Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

"New Reagents for the Generation of N-Centered Radicals – Hydroamination of Norbornene"

Jens Kemper and Armido Studer

Experimental Section

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in hot dried glassware under an argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from potassium under argon. Diethylether (Et_2O) was freshly distilled from K/Na under argon. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus(V)oxide (P_2O_5). All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich or Fluka. ^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker AMX* 400, *ARX* 300, *AC* 200, *ARX* 200. Chemical shifts δ in ppm relative to $CHCl_3$ at 7.24 ppm as external standard. TLC was performed using Merck silica gel 60 F_{254} plates; detection with UV or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$) or a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), concentrated H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 µm) applying a pressure of about 0.4 bar. IR spectra were recorded on a *Bruker IFS-200 ,* a *Bruker IFS-28*, a *Digilab FTS 4000* or a *Nicolet Magna-IR 750* spectrophotometer. Mass spectra were recorded on a *Varian CH7* (EI); *Finnigan MAT 95S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI); a *Waters-Micromass Quatro Micro* or a *Finnigan MAT 8230* (GC-MS(CI)) and peaks are given in *m/z* (% of basis peak).

***E*-2,4-Dimethyl-penta-2,4-dienoic acid ethyl ester (4):** To a solution of (carbethoxyethylidene)triphenylphosphorane (19.507 g, 0.054 mol) in CH_2Cl_2 (80 mL) was added dropwise methacroleine (95 %, 3.971 g, 4.7 mL, 0.054 mol). The mixture was refluxed for 3 h and then cooled to room temperature. Half of the solvent was removed under reduced pressure and pentane (200 mL) was added. The precipitated triphenyl-phosphine oxide was filtered off. The solvent was removed under reduced pressure and the residue was purified by distillation (18 mbar, 71 °C) to yield **4** (6.673 g, 80 %). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.05 (*s*, 1 H, CH); 5.02 – 4.91 (*m*, 2 H, CH_2); 4.16 (*q*, 2 H, CH_2, J = 7.1); 1.97 (*s*, 3 H, CH_3); 1.89 (*s*, 3 H, CH_3); 1.30 (*t*, 3 H, CH_3, J = 7.1). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.72 (C), 140.74 (C), 140.30 (CH), 127.60 (C), 119.52 (CH_2), 60.62 (CH_2), 22.74 (CH_3), 14.20 (CH_3), 13.76 (CH_3).[1]

***E*-2,4-Dimethyl-penta-2,4-dienoic acid:** A solution of ester **4** (6.616 g, 0.043 mol) and NaOH (3.432 g, 0.086 mol) in methanol (60 mL) was refluxed for 18 h. After cooling to room temperature the solvent was removed under reduced pressure. The residue was dissolved in water (100 mL) and the solution was acidified by adding H_2SO_4 (aq. 50 %). The mixture was extracted with CH_2Cl_2 (3x) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure to yield **4** (5.221 g, 96 %). The product was used without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 12.26 (*s*, *br*, 1 H, CO_2H); 7.18 (*s*, 1 H, CH); 5.20 (*s*, 1 H, CH_2); 5.06 (*s*, 1 H, CH_2); 1.96 (*s*, 3 H, CH_3); 1.89 (*s*, 3 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 174.69 (C), 142.82 (CH), 140.65 (C), 126.66 (C), 120.85 (CH), 22.60 (CH_3), 13.39 (CH_3). IR (film): 2968*m*, 1686*s*, 1638*w*, 1420*m*, 1283*m*, 1135*w*, 1032*w*, 905*w*, 759*w*. MS (ESI, neg.): 717.26, 569.21, 421.16 ([3M-3H+2Na]$^-$), 273.11 ([2M-2H+Na]$^-$), 125.06 ([M-H]$^-$). MS (ESI, pos.): 615.19 ([4M-4H+5Na]$^+$), 467.14

([3M-3H+4Na]$^+$), 319.09 ([2M-2H+3Na]$^+$), 171.04 ([M-H+2Na]$^+$), 149.06 ([M+Na]$^+$). HRMS (ESI) calcd for $C_7H_{10}NaO_2$ ([M+Na]$^+$): 149.0578; found: 149.0573. Calcd for $C_7H_9O_2$ ([M-H]$^-$): 125.0603; found: 125.0597.[2]

***E*-(1,3-Dimethyl-buta-1,3-dienyl)-carbamic acid *tert*-butyl ester (5):** To a solution of 2,4-dimethyl-penta-2,4-dienoic acid (6.30 g, 0.050 mol) and *p-tert*-butylcatechol (40 mg) in acetone (60 mL) Et_3N (6.064 g, 8.00 mL, 0.060 mol) was added. After cooling to 0 °C a solution of ethyl chloroformate (7.045 g, 6.19 mL, 0.065 mol) in acetone (20 mL) was added dropwise. The mixture was stirred for 30 min at 0 °C and a solution of NaN_3 (4.967 g, 0.076 mol) in water (14 mL) was added slowly (T < 10 °C). After stirring for 2 h at 0 °C the reaction mixture was poured onto ice-water (100 g) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by FC (pentane/ Et_2O 10:1) and 90 % of the solvent was removed under reduced pressure.
A mixture of toluene (60 mL), *tert*-butanol (18.878 g, 24.4 mL, 0.255 mol) and *p-tert*-butylcatechol (40 mg) was heated to reflux. The solution of the azide was diluted with toluene (45 mL) and added within 1 h. After 5 h refluxing and cooling to room temperature the solvent was removed under reduced pressure. Purification of the crude product by FC (pentane/ Et_2O 10:1) yielded **5** (7.004 g, 71 %). Partial isomerisation of **5** was observed in the NMR spectra. ^{1}H-NMR (200 MHz, DMSO): δ= 8.28 (*s*, *br*, 1 H, NH); 6.17 (*s*, 1 H, CH); 4.89 – 4.70 (*m*, 2 H, CH_2); 1.95 (*s*, 3 H, CH_3); 1.82 (*s*, 3 H, CH_3); 1.46 (*s*, 9 H, *t*Bu). ^{13}C-NMR (75 MHz, DMSO): δ= 153.55 (C), 141.84 (C), 134.16 (C), 114.15 (CH), 113.64 (CH_2), 79.34 (C), 29.00 (CH_3), 25.11 (CH_3), 18.29 (CH_3). IR (neat): 3338br. *s*, 3083*w*, 2976*s*, 1707*s*, 1648*m*, 1512*s*, 1455*m*, 1392*s*, 1368*s*, 1241*s*, 1161*s*, 1077*s*, 886*m*, 772*m.* MS (ESI): 417.27 ([2M+Na]$^+$), 337.21, 316.19, 252.16, 222.11, 220.13 ([M+Na]$^+$), 182.08. HRMS (ESI) calcd for $C_{11}H_{19}NO_2Na$ ([M+Na]$^+$): 220.1313; found: 220.1308. Calcd for $C_{22}H_{38}N_2O_4Na_2$ ([2M+Na]$^+$): 417.2729; found: 417.2724.

