Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. 200460811

Catalytic Hydrohydrazination of a Wide Range of Alkenes with a Simple Mn-Complex

Jérôme Waser and Erick M. Carreira*

Laboratorium für Organische Chemie, ETH Hönggerberg, CH-8093 Zürich, Switzerland.

carreira@org.chem.ethz.ch

General. All reactions were carried out in oven dried glassware under an atmosphere of argon or nitrogen. For flash chromatography technical grade solvents were used, which were distilled prior to use. Solvents for reactions were analytical grade purchased from Merck or Baker and used without further purifications except for THF and Et_2O, which were passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; Macherey und Nagel; activated under a flow of N_2 at 300° over night) to remove water. 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, 60Å, using pentanes/diethylether or hexanes/ethyl acetate as eluent with 0.3-0.5 bar pressure.

TLC was performed on Merck silica gel 60 F_{254} 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.

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration; interpretation).

^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard.

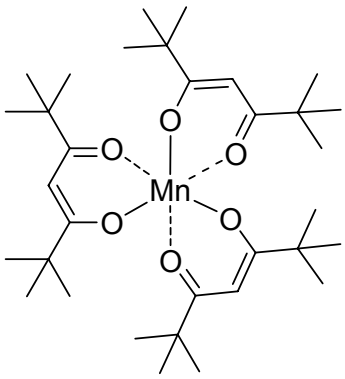
Many NMR measurements were done at 52 °C to minimize signal broadening due to rotamers mixture (temperature given).

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).

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 for high resolution measurements, unless stated otherwise.

Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ. Samples for elemental analysis were further purified through column chromatography or recrystallization.

[Tris-[dipivaloylmethanato]manganese(III)][1] (1) ($Mn(dpm)_3$)



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

Following a slightly modified literature procedure,[1] 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 (560 mg, 2.3 mmol, 1.0 equiv) in methanol (4.5 ml, distilled, degassed (two freeze-thaw cycles)) under nitrogen and the resulting yellow solution was stirred at 23 °C with nitrogen bubbling for 5 min. A solution of sodium hydroxide (180 mg, 4.6 mmol, 2.0 eq) in water (1.25 ml, deionized, degassed (20 min nitrogen bubbling)) was then added, whereas a yellow solid immediately precipitated. The solid was filtred under nitrogen, washed with methanol/water 2:1 (20 ml) and dried 15 h in HV over P_2O_5, whereas a color change to olive green was observed, which shows a partial convertion to $Mn(dpm)_3$. The obtained olive green product (685 mg, 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 (500 mg, 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 (245 mg, 6.1 mmol, 3.0 eq) in water (1.25 ml, deionized) was then added, whereas a green solid immediately precipitated. After diluting with 5.5 ml methanol, the reaction mixture was stirred at 23 °C under air for 13 h and filtered. The green-brown solid was dried in HV at 60° C for 4 h and dissolved in hot *iso*propanol (15 ml). $Mn(dpm)_3$ (**1**) 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, allowing to remove some brown-red impurities. The pentane was removed under reduced pressure and the resulting olive green

solid was dried under HV for 12 h to give $Mn(dpm)_3$ (**1**) as a green powder (759 mg, 1.25 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 characterised.

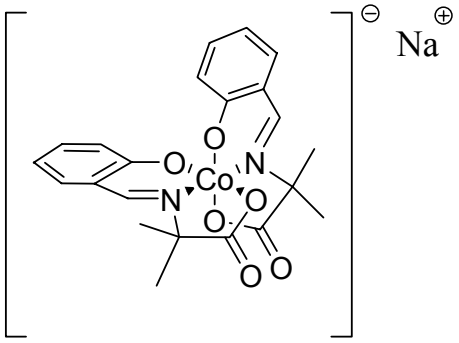
M.p. 164-165 °C;

IR(KBr) 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 $C_{22}H_{38}MnO_4$ $[Mn(dpm)_2]^+$: 421.2145; found: 421.2156;

Elemental analysis calcd for $C_{33}H_{57}MnO_6$: C 65.54, H 9.50; found: C 65.62, H 9.49.

[Sodium-bis-[N-salicylidene-2-amino-isobutyrato]-cobaltate(III)] (5)



Salicylaldehyde (1.1 ml, 10 mmol, 2.0 equiv) and 2-amino-isobutyric acid (1.0 g, 10 mmol, 2.0 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 N_2. The resulting thick yellow suspension was cooled to 0 °C and Cobalt(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 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 CH_2Cl_2 (2x). The resulting dark red-brown residues were suspended in Et_2O, triturated for 1 h and filtered, the obtained fine dark red-brown powder was dried in HV at 70 °C for 12 h to give the active catalyst **5** (2.04 g, 4.14 mmol, 83%).

