Supporting information

In Tandem or Alone: a Remarkably Selective Transfer Hydrogenation of Alkenes Catalyzed by Ruthenium Olefin Metathesis Catalysts

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1. General information

All reactions were carried out in a pressure flask equipped with rotaflo stopcock under argon atmosphere using anhydrous solvents. THF (Aldrich) was dried by heating over sodium benzophenone ketyl and distilled under argon. $^1$H and $^{13}$C NMR spectroscopic data were recorded on Varian Mercury 400 MHz or Agilent 400 MHz spectrometer at room temperature. NMR spectra were calibrated to the solvent residual signals of CDCl$_3$ or TMS. TLC was performed on Sigma Aldrich plates 0.75 mL/g pore volume with fluorescence indicator 254 nm. Column chromatography was carried out using Fluka silica gel (pore size 60 Å, 230-400 mesh size, 40-63 µm partial mesh size) and mixture of distilled ethyl acetate and cyclohexane as an eluent. Calibrating curves and all GC analysis were determined using Clarus 680 spectrometer equipped with a FID detector. MS (ESI) spectra were recorded on SYNAPT G2-S HDMS (Waters). Unless otherwise stated, all chemicals were purchased from Aldrich, Across, TCI or Alfa Aesar and were used without further purification.

2. Synthesis of model substrates

Dienes 1a, 1b and 1d were commercially available or were synthesized by alkylation reaction of corresponding C-H acids following the described procedures. Diene 1c was prepared by Krapcho decarboxylation reaction. Diene 4l was synthesized by Steglich esterification reaction. Olefins 3g, 3h, 3i and 3l were commercially available and were used in transfer hydrogenation reaction without further purification. Cyclic olefins 3a-3e and 3j-3k were synthesized from corresponding dienes by ring closing metathesis reaction according to literature.

Synthesis of dienes 1b, 1c and 1d

Ethyl 1,1-diallyl-1-(phenylsulfonyl)acetate (1b). Compound was prepared according to the literature. Analyses were in accordance with previously reported.$^1$

2-allyl-1-phenylpent-4-en-1-one (1c). Commercially available ethyl 2,2-diallylbenzoylacetae (8.17 g, 30 mmol), LiCl (2.54 g, 60 mmol) and distilled water (50 µl) and DMSO (30 mL) were placed in a microwave tube. The tube
was sealed and the reaction mixture was heated using microwave irradiation at 180 °C for 2 h. After reaction was completed (TLC monitoring) the reaction mixture was poured into brine (400 ml) and extracted with DCM (7x). Collected organic layers were washed with brine, dried over MgSO₄, filtered and evaporated. The crude product was purified using column chromatography to afford ketone 1c (3.15 g, 52%). Analyses were in accordance with previously reported.²

NMR (400 MHz, CDCl₃) δ = 8.00-7.91 (m, 2H), 7.62-7.53 (m, 1H), 7.51-7.43 (m, 2H), 5.74 (ddt, J = 17.0, 10.1, 7.0 Hz, 2H), 5.14-4.88 (m, 4H), 3.72-3.43 (m, 1H), 2.61-2.46 (m, 2H), 2.37-2.23 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ = 202.9, 137.2, 135.5, 133.1, 128.8, 128.4, 117.1, 45.7, 35.9.

Diethyl 2,2-di(but-3-en-1-yl)malonate (1d). Compound 1d was prepared according to procedure reported for synthesis of 7m starting from diethyl malonate (1.60 g, 10 mmol), NaH (0.69 g, 30 mmol) and homoallyl bromide (2.84 g, 21 mmol). Crude product was purified to afford ester 1d (1.50 g, 56%). Analyses were in accordance with previously reported.³

¹H NMR (400 MHz, CDCl₃) δ = 5.90-5.65 (m, 2H), 5.17-4.82 (m, 4H), 4.18 (q, J = 7.1 Hz, 4H), 2.12-1.84 (m, 8H), 1.24 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ = 171.6, 137.7, 115.2, 61.3, 57.1, 31.7, 28.5, 14.2.

