1 General

Chemicals und Solvents. If not indicated, commercial reagents were used without purification. For catalytic reactions, exclusively dried solvents were used. Tetrahydrofuran (THF) was distilled over sodium / benzophenone before use. Iron(II)-chloride (98%) and iron(III) chloride (99.9%, anhydrous) were weighed in a glove box from *MBraun* (Argon 99.996 %). All reactions were carried out using standard Schlenk techniques under nitrogen (99.5%) in rubber septa-capped vials. Solvents for chromatography were distilled under reduced pressure prior to use.

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 A (220-240 mesh) from *Acros*. Pure petroleum ether or mixtures of petroleum ether and 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 0.25, 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 internal standard *n*-pentadecane and analytically pure samples).

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

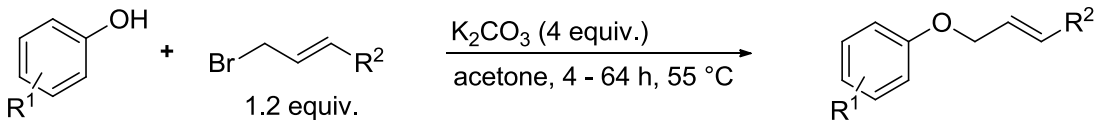
s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of triplet. For yield determinations, hexamethyldisiloxane was used as internal standard.

IR spectroscopy. Infrared spectra were recorded on a *Varian* Scimitar 1000 FT-IR equipped with a ATR unit. Wavenumbers are indicated in cm-1. Intensive absorption bands are indicated with „s“ (strong), medium intensive bands with „m“ (medium) und weak intensive bands with „w“ (weak).

High resolution mass spectrometry (HRMS). The spectra were recorded by the Central Analysis Lab at the Department of Chemistry at the University of Regensburg with a MAT SSQ 710 A from *Finnigan*.

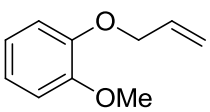
Superscripts behind compound names are literature references.

2 Preparation of *O*-allyl phenyl ethers [1]



Representative procedure for the *O*-allylation of guajacol: To a solution of guajacol (40 mmol, 5.95 g) in acetone (40 mL), anhydrous K_2CO_3 (160 mmol, 22.11 g) and allyl bromide (48 mmol, 4.15 mL) were added. The reaction mixture was heated to reflux for 12 h, cooled to room temperature, filtered and washed with acetone (2 x 10 mL). The filtrate was concentrated under reduced pressure to obtain a residue which was purified by column chromatography.

O-Allyl-2-methoxy phenyl ether[2]



Condition: yellow oil

Chromatography solvent: hexanes/ethyl acetate (3/1)

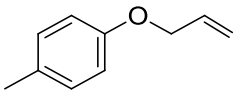
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.98-6.84 (m, 4H), 6.10 (ddt, *J* = 17.2 Hz, 10.7 Hz, 5.4 Hz, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 5.4 Hz, 2H), 3.87 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 149.6, 148.1, 133.5, 121.3, 120.8, 117.9, 113.7, 111.8, 69.3, 51.8

Retention time GC-MS: 6.60 min

LR MS (EI, 70 eV, m/z): 164 [M+], 149, 137, 123, 109, 95, 77, 65, 52

O-Allyl-4-tolyl ether[3]



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

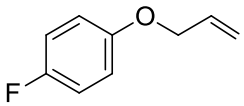
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.04-6.82 (m, 4H), 6.02 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 1H), 5.42 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.30 (d, *J* = 10.5, 1.4 Hz, 1H), 4.50 (dt, *J* = 5.3, 1.5 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.5, 133.6, 130.1, 129.9, 117.5, 114.7, 68.9, 20.5

Retention time GC-MS: 6.02 min

LR MS (EI, 70 eV, m/z): 148 [M+], 133, 119, 107, 91, 77, 63, 51

O-Allyl-4-fluorophenyl ether[4]



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (3/1)

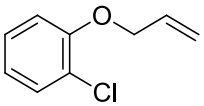
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] =7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.09 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.44 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.54 (d, *J* = 5.3 Hz, 2H), 3.87 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 157.4, 154.7, 133.2, 117.7, 115.9, 115.7, 69.4

Retention time GC-MS: 5.38 min

LR MS (EI, 70 eV, m/z): 152 [M+], 137, 112, 96, 83, 63, 57

O-Allyl 2-chlorophenyl ether[5]



Condition: yellow oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

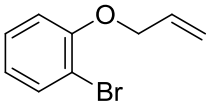
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] =7.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.20 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 6.91 (m, 2H), 6.08 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.62 (dt, *J* = 5.1, 1.6 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 154.1, 132.7, 130.4, 127.6, 123.1, 121.5, 117.9, 113.8, 69.7

Retention time GC-MS: 6.53 min

LR MS (EI, 70 eV, m/z): 168 [M+], 141 133, 113, 105, 99, 92, 75, 63, 51

O-Allyl 2-bromophenyl ether[6]



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

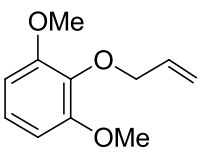
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] =7.55 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.27-7.21 (m, 1H), 6.90 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.84 (ddd, *J* = 8.4, 7.7, 1.4 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.4, 5.0 Hz, 1H), 5.49 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 4.62 (dt, *J* = 5.0, 1.6 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 155.0, 133.4, 132.6, 128.4, 122.0, 117.8, 113.6, 112.3, 69.7

Retention time GC-MS: 7.04 min

LR MS (EI, 70 eV, m/z): 212 [M+], 197, 185, 172, 157, 145, 133, 119, 105, 92, 77, 63, 50

O-Allyl 2,6-dimethoxyphenyl ether[7]



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

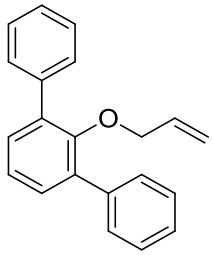
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.95 (t, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.10 (ddt, *J* = 16.4 Hz, 10.3 Hz, 6.1 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.50 (dt, *J* = 6.1 Hz, 2H), 3.80 (s, 6H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 153.7, 136.8, 134.6, 123.7, 117.6, 105.3, 74.1, 56.1

Retention time GC-MS: 7.46 min

LR MS (EI, 70 eV, m/z): 194 [M+], 179,167, 153, 138, 125, 110, 95, 77, 65, 51.

