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

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Contents

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_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_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_{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: ^{1}H- and ^{13}C-NMR spectra were recorded on *Bruker Avance 400* or *300 MHz* machines (400 or 300 MHz for ^{1}H experiments; 101 or 75 MHz for ^{13}C experiments) in commercially available deuterated solvents without TMS. ^{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.[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, ^{13}C-NMR measurements were accompanied by a ^{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 $\tilde{\nu}$ (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.

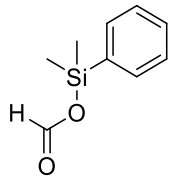
Mass spectrometry: For GC/MS analysis of crude mixtures, an Agilent 6890 N Network GC with an Agilent 5975 Inert Mass Selective Detector was employed. Carrier gas: Dry Hydrogen. The stationary phase was a column type BPX5 (30 m X 0.25 mm X 0.25 µm [film thickness]) from SGE. Program 50-300M: From 50 °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 CO_2 hydrosilylation

Dimethylphenylsilyl formate **9** (quantitative ^{1}H-NMR analysis by conversion into formic acid)[2]



180.3 g/mol

9

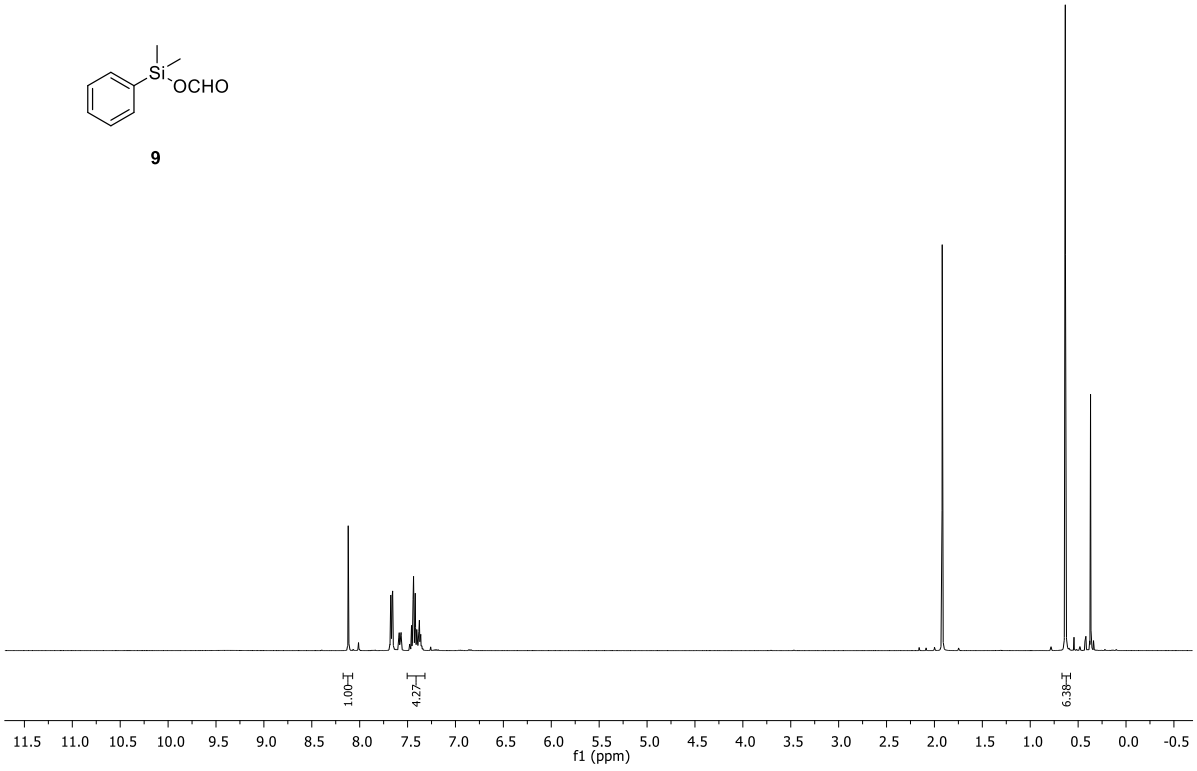
A flame-dried 25 mL Schlenk tube with a stirring bar was charged with $Rh_2(OAc)_4$ (3.3 mg, 7.0 µmol, 0.25 mol%) and K_2CO_3 (2.1 mg, 14 µmol, 0.5 mol%) and then fitted with a rubber septum. The atmosphere in the reaction vessel was exchanged to CO_2 by triple evacuation and refilling with CO_2 (balloon 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 N_2 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 ^{1}H-NMR [400 MHz, $CDCl_3$, δ (ppm): 8.12 (s, 1H, C<u>H</u>O), 7.50 (m, 5H, Ar<u>H</u>), 0.63 (s, 6H, Si(C<u>H</u>$_3$)$_2$] matched with the reported literature data[3] but contained traces of acetonitrile and an unknown impurity, indicating decomposition that occurred while preparing the NMR sample.

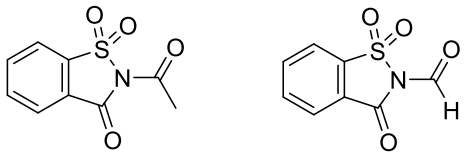
For quantitative ^{1}H-NMR analysis, the silyl formate was treated with 2 mL of dist. H_2O for hydrolysis for 1 h at RT under stirring. As an internal standard, maleic acid (26 mg) was added. An aliquot of this mixture was taken up in D_2O.

For quantitative NMR data evaluation, all spectra were manually phase-corrected and the baseline automatically set. Chemical shifts of components used for evaluation in D_2O (ppm):

Formic acid 8.16 (1H, s, $\underline{H}CO_2H$); Maleic acid 6.34 (2H, s, $HO_2C\text{-}C\underline{H}{=}C\underline{H}\text{-}CO_2H$). Regression analysis of data points from calibration gave a response factor $R_{Formic\ acid}$ =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**[4]



225.2 g/mol 211.2 g/mol

N-acetylsaccharin **1**

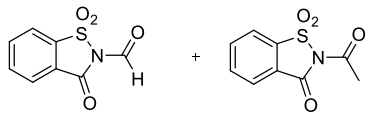
A two-necked, flame-dried RBF equipped with a stirring bar and reflux condenser was charged with acetic anhydride (15.1 mL, 160 mmol, 4 Eqv.) and formic acid (7.80 mL, 208 mmol, 5.2 Eqv.) and heated to reflux for 5 h under stirring. Then, saccharin (7.33 g, 40.0 mmol, 1 Eqv.) was added to the solution and stirred at 60 °C overnight. Then, the reaction vessel was cooled to RT, diluted with dist. H_2O, the precipitate washed with dist. H_2O 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*f**: Decomposition on normal-phase SiO_2.

^{1}H-NMR (300 MHz, CD_3CN): δ (ppm): 9.15 (s, 1H, HetArC<u>H</u>O), 8.31 – 7.72 (m, 4H, HetAr<u>H</u>); minor signals from *N*-acetylsaccharin: 8.31 – 7.72 (m, 4H, HetAr<u>H</u>),), 2.62 (s, 3H, N-COC<u>H$_3$</u>).

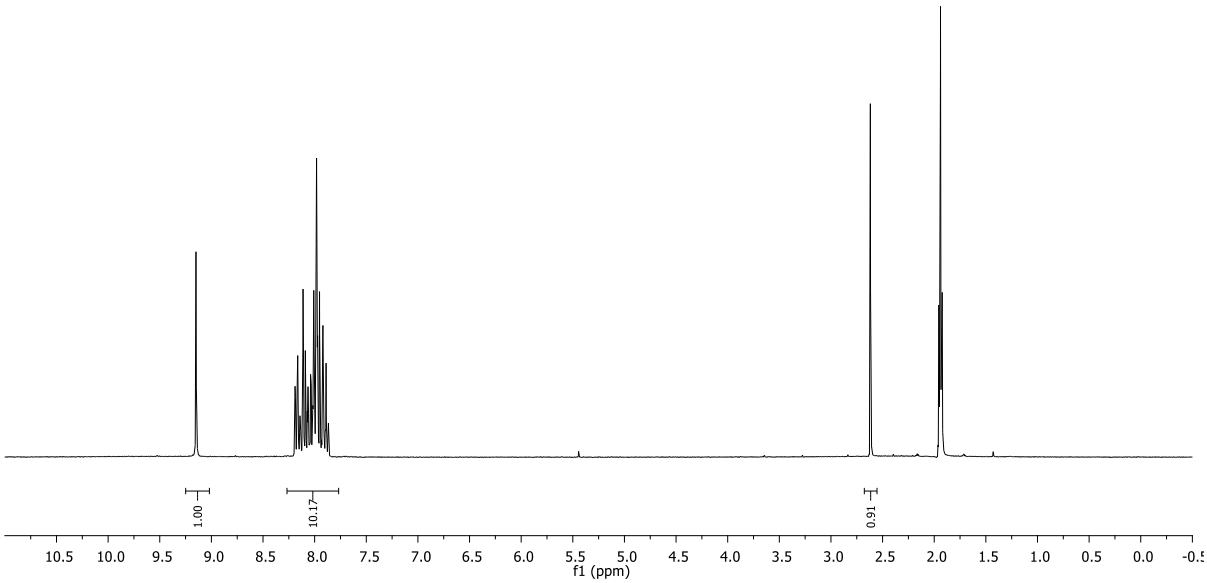
^{13}C-NMR (75 MHz, CD_3CN) δ (ppm): 157.6 , 157.4, 137.8, 137.2, 136.7, 135.3, 135.0, 134.1, 126.0, 125.8, 124.6, 121.2, 120.7, 120.4, 25.1.

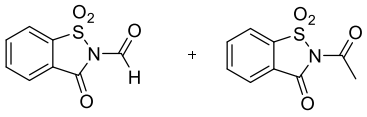
GC/MS (ESI**)**: t_R = 1.63 min (NFS), m/z = 212 (32, [MH^+]), 184 (100, [MH^+]-[CO]); t_R = 1.82 min (NAS), m/z = 226 (100, [MH^+]).



1

N-acetylsaccharin

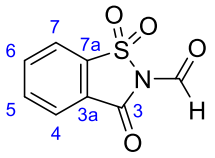




1

N-acetylsaccharin

N-Formylsaccharin **1** (from Formic acid)



211.2 g/mol

1

Using a modified procedure by Goto,[6] a two-necked, flame-dried 500 mL RBF with a N_2 inlet, rubber septum and stirring bar was charged with HCO_2H (98 mL, 2.6 mol, 24 Eqv.) and Ac_2O (113 mL, 1.2 mol, 12 Eqv.) and the resulting solution was stirred vigourosly for 1 h at RT (slightly exothermic). Meanwhile, a flame-dried assembly of a three-necked 500 mL Schlenk RBF with N_2 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 H_2O (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.[4]

$\boldsymbol{R_f}$: Decomposition on normal-phase SiO_2.

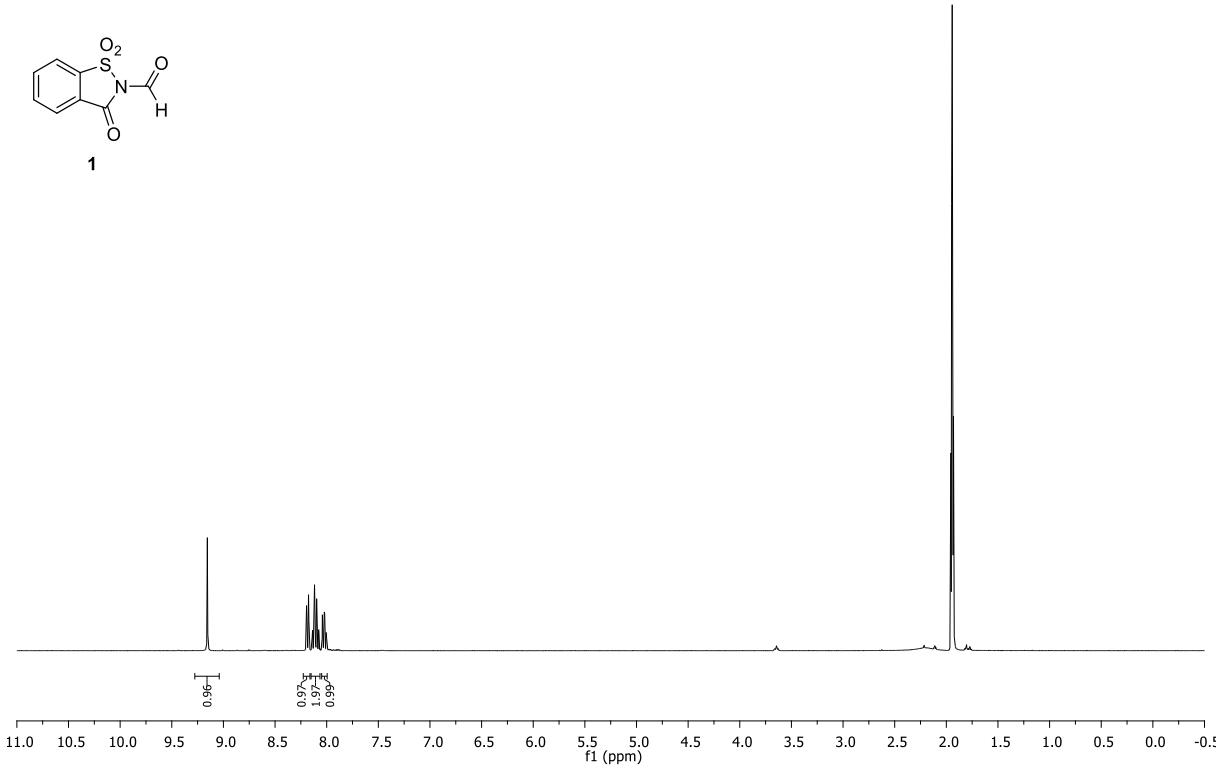
Melting point: 227 °C (a change in crystallinity occurs between 120-150 °C, possibly due to decarbonylation).

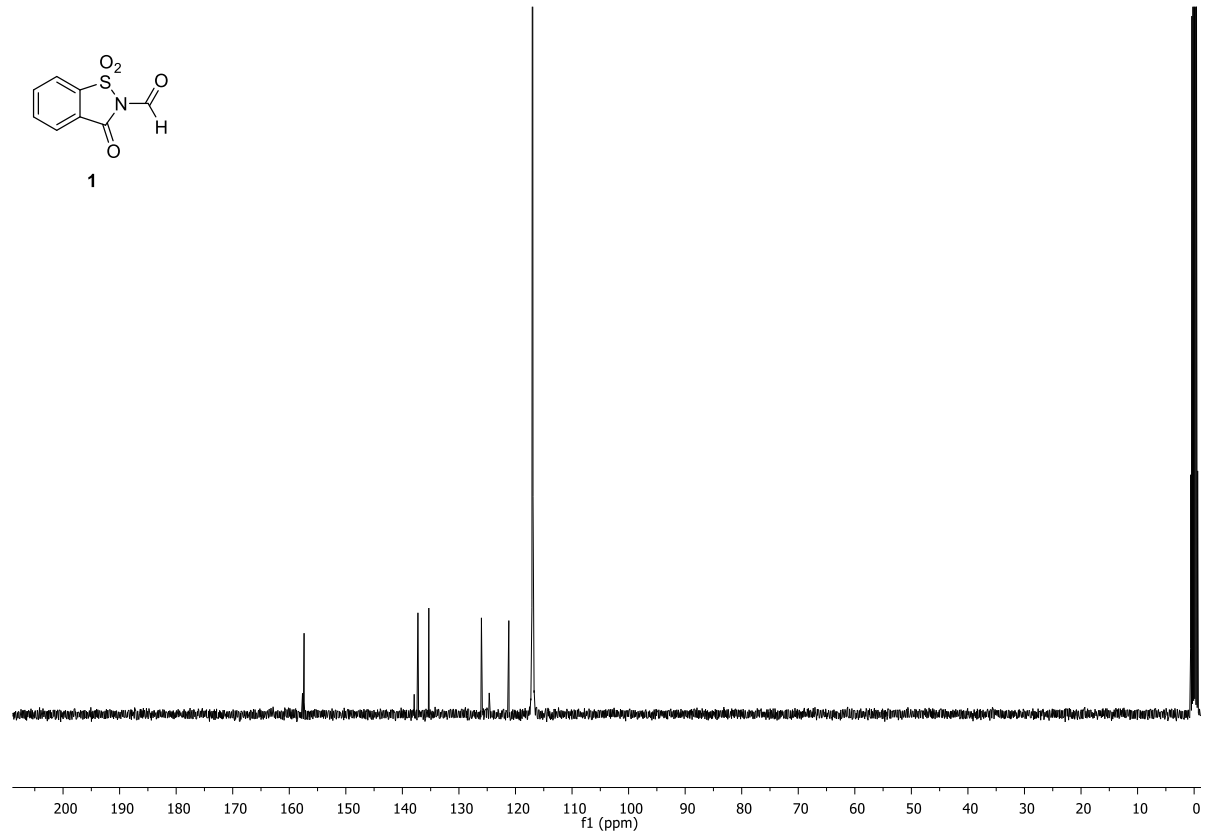
FT-IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 1756 (s, sh), 1716 (s, sh), 1593 (m, sh), 1460 (m, sh), 1345 (s, sh), 1289 (s, sh), 1249 (s), 1175 (s, sh), 1159 (s, sh), 1104 (s, sh), 746 (s, sh), 672 (s, sh), 574 (s, sh).

^{1}H-NMR (400 MHz, CD_3CN) δ (ppm): 9.16 (s, 1H, N-C<u>H</u>O), 8.19 (d, J = 7.7 Hz, 1H, ArH), 8.14 – 8.07 (m, 2H, ArH), 8.04 – 8.00 (m, 1H, ArH).

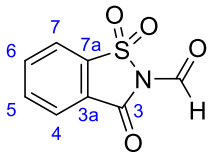
^{13}C-NMR (101 MHz, CD_3CN) δ (ppm): 157.7 (<u>C</u>^{3}), 157.4 (N-<u>C</u>HO), 137.9 (<u>C</u>^{3a}), 137.3 (<u>C</u>^{6}), 135.3 (<u>C</u>^{5}), 126.0 (<u>C</u>^{7}), 124.6 (<u>C</u>^{7a}), 121.2 (<u>C</u>^{4}).

HR-MS (ESI)**:** [MH^+] m/z = calc. for $C_8H_6NO_4S$ 212.0012; found 212.0010.


O2
S
N
O
H
O
1
0.96
0.97
1.97
0.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O2
S
N
O
H
O
1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N-Formylsaccharin **1** (from CO_2)



211.2 g/mol

1

A flame-dried 25 mL Schlenk tube with a stirring bar under N_2 atmosphere was charged with $Rh_2(OAc)_4$ (3.3 mg, 7.5 µmol, 0.25 mol%) and K_2CO_3 (2.1 mg, 15 µmol, 0.5 mol%) and then fitted with a rubber septum. The atmosphere in the reaction vessel was exchanged towards CO_2 by triple evacuation and refilling with CO_2 (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 N_2 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, Ac_2O (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 N_2, 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 Alkoxycarbonylation reactions

General procedure for alkoxycarbonylation 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*-formylsaccharin (**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).

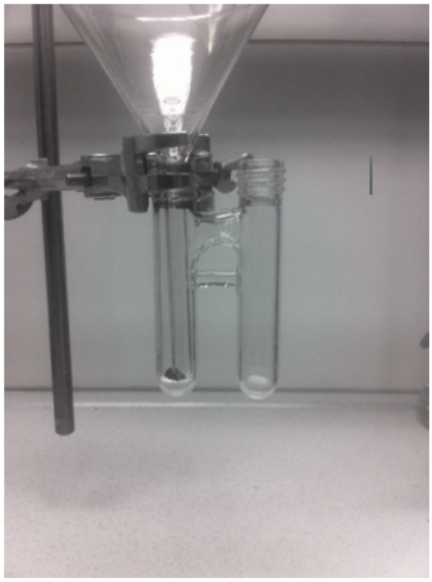
Molar ratios	$Pd(dba)_2$	dtbpx	BNPA
1:4:15 (1 mmol starting material)	**0.5** mol%, 5 µmol, 2.9 mg	2.0 mol%, 20 µmol, 7.9 mg	7.5 mol%, 75 µmol, 26.1 mg
1:4:15 (1 mmol starting material)	**0.75** mol%, 7.5 µmol, 4.4 mg	3.0 mol%, 30 µmol, 11.9 mg	11.25 mol%, 11.3 µmol, 39.2 mg
1:4:15 (0.75 mmol starting material)	**0.75** mol%, 5.6 µmol, 3.3 mg	3.0 mol%, 22.5 µmol, 8.9 mg	11.25 mol%, 8.5 µmol, 29.4 mg
1:4:15 (1 mmol starting material)	**1.0** mol%, 10 µmol, 5.8 mg	4. mol%, 40 µmol, 15.8 mg.	15.0 mol%, 150 µmol, 52.2 mg

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].

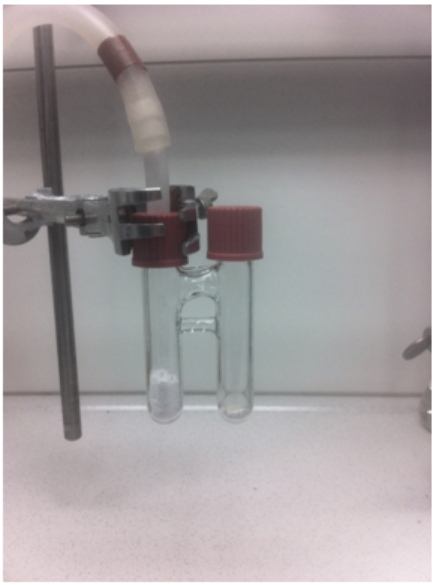
To stop the reaction, the screw caps were loosened in a well-ventilated enviroment (CO evolution may occur!). Excess $NaHCO_3$ in chamber A can be removed by addition of 1 M HCl, further addition of HCl precipitates saccharin which can be recovered (340 mg, 1.83 mmol, 86%) by filtration, washing the filter cake with copious amounts of dist. H_2O to remove NaCl and DMF, and finally drying the solid *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.

a)

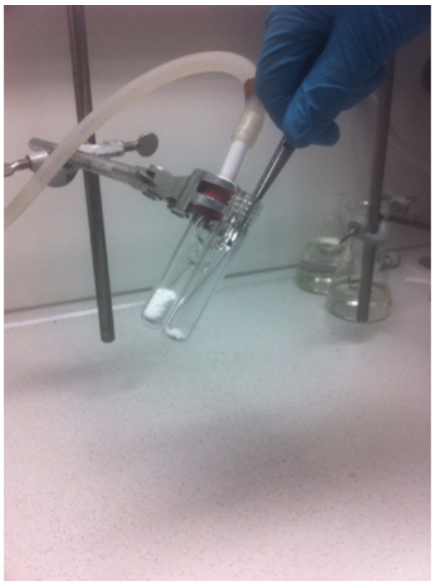


b)

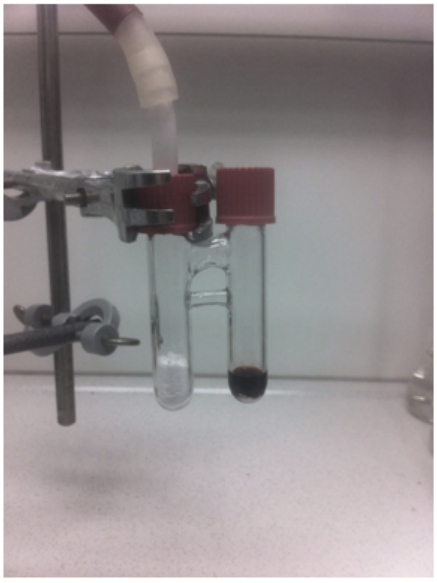
c)



d)



e)



f)

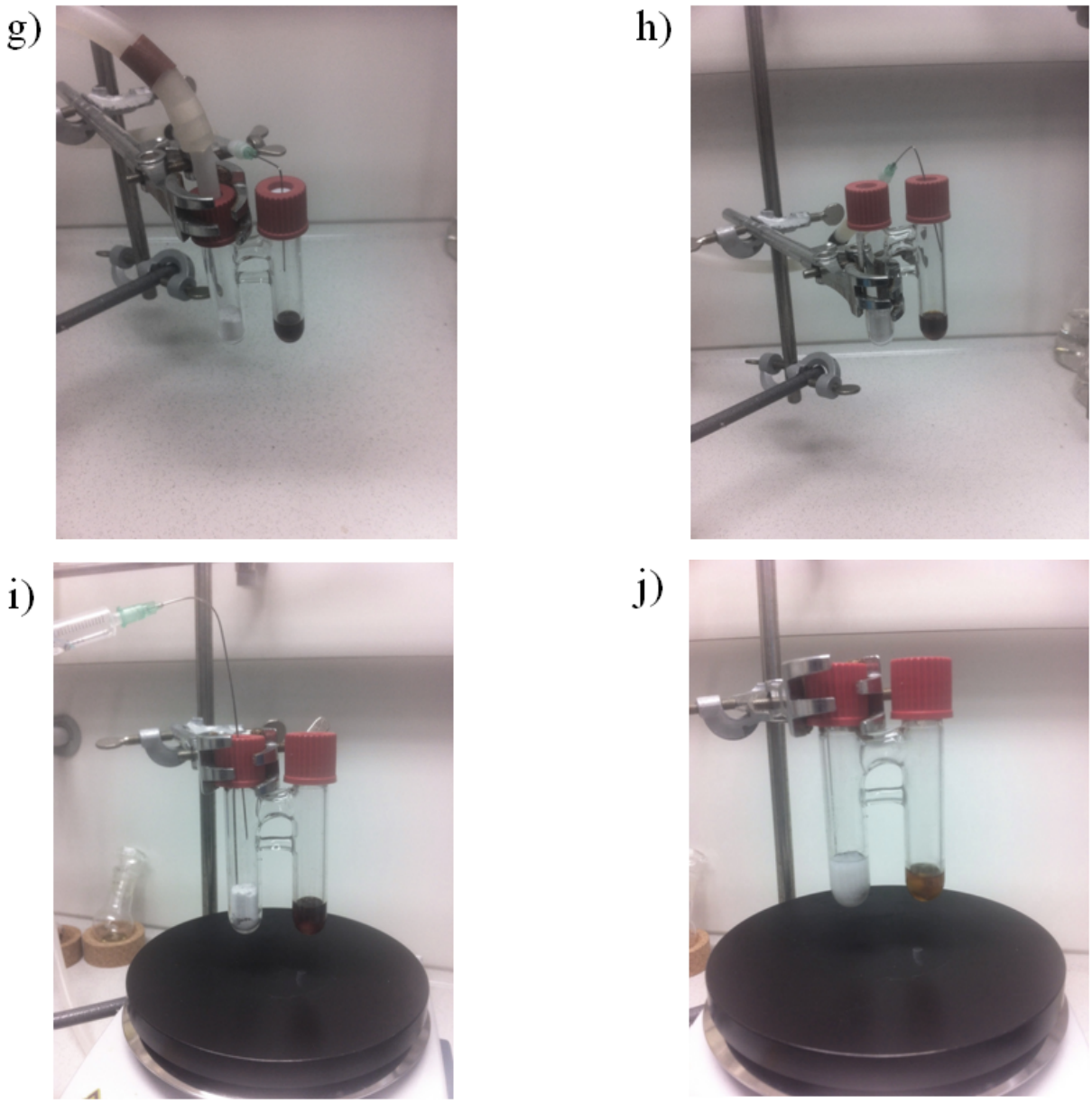


Figure S1: Setup of an alkoxycarbonylation reaction in a two-chambered vessel. See "General Procedure A" for steps a) – j).

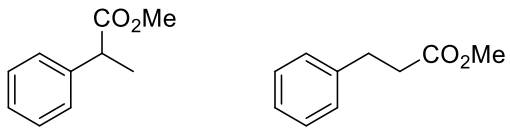
General procedure **B** for Brønsted acid and Pd-precursor screening

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, *p*TsOH, $PhCO_2H$) 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(styrene) = 2.99 min; t_R(*n*-pentadecane) = 6.00 min; t_R(methyl 2-phenylpropanoate **5aa**-b) = 4.99 min; t_R(methyl 3-phenylpropanoate **5aa**-l) = 5.32 min.

Response factors employed for yield calculations were $R_{Styrene}$ = 0.924 and $R_{Product}$ = 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)



164.2 g/mol

5aa-b **5aa**-l

Using dist. styrene (115 µL, 104 mg, 1.00 mmol; long-term storage in the dark under N_2 at -20 °C) as the olefin component and dist. MeOH (250 µL, stored under N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. The b/l ratio of the crude product product was determined by GC-FID analysis to be 88:12. Purification by flash chromatography on SiO_2 (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]

R_f: 0.35 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

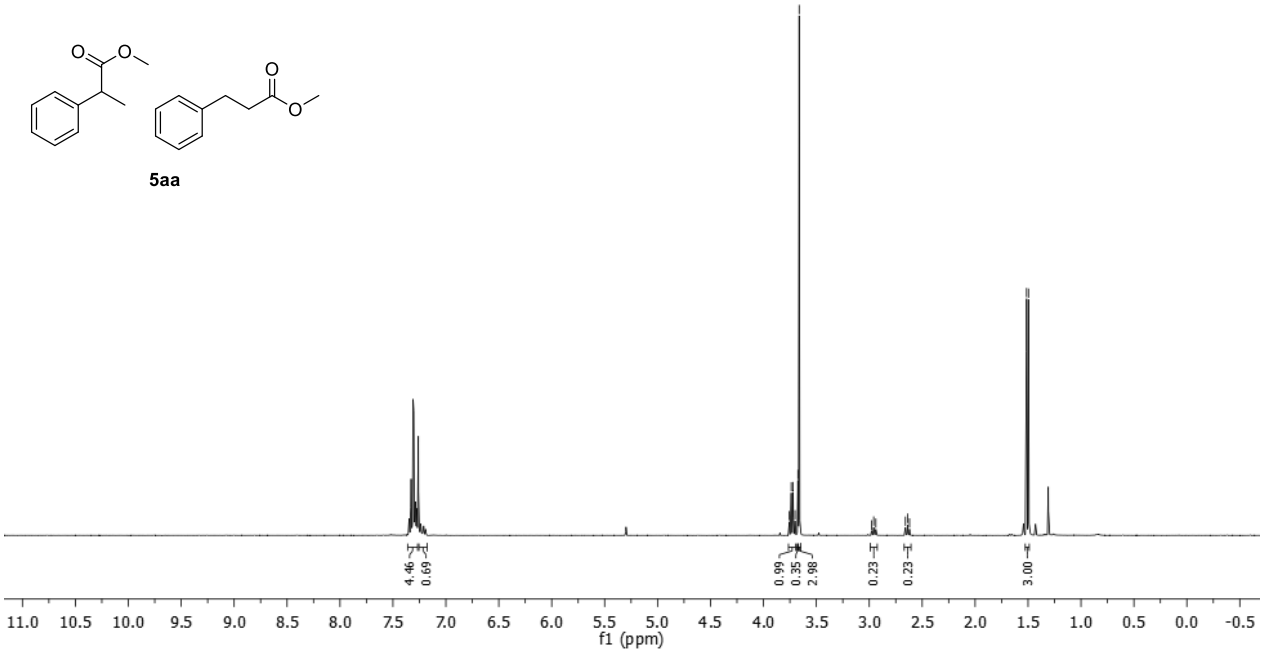
Melting point: Ambient temperature.

