Alkoxide-Catalyzed Addition of Alkyl Carbonates across Alkynes
– Stereoselective Synthesis of (E)-β-Alkoxyacrylates

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Supporting Information

<table>
<thead>
<tr>
<th>General</th>
<th>S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional Screening Experiments</td>
<td>S3</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>S5</td>
</tr>
<tr>
<td>Control Experiments</td>
<td>S20</td>
</tr>
<tr>
<td>Spectra</td>
<td>S22</td>
</tr>
<tr>
<td>References</td>
<td>S50</td>
</tr>
</tbody>
</table>
Experimental procedures and data

**General Methods.** All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum. Solvents were purified and dried by standard procedures prior to use. All reactions were monitored by GC using \( n \)-dodecane as an internal standard. Response factors of the products with regard to \( n \)-dodecane were obtained experimentally by analyzing known quantities of the substances. GC analyses were carried out using a HP6890 with HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30-300/3) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. NMR spectra were obtained on Bruker AMX 400 system using CDCl\(_3\) as solvent, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Mass spectrometric data were acquired on a GC-MS Saturn 2100 T (Varian). Infrared spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer with Universal ATR Sampling Accessory. Melting points were measured on a Mettler FP 61. CHN-elemental analyses were performed with a Hanau Elemental Analyzer vario Micro cube and HRMS with a Waters GCT Premier. Commercial substrates were used as received unless otherwise stated.

Starting materials 2-Ethynynaphthalene (1j) and phenylacetylene-d\(_1\) (1a-d\(_1\)) were synthesized following known procedures.\(^{[1,2]}\)
### Additional Screening Experiments

#### Table S1.

![Chemical Reaction Diagram](image)

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<th>Entry</th>
<th>DMC (eq)</th>
<th>Solvent (mL)</th>
<th>Temp. (°C)</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
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<sup>a</sup> Reaction conditions: 0.50 mmol of 1a, 0.60 mmol of 2a, 0.15 mmol of KOMe, 12 h, rt.

<sup>b</sup> Conversions, yields and E/Z ratios were determined by GC using n-dodecane as internal standard.

<sup>c</sup> H₂O (50 µl) was added.

<sup>d</sup> Under air.
Table S2.

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<th>Solvent (mL)</th>
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<sup>a</sup> Reaction conditions: 0.50 mmol of 1<sub>o</sub>, 1.50 mmol of 2<sub>a</sub>, 0.60 mmol of base, 0.5 mL solvent, 16 h.<br><sup>b</sup> Conversions and yields were determined by GC using n-dodecane as internal standard. No (Z)-product was observed.<br><sup>c</sup> Potassium tert-Amylate (25% (w/v) in toluene).<br><sup>d</sup> 1.00 mmol of KO<sub>b</sub>Bu.<br><sup>e</sup> 1 mL Bu<sub>2</sub>O.
**GP1: General procedure for the synthesis of aromatic β-methoxyacrylates**

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere was changed three times with nitrogen; afterwards DMSO (1 mL) and alkyl carbonate (1.20 mmol) were added via syringe. A stock solution of the liquid alkyne (1.00 mmol) dissolved in DMSO (0.5 mL) was added over 45 min via syringe pump. In case of solid alkynes, those were added directly together with the base. The resulting mixture was stirred (500 rpm) at room temperature for 12 h, diluted with 20 mL of ethyl acetate and washed with 20 mL of water. The aqueous phase was extracted with ethyl acetate (2 x 15 mL), the combined organic layers were washed with brine (15 mL), dried over MgSO$_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (SiO$_2$). The stereochemistry was confirmed by NOE experiments of selected examples.

**GP 2: General procedure for the synthesis of aliphatic β-methoxyacrylates**

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium tert-butoxide (135 mg, 1.20 mmol) and closed with a septum cap. The atmosphere was changed three times with nitrogen; afterwards di-$n$-butyl ether (1 mL), dimethyl carbonate (255 $\mu$L, 3.00 mmol) and the liquid alkyne (1.00 mmol) were added via syringe. The resulting mixture was stirred (500 rpm) at 90 °C for 16 h and then cooled to room temperature. Ethyl acetate (20 mL) was added and the mixture was washed with 20 mL water. The aqueous phase was separated and extracted with ethyl acetate (2 x 15 mL), the combined organic layers were washed with brine (15 mL), dried over MgSO$_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (SiO$_2$, ethyl acetate/cyclohexane gradient). The stereochemistry was confirmed by NOE experiments of selected examples.
Synthesis of \((E)\)-methyl 3-methoxy-3-phenylprop-2-enoate (3aa) [CAS: 60456-20-4]

Compound 3aa was prepared following the general procedure GP1 from phenylacetylene (1a) (102 mg, 110 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, toluene/dichloromethane gradient) yielded 3aa as a colorless oil (144 mg, 75%).

Elemental analysis found: C, 68.5; H, 6.3. \(\text{C}_{11}\text{H}_{12}\text{O}_3\) requires C, 68.7; H, 6.3%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3062, 2988, 2948, 2840, 1717, 1696, 1619, 1597, 1577, 1495, 1434, 1380, 1262, 1219, 1194, 1154, 1112, 1025, 985, 919, 820, 765, 695. \(^1\)H-NMR (400 MHz, CDCl₃) 7.35-7.49 (5 H, m), 5.29 (1 H, s), 3.82 (3 H, s), 3.60 (3 H, s). \(^{13}\)C–NMR (101 MHz, CDCl₃) 171.6, 167.1, 135.0, 129.7, 128.6, 128.6, 127.7, 127.7, 91.9, 56.3, 50.9. MS (Ion trap, EI) \(m/z\) 193.0 (24%), 192.0 (M⁺, 30), 191.0 (81), 161.0 (100), 131.0 (22), 115.1 (30), 105.0 (25). HRMS-EI (TOF) found: 192.0783 [M⁺]. \(\text{C}_{11}\text{H}_{12}\text{O}_3\) requires 192.0786.

