

Supporting information (73 pages)

**Hydrazines and Azides via the Metal-Catalyzed Hydrohydrazination
and Hydroazidation of Olefins**

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1. General Methods

All reactions were carried out in oven dried glassware under an atmosphere of argon or nitrogen, unless stated otherwise. For flash chromatography technical grade solvents were used, which were distilled prior to use. Alcoholic solvents for reactions were analytical grade purchased from Merck, Baker or Fluka and used without further purifications. THF, Et₂O, CH₃CN, toluene and CH₂Cl₂ were purified by distillation and dried by passage over activated alumina under argon atmosphere (H₂O content < 30 ppm, *Karl-Fischer* titration). DCE was distilled under argon from CaH₂. NEt₃ and pyridine were distilled under nitrogen from KOH. All chemicals were purchased from Acros, Aldrich, Fluka, Merck or Lancaster and used as such unless stated otherwise.

Chromatographic purification was performed as flash chromatography using Brunschwig silica 32-63, 60 Å, using the solvents indicated as eluent with 0.3-0.5 bar pressure.

TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates and visualized with UV light and permanganate stain.

Melting points were measured on a Büchi 510 melting point apparatus using open glass capillaries, the data is uncorrected.

¹H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, q_i = quintet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation). NOE-¹H-NMR spectra were measured on a Bruker DMX 500 MHz spectrometer.

²D-NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer in CHCl₃.

¹³C-NMR spectra were recorded with ¹H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films unless stated otherwise and are reported as cm⁻¹ (w = weak, m = medium, s = strong, sh = shoulder).

REACT-IR spectra were recorded on a Mettler Toledo REACT-IR-4000 spectrophotometer and monitored using a Mettler Toledo REACT-IR 3 software.

Gas chromatographic measurements were performed on a Varian 3300 gas chromatographer or a HP 6890 Series gas chromatographer using a Supelco fused silica column β-Dex 120 (length: 30 m, diameter: 0.25 cm, film thickness 0.25 μm), hydrogen as carrier gas and a FID detector.

Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ on a Finnigan TSQ 7000 ESI spectrometer for low resolution measurements and on an IONSPEC Ultima ESI-FT-ICR spectrometer at 4.7 Tesla, on an Ion Spec Ultima HR FT-ICR MS MALDI-FT-ICR MS using the DHB-tl (2,5-Dihydroxy-benzoic acid-two layers) method at 4.7 Tesla or on a EI-HIRES Micromass Autopel-ULTIMA spectrometer at 70 eV for high resolution measurements.

Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ.

Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system. Solvent mixtures, conditions, retention times and columns used are given in parentheses.

Caution: Azides are potentially hazardous compounds and adequate safety measures should be taken. Reaction, especially when involving bigger quantities or heating, should be conducted behind safety shields.

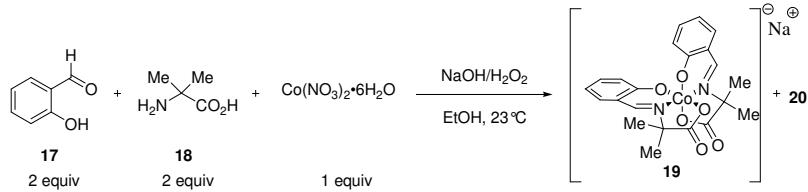
2. The Hydrohydrazination of Olefins

2.1. Ligands and Catalysts

Co(acac)₂, CoCl₂•6H₂O, Co(NO₃)₂•6H₂O and Co(OAc)₂•4H₂O are commercially available and were used as received. Co(OAc)₂ and CoCl₂ were obtained by drying commercially available Co(OAc)₂•4H₂O and CoCl₂•6H₂O 5 h at 100 °C under high vacuo. Co(modp)₂¹ and Co(dpm)₂² were synthesized following reported procedures. Following a reported procedure,³ ligands **7** to **11** and **16** were prepared by condensation of the corresponding amine with salicylaldehyde (**17**) in the presence of triethylamine and the green Co(II) complexes were obtained by mixing two equivalents of the ligand with one equivalent CoCl₂ in acetonitrile for 20 h, followed by solvent removal and drying in high vacuo for at least 5 h. The red-brown Co(III) complexes derived from ligand **12** to **16** were formed in one-pot from the free amino acids, salicylaldehyde (**17**) and Co(NO₃)₂•6H₂O as described in procedure A for Co catalyst **20**.

N-salicylidene-2-amino-isobutyrate -derived cobalt (III) complexes

Procedure A:⁴

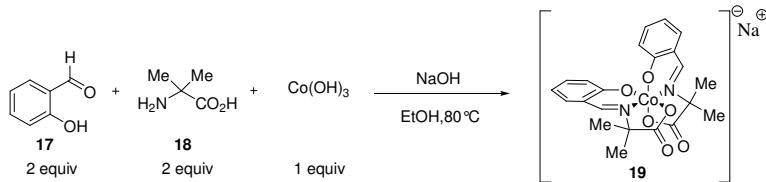


Salicylaldehyde (**17**) (1.06 mL, 10.0 mmol, 2.00 equiv) and 2-aminoisobutyric acid (**18**) (1.03 g, 10.0 mmol, 2.00 equiv) were added to a solution of sodium hydroxide (0.21 g, 5.0 mmol, 1.0 equiv) in ethanol (10 mL) at 23 °C under argon. The resulting thick yellow suspension was cooled to 0 °C and Co(II) nitrate hexahydrate (1.5 g, 5.0 mmol, 1.0 equiv) was added as a cold (0 °C) solution in ethanol (10 mL) and the suspension turned to orange. After stirring 15 min at 0 °C, hydrogen peroxide (35%, 7.0 mL) was added dropwise over 20 min, whereas the reaction mixture immediately turned dark red under gas evolution. The reaction mixture was further stirred at 0 °C for 2 h and then warmed to 23 °C over 3 h. The resulting nearly clear dark red solution was filtered, the solvent was removed under reduced pressure and the residues co- evaporated with methanol (2x) and CH₂Cl₂ (2x). The resulting dark red-brown residues were suspended in Et₂O, triturated for 1 h and filtered, the obtained fine dark red-brown powder was dried in high vacuo at 70 °C for 12 h to afford a dark-red brown solid (2.04 g, 4.14 mmol, 83%).

The identity of the isolated compound was established to be a mixture by NMR analysis. The catalyst was used without further purifications and several batches furnished reproducible results. No loss of activity was observed after several months when the compound was kept in dessicator at 23 °C.

Procedure B:⁴

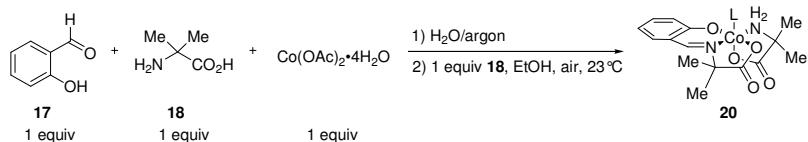
Sodium-bis-[*N*-salicylidene-2-amino-isobutyrate]-cobaltate(III) (**19**)



Sodium peroxide (0.47 g, 6.0 mmol, 1.2 equiv) was added slowly over 10 min to a solution of Co(NO₃)₂·6H₂O (1.5 g, 5.0 mmol, 1.0 equiv) in water (15 mL), whereas black-green Co(OH)₃ precipitated. The reaction mixture was filtered and the precipitate washed with water (2x7 mL) and ethanol (7 mL). The collected Co(OH)₃ gel in ethanol (10 mL) was added to a suspension of salicylaldehyde (**17**) (1.1 mL, 10 mmol, 2.0 equiv) and 2-aminoisobutyric acid (**18**) (1.0 g, 10 mmol, 2.0 equiv) in ethanol (10 mL) and the resulting suspension was refluxed for 18 h. The nearly clear dark red solution was cooled to 23 °C, filtered and the solvent was removed under reduced pressure. After co-evaporating with CH₂Cl₂ (3x), the dark red solid was triturated in Et₂O (50 mL), filtered, washed with Et₂O (50 mL) and dried 6 h in high vacuo at 70 °C. The obtained complex was nearly pure **19**·EtOH, but this complex proved much less active for the hydrohydrazination reaction and not active at all for the hydroazidation reaction. ¹H NMR (CD₃OD, 300 MHz) δ 8.65 (s, 2H, imine H), 7.49 (d, *J* = 8.1 Hz, 2H, Ar H), 7.07-7.01 (m, 2H, Ar H), 6.74 (d, *J* = 8.7 Hz, 2H, Ar H), 6.58-6.53 (m, 2H, Ar H), 3.48 (q, *J* = 7.2 Hz, 2H, ethanol-CH₂), 1.88 (s, 6H, CH₃), 1.87 (s, 6H, CH₃), 1.17 (t, *J* = 7.2 Hz, 3H, ethanol-CH₃); ¹³C NMR (CD₃OD, 75 MHz) δ 188.1, 165.3, 164.6, 135.4, 134.2, 122.5, 120.5, 115.4, 71.2, 66.5, 29.0, 27.8, 15.2; IR (KBr pellets) ν 3412 (m), 3051 (w), 2974 (m), 2930 (w), 2870 (w), 1641 (s), 1602 (s), 1555 (m), 1532 (m), 1466 (s), 1450 (s), 1383 (s), 1350 (s), 1321 (m), 1205 (m), 1173 (m), 1146 (m), 1125 (m), 1108 (w), 1030 (w), 994 (w), 962 (w), 901 (m), 845 (w), 803 (w), 752 (m), 735 (m), 706 (w), 656 (w), 624 (w), 587 (w), 556 (w), 533 (w), 514 (w), 464 (w), 407 (w); HRMS (ESI) calcd for C₂₂H₂₂CoN₂Na₂O₆⁺ (M+Na): 515.0600, found 515.0608; calcd for C₂₂H₂₂CoN₂O₆⁻ (M-Na): 469.0815, found 469.0821.

Procedure C:

[*N*-salicylidene-2-amino-isobutyrate]-[2-amino-isobutyrate]-cobalt (III) (**20**)



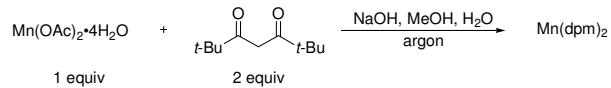
Co(OAc)₂·4H₂O (12.5 g, 50.2 mmol, 1.00 equiv) was added to a suspension of salicylaldehyde (**17**) (5.2 mL, 50 mmol, 1.0 equiv) and 2-aminoisobutyric acid (**18**) (5.1 g, 50 mmol, 1.0 equiv) in water (50 mL) at 23 °C under argon and the reaction mixture was heated to reflux. After refluxing for 2 h, a thick suspension was obtained. The reaction mixture was filtered, the solid washed with water (60 mL) and dried 12 h in high vacuo.

The isolated solid (1.0 g) was then suspended in water (12 mL) and ethanol (30 mL) under air and 2-aminoisobutyric acid (**18**) (0.32 g, 3.1 mmol) was added. The reaction mixture was stirred under air at 23 °C and slowly turned to a dark red solution. After 5 h, the dark red solution was filtered and the solvent was removed under reduced pressure. The residues were co-evaporated with CH₂Cl₂ (2x), dissolved in ethanol, filtered, the solvent was removed under reduced pressure and the isolated product was dried 6 h

in high vacuo at 80 °C. Further purification was achieved via column chromatography (CH₂Cl₂/MeOH, solvent gradient 1:0 to 10:1 to 1:1) to afford **20** (0.92 g, 2.3 mmol, 77%) as a dark red solid. The complex obtained by this procedure contained pure **20** (L = MeOH) as a mixture of isomers (2:1). It shows a slightly increased activity compared to the complex obtained following procedure A. ¹H NMR (CD₃OD, 300 MHz) δ 8.61 (s, 1H (33%), imine H 1. isomer), 8.30 (s, 1H (66%), imine H 2. isomer), 7.56-7.48 (m, 2H, Ar H), 7.29-7.19 (m, 2H, Ar H), 7.09 (d, *J* = 8.7 Hz, 2H, Ar H), 6.70-6.62 (m, 2H, Ar H), 1.84 (s, 3H (33%), CH₃ 1.isomer), 1.82 (s, 3H (33%), CH₃ 1.isomer), 1.79 (s, 3H (66%), CH₃ 2. isomer), 1.70 (s, 3H (33%), CH₃ 1.isomer), 1.67 (s, 3H (66%), CH₃ 2. isomer), 1.62 (s, 3H (33%), CH₃ 1.isomer), 1.32 (s, 3H (66%), CH₃ 2. isomer), 1.26 (s, 3H (66%), CH₃ 2. isomer); ¹³C NMR (DMSO-d₆, 75 MHz) δ 185.5, 184.3, 183.8, 183.2, 166.3, 165.8, 163.8, 163.5, 157.6, 134.7, 134.6, 133.6, 121.9, 121.7, 118.6, 118.2, 114.4, 114.0, 69.6, 69.4, 60.3, 58.2, 29.0, 28.3, 28.2, 27.9, 27.1, 26.6; IR (KBr pellets) v 3410 (m), 3242 (m), 3130 (m), 2978 (m), 1661 (s, sh), 1644 (s), 1600 (s), 1546 (s, sh), 1467 (m), 1450 (s), 1387 (s), 1345 (s), 1310 (m), 1205 (m), 1174 (m), 1147 (m), 1128 (w), 1032 (w), 995 (w), 901 (m), 847 (w), 807 (w), 756 (m), 705 (w), 661 (w), 626 (w), 588 (w), 552 (w), 530 (w), 468 (w), 419 (w); HRMS (MALDI) calcd for C₁₅H₂₀CoN₂O₅⁺ (M+H): 367.0704, found 367.0695; calcd for C₁₅H₁₉CoN₂O₅Na⁺ (M+Na): 389.0524, found 389.0516.

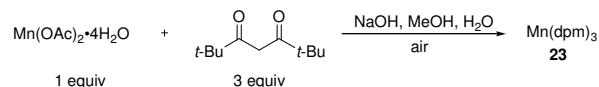
Tris-[dipivaloylmethanato]manganese(III) (23) ($Mn(dpm)_3$)

Procedure A: (“Bis-[dipivaloylmethanato]manganese(II)”)



Following a slightly modified literature procedure,² 2,2,4,4-tetramethylhept-3,5-dione (0.96 mL, 4.6 mmol, 2.0 equiv, freshly distilled) was added to a solution of manganese(II)diacetate tetrahydrate (0.56 g, 2.3 mmol, 1.0 equiv) in methanol (4.5 mL, distilled, degassed (two freeze-thaw cycles)) under argon and the resulting yellow solution was stirred at 23 °C with argon bubbling for 5 min. A solution of sodium hydroxide (0.18 g, 4.6 mmol, 2.0 eq) in water (1.2 mL, deionized, degassed (20 min argon bubbling)) was then added, whereas a yellow solid immediately precipitated. The solid was filtered under argon, washed with methanol/water 2:1 (20 mL) and dried 15 h in high vacuo over P₂O₅, whereas a color change to olive green was observed, which shows a partial conversion to Mn(dpm)₃ (**23**). The obtained olive green Mn(dpm)₂ (0.69 g, 1.6 mmol, 70%) was used without further purification

Procedure B:

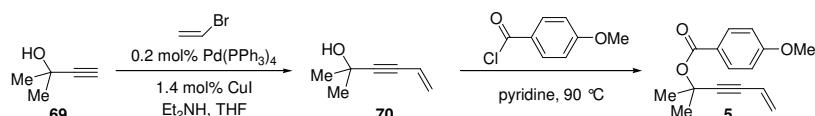


2,2,4,4-Tetramethylhept-3,5-dione (1.3 mL, 6.1 mmol, 3.0 equiv) was added to a solution of manganese(II)diacetate tetrahydrate (0.50 g, 2.0 mmol, 1.0 equiv) in methanol (4.5 mL) under air and the resulting yellow-green solution was stirred at 23 °C. A solution of sodium hydroxide (0.25 g, 6.1 mmol, 3.0 eq) in water (1.2 mL, deionized) was then added, whereas a green solid immediately precipitated. After diluting with methanol (5.5 mL), the reaction mixture was stirred at 23 °C under air for 13 h and filtered. The green-brown solid was dried in high vacuo at 60° C for 4 h, dissolved in hot isopropanol (15 mL), Mn(dpm)₃ (**23**) precipitated partially upon cooling, the precipitation was completed by adding water (3 mL) and the suspension was filtered. The resulting solid was suspended in pentane (10 mL) and the resulting suspension was filtered, removing some brown-red impurities. The pentane was removed under reduced pressure and the resulting olive green solid was dried under high vacuo for 12 h to give Mn(dpm)₃ (**23**) as a green powder (0.76 g, 1.2 mmol, 62 % yield).

The complexes synthesized following either procedure **A** or **B** showed similar activities for the hydrohydrazination reaction. The complexe obtains from **B** was characterized. Mp 164–165 °C; IR ν 2964 (s), 2867 (m), 1593 (s), 1572 (s), 1496 (s), 1402 (s), 1358 (s), 1284 (m), 1246 (m), 1222 (s), 1176 (m), 1134 (s), 1023 (w), 958 (w), 936 (w), 871 (s), 792 (m), 760 (w), 740 (w), 641 (m); HRMS (MALDI) calcd for $Mn(dpm)_2^+$: 421.2145, found 421.2156; Anal. calcd for $C_{33}H_{57}MnO_6$: C, 65.54; H, 9.50. Found: C, 65.62; H, 9.49.

2.2. Synthesis of Alkene Substrates

2-Methyl-hex-5-en-3-yn-2-ol (70) and 4-Methoxy-benzoic acid 1,1-dimethyl-pent-4-en-2-ynyl ester (5)



2-Methyl-hex-5-en-3-vn-2-ol (70)⁵

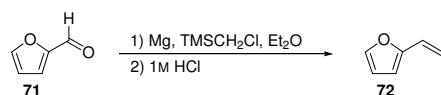
Following a reported procedure,⁶ CuI (0.14 g, 0.72 mmol, 0.014 equiv) and Pd(PPh₃)₄ (0.14 g, 0.12 mmol, 0.0023 equiv) were dissolved in diethylamine (freshly distilled over KOH, 25 mL) at 10 °C under argon. 2-Methyl-3-in-2-ol (**69**) (freshly distilled, 5.0 mL, 52 mmol, 1.0 equiv) and vinyl bromide (1 M in THF, 65 mL, 65 mmol, 1.3 equiv) were added dropwise and the resulting suspension stirred at 23 °C for 2.5 h. The reaction mixture was then poured into water (100 mL) at 0 °C and extracted with Et₂O

(3x125 mL), the combined organic layers were washed with 2 M HCl (2x50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was distilled ($p = 20$ mbar, $bp = 58^\circ\text{C}$) to afford **70** (4.84 g, 43.5 mmol, 84%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 5.81 (dd, $J = 17.4, 10.9$ Hz, 1H, alkene H), 5.62 (dd, $J = 17.7, 2.5$ Hz, 1H, alkene H), 5.46 (dd, $J = 10.9, 2.5$ Hz, 1H, alkene H), 1.97 (bs, OH), 1.54 (s, 6H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 126.8, 116.6, 94.4, 80.7, 65.4, 31.3; IR ν 3350 (s), 3101 (w), 3011 (w), 2982 (s), 2933 (w), 2871 (w), 1844 (w), 1609 (w), 1455 (w), 1411 (m), 1376 (m), 1363 (m), 1240 (s), 1165 (s), 995 (w), 973 (m), 944 (s), 846 (m), 678 (w), 551 (w).

4-Methoxy-benzoic acid 1,1-dimethyl-pent-4-en-2-ynyl ester (**5**)

2-Methyl-hex-5-en-3-yn-2-ol (**70**) (2.24 g, 20.2 mmol, 1.00 equiv) was dissolved in pyridine (distilled, 10 mL) at 23°C under argon. The reaction mixture was cooled to 0°C and anisoyl chloride (3.5 mL, 26 mmol, 1.3 equiv) was added dropwise. The resulting suspension was heated to 90°C for 14 h, cooled to 0°C and quenched with water (10 mL). The mixture was diluted with water (30 mL) and extracted with Et_2O (3x30 mL). The combined organic layers were washed with 2 M HCl (3x50 mL), sat. NaHCO_3 (3x30 mL), brine (2x30 mL), dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography (AcOEt/hexane 1:13) to afford **5** (4.40 g, 17.9 mmol, 89%) as a colorless oil. Enyne **5** polymerised slowly when kept in the air at 23°C , but is stable for months when kept at -20°C under argon. ^1H NMR (CDCl_3 , 300 MHz) δ 7.97 (dd, $J = 7.2, 1.9$ Hz, 2H, Ar H), 6.90 (dd, $J = 7.2, 1.9$ Hz, 2H, Ar H), 5.82 (dd, $J = 17.7, 10.9$ Hz, 1H, alkene H), 5.64 (dd, $J = 17.7, 2.2$ Hz, 1H, alkene H), 5.46 (dd, $J = 10.9, 2.2$ Hz, 1H, alkene H), 3.85 (s, 3H, OCH_3), 1.81 (s, 6H, $(\text{CH}_3)_2\text{COC}$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.4, 163.0, 131.5, 127.1, 123.3, 116.7, 113.4, 90.9, 82.7, 72.5, 55.4, 29.2; IR ν 2987 (m), 2938 (m), 2840 (w), 2044 (w), 1922 (w), 1849 (w), 1719 (s), 1606 (s), 1511 (s), 1465 (m), 1420 (w), 1364 (m), 1316 (m), 1283 (s), 1257 (s), 1170 (s), 1141 (s), 1097 (s), 1030 (m), 921 (m), 848 (m), 770 (s), 697 (m); HRMS(EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3^+$ (M) 244.1099, found 244.1090; Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 73.83; H, 6.79.

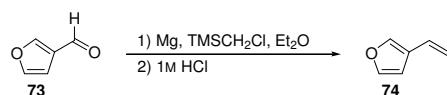
2-Vinyl-furan (**72**)⁷



Following a slightly modified reported procedure,^{7a} Mg (powder, 2.0 g, 82 mmol, 1.5 equiv) was suspended in dry Et_2O (5 mL) at 23°C under argon and TMSCH_2Cl (9.7 mL, 69 mmol, 1.2 equiv) was added dropwise diluted with Et_2O (40 mL) over 30 min. The reaction mixture was heated to reflux (45°C) and dibromoethane (0.10 mL) was added. After 2 h and 11 h, further portions of dibromoethane were added (2x0.10 mL). After a total refluxing time of 18 h, the *Grignard* reaction was finished and the reaction mixture was cooled to 0°C . A solution of furfuraldehyde (**71**) (5.0 mL, 60 mmol, 1.0 equiv) in Et_2O (60 mL) was added over 1 h. After stirring 4 h at 0°C and 14 h at 23°C , the reaction mixture was quenched with sat. NH_4Cl (40 mL) at 0°C , the layers were separated and the water layer extracted with Et_2O (2x50 mL). The combined organic layers were washed with sat. NaHCO_3 (2x30 mL) and brine (30 mL), dried over Na_2SO_4 and the solvent was removed ($p = 100$ mbar, $T = 40^\circ\text{C}$).

The residues were dissolved in Et_2O (20 mL) and the reaction mixture was mixed vigorously together with aqueous 1 M HCl (20 mL) for 75 min until no alcohol was present by TLC (AcOEt/hexane 1:5). The layers were separated, the water layer extracted with Et_2O (2x20 mL), the combined organic layers were washed with sat. NaHCO_3 (20 mL) and brine (20 mL) and dried over Na_2SO_4 . After filtration, 4-*tert*-butyl catechol was added (0.10 g) and the solvent was removed ($p = 700$ mbar, $T = 40^\circ\text{C}$) under nitrogen. Destillation of the crude product ($p = 170$ mbar, $bp = 50\text{--}55^\circ\text{C}$) under nitrogen affords 2-vinylfuran (**72**) in two fractions (1. fraction: 2.2 g, 46% **72**, 2. fraction 4.4 g, 55% **72**, total **72**: 3.4 g, 37 mmol, 61%) as a mixture with TMSOH and Et_2O . This mixture was kept at -20°C protected from light over 4-*tert*-butyl catechol and was used directly as such in the hydrohydrazination reaction. ^1H NMR (CDCl_3 , 300 MHz) δ 7.35 (d, $J = 1.8$ Hz, 1H, furan H), 6.51 (dd, $J = 17.5, 11.3$ Hz, 1H, vinyl H), 6.37 (dd, $J = 3.3, 1.8$ Hz, 1H, furan H), 6.26 (d, $J = 3.3$ Hz, 1H, furan H), 5.66 (dd, $J = 17.5, 1.3$ Hz, 1H, vinyl H), 5.16 (dd, $J = 11.3, 1.3$ Hz, 1H, vinyl H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 153.1, 141.8, 124.9, 112.1, 111.1, 107.9.

3-Vinyl-furan (**74**)^{7c}

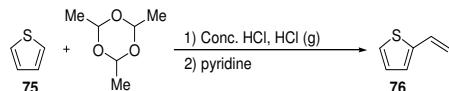


Following a slightly modified reported procedure,^{7a} Mg (powder, 0.38 g, 16 mmol, 1.5 equiv) was suspended in dry Et_2O (1 mL) at 23°C under argon and TMSCH_2Cl (1.7 mL, 12 mmol, 1.1 equiv) was added dropwise diluted with Et_2O (7 mL) over 30 min. The reaction mixture was heated to reflux (45°C) and dibromoethane (50 μL) was added. After a total refluxing time of 19 h, the *Grignard* reaction was finished and the reaction mixture was cooled to 0°C . A solution of furan-3-carbaldehyde (**73**) (1.0 g, 11 mmol, 1.0 equiv) in Et_2O (12 mL) was added over 15 min. After stirring 4 h at 0°C and 14 h at 23°C , the reaction mixture was quenched with sat. NH_4Cl (8 mL) at 0°C , the layers were separated and the water layer extracted with Et_2O (2x10 mL). The combined organic layers were washed with sat. NaHCO_3 (2x10 mL) and brine (10 mL), dried over Na_2SO_4 and the solvent was removed ($p = 100$ mbar, $T = 40^\circ\text{C}$).

The residues were dissolved in Et_2O (4 mL) and the reaction mixture was mixed vigorously together with aqueous 1 M HCl (4 mL) for 60 min until no alcohol was present by TLC (AcOEt: hexane 1:5). The layers were separated, the water layer extracted with Et_2O (2x4 mL), the combined organic layers were washed with sat. NaHCO_3 (5 mL) and brine (5 mL) and dried over Na_2SO_4 . After filtration, 4-*tert*-butyl catechol was added (0.05 g) and the solvent was removed ($p = 700$ mbar, $T = 40^\circ\text{C}$) under

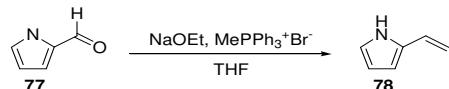
nitrogen. Distillation of the crude product ($p = 150$ mbar, $bp = 40\text{--}45$ °C) under nitrogen gives 3-vinylfuran (**74**) (0.50 g, 41% **74**, total **74**: 0.21 g, 2.2 mmol, 21%) as a mixture with TMSOH and Et₂O. This mixture was kept at -20 °C protected from light over 4-*tert*-butyl catechol and was used directly as such in the hydrohydrazination reaction. ¹H NMR (CDCl₃, 300 MHz) δ 7.42 (s, 1H, furan H), 7.37 (m, 1H, furan H), 6.57 (dd, $J = 17.4, 10.9$ Hz, 1H, vinyl H), 6.56 (d, $J = 0.9$ Hz, 1H, furan H), 5.46 (dd, $J = 17.4, 0.9$ Hz, 1H, vinyl H), 5.14 (dd, $J = 10.9, 1.3$ Hz, 1H, vinyl H); ¹³C NMR (CDCl₃, 75 MHz) δ 143.3, 140.4, 126.4, 124.7, 113.2, 107.1.

2-Vinyl-thiophene (**76**)⁸



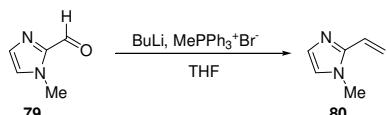
Following a slightly modified reported procedure,^{8a} concentrated HCl (37%, 15 mL) was added at 0 °C under argon to a mixture of thiophene (**75**) (16 mL, 0.20 mol, 1.0 equiv) and paraldehyde (8.9 mL, 67 mmol, 0.33 equiv). Gaseous HCl was bubbled through the reaction mixture at 10 °C for 1 h. The reaction mixture was then poured into crushed ice (15 g), Et₂O (15 mL) was added, the layers were separated, the water layer was extracted with Et₂O (2x15 mL), the organic layers were washed rapidly with ice water (3x10 mL) and dried over Na₂SO₄. After filtration, Et₂O was removed at 50 °C under argon and the residues were poured onto a mixture of pyridine (distilled, 16 mL, 0.20 mol, 1.0 equiv) and α-nitroso-β-naphthol (0.2 g, 1 mmol, 0.005 equiv). After stirring 90 min at 23 °C, the reaction mixture was slowly heated to 100 °C and the pressure lowered to 70 mbar, whereas crude **76** distilled to a flask cooled to 0 °C containing few α-nitroso-β-naphthol. When the distillation was nearly finished, the temperature was increased to 125 °C. Crude **76** was poured onto crushed ice (20 g) and concentrated HCl (37%, 20 mL), the mixture was extracted with Et₂O (3x50 mL), the combined organic layers were washed with 1% HCl (2x20 mL) and 2% NH₃ (2x20 mL) and dried over Na₂SO₄. After filtration, the solvent was removed under nitrogen ($p = 700$ mbar, $T = 40$ °C) and the residues were distilled over α-nitroso-β-naphthol under nitrogen ($p = 70$ mbar, $bp = 60\text{--}66$ °C) to afford **76** with 90% purity (6.1 g, 50 mmol, 25%) contaminated with few paraldehyde. This mixture was kept at -20 °C protected from light over α-nitroso-β-naphthol and was used directly as such in the hydrohydrazination reaction. ¹H NMR (CDCl₃, 300 MHz)^{8b} δ 7.21 (m, 1H, thiophene H), 7.02 (m, 2H, thiophene H), 6.87 (ddd, $J = 17.6, 11.0, 0.8$ Hz, 1H, vinyl H), 5.63 (d, $J = 17.3$ Hz, 1H, vinyl H), 5.19 (d, $J = 11.3$ Hz, 1H, vinyl H); ¹³C NMR (CDCl₃, 75 MHz) δ 142.8, 129.7, 127.1, 125.6, 124.1, 113.1.

2-Vinyl-pyrrole (**78**)⁹



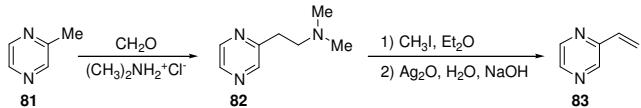
Following a slightly modified reported procedure,⁹ methyltriphenylphosphonium bromide (9.0 g, 25 mmol, 1.0 equiv) was added to a suspension of NaOEt (1.8 g, 26 mmol, 1.1 equiv) in THF (20 mL) at 23 °C under argon. After 2.5 h, pyrrole-2-carbaldehyde (**77**) (2.4 g, 25 mmol, 1.0 equiv) was added dropwise as a solution in THF (10 mL) over 15 min. The yellow suspension was refluxed for 16 h, cooled to 23 °C, filtered and the solvents were removed under reduced pressure. The residues were suspended in CH₂Cl₂ and filtered. The solution was washed with 20% NaHSO₃ (25 mL) and 10% Na₂CO₃ (25 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure under nitrogen. Distillation of the crude product over 4-*tert*-butyl catechol ($p = 0.5$ mbar, $bp = 30\text{--}35$ °C) affords **78** (0.62 g, 6.7 mmol, 27%) as a colorless oil. Compound **78** was kept at -20 °C protected from light over 4-*tert*-butyl catechol. ¹H NMR (CDCl₃, 300 MHz) δ 8.26 (br s, 1H, NH), 6.79 (d, $J = 1.2$ Hz, 1H, pyrrole H), 6.64 (ddm, $J = 17.7, 11.2$, 1H, vinyl H), 6.35-6.28 (m, 2H, pyrrole H), 5.34 (dm, $J = 17.7$ Hz, 1H, vinyl H), 5.09 (dm, $J = 11.2$ Hz, 1H, vinyl H); ¹³C NMR (CDCl₃, 75 MHz) δ 130.6, 126.9, 118.7, 109.2, 108.2, 107.9; IR ν 3400 (s), 3090 (w), 3007 (w), 2980 (w), 1634 (s), 1545 (w), 1459 (w), 1419 (w), 1390 (w), 1356 (w), 1298 (w), 1278 (w), 1231 (w), 1120 (m), 1092 (m), 1035 (m), 1020 (m), 984 (m), 948 (w), 883 (s), 803 (m), 731 (s), 649 (w), 589 (w), 539 (w).

1-Methyl-2-vinyl-1*H*-imidazole (**80**)¹⁰



Following a reported procedure,¹⁰ BuLi (1.6 M in hexane, 4.4 mL, 7.0 mmol, 1.1 equiv) was added to a suspension of methyltriphenylphosphonium bromide (2.3 g, 6.4 mmol, 1.0 equiv) in THF (15 mL) at 0 °C under argon. The reaction mixture was warmed to 23 °C and stirred for 40 min. A solution of **79** (0.71 g, 6.4 mmol, 1.0 equiv) in THF (15 mL) was added dropwise, followed by THF (5 mL). After stirring at 23 °C for 22 h, the mixture was filtered, the filter cake was washed with Et₂O and the solvent was removed. The crude product was purified by column chromatography (acetone:CH₂Cl₂ 7:1) followed by distillation to give **80** (0.30 g, 2.8 mmol, 44%) as a colorless liquid. ¹H NMR (CDCl₃, 300 MHz) δ 7.02 (s, 1H, imidazole H), 6.83 (s, 1H, imidazole H), 6.59 (dd, $J = 17.3, 11.2$, 1H, vinyl H), 6.14 (dd, $J = 17.3, 1.5$ Hz, 1H, vinyl H), 5.40 (dd, $J = 11.2, 1.5$ Hz, 1H, vinyl H), 3.65 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 145.2, 128.3, 122.5, 121.3, 117.8, 32.8;

2-Vinyl-pyrazine (**83**)¹¹



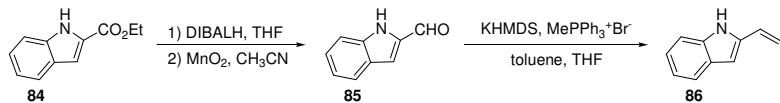
Dimethyl-(2-pyrazin-2-yl-ethyl)-amine (82)

Following a slightly modified reported procedure,¹¹ formaldehyde (37%, 7.2 mL, 96 mmol, 1.7 equiv) was added dropwise over 30 min to a refluxing (135 °C) mixture of 2-methyl-pyrazine (81) (5.0 mL, 55 mmol, 1.0 equiv) and dimethylamine hydrochloride (4.7 g, 58 mmol, 1.1 equiv). After stirring 4 h at reflux, the reaction mixture was cooled to 23 °C, water (15 mL) was added and the pH was adjusted to >12 with NaOH pellets. The reaction mixture was extracted with CH₂Cl₂ (3x25 mL), the combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude mixture was purified by distillation (*p* = 0.5 mbar, *bp* = 55 °C) to give 82 (4.3 g, 29 mmol, 52%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.31–8.19 (m, 3 H, pyrazine H), 2.81–2.75 (m, 2H, CH₂), 2.55–2.48 (m, 2H, CH₂), 2.10 (s, 3H, CH₃), 2.09 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 155.6, 144.4, 143.5, 141.8, 58.4, 45.1, 33.4; IR ν 3054 (w), 2972 (m), 2943 (s), 2859 (m), 2818 (s), 2768 (s), 1578 (w), 1526 (w), 1463 (s), 1403 (s), 1374 (w), 1308 (w), 1266 (w), 1232 (w), 1155 (w), 1123 (m), 1098 (w), 1054 (s), 1016 (m), 920 (w), 879 (w), 837 (m), 778 (w), 656 (w).

2-Vinyl-pyrazine (83)

CH₃I (1.8 mL, 29 mmol, 1.1 equiv) was added dropwise to a solution of 82 (4.2 g, 28 mmol, 1.0 equiv) in Et₂O (28 mL), whereas the ammonium salt precipitated. After 18 h, water (20 mL) and Et₂O (20 mL) were added, the layers were separated and the organic layer was extracted with water (8 mL). The combined water layers were cooled to 0 °C and Ag₂O (13 g, 56 mmol, 2.0 equiv) was added. After 3 h, the reaction mixture was filtered over Celite, the Celite was washed with water (20 mL) and NaOH (1.2 g, 30 mmol, 1.1 equiv) was added. The solution was heated to reflux over 30 min and refluxed for 1 h. After the evolution of trimethyl amine was finished, the reaction mixture was cooled to 23 °C and extracted with CH₂Cl₂ (3x50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure under nitrogen. The crude product was purified by distillation under nitrogen over 4-*tert*-butyl catechol (*p* = 25 mbar, *bp* = 60 °C) to give 83 (1.7 g, 16 mmol, 58%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.45 (d, *J* = 1.2 Hz, 1H, pyrazine H), 8.37 (dd, *J* = 2.5, 1.2 Hz, 1H, pyrazine H), 8.29–8.27 (m, 1H, pyrazine H), 6.68 (ddm, *J* = 17.4, 10.9, 1H, vinyl H), 6.22 (dm, *J* = 17.4 Hz, 1H, vinyl H), 5.47 (dm, *J* = 10.9 Hz, 1H, vinyl H); ¹³C NMR (CDCl₃, 75 MHz) δ 150.7, 143.9, 143.0, 142.8, 133.2, 120.5; IR ν 3064(m), 3028 (w), 1874 (w), 1633 (w), 1567 (w), 1520 (m), 1476 (s), 1416 (s), 1382 (m), 1308 (m), 1231 (w), 1153 (s), 1059 (m), 1030 (s), 1013 (s), 989 (s), 936 (s), 854 (s), 770 (w), 733 (w), 661 (w), 636 (w), 562 (w).

2-Vinyl-1*H*-indole (86)



1*H*-Indole-2-carbaldehyde (85)

Following a reported procedure,¹² a solution of DIBALH (4.3 mL, 26 mmol, 2.4 equiv) in THF (60 mL) was added dropwise to a solution of indole ester 84 (2.0 g, 11 mmol, 1.0 equiv) in THF (70 mL) at -78 °C under argon. The solution was let to warm up to 23 °C over 14 h and sat. Na⁺/K⁺ tartrate solution (120 mL) was added at 0 °C over 30 min. After stirring for 6 h, AcOEt (100 mL) was added, the layers were separated, the water layer was extracted with AcOEt (2x100 mL), the combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure.

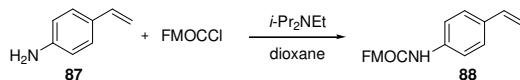
The residues were dissolved in CH₃CN (60 mL) and MnO₂ (5.0 g) was added under argon. After complete oxidation by TLC (AcOEt/hexane 1:2) (18 h), the reaction mixture was filtered over Celite, the Celite was washed with CH₃CN (30 mL) and the solvent was removed under reduced pressure. Recrystallization from AcOEt/hexane 1:4 gives aldehyde 85 (1.21 g, 8.37 mmol, 79%) as slightly brown crystals. Mp (AcOEt/hexane 1:4) 130–132 °C (Lit.:¹² 141–143 °C); ¹H NMR (CDCl₃, 300 MHz) δ 9.86 (s, 1H, aldehyde H), 9.44 (br s, 1H, NH), 7.75 (d, *J* = 8.1 Hz, 1H, indole H), 7.50–7.16 (m, 4H, indole H); ¹³C NMR (CDCl₃, 75 MHz) δ 182.2, 138.2, 135.8, 127.2, 127.1, 123.2, 121.0, 115.2, 112.6; IR (KBr) ν 3179 (m), 3057 (w), 2853 (w), 1683 (w), 1651 (m), 1620 (w), 1528 (m), 1448 (w), 1429 (w), 1363 (w), 1341 (s), 1254 (m), 1231 (m), 1128 (s), 1005 (w), 996 (w), 985 (w), 936 (w), 897 (w), 856 (w), 822 (s), 742 (s), 611 (w), 582 (m), 466 (m), 444 (m).

2-Vinyl-1*H*-indole (86)

A solution of KHMDS (1.2 g, 6.0 mmol, 1.3 equiv) in toluene (12 mL) was added to a suspension of methyltriphenylphosphonium bromide (2.5 g, 7.0 mmol, 1.5 equiv) in THF (34 mL) at 23 °C under argon. After 30 min, the reaction was transferred dropwise *via* canula under argon to a solution of aldehyde 85 (0.67 g, 4.6 mmol, 1 equiv) in THF (23 mL). After stirring at 23 °C for 3 h, the reaction mixture was poured onto Et₂O (50 mL) and water (50 mL), the layers were separated, the water layer was extracted with Et₂O (2x50 mL), the combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:20) to give 86 (0.60 g, 4.2 mmol, 90%) as a colorless solid. Mp 83–85 °C (Lit.:¹² 85–86 °C); ¹H NMR (CDCl₃, 300 MHz) δ 8.14 (br s, 1H, NH), 7.58 (d, *J* = 7.8 Hz, 1H, indole H), 7.34 (dd, *J* = 8.1, 0.9 Hz, 1H, indole H), 7.20 (ddd, *J* = 8.1, 7.2, 1.2 Hz, 1H, indole H), 7.10 (ddd, *J* = 8.1, 7.2, 1.3 Hz, 1H, indole H), 6.75 (dd, *J* = 17.7, 11.2 Hz, 1H, vinyl H), 6.52 (d, *J* = 2.2 Hz, 1H, indole H), 5.56 (d, *J* = 17.7 Hz, 1H, vinyl H), 5.27 (d, *J* = 11.2 Hz, 1H, vinyl H); ¹³C NMR (CDCl₃, 75 MHz) δ 136.4, 136.1, 128.5, 127.4,

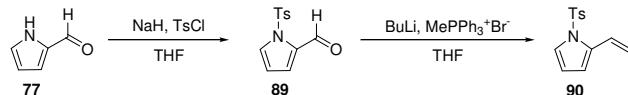
122.7, 120.6, 120.0, 112.0, 110.6, 103.0; IR ν 3405 (s), 3057 (w), 2922 (w), 1892 (w), 1782 (w), 1639 (w), 1612 (w), 1526 (w), 1454 (m), 1424 (m), 1400 (m), 1340 (m), 1292 (m), 1234 (w), 1154 (w), 1132 (w), 1037 (w), 1010 (w), 984 (m), 930 (w), 907 (s), 797 (s), 741 (s), 649 (w), 609 (w), 578 (w), 567 (w), 466 (w).

(4-Vinyl-phenyl)-carbamic acid 9,9a-dihydro-4*A*H-fluoren-9-ylmethyl ester (88)



Fluoranthenylmethoxycarbonyl chloride (1.2 g, 4.8 mmol, 1.2 equiv) and Hünig's base (0.84 mL, 4.8 mmol, 1.2 equiv) were added to a solution of 4-vinylpyridine (**87**) (90%, 0.53 g, 4.0 mmol, 1.0 equiv) in dioxane (8 mL) at 0 °C under argon. The reaction mixture was stirred at 0 °C for 30 min and warmed to 23 °C. After 2 h, CH_2Cl_2 (50 mL), sat. NH_4Cl (20 mL) and brine (20 mL) were added, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (2x40 mL). The combined organic layers were concentrated under reduced pressure and the isolated product was purified via precipitation with hexane from a solution in CH_2Cl_2 to afford **88** (1.28 g, 3.75 mmol, 94%) as a colorless solid. Mp 194–197 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.79 (d, J = 7.5 Hz, 2H, Ar H), 7.62 (d, J = 7.5 Hz, 2H, Ar H), 7.42 (t, J = 7.5 Hz, 2H, Ar H), 7.35–7.30 (m, 6H, Ar H), 6.67 (dd, J = 17.4, 10.9 Hz, 1H, vinyl H), 6.65 (br s, 1H, NH), 5.67 (dd, J = 17.7, 0.9, 1H, vinyl H), 5.19 (dd, J = 10.9, 0.6 Hz, 1H, vinyl H), 4.55 (d, J = 6.5 Hz, 2H, CH_2O), 4.28 (t, J = 6.5 Hz, 1H, CHCH_2O); ^{13}C NMR (CDCl_3 , 75 MHz) δ 153.2, 143.7, 141.4, 137.2, 136.0, 133.1, 127.8, 127.1, 126.9, 124.9, 120.0, 118.7, 112.8, 66.8, 47.1; IR ν 3308 (w), 2361 (w), 1698 (s), 1609 (w), 1586 (w), 1525 (s), 1450 (w), 1414 (w), 1404 (w), 1317 (w), 1236 (m), 1225 (m), 1089 (w), 1053 (w), 1013 (w), 987 (w), 905 (w), 836 (w), 759 (w), 737 (m), 668 (w); HRMS (MALDI) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{Na}^+$ ($\text{M}+\text{Na}$): 364.1308, found 364.1305; Anal. calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.74; H, 5.59; N, 4.05.

1-(Toluene-4-sulfonyl)-2-vinyl-1*H*-pyrrole (90)



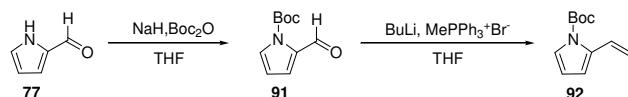
1-(Toluene-4-sulfonyl)-1*H*-pyrrole-2-carbaldehyde (89)¹³

Following a reported procedure,¹⁴ a solution of pyrrole-2-carbaldehyde (**77**) (1.0 g, 11 mmol, 1 equiv) in THF (10 mL) was added over 10 min to a suspension of NaH (0.30 g, 13 mmol, 1.2 equiv) in THF (60 mL) at 23 °C under argon. After 1 h, tosyl chloride (2.2 g, 12 mmol, 1.1 equiv) was added. After stirring for 13 h at 23 °C, the reaction mixture was quenched with sat. NH_4Cl (10 mL), diluted with water (200 mL) and extracted with Et_2O (3x100 mL). The combined organic layer were washed with brine (50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:10) to give **89** (2.5 g, 9.9 mmol, 94%) as a colorless solid. Mp 92–94 °C (Lit.:¹³ 94 °C); ^1H NMR (CDCl_3 , 300 MHz) δ 9.96 (s, 1H, aldehyde H), 7.79 (d, J = 8.4 Hz, 2H, phenyl H), 7.61 (m, 1H, pyrrole H), 7.31 (d, J = 8.1 Hz, 2H, phenyl H), 7.14 (m, 1H, pyrrole H), 6.40 (m, 1H, pyrrole H), 2.40 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 178.7, 145.8, 135.0, 133.3, 130.0, 129.3, 127.3, 124.3, 112.3, 21.7; IR ν 3126 (w), 3066 (w), 2895 (w), 2840 (w), 1672 (s), 1595 (w), 1538 (w), 1494 (w), 1448 (m), 1423 (s), 1409 (m), 1374 (s), 1332 (w), 1308 (w), 1296 (w), 1249 (m), 1234 (w), 1215 (w), 1192 (s), 1175 (s), 1158 (s), 1141 (s), 1090 (m), 1055 (m), 1013 (w), 880 (w), 842 (w), 814 (m), 775 (m), 757 (m), 702 (w), 670 (s), 634 (w), 587 (s), 563 (m), 539 (m), 489 (w), 449 (w), 424 (w).