O-Allyl 2,6-diphenylphenyl ether



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.74 (d, *J* = 7.2 Hz, 4H), 7.57-7.29 (m, 9H), 5.53 (m, 1H), 5.02-4.85 (m, 2H), 3.90-3.79 (m, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 153.8, 138.9, 136.3, 133.8, 130.4, 129.7, 128.2, 127.3, 124.5, 117.3, 73.9

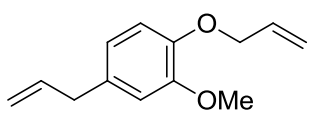
Retention time GC-MS: 10.84 min

LR MS (EI, 70 eV, m/z): 286 [M+], 271, 257, 245, 227, 215, 202, 189, 168, 152, 139, 115, 102, 91, 77, 65, 51

HR MS (CI, m/z): found 287.1438 $[M+H]^+$ (calculated 287.143)

IR in [cm^{-1}]: 3058 (w), 3027 (w), 2863 (w), 1599 (w), 1497 (w), 1461 (m), 1413 (s), 1215 (s), 749 (s), 699 (s)

O-Allyl eugenol



Condition: colorless oil

Chromatography solvent: hexanes/ethyl acetate (20/1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.95 (t, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.10 (ddt, *J* = 16.4 Hz, 10.3 Hz, 6.1 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.50 (dt, *J* = 6.1 Hz, 2H), 3.80 (s, 6H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 149.5, 146.4, 137.7, 133.6, 133.1, 120.4, 117.8, 115.7, 113.7, 112.3, 70.0, 55.9, 39.9

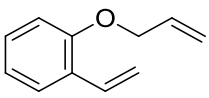
Retention time GC-MS: 6.40 min

LR MS (EI, 70 eV, m/z): 204 [M+], 163, 147, 135, 115, 107, 103, 91, 77, 65, 51

HR MS (CI, m/z): found 205.1224 $[M+H]^+$ (calculated 205.1223)

IR in [cm^{-1}]: 3079 (w), 2935 (w), 2836 (w), 1590 (w), 1510 (s), 1464 (m), 1420 (m), 1259 (s), 1229 (s)

2-Allyloxy styrene[8]



Condition: yellow oil

Chromatography solvent: hexanes/ethyl acetate (10/1)

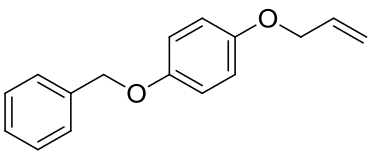
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.50 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.22 (m, 1H), 7.11 (dd, *J* = 17.8, 11.2 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.76 (dd, *J* = 17.8, 1.4 Hz,1H), 5.44 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.34-5.20 (m, 2H), 4.58 (d, *J* = 5.1 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 155.8, 133.4, 131.7, 128.8, 127.1, 126.5, 120.9, 117.3, 114.4, 112.4, 69.2

Retention time GC-MS: 6.61 min

LR MS (EI, 70 eV, m/z): 160 [M+], 145, 131, 119, 103, 91, 77, 65, 51

O-Allyl 4-benzyloxyphenyl ether[9]



Condition: colorless crystalline solid

Chromatography solvent: hexanes/ethyl acetate (10/1)

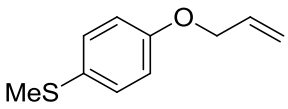
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.45-7.28 (m, 5H), 6.93-6.82 (m, 4H), 6.05 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 5.02 (s, 2H) 4.49 (dt, *J* = 5.3, 1.5 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 153.1, 153.0, 137.3, 133.6, 128.6, 127.9, 127.5, 117.5, 115.8, 115.7, 70.7, 69.5

Retention time GC-MS: 10.13 min

LR MS (EI, 70 eV, m/z): 240 [M+], 200, 165, 149, 128, 115, 91, 77, 65, 51

O-Allyl 4-methylthiophenyl ether[5]



Condition: yellow liquid

Chromatography solvent: hexanes/ethyl acetate (10/1)

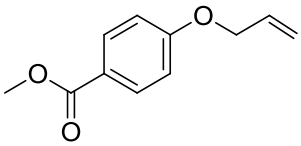
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.27 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.06 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 5.1 Hz, 2H), 2.45 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 157.2, 133.3, 130.3, 130.0, 129.1, 117.7, 115.5, 68.9, 17.9

Retention time GC-MS: 7.85 min

LR MS (EI, 70 eV, m/z): 180 [M+], 165, 139, 125, 111, 96, 85, 77, 67

Methyl 4-allyloxy benzoate[10]



Condition: colorless liquid

Chromatography solvent: hexanes/ethyl acetate (10/1)

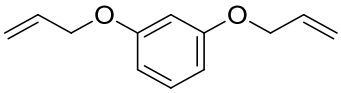
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.04-7.90 (m, 2H), 6.97-6.85 (m, 2H), 6.11-5.96 (m, 1H), 5.41 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.34-5.23 (m, 1H), 4.63-4.49 (m, 2H), 3.87 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δC [ppm] = 166.8, 162.3, 132.6, 132.6, 122.7, 118.6, 114.3, 68.8, 51.7

Retention time GC-MS: 6.06 min

LR MS (EI, 70 eV, m/z): 192 [M+], 177, 161, 152, 133, 121, 105, 92, 77, 63, 51

1,3-Bis(allyloxy)benzene[11]



Condition: yellow liquid

Chromatography solvent: hexanes/ethyl acetate (10/1)

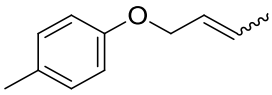
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.24-7.15 (m, 1H), 6.60-6.42 (m, 3H), 6.08 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 2H), 5.44 (d, *J* = 17.3 Hz, 2H), 5.31 (d, *J* = 10.5 Hz, 2H), 4.54 (d, *J* = 5.3 Hz, 4H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 159.9, 133.3, 129.9, 117.7, 107.2, 107.2, 102.2, 68.8

Retention time GC-MS: 7.71 min

LR MS (EI, 70 eV, m/z): 190 [M+], 175, 162, 149, 133, 121, 107, 95, 79, 69, 55

(E/Z)-But-2'-enyl-4-tolyl ether



Condition: yellow liquid

E/Z ratio: 5/1

Chromatography solvent: hexanes/ethyl acetate (10/1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.19-7.10 (m, 2H), 6.93-6.84 (m, 2H), 5.99-5.72 (m, 2H), 4.66-4.59 (m, 2H, (Z)), 4.51-4.45 (m, 2H, (E)), 2.34 (s, 3H), 1.82 (m, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.7, 130.3, 129.9, 129.8, 128.4, 126.4, 126.0, 114.6, 68.8, 63.8, 20.5, 17.9, 13.4

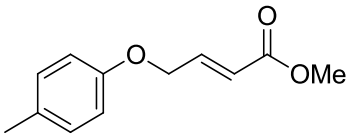
Retention time GC-MS: 6.78 min (E), 6.81 min (Z)

LR MS (EI, 70 eV, m/z): 162 [M+], 147, 131, 119, 108, 91, 77, 65, 55

HR MS (CI, m/z): found 163.1119 $[M+H]^+$ (E), 163.1117 $M+H]^+$ (Z) (calculated 163.1117)

IR in [cm^{-1}]: 3040 (w), 2900 (w), 2880 (w), 1620 (m), 1520 (s), 1450 (m), 1360 (m), 1240 (s), 1160 (m), 1000 (s).

