Reactivity of Sulfur-Centered Radicals with Indolinonic and Quinolinic Aminoxyls

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Indolinonic, phenylimino-indolinonic and quinolinic aromatic aminoxyls readily react with sulfur-centered radicals, generated upon reaction with *p*-methylthiophenol at room temperature. The main product is the deoxygenated derivative i.e. the corresponding amine. The other compounds, obtained in low yields, are *N*-substituted amines and amines substituted in a conjugated position with respect to the amino group by arylthiyl, arylsulphinyl, arylsulphonyl and arylsulphonyloxy radicals. The formation of the products are explained by the initial attack of the thiophenol radical onto the NO· function to give an unstable adduct which decomposes to aminyl and arylsulphinyl radicals. From here the reaction can take two different routes to give the products obtained.

Introduction

The use of aminoxyls as spin probes and spin labels for studies of membranes and proteins[1] and their use (even in living systems) for EPR imaging and *in vivo* EPR spectroscopy[2] has increased significantly recently, and this makes it essential to have better knowledge of the chemical, biochemical and biological interactions of aminoxyls in such systems. The reaction of aminoxyls with SH groups is of particular interest owing to the fact that low-molecular weight SH-containing compounds such as glutathione are important in many cellular functions including protection against oxidative stress. The amino acid cysteine, found in water-soluble and membrane proteins, is also an important source of SH groups. The reaction of aliphatic aminoxyls with these SH-containing compounds has been extensively studied in biological systems,[3] however, the data on their reduction by SH groups are controversial, and the real mechanism of the reaction is not yet known. Therefore, it is of interest to study the reaction between aminoxyls and SH groups in order to understand the products, and possibly elucidate the reaction mechanisms of their interaction. Secondly, clarification on this particular reaction is important considering the role played by aminoxyls during rubber stabilization. In fact, both hindered secondary amines and sulfur-containing compounds are used in polymers as stabilizers, and during their activity aminoxyls and thiyl radicals are formed as intermediates.[4]

As a starting point, we previously studied the reaction of an aliphatic aminoxyl TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) with a series of thiophenols.[5] The main feature of the reaction was the deoxygenation of the aminoxyl with formation of the corresponding tetramethylpiperidinium arylsulphinates and arylsulphonates. Other isolated products were the corresponding amine and *N*-substituted products with arylsulphinyl and arylsulphonyl radicals. This reaction was explained as a consecutive coupling of the arylthiyl radical (or its oxygenated derivatives) with the NO· function, followed by cleavage of the N−O bond.

This study has now been extended to aromatic (namely, indolinonic and quinolinic) aminoxyls, whose NO· function is in conjugation with a π-system. For this reason they display a different reactivity with respect to aminoxyls bearing the NO• function between sp^3 carbons, such as TEMPO.[6] These studies, could therefore contribute to the further understanding of the interaction between aminoxyls and SH groups and of the reactivity of indolinonic and quinolinic aminoxyls with sulfur-centred radicals.

Results

The reactions between indolinonic aminoxyls **1a** and **1b** or quinolinic aminoxyl **1c** with *p*-methylthiophenol (**2**) were carried out in benzene at room temperature, under nitrogen in the ratio 2:1 respectively. The results show that there is interaction of the *p*-methylphenylthiyl (arylthiyl) radicals with the NO• function and/or its conjugated benzene ring. The experiments were each performed twice, and in every case the same products were isolated. The yields reported in Table 1 are the average of the two individual runs and have to be considered indicative since the products were isolated and purified by a series of preparative thin layer chromatographies.

The reaction between 2-methyl-3-oxo-2-phenylindoline-1-oxyl (**1a**) and *p*-methylthiophenol (**2**), led to a number of products. The main product was the amine **10a**[7] corresponding to the starting aminoxyl. Other minor products were differently substituted amines; an amine with an *N*-arylsulphonyl group (**11y/1a**), amines substituted in positions 5 or 7 with an arylthiyl- **12x/1a**, **13x/1a**, arylsulphonyl- **12y/1a**, **13y/1a** or an arylsulphonyloxy group **12z/**

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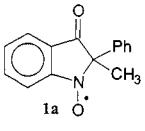
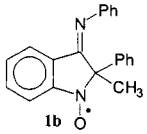
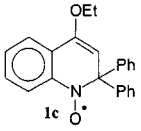
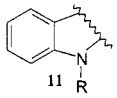
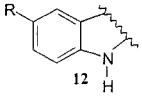
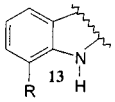
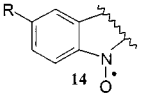
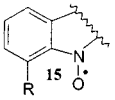
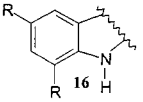
Table 1. Percentage yields of products **4** and **10**−**20** isolated from the reaction of aminoxyls **1a**−**c** with thiyl radicals

Product[a]	Substituent	 1a	 1b	 1c
 1[b]		-	6	46
 4		6	-	-
 10		46	54	13[c]
 11	**x**: R = ArS	-	4	-
	w: R = ArSO	-	4	-
	y: R = $ArSO_2$	4	3	traces
 12	**x**: R = ArS	8	-	2 + traces[d]
	y: R = $ArSO_2$	3	3	3
	z: R = $ArSO_3$	2	3	2
 13	**x**: R = ArS	traces	-	-
	y: R = $ArSO_2$	3	-	2
	z: R = $ArSO_3$	7	traces	-
 14	**y**: R = $ArSO_2$	traces	-	-
 15	**y**: R = $ArSO_2$	traces	-	-
 16	**x**: R = ArS	traces	-	-
ArS−SAr 17		14	traces	7
$ArS-SO_2Ar$ 18		6	-	-

[a] The skeleton of these products corresponds to compounds **1a**−**c** in each column. − [b] Recovered aminoxyl. − [c] Compound **19**. − [d] Compound **20**.