Synthesis of \((E)\)-methyl 3-methoxy-3-(2-methylphenyl)prop-2-enolate (3ba) [CAS:147498-91-7]

Compound 3ba was prepared following the general procedure GP1 from 2-(methyl)phenylacetylene (1b) (120 mg, 130 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3ba as a yellow oil (188 mg, 91%).

Elemental analysis found: C, 69.8; H, 6.9. \(\text{C}_{12}\text{H}_{14}\text{O}_3\) requires C, 69.9; H, 6.8%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3071, 3021, 2950, 1721, 1621, 1599, 1436, 1373, 1264, 1192, 1153, 1122, 1098,
Synthesis of (E)-methyl 3-methoxy-3-(2-methoxyphenyl)prop-2-enoate (3ca) [CAS:82700-88-7]

![Diagram of compound 3ca]

Compound 3ca was prepared following the general procedure GP1 from 2-ethynylanisole (1c) (136 mg, 134 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3ca as a yellow oil (196 mg, 88 %).

Elemental analysis found: C, 64.9; H, 6.4. C₁₂H₁₄O₄ requires C, 64.8; H, 6.4%. IR (ATR)  ν max/cm⁻¹ 3012, 2947, 2840, 1720, 1698, 1625, 1595, 1495, 1460, 1435, 1374, 1246, 1216, 1151, 1123, 1099, 1024, 920, 809, 751. ¹H—NMR (400 MHz, CDCl₃) 7.35—7.39 (1 H, m), 7.20 (1 H, dd, J = 7.5, 1.8 Hz), 6.93—7.00 (2 H, m), 5.36 (1 H, s), 5.36 (1 H, s), 3.81 (3 H, s), 3.79 (3 H, s), 3.55 (3 H, s). ¹³C—NMR (101 MHz, CDCl₃) 168.7, 166.9, 156.5, 130.6, 129.6, 124.7, 120.2, 110.9, 93.7, 56.2, 55.7, 50.8. MS (ion trap, El) m/z 192.0 (13), 190.8 (100), 148.9 (17), 130.9 (23), 120.9 (20), 90.9 (15), 76.9 (14). HRMS-El (TOF) found: 222.0890. [M]⁺. C₁₂H₁₄O₄ requires 222.0892.
Synthesis of \((E)\)-methyl 3-(2-fluorophenyl)-3-methoxyprop-2-enoate (3da)

![Chemical Structure of 3da]

Compound 3da was prepared following the general procedure GP1 from 1-ethynyl-2-fluorobenzene (1d) (124 mg, 117 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3da as a yellow oil (182 mg, 87 %).

Elemental analysis found: C, 62.8; H, 5.4. C_{11}H_{11}FO₃ requires C, 62.9; H, 5.3%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3015, 2950, 2840, 1719, 1633, 1607, 1490, 1452, 1437, 1374, 1267, 1225, 1194, 1149, 1121, 1095, 1028, 987, 922, 826, 758. \(^1\)H—NMR (400 MHz, CDCl₃) 7.37—7.43 (1 H, m), 7.32 (1 H, td, \(J = 7.4, 1.8\) Hz), 7.18 (1 H, td, \(J = 7.4, 1.8\) Hz), 7.08—7.13 (1 H, m), 5.41 (1 H, s), 3.83 (3 H, s), 3.60 (3 H, s). \(^1\)\(^9\)F—NMR (400 MHz, CDCl₃) -114.7. \(^1\)\(^3\)C—NMR (101 MHz, CDCl₃) 166.6 (d, \(J = 111\) Hz), 160.7, 158.2, 131.2 (d, \(J = 9.1\) Hz), 129.9 (d, \(J = 2.7\) Hz), 123.7 (d, \(J = 3.6\) Hz), 123.5, 115.4 (d, \(J = 21.8\) Hz), 94.5, 56.5, 51.0. MS (Ion trap, El) \(m/z\) 211.0 (M⁺, 16%), 210.0 (35), 209.1 (46), 179.1 (100), 149.0 (17), 123.0 (16), 115.0 (22).

Synthesis of \((E)\)-methyl 3-(2-bromophenyl)-3-methoxyprop-2-enoate (3ea) [CAS: 147498-95-1]

![Chemical Structure of 3ea]

Compound 3ea was prepared following the general procedure GP1 from 1-bromo-2-ethynylbenzene (1e) (185 mg, 127 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3ea as an orange oil (250 mg, 92 %).

Gram scale synthesis:
An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (332 mg, 4.50 mmol) and closed with a septum cap. The atmosphere was changed three times with argon; afterwards DMSO (9.90 g, 9 mL) and dimethyl carbonate \((2a)\) (1.64 g, 15.0 mmol) were added via syringe. A stock solution of 1-bromo-2-ethynylbenzene \((1e)\) (2.77 g, 190 ml, 15.0 mmol) dissolved in DMSO (2.20 g, 2 mL) was added over 120 min via syringe pump. The resulting mixture was stirred (500 rpm) at room temperature for 12 h. Purification by Kugelrohr distillation (210°C, 1x10^-2 mbar) yielded \(3ea\) as an orange oil (3.24 g, 80%).