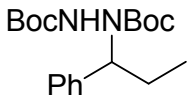
The obtained compound **5** was established to be a mixture by NMR analysis and elemental analysis. Further repeated attempts to purify it via column chromatography or recrystallization were unsuccessful, but high resolution mass spectra confirmed the proposed constitution of **5**. The catalyst was used without further purifications and several batches furnished reproducible results. No lost of activity was observed after several months when the compound was kept in dessicator at 23 °C.

IR(KBr) ν= 3416 (m, br), 3244 (m, br), 2984 (m, br), 1643 (s), 1601 (s), 1470 (m), 1450 (m), 1385 (s), 1361 (s), 1314 (s), 1204 (m), 1148 (m), 1101 (w), 1042 (w), 997 (w), 902 (w), 833 (w), 757 (w);

HRMS calcd for $C_{22}H_{22}N_2O_6^-$ [M-Na]$^-$: 469.0815; found: 469.0821;

General procedure A: Cobalt Catalyst

***N*-(1-Phenyl-propyl)-*N′*-(*tert*-butoxycarbonyl)hydrazine-carboxylic acid *tert*-butyl ester (6)**



The cobalt catalyst **5** (12 mg, 0.025 mmol 0.05 equiv) was dissolved in ethanol (2.5 ml) at 23 °C under N_2. β-methyl-styrene (65 µl, 0.50 mmol, 1.0 equiv) and phenylsilane (65 µl, 0.52 mmol, 1.0 equiv) were added to the brown-red solution, followed by di-*tert*-butyl azodicarboxylate (170 mg, 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 (3 h) 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 FC (AcOEt/hexane 1:10) to afford **6** (154 mg, 0.440 mmol, 88%) as a colorless solid.

General Procedure B: Manganese catalyst

$Mn(dpm)_3$ (**1**) (6 mg, 0.01 mmol 0.02 equiv) was dissolved in *iso*propanol (2.5 ml) at 23 °C under N_2 and the dark brown green solution was cooled to 0 °C. β-methyl-styrene (65 µl, 0.50 mmol, 1.0 equiv) and phenylsilane (65 µl, 0.52 mmol, 1.0 equiv) were added, followed by di-*tert*-butyl azodicarboxylate (170 mg, 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 (2-4 h, 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 FC (AcOEt/hexane 1:10) to afford **6** (165 mg, 0.471 mmol, 94%) as a colorless solid.

R_f (AcOEt/hexane 1:5) 0.30;

M.p. 97-98 °C;

^{1}H 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; CH_2), 1.47 (s, 9H; CCH_3), 1.43 (br s, 9H; CCH_3), 0.96 (t, ^3J(H,H)=7.2 Hz, 3H; CH_2CH_3);

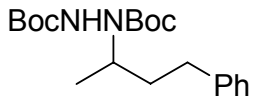
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.5, 154.9, 139.6, 128.2, 128.2, 127.4, 81.2, 80.8, 62.3, 28.4, 28.2, 24.0, 11.3;

IR ν= 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 calcd for $C_{19}H_{30}N_2O_4Na^+$ $[M+Na]^+$: 373.2098; found: 373.2090;

Elemental analysis 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-Phenyl-1-methyl-propyl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (7)**



Following general procedure **A**:

7 (163 mg, 0.448 mmol, 90 %) was obtained as a colorless solid with 4-phenyl butene (75 µl, 0.50 mmol, 1.0 equiv) in 4 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Scale up:

The cobalt catalyst **5** (60 mg, 0.12 mmol, 0.025 equiv) was dissolved in ethanol (20 ml) at 23 °C under N_2. 4-phenyl-butene (675 mg, 0.510 mmol 1.0 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 (1.72 g, 7.47 mmol, 1.5 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 H_2O (3 ml), brine (20 ml) was added and the reaction mixture was extracted with AcOEt (3x50 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 FC (AcOEt/hexane 1:10) to afford **7** (1.75 g, 4.80 mmol, 94 %) as a colorless solid together with recovered 4-phenyl butene (38 mg, 0.28 mmol, 5 %).

Following general procedure **B**:

7 (140 mg, 0.38 mmol, 76 %) together with the primary hydrazide **8** (34 mg, 0.093 mmol, 18%, total 94%) were obtained as colorless solids with 4-phenyl-butene (75 µl, 0.50 mmol, 1.0 eq) in 2.5 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Using PMHS:

7 (140 mg, 0.38 mmol, 76 %) together with the primary hydrazide **8** (22 mg, 0.060 mmol, 12%, total 88%) were obtained as colorless solids with 4-phenyl-butene (75 µl, 0.50 mmol, 1.0 eq) in 12 h at 23 °C with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.35;

M.p. 125-127°C;

^{1}H NMR ($CDCl_3$, 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; $PhCH_2$), 1.90 (m, 1H; CH_2CHN), 1.65 (m, 1H; CH_2CHN), 1.48 (s, 9H; CCH_3), 1.47 (s, 9H; CCH_3), 1.14 (d, ^3J(H,H)=6.9 Hz, 3H; $CHNCH_3$);

