1 General Information

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stir bars contaminated with transition metals were treated with aqua regia (conc. HCl/conc. HNO₃ 3:1) prior to cleaning. For cleaning, glassware and stir bars were kept in a iso-PrOH/KOH bath overnight, rinsed with H₂O, kept in a citric acid/H₂O bath overnight and finally rinsed with deionized H₂O and dried at 120 °C. Solutions and reagents were added with nitrogen-flushed disposable syringes/needles. Solvents were added using glass syringes and stainless steel needles (stored at 120 °C). Analytical thin layer chromatography (TLC) was performed on silica gel 60 G/UV₉₅₄ aluminium sheets (Macherey-Nagel). Flash column chromatography was performed on silica gel Davisil LC60A (40-63 μm, pore size 60 Å, Grace) using the indicated solvents. NMR spectra were recorded on AV400, AV500 or AV700 instruments (Bruker) at the Institut für Chemie of Technische Universität Berlin. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to the standard literature.[¹] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, mₖ = centrosymmetric multiplet), coupling constants (Hz), integration and – if possible – atom assignment. The assignment refers to the atom number shown in the corresponding molecule figure and was achieved by analysis of DEPT (DEPT 135) and 2D-NMR spectra (COSY, HMQC, HSQC, HMBC, NOESY). If a distinct assignment was not possible, atoms were marked with “*” and are interchangeable. Designation “Ar” refers to atoms of an aromatic system where a distinct assignment was not possible. Melting points (m.p.) were determined using a Leica Galen III melting point apparatus (Wagner & Munz). Infrared (IR) spectra were recorded on a Cary 630 FT-IR spectrometer equipped with an ATR unit (Agilent Technologies). Mass spectra (HRMS) were obtained from the Analytical Facility at the Institut für Chemie at Technische Universität Berlin (ESI/APCI: LTQ Orbitrap XL, Thermo Scientific; EI: GC-system 5975C, HP-5MS, Agilent Technologies). Analytical gas chromatography (GC) of reaction mixtures and pure substances was performed using a gas chromatograph 430-GC (Varian Inc.). The instrument was equipped with a FactorFour VF-WAXms capillary column (Varian Inc., length: 30 m, inner diameter: 0.25 mm, film thickness of the stationary phase: 0.25 μm). The following temperature program was used for the analysis: carrier gas N₂; injection temperature 270 °C; detector temperature 270 °C; flow rate 4.0 mL/min; temperature program: 40 °C start temperature, 20 °C/min heating rate to 250 °C for 10 min, then 20 °C/min heating rate to final temperature 260 °C for 5 min. The data was recorded with the program Galaxie 1.9.302.952 (Varian Inc.). Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an
Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OD-H column (n-heptane/iso-propanol = 98:2, 0.5 mL/min, 20 °C, 30 bar).

1.1 Solvents
THF and 1,4-dioxane were dried over sodium/benzophenone and distilled under N₂ atmosphere prior to use. Et₃N and CH₂Cl₂ were dried over CaH₂ and distilled under N₂ atmosphere prior to use. Acetone and EtOH were destilled under reduced pressure prior to use. Solvents (technical grade) for extraction/chromatography (n-pentane, cyclohexane, CH₂Cl₂, tert-butyl methyl ether, EtOAc) were destilled under reduced pressure prior to use. Liquid substrates for hydrogenation reactions were degassed prior to use.

1.2 Reactions under H₂ pressure
All reactions under H₂ pressure were carried out in glass vials (50 x 14 mm, Schütt), equipped with a magnetic stir bar and a rubber septum in autoclaves BR-100 or Br-300 (including the appropriate heating blocks, Berghof). The autoclave was purged with N₂ (3 x 10 bar) before the vials were placed in the autoclave and the septum was pierced under a counter flow of N₂. The autoclave was purged with N₂ (1 x 1 bar, 3 x 10 bar) and H₂ (3 x 10 bar) or D₂ (2 x 5 bar) before the appropriate H₂ or D₂ pressure was applied (pressure is given as initial pressure before heating). The heating block was pre-heated before the autoclave was placed inside. After the respective reaction time the autoclave was allowed to cool to rt and H₂ or D₂ was released. The autoclave was purged with N₂ (3 x 10 bar) before the vials were taken out.

1.3 Chemicals
All reagents were purchased from established commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, Acros, Strem., Merck, ABCR, Fluka, Fisher Scientific) and used without further purification. H₂ (99.999%) and D₂ (99.8%) was purchased from Air Liquide. (1E,2E)-N₁,N₂-dimesitylethane-1,2-diimine,[²] diethyl 3,3’-(1,4-phenylene)(2E,2’E)-bis(but-2-enoate) (8r),[³] ethyl (E)-2-methyl-3-phenylbut-2-enoate (8l),[⁴] ethyl 3-propylhex-2-enoate (8v),[³] ethyl (2E,4E)-5-phenylpenta-2,4-dienoate (12)[⁵], ethyl (E)-3-(4-(dimethylamino)phenyl)but-2-enoate (8n),[⁶] 1-(4-((tert-butyldiphenylsilyl)oxy)phenyl)ethan-1-one[⁷] and (E)-3-phenylbut-2-enoic acid[⁸] were synthesized following known procedures.
2 Additional optimization data

2.1 Influence of catalyst, base, solvent, pressure and temperature

Table S1: Influence of Cu-catalyst. 

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]</th>
<th>Conv. [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>[IMesCuCl] 3</td>
<td>&gt;95</td>
</tr>
<tr>
<td>2</td>
<td>[IPrCuBr] S1</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>[IPrCuCl] 4</td>
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<tr>
<td>4</td>
<td>[SIPrCuCl] 7</td>
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<tr>
<td>5</td>
<td>[SIpOMeMesCuCl] S2</td>
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<tr>
<td>6</td>
<td>[IAdCuCl] 5</td>
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</tr>
<tr>
<td>7</td>
<td>[SIpOMeMesCuCl] S2</td>
<td>&gt;95</td>
</tr>
</tbody>
</table>

All reactions with 4.6 μmol [Cu] in 1.1 mL solvent. Determined by $^1$H NMR spectroscopy.
Table S2: Influence of base.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Conv.(^b) [%]</th>
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<td>1</td>
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<td>2</td>
<td>1.1 equiv NaO(\text{tBu})</td>
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</tr>
<tr>
<td>3</td>
<td>no NaO(\text{tBu})</td>
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</tr>
<tr>
<td>4</td>
<td>no [IMesCuCl] 3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>no NaO(\text{tBu})</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>10 mol% NaO(\text{tBu})</td>
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</tr>
<tr>
<td>7</td>
<td>30 mol% NaO(\text{tBu})</td>
<td>&gt;95</td>
</tr>
<tr>
<td>8</td>
<td>50 mol% NaO(\text{tBu})</td>
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</tr>
<tr>
<td>9</td>
<td>80 mol% NaO(\text{tBu})</td>
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</table>

\(^a\) All reactions with 4.6 μmol [Cu] in 1.1 mL solvent. \(^b\) Determined by \(^1\)H NMR spectroscopy.

---

Table S3: Influence of solvent.\(^a\)

<table>
<thead>
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<th>Entry</th>
<th>solvent</th>
<th>Conv.(^b) [%]</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>1,4-dioxane</td>
<td>&gt;95</td>
</tr>
<tr>
<td>3</td>
<td>2-Me-THF</td>
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</tr>
<tr>
<td>4</td>
<td>DMF</td>
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<td>5</td>
<td>MeCN</td>
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<tr>
<td>6</td>
<td>cyclohexane</td>
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<td>Entry</td>
<td>solvent</td>
<td>Conv. (^b) [%]</td>
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<tr>
<td>-------</td>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>7</td>
<td>(n)-hexane</td>
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<tr>
<td>8</td>
<td>benzene</td>
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<tr>
<td>9</td>
<td>chlorobenzene</td>
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</tr>
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<td>10</td>
<td>1,2-dichlorobenzene</td>
<td>16</td>
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<tr>
<td>11</td>
<td>toluene</td>
<td>44</td>
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</table>

\(^a\) All reactions with 4.6 μmol [Cu] in 1.1 mL solvent. \(^b\) Determined by \(^1\)H NMR spectroscopy.

**Table S4:** Influence of \(\text{H}_2\)-pressure and temperature.\(^a\)

\[
\begin{align*}
\text{Ph} & \quad \text{OEt} & \quad \text{OEt} \\
1 & \quad \quad & \quad \\
\text{Ph} & \quad \quad & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \quad & \quad \text{OEt} \\
2 & \quad \quad & \quad \\
\text{Ph} & \quad \quad & \quad \text{H} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>(\text{H}_2) pressure [bar]</th>
<th>Temperature [°C]</th>
<th>Conv. (^b) [%]</th>
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</thead>
<tbody>
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<td>60</td>
<td>&gt;95</td>
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<td>10</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>100</td>
<td>&gt;95</td>
</tr>
<tr>
<td>4</td>
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<td>120</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>120</td>
<td>0</td>
</tr>
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</table>

\(^a\) All reactions with 5.5 μmol [Cu] in 1 mL solvent. \(^b\) Determined by \(^1\)H NMR spectroscopy. \(^c\) Reaction was performed in an \(\text{H}_2\)-purged pressure tube.
**Table S5**: Performance of Cu catalysts at low H\(_2\) pressure.\(^a\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]</th>
<th>H(_2) pressure [bar]</th>
<th>Temperature [°C]</th>
<th>Conv.(^b) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[IMesCuCl] 3</td>
<td>10</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>[SlpOMeMesCuCl] S2</td>
<td>10</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>[SIMesCuCl] 6</td>
<td>10</td>
<td>60</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>[SIMesCuCl] 6</td>
<td>1(^c)</td>
<td>100</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>[SIMesCuCl] 6</td>
<td>10</td>
<td>100</td>
<td>&gt;95 (71%)(^d)</td>
</tr>
</tbody>
</table>

\(^a\) All reactions with 5.5 μmol [Cu] in 1 mL solvent. \(^b\) Determined by \(^1\)H NMR spectroscopy. \(^c\) Reaction was performed in an H\(_2\)-purged pressure tube. \(^d\) Isolated yield.

**Table S6**: Investigation of E- and Z-enoates.\(^a\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Enoate</th>
<th>Conv.(^b) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>E-1</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Z-1</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

\(^a\) All reactions with 5.5 μmol [Cu] in 1 mL solvent. \(^b\) Determined by GC analysis
3 General procedures

3.1 General procedure 1 – synthesis of α,β-unsaturated esters 8 via Horner-Wadsworth-Emmons reaction (GP1)

According to a literature procedure[3] NaH (60 wt% in mineral oil, 2.00 equiv) is suspended in THF (0.5 M) and cooled to 0 °C. The corresponding phosphonate (2.00 equiv) is added dropwise and the reaction mixture is stirred at 0 °C for 30 min. The corresponding ketone (1.00 equiv) is added (neat for liquids, in solution in THF for solids 0.1 mL/mmol). The cooling bath is removed and the mixture is stirred at 40 °C until full conversion was detected (conversion monitored via TLC). After quenching the reaction by addition of H₂O (2 mL/mmol ketone) the aqueous phase is extracted with tert-butyl methyl ether (3 x 3 mL/mmol) and the combined organic layers are dried over Na₂SO₄ and filtered. All volatiles are removed under reduced pressure and the obtained crude product 8 is purified by flash column chromatography on silica gel.

3.2 General procedure 2 – H₂-mediated conjugate reduction (GP2)

In a 5 mL glass vial equipped with a septum, [SIMesCuCl] (6, 5.1 mg, 13 μmol, 5.0 mol%) is placed and the vial is transferred into a N₂-filled glovebox. NaOtfBu (7.2 mg, 75 μmol, 30 mol%) is added and the solids are dissolved in 1,4-dioxane (1 mL). The mixture is stirred for 5 min at 40 °C. The degassed α,β-unsaturated ester 8 (0.25 mmol, 1.0 equiv) is dissolved in 1,4-dioxane (0.5 mL) and transferred to the reaction vial. The vial is placed in an autoclave and the septum is pierced with a needle under N₂-counterflow. The autoclave is purged with H₂ (3 x 10 bar). The reaction mixture is stirred for 16 h at 100 °C under H₂-atmosphere (10 bar). The crude reaction mixture is filtered over a small plug silica (eluant: CH₂Cl₂,
0.5 x 3 cm, 10 mL) and all volatiles are removed under reduced pressure. The crude product 9 is purified by flash column chromatography on silica gel.

4 Experimental Details

4.1 Syntheses of α,β-unsaturated esters and amides

4.1.1 Ethyl (E)-3-phenylbut-2-enoate (1)

Prepared according to GP1 from acetophenone (2.3 mL, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 100:1) yielded 1 as a colorless oil (2.59 g, 13.6 mmol, 68%).

**Rf** = 0.35 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

**1H NMR** (500 MHz, CDCl3): δ = 1.32 (t, J = 7.1 Hz, 3H), 2.58 (d, J = 1.4 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 6.13 (q, J = 1.3 Hz, 1H), 7.33–7.39 (m, 3H), 7.45–7.50 (m, 2H) ppm.

**13C NMR** (126 MHz, CDCl3): δ = 14.4, 18.0, 59.9, 117.3, 126.4, 128.6, 129.0, 142.3, 155.5, 166.9 ppm.

**HRMS** (APCI) for C12H15O2+ [(M+H)+] calculated: 191.1067, found: 191.1070.
The data is in accordance with literature.[9]

4.1.2 Ethyl (E)-3-(naphthalen-2-yl)but-2-enoate (8a)

Prepared according to GP1 from 2-acetonaphthone (5.11 g, 30.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 2.40 g, 60.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (11.9 mL, 60.0 mmol, 2.00 equiv) in THF (60 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 100:1) yielded 8a as a colorless oil (4.93 g, 20.5 mmol, 68%).

**Rf** = 0.59 (SiO2, cyclohexane/tert-butyl methyl ether = 4:1).

**1H NMR** (500 MHz, CDCl3): δ = 1.35 (m, 3H), 2.70 (m, 3H), 4.26 (m, 2H), 6.29–6.31 (m, 1H), 7.50 (m, 2H), 7.60 (dd, J = 8.6 Hz, J = 1.9 Hz, 1H), 7.81–7.88 (m, 3H), 7.95 (d, J = 1.7 Hz, 1H) ppm.
$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 14.5, 18.0, 60.0, 117.6, 124.0, 126.0, 126.6, 126.8, 127.7, 128.2, 128.6, 133.2, 133.6, 139.5, 155.3, 167.0$ ppm.

HRMS (APCI) for C$_{16}$H$_{17}$O$_2^+$ [$(\text{M}+\text{H})^+$] calculated: 241.1223, found: 241.1228.

The data is in accordance with literature.[10]

4.1.3 tert-Butyl (E)-3-phenylbut-2-enoate (8b)

Prepared according to GP1 from acetophenone (2.1 mL, 18.6 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.48 g, 37.1 mmol, 2.00 equiv) and tert-butyl 2-(diethoxyphosphoryl)acetate (S4, 9.36 g, 37.1 mmol, 2.0 equiv) in THF (35 mL). The reaction mixture was stirred for 7 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 20:1) yielded 8b as a colorless oil (2.10 g, 9.76 mmol, 65%).

$R_f = 0.80$ (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.52$ (s, 9H), 2.53 (d, $J = 1.3$ Hz, 3H), 6.05 (q, $J = 1.3$ Hz, 1H), 7.31–7.37 (m, 3H), 7.43–7.48 (m, 2H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 17.9, 28.4, 80.1, 119.2, 126.4, 128.5, 128.8, 142.7, 154.1, 166.5$ ppm.

HRMS (APCI) for C$_{14}$H$_{19}$O$_2^+$ [$(\text{M}+\text{H})^+$] calculated: 219.1380, found: 219.1375.

IR (ATR): $\tilde{\nu} = 2975$ (w), 1703 (s), 1625 (s), 1445 (m), 1365 (m), 1273 (m), 1203 (w), 1138 (s), 1011 (m), 915 (w), 871 (m), 758 (m), 692 (s) cm$^{-1}$.

