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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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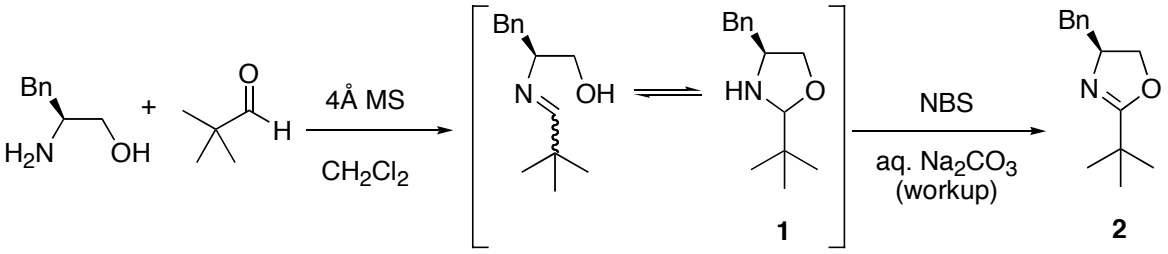
EFFICIENT OXIDATIVE SYNTHESIS OF (-)-2-*TERT*-BUTYL-(4*S*)-BENZYL-(1,3)-OXAZOLINE



Submitted by Björn T. Hahn, Kirsten Schwekendiek and Frank Glorius.[1]
Checked by Björn Gschwend and Andreas Pfaltz.

1. Procedure

*(-)-2-tert-Butyl-(4S)-benzyl-(1,3)-oxazoline (**2**).* In a two-necked, 500-mL round-bottomed flask are placed 12 g of molecular sieves (Note 1). (2*S*)-(-)-2-Amino-3-phenyl-1-propanol ((*S*)-phenylalaninol) (5.20 g, 0.0344 mol) (Note 2) and trimethylacetaldehyde (2.96 g, 0.0344 mol, 1.0 equiv) (Note 3) are dissolved in 150 mL of dichloromethane (Note 4). The resulting slightly turbid solution is added to the flask containing the molecular sieves. The flask is fitted with a glass stopper and a $CaCl_2$-filled drying tube. The reaction mixture is stirred at room temperature for 18 h (Note 5). Subsequently, the glass stopper is replaced by a thermometer, the drying tube is removed and *N*-bromosuccinimide (6.19 g, 0.0348 mol, 1.01 equiv) (Note 6) is added (Note 7). The resulting yellow-orange reaction mixture is stirred for 60 min at room temperature (Note 8). The orange mixture is filtered (Note 9) and the filtrate was transferred to a 500-mL separatory funnel where it is extracted with 50 mL of 0.5 M aq. $Na_2S_2O_3$ solution, 50 mL of sat. aq. Na_2CO_3 solution and 50 mL of water. The combined aqueous phases are then extracted with 50 mL of CH_2Cl_2 in a 500-mL separatory funnel and the combined organic phases are washed with 50 mL of brine in a 500-mL separatory funnel, then are dried over $MgSO_4$ (7 g) and are filtered through a glass funnel with a cotton wool plug. The filtrate is transferred to a 500-mL, round-bottomed flask and is treated with Celite (10 g) and the solvent is removed on a rotary evaporator under reduced pressure (Note 10). The resulting solid is transferred to a column (17 cm x 5 cm, h x d) containing 150 g of silica gel. Elution with pentane/MTBE

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(10:1 to 7:1 to 5:1) (Note 11) affords 5.57-5.72 g (74-76%) of a pale yellow liquid (Notes 12, 13, 14).

2. Notes

1. The 4 Å molecular sieves (beads, 1.7-2.4 mm, purchased from Fluka Chemie GmbH, Buchs) were activated by microwave irradiation (4 times 2 min at 700 Watts) and then cooled under an argon atmosphere in the sealed reaction flask.

2. (*S*)-Phenylalaninol was prepared by reduction of the corresponding amino acid according to the procedure of Abiko and Masamune.[2] Another convenient method has also been reported by McKennon and Meyers,[3a] as well as Gawley and Meyers in *Organic Syntheses.*[3b] Alternatively, (*S*)-phenylalaninol can be purchased from numerous vendors in enantiomerically pure form, e.g. Aldrich Chemical Co., and can be used without further purification.