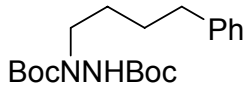
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.7, 154.7, 141.9, 128.2, 128.1, 125.6, 80.8, 53.1, 35.8, 32.9, 28.3, 28.2, 18.2;

IR (KBr) ν= 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 calcd for $C_{20}H_{32}N_2O_4Na^+$ $[M+Na]^+$: 387.2254; found: 387.2255;

Elemental analysis calcd for $C_{20}H_{32}N_2O_4$: 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)hydrazine-carboxylic acid *tert*-butyl ester (8)**



R_f (AcOEt/hexane 1:5) 0.32;

M.p. 54-56°C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 7.29-7.13 (m, 5H; Ar H), 6.21 (br s, 1H; NH), 3.46 (t, ^3J(H,H)=6.5 Hz, 2H; CH_2N), 2.64 (t, ^3J(H,H)=7.2 Hz, 2H; CH_2Ph), 1.70-1.53 (m, 4H; CH_2), 1.47 (s, 9H; CCH_3), 1.46 (s, 9H; CCH_3);

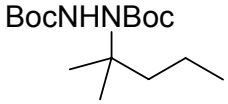
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.2, 142.2, 128.3, 128.2, 125.6, 81.0, 80.9, 49.8, 35.6, 28.5, 28.3, 28.3, 27.2;

IR ν= 3317 (m), 3063 (w), 3026 (w), 2978 (s), 2933 (s), 2863 (w), 1706 (s), 1604 (w), 1496 (s), 1479 (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: m/z (%): 365.1 (100) $[M+H]^+$;

Elemental analysis calcd for $C_{20}H_{32}N_2O_4$: C 65.91, H 8.85, N 7.69; found: C 65.91, H 8.79, N 7.59.

***N*-(1,1-Dimethyl-butyl)-*N'*-(*tert*-butoxycarbonyl)hydrazine-carboxylic acid *tert*-butyl ester (9)**



Following general procedure **A**:

9 (140 mg, 0.443 mmol, 88%) was obtained as a colorless solid with 2-methyl-pentene (62 µl, 0.50 mmol, 1.0 equiv), phenylsilane (90 µl, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (230 mg, 1.0 mmol, 2.0 equiv) in 5 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

9 (137 mg, 0.433 mmol, 86%) was obtained as a colorless solid with 2-methyl-pentene (62 µl, 0.50 mmol, 1.0 equiv), phenylsilane (65 µl, 0.52 mmol, 1.0 equiv) and di-*tert*-butyl azodicarboxylate (170 mg, 0.75 mmol, 1.5 equiv) in 2 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.50;

M.p. 63-64 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.10 (br s, 1H; NH), 1.87 (td, ^3J(H,H)=11.9, 4.9 Hz, 1H; CH_2CN), 1.59 (td, ^3J(H,H)=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, ^3J(H,H)=7.5 Hz, 3H; CH_2CH_3);

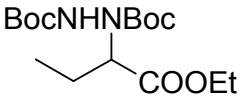
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 156.0, 154.5, 80.5, 62.1, 42.8, 28.4, 28.3, 27.0, 26.4, 17.9, 14.5;

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: m/z (%): 317.3 (100)$[M+H]^+$, 339.2 $[M+Na]^+$ (8);

Elemental analysis 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.

2-(N,N′-Bis-(*tert*-butoxycarbonyl-hydrazino))-butyric acid ethyl ester (10)



Following general procedure **A**:

10 (113 mg, 0.327 mmol, 66%) was obtained as a colorless viscous oil with trans-ethyl crotonate (62 µl, 0.50 mmol, 1.0 equiv), phenylsilane (90 µl, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (230 mg, 1.0 mmol, 2.0 equiv) in 12 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

10 (154 mg, 0.445 mmol, 88%) was obtained as a colorless viscous oil with trans-ethyl crotonate (62 µl, 0.50 mmol, 1.0 equiv), phenylsilane (65 µl, 0.52 mmol, 1.0 equiv) and di-*tert*-butyl azodicarboxylate (170 mg, 0.75 mmol, 1.0 equiv) in 6 h with 2 mol% catalyst after purification by FC (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, ^3J(H,H)=7.2 Hz, 3H; OCH_2CH_3), 1.10 (t, ^3J(H,H)=7.5 Hz, 3H; $CHNCH_2CH_3$);

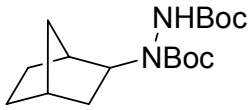
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 171.7, 155.5, 81.7, 80.8, 61.1, 28.3, 28.2, 22.4, 14.2, 11.2;

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 calcd for $C_{16}H_{30}N_2O_6Na^+$ $[M+Na]^+$: 369.1996; found: 369.2000;

