Supporting Information

Palladium-Catalyzed Regio- and Stereoselective Hydrosulfonation of Propiolate Esters

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Content

• Experimental procedure for synthesis of enynoates 5 2-4
• Table S1-S2 5–6
• Copies of $^1$H and $^{13}$C-NMR spectra of alkenyl sulfonates 7–64
• Copies of $^1$H and $^{13}$C-NMR spectra of enynoates 5 65–78
**Experimental procedure for synthesis of (Z)-methyl 5-arylpent-2-en-4-yonoate (5)**

To a pressure-affordable thick-wall glass tube containing 3k (276 mg, 1.0 mmol), Pd(PPh₃)₄ (115 mg, 0.1 mmol), and Cul (57 mg, 0.3 mmol) was added 3 mL of anhydrous THF. Then, the reaction tube was closed with septum and purged argon for 3 min. To this solution, acetylene 4 (3.0 mmol) was added and again purged argon for 5 min. Then, anhydrous (i-Pr)₂NEt (1.5 mL) was added and the solution was bubbled argon for another 1 min. After septum was removed, molecule sieves (4Å) was added to the reaction mixture and closed with a Teflon cap. The reaction mixture was heated 90 °C for 24 h with stirring. Upon cooling down to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate followed by filtration through a short pad of celite. The filtrate was concentrated in vacuum, and then the residue was purified by flash chromatography (eluent: hexane: ethyl acetate) to afford products 5.

**(Z)-methyl 5-phenylpent-2-en-4-yonoate (5a)**

Yield: 82 % (152 mg); colorless oil; \( R_f = 0.25 \) (hexanes/EA = 10/1).

FT-IR (KBr) \( \tilde{\nu} \): 2951, 2920, 2852, 1720, 1713, 1458, 1166, 1097, 1026, 757 cm⁻¹.

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.47–7.49 \) (m, 2H), 7.25–7.26 (m, 3H), 6.28 (d, \( J = 11.4 \) Hz, 1H), 6.07 (d, \( J = 11.4 \) Hz, 1H), 3.69 (s, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta = 165.0, 132.1, 129.2, 128.4, 127.8, 123.1, 122.6, 101.3, 86.5, 51.3 \) ppm.

HRMS (EI⁺): \( m/z [M^+ \text{ calcd for } C_{12}H_{10}O_2: 187.0754; \text{ found: } 187.0753. \)

**(Z)-methyl 3-methyl-5-phenylpent-2-en-4-yonoate (5b)**

Yield: 79 % (158 mg); light yellow oil; \( R_f = 0.29 \) (hexanes/EA = 10/1).

FT-IR (KBr) \( \tilde{\nu} \): 2953, 2919, 2848, 1722, 1715, 1460, 1163, 1090, 1025, 759 cm⁻¹.

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.53–7.55 \) (m, 2H), 7.32–7.34 (m, 3H), 6.03 (d, \( J = 1.4 \) Hz, 1H), 3.75 (s, 3H), 2.12 (d, \( J = 1.4 \) Hz, 1H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta = 165.4, 134.9, 132.0, 129.0, 128.3, 123.8, 122.6, 100.3, 88.2, 51.2, 25.1 \) ppm.

HRMS (EI⁺): \( m/z [M^+ \text{ calcd for } C_{13}H_{12}O_2: 200.0837; \text{ found: } 200.0831. \)

**(Z)-methyl 5-(4-tert-butylphenyl)pent-2-en-4-yonoate (5c)**
Yield: 73 % (176 mg); colorless oil; \( R_f = 0.58 \) (hexanes/EA = 10/1).

FT-IR (KBr) \( \tilde{\nu} \): 3083, 3034, 2962, 2906, 2870, 2199, 1730, 1598, 1503, 1462, 1437, 1405, 1269, 1217, 1170, 1021, 836, 816, 563 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.40 \) (d, \( J = 8.4 \) Hz, 2H), 7.29 (d, \( J = 8.4 \) Hz, 2H), 6.29 (d, \( J = 11.4 \) Hz, 1H), 6.04 (d, \( J = 11.4 \) Hz, 1H), 3.72 (s, 3H), 1.24 (s, 9H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 165.7, 153.1, 132.3, 127.7, 125.8, 120.0, 102.3, 86.4, 51.9, 35.3, 31.5 \) ppm.

HRMS (EI\(^+\)): \( m/z [M^+] \) calcd for C\(_{16}\)H\(_{18}\)O\(_2\): 242.1307; found: 242.1309.

(Z)-methyl 5-p-tolylpent-2-en-4-ynoate (5d)

Yield: 76 % (152 mg); colorless oil; \( R_f = 0.41 \) (hexanes/EA = 10/1).

FT-IR (KBr) \( \tilde{\nu} \): 2957, 2922, 2854, 2199, 1729, 1612, 1436, 1262, 1170, 1095, 1024, 815 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.46 \) (d, \( J = 8.1 \) Hz, 2H), 7.18 (d, \( J = 7.9 \) Hz, 2H), 6.39 (d, \( J = 11.4 \) Hz, 1H), 6.15 (d, \( J = 11.4 \) Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 165.3, 139.7, 132.1, 129.2, 127.2, 123.4, 119.5, 101.9, 86.0, 51.5, 21.6 \) ppm.

HRMS (EI\(^+\)): \( m/z [M^+] \) calcd for C\(_{13}\)H\(_{12}\)O\(_2\): 201.0916; found: 201.0905.

