Supporting Information For

# Tandem reactions of cis-2-acyl-1-alkynyl-1-aryl cyclopropanes tuned by gold(I) and silver(I) catalysts: Efficient synthesis of pyran-fused indene cores and 2,4,6-trisubstitutedphenols

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# **1. Typical Experimental Procedures**

## 1.1 Typical experimental procedures to synthesize (Z)-2-en-4-yn-1-ols



(Z)-2-en-4-yn-1-ols **la** to **le** and **lj** were prepared through a one-pot three-component coupling which was reported by our group.<sup>1</sup>

Aldehyde (2 mmol) was added to the mixture of alkyne (4.4 mmol) and KO<sup>t</sup>Bu (3.6 mmol) in freshly distilled solvent at rt under argon atmosphere. After the reaction was stirred for 3 min, it was cooled to 0°C and neutralized with H<sub>2</sub>SO<sub>4</sub> (10% in water) to acidity. After the product formed in the first step disappeared by TLC, the organic layer was separated followed by the extraction of the aqueous layer with Et<sub>2</sub>O. The combined organic extracts were washed with a saturated solution of NaHCO<sub>3</sub> and brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by the column chromatography on silica gel (petroleum/ethyl acetate = 16/1) to furnish the expected product.



(Z)-2-en-4-yn-1-ols **If** to **Ii** were prepared by the Sonogashira coupling reaction of iodinated allylic alcohols with terminal alkynes. The iodide precursors were conveniently synthesized from the corresponding propargylic alcohols by their reaction with Red-Al (Red-Al = sodium bis(2-methoxyethoxy)aluminumhydride) followed by iodination of the organoaluminum intermediate.<sup>2</sup>

Under an argon atmosphere, to a solution of propargylic alcohols (5 mmol) in dry THF (15 ml) was added Red-Al (8 mmol, 65% w/w in toluene) at 0 $^{\circ}$ C, then the mixture was warmed to room temperature and stirred for 3 h. A solution of I<sub>2</sub> in THF (40 mmol) was added dropwise at -78 $^{\circ}$ C.Then the mixture was warmed up to room temperature and stirred for 1

h. The mixture was treated with saturated  $Na_2S_2O_3$  and extracted with ethyl acetate. The extract was washed with saturated  $Na_2S_2O_3$ , brine, dried over anhydrous  $Na_2SO_4$  and evaporated. Chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) afforded the iodide precursor.

To a solution of the iodide precursor (3 mmol) in THF (12 ml) was added alkyne (3 mmol),  $PdCl_2(PPh_3)_2$  (0.03 mmol), Cul (0.06 mmol) and  $({}^{i}Pr)_2NH$  (9 mmol) at room temperature. Then the mixture was stirred at rt for 3h. The reaction was quenched with 5M HCl solution The residue was extracted with ethyl acetate, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Chromatography on silica gel (petroleum ether/ethyl acetate = 16/1) afforded the expected product.

## 1.2 Typical experimental procedures to synthesize compounds cis-II



A 25 mL round-bottom flask that contained 3 mL of  $CH_2CI_2$  was cooled to  $-30^{\circ}C$ , and 4.3mL (2.2 equiv, 3.72 mmol) of a 15w/w% solution of diethyl zinc in hexane was added under argon atmosphere. This solution was treated with 0.61 mL (4.4 equiv, 7.44 mmol) of methylene iodide, and the reaction was stirred for 30 min at  $-30^{\circ}C$ . To this solution was added 2 mL of a methylene chloride solution that contained 577 mg (1 equiv, 1.86 mmol) 2-en-4-yn-1-ols **Ia**. The reaction mixture was allowed to stir at  $-30^{\circ}C$  for 1 day, then  $-20^{\circ}C$  for 1 day. The reaction was quenched with saturated NH<sub>4</sub>Cl solution, and the aqueous portion was extracted with Et<sub>2</sub>O:CH<sub>2</sub>Cl<sub>2</sub> = 5:1. The combined organic solutions were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated to give a crude oil, which was purified on silica gel (petroleum: ethyl acetate 16:1 to 8:1) to give **IIa** (422 mg 70%).

## 1.3 Typical experimental procedures to synthesize compounds cis-1



A solution of **IIa** (434 mg, 1.34 mmol) in dry  $CH_2CI_2$  (3 mL) was added the PCC (434 mg, 2.01 mmol) and silica gel (434 mg) mixtures at 0 °C. After stirring at room temperature for 5 hours, the reaction mixture was purified through column chromatography first on  $AI_2O_3$  (ethyl acetate) then on silica gel (petroleum: ethyl acetate 40:1) to afford **1a** (280 mg 65%).

## **1.4 Typical experimental procedures of gold(I) catalyzed reaction**

A solution of **1a** (33 mg, 0.10 mmol) in dry  $CH_2CI_2$  (1 mL) was added a solution of  $Ph_3AuOTf$  (generated by mixing equal equivalents of  $PPh_3AuCI$  and AgOTf, with AgCl filtered off) in  $CH_2CI_2$  (0.02 M, 0.5 mL, 0.01 mmol) under argon atmosphere. The mixture was stirred for 2h at room temperature. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum: ethyl acetate 100:1) to afford **2a** (28 mg 85%).

## 1.5 Typical experimental procedures of silver(I) catalyzed reaction

A solution of **1a** (33 mg, 0.10 mmol) in dry  $CH_2Cl_2$  (1 mL) was added NaHCO<sub>3</sub> (9 mg, 0.10 mmol), then AgOTf (5 mg, 0.02mmol) under argon atmosphere. The mixture was stirred for 50 min at room temperature. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum: ethyl acetate 60:1) to afford **3a** (26.5 mg, 80%).