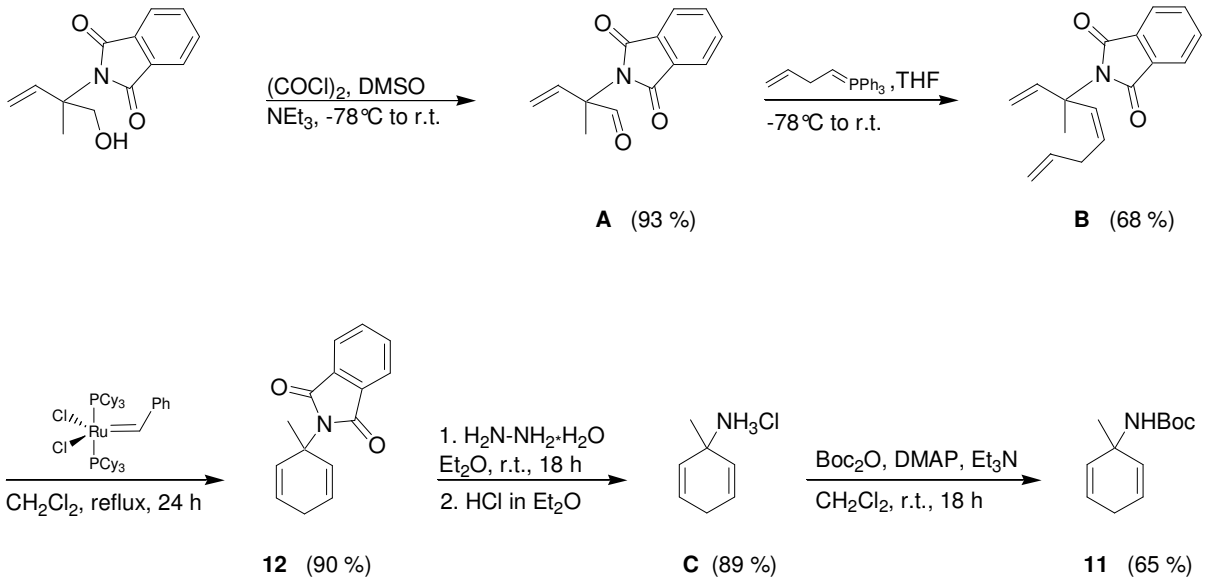
***E*-(1,3-Dimethyl-buta-1,3-dienyl)-carbamic acid methyl ester (6):** To a solution of 2,4-dimethyl-penta-2,4-dienoic acid (3.220 g, 0.026 mol) and *p-tert*-butylcatechol (20 mg) in acetone (30 mL) Et_3N (3.099 g, 4.07 mL, 0.031 mol) was added. After cooling to 0 °C a solution of ethyl chloroformate (3.600 g, 3.16 mL, 0.033 mol) in acetone (15 mL) was added dropwise. The mixture was stirred for 30 min at 0 °C and a solution of NaN_3 (2.539 g, 0.039 mol) in water (8 mL) was added slowly (T < 10 °C). After stirring for 2 h at 0 °C the reaction mixture was poured onto ice-water (30 g) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over $MgSO_4$ and 90 % of the solvent was removed under reduced pressure.
A mixture of toluene (30 mL), methanol (4.171 g, 5.3 mL, 0.130 mol) and *p-tert*-butylcatechol (20 mg) was heated to reflux. The solution of the azide was diluted with toluene (30 mL) and added within 1 h. After 2 h refluxing and cooling to room temperature the solvent was removed under reduced pressure. Purification of the crude product by FC (pentane/ Et_2O 30:1) yielded **6** (3.13 g, 79 %). ^{1}H-NMR (200 MHz, DMSO): δ= 8.72 (*s*, *br*, 1 H, NH); 6.15 (*s*, 1 H, CH); 4.92 – 4.72 (*m*, 2 H, CH_2); 3.60 (*s*, 3 H, CH_3); 1.97 (*s*, 3 H, CH_3); 1.82 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, DMSO): δ = 154.18 (C), 141.07 (C), 133.33 (C), 114.24 (CH), 113.48 (CH_2), 51.54 (CH_3), 24.38 (CH_3), 16.53 (CH_3). IR (neat): 3326br. *m*, 2953*w*, 1709*s*, 1647*m*, 1530*s*, 1441*m*, 1391*m*, 1349*m*, 1226*s*, 1086*s*, 886*m*, 771*m*, 631*m*, 508*m.* MS (ESI): 333.17 ([2M+Na]$^+$), 320.18, 276.15, 248.13, 210.09, 194.07 ([M+K]$^+$), 187.07, 178.08 ([M+Na]$^+$), 156.10 ([M+H]$^+$). HRMS (ESI) calcd for $C_8H_{14}NO_2$ ([M+H]$^+$): 156.1025; found: 156.1019. Calcd for $C_8H_{13}NO_2Na$ ([M+Na]$^+$): 178.0844; found: 178.0838.

