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Synthesis of triaryls: hydroxy and amine dinaphthyl and diphenanthryl aryls by one-pot electron-transfer nucleophilic substitution reactions

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ABSTRACT

A new one-pot synthetic route to achieve the preparation of hydroxy and amine binaphthyl and biphenanthryl aryls is here reported. This approach involves the reaction of 1,4-bromoiodobenzene, 4,4′-diiodobiphenyl, and 1,4- and 1,5-diiodonaphthalene with the anions of 2-naphthylamine, 2-naphthol, and 9-phenanthrylamine under irradiation in liquid ammonia. The reactions proceed to afford triaryl derivatives in moderate to good yields (~45% of 1,4-phenylene- and 1,4-naphthylene-1,1′-dinaphthalen-2-ols as well as 1,4-phenylene-1,1′-dinaphthalen-2-amine and 10,10′-diphenanthren-9-amine). Lower yields (27%) of polyaryl derivatives are obtained by reaction of 4,4′-diiodobiphenyl with anions of 2-naphthol and 9-phenanthrylamine.

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1. Introduction

During the last decades, there has been a steady increase in the report of new aromatic compounds synthesized by different methodologies. Particularly, biaryls and polyaryls are the scope of many laboratories due to their versatile uses such as medicinals (anti-cancer, antifungals), agrochemicals, and even as molecular device precursors.[1] In particular, the development of new organic π-conjugated materials with semiconducting and/or non linear optical properties has been attractive for their potential applications, such as organic light-emitting diodes (OLED) or electronic devices.[2,3] It has been proposed that polyaromatic compounds having naphthyl groups, responsible for their nonplanarity, could improve the device performance in blue-light-emitting materials.[4,5] Hence, the formation of aryl–aryl bonds is of great relevance in modern organic synthesis,[6] and metal catalysis methodology is one of the synthetic procedures most studied nowadays. Aryl boronic acids (Suzuki–Miyaura coupling),[7–9] arylstannanes (Stille reaction),[10,11] and organo-zinc compounds (Negishi coupling)[12] are reagents usually employed in this family of reactions. Another reported alternative to form arene–arene bonds is the direct-coupling of two unfunctionalized aromatic molecules in the presence of an oxidant,[13] or mediated by oxidation of organocuprates.[14] Moreover, organocatalysis or photolysis by free transition-metal-catalyzed direct arylation of aromatic C–H bonds through a homolytic aromatic substitution (HAS) is emerging as a valuable and efficient alternative to traditional cross-couplings in the construction of biaryl compounds and it is a very rapidly growing area of chemical synthesis.[15–17]

The radical nucleophilic substitution mechanism ($S_{RN}1$) is also a metal-free alternative route to the synthesis of biaryls. The versatility of the process mostly derives from the fact that these reactions are generally carried out under mild conditions and the substrates tolerate many functional groups.[18–20] This versatility distinguishes the procedure from other methods used such as Kumada, Suzuki, or Stille coupling using transition-metal-catalyzed reactions. Anions from P, S, Sn, As, Sb, Se, and Te react by this mechanism through the heteroatom to form a C–heteroatom bond. The anions from ketones, esters, amides and thioamides, nitroalkanes, nitriles, arylamines, arylalcohols, and mono and dianions from β-dicarbonyl compounds react at their carbon site to form a C–C bond.[18–20] Thus, different hydroxyl biaryls have been synthesized in good yields by the photoinitiated substitution of haloarenes with arylalkoxides.[21–28] Arylindoles and arylimidazoles can be obtained by this procedure,[29–31] and only a few examples have been reported for the preparation of amino biaryls.[22,25,32]

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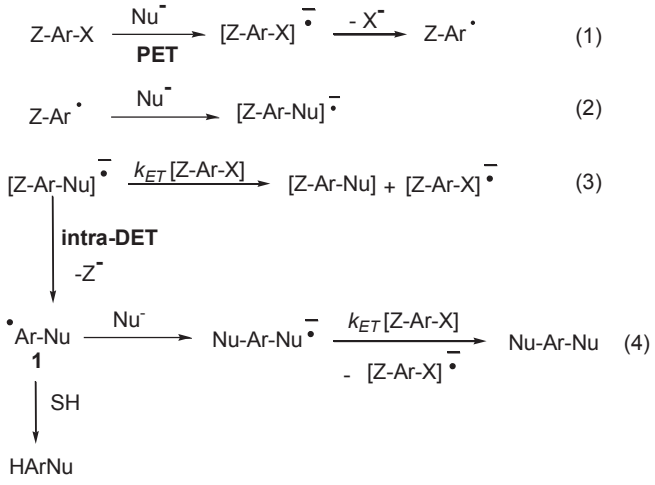
These nucleophilic substitutions involve electron-transfer steps (ET) and the intermediacy of radical and radical anions. The radicals are originated from dissociation of the radical anions of the aromatic substrates ($ZArX^{-\cdot}$, X=halogen, Z=substituent or leaving group), which are formed by a photoinduced electron-transfer (PET) from the nucleophile (Nu^-) (Eq. 1). The radicals can react with the nucleophile to give the radical anion of the substitution product (Eq. 2), also responsible for continuing the propagation chain of the proposed mechanism (Eq. 3) (Scheme 1). The system has attractive synthetic potentialities when Z can act as a leaving group because $Z-Ar-Nu^{-\cdot}$ may cleave through an intramolecular dissociative ET (intra-DET) leading to the monosubstituted radical **1** (Eqs. 3 and 4). This reaction depends on different factors such as the electron affinity of the Nu moiety, its position on the aromatic ring in relation to Z, as well as the electron affinity of Z. Radical **1** can follow different reaction pathways. It can produce the disubstitution compound (NuArNu) by reaction with a second Nu^- (Eq. 4) or it can abstract a hydrogen atom, usually from the solvent,[33] to give the monosubstituted-reduced compound (HArNu).