Calculation of E-factors:

\[
E \text{ (with DMSO)} = \frac{0.332 g + 1.64 g + 2.77 g + 12.1 g}{3.24 g} = 5.2
\]

\[
E \text{ (without DMSO)} = \frac{0.332 g + 1.64 g + 2.77 g}{3.24 g} = 1.5
\]

Elemental analysis found: C, 48.7; H, 4.2. \(C_{11}H_{11}BrO_3\) requires C, 48.8, H, 4.1%. IR (ATR) \(\bar{\nu}_{\text{max}}/\text{cm}^{-1}\) 3062, 2991, 2948, 2837, 1718, 1698, 1627, 1588, 1475, 1435, 1372, 1280, 1220, 1194, 1156, 1117, 1047, 1025, 984, 921, 825, 757, 721, 658. \(^1\)H—NMR (400 MHz, CDCl\(_3\)) 7.58—7.64 (1 H, m), 7.32—7.38 (1 H, m), 7.23—7.30 (2 H, m), 5.39 (1 H, s), 3.83 (3 H, s), 3.57 (3 H, s). \(^{13}\)C—NMR (101 MHz, CDCl\(_3\)) 170.0, 166.4, 137.0, 132.5, 130.3, 129.8, 127.0, 121.7, 94.0, 56.6, 51.0. MS (Ion trap, EI) \(m/z\) 241.0 (9), 238.9 (10), 192.1 (12), 191.1 (100), 148.1 (9), 89.1 (9), 75.0 (7).

Synthesis of \((E)\)-methyl 3-(3-chlorophenyl)-3-methoxprop-2-enoate \((3fa)\)

![Chemical structure of 3fa](image)

Compound \(3fa\) was prepared following the general procedure GP1 from 3-chloro-1-ethynylbenzene \((1f)\) (141 mg, 127 µl, 1.00 mmol) and dimethyl carbonate \((2a)\) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO\(_2\), toluene/dichloromethane gradient) yielded \(3fa\) as a colourless oil (163 mg, 72%).
Elemental analysis found: C, 58.3; H, 5.0. C_{11}H_{11}ClO_3 requires C, 58.3; H, 4.9%. IR (ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 3018, 2982, 2950, 2840, 1716, 1620, 1593, 1567, 1435, 1374, 1258, 1159, 1117, 1034, 990, 924, 816, 787, 698. $^1$H—NMR (400 MHz, CDCl$_3$) 7.42—7.43 (1 H, m), 7.38—7.41 (1 H, m), 7.32—7.33 (2 H, m), 5.29 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s). $^{13}$C—NMR (101 MHz, CDCl$_3$) 169.8, 166.8, 136.6, 133.6, 129.7, 128.9, 128.7, 127.1, 92.5, 56.4, 51.0. MS (Ion trap, EI) m/z 226.9 (M$^+$, 33%), 225.9 (26), 225.0 (60), 197.0 (25), 195.0 (100), 44.0 (28), 40.0 (29). HRMS-EI (TOF) found: 226.0385 [M$^+$]. C_{11}H_{11}ClO_3 requires 226.0397.

Synthesis of (E)-methyl 3-(4-chlorophenyl)-3-methoxyprop-2-enoate (3ga)

![Chemical Structure](image)

Compound 3ga was prepared following the general procedure GP1 from 1-chloro-4-ethynylbenzene (1g) (137 mg, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO$_2$, toluene/ dichloromethane gradient) yielded 3ga as colorless needles (163 mg, 72 %).

mp 67.5—68.0 °C. Elemental analysis found: C, 58.5; H, 5.0. C_{11}H_{11}ClO_3 requires C, 58.3; H, 4.9%. IR (ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 3012, 2991, 2954, 2839, 1718, 1616, 1591, 1568, 1494, 1459, 1431, 1401, 1385, 1259, 1196, 1156, 1116, 1107, 1085, 1016, 984, 922, 831, 819, 783, 739, 722, 665. $^1$H—NMR (400 MHz, CDCl$_3$) 7.32—7.44 (4 H, m), 5.28 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s). $^{13}$C—NMR (101 MHz, CDCl$_3$) 170.2, 166.9, 135.7, 133.3, 130.2, 130.2, 127.9, 127.9, 92.2, 56.4, 51.0. MS (Ion trap, EI) m/z 227.0 (27%), 226.0 (M$^+$, 32), 225.1 (76), 197.0 (37), 195.0 (100), 139.0 (27), 115.1 (27). HRMS-EI (TOF) found: 226.0398 [M$^+$]. C_{11}H_{11}ClO_3 requires 226.0397.
Synthesis of (E)-methyl 3-methoxy-3-[4-(trifluoromethyl)phenyl]prop-2-enoate (3ha)

