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ORIGINAL PAPER

Synthesis of 1,1′-binaphthyl derivatives by Miyaura-Suzuki cross-coupling in cholesteric liquid crystal phase

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Abstract We synthesized 1,1′-binaphthyl and 2-substituted-1,1′-binaphthyl by the Miyaura-Suzuki cross-coupling reaction in cholesteric liquid crystal (CLC) media. The ^{1}H and ^{13}C NMR and UV–Vis absorption spectra of the compounds thus prepared were examined. The liquid crystallinity of the CLC media before and after the reaction was confirmed by differential scanning calorimetry, polarizing optical microscopy, and visual contact in order to characterize the reaction in a CLC phase.

Keywords Cholesteric liquid crystal · Chiral · Binaphthyl · Miyaura-Suzuki cross-coupling

Introduction

The Miyaura-Suzuki cross-coupling is one of the most effective reactions in organic chemistry, since it is an extremely useful and environmentally friendly method for constructing biaryl structures [1, 2]. The Miyaura-Suzuki coupling offers advantages in that the organoboronic acids are air-stable, display low toxicity, and are tolerant of a variety of functional groups during the reaction [3]. Extensive investigations have allowed the performance of various palladium salts, ligands, bases, and solvent systems in this reaction to be evaluated and optimized [4, 5].

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The binaphthyl derivative is known to have axial chirality due to the restricted rotation around the carbon–carbon bond between the 1 and 1′ positions of the binaphthyl rings. The racemization half-life of 1,1′-binaphthyl is 14.5 min at 50 °C ($\Delta G^{\neq}$ = 98.4 kJ/mol) [6]. The chiral conformational stability depends on the bulkiness of the substituent. The introduction of substituents into the 2,2′-position of the binaphthyl compounds provides stability to the chiral configuration [6]. They have been extensively utilized in asymmetric catalysis, molecular recognition, chiral dopant, and synthesis of new materials [6–8].

A cholesteric liquid crystal (CLC) is a chiral photonic crystal with a periodic helical structure of rod-shaped molecules, which exhibit a selective reflection band [7, 9]. The addition of a small amount of chiral molecules to nematic LC can induce the CLC architecture [7, 10]. The chiral molecules containing binaphthyl moiety are reported as powerful inducers due to the axial chirality [7, 11]. The dihedral angle between the two naphthalene rings in a binaphthyl derivative plays a key role in their cholesteric induction behaviors such as helical-pitch and handedness of the induced CLC phase. CLCs have been used as chiral media for asymmetric synthesis of both small molecules and polymers [7, 12–16]. Induction of optical activity in achiral molecules by dissolution in a CLC was reported previously [12]. Verbit et al. [12] concluded that a particularly strong interaction between the solute and solvent molecules may induce optical activity in the product. Recently, we reported synthesis of optically active polymers from achiral monomers using CLC as a reaction solvent [9, 10, 14–16]. During the polymerization reaction, the CLC medium acted as a "one-handed chiral organized matrix" consisting of chiral directors that induced one-handed helical conformation in the polymer. The CLC

