CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201000384

Iron-Catalyzed Carbonylation as a Key Step in the Short and Efficient Syntheses of Himanimide A and B

Saisuree Prateeptongkum, Katrin Marie Driller, Ralf Jackstell, and Matthias Beller*[a]

Substituted maleinimides represent an interesting class of bioactive natural products. Typical examples include himanimides A–D **1**–**2**, **6**, **8**,[1] camphorataimides B–E **3**–**4, 7**, **9**,[2] antrocinnamomins A–B **5**, **10**,[3] polycitrins A–B **11**–**12**,[4] and arcyriarubins A–C **13**–**15**[5] (Figure 1). Synthetic derivatives and natural maleimides are known to exhibit various biological activities, such as antibacterial properties,[1,6] cytotoxicity,[2,7] inhibition of nitric oxide production,[3] inhibition of cell death,[8] and inhibition of different kinases.[9] Because of these attractive biological properties, numerous syntheses of novel maleimides have appeared in the last decade.[10]

Clearly, transition-metal-catalyzed reactions have become an indispensable tool in modern natural-product synthesis.[11] However, from the standpoint of sustainable chemistry, the application of biologically relevant metal complexes based on iron, zinc, copper, etc. instead of precious-metal-based catalysts is desirable. In this respect, especially iron-catalyzed reactions have received increasing attention in organic synthesis.[12,13] For example, we recently developed a straightforward two-step synthesis of *trans*-3,4-diaryl-substituted succinimides using a combination of palladium-catalyzed Sonogashira reactions and iron-catalyzed double amino-carbonylations.[13a] Herein, we report further extensions of our methodology to the total synthesis of himanimide A **1** and B **6**, which were isolated by fermentation from a *Serpula himantoides* strain collected in Chile by Sterner and co-workers.[1] To the best of our knowledge, only one synthesis of himanimide A **1** has been achieved in no more than 11% overall yield.[10a] Moreover, there is no report of the synthesis of himanimide B **6** so far.

As depicted in Scheme 1, the naturally occurring maleimide **1** was obtained by iron-catalyzed carbonylation of the internal alkyne **16** followed by oxidative dehydrogenation.

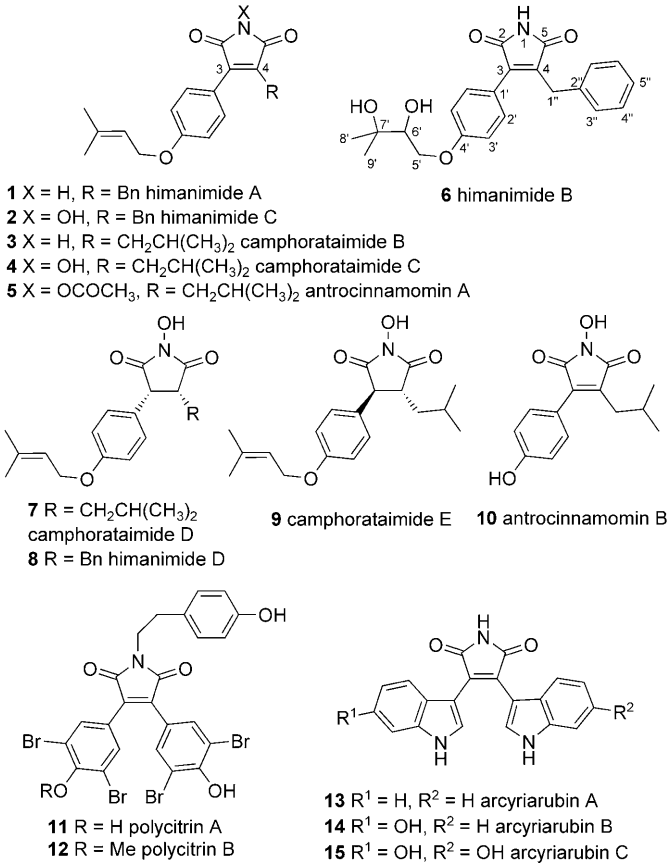
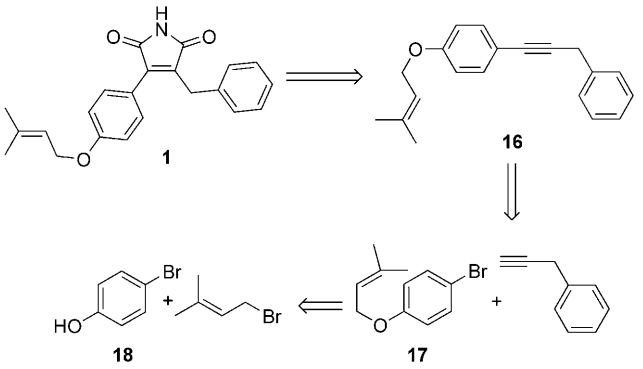


Figure 1. Structures of selected natural products with maleimide subunits.

