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PAPER

Synthesis of α,α -diaryl nitriles by radical nucleophilic substitution†

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The present study shows that the anion of 2-naphthylacetonitrile is substituted selectively at its C_α by aromatic halides, through a radical nucleophilic substitution mechanism, to give the corresponding α,α -diaryl nitriles in good yields. The regioselectivity of this ambident nucleophile changes with the steric hindrance at the radical centre from the aromatic substrate. The selectivity observed was investigated through a computational model of the key reaction step.

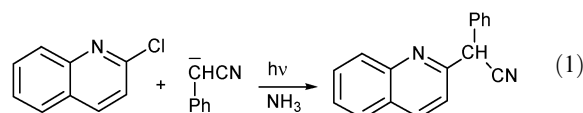
Introduction

The importance of α -aryl-substituted nitriles lies in their potential as building blocks to synthesize amides, carboxylic acids, primary amines, ketones, heterocycles and biologically active compounds with or without the nitrile group.¹ In contrast to α -alkylation of nitriles with alkyl halides,² the direct α -arylation of nitriles appears to be quite difficult to accomplish, and consequently, the chemistry related to this transformation is much less developed. It has been reported that the anions of diphenylacetonitrile, phenylacetonitrile and ethyl cyanoacetate can couple with aryl fluorides under uncatalyzed α -arylations.³

The palladium-catalyzed α -arylation of nitriles has recently emerged as a major advancement; the secondary nitriles afford monoarylation products with aryl halides possessing electron-rich, electron-poor and electron neutral groups.⁴ The reactions of benzyl nitriles take place selectively to form the product of monoarylation in good yields.⁵ The selective monoarylation of acetonitrile and primary nitriles has been achieved using α -silyl nitriles in the presence of ZnF_2 .⁶

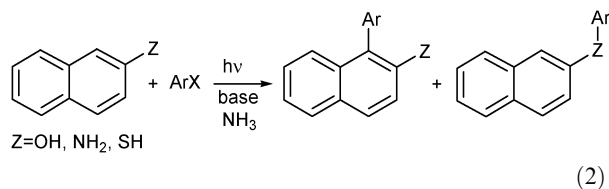
The application of substitution radical nucleophilic reactions to C–C forming processes is a subject of continued interest. The aromatic radical nucleophilic substitution, or $S_{RN}1$ reaction,⁷ has been shown to be an excellent route to perform the nucleophilic substitution of unactivated aromatic compounds with suitable leaving groups. The main feature of the $S_{RN}1$ reaction of nitrile anions centers on the fact that depending on the aryl halides involved, straightforward substitution products with or without retention of the CN group can be formed.⁸ However, α -arylated nitriles are almost exclusively formed by reaction of the alkylnitrile ions (^-CHRCN , R = H, Me) with

stabilized aromatic radicals, such as naphthyl and quinolyl moieties.⁹ Only one aryl nitrile, the anion of phenylacetonitrile, was studied in this reaction type. This anion reacts with heteroaryl halides to afford good yields of the substitution product at C_α (eqn (1)). The substitution at the phenyl moiety of the anion is not observed.



Excellent yields have been obtained with 2-chloropyridine but probably by dual radical chain and addition–elimination mechanisms.¹⁰

On the other hand, a special regiochemistry has been determined in the reactions of radicals with anions able to show ambident behavior.¹¹ The anions of the 2-naphthyl system (Z = O, NH, S) have been reported to react with aryl radicals to give C_1 -substitution at their naphthyl moiety. A preference for heteroatom-arylation has been reported in the reaction of 2-naphthalenethiolate anion **1** (eqn (2)).¹²



In this paper, we present the study of the reaction and regioselectivity of the ambident nucleophile, 2-naphthylacetonitrile anion, with aryl halides. In this anion, all the positions that can be substituted correspond to C atoms. We were interested to inspect the scope of this anion toward the synthesis of α,α -diaryl nitriles.

Results and discussion

The photoinitiated reaction of **1** with 2-iodoanisole (**2a**) in liquid ammonia (nucleophile:substrate ratio = 3) afforded

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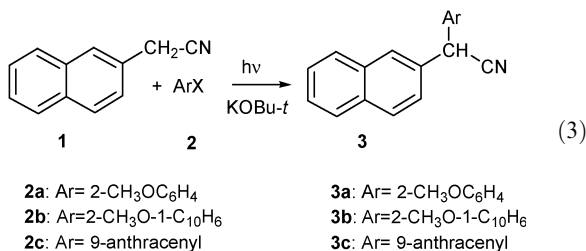
† Electronic supplementary information (ESI) available: ¹H NMR and ¹³C NMR spectra of compounds **3a–g** and **4d–f**. See DOI: 10.1039/c1nj20699k

