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# The First Synthesis of Natural Occurring Juncaceae Coumarin, 9-Hydroxy-8-methyl-3*H*-benzo[*f*]chromen-3-one, Featuring a One-pot Rearrangement and Aromatization Cascade

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The synthesis of benzocoumarins from β-tetralones has been achieved via two pathways in the first total synthesis of the *Juncaceae* natural product, 9-hydroxy-8-methyl-3*H*-benzo[*f*]chromen-3-one, featuring a one-pot rearrangement and aromatization cascade.

**Keywords:** Rearrangement; Total synthesis; Juncaceae; Coumarin.

## INTRODUCTION

Coumarins (*2H*-chromen-2-ones) are found in plants that display a wide spectrum of biological activities, and they have been used widely used in perfumes, foods, and pesticide since their discovery in the 19th century. Many biological studies of coumarins have been reported (Scheme I).[1] Recently, coumarins have been used in the pharmaceutical industry, for example, in the synthetic anticoagulant pharmaceuticals, dicoumarol and warfarin. More recently, several allelopathic phenanthrenoids and benzocoumarins with algicidal activity have been isolated from *Juncus acutus*.[2] Given their history and application potential, extensive efforts have been devoted to the synthesis of coumarin derivatives.[3] Synthetic approaches to the coumarins have employed the Pechmann reaction,[4] Perkin reaction,[5] Knoevenagel condensation,[6] Wittig reaction,[7] Peterson olefination,[8] Claisen rearrangement,[9] Friedel-Craft reaction,[10] and metal catalyzed reactions, including Ni-,[11] Pd-,[12] Ru-,[13] Pt-,[14] Au-,[15] Rh-,[16] Yb-,[17] In-,[18] Hf-,[19] Cu-,[20] Fe-catalyzed reactions.[21]

Continuing of our efforts toward the synthesis of benzocoumarins,[22] we envisioned that an unprecedented and convenient synthesis of 5,6-benzocoumarin from β-tetralone[23] could be achieved via a one-pot rearrangement and aromatization cascade (Scheme II). Herein, we report such a case and describe the first total synthesis of the naturally occurring *Juncaceae* coumarin, 6-hydroxy-7-methyl-5*a*,8*a*-benzocoumarin.[24]

## RESULTS AND DISCUSSION

In a first step, the reaction of β-tetralone (**1a**) with NaH and *tert*-butyl carbonate in toluene at 100 °C for 4 h provided the ketoester **2a** in 82% yield (Scheme II). Treatment of **2a** with DDQ in dioxane at 100 °C for 8 h gave an 89% yield of the enone **3a**. Exposure of **3a** to propargylic acid and trifluoroacetic acid in toluene at 100 °C for 2 h afforded a 74% yield of coumarin **4a**. The mechanism of this transformation probably involved a decarboxylation of **3a** to afford 2-naphthol, followed by esterification with propargylic acid, a subsequent Claisen rearrangement, and aromatization through the Friedel-Crafts alkylation of 2-naphthol and propargylic acid, followed by esterification and aromatization.[25] Alternatively, the mechanism may involve the Michael reaction of ketoester **3a** with propargylic acid, followed by isomerization, decarboxylation, and lactonization to yield **4a**. The three-step transformation of β-tetralone (**1a**) to coumarin **4a** can be achieved in a one-pot synthesis without purification of the intermediates to give a 54% total yield of coumarin **4a**. A series of 5,6-benzocoumarins were then prepared via this protocol (Table 1). Most of the reactions afforded the derivatives in good yields; however, a few examples containing strong electron-donating substituents, for example, methoxy groups, gave particularly low yields at the 3rd step reaction.

On the other hand, coumarin **4a** could be prepared more efficiently in a 66% yield from β-tetralone (**1a**) in a two-step sequence, without isolation of the intermediate **5a**, by a reaction with propargylic acid and trifluoroacetic acid, followed by the subsequent aromatization with DDQ (Scheme II). The methodology was applied toward the synthesis of variant 5,6-benzocoumarins with good yields. Nevertheless, as seen in the previous protocol, much lower

Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

[†] Deceased on June 16, 2011.

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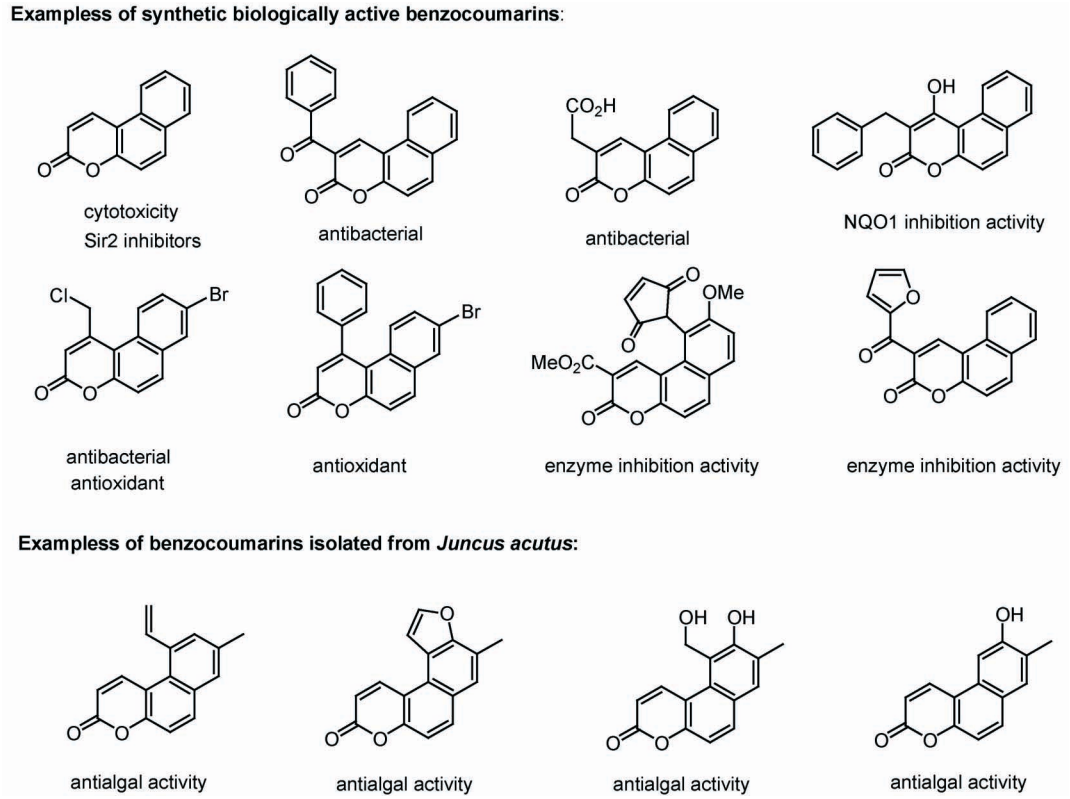
**Scheme I** Select examples of biologically active and natural occurring benzocoumarins




yields were obtained for the derivatives containing methoxy groups (Table 2).

The structure of the product **4i** was confirmed by X-ray analysis of a single crystal (Fig. 1). Deprotection of the methoxy group of **4i** was achieved by treatment with $BBr_3$ in $CH_2Cl_2$ at 0 °C at room temperature for 12 h, which provided 83% yield of the *Juncaceae* coumarin, 9-hydroxy-8-methyl-3*H*-benzo[*f*]chromen-3-one (**6**), Scheme III.[24]

In summary, the synthesis of benzocoumarins from β-tetralones was achieved via two pathways. One of the derivatives prepared by this method, **4i**, was transformed to 9-hydroxy-8-methyl-3*H*-benzo[*f*]chromen-3-one (**6**) to provide a first total synthesis of the *Juncaceae* natural product.

## EXPERIMENTAL SECTION

Reactions were normally carried out under nitrogen atmosphere in glassware. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography.

**Scheme II** Syntheses of 5,6-benzocoumarin from β-tetralone

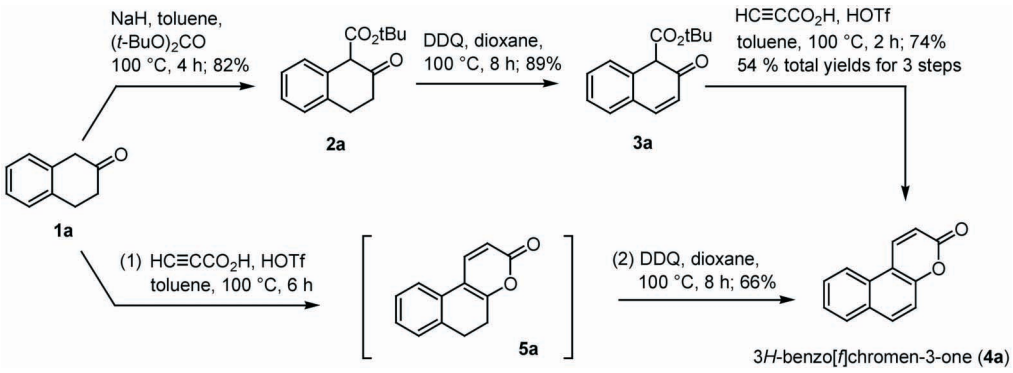
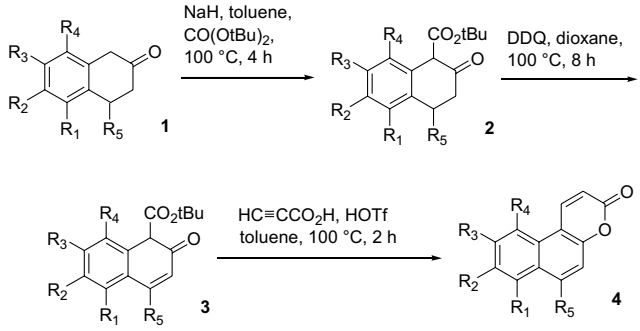


Table 1. First-generation synthesis of 5,6-benzocoumarin from β-tetralone




| Entry | Product | **2** yield[a] (%) | **3** yield[a] (%) | **4** yield[a] (%) |
|---|---|---|---|---|
| 1 | **a** $R_1 = R_2 = R_3 = R_4 = R_5 = H$ | 82 | 89 | 74 |
| 2 | **b** $R_1 = CH_3$, $R_2 = R_3 = R_4 = R_5 = H$ | 76 | 81 | 67 |
| 3 | **c** $R_1 = OCH_3$, $R_2 = R_3 = R_4 = R_5 = H$ | 71 | 65 | 46 |
| 4 | **d** $R_2 = OCH_3$, $R_1 = R_3 = R_4 = R_5 = H$ | 76 | 52 | 64 |
| 5 | **e** $R_3 = OCH_3$, $R_1 = R_2 = R_4 = R_5 = H$ | 85 | 73 | 40 |
| 6 | **f** $R_4 = OCH_3$, $R_1 = R_2 = R_3 = R_5 = H$ | 95 | 79 | 15 |
| 7 | **g** $R_3 = Br$, $R_1 = R_2 = R_4 = R_5 = H$ | 81 | 70 | 79 |
| 8 | **h** $R_1 = R_3 = CH_3$, $R_2 = R_4 = R_5 = H$ | 83 | 63 | 55 |
| 9 | **i** $R_2 = CH_3$, $R_3 = OCH_3$, $R_1 = R_4 = R_5 = H$ | 55 | 72 | 21 |
| 10 | **j** $R_2 = R_3 = OCH_3$, $R_1 = R_4 = R_5 = H$ | 60 | 75 | 27 |
| 11 | **k** $R_1 = R_4 = OCH_3$, $R_2 = R_3 = R_5 = H$ | 86 | 97 | 12 |
| 12 | **l** $R_5 = CH_3$, $R_1 = R_2 = R_3 = R_4 = H$ | 95 | 74 | 65 |
| 13 | **m** $R_5 = Ph$, $R_1 = R_2 = R_3 = R_4 = H$ | 84 | 70 | 60 |
| 14 | **n** $R_3 = CH_3$, $R_1 = R_2 = R_4 = R_5 = H$ | 75 | 82 | 70 |
| 15 | **o** $R_1 = R_4 = CH_3$, $R_2 = R_3 = R_5 = H$ | 71 | 48 | 53 |
| 16 | **p** $R_2 = Br$, $R_1 = R_3 = R_4 = R_5 = H$ | 98 | 81 | 84 |
| 17 | **q** $R_1 = R_2 = R_3 = Ar$, $R_4 = R_5 = H$ | 96 | 86 | 37 |

[a] Isolated yields for the one-step reaction. [b] Isolated yields of **4**, three steps from **1**.

