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Tetrahedron
Tetrahedron 63 (2007) 4535–4542

Lewis acid-catalyzed reactions of mono-aryl group substituted methylenecyclopropanes with diethyl ketomalonate

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Received 24 January 2007; revised 7 March 2007; accepted 7 March 2007
Available online 12 March 2007

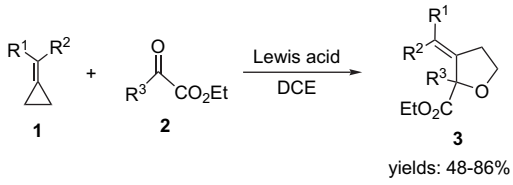
Abstract—Mono-aryl group substituted methylenecyclopropanes (MCPs) **1** react with diethyl ketomalonate **2a**, an activated ketone, to give the corresponding 7-hydroxy-5-oxa-spiro[2,4]heptan-6-one derivatives **6** with *syn*-configuration in moderate yields in the presence of water under the catalysis of Lewis acids such as $Sc(OTf)_3$, $Yb(OTf)_3$ or $In(OTf)_3$ at room temperature. The reaction mechanism has been discussed on the basis of an ^{18}O-labeling experiment.

1. Introduction

Methylenecyclopropanes (MCPs) are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis.[1,2] MCPs undergo a variety of ring-opening reactions in the presence of transition metal or Lewis acid because the relief of ring strain provides a potent thermodynamic driving force.[3,4] Among these reactions, Diels–Alder or 1,3-dipolar cycloaddition reactions have been often witnessed in the literature.[5]

Previously, we reported that MCPs **1** reacted with activated ketone and aldehyde such as diethyl ketomalonate **2a** and ethyl glyoxylate **2b** under the catalysis of various Lewis acids such as $Yb(OTf)_3$, $Sn(OTf)_2$, and $BF_3\cdot OEt_2$ to give the corresponding tetrahydrofuran derivatives **3** via a novel [3+2] cycloaddition approach (Scheme 1).[6] In these reactions, both R^1 and R^2 are aromatic groups in most cases. When 1-(4-methoxyphenyl)methylenecyclopropane **1g**, a single aromatic group substituted MCP, was taken into the reaction, **3g** was obtained in 48% yield along with a byproduct in a low yield, but its structure was not determined at that time (Scheme 2).

Allenes **4** were also employed into the reaction and as a sequence 3-hydroxy-tetrahydrofuran-2-one derivatives **5a** and **5b** were isolated in low yields when phenyl allene **4a** and diethyl ketomalonate **2a** were used as the substrates (Scheme 3).[7] However, efforts to enhance their yields were unsuccessful. Judging from the structures of the products, we assumed that the ambient water in the reaction system took part in the reaction.



Scheme 1. Lewis acid-catalyzed reactions of MCPs with activated ketone or aldehyde.

Afterward, we thought that the reaction of MCPs **1** with diethyl ketomalonate **2a** might also be affected by ambient moisture when single aromatic group substituted MCPs **1** were used as the substrates and the unidentified byproduct might have the similar structure as compounds **5**. Therefore, we envisioned that the yield of the byproduct shown in Scheme 2 would increase if certain amounts of water were added into the reaction system. Herein, we wish to report the Lewis acid-catalyzed reactions of mono-aryl group substituted methylenecyclopropanes **1** with diethyl ketomalonate **2a** in the presence of water under mild conditions to give 7-hydroxy-5-oxa-spiro[2,4]heptan-6-one derivatives **6** as the major products along with the tetrahydrofuran derivatives **3** as the minor products. A plausible mechanism of this reaction was proposed on the basis of an ^{18}O-labeling experiment.

Keywords: Lewis acid-catalyzed reactions; Methylenecyclopropanes; Diethyl ketomalonate; 7-Hydroxy-5-oxa-spiro[2,4]heptan-6-one; Water; $Sc(OTf)_3$.
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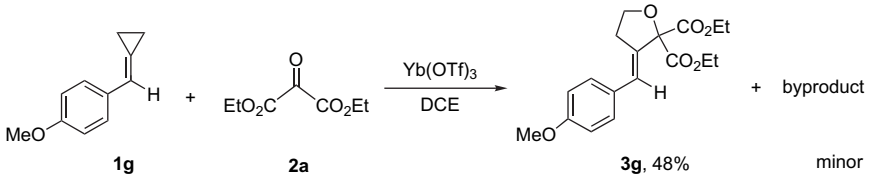
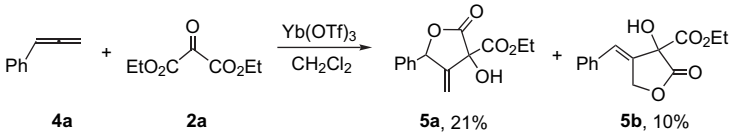
doi:10.1016/j.tet.2007.03.040



Scheme 2. $Yb(OTf)_3$-catalyzed reaction of MCP **1g** with diethyl ketomalonate **2a**.



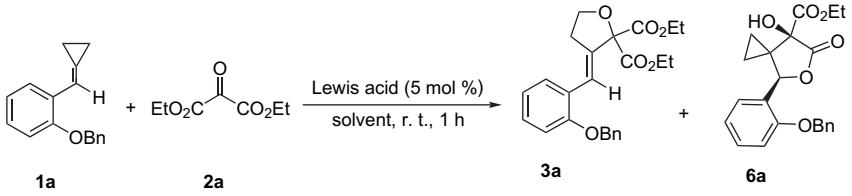
Scheme 3. $Yb(OTf)_3$-catalyzed reaction of allene **4a** with diethyl ketomalonate **2a**.

2. Results and discussion

Lanthanide triflates such as $La(OTf)_3$, $Sc(OTf)_3$, and $Yb(OTf)_3$ were utilized as Lewis acids in the reactions of MCPs **1** with diethyl ketomalonate **2a** in the presence of water since they are stable in air or even water.[8] Using (2-benzyloxy)phenylmethylenecyclopropane **1a** as the substrate, we investigated the Lewis acid-catalyzed reaction with **2a**. It was found that the corresponding 7-hydroxy-5-oxa-spiro[2,4]heptan-6-one derivative **6a** with *syn*-configuration (determined by the X-ray crystal structure of compound **6n** shown in Table 2, see the Supplementary data) was obtained in moderate yields with the addition of water. The reaction conditions were optimized by a variety of Lewis acids in various solvents and the results are summarized in Table 1.

