

Synthesis of a BINOL Derivative Fluorescent Sensor S-N,N'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine)

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Abstract. Optically active fluorescent sensor containing a 1,1'-binaphthyl core and N,N'-diamine was synthesized and characterized by NMR spectroscopy. S-N1,N1'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine) was synthesized by coupling reaction with Pd(dppf)Cl₂ and Cu(phen)Cl₂.

Introduction

Fluorescent probe is a kind of molecules which have character fluorescent from ultraviolet to near-infrared light area, and fluorescent property varies in some degree with the change of the environment. As the advantages of highly sensitivity, highly selectivity and convenient operation, fluorescent probe is widely used for detecting of cation, anion and neutral molecule [1-6]. Optically active fluorescent sensors are also having increased attentions because they can provide real time analysis for the enantiomeric composition of chiral compounds and enhance the sensitivity in the detection of chiral substrates [7-15]. 1-(2-hydroxynaphthalen-1-yl)naphthalen-2-ol, popularly known as BINOL, has the phenomenon of atropisomerism, one stereoisomerism finding in systems where the rotation around a single bond which is restricted to yield different stereoisomers. Among the enantioselective fluorescent sensors synthesized, which based on chiral structure of 1,10-bi-2-naphthol (BINOL) have been highly investigated, and a few highly enantioselective fluorescent sensors have been found for the recognition of R-hydroxycarboxylic acids, chiral amines, amino acids and amino alcohols.

Because BINOL and its derivatives have the obvious different characteristic of special rigid structure, easy modification and the size of angle between two naphthalene ring freely adjusted, they are usually used to design and synthesis of that more efficient fluorescent probes which result in gaining increasing attention. Based on the versatile backbone of 1,1'-binaphthol, one new chiral fluorescent probe S-N1,N1'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine) which may use to detect metal ion was synthesized in this article. It provides a new way of thinking and a certain foundation for the chiral binaphthol fluorescent probes study.

Experimental Section

Characterization: ¹H NMR and ¹³C NMR spectra were collected on a Bruker AM-400WB spectrometer in chloroform-d as solvent and tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained by using a Bruker Daltonics Autoflex II TOF system. Materials: CH₃I (99.8%, anhydrous), dimethyl sulfoxide (DMSO), DCM and Br₂ were purchased from Aldrich. Cu(phen)Cl₂, Pd(dppf)Cl₂, Na₂S₂O₃, was purchased from J&KCHEMICAL Co. All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, and Guoyao) and used without further purification unless stated otherwise. All solvents were distilled over appropriate drying agent(s) prior to use and were purged with nitrogen.

Synthesis of (S) -6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol

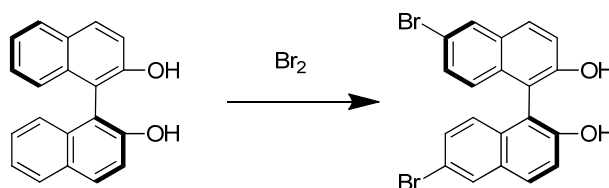


Figure 1 the synthesis of *S*-6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol

To a solution of *S*-[1,1'-binaphthalene]-2,2'-diol (2.86 g, 10 mmol) in DCM (50 mL) was added Br₂ (1.4 mL, 27.3 mmol) dropwise at -78°C. This mixture was stirred for 3 hours. Then the reaction liquid natural at room temperature and continue stirred for 30 minutes, then add Na₂S₂O₃ saturated solution, stirred overnight. The organic layer was separated, and the aqueous phase was extracted with DCM three times, the organic phase was extracted with saturated brine 3 times and dried over Na₂SO₄, concentrated to the presence of a solid solution and then added a large number of petroleum ether, which was a large number of solid precipitation, filtered and washed with petroleum ether. Finally the white solid product was obtained (3.85 g, yield: 86%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.20 (s, 2H), 7.96 (d, 2H, J = 8.0 Hz), 7.45–7.38 (m, 4H) 6.94 (d, 2H, J = 8.0 Hz), 5.35 (s, 2H)