Scheme 1.

Disubstitutions have been obtained, for example, by reaction of $(EtO)_2PO^-$ anions with *o*-[34] and *p*-chloroiodobenzene,[35] whereas the *meta* isomer gives mainly substitution only at the iodine atom, involving the retention of the second halogen atom.[36] Di- and trichlorobenzenes have been di or trisubstituted by Me_3Sn^-,[37,38] respectively. A similar behavior has been observed for the di or trisubstitution of diethylphosphate phenyl esters.[39,40] Disubstitution by $PhSe^-$ has also been achieved with 1,4-$BrIC_6H_4$ as substrate.[41]

The preparation of hydroxyl or amine biaryls has been possible due to the ambident behavior shown by arylamide and arylalkoxide anions. Phenoxide ions react with aromatic radicals at their C_{ortho} and C_{para} positions. Arylation at C_1 is the preferred reaction with 2-naphthoxide and 2-naphthylamide anions.[25] With the anions of 9-phenanthrylamine or 9-phenanthrol the preferred site of arylation is C_{10}.[22] A preference for coupling at C has also been found in the reaction of heteroaryl nitrogen anions with aryl and perfluoroalkyl radicals.[31]

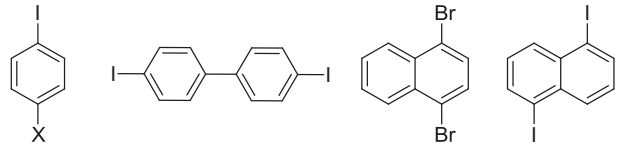
We consider it interesting to take advantage of this regiochemistry to extend the scope of the $S_{RN}1$ mechanism for the preparation of triaryls bearing an amine or hydroxyl substituent, particularly, triaryls from 2-naphthylamine, 9-phenanthrylamine and 2-naphthol. In order to reach these aromatic-type molecules, phenyl, biphenyl and naphthyl moieties holding two halogens as leaving groups were used as substrates.

The possibility to achieve disubstituions with the simultaneous formation of two C_{Ar}-C_{Ar} bonds could represent an interesting alternative route to triaryl alcohols and triaryl amines through a one-pot pathway. The amino or hydroxy substituents on the aromatic skeleton of these compounds would make them suitable for further modifications through their known chemistry. This versatility combined with the spatial disposition of the substituents could improve the potential scope of the new compounds in different areas of interest. Thus, when NH_2 or OH groups are placed in opposite directions, the compounds may prove interesting as cross-linking agents in polymer chemistry as well as in the field of new organic electronic materials.[2,42] Compounds bearing both substituents with similar space orientation may have applications as ligands in metal-catalyzed organic synthesis.[43–45]

Moreover, the amino and hydroxyl groups have been shown to be good leaving groups, acting as radical precursors under ET conditions whenever transformed into trialkyl ammonium and phosphates esters, respectively.[40,46–49]

2. Results

In this work, the five substrates shown in Chart 1 were employed to build up the polyaryl system.

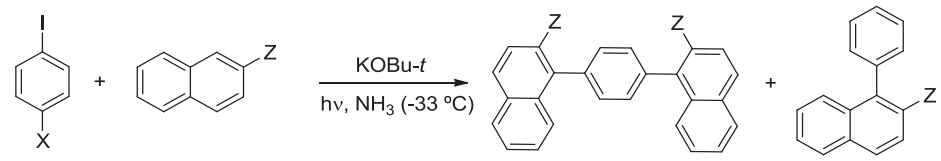


2a, X = I
2b, X = Br
3
4
5

Chart 1.

Table 1 shows the results obtained in the photoinitiated reactions of the anion of 2-aminonaphthalene (**6**) with 1,4-diiodo and 1,4-bromoiodobenzene (**2a** and **2b**, respectively) (Eq. 5).

The highest yield of disubstitution product **7** (50% as isolated product) is obtained through a one-pot reaction of this anion with compound **2b** (X=Br) (Eq. 5, Table 1, expt 3). Arylation is observed in C_1 as in previous studies carried out for 2-aminonaphthalene and 2-naphthol anions under ET conditions.[25] Within this set of reactions, the better yields of disubstitution were observed when the ratio between the nucleophile and the substrate was equal to 6. The yields are also slightly improved by increasing the concentration of the reactants (Table 1, expts 1–3). With substrate **2b**, the monosubstituted-reduced product **8** is formed in yields ranging from 4 to 16% (Eq. 5).



2a X = I
2b X = Br
6, Z = NH_2
10, Z = OH
7, Z = NH_2
11, Z = OH
8, Z = NH_2
12, Z = OH

(5)

Table 1
Photoinitiated reaction of the anions of 2-naphthylamine (**6**), 2-naphthol (**10**), and phenanthryl-9-amine (**13**) with *p*-iodohalobenzenes (**2a** and **2b**)[a]