Table 1 Photoinitiated reactions of aryl halides **2a–c** with the anion of 2-naphthylacetonitrile (**1**) in DMSO^a

Exp.	1 M × 10 ³	Substrate M × 10 ³	Base M × 10 ³	X ^{-b} (%)	Products ^c (% yields)	
					ArH	Substitution
1 ^d	21	2a , 7	42	100	—	3a , 96
2	75	2a , 24	142	85	6	3a , 76
3	65	2a , 32	148	81	8	3a , 65
4	74	2a , 72	140	76	10	3a , 53
5 ^e	68	2a , 32	130	5	—	—
6 ^f	70	2a , 34	133	90	—	3a , 65
7 ^g	75	2a , 73	150	46	6	3a , 25
8 ^h	74	2a , 26	146	42	4	3a , 27
9 ⁱ	70	2a , 31	151	<5	—	—
10 ^d	20	2b , 6	43	100	—	3b , 90
11	77	2b , 26	142	95	10	3b , 84
12	75	2c , 25	143	95	19	3c , 80

^a Photoinitiated reactions (unless indicated), carried out under nitrogen. Reaction time = 180 min. ^b Determined potentiometrically on the basis of the ArX concentration. ^c Determined by GLC and the internal standard method on the basis of the ArX concentration. ^d Solvent = NH₃(l). *T* = -33 °C. ^e Reaction carried out in the dark. ^f Di-*tert*-butylnitroxide (44 mmol%). ^g Di-*tert*-butylnitroxide (64 mmol%). ^h *p*-Dinitrobenzene (36 mmol%). ⁱ Reaction carried out in the dark with FeBr₂ (80 mmol%).

100% yield of iodide ion, and only the product corresponding to substitution at C_α of the acetonitrile moiety, 2-(2-anisyl)-2-(2-naphthyl)acetonitrile **3a** (96%) (eqn (3), Table 1, exp. 1).

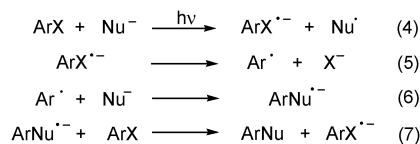


By changing the solvent from NH₃ to DMSO accompanied by a three-fold increase in the concentration of the reactants, **3a** was the main product formed (76%) accompanied by the reduction product anisole (6%) (Table 1, exp. 2). The percentage of substitution product decreased and that of anisole increased with a nucleophile: substrate ratio of 2 or 1 (Table 1, exp. 3 and 4).

No reaction was observed in this solvent in the absence of light (Table 1, exp. 5). When the relation nucleophile: substrate is 2 or 3 the reaction is not inhibited by the addition of di-*tert*-butylnitroxide (DTBN), a radical scavenger (Table 1, exp. 6). Changing the relation nucleophile: substrate to 1, the reaction is inhibited by DTBN or by the addition of a good electron-acceptor such as *p*-dinitrobenzene (*p*-DNB) (Table 1, exp. 7 and 8). The dark reaction in the presence of Fe(II) salt as initiator did not occur.⁷ These facts indicate that a photo-induced nucleophilic substitution with radicals and radical anions as intermediates is in play (Scheme 1).

To examine the scope of this procedure to obtain naphthylacetonitrile derivatives, the reaction with other aryl halides was studied.

In the reaction of **1** with 1-iodo-2-methoxynaphthalene (**2b**), compound **3b** was the main product formed, 90% and 84% yields in liquid ammonia and in DMSO, respectively, accompanied by

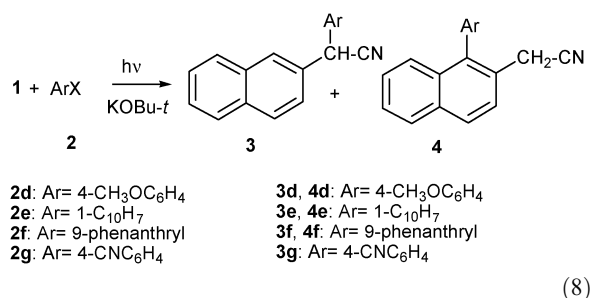


Scheme 1

the reduction product 2-methoxynaphthalene (10%) in the latter solvent (Table 1, exp. 10 and 11).

High yields of the expected substitution product were obtained by reaction with 9-bromoanthracene (**2c**) (80%) (Table 1, exp. 12). In all cases, the reduction product (ArH) formed is ascribed to hydrogen atom abstraction from the solvent by the radicals.