Obviously, alkyne **16** can be prepared in a straightforward manner by palladium-catalyzed Sonogashira reaction of 3-phenyl-1-propyne and aryl bromide **17**, which is accessible from commercially available and inexpensive 4-bromophenol and prenyl bromide.

Indeed, alkylation of 4-bromophenol **18** with prenyl bromide and K_2CO_3 in refluxing acetone gave the corresponding aryl ether **17** in 98% yield.[10d] Subsequent Sonogashira cross-coupling of **17** with 3-phenyl-1-propyne in the presence of 2 mol% of $K_2[PdCl_4]$, CuI, and 2-(di-*tert*-butylphos-

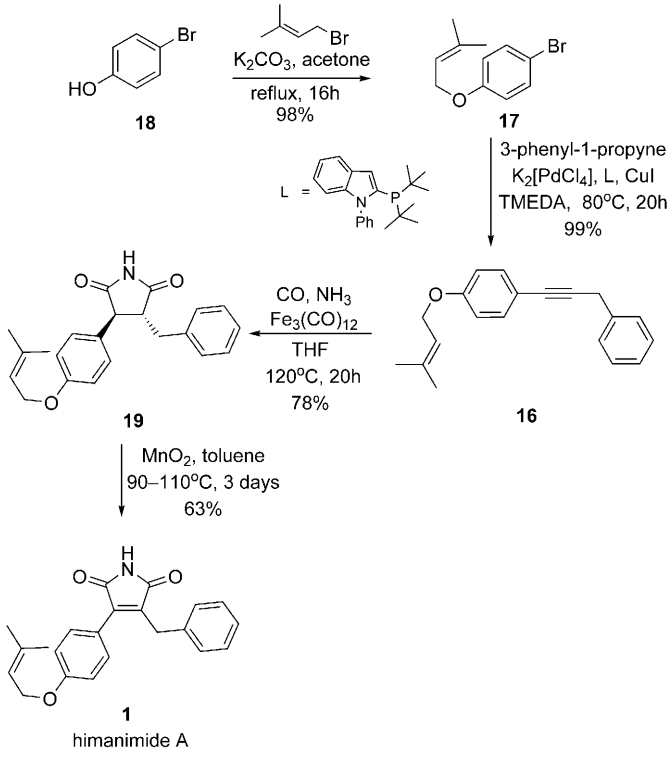
[a] S. Prateeptongkum, K. M. Driller, R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de



Scheme 1. Disconnection strategy for the synthesis of himanimide A **1**.

phino)-*N*-phenylindole as the catalytic system proceeded smoothly in TMEDA at 80 °C, thus providing almost quantitative yield of the desired disubstituted alkyne **16**. Notably, when lower amounts of palladium catalyst, CuI, and ligand (0.5–1 mol %) were employed, the conversion of the Sonogashira reaction was not complete and an inseparable mixture of **17** and **16** was obtained.

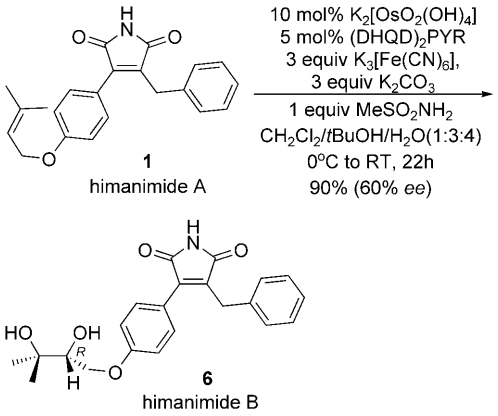
As a key step, the iron-catalyzed carbonylation of alkyne **16** was carried out in tetrahydrofuran at 120 °C for 20 hours in the presence of 3.3 mol % of $Fe_3(CO)_{12}$ and an excess amount of ammonia was added under 20 bar CO to generate (±)-*trans*-3,4-succinimide **19** in 78 % yield (Scheme 2). Notably, the crucial 5-membered maleinimide ring was constructed by a remarkable [2+1+1+1]-annulation strategy. Finally, oxidative dehydrogenation[14] of succinimide **19**, by applying an excess of activated MnO_2 at 90–110 °C, afforded the desired natural product **1** in 63 % yield. We also attempted the dehydrogenation of **19** using DDQ at room temperature and at 80 °C in 1,4-dioxane, but under these conditions no reaction occurred.



