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Synthesis, spectral and electrochemical characterization of novel 2-(fluoroanilino)-1,4-naphthoquinones

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ABSTRACT

The preparation of novel 2-(fluoroanilino)-1,4-naphthoquinones is presented. It takes place under mild conditions by reacting the corresponding fluoroaniline and 1,4-naphthoquinone in the presence of a Lewis acid catalyst with strong oxidation properties such as $CeCl_3 \cdot 7H_2O$. This preparation was also investigated under microwave irradiation. All 1,4-naphthoquinone derivatives were characterized by UV–Vis, IR, ^1H and ^{19}F NMR, MS and cyclic voltammetry, to investigate the effect of the fluoro-substituents on their electronic properties.

1. Introduction

A large number of synthetic and natural organic compounds containing a quinone moiety in their structure have been associated with different biological activities [1]. Many quinones have been used as antituberculosis agents [2], antimalarial agents [3], antimicrobials [4], antitumor agents [5], and fungicides [6,7]. In most cases, the biological activity of quinones has been related to their redox properties and their capacity to accept one or two electrons to form the corresponding radical-anion ($Q^{\bullet -}$) and hydroquinone radical dianion (Q^{2-}) [8]. These intermediate species interact with crucial cellular molecules such as oxygen, DNA and proteins modifying their biological activity [8–10]. Therefore, the studies on mechanisms of biological action, as well as the design and synthesis of novel compounds with more selective biological activities, require the understanding of the factors that modify the physicochemical properties of quinone systems.

The biological importance of this kind of compounds has motivated an extensive research to evaluate the electrochemical behavior of a given quinone and hydroquinone system [11–20]. Many researchers studied the redox kinetics and mechanisms in protic and aprotic solvents [11–13]. Other researchers have centered their studies on the influence of structural parameters on the redox properties of quinones [14–20].

It has been previously demonstrated that the presence of intramolecular hydrogen bonds (O...H–N) is an important factor in the acceptance of the first electron in the electrochemical reduction of the quinone system [21]. The electrochemical studies were performed in acetonitrile since quinones and their corresponding anions are not strongly solvated and intramolecular hydrogen bonds become more important in this solvent [22]. Several investigations have suggested that aprotic solvents indeed mimic cellular nonpolar environment where electron transfer takes place [23].

The electron-accepting capacity and several physicochemical properties of a given quinone can be modified by directly adding a substituted aniline to the quinone system [18]. In this type of compounds, the electron-attracting and donor properties of the substituents on the aniline modify their redox properties either facilitating or interfering with the charge transfer from the substituent to the quinone [19]. Since fluorine atoms are known to form hydrogen bonds and present both, electron-attracting and donor properties, the presence of one or more fluorine atoms on aniline, attached to the quinone structure, must have some interesting effects on the physicochemical properties of 1,4-naphthoquinone.

There are some previous reports on the use of a Lewis acid to catalyze the reaction of an aniline with 1,4-naphthoquinone to

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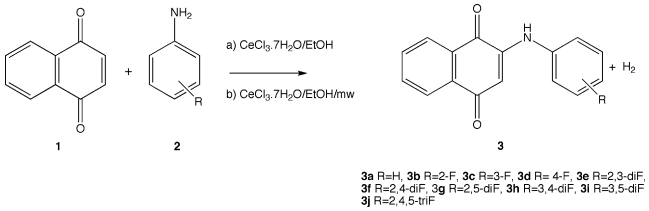
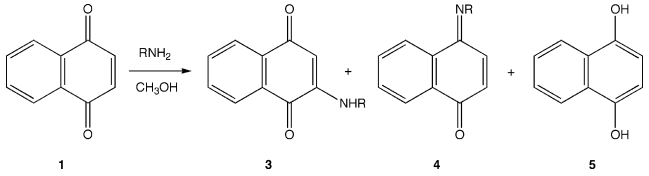


Scheme 1. Catalytic synthesis of 2-(fluoroanilino)-1,4-naphthoquinones.



Scheme 2. Reaction of 1,4-naphthoquinone with amines.

synthesize 2-(R-anilino)-1,4-naphthoquinones [19,24]. However, even in these cases the yields varied from low to moderate and the reactions required long times (days or weeks). In this paper, we report the preparation of several 2-(fluoroanilino)-1,4-naphthoquinones, eight of which have not been previously described, by reaction of a fluoroaniline with 1,4-naphthoquinone in the presence of a strong Lewis acid and a good oxidizing agent such as $CeCl_3{\cdot}7H_2O$. We also investigated this reaction under microwave irradiation (Scheme 1).

All the compounds prepared (Table 1) were characterized by IR, UV–Vis, ^1H and ^{19}F NMR, mass spectrometry and cyclic voltammetry. By means of these studies, the structure and effect of the substituents on the electronic properties of 1,4-naphthoquinone were investigated. Since the biological activity of quinone compounds is related to the redox potentials of the quinone moiety, a systematic investigation of substituent effects on the redox properties of 2-(R-anilino)-1,4-naphthoquinone would be useful for designing new molecules with greater and more specific biological activity.

2. Results and discussion

2.1. Synthesis and reaction pathway

The synthesis of simple alkyl or arylamino derivatives of naphthoquinone and related compounds is of interest due to their broad biological activity [1]. Furthermore, the aminonaphthoquinone moiety is a component of the molecular framework of many natural compounds and has been used as a key intermediate for the synthesis of several compounds with important biological applications [25].

There are two general methods for their preparation. In the first one, an already halogenated naphthoquinone molecule is reacted with an amine to produce the corresponding derivative by nucleophilic displacement [26]. In the second one, an amine is added, in a 1,4-type manner, to the naphthoquinone structure [27]. However, both methods are unpractical and require tedious chromatographic purifications since they give many side products, especially with primary amines.

It has been reported in the literature that when the reaction of 1,4-naphthoquinone **1** with aniline **2** is performed without a catalyst low yields of the 2-(anilino)-1,4-naphthoquinone **3** are obtained (0–50%) and several secondary products are formed [26]. Furthermore, performing this reaction under refluxing conditions leads to even lower yields (0–30%). In fact, the variety of compounds obtained in this reaction are due to two major effects: (a) the presence of several electrophilic centers of comparable reactivity, on the structure of 1,4-naphthoquinone **1**, leading to the formation of 1,4-addition adduct **3** and 1,2-addition adduct **4** as shown in Scheme 2, (b) the redox properties of 1,4-naphthoquinone **1** favoring the formation of an inert 1,4-naphthodiol **5**.

