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Generation of *o*-quinodimethanes (*o*-QDMs) from benzo[*c*]oxepines and the synthetic application for polysubstituted tetrahydronaphthalenes

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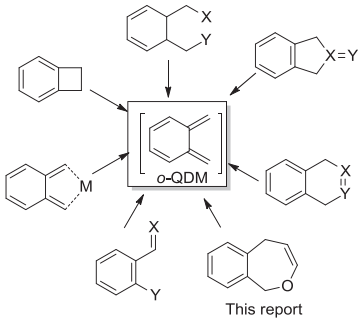
ABSTRACT

A novel method for the generation of *o*-quinodimethane (*o*-QDM) intermediates is reported using a mild and efficient base-promoted ring-opening of benzo[*c*]oxepines. Among the benzo[*c*]oxepines studied, indanone containing analogues demonstrated the greatest variety of reactivity. A number of decay modes were observed, in addition with trapping of the *o*-QDM intermediates using dienophiles for the synthesis of polysubstituted tetrahydronaphthalenes with high regioselectivity. This research provided a novel method to generate *o*-QDM intermediates from benzo[*c*]oxepine precursors.

1. Introduction

Since *o*-quinodimethane (*o*-QDM) was discovered by Cava in 1957,[1] this elusive intermediate has attracted widespread attention from both theoretical and synthetic chemists.[2,3] In recent decades, a significant amount of research has been undertaken in *o*-QDM chemistry with diverse applications in the syntheses of natural products and pharmaceuticals,[4] fullerene chemistry,[5] as building blocks in the syntheses of polymeric materials[6] and materials science,[7] among others.[8] Owing to their utility as synthetic intermediates, considerable attention has been devoted to the development of efficient methods for the generation of *o*-QDM under mild conditions.[2] There are several classic precursors for the generation of *o*-QDM, including benzocyclobutenes,[9] R,R′-substituted *o*-xylenes,[10] benzo-fused heterocyclic compounds,[11] *ortho*-substituted benzaldehydes or benzophenones,[12] *o*-methylstyrenes[13] and *o*-xylylenes metal complexes (Scheme 1).[14] Therefore, the development of a novel process for the generation of *o*-QDM intermediates from unprecedented precursors remains highly significant.



Scheme 1. Various precursors for the generation of *o*-QDM.

We have recently reported a novel synthesis of β-substituted naphthalenes from benzo[*c*]oxepines.[15] The transformation was presumed to occur via the in situ generation of *o*-QDM by the ring opening of benzo[*c*]oxepines (Scheme 2). The benzo[*c*]oxepines were prepared from α-substituted ketones and 1,2-*bis*(halomethyl) benzenes under basic conditions.[16] The key step in the transformations of naphthalene was the presence of the elusive *o*-QDM intermediate, which is generally a highly reactive species with a short lifetime. This highly reactive intermediate could not be isolated as a consequence of an electrocyclic ring closure and

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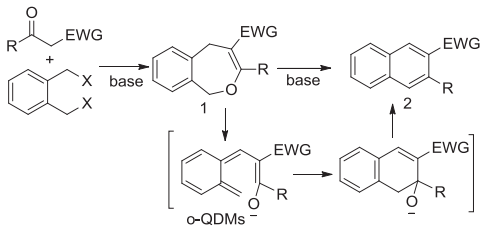
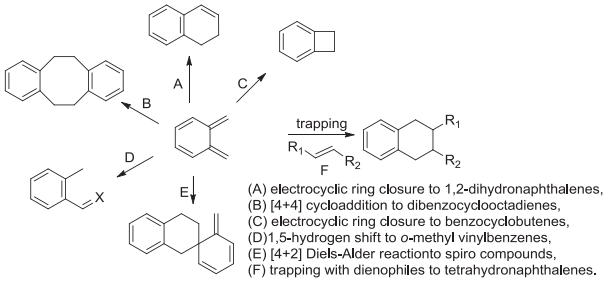
subsequent aromatization, which yielded naphthalene products **2**. The transient *o*-QDM intermediate is mechanistically interesting and provides a potential for the generation of this versatile building block from unprecedented precursors.



Scheme 2. Proposed reaction pathway to synthesize β-substituted naphthalenes from benzo[*c*]oxepines.

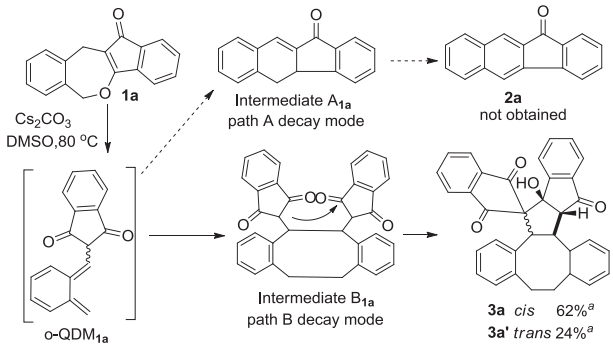
Although there have been reports of *o*-QDM intermediates that exhibit high thermodynamic stability,[17] most of these species are unstable. Their reactions generally occur incidentally, including decay reactions and trapping experiments such as the Diels–Alder reaction with dienophiles. To evaluate our hypothesis for the presence of the *o*-QDM intermediate, we examined the possible decay modes of these intermediates (Scheme 3, path A–D). Additionally, we attempted to trap these intermediates by reaction with dienophiles for the synthesis of tetrahydronaphthalenes (Scheme 3, path F).



Scheme 3. Different reaction pathways for *o*-QDM species.

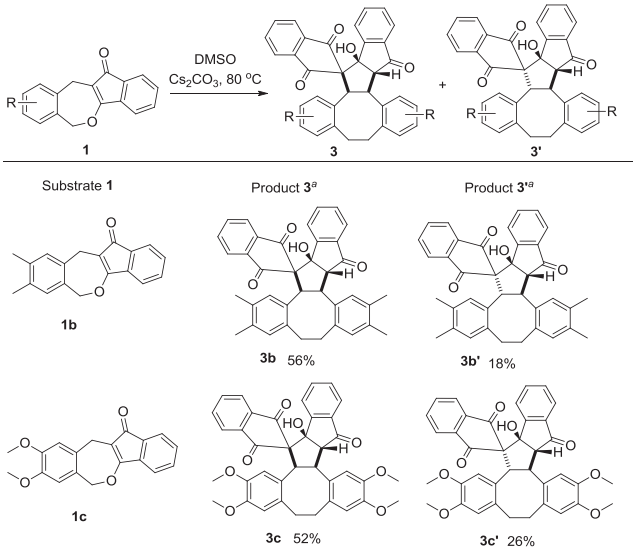
2. Results and discussion

The naphthalene products reported previously were thought to be formed via path A (electrocyclic ring closure with subsequent aromatization).[15] Indanone containing benzo[*c*]oxepine **1a** did not provide the corresponding benzo[*b*]fluorenone **2a** via pathway A, but instead provided a mixture of the *trans*/*cis* isomers **3a** and **3a**′ in yields of 62% and 24%, respectively (Scheme 4). The dibenzocyclooctadiene framework of these compounds indicated that this transformation may have followed pathway B, giving intermediate



Scheme 4. The path A and path B decay modes of *o*-QDM generated by indanone contained benzo[*c*]oxepine precursor. [a]Isolated yields.

B_{1a} in which nucleophilic addition of a tertiary carbon adjacent to a carbonyl afforded the products. Plausibly, the reaction pathway followed by compound **1a** may be attributed to the delocalized π-system by the indanone substituent. This would have the effect of stabilizing, and therefore increasing the lifetime of the *o*-QDM species.[17c,18] Additionally, the internal nucleophilic addition of intermediate B_{1a} provided products with high thermodynamic stability, thus promoting this reaction pathway. To test this hypothesis, several homologues of indanone containing benzo[*c*]oxepines were prepared for mechanistic investigation. Compounds **1b** and **1c** yielded the expected products **3b**, **3b**′, **3c** and **3c**′ in 56, 18, 52 and 26% yields, respectively (Scheme 5). The stereochemistry of compounds **3c** and **3c**′ were determined using X-ray crystallography (Fig. 1).[19] However, the reaction of benzo[*c*]oxepine **1d** gave the benzocyclobutene product **4d**, which suggested that pathway C was followed when certain substituents were present on the benzo[*c*]oxepine derivatives (Scheme 6).