Scheme 2. Total synthesis of himanimide A **1**. TMEDA = tetramethylethylenediamine, THF = tetrahydrofuran.

The relative stereochemistry of **19** was determined to be *trans* on the basis of previous work[13a,15] and from the vicinal coupling constant ($J_{3,4}$ = 5.8 Hz), which was in agreement with those values reported for *trans*-disubstituted succinimides.[10c,16] The spectral data for compound **1** matched those reported for the naturally derived material.[1]

Next, starting from himanimide A, the synthesis of himanimide B **6** was easily accomplished by Sharpless catalytic asymmetric dihydroxylation[17,18] using $(DHQD)_2PYR$ as the chiral ligand in 90 % yield and 60 % *ee* (Scheme 3). Based on the mnemonic device model for predicting the absolute configuration reported by Sharpless, the absolute configuration of C6′ was assigned to be *R* as the chiral ligand prefers to direct dihydroxylation to the top face of the trisubstituted olefin.[17,18e]



Scheme 3. The synthesis of himanimide B **6**. $(DHQD)_2PYR$ = hydroquinidine-2,5- diphenyl-4,6-pyrimidinediyl diether.

In summary, the syntheses of himanimide A **1** and B **6** have been conveniently achieved in only 4 and 5 steps to afford the desired natural products from commercially available starting materials in 48 % and 43 % overall yield, respectively. Whilst **6** was prepared for the first time, the synthesis of **1** has been significantly improved with respect to overall yield. Clearly, this synthetic strategy can be applied to other related bio-active compounds, such as camphorataimides, antrocinnamomins, polycitrins, and arcyriarubins.

Experimental Section

Unless otherwise indicated, all chemicals were obtained from commercial suppliers, and were used without further purification. QuadrasilTM TA was purchased from Sigma–Aldrich. TMEDA was distilled from calcium hydride. THF, acetone, and toluene were distilled from sodium benzophenone ketyl under argon. All reactions were performed under an at-

mosphere of argon. Flash chromatography was performed with FLUKA Silica gel 60 (70–230 mesh) in common glass columns. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV300/AV400 spectrometer. Chemical shifts (δ) are given in ppm and are referenced to TMS or to residual undeuterated solvent as an internal standard. Gas chromatography was performed on a Hewlett–Packard HP 6890 chromatograph with a 30 m HP5 column. EI mass spectra were recorded on an AMD 402 spectrometer (70 eV, AMD Intectra GmbH). IR spectra were recorded on an FTIR Nicolet 6700 (Thermo ELECTRON CORPORATION).

1-Bromo-4-(3-methylbut-2-enyloxy)benzene (**17**):[10c] To a mixture of 4-bromo-phenol (**18**; 1.89 g, 10.9 mmol) and K_2CO_3 (7.53 g, 54.5 mmol) in acetone (35 mL) was added 1-bromo-3-methyl-2-butene (1.26 mL, 10.9 mmol) at room temperature, and the mixture was heated to reflux at 67 °C for 18 h. After cooling, the solid was filtered and the solvent was evaporated. The residue was purified by column chromatography on silica gel to yield **17** (2.58 g, 98 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (d, J = 10.2 Hz, 2H), 6.72 (d, J = 10.2 Hz, 2H), 5.39 (br t, J = 6.7 Hz, 1H), 4.40 (d, J = 6.7 Hz, 2H), 1.72 (s, 3H), 1.66 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 158.0 (*C*), 138.6 (*C*), 132.2 (2x*C*H), 119.3 (*C*H), 116.5 (2x*C*H), 112.7 (*C*), 65.0 (*C*H$_2$), 25.9 (*C*H$_3$), 18.3 ppm (*C*H$_3$); MS (EI) m/z (% rel. intensity) 242 (2), 240 (2), 174 (98), 172 (100), 69 (36), 63 (10), 41 (27); HRMS (ESI-TOF)[$M-$H]$^-$: calcd for $C_{11}H_{12}BrO$: 239.0077; found: 239.0079; calcd for $C_{11}H_{12}BrO$: 241.0057; found: 241.0060.

