Concave Reagents, 22[◇]

Cyclopropanation of Alkenes with Ethyl Diazoacetate: Copper(I) Complexes of Concave 1,10-Phenanthrolines as Diastereoselective Catalysts

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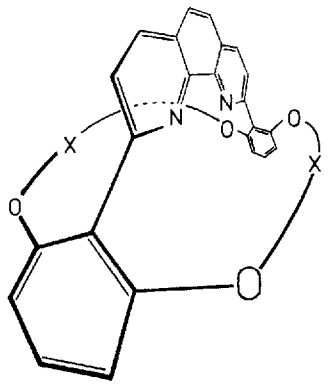
Concave 1,10-phenanthrolines **1a–c** have been used as ligands in the copper(I)-catalyzed cyclopropanation of alkenes **2** with ethyl diazoacetate. The complexes proved to be efficient cyclopropanation catalysts and exhibited an enhanced diastereoselectivity, particularly in the reactions of cyclic alkenes **2b–d**. The preferred formation of *exo*-cyclopropanes **3b–d** can be explained by the concave shape of these catalysts.

Stereoselective synthesis of cyclopropanes is an important goal in organic chemistry. Often cyclopropanes are synthesized by the metal-catalyzed reaction of alkenes with diazo compounds[1]. The reaction between styrene and ethyl diazoacetate has been particularly well-studied. Various ligands have been used in this metal ion catalysis to influence the enantio- and diastereoselectivity of the reaction. The most successful enantioselective catalysts developed to date are C_2-symmetrical chiral metal complexes. Bidentate nitrogen ligands with copper(I) triflate as catalysts show high enantioselectivity but only moderate diastereoselectivity[2].

Diastereoselective cyclopropanation of styrene has been achieved by using bulky diazo compounds such as *tert*-butyl diazoacetate and 2,6-di-*tert*-butyl-4-methylphenyl diazoacetate[3], the latter giving a *trans*/*cis* ratio of 94:6. However, when cycloalkenes were used as substrates, CH insertion was the predominant reaction. Diastereoselective cyclopropanation of styrene has also been achieved using porphyrin complexes as catalysts. A sterically hindered rhodium porphyrin complex gave preferentially the *cis* isomer[4]. Other metal porphyrin complexes were *trans*-selective in the reaction of styrene with ethyl diazoacetate (up to 93:7)[5]. However, these catalysts also gave poor yields in the cyclopropanation of cyclic alkenes, e.g. of cyclohexene and indene. In these instances, the ethyl diazoacetate was largely converted into diethyl fumarate and diethyl maleate[5c]. In the cyclopropanation of styrene, excellent results in both enantioselectivity and diastereoselectivity have been obtained with 2,6-bis(4-isopropyloxazolinyl)pyridine as a ligand for ruthenium[6].

Despite the progress in enantioselective and diastereoselective cyclopropanation of the model system styrene, efficient diastereoselective catalysts for the cyclopropanation of cyclic alkenes have still to be developed. All successful cyclopropanations of cycloalkenes have given only poor diastereomeric excesses[7]. In this paper we present a suitable catalyst for the diastereoselective cyclopropanation of cyclic alkenes.



1a: X = - $(CH_2CH_2O)_2CH_3$ $H_3C(OCH_2CH_2)_2$ -

1b: X = - $CH_2(CH_2OCH_2)_2CH_2$ -

1c: X = - $CH_2(CH_2OCH_2)_3CH_2$ -

Concave 1,10-phenanthrolines[8] **1** have been employed as ligands in the copper-catalyzed cyclopropanation of the alkenes **2** with ethyl diazoacetate. The ligands **1a–c** were synthesized as described previously[8]. The catalysts were prepared in situ by mixing copper(I) triflate with a slight excess of the corresponding bimacrocycles **1b** or **1c** or ligand **1a**. **1a** can be regarded as bimacrocycle **1b** whose side chains X are cut in the middle. Copper(I) was chosen as the metal

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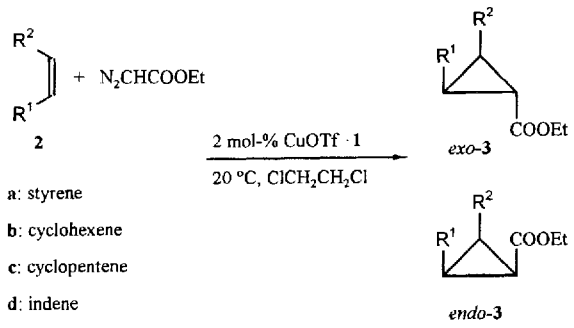
catalyst because of its well-known capability to catalyze the cyclopropanation of alkenes. The association constants of the concave 1,10-phenanthrolines **1** and copper(I) have been reported earlier[8c,d].