1a, **13z**/**1a**, and disubstituted amines **16x**/**1a** with an arylthiyl group in positions 5 and 7. Futhermore, the hydroxylamine **4a**[8] was isolated in addition to the aminoxyls substituted in position 5 **14y**/**1a** or 7 **15y**/**1a** with an arylsulphonyl group. The presence of *p*-methylphenyldisulphide (**17**) and of *S*-(*p*-methylphenyl)-*p*-methylbenzenethiosulphonate (**18**)[9] was confirmed by comparison with authentic samples.

The reaction of 2-methyl-2-phenyl-3-phenyliminoindoline-1-oxyl (**1b**) and *p*-methylthiophenol (**2**) led to the formation of the amine **10b**,[10] to the *N*-substituted amines **11x**/**1b**, **11w**/**1b** and **11y**/**1b** with an arylthiyl-, an arylsulphinyl-, or an arylsulphonyl group, respectively, as well as to the 5-substituted amines with an arylsulphonyl- **12y**/**1b** or an arylsulphonyloxy group **12z**/**1b**. The 7-substituted amine **13z**/**1b** with an arylsulphonyloxy group and traces of *p*-methylphenyldisulphide (**17**) were also isolated.

Finally, the reaction of 4-ethoxy-1,2-dihydro-2,2-diphenylquinoline-1-oxyl (**1c**) with the same thiophenol gave rise to the amine **19**,[11] to the *N*-substituted amine with an arylsulphonyl group **11y**/**1c**, to the 6-substituted amine with an arylthiyl- **12x**/**1c**, an arylsulphonyl- **12y**/**1c**, or an arylsulphonyloxy group **12z**/**1c**, to the 8-substituted amine with an arylsulphonyl group **13y**/**1c** and to *p*-methylphenyldisulphide (**17**). The amine substituted in position 6 with a thiyl group (**20**) was also present in the ketonic form.

All the products were identified by their spectroscopic data (^{1}H NMR, High Resolution Mass Spectroscopy,

FT-IR, EPR) and by comparison with the data for similar compounds.[12]

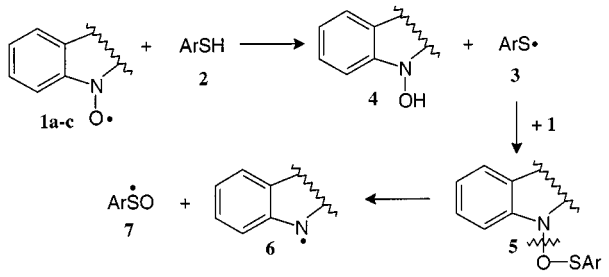
With regards to the substituted amines, the position in which the substituent is attached on the benzene ring of the indolinic and quinolinic moiety was determined by comparing the ^{1}H NMR spectrum of the unsubstituted amine **10** with those of the substituted amines obtained. Differences in the pattern of the H-4 (H-5 for quinolinic derivatives), H-5 (H-6), H-6 (H-7), and H-7 (H-8) signals were observed. These are mainly due to the loss of the signals from H-5 (H-6) and/or H-7 (H-8) to which the substituent is attached; as a consequence there is a loss of the *ortho*-coupling constants for the indolic protons *ortho* to the substituent. Therefore, in the 5-substituted (6-) amines **12**, the signals due to H-4 (H-5) and H-6 (H-7) appear as a doublet (J = 1.9−2.7 Hz) and a doublet of doublets (J = 1.9−2.7 and 8.4−8.8 Hz) respectively. In the 7-substituted amines **13** the signals due to H-6 and H-4 (J = 1.1−1.3 and 7.3−7.8 Hz) differ only by an additional coupling between H-4 and the N−H proton (J = 0.6−0.7 Hz).[13] In the 5,7-disubstituted amine **16**, two doublets due to H-4 and H-6 (J = 1.8 Hz) are observed, with H-4 showing an additional smaller coupling with the N−H proton. On the other hand, in the *N*-substituted amines **11**, H-4, H-5, H-6 and H-7 show similar coupling constants as the unsubstituted amine but at different chemical shifts.

To determine the number of oxygens on the sulfur of the substituent, we compared the chemical shifts of the protons in the thiophenol moiety *ortho* to the sulfur atom of the substituents (namely "arom-S") with those of benzene (δ = 7.25). We also compared the chemical shifts of H-4 and H-6 of 5-substituted amines with those of the unsubstituted amine (δ_{H4} = 7.6 and δ_{H6} = 7.5). Therefore, in the case of ArS substitution (e.g. **12x/1a**), the chemical shifts of the "arom-S" protons (δ = 7.19), of H-4 (δ = 7.67), and of H-6 (δ = 7.55) appear almost unchanged. In the case of $ArSO_2$ (e.g. **12y/1a**) substitution, however, the "arom-S" protons (δ = 7.79), H-4 (δ = 8.13), and H-6 (δ = 7.97) appear deshielded due to the electron-withdrawing character of the SO_2 group. Finally, in the $ArSO_3$-substituted compounds (e.g. **12z/1a**), the "arom-S" protons behave similarly to the $ArSO_2$ derivative (δ = 7.73) but H-4 (δ = 7.08) and H-6 (δ = 7.25) appear shielded, suggesting the presence of a mesomeric effect probably due to an extra oxygen linking the $ArSO_2$ group with the indole moiety. Additional support for the structural assignments was obtained by the IR spectra. The compounds bearing a sulphonyl group attached to the nitrogen show the two typical absorptions between 1365−1315 and 1180−1150 cm^{-1}, while those bearing this group on the benzene ring typically absorb in the 1370−1290 and 1170−1110 cm^{-1} ranges. The sulphonyloxy derivatives show the two characteristic absorption peaks at 1375−1350 and 1185−1145 cm^{-1}. High resolution mass spectra of new compounds were performed whenever possible. In all cases, mass spectra showed the expected molecular ion peak and in most cases the fragmentation due to the different substituents was characteristic.