1-(3-Methylbut-2-enyloxy)-4-(3-phenylprop-1-ynyl)benzene (**16**): A 50 mL Schlenk tube was charged with $K_2[PdCl_4]$ (31.4 mg, 2 mol %), ligand (64.9 mg, 2 mol %), copper iodide (36.6 mg, 2 mol %), and 1-bromo-4-(3-methylbut-2-enyloxy)benzene (**17**; 2.32 g, 9.6 mmol). Then, TMEDA (10 mL) and 3-phenyl-1-propyne (1.6 mL, 12.51 mmol) were added successively under argon atmosphere. The reaction mixture was heated at 80 °C for 20 h. After cooling to room temperature, the mixture was quenched with water (30 mL) and the aqueous phase was extracted with diethyl ether (3x75 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and concentrated in vacuo and the residue was purified by column chromatography on silica gel to give product **16** (2.63 g, 99 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.51–7.26 (m, 7H), 6.90 (d, J = 9.4 Hz, 2H), 5.54 (br t, J = 6.8 Hz, 1H), 4.56 (d, J = 6.8 Hz, 2H), 3.88 (s, 2H), 1.86 (s, 3H), 1.80 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 158.6 (*C*), 138.5 (*C*), 137.1 (*C*), 133.0 (2x*C*H), 128.6 (2x*C*H), 128.0 (2x*C*H), 126.6 (*C*H), 119.4 (*C*H), 115.7 (*C*), 114.6 (2x*C*H), 85.9 (*C*), 82.5 (*C*), 64.8 (*C*H$_2$), 25.9 (*C*H$_3$), 25.8 (*C*H$_2$), 18.3 ppm (*C*H$_3$); IR (ATR): $\tilde{\nu}_{max}$ = 3062, 3029, 2971, 2930, 2876, 2190, 1678, 1601, 1452, 1423, 1383, 1285, 1236, 1168, 1107, 995, 830, 769, 731, 695 cm^{-1}; MS (EI) m/z (% rel. intensity) 276 (M^+, 3), 209 (16), 208 (100), 207 (55), 179 (13), 178 (22), 69 (12), 41 (10); HRMS (EI): calcd for $C_{20}H_{20}O$: 276.1509; found: 276.1508.

3-Benzyl-4-(4-(3-methylbut-2-enyloxy)phenyl)pyrrolidine-2,5-dione (**19**): A mixture of 1-(3-methylbut-2-enyloxy)-4-(3-phenylprop-1-ynyl)benzene (**16**) (0.58 g, 2.1 mmol) and $[Fe_3(CO)_{12}]$ (10 mol % of Fe) were dissolved in THF (20 mL) under an argon atmosphere in a 50 mL Schlenk flask before being transferred into an autoclave. Ammonia (5 g) was condensed from a small bomb into a 100 mL Parr autoclave. Afterwards, the autoclave was pressurized with carbon monoxide (20 bar) and heated to 120 °C. The reaction was carried out for 20 h before the contents were cooled to room temperature. Then, the pressure was released and the reaction mixture was transferred to the 50 mL Schlenk flask. QuadraSil TA (1 g) was added to the reaction mixture and stirred at room temperature for 30 min. After filtration of QuadraSil TA and removal of the solvent in vacuo, the crude succinimide product was purified by column chromatography on silica gel to give product **19** (0.57 g, 78 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.81 (br s, 1H), 7.39–7.19 (m, 5H), 6.96 (d, J = 9.3 Hz, 2H), 6.88 (d, J = 9.3 Hz, 2H), 5.52 (br t, J = 6.8 Hz, 1H), 4.52 (d, J = 6.8 Hz, 2H), 3.73 (d, J = 5.9 Hz, 1H), 3.29 (q, J = 5.9 Hz, 1H), 3.19 (t, J = 5.9 Hz, 2H), 1.85 (s, 3H), 1.78 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 178.5 (*C*), 178.0 (*C*), 158.5 (*C*), 138.5 (*C*), 136.6 (*C*), 129.6 (2x*C*H), 128.92 (2x*C*H), 128.88 (2x*C*H), 128.2 (*C*), 127.2 (*C*H), 119.5 (*C*H), 115.3 (2x*C*H), 64.8 (*C*H$_2$), 51.7 (*C*H), 51.0 (*C*H), 34.9 (*C*H$_2$), 25.9 (*C*H$_3$), 18.3 ppm (*C*H$_3$); IR ν_{max} (ATR)/cm^{-1} 3216, 3063, 3029, 2972, 2923, 2857, 1775, 1704, 1609, 1583, 1510, 1454, 1332, 1300, 1236, 1174, 1113, 999, 912, 824, 790, 753, 733, 699; HRMS (ESI-TOF)[M−H]$^-$: calcd for $C_{22}H_{22}NO_3$: 348.1605; found: 348.1609.