# 2. Spectroscopic and Analytical Data of the Products

## 2.1 Spectroscopic and analytical data of the products cis-lla to cis-llj



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.52-7.60 (d, 2H, J = 7.2 Hz), 7.39-7.45 (m, 2H), 7.31-7.38 (dd, 2H, J = 7.2 Hz and 7.2 Hz), 7.20-7.31 (m, 8H), 7.14-7.20 (dd, 1H, J = 6.8 Hz and 6.8 Hz), 4.88-4.94 (d, 1H, J = 8.0 Hz), 2.24 (s, b, 1H), 1.83-1.92 (ddd, 1H, J = 8.8 Hz and 6.4 Hz), 1.71-1.77 (dd, 1H, J = 6.4 Hz and 5.2 Hz), 1.65-1.71 ppm(dd, 1H, J = 8.8 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 143.5, 141.2, 131.7, 128.5, 128.4, 128.3, 128.0, 127.6, 126.4, 126.0, 125.9, 123.2, 90.9, 82.2, 74.8, 37.6, 23.3, 22.1 ppm; **EI MS** (70 eV): m/z (%): 324 (1) [M]<sup>+</sup>, 228 (2), 122 (76), 120 (100), 91 (56), 77 (56).



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.54-7.60 (d, 2H, *J* = 7.6 Hz), 7.38-7.44 (m, 2H), 7.30-7.38 (dd, 2H, *J* = 7.6 Hz and 7.6 Hz), 7.23-7.30 (m, 4H), 7.16-7.23 (d, 2H, *J* = 8.4 Hz), 6.75-6.81 (d, 2H, *J* = 8.4 Hz), 4.84-4.90 (d, 1H, *J* = 8.4 Hz), 3.73 (s, 3H), 2.30 (s, b, 1H),

1.76-1.85 (ddd, 1H, J = 8.4 Hz, 8.4 Hz and 6.8 Hz), 1.64-1.70 (dd, 1H, J = 6.8 Hz and 5.2 Hz), 1.57-1.64 ppm(dd, 1H, J = 8.4 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta = 158.2$ , 143.6, 133.4, 131.6, 128.5, 128.2, 127.9, 127.6, 127.4, 126.0, 123.3, 113.8, 91.4, 81.7, 74.9, 55.2, 37.0, 22.8, 21.6 ppm; **EI MS** (70 eV): m/z (%): 354 (0.09) [M]<sup>+</sup>, 236 (3), 247 (35), 234 (100), 91 (48), 77 (57).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53-7.60 (d, 2H, *J* = 7.2 Hz), 7.38-7.45 (m, 2H), 7.32-7.38 (dd, 2H, *J* = 7.2 Hz and 7.2 Hz), 7.25-7.32 (m, 4H), 7.19-7.25 (dd, 2H, *J* = 7.6 Hz and 6.4 Hz), 6.90-6.99 (dd, 2H, *J* = 8.4 Hz and 8.4 Hz), 4.85-4.92 (d, 1H, *J* = 8.0 Hz), 2.27 (s, b, 1H), 1.77-1.86 (ddd, 1H, *J* = 8.4 Hz, 8.0 Hz and 6.8 Hz), 1.68-1.75 (dd, 1H, *J* = 6.8 Hz and 5.2 Hz), 1.60-1.68 ppm(dd, 1H, *J* = 8.4 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.7, 160.3, 143.5, 137.0, 137.0, 131.6, 128.5, 128.3, 128.1, 127.8, 127.7, 125.9, 123.1, 115.3, 115.1, 90.8, 82.1, 74.8, 37.4, 23.1, 21.6 ppm; **EI MS** (70 eV): m/z (%): 342 (0.34) [M]<sup>+</sup>, 251 (3), 222 (31), 120 (100), 91 (39), 77 (43).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.90-7.98 (d, 1H, *J* = 8.4 Hz), 7.75-7.80 (d, 1H, *J* = 8.0 Hz), 7.65-7.72 (m, 3H), 7.36-7.46 (m, 5H), 7.25-7.36 (m, 3H), 7.18-7.25 (m, 4H), 4.95-5.05 (d, 1H, *J* = 8.4 Hz), 2.33 (s, b, 1H), 1.87-1.95 (ddd, 1H, *J* = 8.4 Hz, 8.4 Hz and 5.2 Hz), 1.76-1.82 (dd, 1H, *J* = 5.2 Hz and 4.8 Hz), 1.66-1.73 ppm(dd, 1H, *J* = 8.4 Hz and 4.8 Hz); 1<sup>3</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 143.5, 137.5, 133.8, 132.0, 131.6, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 126.6, 126.3, 125.8, 125.6, 125.2, 125.1, 123.3, 91.9, 80.4, 75.8, 34.8, 21.5, 21.1 ppm; **EI MS** (70 eV): m/z (%): 356 (2), 270 (13), 254 (92), 120 (100), 91 (75), 77 (73).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.41-7.46 (m, 2H), 7.35-7.41 (m, 2H), 7.26-7.35 (m, 5H), 7.18-7.25 (dd, 1H, *J* = 7.6 Hz and 7.6 Hz), 3.68-3.78 (m, 1H), 1.80-1.90 (m, 2H), 1.67-1.80

