

# **-Supporting Information-**

**Ru(II)-Catalyzed Oxidative *Hack*-type Olefination of Aromatic Carboxylic Acids with Styrenes  
through Carboxylate Assisted C–H Bond Activation**

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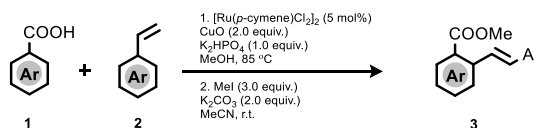
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## General Information

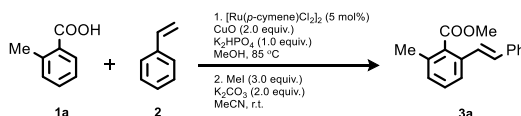
[Ru(p-cymene)Cl<sub>2</sub>]<sub>2</sub> and CuO were purchased from Alfa Aesar company. Benzoic acids and K<sub>2</sub>HPO<sub>4</sub> were purchased from Avra chemicals and Spectrochem. All reactions were monitored by thin layer chromatography (TLC) on Merck 60 F 254 precoated silica plates and visualized using a UV lamp (366 or 254 nm) or by use of potassium permanganate, 5 g K<sub>2</sub>CO<sub>3</sub>, / 100 mL water. Products were isolated by column chromatography (Merck silica gel 100-200μm). Yields refer to chromatographically and spectroscopically homogenous materials unless noted otherwise. <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded on a Bruker 400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak CDCl<sub>3</sub> δ = 7.2600 ppm for <sup>1</sup>H, δ = 77.16 for <sup>13</sup>C; or calibrated to tetramethylsilane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. <sup>1</sup>H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad. Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source.

### Typical Ruthenium(II)-catalyzed *mono*-olefination of benzoic acids (*isolation of ester*):



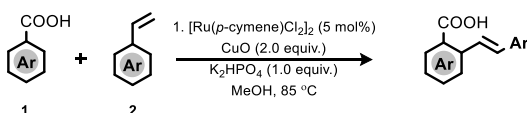
**Procedure:** To an oven dried screw cap reaction tube (10×1.5 cm) corresponding benzoic acid **1a**-**1q** (0.15mmol, 1 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CuO (2.0 equiv), K<sub>2</sub>HPO<sub>4</sub> (1.0 equiv), and styrene (2.0 equiv) were added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the crude reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then solvent was evaporated and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), iodomethane (3.0 equiv), and acetonitrile (1.0 ml) were added to the reaction mixture and stirred for 4 h. Then solvent was evaporated under reduced pressure. In order to get pure 2-styrylbenzoic acid methyl esters, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (2-5% ethyl acetate in hexane).

### Typical Ruthenium(II)-catalyzed *mono*-olefination of benzoic acids (*gram scale*):



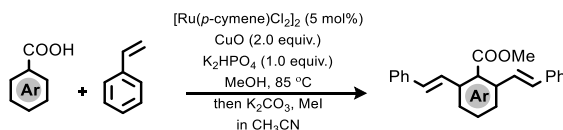
**Procedure:** To an oven dried 50 mL round bottom flask corresponding 2-toluic acid **1a** (1.0 gram, 7.35 mmol, 1 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CuO (2.0 equiv), K<sub>2</sub>HPO<sub>4</sub> (1.0 equiv), and styrene (2.0 equiv) were added in 20 ml MeOH. The RB flask was sealed with a glass stopper and the reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the crude reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then solvent was evaporated and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), iodomethane (3.0 equiv), and acetonitrile (10 ml) were added to the reaction mixture and stirred for 4 h. Then solvent was evaporated under reduced pressure. Pure 2-styrylbenzoic acid methyl ester (**3a**, 1.37 gm, 74% yield) was obtained by column chromatography of the crude mixture on silica gel with a gradient eluent of hexane and ethyl acetate (2-5% ethyl acetate in hexane).

**Typical Ruthenium(II)-catalyzed *mono*-olefination of benzoic acids (*free acid synthesis*; 3aa–3ad, 3ma):**



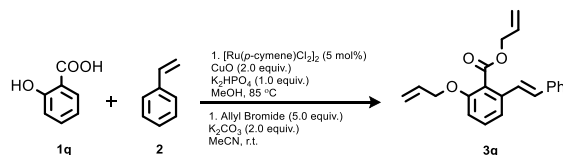
**Procedure:** To an oven dried reaction tube (10 × 1.5 cm) corresponding benzoic acid (**1**) (0.15mmol, 1 equiv.), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CuO (2.0 equiv), K<sub>2</sub>HPO<sub>4</sub>(1.0 equiv), and styrene derivatives (2.0 equiv) were added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air in sealed tube. After completion (monitored by TLC), the reaction was quenched with 0.1 ml of acetic acid. Then solvent was evaporated under reduced pressure. In order to get pure 2-styrylbenzoic acids, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (15-20% ethyl acetate in hexane).

