Regio- and Stereoselective Chan-Lam-Evans Enol Esterification of Carboxylic Acids with Alkenylboroxines

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I. General Information and Materials

NMR spectra were recorded using a Bruker AV-300 or AV-400 MHz spectrometers and calibrated on residual undeuterated solvent signals as internal standard. The data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on a Mass spectrometer (JEOL, Japan). FD/FI probe equipped with FD Emitter, Carbotec or Linden (Germany), FD 10 μm. Current rate 51.2 mA/min over 1.2 min machine using field desorption (FD) as ionization method. Depending on the molecule, either the (M)⁺ or (M+H)⁺ were observed. Reactions were monitored with thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254). SilaFlash® P60 (particle size 40-63 μm) was used for silica column chromatography. Dried CH₂Cl₂ and CH₃CN were obtained by distilling these solvents with CaH₂ as drying agent. Dried THF and Et₂O were obtained by distillation with sodium. All dried solvents were stored under N₂ atmosphere. Dry DMF on 4Å molecular sieves was obtained from Sigma-Aldrich and stored under N₂ atmosphere. Reagents (including trivinylboroxine pyridine complex) were purchased with the highest purity (usually >98%) from Sigma Aldrich and Fluorochem and used as received. Melting points were recorded on a Wagner & Munz Polytherm A melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FTIR machine. All reactions were performed in normal glassware, without drying. Unless stated elsewhere, all reactions were performed under air. Compounds 1a, 1d, 1h, 1i, 1f, 1q, 1r, 1s, 1t, 2a, 2c, 2d, 2e, 2j, 3a, 3c, 4, 8a, 8d, 9a, 9b, 9c, 9d, 10a, 10b, 10c, 10d, 10e, 11a, 11b, 11c, 12b, 13, and 14 have been reported before in literature. Only new compounds and known compounds lacking exact mass data have their HRMS data reported.
II. Synthesis and characterization of boroxines

2-propenylboroxine pyridine complex\(^1\)

60 mL of a 0.5 M solution of 2-propenylmagnesium bromide in THF (30.0 mmol) was added dropwise over 1 h to a solution of 5.0 mL trimethyl borate (45.0 mmol, 1.5 eq) in 45 mL dry THF at -78 °C under N\(_2\) atmosphere. The reaction was stirred at -78 °C for 1 h and room temperature for 1 h. The reaction was cooled in an ice bath and 40 mL 1M HCl was added and stirred for 15 minutes. Next, 40 mL brine was added and the mixture was extracted with 3 \times 80 mL Et\(_2\)O. The combined organic layers were washed with 80 mL brine, dried over MgSO\(_4\) and concentrated to a volume of circa 30 mL. Next, 2.40 mL pyridine (30.0 mmol) and 400 mg MgSO\(_4\) were added and the reaction was stirred for 3 h at room temperature. The MgSO\(_4\) was filtered off and washed with Et\(_2\)O. The organic layer was concentrated in vacuo and the residue was purified by Kugelrohr distillation (0.03 mbar, 110–125 °C) to give a colorless oil, which crystallized over time to a low-melting solid. Yield: 2.50 g (8.84 mmol, 88%).

\(\text{\(^1\)H-NMR (300 MHz, CDCl}_3\)} \(\delta\) 8.87 (d, 2H), 8.07 (t, 1H), 7.64 (t, 2H), 5.70 (d, 3H), 5.48 (d, 3H), 1.82 (s, 9H); \(\text{\(^13\)C-NMR (75 MHz, CDCl}_3\)} \(\delta\) 144.0, 140.8, 125.3, 124.6, 21.1 (carbon attached to B not visible); IR (cm\(^{-1}\)) 3060, 2951, 1620, 1336, 1190

(\(E\))-1-hexenylboroxine pyridine complex

2.30 mL 1-hexyne (20.0 mmol) was dissolved in 10 mL dry CH\(_2\)Cl\(_2\) under N\(_2\) atmosphere and cooled to 0°C. After cooling, 20 mL 1M HBBr\(_2\)SMe\(_2\) in CH\(_2\)Cl\(_2\) (20.0 mmol, 1.0 equiv) was added dropwise and the reaction was stirred at 0 °C for 1 h and overnight at room temperature. The reaction mixture was poured in 20 mL Et\(_2\)O/H\(_2\)O 1:1 and the mixture was stirred vigorously for 30 minutes with ice bath cooling. The layers were separated and the aqueous layer was extracted with 3 \times 10 mL Et\(_2\)O. The combined organic layers were washed with 10 mL H\(_2\)O and 10 mL brine, dried over MgSO\(_4\) and concentrated in vacuo. The residue was dissolved in 10 mL dry Et\(_2\)O and 0.78 mL pyridine (10.0 mmol, 1 equiv) and 100 mg MgSO\(_4\) were added. The reaction was stirred overnight at room temperature and the MgSO\(_4\) was filtered off and washed with Et\(_2\)O. The organic layer was concentrated in vacuo to give a slightly yellow thick oil, which was used without further purification. Yield: 2.51 g (6.13 mmol, 92%). \(\text{\(^1\)H-NMR (300 MHz, CDCl}_3\)} \(\delta\) 8.79 (d, 2H), 7.93 (t, 1H), 7.54 (t, 2H), 6.65 (dt, 3H), 5.57 (d, 3H), 2.17 (q, 6H), 1.38 (m, 12H), 0.93 (t, 9H); \(\text{\(^13\)C-NMR (75 MHz, CDCl}_3\)} \(\delta\) 151.3, 145.8, 139.3, 124.9, 35.4, 30.9, 22.5, 14.1 (carbon attached to B not visible); IR (cm\(^{-1}\)) 2925, 1633, 1394

(\(Z\))-1-propenylboroxine pyridine complex

859 mg Z-1-propeneboronic acid (10.0 mmol), 0.79 mL pyridine (10.0 mmol) and 1.0 gram MgSO\(_4\) were stirred overnight in 10 mL dry Et\(_2\)O at room temperature. The mixture was filtered and concentrated in vacuo. The residue was purified by Kugelrohr distillation (0.04 mbar 100-110 °C) to give a colorless oil. Yield: 784 mg (2.77 mmol, 83%). \(\text{\(^1\)H-NMR (300 MHz, CDCl}_3\)} \(\delta\) 8.86 (d, 2H), 8.03 (t, 1H), 7.54 (t, 2H), 6.65 (dt, 3H), 5.57 (d, 3H), 2.03 (d, 9H); \(\text{\(^13\)C-NMR (75 MHz, CDCl}_3\)} \(\delta\) 145.1, 144.2, 140.5, 125.4, 17.6 (carbon attached to B not visible); IR (cm\(^{-1}\)) 3386, 2988, 2913, 1623, 1414, 1357
II. 2,2-dimethylvinylboroxine

784 mg 2,2-dimethylvinylboronic acid (7.85 mmol), 0.62 mL pyridine (7.85 mmol) and 1.0 gram of MgSO$_4$ were stirred overnight in 20 mL dry Et$_2$O at room temperature. The mixture was filtered and concentrated in vacuo. The residue was purified by Kugelrohr distillation (0.02 mbar, 120-130°C) to give a white solid. Yield: 471 mg (1.92 mmol, 73%). Melting point: 84-87 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 5.25 (s, 3H), 2.13 (s, 9H), 1.95 (s, 9H); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 163.1, 29.8, 22.3 (carbon attached to B not visible); IR (cm$^{-1}$) 2968, 2932, 2909, 1634, 1377, 1349, 1318

III. Synthesis and characterization of enol esters 1a-8t

General procedure for the synthesis of vinyl esters via the Chan-Lam-Evans reaction

In a 10 mL round bottom flask were added 181 mg Cu(OTf)$_2$ (0.50 mmol) and 58 mg 1,3-diethylurea (0.50 mmol). Next, 5 mL dry THF was added and the mixture was stirred to give a (neatly) clear colorless solution. After dissolving, 70 μL Et$_3$N (0.50 mmol) was added to give a dark solution, after which the carboxylic acid (0.50 mmol) was added. Usually the color changed to dark blue or dark green. Lastly, 80 mg trivinylboroxine pyridine complex (0.33 mmol, 0.66 equiv) was added and a balloon filled with air was placed on top of the flask. The reaction was stirred overnight at 50 °C (stirring at 800-1000 rpm), after which the reaction mixture usually had turned light green with precipitation. To the reaction mixture was added ~2 teaspoons of silica gel and the mixture was concentrated in vacuo. The dry-loaded material was purified by column chromatography to give the pure vinyl ester as the most apolar fraction.