Scheme 5. Synthesis of dibenzocyclooctadiene derivatives via path B decay mode of *o*-QDM intermediate form indanone-contained benzo[*c*]oxepine precursors. [a]Isolated yields.

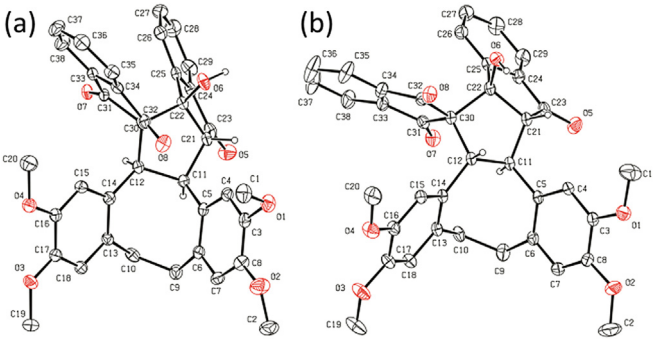
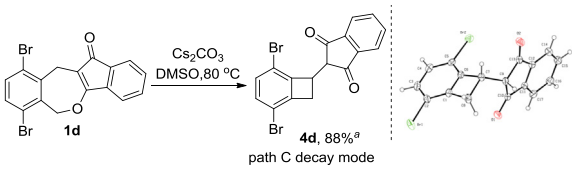


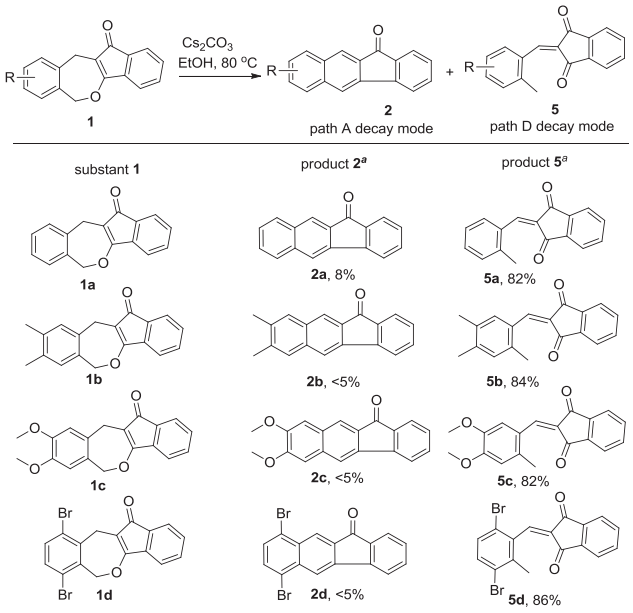
Fig. 1. X-ray structure of compounds (a) **3c** and (b) **3c**′.

As we had benzo[*c*]oxepines derivatives that reacted via pathways B or C, we focused on materials and methods to study the alternative decay modes. To study pathway D, Cs_2CO_3 was added to benzo[*c*]oxepine **1a** in a variety of solvents. There was no reaction observed when the solvents MeOH, MeCN or dioxane were used. When the reaction was performed in DMF, a complex mixture was obtained that could not be identified. However, when the reaction was performed in EtOH at 80 °C, product **5a** was obtained in 82% yield (Scheme 7). The transformation was successfully performed



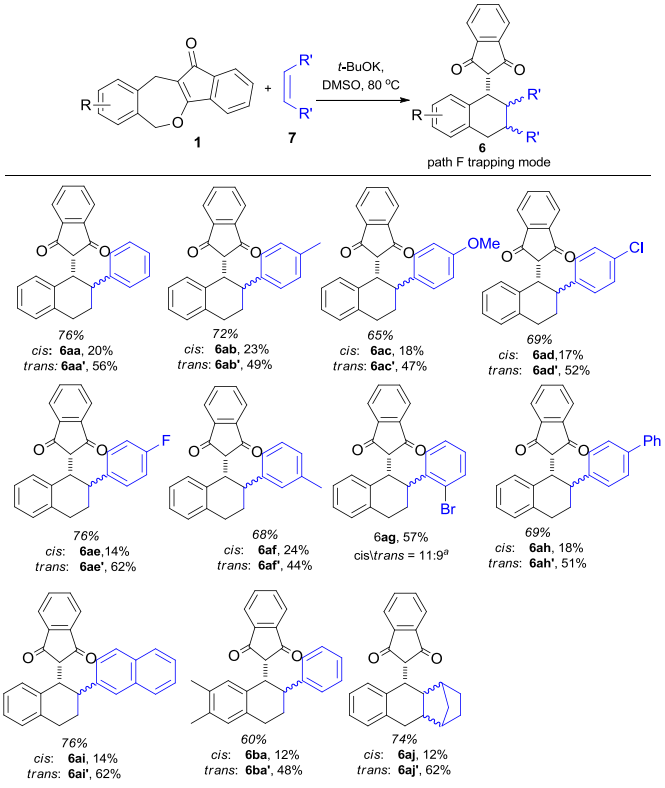
Scheme 6. The path C decay mode of *o*-QDM generated by indanone contained benzo[*c*]oxepine precursor. [a]Isolated yields.

using the indanone containing benzo[*c*]oxepines **1b**–**d** to afford the compounds **5b**–**d**, containing the *o*-methylstyrene moiety in similar yields. In addition to the products resulting from a 1,5-hydrogen shift (path D), the reaction involving compound **1a** also gave benzo[*b*]fluorenone (path A) in low yield (**2a**: 8%). Regrettably, substrates **1b**–**d** only provided these products (path A) in trace amounts and could not be isolated. This indicated the *o*-QDM intermediate, which generated from indanone containing benzo[*c*]oxepine precursors, were in favour of 1,5-hydrogen shift (path D) to provide the *o*-methylstyrenes rather than electrocyclic ring closure (path A)/aromatization to provide benzo[*b*]fluorenone derivatives.[18b]



Scheme 7. The path A and D decay modes of *o*-QDM generated by indanone contained benzo[*c*]oxepine precursors. [a]Isolated yields.

These experiments provided convincing evidence for the generation of the *o*-QDM intermediate from benzo[*c*]oxepines. The synthetic application of the *o*-QDM species, generated from benzo[*c*]oxepines, as a diene in Diels–Alder reactions with various dienophiles was further explored because the polysubstituted tetrahydronaphthalene products (**6**, Scheme 8) generated from these reactions are core structures in numerous naturally occurring and biologically active substances.[2c] When styrene was reacted with **1a** in DMSO containing Cs_2CO_3 at 80 °C, reaction pathway B ([4+4] cycloaddition) predominantly afforded the dibenzocyclooctadienes **3a** and **3a′** in 60% overall yield (46% and 14%, respectively). In addition to pathway B, the tetrahydronaphthalene products **6aa** and **6aa′** from pathway F ([4+2] Diels–Alder reaction) were also isolated in 30% overall yield (6% and 24%, respectively. Table S1, Supplementary data). To avoid reactions from pathway B occurring, the experimental procedure was optimized by adding a solution of **1a** (in DMSO) drop-wise into a mixture of styrene and *t*-BuOK in DMSO at 80 °C. This had the effect of increasing the yield of the Diels–Alder reaction products **6aa** and **6aa′** (pathway F) to an overall yield of 76% (20% and 56%, respectively) and the dibenzocyclooctadiene reaction products from pathway B nearly suppressed (10% yield). With the conditions optimized (for detailed conditions see Supplementary data, Table S1), the scope of the [4+2] Diels–Alder cycloaddition was examined. A series of styrene derivatives effectively reacted with benzo[*c*]oxepine **1a** (Scheme 8, **6aa**–**6ah**). Additionally, reactions involving β-vinylnaphthalene and norbornene were also successful (Scheme 8, **6ai**–**6aj**). The stereochemistry of products **6ab** and **6ab′** was determined using X-ray crystallography (Fig. 2).[19] The formation of the products **6** provided additional evidence for the generation of *o*-QDM intermediate from benzo[*c*]oxepines and developed an efficient approach for the construction of polysubstituted tetrahydronaphthalene.