Based on the results found, we extended our study to 4-iodoanisole (**2d**), a phenyl halide unsubstituted at its *ortho* position. This substrate reacts with anion of **1** to afford two substitution products, the products corresponding to substitution at the C_α (**3**) and at the C₁ of the naphthyl cycle (**4**) in 47% and 22% yields respectively (eqn (8), Table 2, exp 1). Similar results were obtained in DMSO.



The percentages of products do not increase by changing the nucleophile/substrate ratio to 5 (Table 1, exp. 3). No reaction was observed in the absence of light.

Compounds **3e** and **4e** were obtained by reaction of the anion of **1** with 1-iodonaphthalene (**2e**), in 85% and 13% yields, respectively, in NH₃(l) (Table 2, exp. 5).

We observed that both compounds, **3f** and **4f**, were formed in the reaction with 9-bromophenanthrene (**2f**). In both

Table 2 Photoinitiated reactions of aryl halides **2d–f** with the anion of 2-naphthylacetonitrile (**1**) in DMSO^a

Exp.	NuH M × 10 ³	Substrate M × 10 ³	Base M × 10 ³	X ^{-b} (%)	Products ^c (% yields)	
					ArH	Substitution
1 ^d	10	2d , 3	25.3	100	4	3d , 47 4d , 22
2	75	2d , 28	146	93	11	3d , 47 4d , 21
3	120	2d , 26	243	90	nc	3d , 53 4d , 23
4 ^e	83	2d , 32	194	1	—	—
5 ^d	15	2e , 5	30	95	2	3e , 85 4e , 13
6	78	2e , 28	153	90	6	3e , 68 4e , 16
7 ^d	15	2f , 5	32	98	—	3f , 79 4f , 18
8	73	2f , 24	146	100	10	3f , 76 4f , 15

^a Photoinitiated reactions (unless indicated), carried out under nitrogen. Reaction time = 180 min. ^b Determined potentiometrically on the basis of the ArX concentration. ^c Determined by GLC and the internal standard method on the basis of the ArX concentration. ^d Solvent = NH₃(l). *T* = -33 °C. ^e Reaction carried out in the dark.

Table 3 Photoinitiated reactions of aryl halide **2g** with the anion of 2-naphthylacetonitrile (**1**) in DMSO^a

Exp.	NuH M × 10 ³	Substrate M × 10 ³	Base M × 10 ³	X ^{-b} (%)	Substitution product (3g) ^c (% yields)
1 ^d	77	2g , 27	152	100	93
2	75	2g , 26	153	97	95
3 ^e	75	2g , 27	155	83	74
4 ^{e,f}	74	2g , 28	156	66	51
5 ^{e,g}	76	2g , 28	153	82	76
6 ^{e,g}	53	2g , 26	110	56	29
7 ^{e,h}	201	2g , 101	408	60	50 ⁱ

^a Photoinitiated reactions (unless indicated), carried out under nitrogen. Reaction time = 30 min. ^b Determined potentiometrically on the basis of the ArX concentration. ^c Determined by GLC and the internal standard method on the basis of the ArX concentration. ^d Reaction time = 120 min. ^e Reaction carried out in the dark. ^f *p*-Dinitrobenzene (44 mmol% to substrate). ^g Di-*tert*-butylnitroxide (46 mmol%). ^h Reaction time = 60 min. ⁱ Isolated product.

solvents, compound **3f** was the main product (76%) (Table 2, exp. 7 and 8).

These results show that the regioselectivity of the reaction of the anion of **1** is sensitive to the substitution of the aryl radical. The approach of the radical to the naphthyl-C₁ position is more constrained when the hindrance at the radical centre increases (**2a**, **2b**, **2c**). In these reactions only substitution at C_α was observed. Recently, we informed that the rate of a radical-ambident nucleophile coupling is sensitive to steric hindrance.¹³ However, the marked changes in the regioselectivity of the reaction with the nature of the substrate have not been previously shown in the reactions of aryl halides with ambident nucleophiles; this being the first report to show that the steric hindrance increases the selectivity of the coupling.

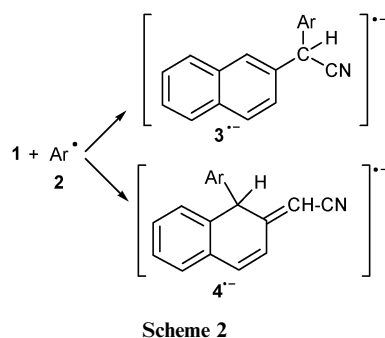
In DMSO, anion **1** reacts with **2g** to give **3g** (93%) and traces of **4g** after 120 minutes of irradiation (eqn (8), Table 3, exp. 1). Similar results were found after 30 min of reaction. When the above reaction was conducted with no illumination, 74% of **3g** was formed but this was significantly inhibited in the presence of *p*-dinitrobenzene (*p*-DNB) (Table 3, exp. 3 and 4). The reaction was not inhibited by the addition of DTBN. In all previous cases, the relation **1/2g** was 3; when this relation decreased to 2, we obtained 29% of product in the reaction with DTBN (Table 3, exp. 6). This would indicate that radicals and radical anions are present in the dark reaction. The synthetic protocol was optimized and **3g** was obtained in good yield.

