A Recyclable CO Surrogate in Regioselective Alkoxy carbonylation of Alkenes: Indirect Use of Carbon Dioxide

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1 General methods

1.1 Reagents and Working Techniques

All chemicals and solvents were purchased from Acros, Merck, TCI, Aldrich or Fluka and used without purification unless otherwise noted. When necessary, purification of chemicals was carried out with the standard methods. Unless otherwise noted, all reactions were carried out air- and moisture-free under an atmosphere of dry nitrogen by employing Schlenk techniques. The reaction glassware was freed from residual moisture by heating under vacuum and subsequent cooling under dry N\textsubscript{2} (3x); this treatment is called "flame-drying" below.

Column chromatography was carried out using normal- (60 Å) or flash-grade (40 Å) Silica gel (SiO\textsubscript{2}) either using gravity flow or air overpressure flow conditions in a standard glass column setup with isocratic or gradient elution (composition of mobile phase noted in each experiment). Chromatography solvents were distilled prior to use.

For TLC analysis of reactions and purification processes, Kieselgel 60 F\textsubscript{254} aluminium-backed plates were employed, visualization was carried out either by fluorescence quenching of UV active compounds or by dipping the developed plates in pre-made solutions of various TLC stains and heating the plate gently until maximum contrast occurred (used stain noted in each experiment).

1.2 Analytical techniques

Melting point: Uncorrected melting points were determined on an Optimelt MPA100 apparatus from Stanford Research Systems. (heating rate 2 °C/min).

NMR spectroscopy: \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectra were recorded on Bruker Avance 400 or 300 MHz machines (400 or 300 MHz for \textsuperscript{1}H experiments; 101 or 75 MHz for \textsuperscript{13}C experiments) in commercially available deuterated solvents without TMS. \textsuperscript{13}C-NMR experiments were recorded in proton-decoupled mode, and this is not explicitly noted below. The chemical shift is noted as δ (ppm) and referenced to the trace solvent signals; these signals and their relation to the 0 ppm TMS signal are available in the literature.\textsuperscript{1} Coupling constants across bonds are given as J (Hz). The nomenclature for spin multiplicities is as follows: s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; sext = sextet; hept = heptet; m = multiplet. Usually, \textsuperscript{13}C-NMR measurements were accompanied by a \textsuperscript{13}C-DEPT135 experiment for further structural elucidation but are not noted explicitly in the
experimental data. Occasionally, 2D-NMR experiments were carried out where assignments were ambiguous, but are not noted explicitly in the experimental data.

**Infrared spectroscopy:** Infrared spectra were measured on a Excalibur FTS3000 MX FT-IR spectrometer from BioRad. The samples were applied neat on an ATR setup. Absorption bands are given in wave numbers $\nu$ (cm$^{-1}$) and peak intensities are abbreviated as follows: s - strong, m - medium, w - weak. Peak form descriptions are as follows: br - broad, sh - sharp.

**Mass spectrometry:** For GC/MS analysis of crude mixtures, an Agilent 6890 N Network GC with an Agilent 5975 Inert Mass Selective Detector was employed. Carrier gas: Dry Hydrogen. The stationary phase was a column type BPX5 (30 m X 0.25 mm X 0.25 µm [film thickness]) from SGE. Program 50-300M: From 50 °C (2 min) by heating 25 °C/min towards 300 °C (5 min). Total time: 17 min; flow rate: 1.0 mL/min. HR-MS and GC/MS analysis for purified compounds was carried out by the Central Analytical Department, University of Regensburg on a Agilent Q-TOF 6540 UHD (APCI/ESI-HRMS) and Finnigan MAT SSQ 710 A (EI/CI-LR-GC/MS) machine respectively.

**Gas chromatography:** Gas chromatography (flame ionization detection) was carried out on a HP6890 GC-System with injector 7683B and Agilent 7820A System, carrier gas: Dry Hydrogen. Program 50-280M12: From 50 °C by heating towards 280 °C in 12 min after injection. In some cases, quantitative instrumental analysis was used to determine reaction yields and conversions by the *internal standard method*. 
2 Experimental procedures and NMR data

2.1 Synthesis of N-formylsaccharin via CO₂ hydrosilylation

Dimethylphenylsilyl formate 9 (quantitative ¹H-NMR analysis by conversion into formic acid)²

\[
\text{Si} \quad \text{H} \quad \text{O} \\
180.3 \text{ g/mol}
\]

A flame-dried 25 mL Schlenk tube with a stirring bar was charged with Rh₂(OAc)₄ (3.3 mg, 7.0 µmol, 0.25 mol%) and K₂CO₃ (2.1 mg, 14 µmol, 0.5 mol%) and then fitted with a rubber septum. The atmosphere in the reaction vessel was exchanged to CO₂ by triple evacuation and refilling with CO₂ (balloon reservoir). The solids were dissolved in dry MeCN (6 mL) by syringe addition under stirring, giving a purple solution. After dissolution of all solid components, the solution was heated to 50 °C and dimethylphenylsilane 8 (460 µL, 3.00 mmol) was added via syringe (gas evolution occurs) and the reaction was further stirred at this temperature for 2 h.

After this time, the reaction was allowed to come to room temperature and the solvent was removed in vacuo (110 mbar, tepid water bath) without subjecting the intermediate silyl formate to atmospheric conditions in the process. The catalyst components were then precipitated under N₂ atmosphere by addition of dry hexane (3 mL) by syringe. The colourless solution was then transferred to a flame-dried 25 mL Schlenk tube by cannula filtration under inert conditions and the solvent subsequently removed again as described above, giving the silyl formate 9 as colourless to bronze liquid with slight turbidity. A qualitative analysis by ¹H-NMR [400 MHz, CDCl₃, δ (ppm): 8.12 (s, 1H, CHO), 7.50 (m, 5H, ArH), 0.63 (s, 6H, Si(CH₃)₂] matched with the reported literature data³ but contained traces of acetonitrile and an unknown impurity, indicating decomposition that occurred while preparing the NMR sample.

For quantitative ¹H-NMR analysis, the silyl formate was treated with 2 mL of dist. H₂O for hydrolysis for 1 h at RT under stirring. As an internal standard, maleic acid (26 mg) was added. An aliquot of this mixture was taken up in D₂O.

For quantitative NMR data evaluation, all spectra were manually phase-corrected and the baseline automatically set. Chemical shifts of components used for evaluation in D₂O (ppm):
Formic acid 8.16 (1H, s, HCO₂H); Maleic acid 6.34 (2H, s, HO₂C-CH=CH-CO₂H). Regression analysis of data points from calibration gave a response factor $R_{\text{Formic acid}} = 1.01$, and by using the obtained integral ratios for calculation, 150 mg (3.25 mmol, quant.) of formic acid was yielded after the hydrolysis.
**N-Acetylsaccharin and N-Formylsaccharin 1**

A two-necked, flame-dried RBF equipped with a stirring bar and reflux condenser was charged with acetic anhydride (15.1 mL, 160 mmol, 4 Eqv.) and formic acid (7.80 mL, 208 mmol, 5.2 Eqv.) and heated to reflux for 5 h under stirring. Then, saccharin (7.33 g, 40.0 mmol, 1 Eqv.) was added to the solution and stirred at 60 °C overnight. Then, the reaction vessel was cooled to RT, diluted with dist. H₂O, the precipitate washed with dist. H₂O over a Buchner funnel and the resulting filter cake dried in vacuo to afford a mixture of N-formyl- and N-acetylsaccharin as a colourless powder (5.10 g, 24 mmol, 60%). Each component matches with the reported literature data.⁴,⁵

*R*<sub>f</sub>: Decomposition on normal-phase SiO₂.

¹H-NMR (300 MHz, CD₃CN): δ (ppm): 9.15 (s, 1H, HetArCHO), 8.31 – 7.72 (m, 4H, HetArH); minor signals from N-acetylsaccharin: 8.31 – 7.72 (m, 4H, HetArH), 2.62 (s, 3H, N-COCH₃).

¹³C-NMR (75 MHz, CD₃CN) δ (ppm): 157.6, 157.4, 137.8, 137.2, 136.7, 135.3, 135.0, 134.1, 126.0, 125.8, 124.6, 121.2, 120.7, 120.4, 25.1.

GC/MS (ESI): *t*<sub>R</sub> = 1.63 min (NFS), m/z = 212 (32, [MH⁺]), 184 (100, [MH⁺]-[CO]); *t*<sub>R</sub> = 1.82 min (NAS), m/z = 226 (100, [MH⁺]).
**N-Formylsaccharin I (from Formic acid)**

![Chemical structure of N-Formylsaccharin](image)

211.2 g/mol

Using a modified procedure by Goto, a two-necked, flame-dried 500 mL RBF with a N₂ inlet, rubber septum and stirring bar was charged with HCO₂H (98 mL, 2.6 mol, 24 Eqv.) and Ac₂O (113 mL, 1.2 mol, 12 Eqv.) and the resulting solution was stirred vigorously for 1 h at RT (slightly exothermic). Meanwhile, a flame-dried assembly of a three-necked 500 mL Schlenk RBF with N₂ inlet, 100 mL dropping funnel and stirring bar and was charged with saccharin (18.3 g, 100 mmol, 1 Eqv.) and dissolved in dry THF (150 mL) under stirring. Upon the addition of pyridine (1.0 mL, 10 mmol, 10 mol%), the solution turned slightly cloudy and was further stirred. The formylating mixture prepared beforehand was then transferred via cannula into the dropping funnel and then added to the stirred saccharin solution dropwise at a rate which keeps the stirred saccharin solution at room temperature. After complete addition, precipitation occurs, and the white suspension is further stirred at RT for 3 h. The precipitate was collected by vacuum filtration, washed with MeOH p.A. (150 mL), then H₂O (150 mL, caution: remaining AcOCHO decomposes exothermically in the filtrate under CO release), and the filter cake was dried in vacuo to yield a colourless crystalline powder (19.4 g, 92.0 mmol, 92%). The analytical data matches with reported literature data.

\[ R_f: \] Decomposition on normal-phase SiO₂.

**Melting point:** 227 °C (a change in crystallinity occurs between 120-150 °C, possibly due to decarboxylation).

**FT-IR (ATR) \( \tilde{\nu} (\text{cm}^{-1}) \):** 1756 (s, sh), 1716 (s, sh), 1593 (m, sh), 1460 (m, sh), 1345 (s, sh), 1289 (s, sh), 1249 (s), 1175 (s, sh), 1159 (s, sh), 1104 (s, sh), 746 (s, sh), 672 (s, sh), 574 (s, sh).