Scheme 8. Pathway F trapping of *o*-QDM generated by indanone contained benzo[*c*]oxepine precursors. Isolated yields. [a]Diastereomeric ratio (dr) was determined using ^{1}H NMR analysis of the crude product.

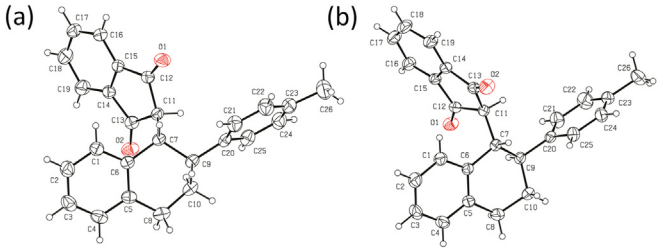


Fig. 2. X-ray crystal structures of compounds (a) **6ab** and (b) **6ab′**.

3. Conclusion

In summary, we have described a novel method for the generation of *o*-QDM intermediates. The starting material benzo[*c*]oxepines were readily prepared and the subsequent formation of the *o*-QDM intermediates was achieved under basic conditions in DMSO. Among the benzo[*c*]oxepines studied, the indanone containing

analogues demonstrated the great varied reactivity. This was attributed to the delocalized π-system of the indanone moiety, which stabilized and increased the lifetime of the *o*-QDM intermediate. By adjusting the reaction conditions when using the indanone containing benzo[*c*]oxepines, the reaction pathway was manipulated to yield a number of different products, including naphthalene, dibenzocyclooctadiene, benzocyclobutene and *o*-methylstyrene. These experiments gave convincing evidence for the presence of the *o*-QDM intermediate. This intermediate, being a *cis*-diene, was highly reactive towards dienophiles in Diels–Alder reactions. As such, it could be used as an important building block in the synthesis of polysubstituted tetrahydronaphthalenes via an intermolecular Diels–Alder reaction. Reaction pathways B, C and F were observed for the indanone contained benzo[*c*]oxepines in DMSO and pathways A and D tended to occur in EtOH; however, trace amounts of alternative reaction pathways were always unavoidable. Further investigations for the synthetic applications of this novel method to generate *o*-QDM intermediates are currently underway in our laboratory.

4. Experimental

4.1. General

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H spectra were recorded in CDCl3 or DMSO-d_6 on 300/400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constants (Hertz) and integration. ^{13}C spectra were recorded in CDCl3 or DMSO on 75/100/150 MHz NMR spectrometers and resonances (δ) are given in parts per million. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. MS was carried out on a Finnigan Trace MS spectrometer (EI, 70 eV). The X-ray crystal-structure determinations of **1a**, **3c**, **3c′**, **4d**, **5a**, **6ab**, and **6ab′** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

*4.1.1. General procedure for the synthesis of **1** (**1a** as an example).* A mixture of 1,2-bis(bromomethyl)benzene **S1a** (3.168 g, 12 mmol), 1*H*-indene-1,3(2*H*)-dione **S2a** (1.46 g, 10 mmol) and Cs_2CO_3 (6.52 g, 20 mmol) in DMSO (20 mL) was stirred at 80 °C for 4 h. The resulting mixture was poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×150 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=40/1) to afford the product **1a** as a yellow solid.

*4.1.2. General procedure for the synthesis of **2** (**2a** as an example).* A mixture of 6*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12(11*H*)-one **1a** (248 mg, 1.0 mmol), and Cs_2CO_3 (652 mg, 2 mmol) in EtOH (5 mL) was stirred at 80 °C for 2 h. The resulting mixture was then poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×100 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=20/1) to afford the products **2a**.

*4.1.3. General procedure for the synthesis of **3** (**3a** as an example).* A mixture of 6*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12(11*H*)-one **1a** (248 mg, 1.0 mmol), and *t*-BuOK (224 mg, 2 mmol) in DMSO (5 mL) was stirred at 80 °C for 2 h. The resulting mixture was then poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×100 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=5/1) to afford the products **3a** and **3a′**.

*4.1.4. General procedure for the synthesis of **4** (**4d** as an example).* A mixture of 7,10-dibromo-6*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12(11*H*)-one **4a** (406 mg, 1.0 mmol), and *t*-BuOK (224 mg, 2 mmol) in DMSO (5 mL) was stirred at 80 °C for 2 h. The resulting mixture was then poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×100 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=30/1) to afford the products **4a**.

*4.1.5. General procedure for the synthesis of **5** (**5a** as an example).* A mixture of 6*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12(11*H*)-one **1a** (248 mg, 1.0 mmol), and Cs_2CO_3 (652 mg, 2 mmol) in EtOH (5 mL) was stirred at 80 °C for 2 h. The resulting mixture was then poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×100 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=20/1) to afford the products **5a**.

*4.1.6. General procedure for the synthesis of **6** (**6aa** and **6aa′** as an example).* A mixture of styrene **7a** (520 mg, 5.0 mmol) and *t*-BuOK (224 mg, 2 mmol) in DMSO (2 mL) was stirred at 80 °C, then the DMSO solution (10 mL) of 7,10-dibromo-6*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12(11*H*)-one **1a** (248 mg, 1.0 mmol) was slowly drop to the mixture by constant pressure funnel. The reaction was last about 1 h and the resulting mixture was then poured into 300 mL 1 M HCl (aq) and extracted with EtOAc 3 times (3×100 mL). The organic extract was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=30/1) to afford the products **6**aa and **6**aa′.

4.2. Characterization data

*4.2.1. Compound **1a**.*[16c] 223.2 mg (Yield 90%); yellow solid; mp 131.9–133.5 °C; IR (KBr): 3452, 1691, 1617, 1584, 1400, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=6.8 Hz, 2H), 7.32 (d, *J*=7.6 Hz, 1H), 7.29–7.26 (m, 3H), 7.24–7.20 (m, 1H), 7.09 (d, *J*=6.8 Hz, 1H), 5.43 (s, 2H), 3.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 173.1, 141.5, 139.5, 133.6, 132.0, 131.7, 130.1, 129.7, 129.4, 128.4, 127.0, 120.7, 117.8, 107.6, 72.6, 26.1. HRMS (APCI): *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{13}O_2$: 249.0912; found: 249.0910.

*4.2.2. Compound **1b**.* 243.0 mg (Yield 88%); yellow solid; mp 162.8–164.4 °C; IR (KBr): 3455, 1717, 1623, 1588, 1394, 711 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J*=7.2 Hz, 1H), 7.28 (d, *J*=7.2 Hz, 1H), 7.21 (t, *J*=7.2 Hz, 1H), 7.14 (s, 1H), 7.08 (d, *J*=6.6 Hz, 1H), 7.04 (s, 1H), 5.38 (s, 2H), 3.70 (s, 2H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 173.2, 139.8, 138.8, 138.2, 135.1, 132.0, 131.8, 131.5, 131.1, 129.8, 129.3, 120.7, 117.8, 108.0, 72.6, 25.7, 19.4, 19.2. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{16}NaO_2$: 299.1042; found: 299.1043.

*4.2.3. Compound **1c**.* 265.0 mg (Yield 86%); yellow solid; mp 181.7–184.0 °C; IR (KBr): 1696, 1624, 1585, 1520, 1393, 1342, 1256, 1110, 709 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J*=7.2 Hz, 1H), 7.29 (t, *J*=7.2 Hz, 1H), 7.22 (t, *J*=7.2 Hz, 1H), 7.09 (d, *J*=6.6 Hz, 1H),

6.91 (s, 1H), 6.79 (s, 1H), 5.39 (s, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 173.1, 149.3, 147.1, 139.5, 134.4, 132.0, 131.6, 129.3, 125.5, 120.6, 117.7, 113.5, 111.7, 107.8, 72.4, 56.0, 55.9, 25.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{17}O_4$: 309.1120; found: 309.1121.

