

Synthesis and Structural Analysis of Oligo(naphthalene-2,3-diyl)s

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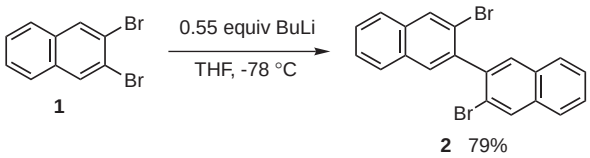
Oligo(naphthalene-2,3-diyl)s are synthesized by the palladium-catalyzed cross-coupling reactions of 2-naphthylzinc compounds with 2-bromonaphthalene derivatives. An NMR analysis together with an X-ray diffraction study supports the conjecture that the helical secondary structure is a common feature of the assemblies in which naphthalene-like aromatic units are linked together between the β-positions in series.

Previous papers from this laboratory have described aromatizing polymerization of 1,2-diisocyanoarenes catalyzed by organopalladium complexes giving poly(quinoxaline-2,3-diyl)s.[1] An X-ray structural study of a quinoxaline pentamer suggested that the main chain of poly(quinoxaline-2,3-diyl) would have a helical secondary structure. Actually, we succeeded in the synthesis of poly(quinoxaline-2,3-diyl)s that are optically active due to their helical secondary structures.[2] These previous studies brought forth the possibility that a similar helical secondary structure might be a common feature of the assemblies in which aromatic units analogous to quinoxaline are linked together between the 2- and 3-positions in series. This conjecture led us to study the structural features of assemblies of naphthalene-like aromatic units. In the first place, naphthalene itself was chosen as the simplest constituent unit for a model assembly.

As for the atropisomerism of naphthalene assemblies, 1,1′-binaphthyl derivatives has attracted much attention, particularly due to their successful applications to chiral ligands for enantioselective reactions.[3] Accordingly, a variety of reactions to form C–C bonds between two α-positions of naphthalene derivatives have been reported.[4] In contrast, much less attention has been directed to the atropisomerism of 2,2′-binaphthyl, and thus synthetic methods of 2,2′-binaphthyl are not as well developed. In this paper, the synthetic study and structural analyses of oligo(naphthalene-2,3-diyl)s are described.

Results and Discussion

Synthesis of Oligo(naphthalene-2,3-diyl)s. Transition metal-catalyzed cross-coupling reactions of two aromatic units have been well studied and utilized for the preparation of aromatic materials.[5] We envisaged that making a bond between the β-positions of naphthalene units by a cross-coupling reaction would be a staightforward and suitable method for the construction of oligo(naphthalene-2,3-diyl)s. Thus, we examined the palladium-catalyzed cross-coupling reaction of bi-



1 **2** 79%

Scheme 1. Synthesis of 3,3′-dibromo-2,2′-binaphthyl (**2**).

naphthyl dibromide with 2-metallonaphthalene in order to synthesize naphthalene tetramers.

3,3′-Dibromo-2,2′-binaphthyl (**2**), a suitable starting platform for the synthesis of quater(naphthalene-2,3-diyl), was successfully prepared in 79% yield from 2,3-dibromonaphthalene (**1**) according to the procedure reported for the synthesis of 2,2′-dibromobiphenyl from 1,2-dibromobenzene (Scheme 1).[6]

The dibromo derivative **2** was reacted with 2-metallonaphthalenes (2.0–2.2 equiv), which were generated in situ by transmetallation from 2-naphthylmagnesium bromide, in the presence of a palladium catalyst (Table 1). 2-Naphthyltin and -boron derivatives afforded naphthalene trimer **3** as the major product (Runs 1 and 2). The desired naphthalene tetramer **4** was obtained only in low yield even when the isolated **3** was subjected to a second coupling reaction with these 2-metallonaphthalenes. On the other hand, 2-naphthylzinc halide generated by transmetallation of 2-naphthylmagnesium bromide with $ZnCl_2$ underwent the double coupling reaction with **2** efficiently to furnish **4** in 55% yield (Run 3). Naphthalene trimer **3b**, concomitantly formed in 45% yield through a single coupling reaction, possessed a chlorine atom instead of a bromine atom. It is likely that halogen exchange on the aromatic ring was also mediated by the palladium catalyst. The decreased reactivity of the resultant chloro derivative **3b** toward oxidative addition to palladium(0) retarded the second coupling reaction. In fact, the use of $ZnBr_2$ instead of $ZnCl_2$ for the transmetallation improved the yield of **4** to 74% (Run 4).

