STEREOCONSERVATIVE CYANATION OF [1,1′-BINAPHTHALENE]-2,2′-DIELECTROPHILES. AN ALTERNATIVE APPROACH TO HOMOCHIRAL C_2-SYMMETRIC [1,1′-BINAPHTHALENE]-2,2′-DICARBONITRILE AND ITS TRANSFORMATIONS

Peter KASÁK[1] and Martin PUTALA[2,*]

Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH-2, SK-842 15 Bratislava, Slovak Republic; e-mail: [1] kasak@pobox.sk, [2] putala@fns.uniba.sk

Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday.

The performed study on the cyanation of [1,1′-binaphthalene]-2,2′-diiodide and [1,1′-binaphthalene]-2,2′-diyl ditriflate showed reactions with zinc cyanide catalyzed by palladium phosphane complex in DMF to be the most effective procedures with almost complete conservation of stereogenic information – affording corresponding highly enantiomerically enriched dinitrile (from diiodide: 94% yield, 92% ee). Dinitrile was successfully transformed into [1,1′-binaphthalene]-2,2′-dicarboxylic acid and -2,2′-dicarbaldehyde in high yields (84–87%).
Key words: Axial chirality; Biaryls; Binaphthyl; C_2-Symmetry; Cyanation; Aryl halides; Nickel; Palladium; Stereoselective reactions; Triflates.

Cyanation (cyanodehalogenation) of aromatic halides is a synthetically important reaction affording valuable intermediates – arenecarbonitriles. The classic method of cyanation exploits copper(I) cyanide at high reaction temperatures[1]. In the meantime, effective methods have been developed for transition metal-catalyzed cyanations[2]. These reactions can be performed under milder conditions and allow transformation also of less reactive substrates to cyanides, including sterically hindered halides, trifluoromethanesulfonates[3–7] (triflates), or even methanesulfonates[8] (mesylates). Complexes of palladium[3,4,9–17] and nickel[5–9,18,19] with phosphane ligands have been widely used as catalysts, but also a cobalt complex in substoichiometric amount was found to be effective[20]. Several zinc mediated cyanations have also been reported[9,21]. Wide variety of cyanation reagents has been used – alkali metal cyanides neat[4–7,10,18] or coated on alumina[11] or in the presence of the phase transfer agents (crown ethers[12,13,19] or ammonium

salts[14,19]) or in the presence of various additives[13,15,20] (most often CuI or zinc salts), zinc cyanide[3,16], copper(I) cyanide[14], trimethylsilyl cyanide[17] (TMSCN), tosyl cyanide[21], and even alkyl cyanides[9] (MeCN and BnCN).

Synthesis of nonracemic C_2-symmetric 1,1′-binaphthalene derivatives[22] bearing carbon substituents in positions 2 and 2′ can be accomplished by three principal methods:

– stereoselective coupling of two 1-halonaphthalene units substituted in position 2 by carbon substituent[23],

– resolution of racemic [1,1′-binaphthalene]-2,2′-dicarboxylic acid[24,25] (**1**), ([1,1′-binaphthalene]-2,2′-diyl)dimethanol[26] or 2,2′-bis(bromomethyl)-[1,1′-binaphthalene][27] to stereoisomers (all three were obtained by nonstereoselective coupling analogous to the method mentioned above and followed by further functional group transformations),

– stereoconservative Pd-catalyzed methoxycarbonylation[28], Ni-catalyzed cross-coupling reaction with Grignard reagent[29] from easily accessible enantiopure [1,1′-binaphthalene]-2,2′-diyl ditriflate (**2**).
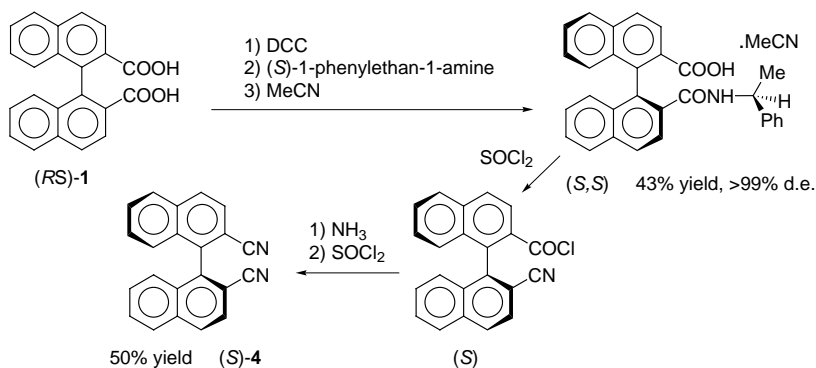
Application of the latter approach for direct cyanation of accessible homochiral binaphthalene dielectrophiles (ditriflate **2** or diiodide **3**) should be a more effective method for the synthesis of [1,1′-binaphthalene]-2,2′-dicarbonitrile (**4**). In addition it could serve as a valuable intermediate for the synthesis of other homochiral 1,1′-binaphthyl derivatives bearing carbon substituents in positions 2 and 2′. Attempts to apply this approach for the synthesis of dinitrile **4** by Ni-catalyzed cyanation of enantiopure ditriflate[5] **2** gave poor yield of the first one (10%), though most probably enantiopure (see the discussion below). Replacement of only one triflate group in position 2 to cyanide of the C_1-symmetric derivative **5** has been effectively performed[6] (Scheme 1), but presence of sterically demanding diphenyl-
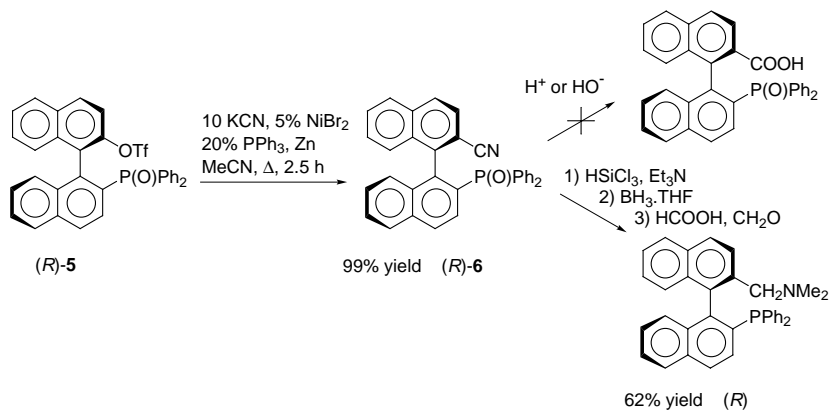
SCHEME 1

