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# Solid-Phase Synthesis of a Combinatorial Methylated (±)-Epigallocatechin Gallate Library and the Growth-Inhibitory Effects of these Compounds on Melanoma B16 Cells

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**Abstract:** We report on the solid-phase synthesis of a combinatorial methylated (±)-epigallocatechin gallate (EGCG) library and its biological evaluation. Epigallocatechin gallate (EGCG) and its methylated derivatives, which are members of the catechin family, exhibit various anti-cancer effects. The solid-phase synthesis of methylated EGCG involves the preparation of the α-acyloxyketone by the coupling of a solid-supported aldehyde with a ketone and an acid. The subsequent release and reductive etherification reaction of the solid-supported α-acyloxyketone provide the protected EGCG in good total yields. Sixty-four methylated EGCGs were successfully prepared. The growth-inhibitory effects of the methylated EGCG library were also examined. Although methylation of EGCG generally causes reduced growth inhibition, the growth-inhibitory effect of 7-OMe EGCGs was comparable to that of EGCG. The 7-OMe EGCGs are attractive drug candidates because of their enhanced bioavailability.

**Keywords:** combinatorial chemistry · microreactors · phytochemistry · receptors · solid-phase synthesis

## Introduction

Combinatorial chemistry greatly facilitates the systematic syntheses of small molecules that involve a common core structure. Solid-phase syntheses that are based on the reactions of solid-supported substrates and the release of products from the solid-support during the final stage have many advantages for the combinatorial synthesis of small molecules. In particular, the use of solid-supported substrates results in easy manipulation and adaptability of the split-and-pool strategy. An effective application of combinatorial chemistry is the synthesis of combinatorial libraries based on the unique structures of natural products with biological activities;[1] these libraries serve as attractive drug candidates and biochemical probes. We have already reported the synthesis of natural-product-based combinatorial libraries, such as terpenoids, macrolides, peptides, heterocycles, and glycoconjugates.[2]

Polyphenols, such as (−)-catechin (**1**) and (−)-epigallocatechin-3-*O*-gallate (EGCG, (−)-**2aa**), are phytochemicals found in tea leaves that exhibit various biological activities (Scheme 1).[3] The 67 kDa laminin receptor (67LR)[4] is a receptor for EGCG that mediates its anti-cancer[5] and anti-allergic[6] actions. However, because EGCGs are highly hydrophilic, they have low bioavailability, which makes them ineffective when administered orally. On the other hand, methylated EGCGs, the phenols of which are partially capped with methyl ethers, have recently attracted considerable attention because the hydrophilicity of the methyl groups improves the bioavailability of the methylated compounds.[7] However, methylated EGCGs isolated from natural sources

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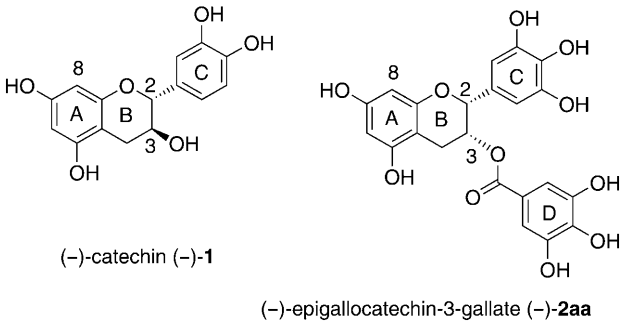


Scheme 1. Structures of catechin and epigallocatechin gallate.

frequently show reduced biological activity in vitro in comparison with EGCG.[8] Furthermore, the structural diversity of both the methylated EGCGs and the catechins is limited. In particular, naturally occurring EGCG derivatives methylated at the phenol on the A ring have not been isolated. Therefore, the systematic chemical synthesis of both natural and unnatural methylated EGCGs, and a survey of the biological activities of these compounds is highly desirable. However, although several reports on the solid-phase syntheses of pyran natural products have been reported,[9] most of the syntheses of acylated epicatechins reported to date have been based on a target-oriented synthesis which involves the preparation of *cis*-benzopyran derivatives, followed by the acylation of the C3 hydroxyl group.[10] Therefore, the goal of this study was to develop an effective method for the synthesis of methylated EGCG derivatives.[11] Herein, we report the solid-phase synthesis of a methylated (±)-EGCG library and the biological evaluation of these compounds.

## Results and Discussion

We planned to synthesize the racemic methylated EGCG library **2–5** involving the natural dihydroxyl A ring (in **2**) and the three unnatural methylated A rings (in **3–5**). Our strategy for the synthesis of methylated EGCG library **2–5** involved the combinatorial synthesis of benzyl-protected, methylated EGCG library **6–9** in the solid-phase from aldehyde **15**, ketone **14**, and carboxylic acid **11**, and the deprotection of the benzyl-protected library **6–9** by utilizing the H-Cube (Scheme 2). H-Cube is a continuous-flow hydrogenation reactor with endogenous on-demand hydrogen generation and a disposable catalyst-cartridge system, and allows precise tuning of the reaction conditions to minimize over-reaction.[12] The solid-phase synthesis of the protected library **6–9** involved four steps: 1) loading of phenol **15** on the polystyrene resin through *para*-alkyloxybenzyl linker (Wang resin) **16** to prepare the solid-supported aldehyde **13**; 2) aldol condensation of ketone **14** with the solid-supported aldehyde **13**, followed by epoxidation of the resulting enone to **12**; 3) regioselective opening of the epoxide **12**, followed by the acylation of the resulting alcohol with acid **11**; and, 4) the construction of the epicatechin skeleton by one-pot release and reductive etherification of the solid-supported α-acyloxyl ketone **10**. The reductive etherification of the α-acyloxyl ketone **10** provided the *cis*-substituted benzopyran by neighboring-group participation.[13] The bromide at the C8 position prevented Friedel–Craft alkylation of the cleaved *para*-alkyloxybenzyl linker at the C8 position.[14] The three-component coupling strategy was effective for the synthesis of combinatorial epicatechin libraries with three different aromatic rings. Furthermore, the solid-phase synthesis allowed the synthesis of all possible methylated EGCGs because the phenol group that is used to link to the solid support becomes an element of the pyran ring. We used this method to synthesize 64 methylated EGCGs from aldehydes **15a–d**, ketones **14a–d**, and carboxylic acids **11a–d** (Scheme 3).

We first examined the solution-phase synthesis of (±)-EGCG **2aa** using *para*-methoxybenzyl ether instead of a Wang resin (Scheme 4). Treatment of triphenol **17** with 2.0 equivalents of *para*-fluorobenzyl bromide under basic conditions provided the dibenzylated product **18** in 81% yield. Subsequent bromination at the *ortho* position of the remaining free phenol group provided the phenyl bromide **15a** in 87% yield. $^1$H NOESY experiments showed 9.5% and 11% NOEs between the hydrogens at the C5 position and the two benzylic positions, respectively, thus indicating that the remaining proton of **19** was located at the C5 position. Protection of the free phenol group of **19** with *para*-methoxybenzyl chloride, followed by aldol condensation with 3,4,5-tribenzyloxyphenylmethyl ketone (**14a**) afforded the *E*-enone **20** in 82% yield in two steps.

Synthesis of precursor **25a** for reductive etherification was examined (Scheme 5). Enone **20** was treated with $H_2O_2$ under basic conditions. After a conventional workup of the reaction, the crude material, which included the epoxide **22**, was exposed to methanol in the presence of $Sc(OTf)_3$ to provide the alcohol **24** in 81% yield from **20** as a mixture of diastereomers. Purification of the epoxide **22** using column chromatography on silica gel was difficult. The corresponding benzyl ether derivative **21** was not converted into the corresponding epoxide **23** under the same reaction conditions. These results suggested that the fluoro substituents might reduce the LUMO level, thereby, enhancing the reactivity of the enone towards nucleophilic epoxidation. The relative stereochemistry of **24** was not determined, but the

**Abstract in Japanese:**

本研究では、固相合成法を用いるメチル化カテキンライブラリーを行った。メチル化カテキンは、水溶性の低下による生体利用率の向上が期待できる。固相上で３成分のビルディングブロックを結合することにより環化前駆体を合成し、切り出しながら立体選択的にエピカテキン骨格を合成した。各々４種のビルディングブロックを用いることで６４種類の保護体のコンビナトリアル合成を行った。保護体の脱保護には、フロー型反応装置を用いた。ライブラリー化合物の細胞増殖抑制作用を調べた結果、D環部メチル化は細胞増殖抑制作用を減弱させる傾向があるものの、７位メチル化は、細胞増殖抑制作用に大きく影響しないことを見出した。

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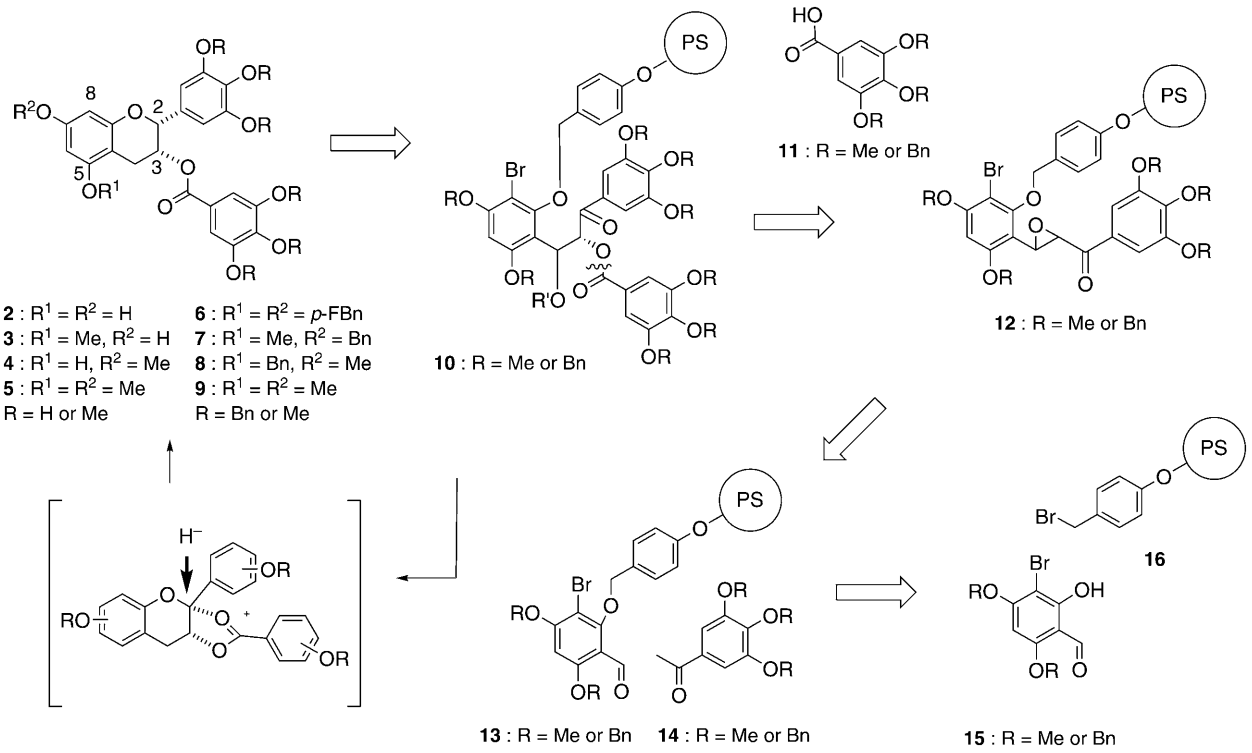
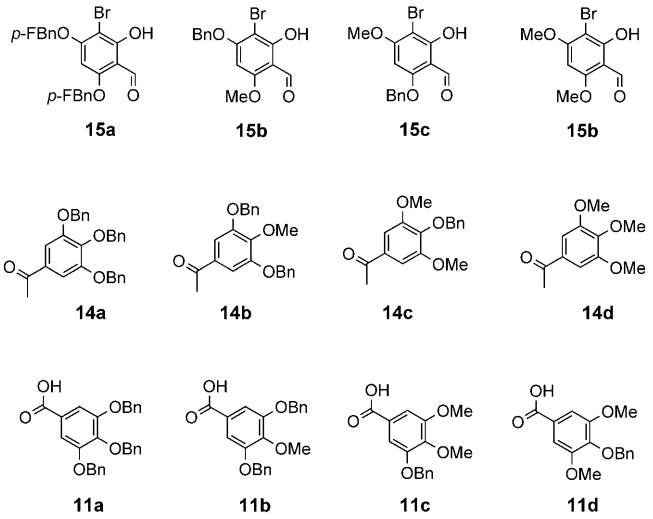
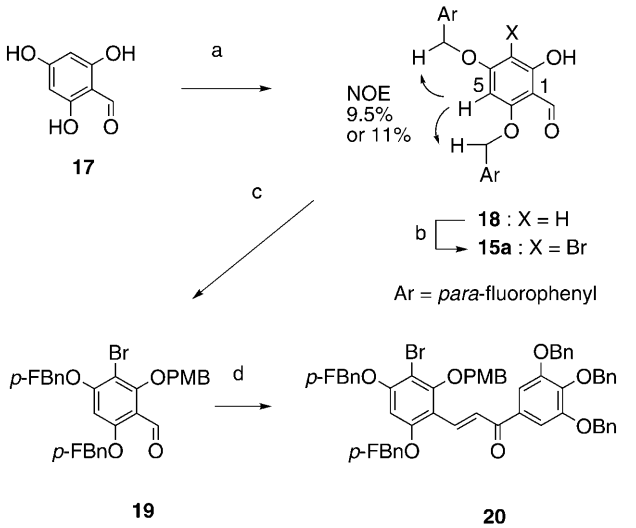



Scheme 2. Strategy for the solid-phase synthesis of methylated EGCG derivatives **2**–**5**.




Scheme 3. Building blocks **15**, **14**, and **11** for the synthesis of the 64-member combinatorial library.




Scheme 4. Reagents and conditions: a) *para*-fluorobenzyl bromide, $Cs_2CO_3$, DMF, 81%; b) bromine, $CH_2Cl_2$, 0°C, 82%; c) *para*-methoxybenzyl chloride, $K_2CO_3$, DMF; d) 3′,4′,5′-tris(benzyloxy)acetophenone (**14a**), NaOMe, THF, 82% based on **15a**. DMF = *N*,*N*-dimethylformamide.

methyl ether was reduced at the final stage. Acylation of the resulting alcohol **24** with the tribenzyl-protected gallic acid, provided the precursor **25a** in 96% yield.

Cyclization of **25a** by reductive etherification was examined (Table 1). Exposure of the precursor **25a** to our previously reported reaction conditions for reductive cyclization of thioether **25b** (15% TFA and 10% $Et_3SiH$ in $CH_2Cl_2$ −20°C) resulted in a high yield of the starting material **25a** and a trace amount of the product **6aa** (Table 1 entry 3).

Table 1. Reductive cyclization of the α-acyloxy ketone **25**.

| Entry | TFA [V V$^{-1}$%] | $Et_3SiH$ [V V$^{-1}$%] | *t* [h] | T [°C] | Yield [%] |
|---|---|---|---|---|---|
| 1 | 5 | 10 | 2 | 0 | 72 |
| 2 | 15 | 10 | 15 | 0 | 28 |
| 3 | 15 | 10 | 10 | -20 | trace |
| 4[a] | 15 | 10 | 5 | -20 | 68 |

[a] Addition of decanethiol to the reaction mixture.

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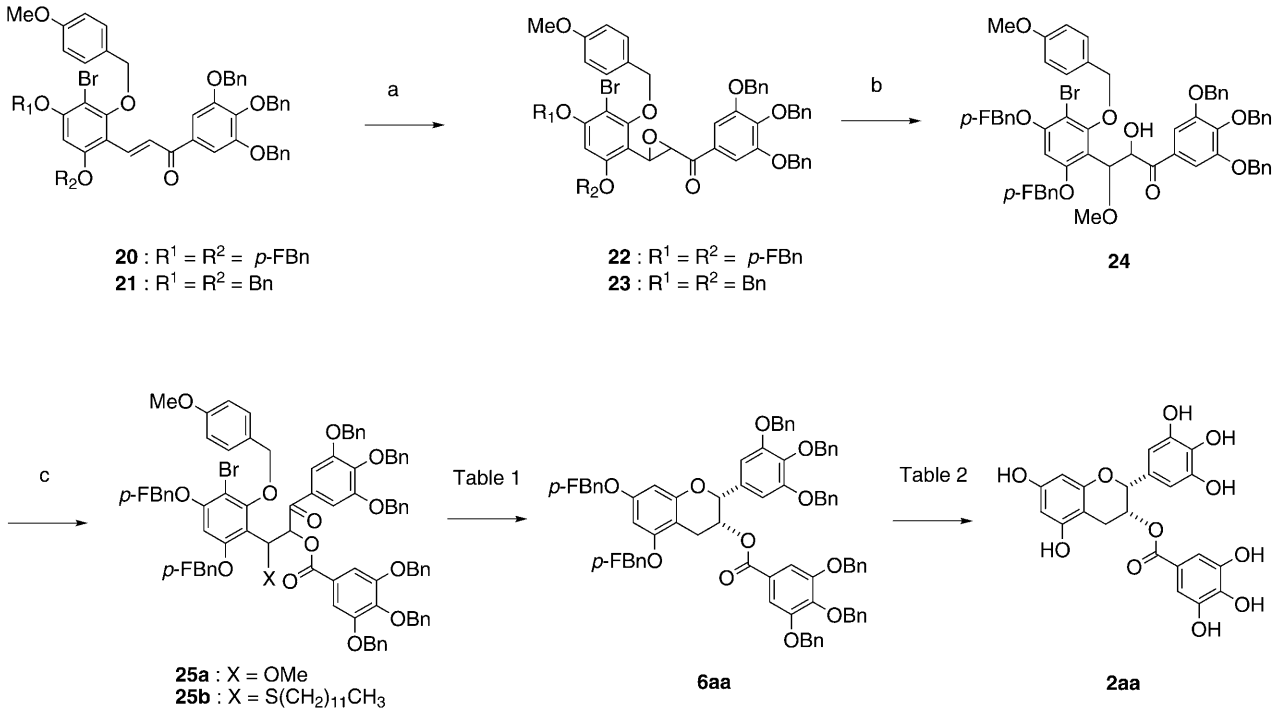


Scheme 5. Reagents and conditions: a) KOH, $H_2O_2$ (aq.), $Bu_4N{\cdot}HSO_4$, $CH_2Cl_2$, room temperature, 30 hours; b) $Sc(OTf)_3$, $MeOH/CH_2Cl_2$ (1:1), room temperature, 3 hours, 81% based on **20**; c) **10a**, EDCI, DMAP, pyridine, 12 h, 96%.

The addition of thiol to the reaction of **25a** under the previously reported conditions provided the protected EGCG **6aa** in 68% yield (Table 1 entry 4). These results suggested that the thiol accelerates cyclization by the removal of the *para*-methoxybenzyl ether. After further optimization of the reaction conditions, we found that treatment of **25a** with trifluoroacetic acid (TFA, 15%) and triethylsilane ($Et_3SiH$, 5%) in dichloromethane at 0°C for 2 hours provided the protected EGCG **6aa** in 72% yield as a single diastereomer (Table 1, entry 1). Both the bromide at the 8-position and a methyloxy group at the 4-position were reduced under the release-and-cyclization conditions. Based on the coupling constant between H2 and H3 ($J_{H2-H3} = < 1$ Hz), the relative stereochemistry between the C2 and C3 positions was determined to be *cis*.

Deprotection of the protected EGCG **6aa** using a continuous-flow hydrogenation reactor (H-Cube) was examined (Table 2). CatCart (70 mm) containing 20% $Pd(OH)_2/C$ was used as the catalyst. A solution of the protected EGCG **6aa** (1 mg mL$^{-1}$ in 1% formic acid in THF/MeOH = 1:1) was injected into the device (the flow ratio was 1 mL min$^{-1}$) at 50°C and 20 bar to provide (±)-EGCG (**2aa**) in 72% yield (Table 2 entry 2). Cleavage of the fluorobenzyl groups was difficult without formic acid (Table 2, entry 1). However, the use of a 5% formic acid solution as a solvent reduced the yield of (±)-EGCG (**2aa**) (28%; Table 2, entry 3). TLC analysis of the reaction mixture indicated that a significant amount of (±)-EGCG (**2aa**) had decomposed under these reaction conditions. The use of the protected EGCG **6aa** from **25b** reduced the recyclability of the catalyst. A trace amount of thiol remaining in **6aa** would poison the catalyst.