Expt	Substrate **2**	Nu^-	Substrate/Nu^- ratio	Halides (%)	Product yields (%)	
					NuC_6H_4Nu	NuC_6H_5
1	**2b**, X=Br	$C_{10}H_7NH^-$(**6**$^-$)	1:3	I^-=82, Br^-=80	**7** (40) (34)[g]	**8** (4)
2	**2b**, X=Br		1:6	I^-=72, Br^-=66	**7**(51)	**8**(11)
3	**2b**, X=Br, 53 mM		1:6	I^-=80, Br^-=76	**7** (56) (50)[g]	**8** (16)
4[c]	**2b**, X=Br		1:6	I^-=30, Br^-=20	**7**(14)	**8** (5)
5[b,d]	**2b**, X=Br, 53 mM		1:6	I^-=68, Br^-=63	**7**(15)	**8** (33)
6[b]	**2a**, X=I, 53 mM		1:6	I^-=80	**7**(29)	**8** (32)
7	**2b**, X=Br, 2.3 mM	$C_{10}H_7O^-$[e]	1:6	I^-=95, Br^-=83	**11** (35)	**12** (6)
8	**2b**, X=Br, 2.3 mM	(**10**$^-$)	1:10	I^-=96, Br^-=88	**11** (44) (40)[g]	**12** (3)
9[d]	**2b**, X=Br, 15 mM		1:10	I^-=97, Br^-=88	**11** (27)	**12** (16)
10[b,f]	**2a**, X=I	$C_{14}H_9NH^-$(**13**$^-$)	1:6	I^-=100	**14** (29)[g]	**15** (22)
11[f,h]	**2b**, X=Br		1:6	I^-=85, Br^-=60	**14** (40)[g]	**15** (17)

[a] Reaction time=120 min, NH_3(l) as solvent (unless otherwise indicated), N_2 atmosphere, [substrate]=8.5 mM, unless indicated. Products were quantified by GC, using the internal standard method, unless indicated. In reactions with **2b** as substrate bromobenzene is found in traces as a sub-product.
[b] Benzene was found at 12% (expt 5), 35% (expt 6), and 30% (expt 10).
[c] 1,4-DNB (37% based on substrate) was added.
[d] DMSO as solvent.
[e] In all the reactions with this anion, benzene was observed but not quantified.
[f] Reaction time=180 min.
[g] Isolated yield.
[h] An 8% of substitution product was also quantified with retention of the second halogen (Br).

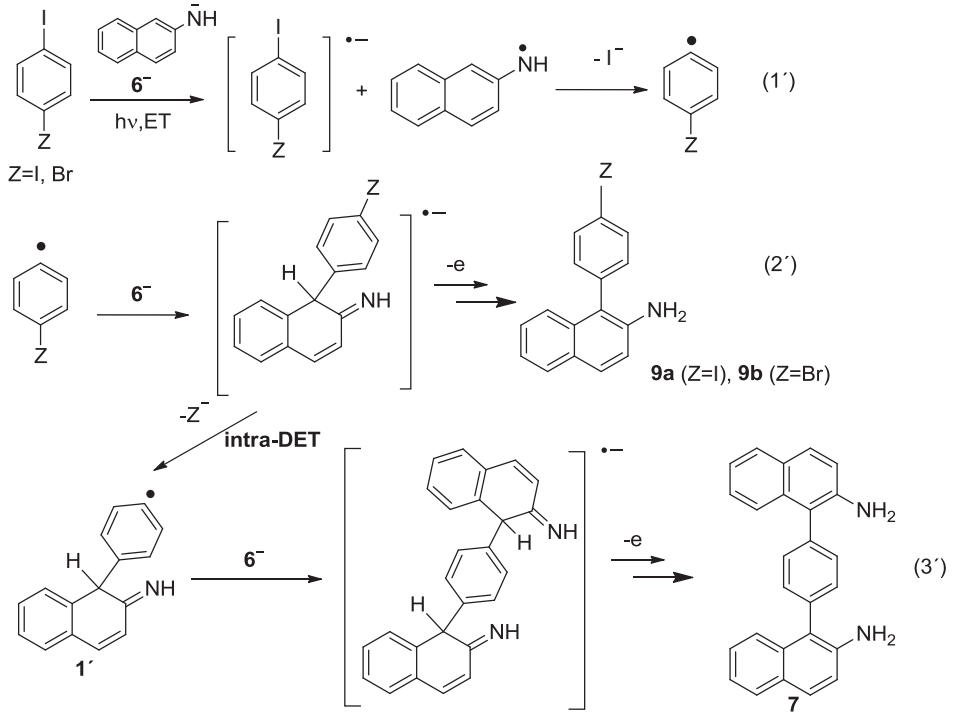
On the other hand, it is observed that **2a**, under the best experimental conditions found for **2b**, is not a recommended substrate (Table 1, expt 6). In this case the main product is benzene, resulting from the reduction of the substrate and the percentage of disubstitution product **7** decreases. Moreover, in these reactions, comparative yields of **7** and **8** are obtained.

Dimethylsulfoxide (DMSO) is a solvent usually employed in nucleophilic substitution reaction under ET. In our case, with substrate **2b** and DMSO as solvent, the yield of the disubstitution product **7** is lower than that in NH_3(l), even at the highest concentration of reactants used (Table 1, expt 5).

The mechanism proposed in these studies is presented in Scheme 2 (Eqs. 1′–3′). As can be seen, the substituted phenyl radicals formed in step 1′ may couple at C_1 of anion **6**$^-$ to finally afford the monosubstituted compounds **9a**,**b** (Eq. 2′). On the other hand, fragmentation of the C–Z bond by intra-DET affords radical intermediate **1**′, which, by reaction with a second nucleophile, will finally produce the disubstitution compound **7** (Eq. 3′).

Following mechanistic studies, we observed that in most of the reactions, the substitution compound with retention of the second halogen (**9a** and **9b** according to the substrate employed) was formed in traces, only detected by GC–MS.