Elemental analysis 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*-(Bicyclo[2.2.1]hept-2-yl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (11)**



Following general procedure **A**:

11 (103 mg, 0.316 mmol, 66%) was obtained as a colorless solid with norbornene (45 mg, 0.48 mmol, 1.0 equiv) in 7 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

11 (179 mg, 0.548 mmol, 98%) was obtained as a colorless solid with norbornene (53 mg, 0.56 mmol, 1.0 equiv) in 3 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.40;

M.p. 169-170 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.06 (br s, 1H; NH), 3.91 (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; $OCCH_3$);

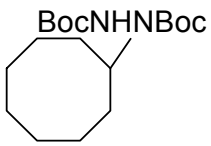
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.7, 155.1, 80.8, 60.6, 41.2, 37.2, 36.2, 35.8, 28.4, 28.3, 27.9;

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: m/z (%): 327.2 (63) $[M+H]^+$, 349.3 (100) $[M+Na]^+$;

Elemental analysis 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 (12)**



Following general procedure **A**:

12 (104 mg, 0.304 mmol, 62 %) was obtained as a colorless solid with cyclooctene (65 µl, 0.49 mmol, 1.0 equiv, freshly distilled), phenylsilane (95 µl, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (230 mg, 1.0 mmol, 2.0 equiv) in 24 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

12 (163 mg, 0.476 mmol, 95 %) was obtained as a colorless solid with cyclooctene (66 µl, 0.50 mmol, 1.0 equiv, freshly distilled) in 2.5 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.35;

M.p. 115-116 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.02 (br s, 1H; NH), 4.16 (br s, 1H; CHN), 1.71-1.40 (m, 14H; CH_2), 1.45 (s, 9H; $OCCH_3$), 1.44 (s, 9H; $OCCH_3$);

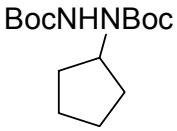
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 156.0, 154.6, 80.7, 57.7, 31.1, 28.3, 28.2, 26.7, 26.3, 24.7;

IR ν= 3317 (m), 2978 (m), 2926 (s), 2857 (m), 1703 (s), 1478 (m), 1455 (m), 1392 (s), 1367 (s), 1315 (s), 1253 (s), 1164 (s), 1111 (m), 1051 (m), 1017 (w), 919 (w), 866 (w), 781 (w), 758 (w), 734 (m), 650 (w), 615 (w);

MS: m/z (%): 343.4 (23)$[M+H]^+$, 365.4 (10)$[M+Na]^+$;

Elemental analysis calcd for $C_{18}H_{34}N_2O_4$: C 63.13, H 10.01, N 8.18; found: C 63.22, H 10.09, N 7.99.

***N*-(Cyclopentyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (13)**



Following general procedure **A**:

13 (111 mg, 0.370 mmol, 74 %) was obtained as a colorless solid with cyclopentene (44 µl, 0.50 mmol, 1.0 equiv), phenylsilane (95 µl, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (230 mg, 1.0 mmol, 2.0 equiv) in 8 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

13 (141 mg, 0.469 mmol, 94 %) was obtained as a colorless solid with cyclopentene (44 µl, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.40;

M.p. 154-155 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °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; $OCCH_3$);

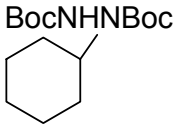
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.9, 154.9, 80.8, 59.0, 29.1, 28.4, 28.3, 23.8;

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: m/z (%): 301.2 (16)$[M+H]^+$, 323.2 (58) $[M+Na]^+$, 623.2 (100) $[2M+Na]^+$;

Elemental analysis 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*-(Cyclohexyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (14)**



Following general procedure **A**:

14 (39 mg, 0.12 mmol, 24 %) was obtained as a colorless solid with cyclohexene (51 µl, 0.50 mmol, 1.0 equiv), phenylsilane (95 µl, 0.75 mmol, 1.5 equiv) and di-*tert*-butyl azodicarboxylate (230 mg, 1.0 mmol, 2.0 equiv) in 24 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

14 (142 mg, 0.452 mmol, 90 %) was obtained as a colorless solid with cyclohexene (51 µl, 0.50 mmol, 1.0 equiv in 2 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.42;

M.p. 147-148 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 5.98 (br s, 1H; NH), 4.93 (br s, 1H; CHN), 1.80-1.06 (m, 10H; CH_2), 1.48 (s, 9H; $OCCH_3$), 1.47 (s, 9H; $OCCH_3$);

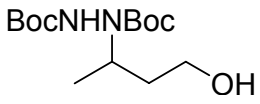
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.8, 154.6, 80.8, 56.9, 30.3, 28.4, 28.3, 25.7, 25.6;

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: m/z (%): 315.3 (11) $[M+H]^+$, 337.3 (44) $[M+Na]^+$, 651.2 (100) $[2M+Na]^+$;

Elemental analysis 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*-(3-Hydroxy-1-methyl-propyl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (15)**



Following general procedure **A**:

15 (67 mg, 0.22 mmol, 44%) was obtained as a colorless viscous oil together with the regioisomeric product **16** (15 mg, 0.05 mmol, 10%) with crotyl alcohol (43 µl, 0.50 mmol, 1.0 equiv), phenylsilane (130 µl, 1.0 mmol, 2 equiv) and di-*tert*-butyl azodicarboxylate (340 mg, 1.5 mmol, 3.0 equiv) in 24 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:3).