3. Trimethylacetaldehyde was purchased from Aldrich Chemical Co. and was distilled prior to use.

4. Methylene chloride was of technical grade (Brenntag Schweizerhall AG) and was distilled under air prior to use. The submitters reported the use of CH_2Cl_2 distilled over CaH_2 which resulted in a slightly increased yield of 79%.

5. The stir rate was adjusted to about 200 rpm to minimize grinding of the molecular sieves.

6. *N*-Bromosuccinimide was purchased from Fluka and was recrystallized from water. The colorless plates were dried thoroughly under vacuum for 1 h.

7. The reaction flask was placed in a water bath (23 °C), and the NBS was added in portions, keeping the internal temperature below 35 °C.

8. The progress of the reaction can be followed by GC-MS analysis (see Note 13).

9. The reaction mixture was filtered through a 2 cm layer of Celite using a sintered glass funnel (porosity 3, 6.5 cm diameter).

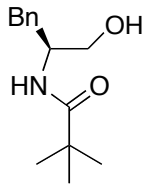
10. The pressure was reduced to 15 mmHg and the heating bath kept at 50 °C. Upon addition of the eluent to the crude product, the formation of a sticky insoluble solid was observed. The crude product was therefore adsorbed on Celite.

11. Flash chromatography: Fluka silica gel 60 (0.040-0.063 mm). Pentane and MTBE were of technical grade (Brenntag Schweizerhall AG) and distilled prior to use. Three different pentane/MTBE mixtures were used successively: 750 mL of a 10:1, 1600 mL of a 7:1 and 1100 mL of a 5:1 mixture. The solvent was collected in 250 mL fractions (from the start) and the product was obtained in fractions 4 to 12.

12. The product is >95% pure, as judged by ^{1}H NMR spectroscopy. If necessary it can be further purified by Kugelrohr distillation (100 °C, 0.06 mmHg, > 95% yield) to give **2** as a colorless liquid (Note 13).

13. Oxazoline **2** displays the following physicochemical data: R_f = 0.3 (0.2 mm silica gel on plastic foil, pentane/MTBE 5:1). $[\alpha]_D^{20}$ = –35.8 (*c* 1.39, $CHCl_3$ (0.75% EtOH)), [lit.[4] $[\alpha]_D^{23}$ = –38.2 (*c* = 1.31, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (s, 9 H), 2.63 (dd, 1 H, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 8.6 Hz), 3.09 (dd, 1 H, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 4.4 Hz), 3.96 (dd, 1 H, $^{2}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 6.8 Hz), 4.11 (dd, 1 H, $^{2}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 9.3 Hz), 4.35 (dddd, 1 H, $^{3}J_{HH}$ = 9.2 Hz, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 4.5 Hz), 7.16 – 7.23 (m, 3 H), 7.24 – 7.31 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ*:* 27.7, 33.0, 41.4, 66.8, 71.3, 126.3, 128.3, 129.4, 137.7, 174.2. IR (NaCl) cm^{-1}: 3062, 3028, 2970, 2928, 1949, 1881, 1807, 1658, 1604, 1482, 1456, 1393, 1361, 1284, 1219, 1140, 1097, 1026, 979, 926, 749, 703; GC-MS: t_R (**2**) = 11.6 min, EI *m/z* (%): 126 (100), 91 (18), 70 (46), 57 (56), 41 (31); t_R (**1**) = 13.5 min, EI *m/z* (%): 188 (23), 162 (76), 128 (100), 117 (53), 91 (79), 57 (15), 41 (43) (Marcherey-Nagel Optima 5 5% PhMeSi, 25 m x 0.2 mm, 0.35 µm film, 1.4 bar He, 100 °C/5 min/10 °C min^{-1}/ 270 °C/10 min); CSP-HPLC: t_R = 10.1 min (Daicel, Chiralpak AS, 25 cm, heptane/2-propanol, 400:1, 20 °C, 0.5 mL/min, 220 nm; UV: l_{max1} = 208 nm, l_{max2} = 259 nm. Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.24; H, 8.80; N, 6.42.

14. The lability of oxazolines strongly depends on their substitution pattern. The product **2** is moisture sensitive. Standing at room temperature in a closed flask led to the formation and precipitation of a small amount of the corresponding hydrolysis product, amido alcohol **3** (a colorless, crystalline solid), within a few weeks. Storing at low temperature and exclusion of moisture is therefore recommended.