phosphoryl group [Ph$_2$P(O)–] in position 2′ of **6** decreased the efficiency of its subsequent transformation (reduction and in particular hydrolysis).

The effective synthesis of enantiopure dinitrile **4** has been reported[30] by four step procedure from racemic [1,1′-binaphthalene]-2,2′-dicarboxylic acid (*RS*)-**1** (Scheme 2). The preparation of the latter in overall 26% yield required six steps[25,31] from commercially available 1-bromo-2-methyl-naphthalene.

(*RS*)-**1**
1) DCC
2) (*S*)-1-phenylethan-1-amine
3) MeCN

.MeCN
COOH
CONH—Me / H / Ph
(*S,S*) 43% yield, >99% d.e.

SOCl$_2$

(*S*)
COCl
CN

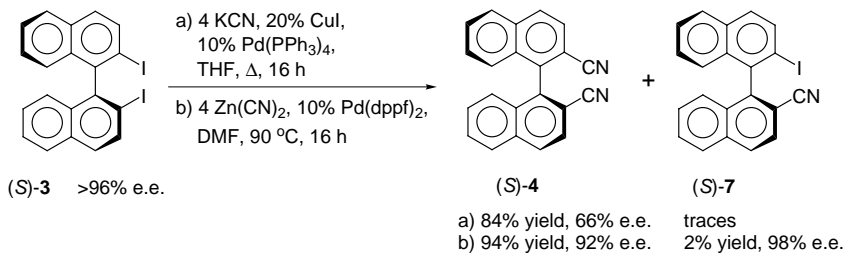1) NH$_3$
2) SOCl$_2$

CN
CN
50% yield (*S*)-**4**

Scheme 2

RESULTS AND DISCUSSION

Methods for cyanation of aromatic halides and triflates are known to be not very reliable; the efficiency of individual methods varies depending on substrate. Binaphthyl electrophiles (ditriflate **2** and diiodide **3**) used by us should be considered as medium electron rich, highly hindered substrates (bulky substituent in *ortho*-position).

Starting from diiodide **3**, we examined basic methods known for cyanation of aromatic halides (Scheme 3, Table I). Classic uncatalyzed cyanation with excess of copper(I) cyanide did not occur in boiling DMF

(*S*)-**3** >96% e.e.

a) 4 KCN, 20% CuI,
10% Pd(PPh$_3$)$_4$,
THF, Δ, 16 h

b) 4 Zn(CN)$_2$, 10% Pd(dppf)$_2$,
DMF, 90 °C, 16 h

I / I

CN / CN
(*S*)-**4**
a) 84% yield, 66% e.e.
b) 94% yield, 92% e.e.

+

I / CN
(*S*)-**7**
traces
2% yield, 98% e.e.

Scheme 3

TABLE I
Cyanation of diiodide **3**[a]

Entry	Catalyst	Cyanide equivalent	Additive mole %	Solvent	Isolated, %			Analogous to ref.
					3	**4**	**7**	
1	–	8 CuCN	–	DMF[b]	90	–	–	1
2	–	8 CuCN	–	NMP[b]	6[c]	26	≤2	1
3	A	4 CuCN	–	DMF	67	13	10	14
4	A	4 KCN	–	NMP	85	–	–	4a,10b
5	B	2 KCN	–	DMF	39	38	12	
6	B	4 KCN[d]	–	DMF	35	40	10	
7	A	4 KCN	4 18C6[e]	DMF	60	15	5	12a
8	A	4 KCN	2 TEBA[f]	PhMe	69	13	10	
9	A	12 NaCN	Al_2O_3	PhMe	67	9	5	11
10	D	4 KCN	4 KOH	HMPA	93	–	–	15a
11[g]	A	4 KCN	20 CuI	THF	≤2	84[h]	≤2	15b,15e
12	A	3 TMSCN	–	NEt_3	65	16	10	17
13	A	BnCN	400 Zn	BnCN	25[c]	5	≤2	9
14	A	2 Zn(CN)$_2$	–	THF	34	32	25	
15	B	2 Zn(CN)$_2$	–	THF	33	26	15	
16	C	2 Zn(CN)$_2$	–	THF	22	32	17	
17	E	2 Zn(CN)$_2$	–	THF	71	18	5	
18	A	2 Zn(CN)$_2$	–	Dioxane	39	39	11	
19	B	2 Zn(CN)$_2$	–	Dioxane	34	26	13	
20	B	2 Zn(CN)$_2$	–	MeCN	59	16	10	
21	A	2 Zn(CN)$_2$	–	DMF	–	86	5	
22	A	2 Zn(CN)$_2$	–	DMF[i]	–	93	3	
23	B	2 Zn(CN)$_2$	–	DMF	5	79	10	14
24	C	2 Zn(CN)$_2$	–	DMF	35	28	26	
25	B	3 Zn(CN)$_2$	–	DMF	–	88	7	
26[g]	B	4 Zn(CN)$_2$	–	DMF	–	94[j]	2[k]	15d