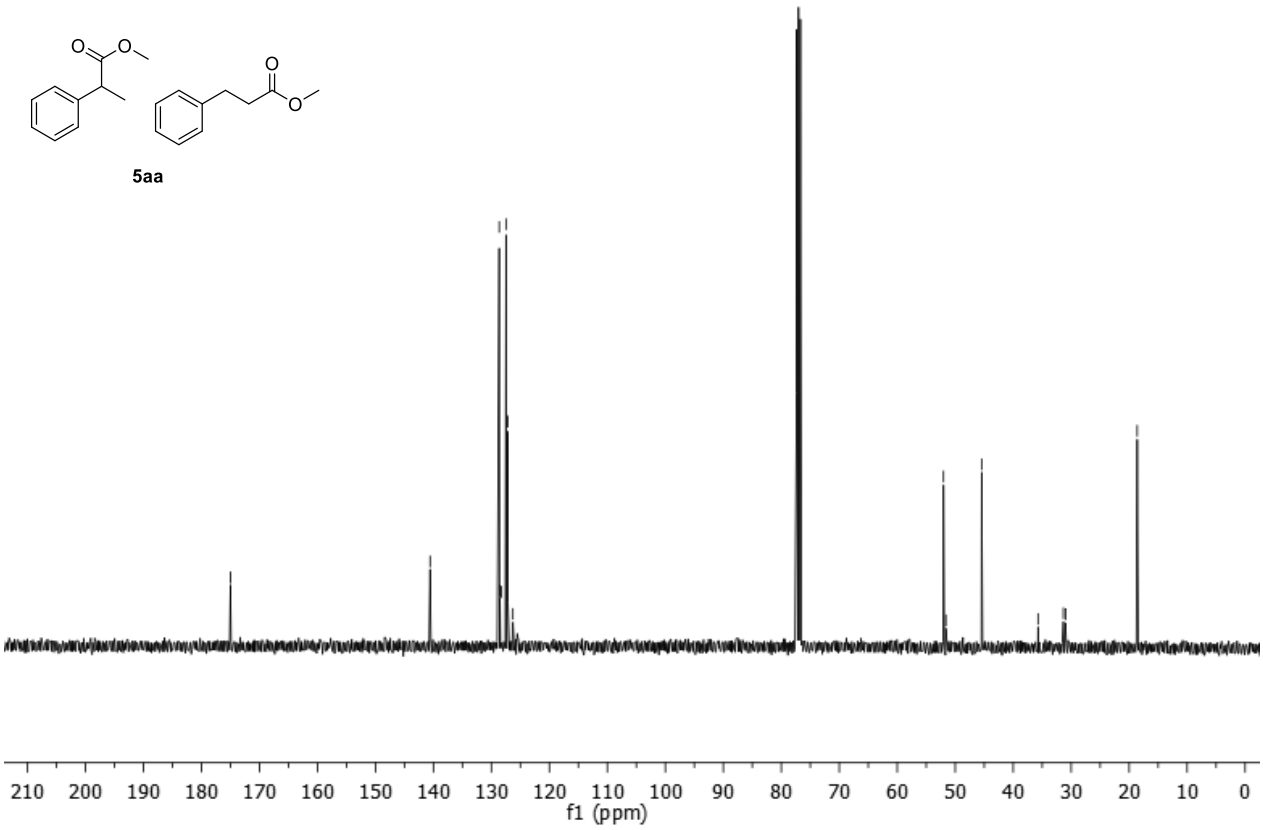
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.18 (m, 5H, ArH), 3.75 (q, J = 7.2 Hz, 1H, ArCH(CO_2Me)CH_3), 3.67 (s, 3H, R-CO_2CH_3), 1.52 (d, J = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3); minor signals for linear regioisomer 2.99 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.66 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 175.0 (R-CO_2CH_3), 140.6 (ArC), 128.7 (ArC), 127.5 (ArC), 127.2 (ArC), 52.0 (R-CO_2CH_3), 45.5 (ArCH(CO_2Me)CH_3), 18.6 (ArCH(CO_2Me)CH_3). minor signals for linear regioisomer: 128.5 (ArC), 128.3 (ArC), 126.3 (ArC), 51.6 (R-CO_2CH_3), 35.7 (Ar$CH_2CH_2CO_2$Me), 31.0 (Ar$CH_2CH_2CO_2$Me).

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 (35, [$MH^{+\bullet}$]), 133 (1, [$MH^{+\bullet}$]-[$OMe^{\bullet}$]), 104 (100, [$MH^{+\bullet}$]-[$OMe^{\bullet}$]-[CO]), t_R = 7.37 min (linear), same m/z and intensity pattern.


5aa
4.46
0.69
0.99
0.35
2.98
0.23
0.23
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Ethyl 2-phenylpropanoate (**5ab**-b) and Ethyl 3-phenylpropanoate (**5ab**-l)

178.2 g/mol

5ab-b **5ab**-l

Using styrene (115 µL, 104 mg, 1.00 mmol) as the olefin component and dist. EtOH (250 µL, stored under N_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_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 (mobile phase 9:1 CyH:EtOAc), 0.34 (mobile phase 95:5 CyH:EtOAc), $KMnO_4$ stain.

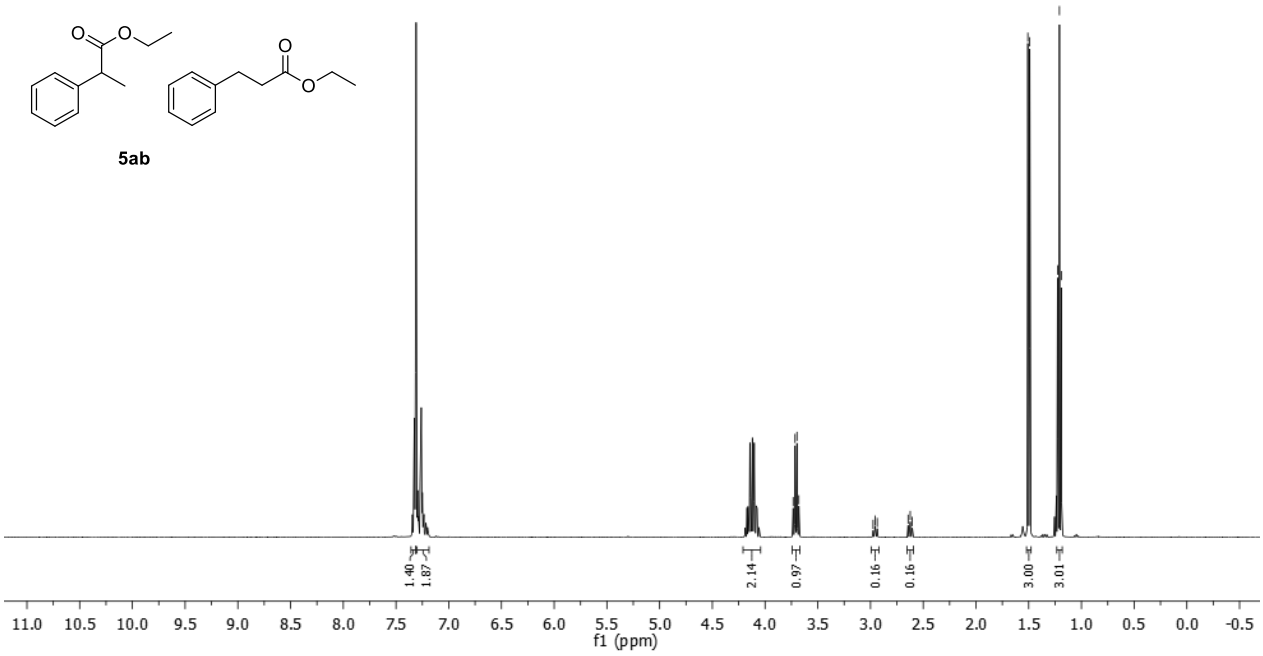
Melting point: Ambient temperature.

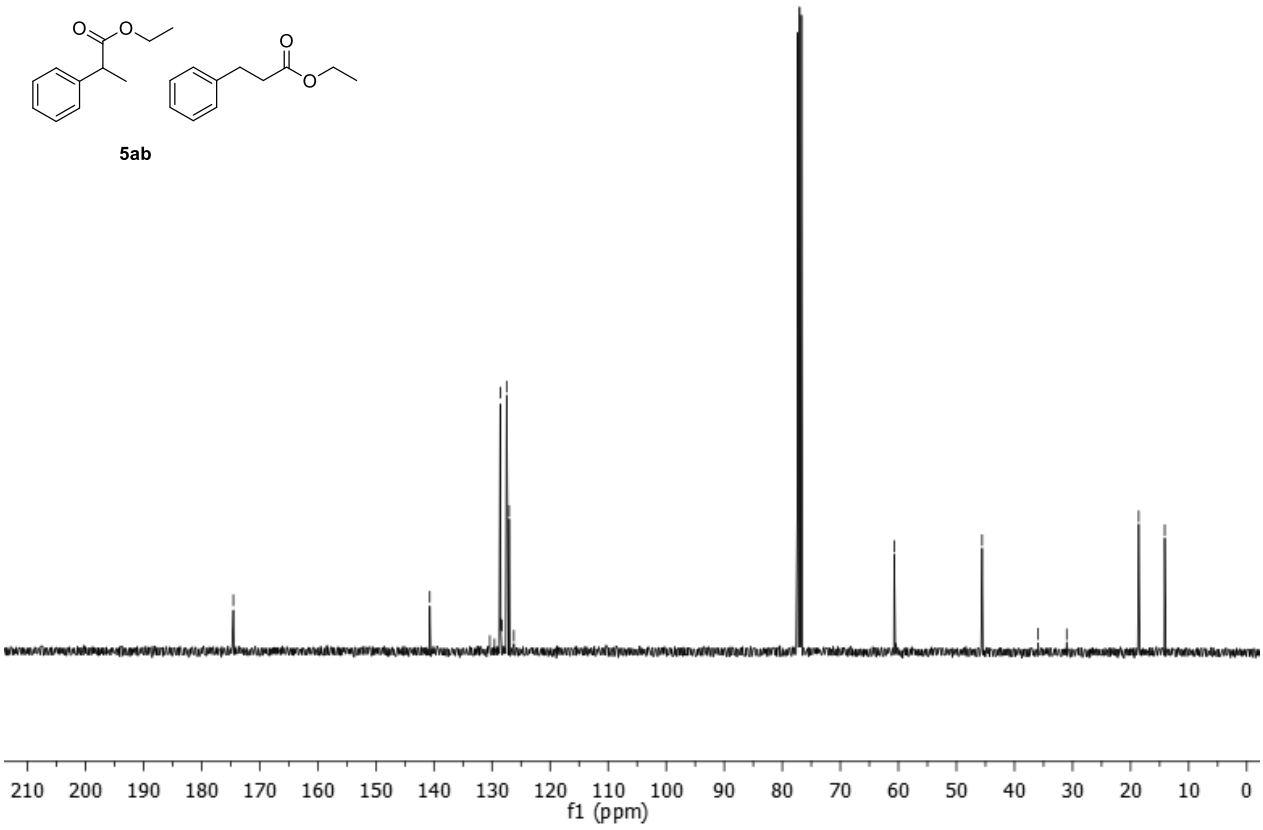
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 - 7.17 (m, 5H, ArH), 4.20 – 4.06 (m, 2H, R-$CO_2CH_2CH_3$), 3.71 (q, *J* = 7.2 Hz, 1H, ArCH(CO_2Et)Me), 1.50 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2Et)CH_3), 1.21 (t, *J* = 7.1 Hz, 3H, R-$CO_2CH_2CH_3$); minor signals from linear regioisomer: 2.96 (t, *J* = 8.0 Hz, 2H, Ar$CH_2CH_2CO_2$Et), 2.63 (t, *J* = 8.0 Hz, 2H, Ar$CH_2CH_2CO_2$Et).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 174.6 (C=O), 140.7 (ArC), 128.6 (ArC), 127.5 (ArC), 127.1 (ArC), 60.7 ($CO_2CH_2CH_3$), 45.6 (ArCH(CO_2Et)Me), 18.6 (ArCH(CO_2Et)CH_3), 14.1 ($CO_2CH_2CH_3$), minor signals from linear regioisomer were not detected due to low concentration.

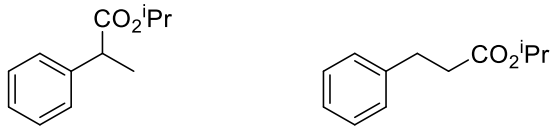
GC-FID (50-280M12): t_R = 5.16 min (branched), t_R = 5.55 min (linear).

GC/MS (EI): t_R = 7.30 min (branched), m/z = 178 (18, [$M^{+\bullet}$]), 105 (100, [$C_8H_9^+$]); t_R = 8.22 min (linear), m/z = 178 (18, [$M^{+\bullet}$]), 133 (100, [$M^{+\bullet}$]-[$OEt^\bullet$]).


5ab
1.40
1.87
2.14
0.97
0.16
0.16
3.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Isopropyl 2-phenylpropanoate (**5ac**-b) and Isopropyl 3-phenylpropanoate (**5ac**-l)



192.3 g/mol

5ac-b **5ac**-l

Using styrene (115 µL, 104.2 mg, 1 mmol) at as the olefin component and dist. ^{i}PrOH (250 µL, stored under N_2) 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 SiO_2 (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]

***R*$_f$**: 0.56 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

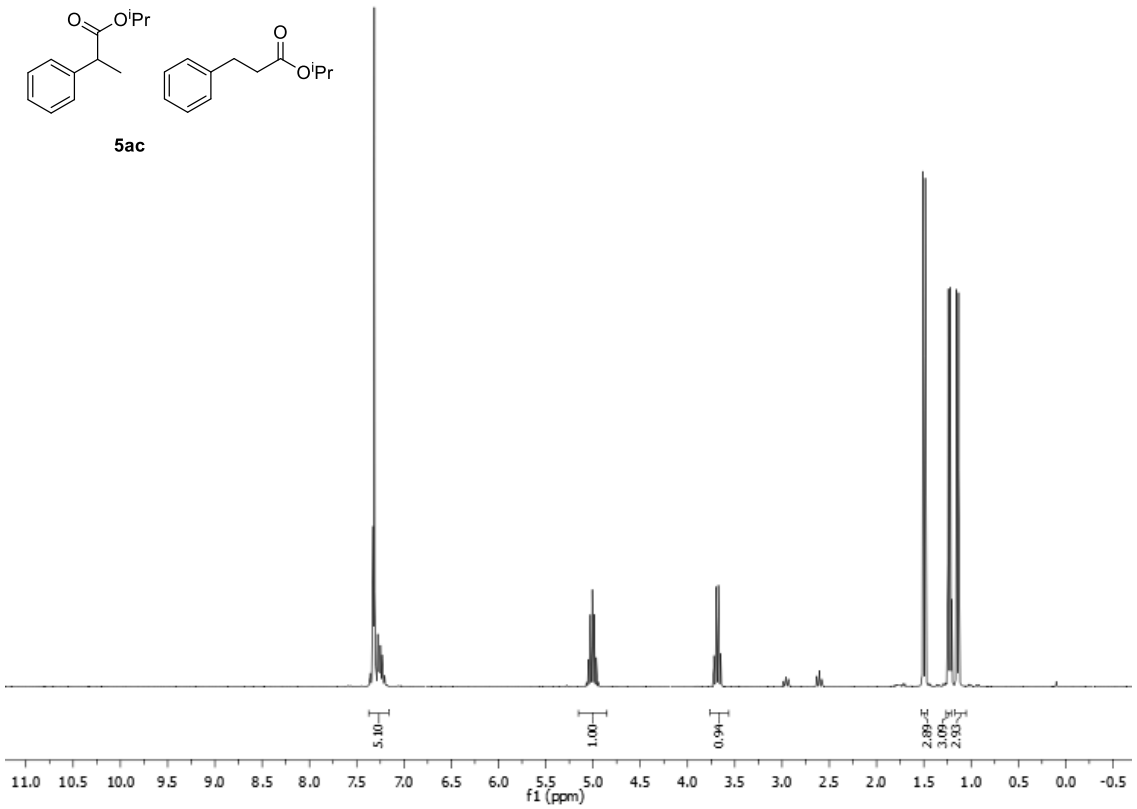
Melting point: Ambient temperature.

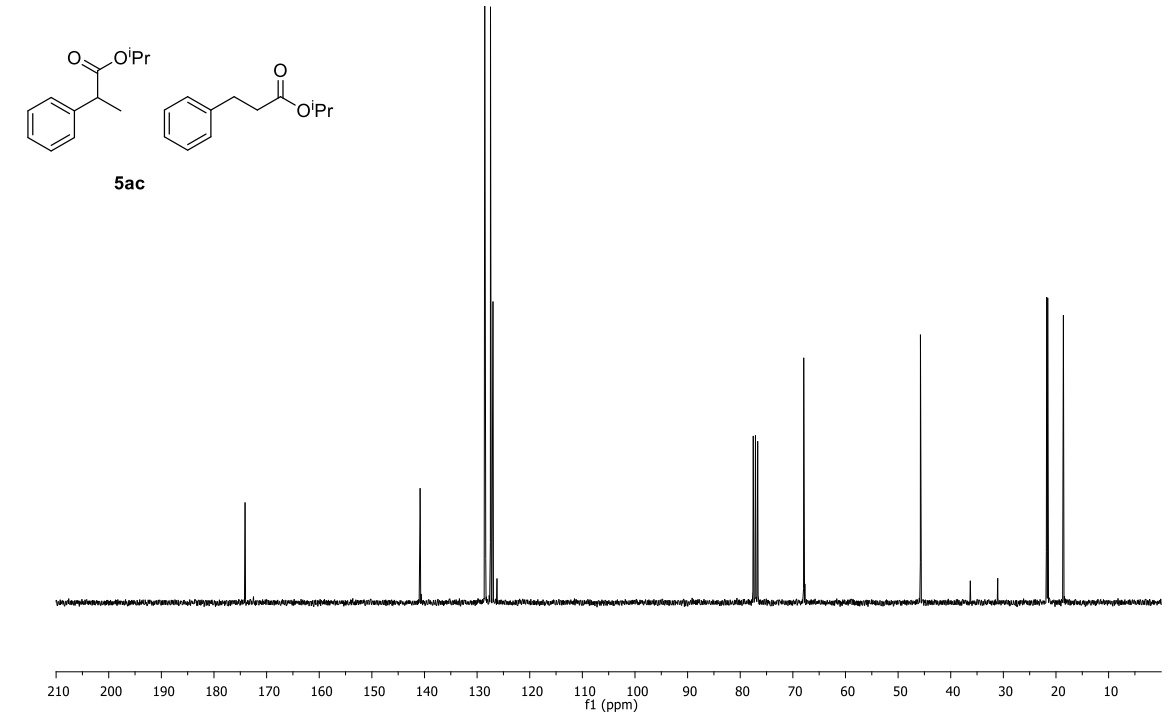
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.40 – 7.18 (m, 5H, ArH), 5.01 (hept, *J* = 6.3 Hz, 1H, R-CO_2C<u>H</u>$(Me)_2$), 3.68 (q, *J* = 7.2 Hz, 1H, ArC<u>H</u>($CO_2{}^{i}$Pr)Me), 1.50 (d, *J* = 7.2 Hz, 3H, ArCH($CO_2{}^{i}$Pr)C<u>H</u>$_3$), 1.23 (d, *J* = 6.3 Hz, 3H, R-CO_2CH(C<u>H</u>$_3)_2$ diastereotopic), 1.14 (d, *J* = 6.3 Hz, 3H, R-CO_2CH(C<u>H</u>$_3)_2$ diastereotopic); minor signals from linear regioisomer: 2.96 (t, *J* = 7.9 Hz, 2H, ArC<u>H</u>$_2$$CH_2CO_2{}^{i}$Pr), 2.61 (t, *J* = 7.9 Hz, 2H, ArCH_2C<u>H</u>$_2$$CO_2{}^{i}$Pr).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.1 (<u>C</u>=O), 140.8 (Ar<u>C</u>), 128.6 (Ar<u>C</u>), 127.5 (Ar<u>C</u>), 127.0 (Ar<u>C</u>), 67.9 (R-CO_2<u>C</u>H$(Me)_2$), 45.8 (Ar<u>C</u>H($CO_2{}^{i}$Pr)CH_3), 21.8 (R-CO_2CH(<u>C</u>H$_3)_2$, 21.6 (R-CO_2CH(<u>C</u>H$_3)_2$, 18.6 (ArCH($CO_2{}^{i}$Pr)<u>C</u>H$_3$); minor signals from linear regioisomer: 140.6 (Ar<u>C</u>), 128.5 (Ar<u>C</u>), 128.4 (Ar<u>C</u>), 126.2 (Ar<u>C</u>), 67.7 (R-CO_2<u>C</u>H$(Me)_2$), 36.3 (ArCH_2<u>C</u>H$_2$$CO_2{}^{i}$Pr), 31.1 (Ar<u>C</u>H$_2$$CH_2CO_2{}^{i}$Pr).

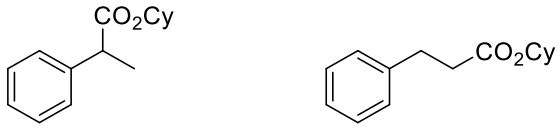
GC-FID (50-280M12): t_R = 5.40 min (branched), t_R = 5.85 min (linear).

GC/MS (EI): t_R = 7.58 min (branched), m/z = 192 (25, [$M^{+\bullet}$]), 105 (100, [$C_8H_9^+$]); t_R = 8.59 min (linear), m/z = 192 (25, [$M^{+\bullet}$]).


O
OiPr
O
OiPr
5ac
5.10
1.00
0.94
2.89
3.09
2.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O
OiPr
O
OiPr
5ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Cyclohexyl 2-phenylpropanoate (**5ae**-b) and Cyclohexyl 3-phenylpropanoate (**5ae**-l)



232.3 g/mol

5ae-b **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 SiO_2 (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]

R_f: 0.47 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

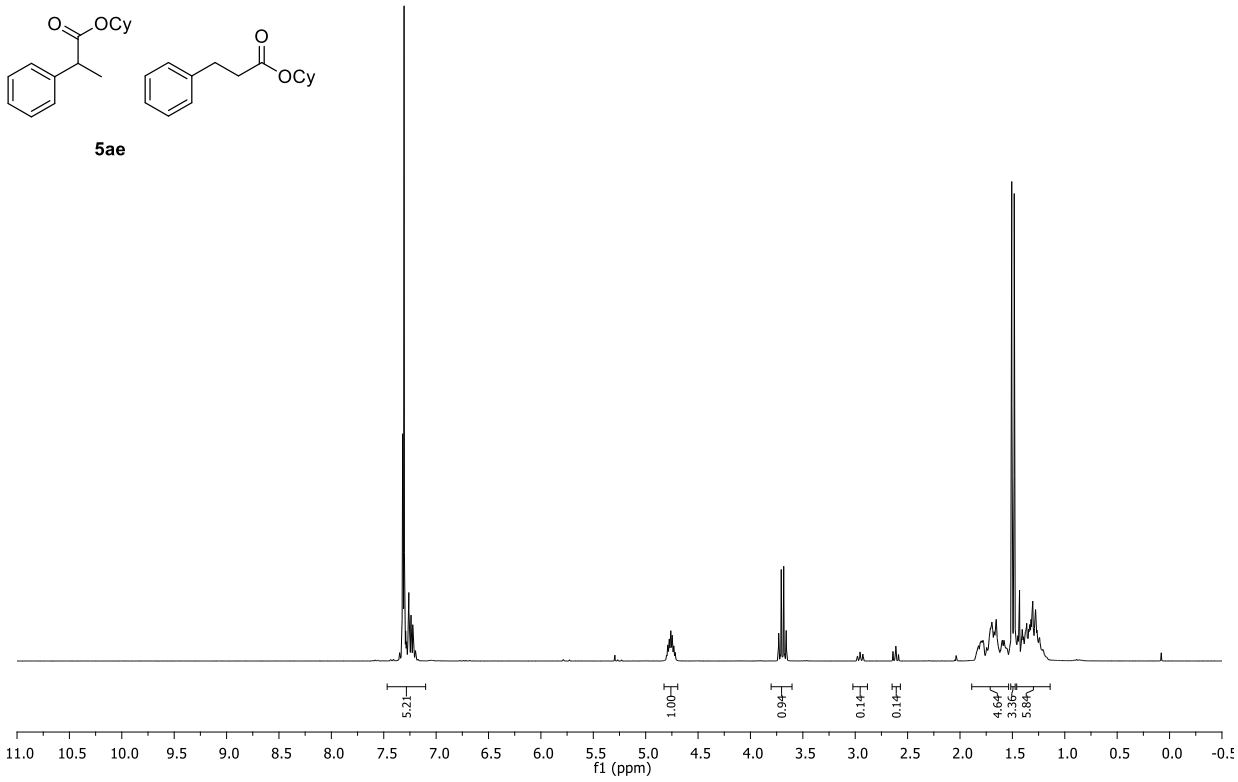
Melting point: Ambient temperature.

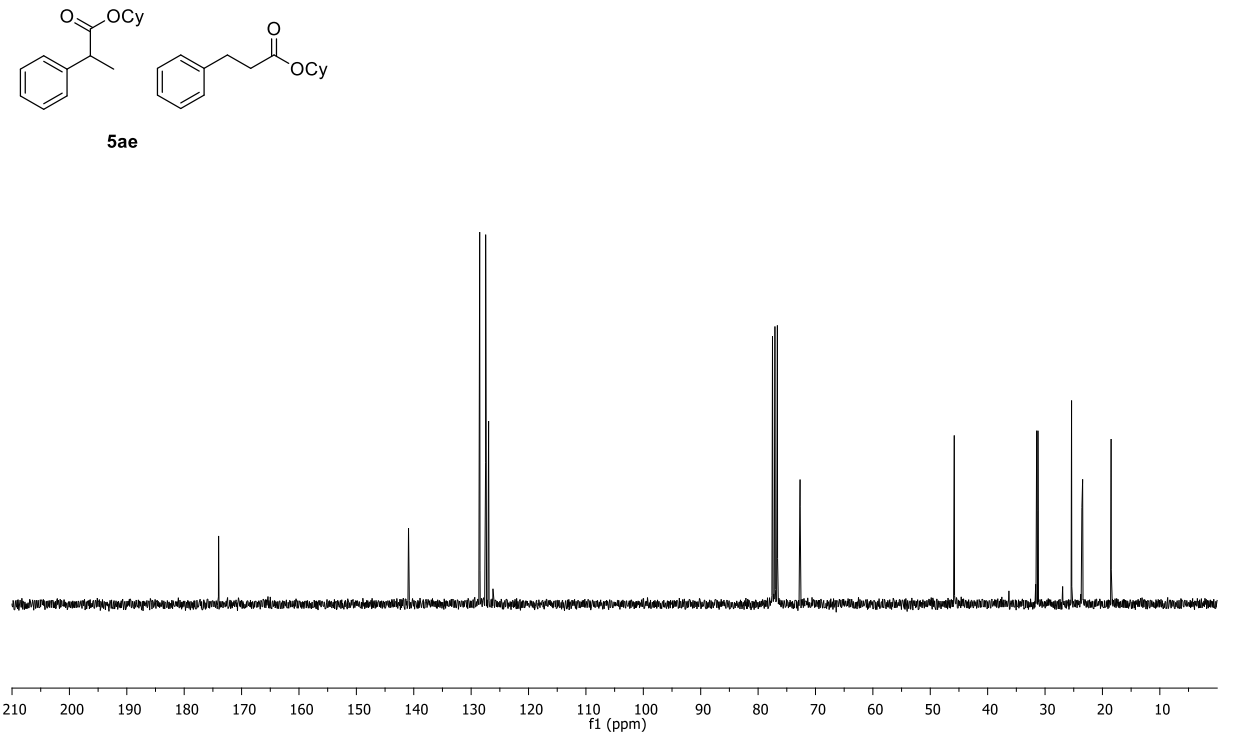
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.40 – 7.14 (m, 5H, ArH), 4.83 – 4.69 (m, 1H, Cyclohexyl-CH), 3.69 (q, J = 7.2 Hz, 1H, ArCH(CO_2Cy)CH_3), 1.88 – 1.54 (m, 5H Cyclohexyl-CH_2), 1.49 (d, J = 7.2 Hz, 3H, ArCH(CO_2Cy)CH_3), 1.43 – 1.17 (m, 5H, Cyclohexyl-CH_2); minor signals from linear regioisomer: 2.95 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Cy), 2.61 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Cy).

^{13}C-NMR (75 MHz, $CDCl_3$) 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(CO_2Cy)CH_3), 25.4 (Cyclohexyl-CH_2), 23.6 (Cyclohexyl-CH_2), 23.5 (Cyclohexyl-CH_2), 18.5 (ArCH(CO_2Cy)CH_3); minor signals from linear regioisomer: 128.5 (ArC), 128.3 ArC), 126.2 (ArC), 31.5 (Ar$CH_2CH_2CO_2$Cy), 31.2 (ArC$H_2CH_2CO_2$Cy).