Copper(I) catalyzes the evolution of N_2 from ethyl diazoacetate and forms a copper carbenoid[9]. This electrophilic species then reacts with an alkene **2** to form the corresponding cyclopropane **3**. A competing reaction is the dimerization of the diazo compound to give diethyl fumarate and diethyl maleate. This reaction can be suppressed by keeping the concentration of ethyl diazoacetate low. A slow and continuous addition of the diazo compound by a syringe pump may avoid the side reaction[2a]. In this work however, all cyclopropanations were carried out as batch reactions so that the yields and diastereoselectivities could be compared for different ligands. Therefore, no special measures were taken to minimise the side reaction; in other words, a larger degree of dimerization was consciously allowed.



Alkenes **2** were used in an 8-fold excess with respect to ethyl diazoacetate. 1–2 mol % of catalyst **1** · CuOTf gave yields of cyclopropanes **3** of up to 83% (see Table 1). Optimization should be possible by using the syringe-pump technique. The reactions were also carried out in the absence of ligand to get some appraisal of the influence of the ligands on the reaction. The *exo*- and *endo*-cyclopropane products **3** were identified and characterized by ^{1}H-NMR spectroscopy and their ratio was determined by gas chromatography. In the ^{1}H-NMR spectra, the hydrogen atoms of the cyclopropane ring possess different coupling constants in the two possible diastereomers; *trans*-coupling gives small J values of 2.5–7.6 Hz while *cis*-coupling leads to larger values of 7.9–9.1 Hz.

Complexation with the ligands **1a–c** did not reduce the catalytic activity of the copper(I) catalyst in the cyclopropanations of the alkenes **2** in Table 1. First the cyclopropanation of styrene (**2a**) was studied. In the absence of a ligand, 70% conversion to cyclopropanes **3a** was obtained, with a slight excess of *trans*-**3a**. Reactions using ligands **1a–c** gave similar yields but larger *trans*/*cis* ratios. In the cyclopropanations of the cyclic alkenes cyclohexene (**2b**), cyclopentene (**2c**) and indene (**2d**), the diastereoselectivity was exceptionally increased when the ligands **1a–c** were used. Diastereomer ratios between 94:6 and 99:1 were obtained. The use of these ligands did not decrease the yields of cyclopropanes **3b–d**.

Table 1. Diastereoselective cyclopropanation of various alkenes **2** with ethyl diazoacetate, catalyzed by CuOTf · **1**

		cyclopropanes **3**		dimerization products	
alkene **2**	ligand **1**	yield / %	*exo* : *endo*[a,b]	yield / %	*E* : *Z*[b]
styrene (**2a**)	-	70	59 : 41	19	57 : 43
styrene (**2a**)	**1a**	66	82 : 18	19	93 : 7
styrene (**2a**)	**1b**	83	86 : 14	10	80 : 20
styrene (**2a**)	**1c**	70	85 : 15	26	96 : 4
cyclohexene (**2b**)	-	37	84 : 16	20	50 : 50
cyclohexene (**2b**)	**1a**	31	99 : 1	21	95 : 5
cyclohexene (**2b**)	**1b**	61	97 : 3	12	82 : 18
cyclohexene (**2b**)	**1c**	49	98 : 2	25	>95 : 5
cyclopentene (**2c**)	-	61	77 : 23	20	43 : 57
cyclopentene (**2c**)	**1a**	51	98 : 2	31	96 : 4
cyclopentene (**2c**)	**1b**	64	94 : 6	17	76 : 24
cyclopentene (**2c**)	**1c**	66	97 : 3	22	>95 : 5
indene (**2d**)	-	53	68 : 32	18	56 : 44
indene (**2d**)	**1a**	61	99 : 1	19	94 : 6
indene (**2d**)	**1b**	72	97 : 3	10	78 : 22
indene (**2d**)	**1c**	61	98 : 2	18	>95 : 5

[a] *trans*:*cis* for styrene. – [b] *exo*/*endo* and *E*/*Z* ratios were determined by GC.