There are few reports on the use of Lewis acids to catalyze the reaction of anilines with 1,4-naphthoquinone [19,24]. We recently reported a bentonitic clay assisted preparation of 2-(chloroanilino)-1,4-naphthoquinones [28]. However, to the best of our knowledge there are no reports on the optimal conditions to prepare 2-(fluoroanilino)-1,4-naphthoquinones. The reaction of 1,4-naphthoquinone **1** with several fluoroanilines **2b**–**2j** gave the corresponding adducts **3b**–**3j** in low to moderate yields (30–60%). Only when the reaction (Table 2) was carried out in the presence of $CeCl_3{\cdot}7H_2O$, there was a high conversion of reactant species and the naphthoquinone derivatives **3b**–**3j** were obtained in very good yields (70–91%). This latter reaction was performed under microwave irradiation and moderate to good yields (55–90%) of adducts **3b**–**3j** were obtained in few minutes (1–3).

In the case of cerium, due to the low redox potential between the two ions (Ce^{3+}/Ce^{4+}, 1.7 V) in solution, the strong oxidant Ce^{4+} predominates in an oxidative atmosphere [29]. Therefore, in this particular reaction the high yield observed is most likely due to the presence of a strong Lewis acid and a strong oxidizing agent. It is envisioned that the Ce^{4+} assisted synthesis proceeds via a four steps mechanism (Scheme 3). First, the quinone **1** is activated by reaction with the Lewis acid catalyst to form an organic complex **6a**. Second, and due to resonance electronic interactions, there is a charge transfer in the activated complex with the 2-position of the quinone ring becoming positively charged **6b**. Third, the activated

Table 1
Structure of 2-(fluoroanilino)-1,4-naphthoquinones synthesized.

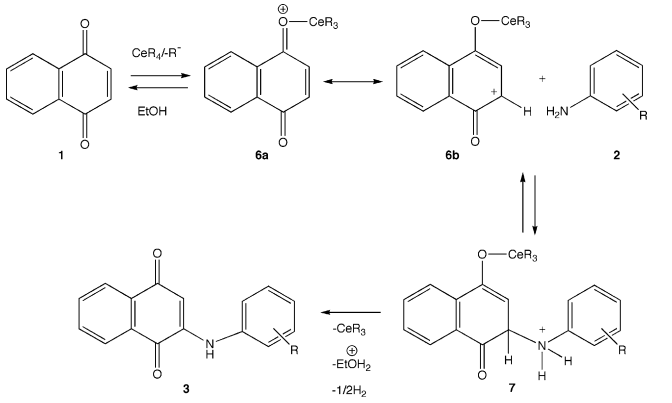
Compound	R_1	R_2	R_3	R_4
PAN **3a**[a,c]	H	H	H	H
2-FPAN **3b**[b]	F	H	H	H
3-FPAN **3c**	H	F	H	H
4-FPAN **3d**[b]	H	H	F	H
2,3-FPAN **3e**[b]	F	F	H	H
2,4-FPAN **3f**[b]	F	H	F	H
2,5-FPAN **3g**[b]	F	H	H	F
3,4-FPAN **3h**[b]	H	F	F	H
3,5-FPAN **3i**[b]	H	F	H	F
2,4,5-FPAN **3j**[b]	F	H	F	F
4-MeOPAN **3k**[c]	H	H	CH_3O	H

[a] It is also known as 2-[(phenyl) amine]-1,4-naphthalenediona or PAN.
[b] These compounds have not been previously described.
[c] These compounds were prepared for comparison.

Table 2
Effect of reaction conditions in the yield of 2-(fluoroanilino)-1,4-naphthoquinones.

Compound	Yield (%)[a]	Yield (%)[b]	Yield (%)[c]
PAN **3a**	60	85	57
2-FPAN **3b**	30	91	55
3-FPAN **3c**	50	72	60
4-FPAN **3d**	55	85	83
2,3-FPAN **3e**	60	85	56[d]
2,4-FPAN **3f**	40	70	55
2,5-FPAN **3g**	35	70	73
3,4-FPAN **3h**	30	74	90
3,5-FPAN **3i**	40	70	78
2,4,5-FPAN **3j**	45	74	55

[a] Without catalyst and 7 days.
[b] With catalyst $CeCl_3{\cdot}7H_2O$ and 4 h.
[c] With catalyst $CeCl_3{\cdot}7H_2O$ under microwave irradiation and 1–3 min.
[d] This reaction required microwave irradiation for 10 min.



Scheme 3. Reaction mechanism for the synthesis of 2-(fluoroanilino)-1,4-naphthoquinones.

Table 3
Spectroscopic data for 2-(R-anilino)-1,4-naphthoquinones synthesized.

Compound	(λ_{1max})[a]	(λ_{2max})[a]	(λ_{4max})[a]
	π–π^*	π–π^*	CT + η–π^*
PAN (**3a**)	207	271	466
2-FPAN (**3b**)	208	268	447
3-FPAN (**3c**)	208	272	458
4-FPAN (**3d**)	207	270	462
2,3-FPAN (**3e**)	209	268	448
2,4-FPAN (**3f**)	208	266	443
2,5-FPAN (**3g**)	208	268	441
3,4-FPAN (**3h**)	208	269	456
3,5-FPAN (**3i**)	209	272	451
2,4,5-FPAN (**3j**)	211	265	438
4-MeOPAN (**3k**)	203	273	480
NQ	200	245	329

[a] The UV–Vis spectra were determined using CH_3OH as solvent and λ_{max} values are in nanometers.

complex undergoes a selective nucleophilic attack, by the aniline **2** to give intermediate **7**. Fourth, under ethanolic conditions, it easily loses a proton and decomposes to produce a reduced ion Ce^{3+} and an oxidized compound or 2-(R-anilino)-1,4-naphthoquinone **3**. As stated above (Table 2), this adduct is obtained in lower yields (30–60%) when the reaction is performed without a catalyst due to the competitive formation of several secondary products. Indeed, Ce^{4+} provides a unique catalytic effect, promoted by Lewis acid and redox properties, with formation of the desired products in very good yields (70–91%). In all the reactions with $CeCl_3{\cdot}7H_2O$, no secondary products were observed and some amounts of the starting materials were recovered.