1-(Toluene-4-sulfonyl)-2-vinyl-1*H*-pyrrole (90)¹⁵

Following a reported procedure,¹⁴ BuLi (1.6 M in hexane, 5.5 mL, 8.8 mmol, 1.1 equiv) was added to a suspension of methyltriphenylphosphonium bromide (3.4 g, 9.5 mmol, 1.2 equiv) in THF (70 mL) at 0 °C under argon. After stirring for 2 h, the reaction mixture was cooled to -78 °C and a solution of **89** (2.0 g, 8.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. The reaction was let to warm up to 23 °C over 12 h, quenched with water (150 mL) and extracted with Et_2O (3x100 mL). The combined organic layer were washed with water (50 mL) and brine (50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:15) to give **90** (1.8 g, 7.3 mmol, 91%) as a colorless solid. Mp 66–67 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.69 (d, J = 8.4 Hz, 2H, phenyl H), 7.31–7.28 (m, 1H, pyrrole H), 7.27 (d, J = 8.1 Hz, 2H, phenyl H), 7.10 (dd, J = 17.4, 11.2 Hz, 1H, vinyl H), 6.44 (m, 1H, pyrrole H), 6.24 (m, 1H, pyrrole H), 5.48 (dd, J = 17.4, 1.2 Hz, 1H, vinyl H), 5.15 (dd, J = 11.2, 1.5 Hz, 1H, vinyl H), 2.39 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 144.8, 135.8, 133.8, 129.7, 126.7, 125.3, 123.0, 114.9, 112.1, 111.6, 21.6; IR ν 3150 (w), 2926 (w), 1596 (w), 1494 (w), 1465 (w), 1421 (w), 1368 (s), 1309 (w), 1294 (w), 1244 (w), 1190 (s), 1179 (s), 1154 (s), 1129 (m), 1091 (m), 1060 (w), 1039 (w), 1018 (w), 1000 (w), 910 (w), 874 (w), 813 (m), 726 (m), 704 (m), 690 (m), 659 (m), 586 (s), 554 (w), 535 (w), 489 (w).

2-Vinyl-pyrrole-1-carboxylic acid *tert*-butyl ester (92)¹⁴



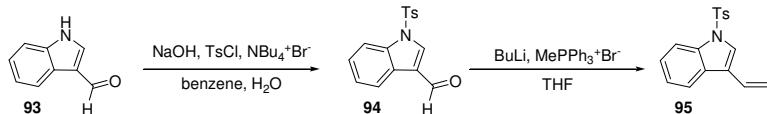
2-Formyl-pyrrole-1-carboxylic acid *tert*-butyl ester (91)¹⁴

Following a reported procedure,¹⁴ a solution of pyrrole-2-carbaldehyde (**77**) (1.0 g, 11 mmol, 1.0 equiv) in THF (10 mL) was added over 10 min to a suspension of NaH (0.30 g, 13 mmol, 1.2 equiv) in THF (60 mL) at 23 °C under argon. After 1 h, Boc anhydride (2.5 g, 12 mmol, 1.1 equiv) was added. After stirring for 13 h at 23 °C, the reaction mixture was quenched with sat. NH₄Cl (10 mL), diluted with water (200 mL) and extracted with Et₂O (3x100 mL). The combined organic layer were washed with brine (50 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:30) to give **91** (2.0 g, 10 mmol, 97%) as an oil. ¹H NMR (CDCl₃, 300 MHz) δ 10.29 (s, 1H, aldehyde H), 7.41 (m, 1H, pyrrole H), 7.14 (m, 1H, pyrrole H), 6.24 (m, 1H, pyrrole H), 1.61 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 182.0, 148.1, 134.5, 127.1, 120.9, 111.5, 85.7, 27.9. IR v 3150 (w), 2982 (m), 2936 (w), 2906 (w), 1749 (s), 1668 (s), 1544 (s), 1477 (w), 1442 (s), 1390 (m), 1372 (s), 1339 (s), 1300 (s), 1251 (s), 1166 (s), 1126 (s), 1066 (s), 1016 (w), 894 (m), 846 (s), 771 (m), 749 (s), 596 (w), 486 (w).

2-Vinyl-pyrrole-1-carboxylic acid *tert*-butyl ester (**92**)

Following a reported procedure,¹⁴ BuLi (1.6 M in hexane, 5.5 mL, 8.8 mmol, 1.1 equiv) was added to a suspension of methyltriphenylphosphonium bromide (3.4 g, 9.5 mmol, 1.2 equiv) in THF (70 mL) at 0 °C under argon. After stirring for 2 h, the reaction mixture was cooled to -78 °C and a solution of **91** (1.6 g, 8.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. The reaction was let to warm up to 23 °C over 12 h, quenched with water (150 mL) and extracted with Et₂O (3x100 mL). The combined organic layer were washed with water (50 mL) and brine (50 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:30) to give **92** (1.22 g, 6.33 mmol, 79%) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.25 (m, 1H, pyrrole H), 7.23 (dd, *J* = 17.4, 11.2 Hz, 1H, vinyl H), 6.43 (m, 1H, pyrrole H), 6.14 (m, 1H, pyrrole H), 5.53 (dd, *J* = 17.4, 1.6 Hz, 1H, vinyl H), 5.12 (dd, *J* = 11.2, 1.6 Hz, 1H, vinyl H), 1.61 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 149.2, 134.3, 127.9, 121.7, 113.1, 110.6, 110.6, 83.7, 28.0; IR v 3160 (w), 3093 (w), 2980 (m), 2935 (w), 2874 (w), 1743 (s), 1618 (w), 1557 (w), 1477 (m), 1458 (w), 1423 (m), 1396 (m), 1371 (s), 1336 (s), 1308 (s), 1286 (m), 1245 (m), 1168 (s), 1124 (s), 1066 (m), 1044 (w), 1013 (w), 985 (w), 902 (w), 884 (w), 851 (w), 813 (w), 772 (w), 729 (m), 701 (w), 672 (w), 595 (w), 480 (w), 460 (w).

1-(Toluene-4-sulfonyl)-2-vinyl-1*H*-indole (**95**)¹⁶



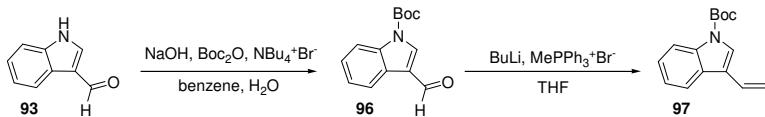
1-(Toluene-4-sulfonyl)-1*H*-indole-2-carbaldehyde (**94**)¹⁷

Following a reported procedure,¹⁸ aqueous 30% NaOH (25 mL), tosyl chloride (1.4 g, 7.2 mmol, 1.1 equiv) and tetrabutylammonium bromide (0.22 g, 0.69 mmol, 0.10 equiv) were added to a suspension of indole aldehyde **93** (1.0 g, 6.9 mmol, 1.0 equiv) in benzene (25 mL). After stirring vigorously for 30 min, the layers were separated and the water layer was extracted with benzene (10 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from CH₂Cl₂/hexane to afford aldehyde **94** (1.44 g, 4.82 mmol, 70%) as a colorless solid. Mp (CH₂Cl₂/hexane) 146-147 °C (Lit.:¹⁸ 147-149 °C); ¹H NMR (CDCl₃, 300 MHz) δ 10.09 (s, 1H, aldehyde H), 8.25 (dm, *J* = 7.2 Hz, 1H, indole H), 8.23 (s, 1H, indole H), 7.95 (d, *J* = 8.4 Hz, 1H, indole H), 7.85 (d, *J* = 8.4 Hz, 2H, phenyl H), 7.44-7.31 (m, 2H, indole H), 7.30 (d, *J* = 8.1 Hz, 2H, phenyl H), 2.38 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 185.1, 146.0, 136.1, 135.0, 134.1, 130.1, 127.1, 126.1, 124.9, 122.4, 122.2, 113.1, 21.7; IR v 3128 (w), 3064 (w), 2922 (w), 2824 (w), 2740 (w), 1920 (w), 1807 (w), 1679 (s), 1596 (w), 1542 (m), 1493 (w), 1480 (w), 1446 (s), 1380 (s), 1334 (w), 1307 (w), 1293 (w), 1277 (m), 1233 (m), 1214 (w), 1190 (s), 1178 (s), 1142 (m), 1127 (s), 1100 (s), 1085 (m), 1039 (w), 1018 (w), 971 (s), 911 (w), 813 (w), 781 (m), 749 (s), 710 (m), 662 (s), 589 (s), 572 (s), 537 (m), 515 (w).

1-(Toluene-4-sulfonyl)-2-vinyl-1*H*-indole (**95**)

Following a reported procedure,¹⁴ BuLi (1.6 M in hexane, 2.7 mL, 4.3 mmol, 1.1 equiv) was added to a suspension of methyltriphenylphosphonium bromide (1.7 g, 4.8 mmol, 1.2 equiv) in THF (40 mL) at 0 °C under argon. After stirring for 2 h, the reaction mixture was cooled to -78 °C and a solution of **94** (1.2 g, 3.9 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. The reaction was let to warm up to 23 °C over 12 h, quenched with water (60 mL) and extracted with Et₂O (3x60 mL). The combined organic layer were washed with water (30 mL) and brine (30 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:20) to give **95** (0.98 g, 3.3 mmol, 85%) as a colorless solid. Mp 93-94 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.01 (dm, *J* = 8.1 Hz, 1H, indole H), 7.82-7.73 (m, 1H, indole H), 7.78 (d, *J* = 8.7 Hz, 2H, phenyl H), 7.62 (s, 1H, indole H), 7.37-7.24 (m, 2H, indole H), 7.20 (d, *J* = 7.8 Hz, 2H, phenyl H), 6.77 (ddm, *J* = 17.7, 11.2 Hz, 1H, vinyl H), 5.80 (dm, *J* = 18.0 Hz, 1H, vinyl H), 5.35 (dm, *J* = 11.2 Hz, 1H, vinyl H), 2.31 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 144.9, 135.3, 134.9, 129.7, 129.6, 128.8, 127.7, 127.4, 126.7, 124.8, 123.9, 123.4, 120.8, 115.2, 113.6, 21.6; IR v 3126 (w), 3066 (w), 2961 (w), 2925 (w), 1917 (w), 1637 (w), 1597 (w), 1542 (w), 1494 (w), 1447 (m), 1416 (w), 1400 (w), 1373 (s), 1306 (w), 1293 (w), 1268 (m), 1217 (m), 1188 (s), 1176 (s), 1146 (w), 1124 (s), 1089 (m), 1042 (w), 1020 (w), 989 (w), 962 (m), 939 (w), 907 (w), 812 (m), 766 (m), 747 (m), 703 (w), 668 (s), 625 (w), 594 (m), 575 (s), 536 (m), 510 (w), 487 (w).

2-Vinyl-indole-1-carboxylic acid *tert*-butyl ester (**97**)¹⁹



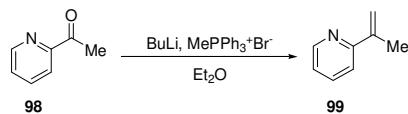
2-Formyl-indole-1-carboxylic acid *tert*-butyl ester (96)²⁰

Following a reported procedure,¹⁸ aqueous 30% NaOH (25 mL), Boc anhydride (1.6 g, 7.2 mmol, 1.1 equiv) and tetrabutylammonium bromide (0.22 g, 0.69 mmol, 0.10 equiv) were added to a suspension of indole aldehyde **93** (1.0 g, 6.9 mmol, 1.0 equiv) in benzene (25 mL). After stirring vigorously for 30 min, the layers were separated and the water layer was extracted with benzene (10 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from AcOEt/hexane to afford aldehyde **96** (1.05 g, 4.28 mmol, 62%) as a colorless solid. Mp (AcOEt/hexane) 124-126 °C (Lit.:¹⁸ 123-125 °C); ¹H NMR (CDCl₃, 300 MHz) δ 10.10 (s, 1H, aldehyde H), 8.29 (m, 1H, indole H), 8.24 (s, 1H, indole H), 8.15 (d, *J* = 7.8 Hz, 1H, indole H), 7.45-7.34 (m, 2H, indole H), 1.71 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 185.4, 148.5, 136.3, 135.7, 125.8, 124.3, 121.8, 121.3, 114.9, 85.5, 28.0; IR ν 3144 (w), 3077 (w), 3054 (w), 3002 (w), 2979 (m), 2939 (w), 2816 (m), 2763 (w), 2740 (w), 1967 (w), 1928 (w), 1829 (w), 1806 (w), 1746 (s), 1681 (s), 1609 (w), 1558 (m), 1481 (m), 1452 (m), 1434 (w), 1398 (s), 1369 (s), 1332 (m), 1310 (m), 1276 (m), 1259 (s), 1243 (s), 1155 (s), 1134 (s), 1101 (s), 1046 (w), 1017 (w), 946 (w), 909 (m), 840 (s), 786 (m), 761 (s), 750 (s), 668 (w), 649 (w), 596 (w), 518 (w).

2-Vinyl-indole-1-carboxylic acid *tert*-butyl ester (97)

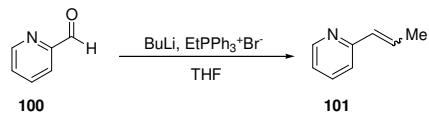
Following a reported procedure,¹⁴ BuLi (1.6 M in hexane, 2.6 mL, 4.2 mmol, 1.1 equiv) was added to a suspension of methyltriphenylphosphonium bromide (1.6 g, 4.5 mmol, 1.2 equiv) in THF (40 mL) at 0 °C under argon. After stirring for 2 h, the reaction mixture was cooled to -78 °C and a solution of **96** (0.90 g, 3.7 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. The reaction was let to warm up to 23 °C over 12 h, quenched with water (60 mL) and extracted with Et₂O (3x60 mL). The combined organic layer were washed with water (30 mL) and brine (30 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:30) to give **97** (0.72 g, 3.0 mmol, 80%) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.21 (d, *J* = 7.9 Hz, 1H, indole H), 7.81 (d, *J* = 7.6 Hz, 1H, indole H), 7.65 (s, 1H, indole H), 7.39-7.25 (m, 2H, indole H), 6.83 (dd, *J* = 17.8, 11.3 Hz, 1H, vinyl H), 5.84 (d, *J* = 17.8 Hz, 1H, vinyl H), 5.35 (d, *J* = 11.3 Hz, 1H, vinyl H), 1.70 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 149.4, 135.8, 128.5, 128.0, 124.4, 123.8, 122.8, 119.8, 119.1, 115.2, 114.2, 83.7, 28.2; IR ν 3139 (w), 3083 (w), 3053 (w), 2979 (m), 2933 (w), 1732 (s), 1637 (m), 1607 (w), 1558 (w), 1550 (w), 1477 (m), 1453 (s), 1418 (m), 1371 (s), 1326 (m), 1308 (s), 1255 (s), 1235 (s), 1225 (s), 1158 (s), 1100 (s), 1079 (m), 1049 (m), 1034 (w), 1024 (m), 988 (m), 935 (w), 898 (w), 857 (m), 836 (w), 814 (w), 765 (m), 746 (s), 706 (w), 686 (w), 639 (w), 590 (w), 569 (w), 534 (w), 512 (w), 471 (w), 441 (w).

2-Isopropenyl-pyridine (99)²¹



Following a reported procedure,²² BuLi (1.6 M in hexane, 10 mL, 16 mmol, 1.0 equiv) was added to a suspension of methyltriphenylphosphonium bromide (5.7 g, 16 mmol, 1.0 equiv) in Et₂O (20 mL) at 0 °C under argon. The reaction mixture was warmed to 23 °C and stirred for 40 min. A solution of **98** (2.0 g, 16 mmol, 1.0 equiv) in Et₂O (15 mL) was added dropwise, followed by Et₂O (15 mL). After stirring at reflux for 2 h, the mixture was quenched with water (100 mL) and extracted with Et₂O (2x150 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:1) to give pyridine **99** (0.35 g, 2.9 mmol, 18%) as an oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.59 (dq, *J* = 4.8, 0.9 Hz, 1H, pyridine H), 7.65 (ddd, *J* = 8.0, 7.5, 1.9 Hz, 1H, pyridine H), 7.49 (dt, *J* = 8.0, 1.1 Hz, 1H, pyridine H), 7.17 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H, pyridine H), 5.85 (sextet, *J* = 0.8 Hz, 1H, vinyl H), 5.30, (qi, *J* = 1.6 Hz, 1H, vinyl H), 2.22 (dd, *J* = 1.5, 0.8 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 158.0, 148.7, 143.0, 136.0, 121.9, 120.0, 115.5, 20.5.

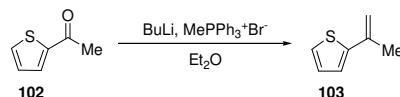
2-Propenyl-pyridine (101)²³



Following a reported procedure,²³ BuLi (1.6 M in hexane, 12 mL, 19 mmol, 1.0 equiv) was added to a suspension of ethyltriphenylphosphonium bromide (7.3 g, 20 mmol, 1.1 equiv) in THF (35 mL) at 23 °C under argon. After 30 min, a solution of **100** (2.0 g, 19 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. After stirring at 23 °C for 66 h, the mixture was quenched with water (100 mL), THF was removed under reduced pressure and the reaction mixture was extracted with CH₂Cl₂ (3x75 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:1) to give pyridine **101** (1.13 g, 9.45 mmol, 50%, 2:1 *E/Z* mixture) as an oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.60 (d, *J* = 4.5 Hz, 1H (*Z*)), 8.51 (d, *J* = 4.5 Hz, 1H (*E*)), 7.66-7.56 (m, 1H, pyridine H (*E* and *Z*)), 7.32-7.20 (m, 1H, pyridine H (*E* and *Z*)), 7.11-7.06 (m, 1H, pyridine H (*E*)),

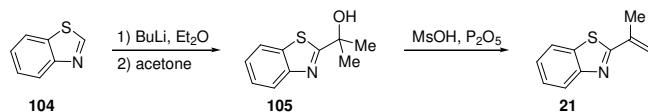
(*E* and *Z*)), 6.80-6.68 (m, 1H (66%), vinyl H (*E*)), 6.52-6.47 (m, 1H, vinyl H (*E* and *Z*)), 6.06-5.95 (m, 1H (33%), vinyl H (*Z*)), 2.09 (dd, *J* = 7.2, 1.3 Hz, 3H (33%), CH₃ (*Z*)), 1.93 (d, *J* = 6.6 Hz, 3H (66%), CH₃ (*E*)); ¹³C NMR (CDCl₃, 75 MHz) δ 156.5, 155.8, 149.1, 148.9, 136.0, 135.6, 131.1, 130.9, 130.4, 129.3, 123.6, 121.2, 120.8, 120.6, 18.3, 15.0.

2-Isopropenyl-thiophene (103)²⁴



Following a reported procedure,²² BuLi (1.6 M in hexane, 10 mL, 16 mmol, 1.0 equiv) was added to a suspension of methyltriphenylphosphonium bromide (5.7 g, 16 mmol, 1.0 equiv) in Et₂O (15 mL) at 0 °C under argon. The reaction mixture was warmed to 23 °C and stirred for 40 min. A solution of **102** (2.1 g, 16 mmol, 1.0 equiv) in Et₂O (20 mL) was added dropwise. After stirring at reflux for 2 h, the mixture was quenched with water (100 mL) and extracted with Et₂O (2x150 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/hexane 10:1) to give thiophene **103** (0.52 g, 4.2 mmol, 25%) as an oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.18 (d, *J* = 5.1 Hz, 1H, thiophene H), 7.05-6.97 (m, 2H, thiophene H), 5.40 (s, 1H, vinyl H), 4.97 (s, 1H, vinyl H), 2.17 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 146.0, 137.4, 127.5, 124.4, 123.8, 111.4, 22.0.

2-Isopropenyl-benzothiazole (21)²⁵



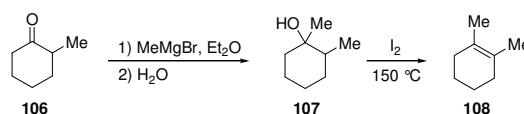
2-Benzothiazol-2-yl-propan-2-ol (105)²⁵

Following a reported procedure,²⁵ benzothiazole (**104**) (freshly distilled, 3.0 mL, 27 mmol, 1.0 equiv) was added dropwise over 20 min to a mixture of BuLi (1.6 M in hexane, 18 mL, 29 mmol, 1.1 equiv) and Et₂O (60 mL) at -78 °C under argon. After 25 min, a solution of acetone (2.2 mL, 30 mmol, 1.1 equiv) in Et₂O (10 mL) was added dropwise and the resulting suspension was stirred below -50 °C for 3 h. The reaction mixture was quenched with sat. NH₄Cl (5 mL) and heated to 23 °C. Sat. NH₄Cl (50 mL) and water (10 mL) were added and the layers were separated and the water layer was extracted with Et₂O (50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from hexane to afford alcohol **105** (4.8 g, 25 mmol, 92%) as slightly yellow crystals. ¹H NMR (CDCl₃, 300 MHz) δ 7.98 (dm, *J* = 8.1 Hz, 1H, Ar H), 7.88 (dm, *J* = 8.1 Hz, 1H, Ar H), 7.49-7.43 (m, 1H, Ar H), 7.39-7.33 (m, 1H, Ar H), 3.29 (br s, 1H, OH), 1.75 (s, 6H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 180.0, 152.8, 135.1, 125.8, 124.7, 122.7, 121.6, 73.5, 30.8; IR ν 3370 (m), 3064 (w), 2978 (m), 2932 (w), 1910 (w), 1788 (w), 1594 (w), 1560 (w), 1515 (m), 1456 (m), 1439 (s), 1363 (m), 1315 (m), 1277 (m), 1243 (s), 1181 (s), 1142 (m), 1091 (m), 1048 (s), 1015 (w), 961 (m), 871 (w), 825 (w), 759 (s), 730 (s), 698 (w), 656 (w), 621 (w), 540 (w), 460 (w).

2-Isopropenyl-benzothiazole (21)

Phosphorous pentoxide (2.0 g) was added to methanesulfonic acid (20 g) at 23 °C under argon and the resulting suspension was stirred for 12 h and became a clear solution. Alcohol **105** (1.54 g, 7.97 mmol, 1.00 equiv) was added and the reaction mixture was heated to 60 °C for 10 h. The reaction mixture was cooled to 23 °C and poured onto sat. NaHCO₃ (50 mL) at 0 °C. Solid NaHCO₃ was added until gas evolution stopped. The reaction mixture was extracted with CH₂Cl₂ (3x50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:20) to give benzothiazole **21** (1.17 g, 6.64 mmol, 83%) as a low melting solid. Mp 25-30 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.02 (dm, *J* = 8.1 Hz, 1H, Ar H), 7.84 (dm, *J* = 8.1 Hz, 1H, Ar H), 7.49-7.33 (m, 2H, Ar H), 5.96 (s, 1H, alkene H), 5.52 (m, 1H, alkene H), 2.34 (m, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 169.2, 153.6, 138.9, 134.6, 125.9, 125.2, 123.1, 121.3, 119.7, 20.4; IR ν 3062 (w), 2979 (w), 2959 (w), 2922 (w), 1816 (w), 1629 (w), 1592 (w), 1557 (w), 1494 (s), 1456 (m), 1435 (m), 1375 (w), 1317 (m), 1298 (w), 1274 (w), 1244 (w), 1160 (w), 1124 (w), 1088 (m), 1050 (m), 1016 (w), 995 (w), 903 (m), 860 (w), 758 (s), 728 (s), 697 (w), 626 (w), 603 (w), 550 (w), 502 (w).

1,2-Dimethyl-cyclohexene (108)²⁶



1,2-Dimethyl-cyclohexanol (107)

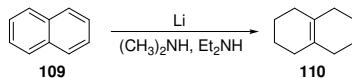
2-Methyl-cyclohexanone (**106**) (5.0 mL, 41 mmol, freshly distilled, 1.0 equiv) was diluted in Et₂O (9 mL, dry) at 0 °C under argon and a solution of methylmagnesium bromide (3 M in Et₂O, 16 mL, 48 mmol, 1.2 equiv) was added dropwise over 45 min. The reaction mixture was then allowed to warm to 23 °C over night, quenched with a crushed ice/water mixture and the pH was adjusted to 1 with concentrated HCl. The layers were separated and the organic layer was washed with sat. NaHSO₃ solution (2x10 mL), water (4x10 mL), brine (10 mL), dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure.

The crude product was purified by distillation ($p = 100$ mbar, $bp = 80$ °C) to afford **107** (4.4 g, 34 mmol, 83%, 1:1 mixture of diastereomers) as a slightly yellow liquid. ^1H NMR (CDCl_3 , 300 MHz)^{26b} δ 1.70-1.10 (m, 10H), 1.19 (s, 2.25H, COHCH_3 , major diastereoisomer), 1.10 (0.7 H, s, COHCH_3 , minor diastereoisomer), 0.93 (d, 0.75H, $J = 6.9$ Hz, CHCH_3 , minor diastereoisomer), 0.91 (d, $J = 6.2$ Hz, CHCH_3 , major diastereoisomer).

1,2-Dimethyl-cyclohexene (108)

1,2-Dimethyl-cyclohexanol (**107**) (4.1 g, 32 mmol, 1.0 equiv) and iodine (50 mg, 0.20 mmol, 0.0060 equiv) were mixed at 23 °C under argon and the solution was heated to 150 °C and directly distilled ($p = 100$ mbar, $bp = 60$ °C). The distilled liquid was dried 2 h over CaCl_2 and filtered to give 1,2-dimethyl-cyclohexene (**108**) together with 1,6-dimethyl-cyclohexene (5:1 ratio, 3.1 g, 28 mmol, 89%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz)^{26c} δ 2.06-0.90 (m, 8 H, CH_2), 1.60 (s, 6H, CH_3).

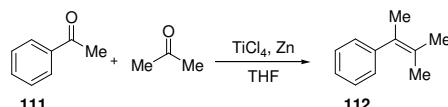
1,2,3,4,5,6,7,8-Octahydro-naphthalene (110)²⁷



Naphthalene (**109**) (2.6 g, 20 mmol, 1.0 equiv) was dissolved in dimethylamine (25 mL) and ethylamine (25 mL) at 0 °C under argon. Lithium (1.2 g, 0.17 mol, 8.3 equiv, wires, freshly cut in 0.5 cm pieces and washed with hexane) was added over 45 min, whereas the reaction mixture turned red, then blue-red. The reaction mixture was stirred at reflux (15 °C, dry ice cooling) for 13 h, the dry ice condenser was removed and the solvents were evaporated at 23 °C over night. The greyish residues were quenched with water (50 mL, caution, violent reaction!) and the suspension was filtered, the residues were washed with Et_2O (3x10 mL), the layers were separated, the water layer was extracted with Et_2O (5x20 mL), the combined organic layers were dried over Na_2SO_4 and the solvents were removed under reduced pressure ($p = 100$ mbar, $T = 40$ °C). The crude product was distilled ($p = 20$ mbar, $bp = 80$ °C) to give octahydronaphthalene **110** (1.9 g, 14 mmol, 70%) as a 5.5:1 mixture of isomers.

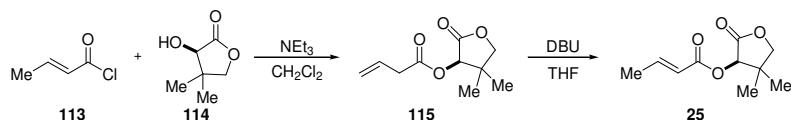
NaBH_4 (0.24 g, 6.2 mmol, 0.60 equiv) was suspended in THF (12 mL) at 23 °C under argon and 2-methyl-2-butene (1.7 mL, 16 mmol, 1.5 equiv) and a solution of $\text{BF}_3\bullet\text{Et}_2\text{O}$ (1.0 mL, 8.3 mmol, 0.75 equiv, freshly distilled) in THF (3.0 mL) were added dropwise. The crude octahydronaphthalene (1.8 g, 11 mmol **110**, 1 equiv) was added dropwise to the resulting suspension, the reaction mixture was stirred at 23 °C for 2 h and quenched with water (5 mL) and 3 M NaOH (3.5 mL). 30% H_2O_2 (3.5 mL) was then added dropwise, the reaction mixture was heated to 45 °C and stirred at that temperature for 5 h. After cooling to 23 °C, the layers were separated, the water layer extracted with Et_2O (2x10 mL), the combined organic layers washed with water (4x10 mL), dried over Na_2SO_4 and the solvents removed under reduced pressure ($p = 100$ mbar, $T = 40$ °C). Distillation ($p = 20$ mbar, $bp = 80$ °C) furnished **110** (1.2 g, 9.0 mmol, 82%) containing less than 7% of 2,3,4,5,6,7,9-Octahydro-naphthalene. ^1H NMR (CDCl_3 , 300 MHz)^{27b} δ 1.84 (m, 8H, CH_2), 1.59 (m, 8H, CH_2).

3-Methyl-2-phenyl-but-2-ene (112)²⁸



TiCl_4 (6.0 mL, 55 mmol, 5.5 equiv, freshly distilled) was added dropwise to THF (150 mL, dry) at 0 °C under argon over 40 min and a yellow suspension was formed in a violent reaction. After stirring for 20 min, Zn (7.3 g, 0.11 mol, 11 equiv, activated) was added in small portions at 0 °C over 1 h, whereas the reaction mixture turned black-red. A mixture of acetophenone (**111**) (1.2 mL, 9.7 mmol, 1.0 equiv) and acetone (3.0 mL, 41 mmol, 4.2 equiv, freshly distilled) in THF (20 mL) was added dropwise over 30 min and the reaction mixture was heated to reflux for 22 h. After cooling to 23 °C, the reaction was quenched with 10% K_2CO_3 solution (150 mL), the layers were separated, the water layer extracted with Et_2O (4x50 mL), the combined organic layers washed with water (50 mL), brine (50 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (pentane) to give 3-methyl-2-phenyl-but-2-ene (**112**) (0.26 g, 1.8 mmol, 19%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz)^{28b} δ 7.33-7.11 (m, 5H, Ar H), 1.96 (m, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.59 (q, $J = 1.4$ Hz, 3H, CH_3).

(R)-(E)-But-2-enoic acid 4,4-dimethyl-2-oxo-tetrahydro-furan-3-yl ester (25)



(R)-But-3-enoic acid 4,4-dimethyl-2-oxo-tetrahydro-furan-3-yl ester (115)

Triethylamine (distilled, 2.1 mL, 15 mmol, 1.5 equiv) was added to a solution of D-Pantolactone (**114**) (1.30 g, 10.0 mmol, 1.00 equiv) in CH_2Cl_2 (17 mL) at -20 °C under argon. Crotonyl chloride (**113**) (freshly distilled, 1.2 mL, 13 mmol, 1.3 equiv) was then added dropwise over 30 min. After warming up to 23 °C over 4 h, the reaction mixture was washed with 1 M HCl (2x15 mL), sat. NaHCO_3 (2x15 mL) and water (15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:4) to give product **115** (1.77 g, 8.93 mmol, 89%) as an oil. R_f (AcOEt/hexane 1:5) 0.20; ^1H NMR (CDCl_3 , 300 MHz) δ 5.99-5.89 (m, 1H, alkene H), 5.38 (s, 1H, C_2CHOH), 5.27-5.20 (m, 2H, alkene H), 4.08-4.00 (m, 2H, CH_2O), 3.27-3.24 (m, 2H, alkene CH_2), 1.21 (s, 3H, CH_3), 1.11 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75

MHz) δ 172.0, 170.1, 129.1, 119.2, 76.1, 75.1, 40.2, 38.5, 23.1, 19.9; IR ν 3085 (w), 2970 (m), 2936 (w), 2912 (w), 2880 (w), 1792 (s), 1750 (s), 1644 (w), 1467 (m), 1426 (w), 1402 (m), 1377 (m), 1370 (m), 1349 (w), 1325 (m), 1297 (m), 1249 (m), 1200 (m), 1153 (s), 1106 (s), 1081 (s), 1033 (m), 1014 (s), 997 (s), 927 (m), 813 (w), 708 (w), 558 (w); HRMS (EI) calcd for $C_{10}H_{14}O_4^+$ (M): 198.0892, found 198.0891; Anal. calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.82; H, 7.10.

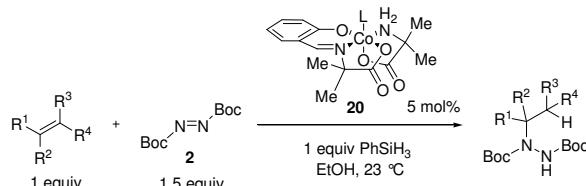
(R)-(E)-But-2-enoic acid 4,4-dimethyl-2-oxo-tetrahydro-furan-3-yl ester (25)

DBU (1.0 mL, 6.2 mmol, 1.3 equiv) was added dropwise to a solution of **115** (1.0 g, 5.0 mmol, 1.0 equiv) in THF (5 mL) at 0 °C under argon. The reaction mixture was stirred 30 min at 0 °C and 5 h at 23 °C, diluted with Et_2O (20 mL), washed with 3 M HCl (3x15 mL) and the water layers were extracted with Et_2O (3x15 mL). The combined organic layers were washed with 10% NaOH (2x15 mL), 2 M HCl (2x15 mL) and water (15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to give product **25** (0.84 g, 4.2 mmol, 84%) as a yellow oil. R_f (AcOEt/hexane 1:5) 0.20; 1H NMR ($CDCl_3$, 300 MHz) δ 7.12 (dq, J = 15.6, 6.8 Hz, 1H, alkene H), 5.96 (dq, J = 15.6, 1.9 Hz, 1H, alkene H), 5.43 (s, 1H, C_2CHO), 4.08 (d, J = 9.0 Hz, 1H, CH_2O), 4.03 (d, J = 9.0 Hz, 1H, CH_2O), 1.93 (dd, J = 6.8, 1.9 Hz, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.4, 164.8, 147.1, 121.1, 76.2, 74.7, 40.4, 23.1, 20.0, 18.3; IR ν 2970 (m), 2936 (w), 2915 (w), 2879 (w), 1794 (s), 1731 (s), 1656 (m), 1466 (w), 1444 (m), 1401 (w), 1377 (m), 1344 (w), 1294 (m), 1256 (s), 1171 (s), 1107 (s), 1087 (s), 1032 (m), 1014 (m), 997 (m), 970 (m), 915 (w), 894 (w), 836 (w), 732 (w), 685 (w), 650 (w), 562 (w), 516 (w); HRMS (EI) calcd for $C_{10}H_{14}O_4^+$ (M): 198.0892, found 198.0891; Anal. calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.76; H, 7.17.

2.3. The Co- and Mn- Catalyzed Hydrohydrazination of Olefins

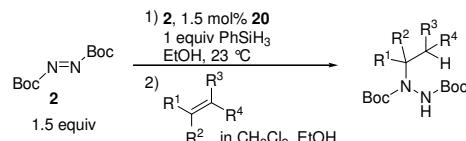
2.3.1. General Procedures

General Procedure for the Co-Catalyzed Hydrohydrazination of Olefins (GP1)



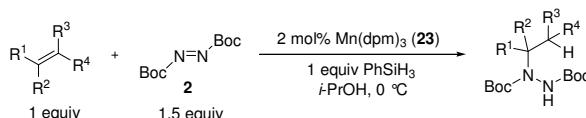
The Co catalyst **20** (10 mg, 0.025 mmol 0.050 equiv) was dissolved in ethanol (2.5 mL) at 23 °C under argon. The olefin (0.50 mmol, 1.0 equiv) and phenylsilane (65 μ L, 0.52 mmol, 1.0 equiv) were added to the brown-red solution, followed by di-*tert*-butyl azodicarboxylate (**2**) (0.17 g, 0.75 mmol, 1.5 equiv) in one portion. The resulting solution was stirred at 23 °C and monitored by TLC (AcOEt/hexane 1:5). After completion the reaction was quenched with H_2O (1 mL), brine (5 mL) was added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography.

General Procedure for the Co-Catalyzed Hydrohydrazination of Polymerization-Sensitive Olefins (GP2)



The Co catalyst **20** (3.0 mg, 0.0075 mmol, 0.016 equiv, in the case of vinyl heterocycles: 5.0 mg, 0.012 mmol, 0.025 equiv) was dissolved in ethanol (2.5 mL) at 23 °C under argon. Phenylsilane (65 μ L, 0.52 mmol, 1.0 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.17 g, 0.75 mmol, 1.5 equiv) were added to the brown-red solution, followed by a solution of olefin (0.50 mmol, 1.0 equiv) in ethanol (0.5 mL, in the case of vinyl heterocycles: 1.0 mL) and CH_2Cl_2 (0.5 mL, in the case of vinyl heterocycles: 1.0 mL). The resulting solution was stirred at 23 °C and monitored by TLC (AcOEt/hexane 1:5). After completion the reaction was quenched with H_2O (1 mL), brine (5 mL) was added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography.

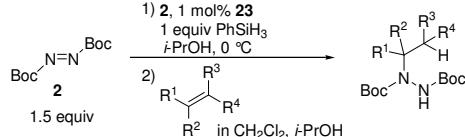
General Procedure for the Mn-Catalyzed Hydrohydrazination of Olefins (GP3)



$Mn(dpm)_3$ (**23**) (6 mg, 0.01 mmol, 0.02 equiv) was dissolved in isopropanol (2.5 mL) at 23 °C under argon and the dark brown-green solution was cooled to 0 °C. The olefin (0.50 mmol, 1.0 equiv) and phenylsilane (65 μ L, 0.52 mmol, 1.0 equiv) were added, followed by di-*tert*-butyl azodicarboxylate (**2**) (0.17 g, 0.75 mmol, 1.5 equiv) in one portion. The resulting suspension was stirred at 0 °C and monitored by TLC (AcOEt/hexane 1:5). After completion (color change to yellow) the reaction was quenched with H_2O (1 mL), brine (5 mL) was added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic

layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography.

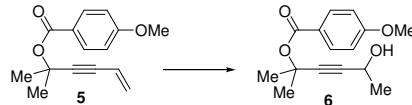
General Procedure for the Mn-Catalyzed Hydrohydrazination of Polymerization-Sensitive Olefins (GP4)



The Mn catalyst **23** (3 mg, 0.005 mmol, 0.01 equiv) was dissolved in isopropanol (2.5 mL) at 23 °C under argon and the dark brown-green solution was cooled to 0 °C. Phenylsilane (65 μL , 0.52 mmol, 1.0 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.17 g, 0.75 mmol, 1.5 equiv) were added, followed by a solution of olefin in isopropanol (1 mL) and CH_2Cl_2 (1 mL). The resulting solution was stirred at 0 °C and monitored by TLC (AcOEt/hexane 1:5). After completion (color change to yellow) the reaction was quenched with H_2O (1 mL), brine (5 mL) was added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography.

2.3.2. Hydration of enyne 5

4-Methoxy-benzoic acid 4-hydroxy-1,1-dimethyl-pent-2-ynyl ester (6)



With Co catalyst from ligand 7

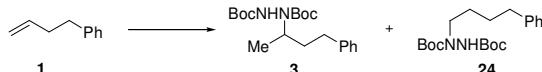
The catalyst (18 mg, 0.036 mmol, 0.13 equiv) was dissolved in CH_2Cl_2 (3 mL) at 23 °C under O_2 (1 atm, balloon). Enyne **5** (69 mg, 0.28 mmol, 1.0 equiv) and PhSiH_3 (75 μL , 0.60 mmol, 2.2 equiv) were added and the resulting green-brown solution was stirred at 23 °C and the reaction was monitored by TLC (AcOEt/hexane 1:2). After completion (9 h), the solvent was removed under reduced pressure, the residues were dissolved in MeOH (3 mL), sat. $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) was added, the mixture stirred vigorously for 30 min and quenched with sat. NaCl (5 mL). The reaction mixture was then extracted with AcOEt (3x10 mL), the organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:2) to afford propargylic alcohol **6** (57 mg, 0.22 mmol, 77%) as a colorless oil.

With Co catalyst 20

Catalyst **20** (0.8 mg, 2 μmol , 0.01 equiv) was dissolved in ethanol (2 mL) at 23 °C under O_2 (1 atm, balloon). Enyne **5** (48 mg, 0.20 mmol, 1.0 equiv) and PhSiH_3 (50 μL , 0.40 mmol, 2.0 equiv) were added and the resulting dark brown red solution was stirred at 23 °C and the reaction was monitored by TLC (AcOEt/hexane 1:2). After completion (45 min), the solvent was removed under reduced pressure, the residues were dissolved in MeOH (3 mL), sat. $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) was added, the mixture stirred vigorously for 30 min and quenched with sat. NaCl (5 mL). The reaction mixture was then extracted with AcOEt (3x10 mL), the organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/hexane 1:2) to afford propargylic alcohol **6** (47 mg, 0.18 mmol, 91%) as a colorless oil. R_f (AcOEt/hexane 1:2) 0.30; ^1H NMR (CDCl_3 , 300 MHz) δ 7.94 (dd, J = 6.9, 2.2 Hz, 2H, Ar H), 6.89 (dd, J = 6.9, 1.9 Hz, 2H, Ar H), 4.56 (q, J = 6.5 Hz, 1H, CHOHCH_3), 3.84 (s, 3H, OCH_3), 2.77 (bs, OH), 1.76 (s, 6H, $(\text{CH}_3)_2\text{COC}$), 1.43 (d, J = 6.5 Hz, 3H, CHOHCH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.5, 163.1, 131.5, 123.2, 113.4, 86.2, 84.9, 72.2, 58.2, 55.4, 29.2, 24.1; IR v 3448 (m), 2985 (m), 2936 (m), 2841 (w), 1717 (s), 1607 (s), 1582 (w), 1511 (m), 1465 (m), 1421 (m), 1383 (w), 1365 (m), 1318 (m), 1286 (s), 1258 (s), 1171 (m), 1140 (s), 1100 (s), 1029 (m), 983 (w), 925 (m), 848 (m), 771 (m), 698 (m), 622 (w); HRMS(EI) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4^+$ (M) 262.1205, found 262.1195.

2.3.3. Hydrohydrazination Products

N-(3-Phenyl-1-methyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (3) and *N*-(4-Phenylbutyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (24)



Following GP1 Hydrohydrazination product **3** (155 mg, 0.425 mmol, 85%) was obtained as a colorless solid with 4-phenylbutene (**1**) (75 μL , 0.50 mmol, 1.0 equiv) in 4 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Scale up** The cobalt catalyst **20** (60 mg, 0.12 mmol 0.025 equiv) was dissolved in ethanol (20 mL) at 23 °C under argon. 4-Phenylbutene (**1**) (675 mg, 0.510 mmol 1.00 equiv) and phenylsilane (0.65 mL, 5.2 mmol, 1.0 equiv) were added to the brown-red solution, followed by di-*tert*-butyl azodicarboxylate (**2**) (1.72 g, 7.47 mmol, 1.50 equiv) portionswise. The resulting solution was stirred at 23 °C and monitored by TLC (AcOEt/hexane 1:5). After completion (5 h) the reaction mixture

was concentrated under reduced pressure to about 3 mL, quenched with H₂O (3 mL), brine (20 mL) was added and the reaction mixture was extracted with AcOEt (3x50 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 1:10) to afford **3** (1.75 g, 4.80 mmol, 94%) as a colorless solid together with recovered 4-phenylbutene (**1**) (38 mg, 0.28 mmol, 5 %). **Following GP1, but using TMDSO** Hydrohydrazination product **3** (156 mg, 0.428 mmol, 86%) was obtained as a colorless solid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) and TMDSO (0.13 mL, 0.75 mmol, 1.5 equiv) in 4 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **3** (140 mg, 0.384 mmol, 76%) together with the primary hydrazide **24** (34 mg, 0.093 mmol, 18%, total 94%) were obtained as colorless solids with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 eq) in 2.5 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3, but with PMHS** Hydrohydrazination product **3** (142 mg, 0.390 mmol, 78%) together with the primary hydrazide **24** (20 mg, 0.056 mmol, 11%, total 89%) were obtained as colorless solids with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 eq) and PMHS (0.10 mL, 1.6 H equiv) in 20 h at 23 °C with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10).

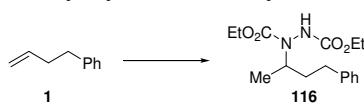
N-(3-Phenyl-1-methyl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (3)

R_f (AcOEt/hexane 1:5) 0.35; Mp 125-127°C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.29-7.14 (m, 5H, Ar H), 5.86 (br s, 1H, NH), 4.25 (br s, 1H, CHN), 2.63 (m, 2H, PhCH₂), 1.90 (m, 1H, CH₂CHN), 1.65 (m, 1H, CH₂CHN), 1.48 (s, 9H, CCH₃), 1.47 (s, 9H, CCH₃), 1.14 (d, J = 6.9 Hz, 3H, CHNCH₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.7, 154.7, 141.9, 128.2, 128.1, 125.6, 80.8, 53.1, 35.8, 32.9, 28.3, 28.2, 18.2; IR (KBr) v 3290 (s), 3070 (w), 2977 (s), 2927 (m), 1744 (s), 1665 (s), 1514 (s), 1411 (s), 1369 (s), 1346 (s), 1245 (s), 1153 (s), 1116 (s), 1074 (m), 1004 (m), 909 (m), 898 (m), 858 (m), 784 (m), 747 (s), 702 (s), 592 (m); HRMS (ESI) calcd for C₂₀H₃₂N₂O₄Na⁺ (M+Na): 387.2254, found 387.2255; Anal. calcd for C₂₀H₃₂N₂O₄: C, 65.91; H, 8.85; N, 7.69. Found: C, 65.69; H, 8.77; N, 7.60.

N-(4-Phenyl-butyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (24)

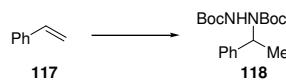
R_f (AcOEt/hexane 1:5) 0.32; Mp 54-56°C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.29-7.19 (m, 2H, Ar H), 7.18-7.13 (m, 3H, Ar H), 6.21 (br s, 1H, NH), 3.46 (t, J = 6.5 Hz, 2H, CH₂N), 2.64 (t, J = 7.2 Hz, 2H, CH₂Ph), 1.70-1.53 (m, 4H, CH₂), 1.47 (s, 9H, CCH₃), 1.46 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.2, 142.2, 128.3, 128.2, 125.6, 81.0, 80.9, 49.8, 35.6, 28.5, 28.3, 28.3, 27.2; IR v 3317 (m), 3063 (w), 3026 (w), 2978 (s), 2933 (s), 2863 (w), 1706 (s), 1604 (w), 1496 (s), 1479 (s), 1454 (s), 1393 (s), 1367 (s), 1254 (s), 1153 (s), 1090 (w), 1074 (w), 1053 (w), 1017 (w), 932 (w), 856 (w), 750 (m), 700 (m), 584 (w), 494 (w); MS 365.1 (M+H); Anal. calcd for C₂₀H₃₂N₂O₄: C, 65.91; H, 8.85; N, 7.69. Found: C, 65.91; H, 8.79; N, 7.59.

N-(3-Phenyl-1-methyl-propyl)-N'-(ethoxycarbonyl)hydrazinecarboxylic acid ethyl ester (116)



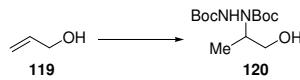
Following GP1, but using DEAD Hydrohydrazination product **116** (51 mg, 0.17 mmol, 34%) was obtained as a colorless viscous oil with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) and diethyl azodicarboxylate (0.12 mL, 0.75 mmol, 1.5 equiv) in 1.5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:5). R_f (AcOEt/hexane 1:5) 0.20; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.36-7.21 (m, 5H, Ar H), 6.19 (br s, 1H, NH), 4.35 (br s, 1H, CHN), 4.30-4.21 (m, 4H, OCH₂), 2.74 (m, 2H, CH₂Ph), 1.99 (m, 1H, CH₂CHN), 1.75 (m, 1H, CH₂CHN), 1.33 (m, 6H, OCH₂CH₃), 1.23 (d, J = 6.5 Hz, 3H, CH₂CHN); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 156.9, 155.9, 141.8, 128.2, 125.7, 109.9, 62.3, 62.0, 53.8, 35.7, 33.0, 18.2, 14.6, 14.5; IR v 3289 (m), 3085 (w), 3062 (w), 3027 (w), 2981 (m), 2934 (m), 2871 (m), 1755 (s), 1711 (s), 1604 (w), 1519 (m), 1496 (m), 1454 (m), 1415 (s), 1378 (m), 1327 (m), 1228 (s), 1174 (m), 1114 (m), 1097 (m), 1061 (m), 915 (w), 850 (w), 760 (m), 701 (m), 621 (w), 594 (w), 488 (w); HRMS (ESI) calcd for C₁₆H₂₄N₂O₄Na⁺ (M+Na) 331.1628, found 331.1630; Anal. calcd for C₁₆H₂₄N₂O₄: C, 62.32; H, 7.84; N, 9.08. Found: C, 62.30; H, 7.75; N, 8.90.