Melting points are uncorrected. $^1$H NMR spectra were obtained in $CDCl_3$ unless otherwise noted at 400 MHz (Bruker DPX-400) or 500 MHz (Varian-Unity INOVA-500). $^{13}$C NMR spectra were obtained at 100 MHz or 125 MHz. The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected.

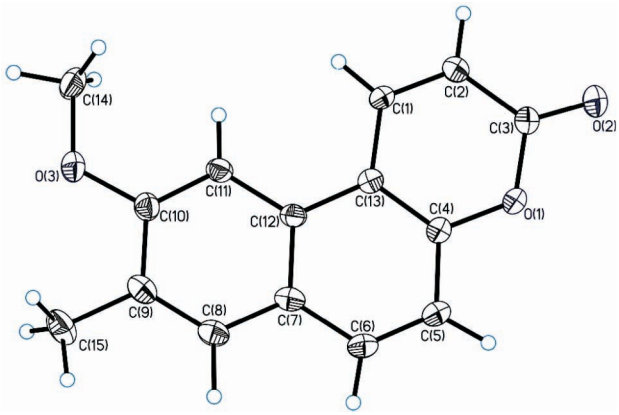



Fig. 1. ORTEP plot of the X-ray crystal structure of **4i**.

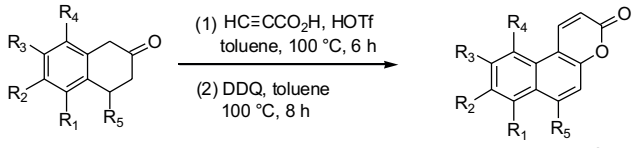
**Typical experimental procedure for the preparation of coumarin 4a (1st generation)**

**Preparation of 2a**

To a solution of NaH (219 mg, 5.47 mmol) in toluene (3 mL) was added dropwise a solution of β-tetralone (**1a**, 200 mg, 1.37 mmol) in toluene (4 mL), followed by the addition of di-*tert*-butyl dicarbonate (0.47 mL, 2.05 mmmol). The solution was heated to 100 °C and stirred for 4 h until the completion of reaction, monitored by TLC. The solution was cooled to 0 °C, followed by slow addition of 1 N aqueous HCl solution to quench the reaction. The reaction mixture was extracted by EtOAc, and the organic extract was dried over $MgSO_4$, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 4% EtOAc-hexane ($R_f$ = 0.69 for **2a**, in 1:10 EtOAc-hexane) to give **2a** as a white solid

Table 2. One-pot synthesis of 5,6-benzocoumarin from β-tetralone

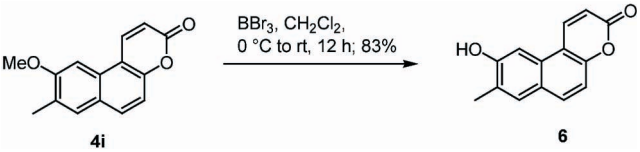



1 4

| Entry | Product | Time (h)[a] | Yield[b] (%) |
|---|---|---|---|
| 1 | **4a** $R_1 = R_2 = R_3 = R_4 = R_5 = H$ | 6/8 | 66 |
| 2 | **4b** $R_5 = CH_3$, $R_1 = R_2 = R_3 = R_4 = H$ | 4/6 | 75 |
| 3 | **4c** $R_1 = OCH_3$, $R_2 = R_3 = R_4 = R_5 = H$ | 2/4 | 23 |
| 4 | **4d** $R_2 = OCH_3$, $R_1 = R_3 = R_4 = R_5 = H$ | 2/4 | 20 |
| 5 | **4e** $R_3 = OCH_3$, $R_1 = R_2 = R_4 = R_5 = H$ | 2/4 | 27 |
| 6 | **4f** $R_4 = OCH_3$, $R_1 = R_2 = R_3 = R_5 = H$ | 2/4 | 17 |
| 7 | **4g** $R_2 = Br$, $R_1 = R_3 = R_4 = R_5 = H$ | 8/10 | 84 |
| 8 | **4h** $R_1 = R_3 = CH_3$, $R_2 = R_4 = R_5 = H$ | 4/6 | 43 |
| 9 | **4i** $R_2 = CH_3$, $R_3 = OCH_3$, $R_1 = R_4 = R_5 = H$ | 3/5 | 22[e] |

[a] Reaction times for the 1st and 2nd reaction steps. [b] Isolated yields of the two steps.

**Scheme III** Completion of the synthesis of 6-hydroxy-7-methyl-5*a*,8*a*-benzocoumarin (**6**)




4i 6

(280 mg, 82% yield). Mp 48-50 °C. Spectroscopic data for **2a**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.09 (m, 3 H), 7.0 (d, $J$ = 6.6 Hz, 1 H), 6.29 (s, 1 H), 2.99 (t, $J$ = 8.4 Hz, 2 H), 2.57-2.53 (m, 2 H), 1.54 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 150.1 (C), 150.8 (C), 133.2 (C), 133.1 (C), 127.2 (CH), 126.8 (CH), 126.6 (CH), 126.3 (CH), 114.2 (CH), 83.3 (C), 28.6 ($CH_2$), 27.7 (three $CH_3$), 26.1 ($CH_2$); IR (neat): 3059, 2981, 2934, 1755, 1631, 1601, 1510, 1465, 1395, 1370, 1239, 1145, 958, 866, 812, 754 cm$^{-1}$; MS (*m/z*, relative intensity): 246 ($M^+$, 100), 146 (91), 129 (20), 128 (11), 117 (30), 116 (11), 115 (27), 104 (25), 91 (12), 57 (100); exact mass calculate for $C_{15}H_{18}O_3$ ($M^+$): 246.1256; found 246.1246.

**Preparation of 3a**

To a solution of **2a** (200 mg, 0.812 mmol) in 1,4-dioxane (4 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 221 mg, 1.057 mmol). The solution was heated to 100 °C and stirred for 8 h until the completion of reaction, monitored by TLC. The solution was concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 4% EtOAc-hexane ($R_f$ = 0.69 for **3a**, in 1:10 EtOAc-hexane; dark purple color for **3a**, and sky blue color for **2a** on TLC with the Vanillin stain) to give **3a** as a white solid (162 mg, 89% yield). Mp 74-76 °C. Spectroscopic data for **3a**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.79 (m, 3 H), 7.63 (d, $J$ = 2.4 Hz, 1 H), 7.49-7.45 (m, 2 H), 7.31 (dd, $J$ = 8.8, 2.4 Hz, 1 H), 1.59 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.0 (C), 148.7 (C), 133.7 (C), 131.4 (C), 129.4 (CH), 127.70 (CH), 127.67 (CH), 126.5 (CH), 125.7 (CH), 120.9 (CH), 118.1 (CH), 83.6 (C), 27.7 (three $CH_3$); IR (neat): 3058, 2980, 2931, 1753, 1634, 1601, 1510, 1465, 1370, 1277, 1239, 1145, 957, 867, 754 cm$^{-1}$; MS (*m/z*, relative intensity): 244 ($M^+$, 23), 145 (11), 144 (100), 127 (22), 115 (67), 57 (80); exact mass calculate for $C_{15}H_{16}O_3$ ($M^+$): 244.1099; found 244.1105.

**Preparation of 4a**

To a solution of **3a** (142 mg, 0.634 mmol) in toluene (6.3 mL) was sequentially added propiolic acid (0.08 mL, 2.69 mmol) and trifluoromethanesulfonic acid (TfOH, 0.04 mL, 0.507 mmol). The solution was heated to 100 °C for 2 h until the completion of reaction, monitored by TLC. The residue was purified by flash column chromatography (Aluminum oxide 90 active basic) with EtOAc ($R_f$ = 0.47 for **4a**, in 1:5 EtOAc-hexane) to give **4a** as a pale yellow solid (930 mg, 74% yield); mp 115-116 °C. Spectroscopic data for **4a**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.47 (d, $J$ = 10.0 Hz, 1 H), 8.21 (d, $J$ = 8.4 Hz, 1 H), 7.97 (d, $J$ = 9.2 Hz, 1 H), 7.90 (d, $J$ = 8.0 Hz, 1 H), 7.68 (dd, $J$ = 8, 7.6 Hz, 1 H), 7.57 (dd, $J$ = 7.6, 7.6 Hz, 1 H), 7.44 (d, $J$ = 9.2 Hz, 1 H), 6.56 (d, $J$ = 10 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 153.8 (C), 139.0 (CH), 133.1 (CH), 130.2 (C), 129.0 (C, CH), 128.3 (CH), 126.0 (CH), 121.3 (CH), 117.0 (CH), 115.6 (CH), 112.9 (C); IR (neat): 2921, 2853, 1719, 1631, 1584, 1563, 1513, 1461, 1434, 1334, 1279, 1245, 1221, 1206, 1173, 1109, 1082, 897, 811, 781, 753 cm$^{-1}$; EI MS (*m/z*): 196 ($M^+$, 31), 168 (72), 140 (27), 139 (100), 70 (23); MS (*m/z*, relative intensity): 196 ($M^+$, 17), 195 (11), 168 (100), 140 (19), 139 (55), 84 (11), 58 (10); exact mass calculate for $C_{13}H_8O_2$ ($M^+$): 196.0524; found 196.0529.

**Typical experimental procedure for the preparation of coumarin 4a (2nd generation)**

A solution of β-tetralone (100 mg, 0.684 mmol), propiolic acid (0.08 mL, 1.37 mmol), trifluoromethanesulfonic acid (HOTf, 0.04 mL, 0.547 mmol) in toluene (6.8

mL) was heated to 100 °C for 6 h until the completion of reaction, monitored by TLC. To the solution was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 200 mg, 0.821 mmol) and the resulting solution was kept at 100 °C for additional 8 h until the completion of reaction, monitored by TLC. The resulting reside was purified by passing through a chromatography, packing with aluminum oxide 90 active basic, to give **4a** as a light yellow solid (891 mg, 66% yield).

