

Supporting Information

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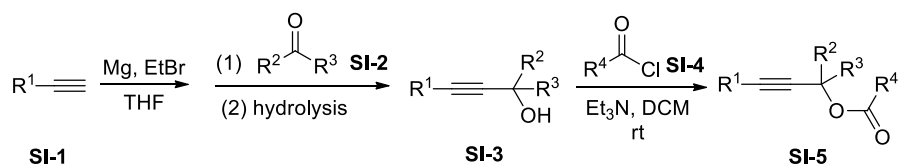
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I. General Information

Organic solvents (Aldrich) were used without further purification. Purifications of reaction products were carried out by flash chromatography using Merck silica gel (40-63 μm). ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvent peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

II. The General Synthetic Procedure and Analytical Data for Propargylic Acetates (Path a)

Propargylic alcohols (Path a) **SI-3** were prepared through alkynyl Grignard reagent with aldehydes or ketones **SI-2**. Esterification of **SI-3** gave Propargylic acetates **SI-5**.

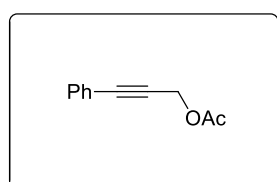


General Procedure:

Drops of ethyl bromide were added to Mg (72.9 mg, 3.0 mmol) in 2 mL anhydrous THF under N₂ condition, heating by blower to initiate the reaction. The rest of ethyl bromide (326.9 mg, 3.0 mmol) was dissolved in 3 mL THF and added drop by drop. Keep stirring for 1 hour at room temperature until no Mg left. The terminal alkyne **SI-1** (2.7 mmol) was added with constant pressure and the solution turned from light brown to brown. The mixture was stirred at r.t. for 30 min after the **SI-2** (2.7 mmol) was added. Hydrochloric acid (5 mL, 1 mol/L) was dropwise added to quench the reaction. The mixture was extracted by EA (30 mL x 3). Desired propargylic alcohols **SI-3** were synthesized with further purified by flash chromatography.

Dropwise adding acyl chloride **SI-4** (3.0 mmol) to the mixture of **SI-3** (1.5 mmol), triethylamine (303.6 mg, 3.0 mmol) and DCM (4.0 mL). Stirring the solution rapidly for 10 minutes and quenched by 10 mL water. The mixture was extracted by EA (30 mL x 3) and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na₂SO₄, evaporated and purified by flash chromatography. The purified propargylic acetates **SI-5** were dried by vacuum.

Analytical Data:



C₁₁H₁₀O₂

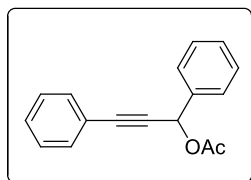
MW: 174.07 g.mol⁻¹

Yellow liquid

Yield: 82%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.47-7.45 (m, 2H), 7.36-7.29 (m, 3H), 4.91 (s, 2H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 170.4, 131.9, 128.8, 128.3, 122.1, 86.5, 82.9, 52.9, 20.9.



$\text{C}_{17}\text{H}_{14}\text{O}_2$

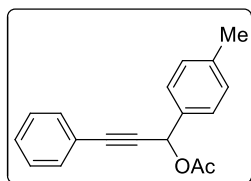
MW: 250.10 g.mol^{-1}

Colourless liquid

Yield: 81%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.62-7.60 (m, 2H), 7.45-7.48 (m, 2H), 7.44-7.38 (m, 3H), 7.35-7.32 (m, 3H), 6.70 (s, 1H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.9, 137.1, 132.0, 129.0, 128.9, 128.7, 128.3, 127.9, 122.1, 87.1, 85.5, 66.1, 21.2.



$\text{C}_{18}\text{H}_{16}\text{O}_2$

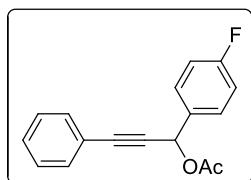
MW: 264.12 g.mol^{-1}

Colourless liquid

Yield: 43.7%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.51-7.47 (m, 4H), 7.34-7.29 (m, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.67 (s, 1H), 2.38 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 170.0, 139.0, 134.3, 131.9, 129.4, 128.8, 128.3, 127.9, 122.2, 86.9, 85.8, 66.0, 21.3, 21.2.



$\text{C}_{17}\text{H}_{13}\text{FO}_2$

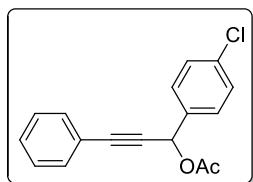
MW: 286.09 g.mol^{-1}

Colourless liquid

Yield: 55.2%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.59 (dd, $J = 8.4$ Hz, $J = 5.2$ Hz, 2H), 7.48 (dd, $J = 7.2$ Hz, $J = 1.6$ Hz, 2H), 7.35-7.30 (m, 3H), 7.09 (t, $J = 8.86$ Hz, 2H), 6.67 (s, 1H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm):169.9, 163.0 (d, $J = 246.6$ Hz), 133.1 (d, $J = 3.2$ Hz), 131.9, 129.8 (d, $J = 8.4$ Hz), 129.0, 128.4, 121.9, 115.6 (d, $J = 21.7$ Hz), 87.2, 85.3, 65.4, 21.2.