3

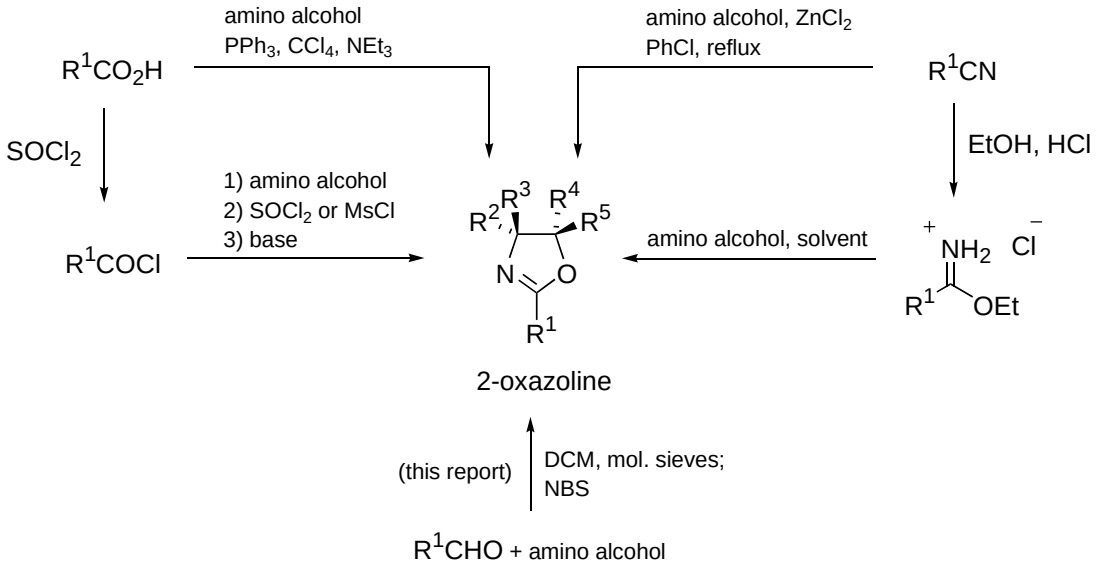
Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Chiral 2-oxazolines (IUPAC: 4,5-dihydrooxazoles)[5] have attracted increasing interest in the last decades, because of their multiple roles in biologically active compounds,[6] chiral ligands for asymmetric catalysis[7] like bisoxazolines and phosphinooxazolines and many other areas of chemistry.[8] Consequently, numerous methods have been developed for the efficient synthesis of oxazolines.[5] Most often, amino alcohols are reacted with either acid chlorides,[5] carboxylic acids,[9] nitriles[10] or imino ethers[11] (Scheme 1). However, despite their broad applicability, some disadvantages of these methods can be identified. Starting from acid chlorides, three steps are needed to form the oxazoline products. The direct use of carboxylic acids under Appel conditions most often leads to the formation of a number of byproducts requiring elaborate purification steps. Starting from nitriles, rather forcing conditions (Lewis acid catalysis in refluxing chlorobenzene) have to be used. Finally, imino ethers are generally not commercially available and have to be prepared in an additional step, either by using primary amides in conjunction with Meerwein's salt or from nitriles employing HCl gas in an alcohol.

Scheme 1



Several oxidative methods for the formation of benzoxazoles,[12] benzimidazoles[12] and imidazolines[13] from aldehydes are described. Thus, recently, we and others have developed complementary, oxidative procedures for the formation of 2-oxazolines starting from the corresponding aldehydes.[14,15] In a typical procedure, (-)-2-*tert*-butyl-(4*S*)-benzyl-(1,3)-oxazoline can be formed from pivaldehyde and L-phenylalaninol using NBS as the oxidizing agent. Under optimized conditions, the in situ formation of the oxazolidine **1** is followed by the addition of one equivalent NBS, resulting in the formation of the oxazoline hydrobromide salts. Following the standard procedure, this salt was deprotonated subsequently using an aqueous basic work-up, also allowing for the separation of the oxazoline from the water-soluble succinimide byproduct. The product **2** was obtained with unchanged high enantiomeric excess of above 99%, as determined by HPLC using a chiral column (see above).