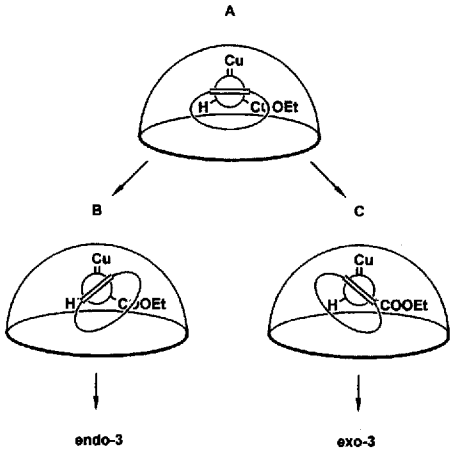
With bulkier alkenes such as norbornene, an increased diastereoselectivity was also found, but the yields of the desired cyclopropanes were low and formation of diethyl fumarate and diethyl maleate predominated. The cavity of the ligands **1** is probably too small for norbornene.

Reactions with less nucleophilic substrates such as *cis*-stilbene also gave fumarate and maleate as the major products. Here the formation of cyclopropanes was retarded by electronic rather than steric effects, because even in the absence of ligands only dimerization was observed.

The cyclopropanation of styrene (**2a**) with ethyl diazoacetate was also carried out in the presence of copper(I) triflate at 0°C, giving the same results as at 20°C. The complex of copper(I) with **1a** gave the same yield but a slightly larger *trans*/*cis* ratio of 88:12, as compared to 82:18 at 20°C. Similar results were expected for the copper(I) complexes of **1b** and **1c**, but the decrease in temperature gave lower yields of both the cyclopropanes **3** and the dimerization products, while the diastereoselectivities were essentially unaffected.

The enhanced diastereoselectivities listed in Table 1 can be explained by the influence of the concave ligands **1** on the transition states leading to the two diastereomers (see Figure 1). Without concave ligands **1**, the alkene **2** can reach the copper(I) carbenoid unhindered. However, in the presence of a 1,10-phenanthroline ligand, copper is strongly bound by the nitrogen atoms[8]. Therefore the reaction of ethyl diazoacetate with the copper ion will form a carbenoid which is bound to the concave ligand. The concave shielding in these complexes restricts the number of possible arrangements of the catalyst and the cycloalkene **2**. An attack from the opposite side of the ligand seems to be favorable. This approach, shown in diagram **A** of Figure 1, minimizes the steric interactions between the cycloalkene **2** and the concave ligand **1**. However, this arrangement is unproductive since the double bonds of alkene **2** and copper(I) carbenoid are perpendicular to one another. Formation of a

Figure 1. Newman projection of the approach of an alkene **2** to a copper(I) carbene formed by reaction of ethyl diazoacetate with a complex of Cu^+ with a concave 1,10-phenanthroline ligand **1**: the ligand **1** shielding the copper(I) carbene is shown as a half bowl



cyclopropane **3** can only occur if the cyclic alkene **2** rotates with respect to the carbenoid. A counterclockwise turn, shown in diagram **B** of Figure 1, will lead to the *endo*-product. Such a turn will however increase the steric interactions between cycloalkene **2** and the ester group. The clockwise turn in diagram **C** of Figure 1 avoids these interactions and accounts for the preferred formation of the *exo*-products (see Table 1).

Changes of the *E*/*Z* ratios in the competing dimerization reactions of ethyl diazoacetate support this explanation. Equal amounts of diethyl fumarate and diethyl maleate were formed in the reaction without a ligand. A copper(I) complex with ligand **1b** gave *E*/*Z* ratios of 80:20, and an even higher ratio, greater than 95:5, was seen with **1c** as the ligand.

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Experimental Section

Equipment: ^{1}H-NMR spectroscopy: Bruker AM 300, 300 MHz, $CDCl_3$, δ in ppm vs. TMS. – GC: HRGC 5300 Mega Series MFC 500, Carlo Erba Instruments. SE 30/25 m column, 0.32 mm ID; 0.25 μm DF, Macherey-Nagel. – MS: Finnigan MAT 8200.

General Procedure for Cyclopropanations: All reactions were carried out under nitrogen. 8.75 mmol of the alkene **2** and a solution of 24 μmol of the ligand **1** in 1.0 ml of 1,2-dichloroethane were added to 5.0 mg (20 μmol) of CuOTf · $(C_6H_6)_{0.5}$. The solid was dissolved with the aid of ultrasound and 1.00 mmol of ethyl diazoacetate dissolved in dichloromethane[10] and 1.0 ml of 1,2-dichloroethane were added to the solution at 20°C. After stirring for 24 h, the mixture was filtered through silica gel (5 cm × 3 cm) with 150 ml of diethyl ether and the solution was concentrated in vacuo. After addition of 50.0 mg (0.221 mmol) of *n*-hexadecane as internal standard, the reaction mixture was diluted to 12.5 ml with 1,2-dichloroethane and analyzed by GC. The results are listed in Table 1.

