Supporting Information

Chemoselective Aldol Reactions of Silyl Enolates Catalyzed by MgI_2 Etherate

Wei-Dong Z. Li* and Xing-Xian Zhang

National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

Experimental

General

For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (PE, b.p. 60~90 °C) are used. All solvents were purified and dried by standard techniques, and distilled prior to use. IR spectra were recorded on a Nicolet FT-170SX spectrometer as liquid film. ^1H and ^{13}C NMR spectra were taken on a Bruker AC-80, AM-200 or AM-400 spectrometer with TMS as an internal standard and CDCl_3 as solvent. HRMS were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. Melting points were measured on Kofler hot stage and uncorrected.

Representative experimental procedure of MgI_2 etherate-catalyzed Mukaiyama aldol reaction. To a stirred solution of piperonal (5 mmol) in dry CH_2Cl_2 (8 mL) was added a freshly prepared stock solution of MgI_2 etherate (**1**) in Et_2O /Benzene (v/v 1:2, 0.2 M, 0.25 mL, 1 mol % of **1**) at 22 °C. After stirring for 10 min, a solution of silyl enolate **4** (5.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise via a syringe under Ar. The resulting homogeneous reaction mixture was stirred at r.t. for 30 min and quenched with saturated aqueous NaHCO_3 . Extractive workup with ether and chromatographic purification of the crude product on silica gel gave the silylated aldol adduct **7a** (R = piperonyl) in 96% yield as a mixture of diastereomers (*dr* 3:2).

Typical experimental procedure of the MgI_2 etherate-catalyzed aldol discrimination of benzaldehyde and its dimethyl acetal. A freshly prepared stock solution of MgI_2 etherate (**1**) in Et_2O /Benzene (v/v 1:2, 0.2 M, 0.125 mL, 5 mol % of **1**) was added to a solution of benzaldehyde (53 mg, 0.5 mmol) and its dimethyl acetal (76 mg, 0.5 mmol) in CH_2Cl_2 (4 mL) at 22 °C, followed by the addition of 1, 2-bis(trimethylsiloxy)cyclobutene **4** (115 mg, 0.5 mmol) in CH_2Cl_2 (2 mL). After stirring for 30 min at room temperature, the reaction mixture was poured into saturated aqueous NaHCO_3 solution (2 mL). The resultant mixture was extracted with Et_2O (2 × 40 mL) and combined organic layers were washed with water (2 × 10 mL), brine (2 × 15 mL), dried over MgSO_4 , and concentrated. The crude product was purified by flash chromatography on silica gel eluting with PE / EtOAc (v/v 35:1) to provide 137 mg (99%) of 2-[(methoxy)benzyl]-2-(trimethylsiloxy)cyclobutanone **7c** (R = Ph).

Typical experimental procedure of the MgI_2 etherate-catalyzed Mukaiyama Aldol discrimination of substituted benzaldehydes. A freshly prepared stock solution of MgI_2 etherate (**1**) in Et_2O /Benzene (v/v 1:2, 0.2 M, 0.125 mL, 5 mol % of **1**) was added to a solution of *o*-nitrobenzaldehyde (75 mg, 0.5 mmol) and benzaldehyde (53 mg, 0.5 mmol) in CH_2Cl_2 (4 mL) at room temperature, followed by **1**, 2-bis(trimethylsiloxy)cyclobutene (115 mg, 0.5 mmol) in CH_2Cl_2 (2 mL). After stirring for 30 min at room temperature under Ar, the reaction mixture was poured into saturated aqueous NaHCO_3 (2 mL) solution, extracted with Et_2O (2×40 mL). The combined organic layers were washed with water (2×10 mL), brine (2×15 mL), dried over MgSO_4 , and concentrated. The crude product was purified by flash chromatography on silica gel eluting with PE / EtOAc (v/v 30:1) to provide 167 mg (99%) of 2-[(trimethylsiloxy)benzyl]-2-(trimethylsiloxy)cyclobutanone **7a** (R = Ph).

Table 1. MgI_2 etherate-catalyzed Mukaiyama-type aldol coupling of aldehydes with silyl enolates^a

$\text{RCHO} + \mathbf{2-4} \xrightarrow[\text{CH}_2\text{Cl}_2]{\mathbf{1} (1-5 \text{ mol } \%)} \mathbf{5-7(a, b)}$			
R / aldehyde	1 (mol %)	Enolate / T / t	Prod./Yield (%) ^b
Ph	5	2 / r.t. / 1 h	5 / 90
Ph	5	3 / r.t. / 2 h	6 / 85
Ph	5	4 / r.t. / 1 h	7 / 98 (<i>dr</i> 3:2)
2-MeOC ₆ H ₄	1	2 / -78 °C / 0.3 h	5 / 99
2-MeOC ₆ H ₄	1	3 / -10 °C / 1 h	6 / 99
2-MeOC ₆ H ₄	1	4 / r.t. / 0.3 h	7 / 99 (<i>dr</i> 7:2)
4-MeOC ₆ H ₄	1	4 / r.t. / 0.5 h	7 / 98 (<i>dr</i> 1:1)
Piperonal	1	2 / -78 °C / 0.5 h	5 / 98
Piperonal	1	4 / r.t. / 0.5 h	7 / 99 (<i>dr</i> 3:2)
PhCH=CH	5	2 / -78 °C / 3 h	85 (72:28) ^c
PhCH=CH	5	3 / r.t. / 2 h	6 / 75
PhCH=CH	5	4 / r.t. / 0.5 h	7 / 98 (<i>dr</i> 3:2)
Geranial	5	2 / -78 °C / 4 h	5 / 78
2,5-(MeO) ₂ C ₆ H ₃	1	4 / r.t. / 15 min	7 / 99 (<i>dr</i> 1:1)
Furfural	1	4 / r.t. / 0.5 h	7 / 99 (<i>dr</i> 1:1)
α-Naphthyl	1	4 / r.t. / 1 h	7 / 90 ^d
6-Me-2-pyridyl	5	2 / r.t. / 2 h	5 / 90
2-NO ₂ C ₆ H ₄	1	4 / r.t. / 10 h	7 / 53 (<i>dr</i> 3:2)
4-NO ₂ C ₆ H ₄	1	4 / r.t. / 10 h	7 / 70 (<i>dr</i> 2:1)
2-ClC ₆ H ₄	1	4 / r.t. / 10 h	7 / 50 ^d
2-CF ₃ C ₆ H ₄	1	4 / r.t. / 10 h	7 / 20 ^d
<i>n</i> -Octanal	5	2 / r.t. / 2 h	5 / 50
<i>n</i> -Octanal	5	3 or 4 / r.t. / 12 h	<i>N. R.</i>
PhCH ₂ CH ₂	5	2 or 3 / r.t. / 8 h	trace
PhCH ₂ CH ₂	5	4 / r.t. / 5 h	<i>N. R.</i>
<i>i</i> -Propanal	5	3 or 4 / r.t. / 12 h	<i>N. R.</i>
3	2 / -78 °C / 2 h	80 (<i>syn</i> / <i>anti</i> 6:1)

