Tetrahedron Letters, Vol.30, No.2, pp 215-218, 1989   0040-4039/89 $3.00 + .00
Printed in Great Britain   Pergamon Press plc

ASYMMETRIC SYNTHESIS OF AXIALLY CHIRAL 1,1':5',1''- AND 1,1':4',1''-TERNAPHTHALENES BY ASYMMETRIC CROSS-COUPLING WITH A CHIRAL FERROCENYLPHOSPHINE-NICKEL CATALYST

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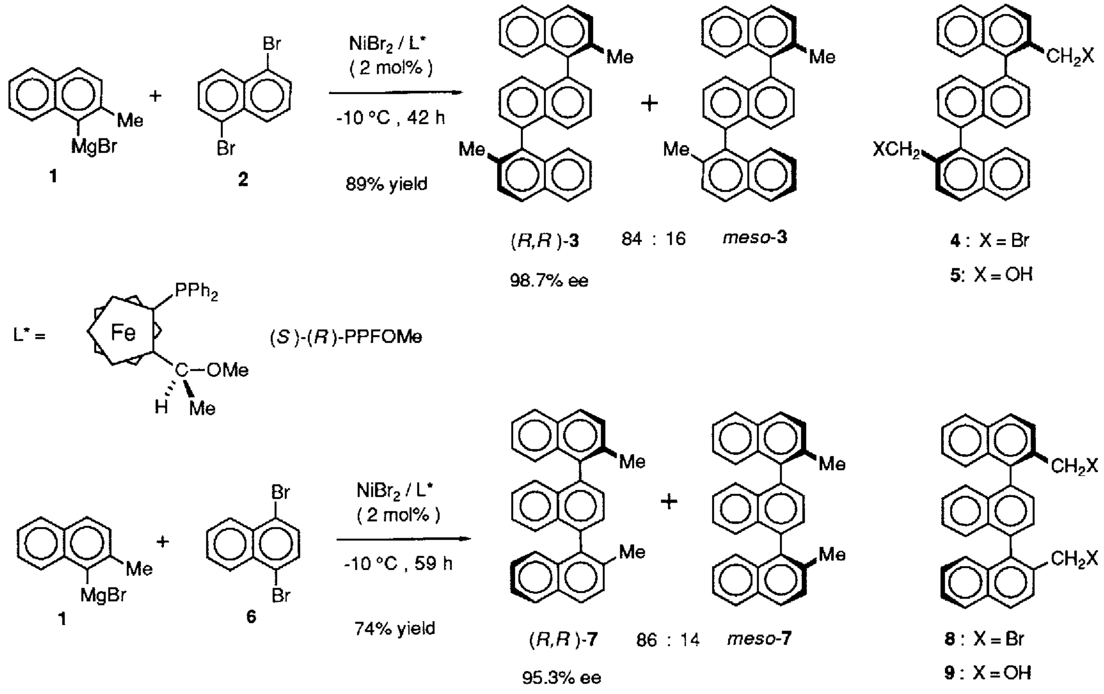
Summary: Cross-coupling of 2-methyl-1-naphthylmagnesium bromide with 1,5- and 1,4-dibromonaphthalenes in the presence of a chiral ferrocenylphosphine-nickel catalyst [(S)-(R)-PPFOMe/Ni] gave axially chiral ternaphthalenes, (R,R)-2,2''-dimethyl-1,1':5',1''-ternaphthalene (98.7% ee) and its 1,1':4',1'' isomer (95.3% ee), respectively.

We recently reported that highly stereoselective asymmetric cross-coupling of 2-methyl-1-naphthylmagnesium bromide (**1**) with 1-bromonaphthalenes producing optically active 1,1'-binaphthalenes is accomplished by the use of nickel catalyst coordinated with a chiral ferrocenylphosphine ligand, (S)-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethyl methyl ether [(S)-(R)-PPFOMe].[1] Here we describe the nickel-catalyzed cross-coupling of the Grignard reagent 1 with 1,5- and 1,4-dibromonaphthalenes which gives optically active ternaphthalenes[2] of over 95% ee (Scheme 1).