Ethyl trans-2-Phenylcyclopropanecarboxylate (*trans*-**3a**)[2a]: For characterization, *trans*-**3a** was isolated by chromatography (silica gel, *n*-pentane/diethyl ether, 10:1). – ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz, 3H, CH_3), 1.31 (ddd, *J* = 4.5 Hz, *J* = 6.5 Hz, *J* = 8.4 Hz, 1H, *trans*-3-H), 1.60 (ddd, *J* = 4.5 Hz, *J* = 5.3 Hz, *J* = 9.1 Hz, 1H, *cis*-3-H), 1.90 (ddd, *J* = 4.2 Hz, *J* = 5.3 Hz, *J* = 8.4 Hz, 1H, 1-H), 2.51 (ddd, *J* = 4.1 Hz, *J* = 6.5 Hz, *J* = 9.1 Hz, 1H, 2-H), 4.17 (q, *J* = 7.1 Hz, 2H, CH_2), 7.0–7.3 (m, 5H, Ph).

Ethyl cis-2-Phenylcyclopropanecarboxylate (*cis*-**3a**) *(Mixture with Diethyl Fumarate)*[2a]: Chromatography (silica gel, *n*-pentane/diethyl ether, 10:1) gave a mixture of *cis*-**3a** and diethyl fumarate. – ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, *J* = 7.1 Hz, 3H, CH_3), 1.31, 1.32 (t, *J* = 7.1 Hz, fumarate CH_3, ddd, *J* = 5.1 Hz, *J* = 7.9 Hz, *J* = 8.8 Hz, *trans*-3-H, 3.5H), 1.71 (ddd, *J* = 5.1 Hz, *J* = 5.6 Hz, *J* = 7.6 Hz, 1H, *cis*-3-H), 2.07 (ddd, *J* = 5.6 Hz, *J* = 7.8 Hz, *J* = 9.2 Hz, 1H, 1-H), 2.58 (dt, J_d = 7.6 Hz, J_t = 9.0 Hz, 1H, 2-H), 3.87 (q, *J* = 7.1 Hz, 2H, CH_2), 4.26 (q, *J* = 7.1 Hz, 1.4H, fumarate CH_2), 6.85 (s, >0.5H, fumarate CH), 7.1–7.3 (m, ca. 5H, aromatic H).

Identification of Cyclopropanes **3b–d**: The products of the reaction of the alkenes **2b–d** with ethyl diazoacetate were analyzed by GC-MS. The *exo*-cyclopropanes *exo*-**3** were isolated by preparative HPLC (Si-60, *n*-hexane) and were identified by ^{1}H NMR. The *endo*-products showed identical GC-MS decomposition patterns and were not isolated.

Ethyl exo-7-Bicyclo[4.1.0]heptanecarboxylate (*exo*-**3b**)[11]: GC-MS (EI, 70 eV); *m/z* (%): 168 (40) [M^+], 140 (60) [$M^+ - C_2H_4$], 139 (40) [$M^+ - C_2H_5$], 123 (100) [$M^+ - OC_2H_5$], 95 (80) [$M^+ - COOC_2H_5$], 81 (60) [$C_6H_9^+$], 80 (95) [$C_6H_8^+$], 79 (80) [$C_6H_7^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.1–1.3 (m, 4H, $CH_2CH_2CH_2$), 1.23 (t, *J* = 7.3 Hz, 3H, CH_3), 1.35 (t, *J* = 4.3 Hz, 1H, C*H*COOEt), 1.58 (m_c, 2H, $(CH)_2CHCH_2$), 1.60–1.75 (m, 2H, CH_2CH_2CH), 1.80–1.95 (m, 2H, CH_2CH_2CH), 4.08 (q, *J* = 7.3 Hz, 2H, OCH_2).

Ethyl endo-7-Bicyclo[4.1.0]heptanecarboxylate (*endo*-**3b**)[11]: GC-MS (EI, 70 eV); *m/z* (%): 168 (80) [M^+], 140 (65) [$M^+ - C_2H_4$], 139 (30) [$M^+ - C_2H_5$], 123 (85) [$M^+ - OC_2H_5$], 95 (75) [$M^+ - COOC_2H_5$], 81 (55) [$C_6H_9^+$], 80 (100) [$C_6H_8^+$], 79 (70) [$C_6H_7^+$].