[a] Diiodide **3** 0.50 mmol, cyanide, additive, 10 mole % (relative to **3**) of palladium catalyst; 16 h at 90 °C (bath); aqueous work-up; flash chromatography on silica gel. [b] Heated to reflux. [c] Complex reaction mixture. [d] Cyanide was added portionwise. [e] 18-Crown-6. [f] Benzyl-(triethyl)ammonium chloride. [g] From (*S*)-**3**, >96% e.e. (polarimetry). [h] 66% e.e. (HPLC), 65% ee (polarimetry). [i] 3 days. [j] 92% e.e. (HPLC), 95% e.e. (polarimetry). [k] 98% e.e. (HPLC). *A* Pd(dba)$_2$ + PPh$_3$ (1 : 4); *B* Pd(dba)$_2$ + dppf (1 : 2); *C* Pd(dba)$_2$ + dppf (1 : 4); *D* Pd(OAc)$_2$; *E* Pd(dba)$_2$ + P(*o*-tolyl) (1 : 4).

(entry 1). Further increase of temperature (boiling NMP) resulted in partial decomposition of the reaction mixture (black viscous mass) and low yield of the desired product **4** (entry 2). Using the palladium complex Pd(PPh$_3$)$_4$ at a lower temperature with the same cyanation reagent (entry 3) gave poor conversion of diiodide **3**.

Experiments using alkali metal cyanide as a cyanation reagent in the presence of palladium catalyst, and without or with various additives (crown ether, ammonium salt, base, solid support), yielded low to moderate conversions of diiodide **3** to target dinitrile **4** (entries 4–10). Mode of the cyanide addition (in one portion or portionwise) did not affect the results (entries 5, 6). DMF was found to be a key solvent for at least partly effective cyanation, since the presence of the mentioned additives (entries 8–10) decreased the yield remarkably when accompanied by the change of the solvent. The only really effective method for palladium-catalyzed cyanation of diiodide **3** with potassium cyanide required the presence of copper(I) iodide as cocatalyst (entry 11). Dinitrile **4** in high yield (84%) and only traces of the starting material **3** and the intermediate **7** were isolated from the reaction mixture.

More curious palladium-catalyzed cyanation methods exploring trimethylsilyl and benzyl cyanides (entries 12, 13) gave poor conversion, or in the latter case, a low amount of the desired product in a complex reaction mixture.

Cyanation with zinc cyanide in the presence of palladium catalyst [Pd(PPh$_3$)$_4$, Pd(dppf)$_2$] afforded the best result (entries 22, 26) – complete conversion of diiodide **3** to dinitrile **4**, and the highest yield of the latter (93–94%), although some optimization of reaction conditions was inevitable (entries 14–26). First, DMF was found the most suitable among the tested solvents (acetonitrile, DMF, dioxane, THF; entries 20, 23, 19, 15) under comparable conditions (heating to reflux or to 90 °C if the boiling point of the solvent is higher). The use of 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) and triphenylphosphane (PPh$_3$) as ligands to palladium gave comparable results in most of the solvents (entries 14/15, 18/19, 21/23). Yields of the product were slightly higher with triphenylphosphane. In order to obtain the same result, the reaction using dppf required three equivalents of zinc cyanide instead of two with PPh$_3$ (entry 25 *vs* 21). An excess of dppf over palladium (Pd : dppf > 1 : 2) in DMF decreased the conversion of diiodide **3** (entry 24). A longer reaction time (entry 22) or a higher excess of zinc cyanide (4 equivalents, entry 26) shifted the yield of the desired product above 90%. Tris(2-tolyl)phosphane complex of palladium was the least effective of those tested (entry 17).

In all successful cases (except entries 1, 4, and 10), small amounts of intermediate iodonitrile **7** was isolated from the reaction mixture, together with starting diiodide **3** and dinitrile **4**. The amount of iodonitrile **7** was always lower than that of dinitrile **4**. This observation is well understandable since iodonitrile **7** should be more reactive than the starting diiodide **3** due to electronic (electron withdrawing nature of the already present cyano group) and steric reasons as well (small cyano group compared with large iodine atom). Products of hydrodehalogenation were not detected in any reaction.

We failed to find a procedure for the effective cyanation of ditriflate **2** (Scheme 4, Table II). Ditriflate **2** would be a better candidate for practical application of cyanation procedure, since it is more easily accessible than

(R)-**2**
92% e.e.

1.2 Zn(CN)$_2$, 10% Pd(dppf)$_2$
DMF, 90 °C, 16 h

(R)-**4**
17% yield, 93% e.e.