**Synthesis of 3f**

![Scheme 1. Synthesis of 3f. Reaction conditions: a) LiAlH₄, Et₂O, 48 h, RT; b) NaH, BnBr, THF, 4 h, 50 °C.](image)

(1S,2R)-2-(2-hydroxyethyl)cyclopent-3-enol (4f). To a suspension of LiAlH₄ (1.52 g, 40 mmol) in anhydrous diethyl ether (25 mL) a solution of commercially available Grieco lactone ((1S,5R)-2-oxabicyclo[3.3.0]oct-6-en-3-one) (1.24 g, 10 mmol) was added dropwise at 0 °C. Reaction mixture was left stirring for 2 h at room temperature. After full conversion of substrate was observed
(TLC monitoring) the reaction mixture was cooled down to 0 °C and a solution of Na₂SO₄ was added dropwise (CAUTION: extremely exothermic reaction). The granular solid (formed in 10 min) was filtered off and rinsed with ether (ca. 50 mL). The filtrate was washed with brine and organic layer was separated, dried over MgSO₄, filtered and evaporated to obtain crude diol 4f (0.97 g, 75%) that was spectrally pure and was used in next step without further purification.⁴

¹H NMR (400 MHz, CDCl₃) δ = 5.78-5.65 (m, 1H), 5.58-5.49 (m, 1H), 4.44 (td, J = 6.1, 2.3 Hz, 1H), 3.85-3.73 (m, 1H), 3.65 (m, 1H), 3.45 (s, 2H), 2.76-2.67 (m, 1H), 2.59 (dd, J = 6.2, 2.6 Hz, 1H), 2.39-2.26 (m, 1H), 1.93-1.69 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ = 133.0, 128.1, 72.2, 61.8, 49.5, 41.7, 30.2.

(1S,2R)-1-benzyloxy-2-(2-benzyloxyethyl)cyclopent-3-en (3f). To a solution of diol 4f (0.94 g, 7.3 mmol) in 25 mL of anhydrous THF NaH (0.70 g, 29.2 mmol) was carefully added at 0 °C. The suspension was stirred for 1 h at room temperature and then benzyl bromide (5.00 g, 29.2 mmol) was added dropwise over 5 min. The reaction mixture was stirred at 50 °C for 4 h. Excess of NaH was quenched with MeOH and reaction mixture was diluted with water (50 mL). Aqueous layer was extracted with TBME (3x), collected organic layers were combined, washed with brine and distilled water, dried over MgSO₄, filtered and evaporated to obtain crude product, that was purified using column chromatography to yield compound 3f (1.60 g, 71%).

¹H NMR (400 MHz, CDCl₃) δ = 7.55-7.10 (m, 10H), 5.90-5.56 (m, 2H), 4.52 (s, 2H), 4.50 (dd, J = 40.4, 11.9 Hz, 4H), 4.26-4.10 (m, 1H), 3.58 (t, J = 6.6 Hz, 2H), 3.00-2.76 (m, 1H), 2.16-1.98 (m, 1H), 1.89-1.66 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 138.8, 138.8, 133.7, 128.4, 128.3, 127.8, 127.6, 127.5, 127.5, 127.5, 80.1, 72.9, 71.4, 69.3, 44.9, 37.5, 28.4.


Synthesis of olefins 3a, 3b, 3c, 3d, 3e, 3j, 3k

Diethyl cyclopent-3-ene-1,1-dicarboxylate (3a). Diene 1a (1.68 g, 7 mmol) was placed in a dry flask, degassed and diluted with anhydrous DCM (C=0.2M). Gru-II (5.94 mg, 0.007 mmol) was added and reaction
mixture was heated at 40 °C for 1 h. After that time solvent was removed under reduced pressure and then purification of crude product using column chromatography afforded spectrally pure ester 3a (1.42 g, 95%). Analyses were in accordance with previously reported.\textsuperscript{5}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 5.73-5.50\) (m, 2H), \(4.19\) (q, \(J = 7.1\) Hz, 4H), \(3.06-2.92\) (m, 4H), \(1.24\) (t, \(J = 7.1\) Hz, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 172.3, 127.9, 61.6, 58.9, 41.0, 14.2\).

**Ethyl 1-(phenylsulfonyl)cyclopent-3-enecarboxylate** (3b). Compound 3b was prepared according to procedure reported for synthesis of 3a starting from 1b (1.29 g, 4.2 mmol), Gru-II (7.11 mg, 0.0084 mmol). Crude product was purified by column chromatography to afford ester 3b (1.16 g, 99%). Analyses were in accordance with previously reported.\textsuperscript{1}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.91-7.83\) (m, 2H), \(7.72-7.63\) (m, 1H), \(7.58-7.50\) (m, 2H), \(5.72-5.54\) (m, 2H), \(4.13\) (q, \(J = 7.2\) Hz, 2H), \(3.42-3.06\) (m, 4H), \(1.18\) (t, \(J = 7.1\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 168.7, 136.8, 134.2, 130.1, 128.9, 127.7, 78.1, 62.8, 38.9, 13.9\).