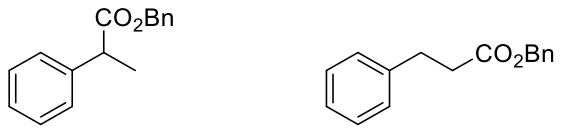
GC-FID (50-280M12): t_R = 7.38 min (branched), t_R = 7.82 min (linear).

GC/MS (EI): t_R = 11.86 min (branched), m/z = 232 (4, [$M^{+\bullet}$]); t_R = 12.79 min (linear), m/z = 232 (8, [$M^{+\bullet}$]).


O
OCy
O
OCy
5ae
5.21
1.00
0.94
0.14
0.14
4.64
3.36
5.84
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
OCy
O
OCy
5ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Benzyl 2-phenylpropanoate (**5af**-b) and Benzyl 3-phenylpropanoate (**5af**-l)



240.3 g/mol

5af-b **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]

$\boldsymbol{R_f}$: 0.42 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

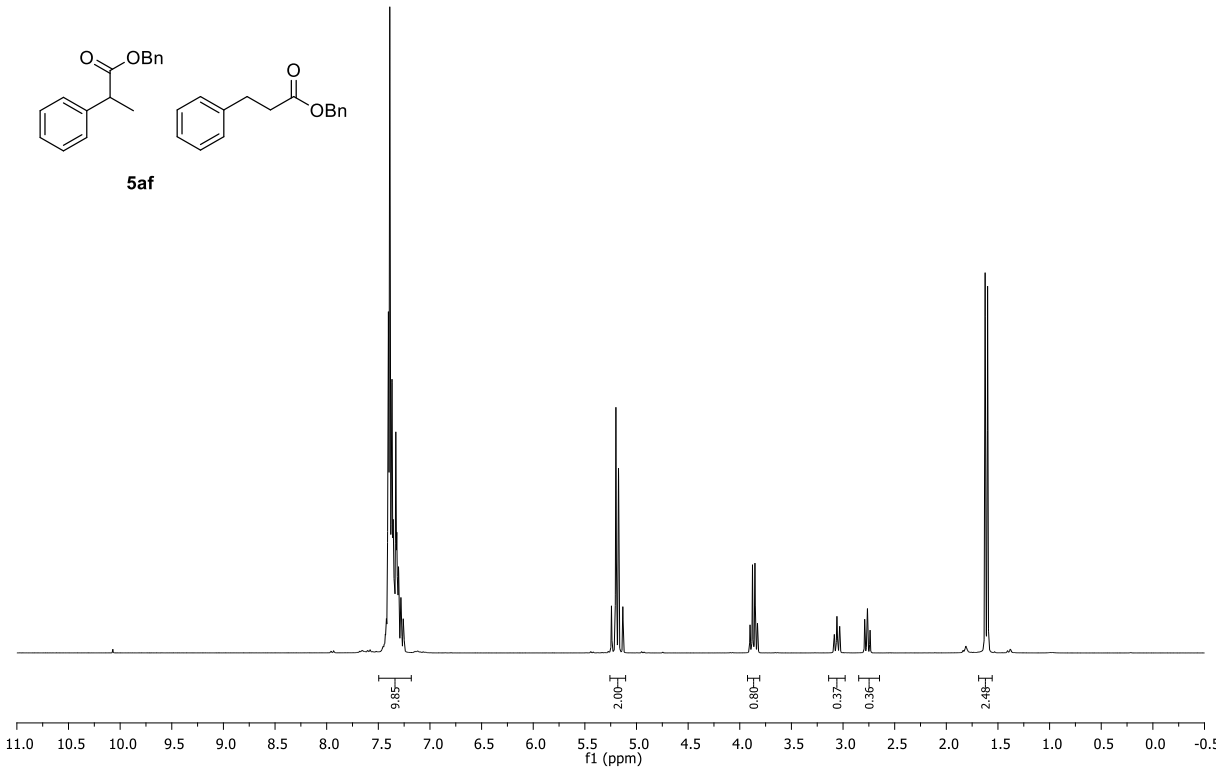
Melting point: Ambient temperature.

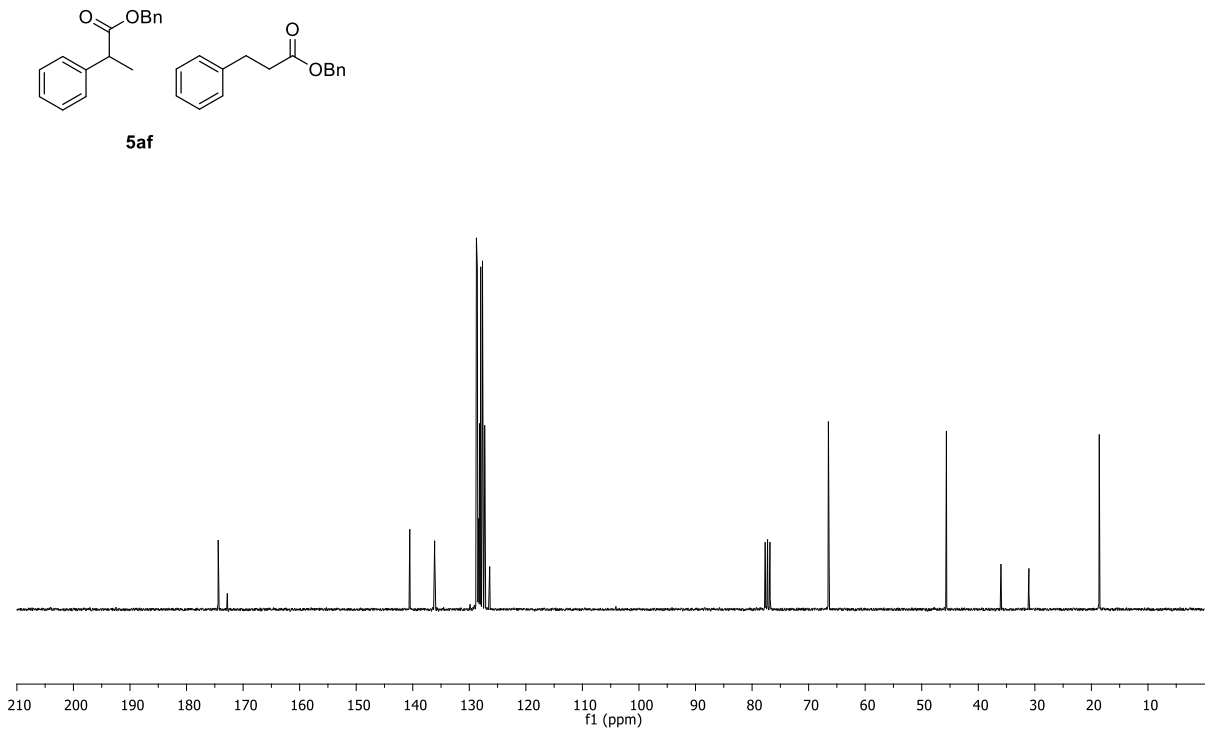
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.22 (m, 10H, ArH), 5.19 (ABq, $\Delta\delta_{AB}$ = 0.05, J = 12.9 Hz, 2H, CH_2Ph), 3.86 (q, J = 7.2 Hz, 1H, ArCH(CO_2CH_2Ph)Me), 1.61 (d, J = 7.2 Hz, 3H, ArCH(CO_2CH_2Ph)CH_3); minor signals from linear regioisomer: 3.06 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2Bn$), 2.76 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2Bn$).

^{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_2CH_2Ph)Me), 45.6 (ArCH(CO_2CH_2Ph)Me), 18.6 (ArCH(CO_2CH_2Ph)CH_3); minor signals from linear regioisomer: 172.8 (C=O), 136.1 (ArC), 66.4 (Ar$CH_2CH_2CO_2CH_2Ph$), 36.0 (Ar$CH_2CH_2CO_2Bn$), 31.1 (Ar$CH_2CH_2CO_2Bn$).

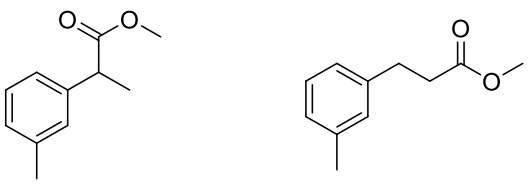
GC-FID (50-280M12): t_R = 7.94 min (branched), t_R = 8.35 min (linear).

GC/MS (EI): t_R = 13.00 min (branched), m/z = 240 (12, $[M^{+\bullet}]$), 105 (100, $[C_8H_9^+]$), 91 (75, $[C_7H_7^+]$); t_R = 13.91 min (linear), m/z = 240 (4, $[M^{+\bullet}]$), 107 (100, $[C_7H_7O^+]$), 91 (100, $[C_7H_7^+]$).


O
OBn
O
OBn
5af
9.85
2.00
0.80
0.37
0.36
2.40
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
OBn
O
OBn
5af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Methyl 2-(m-tolyl)propanoate (**5ba**-b) and Methyl 3-(m-tolyl)propanoate (**5ba**-l)



178.2 g/mol

5ba-b **5ba**-l

Using 3-methylstyrene (130 µL, 118 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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).

R_f: 0.34 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ 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), 1335 (m, br), 1238 (m, br), 1196 (s, br), 1168 (s, br), 1067 (m, br).

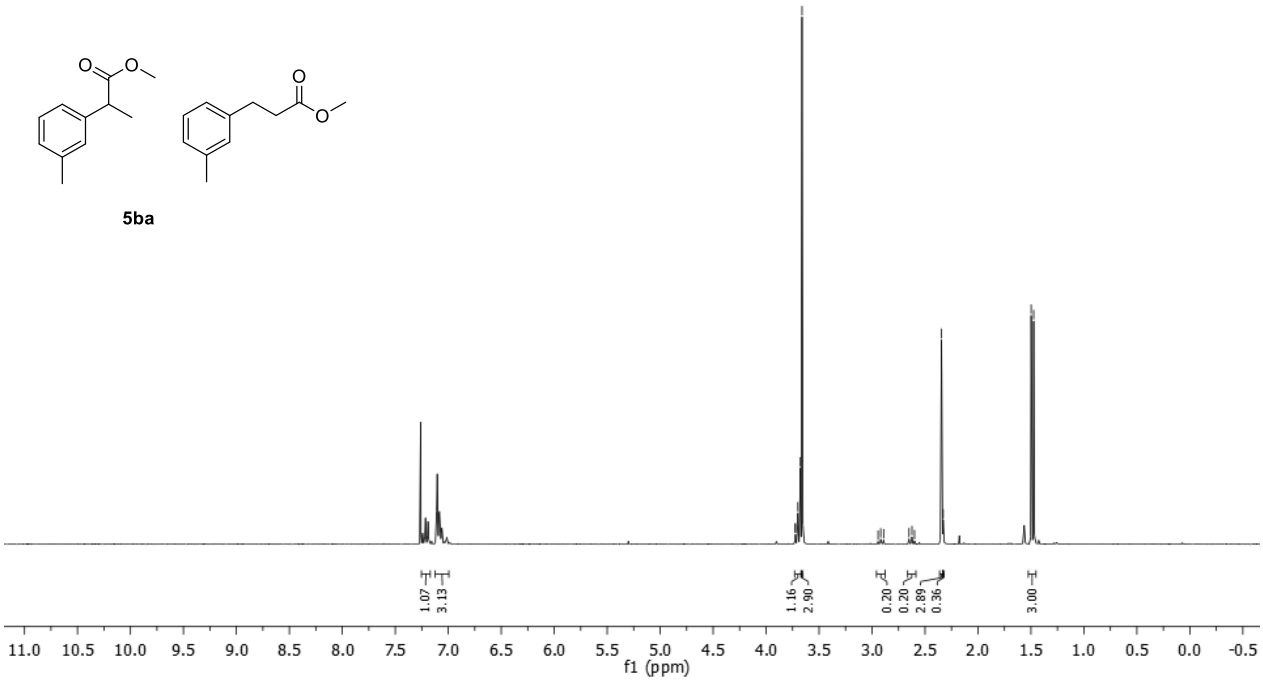
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.25 – 7.17 (m, 1H, ArH), 7.12 – 6.99 (m, 3H, ArH), 3.70 (q, *J* = 7.2 Hz, 1H, ArCH), 3.66 (s, 3H, OCH_3), 2.34 (s, 3H, $ArCH_3$), 1.49 (d, *J* = 7.2 Hz, 3H, $ArCHCH_3$); minor signals from linear regioisomer: 2.33 (s, 3H, $ArCH_3$), 2.92 (t, *J* = 7.5 Hz, 2H, $ArCH_2CH_2CO_2Me$), 2.62 (t, *J* = 7.5 Hz, 2H, $ArCH_2CH_2CO_2Me$).

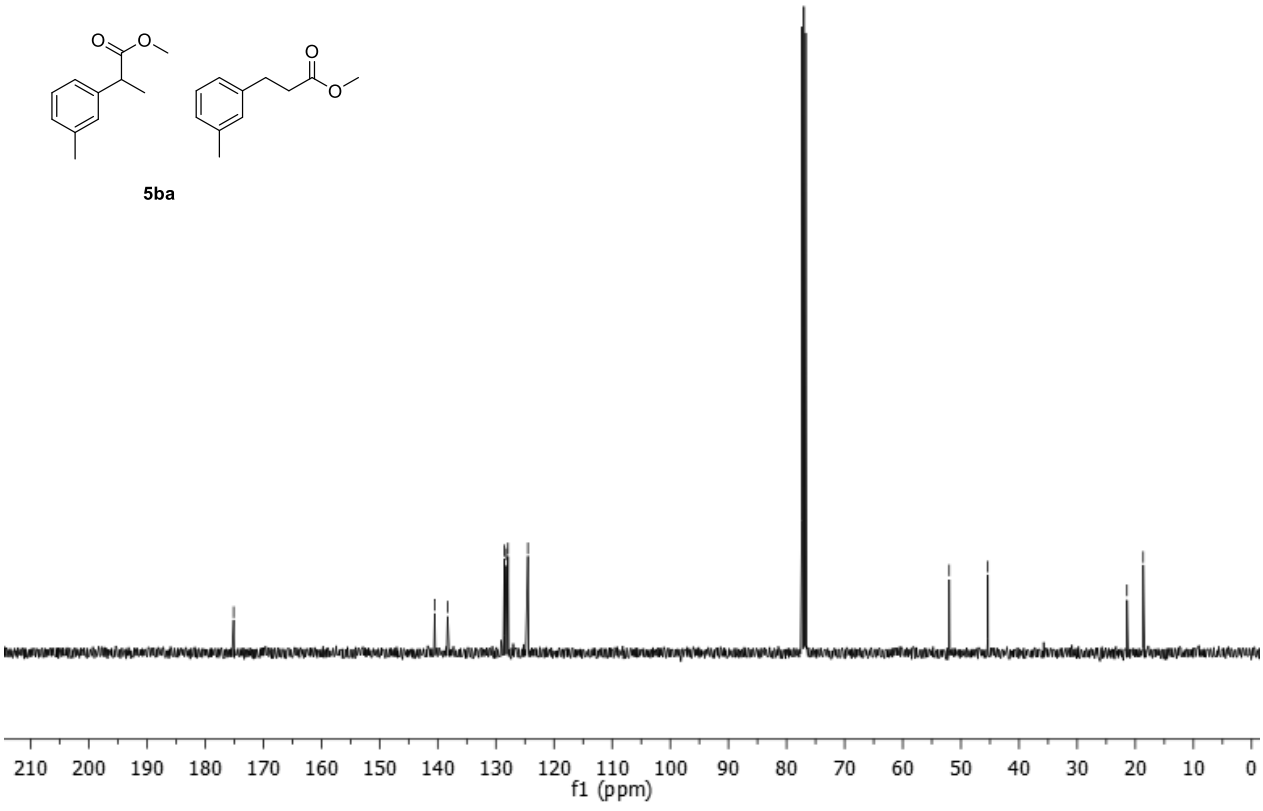
^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 175.1 (C=O), 140.5 (ArC), 138.3 (ArC), 128.5 (ArC), 128.2 (ArC), 127.9 (ArC), 124.5 (ArC), 52.0 ($ArCH(CO_2CH_3)Me$), 45.4 ($ArCH(CO_2Me)Me$), 21.4 ($ArCH_3$), 18.6 ($ArCH(CO_2Me)CH_3$). Due to low concentration no signals from the linear regioisomer were observed.

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

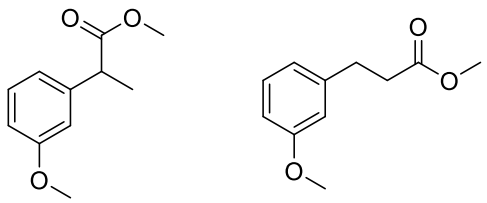
GC-MS: t_R = 6.03 min (branched), m/z = 178 (33, $[M^{+\bullet}]$), 119 (100, $[M^{+\bullet}]$-$[^{\bullet}CO_2Me]$, 91 (28, $[M^{+\bullet}]$-$[CO_2Me^{\bullet}]$-$[CH_3^{\bullet}]$); t_R = 6.77 min (linear), m/z = 178 (24, $[M^{+\bullet}]$), 147 (8, $[M^{+\bullet}]$-$[OMe^{\bullet}]$), 118 (100, $[C_9H_{10}^{+\bullet}]$), 105 (54, $[M^{+\bullet}]$-$[CH_2CO_2Me^{\bullet}]$).

HR-MS (APCI): m/z = $[MH^+]$ calc. for $C_{11}H_{14}O_2$ 179.1067, found 179.1067.


5ba
1.07
3.13
1.16
2.90
0.20
0.20
2.89
0.36
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-(3-methoxyphenyl)propanoate **(5ca**-b**)** and methyl 3-(3-methoxyphenyl)propanoate **(5ca**-l**)**



194.2 g/mol

5ca-b **5ca**-l

Using 3-vinylanisole (140 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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]

R_f: 0.21 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

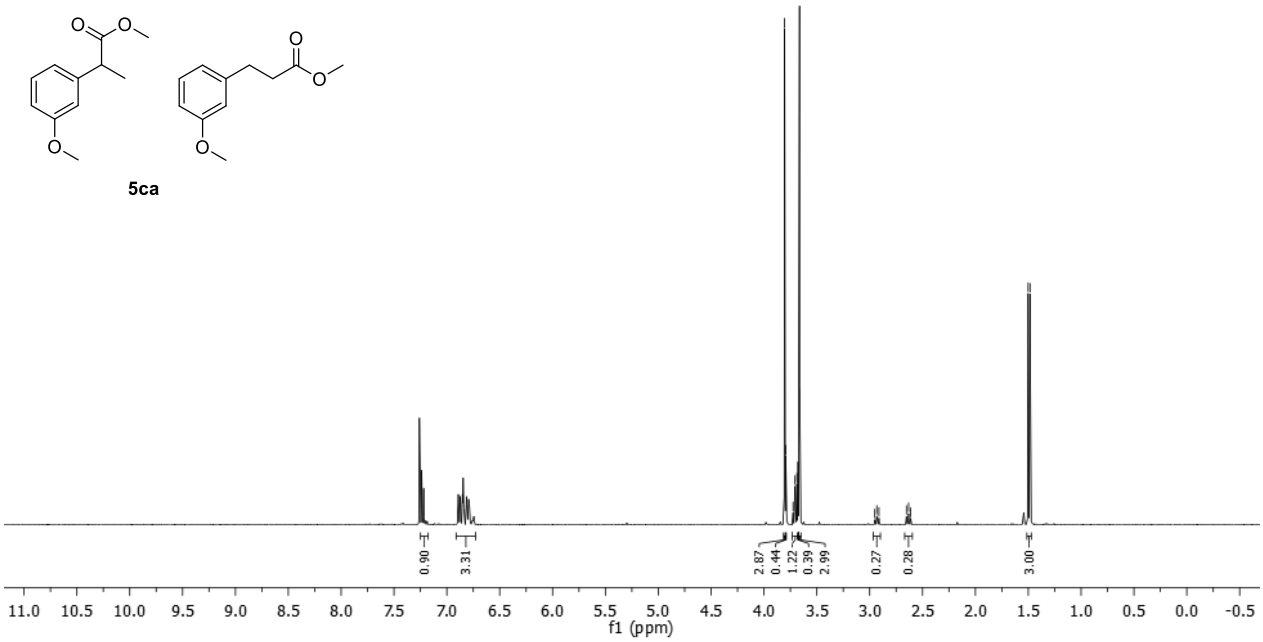
Melting point: Ambient temperature.

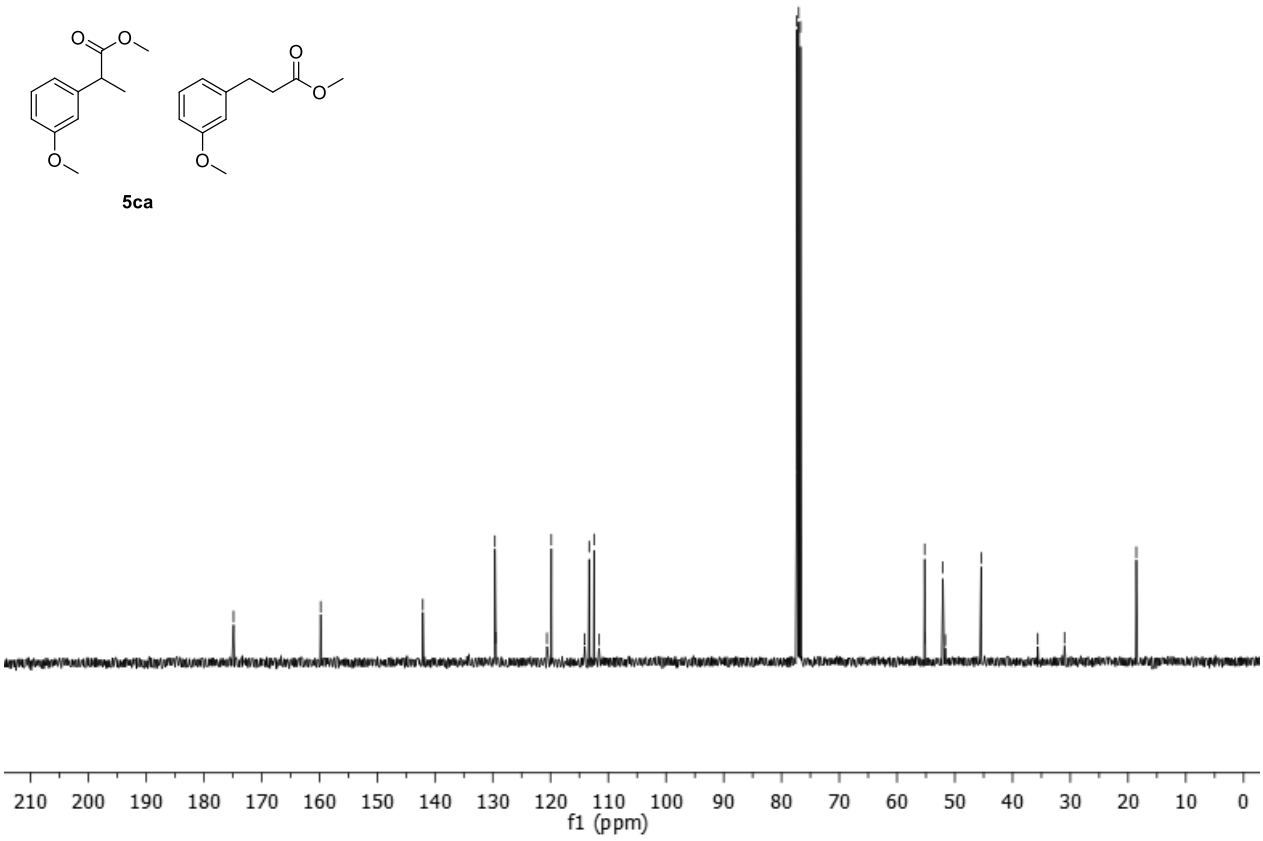
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 – 7.18 (m, 1H, ArH), 6.91 – 6.73 (m, 3H, ArH), 3.80 (s, 3H, $ArOCH_3$), 3.70 (q, J = 7.2 Hz, 1H, $ArCH(CO_2Me)Me$), 3.67 (s, 3H, RCO_2CH_3), 1.49 (d, J = 7.2 Hz, 3H, $ArCH(CO_2Me)CH_3$); minor signals from linear regioisomer: 3.79 (s, 3H, $ArOCH_3$), 3.68 (s, 3H, $ArCH_2CH_2COOCH_3$), 2.93 (t, J = 7.9 Hz, 2H, $ArCH_2CH_2CO_2Me$), 2.63 (t, J = 7.9 Hz, 2H, $ArCH_2CH_2CO_2Me$).

^{13}C-NMR (101 MHz, $CDCl_3$) 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 ($ArOCH_3$), 52.1 (RCO_2CH_3), 45.4 ($ArCH(CO_2Me)Me$), 18.6 ($ArCH(CO_2Me)CH_3$); minor signals from linear regioisomer: 129.5 (ArC), 120.6 (ArC),114.1 (ArC), 111.6 (ArC), 51.6 (RCO_2CH_3), 35.6 ($ArCH_2CH_2CO_2Me$), 31.0 ($ArCH_2CH_2CO_2Me$).

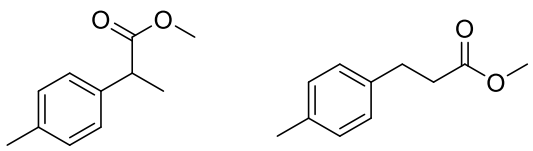
GC-FID: (50-280M12): t_R = 6.13 min (branched), t_R = 6.47 min (linear).

GC-MS: t_R = 7.56 min (branched), m/z = 194 (40, $[M^{+\bullet}]$), 135 (100, $[M^{+\bullet}]$-$[^{\bullet}CO_2Me]$; t_R = 8.34 min (linear), m/z = 194 (46, $[M^{+\bullet}]$), 163 (11, $[M^{+\bullet}]$-$[OMe^{\bullet}]$), 134 (100, $[C_9H_{10}O^{+\bullet}]$).


5ca
0.90
3.31
2.87
0.44
1.22
0.39
2.99
0.27
0.28
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-(p-tolyl)propanoate **(5da**-b**)** and methyl 3-(p-tolyl)propanoate **(5da**-l**)**



178.2 g/mol

5da-b **5da**-l

Using 4-methylstyrene (130 µL, 118, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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]

R_f: 0.32 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

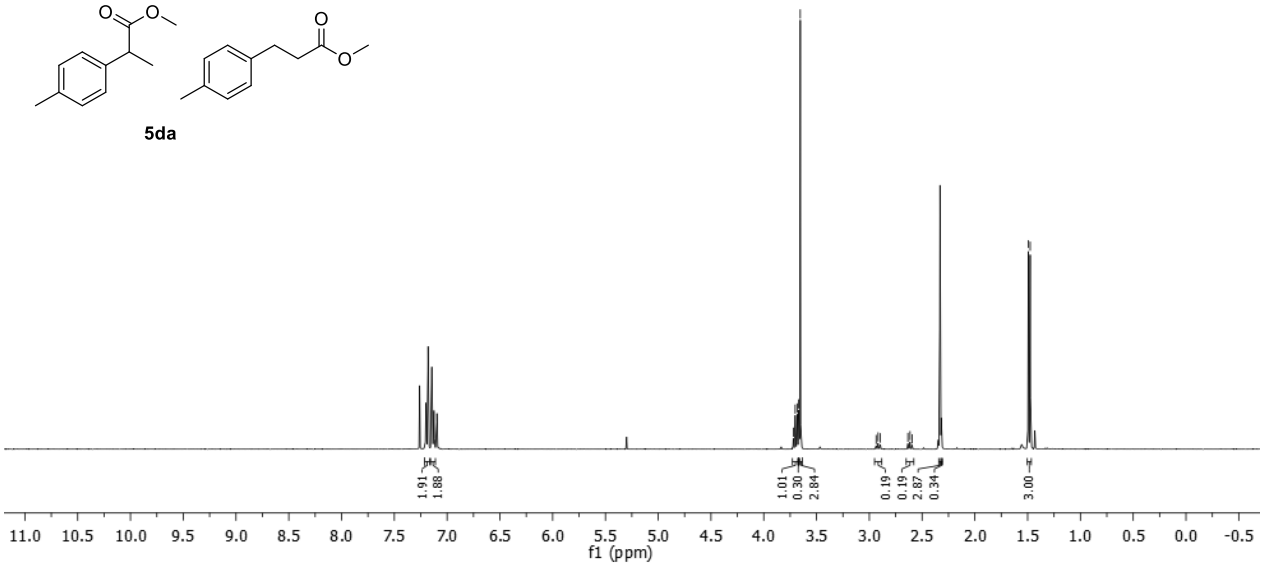
Melting point: Ambient temperature.