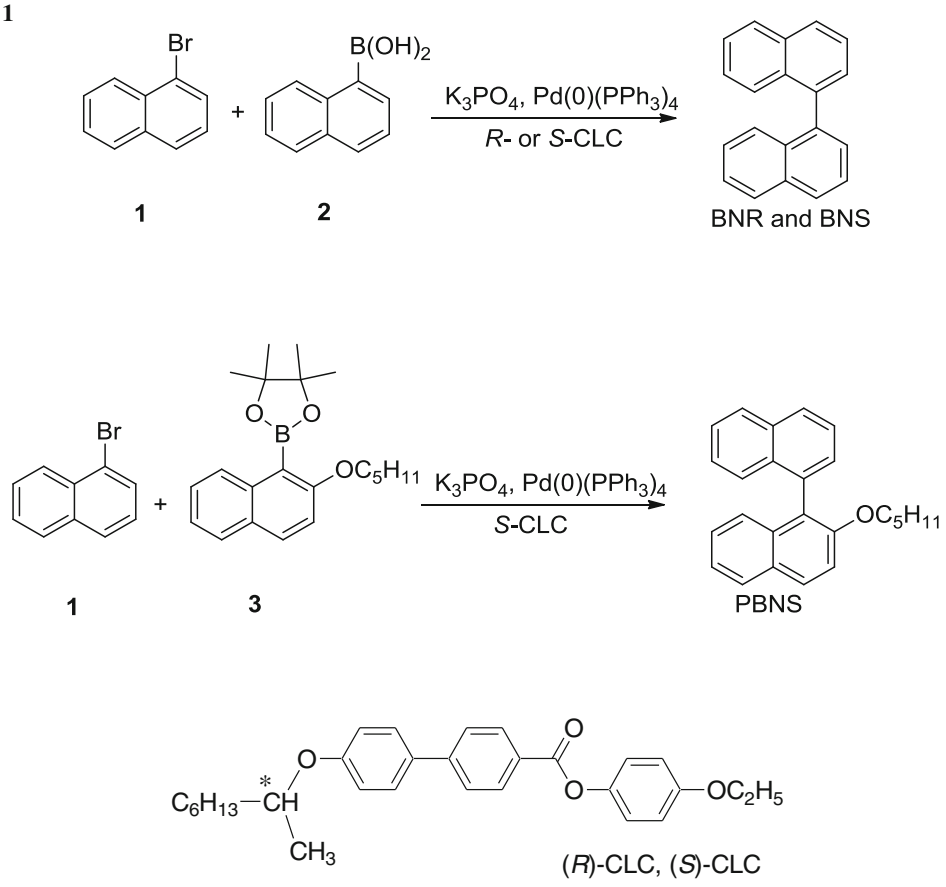
phase exists over a certain temperature range and produces optical activity in polymers depending on an excluded volume effect between the monomers and CLC molecules [15]. This study represents the very first report of the Miyaura-Suzuki coupling reaction in CLC media. Its results may present a possibility of conducting condensation reactions in an ordered environment.

Results and discussion

A series of binaphthyl derivatives (BNR, BNS, and PBNS) were synthesized by the Miyaura-Suzuki coupling reaction in CLC media (Scheme 1). 2,2′-Bis(pentyloxy)-1,1′-binaphthyl was not obtained under the same conditions due to the steric hindrance. The chemical structures of BNR, BNS, and PBNS were confirmed by ^{1}H and ^{13}C NMR spectroscopy and GC–MS analysis.

Liquid crystallinity of the CLC media was examined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Figure 1 (top) shows the DSC curves of the CLC reaction mixture of BNS (a before and b after the reaction). These DSC curves indicated that the reaction mixture exhibited the presence of a CLC phase in the temperature range of 99–133 °C. The CLC media of PBNS showed a CLC phase from 94 to 120 °C. The POM images of several CLC reaction mixtures are shown in Fig. 1 (bottom). Figure 1c, e show the POM images for the reaction mixture of BNS and PBNS containing CLC solvent, tripotassium phosphate, aryl bromide, and arylboronic acid precursors (before the reaction). Panels d and f of Fig. 1 show the POM images of the reaction mixture of BNS and PBNS containing CLC solvent, tripotassium phosphate, $Pd(PPh_3)_4$, reaction products, and unreacted aryl bromide and arylboronic acids (after the reaction). Figure 1c–f suggested that the reaction mixtures displayed the Grandjean texture typically observed in a CLC phase. The DSC curves and POM images support the fact that the reaction was performed in a CLC phase. Besides, the liquid crystallinity of the reaction mixture was checked by visual observations during the reaction. The selective light reflection derived from a CLC phase was confirmed in the CLC media of BNR, BNS, and PBNS at the reaction temperature (before and after the reaction). These results indicated that the entire reaction was performed in CLC phases. The addition of a base compound