^a Reactions were run on 1 mmol scale in dry CH_2Cl_2 with 1.1 equiv of silyl enolate and 1–5 mol % MgI_2 etherate (**1**) (0.2 M solution in Et_2O /benzene (v/v 1:2)), r.t. refers to 22 °C. ^b Isolated yield, *dr* was determined by ¹H NMR analysis. ^c Overall yield, aldol and Michael adduct ratio in parenthesis. ^d *dr* not determined.

Table 2. MgI₂ etherate-catalyzed aldolization of dimethyl acetals with silyl enolates^a

$$\text{RCH(OMe)}_2 + \mathbf{2-4} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ r.t.}]{\mathbf{1} \text{ (5 mol \%)}} \mathbf{5-7(c)}$$

Entry	R / acetal	Enolate / time	Product / Yield (%) ^b
1	Ph	2 / 30 min	5 / 99
2	Ph	3 / 20 min	6 / 99
3	Ph	4 / 25 min	7 / 99 (<i>dr</i> 5:2)
4	PhCH=CH	2 / 30 min	5 / 97
5	PhCH=CH	3 / 15 min	6 / 96
6	PhCH=CH	4 / 20 min	7 / 97 (<i>dr</i> 3:1)
7	PhCH ₂ CH ₂	2 / 3 h	5 / 85
8	PhCH ₂ CH ₂	3 / 1 h	6 / 90
9	PhCH ₂ CH ₂	4 / 2 h	7 / 75 ^c
10	<i>n</i> -C ₇ H ₁₅	2 / 30 min	5 / 97
11	<i>n</i> -C ₇ H ₁₅	3 / 30 min	6 / 90
12	<i>n</i> -C ₇ H ₁₅	4 / 30 min	7 / 80 ^c

^a Reactions were run on 1 mmol scale in dry CH₂Cl₂ with 1.1 equiv of silyl enolate and MgI₂ etherate (**1**) (0.25 mL, 0.2 M solution in Et₂O/benzene (v/v 1:2)). ^b Isolated yield, *dr* was determined by ¹H NMR analysis. ^c *dr* not determined.

Table 3. Comparison of relative reactivity of aldehyde and its dimethyl acetal in Mg-catalyzed aldolization with silyl enolate **2**^a

$$\text{RCH(OMe)}_2 \text{ or RCHO} + \mathbf{2} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ r.t.}]{\mathbf{1} \text{ (5 mol \%)}} \mathbf{5c} \text{ or } \mathbf{5a}$$

R	Reaction time (acetal / aldehyde)	Yield (%) (5c / 5a)
Ph	0.5 h / 1 h	99 / 90
<i>n</i> -C ₇ H ₁₅	0.5 h / 2 h	97 / 50
PhCH ₂ CH ₂	3 h / 8 h	85 / trace
PhCH=CH	0.5 h / 3 h (−78 °C)	97 / 85 ^b

^a Results selected from Table 1 and Table 2. ^b The ratio of aldol / Michael adduct is 72 : 28.

Table 4. Comparison of relative reactivity of aldehyde and its acetal in Mg-catalyzed aldolization with silyl enolate **3**^a

$$\text{RCH(OMe)}_2 \text{ or RCHO} + \mathbf{3} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ r.t.}]{\mathbf{1} \text{ (5 mol \%)}} \mathbf{6c} \text{ or } \mathbf{6a}$$

R	Reaction time (acetal / aldehyde)	Yield (%) (6c / 6a)
Ph	20 min / 2 h	99 / 85
<i>n</i> -C ₇ H ₁₅	0.5 h / 6 h	90 / –
PhCH ₂ CH ₂	1 h / 8 h	90 / trace
PhCH=CH	15 min / 2 h	96 / 75

^a Results selected from Table 1 and Table 2.

Table 5. Comparison of relative reactivity of aldehyde and its acetal in Mg-catalyzed aldolization with silyl enolate **4**^a

R	Reaction time (acetal / aldehyde)	Yield (%) ^b (7c / 7a)
Ph	25 min / 1 h	99 / 98
<i>n</i> -C ₇ H ₁₅	0.5 h / 2 h	80 / –
PhCH ₂ CH ₂	2 h / 5 h	75 / –
PhCH=CH	20 min / 0.5 h	97 / 98

^a Results selected from Table 1 and Table 2.