Table 2. Deprotection of protected EGCG **6aa** using a continuous-flow hydrogenation reactor (H-Cube).

| Entry | Cat. cartridge | $HCO_2H$ [V V$^{-1}$%] | $T$ [°C] | Cycles | Yield [%] |
|---|---|---|---|---|---|
| 1 | $Pd(OH)_2$ | – | 50 | 3 | 42 |
| 2 | $Pd(OH)_2$ | 1 | 50 | 1 | 72 |
| 3 | $Pd(OH)_2$ | 5 | 50 | 1 | 28 |

The solid-phase synthesis of EGCG is shown in Scheme 6. Treatment of a solution of the aldehyde **15a** (2.0 M) with the *para*-alkyloxybenzyl bromide on polystyrene resin **16** (PS-Wang bromide, 1.6 mmol g$^{-1}$) provided the solid-supported aldehyde **26**.[15] The loading yield was 67%, as estimated by the cleavage from the resin. Treatment of the solid-supported aldehyde **26** with ketone **14a** under basic conditions provided the solid-supported enone **27**. Epoxidation of the solid-supported enone **27** with *tert*-butyl hydrogen peroxide (TBHP) under basic conditions, followed by the regioselective opening of the solid-supported epoxide **28** with methanol in the presence of $Sc(OTf)_3$ without cleavage of the Wang linker afforded the solid-supported α-hydroxyl ketone **29**. Acylation of the resulting alcohol **29** with 3,4,5-tribenzyloxybenzoic acid **11a** afforded the precursor **30** for reductive cyclization. Reactions **26–30** were monitored using infrared analysis of the solid-supported compounds **26–30**. A release and cyclization reaction of **30** was then conducted. Exposure of **30** to trifluoroacetic acid (1%) in dichloromethane in the presence of $Et_3SiH$ (10%) also in dichloromethane, provided the protected EGCG **6aa**. The crude material, after purification by gel permeation chromatography, gave the protected EGCG **6aa** in 47% yield based on the solid-support-

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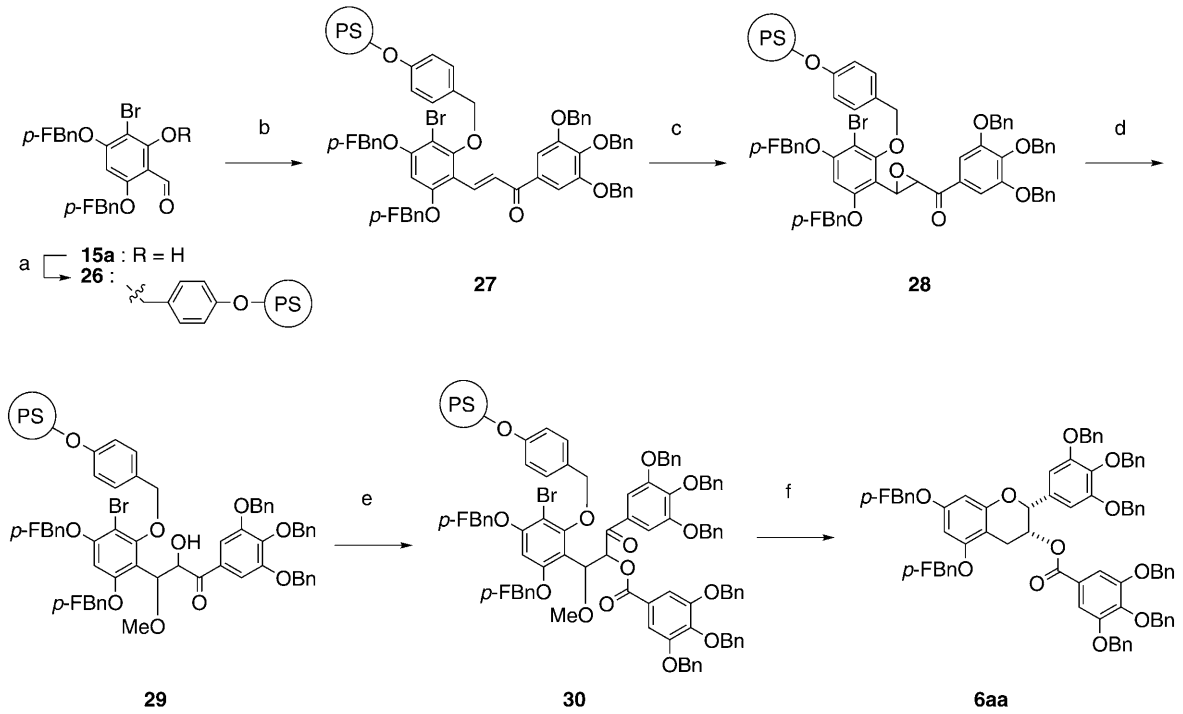


Scheme 6. Reagents and conditions: a) PS-Wang-Br (1.6 mmol g)$^{-1}$, $Cs_2CO_3$ (0,2 M), NaI (0.06 M), DMF, room temperature, 24 hours, 58% based on the resin; b) **11a** (0.5 M), NaOMe (0.1 M), THF/MeOH (4:1), room temperature, 24 hours; c) TBHP (1.5 M), KOH (0.2 M), $CH_2Cl_2$/MeOH:decane (19:2:9), room temperature, 72 hours; d) $Sc(OTf)_3$ (0.01 M), MeOH/$CH_2Cl_2$ (1:1), room temperature, 3 hours; e) **7a** (0.2 M), DIC (0.2 M), DMAP (0.06 M), $CH_2Cl_2$/DMF (4:1), room temperature, 48 hours; f) TFA (5%), $Et_3SiH$ (10%), $CH_2Cl_2$, 0 °C, 6 hours, 47% based on **26**.

ed aldehyde **26**. The previous reported method involving the use of a thiol instead of methanol resulted in a total yield of **6aa** of 19%. These results indicated that the second generation of the solid-phase synthesis of EGCG derivatives was successfully optimized and clearly improved in comparison with the previously reported one.

The synthesis of the methylated EGCG library **2–5** containing 64 compounds was achieved based on the split-and-pool strategy using 64 IRORI MiniKans. The polystyrene Wang-Br resin (70 mg) and a radiofrequency tag were packed in IRORI MiniKans.[13] The content in each of MiniKans™ was encoded by the radiofrequency tag. Coupling of the building blocks **11a–d**, **14a–d**, and **15a–d** was achieved in separate vessels. The processes of workup and other reactions were also achieved in a single vessel. Yields of the isolated protected EGCG library compounds ranged from 29 to 58%. Deprotection of the protected EGCGs with *para*-fluorobenzyl ethers was achieved by utilizing H-Cube under the established conditions. Deprotection of the other benzyl-protected EGCG derivatives did not require the addition of formic acid. The yields of the 64 methylated EGCG derivatives ranged from 33 to 77%. Scheme 7 shows the 64 compounds in the library.

We next examined the effects of library compounds **2ab–2dd**, **3–5**, and (−)-EGCG (**2aa**) on a sample of B16 cells (a mouse melanoma cell line; Figure 1). The B16 cells were incubated with each of the methylated EGCGs **2–5** (0, 1.0, or 5.0 μM) for 96 hours at 37 °C. The viability of the B16 cells incubated with compounds **2–5** was almost 100% as assessed by trypan-blue staining. The growth-inhibitory effects of methylated EGCGs **2–5** on the B16 cells were estimated by the comparison with the number of the remaining cells. Methylation of phenols on the D rings reduced the biological activity of these compounds. On the other hand, most of the 7-methoxy-methylated EGCGs **4** exhibited biological activity comparable to that of the naturally occurring EGCG. These results suggest that 7-OMe-methylated EGCGs **4** are attractive drug candidates because of their enhanced bioavailability.

## Conclusions

The solid-phase synthesis of a combinatorial methylated epigallocatechin gallate (EGCG) library and its biological evaluation has been performed. The solid-phase synthesis of methylated EGCGs involved the preparation of the α-acyloxyketone by coupling of the solid-supported aldehyde with a ketone and an acid. The subsequent release and reductive etherification reaction of the solid-supported α-acyloxyketone provide protected EGCGs in good total yields. Deprotection of the protected EGCGs is achieved by utilizing a continuous-flow hydrogenation reactor (H-Cube). Combinatorial synthesis of 64 methylated EGCGs from four aldehydes, four ketones, and four carboxylic acids was successfully achieved using this method. The 7-OMe EGCGs **4** exhibited growth-inhibitory effects which were comparable to that of the naturally occurring EGCG. Thus, the 7-OMe

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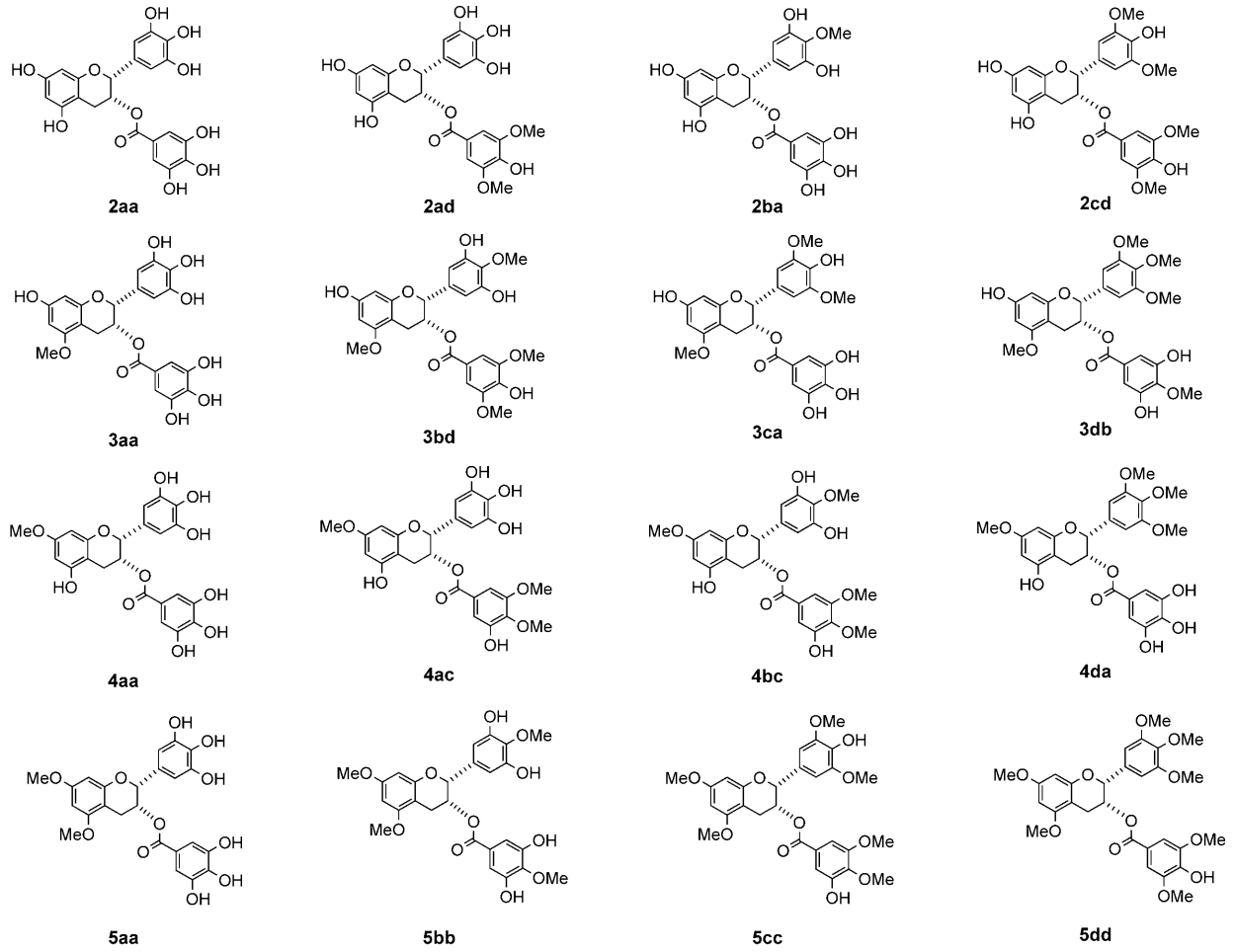


Scheme 7. Structures of the representing compounds of the methylated EGCG library **2–5**.

EGCGs are attractive drug candidates because of their enhanced bioavailability. Synthesis of optically active EGCG derivatives and further biological evaluation of the 7-OMe EGCGs is in progress.

## Experimental Section

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for $^{1}$H, 100 MHz for $^{13}$C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0 ppm) for internal tetramethylsilane for solutions in deuterated chloroform ($CDCl_3$). $^{1}$H NMR spectrum data are reported as follows: $CDCl_3$ (7.26 ppm) or perdeuterated methanol ($CD_3OD$, 3.30 ppm), [$D_6$]acetone (2.00 ppm), dimethyl-d6 sulfoxide ([$D_6$]DMSO, 2.50 ppm). $^{13}$C NMR spectrum data are reported as follows: $CDCl_3$ (77.1 ppm) or [$D_6$]acetone (30.3 ppm) as internal standard for deuterium oxide ($D_2O$). Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constants in Hertz. Zodiac is a parallel synthesizer purchased by TOKYO RIKAKIKAI CO., LTD.

*Syntheses*

**18**: To a solution of **17** (3.04 g, 19.7 mmol) in dimethylformamide (DMF, 55.0 mL) was added $K_2CO_3$ (6.30 g, 45.4 mmol) at 0 °C under argon. After 5 minutes, a solution of 4-fluorobenzyl bromide (4.90 mL, 39.5 mmol) in DMF (5.00 mL) was added to the reaction mixture at the same temperature. After being stirred at room temperature for 12 hours, the reaction mixture was poured into a mixture of an aqueous solution of HCl (1 M) and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with $H_2O$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform), and recrystallized from $CH_2Cl_2$-hexane to afford **18** (5.93 g, 16.0 mmol, 81 %) as a white solid. $R_f$ = 0.48 (hexane/ethyl acetate = 2/1); FTIR (solid): $\tilde{\nu}$ = 3041, 2891, 1600, 1508, 1220, 1096, 814, 773, 646, 502, 494 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 12.5 (s, 1H), 10.1 (s, 1H), 7.38 (dd, $J$ = 8.2 Hz, $J_{H,F}$ = 4.3 Hz, 2H), 7.37 (dd, $J$ = 8.2 Hz, $J_{H,F}$ = 4.3 Hz, 2H), 7.09 (dd, $J$ = 8.2 Hz, $J_{H,F}$ = 8.7 Hz, 4H), 6.10 (s, 1H), 6.04 (s, 1H), 5.04 (s, 2H), 5.02 ppm (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 191.8, 166.8, 166.3, 162.7 × 2 ($J_{C,F}$ = 247 Hz), 162.4, 131.4 ($J_{C,F}$ = 3.0 Hz), 131.3 ($J_{C,F}$ = 3.0 Hz), 129.5 ($J_{C,F}$ = 7.6 Hz), 129.3 ($J_{C,F}$ = 8.4 Hz), 115.7 ($J_{C,F}$ = 21.3 Hz), 106.3, 94.1, 92.3, 69.9, 69.7 ppm; elemental analysis: calcd (%) for $C_{21}H_{16}F_2O_4$: C 68.11, H 4.35; found: C 67.80, H 4.47.

**15a:** To a solution of **18** (2.79 g, 7.54 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise a solution of bromine (385 μL, 7.54 mmol) in $CH_2Cl_2$ (5.0 mL) at 0 °C under argon. After being stirred at the same temperature for 30 minutes, the reaction mixture was poured into a mixture of aqueous solution of $Na_2S_2O_3$ (10 %), saturated aqueous solution of $NaHCO_3$, and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was recrystallized from $CH_2Cl_2$-hexane to afford **15a** (2.97 g, 6.62 mmol, 87 %) as a pale yellow solid. $R_f$ = 0.40 (hexane:ethyl acetate = 2:1); FTIR (solid): $\tilde{\nu}$ = 3048, 2905, 1633,

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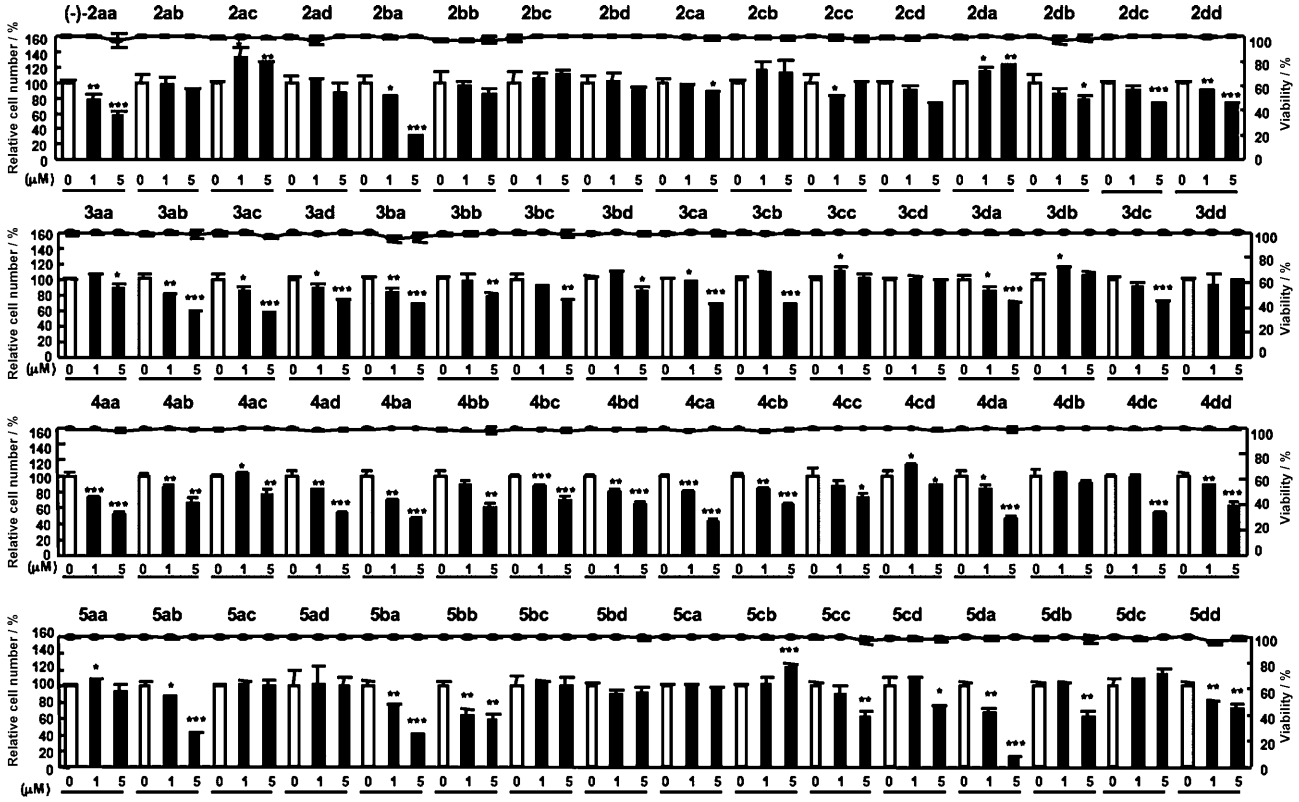


Figure 1. Growth inhibitory effects of the methylated EGCG library **2**–**5** on the B16 cells.

1608, 1509, 1294, 1219, 1197, 1120, 1097, 981, 823, 814, 792, 716 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 12.9$ (s, 1H), 10.2 (s, 1H), 7.40 (dd, $J =$ 8.1 Hz, $J_{H,F} = 5.3$ Hz, 2H), 7.33 (dd, $J = 8.1$ Hz, $J_{H,F} = 5.3$ Hz, 2H), 7.09 (dd, $J = 8.1$ Hz, $J_{H,F} = 8.8$ Hz, 4H), 6.08 (s, 1H), 5.14 (s, 2H), 5.08 ppm (s, 2H); elemental analysis: calcd (%) for $C_{21}H_{15}BrF_2O_4$: C 56.14, H 3.37; found: C 56.26, H 3.37.

**19**: To a solution of **15a** (1.36 g, 3.02 mmol) and $Cs_2CO_3$ (1.97 g, 6.05 mmol) in DMF (15 mL) was added 4-methoxybenzyl bromide (430 μL, 3.18 mmol) and sodium iodide (181 mg, 1.21 mmol) at room temperature under argon. After being stirred at the same temperature for 20 hours, the reaction mixture was poured into a mixture of $H_2O$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with $H_2O$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was recrystallized from diethylether-hexane to afford **19** (1.14 g, 2.00 mmol, 66%) as a pale white solid. $R_f = 0.36$ (hexane:ethyl acetate = 2:1); FTIR (solid): $\tilde{\nu} = 2919$, 1673, 1604, 1584, 1510, 1367, 1249, 1186, 1079, 857, 829, 612 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 10.3$ (s, 1H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.37–7.43 (m, 4H), 7.05–7.13 (m, 4H), 6.92 (d, $J = 8.6$ Hz, 2H), 6.38 (s, 1H), 5.12 (s, 2H), 5.10 (s, 2H), 4.98 (s, 2H), 3.82 ppm (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 187.2$, 164.0, 161.5, 160.7, 160.0, 159.7, 131.5, 131.2, 130.8, 129.0 ($J_{C,F} = 6.1$ Hz), 128.9 ($J_{C,F} = 6.1$ Hz), 128.6, 128.3, 115.9 ($J_{C,F} =$ 21.3 Hz), 115.9 ($J_{C,F} = 21.3$ Hz), 115.2, 114.0, 101.1, 95.6, 76.7, 70.6, 70.6, 55.4 ppm; elemental analysis: calcd (%) for $C_{58}H_{47}BrF_2O_8$: C 70.37, H 4.79; found: C 70.22, H 4.81.