Scheme 1



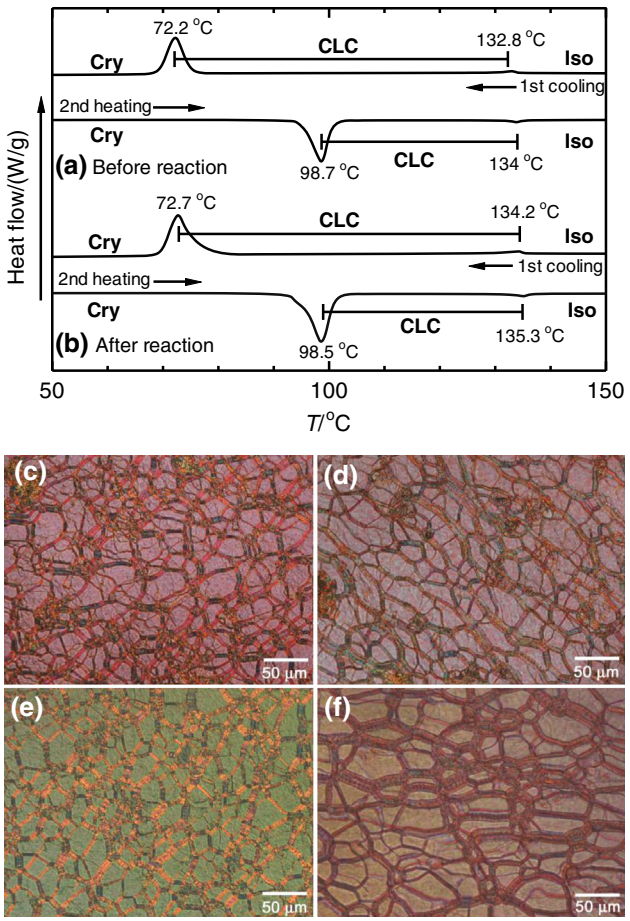


Fig. 1 (*Top*) DSC results for CLC media of BNS. **a** Before the reaction (containing (*S*)-CLC, **1**, **2**, and tripotassium phosphate); **b** after the reaction (containing (*S*)-CLC, **1**, **2**, tripotassium phosphate, and $Pd(PPh_3)_4$). (*Bottom*) polarizing optical microscopy images of the CLC mixture of BNS at 100 °C (**c**) and PBNS at 96 °C (**e**) before the reaction containing (*S*)-CLC, tripotassium phosphate, precursor aryl bromide, and arylboronic acid. CLC reaction mixtures of BNS at 100 °C (**d**) and PBNS 96 °C (**f**) after the reaction containing (*S*)-CLC, tripotassium phosphate, $Pd(PPh_3)_4$, products, unreacted aryl bromide, and arylboronic acids

decreased the stability of a CLC phase. In order to preserve the CLC phase of the CLC media, a minimal amount of base was employed in the reaction, resulting in a relatively low product yield. The GC–MS spectrum of PBNS showed two prominent ions at $m/z = 340$ and 270. The intense fragment at $m/z = 270$ corresponds to a loss of alkyl chain.

UV–Vis absorption spectra of BNR and BNS were obtained in *n*-hexane solution (Fig. S1). The absorption bands in the 210–230 nm region correspond to the π-π* transitions of the binaphthyl units. At the present stage, we could not confirm chiroptical activity of the product prepared in the CLC. The enantiomeric excess of the compound thus prepared in the CLC was not significant for chiroptical activity. This can be due to the fact that the twist of the directors between neighboring molecules in the CLC matrix is quite small. A sequential twist in one direction (left or right) is integrated to form a helical aggregation structure as a super molecular form. The molecules synthesized in this study received a small twist in the CLC at a molecular level resulting in the lack of definitive chiroptical activity. However, the helical twisting of CLCs may result in binaphthyl displaying axial chirality. At the present stage, we succeeded in performing the aromatic condensation reaction in the CLC. Furthermore, improved affinity of the naphthyl compounds towards the CLC is required for a transcription of chirality from the CLC media. Introduction of bulky rod-like aromatic groups may result in enhanced affinity towards CLC media, which may be expected to be preferable for chiral transcription from central chirality of CLCs to axial chirality.

Conclusion

A series of binaphthyl derivatives were synthesized for the very first time by the Miyaura-Suzuki cross-coupling reaction in CLC media, which may open a new possibility for conducting reactions in liquid crystals as solvents. The amount of base compound was limited due to the destabilization of the CLC phase, resulting in a relatively low yield of products. To improve the product yield and stability of the CLC phase, the affinity between the CLC molecule and base compound needs to be improved.

