Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Iron-Catalysed Allylation-Hydrogenation Sequences as Masked Alkyl-Alkyl Cross-Couplings

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1 General

Chemicals and Solvents. If not indicated, commercial reagents were used without purification. For catalytic reactions, exclusively dried solvents were used. Liquid substrates were distilled prior to use.THF was dried over sodium/benzophenoneand distilled.All Fe-catalyzed reactions were performed under an atmosphere of dry argon using standard Schlenk and glovebox techniques.

Analytical thin-layer chromatography. TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, $60F_{254}$). Thin-layer chromatography plates were visualized by exposure to UV light and/or by immersion in an aqueous staining solution of $KMnO_4$.

Column chromatography. Flash column chromatography with silica gel 60 Å (220-240 mesh) from *Acros*. Mixtures of pentane with ethyl acetate were used as eluents.

Gas chromatography with mass-selective detector. *Agilent* 6890N Network GC-System, mass detector 5975 MS. Column BPX5 (30m x 0.25 mm x 0.25µm) from *SGE*, carrier gas: H_2. Standard heating procedure: 50°C (2 min), 25°C/min -> 300°C (5 min).

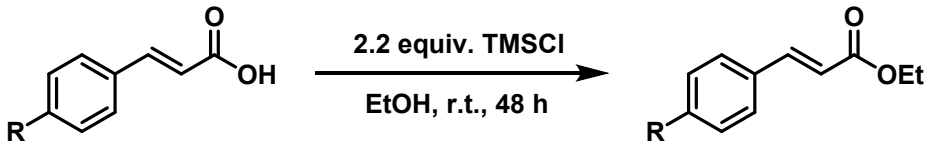
Gas chromatography with FID. *Agilent* 7820A GC-Systems. Column: HP 5 19091J 413 (30 m x 0.32 mm x 0.25 µm) from *Agilent*, carrier gas: N_2. GC-FID was used for catalyst screening (calibration with analytically pure samples vs. internal *n*-pentadecane).

NMR. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a *Bruker* Avance 300 (300 MHz ^{1}H; 75 MHz ^{13}C) and *Bruker* Avance 400 (400 MHz ^{1}H, 101 MHz ^{13}C) spectrometers. Chemicals shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS). Coupling constants (*J*) are reported in Hertz (Hz).

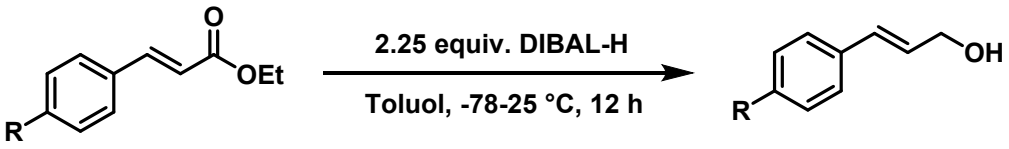
High resolution mass spectrometry (HRMS). The spectra were recorded by the Central Analytics Lab at the Department of Chemistry, University of Regensburg.

2 Preparation of Starting Materials

Preparation of Allylic Alcohols - Procedure 1



R = OMe, Me, Cl



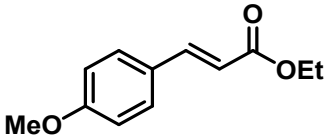
R = OMe, Me, Cl

Representative procedure on the example of 4-methoxy cinnamyl alcohol:

1) Chlorotrimethylsilane (TMSCl, 33 mmol, 4.2 mL) was added to a solution of 4-methoxycinnamic acid (15 mmol, 2.67 g) in 75 ml of ethanol. The solution was stirred at room temperature for 48 hours. The solvent was then removed under reduced pressure.

2) 13.5 ml of a 1.0 M diisobutylaluminum hydride (DIBAL-H) solution in toluene was added dropwise at -78 °C to a solution of 4-methoxy ethyl cinnamate (6 mmol, 1.24 g) in toluene (18 mL) over 45 minutes. The reaction was stirred at room temperature for 12 hours before gently hydrolyzing with ice-cooled 1.0 M aqueous HCl solution (15 mL). The aqueous phase was extracted with Et_2O and the combined organic phases were then dried over $NaSO_4$. After filtering off the drying agent, the solvent was distilled off under reduced pressure. No further purification was required.[1]

4-methoxyethyl cinnamate



$C_{12}H_{14}O_3$ 206.24 g/mol

Yield 3.07 g, 14.9 mmol, 99%

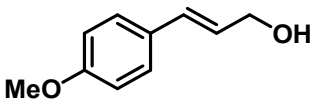
^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.64 (d, *J* = 16.0 Hz, 1H), 7.54 - 7.43 (m, 2H), 6.96 - 6.82 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 167.4, 161.3, 144.3, 129.7, 127.2, 115.7, 114.3, 60.4, 55.4, 14.4.

GC-MS (EI, 70 eV, m/z): 206 $[M]^+$, 194, 181, 161, 149, 136, 121, 110, 78, 69, 51.

The data corresponds to the literature values.[2]

4-methoxy cinnamyl alcohol



$C_{10}H_{12}O_2$ 164.20 g/mol

Yield 879 mg, 5.4 mmol, 89%

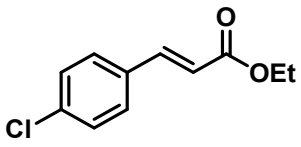
^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.36 - 7.29 (m, 2H), 6.90 - 6.81 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.30 (d, *J* = 5.6 Hz, 2H), 3.81 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 159.4, 131.0, 129.4, 127.7, 126.3, 114.0, 64.0, 55.3.

GC-MS (EI, 70 eV, m/z): 164 $[M]^+$, 147, 136, 121, 110, 78, 50.

The data corresponds to the literature values.[3]

4-chloroethyl cinnamate



$C_{11}H_{11}ClO_2$ 210.66 g/mol

Yield 3.15 g, 15 mmol, 100%

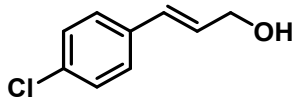
^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.63 (d, *J* = 16.0 Hz, 1H), 7.51 - 7.29 (m, 4H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 166.8, 143.2, 136.1, 133.0, 129.2, 129.2, 118.9, 60.7, 14.3.

GC-MS (EI, 70 eV, m/z): 210 $[M]^+$, 182, 165, 138, 102, 75, 63, 50.

The data corresponds to the literature values.[2]

4-chloro cinnamyl alcohol



C_9H_9ClO 168.62 g/mol

Yield 877 mg, 5.2 mmol, 87%

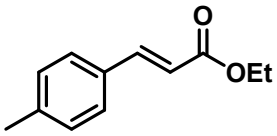
^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.39-7.26 (m, 4H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.33 (dd, *J* = 5.6, 1.5 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 135.2, 133.3, 129.8, 129.2, 128.8, 127.7, 63.6.

GC-MS (EI, 70 eV, m/z): 168 $[M]^+$, 151, 122, 115, 91, 61.

The data corresponds to the literature values.[3]

4-methyl ethyl cinnamate



$C_{12}H_{14}O_2$ 190.24 g/mol

Yield 2.86 g, 15 mmol, 100%

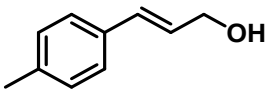
^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.66 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 167.3, 144.6, 140.7, 131.7, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4.

GC-MS (EI, 70 eV, m/z): 190 $[M]^+$, 172, 162, 145, 132, 115, 103, 91, 76, 63, 51.

The data corresponds to the literature values.[2]

4-methyl cinnamyl alcohol



$C_{10}H_{12}O$ 148.21 g/mol

Yield 629 mg, 4.2 mmol, 71%

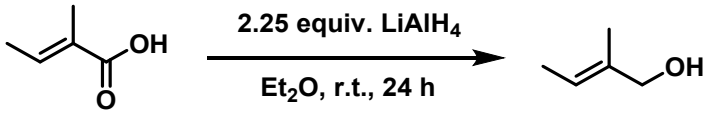
^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.31 (dd, *J* = 5.8, 1.3 Hz, 2H), 2.34 (s, *J* = 8.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 137.6, 133.9, 131.3, 129.3, 127.4, 126.4, 63.9, 21.2.

GC-MS (EI, 70 eV, m/z): 148 $[M]^+$, 131, 105, 71, 55.

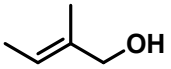
The data corresponds to the literature values.[3]

Preparation of Allylic Alcohols - Procedure 2



Under inert gas atmosphere (N_2), lithiumaluminum hydride (34 mmol, 1.29 g) was charged in 40 mL of absolute Et_2O. Tiglic acid (15 mmol, 1.5 g) was dissolved in 20 mL of absolute Et2O and added dropwise over a period of 2 hours with the aid of a dropping funnel. The suspension was stirred for 24 hours at room temperature and then carefully hydrolyzed with ice water and 15% aqueous NaOH solution (2 mL each). After addition of another 25 mL of ice water, the reaction mixture was filtered and the aqueous phase was extracted with Et_2O. The collected organic phases were dried over $NaSO_4$. The drying agent was filtered off and the solvent was carefully removed at 50 °C at ambient pressure. The product was purified by distillation at 60 °C at 20 mbar.[4]

(*E*)-2-methylbut-2-en-1-ol



$C_5H_{10}O$ 86.13 g/mol

Yield 586 mg, 6.8 mmol, 45%

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 5.58 - 5.39 (m, 1H), 3.98 (d, *J* = 5.9 Hz, 2H), 1.65 (d, *J* = 1.0 Hz, 3H), 1.61 (ddd, *J* = 6.7, 2.1, 1.0 Hz, 4H).

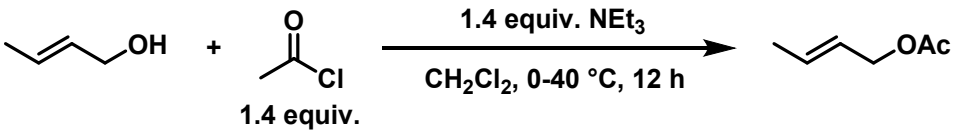
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 135.5, 120.7, 69.1, 13.4, 13.1.

GC-HRMS (CI, m/z): found 86.07269 $[M]^+$ (calculated 86.07262).