N-(1-Phenyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (118)



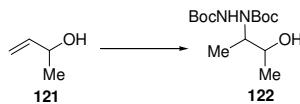
Following GP2 Hydrohydrazination product **118** (145 mg, 0.431 mmol, 86%) was obtained as a colorless solid with styrene (**117**) (freshly filtered through neutral Al₂O₃, 57 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:3) 0.43; Mp 87-88 °C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.34-7.20 (m, 5H, Ar H), 5.95 (br s, 1H, NH), 5.43 (br m, 1H, CHN), 5.12 (d, J = 7.2 Hz, 3H, CHCH₃), 1.46 (s, 9H, CCH₃), 1.43 (br s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.6, 154.6, 141.2, 128.2, 127.2, 81.1, 80.8, 55.8, 28.3, 28.2, 17.0; IR v 3311 (m), 3088 (w), 3064 (w), 3032 (w), 2979 (m), 2934 (m), 1702 (s), 1495 (m), 1479 (m), 1455 (m), 1393 (s), 1367 (s), 1316 (s), 1251 (s), 1168 (s), 1048 (m), 1030 (m), 990 (w), 912 (w), 860 (w), 760 (m), 700 (m), 580 (w); HRMS (ESI) calcd for C₁₈H₂₈N₂O₄Na⁺ (M+Na): 359.1941, found 359.1945; Anal. calcd for C₁₈H₂₈N₂O₄: C, 64.26; H, 8.39; N, 8.33. Found: C, 63.99; H, 8.36; N, 8.29.

N-(2-Hydroxy-1-methyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (120)



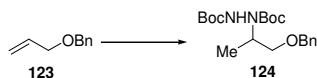
Following GP1 Hydrohydrazination product **120** (113 mg, 0.390 mmol, 78%) was obtained as a colorless solid with allyl alcohol (**119**) (34 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:2). R_f (AcOEt/hexane 1:2) 0.40; Mp 119-120 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.26 (br s, 1H, NH), 4.35 (br s, 1H, CHN), 4.08 (br s, 1H, OH), 3.42 (m, 2H, CH_2), 1.46 (s, 9H, CCH_3), 1.44 (s, 9H, CCH_3), 0.97 (d, J = 6.9 Hz, 3H, $CHNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 157.9, 155.3, 82.0, 81.5, 63.5, 55.3, 28.2, 28.1, 13.6; IR v 3358 (m), 3234 (m), 2978 (m), 2935 (m), 2876 (w), 1713 (s), 1511 (m), 1460 (m), 1395 (s), 1368 (s), 1338 (s), 1292 (s), 1259 (s), 1156 (s), 1114 (s), 1061 (s), 1013 (m), 898 (w), 858 (m), 763 (m), 698 (w), 625 (w), 538 (w); MS (ESI) 291.2 (M+H), 313.1 (M+Na); Anal. calcd for $C_{13}H_{26}N_2O_5$: C, 53.78; H, 9.03; N, 9.65. Found: C, 53.92; H, 8.92; N, 9.52.

N-(2-Hydroxy-1-methyl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (122)



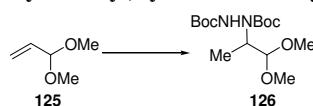
Following GP1 Hydrohydrazination product **122** (1. diastereoisomer: 57 mg, 0.19 mmol, 38%; 2. diastereoisomer: 55 mg, 0.18 mmol, 36%) was obtained as a colorless solid with but-3-en-2-ol (**121**) (43 μ L, 0.50 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:5-1:3). **Diastereoisomer 1** R_f (AcOEt/hexane 1:2) 0.33; Mp 111-113 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.19 (br s, 1H, NH), 4.70 (br s, 1H, OH), 3.99 (br s, 1H, $CHOH$), 3.52 (1H, br s, CHN), 1.48 (s, 9H, CCH_3), 1.46 (s, 9H, CCH_3), 1.18 (d, J = 6.3 Hz, 3H, CH_3), 1.03 (d, J = 6.9 Hz, 3H, $CHCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 157.9, 155.3, 82.1, 81.6, 67.9, 59.8, 28.2, 28.1, 19.2, 14.5; IR v 3387 (m), 3302 (m), 2980 (s), 2935 (m), 2883 (w), 1714 (s), 1516 (m), 1480 (m), 1456 (m), 1395 (s), 1368 (s), 1333 (s), 1288 (s), 1252 (s), 1159 (s), 1102 (s), 1051 (w), 1013 (m), 923 (m), 911 (m), 851 (w), 827 (w), 784 (w), 759 (w), 734 (m), 647 (w), 609 (w), 531 (w); MS (ESI) 305.4 (M+H), 327.4 (M+Na); Anal. calcd for $C_{14}H_{28}N_2O_5$: C, 55.24; H, 9.27; N, 9.20. Found: C, 55.24; H, 9.41; N, 8.96. **Diastereoisomer 2** R_f (AcOEt/hexane 1:2) 0.20; Mp 143-145 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.26 (br s, 1H, NH), 4.10-3.97 (m, 2H, CHN and $CHOH$), 3.53 (br s, 1H, OH), 1.47 (s, 9H, CCH_3), 1.46 (s, 9H, CCH_3), 1.12 (m, 6H, $CHCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 157.2, 154.9, 81.9, 81.5, 69.1, 58.8, 28.2, 28.1, 19.1, 10.0; IR v 3391 (m, sh), 3309 (m), 2980 (s), 2935 (m), 1707 (s), 1480 (m), 1456 (m), 1394 (s), 1368 (s), 1292 (s), 1254 (s), 1160 (s), 1089 (s), 1005 (m), 978 (w), 919 (m), 909 (m), 858 (w), 785 (w), 760 (w), 734 (m), 647 (w); HRMS (ESI) calcd for $C_{14}H_{28}N_2O_5Na^+$ (M+Na): 327.1890, found 327.1888; Anal. calcd for $C_{14}H_{28}N_2O_5$: C, 55.24; H, 9.27; N, 9.20. Found: C, 55.39; H, 9.22; N, 9.13.

N-(2-Benzyl-1-methyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (124)



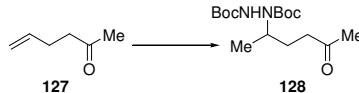
Following GP1 Hydrohydrazination product **124** (143 mg, 0.376 mmol, 76%) was obtained as a colorless solid with benzyl-vinyl ether (**123**) (77 μ L, 0.50 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.27; Mp 99-100 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 7.36-7.23 (m, 5H, Ar H), 5.99 (br s, 1H, NH), 4.54 (d, J = 12.1 Hz, 1H, $PhCH_2$), 4.48 (br s, 1H, CHN), 4.45 (d, J = 12.1 Hz, 1H, $PhCH_2$), 3.49 (m, 1H, $CHNCH_2$), 3.38 (m, 1H, $CHNCH_2$), 1.46 (s, 9H, CCH_3), 1.46 (s, 9H, CCH_3), 1.13 (d, 3H, J = 6.9 Hz, $CHNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.9, 155.0, 138.4, 128.3, 127.6, 80.9, 80.8, 72.8, 71.3, 52.0, 28.3, 28.2, 14.4; IR v 3307 (m), 3065 (w), 3030 (w), 2979 (s), 2933 (m), 2869 (m), 1746 (s), 1707 (s), 1496 (m), 1479 (m), 1455 (m), 1392 (s), 1367 (s), 1337 (s), 1250 (s), 1155 (s), 1096 (s), 1064 (s), 1014 (m), 914 (w), 857 (w), 839 (w), 782 (w), 738 (m), 698 (m), 608 (w); MS (ESI) 403.1 (M+Na); Anal. calcd for $C_{20}H_{32}N_2O_5$: C, 63.14; H, 8.48; N, 7.36. Found: C, 62.85; H, 8.33; N, 7.49.

N-(2-Dimethoxy-1-methyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (126)



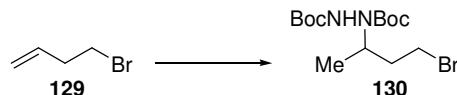
Following GP1 Hydrohydrazination product **126** (117 mg, 0.350 mmol, 70% (40 % pure, 30 % co-fraction with N,N' -di-*tert*-butoxycarbonylhydrazine (**4**))) was obtained as a colorless viscous oil with acrolein-dimethylacetal (**125**) (freshly distilled, 59 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (96 μ L, 0.77 mmol, 1.5 equiv) and di-*tert*-butylazodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 7 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:2) 0.36; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.09 (br s, 1H, NH), 4.26 (br s, 1H, CHN), 4.26 (d, J = 5.3 Hz, 1H, acetal H), 3.35 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 1.46 (s, 18H, CCH_3), 1.14 (d, J = 6.5 Hz, 3H, $CHNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.5, 154.7, 105.2, 81.0, 80.7, 54.8, 53.1, 28.3, 28.3, 12.9; IR v 3295 (m), 2979 (m), 2936 (m), 2836 (w), 1749 (s), 1708 (s), 1479 (m), 1456 (m), 1394 (s), 1367 (s), 1319 (m), 1241 (m), 1155 (s), 1102 (s), 1051 (m), 1012 (w), 973 (w), 952 (w), 859 (w), 846 (w), 782 (w), 758 (w); HRMS (ESI) calcd for $C_{15}H_{30}N_2O_6Na^+$ (M+Na): 357.1996, found 357.1993; Anal. calcd for $C_{15}H_{30}N_2O_6$: C, 53.88; H, 9.04; N, 8.38. Found: C, 53.60; H, 8.98; N, 8.21.

N-(1-Methyl-4-oxo-pentyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (128)



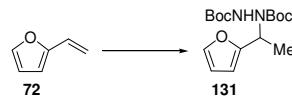
Following GP1 Hydrohydrazination product **128** (125 mg, 0.379 mmol, 76 %) was obtained as a colorless viscous oil with hexan-5-en-2-one (**127**) (freshly distilled, 56 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:5). R_f (AcOEt/hexane 1:2) 0.37; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.11 (br s, 1H, NH), 4.18 (br s, 1H, CHN), 2.51 (br s, 2H, CH_2), 2.09 (s, 3H, $COCH_3$), 1.79 (br s, 1H, CH_2), 1.52 (br s, 1H, CH_2), 1.45 (s, 9H, CCH_3), 1.43 (s, 9H, CCH_3), 1.10 (d, J = 6.5 Hz, 3H, $CHNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 208.5, 155.5, 155.0, 81.2, 80.8, 52.9, 40.8, 30.0, 28.3, 28.2, 27.8, 18.2; IR v 3318 (m), 2979 (s), 2934 (m), 1746 (s), 1710 (s), 1480 (m), 1456 (m), 1394 (s), 1367 (s), 1338 (s), 1246 (s), 1160 (s), 1117 (s), 1082 (m), 1047 (m), 1014 (m), 917 (w), 858 (w), 782 (w), 760 (m), 736 (w), 689 (w), 647 (w), 598 (w); HRMS (ESI) calcd for $C_{16}H_{30}N_2O_5Na^+$ (M+Na): 353.2047, found 353.2060; Anal. calcd for $C_{16}H_{30}N_2O_5$: C, 58.16; H, 9.10; N, 8.48. Found: C, 58.36; H, 9.10; N, 8.29.

N-(3-Bromo-1-methyl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (130)



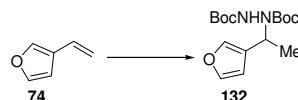
Following GP1 Hydrohydrazination product **130** (166 mg, 0.452 mmol, 90 %) was obtained as a colorless solid with 4-bromobutene (**129**) (51 μ L, 0.50 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.33; Mp 88-90 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.06 (br s, 1H, NH), 4.38 (m, 1H, CHN), 3.45 (m, 2H, CH_2Br), 2.13 (m, 1H, CH_2CHN), 1.82 (m, 1H, CH_2CHN), 1.46 (s, 18H, CCH_3), 1.12 (d, J = 6.5 Hz, 3H, $CHNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 156.0, 154.7, 81.3, 52.2, 37.5, 30.5, 28.3, 28.2, 18.0; IR v 3315 (m), 2979 (s), 2934 (m), 1707 (s), 1479 (m), 1456 (m), 1394 (s), 1368 (s), 1336 (m), 1305 (m), 1243 (s), 1160 (s), 1113 (m), 1085 (w), 1054 (m), 1018 (w), 1008 (w), 912 (w), 856 (w), 784 (w), 760 (m), 649 (w), 558 (w); HRMS (ESI) calcd for $C_{14}H_{27}N_2O_4BrNa^+$ (M+Na): 389.1052, 391.1031, found 389.1050, 391.1031; Anal. calcd for $C_{14}H_{27}N_2O_4Br$: C, 45.78; H, 7.41; N, 7.63. Found: C, 45.98; H, 7.48; N, 7.63.

N-(1-Furan-2-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (131)



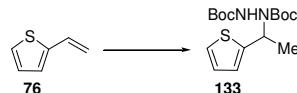
Following GP2 Hydrohydrazination product **131** (110 mg, 0.337 mmol, 68%) was obtained as a colorless solid with vinylfuran **72** (55% pure, 86 mg, 0.50 mmol, 1.0 equiv) in 12 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP4** Hydrohydrazination product **131** (103 mg, 0.316 mmol, 63%) was obtained as a colorless solid with vinylfuran **72** (55% pure, 86 mg, 0.50 mmol, 1.0 equiv) in 12 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.40; Mp 110-111 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.31 (m, 1H, furan H), 6.27 (m, 1H, furan H), 6.17 (m, 1H, furan H), 5.96 (br s, 1H, NH), 5.42 (br m, 1H, CHN), 1.50 (m, 3H, $CHCH_3$), 1.47 (s, 9H, CCH_3), 1.43 (br s, 9H, CCH_3); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.5, 154.6, 141.7, 110.1, 106.8, 81.4, 80.8, 50.7, 28.2, 28.1, 15.7; IR v 3317 (m), 3153 (w), 2980 (m), 2935 (m), 1705 (s), 1504 (m), 1479 (m), 1456 (m), 1393 (s), 1368 (s), 1311 (s), 1242 (s), 1161 (s), 1084 (w), 1053 (m), 1010 (m), 995 (m), 922 (w), 909 (w), 885 (w), 858 (w), 845 (w), 810 (w), 754 (m), 691 (w), 648 (w), 600 (w), 485 (w), 460 (w); MS (ESI) 327.1 (M+H), 349.1 (M+Na); Anal. calcd for $C_{16}H_{26}N_2O_5$: C, 58.88; H, 8.03; N, 8.58. Found: C, 59.05; H, 8.10; N, 8.56.

N-(1-Furan-3-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (132)



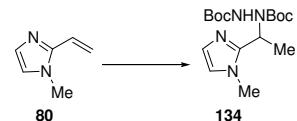
Following GP2 Hydrohydrazination product **132** (130 mg, 0.398 mmol, 75%) was obtained as a colorless solid with vinylfuran **74** (41% pure, 121 mg, 0.527 mmol, 1.00 equiv) in 18 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:9). **Following GP3** Hydrohydrazination product **132** (115 mg, 0.352 mmol, 72%) was obtained as a colorless solid with vinylfuran **74** (41% pure, 112 mg, 0.488 mmol, 1.00 equiv) in 18 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.40; Mp 79-81 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.35 (m, 2H, furan H), 6.35 (s, 1H, furan H), 5.87 (br s, 1H, NH), 5.35-5.29 (br m, 1H, CHN), 1.49 (s, 9H, CCH_3), 1.47 (m, 3H, $CHCH_3$), 1.45 (br s, 9H, CCH_3); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.5, 154.5, 142.8, 139.7, 125.8, 109.7, 81.2, 80.8, 48.9, 28.3, 28.2, 17.2; IR v 3314 (m), 3150 (w), 2980 (m), 2935 (m), 1704 (s), 1504 (m), 1479 (m), 1456 (m), 1393 (s), 1368 (s), 1316 (m), 1251 (m), 1163 (s), 1098 (m), 1058 (m), 1019 (m), 998 (m), 952 (w), 910 (w), 875 (m), 858 (w), 844 (w), 798 (w), 756 (w), 733 (w), 684 (w), 648 (w), 601 (m), 485 (w), 459 (w), 440 (w), 420 (w); MS (ESI) 327.1 (M+H), 349.1 (M+Na), 675.0 (2M+Na); Anal. calcd for $C_{16}H_{26}N_2O_5$: C, 58.88; H, 8.03; N, 8.58. Found: C, 58.97; H, 8.12; N, 8.60.

N-(1-Thiophene-2-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid tert-butyl ester (133)



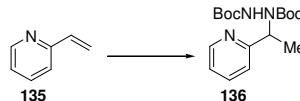
Following GP2 Hydrohydrazination product **133** (144 mg, 0.420 mmol, 84%) was obtained as a colorless solid with vinylthiophene **76** (90% pure, 62 mg, 0.50 mmol, 1.0 equiv) in 18 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP4** Hydrohydrazination product **133** (146 mg, 0.426 mmol, 85%) was obtained as a colorless solid with vinylthiophene **76** (90% pure, 62 mg, 0.50 mmol, 1.0 equiv) in 18 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.40; Mp 73–75 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.19–7.16 (m, 1H, furan H), 6.94–6.91 (m, 2H, furan H), 5.96 (br s, 1H, NH), 5.65 (br m, 1H, CHN), 1.57 (d, J = 6.9 Hz, 3H, CHCH_3), 1.48 (s, 9H, CCH_3), 1.44 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.4, 154.2, 144.8, 126.4, 124.6, 124.3, 81.5, 80.9, 51.9, 28.3, 28.2, 18.4; IR ν 3316 (m), 3106 (w), 2979 (m), 2934 (m), 1704 (s), 1479 (m), 1456 (m), 1392 (s), 1368 (s), 1315 (s), 1239 (s), 1164 (s), 1087 (w), 1058 (m), 1030 (w), 1015 (m), 984 (w), 910 (w), 854 (m), 842 (w), 756 (m), 699 (m), 582 (w), 475 (w); MS (ESI) 343.0 ($\text{M}+\text{H}$), 365.1 ($\text{M}+\text{Na}$); Anal. calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.35; H, 7.70; N, 8.22.

N-(1-(1-Methyl-1*H*-imidazole-2-yl)-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (134)



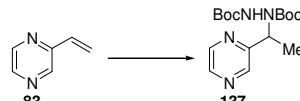
Following GP2 Hydrohydrazination product **134** (102 mg, 0.300 mmol, 60%) was obtained as a colorless solid with vinylimidazole **80** (54 mg, 0.50 mmol, 1.0 equiv) in 8 h with 2.5 mol% catalyst **20** after purification by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 14:1). **Following GP4** Hydrohydrazination product **134** (142 mg, 0.417 mmol, 83%) was obtained as a colorless solid with vinylimidazole **80** (54 mg, 0.50 mmol, 1.0 equiv) in 5 h with 1 mol% catalyst **23** after purification by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 14:1). Mp 131–135 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.90 (d, J = 0.8 Hz, 1H, imidazole H), 6.77 (d, J = 1.1 Hz, 1H, imidazole H), 6.40 (br s, 1H, NH), 5.54 (br m, 1H, CHN), 3.67 (s, 3H, NCH_3), 1.57 (d, J = 7.0 Hz, 3H, CHCH_3), 1.46 (s, 9H, CCH_3), 1.37 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 25 °C, mixture or rotamers) δ 154.9, 154.4, 147.7, 147.0, 145.7, 144.8, 126.8, 120.9, 81.2, 80.3, 47.5, 46.9, 32.7, 28.1, 16.1; IR ν 3314 (w), 3166 (w), 2980 (m), 2934 (w), 1731 (s), 1697 (s), 1642 (w), 1547 (w), 1496 (m), 1479 (m), 1454 (m), 1393 (s), 1367 (s), 1319 (s), 1282 (s), 1245 (s), 1170 (s), 1125 (w), 1094 (w), 1057 (m), 1023 (w), 994 (w), 922 (w), 858 (w), 756 (w), 733 (m), 646 (w), 590 (w), 521 (w); MS (ESI) 341.4 ($\text{M}+\text{H}$), 363.2 ($\text{M}+\text{Na}$); Anal. calcd for $\text{C}_{16}\text{H}_{28}\text{N}_4\text{O}_4$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.54; H, 8.43; N, 16.17.

N-(1-Pyridin-2-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (136)



Following GP2 Hydrohydrazination product **136** (130 mg, 0.385 mmol, 77%) was obtained as a colorless gel with vinylpyridine **135** (filtered over Al_2O_3 , 54 μL , 0.50 mmol, 1.0 equiv) in 4 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:5:1:2). **Following GP4** Hydrohydrazination product **136** (132 mg, 0.391 mmol, 78%) was obtained as a colorless gel with vinylpyridine **135** (filtered over Al_2O_3 , 54 μL , 0.50 mmol, 1.0 equiv) in 13 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:3). R_f (AcOEt/hexane 1:2) 0.30; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 8.47 (d, J = 4.7 Hz, 1H, pyridine H), 7.59 (dd, J = 9.4, 7.7 Hz, 1H, pyridine H), 7.22 (br m, 1H, pyridine H), 7.10 (dd, J = 7.2, 5.2 Hz, 1H, pyridine H), 6.80 (br s, 1H, NH), 5.37 (br m, 1H, CHN), 1.53 (d, J = 7.1 Hz, 3H, CHCH_3), 1.44 (s, 9H, CCH_3), 1.38 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 161.6, 155.4, 148.7, 136.3, 134.0, 121.8, 121.2, 81.1, 80.4, 57.2, 28.3, 28.2, 17.5; IR ν 3312 (w), 2980 (m), 2934 (w), 1708 (s), 1594 (w), 1572 (w), 1477 (m), 1456 (m), 1435 (w), 1392 (s), 1367 (s), 1317 (m), 1245 (s), 1161 (s), 1092 (w), 1049 (w), 1021 (w), 989 (w), 913 (w), 858 (w), 779 (w), 751 (w), 734 (w), 700 (w), 668 (w), 592 (w), 501 (w); MS (ESI) 338.1 ($\text{M}+\text{H}$), 360.0 ($\text{M}+\text{Na}$); Anal. calcd for $\text{C}_{17}\text{H}_{27}\text{N}_3\text{O}_4$: C, 60.51; H, 8.07; N, 12.45. Found: C, 60.36; H, 8.11; N, 12.26.

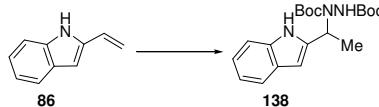
N-(1-Pyrazin-2-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (137)



Following GP2 Hydrohydrazination product **137** (110 mg, 0.325 mmol, 63%) was obtained as a colorless gel with vinylpyrazine **83** (55 mg, 0.52 mmol, 1.0 equiv) in 24 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:2). **Following GP4** Hydrohydrazination product **137** (112 mg, 0.331 mmol, 64%) was obtained as a colorless gel with vinylpyrazine **83** (55 mg, 0.52 mmol, 1.0 equiv) in 10 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:4:1:2). R_f (AcOEt/hexane 1:2) 0.20; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 8.58 (s, 1H, pyrazine H), 8.41 (m, 2H, pyrazine H), 6.52 (br s, 1H, NH), 5.45 (br m, 1H, CHN), 1.56 (d, J = 7.2 Hz, 3H, CHCH_3), 1.42 (s, 9H,

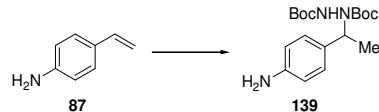
CCH_3), 1.39 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 156.8, 155.3, 154.9, 143.6, 143.3, 142.9, 81.5, 80.8, 55.6, 28.2, 16.8; IR ν 3312 (w), 2980 (m), 2935 (w), 1706 (s), 1477 (m), 1456 (m), 1392 (s), 1368 (s), 1317 (s), 1247 (s), 1159 (s), 1095 (m), 1053 (m), 1019 (m), 994 (w), 913 (w), 852 (m), 762 (w), 734 (m), 648 (w), 595 (w), 461 (w); MS (ESI) 361.2 (M+Na); Anal. calcd for $\text{C}_{16}\text{H}_{26}\text{N}_4\text{O}_4$: C, 56.79; H, 7.74; N, 16.56. Found: C, 56.99; H, 7.85; N, 16.35.

***N*-(1-(1*H*-Indol-2-yl)-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (138)**



Following GP2 Hydrohydrazination product **138** (153 mg, 0.408 mmol, 82%) was obtained as a colorless solid with vinylindole **86** (73 mg, 0.50 mmol, 1.0 equiv) in 5 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:7). **Following GP4** Hydrohydrazination product **138** (135 mg, 0.360 mmol, 72%) was obtained as a colorless solid with vinylindole **86** (73 mg, 0.50 mmol, 1.0 equiv) in 5 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:5). R_f (AcOEt/hexane 1:5) 0.35; Mp 73–75 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 9.46 (br s, 1H, indole NH), 7.55 (d, J = 7.8 Hz, 1H, indole CH), 7.34 (d, J = 8.1 Hz, 1H, indole CH), 7.17–7.04 (m, 2H, indole CH), 6.35 (s, 1H, indole CH), 6.24 (br s, 1H, hydrazine NH), 5.47 (br m, 1H, CHN), 1.64 (d, J = 7.2 Hz, 3H, CHCH_3), 1.46 (s, 18H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 156.1, 154.9, 139.3, 136.1, 133.9, 128.1, 121.5, 120.0, 119.3, 110.9, 99.5, 81.9, 81.5, 52.6, 28.2, 28.1, 16.7; IR ν 3320 (m), 3059 (w), 2980 (m), 2935 (w), 1694 (s), 1619 (w), 1585 (w), 1479 (m), 1456 (m), 1393 (s), 1368 (s), 1302 (m), 1281 (m), 1252 (m), 1157 (s), 1092 (w), 1061 (w), 1025 (w), 1000 (w), 959 (w), 910 (m), 855 (w), 789 (w), 735 (m), 700 (w), 649 (w), 555 (w); MS (ESI) 376.3 (M+H), 398.2 (M+Na); Anal. calcd for $\text{C}_{20}\text{H}_{29}\text{N}_3\text{O}_4$: C, 63.98; H, 7.78; N, 11.19. Found: C, 64.18; H, 7.92; N, 10.95.

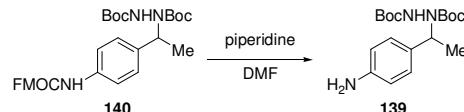
***N*-[1-(4-Amino-phenyl)-ethyl]-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (139)**



Following GP2 Hydrohydrazination product **139** was obtained as the minor product (< 40%) of a mixture of non-identified products with 4-vinylaniline **87** (90%, 67 mg, 0.50 mmol, 1.0 equiv) in 20 h with 2.5 mol% catalyst **20**. Purification by column chromatography (AcOEt/hexane 1:1) was not successful.

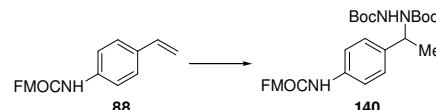
Following GP4 Hydrohydrazination product **139** (144 mg, 81% pure, 0.332 mmol, 66%) was obtained as a colorless solid with 4-vinylaniline **87** (90%, 67 mg, 0.50 mmol, 1.0 equiv) in 4 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:1).

Via Deprotection of 140



A mixture of piperidine (0.16 mL, 1.6 mmol, 9.2 equiv) and DMF (2.8 mL) was added to hydrohydrazination product **140** (100 mg, 0.174 mmol, 1.00 equiv) and the reaction mixture was stirred 14 h at 23 °C. The solvent was removed under reduced pressure and the isolated product was purified by column chromatography (AcOEt/hexane 1:1) to afford **139** (55 mg, 0.16 mmol, 90%) as a colorless solid. R_f (AcOEt/hexane 1:1) 0.35; Mp 62–67 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.12 (d, J = 8.2 Hz, 2H, Ar H), 6.62 (d, J = 8.5 Hz, 2H, Ar H), 5.83 (br s, 1H, hydrazine NH), 5.35 (br m, 1H, CHN), 3.61 (br s, 2H, NH_2), 1.49–1.47 (m, 3H, CHCH_3), 1.47 (s, 9H, CCH_3), 1.44 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.7, 154.8, 145.8, 131.1, 128.4, 114.9, 81.0, 80.7, 55.3, 28.3, 28.1, 16.9; IR ν 3366 (w), 2979 (m), 2933 (w), 1694 (s), 1626 (m), 1548 (w), 1518 (m), 1479 (m), 1454 (m), 1392 (s), 1367 (s), 1317 (m), 1253 (m), 1172 (s), 1048 (w), 1022 (w), 992 (w), 911 (w), 832 (w), 756 (w), 734 (m), 647 (w), 620 (w), 535 (w); MS (ESI) 352.2 (M+H), 374.2 (M+Na), 703.0 (2M+H), 725.0 (2M+Na); Anal. calcd for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{O}_4$: C, 61.52; H, 8.32; N, 11.96. Found: C, 61.81; H, 8.58; N, 11.72.

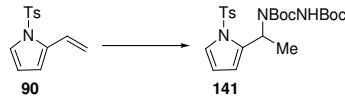
***N*-(4-(9,9a-Dihydro-4a*H*-fluoren-9-ylmethoxycarbonylamino)-phenyl)-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (140)**



Following GP2 Hydrohydrazination product **140** (282 mg, 0.492 mmol, 98%) was obtained as a colorless solid with protected vinylaniline **88** (171 mg, 0.501 mmol, 1.00 equiv) in 4 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/CH₂Cl₂ 1:10). **Following GP4** Hydrohydrazination product **140** (202 mg, 0.352 mmol, 70%) was obtained as a colorless solid with protected vinylaniline **88** (171 mg, 0.501 mmol, 1.00 equiv) in 4 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/CH₂Cl₂ 1:10). Mp 105–112 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.77 (d, J = 7.5 Hz, 2H, Ar H),

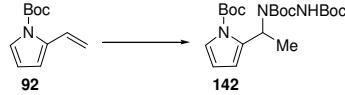
7.61 (d, J = 7.5 Hz, 2H, Ar H), 7.41 (t, J = 7.2 Hz, 2H, Ar H), 7.34-7.25 (m, 6H, Ar H), 6.65 (s, 1H, FMOCNH), 5.88 (br s, 1H, hydrazine NH), 5.40 (br m, 1H, CHN), 4.54 (d, J = 6.5 Hz, 2H, CH_2O), 4.27 (t, J = 6.5 Hz, 1H, CHCH_2O), 1.51 (d, J = 7.2 Hz, 3H, CHNCH_3), 1.48 (s, 9H, CCH_3), 1.45 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.7, 154.8, 153.4, 143.8, 141.5, 137.0, 128.0, 127.8, 127.1, 124.9, 120.0, 119.0, 81.3, 81.0, 66.9, 55.3, 47.3, 28.3, 28.2, 16.9; IR v 3313 (m), 3066 (w), 2979 (m), 2935 (w), 1702 (s), 1601 (m), 1535 (s), 1478 (m), 1451 (m), 1393 (s), 1368 (s), 1316 (s), 1222 (s), 1166 (s), 1106 (w), 1086 (m), 1055 (m), 1018 (w), 993 (w), 910 (m), 841 (w), 758 (m), 737 (s), 668 (w), 648 (w), 622 (w); MS (ESI) 596.0 (M+Na); Anal. calcd for $\text{C}_{33}\text{H}_{39}\text{N}_3\text{O}_6$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.12; H, 7.04; N, 7.08.

N-[1-[1-(Toluene-4-sulfonyl)-1*H*-pyrrol-2-yl]-ethyl]-N'-(*tert*-butoxycarbonyl)hydrazine carboxylic acid *tert*-butyl ester (141)



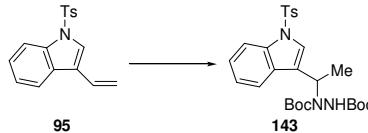
Following GP2 Hydrohydrazination product **141** (168 mg, 0.350 mmol, 74%) was obtained as a colorless solid with vinylpyrrole **90** (96% pure, 122 mg, 0.474 mmol, 1.00 equiv) in 11 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:6). **Following GP4** Hydrohydrazination product **141** (161 mg, 0.336 mmol, 70%) was obtained as a colorless solid with vinylpyrrole **90** (96% pure, 124 mg, 0.481 mmol, 1.00 equiv) in 11 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:6). R_f (AcOEt/hexane 1:5) 0.25; Mp 58-60 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.68 (d, J = 8.1 Hz, 2H, tosyl CH), 7.34 (m, 1H, pyrrole H), 7.28 (d, J = 8.1 Hz, 2H, tosyl CH), 6.31 (m, 1H, pyrrole H), 6.22 (t, J = 3.4 Hz, 1H, pyrrole H), 5.57 (br m, 2H, NH and CHN), 2.40 (s, 3H, tosyl CH_3), 1.51 (s, 9H, CCH_3), 1.46 (m, 3H, CHCH_3), 1.41 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.5, 153.8, 144.7, 136.3, 133.7, 129.8, 126.7, 123.7, 115.4, 110.9, 81.0, 80.6, 49.9, 28.3, 28.2, 21.5, 18.4; IR v 3375 (w), 3153 (w), 2980 (m), 2934 (w), 1748 (m), 1707 (s), 1597 (w), 1479 (m), 1456 (m), 1393 (s), 1368 (s), 1310 (m), 1254 (m), 1176 (s), 1155 (s), 1094 (m), 1080 (m), 1048 (m), 981 (w), 912 (w), 874 (w), 858 (w), 814 (w), 756 (w), 733 (m), 705 (m), 686 (m), 670 (m), 590 (s), 545 (m); MS (ESI) 480.2 (M+H), 502.2 (M+Na), 981.4 (2M+Na); Anal. calcd for $\text{C}_{23}\text{H}_{33}\text{N}_3\text{O}_6\text{S}$: C, 57.60; H, 6.94; N, 8.76. Found: C, 57.68; H, 6.96; N, 8.63.

2-[1-(*N,N'*-Di-*tert*-butoxycarbonyl-hydrazino)-ethyl]-pyrrole-1-carboxylic acid *tert*-butyl ester (142)



Following GP2 Hydrohydrazination product **142** (135 mg, 0.317 mmol, 67%) was obtained as a colorless solid with vinylpyrrole **92** (92% pure, 100 mg, 0.476 mmol, 1.00 equiv) in 11 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:8). **Following GP4** Hydrohydrazination product **142** (146 mg, 0.343 mmol, 73%) was obtained as a colorless solid with vinylpyrrole **92** (92% pure, 99 mg, 0.47 mmol, 1.0 equiv) in 11 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:7). R_f (AcOEt/hexane 1:5) 0.30; Mp 54-55 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.18 (dd, J = 3.1, 1.9 Hz, 1H, pyrrole H), 6.22 (m, 1H, pyrrole H), 6.07 (t, J = 3.1 Hz, 1H, pyrrole H), 5.92 (br m, 2H, NH and CHN), 1.59 (s, 9H, pyrrole-Boc CH_3), 1.52 (d, J = 6.9 Hz, 3H, CHCH_3), 1.46 (s, 9H, hydrazine-Boc CH_3), 1.42 (br s, 9H, hydrazine-Boc CH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.4, 154.2, 134.4, 121.9, 112.9, 109.5, 83.6, 80.6, 51.1, 28.3; 28.2, 28.0, 17.7; IR v 3335 (w), 3159 (w), 2979 (m), 2935 (m), 1748 (s), 1710 (s), 1479 (m), 1456 (m), 1393 (s), 1368 (s), 1328 (s), 1253 (s), 1167 (s), 1137 (s), 1088 (w), 1054 (m), 1013 (m), 987 (m), 912 (m), 883 (w), 851 (m), 819 (w), 772 (m), 733 (m), 648 (w), 597 (w), 564 (w), 486 (w), 458 (w); MS (ESI) 448.3 (M+Na); Anal. calcd for $\text{C}_{21}\text{H}_{35}\text{N}_3\text{O}_6$: C, 59.28; H, 8.29; N, 9.87. Found: C, 59.13; H, 8.34; N, 9.83.

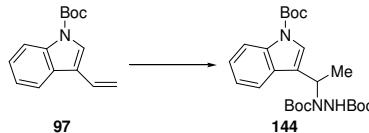
N-[1-[1-(Toluene-4-sulfonyl)-1*H*-indol-3-yl]-ethyl]-N'-(*tert*-butoxycarbonyl)hydrazine carboxylic acid *tert*-butyl ester (143)



Following GP2 Hydrohydrazination product **143** (220 mg, 0.415 mmol, 85%) was obtained as a colorless solid with vinylindole **95** (92% pure, 157 mg, 0.486 mmol, 1.00 equiv) in 11 h with 2.5 mol% catalyst **20** after purification by column chromatography (pentane/CH₂Cl₂/Et₂O 1:1:0.2). **Following GP4** Hydrohydrazination product **143** (126 mg, 0.238 mmol, 51%) was obtained as a colorless solid with vinylindole **95** (92% pure, 150 mg, 0.464 mmol, 1.00 equiv) in 11 h with 1 mol% catalyst **23** after purification by column chromatography (pentane/CH₂Cl₂/Et₂O 1:1:0.2). R_f (AcOEt/hexane 1:3) 0.30; Mp 168-169 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 7.95 (dm, J = 8.1 Hz, 1H, indole CH), 7.75 (d, J = 8.4 Hz, 2H, tosyl CH), 7.57 (br m, 1H, indole CH), 7.51 (s, 1H, indole CH), 7.32-7.18 (m, 2H, indole CH), 7.22 (d, J = 7.8 Hz, 2H, tosyl CH), 5.70 (br m, 2H, NH and CHN), 2.34 (s, 3H, tosyl CH_3), 1.60 (d, J = 6.9 Hz, 3H, CHCH_3), 1.49 (s, 9H, CCH_3), 1.44 (br s, 9H, CCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.4, 154.3, 144.7, 135.3, 135.3, 129.7, 126.6, 124.7, 124.5, 123.3, 122.7, 120.1, 113.6, 81.3, 80.9, 48.5, 28.3, 28.1, 21.5, 16.7; IR v 3354 (w), 3153 (w), 3053 (w), 2980 (m), 2934 (w), 1698 (s), 1598 (w), 1564 (w), 1494 (m), 1477 (m), 1450 (s), 1393 (s), 1368 (s), 1313 (s), 1279 (m), 1256 (m), 1214 (m), 1175 (s), 1129 (s), 1091 (s), 1060 (m), 1020 (m), 995 (w), 960 (m), 911 (m), 856 (w),

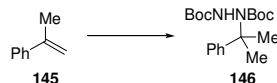
843 (w), 813 (m), 734 (s), 704 (w), 670 (s), 648 (w), 618 (w), 578 (s), 538 (m); MS (ESI) 552.0 (M+Na); Anal. calcd for $C_{27}H_{35}N_3O_6S$: C, 61.23; H, 6.66; N, 7.93. Found: C, 61.13; H, 6.85; N, 7.78.

3-[1-(*N,N'*-Di-*tert*-butoxycarbonyl-hydrazino)-ethyl]-indole-1-carboxylic acid *tert*-butyl ester (144)



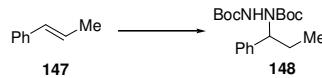
Following GP2 Hydroxylation product **144** (172 mg, 0.362 mmol, 76%) was obtained as a colorless solid with vinylindole **97** (92% pure, 126 mg, 0.476 mmol, 1.00 equiv) in 11 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:7). **Following GP4** Hydroxylation product **144** (169 mg, 0.355 mmol, 73%) was obtained as a colorless solid with vinylindole **97** (92% pure, 128 mg, 0.484 mmol, 1.00 equiv) in 11 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:7). R_f (AcOEt/hexane 1:5) 0.40; Mp 79-80 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 8.12 (d, J = 8.1 Hz, 1H, indole CH), 7.61 (br m, 1H, indole CH), 7.51 (s, 1H, indole CH), 7.33-7.18 (m, 2H, indole CH), 5.75 (br m, 2H, NH and CHN), 1.69 (s, 9H, indole-Boc CH₃), 1.61 (d, J = 6.8 Hz, 3H, CHCH₃), 1.52 (s, 9H, hydrazine-Boc CH₃), 1.44 (br s, 9H, hydrazine-Boc CH₃); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.4, 154.3, 149.5, 135.5, 129.3, 124.4, 123.9, 122.6, 120.7, 119.5, 115.1, 83.7, 81.1, 80.7, 48.7, 28.3, 28.3, 16.8; IR v 3326 (w), 3159 (w), 3053 (w), 2980 (s), 2935 (m), 1732 (s), 1609 (w), 1570 (w), 1478 (m), 1455 (s), 1369 (s), 1310 (s), 1256 (s), 1224 (s), 1160 (s), 1108 (s), 1064 (m), 1026 (m), 1010 (m), 973 (w), 911 (m), 857 (m), 768 (m), 734 (s), 648 (w), 582 (w), 457 (w); MS (ESI) 498.2 (M+Na); Anal. calcd for $C_{25}H_{37}N_3O_6$: C, 63.14; H, 7.84; N, 8.84. Found: C, 63.05; H, 7.84; N, 8.66.

***N*-(1-Methyl-1-phenyl-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (146)**



Following GP2 Hydroxylation product **146** (155 mg, 0.443 mmol, 88%) was obtained as a viscous oil with α -methyl styrene (**145**) (freshly filtered through neutral Al_2O_3 , 65 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 5 mol% catalyst after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.33; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.45 (d, J = 7.5 Hz, 2H, Ar H), 7.27 (t, J = 7.5 Hz, 2H, Ar H), 7.16 (t, J = 7.5 Hz, 2H, Ar H), 6.42 (br s, 1H, NH), 1.71 (s, 3H, CNCH₃), 1.56 (s, 3H, CNCH₃), 1.52 (s, 9H, CCH₃), 1.16 (s, 9H, CCH₃); ^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ 156.6, 154.6, 149.0, 127.9, 125.9, 124.6, 81.0, 63.8, 28.7, 28.3, 28.0, 27.9; IR v 3269 (m), 3089 (w), 3061 (w), 2979 (s), 2933 (m), 2175 (w), 1949 (w), 1712 (s), 1602 (w), 1495 (m), 1479 (m), 1450 (m), 1390 (s), 1367 (s), 1341 (s), 1250 (s), 1158 (s), 1114 (m), 1097 (m), 1078 (m), 1047 (m), 1019 (m), 911 (m), 857 (w), 764 (m), 734 (m), 700 (s), 648 (w), 602 (w); HRMS (ESI) calcd for $C_{19}H_{30}N_2O_4Na^+$ (M+Na) 373.2098, found 373.2103; Anal. calcd for $C_{19}H_{30}N_2O_4$: C, 65.12; H, 8.63; N, 7.99. Found: C, 65.23; H, 8.50; N, 8.10.

***N*-(1-Phenyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (148)**



Following GP1 Hydroxylation product **148** (154 mg, 0.440 mmol, 88%) was obtained as a colorless solid with β -methylstyrene (**147**) (65 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP2** Hydroxylation product **148** (165 mg, 0.471 mmol, 94%) was obtained as a colorless solid with β -methyl-styrene (**147**) (65 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.30; Mp 97-98 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.33-7.22 (m, 5H, Ar H), 5.78 (br s, 1H, NH), 5.12 (br m, 1H, CHN), 2.11-1.81 (m, 2H, CH₂), 1.47 (s, 9H, CCH₃), 1.43 (br s, 9H, CCH₃), 0.96 (t, J = 7.2 Hz, 3H, CH₂CH₃); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.5, 154.9, 139.6, 128.2, 128.2, 127.4, 81.2, 80.8, 62.3, 28.4, 28.2, 24.0, 11.3; IR v 3221 (m), 3151 (m), 2970 (m), 2935 (m), 2878 (w), 1714 (s), 1694 (s), 1497 (m), 1478 (m), 1456 (m), 1404 (s), 1366 (s), 1319 (s), 1283 (m), 1258 (m), 1169 (s), 1138 (s), 1082 (m), 1050 (m), 1017 (m), 942 (m), 907 (w), 875 (m), 767 (m), 749 (m), 698 (s), 632 (m), 603 (w), 521 (w); HRMS (ESI) calcd for $C_{19}H_{30}N_2O_4Na^+$ (M+Na) 373.2098, found 373.2090; Anal. calcd for $C_{19}H_{30}N_2O_4$: C, 65.12; H, 8.63; N, 7.99. Found: C, 64.88; H, 8.43; N, 8.03.

***N*-(3-Hydroxy-1-phenyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (150)**



Following GP1 Hydroxylation product **150** (167 mg, 0.456 mmol, 91%) was obtained as a colorless solid with cinnamyl alcohol (**149**) (67 mg, 0.50 mmol, 1.0 equiv) in 1 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:5-1:1). R_f (AcOEt/hexane 1:2) 0.20; Mp 102-104 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.31-7.21 (m, 5H, Ar H), 5.96 (br s, 1H, NH), 5.40 (br s, 1H, CHN), 3.89 (br s, 1H, CH₂OH), 3.73 (br s, 1H, CH₂OH), 3.18 (br s, 1H, CH₂OH), 2.22 (br m, 1H, CHNCH₂), 1.99 (br m, 1H, CHNCH₂), 1.46 (s, 9H, CCH₃), 1.42 (br s, 9H, CCH₃); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.6, 155.3, 139.3, 128.2, 127.9, 127.5, 81.6, 81.1, 59.7, 57.4, 33.7, 28.3, 28.1; IR v 3425 (w, sh), 3306 (m), 3032 (w), 2979 (m), 2933 (m), 1703 (s), 1478 (m), 1455 (m), 1393 (s), 1368 (s), 1324 (s), 1253 (s), 1162 (s), 1050 (m), 912 (m), 863 (w), 734

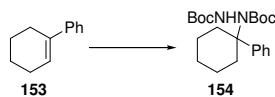
(m), 700 (m); MS (ESI) 367.1 (M+H), 389.2 (M+Na), 755.1 (2M+Na); Anal. calcd for $C_{19}H_{30}N_2O_5$: C, 62.27; H, 8.25; N, 7.64. Found: C, 62.20; H, 8.18; N, 7.60.

N-(1H-Inden-1-yl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (152)



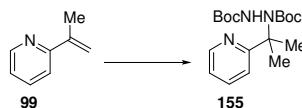
Following GP1 Hydroboration product **152** (163 mg, 0.468 mmol, 94%) was obtained as a colorless solid with indene (**151**) (59 μ L, 0.50 mmol, 1.0 equiv) in 1 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.35; Mp 93–95 $^{\circ}$ C; 1H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 7.22–7.14 (m, 4H, Ar H), 5.93 (br s, 1H, NH), 5.76 (br s, 1H, CHN), 3.00 (m, 1H, CH_2), 2.81 (m, 1H, CH_2), 2.38 (m, 1H, CH_2), 2.17 (m, 1H, CH_2), 1.51 (s, 9H, CCH_3), 1.42 (br s, 9H, CCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.5, 155.1, 144.1, 141.2, 127.9, 126.4, 124.8, 124.2, 81.3, 80.9, 63.1, 30.5, 29.0, 28.3, 28.1; IR v 3314 (m), 3072 (w), 2979 (m), 2933 (m), 1705 (s), 1480 (m), 1458 (m), 1393 (s), 1367 (s), 1332 (m), 1297 (m), 1246 (s), 1161 (s), 1052 (m), 1020 (w), 940 (w), 920 (w), 854 (w), 830 (w), 758 (m), 737 (m), 647 (w), 591 (w); MS (ESI) 349.3 (M+H), 371.1 (M+Na); Anal. calcd for $C_{19}H_{28}N_2O_4$: C, 65.49; H, 8.10; N, 8.04. Found: C, 65.31; H, 8.13; N, 7.87.