Firstly, we utilized $Yb(OTf)_3$ as the Lewis acid and 1,2-dichloroethane (DCE) as a solvent to examine the influence of different equivalents of water on this reaction (Table 1, entries 1–5). It was found that the concentration of water in the reaction system affected the yield of product **6a** significantly. Compound **3a** was isolated as the major product (52% yield, *E*/*Z*>15/1) along with 8% yield of **6a** in the absence of water. However, with the addition of 1 equiv of water, **6a** was obtained in 52% yield, indicating that water indeed takes part in the reaction (Table 1, entries 1 and 2). Increasing the amount of water, the yield of the product **6a**, on the contrary,

Table 1. Lewis acid-catalyzed reactions of MCP **1a** (0.3 mmol) with diethyl ketomalonate **2a** (0.36 mmol) in the presence of water



Entry	Lewis acid	Solvent (2 mL)	Water (equiv)	Yield[a] [%]	
				3a[b]	**6a**
1	$Yb(OTf)_3$	DCE	0	52	8
2	$Yb(OTf)_3$	DCE	1	16	52
3	$Yb(OTf)_3$	DCE	2	6	40
4	$Yb(OTf)_3$	DCE	5	Trace	26
5	$Yb(OTf)_3$	DCE	10	Trace	Trace
6	$La(OTf)_3$[c]	DCE	1	Trace	Trace
7	$Sc(OTf)_3$	DCE	1	8	66
8	$In(OTf)_3$	DCE	1	20	35
9	$Sn(OTf)_2$	DCE	1	10	22
10	$Sc(OPf)_3$[c]	DCE	1	Trace	Trace
11	$Zr(OTf)_4$	DCE	1	Complex	
12	TMSOTf	DCE	1	Complex	
13	$Sc(OTf)_3$	CH_2Cl_2	1	14	38
14	$Sc(OTf)_3$	Toulene	1	16	41
15	$Sc(OTf)_3$	Et_2O	1	11	36
16	$Sc(OTf)_3$	$CHCl_3$	1	12	43
17	$Sc(OTf)_3$	CH_3CN	1	Trace	Trace
18	$Sc(OTf)_3$	THF	1	Trace	Trace
19	$Sc(OTf)_3$	Acetone	1	Trace	Trace

[a] Isolated yields.
[b] *E*/*Z*>15/1 determined by ^1H NMR spectroscopic data.
[c] Reaction time was prolonged to 12 h. $Sc(OPf)_3$=scandium perfluorooctanesulfonate.

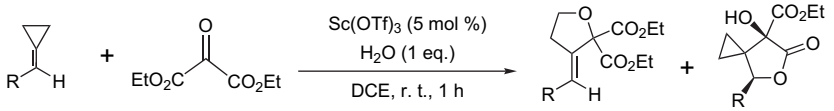
decreased. With the addition of 10 equiv of water, this reaction was almost stopped, producing only trace of the product **6a** on the basis of TLC plates and most of the starting materials remained unchanged even after a prolonged reaction time (Table 1, entries 3–5).

Secondly, various Lewis acids were tested in the reaction as described in Table 1, entries 6–12. $Sc(OTf)_3$ was identified as the most efficient catalyst for the reaction in the presence of 1 equiv of water to give **6a** in 66% yield. $In(OTf)_3$ and $Sn(OTf)_2$ could also catalyze the reaction but gave **6a** in lower yields under otherwise identical conditions. $La(OTf)_3$ and $Sc(OPf)_3$ (scandium perfluorooctanesulfonate) did not catalyze this reaction effectively, producing only trace of **6a** along with most of the starting materials. $Zr(OTf)_4$ and TMSOTf disordered the reaction, presumably due to that these Lewis acids were decomposed in the presence of water. In addition, we also examined the solvent effect of the reaction (Table 1, entries 13–19). Using $Sc(OTf)_3$ as the catalyst, we found that the reaction could proceed smoothly in toluene, dichloromethane, diethyl ether, and chloroform under mild conditions. However, no reaction occurred in acetonitrile, tetrahydrofuran, and acetone under the same conditions. The best reaction conditions are to carry out the reaction in DCE at room temperature (20 °C) using $Sc(OTf)_3$ (5 mol %) as a catalyst with the addition of 1 equiv of water (Table 1, entry 7).

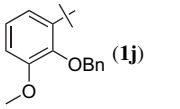
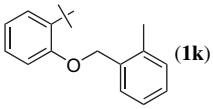
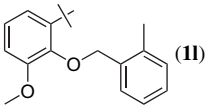
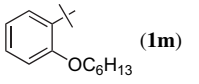
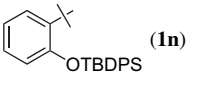
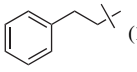
Under these optimal reaction conditions, we next carried out the reactions of various MCPs **1** with **2a** to examine the scope of substrates. The results are summarized in Table 2.

We found that the substituents on the aromatic ring have a remarkable effect on the reaction rate. Electron-donating substituents on the aromatic ring of MCPs **1** significantly promoted the reaction rate and these reactions completed within 1 h at room temperature to give the corresponding products in moderate yields even for sterically hindered substrates (Table 2, entries 2–6 and 9–13). On the other hand, either an electron-withdrawing group or no substituent on the aromatic ring retarded the reaction

Table 2. $Sc(OTf)_3$-catalyzed reactions of MCPs (0.3 mmol) with diethyl ketomalonate (0.36 mmol) in the presence of water (1 equiv)



1 **2a** **3** **6**

Entry	R	Yield[a] [%]		Entry	R	Yield[a] [%]	
		3[b]	**6**			**3**[b]	**6**
1[c]	C_6H_5 (**1b**)	**3b**, 10	**6b**, 52	9	 (**1j**)	**3j**, 6	**6j**, 72
2	*o*-$CH_3C_6H_4$ (**1c**)	**3c**, 8	**6c**, 55	10	 (**1k**)	**3k**, 7	**6k**, 75
3	*m*-$CH_3C_6H_4$ (**1d**)	**3d**, 11	**6d**, 56	11	 (**1l**)	**3l**, 11	**6l**, 56
4	*p*-$CH_3C_6H_4$ (**1e**)	**3e**, 10	**6e**, 59	12	 (**1m**)	**3m**, 30	**6m**, 41
5	*o*-$CH_3OC_6H_4$ (**1f**)	**3f**, 9	**6f**, 50	13	 (**1n**)	**3n**, 10	**6n**, 52
6	*p*-$CH_3OC_6H_4$ (**1g**)	**3g**, 12	**6g**, 54				
7[d]	*p*-ClC_6H_4 (**1h**)	**3h**, trace	**6h**, 28				
8[c]	 (**1i**)	**3i**, trace	**6i**, 42				

[a] Isolated yields.
[b] *E*/*Z*>15/1 determined by ^1H NMR spectroscopic data.
[c] Reaction time was prolonged to 12 h.
[d] Reaction time was prolonged to 12 h and 46% of the starting material was recovered.