Discussion

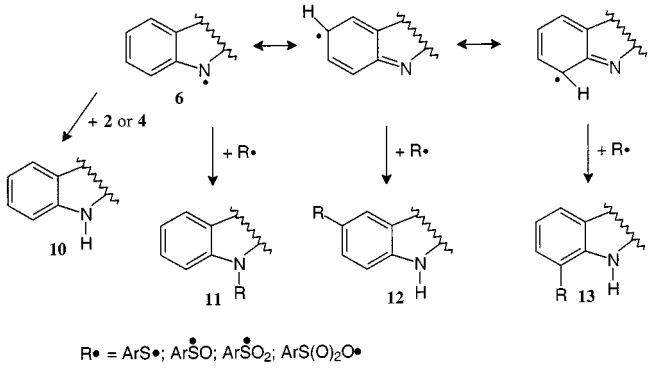
It has been well established that indolinonic aminoxyls are extremely versatile in reacting with oxygen-centered radicals, such as peroxyl[14] and alkoxyl,[15] with nitrogen-centered radicals such as aminyl,[16] and with carbon-centered radicals[17] yielding products substituted on the benzene ring in the three former cases and alkylated hydroxylamines in the latter case. To gain more information on the reactivity of this class of aminoxyls towards different types of radicals, their reaction with sulfur-centered radicals was considered. These were generated from *p*-methylthiophenol as reported previously.[5]

The molecular ratio 2:1 between aminoxyl and *p*-methylthiophenol was chosen with the aim of generating arylthiyl radicals via hydrogen abstraction from the thiophenol by one mole of aminoxyl, followed by entrapment of the arylthiyl radical with a second mole of aminoxyl as reported in Scheme 1.



Scheme 1

The main product in all the reactions was the amine **10** corresponding to the starting aminoxyl. We hypothesize that the most likely pathway for its formation (Scheme 2) is via aminyl **6**, formed from decomposition of adduct **5** (Scheme 1).



Scheme 2

This proposed intermediate could readily form through coupling of ArS$^\bullet$ with the NO$^\bullet$ function (Scheme 1), however, it was never isolated. The instability of intermediate **5** due to the facile homolysis of the oxygen-nitrogen bond is supported by the fact that the same bond in arylsulphinyl nitrate[18] or in the pyridine *N*-oxide-arylsulphenyl chloride adduct[19] behaves in a similar way. Furthermore, similar intermediates have been previously characterized only at

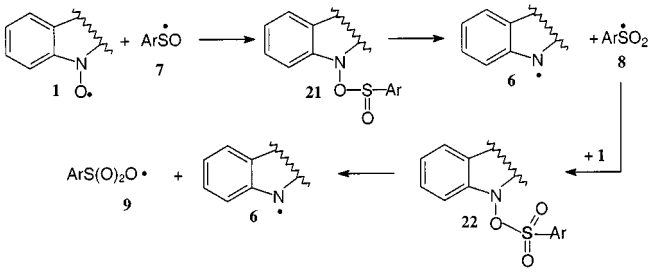
low temperatures, but were never isolated.[20] In addition, semiempirical calculations of compound **5** show that the N−O bond is weaker [Bond Dissociation Energy (*BDE*) = −10.78 kcal/mol] than the O−S bond (*BDE* = 21.77 kcal/mol) (see Experimental Section). Heterolytic cleavage of intermediate **5** to give a nitrenium ion and the sulphinyl anion can be excluded since no methoxylated products[21] were obtained when methanol was used instead of benzene as solvent.

In order to give a possible explanation for the formation of all the other reaction products bearing sulfur-oxygenated substituents, namely the arylsulphinyl, arylsulphonyl and arylsulphonyloxy groups, it is important to first understand how these are formed. Arylsulphinyl radical **7**, arising from the decomposition of adduct **5**, may disproportionate to arylthiyl **3** and arylsulphonyl **8** according to the literature reports[22] (Equation 1). The latter in turn further disproportionates, faster than the arylsulphinyl radical, to arylsulphinyl and arylsulphonyloxy **9** (Equation 2).[23]

$$2\ ArSO^{\bullet}\ (\mathbf{7}) \rightarrow ArS^{\bullet}\ (\mathbf{3}) + ArSO_2^{\bullet}\ (\mathbf{8}) \quad (1)$$

$$2\ ArSO_2^{\bullet}\ (\mathbf{8}) \rightarrow ArSO^{\bullet}\ (\mathbf{7}) + ArSO_2O^{\bullet}\ (\mathbf{9}) \quad (2)$$

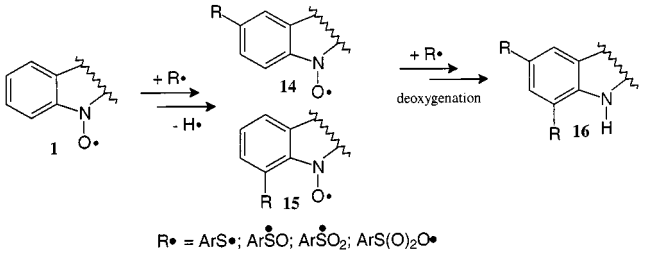
However, these radicals may also be formed through an alternative route, as reported in Scheme 3, by reaction of the starting aminoxyls with all the sulfur-containing radicals at the NO· function.