6-*tert*-Butoxycarbonylamino-4,6-dimethyl-cyclohexa-1,4-dienecarboxylic acid methyl ester (7): A solution of diene **5** (315 mg, 2 mmol), methyl propiolate (0.5 mL, 504 mg, 6 mmol) and *p-tert*-butylcatechol (~ 20 mg) in dioxane (2 mL) was stirred for 18 h at 110 °C in a sealed tube. After cooling to room temperature the solvent was removed under reduced pressure. FC (pentane/ Et_2O 3:1) yielded **7** (215 mg, 38 %). ^{1}H-NMR (400 MHz, C_6D_6): δ = 6.98 (*t*, 1 H, CH, *J* = 3.6); 5.41 (*s*, 1H, CH); 5.25 (*s*, *br*, 1 H, NH); 3.38 (*s*, 3 H, CH_3); 2.54 – 2.15 (*m*, 2 H, CH_2); 1.47 (*s*, 3 H, CH_3); 1.40 (*s*, 3 H, CH_3); 1.38 (*s*, 9 H, CH_3). ^{13}C-NMR (100 MHz, C_6D_6): δ = 166.71 (C), 155.19 (C), 139.52 (CH), 132.64 (C), 129.22 (C), 128.78 (CH), 78.78 (C), 52.38 (C), 51.55 (CH_3), 32.79 (CH_2), 29.54 (CH_3), 29.12 (CH_3), 22.77 (CH_3). IR (neat): 3383br. *m*, 2975*w*, 2932*w*, 2879*w*, 1711*s*, 1511*s*, 1433*w*, 1361*w*, 1248*s*, 1166*s*, 1049*s*, 942*m*, 750*m*. MS (ESI): 304.15 ($[M+Na]^+$), 248.09, 204.10, 187.07, 165.09, 133.07, 121.10. HRMS (ESI) calcd for $C_{15}H_{23}NNaO_4$ ($[M+Na]^+$): 304.1525; found: 304.1519.

3-*tert*-Butoxycarbonylamino-3,5-dimethyl-cyclohexa-1,4-dienecarboxylic acid methyl ester (8): To a solution of diene **5** (7.00 g, 0.036 mol) in benzene (30 mL) 3-nitro-acrylic acid methyl ester (4.651 g, 0.036 mol) was added at 0 °C. After 1 h stirring at 0 °C and 2 h stirring at room temperature the mixture was again cooled to 0 °C. DBU (8.08 mL, 8.221 g, 0.054 mol) was added dropwise. After 6 h stirring at room temperature brine was added and the reaction mixture was extracted with Et_2O (3x). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. FC (pentane/ *tert*-butyl-methyl ether 6:1) and washing with pentane yielded **8** (6.799 g, 68 %). ^{1}H-NMR (200 MHz, DMSO): δ = 6.88 (*s*, *br*, 1 H, NH); 6.74 (*s*, 1 H, CH); 5.28 (*s*, 1 H, CH); 3.68 (*s*, 3H, CH_3); 2.77 – 2.50 (*m*, 2 H, CH_2); 1.70 (*s*, 3 H, CH_3); 1.30 (*s*, 9 H, *t*Bu); 1.19 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, DMSO): δ = 167.48 (C), 155.03 (C), 142.54 (CH), 130.94 (C), 126.81 (C), 126.10 (CH), 78.41 (C), 52.49 (CH_3), 52.35 (C), 30.92 (CH_2), 29.25 (CH_3), 29.09 (CH_3), 23.17 (CH_3). IR (KBr): 3265br. *m*, 2980*m*, 1719*s*, 1689*s*, 1437*w*, 1384*m*, 1259*s*, 1198*w*, 1169*m*, 1093*m*, 1058*w*, 749*w*. MS (EI): 281 (< 1, $[M]^+$), 266 (8, $[M-CH_3]^+$), 210 (41), 178 (62), 165 (62), 164 (100), 134 (27), 133 (90), 122 (25), 57 (37). Elemental analysis calcd (%) for $C_{15}H_{23}NO_4$ (281.35): C 64.03, H 8.24, N 4.98; found: C 64.03, H 8.20, N 4.87.

3-Methoxycarbonylamino-3,5-dimethyl-cyclohexa-1,4-dienecarboxylic acid methyl ester (9): To a solution of diene **6** (9.098 g, 0.059 mol) and *p-tert*-butylcatechol (100 mg, 0.6 mmol) in benzene (60 mL) a solution of 3-nitro-acrylic acid methyl ester (6.986 g, 0.053 mol) in benzene (15 mL) was added dropwise at 0 °C. After 18 h stirring at room temperature the reaction mixture was again cooled to 0 °C. After addition of DBU (17.5 mL, 17.849 g, 0.117 mol) and 18 h stirring at room temperature the reaction mixture was washed with brine (3x) and water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by FC (pentane/ *tert*-butyl-methyl ether 2:1 – 1:1) yielded **9** (9.975 g, 78 %). ^{1}H-NMR (200 MHz, C_6D_6): δ = 7.13 – 7.12 (*m*, 1 H, CH); 5.16 – 5.15 (*m*, 1 H, CH); 4.73 (*s*, *br*, 1 H, NH); 3.38 (*s*, 3H, CH_3); 3.35 (s, 3 H, CH_3); 2.95 – 2.58 (*m*, 2 H, CH_2); 1.48 (*s*, 3 H, CH_3); 1.19 (*s*, 3 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 167.09 (C), 155.11 (C), 139.57 (CH), 132.71 (C), 127.83 (C), 123.70 (CH), 52.12 (C), 51.65 (CH_3), 51.55 (CH_3), 30.35 (CH_2), 28.31 (CH_3), 22.52 (CH_3). IR (KBr): 3347br. *m*, 2954*m*, 1719*s*, 1522*m*, 1439*m*, 1375*w*, 1259*s*, 1195*m*, 1069*m*, 929*w*, 780*w*. MS (EI): 224 (26, $[M-CH_3]^+$), 192 (100), 180 (20), 165 (19), 133 (82), 111 (39), 59 (12). MS (ESI): 333.18, 278.10 ($[M+K]^+$), 262.10 ($[M+Na]^+$), 187.07, 165.09, 121.10. HRMS (ESI) calcd for $C_{12}H_{17}NNaO_4$ ($[M+Na]^+$): 262.1055; found: 262.1050. 3,5-dimethyl-benzoic acid methyl ester was observed as a side product: ^{1}H-NMR (200 MHz, C_6D_6): δ = 7.86 (*s*, 2 H, CH); 6.80 (*s*, 1 H, CH); 3.52 (*s*, 3 H, CH_3); 2.01 (*s*, 6 H, CH_3).[3]

