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Photoinduced Decarbonylative Rearrangement of Bicyclo[2.2.2]Octenones: Synthesis of the Marasmane Skeleton

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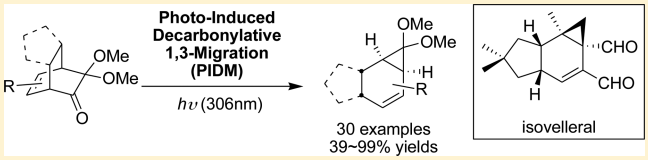
Supporting Information

ABSTRACT: The marasmane sesquiterpenoid structure can be found in the skeleton of a variety of natural products bearing interesting bioactivity. The unique fused-5,6,3-tricyclic ring structure, in which the rings are *cis*-fused and the five- and three-membered rings are mutually *trans*, provides a synthetic challenge for organic chemists. In this work, we took advantage of the photoinduced decarbonylative rearrangement of bicyclo[2.2.2]octenone to develop a new methodology for construction of the highly functionalized fused-5,6,3-tricyclic ring structure in a concise reaction sequence.



INTRODUCTION

Isolated from the basidiomycete species of the genus *Lactarius*,[1] marasmane sesquiterpenoids are known for their unique fused-5,6,3-tricyclic ring skeleton[2](Figure 1). Aside from being a

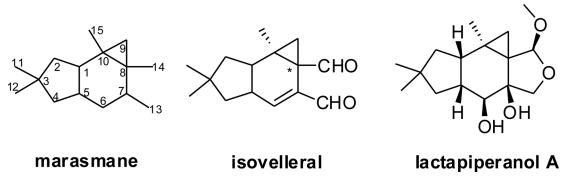
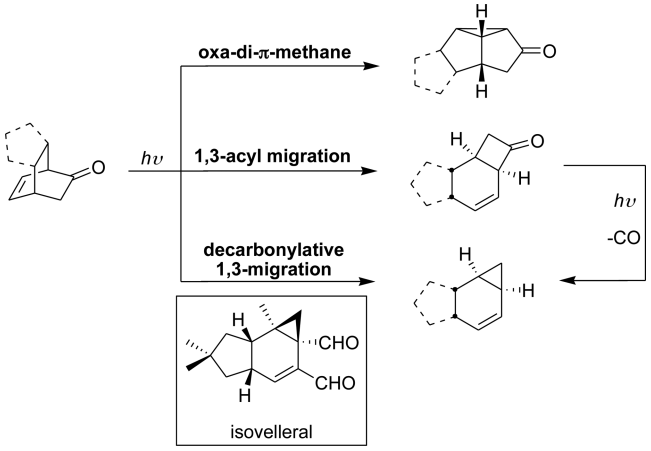


Figure 1. Marasmane skeleton and related natural products.

synthetic challenge for organic chemists, the antifeedant,[3] antifungal, antibacterial,[4] and other bioactivities of these secondary metabolites are also of interest to medicinal chemists.[5] Over the years, Heathcock,[6] Wilson,[7] Groot,[8] Woodward,[9] and others have demonstrated a variety of methods to synthesize members of the marasmane family of natural products.[10] Within the marasmane family, isovelleral caught our attention with its densely functionalized tricyclic ring structure, in which the five-membered ring and cyclopropane ring are fused to a cyclohexene core at adjacent carbons and a dialdehyde group is featured. Isovelleral was also identified to be antibiotic and mutagenic.[5a,11] In previously reported syntheses of isovelleral and its derivatives,[6,12] multiple steps were needed to assemble the fused-5,6,3-tricyclic core structure. We envisioned that a short and functional group compatible construction of the isovelleral skeleton could be potentially important for evaluation of bioactivities of this family of compounds.

Photochemical rearrangement of bicyclo[2.2.2]octenones has been a fruitful area in natural product synthesis; namely, the oxa-di-π-methane rearrangement of bicyclo[2.2.2]octenones has been utilized in the synthesis of a number of complex molecules.[13] Pioneered by Yates and Stevens in the early 1980s,[14] Singh,[15] Banwell,[16] Liao,[17] and other groups have successfully employed the oxa-di-π-methane (ODPM) rearrangement of bicyclo[2.2.2]octenones in syntheses of a great diversity of natural products.[18] Additionally, the photoinduced 1,3-acyl migration of bicyclo[2.2.2]octenones has also been demonstrated as an effective method in natural product synthesis.[15a,19] As shown in Scheme 1, it has been reported

Scheme 1. Photochemical Rearrangement of Bicyclo[2.2.2]octenones



that, in some cases of the 1,3-acyl migration pathway, a secondary product was found that resulted from an additional decarbonylation.[14b,16g,17b,20] With the structural resemblance of this secondary product to marasmane's skeleton, we anticipated that this photoinduced decarbonylative 1,3-migration (PIDM) of bicyclo[2.2.2]octenones could be an effective synthetic pathway for isovelleral and related compounds. We herein

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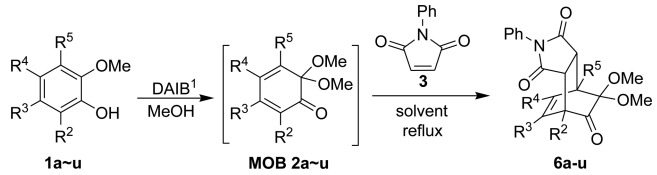
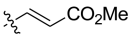
Table 1. Diels–Alder Reaction of 2a–u with 3, *N*-Phenylmaleimide



Entry	Diels-Alder Product R^2	R^3	R^4	R^5	Product	Solvent	Yield[a] (%)
1	H	H	H	H	**6a**	Mesitylene	92[b]
2	H	H	CH_3	H	**6b**	Toluene	68
3	CH_3	H	H	H	**6c**	MeOH	74
4	H	CH_3	H	H	**6d**	Mesitylene	87[b]
5	H	H	H	CH_3	**6e**	Toluene	68
6		H	H	H	**6f**	MeOH	72[c]
7	H		H	H	**6g**	MeOH	70[c]
8	H	H		H	**6h**	Toluene	72
9	H	CO_2Me	H	H	**6i**	MeOH	88
10	H	H	CO_2Me	H	**6j**	MeOH	74[c]
11	OMe	H	CO_2Me	H	**6k**	MeOH	80[c]
12	H	H	Acetyl	H	**6l**	MeOH	55
13	OMe	H	H	H	**6m**	MeOH	62
14	H	H	H	OMe	**6n**	Toluene	88
15	H	H	CN	H	**6o**	MeOH	25
16	H	H	TMS	H	**6p**	MeOH	74
17	H	H	allyl	H	**6q**	MeOH	84
18	OMe	H		H	**6r**	Toluene	72
19	OMe	H		H	**6s**	MeOH	37
20	H	tBu	H	H	**6t**	MeOH	51
21	H	H	tBu	H	**6u**	MeOH	60

[a]DAIB: (diacetoxy)iodobenzene. [b]Reaction done by using dimer of MOB in retro-Diels–Alder reaction with **3**. [c]Reaction at rt.

report a rapid synthesis of functionalized marasmane anolgues by PIDM of bicyclo[2.2.2]octenones.

RESULTS

In order to construct the bicyclo[2.2.2]octenone starting materials with diverse functionalities, we took advantage of the Diels–Alder (D-A) reaction chemistry of masked-*o*-benzoquinone (MOB) developed by Liao and Quideau.[21] Using readily available 2-methoxyphenols, with an oxidative dearomatization using hypervalent iodine reagent ($PhI(OAc)_2$) in MeOH, MOBs were formed for the subsequent D-A reaction. We selected three dienophiles: *N*-phenylmaleimide (**3**) for its high reactivity allowing for the generation of a wide variety of D-A adducts, and 2,2-dimethylcyclopent-4-ene-1,3-dione (**4**) and cyclopentadiene (**5**) for their all-carbon ring structures that resemble the five-membered ring in marasmane. The results of the D-A reaction of MOB with **3** are shown in Table 1.

As shown in Table 1, yields of D-A reaction of MOBs **2a–2u** with **3** range from 25% to 92%. It should be noted that, because of the rapid self-dimerization of some MOBs, the generation of **6a** and **6d** (entries 1 and 4, Table 1) were carried out by the cycloaddition using the dimer of the corresponding MOB and dienophile, **3**, in a retro-D-A/D-A reaction sequence.[22] In most examples, the product bicyclo[2.2.2]octenones (**6**) were isolated in moderate yield. To further expand the diversity of functionality in our photorearrangement precursors, we hydrolyzed **6g** and **6h** to form **6v** and **6w**. The aldehyde moieties

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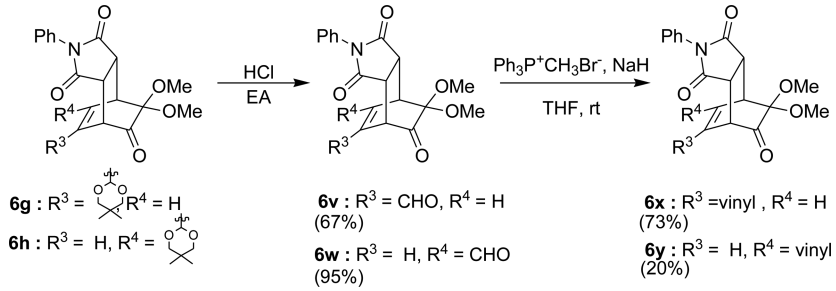
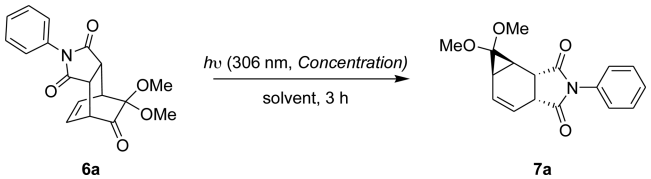
Scheme 2. Syntheses of 6v, 6w, 6x, and 6y



were found to be important for the bioactivities of isovelleral and its analogous natural products.[5a] Thus, we wanted to inspect the necessity of aldehyde protection during the photorearrangement. To examine the compatibility of conjugate extension at olefinic position 6 in the photolysis, we also synthesized vinylated **6x** and **6y** from **6v** and **6w** by Wittig reaction (Scheme 2). This wide variety of substituents on the bicyclo[2.2.2]-core structure is useful for later examination of substitution effects on the photochemical reaction.

We next examined the photoinduced rearrangement of **6**. As shown in Table 2, parent compound **6a** was selected as the initial substrate. We were pleased to find that, using benzene or acetonitrile as solvent, compound **6a** was transformed into the desired **7a** as the sole detectable product after 3 h irradiation with a broad-band UV light centered at 306 nm. Product from the competing oxa-di-π-methane rearrangement was not observed. In addition, we were not able to detect the product from 1,3-acyl migration of **6a**, neither at partial conversion nor upon total consumption of starting material. This efficient decarbonylation process could be explained by the dimethyl ketal group adjacent to the carbonyl group: the decarbonylation of biradical-I (resulting from Norrish type I cleavage) would be favored due to formation of the more stable dimethoxy radical terminus of biradical-II, thus facilitating the sequential extrusion of CO and recombination of the biradical species to form product **7a** (Scheme 3). As an optimized condition for the irradiation of other substrates, acetonitrile was selected as solvent, with a concentration of 1 mg/mL (selected for economical reasons, although 0.5 mg/mL resulted in slightly higher yields).

Table 2. Optimization of Photoinduced Decarbonylative 1,3-Migration of 6a



entry	solvent	concentration (mg/mL)	isolated yield (%)
1	acetone	1	26
2	benzene	1	85
3	methanol	1	83
4	ACN	1	85
5	ACN	0.5	89
6	ACN	2	78
7	ACN	3	76

We then applied the optimized conditions for the photolysis of **6a**–**y**. The result of cases where decarbonylated 1,3-migrated products **7** were successfully obtained are shown in Table 3. The structures of photoreaction products **7** were established by ^{1}H, ^{13}C, DEPT NMR, and HRMS. As shown in Figure 2, the stereochemistry of photoproduct **7** was confirmed by X-ray crystallography and NOE experiments, using compound **7d** as a representative example. As desired, the five-membered ring from phthalimide is *cis*-fused to the cyclohexene, and is *trans* to the neighboring cyclopropane ring. In all cases, no product from 1,3-acyl migration without decarbonylation was found. Substrates **6** with alkyl groups at olefinic and bridgehead positions resulted in 69–99% isolated yield of the corresponding PIDM product **7** (entries 1–4, 14, and 15, Table 3). It should be noted that the *tert*-butyl group shows no retardation of the rearrangement, even in the generation of **7u** (entry 15, Table 3), in which three tetrasubstituted carbon centers (*t*-Bu, and two of the carbons on the cyclopropane ring) were formed in close proximity. Starting materials with six-membered ring

Scheme 3. Proposed Reaction Pathway for the Generation of 7a from 6a

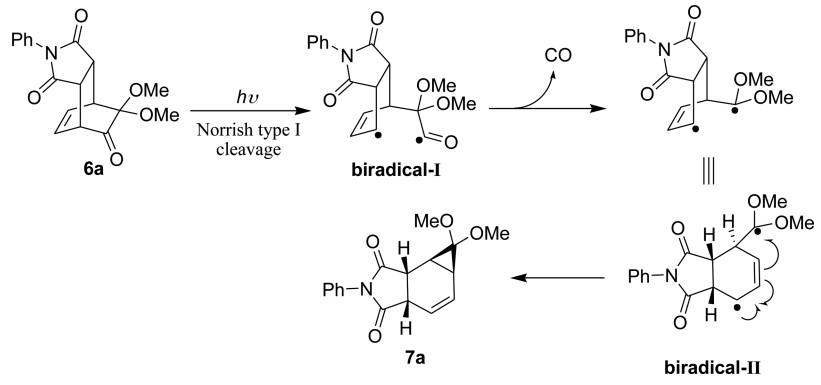


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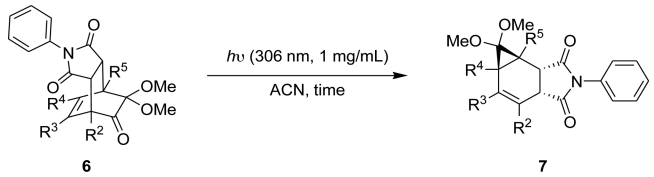
Table 3. Photoinduced Decarbonylative 1,3-Migration of 6



