Steric effects in the synthesis of ortho-substituted 1,1'-binaphthalene derivatives by the $S_{RN}1$ and the Stille Reaction

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Dedicated to Professors Roberto A. Rossi and Edmundo A. Rúveda

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Abstract

The scope of the $S_{RN}1$ mechanism and the Stille reaction to synthesize 1,1´-binaphthalene derivatives was investigated. The best yield of 2'-methoxy-1,1'-binaphthalenyl-2-ol (52%) was obtained in liquid ammonia or DMSO by the $S_{RN}1$ irradiated reaction of 1-iodo-2-methoxynaphthalene with the anion of 2-naphthol. A lower yield (40%) of BINOL is obtained in water with 1-iodo-2-hydroxynaphthalene as substrate when the reaction is sonicated before irradiation. The Stille reaction between (2-methoxy-1-naphthyl)-trimethylstannane and 1-iodo-2-methoxynaphthalene afforded low yields (15-11%) of the 1,1´-binaphthalene derivative. Based on AM1 and B3LYP calculations the yields of the 1,1´-binaphthalene derivatives obtained through the electron transfer $S_{RN}1$ reaction can be attributed to kinetic factors of the radical-nucleophile coupling step.

Keywords: 1,1´-Binaphthtyl derivatives, BINOL, $S_{RN}1$, Stille

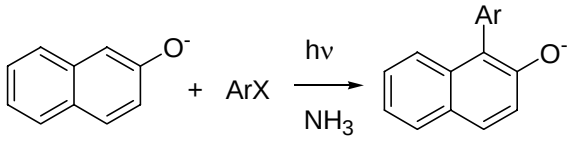
Introduction

The synthesis of biaryls, compounds present in a large number of natural products, is a subject of current interest. In this family, the chiral 1,1'-binaphthyl derivatives are of relevance mainly due to their applications as inducers for stereoselective reactions,[1] as stationary phases,[2] and reagents for chiral NMR resolution.[3]

Several procedures have been reported for the synthesis of binaphthyl derivatives, the most commonly used one being oxidative coupling. The reactions are carried out with a variety of oxidants[4] either in organic solvents,[5] aqueous solution[6] or in the solid state.[7]

Symmetric and asymmetric biaryls can also be synthesised by the electron transfer (ET) $S_{RN}1$ mechanism[8] through the substitution of an haloaromatic substrate by a β-naphthyl nucleophile,

such as the anion of 2-naphthol and 2-naphthylamine.[9] In this system, we have determined that the 2-naphthoxide anion (**1**) reacts with aromatic radicals regiospecifically by coupling at the C_1 of its naphthyl ring (eq 1).[9]

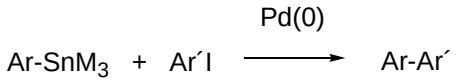


(1)

1 Ar = *p*-$MeOC_6H_4$, 2-$C_{10}H_7$,1-$C_{10}H_7$

We were interested in evaluating the scope of this reaction toward the synthesis of 1,1'-binaphthyl derivatives, mainly 1,1'-binaphthalenyl-2,2'-diol (BINOL). For this reason, we performed the reaction of 1-halo-2-methoxy or 2-hydroxynaphthalenes with anion **1**. Different experimental conditions (solvent, nucleophile/substrate ratio**,** temperature, among others) were investigated to improve the yield of the 1,1´-binaphthyl derivative. Initially, the 2-hydroxyl group of the halide was protected as the methyl ether, as it is known that haloaryl compounds substituted by an ionizable OH group react poorly under $S_{RN}1$ conditions.[8]

Another approach we followed was the Stille procedure[10] through which 1,1'-binaphthalenes can be obtained by the palladium catalyzed cross-coupling reaction of an organostannyl compound with an aryl halide.[11] In this approach we performed the reaction of (2-methoxy-1-naphthyl)-trimethylstannane, synthesized by the $S_{RN}1$ procedure, with 1-iodo-2-methoxynaphthalene (eq 2). The reaction was also evaluated with other aromatic halides such as 1-iodonaphthalene and 1-iodo-2-methylbenzene.



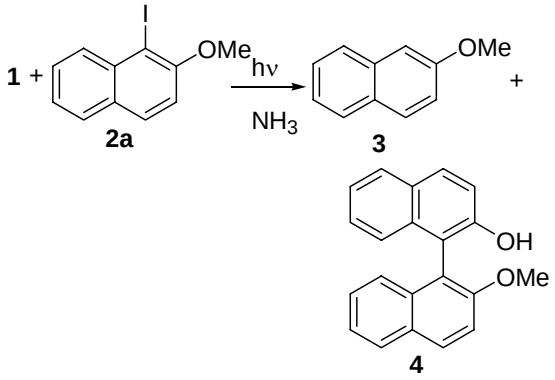
(2)

From the two approaches used the highest yield of 2'-methoxy-1,1'-binaphthalenyl-2-ol (52%) was achieved through the $S_{RN}1$ procedure. In the Stille reaction between (2-methoxy-1-naphthyl)-trimethylstannane and an ortho-substituted iodide mainly methyl transfer instead of 2-methoxy-1-naphthyl transfer was obtained.