2-Bromo-3-methoxynaphthalene (**8**) and 2-bromo-3-methylnaphthalene (**12**) were employed as the precursors of 2-metallonaphthalenes for the cross-coupling reaction. The 2-bromonaphthalene derivative **8** was prepared from 3-hydroxy-2-naphthoic acid **5** via **6** according to the reaction sequences

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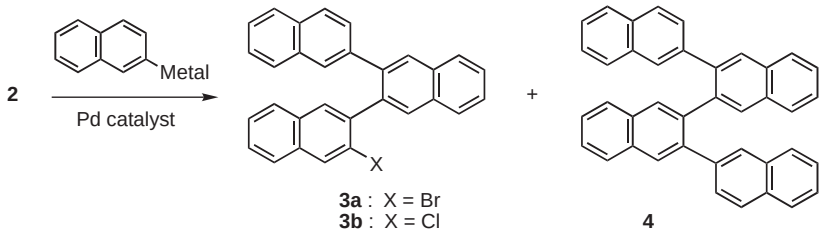
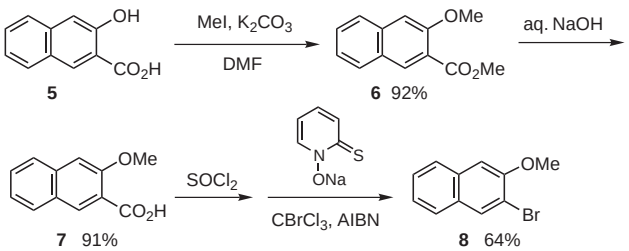
Table 1. Cross-Coupling Reactions of 2-Metallonaphthalenes with **2**

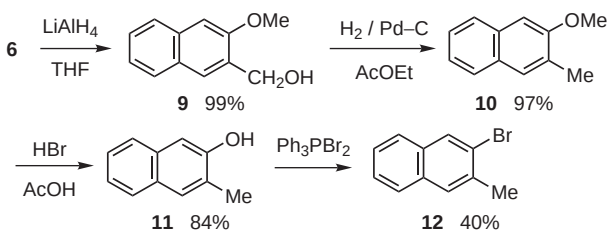


Run	Metal	Catalyst	Solvent	Conditions	**3**, %	**4**, %
1	$-SnBu_3$	$Pd(PPh_3)_4$, LiCl	DMF	100 °C, 5 d	**3b**, 66	0
2	$-B(OH)_2$	$Pd(PPh_3)_4$, Na_2CO_3	THF	reflux, 21 h	**3a**, 38	7
3	$-ZnX$[a)]	$PdCl_2$(dppp)	THF	reflux, 13 h	**3b**, 45	55
4	$-ZnBr$[b)]	$PdCl_2$(dppp)	THF	reflux, 31 h	**3a**, 12	74

a) Prepared by transmetallation of 2-naphthylmagnesium bromide with $ZnCl_2$. b) Prepared by transmetallation of 2-naphthylmagnesium bromide with $ZnBr_2$.



Scheme 2. Synthesis of 2-bromo-3-methoxynaphthalene (**8**).



Scheme 3. Synthesis of 2-bromo-3-methylnaphthalene (**12**).

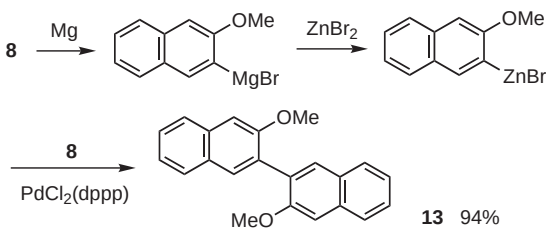
shown in Scheme 2.

2-Bromo-3-methylnaphthalene (**12**) was also prepared from the intermediate **6** (Scheme 3).

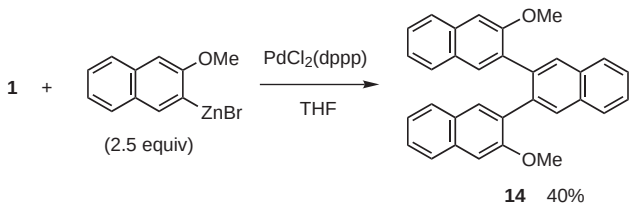
Symmetrical naphthalene dimer and trimer with both ends substituted by two methoxy groups were synthesized using the building block **8**. Initially, the bromonaphthalene (**8**) was converted to the corresponding 2-naphthylzinc bromide via the Grignard reaction and the following transmetallation with $ZnBr_2$. (3-Methoxy-2-naphthyl)zinc bromide was then subjected to the palladium-catalyzed coupling reactions. Coupling with **8** in the presence of $PdCl_2$(dppp) afforded the symmetrical 3,3′-dimethoxy-2,2′-binaphthyl (**13**) in 94% yield (Scheme 4).