4.1.4 Ethyl 3,3-diphenylacrylate (8c)

Prepared according to GP1 from benzophenone (3.64 g, 20.0 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8c as a colorless oil (2.87 g, 11.4 mmol, 57%).

$R_f = 0.46$ (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.11$ (t, $J = 7.1$ Hz, 3H), 4.05 (q, $J = 7.1$ Hz, 2H), 6.37 (s, 1H), 7.19–7.24 (m, 2H), 7.28–7.42 (m, 8H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 14.1, 60.1, 117.6, 127.9, 128.2, 128.4, 128.9, 140.9, 156.5, 166.2$ ppm.
HRMS (APCI) for C_{13}H_{17}O_{2}^{+} [(M+H)^{+}] calculated: 253.1223, found: 253.1217.

The data is in accordance with literature.[3]

4.1.5 Ethyl (E)-3-(4-methoxyphenyl)but-2-enoate (8d)

Prepared according to GP1 from 4-methoxy acetophenone (3.00 g, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8d as a yellow oil (2.87 g, 13.0 mmol, 65%).

R_f = 0.36 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.31 (t, J = 7.2 Hz, 3H), 2.56 (d, J = 1.3 Hz, 3H), 3.83 (s, 3H), 4.21 (q, J = 7.1 Hz, 2H), 6.11 (q, J = 1.3 Hz, 1H), 6.89 (m, 2H), 7.45 (m, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): δ = 14.4, 17.7, 55.4, 59.8, 113.9, 115.4, 127.7, 134.4, 154.9, 160.5, 167.1 ppm.

HRMS (APCI) for C_{13}H_{17}O_{3}^{+} [(M+H)^{+}] calculated: 221.1172, found: 221.1165.

The data is in accordance with the literature.[3]

4.1.6 Ethyl (E)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (8e)

Prepared according to GP1 from 4-trifluoroacetophenone (3.76 g, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8e as a colorless oil (3.31 g, 12.8 mmol, 65%).

R_f = 0.46 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.32 (t, J = 7.1 Hz, 3H), 2.57 (d, J = 1.3 Hz, 3H), 4.23 (q, J = 7.1 Hz, 2H), 6.14 (q, J = 1.3 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): δ = 14.4, 18.0, 60.2, 119.1, 124.1 (q, J = 272.2 Hz), 125.6 (q, J = 3.8 Hz), 126.7, 130.9 (q, J = 32.7 Hz), 145.9, 153.8, 166.5 ppm.

^{19}F NMR (659 MHz, CDCl_3): δ = –62.7 ppm.

HRMS (APCI) for C_{13}H_{14}F_{3}O_{2}^{+} [(M+H)^{+}] calculated: 259.0940, found: 259.0935.

The data is in accordance with literature.[9]
4.1.7 Ethyl (E)-3-(4-bromophenyl)but-2-enoate (8f)

Prepared according to GP1 from 1-(4-bromophenyl)ethan-1-one (2.99 g, 15 mmol, 1.0 equiv), NaNH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8f as a colorless oil (2.54 g, 9.44 mmol, 63%).

R_F = 0.44 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.31 (t, J = 7.1 Hz, 3H), 2.54 (d, J = 1.3 Hz, 3H), 4.21 (q, J = 7.1 Hz, 2H), 6.11 (m, 1H), 7.33 (m, 2H), 7.49 (m, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): δ = 14.4, 17.9, 60.1, 117.7, 123.3, 128.0, 131.8, 141.2, 154.1, 166.7 ppm.

HRMS (APCI) for C_{12}H_{14}BrO_2 ([M+H]^+) calculated: 269.0172, found: 269.0168.

The data is in accordance with literature.^[9]

4.1.8 Ethyl (E)-3-(4-chlorophenyl)but-2-enoate (8g)

Prepared according to GP1 from 1-(4-chlorophenyl)ethan-1-one (2.0 mL, 15 mmol, 1.0 equiv), NaNH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8g as a colorless oil (2.15 g, 10.0 mmol, 67%).

R_F = 0.48 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.31 (t, J = 7.1 Hz, 3H), 2.54 (d, J = 1.3 Hz, 3H), 4.21 (q, J = 7.1 Hz, 2H), 6.10 (d, J = 1.3 Hz, 1H), 7.33 (m, 2H), 7.49 (m, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): δ = 14.4, 17.9, 60.0, 117.7, 123.0, 128.0, 131.8, 141.2, 154.1, 166.7 ppm.

HRMS (APCI) for C_{12}H_{14}ClO_2 ([M+H]^+) calculated: 225.0677, found: 225.0672.

The data is in accordance with literature.^[9]

4.1.9 Ethyl (E)-3-(o-tolyl)but-2-enoate (8h)

Prepared according to GP1 from 1-(o-tolyl)ethan-1-one (2.0 mL, 15 mmol, 1.0 equiv), NaNH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and
triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8h as a colorless oil (1.97 g, 9.66 mmol, 64%).

\[ R_f = 0.55 \text{ (SiO}_2\text{, cyclohexane/tert-butyl methyl ether = 10:1).} \]

**^1H NMR** (500 MHz, CDCl\textsubscript{3}): \( \delta = 1.31 \text{ (t, } J = 7.1 \text{ Hz, 3H), 2.29 \text{ (s, 3H), 2.44 \text{ (d, } J = 1.4 \text{ Hz, 3H), 4.21 \text{ (q, } J = 7.1 \text{ Hz, 2H), 5.76 \text{ (q, } J = 1.4 \text{ Hz, 1H), 7.05–7.08 \text{ (m, 1H), 7.14–7.23 \text{ (m, 3H) ppm.}}} \]

**^13C NMR** (126 MHz, CDCl\textsubscript{3}): \( \delta = 14.4, 19.8, 20.9, 59.9, 119.5, 125.8, 127.2, 127.8, 130.5, 134.0, 144.0, 158.3, 166.8 \text{ ppm.} \)

**HRMS** (APCI) for C\textsubscript{13}H\textsubscript{17}O\textsubscript{2} \([\text{M+H}]^+\) calculated: 205.1223, found: 205.1218.

The data is in accordance with literature.\textsuperscript{[11]}

**4.1.10 Ethyl (E)-3-(4-nitrophenyl)but-2-enoate (8i)**

Prepared according to GP1 from 4-nitroacetophenone (2.48 g, 15.0 mmol, 1.00 equiv), NaH (60 wt\% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 6.78 g, 30.0 mmol, 2.00 equiv) in THF (40 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/tert-butyl methyl ether = 20:1 yielded 8i as a colorless oil (E/Z = 88:12, 1.20 g, 5.12 mmol, 34%).

\[ R_f = 0.37 \text{ (SiO}_2\text{, cyclohexane/tert-butyl methyl ether = 9:1).} \]

**^1H NMR** (500 MHz, CDCl\textsubscript{3}): \( \delta = 1.32 \text{ (t, } J = 7.2 \text{ Hz, 3H), 2.58 \text{ (d, } J = 1.2 \text{ Hz, 3H), 4.24 \text{ (q, } J = 7.2 \text{ Hz, 2H), 6.18 \text{ (m, 1H), 7.61 \text{ (m, 2H), 8.21 \text{ (m, 2H) ppm.}}} \]

**^13C NMR** (126 MHz, CDCl\textsubscript{3}): \( \delta = 14.4, 18.0, 60.4, 120.3, 123.9, 127.4, 148.1, 148.7, 152.8, 166.2 \text{ ppm.} \)

**HRMS** (APCI) for C\textsubscript{14}H\textsubscript{18}N\textsubscript{2}O\textsubscript{3}\textsuperscript{+} \([\text{M+H+MeCN}]^+\) calculated: 262.1306, found: 262.1158.

**IR** (ATR): \( \tilde{\nu} = 2986 \text{ (w), 2907 \text{ (w), 2114 \text{ (w), 1709 \text{ (s), 1594 \text{ (m), 1511 \text{ (s), 1339 \text{ (s), 1274 \text{ (m), 1177 \text{ (s), 1039 \text{ (m), 846 \text{ (s.}})}} \]

**4.1.11 Ethyl (E)-3-(4-cyanophenyl)but-2-enoate (8j)**

Prepared according to GP1 from 4-acetylbenzonitrile (2.17 g, 15 mmol, 1.0 equiv), NaH (60 wt\% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.00 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel
cyclohexane/tert-butyl methyl ether = 20:1) yielded 8j as a colorless oil (2.10 g, 9.76 mmol, 65%).

R_f = 0.21 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.31 (t, J = 7.1 Hz, 3H), 2.55 (d, J = 1.3 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 6.13 (q, J = 1.3 Hz, 1H), 7.54 (m, 2H), 7.66 (m, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): δ = 14.4, 17.8, 60.3, 112.6, 118.5, 119.8, 127.1, 132.4, 146.8, 153.1, 166.2 ppm.

HRMS (APCI) for C_{13}H_{14}NO_2 \[ \text{[(M+H)]^+} \] calculated: 216.1019, found: 216.1020.

The data is in accordance with literature.\[9\]

4.1.12 Ethyl (E)-3-(4-acetylphenyl)but-2-enoate (8k)

Prepared according to GP1 from 1,1’-(1,4-phenylene)bis(ethan-1-one) (2.43 g, 15.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 0.670 g, 16.5 mmol, 1.1 equiv) and triethyl phosphonoacetate (3.3 mL, 17 mmol, 1.1 equiv) in THF (40 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/tert-butyl methyl ether = 10:1) yielded 8k as a colorless oil (E/Z = 87:13, 1.29 g, 5.54 mmol, 37%).

R_f = 0.23 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.32 (t, J = 7.2 Hz, 3H), 2.58 (d, J = 1.4 Hz, 3H), 2.61 (s, 3H), 4.23 (q, J = 7.2 Hz, 2H), 6.17 (q, J = 1.3 Hz, 1H), 7.55 (m, 2H), 7.95 (m, 2H) ppm.

Indicative signals for the Z-isomer are at δ = 1.10, 4.00, 5.95, 7.28.

^13C NMR (126 MHz, CDCl_3): δ = 14.5 (C-2’’), 18.0 (C-4), 26.8 (C-6’), 60.2 (C-1’’), 119.0 (C-2), 126.7 (C-2’), 128.7 (C-3’), 137.3 (C-4’), 146.9 (C-1’), 154.1 (C-3), 166.6 (C-1), 197.6 (C-5’) ppm.

HRMS (APCI) for C_{14}H_{17}O_3 \[ \text{[(M+H)]^+} \] calculated: 233.1172, found: 233.1169.

IR (ATR): ν = 2975 (w), 1681 (m), 1626 (m), 1358 (m), 1261 (s), 1159 (s), 1039 (m), 829 (m).

The data is in accordance with literature.\[12\]

4.1.13 Ethyl (E)-3-(4-hydroxyphenyl)but-2-enoate (8l)

In a 10 mL-schlenkflask ethyl (E)-3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (8m, 204 mg, 1.24 mmol, 1.00 equiv) was desolved in THF (5 mL). Tetrabutylammonium fluoride solution (1M, 1.4 mL, 1.4 mmol, 1.1 equiv) was added. The resulting solution was stirred for 1 h at rt until full conversion
(conversion monitored via TLC). After quenching the reaction by addition of saturated aqueous NH₄Cl solution (10 mL) the aqueous phase was extracted with tert-butyl methyl ether (3 x 10 mL) and the combined organic layers were dried over MgSO₄ and filtered. All volatiles were removed and the obtained crude product 8l was purified by flash column chromatography on silica gel (cyclohexane/ tert-butyl methyl ether = 10:1). The product 8l was obtained as a white solid (150 mg, 0.728 mmol, 59%).

Rₛ = 0.57 (SiO₂, cyclohexane/tert-butyl methyl ether = 2:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.31 (t, J = 7.1 Hz, 3H), 2.55 (d, J = 1.3 Hz, 3H), 4.21 (q, J = 7.1 Hz, 2H), 5.15 (br s, 1H), 6.09 (q, J = 1.3 Hz, 1H), 6.83 (m, 2H), 7.40 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 14.4, 17.8, 59.9, 115.4, 115.5, 128.0, 134.7, 155.0, 156.7, 167.3 ppm.

HRMS (APCI) for C₁₃H₁₄NO₂⁺ [(M+H)⁺] calculated: 207.1016, found: 207.1011.

IR (ATR): 𝜐̃ = 3340 (m), 1676 (m), 1595 (m), 1509 (w), 1435 (w), 1274 (m), 1171 (m), 1041 (w), 869 (w), 835 (m) cm⁻¹.

M.p.: T = 94 °C.

4.1.14 Ethyl (E)-3-(4-((tert-butylidiphenylsilyl)oxy)phenyl)but-2-enoate (9m)

Prepared according to GP1 from 1-(4-((tert-butylidiphenylsilyl)oxy)phenyl)ethan-1-one (1.7 g, 4.6 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 0.40 g, 10.0 mmol, 2.2 equiv) and triethyl phosphonoacetate (2.0 mL, 10 mmol, 2.2 equiv) in THF (10 mL). The reaction mixture was stirred for 20 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/tert-butyl methyl ether = 100:1) yielded 9m as a white solid (E/Z = 93:7, 0.550 g, 1.24 mmol, 27%).

Rₛ = 0.69 (SiO₂, cyclohexane/tert-butyl methyl ether = 9:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.10 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H), 2.49 (d, J = 1.2 Hz, 3H), 4.18 (q, J = 7.1 Hz, 2H), 6.03 (q, J = 1.2 Hz, 1H), 6.74 (m, 2H), 7.25 (m, 2H), 7.34–7.40 (m, 4H), 7.41–7.46 (m, 2H), 7.69–7.73 (m, 4H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 14.4, 17.6, 19.6, 26.6, 59.7, 115.4, 119.7, 127.5, 127.9, 130.1, 132.7, 134.7, 135.6, 155.0, 156.7, 167.2 ppm.

The NMR spectra contain 7% of the Z-Isomer, indicative signals in ¹H NMR are at 1.20, 3.74, 5.29 and 7.68 ppm.

²⁹Si DEPT NMR (99MHz, J = 20 Hz, CDCl₃): δ = −5.6 ppm.
HRMS (APCI) for C_{28}H_{33}O_{3}Si^{+} [(M+H)^{+}] calculated: 445.2193, found: 445.2184.

IR (ATR): v = 2930 (w), 2892 (w), 2857 (w), 1703 (m), 1598 (m), 1507 (m), 1424 (w), 1372 (w), 1258 (s), 1112 (s), 1044 (m), 1007 (w), 916 (s), 819 (s), 696 (s) cm^{-1}.

M.p.: T = 69 °C.

4.1.10 Ethyl (E)-3-(thiophen-2-yl)but-2-enoate (8o)

Prepared according to GP1 from 1-(thiophen-2-yl)ethan-1-one (1.6 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 36 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8o as a colorless oil (1.64 g, 8.33 mmol, 56%).

R_f = 0.43 (SiO_2, cyclohexane/tert-butyl methyl ether = 10:1).

^1H NMR (500 MHz, CDCl_3): \( \delta = 1.31 \) (t, \( J = 7.1 \) Hz, 3H), 2.60 (d, \( J = 1.2 \) Hz, 3H), 4.20 (q, \( J = 7.1 \) Hz, 2H), 6.25 (q, \( J = 1.2 \) Hz, 1H), 7.04 (m, 1H), 7.30–7.32 (m, 2H) ppm.

^13C NMR (126 MHz, CDCl_3): \( \delta = 14.4 \), 17.4, 59.9, 114.4, 126.7, 127.1, 128.0, 145.7, 147.8, 166.8 ppm.

HRMS (APCI) for C_{10}H_{13}O_{2}S^{+} [(M+H)^{+}] calculated: 197.0631, found: 197.0626.

The data is in accordance with literature.^[9]

4.1.15 Ethyl (E)-3-cyclopropyl-3-phenylacrylate (8p)

Prepared according to GP1 from cyclopropyl(phenyl)methanone (2.1 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8p as a colorless oil (0.64 g, 3.0 mmol, 35%).