**20:** To a solution of **19** (156 mg, 274 μmol) in tetrahydrofuran (THF, 1.9 mL) was added **14a** (124 mg, 283 μmol) and sodium methoxide (44.5 mg, 830 μmol) at room temperature under argon. After being stirred at the same temperature for 5 hours, the reaction mixture was poured into a mixture of $H_2O$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was recrystallized from $CH_2Cl_2$-hexane to afford **20** (247 mg, 250 μmol, 91%) as a pale yellow solid. $R_f = 0.38$ (hexane:ethyl acetate = 2:1); FTIR (solid): $\tilde{\nu} = 2941$, 1642, 1585, 1513, 1319, 1251, 1183, 1158, 1093, 1030, 829, 749, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 8.16$ (d, $J = 15.8$ Hz, 1H), 7.92 (d, $J = 15.8$ Hz, 1H), 7.31–7.46 (m, 21H, aromatic), 7.23 (s, 2H), 7.10 (dd, $J = 8.2$ Hz, $J_{H,F} = 8.7$ Hz, 2H), 7.04 (dd, $J = 8.2$ Hz, $J_{H,F} = 8.7$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 6.42 (s, 1H), 5.11 (s, 4H), 5.09 (s, 2H), 4.95 (s, 4H), 4.85 (s, 2H), 3.64 ppm (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta =$ 189.7, 162.7 ($J_{C,F} = 248$ Hz), 160.0, 158.9, 157.6, 157.5, 152.7, 142.5, 137.6, 136.7, 135.3, 133.8, 131.6×2 ($J_{C,F} = 3.0$ Hz), 130.8, 129.1 ($J_{C,F} = 7.6$ Hz), 128.9 ($J_{C,F} = 8.4$ Hz), 128.5, 128.2×2, 128.0×2, 127.8, 123.9, 115.9 ($J_{C,F} =$ 21.3 Hz), 115.8 ($J_{C,F} = 21.3$ Hz), 114.0, 113.8, 108.3, 101.1, 96.0, 75.3, 71.2, 70.6×2, 55.2 ppm.

**24**: To a solution of **20** (214 mg, 216 μmol) in $CH_2Cl_2$ (3.3 mL) was added aqueous $H_2O_2$ (30%, 2.40 mL, 21.6 mmol), aqueous KOH (1.1 mL, 3M), and $Bu_4N{\cdot}HSO_4$ (147 mg, 432 μmol) at room temperature under argon. After being stirred at the same temperature for 30 hours, the reaction mixture was poured into a mixture of aqueous $Na_2S_2O_3$ (10%) and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with aqueous $Na_2S_2O_3$ (10%) and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a solution of the above residue in methanol (1.5 mL) and $CH_2Cl_2$ (1.5 mL) was added $Sc(OTf)_3$ (21.2 mg, 43.2 μmol) at room temperature under argon. After being stirred at the same temperature for 3 hours, the reaction mixture was poured into a mixture of saturated aqueous solution of $NaHCO_3$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (2% ethyl acetate in toluene) to afford **24** (180 mg, 174 μmol, 81% in 2 steps, a mixture of diastereomers) as a white solid. $R_f = 0.23$ (hexane:ethyl acetate = 2:1); FTIR (solid): $\tilde{\nu} = 3474$, 3033, 2934, 1674, 1604, 1587, 1513, 1455, 1427, 1372, 1332, 1250, 1226, 1158, 1103, 1031, 827, 751, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (d, $J = 8.2$ Hz, 2H), 7.20–7.37 (m, 19H, aromatic), 7.10 (brt, $J = 8.2$ Hz, 2H), 6.99 (s, 2H), 6.97 (brt, $J =$ 8.2 Hz, 2H), 6.88 (d, $J = 8.2$ Hz, 2H), 6.09 (s, 1H,), 5.83 (brt, $J = 7.3$ Hz,

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1H), 4.72–5.06 (m, 13H), 3.77 (s, 3H), 3.52 (d, $J$=7.3 Hz, 1H), 3.39 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=200.2, 162.7 ($J_{C,F}$=247 Hz), 162.6 ($J_{C,F}$=247 Hz), 159.9, 157.3, 156.7, 152.3, 142.7, 137.5, 136.8, 132.1 ($J_{C,F}$=3.0 Hz), 131.7 ($J_{C,F}$=3.0 Hz), 131.1, 131.0, 129.1 ($J_{C,F}$=8.4 Hz), 128.9 ($J_{C,F}$=8.4 Hz), 128.5, 128.4, 128.2, 128.0, 127.5, 115.8 ($J_{C,F}$= 21.4 Hz), 115.7 ($J_{C,F}$=21.4 Hz), 114.4, 114.1, 107.7, 101.5, 96.0, 79.4, 75.3, 75.1, 73.9, 70.9, 70.8, 70.4, 57.7, 55.3 ppm.

**25**: To a solution of **24** (484 mg, 466 μmol) in pyridine (3.30 mL) was added **11a** (226 mg, 513 μmol), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDCI·HCl, 134 mg, 700 μmol, 1.50 equiv), and 4-dimethylaminopyridine (DMAP, 11.0 mg, 93.3 μmol, 0.200 equiv) at room temperature under argon. After being stirred at the same temperature for 12 hours, the reaction mixture was poured into a mixture of aqueous HCl (1 M) and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with aqueous HCl (1 M), saturated aqueous solution of $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexane) to afford **26** (654 mg, 448 μmol, 96%) as a white solid. $R_f$=0.36 (hexane:ethyl acetate=2:1); FTIR (solid): $\tilde{\nu}$=3033, 2926, 1715, 1685, 1589, 1512, 1455, 1428, 1372, 1327, 1227, 1112, 911, 827, 736, 697, 498 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.59 (d, $J$=8.2 Hz, 2H), 7.52 (s, 2H), 7.08–7.44 (m, 38H, aromatic), 6.96 (brt, $J$=8.7 Hz, 2H), 6.81 (d, $J$=8.2 Hz, 2H), 6.09 (s, 1H), 5.38 (d, $J$=9.2 Hz, 1H), 4.74–5.20 (m, 19H), 3.69 (s, 3H), 3.42 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=166.0, 162.6×2 ($J_{C,F}$= 247 Hz), 159.8, 157.0, 152.7, 152.4, 142.9, 138.0, 137.7, 137.5, 136.8×2, 132.3 ($J_{C,F}$=3.0 Hz), 131.7 ($J_{C,F}$=3.0 Hz), 130.8, 129.2 ($J_{C,F}$=8.4 Hz), 129.0 ($J_{C,F}$=8.4 Hz), 128.8, 128.7×2, 128.5, 128.4, 128.3, 128.2, 128.1×2, 127.9×2, 127.8, 127.7, 125.4, 124.7, 120.8, 115.9 ($J_{C,F}$=21.3 Hz), 115.6 ($J_{C,F}$=21.3 Hz), 114.0, 109.8, 107.8, 99.7, 95.9, 76.7, 76.6, 75.3, 71.4, 71.0, 70.7, 70.3, 58.0, 55.2, 21.6 ppm.

**6aa**: To a solution of **25** (20.9 mg, 14.3 μmol) in $CH_2Cl_2$ (850 μL) was added triethylsilane (100 μL) and trifluoroacetic acid (50 μL) at 0°C under argon. After being stirred at the same temperature for 2 hours, the reaction mixture was poured into a mixture of saturated aqueous $NaHCO_3$ and ethyl acetate at 0°C. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexane) to afford **6aa** (12.5 mg, 103 μmol, 72%) as a white solid. $R_f$=0.44 (hexane:ethyl acetate=2:1); FTIR (solid): $\tilde{\nu}$= 3033, 2927, 1716, 1616, 1593, 1512, 1455, 1430, 1372, 1227, 1114, 911, 826, 752, 697, 504 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.39 (m, 36H, aromatic), 7.01–7.07 (m, 4H, aromatic), 6.73 (s, 2H), 6.38 (d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 5.04 (s, 1H), 4.66–5.01 (m, 16H), 3.10 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (dd, $J_{gem}$= 17.9 Hz, $J$=2.4 Hz, 1H, f); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=164.9, 162.7 ($J_{C,F}$=247 Hz), 162.6 ($J_{C,F}$=247 Hz), 158.8, 158.0, 155.8, 153.0, 152.5, 142.9, 138.6, 137.8, 137.5, 137.0, 136.5, 136.2, 133.2, 132.6 ($J_{C,F}$=3.0 Hz), 132.5 ($J_{C,F}$=3.0 Hz), 129.4 ($J_{C,F}$=8.4 Hz), 129.1 ($J_{C,F}$=8.4 Hz), 128.6×2, 128.5, 128.4, 128.3, 128.2×2, 128.0, 127.9, 127.8, 127.6×2, 125.0, 115.6 ($J_{C,F}$=21.8 Hz), 109.3, 106.9, 101.2, 94.8, 94.1, 78.1, 75.2, 75.1, 71.3, 71.2, 69.6, 69.5, 68.3, 26.3 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{78}H_{64}F_2O_{11}$: 1215.4495 $[M+H]^+$; found: 1215.4495; elemental analysis: calcd (%) for $C_{78}H_{64}F_2O_{11}$: C 77.08, H 5.31; found: C 76.76, H 5.41.

**2aa:** H-Cube system was charged with $Pd(OH)_2$:C CatCart column and heated to 50°C. The hydrogen pressure was set to 20 bar. **6aa** (11.4 mg, 9.38 μmol) was dissolved in methanol:THF (1:1, 10.0 mL), and the solution was pumped through the system with a flow rate of 1 mL min$^{-1}$. After passing through the instrument, the reaction mixture was collected, and the column was washed with methanol (7.00 mL). The collected solutions were combined and concentrated in vacuo. The residue was purified by reverse-phase column chromatography (VARIAN Bond ELUT C18) to afford **2aa** (3.10 mg, 6.76 μmol, 72%) as a white solid. FTIR (solid): $\tilde{\nu}$=3508, 1687, 1608, 1451, 1227, 1029, 730, 549 cm$^{-1}$; $^1$H NMR (400 MHz, [$D_6$]acetone:$D_2O$=1:1): $\delta$=6.86 (s, 2H), 6.51 (s, 2H), 5.89 (s, 2H), 5.27 (brs, 1H), 4.89 (s, 1H), 2.87 (dd, $J_{gem}$=17.4 Hz, $J$=4.4 Hz, 1H), 2.76 ppm (brd, $J_{gem}$=17.4 Hz, 1H); $^{13}$C NMR (100 MHz, [$D_6$]acetone:$D_2O$=1:1): $\delta$=167.3, 157.0, 156.9, 156.8, 146.0, 145.7, 139.3, 133.0, 130.6, 121.0, 110.2, 106.8, 99.0, 96.5, 95.8, 77.9, 70.3, 26.4 ppm.

**26:** PS-Wang-Br resin (Novabiochem, 1.60 mmol g$^{-1}$ loading, 282 mg) was placed in a syringe-shaped vessel. To this reaction vessel was added a suspension of **15a** (360 mg, 800 μmol, 200 μM) in DMF (4.00 mL), $Cs_2CO_3$ (260 mg, 800 μmol, 200 μM), and sodium iodide (30.0 mg, 240 μmol, 60.0 μM) at room temperature. After being shaken for 24 hours, the solvent was removed and the resin was rinsed with DMF (5 min). The remaining resin was washed consecutively with DMF:$H_2O$ (2:1, 5 min x3), DMF (5 min x3), methanol (5 min x3), and $CH_2Cl_2$ (5 min x3), and dried under reduced pressure to afford polymer-supported benzaldehyde **26**. FTIR (solid): $\tilde{\nu}$=3026, 2925, 1677, 1591, 1559, 1520, 1354, 1250, 1189, 1083, 855, 813, 734, 576 cm$^{-1}$.

*Procedure for Cleavage from PS Resins*

Polymer-supported benzaldehyde **9** was placed in a syringe-shaped vessel. To this reaction vessel was added a solution of trifluoroacetic acid (50.0 μL) in $CH_2Cl_2$ (950 μL) at room temperature. After being shaken at the same temperature for 1 hour, the reaction mixture was filtered and washed with $CH_2Cl_2$ (5 min x3). The filtrate was concentrated in vacuo. The residue was purified by short-pad column chromatography.

**27**: **26** was placed in a syringe-shaped vessel. To this reaction vessel was added **14a** (330 mg, 750 μmol, 500 μM) in THF (1.20 mL) at room temperature. After being shaken for 15 minutes, a solution of sodium methoxide (8.10 mg, 150 μmol, 100 μM) in methanol (300 μL) was added to the reaction mixture at room temperature. After being shaken for 24 hours, the solvent was removed, and the resin was rinsed with THF (5 min). The remaining resin was washed consecutively with THF (5 min x3), methanol (5 min x3), and $CH_2Cl_2$ (5 min x3), and dried under reduced pressure to afford polymer-supported chalcone **27**. FTIR (solid): $\tilde{\nu}$=3033, 2919, 1659, 1591, 1555, 1337, 1287, 1188, 1148, 1083, 989, 857, 729, 693 cm$^{-1}$.

**28**: **27** was placed in a syringe-shaped vessel. To this reaction vessel was added *tert*-butyl hydrogen peroxide (TBHP, 5.5 M) in decane (450 μL, 2.25 mmol, 1.50 M), $CH_2Cl_2$ (950 μL), and KOH (3 M) in methanol (100 μL, 300 μmol, 200 μM) at room temperature. After being shaken for 72 hours, the solvent was removed, and the resin was rinsed with $CH_2Cl_2$ (5 min). The remaining resin was washed consecutively with methanol (5 min x4) and $CH_2Cl_2$ (5 min x4), and dried under reduced pressure to afford **28**. FTIR (solid): $\tilde{\nu}$=3028, 2928, 1675, 1608, 1512, 1168, 1113, 1016, 825, 736 cm$^{-1}$.

**29**: **28** was placed in a syringe-shaped vessel. To this reaction vessel was added $CH_2Cl_2$ (700 μL) at room temperature. After being shaken for 15 minutes, the reaction mixture was added with $Sc(OTf)_3$ (6.90 mg, 14.0 μg, 10.0 μM) in methanol (700 μL). After being shaken for 3 hours, the solution was quenched with triethylamine. Then, the solvent was removed and the resin was rinsed with $CH_2Cl_2$ (5 min). The remaining resin was washed consecutively with methanol (5 min x4) and $CH_2Cl_2$ (5 min x4), and dried under reduced pressure to afford **29**. FTIR (solid): $\tilde{\nu}$=3368, 3027, 2927, 1677, 1604, 1512, 1453, 1427, 1376, 1233, 1158, 1030, 827, 730, 706 cm$^{-1}$.

**30**: **29** was placed in a syringe-shaped vessel. To this reaction vessel was added **11a** (100 mg, 225 μmol, 150 μM), http://en.wikipedia.org/wiki/N,N%27-Diisopropylcarbodiimide (DIC, 46.0 μL, 300 μmol, 200 μM), and DMAP (11.0 mg, 90.0 μmol, 60.0 μM) in $CH_2Cl_2$:DMF (4:1, 1.50 mL) at room temperature. After being shaken for 48 hours, the solvent was removed, and the resin was rinsed with DMF (5 mL). The remaining resin was washed consecutively with DMF:$H_2O$ (2:1, 5 mL x3), DMF (5 mL x3), methanol (5 mL x3), and $CH_2Cl_2$ (5 mL x3), and dried under reduced pressure to afford polymer-supported acyloxyketone **30**. FTIR (solid): $\tilde{\nu}$=3029, 2926, 1720, 1686, 1592, 1513, 1453, 1427, 1364, 1326, 1219, 1116, 915, 827, 738, 703, 592 cm$^{-1}$.

**6aa**: To a suspension of **30** packed into MiniKan in $CH_2Cl_2$ (8.50 mL) was added a solution of trifluoroacetic acid (500 μL) and triethylsilane (1.00 mL) at 0°C. After being shaken at the same temperature for 6 hours, the reaction mixture was filtered. The remaining resin was rinsed with ethyl acetate, and the filtrate was concentrated in vacuo. The residue was purified by gel permeation chromatography (GPC) to afford chroman **6aa** (9.20 mg, 7.57 μmol, 47% yield in 5 steps).

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*Solid-Phase Synthesis of the Protected Methylated EGCGs **6–9**.*

**Loading of building blocks 15:** Each MiniKans contained PS-Wang-Br resin (Novabiochem, 1.60 mmol $g^{-1}$ loading, ca. 70.0 mg) and a radiofrequency tag. The 64 MiniKans were encoded and distributed into four vials (A-1,2,3,4: 16 MiniKans in each). To a suspension of a set of MiniKan and DMF solution of **15a–d** (32.0 mL, 0.2 M), was added $Cs_2CO_3$ (0.2 M) and sodium iodide (0.06 M) at room temperature. After being shaken for 24 hours, the reaction mixture was filtered, and the MiniKans™ were rinsed with DMF (80 mL). All MiniKans were pooled together, and washed consecutively with DMF:$H_2O$ (2:1, 80 mL x3), DMF (80 mL x3), methanol (80 mL x3), and $CH_2Cl_2$ (80 mL x3), and dried under reduced pressure.

**Aldol condensation of ketone 14:** The 64 MiniKans were sorted and distributed into four vials (B-1,2,3,4: 16 MiniKans in each). To a suspension of each MiniKan and THF solution of **14a–d** (22.4 mL, 0.3 M) was added a methanol solution of sodium methoxide (4.80 mL, 0.1 M) at room temperature. After being shaken for 24 hours, the reaction mixture was filtered, and the MiniKans were rinsed with THF (80 mL). All MiniKans were pooled together, and washed consecutively with THF (80 mL x3), methanol (80 mL x3), $CH_2Cl_2$ (80 mL x3), and dried under reduced pressure.

**Epoxidation:** The 64 MiniKans in $CH_2Cl_2$ (96.0 mL) were treated with a decan solution of *tert*-butyl hydrogen peroxide (36.5 mL, 5.5 M) and methanol solution of KOH (17.3 mL, 2.5 M) at room temperature. After being shaken for 72 hours, the solvent was removed, and the MiniKans were rinsed with $CH_2Cl_2$ (480 mL). The MiniKans were washed consecutively with methanol (480 mL x4) and $CH_2Cl_2$ (480 mL x4), and dried under reduced pressure.

**Epoxide opening:** The 64 MiniKans in $CH_2Cl_2$ (64.0 mL) were treated with a methanol suspension of $Sc(OTf)_3$ (64.0 mL, 0.01 M). After being shaken for 3 hours, the solution was quenched by the addition of triethylamine. Then, the solvent was removed, and the MiniKans were rinsed with $CH_2Cl_2$ (480 mL). The MiniKans was washed consecutively with methanol (480 mL x4) and $CH_2Cl_2$ (480 mL x4), and dried under reduced pressure.

**Esterification with 11:** The 64 MiniKans were sorted and distributed into four vials (D-1,2,3,4: 16 MiniKans in each). To a suspension of each MiniKan and a $CH_2Cl_2$:DMF (4:1) solution of **11** (32.0 mL, 0.2 M) was added DIC (0.2 M) and DMAP (0.06 M) at room temperature. After being shaken for 36 hours, the reaction mixture was filtered and rinsed with DMF (80 mL). All MiniKans™ were pooled together, and washed consecutively with DMF:$H_2O$ (2:1, 80 mL x3), DMF (80 mL x3), methanol (80 mL x3), and $CH_2Cl_2$ (80 mL x3), and dried under reduced pressure.

**Release and reductive etherification:** The 64 MiniKans were sorted and distributed into 64 reaction vessels containing a magnetic stirring bar in each. Then, each vessel was inserted into a Zodiac, and a solution of trifluoroacetic acid (500 μL) and triethylsilane (1.00 mL) in $CH_2Cl_2$ (8.50 mL) was added at 0 °C. After being stirred for 6 hours, the reaction mixtures were filtered, diluted with ethyl acetate, and concentrated in vacuo. The residues were purified by column chromatography (hexane:ethyl acetate) to afford EGCG analogues.

**6ab** (54%): $R_f$=0.43 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.39 (m, 31H,aromatic), 6.99–7.07 (m, 4H, aromatic), 6.71 (s, 2H), 6.39(d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz,1H), 5.65 (brs, 1H), 4.94–5.03 (m, 11H), 4.74 (d, $J$=11.6 Hz, 2H), 4.62 (d, $J$=11.6 Hz, 2H), 3.77 (s, 3H), 3.09 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=164.8, 162.6×2 ($^1J_{C,F}$=247 Hz), 158.8, 158.0, 155.8, 153.0, 152.1,143.9, 138.6, 137.8, 137.0, 136.6, 136.5, 133.2, 132.6 ($^4J_{C,F}$=2.3 Hz), 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=8.4 Hz), 128.7, 128.6, 128.5, 128.4, 128.3×2, 128.2, 127.8×2, 127.7, 127.6×2, 127.5, 124.7, 115.6 ($^2J_{C,F}$=22.1 Hz), 109.3, 106.9, 101.2, 94.8, 94.1, 78.1, 75.2, 71.3, 71.1, 69.6, 69.5, 68.2, 60.9, 26.4 ppm.