4.2.4. Compound ***1d***. 354.5 mg (Yield 88%); yellow solid; mp 205.8–207.6 °C; IR (KBr): 3450, 1708, 1627, 1592, 1399, 1140, 717 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J=8.4 Hz, 1H), 7.38 (d, J=6.6 Hz, 1H), 7.35 (d, J=8.4 Hz, 1H), 7.29 (t, J=7.2 Hz, 1H), 7.23 (t, J=7.2 Hz, 1H), 7.10 (d, J=7.2 Hz, 1H), 5.72 (s, 2H), 4.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 173.3, 143.4, 138.8, 134.9, 134.6, 132.2, 132.2, 131.6, 124.5, 122.6, 121.0, 118.2, 106.2, 71.1, 26.0. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}Br_2NaO_2$: 426.8935; found: 426.8939.

4.2.5. Compound ***2a***.[15b] 18.2 mg (Yield 8%); Yellow solid; mp 151.2–152.1 °C; IR (KBr): 2963, 2926, 1708, 1632, 1602, 1262, 1102, 1021 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.90 (d, J=7.8 Hz, 1H), 7.88 (s, 1H), 7.84 (d, J=7.8 Hz, 1H), 7.76 (d, J=7.8 Hz, 1H), 7.73 (d, J=7.2 Hz, 1H), 7.55 (t, J=7.8 Hz, 2H). 7.48 (t, J=7.2 Hz, 1H), 7.36 (t, J=7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 144.8, 138.3, 136.8, 136.1, 135.0, 133.5, 130.8, 129.1, 129.0, 128.7. 126.9, 125.6, 124.4, 120.9, 119.0, 109.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{11}O$: 231.0804; found: 231.0804.

4.2.6. Compound ***3a***. 308.8 mg (Yield 62%); pale yellow solid; mp 115.2–116.1 °C; IR (KBr): 3468, 2897, 1697, 1594, 1257, 762 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J=7.8 Hz, 1H), 7.77 (d, J=7.8 Hz, 1H), 7.72 (t, J=7.2 Hz, 1H), 7.63 (t, J=7.2 Hz, 1H), 7.54 (d, J=7.8 Hz, 1H), 7.50 (d, J=7.2 Hz, 1H), 7.41 (t, J=7.8 Hz, 1H), 7.36 (t, J=7.2 Hz, 1H), 7.19 (t, J=7.8 Hz, 1H), 7.00 (t, J=7.8 Hz, 1H), 6.92 (t, J=8.4 Hz, 2H), 6.85 (d, J=6.0 Hz, 1H), 6.81 (t, J=6.6 Hz, 1H), 6.74 (d, J=7.8 Hz, 1H), 6.70 (t, J=7.2 Hz, 1H), 5.52 (br, 1H), 5.45 (br, 1H), 4.53 (br, 1H), 3.85 (br, 1H), 3.84 (br, 1H), 3.63 (br, 1H), 2.96 (br, 1H), 2.71 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 202.4, 199.0, 142.6, 142.0, 139.2, 138.7, 138.6, 137.3, 136.5, 135.8, 134.9, 132.7, 132.3, 131.3, 130.9, 129.9, 127.6, 126.1, 124.9, 123.5, 123.1, 89.8, 68.4, 66.9, 64.8, 44.2, 35.9, 33.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{34}H_{24}NaO_4$: 519.1563; found: 519.1567.

4.2.7. Compound ***3a′***. 119.5 mg (Yield 24%); pale yellow solid; mp 134.0–136.1 °C; IR (KBr): 3433, 1746, 1708, 1262, 762 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J=7.2 Hz, 1H), 7.96 (d, J=7.2 Hz, 1H), 7.93–7.90 (m, 2H), 7.82 (d, J=7.2 Hz, 1H), 7.70 (d, J=7.8 Hz, 1H), 7.56–7.51 (m, 2H), 7.16 (t, J=7.2 Hz, 1H), 7.11 (d, J=7.3 Hz, 1H), 7.00–6.96 (m, 2H), 6.87–6.83 (m, 3H), 6.76 (t, J=7.2 Hz, 1H), 4.60–4.55 (m, 2H), 4.10 (d, J=6.0 Hz, 1H), 4.00 (br, 1H), 3.35–3.30 (m, 1H), 3.17–3.12 (m, 1H), 2.94–2.90 (m, 1H), 2.84–2.79 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 199.6, 199.4, 152.6, 143.2, 141.4, 139.4, 138.9, 137.5, 136.3, 136.2, 136.0, 135.4, 135.1, 130.4, 130.1, 129.7, 128.2, 127.9, 126.7, 126.7, 126.0, 125.9, 124.5, 124.1, 123.8, 123.8, 89.7, 68.2, 65.4, 56.8, 48.7, 34.4, 34.3. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{34}H_{24}NaO_4$: 519.1565; found: 519.1567.

4.2.8. Compound ***3b***. 310.2 mg (Yield 56%); yellow solid; mp 288.3–290.5 °C; IR (KBr): 3452, 1700, 1597, 1259, 771 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J=7.8 Hz, 1H), 7.76 (d, J=7.8 Hz, 1H), 7.71 (t, J=7.2 Hz, 1H), 7.61 (t, J=7.2 Hz, 1H), 7.47 (d, J=7.8 Hz, 1H), 7.39 (t, J=7.2 Hz, 1H), 7.35 (t, J=7.2 Hz, 1H), 6.91 (d, J=7.2 Hz, 1H), 6.67 (s, 1H), 6.57 (s, 1H), 6.47 (s, 1H), 5.59 (br, 1H), 5.35 (br, 1H), 4.44 (br, 1H), 3.83 (br, 1H), 3.73 (br, 1H), 3.54 (br, 1H), 2.88 (br, 1H), 2.59 (br, 1H), 2.19 (br, 3H), 2.07 (s, 3H), 1.89 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 202.6, 198.9, 150.7, 142.7, 142.3, 137.4, 136.5, 136.3, 135.9, 135.8, 135.6, 135.5, 134.8, 134.6, 133.8, 133.6, 132.8, 129.9, 129.8, 123.5, 123.4, 123.0, 122.8, 89.7, 68.6, 64.9, 35.6, 33.4, 19.4, 19.1, 18.8, 18.7. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{38}H_{32}NaO_4$: 575.2191; found: 575.2193.

4.2.9. Compound ***3b′***. 99.7 mg (Yield 18%); yellow solid; mp>300 °C; IR (KBr): 3483, 2922, 1710, 1264, 770 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J=7.2 Hz, 1H), 7.98 (d, J=7.2 Hz, 1H), 7.94–7.89 (m, 2H), 7.84 (d, J=7.2 Hz, 1H), 7.59–7.52 (m, 2H), 7.46 (s, 1H), 7.13 (d, J=7.8 Hz, 1H), 6.62 (d, J=13.8 Hz, 2H), 6.53 (s, 1H), 4.55–4.48 (m, 2H), 4.07 (d, J=6.6 Hz, 1H), 3.77 (br, 1H), 3.29–3.25 (m, 1H), 3.09–3.05 (m, 1H), 2.86–2.81 (m, 1H), 2.75–2.70 (m, 1H), 2.25 (s, 3H), 2.10 (s, 3H), 1.96 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.6, 199.6, 199.5, 152.9, 143.3, 141.6, 136.8, 136.3, 136.2, 136.1, 135.8, 135.3, 134.9, 134.5, 134.3, 133.4, 133.1, 132.6, 131.5, 131.3, 130.3, 130.1, 129.4, 124.6, 124.0, 123.7, 123.6, 89.8, 68.8, 66.1, 56.5, 48.5, 34.4, 33.8, 19.7, 19.5, 19.1, 18.9. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{38}H_{32}NaO_4$: 575.2189; found: 575.2193.

4.2.10. Compound ***3c***. 321.4 mg (Yield 52%); yellow solid; mp 176.5–179.7 °C; IR (KBr): 3459, 2935, 1701, 1603, 1518, 1259, 771 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J=7.8 Hz, 1H), 7.79–7.74 (m, 2H), 7.67 (t, J=7.5 Hz, 1H), 7.52 (d, J=7.5 Hz, 1H), 7.45–7.35 (m, 2H), 7.02 (br, 1H), 6.96 (br, 1H), 6.94 (br, 1H), 6.45 (br, 1H), 6.32 (br, 1H), 6.25 (br, 1H), 5.52 (br, 1H), 5.40 (br, 1H), 4.45 (br, 1H), 3.92 (s, 3H), 3.78–3.74 (m, 4H), 3.68 (s, 3H), 3.60 (br, 3H), 2.87 (br, 1H), 2.57 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 202.4, 198.9, 150.4, 147.8, 147.5, 147.4, 146.4, 142.7, 142.2, 137.3, 136.6, 136.0, 135.0, 131.6, 130.9, 130.4, 130.0, 123.5, 123.4, 123.2, 122.9, 115.0, 114.7, 89.6, 65.1, 56.2, 55.7, 55.5, 55.4, 35.8, 33.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{38}H_{33}O_8$: 617.2166; found: 617.2170.