Table 6. Aldol discrimination of aryl aldehydes with silyl enolates catalyzed by etherate **1** or **1b**^a

Ar	Ar'	Enolate / cat. / t	Ratio (5/5' or 7/7')	Yield (%) ^b
Ph	2-NO ₂ C ₆ H ₄	2 / 1 / 2 h	80 / 20	99
Ph	2-NO ₂ C ₆ H ₄	2 / 1b / 3 h	38 / 62	65
2-MeOC ₆ H ₄	2-NO ₂ C ₆ H ₄	2 / 1 / 10 min	> 99 / < 1	99
2-MeOC ₆ H ₄	2-NO ₂ C ₆ H ₄	2 / 1b / 1 h	40 / 60 ^c	99
2-MeOC ₆ H ₄	3-MeOC ₆ H ₄	2 / 1 / 15 min	> 99 / < 1	99
2-MeOC ₆ H ₄	3-MeOC ₆ H ₄	2 / 1b / 3 h	70 / 30 ^c	75
4-MeOC ₆ H ₄	4-NO ₂ C ₆ H ₄	2 / 1 / 10 min	> 99 / < 1	99
4-MeOC ₆ H ₄	4-Me ₂ NC ₆ H ₄	2 / 1 / 10 min	< 1 / > 99	99
4-Me ₂ NC ₆ H ₄	4-NO ₂ C ₆ H ₄	2 / 1b / 30 min	55 / 45 ^c	99
4-Me ₂ NC ₆ H ₄	4-MeOC ₆ H ₄	2 / 1b / 45 min	> 99 / < 1	98
2-MeOC ₆ H ₄	2-NO ₂ C ₆ H ₄	4 / 1 / 20 min	> 99 / < 1	99
2-MeOC ₆ H ₄	2-NO ₂ C ₆ H ₄	4 / 1b / 5 h	<i>N. R.</i>	–

^a Reactions were run with a mixture of 0.5 mmol of each aldehyde, 0.5 mmol of silyl enolate and 5 mol % of MgI₂ etherate (**1**) or MgBr₂ etherate (**1b**) (0.125 mL, 0.2 M solution in Et₂O/benzene (v/v 1:2)). ^b Isolated overall yield. ^c Ratio determined by ¹H NMR analysis of desilylated products.

Table 7. Solvent effect of MgI₂ etherate-catalyzed aldol reaction^a

Entry	Solvent	time	Yield (%) ^b
1	Et ₂ O	5 h	15
2	THF	6 h	<i>N. R.</i>
3	DMF	4 h	trace
4	CH ₃ CN	5 h	72
5	Benzene	0.5 h	94
6	Toluene	1 h	96
7	CH ₂ Cl ₂	15 min	99

^a Reactions were run with 1.0 mmol of *o*-anisaldehyde and 1.1 mmol of silyl enolate **2**, and 1 mol % of MgI₂ etherate (**1**) (0.05 mL, 0.2 M solution in Et₂O/benzene (v/v 1:2)). ^b Isolated yield.

Colorless oil,¹ IR(film) $\nu_{\max}$ 3495, 2927, 1732, 1466, 1271, 1142, 1077 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.84–0.95 (m, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.27–1.58 (m, 12H, CH_2), 2.60 (br, OH), 3.60 (br d, 1H, $J = 9.6$ Hz), 3.69 (s, 3H, OCH_3) *ppm*. EIMS m/z 215 (M–15), 212 (M–28), 199, 102(100).

Colorless oil,² IR(film) $\nu_{\max}$ 3207, 2927, 1738, 1613, 1471, 1161 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.77–0.88 (m, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.26–1.60 (m, 12H, CH_2), 3.29–3.32 (m, 1H), 3.40 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 3456, 2949, 1725, 1601, 1454, 1268, 1134, 749, 700 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.17 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.61–1.85 (m, 2H), 2.59–2.97 (m, 2H), 3.61–3.74 (m, 1H), 3.70 (s, 3H, OCH_3), 7.21–7.38 (m, 5H) *ppm*. EIMS m/z 236 (M^+), 218, 151, 117, 102, 91(100).

Colorless oil, IR (film) $\nu_{\max}$ 2949, 1734, 1602, 1496, 1454, 1129, 749, 700 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.13 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.67–1.82 (m, 2H), 2.85–2.97 (m, 2H), 3.41–3.50 (m, 1H), 3.49 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 7.20–7.36 (m, 5H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 2980, 1732, 1682, 1466, 1450, 1273, 1090, 973, 749, 696 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.11 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 3.30 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.94 (d, 1H, $J = 8.2$ Hz), 6.09 (dd, 1H, $J = 16.0, 8.2$ Hz), 6.60 (d, 1H, $J = 16.0$ Hz), 7.20–7.45 (m, 5H) *ppm*. EIMS m/z 248 (M^+), 233, 205, 147(100).

Pale yellowish oil, IR(film) $\nu_{\max}$ 3427, 1725, 1648, 1452, 1033, 770, 752 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.23(s, 3H), 1.24 (s, 3H), 2.75 (br, OH), 3.72 (s, 3H, OCH_3), 4.35 (d, 1H, $J = 7.0\text{Hz}$), 6.21 (dd, 1H, $J = 16.0, 7.2$ Hz), 6.64 (d, 1H, $J = 16.0$ Hz), 7.24–7.41 (m, 5H) *ppm*. EIMS m/z 234 (M^+), 133 (100), 115, 102, 91.

¹ Ooi, T.; Tayama, E.; Takahashi, M.; Maruoka, K. *Tetrahedron Lett.* **1997**, 38, 7403.

Colorless oil (80%, *syn* / *anti* 6:1); *syn* isomer, IR(film) $\nu_{\max}$ 3552, 3452, 1733, 1613, 1514, 1463, 1249 cm^{-1} ; ^1H NMR(CDCl_3 , 200 MHz) δ 1.08 (s, 3H), 1.18 (s, 3H), 1.20 (d, 3H, $J = 6.0$ Hz, CH_3), 3.20 (d, 1H, $J = 1.8$ Hz, CHOH), 3.22 (s, 3H), 3.58 (q, 1H, $J = 6.0$ Hz, CH_3CHO), 3.70 (s, 3H), 4.12 (d, 1H, $J = 10.8$ Hz, ArCH_2O), 4.45 (d, 1H, $J = 10.8$ Hz, ArCH_2O), 6.78 (d, 1H, $J = 8.4$ Hz, ArH), 7.16 (d, 1H, $J = 8.4$ Hz, ArH) *ppm*; EIMS m/z 296 (M^+), 278, 121 (100).

Colorless oil, IR(film) $\nu_{\max}$ 1726(s), 1645, 1454, 1130, 771, 706 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.1 (s, 3H), 1.16 (s, 3H), 2.69 (ddd, 1H, $J = 16.8, 4.2, 1.4$ Hz), 2.97 (ddd, 1H, $J = 16.8, 11.0, 2.6$ Hz), 3.62 (dd, 1H, $J = 11.0, 4.2$ Hz), 3.66 (s, 3H, OCH_3), 7.14–7.30 (m, 5H), 9.53 (dd, 1H, $J = 2.6, 1.4$ Hz) *ppm*. EIMS m/z 234 (M^+), 203, 133, 105(100).