Theoretical studies were performed to interpretate the low yield of 2,2'-disubstituted binaphthyls obtained through the ET pathway.

Results and Discussion

The photoinitiated reaction of **1** with 1-iodo-2-methoxynaphthalene (**2a**) in liquid ammonia (nucleophile/substrate ratio = 4) afforded a 91% yield of iodide ions, 2-methoxynaphthalene **3** (56%) and 2'-methoxy-1,1'-binaphthalenyl-2-ol **4** (35%) (eq 3, Table 1, entry 1).



(3)

Table 1. Photostimulated reaction of the anion of β-naphthol **1** with 1-iodo-2-methoxynaphthalene (**2a)** in different solvents[a]

Exp	Nu^- $Mx10^3$	Substrate $Mx10^3$	KBuO-*t* $Mx10^3$	Solvent	X^- (%)[b]	Products (%)[c]	
						3	**4**
1	9.6	2.2	17.8	NH_3	91	56	35
2	10.1	0.8	18.7	NH_3	*d*	57	42
3	90	8.6	163.8	DMSO	*d*	54	41
4	616	59.2	714	DMSO	100	39	52
5	549	54.8	527	DMSO	99	41	52
6	598	59.8	748	DMSO/crown(185)	100	66	33
7	99.9	9.7	187.5	DMSO/65°C	71	*d*	23
8	570	58.8	704	DMSO/$FeBr_2$	*d*	9	7
9[e]	94.4	9.2	176	DMSO	6		
10[f]	90.6	9	164	DMSO	99	52	42
11[g]	89.3	8.7	163	DMSO	90	54	17
12	--	9.8	--	DMSO	< 5		
13	--	9.2	105.7	DMSO	88	61	--
14	93.9	10.3	176.6	DMPU	86	*d*	21
15	206	20	415.0	CH_3CN	70	38	10
16[h]	154.9	25.2	700	Tetraglyme	100	97	--
17	544	59.2	690	HMPA	86	*i*	--

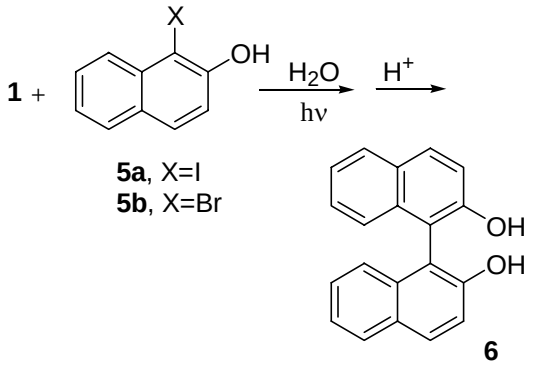
[a]Irradiation time=180 min, unless otherwise indicated. [b]Percentage of halogen quantified potentiometrically on the basis of the substrate concentration. [c]Quantified by GLC using the

internal standard method. [d]Not quantified. [e]Dark reaction. [f]*p*-Dinitrobenzene (40 mol %). [g]di-*t*-Butylnitroxide (50 mol %). [h]Irradiation time = 300 min. [i]Only product formed. Not quantified.

The percentage of **4** increases to 42% with a nucleophile /substrate ratio of 12 (Table 1, entry 2). Changing the solvent from NH_3 to DMSO (rt) accompanied by a 10 fold increment in the concentration of the reactants improved the yield of **4** to 52%. In these reactions the reduction product **3** was also formed (Table 1, entries 3-5). No reaction was observed in this solvent in the absence of light or in the presence of Fe(II) salts as initiators (Table 1, entries 8, 9).

The reaction is not inhibited by the addition of *p*-dinitrobenzene, a well known radical anion scavenger, but the yield of substitution decreases in the presence of di-*t*-butylnitroxide, a radical scavenger (Table 1, entries 10, 11). The deiodination of **2a** fails when it is irradiated in the absence of **1** but it releases 88% of iodide ions when irradiated in the presence of an excess of KOBu-*t* (Table 1, entries 12, 13). Besides, the yield of products was shown to be invariant to the presence of excess KOBu-*t* (Table 1, entry 5). A higher reaction temperature or the presence of crown ether did not improve the yield of substitution.