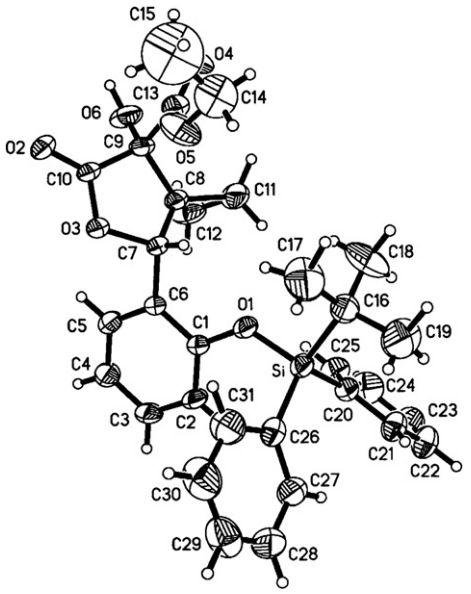
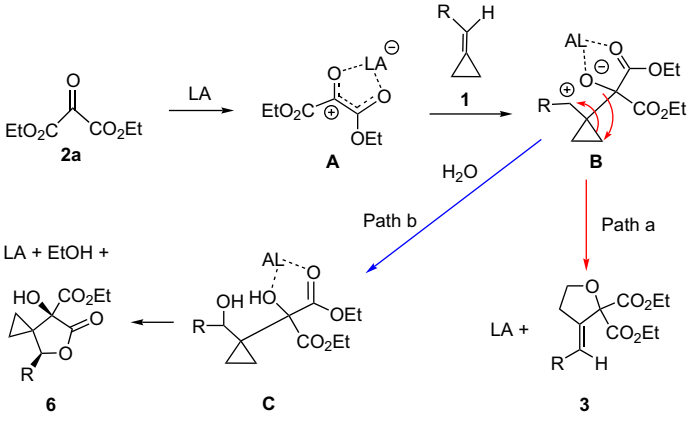


Figure 1. ORTEP drawing of **6n**.

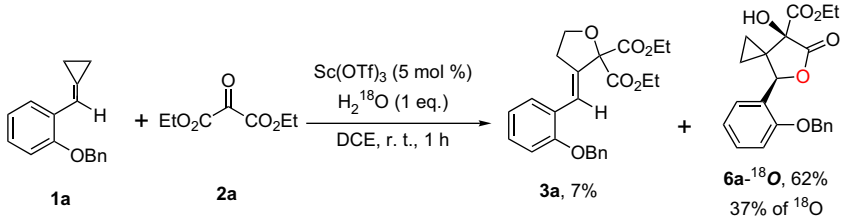
rate (Table 2, entries 1 and 7). For example, using *p*-chlorophenylmethylenecyclopropane **1h** as substrate, the corresponding cyclized product **6h** was obtained in lower yield even under a prolonged reaction time. 1-(2-Phenylethyl)-methylenecyclopropane **1i**, an aliphatic group substituted MCP, was also employed in the reaction and the corresponding product **6i** was isolated in moderate yield after 12 h (Table 2, entry 8). Nevertheless, cyclized products **3** were isolated in low yields as the side products in most cases. The product structures of **3** and **6** were determined by ^{1}H and ^{13}C NMR spectroscopic data, HRMS, microanalysis and the crystal structure of compound **6n** was further determined by X-ray diffraction.[9] The ORTEP drawing of **6n** is shown in Figure 1. The configurations of products **3** and their *E*/*Z* ratios were determined by NOESY spectroscopy and ^{1}H NMR spectroscopic data (see the Supplementary data).

The mechanism for this Lewis acid-catalyzed reaction of MCPs **1** with diethyl ketomalonate **2a** is outlined in Scheme 4. Lewis acid activated diethyl ketomalonate **2a** to generate intermediate **A**, which attacked MCP **1** to form the key intermediate **B**. The intermediate **B** could undergo a cyclopropylmethyl carbocationic rearrangement by the attack of oxygen atom to give the corresponding [3+2] cycloaddition product **3** (path a, the red arrows in Scheme 4). If there was one molecule of water in the reaction system, intermediate **B** could be hydrolyzed to produce intermediate **C** and subsequently afforded the product **6** by intramolecular transesterification (path b, the blue arrow in Scheme 4). The steric hindrance between aromatic R group and ethoxycarbonyl group in intermediate **C** resulted in product **6** being formed as *syn*-configuration.

To confirm the proposed mechanism for the reaction, an ^{18}O-labeling experiment was conducted under the same conditions (Scheme 5). Using (2-benzyloxy)phenylmethylenecyclopropane **1a** as the substrate, we added 1 equiv of $H_2{}^{18}O$ (94% ^{18}O content), instead of H_2O, into the reaction mixture. It was found that the reaction gave the corresponding product **6a**-^{18}O in 62% isolated yield with 37% ^{18}O content determined by EI mass spectroscopy (see the Supplementary data). This result clearly indicates that one oxygen atom (the red one in Scheme 5) in the cyclized product **6** comes from H_2O in the reaction system.



Scheme 4. A plausible mechanism for the Lewis acid-catalyzed reaction.



Scheme 5. ^{18}O-labeling experiment.

3. Conclusion

We have found that the Lewis acid-catalyzed reactions of mono-aryl group substituted MCPs **1** with diethyl ketomalonate **2a** in the presence of water (1.0 equiv) proceeded smoothly under mild conditions (room temperature) to give the corresponding 7-hydroxy-5-oxa-spiro[2,4]heptan-6-one derivatives **6** with *syn*-configuration in moderate yields along with the [3+2] cycloaddition products **3** in low yields. A plausible mechanism has been proposed based on the ^{18}O-labeling experiment.