(Z)-methyl 5-(4-methoxyphenyl)pent-2-en-4-ynoate (5e)

Yield: 68 % (146 mg); colorless oil; \( R_f = 0.26 \) (hexanes/EA = 5/1).

FT-IR (KBr) \( \tilde{\nu} \): 2951, 2909, 2839, 2195, 1725, 1597, 1510, 1461, 1439, 1297, 1165, 1031, 834, 538 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.50 \) (d, \( J = 8.9 \) Hz, 2H), 6.88 (d, \( J = 8.9 \) Hz, 2H), 6.37 (d, \( J = 11.4 \) Hz, 1H), 6.11 (d, \( J = 11.4 \) Hz, 1H), 3.81 (s, 3H) ppm.

\(^13\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 165.4, 160.4, 133.8, 126.5, 123.5, 114.6, 114.0, 102.1, 85.7, 55.2, 51.4 \) ppm.

HRMS (EI\(^+\)): \( m/z [M^+] \) calcd for C\(_{13}\)H\(_{12}\)O\(_3\): 216.0786; found: 216.0784.

(Z)-methyl 5-(4-fluorophenyl)pent-2-en-4-ynoate (5f)

Yield: 49 % (100 mg); colorless oil; \( R_f = 0.4 \) (hexanes/EA = 10/1).

FT-IR (KBr) \( \tilde{\nu} \): 2952, 2926, 2853, 2203, 1725, 1596, 1506, 1230, 1173, 837, 816, 531 cm\(^{-1}\).
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 7.50-7.55 \) (m, 2H), 7.04 (t, \( J = 8.7 \) Hz, 2H), 6.35 (d, \( J = 11.4 \) Hz, 1H), 6.15 (d, \( J = 11.4 \) Hz, 1H), 3.79 (s, 3H) ppm.

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta = 165.2, 163.1 \) (d, \( \text{J}_{\text{C-F}} = 250.0 \) Hz), 134.2 (d, \( \text{J}_{\text{C-F}} = 8.4 \) Hz), 127.8, 123.1, 118.7 (d, \( \text{J}_{\text{C-F}} = 3.4 \) Hz), 115.8 (d, \( \text{J}_{\text{C-F}} = 22.0 \) Hz), 100.3, 86.1, 51.4 ppm.

HRMS (EI\textsuperscript{+}): \( m/z \) [M\textsuperscript{+}] calcd for C\textsubscript{12}H\textsubscript{9}FO\textsubscript{2}: 204.0587; found: 204.0582.

(Z)-methyl 5-(4-chlorophenyl)pent-2-en-4-ynoate (5g)

Yield: 27\% (59 mg); colorless oil; \( R_f = 0.37 \) (hexanes/EA = 10/1).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 7.48 \) (d, \( J = 8.5 \) Hz, 2H), 7.33 (d, \( J = 8.5 \) Hz, 2H), 6.36 (d, \( J = 11.4 \) Hz, 1H), 6.18 (d, \( J = 11.4 \) Hz, 1H), 3.81 (s, 3H) ppm.

HRMS (EI\textsuperscript{+}): \( m/z \) [M\textsuperscript{+}] calcd for C\textsubscript{12}H\textsubscript{9}ClO\textsubscript{2}: 220.0291; found: 220.0285.
Table S1. Condition Optimization of Sonogashira Cross-coupling Reaction

![Chemical Structure](https://example.com/structure.png)

<table>
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<tr>
<th>Entry</th>
<th>Pd(PPh₃)₄ (mol %)</th>
<th>4a (equiv)</th>
<th>CuI (equiv)</th>
<th>iPr₂NEt (mL)</th>
<th>Solvent (mL)</th>
<th>Temp (℃)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>3k recovery (%)</th>
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<tbody>
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<td>1</td>
<td>0.15</td>
<td>1</td>
<td>THF (1.5)</td>
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<td>trace</td>
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<td>5</td>
<td>1.5</td>
<td>0.15</td>
<td>1</td>
<td>THF (3)</td>
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<tr>
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<td>3</td>
<td>0.15</td>
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<td>5</td>
<td>5</td>
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<td>THF (4)</td>
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<td>THF (4)</td>
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ᵇ The reactions of were performed with 1.0 mmol of alkenyl sulfonate 3k, 3.0 mmol of alkyne 4a, Pd(PPh₃)₄, CuI, and iPr₂NEt/THF for 24 h unless otherwise noted. ᵇ The (Z)-methyl 3-(tosyloxy)acrylate (3a) was used instead of 3k.
Table S2. Sonogashira Cross-coupling Reaction.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
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<th>product¹</th>
<th>Yield (%)</th>
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<tr>
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<td>Me</td>
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<td>H</td>
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<td>H</td>
<td>4-Cl-Ph (4f)</td>
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</tbody>
</table>

ᵃ All reactions were performed with 1.0 mmol of alkenyl sulfonates, 3.0 mmol of alkynes, 10 mol % of Pd(PPh₃)₄ and 30 mol % of CuI in 1.5 mL of Pr₂NEt and 4 mL of THF for 24 h unless otherwise noted. ᵇ The (Z)-ethyl 3-(p-toluenesulfonyloxy)-butenoate (3x) was used instead of 3k. ᶜ 5a-g are known compounds.

* indicates signals for E-isomer