Changing the solvent from DMSO to DMPU (N,N´-dimethylpropyleneurea), MeCN, tetraglyme or HMPA decreases the percentage of **4** with a considerable increase in the amount of reduction. There was no reaction between **1** and **2a** either in toluene, water, or water:DMSO (10:1), DMSO being added to favour the solubility of the substrate. A low degree of substitution occurs in water when **5a**, the hydroxy derivative of **2a**, is the substrate. On the other hand, the bromo derivative **5b** reacts in water to give BINOL[12] in 34% yield (eq 4, Table 2, entry 1, 4).



(4)

As it is known, the thermal reaction of **1** with **5b**, which can be deprotonated in the reaction medium, depends on the concentration of the base being used.[13] A similar base dependent behavior was observed under our irradiated reaction conditions (see Table 2). The lower overall yield determined with the iodine derivative **5a** with respect to that of **5b** is mainly ascribed to the lower solubility of the former compound in the reaction medium. Interestingly, the yield of BINOL obtained from **5a** increases (40% after 6 h irradiation) when the reaction mixture is treated under ultrasound (20 min) before being irradiated (Table 2, entry 3). On the other hand, high yields of reduction and very low yields of substitution are obtained by reaction of either **5a** or **5b** under irradiation in DMSO (Table 2).

Table 2. Photostimulated reaction of anion **1** with 1-halo-2-naphthol **5** in different solvents

Exp	Nucleophile Mx10^3	Substrate Mx10^3	Base[a] Mx10^3	Solvent	Time h	X^- (%)[b]	**6** (%)[c]
1	126	5a, 32	119	H_2O	10	30	5
2[d]	113	5a, 36	125	H_2O	10	2	
3[e]	139	5a, 36	147	H_2O	6	71	40
4	111	5b, 29.9	106	H_2O	10	77	34
5	262	5b, 30.2	281	H_2O	10	37	17
6	106	5b, 101	120	H_2O	10	7	---
7[f]	138	5b, 23.5	146	DMSO	6	85	18
8[f]	162	5a, 14.6	158	DMSO	3	91	13
9[f]	148	5a, 32	312	DMSO	3	89	traces

[a]NaOH as base unless otherwise indicated. [b]Percentage of halogen quantified potentiometrically on the basis of the substrate concentration. [c]Quantified by GLC using the internal standard method. [d]Dark reaction. [e]20 min sonication before irradiation. [f]KBuO-*t* as base.

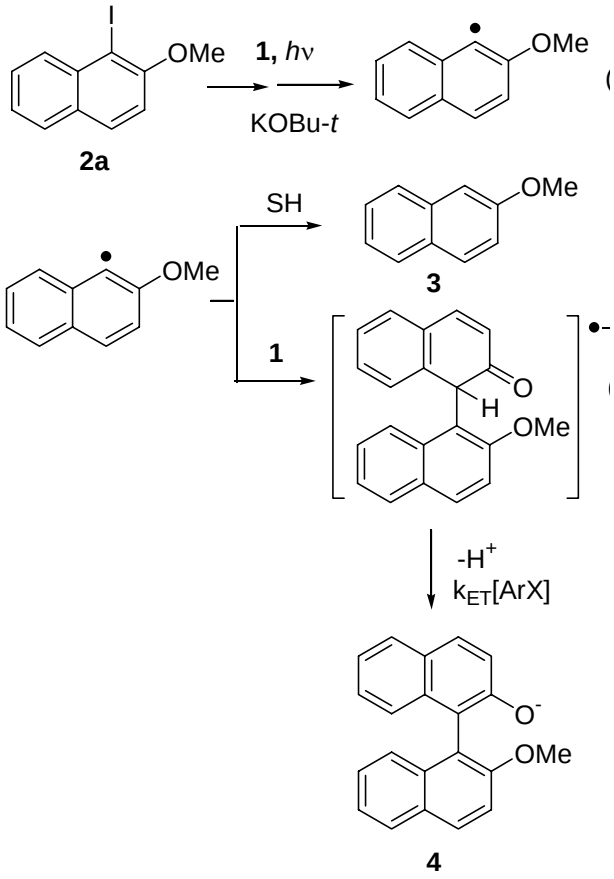
The experimental evidence obtained can be taken as indicative of the presence of radicals as reaction intermediates. In the initiation step, 2-naphthoxide anion or KOBu-*t* ultimately forms the 2-methoxy-1-naphthyl radical by ET to **2** (eq 5). This radical can couple with the nucleophile to form the radical anion of the substitution product or can be reduced to afford compound **3** (Scheme 1).

DMSO or liquid ammonia are the solvents in which the radical-nucleophile coupling step (eq 7) competes more efficiently with the reduction of the radical (eq 6). For this to happen, a higher concentration of reactants is required in DMSO.