(m, 1H), 1.50-1.63 (m, 3H), 1.03-1.11 ppm(t, 3H, J = 7.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta = 141.6, 131.6, 128.4, 128.3, 127.9, 126.3, 125.7, 123.3, 90.6, 81.6, 74.7, 36.3, 30.1, 23.2, 21.4, 10.0 ppm;$ **EI MS**(70 eV): m/z (%): 276 (3) [M]<sup>+</sup>, 247 (22), 217 (54), 204 (100), 189 (33), 115 (24).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.25-7.32 (m, 4H), 7.14-7.21 (m, 1H), 3.57-3.67 (m, 1H), 1.93 (s, b, 1H), 1.69-1.80 (m, 1H), 1.60-1.69 (m, 1H), 1.32-1.44 (m, 3H), 1.21-1.31 (m, 1H), 0.98-1.08 (t, 3H, J = 7.2 Hz), 0.71-0.79 (m, 2H), 0.61-0.67 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 142.3, 128.3, 126.0, 125.5, 85.1, 75.9, 74.2, 35.7, 30.0, 22.5, 20.7, 9.9, 8.3, 8.2, 0.0 ppm; **EI MS** (70 eV): m/z (%): 240 (0.36) [M]<sup>+</sup>, 211 (15), 182 (24), 167 (100), 153 (74), 115 (50).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.55-7.60 (d, 2H, *J* = 7.6 Hz), 7.39-7.45 (m, 2H), 7.33-7.39 (dd, 2H, *J* = 7.6 Hz and 7.6 Hz), 7.26-7.33 (m, 4H), 7.05-7.10 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz), 6.85-6.90 (d, 2H, *J* = 3.2 Hz), 4.83-4.90 (d, 1H, *J* = 7.6 Hz), 2.24 (s, b, 1H), 1.91-2.00 (ddd, 1H, *J* = 8.8 Hz, 7.6 Hz and 6.8 Hz), 1.79-1.85 (dd, 1H, *J* = 6.8 Hz and 5.2 Hz), 1.66-1.74 ppm(dd, 1H, *J* = 8.8 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 146.9, 143.2, 131.7, 128.5, 128.3, 128.2, 127.7, 126.8, 126.0, 123.2, 123.0, 122.9, 90.0, 81.9, 74.4, 39.0, 25.2, 19.0 ppm; **EI MS** (70 eV): m/z (%): 255 (11), 223 (14), 192 (18), 84 (65), 64 (95), 41 (100).

#### 2.2 Spectroscopic and analytical data of the products cis-1a to cis-1j



Following the typical experimental procedures **1a** was prepared in 52% yield over two steps from (Z)-2-en-4-yn-1-ol **Ia**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92-8.00 (d, 2H, *J* = 7.6 Hz), 7.50-7.58 (m, 3H), 7.38-7.48 (m, 4H), 7.25-7.35 (m, 3H), 7.16-7.24 (m, 3H), 3.14-3.22 (dd, 1H, *J* = 7.6 Hz and 7.2 Hz), 2.47-2.54 (dd, 1H, *J* = 7.2 Hz and 5.2 Hz), 1.92-2.00 ppm(dd, 1H, *J* = 7.6 Hz and 5.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 193.7, 140.2, 137.9, 132.9, 131.8, 128.8, 128.6, 128.3, 128.0, 127.8, 127.1, 125.8, 123.0, 88.0,

82.2, 38.3, 27.6, 22.6 ppm; **EI MS** (70 eV): m/z (%): 322 (19)  $[M]^+$ , 217 (20), 189 (26), 105 (78), 77 (100), 51 (39); **HRMS** (ESI): m/z calcd for C<sub>24</sub>H<sub>18</sub>O  $[M+H]^+$ : 323.1430; found: 323.1423.



Following the typical experimental procedures **1b** was prepared in 50% yield over two steps from (*Z*)-2-en-4-yn-1-ol **Ib**. <sup>1</sup>**H NMR** (400 MHz, Acetone-d6):  $\delta = 7.98-8.05$  (d, 2H, J = 7.6 Hz), 7.58-7.65 (m, 1H), 7.49-7.57 (m, 4H), 7.25-7.30 (m, 5H), 6.97-7.02 (dd, 2H, J = 6.8 Hz and 2.0 Hz), 3.83 (s, 3H), 3.37-3.43 (dd, 1H, J = 7.6 Hz and 7.2 Hz), 2.32-2.37 (dd, 1H, J = 7.2 Hz and 4.8 Hz), 1.98-2.03 ppm(dd, 1H, J = 7.6 Hz and 4.8 Hz); <sup>13</sup>**C NMR** (100 MHz, Acetone-d6):  $\delta = 194.0$ , 160.0, 139.0, 133.9, 133.0, 132.4, 129.6, 129.2, 129.0, 128.9, 128.1, 124.2, 115.0, 90.0, 82.3, 55.7, 38.6, 27.6, 22.8 ppm; **EI MS** (70 eV): m/z (%): 352 (1) [M]<sup>+</sup>, 247 (4), 236 (75), 208 (78), 129 (100), 77 (55). **HRMS** (APCI): m/z calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 353.1536; found: 353.1539.



Following the typical experimental procedures **1c** was prepared in 45% yield over two steps from (*Z*)-2-en-4-yn-1-ol **Ic**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.15-8.20 (d, 2H, *J* = 8.0 Hz), 7.52-7.60 (dd, 1H, *J* = 7.2 Hz and 7.2 Hz), 7.40-7.52 (m, 3H), 7.20-7.32 (m, 3H), 7.12-7.18 (m, 3H), 6.90-7.00 (m, 2H), 3.80 (s, 3H), 3.16-3.22 (dd, 1H, *J* = 7.6 Hz and 6.4 Hz), 2.36-2.43 (dd, 1H, *J* = 6.4 Hz and 4.8 Hz), 1.80-2.87 ppm(dd, 1H, *J* = 7.6 Hz and 4.8 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 194.8, 158.3, 138.5, 132.5, 131.8, 129.9, 129.3, 129.0, 128.5, 128.3, 127.8, 127.4, 123.7, 120.6, 111.3, 89.4, 79.6, 55.2, 34.2, 26.1, 21.7 ppm; **EI MS** (70 eV): m/z (%): 352 (6) [M]<sup>+</sup>, 247 (28), 135 (46), 105 (100), 77 (64), 51 (24); **HRMS** (ESI): m/z calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 353.1536; found: 353.1534.