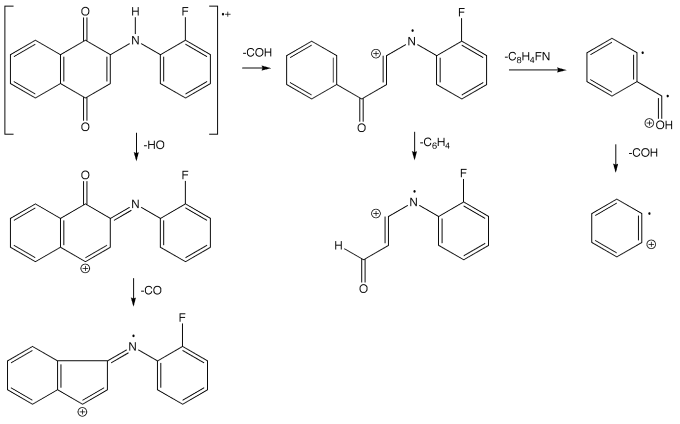
2.2. Mass spectrometry characterization

All the quinones obtained were characterized by mass spectrometry and the molecular radical ion for each quinone was determined. In addition, all the compounds showed analogous fragments (Scheme 4) suggesting a common fragmentation pattern [30].

2.3. UV–Vis spectroscopy studies

In general, PAN derivatives containing fluoro-substituents on their structure were found to be less soluble than PAN in acetonitrile and ethanol. PAN and FPAN derivatives gave orange to dark red solutions in ethanol (Table 3). UV–Vis electronic absorption spectra of **3a**–**3k** (Fig. 1) showed the expected π–π^* electron transitions bands associated with benzene and naphthoquinone in the region 203–211 nm (λ_1) and around 265–273 nm (λ_2). Furthermore, a weak η–π^* transition band is observed at 310–330 nm (λ_3). We also observed a broad and low energy band in the visible region centered between 438 and 480 nm (λ_4). This latter absorption is typical of amino substituted quinones and it has been previously assigned to charge-transfer (CT) transitions and weak η–π^* electron transitions of the carbonyl group in the quinone [31]. This absorption is strongly shifted to the visible region in PAN and FPAN derivatives relative to 1,4-naphthoquinone (NQ). Indeed, when a substituted aniline is added to the C_2 position of 1,4-naphthoquinone, bathochromic shifts of the absorption bands are observed with changes in the intensity and width [19]. In this case, the substitution of a fluoroaniline on NQ to give an FPAN compound, produces bathochromic shifts (relative to NQ) due to an increase in both, the π–π^* electron transition probability and interactions between the η electrons of the amine with the π system. This behavior has been previously discussed indicating that substituents on the aniline have an important role modulating the electronic properties of PAN compounds.

Indeed, electron-accepting and electron-donating substituents move the π–π^* absorptions, contributed from the HOMO-LUMO configuration, to longer wavelengths [32]. However we observed (Table 3) that the two bands (λ_1 and λ_2) frequently associated with these absorptions are not strongly shifted by modification of the substituent. In contrast, the low energy band (λ_4) observed in the visible region centered between 438 and 480 nm shifted when the substituent is modified. As we mentioned earlier, this latter band has been assigned to CT transitions and weak η–π^* transitions [31]. Both types of transitions are expected to be modified by nonbonding



Scheme 4. MS fragmentation pattern for 2-(2-fluoroanilino)-1,4-naphthoquinone.

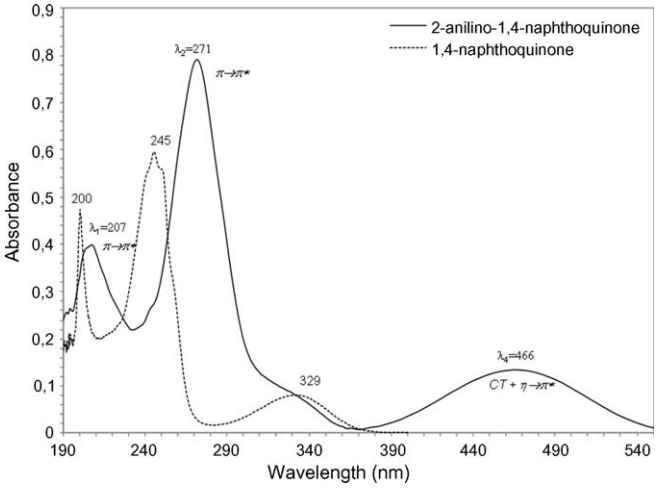


Fig. 1. UV–Vis electronic absorption spectra of 2-anilino-1,4-naphthoquinone and 1,4-naphthoquinone in methanol.

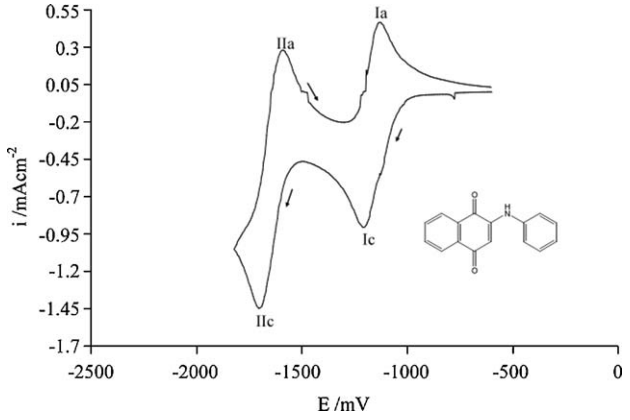


Fig. 2. Voltammetric response of PAN obtained at 100 mV/s in Et4NBF4 0.1 M/AcN.

electrons (η electrons) present in the nitrogen atom of aniline. When these η electrons are more available for interactions with the π system of the quinone, larger bathochromic shifts are observed. Some substituent effect on the position of this band is observed in Table 3. A strong bathochromic shift (relative to PAN) was observed for p-methoxyaniline due to an electron-donating effect of the substituent that makes the η electrons more available. In contrast, all FPAN derivatives exhibited hypsochromic shifts (relative to PAN) to shorter wavelenghts due to an electron-accepting effect of the substituents. This shift increased with the number of fluorine atoms in the aniline and the largest shift was observed for 2,4,5-FPAN. Particularly larger hypsochromic shifts were observed in FPAN compounds with an ortho-fluoro-substituted aniline.