Colorless oil, IR(film) $\nu_{\max}$ 1739(s), 1456, 1383, 1254, 1063, 882 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 0.93 (s, 3H), 1.12 (s, 3H), 1.54–1.72 (m, 9H, 3 X CH_3), 1.97–2.10 (m, 4H, 2 CH_2), 3.63 (s, 3H, OCH_3), 4.59 (d, 1H, $J = 9.4$ Hz), 5.06–5.11 (m, 2H) *ppm*. EIMS m/z 326 (M^+), 311, 225(100), 157, 131.

Colorless oil,² IR(film) $\nu_{\max}$ 3206, 1739, 1611, 1514, 1470, 1161, 1099, 706 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 1.03 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 3.20 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 4.50 (s, 1H), 7.31 (s, 5H) *ppm*.

Colorless oil,² IR (film) $\nu_{\max}$ 2954, 1741 (s), 1586, 1452, 1434, 1251, 1067 cm^{-1} ; ^1H NMR (CDCl_3 , 80 MHz) δ 0.01 (s, 9H), 1.01 (s, 3H), 1.14 (s, 3H), 3.69 (s, 3H, OCH_3), 5.00 (s, 1H), 7.30 (s, 5H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 3449, 1726(s), 1468, 1453, 1135, 1060, 706 cm^{-1} . ^1H NMR

² Odekirk, W.; Whelan, J.; Bosnich, B. *Tetrahedron Lett.* **1992**, 33, 5729.

(CDCl₃, 400 MHz) δ 1.03 (s, 3H, CH₃), 1.12 (s, 3H, CH₃), 2.42 (br, OH), 3.29–3.34 (m, 1H), 3.50–3.55 (m, 1H), 3.63–3.67 (m, 2H), 3.75 (s, 3H, OCH₃), 4.72 (s, 1H), 7.28–7.38 (m, 5H) *ppm*. EIMS *m/z* 221(M⁺–31), 207, 191, 175, 151, 107(100).

Colorless oil, ³ IR(film) $\nu_{\max}$ 2957, 1685(s), 1598, 1493, 1254, 1096, 845 cm⁻¹. ¹H NMR (CDCl₃, 80 MHz) δ 0.02 (s, 9H), 3.05 (dd, 1H, *J* = 15.4, 4.0 Hz), 3.63 (dd, 1H, *J* = 15.4, 8.6 Hz), 5.43 (dd, 1H, *J* = 8.6, 4.0 Hz), 7.32–8.07 (m, 10H) *ppm*.

Pale yellowish oil, IR(film) $\nu_{\max}$ 3445, 2928, 1680(s), 1598, 1494, 1450, 1212, 1052 cm⁻¹. ¹H NMR (CDCl₃, 200 MHz) δ 1.70–2.10 (m, 2H), 2.63–2.96 (m, 2H), 3.10–3.22 (m, 1H), 3.29–3.50 (m, 1H), 4.18–4.35 (m, 1H), 7.20–7.97 (m, 10H) *ppm*. EIMS *m/z* 254 (M⁺), 236, 105(100).

Pale yellowish oil, IR(film) $\nu_{\max}$ 2928, 1681(s), 1621, 1598, 1580, 1450, 1057, 1106 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.86–1.97 (m, 2H), 2.62–2.85 (m, 2H), 2.98 (dd, 1H, *J* = 16.2, 5.6 Hz), 3.34 (dd, 1H, *J* = 16.2, 6.6 Hz), 3.38 (s, 3H, OCH₃), 3.88–4.00 (m, 1H), 7.19–7.99 (m, 10H) *ppm*. EIMS *m/z* 268 (M⁺), 236, 105 (100), 91.

Colorless oil,³ IR(film) $\nu_{\max}$ 3208, 2931, 1685(s), 1607, 1510, 1215, 1102, 750 cm⁻¹. ¹H NMR(CDCl₃, 80 MHz) δ 3.09 (dd, 1H, *J* = 16.6, 4.6 Hz), 3.27 (s, 3H, OCH₃), 3.64 (dd, 1H, *J* = 16.6, 8.2 Hz), 4.92 (dd, 1H, *J* = 8.2, 4.6 Hz), 7.29–8.03 (m, 10H) *ppm*. EIMS *m/z* 240 (M⁺), 225, 121(100), 105, 91.

Colorless oil, IR(film) $\nu_{\max}$ 3207, 1613(s), 1510, 1475, 1414, 1161 cm⁻¹. ¹H NMR (CDCl₃, 200 MHz) δ 0.85–0.95 (m, 3H, CH₃), 1.20–1.65 (m, 12H), 2.93 (dd, 1H, *J* = 16.2, 5.4 Hz), 3.28 (dd, 1H, *J* = 16.2, 6.8 Hz), 3.37 (s, 3H, OCH₃), 3.84–3.93 (m, 1H), 7.42–7.98 (m, 5H) *ppm*. EIMS *m/z* 262 (M⁺), 247, 163, 105(100).

Pale yellowish oil, IR(film) $\nu_{\max}$ 3058, 1684(s), 1657, 1580, 1447, 1097 cm⁻¹. ¹H NMR (CDCl₃, 200 MHz) δ 3.09 (dd, 1H, *J* = 16.2, 5.0 Hz), 3.35 (s, 3H, OCH₃), 3.49 (dd, 1H, *J* = 16.2, 7.6 Hz), 4.42–4.51 (m, 1H), 6.18 (dd, 1H, *J* = 16.0, 7.6 Hz), 6.69 (d, 1H, *J* = 16.0 Hz), 7.02–8.00 (m, 10H) *ppm*. EIMS

m/z 266 (M^+), 251, 147, 105(100).