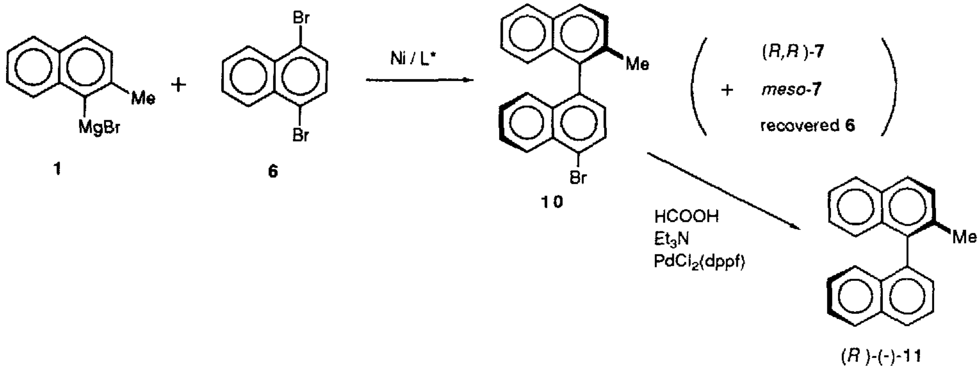
Scheme 1



To a mixture of anhydrous nickel bromide (0.02 mmol), ferrocenylphosphine [(*S*)-(*R*)-PPFOMe] (0.04 mmol), and 1,5-dibromonaphthalene[3] (**2**) (1.05 mmol), was added methylmagnesium bromide (0.1 mmol) in ether and toluene. The mixture was refluxed for 10 min to activate the nickel catalyst.[1,4] 2-Methyl-1-naphthylmagnesium bromide (**1**) (2.2 mmol) in ether and toluene was added at -10 °C. The mixture was stirred at -10 °C for 42 h, and hydrolyzed with diluted hydrochloric acid. Extraction with ether followed by silica gel column chromatography with hexane/benzene gave optically active 2,2''-dimethyl-1,1':5',1''-ternaphthalene (**3**) ($[\alpha]^{20}_{D}$ +78.4° (*c* 1.0, chloroform)[5]) in 89% yield, which was shown by ^{1}H NMR analysis to be a mixture of dl and meso isomers in a ratio of 84 to 16.[6] The ternaphthalene 3 was converted into diol 5[7] by benzylic bromination with NBS in benzene followed by treatment of the resulting dibromide **4**[8] with silver nitrate in acetone/H_2O (1/1). The enantiomeric purity of dl isomer was determined to be 98.7% by HPLC analysis of 5 with a chiral stationary phase column (Sumipax OA-2000, hexane/dichloroethane/ethanol = 50/15/1). Asymmetric cross-coupling of the Grignard reagent 1 with 1,4-dibromonaphthalene[9] (**6**) proceeded in a similar manner (at -10 °C for 59 h) to give 74% yield of 2,2''-dimethyl-1,1':4',1''-ternaphthalene **7**[10] (dl/meso = 86/14, $[\alpha]^{20}_{D}$ +7.0° (*c* 1.0, chloroform)[5]). The enantiomeric purity determined by the HPLC analysis of diol **9**[11] was 95.3%.