+

(R)-**8**
3% yield
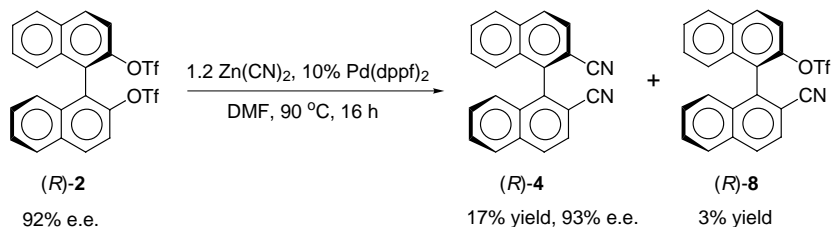
SCHEME 4

TABLE II
Cyanation of ditriflate **2**[a]

Entry	Catalyst	Cyanide equivalent	Solvent	Isolated, %			Analogous to ref.
				2	**4**	**8**	
1[b]	A	2.2 KCN	MeCN	34	10[c]	40	
2[d]	B	1.2 Zn(CN)$_2$	DMF	69	17[e]	3	3a,16a
3	B	1.2 Zn(CN)$_2$[f]	DMF	61	16	5	3c
4	B	1.2 Zn(CN)$_2$	DMF[g]	56	21	5	
5	B	4 Zn(CN)$_2$	DMF	76	8	≤2	15d

[a] Ditriflate **2** 0.50 mmol, cyanide, 10 mole % of catalyst (relative to **2**); 16 h at 90 °C (bath); aqueous work-up; flash chromatography on silica gel. [b] From (R)-**2**, e.e. was not given. [c] Claimed enantiopure (HPLC), calculated 89% e.e. (polarimetry). [d] From (R)-**2**, 92% e.e. (HPLC), >96% e.e. (polarimetry). [e] 93% e.e. (HPLC), 94% e.e. (polarimetry). [f] Cyanide was added portionwise. [g] 150 °C. A NiBr$_2$, 4 PPh$_3$, 3 Zn; B Pd(dba)$_2$ + dppf (1 : 2).

diiodide **3**. We did not succeed to improve result of the method exploring potassium cyanide in the presence of *in situ* formed nickel catalyst (10% of dinitrile **4**, entry 1 (ref.[5])), though this method has been applied for very efficient transformation of monotriflate **5** to the corresponding nitrile[6] **6**. Observed low conversion of ditriflate **2** to dinitrile **4** was quite surprising – diphenylphosphoryl group (in position 2' of monotriflate **5**) should be sterically more demanding than the second triflate group in our case (in **8**). Perhaps an explanation could be that the –P(O)Ph$_2$ group has a remarkable electron withdrawal character in contrast to –OSO$_2$CF$_3$, but also more electron rich aryltriflates have been converted to nitriles[3d]. We suppose that a probable reason for the failure of effective cyanation of ditriflate **2** by nickel catalyst should be that the partially introduced first nitrile group coordinates nickel complex and nickel therefore cannot reach then the second triflate position. This could also explain why in these single case more of mononitrile **8** than nitrile **4** was obtained. Change of catalyst to palladium complex and cyanation reagent to zinc cyanide did not yield a higher conversion of ditriflate **2**, but it afforded slightly higher yield of dinitrile **4** (16–17%, entries 2, 3). In contrast to the cyanation of diiodide **3** in our case and some aryl triflates[15d], an excess of zinc cyanide decreased the conversion of ditriflate **2** (entry 5). The mode of the addition of cyanation reagent (in one portion or stepwise) and performing the reaction at higher temperature did not influence the result (entry 2 *vs* 3 and entry 4).

Having found the optimum procedure for the synthesis of dinitrile **4** from diiodide **3**, we investigated stereochemical behavior of axially chiral binaphthalene moiety in the course of the reaction – whether the stereogenic information would be conserved. This is the unique peculiarity of the 2,2'-substituted 1,1'-binaphthyl derivatives, since the steric hindrance of the groups in positions 2 and 2' is crucial for configurational (atropoisomeric) stability of these derivatives and exchange of this groups (especially simultaneous) may cause racemization of the binaphthyl unit. We found[22,32] that the Negishi palladium-catalyzed cross-coupling reactions in both 2,2'-positions of diiodide **3** proceeds stereoconservatively (stereoselectively), while in the Suzuki and Stille couplings (with less reactive organometallics), almost full racemization of binaphthyl moiety took place. Therefore the prediction of the stereochemical result was not that trivial. Starting from enantiopure diiodide (*S*)-**3** (>96% ee), we examined only those methods which gave high yields of dinitrile **4** – palladium-catalyzed reactions with potassium cyanide as cyanation reagent in the presence of copper(I) iodide (Table I, entry 11) and with zinc cyanide (Table I, entry 26). The former afforded dinitrile **4** with 66% ee. This result

is surprising, because on the basis of the previous results with cross-coupling reactions, one would expect extreme results as more probable (full racemization for simultaneous process or full conservation of stereogenic information for stepwise reaction). The latter cyanation method (with zinc cyanide) yielded highly enriched dinitrile **4** (92% ee) with almost complete conservation of stereogenic information from the substrate. Mononitrile **7** was enantiopure (98% ee), since its transformation regards only one of critical positions 2 and 2′.

Cyanation of ditriflate (*R*)-**2** with potassium cyanide in the presence of nickel catalyst was reported[5] to proceed with complete conservation of stereogenic information giving (*R*)-**4** (Table II, entry 1; claimed as enantiopure based on HPLC). However, the given value of specific optical rotation for (*R*)-**4** compared with our points to only 89% ee. We examined cyanation of ditriflate (*R*)-**2** (92% ee) with zinc cyanide in the presence of palladium catalyst in DMF (Table II, entry 5) which took place with complete retention of configuration on the binaphthalene moiety, affording dinitrile **4** with 93% ee.