On the other hand, the double coupling reaction of **1** with (3-methoxy-2-naphthyl)zinc bromide (2.5 equiv) furnished the symmetrical naphthalene trimer **14** in 40% yield (Scheme 5). The homo-coupling dimer **13** and the mono-coupling product, e.g., bromobinaphthyl **15**, were also formed as the side products.

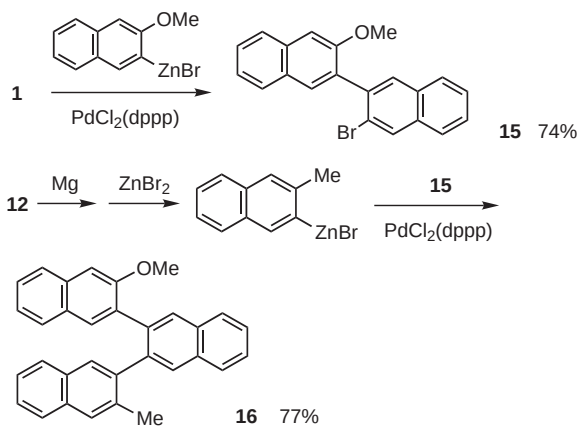
Unsymmetrical naphthalene trimer was also synthesized



Scheme 4. Synthesis of 3,3′-dimethoxy-2,2′-binaphthyl (**13**).



Scheme 5. Synthesis of symmetrical naphthalene trimer **14**.



Scheme 6. Synthesis of unsymmetrical naphthalene trimer **16**.

(Scheme 6). The bromonaphthalene **12** was converted to the corresponding 2-naphthylzinc bromide via the Grignard reagent. Bromobinaphthyl **15** was prepared by a controlled coupling reaction of 2,3-dibromonaphthalene (**1**) with (3-me-

thoxy-2-naphthyl)zinc bromide (1.1 equiv). The successive cross-coupling reaction of **15** with (3-methyl-2-naphthyl)zinc bromide furnished the unsymmetrical naphthalene trimer **16** in 77% yield.

Finally, naphthalene pentamer **18** was synthesized (Scheme 7). Bromobinaphthyl **17** was produced by a single coupling reaction of (3-methyl-2-naphthyl)zinc bromide (1.1 equiv) with 2,3-dibromonaphthalene (**1**). The palladium-catalyzed double coupling reaction of **1** with the 2-naphthylzinc derivative generated from **17** (2.5 equiv) successfully produced naphthalene pentamer **18**.

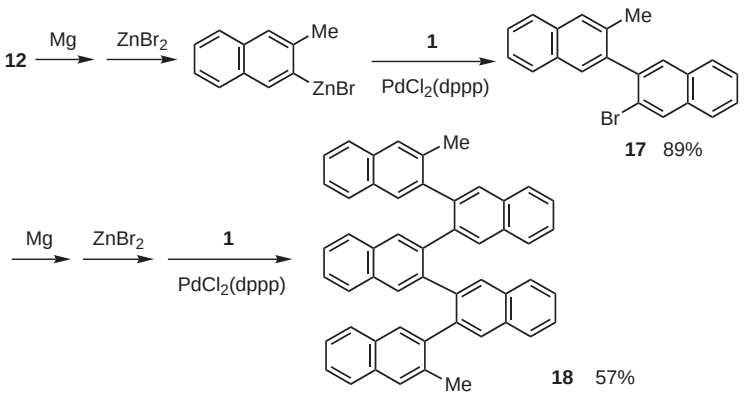
Structural Analysis of Ter(naphthalene-2,3-diyl)s in Solution. The ^{1}H NMR studies on the naphthalene monomer, dimer, and trimers provided a basis for deduction of the structures of oligo(naphthalene-2,3-diyl)s in solution (Fig. 1). 2-Methoxynaphthalene and 3,3′-dimethoxy-2,2′-binaphthalene (**13**) showed their methoxy signals at δ 3.92 and 3.90, respectively. On the other hand, the methoxy groups of the ter(naphthalene-2,3-diyl)s **14** and **16** resonated at δ 3.50 and 3.52, respectively. These large high-field shifts peculiar to naphthalene trimers are reasonably ascribed to their folded conformations where the methoxy group of the head (first) naphthalene is disposed over the tail (third) naphthalene ring. The signal of the methoxy group of **14** was significantly broadened, suggesting that the flipping of the naphthalene units is occurring at the rate comparable to the NMR time-scale (200 MHz) at room temperature.