Compound 3ha was prepared following the general procedure GP1 from 4-(trifluoromethyl)phenylacetylene (1h) (170 mg, 164 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/dichloromethane gradient) yielded 3ha as an orange solid (198 mg, 76 %). mp 37.5—38.0 °C. Elemental analysis found: C, 55.5; H, 4.5. C₁₂H₁₁F₃O₃ requires C, 55.4; H, 4.3%. IR (ATR) ν max/cm⁻¹ 3080, 3036, 3012, 2985, 2948, 2845, 1713, 1664, 1631, 1608, 1520, 1458, 1437, 1408, 1382, 1325, 1277, 1196, 1153, 1104, 1061, 1034, 1019, 983, 922, 841, 830, 748, 721. \(^1\)H—NMR (400 MHz, CDCl₃) 7.66 (2 H, d, J = 8.3 Hz), 7.55 (2 H, d, J = 8.3 Hz), 5.35 (1 H, s), 3.84 (3 H, s), 3.61 (3 H, s). \(^1^9\)F–NMR (400 MHz, CDCl₃) -62.8. \(^1^3\)C–NMR (101 MHz, CDCl₃) 169.9, 166.8, 138.5, 131.4 (q, \(^2\)J(C,F) = 32.7 Hz), 129.2, 129.2, 124.7 (q, \(^3\)J(C,F) = 3.6 Hz), 124.7 (q, \(^3\)J(C,F) = 3.6 Hz), 124.3 (q, \(^1\)J(C,F) = 271.6 Hz), 92.8, 56.5, 51.1. MS (Ion trap, EI) m/z 260.0 (M⁺, 26%), 259.0 (58), 240.9 (19), 229.0 (100), 145.0 (17), 68.8 (18), 58.8 (20). HRMS-EI (TOF) found: 260.0654. [M⁺]. C₁₂H₁₁F₃O₃ requires 260.0660.

Synthesis of (E)-methyl 3-methoxy-3-(4-propylphenyl)prop-2-enoate (3ia)

Compound 3ia was prepared following the general procedure GP1 from 1-ethynyl-4-propylbenzene (1i) (147 mg, 162 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, toluene/dichloromethane gradient) yielded 3ia as a colorless oil (210 mg, 90 %).
Elemental analysis found: C, 71.9; H, 7.5. C_{14}H_{18}O_{3} requires C, 71.8; H, 7.7%. IR (ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 3012, 2958, 2875, 1720, 1698, 1605, 1513, 1435, 1380, 1260, 1218, 1154, 1111, 1035, 921, 816. $^1$H—NMR (400 MHz, CDCl$_3$) 7.37 (2 H, d, $J = 8.3$ Hz), 7.21 (2 H, d, $J = 8.3$ Hz), 5.26 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s), 2.60 (1 H, t, $J = 7.5$ Hz), 1.66 (2 H, sxt, $J = 7.4$ Hz), 0.96 (3 H, t, $J = 7.3$ Hz). $^{13}$C—NMR (101 MHz, CDCl$_3$) 171.7, 167.3, 144.6, 132.2, 128.6, 128.6, 127.8, 127.8, 91.5, 56.3, 50.9, 38.0, 24.3, 13.9. MS (Ion trap, EI) m/z 235.0 (100), 234.1 (M$^+$, 47), 233.2 (70), 203.2 (71), 191.0 (96), 149.2 (45), 131.0 (38). HRMS-EI (TOF) found: 234.1250 [M$^+$]. C$_{14}$H$_{18}$O$_3$ requires 234.1256.

**Synthesis of (E)-methyl 3-methoxy-3-(naphthalen-2-yl)prop-2-enoate (3ja)**

![Chemical structure](image)

Compound 3ja was prepared following the general procedure GP1 from 2-ethynyl-naphthalene (1j) (152 mg, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO$_2$, cyclohexane/ dichloromethane gradient) yielded 3ja as a yellow oil (161 mg, 67%).

Elemental analysis found: C, 74.2; H, 6.0. C$_{15}$H$_{14}$O$_3$ requires C, 74.4; H, 5.8%. IR (ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 3059, 3024, 2947, 2831, 1715, 1696, 1613, 1594, 1575, 1502, 1472, 1434, 1383, 1358, 1264, 1215, 1190, 1148, 1129, 1102, 1033, 995, 946, 921, 857, 815, 748. $^1$H—NMR (400 MHz, CDCl$_3$) 7.97 (1 H, s), 7.85—7.89 (3 H, m), 7.48—7.55 (3 H, m), 5.37 (1 H, s), 3.88 (3 H, s), 3.60 (3 H, s). $^{13}$C—NMR (101 MHz, CDCl$_3$) 171.4, 167.2, 133.8, 132.6, 132.4, 128.6, 128.5, 127.7, 127.1, 126.8, 126.2, 126.1, 92.2, 56.5, 51.0. MS (Ion trap, EI) m/z 241.9 (M$^+$, 100%), 241.1 (52), 211.0 (51), 169.0 (19), 168.1 (19), 155.1 (26), 152.2 (18).
Synthesis of (E)-methyl 3-methoxy-3-(pyridin-2-yl)prop-2-enoate (3ka)

Compound 3ka was prepared following the general procedure GP1 from 2-ethynylpiridine (1k) (105 mg, 103 μl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 μl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate/trimethylamine (10%) gradient) yielded 3ka as a yellow oil (139 mg, 72%).