R_f = 0.5 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

^1H NMR (500 MHz, CDCl_3): \( \delta = 0.47 \) (m, 2H), 0.89 (m, 2H), 1.30 (t, \( J = 7.1 \) Hz, 3H), 3.12 (m, 1H), 4.21 (q, \( J = 7.1 \) Hz, 2H), 5.79 (d, \( J = 0.8 \) Hz, 1H), 7.11–7.15 (m, 2H), 7.27–7.33 (m, 3H) ppm.

^13C NMR (126 MHz, CDCl_3): \( \delta = 7.0 \), 13.6, 14.4, 59.8, 118.9, 127.8, 127.8, 128.1, 138.9, 163.2, 167.0 ppm.

S16
HRMS (APCI) for C_{16}H_{21}O_{2}^{+} [(M+H)^{+}] calculated: 245.1536, found: 245.1532.

The data is in accordance with literature.\[^9\]

4.1.16 Hex-5-en-1-yl (E)-3-phenylbut-2-enoate (8q)

Following a literature procedure,\[^{13}\] in a 25 mL-schlenk tube, (E)-3-phenylbut-2-enoic acid (0.50 g, 3.1 mmol, 1.00 equiv) was dissolved in CH_{2}Cl_{2} (10 mL). DMAP (452 mg, 3.70 mmol, 1.20 equiv) and hex-5-en-1-ol (0.73 mL, 6.2 mmol, 2.0 equiv) were added. The resulting solution was cooled to 0 °C and DCC (954 mg, 4.62 mmol, 1.50 equiv) was added. The solution was stirred for 5 min at 0 °C and 18 h at rt until full conversion was detected (conversion monitored via TLC). Precipitated urea was filtered off over a plug of silica gel (3 x 3 cm, eluent: CH_{2}Cl_{2}, 30 mL). The filtrate was evaporated and the obtained crude product 8q was purified by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 100:1). Remaining urea residues were removed by dissolving the product 8q in Et_{2}O (10 mL) and washing the organic layer with aqueous HCl (2M, 3 x 10 mL). The organic layer was dried over MgSO_{4}, filtered and all volatiles were removed. The product 8q was obtained as a yellow oil (330 mg, 1.35 mmol, 44%).

R_{f} = 0.73 (SiO_{2}, cyclohexane/tert-butyl methyl ether = 9:1).

\[^1\]H NMR (500 MHz, CDCl_{3}): δ = 1.46–1.55 (m, 2H), 1.66–1.74 (m, 2H), 2.11 (m, 2H), 2.57 (d, J = 1.3 Hz, 3H), 4.16 (t, J = 6.6 Hz, 2H), 4.97 (m, 1H), 5.02 (m, 1H), 5.81 (m, 1H), 6.13 (q, J = 1.3 Hz, 1H), 7.34–7.40 (m, 3H), 7.45–7.50 (m, 2H) ppm.

\[^{13}\]C NMR (126 MHz, CDCl_{3}): δ = 18.0, 25.4, 28.3, 33.4, 63.9, 114.9, 117.3, 126.4, 128.6, 129.0, 138.5, 142.3, 155.6, 167.0 ppm.

HRMS (APCI) for C_{16}H_{21}O_{2}^{+} [(M+H)^{+}] calculated: 245.1536, found: 245.1532.

IR (ATR): \bar{\nu} = 2934 (w), 1709 (s), 1575 (w), 1445 (w), 1379 (w), 1270 (m), 1154 (s), 1023 (m), 870 (m), 764 (s), 692 (m) cm\(^{-1}\).

4.1.17 Ethyl (E)-3-cyclohexylbut-2-enoate (8t)

Prepared according to GP1 from 1-cyclohexylethan-1-one (2.1 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8t as a colorless oil (E/Z = 90:10, 2.22 g, 11.3 mmol, 75%).
$R_f = 0.56$ (SiO$_2$, cyclohexane/tert-butyl methyl ether = 10:1).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.11$–1.39 (m, 8H), 1.55–1.82 (m, 5H), 1.96 (tt, $J = 1.9$ Hz, $J = 2.8$ Hz, 1H), 2.13 (d, $J = 1.2$ Hz, 3H), 4.13 (q, $J = 7.1$ Hz, 2H), 5.64 (m, 1H) ppm.

The sample contains 10% of the Z-isomer (detected via $^1$H NMR and $^1$H-$^1$H NOESY). Therefore, the value of the integration for the cyclohexyl substituent is too high (see the attached spectra).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 14.4$, 17.5, 26.2, 26.5, 31.5, 48.8, 59.5, 114.0, 164.9, 167.4 ppm.

HRMS (APCI) for C$_{12}$H$_{21}$O$_2$ $^{+}$ [(M+H)$^+$] calculated: 197.1536, found: 197.1531.

The data is in accordance with literature.[14]

### 4.1.18 Ethyl (E)-3-methylundec-2-enoate (8u)

Prepared according to GP1 from decan-2-one (2.8 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 50:1) yielded 8u as a colorless oil ($E/Z = 77:23$, 3.17 g, 14.0 mmol, 93%).

$R_f = 0.59$ (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

**E-isomer:**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 6.9$ Hz, 3H), 1.16–1.36 (m, 13H), 1.41–1.49 (m, 2H), 2.12 (m, 2H), 2.14 (d, $J = 1.3$ Hz, 3H), 4.14 (q, $J = 7.1$ Hz, 2H), 5.65 (q, $J = 1.2$ Hz, 1H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 14.2$, 14.4, 18.9, 22.7, 27.5, 29.3, 29.3, 29.5, 31.9, 41.0, 49.5, 115.5, 160.4, 167.0 ppm.

**Z-isomer:**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 0.87$ (t, $J = 7.0$ Hz, 3H), 2.54 (d, $J = 1.3$ Hz, 3H), 4.21 (q, $J = 7.1$ Hz, 2H), 6.10 (d, $J = 1.3$ Hz, 1H), 1.87 (d, $J = 1.3$ Hz, 3H), 4.13 (q, $J = 7.1$ Hz, 2H), 5.63 (m, 1H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 14.2$, 14.4, 25.2, 28.3, 29.3, 29.5, 29.8, 33.5, 59.4, 116.0, 160.8 ppm.

E- and Z-Isomer could be identified via $^1$H-$^1$H NOESY.

Not all signals for the Z-isomer could be detected in $^1$H and $^{13}$C NMR due to low concentration and overlay with signals of the E-isomer.
HRMS (APCI) for C$_{14}$H$_{27}$O$_2$·[(M+H)$^+$] calculated: 227.2006, found: 227.1997.

The data is in accordance with literature.$^{[14]}$

4.1.19 (E)-N,N-diethyl-3-phenylbut-2-enamide (10)

Prepared according to GP1 from acetophenone (0.47 mL, 4.0 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 316 mg, 7.96 mmol, 2.00 equiv) and diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (S6, 1.8 mL, 8.0 mmol, 2.0 equiv) in THF (8 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 4:1) yielded 10 as a colorless oil (589 mg, 2.71 mmol, 68%).

R$_f$ = 0.16 (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

$^1$H NMR (500 MHz, CDCl$_3$): δ = 1.18 (t, J = 7.0 Hz, 6H), 2.30 (d, J = 1.2 Hz, 3H), 3.43 (m, 4H), 6.29 (d, J = 1.2 Hz, 1H), 7.29–7.38 (m, 3H), 7.42–7.46 (m, 2H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): δ = 13.3, 14.5, 18.0, 39.7, 42.7, 120.3, 126.1, 128.2, 128.5, 142.3, 145.6, 167.7 ppm.

HRMS (APCI) for C$_{14}$H$_{20}$N.O$^+$ [(M+H)$^+$] calculated: 218.1539, found: 218.1531.

The data is in accordance with literature.$^{[15]}$

4.1.20 Ethyl (E)-3-(4-(phenylethynyl)phenyl)but-2-enoate (S3)

Prepared according to GP1 from 1-(4-(phenylethynyl)phenyl)ethan-1-one (1.65 g, 7.50 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 0.60 g, 15 mmol, 2.0 equiv) and triethyl phosphonoacetate (3.0 mL, 3.4 g, 15 mmol, 2.0 equiv) in THF (20 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/tert-butyl methyl ether = 70:1) yielded S3 as a colorless oil (1.36 g, 4.96 mmol, 66%).

R$_f$ = 0.46 (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

$^1$H NMR (500 MHz, CDCl$_3$): δ = 1.33 (t, J = 7.0 Hz, 3H), 2.58 (d, J = 1.3 Hz, 3H), 4.23 (q, J = 7.3 Hz, 2H), 6.17 (d, J = 1.3 Hz, 1H), 7.34–7.38 (m, 2H), 7.45–7.49 (m, 2H), 7.51–7.56 (m, 5H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): δ = 14.4, 17.7, 60.0, 89.1, 90.9, 117.7, 123.2, 124.1, 126.4, 128.5, 131.7, 131.8, 141.9, 154.5, 166.8 ppm.
HRMS (APCI) for C_{20}H_{19}O_{2}^+ [(M+H)^+] calculated: 291.1380, found: 291.1383.

IR (ATR): \tilde{\nu} = 2978 (w), 2908 (w), 2117 (w), 1705 (m), 1619 (m), 1440 (m), 1342 (m), 1272 (m), 1167 (s), 1039 (m), 879 (m), 831 (s), 756 (s).

4.2 Syntheses of alkyl phosphonates

4.2.1 tert-Butyl 2-(diethoxyphosphoryl)acetate (S4)

According to a literature procedure\[16]\ a 25 mL two neck flask with reflux condenser was charged with tert-butyl bromoacetate (7.2 mL, 50 mmol, 1.0 equiv) and triethylphosphite (8.6 mL, 50 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 1 h at 100 °C and heated to reflux for 14 h until full conversion was detected (conversion monitored via TLC). The obtained crude product S4 was purified by fractional distillation (106 °C, 8.6·10^{-1} mbar) and yielded S4 as a colorless oil (10.8 g, 43.0 mmol, 86%).

R_f = 0.56 (SiO_2, cyclohexane/tert-butyl methyl ether = 9:1).

\[^1\text{H}\text{ NMR}\ (500 \text{ MHz, CDCl}_3): \delta = 1.34 \text{ (t, } J = 7.1 \text{ Hz, 6H), 1.46 \text{ (s, 9H), 2.87 \text{ (d, } J = 21.4 \text{ Hz, 2H), 4.15 \text{ (m, 4H) ppm.}}

\[^{13}\text{C} \text{ NMR}\ (126 \text{ MHz, CDCl}_3): \delta = 16.4 \text{ (d, } J = 6.1 \text{ Hz), 28.0, 35.7 \text{ (d, } J = 133.1 \text{ Hz), 62.5 \text{ (d, } J = 6.0 \text{ Hz), 82.1, 165.0 \text{ (d, } J = 6.3 \text{ Hz) ppm.}}

\[^{31}\text{P} \text{ NMR}\ (202 \text{ MHz, CDCl}_3): \delta = 20.5 \text{ (m) ppm.}}

HRMS (APCI) for C_{10}H_{22}O_{5}P^+ [(M-H)^+] calculated: 253.1199, found: 253.1191.

The data is in accordance with literature.\[16,17\]

4.2.2 2-Chloro-N,N-diethylacetamide (S5)

According to a literature procedure\[18\] diethylamine (3.1 mL, 30 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (150 mL). Triethylamine (4.8 mL, 38 mmol, 1.3 equiv) was added and chloroacetylchloride (2.6 mL, 33 mmol, 1.1 equiv) was added dropwise over 15 min. The reaction mixture was stirred for 16 h at rt until full conversion (conversion monitored via TLC). The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous HCl (1M, 3 x 40 mL). The organic layer was dried over MgSO_4 and filtered. The obtained crude product S5 was purified by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 2:1) and yielded S5 as a orange oil (3.18 g, 21.3 mmol, 71%).

R_f = 0.28 (SiO_2, cyclohexane/tert-butyl methyl ether = 1:1).

\[^1\text{H} \text{ NMR}\ (500 \text{ MHz, CDCl}_3): \delta = 1.13 \text{ (t, } J = 7.1 \text{ Hz, 3H), 1.22 \text{ (t, } J = 7.1 \text{ Hz, 3H), 3.37 \text{ (m,}}

S20
4H), 4.04 (s, 2H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): δ = 12.7, 14.4, 40.6, 41.3, 42.5, 165.8 ppm.

HRMS (APCI) for C$_6$H$_{13}$ClNO$^+$ [(M+H)$^+$] calculated: 150.0680, found: 150.0677.

IR (ATR): $\tilde{\nu}$ = 2973 (w), 1639 (s), 1429 (m), 1380 (m), 1315 (w), 1253 (m), 1218 (m), 1120 (m), 1098 (m), 1016 (w), 950 (w), 788 (m), 721 (w) cm$^{-1}$.

4.2.3 Diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (S6)

According to a literature procedure$^{[15]}$ a 25 mL two neck flask with reflux condenser was charged with 2-chloro-N,N-diethylacetamide (S6, 3.00 g, 20.0 mmol, 1.0 equiv) and triethylphosphite (3.6 mL, 21.1 mmol, 1.15 equiv) was added. The reaction mixture was stirred for 8 h at 180 °C. The obtained crude product S6 was purified by fractional distillation (125 °C, 1.2·10$^{-1}$ mbar) and yielded S6 as a colorless oil (4.01 g, 15.9 mmol, 80%).

Bp = 125 °C (1.2·10$^{-1}$ mbar).

$^1$H NMR (500 MHz, CDCl$_3$): δ = 1.12 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.0 Hz, 6H), 3.00 (d, J = 22.0 Hz, 2H), 3.40 (m, 4H), 4.16 (m, 4H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): δ = 13.0, 14.2, 16.4 (d, J = 6.3 Hz), 33.5 (d, J = 134.0 Hz), 40.6, 43.1, 62.6 (d, J = 6.5 Hz), 164.0 (d, J = 5.6 Hz) ppm.

$^{31}$P NMR (202 MHz, CDCl$_3$): δ = 21.4 (m) ppm.

HRMS (APCI) for C$_{10}$H$_{23}$NO$_4$P$^+$ [(M+H)$^+$] calculated: 252.1359, found: 252.1351.

The data is in accordance with literature.$^{[15]}$

4.3 Synthesis of [SIMesCuCl] 6

4.3.1 Synthesis of N$^1$N$^2$-dimesitylethane-1,2-diaminium chloride (S7)

Following a literature procedure$^{[2]}$ in a 250 mL-schlenk flask, N$^1$N$^2$-dimesitylethane-1,2-diimine (5.00 g, 17.1 mmol, 1.00 equiv) was dissolved in THF (80 mL) and and the solution was cooled to 0 °C. NaBH$_4$ (2.59 g, 68.4 mmol, 4.00 equiv) was added and the suspension was stirred for 15 min at 0 °C. Concentrated aqueous HCl (2.9 ml, 34 mmol, 2.0 equiv) was added dropwise over 30 min. The suspension was stirred for 1 h at 0 °C. Aqueous HCl (3M, 130 mL) was added and the suspension was stirred for 16 h at rt. The precipitate was collected on a sintered funnel and washed with H$_2$O (100 mL). The obtained product was dried under reduced pressure (2·10$^{-2}$ mbar) and used without further purification. The product S7 (4.88 g, 13.2 mmol, 77%) was obtained as a white solid.
\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 2.22\) (s, 6H, H-2”), 2.31–2.40 (m, 12H, H-1”), 3.34–3.49 (m, 4H, H-1), 6.91 (s, 4H, H-3’) ppm.

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)): \(\delta = 18.0\) (C-1”), 20.2 (C-2”), 46.9 (C-4), 129.8 (C-3’), 130.9 (C-1’), 135.8 (C-4’) ppm. C-2’ could not be detected in \(^{13}\)C NMR.

HRMS (APCI) for \(C_{20}H_{29}N_2^+\) [\((M-2Cl-H)^+]\): calculated: 297.2325, found: 297.2320.