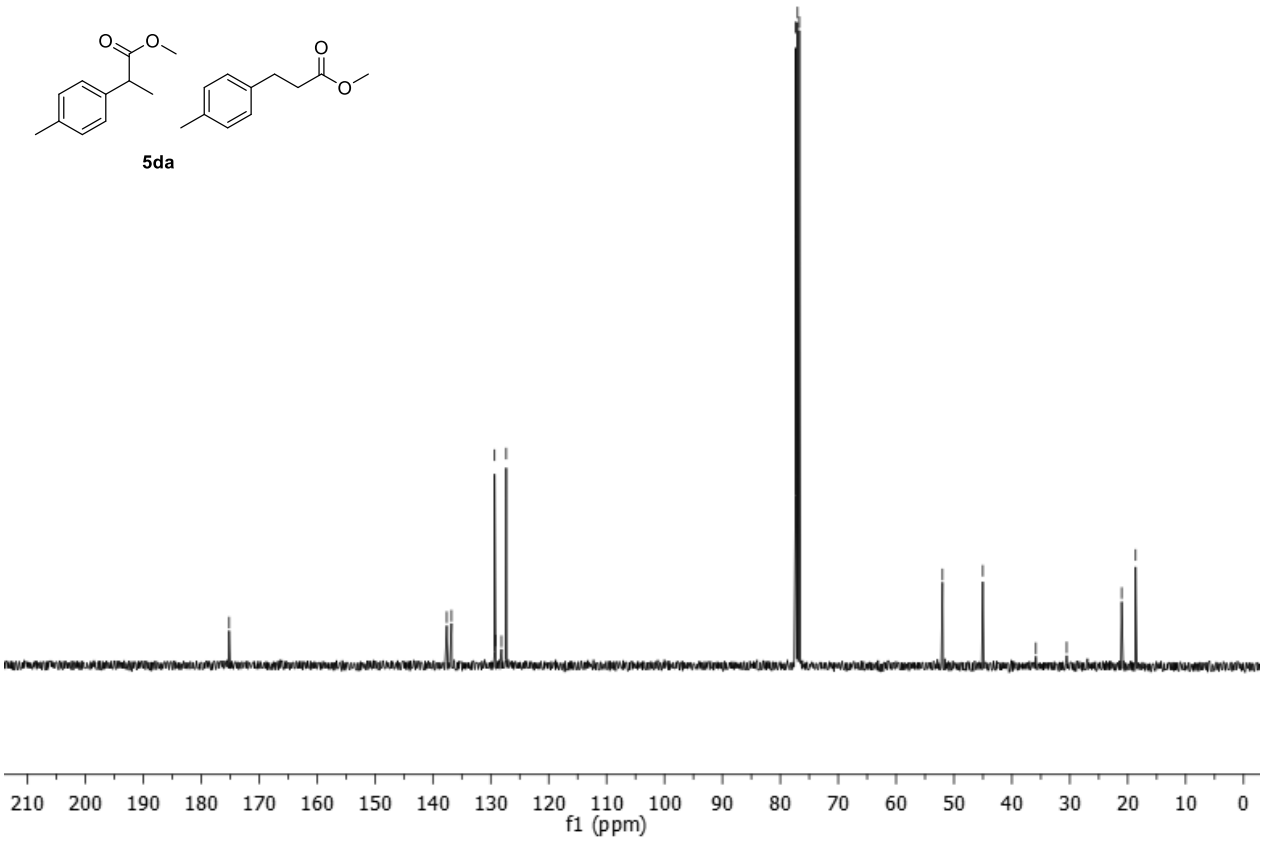
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.19 (d, *J* = 8.1 Hz, 2H, ArH), 7.13 (d, *J* = 8.1 Hz, 2H, ArH), 3.69 (q, *J* = 7.2 Hz, 1H, ArCH), 3.65 (s, 3H, ArCH(CO_2CH_3)Me), 2.33 (s, 3H, ArCH_3), 1.48 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3); minor signals from linear regioisomer: 3.67 (s, 3H, Ar$CH_2CH_2CO_2CH_3$), 2.32 (s, 3H, ArCH_3), 2.92 (t, *J* = 7.9 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.61 (t, *J* = 7.9 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 175.2 (C=O), 137.6 (ArC), 136.8 (ArC), 129.3 (ArC), 127.3 (ArC), 52.0 (RCO_2CH_3), 45.0 (ArCH(CO_2CH_3)CH_3), 21.0 (ArCH_3), 18.6 (ArCH(CO_2CH_3)CH_3); minor signals from linear regioisomer: 129.2 (ArC), 128.2 (ArC), 52.0 RCO_2CH_3), 35.9 (Ar$CH_2CH_2CO_2$Me), 30.6 (ArCH$_2$CH$_2$CO$_2$Me).

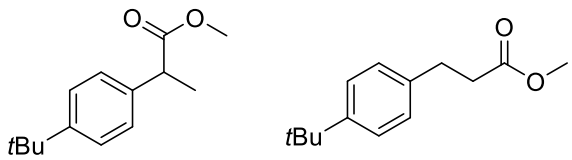
GC-FID: (50-280M12): t_R = 5.47 min (branched), t_R = 5.79 min (linear).

GC-MS: t_R = 6.03 min (branched), m/z = 178 (17, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$]-[$^\bullet CO_2$Me], 91 (19, [$M^{+\bullet}$]-[$CH_2CH_2CO_2Me^\bullet$]); t_R = 6.87 min (linear), m/z = 178 (25, [$M^{+\bullet}$]), 118 (93, [$C_9H_{10}^{+\bullet}$]), 105 (100, [$M^{+\bullet}$]-[$CH_2CO_2Me^\bullet$]).


5da
1.91
1.88
1.01
0.30
2.84
0.19
0.19
2.87
0.34
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5da
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-(4-(*tert*-butyl)phenyl)propanoate **(5ea**-b**)** and methyl 3-(4-(*tert*-butyl)phenyl) propanoate **(5ea**-l**)**



220.3 g/mol

5ea-b **5ea**-l

Using 4-*tert*-butylstyrene (200 µL, 163 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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. [13]

R_f: 0.32 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

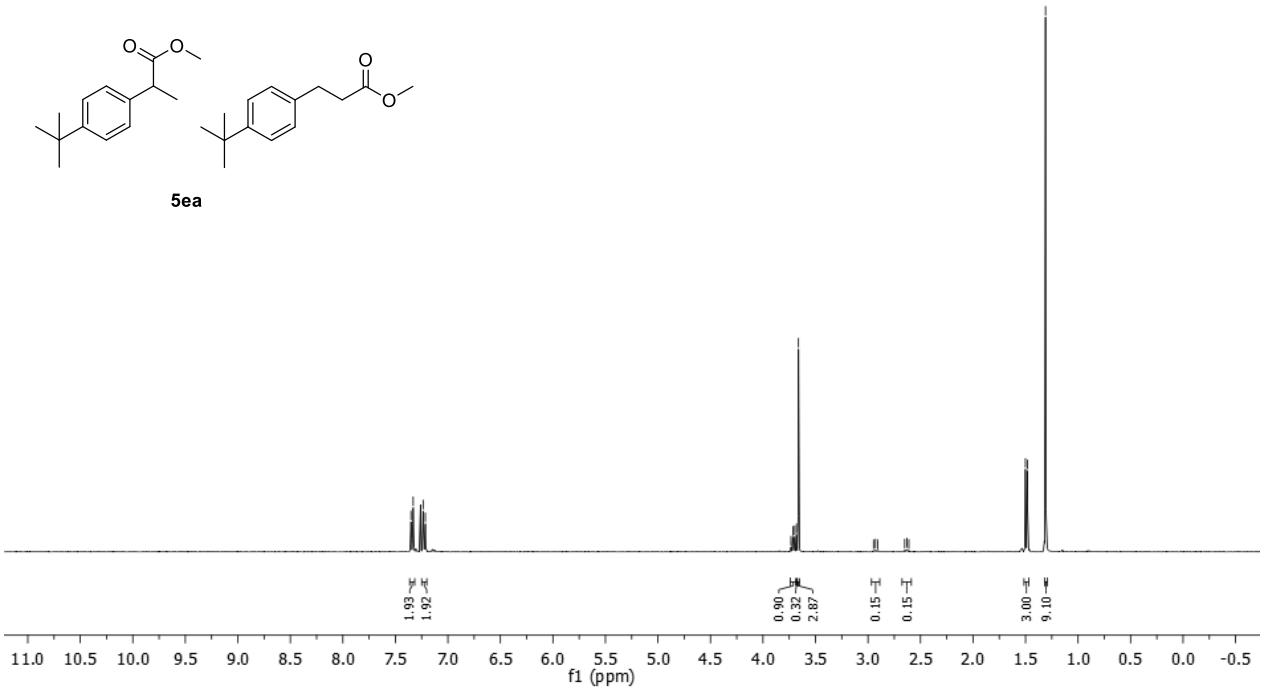
Melting point: Ambient temperature.

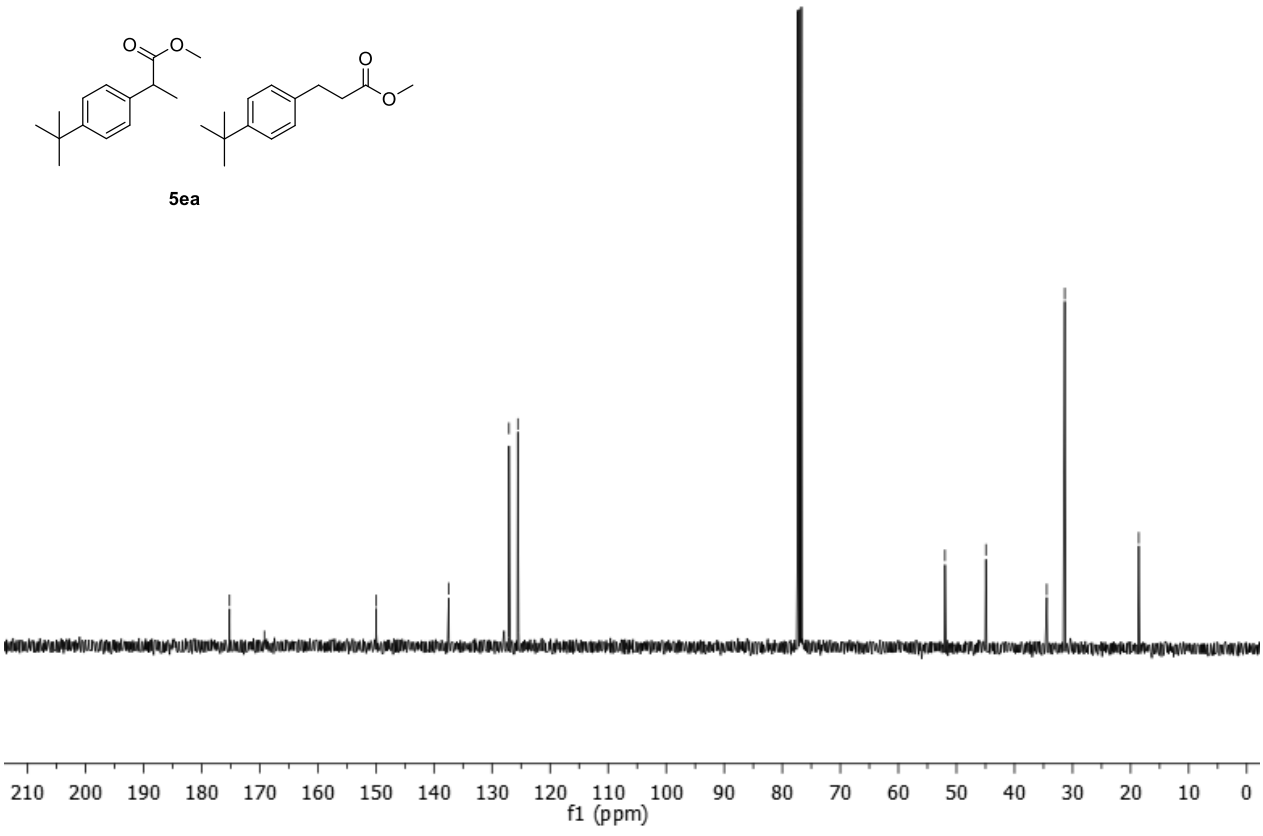
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (d, *J* = 8.4 Hz, 2H, ArH), 7.23 (d, *J* = 8.4 Hz, 2H, ArH), 3.72 (q, *J* = 7.2 Hz, 1H, ArCH(CO_2CH_3)Me), 3.66 (s, 3H, ArCH(CO_2CH_3)Me), 1.49 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3), 1.31 (s, 9H, Ar-C(CH_3)$_3$); minor signals from linear regioisomer: 3.68 (s, 2H, RCO_2CH_3), 2.93 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.63 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (101MHz, $CDCl_3$) δ (ppm): 175.2 (C=O), 150.00 (ArC), 137.5 (ArC), 127.1 (ArC), 125.6 (ArC), 52.0 (RCO_2CH_3), 44.9 (ArCH(CO_2CH_3)Me), 34.5 (Ar-C(CH_3)$_3$), 31.3 (Ar-C(CH_3)$_3$), 18.6 (ArCH(CO_2Me)CH_3); due to low concentration, signals from the minor regioisomer were not detected.

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

GC-MS: t_R = 8.42 min (branched), m/z = 220 (25, [$M^{+\bullet}$]), 205 (100, [$M^{+\bullet}$]-[$CH_3^\bullet$]), 161 (75, [$M^{+\bullet}$]-[$^\bullet CO_2$Me]; t_R = 9.11 min (linear), m/z = 220 (21, [$M^{+\bullet}$]), 205 (100, [$M^{+\bullet}$]-[$CH_3^\bullet$]).


5ea
1.93
1.92
0.90
0.32
2.87
0.15
0.15
3.00
9.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-(4-methoxyphenyl)propanoate (**5fa**-b) and Methyl 3-(4-ethoxyphenyl)propanoate (**5fa**-l)

194.2 g/mol

5fa-b **5fa**-b

Using dist. 4-vinylanisole (135 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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]

***R*f**: 0.31 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

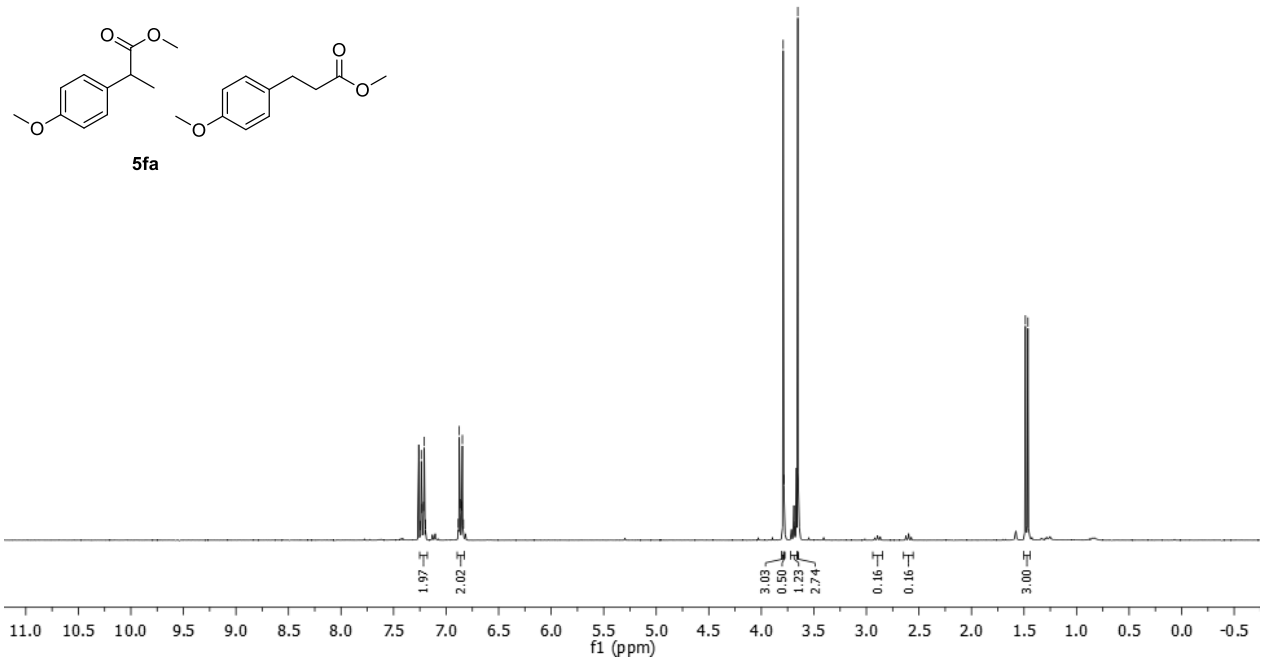
Melting point: Ambient temperature.

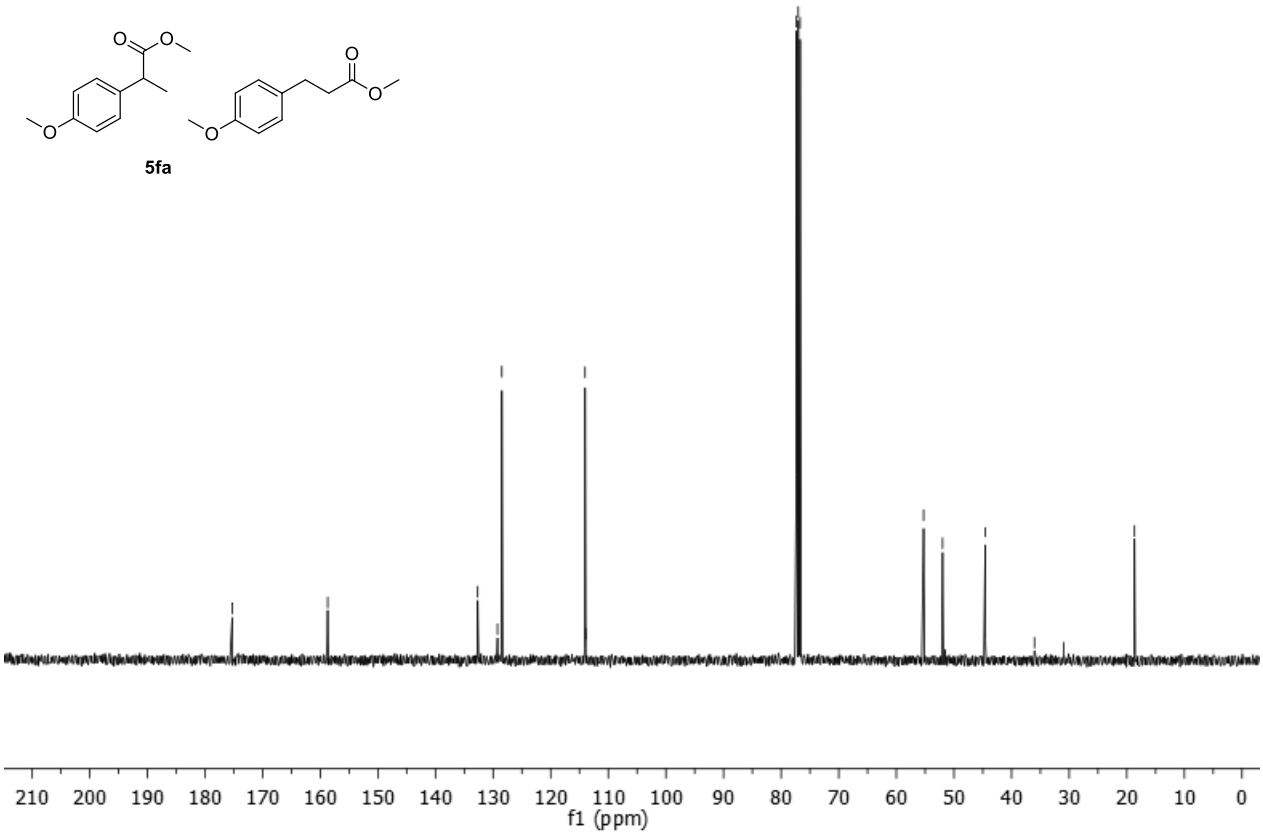
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 – 7.20 (m, 2H, ArH), 6.89 – 6.83 (m, 2H, ArH), 3.78 (s, 3H, ArOCH_3), 3.69 (q, *J* = 7.2 Hz, 1H, ArCH(CO_2Me)Me), 3.65 (s, 3H, ArCH($CO_2C H_3$)Me), 1.48 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3); minor signals for linear regioisomer: 2.90 (t, *J* = 7.8 Hz, 2H, ArC$H_2CH_2CO_2$Me), 2.60 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 175.3 (C=O), 158.7 (ArC), 132.7 (ArC), 128.5 (ArC), 114.0 (ArC), 55.2 (ArOCH_3), 51.9 (R-CO_2CH_3), 44.6 (ArCH(CO_2Me)CH_3), 18.7 (ArCH(CO_2Me)CH_3); minor signals for linear regioisomer: 129.2 (ArC), 113.9 (ArC), 55.3 (ArOCH_3), 52.0 (RCO_2CH_3), 36.0 (Ar$CH_2CH_2CO_2$Me), 30.9 (ArC$H_2CH_2CO_2$Me).

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

GC/MS (EI): t_R = 9.46 min (branched), m/z = 194 (18, [$MH^{+\bullet}$]), 135 (100, [$MH^{+\bullet}$]-[$CO_2Me^{\bullet}$]); t_R = 10.14 min (linear), m/z = 194 (18, [$MH^{+\bullet}$]), 121 (100, [$MH^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).


5fa
1.97
2.02
3.03
0.50
1.23
2.74
0.16
0.16
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 4-(1-methoxy-1-oxopropan-2-yl)benzoate (**5ga**-b) and Methyl 4-(3-methoxy-3-oxopropyl)benzoate (**5ga**-l)

222.2 g/mol

5ga-b **5ga**-l

Using 4-vinylbenzoic acid (148 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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]

***R*$_f$**: 0.22 (mobile phase 8:2 DCM:MeOH, $KMnO_4$ stain)

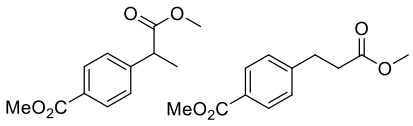
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.34 – 7.28 (m, 2H, ArH), 7.07 – 7.01 (m, 2H, ArH), 3.73 (q, *J* = 7.2 Hz, 1H, ArCH(CO_2Me)CH_3), 3.63 (s, 3H, ArCH(CO_2CH_3)CH_3), 2.29 (s, 3H, ArCO_2CH_3), 1.49 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2CH_3)CH_3); minor signals from linear regioisomer: 3.65 (Ar$CH_2CH_2CO_2CH_3$), 2.94 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2Me$), 2.63 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2Me$).

^{13}C-NMR (75 MHz, $CDCl_3$) 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(CO_2CH_3)Me), 44.8 (ArCH(CO_2CH_3)CH_3), 21.1 (Ar-CO_2CH_3), 18.6 (ArCH(CO_2CH_3)CH_3); minor signals from linear regioisomer: 51.7 (ArCH(CO_2CH_3)Me), 35.6 (Ar$CH_2CH_2CO_2Me$), 30.3 (Ar$CH_2CH_2CO_2Me$).

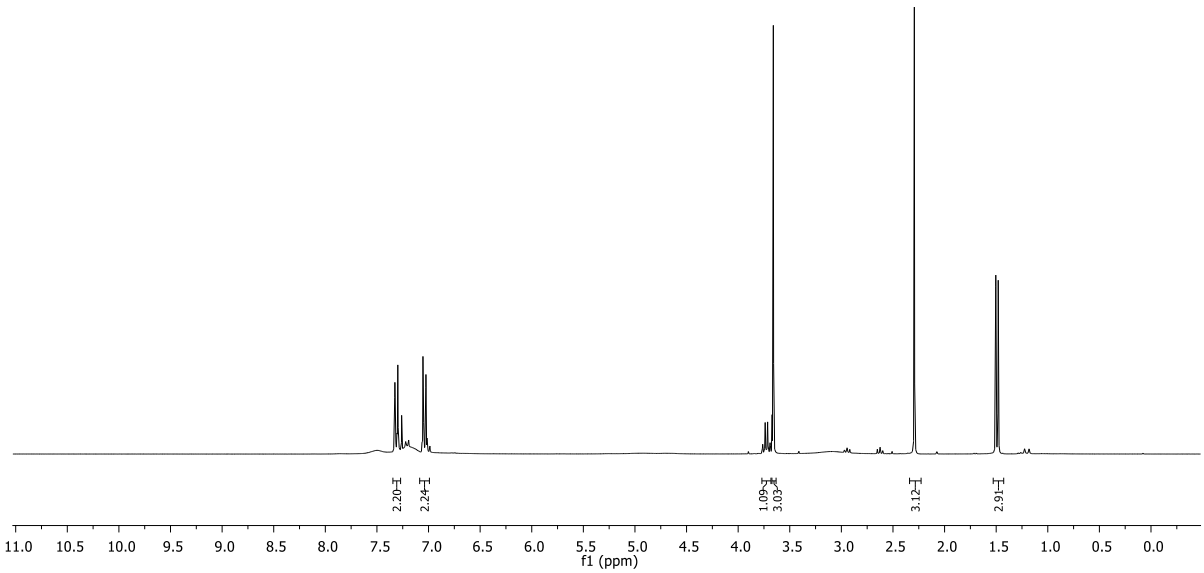
GC-FID (50-280M12): t_R = 7.45 min (branched), t_R = 7.73 min (linear).

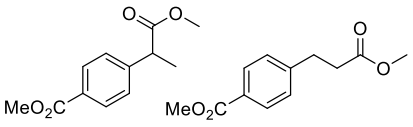
GC/MS (APCI)**:** t_R = 8.35 min (branched), m/z = 240.123 [M+NH_4^+]; t_R = 8.90 min (linear), m/z = 240.123 [M+NH_4^+].

HR-MS (APCI)**:** [MH^+] m/z = calc. for $C_{12}H_{14}O_4$ 223.0965; found 223.0968.



5ga


2.20
2.24
1.09
3.03
3.12
2.91
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



5ga

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Methyl 2-(4-chlorophenyl)propanoate (**5ia**-b) and Methyl 3-(4-chlorophenyl)propanoate (**5ia**-l)

198.6 g/mol

5ia-b **5ia**-l

Using 4-chlorostyrene (120 µL, 139 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) as the alcohol component, general procedure **A** was employed using 1.0 mol% [Pd]. The b/l ratio of the crude product was determined by GC-FID analysis to be 92:8. Purification by chromatography on SiO_2 (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]

$\boldsymbol{R_f}$: 0.29 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain) .

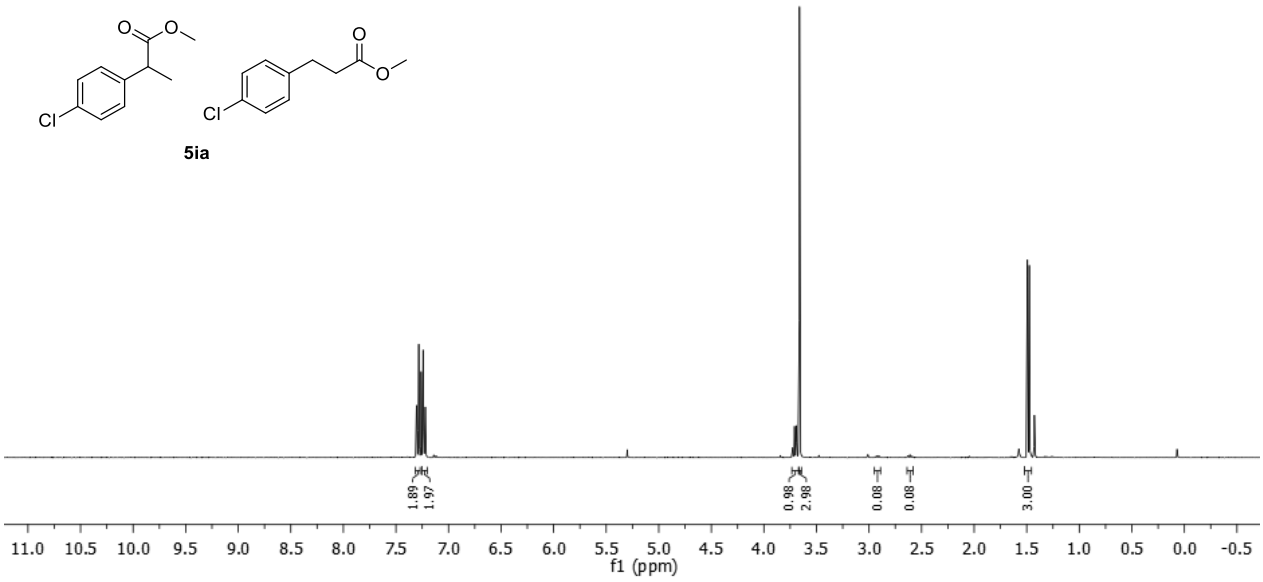
Melting point: Ambient temperature.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 – 7.27 (m, 2H, ArH), 7.25 – 7.21 (m, 2 H, ArH), 3.70 (q, J = 7.2 Hz, 1H, ArCH(CO_2Me)CH_3), 3.66 (s, 3H, ArCH(CO_2CH_3)CH_3), 1.48 (d, J = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3); minor signals from linear regioisomer: 2.92 (t, J = 7.7 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.61 (t, J = 7.7 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 174.6 (C=O), 138.97 (ArC), 133.0 (ArC), 128.9 (ArC), 128.8 (ArC), 52.1 (ArCH(CO_2CH_3)CH_3), 44.8 ArCH(CO_2Me)CH_3), 18.5 ArCH(CO_2Me)CH_3); minor signals from linear regioisomer: 173.0 (C=O), 132.1 (ArC), 129.7 (ArC), 128.6 (ArC) 51.7 (Ar$CH_2CH_2CO_2CH_3$), 35.5 (Ar$CH_2CH_2CO_2$Me), 30.3 (Ar$CH_2CH_2CO_2$Me).