Yellowish oil, IR(film) $\nu_{\max}$ 3447, 3027, 1718(w), 1681(s), 1597, 1097, 1211 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 3.30 (d, 2H, $J = 6.0$ Hz), 3.52 (br, OH), 4.98 (dd, 1H, $J = 7.4, 6.0$ Hz), 6.34 (dd, 1H, $J = 16.2, 6.0$ Hz), 6.73 (d, 1H, $J = 16.2$ Hz), 7.24–8.05 (m, 10H) ppm. EIMS m/z 252 (M^+), 234, 105(100).

Colorless oil,³ IR(film) $\nu_{\max}$ 1789(s), 1494, 1452, 1253, 1098, 845 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 18H), 1.76–2.81 (m, 4H), 4.71 (s, 0.4H) and 4.75 (s, 0.6H), 7.29–7.36 (m, 5H) ppm.

Colorless oil,⁴ IR(film) $\nu_{\max}$ 1789(s), 1492, 1452, 1252, 1101, 866 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 1.70–2.86 (m, 4H), 3.25 (s, 2.0 H) and 3.28 (s, 1.0 H), 4.26 (s, 0.33 H) and 4.27 (s, 0.67 H), 7.29–7.34 (m, 5 H) ppm.

Colorless oil, IR(film) $\nu_{\max}$ 1789(s), 1614, 1161, 1072, 844 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.13 (s, 9H), 0.84–0.90 (m, 3H), 1.15–1.60 (m, 12H), 1.70–2.82 (m, 4H), 3.15–3.18 (m, 1H), 3.29 (s, 1.5 H, OCH_3) and 3.44 (s, 1.5 H, OCH_3). EIMS m/z 300 (M^+), 285, 272, 73(100).

Colorless oil, IR(film) $\nu_{\max}$ 1788(s), 1602, 1252, 1064, 844 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.17 (s, 9H), 1.80–2.83 (m, 8H), 3.25 (dd, 1H, $J = 7.8, 4.0$ Hz), 3.33 (s, 1.1 H, OCH_3) and 3.46 (s, 1.9 H, OCH_3), 7.18–7.28 (m, 5H) ppm. EIMS m/z 306 (M^+), 291, 174, 111, 91(100).

Colorless oil,⁵ IR(film) $\nu_{\max}$ 1788(s), 1650, 1494, 1252, 1070, 844 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.15 (s, 9H), 1.85–2.91 (m, 4H), 3.34 (s, 3H, OCH_3), 3.80 (d, 0.25 H, $J = 8.2$ Hz) and 3.88 (d, 0.75 H, $J = 6.6$ Hz), 6.08–6.20 (m, 1H), 6.55–6.70 (m, 1H), 7.30–7.41 (m, 5H) ppm. EIMS m/z 304 (M^+), 289,

³ Naramura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, 48, 932.

⁴ Shimadam, J.; Hashimoto, K.; Kim, B. H.; Naramura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, 106, 1759.

262, 159, 147, 115, 73(100).

Colorless oil, IR(film) $\nu_{\max}$ 1788 (s), 1650, 1494, 1252, 1070, 844 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.10–0.18 (m, 18 H), 1.69–2.81 (m, 4H), 4.32 (d, 0.6 H, $J = 6.6$ Hz) and 4.42 (d, 0.4 H, $J = 5.8$ Hz), 6.19–6.31 (m, 1H), 6.53–6.65 (m, 1H), 7.26–7.43 (m, 5H) *ppm*. EIMS m/z 362 (M^+), 347, 147, 129, 73(100); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3\text{Si}_2\text{Na}$ 385.1626, found for $[\text{M}+\text{Na}]^+$ 385.1624.

Colorless oil, IR(film) $\nu_{\max}$ 2954, 1684(s), 1596, 1495, 1215, 1047, 844 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 0.03 (s, 9H), 3.26 (d, 2H, $J = 6.0$ Hz), 3.82 (s, 6H, OCH_3), 5.70 (br t, 1H, $J = 6.0$ Hz), 6.79–8.10 (m, 10H) *ppm*. EIMS m/z 358 (M^+), 343, 239 (100), 105.

Colorless oil, IR(film) $\nu_{\max}$ 2958, 1686(s), 1598, 1489, 1247, 1085, 842 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 3.18–3.30 (m, 2H), 3.86 (s, 3H, OCH_3), 5.73(dd, 1H, $J = 8.2, 3.6$ Hz), 6.85–8.06 (m, 9H) *ppm*. EIMS m/z 328 (M^+), 313, 209, 105, 73(100).

Colorless oil, IR(film) $\nu_{\max}$ 2956, 1686 (s), 1596, 1495, 1215, 1047, 844 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 3.03 (dd, 1H, $J = 15.4, 4.2$ Hz), 3.56 (dd, 1H, $J = 15.4, 8.6$ Hz), 3.78 (s, 3H, OCH_3), 5.36 (dd, 1H, $J = 8.6, 4.2$ Hz), 6.84–8.10 (m, 9H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1785(s), 1497, 1462, 1252, 1075, 844 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.02 (s, 9H), 0.05 (s, 9H), 1.80–2.83 (m, 4H), 3.71 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.29 (s, 1H), 6.75–7.88 (m, 3H) *ppm*. EIMS m/z 396 (M^+), 381, 368, 239, 73(100).

Colorless oil, IR(film) $\nu_{\max}$ 1784(s), 1597, 1491, 1247, 1074, 845 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.02 (s, 9H), 0.03 (s, 9H), 1.79–2.76 (m, 4H), 3.76 (s, 3H, OCH_3), 5.34 (s, 1H), 6.78–7.50 (m, 4H)

ppm. EIMS m/z 366 (M^+), 351, 338, 209, 147, 73(100).

Colorless oil, IR(film) $\nu_{\max}$ 1786(s), 1612, 1512, 1250, 1085, 846 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 0.02 (s, 9H), 1.65–2.80 (m, 4H), 3.80 (s, 3H, OCH_3), 4.66 (s, 0.5 H) and 4.70 (s, 0.5 H), 6.80–7.31 (m, 4H) *ppm*. EIMS m/z 366 (M^+), 351, 323, 209, 147, 73(100).