$\text{C}_{17}\text{H}_{13}\text{ClO}_2$

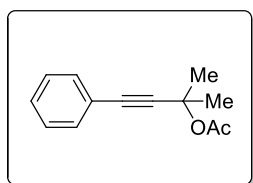
MW: 284.04 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 93%

^1H NMR (400 MHz, CDCl_3 , δ ppm):7.54 (dt, $J = 8.4\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 7.48 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 2H), 7.38 (dt, $J = 8.8$ Hz, $J = 2.4$ Hz, 2H), 7.35-7.30 (m, 3H), 6.67 (s, 1H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.8, 135.8, 134.9, 131.9, 129.2, 129.0, 128.9, 128.4, 121.9, 87.4, 85.1, 65.4, 21.1.



$\text{C}_{13}\text{H}_{14}\text{O}_2$

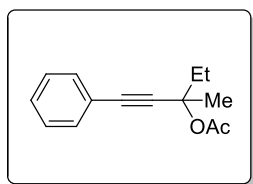
MW: 202.10 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 28.8%

^1H NMR (400 MHz, CDCl_3 , δ ppm):7.43-7.42 (m, 2H), 7.30-7.28 (m, 3H), 2.05 (s, 3H), 1.75 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm):169.4, 131.8, 128.3, 128.2, 122.6, 90.2, 84.0, 72.5, 29.1, 22.1.



$\text{C}_{14}\text{H}_{16}\text{O}_2$

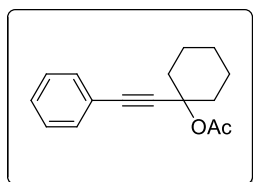
MW: 216.12 $\text{g}\cdot\text{mol}^{-1}$

Yellow liquid

Yield: 16.2%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.45-7.42 (m, 2H), 7.31-7.28 (m, 3H), 2.05, (s, 3H), 2.09-1.87 (m, 2H), 1.74 (s, 3H), 1.08 (t, $J = 7.6$, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.5, 131.9, 131.8, 128.3, 128.2, 122.7, 89.3, 85.0, 76.2, 34.6, 26.1, 22.1, 8.7.



$\text{C}_{16}\text{H}_{18}\text{O}_2$

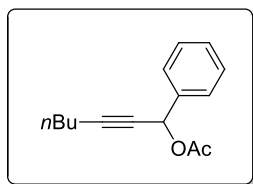
MW: 242.13 $\text{g}\cdot\text{mol}^{-1}$

Yellow liquid

Yield: 16.2 %

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.46-7.43 (m, 2H), 7.31- 7.28 (m, 3H), 2.24-2.21 (m, 2H), 2.07 (s, 3H), 1.93-1.87 (m, 2H), 1.70-1.64 (m, 4H), 1.58-1.55 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.3, 131.9, 128.2, 122.8, 89.2, 86.2, 53.5, 37.2, 25.3, 22.8, 22.1.



$\text{C}_{15}\text{H}_{18}\text{O}_2$

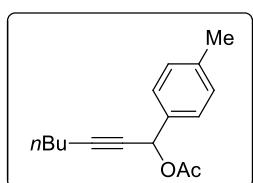
MW: 230.13 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 71.1%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.54-7.51 (m, 2H), 7.40-7.34 (m, 3H), 6.46 (t, $J = 2.0$ Hz, 1H), 2.27 (td, $J = 7.2$ Hz, $J = 2.0$ Hz, 2H), 2.10 (s, 3H), 1.55-1.49 (m, 2H), 1.44-1.38 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 167.0, 137.7, 128.8, 128.6, 127.7, 88.4, 66.1, 30.5, 22.2, 21.2, 18.6, 13.6.



$\text{C}_{16}\text{H}_{20}\text{O}_2$

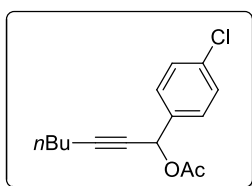
MW: 244.15 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 57.6%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.41 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.42 (t, $J = 2.0$ Hz, 1H), 2.35 (s, 3H), 2.27 (td, $J = 6.8$ Hz, $J = 2.0$ Hz, 2H), 2.08 (s, 3H), 1.54-1.48 (m, 2H), 1.43-1.38 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 167.0, 138.7, 134.8, 129.2, 127.7, 88.2, 66.0, 30.5, 22.0, 21.2, 21.2, 18.6, 13.6.



$\text{C}_{15}\text{H}_{17}\text{ClO}_2$

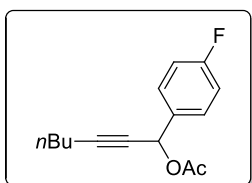
MW: 264.09 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 47.1%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.45 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.41 (t, $J = 2.0$ Hz, 1H), 2.27 (td, $J = 6.8$ Hz, $J = 2.0$ Hz, 2H), 2.09 (s, 3H), 1.54-1.48 (m, 2H), 1.43-1.37 (m, 2H), 0.91 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.8, 136.3, 134.7, 129.1, 128.8, 88.8, 65.4, 30.4, 22.0, 21.1, 18.5, 13.6.