2.4. Electrochemical studies

Redox potentials of all FPAN evaluated in this study were measured by cyclic voltammetry at 25 °C using a Pt disk electrode and 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile as the electrolytic medium [33]. The typical electrochemical behavior of PAN and FPANs was investigated and presented two reversible waves (Fig. 2). In the first wave, a semiquinone radical anion ($Q^{\bullet -}$) is generated by the addition of an electron to the quinone structure (Q). In the second wave, a dianion hydroquinone Q^{2-} is produced by the subsequent addition of an electron to the semiquinone radical anion [11–13]. These oxidation–reduction reactions could be represented by the following equations:

$$Q + e^- = Q\cdot^- \quad E^{I}_{1/2} \tag{1}$$

$$Q\cdot^- + e^- = Q^{2-} \quad E^{II}_{1/2} \tag{2}$$

Several parameters were evaluated from the voltammetric curves obtained over a potential range between −600 and −2020 mV with a sweep rate of 100 mV/s. The two half-wave potentials are associated with waves I and II, $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} corresponds to the anodic peak potential and E_{pc} corresponds to the cathodic peak potential. With the exception of 2,5-FPAN that presented a more complex cyclic voltammogram, the electrochemical behavior of all FPAN derivatives studied was quite similar to PAN indicating that all quinones oxidize by means of the same mechanism [14]. The cathodic peak current (i_{pc}) versus the square root of the sweep rate ($\nu^{1/2}$), produced a linear relationship with zero intercept for both peaks indicating no complications [34]. In addition to this, there was consistency of the voltammetric function with the sweep rate. In the voltammetric studies, the concentration of a given FPAN compound varied due to differences in solubility. Voltammetric function values were standardized for concentration and reported as $i_{pc}\nu^{-1/2}c^{-1}$. In this function, i_{pc} represents the cathodic peak current at the first or second reduction peak, ν is the scan rate and c is the concentration of compound in mol/cm^3.

In most of the cases, the values of the current function, i_{pc}, for both waves are approximately the same. This is generally associated with a one electron transfer for each wave and quite similar diffusion coefficients [35]. Indeed this result is expected, since most of the FPAN studied present a quite similar structure. In addition to this, the reversibility of the process is indicated by the relationship i_{pa}/i_{pc} and it has a value close to one for most cases studied [19]. The value $\Delta E_p = (E_{pa} - E_{pc})$ approaches the theoretical value reported for one-electron reversible system. In terms of the similarities in the voltammetric measurements (Table 4), we can presume that all the quinones studied are reduced by the same mechanism [14]. Therefore, one would expect to find consistency in several physicochemical properties such as substituent electronic effects and spectroscopic parameters.

A particularly different voltammetric behavior was observed in the case of 2,5-FPAN (Fig. 3). In this case, it was not possible to determine the E_{pa} and E_{pc} values since it was observed an intercrossing of current in the cathodic side of the voltammogram. This behavior could be due to an autocatalytic reaction [36]. In fact, there are several examples in the literature in which this type of chemistry has been reported.

More negative $E_{1/2}$ potentials were obtained for PAN and FPANs than the one reported for naphthoquinone. Therefore, the substitution of aniline and fluoroaniline increases electron density on the quinone structure [21]. In the FPAN compounds the lone pair on nitrogen (α to the $C_1 = O_1$ carbonyl) is displaced towards the enone structure. For a single fluoro-substituent, the $E_{1/2}$ potentials, corresponding to the first wave and second wave, presented the same trend. A moderate effect was observed to less negative values, with the following order 2F > 3F > 4F. An increase

Table 4
Electrochemical parameters[a] of 2-(fluoroanilino)-1,4-naphthoquinones.

Compound	$i_{pa}\nu^{-1/2}c^{-1}$ Wave I	$i_{pa}\nu^{-1/2}c^{-1}$ Wave II	E_{pa} Wave I	E_{pa} Wave II	$i_{pa}\nu^{-1/2}c^{-1}$ Wave I	$i_{pa}\nu^{-1/2}c^{-1}$ Wave II	E_{pc} Wave I	E_{pc} Wave II	i_{pa}/i_{pc} Wave I	i_{pa}/i_{pc} Wave II	ΔE_p Wave I	ΔE_p Wave II
PAN	369	545	−1133	−1587	−478	−419	−1204	−1693	0.77	1.3	71	106
2-FPAN	335	553	−1094	−1555	−503	−453	−1178	−1717	0.66	1.2	84	162
3-FPAN	823	841	−1102	−1551	−893	−645	−1198	−1727	0.92	1.3	96	176
4-FPAN	254	329	−1091	−1642	−368	−368	−1215	−1755	0.69	0.89	124	113
2,3-FPAN	187	491	−1124	−1604	−471	−461	−1169	−1774	0.4	1.06	45	170
2,4-FPAN	471	500	−1102	−1568	−520	−393	−1197	−1704	0.9	1.27	95	136
2,5-FPAN	359	[b]	−1051	[b]	−378	[b]	−1169	[b]	0.95	[b]	118	[b]
3,4-FPAN	236	470	−1130	−1593	−324	−429	−1203	−1723	0.73	1.09	73	130
3,5-FPAN	[b]	648	[b]	−1597	−443	−738	−1110	−1691	[b]	0.88	[b]	94
2,4,5-FPAN	422	546	−1072	−1556	−556	−431	−1172	−1667	0.76	1.27	100	111

[a] Determined by cyclic voltammetry at 100 mV/s. The potentials are given with respect to the Fc/Fc^+ redox couple.
[b] Since the waves were not well defined, these values could not be accurately determined.

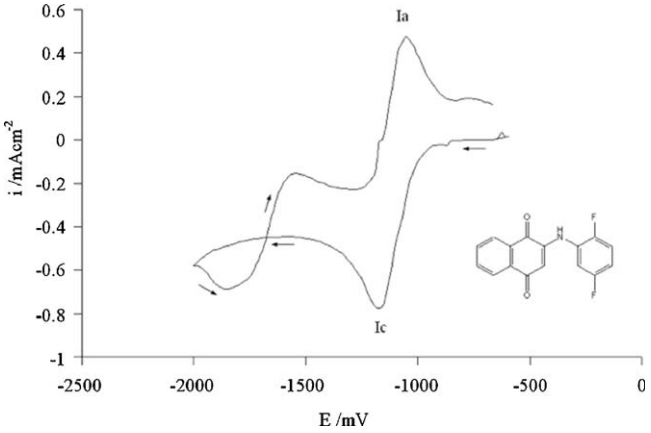
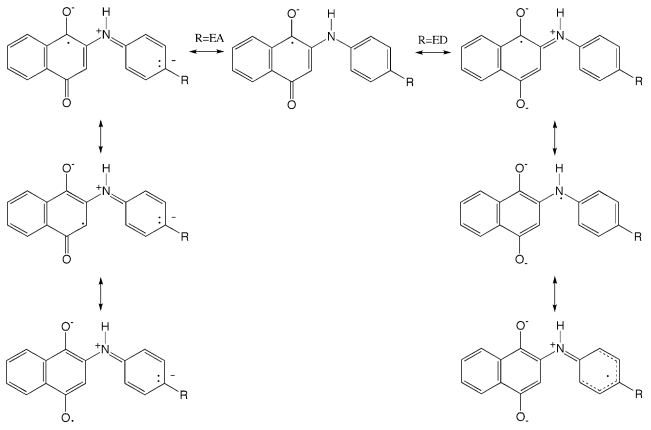