Colorless crystals, mp. 43–44 $^{\circ}\text{C}$, IR(film) $\nu_{\max}$ 2957, 1788, 1730 (s), 1500, 1466, 1254, 1077, 841 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ –0.07 (s, 9H), 0.98 (s, 3H), 1.13 (s, 3H), 3.69 (s, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 5.53 (s, 1H), 6.75–7.00 (m, 3H) *ppm*. EIMS m/z 340(M^+), 325, 265, 239(100).

Yellowish oil, IR(film) $\nu_{\max}$ 3489, 2985, 1724(s), 1604, 1529, 1470, 1136, 854 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.08 (s, 3H), 1.12 (s, 3H), 3.72 (s, 3H, OCH_3), 5.86 (s, 1H), 7.38–7.80 (m, 4H) *ppm*.

Colorless crystals, 3 mp. 63–64 $^{\circ}\text{C}$, ^1H NMR (CDCl_3 , 200 MHz) δ 1.12 (s, 3H), 1.16 (s, 3H), 3.23 (br s, OH), 3.70 (s, 3H, OCH_3), 4.91 (s, 1H), 7.30 (s, 5H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 3432, 2949, 1722, 1612, 1513, 1465, 1248, 1133, 837 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.11 (s, 3H), 1.21 (s, 3H), 3.60 (br, OH), 3.70 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.28 (s, 1H), 6.83–7.32 (m, 4H) *ppm*.

Yellowish oil, IR(film) $\nu_{\max}$ 3437, 2949, 1721, 1637, 1606, 1466, 1258, 1134, 857 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.14 (s, 3H), 1.18 (s, 3H), 3.11 (br, OH), 3.74 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.89 (s, 1H), 6.82–7.56 (m, 4H) *ppm*.

Yellowish oil, IR(film) $\nu_{\max}$ 3433, 2950, 1724, 1612, 1466, 1249, 1134, 837 cm^{-1} .

^1H NMR (CDCl_3 , 200 MHz) δ 1.06 (s, 3H), 1.17 (s, 3H), 3.15 (br, OH), 3.69 (s, 3H), 3.77 (s, 3H), 4.82 (s, 1H), 6.79–7.27 (m, 4H) *ppm*.

Pale yellowish crystals, mp. 94–95 °C, IR(film) ν_{max} 3405, 2980, 1727, 1612, 1458, 1249, 1133, 823 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 1.11 (s, 3H), 1.16 (s, 3H), 2.96 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.73 (s, 3H, OCH_3), 4.84 (s, 1H), 6.73 (br d, 2H, $J = 8.8$ Hz), 7.20 (br d, 2H, $J = 8.8$ Hz) *ppm*.

Yellowish crystals, mp. 113–114 °C, IR(film) ν_{max} 3495(s), 2952, 1728(s), 1606, 1531, 1470, 1052, 854 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 1.17 (s, 3H), 1.18 (s, 3H), 3.41 (d, 1H, $J = 4.2$ Hz, OH), 5.04 (d, 1H, $J = 4.2$ Hz), 7.53 (d, 2H, $J = 8.8$ Hz), 8.23 (d, 2H, $J = 8.8$ Hz) *ppm*.

Colorless crystal, mp 45–46 °C, IR(film) ν_{max} 3449, 1735 (s), 1594, 1461, 1264, 1063 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.06 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 3.70 (s, 3H, CH_3O), 4.87 (s, 1H), 6.92 (d, 1H, $J = 7.8$ Hz), 7.04 (d, 1H, $J = 7.6$ Hz), 7.50 (t, 1H, $J = 7.8$ Hz) *ppm*.

Colorless oil, ^1H NMR (200 MHz, CDCl_3) δ 0.02 (s, 9H), 0.98 (s, 3H), 1.17 (s, 3H), 2.49 (s, 3H), 3.70 (s, 1H), 5.06 (s, 3H), 6.98 (d, 1H, $J = 7.6$ Hz), 7.22 (d, 1H, $J = 7.6$ Hz), 7.53 (t, 1H, $J = 7.6$ Hz) *ppm*.

Pale yellowish oil, IR(film) ν_{max} 1786(s), 1603, 1523, 1347, 1254, 1096, 850 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.03–0.20 (m, 18H), 1.65–2.90 (m, 4H), 4.77 (s, 0.4 H) and 4.83 (s, 0.6 H), 7.43–8.22 (m, 4H) *ppm*.

Pale yellowish oil, IR(film) ν_{max} 1788(s), 1607, 1532, 1253, 1106, 847 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.01–0.21 (m, 18H), 1.62–2.91 (m, 4H), 5.81 (s, 0.6 H) and 5.86 (s, 0.4 H), 7.35–7.91 (m, 4H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1788(s), 1594, 1573, 1473, 1440, 1252, 1091, 844, 753 cm^{-1} .

^1H NMR (CDCl_3 , 200 MHz) δ 0.002–0.017 (m, 18H), 1.76–2.90 (m, 4H), 5.35 (s, 1H), 7.21–7.64 (m, 4H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1790(s), 1607, 1451, 1375, 1309, 1255, 1089, 847, 760 cm^{-1} . ^1H

NMR (CDCl_3 , 200 MHz) δ –0.04 (s, 9H), –0.02 (s, 9H), 1.84–2.87 (m, 4H), 5.26 (s, 1H), 7.34–7.89 (m, 4H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1786(s), 1504, 1489, 1443, 1251, 1039, 845 cm^{-1} . ^1H NMR

(CDCl_3 , 200 MHz) δ –0.03 (s, 9H), 0.01 (s, 9H), 1.60–2.82 (m, 4H), 4.56 (s, 0.6 H) and 4.63 (s, 0.4 H), 5.89 (s, 2H), 6.66–6.84 (m, 3H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1786(s), 1595, 1512, 1389, 1252, 1089, 844 cm^{-1} . ^1H NMR

(CDCl_3 , 200 MHz) δ –0.33 ~ –0.28 (m, 9H), –0.05 ~ 0.05 (m, 9H), 1.75–2.90 (m, 4H), 5.68 (s, 0.5 H) and 5.75 (s, 0.5 H), 7.43–8.30 (m, 7H) *ppm*.