4.2.11. Compound ***3c′***. 160.7 mg (Yield 26%); yellow solid; mp 177.1–179.5 °C; IR (KBr): 3446, 1709, 1632, 1517, 1266, 775 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J=6.6 Hz, 1H), 7.97 (d, J=7.2 Hz, 1H), 7.91–7.87 (m, 2H), 7.80 (d, J=7.2 Hz, 1H), 7.56–7.50 (m, 2H), 7.38 (s, 1H), 7.11 (d, J=7.2 Hz, 1H), 6.67 (s, 1H), 6.38 (s, 1H), 6.32 (s, 1H), 4.50 (d, J=9.6 Hz, 1H), 4.46–4.43 (m, 1H), 4.06 (d, J=6.6 Hz, 1H), 3.94 (s, 3H), 3.75 (s, 3H), 3.68 (s, 3H), 3.33 (s, 3H), 3.25–3.20 (m, 1H), 3.08–3.03 (m, 1H), 2.80–2.76 (m, 1H), 2.71–2.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 199.4, 199.3, 152.7, 147.4, 146.9, 146.7, 146.2, 143.2, 141.4, 136.2, 136.0, 135.4, 131.7, 131.1, 130.3, 130.1, 127.2, 124.3, 124.1, 123.8, 123.6, 113.5, 113.4, 113.1, 112.5, 89.5, 67.9, 65.9, 57.6, 56.0, 55.9, 55.7, 55.6, 48.5, 33.9, 29.6. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{38}H_{32}NaO_8$: 639.1983; found: 639.1989.

4.2.12. Compound ***4d***. 357.3 mg (Yield 88%); yellow solid; mp 130.1–133.2 °C; IR (KBr): 2928, 1707, 1590, 1275, 760 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99–7.98 (m, 1H), 7.93–7.92 (m, 1H), 7.87–7.83 (m, 2H), 7.19 (d, J=8.4 Hz, 1H), 7.09 (d, J=9.0 Hz, 1H), 4.26–4.24 (m, 1H), 3.62 (d, J=3.6 Hz, 1H), 3.28 (dd, J=15.0, 5.4 Hz, 1H), 3.16 (dd, J=11.4, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 198.0, 145.7, 145.0, 142.7, 142.1, 135.9, 135.7, 132.5, 131.8, 123.4, 123.3, 115.0, 114.3, 52.8, 39.1, 32.9. HRMS (APCI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}Br_2NaO_2$: 426.8940; found: 426.8940.

4.2.13. Compound ***5a***.[20] 203.4 mg (Yield 82%); yellow solid; mp 159.6–161.3 °C; IR (KBr): 1681, 1582, 1378, 1346, 1210, 737 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J=7.8 Hz, 1H), 8.24 (s, 1H), 8.01 (d, J=16.2 Hz, 2H), 7.82 (s, 2H), 7.42 (t, J=7.2 Hz, 1H), 7.33 (t, J=7.2 Hz, 1H), 7.28 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 188.6, 144.1, 142.4, 140.7, 139.9, 135.3, 135.1, 132.7, 132.4, 131.3, 130.5, 129.0, 125.8, 123.2, 20.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}O_2$: 249.0909; found: 249.0910.

4.2.14. Compound ***5b***. 231.8 mg (Yield 84%); yellow solid; mp 184.0–185.9 °C; IR (KBr): 1681, 1577, 1385, 1344, 1236, 743 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.23 (s, 1H), 8.00 (s, 2H), 7.81

(s, 2H), 7.07 (s, 1H), 2.51 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 188.9, 144.3, 143.1, 142.3, 139.7, 139.1, 135.1, 134.6, 134.1, 133.7, 132.0, 129.0, 127.6, 123.0, 20.1, 19.7, 19.2. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{16}NaO_2$: 299.1043; found: 299.1043.

4.2.15. Compound ***5c***. 252.6 mg (Yield 82%); yellow solid; mp 229.0–231.3 °C; IR (KBr): 3448, 1678, 1569, 1513, 1285, 1240, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.24 (s, 1H), 8.00–7.98 (m, 2H), 7.80–7.79 (m, 2H), 6.77 (s, 1H), 4.09 (s, 3H), 3.98 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 189.8, 153.7, 146.8, 144.0, 142.4, 139.7, 138.4, 135.0, 134.8, 125.8, 124.6, 123.0, 122.9, 115.8, 113.1, 56.2, 56.0, 20.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{17}O_4$: 309.1115; found: 309.1121.

4.2.16. Compound ***5d***. 347.4 mg (Yield 86%); yellow solid; mp 201.3–204.5 °C; IR (KBr): 1733, 1697, 1641, 1237, 1012, 737 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J=7.2 Hz, 1H), 7.96 (d, J=7.2 Hz, 1H), 7.90 (s, 1H), 7.88–7.84 (m, 2H), 7.48 (d, J=8.4 Hz, 1H), 7.35 (d, J=8.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 187.5, 142.2, 141.8, 141.0, 138.1, 135.9, 135.7, 135.0, 133.9, 133.2, 130.8, 124.6, 123.7, 123.5, 121.2, 21.5. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}Br_2NaO_2$: 426.8940; found: 426.8940.

4.2.17. Compound ***6aa***. 70.4 mg (Yield 20%); white solid; mp 182.5–184.0 °C; IR (KBr): 3435, 1708, 1255, 803 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J=7.2 Hz, 1H), 7.71 (t, J=7.8 Hz, 1H), 7.65 (q, J=7.2 Hz, 2H), 7.41 (d, J=7.8 Hz, 2H), 7.35 (t, J=7.8 Hz, 2H), 7.22 (t, J=7.2 Hz, 1H), 7.13 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.8 Hz, 1H), 6.75 (t, J=7.2 Hz, 1H), 6.62 (d, J=7.8 Hz, 1H), 4.23 (d, J=4.8 Hz, 1H), 3.45–3.42 (m, 1H), 3.23–3.20 (m, 1H), 3.03–2.89 (m, 3H), 2.20–2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 198.6, 143.5, 142.8, 142.3, 136.9, 135.8, 135.2, 135.0, 129.3, 128.6, 127.9, 127.3, 126.7, 125.2, 122.8, 122.8, 56.4, 43.8, 42.9, 29.6, 22.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{20}NaO_2$: 375.1358; found: 375.1356.

4.2.18. Compound ***6aa′***. 197.1 mg (Yield 56%); white solid; mp 194.3–196.0 °C; IR (KBr): 2933, 1712, 1493, 1269, 768, 739 cm^{-1}. NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J=7.8 Hz, 1H), 7.81–7.78 (m, 1H), 7.76–7.74 (m, 2H), 7.32–7.28 (m, 4H), 7.21 (t, J=7.2 Hz, 1H), 7.11 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.2 Hz, 1H), 6.79 (t, J=7.8 Hz, 1H), 6.64 (d, J=7.8 Hz, 1H), 4.14 (d, J=10.8 Hz, 1H), 3.60–3.56 (m, 1H), 3.35 (s, 1H), 3.18–3.10 (m, 1H), 2.86 (d, J=16.2 Hz, 1H), 2.15–2.12 (m, 1H), 2.01–1.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 199.3, 144.7, 142.7, 141.9, 137.9, 136.2, 135.1, 129.3, 128.7, 127.9, 126.8, 126.3, 126.0, 125.6, 122.9, 122.7, 56.8, 45.9, 43.7, 31.8, 30.6. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{20}NaO_2$: 375.1360; found: 375.1356.