The data corresponds to the literature values.[4]

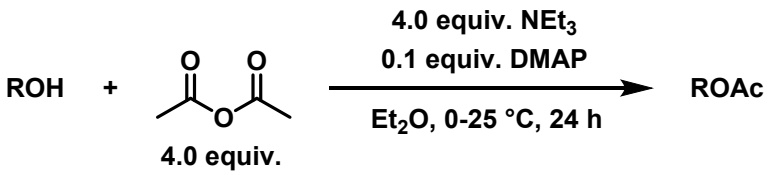
Acetylation reactions

Procedure A



Representative procedure on the example of Crotylacetate: Crotyl alcohol (50 mmol, 3.6 g) and triethylamine (70 mmol, 9.0 mL) were dissolved in dichloromethane (25 mL) in a dry three-necked flask. The solution was cooled to 0 °C and acetyl chloride (70 mmol, 4.6 mL) in 25 mL dichloromethane was slowly added dropwise via a dropping funnel. The mixture was subsequently heated under reflux for 12 hours and, after cooling to room temperature, the precipitate formed was filtered off. The yellow solution was washed with saturated $NaHCO_3$ solution and with distilled water. The organic phase was dried over $NaSO_4$. After filtering off the drying agent, the solvent was carefully distilled off under reduced pressure (500 mbar). Product purification was carried out by distillation at 80 °C under a pressure of 20 mbar.[5]

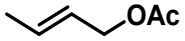
Procedure B



Representative procedure on the example of 4-methoxycinnamylacetate: 4-methoxycinnamyl alcohol (4 mmol, 657 mg), triethylamine (16 mmol, 2.2 ml) and 4-(dimethylamino)-pyridine (DMAP) (0.4 mmol, 49 mg) were dissolved in absolute Et_2O (20 mL). The solution was cooled to 0 °C. and acetic anhydride (16 mmol, 1.5 mL) was added dropwise. The mixture was stirred at room temperature for 24 hours. The reaction solution was then washed with saturated $NaHCO_3$ solution, 10% aqueous NaOH solution and saturated NaCl solution, and the organic phase was dried over $NaSO_4$. After filtering off the drying agent, the solvent was distilled off under reduced pressure. The crude product was purified by flash chromatography when necessary.[6]

Crotyl acetate

Synthesized according to procedure A.



$C_6H_{10}O_2$ 114.14 g/mol

Yield 1.92 g, 16.8 mmol, 34%

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 5.80 (dq, *J* = 12.8, 6.4 Hz, 1H), 5.59 (dtd, *J* = 8.1, 6.5, 1.5 Hz, 1H), 4.49 (d, *J* = 6.5 Hz, 2H), 2.06 (s, 3H), 1.72 (dd, *J* = 6.4, 1.0 Hz, 3H).

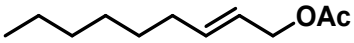
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 170.9, 131.5, 125.1, 65.2, 21.0, 17.8.

GC-HRMS (CI, m/z): found 114.0667 $[M]^+$ (calculated 114.0681).

The data corresponds to the literature values.[7]

(E)-non-2-en-1-yl acetate

Synthesized according to procedure A.



$C_{11}H_{20}O_2$ 184.15 g/mol

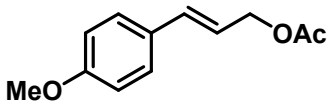
^{1}H-NMR (300 MHz, Chloroform-d) δ 5.77 (dtt, J = 15.5, 6.6, 1.1 Hz, 1H), 5.55 (dtt, J = 15.5, 6.5, 1.4 Hz, 1H), 4.50 (dt, J = 6.5, 1.1 Hz, 2H), 2.06 (d, J = 1.8 Hz, 5H), 1.49 – 1.17 (m, 8H), 0.96 – 0.78 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 170.94, 136.82, 123.62, 65.39, 32.28, 31.68, 28.85, 22.61, 21.09, 14.10.

GC-HRMS (EI, 70 eV m/z): found 184.14653 $[M]^{+\bullet}$ (calculated 184.14578).

4-methoxycinnamyl acetate

Synthesized according to procedure B.



$C_{12}H_{14}O_3$ 206.24 g/mol

Yield 644 mg, 3.1 mmol, 78%

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.39 - 7.30 (m, 2H), 6.92 - 6.79 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.70 (dd, *J* = 6.6, 1.1 Hz, 2H), 3.81 (s, 3H), 2.09 (s, 3H).

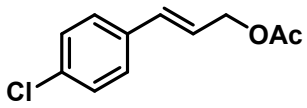
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 170.9, 159.6, 134.1, 129.0, 127.9, 120.9, 114.0, 65.4, 55.3, 21.1.

GC-MS (EI, 70 eV, m/z): 206 $[M]^+$, 163, 147, 135, 115, 103, 91, 78, 63, 51.

The data corresponds to the literature values.[8]

4-chlorocinnamyl acetate

Synthesized according to procedure B.



$C_{11}H_{11}ClO_2$ 210.66 g/mol

Yield 608 mg, 2.9 mmol, 73%

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.34 - 7.27 (m, 4H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.72 (dd, *J* = 6.4, 1.2 Hz, 2H), 2.10 (s, 3H).

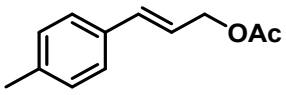
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 170.8, 134.7, 133.8, 132.9, 128.8, 127.8, 123.9, 64.9, 21.0.

GC-MS (EI, 70 eV, m/z): 210 $[M]^+$, 168, 151, 133, 115, 103, 89, 77, 63, 51.

The data corresponds to the literature values.[8]

4-methylcinnamyl acetate

Synthesized according to procedure B.



$C_{12}H_{14}O_2$ 190.24 g/mol

Yield 613 mg, 3.2 mmol, 81%

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.72 (dd, *J* = 6.5, 1.1 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H).

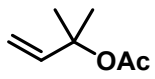
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 170.9, 138.0, 134.3, 133.4, 129.3, 126.6, 122.1, 65.3, 21.2, 21.0.

GC-MS (EI, 70 eV, m/z): 190 $[M]^+$, 148, 131, 115, 103, 91, 77, 65, 51.

The data corresponds to the literature values.[8]

2-methylbut-3-en-2-yl acetate

Synthesized according to procedure B.



$C_7H_{12}O_2$ 128.17 g/mol

Yield 548 mg, 4.3 mmol, 22%

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 6.07 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.16 (d, *J* = 17.5 Hz, 1H), 5.06 (dd, *J* = 10.9, 0.5 Hz, 1H), 1.98 (s, 3H), 1.51 (s, 6H).

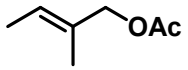
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 170.1, 142.6, 112.6, 80.6, 29.4, 26.5, 22.3.

GC-HRMS (CI, m/z): found 128.0795 $[M]^+$ (calculated 128.0788).

The data corresponds to the literature values.[6]

(*E*)-2-methylbut-2-en-1-ylacetate

Synthesized according to procedure B.



$C_7H_{12}O_2$ 128.17 g/mol

Yield 344 mg, 2.7 mmol, 67%

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 5.64 - 5.45 (m, 1H), 4.45 (s, 2H), 2.07 (s, 3H), 1.73 - 1.55 (m, 6H).

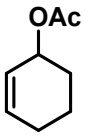
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 171.1, 130.8, 124.2, 70.4, 21.0, 13.6, 13.3.

GC-HRMS R_t = 4.49 min
(CI, m/z): found 129.0909 $[M+H]^+$ (calculated 129.0910).

The data corresponds to the literature values.[9]

Cyclohex-2-en-1-yl acetate

Synthesized according to procedure B.



$C_8H_{12}O_2$ 140.18 g/mol

Yield 1.20 g, 8.6 mmol, 57%

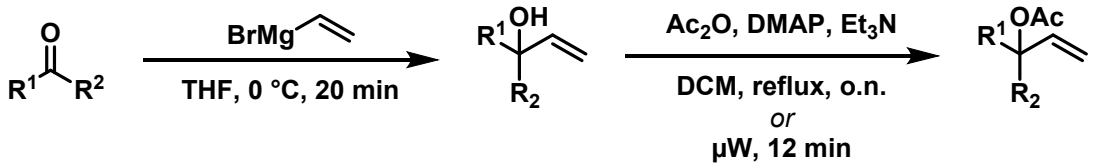
^{1}H-NMR (300 MHz, Chloroform-d) δ 5.95 (dtd, J = 10.1, 3.7, 1.3 Hz, 1H), 5.70 (ddt, J = 10.1, 4.0, 2.2 Hz, 1H), 5.25 (tdq, J = 5.6, 3.5, 2.0 Hz, 1H), 2.22 – 1.75 (m, 6H), 1.75 – 1.53 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 170.79, 132.71, 125.66, 68.08, 28.28, 24.86, 21.45, 18.85.

GC-MS R_t = 5.22 min
(EI, 70 eV, m/z): 140 $[M]^+$, 98, 79, 77, 70, 65, 53, 51.

The data corresponds to the literature values.[7]

Alkenylation-Acetylation Reactions

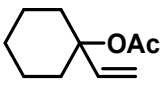


General procedures:

Alkenylation: To a solution of the ketone (10 mmol, 1 equiv.) in THF (20 mL) was added vinylmagnesium bromide (1.0 M in THF, 12 mmol, 1.2 equiv.) under nitrogen at 0 ºC and the reaction was stirred for 20 minutes. The reaction was then quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and evaporated to give the crude allylic alcohol that was engaged in the next step without further purification.

Acylation: The acylation of allylic alcohols was carried out using microwaveassisted heating conditions described as follow. The allylic alcohol (10 mmol, 1 equiv.), Et_3N (5.6 mL, 40 mmol, 4 equiv.), Ac_2O (1.8 mL, 20 mmol, 2 equiv.) and DMAP (0.360 g, 3.0 mmol, 0.3 equiv), were added in turn in a microwave-designed vial. The reaction mixture was heated under microwave-assisted heating at 100 °C for 12 min. The reaction was then quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and evaporated to give a crude product that was purified by flash chromatography on silica gel.

1-vinylcyclohexyl acetate



$C_{10}H_{16}O_2$ 168.24 g/mol

Yield 350 mg, 2.1 mmol, 27%

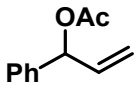
^{1}H-NMR (300 MHz, Chloroform-d) δ 6.10 (dd, J = 17.7, 11.0 Hz, 1H), 5.22 – 5.07 (m, 2H), 2.17 (q, J = 6.5, 6.1 Hz, 2H), 2.02 (s, 3H), 1.65 – 1.39 (m, 6H), 1.35 – 1.20 (m, 2H).

^{13}C-NMR (75 MHz, CDCl3) δ 169.94, 141.97, 113.54, 81.78, 34.88, 25.37, 22.17, 21.88.

GC-MS R_t = 4.70 min
(EI, 70 eV, m/z): 126 $[M\text{-}Ac]^+$, 111, 108, 93, 91, 83, 79, 77, 55.