$\text{C}_{15}\text{H}_{17}\text{FO}_2$

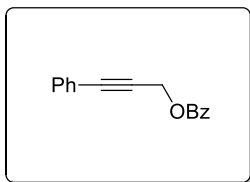
MW: 248.12 $\text{g}\cdot\text{mol}^{-1}$

Colourless liquid

Yield: 53%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.52-7.48 (m, 2H), 7.05 (t, $J = 8.8$ Hz, 2H), 6.43 (t, $J = 2.0$ Hz, 1H), 2.27 (td, $J = 6.8$ Hz, $J = 2.0$ Hz, 2H), 2.08 (s, 3H), 1.54-1.49 (m, 2H), 1.43-1.37 (m, 2H), 0.91 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 169.9, 162.9 (d, $J = 246.2$ Hz), 133.7 (d, $J = 3.2$ Hz), 129.7 (d, $J = 8.3$ Hz), 115.5 (d, $J = 21.6$), 88.6, 65.4, 30.5, 22.0, 21.2, 18.5, 13.6.



$C_{16}H_{12}O_2$

MW:236.08 g.mol⁻¹

Yellow liquid

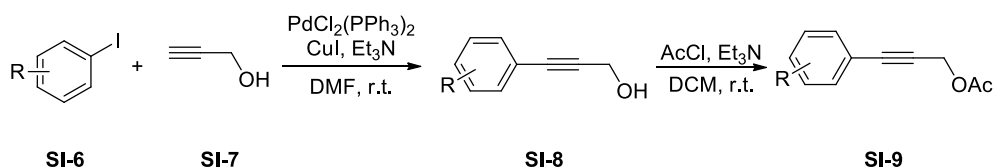
Yield: 85%

¹H NMR (400 MHz, DMSO-d₆, δ ppm):8.11 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 6.8 Hz, 1H), 7.48-7.45 (m, 4H), 7.33-7.30 (m, 3H), 5.16 (s, 2H).

¹³C NMR (100 MHz, DMSO-d₆, δ ppm):166.0, 133.3, 132.0, 129.9, 129.6, 128.8, 128.5, 128.3, 122.2, 86.6, 83.1, 53.4.

III. The General Synthetic Procedure and Analytical Data for Propargylic Acetates (Path b)

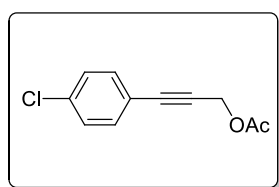
Propargylic alcohols (Path b) **SI-8** were synthesized from aryl iodides and propargylic alcohols through Sonogashira reaction. Esterification of **SI-8** gave Propargylic acetates **SI-9**.



To a solution of **SI-6** (3.0 mmol), CuI (32.8 mg, 0.3 mmol) and PdCl₂(PPh₃)₂ (63.2 mg, 0.09 mmol) in Et₃N (5 mL) was added propargyl alcohol **SI-7** (185.0 mg, 3.3 mmol) and DMF (3 mL) at r.t. under N₂. After stirring for 1 hour, the mixture was extracted by EA and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na₂SO₄ and evaporated to solid in the addition of silica gel. The crude phenyl propargylic alcohols **SI-8** were purified by flash chromatography.

Dropwise adding acetyl chloride (235.5 mg, 3.0 mmol) to the mixture of **SI-8** (1.5 mmol), triethylamine (303.6 mg, 3.0 mmol) and DCM (4.0 mL). Stirring the solution rapidly for 10 minutes and quenched by 10 mL water. The mixture was extracted by EA (30 mL x 3) and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The crude products were dried over Na₂SO₄, evaporated and purified by flash chromatography. Dried by vacuum, the purified propargylic acetates **SI-9** were gained.

Analytical Data:



C₁₁H₉ClO₂

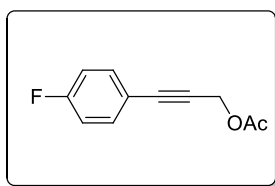
MW: 208.03 g.mol⁻¹

Light-Yellow liquid

Yield: 38%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.36 (dd, *J* = 36.4 Hz, *J* = 8.4 Hz, 4H), 4.89 (s, 2H), 2.13 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 170.3, 134.9, 133.2, 128.7, 120.6, 85.3, 83.9, 52.7, 20.8.



$C_{11}H_9FO_2$

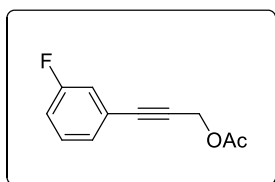
MW: 192.06 g.mol⁻¹

Light-Yellow liquid

Yield: 88.9%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.44 (dd, $J = 8.2$ Hz, $J = 5.6$ Hz, 2H), 7.00 (t, $J = 2.1$ Hz, 2H), 4.89 (s, 2H), 2.13 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 170.4, 162.8 (d, $J = 248.6$ Hz), 133.9 (d, $J = 8.4$ Hz), 118.2 (d, $J = 3.6$ Hz), 115.7 (d, $J = 21.9$), 85.4, 82.7, 52.8, 20.8.