6 7

Entry	Substituents on **6** and **7** R^2	R^3	R^4	R^5	Product	Time (hr)	Isolated Yield (%)
1	H	H	CH_3	H	**7b**	5	90
2	CH_3	H	H	H	**7c**	3	77
3	H	CH_3	H	H	**7d**	3	69
4	H	H	H	CH_3	**7e**	3	92
5		H	H	H	**7f**	5	52
6	H		H	H	**7g**	5	75
7	H	H		H	**7h**	5	90
8	H	CO_2Me	H	H	**7i**	3	69
9	OMe	H	H	H	**7m**	3	86
10	H	H	H	OMe	**7n**	3	90
11	H	H	TMS	H	**7p**	3	99
12	H	H	allyl	H	**7q**	3	90
13	OMe	H		H	**7r**	3	49
14	H	tBu	H	H	**7t**	3	87
15	H	H	tBu	H	**7u**	3	85
16	H	CHO	H	H	**7v**	4	86
17	H	vinyl	H	H	**7x**	3	33
18	H	H	vinyl	H	**7y**	4	87

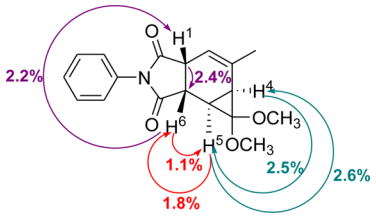


Figure 2. NOE correlations of **7d**.

acetals at R^2, R^3, or R^4 showed moderate yields of 75−90% in the photoreaction. (entries 5−7, Table 3). Substrate **6** with a methoxy group installed at the bridgehead positions gave the corresponding products in high yield (entries 9 and 10, Table 3), whereas **7r** was isolated in 49% yield. The PIDM products with trimethylsilyl, allyl, or vinyl substituents at R^4 were also isolated in 87−99% yield from their photoprecursors. Substrates with electron-withdrawing CO_2Me or formyl groups at R^3 showed moderate reactivity (entries 8 and 16, Table 3); however, product **7x** with a vinyl group at the same position was isolated in only 33%.

During the photolysis of bicyclooctenones **6**, examples of incompatibility of the substitution pattern on the starting compound to the desired PIDM were also found. In cases where an electron-withdrawing group (EWG) is installed at the R^4 position, either the oxa-di-π-methane rearrangement is the preferred photoreaction pathway or complex mixtures were produced. As shown in Scheme 4, acetyl and formyl groups at R^4 (**6l** and **6w**) lead to the formation of ODPM products (**8l** and **8w**, respectively) in optimized conditions for the desired PIDM reaction. When R^4 = CO_2Me, or CN (**6j**, **6k**, and **6o**), or is a conjugated elongation of an ester (**6s**), inseparable mixtures were found during the photolysis. This observation is in accordance with a previous report, where EWG at R^4 governed the photoreaction pathway and yielded primarily ODPM products.[17b]

As the intended PIDM reaction was successful for a wide variety of bicyclo[2.2.2]octenones **6**, we next investigated examples where the embedded five-membered ring is

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Scheme 4. Photolysis of 6j–l, 6o, 6s, and 6w

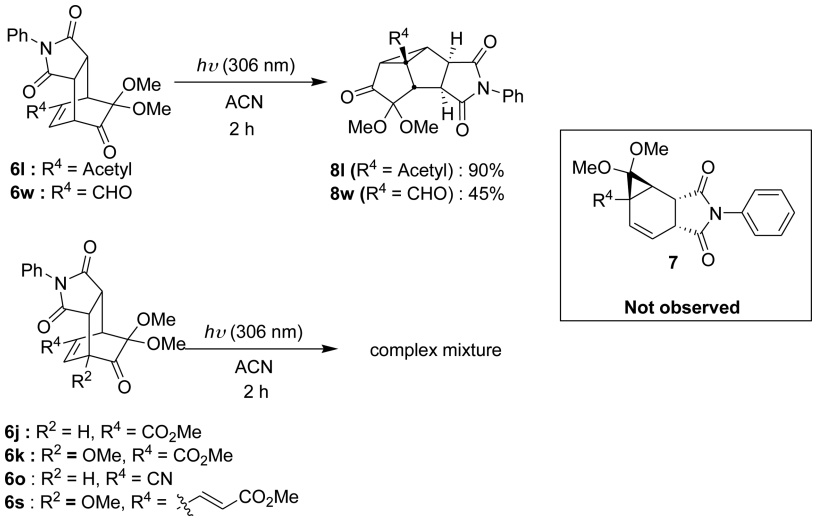
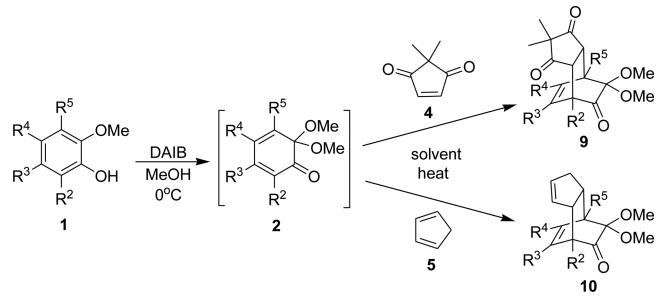


Table 4. Diels–Alder Reactions of MOBs with 4 and 5



Entry	Diels-Alder Product R^2	R^3	R^4	R^5	Dienophile	Product	Yield[a] (%)
1	H	H	H	H	**4**	**9a**	51[b]
2	H	H	CH_3	H	**4**	**9b**	23[a]
3	CH_3	H	H	H	**4**	**9c**	75[b]
4	H	CH_3	H	H	**4**	**9d**	75[b]
5	H	H	H	CH_3	**4**	**9e**	42[b]
6		H	H	H	**4**	**9f**	15[b]
7	H		H	H	**4**	**9g**	0[b]
8	H	H		H	**4**	**9h**	62[a]
9	H	H	H	OMe	**4**	**9i**	74[b]
10	H		H	H	**5**	**10a**	53[b]
11	H	H		H	**5**	**10b**	75[a]

[a]Diels–Alder reaction carried out in refluxing toluene. [b]Reaction done by using dimer of MOB in retro-Diels–Alder reaction at 220 °C in mesitylene.

constructed with an all-carbon unit, as in the skeleton of marasmane (Figure 1). Substrates **4** (2,2-dimethylcyclopent-4-ene-1,3-dione) and **5** (cyclopentadiene) were selected as dienophiles for the construction of bicyclo[2.2.2]octenones with all-carbon frameworks via Diels–Alders reaction. The geminal dimethyls on **9** or the extra olefin on **10** would provide synthetic handles to facilitate later conversion of the cyclopentane ring to mimic the natural product skeleton if needed.

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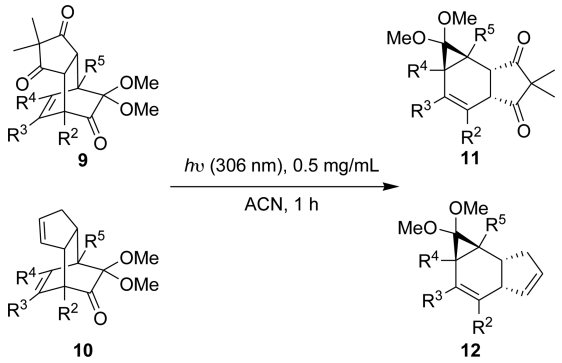
Table 5. Photolysis of Compounds 9 and 10



Entry	Substituents on **6** and **7** R^2	R^3	R^4	R^5	Starting material	Product	Isolated Yield (%)
1	H	H	H	H	**9a**	**11a**	50
1	H	H	CH_3	H	**9b**	**11b**	40
2	CH_3	H	H	H	**9c**	**11c**	40
3	H	CH_3	H	H	**9d**	**11d**	80
4	H	H	H	CH_3	**9e**	**11e**	39
5		H	H	H	**9f**	**11f**	trace
7	H	H		H	**9g**	**11g**	43
10	H	H	H	OMe	**9h**	**11h**	44
11	H		H	H	**10a**	**12a**	61
12	H	H		H	**10b**	**12b**	95

The result of D-A reactions of **4** and **5** with selected MOBs is shown in Table 4. The structures of the Diels–Alder adducts were identified by ^{1}H and ^{13}C NMR, and HRMS.[23] Comparing to **3** in the synthesis of compounds **6**, **4** was found to be less reactive in the cycloaddition, as a retro-Diels–Alder procedure was required to obtain the corresponding cycloadducts **9** (Table 3, entries 1, 3–6, and 9). Isolated yields of bicyclo[2.2.2]octeneones **9** were lower comparing to **6**. In the case of R^3 = acetal, **9g** was not found in the reaction mixture. In this series of photoreaction precursors, our intention was to examine the application of the PIDM strategy in the synthesis of isovelleral derivatives; thus, we focused on examples of acetal (protected formyl group) substituted compounds. In the case of using **5** as dienophile, **10a** and **10b** were obtained in 53% and 75% yields, respectively.

We then applied our optimized PIDM conditions to cycloadducts **9** and **10**, to inspect whether their reactivity is similar to **6**. In preliminary results, products **11** from the photoreaction of **9** were not stable under the conditions of the photolysis process and were isolated in <10% yield. Consequently, we lowered the concentration of the reactant and shortened the reaction time to 1 h to reduce the decomposition of **11** during photolysis. As shown in Table 5, a series of products **11** were obtained from the PIDM reaction of the corresponding starting material **9** in 39–80% yield. Unfortunately, **9f** resulted in a complex mixture with only trace amounts of desired product detected in the ^{1}H NMR of the crude product mixture. In most cases, reaction yields of **11** were found to be lower when comparing to the photoreactions of **6** bearing the same substitution pattern. This phenomenon is presumably due to the β,γ-unsaturated ketone moiety in **11**, which could lead to the aforementioned decomposition of **11** during photolysis. In comparison, **10a** and **10b** underwent the PIDM reaction to give 61% and 95% yields of **12a** and **12b**, respectively, which is comparable to the yields of counterparts **7g** and **7h** in Table 3.

DISCUSSION

From the result of photoinduced decarbonylative 1,3-migration of **6** to form **7** (Table 3), most substitutions at the olefin (R^3 and R^4) and bridgehead (R^2 and R^5) positions show high compatibility during the photoreaction. Only electron-withdrawing groups at R^4 were found to be incompatible with the desired PIDM process and led to ODPM reaction or complex reaction mixtures. A possible explanation of this observed phenomenon could be that, during the photolysis, the conjugated carbonyl group at R^4 served as a sensitizer and enabled a self-sensitized triplet process, and led to ODPM reaction as the major pathway or a complex mixture of products from competing reactions. The extra carbonyl groups on the five-membered ring of bicyclo[2.2.2]octenones **9** were the likely reason for lower yields of **11**. The α-geminal dimethyl ketal facilitated the decarbonylation process by stabilizing the radical terminus of biradical-II (Scheme 3), as in all cases of photolysis of **6**, **9** and **10** 1,3-acyl migration was not found.

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CONCLUSION

In summary, we have disclosed a facile construction of functionalized, marasmane-like skeletons via photochemical rearrangement of bicyclo[2.2.2]octenone precursors, which could easily be obtained by the sequential oxidative dearomatization and cycloaddition of readily available 2-methoxyphenols. Functional group compatibility with respect to the photoreaction precursor was high, and the fused-5,6,3-tricyclic ring structures could be obtained in 33−99% yields. We anticipate that this PIDM strategy may be useful in the syntheses of natural products and analogues of the bioactive isovelleral skeleton.

EXPERIMENTAL SECTION

General Procedure of Diels−Alder Reaction of MOBs Using MeOH as Solvent: (Synthesis of 6c as Example). To a solution of **1c** (0.414 g, 3.00 mmol) and **3** (1.04 g, 6.00 mmol) in 5 mL of MeOH at refluxing temperature was slowly added a solution of diacetoxyiodobenzene (1.16 g, 3.60 mmol) in 10 mL of MeOH over 8 h using a syringe pump. The reaction was stirred at refluxing temperature for 4 h and then cooled to rt. 50 mL of saturated $NaHCO_3$(aq) was added to the reaction mixture and then extracted with CH_2Cl_2. The organic phase was collected and dried with anhydrous $MgSO_4$, and solvent was removed using a rotavap. The crude was then recrystallized in ether to obtain 755 mg of **6c** as a white powder in 74% yield.

General Procedure of Diels−Alder Reaction of MOBs Using Toluene as Solvent: (Synthesis of 6b as Example). To a solution of **1b** (1.39 g, 10.0 mmol) in 25 mL of MeOH at 0 °C was added diacetoxyiodobenzene (3.86 g, 12.0 mmol). The reaction mixture was then warmed to rt and stirred for 30 min. 10 mL of saturated $NaHCO_3$(aq) was then added to the reaction mixture and extracted with CH_2Cl_2. The organic phase was collected and dried with anhydrous $MgSO_4$, and solvent was exchanged to toluene (∼50 mL) using a rotavap. **3** (2.60 g, 15.0 mmol) was added to the toluene solution and stirred at refluxing temperature for 12 h. The crude was then concentrated. **6b** (2.34 g, R_f = 0.11, EA:Hexanes = 1:3) was isolated using column chromatography of the reaction crude in 68% yield as a white solid.