In addition, a distinct NOE was observed between the methoxy group on the head naphthalene and the methyl group on the tail naphthalene of **16**. This result also indicates that the three naphthalene units are not extended but folded, and that both ends are brought in close proximity to each other.

These results of the NMR studies suggest clearly that naphthalene trimers take a helical secondary structure in solution.

Crystal Structure of Quater(naphthalene-2,3-diyl) (4). Recrystallization of quater(naphthalene-2,3-diyl) (**4**) from hexane provided single crystals and so an X-ray structural analysis was conducted. The ORTEP view is shown in Fig. 2. The three serial naphthalene units A–C constitute almost one cycle of the helical structure, which was similar to that observed with a quinoxaline pentamer.[2a] The terminal D ring is oriented out of the helical array. The dihedral angles between two adjacent naphthalene units are as follows: C1–C10–C11–C20 = 48.3°, C11–C20–C21–C30 = 61.8°, C21–C30–C31–C40 = −135.3°.[2b]

Thus, a helical folding was observed also in the crystal structure of **4**. However, we have been unsuccessful so far in obtaining single crystals of the naphthalene pentamer **18**.



Scheme 7. Synthesis of naphthalene pentamer **18**.

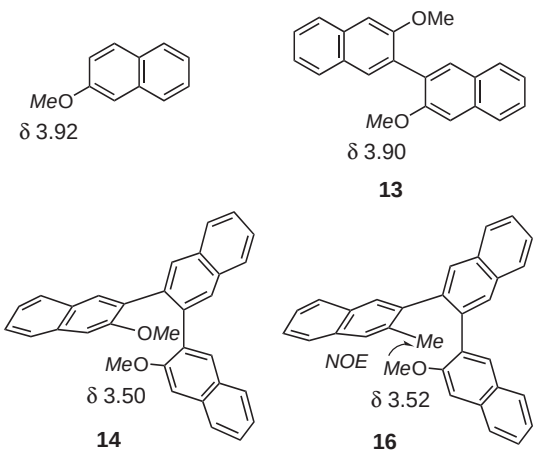


Fig. 1. Chemical shifts of 2-methoxy-substituted naphthalene derivatives.

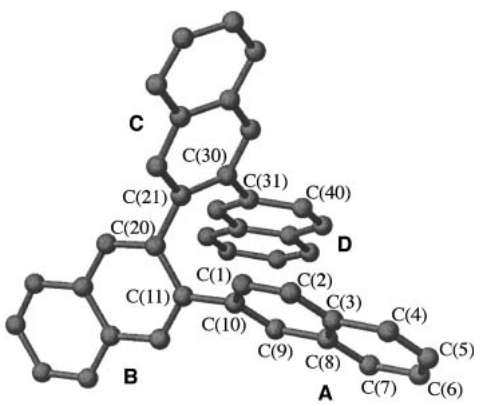


Fig. 2. Crystal structure of naphthalene tetramer **4**.

Conclusion

The palladium-catalyzed cross-coupling reactions of 2-naphthylzinc bromide with 2-bromonaphthalene derivatives offered straightforward synthetic pathways leading to oligo(naphthalene-2,3-diyl)s. The present structural studies on the naphthalene trimers in solution and on the naphthalene tetramer in crystal provided a convincing support for the conjecture that organic assemblies in which naphthalene-like aromatic units are linked together between the β-positions would have the helical secondary structures similar to those of poly(quinoxaline-2,3-diyl)s.