$C_{11}H_9FO_2$

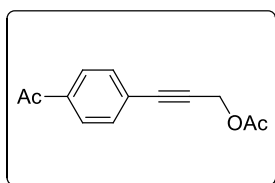
MW: 192.06 g.mol⁻¹

Light-Yellow liquid

Yield: 89.6%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.31-7.22 (m, 2H), 7.14 (d, $J = 9.6$ Hz, 1H), 7.07-7.02 (m, 1H), 4.89 (s, 2H), 2.13 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 170.3, 162.8 (d, $J = 245.1$), 129.9 (d, $J = 8.6$ Hz), 127.8 (d, $J = 3.1$ Hz), 123.9 (d, $J = 9.4$ Hz), 118.7 (d, $J = 22.7$ Hz), 116.2 (d, $J = 21.0$ Hz), 85.2 (d, $J = 3.4$ Hz), 85.2 (d, $J = 3.4$ Hz), 83.9, 52.6, 20.8.



$C_{13}H_{12}O_3$

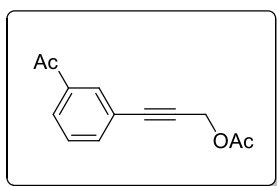
MW: 216.08 g.mol⁻¹

White solid

Yield: 99%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.82 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 4.84 (s, 2H), 2.51 (s, 3H), 2.06 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 197.1, 170.1, 136.6, 131.9, 128.1, 126.9, 86.2, 85.4, 52.5, 26.5, 20.7.



$C_{13}H_{12}O_3$

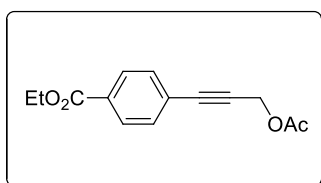
MW: 216.08 g.mol⁻¹

Light-Yellow solid

Yield: 85.5%

¹H NMR (400 MHz, CDCl₃, δ ppm): 8.04 (t, *J* = 1.6 Hz, 1H), 7.93 (dt, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 7.64 (dt, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 4.92 (s, 2H), 2.61 (s, 3H), 2.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 197.3, 170.3, 137.1, 136.1, 131.9, 128.7, 128.4, 122.8, 85.4, 84.0, 52.7, 26.7, 20.8.



$C_{14}H_{14}O_4$

MW: 246.09 g.mol⁻¹

White solid

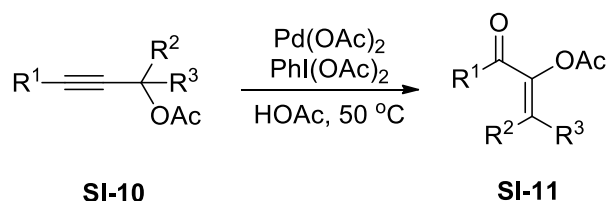
Yield: 97%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.99 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 4.91 (s, 2H), 4.37 (dd, *J* = 14.4 Hz, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

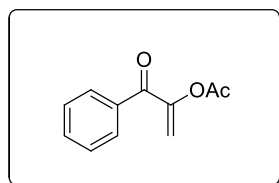
¹³C NMR (100 MHz, CDCl₃, δ ppm): 170.2, 165.9, 131.7, 130.4, 129.4, 126.7, 85.8, 85.6, 61.2, 52.6, 20.7, 14.3.

IV. Tahe General Synthetic Procedure and Analytical Data for acetoxyenones

To a solution of Pd(OAc)₂ (3.4mg, 0.015 mmol) and PhI(OAc)₂ (106.3mg, 0.33 mmol) in HOAc (3 mL) was added **SI-10** (0.3 mmol). Stirring for 10 minutes at 50 °C, 5 mL water was added to quench the reaction. Then the mixture was extracted by EA and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na₂SO₄, evaporated and purified by flash chromatography. The purified acetoxyenones **SI-11** were dried by vacuum.



Analytical Data:



C₁₁H₁₀O₃

MW: 190.06 g.mol⁻¹

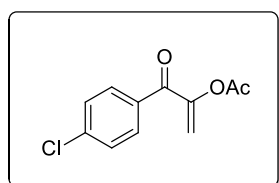
Light-Yellow liquid

Yield: 81%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.87-7.84 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.72 (d, *J* = 2.0 Hz, 1H), 5.59 (d, *J* = 2.0 Hz, 1H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 189.8, 169.0, 151.2, 136.2, 133.0, 129.6, 128.4, 114.6, 20.4.

MS (EI) *m/z*: 190(M⁺); HRMS: Calcd for C₁₁H₁₀O₃ 190.0630, found 190.0633.