**Spectroscopic data for 2b**

TLC $R_f$ = 0.69 (Hexane/EtOAc = 10:1); colorless liquid. Spectroscopic data for **2b**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.04 (dd, *J* = 7.4 Hz, 1 H), 6.98 (d, *J* = 7.2 Hz, 1 H), 6.87 (d, *J* = 7.2 Hz, 1 H), 6.27 (s, 1 H), 2.94 (t, *J* = 8.4 Hz, 2 H), 2.58-2.54 (m, 2 H), 2.26 (s, 3H), 1.54 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.2 (C), 134.8 (C), 133.1 (C), 131.2 (C), 128.9 (CH), 126.1 (CH), 124.5 (CH), 114.4 (CH), 83.2 (C), 27.7 (three $CH_3$), 25.7 ($CH_2$), 24.9 ($CH_2$), 19.5 ($CH_3$); IR (neat): 3065, 2979, 2833, 1752, 1671, 1468, 1394, 1370, 1319, 1273, 1135, 1084, 880, 820, 779, 721 cm$^{-1}$; MS (*m/z*, relative intensity): 260 ($M^+$, 100), 160 (85), 145 (16), 143 (14), 131 (13), 128 (12), 115 (16), 91 (14), 57 (100); exact mass calculate for $C_{16}H_{20}O_3$ ($M^+$): 260.1412; found 260.1407.

**Spectroscopic data for 3b**

TLC $R_f$ = 0.69 (Hexane/EtOAc = 10:1); pale yellow liquid. Spectroscopic data for **3b**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 9.2 Hz, 1 H), 7.66-7.61 (m, 2 H), 7.37-7.32 (m, 2 H), 7.27 (d, *J* = 6.8 Hz, 1 H), 2.66 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.0 (C), 148.5 (C), 134.3 (C), 134.0 (C), 130.6 (C), 126.40 (CH), 126.37 (CH), 126.2 (CH), 125.7 (CH), 120.5 (CH), 118.6 (CH), 83.5 (C), 27.7 (three $CH_3$), 19.4 ($CH_3$); IR (neat): 3053, 2980, 2935, 2291, 2178, 2161, 2084, 1752, 1628, 1600, 1510, 1456, 1426, 1394, 1370, 1238, 1214, 1136, 1045, 1020, 980, 942, 884, 835, 819, 780, 760, 698 cm$^{-1}$; MS (*m/z*, relative intensity): 258 ($M^+$, 100), 199 (19), 159 (40), 158 (100), 157 (58), 141 (20), 129 (23), 128 (31), 127 (12), 115 (12), 57 (84); exact mass calculate for $C_{16}H_{18}O_3$ ($M^+$): 258.1256; found 258.1261.

**Spectroscopic data for 4b**

TLC $R_f$ = 0.39 (Hexane/EtOAc = 5:1); pale yellow solid; mp 126-128 °C. Spectroscopic data for **4b**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.43 (d, *J* = 10 Hz, 1 H), 8.13 (d, *J* = 9.2 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.55 (dd, *J* = 8.4, 7.2 Hz, 1 H), 7.43 (d, *J* = 9.2 Hz, 1 H), 7.39 (d, *J* = 7.2 Hz, 1 H), 6.53 (d, *J* = 10 Hz, 1 H), 2.71 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.8 (C), 153.5 (C), 139.3 (CH), 135.6 (C), 129.32 (C), 129.25 (C), 129.16 (CH), 128.0 (CH), 126.9 (CH), 119.5 (CH), 116.4 (CH), 115.5 (CH), 113.2 (C), 19.6 ($CH_3$); IR (neat): 3068, 2920, 2848, 1721, 1592, 1567, 1513, 1457, 1375, 1233, 1204, 1180, 1121, 1050, 812, 795, 752 cm$^{-1}$; MS (*m/z*, relative intensity): 210 ($M^+$, 57), 194 (32), 182 (70), 181 (31), 153 (19), 152 (29), 151 (10), 76 (14); exact mass calculate for $C_{14}H_{10}O_2$ ($M^+$): 210.0681; found 210.0687.

**Spectroscopic data for 2c**

TLC $R_f$ = 0.58 (Hexane/EtOAc = 10:1); pale yellow liquid. Spectroscopic data for **2c**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.10 (dd, *J* = 8.4, 7.6 Hz, 1 H), 6.73 (d, *J* = 8.4 Hz, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 6.26 (s, 1 H), 3.82 (s, 3 H), 2.99 (t, *J* = 8.4 Hz, 2 H), 2.52 (t, *J* = 8.4 Hz, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 156.2 (C), 151.0 (two C), 134.5 (C), 127.0 (CH), 120.7 (C), 119.3 (CH), 113.9 (CH), 109.5 (CH), 83.2 (C), 55.5 ($CH_3$), 27.7 (three $CH_3$) , 25.5 ($CH_2$), 21.1 ($CH_2$); IR (neat): 3062, 2979, 2837, 2290, 2178, 2090, 1976, 1910, 1753, 1668, 1576, 1471, 1394, 1370, 1258, 1132, 1045, 1016, 967, 885, 815, 779, 717, 644 cm$^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$, 87), 177 (12), 176 (96), 175 (11), 159 (23), 134 (11), 115 (13), 57 (100); exact mass calculate for $C_{16}H_{20}O_4$ ($M^+$): 276.1362; found 276.1365.

**Spectroscopic data for 3c**

TLC $R_f$ = 0.58 (Hexane/EtOAc = 10:1); white solid; mp 67-69 °C. Spectroscopic data for **3c**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 9.6 Hz, 1 H), 7.58 (d, *J* = 2.4 Hz, 1 H), 7.40-7.37 (m, 2 H), 7.37 (s, 1 H), 7.27 (dd, *J* = 9.6, 2.4 Hz, 1 H), 6.79-6.77 (m, 1 H), 3.98 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 155.5 (C), 151.9 (C), 149.4 (C), 135.0 (C), 126.9 (CH), 123.8 (CH), 123.5 (C), 120.0 (CH), 119.9 (CH), 117.7 (CH), 103.7 (CH), 83.5 (C), 55.5 ($CH_3$), 27.7 (three $CH_3$); IR (neat): 3060, 2980, 2935, 2843, 2291, 2160, 2092, 1917, 1756, 1632, 1583, 1510, 1448, 1428, 1387, 1370, 1274, 1218, 1149, 1104, 1070, 1048, 1020, 942, 889, 871, 831, 781, 756, 724, 702 cm$^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 100), 175 (12), 174 (100), 131 (43), 115 (31), 102 (14), 57 (16); exact mass calculate for $C_{16}H_{18}O_4$ ($M^+$): 274.1205; found 274.1207.

**Spectroscopic data for 4c**

TLC $R_f$ = 0.31 (Hexane/EtOAc = 5:1); bright yellow solid; mp 189-191 °C. Spectroscopic data for **4c**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, *J* = 9.2 Hz, 1 H), 8.44 (d, *J* = 10.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.59 (dd, *J* = 8.0, 8.0 Hz, 1 H), 7.41 (d, *J* = 9.2 Hz, 1 H), 6.91 (d, *J* = 8.0 Hz, 1

H), 6.54 (d, $J$ = 10.0 Hz, 1 H), 4.03 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 156.1 (C), 154.4 (C), 139.6 (CH), 130.4 (C), 128.8 (CH), 127.4 (CH), 122.2 (C), 115.9 (CH), 115.4 (CH), 113.4 (CH), 112.7 (C), 104.4 (CH), 55.7 ($CH_3$); IR (neat): 2955, 2916, 2833, 1707, 1588, 1566, 1472, 1251, 1237, 1179, 1120, 1078, 1018, 910, 831, 793, 750 cm$^{-1}$; MS (*m/z*, relative intensity): 226 ($M^+$, 100), 198 (26), 194 (19), 182 (39), 155 (42), 139 (11), 127 (20), 126 (16), 77 (10); exact mass calculate for $C_{14}H_{10}O_3$ ($M^+$): 226.0630; found 226.0623.

**Spectroscopic data for 2d**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); colorless solid; mp 88-90 °C. Spectroscopic data for **2d**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.93 (d, $J$ = 8.0 Hz, 1 H), 6.68-6.63 (m, 2 H), 6.24 (s, 1 H), 3.78 (s, 3 H), 2.96 (t, $J$ = 8.4 Hz, 2 H), 2.52 (t, $J$ = 8.0 Hz, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 158.6 (C), 151.3 (C), 148.7 (C), 134.8 (C), 127.2 (CH), 126.0 (C), 113.7 (two CH), 111.2 (CH), 83.2 (C), 55.3 ($CH_3$), 29.1 ($CH_2$), 27.7 (three $CH_3$), 25.9 ($CH_2$); IR (neat): 2976, 2937, 2837, 1749, 1664, 1609, 1576, 1498, 1461, 1427, 1369, 1274, 1244, 1162, 1134, 1113, 1038, 886 cm$^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$, 41), 177 (12), 176 (100), 161 (22), 159 (17), 147 (18), 57 (77); exact mass calculate for $C_{16}H_{20}O_4$ ($M^+$): 276.1362; found 276.1363.

**Spectroscopic data for 3d**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); white solid; mp 135-137 °C. Spectroscopic data for **3d**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, $J$ = 8.8 Hz, 1 H), 7.69 (d, $J$ = 8.8 Hz, 1 H), 7.55 (d, $J$ = 2.0 Hz, 1 H), 7.28 (d, $J$ = 2.0 Hz, 1 H), 7.17-7.14 (m, 2H), 3.91 (s, 3 H), 1.54 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 157.7 (C), 152.2 (C), 147.1 (C), 132.5 (C), 129.1 (CH), 129.0 (C), 128.0 (CH), 121.2 (CH), 119.4 (CH), 118.1 (CH), 105.8 (CH), 83.5 (C), 55.3 ($CH_3$), 27.7 (three $CH_3$); IR (neat): 3002, 2970, 2938, 1752, 1708, 1633, 1606, 1509, 1482, 1456, 1390, 1370, 1336, 1287, 1262, 1226, 1166, 1150, 1048, 1025, 965, 937, 896, 856, 820, 810, 780, 743 cm$^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 63), 175 (11), 174 (100), 159 (35), 145 (14), 131 (67), 103 (13), 102 (33), 77 (14), 57 (40); exact mass calculate for $C_{16}H_{18}O_4$ ($M^+$): 274.1205; found 274.1204.

**Spectroscopic data for 4d**

TLC $R_f$ = 0.23 (Hexane/EtOAc = 5:1); pale yellow solid; mp 167-169 °C. Spectroscopic data for **4d**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, $J$ = 9.6 Hz, 1 H), 8.10 (d, $J$ = 9.2 Hz, 1 H), 7.87 (d, $J$ = 9.2 Hz, 1 H), 7.42 (d, $J$ = 9.2 Hz, 1 H), 7.33 (dd, $J$ = 9.2 Hz, 2.4 Hz, 1 H), 7.21 (d, $J$ = 2.4 Hz, 1 H), 6.55 (d, $J$ = 9.6 Hz, 1 H), 3.95 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 161.0 (C), 157.7 (C), 152.4 (C), 139.1 (CH), 131.8 (CH), 131.6 (C), 123.8 (C), 122.8 (CH), 120.4 (CH), 117.4 (CH), 115.8 (CH), 113.2 (C), 107.5 (CH), 55.4 ($CH_3$); IR (neat): 2961, 2923, 2849, 1710, 1612, 1590, 1566, 1517, 1468, 1374, 1337, 1253, 1177, 1113, 1080, 1031, 989, 898, 851, 800 cm$^{-1}$; MS (*m/z*, relative intensity): 226 ($M^+$, 100), 198 (50), 183 (43), 156 (11), 155 (98), 139 (17), 127 (60), 126 (36), 101 (12), 77 (14), 75 (12); exact mass calculate for $C_{14}H_{10}O_3$ ($M^+$): 226.0630; found 226.0639.