4. Experimental procedures

4.1. General methods

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), Bruker FT mass spectrometer (ESI), and IonSpec 4.7 Tesla FTMS (MALDI). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Yinlong GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.2. Typical reaction procedure for the Lewis acid-catalyzed reaction of MCPs with diethyl ketomalonate in the presence of water

Water (5.0 μL, 0.3 mmol) was added to a solution of (2-benzyloxy)phenylmethylenecyclopropane **1a** (71 mg, 0.3 mmol) in DCE (2.0 mL) and the mixture was stirred for 0.5 h at room temperature. Afterward, $Sc(OTf)_3$ (7.0 mg, 0.014 mmol, 5 mol %) and diethyl ketomalonate (62 mg, 0.36 mmol) were added to the solution and the mixture was stirred for another 1 h at room temperature (monitored by TLC). Then the solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate= 8/1) to give the product **3a** (10 mg, 8%) as a colorless oil and **6a** (76 mg, 66%) as a white solid.

4.2.1. Compound 3a (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 3064, 2982, 1743, 1598, 1451, 1270, 1039, 753, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.20 (6H, t, J=7.2 Hz, $2CH_3$), 2.90 (2H, dt, J=2.4, 6.9 Hz, CH_2), 4.13–4.24 (6H, m, $3OCH_2$), 5.07 (2H, s, CH_2), 6.94–7.00 (2H, m, 1H for =CH and 1H for Ar), 7.22–7.45 (8H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 31.2, 62.1, 69.3, 70.2, 87.9, 112.0, 120.5, 122.0, 126.3, 127.3, 127.8, 128.4, 128.8, 128.9, 136.3, 136.9, 156.3, 168.0; MS (EI) *m*/*z* 4 10 (M^+, 1), 337 (25), 263 (12), 231 (15), 173 (19), 91 (100); HRMS (EI) calcd for $C_{24}H_{26}O_6$ (M^+) requires 410.1729, found: 410.1740.

4.2.2. Compound 3b (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 3053, 2981, 1743, 1492, 1268, 1100, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.32 (6H, t, J=7.2 Hz, $2CH_3$), 2.96 (2H, dt, J=2.7, 6.9 Hz, CH_2), 4.22 (2H, t, J=7.2 Hz, CH_2), 4.26–4.34 (4H, m, $2CH_2$), 6.92 (1H, t, J=2.7 Hz, =CH), 7.24–7.31 (1H, m, Ar), 7.36–7.37 (4H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 31.2, 62.1, 69.2, 87.9, 126.9, 127.4, 128.3, 128.5, 136.1, 136.5, 167.9; MS (EI) *m*/*z* 304 (M^+, 3), 231 (100), 203 (8), 157 (41), 129 (55); HRMS (EI) calcd for $C_{17}H_{20}O_5$ (M^+) requires 304.1311, found: 304.1310.

4.2.3. Compound 3c (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 3060, 2981, 1744, 1508, 1268, 1096, 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.33 (6H, t, J=7.2 Hz, $2CH_3$), 2.31 (3H, s, CH_3), 2.81 (2H, dt, J=2.4, 6.6 Hz, CH_2), 4.16 (2H, t, J=6.9 Hz, CH_2), 4.31 (4H, q, J=4.2 Hz, $2CH_2$), 7.02 (1H, t, J=2.4 Hz, =CH), 7.18–7.19 (3H, m, Ar), 7.26–7.30 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 19.7, 30.8, 62.1, 69.1, 87.5, 125.59, 125.63, 127.5, 127.7, 129.9, 135.8, 136.5, 137.0, 168.0; MS (EI) *m*/*z* 318 (M^+, 6), 245 (100), 171 (82), 143 (47), 128 (29); HRMS (EI) calcd for $C_{18}H_{22}O_5$ (M^+) requires 318.1467, found: 318.1490.

4.2.4. Compound 3d (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 3060, 2981, 1744, 1604, 1272, 1096, 793, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.32 (6H, t, J=7.2 Hz, $2CH_3$), 2.36 (3H, s, CH_3), 2.96 (2H, dt, J=2.4, 6.9 Hz, CH_2), 4.20–4.35 (6H, m, $3CH_2$), 6.88 (1H, t, J=2.4 Hz, =CH), 7.07–7.29 (4H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 21.4, 31.2, 62.1, 69.2, 87.9, 125.6, 127.0, 128.21, 128.23, 129.4, 136.0, 136.6, 137.9, 168.0; MS (EI) *m*/*z* 318 (M^+, 5), 245 (100), 171 (32), 143 (37), 128 (31); HRMS (EI) calcd for $C_{18}H_{22}O_5$ (M^+) requires 318.1467, found: 318.1467.

4.2.5. Compound 3e (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 2983, 1748, 1513, 1284, 1039, 819 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.31 (6H, t, J=7.2 Hz, $2CH_3$), 2.35 (3H, s, CH_3), 2.95 (2H, dt, J=2.4, 6.9 Hz, CH_2), 4.20–4.35 (6H, m, $3CH_2$), 6.87 (1H, t, J=2.4 Hz, =CH), 7.17 (2H, d, J=7.8 Hz, Ar), 7.26 (2H, d, J=7.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 21.1, 31.1, 62.0, 69.2, 87.9, 126.7, 128.5, 129.0, 133.7, 135.1, 137.3, 167.9; MS (EI) *m*/*z* 318 (M^+, 5), 245 (100), 171 (51), 143 (47), 128 (36); HRMS (EI) calcd for $C_{18}H_{22}O_5$ (M^+) requires 318.1467, found: 318.1475.

4.2.6. Compound 3f (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 2981, 1743, 1598, 1489, 1247, 1134, 1039, 859, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.33 (6H, t, J=7.2 Hz, $2CH_3$), 2.89 (2H, dt, J=2.7, 6.9 Hz, CH_2), 3.83 (3H, s, CH_3), 4.19 (2H, t, J=6.9 Hz, CH_2), 4.24–4.40 (4H, m, $2CH_2$), 6.87–6.98 (2H, m, Ar), 7.19 (1H, t, J=2.7 Hz, =CH), 7.23–7.35 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 31.2, 55.4, 62.1, 69.3, 87.8, 110.5, 120.1, 122.0, 125.8, 128.7, 128.9, 136.0, 157.1, 168.0; MS (EI) *m*/*z* 334 (M^+, 2), 261 (100), 187 (18), 159 (16); HRMS (EI) calcd for $C_{18}H_{22}O_6$ (M^+) requires 334.1416, found: 334.1416.