Colorless oil, IR(film) $\nu_{\max}$ 1789(s), 1592, 1501, 1387, 1252, 1091, 844, 754 cm^{-1} . ^1H

NMR (CDCl_3 , 200 MHz) δ 0.002–0.043 (m, 18H), 1.95–2.86 (m, 4H), 4.88 (s, 0.67 H) and 4.89 (s, 0.33 H), 6.26–6.35 (m, 2H), 7.35–7.39 (m, 1H) *ppm*.

Colorless crystal, mp 69–70 $^{\circ}\text{C}$, IR(film) $\nu_{\max}$ 3497, 1721, 1501, 1489, 1442, 1247,

1040 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 1.13 (s, 3H), 1.17 (s, 3H), 3.03 (d, 1H, J = 4.0 Hz, OH), 3.75(s, 3H, OCH_3), 4.84 (d, 1H, J = 4.0 Hz), 5.97 (s, 2H), 6.77–6.85 (m, 3H) *ppm*.

Colorless crystal, mp. 54–55 °C, IR(film) $\nu_{\max}$ 1737 (s), 1501, 1488, 1442, 1250, 1076 cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz) δ 0.01 (s, 9H), 1.01 (s, 3H), 1.14 (s, 3H), 3.69 (s, 3H, OCH_3), 4.91 (s, 1H), 5.97 (s, 2H), 6.73–6.82 (m, 3H) ppm.

colorless crystal : mp 68–69 °C IR(film) $\nu_{\max}$ 3445(s), 1722(s), 1652, 1541, 1514, 1466, 1278, 1055, 827 cm^{-1} ; ^1H NMR(200 MHz, CDCl_3) δ 1.12 (s, 3H), 1.15 (s, 3H), 2.35(s, 3H), 3.03 (br s, OH), 3.72 (s, 3H, OCH_3), 4.87 (s, 1H), 7.13 (d, 2H, $J = 8.2$ Hz), 7.20 (d, 2H, $J = 8.2$ Hz).

colorless oil (dr 2:1), IR(film) $\nu_{\max}$ 1788(s), 1613, 1513, 1441, 1253, 1090, 862, 844 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 0.01 (s, 9H), 0.03 (s, 9H), 1.60–2.84 (m, 4H), 2.33 (s, 1.0H, CH_3) and 2.36 (s, 2.0H, CH_3), 4.69 (s, 0.33 H) and 4.73 (s, 0.67 H), 7.07–7.29 (m, 4H); EIMS m/z 350 (M^+), 335, 322, 294, 193, 73 (100).

colorless oil, IR(film) $\nu_{\max}$ 1687(s), 1598, 1575, 1513, 1252, 1090, 844. ^1H NMR (CDCl_3 , 200 MHz) δ 0.002 (s, 9H), 2.35 (s, 3H, CH_3), 3.02 (dd, 1H, $J = 3.8, 15.4$ Hz), 3.57 (dd, 1H, $J = 8.8, 15.4$ Hz), 5.37 (dd, 1H, $J = 3.8, 8.8$ Hz), 7.14–8.00 (m, 9H).

colorless crystal mp. 58–59 °C, IR(film) $\nu_{\max}$ 3488(s), 1722(s), 1596, 1491, 1470, 1435, 1134, 1012, 837 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.09 (s, 3H), 1.12 (s, 3H), 3.24 (d, 1H, OH, $J = 3.0$ Hz), 3.71 (s, 3H, OCH_3), 4.86 (d, 1H, $J = 3.0$ Hz), 7.23 (dd, 2H, $J = 2.2, 6.6$ Hz), 7.30 (dd, 2H, $J = 2.4, 6.4$ Hz).

^1H NMR (CDCl_3 , 200 MHz) δ 1.23 (s, 6H), 3.40 (d, 1H, OH, $J = 4.4$ Hz), 3.79 (s, 3H, OCH_3), 5.55 (d, 1H, $J = 4.4$ Hz), 7.25–7.57 (m, 4H).

colorless crystal, mp. 64–65 °C, IR(film) $\nu_{\max}$ 3488(s), 1722(s), 1592, 1487, 1469, 1434,

1134, 1010, 834 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.10 (s, 3H), 1.12 (s, 3H), 3.21 (br s, OH), 4.86 (s, 1H), 7.18 (d, 2H, $J = 8.2$ Hz), 7.45 (d, 2H, $J = 8.6$ Hz).

78%, Colorless oil, R(film) ν_{max} 1784(s), 1736(s), 1600, 1502, 1455, 1269, 1044, 701 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 2.60–2.98 (m, 4H), 5.65 (s, 1H), 7.34 (br s, 5H, ArH) *ppm*. EIMS m/z 190 (M^+), 162, 122, 107, 105(100).

60%, Colorless oil, IR(film) ν_{max} 1757(s), 1736(s), 1491, 1446, 1250, 1036, 930 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 2.75–2.95 (m, 4H), 5.59 (s, 1H), 5.99 (s, 2H), 6.82 (br s, 3H, ArH) *ppm*. EIMS m/z 234 (M^+), 206, 162, 151(100).

50%, mp. 85–87 $^{\circ}\text{C}$, IR(film) ν_{max} 1759 (s), 1737 (s), 1605, 1567, 1494, 1451, 1261, 1164, 910 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 2.75–2.87 (m, 4H), 2.93–3.61 (m, 2H), 5.36 (dd, 1H, $J = 4.8, 1.6$ Hz), 6.25 (dd, 1H, $J = 16.0, 4.8$ Hz), 6.76 (dd, 1H, $J = 16.0, 1.6$ Hz), 7.30–7.44 (m, 5H) *ppm*. EIMS m/z 216 (M^+), 188, 131(100), 115, 103. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3$ 217.0859, found for $[\text{M}+1]^+$ 217.0852.

Colorless oil (88%, *syn* or *threo*), IR(film) ν_{max} 3400, 1768, 1600, 1492, 1443, 1033, 778 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.90–2.10 (m, 2H), 2.48 (dd, 2H, $J = 9.0, 7.8$ Hz), 4.50–4.65 (m, 2H), 5.98 (s, 2H), 6.75–6.95 (m, 3H) *ppm*. ^{13}C NMR (50 MHz, CDCl_3) δ 176.8, 147.9, 147.8, 132.3, 120.6, 108.3, 107.2, 101.2, 83.5, 60.4, 28.4, 24.0 *ppm*. EIMS m/z 236 (M^+), 151(100).