The substrate scope of this transformation is rather broad.[14a] Differently substituted aliphatic and aromatic aldehydes and various 1,2-aminoalcohols can be successfully employed (Table 1). A number of different benzaldehyde derivatives provide oxazolines in good yields. However, electron-rich aromatic aldehydes like salicylaldehyde, 4-hydroxybenzaldehyde, or pyrrole-2-carbaldehyde are unsuitable, since they were found to undergo an undesired electrophilic aromatic bromination. Nevertheless, moderately electron-rich aldehydes like methyl-substituted benzaldehydes are suitable substrates, although the reactions proceed with a significantly reduced rate (entries 2,3). Benzaldehyde derivatives bearing electron-withdrawing groups (entries 4-6,9) and other electron-poor

substrates (entries 7,8) are generally good substrates. However, due to the increased acid-sensitivity of the oxazolines obtained from these latter substrates, slightly modified reaction conditions were required. Namely, these reactions were run in the presence of a solid inorganic base (K_2CO_3 or K_3PO_4) in toluene as the solvent. Aliphatic aldehydes were also used with good success (entries 16-20).

No limitation in the scope of the amino alcohol component was found. Unsubstituted (entry 9), mono- (entries 1-8,10,11,16-18) or disubstituted (entries 12-15,19,20) amino alcohols were converted into the oxazoline products with the method described. In addition, it seems that the enantiomeric purity of enantiomerically pure aminoalcohols (entries 10-13, 16-19) generally remains intact.[14a] This can be deduced from the following observations: First, in cases where values for optical rotation of optically pure 2-oxazolines were published in the literature, these values were found to be comparable to the ones obtained for the products of this study (entries 10-13,16,17). The deviations observed were less than 4% for these samples. Second, in cases where the oxazoline product bears two stereocenters an epimerization would lead to a mixture of diastereomers (entries 12,13,18,19). However, GC-MS and ^{1}H NMR analysis of these products revealed only a single diastereomer, indicating that no loss of enantiomeric purity had occured. Most importantly, however, for (-)-2-*tert*-butyl-(4*S*)-benzyl-(1,3)-oxazoline, the title compound of this publication, the enantiomeric purity was unequivocally established by an HPLC measurement using a chiral column.

In conclusion, this one-pot synthesis is characterized by mild reaction conditions, broad scope, high yield and its preparative simplicity.

Table 1. Oxidative formation of substituted oxazolines starting from various aldehydes and aminoalcohols.

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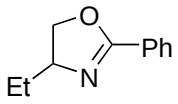
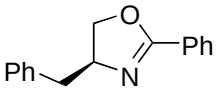
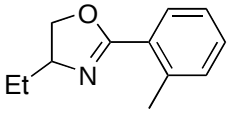
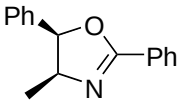
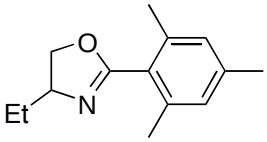
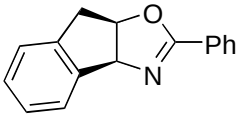
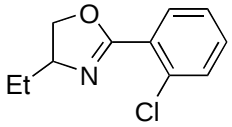
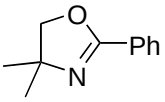
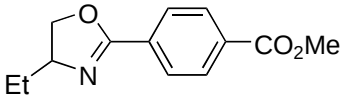
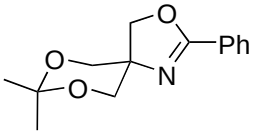
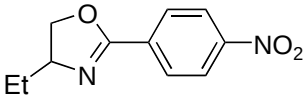
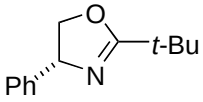
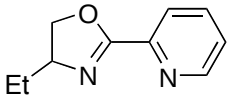
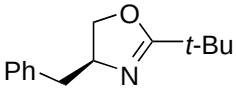
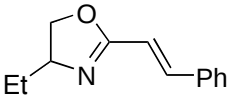
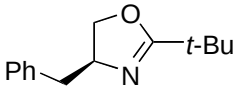
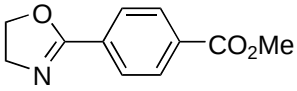
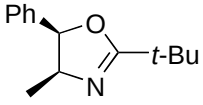
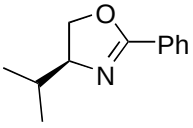
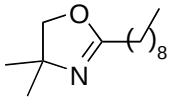
1		91	11		80
2		93	12		81
3[b]		42	13		65
4[b]		76	14		82
5		83	15		88
6[b]		68	16		89
7[b]		77	17		85
8[b]		30	18[c]		76
9		88	19		91
10		70	20[c]		75

