862. Found: m/z 373.1867.

*4.3.58. 2,4-Diphenyl-6-methoxy-4-trimethylsilyloxy-1,2,3,4-tetrahydroquinoline (**13ba**) (single diastereomer).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS as an external standard) δ −0.05 (s, 9H), 2.05–2.11 (m, 2H), 3.57 (s, 3H), 4.08 (s, 1H), 4.69 (dd, J=8.7 and 6.0 Hz, 1H), 6.39 (d, J=3.0 Hz, 1H), 6.55 (d, J=8.7 Hz, 1H), 6.74 (dd, J=8.7 and 3.0 Hz, 1H), 7.18–7.33 (m, 6H), 7.42 (d, J=7.6 Hz, 2H), 7.45 (d, J=7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.8 (3C), 50.6, 53.4, 55.9, 76.6, 115.6, 116.1, 116.3, 124.7, 126.47, 126.52 (2C), 126.8 (2C), 127.5, 127.6 (2C), 128.5 (2C), 140.4, 143.8, 147.6, 151.1. HRMS: calcd for $C_{25}H_{29}NO_2Si$ ($[M]^+$), 403.1968. Found: m/z 403.1971.

*4.3.59. Methyl 3-amino-2,2-dimethyl-3-phenyl-propanoate (**10**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.08 (s, 3H), 1.14 (s, 3H), 1.64 (s, 2H), 3.69 (s, 3H), 4.23 (s, 1H), 7.24–7.32 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 23.5, 47.7, 51.8, 61.9, 127.3, 127.7 (2C), 128.0 (2C), 141.8, 177.8. HRMS: calcd for $C_{12}H_{18}NO_2$ ($[M+H]^+$), 208.1338. Found: m/z 208.1341.

Acknowledgements

This research was supported financially by a grant from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supplementary data

^{1}H, ^{13}C, and ^{31}P NMR spectra of products. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.015. These data include MOL files and InChIKeys of the most important compounds described in this article.

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