Ethyl exo-6-Bicyclo[3.1.0]hexanecarboxylate (*exo*-**3c**)[12]: GC-MS (EI, 70 eV); *m/z* (%): 154 (25) [M^+], 126 (45) [$M^+ - C_2H_4$] 125 (20) [$M^+ - C_2H_5$], 109 (65) [$M^+ - OC_2H_5$], 81 (100) [$M^+ - COOC_2H_5$], 67 (40) [$M^+ - CH_2COOC_2H_5$]. – ^{1}H NMR ($CDCl_3$): δ = 0.85–1.15 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 1.39 (t, *J* = 2.7 Hz, 1H, CHCOOEt), 1.55–1.90 (m, 7H), 4.10 (q, *J* = 7.1 Hz, 2H, OCH_2).

Ethyl endo-6-Bicyclo[3.1.0]hexanecarboxylate (*endo*-**3c**)[12]: GC-MS (EI, 70 eV); *m/z* (%): 154 (10) [M^+], 126 (20) [$M^+ - C_2H_4$] 125 (20) [$M^+ - C_2H_5$], 109 (50) [$M^+ - OC_2H_5$], 81 (100) [$M^+ - COOC_2H_5$], 67 (30) [$M^+ - CH_2COOC_2H_5$].

Ethyl exo-3-Tricyclo[4.4.0.0^{2,4}]deca-1(6),7,9-trienecarboxylate (*exo*-**3d**)[13]: GC-MS (EI, 70 eV); *m/z* (%): 202 (20) [M^+], 173 (20) [$M^+ - C_2H_5$], 157 (15) [$M^+ - OC_2H_5$], 129 (100) [$M^+ - COOC_2H_5$], 116 (5) [$M^+ - CHCOOC_2H_5$, indene$^+$]. – GC-MS (CI-isobutane); *m/z* (%): 203 (100) [$M^+ + H$], 157 (15) [$M^+ - OC_2H_5$], 129 (35) [$M^+ - COOC_2H_5$]. – ^{1}H NMR ($CDCl_3$): δ = 1.24 (dd, *J* = 3.3 Hz, *J* = 2.5 Hz, 1H, CHCOOEt), 1.30 (t, *J* = 7.3 Hz, 3H, CH_3), 2.44 (ddt, J_t = 6.5 Hz, J_d = 3.3 Hz, J_d = 0.9 Hz, 1H, $(CH)_2CHCH_2$), 2.95 (ddd, *J* = 6.5 Hz, *J* = 2.5 Hz, *J* = 1.4 Hz, 1H, $CCH(CH)_2$), 3.04 (ddd, *J* = 17.5 Hz, *J* = 1.4 Hz, *J* = 0.9 Hz, 1H, *endo*-CH_2), 3.28 (ddd, *J* = 17.5 Hz, *J* = 6.5 Hz, *J* = 1.0 Hz, 1H, *exo*-CH_2), 4.15 (q, *J* = 7.3 Hz, 2H, OCH_3), 7.1–7.2 (m, 3H, aromatic H), 7.3–7.4 (m, 1H, aromatic H).

Ethyl endo-3-Tricyclo[4.4.0.0^{2,4}]deca-1(6),7,9-trienecarboxylate (*endo*-**3d**)[13]: GC-MS (EI, 70 eV); *m/z* (%): 202 (15) [M^+], 173 (15)

$[M^+ - C_2H_5]$, 157 (15) $[M^+ - OC_2H_5]$, 129 (100) $[M^+ - COOC_2H_5]$, 116 (5) $[M^+ - CHCOOC_2H_5$, indene$^+]$. – GC-MS (CI-isobutane); *m/z* (%): 203 (100) $[M^+ + H]$, 157 (10) $[M^+ - OC_2H_5]$, 129 (25) $[M^+ - COOC_2H_5]$.

[1] [1a] P. Eilbracht, *Methoden Org. Chem.* (Houben-Weyl) 4th ed. **1995**, vol. E21c, 2650–2658. – [1b] H.-U. Reißig, *ibid.* **1995**, vol. E21c, 3179–3270.