(3-Cyano-1,5-dimethyl-cyclohexa-2,5-dienyl)-carbaminc acid *tert*-butyl ester (10): To a solution of diene **5** (434 mg, 2.2 mmol) and *p-tert*-butylcatechol (10 mg) in benzene (2.5 mL) was added 3-nitro-acrylonitrile (196 mg, 2.0 mmol) at room temperature. After 45 min stirring at room temperature the solvent was removed under reduced pressure. Washing of the crude product with pentane/ Et_2O (50:1) yielded (5-cyano-1,3-dimethyl-6-nitro-cyclohex-2-enyl)-carbamic acid *tert*-butyl ester (522 mg, 88 %). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 5.71 (*d*, 1 H, CH, *J* = 12.0); 5.24 (*s*, 1 H, CH); 4.65 (*s*, *br*, 1 H, NH); 3.53 – 3.38 (*m*, 1 H, CH); 2.69 – 2.43 (*m*, 2 H, CH_2); 1.72 (*s*, 3 H, CH_3); 1.44 (s, 9 H, CH_3); 1.12 (*s*, 3 H, CH_3). IR (KBr): 3325br. *s*, 2981*m*, 2240*w*, 1692*s*, 1553*s*, 1537*s*, 1453*w*, 1393*m*, 1368*m*, 1310*w*, 1285*m*, 1256*m*, 1205*w*, 1164*m*, 1072*m*. MS (EI): 295 (1, $[M]^+$), 239 (67), 209 (31), 165 (55), 148 (54), 132 (100), 96 (39), 62 (79), 57 (82). HRMS (EI) calcd for $C_{14}H_{21}N_3O_4$ ($[M]^+$): 295.1532; found: 295.1556. To a suspension of (5-cyano-1,3-dimethyl-6-nitro-cyclohex-2-enyl)-carbamic acid *tert*-butyl ester (462 mg, 1.56 mmol) in Et_2O (5 mL) was added dropwise a solution of DBU (0.23 mL, 231 mg, 1.52 mmol) in Et_2O (3 mL). After 1 h refluxing the reaction mixture was cooled to room temperature and then washed with brine. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. FC (pentane/ Et_2O 4:1) yielded **10** (253 mg, 69 %). ^{1}H-NMR (200 MHz, C_6D_6): δ = 6.18 (*s*, 1 H, CH); 4.93 (*s*, 1 H, CH); 4.27 (*s*, *br*, 1 H, NH); 2.29 – 1.89 (*m*, 2 H, CH_2); 1.35 (*s*, 9 H, CH_3); 1.22 (*s*, 3 H, CH_3); 0.85 (*s*, 3 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 154.71 (C), 145.69 (CH), 128.90 (C), 125.28 (CH), 119.19 (C), 111.06 (C), 79.60 (C), 51.60 (C), 32.56 (CH_2), 28.96 (CH_3), 28.44 (CH_3), 22.62 (CH_3). IR (KBr): 3325br. *s*, 2984*m*, 2934*w*, 2220*m*, 1694*s*, 1518*s*, 1450*m*, 1410*w*, 1365*m*, 1274*s*, 1253*s*, 1172*s*, 1058*s*. MS (EI): 248 (< 1, $[M]^+$), 233 (6, $[M\text{-}CH_3]^+$), 192 (69), 177 (99), 159 (26), 133 (47), 132 (100), 131 (93), 116 (17), 62 (98). HRMS (EI) calcd for $C_{14}H_{20}N_2O_2$ ($[M]^+$): 248.1525; found: 248.1524.



Scheme. Synthesis of **11** and **12**.

2-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-2-methyl-but-3-enal (A): To a solution of oxalyl chloride (205 mg, 0.14 mL, 1.62 mmol) in CH_2Cl_2 (5 mL) DMSO (252 mg, 0.23 mL, 3.23 mmol) was added dropwise at -78 °C. After 10 min stirring at -78 °C a solution of 2-(1-hydroxymethyl-1-methyl-allyl)-isoindole-1,3-dione[4] (340 mg, 1.47 mmol) in CH_2Cl_2 (~ 5 mL) was slowly added. The reaction mixture was allowed to warm to -60 °C within 1 h. NEt_3 (713 mg, 0.98 mL, 7.22 mmol) was added and the reaction mixture was allowed to warm to -40 °C within 1 h. After stirring 1 h at room temperature, water (3 mL) was added