Fig. 3. Voltammetric response of 2,5-FPAN obtained at 100 mV/s in Et4NBF4 0.1 M/AcN.

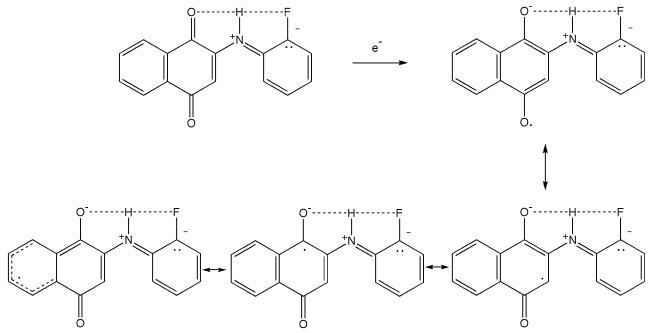
in number of the fluoro-substituents also shows a quite moderate effect to less negative values. These results are in agreement with previous studies on PAN and its derivatives [19–21]. In fact, the introduction of electron-donor groups displaced $E_{1/2}$ potentials for the first wave to more negative values than the one obtained for PAN. In contrast, introduction of electron-accepting substituents changed the $E_{1/2}$ potentials to less negative region. Electron-accepting substituents strongly unsaturated like cyano, acetyl and nitro were more powerful electron-acceptors than halogens. In general, electron-acceptor groups reduced the electron density of the electroactive group and facilitated the reduction process. However, in the case of fluoro-substituents this effect is rather weak due to simultaneous electron-attracting and donor properties of the substituents (Scheme 5).

In the case of PAN, electron-donor groups favor displacement of the free pair of electrons on nitrogen towards the quinone system, while electron-accepting groups facilitate displacement of electron density of nitrogen toward the aniline ring. A slightly larger electron-attracting effect is observed when an ortho-fluoro-substituent is present in the aniline. In this case, the intramolecular hydrogen bond C═O···H···F (Scheme 6) favors the reduction by enhancing the inductive effect of the substituent. Indeed, there are previous reports in the literature that evidence the thermodynamic stability in a three centered hydrogen bond present in similar aromatic ortho-substituted amides [37].

Analyzing substituent effects, we observe that the anodic shift (Table 4) was greater with a fluoro-substituent in meta-position



Scheme 5. Resonance hybrids showing stabilization of the radical anion ($Q^{\cdot -}$) when *R* is an electron-donor (ED) or an electron-acceptor (EA).



Scheme 6. Resonance hybrids showing stabilization of the radical anion ($Q^{\cdot -}$) where the substituent F acts as an electron-acceptor and a hydrogen bond forming atom.

than in para-position. This confirmed that the inductive effect of the halogen in this meta-position is more pronounced than the resonance effect. In previous studies on anilino-1,4-naphthoquinones [19] it was found that the first reduction corresponds to the reduction of the carbonyl (C_1═O) α to the amino group and the second reduction is associated with the other carbonyl (C_4═O). Displacement of the electron pair in amine nitrogen mainly affects the electron density on (C_4═O) carbonyl and a greater susceptibility of the second reduction to the electronic effect of the substituents is observed (Table 4). In general, it has been observed that increasing the amount of fluorine atoms in the structure favors both reduction waves but a small effect is still observed.

3. Conclusions

We synthesized nine FPANs, eight of which have not been previously reported. These compounds were prepared by reaction of the corresponding fluoroaniline with 1,4-naphthoquinone in the presence of a Lewis acid catalyst with strong oxidation properties such as $CeCl_3{\cdot}7H_2O$. This preparation was also achieved under microwave irradiation in several minutes. UV–Vis spectra of FPANs show the existence of an intramolecular electronic transfer from the fluoro-substituent to the 1,4-naphthoquinone moiety. In agreement with this donor-acceptor character, the cyclic voltammograms of FPANs exhibit two one-electron reduction waves to the corresponding radical-anion and dianion. In general, fluoro-substituents reduced the electron density of the electroactive group and facilitated the reduction process. However, this effect is rather weak due to simultaneous electron-attracting and donor properties of the substituents. Furthermore, a slightly larger effect is observed when an ortho-fluoro-substituent is present in the aniline due to an intramolecular three centered hydrogen bond. A different voltammetric behavior was observed for 2,5-FPAN that presented an intercrossing of current in the cathodic side of the voltammogram indicating an autocatalytic reaction.

4. Experimental

4.1. General methods

Melting points were measured with a Fisher Johns apparatus. UV–Vis spectra were obtained on a Shimadzu UV-2401 PC spectrophotometer. IR spectra were recorded on a Nicolet Nexus 470 FTIR spectrophotometer. NMR spectra were obtained on a Varian, Mercury 400 MHz nuclear magnetic resonance spectrometer. ^{1}H NMR spectra were recorded in ppm from tetramethylsilane and ^{19}F NMR spectra were recorded in ppm from trifluoroacetic acid. Mass spectra were recorded on an Finnigan MAT 8200 spectrometer at 70 eV. All the starting compounds were

purchased from Aldrich. Reactions under microwave irradiation were performed in a CEM microwave reactor, Discover System No. DU8756.

4.2. Electrochemical procedure. Solvent and supporting electrolyte

Acetonitrile was dried overnight with $CaCl_2$ and purified by distillation on P_2O_5 under vacuum [38]. Traces of water in the solvent were eliminated by contact with a molecular sieve 3 Å in the absence of light. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was dried under vacuum at 60 °C.