[2] Different ligands in copper-catalyzed enantioselective cyclopropanations of styrene: [2a] H. Fritschi, U. Leutenegger, A. Pfaltz, *Helv. Chim. Acta* **1988**, *71*, 1553–1565. – [2b] D. A. Evans, K. A. Woerpel, M. M. Hinman, M. M. Faul, *J. Am. Chem. Soc.* **1991**, *113*, 726–728. – [2c] U. Leutenegger, G. Umbricht, C. Fahrni, P. v. Matt, A. Pfaltz, *Tetrahedron* **1992**, *48*, 2143–2156. – [2c] A. V. Bedekar, P. G. Andersson, *Tetrahedron Lett.* **1996**, *37*, 4073–4076.

[3] M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle, K.-L. Loh, *J. Am. Chem. Soc.* **1990**, *112*, 1906–1912.

[4] H. J. Callot, C. Piechocki, *Tetrahedron Lett.* **1980**, *21*, 3489–3492.

[5] Different metal porphyrin catalysts in diastereoselective cyclopropanations: [5a] K. C. Brown, T. Kodadek, *J. Am. Chem. Soc.* **1992**, *114*, 8336–8338, and references therein. – [5b] D. A. Smith, D. N. Reynolds, L. K. Woo, *J. Am. Chem. Soc.* **1993**, *115*, 2511–2513. – [5c] J. R. Wolf, C. G. Hamaker, J.-P. Djukic, T. Kodadek, L. K. Woo, *J. Am. Chem. Soc.* **1995**, *117*, 9194–9199.

[6] [6a] Chiral bis(oxazolinyl)pyridines as ligands in ruthenium-catalyzed cyclopropanations of styrene: H. Nishiyama, Y. Ito, H. Matsumoto, S.-B. Park, K. Itoh, *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224. – [6b] Electronic control in asymmetric cyclopropanations with ruthenium catalysts: S.-B. Park, K. Murate, H. Matsumoto, H. Nishiyama, *Tetrahedron: Asymmetry* **1995**, *6*, 2487–2494. – [6c] Isolation of a ruthenium carbenoid: S.-B. Park, N. Sakata, H. Nishiyama, *Chem. Eur. J.* **1996**, *2*, 303–306.

[7] Different catalysts in diastereoselective cyclopropanations of cyclic alkenes: [7a] A. Demonceau, A. F. Noels, A. J. Hubert, *Tetrahedron* **1990**, *46*, 3889–3896. – [7b] A. Demonceau, E. Saive, Y. de Froidmont, A. F. Noels, A. J. Hubert, *Tetrahedron Lett.* **1992**, *33*, 2009–2012. – [7c] A. Demonceau, C. A. Lemoine, A. F. Noels, I. T. Chizhevsky, P. V. Sorokin, *Tetrahedron Lett.* **1995**, *36*, 8419–8422. – [7d] A. Demonceau, C. A. Lemoine, A. F. Noels, *Tetrahedron Lett.* **1996**, *37*, 1025–1026.

[8] [8a] U. Lüning, M. Müller, *Chem. Ber.* **1990**, *123*, 643–645. – [8b] M. Müller, Dissertation, Universität Freiburg, **1991**. – [8c] U. Lüning, M. Müller, M. Gelbert, K. Peters, H. G. von Schnering, M. Keller, *Chem. Ber.* **1994**, *127*, 2297–2306. – [8d] M. Gelbert, *Dissertation*, Universität Freiburg, **1995**.

[9] M. P. Doyle, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 305–316.

[10] Preparation of ethyl diazoacetate: M. S. Newman, G. F. Ottmann, C. F. Grundmann, *Org. Synth. Coll. Vol. IV* **1963**, 424–426. The concentration of ethyl diazoacetate in dichloromethane was determined by ^{1}H-NMR spectroscopy.

[11] H. O. Krabbenhoft, *J. Org. Chem.* **1979**, *44*, 4285–4294.

[12] [12a] R. H. Rynbrandt, E. S. Cerda, F. L. Schmidt (Upjohn Co.), *Ger. Offen.* 2201358, 27 Jul 1972, *US Appl.* 106601, 14 Jan 1971; *Chem. Abstr.* **1972**, *77*, 126147m. – [12b] R. H. Rynbrandt (Upjohn Co.), *Ger. Offen.* 2200091, 27 Jul 1972, *US Appl.* 103878, 4 Jan 1971; *Chem. Abstr.* **1972**, *77*, 126148n.

[13] M. E. Alonso, S. V. Pekerar, *Magn. Reson. Chem.* **1991**, *29*, 587–593.

[96158]