**6ac** (56%): $R_f$=0.36 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.18–7.38 (m, 26H, aromatic), 7.04×2 (t, $J$=8.7 Hz, 4H), 6.74 (s, 2H, c), 6.35(d, $J$=2.4 Hz, 1H), 6.28 (d, $J$=2.4 Hz, 1H), 5.65 (brs, 1H), 5.07 (s, 1H), 4.93–5.05 (m, 8H), 4.84 (d, $J$=11.6 Hz, 2H), 4.71 (d, $J$=11.6 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 162.6×2 ($^1J_{C,F}$=247 Hz), 158.8, 158.0, 155.8, 153.3, 153.0, 151.8, 143.3, 137.8, 137.0, 136.5, 133.3, 132.6 ($^4J_{C,F}$=1.7 Hz), 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=8.4 Hz), 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 124.9, 115.6×2 ($^2J_{C,F}$=22.1 Hz), 109.2, 107.5, 106.9, 101.2, 94.8, 94.7, 78.0, 75.2, 71.4, 71.1, 69.6, 68.4, 60.9, 56.4, 26.3 ppm.

**6ad** (43%): $R_f$=0.39 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.42 (m, 26H, aromatic), 7.08 (t, $J$=8.7 Hz, 2H), 7.05 (t, $J$=8.7 Hz, 2H), 6.80 (s, 2H, c), 6.31 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.63 (brs, 1H), 5.07 (s, 1H), 4.93–5.02 (m, 10H), 4.85 (d, $J$=11.6 Hz, 2H), 3.76 (s, 6H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.06 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 164.4, 158.7, 157.9, 155.7, 153.3, 153.0, 141.7, 138.7, 137.5, 137.0, 133.4, 132.7 ($^4J_{C,F}$=3.4 Hz), 132.6 ($^4J_{C,F}$=3.9 Hz), 129.4 ($^3J_{C,F}$=7.8 Hz), 129.1 ($^3J_{C,F}$=7.8 Hz), 128.6, 128.5, 128.3, 128.2, 128.0×2, 127.9, 127.6, 127.5, 125.2, 115.6×2 ($^2J_{C,F}$=21.8 Hz), 107.4, 107.0, 101.1, 94.8, 94.0, 77.8, 75.3, 75.0, 71.6, 69.6, 69.5, 68.7, 56.4, 26.3 ppm.

**6ba** (41%): $R_f$=0.46 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.22–7.37 (m, 31H, aromatic), 7.04 (t, $J$=8.7 Hz, 2H), 7.02 (t, $J$=8.7 Hz, 2H), 6.71 (s, 2H), 6.36 (d, $J$=1.9 Hz, 1H), 6.29 (d, $J$=1.9 Hz, 1H), 5.63 (brs, 1H, f), 5.05 (s, 1H), 4.92–5.03 (m, 10H), 4.82 (d, $J$=11.6 Hz, 2H), 4.71 (d, $J$=11.6 Hz, 2H), 3.80 (s, 3H), 3.09 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H, i), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.3, 158.7, 157.9, 155.7, 152.6, 152.4, 142.8, 139.5, 137.4, 136.9, 136.4, 132.9, 132.5 ($^3J_{C,F}$=3.4 Hz),, 129.3 ($^3J_{C,F}$=7.8 Hz), 129.0 ($^3J_{C,F}$=7.8 Hz), 128.5×2, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4×2, 127.3, 124.8, 115.5 ($^2J_{C,F}$=21.8 Hz), 109.2, 106.9, 101.1, 94.7, 94.0, 77.9, 75.0, 71.2, 71.1, 69.5, 69.4, 68.2, 60.9, 26.2 ppm.

**6bb** (58%): $R_f$=0.41 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.21–7.38 (m, 26H, aromatic), 7.04 (t, $J$=8.7 Hz, 2H), 7.02 (t, $J$=8.7 Hz, 2H), 6.68 (s, 2H), 6.36 (d, $J$=1.4 Hz, 1H), 6.29 (d, $J$=1.4 Hz, 1H), 5.63 (brs, 1H), 5.05 (s, 1H), 4.98–5.02 (m, 8H), 4.77 (d, $J$=11.6 Hz, 2H), 4.66 (d, $J$=11.6 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 162.5 ($^1J_{C,F}$=246 Hz), 158.7, 158.0, 155.8, 152.7, 152.1, 143.9, 139.7, 137.0, 136.5, 132.9, 132.6 ($^4J_{C,F}$=2.8 Hz), 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=7.8 Hz), 128.7, 128.5×2, 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 124.7, 115.6 ($^2J_{C,F}$=21.8 Hz), 109.3, 107.0, 101.2, 94.8, 94.0, 78.1, 71.2, 71.1, 69.6, 69.4, 68.2, 60.9, 26.4 ppm.

**6bc** (57%): $R_f$=0.32 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.39 (m, 21H, aromatic), 7.04 (brt, $J$=8.7 Hz, 4H), 6.72 (s, 2H), 6.33 (d, $J$=1.9 Hz, 1H), 6.27 (d, $J$=1.9 Hz, 1H), 5.63 (brs, 1H), 5.00 (s, 1H), 4.98–5.04 (m, 6H), 4.86 (d, $J$=11.6 Hz, 2H), 4.74 (d, $J$=11.6 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 6H), 3.09 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 161.4, 158.8, 158.0, 155.8, 153.3,152.7, 151.8, 143.3, 139.8, 137.0, 136.5, 133.0, 132.6, 129.4 ($^3J_{C,F}$=7.6 Hz), 129.1 ($^3J_{C,F}$=7.6 Hz), 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 124.9, 115.7 ($^2J_{C,F}$=22.1 Hz), 115.5 ($^2J_{C,F}$=21.3 Hz), 109.2, 107.5, 107.1, 101.2, 94.8, 94.1, 77.9, 77.6, 71.4, 71.1, 69.5×2, 68.4, 61.0, 56.4, 56.3, 25.7 ppm.

**6bd** (57%): $R_f$=0.36 (hexane:ethyl acetate=2:1); $^1$H NMR (270 MHz, $CDCl_3$): $\delta$=7.29–7.42 (m, 19H, aromatic), 7.18 (s, 2H), 7.07 (t, $J$=8.6 Hz, 2H7.04 (t, $J$=8.6 Hz, 2H), 6.78 (s, 2H), 6.29 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.61 (brs, 1H), 5.04 (s, 1H), 4.86–5.02 (m, 10H), 3.83 (s, 3H), 3.76 (s, 6H), 3.10 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.3, 162.6×2 ($^1J_{C,F}$=247 Hz), 158.7, 157.9, 155.7, 153.3, 152.7, 141.7, 139.8, 137.4, 137.0, 133.1, 132.7, 132.6 ($^4J_{C,F}$=3.4 Hz), 129.4 ($^3J_{C,F}$=7.8 Hz), 129.1 ($^3J_{C,F}$=8.4 Hz), 128.6, 128.4, 128.3×2, 128.0×2, 127.5, 127.4, 125.2, 115.6×2 ($^2J_{C,F}$=21.8 Hz), 107.4, 107.1, 101.1, 94.8, 94.0, 77.7, 75.0, 71.5, 69.6, 69.4, 68.6, 61.0, 56.4, 26.0 ppm.

**6ca** (52%): $R_f$=0.42 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.26–7.43 (m, 26H, aromatic), 7.05 (t, $J$=8.7 Hz, 2H), 7.03 (t, $J$=8.7 Hz, 2H), 6.60 (s, 2H), 6.40 (d, $J$=1.9 Hz, 1H), 6.29 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.93–5.08 (m, 13H), 3.50 (s, 6H), 3.11 (dd,

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$J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.4 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 162.5 ($^1J_{C,F}$=247 Hz), 158.7, 157.9, 155.7, 153.5, 152.3, 142.5, 137.7, 137.3, 137.0, 136.5, 133.4, 132.5, 129.3 ($^3J_{C,F}$=8.4 Hz), 129.0 ($^3J_{C,F}$=8.4 Hz), 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 124.9, 115.5 ($^2J_{C,F}$=21.8 Hz), 109.2, 104.2, 101.1, 94.7, 94.0, 78.1, 75.1, 74.9, 71.1, 69.5, 69.4, 68.3, 55.9, 26.3 ppm.

**6cb** (56%): $R_f$=0.41 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.42 (m, 21H, aromatic), 7.12 (t, $J$=8.7 Hz, 2H), 7.03 (t, $J$=8.7 Hz, 2H), 6.60 (s, 2H), 6.41 (d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.92–5.07 (m, 11H), 3.89 (s, 3H, h), 3.50 (s, 6H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.8 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 160.8, 158.8, 158.0, 155.8, 153.6, 152.3, 152.1, 144.0, 137.8, 137.1, 136.6, 133.3, 132.6, 129.4 ($^3J_{C,F}$=8.4 Hz), 129.3 ($^3J_{C,F}$=8.4 Hz), 128.7, 128.5, 128.2, 127.8×2, 127.6, 124.8, 115.6 ($^2J_{C,F}$=21.8 Hz), 110.4, 109.5, 104.2, 101.2, 94.9, 94.1, 78.2, 75.0, 71.2, 69.6, 69.5, 68.3, 61.1, 56.0, 26.4 ppm.

**6cc** (47%): $R_f$=0.35 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.16–7.43 (m, 16H, aromatic), 7.04 (brt, $J$=8.7 Hz, 4H), 6.63 (s, 2H), 6.38 (d, $J$=1.9 Hz, 1H), 6.28 (d, $J$=1.9 Hz, 1H), 5.67 (brs, 1H, f), 4.93–5.06 (m, 9H), 3.88 (s, 3H), 3.81 (s, 3H), 3.57 (s, 6H, j), 3.12 (dd, $J_{gem}$=17.9 Hz, $J$=4.9 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 164.4, 158.8, 158.0, 155.8, 153.6, 153.2, 151.9, 144.1, 143.4, 137.8, 137.1, 136.6, 133.4, 132.6, 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=7.8 Hz), 128.7×2, 128.5, 128.2×2, 127.9, 124.9, 115.6 ($^2J_{C,F}$=22.9 Hz), 109.3, 107.5, 104.2, 101.2, 94.9, 94.1, 78.1, 75.1, 71.2, 69.6, 69.5, 68.5, 61.0, 56.4, 56.1, 26.3 ppm.

**6cd** (55%): $R_f$=0.37 (hexane:ethyl acetate=2:1); FTIR (neat): $\tilde{\nu}$=2939, 1715, 1618, 1592, 1512, 1463, 1417, 1360, 1333, 1225, 1183, 1149, 1128, 1039, 826, 756, 734, 698 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.43 (m, 14H, aromatic), 7.16 (s, 2H), 7.03–7.10 (m, 4H, aromatic), 6.67 (s, 2H), 6.33 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 5.08 (s, 1H), 5.05 (s, 2H, Bn), 5.00 (s, 2H, Bn), 4.98 (s, 2H, Bn), 4.95 (s, 2H, Bn), 3.78 (s, 6H), 3.65 (s, 6H), 3.12 (dd, $J_{gem}$=17.9 Hz, $J$=4.8 Hz, 1H), 3.06 ppm (d, $J_{gem}$=17.9 Hz, 1H).

**6da** (48%): $R_f$=0.38 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.26–7.36 (m, 21H, aromatic), 7.00–7.06 (m, 4H, aromatic), 6.60 (s, 2H), 6.39 (d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.98–5.08 (m, 11H), 3.78 (s, 3H), 3.52 (s, 6H), 3.11 (dd, $J_{gem}$=17.4 Hz, $J$=3.9 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.4 Hz, 1H).

**6db** (53%): $R_f$=0.36 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.40 (m, 16H, aromatic), 7.04 (t, $J$=8.7 Hz, 2H), 7.02 (t, $J$=8.7 Hz, 2H), 6.60 (s, 2H), 6.40 (d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz, 1H), 5.67 (brs, 1H), 5.02 (s, 1H), 4.99–5.06 (m, 8H, Bn), 3.89 (s, 3H), 3.78 (s, 3H), 3.53 (s, 6H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 162.6, 158.8, 158.0, 155.8, 153.2, 152.1, 144.0, 140.5, 138.1, 136.6, 133.1, 132.6, 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=8.4 Hz), 128.7, 128.2, 127.8, 124.8, 115.6 ($^2J_{C,F}$=21.8 Hz), 109.4, 104.1, 101.2, 94.8, 94.1, 78.2, 71.1, 69.6, 69.5, 68.3, 61.1, 60.9, 56.0, 26.4 ppm.

**6dc** (49%): $R_f$=0.30 (hexane:ethyl acetate=2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.26–7.40 (m, 11H, aromatic), 7.04 (t, $J$=8.7 Hz, 4H), 6.64 (s, 2H), 6.38 (d, $J$=2.4 Hz, 1H), 6.28 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 4.99–5.08 (m, 7H), 3.88 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.60 (s, 6H), 3.12 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.06 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 160.7, 158.7, 158.0, 155.8, 153.2, 151.8, 143.3, 138.0, 136.5, 133.2, 132.6 ($^4J_{C,F}$=2.2 Hz), 132.5 ($^4J_{C,F}$=2.2 Hz), 129.4 ($^3J_{C,F}$=8.4 Hz), 129.1 ($^3J_{C,F}$=8.4 Hz), 128.7, 128.3, 127.9, 124.9, 115.6×2 ($^2J_{C,F}$=21.2 Hz), 109.2, 107.5, 104.1, 101.2, 94.8, 94.1, 78.1, 71.1, 69.6, 69.5, 68.4, 61.0, 60.9, 56.4, 56.0, 26.4 ppm.

**6dd** (50%): $R_f$=0.31 (hexane:ethyl acetate=2:1); FTIR (neat): $\tilde{\nu}$=3010, 2939, 2841, 1715, 1621, 1593, 1512, 1463, 1417, 1361, 1334, 1228, 1183, 1149, 1129, 1040, 1014, 827, 756, 699, 506 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.44 (m, 9H, aromatic), 7.16 (s, 2H), 7.08 (t, $J$=8.7 Hz, 2H), 7.04 (t, $J$=8.7 Hz, 2H), 6.68 (s, 2H, d), 6.33 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 5.08 (s, 1H), 5.05 (s, 2H), 5.00 (s, 2H), 4.98 (s, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.69 (s, 6H), 3.12 (dd, $J_{gem}$=18.4 Hz, $J$=4.8 Hz, 1H), 3.06 ppm (dd, $J_{gem}$=18.4 Hz, $J$=2.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 162.6 ($^1J_{C,F}$=247 Hz), 162.5 ($^1J_{C,F}$=247 Hz), 158.7, 157.9, 155.8, 153.3×2, 141.5, 138.1, 137.3, 133.3, 132.6 ($^4J_{C,F}$=1.7 Hz), 132.5 ($^4J_{C,F}$=1.7 Hz), 129.4 ($^3J_{C,F}$=7.8 Hz), 129.1 ($^3J_{C,F}$=7.8 Hz), 128.5, 128.3, 128.1, 125.2, 115.6×2 ($^2J_{C,F}$=21.8 Hz), 107.4, 104.1, 101.1, 94.8, 94.0, 78.0, 69.6, 69.5, 68.6, 60.9, 56.4, 56.1, 26.2 ppm.

**7aa** (40%): $R_f$=0.68 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.42 (m, 37H, aromatic), 6.73 (s, 2H), 6.38 (d, $J$=1.9 Hz, 1H), 6.30 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.95–5.04 (m, 9H), 4.90 (s, 2H, Bn), 4.80 (d, $J_{gem}$=11.6 Hz, 2H), 4.67 (d, $J_{gem}$=11.6 Hz, 2H), 3.80 (s, 3H), 3.10 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 158.9×2, 155.5, 152,8, 152.3, 142.7, 138.4, 137.7, 137.4, 136.8×2, 136.4, 133.3, 128.6, 128.5, 128.4×2, 128.3, 128.2, 128.1, 128.0×3, 127.8, 127.7, 127.5×2, 127.4, 124.9, 109.1, 106.6, 100.5, 94.2, 92.7, 77.9, 75.1, 75.0, 71.1, 71.0, 70.1, 68.2, 55.4, 26.0 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{72}H_{66}NO_{11}$: 1120.4636 $[M+NH_4]^+$; found: 1120.4679.

**7ab** (38%): $R_f$=0.66 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$=2964, 1716, 1621, 1591, 1496, 1427, 1370, 1261, 1213, 1102, 1047, 801, 736, 697 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.41 (m, 32H, aromatic), 6.71 (s, 2H), 6.38(d, $J$=2.4 Hz, 1H), 6.26 (d, $J$=2.4 Hz, 1H), 5.65 (brs, 1H), 4.94–5.06 (m, 9H), 4.75 (d, $J_{gem}$=11.6 Hz, 2H), 4.62 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.80 (s, 3H), 3.77 (s, 3H), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.98 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.1, 159.0, 155.6, 152,9, 152.1, 143.7, 138.5, 137.8, 137.0, 136.9, 136.5, 133.3, 128.7, 128.6, 128.4, 128.1×2, 127.8×2, 127.6×3, 127.5, 124.8, 109.2, 106.7, 100.6, 94.3, 92.8, 78.0, 75.2, 71.2, 71.0, 70.2, 68.3, 60.9, 55.5, 26.2 ppm; HRMS (ESI-TOF): $m/z$ (%)calcd for $C_{66}H_{62}NO_{11}$: 1044.4323 $[M+NH_4]^+$; found: 1044.4332.

**7ac** (39%): $R_f$=0.61 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.17–7.43 (m, 27H, aromatic), 6.75 (s, 2H), 6.35 (d, $J$=2.4 Hz, 1H), 6.24 (d, $J$=2.4 Hz, 1H), 5.65 (brs, 1H), 4.96–5.14 (m, 7H), 4.84 (d, $J_{gem}$=11.6 Hz, 2H), 4.71 (d, $J_{gem}$=11.6 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.77 (s, 3H), 3.07 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (dd, $J_{gem}$=17.9 Hz, $J$=3.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 159.0×2, 155.5, 153,2, 152.9, 151.8, 137.8, 137.0, 136.9, 136.5, 133.4, 128.7, 128.6, 128.5, 128.4, 128.2×2, 128.1, 128.0, 127.9×2, 127.8, 127.6×3, 127.5, 124.9, 109.1, 107.3, 106.8, 100.5, 94.3, 92.8, 77.9, 75.2, 71.3, 71.0, 70.2, 68.5, 60.9, 56.3, 55.5, 26.1 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4053.

**7ad** (41%): $R_f$=0.63 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=d 7.18–7.45 (m, 27H, aromatic), 6.80 (s, 2H), 6.30(d, $J$=2.4 Hz, 1H), 6.21 (d, $J$=2.4 Hz, 1H,), 5.63 (brs, 1H), 4.84–5.06 (m, 11H), 3.78 (s, 3H), 3.75 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.3, 159.0, 155.5, 153,3, 152.9, 141.5, 138.5, 137.8, 137.4, 137.0×2, 133.5, 128.7, 128.6, 128.5, 128.3×2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6×2, 127.5, 125.3, 107.3, 106.9, 100.5, 92.8, 77.0, 75.2, 75.0, 71.5, 70.2, 68.7, 56.4, 55.5, 25.9 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4009.

**7ba** (44%): $R_f$=0.66 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.41 (m, 32H, aromatic), 6.71 (s, 2H), 6.35 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.63 (brs, 1H), 5.04 (s, 1H, e), 4.91–5.03 (m, 8H, Bn), 4.82 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.71 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.80 (s, 3H), 3.80 (s, 3H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.98 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 159.0×2, 155.6, 152,7, 152.4, 142.8, 139.6, 137.5, 137.0, 136.9, 136.5, 133.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 125.0, 109.2, 106.9, 100.6, 94.3, 92.8, 77.9, 75.1, 71.2, 71.1, 70.2, 68.3, 60.9, 55.5, 26.1 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{66}H_{62}NO_{11}$: 1044.4323 $[M+NH_4]^+$; found: 1044.4333.

**7bb** (49%): $R_f$=0.64 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.46 (m, 27H, aromatic), 6.69 (s, 2H), 6.36 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.63 (brs, 1H), 5.06 (s, 1H), 4.99–5.03 (m, 6H), 4.77 (d, $J_{gem}$=11.6 Hz, 2H), 4.65 (d, $J_{gem}$=11.6 Hz, 2H), 3.80 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.03 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.97 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.1×2, 155.6, 152,7, 152.1, 143.9, 139.7, 137.1, 136.9, 136.6, 133.1, 128.7, 128.5×2, 128.1, 127.8×2, 127.6, 127.5×2, 127.4, 124.8,

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109.4, 107.0, 100.6, 94.4, 92.9, 78.0, 71.3, 71.1, 70.3, 68.3, 60.9, 55.5, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4009.

