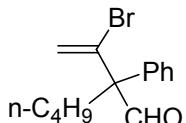


## Supporting Information

### Experimental section

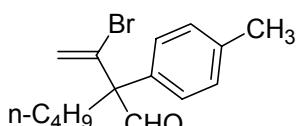
#### (1) Synthesis of 3-Bromo-2-butyl-2-phenyl-3-butenal (**2a**).



**2a**

**Typical procedure.** To a solution of **1a** (81.3 mg, 0.4 mmol) in 2.4 mL of MeCN and 0.27 mL of H<sub>2</sub>O was added with stirring 1.6 mL (0.5 M in MeCN, 0.8 mmol) of Br<sub>2</sub> at 25 °C. After 0.5 h as monitored by TLC (petroleum ether/ethyl acetate = 40:1), the mixture was quenched with water (6 mL) followed by the addition of a saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, extracted with diethyl ether (25 mL×3), washed with NaCl, and dried over *anhydrous* Na<sub>2</sub>SO<sub>4</sub>. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) afforded **2a** (86.4 mg, 77%). Oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.68(s, 1H), 7.33-7.43(m, 5H), 6.05(d, *J* = 2.4 Hz, 1H), 5.97(d, *J* = 2.4 Hz, 1H), 2.20-2.24(m, 1H), 2.12-2.16(m, 1H), 1.39-1.45(m, 2H), 1.18-1.28(m, 2H), 0.94(t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub> ) δ 196.2, 136.9, 133.9, 128.9, 128.2, 128.0, 121.4, 65.7, 31.7, 26.9, 23.1, 13.9; IR(KBr) ν (cm<sup>-1</sup>) 1730, 1619; MS(70eV, EI) m/z(%):283 (M<sup>+</sup>+1(<sup>81</sup>Br), 2.69), 281 (M<sup>+</sup>+1(<sup>79</sup>Br), 3.81), 105(100); HRMS Calcd for C<sub>14</sub>H<sub>18</sub><sup>79</sup>BrO(M<sup>+</sup>+1): 281.0536. Found: 281.0549.

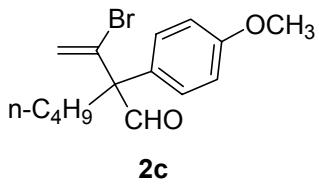
#### (2) Synthesis of 3-Bromo-2-butyl-2-(4'-methylphenyl)-3-butenal



**2b**

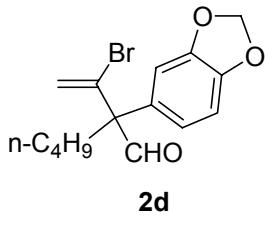
The reaction of 85.7 mg (0.4 mmol) of **1b** and 1.6 mL (0.5 M in MeCN, 0.8 mmol) of Br<sub>2</sub> afforded 84.9 mg (73%) of **2b**; The reaction of 64.1 mg (0.3 mmol) of **1b** and 65.5 mg (0.36 mmol) of NBS afforded 78.9 mg (90%) of **2b**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.65(s, 1H), 7.22(s, 4H), 6.04(d, *J* = 2.4 Hz, 1H), 5.96(d, *J* = 2.4 Hz, 1H), 2.35(s, 3H), 2.20-2.23(m, 1H), 2.09-2.13(m, 1H), 1.39-1.45(m, 2H), 1.20-1.29(m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ 196.1, 137.9, 134.2, 133.8, 129.6, 128.0, 121.2, 65.4, 31.6, 26.9, 23.1, 21.0, 13.9; IR(KBr) ν (cm<sup>-1</sup>) 1730, 1619; MS(70eV, EI) m/z(%): 296(M<sup>+</sup>+1(<sup>81</sup>Br), 1.30), 294(M<sup>+</sup>+1(<sup>79</sup>Br), 1.31), 143(100); HRMS Calcd for C<sub>15</sub>H<sub>20</sub><sup>79</sup>BrO(M<sup>+</sup>+1): 295.0692. Found: 295.0677.