There was no reaction in the dark and inhibition was observed when the irradiated reaction was performed in the presence of 1,4-dinitrobenzene (1,4-DNB), known as an electron acceptor and



Scheme 2.

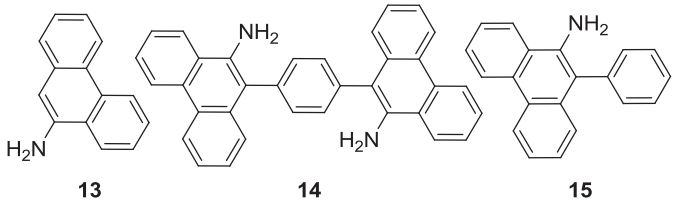
able to interfere at the propagation steps, thus reducing the overall yield of substitution compounds (Table 1, expt 4). The two last reactions are mechanistic evidences of an $S_{RN}1$ type mechanism.

On the basis of sampling experiments (see Supplementary data, Fig. 1), we were able to prove that in the reaction of **2a**,**b**, the monosubstitution product (**9a**,**b**) is not an intermediate in the formation of **7**. It is interesting to notice that in the case of substrate **2a**, a high yield of benzene is detected at a short reaction time. Its formation increases during the irradiation time being the major product at the end of the reaction.

A similar overall behavior was observed in reactions carried out with the anion of 2-naphthol (**10**) in DMSO or NH_3(l) (Eq. 5). Yields were found to range from moderate to good, the highest yield of **11** (40% as isolated product) was obtained in NH_3(l) as solvent with a $\mathbf{10}^-/\mathbf{2b}$ ratio equal to 10. The increase in yield, in relation to the reaction performed with a $\mathbf{10}^-/\mathbf{2b}$ ratio equal to 6, is not significant considering the excess of **10** used (Table 1, expt 7 vs 8). However, this excess of **10** is easily recovered.

When solvent is changed to DMSO, the reduction pathway becomes the main reaction and the yield of disubstitution compound **11** is lower than in NH_3(l) (Table 1, expt 9). The mono- and disubstitution products **11** and **12** derived from 2-naphthol were obtained with similar yields to those of amine derivatives **7** and **8**; however, they show good solubility in most polar organic solvents, thus their manipulation is less complex than that of the corresponding amino derivatives.

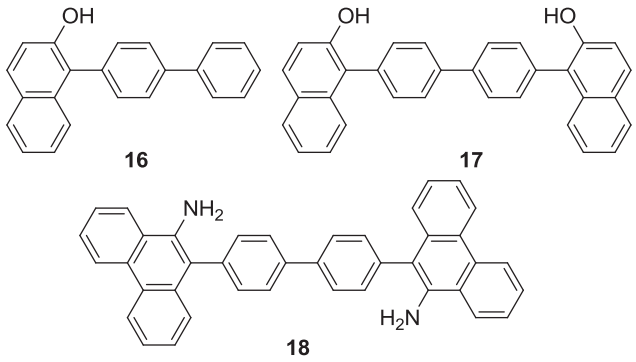
Reactions of **2a** and **2b** with the anion of 9-phenanthrylamine (**13**) are also presented in Table 1. Yields for **14** and **15**, disubstitution and reduced monosubstitution compounds, respectively (Chart 2, Table 1, expts 10 and 11), are as good as for reactions with 2-naphthylamine anion. The maximum isolated yield of **14** (40%) was achieved by reaction of the anion of **13** with substrate **2b**. Compound **14** is a solid that shows low solubility in most common organic solvents.



13 14 15

Chart 2.

Reactivity of **6**, **10**, and **13** was also studied with 4,4′-diiodobiphenyl (**3**), under the same ET conditions. The best yields of reaction with this substrate, insoluble in NH_3(l), were obtained in DMSO. The disubstitution product **17** from anion of 2-naphthol was formed in 26% (Chart 3, Table 2, expt 1).



16 17 18

Chart 3.

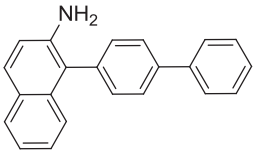
Table 2
Photoinitiated reaction of anions of 2-naphthol (**10**) and phenanthryl-9-amine (**13**) with 4,4′-diiodobiphenyl (**3**)[a]

Expt	Nu^-	Substrate/Nu^- ratio	Halides (%)	Product yields (% isolated)
1[b]	$C_{10}H_7O^-$(**10**$^-$)	1:10	I^-=79	**16** (11) **17** (26)
2[c,d,e]	$C_{14}H_9NH^-$ (**13**$^-$)	1:6	I^-=50	**18** (19)[f]
3[e]		1:6	I^-=70	**18** (28)[f]

[a] Reaction time=240 min, DMSO as solvent, [substrate]=15 mM.
[b] Biphenyl was found but not quantified.
[c] Reaction time=180 min.
[d] NH_3(l) as solvent, substrate dissolved in DMSO when added.
[e] Biphenyl was found at 20% (expt 2) and 26% (expt 3).
[f] Traces of the monosubstituted-reduced product were observed.

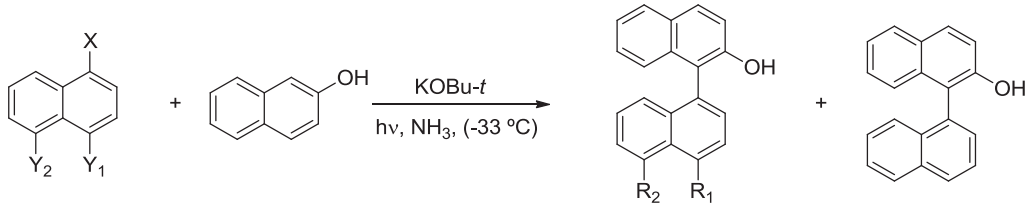
This compound was easily isolated as a solid. From the same reaction, the monosubstituted-reduced product **16** was isolated in 11% yield. Moreover, a similar yield for the disubstitution product **18** (28%) was obtained with anion **13**$^-$ (Table 2).