**Typical Ruthenium(II)-catalyzed *di*-olefination of benzoic acids (*isolation of ester*):**



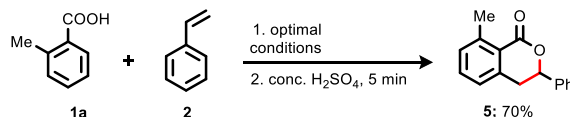
**Procedure:** To an oven dried screw cap reaction tube (10 × 1.5 cm) corresponding benzoic acid (0.15mmol, 1.0 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CuO (2.0 equiv), K<sub>2</sub>HPO<sub>4</sub>(1.0 equiv), and styrene (3.5 equiv) were added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the crude reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then the methanol was evaporated and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), iodomethane (3.0 equiv), and acetonitrile (1.0 ml) were added to the reaction mixture and stirred for 4 h. Then solvent was evaporated under reduced pressure. In order to get pure 2-styrylbenzoic acid methyl esters, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (2-5% ethyl acetate in hexane).

### Typical Ruthenium(II)-catalyzed olefination of salicylic acid (*isolation of allyl ester*):



**Procedure:** To an oven dried screw cap reaction tube (10×1.5 cm) corresponding salicylic acid **1q** (0.15mmol, 1 equiv),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (5 mol %), CuO (2.0 equiv),  $\text{K}_2\text{HPO}_4$  (1.0 equiv), and styrene (2.0 equiv) were added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the crude reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then solvent was evaporated and  $\text{K}_2\text{CO}_3$  (2.0 equiv), allyl bromide (5.0 equiv), and acetonitrile (1.0 ml) were added to the reaction mixture and stirred for 4 h. Then solvent was evaporated under reduced pressure. In order to get pure 2-styrylbenzoic acid methyl esters, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (2-5% ethyl acetate in hexane).

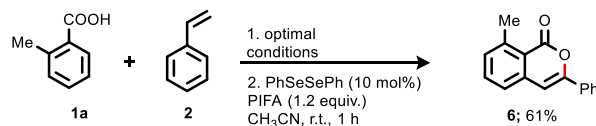
### Sequential Synthesis of Isochromone (**5**):



**Procedure:** To an oven dried screw cap reaction tube (10 × 1.5 cm) corresponding 2-toluic acid **1a** (0.25mmol, 1.0 equiv),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (5 mol %), CuO (2.0 equiv),  $\text{K}_2\text{HPO}_4$  (1.0 equiv), and styrene (2.0 equiv) was added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then the methanol was evaporated and conc.  $\text{H}_2\text{SO}_4$  (3.0 ml) was added to the crude reaction mixture and stirred for 5 min. The reaction mixture was transferred to ice-water and neutralized by saturated bicarbonate solution. The compound was extracted through work up with ethyl acetate. The solvent was evaporated under reduced pressure. In order to get pure product, the resulting residue was purified by

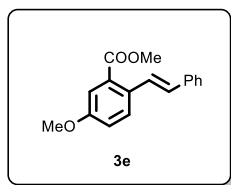
column chromatography on silica gel with a gradient eluent of hexane-ethyl acetate mixture (5-10% ethyl acetate in hexane) and 70% yield (41 mg) of the product was obtained.

### Sequential Synthesis of 1H-Isochromone (6):

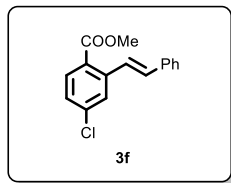


**Procedure:** To an oven dried screw cap reaction tube (10 × 1.5 cm) corresponding 2-toluic acid **1a** (0.25mmol, 1.0 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CuO (2.0 equiv), K<sub>2</sub>HPO<sub>4</sub>(1.0 equiv), and styrene (2.0 equiv) was added in 0.5 ml MeOH. The reaction mixture was stirred at 85 °C for 24 h under air. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate and filtered through a celite pad. Then the solvent was evaporated and diphenyl diselenide (0.1equiv) and PIFA (1.2 equiv) were added to the reaction mixture in presence of acetonitrile solvent (1.5 ml) under N<sub>2</sub> atmosphere and stirred for one hour. In order to get pure product, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane-ethyl acetate mixture (3-7% ethyl acetate in hexane) and 58% yield (34 mg) of the desired product was obtained (cyclization is performed using the crude reaction mixture following previous literature procedure- *Eur. J. Org. Chem.* **2010**, 3465–3472).