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

GC/MS (EI): t_R = 8.73 min (branched), m/z = 198 (21, [$MH^{+\bullet}$]), 139 (100, [$MH^{+\bullet}$]-[$CO_2Me^{\bullet}$]); t_R = 10.14 min (linear), m/z = 198 (21, [$MH^{+\bullet}$]), 167 (17, [$MH^{+\bullet}$]-[$OMe^{\bullet}$]), 125 (80, [$MH^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).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Cl
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1.97
0.98
2.98
0.08
0.08
3.00
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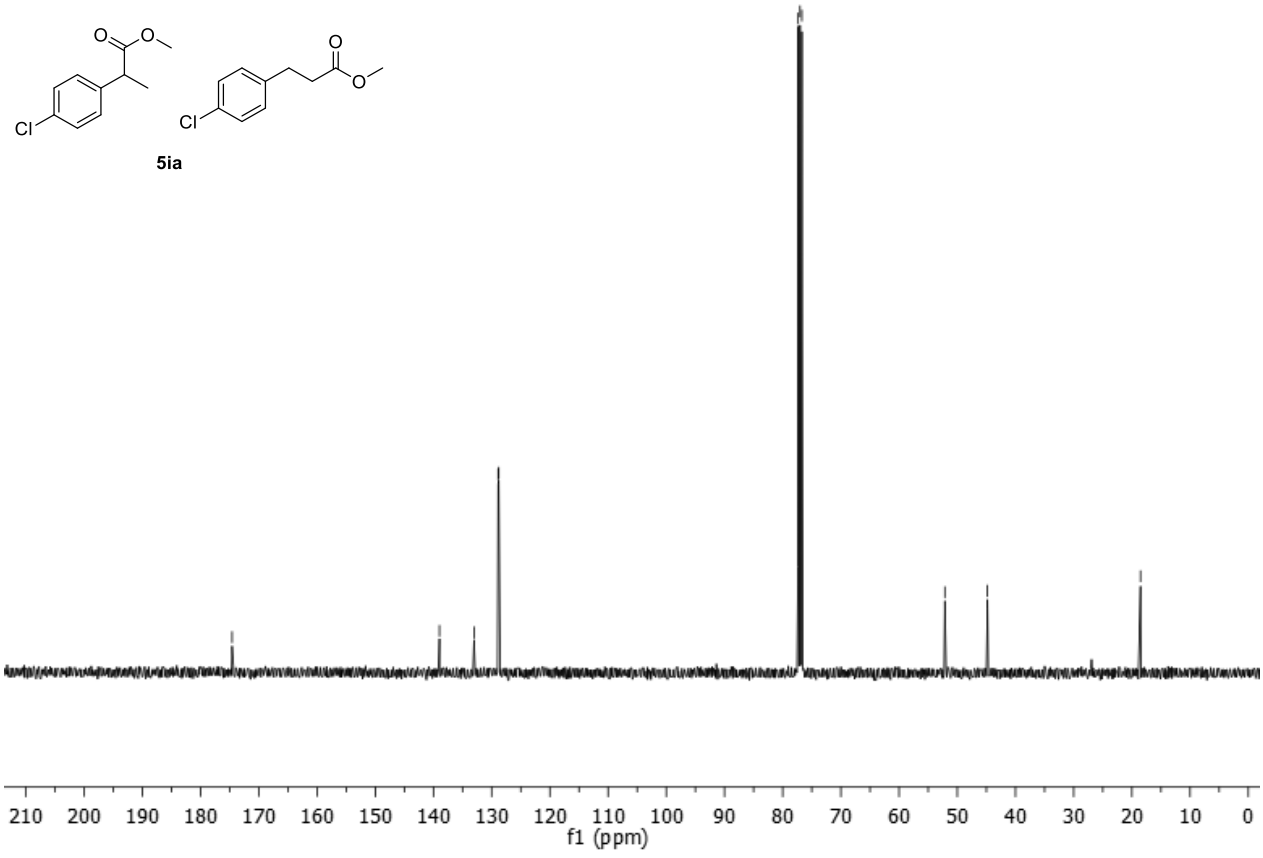
f1 (ppm)


Cl
Cl
5ia
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f1 (ppm)

Methyl 2-(4-acetoxyphenyl)propanoate (**5ja**-b) and Methyl 3-(4-acetoxyphenyl)propanoate (**5ja**-l)

222.2 g/mol

5ja-b **5ja**-l

Using 4-vinylphenyl acetate (150 µL, 162 mg, 1.00 mmol) as the olefin component and dist. MeOH (stored under N_2) as the alcohol component, general procedure **A** was employed using 1.0 mol% [Pd]. Purification by flash chromatography on SiO_2 (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]

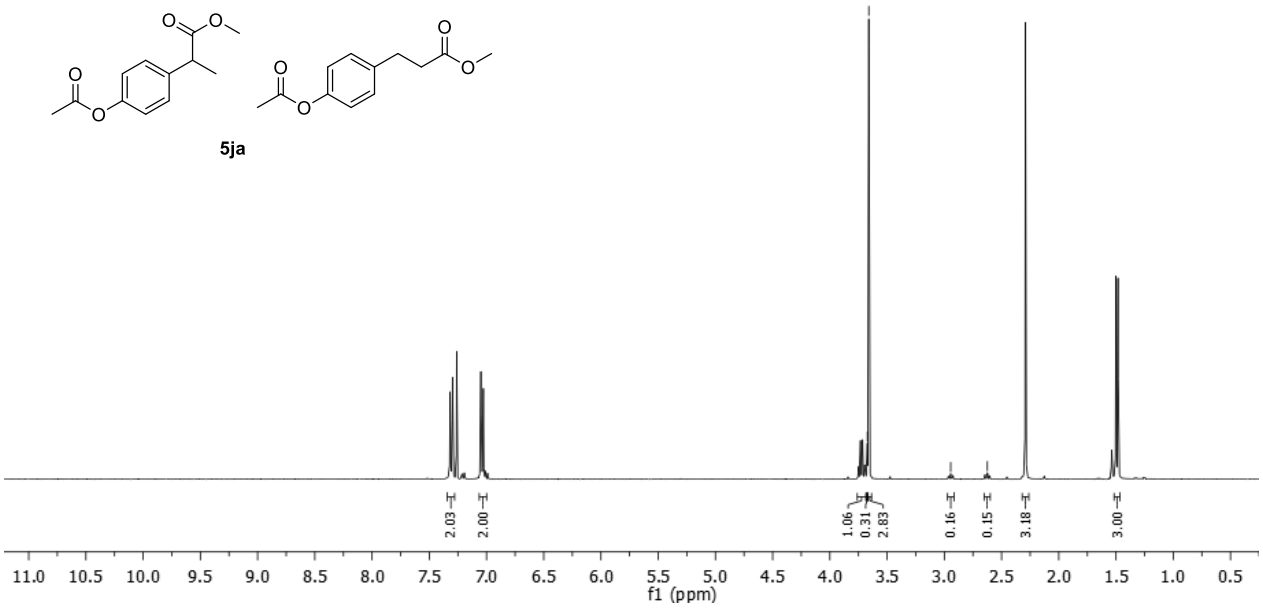
***R*f**: 0.31 (mobile phase 8:2 DCM:MeOH, $KMnO_4$ stain).

^{1}H-NMR (300 MHz, $CDCl_3$) 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(CO_2Me)CH_3), 3.63 (s, 3H, ArCH(CO_2CH_3)CH_3), 2.26 (s, 3H, Acetyl-CH_3), 1.47 (d, *J* = 7.2 Hz, 3H, ArCH(CO_2CH_3)CH_3); minor signals from linear regioisomer: 2.93 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.61 (t, *J* = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (75 MHz, $CDCl_3$) 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-CO_2CH_3), 44.8 ArCH(CO_2Me)CH_3, 21.1 (acetyl CH_3), 18.6 (ArCH(CO_2Me)CH_3); minor signals from linear regioisomer: 35.6 (Ar$CH_2CH_2CO_2$Me), 30.3 (Ar$CH_2CH_2CO_2$Me).

GC-FID (50-280M12, from crude): t_R = 6.80 min (branched), t_R = 7.10 min (linear).

GC/MS (EI): Main product - t_R = 10.82 min (branched), m/z = 222 (8, [$MH^{+\bullet}$]), 180 (38, [$MH^{+\bullet}$]-[CH_2CO]), 121 (100, [$MH^{+\bullet}$]-[CH_2CO]-[$CO_2Me^{\bullet}$]); t_R = 11.84 min (linear), m/z = 222 (8, [$MH^{+\bullet}$]), 180 (65, [$MH^{+\bullet}$]-[CH_2CO]), 107 (100, [$MH^{+\bullet}$]-[CH_2CO]-[$CH_2CO_2Me^{\bullet}$]). Deacetylated product - t_R = 10.01 min (branched), m/z = 180 (30, [$MH^{+\bullet}$]), 121 (100, [$MH^{+\bullet}$]-[$CO_2Me^{\bullet}$]); t_R = 10.80 min (linear), m/z = 180 (30, [$MH^{+\bullet}$]), 107 (100, [$MH^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).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1.06
0.31
2.83
0.16
0.15
3.18
3.00
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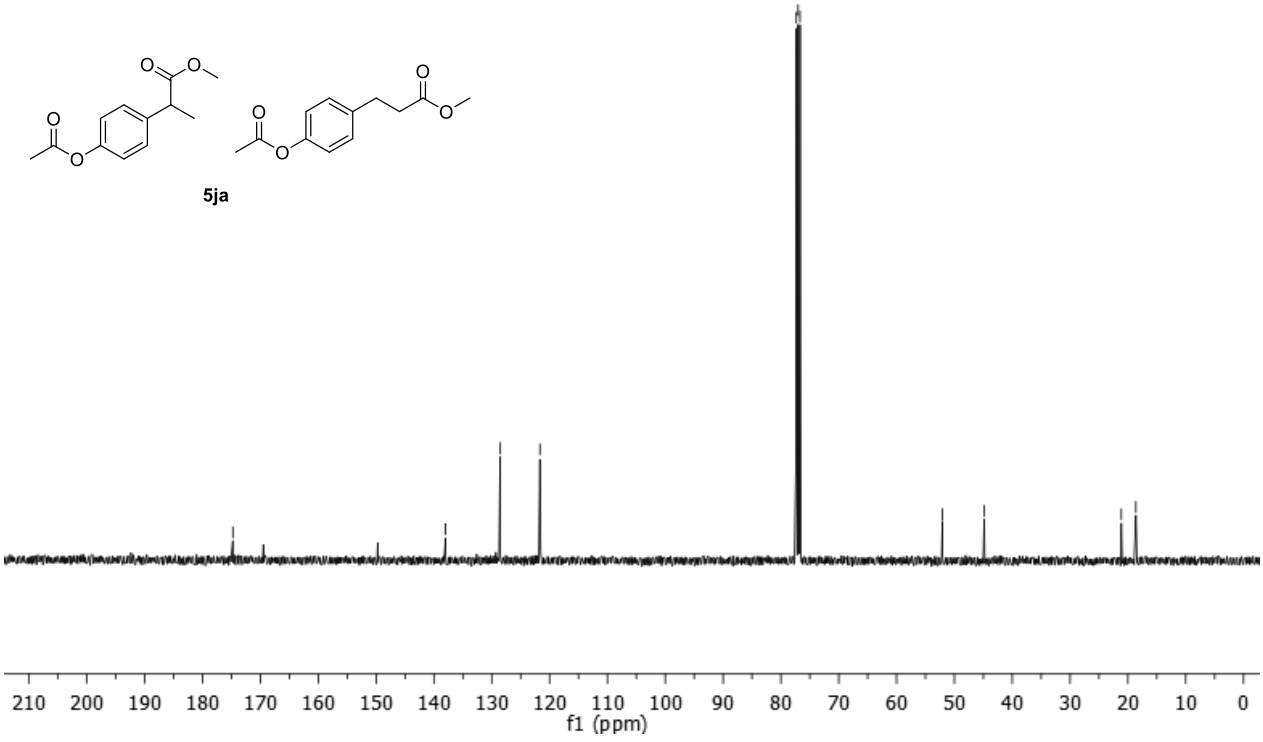
f1 (ppm)


5ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-(4-hydroxyphenyl)propanoate (**5ka**-b) and Methyl 3-(4-hydroxyphenyl)propanoate (**5ka**-l)

180.2 g/mol

5ka-b **5ka**-l

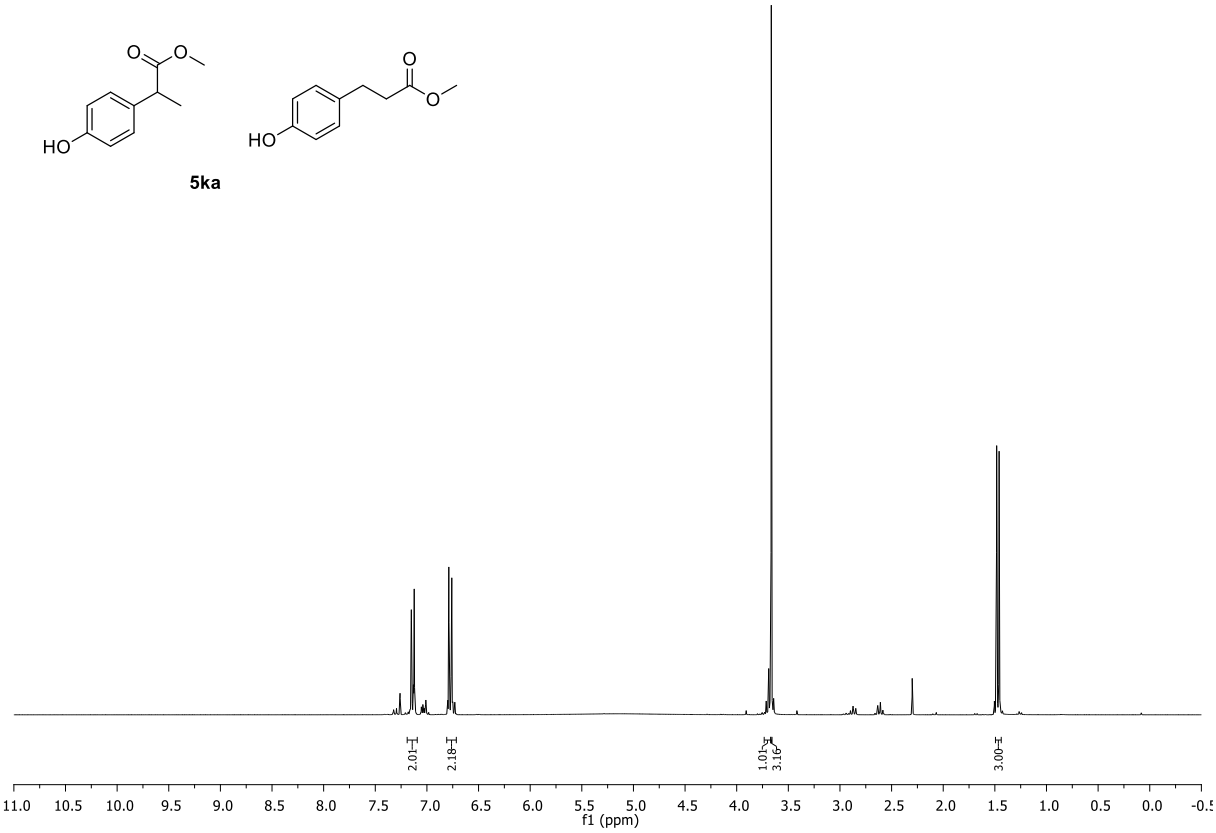
Using 4-vinylphenyl acetate (150 µL, 162 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) as the alcohol component, general procedure **A** was employed using 1.0 mol% [Pd] at 50 °C. Purification by flash chromatography on SiO_2 (mobile phase: 8:2 CyH:EtOAc) gave the regioisomeric 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, $KMnO_4$ stain).

^{1}H-NMR (300 MHz, $CDCl_3$) 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(CO_2Me)CH_3), 3.63 (s, 3H, ArCH(CO_2CH_3)CH_3), 1.47 (d, J = 7.2 Hz, 3H, ArCH(CO_2CH_3)CH_3); minor signals from linear regioisomer: 2.93 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.61 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.8 (methyl ester C=O), 151.7 (ArC), 138.0 (ArC), 128.6 (ArC), 121.7 (ArC), 52.1 (R-CO_2CH_3), 44.8 ArCH(CO_2Me)CH_3, 18.6 ArCH(CO_2Me)CH_3; minor signals from linear regioisomer: 35.6 (Ar$CH_2CH_2CO_2$Me), 30.3 (Ar$CH_2CH_2CO_2$Me).

GC/MS (EI): t_R = 10.01 min (branched), m/z = 180 (30, [$MH^{+\bullet}$]), 121 (100, [$MH^{+\bullet}$]-[$CO_2Me^{\bullet}$]); t_R = 10.80 min (linear), m/z = 180 (30, [$MH^{+\bullet}$]), 107 (100, [$MH^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).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HO
O
O
5ka
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2.18
1.01
3.16
3.00
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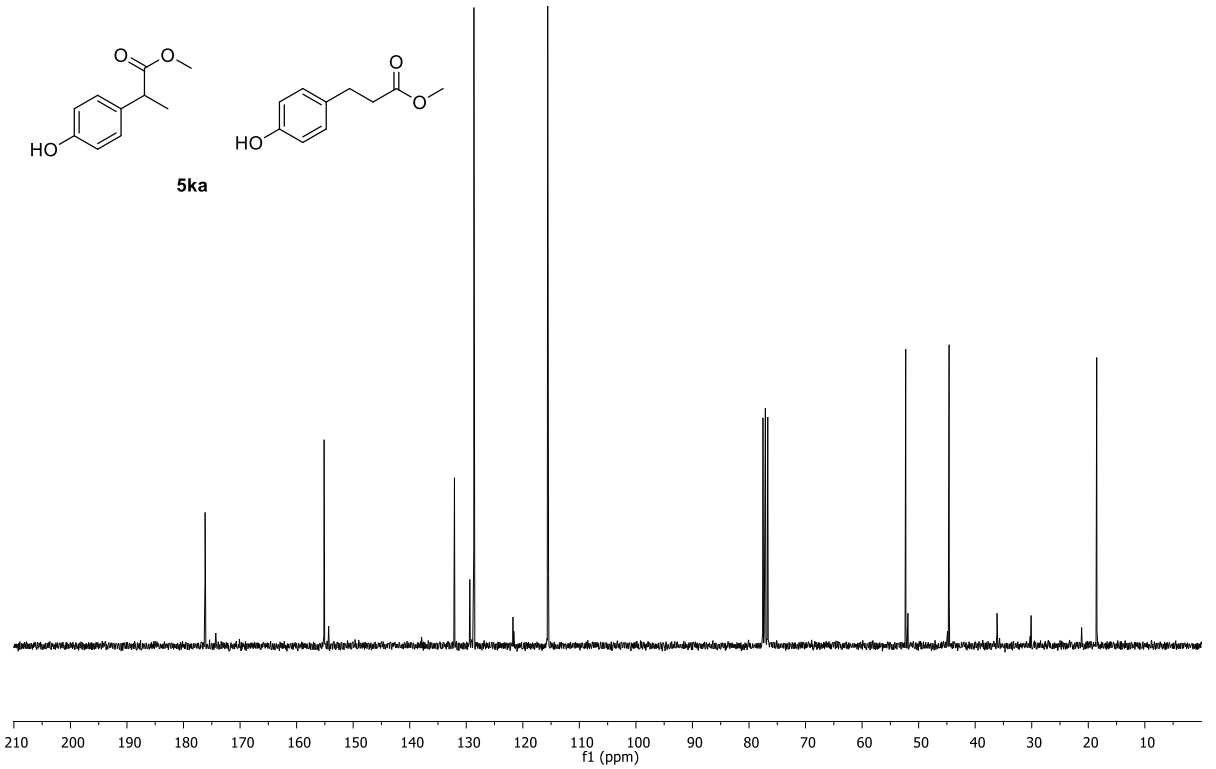
f1 (ppm)


HO
O
O
HO
O
O
5ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Methyl 2-(2-methoxyphenyl)propanoate (**5la**-b) and Methyl 3-(2-methoxyphenyl)propanoate (**5la**-l)

194.3 g/mol

5la-b **5la**-l

Using 2-vinylanisole (135 µL, 134 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_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 46:54. Purification by flash chromatography on SiO_2 (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]

R_f: 0.22 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

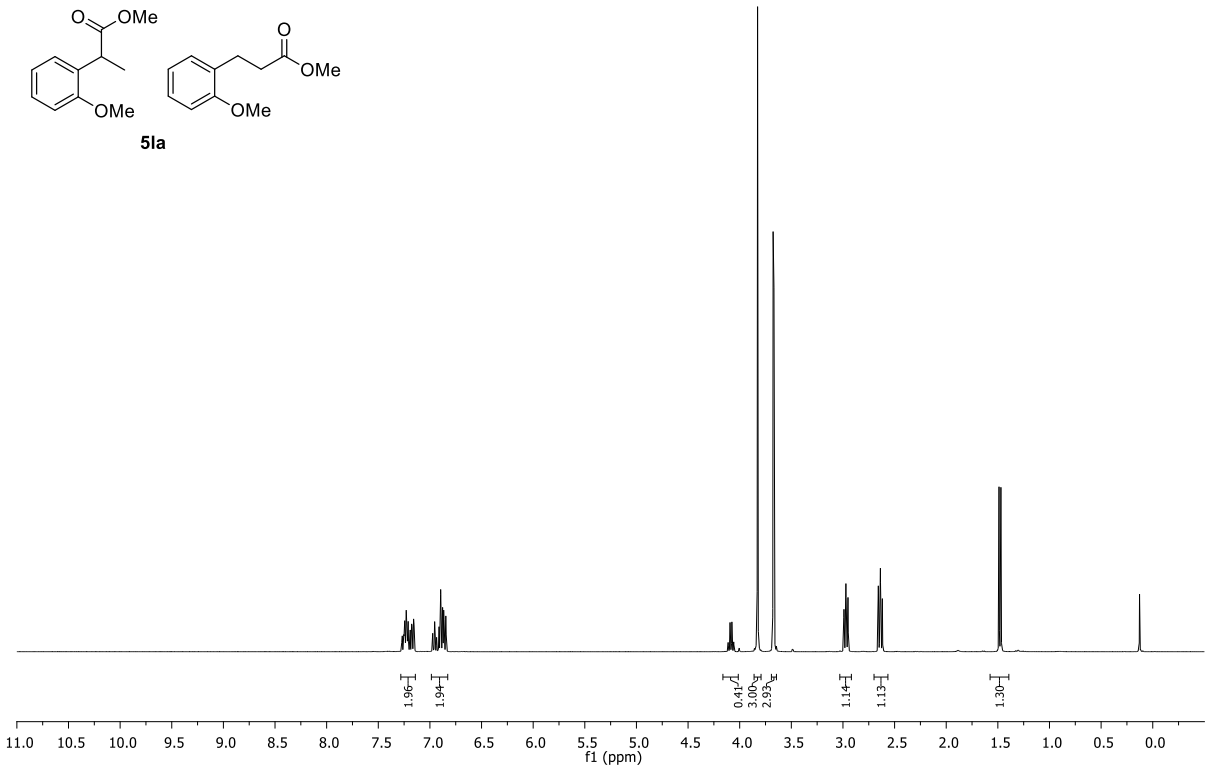
Melting point: Ambient temperature.

^{1}H-NMR (400 MHz, $CDCl_3$) 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(CO_2Me)CH_3), 3.83 (s, 3H, R-CO_2CH_3) 3.67 (s, 3H, ArOCH_3), 1.48 (d, J = 7.2 Hz, 3H, ArCH(CO_2Me)CH_3); signals from linear regioisomer: 3.68 (s, 3H, ArOCH_3), 2.97 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.64 (t, J = 7.8 Hz, 2H, Ar$CH_2CH_2CO_2$Me).

^{13}C-NMR (101 MHz, $CDCl_3$) 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 (ArOCH_3), 50.8 (R-CO_2CH_3), 38.1 (ArCH(CO_2CH_3)CH_3), 16.3 (ArCH(CO_2Me)CH_3); 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 (ArOCH_3), 50.4 (R-CO_2CH_3), 33.0 (Ar$CH_2CH_2CO_2$Me), 25.1 (Ar$CH_2CH_2CO_2$Me).

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

GC/MS (EI): t_R = 8.88 min (branched), m/z = 194 (28, [$M^{+\bullet}$]), 135 (100, [$M^{+\bullet}$]-[$^{\bullet}CO_2$Me]); t_R = 9.67 min (linear), m/z = 194 (56, [$M^{+\bullet}$]), 163 (16, [$M^{+\bullet}$]-[$OMe^{\bullet}$]), 121 (100, [$M^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).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OMe
O
OMe
OMe
5la
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1.94
0.41
3.00
2.93
1.14
1.13
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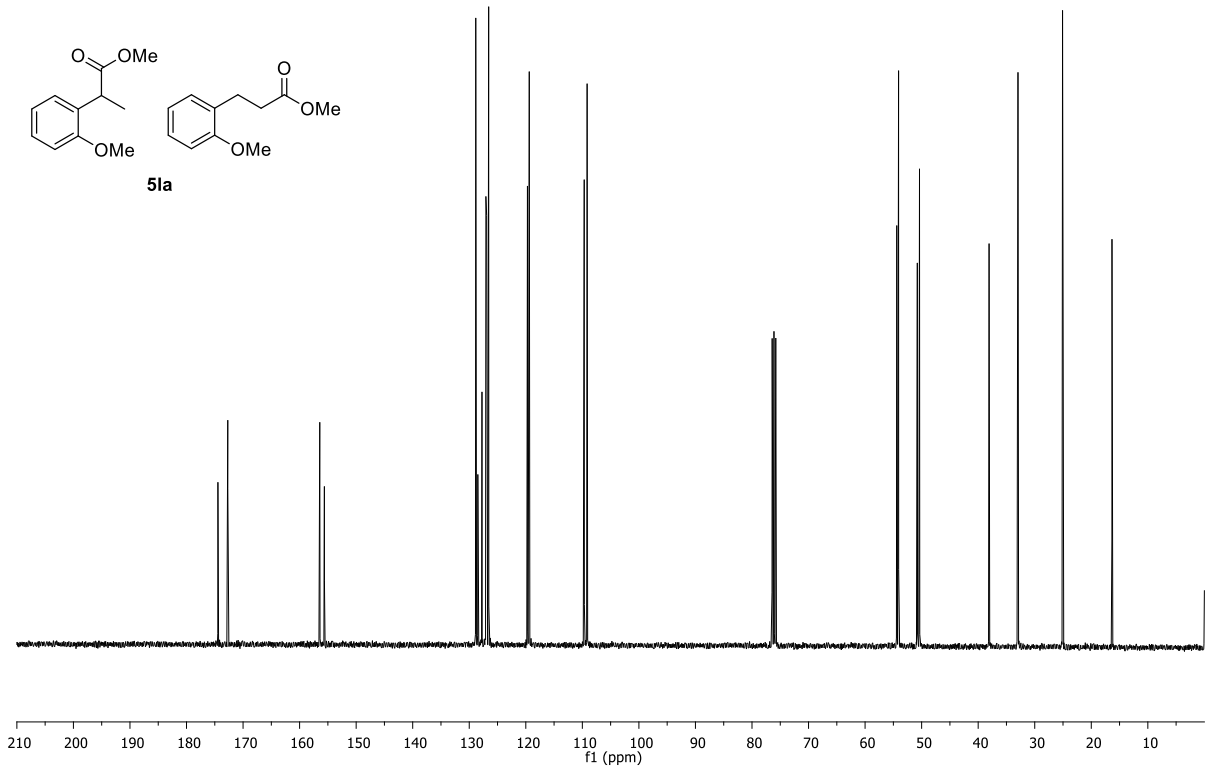
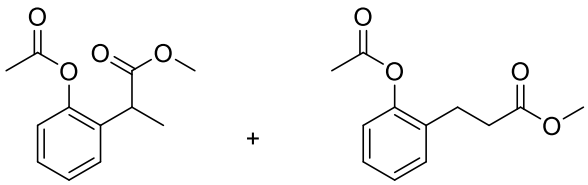
f1 (ppm)


OMe
OMe
O
OMe
OMe
5la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Methyl 2-(2-acetoxyphenyl)propanoate (**5ma**-b) and Methyl 3-(2-acetoxyphenyl)propanoate (**5ma**-l)



222.2 g/mol

5ma-b **5ma**-l

Using 2-acetoxystyrene (117 mg, 720 µmol) as the olefin component and dist. MeOH (250 µL, stored under N_2) 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 SiO_2 (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).

R_f: 0.32 (mobile phase 80:20 CyH:EtOAc, $KMnO_4$ 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), 1099 (m, sh), 1068 (w, sh), 1041 (m, sh), 1011 (m, sh), 913 (m, sh).

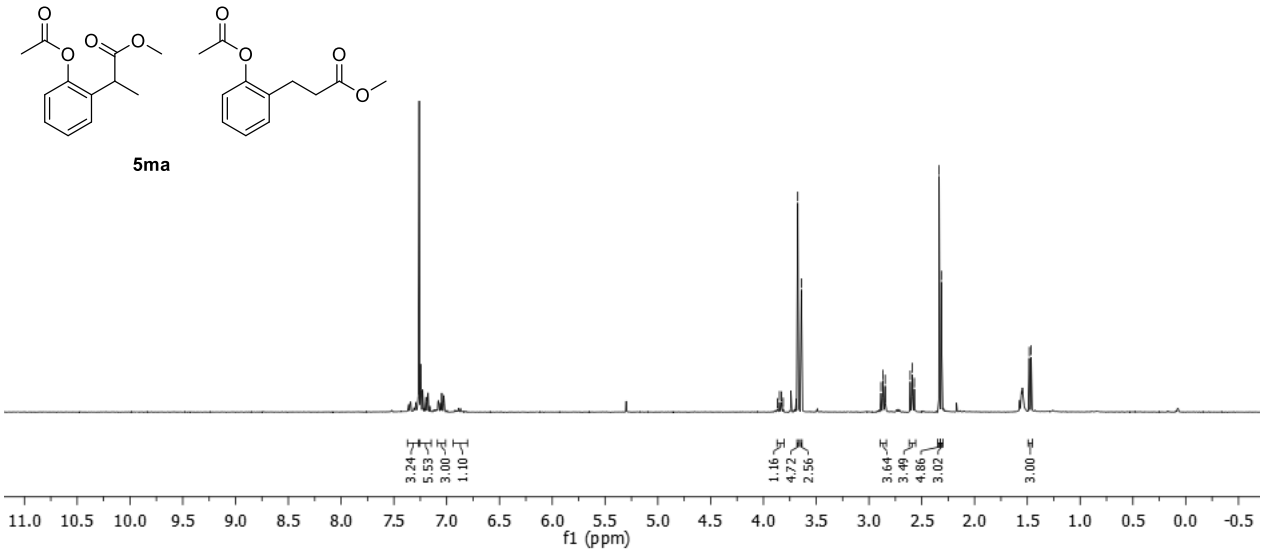
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.27 (m, 1H, ArH), 7.25 – 7.15 (m, 2H, ArH), 7.09 – 7.01 (m, 1H, ArH), 3.84 (q, *J* = 7.2 Hz, 1H, ArCH(CO$_2$Me)Me), 3.64 (s, 3H, ArCH(COOCH$_3$)Me), 2.31 (s, 3H, ArOCOCH$_3$), 1.47 (d, *J* = 7.2 Hz, 3H, ArCH(CO$_2$Me)CH$_3$); signals from linear regioisomer: 3.67 (s, 3H, ArCH$_2$CH$_2$CO$_2$CH$_3$), 2.89 – 2.84 (m, 2H, ArCH$_2$CH$_2$CO$_2$Me), 2.62 – 2.56 (m, 2H, ArCH$_2$CH$_2$CO$_2$Me), 2.34 (s, 3H, ArOCOCH$_3$).