Himanimide A (**1**): 3-Benzyl-4-(4-(3-methylbut-2-enyloxy)phenyl)pyrrolidine-2,5-dione (**19**; 0.16 g, 0.46 mmol) was dissolved in toluene (8 mL) and activated MnO_2 (0.4 g, 4.6 mmol) was added. The black suspension was stirred at 90 °C for 2 days and at 110 °C for 1 day. After cooling, the solid was filtered off, the filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to give himanimide A (**1**) (0.10 g, 63 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, J = 9.0 Hz, 2H), 7.41 (br s, 1H), 7.39–7.22 (m, 5H), 7.02 (d, J = 9.0 Hz, 2H), 5.54 (br t, J = 6.8 Hz, 1H), 4.60 (d, J = 6.8 Hz, 2H), 4.00 (s, 2H), 1.86 (s, 3H), 1.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.5 (*C*), 171.0 (*C*), 160.5 (*C*), 139.2 (*C*), 138.9 (*C*), 137.2 (*C*), 136.9 (*C*), 131.2 (2x*C*H), 128.9 (2x*C*H), 128.4 (2x*C*H), 126.9 (*C*H), 120.8 (*C*), 119.2 (*C*H), 115.0 (2x*C*H), 64.9 (*C*H$_2$), 29.8 (*C*H$_2$), 25.9 (*C*H$_3$), 18.3 (*C*H$_3$); IR (ATR): $\tilde{\nu}_{max}$ = 3205, 3058, 2966, 2918, 2851, 1772, 1710, 1629, 1601, 1564, 1511, 1496, 1457, 1423, 1378, 1351, 1294, 1244, 1178, 1153, 1122, 1087, 1017, 1010, 994, 957, 841, 783, 756, 738, 699 cm^{-1}; MS (EI) m/z (% rel. intensity) 347 (M^+, 1), 279 (100), 236 (18), 208 (10), 207 (11), 178 (10), 69 (17), 41 (9); HRMS (EI): calcd for $C_{22}H_{21}NO_3$: 347.1516; found: 347.1511.

Himanimide B (**6**): In a 10 mL Schlenk, $K_2OsO_2(OH)_4$ (10.7 mg, 10 mol %), 5 mol % $(DHQD)_2PYR$ (12.8 mg, 5 mol %), $K_3Fe(CN)_6$ (286.4 mg, 0.87 mmol), K_2CO_3 (120.2 mg, 0.87 mmol), and $CH_3SO_2NH_2$ (27.6 mg, 0.29 mmol) were dissolved in CH_2Cl_2 (0.5 mL), *tert*-BuOH (1.5 mL), and H_2O (2 mL) at room temperature. The mixture was cooled to 0 °C and himanimide A (**1**; 100 mg, 0.29 mmol) was added. The reaction mixture was stirred vigorously at 0 °C for 4 h and warmed slowly to room temperature and stirred for 18 h. Then Na_2SO_3 (450 mg) was added under stirring. The mixture was extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo and the residue was purified by column chromatography on silica gel to give himanimide B (**6**; 100 mg, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.46 (d, J = 8.9 Hz, 2H), 7.44 (br s, 1H), 7.27–7.09 (m, 5H), 6.91 (d, J = 8.9 Hz, 2H), 4.12 (dd, J = 9.6, 3.0 Hz, 1H), 3.99 (dd, J = 9.6, 7.6 Hz, 1H), 3.87 (s, 2H), 3.76 (dd, J = 7.6, 3.0 Hz, 1H), 2.72 (br s, 1H), 2.26 (br s, 1H), 1.27 (s, 3H), 1.21 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.3 (*C*), 170.9 (*C*), 159.9 (*C*), 138.9 (*C*), 137.4 (*C*), 137.1 (*C*), 131.3 (2x*C*H), 129.0 (2x*C*H), 128.4 (2x*C*H), 126.9 (*C*H), 121.6 (*C*), 114.9 (2x*C*H), 75.7 (*C*H), 71.7 (*C*), 69.3 (*C*H$_2$), 29.8 (*C*H$_2$), 26.7 (*C*H$_3$), 25.0 ppm (*C*H$_3$); IR (ATR): $\tilde{\nu}_{max}$ = 3550, 3246, 3057, 2969, 2926, 1772, 1710, 1638, 1601, 1568, 1512, 1496, 1455, 1423, 1340, 1292, 1245, 1179, 1153, 1087, 1027, 990, 957, 881, 839, 741, 700 cm^{-1}; Enantiomeric excess was determined to be 60 % *ee* by HPLC on a chiral stationary phase (Chiralpak AS-H, heptane/EtOH = 95:5, 1.0 mL min^{-1}, t_1 = 65.67 min (major), t_2 = 71.79 min); HRMS (ESI-TOF)[M+H]$^+$: calcd for $C_{22}H_{24}NO_5$: 382.1649; found: 382.1652.