**1-benzoylcyclopent-3-en** (3c). Compound 3c was prepared according to procedure reported for synthesis of 3a starting from 1c (1.00 g, 5 mmol), Gru-II (21.2 mg, 0.025 mmol). Crude product was purified by column chromatography to afford ketone 3c (0.85 g, 98%). Analyses were in accordance with previously reported.\textsuperscript{6}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 8.03-7.94\) (m, 2H), \(7.61-7.52\) (m, 1H), \(7.51-7.43\) (m, 2H), \(5.82-5.58\) (m, 2H), \(4.08\) (tt, \(J = 9.5, 6.3\) Hz, 1H), \(2.93-2.58\) (m, 4H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 201.5, 136.6, 133.0, 129.0, 128.7, 128.7, 44.2, 36.4\).

**Diethyl cyclohept-4-ene-1,1-dicarboxylate** (3d). Compound 3d was prepared according to procedure reported for synthesis of 3a starting from 1d (1.61 g, 6 mmol), Gru-II (25.5 mg 0.03 mmol). Crude product was purified by column chromatography to afford ester 3d (1.41 g, 98%). Analyses were in accordance with previously reported.\textsuperscript{3}
$^1$H NMR (400 MHz, CDCl$_3$) δ = 5.66 (s, 2H), 4.17 (q, $J = 7.1$ Hz, 4H), 2.32-2.12 (m, 8H), 1.23 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 172.4, 131.0, 61.3, 58.1, 32.1, 24.6, 14.2.

**PhOC**

![3e]

**Ethyl 1-benzoylcyclopent-3-enecarboxylate (3e).** Compound 3e was prepared according to procedure reported for synthesis of 3a starting from commercially available ethyl 2,2-allylbenzoylacetate (2.53 g, 9.3 mmol), Gru-II (7.9 mg, 0.0093 mmol). Crude product was purified by column chromatography to afford ketone 3e (2.25 g, 99%). Analyses were in accordance with previously reported.\(^7\)

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.91-7.80 (m, 2H), 7.60-7.47 (m, 1H), 7.46-7.36 (m, 2H), 5.66-5.55 (m, 2H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.32-3.03 (m, 4H), 0.98 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 194.9, 174.3, 135.0, 132.9, 128.9, 128.64, 127.7, 62.3, 61.7, 41.4, 13.8.

**EtO$_2$C**

![3j]

**Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (3j).** Compound 3j was prepared according to the literature. Analyses were in accordance with previously reported. Analyses were in accordance with previously reported.\(^5\)

$^1$H NMR (400 MHz, CDCl$_3$) δ = 6.39-5.25 (m, 1H), 4.40 (q, $J = 7.1$ Hz, 4H), 3.37-2.98 (m, 4H), 1.91 (s, 3H), 1.45 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 172.4, 137.5, 121.4, 61.5, 59.5, 44.7, 40.9, 15.1, 14.1.

**EtO$_2$C**

![3k]

**Diethyl cyclohex-3-ene-1,1-dicarboxylate (3k).** Compound 3k was prepared according to procedure reported for synthesis of 3a starting from 7m (1.53 g, 6 mmol), Gru-II (25.5 mg, 0.03 mmol). Crude product was purified by column chromatography to afford ester 3k (1.00 g, 74%). Analyses were in accordance with previously reported.\(^5\)

$^1$H NMR (400 MHz, CDCl$_3$) δ = 5.70-5.63 (m, 2H), 4.18 (q, $J = 7.1$ Hz, 4H), 2.60-2.47 (m, 2H), 2.17-2.04 (m, 4H), 1.24 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 171.8, 126.2, 124.1, 61.4, 53.1, 30.5, 27.5, 22.4, 14.2.
Synthesis of tetraene 1m

Scheme 1. Synthesis of tetraene 1m. Reaction conditions: a) KOH, EtOH/H₂O, 4 h, reflux; b) Δ, 140 °C MW irradiation, 3 h; c) NaH, homoallyl bromide, DMF, 4 h, 50 °C; d) KOH, EtOH/H₂O, 4 h, reflux; e) 1. Δ, 140 °C MW irradiation 3 h; 2. MeOH, H+; 12 h, reflux; f) LiAlH₄, Et₂O, 48 h; g) DMAP, EDCI, DCM, overnight, RT.