Experimental

Column chromatography was performed with silica gel 60 (E. Merck, Darmstadt), 230–400 mesh. Preparative thin-layer chromatography (TLC) was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). ^{1}H and ^{13}C NMR spectra were acquired in chloroform-*d* at 200 MHz and 50 MHz, respectively. The carbon chemical shifts were recorded relative to chloroform-*d* (δ 77.0). Na_2SO_4 was used to dry the organic layers after extraction. All of the reactions were performed under a dry nitrogen atmosphere. Unless otherwise noted, all materials were obtained from commercial sources. THF was distilled from sodium diphenylketyl. Dichloromethane was distilled under N_2 over CaH_2. 2,3-Dibromonaphthalene (**1**) was prepared according to the literature procedure.[7]

3,3′-Dibromo-2,2′-binaphthyl (2). To a stirred solution of **1** (4.00 g, 14.0 mmol) in THF (100 mL) at −78 °C was added a solution of butyllithium in hexane (4.90 mL, 7.74 mmol) over 3 min. After the reaction mixture was stirred for 10 min, MeOH (1 mL) was added. The mixture was subjected to aqueous extractive workup. Evaporation and the following recrystallization of the organic extracts from benzene–EtOH afforded **2** as white needles (2.28 g, 79%): IR (KBr) 3056, 748, 740 cm^{-1}; ^{1}H NMR δ 7.50–7.64 (m, 4H), 7.80–7.92 (m, 6H), 8.23 (s, 2H); ^{13}C NMR δ 122.3, 127.2, 127.3, 127.7, 128.5, 130.6, 131.5, 132.5, 134.5, 140.0. Found: C, 58.55; H, 3.09; Br, 38.82%. Calcd for $C_{20}H_{12}Br_2$: C, 58.29; H, 2.93; Br, 38.78%.

Quarter(naphthalene-2,3-diyl) (4). To a stirred solution of $ZnBr_2$ (455 mg, 2.0 mmol) in THF (3 mL) at room temperature was added a solution of 2-naphthylmagnesium bromide in THF (2.6 mL, 2.0 mmol). After the reaction mixture was stirred for 30 min, **2** (206 mg, 0.50 mmol) and $PdCl_2$(dppp) (15 mg, 26 μmol) was added. The mixture was stirred at 80 °C for 31 h, and then cooled. Aqueous HCl (1 mol L^{-1}, 5 mL) was added to the mixture, which was then subjected to aqueous extractive workup. After evaporation, the mixture was separated by GPC to afford **4** (188 mg, 74%) and **3a** (28 mg, 12%) as white solids. **3a**: ^{1}H NMR δ 7.34–7.53 (m, 4H), 7.44 (s, 1H), 7.53–7.66 (m, 2H), 7.59 (s, 1H), 7.66–7.82 (m, 4H), 7.83–8.06 (m, 6H), 8.10 (s, 1H); ^{13}C NMR δ 122.3, 127.2, 127.3, 127.7, 128.5, 130.6, 131.5, 132.5, 134.5, 140.0. **4**: ^{1}H NMR δ 6.20–6.70 (m, 2H), 6.71–6.80 (m, 2H), 7.02–7.11 (m, 2H), 7.18–7.33 (m, 4H), 7.35–7.45 (m, 2H), 7.52–7.61 (m, 4H), 7.61–7.74 (m, 2H), 7.63 (s, 2H), 7.81–7.90 (m, 2H), 7.97–8.10 (m, 2H), 8.24 (s, 2H); ^{13}C NMR δ 125.37, 125.43, 126.2, 126.3, 127.1, 127.3, 127.7, 127.8, 128.0, 128.1, 129.0, 130.8, 131.6, 132.7, 133.0, 133.1, 138.3, 139.2, 139.5. HRMS Found: m/z 506.2045. Calcd for $C_{40}H_{26}$: M, 506.2034.

Methyl 3-Methoxy-2-naphthoate (6). To a stirred mixture of 3-hydroxy-2-naphthoic acid (15.1 g, 80 mmol) and K_2CO_3 (33.4 g, 241 mmol) in DMF (120 mL) at room temperature was added MeI (68.4 g, 482 mmol). The reaction mixture was stirred at 50 °C for 4 d. After removal of DMF at a reduced pressure, the residue was subjected to aqueous extractive workup. Column chromatography of the organic extracts (silica gel, ether:hexane = 2:1) afforded **6** as yellow oil (15.9 g, 92%): ^{1}H NMR δ 3.96 (s, 3H), 4.00 (s, 3H), 7.21 (s, 1H), 7.33–7.43 (m, 1H), 7.47–7.57 (m, 1H), 7.70–7.87 (m, 2H), 8.31 (s, 1H).[8]