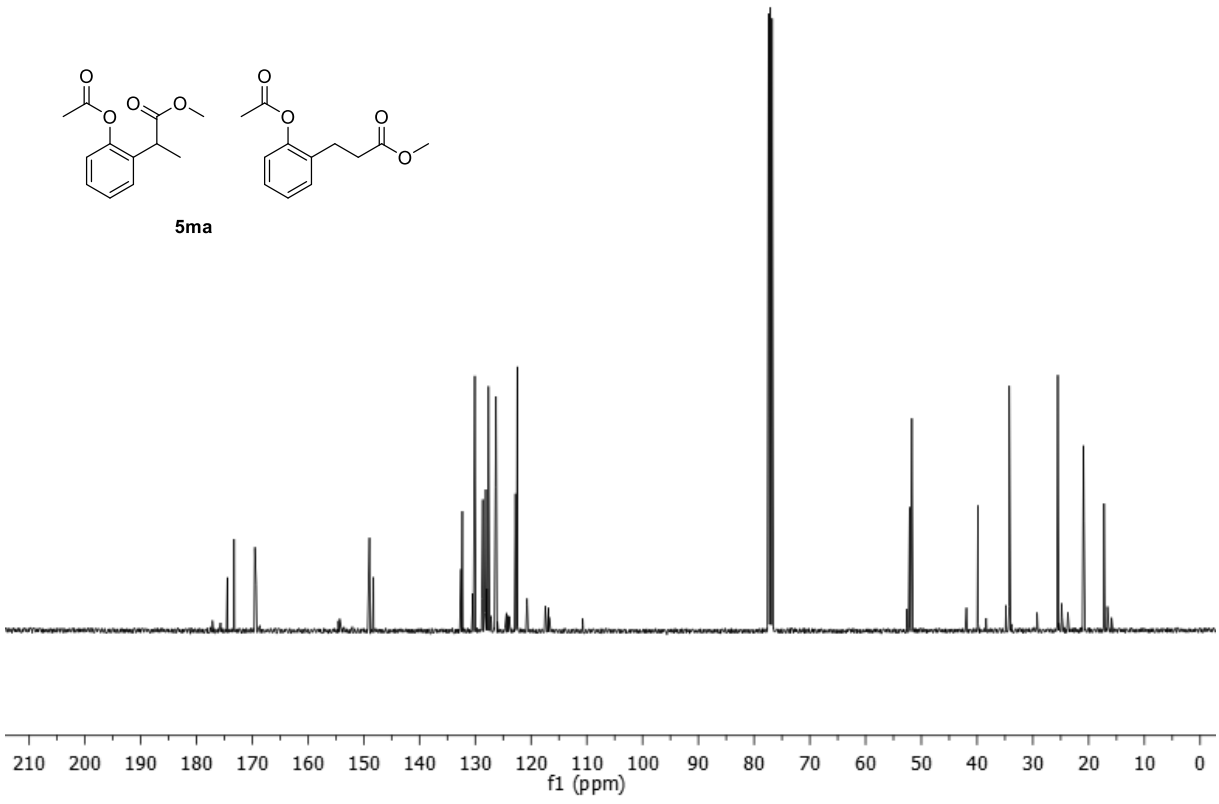
^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 174.5 (methyl ester C=O), 169.3 (acetate C=O), 148.3 (ArC), 132.3 (ArC), 128.7 (ArC), 128.1 (ArC), 126.4 (ArC), 122.8 (ArC), 52.1 (ArCH(CO$_2$CH$_3$)Me), 39.9 (ArCH(CO$_2$Me)Me), 20.8 (ArOCOCH$_3$), 17.2 (ArCH(CO$_2$Me)CH$_3$); signals from linear regioisomer: 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 (ArCH$_2$CH$_2$CO$_2$CH$_3$), 34.2 (ArCH$_2$CH$_2$CO$_2$CH$_3$), 25.5 (ArCH$_2$CH$_2$CO$_2$CH$_3$), 20.9 (ArOCOCH$_3$).

GC-FID (50-280M12): t_R = 6.44 min (branched), t_R = 6.84 min (linear).

GC-MS: t_R = 7.54 min (branched), m/z = 223 (100, [MH^+]), 163 (20, [MH^+]-[$^{\bullet}CO_2Me$]), 149 (31, [MH^+]-[$CO_2Me^{\bullet}$]-[$CH_3^{\bullet}$]); t_R = 8.20 min (branched), m/z = 223 (100, [MH^+]), 163 (14, [MH^+]-[$^{\bullet}CO_2Me$]), 149 (64, [MH^+]-[$CH_2CO_2Me^{\bullet}$].

HR-MS (APCI): m/z = [MH^+] calc. for $C_{12}H_{14}O_4$ 223.0965, found 233.0967





Methyl 2-(*o*-tolyl)propanoate (**5na**-b) and Methyl 2-(*o*-tolyl)propanoate (**5na**-l)

178.2 g/mol

5na-b **5na**-l

Using 2-methylstyrene (130 µL, 118 mg, 1.00 mmol) as the olefin component and dist. MeOH (250 µL, stored under N_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 50:50. Purification by flash chromatography on SiO_2 (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, $KMnO_4$ stain)

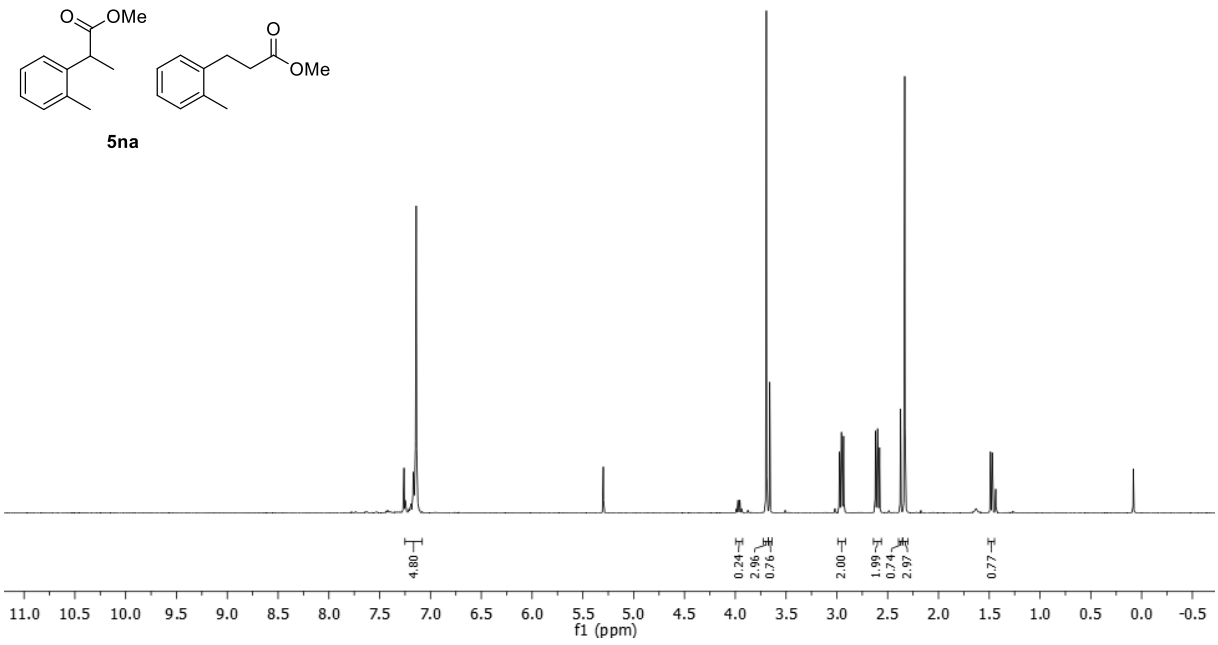
Melting point: Ambient temperature.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 – 7.06 (m, 4H, ArH), 3.96 (q, *J* = 7.1 Hz, 1H, ArCH(CO_2Me)Me), 3.66 (s, 3H, ArCH(CO_2CH_3)Me), 2.37 (s, 3H, ArCH_3), 1.48 (d, *J* = 7.1 Hz, 3H, ArCH(CO_2Me)CH_3); signals from linear regioisomer: 3.69 (s, 3H, Ar$CH_2CH_2CO_2CH_3$), 2.95 (t, *J* = 8.1 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.60 (t, *J* = 8.1 Hz, 2H, Ar$CH_2CH_2CO_2$Me), 2.33 (s, 3H, ArCH_3).

^{13}C-NMR (101 MHz, $CDCl_3$) 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(CO_2CH_3)Me), 41.3 (ArCH(CO_2CH_3)Me), 19.6 (ArCH_3), 18.0 (ArCH(CO_2CH_3)CH_3); 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 (RCO_2CH_3), 34.4 (Ar$CH_2CH_2CO_2$Me), 28.4 (Ar$CH_2CH_2CO_2$Me), 19.2 (ArCH_3).

GC-FID (50-280M12): t_R = 4.58 min (branched), t_R = 4.81 min (linear).

GC/MS (EI): t_R = 7.68 min (branched), m/z = 178 (18, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$]-[$CO_2Me^{\bullet}$]); t_R = 8.56 min (linear), m/z = 178 (18, [$M^{+\bullet}$]), 105 (100, [$M^{+\bullet}$]-[$CH_2CO_2Me^{\bullet}$]).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OMe
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0.74
2.97
0.77
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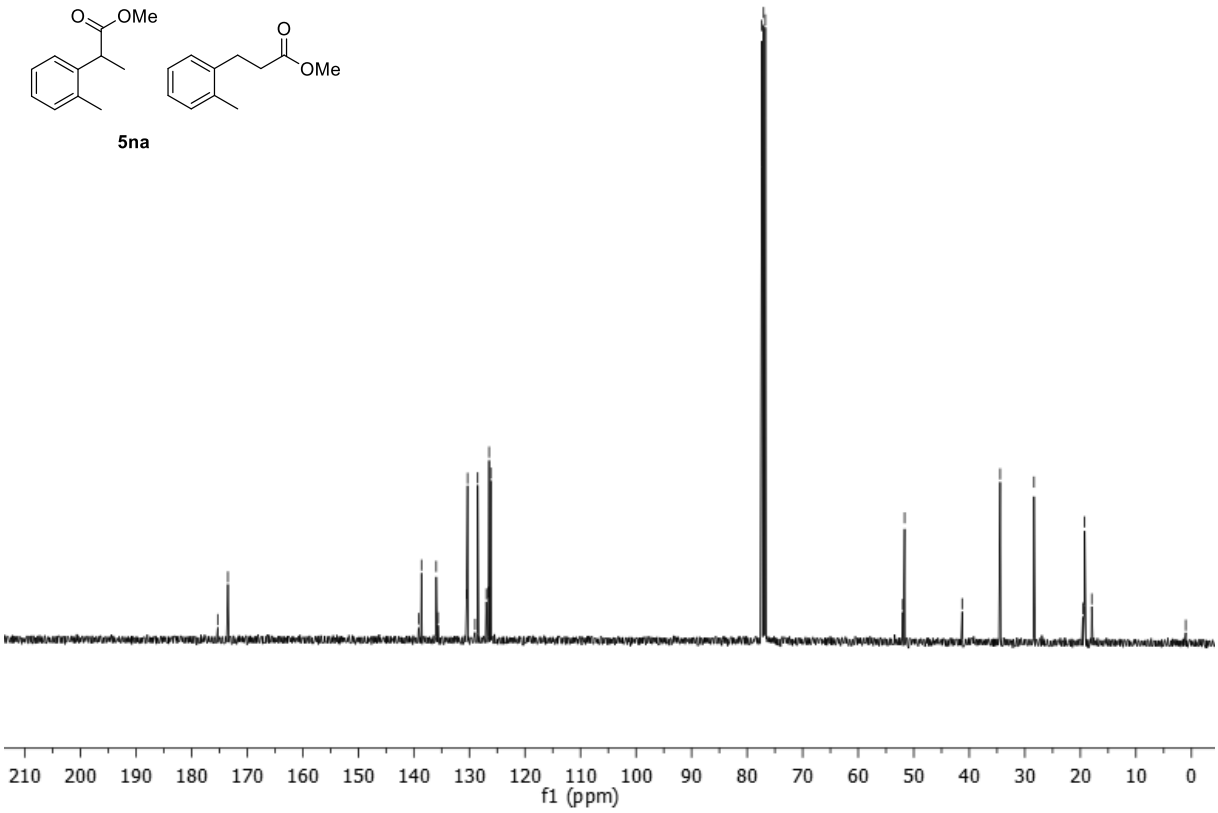
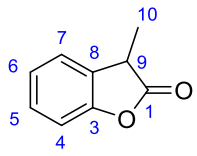
f1 (ppm)


OMe
O
O
OMe
5na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3-Methylbenzofuran-2(3*H*)-one (**5p**)



148.2 g/mol

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 N_2) as the alcohol component to dissolve the organophosphoric acid, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash chromatography on SiO_2 (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]

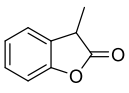
***R*f**: 0.36 (mobile phase 8:2 CyH:EtOAc, $KMnO_4$ stain)

Melting point: Ambient temperature.

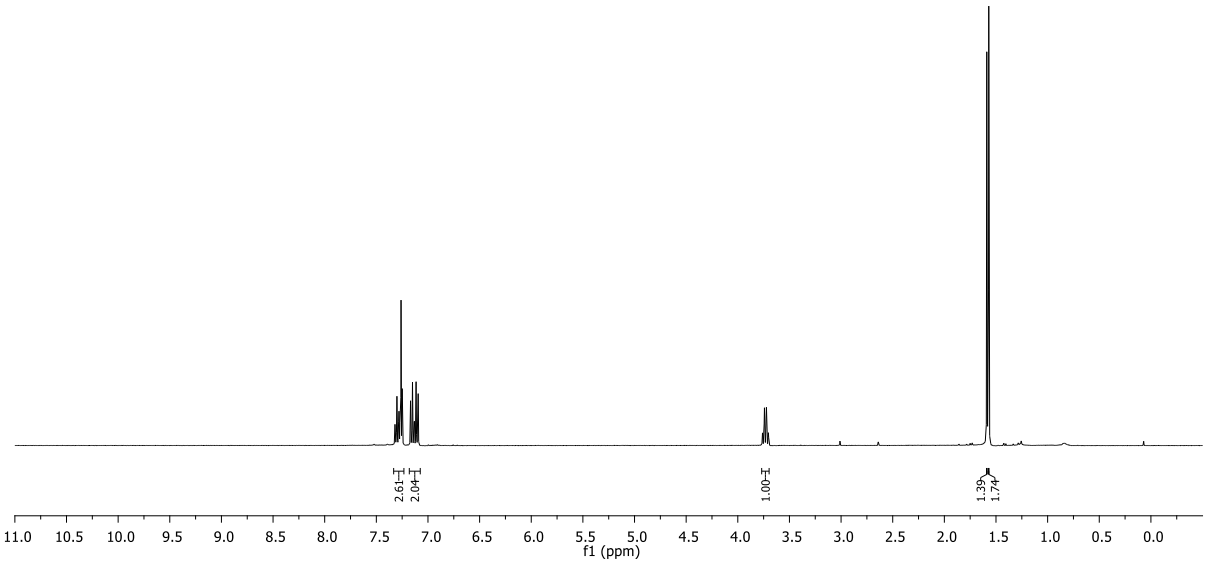
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 – 7.23 (m, 2H, ArH), 7.18 – 7.08 (m, 2H, ArH), 3.73 (q, *J* = 7.6 Hz, 1H, C^9-H), 1.58 (d, *J* = 7.6 Hz, 3H, CH_3).

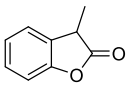
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 178.0 (C=O), 153.5 (ArC) , 131.7 (ArC), 128.8 (ArC), 124.2 (ArC), 123.9 (ArC), 110.8 (ArC), 38.4 (C^9), 15.9 (C^{10}).

GC/MS (EI): t_R = 7.11, m/z = 148 (100, $[MH^{+\bullet}]$), 120 (78, $[MH^{+\bullet}]$-[CO]), 91 (80, $[C_7H_7^+]$).



5p

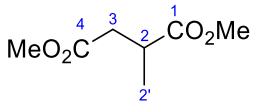

2.61
2.04
1.00
1.39
1.74
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



5pa

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Dimethyl 2-methylsuccinate (**21**)



160.2 g/mol

21

Using methyl methacrylate (**11**) (105 µL, 100 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO_2 (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.[26]

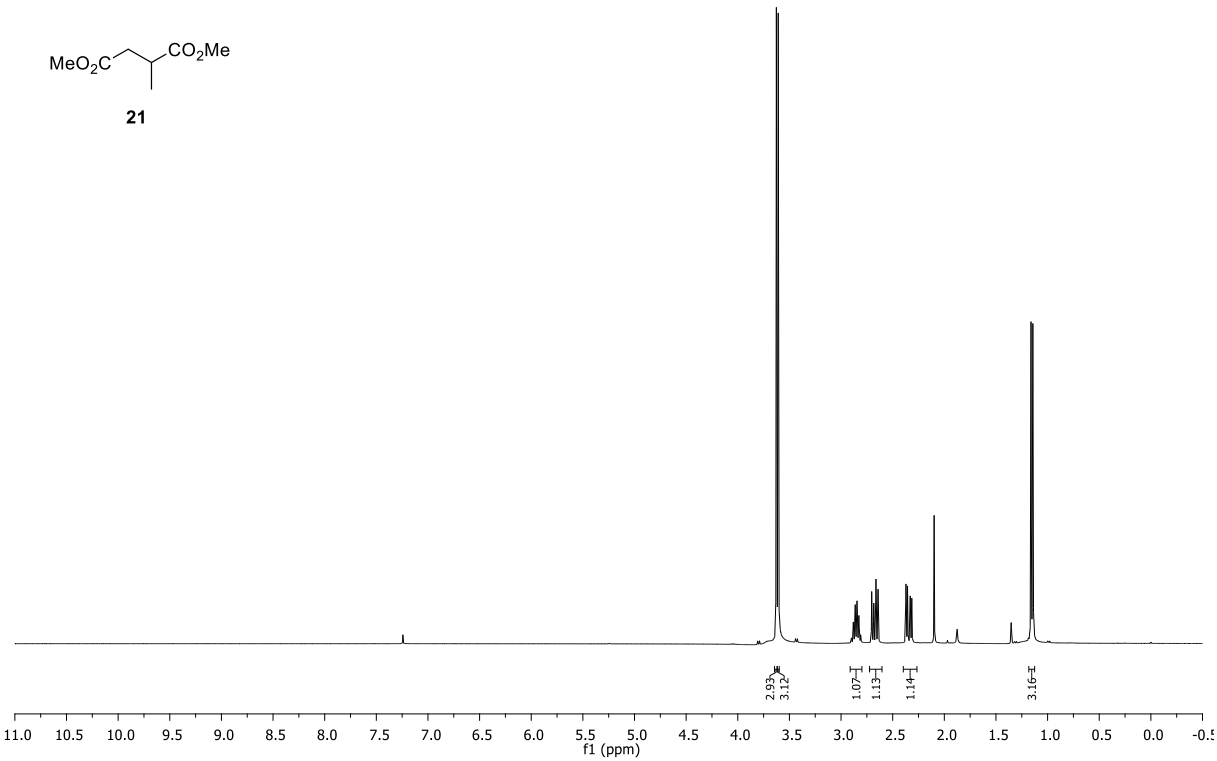
R_f: 0.30 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

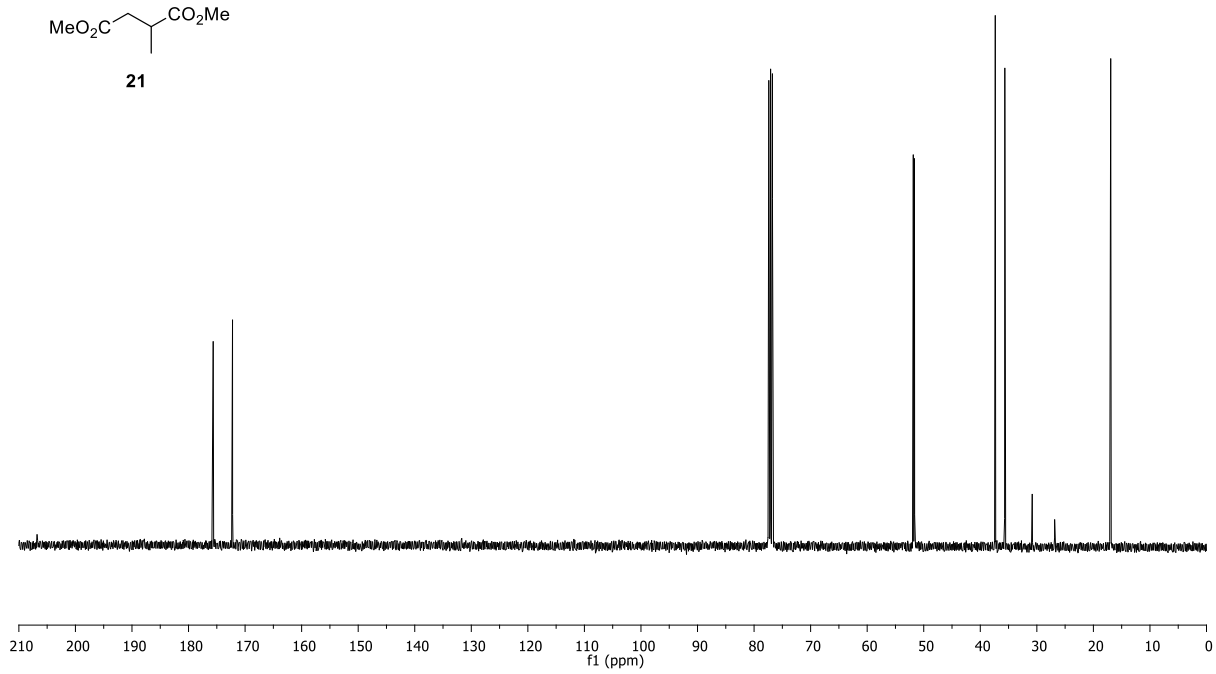
Melting point: Ambient temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.63 (s, 3H, $RC^1O_2C\underline{H}_3$), 3.61 (s, 3H, $R\text{-}C^4O_2C\underline{H}_3$), 2.94 – 2.78 (m, 1H, $\text{-}C^2\underline{H}(C^{2'}H_3)\text{-}$), 2.67 (m, 1H, diastereotopic $\text{-}C^3\underline{H}_2C^4O_2CH_3\text{-}$), 2.34 (m, 1H, diastereotopic $\text{-}C^3\underline{H}_2C^4O_2CH_3\text{-}$), 1.15 (d, J = 7.2 Hz, 3H, $\text{-}C^2H\text{-}C^{2'}\underline{H}_3$).

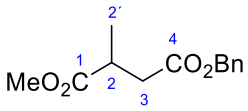
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 175.6 ($\underline{C}^1$), 172.2 ($\underline{C}^4$), 51.9 ($\underline{C}^1\text{-}O\underline{C}H_3$), 51.6 ($\underline{C}^4\text{-}O\underline{C}H_3$), 37.4 ($\underline{C}^3$), 35.7 ($\underline{C}^2$), 16.9 ($C^2\text{-}\underline{C}H_3$).

GC/MS (EI): t_R = 4.78 min, m/z = 129 (50, $[M^{+\bullet}]\text{-}[OMe^{\bullet}]$), 128 (36, $[M^{+\bullet}]\text{-}[HOMe]$), 59 (100, $[CO_2Me^+]$).


MeO2C
CO2Me
21
2.93
3.12
1.07
1.13
1.14
3.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MeO2C
CO2Me
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4-Benzyl 1-methyl 2-methylsuccinate (**22**)



236.27 g/mol

22

Using methyl methacrylate (**11**) (155 µL, 146.0 mg, 1.5 mmol) as the alkene component and degassed BnOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 0.75 mol% [Pd]. Purification by flash column chromatography on SiO_2 (mobile phase: 95:5 CyH:EtOAc) gave the compound as a colourless liquid (176 mg, 0.75 mmol, 51%).

R_f: 0.10 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

Melting point: Ambient temperature.

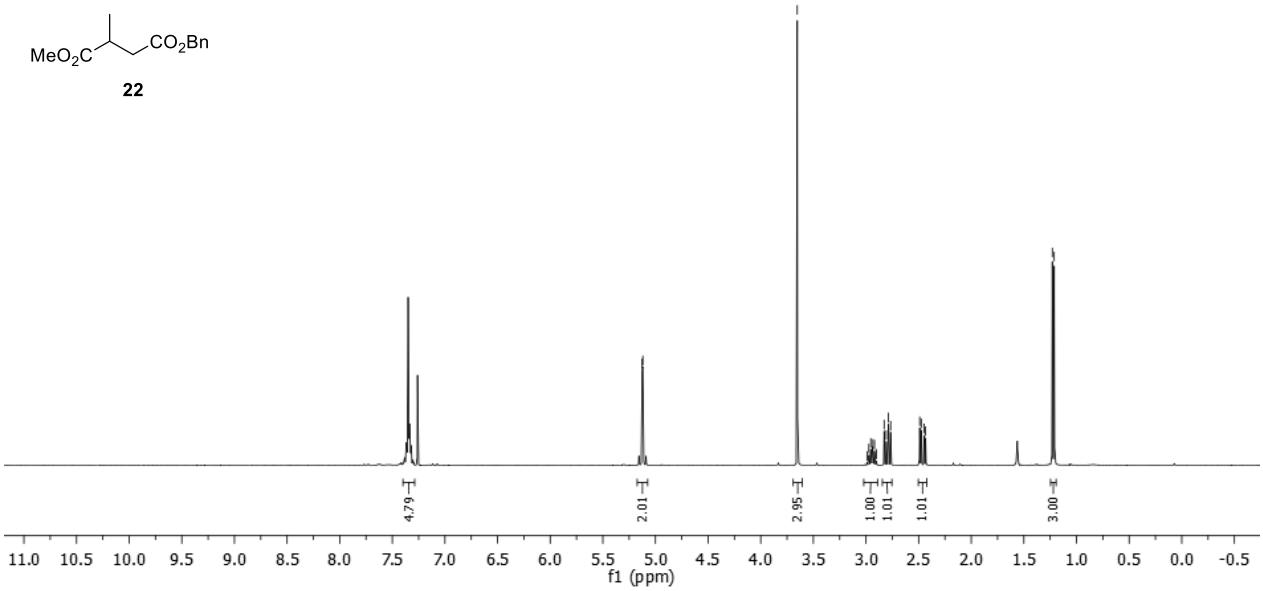
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.29 (m, 5H, Ar<u>H</u>), 5.12 (ABq, $\Delta\delta_{AB}$ = 0.02, *J* = 12.3 Hz, 2H, C<u>H$_2$</u>Ph), 3.65 (s, 3H, RC^{1}O$_2$C<u>H$_3$</u>), 2.95 (sext, *J* = 7.2 Hz, 1H, -C^2<u>H</u>(C$^{2'}$H$_3$)-), 2.80 (m, 1H, diastereotopic C^3<u>H$_2$</u>C^{4}O$_2$Bn-), 2.46 (m, 1H, diastereotopic C^3<u>H$_2$</u>C^{4}O$_2$Bn-), 1.22 (d, *J* = 7.2 Hz, 3H, -C^{2}H-C$^{2'}$<u>H$_3$</u>).

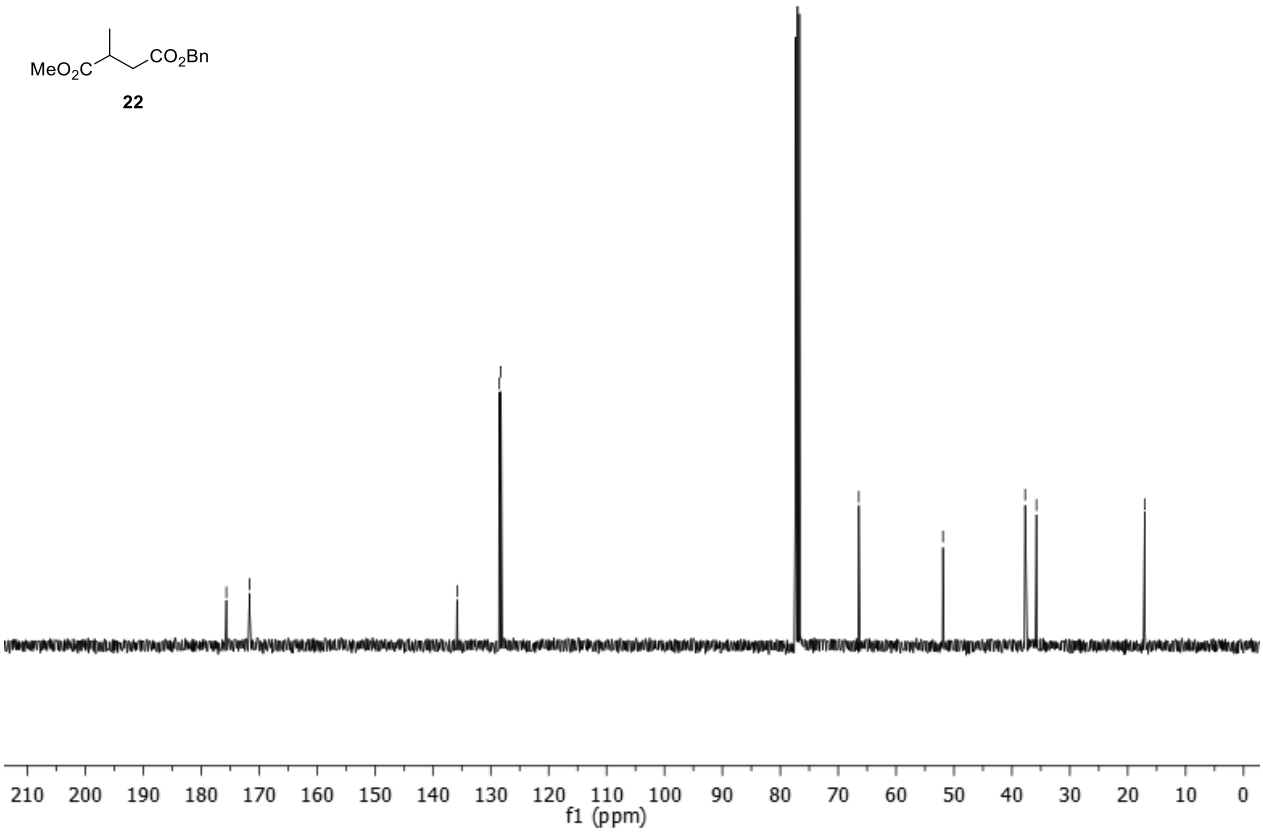
^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 175.7 (<u>C</u>^{1}), 171.6 (<u>C</u>^{4}), 135.8 (Ar<u>C</u>), 128.6 (Ar<u>C</u>), 128.3 (Ar<u>C</u>), 128.3 (Ar<u>C</u>), 66.5 (Ar<u>C</u>H$_2$), 51.9 (C^1-O<u>C</u>H$_3$), 37.7 (<u>C</u>^{3}), 35.8 (<u>C</u>^{2}), 17.0 (C^2-<u>C</u>H$_3$).