### (3) Synthesis of 3-Bromo-2-butyl-2-(4'-methoxyphenyl)-3-butenal



The reaction of 86.8 mg (0.37 mmol) of **1c** and 1.6 mL (0.5 M in MeCN, 0.8 mmol) of Br<sub>2</sub> afforded 82.2 mg (71%) of **2c**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.55(s, 1H), 7.18(d, *J* = 8.8 Hz, 2H), 6.86(d, *J* = 8.8 Hz, 2H), 5.97(d, *J* = 2.4 Hz, 1H), 5.88(d, *J* = 2.4 Hz, 1H), 3.75(s, 3H), 2.11-2.15(m, 1H), 2.01-2.05(m, 1H), 1.31-1.38(m, 2H), 1.13-1.25(m, 2H), 0.88(t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ 195.8, 159.3, 134.4, 129.4, 128.7, 121.1, 114.3, 65.0, 55.2, 31.6, 26.9, 23.1, 13.9; IR(KBr) ν (cm<sup>-1</sup>) 1728, 1608; MS(70eV, EI) m/z(%): 312(M<sup>+</sup>(<sup>81</sup>Br), 3.14), 310(M<sup>+</sup>(<sup>79</sup>Br), 3.18), 160(100); HRMS Calcd for C<sub>15</sub>H<sub>19</sub><sup>79</sup>BrO<sub>2</sub>Na(M<sup>+</sup>+Na) □ 333.0461. Found: 333.0480.

### (4) Synthesis of 3-Bromo-2-butyl-2-(3',4'-methylenedioxyphenyl)-3-butenal



**2d**

The reaction of 96.2 mg (0.4 mmol) of **1d** and 1.6 mL (0.5 M in MeCN, 0.8 mmol) of Br<sub>2</sub> afforded 98.7 mg (78%) of **2d**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.58(s, 1H), 6.77-6.82(m, 3H), 6.04(d, *J* = 2.4 Hz, 1H), 5.97(s, 2H), 5.93(d, *J* = 2.4 Hz, 1H), 2.12-2.18(m, 1H), 2.03-2.07(m, 1H), 1.35-1.43(m, 2H), 1.17-1.29(m, 2H), 0.95(t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ 195.5, 148.3, 147.3, 134.1, 130.5, 121.8, 121.2, 108.44, 108.41, 101.3, 65.2, 31.7, 26.9, 23.0, 13.9; IR(KBr) ν (cm<sup>-1</sup>) 1728, 1618; MS(70eV, EI) m/z(%): 326(M<sup>+</sup>(<sup>81</sup>Br), 35.90), 324(M<sup>+</sup>(<sup>79</sup>Br), 37.88), 297(95.82), 295(100); HRMS Calcd for C<sub>15</sub>H<sub>18</sub><sup>79</sup>BrO<sub>3</sub>(M<sup>+</sup>+1): 325.0434. Found: 325.0461.

### (5) Synthesis of 2-Allyl-3-bromo-2-(4'-methoxyphenyl)-3-butenal



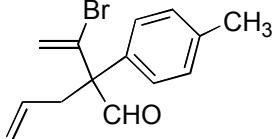
**2e**

The reaction of 329.4 mg (1.53 mmol) of **1e** and 3.84 mL (0.5 M in MeCN, 1.92 mmol) of Br<sub>2</sub> afforded 256.3 mg (57%) of **2e**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.57(s, 1H), 7.15(d, *J* = 8.8 Hz, 2H), 6.85(d, *J* = 8.8 Hz, 2H), 5.86-5.88(s, 2H), 5.60-5.69(m, 1H), 5.11(d, *J* = 17.2 Hz, 1H), 5.03(d, *J* = 9.2 Hz, 1H), 3.73(s, 3H), 2.96(dd, *J* = 7.6 Hz, *J* = 14 Hz, 1H), 2.79(dd, *J* = 7.6 Hz, *J* = 14 Hz, 1H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ 195.8, 159.3, 133.7, 132.7, 129.4, 128.0, 121.5, 118.8, 114.3, 64.8, 55.2, 36.5; IR(KBr) ν (cm<sup>-1</sup>) 1727, 1608; MS(70eV, EI) m/z(%): 296(M<sup>+</sup>(<sup>81</sup>Br), 2.63),

294( $M^+(^{79}\text{Br})$ , 2.45), 145(100); HRMS Calcd for  $C_{14}\text{H}_{16}^{79}\text{BrO}_2\Box M^++1\Box$ : 295.0328.