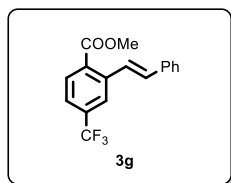
## Spectroscopic data of synthesized compounds:



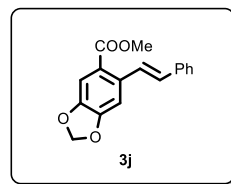
**Methyl (E)-5-methoxy-2-styrylbenzoate (3e):** white solid; yield 54% (22 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 16.2$  Hz, 1H), 7.66 (d,  $J = 8.7$  Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 (d,  $J = 2.8$  Hz, 1H), 7.35 (dd,  $J = 10.4, 4.7$  Hz, 2H), 7.28 – 7.21 (m, 1H), 7.07 (dd,  $J = 8.7, 2.8$  Hz, 1H), 6.92 (d,  $J = 16.2$  Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.89, 158.77, 137.83, 132.00, 129.95, 128.78, 128.42, 127.67, 127.11, 126.80, 119.01, 114.96, 55.67, 52.36 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 291.0990  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}$ ; Found 291.0997.



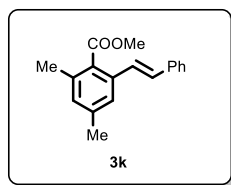
**Methyl (E)-4-chloro-2-styrylbenzoate (3f):** white solid; yield 47% (19 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 16.2$  Hz, 1H), 7.89 (d,  $J = 8.4$  Hz, 1H), 7.70 (d,  $J = 2.1$  Hz, 1H), 7.55 (d,  $J = 7.5$  Hz, 2H), 7.38 (dd,  $J = 10.4, 4.9$  Hz, 2H), 7.32 – 7.27 (m, 2H), 7.01 (d,  $J = 16.2$  Hz, 1H), 3.92 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.16, 141.37, 138.63, 137.09, 132.79, 132.39, 128.88, 128.38, 127.27, 127.16, 127.06, 126.80, 126.35, 52.40 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 295.0502  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{ClNa}$ ; Found 295.0510.



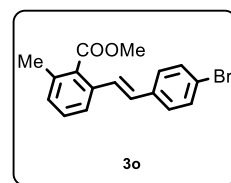
**Methyl (E)-2-styryl-4-(trifluoromethyl)benzoate (3g):** white solid; yield 44% (20 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.2$  Hz, 1H), 7.99 – 7.92 (m, 2H), 7.56 (t,  $J = 6.8$  Hz, 3H), 7.39 (t,  $J = 7.5$  Hz, 2H), 7.32 (d,  $J = 7.1$  Hz, 1H), 7.08 (d,  $J = 16.3$  Hz, 1H), 3.96 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.05, 140.04, 136.94, 134.29, 133.91 (q,  $J = 32.7$  Hz), 131.61, 131.37, 128.92, 128.54, 127.20, 126.04, 123.92 (q,  $J = 3.6$  Hz), 123.75 (q,  $J = 273.2$  Hz), 123.66 (q,  $J = 3.5$  Hz), 52.67 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 307.0946  $[\text{M} + \text{H}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{F}_3$ ; Found 307.0914.



**Methyl (E)-6-styrylbenzo[d][1,3]dioxole-5-carboxylate (3j):** white solid; yield 61% (26 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 16.6$  Hz, 1H), 7.59 (d,  $J = 8.3$  Hz, 1H), 7.57 – 7.53 (m, 2H), 7.45 (d,  $J = 16.6$  Hz, 1H), 7.35 (dd,  $J = 10.5, 4.8$  Hz, 2H), 7.30 – 7.24 (m, 1H), 6.73 (d,  $J = 8.3$  Hz, 1H), 6.12 (s, 2H), 3.89 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.54, 150.72, 146.03, 137.92, 134.99, 128.75, 128.03, 126.93, 126.73, 122.85, 122.07, 121.89, 106.51, 101.75, 52.17 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 305.0790  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Na}$ ; Found 305.0789.