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).

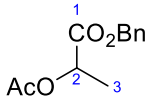
GC-MS: t_R = 8.98 min, m/z = 237 (77, [MH$^+$]), 129 (29, [MH$^+$]-[BnO$^•$]), 91 (100, [MH$^+$]-[C$_7$H$_7^•$]).

HR-MS (APCI): m/z = [MH$^+$] calc. for $C_{13}H_{16}O_4$ 237.1121, found 237.1126.


MeO2C
CO2Bn
22
4.79
2.01
2.95
1.00
1.01
1.01
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


MeO2C
CO2Bn
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Benzyl 2-acetoxypropanoate (**23**)



222.4 g/mol

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 SiO_2 (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]

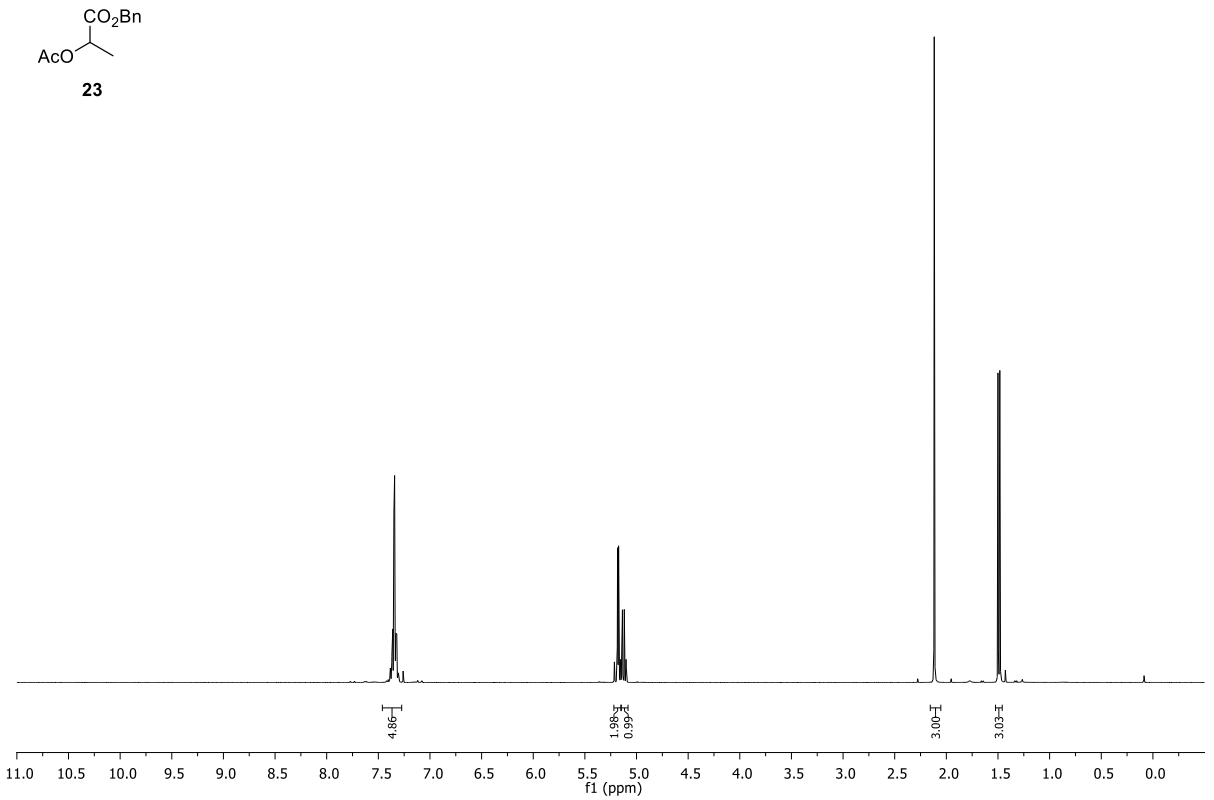
$\boldsymbol{R_f}$: 0.10 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

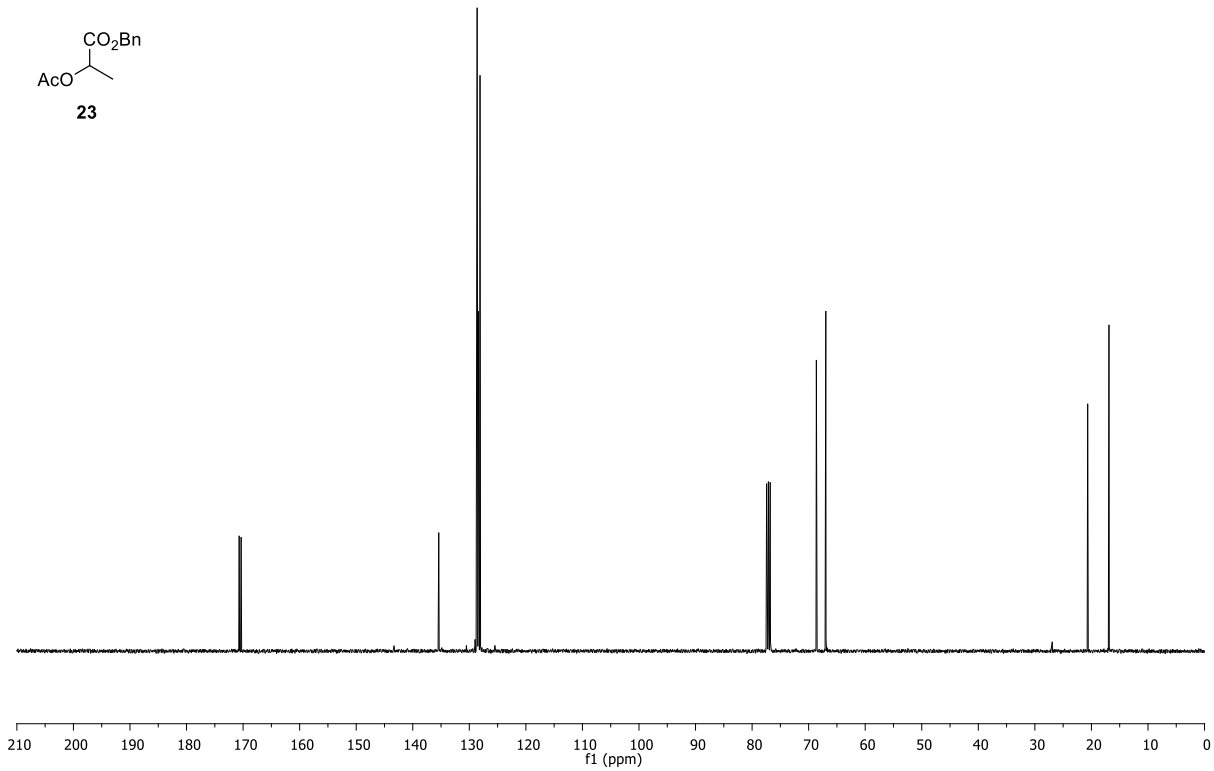
Melting point: Ambient temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 – 7.17 (m, 5H, Ar<u>H</u>), 5.18 (ABq, $\Delta\delta_{AB}$ = 0.03, J = 12.3 Hz, 2H, C<u>H$_2$</u>Ph), 5.13 (q, J = 7.1 Hz, 1H, -C^{2}H-), 2.12 (s, 3H, Acetyl-C<u>H$_3$</u>), 1.49 (d, J = 7.1 Hz, 3H,-C^3<u>H$_3$</u>).

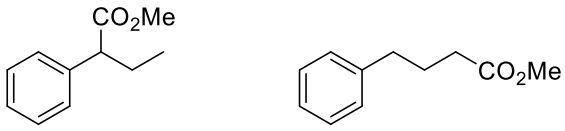
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.7 (<u>C</u>^{1}), 170.4 (Acetyl <u>C</u>=O), 135.4 (Ar<u>C</u>), 128.6 (Ar<u>C</u>), 128.4 (Ar<u>C</u>), 128.1 (Ar<u>C</u>), 68.6 (<u>C</u>^{2}), 66.7 (<u>C</u>H$_2$Ph), 20.7 (Acetyl-<u>C</u>H$_3$), 16.0 (<u>C</u>^{3}).

GC/MS (EI): t_R = 10.16 min, m/z = 162 (30, [$M^{+\bullet}$]-[AcOH]), 91 (80, [$C_7H_7^+$]), 43 (100, [AcO^+]).


CO2Bn
AcO
23
4.86
1.98
0.99
3.00
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CO2Bn
AcO
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 2-Phenylbutanoate (**24**-b) and Methyl 4-Phenylbutanoate (**24**-l) (from β-Methylstyrene **14**)



178.2 g/mol

24-b **24**-l

Using β-methylstyrene (100 µL, 89 mg, 0.750 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 1.0 mol% [Pd]. Purification by flash column chromatography on SiO_2 (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 NMR[1]). The analytical data matched the reported literature data.[28-30]

***R*$_f$** (linear isomer): 0.33 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain).

***R*$_f$** (C^2-branched isomer): 0.42 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain).

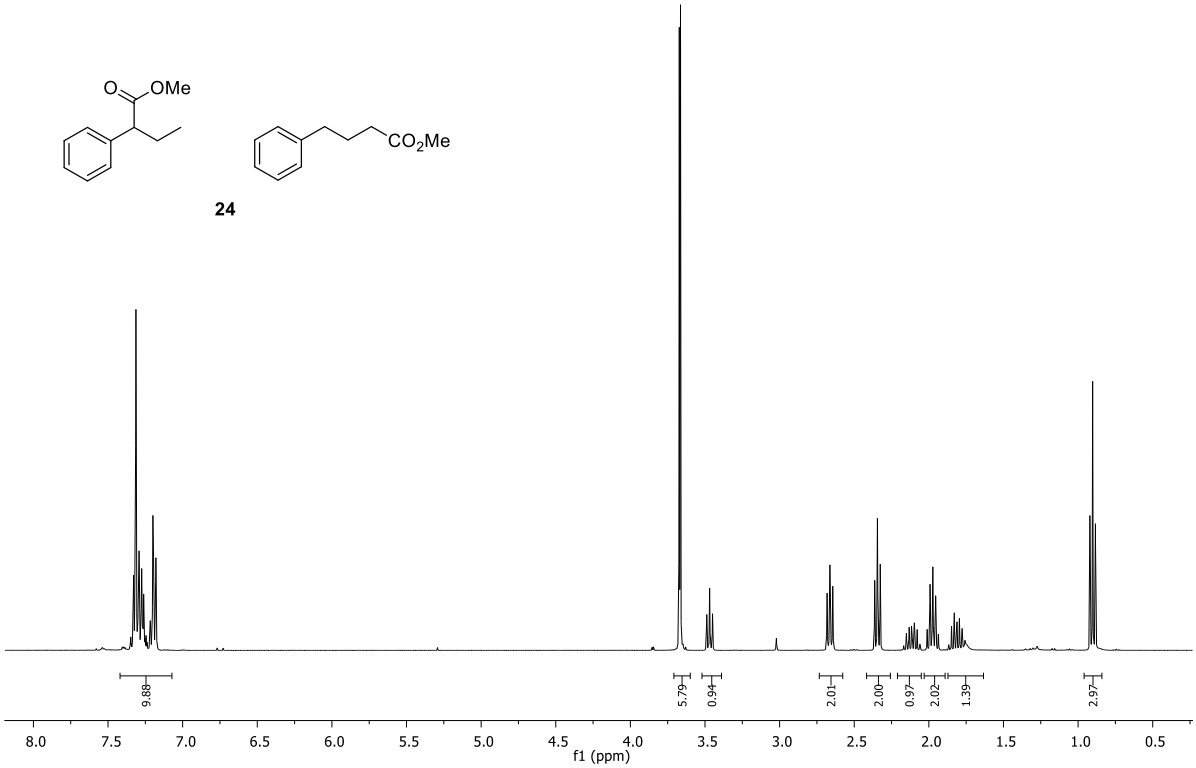
Melting point: Ambient temperature.

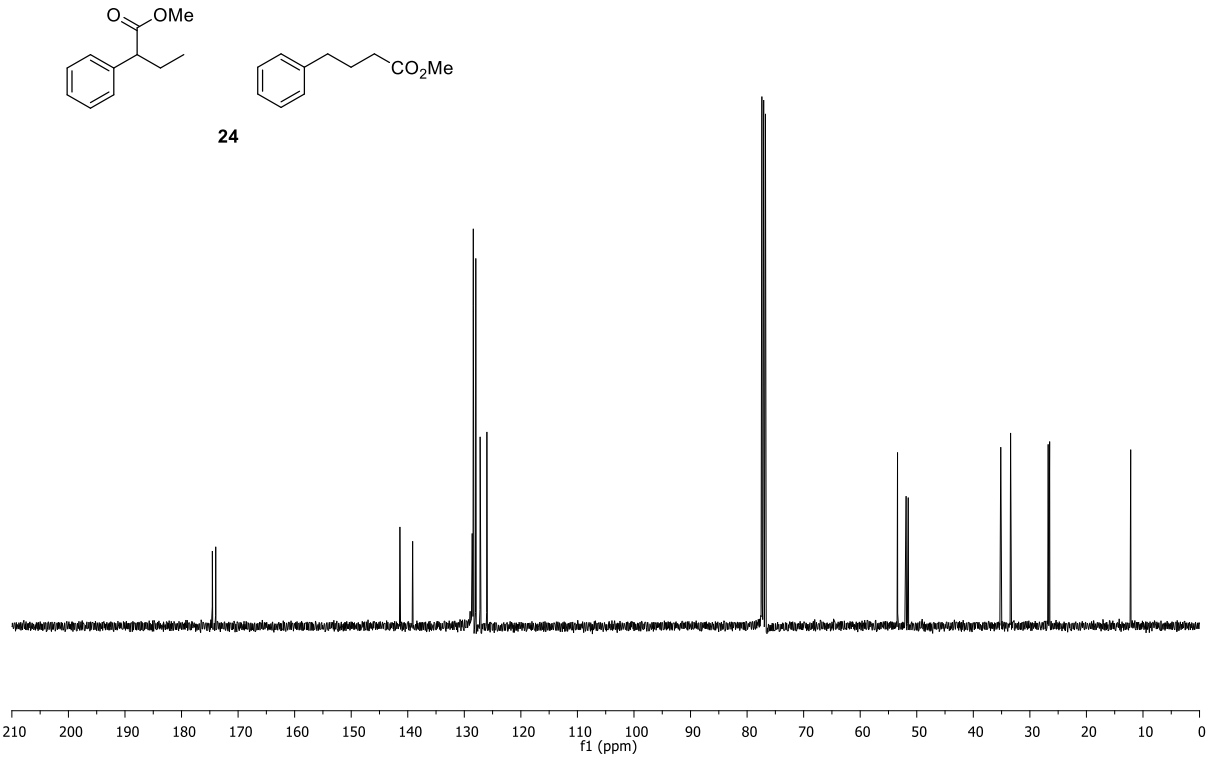
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): signals from linear isomer: 7.44 – 7.09 (m, 5H, Ar<u>H</u>), 3.67 (s, 3H, R-$CO_2C\underline{H}_3$), 2.71 – 2.59 (m, 2H, $ArCH_2CH_2C\underline{H}_2CO_2CH_3$), 2.34 (t, *J* = 7.5 Hz, 2H, $ArC\underline{H}_2CH_2CH_2CO_2CH_3$), 2.02 – 1.88 (m, 2H, $ArCH_2C\underline{H}_2CH_2CO_2CH_3$); signals from C2-branched isomer: 3.47 (t, *J* = 7.7 Hz, 1H, $ArC\underline{H}(CO_2Me)CH_2CH_3$), 2.18 – 2.05 (m, 1H, diastereotopic $ArCH(CO_2Me)C\underline{H}_2CH_3$), 1.81 (m, 1H, diastereotopic $ArCH(CO_2Me)C\underline{H}_2CH_3$), 0.90 (t, *J* = 7.4 Hz, 3H, $ArCH(CO_2Me)CH_2C\underline{H}_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 174.0 (<u>C</u>=O), 141.4 (Ar<u>C</u>), 128.5 (Ar<u>C</u>), 128.4 (Ar<u>C</u>), 126.0 (Ar<u>C</u>), 51.6 (R-$CO_2\underline{C}H_3$), 35.1 ($ArCH_2CH_2\underline{C}H_2CO_2CH_3$), 33.4 ($Ar\underline{C}H_2CH_2CH_2CO_2CH_3$), 26.5 ($ArCH_2\underline{C}H_2CH_2CO_2CH_3$); signals from C2-branched isomer: 174.6 (<u>C</u>=O), 139.1 (Ar<u>C</u>), 128.6 (Ar<u>C</u>), 128.0 (Ar<u>C</u>), 127.2 (Ar<u>C</u>), 53.4 (R-$CO_2\underline{C}H_3$), 51.9 ($Ar\underline{C}H(CO_2Me)CH_2CH_3$), 26.5 ($ArCH(CO_2Me)\underline{C}H_2CH_3$), 12.2 ($ArCH(CO_2Me)CH_2\underline{C}H_3$)

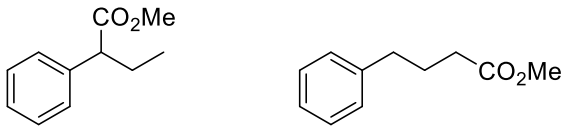
GC/MS (EI): t_R = 7.41 min (C2-branched), m/z = 178 (20, $[M^{+\bullet}]$), 163 (2, $[M^{+\bullet}]$-$[Me^{\bullet}]$), 150 (8, $[M^{+\bullet}]$-[CO]-$[OMe^{\bullet}]$); t_R = 8.58 min (linear), m/z = 178 (40, $[M^{+\bullet}]$), 147 (40, $[M^{+\bullet}]$ - $[OMe^{\bullet}]$), 146 (40, $[M^{+\bullet}]$-[MeOH]).

[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.


O
OMe
CO2Me
24
9.88
5.79
0.94
2.01
2.00
0.97
2.02
1.39
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
OMe
CO2Me
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Methyl 2-Phenylbutanoate (**24**-b) and Methyl 4-Phenylbutanoate (**24**-l) (from Allylbenzene **13**)



178.2 g/mol

24-b **24**-l

Using allylbenzene (130 µL, 118 mg, 0.750 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO_2 (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-dioxoisoindolin-2-yl)propanoate (**25**-b) and Methyl 2-(1,3-dioxoisoindolin-2-yl)propanoate (**25**-l)

233.2 g/mol

25-b **25**-l

Using *N*-vinylphthalimide (**15**) (173 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) 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 SiO_2 (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]

R_f: 0.39 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

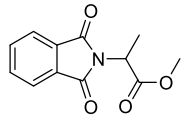
Melting point: 60 °C.

^{1}H NMR (400 MHz, $CDCl_3$) 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, $NCH_2CH_2CO_2CH_3$), 3.60 (s, 3H, $NCH_2CH_2CO_2CH_3$), 2.65 (t, J = 7.2 Hz, 2H, $NCH_2CH_2CO_2CH_3$); minor signals from branched regioisomer: 4.97 (q, J = 7.3 Hz, 1H, $NCH(CO_2Me)CH_3$), 3.74 (s, 3H, $NCH(CO_2CH_3)CH_3$), 1.69 (d, J = 7.3 Hz, 3H, $NCH(CO_2CH_3)CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.2 (Ester C=O), 167.9 (Imide C=O), 134.0 (ArC), 132.0 (ArC), 123.3 (ArC), 51.9 ($NCH_2CH_2CO_2CH_3$), 33.7 ($NCH_2CH_2CO_2CH_3$), 32.7 ($NCH_2CH_2CO_2CH_3$); 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 ($NCH(CO_2CH_3)CH_3$), 47.4 ($NCH(CO_2CH_3)CH_3$), 15.3 ($NCH(CO_2CH_3)CH_3$).

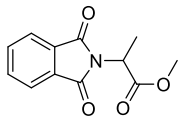
GC-FID (50-280M12, from crude): t_R = 7.77 min (branched), t_R = 8.12 (linear).

GC/MS (EI): t_R = 12.56 min (branched), m/z = 233 (2, $[M^{+\bullet}]$), 202 (1, $[M^{+\bullet}]$-$[OMe^{\bullet}]$), 174 (100, $[M^{+\bullet}]$-$[OMe^{\bullet}]$-[CO]), t_R = 13.45 min (linear), m/z = 233 (15, $[M^{+\bullet}]$), 202 (8, $[M^{+\bullet}]$-$[OMe^{\bullet}]$), 173 (100, $[M^{+\bullet}]$-$[OMe^{\bullet}]$-[CO]), 160 (100, $[PhthalN^{+}=CH_2]$).



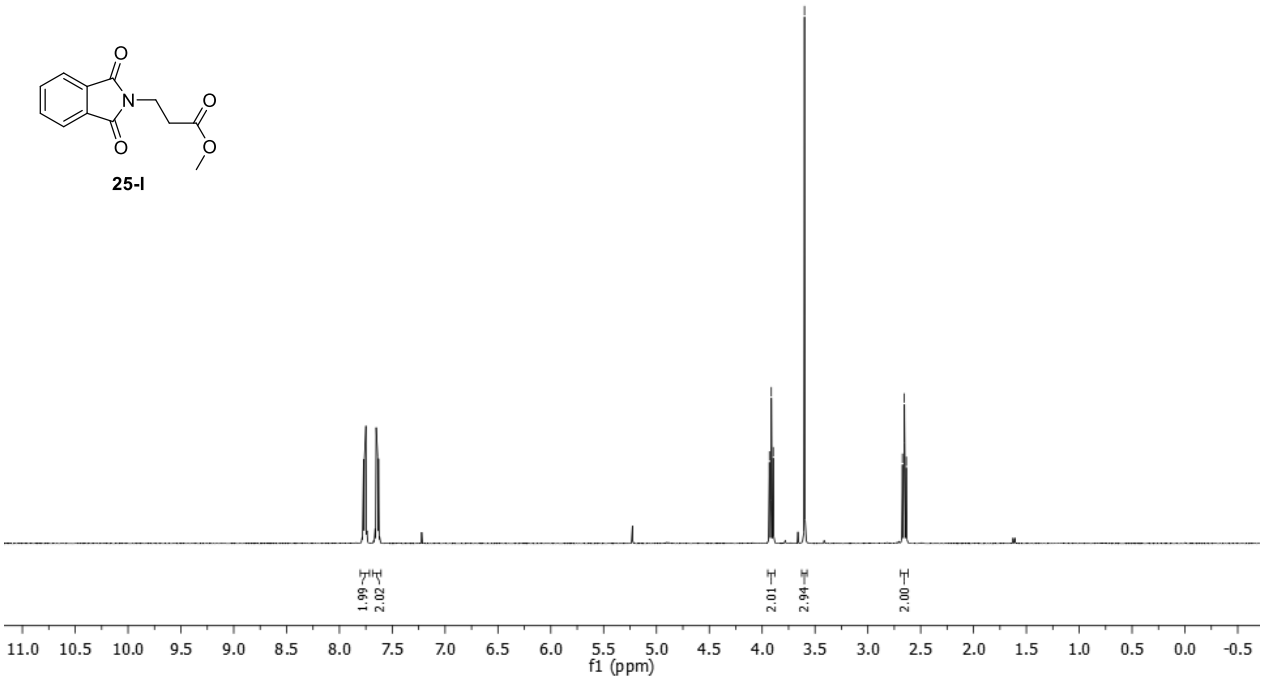
25-b

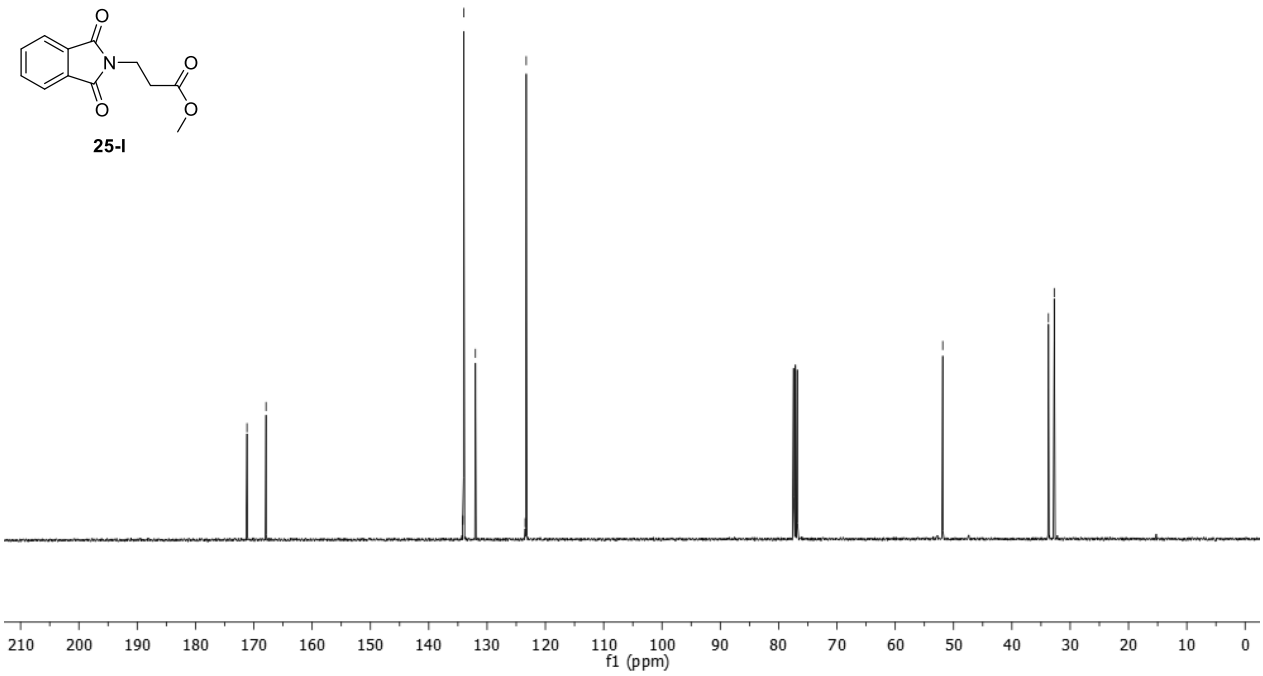
2.01
2.05
1.00
3.01
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



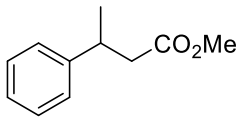
25-b

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


25-I
1.99
2.02
2.01
2.94
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


25-I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 3-Phenylbutanoate (**26**) (from α-Methylstyrene **16**)



178.2 g/mol

26

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 N_2) as the alcohol component, general procedure **A** was employed at RT or 50 °C (in DCE), respectively. Purification by flash column chromatography on SiO_2 (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]

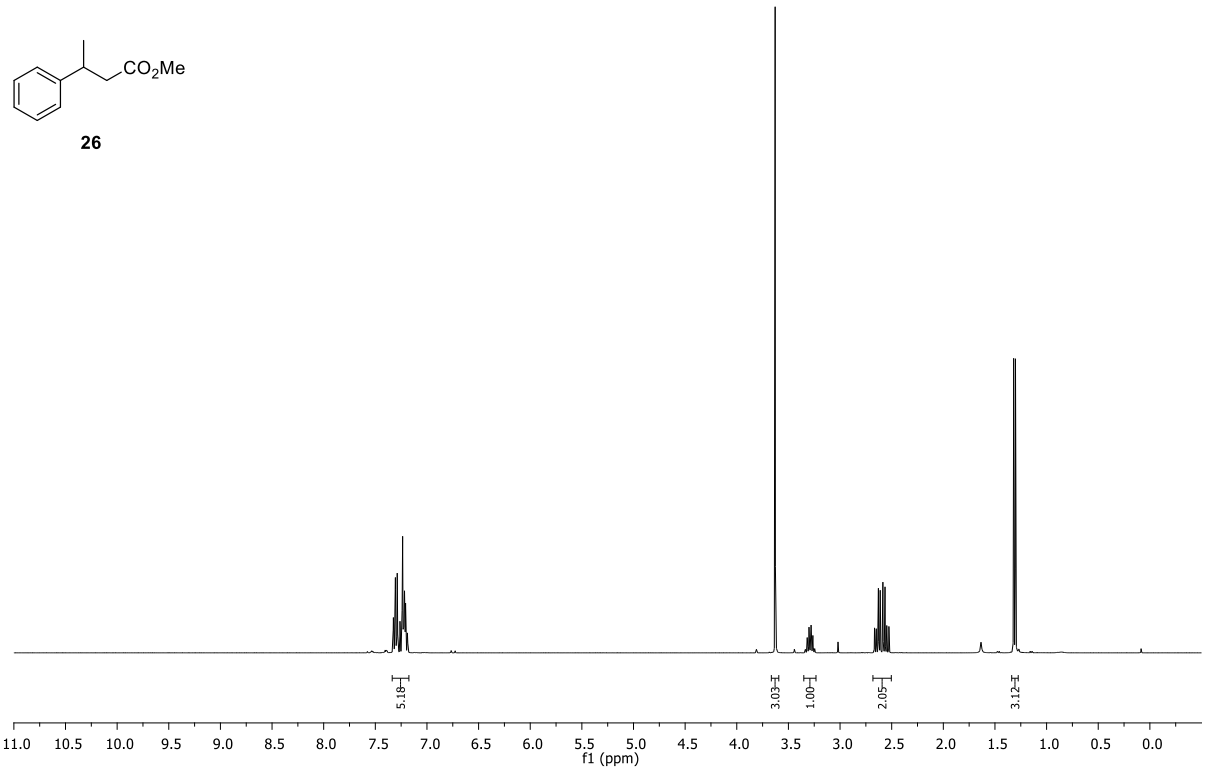
$\boldsymbol{R_f}$: 0.48 (mobile phase 9:1 CyH:EtOAc, $KMnO_4$ stain)

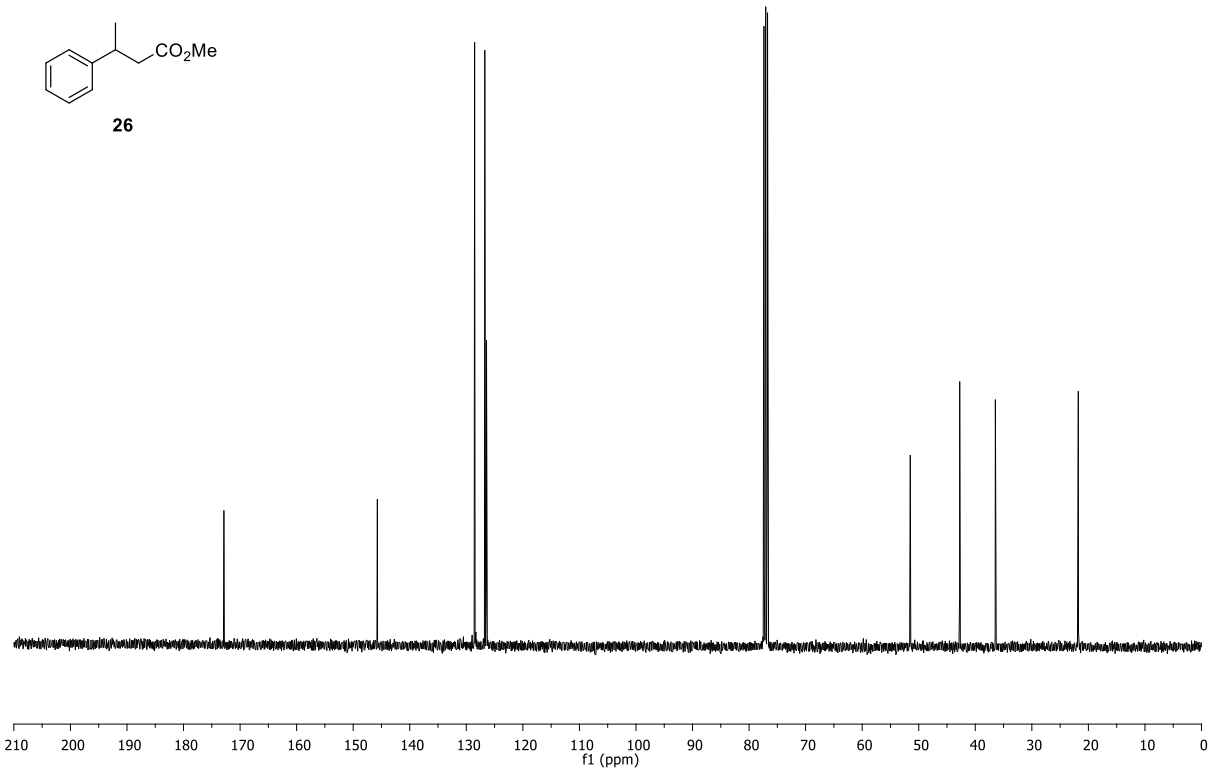
Melting point: Ambient temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.16 (m, 5H, ArH), 3.63 (s, 3H, R-CO_2CH_3), 3.34 – 3.24 (m, 1H, ArCH(Me)CH_2CO_2Me), 2.60 (m, 2H, ArCH(Me)CH_2CO_2Me), 1.31 (d, J = 7.0 Hz, 3H, ArCH(CH_3)CH_2CO_2Me).