**Vinyl benzoate (1a)$^2$**

The reaction was performed with 40 mol% Cu(OTf)$_2$ and 40 mol% 1,3-diethylurea. Column chromatography with PE/EtOAc 99:1 ($R_t=0.41$). Yield: 72 mg (0.486 mmol, 97%) as a colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 8.14 (d, 2H), 7.65-7.46 (m, 4H), 5.10 (d, 1H), 4.73 (d, 1H); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 163.7, 141.5, 133.7, 130.1, 129.0, 128.6, 98.3; IR (cm$^{-1}$) 3091, 1728, 1644, 1245

**Vinyl 2,4,6-trimethylbenzoate (1b)**

Column chromatography with PE/EtOAc 98:2 ($R_t=0.28$ in pure PE). Yield: 89 mg (0.468 mmol, 94%) as a colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.58 (dd, 1H), 5.04 (d, 1H), 4.73 (d, 1H), 2.39 (s, 6H), 2.34 (s, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 166.9, 141.3, 140.2, 136.1, 129.4, 128.7, 98.3, 21.2, 20.1; IR (cm$^{-1}$) 2924, 1735, 1644, 1611, 1241, 1070; HRMS (EI), calcd. for C$_{12}$H$_{14}$O$_2$ (M$^+$): 190.0988, found: 190.1009

**Vinyl 2,6-dimethoxybenzoate (1c)**

Column chromatography with PE/EtOAc 10:1 ($R_t=0.14$ in 20:1 ratio). Yield: 99 mg (0.475 mmol, 95%) as a colorless solid. Melting point: 60-62 °C. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.52 (dd, 1H), 7.33 (t, 1H), 6.58 (d, 2H), 5.00 (d, 1H), 4.68 (d, 1H), 3.83 (s, 6H); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 163.6, 157.7, 141.7, 131.8, 111.8, 103.9, 98.2, 56.1; IR (cm$^{-1}$) 2973, 2940, 2843, 1746, 1594, 1476, 1239, 1099; HRMS (EI), calcd. for C$_{13}$H$_{14}$O$_4$ (M$^+$): 208.0730, found: 208.0720
Vinyl 4-methoxybenzoate (1d)

Column chromatography with PE/EtOAc 99:1 -> 98:2 (Rf=0.48 in 20:1 ratio). Yield: 77 mg (0.432 mmol, 86%) as a colorless solid. Melting point: 53-54 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.07 (d, 2H), 7.53 (dd, 1H), 6.95 (d, 2H), 5.05 (d, 1H), 4.68 (d, 1H), 3.87 (s, 3H); 13C-NMR (75 MHz, CDCl₃) δ 163.9, 163.4, 141.5, 132.2, 121.2, 113.9, 97.7, 55.5; IR (cm⁻¹) 2843, 1715, 1603, 1510; HRMS (EI), calcd. for C₁₀H₁₀O₃ (M⁺): 178.0624, found: 178.0636

Vinyl 4-iodobenzoate (1e)

Column chromatography with PE/EtOAc 98:2 (Rf=0.48 in pure PE). Yield: 125 mg (0.456 mmol, 91%) as a colorless solid. Melting point: 41-44 °C; 1H-NMR (300 MHz, CDCl₃) δ 7.85 (d, 2H), 7.81 (d, 2H), 7.50 (dd, 1H), 5.09 (d, 1H), 4.74 (d, 1H); 13C-NMR (75 MHz, CDCl₃) δ 163.2, 141.3, 138.0, 131.4, 128.4, 101.8, 98.7; IR (cm⁻¹) 3087, 1729, 1647, 1581, 1527; HRMS (EI), calcd. for C₉H₇IO₂ (M⁺): 273.9485, found: 273.9495

Vinyl 4-formylbenzoate (1f)

Column chromatography with PE/EtOAc 99:1 -> 98:2 (Rf=0.25 in 20:1 ratio). Yield: 62 mg (0.352 mmol, 70%) as a colorless solid. Melting point: 57-58 °C; 1H-NMR (300 MHz, CDCl₃) δ 10.12 (s, 1H), 8.26 (d, 2H), 7.98 (d, 2H), 7.51 (dd, 1H), 5.13 (d, 1H), 4.77 (d, 1H); 13C-NMR (75 MHz, CDCl₃) δ 191.6, 162.7, 141.3, 139.6, 133.9, 130.6, 129.6, 99.1; IR (cm⁻¹) 2857, 1731, 1693, 1651, 1261; HRMS (ESI), calcd. for C₁₀H₇O₂ (M⁺): 176.0468, found: 176.0468

Vinyl 4-cyanobenzoate (1g)

Column chromatography with PE/EtOAc 20:1 (Rf=0.17). Yield: 81 mg (0.468 mmol, 94%) as a colorless solid. Melting point: 38-40 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.20 (d, 2H), 7.78 (d, 2H), 7.49 (dd, 1H), 5.13 (d, 1H), 4.78 (d, 1H); 13C-NMR (75 MHz, CDCl₃) δ 162.0, 141.1, 132.8, 130.5, 117.8, 117.0, 99.4; IR (cm⁻¹) 3099, 2233, 1731, 1646, 1259, 1129; HRMS (EI), calcd. for C₁₀H₇NO₂ (M⁺): 173.0471, found: 173.0478

Vinyl 4-nitrobenzoate (1h)

Column chromatography with PE/EtOAc 99:1 -> 98:2 (Rf=0.15 in pure PE). Yield: 68 mg (0.352 mmol, 70%) as a slightly yellow solid. Melting point: 69-70 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.31 (d, 2H), 8.28 (d, 2H), 7.51 (dd, 1H), 5.16 (d, 1H), 4.81 (d, 1H); 13C-NMR (75 MHz, CDCl₃) δ 161.9, 150.9, 141.2, 134.4, 131.2, 123.8, 99.6; IR (cm⁻¹) 3110, 1729, 1523, 1266; HRMS (EI), calcd. for C₉H₇NO₄ (M⁺): 193.0370, found: 193.0366

Vinyl 4-hydroxybenzotate (1i)

Column chromatography with PE/EtOAc 8:1 (Rf=0.27). Yield: 55 mg (0.335 mmol, 67%) as a colorless solid. Melting point: 117-120 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.04 (d, 2H), 7.50 (dd, 1H), 6.95 (d, 2H), 6.86 (bs, 1H), 5.09 (d, 1H), 4.73 (d, 1H); 13C-NMR (75 MHz, CDCl₃) δ 164.3, 161.1, 141.4, 132.7, 120.9, 115.7, 98.5; IR (cm⁻¹) 3278, 1686, 1645, 1589, 1274, 1227, 1129; HRMS (EI), calcd. for C₈H₇O₃ (M⁺): 164.0468, found: 164.0473
Vinyl 4-vinylxybenzoate (1j)

Column chromatography with PE/EtOAc 20:1 (Rf=0.82 in 8:1 ratio). Yield: 20 mg (0.105 mmol, 21%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, 2H), 7.51 (dd, 1H), 7.07 (d, 2H), 6.72 (dd, 1H), 5.08 (d, 1H), 5.02 (d, 1H), 4.71 (d, 1H), 4.62 (d, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 163.2, 161.1, 146.6, 141.5, 132.3, 123.5, 116.4, 98.1, 97.9; IR (cm\(^{-1}\)) 1727, 1645, 1600, 1505, 1241, 1134; HRMS (EI), calcd. for C\(_{11}\)H\(_{10}\)O\(_3\) (M\(^+\)): 190.0624, found: 190.0639

Divinyl terephthalate (1k)

Column chromatography with PE/EtOAc 99:1 \(\rightarrow\) 98:2 (Rf=0.39 in pure PE). Yield: 88 mg (0.403 mmol, 81%) as a colorless solid. Melting point: 77-80 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.20 (s, 4H), 7.53 (dd, 2H), 5.14 (d, 2H), 4.77 (d, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.7, 141.3, 133.3, 130.1, 99.0; IR (cm\(^{-1}\)) 1727, 1648, 1235; HRMS (EI), calcd. for C\(_{12}\)H\(_{10}\)O\(_4\) (M\(^+\)): 218.0574, found: 218.0587

Vinyl pentafluorobenzoate (1l)

Column chromatography with PE/EtOAc 99:1 \(-\) 98:2 (Rf=0.14 in pure PE). Yield: 54 mg (0.227 mmol, 45%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.46 (dd, 1H), 5.14 (d, 1H), 4.84 (d, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.3, 140.7, 100.5; \(^{19}\)F-NMR (300 MHz, CDCl\(_3\)) \(\delta\) -137.0, -147.0, -160.0; IR (cm\(^{-1}\)) 1748, 1646, 1495, 1329, 1210; HRMS (EI), calcd. for C\(_9\)H\(_3\)O\(_2\)F\(_5\) (M\(^+\)): 238.0048, found: 238.0050

2-pyrrolecarboxylic acid vinyl ester (1p)

