Efforts are underway to access the alternate transannular [4+2] cycloaddition pathway leading to the hexacyclinic acid framework, and will be reported in due course.

Received: March 15, 2002 [Z18907]

[1] a) H. Muramatsu, M. Miyauchi, B. Sato, S. Yoshimura, *40th Symposium on the Chemistry of Natural Products* (Fukuoka, Japan), **1998**, Paper 83, p. 487; b) B. Sato, H. Muramatsu, M. Miyauchi, Y. Hori, S. Takese, M. Mino, S. Hashimoto, H. Terano, *J. Antibiot.* **2000**, *53*, 123. Susceptible cell lines were : MCF-7 ($IC_{50} = 27\,ng\,mL^{-1}$), A549 ($IC_{50} = 73\,ng\,mL^{-1}$), HT-29 ($IC_{50} = 73\,ng\,mL^{-1}$), Jurkat ($IC_{50} = 33\,ng\,mL^{-1}$), P388 ($IC_{50} = 21\,ng\,mL^{-1}$), and B16 ($IC_{50} = 67\,ng\,mL^{-1}$); c) B. Sato, H. Makajima, Y. Hori, M. Hino, S. Hashimoto, H. Terano, *J. Antibiot.* **2000**, *53*, 204; d) S. Yoshimura, B. Sato, T. Kinoshita, S. Takese, H. Terano, *J. Antibiot.* **2000**, *53*, 615; e) S. Yoshimura, B. Sato, T. Kinoshita, S. Takese, H. Terano, *J. Antibiot.* **2002**, *55*, C-1.
[2] R. Höfs, M. Walker, A. Zeeck, *Angew. Chem.* **2000**, *39*, 3400; *Angew. Chem. Int. Ed.* **2000**, *39*, 3258.
[3] a) For a review of TADA reactions, see E. Marsault, A. Toro, P. Nowak, P. Deslongchamps, *Tetrahedron* **2001**, *57*, 4243; b) for a recent example in synthesis, see also longithorone A: M. E. Layton, C. A. Morales, M. D. Shair, *J. Am. Chem. Soc.* **2002**, *124*, 773; c) for the use of a bromodiene in a TADA reaction, see W. R. Roush, K. Koyama, M. L. Curtin, K. J. Moriarty, *J. Am. Chem. Soc.* **1996**, *118*, 7502; d) for this type of hetero-[4+2] cycloaddition, see K. Shin, M. Moriya, K. Ogasawara, *Tetrahedron Lett.* **1998**, *39*, 3765; e) S. Takano, S. Satoh, K. Ogasawara, *J. Chem. Soc. Chem. Commun.* **1988**, 59; f) S. Takano, S. Satoh, K. Ogasawara, K. Aoe, *Heterocycles* **1990**, *30*, 583; g) M. Yamauchi, S. Katayama, O. Baba, T. Watanabe, *J. Chem. Soc. Chem. Commun.* **1983**, 281.
[4] Sorensen and co-workers have recently completed a synthesis of FR182877 through an approach that is closely related to the route described in this Communication: D. A. Vosburg, C. D. Vanderwal, E. J. Sorenson, *J. Am. Chem. Soc.* **2002**, *ASAP.*
[5] I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc.* **1991**, *113*, 4092. See also ref. [1d] for analytical data on the Mosher esters of FR182877.
[6] J. R. Gage, D. A. Evans, *Org. Synth.* **1990**, *68*, 77.
[7] H. Ishiwata, H. Sone, H. Kigoshi, K. Yamada, *J. Org. Chem.* **1994**, *59*, 4712.
[8] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277.
[9] E. J. Corey, P. L. Fuchs, *Tetrahedron Lett.* **1972**, 3769.
[10] M. A. Brodney, J. P. O'Leary, J. A. Hansen, R. J. Giguere, *Synth. Commun.* **1995**, *25*, 521.
[11] S.-i. Kiyooka, H. Kuroda, Y. Shimasaki, *Tetrahedron Lett.* **1986**, *27*, 3009.
[12] A. Arase, M. Hoshi, A. Mijin, K. Nishi, *Syn. Commun.* **1995**, *25*, 1957.
[13] a) For a review, see N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) for the use of TlOH, see J. Uenishi, J. M. Beau, R. W. Armstrong, Y. Kishi, *J. Am. Chem. Soc.* **1987**, *109*, 4756; c) for the use of TlOEt, see S. A. Frank, H. Chen, R. K. Kunz, M. J. Schnaderbeck, W. R. Roush, *Org. Lett.* **2000**, *2*, 2691; d) for the use of Tl_2CO_3, see I. E. Marko, F. Murphy, S. Dolan, *Tetrahedron Lett.* **1996**, *37*, 2507; e) for the first Suzuki coupling with vinyldibromide, see W. R. Roush, R. Riva, *J. Org. Chem.* **1988**, *53*, 710.
[14] C. R. Holmquist, E. J. Roskamp, *J. Org. Chem.* **1989**, *54*, 3258.
[15] S. Higashibayashi, K. Shinko, T. Ishizu, K. Hashimoto, H. Shirahama, M. Nakata, *Synlett* **2000**, 1306.
[16] For a Cs_2CO_3-mediated macrocarbocyclization, see S. Phoenix, E. Bourque, P. Deslongchamps, *Org. Lett.* **2000**, *2*, 4149.
[17] L. Ouellet, P. Langlois, P. Deslongchamps, *Synlett* **1997**, 689, and references therein.
[18] a) C. D. Vanderwal, D. A. Vosberg, S. Weiler, E. J. Sorensen, *Org. Lett.* **1999**, *1*, 645; b) C. D. Vanderwal, D. A. Vosberg, E. J. Sorensen, *Org. Lett.* **2001**, *3*, 4307.
[19] M. Gray, I. P. Andrews, D. F. Hook, J. Kitteringham, M. Voyle, *Tetrahedron Lett.* **2000**, *41*, 6237.
[20] E. D. Laganis, B. L. Chenard, *Tetrahedron Lett.* **1984**, *25*, 5831.
[21] T. Mukaiyama, M. Usui, K. Saigo, *Chem. Lett.* **1976**, 49.
[22] A sample of natural FR182877 was not available for direct comparison.