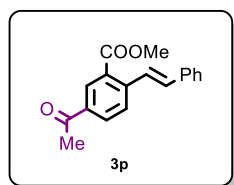


**Methyl (E)-2,4-dimethyl-6-styrylbenzoate (3k):** white solid; yield 91% (36 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 16.2$  Hz, 1H), 7.73 (s, 1H), 7.58 – 7.53 (m, 2H), 7.50 (s, 1H), 7.36 (dd,  $J = 10.4, 4.9$  Hz, 2H), 7.29 – 7.23 (m, 1H), 6.98 (d,  $J = 16.2$  Hz, 1H), 3.91 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.11, 141.51, 137.82, 137.06, 136.01, 131.95, 130.51, 128.75, 128.27, 127.72, 127.69, 126.90, 126.02, 52.06, 20.09, 19.51 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 289.1204  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Na}$ ; Found 289.1218.

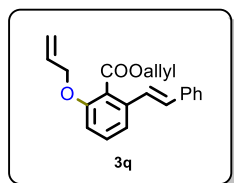


**Methyl (E)-2-(4-bromostyryl)-6-methylbenzoate (3o):** White solid; yield 53% (26 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.43 (m, 3H), 7.37 – 7.27 (m, 3H), 7.18 – 7.05 (m, 2H), 7.02 – 6.93 (m, 1H), 3.95 (s, 3H), 2.35 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.28, 136.18, 135.58, 134.80, 131.95, 130.25, 129.78, 129.71, 128.31, 126.52, 123.18, 121.85, 52.36, 19.90 ppm; **HRMS** (ESI/TOF-Q)  $m/z$ : 331.0334  $[\text{M} + \text{H}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{16}\text{BrO}_2$ ; Found 331.0365.

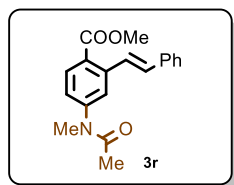




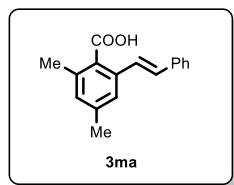
**Methyl (E)-5-acetyl-2-styrylbenzoate (3p):** white solid; yield 63% (26 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J$  = 1.9 Hz, 1H), 8.08 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 8.03 (d,  $J$  = 16.3 Hz, 1H), 7.83 (d,  $J$  = 8.3 Hz, 1H), 7.57 (dd,  $J$  = 5.1, 3.4 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.31 (dt,  $J$  = 4.7, 1.9 Hz, 1H), 7.14 (t,  $J$  = 9.3 Hz, 1H), 3.96 (s, 3H), 2.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.87, 167.29, 143.69, 137.00, 135.59, 133.96, 131.49, 131.26, 128.91, 128.62, 127.28, 127.25, 126.36, 52.53, 26.71 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 281.1178  $[\text{M} + \text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{17}\text{O}_3$ ; Found 281.1159.



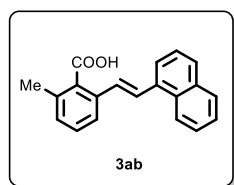
**Allyl (E)-2-(allyloxy)-6-styrylbenzoate (3q):** colorless liquid; yield 65% (31 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J$  = 7.4 Hz, 2H), 7.32–7.14 (m, 5H), 7.01 (d,  $J$  = 1.0 Hz, 2H), 6.75 (d,  $J$  = 8.0 Hz, 1H), 6.05–5.85 (m, 2H), 5.34 (t,  $J$  = 17.2 Hz, 2H), 5.25 – 5.11 (m, 2H), 4.80 (d,  $J$  = 5.3 Hz, 2H), 4.58 – 4.42 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.76, 155.77, 137.09, 136.39, 132.92, 132.15, 131.96, 130.51, 128.79, 128.16, 126.91, 125.09, 123.46, 119.04, 118.00, 117.54, 111.59, 69.58, 66.08 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 291.0990  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}$ ; Found 291.0997.



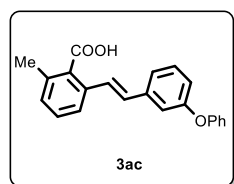
**Methyl (E)-2-methyl-4-(N-methylacetamido)-6-styrylbenzoate (3r):** colorless liquid; yield 65% (26 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 7.94 (m, 2H), 7.56 (d,  $J$  = 7.0 Hz, 3H), 7.38 (t,  $J$  = 7.4 Hz, 2H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.15 (d,  $J$  = 8.7 Hz, 1H), 7.01 (d,  $J$  = 16.3 Hz, 1H), 3.95 (s, 3H), 3.33 (s, 3H), 1.98 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.36, 167.20, 147.91, 138.72, 136.98, 132.66, 132.52, 128.97, 128.91, 128.45, 127.13, 126.43, 125.46, 125.30, 52.51, 22.72 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 310.1443  $[\text{M} + \text{H}]^+$  Calcd. For  $\text{C}_{19}\text{H}_{20}\text{NO}_3$ ; Found 310.1478.