N-(1-Phenyl-cyclohexyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (154)



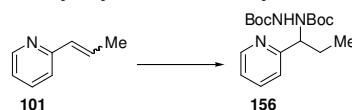
Following GP1 Hydroboration product **154** (157 mg, 0.403 mmol, 80%) was obtained as a colorless viscous oil with 1-phenyl cyclohexene (**153**) (80 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (97 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.26 g, 1.1 mmol, 2.2 equiv) in 8 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.35; 1H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 7.46 (d, J = 7.5 Hz, 2H, Ar H), 7.27 (m, 2H, Ar H), 7.17 (m, 1H, Ar H), 6.11 (br s, 1H, NH), 2.52 (m, 1H, CH_2), 2.35–2.06 (m, 3H, CH_2), 1.83–1.34 (m, 6H, CH_2), 1.47 (s, 9H, CCH_3), 1.26 (s, 9H, CCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 156.3, 155.0, 145.7, 127.9, 126.4, 126.4, 81.0, 80.8, 66.3, 36.1, 35.6, 28.2, 28.0, 25.7, 23.0, 22.7; IR v 3263 (m), 3156 (w), 3093 (w), 3059 (w), 2977 (s), 2933 (s), 2866 (m), 1705 (s), 1602 (w), 1479 (m), 1454 (s), 1392 (s), 1367 (s), 1332 (s), 1248 (s), 1163 (s), 1108 (m), 1085 (m), 1047 (m), 1015 (m), 911 (m), 884 (w), 857 (w), 754 (m), 734 (s), 700 (m), 647 (w), 613 (w), 576 (w), 529 (w); MS (ESI) 413.2 (M+Na); Anal. calcd for $C_{22}H_{34}N_2O_4$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.67; H, 8.92; N, 7.45.

N-(1-Methyl-1-pyridin-2-yl-ethyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (155)



Following GP2 Hydroboration product **155** (106 mg, 0.302 mmol, 60%) was obtained as a colorless gel with vinylpyridine **99** (60 mg, 0.50 mmol, 1.0 equiv) in 5 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:4). **Following GP4** Hydroboration product **155** (75 mg, 0.21 mmol, 42%) was obtained as a colorless gel with vinylpyridine **99** (60 mg, 0.50 mmol, 1.0 equiv) in 5 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:4). 1H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 8.42 (m, 1H, pyridine CH), 7.66–7.54 (m, 2H, pyridine CH), 7.04 (m, 1H, pyridine CH), 6.65 (br s, 1H, NH), 1.74 (s, 3H, $C(CH_3)_2$), 1.54 (s, 3H, $C(CH_3)_2$), 1.48 (s, 9H, $OC(CH_3)_3$), 1.15 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 $^{\circ}$ C) δ 166.5, 156.3, 154.7, 147.7, 136.1, 121.0, 119.9, 80.9, 80.5, 65.3, 28.3, 27.9, 27.2; IR v 3286 (m), 3053 (w), 2980 (s), 2934 (s), 1715 (s), 1593 (s), 1571 (m), 1480 (s), 1430 (s), 1368 (s), 1249 (s), 1157 (s), 1082 (m), 1048 (m), 1020 (m), 995 (w), 911 (m), 858 (w), 839 (w), 788 (m), 733 (s), 647 (m), 605 (s); MS (ESI) 374.4 (M+Na); Anal. calcd for $C_{18}H_{29}N_3O_4$: C, 61.52; H, 8.32; N, 11.96. Found: C, 61.44; H, 8.36; N, 11.86.

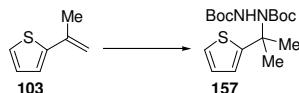
N-(1-pyridin-2-yl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (156)



Following GP2 Hydroboration product **156** (96 mg, 0.27 mmol, 54%) was obtained as a colorless gel with vinylpyridine **101** (60 mg, 0.50 mmol, 1.0 equiv) in 5 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:2). **Following GP4** Hydroboration product **156** (94 mg, 0.27 mmol, 54%) was obtained as a colorless gel with vinylpyridine **101** (60 mg, 0.50 mmol, 1.0 equiv) in 5 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:4). R_f (AcOEt/hexane 1:2) 0.40; 1H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 8.50 (dm, J = 4.8 Hz, 1H, pyridine CH), 7.61 (td, J = 7.7, 1.8 Hz, 1H, pyridine CH), 7.23 (m, 1H, pyridine CH), 7.14 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H, pyridine CH), 6.84 (br s, 1H, NH), 5.11 (br m, 1H, CHN), 2.04–1.92 (m, 2H, CH_2), 1.46 (s, 9H, $OC(CH_3)_3$), 1.41 (s, 9H, $OC(CH_3)_3$), 1.02 (t, J = 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 $^{\circ}$ C) δ 160.5, 156.0, 155.0, 148.9, 136.1, 122.0, 122.0, 81.0, 80.2, 62.8, 28.1, 28.0, 24.8, 11.1; IR v 3306 (w), 3054 (w), 2978 (m), 2934 (m), 2879 (w), 1746 (s), 1710 (s), 1642 (w), 1592 (m), 1572 (m), 1548 (w), 1512

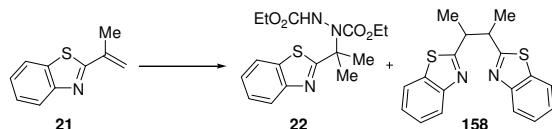
(w), 1478 (m), 1461 (m), 1435 (m), 1392 (s), 1367 (s), 1333 (m), 1307 (m), 1254 (s), 1163 (s), 1104 (m), 1050 (m), 1017 (m), 996 (w), 940 (w), 920 (w), 858 (w), 758 (m), 647 (w), 602 (w), 534 (w); MS (ESI) 374.2 (M+Na); Anal. calcd for $C_{18}H_{29}N_3O_4$: C, 61.52; H, 8.32; N, 11.96. Found: C, 61.55; H, 8.44; N, 11.78.

***N*-(1-Methyl-1-thiophen-2-yl-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (157)**



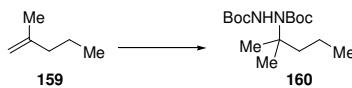
Following GP2 Hydrohydrazination product **157** (103 mg, 0.289 mmol, 58%) was obtained as a colorless gel with vinylthiophene **103** (62 mg, 0.50 mmol, 1.0 equiv) in 7 h with 2.5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:6). **Following GP4** Hydrohydrazination product **157** (110 mg, 0.309 mmol, 62%) was obtained as a colorless gel with vinylthiophene **103** (62 mg, 0.50 mmol, 1.0 equiv) in 7 h with 1 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:6). ¹H NMR (CDCl₃, 300 MHz, 25 °C) δ 7.11 (m, 1H, thiophene CH), 6.95-6.87 (m, 2H, thiophene CH), 6.35-6.00 (br s, 1H, NH), 1.89 (s, 3H, C(CH₃)₂), 1.65 (s, 3H, C(CH₃)₂), 1.49 (s, 9H, OC(CH₃)₃), 1.29 (s, 9H, OC(CH₃)₃); ¹³C NMR (CDCl₃, 75 MHz, 25 °C) δ 156.0, 154.1, 153.7, 126.0, 122.6, 122.1, 81.3, 80.8, 62.0, 30.5, 29.0, 28.3, 28.1; IR ν 3273 (m), 2980 (s), 2933 (m), 1714 (s), 1479 (m), 1456 (m), 1391 (s), 1367 (s), 1249 (s), 1156 (s), 1106 (m), 1080 (m), 1047 (m), 1018 (m), 911 (m), 853 (m), 831 (w), 734 (m), 693 (m), 647 (w), 621 (w); MS (ESI) 379.4 (M+Na); Anal. calcd for C₁₇H₂₈N₂O₄S: C, 57.28; H, 7.92; N, 7.86. Found: C, 57.05; H, 8.08; N, 7.74.

***N*-(1-Benzothiazol-2-yl-1-methyl-ethyl)-*N'*-(ethoxycarbonyl)hydrazinecarboxylic acid ethyl ester (158)**



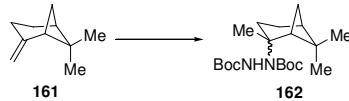
Following GP2 (slightly modified) The hydrohydrazination reaction of **21** under standard conditions **GP2** or **GP4** with di-*tert*-butyl azodicarboxylate (**2**) was not successful due to extensive dimerization of **21**. However, hydrohydrazination product **22** (95 mg, 0.27 mmol, 54%) was obtained as a colorless solid with vinyl benzothiazole **21** (88 mg, 0.50 mmol, 1.0 equiv), diethyl azodicarboxylate (0.24 mL, 1.5 mmol, 3.0 equiv) and phenylsilane (0.13 mL, 1.0 mmol, 2.0 equiv) in 2 d with 0.25 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:3). About 30% of dimer **158** was still detected in the crude mixture *via* ¹H-NMR. R_f (AcOEt/hexane 1:2) 0.25; Mp 43–45 °C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.95 (dd, *J* = 8.1, 0.6 Hz, 1H, Ar H), 7.82 (dt, *J* = 8.1, 0.6 Hz, 1H, Ar H), 7.43 (m, 1H, Ar H), 7.33 (m, 1H, Ar H), 6.77 (br s, 1H, NH), 4.35–4.20 (m, 2H, CH₂), 4.10–4.00 (m, 2H, CH₂), 2.03 (s, 3H, C(CH₃)₂), 1.75 (s, 3H, C(CH₃)₂), 1.36–1.26 (m, 3H, CH₂CH₃), 1.12–1.03 (m, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 178.0, 156.8, 155.3, 152.6, 135.2, 125.6, 124.6, 122.8, 121.4, 65.0, 62.4, 62.1, 28.5, 27.4, 14.5, 14.2; IR ν 3299 (m), 3063 (w), 2986 (m), 2938 (w), 1723 (s), 1519 (m), 1456 (m), 1440 (m), 1402 (m), 1377 (m), 1339 (m), 1314 (m), 1255 (s), 1190 (m), 1174 (m), 1098 (s), 1057 (m), 1015 (m), 915 (m), 865 (w), 824 (w), 762 (m), 731 (m), 647 (w), 522 (w); MS (ESI) 374.1 (M+Na); Anal. calcd for C₁₆H₂₁N₃O₄S: C, 54.68; H, 6.02; N, 11.96. Found: C, 54.50; H, 6.18; N, 11.79. Characteristic ¹H-NMR peaks for dimer **158**: ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 8.02 (d, *J* = 8.1 Hz, 2H, Ar H), 7.75 (dm, *J* = 8.1 Hz, 2H, Ar H), 7.44 (m, 2H, Ar H), 7.31 (m, 2H, Ar H), 1.71 (s, 12H, C(CH₃)₂).

***N*-(1,1-Dimethyl-butyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (160)**



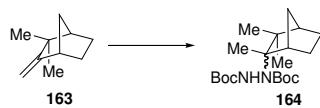
Following GP1 Hydrohydrazination product **160** (140 mg, 0.443 mmol, 88%) was obtained as a colorless solid with 2-methylpentene (**159**) (62 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (90 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **160** (137 mg, 0.433 mmol, 86%) was obtained as a colorless solid with 2-methylpentene (**159**) (62 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.50; Mp 63–64 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.10 (br s, 1H, NH), 1.87 (td, J = 11.9, 4.9 Hz, 1H, CH_2CN), 1.59 (td, J = 11.9, 4.9 Hz, 1H, CH_2CN), 1.44 (s, 9H, $OCCH_3$), 1.43 (s, 9H, $OCCH_3$), 1.39 (s, 3H, $CNCH_3$), 1.36–1.08 (m, 2H, CH_2CH_3), 1.22 (s, 1H, $CNCH_3$), 0.87 (t, J = 7.5 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 156.0, 154.5, 80.5, 62.1, 42.8, 28.4, 28.3, 27.0, 26.4, 17.9, 14.5; IR ν 3340 (m), 3272 (m), 3158 (w), 2978 (s), 2933 (m), 2874 (m), 1701 (s), 1477 (m), 1456 (m), 1392 (s), 1367 (s), 1272 (s), 1252 (s), 1166 (s), 1085 (s), 1064 (m), 1047 (m), 1018 (m), 911 (m), 860 (m), 786 (m), 764 (m), 736 (m), 679 (w), 647 (w), 603 (w), 560 (w); MS (ESI) 317.3 (M+H), 339.2 (M+Na); Anal. calcd for $C_{16}H_{32}N_2O_4$: C, 60.73; H, 10.19; N, 8.85. Found: C, 60.70; H, 10.06; N, 8.75.

(1*R*,5*S*)-*N*-(2,6,6-Trimethyl-bicyclo[3.1.1]hept-2-yl)-*N*'-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (162)



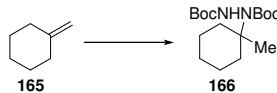
Following GP1 Hydroboration product **162** (155 mg, 0.421 mmol, 84 %, mixture of diastereoisomers (1:2-1:3)) was obtained as a colorless viscous oil with L- β -Pinene (**161**) (78 μ L, 0.50 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.65; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.03 (br s, 1H, NH), 2.52-2.09 (m, 3H, CH_2 or CH), 1.88-1.75 (m, 2H, CH_2 or CH), 1.82 (s, 3H, $CNCH_3$), 1.52 (m, 2H, CH_2 or CH), 1.45 (s, 9H, $OCCH_3$), 1.45 (s, 9H, $OCCH_3$), 1.44 (s, 9H, $OCCH_3$), 1.43 (s, 9H, $OCCH_3$), 1.25 (s, 3H, $C(CH_3)_2$), 1.13 (m, 1H, CH_2 or CH), 1.01 (s, 3H (33%), $C(CH_3)_2$ 1. diastereoisomer), 0.99 (s, 3H (66%), $C(CH_3)_2$ 2. diastereoisomer); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.8, 154.6, 80.5, 68.0, 67.8, 52.1, 51.9, 40.0, 39.4, 38.5, 37.8, 30.0, 29.2, 28.9, 28.5, 28.4, 28.4, 27.0, 26.8, 26.5, 26.3, 23.8, 23.7; IR ν 3333 (m), 3267 (m), 3157 (w), 2979 (s), 2932 (s), 2870 (m), 1707 (s), 1478 (m), 1456 (m), 1391 (s), 1367 (s), 1251 (s), 1163 (s), 1072 (m), 1049 (m), 1012 (m), 920 (m), 858 (m), 783 (m), 762 (m), 734 (m), 647 (w); HRMS (ESI) calcd for $C_{20}H_{36}N_2O_4Na^+$ (M+Na) 391.2567, found 391.2555; Anal. calcd for $C_{20}H_{36}N_2O_4$: C, 65.19; H, 9.85; N, 7.60. Found: C, 64.98; H, 9.98; N, 7.50.

(1*S*,4*R*)-*N*-(2,3,3-Trimethyl-bicyclo[2.2.1]hept-2-yl)-*N*'-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (164)



Following GP1 Hydroboration product **164** (124 mg, 0.337 mmol, 70 %, mixture of diastereoisomers (1:5)) was obtained as a colorless solid with D-camphene (**163**) (94%, 70 mg, 0.48 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.50; Mp 113-114 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.08-5.91 (br s, 1H, NH), 2.22 (m, 2H, CH_2 or CH), 1.92-1.11 (m, 9H, CH_2 or CH), 1.47 (s, 9H, $OCCH_3$), 1.44 (s, 9H, $OCCH_3$), 1.05 (s, 3H (82%), CCH_3 1. diastereoisomer), 1.02 (s, 3H (18%), CCH_3 2. diastereoisomer), 0.97 (s, 3H, CCH_3); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 156.2, 155.4, 80.5, 72.9, 72.2, 51.7, 50.6, 48.2, 47.3, 36.7, 35.0, 28.4, 28.4, 27.2, 26.8, 24.8, 22.6, 22.0, 19.5; IR ν 3262 (m), 3156 (w), 2978 (s), 2937 (m), 1704 (s), 1478 (m), 1455 (m), 1391 (s), 1367 (s), 1335 (s), 1253 (s), 1171 (s), 1067 (m), 1047 (m), 1018 (m), 910 (m), 860 (w), 782 (w), 765 (w), 734 (m), 648 (w), 618 (w), 569 (w); MS (ESI) 369.2 (M+H); Anal. calcd for $C_{20}H_{36}N_2O_4$: C, 65.19; H, 9.85; N, 7.60. Found: C, 65.02; H, 9.82; N, 7.39.

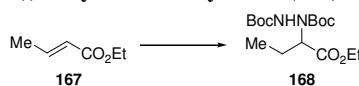
***N*-(1-Methyl-cyclohexyl)-*N*'-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (166)**



Following GP1

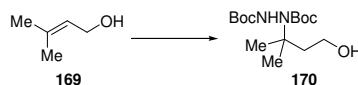
Hydroboration product **166** (147 mg, 0.448 mmol, 90%) was obtained as a colorless solid with methylene cyclohexane (**165**) (60 μ L, 0.50 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.54; Mp 101-102 °C; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.11 (br s, 1H, NH), 2.17 (m, 1H, CH_2), 1.98 (m, 1H, CH_2), 1.68-1.37 (m, 8H, CH_2), 1.47 (s, 9H, $OCCH_3$), 1.45 (s, 9H, $OCCH_3$), 1.37 (s, 3H, $CNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 156.3, 80.5, 62.1, 36.8, 36.2, 28.4, 28.3, 25.8, 23.9, 23.2, 22.7; IR ν 3344 (w), 2978 (m), 2932 (m), 2863 (w), 1705 (s), 1479 (m), 1454 (m), 1391 (m), 1366 (s), 1341 (s), 1252 (s), 1163 (s), 1083 (m), 1069 (m), 1048 (w), 1018 (w), 962 (w), 908 (w), 857 (w), 783 (w), 762 (w), 734 (w); MS (ESI) 329.4 (M+H), 351.3 (M+Na); Anal. calcd for $C_{17}H_{32}N_2O_4$: C, 62.17; H, 9.82; N, 8.53. Found: C, 62.29; H, 9.54; N, 8.50.

2-(*N*,*N*'-Bis-(*tert*-butoxycarbonyl-hydrazino))-butyric acid ethyl ester (168)



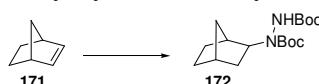
Following GP1 Hydroboration product **168** (113 mg, 0.327 mmol, 66%) was obtained as a colorless viscous oil with *trans*-ethyl crotonate (**167**) (62 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (90 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 12 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydroboration product **168** (154 mg, 0.445 mmol, 88%) was obtained as a colorless viscous oil with *trans*-ethyl crotonate (**167**) (62 μ L, 0.50 mmol, 1.0 equiv) in 6 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.30; 1 H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.32 (br s, 1H, NH), 4.61 (br s, 1H, CHN), 4.23-4.10 (m, 2H, OCH_2), 1.97-1.75 (m, 1H, CH_2CHN), 1.48 (s, 9H, $OCCH_3$), 1.48 (s, 9H, $OCCH_3$), 1.28 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.10 (t, J = 7.5 Hz, 3H, $CHNCH_2CH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 171.7, 155.5, 81.7, 80.8, 61.1, 28.3, 28.2, 22.4, 14.2, 11.2; IR ν 3326 (w), 2980 (m), 2936 (m), 1738 (s), 1714 (s), 1479 (m), 1393 (m), 1368 (s), 1330 (m), 1299 (m), 1237 (m), 1155 (s), 1087 (m), 1021 (m), 940 (w), 856 (w), 782 (w), 700 (w); HRMS (ESI) calcd for $C_{16}H_{30}N_2O_6Na^+$ (M+Na) 369.1996, found 369.2000; Anal. calcd for $C_{16}H_{30}N_2O_6$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.68; H, 8.53; N, 8.00.

***N*-(3-Hydroxy-1,1-dimethyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (170)**



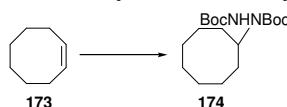
Following GP1 Hydrohydrazination product **170** (111 mg, 0.350 mmol, 70%) was obtained as a colorless solid with 2-methyl-2-butene-4-ol (**169**) (51 μ L, 0.50 mmol, 1.0 equiv) in 8 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:7-1:2). R_f (AcOEt/hexane 1:2) 0.18; Mp 100-101 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.37 (br s, 1H, NH), 3.77-3.71 (m, 2H, CH_2OH), 3.18 (br s, 1H, OH), 2.22 (br s, 1H, CH_2CN), 1.86 (br s, 1H, CH_2CN), 1.45 (s, 9H, $OCCH_3$), 1.44 (s, 9H, $OCCH_3$), 1.40 (s, 3H, $CNCH_3$), 1.30 (s, 3H, $CNCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 156.7, 154.6, 81.0, 61.0, 59.4, 42.2, 28.4, 28.3, 27.9, 27.5; IR ν 3447 (m, sh), 3329 (m), 2980 (s), 2933 (m), 1713 (s), 1479 (m), 1456 (m), 1392 (s), 1368 (s), 1255 (s), 1161 (s), 1081 (s), 1050 (m), 1023 (m), 976 (w), 911 (m), 858 (w), 785 (w), 763 (m), 734 (m), 647 (w), 609 (w); MS (ESI) 341.3 (M+Na); Anal. calcd for $C_{15}H_{30}N_2O_5$: C, 56.58; H, 9.50; N, 8.80. Found: C, 56.51; H, 9.54; N, 8.83.

***N*-(Bicyclo[2.2.1]hept-2-yl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (172)**



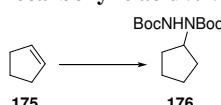
Following GP1 Hydrohydrazination product **172** (103 mg, 0.316 mmol, 66%) was obtained as a colorless solid with norbornene (**171**) (45 mg, 0.48 mmol, 1.0 equiv) in 7 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **172** (179 mg, 0.548 mmol, 98%) was obtained as a colorless solid with norbornene (**171**) (53 mg, 0.56 mmol, 1.0 equiv) in 7 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.40; Mp 169-170 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.06 (br s, 1H, NH), 3.92 (m, 1H, CHN), 2.35-2.23 (m, 2H, CH), 1.68-1.08 (m, 8H, CH_2), 1.47 (s, 9H, $OCCH_3$), 1.46 (s, 9H, $OCCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.7, 155.1, 80.8, 60.6, 41.2, 37.2, 36.2, 35.8, 28.4, 28.3, 27.9; IR ν 3318 (w), 2958 (m), 2874 (m), 1701 (s), 1516 (m), 1479 (m), 1454 (w), 1410 (m), 1392 (m), 1366 (s), 1348 (s), 1286 (s), 1253 (s), 1163 (s), 1130 (m), 1111 (m), 1067 (m), 966 (m), 918 (w), 898 (w), 859 (w), 834 (w), 784 (w), 760 (w), 735 (w), 600 (w); MS (ESI) 327.2 (M+H), 349.3 (M+Na); Anal. calcd for $C_{17}H_{30}N_2O_4$: C, 62.55; H, 9.26; N, 8.58. Found: C, 62.70; H, 8.98; N, 8.50.

***N*-(Cyclooctyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (174)**



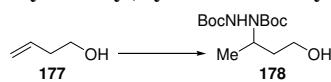
Following GP1 Hydrohydrazination product **174** (104 mg, 0.304 mmol, 62%) was obtained as a colorless solid with cyclooctene (**173**) (freshly distilled, 65 μ L, 0.49 mmol, 1.0 equiv), phenylsilane (95 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 24 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **174** (163 mg, 0.476 mmol, 95%) was obtained as a colorless solid with cyclooctene (**173**) (freshly distilled, 65 μ L, 0.49 mmol, 1.0 equiv) in 2.5 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10).

***N*-(Cyclopentyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (176)**



Following GP1 Hydrohydrazination product **176** (111 mg, 0.370 mmol, 74 %) was obtained as a colorless solid with cyclopentene (**175**) (44 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (95 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 8 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **176** (141 mg, 0.469 mmol, 94 %) was obtained as a colorless solid with cyclopentene (**175**) (44 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.40; Mp 154-155 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.00 (br s, 1H, NH), 4.46 (m, 1H, CHN), 1.83-1.26 (m, 8H, CH_2), 1.48 (s, 9H, $OCCH_3$), 1.47 (s, 9H, $OCCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.9, 154.9, 80.8, 59.0, 29.1, 28.4, 28.3, 23.8; IR ν 3312 (w), 2976 (m), 2869 (m), 1700 (s), 1517 (m), 1480 (w), 1453 (w), 1405 (s), 1366 (m), 1345 (m), 1292 (m), 1250 (m), 1157 (s), 1126 (m), 1054 (w), 1028 (w), 948 (w), 894 (w), 858 (w), 758 (w), 736 (w), 607 (w); MS (ESI) 301.2 (M+H), 323.2 (M+Na), 623.2 (2M+Na); Anal. calcd for $C_{15}H_{28}N_2O_4$: C, 59.98; H, 9.39; N, 9.33. Found: C, 60.07; H, 9.39; N, 9.15.

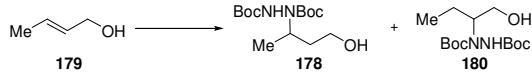
***N*-(3-Hydroxy-1-methyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (178)**



Following GP1 Hydrohydrazination product **178** (34 mg, 0.11 mmol, 22%) was obtained as a colorless viscous oil with but-1-ene-4-ol (**177**) (43 μ L, 0.50 mmol, 1.0 equiv) in 12 h with 5 mol% catalyst **20** after purification by column chromatography

(AcOEt/hexane 1:2). **Following GP3** Hydrohydrazination product **178** (111 mg, 0.36 mmol, 72%) was obtained as a colorless viscous oil with but-1-ene-4-ol (**177**) (43 μ L, 0.50 mmol, 1.0 equiv) in 2.5 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:2). **Following GP3, but with PMHS** Hydrohydrazination product **178** (90 mg, 0.30 mmol, 60%) was obtained as colorless viscous oil with but-1-ene-4-ol (**177**) (43 μ L, 0.50 mmol, 1.0 equiv) and PMHS (0.10 mL, 1.6 H equiv) in 10 h at 23 °C with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:2). R_f (AcOEt/hexane 1:2) 0.20; 1 H NMR (CDCl₃, 300 MHz, 52 °C) δ 6.11 (br s, 1H, NH), 4.38 (br s, 1H, CHN), 3.73-3.63 (m, 2H, CH₂OH), 2.77 (br s, 1H, OH), 1.68-1.51 (m, 2H, CH₂CN), 1.47 (s, 9H, OCCH₃), 1.47 (s, 9H, OCCH₃), 1.15 (d, J = 6.9 Hz, 3H, CNCH₃); 13 C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.9, 155.6, 81.4, 81.1, 59.7, 50.0, 37.2, 28.3, 18.3; IR v 3449 (w, sh), 3312 (m), 2979 (m), 2935 (m), 1705 (s), 1479 (m), 1456 (m), 1394 (s), 1368 (s), 1251 (s), 1162 (s), 1080 (m), 1047 (m), 1017 (m), 914 (w), 854 (w), 761 (w), 735 (m), 647 (w), 577 (w); HRMS(ESI) calcd for C₁₄H₂₈N₂O₅Na⁺ (M+Na) 327.1890, found 327.1888; Anal. calcd for C₁₄H₂₈N₂O₅; C, 55.24; H, 9.27; N, 9.20. Found: C, 55.40; H, 9.51; N, 8.93.

N-(3-Hydroxy-1-methyl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (178**) and *N*-(2-Hydroxy-1-ethyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazine carboxylic acid *tert*-butyl ester (**180**)**



Following GP1 Hydrohydrazination product **178** (67 mg, 0.22 mmol, 44%) was obtained as a colorless viscous oil together with the regiosomeric product **180** (15 mg, 0.05 mmol, 10%) with crotol alcohol (**179**) (43 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (0.12 mL, 1.0 mmol, 2.0 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.34 g, 1.5 mmol, 3.0 equiv) in 24 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:3). **Following GP3** Hydrohydrazination product **178** (88 mg, 0.29 mmol, 58%) was obtained as a colorless viscous oil together with the regiosomeric product **180** (49 mg, 0.16 mmol, 32%, colorless solid) with crotol alcohol (**179**) (43 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst after purification by column chromatography (AcOEt/hexane 1:6-1:1).

N-(2-Hydroxy-1-ethyl-ethyl)-N'-(tert-butoxycarbonyl)hydrazine carboxylic acid *tert*-butyl ester (180**)**

R_f (AcOEt/hexane 1:2) 0.33; Mp 144-145 °C; 1 H NMR (CDCl₃, 300 MHz, 52 °C) δ 6.17 (br s, 1H, NH), 4.12 (br s, 1H, CHN), 3.42-3.39 (m, 2H, CH₂OH), 1.48 (s, 9H, OCCH₃), 1.46 (s, 9H, OCCH₃), 1.40-1.23 (m, 2H, CH₂CH₃), 0.86 (t, J = 7.5 Hz, 3H, CH₂CH₃); 13 C NMR (CDCl₃, 75 MHz, 25 °C) δ 158.3, 157.7, 156.1, 155.2, 82.3, 82.1, 81.8, 81.2, 62.2, 61.9, 59.8, 28.2, 28.1, 22.0, 21.2, 10.6; IR v 3363 (w), 3206 (w), 2973 (m), 1712 (s), 1538 (w), 1456 (w), 1394 (m), 1367 (m), 1342 (m), 1289 (m), 1256 (m), 1150 (s), 1101 (m), 1071 (m), 1001 (w), 968 (w), 914 (w), 759 (w), 609 (w), 555 (w); HRMS (ESI) calcd for C₁₄H₂₈N₂O₅Na⁺ (M+Na) 327.1890, found 327.1885; Anal. calcd for C₁₄H₂₈N₂O₅; C, 55.24; H, 9.27; N, 9.20. Found: C, 55.32; H, 9.18; N, 9.22.

N-(1-Cyano-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (182**)**



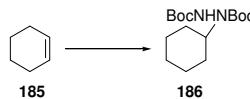
Following GP1 Hydrohydrazination product **182** (69 mg, 0.23 mmol, 46%) was obtained as a colorless solid with crotol nitrile (**181**) (41 μ L, 0.50 mmol, 1.0 equiv) in 18 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **182** (67 mg, 0.22 mmol, 44%) was obtained as a colorless solid with crotol nitrile (**181**) (41 μ L, 0.50 mmol, 1.0 equiv) in 2.5 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.30; Mp 105-107 °C; 1 H NMR (CDCl₃, 300 MHz, 52 °C) δ 6.31 (br s, 1H, NH), 4.91 (br s, 1H, CHN), 1.95-1.85 (m, 2H, CH₂), 1.49 (s, 9H, OCCH₃), 1.48 (s, 9H, OCCH₃), 1.07 (t, J = 7.5 Hz, 3H, CH₂CH₃); 13 C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.0, 153.5, 117.0, 83.1, 82.0, 51.9, 28.2, 25.0, 10.3; IR v 3316 (m), 2980 (s), 2938 (s), 2883 (w), 2254 (w), 2176 (w), 1714 (s), 1479 (m), 1459 (m), 1393 (s), 1370 (s), 1299 (s), 1254 (s), 1151 (s), 1110 (m), 1093 (m), 1051 (m), 1017 (m), 936 (m), 891 (w), 848 (m), 785 (w), 761 (m), 737 (w), 597 (w); HRMS (ESI) calcd for C₁₄H₂₅N₃O₄Na⁺ (M+Na) 322.1737, found 322.1735; Anal. calcd for C₁₄H₂₅N₃O₄; C, 56.17; H, 8.42; N, 14.04. Found: C, 56.02; H, 8.40; N, 13.97.

N-(1-ethyl-propyl)-N'-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (184**)**



Following GP1 Hydrohydrazination product **184** (25 mg, 0.079 mmol, 16%) was obtained as a colorless solid with *trans*-3-hexene (**182**) (62 μ L, 0.50 mmol, 1.0 equiv) in 10 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). **Following GP3** Hydrohydrazination product **184** (105 mg, 0.332 mmol, 66%) was obtained as a colorless solid with *trans*-3-hexene (**182**) (62 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.50; Mp 80-82 °C; 1 H NMR (CDCl₃, 300 MHz, 52 °C) δ 5.87 (br s, 1H, NH), 3.94 (br s, 1H, CHN), 1.57-1.23 (m, 6H, CH₂), 1.46 (s, 9H, OCCH₃), 1.45 (s, 9H, OCCH₃), 0.89 (t, J = 7.2 Hz, 6H, CH₂CH₃); 13 C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.5, 80.7, 58.6, 34.5, 28.3, 28.3, 25.6, 19.8, 14.0, 11.2; IR v 3362 (m), 2968 (s), 2934 (s), 2875 (m), 1750 (s), 1705 (s), 1479 (m), 1456 (m), 1393 (s), 1367 (s), 1338 (s), 1303 (m), 1254 (s), 1156 (s), 1106 (s), 1046 (m), 1016 (m), 935 (m), 858 (w), 797 (w), 760 (m), 617 (w); MS (ESI) 317.1 (M+H), 339.1 (M+Na); Anal. calcd for C₁₆H₃₂N₂O₄; C, 60.73; H, 10.19; N, 8.85. Found: C, 60.50; H, 10.43; N, 8.78.

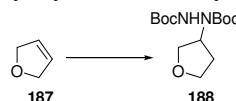
***N*-(Cyclohexyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (186)**



Following GP1 Hydroxylation product **186** (39 mg, 0.12 mmol, 24 %) was obtained as a colorless solid with cyclohexene (**185**) (51 μ L, 0.50 mmol, 1.0 equiv), phenylsilane (95 μ L, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (**2**) (0.23 g, 1.0 mmol, 2.0 equiv) in 24 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10).

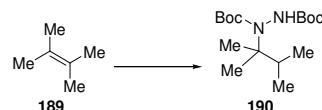
Following GP3 Hydroxylation product **186** (142 mg, 0.452 mmol, 90 %) was obtained as a colorless solid with cyclohexene (**185**) (51 μ L, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.42; Mp 147-148 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 5.98 (br s, 1H, NH), 3.93 (br s, 1H, CHN), 1.80-1.06 (m, 10H, CH_2), 1.48 (s, 9H, $OCCH_3$), 1.47 (s, 9H, $OCCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.8, 154.6, 80.8, 56.9, 30.3, 28.4, 28.3, 25.7, 25.6; IR ν 3314 (m), 2976 (m), 2931 (s), 2857 (m), 1699 (s), 1519 (s), 1453 (m), 1398 (s), 1365 (s), 1318 (s), 1290 (s), 1268 (s), 1256 (s), 1236 (s), 1172 (s), 1152 (s), 1116 (m), 1060 (m), 1026 (w), 1003 (m), 932 (w), 904 (m), 869 (m), 858 (m), 784 (w), 758 (m), 611 (w); MS (ESI) 315.3 (M+H), 337.3 (M+Na), 651.2 (2M+Na); Anal. calcd for $C_{16}H_{30}N_2O_4$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.26; H, 9.73; N, 8.91.

***N*-(Tetrahydro-furan-3-yl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (188)**



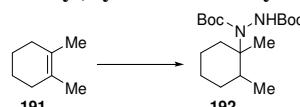
Following GP1 Hydroxylation product **188** (47 mg, 0.16 mmol, 31%) was obtained as a colorless solid with 2,4-dehydrofuran (187) (38 μ L, 0.50 mmol, 1.0 equiv) in 12 h with 5 mol% catalyst **20** after purification by column chromatography (pentane/CH₂Cl₂/Et₂O 2:1:1). **Following GP3** Hydroxylation product **188** (123 mg, 0.407 mmol, 81%) was obtained as a colorless solid with 2,4-dehydrofuran (187) (38 μ L, 0.50 mmol, 1.0 equiv) in 4 h with 2 mol% catalyst **23** after purification by column chromatography (pentane/CH₂Cl₂/Et₂O 2:1:1). R_f (pentane/CH₂Cl₂/Et₂O 2:1:1) 0.30; Mp 121-122 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.36 (br s, 1H, NH), 4.72 (br s, 1H, CHN), 3.93-3.68 (m, 4H, CH_2O), 2.07-2.03 (m, 2H, C_2CH_2), 1.44 (s, 9H, $OCCH_3$), 1.43 (s, 9H, $OCCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 155.8, 154.8, 81.4, 70.3, 67.5, 57.7, 29.6, 28.1, 28.1; IR (KBr) ν 3314 (m), 2980 (m), 2935 (w), 2872 (w), 1704 (s), 1518 (m), 1458 (w), 1407 (m), 1367 (s), 1344 (m), 1299 (m), 1254 (s), 1160 (s), 1083 (m), 1024 (w), 951 (m), 918 (w), 857 (w), 785 (w), 757 (m), 616 (w), 463 (w); MS (ESI) 303.1 (M+H), 325.0 (M+Na); Anal. calcd for $C_{14}H_{26}N_2O_5$: C, 55.61; H, 8.67; N, 9.26. Found: C, 55.34; H, 8.81; N, 9.16.

***N*-(1,1,2-Trimethyl-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (190)**



Following GP1 Hydroxylation product **190** (22 mg, 0.070 mmol, 14%) was obtained as a colorless solid with 2,3-dimethylbutene (189) (60 μ L, 0.50 mmol, 1.0 equiv) in 10 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). **Following GP3** Hydroxylation product **190** (123 mg, 0.389 mmol, 78%) was obtained as a colorless solid with 2,3-dimethylbutene (189) (60 μ L, 0.50 mmol, 1.0 equiv) in 3 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15). **Following GP3, but with PMHS** Hydroxylation product **190** (94 mg, 0.30 mmol, 60%) was obtained as colorless solid with 2,3-dimethylbutene (189) (60 μ L, 0.50 mmol, 1.0 equiv) and PMHS (0.10 mL, 1.6 H equiv) in 10 h at 23 $^{\circ}$ C with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.60; Mp 101-102 $^{\circ}$ C; 1 H NMR ($CDCl_3$, 300 MHz, 52 $^{\circ}$ C) δ 6.03 (br s, 1H, NH), 2.57 (septet, J = 6.9 Hz, 1H, $CHCH_3$), 1.47 (s, 3H, $CNCH_3$), 1.45 (s, 9H, $OCCH_3$), 1.43 (s, 9H, $OCCH_3$), 1.09 (s, 3H, $CNCH_3$), 0.85 (d, J = 6.9 Hz, 3H, $CHCH_3$), 0.79 (d, J = 6.9 Hz, 3H, $CHCH_3$); 13 C NMR ($CDCl_3$, 75 MHz, 52 $^{\circ}$ C) δ 156.1, 154.5, 80.5, 65.8, 34.0, 28.4, 28.3, 24.9, 20.8, 18.1, 17.8; IR ν 3339 (m), 3268 (m), 3158 (w), 2977 (s), 2934 (s), 2879 (m), 1714 (s), 1477 (s), 1456 (s), 1367 (s), 1252 (s), 1171 (s), 1082 (s), 1065 (s), 1046 (m), 1018 (s), 908 (m), 889 (w), 858 (m), 835 (w), 785 (m), 762 (m), 735 (m), 710 (w), 593 (w), 462 (w); MS (ESI) 317.1 (M+H); Anal. calcd for $C_{16}H_{32}N_2O_4$: C, 60.73; H, 10.19; N, 8.85. Found: C, 60.51; H, 10.45; N, 8.72.

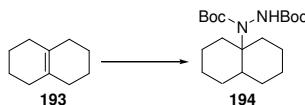
***N*-(1,2-Dimethyl-cyclohexyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (192)**



Following GP1 Hydroxylation product **192** (30 mg, 0.088 mmol, 17%, 1:1 mixture of diastereoisomers) was obtained as a colorless solid with 1,2-dimethyl-cyclohexene (191) (57 mg, 0.52 mmol, 1.0 equiv, contains < 17% 1,6-dimethyl-cyclohexene) in 20 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). **Following GP3** Hydroxylation product **192** (144 mg, 0.420 mmol, 79%, 1:1 mixture of diastereoisomers) was obtained as a colorless solid with 1,2-dimethyl-cyclohexene (191) (58 mg, 0.53 mmol, 1.0 equiv, contains < 17% 1,6-dimethyl-cyclohexene) in 3 h with 2

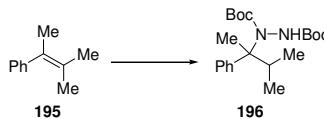
mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.50; Mp 97-99 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.07 (br s, 2H, NH (2 diastereoisomers)), 2.70-2.45 (m, 3H, CHCH_3 and CH_2), 1.92-1.11 (m, 15H, CHCH_3 and CH_2), 1.48 (s, 9H, OCCH_3), 1.48 (s, 9H, OCCH_3), 1.46 (s, 9H, OCCH_3), 1.46 (s, 9H, OCCH_3), 1.29 (s, 3H, CNCH_3), 1.17 (s, 3H, CNCH_3), 0.88 (d, J = 6.9 Hz, 3H, CHCH_3), 0.78 (d, J = 6.9 Hz, 3H, CHCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 156.0, 154.7, 80.4, 66.9, 66.4, 40.0, 35.5, 35.4, 35.2, 32.1, 31.8, 28.4, 28.4, 28.3, 25.5, 25.2, 23.7, 23.3, 18.0, 17.0, 16.5, 16.3; IR ν 3340 (w), 3267 (w), 3156 (w), 2977 (m), 2929 (m), 2862 (w), 1705 (s), 1477 (m), 1458 (m), 1391 (s), 1367 (s), 1340 (m), 1329 (m), 1285 (m), 1252 (m), 1172 (s), 1092 (m), 1074 (m), 1046 (m), 1017 (m), 894 (w), 862 (w), 783 (w), 761 (w), 701 (w), 621 (w); MS (ESI) 343.2 (M+H); Anal. calcd for $\text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_4$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.04; H, 10.05; N, 8.05.

Octahydro-naphthalen-4a-yl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid-*tert*-butyl ester (194)



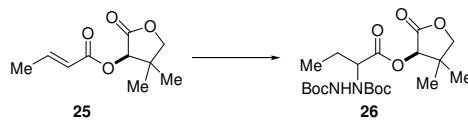
Following GP1 Hydroboration product **194** (18 mg, 0.049 mmol, 10%) was obtained as a colorless solid with octalin **193** (70 mg, 0.51 mmol, 1.0 equiv, contains < 7% trisubstituted olefin) in 18 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15). **Following GP3** Hydroboration product **194** (140 mg, 0.380 mmol, 74%) was obtained as a colorless solid with octalin **193** (70 mg, 0.51 mmol, 1.0 equiv, contains < 7% trisubstituted olefin) in 18 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15). R_f (AcOEt/hexane 1:5) 0.50; Mp 54-56 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.12 (br s, 1H, NH), 2.51 (br s, 1H, CH), 2.20-1.96 (m, 2H, CH_2), 1.80-1.72 (m, 2H, CH_2), 1.60-1.23 (m, 12H, CH_2), 1.47 (s, 9H, OCCH_3), 1.44 (s, 9H, OCCH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 156.2, 154.7, 80.4, 77.2, 66.2, 36.6, 30.9, 29.0, 28.8, 28.4, 28.2, 23.2, 23.0; IR ν 3331 (w), 3261 (w), 3156 (w), 2977 (s), 2930 (s), 2865 (s), 1749 (s), 1704 (s), 1478 (m), 1454 (m), 1392 (s), 1367 (s), 1328 (s), 1308 (m), 1292 (m), 1253 (s), 1161 (s), 1104 (m), 1081 (m), 1047 (m), 1020 (m), 978 (m), 914 (m), 857 (w), 762 (w), 734 (m), 647 (w), 618 (w), 463 (w); MS (ESI) 369.2 (M+H); Anal. calcd for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}_4$: C, 65.19; H, 9.85; N, 7.60. Found: C, 65.03; H, 9.85; N, 7.41.

N-(1,2-Dimethyl-1-phenyl-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (196)



Following GP1 Hydroboration product **196** (24 mg, 0.063 mmol, 13%) was obtained as a gel with 2-methyl-1-phenylbutene (195) (71 mg, 0.49 mmol, 1.0 equiv) in 20 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydroboration product **196** (94 mg, 0.25 mmol, 51%) was obtained as a gel with 2-methyl-1-phenylbutene (195) (71 mg, 0.49 mmol, 1.0 equiv) in 4 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.50; ^1H NMR (CDCl_3 , 300 MHz, 52 °C, mixture of rotamers major/minor: 7:3) δ 7.50-7.47 (m, 2H, Ar H), 7.30-7.13 (m, 3H, Ar H), 6.19-5.95 (br m, 1H, NH), 2.95 (br s, 0.3H, CH, minor rotamer), 2.78 (quintet, J = 6.9 Hz, 0.7H, CH, major rotamer), 1.61 (s, 0.9H, CNCH_3 , minor rotamer), 1.58 (s, 2.7H, OCCH_3 , minor rotamer), 1.52 (s, 6.3H, OCCH_3 , major rotamer), 1.49 (s, 2.1H, CNCH_3 , major rotamer), 1.28 (s, 2.7H, OCCH_3 , minor rotamer), 1.15 (s, 6.3H, OCCH_3 , major rotamer), 1.00 (d, J = 6.9 Hz, 0.9H, CHCH_3 , minor rotamer), 0.92-0.87 (m, 4.2H, CHCH_3 , major rotamer), 0.69 (d, J = 6.9 Hz, 0.9 H, minor rotamer); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 156.4, 155.1, 154.8, 146.3, 144.4, 127.4, 127.3, 126.5, 126.2, 125.7, 81.0, 70.9, 69.4, 34.7, 34.0, 28.4, 28.1, 28.0, 21.8, 19.8, 19.1, 18.9, 18.3; IR ν 3263 (m), 3090 (w), 3058 (w), 2978 (s), 2933 (m), 2882 (m), 1711 (s), 1602 (w), 1495 (m), 1478 (m), 1455 (m), 1392 (s), 1367 (s), 1248 (s), 1163 (s), 1093 (m), 1047 (m), 1018 (m), 911 (m), 855 (m), 759 (m), 734 (s), 703 (s), 646 (w), 609 (w); MS (ESI) 401.2 (M+Na); Anal. calcd for $\text{C}_{21}\text{H}_{34}\text{N}_2\text{O}_4$: C, 66.64; H, 9.05; N, 7.40. Found: C, 66.44; H, 9.01; N, 7.25.

2-(*N,N'*-Di-*tert*-butoxycarbonyl-hydrazino)-butyric acid 4,4-dimethyl-2-oxo-tetrahydro-furan-(*R*)-3-yl ester (26)



Following GP1 Hydroboration product **26** (156 mg, 0.362 mmol, 74%, 78:22 mixture of diastereoisomers by integration of the singlet at 5.30 respectively 5.33 in the ^1H -NMR) was obtained as a colorless solid with olefin **25** (97 mg, 0.49 mmol, 1.0 equiv) in 20 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/CH₂Cl₂ 1:50). **Following GP3** Hydroboration product **26** (145 mg, 0.337 mmol, 75%, 81:19 mixture of diastereoisomers by integration of the singlet at 5.30 respectively 5.33 in the ^1H -NMR) was obtained as a colorless solid with olefin **25** (90 mg, 0.45 mmol, 1.0 equiv) in 3 h with 2.5 mol% catalyst **23** after purification by column chromatography (AcOEt/CH₂Cl₂ 1:50). R_f (AcOEt/CH₂Cl₂ 1:20) 0.40; Mp 107-108 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.34 (br s, 1H, NH), 5.33 (s, 1H, C_2CHO , minor diastereoisomer), 5.30 (s, 1H, C_2CHO , major diastereoisomer), 4.68 (br m, 1H, CHN), 4.04-3.97 (m, 2H, CH_2O), 2.01-1.81 (m, 2H, CH_2CH_3), 1.45 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.20 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.11 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.16-1.06 (m, 3H, CH_2CH_3); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 171.4, 171.2, 155.3, 155.1, 82.1, 81.0, 76.3, 76.2, 75.7, 61.7, 40.3, 40.2, 29.7, 28.2, 28.0, 23.0,

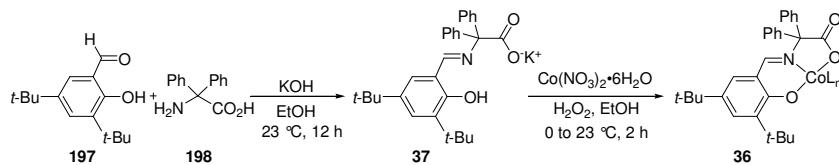
22.9, 22.4, 19.9, 11.1; IR ν 3337 (m), 2979 (s), 2936 (m), 2881 (m), 1795 (s), 1753 (s), 1480 (s), 1393 (s), 1369 (s), 1299 (s), 1255 (s), 1156 (s), 1112 (s), 1089 (s), 1033 (m), 1014 (m), 998 (m), 943 (m), 917 (m), 856 (m), 770 (m), 734 (m), 648 (w), 562 (w), 544 (w); MS (ESI) 431.3 (M+H), 453.2 (M+Na), 469.1 (M+2Na); Anal. calcd for $C_{20}H_{34}N_2O_8$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.54; H, 7.90; N, 6.40.