The rate constant for reduction of naphthyl radicals has been determined to be 6.4×10^6 M^{-1} s^{-1} in DMSO,[14] and that for phenyl radicals 2.8×10^6 M^{-1} s^{-1} and 6.7×10^6 M^{-1} s^{-1} in DMSO and MeCN, respectively. Based on these data and our experimental results a higher rate constant for hydrogen transfer to naphthyl radicals is expected from MeCN than from DMSO.

It is known that the nucleophile – radical coupling reaction has been determined to be less sensitive than expected to steric hindrance.[15] For example, in the reaction of the enolate anion of acetone with 2,4,6-triethylphenyl radical a 70% yield of coupling has been determined. The yield decreases considerably, accompanied by an increment in reduction, when two *i*-Pr groups are adjacent to the radical center.[15] Despite this fact, the reaction of **1** with the 2-methoxy-1-naphthyl radical affords the highest yield of reduction when compared to the reaction of **1** with 1-naphthyl

and *p*-anisyl radicals in which 53% and 42 % yields of substitution are obtained together with 20% and 13% yields of naphthalene and anisole, respectively; all the reactions in liquid ammonia under irradiation.[9] In order to explain these results the potential energy surface for the reaction of **1** with phenyl, 1-naphthyl and 2-methoxy-1-naphthyl radicals was calculated by the semiempirical AM1/UHF[16] method and the global enthalpy of reaction by the DFT B3LYP[17] procedure.[18]



(5)

(6)

(7)

Scheme 1

The potential energy surface calculated for the coupling step shows the same general shape for all the radicals under study. These radicals combined with the anion to form an electrostatic encounter complex in which the hydrogen atoms of the radical interact with the oxygen center of the nucleophile. The change in hybridization (sp^2 - sp^3) at C_1 of the anionic naphthyl moiety and the C-C bond formation are the more relevant reaction coordinates in the formation of the radical anion of the substitution compounds from this complex.

Based on our calculations, **1** combined exothermically with all the radicals to form the corresponding radical anion; the exothermicity calculated being -45.93 kcal/mol (phenyl radical), -43.02 kcal/mol (1-naphthyl radical), and -45.99 kcal/mol (2-methoxy-1-naphthyl radical). The relative thermodynamic stability obtained is thus: 2-metoxy-1-naphthyl ≈ phenyl > 1-naphthyl. UB3LYP calculations afford similar results.

The higher percentage of reduction *vs.* coupling obtained in the reaction of 2-methoxy-1-naphthyl radical with **1**, despite the fact it affords the most stable radical anion of the series, can be indicating the importance of the kinetics factors in this reaction. From the computational analysis of the coupling reaction the following activation energies are evaluated: 3.20 kcal/mol (1-naphthyl radical), 3.80 kcal/mol (phenyl radical), and 4.00 kcal/mol (2-methoxy-1-naphthyl radical). The calculated higher activation energy for coupling of the ortho-substituted naphthyl radical can be interpreted on the basis of steric interactions in the corresponding TS as shown in Figure 1 in which the TS for the coupling with 1-naphthyl radicals is also presented for comparison. Given these steric constrains the hydrogen abstraction competes more efficiently with the radical-nucleophile coupling when the 1-naphthyl radicals bear a 2-methoxy substituent.

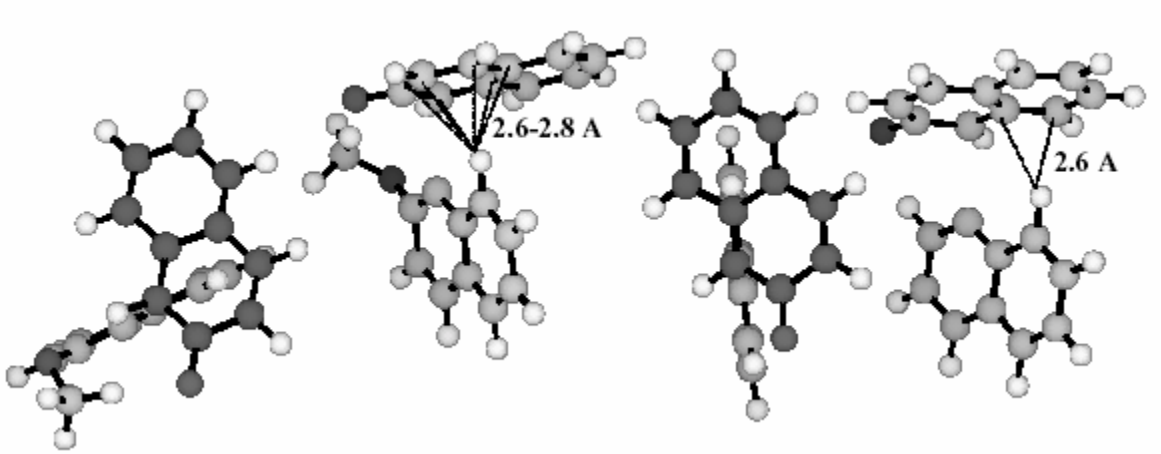
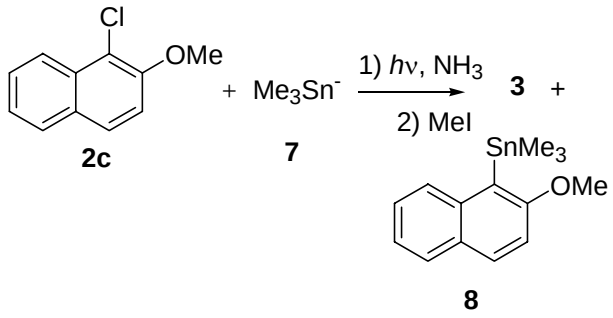