Acknowledgements

This work was funded by the State of Mecklenburg-Western Pomerania, the BMBF (Bundesministerium für Bildung und Forschung), and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 1213 and Leibnizprice).

Keywords: carbonylation · himanimide A and B · iron · natural products · Sonogashira reactions

[1] P. Aqueveque, T. Anke, O. Sterner, *Z. Naturforsch.* **2002**, *57c*, 257–262.

[2] N. Nakamura, A. Hirakawa, J.-J. Gao, H. Kakuda, M. Shiro, Y. Kamatsu, C.-C. Sheu, M. Hattori, *J. Nat. Prod.* **2004**, *67*, 46–48.

[3] M.-D. Wu, M.-J. Cheng, B.-C. Wang, Y.-J. Yech, J.-T. Lai, Y.-H. Kuo, G.-F. Yuan, I.-S. Chen, *J. Nat. Prod.* **2008**, *71*, 1258–1261.

[4] A. Rudi, I. Goldberg, Z. Stein, F. Frolow, Y. Benayahu, M. Schleyer, Y. Kashman, *J. Org. Chem.* **1994**, *59*, 999–1003.
[5] a) W. Steglich, *Pure Appl. Chem.* **1981**, *53*, 1233–1240; b) W. Steglich, B. Steffan, L. Kopanski, G. Eckhardt, *Angew. Chem.* **1980**, *92*, 463–464; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 459–460.
[6] a) S. Mahboobi, E. Eichhorn, A. Popp, A. Sellmer, S. Elz, U. Möllmann, *Eur. J. Med. Chem.* **2006**, *41*, 176–191; b) D. H. Marrian, E. Friedmann, J. L. Ward, *Biochem. J.* **1953**, *54*, 65–68.
[7] a) G.-Q. Xu, P. Guo, C. Zhang, Q.-J. He, B. Yang, Y.-Z. Hu, *Chem. Pharm. Bull.* **2007**, *55*, 1302–1307; b) S. R. T. Prado, V. Cechinel-Filho, F. Campo *s*Buzzi, R. Corrêa, S. M. C. S. Cadena, M. B. M. d. Oliveira, *Z. Naturforsch.* **2004**, 59c, 663–672.
[8] a) K. Dodo, M. Katoh, T. Shimizu, M. Takahashi, M. Sodeoka, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3114–3118; b) M. Katoh, K. Dodo, M. Fujita, M. Sodeoka, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3109–3113; c) J. Ni, S. Singh, L.-X. Wang, *Bioconjugate Chem.* **2003**, *14*, 232–238.
[9] For selected examples, see: a) I. N. Gaisina, F. Gallier, A. V. Ougolkov, K. H. Kim, T. Kurome, S. Guo, D. Holzle, D. N. Luchini, S. Y. Blond, D. D. Billadeau, A. P. Kozikowski, *J. Med. Chem.* **2009**, *52*, 1853–1863; b) Q. Ye, G. Xu, D. Lv, Z. Cheng, J. Li, Y. Hu, *Bioorg. Med. Chem.* **2009**, *17*, 4302–4312; c) D. E. Levy, D.-X. Wang, Q. Lu, Z. Chen, J. Perumattam, Y.-J. Xu, J. Higaki, H. Dong, A. Liclican, M. Laney, B. Mavunkel, S. Dugar, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 2395–2398; d) A. P. Kozikowski, I. N. Gasina, H. Yuan, P. A. Petukhov, S. Y. Blond, A. Fedolak, B. Caldarone, P. McGonigle, *J. Am. Chem. Soc.* **2007**, *129*, 8328–8332; e) A. P. Kozikowski, I. N. Gasina, P. A. Petukhov, J. Sridhar, L. T. King, S. Y. Blond, T. Duka, M. Rusnak, A. Sidhu, *ChemMedChem* **2006**, *1*, 256–266; f) C. Pardin, S. M. F. G. Gillet, J. W. Keillor, *Bioorg. Med. Chem.* **2006**, *14*, 8379–8385; g) T. A. Engler, S. Malhotra, T. P. Burkholder, J. R. Henry, D. Mendel, W. J. Porter, K. Furness, C. Diefenbacher, A. Marquart, J. K. Reel, Y. Li, J. Clayton, B. Cunningham, J. McLean, J. C. O'Toole, J. Brozinick, E. Hawkins, E. Misener, D. Briere, R. A. Brier, J. R. Wagner, R. M. Campbell, B. D. Anderson, R. Vaughn, D. B. Bennett, T. I. Meier, J. A. Cook, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 899–903; h) H.-C. Zhang, H. Ye, B. R. Conway, C. K. Derian, M. F. Addo, G.