The data corresponds to the literature values.[10]

1-phenylallyl acetate



$C_{11}H_{12}O_2$ 176.22 g/mol

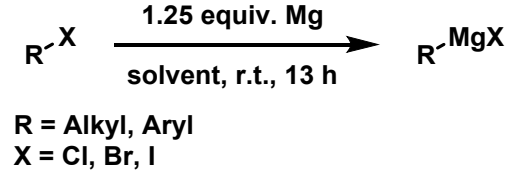
Yield 1.41 g, 8.0 mmol, 89%

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.44 – 7.24 (m, 5H), 6.27 (dt, J = 5.9, 1.4 Hz, 1H), 6.01 (ddd, J = 17.1, 10.4, 5.9 Hz, 1H), 5.37 – 5.20 (m, 2H), 2.12 (s, 3H).

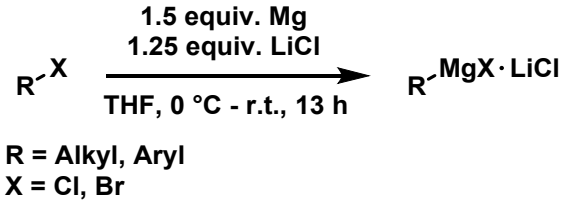
GC-MS R_t = 6.58 min
(EI, 70 eV, m/z): 176 $[M]^+$, 134, 116, 105, 91, 77, 65, 55.

The data corresponds to the literature values.[10]

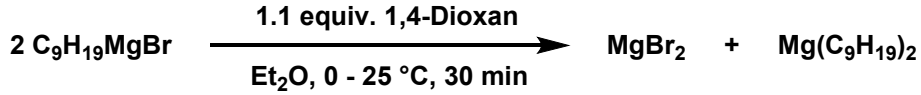
Synthesis of the Grignard reagents



Representative procedure on the example of 1-Bromononane in Et_2O: All reaction steps were carried out under inert gas atmosphere (N_2). 1-Bromononane (40 mmol, 7.6 mL) was added dropwise to a suspension of magnesium turnings (50 mmol, 1.22 g) in Et_2O (30 mL) at room temperature over a period of 1 hour using a syringe pump. The reaction solution was then stirred at room temperature for 12 hours.[11]



Representative procedure on the example of 1-Bromononane: All reaction steps were carried out under inert gas atmosphere (N_2). 1-Bromononane (20 mmol, 3.8 mL) was added dropwise to a suspension of magnesium turnings (30 mmol, 0.73 g) and LiCl (25 mmol, 1.06 g) in THF (15 mL) at 0 °C over a period of 1 hour using a syringe pump. The reaction solution was then stirred at room temperature for 12 hours.



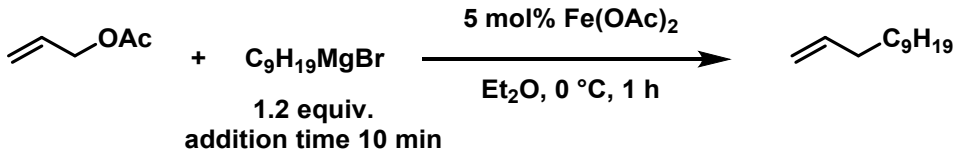
All reaction steps were carried out in an Argon-filled glovebox. A 1.0 M *n*-nonylmagnesium bromide solution in Et_2O (3 mmol, 3 mL) was added dropwise over a period of 5 minutes to a solution of dry 1,4-dioxane (3.3 mmol, 291 mg) in absolute Et_2O (2 mL) at 0 °C. The mixture was then stirred at room temperature for 30 minutes and the precipitate formed was filtered off by means of a syringe filter.

Grignard solutions were titrated with salicylaldehyde phenylhydrazone (0.25 mmol, 53 mg) as indicator in THF (4 mL) to determine their concentration.[12]

3 Iron-catalysed cross-coupling reactions

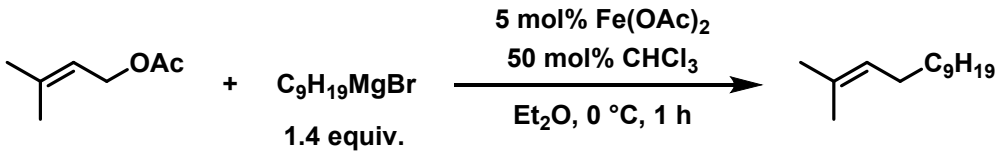
Procedures

Procedure during optimization



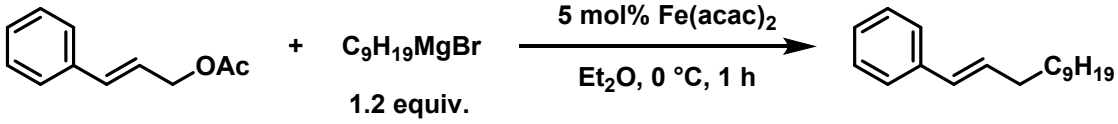
A suspension of $Fe(OAc)_2$ (0.025 mmol, 4.3 mg) in absolute Et_2O (2 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried reaction tube. After the addition of freshly distilled allyl acetate (0.5 mmol, 54 µL), a 1.0 M *n*-nonylmagnesium bromide solution (0.6 mmol, 0.6 mL) in Et_2O was added dropwise over a period of 10 minutes and the mixture was stirred at 0 °C for 1 hour. The reaction mixture was then hydrolyzed with a saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc. Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane.

Protocol A



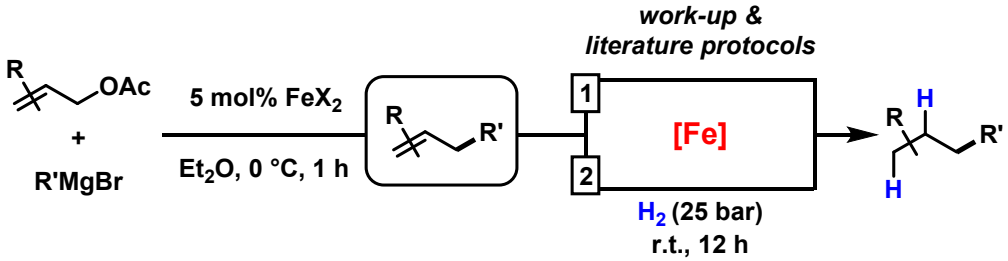
Representative procedure on the example of 2-methyltridec-2-ene: A suspension of $Fe(OAc)_2$ (0.025 mmol, 4.3 mg) and dry $CHCl_3$ (0.25 mmol, 20 µl) in absolute Et_2O (2 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried reaction tube. After the addition of freshly distilled prenyl acetate (0.5 mmol, 70 µL), a 1.0 M n-nonyl-magnesium bromide solution (0.7 mmol, 0.7 mL) in Et2O was added dropwise over a period of 45 minutes and the mixture was stirred at 0 °C for 1 hour. The reaction mixture was then hydrolyzed with a saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc. The solvent was removed under reduced pressure. Product purification was carried out by kugelrohr distillation at 150 °C at 20 mbar.

Protocol B



Representative procedure on the example of (*E*)-1-phenyldodec-1-ene: A suspension of $Fe(acac)_2$ (0.025 mmol, 6.4 mg) in absolute Et_2O (2 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried reaction tube. After the addition cinnamyl acetate (0.5 mmol, 84 µL), a 1.0 M *n*-nonylmagnesium bromide solution (0.7 mmol, 0.7 mL) in Et_2O was added dropwise over a period of 10 minutes and the mixture was stirred at 0 °C for 1 hour. The reaction mixture was then hydrolyzed with a saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc. The solvent was removed under reduced pressure. The crude product was purified by column chromatography.

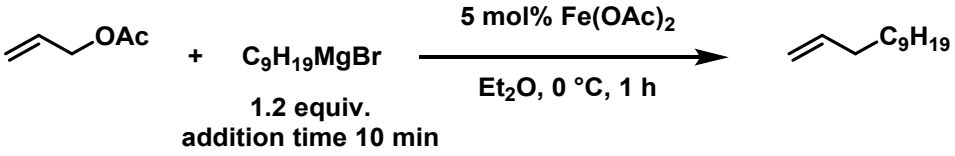
Cross Coupling with subsequent hydrogenation



For Route 1, the isolated product of the coupling reaction was hydrogenated according to literature.[13] The products were analyzed via GC-MS and GC-FID.

For Route 2, the reaction was carried out according to Condition A (without addition of $CHCl_3$) or B in an autoclave vial. After completion of the reaction, a small sample was taken out for quantitative GC-FID, and the vial was transferred into an argon-filled glovebox. The septum was penetrated with a cannula and the reaction vial was put into an autoclave, which was set under a pressure of 25 bar of H_2. The reaction was stirred overnight and then quenched with aqueous NH_4Cl solution. The organic phase was extracted with ethyl acetate, dried over sodium sulfate and filtered over a short layer of silica. The products were analyzed via GC-MS and GC-FID.

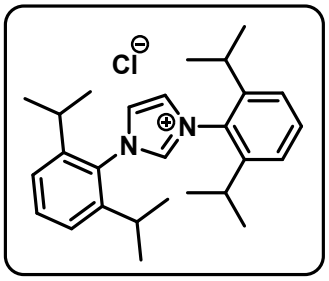
Optimization experiments with allyl acetate



Entry	Change of reaction conditions		Yield [%][a]
1	Metal Precursor	$Fe(OAc)_2$ (99.99%)	73
2		$Pd(OAc)_2$	Traces
3		$Pd(PPh_3)_4$	Traces
4		$Co(OAc)_2$	Traces
5		$NiBr_2$	Traces
6		CuBr	78 (<5[b])
7	Iron Precursor	none	0
8		$FeCl_2$	58
9		$FeCl_3$	61
10		$FeBr_2$	66
11		FeI_2 x 2 THF	51
12		**$Fe(OAc)_2$**	**71**
13		$Fe(acac)_2$	66
14		$Fe(acac)_3$	59
15		$Fe(N(TMS)_2)_2$	45
16		$Fe(OTf)_3$	48
17	1 – 15 mol% $Fe(OAc)_2$	1	62
18		3	54
19		5	71
20		8	72
21		**10**	**78**
22		12	77
23		15	78
24	Solvent	Heptane	4
25		**Et_2O**	**71**
26		Et_2O/NMP (20/1)	20
27		Toluene	41
28		Et_2O/Toluene (3/1)	70
29		Et_2O/Toluene (1/1)	71
30		Et_2O/Toluene (1/3)	70
31		EtOAc	63
32		DME	44

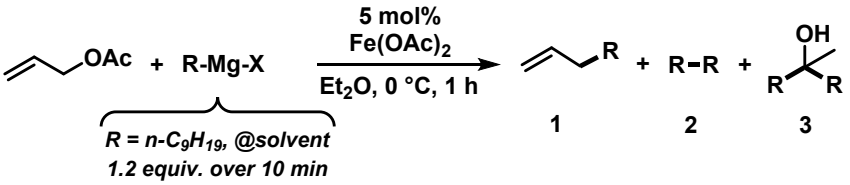
33		MTBE	55
34	Grignard concentration [M]	0.5	75[c]
35		1.0	78[c]
36		2.0	78[c]
37	Temperature [°C]	-20	30[c]
38		-10	66[c]
39		**0**	**78**[c]
40		25	73[c]
41	Additives	12.5 mol% dppp	0[c]
42		25 mol% IPr·HCl	52[c]
43		25 mol% NEt_3	61[c]
44		12.5 mol% TMEDA	62[c]
45		12.5 mol% DABCO	62[c]
46		12.5 mol% CH_2Cl_2	55[c]
47		12.5 mol% Glucosamin·HCl	70[c]

[a] Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. [b] 0.01 mol% CuBr [c] 10 mol% $Fe(OAc)_2$.