The data is in accordance with literature.\[^{19}\]

4.3.2 Synthesis of 1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride (S8)

Following a literature procedure\[^{20}\], in a 100 mL-two-necked flask, \(N^1,N^2\)-dimesitylethane-1,2-diaminium chloride (S7, 4.80 g, 13.0 mmol, 1.00 equiv) was suspended in triethylorthoformate (65 mL) and formic acid (3 drops) was added. The resulting suspension was stirred for 48 h at 120 °C. The precipitate was filtered off and washed with \(\text{Et}_2\text{O}\) (30 mL). The obtained crude product was purified by flash column chromatography on silica gel (\(\text{CH}_2\text{Cl}_2/\text{MeOH} = 50:1\)) and yielded S8 (3.09 mg, 9.01 mmol, 69%) as yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 2.25\) (s, 6H, H-2”), 2.32–2.39 (m, 12H, H-1”), 4.50–4.59 (m, 4H, H-4), 6.86–6.94 (m, 4H, H-3’), 9.41 (m, 1H, H-2) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta = 18.0\) (C-1”), 21.1 (C-2”), 52.0 (C-4), 130.1 (C-3’), 130.3 (C-1’), 135.0 (C-2”), 140.5 (C-4’), 160.0 (C-2) ppm.

HRMS (APCI) for \(C_{21}H_{27}C\text{Ni}^+\) [\((M-\text{Cl})^+]\): calculated: 307.2169, found: 442.1559.

IR (ATR): \(\tilde{\nu} = 3242\) (w), 2953 (w), 2914 (w), 2830 (w), 1620 (s), 1481 (m), 1450 (m), 1376 (w), 1266 (s), 1216 (s), 1151 (w), 1042 (m), 984 (w), 936 (w), 845 (m), 819 (m), 731 (s) cm\(^{-1}\).

The data is in accordance with literature.\[^{20}\]

4.3.3 Synthesis of (1,3-dimesitylimidazolidin-2-yliden)copper(I) chloride (6)

Following a literature procedure\[^{21}\] a 25 mL-two-necked flask was charged with copper(I) chloride (99.99%, 289 mg, 2.92 mmol, 1.00 equiv), 1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride (S8, 1.00 g, 2.92 mmol, 1.00 equiv) and \(\text{K}_2\text{CO}_3\) (806 mg, 5.83 mmol, 2.00 equiv). The flask was evacuated and backfilled with nitrogen (2 x). Acetone (12 mL) was added and the resulting yellow suspension was
stirred for 24 h at 60 °C. The reaction mixture was filtered over a plug of silica (3 x 2 cm, eluent: CH₂Cl₂, 2 x 30 mL) and the yellow filtrate was concentrated under reduced pressure to ~5 mL. n-Pentane (50 mL) was added rapidly to precipitate the crude product, which was collected on a funnel and washed with n-pentane (2 x 20 mL). The resulting yellow crystals were dried under reduced pressure. Copper(I)/NHC complex 6 (845 mg, 2.09 mmol, 72%) was obtained as yellow crystals.

¹H NMR (500 MHz, CDCl₃): δ = 2.29 (s, 6H, H-2''), 2.31 (s, 12H, H-1''), 3.94 (br s, 4H, H-4), 6.95 (s, 4H, H-3') ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 18.1 (C-1''), 21.1 (C-2''), 51.1 (C-4), 129.9 (C-3'), 135.1 (C-4'), 135.5 (C-1'), 138.8 (C-1') ppm. The ¹³C-NMR resonance of C-2 could not be detected.

HRMS (APCI) for C₂₃H₂₉CuN₃⁺ [(M–Cl)MeCN⁺]: calculated: 410.1657, found: 410.1649.

IR (ATR): ν = 2909 (w), 1607 (w), 1485 (s), 1438 (m), 1315 (w), 1270 (s), 1189 (w), 1020 (w), 849 (s), 802 (w), 731 (w) cm⁻¹.

M.p.: T = 205 °C.
The data is in accordance with literature.²¹

4.4 Conjugate reduction products

4.4.1 Ethyl 3-phenylbutanoate (2)

 Prepared according to GP2 from ethyl (E)-3-phenylbut-2-enoate (1, 95 mg, 0.50 mmol, 1.0 equiv), [SiMesCuCl] (6, 10 mg, 25 µmol, 5.0 mol%) and NaOtfBu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (2.0 mL). The reaction mixture was stirred for 16 h at 100 °C.

Purification by flash column chromatography on silica gel (cyclohexane/tert-butyl methyl ether = 30:1) yielded 2 as a colorless oil (68 mg, 0.35 mmol, 71%).

Rₓ = 0.33 (SiO₂, cyclohexane/tert-butyl methyl ether = 20:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.18 (m, 3H, H-1), 1.31 (d, 3J₁₀,₅ = 7.0 Hz, 3H, H-10), 2.58 (m, 2H, H-4), 3.28 (m, 1H, H-5), 4.08 (q, 3J₀₂,₁ = 7.1 Hz, 2H, H-2), 7.18–7.24 (m, 3H, H-7, H-9), 7.28–7.33 (m, 2H, H-8)ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 14.2 (C-1), 21.9 (C-10), 36.6 (C-5), 43.1 (C-4), 60.3 (C-2), 126.4 (C-7)*, 126.8 (C-9)*, 128.5 (C-8), 145.8 (C-6), 172.5 (C-3) ppm.

HRMS (APCI) for C₁₂H₁₇O₂⁺ [(M+H)⁺] calculated: 193.1223, found: 193.1222.
The data is in accordance with literature.²²
4.4.2 Ethyl 3-(naphthalen-2-yl)butanoate (9a)

Prepared according to GP2 from ethyl (E)-3-(naphthalen-2-yl)but-2-enoate (8a, 60 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9a as a colorless oil (41.1 mg, 0.170 mmol, 68%).

Rf = 0.45 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

1H NMR (500 MHz, CDCl3): δ = 1.16 (t, 3J1,2 = 7.1 Hz, 3H, H-1), 1.39 (d, 3J16,5 = 6.9 Hz, 3H, H-16), 2.67 (m, 2H, H-4), 3.46 (m, 1H, H-5) 4.07 (m, 2H, H-2), 7.38 (dd, 3J15,14 = 8.4 Hz, 4J15,7 = 1.8 Hz, 1H, H-15), 7.44 (m, 2H, H-10/H-11)*, 7.65 (m, 1H, H-7), 7.77–7.82 (m, 3H, H-9/H-12/H-14)* ppm.

13C NMR (126 MHz, CDCl3): δ = 14.2 (C-1), 21.9 (C-16), 36.7 (C-5), 43.0 (C-4), 60.4 (C-2), 125.0 (C-7), 125.4 (C-10)*, 125.6 (C-15), 126.0 (C-11)*, 127.6 (C-9)*, 127.7 (C-12)*, 128.2 (C-14)*, 132.4 (C-13), 133.6 (C-8), 143.3 (C-6), 172.4 (C-3) ppm.


The data is in accordance with literature.[23]

4.4.3 tert-Butyl 3-phenylbutanoate (9b)

Prepared according to GP2 from tert-butyl (E)-3-phenylbut-2-enoate (8b, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9b as a colorless oil (46 mg, 0.21 mmol, 84%).

Rf = 0.65 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

1H NMR (500 MHz, CDCl3): δ = 1.28 (d, 3J10,5 = 7.0 Hz, 3H, H-10), 1.35 (s, 9H, H-1), 2.49 (m, 2H, H-4), 3.22 (m, 1H, H-5), 7.00–7.23 (m, 3H, H-7/H-9), 7.26–7.31 (m, 2H, H-8) ppm.

13C NMR (126 MHz, CDCl3): δ = 22.0 (C-10), 28.1 (C-1), 36.9 (C-5), 44.3 (C-4), 80.3 (C-2), 126.3 (C-9), 126.9 (C-7), 128.4 (C-8), 146.0 (C-6), 171.8 (C-3) ppm.

HRMS (EI) for C14H20O2•+ [(M•+)] calculated: 220.1457, found: 220.1467.

IR (ATR): v = 2969 (w), 1724 (s), 1603 (w), 1452 (w), 1365 (m), 1255 (w), 1144 (s), 1082 (w), 1018 (m), 956 (m), 907 (w), 843 (m), 754 (m), 697 (s) cm⁻¹.
4.4.4 Ethyl 3,3-diphenylpropanoate (9c)

Prepared according to GP2 from ethyl 3,3-diphenylacrylate (8c, 63 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9c as a colorless oil (50.1 mg, 0.197 mmol, 79%). 

Rf = 0.45 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

1H NMR (500 MHz, CD2Cl2): δ = 1.11 (t, $^3J_{1,2} = 7.1$ Hz, 3H, H-1), 3.04 (d, $^3J_{4,5} = 8.0$ Hz, 2H, H-4), 4.01 (q, $^3J_{2,1} = 7.1$ Hz, 2H, H-2), 4.52 (t, $^3J_{5,4} = 8.0$ Hz, 1H, H-5), 7.16–7.21 (m, 2H, H-9), 7.22–7.31 (m, 8H, H-7/H-8) ppm.

13C NMR (126 MHz, CDCl3): δ = 14.2 (C-1), 40.9 (C-4), 47.4 (C-5), 60.7 (C-2), 126.8 (C-7), 128.0 (C-8), 144.2 (C-6), 171.9 (C-3) ppm.

HRMS (APCI) for C17H19O2 + [(M+H)⁺] calculated: 255.1380, found: 255.1374.

The data is in accordance with literature.[24]

4.4.5 Ethyl 3-(4-methoxyphenyl)butanoate (9d)

Prepared according to GP2 from ethyl (E)-3-(4-methoxyphenyl)but-2-enooate (8d, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 30:1) yielded 9d as a colorless oil (42.4 mg, 0.191 mmol, 76%).

Rf = 0.30 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

1H NMR (500 MHz, CDCl3): δ = 1.18 (t, $^3J_{1,2} = 7.1$ Hz, 3H, H-1), 1.27 (d, $^3J_{11,5} = 7.0$ Hz, 3H, H-11), 2.53 (m, 2H, H-4), 3.23 (m, 1H, H-5), 3.78 (s, 3H, H-10), 4.07 (m, 2H, H-2), 6.83 (m, 2H, H-8), 7.14 (m, 2H, H-7) ppm.

13C NMR (126 MHz, CDCl3): δ = 14.3 (C-1), 22.1 (C-11), 35.8 (C-5), 43.3 (C-4), 55.3 (C-10), 60.3 (C-2), 113.9 (C-8), 127.7 (C-7), 138.0 (C-6), 158.2 (C-9), 172.5 (C-3) ppm.

HRMS (APCI) for C13H19O3⁺ [(M+H)⁺] calculated: 223.1329, found: 223.1324.

The data is in accordance with literature.[25,26]
4.4.6 Ethyl 3-(4-(trifluoromethyl)phenyl)butanoate (9e)

Prepared according to GP2 from ethyl (E)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (8e, 64 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9e as a colorless oil (41.4 mg, 0.159 mmol, 64%).

\[ R_f = 0.45 \] (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\[ \text{\(^1\)H NMR (500 MHz, CDCl}_3\):} \delta = 1.17 (t, \(3J_{1,2} = 7.1\) Hz, 3H, H-1), 1.31 (d, \(3J_{10,5} = 7.0\) Hz, 3H, H-10), 2.59 (m, 2H, H-4), 3.34 (m, 1H, H-5), 4.07 (m, 2H, H-2), 7.33 (d, \(3J_{7,8} = 8.2\) Hz, 2H, H-7), 7.41 (d, \(3J_{8,7} = 8.3\) Hz, 2H, H-8) ppm.

\[ \text{\(^{13}\)C NMR (126 MHz, CDCl}_3\):} \delta = 14.2 (C-1), 21.9 (C-10), 36.5 (C-5), 42.6 (C-4), 60.5 (C-2), 124.4 (q, \(3J_{10,F} = 271.5\) Hz, C-10), 125.5 (q, \(3J_{8,F} = 3.6\) Hz, C-8), 127.3 (C-7), 128.8 (q, \(2J_{9,F} = 32.2\) Hz, C-9), 149.8 (C-6), 172.0 (C-3) ppm.

\[ \text{\(^{19}\)F NMR (659 MHz, CDCl}_3\):} \delta = -62.4 ppm.

HRMS (APCI) for C\(_{13}\)H\(_{16}\)F\(_3\)O\(_2\) + [(M+H)\(^+\)] calculated: 261.1097, found: 261.1090.

IR (ATR): \(\tilde{\nu} = 2970\) (w), 1731 (s), 1618 (m), 1457 (w), 1419 (w), 1371 (w), 1322 (s), 1268 (w), 1160 (s), 1112 (s), 1066 (s), 1015 (m), 953 (w), 838 (s), 712 (w) cm\(^{-1}\).

The \(^1\)H and \(^{13}\)C NMR data is in accordance with literature.[27]

4.4.7 Ethyl 3-(4-bromophenyl)butanoate (9f)

Prepared according to GP2 from ethyl (E)-3-(4-bromophenyl)but-2-enoate (8f, 67 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9f as a colorless oil (57.9 mg, 0.214 mmol, 85%).

\[ R_f = 0.48 \] (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\[ \text{\(^1\)H NMR (500 MHz, CDCl}_3\):} \delta = 1.18 (t, \(3J_{1,2} = 7.1\) Hz, 3H, H-1), 1.27 (d, \(3J_{10,5} = 6.9\) Hz, 3H, H-10), 2.54 (m, 2H, H-4), 3.24 (m, 1H, H-5), 4.07 (m, 2H, H-2), 7.09 (m, 2H, H-7), 7.41 (m, 2H, H-8) ppm.

\[ \text{\(^{13}\)C NMR (126 MHz, CDCl}_3\):} \delta = 14.2 (C-1), 21.9 (C-10), 36.1 (C-5), 42.8 (C-4), 60.4 (C-2), 120.1 (C-9), 128.7 (C-7), 131.6 (C-8), 144.8 (C-6), 172.1 (C-3) ppm.
HRMS (APCI) for C₁₂H₁₆⁷⁸BrO₂⁺ [(M+H)⁺] calculated: 271.0328, found: 271.0323.

IR (ATR): ʋ = 2966 (w), 1729 (s), 1488 (m), 1455 (w), 1369 (m), 1260 (m), 1160 (s), 1071 (m), 1031 (m), 949 (w), 821 (s), 762 (w), 716 (w) cm⁻¹.

The ¹H and ¹³C NMR data is in accordance with literature.[²⁸]

4.4.8 Ethyl 3-(4-chlorophenyl)butanoate (9g)

Prepared according to GP2 from ethyl (E)-3-(4-chlorophenyl)but-2-enoate (8g, 56 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9g as a colorless oil (37 mg, 0.16 mmol, 65%).

Rᵣ = 0.52 (SiO₂, cyclohexane/tert-butyl methyl ether = 9:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.17 (t, 3J₁,₂ = 7.1 Hz, 3H, H-1), 1.27 (d, 3J₁₀,₅ = 7.0 Hz, 3H, H-10), 2.54 (m, 2H, H-4), 3.25 (m, 1H, H-5), 4.06 (m, 2H, H-2), 7.15 (m, 2H, H-7), 7.25 (m, 2H, H-8) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 14.2 (C-1), 21.9 (C-10), 36.0 (C-5), 42.9 (C-4), 60.4 (C-2), 128.3 (C-7), 128.7 (C-8), 132.1 (C-9), 144.3 (C-6), 172.2 (C-3) ppm.

HRMS (APCI) for C₁₂H₁₆³⁵ClO₂⁺ [(M+H)⁺] calculated: 227.0833, found: 227.0828.

IR (ATR): ʋ = 2965 (w), 2115 (w), 1729 (s), 1492 (m), 1457 (w), 1410 (w), 1369 (m), 1259 (m), 1161 (s), 1093 (s), 1032 (s), 950 (w), 825 (s), 732 (w) cm⁻¹.

4.4.9 Ethyl 3-(o-tolyl)butanoate (9h)

Prepared according to GP2 from ethyl (E)-3-(o-tolyl)but-2-enoate (8h, 51 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9h as a colorless oil (90% conversion, 28.6 mg, 0.138 mmol, 55%).