3. The Co-Catalyzed Hydroazidation of Olefins

3.1. Catalysts and Azide Transfer Reagents

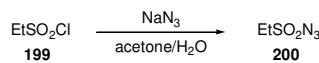
The Co-salen catalysts described in this work (28-31) were all prepared using the same known procedure,²⁹ and were used as obtained without further purification and characterization. Co catalysts **32a-32g** were synthesized following the same procedure as for **20** and were used as obtained without further purification and characterization.

Potassium{[1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-meth-(E)-ylidene]-amino}-diphenyl-acetate (37) and [N-3,5-di-*tert*-butyl-salicylidene-2,2-diphenyl-glycinato]- cobalt (III) (36)



Potassium hydroxide (0.5 M in EtOH, 9.3 mL, 4.6 mmol, 1.1 equiv) was added to a suspension of α,α -diphenyl glycine (**198**) (1.0 g, 4.4 mmol, 1.1 equiv) in ethanol (50 mL) at 23 °C under argon. After 30 min, 3,5-di-*tert*-butyl-salicylaldehyde (**197**) (1.0 g, 4.4 mmol, 1.0 equiv) was added to the clear colorless solution, and the color changed to intensive yellow. The reaction mixture was stirred at 23 °C for 10 h and the solvent was removed under reduced pressure. The isolated hygroscopic yellow solid was further dried in high vacuo for 8 h to furnish **43** (2.2 g, 4.5 mmol, 100%), which was used without further purifications. A solution of $Co(NO_3)_2 \cdot 6H_2O$ (61 mg, 0.21 mmol, 1.0 equiv) in ethanol (1 mL) was added to a solution of ligand **43** (100 mg, 0.21 mmol, 1.0 equiv) in ethanol (0.5 mL) and CH_2Cl_2 (1.5 mL) at 0 °C under argon, whereas an orange solid precipitated. The reaction mixture was warmed to 23 °C, stirred for 6 h and hydrogen peroxide (43 μ L, 0.42 mmol, 2.0 equiv) was added dropwise at 0 °C. After 30 min, the reaction mixture was warmed to 23 °C, stirred for 1.5 h and the dark red solution was filtered. The solvent was removed under reduced pressure, co-evaporated with CH_2Cl_2 (2x), the residues were dissolved in CH_2Cl_2 (10 mL) and filtered. The solvent was removed under reduced pressure and the remaining solid dissolved in Et_2O (20 mL) and filtered. The solvent was removed under reduced pressure and the obtained dark red solid triturated in hexane (30 mL), filtered, washed with hexane (10 mL) and dried 12 h in high vacuo to afford a dark red solid (84 mg), which appear to be the nearly pure 1:1 complex **42** by 1H -NMR, the coordination sphere of the complex being probably completed with water. 1H NMR (DMSO-d₆, 300 MHz) δ 8.03 (s, 1H, imine H), 7.48-7.41 (m, 4H, Ar H), 7.27-7.20 (m, 6H, ArH), 6.87-6.85 (m, 2H, Ar H), 3.53 (br s, 5 to 10H, H_2O), 1.08 (s, 9H, CCH_3), 0.70 (s, 9H, CCH_3); ^{13}C NMR (DMSO-d₆, 75 MHz)³⁰ δ 168.9, 163.1, 143.8, 143.1, 140.9, 133.4, 130.0, 129.7, 129.6, 128.4, 127.6, 127.5, 127.0, 126.9, 126.6, 118.9, 82.5, 34.6, 33.2, 31.2, 29.5; IR (KBr) ν 3390 (m), 2955 (m), 1762 (w), 1635 (s), 1527 (w), 1431 (m), 1385 (s), 1270 (w), 1254 (w), 1200 (w), 1169 (w), 1090 (w), 1049 (w), 1027 (w), 916 (w), 870 (w), 844 (w), 826 (w), 743 (w), 700 (m), 595 (w), 545 (w); HRMS (MALDI) calcd for $C_{29}H_{31}CoNNaO_3^+$ (M+Na): 523.1528, found 523.1519.

Ethanesulfonyl azide (200)³¹



Following a reported procedure,³¹ a solution of sodium azide (9.5 g, 0.15 mol, 1.5 equiv) in water (60 mL) was added dropwise over 1 h to a solution of ethanesulfonyl chloride (**199**) (8.9 mL, 93 mmol, 1.0 equiv) in acetone (200 mL) at 0 °C. The reaction was let to warm up to 23 °C and stirred for 11 h, the acetone was removed under reduced pressure at 25 °C and the reaction mixture was extracted with $AcOEt$ (2x100 mL). The combined organic layers were washed with water (2x100 mL), 5% Na_2CO_3 (2x100 mL) and water (2x100 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by distillation ($p = 0.6$ mbar, $bp = 45-48$ °C) to afford ethanesulfonyl azide (**200**) (10.5 g, 7.77 mmol, 83%) as a colorless liquid. 1H NMR ($CDCl_3$, 300 MHz) δ 3.33 (q, $J = 7.2$ Hz, 2H, CH_2), 1.45 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 50.4, 8.0; IR ν 3309 (w), 2987 (w), 2948 (w), 2886 (w), 2369 (w), 2138 (s), 1458 (m), 1411 (w), 1360 (s), 1289 (w), 1199 (s), 1159 (s), 1050 (m), 978 (w), 783 (s), 745 (m), 613 (m), 568 (m), 519 (m).

Methanesulfonyl azide (**201**), benzenesulfonyl azide (**202**), toluenesulfonyl azide (**203**) mesitylenesulfonyl azide (**204**), *p*-nitro-toluenesulfonyl azide (**205**), *p*-methoxy-benzenesulfonyl azide (**42**) and camphor-derived sulfonyl azide **41** were synthesized following the same procedure,³¹ but distillation was omitted, as these compounds were already pure enough.

Methanesulfonyl azide (201)³²

1H NMR ($CDCl_3$, 300 MHz) δ 3.24 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.6; IR ν 3318 (w), 3036 (w), 2938 (w), 2141 (s), 1413 (w), 1360 (s), 1167 (s), 968 (m), 781 (s), 730 (m), 574 (s), 509 (s).

Benzenesulfonyl azide (202)³¹

¹H NMR (CDCl₃, 300 MHz) δ 7.96-7.92 (m, 2H, Ar H), 7.75-7.69 (m, 1H, Ar H), 7.64-7.57 (m, 2H, Ar H); ¹³C NMR (CDCl₃, 75 MHz) δ 138.1, 134.6, 129.5, 127.2; IR ν 3276 (w), 3069 (w), 2347 (w), 2129 (s), 1584 (w), 1477 (w), 1450 (m), 1372 (s), 1313 (w), 1298 (w), 1170 (s), 1088 (m), 1023 (w), 1000 (w), 751 (m), 685 (m), 601 (s), 564 (s).

Toluenesulfonyl azide (203)³³

¹H NMR (CDCl₃, 300 MHz) δ 7.80 (d, *J* = 8.4 Hz, 2H, Ar H), 7.38 (d, *J* = 8.7 Hz, 2H, Ar H), 2.45 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 146.0, 135.1, 130.0, 127.2, 21.6; IR ν 3275 (w), 3068 (w), 2927 (w), 2872 (w), 2351 (w), 2127 (s), 1924 (w), 1808 (w), 1596 (m), 1495 (w), 1451 (w), 1399 (w), 1372 (s), 1308 (w), 1297 (w), 1168 (s), 1121 (w), 1086 (m), 1041 (w), 1018 (w), 814 (m), 800 (w), 748 (s), 703 (m), 662 (s), 593 (s), 540 (s), 501 (w).

Mesitylenesulfonyl azide (204)³⁴

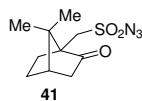
¹H NMR (CDCl₃, 300 MHz) δ 7.01 (s, 2H, Ar H), 2.65 (s, 6H, CH₃), 2.33 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 144.4, 139.6, 132.9, 131.9, 22.7, 21.0; IR ν 3276 (w), 2982 (w), 2943 (w), 2362 (w), 2123 (s), 1603 (m), 1565 (w), 1455 (m), 1405 (m), 1366 (s), 1292 (w), 1278 (w), 1191 (s), 1167 (s), 1052 (m), 1035 (m), 965 (w), 854 (m), 744 (m), 658 (s), 596 (s), 572 (m), 530 (s).

p-Nitro-toluenesulfonyl azide (205)³⁵

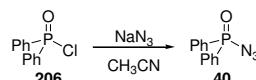
¹H NMR (CDCl₃, 300 MHz) δ 8.46 (d, *J* = 9.0 Hz, 2H, Ar H), 8.17 (d, *J* = 9.0 Hz, 2H, Ar H); ¹³C NMR (CDCl₃, 75 MHz) δ 151.0, 143.5, 128.8, 124.8. IR ν 3107 (w), 2311 (w), 2142 (s), 1605 (w), 1535 (m), 1477 (w), 1404 (w), 1369 (m), 1350 (m), 1311 (w), 1177 (s), 1159 (s), 1110 (w), 1085 (m), 1013 (w), 907 (w), 868 (w), 854 (m), 770 (m), 744 (m), 732 (m), 681 (m), 607 (s), 585 (s), 545 (m), 461 (m).

p-Methoxy-benzenesulfonyl azide (42)³⁵

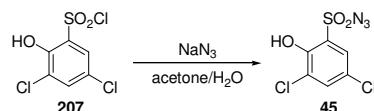
¹H NMR (CDCl₃, 300 MHz) δ 7.86 (d, *J* = 9.0 Hz, 2H, Ar H), 7.04 (d, *J* = 9.0 Hz, 2H, Ar H), 3.89 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 129.7, 129.4, 114.7, 55.8; IR ν 3276 (w), 3102 (w), 3080 (w), 3015 (w), 2977 (w), 2949 (w), 2845 (w), 2350 (w), 2128 (s), 1909 (w), 1811 (w), 1772 (w), 1595 (s), 1578 (s), 1499 (s), 1463 (m), 1442 (m), 1418 (m), 1370 (s), 1315 (m), 1267 (s), 1163 (s), 1114 (m), 1089 (s), 1023 (m), 915 (w), 836 (s), 806 (s), 748 (s), 715 (w), 668 (m), 628 (m), 594 (s), 551 (s), 521 (w), 486 (w).

(7,7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-methanesulfonyl azide (41)³⁶

¹H NMR (CDCl₃, 300 MHz) δ 3.79 (d, *J* = 14.9 Hz, 1H, CH₂SO₂N₃), 3.21 (d, *J* = 14.9 Hz, 1H, CH₂SO₂N₃), 2.43-2.27 (m, 2H, CH₂ or CH), 2.27-1.92 (m, 3H, CH₂ or CH), 1.80-1.51 (m, 1H, CH₂ or CH), 1.51-1.42 (m, 1H, CH₂ or CH), 1.06 (s, 3H, CH₃), 0.87 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 213.8, 58.4, 53.4, 48.4, 42.7, 42.4, 26.9, 24.9, 19.7, 19.5; IR ν 2964 (m), 2892 (w), 2357 (w), 2139 (s), 1748 (s), 1472 (w), 1456 (w), 1417 (w), 1395 (w), 1366 (s), 1280 (w), 1198 (m), 1162 (s), 1106 (w), 1069 (w), 1052 (m), 1028 (w), 1002 (w), 968 (w), 936 (w), 907 (w), 854 (w), 815 (w), 795 (m), 734 (m), 681 (w), 615 (m), 572 (m), 545 (m), 519 (m), 469 (w), 446 (w).

Diphenylphosphonyl azide (40)³⁷

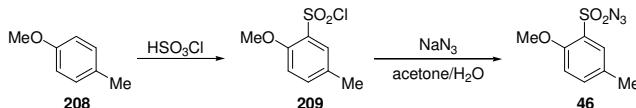
Following a reported procedure,³⁷ diphenylphosphonyl chloride (206) (1.0 mL, 5.1 mmol, 1.0 equiv) was added dropwise to a suspension of sodium azide (0.51 g, 7.8 mmol, 1.5 equiv) in acetonitrile (10 mL) at 0 °C under argon. After stirring at 23 °C for 12 h, the reaction mixture was filtered, the solvent was removed under reduced pressure at 25 °C and the reaction mixture was diluted with AcOEt (20 mL). The organic layer was washed with water (2x5 mL), 5% Na₂CO₃ (2x5 mL), water (5 mL) and brine (5 mL), dried over Na₂SO₄, the solvent was removed under reduced pressure and the residues dried 3 h in high vacuo to yield azide 40 (1.3 g, 5.3 mmol, 100%). ¹H NMR (CDCl₃, 300 MHz) δ 7.79-7.72 (m, 6H, Ar H), 7.53-7.37 (m, 9H, Ar H); ¹³C NMR (CDCl₃, 75 MHz) δ 132.7, 132.7, 131.1, 130.9, 130.8, 130.5, 128.7, 128.6, 128.4; IR ν 3533 (w), 3059 (m), 2994 (w), 2507 (w), 2144 (s), 1971 (w), 1905 (w), 1824 (w), 1779 (w), 1616 (w), 1591 (m), 1484 (m), 1439 (s), 1392 (w), 1311 (m), 1262 (s), 1227 (s), 1184 (m), 1161 (m), 1128 (s), 1107 (m), 1072 (m), 1028 (w), 998 (m), 935 (w), 853 (w), 729 (s), 694 (s), 618 (m), 590 (s), 532 (s), 505 (m).

3,5-Dichloro-2-hydroxy-benzenesulfonyl azide (45)

A solution of sodium azide (0.37 g, 5.7 mmol, 1.5 equiv) in water (2.7 mL) was added dropwise over 20 min to a solution of sulfonyl chloride 207 (1.0 g, 3.8 mmol, 1.0 equiv) in acetone (8.7 mL) at 0 °C. The reaction was let to warm up to 23 °C and

stirred for 12 h, the acetone was removed under reduced pressure at 25 °C and the reaction mixture was extracted with AcOEt (2x30 mL). The combined organic layers were washed with water (2x20 mL), and brine (20 mL), dried over Na_2SO_4 , the solvent was removed under reduced pressure and the residues were dried under high vacuo for 2 h to afford sulfonyl azide **45** (0.55 g, 2.1 mmol, 54%) as a colorless solid. Mp 94–95 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.74 (d, J = 2.5 Hz, 1H, Ar H), 7.67 (d, J = 2.7 Hz, 1H, Ar H), 7.50 (s, 1H, OH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 149.1, 135.8, 127.4, 125.9, 125.8, 124.1; IR v 3416 (w), 3086 (w), 2356 (w), 2149 (s), 1573 (w), 1469 (s), 1395 (m), 1368 (m), 1316 (m), 1277 (m), 1233 (m), 1178 (s), 1083 (w), 869 (m), 810 (m), 752 (m), 621 (m), 597 (m), 556 (m), 521 (w), 446 (w); MS (ESI) 266.1 ($\text{M}^{35}\text{Cl}^{35}\text{Cl}$ -H), 268.1 ($\text{M}^{37}\text{Cl}^{35}\text{Cl}$ -H), 270.1 ($\text{M}^{37}\text{Cl}^{37}\text{Cl}$ -H); Anal. calcd for $\text{C}_6\text{H}_3\text{N}_3\text{O}_3\text{SCl}_2$: C, 26.88; H, 1.13; N, 15.67. Found: C, 26.99; H, 1.16; N, 15.64.

5-Methyl-2-methoxy-benzenesulfonyl chloride (**209**) and 5-Methyl-2-methoxy-benzenesulfonyl azide (**46**)



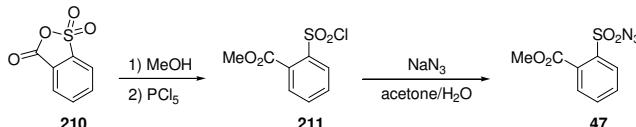
5-Methyl-2-methoxy-benzenesulfonyl chloride (**209**)³⁸

Following a reported procedure,³⁸ *p*-methoxy toluene (**208**) (10 mL, 79 mmol, 1.0 equiv) was added dropwise over 20 min to chlorosulfonic acid (26 mL, 0.39 mol, 5.0 equiv) at 0 °C under argon. The reaction mixture was stirred at 0 °C for 30 min and at 23 °C for 5 h, poured carefully onto crushed ice (80 g) and extracted with CH_2Cl_2 (3x80 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The isolated product was recrystallized from hexane/ CH_2Cl_2 to yield sulfonyl chloride **209** (11.2 g, 50.8 mmol, 64%) as a colorless solid. ^1H NMR (CDCl_3 , 300 MHz) δ 7.74 (d, J = 1.9 Hz, 1H, Ar H), 7.47 (dm, J = 8.5 Hz, 1H, Ar H), 7.02 (d, J = 8.5 Hz, 1H, Ar H), 4.02 (s, 3H, OCH_3), 2.35 (s, 3H, Ar CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.2, 137.8, 131.3, 130.0, 129.6, 113.2, 56.6, 20.2; IR v 3122 (w), 2991 (w), 2958 (w), 2925 (w), 2851 (w), 1608 (w), 1580 (w), 1563 (w), 1506 (m), 1459 (w), 1441 (w), 1398 (w), 1369 (s), 1290 (m), 1264 (m), 1220 (w), 1175 (s), 1064 (w), 1016 (m), 958 (w), 885 (w), 822 (m), 745 (w), 716 (w), 692 (w), 587 (s), 550 (m), 525 (m), 445 (w).

5-Methyl-2-methoxy-benzenesulfonyl azide (**46**)

A solution of sodium azide (4.5 g, 69 mol, 1.5 equiv) in water (30 mL) was added dropwise over 30 min to a solution of sulfonyl chloride (**209**) (10.1 g, 45.7 mmol, 1.00 equiv) in acetone (100 mL) at 0 °C. The reaction was let to warm up to 23 °C and stirred for 11 h, the acetone was removed under reduced pressure at 25 °C and the reaction mixture was extracted with AcOEt (3x50 mL). The combined organic layers were washed with water (2x50 mL), 5% Na_2CO_3 (2x50 mL), water (50 mL) and brine (50 mL), dried over Na_2SO_4 , the solvent was removed under reduced pressure and the isolated product was dried 2 h in high vacuo to afford sulfonyl azide **46** (10.3 g, 45.2 mmol, 99%) as a colorless solid. Mp 72–73 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.68 (d, J = 1.9 Hz, 1H, Ar H), 7.41 (dm, J = 9.0 Hz, 1H, Ar H), 6.99 (d, J = 9.0 Hz, 1H, Ar H), 3.99 (s, 3H, OCH_3), 2.33 (s, 3H, Ar CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 154.9, 136.7, 130.2, 130.2, 127.0, 112.2, 56.3, 20.2; IR v 2955 (w), 2361 (w), 2142 (s), 1606 (w), 1585 (w), 1569 (w), 1498 (s), 1465 (m), 1441 (w), 1402 (w), 1360 (s), 1286 (m), 1259 (m), 1221 (w), 1168 (s), 1068 (m), 1019 (m), 888 (m), 814 (m), 749 (s), 692 (m), 612 (s), 593 (s), 560 (m), 544 (m), 477 (w), 459 (w), 431 (w); MS (ESI) 250.2 ($\text{M}+\text{Na}$); Anal. calcd for $\text{C}_8\text{H}_9\text{N}_3\text{O}_3\text{S}$: C, 42.28; H, 3.99; N, 18.49. Found: C, 42.52; H, 4.05; N, 18.29.

2-Chlorosulfonyl-benzoic acid methyl ester (**211**) and 2-Azidosulfonyl-benzoic acid methyl ester (**47**)



2-Chlorosulfonyl-benzoic acid methyl ester (**211**)³⁹

Following a known procedure,⁴⁰ a suspension of mixed anhydride **210** (2.0 g, 11 mmol, 1.0 equiv) in methanol (5 mL) was heated to reflux for 1 h. The clear solution was cooled to 23 °C, the solvent was removed under reduced pressure and the isolated sulfonic acid was dried 2 h in high vacuo. PCl_5 (5.7 g, 27 mmol, 2.5 equiv) was then added slowly and the viscous mixture was heated to 95 °C and stirred at this temperature for 2.5 h. The reaction mixture was cooled to 23 °C and POCl_3 was removed under reduced pressure. The residues were suspended in Et_2O (30 mL), washed rapidly with ice-water (caution: exothermic reaction, 4x10 mL), dried over Na_2SO_4 , the solvent was removed under reduced pressure and the isolated product was dried 3 h in high vacuo to yield sulfonyl chloride **211** (2.51 g, 10.7 mmol, 97%) as a viscous oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.14 (dm, J = 8.4 Hz, 1H, Ar H), 7.82–7.68 (m, 3H, Ar H), 3.97 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.0, 141.3, 135.1, 132.1, 131.3, 129.9, 128.9, 53.4; IR v 3100 (w), 3012 (w), 2956 (w), 2844 (w), 1792 (w), 1739 (s), 1592 (w), 1571 (w), 1434 (m), 1378 (s), 1298 (s), 1260 (s), 1185 (s), 1132 (m), 1119 (m), 1054 (m), 989 (w), 955 (w), 867 (w), 830 (w), 784 (m), 759 (m), 730 (m), 712 (m), 651 (m), 580 (s), 559 (s), 468 (w).

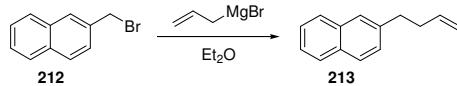
2-Azidosulfonyl-benzoic acid methyl ester (**47**)

A solution of sodium azide (1.0 g, 15 mol, 1.5 equiv) in water (7.3 mL) was added dropwise over 30 min to a solution of sulfonyl chloride (**211**) (2.33 g, 9.93 mmol, 1.00 equiv) in acetone (24 mL) at 0 °C. The reaction was let to warm up to 23 °C and stirred for 11 h, the acetone was removed under reduced pressure at 25 °C and the reaction mixture was extracted with AcOEt (3x15 mL). The combined organic layers were washed with water (2x15 mL), 5% Na_2CO_3 (2x15 mL), water (15 mL) and brine (15 mL), dried over Na_2SO_4 , the solvent was removed under reduced pressure and the isolated product was dried 3 h in high

vacuo to afford sulfonyl azide **47** (2.15 g, 8.91 mmol, 90%) as a colorless solid. Mp 63–64 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.11 (dm, *J* = 8.4 Hz, 1H, Ar H), 7.78–7.66 (m, 3H, Ar H), 3.99 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 166.5, 137.1, 134.5, 132.3, 131.5, 130.2, 130.1, 53.5; IR v 3102 (w), 3012 (w), 2957 (w), 2845 (w), 2364 (w), 2146 (s), 1738 (s), 1626 (w), 1592 (w), 1572 (w), 1476 (w), 1435 (m), 1370 (s), 1297 (s), 1259 (m), 1175 (s), 1119 (m), 1058 (m), 955 (w), 889 (w), 831 (w), 785 (w), 744 (s), 655 (m), 610 (s), 568 (s); MS (ESI) 264.3 (M+Na); Anal. calcd for C₈H₇N₃O₄S: C, 39.83; H, 2.92; N, 17.42. Found: C, 40.04; H, 3.09; N, 17.37.

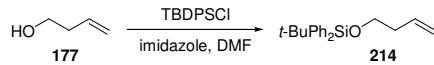
3.2. Synthesis of Alkene Substrates

(3-Methyl-but-3-enyl)-naphthalene (213)⁴¹



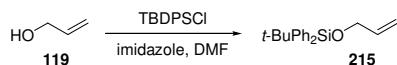
A solution of 2-bromomethyl-naphthalene (**212**) (5.0 g, 23 mmol, 1.0 equiv) in dry Et₂O (25 mL) was added dropwise over 90 min to a solution of allyl magnesium bromide (1 M in Et₂O, 45 mL, 45 mmol, 2.0 equiv) at 0 °C under argon. The reaction mixture was warmed to 23 °C over 14 h, cooled to 0 °C and quenched with sat. NH₄Cl solution (30 mL). After diluting with H₂O (30 mL), the reaction mixture was extracted with Et₂O (3x50 mL), the combined organic layers were washed with brine (30 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (hexane) to afford (3-methyl-but-3-enyl)-naphthalene (**213**) (3.09 g, 16.9 mmol, 73%) as a colorless oil. R_f (hexane) 0.35; ¹H NMR (CDCl₃, 300 MHz) δ 7.82–7.76 (m, 3H, naphthyl H), 7.63 (d, *J* = 0.6 Hz, 1H, naphthyl H), 7.48–7.39 (m, 3H, naphthyl H), 7.35 (dd, *J* = 8.4, 1.9 Hz, 1H, naphthyl H), 5.95–5.84 (m, 1H, alkene H), 5.11–4.98 (m, 2H, alkene H), 2.91 (t, *J* = 7.5 Hz, 2H, naphthyl-CH₂), 2.51–2.44 (m, 2H, alkene-CH₂); ¹³C NMR (CDCl₃, 75 MHz) δ 139.3, 138.0, 133.6, 132.0, 127.8, 127.6, 127.4, 127.3, 126.4, 125.8, 125.1, 115.0, 35.5, 35.4; IR v 3053 (m), 3018 (w), 2977 (w), 2925 (m), 2853 (w), 1912 (w), 1821 (w), 1639 (m), 1600 (m), 1508 (m), 1439 (w), 1365 (w), 1332 (w), 1270 (w), 1169 (w), 1143 (w), 1125 (w), 1017 (w), 996 (w), 959 (w), 911 (s), 889 (w), 853 (s), 815 (s), 745 (s), 648 (w), 617 (w), 475 (s).

But-3-enyloxy-*tert*-butyl-diphenyl-silane (214)⁴²



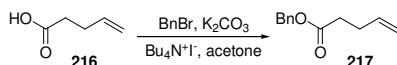
tert-Butyldiphenyl-silyl-chloride (3.1 mL, 12 mmol, 1.2 equiv) was added dropwise to a solution of 3-butanol (**177**) (0.86 mL, 10 mmol, 1.0 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in dry DMF (15 mL) at 23 °C under argon. After stirring for 20 h, the reaction mixture was quenched with water (30 mL) and extracted with AcOEt (3x30 mL). The combined organic layers were washed with water (4x20 mL) and brine (20 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (gradient: hexane, then hexane/ AcOEt 200:1) to afford **214** (3.0 g, 9.8 mmol, 98%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.70–7.66 (m, 4H, Ar H), 7.45–7.35 (m, 6H, Ar H), 5.89–5.77 (m, 1H, alkene-H), 5.10–4.99 (m, 2H, alkene-H), 3.72 (t, *J* = 6.5 Hz, 2H, CH₂O), 2.36–2.28 (m, 2H, alkene-CH₂), 1.06 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 135.6, 135.4, 134.0, 129.5, 127.6, 116.4, 63.5, 37.2, 26.8, 19.2; IR v 3071 (m), 3050 (w), 3013 (w), 2958 (m), 2930 (m), 2894 (m), 2857 (m), 1958 (w), 1887 (w), 1822 (w), 1641 (w), 1589 (w), 1472 (m), 1462 (w), 1428 (m), 1389 (w), 1361 (w), 1329 (w), 1305 (w), 1263 (w), 1227 (w), 1188 (w), 1111 (s), 1007 (w), 998 (w), 988 (w), 912 (m), 823 (m), 737 (m), 701 (s), 689 (m), 613 (m), 506 (s), 491 (m).

Prop-2-enyloxy-*tert*-butyl-diphenyl-silane (215)⁴³



tert-Butyldiphenyl-silyl-chloride (8.4 mL, 32 mmol, 1.1 equiv) was added dropwise to a solution of allyl alcohol (**119**) (2.0 mL, 29 mmol, 1.0 equiv) and imidazole (2.4 g, 35 mmol, 1.2 equiv) in dry DMF (25 mL) at 23 °C under argon. After stirring for 2 h, the reaction mixture was quenched with water (60 mL) and extracted with Et₂O (3x60 mL). The combined organic layers were washed with water (4x40 mL) and brine (40 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (hexane/AcOEt 50:1) to afford **215** (8.91 g, 30.0 mmol, 100%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.71–7.67 (m, 4H, Ar H), 7.46–7.35 (m, 6H, Ar H), 5.98–5.87 (m, 1H, alkene-H), 5.42–5.34 (m, 1H, alkene-H), 5.15–5.09 (m, 1H, alkene-H), 4.22–4.20 (m, 2H, CH₂O), 1.07 (s, 9H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 136.9, 135.4, 135.4, 133.6, 129.5, 127.5, 113.8, 64.6, 26.9, 19.4; IR v 3070 (m), 3050 (w), 3013 (w), 2998 (w), 2958 (m), 2930 (m), 2891 (m), 2857 (s), 1959 (w), 1888 (w), 1824 (w), 1771 (w), 1646 (w), 1589 (w), 1487 (w), 1472 (m), 1462 (m), 1427 (s), 1402 (w), 1398 (w), 1378 (w), 1361 (w), 1306 (w), 1288 (w), 1261 (w), 1188 (w), 1134 (m), 1112 (s), 1079 (m), 1035 (m), 1008 (m), 998 (m), 916 (m), 824 (m), 811 (m), 740 (m), 701 (s), 620 (m), 616 (m), 564 (w), 505 (s), 490 (m).

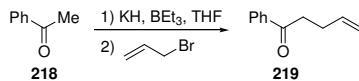
Pent-4-enoic acid benzyl ester (217)⁴⁴



Benzyl bromide (1.3 mL, 12 mmol, 1.2 equiv) was added to a solution of 4-pentanoic acid (**216**) (1.0 mL, 9.8 mmol, 1.0 equiv) in acetone (20 mL) at 23 °C under argon. Potassium carbonate (6.8 g, 49 mmol, 5.0 equiv) and tetrabutylammonium iodide (0.24 g, 1.0 mmol, 0.10 equiv) were added and the resulting colorless suspension was stirred for 15 h, filtered and the solvent was

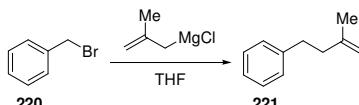
removed under reduced pressure. The reaction mixture was then dissolved in AcOEt (40 mL), washed with 2 M HCl (30 mL, sat. NaHCO₃ (30 mL) and brine (30 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 30:1) to afford **217** (1.65 g, 8.67 mmol, 88%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.39-7.33 (m, 5H, Ar H), 5.91-5.78 (m, 1H, alkene-H), 5.14 (s, 2H, PhCH₂), 5.14-5.00 (m, 2H, alkene-H), 2.52-2.39 (m, 4H, CH₂CO and alkene-CH₂); ¹³C NMR (CDCl₃, 75 MHz) δ 172.6, 136.4, 135.8, 128.4, 128.0, 115.4, 66.1, 33.5, 28.9; IR v 3067 (w), 3034 (w), 2979 (w), 2959 (w), 1738 (s), 1642 (w), 1608 (w), 1587 (w), 1498 (w), 1455 (m), 1418 (w), 1381 (m), 1350 (m), 1257 (m), 1213 (m), 1165 (s), 1115 (w), 1002 (m), 916 (m), 844 (w), 825 (w), 786 (w), 751 (m), 698 (s), 577 (w), 500 (w), 450 (w).

1-Phenyl-pent-4-en-1-one (219)⁴⁵



A solution of acetophenone (**218**) (2.6 mL, 22 mmol, 1.0 equiv) in dry THF (8 mL) was added dropwise over 10 min to a suspension of potassium hydride (1.1 g, 27 mmol, 1.2 equiv) in dry THF (45 mL) at 0 °C under argon. The yellow suspension was stirred at 23 °C for 30 min and BEt₃ (4.0 mL, 28 mmol, 1.2 equiv) was added dropwise at 15 °C over 15 min. After stirring the resulting clear yellow solution at 23 °C for 15 min, allyl bromide (freshly distilled, 2.9 mL, 34 mmol, 1.5 equiv) was added dropwise over 10 min and the resulting suspension was stirred for 4 h at 23 °C and quenched with a 1:1 mixture of 30% NaOH and 30% H₂O₂ (24 mL) at 0°C over 15 min. The reaction mixture was then diluted with H₂O (40 mL), the layers were separated and the organic layer diluted with Et₂O (100 mL) and washed with water (2x50 mL). The combined water layers were extracted with CH₂Cl₂ (2x50 mL) and the combined organic layers were dried over Na₂SO₄ and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 1:30) to afford **219** (2.85 g, 17.8 mmol, 80%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.97 (d, *J* = 7.2 Hz, 2H, Ar H), 7.59-7.43 (m, 3H, Ar H), 5.98-5.84 (m, 1H, alkene-H), 5.13-4.99 (m, 2H, alkene-H), 3.11-3.06 (m, 2H, CH₂CO), 2.54-2.46 (m, 2H, alkene-CH₂); ¹³C NMR (CDCl₃, 75 MHz) δ 199.1, 137.1, 136.8, 132.9, 128.4, 127.9, 115.2, 37.8, 28.2; IR v 3067 (w), 2977 (w), 2922 (w), 2855 (w), 1820 (w), 1687 (s), 1641 (w), 1597 (w), 1580 (w), 1448 (m), 1411 (w), 1361 (w), 1268 (w), 1207 (m), 1180 (w), 1159 (w), 1102 (w), 1076 (w), 1001 (w), 971 (w), 913 (m), 744 (m), 690 (m), 656 (w), 567 (w).

(3-Methyl-but-3-enyl)-benzene (221)⁴⁶



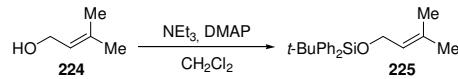
Methylmagnesium chloride (5.3 mL, 54 mmol, 2.5 equiv) was added slowly (10 min) to a suspension of magnesium turnings (1.3 g, 55 mmol, 2.5 equiv) in dry THF (40 mL) at 15 °C. The resulting suspension was stirred at 23 °C for 2 h and refluxed for 2 h. After cooling to 23 °C, the suspension was decanted and transferred *via* canula to a 100 mL-Schlenk flask. The solution was titrated (quenched with exact amount of 0.2 M HCl, neutralisation of excess HCl with 0.2 M NaOH over phenolphthalein) and appeared to be 0.6 M (24 mmol Grignard reagent, 1.1 equiv). Benzyl bromide (**220**) (2.6 mL, 22 mmol, 1.0 equiv) was then added at 0 °C over 3 h *via* syringe pump and the reaction mixture was refluxed for 3 h, cooled to 0 °C and quenched with sat. NH₄Cl (20 mL). After diluting with H₂O (20 mL), the reaction mixture was extracted with Et₂O (3x40 mL), the combined organic layers were washed with brine (20 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure (*p* = 50 mbar, *T* = 40 °C). The isolated product was purified by column chromatography (pentane) to afford (3-methyl-but-3-enyl)-benzene (**221**) (2.22 g, 15.2 mmol, 69%) as a colorless liquid. *R*_f (hexane) 0.60; ¹H NMR (CDCl₃, 300 MHz) δ 7.34-7.18 (m, 5H, Ar H), 4.78-4.75 (m, 2H, alkene H), 2.82-2.76 (m, 2H, PhCH₂), 2.38-2.33 (m, 2H, alkene-CH₂), 1.81 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 145.2, 142.1, 128.2, 125.6, 110.1, 39.7, 34.3, 22.7; IR v 3064 (w), 3027 (m), 2968 (m), 2936 (m), 2857 (w), 1800 (w), 1649 (m), 1604 (w), 1495 (m), 1453 (s), 1374 (w), 1078 (w), 1031 (w), 887 (s), 745 (m), 697 (s), 574 (w), 520 (w).

tert-Butyl-(2-methyl-allyloxy)-diphenyl-silane (223)⁴⁷



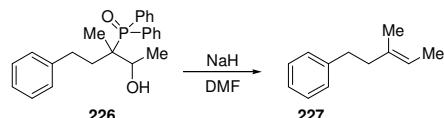
tert-Butyldiphenyl-silyl-chloride (3.1 mL, 12 mmol, 1.2 equiv) was added dropwise to a solution of methallyl alcohol (**222**) (0.85 mL, 10 mmol, 1.0 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in dry DMF (15 mL) at 23 °C under argon. After stirring for 15 h, the reaction mixture was quenched with water (30 mL) and extracted with AcOEt (3x30 mL). The combined organic layers were washed with water (4x20 mL) and brine (20 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (pentane/Et₂O 100:1) to afford **223** (3.1 g, 9.9 mmol, 99%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.71-7.68 (m, 4H, Ar H), 7.43-7.35 (m, 6H, Ar H), 5.13 (s, 1H, alkene-H), 4.86 (s, 1H, alkene-H), 4.07 (s, 2H, CH₂O), 1.69 (s, 3H, alkene-CH₃), 1.07 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 144.0, 135.4, 133.6, 129.5, 127.6, 109.1, 67.3, 26.9, 19.4, 19.1; IR v 3071 (w), 3050 (w), 2998 (w), 2959 (m), 2931 (m), 2893 (m), 2857 (m), 1959 (w), 1889 (w), 1822 (w), 1659 (w), 1589 (w), 1486 (w), 1472 (m), 1462 (w), 1428 (m), 1390 (w), 1361 (w), 1306 (w), 1262 (w), 1188 (w), 1112 (s), 1029 (w), 1007 (w), 998 (w), 938 (w), 896 (m), 826 (m), 740 (m), 701 (s), 614 (m), 504 (s), 490 (m), 436 (w).

tert-Butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (225)⁴⁸



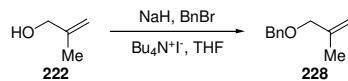
tert-Butyl diphenyl-silyl-chloride (2.1 mL, 22 mmol, 1.2 equiv) was added dropwise to a solution of 3-methyl-2-butanol (**224**) (1.0 mL, 10 mmol, 1.0 equiv) in dry CH_2Cl_2 (17 mL) at 23 °C under argon. Triethylamine (freshly distilled, 1.7 mL, 12 mmol, 1.2 equiv) and 4-dimethylamino-pyridine (48 mg, 0.39 mmol, 0.039 equiv) were added. After stirring 48 h at 23 °C the reaction mixture was diluted with CH_2Cl_2 and washed with water (2x50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 1:100) to afford **225** (2.54 g, 7.83 mmol, 78%) as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.75-7.71 (m, 4H, Ar H), 7.47-7.37 (m, 6H, Ar H), 5.44-5.38 (m, 1H, alkene-H), 4.23 (d, J = 6.5 Hz, 2H, CH_2O), 1.72 (m, 3H, alkene-CH₃), 1.48 (s, 3H, alkene-CH₃), 1.08 (s, 9H, CCH₃); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.6, 134.0, 133.8, 129.5, 127.6, 124.2, 61.1, 26.8, 25.7, 19.2, 17.9; IR v 3070 (w), 3049 (w), 2960 (m), 2930 (m), 2891 (m), 2857 (m), 2104 (w), 1958 (w), 1888 (w), 1824 (w), 1771 (w), 1722 (w), 1675 (w), 1589 (w), 1487 (w), 1472 (m), 1462 (w), 1446 (w), 1428 (m), 1380 (w), 1361 (w), 1329 (w), 1261 (w), 1189 (w), 1112 (s), 1062 (s), 1028 (m), 1007 (w), 998 (w), 938 (w), 913 (w), 855 (w), 823 (m), 774 (w), 739 (m), 701 (s), 689 (m), 613 (m), 504 (s), 440 (w).

(E)-3-Methyl-pent-3-enyl-benzene (227)⁴⁹



A suspension of 3-(diphenyl-phosphinoyl)-3-methyl-5-phenyl-pentan-2-ol (**226**) (666 mg, 1.76 mmol, 1.00 equiv, diastereomerically pure, synthesized following a published procedure)⁴⁹ in dry DMF (30 mL) was added to a suspension of sodium hydride (45 mg, 1.8 mmol, 1.0 equiv) in dry DMF (15 mL). After heating the resulting suspension at 50 °C for 1 h, the reaction mixture was cooled to 0 °C, quenched with water (50 mL), diluted with water (20 mL) and brine (70 mL) and extracted with Et_2O (3x50 mL). The combined organic layers were washed with water (4x50 mL) and brine (50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure (p = 100 mbar, T = 40 °C). The isolated product was purified by column chromatography (pentane) to afford **227** (101 mg, 0.631 mmol, 36%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 7.31-7.25 (m, 2H, Ar H), 7.20-7.15 (m, 3H, Ar H), 5.27-5.20 (m, 1H, alkene-H), 2.73-2.68 (m, 2H, PhCH_2), 2.30-2.25 (m, 2H, alkene- CH_2), 1.66 (s, 3H, CH_3), 1.58 (d, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 142.4, 135.2, 128.3, 128.1, 125.5, 118.7, 41.7, 34.9, 15.9, 13.5; IR v 3026 (w), 2922 (m), 2858 (w), 1602 (w), 1496 (w), 1453 (w), 1380 (w), 1030 (w), 913 (m), 807 (w), 743 (s), 697 (s), 516 (w), 451 (w).

(2-Methyl-allyloxy)methyl-benzene (228)⁵⁰

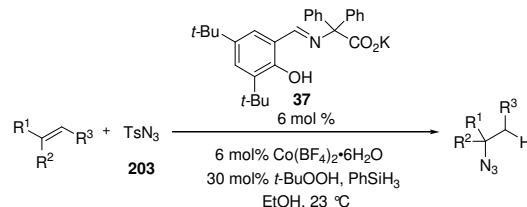


A solution of methallyl alcohol (**222**) (2.0 mL, 24 mmol, 1.0 equiv) in THF (8 mL) was added dropwise to a suspension of NaH (0.63 g, 25 mmol, 1.0 equiv) in THF (8 mL) at 23 °C under argon. After 1 h, a solution of benzyl bromide (2.8 mL, 24 mmol, 1 equiv) in THF (8 mL) and tetrabutylammonium iodide (0.24 g, 0.65 mmol, 0.027 equiv) were added slowly and the reaction mixture was heated to 40°C for 3.5 h. After cooling to 23 °C, the reaction mixture was quenched with water (20 mL) and extracted with Et_2O (3x50 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The isolated product was distilled (p = 0.5 mbar, bp = 45 °C) to afford **228** (3.58 g, 22.1 mmol, 92%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 7.46-7.33 (m, 5H, Ar H), 5.11 (m, 1H, alkene H), 5.02 (m, 1H, alkene H), 4.58 (s, 2H, CH_2O), 4.02 (s, 2H, CH_2O), 1.87 (d, J = 0.6 Hz, 3H, alkene CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 141.9, 138.2, 128.1, 127.4, 127.3, 112.1, 74.0, 71.7, 19.5; IR v 3066 (w), 3031 (w), 2974 (w), 2915 (m), 2854 (m), 1950 (w), 1870 (w), 1809 (w), 1656 (w), 1605 (w), 1496 (m), 1453 (s), 1363 (m), 1350 (m), 1310 (w), 1254 (w), 1203 (w), 1099 (s), 1075 (s), 1028 (m), 985 (w), 944 (w), 901 (s), 819 (w), 736 (s), 697 (s), 610 (w), 553 (w), 467 (w).

3.3. The Hydroazidation of Olefins

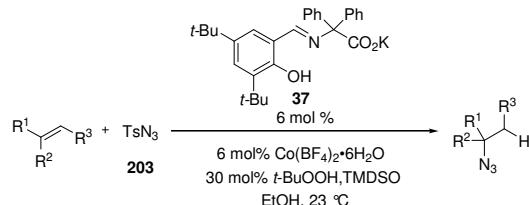
3.3.1. General Procedures

General Procedure for the Co-Catalyzed Hydroazidation of Olefins with Phenylsilane (GP5)



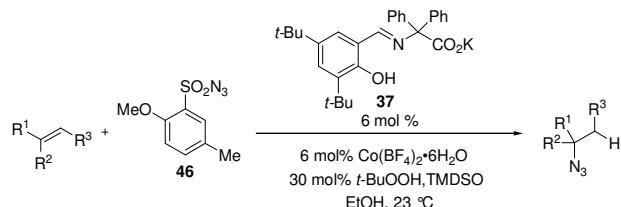
$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, the alkene (0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (**203**) (0.23 mL, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min, phenylsilane (0.10 mL, 0.80 mmol, 1.6 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After completion the reaction was quenched with H_2O (2 mL). Sat. NaHCO_3 (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The isolated product was purified by column chromatography to afford the desired alkyl azide.

General Procedure for the Co-Catalyzed Hydroazidation of Olefins with TMDSO (260) (GP6)



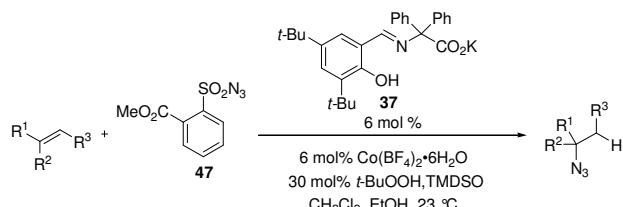
$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, the alkene (0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (**203**) (0.23 mL, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min, TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv, for some substrates: 0.26 mL, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting dark brown-green solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After completion the reaction was quenched with H_2O (2 mL). Sat. NaHCO_3 (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The isolated product was purified by column chromatography to afford the desired alkyl azide.

General Procedure for the Co-Catalyzed Hydroazidation of Olefins with TMDSO and sulfonylazide 52 (GP7)



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, the alkene (0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by sulfonyl azide **46** (0.17 g, 0.75 mmol, 1.5 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min, TMDSO (0.13 mL, 0.75 mmol, 1.5 equiv) was added dropwise. The resulting dark brown-green to dark green solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After completion the reaction was quenched with H_2O (2 mL). Sat. NaHCO_3 (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The isolated product was purified by column chromatography to afford the desired alkyl azide.

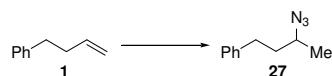
General Procedure for the Co-Catalyzed Hydroazidation of Olefins with TMDSO and sulfonylazide 47 (GP8)



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, the alkene (0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by sulfonyl azide **46** (0.18 g, 0.75 mmol, 1.5 equiv), CH_2Cl_2 (1.0 mL) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min, TMDSO (0.13 mL, 0.75 mmol, 1.5 equiv) was added dropwise. The resulting dark brown-green to dark green solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After completion the reaction was quenched with H_2O (2 mL). Sat. NaHCO_3 (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The isolated product was purified by column chromatography to afford the desired alkyl azide.