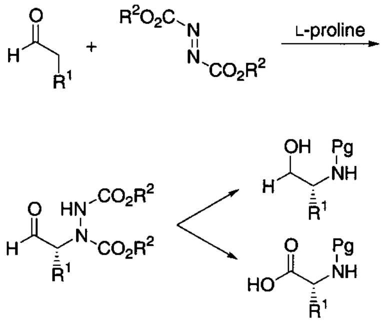
Direct Organo-Catalytic Asymmetric α-Amination of Aldehydes—A Simple Approach to Optically Active α-Amino Aldehydes, α-Amino Alcohols, and α-Amino Acids[**]

Anders Bøgevig, Karsten Juhl,
Nagaswamy Kumaragurubaran, Wei Zhuang, and
Karl Anker Jørgensen[*]

One of the ultimate goals and challenges in chemistry is to develop stereoselective transformations for the creation of functionalized optically active molecules with structural diversity from simple and easily available starting materials. Several procedures to generate optically active molecules are known and among these asymmetric catalysis plays an important role.

The importance of optically active α-amino acids, α-amino aldehydes, and α-amino alcohols, formed by asymmetric catalysis,[1] has stimulated an enormous development in synthetic strategies, and two different catalytic, enantioselective approaches are attractive: the C–C and the C–N bond-forming reactions. The catalytic enantioselective C–C bond-forming reactions include the addition to imines, such as the Strecker[2] and Mannich[3] reactions.

The catalytic, enantioselective, direct C–N bond-forming reaction using aldehydes and a nitrogen source, such as azodicarboxylates, would constitute one of the simplest procedures for the construction of a stereogenic carbon center attached to a nitrogen atom (Scheme 1). Recently, we presented the first direct, enantioselective α-amination of 2-keto esters catalyzed by chiral copper(II)–bisoxazoline complexes.[4, 5] This development led to a simple synthetic approach to optically active *syn*-β-amino-α-hydroxy esters.



Scheme 1. Pg = protecting group.