Synthesis of *S*-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene

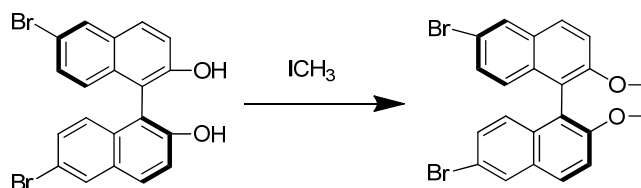


Figure 2 the synthesis of *S*-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene

To a solution of *S*-[1,1'-binaphthalene]-2,2'-diol (2.86 g, 10mmol) in acetone (15 mL) was added K₂CO₃ (1.87 g, 13.5 mmol) and CH₃I (1.68mL, 27mmol). The mixture was stirred and heated to reflux for 12 hours. The liquid was cooled to 25°C and then CH₃I (0.8 mL, 12.9 mmol) and H₂O (7.5 mL) was added to the solution. The reaction was stirred for 8 hour. Filtered and compound was washed with petroleum ether and water. After dried over MgSO₄, light brown solid (1.79 g, yield: 84%) was obtained. ¹H NMR (400 MHz, CDCl₃, TMS): δ ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.20 (s, 2H), 7.96 (d, 2H, J = 8.0 Hz), 7.45–7.38 (m, 4H) 6.94(d, 2H, J = 8.0 Hz), 3.86(s, 6H).

Synthesis of *S*-N1,N1'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine)

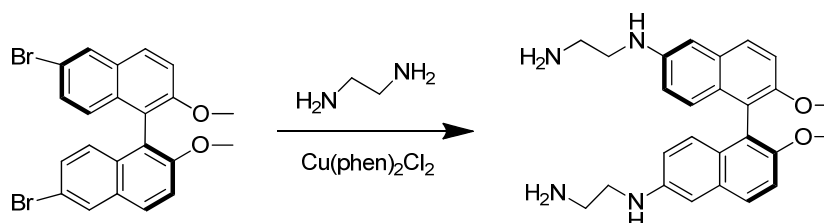


Figure 3 the synthesis of *S*-N1,N1'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine)

To a solution of CuCl₂ (5.6 mg, 0.04 mmol) and 1,10- phenanthroline (15.3 mg, 0.08 mmol) and 1,10- phenanthroline (15.3 mg, 0.08 mmol) in DCM (2 mL) . This mixture was stirred for 1 hour at 50 °C. Then (*S*) -6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (100mg, 0.2mmol) and Pd(dppf)Cl₂ (30 mg, 0.04 mmol) in DMF (10 mL) were added to the mixture. The reaction solution was heated to 120 °C to clarify, then ethane-1,2-diamine (2 mL) was added. The mixture was stirred

overnight. The organic phase was extracted with DCM and saturated brine. The combined organic layers were dried over MgSO_4 . The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel, finally yellow green solid product was obtained (25.1 mg yield: 27.5%). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.15 (s, 2H), 7.72 (d, J = 8.9 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.85 (s, 2H), 6.61 (d, J = 8.3 Hz, 2H), 5.96 (s, 2H), 5.30 (s, 2H), 3.69 (s, 6H), 3.57 (d, J = 5.4 Hz, 4H), 3.37 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.70 (s), 152.73 (s), 143.72 (s), 130.77 (s), 128.17 (s), 127.11 (s), 120.54 (s), 118.58 (s), 115.49 (s), 104.90 (s), 57.29 (s), 43.85 (s), 37.70 (s).

Summary

We have developed an efficient method for the synthesis of binaphthyl derivatives bearing both OH functionalities (in the 2,2' and 6,6' positions of the aromatic skeleton). The key step was the coupling reaction by $\text{Pd}(\text{dppf})\text{Cl}_2$ to synthesis the *S*-N1,N1'-(2,2'-dimethoxy-[1,1'-binaphthalene]-6,6'-diyl)bis (ethane-1,2-diamine).

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