**\(^1\)H-NMR (400 MHz, CD₃CN) \( \delta \) (ppm):** 9.16 (s, 1H, N-CHO), 8.19 (d, \( J = 7.7 \) Hz, 1H, ArH), 8.14 – 8.07 (m, 2H, ArH), 8.04 – 8.00 (m, 1H, ArH).

**\(^13\)C-NMR (101 MHz, CD₃CN) \( \delta \) (ppm):** 157.7 (C⁶), 157.4 (N-CHO), 137.9 (C₃a), 137.3 (C⁶), 135.3 (C⁵), 126.0 (C⁷), 124.6 (C₇a), 121.2 (C⁴).

**HR-MS (ESI):** [MH⁺] m/z = calc. for C₈H₆NO₄S 212.0012; found 212.0010.
**N-Formylsaccharin I (from CO₂)**

A flame-dried 25 mL Schlenk tube with a stirring bar under N₂ atmosphere was charged with Rh₂(OAc)₄ (3.3 mg, 7.5 µmol, 0.25 mol%) and K₂CO₃ (2.1 mg, 15 µmol, 0.5 mol%) and then fitted with a rubber septum. The atmosphere in the reaction vessel was exchanged towards CO₂ by triple evacuation and refilling with CO₂ (balloon reservoir). The solids were dissolved in dry MeCN (6 mL) by syringe addition under stirring, giving a purple solution. After dissolution of all solid components, the solution was heated to 50 °C and dimethylphenylsilane (460 µL, 3.0 mmol) was added via syringe (gas evolution may occur) and the reaction was further stirred at this temperature for 2 h.

After this time, the reaction was allowed to cool down to room temperature and the solvent was removed *in vacuo* (110 mbar, tepid water bath) without subjecting the intermediate silyl formate to atmospheric conditions in the process. The catalyst components were then precipitated under N₂ atmosphere by addition of dry hexane (6 mL) by syringe. The colourless solution was then transferred to a flame-dried 25 mL Schlenk tube by cannula filtration under inert conditions and the solvent subsequently removed again as described above, giving the silyl formate 9 as colourless to bronze liquid with slight turbidity.

To the neat silyl formate, Ac₂O (284 µL, 3.00 mmol) was added and stirred for 4 h at 40 °C to generate the formylating mixture. Meanwhile, an oven-dried 5 mL screw-capped glass vessel with septum inlet and stirring bar was filled with N₂, then charged with saccharin (0.30 mmol, 55 mg) and imidazole (10 mol%, 0.030 mmol, 2.0 mg). The solids were dissolved with dry THF (430 µL) under stirring. The formylating mixture was added dropwise under vigorous stirring *via* syringe. After complete addition, precipitation occurs, and the white suspension is further stirred at RT for 3 h. After the end of the reaction, the vessel contents were transferred to a Pasteur pipette plugged with cotton and filter paper. The resulting filter cake was washed with three pipette volumes of MeOH p.A., then three pipette volumes of cyclohexane, and the filtrate was discarded. The filter cake was then dissolved by addition of three pipette volumes MeCN, and the filtrate collected in a tared 5 mL RBF. The solvent was removed *in vacuo* to give the product as a colourless powder (36 mg, 0.17 mmol, 57% based on saccharin).
Analytical data as above.

### 2.2 Alkoxy carbonylation reactions

**General procedure for alkoxy carbonylation of olefins A**

A two-chambered pressure vessel (COware 20 mL, SyTracks A/S, Sigma-Aldrich article #744077) equipped with stirring bars was charged with N-formyl saccharin (1) (450 mg, 2.13 mmol) and sodium carbonate (339 mg, 3.20 mmol) in chamber A [Figure S1, a]); chamber B was charged with BNPA (3) (7.5 mol% up to 15 mol%, 15 eq. relative to Pd(dba)$_2$) [Figure S1, b]) and sealed with a septum-containing screw cap assembly (COware type, Sigma-Aldrich articles #743852 and #743968). Chamber A was fitted with a vacuum adapter screw cap and the reaction vessel was evacuated for 10 min [Figure S1, c)]. Under a N$_2$ backcurrent, Pd(dba)$_2$ (0.5 mol% up to 1.0 mol%, amounts specified below and referred to in each single experiment), dtbpx (2) (2.0 mol% up to 4.0 mol%, 4 eq. relative to Pd(dba)$_2$) were added in chamber B [Figure S1, d]), the vessel was then subjected to evacuation/N$_2$-backfilling (3x).

<table>
<thead>
<tr>
<th>Molar ratios</th>
<th>Pd(dba)$_2$</th>
<th>dtbpx</th>
<th>BNPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4:15 (1 mmol</td>
<td>0.5 mol%, 5 µmol, 2.9 mg</td>
<td>2.0 mol%, 20 µmol, 7.9 mg</td>
<td>7.5 mol%, 75 µmol, 26.1 mg</td>
</tr>
<tr>
<td>starting material)</td>
<td></td>
<td>3.0 mol%, 30 µmol, 11.9 mg</td>
<td></td>
</tr>
<tr>
<td>1:4:15 (0.75 mmol</td>
<td>0.75 mol%, 7.5 µmol, 4.4 mg</td>
<td>11.25 mol%, 11.3 µmol, 39.2 mg</td>
<td></td>
</tr>
<tr>
<td>starting material)</td>
<td></td>
<td>3.0 mol%, 22.5 µmol, 8.9 mg</td>
<td></td>
</tr>
<tr>
<td>1:4:15 (1 mmol</td>
<td>1.0 mol%, 10 µmol, 5.8 mg</td>
<td>4. mol%, 40 µmol, 15.8 mg, 15.0 mol%, 150 µmol, 52.2 mg</td>
<td></td>
</tr>
<tr>
<td>starting material)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Then, anhydrous DCM (750 µL) [Figure S1, e]), the alcohol (250 µL) [Figure S1, f]) and the olefin (1 mmol or 0.75 mmol, 100 mol%) were added to chamber B in exactly this order (solid olefins can be added at the beginning), resulting in a dark-red solution which was stirred at 750 rpm. The vacuum adapter screw cap of chamber A was exchanged to a septum-containing screw cap under positive N$_2$ pressure (using the septum inlet of chamber B) [Figure S1, g) and h)]. To start the decarbonylation, dry DMF (1 mL) was added to chamber A via septum addition [Figure S1, i]). This resulted in a suspension in chamber A where gas
evolution could be observed. Both reaction chambers were stirred at 750 rpm for 14 h at RT [Figure S1, j) after 14 h reaction time].

To stop the reaction, the screw caps were loosened in a well-ventilated environment (CO evolution may occur!). Excess NaHCO$_3$ in chamber A can be removed by addition of 1 M HCl, further addition of HCl precipitates saccharin which can be recovered (340 mg, 1.83 mmol, 86%) by filtration, washing the filter cake with copious amounts of dist. H$_2$O to remove NaCl and DMF, and finally drying the solid \textit{in vacuo}. The crude product can be subjected to GC analysis at this point, by adding a Pd metal scavenger (QuadraSil MP) and then filtering the crude solution through a cotton-plugged pasteur pipette filled with celite and basic aluminium oxide. Reaction mixtures giving non-volatile products can be adsorbed on Silica gel without further workup. Generally, special care must be taken to separate the products from catalyst components, which in the case of styrene derivatives as starting materials, often show retention behaviour similar the corresponding products. These impurities may give spectroscopically pure products a yellow appearance.
Figure S1: Setup of an alkoxy carbonylation reaction in a two-chambered vessel. See "General Procedure A" for steps a) – j)
General procedure B for Brønsted acid and Pd-precursor screening

General procedure A was followed using styrene as the olefin component and dist. MeOH as the alcohol, but with equimolar amounts of different acids or Pd precursors employed and 2 h reaction time. Solid acids (BNPA, pTsOH, PhCO₂H) were added at the start, while liquid acids (TFA, MsOH) were added via microsyringe to the olefin/MeOH/Pd(dba)₂/ligand DCM solution.

For quantitative GC-FID analysis of these catalytic carbonylation reactions, n-pentadecane (76.9 mg, 100 µL) was added to the crude reaction mixture with a 100 µL teflon microsyringe, the two-phase system vigorously stirred and diluted with DCM (2 mL) until a homogenous solution was obtained. A suitable Pd metal scavenger was added (QuadraSil MP) and the solution was then filtered through a cotton-plugged Pasteur pipette filled with celite and basic aluminium oxide and the sample in the GC vial was further diluted with DCM. The vial caps were sealed with parafilm to avoid evaporation of volatile components. Retention times under GC temperature program described above: \( t_R(\text{styrene}) = 2.99 \) min; \( t_R(n\text{-pentadecane}) = 6.00 \) min; \( t_R(\text{methyl 2-phenylpropanoate 5aa-b}) = 4.99 \) min; \( t_R(\text{methyl 3-phenylpropanoate 5aa-l}) = 5.32 \) min.

Response factors employed for yield calculations were \( R_{\text{Styrene}} = 0.924 \) and \( R_{\text{Product}} = 0.649 \) derived from calibration data by linear regression. b:l ratios were determined by comparison of the area integrals from the branched and linear product from the same GC-FID data.
Methyl 2-Phenylpropanoate (5aa-b) and Methyl 3-Phenylpropanoate (5aa-l)

Using dist. styrene (115 µL, 104 mg, 1.00 mmol; long-term storage in the dark under N₂ at -20 °C) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 88:12. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (124 mg, 0.76 mmol, 76%, b/l ratio 97:3 by NMR). The analytical data matches with reported literature data.⁷,⁸

Rₜ: 0.35  (mobile phase 9:1 CyH:EtoAc, KMN₅ stain)

**Melting point:** Ambient temperature.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.43 – 7.18 (m, 5H, ArH), 3.75 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)CH₃), 3.67 (s, 3H, R-CO₂CH₃), 1.52 (d, J = 7.2 Hz, 3H, ArCH(CO₂Me)CH₃); minor signals for linear regioisomer 2.99 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.66 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

¹³C-NMR (101 MHz, CDCl₃) δ (ppm): 175.0 (R-CO₂CH₃), 140.6 (ArC), 128.7 (ArC), 127.5 (ArC), 127.2 (ArC), 52.0 (R-CO₂CH₃), 45.5 (ArCH(CO₂Me)CH₃), 18.6 (ArCH(CO₂Me)CH₃). minor signals for linear regioisomer: 128.5 (ArC), 128.3 (ArC), 126.3 (ArC), 51.6 (R-CO₂CH₃), 35.7 (ArCH₂CH₂CO₂Me), 31.0 (ArCH₂CH₂CO₂Me).