**7bc** (45%): $R_f$=0.57 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.17–7.42 (m, 22H, aromatic), 6.72 (s, 2H), 6.33 (d, $J$=2.4 Hz, 1H), 6.23 (d, $J$=2.4 Hz, 1H,), 5.63 (brs, 1H), 5.01–5.03 (m, 4H, Bn), 5.00 (s, 1H), 4.86 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.74 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81(s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.98 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 159.0, 155.6, 153.2, 152,7, 151.8, 143.2, 139.7, 137.0, 136.9, 136.5, 133.1, 128.7, 128.6, 128.5×2, 128.2, 128.1, 127.9, 127.5×2, 127.4, 124.9, 109.2, 107.4, 107.0, 100.6, 94.3, 92.8, 77.8, 71.3, 71.1, 70.2, 68.4, 60.9×2, 56.3, 55.5, 26.0 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3698.

**7bd** (48%): $R_f$=0.59 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.26–7.45 (m, 20H, aromatic), 7.17 (s, 2H), 6.78 (s, 2H), 6.28 (d, $J$=1.9 Hz, 1H), 6.21 (d, $J$=1.9 Hz, 1H), 5.60 (brs, 1H), 4.87–5.04 (m, 9H), 3.83 (s, 3H), 3.78 (s, 3H), 3.75 (s, 6H), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 158.8, 155.3, 153.2, 152,5, 141.4, 139.6, 137.3, 136.9, 136.8, 133.2, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.5, 127.4, 127.3, 125.2, 107.2, 106.9, 100.4, 94.1, 92.6, 77.5, 74.9, 71.3, 70.1, 68.6, 60.9, 56.2, 55.4, 25.7 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3697.

**7ca** (41%): $R_f$=0.57 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 3031, 2938, 1716, 1621, 1593, 1499, 1455, 1429, 1369, 1328, 1214, 1148, 1124, 1030, 1002, 911, 815, 752, 697, 481 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.42 (m, 27H, aromatic), 6.61 (s, 2H), 6.39 (d, $J$= 1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 5.02–5.07 (m, 9H), 4.93 (s, 2H), 3.80 (s, 3H), 3.50 (s, 6H), 3.07 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.6, 158.7×2, 155.3, 153.2, 152,1, 142.2, 137.5, 137.1, 136.6, 136.2, 133.1, 128.8, 128.3×2, 128.2, 128.0, 127.9, 127.8, 127.6, 127.3, 125.1, 124.7, 108.9, 103.8, 100.3, 94.0, 92.5, 77.8, 74.8, 74.7, 70.8, 69.9, 68.1, 55.7, 55.2, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4010.

**7cb** (43%): $R_f$=0.51 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 3031, 2938, 1716, 1620, 1593, 1499, 1455, 1428, 1370, 1329, 1216, 1148, 1124, 1030, 1002, 910, 842, 814, 753, 698, 477 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.42 (m, 22H, aromatic), 6.60 (s, 2H), 6.40 (d, $J$= 1.9 Hz, 1H), 6.26 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 5.02–5.06 (m, 7H), 4.92 (s, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 3.50 (s, 6H), 3.06 (dd, $J_{gem}$= 17.9 Hz, $J$=4.3 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.7, 159.0, 158.9, 155.5, 153.4, 151,9, 143.7, 137.7, 136.8, 136.4, 133.3, 128.6, 128.4, 128.1, 128.0, 127.7×2, 127.5, 124.7, 109.2, 103.9, 100.5, 94.2, 92.7, 78.0, 74.9, 71.0, 70.1, 68.3, 61.0, 55.8, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3697.

**7cc** (40%): $R_f$=0.38 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 2936, 1715, 1620, 1592, 1500, 1454, 1421, 1358, 1330, 1218, 1147, 1122, 1029, 1001, 814, 753, 698 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.24–7.43 (m, 16H), 7.16 (d, $J$=1.4 Hz, 1H), 6.63 (s, 2H), 6.37 (d, $J$=2.4 Hz, 1H), 6.24 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 5.02–5.09 (m, 5H), 4.93 (s, 2H, Bn), 3.87 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.57 (s, 6H), 3.07 (dd, $J_{gem}$= 17.4 Hz, $J$=4.3 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.4 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 158.9×2, 155.5, 153.4, 153,0, 151.7, 143.0, 137.7, 136.8, 136.4, 133.4, 128.6×2, 128.4, 128.1×2, 128.0, 127.8, 127.5, 124.9, 109.0, 107.3, 103.9, 100.4, 94.2, 92.7, 77.9, 74.9, 71.0, 70.1, 68.4, 60.9, 56.2, 55.9, 55.4, 26.0 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+NH_4]^+$; found: 816.3380.

**7cd** (44%): $R_f$=0.39 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.43 (m, 15H, aromatic), 7.16 (s, 2H), 6.67 (s, 2H), 6.33 (d, $J$=2.4 Hz, 1H), 6.21 (d, $J$=2.4 Hz, 1H), 5.65 (brs, 1H), 5.08 (s, 1H), 5.05 (s, 4H, Bn), 4.95 (s, 2H, Bn), 3.78 (s, 3H), 3.77 (s, 6H), 3.65 (s, 6H), 3.08 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$= 2.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+NH_4]^+$; found: 816.3384.

**7da** (47%): $R_f$=0.40 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 3031, 2937, 1716, 1620, 1592, 1499, 1455, 1429, 1367, 1328, 1214, 1148, 1123, 1029, 1006, 910, 814, 753, 697 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.41 (m, 22H, aromatic), 6.61 (s, 2H), 6.39 (d, $J$=2.4 Hz, 1H), 6.26 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 4.99–5.07 (m, 9H), 3.80 (s, 3H), 3.78 (s, 3H), 3.53 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 158.9×2, 155.5, 153.1, 152,2, 142.3, 137.8, 137.2, 136.7, 136.4, 133.2, 128.5×2, 128.2, 128.1, 128.0, 127.7, 127.5, 124.9, 109.0, 103.9, 100.4, 94.2, 92.7, 78.0, 75.0, 71.0, 70.1, 68.3, 60.7, 55.8, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3724.

**7db** (46%): $R_f$=0.34 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 2939, 1716, 1620, 1592, 1499, 1455, 1428, 1369, 1329, 1216, 1148, 1123, 1037, 1004, 814, 754, 698 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.41 (m, 15H, aromatic), 7.25 (s, 2H), 6.60 (s, 2H), 6.40 (d, $J$=2.4 Hz, 1H), 6.26 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 5.01–5.09 (m, 7H), 3.88 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.53 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.00 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.7, 159.0, 158.9, 155.5, 153.1, 151,9, 143.7, 137.8, 136.7, 136.4, 133.2, 128.6, 128.1, 128.0, 127.7, 127.5, 124.7, 109.1, 103.9, 100.5, 94.2, 92.7, 78.0, 70.9, 70.1, 68.2, 61.0, 60.7, 55.8, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+NH_4]^+$; found: 816.3384.

**7dc** (49%): $R_f$=0.27 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$= 2939, 1716, 1620, 1593, 1500, 1455, 1421, 1358, 1331, 1219, 1148, 1123, 1037, 1005, 814, 756, 698 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.26–7.43 (m, 11H, aromatic), 7.15 (d, $J$=1.9 Hz, 1H), 6.64 (s, 2H), 6.37 (d, $J$= 1.9 Hz, 1H,), 6.24 (d, $J$=1.9 Hz, 1H), 5.67 (brs, 1H), 5.02–5.09 (m, 5H), 3.87 (s, 3H), 3.80 (s, 3H), 3.79×2 (s, 3H), 3.60 (s, 6H), 3.07 (dd, $J_{gem}$= 17.4 Hz, $J$=4.4 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 159.0, 158.9, 155.5, 153.2, 151,7, 143.1, 137.9, 136.8, 136.5, 133.3, 128.7×2, 128.2, 128.1, 127.9, 127.6, 124.9, 109.0, 107.3, 103.9, 100.5, 94.2, 92.8, 78.0, 71.0, 70.2, 68.5, 61.0, 60.8, 56.3, 55.9, 55.5, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{42}H_{46}NO_{11}$: 740.3071 $[M+NH_4]^+$; found: 740.3073.

**7dd** (43%): $R_f$=0.28 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.43 (m, 10H, aromatic), 7.16 (s, 2H), 6.68 (s, 2H, b), 6.32 (d, $J$=1.9 Hz, 1H), 6.21 (d, $J$=1.9 Hz, 1H), 5.65 (brs, 1H), 5.07 (s, 1H), 5.05 (s, 4H, Bn), 3.80 (s, 3H), 3.78 (s, 3H), 3.77 (s, 6H), 3.69 (s, 6H j), 3.05 (brs, 1H), 3.04 ppm (brs, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$= 165.1, 158.8×2, 155.4, 153.1×2, 141.1, 137.8, 137.2, 136.8, 133.3, 128.6, 128.4, 128.2, 128.0×2, 127.5 125.1, 107.1, 103.8, 100.4, 94.1, 92.6, 77.8, 74.9, 70.1, 68.6, 60.8, 56.2, 55.9, 55.4, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{42}H_{46}NO_{11}$: 740.3071 $[M+NH_4]^+$; found: 740.3101.

**8aa** (39%): $R_f$=0.66 (toluene:ethyl acetate=9:1); FTIR (neat): $\tilde{\nu}$=3031, 2935, 1717, 1620, 1592, 1499, 1454, 1429, 1370, 1328, 1196, 1148, 1112, 1029, 909, 814, 736, 696, 476 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.43 (m, 37H, aromatic), 6.74 (s, 2H), 6.32 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 4.91–5.06 (m, 11H), 4.81 (d, $J_{gem}$= 11.6 Hz, 2H), 4.68 (d, $J_{gem}$=11.6 Hz, 2H), 3.78 (s, 3H), 3.12 (dd, $J_{gem}$= 17.9 Hz, $J$=4.3 Hz, 1H), 3.06 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.0, 155.6, 152,8, 152.4, 142.7, 138.4, 137.7, 137.4, 136.9, 136.8, 136.4, 133.2, 128.5×3, 128.3×2, 128.2, 128.1, 128.0, 127.9, 127.8×2, 127.7, 127.6, 127,5, 127.2, 125.0, 109.1, 106.7, 100.7, 93.6, 93.3, 77.9, 75.1, 75.0, 71.2, 71.0, 70.0, 68.3, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{72}H_{66}NO_{11}$: 1120.4636 $[M+NH_4]^+$; found: 1120.4625.

**8ab** (41%): $R_f$=0.61 (toluene:ethyl acetate=9:1); FTIR (neat): $\tilde{\nu}$=3032, 2925, 1716, 1621, 1592, 1499, 1454, 1371, 1329, 1217, 1197, 1148, 1113, 1029, 1003, 909, 814, 737, 697, 477 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$= 7.19–7.42 (m, 32H, aromatic), 6.72 (s, 2H), 6.33 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.90–5.06 (m, 9H), 4.76 (d, $J_{gem}$= 11.6 Hz, 2H), 4.63 (d, $J_{gem}$=11.6 Hz, 2H), 3.78 (s, 6H), 3.12 (dd, $J_{gem}$= 17.9 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.7, 159.7, 158.0, 155.7, 152,8, 152.0, 142.0, 137.7, 136.9, 136.8, 136.4, 133.2, 128.6, 128.5, 128.3, 128.0, 127.9, 127.7×2, 127.5, 127.4, 127.2, 124.7, 109.2, 106.7, 100.7, 93.6, 93.3, 77.9,

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75.1, 71.1, 71.0, 70.0, 68.2, 60.8, 55.4, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{66}H_{62}NO_{11}$: 1044.4323 $[M+NH_4]^+$; found: 1044.4319.

**8ac** (43%): $R_f$=0.49 (toluene:ethyl acetate=9:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.21–7.43 (m, 27H, aromatic), 6.75 (s, 2H), 6.29 (d, $J$=1.9 Hz, 1H), 6.23 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 4.96–5.15 (m, 7H), 4.85 (d, $J_{gem}$=11.6 Hz, 2H), 4.71 (d, $J_{gem}$=11.6 Hz, 2H), 3.78 (s, 3H, f), 3.77 (s, 3H), 3.75 (s, 3H), 3.12 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4011.

**8ad** (40%): $R_f$=0.53 (toluene:ethyl acetate=9:1); FTIR (neat): $\tilde{\nu}$=3032, 2937, 1716, 1621, 1593, 1500, 1455, 1436, 1416, 1360, 1333, 1218, 1198, 1148, 1126, 1029, 911, 815, 751, 735, 697, 476 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.44 (m, 27H, aromatic), 6.80 (s, 2H), 6.24 (d, $J$=2.4 Hz, 1H), 6.20 (d, $J$=2.4 Hz, 1H), 5.64 (brs, 1H), 4.93–5.07 (m, 9H), 4.85 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.78 (s, 3H), 3.76 (s, 6H), 3.12 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 159.7, 157.9, 155.5, 153.2, 153,0, 152.8, 137.7, 137.4, 136.9, 136.8, 133.4, 128.5×2, 128.4, 128.2×2, 128.1, 127.9, 127.8, 127.7, 127.5×2, 127.4, 127.2, 125.2, 107.2, 106.8, 100.6, 93.6, 93.2, 77.6, 75.1, 74.9, 71.4, 69.9, 68.6, 56.3, 55.4, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4017.

**8ba** (47%): $R_f$=0.51 (toluene:ethyl acetate=9:1); FTIR (neat): $\tilde{\nu}$=3032, 2936, 1716, 1621, 1592, 1500, 1455, 1435, 1367, 1332, 1218, 1197, 1148, 1115, 1029, 814, 736, 697, 474 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.22–7.42 (m, 32H, aromatic), 6.71 (s, 2H), 6.29 (d, $J$=2.4 Hz, 1H), 6.24 (d, $J$=2.4 Hz, 1H), 5.64 (brs, 1H), 5.01–5.05 (m, 7H), 4.92 (s, 2H, Bn), 4.83 (d, $J_{gem}$=11.6 Hz, 2H), 4.72 (d, $J_{gem}$=11.6 Hz, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.0, 155.6, 152.6, 152.3, 142.7, 139.5, 137.4, 136.9, 136.8, 136.4, 133.0, 130.0, 128.5, 128.4×2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 124.9, 115.0, 109.2, 106.8, 100.6, 93.6, 93.2, 77.8, 75.0, 71.1, 71.0, 70.0, 68.2, 60.8, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{66}H_{62}NO_{11}$: 1044.4323 $[M+NH_4]^+$; found: 1043.4330.

**8bb** (58%): $R_f$=0.43 (toluene:ethyl acetate=9:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.44 (m, 27H, aromatic), 6.69 (s, 2H, a), 6.30 (d, $J$=1.9 Hz, 1H), 6.25 (d, $J$=1.9 Hz, 1H), 5.64 (brs, 1H), 5.03–5.05 (m, 6H, Bn), 4.99 (s, 1H), 4.79 (d, $J$=11.6 Hz, 2H, Bn), 4.67 (d, $J$=11.6 Hz, 2H, Bn), 3.80 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.10 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.7, 159.7, 158.0, 155.7, 152.6, 143.7, 139.5, 136.9, 136.8, 136.4, 133.0, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7×2, 127.4, 127.3, 127.2, 124.7, 109.2, 106.8, 100.7, 93.6, 93.3, 77.9, 71.1, 71.0, 70.0, 68.2, 60.8, 55.4, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4034.

**8bc** (54%): $R_f$=0.29 (toluene:ethyl acetate=9:1); FTIR (neat): $\tilde{\nu}$=2925, 1716, 1620, 1592, 1500, 1434, 1373, 1331, 1219, 1147, 1115, 1029, 1006, 814, 772, 697 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.41 (m, 22H, aromatic), 6.73 (s, 2H), 6.27 (d, $J$=1.9 Hz, 1H), 6.23 (d, $J$=1.9 Hz, 1H), 5.64 (brs, 1H), 5.03–5.05 (m, 4H), 5.00 (s, 1H), 4.87 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.75 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81 (s, 3H), 3.78 (s, 3H), 3.78 (s, 6H), 3.11 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.04 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3684.

**8bd** (51%): $R_f$=0.34 (toluene:ethyl acetate=9:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.29–7.44 (m, 20H, aromatic), 7.18 (s, 2H), 6.78 (s, 2H), 6.22 (d, $J$=1.9 Hz, 1H), 6.20 (d, $J$=1.9 Hz, 1H), 5.62 (brs, 1H), 5.05 (s, 1H), 5.03 (s, 2H), 4.99 (d, $J_{gem}$=11.6 Hz, 2H), 4.94 (s, 2H), 4.89 (d, $J$=11.6 Hz, 2H, Bn), 3.83 (s, 3H), 3.78 (s, 3H), 3.76 (s, 6H), 3.12 (dd, $J_{gem}$=18.4 Hz, $J$=4.3 Hz, 1H), 3.05 ppm (dd, $J_{gem}$=18.4 Hz, $J$=2.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 159.7, 157.9, 155.5, 153.2, 152.6, 141.5, 139.6, 137.3, 136.9, 136.8, 133.1, 128.5, 128.4, 128.2×2, 127.9×2, 127.8, 127.3, 127.1, 125.2, 107.2, 106.9, 100.6, 93.5, 93.1, 77.5, 74.9, 71.3, 69.9, 68.6, 60.9, 56.2, 55.4, 25.8 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3695.

**8ca** (43%): $R_f$=0.49 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.43 (m, 27H, aromatic), 6.61 (s, 2H), 6.34 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.02–5.07 (m, 9H), 4.92 (s, 2H, Bn), 3.78 (s, 3H), 3.51 (s, 6H), 3.13 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.07 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{60}H_{58}NO_{11}$: 968.4010 $[M+NH_4]^+$; found: 968.4044.

**8cb** (38%): $R_f$=0.44 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.42 (m, 22H, aromatic), 6.60 (s, 2H), 6.34 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.02–5.09 (m, 7H), 4.92 (s, 2H), 3.88 (s, 3H), 3.78 (s, 3H), 3.50 (s, 6H), 3.13 (dd, $J_{gem}$=17.9 Hz, $J$=3.9 Hz, 1H), 3.07 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.0, 155.7, 153.4 152.0, 137.7, 136.8, 136.5, 133.3, 128.6, 128.5, 128.4, 128.1, 127.9, 127.7×2, 127.2, 124.8, 109.3, 104.0, 100.7, 93.6, 93.3, 78.0, 74.9, 71.0, 70.0, 68.3, 61.0, 55.9, 55.4, 26.3 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$: 892.3697 $[M+NH_4]^+$; found: 892.3690.

**8cc** (39%): $R_f$=0.31 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.43 (m, 16H, a and aromatic), 7.16 (d, $J$=1.9 Hz, 1H), 6.64 (s, 2H), 6.32 (d, $J$=1.9 Hz, 1H), 6.23 (d, $J$=1.9 Hz, 1H), 5.68 (brs, 1H), 5.09 (s, 1H), 5.05 (s, 4H, Bn), 4.93 (s, 2H, Bn), 3.88 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 3.58 (s, 6H), 3.14 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 3.08 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 159.7, 158.0, 155.7, 153.4, 153.1, 151.7, 143.1, 137.7, 136.8, 136.5, 133.3, 128.6, 128.5, 128.4, 128.1×2, 127.9, 127.7, 127.2, 124.9, 109.1, 107.3, 104.0, 100.6, 93.6, 93.3, 77.9, 74.9, 71.0, 70.0, 68.4, 60.9, 56.2, 55.9, 55.4, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+NH_4]^+$; found: 816.3392.

**8cd** (39%): $R_f$=0.33 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.17–7.35 (m, 15H, aromatic), 7.09 (s, 2H), 6.61 (s, 2H), 6.20 (d, $J$=2.4 Hz, 1H), 6.13 (d, $J$=2.4 Hz, 1H), 5.60 (brs, 1H), 5.02 (s, 1H), 4.97 (s, 2H, Bn), 4.96 (s, 2H, Bn), 4.87 (s, 2H, Bn), 3.85 (s, 6H), 3.76 (s, 3H), 3.73 (s, 3H), 3.04 (dd, $J_{gem}$=16.9 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.4 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.3, 159.7, 157.9, 155.6, 153.4, 153.2, 141.3, 137.7, 137.2, 136.8, 133.4, 128.5, 128.4, 128.2, 128.1, 129.0, 127.9, 127.7, 127.2, 125.2, 107.2, 104.0, 100.6, 93.6, 93.2, 77.9, 74.9, 70.0, 68.6, 56.2, 56.0, 55.3, 25.7 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+H]^+$; found: 816.3383.

**8da** (52%): $R_f$=0.32 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.42 (m, 22H, aromatic), 6.61 (s, 2H), 6.33 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.68 (brs, 1H), 5.02–5.08 (m, 9H), 3.78 (s, 3H), 3.78 (s, 3H), 3.53 (s, 6H), 3.13 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.07 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.0, 155.7, 153.1, 152.3, 142.4, 137.9, 137.3, 136.8, 136.5, 133.2, 128.5×2, 128.2, 128.1, 128.0×2, 127.9, 127.7, 127.2, 124.9, 109.1, 104.0, 100.7, 93.6, 93.3, 78.1, 75.0, 71.0, 70.0, 68.3, 60.7, 55.8, 55.4, 26.3 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{54}H_{54}NO_{11}$ 892.3697 $[M+NH_4]^+$; found: 892.3719.