---

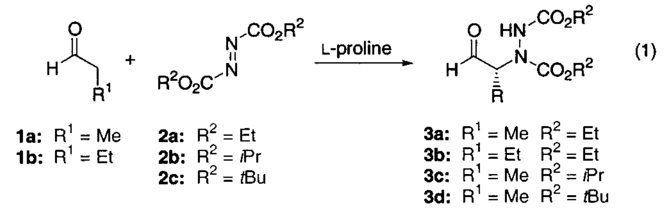
[*] Prof. Dr. K. A. Jørgensen, Dr. A. Bøgevig, Dr. K. Juhl,
Dr. N. Kumaragurubaran, W. Zhuang
Center for Catalysis
Department of Chemistry
Aarhus University
8000 Aarhus C (Denmark)
Fax: (+45) 8919-6199
E-mail: kaj@chem.au.dk

[**] This work was made possible by a grant from The Danish National Research Foundation.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

Herein we present the first catalytic, enantioselective, direct α-amination of aldehydes, that is, the successful and unprecedented use of unmodified aldehydes for the stereoselective creation of C–N bonds using L-proline[3c,d, 6, 7] as the catalyst (Scheme 1). These reactions give an easy and simple access to many classes of optically active molecules with high structural diversity. The molecules include α-amino aldehydes, α-amino alcohols, and α-amino acids, all key chiral elements in many natural products as well as in medicinal chemistry.

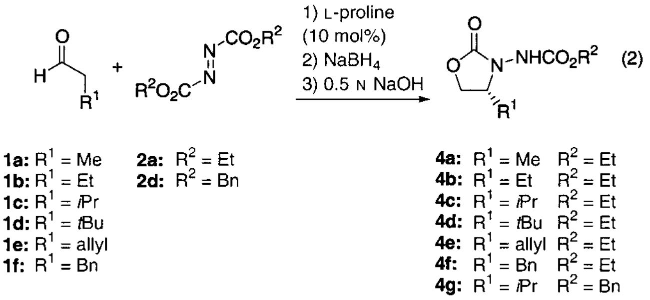
The results for the direct α-amination of some representative aldehydes **1a**, **b** with different azodicarboxylates **2a–c** catalyzed by L-proline [Eq. (1)] under various reaction conditions are presented in Table 1.



Propanal **1a** reacts with diethyl azodicarboxylate (DEAD) **2a** catalyzed by L-proline at room temperature under ambient conditions in CH_2Cl_2 and the α-aminated product **3a** is formed in 93 % yield and with 92 % *ee* (Table 1, entry 1). The procedure for the isolation of the α-aminated product is remarkable: addition of H_2O and extraction with Et_2O followed by evaporation of the excess aldehyde and the solvent gives pure **3a**. At 0 °C the enantioselectivity of the reaction is not significantly improved (93 % *ee*). However, the reaction also proceeds with lower catalyst loadings (Table 1, entries 2–4) and a highly enantioselective reaction takes place using only 2 mol % of L-proline as the catalyst. A variety of other solvents can also be applied with success for the catalytic, enantioselective, direct α-amination reaction (Table 1, entries 5–9). Butanal **1b** is α-aminated, in good yield, and high enantioselectivity using DEAD **2a** to give **3b** in 77 % yield and 90 % *ee* (Table 1, entry 10). The direct α-amination of **1a** was also investigated for the azodicarboxylates **2b**, **c** (Table 1, entries 11 and 12) to introduce more useful *N*-protecting groups (see below).

Further attractive features of the L-proline-catalyzed direct α-amination reactions are: 1) the neat reaction proceeds smoothly in, for example, propanal with only a slight decrease in enantioselectivity,[8] and 2) the reaction can also be performed in gram scale with the same high yield and enantioselectivity (e.g. propanal reacts with DEAD (10 mmol scale) to give the α-aminated product **3a** in 98 % yield and 92 % *ee*).

The enantiomeric excesses of the products formed by the direct α-amination of aldehydes decrease slowly because of the acidity of the α-position next to the carbonyl group. This problem can easily be solved by the in situ reduction of the aldehyde group of the α-aminated aldehydes. This approach leads to a simple, catalytic, enantioselective procedure for the formation of valuable α-amino alcohols [Eq. (2)]. To simplify the isolation and analytical procedures the α-amino alcohols were converted into the *N*-amino oxazolidinones **4**. The results are presented in Table 2.