The radical **2g** reacts only at the C_α position. This behaviour is in contrast with the one shown by **2d**, and may be due to the more electrophilic character of the radical, that directs the reaction to the slightly more nucleophilic part of the ambident nucleophile.

Theoretical calculations

In order to complement the experimental results, quantum mechanical calculations could be of use to explain the regiochemistry observed.

We have demonstrated that the carbon *vs.* heteroatom regioselectivity of the reactions of the aryl radicals toward ambident nucleophiles is kinetically controlled.¹⁴



In this context, the intermolecular addition of the aryl radicals (Ar•) can take place at two different positions of the anion of **1**, C₁ of the naphthyl moiety, or C_α of the substituent (Scheme 2). The reaction at the C₁ forms the radical anion intermediate **3**^{•-}, which gives the biaryl system. Attack at the C_α produces the three substituted asymmetric carbons.

The potential energy surfaces (PESs) for the coupling step were calculated. The PESs were inspected from the most stable conformer of the radical anions (**3**^{•-} and **4**^{•-}). The optimized geometries of radical anions and the transition states corresponding to their formation were calculated by the unrestricted Density Functional Theory (DFT) with the B3LYP functional and the 6-31G(d) basis set, as implemented in Gaussian 03.¹⁵ Vibrational frequencies were computed for the stationary points.

The change in hybridization from sp² (in the anion of **1**) to sp³ occurs by the coupling at either position (C₁ and C_α) to form the radical anions of the corresponding substitution products (Fig. 1). The TSs of these couplings are located early along the reaction coordinates; the hybridization changes at the C₁ and C_α take place at shorter C–C distances than those of the localized TSs (Fig. 2).

Table 4 shows the difference in energy between the critical structures located along the PESs.

The radicals combine exothermically with the anion to form the radical anion of the product.

In the gas phase, the reactions take place without energy barriers (negative ΔE_a) evaluated as the energy difference

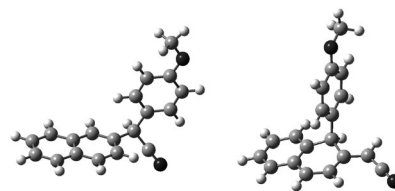


Fig. 1 B3LYP/6-31G* calculated **3e** and **4e** radical anions.

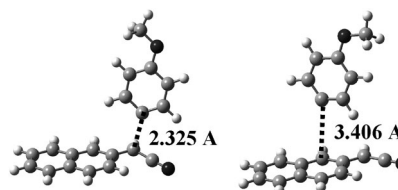


Fig. 2 B3LYP/6-31G* calculated TSs for formation of **3e** and **4e** radical anions.

Table 4 Energy differences between PES relevant points of the reaction of the 2-naphthylacetonitrile anion with different aryl radicals

Ar	Gas phase			Continuum solvent ^e					
	ΔE_{r}^a	ΔE_{a}^b	ΔG^c	$\Delta G^{\ddagger d}$	ΔE_{r}	ΔE_{a}	ΔG^f	$\Delta G^{\ddagger f}$	
2b	C ₁	-31.95	-5.83	-17.91	6.75	-25.49	4.68	-11.44	17.26
	C _α	-36.47	-10.80	-22.59	2.11	-24.55	-2.70	-10.67	10.21
2d	C ₁	-37.26	-4.65	-23.23	6.33	-33.02	0.44	-18.99	11.42
	C _α	-32.34	-7.59	-19.51	3.41	-25.92	-0.37	-13.10	10.63
2g	C ₁	-44.72	-11.49	-30.24	-0.77	-34.70	1.70	-20.22	12.42
	C _α	-46.34	-17.81	-32.62	-5.92	-34.70	-5.49	-20.97	6.40

^a ΔE_{r} (kcal mol⁻¹) = energy difference between radical anions and reactants (anion of **1** + radical). ^b ΔE_{a} (kcal mol⁻¹) = energy difference between transition states and reactants (anion of **1** + radical). ^c ΔG (kcal mol⁻¹) = free energy difference between radical anions and reactants. ^d ΔG^{\ddagger} (kcal mol⁻¹) = free energy difference between transition states and reactants. ^e Continuum solvent model for DMSO, without geometry optimization. Differences in the total solution phase energies informed. ^f The energy correction was taken to be the same as in the gas phase.