Column chromatography with PE/EtOAc 98:2 \(\rightarrow\) 96:4 \(\rightarrow\) 94:6 (Rf=0.11 in 20:1 ratio). Yield: 52 mg (0.379 mmol, 76%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.73 (bs, 1H), 7.50 (dd, 1H), 7.07 (m, 2H), 6.34 (q, 1H), 5.04 (d, 1H), 4.68 (d, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 158.4, 141.0, 124.6, 121.3, 117.1, 111.0, 97.7; IR (cm\(^{-1}\)) 3324, 1684, 1644, 1405, 1310, 1154; HRMS (EI), calcd. for C\(_7\)H\(_7\)NO\(_2\) (M\(^+\)): 137.0471, found: 137.0483

2-Thiophenecarboxylic acid vinyl ester (1q)

Yield: 35 mg (0.23 mmol, 45%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, 1H), 7.66 (d, 1H), 7.47 (dd, 1H), 7.16 (t, 1H), 5.08 (d, 1H), 4.71 (d, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 159.4, 141.2, 134.7, 133.7, 132.4, 128.1, 98.4; IR (cm\(^{-1}\)) 3094, 2923, 2853, 1721, 1647, 1522, 1462, 1250; HRMS (FD), calcd. for C\(_7\)H\(_6\)O\(_2\)S (M\(^+\)): 154.0083, found: 154.0083

Vinyl octanoate (2a)

Column chromatography with PE/EtOAc 99:1 (Rf=0.14 in pure PE). Yield: 79 mg (0.464 mmol, 93%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.30 (dd, 1H), 4.88 (d, 1H), 4.57 (d, 1H), 2.40 (t, 2H), 1.67 (quint, 2H), 1.33 (m, 8H), 0.90 (t, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.0, 141.3, 97.5, 34.1, 31.7, 29.1, 29.0, 24.7, 22.7, 14.2; IR (cm\(^{-1}\)) 2928, 2858, 1757, 1647, 1149
6-bromohexanoic acid vinyl ester (2b)

Column chromatography with PE/EtOAc 99:1 (Rf=0.24 in pure PE).

Yield: 107 mg (0.484 mmol, 97%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.28 (dd, 1H), 4.88 (d, 1H), 4.57 (d, 1H), 3.41 (t, 2H), 2.41 (t, 2H), 1.89 (quint, 2H), 1.69 (quint, 2H), 1.52 (quint, 2H); 13C-NMR (75 MHz, CDCl3) δ 170.5, 141.2, 97.7, 33.7, 33.5, 32.4, 27.6, 23.8; IR (cm⁻¹) 2943, 1753, 1646, 1145; HRMS (EI), calcd. for C₈H₁₃BrO₂ (M⁺): 220.0093, found: 220.0109

Phenylacetic acid vinyl ester (2c)

Column chromatography with PE/EtOAc 99:1 (Rf=0.21 in pure PE).

Yield: 78 mg (0.481 mmol, 96%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.38 (m, 6H), 4.97 (d, 1H), 4.64 (d, 1H), 3.75 (s, 2H); 13C-NMR (75 MHz, CDCl3) δ 168.7, 141.3, 133.2, 129.4, 128.7, 127.4, 98.1, 41.0; IR (cm⁻¹) 3033, 1749, 1645, 1131; HRMS (EI), calcd. for C₁₀H₁₁O₂ ([M+H]⁺): 162.0675, found: 162.0691

Diphenylacetic acid vinyl ester (2d)

Column chromatography with PE/EtOAc 99:1 (Rf=0.23 in pure PE).

Yield: 113 mg (0.474 mmol, 95%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.42 (m, 11H), 5.21 (s, 1H), 5.01 (d, 1H), 4.69 (d, 1H); 13C-NMR (75 MHz, CDCl3) δ 169.7, 141.4, 138.0, 128.8, 128.7, 127.6, 98.5, 56.8; IR (cm⁻¹) 3030, 1747, 1644, 1129

Vinyl cinnamate (2e)

Column chromatography with PE/EtOAc 99:1 → 98:2 (Rf=0.18 in pure PE).

Yield: 77 mg (0.442 mmol, 88%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.83 (d, 1H), 7.59-7.41 (m, 6H), 6.49 (d, 1H), 5.02 (d, 1H), 4.67 (d, 1H); 13C-NMR (75 MHz, CDCl3) δ 163.9, 146.7, 141.4, 134.1, 130.8, 129.0, 128.4, 116.7, 97.8; IR (cm⁻¹) 1720, 1630, 1143; HRMS (EI), calcd. for C₁₁H₁₀O₂ (M⁺): 174.0675, found: 174.0686

2-hexynoic acid vinyl ester (2f)

Column chromatography with PE/EtOAc 99:1 (Rf=0.29 in pure PE).

Yield: 17 mg (0.123 mmol, 25%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.31 (dd, 1H), 5.00 (d, 1H), 4.66 (d, 1H), 2.37 (t, 2H), 1.66 (sext, 2H), 1.05 (t, 3H); 13C-NMR (75 MHz, CDCl3) δ 150.7, 140.9, 98.9, 92.1, 72.6, 21.1, 20.8, 13.6; IR (cm⁻¹) 2927, 2231, 1725, 1645, 1229; HRMS (EI), calcd. for C₈H₁₀O₂ (M⁺): 138.0675, found: 138.0689

1-adamantylcarboxylic acid vinyl ester (2i)

Column chromatography with PE/EtOAc 99:1 (Rf=0.30). Yield: 93 mg (0.451 mmol, 90%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.28 (dd, 1H), 4.88 (d, 1H), 4.56 (d, 1H), 2.03 (bs, 3H), 1.94 (s, 6H), 1.73 (q, 6H); 13C-NMR (75 MHz, CDCl3) δ 174.7, 141.6, 97.3, 40.7, 38.6, 36.5, 27.9; IR (cm⁻¹) 2905, 2852, 1741, 1644, 1453; HRMS (FD), calcd. for C₁₃H₁₈O₂ (M⁺): 206.1301, found: 206.1334
The following esters were synthesized in an identical method as described in the general procedure, except by using 0.66 equivalents of the respective alkenyl boroxine pyridine complex (except 1s, which used the normal alkenyl boroxine, as it did not form the pyridine complex).

**Isopropenyl benzoate (1r)**

Column chromatography with PE/EtOAc 99:1 (Rf=0.29 in pure PE). Yield: 70 mg (0.432 mmol, 86%) as colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 8.11 (d, 2H), 7.59 (t, 1H), 7.49 (t, 2H), 4.85 (m, 2H), 2.08 (s, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 164.8, 153.3, 133.4, 130.0, 128.5, 102.4, 19.7; IR (cm\(^{-1}\)) 1728, 1668, 1275, 1209, 1091

**2-methyl-1-propenyl benzoate (1s)**

Column chromatography with PE/EtOAc 99:1 \(\rightarrow \) 98:2 (Rf=0.15 in 99:1 ratio). Yield: 58 mg (0.329 mmol, 66%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 8.14 (d, 2H), 7.61 (t, 1H), 7.49 (t, 2H), 7.14 (s, 1H), 1.83 (s, 3H), 1.75 (s, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 163.9, 133.4, 130.1, 129.9, 129.8, 128.6, 119.0, 19.9, 16.0; IR (cm\(^{-1}\)) 2859, 1724, 1370, 1263

**\((E)\)-1-hexenyl acetate (2j)**

Column chromatography with PE/EtOAc 99:1 (Rf=0.19 in pure PE). Yield: 39 mg (0.274 mmol, 55%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.07 (dt, 1H), 5.41 (m, 1H), 2.10 (s, 3H), 1.98 (q, 2H), 1.35 (m, 4H), 0.90 (t, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 168.4, 135.4, 115.1, 31.8, 27.0, 22.2, 20.8, 13.9; IR (cm\(^{-1}\)) 2928, 1751, 1370, 1214

**\((E)\)-1-hexenylbenzoate (1u)**

The reaction was stirred at 50 °C for 2 days. Column chromatography with PE/EtOAc 99:1 (Rf=0.22 in pure PE). Yield: 81 mg (0.397 mmol, 79%) as colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 8.13 (d, 2H), 7.61 (t, 1H), 7.48 (t, 2H), 7.35 (d, 1H), 5.64 (m, 1H), 2.12 (q, 2H), 1.43 (m, 4H), 0.97 (t, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 164.0, 135.6, 133.4, 130.0, 129.4, 128.5, 115.8, 31.8, 27.2, 22.2, 14.0; IR (cm\(^{-1}\)) 2927, 1728, 1370, 1260

**\((Z)\)-1-propenyl benzoate (1v)**

Yield: 59 mg (0.364 mmol, 73%) as a colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 8.15 (d, 2H), 7.63 (t, 1H), 7.50 (t, 2H), 7.30 (d, 1H), 5.09 (quint, 1H), 1.84 (d, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 163.7, 135.1, 133.5, 130.0, 129.6, 128.6, 109.4, 10.2; IR (cm\(^{-1}\)) 2923, 1730, 1264

**Note:**

The following compounds were synthesized according to the general procedure, except by using 1.0 equivalent (0.50 mmol) of N-hydroxyphthalimide, phthalimide or saccharine as the nucleophile and 0.66 equivalents of the respective boroxine pyridine complex.
**N-vinlyoxphthalimide (3a)**

Column chromatography with PE/EtOAc 10:1 → 8:1 (R_f=0.19 in 10:1 ratio).