Found: 295.0322.

**(6) Synthesis of 2-Allyl-3-bromo-2-(4'-methylphenyl)-3-butenal**

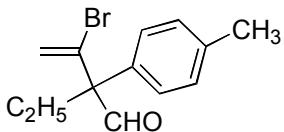


**2f**

The reaction of 78.4 mg (0.4 mmol) of **1f** and 0.88 mL (0.5 M in MeCN, 0.44 mmol) of  $\text{Br}_2$  afforded 56.6 mg (52%) of **2f**; The reaction of 57.6 mg (0.3 mmol) of **1f** and 63.1 mg (0.36 mmol) of NBS afforded 56.8 mg (71%) of **2f**: oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69(s, 1H), 7.22(s, 4H), 5.95-5.96(m, 2H), 5.69-5.76(m, 1H), 5.19(d,  $J = 17.2$  Hz, 1H), 5.12(d,  $J = 9.2$  Hz, 1H), 3.06(dd,  $J = 8.0$  Hz,  $J = 14$  Hz, 1H), 2.89(dd,  $J = 8.0$  Hz,  $J = 14$  Hz, 1H), 2.36(s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 138.0, 133.5, 133.2, 132.7, 129.7, 128.1, 121.6, 118.8, 65.1, 36.5, 21.0; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 1728, 1641; MS(70eV, EI) m/z(%): 280( $M^+(^{81}\text{Br})$ , 3.67), 278( $M^+(^{79}\text{Br})$ , 3.75), 129(100); HRMS Calcd for  $C_{14}\text{H}_{16}^{79}\text{BrO}(M^++1)$ : 279.0379.

Found: 279.0351.

**(7) Synthesis of 2-Ethyl-3-bromo-2-(4'-methylphenyl)-3-butenal**

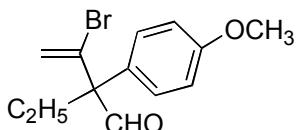


**2g**

The reaction of 73.5 mg (0.4 mmol) of **1g** and 1.6 mL (0.5 M in MeCN, 0.8 mmol) of  $\text{Br}_2$  afforded 74.4 mg (71%) of **2g**: oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.65(s, 1H), 7.23(s, 4H), 6.03(d,  $J = 2.4$  Hz, 1H), 5.97(d,  $J = 2.4$  Hz, 1H), 2.35(s, 3H), 2.28-2.33

(m, 1H), 2.13-2.17(m, 1H), 0.94(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 137.9, 133.8, 133.7, 129.6, 128.1, 121.5, 65.9, 24.6, 21.0, 9.2; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 1730, 1620; MS(70eV, EI) m/z(%): 268( $\text{M}^+(^{81}\text{Br})$ , 2.02), 266( $\text{M}^+(^{79}\text{Br})$ , 2.26), 157(100); HRMS Calcd for  $\text{C}_{13}\text{H}_{16}^{79}\text{BrO}(\text{M}^++1)$ : 267.0379. Found: 267.0356.

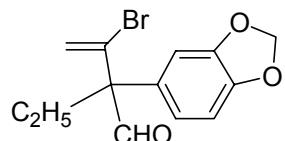
**(8) Synthesis of 2-Ethyl-3-bromo-2-(4'-methoxyphenyl)-3-butenal**