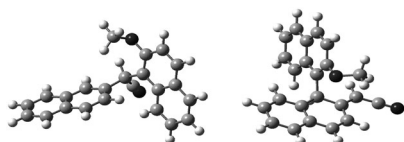


Fig. 3 B3LYP/6-31G* calculated **3b** and **4b** radical anions.

between the TS and the reactants. Different results are obtained for ΔG^{\ddagger} at 298 K.

The different regioselectivity of radicals **2a**, **2b** and **2c** compared with *p*-substituted radicals **2d** can be explained in terms of the steric hindrance to the coupling at the radical centre to form the radical anion intermediates **4**. The C₁ radical anion (**4^{•-}**) has a more rigid structure than that of radical anion **3^{•-}** (Scheme 2). Moreover, in radical **2b**, the *ortho* substituents beside the radical centre (MeO group and the aryl moiety) increased the steric compression (Fig. 3). As a consequence, the energy barrier for C₁-coupling is higher than the barrier for C_α-coupling (Table 4) and the reactivity of this position is smaller in agreement with the experimental results.

Radical **2g** reacts without activation energy, while radical **2d** coupled at both positions of the nucleophile with activation energy. For radicals **2d** and **2g**, the energy barriers for C₁-coupling (Table 4) are higher than those for C_α-coupling.

The solvent effect was taken into consideration with the Tomasi's polarized continuum model (PCM).¹⁶ In the presence of DMSO, the solvent of the experimental reactions, the PESs were similar to those calculated in the gas phase. The solvent affects the energies of TSs in a similar way for all radicals and the barriers ordering determined in the gas phase is maintained under a continuum; the $\Delta G^{\ddagger}_{\text{C}_1}$ are higher than the corresponding $\Delta G^{\ddagger}_{\text{C}_\alpha}$. These results show that the C₁ substitution is more likely to be found for radical **2d** than for radical **2g**. For this radical, the C_α substitution has the lowest activation energy compared with all previous results.

The relation of $k_{3(2d)}/k_{4(2d)}$ is given by: $k_{3(2d)}/k_{4(2d)} \propto e^{(\Delta\Delta G^{\ddagger}/RT)}$. Considering that TS_{3(2d)}} is 0.79 kcal mol⁻¹ more stable than TS_{4(2d)}}, the calculated ratio of constants is 3.9. For **2b** and **2g**, the calculated ratio is $>3 \times 10^4$. Experimentally, radical **2d** gives

68% of **3d** and 16% of **4d**, and the ratio **3/4** observed is 4.25. In contrast with this behavior, **3g** is the only product formed with **2g** radical, in agreement with the theoretical results.

Conclusions

In summary, the photoinduced reaction of the 2-naphthylacetonitrile anion with radicals gives the C_α substitution selectively. We have developed a simple and versatile system for the synthesis of α,α -diarylsubstituted nitriles. It should be noted that product yields are better with hindered radicals.

The key reaction step has been modeled and is predicted to be under kinetic control, with the observed regioselectivity resulting mainly from the steric factors within the TSs. The theoretical calculations show that the activation energy by C₁ substitution is higher than that by C_α substitution and the energy difference order is 2-methoxy-1-naphthyl > 4-benzonitril >> 4-anisyl, in agreement with the experimental results.

Experimental section

General experimental methods

¹H and ¹³C NMR spectra were recorded on a 200 or a 400 nuclear magnetic resonance spectrometer. All NMR spectra were measured in CDCl₃ or DMSO-d₆ using tetramethylsilane as a reference. High-resolution mass spectra (HRMS) for all compounds were measured using electron impact ionization mode. Irradiation was performed in a reactor equipped with two water-cooled lamps. Gas chromatographic analyses were performed on a chromatograph with a flame-ionization detector and using a HP-1 capillary column (methyl silicone, 10 m × 0.53 mm × 2.65 μm film thickness). The GS/MS analyses were carried out employing a column of 30 metres packed with 5% diphenyl and 95% dimethylpolysiloxane of 0.53 mm × 2.65 mm film thickness using electron impact ionization mode. Potentiometric titration of halide ions was performed in a pH meter using an Ag/Ag⁺ electrode. Melting points were not corrected. Silica gel (70–270 mesh ASTM) was used for chromatographic purifications. Radial chromatographic separations used a silica gel 60 PF-254 with gypsum. Solvents were purified by distillation. All reagents obtained from commercial suppliers were used without further purification. DMSO was stored under molecular sieves (4 Å). 1-Iodo-2-methoxynaphthalene (**2b**) was prepared by reaction of 1-iodo-2-naphthol, potassium *tert*-butoxide in DMSO with methyl iodide. 1-Iodo-2-naphthol was prepared by reaction of 2-naphthol, iodide and H₂O₂ in ethanol.¹⁷