General Procedure of Diels−Alder Reaction of MOBs Using Mesitylene as Solvent: (Synthesis of 6a as Example). A solution of the dimer of MOB **2a** (0.0770 g, 0.250 mmol), **3** (0.433 g, 2.50 mmol), and BHT (5.50 mg, 0.0250 mmol) in 1 mL of degassed (freeze−pump−thaw) mesitylene in a sealed tube was heated to 220 °C for 3 h. Mesitylene was then removed by kugelrohr. **6a** (0.151 g, R_f = 0.10, EA:Hexanes = 1:4) was isolated using column chromatography of the reaction crude in 92% yield as a white solid.

Spectral Data of ***6a****.* White solid, 151 mg, 92% yield, mp 229.7−232.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.37−7.49 (m, 3H), 7.16−7.20 (m, 2H), 6.44 (ddd, J = 1.4, 6.4, 8.1 Hz, 1H), 6.27 (ddd, J = 1.3, 6.2, 8.1 Hz, 1H), 3.82 (ddd, J = 1.6, 3.3, 6.4 Hz, 1H), 3.76 (ddd, J = 1.4, 3.1, 6.2 Hz, 1H), 3.58 (dd, J = 3.3, 8.4 Hz, 1 H), 3.42 (s, 3H), 3.41 (dd, J = 3.0 and 8.4 Hz, 1H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.4 (C), 176.3 (C), 174.9 (C), 133.1 (CH), 131.5 (C), 129.2 (2 × CH), 129.0 (CH), 127.1 (CH), 126.3 (2 × CH), 93.0 (C), 50.4 (CH_3), 50.3 (CH_3), 48.8 (CH), 40.7 (CH), 40.7 (CH), 40.0 (CH). HMRS (ESI-TOF) calcd for $C_{18}H_{17}NO_5Na$ [M + Na]$^+$, 350.0999. Found, 350.1012. IR (neat, cm^{-1}): 2941, 2841, 1778, 1744, 1711, 1597, 1545, 1498, 1456, 1386, 1188, 1140, 1092, 1057, 752, 733, 692.

Spectral Data of ***6b****.* White solid, 2.34 g, 68% yield, mp 155.4−159.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.50−7.37 (m, 3H), 7.17−7.13 (m, 2H), 5.84 (dd, J = 4.4, 1.7 Hz, 1H), 3.67−3.62 (m, 2H), 3.54 (dd, J = 8.4, 3.5 Hz, 1H), 3.40 (s, 6H), 3.37 (d, J = 3.0 Hz, 1H), 1.93 (d, J = 1.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 198.5 (C), 176.2 (C), 175.1 (C), 144.1 (C), 131.5 (C), 129.2 (CH), 128.8 (CH), 126.2 (CH), 118.1 (CH), 93.1 (C), 50.7 (CH_3), 50.1 (CH_3), 48.7 (CH), 45.3 (CH), 41.0 (CH), 39.9 (CH), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{19}H_{19}NO_5Na$ [M + Na]$^+$, 364.1155. Found, 364.1173. IR (neat, cm^{-1}): 2945, 1741, 1713, 1597, 1498, 1441, 1384, 1187, 1086, 1061, 908, 757, 691.

Spectral Data of ***6c****.* White solid, 755 mg, 74% yield, mp 178.1−181.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.36−7.50 (m, 3 H), 7.17−7.21 (m, 2 H), 6.40 (dd, J = 6.5, 8.2 Hz, 1H), 5.95 (ddd, J = 0.7, 1.5, 8.2 Hz, 1H), 3.79 (ddd, J = 1.6, 3.3, 6.5 Hz, 1H), 3.60 (dd, J = 3.2, 8.4 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H), 3.01 (dd, J = 0.6, 8.4 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ):200.1 (C), 176.2 (C), 174.2 (C), 132.6 (CH), 131.5 (C), 132.0 (CH), 129.1 (2 × CH), 128.8 (CH), 126.3 (2 × CH), 92.6 (C), 51.0 (C), 50.2 (CH_3), 50.1 (CH_3), 44.6 (CH), 41.4 (CH), 40.0 (CH), 14.7 (CH_3); HMRS (ESI-TOF) calcd for $C_{19}H_{20}NO_5$ [M + H]$^+$, 342.1336. Found, 342.1342. IR (neat, cm^{-1}): 2974, 2943, 2834, 1779, 1735, 1712, 1594, 1497, 1455, 1385, 1282, 1225, 1186, 1155, 1037, 752, 731, 692.

Spectral Data of ***6d****.* White solid, 148 mg, 87% yield, mp 113.3−114.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.37−7.50 (m, 3 H), 7.13−7.18 (m, 2 H), 6.03 (dt, J = 1.7 and 6.5 Hz, 1H), 3.71 (dd, J = 3.2, 6.5 Hz, 1H), 3.58 (dd, J = 1.7, 3.1 Hz, 1H), 3.57 (dd, J = 3.3, 8.4 Hz, 1H), 3.42 (dd, J = 3.1, 8.2 Hz, 1H), 3.40 (s, 3H), 3.36 (s, 3*H*), 1.88 (d, J = 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.2 (C), 176.5 (C), 174.9 (C), 137.2 (C), 131.5 (C), 129.2 (2 × CH), 128.9 (CH), 126.1 (2 × CH), 124.5 (CH), 93.2 (C), 53.8 (CH), 50.3 (CH_3), 50.0 (CH_3), 40.6 (CH), 40.5 (CH), 40.4 (CH), 20.7 (CH_3); HMRS (ESI-TOF) calcd for $C_{19}H_{20}NO_5$ [M + H]$^+$, 342.1336. Found, 342.1329. IR (neat, cm^{-1}): 2971, 2935, 2835, 1743, 1712, 1597, 1497, 1384, 1190, 1138, 1095, 1059, 968, 753, 685.

Spectral Data of ***6e****.* White solid, 699 mg, 68% yield, mp 174.6−176.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.36−7.48 (m, 3 H), 7.16−7.19 (m, 2 H), 6.21 (dd, J = 1.7, 8.2 Hz, 1H), 6.17 (dd, J = 5.9, 8.2 Hz, 1H), 3.76 (ddd, J = 1.7, 2.5, 5.9 Hz, 1H), 3.46 (d, J = 8.2 Hz, 1H), 3.44 (s, 3H), 3.42 (dd, J = 2.5, 8.3 Hz, 1H), 3.33 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.0 (C), 175.8 (C), 174.8 (C), 140.7 (CH), 131.5 (C), 129.0 (2 × CH), 128.7 (CH), 126.3 (2 × CH), 124.1 (CH), 94.6 (C), 54.7 (CH), 51.9 (CH_3), 49.0 (CH_3), 48.9 (C), 45.0 (CH), 41.5 (CH), 14.8 (CH_3); HMRS (ESI-TOF) calcd for $C_{19}H_{20}NO_5$ [M + H]$^+$, 342.1336. Found, 342.1351. IR (neat, cm^{-1}): 2988, 2945, 2837, 1774, 1736, 1711, 1596, 1497, 1457, 1383, 1288, 1218, 1186, 1103, 1000, 898, 799, 751, 734, 692, 620.

Spectral Data of ***6f****.* Yellowish solid, 317 mg, 72% yield, mp 200.8−203.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.49−7.36 (m, 3H), 7.20−7.16 (m, 2H), 6.42 (dd, J = 8.3, 6.4 Hz, 1H), 6.20 (dd, J = 8.3, 1.3 Hz, 1H), 5.17 (s, 1H), 3.79−3.72 (m, 2H), 3.70 (dd, J = 10.9, 2.7 Hz, 1H), 3.68−3.65 (m, 1H), 3.58 (dd, J = 8.6, 3.3 Hz, 1H), 3.6−3.5 (m, 1H), 3.49−3.44 (m, 1H), 3.45 (s, 3H), 3.34 (s 3H), 1.42 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 195.0 (C), 176.2 (C), 173.8 (C), 131.5 (CH), 129.1 (CH), 128.8 (CH), 126.4 (CH), 99.6 (CH), 92.6 (C), 78.0 (CH_3), 77.6 (CH_3), 56.0 (C), 50.3 (CH_3), 50.2 (CH_3), 41.2 (CH), 40.7 (CH), 40.3 (CH), 30.6 (C), 22.9 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) calcd for $C_{24}H_{27}NO_7Na$ [M + Na]$^+$, 464.1680. Found, 464.1701. IR (neat, cm^{-1}): 2952, 2850, 1750, 1714, 1498, 1385, 1190, 1108, 1042, 753, 732, 691.

Spectral Data of ***6g****.* White solid, 932 mg, 70% yield, mp 132.1−133.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.45−7.34 (m, 3H), 7.25−7.21 (m, 2H), 6.45−6.40 (d, J = 6.6 Hz, 1H), 4.80 (s, 1H), 3.95 (dd, J = 2.7, 1.8 Hz, 1H), 3.84 (dd, J = 3.7, 6.7 Hz, 1H), 3.67−3.54 (m, 3H), 3.45 (d, J = 3.3 Hz, 1H), 3.42 (d, J = 3.4 Hz, 1H), 3.41 (s, 3H), 3.38 (d, J = 2.9 Hz, 1H), 3.36 (s, 3H), 1.16 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 197.8 (C), 176.2 (C), 174.0 (C), 136.9 (C), 131.7 (C), 128.9 (CH), 128.6 (CH), 128.3 (CH), 126.5 (CH), 98.4 (CH), 93.0 (C), 77.1 (CH_2), 76.9 (CH_2), 50.3 (CH_3), 48.8 (CH), 40.8 (CH), 40.4 (CH), 39.9 (CH), 30.1 (C), 22.9 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) calcd for $C_{24}H_{27}NO_7Na$ [M + Na]$^+$, 464.1679. Found, 464.1700. IR (neat, cm^{-1}): 2954, 2853, 1746, 1715, 1598, 1499, 1456, 1385, 1190, 1136, 1098, 1057, 1030, 987, 751, 692.

Spectral Data of ***6h****.* White solid, 976 mg, 72% yield, mp 222.7−225.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.46−7.34 (m, 3H), 7.25−7.20 (m, 2H), 6.29 (d, J = 6.4 Hz, 1H), 4.90 (d, J = 1.0 Hz, 1H), 3.97 (dd, J = 3.0, 2.1 Hz, 1H), 3.78 (dd, J = 6.5, 3.2 Hz, 1H), 3.67 (dd, J = 11.1, 2.7 Hz, 1H), 3.63 (m, 1H), 3.58 (dd, J = 8.4, 3.1 Hz, 1H),

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3.50 (s, 1H), 3.48 (s, 1H), 3.43−3.39 (m, 1H), 3.41 (s, 3H), 3.37 (s, 3H), 1.17 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 198.6 (C), 175.4 (C), 174.9 (C), 143.2 (C), 131.8 (C), 129.0 (CH), 128.7 (CH), 126.6 (CH), 122.5 (CH), 98.8 (CH), 93.1 (C), 77.3 (CH_2), 77.0 (CH_2), 50.3 (CH_3), 50.2 (CH_3), 48.2 (CH), 41.4 (CH), 41.1 (CH), 39.9 (CH), 30.1 (C), 22.9 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{24}H_{27}NO_7Na$ $[M + Na]^+$, 464.1680. Found, 464.1705. IR (neat, cm^{-1}): 2951, 2851, 1741, 1716, 1499, 1386, 1191, 1103, 1029, 751.

Spectral Data of ***6i***. White solid, 1690 mg, 88% yield, mp 195.3−201.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.36−7.47 (m, 3 H), 7.34 (dd, *J* = 1.7, 6.7 Hz, 1H), 7.07−7.12 (m, 2 H), 4.35 (dd, *J* = 1.8, 3.0 Hz, 1H), 4.00 (dd, *J* = 3.3, 6.8 Hz, 1H), 3.60 (dd, *J* = 3.2, 8.5 Hz, 1H), 3.49 (dd, *J* = 3.1, 8.5 Hz, 1H), 3.44 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 197.1 (C), 175.4 (C), 173.7 (C), 162.6 (C), 140.9 (CH), 131.2 (C), 130.8 (C), 129.1 (2 × CH), 128.8 (CH), 126.1 (2 × CH), 92.3 (C), 52.4 (CH_3), 50.4 (CH_3), 50.1 (CH_3), 48.0 (CH), 41.4 (CH), 40.5 (CH), 39.5 (CH); HMRS (ESI-TOF) calcd for $C_{20}H_{20}NO_7$ $[M + H]^+$, 386.1234. Found, 386.1248. IR (neat, cm^{-1}): 2948, 2837, 1746, 1717, 1633, 1601, 1499, 1438, 1385, 1273, 1225, 1188, 1133, 1098, 1059, 995, 794, 748, 692.

Spectral Data of ***6j***. White solid, 786 mg, 74% yield, mp 222.3−227.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.50−7.33 (m, 3H), 7.18 (dd, *J* = 6.4, 2.1 Hz, 1H), 7.13−7.09 (m, 2H), 4.44 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.94 (dd, *J* = 6.5, 3.0 Hz, 1H), 3.01 (s, 3H), 3.69 (dd, *J* = 8.5, 3.5, Hz, 1H), 3.49 (dd, *J* = 8.4, 2.9, Hz, 1H), 3.44 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 197.1 (C), 175.2 (C), 174.1 (C), 163.0 (C), 136.4 (C), 135.0 (CH), 131.3 (C), 129.2 (CH), 129.0 (CH), 126.2 (CH), 92.3 (C), 52.5 (CH_3), 50.5 (CH_3), 49.6 (CH_3), 40.7 (CH), 40.6 (CH), 39.9 (CH); HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_7Na$ $[M + Na]^+$, 408.1054. Found, 408.1069. IR (neat, cm^{-1}): 2951, 2840, 1714, 1498, 1438, 1384, 1253, 1189, 1129, 1081, 747, 693.