3.3.2. Hydroazidation Products

(3-Azido-butyl)-benzene (27)⁵¹



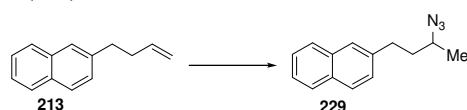
First Lead Result Phenylsilane (65 μ L, 0.52 mmol, 1.0 equiv) and ethanesulfonyl azide (**200**) (0.10 g, 0.75 mmol, 1.5 equiv) were added to a solution of Co catalyst **20** (10 mg, 0.025 mmol, 0.050 equiv) and 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) at 23 °C under argon. The resulting dark red solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 48 h, the reaction was still not completed and was quenched with H₂O (2 mL). Sat. NaHCO₃ (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (p = 50 mbar, T = 40 °C). The isolated product was purified by column chromatography (AcOEt/hexane 1:60) to afford the desired alkyl azide **33** (45 mg, 0.25 mmol, 50%) as a colorless liquid and recovered alkene **1** (11 mg, 0.083 mmol, 16%). **Following GP5** Azide **33** (79 mg, 0.45 mmol, 90%) was obtained as a colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) in 2 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). Gas chromatography showed full conversion (> 99%) after 2 h and a selectivity of 89:11 for the azidation of the alkene compared to simple reduction. **Following GP6** Azide **33** (75 mg, 0.43 mmol, 86%) was obtained as colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 3 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). Gas chromatography showed full conversion (> 99%) after 3 h and a selectivity of 96:4 for the azidation of the alkene compared to simple reduction. **Following GP7 (slightly modified)** Azide **33** (83 mg, 0.47 mmol, 94%) was obtained as colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv), TMDSO (88 μ L, 0.50 mmol, 1.0 equiv) and azide **52** (0.14 g, 0.60 mmol, 1.2 equiv) in 5 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). **Following GP8** Azide **33** (80 mg, 0.46 mmol, 91%) was obtained as colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) in 4 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). **Following GP5, but with Co-Salen Complex 34b** Azide **33** (60 mg, 0.34 mmol, 68%) was obtained as colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv), Co-salen catalyst **34b** (15 mg, 0.025 mmol, 0.050 equiv) in 5 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). Separation of the two enantiomers of **33** via HPLC was not directly possible. However, separation of the two enantiomers of the triazole obtained from the cycloaddition reaction of **33** with phenyl acetylene following a reported procedure⁵² was easy, but the obtained triazole was racemic (Daicel Chiracel OD-H column 250x4.6 mm, hexane/i-PrOH 80:20, flow: 1.0 mL/min, t_R : 12.0, 15.4 min, detector: 254 nm).

Gas chromatographic measurements:

An aliquot of 0.10 mL of the reaction mixture was diluted with 0.90 mL hexane and filtered through a short silica gel plug (2.5 cm) to remove the catalyst. 2 μ L of the obtained solution were injected in the gas chromatographer (Varian 3300 gas chromatographer) and the following temperature program was followed:- 10 min at 60 °C - to 110 °C with a temperature gradient of 8 °C/min - 1 min at 110 °C - to 180 °C with a temperature gradient of 20 °C/min. Using this procedure, 4-phenylbutene (**1**) eluted after 12.8 min, 4-phenylbutane (**44**) after 13.5 min and (3-azido-butyl)-benzene (**33**) after 23.8 min.

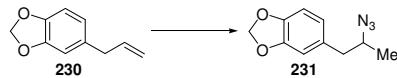
R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.37-7.32 (m, 2H, Ar H), 7.27-7.22 (m, 3H, Ar H), 3.52-3.43 (m, 1H, CHN₃), 2.86-2.66 (m, 2H, PhCH₂), 1.92-1.75 (m, 2H, CH₂CHN₃), 1.33 (d, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 141.1, 128.4, 128.3, 126.0, 57.1, 37.8, 32.2, 19.4; IR v 3064 (w), 3028 (m), 2972 (m), 2931 (m), 2862 (w), 2100 (s), 1947 (w), 1881 (w), 1805 (w), 1604 (w), 1496 (m), 1454 (m), 1380 (m), 1330 (m), 1250 (s), 1125 (w), 1047 (w), 1031 (w), 916 (w), 857 (w), 832 (w), 800 (w), 747 (m), 699 (s), 578 (w), 562 (w), 515 (w), 466 (w).

(3-Azido-3-methyl-butyl)-naphthalene (229)



Following GP5 Azide **229** (80 mg, 0.36 mmol, 72%) was obtained as an oil with (3-methylbut-3-enyl)-naphthalene (**213**) (89 mg, 0.49 mmol, 1.0 equiv) in 8 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). **Following GP6** Azide **229** (76 mg, 0.34 mmol, 69%) and (3-methylbut-3-enyl)-naphthalene (**213**) (23 mg, 0.13 mmol, 26% recovery) were obtained as oils with (3-methylbut-3-enyl)-naphthalene (**213**) (77 mg, 0.53 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 12 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.85-7.79 (m, 3H, naphthyl H), 7.65 (s, 1H, naphthyl H), 7.51-7.42 (m, 3H, naphthyl H), 7.35 (dd, J = 8.4, 1.9 Hz, 1H, naphthyl H), 3.52-3.45 (m, 1H, CHN₃), 2.99-2.80 (m, 2H, naphthyl-CH₂), 2.00-1.82 (m, 2H, CH₂CHN₃), 1.33 (d, J = 6.5 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 139.0, 133.9, 132.3, 128.4, 127.9, 127.7, 127.4, 126.8, 126.3, 125.6, 57.4, 38.0, 32.7, 19.8; IR v 3052 (w), 3019 (w), 2969 (m), 2929 (m), 2861 (w), 2099 (s), 1633 (w), 1600 (w), 1507 (m), 1452 (m), 1379 (m), 1332 (m), 1270 (m), 1246 (m), 1125 (w), 1059 (w), 1018 (w), 960 (w), 891 (w), 854 (m), 818 (s), 746 (s), 650 (w), 621 (w), 560 (w), 477 (m); MS (EI-HIRES) 182.0974 (M-HN₃), 196.1130 (M-HN₂), 197.1201 (M-N₂), 219.1375 (M-HN₂+Na); Anal. calcd for C₁₄H₁₅N₃: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.71; H, 6.88; N, 18.37.

5-(2-Azido-propyl)-benzo[1,3]dioxole (231)



Following GP5 Azide **231** (67 mg, 0.33 mmol, 66%) and safrole (**230**) (9 mg, 0.06 mmol, 11% recovery) were obtained as oils with safrole (**230**) (74 μ L, 0.50 mmol, 1.0 equiv) in 20 h after purification by column chromatography (pentane/Et₂O 120:1). **Following GP6** Azide **231** (64 mg, 0.31 mmol, 62%) and safrole (**230**) (12 mg, 0.075 mmol, 15% recovery) were obtained as oils with safrole (**230**) (74 μ L, 0.50 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 20 h after purification by column chromatography (pentane/Et₂O 120:1). R_f (AcOEt/hexane 1:40) 0.25; ¹H NMR (CDCl₃, 300 MHz) δ 6.96-6.63 (m, 3H, Ar H), 5.94 (s, 2H, acetal-H), 3.66-3.60 (m, 1H, CHN₃), 2.77-2.61 (m, 2H, ArCH₂), 1.25 (d, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 147.5, 146.2, 131.3, 122.2, 109.5, 108.2, 100.9, 59.2, 42.3, 19.1; IR ν 2973 (w), 2894 (w), 2105 (s), 1844 (w), 1608 (w), 1503 (s), 1490 (s), 1443 (m), 1379 (w), 1362 (w), 1327 (w), 1250 (s), 1190 (m), 1123 (w), 1100 (w), 1040 (s), 931 (m), 913 (w), 862 (w), 808 (w), 772 (w), 743 (w), 650 (w), 619 (w), 602 (w), 560 (w), 526 (w), 452 (w); HRMS (EI) calcd for C₁₀H₁₁N₃O₂⁺ (M): 205.0846, found 205.0846; Anal. calcd for C₁₀H₁₁N₃O₂: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.53; H, 5.52; N, 20.41.

(3-Azido-butoxy)-*tert*-butyl-diphenyl-silane (232)



Following GP5 Azide **232** (127 mg, 0.359 mmol, 73%) and butoxy-*tert*-butyl-diphenyl-silane (25 mg, 0.080 mmol, 16%) were obtained as oils with but-3-enyloxy-*tert*-butyl-diphenyl-silane (**214**) (152 mg, 0.490 mmol, 1.00 equiv) in 3 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). **Following GP6** Azide **232** (146 mg, 0.413 mmol, 85%) and butoxy-*tert*-butyl-diphenyl-silane (9 mg, 0.03 mmol, 6%) were obtained as oils with but-3-enyloxy-*tert*-butyl-diphenyl-silane (**214**) (150 mg, 0.483 mmol, 1.00 equiv) and TMDSO (0.26 mL, 1.5 mmol, 3.0 equiv) in 3 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). R_f (AcOEt/hexane 1:40) 0.27; ¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.66 (m, 4H, Ar H), 7.45-7.38 (m, 6H, Ar H), 3.81-3.70 (m, 3H, CH₂O and CHN₃), 1.74-1.67 (m, 2H, CH₂CHN₃), 1.29 (d, J = 6.6 Hz, 3H, CHN₃CH₃), 1.07 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 135.5, 133.7, 129.7, 127.7, 60.4, 54.8, 38.8, 26.8, 19.6, 19.2; IR ν 3070 (w), 3049 (w), 2959 (m), 2931 (m), 2878 (m), 2857 (m), 2103 (s), 1959 (w), 1887 (w), 1822 (w), 1657 (w), 1589 (w), 1472 (m), 1462 (w), 1428 (m), 1389 (w), 1361 (w), 1332 (w), 1268 (w), 1188 (w), 1112 (s), 1007 (w), 997 (w), 982 (w), 939 (w), 899 (w), 868 (w), 823 (m), 737 (m), 702 (s), 614 (m), 505 (s), 488 (m); MS (ESI) 354.3 (M+H), 376.3 (M+Na); Anal. calcd for C₂₀H₂₇N₃OSi: C, 67.95; H, 7.70; N, 11.89. Found: C, 68.16; H, 7.66; N, 11.91.

(3-Azido-butoxy)-*tert*-butyl-diphenyl-silane (233)



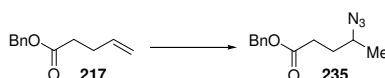
Following GP5 Azide **233** (93 mg, 0.27 mmol, 55%, about 95% purity in ¹H-NMR) and propoxy-*tert*-butyl-diphenyl-silane (36 mg, 0.12 mmol, 24%) were obtained as oils with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (148 mg, 0.499 mmol, 1.00 equiv) in 2 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP6** Azide **233** (114 mg, 0.34 mmol, 67%, about 90% purity in ¹H-NMR), propoxy-*tert*-butyl-diphenyl-silane (7 mg, 0.02 mmol, 4%) and prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (18 mg, 0.061 mmol, 12% recovery) were obtained as oils with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (147 mg, 0.496 mmol, 1.00 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 18 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP7** Azide **233** (32 mg, 0.95 mmol, 19%, about 95% purity in ¹H NMR), was obtained as a colorless oil with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (148 mg, 0.499 mmol, 1.00 equiv) in 18 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP8** Azide **233** (89 mg, 0.22 mmol, 44%, about 90% purity in ¹H-NMR), propoxy-*tert*-butyl-diphenyl-silane (18 mg, 0.060 mmol, 12%) and prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (5 mg, 0.02 mmol, 4% recovery) were obtained as oils with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**215**) (148 mg, 0.499 mmol, 1.00 equiv) in 18 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). Analytically pure samples of the desired product **233** were obtained after a second purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.71-7.66 (m, 4H, Ar H), 7.47-7.37 (m, 6H, Ar H), 3.67-3.53 (m, 3H, CH₂O and CHN₃), 1.17 (d, J = 6.5 Hz, 3H, CHN₃CH₃), 1.08 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 135.5, 133.0, 129.7, 127.6, 68.0, 58.9, 26.8, 19.3, 16.0; IR ν 3070 (w), 3050 (w), 2959 (m), 2931 (m), 2893 (w), 2858 (m), 2123 (s), 2109 (s), 1890 (w), 1824 (w), 1652 (w), 1589 (w), 1472 (w), 1463 (w), 1428 (m), 1390 (w), 1362 (w), 1332 (w), 1271 (m), 1188 (w), 1112 (s), 1022 (w), 1008 (w), 938 (w), 912 (m), 824 (m), 805 (w), 741 (s), 702 (s), 615 (m), 504 (s), 489 (m); MS (ESI) 339.2 (M), 362.0 (M+Na); Anal. calcd for C₁₉H₂₅N₃OSi: C, 67.22; H, 7.42; N, 12.38. Found: C, 67.48; H, 7.56; N, 12.29.

(2-Azido-propoxymethyl)-benzene (234)



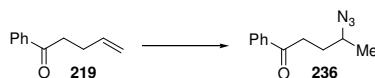
Following GP5 Azide **234** (33 mg, 0.17 mmol, 35%) and allyl benzyl ether (**123**) (14 mg, 0.094 mmol, 19% recovery) were obtained as oils with allyl benzyl ether (**123**) (77 μ L, 0.50 mmol, 1.0 equiv) in 48 h after purification by column chromatography (pentane/Et₂O 100:1). **Following GP6** Azide **234** (37 mg, 0.19 mmol, 39%) and allyl benzyl ether (**123**) (16 mg, 0.11 mmol, 22% recovery) were obtained as oils with allyl benzyl ether (**123**) (77 μ L, 0.50 mmol, 1.0 equiv) and TMDSO (0.26 mL, 1.5 mol, 3.0 equiv) in 48 h after purification by column chromatography (pentane/Et₂O 100:1). **Following GP7** Azide **234** was detected only as a minor product (< 20%) in the crude ¹H-NMR of the reaction mixture and was not isolated. **Following GP8** Azide **234** (27 mg, 0.14 mmol, 28%) and allyl benzyl ether (**123**) (8 mg, 0.05 mmol, 10% recovery) were obtained as oils with allyl benzyl ether (**123**) (77 μ L, 0.50 mmol, 1.0 equiv) in 48 h after purification by column chromatography (pentane/Et₂O 100:1). R_f (AcOEt/hexane 1:40) 0.25; ¹H NMR (CDCl₃, 300 MHz) δ 7.38-7.28 (m, 5H, Ar H), 4.58 (s, 2H, PhCH₂), 3.74-3.68 (m, 1H, CHN₃), 3.54-3.42 (m, 2H, CH₂O), 1.22 (d, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 137.7, 128.3, 127.6, 127.5, 73.8, 73.3, 57.0, 16.3; IR v 3064 (w), 3030 (w), 2976 (w), 2861 (w), 2124 (s), 2103 (s), 1496 (w), 1453 (w), 1379 (w), 1362 (w), 1330 (w), 1266 (m), 1206 (w), 1102 (m), 1028 (w), 998 (w), 913 (s), 743 (s), 698 (m), 651 (w), 621 (w), 558 (w), 458 (w), 441 (w); MS (EI-HIRES) 162.0912 (M-HN₂), 163.0947 (M-N₂); Anal. calcd for C₁₀H₁₃N₃O: C, 62.81; H, 6.85; N, 21.97. Found: C, 63.04; H, 7.00; N, 21.79.

4-Azido-pentanoic acid benzyl ester (**235**)



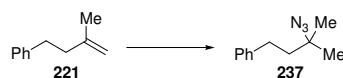
Following GP5 Azide **235** (86 mg, 0.37 mmol, 75%) was obtained as an oil with pent-4-enoic acid benzyl ester (**217**) (94 mg, 0.49 mmol, 1.0 equiv) in 10 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1). **Following GP6** Azide **235** (90 mg, 0.39 mmol, 77%) was obtained as an oil with pent-4-enoic acid benzyl ester (**217**) (95 mg, 0.50 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 10 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1). R_f (AcOEt/hexane 1:10) 0.40; ¹H NMR (CDCl₃, 300 MHz) δ 7.42-7.31 (m, 5H, Ar H), 5.14 (s, 2H, PhCH₂), 3.55-3.48 (m, 1H, CHN₃), 2.51-2.42 (m, 2H, CH₂CO), 1.92-1.71 (m, 2H, CH₂CHN₃), 1.29 (d, J = 6.5 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 172.5, 135.6, 128.4, 128.1, 128.1, 66.3, 57.0, 31.2, 30.8, 19.3; IR v 3336 (w), 3066 (w), 3034 (w), 2972 (m), 2102 (s), 1736 (s), 1498 (w), 1455 (m), 1382 (m), 1339 (m), 1269 (s), 1167 (s), 1127 (m), 1028 (m), 965 (m), 913 (w), 868 (w), 739 (m), 697 (m); MS (EI-HIRES) 204.1027 (M-HN₂), 205.1074 (M-N₂); Anal. calcd for C₁₂H₁₅N₃O₂: C, 61.79; H, 6.48; N, 18.01. Found: C, 62.04; H, 6.40; N, 17.88.

4-Azido-1-phenyl-pentan-1-one (**236**)



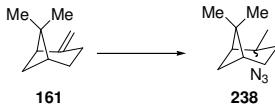
Following GP5 Azide **236** (51 mg, 0.25 mmol, 49%) and 1-phenyl-pent-4-en-1-one (**219**) (26 mg, 0.16 mmol, 32% recovery) were obtained as oils with 1-phenyl-pent-4-en-1-one (**219**) (82 mg, 0.51 mmol, 1.0 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1). **Following GP6** Azide **236** (46 mg, 0.23 mmol, 46%) and 1-phenyl-pent-4-en-1-one (**219**) (30 mg, 0.19 mmol, 38% recovery) were obtained as oils with 1-phenyl-pent-4-en-1-one (**219**) (79 mg, 0.49 mmol, 1.0 equiv) and TMDSO (0.26 mL, 1.5 mol, 3.0 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1). R_f (AcOEt/hexane 1:10) 0.40; ¹H NMR (CDCl₃, 300 MHz) δ 7.99-7.95 (m, 2H, Ar H), 7.60-7.51 (m, 1H, Ar H), 7.50-7.43 (m, 2H, Ar H), 3.62-3.53 (m, 1H, CHN₃), 3.18-3.00 (m, 2H, CH₂CO), 2.05-1.76 (m, 2H, CH₂CHN₃), 1.34 (d, J = 6.5 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 198.9, 136.6, 133.0, 128.5, 127.9, 57.3, 34.8, 30.4, 19.6; IR v 3353 (w), 3062 (w), 2972 (w), 2931 (w), 2105 (s), 1686 (s), 1597 (w), 1580 (w), 1448 (m), 1413 (w), 1381 (w), 1342 (w), 1218 (m), 1208 (m), 1180 (w), 1126 (w), 1071 (w), 1017 (w), 1002 (w), 970 (w), 913 (m), 744 (s), 690 (m), 654 (w), 616 (w), 564 (w), 506 (w); MS (EI-HIRES) 161.0924 (M-N₃), 175.0989 (M-N₂); Anal. calcd for C₁₁H₁₃N₃O: C, 65.01; H, 6.45; N, 20.67. Found: C, 64.82; H, 6.59; N, 20.76.

(3-Azido-3-methyl-butyl)-benzene (**237**)⁵¹



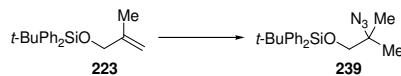
Following GP5 Azide **237** (81 mg, 0.43 mmol, 86%) was obtained as an oil with (3-methylbut-3-enyl)-benzene (**221**) (73 mg, 0.50 mmol, 1.0 equiv) in 3 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). **Following GP6** Azide **237** (90 mg, 0.48 mmol, 90%) was obtained as an oil with (3-methylbut-3-enyl)-benzene (**221**) (77 mg, 0.53 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 12 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.34-7.20 (m, 5H, Ar H), 2.73-2.67 (m, 2H, PhCH₂), 1.84-1.79 (m, 2H, CH₂CN₃), 1.35 (s, 6H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 141.8, 128.4, 128.3, 125.9, 61.4, 43.5, 30.7, 26.0; IR v 3329 (w), 3086 (w), 3062 (w), 3027 (w), 2972 (m), 2099 (s), 1603 (w), 1497 (w), 1454 (m), 1388 (w), 1370 (m), 1255 (s), 1204 (m), 1163 (w), 1124 (w), 1073 (w), 1030 (w), 871 (w), 850 (w), 822 (w), 767 (w), 744 (m), 699 (s), 631 (w), 565 (w), 512 (w).

2-Azido-2,6-trimethyl-bicyclo[3.1.1]heptane (**238**)



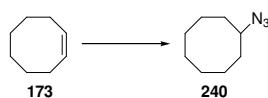
Following GP5 Azide **238** (80 mg, 0.45 mmol, 89%, mixture of diastereoisomers: 4:1) was obtained as an oil with β -pinene (**161**) (78 μ L, 0.50 mmol, 1.0 equiv) in 12 h after purification by column chromatography (pentane/Et₂O 100:1). **Following GP6** Azide **238** (68 mg, 0.38 mmol, 76%, mixture of diastereoisomers: 4:1) was obtained as an oil with β -pinene (**161**) (78 μ L, 0.50 mmol, 1.0 equiv) and TMDSO (0.26 mL, 1.5 mol, 3.0 equiv) in 12 h catalyst after purification by column chromatography (pentane/Et₂O 100:1). **Caution:** As the desired product displayed a very high tendency to co-evaporate with many solvents, the following work-up was substituted to the one described in the general procedure: After completion (12 h) the reaction was quenched with H₂O (2 mL). Sat. NaHCO₃ (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with Et₂O (3x10 mL). The combined organic layers were washed with water (3x10 mL) and brine (10 mL), dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (p = 700 mbar, T = 40 °C). After column chromatography, the fractions were not fully concentrated and the yield was determined via ¹H-NMR. R_f (AcOEt/hexane 1:40) 0.40; ¹H NMR (CDCl₃, 300 MHz) δ 2.27-2.19 (m, 1H, CH₂ or CH), 1.97-1.64 (m, 7H, CH₂ or CH), 1.42 (s, 3H (80%), CH₃ 1. diastereoisomer), 1.41 (s, 3H (20%), CH₃ 2. diastereoisomer), 1.26 (s, 3H (80%), CH₃ 1. diastereoisomer), 1.23 (s, 3H (20%), CH₃ 2. diastereoisomer), 0.99 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 67.6, 51.5, 40.2, 38.4, 28.9, 28.7, 27.8, 27.3, 25.1, 24.1, 23.4, 23.2; IR v 2917 (m), 2099 (s), 1465 (w), 1378 (w), 1252 (m), 1161 (w), 1133 (w), 1095 (w), 1075 (w), 1011 (w), 911 (w), 831 (w); MS (EI-HIRES) 137.1346 (M-N₃); Anal. calcd for C₁₀H₁₇N₃: C, 67.00; H, 9.56; N, 23.44. Found: C, 66.95; H, 9.38; N, 23.37.

(2-Azido-2-methyl-propoxy)-*tert*-butyl-diphenyl-silane (239)



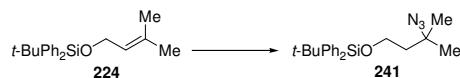
Following GP5 Azide **239** (130 mg, 0.368 mmol, 74%) and *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (31 mg, 0.10 mmol, 20% recovery) were obtained as oils with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (156 mg, 0.502 mmol, 1.00 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP6** Azide **239** (101 mg, 0.286 mmol, 58%) and *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (50 mg, 0.16 mmol, 33% recovery) were obtained as oils with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (152 mg, 0.490 mmol, 1.00 equiv) and TMDSO (0.26 mL, 1.5 mmol, 3.0 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP7** Azide **239** (155 mg, 0.439 mmol, 89%) was obtained as an oil with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (154 mg, 0.496 mmol, 1.00 equiv) in 20 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP8** Azide **239** (162 mg, 0.458 mmol, 91%) was obtained as an oil with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**223**) (156 mg, 0.502 mmol, 1.00 equiv) in 20 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.66 (m, 4H, Ar H), 7.45-7.38 (m, 6H, Ar H), 3.51 (s, 2H, CH₂O), 1.25 (s, 6H, CN₃CH₃), 1.09 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 135.5, 132.9, 129.7, 127.6, 71.5, 61.9, 26.8, 23.1, 19.4; IR v 3070 (w), 3050 (w), 2961 (w), 2931 (m), 2895 (w), 2858 (m), 2134 (m), 2098 (s), 2035 (w), 1890 (w), 1824 (w), 1589 (w), 1472 (w), 1428 (m), 1392 (w), 1365 (w), 1265 (m), 1164 (w), 1112 (s), 1007 (w), 998 (w), 938 (w), 913 (w), 866 (w), 825 (m), 773 (w), 741 (m), 702 (s), 614 (m), 504 (m), 489 (m); MS (ESI) 376.1 (M+Na); Anal. calcd for C₂₀H₂₇N₃OSi: C, 67.95; H, 7.70; N, 11.89. Found: C, 68.16; H, 7.93; N, 11.82.

Azidocyclobutane (240)⁵³



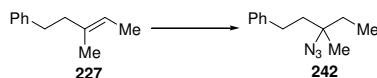
Co(BF₄)₂•6H₂O (20 mg, 0.060 mmol, 0.060 equiv) and ligand **43** (28 mg, 0.060 mmol, 0.060 equiv) were dissolved in ethanol (5 mL) at 23 °C under argon. After 10 min, cyclooctene (**173**) (0.13 mL, 1.0 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (**203**) (0.46 mL, 3.0 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 50 μ L, 0.28 mmol, 0.28 equiv). After 5 min, phenylsilane (0.20 mL, 1.6 mmol, 1.6 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After completion (12 h) the reaction was quenched with H₂O (5 mL). Sat. NaHCO₃ (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with Et₂O (3x20 mL). The combined organic layers were washed with water (4x10 mL) and brine (10 mL), dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (p = 700 mbar, T = 40 °C). The isolated product was purified by column chromatography (pentane/Et₂O 100:1) to afford the desired alkyl azide **240** (86 mg, 0.56 mmol, 56%) as a colorless liquid. R_f (AcOEt/hexane 1:40) 0.50; ¹H NMR (CDCl₃, 300 MHz) δ 3.59-3.52 (m, 1H, CHN₃), 1.92-1.42 (m, 14H, CH₂); ¹³C NMR (CDCl₃, 75 MHz) δ 62.2, 30.8, 27.2, 25.1, 23.1; IR v 2924 (s), 2855 (m), 2091 (s), 1474 (m), 1447 (m), 1362 (w), 1251 (m), 1095 (w), 1047 (w), 940 (w), 872 (w), 806 (w), 668 (w).

(3-Azido-3-methyl-butoxy)-*tert*-butyl-diphenyl-silane (241)



Following GP5 Azide **241** (116 mg, 0.316 mmol, 66%) and *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (34 mg, 0.10 mmol, 21% recovery) were obtained as oils with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (157 mg, 0.484 mmol, 1.00 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP6** Azide **241** (85 mg, 0.23 mmol, 50%) and *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (74 mg, 0.23 mmol, 50% recovery) were obtained as oils with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (150 mg, 0.462 mmol, 1.00 equiv) and TMDSO (0.26 mL, 1.5 mmol, 3.0 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP7** Azide **241** (151 mg, 0.411 mmol, 83%) and *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (9 mg, 0.03 mmol, 6% recovery) were obtained as oils with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (161 mg, 0.496 mmol, 1.00 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). **Following GP8** Azide **241** (142 mg, 0.386 mmol, 79%) was obtained as an oil with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**224**) (158 mg, 0.487 mmol, 1.00 equiv) in 24 h after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5). R_f (AcOEt/hexane 1:40) 0.35; ¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.67 (m, 4H, Ar H), 7.45-7.37 (m, 6H, Ar H), 3.79 (t, J = 6.8 Hz, 2H, CH₂O), 1.81 (t, J = 6.8 Hz, 2H, CN₃CH₂), 1.28 (s, 6H, CN₃CH₃), 1.06 (s, 9H, CCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 135.4, 133.5, 129.6, 127.6, 60.7, 60.3, 43.5, 26.9, 26.6, 19.2; IR ν 3070 (w), 3050 (w), 2962 (m), 2931 (m), 2887 (m), 2857 (m), 2099 (s), 1889 (w), 1824 (w), 1652 (w), 1589 (w), 1472 (w), 1428 (m), 1389 (w), 1370 (w), 1304 (w), 1260 (m), 1186 (w), 1144 (w), 1112 (s), 1048 (w), 997 (w), 938 (w), 913 (w), 893 (w), 823 (w), 758 (w), 738 (m), 702 (s), 689 (w), 613 (m), 505 (m), 490 (m), 416 (s); MS (ESI) 362.1 (M-N₂+Na), 390.0 (M+Na); Anal. calcd for C₂₁H₂₉N₃OSi: C, 68.62; H, 7.95; N, 11.43. Found: C, 68.46; H, 7.74; N, 11.28.

(3-Azido-3-methyl-pentyl)-benzene (242)



Following GP5 (slightly modified) Co(BF₄)₂•6H₂O (6 mg, 0.02 mmol, 0.06 equiv) and ligand **43** (8 mg, 0.02 mmol, 0.06 equiv) were dissolved in ethanol (1.5 mL) at 23 °C under argon. After 10 min, ((E)-3-methyl-pent-3-enyl)-benzene (**227**) (46 mg, 0.29 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosylazide (**203**) (0.14 mL, 0.90 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 15 μ L, 0.083 mmol, 0.28 equiv). After 5 min phenylsilane (60 μ L, 0.48 mmol, 1.6 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 30 h the reaction was quenched with H₂O (2 mL). Sat. NaHCO₃ (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (p = 50 mbar, T = 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1) to afford **242** (39 mg, 0.19 mmol, 66%) as a colorless liquid. **Following GP11 (slightly modified)** Co(BF₄)₂•6H₂O (6 mg, 0.02 mmol, 0.06 equiv) and ligand **43** (8 mg, 0.02 mmol, 0.06 equiv) were dissolved in ethanol (1.5 mL) at 23 °C under argon. After 10 min, ((E)-3-methyl-pent-3-enyl)-benzene (**227**) (46 mg, 0.29 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosylazide (**203**) (0.14 mL, 0.90 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 15 μ L, 0.083 mmol, 0.28 equiv). After 5 min TMDSO (0.16 mL, 0.90 mmol, 3.0 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 30 h the reaction was quenched with H₂O (2 mL). Sat. NaHCO₃ (2 mL) and brine (5 mL) were added and the reaction mixture was extracted with AcOEt (3x10 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (p = 50 mbar, T = 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1) to afford **242** (28 mg, 0.14 mmol, 48%) as a colorless liquid. R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.33-7.18 (m, 5H, Ar H), 2.69-2.63 (m, 2H, PhCH₂), 1.83-1.76 (m, 2H, CH₂CN₃), 1.63 (q, J = 7.5 Hz, 2H, CH₂CH₃), 1.30 (s, 3H, CN₃CH₃), 0.97 (t, J = 7.5 Hz, 3H, CH₂CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 141.8, 128.4, 128.2, 125.8, 64.3, 41.1, 32.1, 30.5, 22.9, 8.5; IR ν 3063 (w), 3026 (w), 2971 (w), 2939 (w), 2880 (w), 2092 (s), 1603 (w), 1497 (w), 1455 (w), 1381 (w), 1256 (m), 1190 (w), 1136 (w), 1074 (w), 1030 (w), 912 (w), 856 (w), 741 (m), 698 (m), 565 (w), 510 (w), 460 (w), 450 (w); MS (EI-HREES) 160.1171 (M-HN₃), 174.1281 (M-HN₂), 175.1343 (M-N₂); Anal. calcd for C₁₂H₁₇N₃: C, 70.90; H, 8.43; N, 20.67. Found: C, 71.15; H, 8.52; N, 20.76.

(2-Azido-2-methyl-propoxymethyl)-benzene (243)



Following GP6 Azide **243** (41 mg, 0.20 mmol, 40%) and alkene **228** (22 mg, 0.13 mmol, 26% recovery) were obtained as oils with alkene **228** (81 mg, 0.50 mmol, 1.0 equiv) and TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) in 24 h after purification by column chromatography (pentane/Et₂O 60:1). **Following GP7** Azide **243** (66 mg, 0.32 mmol, 64%) was obtained as an oil with alkene **228** (81 mg, 0.50 mmol, 1.0 equiv) in 24 h after purification by column chromatography (solvent gradient: pentane/Et₂O 80:1, then pentane/Et₂O 40:1). **Following GP8** Azide **243** (79 mg, 0.38 mmol, 76%) was obtained as an oil with alkene **228** (81 mg, 0.50 mmol, 1.0 equiv) in 24 h after purification by column chromatography (pentane/Et₂O 60:1). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.39-7.30 (m, 5H, Ar H), 4.60 (s, 2H, PhCH₂O), 3.38 (s, 2H, CH₂OBn, 1.30 (s, 6H, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 137.9, 128.2, 127.5, 127.3, 77.3, 73.3, 61.0, 23.5; IR ν 3090 (w), 3066 (w), 3031 (w), 2977 (m), 2935 (w), 2861 (m), 2502 (w), 2100 (s), 2043 (w), 1587 (w), 1497 (w), 1470 (w), 1454 (m), 1410 (w), 1384 (w), 1368 (m), 1265 (s), 1208

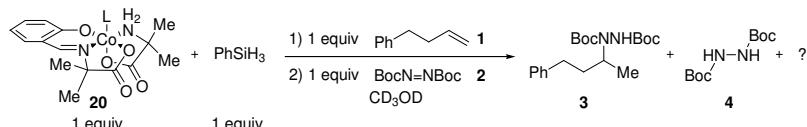
(w), 1164 (w), 1104 (s), 1029 (m), 981 (w), 960 (w), 906 (w), 870 (w), 783 (w), 737 (m), 698 (m), 620 (w), 605 (w), 562 (w); MS (ESI) 228.0 (M+Na); Anal. calcd for $C_{11}H_{15}N_3O$: C, 64.37; H, 7.37; N, 20.47. Found: C, 64.55; H, 7.47; N, 20.36.

4. Mechanistic Investigations

4.1. NMR and Deuterium-Labeling Experiments

NMR Experiments

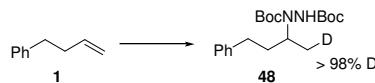
Stoichiometric Reaction with Complex 20



Complex **20** (10 mg, 0.025 mmol, 1.0 equiv) was dissolved in CD_3OD (0.75 mL) at 23 °C under argon and the first 1H -NMR (300 MHz) spectrum **A** was measured. Phenylsilane (3.1 μ L, 0.025 mmol, 1.0 equiv) was added and the second 1H -NMR spectrum **B** was measured as fast as possible, showing no peaks anymore corresponding to **20**. The reaction mixture was then heated progressively to 40 °C and monitored by 1H -NMR spectroscopy. After 20 min, at 40 °C, spectrum **C** was measured. At this point, the reaction mixture was cooled to 23 °C and 4-phenylbutene (**1**) (3.8 μ L, 0.025 mmol, 1.0 equiv) was added and the spectrum **D** was measured. Finally, after 5 min, azodicarboxylate **2** (6.0 mg, 0.026 mmol, 1.0 equiv) was added and the reaction monitored via 1H -NMR spectroscopy for the following 30 min. After 30 min, spectrum **E** was obtained and no major changes were observed afterwards.

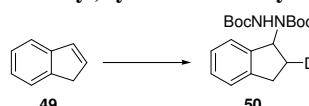
Deuterium-Labeling Experiments

N-(3-Phenyl-1-deuteromethyl-propyl)-*N'*-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**48**)



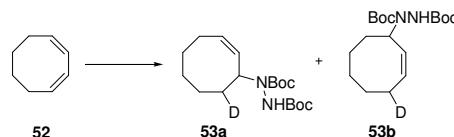
Following GP2 (with PhSiD₃) Hydrohydrazination product **48** (132 mg, 0.361 mmol, 72%) was obtained as a colorless solid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) and PhSiD₃ (synthesized following a reported procedure,⁵⁴ > 98% D, 82% in Et_2O , 70 mg, 0.52 mmol, 1.0 equiv) in 10 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.35; Mp 127-128°C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.29-7.14 (m, 5H, Ar H), 5.86 (br s, 1H, NH), 4.24 (br s, 1H, CHN), 2.65 (m, 2H, PhCH₂), 1.88 (m, 1H, CH_2CHN), 1.65 (m, 1H, CH_2CHN), 1.48 (s, 9H, CCH₃), 1.47 (s, 9H, CCH₃), 1.12 (d, J = 6.5 Hz, 2H, CHNCH₂D); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 156.0, 155.0, 142.1, 128.3, 128.3, 125.7, 80.9, 53.0, 35.8, 32.9, 28.3, 28.2, 17.8 (t, J = 19 Hz); IR v 3269 (m), 3159 (w), 3085 (w), 3062 (w), 3026 (w), 2977 (s), 2932 (m), 2864 (w), 2252 (w), 2185 (w), 1945 (w), 1746 (s), 1703 (s), 1604 (w), 1495 (m), 1478 (m), 1454 (m), 1392 (s), 1366 (s), 1273 (s), 1249 (s), 1159 (s), 1099 (m), 1079 (m), 1052 (m), 1032 (m), 1015 (m), 911 (m), 859 (m), 748 (m), 755 (m), 700 (m), 647 (w); MS (ESI) 366.4 (M+H), 388.2 (M+Na); Anal. calcd for $C_{20}H_{31}DN_2O_4$: C, 65.73; H+D, 8.85; N, 7.66. Found: C, 65.99; H+D, 8.93; N, 7.58.

N-(2-Deutero-1*H*-inden-1-yl)-*N'*-(tert-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**50**)



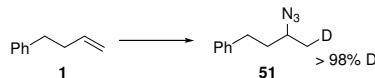
Following GP1 (with PhSiD₃) Hydrohydrazination product **50** (1:1 mixture of diastereoisomers, 154 mg, 0.441 mmol, 88%) was obtained as a colorless solid with indene (**49**) (59 μ L, 0.50 mmol, 1.0 equiv) and PhSiD₃ (synthesized following a reported procedure,⁵⁴ > 98% D, 82% in Et_2O , 70 mg, 0.52 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:5) 0.35; Mp 95-97 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 7.23-7.15 (m, 4H, Ar H), 5.88 (br s, 1H, NH), 5.75 (br s, 1H, CHN), 2.99 (m, 1H, CH_2), 2.81 (dd, J = 15.9, 8.0 Hz, 1H, CH_2), 2.37 (m, 0.5H, CHD), 2.17 (m, 0.5H, CHD), 1.51 (s, 9H, CCH₃), 1.43 (br s, 9H, CCH₃); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.4, 155.0, 144.0, 141.1, 127.8, 126.4, 124.8, 124.1, 81.2, 80.8, 62.4, 30.3, 28.8 (m), 28.2, 28.1; IR v 3313 (m), 3071 (w), 2977 (s), 2932 (m), 2855 (w), 2252 (w), 2201 (w), 1742 (s), 1704 (s), 1606 (w), 1479 (m), 1458 (m), 1392 (s), 1367 (s), 1327 (s), 1254 (s), 1158 (s), 1100 (m), 1052 (m), 1023 (m), 987 (w), 940 (w), 918 (w), 874 (w), 854 (w), 750 (s), 700 (w), 647 (w); MS (ESI) 350.2 (M+H), 372.2 (M+Na); Anal. calcd for $C_{19}H_{27}DN_2O_4$: C, 65.31; H+D, 8.10; N, 8.02. Found: C, 65.28; H, 8.10; N, 7.85.

Di-*tert*-butyl-1-(8-deutero-cyclooct-2-enyl)hydrazine-1,2-dicarboxylate (**53a**) and Di-*tert*-butyl-1-(4-deutero-cyclooct-2-enyl)hydrazine-1,2-dicarboxylate (**53b**)



Following GP1 (with PhSiD₃) Hydrohydrazination product **53** (1:1 mixture of regioisomers **53a**, **53b**, each regioisomer 1:1 mixture of diastereoisomers, 88 mg, 0.26 mmol, 52%) was obtained as a colorless solid with cyclooctadiene (**52**) (62 μ L, 0.50 mmol, 1.0 equiv) and PhSiD₃ (synthesized following a reported procedure,⁵⁴ > 98% D, 82% in Et₂O, 70 mg, 0.52 mmol, 1.0 equiv) in 6 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:10) 0.25; Mp 121-123 °C; ¹H NMR (CDCl₃, 300 MHz, 50 °C) δ 6.09 (br s, 1H, NH), 5.70-5.52 (m, 2H, C=CH), 5.02 (m, 1H, CHN), 2.30-2.19 (m, 0.7-0.8H, CH₂C= and CHD=), 2.13-2.01 (m, 0.7-0.8H, CH₂C= and CHD=), 1.68-1.24 (m, 7.5-8H), 1.46 (s, 9H, C(CH₃)₃), 1.45 (s, 9H, C(CH₃)₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.9, 154.5, 129.3, 128.7, 81.0, 55.4, 33.3, 33.0 (m), 32.7 (m), 29.3, 29.2 (m), 28.4, 28.3, 26.8, 26.6, 24.5, 24.4; ²D NMR (CHCl₃, 300 MHz, 23 °C) δ 2.24 (s, 1D, CHD=, **53b**), 2.09 (s, 1D, CHD=, **53b**), 1.75 (s, 1D, CHDCHN, **53a**), 1.58 (s, 1D, CHDCHN, **53a**); IR v 3319 (w), 2978 (m), 2929 (m), 2858 (w), 2157 (w), 1704 (s), 1479 (m), 1455 (m), 1412 (m), 1391 (s), 1367 (s), 1315 (m), 1246 (m), 1161 (s), 1050 (w), 1022 (w), 937 (w), 859 (w), 759 (w); MS (ESI) 342.2 (M+H), 364.2 (M+Na), 705.2 (2M+Na); Anal. calcd for C₁₈H₃₁DN₂O₄: C, 63.31; H+D, 9.47; N, 8.20. Found: C, 63.35; H+D, 9.52; N, 8.22.

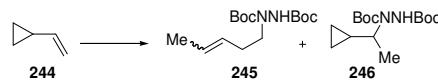
(3-Azido-4-deutero-butyl)-benzene (**51**)



Following GP10 (with PhSiD₃) Azide **51** (83 mg, 0.47 mmol, 94%) was obtained as a colorless liquid with 4-phenylbutene (**1**) (75 μ L, 0.50 mmol, 1.0 equiv) and PhSiD₃ (synthesized following a reported procedure,⁵⁴ > 98% D, 82% in Et₂O, 0.10 g, 0.74 mmol, 1.5 equiv) in 3 h after purification by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1). R_f (AcOEt/hexane 1:40) 0.30; ¹H NMR (CDCl₃, 300 MHz) δ 7.33-7.18 (m, 5H, Ar H), 3.43 (qi, *J* = 6.9 Hz, 1H, CHN₃), 2.81-2.62 (m, 2H, PhCH₂), 1.90-1.72 (m, 2H, CH₂CHN₃), 1.28 (dt, *J* = 6.5 Hz, 1.9Hz, 2H, CHNCH₂D); ¹³C NMR (CDCl₃, 75 MHz) δ 141.1, 128.3, 128.3, 125.9, 57.1, 37.9, 32.4, 19.3 (t, *J* = 19 Hz); IR v 3063 (w), 3027 (w), 2941 (m), 2860 (w), 2100 (s), 1603 (w), 1496 (w), 1454 (w), 1333 (w), 1261 (m), 1030 (w), 745 (w), 699 (m); HRMS (EI) calcd for C₁₀H₁₁DN⁺ (M-HN₂): 147.1027, found 147.1029; Anal. calcd for C₁₀H₁₂DN₃: C, 68.15; H+D, 7.48; N, 23.84. Found: C, 68.15; H+D, 7.70; N, 23.93.

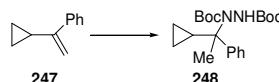
4.2. Radical Clocks

(*N*-Pent-3-enyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**245**)



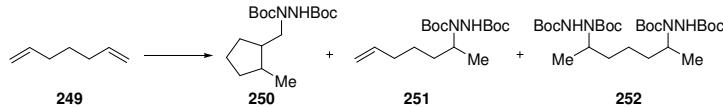
Following GP1 Hydrohydrazination product **245** (80 mg, 0.27 mmol, 59 %, mixture of *Z/E* olefins (1/5, not assigned), containing traces (<5%) of **246** (not isolated)) was obtained as a colorless solid with vinylcyclopropane (**244**) (synthesized following a reported procedure,⁵⁵ 93% pure, 33 mg, 0.45 mmol, 1.0 eq) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15-1:2). R_f (AcOEt/hexane 1:5) 0.35; Mp 51-55 °C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 6.24 (br s, 1H, NH), 5.55-5.31 (m, 2H, alkene H), 3.44 (dd, *J* = 6.9, 7.5 Hz, 2H, CH₂Ph), 2.35-2.19 (m, 2H, alkene-CH₂), 1.62 (dd, *J* = 5.9, 1.2 Hz, 3H (83 %), alkene-CH₃, 1. diastereoisomer), 1.46 (s, 9H, CCH₃), 1.44 (s, 9H, CCH₃), 1.19 (d, *J* = 6.9 Hz, alkene-CH₃, 3H (17 %), 2. diastereoisomer); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 155.0, 127.8, 126.7, 125.8, 80.9, 80.8, 80.6, 49.7, 30.9, 28.2, 28.2, 25.4, 17.8, 17.4, 15.1, 12.7; IR v 3318 (m), 2980 (s), 2934 (m), 1706 (s), 1480 (m), 1455 (m), 1393 (s), 1367 (s), 1290 (s), 1252 (s), 1161 (s), 1051 (m), 1019 (m), 967 (w), 932 (w), 857 (w), 758 (m), 701 (w), 605 (w); MS (ESI) 301.2 (M+H), 323.2 (M+Na); Anal. calcd for C₁₅H₂₈N₂O₄: C, 59.98; H, 9.39; N, 9.33. Found: C, 59.77; H, 9.17; N, 9.14.

N-(1-Cyclopropyl-1-phenyl-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**248**)



Following GP1 Hydrohydrazination product **248** (91 mg, 0.24 mmol, 48%) was obtained as a colorless solid with vinylcyclopropane **247** (synthesized following a reported procedure,⁵⁶ 72 mg, 0.50 mmol, 1.0 eq) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:15-1:2). A fraction containing a mixture of ring-opened and multi-aminated products (61 mg, about 20-30%, exact structure not assigned) was also isolated. **Following GP3** Hydrohydrazination product **248** (114 mg, 0.303 mmol, 60%) was obtained as a colorless solid with vinylcyclopropane **247** (synthesized following a reported procedure,⁵⁶ 72 mg, 0.50 mmol, 1.0 eq) in 3 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:15-1:2). A fraction containing a mixture of ring-opened and multi-aminated products (48 mg, about 20%, exact structure not assigned) was also isolated. R_f (AcOEt/hexane 1:5) 0.30; Mp 53-55 °C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 7.56 (br m, 2H, Ar H), 7.29-7.14 (m, 3H, Ar H), 6.40 (br s, 1H, NH), 1.65-1.50 (m, 1H, CH), 1.53 (s, 9H, OC(CH₃)₃), 1.39 (s, 3H, CNCH₃), 1.15 (s, 9H, OC(CH₃)₃), 0.62-0.08 (m, 4H, CH₂); ¹³C NMR (CDCl₃, 75 MHz, mixture of rotamers) δ 156.3, 154.5, 147.9, 146.0, 128.5, 127.6, 127.4, 125.8, 125.3, 81.0, 67.7, 67.1, 28.4, 28.0, 23.2, 21.7, 21.0, 19.1, 2.6, 2.4, 0.6; IR v 3270 (m), 3086 (w), 3061 (w), 3006 (m), 2978 (s), 2932 (m), 1952 (w), 1711 (s), 1602 (w), 1493 (m), 1478 (m), 1455 (m), 1392 (s), 1367 (s), 1338 (s), 1250 (s), 1161 (s), 1085 (m), 1073 (m), 1048 (m), 1020 (m), 912 (m), 851 (m), 764 (m), 733 (s), 703 (s), 646 (w), 615 (w); MS (ESI) 399.3 (M+Na); Anal. calcd for C₂₁H₃₂N₂O₄: C, 66.99; H, 8.57; N, 7.44. Found: C, 67.01; H, 8.47; N, 7.28.