Methyl (E)-4-(4′-tolyloxy) 2-butenoate[12]



Condition: colorless solid

Chromatography solvent: hexanes/ethyl acetate (100/1)

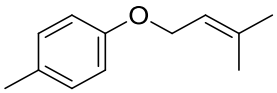
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.05-6.97 (m, 3H), 6.77-6.71 (m, 2H), 6.16 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.51 (dd, *J* = 4.0 Hz, 2H), 3.68 (s, 3H), 2.23 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.5, 156.0, 143.3, 130.4, 130.0, 114.4, 66.3, 51.4, 20.3

Retention time GC-MS: 8.67 min

LR MS (EI, 70 eV, m/z): 206 [M+], 174, 159, 147, 132, 119, 107, 99, 91, 77, 68, 59, 51

(*E*)-Prenyl-4-tolyl ether



Condition: colorless liquid

Chromatography solvent: hexanes/ethyl acetate (100/1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.14 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.57 (t, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 1.86 (s, 3H), 1.80 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.9, 137.9, 129.9, 129.8, 120.1, 114.6, 64.8, 25.9, 20.5, 18.2

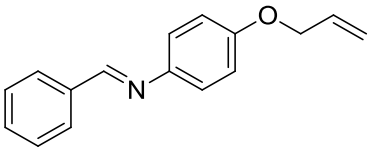
Retention time GC-MS: 7.33 min

LR MS (EI, 70 eV, m/z): 176 [M+], 161, 133, 121, 108, 91, 77, 69, 65, 51

HR MS (CI, m/z): found 177.1274 $[M+H]^+$ (calculated 177.1274)

IR in [cm^{-1}]: 3000 (w), 2950 (w), 2850 (w), 1620 (m), 1520 (s), 1440 (m), 1400 (m), 1240 (s), 1160 (m), 1000 (s)

(E)-4-(Allyloxy)-*N*-benzylidene aniline



Condition: yellow solid

Chromatography solvent: hexanes/ethyl acetate (3/2)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.48 (s, 1H), 7.94-7.84 (m, 2H), 7.51-7.43 (m, 3H), 7.29-7.18 (m, 2H), 7.00-6.91 (m, 2H), 6.08 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.44 (m, 1H), 5.31 (m, 1H), 4.56 (dt, *J* = 5.3, 1.5 Hz, 2 H)

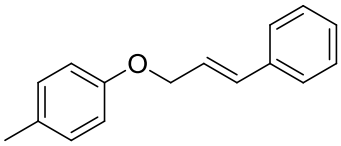
^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 158.5, 157.3, 145.1, 136.5, 133.3, 131.1, 128.8, 128.6, 122.2, 117.7, 115.3, 69.1

Retention time GC-MS: 10.69 min

LR MS (EI, 70 eV, m/z): 237 [M+], 196, 167, 141, 115, 103, 89, 77, 63, 51

HR MS (CI, m/z): found 237.1151[M+] (calculated 237.1154)

(*E*)-Cinnamyl-4-tolyl ether[13]



Condition: colorless solid

Recrystallization solvent: Methanol

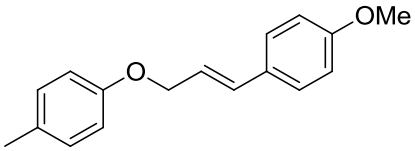
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.44–7.39 (m, 2H), 7.36–7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.13- 7.07 (m, 2H), 6.90–6.85 (m, 2H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.43 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.68 (dd, *J* = 5.8, 1.5 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.6, 136.5, 132.9, 130.2, 130.0 2, 128.6, 127.9, 126.6, 124.8, 114.7 2, 68.8, 20.5

Retention time GC-MS: 10.10 min

LR MS (EI, 70 eV, m/z): 224 [M+], 209, 195, 178, 152, 133, 117, 91, 77

(*E*)-4-Methoxycinnamyl-4'-tolyl ether[14]



Condition: colorless solid

Recrystallization solvent: methanol

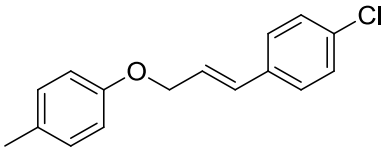
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39-7.32 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.91-6.82 (m, 4H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.65 (dd, *J* = 6.0, 1.4 Hz, 2H), 3.81 (s, 3H), 2.29 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 159.4, 156.6, 132.7, 130.1, 129.9, 129.3, 127.8, 122.4, 114.7, 114.0, 69.0, 55.3, 20.5

Retention time GC-MS: 11.17 min

LR MS (EI, 70 eV, m/z): 254 [M+], 147, 131, 122, 115, 103, 91, 77, 63, 51

(*E*)-4-Chlorocinnamyl-4'-tolyl ether[15]



Condition: colorless solid

Recrystallization solvent: Methanol

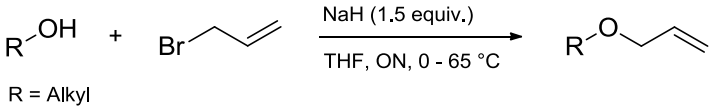
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.35-7.27 (m, 4H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.88-6.83 (m, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.39 (dt, *J* = 16.0, 5.7 Hz, 1H), 4.66 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.29 (s, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.5, 133.5, 131.5, 130.3, 123.0, 128.8, 127.8, 125.5, 114.7, 68.5, 20.5

Retention time GC-MS: 10.92 min

LR MS (EI, 70 eV, m/z): 258 [M+], 179, 151, 138, 125, 115, 107, 91, 77, 63, 51

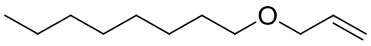
3 Synthesis of *O*-allyl alkylethers[16]



Representative procedure for the O-allylation of 1-octanol: The reaction was carried out under an inert atmosphere (N_2). To a suspension of NaH, a 60 % dispersion in mineral oil (0.60 g, 15 mmol) in dry THF (20 mL), was added at 0 °C 1-octanol (1.5 mL, 10 mmol). The reaction mixture was stirred at room temperature for 30 min. The allyl bromide (1.3 mL, 15 mmol) was added slowly and the reaction was heated to reflux overnight. The reaction mixture was allowed to cool to room temperature. Excess NaH was quenched with 1.5 M aqueous NH_4Cl-solution (5 mL). The organic

layer was separated and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL) and dried over Na_2SO_4. The product was purified via column chromatography.