4.3. Electrodes, apparatus and instrumentation

Cyclic voltammetry measurements were carried out in a conventional BASS model C3 three-electrode cell. A polished Pt-disk BASS electrode with a diameter of 0.2 cm was used as a working electrode. Prior to measurements, this electrode was polished and cleaned with 15 μm and 3 μm alumina, washed with distilled water and sonicated in ethanol for 3 min. The auxiliary electrode consisted of a piece of platinum wire with an area of 0.475 cm^2. The reference electrode was a silver wire in a solution of $AgNO_3$ 3 M (Ag/Ag^+) with acetonitrile. This electrode was isolated from the main cell body by a Luggin tube filled with 0.1 M Et_4NBF_4/acetonitrile.

The half-wave potentials were measured at room temperature in acetonitrile solutions using 0.1 M Et_4NBF_4 as the supporting electrolyte. The concentration for the PAN solutions were 5×10^{-3} M. Voltametric curves were recorded using a Tacussel 1MT 101 Electrochemical Analyzer with a signals generator DEA 332 interfaced with a personal computer with a Voltamaster 2-X9725-2.0 program. Measurements were made over a potencial range between −600 and −2020 mV with a sweep rate of 100 mV/s. Prior to the experiments, solutions were purged with nitrogen. All potentials were determined under the same conditions in order to obtain a consistent data set [39].

4.4. Synthetic procedures

4.4.1. Preparation of 2-(fluoroanilino)-1,4-naphthoquinones by method A

The substituted naphthoquinones were prepared by the method reported in the literature [24] with several modifications. 1,4-Naphthoquinone (1 mmol) was dissolved in ethanol (30 mL). A solution of fluoroaniline (1 mmol) in ethanol (30 mL) was slowly added and the reaction mixture was allowed to react for seven days. The reaction vessel was equipped with a reflux condenser to minimize ethanol losses during the experiment. The solution turned deep red or orange-yellow when the corresponding 2-(fluoroanilino)-1,4-naphthoquinone was formed. The resulting solid was filtered and washed with cold ethanol. After recrystallization from ethanol, the desired product was obtained as a pure and crystalline colored solid.

4.4.2. Preparation of 2-(fluoroanilino)-1,4-naphthoquinones by method B

The substituted naphthoquinones were prepared by the method reported in the literature [24] with several modifications. 1,4-Naphthoquinone (1 mmol) was dissolved in ethanol (10 mL) and $CeCl_3.7H_2O$ (0.1 mmol) was added. The reaction mixture was stirred at least 60 min to allow the reaction between the Lewis base (1,4-naphthoquinone) and the Lewis acid ($CeCl_3{\cdot}7H_2O$). A solution of fluoroaniline (1 mmol) in ethanol (10 mL) was slowly added and the mixture was allowed to react for 4 h. The reaction vessel was equipped with a reflux condenser to minimize ethanol losses during the experiment. The progress of the reaction was monitored by TLC and only one product was formed. The solution turned deep red or orange-yellow when the corresponding 2-(fluoroanilino)-1,4-naphthoquinone was formed. The resulting solid was filtered and washed with cold ethanol. After recrystallization from ethanol, the desired product was obtained as a pure and crystalline colored solid. Comparing with previous reports, it was found that the yields of this reaction were notoriously improved. In terms of the proposed mechanism, the order in which the reagents are added is quite important.

4.4.3. Preparation of 2-(fluoroanilino)-1,4-naphthoquinones by method C

In a flask were placed 1,4-naphthoquinone (1 mmol), the corresponding aniline (1 mmol), $CeCl_3{\cdot}7H_2O$ (0.1 mmol) and 5 mL of ethanol. The reaction mixture was placed in a microwave reactor and it was irradiated (20–50 W) in an open atmosphere system. The temperature was set at 65 °C for 1–3 min. After this time, the reaction mixture flask was placed in an ice-water bath for 1 h to induce precipitation. A crystalline product was separated by filtration and washed with cold ethanol.

4.5. Characterization of 2-(2-fluoroanilino)-1,4-naphthoquinone (3b)

It was obtained as an orange solid with m.p. 155 °C; IR (KBr, cm^{-1}): 3314 (–NH–), 1667.6, 1644.5 (C=O), 1607, 1594 (C=C aromatic), 1502 (–NH–), 1353 (C–N), 1300 (C–CO–C), 1104 (C–F); UV–Vis (CH_3OH, nm, log ε): 447 (3.73), 268 (4.55), 208 (4.29); ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.19 (1H, s, vinyl H), 7.28 (1H, m, aromatic H), 7.37 (2H, m, aromatic H), 7.44 (1H, t, J_{HF} = 8.5, J_{HH} = 7.42 Hz, aromatic H), 7.79 (1H, td, J = 7.42, 1.37 Hz, aromatic H), 7.85 (1H, td, J = 7.42, 1.37 Hz, aromatic H), 7.93 (1H, dd, J = 7.42, 1.37 Hz, aromatic H), 8.06 (1H, dd, J = 7.42, 1.37 Hz, aromatic H), 9.15 (1H, s, N–H); ^{19}F NMR (DMSO-d_6) δ (ppm): −120.07 (m, J = 8.3, 5.95 Hz aromatic F); EIMS (probe) 70 eV, m/z (rel. int.): 267 [M^+] (100), 250 [M^+–OH] (4.5), 238 [M^+–COH] (30.4), 222 [M^+–OH–CO] (12.5), 162 [M^+–COH–C_6H_4] (20.2), 105 [M^+–COH–C_8H_4FN] (17.6), 76 [M^+–COH–C_8H_4FN–COH] (13.2). The exact mass was 267.0696 amu, the mass observed was 267.0691 amu for $C_{16}H_{10}FNO_2$.