The described effective cyanation procedure (Table I, entry 26) is quite simple and does not require special equipment; it can serve as a convenient route to the valuable intermediate to other nonracemic C_2-symmetric 1,1′-binaphthalene derivatives bearing carbon substituents in positions 2 and 2′. For this purpose, we examined transformations of cyano groups of dinitrile **4** to other functional groups (carboxylic acid, formyl, and aminomethyl, Scheme 5).

84% yield **9**   **4**   87% yield **1**
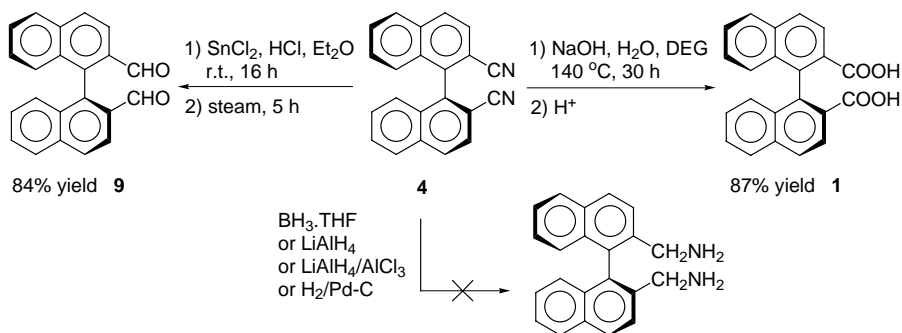
SCHEME 5

Alkaline hydrolysis of dinitrile **4** in diethylene glycol and the following acid work-up afforded the corresponding dicarboxylic acid **1** in high yield (87%). Reduction of **4** with anhydrous tin(II) chloride in the presence of HCl followed by hydrolysis gave dicarbaldehyde **9** in a very good yield

(84%). Reduction of cyano group to aminomethyl one was not successful with the borane complex $BH_3 \cdot THF$ (which was used for reduction of mononitrile[6] **6**). Reduction with a large excess of $LiAlH_4$ occurred only at elevated temperature (in boiling dioxane) with $LiAlH_4/AlCl_3$ (in refluxing THF) or hydrogenation over Pd-C, but in all cases it yielded to complex reaction mixture where only traces of desired 2,2′-bis(aminomethyl)-[1,1′-binaphthalene] were detected (GC).

EXPERIMENTAL

All cyanation experiments were performed in dried deoxygenated solvents under argon atmosphere using Schlenk technique. $Pd(dba)_2$ (ref.[33]), $Ni(PPh_3)_2Cl_2$ (ref.[34]), dppf (ref.[35]), ditriflate[36] (*RS*)-**2**, (*R*)-**2**, diiodide[37] (*RS*)-**3**, (*S*)-**3**, and Me_3SiCN (ref.[38]) were prepared according to literature procedures. KCN, $Zn(CN)_2$, and $SnCl_2$ were dried prior to use.

Melting points were measured on a Kofler block and are uncorrected. IR spectra were recorded on a Specord M 80 spectrophotometer (wavenumbers in cm^{-1}) in chloroform. ^1H NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian Gemini 300 (300 MHz) instrument in $CDCl_3$ with tetramethylsilane as internal standard. Flash column chromatography was performed on 30–60 μm silica gel and thin-layer chromatography (TLC) on Silufol UV 254 foils. HPLC analysis was done on (+)-poly(triphenylmethyl)methacrylate/silica using a Jasco CD-995 detector (CD and UV detection). Specific optical rotation was measured on a Perkin–Elmer 241 polarimeter at temperatures from 19 to 23 °C and are given in 10^{-1} deg cm^2 g^{-1}. Elemental analysis was determined on an Erba Science 1106 instrument.

Cyanation of 2,2′-Diiodo-[1,1′-binaphthalene] (3). General Procedure

The flask containing diiodide **3** (253 mg, 0.50 mmol), cyanide, additive, 10 mole % (relative to **3**) of palladium catalyst was flushed with Ar atmosphere and a deoxygenated dry solvent (2 ml) was added *via* syringe. Reaction mixture was stirred and heated on a bath at 90 °C for 16 h. The solvent was then removed *in vacuo*, and dichloromethane (20 ml) was added. The resulting mixture was washed with 10% aqueous Na_2CO_3 (10 ml), H_2O (10 ml), brine (10 ml) and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue purified by flash chromatography on silica gel, eluent isohexane–dichloromethane (9 : 1) up to isohexane–dichloromethane–diethyl ether (9 : 1 : 2). Results are summarized in Table I.

Cyanation of [1,1′-Binaphthalene]-2,2′-diyl Bis(trifluoromethanesulfonate) (2). General Procedure

The flask containing ditriflate **2** (259 mg, 0.50 mmol), cyanide, 10 mole % (relative to **2**) of catalyst was flushed with Ar atmosphere and a deoxygenated DMF (2 ml) was added *via* syringe. Reaction mixture was stirred and heated on the bath at 90 °C for 16 h. Solvent was then removed under vacuum, and dichloromethane (20 ml) was added. Work-up was the same as from diiodide **3**. Results are summarized in Table II.