The various aldehydes **1a–f** all react with azodicarboxylates affording the α-aminated aldehydes in high yields and enantioselectivities in the presence of L-proline (10 mol %) as the catalyst. Further transformations give the *N*-amino oxazolidinones **4**. The results given in Table 2, entries 1 and

Table 1. Catalytic, enantioselective, direct α-amination of aldehydes **1a**, **b** using the azodicarboxylates **2a–c** catalyzed by L-proline under various reaction conditions.[a]

Entry	Aldehyde	Azodicarboxylate	Solvent	Cat. Load [%]	Reaction time [min]	Yield [%][b]	*ee* [%][c]
1	R^1 = Me (**1a**)	R^2 = Et (**2a**)	CH_2Cl_2	50	45	**3a**–93	92
2	R^1 = Me (**1a**)	R^2 = Et (**2a**)	CH_2Cl_2	20	55	**3a**–82	92
3	R^1 = Me (**1a**)	R^2 = Et (**2a**)	CH_2Cl_2	5	105	**3a**–87	91
4	R^1 = Me (**1a**)	R^2 = Et (**2a**)	CH_2Cl_2	2	300	**3a**–92	84
5	R^1 = Me (**1a**)	R^2 = Et (**2a**)	$ClCH_2CH_2Cl$	50	120	**3a**–87	89
6	R^1 = Me (**1a**)	R^2 = Et (**2a**)	MeCN	50	30	**3a**–70	91
7	R^1 = Me (**1a**)	R^2 = Et (**2a**)	EtOAc	50	300	**3a**–77	81
8	R^1 = Me (**1a**)	R^2 = Et (**2a**)	toluene	50	450	**3a**–81	86
9	R^1 = Me (**1a**)	R^2 = Et (**2a**)	dioxane	50	50	**3a**–86	68
10	R^1 = Et (**1b**)	R^2 = Et (**2a**)	CH_2Cl_2	10	120	**3b**–77	90
11	R^1 = Me (**1a**)	R^2 = *i*Pr (**2b**)	CH_2Cl_2	10	105	**3c**–91	88
12	R^1 = Me (**1a**)	R^2 = *t*Bu (**2c**)	CH_2Cl_2	10	205	**3d**–99	89

[a] Experimental conditions: L-proline was added to a stirred solution of the azodicarboxylate (1.0 mmol) and aldehyde (1.5 mmol) in the solvent (3 mL) at room temperature. The reaction mixture was quenched with H_2O (5 mL), extracted with Et_2O, and dried over anhydrous Na_2SO_4. The solvent and the excess aldehyde were removed by evaporation (see Supporting Information). [b] Yield of isolated product. [c] Enantiomeric excesses determined by GC using a chiral Chrompack CP Chiralsil-Dex Cβ column.

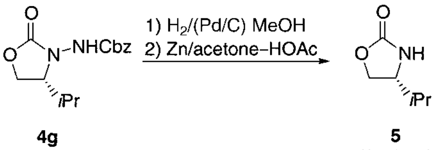
Table 2. Catalytic, enantioselective, direct α-amination of aldehydes **1a–f** with azodicarboxylates **2a**, **d** catalyzed by L-proline (10 mol%) at room temperature in CH_2Cl_2 [Eq. (2)].[a]

Entry	Aldehyde	Azodicarboxylate	Yield [%][b]	*ee* [%][c]
1	R^1 = Me (**1a**)	R^2 = Et (**2a**)	**4a**–67	93
2	R^1 = Et (**1b**)	R^2 = Et (**2a**)	**4b**–77	95
3	R^1 = *i*Pr (**1c**)	R^2 = Et (**2a**)	**4c**–83	93
4	R^1 = *t*Bu (**1d**)	R^2 = Et (**2a**)	**4d**–57	91
5	R^1 = allyl (**1e**)	R^2 = Et (**2a**)	**4e**–92	93
6	R^1 = Bn (**1f**)	R^2 = Et (**2a**)	**4f**–68	89
7	R^1 = *i*Pr (**1c**)	R^2 = Bn (**2d**)	**4g**–70	91