-H. Kuo, L. R. Hecker, D. R. Croll, J. Li, L. Westover, J. Z. Xu, R. Look, K. T. Demarest, P. Andrae-Gordon, B. P. Damiano, B. E. Maryanoff, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3245–3250; i) L. Meijer, M. Flajolet, P. Greengard, *Trends Pharmacol. Sci.* **2004**, *25*, 471–480; j) H.-C. Zhang, K. B. White, H. Ye, D. F. McComsey, C. K. Derian, M. F. Addo, P. Andrade-Gordon, A. J. Eckardt, B. R. Conway, L. Westover, J. Z. Xu, R. Look, K. T. Demarest, S. Emanuel, B. E. Maryanoff, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3049–3053.
[10] For selected examples, see: a) D. Basavaiah, B. Devendar, K. Aravindu, A. Veerendhar, *Chem. Eur. J.* **2010**, *16*, 2031–2035; b) S. G. Stewart, L. A. Ho, M. E. Polomska, A. T. Percival, G. C. T. Yeoh, *ChemMedChem* **2009**, *4*, 1657–1667; c) C.-F. Cheng, Z.-C. Lai, Y.-J. Lee, *Tetrahedron* **2008**, *64*, 4347–4353; d) S. G. Stewart, M. E. Polomska, R. W. Lim, *Tetrahedron Lett.* **2007**, *48*, 2241–2244; e) P. Sellès, *Org. Lett.* **2005**, *7*, 605–608; f) M. M. Faul, L. L. Winneroski, C. A. Krumrich, *Tetrahedron Lett.* **1999**, *40*, 1109–1112; g) A. Terpin, C. Winklhofer, S. Schumann, W. Steglich, *Tetrahedron* **1998**, *54*, 1745–1752; h) M. M. Faul, L. L. Winneroski, C. A. Krumrich, *J. Org. Chem.* **1998**, *63*, 6053–6058; i) M. Brenner, G. Mayer, A. Terpin, W. Steglich, *Chem. Eur. J.* **1997**, *3*, 70–74; j) G. Mayer, W. Steglich, *Tetrahedron Lett.* **1996**, *37*, 4483–4486; k) M. M. Faul, K. A. Sullivan, L. L. Winneroski, *Synthesis* **1995**, 1511–1516; l) M. Brenner, H. Rexhausen, B. Steffen, W. Steglich, *Tetrahedron* **1988**, *44*, 2887–2892.
[11] For selected examples, see: a) S. E. Denmark, J. H.-C. Liu, *Angew. Chem.* **2010**, *122*, 3040–3049; *Angew. Chem. Int. Ed.* **2010**, *49*, 2978–2986; b) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; c) B. B. Toure, D. G. Hall, *Chem. Rev.* **2009**, *109*, 4439–4486; d) S. Nakamura, F. Kikuchi, S. Hashimoto, *Angew. Chem.* **2008**, *120*, 7199–7202; *Angew. Chem. Int. Ed.* **2008**, *47*, 7091–7094; e) A. L. K. Shi Shun, R. R. Tykwinski, *Angew. Chem.* **2006**, *118*, 1050–1073; *Angew. Chem. Int. Ed.* **2006**, *45*, 1034–1057; f) S. Kotha, E. Brahmachary, K. Lahiri, *Eur. J. Org. Chem.* **2005**, 4741–4767; g) H. M. L. Davies, M. S. Long, *Angew. Chem.* **2005**, *117*, 3584–3586; *Angew. Chem. Int. Ed.* **2005**, *44*, 3518–3520; h) H. Brunner, *Pure Appl. Chem.* **1994**, *66*, 2033–2036; i) B. M. Trost, *Pure Appl. Chem.* **1994**, *66*, 2007–2014.
[12] For recent reviews and highlights on iron catalysis, see: a) *Iron Catalysis in Organic Chemistry* (Ed.: B. Plietker), Wiley-VCH, **2008**; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363–3367; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; c) S. Gaillard, J.-L. Renaud, *ChemSusChem* **2008**, *1*, 505–509; d) C. Bolm, J. Legros, J. L. Paith, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; e) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108–1117; f) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511; g) A. Fürstner, *Angew. Chem.* **2009**, *121*, 1390–1393; *Angew. Chem. Int. Ed.* **2009**, *48*, 1364–1367; h) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504–7507; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363.