**GC-FID** (50-280M12, from crude): t_R = 4.99 min (branched), t_R = 5.32 min (linear).

**GC/MS (EI):** t_R = 6.61 min (branched), m/z = 164 ([MH⁺]), 133 (1, [MH⁺]-[Ome⁻]), 104 (100, [MH⁺]-[Ome⁻]-[CO]), t_R = 7.37 min (linear), same m/z and intensity pattern.
Ethyl 2-phenylpropanoate (5ab-b) and Ethyl 3-phenylpropanoate (5ab-l)

![Chemical Structures](image.png)

Using styrene (115 µL, 104 mg, 1.00 mmol) as the olefin component and dist. EtOH (250 µL, stored under N\textsubscript{2}) as the alcohol component, general procedure A was employed using 0.5 mol\% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 93:7. Purification by column chromatography on SiO\textsubscript{2} (95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (150 mg, 0.84 mmol, 84\%, b/l ratio 97:3 by NMR). Analytical data matched with the reported literature data.9,10

\[
R_f : 0.44 \text{ (mobile phase 9:1 CyH:EtOAc), 0.34 \text{ (mobile phase 95:5 CyH:EtOAc), KMnO}_4 \text{ stain.}}
\]

**Melting point**: Ambient temperature.

\[^{1}H\text{-NMR} \text{ (400 MHz, CDCl}_3 \text{) } \delta \text{ (ppm): 7.40 - 7.17 (m, 5H, ArH), 4.20 - 4.06 (m, 2H, R-CO}_2\text{CH}_2\text{CH}_3 \text{), 3.71 (q, } J = 7.2 \text{ Hz, 1H, ArCH(CO}_2\text{Et)Me), 1.50 (d, } J = 7.2 \text{ Hz, 3H, ArCH(CO}_2\text{Et)CH}_3 \text{), 1.21 (t, } J = 7.1 \text{ Hz, 3H, R-CO}_2\text{CH}_2\text{CH}_3 \text{); minor signals from linear regioisomer: 2.96 (t, } J = 8.0 \text{ Hz, 2H, ArCH}_2\text{CH}_2\text{CO}_2\text{Et), 2.63 (t, } J = 8.0 \text{ Hz, 2H, ArCH}_2\text{CH}_2\text{CO}_2\text{Et).}}
\]

\[^{13}C\text{-NMR} \text{ (101 MHz, CDCl}_3 \text{) } \delta \text{ (ppm): 174.6 (C=O), 140.7 (ArC), 128.6 (ArC), 127.5 (ArC), 127.1 (ArC), 60.7 (CO}_2\text{CH}_2\text{CH}_3 \text{), 45.6 (ArCH(CO}_2\text{Et)Me), 18.6 (ArCH(CO}_2\text{Et)CH}_3 \text{), 14.1 (CO}_2\text{CH}_2\text{CH}_3 \text{), minor signals from linear regioisomer were not detected due to low concentration.}}
\]

**GC-FID** (50-280M12): \(t_R = 5.16 \text{ min (branched), } t_R = 5.55 \text{ min (linear).}
\)

**GC/MS** (EI): \(t_R = 7.30 \text{ min (branched), } m/z = 178 \text{ (18, [M\textsuperscript{++}]}, 105 \text{ (100, [C}_8\text{H}_9\text{]} \textsuperscript{+})); t_R = 8.22 \text{ min (linear), } m/z = 178 \text{ (18, [M\textsuperscript{++}]}, 133 \text{ (100, [M\textsuperscript{++}]-[OEt\textsuperscript{+}]).}}
\)
Isopropyl 2-phenylpropanoate (5ac-b) and Isopropyl 3-phenylpropanoate (5ac-l)

Using styrene (115 µL, 104.2 mg, 1 mmol) as the olefin component and diisopropyl ether (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 89:11. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (90 mg, 0.47 mmol, 47%, b/l ratio 93:7 by NMR). Analytical data matched with the reported literature data.⁹,¹⁰

Rᵣ: 0.56 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

Melting point: Ambient temperature.

¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.40 – 7.18 (m, 5H, ArH), 5.01 (hept, J = 6.3 Hz, 1H, R-CO₂CH(Me)₂), 3.68 (q, J = 7.2 Hz, 1H, ArCH(CO₂Pr)Me), 1.50 (d, J = 7.2 Hz, 3H, ArCH(CO₂Pr)CH₃), 1.23 (d, J = 6.3 Hz, 3H, R-CO₂CH(CH₃)₂ diastereotopic), 1.14 (d, J = 6.3 Hz, 3H, R-CO₂CH(CH₃)₂ diastereotopic); minor signals from linear regioisomer: 2.96 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Pr), 2.61 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Pr).

¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 174.1 (C=O), 140.8 (ArC), 128.6 (ArC), 127.5 (ArC), 127.0 (ArC), 67.9 (R-CO₂CH(Me)₂), 45.8 (ArCH(CO₂Pr)CH₃), 21.8 (R-CO₂CH(CH₃)₂), 21.6 (R-CO₂CH(CH₃)₂), 18.6 (ArCH(CO₂Pr)CH₃); minor signals from linear regioisomer: 140.6 (ArC), 128.5 (ArC), 128.4 (ArC), 126.2 (ArC), 67.7 (R-CO₂CH(Me)₂), 36.3 (ArCH₂CH₂CO₂Pr), 31.1 (ArCH₂CH₂CO₂Pr).

GC-FID (50-280 M12): tᵣ = 5.40 min (branched), tᵣ = 5.85 min (linear).

GC/MS (EI): tᵣ = 7.58 min (branched), m/z = 192 (25, [M⁺]), 105 (100, [C₈H₉⁺]); tᵣ = 8.59 min (linear), m/z = 192 (25, [M⁺]).
Cyclohexyl 2-phenylpropanoate (5ae-b) and Cyclohexyl 3-phenylpropanoate (5ae-l)

Using styrene (115 µL, 104 mg, 1.00 mmol) as the olefin component and cyclohexanol (250 µL) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 93:7. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (48 mg, 0.21 mmol, 21%, b/l ratio 92:8 by NMR). The analytical data matches with reported literature data.¹¹,¹²

*Rf*: 0.47 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

**Melting point**: Ambient temperature.

¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.40 – 7.14 (m, 5H, ArH), 4.83 – 4.69 (m, 1H, Cyclohexyl-CH), 3.69 (q, J = 7.2 Hz, 1H, ArCH(CO₂Cy)CH₃), 1.88 – 1.54 (m, 5H Cyclohexyl-CH₂), 1.49 (d, J = 7.2 Hz, 3H, ArCH(CO₂Cy)CH₃), 1.43 – 1.17 (m, 5H, Cyclohexyl-CH₂); minor signals from linear regioisomer: 2.95 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Cy), 2.61 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Cy).

¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 174.0 (C=O), 140.9 (ArC), 128.5 (ArC), 127.5 (ArC), 127.0 (ArC), 72.7 (Cyclohexyl-CH), 45.8 (ArCH(CO₂Cy)CH₃), 25.4 (Cyclohexyl-CH₂), 23.6 (Cyclohexyl-CH₂), 23.5 (Cyclohexyl-CH₂), 18.5 (ArCH(CO₂Cy)CH₃); minor signals from linear regioisomer: 128.5 (ArC), 128.3 ArC), 126.2 (ArC), 31.5 (ArCH₂CH₂CO₂Cy), 31.2 (ArCH₂CH₂CO₂Cy).

**GC-FID** (50-280M12): *tᵣ =* 7.38 min (branched), *tᵣ =* 7.82 min (linear).

**GC/MS (EI)**: *tᵣ =* 11.86 min (branched), *m/z =* 232 (4, [M⁺⁺⁺⁺]); *tᵣ =* 12.79 min (linear), *m/z =* 232 (8, [M⁺⁺⁺⁺]).
Benzyl 2-phenylpropanoate (5af-b) and Benzyl 3-phenylpropanoate (5af-l)

Using styrene (115 µL, 104 mg, 1.00 mmol) as the olefin component and benzyl alcohol (250 µL) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 82:18. Purification by flash chromatography on SiO$_2$ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil with a pleasant smell (191 mg, 0.80 mmol, 80%, b/l ratio 77:23 by NMR). The analytical data matches with reported literature data.$^7,^9$

$R_f$: 0.42 (mobile phase 9:1 CyH:EtOAc, KMnO$_4$ stain)

**Melting point:** Ambient temperature.

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.50 – 7.22 (m, 10H, ArH), 5.19 (ABq, $\Delta\delta_{AB} = 0.05$, $J = 12.9$ Hz, 2H, CH$_2$Ph), 3.86 (q, $J = 7.2$ Hz, 1H, ArCH(CO$_2$CH$_2$Ph)Me), 1.61 (d, $J = 7.2$ Hz, 3H, ArCH(CO$_2$CH$_2$Ph)CH$_3$); minor signals from linear regioisomer: 3.06 (t, $J = 7.8$ Hz, 2H, ArCH$_2$CH$_2$CO$_2$Bn), 2.76 (t, $J = 7.8$ Hz, 2H, ArCH$_2$CH$_2$CO$_2$Bn).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 174.4 (C=O), 140.5 (ArC), 136.1 (ArC), 128.7 (ArC), 128.7 (ArC), 128.6 (ArC), 128.4 (ArC), 128.3 (ArC), 128.2 (ArC), 128.0 (ArC), 127.7 (ArC), 127.3 (ArC), 126.4 (ArC), 66.5 (ArCH(CO$_2$CH$_2$Ph)Me), 45.6 (ArCH(CO$_2$CH$_2$Ph)Me), 18.6 (ArCH(CO$_2$CH$_2$Ph)CH$_3$); minor signals from linear regioisomer: 172.8 (C=O), 136.1 (ArC), 66.4 (ArCH$_2$CH$_2$CO$_2$CH$_2$Ph), 36.0 (ArCH$_2$CH$_2$CO$_2$Bn), 31.1 (ArCH$_2$CH$_2$CO$_2$Bn).