Scheme 3

At this stage, the formation of amines **11**, **12** and **13** could be explained by the interaction of aminyl **6** with all the sulfur-centered radicals (**3**, **7** and **8**) and the arylsulphonyloxy radical **9** (Scheme 2). The probability that radicals **7** and **8** give O−C instead of S−C coupling on the benzene ring was ruled out since several studies have demonstrated that the unpaired electron resides essentially on the sulfur.[20][24]

Another alternative route for the formation of the products, is the interaction of the sulfur-centered radicals with the starting aminoxyl itself at the conjugated positions with the NO• function as shown in Scheme 4. This route explains the formation of the substituted aminoxyls **14** and **15** obtained in traces, which can subsequently undergo deoxygenation as shown in Scheme 1 and Scheme 3 to give the monosubstituted amines **12** and **13**. The substituted aminoxyls may also undergo further substitution on the conjugated benzene ring and deoxygenation leading to the disubstituted amine **16** (Scheme 4).



Scheme 4

In the case of aminoxyl **1c**, compounds **19** and **20** (Figure 1) were isolated.

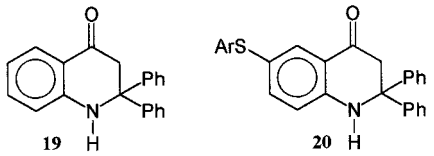


Figure 1. Chemical structure of compounds **19** and **20**

A similar result was previously observed apon acid treatment of **1c**;[11] in fact enol ethers are readily hydrolysed by acids. In our case, even if they were not isolated, arylsulphinic and arylsulphonic acids may be formed in the reaction medium, and these may promote the hydrolysis of the enol ether moiety to the corresponding ketone form. It is worth recalling that in the reactions between TEMPO and thiophenols,[5] the main products were the tetramethylpiperidinium arylsulphinates and arylsulphonates arising from the formation of arylsulphinic and arylsulphonic acids as stated in the introduction.

Aminoxyls **1a** and **1b** have a similar basic structure, therefore their reactivities might be comparable; however the products obtained (Table 1) are not always the same. The possibility that different mechanisms can take place during these reactions is such that, small variations in the rate of each step could lead to the formation of the different products.

Conclusion

Aminoxyls **1** react with nucleophilic radicals, such as alkyl radicals, at the NO• function affording alkoxyamines[17] and with electrophilic radicals such as alkoxyl[15] and alkylperoxyl[14] radicals at the conjugated benzene ring. In the present work, it is interesting to observe that sulfur-centered radicals **3**, **7** and **8** and arylsulphonyloxy radical **9** react at both positions, and this could be ascribed to their polar character, which may be considered somewhere between electrophilic and nucleophilic.

The reactions described in this paper cannot be considered of synthetic value due to the number of products isolated, even if the amines are obtained in good yield based on the conversion of the starting aminoxyl. However, they represent an interesting example for understanding the re-

activity of sulphydrilic groups with aminoxyls, particularly when considering the applications of the latter in biology and in polymer stabilization. Secondly, the results described give further insights on the reactivity of this class of aromatic aminoxyls towards radical species, demonstrating that these aminoxyls are also capable of efficiently reacting with sulfur-centered radicals

Experimental Section

General Remarks: IR spectra were measured on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spectra Tech "Collector" for DRIFT measurements, or on a Perkin−Elmer 298 infrared spectrometer. − ^{1}H NMR spectra were recorded at room temperature as a solution in $CDCl_3$ or C_6D_6 on a Varian Gemini 200 spectrometer (δ in ppm are relative to Me_4Si). Where compounds are marked by #, the spectroscopic data reported in the reference are incomplete. − High resolution mass spectra were recorded on a VG7070-E 5000 spectrometer with PFK as the resolution and calibration standard. In some cases, mass spectra were recorded on a Carlo Erba QMD 1000 spectrometer in EI^+ or CI^+ mode. − EPR spectra were recorded on a Varian E4 spectrometer interfaced with a computer. − Calculations were performed by using the semiempirical quantum-mechanical method AM1 enclosed in the software package HyperChem 4.5.[25] − Aminoxyls **1a**,[8] **1b**[8]and **1c**[26] were prepared according to the literature methods. *p*-Methylthiophenol was an Aldrich commercial reagent grade product and used as purchased.

Reaction of Nitroxides (1a−c) with *p*-Methylthiophenol (2). − General Procedure: A solution of nitroxide (300 mg) in 10 mL of anhydrous benzene and a solution of thiophenol (half equivalent) in 7 mL of the same solvent were each degassed separately under nitrogen for 10 min. The thiophenol was then added dropwise to the solution of nitroxide under magnetic stirring over 10 minutes. With nitroxide **1a**, the reaction mixture immediately darkened and after 10 min from the addition the reaction was completed as the nitroxide had disappeared (TLC analysis using benzene/acetone 9.8:0.2 as eluant). With nitroxide **1b**, the reaction was slower, and after 2 h there was no more change according to TLC analysis (same eluant as above). With nitroxide **1c** the reaction was even slow and after 3 h there was no variation according to TLC analysis (ethyl acetate/cyclohexane 8.5:1.5). At the end of the reaction, the reaction mixture was evaporated under reduced pressure, taken up with benzene and purified on silica-gel preparative chromatography plates, by eluting with different eluants according to the reaction. All the products were extracted from the silica-gel with ethyl acetate.