***O*-Allyl *n*-octyl ether**[17]



Condition: colorless liquid

Chromatography solvent: hexanes/ethyl acetate (10/1)

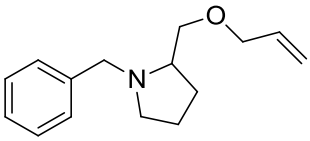
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.90 (ddt, *J* = 17.1, 10.6, 5.6 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 3.95 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.63-1.51 (m, 2H), 1.43-1.16 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.1, 116.5, 71.8, 70.5, 31.8, 29.8, 29.5, 29.3, 26.2, 22.7, 14.1

Retention time GC-MS: 5.94 min

LR MS (EI, 70 eV, m/z): 170 [M+], 141, 127, 112, 97, 83, 71, 57

2-(Allyloxy)-1-benzylpyrrolidine



Condition: yellow liquid

Chromatography solvent: hexanes/ethyl acetate (2/1 +0.1 % NEt_3)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.40-7.16 (m, 5H), 5.95 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.35-5.27 (m, 1H), 5.21 (m, 1H), 4.16 (d, *J* = 13.0 Hz, 1H), 4.03 (dt, *J* = 5.5, 1.4 Hz, 2H), 3.65 (dd, *J* = 9.4, 5.3 Hz, 1H), 3.46-3.38 (m, 2H), 3.00-2.93 (m, 1H), 2.79 (ddd, *J* = 11.1, 8.4, 5.8 Hz, 1H), 2.29-2-19 (m, 1H), 2.04-1.91 (m, 1H), 1.83-1.63 (m, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.8, 135.0, 129.0, 128.1, 126.8, 116.8, 74.2, 72.3, 128.6, 63.0, 59.7, 54.6, 28.7, 22.9

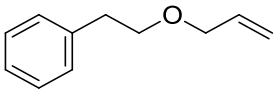
Retention time GC-MS: 8.73 min

LR MS (EI, 70 eV, m/z): 231 [M+], 172, 160, 130, 104, 91, 77, 65, 51

HR MS (ESI, 170 V, m/z): found 232.1693 $[M+H]^+$ (calculated 232.1696)

IR in [cm^{-1}]: 2953 (w), 2915 (w), 2850 (w), 2788 (w), 1495 (w), 1453 (w), 1098 (s), 989 (m)

2-Phenylethyl allyl ether[18]



Condition: yellow liquid

Chromatography solvent: hexanes/ethyl acetate (2/1)

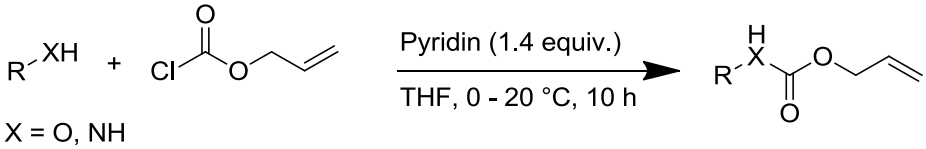
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.38-7.15 (m, 5H), 5.91 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.26 (m, 1H), 5.17 (m, 1H), 4.00 (dt, *J* = 5.6, 1.4 Hz, 1H), 3.65 (t, *J* = 7.3 Hz, 1H), 2.91 (t, *J* = 7.3 Hz, 1H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.0, 134.9, 128.9, 128.4, 126.2, 116.9, 71.9, 71.3, 36.4.

Retention time GC-MS: 6.36 min

LR MS (EI, 70 eV, m/z): 162 [M+], 129, 105, 91, 77, 71, 65, 57, 51.

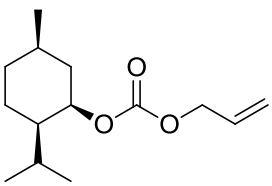
4 Synthesis of *O*/*N*-Allyloxycarbonyl compounds[19]



Representative procedure for the synthesis of (-)-menthyl *O*-allylcarbonate:

To a solution of (-)-menthol (20.0 mmol, 3.13 g) in freshly dried/distilled THF (20 mL) was added pyridine (28.0 mmol, 2.26 mL). The reaction mixture was cooled to 0 °C and allyl chloroformate (24.0 mmol, 2.56 mL) was added slowly. The suspension was stirred at room temperature for 10 h. After addition of water (5 mL), the mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were successively washed with 1 N HCl (2x10 mL), saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). After drying over Na_2SO_4 and removal of the solvent under reduced pressure, the crude product was purified by column chromatography.

(-)-Menthyl *O*-allyl carbonate[19]



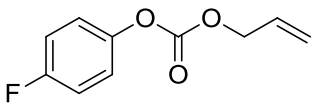
Condition: colorless liquid

Chromatography solvent: hexanes/ethyl acetate (10/1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.94 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.35 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.61 (ddd, *J* = 5.8, 2.6, 1.2 Hz, 2H), 4.57 – 4.46 (m, 1H), 2.12 – 2.03 (m, 2H), 1.97 (tt, *J* = 9.6, 3.5, 1H), 1.68 (qd, *J* = 5.8, 3.1 Hz, 2H), 1.54 – 1.35 (m, 2H), 1.12 – 0.97 (m, 2H), 0.90 (dd, *J* = 6.8, 5.5 Hz, 6H), 0.79 (d, *J* = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 154.7, 131.8, 118.6, 78.5, 68.2, 47.0, 40.7, 34.1, 31.4, 26.0, 23.3, 22.0, 20.7, 16.2.

O-Allyl (4-fluorophenyl) carbonate



Condition: yellowish liquid

Chromatography solvent: hexanes/ethyl acetate (10/3)

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.22 – 6.99 (m, 4H), 6.10 – 5.89 (m, 1H), 5.43 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.77 – 4.68 (m, 2H).

^{13}C-NMR (300 MHz, $CDCl_3$): δ [ppm] = 194.6, 162.0, 147.0, 131.0, 122.6, 119.7, 116.2, 69.3.

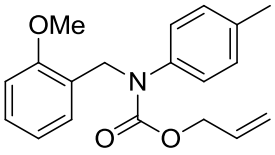
Retention time GC-MS: 6.71 min

LR MS (EI, 70 eV, m/z): 196 [M+], 152, 137, 123, 112, 195, 83, 69, 57.

HR MS (EI, 70 V, m/z): found 196.0538 $[M+H]^+$ (calculated 196.0536).

IR in [cm^{-1}]: 3084 (w), 2949 (w), 1758 (s), 1650 (m), 1504 (s), 1454 (m), 1365 (m), 1236 (s), 1190 (s), 1149 (m), 1091 (m).

O-Allyl 2-methoxybenzyl (4'-tolyl) carbamate



Condition: yellowish liquid

Chromatography solvent: hexanes/ethyl acetate (2/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.14 – 6.98 (m, 4H), 6.95 – 6.84 (m, 2H), 6.79 – 6.69 (m, 2H), 5.92 – 5.72 (m, 1H), 5.19 – 5.01 (m, 2H), 4.71 (s, 2H), 3.73 (s, 3H), 2.27 (s, 3H).

^{13}C-NMR (300 MHz, $CDCl_3$): δ [ppm] = 158.8, 155.7, 132.8, 130.1, 129.5, 127.1, 113.7, 66.2, 55.2, 53.9, 21.1.

Retention time GC-MS: 11.31 min

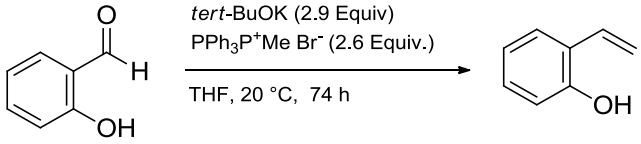
LR MS (EI, 70 eV, m/z): 347 [M+], 311, 270, 227, 211, 198, 167, 152, 134, 121, 106, 91, 77, 64, 51.

HR MS (EI, 70 V, m/z): found 311.1519 $[M+H]^+$ (calculated 311.1521).

IR in [cm^{-1}]: 2934 (w), 2836 (w), 1698 (s), 1647 (w), 1613 (m), 1512 (s), 1441 (m), 1393 (m), 1244 (s), 1175 (m), 1032 (s).