**GC-FID** (50-280M12): $t_R = 7.94$ min (branched), $t_R = 8.35$ min (linear).

**GC/MS (EI):** $t_R = 13.00$ min (branched), m/z = 240 (12, [M$^+$]), 105 (100, [C$_5$H$_5$O$^-$]), 91 (75, [C$_7$H$_7^+$]); $t_R = 13.91$ min (linear), m/z = 240 (4, [M$^+$]), 107 (100, [C$_7$H$_5$O$^+$]), 91 (100, [C$_7$H$_7^+$]).
Using 3-methylstyrene (130 μL, 118 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 μL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 91:9. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a bright yellow oil (161 mg, 0.92 mmol, 92%, b/l ratio 91/9 by NMR).

**Rf:** 0.34 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**FT-IR** (ATR) ν (cm⁻¹): 2981 (w, br), 2952 (w, br), 1734 (s, sh), 1608 (w, sh), 1455 (m, br), 1376 (m, br), 1376 (m, br), 1238 (m, br), 1196 (s, br), 1168 (s, br), 1067 (m, br).

**¹H-NMR** (300 MHz, CDCl₃) δ (ppm): 7.25 – 7.17 (m, 1H, ArH), 7.12 – 6.99 (m, 3H, ArH), 3.70 (q, J = 7.2 Hz, 1H, ArCH₂), 3.66 (s, 3H, OC₃H₃), 2.34 (s, 3H, ArCH₃), 1.49 (d, J = 7.2 Hz, 3H, ArCH₂CH₃); minor signals from linear regioisomer: 2.33 (s, 3H, ArCH₃), 2.92 (t, J = 7.5 Hz, 2H, ArCH₂CH₂CO₂Me), 2.62 (t, J = 7.5 Hz, 2H, ArCH₂CH₂CO₂Me). Due to low concentration no signals from the linear regioisomer were observed.

**¹³C-NMR** (101 MHz, CDCl₃) δ (ppm): 175.1 (C=O), 140.5 (ArC), 138.3 (ArC), 128.5 (ArC), 128.2 (ArC), 127.9 (ArC), 124.5 (ArC), 52.0 (ArCH(CO₂CH₃)Me), 45.4 (ArCH(CO₂Me)Me), 21.4 (ArCH₃), 18.6 (ArCH(CO₂Me)CH₃). Due to low concentration no signals from the linear regioisomer were observed.

**GC-FID:** (50-280M12): t_R = 5.42 min (branched), t_R = 5.75 min (linear).

**GC-MS:** t_R = 6.03 min (branched), m/z = 178 (33, [M⁺]), 119 (100, [M⁺][CO₂Me]), 91 (28, [M⁺][CO₂Me][CH₃⁺]); t_R = 6.77 min (linear), m/z = 178 (24, [M⁺]), 147 (8, [M⁺][OMe⁺]), 118 (100, [C₉H₁₀⁺⁺⁺⁺]), 105 (54, [M⁺][CH₂CO₂Me⁺⁺⁺⁺]).

**HR-MS** (APCI): m/z = [MH⁺] calc. for C₁₁H₁₄O₂ 179.1067, found 179.1067.
Methyl 2-(3-methoxyphenyl)propanoate (5ca-b) and methyl 3-(3-methoxyphenyl)propanoate (5ca-l)

![Chemical structures](image)

Using 3-vinylanisole (140 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 89:11. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a bright yellow oil (148 mg, 762 µmol, 76%, b/l ratio 88/12 by NMR). The analytical data for the linear product matches with reported literature.¹³

**Rf:** 0.21 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 7.25 – 7.18 (m, 1H, ArH), 6.91 – 6.73 (m, 3H, ArH), 3.80 (s, 3H, ArOCH₃), 3.70 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)Me), 3.67 (s, 3H, RCO₂CH₃), 1.49 (d, J = 7.2 Hz, 3H, ArCH(CO₂Me)CH₂); minor signals from linear regioisomer: 3.79 (s, 3H, ArOCH₃), 3.68 (s, 3H, ArCH₂CH₂COOCH₃), 2.93 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Me), 2.63 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Me).

**¹³C-NMR** (101 MHz, CDCl₃) δ (ppm): 174.9 (C=O), 159.8 (ArC), 142.1 (ArC), 129.6 (ArC), 119.9 (ArC), 113.3 (ArC), 112.5 (ArC), 55.2 (ArOCH₃), 52.1 (RCO₂CH₃), 45.4 (ArCH(CO₂Me)CH₃), 18.6 (ArCH(CO₂Me)CH₂); minor signals from linear regioisomer: 129.5 (ArC), 120.6 (ArC), 114.1 (ArC), 111.6 (ArC), 51.6 (RCO₂CH₃), 35.6 (ArCH₂CH₂CO₂Me), 31.0 (ArCH₂CH₂CO₂Me).

**GC-FID:** (50-280M12): tᵣ = 6.13 min (branched), tᵣ = 6.47 min (linear).

**GC-MS:** tᵣ = 7.56 min (branched), m/z = 194 (40, [M⁺]), 135 (100, [M⁺]-CO₂Me); tᵣ = 8.34 min (linear), m/z = 194 (46, [M⁺]), 163 (11, [M⁺]-OMe'), 134 (100, [C₅H₁₀O⁺]).
Methyl 2-(p-tolyl)propanoate (5da-b) and methyl 3-(p-tolyl)propanoate (5da-l)

Using 4-methylstyrene (130 µL, 118, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 90:10. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colorless oil (160 mg, 896 µmol, 91%, b/l ratio 91/9 by NMR). The analytical data for the branched product matches with reported literature.¹⁴

Rf: 0.32 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

Melting point: Ambient temperature.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.19 (d, J = 8.1 Hz, 2H, ArH), 7.13 (d, J = 8.1 Hz, 2H, ArH), 3.69 (q, J = 7.2 Hz, 1H, ArCH), 3.65 (s, 3H, ArCH₂CO₂CH₃), 2.33 (s, 3H, ArCH₃), 1.48 (d, J = 7.2 Hz, 3H, ArCH₂CH₂CO₂CH₃); minor signals from linear regioisomer: 3.67 (s, 3H, ArCH₂CH₂CO₂CH₃), 2.32 (s, 3H, ArCH₃), 2.92 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Me), 2.61 (t, J = 7.9 Hz, 2H, ArCH₂CH₂CO₂Me).

¹³C-NMR (101 MHz, CDCl₃) δ (ppm): 175.2 (C=O), 137.6 (ArC), 136.8 (ArC), 129.3 (ArC), 127.3 (ArC), 52.0 (RCO₂CH₃), 45.0 (ArCH(CO₂CH₃)CH₃), 21.0 (ArCH₃), 18.6 (ArCH(CO₂CH₃)CH₃); minor signals from linear regioisomer: 129.2 (ArC), 128.2 (ArC), 52.0 (RCO₂CH₃), 35.9 (ArCH₂CH₂CO₂Me), 30.6 (ArCH₂CH₂CO₂Me).

GC-FID: (50-280M12): tᵣ = 5.47 min (branched), tᵣ = 5.79 min (linear).

GC-MS: tᵣ = 6.03 min (branched), m/z = 178 (17, [M⁺]), 119 (100, [M⁺]-[CO₂Me], 91 (19, [M⁺]-[CH₂CH₂CO₂Me⁺]); tᵣ = 6.87 min (linear), m/z = 178 (25, [M⁺]), 118 (93, [C₉H₁₀⁺]), 105 (100, [M⁺]-[CH₂CO₂Me⁺]).
Methyl 2-(4-(tert-butyl)phenyl)propanoate (5ea-b) and methyl 3-(4-(tert-butyl)phenyl)propanoate (5ea-l)

Using 4-tert-butylstyrene (200 µL, 163 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 1.0 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 94:6. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colorless oil (199 mg, 902 µmol, 89%, b/l ratio 93/7 by NMR). The analytical data for the linear product matches with reported literature.

**(R)/**: 0.32 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.23 (d, J = 8.4 Hz, 2H, ArH), 3.72 (q, J = 7.2 Hz, 1H, ArCH(CO₂CH₃)Me), 3.66 (s, 3H, ArCH(CO₂CH₃)Me), 1.49 (d, J = 7.2 Hz, 3H, ArCH(CO₂Me)CH₂), 1.31 (s, 9H, Ar-CH(CH₃)₃; minor signals from linear regioisomer: 3.68 (s, 2H, RCO₂CH₂), 2.93 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.63 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

**¹³C-NMR** (101MHz, CDCl₃) δ (ppm): 175.2 (C=O), 150.00 (ArC), 137.5 (ArC), 127.1 (ArC), 125.6 (ArC), 52.0 (RCO₂CH₂), 44.9 (ArCH(CO₂CH₃)Me), 34.5 (Ar-CH(CH₃)₃), 31.3 (ArC(CH₃)₃), 18.6 (ArCH(CO₂Me)CH₂); due to low concentration, signals from the minor regioisomer were not detected.

**GC-FID:** (50-280M12): tᵣ = 6.53 min (branched), tᵣ = 6.84 min (linear).

**GC-MS:** tᵣ = 8.42 min (branched), m/z = 220 (25, [M⁺]), 205 (100, [M⁺]-[CH₃]), 161 (75, [M⁺]-[CO₂Me]; tᵣ = 9.11 min (linear), m/z = 220 (21, [M⁺]), 205 (100, [M⁺]-[CH₃]).
Methyl 2-(4-methoxyphenyl)propanoate (5fa-b) and Methyl 3-(4-ethoxyphenyl)propanoate (5fa-l)

Using dist. 4-vinylanisole (135 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 93:7. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (193 mg, 0.97 mmol, 97%, b/l ratio 93:7 by NMR). The analytical data matches with reported literature data.¹⁵⁻¹⁷

**Rₚ:** 0.31 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H NMR** (400 MHz, CDCl₃) δ (ppm): 7.25 – 7.20 (m, 2H, ArH), 6.89 – 6.83 (m, 2H, ArH), 3.78 (s, 3H, ArOCH₃), 3.69 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)Me), 3.65 (s, 3H, ArCH(CO₂CH₂)Me), 1.48 (d, J = 7.2 Hz, 3H, ArCH(CO₂Me)CH₃); minor signals for linear regioisomer: 2.90 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.60 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

**¹³C NMR** (101 MHz, CDCl₃) δ (ppm): 175.3 (C=O), 158.7 (ArC), 132.7 (ArC), 128.5 (ArC), 114.0 (ArC), 55.2 (ArOCH₃), 51.9 (R-CO₂CH₃), 44.6 (ArCH(CO₂Me)CH₃), 18.7 (ArCH(CO₂Me)CH₃); minor signals for linear regioisomer: 129.2 (ArC), 113.9 (ArC), 55.3 (ArOCH₃), 52.0 (RCO₂CH₃), 36.0 (ArCH₂CH₂CO₂Me), 30.9 (ArCH₂CH₂CO₂Me).