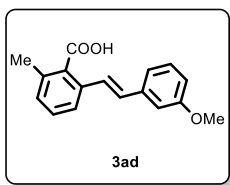
**(E)-2,4-dimethyl-6-styrylbenzoic acid (3ma):** white solid; yield 92% (34 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.45 (m, 2H), 7.43 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 7.09 – 6.96 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.34, 140.34, 137.32, 136.33, 136.05, 131.50, 130.73, 128.82, 128.74, 128.01, 126.90, 126.30, 124.19, 21.52, 20.42 ppm.



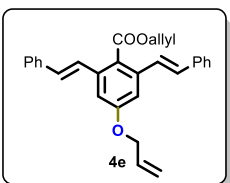
**(E)-2-methyl-6-(2-(naphthalen-1-yl)vinyl)benzoic acid (3ab):** white solid; yield 66% (29 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J$  = 8.4 Hz, 1H), 7.82 – 7.66 (m, 3H), 7.65 – 7.55 (m, 2H), 7.48 – 7.38 (m, 2H), 7.37 – 7.24 (m, 3H), 7.11 (d,  $J$  = 7.7 Hz, 1H), 2.38 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.98, 135.96, 135.89, 134.88, 133.80, 131.83, 131.49, 130.25, 129.79, 129.05, 128.74, 128.48, 127.81, 126.33, 126.00, 125.81, 124.19, 123.90, 123.77, 20.24 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 311.1048  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{Na}$ ; Found 311.1063.



**(E)-2-methyl-6-(3-phenoxy)styryl)benzoic acid (3ac):** white solid; yield 42% (21 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J$  = 7.9 Hz, 1H), 7.39 – 7.21 (m, 6H), 7.12 (dt,  $J$  = 14.8, 8.0 Hz, 3H), 7.05 – 6.96 (m, 3H), 6.89 (d,  $J$  = 7.4 Hz, 1H), 2.45 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.68, 157.68, 157.23, 139.15, 136.01, 135.41, 131.73, 131.18, 130.21, 130.08, 129.91, 129.86, 126.77, 123.52, 123.45, 121.75, 119.02, 118.46, 117.42, 20.28 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 353.1154  $[\text{M} + \text{Na}]^+$  Calcd. For  $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na}$ ; Found 353.1140.



**(E)-2-(3-methoxystyryl)-6-methylbenzoic acid (3ad):** white solid; yield 47% (19 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.7$  Hz, 1H), 7.44 – 7.32 (m, 2H), 7.23 (t,  $J = 7.6$  Hz, 1H), 7.18 (d,  $J = 7.5$  Hz, 1H), 7.15 – 7.06 (m, 2H), 7.03 (s, 1H), 6.86 – 6.77 (m, 1H), 3.81 (s, 3H), 2.48 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.94, 138.64, 136.00, 135.62, 131.78, 131.75, 130.25, 129.79, 129.75, 126.31, 123.54, 119.54, 113.70, 112.31, 55.37, 20.31 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 307.0737  $[\text{M} + \text{K}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{K}$ ; Found 307.0710.



**Allyl 4-(allyloxy)-2,6-di((E)-styryl)benzoate (4e):** colorless liquid; yield 70% (36 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.42 (m, 1H), 7.40 – 7.10 (m, 3H), 7.02 (d,  $J = 16.1$  Hz, 1H), 6.17 – 5.95 (m, 1H), 5.53 – 5.22 (m, 1H), 4.87 (d,  $J = 4.9$  Hz, 1H), 4.65 (d,  $J = 2.2$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.01, 159.63, 137.85, 137.08, 132.98, 132.03, 131.92, 128.81, 128.19, 126.93, 125.93, 125.11, 119.68, 118.18, 111.18, 69.10, 66.16 ppm; HRMS (ESI/TOF-Q)  $m/z$ : 423.1960  $[\text{M} + \text{H}]^+$  Calcd. For  $\text{C}_{29}\text{H}_{27}\text{O}_3$ ; Found 423.1962.

**NMR spectra of synthesized compounds**