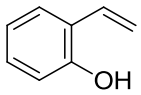
5 Other Starting Materials

Preparation of 2-hydroxy styrene[20]



The reaction was carried out under an inert atmosphere (N_2). Triphenylphosphonium bromide (52.9 mmol, 19.3 g) was dissolved in THF (86 mL) and *tert*-BuOK (57.2 mmol, 6.24 g) was added slowly. The reaction mixture was stirred at room temperature for 1 h. Then, 2-hydroxybenzaldehyde (20.1 mmol, 2.1 mL) was added slowly and the mixture was stirred at room temperature for 73 h. CH_2Cl_2 (200 mL) was added and the solution was washed with water (25 mL) and with brine (25 mL). The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (hexanes/ethyl acetate 10/1).

2-Hydroxy styrene[21]



Condition: yellow liquid

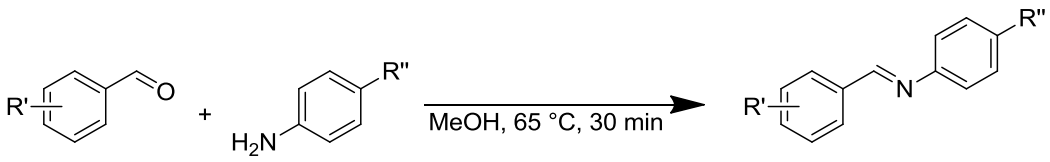
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.44 (d, *J* = 7.7 Hz, 1H), 7.19-7.12 (m, 1H), 7.07-6.90 (m, 2H), 6.81 (dd, *J* = 8.1, 1.0 Hz, 1H), 5.84 (s, 1H), 5.78 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.36 (dd, *J* = 11.2, 1.4 Hz, 1H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 151.9, 130.4, 127.8, 126.1, 123.9, 119.8, 114.8, 114.4

Retention time GC-MS: 5.82 min

LR MS (EI, 70 eV, m/z): 120 [M+], 107, 91, 86, 77, 70, 65, 51

Synthesis of (*E*)-*N*-Benzylideneanilines[22]

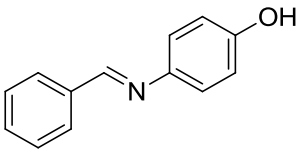


R' = *o*-OMe, H
R"= Me, OH

Representative procedure for the synthesis of (E)-4-Benzylidene aminophenol:

To a solution of 4-hydroxyaniline (4.41 g, 40 mmol) in MeOH (100 mL) was added benzaldehyde (4.1 mL, 40 mmol). The reaction mixture was heated to reflux for 30 min. After removal of solvent the crude product was recrystallized in toluene.

(*E*)-4-Benzylidene aminophenol[22]



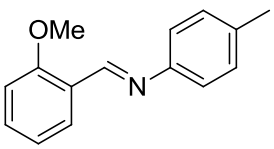
Condition: brown crystalline solid

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.48 (s, 1H), 7.93-7.85 (m, 2H), 7.47 (m, 3H), 7.22-7.16 (m, 2H), 6.89-6.84 (m, 2H), 4.91 (s, 1H)

Retention time GC-MS: 10.29 min

LR MS (EI, 70 eV, m/z): 197 [M+], 167, 152, 141, 120, 104, 93, 77, 65, 51

(E)-*N*-(2-Methoxybenzylidene)-4-toluidine



Condition: yellowish solid

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 8.40 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.17 (q, *J* = 8.3 Hz, 4H), 7.01 – 6.96 (m, 2H), 3.89 (s, 3H), 2.37 (s, 3H).

^{13}C-NMR (300 MHz, $CDCl_3$): δ [ppm] = 159.0, 130.6, 129.8, 120.8, 114.2, 55.5, 21.0.

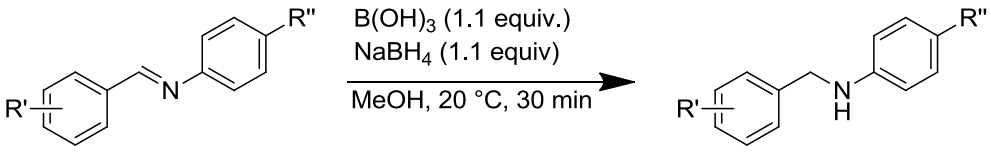
Retention time GC-MS: 10.55 min

LR MS (EI, 70 eV, m/z): 225 [M+], 209, 195, 181, 167, 154, 121, 107, 91, 77, 65, 51.

HR MS (EI, 70 V, m/z): found 225.1155 $[M+H]^+$ (calculated 225.1154).

IR in [cm^{-1}]: 3078 (w), 3006 (w), 2877 (w), 2842 (w), 1602 (m), 1595 (s), 1568 (s), 1505 (s), 1461 (m), 1305 (m), 1246 (s), 1165 (s), 1105 (s), 1023 (s).

Synthesis of 4-(Allyloxy)-*N*-benzylaniline[23]

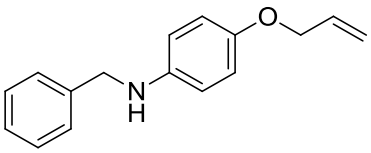


R' = *o*-OMe, H
R''= Me, O-allyl

Representative procedure for the synthesis of (E)-4-Benzylidene aminophenol:

To a solution of (E)-4-(Allyloxy)-N-benzylidene aniline (7 mmol, 1.7 g) and boric acid (7.7 mmol, 0.29 g) in methanol (9 mL) was slowly added sodium borohydride (7.7 mmol, 0.47 g). The reaction mixture was stirred at room temperature for 30 min. Excess sodium borohydride was quenched with water (10 mL). The mixture was filtered and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes / ethyl acetate 3/2).

4-(Allyloxy)-*N*-benzylaniline



Condition: yellow oil

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.41 (m, 5H), 6.84-6.74 (m, 2H), 6.66-6.57 (m, 2H), 6.05 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.38 (m, 1H), 5.25 (m, 1H), 5.44 (m, 1H), 4.71 (s, 1H), 4.46 (dt, *J* = 5.3, 1.5 Hz, 2 H), 4.29 (s, 2 H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 151.3, 142.4, 139.5, 133.9, 129.1, 128.6, 128.2, 127.6, 127.2, 117.3, 114.2, 69.7, 49.4

Retention time GC-MS: 10.67 min

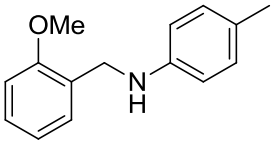
LR MS (EI, 70 eV, m/z): 239 [M+], 198, 168, 108, 91, 77, 65, 51

HR MS (CI, m/z): found 239.1311 [M+] (calculated 239.1310)

IR in [cm^{-1}]: 3394 (w), 3080 (w), 3029 (w), 2911 (w), 2865 (w), 1508 (s), 1465 (m), 1365 (m), 1294 (m), 1230 (s), 1120 (m), 1023 (s).

N-(2-Methoxybenzyl)-4-methylaniline

Differing to the protocol, the crude product was purified by recrystallization in methanol.