Reaction with Aminoxyl 1a: The reaction mixture was purified by eluting the plates with benzene/acetone, 9.8:0.2. Some fractions were further re-purified by eluting with ethyl acetate/cyclohexane, 2.5:7.5 or 1:9, or with petroleum ether/ethyl ether, 7:3, or acetone/benzene, 0.5:9.5, or just benzene. The products isolated were: **4a (2-Methyl-3-oxo-2-phenylindolin-1-hydroxide)**,[8] **10a**,[7] **11y/1a** (R = SO_2Ar), **12x/1a** (R = SAr), **12y/1a** (R = SO_2Ar), **12z/1a** (R = SO_3Ar), **13x/1a** (R = SAr), **13y/1a** (R = SO_2Ar), **13z/1a** (R = SO_3Ar), **14y/1a** (R = SO_2Ar), **15y/1a** (R = SO_2Ar), **16x/1a** (R = SAr), **17**, and **18**.[9] Their spectroscopic data are reported below.

2-Methyl-3-oxo-2-phenylindoline (10a):[7] ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.74 (3 H, s, Ind-CH_3), 5.02 (1 H, br., NH), 6.84 (1 H, ddd, H5, J_1 = 7.85, J_2 = 7.1, J_3 = 0.87 Hz), 6.95 (1 H, dt, H7, J_1 = 8.24 J_2 = 0.83 Hz), 7.3 (3 H, m, arom.), 7.5 (4 H, m, arom.), 7.6 (1 H, ddd, H4, J_1 = 7.75 J_2 = 1.41 J_3 = 0.82 Hz). − MS (EI^+) *m/z* (rel. int.) 223 (M^+, 34%), 194 (100).

2-Methyl-3-oxo-2-phenyl-1-(*p*-tolylsulphonyl)indoline (11y/1a): IR (DRIFT): ṽ = 1721 (C=O), 1603, 1460, 1357 and 1170 (SO_2N). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 2.11 (3 H, s, Ind-CH_3), 2.35 (3 H, s, Ar-CH_3), 7.10 (2 H, d, arom-S, *J* = 8.3 Hz), 7.22 (6 H, m, arom.), 7.39 (2 H, d, arom-S, *J* = 8.3 Hz), 7.72 (1 H, ddd, H6, J_1 = 8.5, J_2 = 7.3, J_3 = 1.5 Hz), 7.76 (1 H, ddd, H7, J_1 = 7.7, J_2 = 1.5, J_3 = 0.8 Hz), 8.03 (1 H, dt, H4, J_1 = 8.3, J_2 = 0.8 Hz). − MS (EI^+) *m/z* (rel. int.) 377 (M^+, 35%), 222 (M−155, 100). − HRMS calcd. for $C_{22}H_{19}NO_3S$ 377.1086, found 377.1089.

2-Methyl-3-oxo-2-phenyl-5-(*p*-tolylsulphanyl)indoline (12x/1a): IR (DRIFT): ṽ = 3370 (NH), 1708 (C=O), 1610, 1476. − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.75 (3 H, s, Ind-CH_3), 2.31 (3 H, s, Ar-CH_3), 5.06 (1 H, br., NH), 6.91 (1 H, dd, H7, J_1 = 8.4, J_2 = 0.6 Hz), 7.08 (2 H, d, arom-S, *J* = 8.4 Hz), 7.19 (2 H, d, arom-S, *J* = 8.4 Hz), 7.4 (3 H, m, arom.), 7.49 (2 H, m, arom.), 7.55 (1 H, dd, H6, J_1 = 8.4, J_2 = 1.9 Hz), 7.67 (1 H, dt, H4, J_1 = 1.9, J_2 = 0.6 Hz). − MS (EI^+) *m/z* (rel. int.) 345 (M^+, 91%), 222 (M−123, 100). − HRMS calcd. for $C_{22}H_{19}NOS$ 345.1187, found 345.1189.

2-Methyl-3-oxo-2-phenyl-5-(*p*-tolylsulphonyl)indoline (12y/1a): IR (DRIFT): ṽ = 3376 (NH), 1709 (C=O), 1620, 1493, 1331 and 1135 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.72 (3 H, s, Ind-CH_3), 2.38 (3 H, s, Ar-CH_3), 5.75 (1 H, br., NH), 6.94 (1 H, dd, H7, J_1 = 8.4, J_2 = 0.6 Hz), 7.3 (5 H, m, arom.), 7.41 (2 H, m, arom.), 7.79 (2 H, d, arom-S, *J* = 8.3 Hz), 7.97 (1 H, dd, H6, J_1 = 8.7, J_2 = 2.1 Hz), 8.13 (1 H, dd, H4, J_1 = 2.0, J_2 = 0.5 Hz). − MS (EI^+) *m/z* (rel. int.) 377 (M^+, 80%), 348 (M−29, 100), 221 (M−156, 3), 193 (M−29−155, 69). − HRMS calcd. for $C_{22}H_{19}NO_3S$ 377.1086, found 377.1089.