**8db** (54%): $R_f$=0.28 (toluene:ethyl acetate=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.42 (m, 17H, aromatic), 6.60 (s, 2H), 6.34 (d, $J$=2.4 Hz, 1H), 6.25 (d, $J$=2.4 Hz, 1H), 5.68 (brs, 1H), 5.02–5.09 (m, 7H), 3.88 (s, 3H), 3.78 (s, 6H), 3.53 (s, 6H), 3.13 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.06 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.0, 155.7, 153.1, 152.0, 143.8, 137.9, 136.8, 136.5, 133.1, 128.6, 128.5, 128.1, 127.9, 127.6, 127.2, 124.7, 109.3, 104.0, 100.6, 93.6, 93.3, 78.0, 71.0, 70.0, 68.2, 60.9, 60.7, 55.8, 55.4, 26.3 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{48}H_{50}NO_{11}$: 816.3384 $[M+NH_4]^+$; found: 816.3375.

**8dc** (58%): $R_f$=0.15 (toluene:ethyl acetate=10:1); FTIR (neat): $\tilde{\nu}$=2927, 1716, 1621, 1593, 1502, 1456, 1422, 1357, 1331, 1221, 1149, 1124, 1004, 814, 756, 699 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.42 (m, 11H), 7.16 (d, $J$=1.9 Hz, 1H), 6.64 (s, 2H), 6.31 (d, $J$=1.9 Hz, 1H), 6.24 (d, $J$=1.9 Hz, 1H), 5.68 (brs, 1H), 5.08 (s, 1H), 5.06 (s, 2H, Bn), 5.05 (s, 2H, Bn), 3.87 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.61 (s, 6H), 3.14 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.08 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 159.7, 158.0, 155.7, 153.1, 151.7, 143.1, 137.9, 136.8, 136.5, 133.2, 128.6, 128.5, 128.1, 127.9, 127.7, 127.5, 127.1, 124.8, 109.1, 107.3, 103.9, 100.6, 93.6, 93.2, 77.9, 71.0, 70.0, 68.4, 60.9, 60.7, 56.2, 55.9, 55.4, 26.2 ppm; HRMS

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(ESI-TOF): *m/z* (%) calcd for $C_{42}H_{46}NO_{11}$: 740.3071 $[M+NH_4]^+$; found: 740.3099.

**8dd** (53%): $R_f$=0.19 (toluene:ethyl acetate=9:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.44 (m, 10H, aromatic), 7.16 (s, 2H), 6.69 (s, 2H), 6.26 (d, $J$=2.4 Hz, 1H), 6.21 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.09 (s, 1H), 5.05 (s, 2H, Bn), 5.04 (s, 2H, Bn), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.69 (s, 6H), 3.14 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.09 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.1, 159.6, 157.9, 155.6, 153.2, 153.1, 141.2, 137.9, 137.2, 136.8, 133.3, 128.5, 128.4, 128.2, 128.0, 127.9, 127.1, 125.2, 107.2, 103.9, 100.6, 93.6, 93.2, 77.9, 74.9, 69.9, 68.6, 60.8, 56.2, 56.0, 55.4, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{42}H_{46}NO_{11}$: 740.3071 $[M+NH_4]^+$; found: 740.3074.

**9aa** (45%): $R_f$=0.60 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.36 (m, 32H, aromatic), 6.74 (s, 2H), 6.30 (d, $J$=2.4 Hz, 1H), 6.17 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 4.90–5.04 (m, 9H), 4.81 (d, $J_{gem}$=11.6 Hz, 2H), 4.68 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81 (s, 3H), 3.79 (s, 3H, f or g), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.00 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H).

**9ab** (51%): $R_f$=0.58 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.19–7.38 (m, 27H, aromatic), 6.72 (s, 2H), 6.30 (d, $J$=1.9 Hz, 1H), 6.17 (d, $J$=1.9 Hz, 1H), 5.65 (brs, 1H), 4.95–5.06 (m, 7H), 4.77 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.64 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=3.9 Hz, 1H), 2.98 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H).

**9ac** (38%): $R_f$=0.53 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.14–7.38 (m, 22H, aromatic), 6.76 (s, 2H), 6.27 (d, $J$=1.9 Hz, 1H), 6.15 (d, $J$=1.9 Hz, 1H), 5.65 (brs, 1H), 4.96–5.07 (m, 5H), 4.85 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.72 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.06 (dd, $J_{gem}$=18.4 Hz, $J$=4.3 Hz, 1H), 3.00 ppm (dd, $J_{gem}$=18.4 Hz, $J$=2.4 Hz, 1H).

**9ad** (29%): $R_f$=0.54 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.18–7.45 (m, 22H, aromatic), 6.81 (s, 2H), 6.22 (d, $J$=1.9 Hz, 1H), 6.12 (d, $J$=1.9 Hz, 1H), 5.63 (brs, 1H, d), 4.97–5.08 (m, 5H), 4.94 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.86 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.80 (s, 3H), 3.79 (s, 3H), 3.76 (s, 6H), 3.07 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.01 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H).

**9ba** (43%): $R_f$=0.58 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.24–7.34 (m, 27H, aromatic), 6.73 (s, 2H), 6.28 (d, $J$=2.4 Hz, 1H), 6.17 (d, $J$=2.4 Hz, 1H), 5.64 (brs, 1H), 5.05 (s, 1H), 5.02 (s, 4H, Bn), 4.92 (s, 2H, Bn), 4.84 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.73 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81 (s, 6H), 3.79 (s, 3H), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.99 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.9, 155.5, 152.5, 152.3, 142.7, 139.4, 137.4, 136.9, 136.4, 133.0, 128.5, 128.4×2, 128.2, 128.1, 128.0, 127.8, 127.7, 127.3, 124.9, 109.1, 106.7, 100.1, 93.2, 91.9, 77.8, 75.0, 71.1, 71.0, 68.2, 60.8, 55.4, 55.3, 26.0 ppm.

**9bb** (47%): $R_f$=0.56 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.22–7.40 (m, 22H, aromatic), 6.70 (s, 2H), 6.28 (d, $J$=2.4 Hz, 1H), 6.16 (d, $J$=2.4 Hz, 1H), 5.63 (brs, 1H), 5.06 (s, 1H), 5.03×2 (s, 4H, Bn), 4.79 (d, $J_{gem}$=12.1 Hz, 2H, Bn), 4.67 (d, $J_{gem}$=12.1 Hz, 2H, Bn), 3.81 (s, 3H), 3.80 (s, 3H), 3.78×2 (s, 3H), 3.03 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.97 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H).

**9bc** (40%): $R_f$=0.51 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27–7.38 (m, 16H, a and aromatic), 7.17 (d, $J$=1.9 Hz, 1H), 6.73 (s, 2H), 6.25 (d, $J$=2.4 Hz, 1H), 6.14 (d, $J$=2.4 Hz, 1H), 5.63 (brs, 1H), 5.01–5.04 (m, 3H), 4.87 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.76 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.98 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.0, 159.9, 159.0, 155.6, 153.2, 152.7, 151.9, 137.1, 136.6, 133.2, 128.7, 128.6, 128.5, 128.2, 127.9, 127.5, 127.4, 125.0, 109.2, 107.5, 100.3, 93.4, 92.0, 77.9, 71.4, 71.1, 68.5, 61.0, 60.9, 56.4, 55.5×2, 26.0 ppm.

**9bd** (32%): $R_f$=0.52 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28–7.42 (m, 15H, aromatic), 7.17 (s, 2H), 6.78 (s, 2H), 6.20 (d, $J$=2.4 Hz, 1H), 6.11 (d, $J$=2.4 Hz, 1H), 5.61 (brs, 1H), 5.04 (s, 1H), 5.00 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 4.93 (s, 2H, Bn), 4.89 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.83 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H, g, h, or i), 3.76 (s, 6H, j), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (brs, 1H).

**9ca** (34%): $R_f$=0.55 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.24–7.34 (m, 27H, aromatic), 6.73 (s, 2H), 6.28 (d, $J$=2.4 Hz, 1H), 6.17 (d, $J$=2.4 Hz, 1H), 5.64 (brs, 1H), 5.05 (s, 1H), 5.02 (s, 2H, Bn), 4.92 (s, 2H, Bn), 4.84 (d, $J$=11.6 Hz, 2H, Bn), 4.73 (d, $J$=11.6 Hz, 2H, Bn), 3.81 (s, 6H), 3.79 (s, 3H), 3.75 (s, 6H), 3.05 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.99 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H).

**9cb** (39%): $R_f$=0.52 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.24–7.42 (m, 17H, aromatic), 6.61 (s, 2H), 6.32 (d, $J$=2.4 Hz, 1H), 6.17 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 5.02–5.09 (m, 5H), 4.92 (s, 2H, Bn), 3.88 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.51 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.03 ppm (brs, 1H).

**9cc** (52%): $R_f$=0.47 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.24–7.43 (m, 11H, a and aromatic), 7.16 (d, $J$=1.9 Hz, 1H), 6.64 (s, 2H), 6.30 (d, $J$=2.4 Hz, 1H), 6.15 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.08 (d, $J_{gem}$=12.1 Hz, 1H, Bn), 5.08 (s, 1H, f), 5.04 (d, $J_{gem}$=12.1 Hz, 1H, Bn), 4.94 (s, 2H, Bn), 3.87 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.58 (s, 6H), 3.07 (dd, $J_{gem}$=17.4 Hz, $J$=3.9 Hz, 1H), 3.04 ppm (brs, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.9, 159.7, 158.9, 155.4, 153.4, 151.7, 143.0, 137.7, 136.8, 133.4, 128.6, 128.4, 128.1×2, 127.7, 127.6, 124.9, 109.0, 107.3, 100.2, 93.2, 77.9, 74.9, 71.0, 68.5, 60.9, 56.2, 55.9, 55.4×2, 26.0 ppm.

**9cd** (54%): $R_f$=0.49 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.43 (d, $J$=6.8 Hz, 2H, aromatic), 7.26–7.34 (m, 8H, aromatic), 7.16 (s, 2H), 6.68 (s, 2H), 6.25 (d, $J$=1.9 Hz, 1H), 6.13 (d, $J$=1.9 Hz, 1H), 5.65 (brs, 1H), 5.08 (s, 1H), 5.04 (s, 2H, Bn), 4.95 (s, 2H, Bn), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.66 (s, 6H), 3.05 ppm (brs, 2H).

**9da** (48%): $R_f$=0.53 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.25–7.38 (m, 17H, aromatic), 6.62 (s, 2H), 6.32 (d, $J$=1.9 Hz, 1H), 6.17 (d, $J$=1.9 Hz, 1H), 5.67 (brs, 1H), 5.07–5.00 (m, 7H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.54 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=3.9 Hz, 1H), 3.01 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.8, 159.7, 158.9, 155.5, 153.1, 152.2, 142.3, 137.8, 137.2, 136.4, 133.2, 128.5×2, 128.2, 128.1, 128.0, 127.7, 124.9, 109.0, 103.9, 100.1, 93.2, 91.9, 78.0, 75.0, 71.0, 68.3, 60.7, 55.8, 55.4×2, 26.1 ppm.

**9db** (51%): $R_f$=0.50 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.29–7.40 (m, 12H, aromatic), 6.61 (s, 2H), 6.32 (d, $J$=1.9 Hz, 1H), 6.17 (d, $J$=1.9 Hz, 1H), 5.67 (brs, 1H), 5.08 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 5.05 (s, 1H), 5.04 (d, $J_{gem}$=11.6 Hz, 2H, Bn), 3.88 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.54 (s, 6H), 3.06 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 3.00 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=164.7, 159.7, 158.9, 155.5, 153.1, 151.9, 143.6, 137.8, 136.4, 133.2, 128.6, 128.1, 127.6, 124.7, 109.1, 103.8, 100.1, 93.2, 91.9, 78.0, 70.9, 68.2, 60.9, 60.7, 55.7, 55.4×2, 26.1 ppm.

**9dc** (47%): $R_f$=0.46 (hexane:ethyl acetate=1:1); FTIR (neat): $\tilde{\nu}$=3031, 2938, 1716, 1621, 1593, 1499, 1455, 1429, 1369, 1328, 1214, 1148, 1124, 1030, 1002, 911, 843, 815, 752, 697, 481 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.29–7.40 (m, 5H, aromatic), 7.27 (d, $J$=1.9 Hz, 1H), 7.15 (d, $J$=1.9 Hz, 1H), 6.64 (s, 2H), 6.29 (d, $J$=2.4 Hz, 1H), 6.15 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.08 (d, $J_{gem}$=11.6 Hz, 1H, Bn), 5.07 (s, 1H, f), 5.04 (d, $J_{gem}$=11.6 Hz, 1H, Bn), 3.87 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79×2 (s, 3H), 3.61 (s, 6H), 3.07 (dd, $J_{gem}$=17.9 Hz, $J$=4.8 Hz, 1H), 3.02 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H).

**9dd** ( 36%): $R_f$=0.48 (hexane:ethyl acetate=1:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.43 (d, $J$=6.8 Hz, 2H, aromatic), 7.28–7.34 (m, 3H, aromatic), 7.16 (s, 2H), 6.69 (s, 2H), 6.24 (d, $J$=2.4 Hz, 1H), 6.12 (d, $J$=2.4 Hz, 1H), 5.66 (brs, 1H), 5.08 (s, 1H), 5.04 (s, 2H, Bn), 3.80×2 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.70 (s, 6H), 3.05 (s, 1H), 3.04 ppm (s, 1H); $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 159.8, 158.9, 155.6, 153.2×2, 141.3, 138.0, 137.3, 133.4, 128.4, 128.2, 128.0, 125.3, 107.3, 104.0, 100.2, 93.3, 91.9, 77.9, 75.0, 68.7, 60.8, 56.3×2, 56.0, 55.4, 26.0 ppm.

**Deprotection**: deprotection of the protected methylated EGCG library was achieved by the same procedure for the synthesis of **2aa**.

**2ab** (49%): $R_f$=0.37 ($CHCl_3$:methanol=2:1); FTIR (solid): $\tilde{\nu}$=1693, 1603, 1522, 1451, 1345, 1234, 1142, 1092, 1038, 882, 727, 636, 492 cm$^{-1}$; $^1$H NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.93 (s, 2H), 6.59 (s,

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2H), 5.97 (d, $J$=2.4 Hz, 1H), 5.95 (d, $J$=1.9 Hz, 1H), 5.39 (brs, 1H), 4.97 (s, 1H), 3.72 (s, 3H), 2.95 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{23}H_{21}O_{11}$: 473.1084 $[M+H]^+$; found: 473.1088.

**2ac** (60%): $R_f$=0.49 ($CHCl_3$:methanol=2:1); FTIR (solid): $\tilde{\nu}$=3282, 1696, 1603, 1607, 1510, 1455, 1340, 1226, 1146, 1112, 824, 803, 755, 645, 533 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.00 (d, $J$=1.9 Hz, 1H), 6.91 (d, $J$=1.9 Hz, 1H), 6.57 (s, 2H), 5.95 (d, $J$=1.9 Hz, 1H), 5.94 (d, $J$=1.9 Hz, 1H), 5.37 (brs, 1H), 4.98 (s, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 2.94 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.85 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1244.

**2ad** (35%): $R_f$=0.49 ($CHCl_3$:methanol=2:1); FTIR (solid): $\tilde{\nu}$=3357, 1611, 1510, 1456, 1339, 1146, 1003, 803, 755, 646, 524 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.07 (s, 2H), 6.59 (s, 2H), 5.96 (s, 1H), 5.96 (s, 1H), 5.35 (brs, 1H), 5.01 (s, 1H), 3.74 (s, 6H), 2.94 (d, $J_{gem}$=18.4 Hz, 1H), 2.72 ppm (d, $J_{gem}$=18.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1239.

**2ba** (68%): $R_f$=0.43 ($CHCl_3$:methanol=2:1); FTIR (solid): $\tilde{\nu}$=3299, 1689, 1605, 1529, 1506, 1441, 1315, 1233, 1195, 1143, 1116, 1029, 1007, 820, 766, 628 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.97 (s, 2H), 6.61 (s, 2H), 5.99 (d, $J$=2.4 Hz, 1H), 5.96 (d, $J$=2.4 Hz, 1H), 5.40 (brs, 1H), 4.99 (s, 1H), 3.67 (s, 3H), 2.95 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.86 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{23}H_{21}O_{11}$: 473.1084 $[M+H]^+$; found: 473.1064.

**2bb** (63%): $R_f$=0.32 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3283, 1693, 1601, 1600, 1510, 1435, 1372, 1193, 1145, 1050, 986, 823, 755, 713, 540 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.89 (s, 2H, a), 6.59 (s, 2H, b), 5.95 (d, $J$=2.4 Hz, 1H, c or d), 5.94 (d, $J$=2.4 Hz, 1H, c or d), 5.39 (brs, 1H, e), 4.98 (s, 1H, f), 3.70 (s, 3H, g or h), 3.64 (s, 3H, g or h), 2.94 (dd, $J_{gem}$=17.9 Hz, $J$=4.8 Hz, 1H, i), 2.82 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H, i); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1238.

**2bc** (51%): $R_f$=0.41 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3283, 1697, 1599, 1509, 1462, 1434, 1366, 1225, 1146, 1099, 1049, 1016, 1003, 824, 755, 714, 548 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.00 (d, $J$=1.9 Hz, 1H, a), 6.91 (d, $J$=1.9 Hz, 1H, a), 6.58 (s, 2H, b), 5.95 (d, $J$=2.4 Hz, 1H, c or d), 5.93 (d, $J$=2.4 Hz, 1H, c or d), 5.39 (brs, 1H, e), 5.00 (s, 1H, f), 3.72 (s, 3H, g, h, or i), 3.67 (s, 3H, g, h, or i), 3.63 (s, 3H, g, h, or i), 2.94 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H, j), 2.87 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.9 Hz, 1H, j); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1390.

**2bd** (34%): $R_f$=0.41 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3387, 1669, 1629, 1515, 1462, 1365, 1207, 1144, 1118, 1044, 960, 803, 755, 606 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.05 (s, 2H), 6.61 (s, 2H), 5.96 (s, 1H), 5.96 (s, 1H), 5.37 (brs, 1H), 5.04 (s, 1H), 3.74 (s, 6H), 3.64 (s, 3H), 2.98 (dd, $J_{gem}$=18.4 Hz, $J$=4.4 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1400.

**2ca** (43%): $R_f$=0.38 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3301, 1689, 1612, 1517, 1462, 1340, 1213, 1146, 1117, 1036, 994, 824, 755, 649, 535 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.95 (s, 2H), 6.90 (s, 2H), 5.98 (d, $J$=2.4 Hz, 1H), 5.96 (d, $J$=2.4 Hz, 1H), 5.43 (brs, 1H), 5.05 (s, 1H), 3.64 (s, 6H), 2.96 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.81 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1235.

**2cb** (57%): $R_f$=0.52 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3337, 1697, 1606, 1517, 1461, 1433, 1372, 1223, 1147, 1113, 1057, 824, 755, 665, 531 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.92 (s, 2H), 6.75 (s, 2H), 5.97 (d, $J$=2.4 Hz, 1H), 5.95 (d, $J$=2.4 Hz, 1H), 5.44 (brs, 1H), 5.06 (s, 1H), 3.70 (s, 3H), 3.63 (s, 6H), 2.97 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.81 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1400.

**2cc** (60%): $R_f$=0.43 ($CHCl_3$:methanol=4:1); $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.06 (d, $J$=1.4 Hz, 1H), 6.94 (d, $J$=1.4 Hz, 1H), 6.78 (s, 2H), 6.00 (d, $J$=1.9 Hz, 1H), 5.97 (d, $J$=1.9 Hz, 1H), 5.50 (brs, 1H), 5.10 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.64 (s, 6H), 2.99 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.86 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1552.

**2cd** (61%): $R_f$=0.43 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3386, 1693, 1602, 1512, 1461, 1423, 1328, 1211, 1146, 1108, 997, 955, 911, 864, 817, 759, 636 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.10 (s, 2H), 6.79 (s, 2H), 6.00 (d, $J$=1.9 Hz, 1H), 5.98 (d, $J$=2.4 Hz, 1H), 5.51 (brs, 1H, e), 5.12 (s, 1H), 3.72 (s, 6H), 3.63 (s, 6H), 3.00 (dd, $J_{gem}$=17.9 Hz, $J$=4.8 Hz, 1H), 2.87 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1552.

**2da** (58%): $R_f$=0.38 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3287, 1682, 1598, 1533, 1505, 1459, 1421, 1368, 1329, 1234, 1193, 1146, 1117, 1031, 997, 968, 874, 818, 721, 586 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.93 (s, 2H), 6.80 (s, 2H), 6.05 (s, 1H), 6.04 (s, 1H), 5.43 (brs, 1H), 5.10 (s, 1H), 3.65 (s, 6H), 3.65 (s, 3H), 2.94 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.79 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1397.

**2db** (52%): $R_f$=0.42 ($CHCl_3$:methanol=4:1); $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.95 (s, 2H), 6.83 (s, 2H), 6.02 (d, $J$=1.9 Hz, 1H), 5.99 (d, $J$=1.9 Hz, 1H), 5.51 (brs, 1H), 5.14 (s, 1H), 3.74 (s, 3H), 3.67 (s, 6H), 3.61 (s, 3H), 3.01 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz 1H), 2.87 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1556.