and the aqueous layer was saturated with NaCl. After extraction with CH_2Cl_2 (3x) the combined organic layers were washed with HCl (aq. 3 M) and brine and dried over $MgSO_4$. Removal of the solvent and FC (pentane/ Et_2O 1:1) yielded **A** (315 mg, 93 %). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 9.52 (*s*, 1 H, CHO); 7.86 – 7.72 (*m*, 4 H, CH); 6.25 – 6.11 (*dd*, 1 H, CH, J_1 = 10.7, J_2 = 17.4); 5.45 – 5.24 (*m*, 2 H, CH_2, J_1 = 10.8, J_2 = 17.2); 1.75 (*s*, 3 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 192.62 (C), 168.03 (C), 134.47 (CH), 133.32 (C), 131.56 (CH), 123.52 (CH), 118.14 (CH_2), 67.07 (C), 18.08 (CH_3). IR (neat): 3458*w*, 3206*w*, 3096*w*, 3070*w*, 2989*w*, 2943*w*, 2868*w*, 1766*m*, 1697*s*, 1608*m*, 1465*m*, 1377*s*, 1355*s*, 1331*s*, 1078*s*, 912*m*, 715*s*, 671*s*, 532*m*. MS (EI): 201 (100), 200 (70, $[M\text{-}CHO]^+$), 183 (20), 148 (19), 130 (33), 104 (47), 76 (8), 53 (17). MS (ESI, MeOH): 609.24, 577.21, 316.12, 284.09 ($[M+MeOH+Na]^+$), 252.06 ($[M+Na]^+$), 163.04. HRMS (ESI) calcd for $C_{13}H_{11}NNaO_3$ ($[M+Na]^+$): 252.0637; found: 252.0631.

***Z*-2-(1-Methyl-1-vinyl-hexa-2,5-dienyl)-isoindole-1,3-dione (B):** To a suspension of but-3-enyl-triphenyl-phosphonium bromide (1.542 g, 3.88 mmol) in THF (15 mL) was added *n*-butyl lithium (1.58 M in hexane, 2.46 mL, 3.88 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 20 min. After cooling to -78 °C a solution of aldehyde **A** (809 mg, 3.53 mmol) in THF (10 mL) was added dropwise. After warming to room temperature within 2 h water (~ 50 mL) was added. After extraction with CH_2Cl_2 (3x) the combined organic layers were dried over $MgSO_4$. Removal of the solvent at reduced pressure and purification by FC yielded **B** (635 mg, 68 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.77 – 7.75 (*m*, 2 H, CH); 7.67 – 7.65 (*m*, 2 H, CH); 6.51 – 6.44 (*dd*, 1 H, CH, J_1 = 10.4, J_2 = 17.2); 5.78 – 5.74 (*dt*, 1 H, CH, J_1 = 11.6, J_2 = 2.0); 5.65 – 5.56 (*m*, 1 H, CH); 5.52 – 5.45 (*m*, 1 H, CH); 5.19 – 5.11 (*m*, 2 H, CH_2, J_1 = 17.2, J_2 = 10.8); 4.85 – 4.76 (*m*, 2 H, CH_2); 2.77 – 2.72 (*m*, 2 H, CH_2); 1.86 (*s*, 3 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.41 (C), 140.45 (CH), 135.49 (CH), 133.84 (CH), 133.32 (CH), 131.76 (C), 128.44 (CH), 122.83 (CH), 115.21 (CH_2), 112.13 (CH_2), 61.39 (C), 32.23 (CH_2), 26.45 (CH_3). IR (film): 3071*m*, 3054*m*, 3002*m*, 2976*m*, 2936*m*, 1774*m*, 1716*s*, 1478*m*, 1468*s*, 1366*s*, 1316*s*, 1232*m*, 1084*s*, 917*m*, 744*s*, 721*s*, 697*s*. MS (ESI): 621.29, 600.23, 557.24, 338.19, 322.14, 301.07, 290.11 ($[M+Na]^+$), 263.10, 170.02. HRMS (ESI) calcd for $C_{17}H_{17}NNaO_2$ ($[M+Na]^+$): 290.1157; found: 290.1151.

2-(1-Methyl-cyclohexa-2,5-dienyl)-isoindole-1,3-dione (12): To a solution of triene **B** (872 mg, 3.26 mmol) in CH_2Cl_2 (80 mL) was added *Grubbs I* catalyst (268 mg, 0.33 mmol). After refluxing for 24 h the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by FC (pentane/ Et_2O 10 : 1) to give **12** (700 mg, 90 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 – 7.71 (*m*, 2 H, CH); 7.67 – 7.61 (*m*, 2 H, CH); 6.12 – 6.06 (*m*, 2 H, CH, CH); 5.91 – 5.85 (*m*, 2 H, CH); 2.83 – 2.54 (*m*, 2 H, CH_2); 1.81 (*s*, 3 H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 168.91 (C), 133.71 (CH), 132.07 (C), 129.06 (CH), 124.66 (CH), 122.66 (CH), 56.48 (C); 28.82 (CH_3); 25.99 (CH_2). IR (KBr): 3039*w*, 2973*w*, 2934*w*, 2866*w*, 2808*w*, 1774*m*, 1709*s*, 1466*w*, 1368*m*, 1314*s*, 1147*m*, 1083*m*, 1048*m*, 944*m*, 870*m*, 775*m*, 715*s*, 682*m*. MS (EI): 239 (7, $[M]^+$), 224 (100, $[M\text{-}CH_3]^+$), 148 (28), 130 (37), 92 (97), 91 (53), 77 (59), 65 (16). HRMS (EI) calcd for $C_{15}H_{13}NO_2$ ($[M]^+$): 239.0946; found: 239.0939.