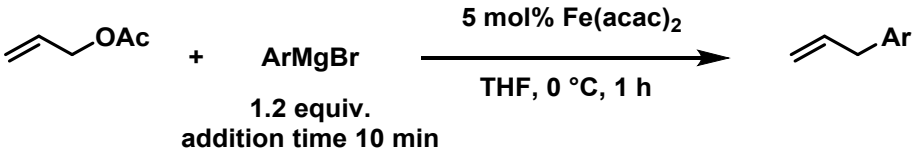
IPr·HCl

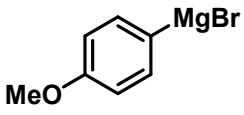
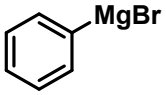
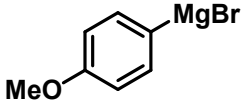
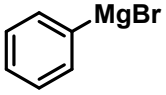
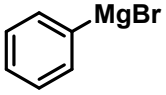
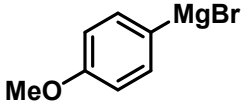
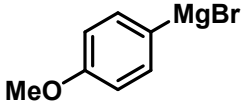
Influence of the Schlenck equilibrium



Entry	X	Solvent (RMgX)	1 [%]	2 [%]	3 [%]
1	Cl	Et_2O	0	<1	52
2	Cl	THF	37	12	11
3	Cl·LiCl	THF	54	5	2
4	Br	Et_2O	76	11	<1
5	Br	THF	69	6	2
6	Br·LiCl	THF	77	5	2
7	I	Et_2O	32	35	0
8	*n*-C_9H_{19}	Dioxane	1	<1	48

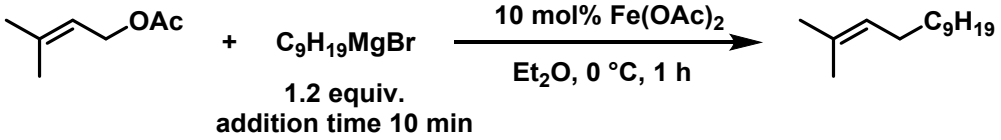
Application of ArMgBr



Entry	Change of reaction conditions		ArMgBr	Yield [%][a]
1	Iron Precursor	None	 in THF	0
2		$FeCl_2$		80
3		$FeBr_2$		66
4		$Fe(OAc)_2$		52
5		**$Fe(acac)_2$**		**83**
6		$Fe(OTf)_3$		65
7		$FeBr_2$	 in Et_2O	52[b]
8		$Fe(OAc)_2$		17[b]
9		**$Fe(acac)_2$**		**65**[b]
10	Solvent	**THF**	 in THF (not soluble in Et_2O)	**83**
11		THF/NMP (20/1)		74
12		Et_2O		81
13		Toluol		82
14		Benzol		68[c]
15		Et_2O	 in THF	55
16		THF		55
17		**Et_2O**	 in Et_2O	**65**
18		THF		61
19	Temperature [°C]	-10	 in THF	79
20		**0**		**83**
21		25		44
22	Additives	6.25 mol% dppp	 in THF	62
23		12.5 mol% IPr·HCl		78
24		12.5 mol% NEt_3		80
25		6.25 mol% TMEDA		77
26		30 mol% CH_2Cl_2		74
27		6.25 mol% Glucosamin·HCl		40

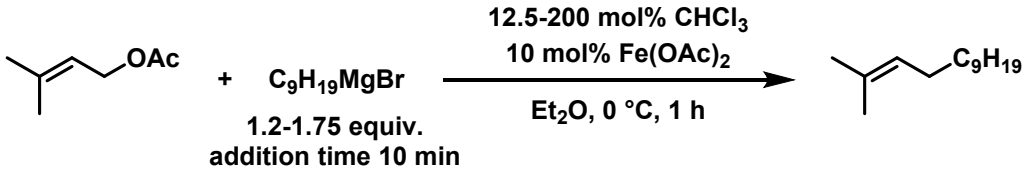
[a] Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. [b] Reaction was run in Et_2O. [c] Reaction temperature 25 °C.

Optimization experiments with alkyl-substituted acetates



Entry	Change of reaction conditions		Conversion [%][a]	Yield [%][a]
1		**$Fe(OAc)_2$**	**89**	**15**
2		$Fe(acac)_2$	84	3
3	Iron Precursor	$FeCl_2$	76	9
4		$FeBr_2$	76	1
5		$Fe(OTf)_3$	76	3
6		25 mol% IPr·HCl	73	3
7		25 mol% NEt_3	81	14
8		12.5 mol% TMEDA	84	5
9	Additives	12.5 mol% DABCO	82	7
10		12.5 mol% CH_2Cl_2	81	21
11		**12.5 mol% $CHCl_3$**	**83**	**38**
12		12.5 mol% Glucosamin·HCl	100	11
13		iPr_2O	69	32
14		Bu_2O	65	17
15		CPME	83	48
16	Solvents	2-Methyl-THF	32	13
17		Dioxane	57	<1
18		Dioxolane	13	<1
19		TEGDME	18	2

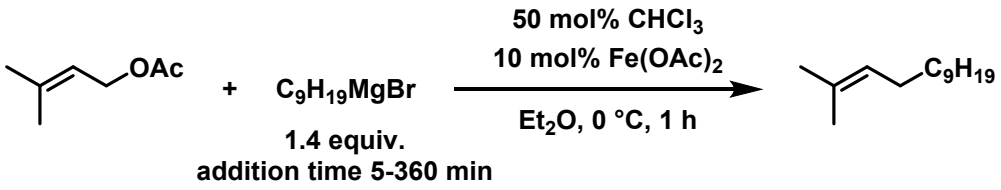
[a] Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane.



Entry	$CHCl_3$ [mol%]	equiv. $C_9H_{19}MgBr$	Conversion[%][a]	Yield [%][a]
1	0	1.2	89	12
2		1.35	90	12
3	12.5	1.2	83	38
4		1.35	93	34
5	25	1.2	85	38
6		1.35	100	42
7		1.5	90	39
8	**50**	1.2	80	41
9		**1.35**	**89**	**46** (42[b], 43[c])
10		1.5	93	50
11		1.75	99	53
12	100	1.2	79	41
13		1.35	77	41
14		1.5	80	42
15		1.75	90	54
16	200	1.2	68	40
17		1.35	75	41
18		1.5	74	43
19		1.75	76	48

[a] Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. [b] Grignard concentration 0.5 M. [c] Grignard concentration 2.0 M.

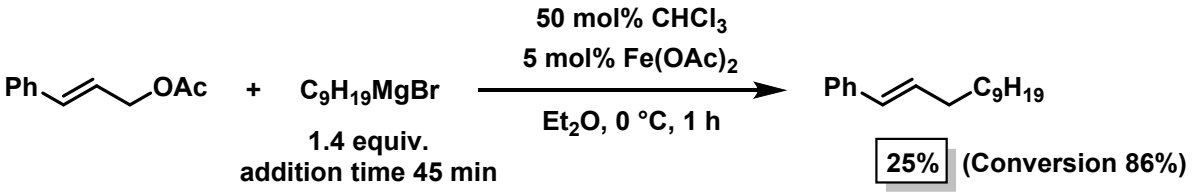
To remain in a reasonable amount of required chloroform and Grignard reagent, the reaction conditions were chosen to be 1.4 equiv. of the organomagnesiumbromide and 50 mol% $CHCl_3$.

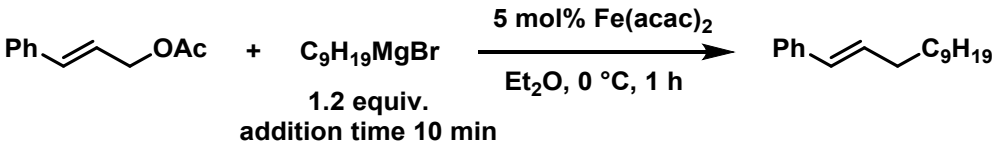


Entry	Addition time [min]	Conversion[%][a]	Yield [%][a]
1	5	68	22
2	10	89 (89[b])	45 (15[b])
3	20	84	52
4	30	100	50
5	**45**	**99** (100[b])	**64** (35[b])
6	60	94 (89[b])	61(31[b])
7	180	100[b]	50[b]
8	360	100[b]	62[b]

[a] Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. [b] Without $CHCl_3$.

Optimization experiments with aryl-substituted acetates



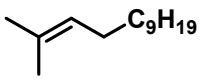


Entry	Change of reaction conditions		Conversion [%][a]	Yield [%][a]
1	Iron Precursor	$Fe(OAc)_2$	65	9
2		**$Fe(acac)_2$**	**100**	**70**
3		$FeCl_2$	100	53
4		$FeBr_2$	100	49
5	Additives	12.5 mol% PPh_3	100	61
6		12.5 mol% IPr·HCl	100	67
7		12.5 mol% NEt_3	100	60
8		6.25 mol% TMEDA	100	58
9		6.25 mol% DABCO	100	53
10		12.5 mol% $CHCl_3$	85	67
11		12.5 mol% Glucosamin·HCl	100	61
12	Addition time [min]	5	100	58
13		20	100	68

Isolated products

2-methyltridec-2-ene

Synthesized according to procedure A.



$C_{14}H_{28}$ 196.38 g/mol

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 5.18 - 5.06 (m, 1H), 2.01 - 1.90 (m, 2H), 1.69 (d, *J* = 1.0 Hz, 3H), 1.60 (s, 3H), 1.26 (s, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

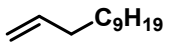
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 131.1, 125.0, 31.9, 29.9, 29.7, 29.7, 29.6, 29.4, 29.4, 28.1, 25.7, 22.7, 17.6, 14.1.

GC-MS (EI, 70 eV, m/z): 196 $[M]^+$, 111, 97, 83, 69, 56.

The data corresponds to the literature values.[14]

dodec-1-ene

Synthesized according to procedure A.



$C_{12}H_{24}$ 168.32 g/mol

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H [ppm] = 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (ddd, *J* = 17.1, 3.6, 1.6 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 2.08 - 2.00 (m, 2H), 1.41 - 1.22 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).