2,2-diallylmalonic acid (4m). To commercially available diethyl diallylmalonate (4.81 g, 20 mmol) placed in a flask, 10 mL of 40% aqueous solution of KOH was poured and 5 mL of ethanol to make mixture homogenous. The reaction mixture was heated under reflux for 4 h. Solvent was removed under reduced pressure to dryness. Solid residue was diluted in distillated water and extracted with n-hexane. The alkaline layer was acidified with cold 10% HCl(aq) and extracted with ether (3x). The combined ethereal extracts were dried over MgSO₄, filtered and evaporated. The residue solidified slowly and crystallization from cyclohexane afforded the pure acid 2m (2.60 g, 70%). Analyses were in accordance with previously reported.⁸

¹H NMR (400 MHz, CD₃OD) δ = 5.71 (ddt, J = 17.5, 10.2, 7.4 Hz, 2H), 5.19-5.06 (m, 4H), 2.67-2.56 (m, 4H); ¹³C NMR (101 MHz, CD₃OD) δ = 174.3, 134.0, 119.2, 58.4, 37.8.
2-allylpent-4-enoic acid (5m). Acid 4m (2.12 g, 11.5 mmol) was placed in a flask and reaction was performed at 140 °C under microwave irradiation for 3h under argon atmosphere. Crude product was purified by distillation under reduced pressure 69-71 °C / 0.4 mBar and spectrally pure acid 5m (1.53 g, 95%) was obtained. Analyses were in accordance with previously reported.\(^9\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.82\) (br, 1H), 5.89-5.68 (m, 2H), 5.22-4.92 (m, 4H), 2.66-2.47 (m, 1H), 2.47-2.34 (m, 2H), 2.34-2.21 (m, 2H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 181.7, 135.0, 117.5, 45.0, 35.6.\)

Diethyl 2-allyl-2-homoallylmalonate (7m). Diethyl allylmalonate (5.00 g, 25 mmol) was placed in a dry flask, degassed and dissolved in anhydrous DMF. NaH (0.86 g, 37.5 mmol) was added to the solution and then the mixture was stirred for 0.5h at room temperature. Homoallyl bromide (4.05 g, 30 mmol) was slowly added dropwise via syringe to the reaction mixture at room temperature. The reaction mixture was heated at 50 °C for 5 h. After the reaction was completed (TLC monitoring) the reaction mixture was cooled down and quenched with 100 mL of saturated aqueous solution of NH\(_4\)Cl. Organic layer was separated and aqueous layer was extracted with EtOAc (3x), combined extracts were washed with brine, dried over MgSO\(_4\), filtered and evaporated to obtain crude product which was purified by filtration through silica gel pad to afford spectrally pure 7m (5.54 g, 87%). Analyses were in accordance with previously reported.\(^5\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 5.87-5.70\) (m, 1H), 5.70-5.56 (m, 1H), 5.17-4.88 (m, 4H), 4.16 (q, \(J = 7.1\) Hz, 4H), 2.73-2.58 (m, 2H), 2.03-1.87 (m, 4H), 1.23 (t, \(J = 7.1\) Hz, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 171.1, 137.6, 132.4, 118.8, 114.9, 61.1, 57.1, 37.0, 31.5, 28.2, 14.0.\)

2-allyl-2-homoallylmalonic acid (8m). Compound 8m was prepared according to procedure reported for synthesis of 4m starting from 7m (6.36 g, 25 mmol), 13 mL of 40% KOH and 7mL of ethanol. Crude product 8m (4.82 g, 97%) was spectrally pure and was used in next step without further purification. Analyses were in accordance with previously reported.\(^10\)
\[^1\text{H} \text{NMR (400 MHz, CDCl}_3 \delta = 11.86 \text{ (br, 2H), 6.04}-5.47 \text{ (m, 2H), 5.35}-4.80 \text{ (m, 4H), 2.71 (d, } J \text{ = 7.4 Hz, 2H), 2.31}-1.83 \text{ (m, 4H); } ^{13}\text{C NMR (101 MHz, CDCl}_3 \delta = 177.2, 137.0, 131.6, 120.1, 115.8, 57.7, 38.1, 32.4, 28.6.}\]

**Methyl 2-allylhex-5-enoate (9m).** 2-allylhex-5-enoic acid was prepared according to procedure reported for synthesis of 5m starting from 8m (4.96 g, 25 mmol). Crude 2-allylhex-5-enoic acid (3.80 g, 98%) was dissolved in MeOH (100 mL), few drops of H\_2SO\_4 was added and the reaction mixture was heated to reflux for 4 h. After reaction was completed solvent was removed under reduced pressure and the residue was dissolved in EtOAc (100 mL), washed with saturated solution of NaHCO\_3 and brine. Organic phase was dried over MgSO\_4, filtered, evaporated to obtain crude ester 9m (2.60 g, 62%) that was used in next step without further purification. Analyses were in accordance with previously reported.\(^{11}\)

Analytical data of 2-allylhex-5-enoic acid:

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3 \delta = 11.71 \text{ (br, 1H), 5.86}-5.67 \text{ (m, 2H), 5.17}-4.92 \text{ (m, 4H), 2.56}-2.43 \text{ (m, 1H), 2.43}-2.34 \text{ (m, 1H), 2.31}-2.2 \text{ (m, 1H), 2.16}-2.01 \text{ (m, 2H), 1.82}-1.69 \text{ (m, 1H), 1.64}-1.54 \text{ (m, 1H); } ^{13}\text{C NMR (101 MHz, CDCl}_3 \delta = 182.2, 137.7, 135.1, 117.3, 115.5, 44.58, 36.2, 31.4, 30.6.}\]

Analytical data of methyl ester 9m:

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3 \delta = 5.84}-5.70 \text{ (m, 2H), 5.10}-4.91 \text{ (m, 4H), 3.65 \text{ (s, 3H), 2.60}-2.45 \text{ (m, 1H), 2.42}-2.37 \text{ (m, 1H), 2.35}-2.22 \text{ (m, 1H), 2.20}-2.07 \text{ (m, 2H), 1.90}-1.73 \text{ (m, 1H), 1.73}-1.61 \text{ (m, 1H); } ^{13}\text{C NMR (101 MHz, CDCl}_3 \delta = 175.2, 137.4, 135.1, 116.5, 114.8, 50.9, 44.4, 36.2, 31.1, 30.6.}\]

**2-allylhex-5-en-1-ol (10m).** To a well stirred suspension of LiAlH\_4 (228 mg, 6 mmol) in anhydrous diethyl ether (15 mL) ethereal solution of ester 9m (252 mg, 1.5 mmol) was added dropwise at 0 °C. The reaction mixture was left stirring for 2 days. After reaction was completed the reaction mixture was cooled down to 0 °C and saturated solution of Na\_2SO\_4 was added dropwise (CAUTION: extremely exothermic reaction). The granular white solid was formed (in ca. 15 min), filtered off and rinsed with ether (50 mL). The filtrate was washed with brine, dried over MgSO\_4, filtered and
evaporated to obtain spectrally pure alcohol 10m (200 mg, 95%). Analyses were in accordance with previously reported.\textsuperscript{12}

\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \( \delta = 6.00-5.64 \) (m, 2H), 5.18-4.85 (m, 4H), 3.55 (d, \( J = 5.5 \) Hz, 2H), 2.19-1.98 (m, 4H), 1.76-1.20 (m, 4H); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \( \delta = 138.9, 137.0, 116.4, 114.7, 65.37, 39.9, 35.8, 31.2, 29.9. \)

**2-allylhex-5-en-1-yl 2-allylpent-4-enoate (1m).** Solution of acid 5m (617 mg, 4.4 mmol), DMAP (977 mg, 8 mmol) and alcohol 10m (561 mg, 4 mmol) was dissolved in DCM. EDCI (1.92 g, 10 mmol) was added in one portion to ice-cooled reaction mixture and stirring was continued at room temperature overnight. Solvent was removed under reduced pressure and the residue was dissolved in EtOAc, washed with distilled water and saturated solution of NaHCO\textsubscript{3}. Combined organic phases were dried over MgSO\textsubscript{4}, filtered and evaporated to obtain crude product. Purification using column chromatography afforded spectrally pure ester 1m (350 mg, 33%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 5.91-5.64 \) (m, 4H), 5.19-4.89 (m, 8H), 3.99 (d, \( J = 5.5 \) Hz, 2H), 2.61-2.48 (m, 1H), 2.43-2.32 (m, 2H), 2.31-2.21 (m, 2H), 2.18-2.01 (m, 4H), 1.87-1.69 (m, 1H), 1.471.36 (m, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta = 175.1, 138.6, 136.1, 135.4, 117.1, 116.9, 114.8, 66.3, 45.2, 36.8, 36.0, 35.7, 31.0, 30.1. \)

HRMS (ESI): m/z [M+Na]\textsuperscript{+} calcd for C\textsubscript{17}H\textsubscript{26}O\textsubscript{2}Na, 285.1830; found, 285.1837.

Elemental analysis calcd (%) for C\textsubscript{17}H\textsubscript{26}O\textsubscript{2} (262.19): C 77.82, H 9.99; found: C 77.70, H 9.89.

IR (film) cm\textsuperscript{-1} 3078, 2979, 2925, 2858, 1736,1641,1442, 1173, 993, 914.