3-Methoxy-2-naphthoic Acid (7). A mixture of **6** (4.19 g, 19.4 mmol) and NaOH (1.71 g, 42.8 mmol) in H_2O (20 mL) was stirred at 100 °C for 90 min. After being cooled, the reaction mixture was neutralized with HCl (1 mol L^{-1}), extracted with CH_2Cl_2, and dried. Evaporation followed by crystallization from EtOH afforded **7** as white solid (3.58 g, 91%): ^{1}H NMR δ 4.18 (s, 3H), 7.31 (s, 1H), 7.40–7.52 (m, 1H), 7.55–7.65 (m, 1H), 7.76–7.84 (m, 1H), 7.88–7.97 (m, 1H), 8.79 (s, 1H), 10.62–11.30 (br, 1H).[9]

2-Bromo-3-methoxynaphthalene (8). A mixture of **7** (3.05 g, 15.1 mmol) and $SOCl_2$ (10 mL, 137 mmol) was stirred at room temperature for 2 h to afford crude 3-methoxy-2-naphthoyl chloride. A mixture of 3-methoxy-2-naphthoyl chloride thus prepared, $CBrCl_3$ (30 mL), and 2,2′-azobis(isobutyronitrile) (AIBN, 0.5 g, 3.0 mmol) was added to a refluxing suspension of sodium salt of 2-mercaptopyridine *N*-oxide (2.75 g, 18.5 mmol) in $CBrCl_3$ (30 mL) over 30 min. The reaction mixture was stirred for an additional 15 min, cooled, and subjected to aqueous extractive workup. Column chromatography of the organic extracts (silica gel, ether:CH_2Cl_2 = 2:1) afforded **8** as white solid (2.30 g, 64%): ^{13}C NMR δ 56.7, 107.2, 113.9, 125.0, 127.1, 127.2, 129.9, 132.8, 134.0, 154.1.[9]

(3-Methoxy-2-naphthyl)methanol (9). To a suspension of $LiAlH_4$ (1.90 g, 50.1 mmol) in ether (40 mL) at 0 °C was added a solution of **6** (10.8 g, 50.1 mmol) in ether (20 mL) over 30 min. The reaction mixture was stirred at reflux for 12 h and then cooled in an ice bath. Water (1.9 mL), 15% aqueous NaOH (1.9 mL), and water (5.7 mL) were added successively in a dropwise manner. Removal of the resultant precipitates by filtration and the following evaporation of the filtrate afforded **9** as white solid (9.34 g, 99%): ^{1}H NMR δ 2.42–2.69 (bs, 1H), 3.96 (s, 3H), 4.83 (s, 2H), 7.13 (s, 1H), 7.31–7.51 (m, 2H), 7.73 (s, 1H), 7.70–7.88 (m, 2H).[8]

2-Methoxy-3-methylnaphthalene (10). A mixture of **9** (8.52 g, 45.3 mmol) and 5% Pd on carbon (1.0 g) in AcOEt (50 mL) was stirred under hydrogen atmosphere for 7.5 h. The reaction mixture was filtered through Celite, washed with ether, and evaporated to give **10** as white solid (7.59 g, 97%).[10]

3-Methyl-2-naphthol (11). A mixture of **10** (6.91 g, 40.1 mmol) and 48% aqueous HBr (25 mL) in AcOH (200 mL) was stirred at 130 °C for 6.5 h. After the reaction mixture was cooled, AcOH was evaporated and the residue was extracted with ether. The organic extracts were washed with water, aqueous $Na_2S_2O_3$, and saturated NaCl. The organic layer was dried and evaporated. Recrystallization of the residue from xylene afforded **11** as a pale brown solid (5.34 g, 84%).[11]

2-Bromo-3-methylnaphthalene (12). To a stirred solution of PPh_3 (28.8 g, 110 mmol) in CH_3CN (50 mL) at 0 °C was added Br_2 (5.5 mL, 110 mmol) over 20 min. After the temperature was raised to room temperature, **11** (14.7 g, 100 mmol) in CH_3CN (50 mL) was added. Then CH_3CN was distilled off at 70 °C. The temperature was then raised to 310 °C. The reaction mixture was heated at that temperature for 90 min and then cooled to 240 °C, where Celite (100 g) was added. At 80 °C, benzene (20 mL) and

hexane (150 mL) were added. The reaction mixture was heated at reflux overnight, cooled, and filtered. The filtrate was passed through a short column of silica gel. The filtrate was evaporated and the residue was recrystallized from ethanol to give **12** as pale yellow solid (8.43 g, 40%).[12]