Figure 1. AM1 geometry of the transition states calculated for the coupling reaction of 2-methoxy-1-naphthyl radical (left) and 1-naphthyl radical (right) with **1**.

Stille Approach. Knowing the scope of this reaction in the synthesis of biaryls, we investigated the possibility it could offer in the synthesis of 1,1'-arylnaphthalenes. Recently, the combination between the $S_{RN}1$ mechanism, an interesting approach to the synthesis of the stannyl derivatives needed as substrates, and the Stille reaction has proved a valuable route to biaryls (eq 8).[19]

$$ArCl \xrightarrow[h\nu]{Me_3Sn^-} Ar\text{-}Sn(Me)_3 + Ar'\text{-}I \xrightarrow[Cl_2Pd(PPh_3)_2]{DMF} Ar\text{-}Ar' \qquad (8)$$

In the irradiated reaction of Me_3Sn^- ion **7** with 1-chloro-2-methoxynaphthalene (**2c**), 93% of the substitution compound **8** was obtained (eq 9), (Table 3).



2c **7** **8** (9)

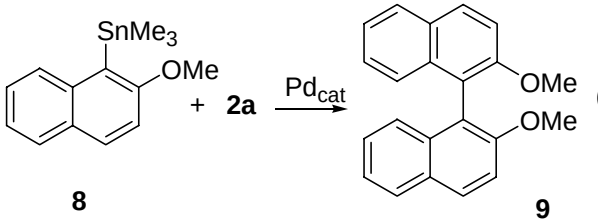
In these reactions, the competition with the halogen metal exchange (HME) mechanism becomes more important with the bromo derivative **2b** as substrate (Table 3).[19] The reaction of **2b** leads to 80% of **3** and 10% of **8**. We have observed that the products distribution is slightly modified by changes in the substrate/nucleophile ratio.

Table 3. Photostimulated reaction of trimethylstannyl anion **8** with 1-halo-2-methoxynaphthalene in liquid ammonia

Exp	Nu^- ($Mx10^3$)	Substrate ($Mx10^3$)	Time min.	Products (%)[a] **3**	**8**
1	11.0	**2b**, X=Br, 9.8	60	80	10
2	11.7	**2c**, X=Cl, 9.7	180	10	93
3	70.0	**2c**, X=Cl, 7.3	180	3/8 =11.4	

[a]Quantified by GLC using the internal standard method.

In a second step, the reaction of **8** with **2a** was performed in the presence of different Pd catalysts to obtain **9**,[20] the 2,2´-dimethoxy derivative of **4** (eq 10).



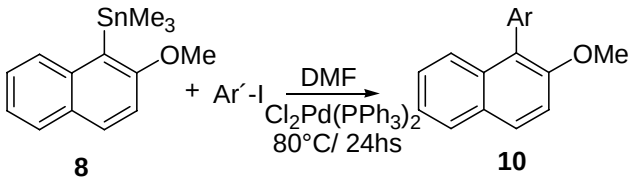
8 **9** (10)

Unfortunately, neither of the reaction conditions or the catalysts used [$Pd(PPh_3)_2Cl_2$, 8% or 10% in DMF (80°C, 24 h); $Pd(dba)_3$ 3% or $Pd(dba)_3$ 3% with (o-biphenyl)$P(t\text{-}Bu)_2$ 6% in toluene (70°C, 72 h), or 9% CuI -Tetrakis 6% in dioxane (80°C, 72 h)] show to be an appropriate route to **9** (yields lower than 11%). We observed a higher yield of methyl transfer from the stannyl derivative to form 2-methoxy-1-methylnaphthalene.