C₁₁H₉ClO₃

MW: 224.02 g.mol⁻¹

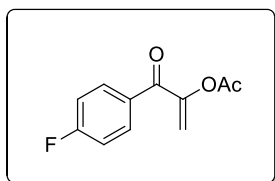
Green-Yellow liquid

Yield: 75%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 6.0 Hz, 2H), 7.44 (d, *J* = 6.0 Hz, 2H), 5.70 (d, *J* = 1.6 Hz, 1H), 5.54 (d, *J* = 1.6 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 188.6, 169.0, 150.9, 137.5, 134.5, 131.1 (d, *J* = 21.1 Hz), 128.1 (d, *J* = 13.2 Hz), 114.3, 20.4.

MS (EI) m/z :224 (M^+); **HRMS:** Calcd for $C_{11}H_9ClO_3$ 224.0240, found 224.0242.



$C_{11}H_9FO_3$

MW: 208.05 g.mol⁻¹

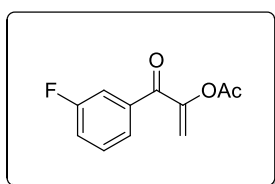
Green-Yellow liquid

Yield: 85%

¹H NMR (400 MHz, CDCl₃, δ ppm):7.93-7.89 (m, 2H), 7.15 (t, J = 8.4 Hz, 2H), 5.70 (d, J = 2.4 Hz, 1H), 5.54 (d, J = 2.0 Hz, 1H), 2.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 188.3, 169.0, 162.9 (d, J = 299.6 Hz), 151.0, 132.4, 132.2 (d, J = 9.3 Hz), 115.7 (d, J = 21.8 Hz), 114.1, 20.4.

MS (EI) m/z :208 (M^+); **HRMS:** Calcd for $C_{11}H_9FO_3$ 208.0536, found 208.0533.



$C_{11}H_9FO_3$

MW: 208.05 g.mol⁻¹

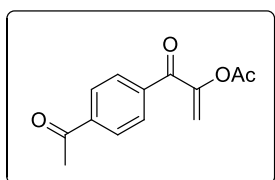
Green-Yellow liquid

Yield: 73%

¹H NMR (400 MHz, CDCl₃, δ ppm):7.65 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.47-7.42 (m, 1H), 7.29 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 5.73 (d, J = 2.0 Hz, 1H), 5.59 (d, J = 2.4 Hz, 1H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 188.4, 169.0, 162.4 (d, J = 246.8 Hz), 150.8, 138.1 (d, J = 6.7 Hz), 130.2 (d, J = 7.7 Hz), 125.3 (d, J = 3.0 Hz), 120.1 (d, J = 21.3 Hz), 116.4 (d, J = 22.6 Hz), 114.8, 20.4.

MS (EI) m/z :208 (M^+); **HRMS:** Calcd for $C_{11}H_9FO_3$ 208.0536, found 208.0534.



$C_{13}H_{12}O_4$

MW: 232.07 g.mol⁻¹

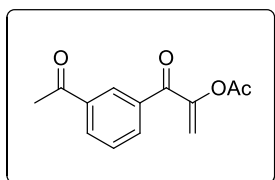
Yellow liquid

Yield: 72%

¹H NMR (400 MHz, CDCl₃, δ ppm):8.02 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 5.76 (d, J = 2.0 Hz, 1H), 5.58 (d, J = 2.0 Hz, 1H), 2.65 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 197.5, 189.1, 169.0, 151.0, 140.0, 139.8, 129.6, 128.2, 115.3, 26.9, 20.4.

MS (EI) m/z :232 (M^+); **HRMS:** Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_4$ 232.0736, found 232.0736.



$\text{C}_{13}\text{H}_{12}\text{O}_4$

MW: 232.07 $\text{g}\cdot\text{mol}^{-1}$

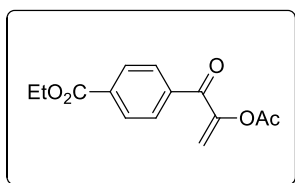
Yellow liquid

Yield: 76%

^1H NMR (400 MHz, CDCl_3 , δ ppm):8.40 (t, J = 1.6 Hz, 1H), 8.17 (dt, J = 8.0 Hz, J = 1.2 Hz, 1H), 8.04 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 5.75 (d, J = 2.0 Hz, 1H), 5.58 (d, J = 2.4 Hz, 1H), 2.64 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 197.2, 189.0, 169.0, 150.9, 137.2, 136.6, 133.8, 132.3, 129.3, 128.9, 114.9, 26.8, 20.4.

MS (EI) m/z :232 (M^+); **HRMS:** Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_4$ 232.0736, found 232.0737.



$\text{C}_{14}\text{H}_{14}\text{O}_5$

MW: 262.08 $\text{g}\cdot\text{mol}^{-1}$

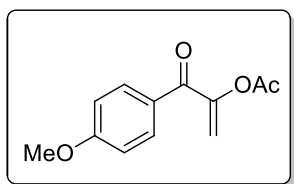
Yield liquid

Yield: 47%

^1H NMR (400 MHz, CDCl_3 , δ ppm):8.12 (d, J = 8.4Hz, 2H), 7.88 (d, J = 8.4Hz, 2H), 5.74 (J = 2.0Hz, 1H), 5.58 (d, J = 2.0Hz, 1H), 4.41 (dd, J = 14.0Hz, J = 6.8Hz, 2H), 2.23 (s, 3H), 1.41 (t, J = 7.2Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm):189.2, 168.9, 165.7, 151.1, 139.8, 134.1, 129.5, 129.3, 115.1, 61.5, 20.4, 14.3.