3,3′-Dimethoxy-2,2′-binaphthyl (13). The title compound was prepared from 2-bromo-3-methoxynaphthalene (**8**) and 3-methoxy-2-naphthylmagnesium bromide (1.1 equiv) by a procedure similar to that used for **4** (94%): ^{1}H NMR δ 3.90 (s, 6H), 7.26 (s, 2H), 7.37–7.47 (m, 2H), 7.47–7.57 (m, 2H), 7.80 (s, 4H), 7.85 (s, 2H); ^{13}C NMR δ 55.7, 105.3, 123.7, 126.2, 126.4, 127.7, 128.7, 129.9, 130.3, 134.4, 156.3. Found: C, 83.93; H, 5.58%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

Dimethoxyternaphthalene (14). The title compound was prepared from 2,3-dibromonaphthalene (**1**) and 3-methoxy-2-naphthylmagnesium bromide (2.5 equiv) by a procedure similar to that used for **4** (40%): ^{1}H NMR δ 3.32–3.65 (br, 6H), 6.76–6.90 (br, 2H), 7.22–7.44 (m, 4H), 7.46–7.85 (m, 8H), 7.86–8.06 (m, 2H), 7.96 (s, 2H); ^{13}C NMR δ 55.4, 105.3, 124.0, 126.4, 126.6, 126.8, 128.0, 128.4, 129.0 (br s), 129.8, 131.1, 133.2, 133.4, 134.5, 137.8 (br s), 155.8. HRMS Found: m/z 440.1787. Calcd for $C_{32}H_{24}O_2$: M, 440.1776.

3-Bromo-3′-methoxy-2,2′-binaphthyl (15). The title compound was prepared from 2,3-dibromonaphthalene (**1**) and 3-methoxy-2-naphthylmagnesium bromide (1.1 equiv) by a procedure similar to that used for **4** (74%): ^{1}H NMR δ 3.92 (s, 3H), 7.26 (s, 1H), 7.36–7.56 (m, 6H), 7.74 (s, 1H), 7.80–7.88 (m, 3H), 8.20 (s, 1H); ^{13}C NMR δ 56.1, 106.0, 123.0, 124.5, 126.9, 127.06, 127.10, 127.26, 127.30, 128.3, 128.4, 129.0, 130.7, 131.3, 132.66, 132.72, 134.3, 135.1, 138.1, 156.2. HRMS Found: m/z 362.0308. Calcd for $C_{21}H_{15}BrO$: M, 362.0307.

2-Methoxy-3′-methylter(naphthalene-2,3-diyl) (16). The title compound was prepared from **15** and 3-methyl-2-naphthylmagnesium bromide (1.1 equiv) by a procedure similar to that used for **4** (77%): ^{1}H NMR δ 2.27 (br s, 3H), 3.52 (s, 3H), 6.81 (s, 1H), 7.27–7.43 (m, 4H), 7.58 (s, 1H), 7.46–7.78 (m, 7H), 7.81 (s, 1H), 7.85 (s, 1H), 7.87 (m, 2H), 8.00 (s, 1H); ^{13}C NMR δ 21.4, 55.3, 105.5, 124.2, 125.4, 126.0, 126.4, 126.8, 126.9, 127.3, 127.9, 128.0, 128.1, 128.3, 128.4, 129.1, 129.5, 129.8, 130.3, 131.3, 131.9, 133.0, 133.2, 133.3, 134.7, 135.3, 137.6, 140.4, 140.7, 155.6. Found: C, 90.38; H, 5.64%. Calcd for $C_{32}H_{24}O$: C, 90.53; H, 5.70%.

3-Bromo-3′-methyl-2,2′-binaphthyl (17). The title compound was prepared from 2-bromo-3-methylnaphthalene (**12**) and 3-methyl-2-naphthylmagnesium bromide (1.1 equiv) by a procedure similar to that used for **4** (89%): ^{1}H NMR δ 2.29 (s, 3H), 7.41–7.62 (m, 4H), 7.67–7.90 (m, 7H), 8.22 (s, 1H). HRMS Found: m/z 346.0355. Calcd for $C_{21}H_{15}Br$: M, 346.0358.