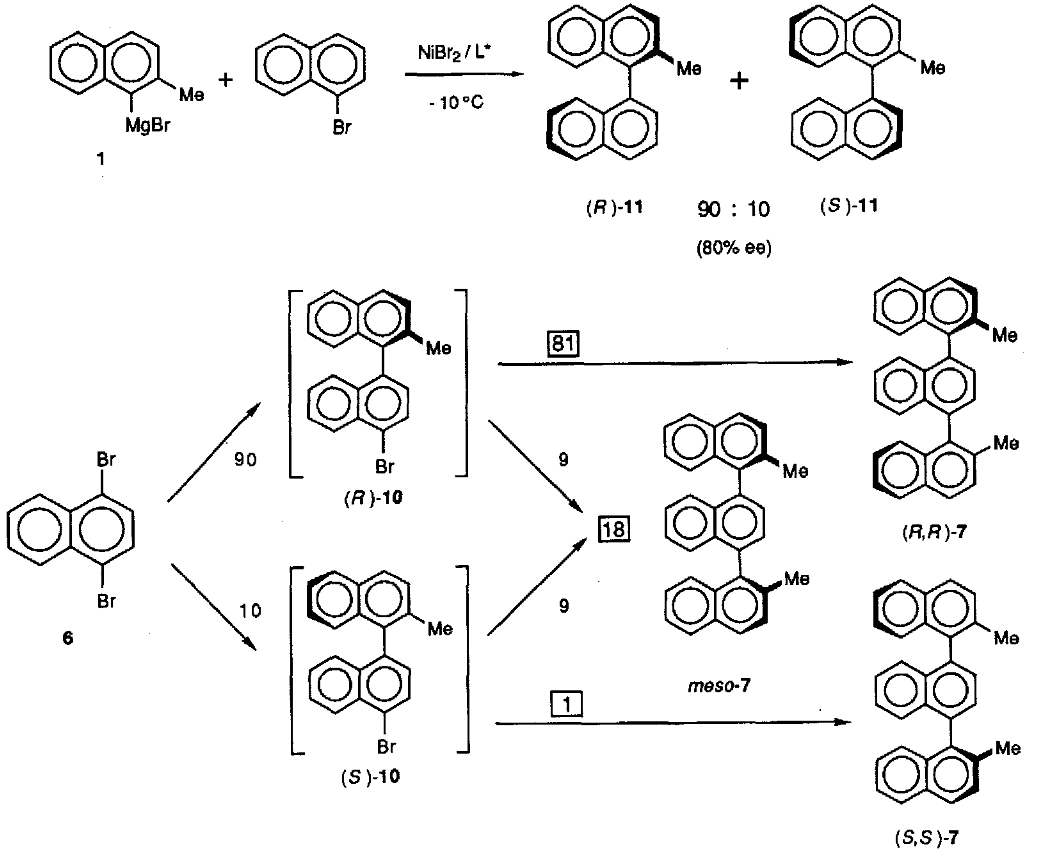
Reaction of dibromonaphthalene **6** with 1 equiv of the Grignard reagent **1** gave a small amount (8% yield) of monoarylation product **10**,[12] along with 33% yield of ternaphthalene **7** as a main product and the recovered dibromide **6** (51%). It seems that the second arylation is faster than the first arylation in the nickel-catalyzed cross-coupling.[13] Absolute configuration of **10** was determined to be (*R*) by reducing it into known (-)-(*R*)-2-methyl-1,1'-binaphthyl (**11**)[1] with triethylamine and formic acid[14] in the presence of $PdCl_2$(dppf)[15] as a catalyst in dimethylformamide (100% yield) (Scheme 2). It follows that (+)-7 has (*R*,*R*) configuration. The configuration is as expected since the dibromonaphthalene is likely to undergo the asymmetric coupling with the same stereochemistry as 1-bromonaphthalene.[1] The ternaphthalene (+)-**3** is assumed to have the configuration (*R*,*R*) as well.

Scheme 2



The stereochemical results of the present cross-coupling forming optically active and meso ternaphthalenes, which are consistent with the stereoselectivity in the reaction of **1** with 1-bromonaphthalene forming (R)-binaphthalene **11** of 80% ee,[1] can be illustrated by Scheme 3. At the first coupling, (R)-**10** and its enantiomer (S)-**10** are expected to be formed in 90% and in 10%, respectively. If the stereoselectivity at the second coupling to form **7** is not affected by the axial chirality in **10**, (R)-**10** will lead to (R,R)-**7** (81%) and (R,S)-meso-**7** (9%) and (S)-**10** to (S,R)-meso-**7** (9%) and (S,S)-**7** (1%). Thus, it is calculated that the ratio of dl to meso isomers of **7** is 82 to 18 and the enantiomeric purity of (R,R)-**7** is 97.6% ee. The calculated values are in good agreement with those observed in the experimental and it may be concluded that both the two coupling steps proceed with the (R) selectivity of about 90% irrespective of the substituent at 4 or 5 position of 1-bromonaphthalenes.