Following the typical experimental procedures **1d** was prepared in 53% yield over two steps from (Z)-2-en-4-yn-1-ol **Id**. <sup>1</sup>**H NMR** (400 MHz,  $CDCI_3$ ):  $\delta$  = 7.92-8.00 (d, 2H, *J* =

7.2 Hz), 7.46-7.56 (m, 3H), 7.40-7.46 (m, 2H), 7.23-7.30 (m, 2H), 7.15-7.23 (m, 3H), 7.04-7.12 (dd, 2H, J = 8.4 Hz and 8.4 Hz), 3.09-3.15 (dd, 1H, J = 8.0 Hz and 6.8 Hz), 2.47-2.54 (dd, 1H, J = 6.8 Hz and 5.2 Hz), 1.88-1.94 ppm(dd, 1H, J = 8.0 Hz and 5.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 193.4, 163.1, 160.7, 137.7, 136.0, 135.9, 132.9, 131.7, 128.6, 128.2, 128.0, 127.9, 127.6, 127.5, 122.8, 115.7, 115.5, 87.8, 82.3, 38.1, 27.0, 22.5 ppm; EI MS (70 eV): m/z (%): 340 (6) [M]<sup>+</sup>, 233 (9), 207 (13), 105 (100), 77 (32), 51 (11); HRMS (ESI): m/z calcd for C<sub>24</sub>H<sub>17</sub>FO [M+H]<sup>+</sup>: 341.1336; found: 341.1336.



Following the typical experimental procedures **1e** was prepared in 50% yield over two steps from (Z)-2-en-4-yn-1-ol **Ie**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.35-8.44 (d, 1H, *J* = 8.0 Hz), 8.05-8.14 (d, 2H, *J* = 8.0 Hz), 7.81-7.88 (d, 1H, *J* = 8.0 Hz), 7.76-7.81 (d, 1H, *J* = 8.0 Hz), 7.52-7.61 (m, 2H), 7.35-7.52 (m, 6H), 7.20-7.25 (m, 2H), 7.05-7.13 (m, 2H), 3.28-3.34 (m, 1H), 2.54-2.62 (m, 1H), 1.90-2.00 ppm(m, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 194.1, 138.0, 137.0, 134.0, 133.0, 131.9, 131.7, 128.6, 128.6, 128.5, 128.5, 127.9, 127.6, 126.2, 126.0, 125.7, 125.4, 125.3, 123.2, 89.1, 81.6, 34.0, 28.2, 22.4 ppm; **EI MS** (70 eV): m/z (%): 372 (6) [M]<sup>+</sup>, 267 (0.2), 239 (13), 105 (100), 77 (64), 51 (19); **HRMS** (ESI): m/z calcd for C<sub>28</sub>H<sub>20</sub>O [M+H]<sup>+</sup>: 373.1587; found: 373.1580.



Following the typical experimental procedures **1f** was prepared in 27% yield over two steps from (Z)-2-en-4-yn-1-ol **If**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.87-7.92$  (d, 2H, J = 8.4 Hz), 7.50-7.56 (d, 2H, J = 7.2 Hz), 7.38-7.46 (m, 4H), 7.30-7.36 (dd, 1H, J = 7.2 Hz and 7.2 Hz), 7.18-7.23 (d, 2H, J = 8.8 Hz), 6.72-6.78 (d, 2H, J = 8.8 Hz), 3.76 (s, 3H), 3.08-3.14 (dd, 1H, J = 7.6 Hz and 6.8 Hz), 2.46-2.54 (dd, 1H, J = 6.8 Hz and 5.2 Hz), 1.94-2.00 ppm(dd, 1H, J = 7.6 Hz and 5.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 192.7$ , 159.4, 140.2, 139.3, 136.2, 133.2, 129.7, 128.9, 128.8, 127.2, 125.7, 115.0, 113.7, 86.1, 82.2, 55.2, 38.3, 27.7, 22.6 ppm; **EI MS** (70 eV): m/z (%): 386 (7) [M]<sup>+</sup>, 254 (12), 247 (73), 139 (100), 111 (77), 75 (36); **HRMS** (ESI): m/z calcd for C<sub>25</sub>H<sub>19</sub>ClO<sub>2</sub> [M+H]<sup>+</sup>: 387.1146; found: 387.1145.



Following the typical experimental procedures **1g** was prepared in 17% yield over two steps from (Z)-2-en-4-yn-1-ol **Ig**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.67-7.73 (d, 1H, *J* = 3.2 Hz), 7.58-7.65 (d, 1H, *J* = 4.8 Hz), 7.48-7.55 (d, 2H, *J* = 7.6 Hz), 7.36-7.43 (m, 2H), 7.26-7.36 (m, 3H), 7.18-7.26 (m, 3H), 7.08-7.14 (dd, 1H, *J* = 4.4 Hz and 4.4 Hz), 3.06-3.14 (dd, 1H, *J* = 7.6 Hz and 6.8 Hz), 2.43-2.50 (dd, 1H, *J* = 6.8 Hz and 5.2 Hz), 1.92-1.98 ppm(dd, 1H, *J* = 7.6 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 186.0, 145.1, 140.2, 133.4, 131.9, 131.8, 128.7, 128.1, 128.0, 127.8, 127.1, 126.0, 123.0, 88.0, 82.3, 38.4, 27.7, 22.3 ppm; **EI MS** (70 eV): m/z (%): 328 (10) [M]<sup>+</sup>, 226 (7), 215 (18), 202 (15), 189 (19), 111 (100); **HRMS** (ESI): m/z calcd for C<sub>22</sub>H<sub>16</sub>OS [M+H]<sup>+</sup>: 329.0995; found: 329.0991.



Following the typical experimental procedures **1h** was prepared in 61% yield over two steps from (*Z*)-2-en-4-yn-1-ol **Ih**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.46-7.51$  (m, 2H), 7.41-7.46 (m, 2H), 7.35-7.41 (m, 2H), 7.26-7.32 (m, 4H), 2.63-2.71 (q, 2H, *J* = 7.2 Hz), 2.57-2.63 (dd, 1H, *J* = 8.0 Hz and 7.2 Hz), 2.27-2.32 (dd, 1H, *J* = 7.2 Hz and 5.2 Hz), 1.77-1.83 (dd, 1H, *J* = 8.0 Hz and 5.2 Hz), 1.15-1.20 ppm(t, 3H, *J* = 7.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta = 204.1$ , 140.4, 131.7, 128.6, 128.1, 127.9, 127.0, 125.9, 123.1, 88.2, 82.0, 40.2, 37.2, 26.8, 22.5, 7.9 ppm; **EI MS** (70 eV): m/z (%): 274 (12) [M]<sup>+</sup>, 245 (12), 217 (100), 202 (58), 189 (34), 57 (68); **HRMS** (ESI): m/z calcd for C<sub>20</sub>H<sub>18</sub>O [M+H]<sup>+</sup>: 275.1430; found: 275.1438.