Following general procedure **B**:

15 (88 mg, 0.29 mmol, 58%) was obtained as a colorless viscous oil together with the regioisomeric product **16** (49 mg, 0.16 mmol, 32%, colorless solid) with crotyl alcohol (43 µl, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:6-1:1).

Starting from but-1-ene-4-ol:

Following general procedure **A**:

15 (34 mg, 0.11 mmol, 22%) was obtained as a colorless viscous oil with but-1-ene-4-ol (43 µl, 0.50 mmol, 1.0 equiv) in 12 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:2).

Following general procedure **B**:

15 (111 mg, 0.36 mmol, 72%) was obtained as a colorless viscous oil with but-1-ene-4-ol (43 µl, 0.50 mmol, 1.0 equiv) in 2.5 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:2).

R_f (AcOEt/hexane 1:2) 0.20;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.11 (br s, 1H; NH), 4.38 (br s, 1H; CHN), 3.73-3.63 (m, 2H; CH_2OH), 2.77 (br s, 1H; OH), 1.68-1.51 (m, 2H; CH_2CN), 1.47 (s, 9H; $OCCH_3$), 1.47 (s, 9H; $OCCH_3$), 1.15 (d, ^3J(H,H)=6.9 Hz, 3H; $CNCH_3$);

^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.9, 155.6, 81.4, 81.1, 59.7, 50.0, 37.2, 28.3, 28.3, 18.3;

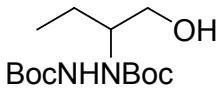
IR ν= 3445 (w, sh), 3312 (m), 2979 (m), 2935 (m), 1705 (s), 1479 (m), 1456 (m), 1394 (s), 1368 (s), 1251 (s), 1162 (s),

1080 (m), 1047 (m), 1017 (m), 914 (w), 854 (w), 761 (w), 735 (m), 647 (w), 577 (w);

HRMS calcd for $C_{14}H_{28}N_2O_5Na^+$ $[M+Na]^+$: 327.1890; found: 327.1888;

Elemental analysis calcd for $C_{14}H_{28}N_2O_5$: C 55.24, H 9.27, N 9.20; found: C 55.40, H 9.51, N 8.93.

***N*-(2-Hydroxy-1-ethyl-ethyl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (16)**



R_f (AcOEt/hexane 1:2) 0.33;

M.p. 144-145 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.17 (br s, 1H; NH), 4.12 (br s, 1H; CHN), 3.42-3.39 (m, 2H; C*H*$_2$OH), 1.48 (s, 9H; OCC*H*$_3$), 1.46 (s, 9H; OCC*H*$_3$), 1.40-1.23 (m, 2H; C*H*$_2$CH$_3$), 0.86 (t, ^3J(H,H)=7.5 Hz, 3H; CH$_2$C*H*$_3$);

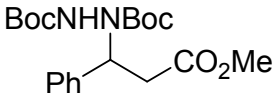
^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C) δ= 158.3, 157.7, 156.1, 155.2, 82.3, 82.1, 81.8, 81.2, 62.2, 61.9, 59.8, 28.2, 28.1, 22.0, 21.2, 10.6;

IR ν= 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 calcd for $C_{14}H_{28}N_2O_5Na^+$ $[M+Na]^+$: 327.1890; found: 327.1885;

Elemental analysis calcd for $C_{14}H_{28}N_2O_5$: C 55.24, H 9.27, N 9.20; found: C 55.32, H 9.18, N 9.22.

3-(*N*,*N'*-Di-*tert*-butoxycarbonyl-hydrazino)-3-phenyl-propionic acid methyl ester (17)



Following general procedure **A**:

17 (178 mg, 0.451 mmol, 90%) was obtained as a colorless solid together with the regioisomeric product (<3 mg, <0.008 mmol, <2%, not isolated) with methyl cinnamate (81 mg, 0.50 mmol, 1.0 equiv) in 4 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

17 (152 mg, 0.385 mmol, 77%) was obtained as a colorless solid together with the regioisomeric product (<18 mg, <0.046 mmol, <9%, not isolated) with methyl cinnamate (81 mg, 0.50 mmol, 1.0 equiv) in 2 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:2) 0.45;