Rᵣ = 0.60 (SiO₂, cyclohexane/tert-butyl methyl ether = 9:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.18 (t, 3J₁,₂ = 6.9 Hz, 3H, H-1), 1.25 (d, 3J₁₃,₄ = 6.9 Hz, 3H, H-13), 2.37 (s, 3H, H-12), 2.57 (m, 2H, H-4), 3.53 (m, 1H, H-5), 4.08 (q, 3J₉,₁ = 7.1 Hz, 2H, H-2), 7.06–7.21 (m, 4H, H-7/H-8/H-9/H-10) ppm.
\[^{13}\text{C NMR}\] (126 MHz, CDCl\(_3\)): \(\delta = 14.2\) (C-1), 19.5 (C-12), 21.4 (C-13), 31.6 (C-5), 42.3 (C-4), 60.3 (C-2), 125.1 (C-7), 126.1 (C-8)*, 126.3 (C-9)*, 130.5 (C-10), 135.4 (C-11), 144.0 (C-6), 172.6 (C-3) ppm.

**HRMS** (APCI) for C\(_{13}\)H\(_{19}\)O\(_2\)^+ [(M+H)^+] calculated: 207.1380, found: 207.1379.

The data is in accordance with literature.\(^{[26]}\)

### 4.4.10 Ethyl 3-(4-nitrophenyl)butanoate (9i)

Prepared according to **GP2** from ethyl (E)-3-(4-nitrophenyl)but-2-enoate (8i, 58 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 \(\mu\)mol, 5.0 mol%) and NaOtBu (7.2 mg, 75 \(\mu\)mol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. No conversion could be observed in \(^1\text{H NMR}, \text{GC and GC-MS.}\)

**Crude \(^1\text{H NMR of conjugate reduction of 8i}**

![NMR spectrum](image)

**GC of conjugate reduction of 8i**

![GC spectrum](image)
### Peak results:

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GC/MS of conjugate reduction of 8i
4.4.11 Ethyl 3-(4-cyanophenyl)butanoate (9j)

Prepared according to GP2 from ethyl (E)-3-(4-cyanophenyl)but-2-enoate (8j, 54 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-
pentane/tert-butyl methyl ether = 15:1) yielded 9j as a colorless oil (9.8 mg, 45 µmol, 5%).

\(R_f = 0.30\) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 4:1).

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)): \(\delta = 1.17\) (t, \(3^J_{1,2} = 7.1\) Hz, 3H, H-1), 1.30 (d, \(3^J_{11,5} = 7.0\) Hz, 3H, H-11), 2.58 (m, 2H, H-4), 3.33 (m, 1H, H-5), 4.06 (m, 2H, H-2), 7.33 (m, 2H, H-7), 7.59 (m, 2H, H-8) ppm.

\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)): \(\delta = 14.2\) (C-1), 21.7 (C-11), 36.7 (C-5), 42.4 (C-4), 60.6 (C-2), 110.5 (C-9), 119.0 (C-10), 127.8 (C-7), 132.5 (C-8), 151.3 (C-6), 171.8 (C-3) ppm.

HRMS (APCI) for C\(_{13}\)H\(_{15}\)NO\(_2\) \([\text{M+H}]^+\) calculated: 218.1176, found: 218.1182.

IR (ATR): \(\tilde{\nu} = 2972\) (w), 2227 (m), 1732 (s), 1608 (w), 1505 (w), 1457 (w), 1416 (w), 1371 (w), 1266 (w), 1174 (m), 1116 (w), 1033 (w), 838 (w) cm\(^{-1}\).

4.4.12 Ethyl 3-(4-acetylphenyl)butanoate (9k)

Prepared according to GP2 from ethyl (E)-3-(4-acetylphenyl)but-2-enoate (8k, 58 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaO\(_{\text{tBu}}\) (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. No conversion could be observed in \(^1\text{H NMR}, \text{GC}\) and GC-MS.

Crude \(^1\text{H NMR}\) of conjugate reduction of 8k
GC of conjugate reduction of 8k

**Peak results:**

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S34
GC/MS data of conjugate reduction of 8k
4.4.13 Ethyl 3-(4-hydroxyphenyl)butanoate (9l)

Prepared according to GP2 from ethyl (E)-3-(4-hydroxyphenyl)but-2-enoate (8l, 45 mg, 0.22 mmol, 1.0 equiv), [SiMesCuCl] (6, 5.1 mg, 13 µmol, 6.0 mol%) and NaOtBu (7.2 mg, 75 µmol, 34 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-
pentane/tert-butyl methyl ether = 10:1) yielded 9l as a colorless oil (conv. 81%, 21.3 mg, 0.102 mmol, 47%).

\[ R_f = 0.44 \text{ (SiO}_2\text{, cyclohexane/tert-butyl methyl ether = 4:1).} \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta = 1.18 \text{ (t, } J_{1,2} = 7.1 \text{ Hz, H-1), 1.26 \text{ (d, } J_{11,5} = 6.9 \text{ Hz, H-11), 2.53 \text{ (m, } 2\text{H, H-4), 3.22 \text{ (m, } 1\text{H, H-5), 4.07 \text{ (m, } 2\text{H, H-2), 4.82 \text{ (s, } 1\text{H,OH), 6.74 \text{ (m, } 2\text{H, H-8), 7.08 \text{ (m, } 2\text{H, H-7) ppm.}} \]

The \(^1H \text{ NMR spectra still contains 9% of the starting material.} \]

\[ ^13C \text{ NMR (126 MHz, CDCl}_3\text{): } \delta = 14.3 \text{ (C-1), 22.1 \text{ (C-10), 35.9 \text{ (C-5), 43.4 \text{ (C-4), 60.4 \text{ (C-2), 115.3 \text{ (C-8), 128.0 \text{ (C-7), 138.0 \text{ (C-6), 154.1 \text{ (C-9), 172.7 \text{ (C-3 ppm).}} \]

\[ \text{HRMS (APCI) for } C_{12}H_{17}O_3^+ \text{[(M+H) } +^1\text{] calculated: } 209.1172, \text{ found: 209.1169.} \]

\[ \text{IR (ATR): } \tilde{\nu} = 3349 \text{ (m), 2965 \text{ (w), 1704 \text{ (s), 1613 \text{ (m), 1515 \text{ (s), 1444 \text{ (m), 1371 \text{ (m), 1266 \text{ (m), 1219 \text{ (m), 1174 \text{ (m), 1032 \text{ (m), 833 \text{ (s) cm}^{-1}.}} \]

4.4.14 Ethyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OEt) and tert-butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OtBu)

Prepared according to GP2 from diethyl ethyl (E)-3-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (104 mg, 0.250 mmol, 1.00 equiv), [SiMesCuCl] (6, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaN(14 mg, 0.15 mmol, 60 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. A crude reaction mixture of the product 9m-OEt and tert-butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OtBu) as a side product (9m-OEt/9m-OtBu = 83:17) was obtained. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 100:1) yielded 9m-OEt as a colorless oil (44.9 mg, 0.101 mmol, 40%) and 9m-OtBu as a colorless oil (8.6 mg, 0.018 mmol, 7%).

Ethyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OEt):

\[ R_f = 0.37 \text{ (SiO}_2\text{, cyclohexane/tert-butyl methyl ether = 9:1).} \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta = 1.08 \text{ (s, 9H, H-15), 1.39 \text{ (t, } J_{1,2} = 7.1 \text{ Hz, H-1), 1.21 \text{ (d, } J_{16,5} = 6.9 \text{ Hz, H-16), 2.46 \text{ (m, } 2\text{H, H-4), 3.14 \text{ (m, } 1\text{H, H-5), 4.03 \text{ (q, } J_{2,1} = 7.1 \text{ Hz, } 2\text{H, H-2), 6.68 \text{ (m, } 2\text{H, H-8), 6.92 \text{ (m, } 2\text{H, H-7), 7.32−7.37 \text{ (m, } 4\text{H, H-12), 7.39−7.43 \text{ (m, } 2\text{H, H-13), 7.67−7.73 \text{ (m, } 4\text{H, H-11) ppm.}} \]
\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ = 14.3 (C-1), 19.6 (C-14), 21.9 (C-16), 26.6 (C-15), 35.9 (C-5), 43.4 (C-4), 60.2 (C-2), 119.6 (C-8), 127.5 (C-7), 127.8 (C-12), 129.9 (C-13), 133.2 (C-10), 135.6 (C-11), 138.3 (C-6), 154.0 (C-9), 172.6 (C-3) ppm.

\(^{29}\)Si DEPT NMR (99MHz, \(J = 20\) Hz, CDCl\(_3\)): δ = -6.6 ppm.

HRMS (APCI) for C\(_{18}\)H\(_{27}\)O\(_3\)\(^+\) \([\text{M+H}]^+\) calculated: 447.2350, found: 447.2343.

IR (ATR): \(\tilde{\nu} = 2930\) (m), 2856 (w), 1731 (s), 1148 (m), 1110 (m), 1011 (w), 920 (m), 834 (m), 779 (w), 741 (w), 701 (s) cm\(^{-1}\).

**tert-Butyl 3-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OtBu):**

\(R_f = 0.47\) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 1.08 (s, 9H, H-15), 1.19 (d, \(^3\)J\(_{16,5}\) = 7.0 Hz, 3H, H-16), 1.31 (s, 9H, H-1), 2.38 (m\(_c\), 2H, H-4), 3.09 (m\(_c\), 1H, H-5), 6.68 (m\(_c\), 2H, H-8), 6.93 (m\(_c\), 2H, H-7), 7.32–7.38 (m, 4H, H-12), 7.38–7.44 (m, 2H, H-13), 7.69–7.72 (m, 4H, H-11) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ = 19.6 (C-14), 22.1 (C-16), 26.6 (C-15), 28.1 (C-1), 36.1 (C-5), 44.5 (C-4), 80.1 (C-2), 119.5 (C-8), 127.6 (C-7), 127.8 (C-12), 129.9 (C-13), 133.2 (C-10), 135.6 (C-11), 138.4 (C-6), 154.0 (C-9), 171.9 (C-1) ppm.

\(^{29}\)Si DEPT NMR (99MHz, \(J = 20\) Hz, CDCl\(_3\)): δ = -6.7 ppm.

HRMS (APCI) for C\(_{20}\)H\(_{29}\)O\(_3\)\(^+\) \([\text{M+H-Ph-tBu}]^+\) calculated: 341.1567, found: 341.1569.

IR (ATR): \(\tilde{\nu} = 2960\) (m), 2857 (w), 1727 (s), 1607 (w), 1509 (s), 1472 (w), 1427 (w), 1365 (w), 1255 (s), 1148 (m), 1110 (m), 1011 (w), 920 (m), 834 (m), 779 (w), 741 (w), 701 (s) cm\(^{-1}\).

### 4.4.15 Ethyl 3-((dimethylamino)phenyl)butanoate (9n)

Prepared according to GP2 from ethyl (t)-3-((dimethylamino)phenyl)but-2-enoate (8n, 61 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 \(\mu\)mol, 5.0 mol%) and NaOtBu (7.2 mg, 75 \(\mu\)mol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9n as a colorless oil (38.1 mg, 0.162 mmol, 65%).

\(R_f = 0.16\) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 1.20 (t, \(^3\)J\(_{1,2}\) = 7.1 Hz, 3H, H-1), 1.26 (d, \(^3\)J\(_{11,5}\) = 6.9 Hz, 2H, H-11), 2.52 (m\(_c\), 2H, H-4), 2.91 (s, 6H, H-10), 3.19 (m\(_c\), 1H, H-5), 4.08 (m\(_c\), 2H, H-2), 6.69 (m\(_c\), 2H, H-8), 7.10 (m\(_c\), 2H, H-7) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ = 14.3 (C-1), 22.0 (C-11), 35.6 (C-5), 40.9 (C-10), 43.5 (C-4), 60.2 (C-2), 113.0 (C-8), 127.4 (C-7), 134.0 (C-6), 149.4 (C-9), 172.8 (C-3) ppm.

HRMS (APCI) for C\(_{14}\)H\(_{22}\)NO\(_2\)\(^+\) \([\text{M+H}]^+\) calculated: 236.1645, found: 236.1640.
The data is in accordance with literature.\[6\]

### 4.4.16 Ethyl 3-(thiophen-2-yl)butanoate (9o)

Prepared according to GP2 from ethyl (E)-3-(thiophen-2-yl)but-2-enooate (8o, 49 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 \( \mu \)mol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 \( \mu \)mol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 30:1) yielded 9o as a colorless oil (38.8 mg, 0.196 mmol, 78%).

\( R_f = 0.55 \) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 1.22 \) (t, 3\( J_{1,2} = 7.1 \) Hz, 3H, H-1), 1.38 (d, 3\( J_{10,5} = 6.9 \) Hz, 3H, H-10), 2.61 (m, 2H, H-4), 3.59 (m, 1H, H-5), 4.12 (q, 3\( J_{2,1} = 7.1 \) Hz, 2H, H-2), 6.83 (m, 1H, H-7), 6.91 (dd, 3\( J_{6,7} = 5.1 \) Hz, 3\( J_{6,9} = 5.1 \) Hz, 1H, H-8), 7.13 (dd, 3\( J_{9,8} = 5.1 \) Hz, 4\( J_{6,7} = 1.1 \) Hz, 1H, H-9) ppm.

\(^13\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 14.3 \) (C-1), 22.7 (C-10), 32.1 (C-5), 44.0 (C-4), 60.5 (C-2), 123.0 (C-7), 123.0 (C-8), 126.7 (C-9), 149.8 (C-6), 172.0 (C-3) ppm.

HRMS (APCI) for C\(_{10}\)H\(_{15}\)O\(_2\)S\(^{+}\) ([M+H\(^+\)]) calculated: 199.0787, found: 199.0782.

IR (ATR): \( \tilde{\nu} = 2971 \) (w), 1729 (s), 1456 (w), 1369 (m), 1344 (w), 1280 (m), 1248 (m), 1160 (m), 1071 (w), 1028 (m), 947 (w), 848 (m), 691 (s) cm\(^{-1}\).

The \(^1\)H NMR data is in accordance with literature.\[29\]

### 4.4.17 Ethyl 3-cyclopropyl-3-phenylpropanoate (9p)

Prepared according to GP2 from ethyl (E)-3-cyclopropyl-3-phenylacrylate (8p, 54 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 \( \mu \)mol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 \( \mu \)mol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9p as a colorless oil (52.0 mg, 0.238 mmol, 95%).

\( R_f = 0.52 \) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 0.14 \) (m, 1H, H-11\(_a\))*, 0.27 (m, 1H, H-11\(_b\))*, 0.41 (m, 1H, H-11\(_b\))*, 0.57 (m, 1H, H-11\(_b\)), 1.03 (m, 1H, H-10), 1.15 (t, 3\( J_{1,2} = 7.1 \) Hz, 3H, H-1), 2.37 (m, 2H, H-2).
1H, H-5), 2.73 (m, 2H, H-4), 4.04 (m, 2H, H-2), 7.18–7.25 (m, 3H, H-7/H-9), 7.26–7.32 (m, 2H, H-8) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ = 4.1 (C-11)*, 5.4 (C-11')*, 14.2 (C-1), 17.2 (C-10), 41.9 (C-4), 47.3 (C-5), 60.3 (C-2), 126.5 (C-9), 127.4 (C-7), 128.4 (C-8), 144.2 (C-6), 172.5 (C-3) ppm.


The data is in accordance with literature.[30]

4.4.18 Hex-5-en-1-yl 3-phenylbutanoate (9q)

Prepared according to GP2 from hex-5-en-1-yl (E)-3-phenylbut-2-enoate (8q, 61 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaO\(_{t}\)Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9q as a colorless oil (40.9 mg, 0.166 mmol, 66%).