2-Methyl-3-oxo-2-phenyl-5-(*p*-tolylsulphonyloxy)indoline (12z/1a): IR (DRIFT): ṽ = 3350 (NH), 1690 (C=O), 1623, 1487, 1370 and 1173 (SO_3). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.72 (3 H, s, Ind-CH_3), 2.44 (3 H, s, Ar-CH_3), 5.05 (1 H, br., NH), 6.87 (1 H, dd, H7, J_1 = 8.8, J_2 = 0.5 Hz), 7.07 (1 H, dd, H4, J_1 = 2.5, J_2 = 0.5 Hz), 7.26 (1 H, dd, H6, J_1 = 8.8, J_2 = 2.5 Hz), 7.34 (5 H, m, arom.), 7.47 (2 H, m, arom.), 7.72 (2 H, d, arom-S, *J* = 8.3 Hz). − MS (EI^+) *m/z* (rel. int.) 393 (M^+, 28%), 238 (M−155, 100). − HRMS calcd. for $C_{22}H_{19}NO_4S$ 393.1035, found 393.1034.

2-Methyl-3-oxo-2-phenyl-7-(*p*-tolylsulphanyl)indoline (13x/1a): IR (DRIFT): ṽ = 3355 (NH), 1708 (C=O), 1602, 1485. − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.67 (3 H, s, Ind-CH_3), 2.34 (3 H, s, Ar-CH_3), 5.24 (1 H, br., NH), 6.84 (1 H, t, H5, *J* = 7.6 Hz), 7.14 (4 H, m, arom.), 7.23 (5 H, m, arom.), 7.6 (1 H, ddd, H4, J_1 = 7.7, J_2 = 1.2, J_3 = 0.7 Hz), 7.69 (1 H, dd, H6, J_1 = 7.3, J_2 = 1.2 Hz). − MS (EI^+) *m/z* (rel. int.) 345 (M^+, 685%), 222 (M−123, 27), 212 (100). − HRMS calcd. for $C_{22}H_{19}NOS$ 345.1187, found 345.1183.

2-Methyl-3-oxo-2-phenyl-7-(*p*-tolylsulphonyl)indoline (13y/1a): IR (DRIFT): ṽ = 3386 (NH), 1711 (C=O), 1611, 1480, 1443, 1296 and 1131 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.77 (3 H, s, Ind-CH_3), 2.44 (3 H, s, Ar-CH_3), 6.82 (1 H, br., NH), 6.88 (1 H, t, H5, *J* = 7.8 Hz), 7.34 (7 H, m, arom.), 7.72 (1 H, ddd, H4, J_1 = 7.5, J_2 = 1.2, J_3 = 0.6 Hz), 7.91 (2 H, d, arom-S, *J* = 8.4 Hz), 7.97 (1 H, dd, H6, J_1 = 7.7, J_2 = 1.2 Hz). − MS (EI^+) *m/z* (rel. int.) 377 (M^+, 29%), 348 (M−29, 20), 285 (M−92, 18), 222 (M^-155, 5), 194 (M−29−154, 20), 149 (100). − HRMS calcd. for $C_{22}H_{19}NO_3S$ 377.1086, found 377.1082.

2-Methyl-3-oxo-2-phenyl-7-(*p*-tolylsulphonyloxy)indoline (13z/1a): IR (DRIFT): ṽ = 3390 (NH), 1710 (C=O), 1625, 1497, 1375 and 1177 (SO_3) − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.66 (3 H, s, Ind-CH_3), 2.46 (3 H, s, Ar-CH_3), 5.33 (1 H, br., NH), 6.69 (1 H, t, H5, *J* = 7.8 Hz), 7.01 (1 H, dd, H6, J_1 = 7.8, J_2 = 1.1 Hz), 7.33 (5 H, m, arom.), 7.47 (3 H, m, arom.), 7.81 (2 H, d, arom-S, *J* =

8.5 Hz). − MS (EI$^+$) *m/z* (rel. int.) 393 (M$^+$, 24%), 238 (M−155, 44), 223 (M−154−16, 45), 194(100). − HRMS calcd. for $C_{22}H_{19}NO_4S$ 393.1035, found 393.1032.

2-Methyl-3-oxo-2-phenyl-5-(*p*-tolylsulphonyl)indoline-1-oxyl (14y/1a): The EPR spectrum was simulated on the basis of the following hyperfine coupling constants (hfccs) in Gauss: a_N (NO·) = 9.01, a_H (H4, H6) = 1.05, a_H (H7) = 2.83, a_H (CH_3) = 0.21 G. − MS(EI$^+$) *m/z* (rel. int.) 392 (M$^+$, 3%), 377 (M−15, 42), 348 (M−15−29, 93), 238 (M−154, 6), 193 (M−15−29−155, 100). To confirm the structure of compound **14y/1a** this was reduced to the corresponding hydroxylamine: IR (DRIFT): $\tilde{\nu}$ = 3363 (NOH), 1723 (C=O), 1608, 1446, 1330 and 1140 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.75 (3 H, s, Ind-CH_3), 2.40 (3 H, s, Ar-CH_3), 6.8 (1 H, br., OH), 7.32 (1 H, dd, H7, J_1 = 8.4, J_2 = 0.6 Hz), 7.35 (7 H, m, arom.), 7.83 (2 H, d, arom-S, J = 8.4 Hz), 8.13 (1 H, dd, H6, J_1 = 8.5, J_2 = 1.9 Hz), 8.20 (1 H, dd, H4, J_1 = 1.9, J_2 = 0.6 Hz).