1-Methyl-cyclohexa-2,5-dienylamine-hydrochloride (C): To a solution of cyclohexadiene **12** (479 mg, 2.0 mmol) in Et_2O (20 mL) was added hydrazine-monohydrate (441 mg, 0.43 mL, 8.8 mmol). After stirring for 18 h at room temperature the precipitated phthalhydrazide was filtered off. The organic layer was washed with brine and dried over $MgSO_4$. To the dried solution a solution of HCl in Et_2O was added until complete precipitation of the amine-hydrochloride. Filtration and drying *in vacuo* yielded **C** (258 mg,

89 %). ^{1}H-NMR (300 MHz, DMSO): δ = 8.47 (*s*, *br*, 3 H, NH_3); 6.08 – 6.04 (*m*, 2 H, CH); 5.86 – 5.83 (*m*, 2 H, CH); 2.78 – 2.61 (*m*, 2 H, CH_2); 1.44 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, DMSO): δ = 128.95 (CH), 127.78 (CH), 50.96 (C), 27.98 (CH_3), 26.77 (CH_2). IR (neat): 2964br. *s*, 2851br. *s*, 2067br. *w*, 1597*m*, 1498*m*, 1402*s*, 1383*s*, 1254*w*, 1195*w*, 1103*s*, 938 *w*, 898*m*, 872*m*, 716*s*. MS (ESI, formation of clusters $[(C_7H_{12}NCl)_nC_7H_{12}N]^+$ was observed): 1419.70 (n = 9), 1274.62 (n = 8), 1129.55 (n = 7), 982.48 (n = 6), 837.42 (n = 5), 692.35 (n = 4), 545.29 (n = 3), 400.23 (n = 2), 255.16 (n = 1). HRMS (ESI) calcd for $C_{14}H_{24}ClN_2$ ($[(C_7H_{12}NCl)_{[n = 1]}C_7H_{12}N]^+$): 255.1628; found: 255.1623.

(1-Methyl-cyclohexa-2,5-dienyl)-carbamic acid *tert*-butyl ester (11): To a suspension of amine-hydrochloride **C** (258 mg, 1.77 mmol) in CH_2Cl_2 (20 mL) was added Boc_2O (464 mg, 2.13 mmol), Et_3N (0.52 mL, 394 mg, 3.89 mmol) und DMAP (22 mg, 0.18 mmol). After stirring for 18 h at room temperature the reaction mixture was washed with NH_4Cl (aq. sat.), water and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by FC (pentane/ *tert*-butyl-methyl ether 10:1) yielded **11** (240 mg, 65 %). ^{1}H-NMR (300 MHz, C_6D_6): δ = 5.78 – 5.74 (*m*, 2 H, CH, *J* = 10.2); 5.56 – 5.51 (*m*, 2 H, CH, *J* = 10.2); 4.37 (*s*, *br*, 1 H, NH); 2.43 – 2.14 (*m*, 2 H, CH_2); 1.42 (*s*, 9 H, CH_3); 1.35 (*s*, *br*, 3 H, CH_3). ^{13}C-NMR (75 MHz, C_6D_6): δ = 131.75 (CH); 125.04 (CH); 79.02 (C); 50.45 (C); 29.39 (CH_2); 29.15 (CH_3), 27.06 (CH_3). IR (neat): 3343br. *m*, 3124*w*, 3023*w*, 3005*m*, 2863*w*, 1692*s*, 1476*w*, 1452*w*, 1380*s*, 1363*s*, 1169*s*, 1062*m*, 720*m*. MS (ESI): 441.27 ($[2M+Na]^+$), 273.16, 232.13 ($[M+Na]^+$). HRMS (ESI) calcd for $C_{12}H_{19}NNaO_2$ ($[M+Na]^+$): 232.1313; found: 232.1308.

Hydroamination of norbornene derivatives

All monosubstituted norbornenes were used as a racemic *endo/exo*-mixture. The hydroamination products were isolated after FC as a 1:1 mixture of the regioisomers. Addition of the carbamoyl radical occured with complete *exo*-selectivity.

General procedure (GP): A solution of the hydroamination reagent (1 eq.), norbornene (3 eq.) and DTBP (0.4 eq.) in benzene was stirred in a sealed tube at 140 °C for 18 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Purification of the residue by FC yielded the hydroamination products as a mixture of isomers.

Hydroamination of norbornene with reagent 9: Bicyclo[2.2.1]hept-2-yl-carbamic acid methyl ester (13): Applying GP with norbornene (282 mg, 3 mmol), reagent **9** (241 mg, 1 mmol) and DTBP (58 mg, 0.4 mmol) in benzene (4 mL). FC (pentane/ *tert*-butyl-methyl ether 3:1) yielded **13** (64 mg, 38 %) as colourless crystalls. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.54 (*s*, *br*, 1 H, NH); 3.61 (s, 3 H, CH_3); 3.46 (*s*, *br*, 1 H, CH); 2.21 (*s*, 1 H, CH); 2.17 (*s*, 1 H, CH); 1.77 – 1.69 (*m*, 1 H, CH_2); 1.53 – 1.35 (*m*, 2 H, CH_2); 1.29 – 1.03 (*m*, 5 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.09 (C), 54.31 (CH_3), 51.79 (CH), 42.51 (CH), 40.43 (CH_2), 35.61 (CH), 35.20 (CH_2), 28.09 (CH_2), 26.29 (CH_2). IR (neat): 3322br. *m*, 2952*s*, 2872*m*, 1689*s*, 1535*s*, 1451*m*, 1365*w*, 1304*m*, 1252*s*, 1190*m*, 1071*s*, 1009*m*, 779*m*, 631*s*.[5]

Hydroamination of norbornene with reagent 8: Bicyclo[2.2.1]hept-2-yl-carbamic acid *tert*-butyl ester (14): Applying GP with norbornene (282 mg, 3 mmol), reagent **8** (281 mg, 1 mmol) and DTBP (58 mg, 0.4 Äquiv.) in benzene (4 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1) yielded **14** (109 mg, 52 %) as colourless crystalls. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.33 (*s*, *br*, 1 H, NH); 3.41 (*s*, *br*, 1 H, CH); 2.21 (*s*, 1 H, CH); 2.16 (*s*, 1 H, CH); 1.76 –