Yield: 91 mg (0.481 mmol, 96%) as a colorless solid. Melting point: 106-109 °C (dec.). ¹H-NMR (300 MHz, CDCl₃) δ 7.87 (m, 2H), 7.81 (m, 2H), 6.68 (dd, 1H), 4.64 (dd, 1H), 4.45 (dd, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 162.4, 151.2, 134.9, 128.7, 123.9, 90.7; IR (cm⁻¹) 1725, 1639, 1121.

**N-isopropenylxophthalimide (3b)**

Column chromatography with PE/EtOAc 10:1 → 8:1 (R_f=0.23 in 10:1 ratio).

Yield: 101 mg (0.497 mmol, 99%) as a colorless solid. Melting point: 113-117 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.90 (m, 2H), 7.81 (m, 2H), 4.22 (m, 2H), 2.08 (t, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 162.6, 159.0, 134.9, 128.8, 123.9, 85.5, 17.3; IR (cm⁻¹) 1789, 1731, 1184, 1124; HRMS (EI), calcd. for C₉H₈NO₃ ([M-isopropenyl]+): 163.0263, found: 163.0267.

**N-1-(E)-hexenyloxphthalimide (3c)**

Column chromatography with PE/EtOAc 10:1 → 8:1 (R_f=0.33 in 10:1 ratio).

Yield: 106 mg (0.432 mmol, 86%) as a waxy solid. Melting point: 33-35 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.88 (m, 2H), 7.80 (m, 2H), 6.47 (d, 1H), 5.30 (m, 1H), 1.96 (q, 2H), 1.30 (m, 4H), 0.87 (t, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 162.7, 145.6, 134.8, 128.7, 123.8, 109.9, 31.6, 26.2, 22.0, 13.9; IR (cm⁻¹) 2957, 2928, 1793, 1731, 1666.

**N-vinylphthalimide (4)**

No Et₃N was added, 93 mg potassium phthalimide (0.50 mmol) was used instead.

Column chromatography with PE/EtOAc 20:1 → 15:1 (R_f=0.23 in 20:1 ratio).

Yield: 52 mg (0.300 mmol, 60%) as a colorless solid. Melting point: 80-83 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.90 (m, 2H), 7.77 (m, 2H), 6.90 (dd, 1H), 6.11 (d, 1H), 5.07 (d, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.6, 134.6, 131.7, 123.9, 123.8, 104.7; IR (cm⁻¹) 2924, 1777, 1721, 1634, 1380.

**N-vinlysaccharine (5a)**

Column chromatography with PE/EtOAc 10:1 → 8:1 (R_f=0.33 in 10:1 ratio).

Yield: 99 mg (0.473 mmol, 95%) as a colorless solid. Melting point: 132-134 °C; ¹H-NMR (300 MHz, CDCl₃) δ 8.09 (d, 1H), 7.96-7.84 (m, 3H), 6.82 (dd, 1H), 5.63 (d, 1H), 5.13 (d, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 165.6, 137.6, 135.3, 134.7, 126.4, 125.7, 121.9, 121.1, 104.2; IR (cm⁻¹) 3089, 1737, 1633, 1334, 1311, 1290; HRMS (FD), calcd. for C₁₀H₉NO₃S (M⁺): 209.0141, found: 209.0143.

**N-isopropenylsaccharine (5b)**

Column chromatography with PE/EtOAc 8:1 (R_f = 0.23 in 10:1 ratio). Yield: 101 mg (0.452 mmol, 90%) as a colorless solid. Melting point: 69-71 °C; ¹H-NMR (300 MHz, CDCl₃) δ 8.06 (d, 1H), 7.94-7.82 (m, 3H), 5.50 (s, 1H), 5.45 (s, 1H), 2.17 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 157.9, 137.9, 135.0, 134.4, 133.7, 127.0, 125.4, 121.1, 118.3, 20.8; IR (cm⁻¹) 1730, 1329, 1300, 1270; HRMS (FD), calcd. for C₁₀H₉NO₃S (M⁺): 223.0298, found: 223.0298.
The following compounds were synthesized according to the general procedure:

**N-1-(E)-hexenylsaccharine (5c)**

Column chromatography PE/EtOAc 8:1 (R_6 = 0.30 in 10:1 ratio). Yield: 79 mg (0.298 mmol, 60%) as a colorless oil. 

*H-NMR (300 MHz, CDCl_3) δ 8.08 (d, 1H), 7.95-7.83 (m, 3H), 6.47 (d, 1H), 6.22 (quint, 1H), 2.23 (q, 2H), 1.50 (quint, 2H), 1.42 (quint, 2H), 0.93 (t, 3H); 13C-NMR (75 MHz, CDCl_3) δ 156.9, 137.6, 135.0, 134.6, 126.8, 125.6, 125.5, 121.1, 115.4, 31.1, 30.4, 22.2, 13.9; IR (cm⁻¹) 2957, 2928, 2858, 1731, 1336, 1292, 1259, 1181; HRMS (FD), calcd. for C_{24}H_{35}NO_3S (M⁺): 337.1880, found: 337.1866.

**(L)-N-acetyl-phenylalanine vinyl ester (8a)**

Column chromatography with PE/EtOAc 4:1 → 3:1 (R_f=0.15 in 4:1 ratio). Yield: 110 mg (0.472 mmol, 94%) as a colorless solid. Melting point: 89-90 °C. 

*H-NMR (300 MHz, CDCl_3) δ 7.30 (m, 4H), 7.12 (d, 2H), 6.32 (d, 1H), 4.96 (m, 2H), 4.67 (d, 1H), 3.14 (m, 2H), 1.96 (s, 3H); 13C-NMR (75 MHz, CDCl_3) δ 169.9, 169.1, 140.8, 135.6, 129.3, 128.7, 127.2, 99.2, 53.0, 37.5, 23.0; IR (cm⁻¹) 3315, 2936, 1769, 1749, 1644, 1536; HRMS (FD), calcd. for C_{15}H_{17}NO_3 (M⁺): 291.1468, found: 291.1465.

**(D)-N-acetyl-phenylalanine vinyl ester (8b)**

Column chromatography with PE/EtOAc 4:1 → 3:1 (R_f=0.15 in 4:1 ratio). Yield: 109 mg (0.467 mmol, 93%) as a colorless solid. Melting point: 89-90 °C. 

*H-NMR (300 MHz, CDCl_3) δ 7.30 (m, 4H), 7.13 (d, 2H), 6.42 (d, 1H), 4.94 (m, 2H), 4.67 (d, 1H), 3.14 (m, 2H), 1.97 (s, 3H); 13C-NMR (75 MHz, CDCl_3) δ 170.0, 169.1, 140.7, 135.6, 129.2, 128.6, 127.2, 99.1, 53.0, 37.5, 22.9; IR (cm⁻¹) 3316, 1769, 1749, 1644, 1535; HRMS (FD), calcd. for C_{15}H_{17}NO_3 (M⁺): 291.1468, found: 291.1465.

**(L)-N-Fmoc-phenylalanine vinyl ester (8c)**

Column chromatography with PE/EtOAc 10:1 (R_f=0.22). Yield: 195 mg (0.472 mmol, 94%) as a colorless solid. Melting point: 145-147 °C. 

*H-NMR (300 MHz, CDCl_3) δ 7.83 (d, 2H), 7.63 (t, 2H), 7.49-7.28 (m, 8H), 7.17 (d, 2H), 5.43 (d, 1H), 5.02 (d, 1H), 4.83 (q, 1H), 4.74 (d, 1H), 4.52 (t, 1H), 4.43 (t, 1H), 4.27 (t, 1H), 3.22 (m, 2H) (rotamers present); 13C-NMR (75 MHz, CDCl_3) δ 168.9, 155.6, 143.8, 143.7, 141.4, 140.8, 135.4, 129.4, 128.7, 127.8, 127.3, 127.1, 125.14, 125.08, 120.1, 99.24, 67.0, 54.7, 47.2, 37.9; IR (cm⁻¹) 3332, 1746, 1688, 1535; HRMS (EI), calcd. for C_{26}H_{29}NO_4 (M⁺): 413.1622, found: 413.1632.

**(L)-N-Boc-phenylalanine vinyl ester (8d)**

Column chromatography with PE/EtOAc 20:1 → 15:1 (R_f=0.11 in 20:1 ratio). Yield: 135 mg (0.463 mmol, 93%) as a colorless oil. 