\(R_f = 0.53\) (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 1.17 (d, \(^3\)J\(_{14,9}\) = 7.0 Hz, 3H, H-14), 1.19–1.27 (m, 2H, H-4), 1.38–1.46 (m, 2H, H-5), 1.90 (m, 2H, H-3), 2.45 (m, 2H, H-8), 3.14 (m, 1H, H-1Z), 3.86 (m, 1H, H-1E), 5.63 (m, 1H, H-2), 7.03–7.11 (m, 3H, H-11/H-13), 7.13–7.19 (m, 2H, H-12) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ = 22.0 (C-14), 25.7 (C-4), 28.1 (C-5), 33.3 (C-3), 36.7 (C-9), 43.1 (C-8), 64.3 (C-6), 114.9 (C-1), 126.5 (C-13), 126.8 (C-11), 128.6 (C-12), 138.4 (C-2), 145.8 (C-10), 172.6 (C-3) ppm.

HRMS (APCI) for C\(_{16}\)H\(_{13}\)O\(_2\)^+ [(M+H)^+] calculated: 247.1693, found: 247.1690.

IR (ATR): \(\tilde{\nu} = 2930\) (w), 1730 (s), 1639 (w), 1602 (w), 1452 (w), 1265 (m), 1162 (m), 1082 (m), 993 (m), 909 (m), 760 (m), 698 (s) cm\(^{-1}\).

4.4.19 Diethyl 3,3'-(1,4-phenylene)bisbutyrate (9r)

Prepared according to GP2 from diethyl 3,3'-(1,4-phenylene)(2\(E\),2\(E\))-bis(but-2-enoate) (8k, 76 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO\(_{t}\)Bu (14 mg, 0.15 mmol, 60 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 25:2) yielded 9r as a colorless oil (47.9 mg, 0.156 mmol, 62%).
**4.4.20 Ethyl 2-methyl-3-phenylbutanoate (9s)**

Prepared according to GP2 from ethyl (E)-2-methyl-3-phenylbut-2-enoate (8s, 51 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10.2 mg, 25.0 μmol, 10.0 mol%) and NaOtfBu (7.2 mg, 75 μmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/Et2O = 50:1) yielded 9 as a colorless oil (66% conversion, 37 mg combined yield of E-8s, Z-8s, syn-9s and anti-9s).

**Rf** = 0.59 (SiO2, cyclohexane/tert-butyl methyl ether = 9:1).

**Major diastereomer:**

1H NMR (500 MHz, CDCl3): \( \delta = 0.93 \text{ (d, }^3J_{1,4} = 6.9 \text{ Hz, 3H, H-11), 1.23–} \\
1.27 \text{ (m, 2H, H-10), 1.28 (t, }^3J_{1,2} = 7.1 \text{ Hz, 3H, H-1), 2.57 (m, 1H, H-4),} \\
2.89 \text{ (m, 1H, H-5), 4.18 (m, 2H, H-2), 7.11–7.23 (m, 3H, H-7/H-9)*,} \\
7.26–7.41 \text{ (m, 2H, H-8)* ppm.}

**Minor diastereomer:**

1H NMR (500 MHz, CDCl3): \( \delta = 1.01 \text{ (t, }^3J_{1,2} = 7.1 \text{ Hz, 3H, H-1), 1.17 (d, }^3J_{1,4} = 6.9 \text{ Hz, 3H, H-11), 1.23–1.27} \\
\text{(m, 2H, H-10), 2.64 (m, 1H, H-4), 3.03 (m, 1H, H-5), 3.91 (m, 2H, H-2),} \\
7.11–7.23 \text{ (m, 3H, H-7/H-9)*, 7.26–7.41 (m, 2H, H-8)* ppm.}

Integrated signals in 1H NMR which are not further listed belong to the starting material (E-8s) and its isomer (Z-8s). Due to overlaying signals, 13C signals have not been correlated. For MS see following GC/MS data.
\(^1\text{H NMR of 9s}\)

\[
\text{GC of 9s}
\]

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GC/MS of 9s minor diastereomer
GC/MS of 9s major diasteromer
GC/MS of E-8s
GC/MS of Z-8s
4.4.21 Ethyl 3-cyclohexylbutanoate (9t)

Prepared according to GP2 from ethyl (E)-3-cyclohexylbut-2-enoate (8t, 49 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9t as a colorless oil (41 mg, 0.21 mmol, 83%).

\[ R_f = 0.63 \text{ (SiO}_2, \text{ cyclohexane/tert-butyl methyl ether = 9:1).} \]

**1H NMR** (500 MHz, CDCl₃): \( \delta = 0.88 \text{ (d, } J_{1,2} = 6.8 \text{ Hz, 3H, H-10), 0.91–1.04 \text{ (m, 2H, H-9*), 1.05–1.23 \text{ (m, 4H, H-6/H-7*/H-7*)), 1.25 \text{ (t, } J_{1,2} = 7.1 \text{ Hz, 3H, H-1), 1.59–1.68 \text{ (m, 3H, H-9*/H-8*), 1.69–1.78 \text{ (m, 2H, H-8*))}, 1.85 \text{ (m, 1H, H-5), 2.21 \text{ (m, 2H, H-4), 4.12 \text{ (q, } J_{2,1} = 7.1 \text{ Hz, 2H, H-2) ppm.}} \]

**13C NMR** (126 MHz, CDCl₃): \( \delta = 14.4 \text{ (C-1), 16.6 \text{ (C-10), 26.7 \text{ (C-7*)}, 26.8 \text{ (C-8*)}, 26.8 \text{ (C-9*), 29.0 \text{ (C-7*)}, 30.4 \text{ (C-8*)}, 35.5 \text{ (C-5), 39.4 \text{ (C-4), 42.7 \text{ (C-6), 60.2 \text{ (C-2), 174.0 \text{ (C-3) ppm.}}}} \]

**HRMS** (APCI) for \( \text{C}_{12}\text{H}_{22}\text{O}_{4}^+ \) [(M+H)⁺] calculated: 199.1693, found: 199.1689.

The data is in accordance with literature.[31]

4.4.22 Ethyl 3-methylundecanoate (9u)

Prepared according to GP2 from ethyl (E)-3-methylundec-2-enoate (8u, 57 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 5.1 mg, 13 µmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9u as a colorless oil (52.7 mg, 0.231 mmol, 92%).

\[ R_f = 0.78 \text{ (SiO}_2, \text{ cyclohexane/tert-butyl methyl ether = 9:1).} \]

**1H NMR** (500 MHz, CDCl₃): \( \delta = 0.87 \text{ (t, } J_{1,2} = 13.9 \text{ Hz, 3H, H-13), 0.92 \text{ (d, } J_{1,5} = 6.6 \text{ Hz, 3H, H-14), 1.12–1.34 \text{ (m, 17H, H-1/H-6/H-7/H-8/H-9/H-10/H-11/H-12), 1.94 \text{ (m, 1H, H-5), 2.18 \text{ (m, 2H, H-4), 4.12 \text{ (q, } J_{2,1} = 7.1 \text{ Hz, 2H, H-7) ppm.}} \]

**13C NMR** (126 MHz, CDCl₃): \( \delta = 14.2 \text{ (C-13), 14.4 \text{ (C-1), 19.8 \text{ (C-14), 22.8 \text{ (C-12*)}, 27.0 \text{ (C-10*)}, 29.4 \text{ (C-9*)}, 29.7 \text{ (C-8*)}, 29.9 \text{ (C-7*)}, 30.5 \text{ (C-5), 32.0 \text{ (C-11*), 36.8 \text{ (C-6), 42.1 \text{ (C-4), 60.1 \text{ (C-2), 173.5 \text{ (C-3) ppm.}}}} \]

**HRMS** (APCI) for \( \text{C}_{14}\text{H}_{24}\text{O}_{2}^+ \) [(M+H)⁺] calculated: 229.2162, found: 229.2157.

**IR** (ATR): \( \tilde{\nu} = 2923 \text{ (m), 2853 \text{ (m), 1735 \text{ (s), 1461 \text{ (m), 1371 \text{ (m), 1250 \text{ (m), 1159 \text{ (m), 1032 \text{ (m), 954 \text{ (w), 844 \text{ (w), 722 \text{ (w) cm}^{-1}.}}}} \]

S50
4.4.23 Ethyl 3-propylhexanoate (9v)

Prepared according to GP2 from ethyl 3-propylhex-2-enoate (46 mg, 0.25 mmol, 1.0 equiv), [SiMesCuCl] (6, 5.1 mg, 13 μmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 μmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/Et₂O = 50:1) yielded 9v as a colorless oil (100% conversion, due to volatility of the product the yield could not be determined).

Rᵣ = 0.78 (SiO₂, cyclohexane/tert-butyl methyl ether = 9:1).

¹H NMR (500 MHz, CD₂Cl₂): δ = 0.88 (t, ³J₈,₇ = 7.0 Hz, 6H, H-8), 1.19–1.33 (m, 11H, H-1/H-6/H-7), 1.84 (m, 1H, H-5), 2.19 (d, ³J₄,₅ = 6.8 Hz, 2H, H-4), 4.08 (q, ³J₂,₁ = 7.1 Hz, 2H, H-2) ppm.

Due to volatility of the product, the sample contains n-pentane residues. Therefore, the value of the integration for H-8 and H1/H-6/H-7 is too high (see the attached spectra).

¹³C NMR (126 MHz, CD₂Cl₂): δ = 14.4 (C-1/C-8), 20.0 (C-7), 35.0 (C-5), 36.6 (C-6), 39.6 (C-4), 60.3 (C-2), 173.7 (C-3) ppm.


IR (ATR): ʋ = 2957 (s), 2929 (m), 2871 (m), 2358 (w), 1735 (s), 1641 (w), 1374 (w), 1247 (m), 1173 (m), 1106 (w), 1036 (m), 854 (w), 739 (w) cm⁻¹.

4.4.24 N,N-diethyl-3-phenylbutanamide (11)

Prepared according to GP2 from (E)-N,N-diethyl-3-phenylbut-2-enamide (10, 46 mg, 0.25 mmol, 1.0 equiv), [SiMesCuCl] (6, 5.1 mg, 13 μmol, 5.0 mol%) and NaOtfBu (7.2 mg, 75 μmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by preparative TLC (Al₂O₃, cyclohexane/ tert-butyl methyl ether = 5:1, Et₃N 2%) yielded 11 as a colorless oil (60% conversion (average of 3 runs), 9.5 mg, 43 μmol, 17%).

Rᵣ = 0.28 (SiO₂, cyclohexane/tert-butyl methyl ether = 2:1).

¹H NMR (500 MHz, CD₂Cl₂): δ = 1.02 (t, ³J₁,₂ = 7.1 Hz, 3H, H-1)*, 1.07 (t, ³J₁',₂ = 7.1 Hz, 3H, H-1')*, 1.28 (d, ³J₄,₅ = 7.0 Hz, 3H, H-10), 2.51 (m, 2H, H-4), 3.19 (t, ³J₂,₁ = 7.1 Hz, 2H, H-2), 3.23–3.38 (m, 3H, H-5/H-2'), 7.14–7.20 (m, 1H, H-9), 7.21–7.31 (m, 4H, H-7/H-8) ppm.

¹³C NMR (126 MHz, CD₂Cl₂): δ = 13.2 (C-1)*, 14.5 (C-1')*, 21.8 (C-10), 36.9 (C-5), 40.39 (C-2)**, 41.8 (C-4), 42.2 (C-2')**, 126.4 (C-9), 127.3 (C-7), 128.6 (C-8), 147.3 (C-6), 170.7 (C-3) ppm.
HRMS (APCI) for C_{14}H_{22}NO^+ [(M+H)^+] calculated: 220.1696, found: 220.1694.

IR (ATR): \tilde{\nu} = 2968 (m), 2931 (w), 2359 (w), 1638 (s), 1454 (m), 1278 (w), 11276 (w), 1222 (w), 1142 (w), 1085 (w), 1021 (w), 761 (w), 701 (m) cm\(^{-1}\).

4.4.25 Ethyl (E)-5-phenylpent-4-enoate (13a)

\[
\text{prepared according to GP2 from ethyl (2E,4E)-5-phenylpenta-2,4-dienoate (12, 51 mg, 0.25 mmol, 1.0 equiv), [SiMesCuCl] (6, 10.2 mg, 25.0 \mu\text{mol}, 10.0 mol\%) and NaOtBu (7.2 mg, 75 \mu\text{mol}, 30 mol\%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/Et,O = 50:1) yielded 13 as a colorless oil (81% conversion, 35 mg combined yield of 12, 13a, 13b and 13c).}
\]

R\(_f\) = 0.61 (SiO\(_2\), cyclohexane/tert-butyl methyl ether = 9:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.26\) (t, 3\(^J\) = 7.1 Hz, 3H, H-1), 2.45–2.57 (m, 4H, H4/H5), 4.15 (q, 3\(^J\) = 7.1 Hz, 2H, H-2), 6.21 (dt, 3\(^J\) = 15.8 Hz, 3\(^J\) = 6.6 Hz, 1H, H-6), 6.43 (d, 3\(^J\) = 15.8 Hz, 1H, H-7), 7.15–7.23 (m, 1H, H-11)*, 7.26–7.37 (m, 4H, H-9/H-10)* ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta = 14.4\) (C-1), 28.4 (C-5), 34.2 (C-4), 60.5 (C-2), 126.1 (C-9), 127.2 (C-11)*, 127.3 (C-10)*, 128.6 (C-6), 131.0 (C-7), 137.5 (C-8), 173.1 (C-3) ppm.

Other unpicked and not integrated signals belong to the starting material or the other products.

Indicative signals for the starting material 12 in the \(^1\)H NMR are at \(\delta = 5.84, 5.99\) and 6.89 ppm. Indicative for the 1,6-conjugate reduction product 13b are the signals at \(\delta = 5.82\) and 7.00 ppm.

HRMS (APCI) for C_{14}H_{17}O_{2}^+ [(M+H)^+] calculated: 205.1223, found: 205.1221.
$^1$H NMR of 13a, 13b, 12

[Diagram of $^1$H NMR spectra for 13a, 13b, and 12 with peaks indicated]
GC of 13

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GC/MS of 13c
GC/MS of 13b
GC/MS of 12
4.4.26 Ethyl 3-(4-styrylphenyl)butanoate (S9)

Prepared according to GP2 from ethyl (E)-3-(4-(phenylethynyl)phenyl)but-2-enoate (S3, 69 mg, 0.25 mmol, 1.0 equiv), [SiMesCuCl] (6, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaOttBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/Et₂O = 50:1) yielded a mixture of S9-E, S9-Z and S10 as a colorless oil (full conversion, 44.6 mg combined yield of S9-E, S9-Z and S10).

Rᵣ = 0.16 (SiO₂, cyclohexane/tert-butyl methyl ether = 50:1).

\(^1\)H NMR (500 MHz, CD₂Cl₂): δ = 1.19 (t, \(^3\)J\(_{1,2}\) = 7.1 Hz, 3H, H-1), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 6.55 (m, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) ppm.

Due to overlaying signals, \(^13\)C signals have not been correlated.

Indicative signals for the alkane product S10 in the \(^1\)H NMR are at δ = 2.89 ppm.

HRMS (APCI) for C\(_{20}\)H\(_{23}\)O\(_2\)\(^{+}\) [(M+H)\(^{+}\)] calculated: 295.1693, found: 295.1691.
$^1$H NMR of S9
GC of S9

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GC/MS of S10
GC/MS of S9-E
4.5 Additives tested in the conjugate reduction

In order to further probe the functional group tolerance of the present protocol, we have added three protic additives (1.0 equivalents with respect to the enoate 1) to the standard conditions, namely $n$-octanol, benzoic acid and aniline. Robustness and functional group tolerance screening experiments\textsuperscript{32} were following GP 2. Additionally to the substrate 1.00 equiv of an additive was added to the reaction mixture together with the starting material.

**Table S7: Influence of additives on the catalytic conjugate reduction.\textsuperscript{a}**

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\textsuperscript{a} All reactions with 5.5 μmol [Cu] in 1 mL solvent. \textsuperscript{b} Determined by \textsuperscript{1}H NMR spectroscopy or GC analysis. \textsuperscript{c} Reaction was performed in an H\textsubscript{2}-purged pressure tube. \textsuperscript{d} Isolated yield.

As can be seen from the table, the copper-catalyzed conjugate reduction tolerates the alcohol additive, with full conversion reached, however, we detect 63% of transesterification product (octyl ester).