4.2.7. Compound 3j (*E*/*Z* > 15/1). A colorless oil; IR (KBr) ν 2981, 1743, 1577, 1476, 1276, 1092, 859, 747, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.23 (6H, t, J=7.2 Hz, $2CH_3$), 2.86 (2H, dt, J=2.7, 6.9 Hz, CH_2), 3.87 (3H, s, CH_3), 4.16–4.23 (6H, m, $3CH_2$), 4.95 (2H, s, CH_2), 6.87–6.90 (1H, m, Ar), 6.95–6.98 (1H, m, Ar), 7.07 (1H, t, J=7.8 Hz, Ar),

7.21 (1H, t, J=2.7 Hz, =CH), 7.30–7.39 (3H, m, Ar), 7.47–7.50 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 31.2, 55.7, 62.0, 69.1, 75.0, 87.9, 111.7, 120.6, 122.0, 123.7, 127.7, 128.1, 128.3, 131.3, 137.35, 137.37, 145.8, 152.9, 167.8; MS (EI) m/z 440 (M^+, 3), 367 (42), 293 (8), 261 (10), 203 (9), 91 (100); HRMS (EI) calcd for $C_{25}H_{28}O_7$ (M^+) requires 440.1835, found: 440.1866.

4.2.8. Compound 3k (E/Z > 15/1). A colorless oil; IR (KBr) ν 2981, 1743, 1594, 1453, 1266, 1110, 855, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.16 (6H, t, J=7.2 Hz, $2CH_3$), 2.36 (3H, s, CH_3), 2.89 (2H, dt, J=2.4, 6.6 Hz, CH_2), 4.07–4.21 (6H, m, $3CH_2$), 5.04 (2H, s, CH_2), 6.97–7.01 (2H, m, Ar), 7.20–7.27 (5H, m, 1H for =CH and 4H for Ar), 7.36–7.45 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 18.7, 31.2, 62.0, 68.6, 69.2, 87.8, 111.6, 120.4, 121.9, 125.8, 126.1, 128.0, 128.4, 128.77, 128.81, 130.1, 134.7, 136.2, 136.5, 156.3, 167.9; MS (EI) m/z 424 (M^+, 1), 351 (12), 279 (4), 231 (8), 149 (22), 105 (100); HRMS (EI) calcd for $C_{25}H_{28}O_6$ (M^+) requires 424.1886, found: 424.1891.

4.2.9. Compound 3l (E/Z > 15/1). A colorless oil; IR (KBr) ν 2978, 1743, 1577, 1476, 1275, 1039, 855, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.21 (6H, t, J=7.2 Hz, $2CH_3$), 2.42 (3H, s, CH_3), 2.89 (2H, dt, J=2.4, 6.6 Hz, CH_2), 3.85 (3H, s, CH_3), 4.13–4.21 (6H, m, $3CH_2$), 4.96 (2H, s, CH_2), 6.88 (1H, d, J=8.1 Hz, Ar), 6.99 (1H, d, J=8.1 Hz, Ar), 7.08 (1H, t, J=8.1 Hz, Ar), 7.18–7.23 (4H, m, 1H for =CH and 4H for Ar), 7.51–7.54 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 18.7, 31.3, 55.7, 62.0, 69.2, 73.0, 87.9, 111.8, 120.6, 121.9, 123.8, 125.7, 127.9, 129.1, 129.9, 131.3, 135.6, 136.6, 137.4, 146.1, 153.0, 167.8; MS (EI) m/z 454 (M^+, 4), 381 (11), 275 (7), 261 (9), 203 (18), 105 (100); HRMS (EI) calcd for $C_{26}H_{30}O_7$ (M^+) requires 454.1992, found: 454.2022.

4.2.10. Compound 3m (E/Z > 15/1). A colorless oil; IR (KBr) ν 2934, 1745, 1597, 1453, 1247, 1111, 1043, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.91 (3H, t, J=6.9 Hz, CH_3), 1.30–1.34 (10H, m, $2CH_3$ and $2CH_2$), 1.42–1.52 (2H, m, CH_2), 1.74–1.84 (2H, m, CH_2), 2.90 (2H, dt, J=2.4, 6.6 Hz, CH_2), 3.96 (2H, t, J=6.6 Hz, CH_2), 4.19 (2H, t, J=6.9 Hz, CH_2), 4.39 (4H, q, J=7.2 Hz, $2CH_2$), 6.85–6.96 (2H, m, Ar), 7.19 (1H, t, J=2.4 Hz, =CH), 7.23–7.35 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.02, 14.04, 22.6, 25.7, 29.3, 31.3, 31.6, 62.0, 68.2, 69.3, 87.9, 111.5, 119.9, 122.0, 125.9, 128.7, 128.8, 135.8, 156.7, 168.0; MS (EI) m/z 404 (M^+, 2), 331 (100), 257 (17), 225 (56), 173 (71), 155 (32); HRMS (EI) calcd for $C_{23}H_{32}O_6$ (M^+) requires 404.2199, found: 404.2247.

4.2.11. Compound 3n (E/Z > 15/1). A colorless oil; IR (KBr) ν 2929, 1744, 1596, 1485, 1260, 1108, 923, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.02 (9H, s, $3CH_3$), 1.21 (6H, t, J=7.2 Hz, $2CH_3$), 2.92 (2H, dt, J=2.4, 6.9 Hz, CH_2), 4.15–4.24 (6H, m, $3CH_2$), 6.34–6.37 (1H, m, Ar), 6.70–6.80 (2H, m, Ar), 7.26–7.35 (7H, m, Ar), 7.41 (1H, t, J=2.4 Hz, =CH), 7.64–7.67 (4H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 19.5, 26.4, 31.4, 62.1, 69.3, 88.1, 119.1, 120.6, 122.1, 127.5, 127.8, 128.3, 128.7, 129.9, 132.5, 135.4, 135.9, 153.4, 168.1; MS (MALDI) m/z 581 (M^++Na); HRMS (MALDI) calcd for $C_{33}H_{38}SiO_6Na^+$ (M^++Na) requires 581.2324, found: 581.2330.