Following the typical experimental procedures **1i** was prepared in 64% yield over two steps from (*Z*)-2-en-4-yn-1-ol **Ii**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34-7.39 (m, 2H), 7.29-7.39 (m, 2H), 7.20-7.26 (m, 1H), 2.53-2.61 (q, 2H, *J* = 7.2 Hz), 2.37-2.44 (dd, 1H, *J* = 7.6 Hz and 7.6 Hz), 2.05-2.10 (dd, 1H, *J* = 7.6 Hz and 5.2 Hz), 1.58-1.64 (dd, 1H, *J* = 7.6 Hz and 5.2 Hz), 1.18-1.26 (m, 1H), 1.09-1.15 (t, 3H, *J* = 7.2 Hz), 0.70-0.75 (m, 2H), 0.60-0.66 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 204.4, 141.1, 128.4, 126.7, 125.8, 85.6, 73.5, 39.9, 37.1, 26.4, 22.3, 8.4, 8.3, 7.8, 0.0 ppm; **EI MS** (70 eV): m/z (%):

238 (11)  $[M]^+$ , 237 (12), 209 (22), 181 (78), 165 (89), 57 (100); **HRMS** (ESI): m/z calcd for C<sub>17</sub>H<sub>18</sub>O  $[M+H]^+$ : 239.1430; found: 239.1434.



Following the typical experimental procedures **1j** was prepared in 54% yield over two steps from (Z)-2-en-4-yn-1-ol **ij**. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.98-8.03 (d, 2H, *J* = 7.6 Hz), 7.54-7.60 (m, 1H), 7.44-7.52 (m, 3H), 7.30-7.35 (m, 2H), 7.24-7.30 (m, 3H), 7.17-7.24 (m, 1H), 7.11-7.15 (m, 1H), 3.23-3.30 (dd, 1H, *J* = 7.6 Hz and 7.6 Hz), 2.54-2.60 (dd, 1H, *J* = 7.6 Hz and 5.2 Hz), 1.91-1.97 ppm(dd, 1H, *J* = 7.6 Hz and 5.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 193.2, 146.0, 137.7, 133.0, 131.8, 128.6, 128.4, 128.3, 128.0, 127.2, 123.9, 123.8, 122.7, 87.4, 81.7, 39.7, 24.6, 24.5 ppm; **EI MS** (70 eV): m/z (%): 328 (2) [M]<sup>+</sup>, 255 (21), 223 (8), 192 (12), 160 (30), 43 (100); **HRMS** (ESI): m/z calcd for C<sub>22</sub>H<sub>16</sub>OS [M+H]<sup>+</sup>: 329.0995; found: 329.0989.

## 2.3 Spectroscopic and analytical data of the products 2a to 2i, 4a, 4i



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.48-7.55 (m, 2H), 7.22-7.36 (m, 9H), 7.17-7.22 (d, 1H, J = 7.2 Hz), 7.13-7.17 (d, 1H, J = 7.2 Hz), 7.08-7.13 (dd, 1H, J = 7.2 Hz and 7.2 Hz), 5.57-5.63 (dd, 1H, J = 3.2 Hz and 3.2 Hz), 4.66 (s, 1H), 3.33-3.39 ppm(dd, 2H, J = 5.6 Hz and 3.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.6, 149.9, 142.7, 141.7, 137.8, 134.3, 128.7, 128.3, 128.2, 128.1, 127.1, 127.0, 124.5, 124.1, 123.5, 117.7, 110.9, 97.3, 52.8, 20.2 ppm; **EI MS** (70 eV): m/z (%): 322 (18) [M]<sup>+</sup>, 217 (14), 191 (18), 149 (70), 105 (100), 77 (49); **HRMS** (APCI): m/z calcd for C<sub>24</sub>H<sub>18</sub>O [M+H]<sup>+</sup>: 323.1430; found: 323.1431.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47-7.52 (d, 2H, *J* = 6.4 Hz), 7.20-7.34 (m, 8H), 7.00-7.05 (d, 1H, *J* = 8.8 Hz), 6.78-6.83 (m, 2H), 5.53-5.58 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz),