### 3. General Procedures

Several general procedures of transfer hydrogenation and sequential ring closing metathesis/transfer hydrogenation reactions were shown below. In every case RCM and transfer hydrogenation reactions were carried out at 40 °C and 80 °C respectively for appropriate period of time (see Tab. 2 and Tab. 3). Unless otherwise noted the obtained hydrogenation products were spectrally pure without further purification. In case of substrates 1d and 3a NaH was used instead of HCO\textsubscript{2}Na.
General Procedure of Transfer Hydrogenation Reaction

Procedure A. Olefin (1 mmol) was placed in a dry pressure ampoule, then it was degassed and diluted in 5mL of anhydrous THF. Catalyst was added to the resulting solution followed by addition of solid HCO$_2$Na (0.2mmol) and HCO$_2$H (50 mmol). Reaction mixture was stirred for appropriate period of time at 80 °C and then allowed to cool down to room temperature and poured into a saturated solution of NaHCO$_3$ (ca. 30 mL) to obtain neutral pH. Aqueous layer was extracted with organic solvent, the combined organic phases were washed with brine, dried over MgSO$_4$, filtered and evaporated to obtain crude product.

General Procedure of Tandem Ring Closing Metathesis / Transfer Hydrogenation Reaction

Procedure B. Diene (1 mmol) was placed in a dry pressure ampoule, then it was degassed and diluted in 5mL of anhydrous THF. Catalyst was added to the resulting solution and the ring closing metathesis reaction was carried out for 0.5 h at 40 °C. Once the RCM reaction was completed, solid HCO$_2$Na (0.2 mmol) and HCO$_2$H (50 mmol) were added and the reaction was continued for appropriate period of time at 80 °C and then the solution was allowed to cool down to room temperature and poured into saturated solution of NaHCO$_3$ (ca. 30 mL) to obtain neutral pH. Aqueous layer was extracted with organic solvent, the combined organic phases were washed with brine, dried over MgSO$_4$, filtered and evaporated to obtain crude product.

4. Transfer hydrogenation of selected olefins

![Diethyl cyclopentane-1,1-dicarboxylate (2a)](image)

Spectrally pure product was synthesized according to general procedure A using 3a as a starting material and NaH instead of HCO$_2$Na without further purification (212 mg, 99%). Analyses were in accordance with previously reported.$^{13}$

Furthermore transfer hydrogenation reaction was also carried out in open flask. The reaction mixture was heated at 80 °C under inert atmosphere for 15 h. GC-FID analysis confirmed 90% starting material conversion to desired product. Duren was used as an internal standard. Reduction product was not isolated.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.20-4.12 (m, 4H), 2.21-2.11 (m, 4H), 1.71-1.62 (m, 4H), 1.23 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.
Ethyl 1-(phenylsulfonyl)cyclopentanecarboxylate (2b). Spectrally pure product was synthesized according to general procedure A without further purification (280 mg, 99%). Analyses were in accordance with previously reported.\(^ {14} \)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.92-7.80\ (m, 2H), 7.73-7.61\ (m, 1H), 7.58-7.48\ (m, 2H), 4.09\ (q, \(J = 7.1\) Hz, 2H), 2.53-2.32\ (m, 4H), 1.92-1.78\ (m, 2H), 1.16\ (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 169.0, 137.4, 134.0, 130.0, 128.8, 79.6, 62.5, 32.5, 25.4, 13.9.\)

Benzoylcyclopentane (2c). Product was synthesized according to general procedure A and then purified by column chromatography to yield title compound as colorless oil (170 mg, 98%). Analyses were in accordance with previously reported.\(^ {15} \)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.03-7.93\ (m, 2H), 7.60-7.50\ (m, 1H), 7.50-7.42\ (m, 2H), 3.72\ (quint, \(J = 7.88\) Hz, 1H), 2.06-1.85\ (m, 4H), 1.83-1.54\ (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.\)

Ethyl 1-benzoylcyclopentanecarboxylate (2e). Crude product was synthesized according to general procedure A using 3e as starting material and NaH instead HCO\(_2\)Na. Purification by bulb-to-bulb distillation yielded title compound as colorless oil (202 mg, 98%). Analyses were in accordance with previously reported.\(^ {16} \)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.87-7.85\ (m, 1H), 7.85-7.83\ (m, 1H), 7.54-7.48\ (m, 1H), 7.44-7.38\ (m, 2H), 4.04\ (q, \(J = 7.1\) Hz, 2H), 2.48-2.20\ (m, 4H), 1.71\ (m, 4H), 0.96\ (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.2, 174.9, 135.4, 132.8, 128.9, 128.5, 63.7, 61.4, 35.1, 26.4, 13.8.\)

(1S,2S)-1-benzyloxy-2-(benzyloxyethyl)cyclopentane (2f). Crude product was synthesized according to general procedure A and then purified by bulb-to-bulb distillation to yield 2f (280 mg, 90%) as colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.48-7.19\ (m, 10H), 4.52\ (s, 2H), 4.48\ (dd, \(J = 84.1, 12.1\) Hz, 2H), 3.88-3.81\ (m, 1H), 3.53\ (t, \(J = 6.6\) Hz, 3H), 2.12-1.44\ (m, 9H); \(^{13}\)C NMR (100 MHz,
CDCl$_3$ δ = 139.5, 139.0, 128.4, 128.3, 127.7, 127.6, 127.5, 127.3, 81.7, 73.0, 70.6, 69.8, 41.8, 30.7, 29.5, 29.3, 22.0.

HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{21}$H$_{26}$O$_2$Na, 333.1830; found, 333.1840.

2-Propylphenol (2g). Crude product was synthesized according to general procedure A and then purified by column chromatography to yield 2g (101 mg, 74%) as colorless oil. Analyses were in accordance with previously reported.$^{17}$

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.23-7.03 (m, 2H), 6.89 (td, $J = 7.4$, 1.1 Hz, 1H), 6.77 (dd, $J = 7.9$, 1.1 Hz, 1H), 4.86 (s, 1H), 2.68-2.55 (m, 2H), 1.74-1.59 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 153.5, 130.4, 128.5, 127.1, 120.8, 115.3, 32.1, 23.0, 14.1.

1-(2,6,6-Trimethylcyclohex-1-en-1-yl)butan-1-one (2h). Spectrally pure product was synthesized according to general procedure A without further purification (161 mg, 83%). Analyses were in accordance with previously reported.$^{18}$

$^1$H NMR (400 MHz, CDCl$_3$) δ = 2.50 (t, $J = 7.4$ Hz, 2H), 1.93 (t, $J = 6.3$ Hz, 2H), 1.69-1.59 (m, 4H), 1.53 (s, 3H), 1.45-1.39 (m, 2H), 1.04 (s, 6H), 0.93 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 212.0, 143.6, 128.7, 47.8, 39.0, 33.3, 31.2, 28.8, 20.95, 19.0, 16.7, 13.9.

1,3-Diphenylpropan-1-one (2i). Crude product was synthesized according to general procedure A and then purified by crystallization to yield 2i (191 mg, 91%) as white crystals. Analyses were in accordance with previously reported.$^{19}$

$^1$H NMR (400 MHz, CDCl$_3$) δ = 8.02-7.92 (m, 2H), 7.60-7.52 (m, 1H), 7.50-7.41 (m, 2H), 7.35-7.17 (m, 5H), 3.34-3.27 (m, 2H), 3.12-3.03 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 199.3, 141.4, 136.9, 133.2, 128.7, 128.6, 128.5, 128.2, 126.3, 40.6, 30.2.

Diethyl 3-methylcyclopentane-1,1-dicarboxylate (2j). Crude product was synthesized according to general procedure A and then purified by bulb-to-bulb distillation (98 mg, 43%). Analyses were in accordance with previously reported.$^{20}$
1H NMR (400 MHz, CDCl₃) δ = 4.16 (q, J = 7.1 Hz, 4H), 2.43 (dd, J = 13.3, 7.1 Hz, 1H), 2.35-2.25 (m, 1H), 2.19-2.08 (m, 1H), 2.07-1.97 (m, 1H), 1.88-1.78 (m, 1H), 1.65 (dd, J = 13.3, 10.1 Hz, 1H), 1.22 (t, J = 7.1 Hz, 6H), 1.00 (d, J = 6.6 Hz, 3H); 13C NMR (101 MHz, CDCl₃) δ = 172.8, 61.2, 60.4, 42.5, 34.4, 34.1, 34.0, 19.6, 14.0.

Diethyl cyclohexane-1,1-dicarboxylate (2k). Incomplete conversion was obtained and crude product was a mixture of substrate and hydrogenation product in ratio 50 : 50 and 20 : 80 when reaction was carried out 120 h and 336 h respectively (determined by NMR). Hydrogenation product was not isolated.

Diethyl cycloheptane-1,1-dicarboxylate (2d). Spectrally pure product was synthesized according to general procedure A without further purification (228 mg, 99%).