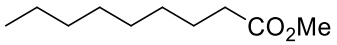
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.9 (ArCH(Me)CH_2CO_2Me), 145.7 (ArC), 128.5 (ArC), 126.7 (ArC), 126.4 (ArC), 51.5 (ArCH(Me)$CH_2CO_2CH_3$), 42.8 (ArCH(Me)CH_2CO_2Me), 36.5 (ArCH(Me)CH_2CO_2Me), 21.8 (ArCH(CH_3)CH_2CO_2Me).

GC/MS (EI): t_R = 7.80 min, m/z = 178 (20, [$M^{+\bullet}$]), 147 (5, [$M^{+\bullet}$]-[$OMe^{\bullet}$]), 105 (100, [$C_8H_9^+$]).


CO2Me
26
5.18
3.03
1.00
2.05
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CO2Me
26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl nonanoate (**27**) (from 1-octene **17**)



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 N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO_2 (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, $KMnO_4$ stain)

Melting point: Ambient temperature.

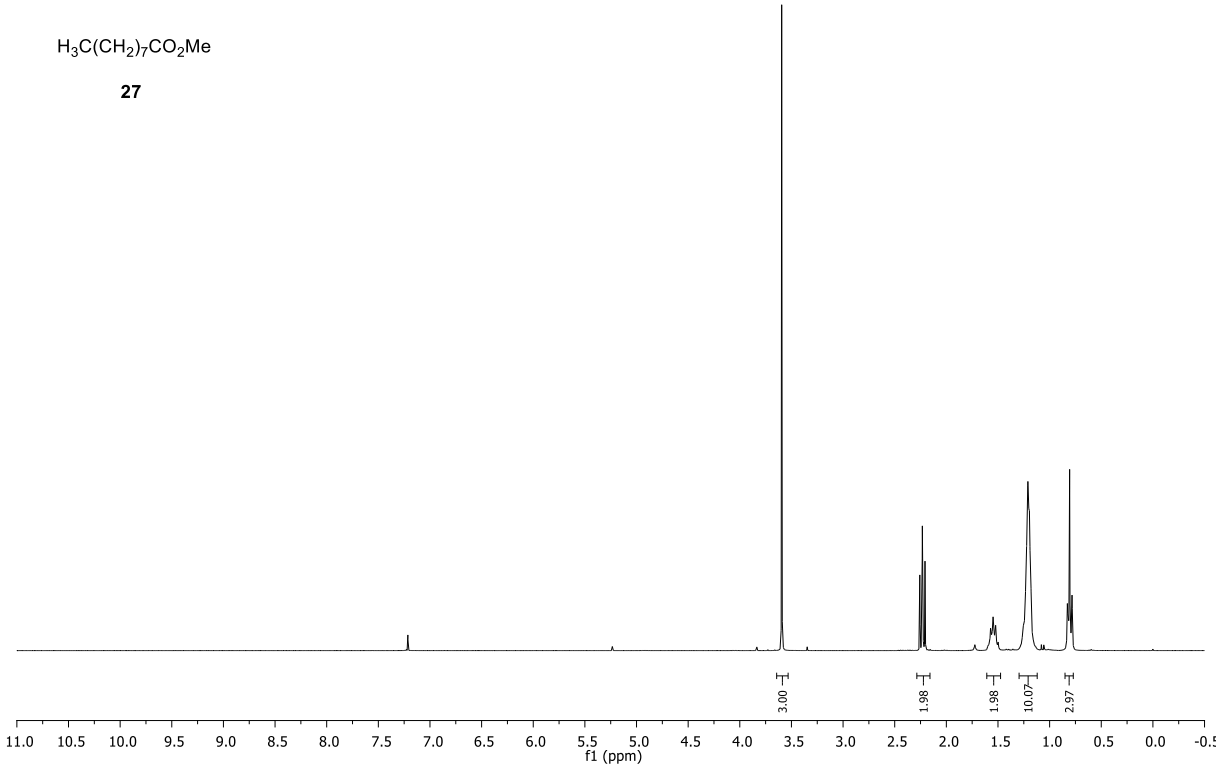
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.59 (s, 3H, $RCO_2C\underline{H_3}$), 2.23 (t, J = 7.5 Hz, 2H, $RC\underline{H_2}$-CO_2Me), 1.55 (sext, J = 7.5 Hz, 2H, R-$C\underline{H_2}$-CH_2-CO_2Me), 1.20 (s br, 10H, Alkane-$C\underline{H_2}$), 0.87 – 0.75 (t, J = 6 Hz, 3H, terminal CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 174.3 (C1), 51.4 (R-$CO_2\underline{C}H_3$), 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 min, m/z = 172 (2, [$M^{+\bullet}$]).

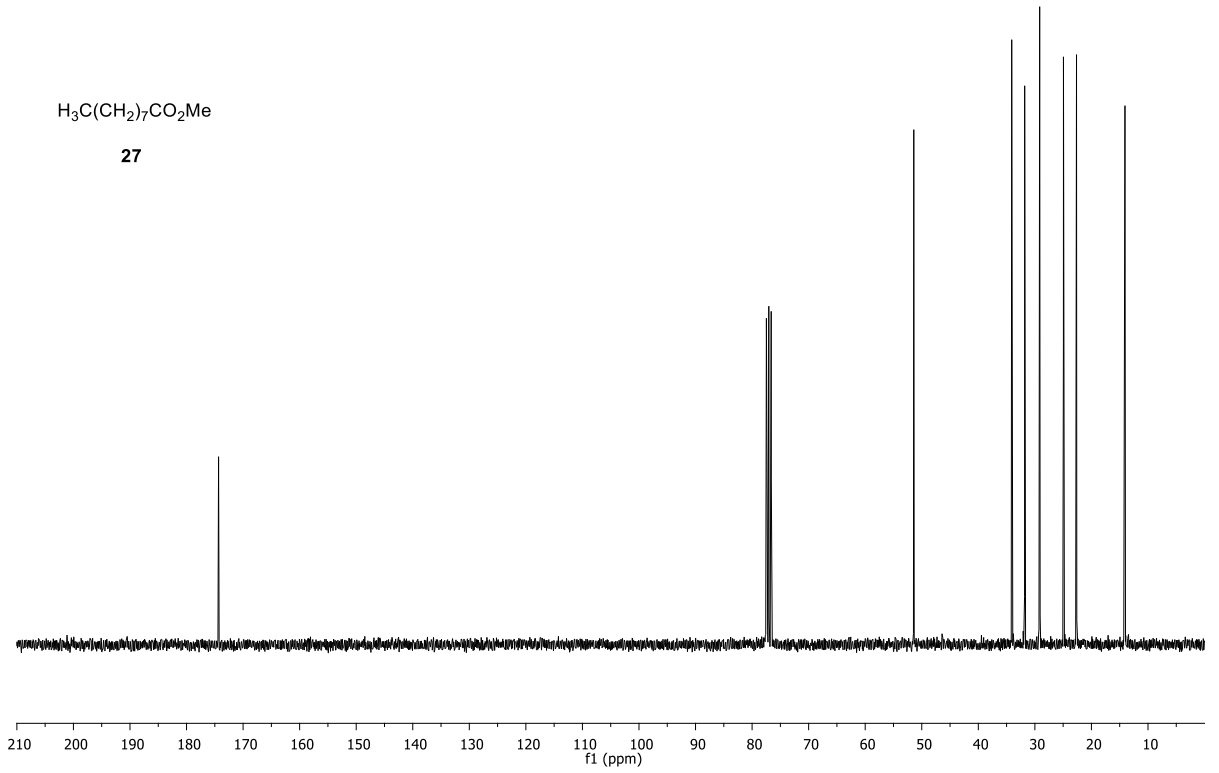
$H_3C(CH_2)_7CO_2Me$

27

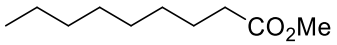


$H_3C(CH_2)_7CO_2Me$

27



Methyl nonanoate (**27**) (from 2-octene **18**)



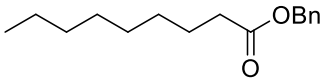
172.3 g/mol

27

Using 2-octene (155 µL, 111 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO_2 (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**)



248.37 g/mol

28

Using 1-octene (160 µL, 113 mg, 1.00 mmol) as the alkene component and degassed BnOH (250 µL; stored under N_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_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.[35]

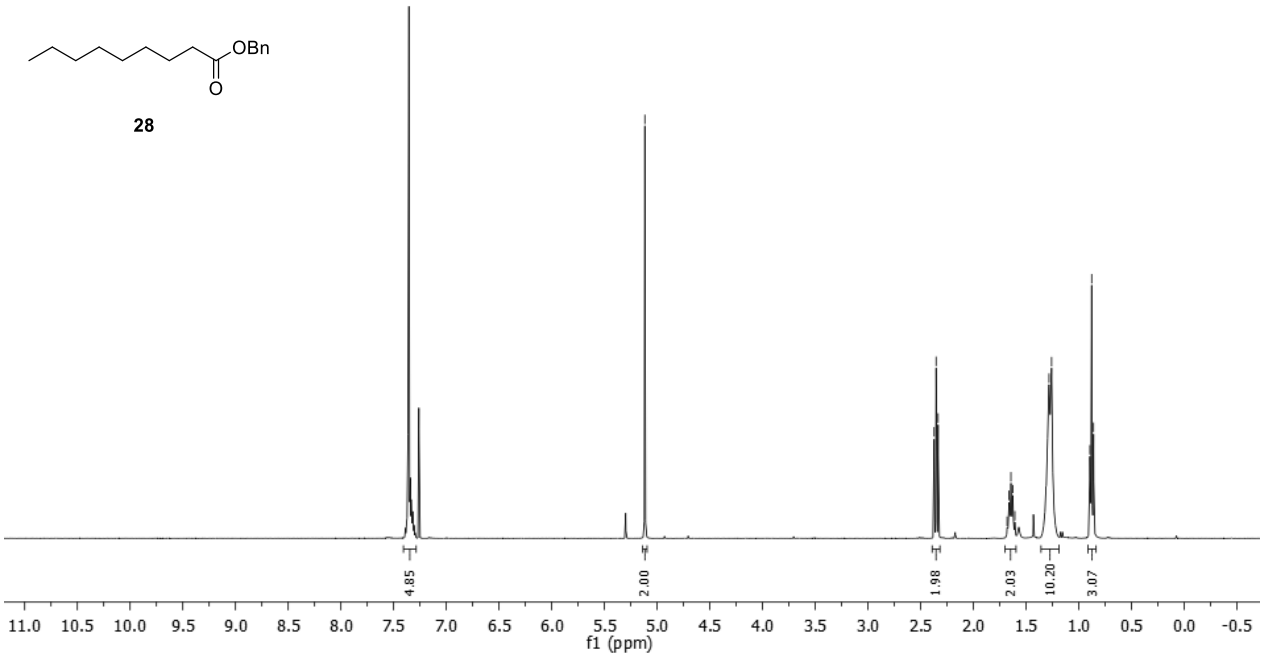
R_f: 0.40 (mobile phase 95:5 CyH:EtOAc, $KMnO_4$ stain)

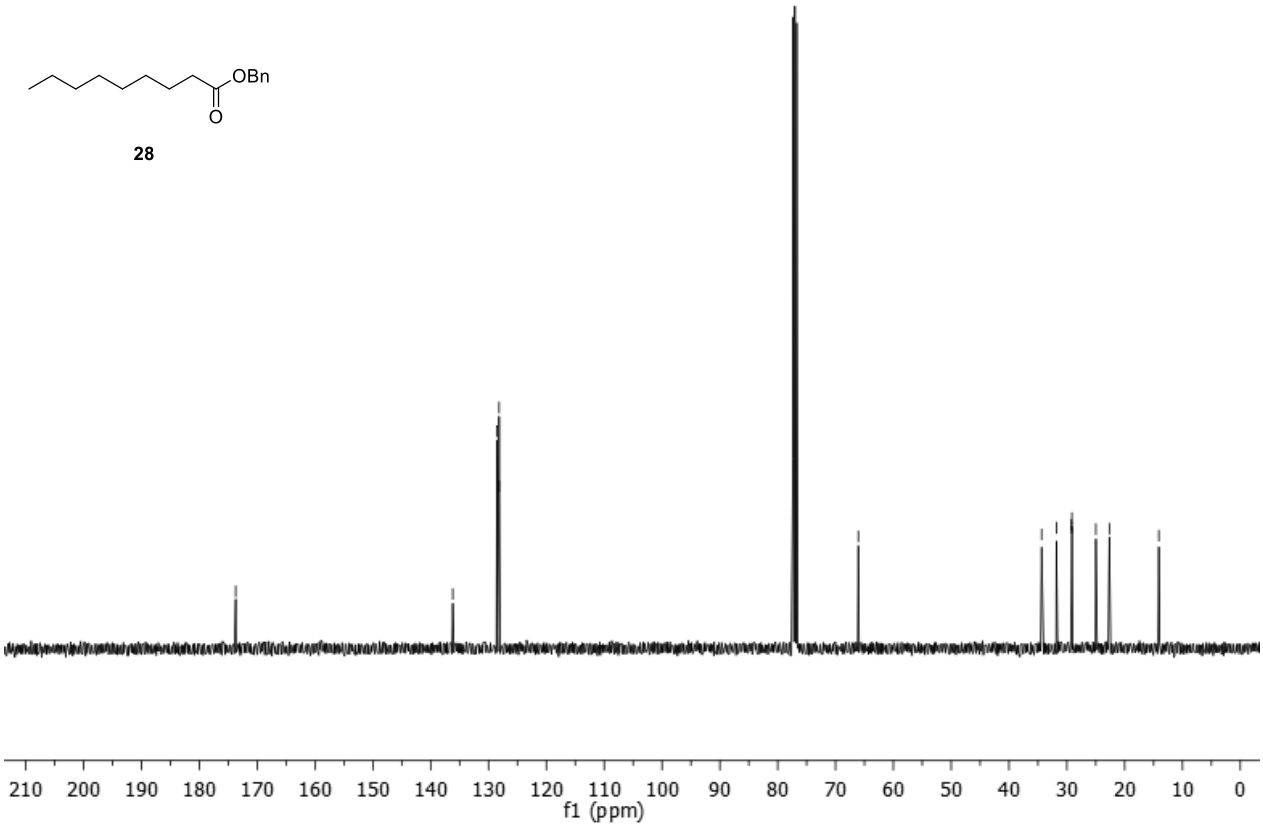
Melting point: Ambient temperature.

^{1}H-NMR (400 MHz, $CDCl_3$) $\delta_{(}$ppm): 7.41 – 7.29 (m, 5H, Ar$\underline{H}$), 5.12 (s, 2H, C$\underline{H_2}$Ph), 2.35 (t, *J* = 7.6 Hz, 2H, PhCH$_2$OCOC$\underline{H_2}$-R), 1.64 (quin, *J* = 7.6 Hz, 2H, ArCH$_2$OCOCH$_2$C$\underline{H_2}$-R), 1.36 – 1.19 (m, 10H, remaining C$\underline{H_2}$), 0.88 (t, *J* = 6.9 Hz, 3H,terminal C$\underline{H_3}$).

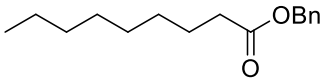
^{13}C-NMR (101 MHz, $CDCl_3$) $\delta_{(}$ppm): 173.7 (C=O), 136.2 (Ar$\underline{C}$), 128.6 (Ar$\underline{C}$), 128.2 (Ar$\underline{C}$), 128.2 (Ar$\underline{C}$), 66.1 (R-$\underline{C}$H$_2$Ph), 34.4 ($\underline{C}$H$_2$), 31.8 ($\underline{C}$H$_2$), 29.2 ($\underline{C}$H$_2$), 29.2 ($\underline{C}$H$_2$), 29.1 ($\underline{C}$H$_2$), 25.0 ($\underline{C}$H$_2$), 22.7 ($\underline{C}$H$_2$), 14.1 (terminal $\underline{C}$H$_3$).

GC-MS: t_R = 9.16 min, m/z = 266 (60, [MNH$_4^+$]), 249 (17, [MH$^+$]), 91 (100, [MH$^+$]-[BnO$^\bullet$]).


OBn
O
28
4.85
2.00
1.98
2.03
10.20
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


OBn
O
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Benzyl nonanoate (**28**) (from (*E*)-2-octene **18**)



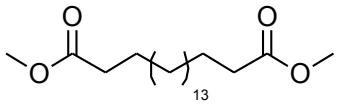
248.37 g/mol

28

Using 2-octene (155 µL, 111 mg, 1.00 mmol) as the alkene component and degassed BnOH (250 µL; stored under N_2) 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 SiO_2 (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**)



356.6 g/mol

29

Using methyl oleate (340 µL, 297 mg, 1.00 mmol) as the alkene component and dist. MeOH (250 µL; stored under N_2) as the alcohol component, general procedure **A** was employed using 0.5 mol% [Pd]. Purification by flash column chromatography on SiO_2 (mobile phase: 95:5 CyH:EtOAc) gave the compound bright yellow liquid (57 mg, 0.16 µmol, 16%).

R_f: 0.18 (CyH/ EtOAc 95:5)

m.p.: 58.5 °C (lit: 56-58°C)[36]

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.66 (s, 6H, R-$CO_2C\underline{H_3}$), 2.30 (t, J = 7.3 Hz, 4H, MeO_2C-$C\underline{H_2}$-R), 1.67 – 1.56 (quin, J = 7.3 Hz, 4H, MeO_2C-$CH_2C\underline{H_2}$-R), 1.35 – 1.20 (m, 26H, remaining $\underline{CH_2}$).

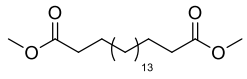
^{13}C-NMR (75 MHz, CDCl3) δ (ppm): 174.4 (C=O), 51.5 ($RCO_2\underline{C}H_3$), 34.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 25.0 (CH_2).

FT-IR (ATR) v (cm^{-1}): 3024 (w, br), 2918 (s, sh), 2850 (m, sh), 1736 (s, sh), 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): t_R = 10.50 min.

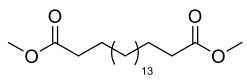
GC-MS: t_R = 14.22 min, m/z = 357 (100, [MH^+]), 325 (22, [MH^+]-[$^\bullet$OMe]), 279 (7, [MH^+]-[$^\bullet CO_2Me$].

HR-MS (APCI): m/z = [MH^+] calc. for $C_{21}H_{40}O_4$ 357.2999, found 357.3004.



29

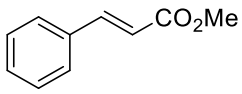
5.99
4.00
4.13
26.55
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



29

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(*E*)-Methyl cinnamate (**30**)



162.2 g/mol

30

Using ethinylbenzene (**20**) (80 µL, 102 mg, 0.750 mmol) as the alkyne component and dist. MeOH (250 µL; stored under N_2) 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 SiO_2 (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]

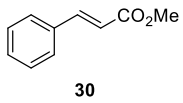
***R*$_f$**: 0.26 (mobile phase 8:2 CyH:EtOAc, $KMnO_4$ stain)

Melting point: 34 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, *J* = 16.0 Hz, 1H, ArCHC<u>H</u>CO_2Me), 7.55 - 7.51 (m, 2H, Ar<u>H</u>), 7.41 – 7.37 (m, 3H, Ar<u>H</u>), 6.45 (d, *J* = 16.0 Hz, 1H, ArC<u>H</u>$CHCO_2$Me), 3.81 (s, 3H, $ArCHCHCO_2C\underline{H_3}$).

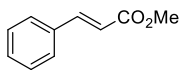
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 167.5 (<u>C</u>=O), 144.9 (ArC<u>H</u>$CHCO_2$Me), 134.4 (*ipso*-ArC), 130.3 (*meta*-ArC), 128.9 (*ortho*-ArC), 128.1 (*para*-ArC), 117.8 (ArCH<u>C</u>HCO_2Me), 51.7 ($ArCHCHCO_2\underline{C}H_3$).

GC/MS (EI): t_R = 8.60 min, m/z = 162 (49, [$M^{+\bullet}$]), 131 (100, [$M^{+\bullet}$]-[$OMe^{\bullet}$]), 103 (61, [$M^{+\bullet}$]-[$OMe^{\bullet}$]-[CO]).


CO2Me

30

1.06
2.08
2.99
1.00
2.91
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CO2Me

30

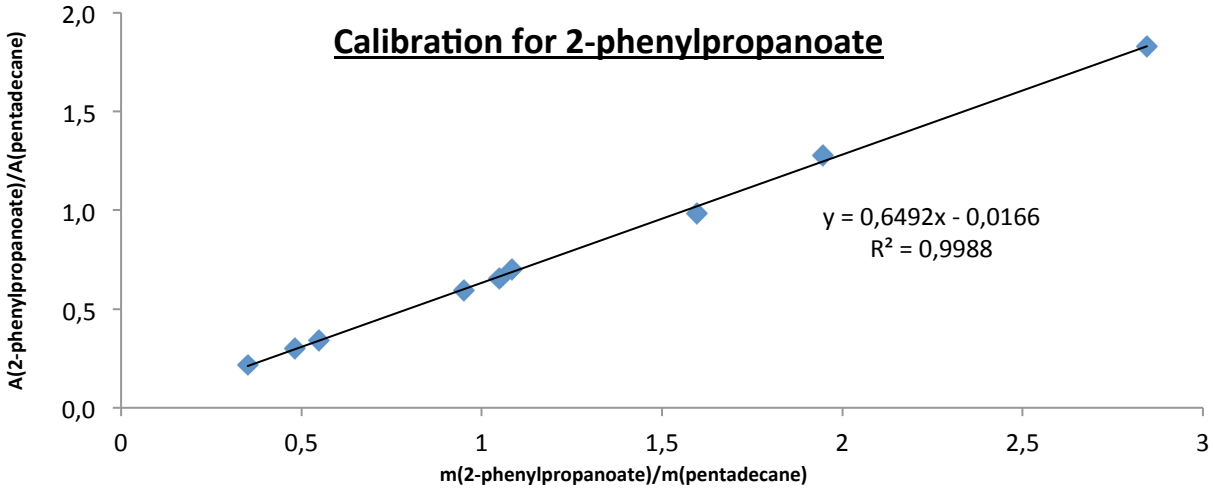
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

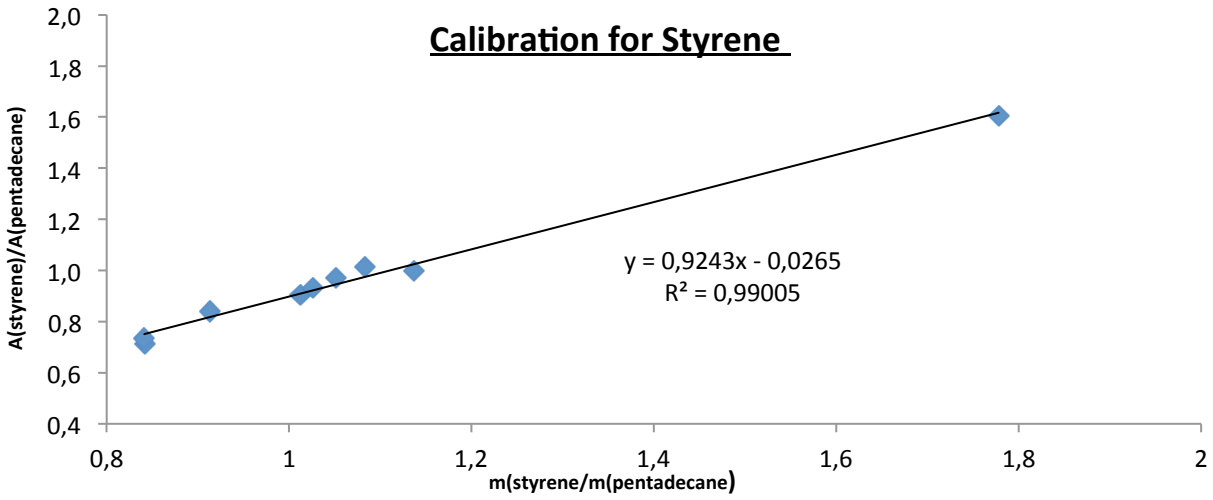
3 Calibration data for quantitative instrumental analysis

3.1 Calibration data for quantitative GC analysis

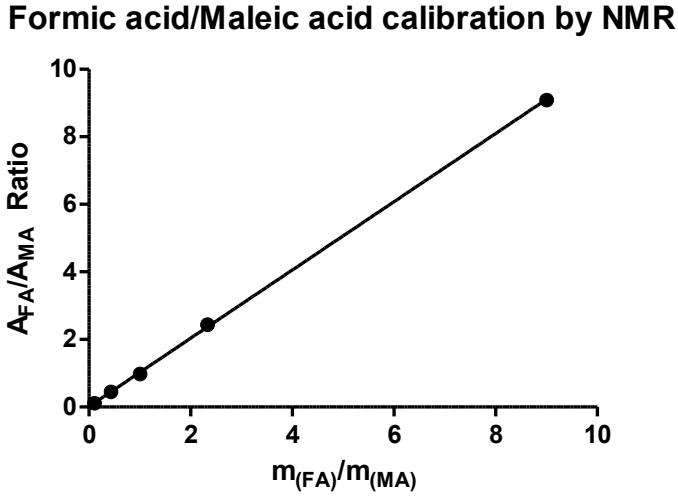
Calibration for Styrene and methyl 2-phenylpropanoate by GC-FID, Internal standard: *n*-Pentadecane (15.4.15)

Entry	m(Styrene) / mg	A(Styrene)	m(2-Phenyl-propanoate) / mg	A(2-Phenyl-propanoate)	m(Pentadecane) / mg	A(Penta-decane)
A1	16.6	11977.5	13.9	7084.9	14.6	11971.6
A2	16.7	12886.9	17.3	9356.4	16.5	14260.2
A3	16.4	12139.9	16.9	8725.9	15.6	12494.6
B1	16	11611.8	25.6	13223.5	9	7232.6
B2	11.8	8989.8	21.2	11328.9	10.9	8865.3
B3	9.6	6450.7	18.2	8922.4	11.4	9063.3
C1	23.1	17151.5	7.9	3974.5	22.5	18418.3
C2	19.6	14648	11.2	6023.8	23.3	19959.8
C3	21	15226.8	12.6	6167.8	23	18134.8





3.2 Calibration data for quantitative NMR analysis



Slope :1,010 ± 0,006852

R square: 0,9999

Mass Ratio	Area Ratio
0.111	0.110
0.429	0.446
1.000	0.980
2.330	2.440
9.000	9.090

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