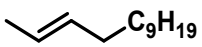
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 139.3, 114.1, 33.8, 31.9, 29.6, 29.6, 29.5, 29.4, 29.2, 29.0, 22.7, 14.1.

GC-MS (EI, 70 eV, m/z): 168 $[M]^+$, 140, 111, 97, 83, 69, 56.

The data corresponds to the literature values.[15]

tridec-2-ene

Synthesized according to procedure A.



$C_{13}H_{26}$ 182.35 g/mol

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 5.44 - 5.37 (m, 2H), 2.00 - 1.90 (m, 2H), 1.66 - 1.62 (m, 3H), 1.36 - 1.21 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

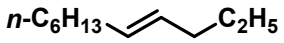
^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 131.7, 124.5, 32.6, 31.9, 31.0, 29.7, 29.7, 29.6, 29.4, 29.2, 22.7, 18.0, 14.1.

GC-MS (EI, 70 eV, m/z): 182 $[M]^+$, 125, 111, 97, 83, 69, 55.

The data corresponds to the literature values.[15]

(*E*)-octadec-7-ene

Synthesized according to procedure A. Product purification by filtration over silica (hexanes).



$C_{11}H_{22}$ 154.30 g/mol

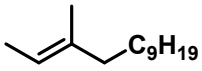
^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 5.45 – 5.30 (m, 2H), 2.06 – 1.84 (m, 4H), 1.38 – 1.21 (m, 10H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 130.6, 130.1, 34.7, 32.7, 31.8, 29.7, 28.9, 22.8, 22.7, 14.1, 13.7.

GC-HRMS (EI, 70 eV m/z): found 154.17198 $[M]^{+\bullet}$ (calculated 154.17160).

(*E*)-3-methyltridec-2-ene

Synthesized according to procedure A.



$C_{14}H_{28}$ 196.38 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 5.17 – 5.06 (m, 1H), 1.87 (m, 2H), 1.54 – 1.42 (m, 6H), 1.19 (m, 16H), 0.86 – 0.75 (m, 3H).

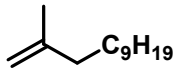
^{13}C-NMR (75 MHz, CDCl3) δ 136.22, 117.93, 39.72, 31.94, 29.67, 29.60, 29.37, 28.02, 22.71, 15.57, 14.14, 13.33.

GC-MS (EI, 70 eV, m/z): 196 $[M]^+$, 111, 97, 83, 70, 55.

The data corresponds to the literature values.[15]

2-methyldodec-1-ene

Synthesized according to procedure A. The purified product contains octadecane, wherein the separation has failed.



$C_{13}H_{26}$ 182.35 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 4.65 – 4.55 (m, 2H), 1.93 (t, J = 7.5 Hz, 2H), 1.65 – 1.62 (m, 3H), 1.28 – 1.10 (m, 16H), 0.87 – 0.75 (m, 3H).

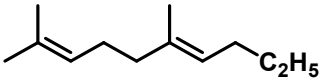
^{13}C-NMR (75 MHz, CDCl3) δ 146.4, 109.5, 37.9, 31.9, 29.6, 29.4, 27.7, 22.7, 22.4, 14.1.

GC-MS (EI, 70 eV, m/z): 182 $[M]^+$, 154, 126, 111, 97, 83, 69, 56.

The data corresponds to the literature values.[16]

(*E*)-2,6-dimethyldeca-2,6-diene

Synthesized according to procedure A.



$C_{12}H_{22}$ 166.31 g/mol

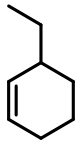
^{1}H-NMR (300 MHz, Chloroform-d) δ 5.10 – 5.00 (m, 2H), 2.05 – 1.80 (m, 6H), 1.64 – 1.59 (m, 6H), 1.56 – 1.54 (s, 3H) 1.34 – 1.20 (m, 2H), 0.86 – 0.69 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 135.1, 131.5, 125.4, 124.4, 32.0, 30.0, 26.7, 25.7, 23.4, 23.2, 17.6, 13.9.

GC-HRMS (EI, 70 eV m/z): found 166.17172 $[M]^{+\bullet}$ (calculated 166.17160).

3-ethylcyclohex-1-ene

Synthesized according to procedure A.



C_8H_{14} 110.20 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 5.72 – 5.51 (m, 2H), 2.03 – 1.89 (m, 3H), 1.85 – 1.10 (m, 6H), 0.91 (t, J = 7.4 Hz, 3H).

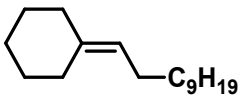
^{13}C-NMR (75 MHz, CDCl3) δ 132.1, 126.74, 36.9, 29.1, 28.7, 25.5, 21.6, 11.5.

GC-MS (EI, 70 eV, m/z): 110 $[M]^{+}$, 95, 81, 67, 53.

The data corresponds to the literature values.[17]

Undecylidenecyclohexane

Synthesized according to procedure A. The purified product contains octadecane, wherein the separation has failed.



$C_{17}H_{32}$ 236.44 g/mol

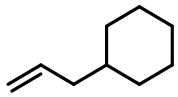
^{1}H-NMR (300 MHz, Chloroform-d) δ 5.06 (tt, J = 7.3, 1.3 Hz, 1H), 2.16 – 1.89 (m, 6H), 1.57 – 1.41 (m, 6H), 1.26 (m, 16H), 0.94 – 0.82 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 130.6, 130.1, 34.7, 32.7, 31.8, 29.7, 28.9, 22.8, 22.7, 14.1, 13.7.

GC-HRMS (EI, 70 eV, m/z): found 236.2500 $[M]^{+\bullet}$ (calculated 235.2499).

Allylcyclohexane

Synthesized according to procedure A.



C_9H_{16} 124.23 g/mol

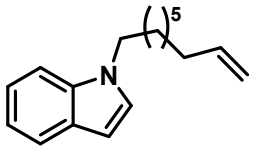
^{1}H-NMR (300 MHz, Chloroform-d) δ 5.72 (ddt, J = 17.4, 10.4, 7.2 Hz, 1H), 4.96 – 4.81 (m, 2H), 1.87 (m, 2H), 1.65 (s, 5H), 1.29 – 0.98 (m, 4H), 0.95 – 0.71 (m, 2H).

^{13}C-NMR (75 MHz, CDCl3) δ 137.71, 115.13, 41.95, 37.67, 33.07, 26.58, 26.34.

GC-MS (EI, 70 eV, m/z): 124 $[M]^+$, 83, 67, 55.

1-(non-8-en-1-yl)-1*H*-indole

Synthesized according to procedure A. The purified product contains 1-hexyl-1H-indole, wherein the separation has failed.



$C_{17}H_{23}N$ 241.38 g/mol

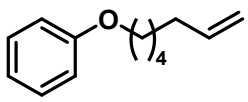
TLC R_f = 0.3 (hexanes/ethylacetate = 200/1)

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.62 – 6.91 (m, 5H), 6.41 (d, J = 3.1 Hz, 1H), 5.81 – 5.61 (m, 1H), 4.99 – 4.78 (m, 2H), 4.03 (td, J = 7.1, 2.2 Hz, 2H), 1.97 (dq, J = 14.1, 7.0 Hz, 2H), 1.83 – 1.68 (m, 2H), 1.35 – 1.04 (m, 8H).

GC-HRMS (EI, 70 eV, m/z): found 241.1824 $[M]^{+\bullet}$ (calculated 241.1825).

(hept-6-en-1-yloxy)benzene

Synthesized according to procedure A. The purified product contains butoxybenzene, wherein the separation has failed.



$C_{13}H_{18}O$ 190.29 g/mol

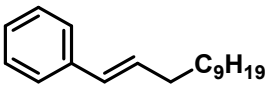
^{1}H-NMR (300 MHz, Chloroform-d) δ 7.26 – 7.11 (m, 2H), 6.91 – 6.73 (m, 3H), 5.74 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.02 – 4.80 (m, 2H), 3.88 (t, J = 6.5 Hz, 2H), 2.00 (m, 2H), 1.80 – 1.62 (m, 2H), 1.40 (m, 4H).

^{13}C-NMR (75 MHz, CDCl3) δ 159.11, 138.85, 129.41, 120.49, 114.50, 67.77, 33.72, 29.18, 28.69, 25.60.

GC-HRMS (EI, 70 eV m/z): found 190.13483 $[M]^{+\bullet}$ (calculated 190.13522).

(*E*)-1-phenyldodec-1-ene

Synthesized according to procedure B.



$C_{18}H_{28}$ 244.42 g/mol

TLC R_f = 0.8 (hexanes)

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.41 - 7.14 (m, 5H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.7 Hz, 1H), 2.21 (td, *J* = 7.7, 1.0 Hz, 2H), 1.56 - 1.40 (m, 2H), 1.28 (s, 14H), 0.89 (t, *J* = 6.7 Hz, 3H).

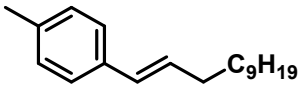
^{13}C-NMR (101 MHz, $CDCl_3$) δ_C [ppm] = 138.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 31.9, 29.6, 29.6, 29.4, 29.4, 29.4, 22.7, 14.1.

GC-MS (EI, 70 eV, m/z): 244 $[M]^{+}$, 171, 145, 129, 117, 104, 91, 77, 67, 55.

The data correspond to the literature values.[18]

(*E*)-1-(4-methylphenyl)-dodec-1-ene

Synthesized according to procedure B. The purified product contains octadecane, wherein the separation has failed.



$C_{19}H_{30}$ 258.45 g/mol

TLC R_f = 0.8 (hexanes)

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.26 - 7.20 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.38 - 6.30 (m, 1H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.32 (s, 3H), 2.19 (q, *J* = 6.8 Hz, 2H), 1.50 - 1.22 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

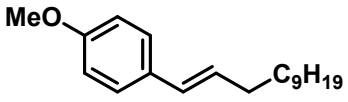
^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 136.4, 135.2, 130.3, 129.5, 129.2, 125.7, 33.1, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 21.2, 14.2.

GC-MS (EI, 70 eV, m/z): 258 $[M]^+$, 143, 131, 115, 106, 91, 77, 67, 55.

The data correspond to the literature values.[19]

(*E*)-1-(4-methoxyphenyl)-dodec-1-ene

Synthesized according to procedure B. The purified product contains octadecane, wherein the separation has failed.



$C_{19}H_{30}O$ 274.45 g/mol

TLC R_f = 0.7 (hexanes)

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.34 - 7.21 (m, 2H), 6.89 - 6.76 (m, 2H), 6.40 - 6.24 (m, 1H), 6.08 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.81 (s, 3H), 2.25 - 2.09 (m, 2H), 1.49 - 1.16 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

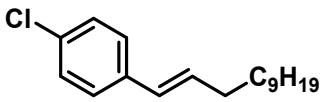
^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 158.6, 130.8, 129.1, 129.0, 126.9, 113.9, 55.3, 33.1, 32.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 22.7, 14.2.