2-Methyl-3-oxo-2-phenyl-7-(*p*-tolylsulphonyl)indoline-1-oxyl (15y/1a): The EPR spectrum was simulated on the basis of the following hyperfine coupling constants (hfccs) in Gauss: a_N (NO·) = 8.09, a_H (H4, H6) = 0.99, a_H (H5) = 3.12, a_H (CH_3) = 0.26 G. − To confirm the structure of compound **15y/1a** this was reduced to the corresponding hydroxylamine: IR (DRIFT): $\tilde{\nu}$ = 3382 (OH), 1723 (C=O), 1600, 1468, 1301 and 1151 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.76 (3 H, s, Ind-CH_3), 2.44 (3 H, s, Ar-CH_3), 7.16 (1 H, t, H5, J = 7.7 Hz), 7.36 (6 H, m, arom.), 7.48 (2 H, m, arom.), 7.83 (2 H, d, arom-S, J = 7.5 Hz), 7.87 (1 H, dd, H6, J_1 = 7.7, J_2 = 1.4 Hz), 8.17 (1 H, dd, H4, J_1 = 7.9, J_2 = 1.4 Hz). − MS (EI$^+$) *m/z* (rel. int.) 393 (M$^+$, 28%), 377 (M−16, 34), 348 (M−16−29, 67), 239 (M−154, 4), 193 (M−15−29−155, 100).

2-Methyl-3-oxo-2-phenyl-5,7-bis(*p*-tolylsulphanyl)indoline (16x/1a): IR (DRIFT): $\tilde{\nu}$ = 3343 (NH), 1703 (C=O), 1599, 1465. − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.66 (3 H, s, Ind-CH_3), 2.32 (3 H, s, Ar-CH_3), 2.35 (3 H, s Ar-CH_3), 5.28 (1 H, br., NH), 7.11 (4 H, m, arom.), 7.2 (9 H, m, arom.), 7.62 (1 H, dd, H4, J_1 = 1.8, J_2 = 0.4 Hz), 7.75 (1 H, d, H6, J = 1.8 Hz). − MS (EI$^+$) *m/z* (rel. int.) 467 (M$^+$, 100%), 334 (56). − HRMS calcd. for $C_{29}H_{25}NOS_2$ 467.1378, found 467.1370.

Reaction with Aminoxyl 1b: The reaction mixture was purified by chromatography by eluting the plates with petroleum ether/ethyl acetate 9.5:0.5 and then some fractions were further purified by eluting with ethyl acetate/cyclohexane 1.5:8.5, or 2:8, or petroleum ether/ethyl ether 8:2 or 8.5:1.5. The products isolated were: **1b**,[8] **10b**,[10] **11x/1b**, **11w/1b**, **11y/1b**, **12y/1b**, **12z/1b**, **13z/1b**. Their spectroscopic data are reported below.

2-Methyl-2-phenyl-3-phenyliminoindoline (10b):[10] ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.92 (3 H, s, Ind-CH_3), 4.76 (1 H, br. s, NH), 6.42 (2 H, m, arom.), 6.81 (3 H, br. d, arom., J = 8.34 Hz), 7.11 (1 H, tt, arom., J_1 = 7.5, J_2 = 1.3), 7.32 (6 H, m, arom.), 7.62 (2 H, br. d, arom., J = 6.5). − MS (EI$^+$) *m/z* (rel. int.) 298 (M$^+$, 73%), 221 (100).

2-Methyl-2-phenyl-3-phenylimino-1-(*p*-tolylsulphanyl)indoline (11x/1b): IR (Nujol): $\tilde{\nu}$ = 1665 (C=N), 1595, 1450,1300, 1085. − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 2.24 (3 H, s, Ind-CH_3), 2.41 (3 H, s, Ar-CH_3), 6.51 (1 H, ddd, arom., J_1 = 8.0, J_2 = 1.3, J_3 = 0.3 Hz), 6.61 (1 H, ddd, arom., J_1 = 8.0, J_2 = 7.1, J_3 = 1.0 Hz), 6.76 (2 H, m, arom.), 6.94 (1 H, dt, arom., J_1 = 8.2, J_2 = 0.7 Hz), 7.11 (2 H, m, arom.), 7.30 (2 H, d, arom-S, J = 8.3 Hz), 7.34 (5 H, m, arom.), 7.54 (2 H, m, arom.), 7.63 (2 H, d, arom-S, J = 8.3 Hz). − MS (EI$^+$) *m/z* (rel. int.) 420 (M$^+$, 2%), 298 (M−122, 77), 139 (100). − HRMS calcd. for $C_{28}H_{24}N_2S$ 420.1660, found 420.1669.

2-Methyl-2-phenyl-3-phenylimino-1-(*p*-tolylsulphinyl)indoline (11w/1b): IR (DRIFT): $\tilde{\nu}$ = 1658 (C=N), 1595, 1458, 1097 (S=O). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 2.37 (6 H, s, Ind-CH_3 and Ar-CH_3), 6.60 (2 H, m, arom.), 6.82 (3 H, m, arom.), 7.10 (3 H, m, arom.), 7.23 (2 H, d, arom-S, J = 8.2 Hz), 7.44 (8 H, m, arom.). − MS (CI$^+$) *m/z* (rel. int.) 437 (M+H, 20%), 298 (M+1−139, 78).

2-Methyl-2-phenyl-3-phenylimino-1-(*p*-tolylsulphonyl)indoline (11y/1b): IR (DRIFT): $\tilde{\nu}$ = 1662 (C=N), 1593, 1458, 1356 and 1171 (SO_2N). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 2.33 (3 H, s, Ind-CH_3), 2.35 (3 H, s, Ar-CH_3), 6.54 (1 H, br. d, arom.), 6.70 (3 H, m, arom.), 7.08 (3 H, m, arom.), 7.30 (12 H, m, arom.), 7.92 (1 H, d, arom., J = 8.4 Hz). − MS (EI$^+$) *m/z* (rel. int.) 452 (M$^+$, 16%), 297 (M−155, 100). − HRMS calcd. for $C_{28}H_{24}N_2O_2S$ 452.1559, found 452.1560.