Unlike anions **10**$^-$ and **13**$^-$, the anion of 2-naphthylamine (**6**) failed to afford disubstitution by reaction with substrate **3**. The monosubstituted-reduced compound **19** was formed in either solvent with a 22% maximum isolated yield in DMSO.



19

The reactivity of anion **10**$^-$ was also studied with substrates 1,4-dibromonaphthalene (**4**) and 1,5-diiodonaphthalene (**5**) (see Table 3, Eq. 6).



4, X=Br, Y_1= Br, Y_2= H
5, X= I, Y_1= H, Y_2= I

10

20, R_1=1-(2-$C_{10}H_6OH$), R_2= H
22, R_1=H, R_2= 1-(2-$C_{10}H_6OH$)

21

(6)

Table 3
Photoinitiated reaction of the anion of 2-naphthol (**10**) with dihalonaphthalenes (**4** and **5**)[a]

Expt	Substrate	Nu^-	Substrate/Nu^- ratio	Halides (%)	Product yields (%)
1	**4**	$C_{10}H_7O^-$ (**10**$^-$)	1:6	Br^-=98	**20***c* (36) **20***t* (12) **21** (21)
2	**4**		1:10	Br^-=100	**20***c* (50) (42)[d] **20***t* (13) (8)[d] **21** (15) (9)[d]
3[b]	**4**		1:10	Br^-=100	**20***c* (15) (9)[d] **20***t* (traces) **21** (32) (27)[d]
4[c]	**5**		1:10	I^-=83	**22***c* (22)[d] **22***t* (15)[d] **21** (12)

[a] Reaction time=180 min, NH_3(l) as solvent (unless otherwise indicated), N_2 atmosphere, [substrate]=1.8 mM, unless indicated. Products were quantified by HPLC, using a calibration curve, unless indicated.
[b] DMSO as solvent, [substrate]=10 mM.
[c] [Substrate]=4.8 mM.
[d] Isolated yield.

Reaction of anion **10**$^-$ with substrate **4** in NH_3(l) proceeds completely in less than 180 min under irradiation. The disubstitution occurs with the formation of two conformational isomers **20***c*,*t* (Chart 4, Table 3, expts 1–3). Their presence is ascribed to the well known high rotational barrier in 1,1′-binaphthalene along the two bulky naphthyl moieties generating additional optical activity.[50] Following our methodology, it was possible to obtain both disubstitution isomers, which were identified as *cisoid* (**20***c*) and *transoid* (**20***t*) [1,1′:4′,1″-ternaphthalene]-2,2″-diol.[51]

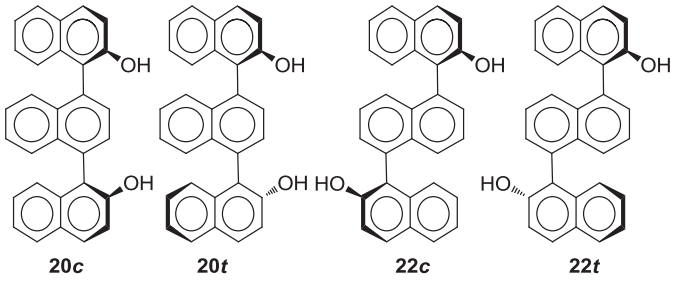


Chart 4.

The best conditions to synthesize compounds **20***c* and **20***t* (42 and 8% as isolated yields, respectively) were obtained in NH_3(l), with a substrate/nucleophile 1:10 ratio (Table 3, expt 2). As in previous examples, the yields of **20***c* and **20***t* decrease when the irradiated reaction is carried out in DMSO (Table 3, expt 3). Reaction of **10**$^-$ with substrate **5** in NH_3(l) shows a similar HPLC chromatographic profile than the one observed with substrate **4** (see Table 3, expt 4); however, products **22***c* and **22***t* were obtained in lower isolated yields under diluted conditions, 22 and 15%, respectively. The solubility of these compounds in common organic solvents, methylene chloride or ethyl acetate, for example, is lower than that of their respective **20**.

Low yields of the disubstitution isomers were obtained by reaction of anion **6**$^-$ with substrates **4** and **5** in NH_3(l), these reactions were not further investigated.

3. Conclusions

Nucleophilic substitution by the $S_{RN}1$ ET mechanism is a good procedure to obtain polyaromatic compounds, with more than 25 carbons, in moderate to good yields through a one-pot reaction. In this work, under the above mechanism, a simple procedure is reported to obtain the aromatic amines and alcohols **7**, **11**, **14**, **20***c* (~50–40% isolated yield) and **17**, **18** (~30% isolated yield) belonging to a large aryl structure. It is worth mentioning that, despite the fact that yields are moderate, two C_{Ar}–C_{Ar} bonds are simultaneously formed and the NH_2 and OH functional groups remain unmodified for further possible reactions.

The experimental workup of the products differs depending on the nucleophile used. The products obtained with the anion of 2-naphthol do not present difficulties in their manipulation and characterization. Those obtained from the anion of 2-naphthylamine are less stable (decompose under light and by exposure to atmospheric air). In addition, when the nucleophile is the anion of 9-phenanthrylamine the solubility of its substitution products decreases in organic solvents considerably. In the case of 1,4-dihalobenzenes as substrates, 1,4-$BrIC_6H_4$ is recommended; for naphthyl substrates, 1,4-dibromonaphthalene affords the best results.