MS (EI) m/z :262 (M^+); **HRMS:** Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_5$ 262.0841, found 264.0842.



$\text{C}_{12}\text{H}_{12}\text{O}_4$

MW: 220.07 $\text{g}\cdot\text{mol}^{-1}$

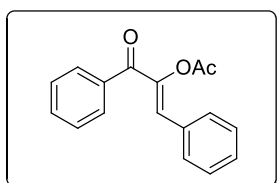
Yellow liquid

Yield: 55%

^1H NMR (400 MHz, CDCl_3 , δ ppm):7.90-7.86 (m, 2H), 6.95-6.91 (m, 2H), 5.63 (d, $J = 2.0$ Hz, 1H), 5.47 (d, $J = 2.0$ Hz, 1H), 3.85 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm):189.4, 169.0, 163.7, 151.2, 132.1, 128.8, 113.8, 113.2, 55.6, 20.5.

MS (EI) m/z :220 (M^+); **HRMS:** Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$ 220.0736, found 220.0735.



$\text{C}_{17}\text{H}_{14}\text{O}_3$

MW: 266.09 $\text{g}\cdot\text{mol}^{-1}$

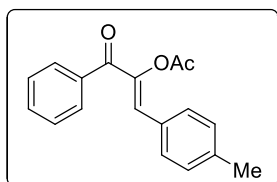
Yellow liquid

Yield: 58%

^1H NMR (400 MHz, CDCl_3 , δ ppm):7.87 (d, $J = 6.8$ Hz, 2H), 7.64-7.61 (m, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.43-7.39 (m, 3H), 6.87 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 190.7, 168.5, 144.6, 137.5, 136.9, 132.6, 132.2, 130.3, 130.0, 129.6, 129.5, 128.9, 128.4, 20.8.

MS (EI) m/z :266 (M^+); **HRMS:** Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3$ 266.0943, found 266.0945.



$\text{C}_{18}\text{H}_{16}\text{O}_3$

MW: 280.11 $\text{g}\cdot\text{mol}^{-1}$

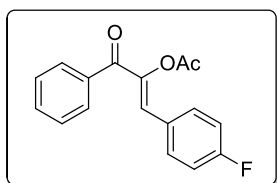
Yellow liquid

Yield: 66%

^1H NMR (400 MHz, CDCl_3 , δ ppm):7.85 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.86 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 190.7, 168.5, 144.1, 140.5, 137.1, 132.4, 130.3, 130.0, 129.6, 129.4, 129.4, 128.4, 21.5, 20.8.

MS (EI) m/z :280 (M^+); **HRMS:** Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3$ 280.1099, found 280.1099.



$\text{C}_{17}\text{H}_{13}\text{FO}_3$

MW: 284.08 $\text{g}\cdot\text{mol}^{-1}$

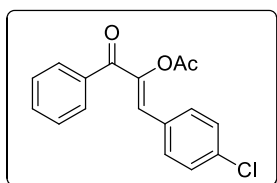
Yellow liquid

Yield: 59%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.86-7.84 (m, 2H), 7.63 (td, $J = 6.4$ Hz, $J = 2.4$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.10 (t, $J = 8.8$ Hz, 2H), 6.83 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 190.5, 168.4, 163.4 (d, $J = 250.7$ Hz), 144.3 (d, $J = 2.4$ Hz), 136.8, 132.6, 132.3 (d, $J = 8.4$ Hz), 129.4, 128.5, 128.3, 116.0 (d, $J = 21.6$ Hz), 20.8.

MS (EI) m/z : 284 (M^+); **HRMS:** Calcd for $\text{C}_{17}\text{H}_{13}\text{FO}_3$ 284.0849, found 284.0848.



$\text{C}_{17}\text{H}_{13}\text{ClO}_3$

MW: 300.06 g.mol $^{-1}$

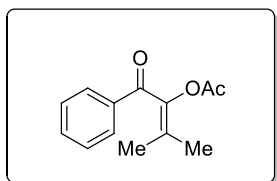
Yellow liquid

Yield: 62%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.86-7.84 (m, 2H), 7.62-7.55 (m, 3H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 6.81 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 190.5, 168.4, 144.9, 136.7, 135.9, 132.7, 131.4, 130.7, 129.5, 129.1, 128.5, 127.9, 20.8.

MS (EI) m/z : 300 (M^+); **HRMS:** Calcd for $\text{C}_{17}\text{H}_{13}\text{ClO}_3$ 300.0553, found 300.0553.