GC-MS (EI, 70 eV, m/z): 274 $[M]^+$, 159, 147, 134, 121, 103, 91, 78, 67, 55.

The data correspond to the literature values.[20]

(*E*)-1-(4-chlorophenyl)-dodec-1-ene

Synthesized according to procedure B.



$C_{18}H_{27}Cl$ 278.86 g/mol

TLC R_f = 0.8 (hexanes)

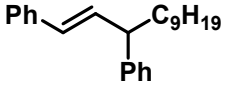
^{1}H-NMR (300 MHz, Chloroform-d) δ 7.18 (s, 4H), 6.25 (d, J = 15.9 Hz, 1H), 6.12 (dt, J = 15.8, 6.6 Hz, 1H), 2.12 (q, J = 7.0 Hz, 2H), 1.38 (t, J = 7.2 Hz, 2H), 1.29 – 1.14 (m, 14H), 0.88 – 0.73 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 136.44, 132.24, 132.02, 128.57, 128.50, 127.09, 33.05, 31.93, 29.64, 29.54, 29.37, 29.31, 29.26, 22.72, 14.15.

GC-HRMS (EI, 70 eV m/z): found 278.17889 $[M]^{+\bullet}$ (calculated 278.17958).

(*E*)-dodec-1-ene-1,3-diyldibenzene

Synthesized according to procedure B.



$C_{24}H_{32}$ 320.52 g/mol

TLC R_f = 0.8 (hexanes)

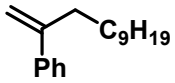
^{1}H-NMR (300 MHz, Chloroform-d) δ 7.33 – 7.02 (m, 10H), 6.38 – 6.17 (m, 2H), 3.32 (q, J = 7.2 Hz, 1H), 1.75 (s, 2H), 1.19 (m, 14H), 0.85 – 0.74 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 144.77, 137.63, 134.51, 129.22, 128.68, 128.47, 128.45, 128.31, 127.64, 126.99, 126.13, 125.74, 49.21, 35.92, 31.90, 29.62, 29.56, 29.33, 27.65, 22.70, 14.14.

GC-HRMS (EI, 70 eV, m/z): found 320.2483 $[M]^{+\bullet}$ (calculated 320.2499).

dodec-1-en-2-ylbenzene

Synthesized according to procedure B.



$C_{18}H_{28}$ 244.42 g/mol

TLC R_f = 0.8 (hexanes)

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.46 – 7.20 (m, 5H), 5.26 (d, J = 1.6 Hz, 1H), 5.05 (q, J = 1.4 Hz, 1H), 2.49 (td, J = 7.4, 1.3 Hz, 2H), 1.44 (s, 1H), 1.43 – 1.19 (m, 15H), 0.93 – 0.82 (m, 3H).

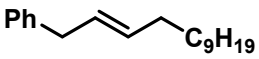
^{13}C-NMR (75 MHz, CDCl3) δ 148.78, 141.47, 128.21, 127.22, 126.11, 112.00, 35.37, 31.93, 29.63, 29.48, 29.38, 28.28, 22.72, 14.16.

GC-MS **(**EI, 70 eV, m/z): 244 $[M]^{+}$, 143, 131, 118, 103, 91, 77, 77, 55.

The data correspond to the literature values.[21]

(*E*)-tridec-2-en-1-ylbenzene

Synthesized according to procedure B.



$C_{19}H_{30}$ 258.45 g/mol

TLC R_f = 0.8 (hexanes)

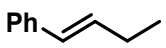
^{1}H-NMR (300 MHz, Chloroform-d) δ 7.40 – 7.24 (m, 2H), 7.24 – 7.09 (m, 3H), 5.67 – 5.42 (m, 2H), 3.33 (d, J = 5.3 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.40 – 1.20 (m, 16 H), 0.96 – 0.83 (m, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 141.16, 132.19, 128.64, 128.48, 128.32, 125.84, 39.09, 32.55, 31.95, 29.66, 29.54, 29.51, 29.38, 29.23, 22.73, 14.17.

GC-HRMS (EI, 70 eV, m/z): found 258.2337 $[M]^{+\bullet}$ (calculated 258.2342).

(*E*)-but-1-en-1-ylbenzene

Synthesized according to procedure B.



$C_{10}H_{12}$ 132.21 g/mol

TLC R_f = 0.8 (hexanes)

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.41 – 7.32 (m, 2H), 7.32 – 7.14 (m, 3H), 6.45 – 6.33 (m, 1H), 6.28 (dt, J = 15.9, 6.1 Hz, 1H), 2.32 – 2.15 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H).

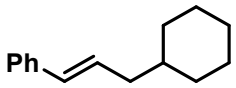
^{13}C-NMR (75 MHz, CDCl3) δ 137.93, 132.66, 128.76, 128.48, 126.76, 125.90, 26.10, 13.68.

GC-MS R_t = 5.72 min
(EI, 70 eV, m/z): 132 $[M]^+$, 117, 104, 91, 77, 63, 51.

The data correspond to the literature values.[22]

(*E*)-(3-cyclohexylprop-1-en-1-yl)benzene.

Synthesized according to procedure B.



$C_{15}H_{20}$ 200.33 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.18 (ddt, J = 27.9, 14.1, 7.3 Hz, 5H), 6.28 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.4, 7.1 Hz, 1H), 2.01 (dd, J = 15.6, 8.7 Hz, 2H), 1.63 (q, J = 13.2, 12.3 Hz, 5H), 1.32 (ddd, J = 11.0, 7.3, 3.6 Hz, 1H), 1.15 (dt, J = 20.3, 7.1 Hz, 3H), 1.00 – 0.74 (m, 2H).

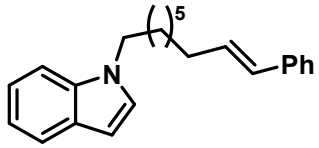
^{13}C-NMR (75 MHz, CDCl3) δ 137.94, 130.68, 129.78, 128.46, 126.74, 125.91, 41.08, 38.22, 33.23, 26.59, 26.38.

GC-MS (EI, 70 eV, m/z): 200 $[M]^+$, 141, 128, 115, 104, 91, 83, 77, 65, 55.

The data correspond to the literature values. [23]

(*E*)-1-(9-phenylnon-8-en-1-yl)-1*H*-indole

Synthesized according to procedure B.



$C_{23}H_{27}N$ 317.48 g/mol

TLC R_f = 0.3 (hexanes/ethylacetate = 200/1)

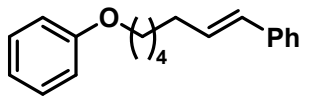
^{1}H-NMR (300 MHz, Chloroform-d) δ 7.64 (d, J = 7.8 Hz, 1H), 7.40 – 7.03 (m, 9H), 6.49 (s, 1H), 6.37 (d, J = 15.9 Hz, 1H), 6.21 (dt, J = 15.8, 6.8 Hz, 1H), 4.19 – 4.01 (m, 2H), 2.26 – 2.04 (m, 2H), 1.86 (q, J = 8.1, 7.0 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.38 – 1.21 (m, 6H).

^{13}C-NMR (75 MHz, CDCl3) δ 137.87, 135.92, 131.02, 129.80, 128.49, 127.81, 126.80, 125.90, 121.28, 120.93, 119.14, 109.38, 100.82, 46.42, 32.98, 30.26, 29.27, 29.15, 29.07, 26.99.

GC-HRMS (EI, 70 eV m/z): found 317.21286 $[M]^{+\bullet}$ (calculated 317.21380).

(*E*)-(7-phenoxyhept-1-en-1-yl)benzene

Synthesized according to procedure B.



$C_{19}H_{22}O$ 266.38 g/mol

TLC R_f = 0.4 (hexanes/ethylacetate = 200/1)

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.40 – 7.27 (m, 6H), 7.27 – 7.11 (m, 1H), 7.07 – 6.84 (m, 3H), 6.46 – 6.33 (m, 1H), 6.23 (dt, J = 15.8,

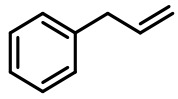
6.8 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 2.25 (tdd, J = 7.0, 5.6, 1.4 Hz, 2H), 1.90 – 1.72 (m, 2H), 1.65 – 1.44 (m, 4H).

^{13}C-NMR (75 MHz, CDCl3) δ 159.05, 137.81, 130.79, 129.97, 129.42, 128.49, 126.83, 125.92, 120.48, 114.47, 67.73, 32.97, 29.19, 29.13, 25.68.

GC-HRMS (EI, 70 eV, m/z): found 266.1661 $[M]^{+\bullet}$ (calculated 266.1665).

Allylbenzene

Synthesized according to procedure B.



C_9H_{10} 118.18 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.30 – 6.96 (m, 5H), 5.89 (m, 1H), 5.09 – 4.89 (m, 2H), 3.31 (d, J = 6.6 Hz, 2H).

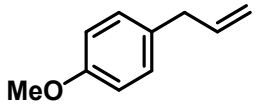
^{13}C-NMR (75 MHz, CDCl3) δ 140.07, 137.48, 128.61, 128.44, 126.08, 115.80, 40.28.

GC-MS (EI, 70 eV, m/z): 118 $[M]^{+}$, 91, 65.

The data corresponds to the literature values.[24]

4-allylanisole

Synthesized according to procedure B.



$C_{10}H_{12}O$ 148.21 g/mol

TLC R_f = 0.6 (hexanes/ethylacetate 20/1)

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.16 - 7.08 (m, 2H), 6.89 - 6.81 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.4, 6.6 Hz, 1H), 5.12 - 5.06 (m, 1H), 5.04 (d, *J* = 0.7 Hz, 1H), 3.80 (s, 3H), 3.34 (d, *J* = 6.6 Hz, 2H).

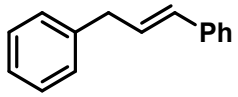
^{13}C-NMR (75 MHz, $CDCl_3$) δ_C [ppm] = 158.0, 137.9, 132.1, 129.5, 115.5, 113.8, 55.3, 39.4.

GC-MS (EI, 70 eV, m/z): 148 $[M]^+$.

The data corresponds to the literature values.[25]

(*E*)-prop-1-ene-1,3-diyldibenzene

Synthesized according to procedure B.



$C_{15}H_{14}$ 194.28 g/mol

TLC R_f = 0.3 (hexanes)

^{1}H-NMR (300 MHz, $CDCl_3$) δ_H [ppm] = 7.30 - 7.08 (m, 10H), 6.42 - 6.27 (m, 2H), 3.47 (d, *J* = 6.4 Hz, 2H).