Photoinduced reaction of the anion of 2-naphthylacetonitrile (**1**) with **2b** in liquid ammonia

The following procedure is representative of these reactions. The reactions were carried out in a 250 mL three-neck round-bottom flask equipped with a nitrogen inlet and a magnetic stirrer. Potassium *tert*-butoxide 4.3 mmol (490 mg) was added to distilled ammonia (100 mL) under nitrogen and 2-naphthylacetonitrile 2 mmol (332 mg) was added following 5 minutes. After 15 min 1-iodo-2-methoxynaphthalene 0.6 mmol (166.8 mg) was added and the reaction mixture was irradiated for 120 min. The reaction was quenched with an excess of ammonium nitrate.

The ammonia was allowed to evaporate and water (50 mL) was added to the residue and extracted twice with CH₂Cl₂ (20 mL). The iodide ions in the aqueous solution were determined potentiometrically. The organic extract was dried (MgSO₄), filtered and quantified by GLC. The reduction products (ArH) were compared by CGL with authentic commercial samples. The solvent was removed under reduced pressure. The crude residue was then purified by column chromatography.

Photoinduced reaction of the anion of 2-naphthylacetonitrile (1) with 2b in DMSO

By way of example, the technique followed for the reaction of 1-iodo-2-methoxynaphthalene with the anion of 2-naphthylacetonitrile is described. In a 50 mL three-neck ball, to 10 mL of dry and degassed DMSO under nitrogen was added 14.2 mmol (1590 mg) of potassium *tert*-butoxide, followed by 7.7 mmol (1278 mg) of 2-naphthylacetonitrile 5 minutes later. After 15 minutes 2.6 mmol (722 mg) of 1-iodo-2-methoxynaphthalene were added and irradiated for 180 minutes in a photochemical reactor. After the irradiation time the reaction was stopped by the addition of ammonium nitrate and water. The extraction of the reaction was carried out with 60 mL of water and three fractions of 20 mL of methylene chloride. The organic extract was subsequently washed with two fractions of 20 mL of water. Finally, the extract was dried with anhydrous MgSO₄ and analyzed by GC. Halide ions in water were determined by potentiometric titration with AgNO₃ solution.

In general, the products were isolated using the following method: the solvent of the organic extract was removed. The crude residue was distilled under reduced pressure in the Kugelrohr (<100 °C) and most of the nucleophile (in excess) was removed. The remaining solid was purified by column or radial chromatography (petroleum ether : acetone, 98 : 2).

α -(2-Methoxyphenyl)-2-naphthylacetonitrile (3a). Mp 141–142 °C. ¹H NMR δ_{H} 3.81 (s, 3H); 5.66 (s, 1H); 6.48–6.94 (m, 2H); 7.19–7.45 (m, 5H); 7.72–7.86 (m, 4H). ¹³C NMR δ_{C} 36.32; 55.62, 111.04; 119.88 (q); 121.09; 124.43; 125.43; 126.37; 126.51; 126.56; 127.61; 127.94; 128.74; 129.04; 129.74; 132.68 (q); 132.89 (q); 133.24 (q); 156.18 (q). m/z = 274 (21); 273 (100); 272 (22); 258 (41); 257 (10); 243 (10); 242 (43); 241 (13); 240 (24); 231 (36); 230 (20); 215 (17); 203 (15); 202 (25); 115 (10); 101 (19). Exact mass calcd for C₁₉H₁₅NO: 273.11536; found: 273.11540.

α -(2-Methoxynaphthyl)-2-naphthylacetonitrile (3b). Mp 137–138 °C. ¹H NMR δ_{H} 4.02 (s, 3H); 6.58 (s, 1H); 7.32–7.50 (m, 6H); 7.72–7.99 (m, 8H). ¹³C NMR δ_{C} 32.26; 56.76; 113.03; 119.74 (q); 123.30; 123.92; 124.54; 125.59; 126.18; 126.46; 127.43; 127.56; 127.94; 128.69; 128.85; 129.61 (q); 131.28; 131.60 (q); 132.52 (q); 132.76 (q); 133.22 (q); 154.81 (q). m/z = 324 (26); 323 (100); 322 (33); 309 (9); 308 (27); 307 (10); 293 (17); 292 (55); 291 (13); 290 (22); 281 (15); 280 (20); 279 (9); 278 (10); 277 (11); 266 (10); 265 (16); 250 (9); 153 (10); 148 (21); 141 (16); 140 (15); 139 (19); 132 (9); 127 (12); 126 (21); 113 (11). Exact mass calcd for C₂₃H₁₇NO: 323.13101; found: 323.13102.