4.62 (s, 1H), 3.75 (s, 3H), 3.30-3.35 ppm(dd, 2H, J = 5.6 Hz and 3.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta = 157.5$ , 155.7, 149.8, 143.4, 138.0, 135.5, 134.4, 128.7, 128.2, 128.1, 127.0, 124.5, 117.9, 111.7, 111.3, 110.5, 97.1, 55.6, 52.8, 20.3 ppm; **EI MS** (70 eV): m/z (%): 352 (27) [M]<sup>+</sup>, 247 (17), 222 (11), 179 (18), 149 (50), 105 (100); **HRMS** (APCI): m/z calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 353.1536; found: 353.1542.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.46-7.50 (d, 2H, *J* = 7.2 Hz), 7.20-7.33 (m, 8H), 6.98-7.04 (dd, 1H, *J* = 8.4 Hz and 7.2 Hz), 6.76-6.83 (dd, 2H, *J* = 8.4 Hz and 7.2 Hz), 5.48-5.55 (dd, 1H, *J* = 3.6 Hz and 3.6 Hz), 4.56 (s, 1H), 3.83 (s, 3H), 3.59-3.63 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 155.9, 153.5, 149.3, 143.3, 138.0, 134.4, 130.5, 128.7, 128.2, 128.1, 127.0, 125.0, 124.4, 116.8, 110.5, 110.0, 98.2, 55.6, 53.1, 20.8 ppm; **EI MS** (70 eV): m/z (%): 352 (17) [M]<sup>+</sup>, 247 (17), 207 (26), 133 (24), 105 (100), 77 (38); **HRMS** (APCI): m/z calcd for  $C_{25}H_{20}O_2$  [M+H]<sup>+</sup>: 353.1536; found: 353.1540.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46-7.51 (m, 2H), 7.25-7.35 (m, 4H), 7.18-7.25 (m, 4H), 7.00-7.05 (m, 1H), 6.95-7.00 (m, 1H), 6.88-6.95 (m, 1H), 5.53-5.58 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz), 4.61 (s, 1H), 3.29-3.34 ppm(dd, 2H, *J* = 6.0 Hz and 3.2 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.1, 159.7, 156.9, 156.8, 149.8, 143.7, 143.6, 138.4, 138.4, 137.2, 134.2, 128.8, 128.3, 128.2, 128.1, 127.3, 124.5, 118.1, 118.0, 113.6, 113.4, 112.0, 111.7, 110.4, 97.1, 52.9, 52.8, 20.2 ppm; **EI MS** (70 eV): m/z (%): 340 (40) [M]<sup>+</sup>, 233 (16), 209 (37), 133 (23), 105 (100), 77 (72); **HRMS** (APCI): m/z calcd for C<sub>24</sub>H<sub>17</sub>FO [M+H]<sup>+</sup>: 341.1336; found: 341.1340.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 8.25-8.30 (d, 1H, *J* = 7.6 Hz), 7.80-7.88 (d, 1H, *J* = 8.0 Hz), 7.58-7.63 (d, 1H, *J* = 7.6 Hz), 7.49-7.58 (m, 3H), 7.39-7.49 (m, 3H), 7.20-7.39 (m, 7H), 5.59-5.64 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz), 4.70 (s, 1H), 4.00-4.06 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 158.7, 149.4, 138.4, 138.3, 137.3, 134.1, 133.7, 128.9, 128.7, 128.6, 128.3, 128.2, 127.1, 126.7, 125.3, 125.0, 124.5, 124.2, 123.8, 122.0, 111.6, 97.3, 53.3, 24.3 ppm; **EI MS** (70 eV): m/z (%): 372 (9) [M]<sup>+</sup>, 241 (15), 180 (15), 165 (20), 105 (100), 77 (73); **HRMS** (APCI): m/z calcd for  $C_{28}H_{20}O$  [M+H]<sup>+</sup>: 373.1587; found: 373.1586.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40-7.46 (d, 2H, *J* = 8.4 Hz), 7.23-7.30 (m, 2H), 7.08-7.20 (m, 6H), 6.82-6.88 (d, 2H, *J* = 8.4 Hz), 5.53-5.58 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz), 4.59 (s, 1H), 3.78 (s, 3H), 3.27-3.35 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.7, 157.6, 149.0, 142.5, 141.9, 134.0, 132.8, 129.5, 129.1, 128.4, 127.1, 125.8, 124.2, 123.5, 117.7, 114.1, 110.6, 97.8, 55.2, 52.0, 20.1 ppm; **EI MS** (70 eV): m/z (%): 386 (29) [M]<sup>+</sup>, 276 (4), 247 (100), 178 (56), 136 (66); **HRMS** (APCI): m/z calcd for C<sub>25</sub>H<sub>19</sub>ClO<sub>2</sub> [M+H]<sup>+</sup>: 387.1146; found: 387.1150.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.28-7.35 (m, 3H), 7.19-7.28 (m, 3H), 7.08-7.19 (m, 5H), 6.91-6.97 (dd, 1H, *J* = 4.0 Hz and 4.0 Hz), 5.42-5.52 (dd, 1H, *J* = 3.2 Hz and 3.2 Hz), 4.64 (s, 1H), 3.26-3.37 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 157.2, 145.8, 142.6, 141.5, 137.9, 137.6, 128.6, 128.1, 127.2, 127.1, 127.1, 124.6, 124.2, 123.6, 123.4, 117.7, 110.9, 96.7, 52.6, 20.0 ppm; **EI MS** (70 eV): m/z (%): 328 (81) [M]<sup>+</sup>, 217 (31), 191 (69), 165 (21), 111 (100); **HRMS** (APCI): m/z calcd for C<sub>22</sub>H<sub>16</sub>OS [M+H]<sup>+</sup>: 329.0995; found: 329.0993.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.20-7.31 (m, 4H), 7.14-7.20 (m, 2H), 7.10-7.14 (m, 1H), 7.01-7.09 (m, 2H), 4.74-4.80 (m, 1H), 4.51 (s, 1H), 3.11-3.19 (m, 2H), 2.07-2.15 (q, 2H, *J* = 7.6 Hz), 0.99-1.05 ppm(t, 3H, *J* = 7.6 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.6, 154.0, 142.9, 141.7, 138.0, 128.6, 128.1, 127.0, 126.9, 123.8, 123.3, 117.4, 111.1, 94.7, 52.6, 26.3, 19.7, 11.3 ppm; **EI MS** (70 eV): m/z (%): 274 (69) [M]<sup>+</sup>, 217 (100), 202 (31), 189 (21), 57 (87); **HRMS** (APCI): m/z calcd for C<sub>20</sub>H<sub>18</sub>O [M+H]<sup>+</sup>: 275.1430; found: 275.1428.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.77-7.82 (d, 2H, *J* = 8.0 Hz), 7.64-7.70 (d, 2H, *J* = 7.2 Hz), 7.55-7.60 (d, 1H, *J* = 7.6 Hz), 7.47-7.55 (dd, 2H, *J* = 7.6 Hz and 7.6 Hz), 7.42-7.47 (d, 1H, *J* = 7.6 Hz), 7.28-7.42 (m, 4H), 7.18-7.24 (dd, 1H, *J* = 7.6 Hz and 7.6 Hz), 5.62-5.68 (dd, 1H, *J* = 6.8 Hz and 2.4 Hz), 3.47-3.55 (dd, 1H, *J* = 12.8 Hz and 8.0 Hz), 2.97-3.08 (ddd, 1H, *J* = 16.8 Hz, 8.0 Hz and 6.8 Hz), 2.18-2.28 ppm(ddd, 1H, *J* = 16.8 Hz, 12.8 Hz and 2.4 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 156.3, 150.9, 143.2, 140.4, 134.1, 132.8, 128.6, 128.5, 128.4, 128.4, 127.2, 126.9, 124.6, 123.7, 122.9, 119.5, 116.8, 95.8, 39.6, 23.8 ppm; **EI MS** (70 eV): m/z (%): 322 (27) [M]<sup>+</sup>, 217 (13), 178 (17), 115 (25), 105 (100), 77 (45).