Experimental

1-Naphthaleneboronic acid (TCI: Tokyo Chemical Industry Co., Ltd., 97 %), 1-bromonaphthalene (TCI, 95 %), 1-bromopentane (TCI, 98 %), bis(pinacolato)diboron (TCI, 97 %), tetrakis(triphenylphosphine)palladium(0) (TCI, 97 %), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Aldrich, 98 %), potassium carbonate (Kanto Chemical Co. Inc., 99.5 %), 1-bromo-2-naphthol (MERCK, 97 %), *n*-butyl lithium (Nakarai Tesque Inc., 1.6 M in *n*-hexanes), and tripotassium phosphate (Wako, 95 %) were used as received. Tetrahydrofuran (THF) was distilled before use.

Confirmatory mass spectra (electron impact, EI) of target compounds were determined using a Shimadzu gas chromatograph-mass spectrometer model GCMS-QP2010 Plus and mass selective detector equipped with a Rxi-5 ms silica capillary column (30 m × 0.25 mm id, 0.25 µm film thickness). The ^{1}H and ^{13}C NMR spectra were recorded using a ECS 400 spectrometer with $CDCl_3$ as the deuterated solvent and tetramethylsilane (TMS) as the internal standard. The chemical structure and optical property were confirmed by UV–Vis spectroscopy (JASCO, U-3500

spectrophotometer, Japan). Differential scanning calorimetry (DSC) curves were obtained with a Seiko Instruments Inc. EXSTRAR7000: TG/DTA7300: X-DSC7000 (Japan). Polarizing optical microscopic images were captured with a Nikon ECLIPSE LV100 camera (Japan).

Synthesis of 1,1′-binaphthyl in CLC phase (BNS and BNR, $C_{20}H_{14}$)

Tetrakis(triphenylphosphine)palladium(0) (1 mg) was added to a solution of 28 mg 1-bromonaphthalene (0.137 mmol), 35 mg 1-naphthylboronic acid (0.200 mmol), and 15 mg tripotassium phosphate (0.069 mmol) in 0.48 g (*S*)-CLC at 100 °C stirred at 74 rpm. After 48 h, the reaction vessel was cooled to 0 °C. Then, the mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and purified by silica gel column chromatography (eluent: pentane, $R_f = 0.41$). The purification was performed below 38 °C in order to prevent the free rotation around a covalent single C−C′ bond connecting the two naphthyl moieties. The desired product BNS was obtained as a white solid (6.7 mg, 0.026 mmol, 20 %) [17]. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (dd, 4H), 7.58 (dd, 2H), 7.50–7.44 (m, 4H), 7.38 (d, 2H), 7.30–7.26 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.5$, 133.5, 132.8, 128.1, 127.9, 127.8, 126.5, 126.0, 125.8, 125.4 ppm; GC–MS (EI): *m/z* (relative intensity) = 252 (78), 253 (100), 254 (M^+, 89).

BNR was synthesized by the same method as in the case of BNS. Quantities: 0.58 g (*R*)-CLC, 30 mg 1-bromonaphthalene (0.145 mmol), 38 mg 1-naphthylboronic acid (0.221 mmol), 15 mg tripotassium phosphate (0.069 mmol), 1 mg tetrakis(triphenylphosphine)palladium(0). Yield: BNR (9.6 mg, 0.038 mmol, 26 %); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$ (dd, 4H), 7.59 (dd, 2H), 7.57–7.45 (m, 4H), 7.39 (d, 2H), 7.30–7.25 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.4$, 133.5, 132.8, 128.1, 127.9, 127.8, 126.5, 126.0, 125.8, 125.4 ppm; GC–MS (EI): *m/z* (relative intensity) = 252 (78), 253 (100), 254 (M^+, 89).