4.6. Characterization of 2-(3-fluoroanilino)-1,4-naphthoquinone (3c)

It was obtained as a red solid with m.p. 200 °C; IR (KBr, cm^{-1}) 3192 (–NH–), 1681.5, 1624.9 (C=O), 1599.5 (C=C aromatic), 1529 (–NH–), 1358 (C–N), 1300 (C–CO–C), 1221 (C–F); UV–Vis (CH_3OH, nm, log ε): 458 (3.61), 272 (4.38), 208 (4.119); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.46 (1H, s, vinyl H), 6.9 (1H, td, J_{HF} = 8.2, J_{HH} = 2.34 Hz, aromatic H), 7.01 (1H, dt, J_{HF} = 9.77, J_{HH} = 2.01 Hz, aromatic H), 7.05 (1H, dd, J = 8.01, 1.1 Hz, aromatic H), 7.37 (1H, m, J_{HH} = 8.2, J_{HF} = 6.5 Hz, aromatic H), 7.56 (1H, s, N–H), 7.68 (1H, td, J = 7.62, 1.17 Hz, aromatic H), 7.77 (1H, td, J = 7.62, 1.37 Hz, aromatic H), 8.12 (2H, td, J = 7.42, 0.8 Hz, aromatic H); ^{19}F NMR ($CDCl_3$) δ (ppm): −110.77 (sextet, J = 9.3, 6.7 Hz, aromatic F); EIMS (probe) 70 eV, m/z (rel. int.): 267 [M^+] (100), 250 [M^+–OH] (7), 238 [M^+–COH] (30), 222 [M^+–OH–CO] (18), 162 [M^+–COH–C_6H_4] (15), 105 [M^+–COH–C_8H_4FN] (16). The exact mass was 267.0696 amu, the mass observed was 267.0690 amu for $C_{16}H_{10}FNO_2$.

4.7. Characterization of 2-(4-fluoroanilino)-1,4-naphthoquinone (3d)

It was obtained as a violet solid with m.p. 244 °C; IR (KBr, cm^{-1}) 3317.1 (–NH–), 1676.8, 1645 (C=O), 1609.7 (C=C aromatic), 1509 (–NH–), 1354 (C–N), 1300 (C–CO–C), 1226 (C–F); UV–Vis (CH_3OH, nm, log ε): 462 (3.678), 270 (4.45), 207 (4.19); ^1H NMR (DMSO-d_6) δ (ppm): 5.98 (s, 1H, vinyl H), 7.27 (2H, t, J_{HF} = 8.79, J_{HH} = 6.75, 2.34 Hz, aromatic H), 7.4 (2H, dd, J_{HH} = 7.23, 2.15 J_{HF} = 5.27 Hz, aromatic H), 7.77 (1H, td, J = 7.62, 1.37 Hz, aromatic H), 7.84 (1H, td, J = 7.62, 1.37 Hz, aromatic H), 7.93 (1H, dd, J = 7.62, 1.37 Hz, aromatic H), 8.04 (1H, dd, J = 7.62, 1.37 Hz, aromatic H), 9.26 (1H, s,

N–H); ^{19}F NMR (DMSO-d_6) δ (ppm): −117.04 (s, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 267 [M^+] (100), 250 [M^+–OH] (6), 238 [M^+–COH] (29), 222 [M^+–OH–CO] (14), 162 [M^+–COH–C_6H_4] (21), 105 [M^+–COH–C_8H_4FN] (22). The exact mass was 267.0696 amu, the mass observed was 267.0691 amu for $C_{16}H_{10}FNO_2$.

4.8. Characterization of 2-(2,3-difluoroanilino)-1,4-naphthoquinone (3e)

It was obtained as an orange solid with m.p. 154 °C; IR (KBr, cm^{-1}) 3316 (–NH–), 1666 (C=O), 1608 (C=C aromatic), 1525 (–NH–), 1348 (C–N), 1301 (C–CO–C), 1248 (C–F); UV–Vis (CH_3OH, nm, log ε): 448 (3.65), 268 (4.47), 209 (4.23); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.32 (1H, s, vinyl H), 7.21 (2H, m, aromatic H), 7.45 (1H, m, aromatic H), 7.55 (1H, s, N–H), 7.7 (1H, td, *J* = 7.44, 1.5 Hz, aromatic H), 7.77 (1H, td, *J* = 7.47, 1.48 Hz, aromatic H), 8.13 (2H, m, *J* = 7.25 Hz, aromatic H); ^{19}F NMR ($CDCl_3$) δ (ppm): −124.98 (s, aromatic F), −125.01 (s, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 285 [M^+] (100), 266 [M^+–F] (8.3), 256 [M^+–COH] (23.7), 180 [M^+–COH–C_6H_4] (22%), 105 [M^+–COH–$C_8H_3F_2N$] (20.6), 76 [M^+–COH–$C_8H_3F_2N$–COH] (14). The exact mass was 285.0601 amu, the mass observed was 285.06 amu for $C_{16}H_9F_2NO_2$.

4.9. Characterization of 2-(2,4-difluoroanilino)-1,4-naphthoquinone (3f)

It was obtained as an orange solid with m.p. 205 °C; IR (KBr, cm^{-1}) 3313 (–NH–), 1665, 1643 (C=O), 1612 (C=C aromatic), 1530 (–NH–), 1355 (C–N), 1306 (C–CO–C), 1148 (C–F); UV–Vis (CH_3OH, nm, log ε): 443 (3.63), 266 (4.55), 208 (4.21); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.13 (1H, s, vinyl H), 6.96 (2H, m, aromatic H), 7.33 (1H, s, N–H), 7.38 (1H, m, *J* = 7.23, J_{HF} = 5.67 Hz, aromatic H), 7.68 (1H, td, *J* = 7.62, 1.37 Hz, aromatic H), 7.76 (1H, td, *J* = 7.62, 1.37 Hz, aromatic H), 8.10 (1H, dd, *J* = 7.62, 0.78 Hz, aromatic H), 8.13 (1H, dd, *J* = 7.62, 0.78 Hz, aromatic H); ^{19}F NMR ($CDCl_3$) δ (ppm): −111.6 (s, aromatic F), −119.02 (s, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 285 [M^+] (100), 266 [M^+–F] (6.6), 256 [M^+–COH] (22.7), 180 [M^+–COH–C_6H_4] (19.8), 105 [M^+–COH–$C_8H_3F_2N$] (25), 76 [M^+–COH–$C_8H_3F_2N$–COH] (12). The exact mass was 285.0601 amu, the mass observed was 285.06 amu for $C_{16}H_9F_2NO_2$.