4.2.12. Compound 6a. A white solid, mp 118–120 °C; IR (KBr) ν 3473, 2982, 1782, 1740, 1603, 1495, 1149, 1002, 859, 750, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.08–0.16 (1H, m, CH_2), 0.45–0.52 (1H, m, CH_2), 0.76–0.83 (1H, m, CH_2), 1.04–1.11 (1H, m, CH_2), 1.20 (3H, t, J=7.2 Hz, CH_3), 3.67 (1H, s, OH), 4.20–4.31 (1H, m, CH_2), 4.37–4.48 (1H, m, CH_2), 5.00 (1H, d, J=11.4 Hz, CH_2), 5.08 (1H, d, J=11.4 Hz, CH_2), 6.33 (1H, s, CH), 6.96 (1H, d, J=7.8 Hz, Ar), 7.04 (1H, t, J=7.5 Hz, Ar), 7.26–7.41 (7H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.7, 7.9, 13.8, 31.1, 63.4, 70.1, 77.5, 78.2, 111.5, 121.1, 123.1, 127.3, 128.0, 128.2, 128.5, 129.9, 136.2, 155.9, 169.9, 172.7; MS (EI) m/z 382 (M^+, 1), 309 (3), 291 (5), 247 (4), 173 (8), 145 (9), 91 (100); HRMS (EI) calcd for $C_{22}H_{22}O_6$ (M^+) requires 382.1416, found: 382.1421. Compound **6a**-^{18}O (37% ^{18}O determined by EI mass spectrum): MS (EI) m/z 384 (M^+, 58), 382 (M^+, 100); HRMS (EI) calcd for $C_{22}H_{22}O_5{}^{18}O$ (M^+) requires 384.1459, found: 384.1407.

4.2.13. Compound 6b. A white solid, mp 118–120 °C; IR (KBr) ν 3468, 2985, 1785, 1747, 1496, 1221, 1151, 1000, 809, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.04–0.03 (1H, m, CH_2), 0.54–0.66 (2H, m, CH_2), 1.04–1.12 (1H, m, CH_2), 1.38 (3H, t, J=6.9 Hz, CH_3), 4.03 (1H, s, OH), 4.32–4.50 (2H, m, CH_2), 5.76 (1H, s, CH), 7.19–7.22 (2H, m, Ar), 7.33–7.38 (3H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 3.9, 7.4, 14.1, 31.3, 63.6, 77.4, 83.1, 126.6, 128.5, 129.0, 134.3, 169.8, 172.6; MS (EI) m/z 276 (M^+, 19), 233 (59), 203 (24), 158 (100), 130 (76). Anal. Calcd for $C_{15}H_{16}O_5$ requires C, 65.21; H, 5.84%. Found: C, 65.10; H, 5.86%.

4.2.14. Compound 6c. A white solid, mp 74–76 °C; IR (KBr) ν 3470, 2983, 1786, 1744, 1466, 1321, 1221, 1178, 1034, 767, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.09–0.17 (1H, m, CH_2), 0.55–0.67 (2H, m, CH_2), 1.16–1.23 (1H, m, CH_2), 1.40 (3H, t, J=7.2 Hz, CH_3), 2.32 (3H, s, CH_3), 4.13 (1H, s, OH), 4.32–4.55 (2H, m, CH_2), 6.05 (1H, s, CH), 7.15–7.28 (4H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.7, 8.1, 14.1, 19.4, 30.7, 63.5, 77.4, 81.7, 126.0, 128.6, 128.9, 130.9, 131.8, 136.1, 169.9, 172.7; MS (EI) m/z 290 (M^+, 1), 217 (28), 171 (78), 157 (100), 143 (58), 129 (89). Anal. Calcd for $C_{16}H_{18}O_5$ requires C, 66.19; H, 6.25%. Found: C, 66.18; H, 6.31%.

4.2.15. Compound 6d. A white solid, mp 98–100 °C; IR (KBr) ν 3473, 2984, 1786, 1743, 1455, 1326, 1224, 1039, 790, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.02–0.05 (1H, m, CH_2), 0.54–0.65 (2H, m, CH_2), 1.04–1.11 (1H, m, CH_2), 1.38 (3H, t, J=7.2 Hz, CH_3), 2.33 (3H, s, CH_3), 4.03 (1H, s, OH), 4.31–4.50 (2H, m, CH_2), 5.72 (1H, s, CH), 6.99–7.02 (2H, m, Ar), 7.14 (1H, d, J=7.8 Hz, Ar), 7.23 (1H, t, J=7.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.0, 7.5, 14.1, 21.3, 31.2, 63.6, 77.4, 83.2, 123.7, 127.2, 128.3, 129.7, 134.2, 138.3, 169.9, 172.6; MS (EI) m/z 290 (M^+, 2), 217 (24), 172 (100), 157 (34), 143 (52), 129 (78); HRMS (EI) calcd for $C_{16}H_{18}O_5$ (M^+) requires 290.1154, found: 290.1159.

4.2.16. Compound 6e. A white solid, mp 114–116 °C; IR (KBr) ν 3471, 2982, 1781, 1745, 1452, 1170, 1028, 829, 786, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.01–0.08 (1H, m, CH_2), 0.52–0.64 (2H, m, CH_2), 1.05–1.12 (1H, m, CH_2), 1.39 (3H, t, J=7.2 Hz, CH_3), 2.34 (3H, s, CH_3), 3.94 (1H, s, OH), 4.33–4.51 (2H, m, CH_2), 5.74 (1H, s, CH), 7.09 (2H, d, J=7.8 Hz, Ar), 7.17 (2H, d, J=7.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 3.9, 7.5, 14.1, 21.1, 31.2, 63.7, 77.4, 83.2, 126.7, 129.2, 131.2, 139.0, 170.0, 172.6; MS (EI) m/z 290 (M^+, 2), 217 (22), 171 (89), 157 (100), 143 (42), 129 (54); HRMS (EI) calcd for $C_{16}H_{18}O_5$ (M^+) requires 290.1154, found: 290.1155.