**Spectroscopic data for 2e**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); white solid; mp 46-48 °C. Spectroscopic data for **2e**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.01 (d, $J$ = 8.4 Hz, 1 H), 6.65 (dd, $J$ = 8.4, 2.4 Hz, 1 H), 6.59 (d, $J$ = 2.4 Hz, 1 H), 6.26 (s, 1 H), 3.77 (s, 3H), 2.92 (t, $J$ = 8.4 Hz, 2 H), 2.55-2.51 (m, 2 H), 1.54 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 158.4 (C), 151.5 (C), 151.0 (C), 134.3 (C), 127.9 (CH), 125.2 (C), 114.2 (CH), 112.1 (CH), 111.7 (CH), 83.3 (C), 55.3 ($CH_3$), 27.74 ($CH_2$), 27.67 (three $CH_3$), 26.4 ($CH_2$); IR (neat): 2980, 2937, 2834, 1752, 1665, 1607, 1575, 1499, 1463, 1423, 1394, 1370, 1311, 1248, 1215, 1132, 1039, 888, 809, 784, 732 cm$^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$, 62), 176 (37), 159 (11), 134 (10), 115 (10), 57 (100); exact mass calculate for $C_{16}H_{20}O_4$ ($M^+$): 276.1362; found 276.1367.

**Spectroscopic data for 3e**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); white solid; mp 74-76 °C. Spectroscopic data for **3e**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, $J$ = 8.8 Hz, 1 H), 7.71 (d, $J$ = 8.8 Hz, 1 H), 7.53 (d, $J$ = 2.0 Hz, 1 H), 7.15 (dd, $J$ = 8.8, 2.0 Hz, 1 H), 7.12-7.09 (m, 2H), 3.90 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 158.2 (C), 152.0 (C), 149.3 (C), 135.1 (C), 129.2 (CH), 129.1 (CH), 126.8 (C), 118.6 (CH), 118.3 (CH), 117.2 (CH), 105.6 (CH), 83.6 (C), 55.3 ($CH_3$), 27.7 (three $CH_3$); IR (neat): 3063, 2980, 2937, 1755, 1634, 1609, 1513, 1467, 1427, 1391, 1371, 1276, 1245, 1216, 1145, 1031, 955, 892, 835, 811, 781, 751 cm$^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 100), 175 (12), 174 (100), 157 (11), 145 (24), 131 (27), 102 (25), 57 (47); exact mass calculate for $C_{16}H_{18}O_4$ ($M^+$): 274.1205; found 274.1204.

**Spectroscopic data for 4e**

TLC $R_f$ = 0.22 (Hexane/EtOAc = 5:1); white solid; mp 168-170 °C. Spectroscopic data for **4e**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, $J$ = 9.6 Hz, 1 H), 7.89 (d, $J$ = 8.8 Hz, 1 H), 7.82 (d, $J$ = 8.8 Hz, 1 H), 7.49 (d, $J$ = 2.4 Hz, 1 H), 7.32 (d, $J$ = 8.8 Hz, 1 H), 7.21 (dd, $J$ = 8.8, 2.4 Hz, 1 H),

6.54 (d, $J$ = 9.6 Hz, 1 H), 4.00 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 161.0 (C), 159.7 (C), 154.6 (C), 139.2 (CH), 132.9 (CH), 130.7 (C), 130.6 (CH), 125.5 (C), 117.6 (CH), 114.9 (CH), 114.5 (CH), 112.2 (C), 101.2 (CH), 55.5 ($CH_3$); IR (neat): 2994, 2961, 2920, 2851, 1731, 1706, 1631, 1571, 1513, 1459, 1376, 1286, 1247, 1227, 1172, 1114, 1030, 910, 824 cm$^{-1}$; ESI MS (*m/z*): 249 ($M^+$, +23) ; MS (*m/z*, relative intensity): 226 ($M^+$, 49), 198 (48), 195 (27), 183 (15), 155 (31), 139 (10), 127 (19), 121 (66), 117 (38), 111 (10), 99 (13), 97 (17), 91 (57), 85 (24), 83 (17), 71 (32), 69 (17), 57 (45), 55 (17); exact mass calculate for $C_{14}H_{10}O_3$ ($M^+$): 226.0630; found 226.0636.

**Spectroscopic data for 2f**

TLC $R_f$ = 0.53 (Hexane/EtOAc = 10:1); white solid; mp 48-50 °C. Spectroscopic data for **2f**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.07 (t, $J$ = 8.0 Hz, 1 H), 6.73 (d, $J$ = 8.0 Hz, 1 H), 6.70 (d, $J$ = 8.0 Hz, 1 H), 6.66 (s, 1 H), 3.80 (s, 3 H), 2.96 (t, $J$ = 8.0 Hz, 2 H), 2.54-2.49 (m, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 154.8 (C), 151.2 (C), 149.9 (C), 134.5 (C), 127.2 (CH), 121.9 (C), 119.8 (CH), 108.9 (CH), 108.5 (CH), 83.1 (C), 55.5 ($CH_3$), 29.0 ($CH_2$), 27.7 (three $CH_3$), 25.8 ($CH_2$); IR (neat): 3072, 2980, 2935, 2836, 1752, 1663, 1578, 1472, 1439, 1370, 1323, 1252, 1212, 1139, 1086, 893, 859, 780, 739, 702, 651 cm$^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$, 18), 177 (12), 176 (100), 161 (18), 159 (17), 115 (11), 57 (80); exact mass calculate for $C_{16}H_{20}O_4$ ($M^+$): 276.1362; found 276.1366.

**Spectroscopic data for 3f**

TLC $R_f$ = 0.53 (Hexane/EtOAc = 10:1); white solid; mp 85-87 °C. Spectroscopic data for **3f**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, $J$ = 2.4 Hz, 1 H), 7.79 (d, $J$ = 8.8 Hz, 1 H), 7.41 (d, $J$ = 8.0 Hz, 1 H), 7.36 (t, $J$ = 8.0 Hz, 1 H), 7.30 (dd, $J$ = 8.8, 2.4 Hz, 1 H), 6.82 (d, $J$ = 8.0 Hz, 1 H), 3.99 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 155.2 (C), 152.1 (C), 148.4 (C), 132.4 (C), 128.9 (CH), 125.9 (C), 125.7 (CH), 121.3 (CH), 119.9 (CH), 113.1 (CH), 104.3 (CH), 83.5 (C), 55.4 ($CH_3$), 27.7 (three $CH_3$); IR (neat): 3064, 2980, 2934, 1757, 1601, 1585, 1510, 1465, 1437, 1371, 1272, 1235, 1215, 1201, 1149, 1100, 1066, 997, 887, 864, 826, 781, 747 cm$^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 100), 175 (13), 174 (100), 159 (38), 131 (11), 115 (26), 102 (15), 57 (56); exact mass calculate for $C_{16}H_{18}O_4$ ($M^+$): 274.1205; found 274.1211.

**Spectroscopic data for 4f**

TLC $R_f$ = 0.22 (Hexane/EtOAc = 5:1); yellow solid; mp 122-124 °C. Spectroscopic data for **4f**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.45 (d, $J$ = 10.0 Hz, 1 H), 7.89 (d, $J$ = 8.8 Hz, 1 H), 7.49 -7.43 (m, 2 H), 7.41 (d, $J$ = 8.8 Hz, 1 H), 7.07 (dd, $J$ = 6.4, 2.4 Hz, 1 H), 6.45 (d, $J$ = 10.0 Hz, 1 H), 4.06 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.7 (C), 157.1 (C), 154.6 (C), 144.7 (CH), 133.2 (CH), 132.4 (C), 126.0 (CH), 121.8 (CH), 120.1 (C), 117.7 (CH), 114.1 (CH), 113.6 (C), 108.5 (CH), 55.6 ($CH_3$); IR (neat): 3066, 2922, 2838, 1731, 1606, 1557, 1514, 1462, 1441, 1353, 1330, 1268, 1255, 1214, 1175, 1113, 1062, 985, 904, 828, 794, 756, 722 cm$^{-1}$; MS (*m/z*, relative intensity): 226 ($M^+$, 100), 199 (10), 198 (70), 183 (58), 167 (35), 155 (66), 139 (19), 127 (29), 126 (16), 75 (12), 63 (11); exact mass calculate for $C_{14}H_{10}O_3$ ($M^+$): 226.0630; found 226.0638.

**Spectroscopic data for 2g**

TLC $R_f$ = 0.62 (Hexane/EtOAc = 5:1); white solid; mp 87-89 °C. Spectroscopic data for **2g**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.21 (dd, $J$ = 8.0, 2.0 Hz, 1 H), 7.14 (d, $J$ = 2.0 Hz, 1 H), 6.96 (d, $J$ = 8.0 Hz, 1 H), 6.23 (s, 1 H), 2.92 (t, $J$ = 8.0 Hz, 2 H), 2.54 (t, $J$ = 8.0 Hz, 2 H), 1.55 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.9 (C), 150.9 (C), 135.4(C), 131.9(C), 129.4 (CH), 128.9 (CH), 128.7 (CH), 120.1 (C), 113.2 (CH), 83.6 (C), 28.1 ($CH_2$), 27.7 (three $CH_3$), 25.9 ($CH_2$); IR (neat): 2980, 2937, 1753, 1666, 1591, 1482, 1395, 1370, 1300, 1274, 1255, 1233, 1133, 1076, 888, 813, 782, 673 cm$^{-1}$; MS (*m/z*, relative intensity): 324 ($M^+$, 100), 226 (31), 224 (33), 209 (9), 207 (9), 139 (10), 116 (18), 115 (19), 57 (100); exact mass calculate for $C_{15}H_{17}BrO_3$ ($M^+$): 324.0361; found 324.0364.

**Spectroscopic data for 3g**

TLC $R_f$ = 0.62 (Hexane/EtOAc = 5:1); white solid; mp 110-112 °C. Spectroscopic data for **3g**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1 H), 7.78 (d, $J$ = 8.8 Hz, 1 H), 7.66 (d, $J$ = 8.8 Hz, 1 H), 7.54 (s, 1 H), 7.50 (d, $J$ = 8.8 Hz, 1 H), 7.31 (d, $J$ = 8.8 Hz, 1 H), 1.55 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.7 (C), 149.4 (C), 134.8 (C), 129.7 (C), 129.6 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 121.3 (CH), 120.7 (C), 117.3 (CH), 83.8 (C), 27.7 (three $CH_3$); IR (neat): 3003, 2980, 2923, 1753, 1626, 1577, 1503, 1450, 1369, 1321, 1280, 1258, 1234, 1201, 1150, 1062, 959, 921, 903, 842, 781, 717 cm$^{-1}$; MS (*m/z*, relative intensity): 322 ($M^+$, 35), 224 (55), 222 (49), 207 (4), 205 (4), 195 (7), 193 (8), 143 (7), 141 (5), 139 (13), 126 (11), 114 (17), 57 (100); exact mass calculate for $C_{15}H_{15}BrO_3$ ($M^+$): 322.0205; found 322.0206.