The results obtained by this approach evidence a considerable inefficient 2-methoxy-1-naphthyl transfer step, which could be attributed to the presence of the ortho substituent on the

rings. In order to test this effect the reaction of **8** with PhI, o-iodotoluene and 1-iodonaphthalene were carried our under the best experimental conditions [($Pd(PPh_3)_2Cl_2$, 8% in DMF (80°C, 24 h)].[19]

As can be seen, the transfer of the naphthyl ring (60%) is considerable more efficient than the transfer of the phenyl ring (41%) (eq 11). On the other hand, while the presence of an *o*-methyl substituent on the phenyl ring decreases the efficiency of the transfer to 31%, the presence of an *o*-hydroxy or *o*-methoxy group on the naphthyl system has a considerable more depressing effect and the percentage of transfer decreases from 60% to 15% and 11% yields respectively.



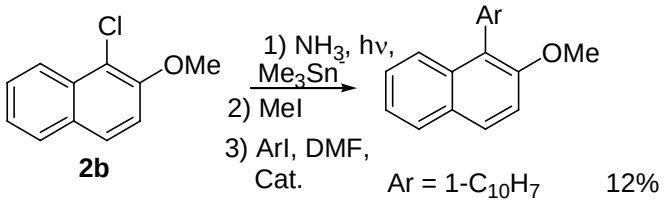
8 **10**

Ar´=Ph, o-CH_3Ph, 41, 31%

1-$C_{10}H_7$, 2-CH_3O-1-$C_{10}H_6$, 2-HO-1-$C_{10}H_6$ 60, 11, 15%

(11)

The one-pot reaction shown in eq 12, in which compound **8** is formed in a first step by substitution of **2b** with $(Me)_2Sn^-$ ions in liquid ammonia and after ammonia evaporation the catalyst, DMF and the aryl halide are added, affords considerable lower yields of biaryls than the reaction performed in two steps.



2b

Ar = 1-$C_{10}H_7$ 12%

Ar = *o*-$CH_3C_6H_4$- 5%

(12)

Conclusions

To our knowledge, this is the first report of an $S_{RN}1$ reaction between a bidentate nucleophile and a 1-halonaphthalene derivative to afford a moderate yield of BINOL in water under irradiation. The reaction can be used as an alternative synthetic path to 2,2'-disustituted 1,1'-binaphthalenes. The scope of water as solvent in these reactions remains to be further investigated, mainly in relation to the substrates able to be substituted in this medium.

Although a low sensitivity to steric effects has been reported for the reaction of substituted phenyl radicals with nucleophiles, we present evidence of a considerable effect exerted by a OCH_3 group ortho to the radical center of a 1-naphthyl radical. In its presence, the yield of substitution decreases from 53% (1-naphthyl radicals) to 35% (2-methoxy-1-naphthyl radicals),

with the corresponding increment in the percentage of reduction product with all the reactions in liquid ammonia under photoinitiation.

A similar effect is informed for the Stille reaction. The yield of the phenyl transfer product decreases ≈10% by *o*-CH_3 substitution of the phenyl radicals while it decreases ≈50% by *o*-CH_3O substitution in the naphthyl system.

Experimental Section

General Procedures. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Brucker 200 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Shimatzu GC-8A or Hewlett Packard 5890 Series II with a flame-ionization detector and the Shimatzu CR-3A or data system Hewlett Packard 3396 Series II integrator, using a column packed with 5% OV17 on chromosorb G (3m x 3mm.), or a HP-1 capillary column (methyl silicone, 10 m x 0.53 mm x 2.65 μm film thickness). The GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 30 m x 0.12 mm DB-5 MS column. The distillation at reduced pressure was performed with a Kügelrohl. Irradiation was conduced in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (Philips Model HPT, air and water refrigerated). Potentiometric titration of halide ions was performed in a pH meter using an Ag/Ag+ electrode. Melting points were not corrected. Column chromatography was performed on silica gel (70-270 mesh ASTM).

Materials. Potassium *tert*-butoxide, iodobenzene, 1-iodonaphthalene, 1-bromo-2-naphthol, 2-iodotoluene, trimethyltin chloride, HMPA and MeCN were commercially available and used as received. The 2-naphthol was recrystallized from ethanol/water.[21] The DMSO was stored under molecular sieves (4Å). DMPU, toluene and tetraglime were distilled under vacuum. The 1-halo-2-methoxynaphthalene (**2**) was prepared from the reaction of 1-halo-2-naphthol, potassium *tert*-butoxide in DMSO with methyl iodide. The 1-iodo-2-naphthol was prepared from the reaction of 2-naphthol, iodide and H_2O_2 in ethanol.[22] The 1-chloro-2-naphthol was prepared from reaction of 2-naphthol with *t*-butyl hypochlorite in CCl_4.[23]