Condition: yellowish solid

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.24 (d, J = 8.7 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.79 (m, 2H), 6.55 (dd, *J* = 8.4, 1.9 Hz, 2H), 4.19 (s, 2H), 3.75 (s, 3H), 2.19 (s, 3H).

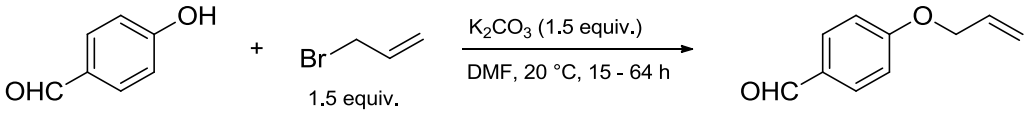
Retention time GC-MS: 10.52 min

LR MS (EI, 70 eV, m/z): 227 [M+], 212, 197, 182, 167, 152, 134,121, 107, 91, 77, 65, 51.

HR MS (EI, 70 V, m/z): found 227.1312 $[M+H]^+$ (calculated 227.1310).

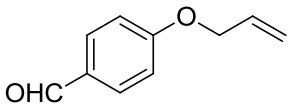
IR in [cm^{-1}]: 3009 (w), 2841 (w), 1604 (m), 1569 (m), 1508 (s), 1462 (m), 1422 (m), 1298 (m), 1246 (s), 1165 (s)m 1106 (s).

Allylation of 4-hydroxybenzaldehyde[24]



4-Hydroxybenzaldehyde (20 mmol, 2.44 g) and allyl bromide (30 mmol, 5.04 mL) were dissolved in DMF (25 mL). After addition of K_2CO_3 (30 mmol, 4.15 g), the reaction mixture was stirred at room temperature for 64 h and then hydrolyzed with water (100 mL). The aqueous phase were separated and extracted with *n*-pentane (3*50 mL). The combined organic phases were diluted with brine, dried with Na_2SO_4 and filtered. The crude product was concentrated under vacuum and purified via column chromatography.

4-Allyloxybenzaldehyde[25]



Condition: yellow liquid

Chromatography solvent: hexanes/ethyl acetate (3/1)

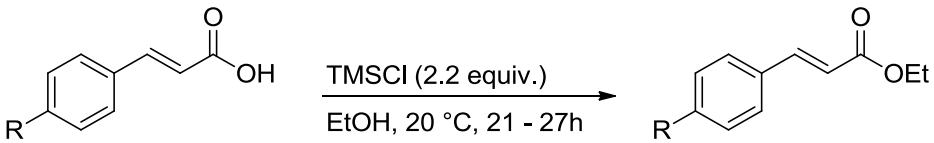
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.80 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.97 (ddt, *J* = 17.4, 10.5 Hz, 5.2 Hz, 1H), 5.36 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 4.54 (d, *J* = 5.2 Hz, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 189.6, 162.5, 131.3, 130.9, 129.0, 117.2, 113.9, 67.9

Retention time GC-MS: 7.47 min

LR MS (EI, 70 eV, m/z): 162 [M+], 147, 133, 121, 105, 93, 77, 65, 51

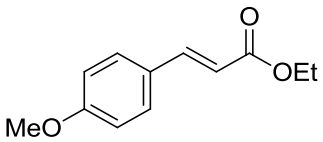
Synthesis of Ethyl cinnamates[26]



R = Cl,OMe

Representative procedure for the esterification of 4-methoxycinnamic acid: To a solution of 4-methoxycinnamic acid (4.74 g, 26.6 mmol) in ethanol (130 mL) was added TMSCl (7.5 mL, 59 mmol). The solution was stirred for 21 h at room temperature. The product was concentrated under vacuum. A purification process was not necessary.

Ethyl 4-methoxycinnamate[27]



Condition: colorless liquid

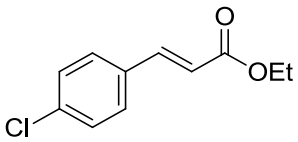
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.64 (d, *J* = 16.0 Hz, 1H), 7.50- 7.44 (m, 2H), 6.94-6.87 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.83 (s, *J* = 4.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 167.4, 161.3, 144.3, 129.7 2, 127.2, 115.8, 114.3, 60.4, 55.38, 14.4

Retention time GC-MS: 9.10 min

LR MS (EI, 70 eV, m/z): 206 [M+], 191, 178, 161, 147, 134, 118, 103, 89, 77, 63, 51

Ethyl 4-chlorocinnamate[27]



Condition: colorless solid

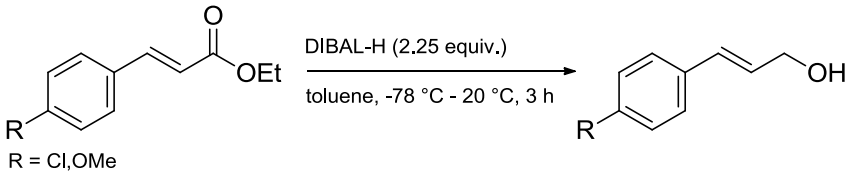
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.63 (d, *J* = 16.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.38-7.33 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.8, 143.1, 136.14, 133.0, 129.2, 118.9, 60.6, 14.3

Retention time GC-MS: 8.64 min

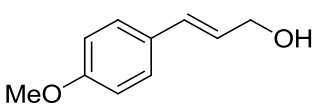
LR MS (EI, 70 eV, m/z): 210 [M+], 182, 165, 157, 147, 137, 129, 110, 102, 91, 75, 63, 51

Synthesis of Cinnamyl alcohols[25]



Representative procedure for the reduction of ethyl 4-methoxycinnamate: To a suspension of ethyl 4-cinnamate (2.85 g, 13.8 mmol) in toluene (40 mL) was added a solution of 1.2 M DIBAL-H in toluene (25.9 mL, 31.1 mmol) over a period of 45 min at -78 °C. The reaction mixture was then stirred for 2.5 h at room temperature. The reaction was carefully hydrolyzed with aqueous 1.5 M NH_4Cl-solution. The suspension was filtered and extracted diethyl ether (3*30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.