[a] Experimental conditions: L-proline (11.5 mg, 0.10 mmol) was suspended in CH_2Cl_2 (2.5 mL) followed by the addition of the aldehyde (1.50 mmol) and the azodicarboxylate (1.00 mmol). The reaction mixture was stirred at room temperature until the yellow color of the azodicarboxylate disappeared. MeOH (2.5 mL) was added followed by careful addition of $NaBH_4$ (50 mg). After 20 min, NaOH (0.5 N, 2.5 mL) was added and after 2 h the organic solvents were removed in vacuo. The aqueous phase was diluted and extracted with EtOAc and the organic phase dried over anhydrous $MgSO_4$ and concentrated in vacuo to give pure *N*-amino oxazolidinones (see Supporting Information). [b] Yield of isolated product. [c] *ee* values determined by GC using a chiral Chrompack CP Chiralsil-Dex Cβ column or by chiral HPLC.

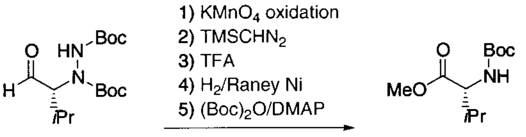
2 show that the masked α-amino alcohols are obtained with excellent enantioselectivity and that a slightly higher enantioselectivity is obtained when the aldehyde is reduced to the alcohol prior to workup. The other aldehydes **1c–f** are directly α aminated in a highly enantioselective fashion with DEAD **2a** in the presence of L-proline as the catalyst to give, after reduction and cyclization, the corresponding oxazolidinones in high yields and very high enantioselectivities (Table 2, entries 3–6, 89% to 93% *ee*). To expand the scope of the reaction we also treated **1c** with dibenzyl azodicarboxylate **2d** in the presence of L-proline (10 mol%) as the catalyst. The *N*-Cbz protected (Cbz = phenylmethoxycarbonyl) *N*-amino oxazolidinone **4g** was isolated in 70% yield and 91% *ee* (Table 2, entry 7) thus showing that a readily removable protecting group can be introduced.

The *N*-protecting group and the N–N bond in the *N*-amino oxazolidinone **4g** can be removed and cleaved, respectively. The α-aminated product **4g** is first treated with H_2/(Pd/C), followed by reaction with Zn/acetone in acetic acid to afford oxazolidinone **5** in 31% overall yield based on **2d** [Eq. (3)]. The absolute configuration of **5** has been assigned as *R*.[9] Hydrolysis of the oxazolidinones at this point would give the α-amino alcohols.[10]



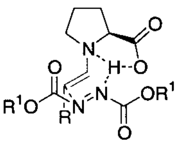
4g **5** (90% ee) (3)

A very important aspect of the direct α-amination reaction is the easy and attractive access it gives to optically active nonproteogenic α-amino acids. Reaction of 3-methyl butanal (**1c**) with di-*tert*-butyl azodicarboxylate (**2c**) catalyzed by L-proline (10 mol%, CH_2Cl_2, 4 h, RT) gives the α-hydrazino aldehyde **3e** (>90% yield). Oxidation of the aldehyde by $KMnO_4$ to the carboxylic acid and esterification followed by hydrolysis of the Boc groups (Boc = *tert*-butoxycarbonyl), reduction, and finally a *N*-Boc protection gives the *N*-Boc-protected valine methyl ester **6** [Eq. (4); TMS = trimethylsilyl, TFA = trifluoroacetic acid, DMAP = 4-dimethylaminopyridine] maintaining the enantiomeric excess obtained in the enantioselective amination step (90% *ee*). The absolute configuration of the chiral carbon center in **6** was assigned as *R*.[11]



3e **6** (4)

Based on the absolute configuration of the α-aminated products, we propose the transition-state model **7** for the reaction. The approach of the azodicarboxylate might be directed by interaction of the incoming nitrogen atom with the proton of the carboxylic acid of the L-proline–enamine intermediate.