**2h**

The reaction of 79.5 mg (0.4 mmol) of **1h** and 1.0 mL (0.5 M in MeCN, 0.50 mmol) of  $\text{Br}_2$  afforded 87.8 mg (80%) of **2h**; The reaction of 82.0 mg (0.4 mmol) of **1h** and 74 mg (0.42 mmol) of NBS afforded 99.7 mg (88%) of **2h**: oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.53(s, 1H), 7.16(d,  $J = 10.8$  Hz, 2H), 6.87(d,  $J = 10.8$  Hz, 2H), 5.94(d,  $J = 2.4$  Hz, 1H), 5.88(d,  $J = 2.4$  Hz, 1H), 3.73(s, 3H), 2.16-2.28 (m, 1H), 1.96-2.08(m, 1H), 0.85(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 159.2, 134.0, 129.4, 128.5, 121.3, 114.3, 65.5, 55.2, 24.6, 9.2; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 1718, 1609; MS(70eV, EI) m/z(%): 284( $\text{M}^+(^{81}\text{Br})$ , 3.20), 282( $\text{M}^+(^{79}\text{Br})$ , 3.20), 174(100); HRMS Calcd for  $\text{C}_{13}\text{H}_{16}^{79}\text{BrO}_2(\text{M}^++1)$ : 283.0328. Found: 283.0352.

**(9) Synthesis of 2-Ethyl-3-bromo-2-(3',4'-methylenedioxyphenyl)-3-butenal**

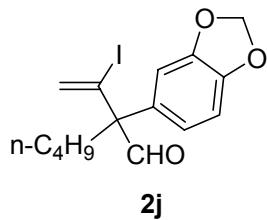


**2i**

The reaction of 87.6 mg (0.4 mmol) of **1i** and 1.6 mL (0.5 M in MeCN, 0.8 mmol) of  $\text{Br}_2$  afforded 76.2 mg (64%) of **2i**; The reaction of 67.1 mg (0.3 mmol) of **1i** and

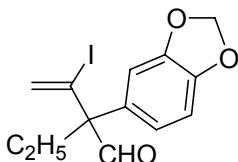
62.4 mg (0.36 mmol) of NBS afforded 76.6 mg (84%) of **2i**: oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.59(s, 1H), 6.78-6.84(m, 3H), 6.04(d,  $J = 2.8$  Hz, 1H), 5.98(s, 2H), 5.96(d,  $J = 2.8$  Hz, 1H), 2.23-2.28(m, 1H), 2.06-2.12(m, 1H), 0.92(t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 148.3, 147.4, 133.8, 130.4, 121.9, 121.4, 108.48, 108.46, 101.3, 65.7, 24.8, 9.3; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 1728, 1618; MS(70eV, EI) m/z(%): 298( $\text{M}^+{^{81}\text{Br}}$ , 10.21), 296( $\text{M}^+{^{79}\text{Br}}$ , 10.61), 130(100); HRMS Calcd for  $\text{C}_{13}\text{H}_{14}{^{79}\text{BrO}_3}(\text{M}^++1)$ : 297.0121. Found: 297.0111.

**(10) Synthesis of 2-Butyl-3-iodo-2-(3',4'-methylenedioxyphenyl)-3-butenal**



The reaction of 99.1 mg (0.4 mmol) of **1d** and 204.6 mg (0.8 mmol) of  $\text{I}_2$  afforded 119.1 mg (80%) of **2j**: solid, Mp: 57-59 °C (petroleum ether ethyl acetate).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.62(s, 1H), 6.77-6.85(m, 3H), 6.50(d,  $J = 2.4$  Hz, 1H), 6.29(d,  $J = 2.4$  Hz, 1H), 5.99(s, 2H), 2.14(dt,  $J = 2.8$  Hz,  $J = 8.8$  Hz, 1H), 1.96(dt,  $J = 2.8$  Hz,  $J = 8.8$  Hz, 1H), 1.40-1.44(m, 2H), 1.18-1.29(m, 2H), 0.94(t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.5, 148.3, 147.4, 131.5, 129.2, 121.9, 114.4, 108.5, 108.4, 101.3, 66.0, 32.2, 27.0, 23.1, 13.9; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 1725, 1605; MS(70eV, EI) m/z(%): 372( $\text{M}^+$ , 19.41), 174(100); HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{IO}_3(\text{M}^++1)$ : 373.0295. Found: 373.0294.