4.2.17. Compound 6f. A white solid, mp 92–94 °C; IR (KBr) ν 3470, 2982, 1786, 1743, 1604, 1495, 1250, 1152, 1028, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.04–0.12 (1H, m, CH_2), 0.52–0.60 (1H, m, CH_2), 0.76–0.83 (1H, m, CH_2), 1.05–1.13 (1H, m, CH_2), 1.40 (3H, t, J=7.2 Hz, CH_3), 3.80 (3H, s, CH_3), 3.95 (1H, s, OH), 4.31–4.54 (2H, m, CH_2), 6.17 (1H, s, CH), 6.88 (1H, d, J=8.4 Hz, Ar), 6.99 (1H, t, J=7.5 Hz, Ar), 7.25–7.34 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 5.6, 8.3, 14.1, 30.8, 55.3, 63.5, 77.7, 78.9, 110.5, 120.7, 123.1, 128.3, 130.0, 156.9, 170.2, 172.9; MS (EI) m/z 306 (M^+, 3), 233 (32), 187 (100), 157 (79), 145 (38), 129 (33); HRMS (EI) calcd for $C_{16}H_{18}O_6$ (M^+) requires 306.1103, found: 306.1085.

4.2.18. Compound 6g. A white solid, mp 96–98 °C; IR (KBr) ν 3462, 2983, 1786, 1743, 1613, 1516, 1306, 1252, 1033, 835, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.06–0.13 (1H, m, CH_2), 0.51–0.65 (2H, m, CH_2), 1.07–1.15 (1H, m, CH_2), 1.40 (3H, t, J=7.2 Hz, CH_3), 3.82 (3H, s, CH_3), 3.86 (1H, s, OH), 4.34–4.52 (2H, m, CH_2), 5.73 (1H, s, CH), 6.90 (2H, d, J=8.7 Hz, Ar), 7.15 (2H, d, J=8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.0, 7.6, 14.2, 31.3, 55.3, 63.7, 77.5, 83.2, 114.0, 126.2, 128.4, 160.1, 170.0, 172.5; MS (EI) m/z 306 (M^+, 5), 233 (30), 187 (100), 159 (35), 145 (19), 121 (28); HRMS (EI) calcd for $C_{16}H_{18}O_6$ (M^+) requires 306.1103, found: 306.1107.

4.2.19. Compound 6h. A white solid, mp 100–102 °C; IR (KBr) ν 3468, 2985, 1786, 1744, 1599, 1493, 1318, 1224, 1151, 1004, 832, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.05–0.03 (1H, m, CH_2), 0.53–0.67 (2H, m, CH_2), 1.06–1.13 (1H, m, CH_2), 1.38 (3H, t, J=7.2 Hz, CH_3), 4.00 (1H, s, OH), 4.32–4.50 (2H, m, CH_2), 5.73 (1H, s, CH), 7.15 (2H, d, J=8.7 Hz, Ar), 7.35 (2H, d, J=8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.0, 7.4, 14.1, 31.2, 63.8, 77.2, 82.3, 128.1, 128.8, 132.9, 135.0, 169.7, 172.3; MS (EI) m/z 310 (M^+, 1), 237 (7), 193 (28), 165 (17), 157 (100), 129 (57). Anal. Calcd for $C_{15}H_{15}ClO_5$ requires C, 57.98; H, 4.87%. Found: C, 57.90; H, 4.88%.

4.2.20. Compound 6i. A colorless oil; IR (KBr) ν 3468, 2939, 1792, 1751, 1496, 1203, 1026, 916, 858, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.55–0.61 (2H, m, CH_2), 0.77–0.84 (1H, m, CH_2), 1.13–1.20 (1H, m, CH_2), 1.29 (3H, t, J=7.2 Hz, CH_3), 1.42–1.52 (1H, m, CH_2), 1.74–1.83 (1H, m, CH_2), 2.67–2.77 (1H, m, CH_2), 2.93–3.03 (1H, m, CH_2), 3.78 (1H, s, OH), 4.24–4.42 (2H, m, CH_2), 4.78 (1H, dd, J=1.8, 10.2 Hz, CH), 7.18–7.33 (5H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.7, 5.8, 14.0, 29.3, 31.9, 33.1, 63.6, 77.4, 80.1, 126.2, 128.4, 128.5, 140.6, 170.0, 172.4; MS (EI) m/z 304 (M^+, 1), 213 (2), 187 (3), 169 (8), 157 (6), 129 (7), 91 (100); HRMS (EI) calcd for $C_{17}H_{20}O_5$ (M^+) requires 304.1311, found: 304.1320.

4.2.21. Compound 6j. A white solid, mp 104–106 °C; IR (KBr) ν 3465, 2981, 1789, 1747, 1589, 1481, 1274, 1152, 1002, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.00–0.07 (1H, m, CH_2), 0.43–0.50 (1H, m, CH_2), 0.82–0.89 (1H, m, CH_2), 1.00–1.07 (1H, m, CH_2), 1.18 (3H, t, J=7.2 Hz, CH_3), 3.86 (1H, s, OH), 3.89 (3H, s, CH_3), 4.20–4.37 (2H, m, CH_2), 4.85 (1H, d, J=11.4 Hz, CH_2), 5.23 (1H, d, J=11.4 Hz, CH_2), 6.15 (1H, s, CH), 6.90–6.94 (2H, m, Ar), 7.12 (1H, t, J=7.8 Hz, Ar), 7.32–7.42 (5H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.5, 8.0, 13.9, 31.1, 55.6, 63.5, 74.9, 77.4, 78.3, 112.3, 119.5, 124.4, 127.7, 128.0, 128.3, 128.5, 137.2, 145.5, 152.0, 169.9, 127.6; MS (EI) m/z 412 (M^+, 2), 339 (1), 321 (2), 277 (4), 203 (8), 175 (16), 91 (100); HRMS (EI) calcd for $C_{23}H_{24}O_7$ (M^+) requires 412.1522, found: 412.1524.