Methyl 3-phenylpropanoate (2l). Crude product was synthesized according to general procedure A and then purified by column chromatography to yield 2l (158 mg, 96%). Analyses were in accordance with previously reported.²¹

Sequential Ring Closing Metathesis / Transfer Hydrogenation Reaction of selected diens

Diethyl cyclopentane-1,1-dicarboxylate (2a). Product was synthesized according to general procedure B using diene 1a as a starting material and NaH instead of HCO₂Na. Spectrally pure product was isolated by extraction (214 mg, 99%). Analyses were in accordance with previously reported.¹³
Ethyl 1-(phenylsulfonyl)cyclopentanecarboxylate (2b). Product was synthesized according to general procedure B using diene 1b as a starting material. Purification by using column chromatography afforded spectrally pure product 2b (273 mg, 97%). Analyses were in accordance with previously reported.\(^\text{14}\)

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 7.92-7.80 (m, 2H), 7.73-7.61 (m, 1H), 7.58-7.48 (m, 2H), 4.09 (q, J = 7.1 Hz, 2H), 2.53-2.32 (m, 4H), 1.92-1.78 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H); \[^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 169.0, 137.4, 134.0, 130.0, 128.8, 79.6, 62.5, 32.5, 25.45, 13.9.\]

Benzoylcyclopentane (2c). Product was synthesized according to general procedure B using 1c as a starting material. Purification by using column chromatography afforded spectrally pure product 2c (160 mg, 92%). Analyses were in accordance with previously reported.\(^\text{15}\)

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 8.03-7.93 (m, 2H), 7.60-7.50 (m, 1H), 7.50-7.42 (m, 2H), 3.72 (quint, J = 7.88 Hz, 1H), 2.06-1.85 (m, 4H), 1.83-1.54 (m, 4H); \[^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.\]

Diethyl cycloheptane-1,1-dicarboxylate (2d). Product was synthesized according to general procedure B using 1c as a starting material. Spectrally pure product was isolated by extraction (204 mg, 89%).

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 4.14 (q, J = 7.1 Hz, 4H), 2.11-2.05 (m, 4H), 1.60-1.47 (m, 8H), 1.21 (t, J = 7.1 Hz, 6H); \[^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 173.1, 61.2, 57.7, 33.8, 29.9, 23.9, 14.2.\]

6. Ring Closing Metathesis and transfer hydrogenation reaction sequence of tetraene 1m

Cyclohex-3-en-1-ylmethyl cyclopent-3-enecarboxylate (3m). Compound 3m was prepared according to procedure reported for synthesis of 3a starting from 1m (64 mg, 0.243 mmol), Gru-II (6 mg,
0.0073 mmol). Crude product was purified by column chromatography to afford title ester 3I (44 mg, 88%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.74-5.57 (m, 4H), 3.99 (d, $J$ = 6.6 Hz, 2H), 3.25-3.04 (m, 1H), 2.75-2.57 (m, 4H), 2.16-2.02 (m, 3H), 2.02-1.89 (m, 1H), 1.82-1.70 (m, 2H), 1.39-1.18 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 176.2, 129.0, 127.0, 125.5, 68.8, 41.7, 36.3, 33.1, 28.2, 25.3, 24.4.

HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{13}$H$_{18}$O$_2$Na, 229.1204; found, 229.1215.

Procedure A

**Cyclohex-3-en-1-ylmethyl cyclopentancarboxylate (2m).** Compound 2m was synthesized according to general procedure A using 3m (20.6 mg 0.1 mmol), Gru-II (1.7 mg, 0.002 mmol), HCO$_2$Na (1.4 mg, 0.02 mmol), HCO$_2$H (189 µL, 5 mmol) and durene (5.4 mg, 0.04 mmol) as internal standard. Crude product was isolated according to procedure A and was analyzed by GC-FID (92% GC yield).

**Procedure B**

Compound 2m was synthesized according to general procedure B using 1m (20.6 mg 0.1 mmol), Gru-II (1.7 mg, 0.002 mmol). RCM reaction was carried out for 0.5 h at 40 °C. Then second portion of Gru-II (1.7 mg, 0.002 mmol), HCO$_2$Na (1.36 mg, 0.02 mmol), HCO$_2$H (189 µL, 5 mmol) and durene (5.4 mg, 0.04 mmol) as internal standard were added and reaction mixture was stirred for 4 h at 80 °C. Crude product was isolated according to procedure B and was analyzed by GC-FID (90% GC yield).

7. **Evidence of ruthenium hydride species**

Grubbs second generation catalyst (17 mg, 0.02 mmol) was placed in dry NMR tube and diluted with THF-$d_8$ (0.5mL) followed by addition of formic acid (15µL, 0.4 mmol). Then the tube was closed and reaction mixture was heated at 50 °C for 4h. After that time the reaction mixture was cooled down to room temperature and NMR spectrum was measured. A new signal with chemical shift -6.86 ppm appeared. This chemical shift is in the range characteristic for ruthenium hydride species.22
8. NMR spectra