Scheme 3



We thank the Ministry of Education, Japan, for Grant-in-Aid for Scientific Research (No. 63550622) for partial financial support of this work.

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4 During the activation of the nickel catalyst, 0.05 mmol of dibromonaphthalene was consumed by methylation to dimethylnaphthalene.

5 Optical rotation of the mixture of dl and meso isomers.

6 ^{1}H NMR ($CDCl_3$). dl-**3**: δ 2.17 (s, 6 H), 7.22-7.48 (m, 12 H), 7.53 (d, *J* = 8 Hz, 2 H), 7.91 (d, *J* = 8 Hz, 4 H). meso-**3**: δ 2.21 (s, 6 H), 7.22-7.48 (m, 12 H), 7.54 (d, *J* = 8 Hz, 2 H), 7.91 (d, *J* = 8 Hz, 4 H).

7 $[\alpha]_D^{20}$ +45° (*c* 0.2, chloroform). ^{1}H NMR ($CDCl_3$) for **5**: δ 4.49 (s, 4 H), 7.30-7.48 (m, 10 H), 7.51 (ddd, *J* = 8, 6, and 2 Hz, 2 H), 7.85 (d, *J* = 8 Hz, 2 H), 7.97 (d, *J* = 8 Hz, 2 H), 8.05 (d, *J* = 8 Hz, 2 H).

8 ^{1}H NMR ($CDCl_3$) for **4**: δ 4.23 (d, *J* = 10 Hz, 2 H), 4.49 (d, *J* = 10 Hz, 2 H), 7.27-7.57 (m, 12 H), 7.74 (d, *J* = 9 Hz, 2 H), 7.94 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 9 Hz, 2 H).

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10 ^{1}H NMR ($CDCl_3$). dl-**7**: δ 2.27 (s, 6 H), 7.21-7.49 (m, 10 H), 7.51 (s, 2 H), 7.56 (d, *J* = 8 Hz, 2 H), 7.92 (d, *J* = 8 Hz, 4 H). meso-**7**: δ 2.20 (s, 6 H), 7.21-7.49 (m, 10 H), 7.51 (s, 2 H), 7.54 (d, *J* = 8 Hz, 2 H), 7.92 (d, *J* = 8 Hz, 4 H).

11 ^{1}H NMR ($CDCl_3$). **8**: δ 4.37 (d, *J* = 10 Hz, 2 H), 4.55 (d, *J* = 10 Hz, 2 H), 7.22-7.41 (m, 8 H), 7.51 (ddd, *J* = 8, 6, and 2 Hz, 2 H), 7.68 (s, 2 H), 7.76 (d, *J* = 8 Hz, 2 H), 7.93 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 9 Hz, 2 H). **9**: δ 4.58 and 4.63 (AB, *J* = 13 Hz, 4 H), 7.23-7.41 (m, 8 H), 7.51 (ddd, *J* = 8, 6, and 2 Hz, 2 H), 7.56 (s, 2 H), 7.87 (d, *J* = 9 Hz, 2 H), 7.97 (d, *J* = 8 Hz, 2 H), 8.07 (d, *J* = 9 Hz, 2 H).

12 ^{1}H NMR ($CDCl_3$) for **10**: δ 2.08 (s, 3 H), 7.11 (d, *J* = 9 Hz, 1 H), 7.16-7.34 (m, 3 H), 7.22 (d, *J* = 8 Hz, 1 H), 7.38 (ddd, *J* = 8, 7, and 1 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 1 H), 7.56 (ddd, *J* = 8, 6, and 2 Hz, 1 H), 7.87 (d, *J* = 8 Hz, 2 H), 7.90 (d, *J* = 8 Hz, 1 H), 8.36 (d, *J* = 8 Hz, 1 H).

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(Received in Japan 9 November 1988)