**2dc** (49%): $R_f$=0.54 ($CHCl_3$:methanol=4:1); $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.07 (d, $J$=1.9 Hz, 1H), 6.94 (d, $J$=1.9 Hz, 1H), 6.83 (s, 2H), 6.02 (d, $J$=2.4 Hz, 1H), 5.99 (d, $J$=2.4 Hz, 1H), 5.54 (brs, 1H), 5.16 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.66 (s, 6H, j), 3.61 (s, 3H), 3.01 (dd, $J_{gem}$=17.4 Hz, $J$=3.9 Hz, 1H), 2.89 ppm (dd, $J_{gem}$=16.4 Hz, $J$=0.97 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1716.

**2dd** (50%): $R_f$=0.55 ($CHCl_3$:methanol=4:1); $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.06 (s, 2H), 6.82 (s, 2H), 6.08 (d, $J$=2.4 Hz, 1H), 6.05 (d, $J$=1.9 Hz, 1H), 5.54 (brs, 1H), 5.16 (s, 1H), 3.70 (s, 6H), 3.66 (s, 3H), 3.64 (s, 6H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.4 Hz 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1712.

**3aa** (40%) $R_f$=0.37 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3271, 2962, 1654, 1601, 1513, 1432, 1370, 1200, 1145, 1118, 1042, 799, 668, 524 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.94 (d, $J$=2.9 Hz, 2H), 6.58 (d, $J$=2.4 Hz, 2H), 6.03 (s, 1H), 6.01 (s, 1H), 5.33 (brs, 1H), 4.95 (s, 1H), 3.64 (s, 3H), 2.91 (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz), 2.72 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{23}H_{21}O_{11}$: 473.1084 $[M+H]^+$; found: 473.1084.

**3ab** (37%): $R_f$=0.46 ($CHCl_3$:methanol=3:1); FTIR (solid): $\tilde{\nu}$=3401, 1627, 1444, 1371, 1212, 1043, 866, 621, 481 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.91 (s, 2H), 6.58 (s, 2H), 6.03 (s, 1H), 6.02 (s, 1H), 5.29 (brs, 1H), 5.13 (s, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 2.83 (dd, $J_{gem}$=17.4 Hz, $J$=4.4 Hz, 1H), 2.72 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1230.

**3ac** (56%): $R_f$=0.55 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3332, 1693, 1595, 1534, 1506, 1463, 1426, 1364, 1338, 1195, 1140, 1111, 1029, 1003, 821, 761, 667, 524 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.04 (d, $J$=1.9 Hz, 1H), 6.95 (d, $J$=1.9 Hz, 1H), 6.60 (s, 2H), 6.06 (d, $J$=1.9 Hz, 1H), 6.03 (d, $J$=1.9 Hz, 1H), 5.40 (brs, 1H), 5.02 (s, 1H), 3.76 (s, 3H) 3.71 (s, 3H), 3.66 (s, 3H), 2.83 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.72 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, acetone$d_6$:$D_2O$=2:1): $\delta$=166.2, 159.4, 157.5, 156.0, 153.5, 150.6, 145.9, 141.3, 130.1, 125.8, 111.2, 106.1, 105.6, 99.1, 96.1, 92.7, 77.4, 70.2, 60.6, 56.2, 55.6, 25.9 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1394.

**3ad** (33%): $R_f$=0.54 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3232, 1688, 1607, 1532, 1513, 1463, 1425, 1364, 1331, 1212, 1144, 1112, 1029, 958, 913, 821, 760, 738, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.06 (s, 2H), 6.59 (s, 2H), 6.05 (s, 1H), 6.02 (s, 1H), 5.35 (brs,

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1H), 5.02 (s, 1H), 3.74 (s, 6H), 3.65 (s, 3H), 2.94 (d, $J_{gem}$=18.4 Hz, 1H), 2.72 ppm (d, $J_{gem}$=18.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1392.

**3ba** (68%): $R_f$=0.47 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3299, 1689, 1605, 1529, 1506, 1441, 1315, 1233, 1195, 1143, 1116, 1029, 1007, 820, 766, 628 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.95 (s, 2H), 6.60 (s, 2H), 6.05 (d, $J$=2.4 Hz, 1H), 6.03 (d, $J$=2.4 Hz, 1H), 5.38 (brs, 1H), 4.99 (s, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.93 (dd, $J_{gem}$= 17.9 Hz, $J$=4.4 Hz, 1H), 2.82 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.7, 159.3, 157.0, 155.7, 150.3, 145.4, 135.3, 134.8, 120.6, 109.7, 106.5, 99.2, 96.0, 92.7, 77.4, 69.4, 60.5, 55.6, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{24}H_{23}O_{11}$ 487.1240 $[M+H]^+$; found: 487.1260.

**3bb** (55%): $R_f$=0.57 ($CHCl_3$:methanol=4:1); FTIR (solid): $\tilde{\nu}$=3315, 1693, 1601, 1524, 1506, 1436, 1343, 1140, 1113, 1042, 990, 843, 816, 760, 714, 645, 530 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.87 (s, 2H), 6.57 (s, 2H), 6.02 (d, $J$=2.4 Hz, 1H), 6.00 (d, $J$=2.4 Hz, 1H), 5.37 (brs, 1H), 4.97 (s, 1H), 3.68 (s, 3H), 3.62 (s, 3H), 3.62 (s, 3H), 2.93 (dd, $J_{gem}$=17.4 Hz, $J$=4.4 Hz, 1H), 2.82 ppm (d, $J_{gem}$=17.4 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.2, 159.3, 157.2, 155.7, 150.7, 150.5, 140.4, 135.3, 134.8, 125.6, 109.5, 106.4, 99.0, 96.0, 92.6, 77.3, 69.7, 60.4, 55.5, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1397.

**3bc** (67%): $R_f$=0.65 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3401, 1686, 1598, 1512, 1459, 1425, 1358, 1326, 1201, 1139, 1110, 1044, 1002, 955, 911, 864, 819, 757, 717, 621 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.98 (d, $J$=1.9 Hz, 1H), 6.90 (d, $J$=1.9 Hz, 1H), 6.58 (s, 2H), 6.03 (d, $J$=2.4 Hz, 1H), 6.01 (d, $J$=1.9 Hz, 1H), 5.38 (brs, 1H), 5.01 (s, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.63 (s, 3H), 3.63 (s, 3H), 2.93 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.84 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.2, 159.3, 157.4, 155.7, 153.4, 150.6, 150.5, 141.2, 135.3, 134.9, 125.6, 111.1, 106.2, 105.4, 98.9, 95.9, 92.6, 77.2, 70.1, 60.6, 60.4, 5 6.1, 55.5, 25.7 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1567.

**3bd** (61%): $R_f$=0.64 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3401, 1686, 1598, 1512, 1459, 1425, 1358, 1326, 1201, 1139, 1110, 1044, 1002, 955, 911, 864, 819, 757, 717, 621 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta$=7.10 (s, 2H), 6.63 (s, 2H), 6.08 (d, $J$=2.4 Hz, 1H), 6.05 (d, $J$=2.4 Hz, 1H), 5.40 (brs, 1H), 5.08 (s, 1H), 3.84 (s, 6H), 3.77 (s, 3H), 3.68 (s, 3H), 2.98 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.9 Hz, $J$= 2.9 Hz 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.6, 159.3, 157.4, 155.7, 150.6, 147.9,135.3, 135.0, 120.4, 107.3, 106.5, 106.1, 99.0, 95.9, 92.6, 77.1, 70.1, 60.4, 56.3, 55.5, 25.6 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1555.

**3ca** (54%): $R_f$=0.29 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3335, 1687, 1606, 1519, 1460, 1314, 1211, 1143, 1111, 1030, 996, 967, 911, 874, 819, 767, 663, 634, 544 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.96 (s, 2H), 6.77 (s, 2H), 6.05 (s, 1H), 6.04 (s, 1H), 5.43 (brs, 1H), 5.06 (s, 1H), 3.65 (s, 3H), 3.64 (s, 6H), 2.94 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.79 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{25}H_{28}NO_{11}$: 518.1662 $[M+NH_4]^+$; found: 518.1675.

**3cb** (60%): $R_f$=0.34 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3371, 1696, 1600, 1519, 1458, 1429, 1346, 1233, 1200, 1144, 1110, 1053, 996, 966, 912, 820, 744, 714, 624 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.91 (d, $J$=2.4 Hz, 2H), 6.75 (d, $J$=2.4 Hz, 2H), 6.05 (s, 1H), 6.05 (s, 1H), 5.45 (brs, 1H), 5.08 (s, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.63 (s, 6H), 2.96 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.80 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.7, 159.6, 157.7, 156.2, 151.0, 148.1,140.4, 129.5, 125.7, 118.2, 109.5, 104.7, 99.1, 96.1, 92.7, 78.0, 69.6, 60.4, 56.2, 55.6, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1546.

**3cc** (58%): $R_f$=0.54 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3379, 1697, 1603, 1503, 1459, 1427, 1341, 1213, 1144, 1107, 1029, 996, 957, 910, 871, 821, 761, 746, 720, 665, 632, 533 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.05 (d, $J$=1.9 Hz, 1H), 6.92 (d, $J$=1.9 Hz, 1H), 6.77 (s, 2H), 6.06 (s, 1H), 6.05 (s, 1H), 5.49 (brs, 1H), 5.10 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.70 (s, 3H), 3.63 (s, 6H), 2.97 (dd, $J_{gem}$= 17.9 Hz, $J$=4.3 Hz, 1H), 2.83 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.4 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.7, 159.5, 157.7, 156.1, 153.7, 150.8, 148.1, 141.5, 135.7, 129.5, 125.7, 111.3, 105.5, 104.7, 99.0, 96.1, 92.7, 77.9, 69.9, 60.7, 56.2, 56.2, 55.6, 26.2 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1727.

**3cd** (49%): $R_f$=0.54 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3386, 1693, 1602, 1512, 1461, 1423, 1328, 1211, 1146, 1108, 997, 955, 911, 864, 817, 759, 636 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta$=7.18 (s, 2H), 6.86 (s, 2H), 6.14 (d, $J$=1.9 Hz, 1H), 6.10 (d, $J$=1.9 Hz, 1H), 5.59 (brs, 1H), 5.20 (s, 1H), 3.79 (s, 6H), 3.74 (s, 3H), 3.69 (s, 6H), 3.04 (dd, $J_{gem}$= 17.9 Hz, $J$=4.8 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1689.

**3da** (55%): $R_f$=0.32 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3287, 1682, 1598, 1533, 1505, 1459, 1421, 1368, 1329, 1234, 1193, 1146, 1117, 1031, 997, 968, 874, 818, 721, 586 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.93 (s, 2H), 6.80 (s, 2H), 6.05 (s, 1H), 6.04 (s, 1H), 5.43 (brs, 1H), 5.10 (s, 1H), 3.65 (s, 6H), 3.65 (s, 3H),3.59 (s, 3H), 2.94 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.79 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{30}NO_{11}$: 532.1819 $[M+NH_4]^+$; found: 532.1842.

**3db** (53%): $R_f$=0.37 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3375, 1698, 1593, 1502, 1459, 1343, 1230, 1116, 1058, 995, 968, 922, 872, 815, 759, 731, 714, 670, 631 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.88 (d, $J$=3.4 Hz, 2H), 6.78 (d, $J$=2.9 Hz, 2H), 6.04 (s, 1H), 6.04 (s, 1H), 5.46 (brs, 1H), 5.10 (s, 1H), 3.68 (s, 3H), 3.64 (s, 6H), 3.59 (s, 3H), 3.58 (s, 3H), 2.95 (d, $J_{gem}$=17.9 Hz, 1H), 2.80 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.7, 159.4,157.5, 155.9, 153.3, 150.9, 140.5, 137.7, 125.5, 109.5, 104.5, 99.0, 96.1, 92.7, 78.8, 77.8, 69.5, 60.5, 60.4, 56.0, 55.6, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1732.

**3dc** (73%): $R_f$=0.53 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3368, 1709, 1591, 1503, 1458, 1421, 1366, 1343, 1196, 1145, 1119, 1035, 999, 945, 813, 757, 720, 671, 629 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.03 (d, $J$=1.9 Hz, 1H), 6.91 (d, $J$=1.9 Hz, 1H), 6.80 (s, 2H), 6.07 (d, $J$=2.4 Hz, 1H), 6.05 (d, $J$=1.9 Hz, 1H), 5.51 (brs, 1H), 5.14 (s, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.64 (s, 6H), 3.59 (s, 3H), 2.98 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.83 ppm (d, $J_{gem}$=17.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$=165.2, 159.0, 155.6, 155.3, 153.0, 151.9, 148.7, 139.5, 137.6, 133.4, 125.4, 109.8, 105.9, 103.7, 99.8, 96.0, 92.1, 77.8, 68.7, 61.0, 60.8, 56.0, 55.9, 55.4, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1887.

**3dd** (69%): $R_f$=0.53 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3378, 1708, 1597, 1504, 1461, 1421, 1358, 1327, 1279, 1211, 1118, 1034, 1002, 955, 955, 914, 866, 819, 759, 721, 668, 632, 528 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.06 (s, 2H), 6.82 (s, 2H), 6.08 (d, $J$=2.4 Hz, 1H), 6.05 (d, $J$=1.9 Hz, 1H), 5.54 (brs, 1H), 5.16 (s, 1H), 3.70 (s, 6H), 3.66 (s, 3H), 3.64 (s, 6H), 3.60 (s, 3H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$=165.4, 158.8, 156.6, 155.3, 152.9, 146.8, 139.9, 133.5, 120.5, 106.9, 103.9, 99.1, 95.5,,92.2, 77.6, 68.5, 60.7, 56.2, 55.8, 55.2, 50.2, 25.8 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1865.

**4aa** (36%): $R_f$=0.19 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3264, 1686, 1616, 1594, 1533, 1499, 1440, 1368, 1340, 1192, 1144, 1114, 1030, 884, 816, 737, 698, 630, 477 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$= 2:1): $\delta$=6.92 (s, 2H), 6.58 (s, 2H), 6.15 (s, 1H), 6.12 (s, 1H), 5.36 (brs, 1H), 4.99 (s, 1H), 3.67 (s, 3H), 2.91 (dd, $J_{gem}$=17.9 Hz, $J$=1.9 Hz, 1H), 2.72 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{23}H_{21}O_{11}$: 473.1084 $[M+H]^+$; found: 473.1070.

**4ab** (43%): $R_f$=0.31 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3304, 1694, 1619, 1596, 1516, 1438, 1373, 1342, 1231, 1192, 1142, 1039, 871, 759, 710, 668, 541 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.89 (s, 2H), 6.58 (s, 2H), 6.02 (d, $J$=1.9 Hz, 1H), 5.99 (d, $J$=2.4 Hz, 1H), 5.38 (brs, 1H), 4.98 (s, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 2.95 (dd, $J_{gem}$= 17.9 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1223.

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**4ac** (45%): $R_f$=0.45 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3357, 1686, 1619, 1595, 1514, 1448, 1426, 1362, 1330, 1196, 1145, 1112, 1039, 868, 821, 765, 639, 626, 554, 503 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.06 (s, 1H), 7.06 (d, $J$=1.9 Hz, 0.5H), 6.95 (d, $J$=1.9 Hz, 0.5H), 6.60 (s, 2H), 6.06 (d, $J$=1.9 Hz, 1H), 6.03 (d, $J$=1.9 Hz, 1H), 5.40 (brs, 1H), 5.02 (s, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.66 (s, 3H), 2.83 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.72 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1394.

**4ad** (40%): $R_f$=0.44 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3366, 1686, 1618, 1597, 1514, 1460, 1425, 1325, 1183, 1144, 1112, 1035, 996, 962, 912, 818, 756, 734, 538 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.04 (s, 2H), 6.59 (s, 2H), 6.03 (d, $J$=2.4 Hz, 1H), 6.02 (d, $J$=2.4 Hz, 1H), 5.36 (brs, 1H), 5.03 (s, 1H), 3.72 (s, 6H), 3.61 (s, 3H), 2.94 (d, $J_{gem}$=17.9 Hz, 1H), 2.72 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.7, 159.7, 156.9, 156.2, 147.8, 145.8, 132.6, 130.2, 120.4, 120.3, 107.3, 105.9, 99.5, 94.9, 93.4, 77.4, 70.3, 56.3, 55.3, 25.7 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1399.

**4ba** (48%): $R_f$=0.29 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3340, 1686, 1596, 1512, 1444, 1317, 1193, 1144, 1034, 973, 819, 768, 684, 648 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.97 (s, 2H), 6.63 (s, 2H), 6.07 (d, $J$=2.4 Hz, 1H), 6.02 (d, $J$=2.4 Hz, 1H), 5.42 (brs, 1H), 5.03 (s, 1H), 3.68 (s, 3H), 3.65 (s, 3H), 2.99 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.89 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.7, 159.7, 156.9, 156.2, 150.4, 145.5, 138.9, 135.3,134.8, 120.6, 109.7, 106.5, 99.6, 95.0, 93.5, 77.5, 69.5, 60.5, 55.3, 26.0 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1250.

**4bb** (47%): $R_f$=0.55 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3333, 1692, 1624, 1592, 1513, 1434, 1376, 1233, 1194, 1145, 1044, 987, 818, 757, 711, 525 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.90 (s, 2H), 6.61 (s, 2H), 6.05 (d, $J$=2.4 Hz, 1H), 6.01 (d, $J$=2.4 Hz, 1H), 5.43 (brs, 1H), 5.02 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 2.98 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.87 ppm (d, $J_{gem}$=17.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1405.

**4bc** (50%): $R_f$=0.36 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3357, 1696, 1623, 1591, 1509, 1430, 1365, 1343, 1192, 1143, 1101, 1045, 998, 945, 815, 757, 712, 538 $cm^{-1}$; $^1H$ NMR (270 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.01 (d, $J$=1.9 Hz, 1H), 6.92 (d, $J$=1.9 Hz, 1H), 6.61 (s, 2H), 6.05 (d, $J$=2.0 Hz, 1H), 6.01 (d, $J$=2.0 Hz, 1H), 5.42 (brs, 1H), 5.05 (s, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.65 (s, 3H), 3.63 (s, 3H), 2.93 (dd, $J_{gem}$=17.1 Hz, $J$=4.0 Hz, 1H), 2.84 ppm (d, $J_{gem}$=17.1 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1578.

**4bd** (39%): $R_f$=0.35 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3408, 1685, 1595, 1512, 1426, 1363, 1330, 1184, 1144, 1115, 997, 817, 752, 713, 554 $cm^{-1}$; $^1H$ NMR (270 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.03 (s, 2H), 6.60 (s, 2H), 6.03 (d, $J$=1.9 Hz, 1H), 6.01 (d, $J$=1.9 Hz, 1H), 5.37 (brs, 1H), 5.06 (s, 1H), 3.72 (s, 6H), 3.62 (s, 3H), 3.61 (s, 3H), 2.96 (brs, 1H), 2.95 ppm (brs, 1H); $^{13}C$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.6, 159.8, 157.0, 156.1, 150.6, 147.9, 135.3, 135.0, 120.5, 107.3, 106.1, 99.5, 94.9, 93.4, 77.3, 70.2, 60.4, 56.4, 55.3, 25.7 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1567.

**4ca** (55%): $R_f$=0.50 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3373, 1681, 1619, 1595, 1517, 1430, 1348, 1195, 1144, 1111, 1056, 994, 914, 872, 822, 761, 713, 524 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.90 (s, 2H), 6.75 (s, 2H), 6.05 (d, $J$=2.4 Hz, 1H), 6.01 (d, $J$=1.9 Hz, 1H), 5.46 (brs, 1H), 5.09 (s, 1H), 3.69 (s, 3H), 3.63 (s, 6H), 2.99 (dd, $J_{gem}$=17.4 Hz, $J$=3.9 Hz, 1H), 2.83 ppm (d, $J_{gem}$=16.9 Hz, 1H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1388.

**4cb** (65%): $R_f$=0.56 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3343, 1685, 1619, 1592, 1514, 1448, 1434, 1344, 1212, 1144, 1113, 1056, 995, 973, 911, 872, 821,759, 739, 712, 585 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.89 (s, 2H), 6.75 (s, 2H), 6.04 (d, $J$=2.4 Hz, 1H), 6.02 (d, $J$=2.4 Hz, 1H), 5.45 (brs, 1H), 5.08 (s, 1H, f), 3.68 (s, 3H), 3.64 (s, 3H), 3.62 (s, 6H), 2.99 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.82 ppm (d, $J_{gem}$=16.9 Hz, 1H); $^{13}C$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.8, 159.8, 157.0, 156.4, 150.9, 148.0, 140.5, 135.4, 129.4, 125.6, 109.6, 104.6, 99.6, 95.0, 93.5, 78.0, 69.7, 60.4, 56.2, 55.3, 26.2 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1556.