**GC-FID** (50-280M12, from crude): tᵣ = 6.37 min (branched), tᵣ = 6.61 min (linear).

**GC/MS (EI):** tᵣ = 9.46 min (branched), m/z = 194 (18, [MH⁺]), 135 (100, [MH⁺]-[CO₂Me⁺]); tᵣ = 10.14 min (linear), m/z = 194 (18, [MH⁺]), 121 (100, [MH⁺]-[CH₂CO₂Me⁺]).
Methyl 4-(1-methoxy-1-oxopropan-2-yl)benzoate (5ga-b) and Methyl 4-(3-methoxy-3-oxopropyl)benzoate (5ga-l)

Using 4-vinylbenzoic acid (148 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed with 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 77:23. Purification by flash chromatography on SiO₂ (mobile phase: 90:10 DCM:MeOH) gave the regioisomeric compounds as a colourless solid paste (44 mg, 0.21 mmol, 21%, b/l ratio 91:9 by NMR). The analytical data matches with reported literature data.¹⁸,¹⁹

Rᵣ: 0.22 (mobile phase 8:2 DCM:MeOH, KMnO₄ stain)

¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.34 – 7.28 (m, 2H, ArH), 7.07 – 7.01 (m, 2H, ArH), 3.73 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)CH₃), 3.63 (s, 3H, ArCH(CO₂CH₂)CH₃), 2.29 (s, 3H, ArCO₂CH₃), 1.49 (d, J = 7.2 Hz, 3H, ArCH(CO₂CH₂)CH₃); minor signals from linear regioisomer: 3.65 (ArCH₂CH₂CO₂CH₃), 2.94 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.63 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 174.8 (C=O), 169.6 (C=O), 149.7 (ArC), 138.0 (ArC), 129.3 (ArC), 128.6 (ArC), 121.7 (ArC), 121.6 (ArC), 52.1 (ArCH(CO₂CH₃)Me), 44.8 (ArCH(CO₂CH₂)CH₃), 21.1 (Ar-CO₂H), 18.6 (ArCH(CO₂CH₂)CH₃); minor signals from linear regioisomer: 51.7 (ArCH(CO₂CH₃)Me), 35.6 (ArCH₂CH₂CO₂Me), 30.3 (ArCH₂CH₂CO₂Me).

GC-FID (50-280M12): tᵣ = 7.45 min (branched), tᵣ = 7.73 min (linear).

GC/MS (APCI): tᵣ = 8.35 min (branched), m/z = 240.123 [M+NH₄⁺]; tᵣ = 8.90 min (linear), m/z = 240.123 [M+NH₄⁺].

HR-MS (APCI): [MH⁺] m/z = calc. for C₁₂H₁₄O₄ 223.0965; found 223.0968.
Methyl 2-(4-chlorophenyl)propanoate (5ia-b) and Methyl 3-(4-chlorophenyl)propanoate (5ia-l)

Using 4-chlorostyrene (120 µL, 139 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed using 1.0 mol% [Pd]ₐ. The b/l ratio of the crude product was determined by GC-FID analysis to be 92:8. Purification by chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (180 mg, 0.90 mmol, 90%, b/l ratio 96:4 by NMR). The analytical data matches with reported literature data.¹⁵,²⁰

\( R_\text{f} \): 0.29 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain).

**Melting point:** Ambient temperature.

\( ^{1}H\)-NMR (400 MHz, CDCl₃) δ (ppm): 7.31 – 7.27 (m, 2H, ArH), 7.25 – 7.21 (m, 2H, ArH), 3.70 (q, \( J = 7.2 \text{ Hz} \), 1H, ArCH(CO₂Me)CH₃), 3.66 (s, 3H, ArCH(CO₂C₃H₃)CH₃), 1.48 (d, \( J = 7.2 \text{ Hz} \), 3H, ArCH(CO₂Me)CH₃); minor signals from linear regioisomer: 2.92 (t, \( J = 7.7 \text{ Hz} \), 2H, ArCH₂CH₂CO₂Me), 2.61 (t, \( J = 7.7 \text{ Hz} \), 2H, ArCH₂CH₂CO₂Me).

\( ^{13}C\)-NMR (101 MHz, CDCl₃) δ (ppm): 174.6 (C=O), 138.97 (ArC), 133.0 (ArC), 128.9 (ArC), 128.8 (ArC), 52.1 (ArCH(CO₂C₃H₃)CH₃), 44.8 ArCH(CO₂Me)CH₃), 18.5 ArCH(CO₂Me)CH₃); minor signals from linear regioisomer: 173.0 (C=O), 132.1 (ArC), 129.7 (ArC), 128.6 (ArC) 51.7 (ArCH₂CH₂CO₂CH₃), 35.5 (ArCH₂CH₂CO₂Me), 30.3 (ArCH₂CH₂CO₂Me).

**GC-FID** (50-280M12, from crude): \( t_R = 5.99 \text{ min} \) (branched), \( t_R = 6.31 \text{ min} \) (linear).

**GC/MS** (EI): \( t_R = 8.73 \text{ min} \) (branched), m/z = 198 (21, [MH⁺]), 139 (100, [MH⁺]-[CO₂Me⁺]); \( t_R = 10.14 \text{ min} \) (linear), m/z = 198 (21, [MH⁺]), 167 (17, [MH⁺]-[OME⁺]), 125 (80, [MH⁺]-[CH₂CO₂Me⁺]).
Methyl 2-(4-acetoxyphenyl)propanoate (5ja-b) and Methyl 3-(4-acetoxyphenyl)propanoate (5ja-l)

Using 4-vinylphenyl acetate (150 µL, 162 mg, 1.00 mmol) as the olefin component and dist. MeOH (stored under N₂) as the alcohol component, general procedure A was employed using 1.0 mol% [Pd]. Purification by flash chromatography on SiO₂ (mobile phase: 8:2 CyH:EtOAc) gave the regioisomeric compounds as a yellow oil (93 mg, 0.43 mmol, 43%) and the corresponding deacetylated byproducts (detected by NMR) as a yellow oil. The analytical data of the main product matches with reported literature data.²¹,²²

R<sub>f</sub>: 0.31 (mobile phase 8:2 DCM:MeOH, KMnO₄ stain).

¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.30 (d, J = 8.5 Hz, 2H, ArH), 7.02 (d, J = 8.6 Hz, 2H, ArH), 3.71 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)CH₃), 3.63 (s, 3H, ArCH(CO₂C₃H₃)CH₃), 2.26 (s, 3H, Acetyl-C₃H₃), 1.47 (d, J = 7.2 Hz, 3H, ArCH(CO₂C₃H₃)C₃H₃); minor signals from linear regioisomer: 2.93 (t, J = 7.8 Hz, 2H, ArCH₂C₃H₂CO₂Me), 2.61 (t, J = 7.8 Hz, 2H, ArCH₂C₃H₂CO₂Me).

¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 174.8 (methyl ester C=O), 169.5 (acetyl C=O), 149.7 ArC, 138.0 (ArC), 128.6 (ArC), 121.7 (ArC), 52.1 (R-CO₂C₃H₃), 44.8 ArCH(CO₂C₃H₃)CH₃, 21.1 (acetyl C₃H₃), 18.6 (ArCH(CO₂C₃H₃)CH₃); minor signals from linear regioisomer: 35.6 (ArCH₂C₃H₂CO₂Me), 30.3 (ArCH₂C₃H₂CO₂Me).

GC-FID (50-280M12, from crude): t<sub>R</sub> = 6.80 min (branched), t<sub>R</sub> = 7.10 min (linear).

GC/MS (EI): Main product - t<sub>R</sub> = 10.82 min (branched), m/z = 222 (8, [MH⁺]), 180 (38, [MH⁺]-[CH₂CO]), 121 (100, [MH⁺]-[CH₂CO]-[CO₂Me⁺]); t<sub>R</sub> = 11.84 min (linear), m/z = 222 (8, [MH⁺]), 180 (65, [MH⁺]-[CH₂CO]), 107 (100, [MH⁺]-[CH₂CO]-[CO₂Me⁻]).

Deacetylated product - t<sub>R</sub> = 10.01 min (branched), m/z = 180 (30, [MH⁺]), 121 (100, [MH⁺]-[CO₂Me⁺]); t<sub>R</sub> = 10.80 min (linear), m/z = 180 (30, [MH⁺]), 107 (100, [MH⁺]-[CH₂CO₂Me⁻]).
Methyl 2-(4-hydroxyphenyl)propanoate (5ka-b) and Methyl 3-(4-hydroxyphenyl)propanoate (5ka-l)

Using 4-vinylphenyl acetate (150 µL, 162 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed using 1.0 mol% [Pd] at 50 °C. Purification by flash chromatography on SiO₂ (mobile phase: 8:2 CyH:EtOAc) gave the regioisomeric deacetylated compounds as a yellow oil (125 mg, 0.69 mmol, 69%) and the corresponding acetylated byproducts (27 mg, 0.12 mmol, 12%) as a yellow oil. The analytical data of the main product matches with reported literature data.²¹,²²

\[ R_f : 0.20 \] (mobile phase 8:2 DCM:MeOH, KMnO₄ stain).

\[ ^1H-NMR \] (300 MHz, CDCl₃) δ (ppm): 7.30 (d, J = 8.5 Hz, 2H, ArH), 7.02 (d, J = 8.6 Hz, 2H, ArH), 3.71 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)CH₃), 3.63 (s, 3H, ArCH(CO₂CH₃)CH₃), 1.47 (d, J = 7.2 Hz, 3H, ArCH(CO₂CH₃)CH₃); minor signals from linear regioisomer: 2.93 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.61 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

\[ ^13C-NMR \] (75 MHz, CDCl₃) δ (ppm): 174.8 (methyl ester C=O), 151.7 (ArC), 138.0 (ArC), 128.6 (ArC), 121.7 (ArC), 52.1 (R-CO₂CH₃), 44.8 ArCH(CO₂Me)CH₃, 18.6 ArCH(CO₂Me)CH₃; minor signals from linear regioisomer: 35.6 (ArCH₂CH₂CO₂Me), 30.3 (ArCH₂CH₂CO₂Me).

\[ GC/MS \] (EI): \( t_R = 10.01 \) min (branched), m/z = 180 (30, [MH⁺]), 121 (100, [MH⁺]-[CO₂Me⁺]); \( t_R = 10.80 \) min (linear), m/z = 180 (30, [MH⁺]), 107 (100, [MH⁺]-[CH₂CO₂Me⁺]).
Methyl 2-(2-methoxyphenyl)propanoate (5la-b) and Methyl 3-(2-methoxyphenyl)propanoate (5la-l)

Using 2-vinylanisole (135 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 46:54. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (126 mg, 0.66 mmol, 66%, b/l ratio 46:54 by NMR). The analytical data for the branched product matches with reported literature data.²³

Rᶠ: 0.22 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 7.29 – 7.11 (m, 2H, ArH), 6.99 – 6.82 (m, 2H, ArH), 4.08 (q, J = 7.2 Hz, 1H, ArCH(CO₂Me)CH₃), 3.83 (s, 3H, R-CO₂C₃H), 3.67 (s, 3H, ArOC₃H); signals from linear regioisomer: 3.68 (s, 3H, ArOC₃H), 2.97 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me), 2.64 (t, J = 7.8 Hz, 2H, ArCH₂CH₂CO₂Me).