[13] For selected reports on iron catalysis from our group, see: Double amino-carbonylation; a) S. Prateeptongkum, K. M. Driller, R. Jackstell, A. Spannenberg, M. Beller, *Chem. Eur. J.* **2010**, *16*, 9606–9615; b) K. M. Driller, H. Klein, R. Jackstell, M. Beller, *Angew. Chem.* **2009**, *121*, 6157–6160; *Angew. Chem. Int. Ed.* **2009**, *48*, 6041–6044; Transfer hydrogenation of ketones; c) S. Enthaler, G. Erre, M. K. Tse, K. Junge, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8095–8099; Hydrogenation; d) S. Enthaler, B. Hagemann, G. Erre, K. Junge, M. Beller, *Chem. Asian J.* **2006**, *1*, 598–604; Oxidations; e) G. Anilkumar, B. Bitterlich, F. G. Gelalcha, M. K. Tse, M. Beller, *Chem. Commun.* **2007**, 289–291; f) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem.* **2007**, *119*, 7431–7435; *Angew. Chem. Int. Ed.* **2007**, *46*, 7293–7296; g) F. Shi, M. K. Tse, M.-M. Pohl, A. Brückner, S. Zhang, M. Beller, *Angew. Chem.* **2007**, *119*, 9022–9024; *Angew. Chem. Int. Ed.* **2007**, *46*, 8866–8868; C–H functionalizations; h) J. Kischel, I. Jovel, K. Mertins, A. Zapf, M. Beller, *Org. Lett.* **2006**, *8*, 19–22; i) I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 3981–3985; *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3917.
[14] For selected examples on oxidative dehydrogenation applying MnO_2, see: a) A. T. Soldatenkov, K. B. Polyanskii, N. M. Kolyadina, S. A. Soldatova, *Chem. Heterocycl. Compd.* **2009**, *45*, 633–657; b) A. T. Soldatenkov, K. B. Polyanskii, N. M. Kolyadina, *Chem. Heterocycl. Compd.* **2002**, *38*, 422–493; c) A. J. Fatiadi, *Synthesis* **1976**, 133–167; by DDQ see: d) J. Bergman, E. Koch, B. Pelcman, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2609–2614; e) J. Bergman, E. Desarbre, E. Koch, *Tetrahedron* **1999**, *55*, 2363–2370.
[15] a) M. Periasamy, C. Rameshkumar, A. Mukkati, *J. Organomet. Chem.* **2002**, *649*, 209–213; b) C. Rameshkumar, M. Periasamy, *Synlett* **2000**, *11*, 1619–1621.
[16] For coupling constants of *trans*-3,4-disubstituted succinimides, see: a) M. Isaka, N. Rugseree, P. Maithip, P. Kongsaeree, S. Prabpai, Y. Thebtaranonth, *Tetrahedron* **2005**, *61*, 5577–5583; b) N. Millot, C. Pizza, S. Avolio, P. Knochel, *Synthesis* **2000**, 703–706; c) M. Periasamy, C. Rameshkumar, A. Mukkati, *J. Organomet. Chem.* **2002**, *649*, 209–213.
[17] M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, *2nd ed.*, Wiley-VCH, Weinheim, **2004**, pp. 275–307.
[18] For selected reviews and articles on catalytic asymmetric dihydroxylation, see: a) M. H. Junttila, O. E. O. Hormi, *J. Org. Chem.* **2004**, *69*, 4816–4820; b) G. M. Mehltretter, S. Bhor, M. Klawonn, C. Döbler, U. Sundermeier, M. Eckert, H.-C. Militzer, M. Beller, *Synthesis* **2003**, 295–301; c) B. M. Choudary, K. Jyothi, S. Madhi, M. L. Kantam, *Adv. Synth. Catal.* **2003**, *345*, 1190–1192; d) B. M. Choudary, N. S. Chodari, K. Jyothi, M. L. Kantam, *J. Am. Chem. Soc.* **2002**, *124*, 5341–5349; e) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483–2547.

Received: May 26, 2010
Published online: July 23, 2010