Colorless oil (12%, *anti* or *erythro*), IR(film) ν_{max} 3406, 1768, 1663, 1608, 1492, 1443, 1037, 772 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 1.90–2.60 (m, 4H), 4.64 (ddd, 1H, $J = 7.6, 6.4, 3.4$ Hz), 5.01 (br t, 1H, $J = 3.4$ Hz), 5.97 (s, 2H), 6.80–6.90 (m, 3H) *ppm*. EIMS m/z 236 (M^+), 151(100), 93.

Colorless oil (60%, *syn* or *threo*), IR(film) $\nu_{\max}$ 3409(br s), 1767(s), 1498, 1452, 1416, 1188, 1039, 748 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 2.15–2.35 (m, 2H), 2.50–2.70 (m, 2H), 4.33 (br t, 1H, J = 6.2 Hz), 4.54–4.59 (m, 1H), 6.24 (dd, 1H, J = 16.0, 6.8 Hz), 6.74 (d, 1H, J = 16.0 Hz), 7.20–7.40 (m, 5H) *ppm*. EIMS m/z 218 (M^+), 200, 133(100), 115. HRMS(FAB) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ Na 241.0835, found for $[\text{M}+\text{Na}]^+$ 241.0834.

Colorless oil, IR(film) $\nu_{\max}$ 2851, 1776, 1652, 1601, 1524, 1464, 1095, 843, 778, 735 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.08 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.92 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.15–2.27 (m, 2H), 2.47–2.56 (m, 2H), 4.40–4.43 (m, 1H), 4.52–4.57 (m, 1H), 6.23 (dd, 1H, J = 16.0, 6.8 Hz), 6.64 (d, 1H, J = 16.0 Hz), 7.26–7.41 (m, 5H) *ppm*. ^{13}C NMR (50 MHz, CDCl_3) δ 177.3, 136.3, 132.5, 128.7, 128.0, 127.2, 126.6, 82.7, 75.1, 28.2, 25.8, 23.0, 18.1, –4.3, –4.8 *ppm*. EIMS m/z 317 (M^+-15), 275, 257, 247, 141, 84(100). HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}$ 333.1880, found for $[\text{M}+1]^+$ 333.1878.

Colorless oil (40%, *anti* or *erythro*), IR(film) $\nu_{\max}$ 3423(br s), 1766(s), 1662, 1599, 1490, 1189, 1023, 746 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 2.15–2.20 (m, 1H), 2.25–2.35 (m, 1H), 2.46–2.55 (m, 1H), 2.60–2.70 (m, 1H), 2.98 (br, OH), 4.55–4.70 (m, 2H), 6.13 (dd, 1H, J = 16.0, 5.6 Hz), 6.76 (d, 1H, J = 16.0 Hz), 7.20–7.45 (m, 5H) *ppm*. ^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 136.2, 133.0, 128.7, 128.2, 126.6, 125.6, 82.4, 72.7, 28.6, 21.3 *ppm*. EIMS m/z 218 (M^+), 200, 133(100), 115. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}$ 241.0835, found for $[\text{M}+\text{Na}]^+$ 241.0829.

Colorless oil, ^1H NMR (CDCl_3 , 400 MHz) δ 0.09 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.08–2.14 (m, 1H), 2.31–2.37 (m, 1H), 2.45–2.51 (m, 1H), 2.57–2.66 (m, 1H), 4.54–4.58 (m, 1H), 4.65–4.67 (m, 1H), 6.10 (dd, 1H, J = 16.0, 5.6 Hz), 6.70 (d, 1H, J = 16.0 Hz), 7.25–7.41 (m, 5H) *ppm*. ^{13}C NMR (100 MHz, CDCl_3) δ 177.5, 136.2, 132.2, 128.7, 128.0, 127.1, 126.5, 82.2, 73.9, 28.6, 25.8, 20.6, 18.1, –4.6, –4.9 *ppm*. EIMS m/z 317(M^+-15), 275, 257, 247, 141, 129, 115, 73(100). HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}$ 333.1880, found for $[\text{M}+1]^+$ 333.1871.

65%, Colorless oil (*syn* or *threo*), IR(film) $\nu_{\max}$ 1778, 1758(s), 1654, 1600, 1495, 1467, 1256, 1077, 836 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.08 (s, 3H), 0.11 (s, 3H), 0.92 (s, 9H), 4.57 (br t, 1H, J = 6.2 Hz), 5.02–5.06 (m, 1H), 6.03 (dd, 1H, J = 6.6, 16.0 Hz), 6.16 (dd, 1H, J = 5.8, 1.8 Hz), 6.61 (d, 1H, J = 16.0 Hz), 7.20–7.40 (m, 5H), 7.50 (dd, 1H, J = 5.8, 1.4 Hz) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ 172.7, 153.6, 136.0, 133.3, 128.7, 128.2, 126.7, 126.1, 123.1, 85.7, 73.5, 25.7, 18.2, –4.4, –4.9 ppm. EIMS m/z 315 ($\text{M}^+ - 15$), 273, 247, 113, 73(100).

, Colorless oil (*anti* or *erythro*), IR(film) $\nu_{\max}$ 1789, 1758(s), 1602, 1495, 1468, 1264, 1088, 739 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ 0.06 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.89 (s, 9H, $\text{C}(\text{CH}_3)_3$), 4.57–4.62 (m, 1H), 4.99–5.02 (m, 1H), 6.19 (dd, 1H, J = 5.8, 1.8 Hz), 6.22 (dd, 1H, J = 16.0, 5.6 Hz), 6.71 (d, 1H, J = 16.0 Hz), 7.15–7.45 (m, 5H), 7.49 (dd, 1H, J = 5.8, 1.6 Hz) ppm. EIMS m/z 315 ($\text{M}^+ - 15$), 247, 113, 77, 73(100).