[a] General reaction conditions: **3** (1 mmol), CH_2Cl_2 (6 mL), **2** (1 mmol), mol. sieves (4 Å, 1.5 g), 14 h, rt; NBS (1 mmol), 0.5 h, rt. [b] Modified reaction conditions: **3** (1 mmol), toluene (6 mL), **2** (1 mmol), mol. sieves (4 Å˘, 1.5 g), 14 h, rt; K_3PO_4 (3 mmol), NBS (1 mmol), 1.5 h, rt.

[c] Large scale reaction according to the procedure of this publication.

1. Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstraße 40, 48149 Münster, Germany; glorius@uni-muenster.de
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14. (a) Schwekendiek, K.; Glorius, F. *Synthesis* **2006**, 2996. (b) Sayama, S. *Synlett* **2006**, 1479.

15. In addition to the methods reported in references 13, a few less practical oxidative oxazoline formations appeared, requiring undesirable substrates like 2-azidoethanol derivatives, being unselective or having a very limited substrate scope: (a) Intramolecular redox reaction of 2-formylbenzaldehyde: Shipchandler, M. T. *J. Heterocyclic. Chem.* **1977**, *14*, 305-306. (b) Reaction of aldehydes with 1,2-hydroxyazides: Badiang, J. G.; Aubé, J. *J. Org. Chem.* **1996**, *61*, 2484-2487. (c) Synthesis of 3-oxazolines (with the formation of 2-oxazoline as minor byproducts): Favreau, S.; Lizzani-Cuvelier, L.; Loiseau, M.; Duñach, E.; Fellous, R. *Tetrahedron Lett.* **2000**, *41*, 9787-9790.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

(-)-2-*tert*-Butyl-(4*S*)-benzyl-(1,3)-oxazoline: 4,5-Dihydrooxazole, (4*S*)-benzyl, 2-*tert*-butyl; (75866-75-0)

(2*S*)-(-)-2-Amino-3-phenyl-1-propanol: Phenylalaninol: Propanol, 2-amino-, 3-phenyl, (*S*); (3182-95-4)

Trimethylacetaldehyde: Pivaldehyde: Propanal, 2,2-dimethyl; (630-19-3)