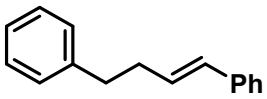
^{13}C-NMR (75 MHz, CDCl3) δ 140.18, 137.49, 131.09, 129.24, 128.76, 128.51, 127.18, 126.19, 126.14, 39.37.

GC-MS (EI, 70 eV, m/z): 194 $[M]^+$, 179, 165, 115, 102, 91, 78, 65, 51.

The data corresponds to the literature values.[26]

(*E*)-but-1-ene-1,4-diyldibenzene

Synthesized according to procedure B.



$C_{16}H_{16}$ 208.30 g/mol

^{1}H-NMR (300 MHz, Chloroform-d) δ 7.32 (m Hz, 10H), 6.47 (d, J = 16.0 Hz, 1H), 6.32 (dt, J = 15.1, 6.7 Hz, 1H), 2.84 (t, J = 7.8 Hz, 2H), 2.58 (q, J = 7.4 Hz, 2H).

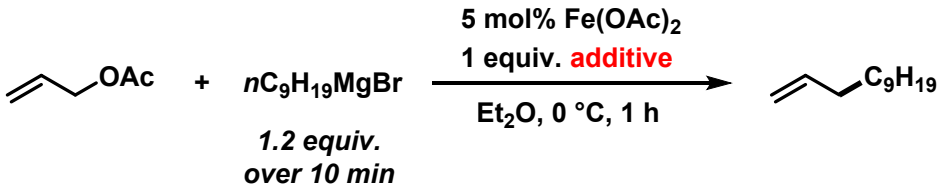
^{13}C-NMR (75 MHz, CDCl3) δ 141.78, 137.74, 130.40, 129.99, 128.50, 128.38, 126.96, 126.02, 125.91, 35.91, 34.91.

GC-MS (EI, 70 eV, m/z): 208 $[M]^+$, 117, 102, 91, 77, 65, 51.

The data corresponds to the literature values.[26]

4 Mechanistic Investigations

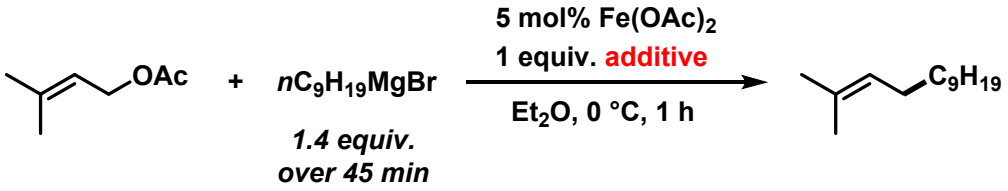
External Functional Group Test / Effect of electrophiles

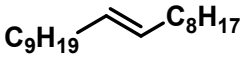
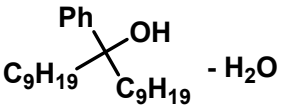


A suspension of $Fe(OAc)_2$ (0.025 mmol, 4.3 mg) in absolute Et_2O (2 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried reaction tube. After the addition of freshly distilled allyl acetate (0.5 mmol, 54 µL) and additive, a 1.0 M *n*-nonylmagnesium bromide solution (0.6 mmol, 0.6 mL) in Et_2O was added dropwise over a period of 10 minutes and the mixture was stirred at 0 °C for 1 hour. The reaction mixture was then hydrolyzed with a saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc. Products were were analyzed via GC-MS and GC-FID.

Entry	**Additive**	Additive conversion [%] [a]	Yield [%] [a]
1	-	-	77
2	PhCN	0	21
3	*n*-C_3H_7CN	9	49
4	$PhNO_2$	90	<1
5	$EtNO_2$	87	8
6	$PhNH_2$	77	9
7	*n*-$C_6H_{13}NH_2$	0	80
8	PhCHO	100	16
9	**$PhCO_2Me$**	**0**	**82**
10	*n*-$C_3H_7CO_2Me$	4	72
11	PhOH	0	75 [b]
12	*n*-$C_5H_{11}OH$	6	79 [b]

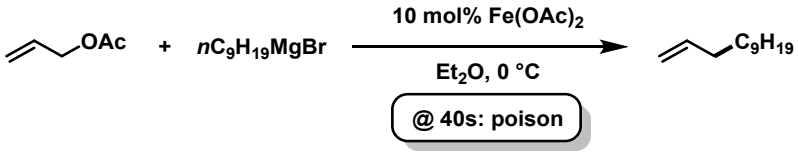
[a] Yields were determined by quantitative GC-FID vs. internal n-pentadecane. [b] 2.2 equiv. n-$C_9H_{19}MgBr$.



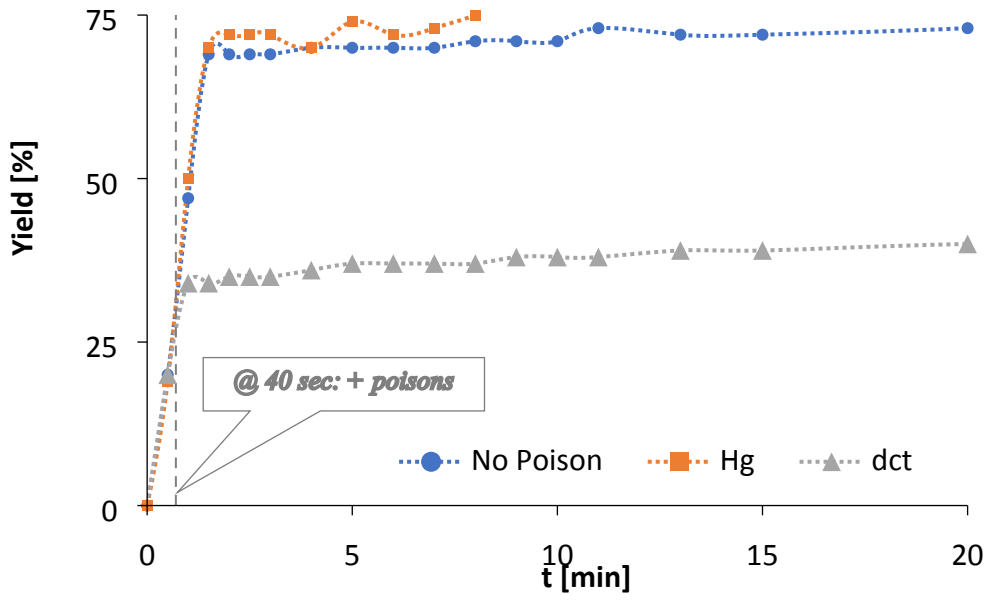
Entry	Additive	Yield [%] [a]	Estimated sideproduct [b]
1	-	27	-
2	1,2- Dichloroethane	27	-
3	Chlorobenzene	24	-
4	Chloroform	58	 **m/z = 266**
5	Air	37	**$C_9H_{19}OH$ - H_2O** **m/z = 126** [c]
6	$PhCO_2Me$	31	 **m/z = 342**

[a] Yields were determined by quantitative GC-FID vs. internal n-pentadecane. [b] Masses recorded by GC-MS. [c] Retention time at 6.0 min vs. actual Nonenes at 3.7-4.0 min.

Kinetic Poisoning



A suspension of $Fe(OAc)_2$ (0.05 mmol, 8.7 mg) and *n*-pentadecane (0.18 mmol, 50 µL) in absolute Et_2O (4 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried schlenk flask. After the addition of freshly distilled allyl acetate (0.50 mmol, 54 µL), a 1.0 M *n*-nonylmagnesium bromide solution (0.50 mmol, 0.5 mL) in Et_2O was added dropwise over a period of 2 minutes and the mixture was stirred at 0 °C. Samples of 0.1 mL were taken out during the reaction and hydrolyzed with a saturated NH_4Cl solution. In case of poisoning, the Hg (5.00 mmol, 148 µL) or Dibenzocyclooctatetrene (dct, 0.25 mmol, 51 mg, dissolved in 0.4 mL absolute Et_2O) respectively was added after 40 seconds. The yields were determined by quantitative GC-FID vs. *n*-pentadecane as internal standard.



Filtration Test

A suspension of $Fe(OAc)_2$ (0.05 mmol, 8.7 mg) in absolute Et_2O (2 mL) was cooled to 0 °C under a nitrogen atmosphere in a flame dried schlenk flask. After the addition of

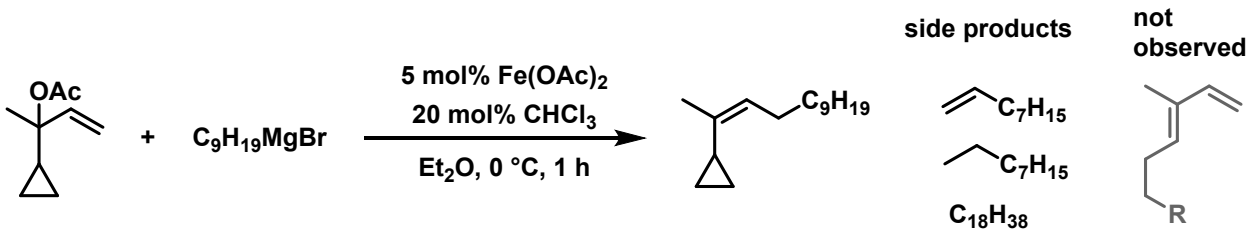
freshly distilled allyl acetate (0.50 mmol, 54 µL), a 1.0 M *n*-nonylmagnesium bromide solution (0.50 mmol, 0.5 mL) in Et_2O was added dropwise over a period of 10 minutes and the mixture was stirred at 0 °C for 1 hour. A sample was taken out (Yield coupling product 78%) and the reaction mixture was filtered.

To the filtrate another 0.5 mmol of allyl acetate and *n*-nonylmagnesium bromide (over 10 min) was added at 0 °C and another reaction cycle was run (Yield 2nd cycle filtrate 61%).