4.10. Characterization of 2-(2,5-difluoroanilino)-1,4-naphthoquinone (3g)

It was obtained as an orange solid with m.p. 190 °C; IR (KBr, cm^{-1}) 3318 (–NH–), 1666.8, 1642.9 (C=O), 1600 (C=C aromatic), 1505 (–NH–), 1348 (C–N), 1301 (C–CO–C), 1251 (C–F); UV–Vis (CH_3OH, nm, log ε): 441 (3.65), 268 (4.42), 208 (4.24); ^{1}H NMR (DMSO-d_6) δ (ppm): 5.63 (1H, s, vinyl H), 7.21 (1H, m, J_{HF} = 9.6, 5.34, J_{HH} = 9, 3.4 Hz, aromatic H), 7.34 (1H, m, J_{HH} = 8.8, 3.1, J_{HF} = 6.2 Hz, aromatic H), 7.43 (1H, m, J_{HF} = 9.65, 5, J_{HH} = 9.45 Hz, aromatic H), 7.79 (1H, td, *J* = 7.4, 1.3 Hz, aromatic H), 7.86 (1H, td, *J* = 7.4, 1.25 Hz, aromatic H), 7.94 (1H, d, *J* = 7.4 Hz, aromatic H), 8.055 (1H, d, *J* = 7.4, aromatic H), 9.17 (1H, s, N–H); ^{19}F NMR (DMSO-d_6) δ (ppm): −117.24 (s, aromatic F), −124.59 (s, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 285 [M^+] (100), 266 [M^+–F] (7.5), 256 [M^+–COH] (22.6), 180 [M^+–COH–C_6H_4] (18.5), 105 [M^+–COH–$C_8H_3F_2N$] (20.4), 76 [M^+–COH–$C_8H_3F_2N$–COH] (13.2). The exact mass was 285.0601 amu, the mass observed was 285.06 amu for $C_{16}H_9F_2NO_2$.

4.11. Characterization of 2-(3,4-difluoroanilino)-1,4-naphthoquinone (3h)

It was obtained as an orange solid with m.p. 260 °C; IR (KBr, cm^{-1}) 3192 (–NH–), 1679.3 (C=O), 1616 (C=C aromatic), 1514 (–NH–), 1358 (C–N), 1260 (C–F); UV–Vis (CH_3OH, nm, log ε): 456 (3.54), 269 (4.35), 208 (4.06); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.31 (1H, s, vinyl H), 7.01 (1H, m, *J* = 8.6 Hz, aromatic H), 7.13 (1H, ddd, J_{HF} = 10.98, 6.74, J_{HH} = 2.64 Hz, aromatic H), 7.22 (1H, q, J_{HF} = 9.57, J_{HH} = 8.79 Hz, aromatic H), 7.44 (1H, s, N–H), 7.69 (1H, td, *J* = 7.62, 1.37 Hz, aromatic H); 7.78 (1H, td, *J* = 7.42, 1.17 Hz, aromatic H), 8.11 (2H, t, *J* = 7.62, 0.78 Hz, aromatic H); ^{19}F NMR ($CDCl_3$) δ (ppm): −134.46 and −140.24 (s, *J* = 9.3, 6.7 Hz, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 285 [M^+] (100), 268 [M^+–OH] (19.5), 256 [M^+–COH] (63), 240 [M^+–CO–OH] (44.5), 180 [M^+–COH–C_6H_4] (45.5), 105 [M^+–COH–$C_8H_3F_2N$] (49.5), 76 [M^+–COH–$C_8H_3F_2N$–COH] (13.2). The exact mass was 285.0601 amu, the mass observed was 285.06 amu for $C_{16}H_9F_2NO_2$.

4.12. Characterization of 2-(3,5-difluoroanilino-1,4-naphthoquinone (3i)

It was obtained as an orange solid with m.p. 261 °C; IR (KBr, cm^{-1}) 3322 (–NH–), 1666.3, 1646.3 (C=O), 1614 (C=C aromatic), 1536 (–NH–), 1304 (C–N), 1248 (C–CO–C), 1116 (C–F); UV–Vis (CH_3OH, nm, log ε): 451 (3.42), 272 (4.21), 209 (3.95); ^{1}H NMR (DMSO-d_6) δ (ppm): 6.31 (1H, s, vinyl H), 7.03 (1H, tt, J_{HF} = 9.38, J_{HH} = 2.34, aromatic H), 7.15 (2H, dd, J_{HF} = 9.18, J_{HH} = 2.34 Hz, aromatic H), 7.79 (1H, td, *J* = 7.42, 1.37 Hz, aromatic H), 7.86 (1H, td, *J* = 7.42, 1.37 Hz, aromatic H), 7.95 (1H, dd, *J* = 7.62, 1.17 Hz, aromatic H), 8.05 (1H, dd, *J* = 7.62, 1.17 Hz, aromatic H), 9.38 (1H, s, N–H); ^{19}F NMR (DMSO-d_6) δ (ppm): −109.19 (t, *J* = 9.29 Hz, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 285 [M^+] (100), 268 [M^+–OH] (9), 256 [M^+–COH] (41), 240 [M^+–CO–OH] (26.6), 180 [M^+–COH–C_6H_4] (16.4), 105 [M^+–COH–$C_8H_3F_2N$] (17.4), 76 [M^+–COH–$C_8H_3F_2N$–COH] (13.6). The exact mass was 285.0601 amu, the mass observed was 285.06 amu for $C_{16}H_9F_2NO_2$.

4.13. Characterization of 2-(2,4,5-trifluoroanilino)-1,4-naphthoquinone (3j)

It was obtained as an orange solid with m.p. 202 °C; IR (KBr, cm^{-1}) 3186 (–NH–), 1686 (C=O), 1607, 1619 (C=C aromatic), 1502 (–NH–), 1347 (C–N), 1277 (C–F); UV–Vis (CH_3OH, nm, log ε): 438 (3.49), 265 (4.34), 211 (4.12); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.21 (1H, s, vinyl H), 7.10 (1H, sextet, J_{HF} = 9.8, 7.3 Hz, aromatic H), 7.28 (1H, m, J_{HF} = 10.36, 7.6 Hz, aromatic H), 7.39 (1H, s, N–H), 7.70 (1H, td, *J* = 7.62, 1.17 Hz, aromatic H), 7.78 (1H, td, *J* = 7.62, 1.17 Hz, aromatic H), 8.12 (2H, t, *J* = 7.82 Hz, aromatic H); ^{19}F NMR ($CDCl_3$) δ (ppm): −125.58 (s, aromatic F), −135.95 (s, aromatic F), −139.63 (s, aromatic F); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 303 [M^+], (100), 275 [M^+–CO] (15), 274 [M^+–COH] (19), 258 [M^+–CO–OH] (9.5), 198 [M^+–COH–C_6H_4] (30), 127 [M^+–CO–OH–$C_6H_2F_3$] (26). The exact mass was 303.0507 amu, the mass observed was 303.050 amu for $C_{16}H_8F_3NO_2$.

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