Elemental analysis found: N, 7.2, C, 62.0; H, 5.9. C₁₀H₁₁NO₃ requires N, 7.3, C, 62.2; H, 5.7%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3068; 3015; 2991; 2948; 2843; 1714; 1625; 1584; 1568; 1474; 1434; 1375; 1283; 1222; 1194; 1165; 1124; 1031; 986; 922; 825; 798; 777; 746. \(^1\)H—NMR (400 MHz, CDCl₃) 8.65 (1 H, d, \(^3\)J = 4.2 Hz), 7.73 (1 H, td, \(J = 7.8 \text{ Hz}\)), 7.43 (1 H, td, \(J = 7.8 \text{ Hz}\)), 7.32 (1 H, dd, \(J = 8.8 \text{ Hz}\)), 5.36 (1 H, s), 3.84 (3 H, s), 3.57 (3 H, s). \(^1\)C–NMR (101 MHz, CDCl₃) 169.1, 166.9, 153.5, 149.2, 136.0, 124.0, 123.9, 93.4, 56.6, 51.1. MS (Ion trap, EI) m/z 193.8 (M⁺, 50%), 177.8 (43), 161.9 (60), 147.8 (56), 133.9 (46), 103.9 (100), 77.9 (50). HRMS-EI (TOF) found: 193.0743. [M⁺]. C₁₀H₁₁NO₃ requires 193.0739.

Synthesis of (E)-methyl 3-methoxy-3-(pyridin-3-yl)prop-2-enoate (3la)

Compound 3la was prepared following the general procedure GP1 from 3-ethynylpyridine (1l) (105 mg, 1.00 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient/trimethylamine (10%) gradient) yielded 3la as a white solid (131 mg, 68%).

mp. 62.0—62.5 °C. Elemental analysis found: N, 7.2, C, 62.2; H, 5.9. C₁₀H₁₁NO₃ requires N, 7.3, C, 62.2; H, 5.7%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3033, 2988, 2950, 2846, 1709, 1611, 1586, 1460, 1437, 1616, 1377, 1274, 1191, 1157, 1122, 1044, 1024, 983, 920, 818, 782, 710. \(^1\)H—NMR
(400 MHz, CDCl$_3$) 8.62—8.66 (2 H, m), 7.77 (1 H, d, $J = 8.0$), 7.31—7.33 (1 H, m), 5.35 (1 H, s), 3.83 (3 H, s), 3.60 (3 H, s). $^{13}$C–NMR (101 MHz, CDCl$_3$) 168.5, 166.8, 150.5, 149.5, 136.3, 130.9, 122.4, 93.2, 56.5, 51.1. MS (ion trap, EI) $m/z$ 192.9 (M$^+$, 24%), 192.0 (70), 162.0 (100), 118.1 (19), 91.0 (20), 78.0 (21), 50.0 (23). HRMS-EI (TOF) found: 193.0733. [M]$^+$. C$_{10}$H$_{11}$NO$_3$ requires 193.0739.

Synthesis of (E)-methyl 3-methoxy-3-(thiophen-3-yl)prop-2-enoate (3ma) [CAS: 1161948-25-9]

![Chemical Structure of 3ma](image)

Compound 3ma was prepared following the general procedure GP1 from 3-ethynylthiophene (1m) (112 mg, 101 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO$_2$, toluene/ dichloromethane gradient) yielded 3ma as a colourless oil (119 mg, 60 %).

Elemental analysis found: C, 54.5; H, 5.1, S, 16.0. C$_9$H$_{10}$O$_3$S requires C, 54.5; H, 5.1, S, 16.2%. IR (ATR) $\bar{\nu}_{\text{max}}$/cm$^{-1}$ 3110, 3009, 2947, 2843, 1712, 1605, 1435, 1345, 1253, 1191, 1143, 1107, 1034, 992, 924, 867, 793, 681. $^1$H–NMR (400 MHz, CDCl$_3$) 7.80 (1 H, dd, $J = 3.0, 1.3$ Hz), 7.32 (1 H, dd, $J = 5.1, 1.4$ Hz), 7.22—7.28 (1 H, m), 5.24 (1 H, s), 3.77 (3 H, s), 3.64 (3 H, s). $^{13}$C–NMR (101 MHz, CDCl$_3$) 167.1, 165.4, 134.9, 128.3, 128.2, 124.0, 91.5, 56.0, 50.9. MS (ion trap, EI) $m/z$ 197.8 (M$^+$, 79%), 166.9 (100), 123.8 (43), 110.8 (33), 96.8 (25), 68.8 (23), 44.9 (32). HRMS-EI (TOF) found: 198.0356. [M]$^+$. C$_9$H$_{10}$O$_3$S requires 198.0351.
Synthesis of \((E)\)-methyl 3-methoxy-3-(thiophen-2-yl)prop-2-enoate (3na)

Compound 3na was prepared following the general procedure GP1 from 2-ethynylthiophene (1n) (114 mg, 99.9 µl, 1.00 mmol) and dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3na as a brown oil (153 mg, 77 %).

Elemental analysis found: C, 54.8; H, 5.0, S, 16.3. C₉H₁₀O₃S requires C, 54.5; H, 5.1, S, 16.2%. IR (ATR) ν_max/cm⁻¹ 3107, 2955, 1736, 1657, 1519, 1436, 1412, 1357, 1325, 1273, 1217, 1146, 1062, 1017, 926, 859, 723. ¹H—NMR (400 MHz, CDCl₃) 7.95 (1 H, dd, J = 3.8, 1.4 Hz), 7.46 (1 H, dd, J = 5.0, 1.3 Hz), 7.08 (1 H, dd, J = 5.3, 3.8 Hz), 5.27 (1 H, s), 3.81 (3 H, s), 3.70 (3 H, s. ¹³C–NMR (101 MHz, CDCl₃) 166.9, 162.2, 135.4, 131.5, 128.8, 126.8, 91.2, 56.2, 51.0. MS (Ion trap, EI) m/z 198.0 (M⁺, 20%), 125.8 (49), 110.9 (100), 82.9 (22), 45.0 (28), 43.9 (34), 43.0 (41). HRMS-EI (TOF) found: 198.0351. [M]⁺. C₉H₁₀O₃S requires 198.0351.