[1,1′-Binaphthalene]-2,2′-dicarbonitrile[30] (**4**): M.p. 239–241 °C (ref.[30]: 232 °C). IR: 2 235 (C≡N). ^1H NMR: 8.12 d, 2 H, *J*(4,3) = 8.5 (H-4); 8.03 broad d, 2 H, *J*(5,6) = 8.2 (H-5); 7.85 d, 2 H, *J*(3,4) = 8.5 (H-3); 7.66 ddd, 2 H, *J*(6,8) = 1.1, *J*(6,7) = 6.9, *J*(6,5) = 8.5 (H-6); 7.44 ddd,

2 H, $J(6,8)$ = 1.1, $J(7,6)$ = 6.9, $J(7,8)$ = 8.5 (H-7); 7.17 broad d, 2 H, $J(8,7)$ = 8.5 (H-8). TLC: R_F 0.35 (isohexane–diethyl ether 4 : 1). HPLC separation (eluent methanol, 15 °C, flow 1.00 ml min^{-1}, λ (UV, CD) 230 nm); k': 0.7 (–)-(*R*)-**4**, 1.0 (+)-(*S*)-**4**. Polarimetry: Table I, entry 11, $[\alpha]_D$ +45.5 (*c* 0.96, CHCl$_3$); Table I, entry 26, $[\alpha]_D$ +67.0 (*c* 0.90, CHCl$_3$), +55.6 (*c* 0.98, CH$_2$Cl$_2$); Table II, entry 5, $[\alpha]_D$ –66.0 (*c* 0.91, CHCl$_3$); ref.[6], (*R*)-**4**: $[\alpha]_D$ –53.95 (*c* 1.01, CH$_2$Cl$_2$); ref.[30], (*R*)-**4**: $[\alpha]_D$ –70.5 (*c* 1.00, CHCl$_3$), (*S*)-**4**: $[\alpha]_D$ +68.6 (*c* 1.54, CHCl$_3$).

2′-Iodo-[1,1′-binaphthalene]-2-carbonitrile (**7**): M.p. 225–227 °C. For C$_{21}$H$_{12}$IN (405.3) calculated: 62.23% C, 2.98% H, 3.45% N; found: 62.41% C, 3.07% H, 3.39% N. IR: 2 230 (C≡N). ^{1}H NMR: 8.07 d, 1 H, J = 8.5; 8.06 d, 1 H, J = 8.5; 8.01 broad d, 1 H, J = 8.5; 7.92 broad d, 1 H, J = 8.5; 7.80 d, 1 H, J = 8.5; 7.74 d, 1 H, J = 8.5; 7.64 ddd, 1 H, J = 1.2, 7.0, 8.5; 7.50 ddd, 1 H, J = 1.1, 7.2, 8.5; 7.42 ddd, 1 H, J = 1.2, 7.0, 8.5; 7.27 ddd, 1 H, J = 1.1, 7.2, 8.5; 7.22 broad d, 1 H, J = 8.5; 6.98 broad d, 1 H, J = 8.5. TLC: R_F 0.50 (isohexane–diethyl ether–dichloromethane 8 : 1 : 2). HPLC separation (eluent heptane–isopropanol 9 : 1, 15 °C, flow 0.50 ml min^{-1}, λ (UV, CD) 230 nm); k': 2.3 (–)-(*R*)-**7**, 2.8 (+)-(*S*)-**7**. Polarimetry, (*S*)-**7**: Table I, entry 26, $[\alpha]_D$ 14.2 (*c* 0.93, CHCl$_3$).

2′-Trifluoromethanesulfonyloxy-[1,1′-binaphthalene]-2-carbonitrile (**8**): M.p. 101–105 °C. IR: 2 230 (C≡N). ^{1}H NMR: 8.16 d, 1 H, J = 8.9; 8.11 d, 1 H, J = 8.9; 8.04 d, 1 H, J = 8.5; 8.01 d, 1 H, J = 8.5; 7.83 d, 1 H, J = 8.9; 7.71 d, 1 H, J = 8.9; 7.70 d, 1 H, J = 8.9; 7.66–7.44 m, 4 H; 7.16 broad d, 1 H, J = 8.5. TLC: R_F 0.22 (isohexane–dichloromethane 4 : 1).

[1,1′-Binaphthalene]-2,2′-dicarboxylic Acid (**1**) (Analogous to ref.[39])

Mixture of dinitrile **4** (152 mg, 0.50 mmol), NaOH (90 mg, 2.25 mmol), and one drop of water in 1.5 ml of diethylene glycol was stirred at 140 °C for 30 h. After cooling down, it was poured into 20 ml of water. The resulting mixture was extracted with diethyl ether (2 × 15 ml). To the aqueous layer, 10% aqueous HCl (15 ml) was added and the obtained mixture was stirred for 1 h. White precipitate was filtered off under reduced pressure, washed with water to neutral reaction, and dried. Yield: 148 mg (87%). M.p. 277–279 °C (ref.[31]: 272–274 °C). Spectra were in good agreement with ref.[31].

[1,1′-Binaphthalene]-2,2′-dicarbaldehyde (**9**) (Analogous to ref.[40])

A mixture of anhydrous SnCl$_2$ (473 mg, 2.5 mmol) in absolute diethyl ether (2 ml) was saturated with dry HCl and was slowly stirred at room temperature for 2 h. A solution of dinitrile **4** (128 mg, 0.43 mmol) in absolute diethyl ether (5 ml) was added to this mixture. The color turned yellow. Dry HCl was again bubbled through the mixture for 2 h and then it was allowed to stand overnight. The organic layer was decanted and the steam was passed through the residue for 5 h. After cooling, the resulting mixture was extracted with ethyl acetate (3 × 20 ml). Combined organic layers were washed with water (2 × 20 ml), brine (15 ml), and then dried over anhydrous Na$_2$SO$_4$. Evaporation of solvent gave 108 mg (84%) of **10** as a yellowish crystalline solid. M.p. 125–129 °C (ref.[41]: 124–126 °C). Spectra were in good agreement with ref.[41].