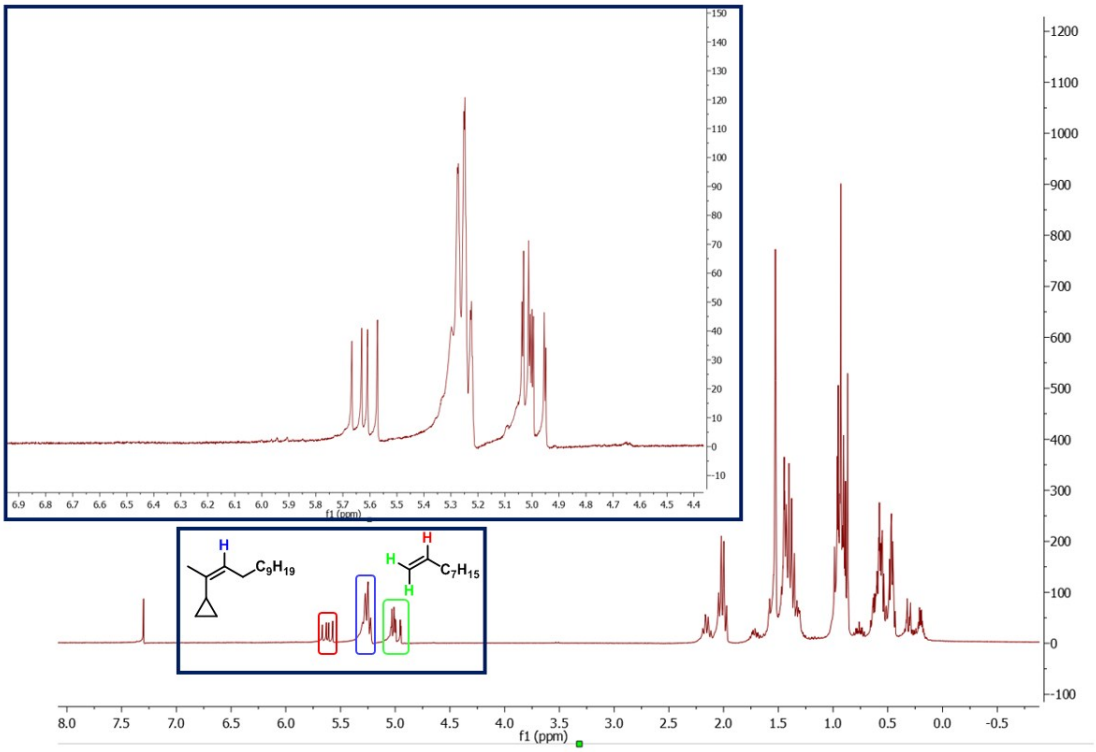
The residue of the filtration was washed with absolute Et_2O (2 x 2 mL) and added to 0.5 mmol allyl acetate in 2 mL absolute Et_2O. 0.5 mmol of *n*-nonylmagnesium bromide was added at 0 °C over 10 min and another reaction cycle was run (Yield 2nd cycle residue 45%).

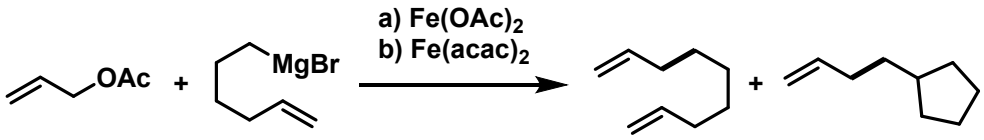
The yields were determined by quantitative GC-FID vs. *n*-pentadecane as internal standard.

Radical Clock Experiments



The reaction was carried out as described in Protocol A. The crude NMR showed no ring opening of the cyclopropane as no signal evolved at around 6.X ppm, which would indicate the presence of the diene moiety.[27]

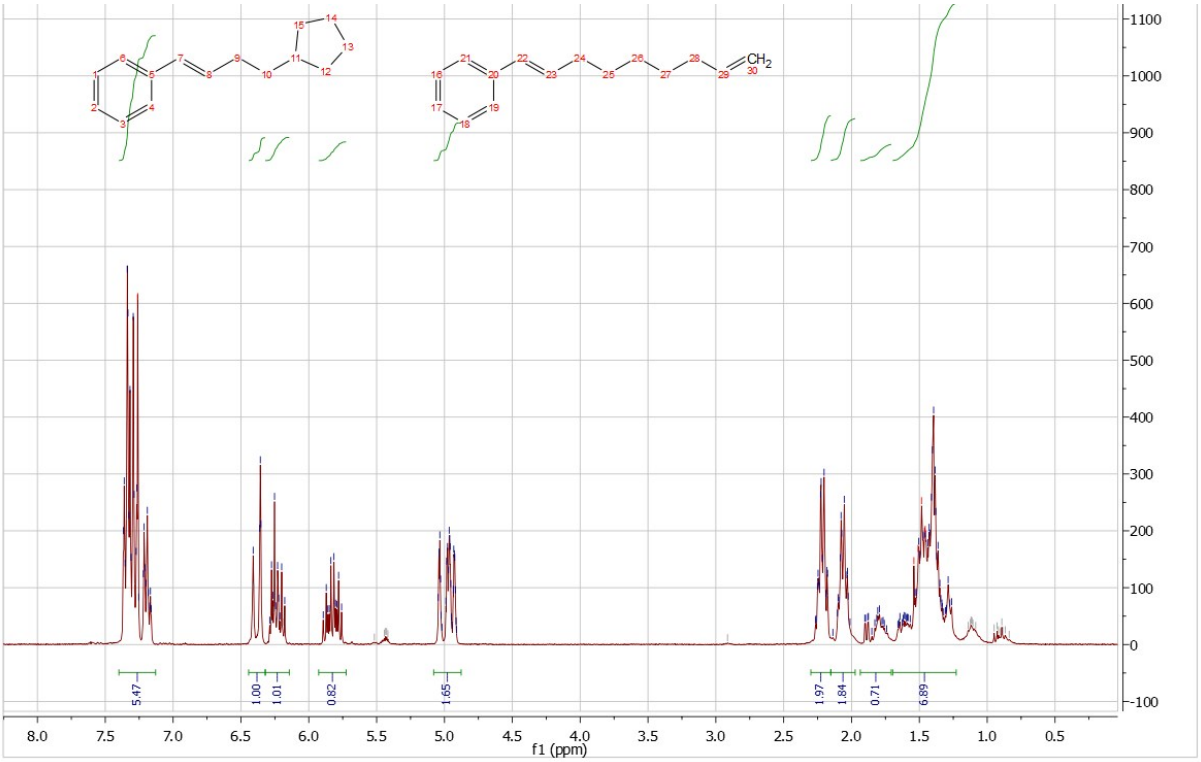




a)	95	:	5
b)	85	:	15

The reaction was carried out as described in a) Protocol A without addition of $CHCl_3$ and b) Protocol B. The Grignard reagent (2% ring closure) and the reactions were

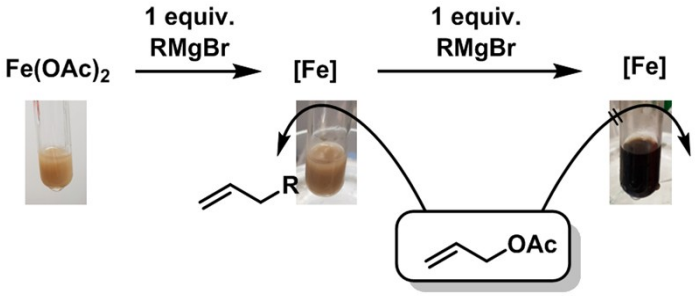
analyzed by GC-MS and GC-FID. When using cinnamylacetate as the starting material, isolation and NMR analysis of the coupling products was possible, showing roughly 15% of additional ring closure.



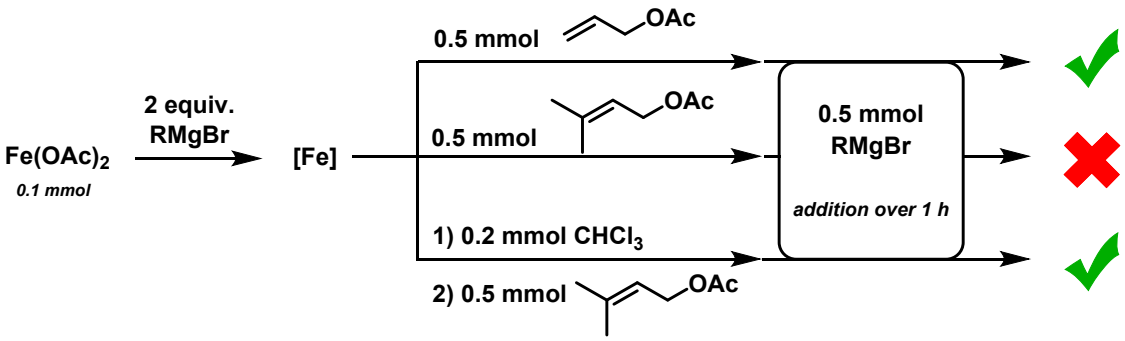
Stoichiometric Reduction Experiments

For determining the oxidation states of the active catalyst, the following experiments have been done:

A solution of $Fe(OAc)_2$ (17.4 mg, 0.1 mmol) in 1 mL diethylether was mixed with **A)** 1 equiv. or **B)** 2 equiv. of $C_9H_{19}MgBr$ (1 M in diethylether).

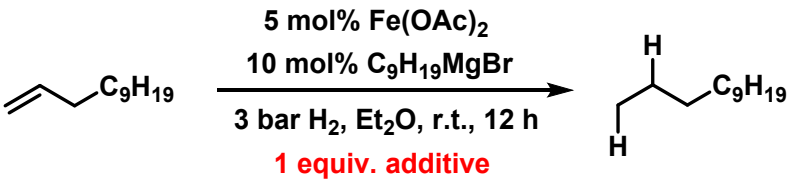


- These suspensions were then added dropwise to separate solutions of allylacetate (0.1 mmol) in 1 mL diethylether. In case of **A** formation of cross coupling product dodecene could be observed (29%), whereas in **B** only traces could be observed.



- To a solution of **B** was added **B1)** 0.5 mmol of allylacetate, **B2)** 0.5 mmol prenyl acetate or **B3)** 0.2 mmol chloroform and 0.5 mmol prenylacetate. To these solutions was added 0.5 mmol $C_9H_{19}MgBr$ over a period of 1 hour. In case of **B1** and **B3** catalytic activity was observed, whereas in **B2** it was not, showing that allylacetate could possibly reoxidize the catalyst, where in the case of prenylacetate $CHCl_3$ was necessary as an oxidizing agent.

Hydrogenation Poisoning studies



1-Dodecene (0.25 mmol), 5 mol% $Fe(OAc)_2$ and 1 equiv. of additive were mixed in a flame dried autoclave vial in an argon-filled glovebox. 10 mol% of $C_9H_{19}MgBr$ was added and the mixture was stirred vigorously for 2 min. The rubber septum was penetrated with a cannula and the reaction vial was put into an autoclave, which was set under a pressure of 3 bar of H_2. The reaction was stirred overnight at r.t. and then quenched with aqueous NH_4Cl solution. The organic phase was extracted with ethyl acetate, dried over sodium sulfate and filtered over a short layer of silica. The yields were determined by quantitative GC-FID vs. *n*-pentadecane as internal standard.

Entry	**Additive**	Conversion [%]	Yield [%]
1	-	100	77
2	**$MgBr_2$**	**19**	**<1**
3	$MgCl_2$	100	72
4	LiBr	3	<1

[a] 25 bar H_2.

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