4.2.19. Compound ***6ab***. 84.2 mg (Yield 23%); pale yellow solid; mp 126.1–128.3 °C; IR (KBr): 2867, 1709, 1259, 765 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J=7.2 Hz, 1H), 7.71 (t, J=7.2 Hz, 1H), 7.67–7.63 (m, 2H), 7.29 (d, J=7.8 Hz, 2H), 7.15–7.12 (m, 3H), 7.01 (t, J=7.2 Hz, 1H), 6.75 (t, J=7.2 Hz, 1H), 6.62 (d, J=7.2 Hz, 1H), 4.22 (d, J=5.4 Hz, 1H), 3.40 (d, J=13.2 Hz, 1H), 3.22–3.18 (m, 1H), 3.02–2.96 (m, 2H), 2.92–2.85 (m, 1H), 2.31 (s, 3H), 2.18–2.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 199.5, 142.8, 142.0, 141.7, 138.1, 136.4, 135.2, 129.4, 127.9, 126.4, 126.0, 125.7, 123.1, 122.8, 56.9, 45.6, 44.0, 32.0, 30.7, 21.0. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{22}NaO_2$: 389.1516; found: 389.1512.

4.2.20. Compound ***6ab′***. 179.3 mg (Yield 49%); pale yellow solid; mp 204.1–206.7 °C; IR (KBr): 2833, 1711, 1268, 737 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J=7.2 Hz, 1H), 7.79–7.76 (m, 1H), 7.74–7.71 (m, 2H), 7.20 (d, J=7.8 Hz, 2H), 7.09 (d, J=7.8 Hz, 3H), 7.01–6.98 (m, 1H), 6.77 (t, J=7.8 Hz, 1H), 6.61 (d, J=7.98 Hz, 1H), 4.10 (d, J=10.8 Hz, 1H), 3.56–3.51 (m, 1H), 3.36 (d, J=1.8 Hz, 1H), 3.15–3.09 (m, 1H), 2.84 (d, J=16.2 Hz, 1H), 2.29 (s, 3H), 2.12–2.09 (m, 1H), 1.99–1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 199.5, 142.8, 142.0, 141.7, 138.0, 136.4, 136.4, 135.2, 129.4, 127.9, 126.43, 126.0, 125.7, 123.0, 122.8, 56.9, 45.6, 44.0, 31.9, 30.7, 21.0. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{22}NaO_2$: 389.1514; found: 389.1512.

4.2.21. Compound ***6ac***. 68.8 mg (Yield 18%); pale yellow solid; mp 168.2–170.3 °C; IR (KBr): 2933, 1706, 1514, 1249, 868 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J=7.2 Hz, 1H), 7.69 (t, J=7.0 Hz, 1H), 7.65–7.60 (m, 2H), 7.30 (d, J=8.4 Hz, 2H), 7.11 (d, J=7.6 Hz, 1H), 6.99 (d, J=7.2 Hz, 1H), 6.86 (d, J=8.4 Hz, 2H), 6.74 (t, J=7.2 Hz, 1H), 6.62 (d, J=7.6 Hz, 1H), 4.20 (d, J=4.8 Hz, 1H), 3.76 (s, 3H), 3.36 (d, J=11.2 Hz, 1H), 3.21–3.16 (m, 1H), 3.02–2.81 (m, 3H), 2.16–2.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 198.6, 158.2, 142.7, 142.3, 136.9, 135.9, 135.4, 135.1, 134.9, 129.3, 128.9, 127.3, 126.6, 125.2, 122.7, 122.7, 113.9, 56.4, 55.1, 43.9, 42.0, 29.6, 23.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{22}NaO_3$: 405.1467; found: 405.1461.

4.2.22. Compound ***6ac′***. 179.5 mg (Yield 47%); pale yellow solid; mp 130.1–132.3 °C; IR (KBr): 2930, 1707, 1511, 1259, 739 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J=7.8 Hz, 1H), 7.76 (t, J=7.2 Hz, 1H), 7.73–7.69 (m, 2H), 7.21 (d, J=8.4 Hz, 2H), 7.08 (d, J=7.2 Hz, 1H), 6.99 (t, J=7.2 Hz, 1H), 6.83–6.76 (m, 3H), 6.63 (d, J=7.8 Hz, 1H), 4.07 (d, J=10.8 Hz, 1H), 3.74 (s, 3H), 3.50 (t, J=12.0 Hz, 1H), 3.37 (s, 1H), 3.13–3.08 (m, 1H), 2.83 (d, J=16.2 Hz, 1H), 2.21–2.08 (m, 1H), 1.96–1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 199.2, 158.2, 142.5, 141.8, 137.8, 136.5, 136.3, 135.0, 129.2, 128.7, 126.2, 125.8, 125.5, 122.8, 122.5, 113.9, 56.6, 54.9, 44.9, 44.0, 31.8, 30.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{23}O_3$: 383.1644; found: 383.1642.

4.2.23. Compound ***6ad***. 65.6 mg (Yield 17%); white solid; mp 151.2–153.2 °C; IR (KBr): 2829, 1739, 1209, 1489, 1269, 1091, 735 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J=7.8 Hz, 1H), 7.74 (t, J=7.2 Hz, 1H), 7.68 (t, J=7.2 Hz, 1H), 7.64 (d, J=7.8 Hz, 1H), 7.32 (q, J=8.0 Hz, 4H), 7.13 (d, J=7.8 Hz, 1H), 7.02 (t, J=7.8 Hz, 1H), 6.76 (t, J=7.2 Hz, 1H), 6.62 (d, J=7.2 Hz, 1H), 4.20 (d, J=4.8 Hz, 1H), 3.42–3.38 (m, 1H), 3.23–3.19 (m, 1H), 3.02–2.97 (m, 1H), 2.91–2.84 (m, 2H), 2.17–2.14 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.0, 198.4, 142.7, 142.2, 141.9, 136.7, 135.5, 135.3, 135.1, 132.5, 129.3, 128.7, 127.2, 126.8, 125.3, 122.9, 122.8, 56.3, 43.5, 42.3, 29.4, 22.9. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{19}ClNaO_2$: 409.097; found: 409.0966.

4.2.24. Compound ***6ad′***. 200.7 mg (Yield 52%); pale yellow solid; mp 185.3–187.2 °C; IR (KBr): 3432, 1709, 1489, 1270, 735 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J=7.2 Hz, 1H), 7.80 (q, J=3.6 Hz, 1H), 7.75 (d, J=3.0 Hz, 2H), 7.24 (s, 4H), 7.10 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.2 Hz, 1H), 6.79 (t, J=7.2 Hz, 1H), 6.63 (d, J=7.8 Hz, 1H), 4.08 (d, J=10.8 Hz, 1H), 3.56 (t, J=11.2 Hz, 1H), 3.30 (s, 1H), 3.11 (t, J=12.0 Hz, 1H), 2.85 (d, J=16.2 Hz, 1H), 2.10 (d, J=13.0 Hz, 1H), 1.93 (qd, J=13.2, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 199.4, 143.3, 142.8, 142.0, 137.8, 136.0, 135.4, 132.5, 129.5, 129.4, 128.9, 126.4, 126.2, 125.8, 123.1, 122.9, 56.8, 45.4, 43.8, 31.8, 30.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{20}ClO_2$: 387.1151; found: 387.1146.

4.2.25. Compound ***6ae***. 51.8 mg (Yield 14%); white solid; mp 157.2–159.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J=7.2 Hz, 1H), 7.73 (t, J=7.2 Hz, 1H), 7.69–7.64 (m, 2H), 7.37–7.35 (m, 2H), 7.13 (d, J=7.8 Hz, 1H), 7.05–7.00 (m, 3H), 6.76 (t, J=7.2 Hz, 1H), 6.62 (d, J=7.8 Hz, 1H), 4.20 (d, J=4.8 Hz, 1H), 3.41 (d, J=13.2 Hz, 1H), 3.21 (dd, J=17.2, 5.6 Hz, 1H), 3.02–2.96 (m, 1H), 2.91 (s, 1H), 2.89–2.83 (m, 1H), 2.17–2.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 198.5, 142.8, 142.3, 139.1, 136.8, 135.6, 135.3, 135.1, 129.5, 129.4, 129.3, 127.3, 126.8, 125.3, 122.9, 122.8, 115.5, 115.3, 56.3, 43.8, 42.2, 29.5,

23.1. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{25}H_{19}FNaO_2$: 393.1261; found: 393.1261.