REFERENCES

1. Ellis G. P., Romney-Alexander T. M.: *Chem. Rev. (Washington, D.C.)* **1987**, *87*, 779.
2. a) Brandsma L., Vasilievsky S. F., Verkruijsse H. D.: *Application of Transition Metal Catalysts in Organic Synthesis*, p. 149. Springer, Berlin 1998; b) Farina V. in: *Comprehensive Organometallic Chemistry* (G. Willkinson, F. G. A. Stone and E. W. Abel, Eds), 2nd ed., Vol. 12/1, p. 225. Pergamon Press, New York 1995.
3. a) Selnick H. G., Smith G. R., Tebben A. J.: *Synth. Commun.* **1995**, *25*, 3255; b) Kehr C., Neidlein R., Engh R. A., Brandstetter H., Kucznierz R., Leinert H., Marzenell K., Strein K., von der Saal W.: *Helv. Chim. Acta* **1997**, *80*, 892; c) Drechsler U., Hanack M.: *Synlett* **1998**, 1207; d) Kubota H., Rice K. C.: *Tetrahedron Lett.* **1998**, *39*, 2907.
4. a) Takagi K., Sasaki K., Sakakibara Y.: *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1118; b) Kraus G. A., Maeda H.: *Tetrahedron Lett.* **1994**, *35*, 9189; c) Nelson P. H., Carr S. F., Devens B. H., Eugui E. M., Franco F., Gonzalez C., Hawley R. C., Loughhead D. G., Milan D. J., Papp E., Patterson J. W., Rouhafza S., Sjogren E. B., Smith D. B., Stephenson R. A., Talamas F. X., Waltos A.-M., Weikert R. J., Wu J. C.: *J. Med. Chem.* **1996**, *39*, 4181.
5. Kurz L., Lee G., Morgans D., Waldyke M. J., Ward T.: *Tetrahedron Lett.* **1990**, *31*, 6321.
6. Uozomi Y., Suzuki N., Ogiwara A., Hayashi T.: *Tetrahedron* **1994**, *50*, 4293.
7. a) Chambers M. R. I., Widdowson D. A.: *J. Chem. Soc., Perkin Trans. 1* **1989**, 1365; b) Takagi K., Sakakibara Y.: *Chem. Lett.* **1989**, 1957; c) Almansa C., Carceller E., Bartolí J., Forn J.: *Synth. Commun.* **1993**, *23*, 2965; d) Herdbreg M. H., Linnanen T., Jansen J. M., Nordvall G., Hjorth S., Unelius L., Johansson A. M.: *J. Med. Chem.* **1996**, *39*, 3503.
8. Percec V., Bae J.-Y., Hill D. H.: *J. Org. Chem.* **1995**, *60*, 6895.
9. Luo F.-H., Chu C.-I., Cheng C.-H.: *Organometallics* **1998**, *17*, 1025.
10. a) Sekiya A., Ishikawa N.: *Chem. Lett.* **1975**, 227; b) Akita Y., Shimazaki M., Ohta A.: *Synthesis* **1981**, 974; c) Andersson Y., Lång ström B.: *J. Chem. Soc., Perkin Trans. 1* **1994**, 1395.
11. a) Dalton J. R., Regen S. L.: *J. Org. Chem.* **1979**, *44*, 4443; b) Oppolzer W., Roberts D. A.: *Helv. Chim. Acta* **1980**, *63*, 1703.
12. a) Procházka M., Široký M.: *Collect. Czech. Chem. Commun.* **1983**, *48*, 1765; b) Okano T., Iwahara M., Kiji J.: *Synlett* **1998**, 243.
13. Sato N., Suzuki M.: *J. Heterocycl. Chem.* **1987**, *24*, 1371.
14. Sakamoto T., Ohsawa K.: *J. Chem. Soc., Perkin Trans. 1* **1999**, 2323.
15. a) Takagi K., Okamoto T., Sazakibara Y., Ohno A., Oka S., Hayama N.: *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3298; b) Anderson B. A., Becke L. M., Booher R. N., Flaugh M. E., Harn N. K., Kress T. J., Varie D. L., Wepsiec J. P.: *J. Org. Chem.* **1997**, *62*, 8634; c) Okano T., Kiji J., Toyooka Y.: *Chem. Lett.* **1998**, 425; d) Okano M., Amano M., Takagi K.: *Tetrahedron Lett.* **1998**, *39*, 3001; e) Anderson B. A., Bell E. C., Ginah F. O., Harn N. K., Pagh L. M., Wepsiec J. P.: *J. Org. Chem.* **1998**, *63*, 8224.
16. a) Tschaen D. M., Desmond R., King A. O., Fortin M. C., Pipik B., King S., Verhoeven T. R.: *Synth. Commun.* **1994**, *24*, 887; b) Gundersen L.-L.: *Acta Chem. Scand.* **1996**, *50*, 58; c) Maligres P. E., Waters M. S., Fleitz F., Askin D.: *Tetrahedron Lett.* **1999**, *40*, 8193.
17. Chatani N., Hanafusa T.: *J. Org. Chem.* **1986**, *51*, 4714.
18. a) Cassar L.: *J. Organomet. Chem.* **1973**, *54*, C57; b) Cassar L., Ferrara S., Foà M.: *Adv. Chem. Ser.* **1974**, *132*, 252; c) Sakakibara Y., Okuda F., Shimobayashi A., Kirino K., Sakai M., Uchino M., Takagi K.: *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1985; d) van Soolingen J., Verkruijsse H. D., Keegstra M. A., Brandsma L.: *Synth. Commun.* **1990**, *20*, 3153;

e) Sakakibara Y., Ido Y., Sasaki K., Sakai M., Uchino N.: *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2776.