4-Methoxy cinnamyl alcohol[25]



Condition: yellowish crystalline solid

Chromatography solvent: hexanes/ethyl acetate (1/1)

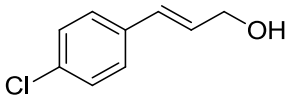
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.35-7.30 (m, 2H), 6.89-6.84 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.0 Hz, 1H), 4.30 (d, *J* = 5.6 Hz, 2H), 3.81 (s, 3H)

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

Retention time GC-MS: 8.26 min

LR MS (EI, 70 eV, m/z): 164 [M+], 147, 135, 121, 108, 91, 77, 63, 51

4-Chlorocinnamyl alcohol[26]



Condition: colorless crystalline solid

Chromatography solvent: hexanes/ethyl acetate (1/1)

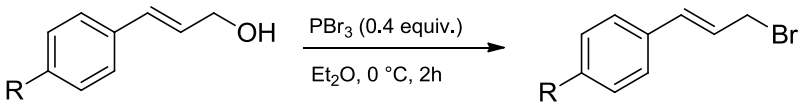
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37-7.17 (m, 4H), 6.53 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.29 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.28 (dd, *J* = 5.6, 1.5 Hz, 2H) 1.50 (s, 1H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.2, 133.3, 129.8, 129.2, 128.8, 127.3, 63.6

Retention time GC-MS: 7.99 min

LR MS (EI, 70 eV, m/z): 168 [M+], 150, 133, 125, 115, 103, 91, 77, 63, 55

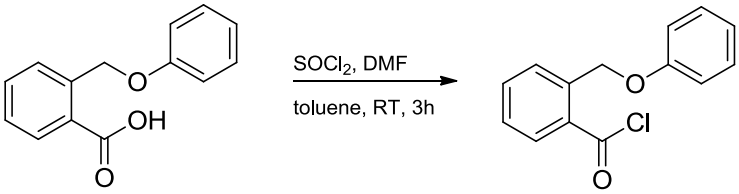
Bromination of cinnamyl alcohols[27]



R = Cl, OMe

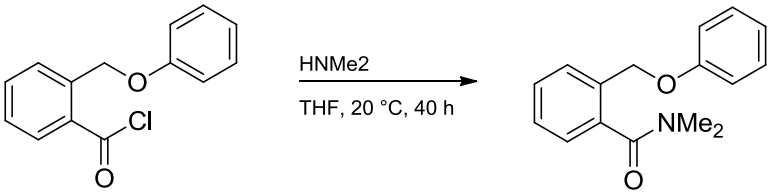
Representative procedure for the bromination of 4-methoxycinnamyl alcohol: The reaction was carried out under an inert atmosphere (N_2). To a solution of 4-methoxy cinnamyl alcohol (1.68 g, 10 mmol) in dry diethyl ether (40 mL) was added PBr_3 (260 µL, 2.8 mmol) at 0 °C. The solution was then stirred for 2 h at room temperature, hydrolyzed with an saturated aqueous $NaHCO_3$ solution (50 mL) and diluted with brine (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were directly used in the next step without further purification.

Synthesis of 2-(phenoxymethyl)benzoyl chloride[28]



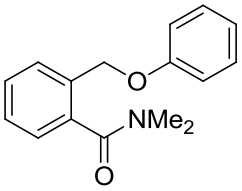
The reaction was carried out under an inert atmosphere (N_2). To a suspension of 2-(phenoxymethyl)benzoic acid (0.98 g, 4.3 mmol) in 2.3 mL toluene was added thionyl chloride (0.35 mL, 4.8 mmol) and DMF (0.15 mL, 1.9 mmol). The reaction mixture was stirred at room temperature for 3 h. The crude product was concentrated under reduced pressure and directly used in the next step without purification.

Synthesis of N,N-dimethyl-2-(phenoxymethyl) benzamide[30]



The reaction was carried out under an inert atmosphere (N_2). To the crude 2-(phenoxymethyl)benzoylchloride was added a 2.0 M solution of dimethyl amine (7.7 mL, 15.4 mmol), The reaction mixture was stirred at room temperature for 40 h. The reaction was hydrolyzed with a saturated aqueous $NHCO_3$-solution (8 mL). The organic layer was separated and the aqueous phase was extracted with DCM (3*7 mL). The combined organic layers were diluted with water (7 mL) and dried over Na_2SO_4, filtered and concentrated under reduced pressure. A purification process was not necessary.

***N*,*N*-dimethyl-2-(phenoxymethyl) benzamide**



Condition: brown oil

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.61-7.48 (m, 1H), 7.44-7.33 (m, 2H), 7.32-7.22 (m, 3H), 7.02-6.86 (m, 3H), 5.08 (s, 2H), 3.07 (s, 3H), 2.85 (s, 3H)

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.8, 158.6, 136.2, 133.9, 129.5, 129.2, 129.1, 128.1, 126.2, 121.1, 114.7, 67.7, 39.1, 34.7

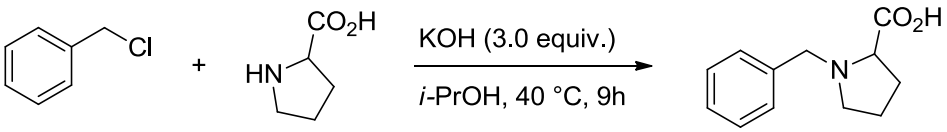
Retention time GC-MS: 10.68 min

LR MS (EI, 70 eV, m/z): 255 [M+], 210, 181, 162, 133, 119, 91, 65, 51

HR MS (CI, m/z): found 255.1256 [M+] (calculated 255.1259)

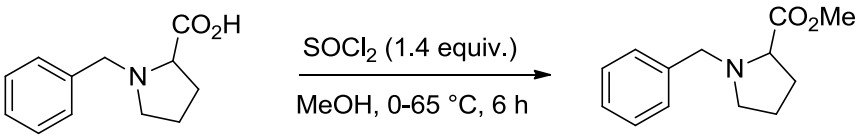
IR in [cm^{-1}]: 3063 (w), 3031 (w), 2885 (w), 1630 (s), 1492 (m), 1456 (m), 1237 (m), 750 (m), 690 (m)

Synthesis of 1-(phenylmethyl)-L-proline[31]



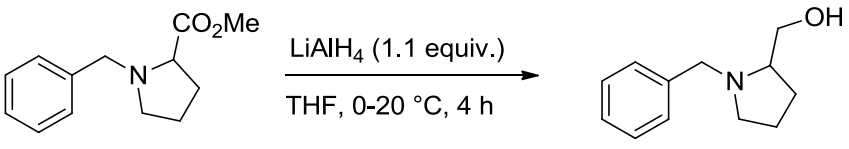
L-Proline (2.3 g, 20 mmol) and potassium hydroxide (3.4 g, 60 mmol) were dissolved in *i*-propanol and the reaction heated at 40 °C. Then, benzyl chloride was added over 1 h with a syringe pump. The reaction mixture was stirred at 40 °C for 8 h. After cooling to room temperature, the reaction mixture was acidified with conc. HCl (6 mL) until a pH of 4-5 was reached. The mixture was diluted with chloroform and stirred over night at room temperature. The colorless precipitate was removed through filtration and the solvent removed under reduced pressure. The resulting yellow solid was directly used in the next step without purification.

Synthesis of methyl 1-benzylpyrrolidine-2-carboxylate[31]



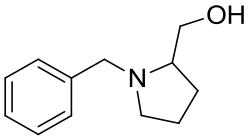
Thionyl chloride (2.0 mL, 27 mmol) was added slowly to methanol (30 mL) at 0 °C. Then 1-(phenylmethyl)-*L*-proline (4.5 g, 20 mmol) was added at 0°C. The reaction was heated to reflux for 6 h. The reaction was allowed to cool to room temperature overnight and the solvent was removed under reduced pressure. The crude product, a brown oil, was directly used in the next step.