4.2.26. Compound ***6ae′***. 229.4 mg (Yield 62%); white solid; mp 162.3–164.1 °C; IR (KBr): 2925, 1710, 1508, 1267, 1225, 738 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J*=7.2 Hz, 1H), 7.81–7.78 (m, 1H), 7.74–7.72 (m, 2H), 7.29–7.25 (m, 2H), 7.10 (d, *J*=7.8 Hz, 1H), 7.01 (t, *J*=7.8 Hz, 1H), 6.96 (t, *J*=8.4 Hz, 2H), 6.80 (t, *J*=7.8 Hz, 1H), 6.65 (d, *J*=7.8 Hz, 1H), 4.08 (d, *J*=10.2 Hz, 1H), 3.58–3.53 (m, 1H), 3.32 (s, 1H), 3.14–3.09 (m, 1H), 2.85 (d, *J*=16.2 Hz, 1H), 2.11–2.09 (m, 1H), 1.96–1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 199.4, 142.8, 142.0, 140.4, 137.9, 136.1, 135.3, 129.5, 129.4, 129.4, 126.4, 126.1, 125.8, 123.1, 122.8, 115.6, 115.4, 56.8, 45.2, 44.1, 32.0, 30.6. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{25}H_{19}FNaO_2$: 393.1268; found: 393.1261.

4.2.27. Compound ***6af***. 87.8 mg (Yield 24%); pale yellow solid; mp 102.1–104.3 °C; IR (KBr): 2924, 1709, 1599, 1257, 765 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J*=7.8 Hz, 1H), 7.61 (t, *J*=6.6 Hz, 1H), 7.57–7.53 (m, 2H), 7.15–7.01 (m, 3H), 7.04 (d, *J*=7.8 Hz, 1H), 6.94–6.90 (m, 2H), 6.66 (t, *J*=7.8 Hz, 1H), 6.54 (d, *J*=7.2 Hz, 1H), 4.14 (d, *J*=4.8 Hz, 1H), 3.29 (d, *J*=13.8 Hz, 1H), 3.13–3.09 (m, 1H), 3.92–2.78 (m, 3H), 2.24 (s, 3H), 2.09–2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 198.6, 143.4, 142.7, 142.3, 138.1, 136.9, 135.9, 135.1, 134.9, 129.3, 128.6, 128.4, 127.4, 127.3, 126.6, 125.2, 125.0, 122.8, 122.7, 56.5, 43.7, 42.8, 29.6, 22.9, 21.5. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{26}H_{22}NaO_2$: 389.1511; found: 389.1512.

4.2.28. Compound ***6af′***. 161.1 mg (Yield 44%); yellow solid; mp 92.1–95.2 °C; IR (KBr): 2922, 1709, 1597, 1489, 1265, 755 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J*=7.2 Hz, 1H), 7.58–7.54 (m, 2H), 7.50 (t, *J*=7.2 Hz, 1H), 7.01 (t, *J*=7.8 Hz, 1H), 6.97–6.91 (m, 3H), 6.85–6.82 (m, 2H), 6.62 (t, *J*=7.2 Hz, 1H), 6.51 (d, *J*=7.8 Hz, 1H), 3.98 (d, *J*=10.8 Hz, 1H), 3.41–3.37 (m, 1H), 3.23 (d, *J*=1.8 Hz, 1H), 2.98–2.93 (m, 1H), 2.69–2.66 (m, 1H), 2.12 (s, 3H), 1.96–1.93 (m, 1H), 1.83–1.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 199.1, 144.5, 142.5, 141.8, 138.0, 137.8, 136.3, 135.0, 135.0, 129.2, 128.7, 128.5, 127.4, 126.2, 125.8, 125.5, 124.7, 122.8, 122.5, 56.7, 45.7, 4.72, 31.7, 30.5, 21.2. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{23}O_2$: 367.1689; found: 367.1693.

4.2.29. Compound ***6ag***. (dr=11:9), 245.7 mg (Yield 57%); pale yellow solid; mp 83.7–89.1 °C; IR (KBr): 2925, 1708, 1593, 1257, 753 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J*=7.8 Hz, 1H), 7.89 (d, *J*=7.8 Hz, 1H), 7.80–7.78 (m, 1H), 7.75–7.71 (m, 3H), 7.68–7.64 (m, 3H), 7.50 (d, *J*=7.8 Hz, 1H), 7.47 (d, *J*=7.8 Hz, 1H), 7.34 (t, *J*=7.2 Hz, 1H), 7.30 (d, *J*=7.8 Hz, 1H), 7.21 (t, *J*=7.2 Hz, 1H), 7.14–7.06 (m, 4H), 7.02 (t, *J*=7.2 Hz, 2H), 6.81 (t, *J*=7.2 Hz, 1H), 6.76 (t, *J*=7.2 Hz, 1H), 6.68–6.64 (m, 2H), 4.52 (d, *J*=4.8 Hz, 1H), 4.22–4.18 (m, 2H), 3.75–3.72 (m, 1H), 3.30 (s, 1H), 3.20–3.15 (m, 2H), 3.06–3.02 (m, 2H), 2.93 (s, 1H), 2.82 (d, *J*=16.2 Hz, 1H), 2.12 (d, *J*=13.8 Hz, 1H), 2.05–2.01 (m, 1H), 1.31–1.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 200.6, 198.8, 198.5, 143.7, 142.9, 142.7, 142.34, 142.3, 142.0, 138.1, 136.6, 136.1, 135.6, 135.4, 135.2, 135.1, 133.5, 133.0, 129.4, 129.3, 128.9, 128.3, 128.2, 128.2, 127.5, 127.4, 126.7, 126.5, 126.1, 125.8, 125.6, 125.3, 123.1, 122.9, 122.8, 122.7, 57.3, 56.5, 44.2, 43.1, 42.8, 40.3, 31.0, 30.5, 29.7, 23.7. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{20}BrO_2$: 431.0642; found: 431.0641.

4.2.30. Compound ***6ah***. 77 mg (Yield 18%); white solid; mp 173.9–175.6 °C; IR (KBr): 2929, 1707, 1486, 1253, 744 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J*=7.8 Hz, 1H), 7.72–7.69 (m, 1H), 7.65–7.63 (m, 2H), 7.57 (d, *J*=8.4 Hz, 4H), 7.47 (d, *J*=8.4 Hz, 2H), 7.42 (t, *J*=7.8 Hz, 2H), 7.32 (t, *J*=7.2 Hz, 1H), 7.14 (d, *J*=7.8 Hz, 1H), 7.02 (t, *J*=7.2 Hz, 1H), 6.77 (t, *J*=7.2 Hz, 1H), 6.66 (d, *J*=7.8 Hz, 1H). 4.30 (d, *J*=4.8 Hz, 1H), 3.49–3.46 (m, 1H), 3.25–3.21 (m, 1H), 3.04–2.92 (m, 3H), 2.24–3.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 198.6, 142.8, 142.5, 142.3, 140.7, 139.5, 136.9, 135.8, 135.2, 135.0, 129.4, 128.7, 128.4, 127.4, 127.3, 127.1, 127.0, 126.7, 125.3, 122.8, 122.8, 56.6, 43.7, 42.6, 29.6, 23.0. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{31}H_{24}NaO_2$: 451.1674; found: 451.1669.

4.2.31. Compound ***6ah′***. 218.3 mg (Yield 51%); white solid; mp 150.3–152.1 °C; IR (KBr): 2913, 1709, 1487, 1266, 736 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J*=7.8 Hz, 1H), 7.75 (t, *J*=7.2 Hz, 1H), 7.73–7.68 (m, 2H), 7.53 (d, *J*=7.8 Hz, 2H), 7.50 (d, *J*=8.2 Hz, 2H), 7.41–7.37 (m, 4H), 7.30 (t, *J*=7.2 Hz, 1H), 7.10 (d, *J*=7.2 Hz, 1H), 7.01 (t, *J*=7.2 Hz, 1H), 6.79 (t, *J*=7.2 Hz, 1H), 6.66 (d, *J*=7.8 Hz, 1H), 4.17 (d, *J*=10.8 Hz, 1H), 3.65–3.60 (m, 1H), 3.40 (s, 1H), 3.17–3.11 (m, 1H), 2.87 (d, *J*=16.2 Hz, 1H), 2.16 (d, *J*=13.2 Hz, 1H), 2.03–1.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 199.4, 143.8, 142.8, 142.0, 140.7, 139.7, 138.0, 136.3, 135.2, 129.4, 128.7, 128.4, 127.4, 127.1, 126.9, 126.4, 126.1, 125.7, 123.0, 122.8, 56.9, 45.6, 43.9, 31.9, 30.6. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{31}H_{24}NaO_2$: 451.1673; found: 451.1669.