Synthesis of \((E)\)-ethyl 3-ethoxy-3-(2-methylphenyl)prop-2-enoate (3bb) [CAS:147499-01-2]

Compound 3bb was prepared following the general procedure GP1 from 2-ethynyltoluene (1b) (120 mg, 130 µl, 1.00 mmol) and diethyl carbonate (2b) (143 mg, 147 µl, 1.20 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3bb as a colourless oil (140 mg, 60 %).
Elemental analysis found: C, 71.6; H, 7.7. C_{14}H_{18}O_{3} requires C, 71.8; H, 7.7%. IR (ATR) \tilde{\nu}_{\text{max}}/\text{cm}^{-1} 3065, 2982, 1718, 1695, 1620, 1599, 1446, 1374, 1355, 1262, 1262, 1217, 1201, 1155, 1123, 1095, 1043, 1021, 896, 815, 761, 726. \textsuperscript{1}H—NMR (400 MHz, CDCl\textsubscript{3}) 7.27-7.33 (m, 1 H), 7.14-7.26 (m, 3 H), 5.34 (s, 1 H), 3.96-4.04 (m, 4 H), 2.28 (s, 3 H), 1.41 (t, \textit{J} = 7.0 Hz, 3 H), 1.08 (t, \textit{J} = 7.0 Hz, 3 H). \textsuperscript{13}C—NMR (101 MHz, CDCl\textsubscript{3}) 171.0, 166.6, 136.0, 135.6, 129.8, 129.0, 128.3, 125.3, 93.9, 84.7, 59.4, 19.1, 14.3, 14.1. MS (Ion trap, EI) \textit{m/z} 235.0 (M\textsuperscript{+}, 55%), 219.1 (44), 189.1 (100), 161.2 (25), 119.0 (48), 118.1 (29), 91.1 (23). HRMS-EI (TOF) found: 234.1267. [M]\textsuperscript{+}. C_{14}H_{18}O_{3} requires 234.1256.

**Synthesis of prop-2-en-1-yl (2E)-3-(2-methylphenyl)-3-(prop-2-en-1-yloxy)prop-2-enoate (3bc)**

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{compound3bc.png}
\end{center}}
\]

Compound 3bc was prepared following the general procedure GP1 from 2-ethynyltoluene (1b) (120 mg, 130 \textmu l, 1.00 mmol) and diallyl carbonate (2c) (172 mg, 174 \textmu l, 1.20 mmol). Purification by column flash chromatography (SiO\textsubscript{2}, cyclohexane/ethyl acetate gradient) yielded 3bc as a yellow oil (162 mg, 63\%).

Elemental analysis found: C, 74.4; H, 7.0. C_{16}H_{18}O_{3} requires C, 74.4; H, 7.0%. IR (ATR) \tilde{\nu}_{\text{max}}/\text{cm}^{-1} 3080, 3023, 2923, 2872, 1720, 1695, 1619, 1599, 1380, 1260, 1155, 1119, 1090, 1029, 987, 925, 822, 767, 728. \textsuperscript{1}H—NMR (400 MHz, CDCl\textsubscript{3}) 7.29—7.33 (1 H, m), 7.21—7.24 (3 H, m), 6.02 (1 H, ddt, \textit{J} = 17.3, 10.7, 5.5), 5.80 (1 H, ddt, \textit{J} = 17.3, 10.4, 5.7), 5.42 (1 H, dq, \textit{J} = 17.3, 1.3), 5.41 (1 H, s), 5.32 (1 H, dq, \textit{J} = 10.5, 1.2), 5.13—5.21 (2 H, m), 4.51 (2 H, dt, \textit{J} = 5.6, 1.6), 4.46 (2 H, dt, \textit{J} = 5.8, 1.5), 2.29 (3 H, s). \textsuperscript{13}C—NMR (101 MHz, CDCl\textsubscript{3}) 170.8, 165.9, 135.6, 135.4, 132.5, 131.7, 129.9, 129.1, 128.4, 125.3, 118.8, 117.6, 94.2, 69.8, 64.3, 19.1. MS (Ion trap, EI) \textit{m/z} 120.0 (9\%), 119.0 (100), 91.0 (36), 65.0 (14). HRMS-EI (TOF) found: 258.1267. [M]\textsuperscript{+}. C_{16}H_{18}O_{3} requires 258.1256.
Synthesis of (E)-methyl 3-methoxyundec-2-enoate (3oa) [CAS: 1161948-21-5]

Compound 3oa was prepared following the general procedure GP2 from 1-decyne (1o) (146 mg, 190 µl, 1.00 mmol) and dimethyl carbonate (2a) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3oa as a colourless oil (128 mg, 56 %).