Synthesis of 1- (Benzyl)-2-pyrrolidine methanol[31]



Molecular Weight: 191,27

The synthesis was carried out under dry and inert conditions. To a suspension of $LiAlH_4$ (0.84 g, 22 mmol) in abs. THF (20 mL) was added at 0°C a solution of methyl 1-benzylpyrrolidine-2-carboxylate (5.4 g, 20 mmol) in abs. THF (10 mL) over 1 h via syringe pump. The reaction was allowed to warm to room temperature and was stirred for 3 h. The reaction mixture was hydrolyzed at 0 °C with 1 M NaOH (1.5 mL). The grey participate was filtered and washed with diethyl ether four times. The filtrate was dried over Na_2SO_4.The product was purified via column chromatography (*n*-pentane/ethyl acetate 99/1). The obtained product was an orange oil.



Condition: yellow oil

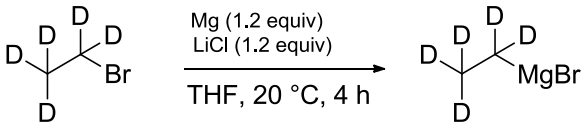
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.41-7.13 (m, 5H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.65 (dt, *J* = 10.7, 3.4 Hz, 1H), 3.43 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.36 (d, *J* = 13.0 Hz, 1H), 3.05-2.92 (m, 1H), 2.74 (ddd, *J* = 9.1, 5.8, 2.7 Hz, 1H), 2.28 (tt, *J* = 16.4, 8.0 Hz, 1H), 2.02-1.77 (m, 2H), 1.77-1.60 (m, 2H)

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 139.4, 128.7, 128.4, 127.1, 64.3, 61.8, 58.6, 54.5, 27.8, 23.5

Retention time GC-MS: 8.32 min

LR MS (EI, 70 eV, m/z): 190 [M+], 172, 160, 130, 104, 91, 77, 65, 51

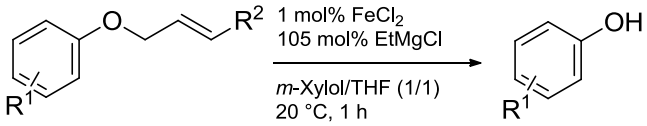
Synthesis of d_5-ethylmagnesium bromide (d^5-EtMgBr) in THF[32]



A modified protocol of Knochel *et al.* was followed. The reaction was carried out under an inert atmosphere (N_2). To magnesium turnings (117 mg, 4.8 mmol) and anhydrous LiCl (203 mg, 4.8 mmol) was added a solution of d_5-bromoethane from *Deutero* (456 mg, 4.0 mmol) in abs. THF (2 mL). After addition, the reaction mixture was stirred at room temperature for 4 h. The resulting dark brown solution was directly used in the ether cleavage reaction.

5 Iron-Catalyzed Ether Cleavage Reactions

Standard procedure:



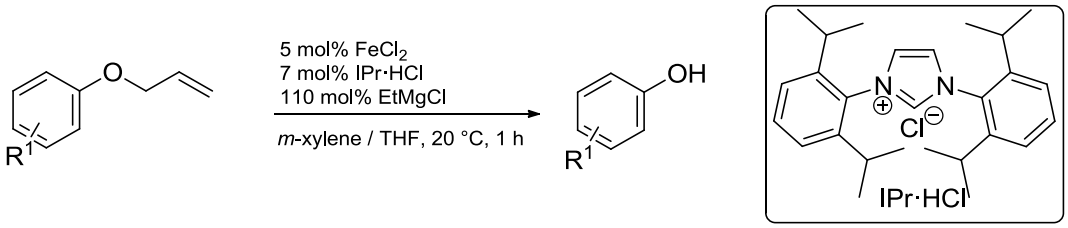
Representative protocol with 1 mol% $FeCl_2$ and 105 mol% EtMgCl:

The reaction was carried out under dry and inert conditions. Firstly, a $FeCl_2$-stock solution was prepared. $FeCl_2$ (5.7 mg, 45 µmol) was dissolved in abs. THF (6 mL) and stirred at room temperature for 2 h.

To a solution of 2-(allyloxy) anisole (0.074 g, 0.45 mmol) in *m*-xylene (0.6 mL) was added the $FeCl_2$-stock solution (0.6 mL). The reaction mixture was degassed twice by the freeze-pump-thaw method. Then, a 2.0 M solution of ethyl magnesium chloride in THF (240 µL, 0.48 mmol, 1.05 equiv.) was added over 20 sec. The reaction was stirred at room temperature for 1 h and hydrolyzed with 1.5 M aqueous NH_4Cl solution (1 mL). After addition of *n*-pentadecane (50µL, 0.18 mmol, internal GC reference), the product was extracted with diethyl ether (2*1 mL). The combined organic layers were dried over Na_2SO_4 and directly analysed by quantitative GC-FID.

Preparative reactions were performed on 5-fold scales and the crude products purified by SiO_2 column chromatography.

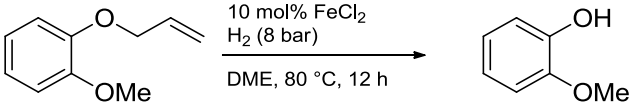
Iron/NHC-catalyzed deallylation



Firstly, a $FeCl_2$-stock solution was prepared. $FeCl_2$ (5.7 mg, 45 µmol) was dissolved in abs. THF (6 mL) and stirred at room temperature for 2 h.

A glass vial was charged with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) (134 mg, 0.32 mmol) and purged with nitrogen. 6 mL of the $FeCl_2$ stock solution was added, and the resulting solution stirred at room temperature for 1 h. The next operations followed the standard procedure above.

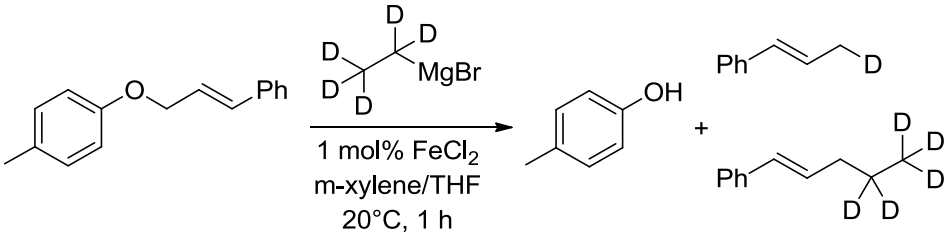
Reactions in high-pressure reactors:



Firstly, a $FeCl_2$-stock solution was prepared in 1,2-dimethoxyethane (DMF): $FeCl_2$ (5.7 mg, 45 µmol) was dissolved in abs. DME (6 mL) and stirred at room temperature for 2 h.

To a solution of 2-(allyloxy) anisole (0.074 g, 0.45 mmol) in *m*-xylene (0.6 mL) was added the $FeCl_2$-stock solution (0.6 mL). The reaction mixture was degassed twice by the freeze-pump-thaw method. The reaction vessels were transferred into a Parr high-pressure stainless steel reactor, and the reactor purged with H_2. Pressure and temperature were set.

Iron catalyzed deuterium transfer from d^5-EtMgBr



Freshly prepared d_5-EtMgBr in THF was used. Otherwise, see standard procedure.

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