*H-NMR (300 MHz, CDCl_3) δ 7.32 (m, 3H), 7.16 (d, 2H), 5.08 (d, 1H), 4.95 (d, 1H), 4.67 (d, 2H), 3.15 (m, 2H), 1.45 (s, 9H); 13C-NMR (75 MHz, CDCl_3) δ 155.1, 140.9, 135.7, 129.3, 128.7, 127.2, 98.9, 80.1, 54.3, 38.0, 28.3; IR (cm⁻¹) 3370, 2978, 1756, 1707, 1646, 1153; HRMS (FD), calcd. for C_{16}H_{27}NO_4 (M⁺): 291.1465, found: 291.1468.
(L)-N-Cbz-phenylalanine vinyl ester (8e)

Column chromatography with PE/EtOAc 15:1 ($R_f$=0.36 in 10:1 ratio). Yield: 153 mg (0.470 mmol, 94%) as a thick colorless oil. $^1$H-NMR (300 MHz, CDCl₃) δ 7.36 (m, 3H), 7.16 (d, 2H), 5.38 (d, 1H), 5.15 (s, 2H), 4.99 (d, 1H), 4.80 (q, 1H), 4.71 (d, 1H), 3.19 (m, 2H); $^{13}$C-NMR (75 MHz, CDCl₃) δ 168.9, 155.7, 140.8, 136.2, 135.4, 129.3, 128.7, 128.6, 128.3, 128.1, 127.3, 99.2, 67.1, 54.7, 37.9; IR (cm⁻¹) 3329, 2953, 1756, 1705, 1646, 1586, 1168; HRMS (FD), calcd. for C₁₉H₁₈NO₅ (M⁺): 325.1309, found: 325.1322

(L)-N-Fmoc-tryptophan vinyl ester (8f)

Column chromatography with PE/EtOAc 4:1 → 3:1 ($R_f$=0.40 in 3:1 ratio). Yield: 202 mg (0.446 mmol, 89%) as a slightly yellow foam. $^1$H-NMR (300 MHz, CDCl₃) δ 8.43 (bs, 1H), 7.84 (d, 2H), 7.69-7.57 (m, 3H), 7.48 (t, 2H), 7.41-7.21 (m, 6H), 6.96 (s, 1H), 5.60 (d, 1H), 5.05 (d, 1H), 4.93 (q, 1H), 4.73 (d, 1H), 4.48 (m, 2H), 4.27 (t, 1H), 3.45 (d, 2H) (rotamers present); $^{13}$C-NMR (75 MHz, CDCl₃) δ 169.3, 155.9, 143.8, 143.7, 141.2, 140.9, 136.2, 127.7, 127.5, 127.1, 125.1, 123.1, 122.2, 120.0, 119.7, 118.5, 111.4, 109.2, 99.1, 67.1, 54.6, 47.0, 27.6; IR (cm⁻¹) 3420, 1754, 1707, 1646, 1509; HRMS (FD), calcd. for C₁₂H₂₃N₂O₄ (M⁺): 452.1731, found: 452.1742

(L)-N-Fmoc-valine vinyl ester (8g)

Column chromatography with PE/EtOAc 10:1 ($R_f$=0.31). Yield: 183 mg (0.498 mmol, 99%) as a thick colorless oil, which slowly crystallized. Melting point: 85-87 °C. $^1$H-NMR (300 MHz, CDCl₃) δ 7.80 (d, 2H), 7.64 (d, 2H), 7.44 (t, 2H), 7.35 (t, 2H), 7.30 (dd, 1H), 5.41 (d, 1H), 5.02 (d, 1H), 4.71 (d, 1H), 4.44 (m, 3H), 4.27 (t, 1H), 2.27 (snt, 1H), 1.05 (d, 3H), 0.97 (d, 3H); $^{13}$C-NMR (75 MHz, CDCl₃) δ 169.5, 156.3, 143.9, 143.8, 141.4, 140.9, 127.8, 127.2, 125.2, 120.1, 99.1, 67.2, 58.9, 47.3, 31.2, 19.1, 17.6; IR (cm⁻¹) 3311, 2965, 1751, 1694, 1647, 1534; HRMS (FD), calcd. for C₁₀H₁₅NO₅ (M⁺): 365.1618; found: 365.1618

(L)-N-Boc-asparagine vinyl ester (8h)

Column chromatography with PE/EtOAc 3:2 → 1:1 ($R_f$=0.21 in 1:1 ratio). Yield: 109 mg (0.422 mmol, 84%) as a waxy solid. Melting trajectory: 69-82 °C (stays waxy); $^1$H-NMR (300 MHz, CDCl₃) δ 7.21 (dd, 1H), 6.29 (d, 2H), 5.88 (d, 1H), 4.90 (d, 1H), 4.58 (m, 2H), 2.94 (d, 1H), 2.75 (d, 1H), 1.42 (s, 9H); $^{13}$C-NMR (75 MHz, CDCl₃) δ 172.6, 169.2, 155.7, 141.2, 98.8, 80.2, 50.1, 37.1, 28.3; IR (cm⁻¹) 3405, 3346, 3204, 2984, 1757, 1692, 1655, 1644, 1523; HRMS (CS), calcd. for C₁₉H₁₇NO₄ (dimer + Na⁺): 539.2329, found: 539.2314

(L)-N-Fmoc-tyrosine vinyl ester (8i)

Column chromatography with PE/EtOAc 4:1 ($R_f$=0.25 in 3:1 ratio). Yield: 160 mg (0.372 mmol, 75%) as a colorless foam. $^1$H-NMR (300 MHz, CDCl₃) δ 7.79 (d, 2H), 7.60 (d, 2H), 7.46-7.25 (m, 5H), 6.99 (d, 2H), 6.90 (bs, 1H), 6.80 (d, 2H), 5.54 (d, 1H), 5.01 (d, 1H), 4.80-4.70 (m, 2H), 4.44 (quint, 2H), 4.20 (t, 1H), 3.12 (m, 4H) (rotamers present); $^{13}$C-NMR (75 MHz, CDCl₃) δ 169.1, 156.0, 155.5, 143.7, 143.6, 141.3, 140.8, 130.4, 127.8, 127.1, 126.6, 125.1, 125.0, 120.0, 115.7, 99.4, 67.2, 54.9, 47.1, 37.1; IR (cm⁻¹) 3331, 1755, 1694, 1514, 1122; HRMS (FD), calcd. for C₁₀H₁₅NO₅ (M⁺): 429.1571, found: 429.1563
(L)-N-Fmoc-tyrosine(O-vinyl) vinyl ester (8j)

Column chromatography with PE/EtOAc 10:1 (R_f=0.24). Yield: 45 mg (0.099 mmol, 20%) as a faint yellow waxy solid. Melting point: 100-105 °C. ^1H-NMR (300 MHz, CDCl_3) δ 7.80 (d, 2H), 7.60 (bs, 2H), 7.47-7.24 (m, 5H), 7.07 (d, 2H), 6.95 (d, 2H), 6.63 (dd, 1H), 5.30 (d, 1H), 5.00 (d, 1H), 4.75 (m, 3H), 4.48 (m, 3H), 4.24 (t, 1H), 3.18 (m, 2H) (rotamers present); ^13C-NMR (75 MHz, CDCl_3) δ 168.9, 156.1, 155.6, 148.1, 143.9, 143.7, 141.4, 140.8, 130.7, 130.0, 127.9, 127.2, 125.2, 125.1, 120.1, 117.3, 99.4, 95.5, 67.1, 54.7, 47.3, 37.3; IR (cm^-1) 3322, 1756, 1749, 1699, 1641, 1537, 1506; HRMS (FD), calcd. for C_{26}H_{23}NO_5 (M^+): 455.1727, found: 455.1710

(L)-N-Fmoc-tyrosine(OtBu) vinyl ester (8k)

Column chromatography with PE/EtOAc 10:1 (R_f = 0.28). Yield: 243 mg (0.498 mmol, 99%) as a colorless foam. ^1H-NMR (300 MHz, CDCl_3) δ 7.80 (d, 2H), 7.62 (t, 2H), 7.44 (t, 2H), 7.36 (t, 2H), 7.05 (d, 2H), 6.96 (d, 1H), 5.47 (d, 1H), 4.77 (q, 1H), 4.69 (d, 1H), 4.51-4.39 (m, 2H), 4.25 (t, 1H), 3.15 (m, 2H), 1.37 (s, 9H) (rotamers present); ^13C-NMR (75 MHz, CDCl_3) δ 168.9, 155.6, 154.6, 143.8, 143.7, 141.3, 140.8, 130.1, 129.8, 127.7, 127.1, 125.09, 125.06, 124.3, 120.01, 119.99, 78.5, 67.0, 54.8, 47.2, 37.4, 28.8; IR (cm^-1) 3324, 2976, 1757, 1706, 1505; HRMS (FD), calcd. for C_{30}H_{31}NO_5 ([M+H]^+): 485.2219, found: 485.2219