Elemental analysis found: C, 68.6; H, 10.7. C₁₃H₂₄O₃ requires C, 68.4; H, 10.6%. IR (ATR) \( \tilde{\nu}_{\text{max}}/\text{cm}^{-1} \) 2927, 2856, 1714, 1620, 1435, 1378, 1136, 1113, 1053, 930, 819. \(^1H\)-NMR (400 MHz, CDCl₃) 4.98 (1 H, s), 3.67 (3 H, s), 3.62 (3 H, s), 2.73 (2 H, t, \( J = 6.8 \)), 1.53 (2 H, quin, \( J = 7.5 \)), 1.26—1.33 (2 H, m), 0.87 (3 H, t, \( J = 7.5 \)). \(^{13}C\)-NMR (101 MHz, CDCl₃) 177.2, 168.0, 89.9, 55.3, 50.7, 32.0, 31.8, 29.4, 29.3, 29.2, 27.5, 22.7, 14.1. MS (Ion trap, El) \( m/z \) 197.0 (40), 142.9 (90), 129.8 (68), 111.0 (60), 101.0 (100), 87.0 (57), 72.0 (45). HRMS-EI (TOF) found: 197.1547. [M-OMe]+. C₁₂H₂₁O₂ requires 197.1542 (M+—Peak too small for appropriate detection).

Synthesis of (E)-methyl 4-cyclohexyl-3-methoxybut-2-enoate (3pa)

Compound 3pa was prepared following the general procedure GP2 from 3-cyclohexyl-1-propyne (1p) (126 mg, 149 µl, 1.00 mmol) and dimethyl carbonate (2a) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3pa as a colourless oil (127 mg, 60 %).

Elemental analysis found: C, 67.7; H, 9.5. C₁₂H₂₀O₃ requires C, 67.9; H, 9.5%. IR (ATR) \( \tilde{\nu}_{\text{max}}/\text{cm}^{-1} \) 2923, 2851, 1713, 1618, 1435, 1376, 1288, 1249, 1191, 1172, 1140, 1120, 1052,
1012, 930, 894, 817, 747. $^1$H—NMR (400 MHz, CDCl$_3$) 5.02 (1 H, s), 3.66 (3 H, s), 3.61 (3 H, s), 2.65 (2 H, d, $J$ = 6.8), 1.63—1.69 (6 H, m), 1.11—1.26 (3 H, m), 0.95—1.03 (2 H, m). $^{13}$C—NMR (101 MHz, CDCl$_3$) 176.0, 168.1, 90.8, 55.2, 50.7, 39.1, 36.6, 32.9, 26.3, 26.1. MS (Ion trap, EI) m/z 131.0 (79), 129.8 (100), 89.0 (50), 87.0 (63), 72.0 (61), 55.0 (51), 40.0 (64). HRMS-EI (TOF) found: 181.1234 [M-OMe]$^+$. C$_{11}$H$_{17}$O$_2$ requires 181.1229 (M$^+$-Peak too small for appropriate detection).

**Synthesis of (E)-methyl 3-cyclopropyl-3-methoxyprop-2-enoate (3qa) [CAS: 182617-98-7]**

![Structural formula of 3qa](image)

Compound 3qa was prepared following the general procedure GP2 from ethynylcyclopropane (1q) (68.1 mg, 87.3 µl, 1.00 mmol) and dimethyl carbonate (2a) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO$_2$, cyclohexane/ethyl acetate gradient) yielded 3qa as a colourless oil (90 mg, 58%).

Elemental analysis found: C, 61.5; H, 7.6. C$_8$H$_{12}$O$_3$ requires C, 61.5; H, 7.7%. IR (ATR) $\tilde{\nu}$ max/cm$^{-1}$ 3097, 3014, 2950, 1706, 1602, 1435, 1405, 1282, 1235, 1189, 1145, 1104, 1044, 989, 915, 812, 768. $^1$H—NMR (400 MHz, CDCl$_3$) 5.06 (1 H, s), 3.70 (3 H, s), 3.57 (3 H, s), 3.16—3.22 (1 H, m), 0.92—0.96 (2 H, m), 0.77—0.82 (2 H, m). $^{13}$C—NMR (101 MHz, CDCl$_3$) 175.6, 168.8, 89.7, 55.3, 50.7, 11.6, 7.19. MS (Ion trap, EI) m/z 127.9 (100%), 125.0 (15), 113.0 (39), 96.9 (20), 68.9 (13), 67.0 (16), 53.0 (12). HRMS-EI (TOF) found: 156.0780. [M]$^+$. C$_8$H$_{12}$O$_3$ requires 156.0786.

**Synthesis of (E)-methyl 3-methoxy-6-phenylhex-2-enoate (3ra) [CAS: 1161948-18-0]**

![Structural formula of 3ra](image)
Compound 3ra was prepared following the general procedure GP2 from 5-phenyl-1-pentyne (1r) (144 mg, 152 μl, 1.00 mmol) and dimethyl carbonate (2a) (273 mg, 255 μl, 3.00 mmol). Purification by column flash chromatography (SiO₂, cyclohexane/ethyl acetate gradient) yielded 3ra as a colourless oil (112 mg, 48 %).