2-(2-Pentyloxynaphthalene-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**, $C_{21}H_{29}BO_3$)

1-Bromo-2-naphthol (2.00 g, 9.0 mmol), 1.49 g K_2CO_3 (10.8 mmol), and 1.33 cm^3 1-bromopentane (10.7 mmol) were dissolved in 40 cm^3 DMF. The reaction mixture was stirred at 94 °C for 12 h. The resulting mixture was filtered, the product extracted with dichloromethane, and the organic layer was dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by silica gel column chromatography (*n*-hexane/chloroform = 2/1). 1-Bromo-2-pentyloxynaphthalene (2.60 g, 8.9 mmol, 99 %) was obtained as liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (d, 1H), 7.78 (dd, 2H), 7.56 (d, 1H), 7.39 (d, 1H), 7.25 (d, 1H), 4.18 (t, 2H), 1.89 (quin, 2H), 1.53 (quin, 2H), 1.42 (sex, 2H), 0.95 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.4$, 133.2, 129.8, 128.7, 128.0, 127.5, 126.2, 124.2, 115.2, 109.4, 70.2, 29.1, 28.2, 22.4, 14.1 ppm.

1-Bromo-2-pentyloxynaphthalene (1.51 g, 5.1 mmol) was dissolved in THF and the mixture was cooled to −78 °C. Then 3.85 cm^3 *n*-BuLi (1.6 M solution in hexanes, 6.2 mmol) was slowly added dropwise and the mixture was stirred at 0 °C for 60 min. After cooling down to −78 °C, 1.14 cm^3 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.7 mmol) was added dropwise to the solution, which was allowed to warm to room temperature overnight. The resulting mixture was quenched with 20 cm^3 aqueous 1 M HCl and stirred at room temperature for another 30 min. After the solvent was evaporated, the aqueous layer was separated and extracted with dichloromethane, dried over $MgSO_4$, and filtered. The solvent was evaporated, and the residue was purified by silica gel column chromatography (*n*-hexane/chloroform = 1/1, $R_f = 0.22$). The product **3** was obtained as solid (0.96 g, 2.8 mmol, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (d, 1H, $J = 8.4$ Hz), 7.81 (d, 1H, $J = 9.2$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.41 (t, 1H, $J = 7.6$ Hz), 7.28 (t, 2H, $J = 9.2$ Hz), 7.18 (d, 1H, $J = 8.8$ Hz), 4.08 (t, 2H), 1.80 (q, 2H), 1.56–1.36 (m, 16H), 0.93 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.1$, 137.2, 131.5, 128.8, 128.1, 126.8, 126.5, 123.2, 113.7, 83.9, 77.2, 29.4, 28.3, 25.0, 22.6, 14.0 ppm.

Synthesis of 2-pentyloxy-1,1′-binaphthyl in CLC phase (PBNS, $C_{25}H_{24}O$)

Tetrakis(triphenylphosphine)palladium(0) (1 mg) was added to a solution of 37 mg 1-bromonaphthalene (0.126 mmol), 32 mg compound **3** (0.188 mmol), and 13 mg tripotassium phosphate (0.061 mmol) in 0.48 g (*S*)-CLC at 96 °C stirred at 74 rpm. After 24 h, the reaction vessel was cooled to 0 °C. Then, the mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and purified by silica gel column chromatography (eluent: hexane/dichloromethane = 3/2, $R_f = 0.53$). The desired product was obtained as a yellowish solid (7 mg, 0.021 mmol, 16 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$–7.91 (m, 3H), 7.86 (d, 1H, $J = 8$ Hz), 7.58 (t, 1H, $J = 7.8$ Hz), 7.44–7.40 (m, 3H), 7.35–7.31 (m, 2H), 7.25–7.21 (m, 3H), 3.98–3.90 (m, 2H), 1.41–1.37 (m, 2H), 1.01–0.98 (m, 2H), 0.89–0.83 (m, 2H), 0.64 (t, $J = 7.3$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.2$, 139.5, 134.3, 134.2, 133.6, 133.0, 129.6, 129.2, 128.4, 128.0, 127.7, 127.5, 126.3, 126.2, 125.6, 125.6, 125.5, 125.4, 124.1, 123.5, 115.7, 69.8, 28.9, 27.7, 22.1, 13.8 ppm; GC–MS (EI): *m/z* (relative intensity) = 270 (100), 340 (M^+, 50).

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