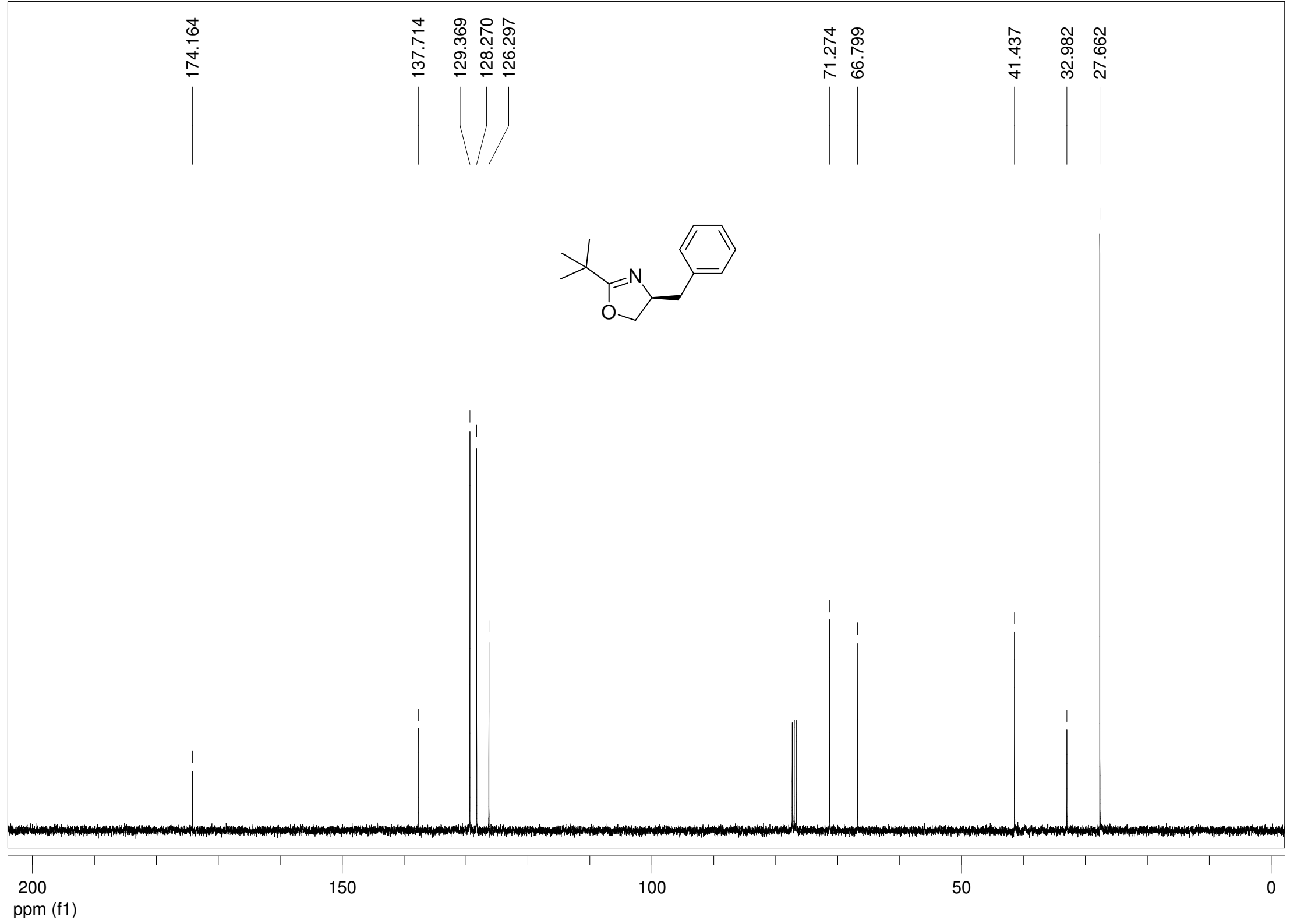
N-Bromosuccinimide; (128-08-5)

Frank Glorius was educated in chemistry at the Universität Hannover, Stanford University (Prof. Paul A. Wender), Max-Planck-Institut für Kohlenforschung and Universität Basel (Prof. Andreas Pfaltz) and Harvard University (Prof. David A. Evans). In 2001 he began his independent research career at the Max-Planck-Institut für Kohlenforschung in Germany (Mentor: Prof. Alois Fürstner). In 2004 he became Assoc. Prof. at the Philipps-Universität Marburg and since 2007 he is a Full Prof. for Organic Chemistry at the Westfälische-Wilhelms-Universität Münster, Germany. He is a dedicated teacher and his research program focuses on the development of new concepts for catalysis and their implementation in organic synthesis.

Björn Hahn was born in Braunschweig (Germany) in 1980 and studied chemistry at the Technische Universität Braunschweig where he obtained his diploma in 2005. He joined the group of Prof. Frank Glorius at the Philipps-Universität Marburg in 2006 as a Ph.D. student. Currently he is working at the Westfälische-Wilhelms-Universität Münster on new catalytic reactions in organic synthesis.

Kirsten Schwekendiek was born in Emden (Germany) in 1981. She studied Chemistry at the Philipps-Universität of Marburg and the University of Melbourne. In 2006 she obtained her diploma degree from Marburg University, where she carried out her graduate work in the field of oxazoline synthesis under the direction of Prof. Frank Glorius. Currently she is a Ph.D. student in the group of Prof. Thisbe K. Lindhorst at the Christian-Albrechts-Universität of Kiel, dealing with the synthesis of photoswitchable glycoconjugates and their evaluation in the field of Biological Chemistry.