19. Cassar L., Foà M., Montanari F., Marinelli G. A.: *J. Organomet. Chem.* **1979**, *173*, 335.

20. Funabiki T., Nakamura H., Yoshida S.: *J. Organomet. Chem.* **1983**, *243*, 95.

21. Klement I., Lennick K., Tucker C. E., Knochel P.: *Tetrahedron Lett.* **1993**, *34*, 4623.

22. Putala M.: *Enantiomer* **1999**, *4*, 243.

23. a) Miyano S., Tobita M., Suzuki S., Nishikawa Y., Hashimoto H.: *Chem. Lett.* **1980**, 1027; b) Miyano S., Hashimoto H., Nawa M., Sato S., Tobita M.: *J. Chem. Soc., Chem. Commun.* **1980**, 1233; b) Miyano S., Tobita M., Hashimoto H.: *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3522; c) Miyano S., Handa S., Shimizu K., Tagami K., Hashimoto H.: *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1943; d) Miyano S., Handa S., Tobita M., Hashimoto H.: *Bull. Chem. Soc. Jpn.* **1986**, *59*, 235; e) Hayashi T., Hayashizaki K., Kiyoi T., Ito Y.: *J. Am. Chem. Soc.* **1988**, *110*, 8153; f) Nelson T. D., Meyers A. I.: *J. Org. Chem.* **1994**, *59*, 2655; g) Andrus M. B., Asgari D., Sclafani J. A.: *J. Org. Chem.* **1997**, *62*, 9365; h) Meyers A. I., Nguyen T., Stoianova D., Sreerama N., Woody R. W., Koslowski A., Fleischhauer J.: *Chirality* **1997**, *9*, 431; i) Sugimura T., Inoue S., Tai A.: *Tetrahedron Lett.* **1998**, *39*, 6487.

24. a) Kanoh S., Hongoh Y., Motoi M., Suda H.: *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1032; b) Uozumi Y., Kyota H., Kishi E., Kitayama K., Hayashi T.: *Tetrahedron: Asymmetry* **1996**, *7*, 1603.

25. Ôi S., Matsuzaka Y., Yamashita J., Miyano S.: *Bull. Chem. Soc. Jpn.* **1989**, *62*, 956.

26. Bringmann G., Hinrichs J.: *Tetrahedron: Asymmetry* **1997**, *8*, 4121.

27. a) Mazaleyrat J.-P.: *Tetrahedron Lett.* **1983**, *24*, 1243; b) Maigrot N., Mazaleyrat J.-P.: *Synthesis* **1985**, 317; c) Mazaleyrat J. P., Wakselman M.: *J. Org. Chem.* **1996**, *61*, 2695; d) Mazaleyrat J.-P.: *Tetrahedron: Asymmetry* **1997**, *8*, 2709.

28. Ohta T., Ito M., Inagaki K., Takaya H.: *Tetrahedron Lett.* **1993**, *34*, 1615.

29. a) Gingras M., Dubois F.: *Tetrahedron Lett.* **1999**, *40*, 1309; b) Xiao D., Zhang Z., Zhang X.: *Org. Lett.* **1999**, *1*, 1679; c) Takashi O., Kameda M., Maruoka K.: *J. Am. Chem. Soc.* **1999**, *121*, 6519.

30. Vodenhof M., Mattay J.: *Chem. Ber.* **1990**, *123*, 2457.

31. Weber E., Csöregh I., Stensland B., Czugler M.: *J. Am. Chem. Soc.* **1984**, *106*, 3297.

32. Kasák P., Mikláš R., Putala M.: Unpublished results.

33. Ukai T., Kawazura H., Ishii Y., Bonnet J. J., Ihers J. A.: *J. Organomet. Chem.* **1974**, *65*, 253.

34. Venanzi L. M.: *J. Chem. Soc.* **1958**, 718.

35. Bishop J. J., Davison A., Kalder B., Lichtenberg J., Merrill A., Smart A.: *J. Organomet. Chem.* **1971**, *27*, 241.

36. a) Toda F., Tanaka K.: *J. Org. Chem.* **1988**, *53*, 3607; b) Ritter K.: *Synthesis* **1993**, 735.

37. a) Brown J. K., Berry M. S., Murdoch J. R.: *J. Am. Chem. Soc.* **1984**, *106*, 4217; b) Brown J. K., Berry M. S., Murdoch J. R.: *J. Org. Chem.* **1985**, *50*, 4345.

38. Reetz M. T., Chatziiosifidis I.: *Synthesis* **1982**, 330.

39. Anzalone L., Hirsch J. A.: *J. Org. Chem.* **1985**, *50*, 2128.

40. *Org. Synth., Coll. Vol. 3* **1965**, 626.

41. a) Bacon R. G. R., Bankhead R.: *J. Chem. Soc.* **1963**, 839; b) Mazaylerat J. P., Wakselman M.: *Synth. Commun.* **1995**, *23*, 3845.