Spectral Data of ***6k***. White solid, 1000 mg, 80% yield, mp 187.7−193.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.47−7.35 (m, 3H), 7.16−7.09 (m, 3H), 4.39 (dd, *J* = 3.4, 2.2, Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.72 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.62 (d, *J* = 8.6 Hz, 1H), 3.45 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): . 196.4 (C), 174.7 (C), 171.4 (C), 162.5 (C), 137.6 (CH), 134.0 (C), 131.2 (C), 129.0 (CH), 128.8 (CH), 126.1 (CH), 92.1 (C), 84.8 (C), 54.1 (CH_3), 52.5 (CH_3), 50.3 (CH_3 × 2), 41.0 (CH), 40.7 (CH), 39.2 (CH); HRMS (ESI-TOF) calcd for $C_{21}H_{21}NO_8Na$ $[M + Na]^+$, 438.1159. Found, 438.1173. IR (neat, cm^{-1}): 2951, 2841, 1715, 1672, 1598, 1499, 1436, 1386, 1246, 1194, 1123, 1092, 1030, 754, 693.

Spectral Data of ***6l***. White solid, 610 mg, 55% yield, mp 215.2−221.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.5−7.3 (m, 3H), 7.14−7.07 (m, 2H), 7.05 (dd, *J* = 6.6, 1.7 Hz, 1H), 4.59−4.54 (m, 1H), 3.94 (dd, *J* = 6.5, 3.0 Hz, 1H), 3.68 (dd, *J* = 8.5, 3.3 Hz, 1H), 3.51 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.44 (s, 3H), 3.33 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 197.4 (C), 192.8 (C), 175.0 (C), 174.2 (C), 144.3 (C), 134.1 (CH), 131.2 (C), 129.1 (CH), 129.0 (CH), 125.9 (CH), 92.4 (C), 50.6 (CH_3), 49.6 (CH), 40.8 (CH), 39.6 (CH), 38.9 (CH), 24.9 (CH_3); HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_6Na$ $[M + Na]^+$, 392.1104. Found, 392.1117. IR (neat, cm^{-1}): 2950, 1743, 1712, 1598, 1499, 1443, 1386, 1198, 1126, 1089, 758, 693.

Spectral Data of ***6m***. White solid, 661 mg, 62% yield, mp 177.1−184.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.49 (m, 3 H), 7.18−7.23 (m, 2 H), 6.34 (dd, *J* = 6.6, 8.6 Hz, 1H), 6.21 (ddd, *J* = 0.7, 1.6, 8.6 Hz, 1H), 3.73−3.79 (m, 4H), 3.57−3.62 (m, 2H), 3.42 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 197.5 (C), 175.6 (C), 172.1 (C), 131.4 (C), 130.8 (CH), 130.3 (CH), 129.0 (2 × CH), 128.7 (CH), 126.2 (2 × CH), 92.8 (C), 83.9 (C), 53.8 (CH_3), 50.1 (CH_3), 50.1 (CH_3), 40.9 (CH), 40.7 (CH), 39.4 (CH); HMRS (ESI-TOF) calcd for $C_{19}H_{20}NO_6$ $[M + H]^+$, 358.1285. Found, 358.1272. IR (neat, cm^{-1}): 2977, 2946, 2841, 1754, 1715, 1597, 1496, 1457, 1386, 1224, 1188, 1139, 1066, 1051, 1021, 998, 862, 751, 729, 692.

Spectral Data of ***6n***. White solid, 945 mg, 88% yield, mp 133.1−136.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.34−7.48 (m, 3 H), 7.18−7.22 (m, 2 H), 6.48 (dt, *J* = 1.0 and 8.6 Hz, 1H), 6.13 (dd, *J* = 6.4 and 8.7 Hz, 1H), 4.03 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 3.77 (ddd, *J* = 1.3, 2.8, and 6.4 Hz, 1H), 3.52 (s, 3H), 3.51 (s, 3H), 3.37 (dd, *J* = 2.7, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 195.5 (C), 174.2 (C), 173.6 (C), 137.3 (CH), 131 (C), 128.9 (2 × CH), 128.6 (CH), 126.2 (2 × CH), 122.2 (CH), 94.9 (C), 83.4 (C), 54.3 (CH_3), 52.7 (CH_3), 51.4 (CH_3), 47.8 (CH), 41.2 (CH), 39.6 (CH); HMRS (ESI-TOF) calcd for $C_{19}H_{19}NO_6Na$ $[M + Na]^+$, 380.1105. Found, 380.1123. IR (neat, cm^{-1}): 2948, 2840, 1779, 1743, 1714, 1597, 1498, 1456, 1385, 1189, 1138, 1115, 1069, 1022, 989, 798, 748, 729, 694, 622.

Spectral Data of ***6o***. White solid, 895 mg, 25% yield, mp 244.3−249.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.40−7.53 (m, 3 H), 7.17−7.22 (m, 2 H), 7.03 (dd, *J* = 1.8, 6.5 Hz, 1H), 4.02 (dd, *J* = 2.1, 3.0 Hz, 1H), 3.96 (dd, *J* = 3.1, 6.5 Hz, 1H), 3.66 (dd, *J* = 3.2, 8.6 Hz, 1H), 3.52 (dd, *J* = 3.0, 8.6 Hz, 1H), 3.46 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 195.5 (C), 174.3 (C), 173.3 (C), 141.3 (CH), 131.0 (C), 129.4 (2 × CH), 129.3 (CH), 126.1 (2 × CH), 117.4 (C), 114.8 (C), 92.0 (C), 51.0 (CH_3), 50.5 (CH_3), 49.6 (CH), 43.9 (CH), 40.8 (CH), 39.3 (CH); HMRS (ESI-TOF) calcd for $C_{19}H_{17}N_2O_5$ $[M + H]^+$, 353.1132. Found, 353.1138. IR (neat, cm^{-1}): 2949, 2841, 1754, 1715, 1596, 1496, 1456, 1384, 1291, 1187, 1157, 1134, 1060, 1032, 980, 927, 754, 691, 589.

Spectral Data of ***6p***. White solid, 883 mg, 74% yield, mp 201.2−203.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3 H), 7.13−7.17 (m, 2 H), 6.48 (dd, *J* = 1.0, 6.0 Hz, 1H), 3.88 (dd, *J* = 1.5, 3.3 Hz, 1H), 3.78 (dd, *J* = 3.0, 6.0 Hz, 1H), 3.53 (dd, *J* = 3.4, 8.6 Hz, 1H), 3.40 (ddd, *J* = 0.5, 3.0, 8.4 Hz, 1H), 3.40 (s, 3H), 3.36 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.9 (C), 176.2 (C), 175.1 (C), 150.5 (C), 133.9 (CH), 131.6 (C), 129.2 (2 × CH), 128.8 (CH), 126.2 (2 × CH), 93.1 (C), 50.8 (CH_3), 49.9 (CH_3), 49.7 (CH), 42.8 (CH), 40.6 (CH), 39.7 (CH), −2.0 (3 × CH_3); HMRS (ESI-TOF) calcd for $C_{21}H_{26}NO_5Si$ $[M + H]^+$, 400.1575. Found, 400.1597. IR (neat, cm^{-1}): 2953, 2834, 1736, 1711, 1597, 1497, 1457, 1385, 1290, 1250, 1911, 1137, 1100, 1059, 972, 834, 792, 751, 691, 622.

Spectral Data of ***6q***. White solid, 883 mg, 84% yield, mp 144.7−146.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.36−7.50 (m, 3 H), 7.11−7.18 (m, 2 H), 5.84 (dd, *J* = 1.8, 6.3 Hz, 1H), 5.74 (qt, *J* = 7.1, 10.2 Hz, 1H), 5.18−5.08 (m, 2H), 3.70 (dd, *J* = 2.9, 6.4 Hz, 1H), 3.65 (dd, *J* = 2.1, 3.3 Hz, 1H), 3.55 (dd, *J* = 3.4, 8.3 Hz, 1H), 3.36−3.45 (m, 7H), 2.98 (dd, *J* = 7.4, 17.0 Hz, 1H), 2.90 (dd, *J* = 6.7, 17.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.3 (C), 176.1 (C), 175.0 (C), 146.3 (C), 132.8 (CH), 131.5 (C), 129.1 (2 × CH), 128.8 (CH), 126.2 (2 × CH), 118.3 (CH_2), 117.9 (CH), 93.0 (C), 50.6 (CH_3), 50.1 (CH_3), 48.7 (CH), 44.4 (CH), 41.0 (CH), 39.9 (CH), 39.8 (CH_2); HMRS (ESI-TOF) calcd for $C_{21}H_{21}NO_5Na$ $[M + Na]^+$, 390.1312. Found, 390.1330. IR (neat, cm^{-1}): 2946, 2837, 1741, 1713, 1597, 1498, 1455, 1384, 1290, 1229, 1187, 1145, 1062, 1032, 981, 920, 750, 691.

Spectral Data of ***6r***. White solid, 976 mg, 72% yield, mp 156.7−165.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.47−7.31 (s, 3H), 7.25−7.22 (s, 2H), 6.30 (s, 1H), 4.89 (s, 1H), 3.92 (m, 1H), 3.71 (s, 3H), 3.70−3.58 (m, 3H), 3.57−3.52 (m, 1H), 3.52−3.46 (m, 2H), 3.42 (3H), 3.38 (3H), 1.16 (3H), 0.73 (3H). ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 197.7 (C), 174.8 (C), 172.2 (C), 141 (C),131.8 (C), 128.9 (CH), 128.7 (CH), 126.6 (CH), 125.4 (CH), 98.4 (CH), 92.9 (C), 84.1 (C), 77.3 (CH_2), 77.1 (CH_2), 54.1 (CH_3), 50.3 (CH_3), 50.3 (CH_3), 42.2 (CH), 40.1 (CH), 40.0 (CH), 30.1 (C), 22.9 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{25}H_{29}NO_8Na$ $[M + Na]^+$, 494.1785. Found, 494.1802. IR (neat, cm^{-1}): 2923, 2851, 1754, 1717, 1500, 1465, 1385, 1188, 1112, 1091, 1030.

Spectral Data of ***6s***. White solid, 328 mg, 37% yield, mp 135.0−138.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.47 (m, 3 H), 7.28 (d, *J* = 15.8 Hz, 1H), 7.08−7.14 (m, 2 H), 6.36 (d, *J* = 1.3 Hz, 1H), 6.21 (d, *J* = 15.8 Hz, 1H), 4.03 (t, *J* = 2.5 Hz, 1H), 3.65−3.72 (m, 2H), 3.45 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 196.4 (C), 174.8 (C), 171.7 (C), 166.6 (C), 139.4 (CH), 139.1 (C), 132.3 (CH), 131.2 (C), 129.2 (2 × CH), 129.0 (CH), 126.2 (2 × CH), 121.3 (CH), 92.8 (C), 84.7 (C), 54.1 (CH_3), 51.9 (CH_3), 51.1

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(CH_3), 50.3 (CH_3), 41.5 (CH), 40.5 (CH), 39.7 (CH); HMRS (ESI-TOF) calcd for $C_{23}H_{24}NO_8$ $[M + H]^+$, 442.1496. Found, 442.1504. IR (neat, cm^{-1}): 2948, 2834, 1755, 1715, 1634, 1594, 1498, 1436, 1384, 1310, 1283, 1229, 1191, 1142, 1049, 1013, 868, 751, 694.

Spectral Data of ***6t***. White solid, 588 mg, 51% yield, mp 204.8−208.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.36−7.49 (m, 3 H), 7.14−7.19 (m, 2 H), 6.07 (dd, J = 1.9, 6.7 Hz, 1H), 3.86 (dd, J = 1.9, 2.8 Hz, 1H), 3.75 (dd, J = 3.5, 6.7 Hz, 1H), 3.56 (dd, J = 3.5, 8.6 Hz, 1H), 3.40 (s, 3H), 3.38 (dd, J = 2.9, 8.6 Hz, 1H), 3.36 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 198.6 (C), 176.6 (C), 174.8 (C), 148.8 (C), 131.6 (C), 129.2 (2 × CH), 128.8 (CH), 126.2 (2 × CH), 121.6 (CH), 93.3 (C), 50.3 (CH_3), 50.2 (CH_3), 50.0 (CH), 40.6 (CH), 40.4 (CH), 39.4 (CH), 34.8 (C), 28.0 (CH_3); HMRS (ESI-TOF) calcd for $C_{22}H_{25}NO_5Na$ $[M + Na]^+$, 406.1625. Found, 406.1635. IR (neat, cm^{-1}): 2965, 1739, 1713, 1594, 1498, 1465, 1384, 1227, 1186, 1136, 1099, 1057, 980, 789, 779, 751, 692, 626.

Spectral Data of ***6u***. White solid, 616 mg, 60% yield, mp 205.3−208.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3 H), 7.14−7.21 (m, 2 H), 5.94 (dd, J = 2.0, 6.6 Hz, 1H), 3.86 (t, J = 2.5 Hz, 1H), 3.73 (dd, J = 3.0, 6.6 Hz, 1H), 3.52 (dd, J = 3.1, 8.6 Hz, 1H), 3.41 (s, 3H), 3.35−3.40 (m, 4H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 199.5 (C), 176.1 (C), 175.2 (C), 155.7 (C), 131.5 (C), 129.2 (2 × CH), 128.8 (CH), 126.2 (2 × CH), 116.1 (CH), 93.5 (C), 51.1 (CH_3), 49.7 (CH_3), 48.0 (CH), 41.6 (CH), 41.1 (CH), 40.1 (CH), 34.7 (C), 29.2 (3 × CH_3); HMRS (ESI-TOF) calcd for $C_{22}H_{25}NO_5Na$ $[M + Na]^+$, 406.1625. Found, 406.1643. IR (neat, cm^{-1}): 2966, 1740, 1713, 1593, 1499, 1458, 1383, 1292, 1190, 1135, 1106, 1052, 1030, 980, 924, 751, 712, 691.

