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A Convenient Synthesis of Optically Pure Dimethyl 1,1'-Binaphthalene-2,2'-dicarboxylate from 1,1'-Binaphthalene-2,2'-diol

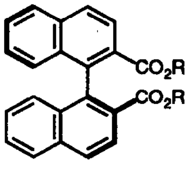
Tetsuo Ohta, Masato Ito, Kohji Inagaki, and Hidemasa Takaya*

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

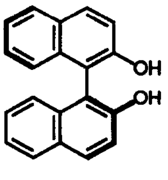
Abstract: *Optically pure dimethyl 1,1'-binaphthalene-2,2'-dicarboxylate has been prepared by methoxycarbonylation of ditriflate of 1,1'-binaphthalene-2,2'-diol catalyzed by Pd(OAc)$_2$—dppp—N,N-diisopropylethylamine in the presence of methanol under CO atmosphere in 83% yield.*

Optically active 1,1'-binaphthalene-2,2'-dicarboxylic acid and its esters (**1**) have been attracting considerable attention as chiral stationary phases for liquid chromatography.[1] The acids (*R*)- and (*S*)-**1a** are also important not only as chiral ligands for palladium catalyzed enyne cyclization,[2a] but also as synthetic intermediates for various chiral auxiliaries.[2b—e] In spite of their high utility, there have been very few efficient synthetic methods for **1**. Generally, **1a** has been obtained by optical resolution[3] of racemate prepared through several steps including Ullman coupling reactions.[2b,4] Herein we report a facile synthesis of optically pure dimethyl 1,1'-binaphthalene-2,2'-dicarboxylate (**1b**) from optically active 1,1'-binaphthalene-2,2'-diol (**2**). The starting (*R*)- and (*S*)-**2** are easily accessible because optical resolution of (±)-**2** via a complex formation with tartaric acid derivatives has been put to practical use.[5]

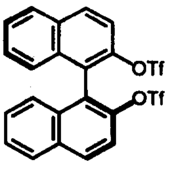
The ditriflate (*S*)-**3**[6] was prepared in 99% yield by the treatment of (*S*)-**2** with triflic anhydride (Tf$_2$O) and 2,6-lutidine in the presence of a catalytic amount of 4-dimethylaminopyridine in dichloromethane.[7] Methanol (7.70 mL, 190 mmol) and *N,N*-diisopropylethylamine (2.91 mL, 16.7 mmol) were added to a solution of (*S*)-**3** (2.09 g, 3.80 mmol) in DMSO (21.0 mL). The resulting solution was degassed by freeze-pump-thaw cycles and transferred to Pd(OAc)$_2$ (128 mg, 0.57 mmol) and 1,3-bis(diphenylphosphino)propane



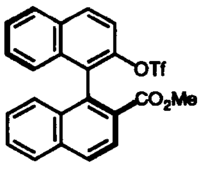
(*S*)-**1a** ; R = H
(*S*)-**1b** ; R = Me



(*S*)-**2**



(*S*)-**3**



(*S*)-**4**

(dppp) (235 mg, 0.57 mmol) placed in a 100-mL pressure bottle. Then the reaction mixture was stirred under CO atmosphere at 80 °C for 72 h, keeping the CO pressure at 1.5 kg/cm^2.[7] The product obtained after dilution of the reaction mixture with brine and extractive work-up with ether was recrystallized from methanol to give 311 mg (26% yield) of (*S*)-**1b**. Concentration of the filtrate followed by silica-gel column chromatography of the residue afforded additional (*S*)-**1b** (861 mg, 57% yield) accompanied by methyl 2-trifluoromethanesulfonyloxy-1,1'-binaphthalene-2'-carboxylate ((*S*)-**4**) (9% yield) and methyl 1,1'-binaphthalene-2-carboxylate-2'-ol (7% yield).[8] Enantiomeric excess of the product (*S*)-**1b** was 100% as determined by HPLC analysis (DAICEL CHIRALCEL OD column, 2-propanol—hexane (1:9), 1 mL/min, (*R*)-**1b**: 19 min; (*S*)-**1b**: 30 min).

Methoxycarbonylation of the ditriflate **3** under similar reaction conditions (in DMSO, 6—15 mol% Pd(OAc)$_2$—dppp, 14 equivs. NEt$_3$, and 494 equivs. MeOH relative to **3**, CO 1.0 kg/cm^2, 70 °C, 18—20 h) has been reported previously.[9] However, only monomethoxycarbonylation product **4** was isolated and no trace of **1b** was obtained. The present method uses relatively small amount of bulky tertiary amine (*N,N*-diisopropylethylamine, 4.4 equivs. to the substrate **3**), which seems important to realize the double methoxycarbonylation effectively. Actually, increase (6.6 equivs.) or decrease (2.2 equivs.) in the amount of the amine resulted in much lower conversion of the intermediary **4** to **1b**. In addition, subtle tuning of other reaction conditions as described above is also crucial for obtaining **1b** in high yield.

Acknowledgments

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8. The yield depends on the purity of the solvent and reagents used. Methanol was distilled over magnesium methoxide under argon. *N,N*-Diisopropylethylamine and DMSO were dried over molecular sieves (MS-4A) and distilled under argon. Commercial samples of dppp and Pd(OAc)$_2$ were used as obtained.
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