**4cc** (59%): $R_f$=0.50 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3372, 1698, 1619, 1592, 1510, 1454, 1426, 1341, 1216, 1199, 1145, 1108, 1033, 995, 981, 913, 872, 821, 759, 728, 712, 526 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.08 (d, $J$=1.9 Hz, 1H), 6.95 (d, $J$=1.9 Hz, 1H), 6.81 (s, 2H), 6.09 (d, $J$=1.9 Hz, 1H), 6.05 (d, $J$=1.9 Hz, 1H), 5.54 (brs, 1H), 5.15 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H), 3.66 (s, 6H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.90 ppm (dd, $J_{gem}$=17.9 Hz, $J$=0.97 Hz, 1H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 159.4, 155.9, 155.0, 151.9, 148.7, 146.8, 139.5, 134.5, 128.8, 125.3, 109.8, 106.0, 103.5, 98.9, 95.5, 94.2, 77.9, 68.8, 61.0, 56.1, 56.0, 55.3, 25.7 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1704.

**4cd** (62%): $R_f$=0.49 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3371, 1698, 1594, 1513, 1459, 1423, 1353, 1329, 1205, 1184, 1145, 1111, 1033, 962, 910, 868, 817, 756, 739, 587 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.19 (s, 2H), 6.69 (s, 2H), 6.24 (d, $J$=2.4 Hz, 1H), 6.06 (d, $J$=2.4 Hz, 1H), 5.67 (brs, 1H), 5.09 (s, 1H), 3.85 (s, 6H), 3.76 (s, 3H), 3.73 (s, 6H), 3.04 (dd, $J_{gem}$=16.9 Hz, $J$=4.3 Hz, 1H), 2.84 ppm (dd, $J_{gem}$=17.4 Hz, $J$=2.4 Hz, 1H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta$=165.3, 159.5, 156.1, 155.0, 151.9, 146.9, 146.6, 139.6, 134.7, 128.8, 120.9, 107.0, 103.7, 99.1, 95.3, 94.2, 77.9, 68.4, 56.4, 56.2, 55.4, 25.7 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$, found: 529.1708.

**4da** (50%): $R_f$=0.38 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3339, 1685, 1593, 1508, 1444, 1422, 1354, 1325, 1227, 1193, 1145, 1125, 1033, 995, 972, 874, 817, 729, 549 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.96 (s, 2H), 6.83 (s, 2H), 6.08 (d, $J$=2.4 Hz, 1H), 6.03 (d, $J$=2.4 Hz, 1H), 5.48 (brs, 1H), 5.14 (s, 1H), 3.67 (s, 6H), 3.60 (s, 3H), 3.22 (s, 3H), 3.01 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.86 ppm (d, $J_{gem}$=16.4 Hz, 1H); $^{13}C$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.2, 159.8, 157.1, 156.3, 153.4, 145.7, 138.9, 137.8, 134.8, 120.6, 109.6, 104.7, 99.7, 95.1, 93.6, 78.1, 69.2, 60.5, 56.1, 55.3, 26.3 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1553.

**4db** (73%): $R_f$=0.51 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3353, 1694, 1628, 1592, 1505, 1446, 1421, 1344, 1227, 1195, 1146, 1123, 1059, 1042, 994, 972, 911, 873, 816, 758, 731, 713, 668, 634 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.94 (s, 2H), 6.84 (s, 2H), 6.09 (d, $J$=2.4 Hz, 1H), 6.04 (d, $J$=2.4 Hz, 1H), 5.52 (brs, 1H), 5.16 (s, 1H), 3.73 (s, 3H), 3.67 (s, 6H), 3.65 (s, 3H), 3.61 (s, 3H), 3.03 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.89 ppm (d, $J_{gem}$=17.4 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.5, 159.2, 155.9, 155.7, 153.0, 149.2, 139.0, 137.5, 133.4, 125.1, 109.3, 103.9, 99.1, 95.2, 93.3, 77.9, 68.6, 60.7, 60.6, 55.9, 55.2, 25.8 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1707.

**4dc** (64%): $R_f$=0.53 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3385, 1711, 1625, 1590, 1504, 1458, 1420, 1342, 1218, 1198, 1145, 1121, 1098, 1035, 998, 872, 814, 759, 729, 668, 640 $cm^{-1}$; $^1H$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.05 (d, $J$=2.0 Hz, 1H), 6.92 (d, $J$=2.0 Hz, 1H), 6.84 (s, 2H), 6.09 (d, $J$=2.3 Hz, 1H), 6.04 (d, $J$=2.3 Hz, 1H), 5.55 (brs, 1H), 5.18 (s, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.66 (s, 6H), 3.64 (s, 3H), 3.61 (s, 3H), 3.04 (dd, $J_{gem}$=17.4 Hz, $J$=4.3 Hz, 1H), 2.90 ppm (d, $J_{gem}$=17.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$=165.2, 159.4, 155.8, 155.1, 153.1, 151.9, 148.7, 139.6, 137.6, 133.3, 127.2, 125.3, 109.8, 105.9, 103.8, 98.9, 95.5, 94.2, 77.9, 68.7, 61.0, 60.8, 56.0, 55.3, 25.7 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1866.

**4dd** (68%): $R_f$=0.52 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3360, 1708, 1626, 1592, 1510, 1460, 1421, 1355, 1329, 1207, 1185, 1146, 1115, 1035, 1002, 962, 914, 818, 761, 730, 712, 666 $cm^{-1}$; $^1H$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.10 (s, 2H), 6.87 (s, 2H), 6.10 (s, 1H), 6.07 (s, 1H), 5.58 (brs, 1H), 5.21 (s, 1H), 3.73 (s, 6H), 3.66 (s, 3H), 3.66 (s, 6H), 3.62 (s, 3H), 3.05 (dd, $J_{gem}$=17.8 Hz, $J$=3.6 Hz, 1H), 2.93 ppm (d, $J_{gem}$=17.8 Hz, 1H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta$=165.4, 159.5, 156.0, 155.1, 153.1, 146.6, 139.6, 137.9, 133.3, 120.9, 107.0, 104.0, 99.1, 95.4, 94.1,

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77.8, 68.4, 60.8, 56.4, 56.0, 55.3, 25.7 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1867.

**5aa** (42%): $R_f$=0.46 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3315, 2943, 2851, 1678, 1602, 1514, 1460, 1434, 1347, 1191, 1144, 1113, 1054, 1016, 819, 800, 760, 663, 653, 511 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.04 (s, 2H), 6.84 (s, 2H), 6.07 (d, $J$=1.9 Hz, 1H), 6.04 (d, $J$=1.9 Hz, 1H), 5.57 (brs, 1H), 5.16 (s, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.07 (dd, $J_{gem}$=17.4 Hz, $J$=4.8 Hz), 2.98 ppm (dd, $J_{gem}$=17.4 Hz, $J$=1.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{24}H_{23}O_{11}$: 487.1240 $[M+H]^+$; found: 487.1247.

**5ab** (51%): $R_f$=0.50 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3260, 2923, 2851, 1693, 1619, 1594, 1525, 1498, 1453, 1437, 1375, 1341, 1215, 1190, 1145, 1120, 1039, 997, 976, 809, 761, 713, 668, 516 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.98 (s, 2H), 6.64 (s, 2H), 6.17 (d, $J$=2.0 Hz, 1H), 6.13 (d, $J$=2.0 Hz, 1H), 5.55 (brs, 1H), 5.09 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.03 (dd, $J_{gem}$=17.8 Hz, $J$=4.6 Hz, 1H), 2.87 ppm (d, $J_{gem}$=17.8 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1406.

**5ac** (56%): $R_f$=0.56 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3279, 2924, 2851, 1707, 1617, 1594, 1512, 1456, 1427, 1364, 1344, 1198, 1146, 1113, 1034, 997, 810, 760, 653, 516 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.07 (d, $J$=1.9 Hz, 1H), 7.01 (d, $J$=1.9 Hz, 1H), 6.66 (s, 2H), 6.18 (d, $J$=2.4 Hz, 1H), 6.13 (d, $J$=2.4 Hz, 1H), 5.53 (brs, 1H), 5.13 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.04 (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H), 2.93 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{30}NO_{11}$: 532.1819 $[M+H]^+$; found: 532.1816.

**5ad** (50%): $R_f$=0.56 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3354, 2923, 2850, 1685, 1593, 1512, 1455, 1425, 1363, 1330, 1183, 1144, 1110, 1030, 999, 816, 799, 761, 667, 652, 514, 501 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=7.04 (s, 2H), 6.59 (s, 2H), 6.03 (d, $J$=2.4 Hz, 1H), 6.02 (d, $J$=2.4 Hz, 1H), 5.36 (brs, 1H), 5.03 (s, 1H), 3.72 (s, 6H), 3.61 (s, 3H), 3.61 (s, 3H), 2.94 (d, $J_{gem}$=17.9 Hz, 1H), 2.72 ppm (dd, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1552.

**5ba** (55%): $R_f$=0.51 ($CHCl_3$:methanol=5:1); FTIR (solid): $\tilde{\nu}$=3294, 2942, 2840, 1687, 1595, 1530, 1499, 1452, 1438, 1372, 1335, 1312, 1191, 1142,1119, 1034, 976, 874, 853, 817, 767, 715, 630, 491 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.96 (s, 2H), 6.63 (s, 2H), 6.13 (d, $J$=2.4 Hz, 1H), 6.08 (d, $J$=2.4 Hz, 1H), 5.41 (brs, 1H), 5.03 (s, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.25 (s, 3H), 2.96 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.86 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=166.6, 160.2, 159.4, 156.0, 150.6, 145.6, 138.9, 135.4, 134.8, 120.8, 109.7, 106.6, 100.5, 94.1, 92.0, 77.7, 69.3, 60.4, 55.7, 55.5, 26.1 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{25}H_{25}O_{11}$: 501.1397 $[M+H]^+$; found: 501.1397.

**5bb** (39%): $R_f$=0.43 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3349, 2935, 2844, 1693, 1619, 1594, 1499, 1453, 1435, 1348, 1267, 1216, 1192, 1141, 1117, 1050, 988, 977, 815, 757, 711, 616 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta$=6.98 (s, 2H), 6.65 (s, 2H), 6.18 (d, $J$=2.4 Hz, 1H), 6.14 (d, $J$=2.4 Hz, 1H,), 5.59 (brs, 1H), 5.12 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.03 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.90 ppm (dd, $J_{gem}$=17.9 Hz, $J$=1.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1575.

**5bc** (52%): $R_f$=0.55 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3344, 2929, 2849, 1697, 1619, 1592, 1500, 1453, 1427, 1365, 1343, 1217, 1197, 1143, 1108, 1049, 997, 948, 814, 760, 714, 519 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.19 (d, $J$=1.9 Hz, 1H), 7.08 (d, $J$=1.9 Hz, 1H), 6.69 (s, 2H), 6.21 (d, $J$=1.9 Hz, 1H), 6.09 (d, $J$=1.9 Hz, 1H), 5.53 (brs, 1H), 5.03 (s, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 3.76 (s, 3H), 3.03 ppm (brs, 2H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1721.

**5bd** (46%): $R_f$=0.55 ($CHCl_3$:methanol=7:1); FTIR (solid): $\tilde{\nu}$=3341, 2917, 2851, 1709, 1618, 1594, 1513, 1499, 1462, 1426, 1362, 1338, 1260, 1216, 1203, 1145, 1113, 1052, 958, 816, 759, 720, 615 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.20 (s, 2H), 6.70 (s, 2H), 6.22 (d, $J$=2.4 Hz, 1H), 6.10 (d, $J$=2.4 Hz, 1H), 5.49 (brs, 1H), 5.06 (s, 1H), 3.90 (s, 6H), 3.83 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.07 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 3.00 ppm (d, $J_{gem}$=17.9 Hz, $J$=2.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{29}O_{11}$: 529.1710 $[M+H]^+$; found: 529.1699.

**5ca** (55%): $R_f$=0.49 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3230, 2924, 2851, 1693, 1594, 1511, 1442, 1371, 1345, 1224, 1189, 1144, 1116, 1039, 823, 764, 721, 510 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.90 (s, 2H), 6.75 (s, 2H), 6.05 (d, $J$=2.4 Hz, 1H), 6.01 (d, $J$=1.9 Hz, 1H), 5.46 (brs, 1H), 5.09 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H), 2.99 (dd, $J_{gem}$=17.4 Hz, $J$=3.9 Hz, 1H), 2.83 ppm (d, $J_{gem}$=17.4 Hz, 1H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{26}H_{27}O_{11}$: 515.1553 $[M+H]^+$; found: 515.1569.

**5cb** (51%): $R_f$=0.61 ($CHCl_3$:methanol=9:1); FTIR (solid): $\tilde{\nu}$=3387, 2925, 2849, 1713, 1620, 1591, 1505, 1460, 1421, 1365, 1344, 1219, 1201, 1147, 1120, 1048, 1001, 948, 872, 814, 759, 732, 718, 669 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.13 (s, 2H), 6.72 (s, 2H), 6.25 (d, $J$=1.9 Hz, 1H), 6.12 (d, $J$=1.9 Hz, 1H), 5.58 (brs, 1H), 5.05 (s, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.80 (s, 6H), 3.78 (s, 3H), 3.03 ppm (brd, $J$=2.9 Hz, 2H); HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{32}NO_{11}$: 546.1975 $[M+H]^+$; found: 546.1987.

**5cc** (57%): $R_f$=0.55 ($CHCl_3$:methanol=12:1); FTIR (solid): $\tilde{\nu}$=3394, 2919, 2849, 1709, 1618, 1592, 1499, 1460, 1427, 1361, 1344, 1217, 1202, 1146, 1111, 1045, 996, 982, 947, 818, 759, 717, 664, 532 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.26 (d, $J$=1.9 Hz, 1H), 7.09 (d, $J$=1.9 Hz, 1H), 6.72 (s, 2H), 6.25 (d, $J$=2.4 Hz, 1H), 6.11 (d, $J$=2.4 Hz, 1H), 5.59 (brs, 1H), 5.05 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 3.78 (s, 6H), 3.04 ppm (d, $J$=3.4 Hz, 2H, l); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta$=165.1, 159.6, 158.8, 155.5, 151.9, 148.6, 146.8, 139.5, 134.4, 128.9, 125.4, 109.8, 106.0, 103.4, 100.0, 93.4, 92.0, 77.9, 77.2, 68.8, 61.0, 56.1, 56.0, 55.4×2, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1881.

**5cd** (53%): $R_f$=0.55 ($CHCl_3$:methanol=12:1); FTIR (solid): $\tilde{\nu}$=3401, 2942, 2839, 1703, 1612, 1592, 1514, 1498, 1454, 1422, 1355, 1325, 1202, 1144, 1145, 1111, 1033, 962, 910, 868, 817, 756, 739, 587 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.20 (s, 2H), 6.70 (s, 2H), 6.25 (d, $J$=1.9 Hz, 1H), 6.12 (d, $J$=1.9 Hz, 1H), 5.66 (brs, 1H), 5.07 (s, 1H), 3.85 (s, 6H), 3.80 (s, 3H), 3.79 (s, 3H), 3.73 (s, 6H) 3.06 (dd, $J_{gem}$=16.9 Hz, $J$=4.3 Hz, 1H), 2.99 ppm (d, $J_{gem}$=16.9 Hz, $J$=2.9 Hz, 1H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta$=165.2, 159.7, 158.9, 155.6, 146.9, 146.5, 139.4, 134.6, 128.9, 121.1, 107.0, 103.6, 100.2, 93.3, 91.9, 77.9, 77.2, 68.5, 56.4, 56.2, 55.4×2, 26.0 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1885.

**5da** (43%): $R_f$=0.24 ($CHCl_3$:methanol=12:1); FTIR (solid): $\tilde{\nu}$=3338, 1691, 1592, 1498, 1453, 1420, 1306, 1191, 1145, 1119, 1035, 972, 813, 758, 631, 461 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.96 (s, 2H), 6.84 (s, 2H), 6.14 (d, $J$=2.4 Hz, 1H), 6.11 (d, $J$=2.4 Hz, 1H), 5.49 (brs, 1H), 5.16 (s, 1H), 3.71 (s, 3H), 3.71 (s, 3H), 3.67 (s, 6H), 3.61 (s, 3H), 3.00 (dd, $J_{gem}$=17.9 Hz, $J$=4.4 Hz, 1H), 2.84 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (67.8 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.9, 159.4, 158.7, 155.2, 152.8, 144.5, 133.4, 109.1, 109.6, 104.7, 99.7, 95.1, 93.6, 78.1, 69.2, 60.5, 56.1, 55.3×2, 26.3 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{27}H_{32}NO_{11}$: 546.1975 $[M+NH_4]^+$; found: 546.1995.

**5db** (55%): $R_f$=0.34 ($CHCl_3$:methanol=12:1); FTIR (solid): $\tilde{\nu}$=3379, 1707, 1618, 1591, 1499, 1454, 1420, 1345, 1219, 1194, 1145, 1116, 1053, 998, 975, 873, 838, 814, 759, 733, 712, 670, 631 $cm^{-1}$; $^1H$ NMR (400 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=6.91 (s, 2H), 6.83 (s, 2H), 6.14 (d, $J$=2.4 Hz, 1H), 6.11 (d, $J$=2.4 Hz, 1H), 5.51 (brs, 1H), 5.17 (s, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.66 (s, 6H), 3.60 (s, 3H), 3.00 (dd, $J_{gem}$=17.9 Hz, $J$=4.3 Hz, 1H), 2.85 ppm (d, $J_{gem}$=17.9 Hz, 1H); $^{13}C$ NMR (100 MHz, [$D_6$]acetone:$D_2O$=2:1): $\delta$=165.5, 159.2, 155.9, 155.7, 153.0, 148.6, 138.6, 137.6, 133.4, 125.7, 109.8, 103.8, 100.0, 93.4, 92.1, 77.9, 68.8, 60.9, 60.8, 56.0, 55.4×2, 25.9 ppm; HRMS (ESI-TOF): *m/z* (%) calcd for $C_{28}H_{31}O_{11}$: 543.1866 $[M+H]^+$; found: 543.1891.

**5dc** (59%): $R_f$=0.66 ($CHCl_3$:methanol=15:1); FTIR (solid): $\tilde{\nu}$=3386, 1710, 1619, 1589, 1503, 1455, 1420, 1362, 1342, 1216, 1196, 1145, 1120, 1048, 999, 982, 948, 872, 814, 758, 734, 717, 667, 631 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.26 (d, $J$=1.4 Hz, 1H), 7.09 (d, $J$=1.4 Hz, 1H), 6.72 (s, 2H), 6.25 (d, $J$=2.4 Hz, 1H), 6.12 (d, $J$=2.4 Hz, 1H), 5.61 (brs, 1H), 5.06 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H),

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3.78 (s, 3H), 3.76 (s, 6H), 3.04 ppm (d, $J=3.4$ Hz, 2H); HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{29}H_{36}NO_{11}$: 574.2288 $[M+NH_4]^+$; found: 574.2317.

**5dd** (68%): $R_f=0.66$ ($CHCl_3$:methanol=15:1); FTIR (solid): $\tilde{\nu}=3387$, 1707, 1618, 1591, 1498, 1453, 1420, 1356, 1329, 1203, 1183, 1145, 1114, 1035, 1005, 954, 915, 816, 758, 717, 668, 633 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta=7.20$ (s, 2H), 6.70 (s, 2H), 6.25 (d, $J=2.4$ Hz, 1H), 6.12 (d, $J=2.4$ Hz, 1H), 5.66 (brs, 1H), 5.09 (s, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.80 (s, 6H), 3.79 (s, 3H), 3.71 (s, 6H), 3.05 (brs, 1H), 3.04 (brs, 1H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$): $\delta=165.3$, 159.8, 158.9, 155.6, 153.2, 146.7, 139.5, 137.9, 133.5, 121.0, 107.0, 104.0, 100.3, 93.3, 91.9, 77.9, 68.5, 60.8, 56.5, 56.5, 56.1, 55.4, 26.0 ppm; HRMS (ESI-TOF): $m/z$ (%) calcd for $C_{29}H_{33}O_{11}$: 557.2023 $[M+H]^+$; found: 557.2022.

*Biological Evaluation*

**Cell culture**: B16 cells (a mouse melanoma) were maintained in Dulbecco's modified Eagle's medium (DMEM) (COSMOBIO Co. Ltd., Tokyo, Japan) supplemented with fetal bovine serum (FBS, 5%) (Biological Industries, Kibbutz Beit Kaemek, Israel) in a humidified atmosphere with $CO_2$ (5%) at 37°C. To assess cell proliferation, cells were plated in 24-well plates at a density of $1\times10^4$ cells/well, and 24 hours later, they were treated with the indicated concentrations of EGCG for 96 hours in DMEM supplemented with FBS (1%), BSA (5 mg $mL^{-1}$), superoxide dismutase (5 U $mL^{-1}$), and catalase (200 U $mL^{-1}$). Cell density is adhesive cell number per well. Cell viability was evaluated by trypan blue dye exclusion assay. Values are means ±S.D. ($n=3$). Data containing star marks are significantly different from the control group at $p<0.05$*, $p<0.01$**, and $p<0.001$*** (Student's $t$-test).

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