Spectral Data of ***6v***. White solid, 27 mg, 67% yield, mp 202.5−211.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 9.58 (s, 1H), 7.46−7.35 (m, 3H), 7.26 (dd, J = 1.7, 6.6 Hz, 1H), 7.10−7.06 (m, 2H), 4.38 (dd, J = 2.9, 1.7 Hz, 1H), 4.10 (dd, J = 6.6, 3.3 Hz, 1H), 3.64 (dd, J = 8.5, 3.3 Hz, 1H), 3.49 (dd, J = 8.5, 3.0 Hz, 1H), 3.45 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 196.7 (C), 186.4 (CH), 175.2 (C), 173.2 (C), 147.1 (CH), 139.3 (C), 131.0 (C), 129.2 (CH), 129.0 (CH), 125.9 (CH), 92.8 (C), 50.8 (CH_3), 50.2 (CH_3), 45.3 (CH), 41.9 (CH), 40.3 (CH), 39.9 (CH); HRMS (ESI-TOF) calcd for $C_{19}H_{17}NO_6Na$ $[M + Na]^+$, 378.0948. Found, 378.0961. IR (neat, cm^{-1}): 2952, 2927, 2655, 1737, 1713, 1694, 1598, 1496, 1455, 1392, 1276, 1203, 1155, 1062, 998, 965.

Spectral Data of ***6w***. White solid, 77 mg, 95% yield, mp 215.9−220.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 9.60 (s, 1H), 7.48−7.35 (m, 3H), 7.15−7.08 (m, 3H), 4.48 (dd, J = 3.2, 2.0 Hz, 1H), 4.05 (dd, J = 6.4, 3.1 Hz, 1H), 3.70 (dd, J = 8.5, 3.3 Hz, 1H), 3.56 (dd, J = 8.6, 3.1 Hz, 1H), 3.46 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 196.6 (C), 186.8 (CH), 174.7 (C), 173.9 (C), 144.9 (C), 141.4 (CH), 129.2 (CH), 126.0 (CH), 92.4 (C), 50.6 (CH_3), 50.5 (CH_3), 50.0 (CH), 41.0 (CH), 39.3 (CH), 37.7 (CH); HRMS (ESI-TOF) calcd for $C_{19}H_{17}NO_6Na$ $[M + Na]^+$, 378.0948. Found, 378.0953. IR (neat, cm^{-1}): 2918, 2849, 1742, 1711, 1597, 1498, 1438, 1387, 1198, 1124, 1088, 754, 692.

Spectral Data of ***6x***. White solid, 72 mg, 73% yield, mp 135.0−137.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.47−7.35 (m, 3H), 7.12−7.08 (m, 2H), 6.38 (dd, J = 17.3, 10.9 Hz, 1H), 6.21 (d, J = 6.4 Hz, 1H), 5.47 (d, J = 17.5 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 4.10 (dd, J = 2.8, 1.9 Hz, 1H), 3.83 (dd, J = 6.7, 3.4 Hz, 1H), 3.60 (dd, J = 8.3, 3.3 Hz, 1H), 3.47 (dd, J = 8.3, 3.1 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 198.0 (C), 176.2 (C), 174.4 (C), 137.2 (C), 132.1 (CH), 131.4 (C), 129.1 (CH), 128.8 (CH), 127.6 (CH), 126.3 (CH), 117.2 (CH_2), 93.1 (C), 50.3 (CH_3), 48.1 (CH), 41.1 (CH), 40.1 (CH), 40.3 (CH); HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_5Na$ $[M + Na]^+$, 376.1155. Found, 376.1172. IR (neat, cm^{-1}): 2949, 2854, 1741, 1713, 1498, 1457, 1384, 1244, 1189, 1136, 1096, 1058, 986, 921, 751, 692.

Spectral Data of ***6y***. White solid, 10 mg, 20% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.46−7.35 (m, 3H), 7.12−7.07 (m, 2H), 6.38 (dd, J = 10.9, 17.5 Hz, 1H), 6.21 (d, J = 6.2 Hz, 1H), 5.47 (d, J = 17.5 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 4.11−4.08 (m, 1H), 3.83 (dd, J = 6.7, 3.4 Hz, 1H), 3.60 (dd, J = 8.3, 3.4 Hz, 1H), 3.46 (dd, J = 8.3, 3.1 Hz, 1H), 3.42 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 197.8 (C), 175.7 (C), 174.9 (C), 143.2 (C), 133.2 (CH), 131.5 (C), 129.1 (CH), 128.9 (CH), 126.2 (CH), 122.1 (CH), 117.0 (CH_2), 93.1 (C), 50.9 (CH_3), 50.4 (CH_3), 49.1 (CH), 41.7 (CH), 40.2 (CH), 39.8 (CH); HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_5H$ $[M + H]^+$, 354.1336. Found, 354.1349. IR (neat, cm^{-1}): 2923, 2849, 1740, 1712, 1498, 1383, 1189, 1135, 1058, 751, 692.

Spectral Data of ***9a***. White solid, 29 mg, 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 6.29 (ddd, J = 1.3, 6.5, 8.1 Hz, 1H), 6.10 (ddd, J = 1.4, 6.2, 8.1 Hz, 1H), 3.78 (ddd, J = 1.6, 3.3, 6.4 Hz, 1H), 3.73 (ddd, J = 1.3, 3.0, 6.1 Hz, 1H), 3.63 (dd, J = 3.2, 10.4 Hz, 1H), 3.47 (dd, J = 3.0, 10.4 Hz, 1H), 3.39 (s, 3H), 3.32 (s, 3H), 1.15 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 216.3 (C), 214.8 (C), 199.5 (C), 134.2 (CH), 127.9 (CH), 93.2 (C), 55.3 (C), 50.3 (CH_3), 50.1 (CH_3), 48.6 (CH), 46.0 (CH), 45.5 (CH), 40.7 (CH), 22.7 (CH_3), 15.7 (CH_3); HMRS (ESI-TOF) calcd for $C_{15}H_{19}O_5$ $[M + H]^+$, 279.1227. Found, 279.1237. IR (neat, cm^{-1}): 2976, 2943, 2887, 1741, 1722, 1461, 1380, 1309, 1286, 1226, 1208, 1142, 1094, 1060, 1006, 972, 891, 783, 728.

Spectral Data of ***9b***. Yellowish solid, 51 mg, 23% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 5.66 (dt. J = 6.2, 1.6 Hz, 1H), 3.61−3.57 (m, 3H), 3.43−3.38 (m, 1H), 3.37 (s, 3H), 3.35 (s, 3H), 1.79 (d, J = 1.6 Hz, 3H), 1.13 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 216.4 (C), 215.5 (C), 199.6 (C), 145.5 (C), 119.2 (CH), 93.3 (C), 54.9 (C), 50.7 (CH_3), 50.01 (CH_3), 48.5 (CH), 46.6 (CH), 45.6 (CH), 45.5 (CH), 22.4 (CH_3), 22.0 (CH_3), 15.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{16}H_{20}O_5Na$ $[M + Na]^+$, 315.1203. Found, 315.1229. IR (neat, cm^{-1}): 2969, 2929, 1723, 1456, 1138, 1019, 1064, 1040.

Spectral Data of ***9c***. White solid, 44 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 6.27 (dd, J = 6.6, 8.2 Hz, 1H), 5.82 (dd, J = 1.2, 8.2 Hz, 1H), 3.76 (ddd, J = 1.6, 3.2, 6.6 Hz, 1H), 3.62 (dd, J = 3.2, 10.3 Hz, 1H), 3.32 (s, 3H), 3.41 (s, 3H), 3.03 (d, J = 10.3 Hz, 1H), 1.57 (d, J = 1.2 Hz, 3H), 1.12 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 217.1 (C), 214.9 (C), 200.9 (C), 133.5 (CH), 133.3 (CH), 92.8 (C), 54.5 (C), 51.3 (C), 50.2 (CH_3), 50.0 (CH_3), 49.7 (CH), 47.3 (CH), 40.1 (CH), 23.0 (CH_3), 16.2 (CH_3), 15.2 (CH_3); HMRS (ESI-TOF) calcd for $C_{16}H_{20}O_5Na$ $[M + Na]^+$, 315.1203. Found, 315.1218. IR (neat, cm^{-1}): 2976, 2938, 2844, 1736, 1720, 1459, 1380, 1283, 1209, 1145, 1099, 1056, 1038, 721.

Spectral Data of ***9d***. White solid, 44 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 5.87 (dt, J = 1.6, 6.4 Hz, 1H), 3.66 (dd, J = 3.2, 6.5 Hz, 1H), 3.60 (dd, J = 3.2, 10.1 Hz, 1H), 3.54 (dd, J = 1.7, 3.1 Hz, 1H), 3.47 (dd, J = 3.1, 10.1 Hz, 1H), 3.38 (s, 3H), 3.32 (s, 3H), 1.72 (d, J = 1.6 Hz, 3H), 1.13 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 216.8 (C), 215.1 (C), 199.4 (C), 138.2 (C), 125.9 (CH), 93.5 (C), 55.1 (C), 53.7 (CH), 50.2 (CH_3), 50.1 (CH_3), 46.2 (CH), 46.1 (CH), 40.6 (CH), 22.4 (CH_3), 20.9 (CH_3), 15.8 (CH_3); HMRS (ESI-TOF) calcd for $C_{16}H_{20}O_5Na$ $[M + Na]^+$, 315.1203. Found, 315.1215. IR (neat, cm^{-1}): 2972, 2940, 2831, 1763, 1723, 1461, 1444, 1379, 1285, 1235, 1203, 1139, 1097, 1080, 1053, 967, 833.

Spectral Data of ***9e***. White solid, 61 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.10 (d, J = 1.3, 8.2 Hz, 1H), 5.97 (dd, J = 6.4, 8.2 Hz, 1H), 3.72 (ddd, J = 1.4, 2.4, 6.4 Hz, 1H), 3.48 (d, J = 10.2 Hz, 1H), 3.45 (dd, J = 2.4, 10.2 Hz, 1H), 3.41 (s, 3H), 3.27 (s, 3H), 1.66 (s, 3H), 1.12 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 216.5 (C), 215.5 (C), 198.8 (C), 142.3 (CH), 124.6 (CH), 94.8 (C), 55.1 (C), 54.7 (CH_3), 51.8 (CH_3), 50.5 (CH), 49.3 (C), 49.0 (CH), 47.0 (CH), 23.0 (CH_3), 15.9 (CH_3), 15.3 (CH_3); HMRS (ESI-TOF) calcd for $C_{16}H_{20}O_5Na$ $[M + Na]^+$, 315.1203. Found, 315.1215. IR (neat, cm^{-1}): 2978, 2944, 2840, 1764, 1736, 1721, 1460, 1379, 1283, 1202, 1096, 896, 785, 726.

Spectral Data of ***9f***. Yellow solid, 23 mg, 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.27 (dd, J = 8.3, 6.5 Hz, 1H), 6.08 (dd, J = 8.3, 1.5 Hz, 1H), 5.24 (s, 1H), 3.75−3.47 (m, 7H), 3.43 (s, 3H), 3.29 (s, 3H), 1.42 (s, 3H), 1.13 (s, 3H), 0.98 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 216.6 (C), 214.4 (C), 195.8 (C), 132.4 (CH), 129.9 (CH), 100.0 (CH), 92.9 (C), 77.9 (CH_2), 77.7 (CH_2), 56.2 (C), 54.9 (C), 50.3 (CH_3), 50.1 (CH_3), 46.7 (CH), 46.5

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(CH), 40.3 (CH), 30.6 (C), 23.1 (CH_3), 23.0 (CH_3), 21.7 (CH_3), 16.2 (CH_3); HRMS (ESI-TOF) calcd for $C_{21}H_{28}O_7Na$ $[M + Na]^+$, 415.1727. Found, 415.1750. IR (neat, cm^{-1}): 2921, 2850, 1748, 1722, 1463, 1394, 1283, 1215, 1140, 1109, 1040, 755.

Spectral Data of ***9h***. White solid, 51 mg, 65% yield, mp 149.4−150.1 °C. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.17 (d, J = 6.5 Hz, 1H), 4.73 (d, J = 1.2 Hz, 1H), 3.89 (dd, J = 3.0, 2.1 Hz, 1H), 3.76 (dd, J = 6.4, 3.2 Hz, 1H), 3.64−3.57 (m, 3H), 3.46−3.40 (m, 3H), 3.39 (s, 3H), 3.33 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 0.99 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 215.9 (C), 215.6 (C), 199.5 (C), 143.9 (C), 123.4 (CH), 98.7 (CH), 93.3 (C), 77.2 (CH_2), 77.1 (CH_2), 54.4 (C), 50.2 (CH_3), 48.3 (CH), 46.6 (CH), 45.6 (CH), 41.2 (CH), 30.1 (C), 29.6 (C), 22.8 (CH_3), 21.7 (CH_3), 16.2 (CH_3); HRMS (ESI-TOF) calcd for $C_{21}H_{28}O_7Na$ $[M + Na]^+$, 415.1727. Found, 415.1747. IR (neat, cm^{-1}): 2953, 2923, 2851, 1725, 1463, 1137, 1106, 1081, 1061, 1030.