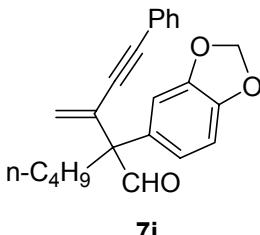
**(11) Synthesis of 2-Ethyl-3-iodo-2-(3',4'-methylenedioxyphenyl)-3-butenal**



2k

The reaction of 88.7 mg (0.4 mmol) of **1d** and 203.2 mg (0.8 mmol) of I<sub>2</sub> afforded 96.3 mg (69%) of **2k**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.62(s, 1H), 6.75-6.83(m, 3H), 6.49(d, *J* = 2.4 Hz, 1H), 6.31(s, *J* = 2.4 Hz, 1H), 5.98(s, 2H), 2.21-2.27(m, 1H), 1.95-2.00(m, 1H), 0.91(t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 194.5, 148.3, 147.4, 131.5, 129.6, 122.0, 114.0, 108.5, 108.4, 101.4, 66.5, 25.2, 9.3; IR(KBr) ν (cm<sup>-1</sup>) 1725, 1606; MS(70eV, EI) m/z(%): 344(M<sup>+</sup>, 9.49), 115(100); HRMS Calcd for C<sub>13</sub>H<sub>14</sub>IO<sub>3</sub>(M<sup>+</sup>+1): 344.9982. Found:344.9970 .

### (12) Synthesis of 7j

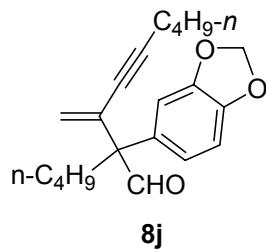


7j

A mixture of 93.3 mg (0.25 mmol) of **2j**, phenylacetylene (30.6 mg, 0.30 mmol), Et<sub>2</sub>NH (22.8 mg, 0.275 mmol), CuI (4.2 mg, 10% mol), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (8.9 mg, 5 % mol) in 2 mL of CH<sub>3</sub>CN was stirred at rt under N<sub>2</sub> for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 40:1). Water (6 mL) was added and the reaction mixture was extracted with ether. The combined extracts were washed with saturated NaCl and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) afforded 83.7 mg (96%) of **7j** as an oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73(s, 1H), 7.27-7.32(m, 5H), 6.77-6.84(m, 3H),

5.97(s, 2H), 5.89(s, 1H), 5.51(s, 1H), 2.06-2.16(m, 2H), 1.35-1.43(m, 2H), 1.22-1.26(m, 2H), 0.91(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 198.3, 148.0, 146.9, 131.73, 131.66, 131.5, 128.4, 128.3, 125.1, 122.7, 122.1, 108.9, 108.2, 101.2, 91.3, 88.2, 62.9, 32.8, 26.9, 23.3, 14.0; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2201, 1725, 1603; MS(70eV, EI) m/z(%): 346( $\text{M}^+$ , 100); HRMS Calcd for  $\text{C}_{23}\text{H}_{22}\text{O}_3(\text{M}^++\text{Na})$ : 369.1461. Found: 369.1467.

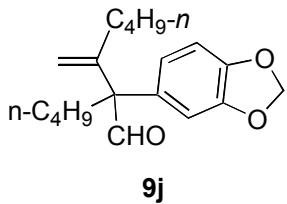
### (13) Synthesis of **8j**



The reaction of 93.2 mg (0.25 mmol) of **2j**, 1-hexyne (28.9mg, 0.325 mmol),  $\text{Et}_2\text{NH}$  (29.2 mg, 0.40 mmol), CuI (5.4 mg, 10 % mol), and  $\text{PdCl}_2(\text{PPh}_3)_2$  (10.0 mg, 5 % mol) in 2 mL of  $\text{CH}_3\text{CN}$  was stirred at  $40^\circ\text{C}$  under  $\text{N}_2$  for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 40:1). Water (6 mL) was added and the reaction mixture was extracted with ether, the combined extracts were washed with saturated  $\text{NaCl}$  and dried over  $\text{Na}_2\text{SO}_4$ . Filtration, column chromatography on silica gel afforded 75.8 mg (93%) of **8j** as an oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.66(s, 1H), 6.78-6.81(m, 2H), 6.70-6.73(m, 1H), 5.96(s, 2H), 5.69(s, 1H), 5.33(s, 1H), 2.20-2.23(t,  $J = 7.2$  Hz, 2H), 1.85-2.16(m, 2H), 1.16-1.41(m, 8H), 0.89(t,  $J = 7.2$  Hz, 3H), 0.84(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 198.7, 147.9, 146.7, 132.02, 132.00, 123.5, 122.0, 109.0, 108.1, 101.1, 92.6, 79.5, 63.0, 32.6, 30.5, 26.9, 23.3, 21.7, 18.8, 13.9, 13.5; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2221, 1726, 1604; MS(70eV, EI) m/z(%):