**Spectroscopic data for 4g**

TLC $R_f$ = 0.33 (Hexane/EtOAc = 5:1); pale orange solid; mp 174-176 °C. Spectroscopic data for **4g**: $^1$H NMR ($CDCl_3$, 400 MHz): $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d,

$J$ = 9.6 Hz, 1 H), 8.33 (s, 1 H), 7.92 (d, $J$ = 8.8 Hz, 1 H), 7.76 (d, $J$ = 8.8 Hz, 1 H), 7.63 (dd, $J$ = 8.8, 1.6 Hz, 1 H), 7.45 (d, $J$ = 8.8 Hz, 1 H), 6.58 (d, $J$ = 9.6 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.3 (C), 154.2 (C), 138.5 (CH), 132.7 (CH), 130.4 (CH), 130.1 (C), 129.4 (CH), 128.6 (C), 124.0 (CH), 122.9 (C), 117.4 (CH), 116.0 (CH), 112.1 (C); IR (neat): 3076, 2922, 2852, 1725, 1627, 1583, 1563, 1498, 1451, 1321, 1245, 1202, 1174, 1113, 1086, 898, 828, 772, 715 cm$^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$+3, 70), 274 ($M^+$+1, 71), 273 ($M^+$, 100), 249 (10), 248 (81), 247 (10), 246 (82), 195 (24), 167 (26), 140 (11), 139 (100), 138 (20), 137 (11), 113 (10), 87 (11), 69 (36), 63 (13); exact mass calculate for$C_{13}H_7BrO_2$ ($M^+$): 273.9629; found 273.9637.

**Spectroscopic data for 2h**

TLC $R_f$ = 0.69 (Hexane/EtOAc = 10:1); white solid; mp 41-43 °C. Spectroscopic data for **2h**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.82 (s, 1 H), 6.70 (s, 1 H), 6.23 (s, 1 H), 2.90 (t, $J$ = 8.4 Hz, 2 H), 2.57-2.52 (m, 2 H), 2.25 (s, 3 H), 2.23 (s, 3 H), 1.56 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.3 (C), 135.5 (C), 134.7 (C), 133.1 (C), 129.6 (CH), 128.2 (C), 125.3 (CH), 114.4 (CH), 83.2 (C), 27.7 (three $CH_3$), 25.9 ($CH_2$), 24.6 ($CH_2$), 20.8 ($CH_3$), 19.4 ($CH_3$); IR (neat): 3006, 2979, 2834, 1752, 1671, 1607, 1577, 1478, 1394, 1370, 1329, 1273, 1134, 1058, 1011, 990, 880, 808, 784, 737, 697 cm$^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 72), 174 (81), 159 (18), 157 (21), 145 (20), 132 (11), 130 (13), 129 (16), 128 (13), 115 (15), 57 (100); exact mass calculate for $C_{17}H_{22}O_3$ ($M^+$): 274.1569; found 274.1559.

**Spectroscopic data for 3h**

TLC $R_f$ = 0.69 (Hexane/EtOAc = 10:1); white solid; mp 58-60 °C. Spectroscopic data for **3h**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, $J$ = 9.0 Hz, 1 H), 7.53 (d, $J$ = 2.4 Hz, 1 H), 7.43 (s, 1 H), 7.26 (dd, $J$ = 9.2, 2.4 Hz, 1 H), 7.13 (s, 1 H), 2.64 (s, 3 H), 2.45 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.0 (C), 148.6 (C), 136.1 (C), 134.3 (C), 134.0 (C), 128.9 (C), 128.8 (CH), 125.5 (CH), 125.1 (CH), 119.5 (CH), 118.0 (CH), 83.5 (C), 27.7 (three $CH_3$), 21.6 ($CH_3$), 19.3 ($CH_3$); IR (neat): 2979, 2936, 1752, 1633, 1611, 1584, 1511, 1455, 1418, 1394, 1370, 1256, 1218, 1147, 1045, 1020, 993, 936, 883, 843, 817, 804, 781, 758, 705 cm$^{-1}$; MS (*m/z*, relative intensity): 272 ($M^+$, 23), 173 (14), 172 (100), 171 (10), 157 (18), 143 (19), 128 (27), 115 (11), 57 (21); exact mass calculate for $C_{17}H_{20}O_3$ ($M^+$): 272.1412; found 272.1409.

**Spectroscopic data for 4h**

TLC $R_f$ = 0.29 (Hexane/EtOAc = 5:1); yellow solid; mp 193-195 °C. Spectroscopic data for **4h**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, $J$ = 10.0 Hz, 1 H), 8.09 (d, $J$ = 9.20 Hz, 1 H), 7.84 (s, 1 H), 7.38 (d, $J$ = 9.20 Hz, 1 H), 7.24 (s, 1 H), 6.52 (d, $J$ = 10.0 Hz, 1 H), 2.68 (s, 3 H), 2.54 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 153.7 (C), 139.4 (CH), 137.9 (C), 135.2 (C), 129.5 (C), 129.0 (CH), 128.9 (CH), 127.5 (C), 118.8 (CH), 115.4 (CH), 115.1 (CH), 112.7 (C), 22.0 ($CH_3$), 19.4 ($CH_3$); IR (neat): 3046, 2917, 2853, 1708, 1625, 1566, 1507, 1443, 1375, 1323, 1261, 1212, 1176, 1120, 1072, 909, 827, 780 cm$^{-1}$; MS (*m/z*, relative intensity): 224 ($M^+$, 100), 209 (47), 196 (41), 181 (19), 165 (14), 152 (24); exact mass calculate for $C_{15}H_{12}O_2$ ($M^+$): 224.0837; found 224.0831.

**Spectroscopic data for 2i**

TLC $R_f$ = 0.68 (Hexane/EtOAc = 5:1); white solid; mp 66-68 °C. Spectroscopic data for **2i**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.87 (s, 1 H), 6.51 (s, 1 H), 6.25 (s, 1 H), 3.79 (s, 3 H), 2.89 (t, $J$ = 8.0 Hz, 2 H), 2.51 (t, $J$ = 8.0 Hz, 2 H), 2.17 (s, 3H), 1.53 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 156.3 (C), 151.1 (C), 150.4 (C), 131.6 (C), 129.6 (CH), 124.7 (C), 124.6 (C), 114.1 (CH), 108.6 (CH), 83.2 (C), 55.5 ($CH_3$), 27.8 ($CH_2$), 27.7 (three $CH_3$), 26.5 ($CH_2$), 15.9 ($CH_3$); IR (neat): 2980, 2937, 2833, 1752, 1665, 1614, 1572, 1506, 1464, 1395, 1370, 1248, 1211, 1162, 1133, 1070, 1032, 889, 838, 783, 752, 704 cm$^{-1}$; MS (*m/z*, relative intensity): 290 ($M^+$,18), 191 (13), 190 (100), 189 (11), 173 (17), 148 (11), 57 (74); exact mass calculate for $C_{17}H_{22}O_4$ ($M^+$): 290.1518; found 290.1513.

**Spectroscopic data for 3i**

TLC $R_f$ = 0.68 (Hexane/EtOAc = 5:1); pale yellow liquid. Spectroscopic data for **3δi**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, $J$ = 8.8 Hz, 1 H), 7.55 (s, 1 H), 7.50 (d, $J$ = 2.4 Hz, 1 H), 7.12 (dd, $J$ = 8.8, 2.4 Hz, 1 H), 7.03 (s, 1 H), 3.92 (s, 3 H), 2.35 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 157.4 (C), 152.1 (C), 148.6 (C), 133.8 (C), 128.5 (CH), 128.3 (C), 128.2 (CH), 126.7 (C), 118.1 (CH), 116.8 (CH), 104.3 (CH), 83.4 (C), 55.3 ($CH_3$), 27.7 (three $CH_3$), 16.8 ($CH_3$); IR (neat): 2977, 2955, 2924, 1754, 1637, 1509, 1462, 1415, 1370, 1279, 1242, 1141, 894, 804, 750 cm$^{-1}$; MS (*m/z*, relative intensity): 288 ($M^+$, 20), 189 (12), 188 (100), 149 (13), 145 (18), 115 (11), 57 (44); exact mass calculate for $C_{17}H_{20}O_4$ ($M^+$): 288.1362; found 288.1367.

**Spectroscopic data for 4i**

TLC $R_f$ = 0.34 (Hexane/EtOAc = 3:1); yellow solid; mp 193-195 °C. Spectroscopic data for **4i**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.38 (d, $J$ = 9.6 Hz, 1 H), 7.79 (d, $J$ = 8.8 Hz, 1 H), 7.59 (s, 1 H), 7.35 (s, 1 H), 7.25 (d, $J$ = 8.8 Hz, 1 H),

6.50 (d, $J$ = 9.6 Hz, 1 H), 4.00 (s, 3 H), 2.37 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 161.1 (C), 158.8 (C), 153.8 (C), 139.2 (CH), 132.1 (CH), 129.9 (CH), 129.2 (C), 128.4 (C), 125.3 (C), 114.7 (CH), 114.1 (CH), 112.1 (C), 98.9 (CH), 55.4 ($CH_3$), 16.5 ($CH_3$); IR (neat): 2996, 2921, 2850, 1729, 1711, 1635, 1571, 1509, 1467, 1320, 1253, 1225, 1148, 1118, 1025, 827 cm$^{-1}$; MS (*m/z*, relative intensity): 240 ($M^+$,100), 212 (54), 209 (27), 197 (28), 169 (36), 152 (10), 141 (14), 139 (18), 115 (19), 113 (14); exact mass calculate for $C_{15}H_{12}O_3$ ($M^+$): 240.0786; found 240.0790.

**Spectroscopic data for 2j**

TLC $R_f$ = 0.31 (Hexane/EtOAc = 5:1); yellow solid; mp 92-96 °C. Spectroscopic data for **2j**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.67 (s, 1 H), 6.57 (s, 1 H), 6.21 (s, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 2.92 (t, $J$ = 8.4 Hz, 2 H), 2.52 (t, $J$ = 8.4 Hz, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.2 (C), 149.2 (C), 147.6 (C), 147.4 (C), 125.7 (CH), 125.4 (C), 113.7 (CH), 111.2 (CH), 110.1 (CH), 83.2 (C), 56.0 (two $CH_3$), 28.4 ($CH_2$), 27.7 (three $CH_3$), 26.1 ($CH_2$); IR (neat): 2977, 2936, 2833, 1751, 1666, 1606, 1516, 1463, 1370, 1322, 1270, 1247, 1213, 1160, 1132, 1026, 980, 889, 784, 753 cm$^{-1}$; MS (*m/z*, relative intensity): 306 ($M^+$, 100), 206 (35), 57 (100); exact mass calculate for $C_{17}H_{22}O_5$ ($M^+$): 306.1467; found 306.1469.