7

In conclusion, we have demonstrated the first organo-catalytic, direct, asymmetric α-amination of aldehydes with azodicarboxylates as the nitrogen source and L-proline as the catalyst. The new reaction provides easy access to optically active α-amino aldehydes, α-amino alcohols, and α-amino acids from simple and easily available starting materials and catalyst. Aldehydes react with azodicarboxylates and the corresponding optically active α-aminated adducts are formed in high yields and enantiomeric excesses, with as little as 2 mol% of L-proline. It is also demonstrated that masked α-amino alcohols are formed in high yields and excellent enantioselectivities (up to 95% *ee*). Furthermore, the formation of oxazolidinones and α-amino acids is demonstrated. This direct α-amination reaction uses readily available and inexpensive achiral starting materials, and can be carried out under environmentally friendly and operationally simple reaction conditions.

Received: March 1, 2002 [Z18800]

---

[1] See for example a) R. M. Williams, *Synthesis of Optically Active α-Amino* Acids, Pergamon, Oxford, **1989**; b) R. M. Williams, J. A. Hendrix, *Chem. Rev.* **1992**, *92*, 889; c) M. Arend, *Angew. Chem.* **1999**, *111*, 3047; *Angew. Chem. Int. Ed.* **1999**, *38*, 2873; d) L. Yet, *Angew. Chem.* **2001**, *113*, 900; *Angew. Chem. Int. Ed.* **2001**, *40*, 875; e) R. O. Duthaler, *Tetrahedron* **1994**, *50*, 1539; f) S. C. Bergmeier, *Tetrahedron* **2000**, *56*, 2561; g) K. L. Reddy, K. B. Sharpless, *J. Am. Chem. Soc.* **1998**, *120*, 1207, and references therein.

[2] See for example: a) M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 5315; b) M. S. Sigman, P. Vachal, E. N. Jacobsen, *Angew. Chem.* **2000**, *112*, 1336; *Angew. Chem. Int. Ed.* **2000**, *39*, 1279; c) M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 4901; d) C. A. Krueger, K. W. Kuntz, C. D. Dzierba, W. G. Wirschun, J. D. Gleason,

M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 4284; e) M. Takamura, Y. Hamashima, H. Usuda, M. Kanai, M. Shibasaki, *Angew. Chem.* **2000**, *112*, 1716; *Angew. Chem. Int. Ed.* **2000**, *39*, 1650; f) E. J. Corey, M. J. Grogan, *Org. Lett.* **1999**, *1*, 157; g) H. Ishitani, S. Komiyama, S. Kobayashi, *Angew. Chem.* **1998**, *110*, 3369; *Angew. Chem. Int. Ed.* **1998**, *37*, 3186; f) H. Ishitani, S. Komiyama, Y. Hasegawa, S. Kobayashi, *J. Am. Chem. Soc.* **2000**, *122*, 762.

[3] Catalytic enantioselective direct Mannich reactions: a) S. Yamasaki, T. Iida, M. Shibasaki, *Tetrahedron* **1999**, *55*, 8857; b) K. Juhl, N. Gathergood, K. A. Jørgensen, *Angew. Chem.* **2001**, *113*, 3083; *Angew. Chem. Int. Ed.* **2001**, *40*, 2995; c) A. Córdova, S.-I. Watanabe, F. Tanaka, W. Notz, C. F. Barbas III, *J. Am. Chem. Soc.* **2002**, *124*, 1842; d) A. Córdova, W. Notz, G. Zhong, J. M. Betancort, C. F. Barbas III, *J. Am. Chem. Soc.* **2002**, *124*, 1866.

[4] K. Juhl, K. A. Jørgensen, *J. Am. Chem. Soc.* **2002**, *124*, 2420.

[5] For an review on asymmetric α-amination reactions see J.-P. Genet, C. Greck, D. Lavergne, *Modern Amination Methods* (Ed.: A. Ricci), Wiley-VCH, Weinheim, **2000**, chap. 3.

[6] D. A. Evans, S. G. Nelson, *J. Am. Chem. Soc.* **1997**, *119*, 6542.

[7] For the use of proline and other chiral amines as catalysts see for example, a) P. I. Dalko, L. Moisan, *Angew. Chem.* **2001**, *113*, 3840; *Angew. Chem. Int. Ed.* **2001**, *40*, 3726; b) A. Córdova, W. Notz, C. F. Barbas III, *J. Org. Chem.* **2002**, *67*, 301; c) K. Sakthivel, W. Notz, T. Bui, C. F. Barbas III, *J. Am. Chem. Soc.* **2001**, *123*, 5260; d) B. List, R. A. Lerner, C. F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2395; e) J. F. Austin, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2002**, *124*, 1172; f) A. B. Northrup, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2002**, *124*, 2458; g) N. A. Paras, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2001**, *123*, 4370; h) W. S. Jen, J. J. M. Wiener, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 9874; i) K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243; j) A. Bøgevig, N. Kumaragurubaran, K. A. Jørgensen, *Chem. Commun.* **2002**, 620.