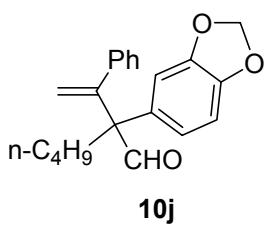
326(M<sup>+</sup>, 15.22), 43(100); HRMS Calcd for C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>: 326.1888. Found: 326.1890.

**(14) Synthesis of 9j**



To a solution of anhydrous ZnBr<sub>2</sub> (103.5 mg, 0.45 mmol) in 2 mL THF was added dropwise *n*-C<sub>4</sub>H<sub>9</sub>Li (0.13 mL, 2.88M in hexane) at 0 °C. After stirring for 10 min, Pd(PPh<sub>3</sub>)<sub>4</sub> (14.8 mg, 5 % mol) and 93.0 mg (0.25 mmol) of **2j** were added and the mixture was stirred for 16 h as monitored by TLC (petroleum ether/ethyl acetate = 40:1). HCl (5 %, 6 mL) was added and the reaction mixture was extracted with ether, washed with saturated NaCl, and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration, evaporation, and column chromatography on silica gel afforded 43.3 mg (57%) of **9j** as an oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.57(s, 1H), 6.71-6.80(m, 3H), 5.96(s, 2H), 5.26(s, 1H), 5.04(s, 1H), 2.04-2.09(m, 1H), 1.85-1.88(m, 1H), 1.75-1.79(m, 2H), 1.23-1.43(m, 6H), 1.06-1.13(m, 2H), 0.89(t, *J* = 7.6 Hz, 3H), 0.85(t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ; 199.4, 148.2, 148.0, 146.6, 132.6, 121.7, 113.9, 108.7, 108.2, 101.1, 63.9, 31.53, 31.48, 29.9, 27.3, 23.3, 22.5, 14.01, 14.00; IR(KBr) ν (cm<sup>-1</sup>) 1723, 1635, 1610; HRMS Calcd for C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>: 302.1876. Found: 302.1886.

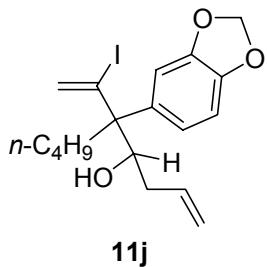
**(15) Synthesis of 10j**



The reaction of 91.8 mg (0.25 mmol) of **2j**, phenyl boronic acid (62.0 mg, 0.5

mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (16.5 mg, 5 mol%), CH<sub>3</sub>OH (0.1 mL) and Na<sub>2</sub>CO<sub>3</sub> (0.3 mL, 2 M in H<sub>2</sub>O) in 2 mL of toluene was refluxed under N<sub>2</sub> for 9 h as monitored by TLC (petroleum ether/ethyl acetate = 40:1). Water (6 mL) was added and the reaction mixture was extracted with ether, washed with saturated NaCl, and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration, evaporation, and column chromatography on silica gel afforded 76.8 mg(98%) of **10j** as an oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.70(s, 1H), 7.18-7.21(m, 3H), 7.04-7.06(m, 2H), 6.89(s, 1H), 6.78-6.83(m, 2H), 5.96(s, 2H), 5.60(s, 1H), 5.35(s, 1H), 2.10-2.14(m, 1H), 1.91-1.96(m, 1H), 1.15-1.27(m, 4H), 0.80(t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.1, 148.7, 148.1, 146.7, 140.6, 132.7, 128.0, 127.9, 127.5, 122.0, 119.4, 108.9, 108.2, 101.2, 62.9, 32.8, 27.1, 23.2, 13.8; IR(KBr) ν (cm<sup>-1</sup>) 1722, 1612; MS(70eV, EI) m/z(%): 322(M<sup>+</sup>, 38.7), 293(100); HRMS Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>3</sub>Na(M<sup>+</sup>+Na): 345.1461. Found: 345.1446.