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.20-7.45 (m, 7H), 7.06-7.18 (m, 2H), 6.98-7.06 (d, 1H, J = 7.6 Hz), 4.72-4.77 (m, 1H), 4.66-4.72 (m, 1H), 3.10-3.19 (dd, 1H, J = 12.4 Hz and 8.0 Hz), 3.03-3.10 (m, 2H), 2.78-2.83 (d, 1H, J = 8.4 Hz), 2.60-2.70 (m, 1H), 2.13-2.35 (m, 5H), 1.80-1.90 (m, 1H), 1.58-1.68 (m, 1H), 1.10-1.20 (m, 6H), 0.80-1.00 (m, 4H), 0.48-0.65 ppm(m, 4H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 158.5, 155.6, 154.8, 153.7, 145.1, 142.9, 141.1, 140.3, 126.9, 126.9, 123.3, 123.0, 122.6, 122.2, 118.5, 117.1, 115.8, 109.6, 94.7,

92.8, 49.9, 39.4, 26.5, 26.4, 23.2, 19.5, 11.6, 11.6, 11.4, 5.5, 4.8, 4.7, 2.3, 2.3 ppm; **EI MS** (70 eV): m/z (%): 238 (82)  $[M]^+$ , 181 (53), 165 (24), 153 (20), 141 (29), 128 (14), 115 (26), 57 (100), 41 (64). **HRMS** (APCI): m/z calcd for C<sub>17</sub>H<sub>18</sub>O  $[M+H]^+$ : 239.1430; found: 239.1425.

#### 2.4 Spectroscopic and analytical data of the products 3a to 3j, 5i



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.60-7.65 (m, 6H), 7.52-7.56 (m, 2H), 7.48-7.52 (m, 4H), 7.39-7.46 (m, 4H), 7.30-7.36 (dd, 1H, *J* = 7.2 Hz and 7.2 Hz), 5.45 ppm(s, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.9, 140.5, 137.5, 133.8, 129.4, 129.1, 128.9, 128.8, 128.6, 127.8, 126.9, 126.8 ppm; **EI MS** (70 eV): m/z (%): 322 (100) [M]<sup>+</sup>, 215 (16), 149 (39), 129 (20), 105 (46), 57 (35); **HRMS** (ESI negative): m/z calcd for C<sub>24</sub>H<sub>18</sub>O [M-H]<sup>+</sup>: 321.1285; found: 321.1287. This known compound has been reported in reference 3.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.59-7.64 (d, 4H, *J* = 7.2 Hz), 7.53-7.58 (d, 2H, *J* = 8.8 Hz), 7.46-7.53 (m, 6H), 7.38-7.46 (dd, 2H, *J* = 7.6 Hz and 7.6 Hz), 6.95-7.00 (d, 2H, *J* = 8.4 Hz), 5.39 (s, 1H), 3.85 ppm(s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 158.9, 148.5, 137.6, 133.5, 133.2, 129.4, 129.1, 128.9, 128.2, 127.8, 127.7, 114.2, 55.4 ppm; **EI MS** (70 eV): m/z (%): 352 (21) [M]<sup>+</sup>, 236 (31), 208 (39), 193 (31), 129 (47), 41 (100); **HRMS** (ESI negative): m/z calcd for  $C_{25}H_{20}O_2$  [M-H]<sup>+</sup>: 351.1391; found: 351.1385. This known compound has been reported in reference 4.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.60-7.65 (d, 4H, J = 7.2 Hz), 7.46-7.52 (m, 6H),

7.37-7.43 (m, 3H), 7.28-7.34 (m, 1H), 6.97-7.06 (m, 2H), 5.46 (s, 1H), 3.84 ppm(s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.4, 148.5, 137.7, 131.1, 130.9, 130.7, 129.9, 129.4, 128.8, 128.4, 128.3, 127.6, 120.8, 111.1, 55.6 ppm; **EI MS** (70 eV): m/z (%): 352 (52) [M]<sup>+</sup>, 149 (100), 135 (76), 77 (51), 57 (83), 43 (75); **HRMS** (ESI negative): m/z calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> [M-H]<sup>+</sup>: 351.1391; found: 351.1384.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.60-7.65 (d, 4H, *J* = 7.6 Hz), 7.54-7.60 (m, 2H), 7.47-7.54 (m, 6H), 7.40-7.47 (m, 2H), 7.09-7.15 (dd, 2H, *J* = 8.8 Hz and 8.8 Hz), 5.45 ppm(s, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 163.4, 161.0, 148.9, 137.4, 136.7, 136.6, 132.9, 129.3, 129.2, 128.9, 128.5, 128.3, 128.2, 127.9, 115.7, 115.5 ppm; **EI MS** (70 eV): m/z (%): 340 (100) [M]<sup>+</sup>, 149 (29), 133 (39), 105 (75), 77 (62), 41 (82); **HRMS** (ESI negative): m/z calcd for C<sub>24</sub>H<sub>17</sub>FO [M-H]<sup>+</sup>: 339.1191; found: 339.1186.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 8.09-8.14 (d, 1H, *J* = 8.0 Hz), 7.90-7.94 (m, 1H), 7.84-7.88 (m, 1H), 7.63-7.69 (m, 4H), 7.44-7.56 (m, 10H), 7.38-7.44 (m, 2H), 5.56 ppm(s, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 148.7, 139.5, 137.4, 133.9, 133.2, 131.7, 131.5, 129.4, 128.9, 128.6, 128.3, 127.8, 127.5, 127.0, 126.1, 126.0, 125.7, 125.4 ppm; **EI MS** (70 eV): m/z (%): 372 (32) [M]<sup>+</sup>, 322 (21), 105 (92), 91 (32), 77 (53), 43 (100); **HRMS** (ESI negative): m/z calcd for C<sub>28</sub>H<sub>20</sub>O [M-H]<sup>+</sup>: 371.1441; found: 371.1437.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55-7.63 (m, 4H), 7.39-7.53 (m, 8H), 7.29-7.35 (m, 1H), 7.03-7.08 (d, 2H, *J* = 8.8 Hz), 5.38 (s, 1H), 3.88 ppm(s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.5, 148.9, 140.4, 136.3, 134.0, 133.5, 130.8, 130.5, 129.1, 129.0, 128.8, 128.8,