1.68 (*m*, 1 H, CH_2); 1.54 – 1.03 (*m*, 7 H, CH_2); 1.41 (*s*, 9 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.23 (C), 79.02 (C), 54.05 (CH), 42.56 (CH), 40.48 (CH_2), 35.61 (CH), 35.25 (CH_2), 28.46 (CH_3), 28.15 (CH_2), 26.39 (CH_2). IR (neat): 3352br. *m*, 2955*m*, 2874*w*, 1680*s*, 1519*s*, 1452*w*, 1365*m*, 1248*s*, 1162*s*, 1066*s*, 997*m*, 780*w*. ESI-MS: 656.46 ($[3M+Na]^+$), 539.38, 445.30 ($[2M+Na]^+$), 423.32, 266.17, 234.15 ($[M+Na]^+$), 156.10. HRMS (ESI) calcd for $C_{12}H_{21}NNaO_2$ ($[M+Na]^+$): 234.1470; found: 234.1465.

with reagent 10: Applying GP with norbornene (141 mg, 1.5 mmol), reagent **10** (125 mg, 0.5 mmol) and DTBP (29 mg, 0.2 mmol) in benzene (2.0 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1) yielded **14** (48 mg, 45 %) as colourless crystalls.
with reagent 11: Applying GP with norbornene (141 mg, 1.5 mmol), reagent **11** (120 mg, 0.5 mmol) and DTBP (29 mg; 0.2 mmol) in benzene (2.0 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1) yielded **14** (50 mg, 47 %) as colourless crystalls.
with reagent 12: Applying GP with norbornene (141 mg, 1.5 mmol), reagent **12** (105 mg, 0.5 mmol) and DTBP (29 mg; 0.2 mmol) in benzene (2.0 mL). During cooling to room temperature a colourless solid, identified as phthalimide, precipitated. Filtration, washing with pentane and drying *in vacuo* yielded phthalimide (45 mg, 61 %). Product **14** was not observed.
with reagent 7: Applying GP with norbornene (36 mg, 0.38 mmol), reagent **7** (36 mg, 0.13 mmol) and DTBP (7.5 mg, 0.05 mmol) in benzene (0.5 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1) yielded **14** (5 mg, 18 %) as colourless crystalls. Furthermore, 2-*tert*-butoxycarbonylamino-4-methyl-benzoic acid methyl ester (15 mg, 44 %) was isolated as a product of the methyl fragmentation process: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.27 (*s*, *br*, 1 H, NH); 8.26 (*s*, 1 H, CH); 7.86 – 7.84 (*m*, 1 H, CH, *J* = 8.4); 6.79 – 6.77 (*m*, 1 H, CH, *J* = 8.4); 3.87 (*s*, 3 H, CH_3); 2.36 (*s*, 3 H, CH_3); 1.51 (*s*, 9 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.59 (C), 152.97 (C), 145.66 (C), 142.25 (C), 130.80 (CH), 122.18 (CH), 119.02 (CH), 111.74 (C), 80.43 (C), 51.99 (CH_3), 28.32 (CH_3), 22.07 (CH_3). IR (neat): 3290br. *w*, 2981*m*, 2953*m*, 2871*w*, 1726*s*, 1689*s*, 1616*w*, 1581*s*, 1527*s*, 1433*s* 1247*s*, 1149*s*, 1095*s*, 1045*s*, 971*w*, 950*w*, 874*m*, 766*s*, 724*m*, 466*s*, 451*s*. MS (ESI): 569 ($[2M+K]^+$), 553 ($[2M+Na]^+$), 531 ($[2M+H]^+$), 304 ($[M+K]^+$), 288 ($[M+Na]^+$), 266 ($[M+H]^+$), 210, 166, 153, 111, 89, 57. HRMS (ESI) calcd for $C_{14}H_{19}NNaO_4$ ($[M+Na]^+$): 288.1212; found: 288.1206.

Hydroamination of 5-phenethyl-bicyclo[2.2.1]hept-2-ene with reagent 8: Product 15: Applying GP with 5-phenethyl-bicyclo[2.2.1]hept-2-ene (617 mg, 3.1 mmol, *endo*:*exo* = 4.2 : 1), reagent **8** (281 mg, 1.0 mmol) und DTBP (57 mg, 0.39 mmol) in benzene (4 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1) yielded **15** (135 mg, 43 %) as a mixture of 4 isomers (1:1 mixture of regioisomers of the *endo* and *exo* product). The isomers could not be separated. Due to the complexity of the NMR spectra of the product mixture, the spectra could not be assigned. IR (film): 3348br. *m*, 3026*m*, 2949*s*, 2866*s*, 1701*s*, 1497*s*, 1454*m*, 1365*m*, 1248*m*, 1172*s*, 1087*w*, 910*m*, 733*m*, 700*m*. GC-MS(CI, NH_3): 333 ($[M+NH_4]^+$), 316 ($[M+H]^+$), 277, 260 ($[M+H-56]^+$). MS (ESI): 354.2 ($[M+K]^+$), 338.2 ($[M+Na]^+$), 260.2 ($[M+H-56]^+$), 199.0. HRMS (ESI) calcd for $C_{20}H_{29}NNaO_2$ ($[M+Na]^+$: 338.2096; found: 338.2096.

Hydroamination of 5-hexyl-bicyclo[2.2.1]hept-2-ene with reagent 8: Product 16: Applying GP with 5-hexyl-bicyclo[2.2.1]hept-2-ene (134 mg, 0.75 mmol, *endo*:*exo* = 4.5 : 1), reagent **8** (70 mg, 0.25 mmol) and DTBP (15 mg, 0.10 mmol) in benzene (1 mL). FC (pentane/ *tert*-butyl-methyl ether 40:1) yielded **16** (31 mg, 42 %) as a mixture of 4 isomers (1:1 mixture of regioisomers of the *endo* and *exo* product). The isomers could not be separated. Due to the complexity of the NMR spectra of the product mixture, the spectra could not be assigned. ESI-MS: 908.73 ($[3M+Na]^+$), 613.48 ($[2M+Na]^+$), 318.24 ($[M+Na]^+$),

240.19 ([M+H-56]$^+$). GC-MS(CI, *iso*-butane): 296.3 ([M+H]$^+$), 240.2 [M+H-56]$^+$), 194.2, 178.2. HRMS(ESI) calcd for $C_{18}H_{33}NNaO_2$ ([M+Na]$^+$): 318.2409; found: 318.2404.