4.2.32. Compound ***6ai***. 56.3 mg (Yield 14%); pale yellow solid; mp 176.1–178.3 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J*=8.4 Hz, 1H), 7.82–7.74 (m, 4H), 7.64 (t, *J*=6.6 Hz, 1H), 7.59–7.57 (m, 3H), 7.43–7.42 (m, 2H), 7.16 (d, *J*=7.2 Hz, 1H), 7.03 (t, *J*=7.2 Hz, 1H), 6.78 (t, *J*=7.2 Hz, 1H), 6.67 (d, *J*=7.8 Hz, 1H), 4.37 (d, *J*=4.8 Hz, 1H), 3.57 (d, *J*=8.4 Hz, 1H), 3.25 (t, *J*=12.0 Hz, 1H), 3.08–3.01 (m, 2H), 2.97 (s, 1H), 2.34–3.312 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 198.6, 142.6, 142.2, 141.1, 136.9, 135.9, 135.1, 134.9, 133.4, 132.4, 129.3, 128.3, 127.8, 127.6, 127.4, 127.0, 126.7, 126.0, 125.6, 125.3, 122.7, 56.6, 43.5, 43.0, 29.6, 23.0. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{29}H_{22}NaO_2$: 425.1513; found: 425.1512.

4.2.33. Compound ***6ai′***. 249.2 mg (Yield 62%); pale yellow solid; mp 114.5–118.3 °C; IR (KBr): 2929, 1708, 1631, 1262, 743 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J*=7.8 Hz, 1H), 7.83 (d, *J*=8.4 Hz, 1H), 7.80–7.79 (m, 1H), 7.77–7.74 (m, 1H), 7.71–7.67 (m, 4H), 7.50 (d, *J*=8.4 Hz, 1H), 7.44–7.41 (m, 2H), 7.13 (d, *J*=7.8 Hz, 1H), 7.04 (t, *J*=7.2 Hz, 1H), 6.82 (t, *J*=7.8 Hz, 1H), 6.67 (d, *J*=7.8 Hz, 1H), 4.25 (d, *J*=11.2 Hz, 1H), 3.76–3.72 (m, 1H), 3.41 (d, *J*=1.8 Hz, 1H), 3.21–3.15 (m, 1H), 2.91 (d, *J*=16.3 Hz, 1H), 2.21–2.19 (m, 1H), 2.13–2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 199.5, 142.7, 142.1, 142.0, 138.1, 136.3, 135.2, 133.4, 132.6, 129.5, 128.8, 127.6, 127.2, 126.5, 126.1, 126.0, 125.8, 125.7, 125.6, 123.0, 122.8, 56.9, 46.2, 43.9, 31.7, 30.7. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{29}H_{23}O_2$: 403.1687; found: 403.1693.

4.2.34. Compound ***6ba***. 45.6 mg (Yield 12%); pale yellow solid; mp 125.1–127.3 °C; IR (KBr): 2929, 1707, 1597, 1256, 752, 701 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J*=7.8 Hz, 1H), 7.73–7.70 (m, 1H), 7.67–7.64 (m, 2H), 7.39 (d, *J*=7.8 Hz, 2H), 7.33 (t, *J*=7.8 Hz, 2H), 7.20 (t, *J*=7.2 Hz, 1H), 6.90 (s, 1H), 6.38 (s, 1H), 4.16 (d, *J*=5.4 Hz, 1H), 3.40–3.37 (m, 1H), 3.14–3.11 (m, 1H), 3.95–2.85 (m, 3H), 2.17–2.13 (m, 1H), 2.08 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4, 198.8, 143.6, 142.8, 142.3, 135.1, 134.9, 134.0, 133.4, 133.1, 130.4, 128.5, 128.4, 128.0, 126.6, 122.9, 122.6, 56.5, 43.51, 43.2, 29.02, 23.00, 19.3, 18.9. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{27}H_{24}NaO_2$: 403.1665; found: 403.1669.

4.2.35. Compound ***6ba′***. 182.4 mg (Yield 48%); pale yellow solid; mp 128.7–130.5 °C; IR (KBr): 2913, 1710, 1597, 1264, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J*=7.2 Hz, 1H), 7.79–7.71 (m, 3H), 7.27–7.18 (m, 5H), 6.85 (s, 1H), 6.40 (s, 1H), 4.06 (d, *J*=10.8 Hz, 1H), 3.54–3.48 (m, 1H), 3.32 (d, *J*=1.6 Hz, 1H), 3.03 (t, *J*=12.4 Hz, 1H), 2.76 (d, *J*=16.0 Hz, 1H), 2.12–2.09 (m, 4H), 1.98–1.87 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 199.7, 144.9, 142.9, 142.2, 135.2, 135.1, 134.2, 133.7, 133.5, 130.6, 128.7, 128.0, 127.8, 126.8,

122.8, 122.8, 56.8, 46.0, 43.8, 32.1, 30.1, 19.2, 19.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{27}H_{24}NaO_2$: 403.1665; found: 403.1669.

4.2.36. Compound ***6aj***. 41.1 mg (Yield 12%); yellow solid; mp 98.5–101.3 °C; IR (KBr): 3446, 2947, 1711, 1593, 1257, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J=7.2 Hz, 1H), 7.96 (d, J=6.6 Hz, 1H), 7.87–7.83 (m, 2H), 7.39 (br, 1H), 7.14–7.13 (m, 2H), 7.08–7.07 (m, 1H), 3.80 (d, J=4.2 Hz, 1H), 3.70 (t, J=4.8 Hz, 1H), 2.83–2.79 (m, 1H), 2.75–2.72 (m, 1H), 2.11–2.08 (m, 1H), 2.05 (s, 1H), 2.00–1.97 (m, 1H), 1.93 (s, 1H), 1.64 (br, 1H)1.36–1.32 (m, 1H), 1.25–1.19 (m, 2H), 1.11–1.07 (m, 1H), 0.79–0.76 (m, 1H), 0.69 (d, J=10.2 Hz, 1H), 0.59 (d, J=10.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 200.4, 142.7, 142.4, 139.6, 137.4, 135.7, 135.5, 127.2, 126.5, 125.8, 125.7, 123.1, 123.1, 54.7, 45.5, 43.7, 43.5, 42.8, 39.8, 34.9, 33.9, 30.6, 30.0. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_2$: 365.1515; found: 365.1512.

4.2.37. Compound ***6aj′***. 212.0 mg (Yield 62%); yellow solid; mp 172.1–174.5 °C; IR (KBr): 3431, 2943, 1705, 1595, 1278, 746 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J=6.0 Hz, 2H), 7.89–7.88 (m, 2H), 7.09–7.07 (m, 2H), 6.98 (t, J=7.8 Hz, 1H), 6.71 (d, J=7.2 Hz, 1H), 3.83 (s, 1H), 3.37 (d, J=12.0 Hz, 1H), 2.76–2.72 (m, 1H), 2.40 (t, J=13.2 Hz, 1H), 2.17 (t, J=10.2 Hz, 1H), 2.11 (s, 1H), 1.90 (s, 1H), 1.86 (d, J=10.2 Hz, 1H), 1.78–1.74 (m, 1H), 1.51–1.49 (m, 1H), 1.44–1.40 (m, 1H), 1.20 (t, J=10.2 Hz, 1H), 1.09 (t, J=10.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 199.4, 142.0, 141.7, 139.3, 138.2, 135.6, 135.5, 127.1, 126.1, 125.9, 123.8, 123.2, 123.2, 54.4, 46.2, 44.4, 42.8, 41.0, 39.5, 33.5, 33.4, 29.5, 29.3. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_2$: 365.1516; found: 365.1512.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.07.062.

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