128.7, 128.3, 127.8, 127.0, 126.8, 114.7, 55.4 ppm; **EI MS** (70 eV): m/z (%): 386 (8) [M]<sup>+</sup>, 223 (5), 205 (4), 149 (100), 69 (48), 57 (64); **HRMS** (ESI negative): m/z calcd for  $C_{25}H_{19}CIO_2$  [M-H]<sup>+</sup>: 385.1001; found: 385.0996.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.64-7.68 (d, 1H, *J* = 8.0 Hz), 7.54-7.58 (dd, 1H, *J* = 3.6 Hz and 1.2 Hz), 7.29-7.38 (m, 4H), 7.20-7.23 (m, 2H), 7.12-7.18 (m, 4H), 7.05-7.11 (m, 3H), 5.64 ppm(s, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 149.1, 141.3, 140.7, 139.4, 134.9, 131.1, 129.6, 129.1, 128.1, 128.0, 127.7, 127.5, 127.3, 126.5, 125.8, 125.5, 122.4, 120.3 ppm; **EI MS** (70 eV): m/z (%): 328 (100) [M]<sup>+</sup>, 215 (15), 191 (14), 111 (27), 45 (25); **HRMS** (ESI negative): m/z calcd for  $C_{22}H_{16}OS$  [M-H]<sup>+</sup>: 327.0849; found: 327.0853.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.57-7.63 (d, 2H, *J* = 7.6 Hz), 7.50-7.57 (m, 4H), 7.39-7.47 (m, 4H), 7.29-7.37 (m, 2H), 5.30 (s, 1H), 2.76-2.83 (q, 2H, *J* = 7.6 Hz), 1.30-1.40 ppm(t, 3H, *J* = 7.6 Hz); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 149.8, 141.0, 137.3, 133.5, 131.0, 129.4, 129.2, 128.7, 128.1, 128.0, 127.6, 126.8, 126.6, 126.4, 23.6, 14.1 ppm; **EI MS** (70 eV): m/z (%): 274 (100) [M]<sup>+</sup>, 259 (37), 244 (16), 215 (16), 152 (9), 77 (13); **HRMS** (ESI negative): m/z calcd for  $C_{20}H_{18}O$  [M-H]<sup>+</sup>: 273.1285; found: 273.1288.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.51-7.56 (d, 2H, *J* = 7.2 Hz), 7.38-7.44 (dd, 2H, *J* = 8.0 Hz and 7.2 Hz), 7.27-7.32 (m, 2H), 7.19-7.24 (m, 1H), 5.62 (s, 1H), 2.70-2.78 (q, 2H, *J* = 7.6 Hz), 1.80-1.89 (m, 1H), 1.25-1.32 (t, 3H, *J* = 7.6 Hz), 0.98-1.04 (m, 2H), 0.69-0.74 ppm(m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 153.0, 141.4, 133.1, 129.9, 128.6, 126.9, 126.8, 126.5, 125.5, 23.3, 14.1, 9.6, 5.2 ppm; **EI MS** (70 eV): m/z (%): 238 (17) [M]<sup>+</sup>, 203 (18), 159 (22), 145 (21), 133 (100), 105 (74); **HRMS** (ESI negative): m/z calcd for C<sub>17</sub>H<sub>18</sub>O [M-H]<sup>+</sup>: 237.1285; found: 237.1292.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38-7.43 (m, 4H), 7.30-7.38 (m, 2H), 6.14-6.18 (m, 2H), 2.12-2.23 (m, 1H), 1.68-1.78 (m, 1H), 1.09-1.18 (m, 1H), 0.74-0.80 (t, 3H, *J* = 7.6 Hz), 0.38-0.46 (m, 2H), 0.28-0.38 (m, 1H), 0.13-0.20 ppm(m, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 205.4, 142.6, 139.0, 138.6, 135.9, 128.8, 127.9, 127.0, 125.7, 54.1, 32.3, 20.2, 9.6, 0.5, 0.1 ppm; **EI MS** (70 eV): m/z (%): 238 (40) [M]<sup>+</sup>, 223 (32), 209 (36), 181 (48), 165 (59), 39 (100). **HRMS** (APCI): m/z calcd for C<sub>17</sub>H<sub>18</sub>O [M+H]<sup>+</sup>: 239.1430; found: 239.1434.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.60-7.67 (d, 4H, *J* = 7.6 Hz), 7.50-7.60 (m, 6H), 7.42-7.50 (m, 2H), 7.25-7.30 (m, 2H), 7.07-7.13 (dd, 1H, *J* = 4.0 Hz and 4.0 Hz), 5.46 ppm(s, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 149.0, 143.9, 137.2, 129.3, 129.2, 128.9, 128.0, 127.9, 127.6, 127.4, 124.1, 122.4 ppm; **EI MS** (70 eV): m/z (%): 328 (8) [M]<sup>+</sup>, 255 (11), 212 (17), 184 (25), 160 (15), 43 (100); **HRMS** (ESI negative): m/z calcd for C<sub>22</sub>H<sub>16</sub>OS [M-H]<sup>+</sup>: 327.0849; found: 327.0854.

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