4.2.22. Compound 6k. A white solid, mp 98–100 °C; IR (KBr) ν 3467, 2982, 1786, 1740, 1604, 1590, 1496, 1151, 1002, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.09–0.16 (1H, m, CH_2), 0.43–0.50 (1H, m, CH_2), 0.71–0.79 (1H, m, CH_2), 1.02–1.10 (1H, m, CH_2), 1.14 (3H, t, J=7.2 Hz, CH_3), 2.36 (3H, s, CH_3), 3.74 (1H, s, OH), 4.16–4.26 (1H, m, CH_2), 4.34–4.45 (1H, m, CH_2), 4.96 (1H, d, J=11.4 Hz, CH_2), 5.05 (1H, d, J=11.4 Hz, CH_2), 6.33 (1H, s, CH), 6.98–7.06 (2H, m, Ar), 7.20–7.37 (6H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.6, 7.9, 13.7, 18.8, 31.1, 63.4, 68.5, 77.5, 78.8, 111.5, 121.4, 123.1, 126.0, 128.2, 128.3, 129.9, 130.3, 134.2, 136.2, 156.0, 170.0, 172.6; MS (EI) m/z 396 (M^+, 1), 323 (1), 276 (2), 247 (3), 173 (4), 145 (4), 105 (100); HRMS (EI) calcd for $C_{23}H_{24}O_6$ (M^+) requires 396.1573, found: 396.1555.

4.2.23. Compound 6l. A white solid, mp 76–78 °C; IR (KBr) ν 3471, 2980, 1789, 1744, 1589, 1481, 1274, 1153, 855, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.00–0.08 (1H, m, CH_2), 0.43–0.50 (1H, m, CH_2), 0.81–0.89 (1H, m, CH_2), 1.01–1.08 (1H, m, CH_2), 1.15 (3H, t, J=7.2 Hz, CH_3), 2.39 (3H, s, CH_3), 3.82 (1H, s, OH), 3.89 (3H, s, CH_3), 4.26 (2H, q, J=7.2 Hz, CH_2), 4.81 (1H, d, J=11.4 Hz, CH_2), 5.28 (1H, d, J=11.4 Hz, CH_2), 6.15 (1H, s, CH), 6.93 (2H, d, J=8.1 Hz, Ar), 7.11–7.23 (4H, m, Ar), 7.40–7.42 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.5, 8.0, 13.9, 18.8, 31.2, 55.7, 63.6, 73.1, 77.4, 78.1, 112.3, 119.5, 124.5, 125.9, 128.1, 128.4, 128.5, 130.2, 135.5, 136.2, 145.8, 152.1, 170.0, 172.6; MS (EI) m/z 426 (M^+, 2), 353 (1), 306 (2), 277 (3), 203 (6), 175 (10), 105 (100); HRMS (EI) calcd for $C_{24}H_{26}O_7$ (M^+) requires 426.1679, found: 426.1687.

4.2.24. Compound 6m. A colorless oil; IR (KBr) ν 3473, 2932, 1786, 1743, 1603, 1495, 1249, 1152, 1004, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.06–0.14 (1H, m, CH_2), 0.50–0.57 (1H, m, CH_2), 0.76–0.83 (1H, m, CH_2), 0.91 (3H, t, J=7.2 Hz, CH_3), 1.05–1.13 (1H, m, CH_2), 1.32–1.51 (9H, m, $1CH_3$ and $3CH_2$), 1.72–1.82 (2H, m, CH_2), 3.80 (1H, s, OH), 3.85–4.02 (2H, m, CH_2), 4.31–4.40 (1H, m, CH_2), 4.46–4.56 (1H, m, CH_2), 6.25 (1H, s, CH), 6.85 (1H, d, J=8.4 Hz, Ar), 6.98 (1H, t, J=7.5 Hz,

Ar), 7.26–7.31 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 5.0, 8.2, 14.0, 14.1, 22.5 (2C), 25.7, 29.1, 31.4, 63.4, 67.9, 77.6, 78.0, 111.1, 120.5, 122.8, 128.3, 129.9, 156.4, 170.2, 172.8; MS (EI) *m/z* 376 (M^+, 3), 303 (21), 257 (32), 201 (18), 173 (100), 157 (30), 145 (58); HRMS (EI) calcd for $C_{21}H_{28}O_6$ (M^+) requires 376.1886, found: 376.1877.

4.2.25. Compound 6n. A white solid, mp 138–140 °C; IR (KBr) ν 3466, 2961, 1787, 1743, 1492, 1257, 1151, 917, 758, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.20–0.27 (1H, m, CH_2), 0.61–0.68 (1H, m, CH_2), 0.96–1.02 (1H, m, CH_2), 1.10 (9H, s, $3CH_3$), 1.14–1.22 (1H, m, CH_2), 1.40 (3H, t, J=7.2 Hz, CH_3), 3.83 (1H, s, OH), 4.31–4.42 (1H, m, CH_2), 4.47–4.58 (1H, m, CH_2), 6.38 (1H, d, J=8.1 Hz, Ar), 6.71 (1H, s, CH), 6.83–6.97 (2H, m, Ar), 7.34–7.48 (7H, m, Ar), 7.64–7.70 (4H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 4.3, 7.8, 14.1, 19.4, 26.5, 31.4, 63.9, 77.3, 77.6, 118.9, 121.5, 124.3, 127.95, 128.03, 128.7, 129.3, 130.2 (2C), 131.1, 131.9, 135.1, 135.3, 152.9, 170.3, 172.7; MS (MALDI) *m/z* 553 (M^++Na); HRMS (MALDI) calcd for $C_{31}H_{34}SiO_6Na^+$ (M^++Na) requires 553.2015, found: 553.2017.

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005), Chinese Academy of Sciences (KGCX2-210-01), and the National Natural Science Foundation of China for financial support (20472096, 203900502, and 20672127).

Supplementary data

The spectroscopic data (^{1}H, ^{13}C, and NOESY spectroscopic data), analytic data, and the X-ray crystal structure of the products shown in Tables 1 and 2, Schemes 1–5 and the detailed description of experimental procedures are included. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.040.

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9. The crystal data of **6n** have been deposited in CCDC with number 279217. Empirical formula: $C_{34}H_{41}O_6Si$; formula weight: 573.76; crystal color, habit: colorless, prismatic; crystal dimensions: 0.516×0.505×0.360 mm; crystal system: triclinic; lattice type: primitive; lattice parameters: a=9.1423(11) Å, b=11.7711(15) Å, c=16.814(2) Å, α=109.480(2)°, β=95.770(2)°, γ=101.167(2)°, V=1646.6(3) $Å^3$; space group: P-1; Z=2; D_{calc}=1.157 g/cm^3; F_{000}=614; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0711, 0.2035.