Spectral Data of ***9i***. White solid, 114 mg, 74% yield. ^1H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 6.34 (ddd, J 0.8, 1.3, 8.8 Hz, 1H), 5.95 (dd, J 6.4, 8.7 Hz, 1H), 4.04 (d, J 10.3 Hz, 1H), 3.79 (s, 3H), 3.69 (ddd, J = 1.3, 2.7, 6.4 Hz, 1H), 3.48 (s, 3H), 3.47 (s, 3H), 3.38 (dd, J = 2.7, 10.4 Hz, 1H), 1.15 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 215.0 (C), 213.9 (C), 196.4 (C), 138.9 (CH), 123.0 (CH), 95.2 (C), 83.9 (C), 54.9 (C), 54.4 (CH_3), 52.9 (CH_3), 51.6 (CH_3), 48.0 (CH), 46.5 (CH), 45.2 (CH), 23.1 (CH_3), 16.2 (CH_3); HMRS (ESI-TOF) calcd for $C_{16}H_{21}O_6$ $[M + H]^+$, 309.1333. Found, 309.1336. IR (neat, cm^{-1}): 2977, 2947, 2840, 1766, 1741, 1721, 1459, 1379, 1354, 1278, 1219, 1193, 1167, 1143, 1114, 1082, 987, 779, 720.

Spectral Data of ***10a***. Yellow oil, 280 mg, 53% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.22 (dt, J = 6.8, 0.8 Hz, 1H), 5.63 (dq, J = 5.7, 2.2 Hz, 1H), 5.43−5.39 (m, 1H), 4.78 (d, J = 0.6 Hz, 1H), 3.61−3.55 (m, 2H), 3.42−3.37 (m, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 3.28−3.22 (m, 1H), 3.15 (dd, J = 6.8, 3.0 Hz, 1H), 2.92−2.85 (m, 1H), 2.53 (dddd, J = 17.1, 10.2, 4.0, 1.8 Hz, 1H), 2.04−1.95 (m, 1H), 1.14 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 203.3 (C), 137.7 (C), 132,1 (CH), 130.5 (CH), 126.9 (CH), 99.5 (CH), 94.9 (C), 76.9 (CH_2), 76.8 (CH_2), 51.6 (CH), 50.5 (CH_3), 49.6 (CH_3), 49.3 (CH), 43.4 (CH), 38.3 (CH_2), 33.6 (CH), 30.0 (C), 22.9 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{19}H_{26}O_5Na$ $[M + Na]^+$, 357.1672. Found, 357.1698. IR (neat, cm^{-1}): 2952, 2845, 1736, 1470, 1393, 1137, 1098, 1056, 1025, 986.

Spectral Data of ***10b***. Colorless oil, 251 mg, 75% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.04 (d, J = 6.6 Hz, 1H), 5.71−5.66 (m, 1H), 5.37 (dd, J = 5.5, 2.4 Hz, 1H), 4.91 (d, J = 1.0 Hz, 1H), 3.66 (dd, J = 9.0, 1.9 Hz, 2H), 3.50 (dd, J = 11.0, 5.2 Hz, 2H), 3.40 (t, J = 2.7 Hz, 1H), 3.38 (s, 3H), 3.33 (s, 3H), 3.28−3.22 (m, 1H), 3.17 (dd, J = 6.6, 2.5 Hz, 1H), 2.99−2.90 (m, 1H), 2.51−2.42 (m, 1H), 2.41−2.32 (m, 1H), 1.19 (s, 3H), 0.74 (s. 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 203.2 (C), 141.9 (C), 133.9 (CH), 129.1 (CH), 123.1 (CH), 99.8 (CH), 94.5 (C), 77.3 (CH_2), 77.0 (CH_2), 52.0 (CH), 49.9 (CH_3), 49.2 (CH), 43.4 (CH), 37.4 (CH_2), 33.8 (CH), 30.1 (C), 22.9 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{19}H_{26}O_5Na$ $[M + Na]^+$, 357.1678. Found, 357.1699. IR (neat, cm^{-1}): 2954, 2850, 1735, 1468, 1393, 1230, 1214, 1138, 1104, 1085, 1050, 1030, 990, 969, 838, 700.

General Procedure of the Photoreaction: (Synthesis of 7a as Example). A solution of **6a** (20 mg, 0.061 mmol) in HPLC-grade acetonitrile (20 mL) in a quartz tube was degassed by sonication for 1 h and then was irradiated with a broad band of UV light centered at 306 nm in a Rayonet-type reaction for 3 h for 10 h. The crude was then concentrated. **7a** (16 mg, R_f = 0.2, EA:Hexanes = 1:4) was isolated using column chromatography of the reaction crude in 85% yield as a white solid.

Spectral Data of ***7a***. White solid, 16 mg, 85% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3 H), 7.25−7.29 (m, 2 H), 6.09 (ddd, J = 1.9, 5.7, 10.1 Hz, 1H). 5.70 (ddd, J = 1.0, 2.1, 10.1 Hz, 1H), 3.47 (m, 2H), 3.43 (s, 3H), 3.31 (s, 3H), 2.22 (d, J = 9.6 Hz, 1H), 1.84 (dd, J = 5.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.3 (C), 176.1 (C), 131.8 (C), 129.0 (2 × CH), 128.5 (CH), 126.3 (2 × CH), 123.4 (CH), 120.3 (CH), 94.5 (C), 54.7 (CH_3), 53.6 (CH_3), 41.4 (CH), 34.8 (CH), 22.2 (CH), 20.8 (CH); HMRS (EI-TOF) calcd for $C_{17}H_{17}NO_4$ $[M]^+$, 299.1158. Found, 299.1160. IR (neat, cm^{-1}): 2936, 2824, 1777, 1714, 1597, 1500, 1442, 1379, 1261, 1242, 1179, 1128, 1099, 1040, 1018, 926, 805, 754, 691, 620.

Spectral Data of ***7b***. White solid, 132 mg, 90% yield, mp 147.5−149.7 °C. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.49−7.43 (m, 2H), 7.41−7.35 (m, 1H), 7.30−7.27 (m, 2H), 5.91 (dd, J = 9.5, 1.00 Hz, 1H), 5.69 (dt, J = 9.8, 1.4, Hz, 1H), 3.45 (m, 2H), 3.44 (s, 3H), 3.24 (s. 3H), 1.83 (s, 1H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 177.5 (C), 176.2 (C), 131.9 (C), 129.3 (CH), 129.0 (CH), 128.4 (CH), 126.3 (CH), 120.1 (CH), 96.0 (C), 54.6 (CH_3), 53.9 (CH_3), 41.4 (CH), 35.4 (CH), 26.1 (CH), 25.9 (C), 18.5 (CH_3); HRMS (ESI-TOF) calcd for $C_{18}H_{19}NO_4Na$ $[M + Na]^+$, 336.1206. Found, 336.1226. IR (neat, cm^{-1}): 2933, 1715, 1598, 1500, 1456, 1381, 1178, 1131, 1026, 802, 760, 721, 691.

Spectral Data of ***7c***. White solid, 14 mg, 77% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3 H), 7.24−7.30 (m, 2 H), 5.74−5.80 (m, 1H), 3.51 (d, J = 9.5 Hz, 1H), 3.41 (s, 3H), 3.26−3.33 (m, 4H), 2.15 (d, J = 9.8 Hz, 3H), 1.94 (s, 3H), 1.81 (dd, J = 5.4, 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.2 (C), 174.7 (C), 131.8 (C), 128.9 (2 × CH), 128.3 (CH), 126.9 (C), 126.3 (2 × CH), 118.5 (CH), 94.0 (C), 54.6 (CH_3), 53.5 (CH_3), 44.3 (CH), 36.9 (CH), 22.7 (CH), 21.6 (CH_3), 19.9 (CH); HMRS (EI-TOF) calcd for $C_{18}H_{19}NO_4$ $[M]^+$, 313.1314. Found, 313.1316. IR (neat, cm^{-1}): 2936, 2831, 1776, 1713, 1597, 1497, 1443, 1409, 1381, 1260, 1239, 1180, 1113, 1043, 840, 798, 749, 691, 517.

Spectral Data of ***7d***. White solid, 13 mg, 69% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3 H), 7.25−7.30 (m, 2 H), 5.44 (dd, J = 1.4, 2.7 Hz, 1H), 3.46 (dt, J = 2.6, 10.1 Hz, 1H), 3.42 (s, 3H), 3.39 (dd, J = 0.8, 9.6 Hz, 1H), 3.30 (s, 3H), 2.25 (d, J = 9.7 Hz, 1H), 1.94 (t, J = 1.8 Hz, 3H), 1.70 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.5 (C), 176.6 (C), 131.9 (C), 131.6 (C), 129.0 (2 × CH), 128.5 (CH), 126.4 (2 × CH), 114.3 (CH), 94.2 (C), 54.1 (CH_3), 53.6 (CH_3), 42.1 (CH), 34.7 (CH), 26.3 (CH), 24.3 (CH_3), 21.9 (CH); HMRS (EI-TOF) calcd for $C_{18}H_{19}NO_4$ $[M]^+$, 313.1314. Found, 313.1316. IR (neat, cm^{-1}): 2936, 2828, 1786, 1714, 1594, 1499, 1442, 1413, 1382, 1241, 1180, 1113, 1096, 1042, 1006, 761, 734, 691.

Spectral Data of ***7e***. White solid, 18 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.34−7.49 (m, 3 H), 7.22−7.27 (m, 2 H), 6.11 (ddd, J = 3.0, 6.0, 10.0 Hz, 1H), 5.65 (dt, J = 2.7, 10.0 Hz, 1H), 3.59 (dt, J = 2.9, 9.3 Hz, 1H), 3.37−3.41 (m, 4H), 3.27 (s, 3H), 1.60 (s, 3H), 1.50 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 176.3 (C), 176.0 (C), 131.7 (C), 129.0 (2 × CH), 128.4 (CH), 126.5 (2 × CH), 124.1 (CH), 120.0 (CH), 96.9 (C), 54.6 (CH_3), 53.8 (CH_3), 44.0 (CH), 38.6 (CH), 28.4 (CH), 27.1 (CH_3), 16.5 (CH_3); HMRS (ESI-TOF) calcd for $C_{18}H_{19}NO_4Na$ $[M + Na]^+$, 336.1206. Found, 336.1221. IR (neat, cm^{-1}): 2937, 2831, 1775, 1715, 1594, 1500, 1457, 1382, 1255, 1200, 1180, 1137, 1094, 1056, 1031, 1007, 797, 752, 691, 633.

Spectral Data of ***7f***. White solid, 39 mg, 52% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.50−7.33 (m, 3H), 7.30−7.25 (m, 2H), 6.50−6.43 (m, 1H), 5.19 (s, 1H), 3.70−3.50 (m, 6H), 3.42 (s, 3H), 3.32 (s, 3H), 2.19 (d, J = 9.7 Hz, 1H), 1.93 (dd, J = 9.7, 6.0 Hz, 1H), 1.19 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 177.2 (C), 174.9 (C), 131.9 (C), 129.0 (CH), 128.5 (CH), 127.7 (C), 126.4 (CH), 120.5 (CH), 98.6 (CH), 94.5 (C), 77.6 (CH_2), 77.3 (CH_2), 55.0 (CH_3), 53.8 (CH_3), 40.5 (CH), 36.6 (CH), 30.3 (C), 23.0 (CH_3), 22.5 (C), 21.7 (CH_3), 20.8 (CH); HRMS (ESI-TOF) calcd for $C_{23}H_{27}NO_6Na$ $[M + Na]^+$, 436.1730. Found, 436.1749. IR (neat, cm^{-1}): 2953, 2930, 2853, 1714, 1498, 1385, 1190, 1108, 1042, 753, 732, 692.

Spectral Data of ***7g***. White solid, 47 mg, 75% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.48−7.41 (m, 2H), 7.40−7.34 (m, 1H), 7.30−7.26 (m, 2H), 5.89 (d, J = 2.9 Hz, 1H), 4.88 (s, 1H), 3.69 (s, 1H), 3.66 (s, 1H), 3.54−3.48 (m, 3H), 3.45 (dd, J = 9.8, 0.7 Hz, 1H), 3.45 (s, 3H), 3.38 (s,3H), 2.29 (d, J = 2.3 Hz, 1H), 2.12 (d, J = 9.8 Hz, 1H), 1.21 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 177.0 (C), 175.8 (C), 133.5 (C), 131.8 (C), 129.0 (CH), 128.5 (CH), 126.4 (CH), 118.3 (CH), 102.1 (CH), 93.8 (C), 77.3 (CH_2), 77.2 (CH_2), 54.0 (CH_3), 53.7 (CH_3), 41.6 (CH), 35.0 (CH), 30.1

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(C), 23.0 (CH_3), 21.8 (CH_3), 21.6 (CH), 21.0 (CH); HRMS (ESI-TOF) calcd for $C_{23}H_{27}NO_6Na$ $[M + Na]^+$, 436.1730. Found, 436.1729. IR (neat, cm^{-1}): 2953, 2928, 2855, 1714, 1498, 1463, 1443, 1383, 1254, 1194, 1098, 1059.

Spectral Data of ***7h***. White solid, 67 mg, 90% yield, mp 183.0−189.1 °C. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.49−7.42 (m, 2H), 7.40−7.34 (m, 1H), 7.33−7.28 (m, 2H), 6.38 (dd, J = 10.4, 2.7 Hz, 1H), 5.80 (dd, = 10.3, 6.2 Hz, 1H), 4.26 (s, 1H), 3.67 (dd, J = 10.7, 2.8 Hz, 1H), 3.58 (dd, J = 11.2, 2.8 Hz, 1H), 3.51−3.42 (m, 3H), 3.46 (s, 3H), 3.39−3.34 (m, 1 H), 3.28 (s, 3H), 2.14 (s, 1H), 1.21 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 176.9 (C), 175.9 (C), 131.8 (C), 128.9 (CH), 128.4 (CH), 126.3 (CH), 123.0 (CH), 120.8 (CH), 101.9 (CH), 95.1 (C), 77.4 (CH_2), 77.3 (CH_2), 55.1 (CH_3), 54.0 (CH_3), 41.6 (CH), 34.9 (CH), 34.1 (C), 29.9 (C), 24.1 (CH), 23.0 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{23}H_{27}NO_6Na$ $[M + Na]^+$, 436.1730. Found, 436.1751. IR (neat, cm^{-1}): 2926, 2850, 1716, 1378, 1182, 1102, 1024.