Addition of the significantly more acidic benzoic acid led to a complete halt of the reaction, most probably due to protonation of the key tert-butoxide additive.

The addition of 1.0 equivalents aniline led to significantly lower conversion (only 62% reached), displaying the limits of the present catalyst. A mixture of products was found, including the corresponding reduced and not reduced amides derived from anilin.

S65
4.5.1 Analytical data for the additives tested:

4.5.1.1 1-Ocantol as additive

5.0 mol% [SiMesCuCl]
30 mol% NaOtBu
1.0 equiv 1-octanol
10 bar H₂

Ph\[OEt\[\rightarrow\]Ph\[OEt\]
1,4-dioxane, 100 °C, 16 h
Ph\[OEt\] + Ph\[OC₆H₁₇\]
2 37%
S11 63%

GC-data

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S66
GC/MS-data
4.5.1.2 Benzoic acid as additive

5.0 mol% [SIMesCuCl]  
30 mol% NaOtBu  
1.0 equiv benzoic acid  
10 bar H₂

1,4-dioxane, 100 °C, 16 h

Ph

OEt

no conversion

Ph

OEt

2

0%

GC-data

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GC/MS-data
4.5.1.3 Anilin as additive

5.0 mol% [SiMesCuCl]
30 mol% NaOtBu
1.0 equiv anilin
10 bar H₂

1,4-dioxane, 100 °C, 16 h
41% conv.

2
X%
S12
X%
S13
X%

GC-data

Peak results:

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GC-MS data
4.6 Deuteration experiments

Deuteration experiments were following GP 2 using D₂ instead of H₂. Deuterium incorporation was determined via quantitative ¹H NMR and comparison of two selected ¹H NMR signals (relaxation delay (d₁), and selected ¹H NMR signals with the respective substrates).

4.6.1 Ethyl 3-phenylbutanoate-d₉ (2-d₉)

Prepared according to GP2 from ethyl (E)-3-phenylbut-2-enoate (1, 48 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10 mg, 25 µmol, 10 mol%) and NaOtBu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 2-d₉ as a colorless oil (38.6 mg, 0.198 mmol, 79%).

R_f = 0.48 (SiO₂, cyclohexane/tert-butyl methyl ether = 9:1).

¹H NMR (700 MHz, CDCl₃): δ = 1.15–1.20 (m, 2.9H, H-1), 1.26–1.30 (m, 2.6H, H-10), 2.49–2.63 (m, 1.4H, H-4), 4.07 (m, 1.8H, H-2), 7.17–7.24 (m, 3H, H-7, H-9), 7.27–7.32 (m, 2H, H-8) ppm.

²H NMR (77 MHz, CDCl₃): δ = 1.30 (s, D-10), 2.55 (m, D-4), 3.25 (s, D-5), 4.07 (s, D-2) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 14.3 (C-1), 21.8 (C-10), 36.6 (C-5), 43.1 (C-4), 60.3 (C-2), 126.4 (C-7)*, 126.8 (C-9)*, 128.5 (C-8), 145.8 (C-6), 172.5 (C-3) ppm. Due to low concentration C-5 could not be detected in ¹³C NMR but was identified via coupling in HMBC.

HRMS (APCI) for C₁₂H₁₅D₂O₂⁺ [(M–D+2H)⁺] calculated: 195.1349, found: 195.1344.

IR (ATR): 䓬 = 2974 (w), 1729 (s), 1603 (w), 1493 (w), 1446 (m), 1367 (m), 1324 (m), 1246 (m), 1178 (s), 1094 (m), 1031 (s), 909 (w), 849 (w), 755 (m), 697 (s) cm⁻¹.

The deuterium incorporation was determined by comparing the integrals of the corresponding ¹H NMR signal H-2 (δ = 4.07 ppm), H-4 (δ = 2.49–2.63 ppm), H-5 (δ = 3.27 ppm) and H-10 (δ = 1.26–1.30 ppm) with H-7/H-9 (δ = 7.17–7.24 ppm) [¹H NMR (700 MHz, CDCl₃), d₁ = 23 s].

4.6.2 Ethyl 3,3-diphenylpropanoate-d₉ (9c-d₉)

Prepared according to GP2 from ethyl ethyl 3,3-diphenylacylate (8c, 63 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10 mg, 25 µmol, 10 mol%) and NaOtBu (14 mg, 0.15 mmol, 30 mol%) in
1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 50:1) yielded 9c-dn as a colorless oil (48.5 mg, 0.188 mmol, 75%).

\[ R_f = 0.40 \text{ (SiO}_2, \text{cyclohexane/tert-butyl methyl ether = 9:1).} \]

\(^1\)H NMR (700 MHz, CDCl\(_3\)): \( \delta = 1.03–1.13 \text{ (m, 2.1H, H-1), 3.01–3.05 \text{ (m, 0.4H, H-4), 3.98–} \]
\( \text{4.05 \text{ (m, 1.2H, H-2), 7.16–7.20 \text{ (m, 2H, H-9), 7.22–7.25 \text{ (m, 4H, H-7)*, 7.26–7.29 \text{ (m, 4H, H-8)* ppm.}} \}

\(^2\)H NMR (77 MHz, CDCl\(_3\)): \( \delta = 1.15 \text{ (s, D-1), 1.27 \text{ (s, D-11), 2.51 \text{ (m c, D-4), 3.21 \text{ (s, D-5), 4.07 \text{ (s, D-2) ppm.}} \}

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 14.5 \text{ (C-1), 41.0 \text{ (C-4), 46.7 \text{ (C-5), 60.5 \text{ (C-2), 126.6 \text{ (C-9),} \]
\( \text{127.8 \text{ (C-7), 128.6 \text{ (C-8), 128.9 \text{ (C-6), 143.5 \text{ (C-6), 171.9 \text{ (C-3) ppm.}} \}

Due to low concentration C-1, C-4, C-5 and C-2 could not be detected in \(^{13}\)C NMR but were identified via coupling in HMQC and HMBC.

HRMS (APCI) for C\(_{17}\)H\(_{16}\)D\(_3\)O\(_2^+\) \([\text{M+H}]^+\) calculated: 258.1568, found: 258.1562.

IR (ATR): \( \tilde{\nu} = 3024 \text{ (w), 2978 \text{ (w), 2127 \text{ (w), 1726 \text{ (s), 1599 \text{ (w), 1492 \text{ (w),} \]
\( \text{1446 \text{ (m), 1351 \text{ (w), 1259 \text{ (w), 1174 \text{ (w), 1122 \text{ (m), 1024 \text{ (m), 909 \text{ (w),} \]
\( \text{741 \text{ (m), 696 \text{ (s) cm}^{-1}.} \)

The deuterium incorporation was determined by comparing the integrals of the corresponding \(^1\)H NMR signal H-1 (\( \delta = 1.03–1.13 \text{ ppm,} \)
\( \text{H-2 (\( \delta = 3.98–4.05 \text{ ppm,} \)
\( \text{H-4 (\( \delta = 3.01–3.05 \text{ ppm) and H-5 (\( \delta = 4.53–4.55 \text{ ppm) with H-9 (\( \delta = 7.16–7.20 \text{ ppm) \}} \)
\[ \text{[}^{1}\text{H NMR (700 MHz, CDCl}_3\text{), } d_1 = 21 \text{ s}. \]

4.6.3 Ethyl 3-(4-methoxyphenyl)butanoate-2,2,3-d\(_5\) (9d-d\(_n\))

Prepared according to GP2 from ethyl (E)-3-(4-methoxyphenyl)but-2-enoate (8d, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10 mg, 25 \( \mu \text{mol, 10 mol%}) \text{ and NaO}^\text{tBu (14 mg,} \]
\( \text{0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction \)
\( \text{mixture was stirred for 48 h at 100 °C. Purification by flash} \)
\( \text{column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 30:1) yielded 9d-dn as a colorless oil (41.4 mg, 0.184 mmol, 74%).} \)

\[ R_f = 0.26 \text{ (SiO}_2, \text{cyclohexane/tert-butyl methyl ether = 9:1).} \]

\(^1\)H NMR (700 MHz, CDCl\(_3\)): \( \delta = 1.14–1.20 \text{ (m, 2.3H, H-1), 1.23–1.28 \text{ (m, 2.7H, H-11), 2.45–} \]
\( \text{2.57 \text{ (m, 0.6H, H-4), 3.78 \text{ (s, 3H, H-10), 4.01–4.10 \text{ (m, 1.4H, H-2), 6.83 \text{ (m, 2H, H-8), 7.13 \text{ (m, 2H, H-7) ppm.}} \}

S79
$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): δ = 13.2–14.5 (m, C-1), 21.4–22.3 (m, C-11), 35.2–36.0 (m, C-5), 42.3–43.4 (m, C-4), 55.5 (C-10), 59.7–60.7 (m, C-2), 114.1 (C-8), 128.0 (C-7), 138.3 (C-6), 158.5 (C-9), 172.5 (C-3) ppm.

$^2$H NMR (77 MHz, CDCl$_3$): δ = 1.15 (s, D-1), 1.27 (s, D-11), 2.51 (m, 0.7D, D-4), 3.21 (s, D-5), 4.07 (s, D-2) ppm.

HRMS (APCI) for C$_{13}$H$_{16}$D$_3$O$_3$ $^*$ [(M+H)$^+$] calculated: 226.1517, found: 226.1508.

IR (ATR): $\tilde{\nu}$ = 2956 (w), 2835 (w), 2133 (w), 1725 (s), 1611 (m), 1511 (s), 1459 (m), 1362 (w), 1241 (s), 1176 (s), 1095 (m), 1031 (s), 829 (s), 725 (w), 633 (w) cm$^{-1}$.

The deuterium incorporation was determined by comparing the integrals of the corresponding $^1$H NMR signal H-1 (δ = 1.14–1.20 ppm), H-2 (δ = 4.01–4.10 ppm), H-4 (δ = 2.45–2.57 ppm), H-5 (δ = 3.21 ppm) and H-11 (δ = 1.23–1.28 ppm) with H-10 (δ = 3.78 ppm) [$^1$H NMR (700 MHz, CDCl$_3$), d$_1$ = 18 s].

4.6.4 Ethyl 3-phenylbutanoate-2,2-d$_2$ (S14-\textit{d}$_n$)

Prepared according to GP2 from ethyl 3-phenylbutanoate (3, 48 mg, 0.25 mmol, 1.0 equiv), [SiMesCuCl] (6, 10 mg, 25 µmol, 10 mol%) and NaO$t$Bu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/tert-butyl methyl ether = 100:1) yielded S14-\textit{d}$_n$ as a colorless oil (26.8 mg, 0.198 mmol, 79%).

R$_f$ = 0.48 (SiO$_2$, cyclohexane/tert-butyl methyl ether = 9:1).

$^1$H NMR (700 MHz, CDCl$_3$): δ = 1.12–1.19 (m, 2.0H, H-1), 1.30 (d, $^3$J$_{10,5}$ = 7.0 Hz, 3H, H-10), 2.48–2.63 (m, 0.4H, H-4), 3.26 (m, 1H, H-5), 4.02–4.10 (m, 1.0H, H-2), 7.17–7.23 (m, 3H, H-7, H-9), 7.27–7.31 (m, 2H, H-8) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$): δ = 13.9–14.4 (m, C-1), 21.8–21.9 (m, C-10), 36.4–36.7 (m, C-5), 42.2–43.3 (m, C-4), 59.7–60.4 (m, C-2), 126.5 (C-9), 126.9 (C-7), 128.6 (C-8), 145.8 (C-6), 172.5 (C-3) ppm.

$^2$H NMR (77 MHz, CDCl$_3$): δ = 1.14 (s, D-1), 2.55 (m, D-4), 4.06 (s, D-2) ppm.

HRMS (APCI) for C$_{12}$H$_{14}$D$_3$O$_2$ $^*$ [(M+D+H)$^+$] calculated: 196.1409, found: 196.1411.
IR (ATR): $\tilde{\nu} = 2962$ (w), 2927 (w), 1731 (s), 1603 (w), 1494 (w), 1453 (w), 1376 (w), 1255 (m), 1173 (w), 802 (w), 759 (w), 700 (m) cm$^{-1}$.

The deuterium incorporation was determined by comparing the integrals of the corresponding $^1$H NMR signal H-2 ($\delta = 4.02$–$4.10$ ppm), H-4 ($\delta = 2.48$–$2.63$ ppm) and H-1 ($\delta = 1.12$–$1.19$ ppm) with H-7/H-9 ($\delta = 7.17$–$7.23$ ppm) [$^1$H NMR (700 MHz, CDCl$_3$), $d_t = 23$ s].
4.7 Competition with alkyne semihydrogenation

4.7.1 Ethyl 3-(4-styrylphenyl)butanoate (S9)

Prepared according to GP2 from ethyl (E)-3-(4-(phenylethynyl)phenyl)but-2-enoate (S3, 69 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (6, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaOEtBu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (n-pentane/Et₂O = 50:1) yielded a mixture of S9-E, S9-Z and S10 as a colorless oil (full conversion, 44.6 mg combined yield of S9-E, S9-Z and S10).

\[ R_f = 0.16 \text{ (SiO}_2, \text{ cyclohexane/tert-butyl methyl ether = 50:1).} \]

\[^{1}H\text{ NMR (500 MHz, CD}_2\text{Cl}_2): \delta = 1.19 (t, J_{1,2} = 7.1 \text{ Hz, 3H, H-1}), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 6.55 (m, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) \text{ ppm.} \]

\[^{13}C\text{ signals have not been correlated.} \]

Indicative signals for the alkane product S10 in the \[^{1}H\text{ NMR are at } \delta = 2.89 \text{ ppm.} \]

\[ \text{HRMS (APCI) for C}_{20}\text{H}_{23}\text{O}_2^+ [(M+H)^+] \text{ calculated: 295.1693, found: 295.1691.} \]
$^1$H NMR of S9
GC of S9

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GC/MS of S9-Z
GC/MS of S10
GC/MS of S9-E
4.8 Circumstantial evidence for possible recycling and re-isolation of the catalyst [SiMesCuCl] (6)

To address the issue of the homogeneous or heterogenous nature of the catalyst, attempts have been carried out to re-isolate the catalyst (6), by quenching the standard conjugate reduction reaction with HCl in Et₂O. These experiments have failed to deliver the desired complex 6. However, in various catalytic conjugate reductions of enoates employing compound 6 as catalyst, we have identified the corresponding mass (Mw = 404) by GC/MS analysis. (see below for a representative GC/MS trace).
From the reaction of 1 with anilin as additive (see section 4.5.1.3): Note the peak at 15.56 min.
5 Asymmetric conjugate reduction of α,β-unsaturated esters

5.1 General procedure 3 – asymmetric conjugate reduction (GP3)

In a glass vial equipped with a septum, CuCl (99.99%, 2.0 mg, 20 μmol, 10 mol%) and \( L^* \) (24 μmol, 12 mol%) are placed and the vial is transferred into a glovebox. Dried NaOtBu (21.4 mg, 0.222 mmol, 1.10 equiv) is added and the solids are dissolved in 1,4-dioxane (1 mL). The mixture is stirred for 10 min at 40 °C. The degassed α,β-unsaturated ester 1 (38.4 mg, 0.202 mmol, 1.00 equiv) is dissolved in 1,4-dioxane (0.2 mL) and transferred to the reaction vial. The vial is placed in an autoclave and the septum is pierced with a needle under \( \text{N}_2 \)-counterflow. The autoclave is purged with \( \text{H}_2 \) (3 x 10 bar). The reaction mixture is stirred for 48 h at 60 °C under \( \text{H}_2 \)-atmosphere (100 bar). The crude reaction mixture is filtered over a small plug silica (eluent: \( \text{CH}_2\text{Cl}_2 \), 0.5 x 3 cm, 10 mL) and all volatiles are removed under reduced pressure. The crude product 2 is purified by flash column chromatography on silica gel.
Table S7: Asymmetric conjugate reduction – Ligand screening.\(^a\)

\[
\begin{align*}
&\text{10.0 mol\% CuCl} \\
&\text{12.0 mol\% } L^* \\
&\text{1.10 equiv NaOfBu} \\
&\text{1,4-dioxane, 60 °C, 48 h} \\
&\text{100 bar } H_2
\end{align*}
\]

\[
\begin{align*}
&\text{Ph-} \quad \text{H} \quad \text{Ph-} \\
&\text{OEt} \quad \text{OEt} \\
&\text{1} \quad \text{2}
\end{align*}
\]

