

# Synthesis of Benzo[*c*]azocanones, Indeno[1,2-*b*]pyrroles and -thiophenes from Indanecarboxylates

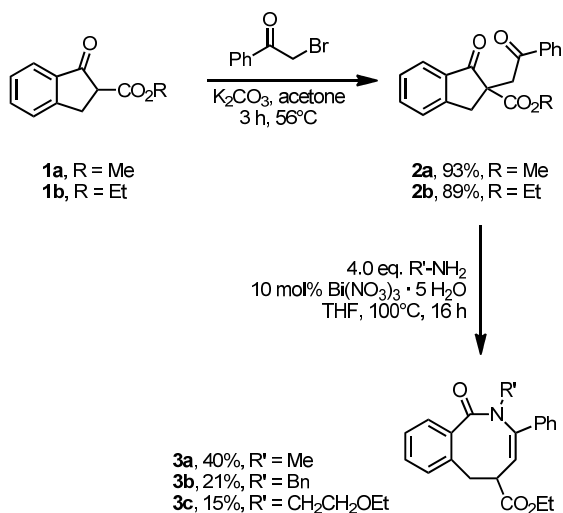
Florian Behler, Florian Habecker, Thorsten Klüner, Jens Christoffers\*

Institut für Chemie, Universität Oldenburg, Carl von Ossietzky-Str. 9–11, D-26111 Oldenburg

Benzo[*c*]azocan-1-ones could be prepared by a ring-expansion reaction of 1-indanone-2-carboxylates containing a 1,4-diketone motif with primary amines. Two diastereomeric boat conformations of these compounds were observed and could be confirmed by DFT calculations and X-ray single structure analysis. Decarboxylation of 1-indanone-2-carboxylates followed by Paal-Knorr reaction led to indeno[1,2-*b*]pyrroles and -thiophenes.

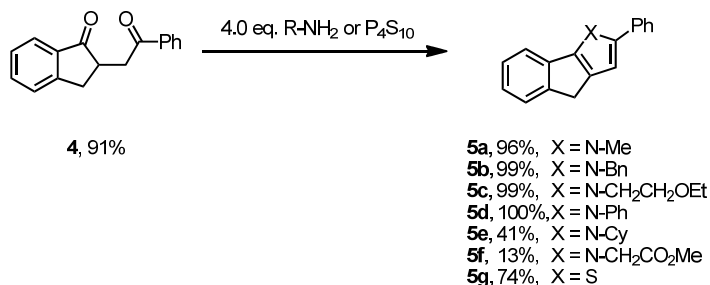
## Preparation of Benzo[*c*]azocan-1-one Derivatives

1-Indanone-2-carboxylate derivatives **1** were prepared from 1-indanone and dialkyl carbonates by literature known procedures.<sup>[1,2]</sup> Further reaction with phenacyl bromide in a nucleophilic substitution reaction gave 1-indanone-2-carboxylate derivatives with 1,4-diketone motifs **2**. Conversion of these compounds **2** with primary amines led to benzo[*c*]azocan-1-one derivatives **3** by a ring-expansion reaction in moderate yields. Because of side reactions of compound **2a** on the methyl ester function we used the ethyl ester **2b** for further reactions.



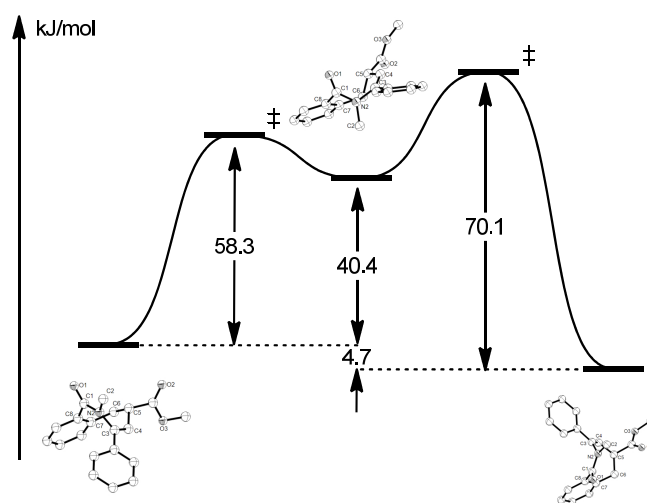
## Preparation of Indeno[1,2-*b*]pyrroles and -thiophenes

Indenopyrroles **5** were observed as byproducts when converting methyl ester **2a** with primary amines. The reaction of 1,4-diketone **4** with primary amines gave these compounds as major products. Many different primary amines could be used though the yields decreased with sterical demand. The use of phosphorus pentasulfide instead of amines led to indeno[1,2-*b*]thiophene. As a heterocyclic fluorene analogue such structures might be suitable for coordination of transition metals. Similar indenoindoles have been used to prepare titanocenes, which turned out to be powerful catalysts for olefin polymerization.<sup>[3]</sup>

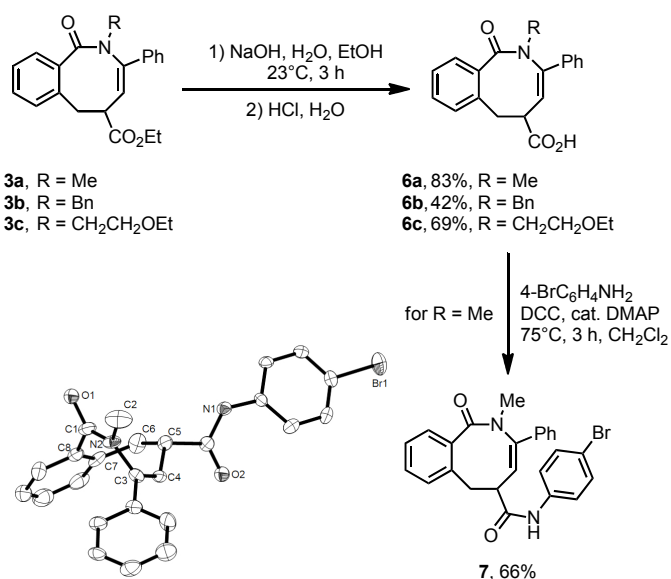


## Benzo[*c*]azocanones Exhibit Planar Chirality

All of the benzo[*c*]azocanone derivatives **4** showed a doubled set of signals in the NMR-spectra although they possess only one stereocenter. Diastereomeric conformers are observed, because the benzo-moiety defines a plane of chirality. DFT calculations on the *N*-methyl derivative **4a** showed two interconverting conformers with a maximum barrier of 70 kJ/mol.



Saponification of the ester function to the free acids **6** and further amidation with 4-bromoaniline gave amide **7**. A single crystal structure from this compound **7** confirmed the calculations at least for one conformer.<sup>[4]</sup>



[1] K. Van Emelen, T. De Wit, G. J. Hoornaert, F. Compennolle, *Org. Lett.* **2000**, *2*, 3083–3086.

[2] D. S. Brown, B. A. Marples, P. Smith, L. Walton, *Tetrahedron* **1995**, *51*, 3587–3606.

[3] J. C. Jewett, E. M. Sletten, C. R. Bertozzi, *J. Am. Chem. Soc.* **2010**, *132*, 3688–3690.

[4] F. Behler, F. Habecker, W. Saak, T. Klüner, J. Christoffers, *Eur. J. Org. Chem.* **2011**, 4231–4240.