Björn Gschwend was born in Basel (Switzerland) in 1980. He studied Chemistry at the University of Basel where he obtained his diploma in 2005 under the supervision of Prof. Edwin C. Constable and Prof. Catherine E. Housecroft. He joined the group of Prof. Andreas Pfaltz in fall 2005 as a Ph.D. student and is currently working on the synthesis of new chiral ligands for metal-catalyzed reactions.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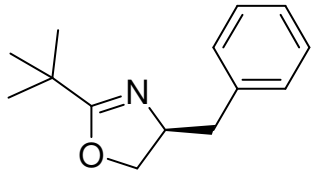
100
50
0
ppm (f1)



before distillation

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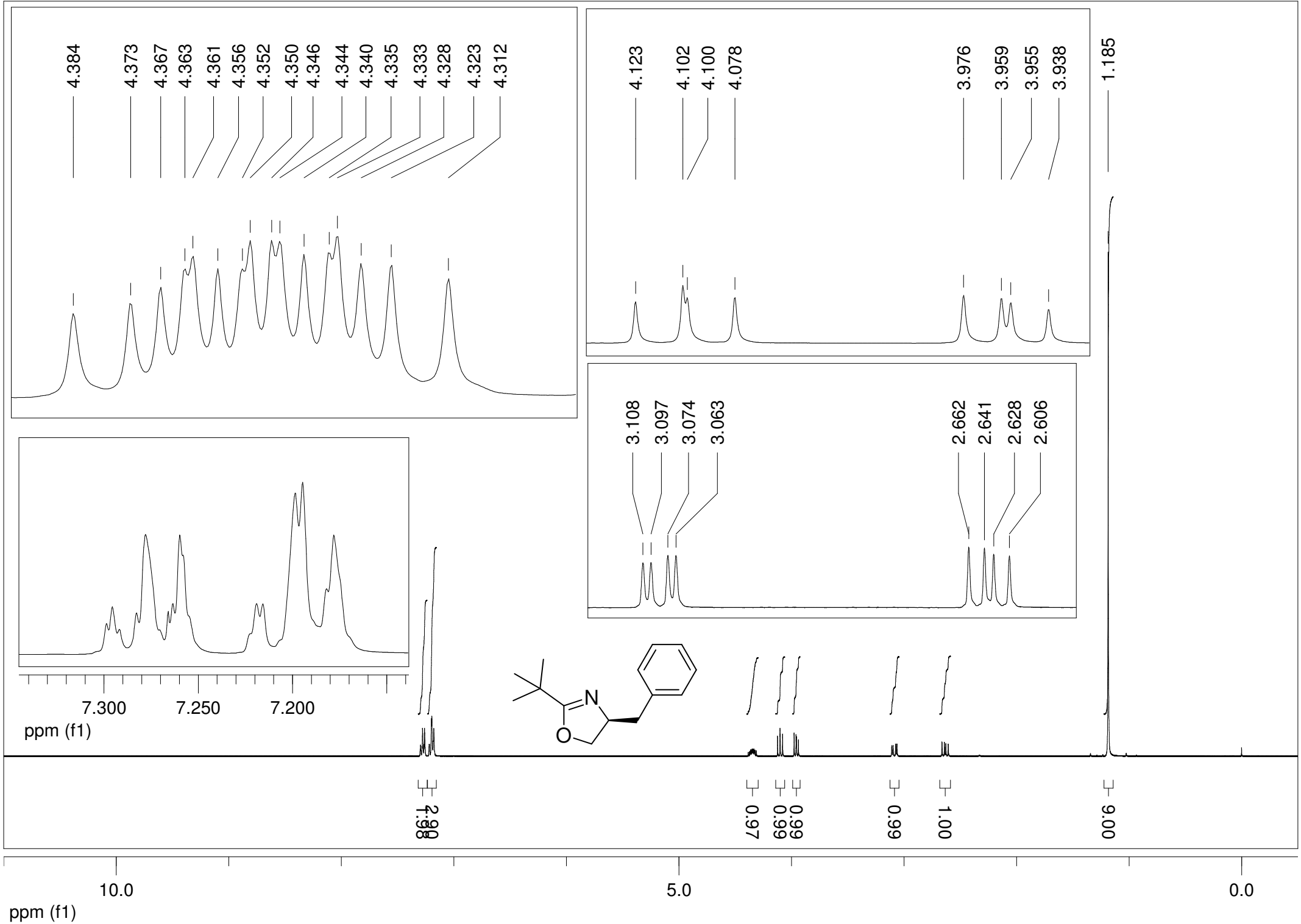
1.00
1.02
1.01
9.21

5.0
0.0

ppm (f1)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4.328
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7.250
7.200
ppm (f1)
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O
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1.98
0.97
0.99
0.99
0.99
1.00
9.00
10.0
5.0
0.0
ppm (f1)