M.p. 102-104 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 7.37-7.22 (m, 5H; Ar H), 6.01 (br s, 1H; NH), 5.71 (br m, 1H; CHN), 3.63 (s, 3H; OCH_3), 3.12 (dd, ^3J(H,H)=15.6, 8.4 Hz, 1H; CH_2), 2.89 (br m, 1H; CH_2), 1.45 (s, 9H; $OCCH_3$), 1.39 (br s, 9H; $OCCH_3$);

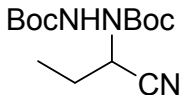
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 171.0, 155.4, 154.3, 138.7, 128.3, 127.7, 127.6, 81.6, 81.0, 57.3, 51.7, 36.6, 28.3, 28.1;

IR ν= 3320 (w), 2979 (m), 2933 (w), 1713 (s), 1497 (m), 1479 (m), 1455 (m), 1437 (m), 1392 (s), 1368 (s), 1296 (s), 1256 (s), 1166 (s), 1083 (w), 1050 (w), 1021 (w), 976 (w), 910 (w), 854 (w), 754 (w), 700 (m);

MS: m/z (%): 395.1 (100) $[M+H]^+$;

Elemental analysis calcd for $C_{20}H_{39}N_2O_6$: C 60.90, H 7.67, N 7.10; found: C 60.71, H 7.65, N 7.10.

N-(1-Cyano-propyl)-*N'*-(*tert*-butoxycarbonyl)hydrazinecarboxylic acid *tert*-butyl ester (18)



Following general procedure **A**:

18 (69 mg, 0.23 mmol, 46%) was obtained as a colorless solid with crotyl nitrile (41 µl, 0.50 mmol, 1.0 equiv) in 18 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

18 (67 mg, 0.22 mmol, 44%) was obtained as a colorless solid with crotyl nitrile (41 µl, 0.50 mmol, 1.0 equiv) in 2.5 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.30;

M.p. 105-107 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.31 (br s, 1H; NH), 4.91 (br s, 1H; CHN), 1.95-1.85 (m, 2H; CH_2), 1.49 (s, 9H; $OCCH_3$), 1.48 (s, 9H; $OCCH_3$), 1.07 (t, ^3J(H,H)=7.5 Hz, 3H; CH_2CH_3);

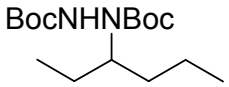
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.0, 153.5, 117.0, 83.1, 82.0, 51.9, 28.2, 25.0, 10.3;

IR ν= 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), 1051 (m), 1017 (m), 936 (m), 891 (w), 848 (m), 785 (w), 761 (m), 737 (w), 597 (w);

HRMS calcd for $C_{14}H_{25}N_3O_4Na^+$ $[M+Na]^+$: 322.1737; found: 322.1735;

Elemental analysis calcd for $C_{14}H_{25}N_3O_4$: 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 (19)



Following general procedure **A**:

19 (25 mg, 0.079 mmol, 16%) was obtained as a colorless solid with trans-3-hexene (62 µl, 0.50 mmol, 1.0 equiv) in 10 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

Following general procedure **B**:

19 (105 mg, 0.332 mmol, 66%) was obtained as a colorless solid with trans-3-hexene (62 µl, 0.50 mmol, 1.0 equiv) in 3 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

R_f (AcOEt/hexane 1:5) 0.50;

M.p. 80-82 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 5.87 (br s, 1H; NH), 3.94 (br s, 1H; CHN), 1.57-1.23 (m, 6H; CH_2), 1.46 (s, 9H; $OCCH_3$), 1.45 (s, 9H; $OCCH_3$), 0.89 (t, ^3J(H,H)=7.2 Hz, 6H; CH_2CH_3);

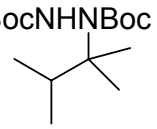
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 155.5, 80.7, 58.6, 34.5, 28.3, 28.3, 25.6, 19.8, 14.0, 11.2;

IR ν= 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: m/z (%): 317.1 (9) $[M+H]^+$, 339.1 (100) $[M+Na]^+$;

Elemental analysis calcd for $C_{16}H_{32}N_2O_4$: C 60.73, H 10.19, N 8.85; found: C 60.50, H 10.43, N 8.78.