**¹³C-NMR** (101 MHz, CDCl₃) δ (ppm): 174.5 (C=O), 155.6 (ArC), 128.9 (ArC), 128.5 (ArC), 127.1 (ArC), 119.7 (ArC), 109.7 (ArC), 54.4 (ArOCH₃), 50.8 (R-CO₂C₃H), 38.1 (ArCH(CO₂CH₂)CH₃), 16.3 (ArCH(CO₂Me)CH₃); signals from linear regioisomer: 172.2 (C=O), 156.4 (ArC), 127.8 (ArC), 126.9 (ArC), 126.6 (ArC), 119.4 (ArC), 109.2 (ArC), 54.1 (ArOCH₃), 50.4 (R-CO₂C₃H), 33.0 (ArCH₂CH₂CO₂Me), 25.1 (ArCH₂CH₂CO₂Me).

**GC-FID** (50-280M12, from crude): tᵣ = 5.92 min (branched), tᵣ = 6.27 min (linear).

**GC/MS** (EI): tᵣ = 8.88 min (branched), m/z = 194 (28, [M⁺]), 135 (100, [M⁺]-[CO₂Me]); tᵣ = 9.67 min (linear), m/z = 194 (56, [M⁺]), 163 (16, [M⁺]-[OMe⁺]), 121 (100, [M⁺]-[CH₃CO₂Me⁺]).
Methyl 2-((2-acetoxyphenyl)propanoate (5ma-b) and Methyl 3-((2-acetoxyphenyl)propanoate (5ma-l)

Using 2-acetoxy styrene (117 mg, 720 µmol) as the olefin component and dist. MeOH (250 µL, stored under N2) as the alcohol component, general procedure C was employed using 0.75 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 39:61. Purification by flash chromatography on SiO2 (mobile phase: 80:20 CyH:EtOAc) gave the regioisomeric compounds as a bright yellow oil (94 mg, 0.42 mmol, 59 %, b/l ratio 36/64 by NMR).

Rf: 0.32 (mobile phase 80:20 CyH:EtOAc, KMnO4 stain)

Melting point: Ambient temperature.

FT-IR (ATR) ν (cm⁻¹): 3062 (w, sh), 2990 (w, sh), 2953 (w, sh), 1806 (w, sh), 1763 (s, br), 1734 (s, br), 1585 (w, br), 1490 (m, sh), 1453 (m, sh), 1436 (m, sh), 1370 (m, sh), 1200 (s, br), 1170 (s, br), 1068 (w, sh), 1041 (m, sh), 1011 (m, sh), 913 (m, sh).

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.37 – 7.27 (m, 1H, ArH), 7.25 – 7.15 (m, 2H, ArH), 7.09 – 7.01 (m, 1H, ArH), 3.84 (q, J = 7.2 Hz, 1H, ArCH₂(CO₂Me)Me), 3.64 (s, 3H, ArCH(COOCH₃)Me), 2.31 (s, 3H, ArOCOC₃H), 1.47 (d, J = 7.2 Hz, 3H, ArCH(CH₂CO₂Me)CH₃); signals from linear regioisomer: 3.67 (s, 3H, ArCH₂CH₂CO₂Me), 2.62 - 2.56 (m, 2H, ArCH₂CH₂CO₂Me), 2.34 (s, 3H, ArOCOCH₃).

¹³C-NMR (101 MHz, CDCl₃) δ (ppm): 174.5 (methyl ester C=O), 169.3 (acetate C=O), 148.3 (ArC), 132.3 (ArC), 128.7 (ArC), 128.1 (ArC), 126.4 (ArC), 122.8 (ArC), 52.1 (ArCH(CH₂CO₂Me)Me), 39.9 (ArCH(CH₂CO₂Me)Me), 20.8 (ArOCOC₃H), 17.2 (ArCH(CH₂CO₂Me)CH₃); signals from linear regioisomer: 173.3 (methyl ester C=O), 169.6 (acetate C=O), 149.0 (ArC), 132.6 (ArC), 130.1 (ArC), 127.6 (ArC), 126.3 (ArC), 122.5 (ArC), 51.7 (ArCH₂CH₂CO₂CH₃), 34.2 (ArCH₂CH₂CO₂CH₃), 25.5 (ArCH₂CH₂CO₂CH₃), 20.9 (ArOCOCH₃).

GC-FID (50-280 M12): tR = 6.44 min (branched), tR = 6.84 min (linear).
GC-MS: $t_R = 7.54$ min (branched), m/z = 223 (100, [MH$^+$]), 163 (20, [MH$^+$]-[$^1$CO$_2$Me$^-$]), 149 (31, [MH$^+$]-[CO$_2$Me$^-$]-[CH$_3$.]); $t_R = 8.20$ min (branched), m/z = 223 (100, [MH$^+$]), 163 (14, [MH$^+$]-[$^1$CO$_2$Me$^-$]), 149 (64, [MH$^+$]-[CH$_2$CO$_2$Me$^-$]).

HR-MS (APCI): m/z = [MH$^+$] calc. for C$_{12}$H$_{14}$O$_4$ 223.0965, found 233.0967
Using 2-methylstyrene (130 µL, 118 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 50:50. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (50 mg, 0.28 mmol, 28%, b/l ratio 20:80 by NMR). The analytical data matches with reported literature data.²³,²⁴

**R_f:** 0.28 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 7.23 – 7.06 (m, 4H, ArH), 3.96 (q, J = 7.1 Hz, 1H, ArCH(CO₂Me)Me), 3.66 (s, 3H, ArCH(CO₂C₃H₃)Me), 2.37 (s, 3H, ArCH₃), 1.48 (d, J = 7.1 Hz, 3H, ArCH(CO₂Me)CH₃); signals from linear regioisomer: 3.69 (s, 3H, ArCH₂CH₂CO₂CH₃), 2.95 (t, J = 8.1 Hz, 2H, ArCH₂CH₂CO₂Me), 2.60 (t, J = 8.1 Hz, 2H, ArCH₂CH₂CO₂Me), 2.33 (s, 3H, ArCH₃).

**¹³C-NMR** (101 MHz, CDCl₃) δ (ppm): 175.3 (C=O), 139.2 (ArC), 135.7 (ArC), 130.5 (ArC), 129.0 (ArC), 127.0 (ArC), 126.5 (ArC), 52.0 (ArCH(CO₂CH₃)Me), 41.3 (ArCH(CO₂CH₃)Me), 19.6 (ArCH₃), 18.0 (ArCH(CO₂CH₃)CH₃); signals from linear regioisomer: 173.5 (C=O), 138.6 (ArC), 136.0 (ArC), 130.3 (ArC), 128.5 (ArC), 126.2 (ArC), 51.7 (RCO₂CH₃), 34.4 (ArCH₂CH₂CO₂Me), 28.4 (ArCH₂CH₂CO₂Me), 19.2 (ArCH₃).

**GC-FID** (50-280M12): tᵣ = 4.58 min (branched), tᵣ = 4.81 min (linear).  
**GC/MS (EI):** tᵣ = 7.68 min (branched), m/z = 178 (18, [M⁺]), 119 (100, [M⁺]-[CO₂Me⁺]); tᵣ = 8.56 min (linear), m/z = 178 (18, [M⁺]), 105 (100, [M⁺]-[CH₂CO₂Me⁺]).
3-Methylbenzofuran-2(3H)-one (5p)

Using freshly purified (column chromatography) 2-vinylphenol (115 µL, 120 mg, 1.00 mmol; storage at 6 °C) as the olefin component and dist. MeOH (50 µL; stored under N₂) as the alcohol component to dissolve the organophosphoric acid, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless oil (25 mg, 0.16 mmol, 16%). The analytical data matches with the reported literature data.²⁵

Rₚ: 0.36 (mobile phase 8:2 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H NMR** (400 MHz, CDCl₃) δ (ppm): 7.35 – 7.23 (m, 2H, ArH), 7.18 – 7.08 (m, 2H, ArH), 3.73 (q, J = 7.6 Hz, 1H, C⁹-H), 1.58 (d, J = 7.6 Hz, 3H, CH₃).

**¹³C NMR** (101 MHz, CDCl₃) δ (ppm): 178.0 (C=O), 153.5 (ArC), 131.7 (ArC), 128.8 (ArC), 124.2 (ArC), 123.9 (ArC), 110.8 (ArC), 38.4 (C⁹), 15.9 (C¹⁰).

**GC/MS (EI):** tᵣ = 7.11, m/z = 148 (100, [MH⁺]), 120 (78, [MH⁺]-[CO]), 91 (80, [C₇H₇⁺]).
Dimethyl 2-methylsuccinate (21)

Using methyl methacrylate (11) (105 µL, 100 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 9:1 CyH:EtOAc) gave the compound as a colourless liquid (74 mg, 0.46 mmol, 46%). The analytical data matches with the reported literature data.

\[ R_f: 0.30 \text{ (mobile phase 9:1 CyH:EtOAc, KMnO}_4\text{ stain)} \]

**Melting point:** Ambient temperature.

**\(^1\)H NMR (400 MHz, CDCl₃)** δ (ppm): 3.63 (s, 3H, RC\(^1\)O₂CH₃), 3.61 (s, 3H, R-C\(^4\)O₂CH₃), 2.94 – 2.78 (m, 1H, -C\(^2\)H(C\(^2\)H₃)-), 2.67 (m, 1H, diastereotopic -C\(^3\)H\(^2\)C\(^4\)O₂CH₃-), 2.34 (m, 1H, diastereotopic -C\(^3\)H\(^2\)C\(^4\)O₂CH₃-), 1.15 (d, J = 7.2 Hz, 3H, -C\(^2\)H-C\(^2\)H₃).