(L)-N-Boc-serine vinyl ester (8l)

Column chromatography with PE/EtOAc 4:1 à 3:1 (R_f = 0.31 in 3:1 ratio) Yield: 63 mg (0.272 mmol, 54%) as a thick colorless oil. ^1H-NMR (300 MHz, CDCl_3) δ 7.27 (dd, 1H), 5.62 (d, 1H), 4.96 (d, 1H), 4.44 (bs, 1H), 4.01 (bs, 1H), 3.93 (bs, 1H), 3.03 (bs, 1H), 1.45 (s, 9H); ^13C-NMR (75 MHz, CDCl_3) δ 168.4, 155.6, 154.6, 143.8, 143.7, 141.3, 140.8, 130.1, 129.8, 127.7, 127.1, 125.09, 125.06, 124.3, 120.01, 119.99, 78.5, 67.0, 54.8, 47.2, 37.4, 28.8; IR (cm^-1) 3400, 2978, 1758, 1691, 1647, 1505, 1153; HRMS (FD), calcd. for C_{10}H_{17}NO_5 ([M+H]^+): 232.1179, found: 232.1173

(L)-N-Fmoc-O-tert-butyl serine vinyl ester (8m)

Column chromatography with PE/EtOAc 12:1 (R_f=0.29). Yield: 203 mg (0.493 mmol, 99%) as a colorless foam. ^1H-NMR (300 MHz, CDCl_3) δ 7.83 (d, 2H), 7.69 (t, 2H), 7.44 (t, 2H), 7.38-7.26 (m, 5H), 5.76 (d, 1H), 5.01 (d, 1H), 4.68 (dd, 1H), 4.63 (dt, 1H), 4.51-4.39 (m, 2H), 4.31 (t, 1H), 3.94 (dd, 1H), 3.68 (dd, 1H), 1.20 (s, 9H) (rotamers present); ^13C-NMR (75 MHz, CDCl_3) δ 168.1, 156.2, 144.0, 143.8, 141.4, 141.2, 127.8, 127.2, 127.1, 125.24, 125.18, 120.1, 98.7, 73.7, 67.3, 61.9, 54.7, 47.2, 27.4; IR (cm^-1) 3437, 2974, 1764, 1719, 1646, 1506; HRMS (FD), calcd. for C_{24}H_{23}NO_5 (M^+): 409.1884, found: 409.1898
(L)-N-Fmoc-arginine(Pmc) vinyl ester (8n)

Column chromatography with PE/EtOAc 1:1 (R<sub>f</sub> = 0.18). Yield: 302 mg (0.438 mmol, 88%) as a colorless foam. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.74 (d, 2H), 7.57 (d, 2H), 7.37 (t, 2H), 7.29-7.18 (m, 3H), 6.30 (bs, 3H), 5.88 (d, 1H), 4.93 (d, 1H), 4.63 (d, 1H), 4.37 (quint, 3H), 3.23 (bs, 2H), 2.57 (d, 8H), 2.07 (s, 3H), 1.87 (bs, 2H), 1.75 (t, 2H), 1.62 (bs, 2H), 1.28 (s, 6H) (rotamers present); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 169.6, 156.4, 156.3, 153.7, 143.8, 143.6, 141.2, 140.9, 135.4, 134.8, 133.1, 127.7, 127.1, 125.2, 124.1, 119.9, 118.0, 99.0, 73.7, 67.2, 53.7, 47.0, 40.6, 32.7, 29.1, 26.7, 25.5, 21.4, 18.6, 17.5, 12.1; IR (cm<sup>-1</sup>) 3435, 3326, 2931, 1717, 1543, 1104; HRMS (FD), calcd. for C<sub>37</sub>H<sub>44</sub>N<sub>4</sub>O<sub>7</sub>S (M<sup>+</sup>): 688.2925, found: 688.2907

(L)-N-Fmoc-lysine(Boc) vinyl ester (8o)

Column chromatography with PE/EtOAc 5:1 à 4:1 (R<sub>f</sub> = 0.30 in 3:1 ratio). Yield: 239 mg (0.483 mmol, 97%) as a colorless foam. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.75 (d, 2H), 7.62 (t, 2H), 7.39 (t, 2H), 7.28 (m, 3H), 5.86 (d, 1H), 4.95 (d, 1H), 4.83 (t, 1H), 4.64 (d, 1H), 4.43 (m, 3H), 4.22 (t, 1H), 3.12 (bs, 2H), 1.89 (quint, 1H), 1.75 (quint, 1H), 1.45 (bs, 13H) (rotamers present); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 169.9, 156.2, 143.9, 143.7, 141.3, 140.9, 127.7, 127.1, 125.1, 120.0, 98.9, 79.1, 67.1, 53.7, 47.1, 39.9, 31.5, 29.6, 28.5, 22.5; IR (cm<sup>-1</sup>) 3329, 2930, 1758, 1689, 1519, 1165; HRMS (FD), calcd. for C<sub>28</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub> (M<sup>+</sup>): 494.2411, found: 494.2401

(L)-N-Fmoc-histidine(Trt) vinyl ester (8p)

Column chromatography with PE/EtOAc 1:1 (R<sub>f</sub> = 0.41). Yield 199 mg (<0.308 mmol, <62%) as a green foam. See spectrum on page 128 for <sup>1</sup>H-spectrum

(L)-N-Boc-histidine(Boc) vinyl ester (8q)

Column chromatography with PE/EtOAc 5:1 → 4:1 (R<sub>f</sub> = 0.23 in 4:1 ratio). Yield: 69 mg (0.181 mmol, 36%) as a colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.99 (s, 1H), 7.22 (dd, 1H), 7.15 (s, 1H), 5.82 (d, 1H), 4.92 (d, 1H), 4.62 (d, 2H), 3.08 (d, 2H), 1.60 (s, 9H), 1.43 (s, 9H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 169.2, 155.5, 146.9, 141.2, 138.4, 137.1, 114.8, 98.6, 85.8, 80.0, 53.2, 29.9, 28.4, 27.9; IR (cm<sup>-1</sup>) 3378, 2979, 2934, 1753, 1713, 1487; HRMS (FD), calcd. for C<sub>18</sub>H<sub>27</sub>N<sub>3</sub>O<sub>6</sub> (M<sup>+</sup>): 381.1894, found: 381.1915

(L)-N-Fmoc-homoserine lactone (8r)

Column chromatography with PE/EtOAc 4:2 à 3:2 (R<sub>f</sub>=0.18 in 4:2 ratio). Yield: 104 mg (0.322 mmol, 64%) as a colorless solid. Melting point: 206-209 °C. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) δ 7.90 (s, 1H), 7.22 (dd, 1H), 7.15 (s, 1H), 5.82 (d, 1H), 4.92 (d, 1H), 4.62 (d, 2H), 3.08 (d, 2H), 1.60 (s, 9H), 1.43 (s, 9H); <sup>13</sup>C-NMR (75 MHz, DMSO-d<sub>6</sub>) δ 169.2, 155.5, 146.9, 141.2, 138.4, 137.1, 114.8, 98.6, 85.8, 80.0, 53.2, 29.9, 28.4, 27.9; IR (cm<sup>-1</sup>) 3378, 2979, 2934, 1753, 1713, 1487; HRMS (FD), calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub> (M<sup>+</sup>): 323.1157, found: 323.1185
(L)-N-Fmoc-cysteine(S-vinyl) vinyl ester (8s)

Column chromatography with PE/EtOAc 6:1 → 5:1 → 4:1 (Rf=0.28 in 5:1 ratio) Yield: 57 mg (0.144 mmol, 29%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.80 (d, 2H), 7.63 (d, 2H), 7.44 (t, 2H), 7.37 (t, 2H), 7.26 (dd, 1H), 6.28 (dd, 1H), 5.71 (d, 1H), 5.34 (s, 1H), 5.26 (d, 1H), 5.03 (d, 1H), 4.82 (q, 1H), 4.74 (d, 1H), 4.44 (m, 2H), 4.29 (t, 1H), 3.25 (m, 2H) (rotamers present); 13C-NMR (75 MHz, CDCl3) δ 167.7, 155.7, 143.8, 143.7, 141.4, 140.93, 140.88, 131.3, 127.9, 127.2, 125.2, 120.1, 114.1, 99.6, 67.4, 53.7, 47.2, 34.3, 29.8; IR (cm⁻¹) 3327, 2925, 1757, 1707, 1646, 1510; HRMS (FD), calcd. for C22H21NO4S (M⁺): 395.1186, found: 395.1194

(L)-N-Boc-cysteine(Boc) vinyl ester (8t)