**Spectroscopic data for 3j**

TLC $R_f$ = 0.31 (Hexane/EtOAc = 5:1); white solid; mp 108-110 °C. Spectroscopic data for **3j**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, $J$ = 8.8 Hz, 1 H), 7.48 (d, $J$ = 2.4 Hz, 1 H), 7.15 (dd, $J$ = 8.8, 2.4 Hz, 1 H), 7.07 (s, 1 H), 7.04 (s, 1 H), 3.96 (s, 3 H), 3.95 (s, 3H), 1.57 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.1 (C), 150.0 (C), 149.2 (C), 147.6 (C), 129.4 (C), 127.4 (CH), 126.9 (C), 118.6 (CH), 116.8 (CH), 106.1 (CH), 106.0 (CH), 83.2 (C), 55.7 (two $CH_3$), 27.6 (three $CH_3$); IR (neat): 3004, 2978, 2936, 1753, 1632, 1609, 1512, 1492, 1463, 1421, 1370, 1278, 1244, 1214, 1144, 1007, 895, 850, 811, 781, 751 cm$^{-1}$; MS (*m/z*, relative intensity): 304 ($M^+$, 51), 204 (57), 57 (100); exact mass calculate for $C_{17}H_{20}O_5$ ($M^+$): 304.1311; found 304.1317.

**Spectroscopic data for 4j**

TLC $R_f$ = 0.18 (Hexane/EtOAc = 3:1); brown solid; mp 194-196 °C. Spectroscopic data for **4j**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, $J$ = 10.0 Hz, 1 H), 7.79 (d, $J$ = 8.4 Hz, 1 H), 7.42 (s, 1 H), 7.28 (d, $J$ = 8.4 Hz, 1 H), 7.16 (s, 1 H), 6.51 (d, $J$ = 10.0 Hz, 1 H), 4.07 (s, 3 H), 4.01 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 161.0 (C), 152.8 (C), 151.2 (C), 149.1 (C), 139.1 (CH), 131.3 (CH), 125.7 (C), 124.6 (C), 115.0 (CH), 114.7 (CH), 112.2 (C), 107.5 (CH), 100.8 (CH), 55.94 ($CH_3$) , 55.89 ($CH_3$); IR (neat): 3004, 2928, 2851, 1729, 1629, 1593, 1570, 1517, 1485, 1434, 1271, 1232, 1163, 1122, 1020, 906, 853, 827, 806 cm$^{-1}$; MS (*m/z*, relative intensity): 256 ($M^+$, 18), 228 (17), 225 (15), 213 (17), 185 (18), 183 (12), 170 (22), 157 (17), 155 (14), 142 (39), 139 (13), 127 (11), 126 (11), 114 (23), 113 (13); exact mass calculate for $C_{15}H_{12}O_4$ ($M^+$): 256.0736; found 256.0731.

**Spectroscopic data for 2k**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); colorless liquid. Spectroscopic data for **2k**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.67-6.63 (m, 2 H), 6.63 (s, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 2.97 (t, $J$ = 8.8 Hz, 2 H), 2.49 (t, $J$ = 8.8 Hz, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.5 (C), 150.4 (C), 149.4 (C), 123.3 (C), 122.4 (C), 109.7 (CH), 109.1 (CH), 108.4 (CH), 83.1 (C), 56.1 ($CH_3$), 55.9 ($CH_3$), 27.7 (three $CH_3$), 25.2 ($CH_2$) , 21.7 ($CH_2$); IR (neat): 2978, 2937, 2832, 1752, 1483, 1370, 1278, 1256, 1138, 1082, 953, 858, 787, 717 cm$^{-1}$; MS (*m/z*, relative intensity): 306 ($M^+$, 81), 207 (17), 206 (100), 191 (50), 189 (20), 57 (65); exact mass calculate for $C_{17}H_{20}O_5$ ($M^+$): 306.1467; found 306.1470.

**Spectroscopic data for 3k**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 10:1); colorless liquid. Spectroscopic data for **3k**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, $J$ = 9.2 Hz, 1 H), 7.98 (d, $J$ = 2.4 Hz, 1 H), 7.31 (dd, $J$ = 9.2, 2.4 Hz, 1 H), 6.66 (d, $J$ = 8.4 Hz, 1 H), 6.61 (d, $J$ = 8.4 Hz, 1 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 1.56 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.9 (C), 149.4 (C), 149.1 (two C), 126.9 (C), 124.2 (C), 123.6 (CH), 120.4 (CH), 112.8 (CH), 104.0 (CH), 103.0 (CH), 83.3 (C), 55.6 (two $CH_3$), 27.7 (three $CH_3$); IR (neat): 3080, 2980, 2937, 2836, 1757, 1633, 1601, 1464, 1426, 1395, 1362, 1269, 1238, 1148, 1099, 1004, 970, 886, 862, 804, 719 cm$^{-1}$; MS (*m/z*, relative intensity): 304 ($M^+$, 32), 205 (12), 204 (89), 189 (100), 175 (10), 146 (11), 57 (35); exact mass calculate for $C_{17}H_{20}O_5$ ($M^+$): 304.1311; found 304.1309.

**Spectroscopic data for 4k**

TLC $R_f$ = 0.19 (Hexane/EtOAc = 5:1); yellow solid; mp 172-173 °C. Spectroscopic data for **4k**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.53 (d, $J$ = 10.0 Hz, 1 H), 8.47 (d, $J$ = 9.2 Hz, 1 H), 7.44 (d, $J$ = 9.2 Hz, 1 H), 7.00 (d, $J$ = 8.4 Hz, 1 H), 6.82 (d, $J$ = 8.4 Hz, 1 H), 6.46 (d, $J$ = 10.0 Hz, 1 H), 4.01 (s, 3 H), 3.98 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.8 (C), 155.2 (C), 151.0 (C), 150.0 (C), 144.9 (CH), 127.3 (CH), 123.7 (C), 121.2 (C), 116.9 (CH), 114.1 (CH), 113.5

(C), 108.6 (CH), 104.1 (CH), 55.92 ($CH_3$), 55.86 ($CH_3$); IR (neat): 2917, 2849, 1725, 1598, 1559, 1462, 1417, 1336, 1243, 1214, 1181, 1109, 1057, 1010, 823, 786 $cm^{-1}$; MS (*m/z*, relative intensity): 256 ($M^+$, 16), 241 (13), 240 (91), 213 (31), 197 (16), 169 (13); exact mass calculate for $C_{15}H_{12}O_4$ ($M^+$): 256.0736; found 256.0729.

**Spectroscopic data for 2l**

TLC $R_f$ = 0.76 (Hexane/EtOAc = 10:1); pale yellow liquid. Spectroscopic data for **2l**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.15-7.12 (m, 3 H), 7.04-7.00 (m, 1 H), 6.28 (s, 1 H), 3.16-3.10 (m, 1 H), 2.77-2.71 (m, 1 H), 2.29 (dd, *J* = 16.8, 6.8 Hz, 1 H), 1.53 (s, 9 H), 1.30 (d, *J* = 6.8 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 149.5 (C), 146.8 (C), 138.3 (C), 132.4 (C), 127.1 (CH), 126.6 (CH), 125.9 (CH), 113.6 (CH), 83.2 (C), 33.7 ($CH_2$), 33.5 (CH), 27.7 (three $CH_3$), 20.5 ($CH_2$); IR (neat): 3068, 2978, 2929, 1753, 1669, 1455, 1395, 1370, 1273, 1252, 1165, 1136, 1073, 846, 753 $cm^{-1}$; MS (*m/z*, relative intensity): 260 ($M^+$, 80), 161 (10), 160 (100), 145 (56), 143 (28), 128 (14), 115 (19), 91 (13); exact mass calculate for $C_{16}H_{20}O_3$ ($M^+$): 260.1412; found 260.1410.

**Spectroscopic data for 3l**

TLC $R_f$ = 0.76 (Hexane/EtOAc = 10:1); pale yellow liquid. Spectroscopic data for **3l**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.98-7.95 (m, 1 H), 7.82-7.78 (m, 1 H), 7.51-7.46 (m, 3 H), 7.16 (d, *J* = 1.2 Hz, 1 H), 2.69 (s, 3 H), 1.58 (s, 9 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 152.1 (C), 148.2 (C), 136.5 (C), 133.9 (C), 130.7 (C), 128.4 (CH), 126.3 (CH), 125.5 (CH), 124.1 (CH), 121.4 (CH), 116.4 (CH), 83.5 (C), 27.7 (three $CH_3$), 19.3 ($CH_3$); IR (neat): 3067, 2980, 2934, 1757, 1626, 1602, 1510, 1464, 1421, 1394, 1370, 1348, 1249, 1147, 1053, 1020, 954, 889, 871, 856, 771, 755, 658 $cm^{-1}$; MS (*m/z*, relative intensity): 258 ($M^+$, 72), 159 (17), 158 (100), 157 (11), 141 (14), 129 (20), 128 (25), 115 (10), 57 (85); exact mass calculate for $C_{16}H_{18}O_3$ ($M^+$): 258.1256; found 258.1251.

**Spectroscopic data for 4l**

TLC $R_f$ = 0.31 (Hexane/EtOAc = 5:1); pale yellow solid; mp 119-121 °C. Spectroscopic data for **4l**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, *J* = 10 Hz, 1 H), 8.24 (d, *J* = 8.0 Hz, 1 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.71-7.67 (m, 1 H), 7.62-7.56 (m, 1 H), 7.32 (s, 1 H), 6.51 (d, *J* = 10.0 Hz, 1 H), 2.77 (s, 3 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 161.1 (C), 153.7 (C), 141.0 (C), 139.1 (CH), 129.8 (C), 129.1 (C), 127.9 (CH), 125.9 (CH), 125.1 (CH), 121.8 (CH), 117.6 (CH), 114.7 (CH), 111.6 (C), 20.0 ($CH_3$); IR (neat): 3075, 2952, 2923, 2857, 1731, 1625, 1590, 1559, 1519, 1458, 1378, 1359, 1224, 1167, 1125, 1009, 896, 825, 756 $cm^{-1}$; MS (*m/z*, relative intensity): 210 ($M^+$, 100), 195 (36), 183 (14), 182 (100), 181 (55), 165 (10), 154 (13), 153 (39), 152 (59), 151 (19), 139 (15), 127 (21), 115 (12), 76 (20), 63 (10); exact mass calculate for $C_{14}H_{10}O_2$ ($M^+$): 210.0681; found 210.0688.

**Spectroscopic data for 2m**

TLC $R_f$ = 0.61 (Hexane/EtOAc = 10:1); pale yellow liquid. Spectroscopic data for **2m**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.34-7.30 (m, 2 H), 7.26-7.24 (m, 3 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 7.09-7.03 (m, 1 H), 6.76 (d, *J* = 7.6 Hz, 1 H), 6.38 (s, 1 H), 4.33 (t, *J* = 9.2 Hz, 1 H), 2.86-2.84 (m, 2 H), 1.51 (s, 9 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 150.9 (C), 149.4 (C), 143.4 (C), 135.9 (C), 133.2 (C), 128.6 (CH), 128.4 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 114.1 (CH), 83.3 (C), 45.3 (CH), 34.4 ($CH_2$), 27.4 (three $CH_3$); IR (neat): 3022, 2980, 2934, 1752, 1667, 1485, 1452, 1370, 1281, 1245, 1161, 1133, 753, 700 $cm^{-1}$; MS (*m/z*, relative intensity): 322 ($M^+$, 9), 223 (18), 222 (100), 220 (13), 205 (20), 179 (28), 178 (15), 57 (81); exact mass calculate for $C_{21}H_{22}O_3$ ($M^+$): 322.1569; found 322.1560.