Photostimulated reaction of 2-naphthoxide ions with 1-iodo-2-methoxynaphthalene

The following procedure is representative. The reactions were carried out in a 30 ml three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 10 mL of dry and degassed DMSO under nitrogen was added potassium *tert*-butoxide (784 mg, 7.0 mmol) and 2-naphthol (864 mg, 6 mmol). After 15 min 1-iodo-2-methoxynaphthalene (170.4 mg, 0.6 mmol) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate and water (50 mL). The mixture was extracted twice with

methylene chloride (20 mL), the organic extract was washed twice with water, dried, and quantified by GLC. The iodide ions in the aqueous solution were determined potentiometrically.

The solvent was removed under reduced pressure. The residue after column chromatography on silica gel [petroleum ether:diethyl ether (95:5)] gave 2-methoxynaphthalene **3**[12] and 2'-methoxy-1,1'-binaphthalenyl-2-ol **4**.[24]

Photostimulated reaction of Me_3Sn^- ions with 1-chloro-2-methoxynaphthalene

The following procedure is representative. The reactions were carried out in a 250 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 100 mL of distilled ammonia was added trimethyltin chloride (1.17 mmol) and then Na metal (2.6 mmol, 10% excess) was added in small pieces, waiting for total decoloration. After 10 min 1-chloro-2-methoxynaphthalene (0.97 mmol) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate and water (50 mL). The mixture was extracted twice with methylene chloride (20 mL), the organic extract was washed twice with water and dried. The solvent was removed under reduced pressure. The mixture was distillate under reduced pressure in the Kügelrohl gave (2-methoxy-1-naphthyl)-trimethylstannane (**8**) ^{1}H NMR (200 MHz, $DCCl_3$, 25°C) δ_H 0.44 (s, 9 H); 3.9 (s, 3 H); 7.20-7.47 (m, 3 H); 7.77-7.89 (m, 3 H). ^{13}C NMR δ_C -6.22($3CH_3$); 56.38; 112.46; 123.2; 125.5(c); 126.2; 128.4; 128.6; 129.9(c); 131; 139.9(c); 162.1(c). *m/z* 326 (1.6); 324 (1.6); 323 (1.1); 322 (8.6); 321 (3.3); 320 (7.2); 319 (3.1); 311 (18.2); 309 (15.4); 308 (10.1); 307 (100); 306 (36.2); 305 (75.7); 304 (29.2); 303 (47.5); 292 (51.7); 291 (16.9); 290 (40.4); 289 (15.5); 288 (21.5); 277 (18.2); 276 (7.2); 275 (13.9); 262 (9.2); 260 (8.1); 247 (25.9); 246 (9.4); 245 (18.7); 234 (9.6); 232 (9.4); 230 (6.7). HRMS calcd for $C_{14}H_{18}SnO$ (Sn 120) 322.0469 found 322.0489 and 320.0498.

Cross Coupling Reaction of **8** with **2** Catalyzed by $Pd(PPh_3)_2Cl_2$. The procedure following is as previously described.[25]

1-Iodo-2-methoxynaphthalene (**2a**)**.** mp 88-9 °C (lit.[12] 88-89).^{1}H NMR δ_H 4.03 (3H, s); 7.2-7.26 (1H, m); 7.34-7.42 (1H, m); 7.5-7.58 (1H, m); 7.73-7.85 (2H, m); 8.14 (1H, d). *m/z* 284 (100); 269 (10); 241 (24); 142 (49); 127 (35); 114 (41).

1-Bromo-2-methoxynaphthalene (**2b**)**.** mp 80-82 °C (lit.[12] 85 (82.5) °C).^{1}H NMR δ_H 4.00 (3H, s); 7.23 (1H, d); 7.35-7.43 (1H, m); 7.53-7.61 (1H, m); 7.76-7.81(2H, m); 8.24 (1H, d).^{13}C NMR δ_C 56.97; 108.61(c); 113.57; 124.24; 126.02; 127.67; 127.97; 128.88; 129.97(c); 133.06(c); 153.70(c).

1-Chloro-2-methoxynaphthalene (**2c**)**.** mp 68-70 °C (lit.[12] 67-69 °C).^{1}H NMR δ_H 3.96 (3H, s); 7.19 (1H, d); 7.31-7.39 (1H, m); 7.48-7.57 (1H, m); 7.67-7.76 (2H, m); 8.19 (1H, d).^{13}C NMR δ_C 56.86; 113.63; 116.81(c); 123.36; 124.22; 127.37; 127.94; 129.44(c); 131.82(c); 152.49(c). *m/z* 194 (20.4); 192 (61.4); 177 (22.5); 151 (32.2); 150 (10.4); 149 (100.0); 126 (10.1); 114 (24.1); 113 (14.5); 63 (12.9).