Column chromatography with PE/EtOAc 3:1 (Rf = 0.19). Yield: 126 mg (0.435 mmol, 87%) as a colorless oil. 1H-NMR (300 MHz, CDCl3) δ 7.17 (dd, 1H), 6.61 (d, 1H), 4.96 (d, 1H), 4.85 (q, 1H), 4.64 (d, 1H), 3.36-3.21 (m, 2H), 2.00 (s, 3H), 1.46 (s, 9H); 13C-NMR (75 MHz, CDCl3) δ 192.2, 170.1, 168.7, 167.7, 140.1, 99.4, 85.9, 52.4, 32.3, 28.1, 22.9; IR (cm⁻¹) 3274, 2981, 1757, 1647, 1534, 1117; HRMS (FD), calcd. for C12H19NO5S ([M+H]+): 290.1057, found: 290.1064

IV. Synthesis and characterization of vinyl benzoate derivates 9a-14

General procedure for the aminolysis or transesterification of vinyl benzoate catalyzed by 1,2,4-triazole and DBU

Firstly a stock solution of the catalyst was made, containing 1.0 M 1,2,4-triazole and 1.0 M DBU in anhydrous CH3CN. Vinyl benzoate (0.138 mL, 1.0 mmol) and the nucleophile (2.4 mmol, 2.4 equiv) were dissolved in 5 mL anhydrous CH3CN and 0.1 mL of the catalyst solution (0.1 mmol, 10 mol%) was added. The reaction was stirred overnight at the specified temperature, or until TLC showed complete conversion of vinyl benzoate. The solution was concentrated in vacuo and the residue was partitioned between 20 mL EtOAc and 20 mL 1M KHSO4. The aqueous layer was extracted with 10 mL EtOAc and the combined organic layers were washed with 10 mL NaHCO3, 10 mL brine, dried over MgSO4 and concentrated in vacuo to give the product. In some cases column purification was required (mentioned below).

N-butyl benzamide (9a) 16

Stirred overnight at room temperature. Yield: 175 mg (0.987 mmol, 99%) as a colorless oil; 1H-NMR (300 MHz, CDCl3) δ 7.78 (d, 2H), 7.40 (t, 1H), 7.33 (t, 2H), 7.05 (t, 1H), 3.37 (q, 2H), 1.54 (quint, 2H), 1.33 (quint, 2H), 0.89 (t, 3H); 13C-NMR (75 MHz, CDCl3) δ 167.7, 134.7, 131.1, 128.3, 127.0, 39.8, 31.6, 20.2, 13.7; IR (cm⁻¹) 3314, 2959, 2932, 1633, 1538

N-benzyl benzamide (9b) 16

Stirred overnight at room temperature. Yield: 208 mg (0.984 mmol, 98%) as a colorless solid. Melting point: 100-102 °C; 1H-NMR (300 MHz, CDCl3) δ 7.81 (d, 2H), 7.47 (t, 1H), 7.40-7.27 (m, 7H), 7.18 (t, 1H), 4.58 (d, 2H); 13C-NMR (75 MHz, CDCl3) δ 167.6, 138.4, 134.3, 131.4, 128.6, 128.5, 127.7, 127.4, 127.1, 43.9; IR (cm⁻¹) 3322, 3058, 3028, 1640, 1539
**N-isopropyl benzamide (9c)**

Stirred at room temperature for 2 days. Purified by column chromatography (PE/EtOAc 6:1, Rf = 0.19) Yield: 132 mg (0.809 mmol, 81%) as a colorless solid.

Melting point: 97-99 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.75 (d, 2H), 7.42 (t, 1H), 7.31 (t, 2H), 6.66 (d, 1H), 4.22 (hept, 1H), 1.21 (s, 3H), 1.19 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.7, 134.9, 131.0, 128.2, 126.9, 41.7, 22.6; IR (cm⁻¹) 3295, 2971, 1630, 1531

**Morpholine benzoate (9d)**

Stirred at room temperature for 3 days. Yield: 192 mg (0.99 mmol, 99%) as a thick, slightly yellow oil; ¹H-NMR (300 MHz, CDCl₃) δ 7.37 (bs, 5H), 3.69-3.30 (bm, 8H); ¹³C-NMR (75 MHz, CDCl₃) δ 170.2, 135.1, 129.7, 128.4, 126.9, 66.7, 48.0, 42.5; IR (cm⁻¹) 2856, 1625, 1426, 1276, 1256, 1112

**Ethyl benzoate (10a)**

Stirred for 3 days at room temperature. Purified by column chromatography (PE/EtOAc 99:1) to give a colorless oil. Yield: 123 mg (0.82 mmol, 82%).

¹H-NMR (300 MHz, CDCl₃) δ 8.07 (d, 2H), 7.53 (t, 1H), 7.44 (t, 2H), 4.38 (q, 2H), 1.40 (t, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.6, 132.8, 130.5, 129.5, 128.3, 60.9, 14.3

**Benzyl benzoate (10b)**

1.2 equiv of benzyl alcohol used. Stirred overnight at room temperature. Purified by column chromatography (PE/EtOAc 98:2) to give a colorless oil. Yield: 185 mg (0.871 mmol, 87%).

¹H-NMR (300 MHz, CDCl₃) δ 8.18 (d, 2H), 7.60-7.41 (m, 8H), 5.45 (s, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.3, 136.1, 133.0, 130.1, 129.7, 128.6, 128.3, 128.2, 128.1, 60.9, 14.3

**Phenyl benzoate (10c)**

1.2 equiv of phenol used. Stirred overnight at 50 °C. Purified by column chromatography (PE/EtOAc 99:1 → 98:2) to give a colorless oil, which solidified upon standing. Yield: 180 mg (0.908 mmol, 91%). Melting point: 64-67 °C.

¹H-NMR (300 MHz, CDCl₃) δ 8.27 (t, 2H), 7.67 (t, 1H), 7.58-7.45 (m, 4H), 7.35-7.25 (m, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 165.3, 151.1, 133.7, 130.3, 129.7, 129.6, 126.0, 121.9; IR (cm⁻¹) 1714, 1497, 1214

**Isopropyl benzoate (10d)**

Stirred overnight at 80 °C. Purified by column chromatography (PE/EtOAc 99:1) to give a colorless oil. Yield: 129 mg (0.785 mmol, 79%).

¹H-NMR (300 MHz, CDCl₃) δ 8.06 (d, 2H), 7.55 (t, 1H), 7.45 (t, 2H), 5.29 (hept, 1H), 1.39 (d, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.1, 132.7, 130.9, 129.5, 128.3, 68.3, 22.0; IR (cm⁻¹) 2980, 2971, 1712, 1270, 1096

**(+) Menthol benzoate (10e)**

1.2 equiv of (+)-menthol used. Stirred overnight at 80 °C. Purified by column chromatography (PE/EtOAc 99:1) to give a colorless oil. Yield: 163 mg (0.626 mmol, 63%).

¹H-NMR (300 MHz, CDCl₃) δ 8.09 (d, 2H), 7.56 (t, 1H), 7.45 (t, 2H), 4.97 (dt, 1H), 2.18 (d, 1H), 2.00 (quint, 1H), 1.74 (d, 2H), 1.58 (d, 2H), 1.15 (quint, 2H), 0.97 (s, 3H), 0.94 (s, 3H), 0.82 (d, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.1, 132.8, 130.9, 129.6, 128.3, 74.9, 47.3, 41.1, 34.4, 31.5, 26.6, 23.7, 22.1, 20.9, 16.6; IR (cm⁻¹) 2954, 2927, 2869, 1712, 1269
S-Ethyl thiobenzoate (11a)\textsuperscript{21}

138 μL vinyl benzoate (1.00 mmol) and 86 μL ethanethiol (1.20 mmol) were dissolved in 5 mL anhydrous CH\textsubscript{3}CN and 166 mg K\textsubscript{2}CO\textsubscript{3} (1.20 mmol) was added. The reaction was stirred overnight at room temperature, after which TLC showed complete conversion. The mixture was diluted with 25 mL Et\textsubscript{2}O and washed with 10 mL H\textsubscript{2}O, 10 mL 1M NaOH and 10 mL brine, dried over MgSO\textsubscript{4} and concentrated in vacuo to give a colorless oil. Yield: 157 mg (0.944 mmol, 94%); \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ 7.98 (d, 2H), 7.54 (t, 1H), 7.43 (t, 2H), 3.08 (q, 4H), 1.34 (t, 3H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) δ 191.9, 137.2, 133.2, 128.5, 127.1, 23.4, 14.8; IR (cm\textsuperscript{-1}) 2969, 2930, 1657, 1448, 1205, 1174