Spectral Data of ***7i***. White solid, 13 mg, 69% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.51 (m, 3 H), 7.24−7.29 (m, 2 H), 6.90 (d, J = 3.3 Hz, 1H), 3.81 (s, 3H), 3.65 (dd, J = 3.3, 9.9 Hz, 1H), 3.49 (dd, J = 0.9, 9.9 Hz, 1H), 3.45 (s, 3H), 3.25 (s, 3H), 2.41 (d, J = 9.8 Hz, 1H), 2.35 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 176.3 (C), 174.2 (C), 165.8 (C), 131.4 (C), 129.8 (CH), 128.9 (2 × CH), 128.5 (CH), 127.4 (C), 126.1 (2 × CH), 93.7 (C), 54.1 (CH_3), 53.7 (CH_3), 52.1 (CH_3), 42.3 (CH), 34.2 (CH), 21.5 (CH), 21.3 (CH); HMRS (EI-TOF) calcd for $C_{19}H_{19}NO_6$ $[M]^+$, 357.1212. Found, 357.1207. IR (neat, cm^{-1}): 2952, 2828, 1776, 1716, 1594, 1497, 1447, 1414, 1385, 1259, 1186, 1114, 1069, 1038, 1008, 761, 693.

Spectral Data of ***7m***. White solid, 17 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.33−7.50 (m, 3 H), 7.27−7.32 (m, 2 H), 4.95 (dd, J = 1.7, 5.7 Hz, 1H), 3.62 (s, 3H), 3.58 (dd, J = 1.0, 9.4 Hz, 1H), 3.49 (dd, J = 1.8, 9.4 Hz, 1H), 3.41 (s, 3H), 3.32 (s, 3H), 2.09 (dd, J = 1.0, 9.9 Hz, 1H), 1.90 (dd, J = 5.7, 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 176.9 (C), 173.0 (C), 148.7 (C), 131.8 (C), 129.0 (2 × CH), 128.4 (CH), 126.3 (2 × CH), 93.6 (CH), 89.9 (CH), 55.0 (CH_3), 54.2 (CH_3), 53.6 (CH_3), 42.7 (CH), 38.5 (CH), 22.2 (CH), 19.5 (CH); HMRS (ESI-TOF) calcd for $C_{18}H_{19}NO_5Na$ $[M + Na]^+$, 352.1155. Found, 352.1157. IR (neat, cm^{-1}): 2936, 2831, 1781, 1716, 1666, 1597, 1500, 1444, 1383, 1334, 1261, 1224, 1180, 1114, 1040, 1022, 814, 749, 692.

Spectral Data of ***7n***. White solid, 18 mg, 90% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.50 (m, 3H), 7.24−7.30 (m, 2H), 6.05 (ddd, J = 0.3, 2.9, 9.9 Hz, 1H). 5.70 (dd, J = 2.9, 9.9 Hz, 1H), 3.77 (d, J = 9.3 Hz, 1H), 3.62 (dtd, J = 0.4, 2.9, 9.3 Hz, 1H), 3.51 (s, 3H), 3.46 (s, 3H), 3.34 (s, 3H), 2.04 (d, J = 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 175.5 (C), 173.6 (C), 131.5 (C), 128.7 (2 × CH), 128.2 (CH), 126.2 (2 × CH), 122.5 (CH), 120.5 (CH), 95.1 (C), 66.5 (C), 56.3 (CH_3), 54.5 (CH_3), 54.0 (CH_3), 44.2 (CH), 36.7 (CH), 27.1 (CH); HMRS (EI-TOF) calcd for $C_{18}H_{19}NO_5$ $[M]^+$, 329.1263. Found, 329.1259. IR (neat, cm^{-1}): 2937, 2834, 1778, 1715, 1593, 1499, 1455, 1386, 1376, 1212, 1180, 1127, 1030, 801, 756, 691, 630.

Spectral Data of ***7p***. White solid, 19 mg, 100% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.51 (m, 3 H), 7.22−7.30 (m, 2 H), 5.92−5.98 (m, 1H), 5.67−5.72 (m, 1H), 3.45 (d, J = 1.4 Hz, 2H), 3.38 (s, 3H), 3.24 (s, 3H), 2.10 (s, 1H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.6 (C), 176.4 (C), 131.9 (C), 129.0 (2 × CH), 128.4 (CH), 126.3 (2 × CH), 126.0 (CH), 119.7 (CH), 97.5 (C), 54.7 (CH_3), 53.3 (CH_3), 41.0 (CH), 35.1 (CH), 23.2 (CH), 21.3 (C), −2.5 (3 × CH_3); HMRS (EI-TOF) calcd for $C_{20}H_{25}NO_4Si$ $[M]^+$, 371.1553. Found, 371.1557. IR (neat, cm^{-1}): 2953, 2902, 2828, 1779, 1716, 1601, 1499, 1440, 1378, 1278, 1247, 1178, 1111, 1066, 1025, 989, 891, 864, 839, 804, 775, 751, 690, 622.

Spectral Data of ***7q***. White solid, 15 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.32−7.50 (m, 3 H), 7.22−7.29 (m, 2 H), 5.95 (dd, J = 1.0, 9.6 Hz, 1H), 5.65−5.80 (m, 2H), 5.00−5.13 (m, 2H), 3.46 (t, J = 1.4 Hz, 2H), 3.44 (s, 3H), 3.22 (s, 3H), 2.31 (m, 2H), 1.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.4 (C), 176.2 (C), 135.6 (CH), 131.8 (C), 129.0 (2 × CH), 128.5 (CH), 127.4 (CH), 126.3 (2 × CH), 120.7 (CH), 116.9 (CH_2), 96.1 (CH), 54.6 (CH_3), 53.9 (CH_3), 41.6 (CH), 36.6 (CH_2), 35.4 (CH), 29.9 (C), 25.8 (CH); HMRS (EI-TOF) calcd for $C_{20}H_{21}NO_4$ $[M]^+$, 339.1471. Found, 339.1469. IR (neat, cm^{-1}): 2935, 2821, 1777, 1715, 1601, 1499, 1441, 1379, 1178, 1129, 1056, 1018, 941, 916, 808, 754, 691, 615.

Spectral Data of ***7r***. White solid, 23 mg, 49% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.50−7.40 (m, 2H), 7.38−7.34 (m, 1H), 7.34−7.30 (m, 2H), 5.22 (d, J = 1.2 Hz, 1H), 4.27 (s, 1H), 3.67 (s, 3H), 3.61−3.46 (m, 4H), 3.42 (s, 3H), 3.39−3.35 (m, 2H), 3.29 (s, 3H), 1.98 (s, 1H), 1.20 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 176.6 (C), 172.9 (C), 149.0 (C), 131.9 (C), 128.9 (CH), 128.4 (CH), 126.4 (CH), 101.9 (CH), 94.6 (C), 89.6 (CH), 77.4 (CH_2), 77.2 (CH_2), 55.1 (CH_3), 54.6 (CH_3), 54.0 (CH_3), 42.7 (CH), 38.4 (CH), 34.9 (C), 30.0 (C), 23.1 (CH), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{24}H_{29}NO_7Na$ $[M + Na]^+$, 466.1836. Found, 466.1844. IR (neat, cm^{-1}): 2920, 2850, 1720, 1660, 1633, 1469, 1455, 1380, 1200, 1129, 1101, 1019.

Spectral Data of ***7t***. White solid, 17 mg, 87% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.33−7.50 (m, 3 H), 7.22−7.28 (m, 2 H), 5.46 (d, J = 2.70 Hz, 1H), 3.50 (dd, J = 2.7, 9.6 Hz, 1H), 3.43 (s, 3H), 3.39 (d, J = 9.6 Hz, 1H), 3.31 (s, 3H), 2.25 (d, J = 9.9 Hz, 1H), 1.90 (d, J = 9.9 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ):177.5 (C), 177.1 (C), 144.1 (C), 131.9 (C), 129.0 (2 × CH), 128.4 (CH), 126.3 (2 × CH), 110.9 (CH), 93.6 (C), 53.3 (CH_3), 42.7 (CH), 36.2 (C), 34.7 (CH), 29.2 (3 × CH_3), 22.9 (CH), 21.5 (CH); HMRS (ESI-TOF) calcd for $C_{21}H_{25}NO_4Na$ $[M + Na]^+$, 378.1676. Found, 378.1692. IR (neat, cm^{-1}): 2964, 2902, 2867, 1777, 1715, 1594, 1500, 1442, 1410, 1383, 1240, 1178, 1134, 1047, 1033, 864, 769, 754, 736, 703, 691.

Spectral Data of ***7u***. White solid, 16 mg, 85% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.34−7.50 (m, 3 H), 7.22−7.27 (m, 2 H), 6.10 (d, J = 10.4 Hz, 1H), 5.67−5.74 (m, 1H), 3.43−3.45 (m, 2H), 3.39 (s, 3H), 3.19 (s, 3H), 2.22 (s, 1H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 177.9 (C), 176.4 (C), 131.9 (C), 129.1 (2 × CH), 128.5 (CH), 127.0 (CH), 126.3 (2 × CH), 120.1 (CH), 96.2 (C), 54.4 (CH_3), 53.3 (CH_3), 41.4 (CH), 38.0 (CH_3), 35.7 (CH), 31.6 (C), 27.9 (3 × CH_3), 21.4 (CH); HMRS (ESI-TOF) calcd for $C_{21}H_{25}NO_4Na$ $[M + Na]^+$, 378.1676. Found, 378.1689. IR (neat, cm^{-1}): 3032, 2955, 2824, 1777, 1716, 1597, 1499, 1457, 1440, 1407, 1378, 1282, 1224, 1206, 1177, 1122, 1082, 1058, 1031, 1000, 825, 809, 782, 752, 691, 615.

Spectral Data of ***7v***. White solid, 36 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 9.67 (s, 1H), 7.44−7.32 (m, 3H), 7.12 (dd, J = 3.5, 1.3 Hz, 1H), 7.06−7.02 (m, 2H), 4.03−4.00 (m, 1H), 3.78−3.74 (m, 1H), 3.67 (qd, J = 7.4, 4.5 Hz, 2H), 3.29 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 186.3 (CH), 175.3 (C), 174.8 (C), 147.3 (CH), 146.4 (C), 131.3 (C), 129.1 (CH), 128.8 (CH), 126.2 (CH), 121.1 (C), 52.5 (CH_3), 50.4 (CH_3), 49.3 (CH), 45.3 (CH), 43.9 (CH), 42.8 (CH); HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_5H$ $[M + H]^+$, 328.1179. Found, 328.1185. IR (neat, cm^{-1}): 2925, 2850, 1713, 1681, 1497, 1455, 1379, 1275, 1183, 1111, 1036, 744, 692.

Spectral Data of ***7x***. White solid, 30 mg, 33% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.50−7.35 (m, 3H), 7.29−7.26 (m, 2H), 6.23−6.18 (m, 1H), 5.84 (dd, J = 17.7, 10.8 Hz, 1H), 5.83−5.79 (m, 1H), 5.18 (dd, J = 15.7, 0.8 Hz, 1H), 5.15 (dd, J = 9.0, 0.9 Hz, 1H), 3.53−3.51 (m, 2H), 3.46 (s, 3H), 3.27 (s, 3H), 2.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 177.3 (C), 176.0 (C), 138.2 (CH), 133.1 (C), 129.1 (CH), 128.6 (CH), 120.1 (CH), 114.0 (CH_2), 93.8 (C), 77.2 (C), 54.0 (CH_3), 53.7 (CH_3), 42.1 (CH). 34.9 (CH), 29.7 (C), 21.5 (CH), 21.4 (CH); HRMS (ESI-TOF) calcd for $C_{19}H_{19}NO_4H$ $[M + H]^+$, 326.1386. Found, 326.1393. IR (neat, cm^{-1}): 2918, 2849, 1714, 1497, 1455, 1384, 1243, 1181, 1042, 749, 691.

Spectral Data of ***7y***. White solid, 8 mg, 87% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.48−7.34 (m, 3H), 7.29−7.27 (m, 2H), 6.20 (d, J = 10.7 Hz, 1H), 5.84 (dd, J = 17.7, 10.8 Hz, 2H), 5.83−5.78 (m, 1H), 5.21−5.12 (m, 1H), 3.53−3.51 (m, 2H), 3.46 (s, 3H), 3.27 (s, 3H), 2.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 177.0 (C),176.0 (C), 136.5 (CH), 131.7 (C), 129.1 (CH), 128.6 (CH), 126.4 (CH), 124.5 (CH), 120.9 (CH), 114.1 (CH_2), 96.6 (C), 54.7 (CH_3), 54.3 (CH_3), 41.5 (CH), 35.3 (CH), 32.3 (C), 27.6 (CH);

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HRMS (ESI-TOF) calcd for $C_{19}H_{19}NO_4Na$ $[M + Na]^+$, 348.1206. Found, 348.1221. IR (neat, cm^{-1}): 2923, 2850, 1714, 1598, 1499, 1382, 1181, 1025, 953, 691.