4. Experimental section

4.1. Materials

Potassium *tert*-butoxide, 1-bromo-4-iodobenzene, *p*-diiodobenzene, 4,4′-diiodobiphenyl, and 2-naphthol are commercially available and used as received, except 2-naphthol, which was sublimed before use. DMSO was provided by Carlo Erba and stored under molecular sieves (4 Å). ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker nuclear magnetic resonance spectrometer. HRMS were recorded on a Bruker, MicroTOF Q II equipment, operated with an ESI source in (positive/negative) mode, using nitrogen as nebulizing and drying gas and sodium formiate 10 mM as internal standard. Gas chromatographic analyses were performed on a Hewlett Packard 5890 Series II with flame ionization detector and the data system Hewlett Packard 3396 Series II integrator, on an HP-1 capillary column (methyl silicone, 5 m, 0.53 mm, 2.65 mm film thickness). GC–MS analyses were carried out on a Shimadzu GC–MS QP5050 spectrometer, employing a 30 m, 0.12 mm DB-5 MS column. Irradiation was performed in a reactor equipped with two 400 W lamps (Philips model Master HPI-T Plus, air- and water-cooled). Potentiometric titration of halide ions was performed with a pH meter using an Ag/AgCl electrode.

4.2. Photoinitiated reaction of the anion of 2-naphthylamine (6) with 1-bromo-4-iodobenzene (2b)

The following procedure is representative for all reactions in NH_3(l) as solvent. The reaction was carried out in a 250-mL three-neck round-bottom flask equipped with nitrogen inlet and magnetic stirrer. To distilled ammonia (150 mL) were added potassium *tert*-butoxide and then 2-naphthylamine in the quantities indicated (see tables). After 15 min, the 1-bromo-4-iodobenzene was added, and the reaction mixture was irradiated for 120 min. The reaction was quenched with an excess of ammonium nitrate as a solid. The ammonia was allowed to evaporate, and Milli-Q water (50 mL) was added to the residue and extracted twice with CH_2Cl_2 (30 mL). The iodide ions in the aqueous solution were determined potentiometrically. The organic extract was dried ($MgSO_4$), filtered, and quantified by GLC. The solvent was removed under reduced pressure. When substrates are **4** or **5** the crude is extracted twice employing ethyl acetate.

4.3. Photoinduced reactions in DMSO

Into a previously dried 25 mL two-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer, 10 mL of dried DMSO stored under molecular sieves (4 Å) was added. The solvent was degassed three times under vacuum and stirring, interspersed with N_2. Afterward, potassium *tert*-butoxide and the anion source (aromatic amines or alcohols) were added and 5 min later, the corresponding amount of substrate. After irradiation, the reaction was quenched by the addition of ammonium nitrate and Milli-Q water. The workup was done adding to the reaction mixture an excess (20 ml) of Milli-Q water and then extraction with CH_2Cl_2 (3×20 mL). The CH_2Cl_2 extract was water washed twice to eliminate the residual DMSO. The organic extract thus obtained was dried with $MgSO_4$. After filtration, the organic solvent was eliminated under reduced pressure. In those reactions where 2-naphthol was employed as nucleophilic precursor in both solvents, the reaction crude was washed with an excess of acidic aqueous solution until an acid pH is obtained. Afterward, the workup followed as it was described before. When substrates are **4** or **5** the crude is extracted twice using ethyl acetate.

4.4. 1,1′-(1,4-Phenylene)dinaphthalen-2-amine (7)

It was isolated by column chromatography, employing a linear gradient of eluent composed by petroleum ether and ethyl acetate, from 0% to 40% of ethyl acetate. Melting point: 240 °C with decomposition. ^{1}H NMR (400 MHz, acetone-d_6): δ 4.64 (s, 4H, NH_2), 7.18–7.24 (m, 4H), 7.45–7.47 (m, 3H), 7.55–7.56 (ds, 4H), 7.72–7.77 (m, 5H). ^{13}C NMR (acetone-d_6) δ 118.8 (Cq), 119.3 (CH), 122.2 (CH), 124.5 (CH), 127.0 (CH), 128.5 (Cq), 128.8 (CH), 128.9 (CH), 129.4 (CH), 129.4 (CH), 132.8 (CH), 135.1 (Cq), 137.6 (Cq), 143.9(Cq). HRMS (ESI): *m*/*z* calcd for $C_{26}H_{20}N_2$+H^+: 361.1699 $[M+H]^+$, found: 361.1677.

4.5. 1,1′-(1,4-Phenylene)bis(naphthalen-2-ol) (11)

Isolated by column chromatography and eluted with petroleum ether/ethyl ether in a polarity gradient starting from 0 to 30 % of diethyl ether. Mp 239.6–240.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (s, 2H, OH), 7.31 (d, 1H, *J*=8.8), 7.33 (d, 1H, *J*=8.8), 7.36–7.48 (m, 4H), 7.53 (d, 1H, *J*=8.37), 7.58 (d, 1H, *J*=8.37), 7.68 (d, 4H, *J*=3.34), 7.88 (br d, 4H, *J*=8.52). ^{13}C NMR(100 MHz, $CDCl_3$): δ 117.7, 120.5, 120.6, 123.7, 124.6, 124.7, 126.9, 128.3, 129.2, 130.0, 130.0, 132.6, 132.6, 133.3, 133.4, 134.7, 134.7, 150.4. HRMS (ESI): *m*/*z* calcd for $C_{26}H_{18}O_2$+H^+: 363.1380 $[M+H]^+$, found: 363.1376.