α -(9-Anthracenyl)-2-naphthylacetonitrile (3c). ¹H NMR δ_{H} 7.29–7.32 (dd, 1H); 7.36 (s, 1H); 7.51–7.54 (m, 2H); 7.58–7.61

(m, 4H); 7.86–7.90 (m, 3H); 7.99 (s, 1H); 8.22–8.25 (m, 2H); 8.46–8.48 (m, 2H); 8.82 (s, 1H). ¹³C NMR δ_{C} 35.09; 119.65(q); 123.95; 124.33; 125.30; 125.37 (2q); 125.96 (q); 126.45; 126.76; 127.22; 127.63; 127.90; 128.98; 129.65 (2q); 129.81; 130.03; 131.92 (2q); 132.67 (q); 133.41 (q); 133.98 (q). m/z = 344 (27); 343 (100); 342 (48); 341 (13); 340 (9); 328 (11); 316 (13); 315 (31); 313 (9); 216 (23); 214 (10); 189 (10); 178 (11); 176 (11); 158 (40); 157 (16). Exact mass calcd for C₂₆H₁₇N: 343.13610; found: 343.13610.

α -(4-Methoxyphenyl)-2-naphthylacetonitrile (3d). Mp 136–137 °C. ¹H NMR δ_{H} 3.80 (s, 3H); 5.25 (s, 1H); 6.87–6.91 (m, 2H); 7.26–7.37 (m, 3H); 7.48–7.53 (m, 2H); 7.80–7.85 (m, 4H). ¹³C NMR δ_{C} 42.01; 55.36; 114.60 (q); 125.19; 126.56; 126.62; 126.75; 127.72; 127.99; 129.04; 129.18 (q); 133.44(q); 161.41(q). m/z 274 (20); 273 (100); 272 (26); 258 (22); 245 (9); 242 (20); 241 (11); 240 (11); 231 (10); 230 (10); 215 (20); 203 (12); 202 (18); 146 (10). Exact mass calcd for C₁₉H₁₅NO: 273.11536; found: 273.11551.

1-(4-Methoxyphenyl)-2-naphthylacetonitrile (4d). Mp 143–144 °C. ¹H NMR δ_{H} 3.62 (s, 2H); 3.19 (s, 3H); 7.05–7.09 (m, 2H); 7.19–7.24 (m, 3H); 7.40–7.53 (m, 3H); 7.61 (d, 1H); 7.87–7.93 (m, 2H). ¹³C NMR δ_{C} 22.53; 55.36; 14.38; 118.34 (q); 125.78; 126.18; 126.56; 126.67; 127.91; 128.53; 129.04 (q); 129.63 (q); 131.04; 133.00 (q); 133.22 (q); 138.99 (q); 159.39 (q). m/z 274 (24); 273 (100); 258 (12); 231 (21); 230 (50); 215 (11); 203 (18); 202 (27); 190 (10); 189 (18). Exact mass calcd for C₁₉H₁₅NO: 273.11536; found: 273.11556.

α -(1-Naphthyl)-2-naphthylacetonitrile (3e). Mp 104–105 °C. ¹H NMR δ_{H} 5.99 (s, 1H); 7.36–7.41 (dd, 1H); 7.45–7.55 (m, 5H); 7.64–7.68 (dd, 1H); 7.79–7.98 (m, 7H). ¹³C NMR δ_{C} 40.04; 119.63 (q); 123.03; 125.19; 125.46; 126.24; 126.67; 126.75; 126.94; 127.10; 127.37; 127.69; 128.04; 129.18; 129.64; 130.44 (q); 130.79 (q); 132.60 (q); 132.87 (q); 133.30 (q); 134.22 (q). m/z = 294 (22); 293 (100); 292 (67); 291 (15); 290 (13); 278 (21); 277 (11); 266 (20); 265 (50); 166 (11); 140 (12); 139 (16); 133 (25); 132 (16). Exact mass calcd for C₂₂H₁₅N: 293.12045; found: 293.12018.