### (16) Synthesis of **11j**

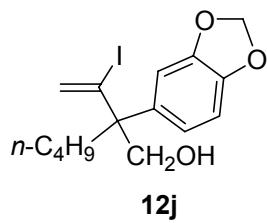


The reaction of 91.5 mg (0.25 mmol) of **2j**, allyl bromide (0.2 mL) and Zn (65.0 mg, 1.0 mmol) in 2 mL of aqueous NH<sub>4</sub>Cl and 0.8 mL of THF afforded 46.3 mg (45%) of **11ja** and 31.3 mg (31%) of **11jb**. **11ja**: oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.95(s, 1H), 6.84(d, *J* = 8 Hz, 1H), 6.78(d, *J* = 8 Hz, 1H), 6.45(d, *J* = 1.6 Hz, 1H), 6.21(d, *J* = 1.6 Hz, 1H), 5.98(s, 1H), 5.96(s, 1H), 5.74-5.83(m, 1H), 5.06(d, *J* = 10.4 Hz, 1H), 5.00(d, *J* = 17.2 Hz, 1H), 4.07-4.12(m, 1H), 2.30-2.35(m, 1H), 1.85(t, *J* =

7.2 Hz, 2H), 1.55-1.59(m, 2H), 1.26-1.44(m, 3H), 1.16-1.21(m, 1H), 0.96(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 146.4, 135.5, 134.6, 128.9, 122.2, 121.0, 117.7, 109.6, 107.5, 101.1, 72.4, 59.2, 39.0, 34.9, 26.6, 23.4, 14.1; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 3557, 1639, 1604, 1503, 1488, 1239; MS(70eV, EI) m/z(%): 414( $\text{M}^+$ , 0.51), 216(100); HRMS Calcd for  $\text{C}_{18}\text{H}_{23}\text{IO}_3\text{Na}$  ( $\text{M}^+ + \text{Na}$ ): 437.0584. Found: 437.0598.

**11jb:** oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83(s, 1H), 6.78(s, 2H), 6.33(s, 1H), 6.27(s, 1H), 5.97(s, 2H), 5.77-5.81(m, 1H), 5.05-5.10(m, 2H), 4.04-4.08(m, 1H), 2.37-2.42(m, 1H), 2.16-2.26(m, 1H), 1.76-1.86(m, 1H), 1.59-1.69(m, 1H), 1.29-1.44(m, 5H), 0.94(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 146.4, 135.5, 134.6, 128.9, 122.1, 121.0, 117.8, 109.6, 107.5, 101.1, 72.3, 59.2, 39.0, 34.8, 26.6, 23.4, 14.1; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 3553, 1639, 1604, 1503, 1342; HRMS Calcd for  $\text{C}_{18}\text{H}_{23}\text{IO}_3$ : 414.0686. Found: 414.0684.

### (17) Synthesis of 12j



The reaction of 72.0 mg (0.2 mmol) of **2j** and 8.0 mg (0.21 mmol) of  $\text{NaBH}_4$  in 2 mL THF afforded 65.7 mg (91%) of **12j**: oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.70-6.77(m, 3H), 6.31(d,  $J = 2.4$  Hz, 1H), 6.14(d,  $J = 2.4$  Hz, 1H), 5.96(s, 2H), 3.88-3.94(m, 2H), 1.87-1.92(m, 2H), 1.26-1.37(m, 4H), 1.04-1.10(m, 1H), 0.90(t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 146.5, 136.5, 127.3, 122.0, 120.4, 108.0, 107.8, 101.1, 64.9, 56.4, 33.9, 26.6, 23.2, 14.0; IR(KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 3558, 3443,

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1605, 1504, 1487, 1243; MS(70eV, EI) m/z(%): 374( $M^+$ , 99.2), 216(100); HRMS

Calcd for  $C_{15}H_{19}IO_3$ : 374.0374. Found: 374.0377.