$\text{C}_{13}\text{H}_{14}\text{O}_3$

MW: 218.09 g.mol $^{-1}$

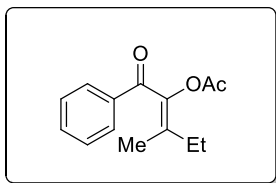
Yellow liquid

Yield: 70%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.82 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 2.04 (s, 3H), 1.88 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 190.9, 169.3, 137.7, 132.6, 129.1, 128.4, 20.3, 20.1, 19.5.

MS (EI) m/z : 218 (M^+); **HRMS:** Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ 218.0943, found 218.0942



$C_{14}H_{16}O_3$

MW: 232.11 g.mol⁻¹

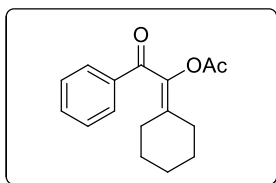
Yellow liquid

Yield: 75%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.85-7.82 (m, 2H), 7.52(t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 2.26-2.22 (m, 2H), 2.04 (s, 1.3H), 2.03 (s, 1.7H), 1.87 (s, 1.7 H), 1.84 (s, 1.3H), 1.08(dd, *J* = 17.2 Hz, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 191.1, 190.8, 169.4, 169.2, 139.8, 139.1, 139.0, 137.8, 137.8, 132.6, 132.6, 129.1, 129.0, 128.3, 128.3, 29.7, 26.2, 26.1, 20.3, 17.5, 16.4, 12.6, 11.9.

MS (EI) *m/z*: 232 (M⁺); **HRMS:** Calcd for C₁₄H₁₆O₃ 232.1099, found 232.1098.



$C_{16}H_{18}O_3$

MW: 258.13 g.mol⁻¹

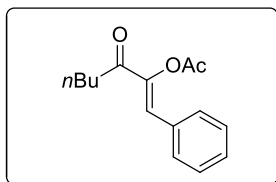
Light-Yellow liquid

Yield: 77%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.88 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 2.34 (t, *J* = 5.6 Hz, 2H), 2.20 (t, *J* = 6.4 Hz, 2H), 2.08 (s, 3H), 1.67 (d, *J* = 7.6 Hz, 2H), 1.58-1.52 (m, 4H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 191.4, 169.5, 140.0, 138.0, 137.0, 132.8, 129.2, 128.4, 29.8, 28.8, 27.5, 27.3, 26.1, 20.4.

MS (EI) *m/z*: 258 (M⁺); **HRMS:** Calcd for C₁₆H₁₈O₃ 258.1256, found 258.1255.



$C_{15}H_{18}O_3$

MW: 246.13 g.mol⁻¹

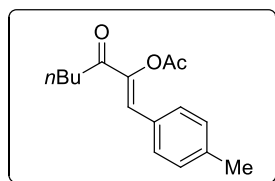
Yellow liquid

Yield: 66%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.61 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 2H), 7.42-7.39 (m, 3H), 7.18 (s, 1H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.72-1.65 (m, 2H), 1.42-1.36 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 194.7, 168.6, 144.7, 132.1, 130.2, 130.0, 128.9, 127.2, 37.0, 26.4, 22.4, 20.8, 13.9.

MS (EI) m/z :246 (M^+); **HRMS:** Calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1258.



$C_{16}H_{20}O_3$

MW: 260.14 $g \cdot mol^{-1}$

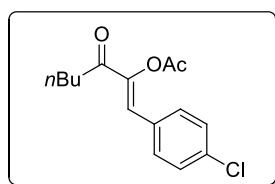
Yellow liquid

Yield: 78%

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.16 (s, 1H), 2.74 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.71-1.64 (m, 2H), 1.41-1.40 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 194.6, 168.6, 144.2, 140.5, 130.2, 129.6, 129.3, 127.4, 37.0, 26.4, 22.4, 21.5, 20.8, 13.9.

MS (EI) m/z :260 (M^+); **HRMS:** Calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1415.



$C_{15}H_{17}ClO_3$

MW:280.09 $g \cdot mol^{-1}$

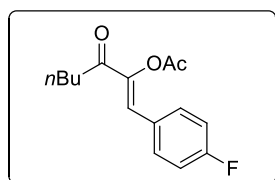
Yellow liquid

Yield: 82%

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.53 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.11 (s, 1H), 2.73 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.70-1.63 (m, 2H), 1.41-1.35 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):194.5, 168.4, 145.0, 135.9, 131.3, 130.6, 129.1, 125.7, 37.0, 26.3, 22.3, 20.7, 13.9.

MS (EI) m/z :280 (M^+); **HRMS:** Calcd for $C_{15}H_{17}ClO_3$ 280.0866, found 280.0867.