Spectral Data of ***8l***. White solid, 143 mg, 90% yield, mp 141.2−142.4 °C. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.53−7.40 (m, 3H), 7.28−7.24 (m, 2H), 3.94 (s, 1H), 3.45 (s, 3H), 3.39 (d, J = 7.2 Hz, 1H), 3.30 (d, J = 7.3 Hz, 1H), 3.28 (s, 3H), 3.07 (d, J = 10.1 Hz, 1H), 2.80 (d, J = 10.1 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 201.9 (C), 199.6 (C), 176.0 (C), 174.9 (C), 131.3 (C), 129.2 (CH), 129.0 (CH), 126.1 (CH), 105.4 (C), 51.5 (CH_3), 50.3 (C), 50.1 (CH_3), 50.0 (C), 48.3 (CH), 46.1 (CH), 44.7 (CH), 40.2 (CH), 27.7 (CH_3); HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_6Na$ $[M + H]^+$, 392.1105. Found, 392.1125. IR (neat, cm^{-1}): 2917, 2849, 1751, 1716, 1496, 1382, 1183, 1143, 1062, 753, 705, 691.

Spectral Data of ***8w***. White solid, 36 mg, 45% yield, mp 211.3−213.5 °C. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 9.60 (s, 1H), 7.47−7.36 (m, 3H), 7.15−7.09 (m, 3H), 4.47 (dd, J = 3.2, 2.0 Hz, 1H), 4.04 (dd, J = 6.3, 3.1 Hz, 1H), 3.69 (dd, J = 8.6, 3.3 Hz, 1H), 3.55 (dd, J = 8.5, 2.9 Hz, 1H), 3.45 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6, 24 °C, δ): 196.7 (C), 186.8 (CH), 174.8 (C), 173.9 (C), 144.9 (C), 141.5 (CH), 131.1 (C), 129.2 (CH), 129.0 (CH), 126.0 (CH), 92.4 (C), 50.6 (CH_3),50.5 (CH_3) 50.0 (C), 41.0 (CH), 39.3 (CH), 37.7 (CH); HRMS (ESI-TOF) calcd for $C_{19}H_{17}NO_6Na$ $[M + Na]^+$, 378.0948. Found, 378.0963. IR (neat, cm^{-1}): 2917, 2850, 1458, 1387, 1711, 1458, 1387, 1097, 1181, 753.

Spectral Data of ***11a***. White solid, 9 mg, 50% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.02 (ddd, J = 3.0, 5.7, 9.9 Hz, 1H), 5.37 (dd, J = 2.4, 9.9 Hz, 1H), 3.43 (dt, J = 2.7, 11.0 Hz, 1H), 3.37 (s, 3H), 3.25 (s, 3H), 3.36 (d, J = 11.0 Hz, 1H), 2.23 (dd, J = 1.1, 9.7 Hz, 1H), 1.77 (dd, J = 5.8, 9.7 Hz, 1H), 1.16 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 216.9 (C), 216.0 (C), 124.8 (CH), 120.6 (CH), 95.2 (C), 54.6 (CH_3), 53.5 (CH_3), 51.3 (C), 49.2 (CH), 40.0 (CH), 22.5 (CH), 22.3 (CH_3), 22.0 (CH), 20.7 (CH_3); HMRS (ESI-TOF) calcd for $C_{14}H_{18}O_4Na$ $[M + Na]^+$, 273.1097. Found, 273.1106. IR (neat, cm^{-1}): 2970, 2935, 2867, 2831, 1767, 1725, 1461, 1442, 1403, 1381, 1259, 1210, 1128, 1040, 1019, 789, 754.

Spectral Data of ***11b***. White solid, 8 mg, 40% yield. ^1H NMR (300 MHz, $CDCl_3$, 24 °C, δ): 6.20 (dd, J = 10.1, 2.6 Hz, 1H), 5.74 (dd, J = 9.8, 2.2 Hz, 1H), 3.74 (s, 3H), 3.73−3.70 (m, 2H), 3.54 (s, 3H), 2.17 (s, 1H), 1.62 (s, 3H), 1.52 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 217.2 (C), 216.1 (C), 130.5 (CH), 120.5 (CH), 54.5 (CH_3), 53.7 (CH_3), 51.4 (C), 49.0 (CH), 40.4 (CH), 29.7 (C), 27.8 (CH), 25.7 (C), 22.3 (CH_3), 20.8 (CH_3), 18.7 (CH_3); HRMS (ESI-TOF) calcd for $C_{15}H_{20}O_4Na$ $[M + Na]^+$, 287.1253. Found, 287.1284. IR (neat, cm^{-1}): 2918, 2847, 1698, 1539, 1470, 1463, 1455.

Spectral Data of ***11c***. White solid, 11 mg, 40% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 5.73−5.78 (m, 1H), 3.37 (s, 3H), 3.31 (d, J = 11.0 Hz, 1H), 3.25 (s, 3H), 3.22 (d, J = 11.0 Hz, 1H), 2.18 (dd, J = 1.3 Hz, 9.9, 1H), 1.79 (dd, J = 5.6, 9.9 Hz, 1H), 1.70 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 216.8 (C), 215.1 (C), 126.8 (C), 119.6 (CH), 94.7 (C), 54.4 (CH_3), 53.4 (CH_3), 52.3 (CH), 50.8 (C), 42.8 (CH), 22.7 (CH), 21.8 (CH), 21.8 (CH_3), 21.3 (CH_3), 20.9 (CH_3); HMRS (ESI-TOF) calcd for $C_{15}H_{21}O_4$ $[M + H]^+$, 265.1434. Found, 265.1441. IR (neat, cm^{-1}): 2969, 2936, 2870, 2824, 1764, 1725, 1463, 1443, 1408, 1379, 1287, 1260, 1222, 1197, 1139, 1114, 1044, 1030, 937, 856, 831.

Spectral Data of ***11d***. White solid, 15 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 5.14 (s, 3H), 3.41 (dd, J = 2.3, 10.4 Hz, 1H), 3.38 (s, 3H), 3.32 (dd, J = 1.3, 10.8 Hz, 1H), 3.25 (s, 3H), 2.27 (d, J = 1.0, 9.8 Hz, 1H), 1.87 (dd, J = 1.5, 2.4 Hz, 1H), 1.66 (d, J = 9.8 Hz, 1H), 1.17 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 217.2 (C), 216.2 (C), 133.1 (C), 114.4 (CH), 94.9 (C), 54.0 (CH_3), 53.4 (CH_3), 51.0 (C), 49.5 (CH), 39.9 (CH), 26.0 (CH), 24.5 (CH_3), 23.4 (CH), 22.4 (CH_3), 20.6 (CH_3); HMRS (ESI-TOF) calcd for $C_{15}H_{21}O_4$ $[M + H]^+$, 265.1434. Found, 265.1438. IR (neat, cm^{-1}): 2970, 2935, 2867, 2831, 1764, 1724, 1442, 1411, 1379, 1267, 1225, 1197, 1162, 1132, 1049, 931, 839.

Spectral Data of ***11e***. White solid, 9 mg, 39% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.07 (ddd, J = 3.4, 6.0, 9.8 Hz, 1H), 5.27 (dd, J = 2.3, 9.8 Hz, 1H), 3.55 (dt, J = 2.8, 9.9 Hz, 1H), 3.35 (s, 3H), 3.26 (d, J = 10.0 Hz, 1H), 3.21 (s, 3H), 1.60 (s, 3H), 1.52 (d, J = 6.1 Hz, 1H), 1.15 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 215.9 (C), 215.9 (C), 126.4 (CH), 119.9 (CH), 97.3 (C), 54.5 (CH_3), 53.6 (CH_3), 52.5 (CH), 51.8 (C), 44.4 (CH), 30.2 (C), 28.5 (CH), 21.8 (CH_3), 21.0 (CH_3), 16.3 (CH_3); HMRS (ESI-TOF) calcd for $C_{15}H_{21}O_4$ $[M + H]^+$, 265.1434. Found, 265.1437. IR (neat, cm^{-1}): 2972, 2937, 2863, 2828, 1736, 1726, 1463, 1442, 1380, 1286, 1239, 1196, 1123, 1103, 1053, 1030, 999, 966, 796, 756.

Spectral Data of ***11g***. White solid, 8 mg, 43% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.31 (dd, J = 10.3, 3.3 Hz, 1H), 5.54 (dd, J = 10.3, 2.8 Hz, 1H), 4.24 (s, 1H), 3.64 (dd, J = 10.9, 2.8 Hz, 1H), 3.53 (dd, J = 11.1, 2.8 Hz, 1H), 3.47−3.43 (m, 1H), 3.40 (t, J = 3.0 Hz, 1H), 3.38−3.29 (m, 2H), 3.23 (s, 3H), 2.11 (s, 1H), 1.16 (s, 6H), 1.12 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 216.4 (C), 216.0 (C), 123.7 (CH), 121.2 (CH), 102.0 (CH), 95.6 (C), 77.4 (CH_2), 77.3 (CH_2), 54.9 (CH_3), 53.8 (CH_3), 51.8 (C), 48.8 (CH), 39.9 (CH), 33.8 (C), 29.9 (C), 25.6 (CH), 22.9 (CH_3), 21.8 (CH_3), 21.7 (CH_3), 21.3 (CH_3); HRMS (ESI-TOF) calcd for $C_{20}H_{28}O_6Na$ $[M + Na]^+$, 387.1178. Found, 387.1792. IR (neat, cm^{-1}): 2925, 2852, 1727, 1461, 1381, 1138, 1105, 1027.

Spectral Data of ***11h***. White solid, 8 mg, 44% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 5.99 (ddd, J = 3.2, 6.3, 9.7 Hz, 1H), 5.32 (dd, J = 2.5, 9.7 Hz, 1H), 3.61 (d, J = 10.0 Hz, 1H), 3.50 (dt, J = 2.6, 10.0 Hz, 1H), 3.46 (s, 3H), 3.45 (s, 3H), 3.26 (s, 3H), 2.06 (d, J = 6.3 Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C, δ): 215.3 (C), 213.5 (C), 124.6 (CH), 121.0 (CH), 95.2 (C), 69.2 (C), 56.2 (CH_3), 54.5 (CH_3), 54.2 (CH_3), 52.6 (CH), 51.9 (C), 42.8 (CH), 27.3 (CH), 21.6 (CH_3), 21.5 (CH_3); HMRS (ESI-TOF) calcd for $C_{15}H_{21}O_5$ $[M + H]^+$, 281.1384. Found, 281.1382. IR (neat, cm^{-1}): 2969, 2937, 2834, 1763, 1728, 1460, 1443, 1381, 1285, 1203, 1134, 1105, 1032.

Spectral Data of ***12a***. Colorless oil, 28 mg, 61% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 5.69−5.64 (m, 1H), 5.60−5.56 (m, 1H), 5.43 (d, J = 2.13 Hz, 1H), 4.79 (s, 1H), 3.68−3.61 (m, 2H), 3.48 (t, J = 10.5 Hz, 2H), 3.39 (s, 6H), 3.07 (d, J = 9.3 Hz, 1H), 2.73 (q, J = 9.4 Hz, 1H), 4.30 (dddd, J = 16.0, 8.5, 2.7, 1.2 Hz, 1H), 2.23−2.14 (m, 1H), 2.01 (d, J = 9.9 Hz, 1H), 1.60 (d, J = 9.9 Hz, 1H), 1.22 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 132.5 (CH), 129.4 (CH), 128.6 (C), 124.6 (CH), 104.0 (CH), 95.1 (C), 77.3 (CH_2), 77.2 (CH_2), 53.6 (CH_3), 53.1 (CH_3), 43.7 (CH), 38.0 (CH_2), 31.0 (CH), 30.1 (C), 26.0 (CH), 23.0 (CH_3), 21.8 (CH_3), 21.3 (CH); HRMS (ESI-TOF) calcd for $C_{18}H_{26}O_4Na$ $[M + Na]^+$, 329.1723. Found, 329.1740. IR (neat, cm^{-1}): 2953, 2921, 2850, 1718, 1439, 1393, 1248, 1101, 1043, 754, 667.

Spectral Data of ***12b***. White solid, 18 mg, 95% yield. ^1H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.06 (dd, J = 10.4, 2.8 Hz, 1H), 5.71−5.66 (m, 1H), 5.58−5.55 (m, 1H), 5.38 (dd, J = 10.4, 2.0 Hz, 1H), 4.21 (s, 1H), 3.69−3.61 (m, 2H), 3.47 (d, J = 11.1 Hz, 1H), 3.42−3.37 (m, 1H), 3.39 (s, 3H), 3.30 (s, 3H), 3.08−3.02 (m, 1H), 2.66 (q, J = 9.2 Hz, 1H), 2.42 (dddd, J = 15.9, 8.4, 2.8, 1.4 Hz, 1H), 2.25−2.15 (m, 1H), 1.40 (s, 1H), 1.22 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C, δ): 132.8 (CH), 129.0 (CH), 126.7 (CH), 117.8 (CH), 103.2 (CH), 96.6 (C), 77.5 (CH_2), 77.4 (CH_2), 54.6 (CH_3), 53.5 (CH_3), 43.9 (CH), 37.7 (CH_2), 34.1 (C), 30.7 (CH), 29.9 (CH), 29.5 (C), 23.1 (CH_3), 21.8 (CH_3); HRMS (ESI-TOF) calcd for $C_{18}H_{26}O_4Na$ $[M + Na]^+$, 329.1723. Found, 329.1754. IR (neat, cm^{-1}): 2952, 2929, 2848, 1458, 1442, 1391, 1245, 1235, 1131, 1105, 1043, 1029, 1019, 968, 702.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02140.

Crystallographic data for **7d** (CIF)

Crystallographic data for **9i** (CIF)

Copies of NMR for **6a−6y**, **7a−7i**, **7m**, **7n**, **7p−7r**, **7t−7v**, **7x**, **7y**, **8l**, **8w**, **9a−9f**, **9h**, **9i**, **10a**, **10b**, **11a−11e**, **11g**,

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11h, **12a**, and **12b**. X-ray single-crystal structure analysis data for **7d** and **9i** (PDF)

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Notes

The authors declare no competing financial interest.

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(23) The ORTEP data of **9i** can be found in the Supporting Information.

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