**Spectroscopic data for 3m**

TLC $R_f$ = 0.61 (Hexane/EtOAc = 10:1); orange solid; mp 76-78 °C. Spectroscopic data for **3m**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 6.4 Hz, 1 H), 7.84 (d, *J* = 6.4 Hz, 1 H), 7.65 (s, 1 H), 7.48-7.35 (m, 7 H), 7.28 (d, *J* = 2.4 Hz, 1 H), 1.57 (s, 9 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 151.9 (C), 148.1 (C), 142.0 (C), 139.7 (C), 134.3 (C), 130.0 (two $CH_2$), 129.7 (C), 128.3 (two CH), 128.1 (CH), 127.6 (CH), 126.5 (CH), 126.0 (CH), 125.8 (CH), 121.7 (CH), 117.6 (CH), 83.6 (C), 27.7 (three $CH_3$); IR (neat): 3058, 2980, 2932, 1757, 1624, 1596, 1493, 1454, 1424, 1393, 1370, 1344, 1296, 1251, 1209, 1145, 1073, 1030, 981, 921, 882, 862, 783, 756, 734, 701 $cm^{-1}$; MS (*m/z*, relative intensity): 320 ($M^+$, 21), 221 (21), 220 (100), 219 (20), 202 (27), 191 (40), 189 (30), 165 (15), 57 (43); exact mass calculate for $C_{21}H_{20}O_3$ ($M^+$): 320.1412; found 320.1417.

**Spectroscopic data for 4m**

TLC $R_f$ = 0.26 (Hexane/EtOAc = 5:1); red brown solid; mp 293-295 °C. Spectroscopic data for **4m**: $^1H$ NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 10.0 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 7.69 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.55-7.47 (m, 6 H), 7.41 (s, 1 H), 6.58 (d, *J* = 10.0 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 153.3 (C), 145.7 (C), 139.0 (CH), 138.9 (C), 129.7 (CH), 129.5 (C), 129.0 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.7

(CH), 126.0 (CH), 121.6 (CH), 117.7 (CH), 115.5 (CH), 112.4 (C); IR (neat): 3061, 2924, 2853, 1733, 1623, 1589, 1555, 1518, 1493, 1445, 1417, 1364, 1227, 1169, 1151, 1116, 995, 903, 878, 826, 772, 702 $cm^{-1}$; MS (*m/z*, relative intensity): 272 ($M^+$, 100), 244 (46), 243 (12), 215 (40), 213 (10), 107 (11); exact mass calculate for $C_{19}H_{12}O_2$ ($M^+$): 272.0837; found 272.0840.

**Spectroscopic data for 2n**

TLC $R_f$ = 0.72 (Hexane/EtOAc = 10:1); pale yellow solid; mp 91-93 °C. Spectroscopic data for **2n**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.99 (d, *J* = 7.6 Hz, 1 H), 6.91 (d, *J* = 7.6 Hz, 1 H), 6.83 (s, 1 H), 6.24 (s, 1 H), 2.94 (t, *J* = 8.0 Hz, 2 H), 2.53 (t, *J* = 8.0 Hz, 2 H), 2.28 (s, 3 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.8 (C), 136.0 (C), 133.1 (C), 130.1 (C), 127.3 (CH), 127.1 (CH), 127.0 (CH), 114.2 (CH), 83.2 (C), 28.2 ($CH_2$), 27.7 (three $CH_3$), 26.3 ($CH_2$), 21.0 ($CH_3$); IR (neat): 3007, 2980, 2936, 1752, 1665, 1497, 1475, 1456, 1394, 1370, 1310, 1243, 1134, 1044, 1022, 981, 891, 852, 812, 784, 736, 664 $cm^{-1}$; MS (*m/z*, relative intensity): 260 ($M^+$, 11), 160 (78), 145 (12), 143 (19), 131 (19), 128 (14), 116 (10), 115 (17), 57 (100); exact mass calculate for $C_{16}H_{20}O_3$ ($M^+$): 260.1412; found 260.1419.

**Spectroscopic data for 3n**

TLC $R_f$ = 0.72 (Hexane/EtOAc = 10:1); pale yellow solid; mp 114-116 °C. Spectroscopic data for **3n**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.8 Hz, 1 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.57 (s, 1 H), 7.53 (d, *J* = 2.4 Hz, 1 H), 7.29-7.27 (m, 1 H), 7.23 (dd, *J* = 8.8, 2.4 Hz, 1 H), 2.50 (s, 3 H), 1.58 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.0 (C), 148.8 (C), 136.3 (C), 134.0 (C), 129.6 (C), 129.0 (CH), 128.0 (CH), 127.5 (CH), 126.7 (CH), 119.9 (CH), 117.5 (CH), 83.5 (C), 27.7 (three $CH_3$), 21.7 ($CH_3$); IR (neat): 3050, 2979, 2925, 1752, 1637, 1510, 1454, 1368, 1280, 1261, 1242, 1206, 1148, 1045, 959, 911, 887, 864, 839, 810, 781, 748 $cm^{-1}$; MS (*m/z*, relative intensity): 258 ($M^+$, 16), 159 (11), 158 (100), 157 (31), 128 (11), 57 (30); exact mass calculate for $C_{16}H_{18}O_3$ ($M^+$): 258.1256; found 258.1263.

**Spectroscopic data for 4n**

TLC $R_f$ = 0.38 (Hexane/EtOAc = 5:1); pale yellow solid; mp 152-154 °C. Spectroscopic data for **4n**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.44 (d, *J* = 9.6 Hz, 1 H), 7.95 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.39-7.34 (m, 2 H), 6.52 (d, *J* = 9.6 Hz, 1 H), 2.59 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 154.0 (C), 139.1 (CH), 138.4 (C), 132.8 (CH), 129.1 (C), 128.7 (CH), 128.4 (C), 128.1 (CH), 120.6 (CH), 116.0 (CH), 115.2 (CH), 112.4 (C), 22.1 ($CH_3$); IR (neat): 3071, 3045, 2911, 2851, 1720, 1632, 1566, 1509, 1446, 1323, 1208, 1171, 1115, 903, 832, 775 $cm^{-1}$; MS (*m/z*, relative intensity): 210 ($M^+$, 100), 195 (31), 183 (13), 182 (89), 181 (29), 153 (24), 152 (33), 151 (13), 77 (10), 76 (20); exact mass calculate for $C_{14}H_{10}O_2$ ($M^+$): 210.0681; found 210.0688.

**Spectroscopic data for 2o**

TLC $R_f$ = 0.67 (Hexane/EtOAc = 10:1); colorless liquid. Spectroscopic data for **2o**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.88 (s, 2 H), 6.46 (s, 1 H), 2.91 (t, *J* = 8.4 Hz, 2 H), 2.53 (t, *J* = 8.4 Hz, 2 H), 2.24 (s, 3 H), 2.23 (s, 3 H), 1.54 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.3 (C), 132.2 (C), 131.4 (C), 131.3 (C), 131.1 (C), 128.5 (CH), 127.8 (CH), 111.4 (CH), 83.2 (C), 27.7 (three $CH_3$), 25.4 ($CH_2$), 25.3 ($CH_2$), 19.5 ($CH_3$), 19.0 ($CH_3$); IR (neat): 3010, 2978, 2938, 1752, 1668, 1482, 1461, 1369, 1270, 1249, 1138, 1049, 872, 860, 804, 784, 694 $cm^{-1}$; MS (*m/z*, relative intensity): 274 ($M^+$, 50), 175 (11), 174 (100), 159 (11), 157 (17), 57 (67); exact mass calculate for $C_{17}H_{22}O_3$ ($M^+$): 274.1569; found 274.1576.

**Spectroscopic data for 3o**

TLC $R_f$ = 0.67 (Hexane/EtOAc = 10:1); colorless liquid. Spectroscopic data for **3o**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, *J* = 9.2 Hz, 1 H), 7.75 (d, *J* = 2.4 Hz, 1 H), 7.36 (dd, *J* = 9.2, 2.4 Hz, 1 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.17 (d, *J* = 7.2 Hz, 1 H), 2.65 (s, 3 H), 2.62 (s, 3 H), 1.59 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.1 (C), 148.5 (C), 133.4 (C), 132.3 (C), 132.2 (C), 130.7 (C), 127.0 (CH), 126.2 (CH), 126.1 (CH), 120.1 (CH), 115.3 (CH), 83.5 (C), 27.8 (three $CH_3$), 19.4 ($CH_3$), 19.3 ($CH_3$); IR (neat): 2978, 2927, 1752, 1667, 1482, 1459, 1369, 1288, 1270, 1250, 1162, 1138, 872, 804 $cm^{-1}$; MS (*m/z*, relative intensity): 272 ($M^+$, 100), 173 (11), 172 (100), 157 (22), 128 (10), 57 (29); exact mass calculate for $C_{17}H_{20}O_3$ ($M^+$): 272.1412; found 272.1417.

**Spectroscopic data for 4o**

TLC $R_f$ = 0.28 (Hexane/EtOAc = 5:1); white solid; mp 180-182 °C. Spectroscopic data for **4o**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.92 (d, *J* = 10.0 Hz, 1 H), 8.21 (d, *J* = 9.2 Hz, 1 H), 7.49 (d, *J* = 9.2 Hz, 1 H), 7.37 (d, *J* = 7.2 Hz, 1 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 6.47 (d, *J* = 10.0 Hz, 1 H), 2.94 (s, 3 H), 2.71 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.4 (C), 155.4 (C), 143.0 (CH), 134.0 (C), 132.4 (CH), 131.6 (C), 130.7 (C), 130.2 (CH), 129.6 (C), 126.8 (CH), 116.7 (CH), 114.8 (C), 113.6 (CH), 26.6 ($CH_3$), 20.1 ($CH_3$); IR (neat): 2965, 2926, 1709, 1614, 1558, 1518, 1449, 1376,

1326, 1229, 1179, 1115, 1027, 993, 911, 831, 785 $cm^{-1}$; MS (*m/z*, relative intensity): 224 ($M^+$, 100), 209 (25), 196 (79), 195 (23), 182 (15), 181 (56), 165 (40), 153 (20), 152 (72), 139 (14), 115 (15), 76 (11); exact mass calculate for $C_{15}H_{12}O_2$ ($M^+$): 224.0837; found 224.0832.

**Spectroscopic data for 2p**

TLC $R_f$ = 0.70 (Hexane/EtOAc = 10:1); white solid; mp 62-64 °C. Spectroscopic data for **2p**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.26-7.24 (m, 2 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.26 (s, 1 H), 2.96 (t, *J* = 8.0 Hz, 2 H), 2.55-2.50 (m, 2 H), 1.53 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.1 (C), 150.9 (C), 135.2 (C), 132.2 (C), 130.2 (CH), 129.5 (CH), 127.6 (CH), 120.0 (C), 113.4 (CH), 83.5 (C), 28.4 ($CH_2$), 27.7 (three $CH_3$), 25.8 ($CH_2$); IR (neat): 2980, 2937, 1753, 1665, 1590, 1479, 1370, 1283, 1271, 1255, 1235, 1163, 1135, 859, 813, 782 $cm^{-1}$; MS (*m/z*, relative intensity): 324 ($M^+$, 11), 226 (9), 224 (9), 116 (12), 115 (15), 57 (46); exact mass calculate for $C_{15}H_{17}BrO_3$ ($M^+$): 324.0361; found 324.0369.