1-(1-Naphthyl)-2-naphthylacetonitrile (4e). ¹H NMR δ_{H} 5.99 (s, 1H); 7.20–8.21 (m, 13H). m/z = 294 (22); 293 (100); 292 (37); 291 (12); 290 (9); 277 (12); 276 (12); 267 (9); 266 (47); 265 (70); 264 (17); 263 (26); 253 (41); 252 (47); 250 (20); 239 (11); 133 (17); 132 (91); 131 (34); 127 (12); 126 (37); 125 (27); 120 (9); 119 (18); 118 (10); 113 (13); 112 (10). MS m/z : 293 (M⁺, 100). Exact mass calcd for C₂₂H₁₅N: 293.12045; found: 293.12018.

α -(9-Phenanthryl)-2-naphthylacetonitrile (3f). ¹H NMR δ_{H} 6.04 (s, 1H); 7.46–7.58 (m, 4H); 7.63–7.69 (t, 2H); 7.72–7.75 (t, 1H); 7.76–7.89 (m, 3H); 7.95–7.99 (m, 3H); 8.02 (s, 1H); 8.72 (d, 1H); 8.78 (d, 1H). ¹³C NMR δ_{C} 40.61; 119.63 (q); 122.60; 123.57; 124.07; 125.25; 126.73; 126.77; 127.16; 127.24; 127.70; 127.74; 128.08; 128.74; 128.95 (q); 129.05; 129.29; 130.64 (q); 130.97 (q); 131.24 (q); 132.32 (q); 132.98 (q); 133.36 (q). m/z = 343 (100); 327 (16); 316 (11); 315 (9); 157 (11). MS m/z : 343 (M⁺, 100). Exact mass calcd for C₂₆H₁₇N: 343.13610; found: 343.13575.

1-(9-Phenanthryl)-2-naphthylacetonitrile (4f). ^1H NMR δ_{H} 3.57 (c, 2H); 7.18–7.21 (dd, 1H); 7.27–7.33 (m, 3H); 7.40–7.43 (cd, 1H); 7.48–7.52 (cd, 1H); 7.66–7.70 (m, 2H); 7.75–7.79 (m, 2H); 7.92 (d, 1H); 7.96 (d, 1H); 8.06 (d, 1H); 8.82 (t, 2H). ^{13}C NMR δ_{C} 22.33; 118.12 (q); 122.71; 123.18; 125.68; 126.25; 126.44; 126.64 (q); 126.74; 126.88; 127.17; 127.20; 127.32; 127.34; 128.05; 129.03; 129.13; 130.44 (q); 130.70 (q); 131.11 (q); 131.40 (q); 133.02 (q); 133.28 (q); 133.64 (q); 136.95 (q). m/z = 344 (40); 343 (60); 316 (100); 304 (11); 303 (15); 302 (14); 157 (18); 151 (26). MS m/z : 343 (M^+ , 100). Exact mass calcd for $\text{C}_{26}\text{H}_{17}\text{N}$: 343.13610; found: 343.13639.

α -(4-Cyanophenyl)-2-naphthylacetonitrile (3g). ^1H NMR δ_{H} 5.35 (s, 1H); 7.31 (d, 1H), 7.52–7.56 (m, 4H); 7.68 (d, 2H); 7.85–7.86 (m, 4H). ^{13}C NMR δ_{C} 42.74; 112.63 (q); 118.05 (q); 118.52 (q); 124.79; 127.06; 127.15; 127.18; 127.83; 128.01; 128.67; 129.76; 131.63 (q); 133.00 (q); 133.04 (q); 133.25 (q); 140.84 (q). m/z = 269 (19); 268 (100); 267 (54); 241 (15); 240 (50); 166 (21); 140 (11); 139 (13); 127 (11); 120 (13); 107 (15); 106 (11); 77 (10); 63 (9). MS m/z : 268 (M^+ , 100). Exact mass calcd for $\text{C}_{19}\text{H}_{12}\text{N}_2$: 268.10004; found: 268.10004.

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- The solvent effect was modelled with Tomasi's polarised continuum model (PCM) [S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117; S. Miertus and J. Tomasi, *Chem. Phys.*, 1982, **65**, 239; M. Cossi, B. Barone, R. Camini and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327]. The solvent effect was evaluated from single point PCM calculations on the gas-phase optimized geometries at the B3LYP/6-31G* theory level, electrostatic and non-electrostatic contributions being considered. In the PCM model the solvent is represented as a polarizable continuum (with dielectric constant ϵ) surrounding the molecular complex at an interface constructed by combining atomic van der Waals radii with the effective probe radius of the solvent. Charges are allowed to develop on this interface according to the electrostatic potential of the solute and ϵ , then the polarized reaction field of the solvent acts back on the quantum mechanical description of the solute. The wave function of the complex is relaxed self-consistently with the reaction field to solve the Poisson–Boltzmann (PB) equations. The solvent was represented with the following parameters: dielectric constant and probe radius.
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