[8] The enantiomeric excess was 77% and full conversion was obtained after only 2 min reaction time!

[9] Absolute configuration of **5**: W. A. Kleschick, M. W. Reed, J. Bordner, *J. Org. Chem.* **1987**, *52*, 3168.

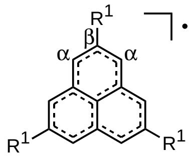
[10] S. J. Katz, S. C. Bergmeier, *Tetrahedron Lett.* **2002**, *43*, 557.

[11] Absolute configuration of **6**: M. J. Burk, J. G. Allen, *J. Org. Chem.* **1997**, *62*, 7054.

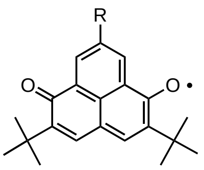
A New Trend in Phenalenyl Chemistry: A Persistent Neutral Radical, 2,5,8-Tri-*tert*-butyl-1,3-diazaphenalenyl, and the Excited Triplet State of the Gable *syn*-Dimer in the Crystal of Column Motif[**]

Yasushi Morita,* Takashi Aoki, Kozo Fukui, Shigeaki Nakazawa, Koichi Tamaki, Shuichi Suzuki, Akira Fuyuhiro, Kagetoshi Yamamoto, Kazunobu Sato, Daisuke Shiomi, Akira Naito, Takeji Takui,* and Kazuhiro Nakasuji*

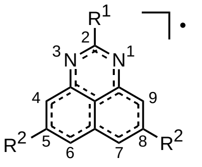
Phenalenyl (**1**) is a highly symmetric (D_{3h}) odd alternating-hydrocarbon π radical, found as early as 1956,[1] and it still plays an important role as a building block for spin-mediated molecular functions in organic molecule-based magnets,[2] and organic metal and conducting materials.[3] Recent progress in phenalenyl chemistry has been made in the isolation of the radical itself in the crystalline state by employing bulky substituents (**2**[4a] and perchlorophenalenyl[4b]), with the exploration of amphoteric redox systems[5] which have intriguing potential applications, such as organic molecular batteries,[6] and with the synthesis of novel phenalenyls with extended conjugation, such as compound **3**.[7] 1,3-Diazaphenalenyl (**4**) is a typical example of the isoelectronic mode of heteroatomic modification for phenalenyl. Successful isolation of **2**[4] aided by the steric hindrance induced by the bulky



1 $R^1 = H$
2 $R^1 = t\mathrm{Bu}$



3



4 $R^1 = R^2 = H$
5 $R^1 = t\mathrm{Bu}$, $R^2 = H$
6 $R^1 = R^2 = t\mathrm{Bu}$

---

[*] Prof. Dr. Y. Morita, Prof. Dr. K. Nakasuji, T. Aoki, Dr. K. Tamaki, S. Suzuki, Prof. Dr. A. Fuyuhiro, Prof. Dr. K. Yamamoto
Department of Chemistry, Graduate School of Science
Osaka University
Toyonaka, Osaka 560-0043 (Japan)
Fax: (+81) 6-6850-5395
E-mail: nakasuji@chem.sci.osaka-u.ac.jp

Prof. Dr. T. Takui, Dr. K. Fukui, Dr. S. Nakazawa, Prof. Dr. K. Sato, Prof. Dr. D. Shiomi
Departments of Chemistry and Materials Science
Graduate School of Science
Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81) 6-6605-3137
E-mail: takui@sci.osaka-cu.ac.jp

Prof. Dr. A. Naito
Faculty of Engineering, Yokohama National University
Hodogaya-ku, Yokohama 240-0085 (Japan)

[**] This work has been supported by Grants-in-Aid for General Scientific Research and Scientific Research on Priority Area "Delocalized π-Electronic Systems (No. 297)" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.