**\(^13\)C NMR (101 MHz, CDCl₃)** δ (ppm): 175.6 (C\(^1\)), 172.2 (C\(^4\)), 51.9 (C\(^1\)-OCH₃), 51.6 (C\(^4\)-OCH₃), 37.4 (C\(^3\)), 35.7 (C\(^2\)), 16.9 (C\(^2\)-CH₃).

**GC/MS (EI):** \( t_R = 4.78 \text{ min, m/z = 129 (50, [M”]-[OMe”]), 128 (36, [M’’]-[HOMe]), 59 (100, [CO₂Me”])}. \)
4-Benzyl 1-methyl 2-methylsuccinate (22)

![Chemical Structure](image)

Using methyl methacrylate (11) (155 µL, 146.0 mg, 1.5 mmol) as the alkene component and degassed BnOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.75 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (176 mg, 0.75 mmol, 51%).

Rᵣ: 0.10 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

Melting point: Ambient temperature.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.44 – 7.29 (m, 5H, ArH), 5.12 (ABq, ∆δ_AB = 0.02, J = 12.3 Hz, 2H, CH₂Ph), 3.65 (s, 3H, RC¹O₂CH₃), 2.95 (s, J = 7.2 Hz, 1H, -C²H(C²H₃)-), 2.80 (m, 1H, diastereotopic C³H₂C⁴O₂Bn⁻), 2.46 (m, 1H, diastereotopic C³H₂C⁴O₂Bn⁻), 1.22 (d, J = 7.2 Hz, 3H, -C²H-C²H₃).

¹³C-NMR (101 MHz, CDCl₃) δ (ppm): 175.7 (C¹), 171.6 (C⁴), 135.8 (ArC), 128.6 (ArC), 128.3 (ArC), 128.3 (ArC), 128.3 (ArC), 66.5 (ArCH₂), 51.9 (C¹-OCH₃), 37.7 (C³), 35.8 (C²), 17.0 (C²-C₃H₃).

FT-IR (ATR) ν (cm⁻¹): 2953 (w, br), 1731 (s, sh), 1456 (m, sh), 1381 (m, sh), 1346 (m, sh), 1273 (m, br), 1159 (s, sh), 1057 (m, sh), 990 (m, br).

GC-MS: t_R = 8.98 min, m/z = 237 (77, [MH⁺]), 129 (29, [MH⁺]-[BnO⁻]), 91 (100, [MH⁺]-[C₇H₇]).

HR-MS (APCI): m/z = [MH⁺] calc. for C₁₃H₁₆O₄ 237.1121, found 237.1126.
Benzyl 2-acetoxypropanoate (23)

Using vinyl acetate (12) (90 µL, 86 mg, 1.00 mmol) as the alkene component and BnOH (250 µL) as the alcohol component, general procedure A was employed using either with 0.5 or 1.0 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (69 mg, 0.32 mmol, 32% with 0.5 mol% [Pd] and 93 mg, 0.43 mmol, 43% with 1.0 mol% [Pd]). The analytical data matched the data reported in the literature.²⁷

*R*<sub>f</sub>: 0.10 (mobile phase 95:5 CyH:EtOAc, KMnO₄ stain)

**Melting point:** Ambient temperature.

**¹H NMR** (400 MHz, CDCl₃) δ (ppm): 7.57 – 7.17 (m, 5H, ArH), 5.18 (ABq, Δδ<sub>AB</sub> = 0.03, J = 12.3 Hz, 2H, CH₂Ph), 5.13 (q, J = 7.1 Hz, 1H, -C⁻²H⁻), 2.12 (s, 3H, Acetyl-CH₃), 1.49 (d, J = 7.1 Hz, 3H,-C⁻³H⁻).

**¹³C NMR** (101 MHz, CDCl₃) δ (ppm): 170.7 (C¹), 170.4 (Acetyl C=O), 135.4 (ArC), 128.6 (ArC), 128.4 (ArC), 128.1 (ArC), 68.6 (C⁻²), 66.7 (CH₂Ph), 20.7 (Acetyl-CH₃), 16.0 (C⁻³).

**GC/MS** (EI): *t*<sub>R</sub> = 10.16 min, m/z = 162 (30, [M⁺]-[AcOH]), 91 (80, [C₇H₇⁺]), 43 (100, [AcO⁻]).
Methyl 2-Phenylbutanoate (24-b) and Methyl 4-Phenylbutanoate (24-l) (from β-Methylstyrene 14)

Using β-methylstyrene (100 µL, 89 mg, 0.750 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 1.0 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 9:1 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil with a pleasant smell (48 mg, 29.3 mmol, 39%, b/l ratio 53:47 by NMR¹). The analytical data matched the reported literature data.²⁸-³⁰

**Rᶠ** (linear isomer): 0.33 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain).

**Rᶠ** (C²-branched isomer): 0.42 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain).

**Melting point:** Ambient temperature.

¹H NMR (400 MHz, CDCl₃) δ (ppm): signals from linear isomer: 7.44 – 7.09 (m, 5H, ArH), 3.67 (s, 3H, R-CO₂C₂H₅), 2.71 – 2.59 (m, 2H, ArCH₂CH₂CH₂CO₂CH₃), 2.34 (t, J = 7.5 Hz, 2H, ArCH₂CH₂CH₂CO₂CH₃), 2.02 – 1.88 (m, 2H, ArCH₂CH₂CH₂CO₂CH₃); signals from C₂-branched isomer: 3.47 (t, J = 7.7 Hz, 1H, ArCH(CO₂Me)CH₂C₂H₅), 2.18 – 2.05 (m, 1H, diastereotopic ArCH(CO₂Me)CH₂C₂H₅), 1.81 (m, 1H, diastereotopic ArCH(CO₂Me)CH₂C₂H₅), 0.90 (t, J = 7.4 Hz, 3H, ArCH(CO₂Me)CH₂C₂H₅).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 174.0 (C=O), 141.4 (ArC), 128.5 (ArC), 128.4 (ArC), 126.0 (ArC), 51.6 (R-CO₂C₂H₅), 35.1 (ArCH₂CH₂CH₂CO₂CH₃), 33.4 (ArCH₂CH₂CH₂CO₂CH₃), 26.5 (ArCH₂CH₂CH₂CO₂CH₃); signals from C₂-branched isomer: 174.6 (C=O), 139.1 (ArC), 128.6 (ArC), 128.0 (ArC), 127.2 (ArC), 53.4 (R-CO₂C₂H₅), 51.9 (ArCH(CO₂Me)CH₂C₂H₅), 26.5 (ArCH(CO₂Me)CH₂C₂H₅), 12.2 (ArCH(CO₂Me)CH₂C₂H₅)

**GC/MS (EI):** tᵣ = 7.41 min (C2-branched), m/z = 178 (20, [M⁺]), 163 (2, [M⁺]-[Me⁺]), 150 (8, [M⁺]-[CO]-[OMe⁺]); tᵣ = 8.58 min (linear), m/z = 178 (40, [M⁺]), 147 (40, [M⁺] - [OMe⁺]), 146 (40, [M⁺]-[MeOH]).

¹ The shown NMR spectra are not representative of the calculated regioselectivity by NMR due to differences in the regioisomeric composition of isolated product fractions.
Methyl 2-Phenylbutanoate (24-b) and Methyl 4-Phenylbutanoate (24-l) (from Allylbenzene 13)

Using allylbenzene (130 µL, 118 mg, 0.750 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the regioisomeric compounds as a colourless oil (41 mg, 29 mmol, 29%, b/l ratio 56:44 by NMR).

Analytical data as above.
Methyl 2-(1,3-dioxoisindolin-2-yl)propanoate (25-b) and Methyl 2-(1,3-dioxoisindolin-2-yl)propanoate (25-l)

Using N-vinylphthalimide (15) (173 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 or 1.0 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 44:56 (with both [Pd] loadings). Purification by flash column chromatography on SiO₂ (mobile phase: 9:1 CyH:EtOAc) gave the regioisomeric compounds as a brown solid (109 mg, 0.47 mmol, 47%, b/l ratio 85:15 by NMR with 0.5 mol% [Pd] and 192 mg, 0.82 mmol, 82%, b/l 45:55 by NMR with 1.0 mol% [Pd]). The analytical data matches with the reported literature data.³¹,³²

Rᵣ: 0.39 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

Melting point: 60 °C.

¹H NMR (400 MHz, CDCl₃) δ (ppm): linear isomer: 7.80 – 7.72 (m, 2H, ArH), 7.69 – 7.61 (m, 2H, ArH), 3.91 (t, J = 7.2 Hz, 2H, NCH₂CH₂CO₂CH₃), 3.60 (s, 3H, NCH₂CH₂CO₂CH₃), 2.65 (t, J = 7.2 Hz, 2H, NCH₂CH₂CO₂CH₃); minor signals from branched regioisomer: 4.97 (q, J = 7.3 Hz, 1H, NC₃H₃(CH(CO₂Me)CH₃)), 3.74 (s, 3H, NCH(CO₂CH₃)CH₃), 1.69 (d, J = 7.3 Hz, 3H, NCH(CO₂CH₃)CH₃).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 171.2 (Ester C=O), 167.9 (Imide C=O), 134.0 (ArC), 132.0 (ArC), 123.3 (ArC), 51.9 (NCH₂CH₂CO₂CH₃), 33.7 (NCH₂CH₂CO₂CH₃), 32.7 (NCH₂CH₂CO₂CH₃); minor signals from branched regioisomer: 170.2 (Ester C=O), 167.4 (Imide C=O), 134.2 (ArC), 132.0 (ArC), 123.5 (ArC), 52.8 (NCH(CO₂CH₃)CH₃), 47.4 (NCH(CO₂CH₃)CH₃), 15.3 (NCH(CO₂CH₃)CH₃).

GC-FID (50-280M12, from crude): tᵣ = 7.77 min (branched), tᵣ = 8.12 (linear).