**Spectroscopic data for 3p**

TLC $R_f$ = 0.79 (Hexane/EtOAc = 10:1); white solid; mp 120-122 °C. Spectroscopic data for **3p**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 2.0 Hz, 1 H), 7.74 (d, *J* = 8.8 Hz, 1 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.61 (d, *J* = 2.4 Hz, 1 H), 7.54 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.33 (dd, *J* = 8.8, 2.4 Hz, 1 H), 1.55 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.8 (C), 148.9 (C), 132.3 (C), 132.1 (C), 129.9 (CH), 129.7 (CH), 129.3 (CH), 128.4 (CH), 122.0 (CH), 119.6 (C), 118.2 (CH), 83.8 (C), 27.7 (three $CH_3$); IR (neat): 3013, 2978, 2938, 1749, 1589, 1499, 1456, 1391, 1371, 1330, 1279, 1264, 1240, 1200, 1164, 1058, 1046, 1015, 964, 915, 883, 861, 810, 779, 741 $cm^{-1}$; MS (*m/z*, relative intensity): 322 ($M^+$, 65), 224 (98), 222 (100), 195 (21), 193 (21), 143 (15), 126 (25), 115 (25), 114 (30), 113 (15), 88 (10), 57 (90); exact mass calculate for $C_{15}H_{15}BrO_3$ ($M^+$): 322.0205; found 322.0202.

**Spectroscopic data for 4p**

TLC $R_f$ = 0.31 (Hexane/EtOAc = 5:1); pale orange solid; mp 198-200 °C. Spectroscopic data for **4p**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.43 (d, *J* = 9.6 Hz, 1 H), 8.11 (s, 1 H), 8.08-8.07 (m, 1 H), 7.90 (d, *J* = 9.2 Hz, 1 H), 7.76 (dd, *J* = 9.2, 1.6 Hz, 1 H), 7.50 (d, *J* = 9.2 Hz, 1 H), 6.60 (d, *J* = 9.6 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.4 (C), 153.8 (C), 138.6 (CH), 131.9 (CH), 131.5 (CH), 131.4 (C), 131.0 (CH), 127.6 (C), 123.1 (CH), 120.0 (C), 118.3 (CH), 116.3 (CH), 113.1 (C); IR (neat): 2920, 2852, 1727, 1563, 1500, 1327, 1188, 1111, 989, 875, 805 $cm^{-1}$; MS (*m/z*, relative intensity): 276 ($M^+$+3, 34), 274 ($M^+$+1, 34), 273 ($M^+$, 54), 248 (49), 246 (50), 195 (11), 167 (18), 140 (12), 139 (100), 138 (21), 137 (13), 113 (13), 87 (14), 69 (10), 63 (15); exact mass calculate for $C_{13}H_7BrO_2$ ($M^+$): 273.9629; found 273.9625.

**Spectroscopic data for 2q**

TLC $R_f$ = 0.50 (Hexane/EtOAc = 10:1); brown solid; mp 161-163 °C. Spectroscopic data for **2q**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 9.2 Hz, 1 H), 8.12 (d, *J* = 2.0 Hz, 1 H), 8.10 (d, *J* = 2.0 Hz, 1 H), 8.05 (d, *J* = 9.2 Hz, 1 H), 7.97-7.92 (m, 3 H), 7.83 (s, 1 H), 6.69 (s, 1H), 3.69 (t, *J* = 8.4 Hz, 2 H), 2.81 (t, *J* = 8.4 Hz, 2 H), 1.58 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 151.4 (C), 151.1 (C), 131.3 (C), 131.2 (C), 130.6 (C), 130.0 (C), 128.0 (C), 127.7 (CH), 127.3 (CH), 127.0 (C), 126.9 (CH), 125.6 (CH), 125.1 (CH), 124.9 (C), 124.8 (CH), 124.3 (C), 123.4 (CH), 123.0 (CH), 115.0 (CH), 83.5 (C), 27.7 (three $CH_3$), 26.0 ($CH_2$), 24.8 ($CH_2$); IR (neat): 3040, 2979, 2930, 1752, 1673, 1600, 1439, 1394, 1370, 1277, 1252, 1223, 1145, 1132, 1069, 890, 841, 824, 705 $cm^{-1}$; MS (*m/z*, relative intensity): 370 ($M^+$, 100), 271 (22), 270 (100), 269 (15), 253 (11), 241 (27), 240 (20), 239 (48), 228 (30), 227 (15), 226 (26), 57 (43); exact mass calculate for $C_{25}H_{22}O_3$ ($M^+$): 370.1569; found 370.1576.

**Spectroscopic data for 3q**

TLC $R_f$ = 0.50 (Hexane/EtOAc = 10:1); brown solid; mp 178-180 °C. Spectroscopic data for **3q**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.01 (d, *J* = 9.2 Hz, 1 H), 8.95 (d, *J* = 9.2 Hz, 1 H), 8.42 (s, 1 H), 8.29 (d, *J* = 9.2 Hz, 1 H), 8.21 (d, *J* = 7.6 Hz, 1 H), 8.09-8.05 (m, 2 H), 7.98-7.94 (m, 2 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.64 (dd, *J* = 9.2, 2.4 Hz, 1 H), 1.64 (s, 9 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 152.0 (C), 149.0 (C), 131.8 (C), 131.4 (C), 131.2 (C), 130.5 (C), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.4 (C), 126.1 (CH), 126.0 (C), 125.7 (CH), 125.2 (C), 125.1 (CH), 124.7 (CH), 124.3 (CH), 123.5 (C), 122.1 (CH), 120.7 (CH), 118.8 (CH), 83.8 (C), 27.8 (three $CH_3$); IR (neat): 3039, 2979, 2928, 1753, 1624, 1460, 1369, 1275, 1253, 1235, 1144, 894, 840, 798, 687 $cm^{-1}$; MS (*m/z*, relative intensity): 368 ($M^+$, 10), 269 (22), 268 (100), 240 (13), 239 (62), 237 (19), 57 (16); exact mass calculate for $C_{25}H_{20}O_3$ ($M^+$): 368.1412; found 368.1417.

**Spectroscopic data for 4q**

TLC $R_f$ = 0.26 (Hexane/EtOAc = 5:1); red brown solid; mp 293-295 °C. Spectroscopic data for **4q**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.08 (d, *J* = 9.6 Hz, 1 H), 8.91 (d, *J* = 9.2 Hz, 1 H), 8.73 (d, *J* = 7.6 Hz, 1 H), 8.35 (d, *J* = 9.2 Hz, 1

H), 8.29 (d, $J$ = 7.6 Hz, 1 H), 8.17 (d, $J$ = 7.6 Hz, 1 H), 8.06-7.99 (m, 3 H), 7.67 (d, $J$ = 9.2 Hz, 1 H), 6.63 (d, $J$ = 9.6 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 160.9 (C), 154.0 (C), 139.5 (CH), 131.4 (C), 131.1 (C), 131.0 (C), 129.2 (CH), 128.7 (CH), 127.97 (CH), 127.86 (C), 127.7 (CH), 127.0 (C), 126.5 (CH), 126.3 (CH), 125.8 (CH), 124.7 (C), 124.4 (C), 123.0 (C), 121.7 (CH), 117.4 (CH), 116.4 (CH), 115.6 (CH), 113.1 (C); IR (neat): 2920, 2849, 1717, 1619, 1559, 1443, 1297, 1261, 1182, 1110, 862, 835, 792 cm$^{-1}$; MS (*m/z*, relative intensity): 320 ($M^+$, 21), 319 (10), 293 (12), 292 (50), 264 (22), 263 (87), 262 (14), 261 (31), 237 (11), 146 (12), 131 (18); exact mass calculate for $C_{23}H_{12}O_2$ ($M^+$): 320.0837; found 320.0834.

**Spectroscopic data for 5a**

TLC $R_f$ = 0.47 (Hexane/EtOAc = 5:1); pale yellow liquid. Spectroscopic data for **5a**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, $J$ = 9.6 Hz, 1 H), 7.38 (d, $J$ = 7.6 Hz, 1 H), 7.31-7.27 (m, 1 H), 7.21-7.19 (m, 2 H), 6.33 (d, $J$ = 9.6 Hz, 1 H), 3.01 (t, $J$ = 8.0 Hz, 2 H), 2.83 (t, $J$ = 8.0 Hz , 2 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 161.8 (C), 161.7 (C), 140.4 (CH), 132.9 (C), 130.0 (C), 128.3 (CH), 127.4 (CH), 127.2 (CH), 121.5 (CH), 114.0 (CH), 112.2 (C), 27.6 ($CH_2$), 26.7 ($CH_2$); IR (neat): 3060, 2922, 2850, 1733, 1632, 1547, 1493, 1451, 1369, 1304, 1210, 1144, 1100, 1074, 999, 856, 823, 766 cm$^{-1}$; MS (*m/z*, relative intensity): 198 ($M^+$, 100), 170 (56), 169 (44), 168 (12), 142 (10), 141 (46), 139 (15), 128 (15), 115 (27), 91 (11); exact mass calculate for $C_{13}H_{10}O_2$ ($M^+$): 198.0681; found 198.0685.

**Preparation of 6**

To a solution of **4i** (1.19 g, 0.495 mmol) in $CH_2Cl_2$ (9.5 mL) was added a solution of $BBr_3$ in $CH_2Cl_2$ (1 M, 4.95 mL) under $N_2$ at 0 °C. The solution was warm up to room temperature and stirred for 12 h until the completion of reaction. The solution was added to a saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with $CH_2Cl_2$. The organic solution was dried over $MgSO_4$, concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 17% EtOAc-hexane ($R_f$ = 0.33 in 50% EtOAc-hexane) to give **6** as a brown solid (0.93 g, 83% yield); mp 248-250 °C. Spectroscopic data for **6**: $^1$H NMR (acetone-$d_6$, 400 MHz): δ 8.52 (d, $J$ = 9.6 Hz, 1 H), 7.95 (d, $J$ = 8.8 Hz, 1 H), 7.74 (s, 1 H), 7.70 (s, 1 H), 7.22 (d, $J$ = 8.8 Hz, 1 H), 6.45 (d, $J$ = 9.6 Hz , 1 H), 2.39 (s, 3H); $^{13}$C NMR (acetone-$d_6$, 100 MHz): δ 159.8 (C), 156.7 (C), 153.7 (C), 139.4 (CH), 132.1 (CH), 130.0 (CH), 129.5 (C), 126.9 (C), 125.0 (C), 114.3 (CH), 113.1 (CH), 111.3 (C), 103.4 (CH), 15.4 ($CH_3$); IR (neat): 3352, 2920, 2853, 1690, 1627, 1560, 1526, 1451, 1429, 1376, 1250, 1213, 1204, 1166, 1142, 1117, 891, 848, 828, 799 cm$^{-1}$; MS (*m/z*, relative intensity): 226 ($M^+$, 100), 209 (11), 199 (13), 198 (88), 197 (25), 169 (16), 141 (18), 139 (15), 115 (18); exact mass calculate for $C_{14}H_{10}O_3$ ($M^+$): 226.0630; found 226.0621.

**Supporting Information Available**

Spectra data for the new compounds.

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