$C_{15}H_{17}FO_3$

MW:264.12 $g \cdot mol^{-1}$

Yellow liquid

Yield: 85%

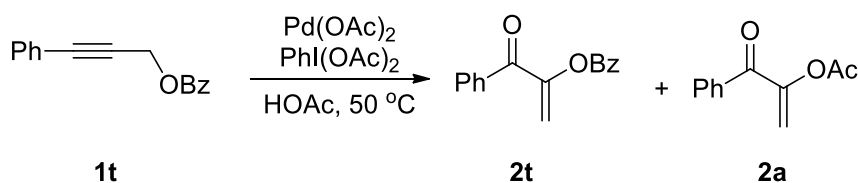
1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.62-7.59 (m, 2H), 7.13 (s, 1H), 7.09 (t, J = 8.8 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.71-1.63 (m, 2H), 1.41-1.35 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm):194.5, 168.5, 163.4 (d, *J* = 250.5 Hz), 144.5 (d, *J* = 2.3 Hz), 132.2 (d, *J* = 8.4 Hz), 128.3 (d, *J* = 3.5 Hz), 125.9, 116.1 (d, *J* = 21.7 Hz),37.0, 26.3, 22.3, 20.7, 13.9.

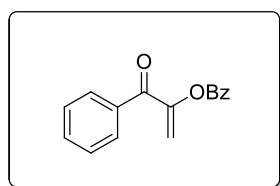
MS (EI) *m/z*:264 (M⁺); **HRMS:** Calcd for C₁₅H₁₇FO₃ 264.1162, found 264.1162.

V. The General Synthetic Procedure and Analytical Data for Compounds 2t.

To a solution of $\text{Pd}(\text{OAc})_2$ (3.4mg, 0.015 mmol) and $\text{PhI}(\text{OAc})_2$ (106.3mg, 0.33 mmol) in HOAc (3 mL) was added **1t** (71.9 mg, 0.3 mmol). Stirring for 10 minutes at 50 °C, 5 mL water was added to quench the reaction. Then the mixture was extracted by EA and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na_2SO_4 , evaporated and purified by flash chromatography. The purified acetoxynones **2t** and **2a** were dried by vacuum.



Analysis Data :



$\text{C}_{16}\text{H}_{12}\text{O}_3$

MW: 252.08 $\text{g}\cdot\text{mol}^{-1}$

Light-Yellow liquid

Yield: 56%

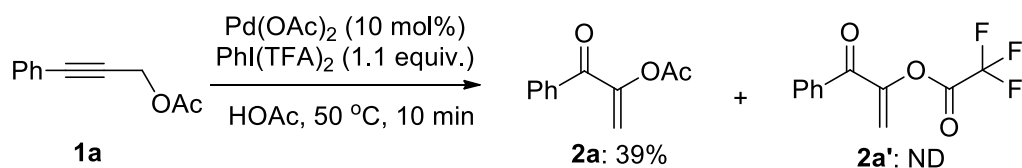
^1H NMR (400 MHz, CDCl_3 , δ ppm): 8.14 (d, $J = 7.2$ Hz, 2H), 7.94 (d, $J = 7.6$ Hz, 2H), 7.65-7.57 (m, 2H), 7.48 (dd, $J = 12.8$ Hz, $J = 8.0$ Hz, 4H), 5.86 (d, $J = 2.0$ Hz, 1H), 5.69 (d, $J = 2.0$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 189.7, 164.8, 151.4, 136.2, 133.9, 133.0, 130.3, 129.7, 128.6, 128.4, 114.6.

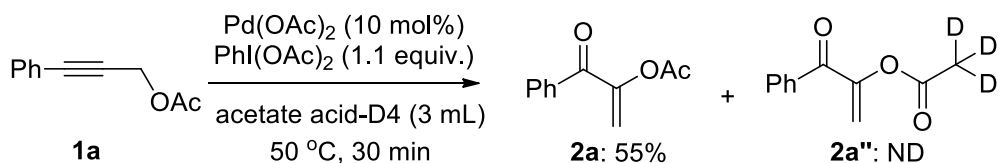
MS (EI) m/z : 252 (M^+); **HRMS:** Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3$ 252.0786, found 252.0788.

VI. The General Synthetic Procedure for Control Experiment.

To a solution of $\text{Pd}(\text{OAc})_2$ (3.4 mg, 0.015 mmol) and $\text{PhI}(\text{TFA})_2$ (141.9 mg, 0.33 mmol) in HOAc (3 mL) was added **1a** (52.3 mg, 0.3 mmol). Stirring for 10 minutes at 50 °C, 5 mL water was added to quench the reaction. Then the mixture was extracted by EA and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na_2SO_4 , evaporated and purified by flash chromatography. The purified acetoxyenones **2a** were dried by vacuum.



To a solution of $\text{Pd}(\text{OAc})_2$ (3.4 mg, 0.015 mmol) and $\text{PhI}(\text{OAc})_2$ (106.3 mg, 0.33 mmol) in deuterium-labelled acetate acid-D₄ (3 mL) was added **1a** (52.3 mg, 0.3 mmol). Stirring for 30 minutes at 50 °C, 5 mL water was added to quench the reaction. Then the mixture was extracted by EA and washed with an aqueous solution of NaCl_{sat} (30 mL x 3). The organic part was dried over Na_2SO_4 , evaporated and purified by flash chromatography. The purified acetoxyenones **2a** were dried by vacuum.



VII. Copies of the ^1H NMR, ^{13}C NMR