4.6. 10,10′-(1,4-Phenylene)diphenanthren-9-amine (14)

Isolated by column chromatography, employing a linear gradient of eluent composed by petroleum ether and diethyl ether, from 0% to 50 % of diethyl ether. Mp: 300 °C with decomposition. ^{1}H NMR (400 MHz, DMSO-d_6 after sonication): δ 5.20 (s, 2H, NH_2), 5.41 (s, 2H, NH_2), 7.34–7.46 (m, 10H), 7.68–7.73 (m, 4H), 8.34–8.39 (m, 2H), 8.74 (d, *J*=8.1, 2H), 8.87 (d, *J*=7.9, 1H). ^{1}H–^{1}H COSY NMR (DMSO-d_6): δ_H/δ_H 7.36/7.34, 7.45/7.35, 7.45/7.44, 7.47/7.35, 7.49/7.35, 8.37/7.72, 8.39/7.71, 8.73/7.36, 8.73/7.40, 8.75/7.59, 8.87, 7.72, 8.89/7.72. ^{1}H–^{13}C HSQC NMR (DMSO-d_6): δ_H/δ_C 7.37/122.5, 7.35/124.3, 7.44/127.2, 7.51/132.6, 7.56/132.6, 7.72/127.0, 8.36/123.5, 8.74/123.0, 8.88/123.5. ^{1}H–^{13}C HMBC NMR (DMSO-d_6): δ_H/δ_C 5.20/115.4, 5.20/125.1, 5.40/114.9, 5.40/125.1, 7.34/114.9, 7.34/124.6, 7.35/122.4, 7.36/114.9, 7.36/122.4, 7.36/124.6, 7.38/125.1, 7.39/124.6, 7.47/123.1, 7.47/133.7, 7.51/114.9, 7.51/132.6, 7.51/137.2, 7.56/115.4, 7.56/137.2, 7.70/123.5, 7.70/125.1, 7.75/123.7, 7.75/130.7, 8.37/127.1, 8.37/130.7, 8.37/139.4, 8.74/127.3, 8.74/130.7, 8.74/133.7, 8.88/124.6, 8.88/125.1, 8.88/126.7. HRMS (ESI): *m*/*z* calcd for $C_{34}H_{24}N_2$+Na^+: 483.1832, found: 483.1827.

4.7. 1-([1,1′-Biphenyl]-4-yl)naphthalen-2-ol (16)

Isolated by column chromatography and eluted with petroleum ether/diethyl ether (95:5). Mp 202.0–203.1 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$):δ 7.29–7.42 (m, 4H), 7.47–7.53 (m, 5H), 7.77–7.86 (m, 6H), 8.13 (s, 1H, OH). ^{13}C NMR(100 MHz, $(CD_3)_2CO$): δ 119.3, 122.3, 123.8, 125.4, 127.2, 127.9, 127.9, 128.4, 129.0, 129.9, 129.9, 130.1, 132.8, 135.0, 136.4, 140.8, 141.8, 152.6. HRMS (ESI): *m*/*z* calcd for $C_{22}H_{16}O$–H^+: 295.1117, $[M-H]^+$ found: 295.1144.

4.8. 1,1′-([1,1′-Biphenyl]-4,4′-di-yl)bis(naphthalen-2-ol) (17)

Isolated by column chromatography and eluted using a gradient of petroleum ether/diethyl ether from 5% of diethyl ether to 80%. Mp 191.0–191.8. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.30–7.39 (m, 6H), 7.54 (d, 6H, *J*=8.24 Hz), 7.84–7.87 (m, 4H), 7.94 (d, 4H, *J*=8.24 Hz), 8.25 (s, 2H, OH). ^{13}C NMR(100 MHz, $(CD_3)_2CO$): δ 119.2, 122.2, 123.7, 125.3, 127.1, 127.8, 128.9, 129.8, 130.0, 132.8, 134.9, 136.4, 140.5, 152.6. For more details in the assignment and 2D-NMR experiments, see Supplementary data. HRMS (ESI): *m*/*z* calcd for $C_{32}H_{22}O_2$–H^+: 437.1620 $[M-H]^+$, found: 437.1611.

4.9. 10,10′-([1,1′-Biphenyl]-4,4′-di-yl)bis(phenanthren-9-amine) (18)

Isolated by precipitation during the workup and washed several times with acetone. Decomposed when heated (ca. 360 °C), mp not determined. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.10 (s, 4H, NH_2), 7.20–7.22 (m, 2H), 7.36–7.42 (m, 4H), 7.50 (d, 4H, *J*=8.2 Hz), 7.68–7.76 (m, 4H), 8.08 (d, 4H, *J*=8.2 Hz), 8.31–8.33 (m; 2H), 8.73–8.75 (m, 2H), 8.86–8.88 (m, 2H). ^{13}C NMR (DMSO-d_6): δ115.0 (q), 122.8 (CH), 123.2 (q), 123.6 (CH), 124.8 (q), 125.0 (CH), 125.1 (CH), 126.9 (CH), 127.3 (CH), 128.2 (CH), 130.7 (q), 132.3 (CH), 133.5 (q), 137.5 (q), 138.8 (q), 139.3 (q). HRMS (ESI): *m*/*z* calcd for $C_{40}H_{28}N_2$+H^+: 537.2253, $[M+H]^+$=found: 537.2335.