GC/MS (EI): tᵣ = 12.56 min (branched), m/z = 233 (2, [M⁺]), 202 (1, [M⁺][OMe⁺]), 174 (100, [M⁺][OMe⁺][CO]), tᵣ = 13.45 min (linear), m/z = 233 (15, [M⁺]), 202 (8, [M⁺][OMe⁺]), 173 (100, [M⁺][OMe⁺][CO]), 160 (100, [PhthalN⁺=CH₂]).
Methyl 3-Phenylbutanoate (26) (from α-Methylstyrene 16)

Using α-methylstyrene (100 µL, 0.75 mmol [0.75 mol% [Pd]] or 130 µL, 1 mmol [1.0 mol% [Pd]]) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed at RT or 50 °C (in DCE), respectively. Purification by flash column chromatography on SiO₂ (mobile phase: 9:1 CyH:EtOAc) gave the compound as a colourless liquid (36 mg, 0.20 mmol, 20% with 0.75 mol% [Pd] and 60 mg, 0.34 mmol, 34% with 1.0 mol% [Pd]). The analytical data matched the data reported in the literature. ³³

R<sub>f</sub>: 0.48 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

**Melting point**: Ambient temperature.

**¹H NMR** (400 MHz, CDCl₃) δ (ppm): 7.37 – 7.16 (m, 5H, ArH), 3.63 (s, 3H, R-CO₂CH₃), 3.34 – 3.24 (m, 1H, ArCH(Me)CH₂CO₂Me), 2.60 (m, 2H, ArCH(Me)CH₂CO₂Me), 1.31 (d, J = 7.0 Hz, 3H, ArCH(CH₃)CH₂CO₂Me).

**¹³C NMR** (101 MHz, CDCl₃) δ (ppm): 172.9 (ArCH(Me)CH₂CO₂Me), 145.7 (ArC), 128.5 (ArC), 126.7 (ArC), 126.4 (ArC), 51.5 (ArCH(Me)CH₂CO₂CH₃), 42.8 (ArCH(Me)CH₂CO₂Me), 36.5 (ArCH(Me)CH₂CO₂Me), 21.8 (ArCH(CH₃)CH₂CO₂Me).

**GC/MS (EI)**: t<sub>R</sub> = 7.80 min, m/z = 178 (20, [M⁺]), 147 (5, [M⁺]-[OMe⁺]), 105 (100, [C₈H₉⁺]).
Methyl nonanoate (27) (from 1-octene 17)

\[
\text{CO}_2\text{Me}
\]

172.3 g/mol

27

Using 1-octene (160 µL, 114 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (91 mg, 0.53 mmol, 53%). The analytical data matches with the reported literature data.³⁴

\( R_f \): 0.50 (mobile phase 9:1 CyH:EtOAc, KMnO₄ stain)

**Melting point**: Ambient temperature.

\(^1\text{H NMR}\) (300 MHz, CDCl₃) \( \delta \) (ppm): 3.59 (s, 3H, RCO₂CH₃), 2.23 (t, \( J = 7.5 \text{ Hz} \), 2H, RCH₂-CO₂Me), 1.55 (sext, \( J = 7.5 \text{ Hz} \), 2H, R-CH₂-CH₂-CO₂Me), 1.20 (s br, 10H, Alkane-CH₂), 0.87 – 0.75 (t, \( J = 6 \text{ Hz} \), 3H, terminal CH₃).

\(^{13}\text{C NMR}\) (75 MHz, CDCl₃) \( \delta \) (ppm): 174.3 (C1), 51.4 (RCO₂CH₃), 34.1 (C2), 31.8 (C3), 29.2 (C4), 29.2 (C5), 29.1 (C6), 25.0 (C7), 22.6 (C8), 14.1 (C9).

**GC/MS** (EI): \( t_R = 6.70 \text{ min} \), m/z = 172 (2, [M⁺]).
Methyl nonanoate (27) (from 2-octene 18)

Using 2-octene (155 µL, 111 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (67 mg, 0.39 mmol, 39%).

Analytical data as above.
Benzyl nonanoate (28) (from 1-octene 17)

Using 1-octene (160 µL, 113 mg, 1.00 mmol) as the alkene component and degassed BnOH (250 µL; stored under N\textsubscript{2}) as the alcohol component, general procedure C was employed using 1 mol\% [Pd] at 50 °C in DCE instead of DCM. Purification by flash column chromatography on SiO\textsubscript{2} (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (229 mg, 0.91 mmol, 91%). The analytical data is in agreement with the reported literature.\textsuperscript{35}

R\textsubscript{f}: 0.40 (mobile phase 95:5 CyH:EtOAc, KMnO\textsubscript{4} stain)

**Melting point**: Ambient temperature.

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta (\text{ppm})\): 7.41 – 7.29 (m, 5H, ArH), 5.12 (s, 2H, CH\textsubscript{2}Ph), 2.35 (t, \(J = 7.6\) Hz, 2H, PhCH\textsubscript{2}OCOCH\textsubscript{2}-R), 1.64 (quin, \(J = 7.6\) Hz, 2H, ArCH\textsubscript{2}OCOCH\textsubscript{2}CH\textsubscript{2}-R), 1.36 – 1.19 (m, 10H, remaining CH\textsubscript{2}), 0.88 (t, \(J = 6.9\) Hz, 3H, terminal CH\textsubscript{3}).

\textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}) \(\delta (\text{ppm})\): 173.7 (C=O), 136.2 (Ar\textsuperscript{C}), 128.6 (Ar\textsuperscript{C}), 128.2 (Ar\textsuperscript{C}), 128.2 (Ar\textsuperscript{C}), 66.1 (R-CH\textsubscript{2}Ph), 34.4 (CH\textsubscript{2}), 31.8 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}), 29.1 (CH\textsubscript{2}), 25.0 (CH\textsubscript{2}), 22.7 (CH\textsubscript{2}), 14.1 (terminal CH\textsubscript{3}).

**GC-MS**: \(t_R = 9.16\) min, m/z = 266 (60, [MNH\textsubscript{4}⁺]), 249 (17, [MH⁺]), 91 (100, [MH⁺]-[BnO⁻]).
Benzyl nonanoate (28) (from (E)-2-octene 18)

Using 2-octene (155 µL, 111 mg, 1.00 mmol) as the alkene component and degassed BnOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 1 mol% [Pd] at 50 °C in DCE instead of DCM. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (225 mg, 0.89 mmol, 89%).

Analytical data as above.
Dimethyl nonadecanedioate (29)

Using methyl oleate (340 µL, 297 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave the compound bright yellow liquid (57 mg, 0.16 µmol, 16%).

**R₉:** 0.18 (CyH/ EtOAc 95:5)

**m.p.:** 58.5 °C (lit: 56-58°C)

**¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 3.66 (s, 6H, R-CO₂CH₃), 2.30 (t, J = 7.3 Hz, 4H, MeO₂C-CH₂-R), 1.67 – 1.56 (quin, J = 7.3 Hz, 4H, MeO₂C-CH₂CH₂-R), 1.35 – 1.20 (m, 26H, remaining CH₂).

**¹³C-NMR** (75 MHz, CDCl₃) δ (ppm): 174.4 (C=O), 51.5 (RCO₂CH₃), 34.1 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 25.0 (CH₂).

**FT-IR** (ATR) ν (cm⁻¹): 3024 (w, br), 2918 (s, sh), 2850 (m, sh), 1736 (s, br), 1463 (w, br), 1437 (m, sh), 1419 (w, sh), 1381 (w, sh), 1343 (w, sh), 1269 (w, sh), 1231 (m, sh), 1215 (m, sh), 1200 (m, br), 1174 (m, br), 1117 (w, br), 1026 (w, br).

**GC-FID:** (50-280M12): tᵣ = 10.50 min.

**GC-MS:** tᵣ = 14.22 min, m/z = 357 (100, [MH⁺]), 325 (22, [MH⁺]-[OMe]), 279 (7, [MH⁺]-[CO₂Me]).

**HR-MS** (APCI): m/z = [MH⁺] calc. for C₂₁H₄₀O₄ 357.2999, found 357.3004.
(E)-Methyl cinnamate (30)

Using ethinylbenzene (20) (80 µL, 102 mg, 0.750 mmol) as the alkyne component and dist.
MeOH (250 µL; stored under N₂) as the alcohol component, general procedure A was
employed using 0.75 mol% [Pd]. Upon addition of ethinylbenzene a highly exothermic
process set in. During workup, an unknown yellow polymeric byproduct was noted.
Purification by flash column chromatography on SiO₂ (mobile phase: 95:5 CyH:EtOAc) gave
the compound as an off-white solid (13 mg, 0.08 mmol, 11%). The analytical data matches
with the reported literature data.³⁷

\[ R_f: 0.26 \] (mobile phase 8:2 CyH:EtOAc, KMnO₄ stain)

Melting point: 34 °C.

\(^1\)H NMR (400 MHz, CDCl₃) δ (ppm): 7.70 (d, \( J = 16.0 \) Hz, 1H, ArCHCHCO₂Me), 7.55 -
7.51 (m, 2H, ArH), 7.41 – 7.37 (m, 3H, ArH), 6.45 (d, \( J = 16.0 \) Hz, 1H, ArCHCHCO₂Me),
3.81 (s, 3H, ArCHCHCO₂CH₃).

\(^1\)H NMR (101 MHz, CDCl₃) δ (ppm): 167.5 (C=O), 144.9 (ArCHCHCO₂Me), 134.4 (ipso-
ArC), 130.3 (meta-ArC), 128.9 (ortho-ArC), 128.1 (para-ArC), 117.8 (ArCHCHCO₂Me),
51.7 (ArCHCHCO₂CH₃).

\(^13\)C NMR (101 MHz, CDCl₃) δ (ppm): 162.2 g/mol

GC/MS (EI): \( t_R = 8.60 \) min, m/z = 162 (49, [M⁺]), 131 (100, [M⁺]-[OMe⁺]), 103 (61, [M⁺]-
[OMe⁺]-[CO]).
3 Calibration data for quantitative instrumental analysis

3.1 Calibration data for quantitative GC analysis

Calibration for Styrene and methyl 2-phenylpropanoate by GC-FID, Internal standard: \(n\)-Pentadecane (15.4.15)

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<th>(A(\text{Styrene}))</th>
<th>(m(2\text{-Phenylpropanoate}) / mg)</th>
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\[ y = 0.6492x - 0.0166 \]

\(R^2 = 0.9988\)
3.2 Calibration data for quantitative NMR analysis

Formic acid/Maleic acid calibration by NMR

Slope : $1.010 \pm 0.0065$

R square: 0.9999

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