S-Benzyl thiobenzoate (11b)\textsuperscript{22}

138 μL vinyl benzoate (1.00 mmol) and 141 μL benzyl mercaptan (1.20 mmol) were dissolved in 5 mL anhydrous CH\textsubscript{3}CN under N\textsubscript{2} atmosphere and 166 mg K\textsubscript{2}CO\textsubscript{3} (1.20 mmol) was added. The reaction was stirred overnight at room temperature under N\textsubscript{2} atmosphere. The mixture was diluted with 20 mL Et\textsubscript{2}O and washed with 10 mL H\textsubscript{2}O, 10 mL 1M NaOH and 10 mL brine, dried over MgSO\textsubscript{4} and concentrated in vacuo to give a very faint yellow oil. Yield: 238 mg (1.04 mmol, 104% (also disulfide present)); \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ 8.08 (d, 2H), 7.62 (t, 1H), 7.52-7.33 (m, 7H), 4.43 (s, 2H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) δ 191.1, 137.5, 136.7, 133.4, 128.9, 128.60, 128.57, 127.3, 127.2, 33.28; IR (cm\textsuperscript{-1}) 3061, 3029, 1657, 1204, 1174

General Procedure for the synthesis of azole-esters

138 μL vinyl benzoate (1.00 mmol) and 1.2 mmol (1.2 equiv) of the azole were dissolved in 5 mL dry CH\textsubscript{3}CN and 0.18 mL DBU (1.20 mmol, 1.2 equiv) was added. The reaction was stirred at room temperature until TLC showed complete conversion of vinyl benzoate and was diluted with 25 mL Et\textsubscript{2}O. The organic layer was washed with 10 mL 1M KHSO\textsubscript{4}, 10 mL NaHCO\textsubscript{3} and 10 mL brine, dried over MgSO\textsubscript{4} and concentrated in vacuo to give the crude azole ester, which was pure enough for practical purposes.

1-(pyrazol-yl)ethyl benzoate (12a)

Yield: 206 mg (0.952 mmol, 95%) as a colorless solid. Melting point: 54-56 °C; \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ 8.01 (d, 2H), 7.72 (t, 1H), 7.58 (s, 1H), 7.49 (t, 1H), 7.37 (t, 2H), 7.05 (q, 1H), 6.26 (d, 1H), 1.98 (d, 3H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) δ 165.2, 140.4, 133.4, 129.78, 129.75, 129.1, 128.3, 106.1, 79.4, 19.3; IR (cm\textsuperscript{-1}) 1717, 1248, 1091; HRMS (EI), calcd. for C\textsubscript{12}H\textsubscript{12}N\textsubscript{2}O\textsubscript{3} (M\textsuperscript{+}): 216.089, found: 216.0890

1-(imidazol-yl)ethyl benzoate (12b)\textsuperscript{23}

Yield: 199 mg (0.920 mmol, 92%) as a colorless solid. Melting point: 85-86 °C; \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ 7.94 (d, 2H), 7.79 (s, 1H), 7.51 (t, 1H), 7.37 (t, 2H), 7.17 (s, 1H), 7.03 (s, 1H), 6.92 (q, 1H), 1.87 (d, 3H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) δ 164.9, 136.5, 133.6, 129.7, 129.6, 128.8, 128.4, 116.7, 75.7, 20.2; IR (cm\textsuperscript{-1}) 3110, 2996, 1715, 1493
1-{1,2,4-triazol-yl}ethyl benzoate (12c)

Yield: 188 mg (0.865 mmol, 87%) as a colorless solid. Melting point: 77-80 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.43 (s, 1H), 7.98 (t, 3H), 7.53 (t, 1H), 7.40 (t, 2H), 7.09 (q, 1H), 2.00 (d, 3H); 13C-NMR (75 MHz, CDCl₃) δ 165.1, 152.1, 144.2, 133.8, 129.9, 128.6, 128.5, 77.0, 19.1; IR (cm⁻¹) 3105, 1722, 1259, 1243, 1067; HRMS (EI), calcd. for C₁₁H₁₁N₃O₂ (M⁺): 217.0846, found: 217.0836

1-{1,2,3-triazol-yl}ethyl benzoate (12d)

Yield: 192 mg (0.884 mmol, 88%) as a colorless solid (mixture of regioisomers); 1H-NMR (300 MHz, CDCl₃) δ 7.97 (d, 2H), 7.66 (t, 2H), 7.46 (t, 1H), 7.40-7.31 (m, 3H), 2.00 (d, 3H) (regioisomer also present); 13C-NMR (75 MHz, CDCl₃) δ 164.7, 164.5, 135.1, 133.7, 133.6, 133.4, 129.8, 128.8, 128.4, 128.3, 123.6, 81.5, 78.0, 19.5, 19.2 (mixture of the two regioisomers); IR (cm⁻¹) 1721, 1263, 1243, 1058; HRMS (EI), calcd. for C₁₁H₁₁N₃O₂ (M⁺): 217.0845, found: 217.0845

1-(benzotriazol-yl)ethyl benzoate (12e)

Residue purified by column chromatography (PE/EtOAc 10:1 → 8:1). Yield: 229 mg (0.897 mmol, 90%) as a colorless solid (mixture of regioisomers). Melting point: 66-71 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.08 (d, 1H), 8.01 (d, 2H), 7.86 (d, 1H), 7.69 (q, 1H), 7.55 (t, 2H), 7.41 (t, 3H), 2.27 (d, 3H) (regioisomer also present); 13C-NMR (75 MHz, CDCl₃) δ 165.0, 146.0, 133.8, 132.4, 130.0, 128.6, 128.5, 128.1, 124.5, 120.1, 110.3, 77.0, 19.6; IR (cm⁻¹) 1722, 1687, 1249; HRMS (EI), calcd. for C₁₅H₁₃N₃O₂ (M⁺): 267.1002, found: 267.0995

1-cyanoethyl benzoate (13)²⁴

138 μL vinyl benzoate (1.00 mmol) was dissolved in 4 mL dry DMF and 78 mg KCN (1.20 mmol, 1.2 equiv) was added. The reaction turned quickly dark yellow. The reaction was stirred at room temperature for 6h and was diluted with 20 mL Et₂O. The organic layer was washed with 10 mL H₂O and the aqueous layer was extracted with 10 mL Et₂O. The combined organic layers were washed with 10 mL H₂O, 10 mL 1M NaOH and 10 mL brine, dried over MgSO₄ and concentrated in vacuo to give a yellow oil. Yield: 72 mg (0.411 mmol, 41%). 1H-NMR (300 MHz, CDCl₃) δ 8.07 (d, 2H), 7.63 (t, 1H), 7.50 (t, 2H), 5.65 (q, 1H), 1.79 (d, 3H); 13C-NMR (75 MHz, CDCl₃) δ 164.8, 134.1, 130.0, 128.7, 128.3, 117.7, 57.8, 19.0; IR (cm⁻¹) 1726, 1452, 1258, 1091

Benzyl alcohol (14)²⁵

138 μL vinyl benzoate (1.00 mmol) was dissolved in 6 mL THF/H₂O 2:1 and cooled to 0 °C. After cooling, 152 mg NaBH₄ (4.00 mmol, 4 equiv) was added portionwise and the reaction was stirred for 30 min at 0 °C and 30 min at room temperature. The mixture was diluted with 20 mL Et₂O and washed with 10 mL 1M KHSO₄ and 10 mL brine, dried over MgSO₄ and concentrated in vacuo to give a colorless oil. Yield: 101 mg (0.934 mmol, 93%). The spectral data were identical to a commercial sample of benzyl alcohol.
V. References

6) Weinhouse, M.I.; Janda, K.D. Synthesis 1993, 1, 81-83
VI. NMR Spectra of compounds
1:3 ratio 2g : 2h

$\text{2g}$

$\text{2h}$
1:3 ratio 2g : 2h
room temperature in DMSO

\[\text{FmocHN} \quad \text{O} \quad \text{allyl} \]

8c

H₂O  DMSO
LC-MS data for 8c

![LC-MS graph](image)

**Time (min)**

- 0.60-1.21
- 2.88-3.24
- 4.25-4.56
- 6.18-6.56
- 7.63-8.47
- 8.91-9.17
- 9.77-10.58
- 12.22

**[M-Fmoc]H^+**
- 192.1

**[M-H]^+**
- 179.1
- 178.1

**[MH]^+**
- 193.2
- 230.0

**[MH]^+**
- 414.0

- 164.1
- 298.3
- 359.4

**Masses**

- 436.3
- 437.3
- 438.4
- 456.2
- 632.2
- 681.5
- 749.7
- 826.7
- 906.4
- 975.8

**Conditions**

- RT: 10.33-10.50
- AV 51 T: ITMS + c ESI
- Full ms [100.00-2000.00]
$\text{Trt} \quad \text{FmocHN}$

$\begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{N}
\end{array} + \text{Cu(II) residues}$

$\text{8p}$
AcHN

8t

$\text{SBoc}$
10c
VII. Chiral HPLC spectra of compounds 8a & 8b

8a: $\frac{95.71}{95.71+0.823} = 99.1\% \text{ ee}$

8b: $\frac{96.24}{96.24+0.091} = 99.9\% \text{ ee}$