N-(2-Methyl-cyclopentylmethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**250**) and *N*-(1-Methyl-hex-5-enyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**251**) and *N*-[5-(*N,N*'-Di-*tert*-butoxycarbonyl-hydrazino)-1-methyl-hexyl]-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**252**)



Following GP1 Hydrohydrazination products **251** together with **250** (mixture **251/250** 5:1, **250** as a 1.4:1 mixture of diastereoisomers, 80 mg, 0.24 mmol, 40% **251** and 8% **250**) and bis-hydrohydrazination product **252** (68 mg, 0.12 mmol, 24%) were obtained as a viscous oil (**250/251** mixture) and a colorless solid (**252**) with 1,6-heptadiene **249** (68 μ L, 0.50 mmol, 1.0 eq) in 20 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10-1:1). Following GP3 Hydrohydrazination products **251** together with **250** (mixture **251/250** 5:1, **251** as a 5:1 mixture of diastereoisomers, 68 mg, 0.20 mmol, 34% **251** and 6% **250**) and bis-hydrohydrazination product **252** (82 mg, 0.15 mmol, 30%) were obtained as a viscous oil (**250/251** mixture) and a colorless solid (**252**) with 1,6-heptadiene **249** (68 μ L, 0.50 mmol, 1.0 eq) in 15 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10-1:1).

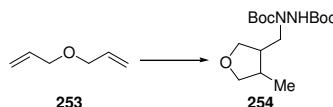
N-(2-Methyl-cyclopentylmethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**250**) and *N*-(1-Methyl-hex-5-enyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**251**)

R_f (AcOEt/hexane 1:5) 0.30; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.23 (br s, 1H, NH, **250**), 5.97 (br s, 1H, NH, **251**), 5.82-5.63 (m, 1H, alkene H, **251**), 4.99-4.88 (m, 2H, alkene H, **251**), 4.15 (m, 1H, CHN, **251**), 3.41-3.27 (m, 2H, CH_2N , **250**), 2.16-1.97 (m, 2H, CH_2 -alkene, **251**), 2.16-1.13 (m, 8H, CH and CH_2 , **250**), 1.82-1.13 (m, 4H, CH_2 , **251**), 1.44 (s, 9H, $OC(CH_3)_3$, **250** and **251**), 1.43 (s, 9H, $OC(CH_3)_3$, **250** and **251**), 1.07 (d, J = 6.8 Hz, 3H, $CHNCH_3$, **251**), 0.95 (d, J = 6.5 Hz, 3H (40%), $CHCH_3$, **250** 1.diastereoisomer), 0.82 (d, J = 6.9 Hz, 3H (60%), $CHCH_3$, **250** 2. diastereoisomer); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.8, 155.4, 154.8, 138.5, 114.4, 114.2, 80.7, 53.1, 50.6, 45.9, 41.2, 38.2, 35.5, 34.7, 33.6, 31.7, 30.7, 28.6, 28.3, 28.2, 27.4, 26.2, 25.8, 23.7, 22.5, 19.8, 18.0, 15.0, 14.0; IR v 3314 (w), 3076 (w), 2978 (m), 2932 (m), 2871 (w), 1704 (s), 1641 (w), 1478 (m), 1455 (m), 1393 (s), 1367 (s), 1333 (m), 1252 (m), 1159 (s), 1113 (m), 1048 (w), 1015 (w), 910 (w), 857 (w), 759 (w); MS(ESI) 329.2 (M+H), 351.2 (M+Na); Anal. calcd for $C_{17}H_{32}N_2O_4$: C, 62.17; H, 9.82; N, 8.53. Found: C, 62.36; H, 9.99; N, 8.69.

N-[5-(*N,N*'-Di-*tert*-butoxycarbonyl-hydrazino)-1-methyl-hexyl]-*N'*-(*tert*-butoxycarbonyl) hydrazinecarboxylic acid *tert*-butyl ester (**252**)

R_f (AcOEt/hexane 1:5) 0.15; Mp 156-158 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.20 (br s, 2H, NH), 4.19 (m, 2H, CHN), 1.76-1.24 (m, 6H, CH_2), 1.49 (s, 18H, $OC(CH_3)_3$), 1.45 (s, 18H, $OC(CH_3)_3$), 1.08 (d, J = 6.8 Hz, 6H, $CHNCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz, 52 °C) δ 155.9, 155.0, 80.7, 52.7, 34.3, 28.4, 23.6, 18.4; IR v 3315 (m), 2978 (m), 2932 (m), 1732 (s), 1707 (s), 1499 (m), 1480 (m), 1456 (m), 1393 (s), 1367 (s), 1343 (m), 1296 (m), 1274 (m), 1245 (s), 1158 (s), 1111 (m), 1096 (m), 1048 (w), 1017 (w), 962 (w), 920 (w), 859 (w), 838 (w), 783 (w), 757 (w), 734 (m), 688 (w), 647 (w); MS(ESI) 583.4 (M+Na); Anal. calcd for $C_{27}H_{52}N_2O_8$: C, 57.83; H, 9.35; N, 9.99. Found: C, 57.67; H, 9.28; N, 10.00.

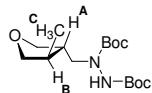
N-(4-Methyl-tetrahydro-furan-3-ylmethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (**254**)



Following GP1 Hydrohydrazination product **254** (mixture of diastereoisomers *trans/cis* 1:1.6, 113 mg, 0.342 mmol, 68%) was obtained as a colorless solid with diallyl ether (**253**) (61 μ L, 0.50 mmol, 1.0 eq) in 15 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10-1:2). Analytically pure samples of the *trans* and the *cis* isomers could be obtained after two more column chromatographies (AcOEt/hexane 1:15-1:5). Following GP3 Hydrohydrazination product **254** (mixture of diastereoisomers *trans/cis* 1:2.5, 145 mg, 0.439 mmol, 88%) was obtained as a colorless solid with diallyl ether (**253**) (61 μ L, 0.50 mmol, 1.0 eq) in 24 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10-1:2). Analytically pure samples of the *trans* and the *cis* isomers could be obtained after two more column chromatographies (AcOEt/hexane 1:15-1:5).

trans-**254**

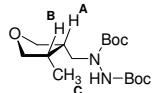
R_f (AcOEt/hexane 1:5) 0.20; Mp 55-57 °C; 1H NMR ($CDCl_3$, 300 MHz, 52 °C) δ 6.25 (br s, 1H, NH), 4.00-3.91 (m, 2H, CH_2O), 3.64-3.50 (m, 2H, CH_2O and/or CH_2N), 3.42-3.28 (m, 2H, CH_2O and/or CH_2N), 2.15-2.03 (m, 1H, $CHCH_2N$), 2.00-1.91 (m, 1H, $CHCH_3$), 1.48 (s, 9H, $OC(CH_3)_3$), 1.47 (s, 9H, $OC(CH_3)_3$), 1.05 (d, J = 6.5 Hz, 3H, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 500 MHz, 23 °C): NOE



pulse on **A** (2.09): NOE on **B** not observed, NOE on **C** strong; pulse on **B** (1.96): NOE on **A** not observed, NOE on **C** strong; pulse on **C** (1.05): NOE on **A** strong, NOE on **B** strong; ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.4, 81.4, 74.9, 72.0, 52.4, 46.1, 37.6, 28.2, 17.0; IR ν 3305 (m), 2977 (s), 2932 (m), 2873 (m), 1713 (s), 1479 (m), 1455 (m), 1393 (s), 1367 (s), 1254 (s), 1149 (s), 1048 (m), 1018 (m), 922 (m), 857 (w), 781 (w), 758 (m), 734 (m), 698 (w), 647 (w); MS(ESI) 331.4 (M+H), 353.4 (M+Na); Anal. calcd for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_5$: C, 58.16; H, 9.15; N, 8.48. Found: C, 57.74; H, 9.39; N, 8.67.

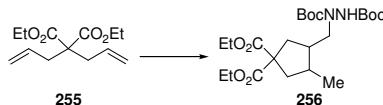
cis-254

R_f (AcOEt/hexane 1:5) 0.20; Mp 88-89 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.30 (br s, 1H, NH), 3.92-3.87 (m, 2H, CH_2O), 3.63-3.41 (m, 4H, CH_2O and CH_2N), 2.58-2.46 (m, 1H, CHCH_2N), 2.41-2.28 (m, 1H, CHCH_3), 1.46 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.45 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 0.96 (d, J = 7.2 Hz, 3H, CHCH_3); ^1H NMR (CDCl_3 , 500 MHz, 23 °C): NOE



pulse on **A** (2.52): NOE on **B** strong, NOE on **C** weak; pulse on **B** (2.34): NOE on **A** strong, NOE on **C** strong; pulse on **C** (0.96): NOE on **A** weak, NOE on **B** strong; ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.2, 81.3, 75.1, 70.9, 48.6, 40.9, 35.5, 28.3, 12.9; IR ν 3309 (m), 2976 (s), 2932 (m), 2877 (m), 1711 (s), 1479 (m), 1455 (m), 1393 (s), 1367 (s), 1320 (m), 1276 (s), 1254 (s), 1148 (s), 1048 (m), 1019 (w), 913 (w), 856 (w), 781 (w), 758 (w), 734 (w), 647 (w); MS(ESI) 331.4 (M+H), 353.4 (M+Na); Anal. calcd for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_5$: C, 58.16; H, 9.15; N, 8.48. Found: C, 58.04; H, 9.17; N, 8.37.

3-(*N,N'*-Di-*tert*-butoxycarbonyl-hydrazinomethyl)-4-methyl-cyclopentane-1,1-dicarboxylic acid diethyl ester (256)



Following GP1 Hydrohydrazination product **256** (mixture of diastereoisomers 7:1, 143 mg, 0.303 mmol, 62%) was obtained as a colorless solid with diallylmalonate **255** (118 mg, 0.491 mmol, 1.00 eq) in 15 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10:1.5). **Following GP3** Hydrohydrazination product **256** (mixture of diastereoisomers 9:1, 221 mg, 0.468 mmol, 93%) was obtained as a colorless solid with diallylmalonate **255** (121 mg, 0.504 mmol, 1.00 eq) in 4 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10:1.5). R_f (AcOEt/hexane 1:2) 0.45; Mp 82-85 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.24 (br s, 1H, NH), 4.19-4.05 (m, 2H, CH_2O), 3.51-3.31 (m, 2H, CH_2N), 2.48-1.64 (m, 6H, CH and CH_2), 1.44 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.43 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.21 (t, J = 7.2 Hz, CH_2CH_3), 0.98 (d, J = 5.9 Hz, 3H, CHCH_3 , minor diastereoisomer), 0.87 (d, J = 6.8 Hz, 3H, CHCH_3 , major diastereoisomer); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 172.5, 172.3, 155.2, 81.1, 61.3, 59.0, 50.2, 41.7, 40.7, 36.9, 35.1, 28.3, 14.9, 14.0, 13.9; IR ν 3337 (w), 2978 (m), 2934 (m), 1731 (s), 1478 (m), 1456 (m), 1393 (m), 1367 (s), 1254 (s), 1152 (s), 1096 (m), 1054 (m), 1018 (m), 918 (w), 859 (w), 782 (w), 758 (w), 734 (w); MS(ESI) 495.4 (M+Na); Anal. calcd for $\text{C}_{23}\text{H}_{40}\text{N}_2\text{O}_8$: C, 58.46; H, 8.53; N, 5.93. Found: C, 58.42; H, 8.43; N, 5.97.

Equation Used for the Estimation of the Reaction Rate⁵⁷

$$\frac{k_1}{k_2} \cdot \left\{ \ln \left(\frac{[XY]_i}{[XY]_f} + \frac{k_1}{k_2} \right) - \ln \left(\frac{[XY]_i}{[XY]_f} + \frac{k_1}{k_2} \right) \right\} = [\text{Sub}]_i \cdot \frac{[R'X]/[RX]}{1 + [R'X]/[RX]}$$

In this equation, k_1 is the rate of the known unimolecular radical reaction, k_2 the unknown rate for the bimolecular amination reaction; $[XY]_i$ is the initial concentration (0.3 M) and $[XY]_f$ is the final concentration (0 M) of the radical trap (azodicarboxylate **2**); $[\text{Sub}]_i$ is the initial concentration of alkene (0.2 M); $[RX]$ and $[R'X]$ are the yields of unarranged and rearranged products respectively. The solution of this equation was approximated numerically.

Specific Values

For α -phenylvinylcyclopropane (247): Co-catalyst **20:** $[RX] = 0.12 \text{ M}$, $[R'X] = 0.04 \text{ M}$, $k_1 = 4 \cdot 10^5 \text{ s}^{-1}$, $k_2 = 1.5 \cdot 10^8 \text{ s}^{-1} \text{ mol}^{-1}$; Mn-catalyst **23:** $[RX] = 0.10 \text{ M}$, $[R'X] = 0.05 \text{ M}$, $k_1 = 4 \cdot 10^5 \text{ s}^{-1}$, $k_2 = 2.5 \cdot 10^8 \text{ s}^{-1} \text{ mol}^{-1}$. **For 1,6-heptadiene (249):** Co-catalyst **20:** $[RX] = 0.13 \text{ M}$, $[R'X] = 0.016 \text{ M}$, $k_1 = 1 \cdot 10^5 \text{ s}^{-1}$, $k_2 = 1.5 \cdot 2.0 \cdot 10^8 \text{ s}^{-1} \text{ mol}^{-1}$; Mn-catalyst **23:** $[RX] = 0.13 \text{ M}$, $[R'X] = 0.013 \text{ M}$, $k_1 = 1 \cdot 10^5 \text{ s}^{-1}$, $k_2 = 2 \cdot 2.5 \cdot 10^8 \text{ s}^{-1} \text{ mol}^{-1}$.

4.3. Kinetic Measurements

4.3.1. Methods and Formula

NMR-Method for the Monitoring of the Hydrohydrazination of 4-phenylbutene (1)

A mixture of Co catalyst **20** and azodicarboxylate **2** were dissolved in CD_3OD (0.75 mL) at 23 °C under argon in a NMR tube. 4-Phenylbutene (**1**) was added, followed by the silane (time set to zero at this point). The reaction was monitored by ^1H -NMR at 300 MHz. Systematic variations of one of the reagent starting from the standard conditions (4-phenyl butene (**1**): 19 μL , 0.13

mmol, 0.17 M, 1.0 equiv; catalyst **20**: 2 mg, 0.005 mmol, 0.007 M, 0.04 equiv; azodicarboxylate **2**: 43 mg, 0.20 mmol, 0.27 M, 1.5 equiv; phenylsilane: 16 μ L, 0.13 mmol, 0.17 M, 1.0 equiv; 25 °C; 0.75 mL CD₃OD) were examined. The ratio of hydrohydrazination product **3** to alkene **1** was calculated from the ratio of the integrals between 1.14 and 1.00 ppm (CH₃ group of **3**) and between 2.40 and 2.23 ppm (alkene-CH₂ group of **1**). The concentration of alkene **1** was then calculated from this ratio and the initial concentration. In this way, the large absolute error of the NMR method was minimized. The relative values obtained present the advantage of being easily compared and requires less experimental work than absolute values based on internal standards.

GC-Method for Monitoring of the Hydrohydrazination of 4-phenylbutene (**1**)

The hydrohydrazination of 4-phenylbutene (**1**) with TMDSO following GP11 was used as reference for these studies. Each reagent was then varied systematically (see Appendix A). **Gas chromatographic measurements:** An aliquot of 0.10 mL of the reaction mixture was diluted with 0.90 mL hexane and filtered through a short silica gel plug (2.5 cm) to remove the catalyst. 2 μ L of the obtained solution were injected in the gas chromatographer (HP 6890 Series GC System) and the following temperature program was followed: - 5 min at 60 °C - to 90 °C with a temperature gradient of 5 °C/min - to 140 °C with a temperature gradient of 12 °C/min - to 180 °C with a temperature gradient of 8 °C/min - 10 min at 180 °C Using this procedure, 4-phenylbutene (**1**) eluted after 12.65 min, 4-phenylbutane (**44**) after 12.48 min and (3-azido-butyl)-benzene (**33**) after 18.00 min. The ratio of hydroazidation product **33** to alkene **1** was calculated from the ratio of the integrals of the signals after 12.65 min and 18.00 min. The concentration of alkene **1** was then calculated from this ratio and the initial concentration. In the rare cases where the formation of 4-phenylbutane (**44**) was significant, the concentration was further corrected.

Statistical Methods and Formula⁵⁸

Reaction Rate

The initial rates r of the reactions were determined using standard linear regression programs (Excel) applied on the linear region of the concentration curves. The standard deviation and the confidence interval of the data were calculated using following formula:

$$\text{Standard deviation of the rate: } s_r^2 = \frac{n}{n \cdot \sum_{i=1}^n t_i^2 - (\sum_{i=1}^n t_i)^2} \cdot \sum_{i=1}^n (c_i - I - r \cdot t_i)^2 \cdot \frac{1}{n-2} \quad \text{Confidence interval (95%)} \text{ of the rate: } v_r = t_s \cdot \frac{s_r}{\sqrt{n}}$$

Whereas n is the amount of data points measured, t is the time of measurement after the addition of the silane, c is the measured concentration of 4-phenylbutene (**1**), r is the calculated reaction rate, I is the calculate intercept of the curve, t_s is the student-t factor corresponding to 95% probability and a degree of freedom of $n-2$.

Van't Hoff Equation

$$\text{Van't Hoff Equation: } y = \log r = O \cdot \log c + I = a \cdot \log c + b;$$

$$\text{Standard deviation, confidence interval for y values: } s_{yi} = \frac{s_r}{\ln(10) \cdot r_i}, \quad v_{yi} = \frac{v_r}{\ln(10) \cdot r_i}$$

$$\text{Standard deviation of the reaction order: } s_O = s_a = \frac{\sum_{i=1}^m \frac{1}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{x_i^2}{s_{yi}^2} - (\sum_{i=1}^m \frac{x_i}{s_{yi}})^2}{\sum_{i=1}^m \frac{1}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{1}{s_{yi}^2} - (\sum_{i=1}^m \frac{1}{s_{yi}})^2}, \quad x_i = \log c_i$$

$$\text{Confidence interval (95%)} \text{ of the reaction order: } v_O = v_a = t_s \cdot \frac{s_a}{\sqrt{m}}$$

$$\text{Correlation factor R: } R = \frac{\sum_{i=1}^m \frac{1}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{x_i y_i}{s_{yi}^2} - \sum_{i=1}^m \frac{x_i}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{y_i}{s_{yi}^2}}{\sqrt{\sum_{i=1}^m \frac{1}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{x_i^2}{s_{yi}^2} - (\sum_{i=1}^m \frac{x_i}{s_{yi}})^2} \cdot \sqrt{\sum_{i=1}^m \frac{1}{s_{yi}^2} \cdot \sum_{i=1}^m \frac{y_i^2}{s_{yi}^2} - (\sum_{i=1}^m \frac{y_i}{s_{yi}})^2}}$$

Whereas r is the calculated reaction rate with standard deviation s_r and confidence interval v_r , O is the reaction order with standard deviation s_O and confidence interval v_O , c is the concentration of the examined reagent, m is the amount of data points measured, R is the correlation factor, t_s is the student-t factor corresponding to 95% probability and a degree of freedom of $n-2$.

Arrhenius Equation

$$\text{Arrhenius equation: } y = \log r = -\frac{E_a}{R} \cdot \frac{1}{T} + \log A + \log K = a \cdot \frac{1}{T} + b \quad \text{Standard deviation, confidence interval for y values: } s_{yi} = \frac{s_{ri}}{r_i}, \quad v_{yi} = \frac{v_{ri}}{r_i}$$

Energy of activation: $E_a = -R \cdot a$ Standard deviation of the energy of activation: $s_{Ea} = R \cdot s_a$ Confidence interval (95%) of the energy of activation: $v_{Ea} = R \cdot v_a$ Whereas r is the calculated reaction rate with standard deviation s_r and confidence interval v_r , $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$, A is the *Arrhenius* parameter, K is a concentration-dependent correction factor, s_a and v_a and the correlation factor R are obtained with the same formula as for the *van't Hoff* equation.

Kinetic Isotope Effect

$$\text{Kinetic isotope effect: } k_{iso} = \frac{r_H}{r_D} \quad \text{Standard deviation of the kinetic isotope effect: } s_{k_{iso}} = \sqrt{\left(\frac{s_{r_H}}{r_D}\right)^2 + \left(\frac{r_H \cdot s_{r_D}}{r_D^2}\right)^2}$$

$$\text{Confidence interval (95%)} \text{ of the kinetic isotope effect: } v_{k_{iso}} = \sqrt{\left(\frac{v_{r_H}}{r_D}\right)^2 + \left(\frac{r_H \cdot v_{r_D}}{r_D^2}\right)^2}$$

Whereas r_H is the calculated reaction rate with PhSiH_3 with standard deviation s_{rH} and confidence interval v_{rH} , r_D is the calculated reaction rate with PhSiD_3 with standard deviation s_{rD} and confidence interval v_{rD} .

All the calculated date in the form value(standard deviation) \pm confidence interval (95%) and the measured data are given in the Appendix A.

4.3.2. Graphical Description of the Results

Figure 1: Hydrohydrazination of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of **1**. The lines represent the calculated initial rates.⁵⁹

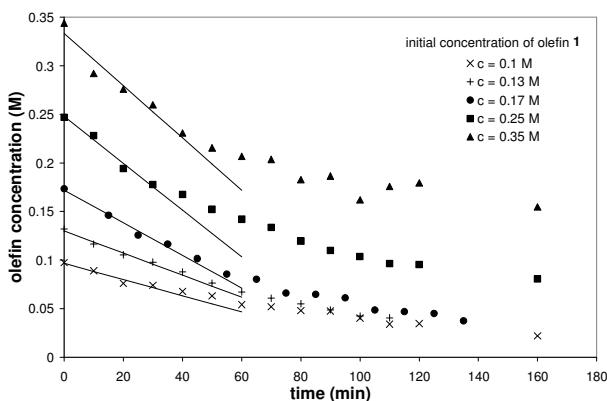


Figure 2: Hydrohydrazination of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of azodicarboxylate **2**. The lines represent the calculated initial rates.

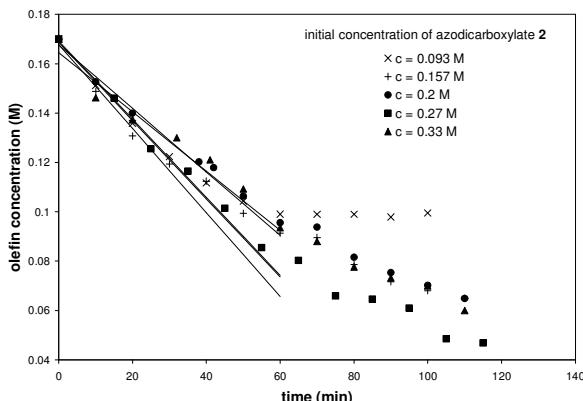


Figure 3: Hydrohydrazination of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of phenylsilane. The lines represent the calculated initial rates.

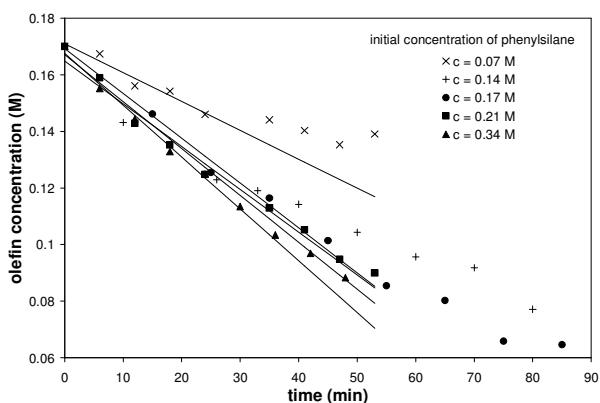


Figure 4: Hydrohydrazination of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of catalyst **20**. The lines represent the calculated initial rates.

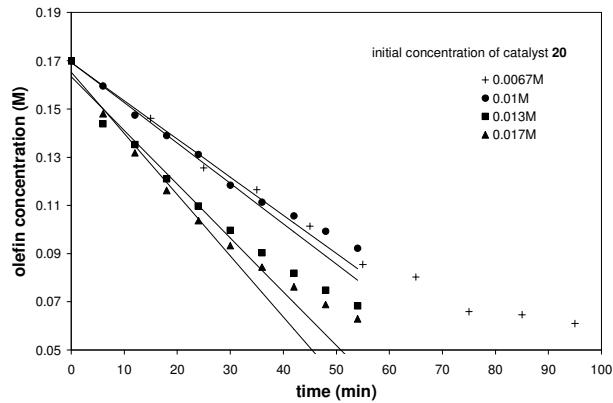


Figure 5: *van't Hoff* plots for the determination of the order of the reactants in the hydrohydrazination of 4-phenylbutene (**1**).

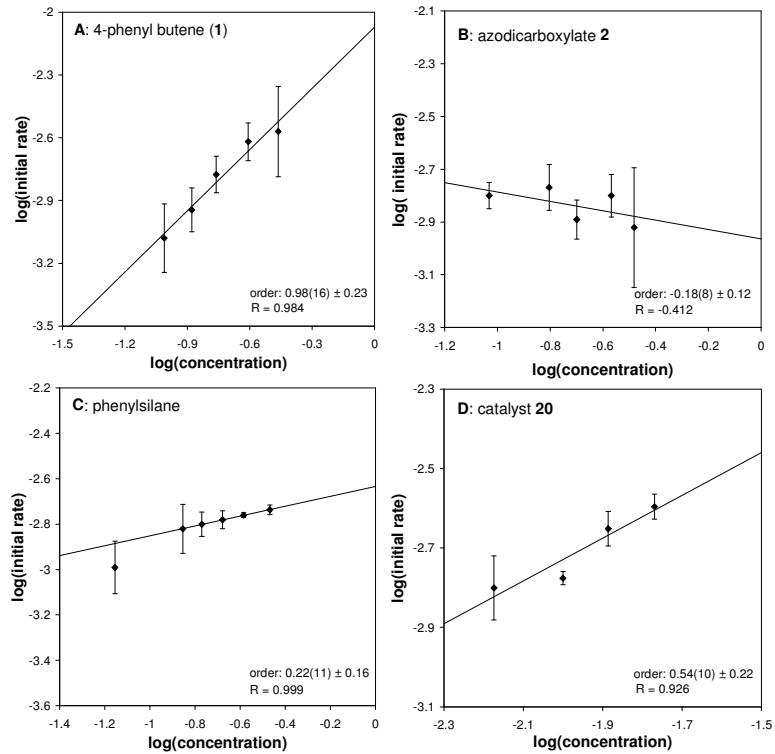


Figure 6: Dependence of the reaction rate on the temperature and *Arrhenius* plot for the hydrohydrazination of 4-phenylbutene (**1**).

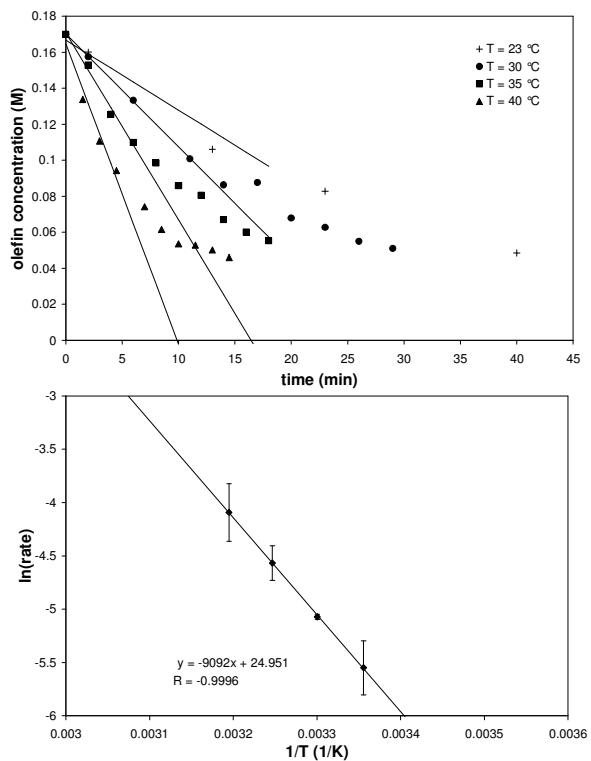


Figure 7: Kinetic isotope effect in the hydrohydrazination of 4-phenylbutene (**1**).

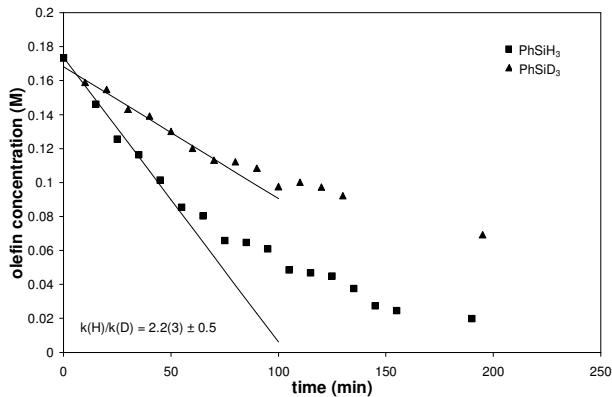


Figure 8: Hydroazidation of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of **1**. The lines represent the calculated initial rates.

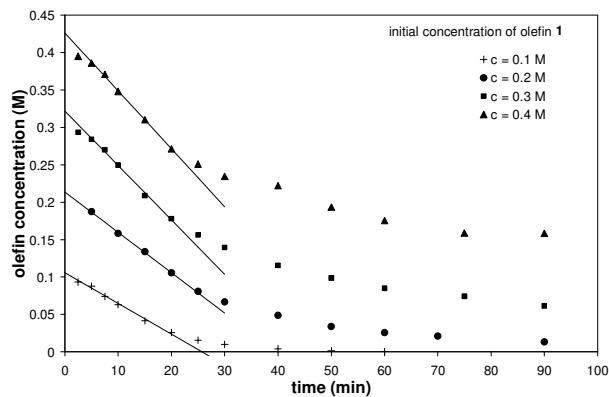


Figure 9 Hydroazidation of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of tosyl azide (**203**). The lines represent the calculated initial rates.

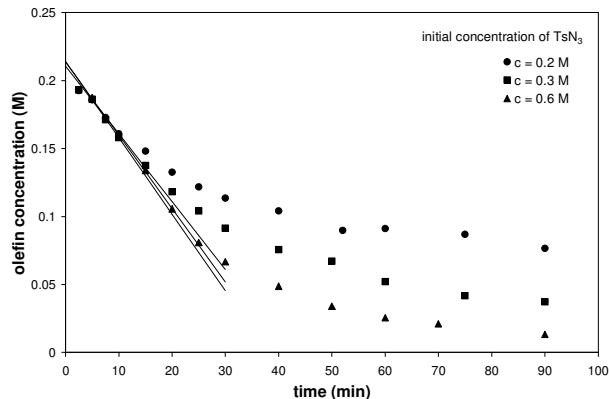


Figure 10: Hydroazidation of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of TMDSO. The lines represent the calculated initial rates.

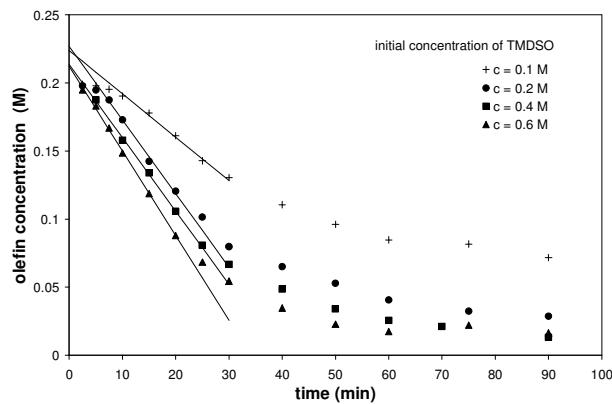


Figure 11: Hydroazidation of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and ligand **43** in ratio 1:1. The lines represent the calculated initial rates.

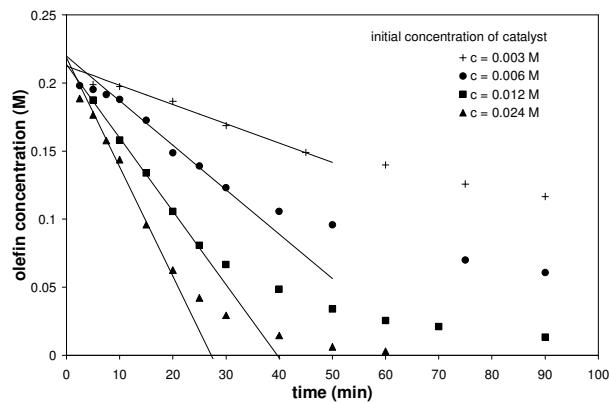


Figure 12: Hydroazidation of 4-phenylbutene (**1**): dependence of the reaction rate on the initial concentration of *tert*-butyl hydroperoxide. The lines represent the calculated initial rates.

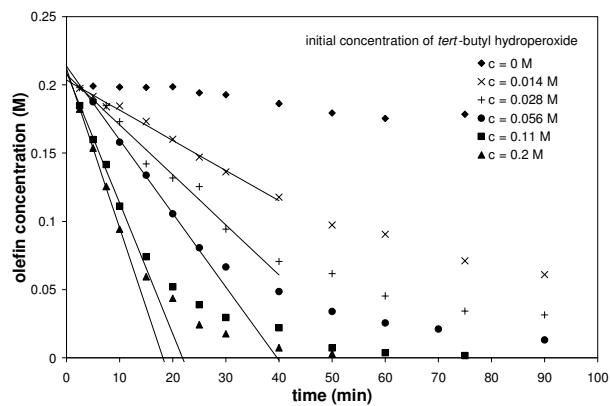


Figure 13: van't Hoff plots for the determination of the order of the reactants in the hydroazidation of 4-phenylbutene (**1**).

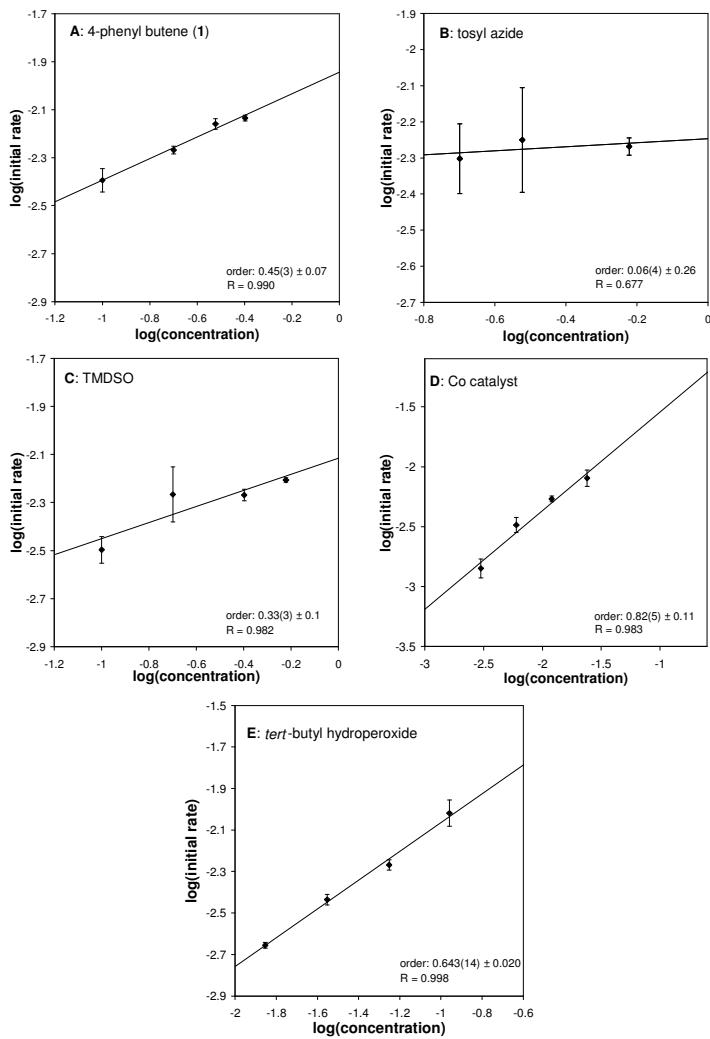


Figure 14: Dependence of the reaction rate on the temperature and *Arrhenius* plot for the hydroazidation of 4-phenylbutene (**1**).

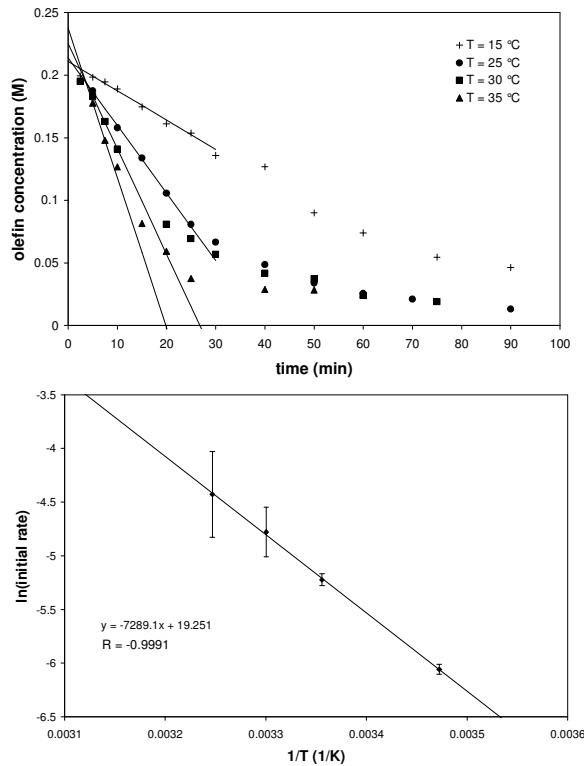
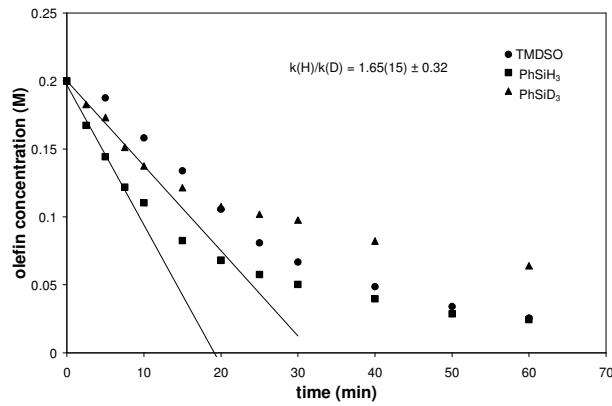


Figure 15: Kinetic isotope effect in the hydroazidation of 4-phenylbutene (**1**).



4.3.3. Kinetics Data

Hydrohydrazination Reaction

Standard Conditions Standard conditions: 4-phenyl butene (**1**) (19 μ L, 0.13 mmol, 0.17 M, 1.0 equiv); catalyst **20** (2 mg, 0.005 mmol, 0.007 M, 0.04 equiv); azodicarboxylate **2** (43 mg, 0.20 mmol, 0.27 M, 1.5 equiv); phenylsilane (16 μ L, 0.13 mmol, 0.17 M, 1.0 equiv); 25 °C; CD₃OD (0.75 mL).

standard conditions		
time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.173
15	0.03	0.146
25	0.19	0.126
35	0.38	0.116
45	0.49	0.101
55	0.71	0.086
65	1.03	0.080
75	1.16	0.066
85	1.63	0.065
95	1.68	0.061
105	1.84	0.049
115	2.57	0.047
125	2.70	0.045
135	2.85	0.038

reaction rate r: 0.00168(16) ± 0.00034

Variation of the concentration of 4-phenylbutene (1) (Figure 1)

standard conditions, concentration 1 = 0.10 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.097
10	0.08	0.089
20	0.22	0.076
30	0.37	0.074
40	0.53	0.068
50	0.61	0.063
60	0.98	0.054
70	0.98	0.052
80	1.28	0.048
90	1.20	0.047
100	1.68	0.040
110	2.34	0.034
120	2.25	0.035
160	4.30	0.022

reaction rate r: 0.00083(15) ± 0.00031

standard conditions, concentration 1 = 0.13 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.132
10	0.31	0.116
20	0.49	0.105
30	0.81	0.098
40	1.08	0.088
50	1.61	0.076
60	1.86	0.067
70	2.34	0.061
80	2.86	0.055
90	3.65	0.049
100	5.07	0.042
110	4.92	0.041

reaction rate r: 0.00114(13) ± 0.00027

standard conditions, concentration 1 = 0.25 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.247
10	0.15	0.228
20	0.37	0.194
30	0.57	0.178
40	0.78	0.167
50	1.01	0.152
60	1.38	0.142
70	1.58	0.133
80	1.96	0.120
90	2.35	0.110
100	2.71	0.104
110	3.16	0.096
120	3.21	0.095
160	4.17	0.081

reaction rate r: 0.0024(2) ± 0.0005

standard conditions, concentration 1 = 0.35 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.344
10	0.10	0.292
20	0.24	0.276
30	0.44	0.260
40	0.60	0.231
50	0.79	0.215
60	0.88	0.207
70	1.12	0.204
80	1.38	0.183
90	1.53	0.186
100	1.50	0.162
110	1.76	0.176
120	2.26	0.179
160	2.46	0.155

reaction rate r: 0.0026(6) ± 0.0013

van't Hoff reaction order

x = log(c)	y = log(r)	s _{yi}	v _{yi}
-1.01	-3.08	-0.08	-0.16
-0.88	-2.94	-0.05	-0.11
-0.76	-2.78	-0.04	-0.09
-0.61	-2.62	-0.04	-0.09
-0.46	-2.57	-0.10	-0.22

reaction order: 0.98(16) ± 0.23

R = 0.984

Variation of the concentration of azodicarboxylate 2 (Figure 2)

standard conditions, concentration **2** = 0.093 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170
10	0.15	0.151
20	0.28	0.136
30	0.51	0.122
40	0.58	0.112
50	0.78	0.104
60	0.84	0.099
70	0.75	0.099
80	0.85	0.099
90	0.78	0.098
100	0.80	0.099
reaction rate <i>r</i> :		0.00158(8) \pm 0.00018

standard conditions, concentration **2** = 0.16 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170
10	0.17	0.149
20	0.37	0.131
30	0.50	0.119
40	0.75	0.112
50	1.00	0.099
60	1.30	0.091
70	1.20	0.090
80	1.48	0.079
90	1.86	0.072
100	1.89	0.068
110	2.10	0.065
reaction rate <i>r</i> :		0.00170(16) \pm 0.0003

standard conditions, concentration **2** = 0.20 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170
10	0.10	0.153
20	0.27	0.140
38	0.55	0.120
42	0.67	0.118
50	0.86	0.106
60	1.11	0.096
70	1.05	0.094
80	1.58	0.082
90	1.71	0.075
100	2.14	0.070
110	2.36	0.065
reaction rate <i>r</i> :		0.00129(10) \pm 0.00022

standard conditions, concentration **2** = 0.33 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170
10	0.15	0.146
20	0.23	0.137
30	0.44	0.130
40	0.67	0.121
50	0.92	0.109
60	1.09	0.094
70	1.20	0.088
80	1.49	0.078
90	1.65	0.073
100	1.95	0.070
110	2.53	0.060
reaction rate <i>r</i> :		0.0012(3) \pm 0.006

van't Hoff reaction order

x = log(c)	y = log(r)	s _{yi}	v _{yi}
-1.03	-2.80	-0.02	-0.05
-0.80	-2.77	-0.04	-0.09
-0.70	-2.89	-0.03	-0.07
-0.57	-2.80	-0.04	-0.08
-0.48	-2.92	-0.11	-0.23

reaction order: $-0.18(8) \pm 0.12$

R = -0.412

Variation of the concentration of phenylsilane (Figure 3)

standard conditions, concentration $\text{PhSiH}_3 = 0.07 \text{ M}$

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.01	0.170
6	0.03	0.167
12	0.06	0.156
18	0.11	0.154
24	0.15	0.146
35	0.23	0.144
41	0.30	0.140
47	0.35	0.135
53	0.38	0.139

reaction rate $r: 0.00102(13) \pm 0.00008$

standard conditions, concentration $\text{PhSiH}_3 = 0.14 \text{ M}$

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170
10	0.19	0.143
26	0.38	0.123
33	0.57	0.119
40	0.65	0.114
50	0.73	0.104
60	0.98	0.096
70	1.09	0.092
80	1.37	0.077
90	1.53	0.077
100	1.89	0.070

reaction rate $r: 0.00151(26) \pm 0.00005$

standard conditions, concentration $\text{PhSiH}_3 = 0.21 \text{ M}$

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.02	0.170
6	0.07	0.159
12	0.20	0.143
18	0.30	0.135
24	0.41	0.125
35	0.65	0.113
41	0.81	0.105
47	0.99	0.095
53	1.17	0.090

reaction rate $r: 0.00166(13) \pm 0.00005$

standard conditions, concentration $\text{PhSiH}_3 = 0.26 \text{ M}$

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.03	0.170
6	0.09	0.160
12	0.18	0.148
18	0.28	0.139
24	0.39	0.127
32	0.60	0.115
38	0.73	0.109
44	0.85	0.103
50	1.04	0.094
56	1.20	0.090

reaction rate $r: 0.00174(4) \pm 0.00005$

van't Hoff reaction order

$x = \log(c)$	$y = \log(r)$	s_{yi}	v_{yi}
-1.15	-2.99	-0.05	-0.12
-0.85	-2.82	-0.08	-0.11
-0.77	-2.80	-0.04	-0.05
-0.68	-2.78	-0.03	-0.04
-0.59	-2.76	-0.010	-0.011
-0.47	-2.74	-0.019	-0.021

reaction order: $0.22(11) \pm 0.16$

$R = 0.999$

standard conditions, concentration $\text{PhSiH}_3 = 0.34 \text{ M}$

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.04	0.170
6	0.11	0.155
12	0.18	0.144
18	0.31	0.133
24	0.43	0.125
30	0.55	0.113
36	0.70	0.103
42	0.85	0.097
48	1.04	0.088
54	1.20	0.082

reaction rate $r: 0.00183(8) \pm 0.00009$

Variation of the concentration of catalyst **20 (Figure 4)**

standard conditions, concentration **20** = 0.010 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.04	0.170
6	0.09	0.159
12	0.20	0.147
18	0.29	0.139
24	0.39	0.131
30	0.52	0.118
36	0.62	0.111
42	0.72	0.106
48	0.85	0.099
54	1	0.092

reaction rate r : 0.00167(5) \pm 0.00007

standard conditions, concentration **20** = 0.013 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.06	0.170
6	0.12	0.144
12	0.40	0.135
18	0.60	0.121
24	0.78	0.110
30	1.06	0.100
36	1.29	0.090
42	1.54	0.082
48	1.82	0.075
54	2.08	0.068

reaction rate r : 0.00223(19) \pm 0.00023

van't Hoff reaction order

x = log(c)	y = log(r)	s_{yi}	v_{yi}
-2.17	-2.80	-0.04	-0.08
-2.00	-2.78	-0.015	-0.017
-1.89	-2.65	-0.04	-0.04
-1.77	-2.60	-0.03	-0.03

reaction order: 0.54(10) \pm 0.22

R = 0.926

standard conditions, concentration **20** = 0.017 M

time(min)	integral ratio 3/1	concentration 1 (M)
0	0.07	0.170
6	0.24	0.148
12	0.42	0.132
18	0.61	0.116
24	0.83	0.104
30	1.09	0.093
36	1.33	0.084
42	1.59	0.076
48	1.91	0.069
54	2.12	0.063

reaction rate r : 0.00254(16) \pm 0.00018

Variation of the temperature (Figure 6)

standard conditions, T = 296 K			standard conditions, T = 303 K		
time(min)	integral ratio 3/1	concentration 1 (M)	time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170	0	0.00	0.170
2	0.06	0.160	2	0.08	0.157
13	0.60	0.106	6	0.28	0.133
23	1.05	0.083	11	0.69	0.101
40	2.50	0.049	14	0.97	0.086
55	3.58	0.037	17	0.94	0.088
74	4.67	0.030	20	1.50	0.068
88	5.66	0.026	23	1.71	0.063
116	6.04	0.024	26	2.09	0.055
reaction rate r:		0.0039(5) ± 0.0010	reaction rate r:		0.0064(4) ± 0.0010

standard conditions, T = 308 K			standard conditions, T = 313 K		
time(min)	integral ratio 3/1	concentration 1 (M)	time(min)	integral ratio 3/1	concentration 1 (M)
0	0.00	0.170	0	0.00	0.170
2	0.11	0.153	1.5	0.27	0.134
4	0.35	0.125	3	0.54	0.111
6	0.55	0.110	4.5	0.80	0.094
8	0.73	0.098	7	1.29	0.074
10	0.98	0.086	8.5	1.76	0.062
12	1.11	0.080	10	2.17	0.054
14	1.54	0.067	11.5	2.22	0.053
16	1.83	0.060	13	2.39	0.050
18	2.08	0.055	14.5	2.70	0.046
reaction rate r:		0.0104(8) ± 0.0017	reaction rate r:		0.0167(21) ± 0.0045