Hydroamination of 9-bicyclo[2.2.1]hept-5-en-2-yl-nonanoic acid ethyl ester with reagent 8: Product 17: Applying GP with 9-bicyclo[2.2.1]hept-5-en-2-yl-nonanoic acid ethyl ester (841 mg, 3.0 mmol, *endo*:*exo* = 4.2 : 1), reagent **8** (281 mg, 1.0 mmol) and DTBP (59 mg, 0.4 mmol) in benzene (4 mL). FC (pentane/ *tert*-butyl-methyl ether 10:1) yielded **17** (220 mg, 56 %) as a mixture of 4 isomers (1:1 mixture of regioisomers of the *endo* and *exo* product). The isomers could not be separated. Due to the complexity of the NMR spectra of the product mixture, the spectra could not be assigned. ESI-MS: 813.59 ([2M+Na]$^+$), 418.29 ([M+Na]$^+$), 396.31 ([M+H]$^+$), 340.25 ([M+H-56]$^+$). GC-MS(CI, *iso*-butane): 396.3 ([M+H]$^+$), 340.2 [M+H-56]$^+$), 296.2, 279.3. HRMS (ESI) calcd for $C_{23}H_{41}NNaO_4$ ([M+Na]$^+$): 418.2933; found: 418.2928.

Hydroamination of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid butyl ester with reagent 8: Product 18: Applying GP with bicyclo[2.2.1]hept-5-en-2-carboxylic acid butyl ester (590 mg, 3.0 mmol, *endo*:*exo* = 2.8 : 1), reagent **8** (280 mg, 1.0 mmol) and DTBP (62 mg, 0.42 mmol) in benzene (4 mL). FC (pentane/ *tert*-butyl-methyl ether 10:1) yielded **18** (166 mg, 53 %) as a mixture of 4 isomers (1:1 mixture of regioisomers of the *endo* and *exo* product). The isomers could not be separated. Due to the complexity of the NMR spectra of the product mixture, the spectra could not be assigned. ESI-MS: 645.40 ([2M+Na]$^+$), 334.20 ([M+Na]$^+$), 312.21 ([M+H]$^+$), 256.15 ([M+H-56]$^+$). GC-MS(CI, *iso*-butane): 312.2 ([M+H]$^+$), 296.2, 256.2 ([M+H-56]$^+$), 238.1, 210.3. HRMS(ESI) calcd for $C_{17}H_{29}NNaO_4$ [M+Na]$^+$: 334.1994; found: 334.1989.

Hydroamination of bicyclo[2.2.1]hept-5-en-2-yl-trimethyl-silane with reagent 8: Product 19: Applying GP with bicyclo[2.2.1]hept-5-en-2-yl-trimethyl-silane (219 mg, 1.5 mmol, *endo*:*exo* = 1.5 : 1), reagent **8** (141 mg, 0.5 mmol) und DTBP (29 mg, 0.2 mmol) in benzene (2 mL). FC (pentane/ Et_2O 20:1) yielded **19** (59 mg, 42 %) as a mixture of 4 isomers (1:1 mixture of regioisomers of the *endo* and *exo* product). The isomers could not be separated. Due to the complexity of the NMR spectra of the product mixture, the spectra could not be assigned. IR (film): 3336br. *m*, 2952*s*, 2866*s*, 1702*s*, 1519*s*, 1365*s*, 1248*s*, 1173*s*, 1058*m*, 989*m*, 921*m*, 833*s*, 748*m*, 688*m*. MS(ESI): 872.57 ([3M+Na]$^+$), 589.37 ([2M+Na]$^+$), 306.18 ([M+Na]$^+$). HRMS(ESI) calcd for $C_{15}H_{29}NNaO_2Si$ ([M+Na]$^+$: 306.1865; found: 306.1860.

Hydroamination of 1,4-dihydro-1,4-methano-naphthalene with reagent 8: (1,2,3,4-Tetrahydro-1,4-methano-naphthalen-2-yl)-carbamic acid *tert*-butyl ester (20): Applying GP with 1,4-dihydro-1,4-methano-naphthalene (213 mg, 1.5 mmol), reagent **8** (141 mg, 0.5 mmol) and DTBP (29 mg, 0.2 mmol) in benzene (2 mL). FC (pentane/ *tert*-butyl-methyl ether 20:1 – 10:1) yielded **20** (52 mg, 40 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 – 7.08 (*m*, 4 H, CH); 4.62 (*s*, *br*, 1 H, NH); 3.65 (*s*, *br*, 1 H, CH); 1.92 – 1.90 (*m*, 2 H, CH); 1.46 (*s*, 9 H, CH_3); 1.48 – 1.20 (*m*, 4 H, CH_2). IR (film): 3339br. *w*, 2971*s*, 2876*w*, 2363*w*, 2248*w*, 1702*s*, 1501*s*, 1459*m*, 1366*m*, 1250*m*, 1166*s*, 1054*m*, 910*m*, 751*s*, 734*s*. ESI-MS: 967.52, 825.44, 800.44 ([3M+Na]$^+$), 683.37, 541.29 ([2M+Na]$^+$), 424.22, 282.14 ([M+Na]$^+$), 204.10. HRMS(ESI) calcd for $C_{16}H_{21}NNaO_2$ ([M+Na]$^+$): 282.1470; found: 282.1465.

[1] Lebarillier, L. et al. *Tetrahedron* **2000**, *56*, 7483
[2] Braude et. al. *J. Chem. Soc.* **1955**, 3337
[3] Kurz et al. *Helv. Chim. Acta* **1996**, *79*, 1967
[4] Trost, B. et al. *J. Am. Chem. Soc.* **2000**, *122*, 5968
[5] Kirmse, W. *J. Am. Chem. Soc.* **1983**, *105*, 950