Naphthalene Pentamer 18. The title compound was prepared from 2,3-dibromonaphthalene (**1**) and the Grignard reagent prepared from **17** (2.5 equiv) by a procedure similar to that used for **4** (57%): ^{1}H NMR δ 0.70–1.94 (m, 6H), 6.05–6.48 (br, 1H), 6.50–7.25 (m, 6H), 7.42 (s, 1H), 7.26–8.40 (m, 22H); ^{13}C NMR δ 20.7, 21.0, 125.2, 126.1, 126.3, 126.4, 126.9, 127.7, 127.8, 128.0, 128.2, 128.5, 129.3, 129.9, 130.4, 131.0, 131.8, 132.2, 132.4, 132.7, 132.8, 133.1, 136.1, 137.7, 138.9, 139.5, 140.0, 140.2. Found: C, 93.08; H, 6.71%. Calcd for $C_{58}H_{50}$ (**18** + hexane): C, 93.25; H, 6.75%.

X-ray Crystallographic Analysis of 4. Crystal data: $C_{40}H_{26}$, $M = 506.4$, orthorhombic, space group $P2_1cn$, $a = 16.650(3)$, $b = 20.223(3)$, $c = 7.989(1)$ Å, $U = 2690.1(8)$ Å^3, $Z = 4$, $D_c = 1.25$ g/cm^3, $\mu = 4.63$ cm^{-1}. Intensity data were measured on a Mac Science MXC^3 diffractometer using ω–2θ scan technique with graphite monochromated Cu K$_\alpha$ radiation ($\lambda = 1.54178$ Å). 2079 unique reflections within $3 \leq 2\theta \leq 120^\circ$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares to $R = 0.051$ ($R_w = 0.058$) for 1752 reflections [$F > 3.0\sigma(F)$], using a Crystan GM package program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found on a difference Fourier map. The thermal parameter of each hydrogen atom was assumed to be isotropic and to be equal to that of the bonded atom.

Supporting Information

Crystallographic coordinates for **4**. This material is available free of charge on the Web at: http//www.csj.jp/journals/bcsj/.

References

1 a) Y. Ito, E. Ihara, M. Murakami, and M. Shiro, *J. Am. Chem. Soc.*, **112**, 6446 (1990). b) Y. Ito, E. Ihara, T. Uesaka, and M. Murakami, *Macromolecules*, **25**, 6711 (1992).

2 a) Y. Ito, E. Ihara, and M. Murakami, *Angew. Chem., Int. Ed. Engl.*, **31**, 1509 (1992). b) Y. Ito, E. Ihara, M. Murakami, and M. Sisido, *Macromolecules*, **25**, 6810 (1992). c) Y. Ito, Y. Kojima, and M. Murakami, *Tetrahedron Lett.*, **34**, 8279 (1993). d) Y. Ito, T. Miyake, S. Hatano, R. Shima, T. Ohara, and M. Suginome, *J. Am. Chem. Soc.*, **120**, 11880 (1998). e) Y. Ito, T. Miyake, and M. Suginome, *Macromolecules*, **33**, 4034 (2000). f) M. Suginome, S. Collet, and Y. Ito, *Org. Lett.*, **4**, 351 (2002).

3 a) R. Noyori and H. Takaya, *Chem. Scr.*, **25**, 83 (1985). b) R. Noyori, "Asymmetric Catalysis in Organic Synthesis," Wiley, New York (1994).

4 a) T. Hattori, H. Hotta, T. Suzuki, and S. Miyano, *Bull. Chem. Soc. Jpn.*, **66**, 613 (1993). b) G. Bringmann, R. Walter, and R. Weirich, *Angew. Chem., Int. Ed. Engl.*, **29**, 977 (1990), and references cited therein.

5 D. W. Knight, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 3, p. 481.

6 H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957).

7 D. H. R. Barton, B. Lacher, and S. Z. Zard, *Tetrahedron*, **43**, 4321 (1987).

8 K. Yamamoto, H. Fukushima, H. Yumioka, and M. Nakazaki, *Bull. Chem. Soc. Jpn.*, **58**, 3633 (1985).

9 J. M. Wilson and D. J. Cram, *J. Org. Chem.*, **49**, 4930 (1984).

10 F. B. Mallory, M. J. Rudolph, and S. M. Oh, *J. Org. Chem.*, **54**, 4619 (1989).

11 G. Coll, J. Morey, A. Costa, and J. M. Saá, *J. Org. Chem.*, **53**, 5345 (1988).

12 J. G. Smith, P. W. Dibble, and R. E. Sandborn, *J. Org. Chem.*, **51**, 3762 (1986).