Elemental analysis found: C, 71.6; H, 7.7. C₁₄H₁₈O₃ requires C, 71.8; H, 7.7%. IR (ATR) \(\tilde{\nu}_{\text{max}}/\text{cm}^{-1}\) 3065, 3027, 2981, 2937, 2905, 1719, 1696, 1620, 1599, 1492, 1477, 1445, 1375, 1355, 1283, 1263, 1217, 1202, 1155, 1124, 1098, 1045, 1021, 1000, 981, 816, 763, 727. \(^1\)H—NMR (400 MHz, CDCl₃) 7.26—7.30 (2 H, m), 7.18—7.22 (3 H, m), 5.01 (1 H, s), 3.68 (3 H, s), 3.62 (3 H, s), 2.82 (2 H, t, \(J = 7.8\)), 2.67 (2 H, t, \(J = 7.8\)), 1.85—1.93 (2 H, m). \(^{13}\)C–NMR (101 MHz, CDCl₃) 176.5, 168.0, 142.2, 128.4, 128.2, 125.7, 90.3, 55.4, 50.7, 36.6, 31.8, 29.2. MS (Ion trap, El) \(m/z\) 129.8 (67), 111.0 (69), 104.0 (100), 101.1 (65), 99.0 (78), 97.9 (66), 91.1 (68). HRMS-EI (TOF) found: 203.1082 [M-OMe]⁺. C₁₃H₁₅O₂ requires 203.1072 (M⁺-Peak too small for appropriate detection).
Control Experiments

Isomerization Experiments

\[
\begin{array}{c}
\text{An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with}
\text{potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere}
\text{was changed three times with argon; afterwards dimethyl carbonate (2a) (109 mg, 102 µl, 1.20}
\text{mmol) and a stock solution of 3aa (E/Z ratio 6:1) (192 mg, 1.00 mmol) in DMSO (1.5 mL) were}
\text{added via syringe. The resulting mixture was stirred (500 rpm) at room temperature for 12 h.}
\text{GC analysis after reaction showed an E/Z ratio of 15 : 1.}
\end{array}
\]

Deuterium Labeling Experiments

Synthesis of (E)-methyl 3-methoxy-3-phenyl(\(^2\)H)prop-2-enoate (3aa-\(d\)_1)

\[
\begin{array}{c}
\text{An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with}
\text{potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere}
\text{was changed three times with argon; afterwards DMSO-d_6 (168 mg, 141 µL, 2.00 mmol),}
\text{dimethyl carbonate (2a) (109 mg, 102 µl, 1.20 mmol) and phenylacetylene (1a) (102 mg, 110}
\text{µl, 1.00 mmol) were added via syringe. The resulting mixture was stirred (500 rpm) at room}
\text{temperature for 12 h. The crude reaction mixture was diluted with DMSO-d_6 (0.5 mL), filtered}
\text{and used for NMR analysis. \(^1\)H-NMR showed a deuterium incorporation of 94 % according to a}
\text{residual proton signal at 5.35 ppm with a relative integral of 0.06.}
\end{array}
\]
B: According to A phenylacetylene-d$_1$ (1a-d$_1$) (102 mg, 110 µl, 1.00 mmol) was reacted in non-deuterated DMSO (168 mg, 141 µL, 2.00 mmol). $^1$H-NMR analysis showed no deuterium incorporation.

C: According to A phenylacetylene-d$_1$ (1a-d$_1$) (102 mg, 110 µl, 1.00 mmol) was reacted with dimethyl carbonate (2a) (455 mg, 425 µl, 5.00 mmol). $^1$H-NMR showed a deuterium incorporation of 96 % according to a residual proton signal at 5.34 ppm with a relative integral of 0.04.
Spectra

(\textit{E})-methyl 3-methoxy-3-phenylprop-2-enoate (3aa)
(E)-methyl 3-methoxy-3-(2-methylphenyl)prop-2-enoate (3ba)
NOE Experiment
(E)-methyl 3-methoxy-3-(2-methoxyphenyl)prop-2-enoate (3ca)
(E)-methyl 3-(2-fluorophenyl)-3-methoxyprop-2-enoate (3da)
(E)-methyl 3-(2-bromophenyl)-3-methoxyprop-2-enoate (3ea)
(E)-methyl 3-(3-chlorophenyl)-3-methoxprop-2-enoate (3fa)
(E)-methyl 3-(4-chlorophenyl)-3-methoxyprop-2-enoate (3ga)
(E)-methyl 3-methoxy-3-[4-(trifluoromethyl)phenyl]prop-2-enooate (3ha)
Chemical Shift (ppm)
((E)-methyl 3-methoxy-3-(4-propylphenyl)prop-2-enoate (3ia)
(E)-methyl 3-methoxy-3-(naphthalen-2-yl)prop-2-enoate (3ja)
(E)-methyl 3-methoxy-3-(pyridin-2-yl)prop-2-enoate (3ka)
NOE Experiment
(E)-methyl 3-methoxy-3-(pyridin-3-yl)prop-2-enoate (3la)
(E)-methyl 3-methoxy-3-(thiophen-3-yl)prop-2-enoate (3ma)
(E)-methyl 3-methoxy-3-(thiophen-2-yl)prop-2-enoate (3na)
(E)-ethyl 3-ethoxy-3-(2-methylphenyl)prop-2-enoate (3bb)
Prop-2-en-1-yl (2E)-3-(2-methylphenyl)-3-(prop-2-en-1-yloxy)prop-2-enoate (3bc)
(E)-methyl 3-methoxyundec-2-enoate (3oa)
NOE Experiment
(E)-methyl 4-cyclohexyl-3-methoxybut-2-enoate (3pa)
(E)-methyl 3-cyclopropyl-3-methoxyprop-2-enoate (3qa)
(E)-methyl 3-methoxy-6-phenylhex-2-enoate (3ra)
(E)-methyl 3-methoxy-3-phenyl(²H)prop-2-enoate (3aa-d₁)

Chemical Shift (ppm)

Chemical Shift (ppm)
References