Arrhenius plot

x = 1/T	y = ln(r)	s _y	v _y
0.00336	-5.55	-0.12	-0.25
0.00330	-5.07	-0.012	-0.03
0.00325	-4.57	-0.08	-0.16
0.00319	-4.09	-0.13	-0.27

activation energy: 76(7) ± 15 KJ/mol

R = -0.9996

Kinetic isotope effect (Figure 7)

standard conditions, with PhSiD₃

time(min)	integral ratio 27/1	concentration 1 (M)
10	0.07	0.159
20	0.10	0.155
30	0.19	0.143
40	0.22	0.139
50	0.31	0.130
60	0.41	0.120
70	0.50	0.113
80	0.52	0.112
90	0.57	0.108
100	0.74	0.098
110	0.70	0.100
120	0.75	0.097
130	0.84	0.092
195	1.46	0.069
reaction rate r:		0.00168(16) ± 0.00034

kinetic isotope effect: 2.2(3) ± 0.5

Hydroazidation Reaction

Standard Conditions Standard conditions: 4-phenylbutene (**1**) (75 µL, 0.50 mmol, 0.20 M, 1.0 equiv); Co(BF₄)₂•6H₂O (10 mg, 0.030 mmol, 0.012 M, 0.060 equiv); ligand **43** (14 mg, 0.030 mmol, 0.012 M, 0.060 equiv); *tert*-butyl hydroperoxide (25 µL, 0.14

mmol, 0. 056 M, 0.28 equiv); tosylazide (**203**) (0.23 mL, 1.5 mmol, 0.60 M, 3.0 equiv); TMDSO (0.18 mL, 1.0 mmol, 0.40 M, 2.0 equiv); 23 °C; EtOH (2.5 mL).

standard conditions

time(min)	integral ratio 33/1	concentration 1 (M)
5	0.07	0.187
10	0.26	0.158
15	0.48	0.134
20	0.87	0.106
25	1.44	0.081
30	1.95	0.067
40	3.02	0.049
50	4.75	0.034
60	6.63	0.026
70	8.26	0.021
90	13.75	0.013

reaction rate *r*: 0.00539(14) ± 0.0003

Variation of the concentration of 4-phenylbutene (1**) (Figure 8)**

standard conditions, concentration **1** = 0.10 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.07	0.093
5	0.14	0.088
7.5	0.34	0.074
10	0.57	0.063
15	1.37	0.042
20	2.82	0.026
25	5.32	0.015
30	8.87	0.010
40	22.58	0.004
50	74.45	0.001
60	363.08	0.000

reaction rate *r*: 0.00411(21) ± 0.0003

standard conditions, concentration **1** = 0.30 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.02	0.293
5	0.05	0.284
7.5	0.11	0.270
10	0.20	0.250
15	0.43	0.209
20	0.67	0.178
25	0.90	0.156
30	1.12	0.139
40	1.56	0.115
50	1.99	0.099
60	2.46	0.085
75	2.96	0.074
90	3.78	0.061

reaction rate *r*: 0.00729(25) ± 0.0004

van't Hoff reaction order

x = log(c)	y = log(r)	s _y	v _y
-1.00	-2.39	-0.023	-0.05
-0.70	-2.27	-0.011	-0.016
-0.52	-2.16	-0.015	-0.022
-0.40	-2.14	-0.009	-0.012

reaction order: 0.45(3) ± 0.07

R = 0.990

standard conditions, concentration **1** = 0.40 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.01	0.395
5	0.04	0.386
7.5	0.08	0.371
10	0.15	0.348
15	0.28	0.310
20	0.46	0.271
25	0.58	0.251
30	0.69	0.235
40	0.78	0.222
50	1.04	0.194
60	1.24	0.176
75	1.48	0.159
90	1.49	0.158

reaction rate *r*: 0.00774(15) ± 0.00021

Variation of the concentration of tosylazide (203) (Figure 9)

standard conditions, concentration $TsN_3 = 0.30\text{ M}$

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.03	0.193
5	0.07	0.186
7.5	0.16	0.171
10	0.26	0.158
15	0.44	0.137
20	0.67	0.118
25	0.90	0.104
30	1.16	0.091
40	1.60	0.076
50	1.93	0.067
60	2.77	0.052
75	3.70	0.042
90	4.27	0.037

reaction rate $r: 0.00562(26) \pm 0.0019$

standard conditions, concentration $TsN_3 = 0.20\text{ M}$

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.04	0.193
5	0.07	0.186
7.5	0.15	0.173
10	0.24	0.161
15	0.34	0.148
20	0.49	0.133
25	0.62	0.122
30	0.74	0.114
40	0.90	0.104
50	1.19	0.090
60	1.16	0.091
75	1.27	0.087
90	1.57	0.077

reaction rate $r: 0.00499(15) \pm 0.0011$

van't Hoff reaction order

$x = \log(c)$	$y = \log(r)$	s_{yi}	v_{yi}
-0.22	-2.27	-0.011	-0.02
-0.52	-2.25	-0.020	-0.145
-0.70	-2.30	-0.013	-0.096

reaction order: $0.06(4) \pm 0.26$

$R = 0.677$

Variation of the concentration of TMDSO (Figure 10)

standard conditions, concentration $TMDSO = 0.10\text{ M}$

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.00	0.199
5	0.01	0.198
7.5	0.02	0.195
10	0.05	0.190
15	0.12	0.178
20	0.23	0.161
25	0.39	0.143
30	0.52	0.130
40	0.79	0.111
50	1.05	0.096
60	1.32	0.085
75	1.41	0.082
90	1.74	0.072

reaction rate $r: 0.00319(19) \pm 0.0004$

standard conditions, concentration $TMDSO = 0.20\text{ M}$

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.01	0.198
5	0.03	0.195
7.5	0.07	0.187
10	0.15	0.173
15	0.39	0.143
20	0.64	0.120
25	0.95	0.101
30	1.47	0.080
40	2.02	0.065
50	2.71	0.053
60	3.82	0.041
75	5.05	0.032
90	5.82	0.029

reaction rate $r: 0.0054(6) \pm 0.0013$

van't Hoff reaction order

$x = \log(c)$	$y = \log(r)$	s_{yi}	v_{yi}
-0.22	-2.21	-0.008	-0.01
-0.40	-2.27	-0.011	-0.024
-0.70	-2.27	-0.053	-0.114
-1.00	-2.50	-0.026	-0.055

reaction order: $0.33(3) \pm 0.10$

$R = 0.982$

standard conditions, concentration $TMDSO = 0.60\text{ M}$

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.03	0.195
5	0.09	0.183
7.5	0.19	0.167
10	0.34	0.149
15	0.67	0.119
20	1.24	0.088
25	1.87	0.068
30	2.60	0.054
40	4.63	0.035
50	7.58	0.023
60	10.22	0.017
75	7.86	0.022
90	10.91	0.016

reaction rate $r: 0.00622(11) \pm 0.00013$

Variation of the concentration of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ / Ligand 43 (Figure 11)

standard conditions, concentration catalyst = 0.003 M

time(min)	integral ratio 33/1	concentration 1 (M)
5	0.01	0.199
10	0.01	0.197
20	0.07	0.187
30	0.18	0.169
45	0.33	0.149
60	0.42	0.140
75	0.57	0.126
90	0.70	0.117
105	0.83	0.108
120	0.91	0.103
150	1.23	0.088
180	1.32	0.085

reaction rate r : $0.00142(12) \pm 0.00026$

standard conditions, concentration catalyst = 0.006 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.01	0.198
5	0.02	0.195
7.5	0.04	0.191
10	0.06	0.188
15	0.15	0.173
20	0.34	0.149
25	0.43	0.139
30	0.61	0.123
40	0.87	0.106
50	1.06	0.096
75	1.81	0.070
90	2.23	0.061

reaction rate r : $0.0033(3) \pm 0.0005$

van't Hoff reaction order

$x = \log(c)$	$y = \log(r)$	s_{yi}	v_{yi}
-1.62	-2.10	-0.032	-0.07
-1.92	-2.27	-0.011	-0.024
-2.22	-2.49	-0.043	-0.062
-2.52	-2.85	-0.037	-0.079

reaction order: $0.82(5) \pm 0.11$

$R = 0.983$

standard conditions, concentration catalyst = 0.024 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.06	0.189
5	0.13	0.177
7.5	0.26	0.158
10	0.38	0.144
15	1.06	0.096
20	2.13	0.063
25	3.65	0.042
30	5.69	0.029
40	12.50	0.014
50	30.53	0.006
60	64.10	0.003

reaction rate r : $0.0080(6) \pm 0.0013$

Variation of the concentration of *tert*-butyl hydroperoxide (Figure 12)

standard conditions, concentration peroxide = 0.0 M

time(min)	integral ratio 33/1	concentration 1 (M)
5	0.00	0.199
10	0.01	0.198
15	0.01	0.198
20	0.01	0.199
25	0.03	0.194
30	0.04	0.193
40	0.07	0.186
50	0.11	0.180
60	0.14	0.175
75	0.12	0.178
90	0.16	0.172

reaction rate r : < 0.00037

standard conditions, concentration peroxide = 0.014 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.01	0.198
5	0.04	0.192
7.5	0.08	0.184
10	0.08	0.185
15	0.15	0.173
20	0.24	0.160
25	0.35	0.147
30	0.46	0.136
40	0.68	0.118
50	1.02	0.097
60	1.17	0.091
75	1.76	0.071
90	2.22	0.061

reaction rate r : 0.00221(9) ± 0.00007

standard conditions, concentration peroxide = 0.028 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.01	0.198
5	0.06	0.189
7.5	0.08	0.185
10	0.15	0.173
15	0.40	0.142
20	0.50	0.132
25	0.58	0.125
30	1.09	0.094
40	1.78	0.071
50	2.18	0.062
60	3.31	0.045
75	4.69	0.034
90	5.22	0.031

reaction rate r : 0.00367(24) ± 0.00021

van't Hoff reaction order

x = log(c)	y = log(r)	S_{yi}	V_{yi}
-0.70	-1.93	-0.007	-0.016
-0.96	-2.02	-0.03	-0.06
-1.25	-2.27	-0.011	-0.024
-1.55	-2.44	-0.03	-0.03
-1.85	-2.66	-0.017	-0.014

reaction order: 0.643(14) ± 0.020

R = 0.998

standard conditions, concentration peroxide = 0.11 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.08	0.185
5	0.24	0.160
7.5	0.40	0.142
10	0.78	0.111
15	1.66	0.074
20	2.75	0.052
25	4.01	0.039
30	5.60	0.030
40	7.85	0.022
50	25.26	0.007
60	51.38	0.004
75	104.77	0.002

reaction rate r : 0.0096(6) ± 0.0014

standard conditions, concentration peroxide = 0.20 M

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.09	0.182
5	0.29	0.154
7.5	0.58	0.126
10	1.09	0.094
15	2.29	0.060
20	3.48	0.044
25	7.02	0.024
30	10.03	0.018
40	25.07	0.007
50	63.68	0.003
60	151.50	0.001

reaction rate r : 0.01168(20) ± 0.0004

Variation of the temperature (Figure 14)

standard conditions, T = 285 K

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.00	0.199
5	0.01	0.198
7.5	0.03	0.195
10	0.06	0.189
15	0.14	0.175
20	0.23	0.161
25	0.29	0.154
30	0.46	0.136
40	0.55	0.127
50	1.18	0.090
60	1.64	0.074
75	2.58	0.055
90	3.20	0.046

reaction rate r: 0.00234(12) ± 0.00011

standard conditions, T = 303 K

time(min)	integral ratio 33/1	concentration 1 (M)
2.5	0.03	0.195
5	0.09	0.183
7.5	0.22	0.163
10	0.40	0.141
20	1.41	0.081
25	1.79	0.069
30	2.39	0.057
40	3.57	0.042
50	4.09	0.037
60	6.97	0.024
75	9.05	0.019

reaction rate r: 0.00841(26) ± 0.0019

Arrhenius plot

x = 1/T	y = ln(r)	s _y	v _y
0.00347	-6.06	-0.05	-0.05
0.00336	-5.22	-0.026	-0.06
0.00330	-4.78	-0.03	-0.23
0.00325	-4.43	-0.22 (5%)	-0.40 (10%)

activation energy: 60(3) ± 6 KJ/mol

R = -0.9991

standard conditions, T = 308 K

time(min)	integral ratio 33/1	concentration 1 (M)
5	0.12	0.178
7.5	0.34	0.148
10	0.55	0.127
15	1.39	0.082
20	2.27	0.059
25	4.13	0.038
40	5.65	0.029
50	5.70	0.028
60	6.61	0.025

reaction rate r: 0.012

Kinetic isotope effect (Figure 15)

standard conditions, with PhSiH₃ (0.20 M)

time(min)	integral ratio 33/1	concentration 1 (M)
0	0.00	0.200
2.5	0.17	0.167
5	0.34	0.144
7.5	0.56	0.122
10	0.71	0.110
15	1.24	0.083
20	1.70	0.068
25	2.18	0.058
30	2.60	0.050
40	3.55	0.040
50	5.33	0.028
60	6.36	0.024
75	8.14	0.019
90	11.43	0.014

reaction rate r: 0.0103(7) ± 0.0015

standard conditions, with PhSiD₃ (0.20 M)

time(min)	integral ratio 54/1	concentration 1 (M)
0	0.00	0.200
2.5	0.09	0.183
5	0.16	0.173
7.5	0.31	0.151
10	0.45	0.137
15	0.64	0.121
20	0.85	0.107
25	0.95	0.102
30	1.03	0.098
40	1.47	0.082
60	2.07	0.064

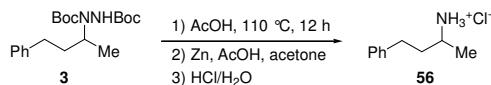
reaction rate r: 0.0063(4) ± 0.0008

kinetic isotope effect: 1.65(15) ± 0.3

5. Useful Transformation of Azide and Hydrazine Products

Conversion of Boc-Protected Hydrazines to Amine Hydrochlorides

1-Methyl-3-phenyl-propylamine hydrochloride (56)

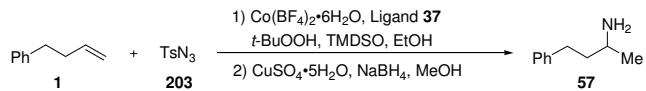


A solution of protected hydrazine **3** (364 mg, 1.00 mmol, 1.00 equiv) in acetic acid (6 mL) was refluxed for 12 h under argon, cooled to 23 °C and acetone (0.6 mL) was added. After 30 min, Zn dust (Aldrich, 3.0 g) was added, the reaction mixture was stirred for 8 h, diluted with CH_2Cl_2 (10 mL), filtered over Celite and the solvents were removed under reduced pressure. The residues were suspended in 1 M HCl (20 mL), the aqueous solution was washed with Et_2O (2x15 mL) and the pH was adjusted to >12 with NaOH pellets. The basic solution was extracted with Et_2O (3x20 mL), the organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure ($p = 100$ mbar, $T = 40$ °C). The crude amine was dissolved in 3 M HCl (20 mL) and the solvent was removed under reduced pressure and the residues were dried for 12 h in high vacuo. The isolated product was recrystallized from AcOEt to afford pure amine hydrochloride **56** (95 mg, 0.51 mmol, 51%) as colorless crystals. Mp (AcOEt) 142–143 °C; ^1H NMR (DMSO-d₆, 300 MHz) δ 8.09 (br s, 3H, NH), 7.33–7.16 (m, 5H, Ar H), 3.11 (br m, 1H, CHN), 2.71–2.61 (m, 2H, CH_2), 1.97–1.85 (m, 1H, CH_2), 1.77–1.66 (m, 1H, CH_2), 1.23 (d, $J = 6.5$ Hz, 3H, CH_3); ^{13}C NMR (DMSO-d₆, 75 MHz) δ 140.8, 128.2, 128.0, 125.8, 46.3, 35.8, 30.8, 18.0; IR (KBr) ν 2891 (br, s), 2615 (m), 2522 (m), 2032 (w), 1605 (m), 1517 (s), 1493 (m), 1454 (m), 1389 (m), 1197 (w), 1180 (w), 1148 (w), 1130 (w), 1111 (w), 1068 (w), 1028 (w), 1010 (w), 766 (m), 746 (m), 701 (s), 586 (w), 514 (m); MS (ESI) 150.2 (M-Cl); Anal. calcd for $\text{C}_{10}\text{H}_{16}\text{NCl}$: C, 64.68; H, 8.68; N, 7.54. Found: C, 64.43; H, 8.42; N, 7.38.

One-pot Conversion of Olefins to Amines

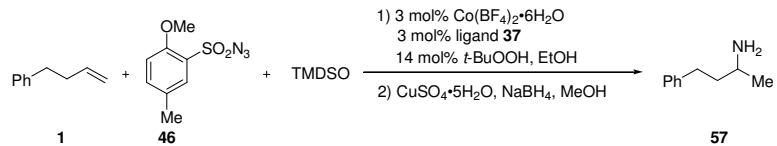
1-Methyl-3-phenyl-propylamine (**57**)⁶⁰

Using TsN_3 (**203**)



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (1.5 mL) at 23 °C under argon. After 10 min, 4-phenylbutene (**1**) (75 μL , 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (**203**) (0.23 mL, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) was added dropwise. The resulting dark brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 4 h, the reaction mixture was cooled to 0 °C and a black suspension of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12 mg, 0.050 mmol, 0.10 equiv) and NaBH_4 (10 mg, 0.26 mmol, 0.50 equiv) in methanol (1.5 mL) was added.⁶¹ Further NaBH_4 (65 mg, 1.7 mmol, 3.4 equiv) was added in small portions over 45 min at 0 °C. At this point, TLC (AcOEt/hexane 1:40) showed a clean reduction of the excess of tosyl azide, but the alkyl azide was not yet totally reduced. Further NaBH_4 (0.10 g, 2.6 mmol, 5.3 equiv) was added in 4 portions over 2 h, whereas TLC showed complete reduction of the alkyl azide. The reaction mixture was allowed to warm to 23 °C over 12 h and filtered over Celite. The Celite was washed with methanol (20 mL) and the solvent was removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The crude product was diluted with water (10 mL) and 1 M HCl (10 mL) and the mixture was extracted with Et_2O (3x20 mL). NaOH pellets were added to the water layer until the pH was higher than 10, and the mixture was extracted with Et_2O (3x20 mL), the organic layers were dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C) to afford the free amine **57** (56 mg, 0.38 mmol, 76%, >95% pure according to ^1H NMR) as a slightly yellow oil.

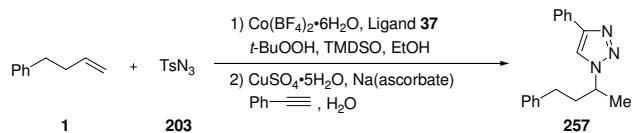
Scale-up with Azide **46**



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.15 mmol, 0.030 equiv) and ligand **37** (70 mg, 0.15 mmol, 0.030 equiv) were dissolved in ethanol (25 mL) at 23 °C under argon. After 10 min, 4-phenylbutene (**1**) (0.75 mL, 5.0 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by azide **46** (1.4 g, 6.2 mmol, 1.2 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 0.13 mL, 0.71 mmol, 0.14 equiv). After 5 min TMDSO (0.88 mL, 5.0 mmol, 1.0 equiv) was added dropwise. The resulting dark green solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 24 h, the reaction mixture was cooled to 0 °C and a black suspension of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (60 mg, 0.24 mmol, 0.050 equiv) and NaBH_4 (50 mg, 1.3 mmol, 0.26 equiv) in methanol (10 mL) was added.⁶² Further NaBH_4 (0.85 g, 22 mmol, 4.5 equiv) was added in small portions over 4 h at 0 °C. At this point, TLC (AcOEt/hexane 1:40) showed complete reduction of the alkyl azide. The reaction mixture was allowed to warm to 23 °C over 12 h and filtered over Celite. The Celite was washed with methanol (100 mL) and the solvent was removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C). The crude product was diluted with 1 M HCl (80 mL) and the mixture was extracted with AcOEt (2x50 mL) and Et_2O (2x50 mL). NaOH pellets were added to the water layer until the pH was higher than 12, and the mixture was extracted with Et_2O (3x100 mL), the organic layers were dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure ($p = 50$ mbar, $T = 40$ °C) to afford the free amine **57** (505 mg, 3.38 mmol, 68%, >95% pure according to ^1H NMR) as a slightly yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.31–7.16 (m, 5H, Ar H), 2.96 (brs, 1H, CHNH_2), 2.76–2.58 (m, 2H, PhCH_2), 1.75–1.66 (m, 2H, CH_2CHNH_2), 1.60–1.00 (br s, 2H, NH₂), 1.13 (d, $J = 6.2$ Hz, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 142.2, 128.3, 128.2, 125.6, 46.4, 41.8, 32.7, 23.9; IR ν 3286 (w), 3061 (w), 3025 (m), 2957 (s), 2925 (s), 2858 (m), 1581 (m), 1495 (m), 1454 (s), 1372 (m), 1294 (w), 1155 (w), 1100 (w), 1067 (w), 1030 (w), 907 (w), 817 (w), 747 (m), 699 (s), 579 (w), 518 (w), 471 (w), 450 (w).

One-pot Conversion of Olefins to Triazoles

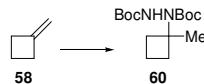
1-(1-Methyl-3-phenyl-propyl)-4-phenyl-1*H*-[1,2,3]triazole (257)



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **37** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, 4-phenylbutene (**1**) (75 μL , 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (**203**) (0.23 mL, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μL , 0.14 mmol, 0.28 equiv). After 5 min, TMDSO (0.18 mL, 1.0 mmol, 2.0 equiv) was added dropwise. The resulting dark brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 4 h, water (2 mL) was added. After further stirring for 30 min, a solution of sodium ascorbate (40 mg, 0.20 mmol, 0.40 equiv) in water (0.10 mL), a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12 mg, 0.050 mmol, 0.10 equiv) in water (0.10 mL) and phenylacetylene (0.28 mL, 2.5 mmol, 5.0 equiv) were added and the heterogeneous mixture stirred at 23 °C for 20 h. The reaction mixture was then diluted with water (5 mL) and brine (5 mL), extracted with AcOEt (3x12 mL), the combined organic layers were dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (solvent gradient: pentane/CH₂Cl₂/Et₂O 50:100:5, then pentane/CH₂Cl₂/Et₂O 50:100:7.5) to afford **257** (83 mg, 0.30 mmol, 60%) as a slightly yellow solid. Analytically pure samples of **257** were obtained after recrystallization from AcOEt/hexane. R_f (pentane/CH₂Cl₂/Et₂O 50:100:7.5) 0.30; Mp (AcOEt/hexane) 72–73 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.88–7.84 (m, 2H, Ar H), 7.75 (s, 1H, triazole H), 7.46–7.13 (m, 8H, Ar H), 4.75–4.68 (m, 1H, CHN), 2.57 (t, *J* = 7.6 Hz, 2H, PhCH₂), 2.41–2.14 (m, 2H, CH₂CHN), 1.63 (d, *J* = 6.8 Hz, CH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 147.4, 140.2, 130.6, 128.7, 128.4, 128.3, 127.9, 126.1, 125.5, 117.4, 56.7, 38.7, 32.1, 21.7; IR ν 3130 (w), 3084 (w), 3061 (w), 3026 (w), 2978 (w), 2935 (w), 2860 (w), 1951 (w), 1883 (w), 1812 (w), 1604 (w), 1580 (w), 1553 (w), 1495 (w), 1482 (m), 1454 (m), 1436 (m), 1383 (w), 1364 (w), 1226 (w), 1180 (w), 1156 (w), 1119 (w), 1074 (m), 1028 (w), 973 (w), 914 (w), 765 (s), 749 (m), 696 (s); HRMS (EI) calcd for C₁₈H₁₉N₃⁺ (M): 277.1579, found 277.1572; Anal. calcd for C₁₈H₁₉N₃: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.87; H, 6.93; N, 15.11.

Case Study: Amination of Methylenecyclobutane and Methylenecyclopropane

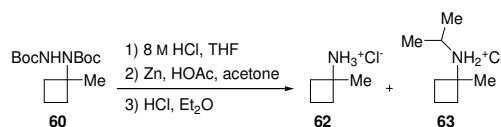
N-(1-Methyl-cyclobutyl)-N'-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (60)



Following GP1 Hydrohydrazination product **60** (540 mg, 1.80 mmol, 90%) was obtained as a colorless solid with methylenecyclobutane (**58**) (0.18 mL, 2.0 mmol, 1.0 equiv) in 5 h with 5 mol% catalyst **20** after purification by column chromatography (AcOEt/hexane 1:10). **Following GP3** Hydrohydrazination product **60** (263 mg, 0.876 mmol, 88%) was obtained as a colorless solid together with the regioisomeric product (<26 mg, <0.087 mmol, <9%, not isolated) with methylenecyclobutane (**58**) (92 μL , 1.0 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst **23** after purification by column chromatography (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:10) 0.20; Mp 118–119 °C; ¹H NMR (CDCl₃, 300 MHz, 52 °C) δ 6.06 (br s, 1H, NH), 2.39–2.29 (m, 2H, CH₂), 1.89–1.84 (m, 2H, CH₂), 1.76–1.65 (m, 2H, CH₂), 1.48 (s, 9H, OCCH₃), 1.46 (s, 9H, OCCH₃), 1.41 (s, 3H, NCC₃); ¹³C NMR (CDCl₃, 75 MHz, 52 °C) δ 156.0, 154.0, 80.9, 80.7, 61.1, 33.6, 28.5, 28.3, 23.0, 13.8; IR ν 3324 (m), 2978 (s), 1706 (s), 1480 (m), 1456 (m), 1428 (w), 1367 (s), 1250 (s), 1163 (s), 1086 (m), 1051 (m), 1017 (m), 919 (w), 876 (w), 856 (w), 780 (w), 760 (m), 734 (m), 691 (w), 647 (w), 602 (w), 489 (w), 462 (w); MS (ESI) 301.2 (M+H), 323.2 (M+Na); Anal. calcd for C₁₅H₂₈N₂O₄: C, 59.98, H, 9.39; N, 9.33. Found: C, 60.25; H, 9.50, N, 9.16.

1-Methylcyclobutylamine hydrochloride (62)

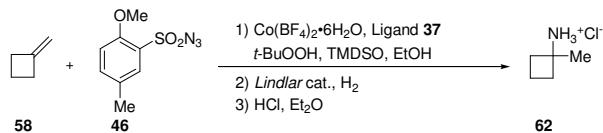
From Hydrazine **60**



Hydrohydrazination product **60** (150 mg, 0.500 mmol, 1.00 equiv) was dissolved in THF (1.5 mL) and 8 M HCl (4.5 mL) was added, whereas partial precipitation of **60** occurred. The reaction mixture was stirred vigorously for 1 h to give a clear solution. The solvents were removed under reduced pressure and the residues dried 3 h in high vacuo. Acetic acid (3 mL) and Zn dust (Acros, freshly activated (Zn dust (30 g) was stirred with 5% HCl (40 mL) for 3 min, filtered and washed with water (3x40 mL), acetone (2x30 mL) and Et₂O (2x30 mL) and dried 2 h in high vacuo, 1.0 g) were added, followed 10 min later by acetone (0.3 mL). After 2 h, the reaction was filtered over Celite, the Celite was washed with MeOH (40 mL), the pH was adjusted to 1 with 37% HCl, and the solvents were removed under reduced pressure. The residues were suspended in 1 M HCl (20 mL), the suspension was washed with Et₂O (3x15 mL) and the pH was adjusted to 12 with NaOH pellets. The resulting solution was extracted with Et₂O (2x20 mL), saturated in NaCl and extracted again with Et₂O (20 mL). The combined organic layers were dried over Na_2SO_4 , filtered, HCl (2 M in Et₂O, 2.5 mL) was added and the solvent was removed under reduced pressure. The

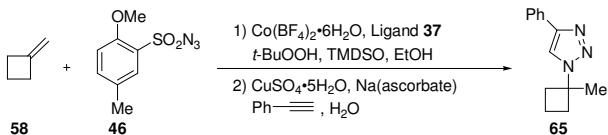
residues were co-evaporated with toluene (2x) and CH_2Cl_2 (2x) and dried 2 h in high vacuo. The isolated product was recrystallized from AcOEt/MeOH to yield amine hydrochloride **62** (51 mg, 0.42 mmol, 84%) together with the reductive amination product **63** (6 mg, 0.04 mmol, 7%). Complete separation of **62** and **63** could not be achieved.

From Methylenecyclobutane **58 via Hydroazidation and Reduction**



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (40 mg, 0.12 mmol, 0.060 equiv) and ligand **37** (56 mg, 0.12 mmol, 0.060 equiv) were dissolved in ethanol (10 mL) at 23 °C under argon. After 10 min, the reaction was cooled to 0 °C and methylenecyclobutane (**58**) (0.18 mL, 2.0 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by azide **46** (0.68 g, 3.1 mmol, 1.5 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 0.10 mL, 0.55 mmol, 0.28 equiv). After 5 min, TMDSO (0.52 mL, 3.0 mmol, 1.5 equiv) was added dropwise to the suspension. The resulting dark brown-green solution was allowed to warm to 23 °C over 2 h and stirred at 23 °C until the color changed back to orange-red (6 h). At this point, Lindlar catalyst (5% Pd, 0.36 g) was added and the reaction was put under H_2 (1 atm, balloon). After 13 h, the reaction was filtered over Celite, the Celite was washed with MeOH (40 mL), the pH was adjusted to 1 with 37% HCl , and the solvents were removed under reduced pressure. The residues were suspended in 1 M HCl (20 mL), the suspension was washed with Et_2O (3x15 mL) and the pH was adjusted to 12 with NaOH pellets. The resulting solution was extracted with Et_2O (2x20 mL), saturated in NaCl and extracted again with Et_2O (20 mL). The combined organic layers were dried over Na_2SO_4 , filtered, HCl (2 M in Et_2O , 2.5 mL) was added and the solvent was removed under reduced pressure. The residues were co-evaporated with toluene (2x) and CH_2Cl_2 (2x) and dried 2 h in high vacuo. The isolated product was recrystallized from AcOEt/MeOH to yield amine hydrochloride **62** (145 mg, 1.19 mmol, 60%) as colorless crystals. **Mp** (AcOEt/MeOH) 241-244 °C; ^1H NMR (CD_3OD , 300 MHz) δ 4.91 (m, >3H, NH and H_2O), 2.36-2.27 (m, 2H, CH_2), 2.11-1.90 (m, 4H, CH_2), 1.50 (s, 3H, CH_3); ^{13}C NMR (CD_3OD , 75 MHz) δ 54.7, 33.0, 23.9, 13.8; IR (KBr) ν 2963 (s, br), 2762 (s), 2696 (m), 2640 (m), 2593 (m), 2539 (m), 2506 (m), 2054 (m), 1920 (w), 1604 (w), 1504 (s), 1456 (w), 1428 (w), 1381 (s), 1323 (w), 1270 (s), 1232 (w), 1206 (w), 1175 (m), 1097 (w), 1051 (w), 980 (w), 924 (w), 905 (w), 712 (w), 608 (w), 417 (m); MS (ESI) 86.4 (M-Cl); Anal. calcd for $\text{C}_5\text{H}_{12}\text{NCl}$: C, 49.38; H, 9.95; N, 11.52. Found: C, 49.31; H, 9.66; N, 11.33.

1-(1-Methyl-cyclobutyl)-4-phenyl-1*H*-[1,2,3]triazole (65)



$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (20 mg, 0.060 mmol, 0.060 equiv) and ligand **37** (28 mg, 0.060 mmol, 0.060 equiv) were dissolved in ethanol (2.5 mL) at 23 °C under argon. After 10 min, the reaction was cooled to 0 °C and methylenecyclobutane (**58**) (92 μL , 1.0 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by azide **46** (0.34 g, 1.5 mmol, 1.5 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 50 μL , 0.28 mmol, 0.28 equiv). After 5 min, TMDSO (0.26 mL, 1.5 mmol, 1.5 equiv) was added dropwise to the suspension. The resulting dark brown-green solution was allowed to warm to 23 °C over 2 h and stirred at 23 °C until the color changed back to orange-red (6 h). Water (3.5 mL) was added. After further stirring for 30 min, a solution of sodium ascorbate (80 mg, 0.40 mmol, 0.40 equiv) in water (0.20 mL), a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (24 mg, 0.10 mmol, 0.10 equiv) in water (0.20 mL) and phenylacetylene (distilled, 0.28 mL, 2.5 mmol, 2.5 equiv) were added and the heterogenous mixture stirred at 23 °C for 20 h. The reaction mixture was then diluted with water (5 mL) and brine (5 mL), extracted with AcOEt (3x15 mL), the combined organic layers were dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (solvent gradient: pentane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 50:100:5, then pentane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 50:100:7.5) to afford **65** (114 mg, 0.53 mmol, 53%) as a slightly yellow solid. Analytically pure samples of **65** were obtained after recrystallization from hexane. R_f (pentane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 50:100:7.5) 0.25; **Mp** (Hexane) 102-104 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.85-7.81 (m, 2H, Ph H), 7.78 (s, 1H, triazole H), 7.43-7.26 (m, 3H, Ph H), 2.89-2.79 (m, 2H, CH_2), 2.37-2.27 (m, 2H, CH_2), 2.07-1.95 (m, 2H, CH_2), 1.79 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 147.2, 130.7, 128.6, 127.7, 125.5, 116.7, 61.0, 34.8, 26.7, 14.2; IR ν 3086 (w), 2976 (m), 2943 (m), 1610 (w), 1483 (m), 1456 (m), 1413 (m), 1381 (w), 1352 (w), 1261 (m), 1227 (m), 1202 (m), 1075 (m), 1027 (m), 973 (w), 921 (w), 827 (w), 768 (s), 697 (s), 513 (w); MS (ESI) 214.3 (M+H), 236.3 (M+Na); Anal. calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.30; H, 7.19; N, 19.42.

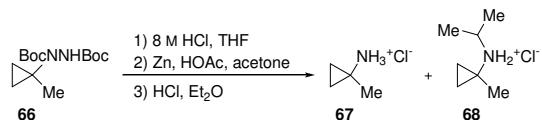
N-(1-Methyl-cyclopropyl)-N'-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (66)



Following **GP3** Hydrohydrazination product **66** (439 mg, 1.53 mmol, 77%) was obtained as a colorless solid with methylenecyclopropane (**59**) (0.15 mL, 2.0 mmol, 2.0 equiv) in 12 h with 2 mol% catalyst **23** after purification by column chromatography ($\text{AcOEt}/\text{hexane}$ 1:10-1:8). R_f ($\text{AcOEt}/\text{hexane}$ 1:5) 0.30; **Mp** 126-127 °C; ^1H NMR (CDCl_3 , 300 MHz, 52 °C) δ 6.23 (br s, 1H, NH), 1.48 (s, 18H, OCCH_3), 1.33 (s, 3H, NCCH_3), 0.99 (br m, 2H, CH_2), 0.67-0.59 (m, 2H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz, 52 °C) δ 155.6, 80.8, 38.6, 28.4, 28.2, 21.2, 15.9; IR ν 3328 (m), 2978 (m), 2933 (m), 1715 (s), 1480 (m), 1456

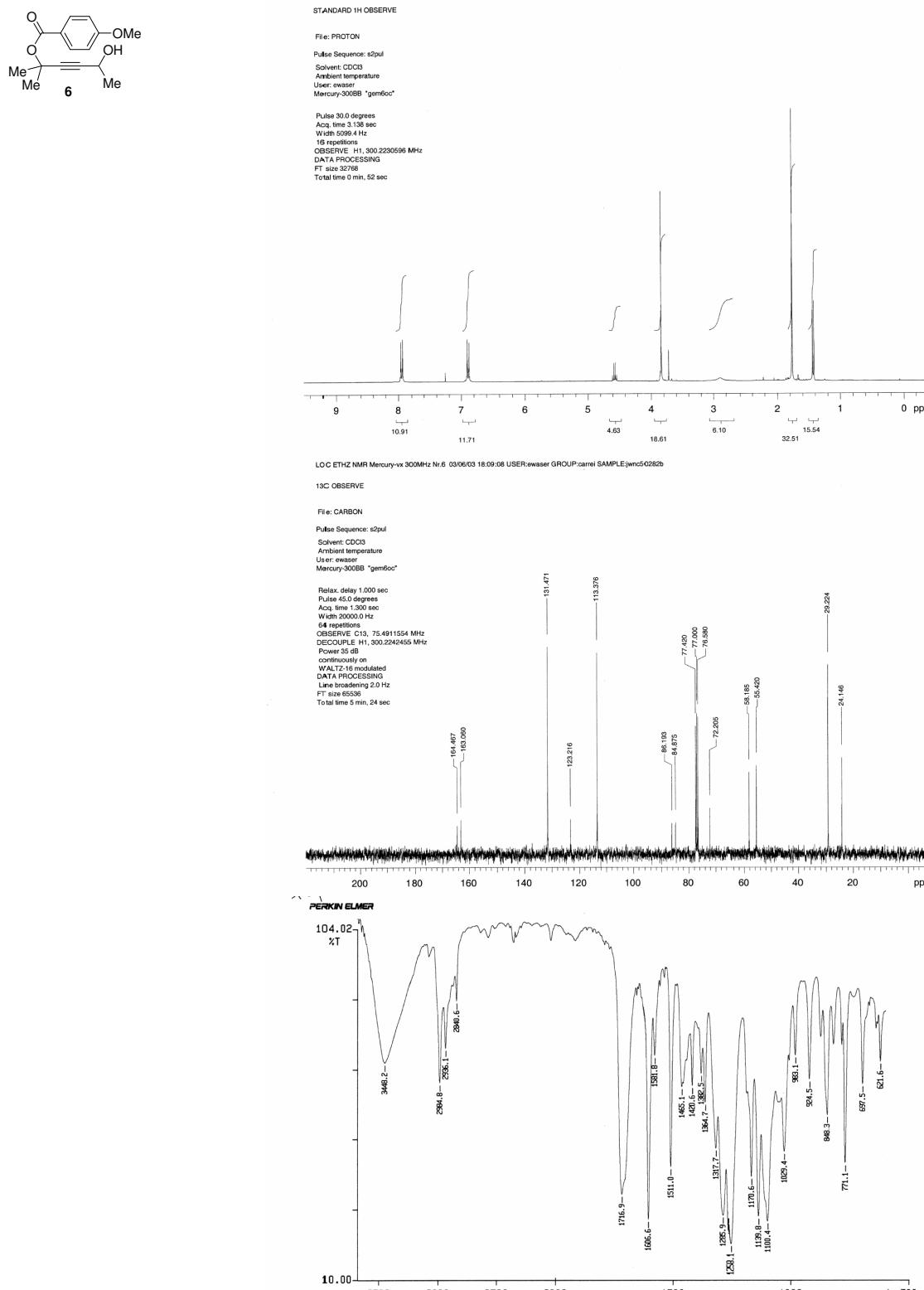
(w), 1385 (s), 1367 (s), 1248 (s), 1166 (s), 1118 (m), 1088 (m), 1048 (m), 1020 (m), 952 (w), 914 (w), 854 (w), 785 (w), 762 (w), 735 (w), 669 (w), 647 (w), 591 (w), 534 (w); MS (ESI) 287.3 (M+H), 309.2 (M+Na); Anal. calcd for $C_{14}H_{26}N_2O_4$: C, 58.72, H, 9.15; N, 9.78. Found: C, 58.51; H, 9.08, N, 9.60.

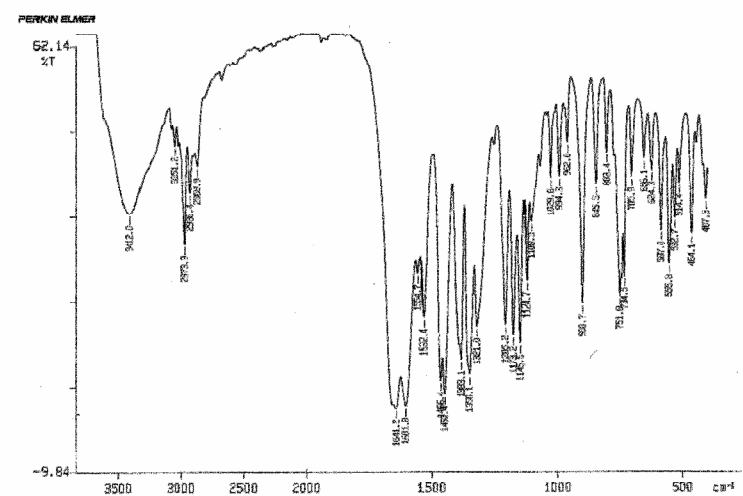
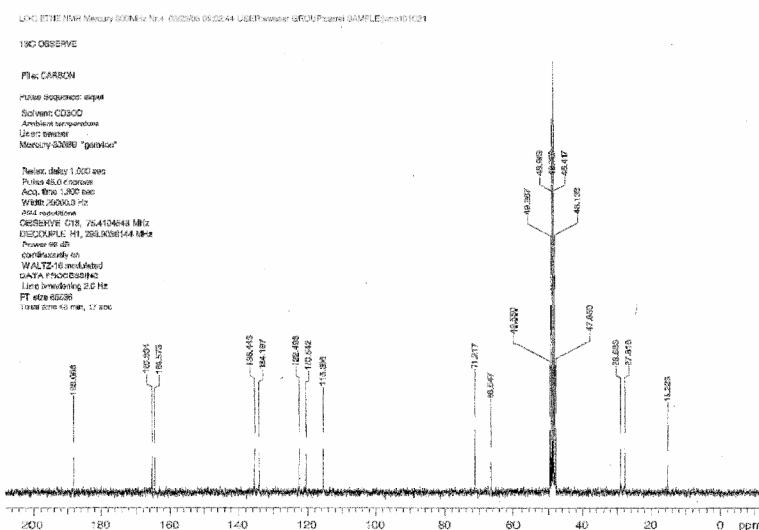
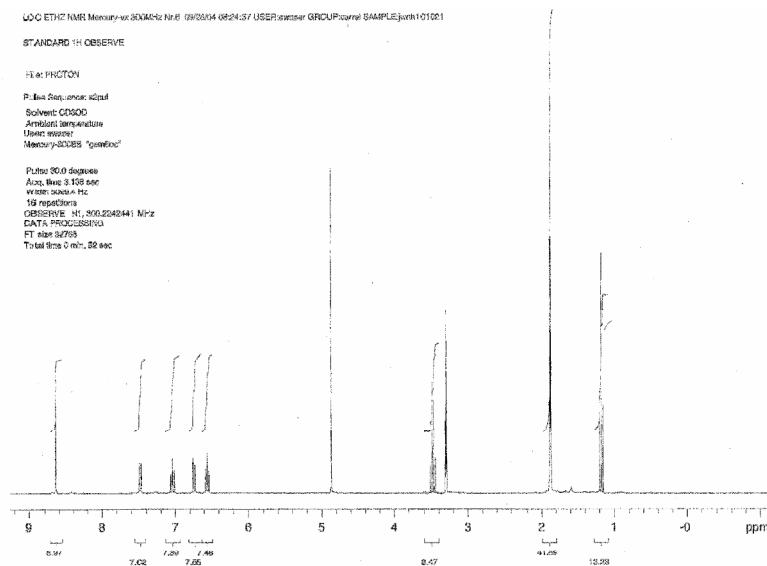
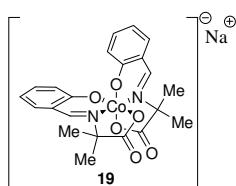
1-Methylcyclopropylamine hydrochloride (68)



Hydrohydrazinization product **66** (509 mg, 1.78 mmol, 1.00 equiv) was dissolved in THF (2 mL) and 8 M HCl (6 mL) was added, whereas partial precipitation of **66** occurred. The reaction mixture was stirred vigorously for 1 h to give a clear solution. The solvents were removed under reduced pressure and the residues dried 3 h in high vacuo. Acetic acid (10 mL) and Zn dust (Acros, freshly activated (Zn dust (30 g) was stirred with 5% HCl (40 mL) for 3 min, filtered and washed with water (3x40 mL), acetone (2x30 mL) and Et₂O (2x30 mL) and dried 2 h in high vacuo), 2.0 g) were added, followed 10 min later by acetone (1.0 mL). After 1 h, the reaction was filtered over Celite, the Celite was washed with MeOH (40 mL), the pH was adjusted to 1 with 37% HCl, and the solvents were removed under reduced pressure. The residues were suspended in 1 M HCl (20 mL), the suspension was washed with Et₂O (3x15 mL) and the pH was adjusted to 12 with NaOH pellets. The resulting solution was extracted with Et₂O (2x20 mL), saturated in NaCl and extracted again with Et₂O (20 mL). The combined organic layers were dried over Na₂SO₄, filtered, HCl (2 M in Et₂O, 2.5 mL) was added and the solvent was removed under reduced pressure. The residues were co-evaporated with toluene (2x) and CH₂Cl₂ (2x) and dried 2 h in high vacuo. The isolated product was recrystallized from AcOEt/MeOH to yield amine hydrochloride **67** (1. crop: pure **67** (90 mg, 0.84 mmol, 47%), 2.crop: **67** (48 mg, 0.45 mmol, 25%) and **68** (4 mg, 0.03 mmol, 2%), combined yield of **67**: 72%) as colorless crystals. Mp (AcOEt/MeOH) 204-205 °C; ¹H NMR (CD₃OD, 300 MHz) δ 4.87 (m, >3H, NH and H₂O), 1.45 (s, 3H, CH₃), 0.95-0.90 (m, 2H, CH₂), 0.77-0.73 (m, 2H, CH₂); ¹³C NMR (CD₃OD, 75 MHz) δ 31.6, 20.8, 11.3; IR (KBr) ν 2906 (s, br), 2695 (s), 2595 (s), 2516 (s), 2432 (m), 2063 (s), 1950 (w), 1806 (w), 1610 (m), 1520 (s), 1470 (m), 1451 (s), 1424 (s), 1395 (s), 1363 (w), 1275 (s), 1208 (m), 1112 (w), 1061 (w), 1027 (s), 1002 (w), 942 (w), 920 (w), 870 (m), 770 (w), 684 (w), 431 (s), 410 (s); MS (ESI) 72.5 (M-Cl); Anal. calcd for C₄H₁₀NCl: C, 44.66; H, 9.37; N, 13.02. Found: C, 44.56; H, 9.18; N, 12.92.

6. Important Spectra for Characterisation





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X: 8 scans, 4.0cm-1, flat