***N*-(1,1,2-Trimethyl-ethyl)-*N'*-(*tert*-butoxycarbonyl)hydrazine-carboxylic acid *tert*-butyl ester (20)**



Following general procedure **A**:

20 (22 mg, 0.070 mmol, 14%) was obtained as a colorless solid with 2,3-dimethyl-butene (60 µl, 0.50 mmol, 1.0 equiv) in 10 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

Following general procedure **B**:

20 (123 mg, 0.389 mmol, 78%) was obtained as a colorless solid with 2,3-dimethyl-butene (60 µl, 0.50 mmol, 1.0 equiv) in 3 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

R_f (AcOEt/hexane 1:5) 0.60;

M.p. 101-102 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.03 (br s, 1H; NH), 2.57 (septet, ^3J(H,H)=6.9 Hz, 1H; C*H*CH_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, ^3J(H,H)=6.9 Hz, 3H; $CHCH_3$), 0.79 (d, ^3J(H,H)=6.9 Hz, 3H; $CHCH_3$);

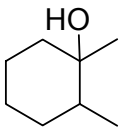
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 156.1, 154.5, 80.5, 65.8, 34.0, 28.4, 28.3, 24.9, 20.8, 18.1, 17.8;

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: m/z (%): 317.1 (100)$[M+H]^+$;

Elemental analysis 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.

1,2-Dimethyl-cyclohexanol[2] (21)

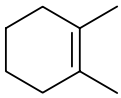


2-Methyl-cyclohexanone (5.0 ml, 41 mmol, freshly distilled, 1.0 equiv) was diluted in Et_2O (9 ml, dry) at 0 °C under argon and a solution of methylmagnesiumbromide (3 M in Et_2O, 16 ml, 48 mmol, 1.2 equiv) was added dropwise over 45 min. The

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 then separated and the organic layer was washed with saturated $NaHSO_3$ solution (2x10 ml), water (4x10 ml), brine (10 ml), dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The crude product was purified by distillation (p = 100 mbar, T = 80 °C) to afford **21** (4.38 g, 34 ml, 83%, 1:1 mixture of diastereoisomers) as a slightly yellow liquid.

^{1}H NMR ($CDCl_3$, 300 MHz, 23 °C)[3] δ= 1.70-1.10 (m, 10H), 1.19 (s, 2.25H; COHCH_3, major diastereoisomer), 1.10 (s, 0.7 H; COHCH_3, minor diastereoisomer), 0.93 (d, 0.75H, ^3J(H,H)=6.9 Hz; CHCH_3, minor diastereoisomer), 0.91 (d, ^3J(H,H)=6.2 Hz, 2.25H; CHCH_3, major diastereoisomer).

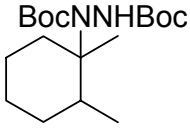
1,2-Dimethyl-cyclohexene[2] **(22)**



1,2-Dimethyl-cyclohexanol (**21**) (4.1 g, 32 mmol, 1.0 equiv) and iodine (50 mg, 0.20 mmol, 0.006 equiv) were mixed at 23 °C under argon and the solution was heated to 150 °C and directly distilled. The distilled liquid was dried 2 h over $CaCl_2$ and filtered to give 1,2-dimethyl-cyclohexene (**22**) together with 1,6-dimethyl-cyclohexene (5:1 ratio, 3.1 g, 28 mmol, 89%) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz)[4] δ= 2.06-0.90 (m, 8 H; CH_2), 1.60 (s, 6H; CH_3).

***N*-(1,2-Dimethyl-cyclohexyl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (23)**



Following general procedure **A**:

23 (30 mg, 0.088 mmol, 17%, 1:1 mixture of diastereoisomers) was obtained as a colorless solid with 1,2-dimethyl-cyclohexene (**22**)(57 mg, 0.52 mmol, 1.0 equiv, contains < 17% 1,6-dimethyl-cyclohexene) in 20 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

Following general procedure **B**:

23 (144 mg, 0.420 mmol, 79%, 1:1 mixture of diastereoisomers) was obtained as a colorless solid with 1,2-dimethyl-cyclohexene (**22**)(58 mg, 0.53 mmol, 1.0 equiv, contains < 17% 1,6-dimethyl-cyclohexene) in 3 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

R_f (AcOEt/hexane 1:5) 0.50;

M.p. 97-99 °C;

^{1}H NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 6.07 (br s, 2H; NH (2 diastereoisomers)), 2.70-2.45 (m, 3H; C*H*CH_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, ^3J(H,H)=6.9 Hz, 3H; $CHCH_3$), 0.78 (d, ^3J(H,H)=6.9 Hz, 3H; $CHCH_3$);

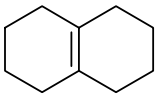
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 156.0, 154.7, 80.4, 66.9, 66.4, 40.0, 35.6, 35.4, 35.2, 32.1, 31.8, 28.4, 28.4, 28.3, 25.5, 25.2, 23.7, 23.3, 18.0, 17.0, 16.5, 16.3;

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: m/z (%): 343.2 (100)$[M+H]^+$;

Elemental analysis calcd for $C_{18}H_{34}N_2O_4$: C 63.13, H 10.01, N 8.18; found: C 63.04, H 10.05, N 8.05.