4.10. 1-([1,1′-Biphenyl]-4-yl)naphthalen-2-amine (19)

It was isolated by column chromatography, employing a linear gradient of eluent composed by petroleum ether and ethyl acetate, from 0% to 15% of ethyl acetate. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 4.485 (s, 2H, NH_2), 7.162–7.184 (m, 1H), 7.224–7.243 (m, 1H), 7.330–7.382 (m, 2H), 7.410–7.431 (m, 2H), 7.478–7.516 (m, 2H), 7.70–7.78 (m, 6H), 7.842–7.863 (m, 2H). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 121.3 (CH), 123.8 (q), 125.9 (CH), 126.7 (CH), 127.3 (CH), 127.5 (CH), 127.8 (CH), 128.4 (CH), 128.8 (CH), 131.4 (CH), 133.9 (Cq), 136.7 (Cq), 139.8 (Cq), 140.5 (Cq), 142.6 (Cq). HRMS (ESI): *m*/*z* calcd for $C_{22}H_{17}N$+H^+: 296.1361, $[M+H]^+$ found: 296.1355.

4.11. [1,1′:4′,1″-Ternaphthalene]-2,2″-diol (20*c*)

Isolated as a white solid from reaction crude by silica gel column chromatography. It was eluted in ether petroleum/ethyl acetate at increased polarity from 0% to 60% of ethyl acetate. Mp: 264.3–265.2 °C. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 7.273–7.369 (m, 8H), 7.40 (d, 2H, *J*=8.9), 7.425–7.450 (dd, 2H, J_1=3.3, J_2=6.5), 7.679 (s, 2H), 7.699 (s, 2H, OH), 7.93–7.95 (dd, 2H, J_1=2.5, J_2=6.7), 7.986 (d, 2H, *J*=8.9). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 119.1 (CH), 120.2 (q), 123.9 (CH), 125.7 (CH), 176.0 (CH), 127.2 (CH), 127.3 (CH), 128.9 (CH), 129.7 (q), 130.1 (CH), 130.5 (CH), 134.6 (q), 134.7 (q), 135.5 (q), 153.4 (q, C–OH). HRMS (ESI): *m*/*z* calcd for $C_{30}H_{20}O_2$+Na^+: 435.1356, $[M+Na]^+$ found: 435.1340.

4.12. [1,1′:4′,1″-Ternaphthalene]-2,2″-diol (20*t*)

Isolated as a pale yellow solid by silica gel column chromatography from reaction mixture. It was eluted in ether petroleum/ethyl

acetate at increased polarity from 0% to 60% of ethyl acetate. Mp: 254.3–255.7 °C. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 7.247–7.350 (m, 8H), 7.423 (d, 2H, J=8.8), 7.449–7.473 (m, 2H), 7.672 (s, 2H), 7.921–7.994 (m, 6H). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 119.4 (CH), 120.5 (q), 123.9 (CH), 126.1 (CH), 126.8 (CH), 127.1 (CH), 127.4 (CH), 128.9 (CH), 129.8 (q), 130.1 (CH), 130.5 (CH), 134.7 (q), 134.9 (q), 135.8 (q), 153.4 (q, C–OH). HRMS (ESI): m/z calcd for $C_{30}H_{20}O_2$–H^+: 411.1380, $[M-H]^+$ found: 411.1305.

4.13. [1,1′:5′,1″-Ternaphthalene]-2,2″-diol (22*c*)

Isolated by silica gel column chromatography from reaction crude. It was eluted in ether petroleum/ethyl ether at increased polarity from 0% to 60% of ethyl ether. Recrystallized from acetonitrile and recovered as a white solid. Mp: 288.4–291.0 °C, decomposed at 315 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.99 (s, 2H, OH), 7.22 (m, 2H), 7.32–7.40 (m, 6H), 7.50–7.54 (m, 2H), 7.58–7.60 (m, 4H), 7.90–7.92 (m, 2H). 7.96 (d, 2H,J=8.9). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 117.6 (CH), 118.7 (q), 123.5 (CH), 125.0 (CH), 126.7 (CH), 126.9 (CH), 127.1 (CH), 128.1 (CH), 129.0 (q), 130.1 (CH), 130.3 (CH), 132.2 (q), 133.7 (q), 134.0 (q), 151.1 (q, C–OH). HRMS (ESI): m/z calcd for $C_{30}H_{20}O_2$–H^+: 411.1380, $[M-H]^+$ found: 411.1409.

4.14. [1,1′:5′,1″-Ternaphthalene]-2,2″-diol (22*t*)

Isolated by silica gel column chromatography from the reaction crude. It was eluted in ether petroleum/ethyl ether at increased polarity from 0% to 60% of ethyl ether. Recrystallized from acetonitrile and recovered as a white solid. Mp: not determined by decomposition at around 312 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.03 (s, 2H, OH), 7.16–7.18 (m, 2H), 7.29–7.41 (m, 6H), 7.49–7.53 (m, 2H), 7.58–7.60 (m, 4H), 7.90–7.91 (m, 2H). 7.95 (d, 2H, J=8.8). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 117.7 (CH), 118.9 (q), 123.7 (CH), 125.1 (CH), 126.9 (CH), 127.1 (CH), 127.3 (CH), 128.3 (CH), 129.2 (q), 130.3 (CH), 130.5 (CH), 132.3 (q), 133.8 (q), 134.1 (q), 151.3 (q, C–OH). HRMS (ESI): m/z calcd for $C_{30}H_{20}O_2$–H^+: 411.1380, $[M-H]^+$ found: 411.1398.

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Supplementary data

General methods and materials, ^{1}H NMR and ^{13}C NMR spectra of new compounds and characterization data for known compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.03.089.

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