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\(^a\) All reactions with 2.0 \(\mu\)mol [Cu] in 1.2 mL solvent. \(^b\) Determined by GC analysis. \(^c\) Determined by HPLC, OD-H, \(n\)-heptane/iPrOH = 98:2, 0.5 mL/min, 20 °C, 30 bar.
HPLC data for racemic mixture

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Totals: 2.01857e4 937.76382
HPLC data for 2 with 14, table S7, entry 1

Signal 3: DAD1 C, Sig=210.4 Ref=360,100

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Totals: 2.12527e4 1350.52026
HPLC data for 2 with 15, table S7, entry 2:

Signal 3: DAD1 C, Sig=210.4 Ref=360,100

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Totals: 1.12433e4 595.44012
HPLC data for 2 with S15, table S7, entry 3:

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HPLC data for 2 with S16, table S7, entry 4:

Signal 3: DAD1 C, Sig=210,4 Ref=360,100

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Totals: 2.05811e4 930.33554
6 References


7 Spectra
\( N_1^1, N_2^2 \)-dimesitylethane-1,2-diaminium chloride (S7)

\(^1\text{H NMR}\)

\[ \begin{align*}
& \text{Chemical Shift} \\
& \text{p.p.m.} \\
& 5.83 \\
& 3.42 \\
& 2.65 \\
& 1.88 \\
& 0.60 \\
\end{align*} \]

S7
$^{1}H-^{1}H$ COSY
$^1$H-$^{13}$C HSQC
1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride (S8)

$^1$H NMR
$^{13}$C DEPT NMR
$^1$H-$^{13}$C HMQC
(1,3-dimesitylimidazolidin-2-yliden)copper(I) chloride (6)

$^1$H NMR
$^{13}$C NMR
$^{13}$C DEPT NMR
$^{1}H-^{1}H$ COSY
$^1$H-$^{13}$C HMQC
$^1$H-$^{13}$C HMBC

S119
Ethyl 3-phenylbutanoate (2)

$^1$H NMR
$^{13}$C NMR

$\text{C NMR}$

$\text{S123}$
$^{13}$C DEPT NMR

![Chemical Structure](image)
$^{1}H^{13}C$ HMQC
$^{1}H^{13}C$ HMBC
$^{1}H-{ }^{1}H$ COSY

[Chemical structure diagram]
Ethyl 3-(naphthalen-2-yl)butanoate (9a)
$^{13}$C DEPT NMR

![Chemical Structure](image)
$^{1}H-^{1}H$ COSY
$^{1}$H-$^{13}$C HMQC
tert-Butyl 3-phenylbutanoate (9b)

$^1$H NMR
$^{13}$C DEPT NMR

![NMR Spectrum](image)

9b
$^{1}H-^{1}H$ COSY
$^1$H-$^{13}$C HMQC
$^1$H-$^{13}$C HMBC
Ethyl 3,3-diphenylpropanoate (9c)

$^1$H NMR
$^{13}$C DEPT NMR

![Carbon-13 DEPT NMR spectrum with a chemical structure of 9c]
Ethyl 3-(4-methoxyphenyl)butanoate (9d)

$^1$H NMR
$^{13}$C DEPT NMR

![Carbon-13 DEPT NMR spectrum](image)

- **Chemical Formula**: 9d

- **ppm Scale**: 10 to 190

S152
$^1H-^{13}C$ HMQC
$^1$H-$^{13}$C HMBC
Ethyl 3-(4-(trifluoromethyl)phenyl)butanoate (9e)

$^1$H NMR

![NMR spectrum of ethyl 3-(4-(trifluoromethyl)phenyl)butanoate (9e)]
$^{13}$C DEPT NMR

9e

Chemical shifts (ppm)
$^{19}$F NMR
$^{1}H-^{1}H$ COSY
$^1H-^{13}C$ HMBC
Ethyl 3-(4-bromophenyl)butanoate (9f)

$^1$H NMR

![Chemical structure of 9f]

ppm
$^{13}$C NMR

---

S167
13C DEPT NMR
S169
$^1$H-\( ^{13}$C HMQC

![Graph of $^1$H-\( ^{13}$C HMQC](image)
$^{1}H - ^{13}C$ HMBC
Ethyl 3-(4-chlorophenyl)butanoate (9g)

$^1$H NMR
$^{13}$C NMR
$^{13}$C DEPT NMR

[Chemical structure image]

S176
Ethyl 3-(o-toly)butanoate (9h)

$^{1}H$ NMR
$^1$H-$^{13}$C HSQC

![Chemical Structure Image]
$^1$H-\textsuperscript{13}C HMBC
Ethyl 3-(4-cyanophenyl)butanoate (9j)

$^1$H NMR
$^1$H-$^{13}$C HMBC
Ethyl 3-(4-hydroxyphenyl)butanoate (9I)

$^1$H NMR
$^{1}\text{H}^{13}\text{C}$ HSQC
$^1$H-$^{13}$C HMBC
Ethyl 3-((tert-butyl)diphenylsilyl)oxy)phenyl)butanoate (9m-OEt)

$^1$H NMR
$^{1}H-^{1}H$ COSY
$^{1}H-^{13}C$ HSQC
$^{1}H^{13}C$ HMBC

9m-OEt

TBOPSO
$^{29}$Si DEPT
tert-Butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OtBu)

$^{1}H$ NMR
$^{1}H-^{1}H$ COSY
$^1$H-$^{13}$C HSQC
$^1H-^{13}C$ HMBC
$^{29}\text{Si DEPT}$

TBOPSO

9m-OrBu
Ethyl 3-(4-(dimethylamino)phenyl)butanoate (9n)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)
$^1\text{H}-^1\text{H COSY}$
$^1$H-$^{13}$C HSQC
$^1$H-$^{13}$C HMBC
Ethyl 3-(thiophen-2-yl)butanoate (9o)

$^1$H NMR
$^{13}$C DEPT NMR
$^{1}H$-$^{13}C$ HMQC
$^1$H-$^{13}$C HMBC
Ethyl 3-cyclopropyl-3-phenylpropanoate (9p)

$^1$H NMR
$\text{H}^{\text{13}C} \text{ HSQC}$
Hex-5-en-1-yl 3-phenylbutanoate (9q)

$^1$H NMR
$^{1}H-{^{13}}C$ HSQC
$^1$H-$^{13}$C HMBC
Diethyl 3,3'-{(1,4-phenylene)dibutyrate (9r)

$^1$H NMR
Ethyl-2-methyl-3-phenylbutanoate (9s)

$^{1}$H NMR
$^{13}$C NMR
$^1H\cdot^1H$ COSY

[Chemical structure image]

ppm

ppm

S254
$^1$H-$^{13}$C HSQC
$^1$H-$^{13}$C HMBC
Ethyl 3-cyclohexylbutanoate (9t)

$^1$H NMR
$^{13}$C DEPT NMR
$^1$H-$^1$H COSY
$^1H^{13}C$ HMBC
Ethyl 3-methylundecanoate (9u)

$^1$H NMR
$^1$H NMR
$^{13}$C DEPT NMR
'$^1$H-$^1$H COSY
$^{1}H-^{13}C$ HMBC
Ethyl 3-propylhexanoate (9v)

$^1$H NMR

![NMR spectrum of ethyl 3-propylhexanoate](image)
$^1$H-$^{13}$C HSQC
$^1$H-$^{13}$C HMBC
\[
\text{S278}
\]
$N,N$-diethyl-3-phenylbutanamide (11)

$^1$H NMR
$^{13}$C NMR
$^1$H-$^{13}$C HSQC
Ethyl (E)-5-phenylpent-4-enoate (13a)

$^1$H NMR
$^{13}$C NMR

![13a](image-url)
\textsuperscript{1}H-\textsuperscript{1}H COSY
$^1$H-$^{13}$C HMBC
Ethyl 3-(4-styrylphenyl)butanoate (S9)

$^1$H NMR
Ethyl 3-phenylbutanoate-2,3-\textit{d}_n (2-\textit{d}_n)

quant. $^1$H NMR
$^{13}$C NMR

![Carbon NMR Spectrum with Chemical Structure](image)
$^{13}$C DEPT NMR

![NMR Spectrogram](image)

S297
$^2$H NMR

![NMR spectrum](image)

2-$d_n$
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HMQC
Ethyl 3,3-diphenylpropanoate-2,2,3-d$_n$ (9c-d$_n$)

quant. $^1$H NMR
$^1$H NMR
$^{13}$C NMR
$^{2}\text{H NMR}$
Ethyl 3-(4-methoxyphenyl)butanoate-2,2,3-$d_n$ (9d-$d_n$)

quant. $^1$H NMR
$^{13}$C NMR

9d-d$_n$
$^{13}$C DEPT NMR
$^2$H NMR

9d-$d_n$
$^1$H-$^{13}$C HMBC
Ethyl 3-phenylbutanoate-2,2-\textsubscript{d}\textsubscript{2} (9d-\textsubscript{d}\textsubscript{n})

quant. \textsuperscript{1}H NMR
$^1$H NMR

$S_{14-d_n}$
$^{13}\text{C NMR}$
$^2$H NMR

![Chemical Structure](image)
$^{1}H-^{1}H$ COSY
$^{1}H^{13}C$ HSQC
$^{1}H-^{13}C$ HMBC

S14-$d_{n}$
Ethyl (E)-3-phenylbut-2-enoate (1)

$^1$H NMR
$^{13}$C NMR
$^{13}$C DEPT NMR
$^1$H-$^{13}$C HMQC
$^1\text{H}-^1\text{H COSY}$
Ethyl (E)-3-(naphthalen-2-yl)but-2-enoate (8a)

$^1$H NMR
$^{13}$C DEPT NMR

8a
$^1$H-$^{13}$C HMQC
$^1$H-$^1$H COSY
tert-Butyl (E)-3-phenylbut-2-enoate (8b)
$^{13}$C NMR
$\textsuperscript{1}H-\textsuperscript{13}C$ HMQC
$^1$H-$^{13}$C HMBC

S354
$^1$H-$^1$H NOESY
Ethyl 3,3-diphenylacrylate (8c)

$^1$H NMR
$^{13}\text{C}$ DEPT NMR

![Chemical Structure](image)

8c
$^{1}H - ^{13}C$ HMBC
Ethyl (E)-3-(4-methoxyphenyl)but-2-enoate (8d)

$^1$H NMR
$^{13}$C NMR

\[\text{8d}\]
$^{13}$C DEPT NMR
$^1$H–$^1$H COSY

S368
$^1H-^{13}C$ HMQC
$^1$H-$^{13}$C HMBC
8d
Ethyl (E)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (8e)

$^1$H NMR
$^{13}$C NMR

- 131.3
- 131.1
- 130.9
- 127.3
- 124.6
- 125.2
- 125.6
- 125.6
- 125.6
- 120.9
- 119.1
- 103.9
- 104.9
- 145.9

8e
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HMQC
$^{1}H-^{13}C$ HMBC

S378
$^{19}$F NMR

![Chemical Structure](image)
Ethyl (E)-3-(4-bromophenyl)but-2-enoate (8f)

$^1$H NMR
$^{13}$C NMR
$^{13}$C DEPT NMR
$^{1}H^{13}C$ HMBC

S387
Br

8f

\[
\text{Structure Image}
\]
Ethyl (E)-3-(4-chlorophenyl)but-2-enoate (8g)

$^1$H NMR
$^1H-^1H$ COSY
Ethyl (E)-3-(o-tolyl)but-2-enoate (8h)

$^1$H NMR
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HSQC
$^{1}{H}^{13}{C}$ HMBC
8h
Ethyl (E)-3-(4-nitrophenyl)but-2-enoate (8i)

$^1$H NMR
$^{13}$C NMR
$\text{H}^-\text{C} \text{ HMQC}$
Ethyl (E)-3-(4-cyanophenyl)but-2-enoate (8j)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

ppm
$^1$H-$^1$H COSY
$^{1}H^{13}C$ HMBC
Ethyl (E)-3-(4-acetylphenyl)but-2-enoate (8k)

$^1$H NMR
$^1$H-$^1$H COSY
Ethyl (E)-3-(4-hydroxyphenyl)but-2-enoate (8l)

$^1$H NMR

S430
$^{13}$C NMR

![Carbon NMR Spectrum](image)

S431
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HSQC
$^{1}H$-$^{13}C$ HMBC

S434
Ethyl (E)-3-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (8m)

$^1$H NMR
$^1$H-$^{13}$C HSQC
$^{29}$Si DEPT
Ethyl (E)-3-(thiophen-2-yl)but-2-enoate (8o)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

$8o$
$^{13}\text{C} \text{ DEPT NMR}$
$^{1}H-^{13}C$ HMQC
$^{1}H-^{1}H$ NOESY
Ethyl (E)-3-cyclopropyl-3-phenylacrylate (9p)

$^1$H NMR

9p
$^{13}$C NMR

![Chemical Structure]

9p
$^1$H-$^{13}$C HMBC
$^1$H-$^1$H NOESY
Hex-5-en-1-yl (E)-3-phenylbut-2-enoate (9q)

$^1$H NMR
$^{13}$C NMR

$9q$

Chemical shifts: 167.1, 157.5, 142.4, 139.5, 129.1, 128.4, 117.3, 114.9, 64.6, 33.5, 28.3, 25.4, 18.1
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HMBC
Ethyl (E)-3-cyclohexylbut-2-enoate (8t)

$^1$H NMR
$^1\text{H}-^{13}\text{C}$ HSQC
$^1$H-$^1$H NOESY
Ethyl (E)-3-methylundec-2-enoate (8u)

$^1$H NMR
$^{13}$C NMR
"H-"H COSY
$^{1}H-^{13}C$ HSQC
$^1$H-$^{13}$C HMBC
(E)-N,N-diethyl-3-phenylbut-2-enamide (10)

$^1$H NMR
$^{13}$C NMR

![Graph showing a carbon-13 NMR spectrum with chemical shifts labeled at various ppm values, including 10.0. A structural formula of a molecule is also present.]
$^{13}$C DEPT NMR
$^{1}H-{^{13}}C$ HMBC
Ethyl (E)-3-cyclohexylbut-2-enoate (8t)

$^1$H NMR

[Chemical structure and NMR spectrum]
$^1$H-$^{13}$C HMBC
Ethyl (E)-3-methylundec-2-enoate (8u)

$^1$H NMR

8u
$^{13}$C NMR

$8u$
$^{1}H-^{1}H$ COSY
$^{1}H$-$^{13}C$ HSQC
$^{1}H^{1}H$ NOESY
Ethyl (E)-3-(4-(phenylethynyl)phenyl)but-2-enolate (S3)

^1H NMR
$^{13}$C DEPT NMR

![Chemical Structure](image)

S3

ppm

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
$^{1}\text{H}^{1}\text{H \text{COSY}}$
$^1$H-$^{13}$C HMQC
tert-Butyl 2-(diethoxyphosphoryl)acetate (S4)

$^1$H NMR
$^{13}$C DEPT NMR

![NMR Spectrum](image-url)
$^1$H-$^1$H COSY
$^1$H-$^{13}$C HMQC
$^1$H-$^{13}$C HMBC
Chloro-N,N-diethylacetamide (S5)

$^1$H NMR

![NMR spectrum of Chloro-N,N-diethylacetamide (S5)]
$^{13}$C NMR
$^{13}$C DEPT NMR

![NMR Spectrum](image)
Diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (S6)

$^1$H NMR
$^{13}$C DEPT NMR
$^1$H-$^{13}$C HMQC

![Chemical Structure Image]

ppm

4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0

S536
$^{31}$P NMR

![Chemical Structure]

- Et$_2$N
- O
- R
- OEt
- S6

![NMR Spectrum]

- 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 ppm