1,2,3,4,5,6,7,8-Octahydro-naphthalene[5] (24)



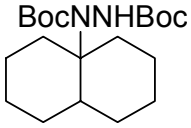
Naphtalene (2.60 g, 20 mmol, 1.0 equiv) was dissolved in dimethylamine (25 ml) and ethylamine (25 ml) at 0 °C under argon. Lithium (1.20 g, 170 mmol, 8.3 equiv, wires, freshly cut in 0.5 cm pieces and washed with hexane) was added over 45 min, whereas the reaction mixture turned red, then blue-red. The 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!), 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 (100 mbar, 40 °C). The crude product was distilled (*p* = 20 mbar, *T* = 80 °C) to give

octahydronaphtalene **24** (1.90 g, 14 mmol, 70%) as a 5.5:1 mixture of isomers.

$NaBH_4$ (240 mg, 6.2 mmol, 0.6 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 $BF_3 \cdot Et_2O$ (1.0 ml, 8.3 mmol, 0.75 equiv, freshly distilled) in THF (3 ml) were added dropwise. The crude octahydronaphtalene (1.79 g, 11 mmol **24**, 1 equiv) was added dropwise to the resulting suspension, the reaction mixture was stirred at rt 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 (100 mbar, 40 °C). Distillation (p = 20 mbar, T = 80 °C) furnished **24** (1.2 g, 9.0 mmol, 82%) containing less than 7% of 2,3,4,5,6,7,9-Octahydro-naphthalene.

^{1}H NMR ($CDCl_3$, 300 MHz)[6] δ= 1.84 (m, 8H; CH_2), 1.59 (m, 8H; CH_2).

Octahydro-naphthalen-4a-yl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid-*tert*-butyl ester (25)



Following general procedure **A**:

25 (18 mg, 0.049 mmol, 10%) was obtained as a colorless solid with octalin **24** (70 mg, 0.51 mmol, 1.0 equiv, contains < 7% trisubstituted olefin) in 18 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

Following general procedure **B**:

25 (140 mg, 0.38 mmol, 74%) was obtained as a colorless solid with octalin **24** (70 mg, 0.51 mmol, 1.0 equiv, contains < 7% trisubstituted olefin) in 18 h with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:15).

R_f (AcOEt/hexane 1:5) 0.50;

M.p. 54-56 °C;

^{1}H 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; $OCCH_3$);

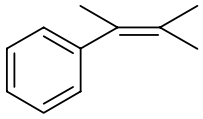
^{13}C NMR ($CDCl_3$, 300 MHz, 52 °C) δ= 156.2, 154.7, 80.4, 77.2, 66.2, 36.6, 30.9, 29.0, 28.8, 28.4, 28.2, 23.2, 23.0;

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: m/z (%): 369.2 (81)$[M+H]^+$;

Elemental analysis calcd for $C_{20}H_{36}N_2O_4$: C 65.19, H 9.85, N 7.60; found: C 65.03, H 9.85, N 7.41.

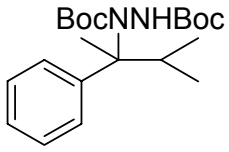
3-Methyl-2-phenyl-but-2-ene[7] (26)



$TiCl_4$ (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, 110 mmol, 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 (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 rt, 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 FC (pentane) to give 3-methyl-2-phenyl-but-2-ene (**26**) (260 mg, 1.8 mmol, 19%) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz)[8] δ= 7.33-7.11 (m, 5H; Ar H), 1.96 (m, 3H; CH_3), 1.81 (s, 3H; CH_3), 1.59 (q, ^3J(H,H)=1.4 Hz, 3H; CH_3).

***N*-(1,2-Dimethyl-1-phenyl-propyl)-*N'*-(*tert*-butoxycarbonyl)-hydrazinecarboxylic acid *tert*-butyl ester (27)**



Following general procedure **A**:

27 (24 mg, 0.063 mmol, 13%) was obtained as a gel with 3-methyl-2-phenyl butene (71 mg, 0.49 mmol, 1.0 equiv) in 20 h

with 5 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

Following general procedure **B**:

27 (94 mg, 0.25 mmol, 51%) was obtained as a gel with 3-methyl-2-phenyl butene (71 mg, 0.49 mmol, 1.0 equiv) in 4 h with 2 mol% catalyst after purification by FC (AcOEt/hexane 1:10).

R_f (AcOEt/hexane 1:5) 0.50;

^{1}H 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, ^3J(H,H)=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, ^3J(H,H)=6.9 Hz, 0.9H; $CHCH_3$, minor rotamer), 0.92-0.87 (m, 4.2H; $CHCH_3$, major rotamer), 0.69 (d, ^3J(H,H)=6.9 Hz, 0.9 H; $CHCH_3$, minor rotamer);

^{13}C NMR ($CDCl_3$, 300 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), 1496 (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: m/z (%): 401.2 (61)$[M+Na]^+$;

Elemental analysis calcd for $C_{21}H_{34}N_2O_4$: C 66.64, H 9.05, N 7.40; found: C 66.44, H 9.01, N 7.25.

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