2-Methoxynaphthalene (**3**)**.** mp 72-3°C (lit[12] mp. 72°C). ^{1}H NMR δ_H 3.9 (3H, s); 7.12-7.16 (2H, m); 7.31-7.43 (2H, m); 7.70-7.77 (3H, m).^{13}C NMR δ_C 55.27; 105.78; 118.69 (c); 123.57;

126.35; 126.72; 127.64; 129.37; 134.57 (c); 157.61 (c). *m/z* 159 (7.2), 158 (60.9); 143 (7.2); 128 (14.4); 116 (10.3); 115 (100.0); 89 (11.5).

2'-Methoxy-1,1'-binaphthalenyl-2-ol (**4**)**.**[24] ^{1}HNMR δ_H 3.79 (3H, s); 4.90 (1H, s); 7.01-7.50 (8H, m); 7.83-7.92 (3H, m); 8.05 (1H, d). *m/z* 301 (16.5); 300 (100.0); 268 (7.6); 239 (7.2), 207 (3.1).

1-Iodo-2-naphthol (**5a**)**.** mp 92-94 °C (lit[12] 91-5 °C). *m/z* 270 (100.0); 142 (26.3); 115 (59.4); 114 (22.4); 88 (11.9); 63 (11.8).

1-Chloro-2-naphthol (**5c**)**.**[23] *m/z* 180 (32.9); 178 (100.0); 115 (35.4); 114 (89.5); 113 (20.9); 89 (15.8); 88 (14.2).

2,2'-Dihydroxy-1,1'-binaphthalene (Binol) (6). mp 214-217 °C (lit.[12] 213-216 °C). ^{1}H NMR (acetone-d_6) δ_H 7.14-7.18 (2H, m); 7.26-7.47 (6H, m); 7.95-8.03 (1H, m).^{13}C NMR (acetone-d_6) 115.04 (c); 119,54; 123.72; 125.50; 127.11; 128.95; 130.05 (c); 130.67; 135.55 (c); 154.58 (c). *m/z* 287 (35.6); 286 (100.0); 285 (30.9); 268 (11.4); 257 (20.2); 239 (20.3); 228 (11.1); 226 (11.2); 134 (15.7); 120 (42.3); 119 (45.5); 118 (17.3); 113 (17.1).

The products **10a – c** were compared by CGL with authentic samples obtained by methylation of the corresponding 1-substituited-2-naphthols with MeI.

1-Phenyl-2-methoxynaphthalene (10a). ^{1}H NMR δ_H 3.82 (3H, s); 7.29-752 (9H, m); 7.79-7.89 (2H, m). ^{13}C NMR δ_C 56.8, 113.9, 123.5, 125.3, 125.5 (c), 126.3, 127.0, 127.8, 128.1 (2c), 129.0, 130.9 (2c), 133.6 (c), 136.4 (c), 153.8 (c).

1-(2-Tolyl)-2-methoxynaphthalene (10b). ^{1}H NMR δ_H 2.00 (3H, s); 3.84(3H, s); 7.16-7.50 (8H, m); 7.8-7.9(2H, m). ^{13}C NMR δ_C 19.7, 56.6, 113.6, 113.9, 123.4, 125.0, 125.3, 125.6, 126.3, 127.0, 127.4, 127.8, 128.1, 128.9, 129.8, 130.8, 130.9, 136.1. *m/z* 249 (16); 248 (100); 233 (15); 218 (36); 217 (28); 216 (15); 215 (31); 203 (21); 202 (28); 189 (20); 115 (9); 107 (16); 101 (20); 95 (14); 88 (9).

1-Naphthyl-2-methoxynaphthalene (10c).[26] ^{1}H NMR δ_H 3.72(3H, s); 7.16-7.47(9H, m); 7.55-7.63 (1H, m); 7.82-7.98(3H,m). *m/z* 285 (21); 284 (100); 283 (11); 269 (31); 268 (26);259 (35); 252 (33); 250 (10); 241 (17); 240 (19); 239 (53); 237 (10); 226 (8); 135 (11); 134 (23); 126 (31); 125 (28); 120 (21); 119 (52); 113 (11); 106 (11).

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18. The AM1 and B3LYP calculations have been performed with the AMPAC 5.0 package (see ref. 16b) and the Gaussian98 program(see ref. 17c), respectively. All the calculations have been performed with complete geometry optimization. The intermediates and transition states were first located through the reaction coordinate method and then refined with the appropriate procedure. The stationary points were located by Hessian matrix calculations: all positive eigenvalues for a minimum energy species and one imaginary frequency for transition states.
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