2-Methyl-2-phenyl-3-phenylimino-5-(*p*-tolylsulphonyl)indoline (12y/1b): IR (DRIFT): $\tilde{\nu}$ = 3355 (NH), 1655 (C=N), 1601, 1481, 1319 and 1153 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.89 (3 H, s, Ind-CH_3), 2.40 (3 H, s, Ar-CH_3), 5.33 (1 H, br. s, NH), 6.74 (3 H, m, arom.), 7.22 (4 H, m, arom.), 7.35 (6 H, m, arom.), 7.50 (3 H, m, arom.), 7.78 (1 H, dd, H6, J_1 = 8.5, J_2 = 1.9 Hz). − MS (EI$^+$) *m/z* (rel. int.) 452 (M$^+$, 1%), 314 (M−138, 2), 223 (1) − MS (CI$^+$) *m/z* (rel. int.) 453 (M+H, 8%), 361 (M−91, 2)

2-Methyl-2-phenyl-3-phenylimino-5-(*p*-tolylsulphonyloxy)indoline (12z/1b): IR (DRIFT): $\tilde{\nu}$ = 3384 (NH), 1649 (C=N), 1604, 1479, 1369 and 1171 (SO_3). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.89 (3 H, s, Ind-CH_3), 2.48 (3 H, s, Ar-CH_3), 4.79 (1 H, br. s, NH), 5.87 (1 H, d, H4, J = 2.4 Hz), 6.60 (2 H, m, arom.), 6.72 (1 H, d, H7, J = 8.5 Hz), 7.04 (2 H, m, arom.), 7.22 (4 H, m, arom.), 7.38 (4 H, m, arom.), 7.52 (3 H, m, arom.). − MS (EI$^+$) *m/z* (rel. int.) 468 (M$^+$, 39%), 313 (M−155, 100), 298 (M−154−16, 17). − HRMS calcd. for $C_{28}H_{24}N_2O_3S$ 468.1508, found 468.1510.

2-Methyl-2-phenyl-3-phenylimino-7-(*p*-tolylsulphonyloxy)indoline (13z/1b): IR (DRIFT): $\tilde{\nu}$ = 3401 (NH), 1654 (C=N), 1489, 1371 and 1176 (SO_3). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.82 (3 H, s, Ind-CH_3), 2.46 (3 H, s, Ar-CH_3), 5.10 (1 H, br. s, NH), 6.25 (2 H, m, arom.), 6.75 (3 H, m, arom.), 7.09 (1 H, m, arom.), 7.30 (6 H, m, arom.), 7.55 (2 H, m, arom.), 7.79 (2 H, d, arom-S, J = 8.4 Hz). − MS (EI$^+$) *m/z* (rel. int.) 468 (M$^+$, 29%), 313 (M−155, 100), 298 (M−154−16, 37). − HRMS calcd. for $C_{28}H_{24}N_2O_3S$ 468.1508, found 468.1508.

Reaction with Aminoxyl 1c: The reaction mixture was purified by chromatography, by eluting the plates twice with ethyl acetate/cyclohexane (8.5:1.5). Some fractions were further purified by eluting with ethyl acetate/cyclohexane (2:8), or petroleum ether/ethyl ether (9:1), or acetone/benzene (1:9), or benzene. The products isolated were **1c**,[26] **17**, **19** (2,3-dihydro-2,2-diphenyl-1*H*-quinolin-4-one),[11] **11y/1c**, **12x/1c**, **20**, **12y/1c**, **12z/1c**, and **13y/1c**. Their spectroscopic data are reported below.

4-Ethoxy-1,2-dihydro-2,2-diphenyl-1-(*p*-tolylsulphonyl)quinoline (11y/1c): IR (DRIFT): $\tilde{\nu}$ = 1608, 1458, 1317 and 1149 (SO_2N). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.43 (3 H, t, CH_2CH_3, J = 7.0 Hz), 2.34 (3 H, s, Ar-CH_3), 4.09 (2 H, q, CH_2CH_3, J = 7.0 Hz), 4.54 (1 H, s, H3), 6.64 (1 H, d, arom., J = 7.8 Hz), 6.61 (1 H, td, arom., J_1 = 7.6, J_2 = 1.0 Hz), 7.10 (5 H, m, arom.), 7.23 (2 H, m, arom.), 7.36 (6 H, m, arom.), 7.67 (3 H, m, arom.). − MS (EI$^+$) *m/z* (rel. int.) 481 (M$^+$, 19%), 452 (M−29, 2), 404 (M−77, 100), 326 (M−155, 24). − HRMS calcd. for $C_{30}H_{27}NO_3S$ 481.1712, found 481.1720.

4-Ethoxy-1,2-dihydro-2,2-diphenyl-6-(*p*-tolylsulphanyl)quinoline (12x/1c): IR (DRIFT): $\tilde{\nu}$ = 3375 (NH), 1649, 1601, 1491. − ^{1}H-

NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.40 (3 H, t, CH_2CH_3, *J* = 7.0 Hz), 2.37 (3 H, s, Ar-CH_3), 3.93 (2 H, q, CH_2CH_3, *J* = 7.0 Hz), 4.63 (1 H, br. s, NH), 4.97 (1 H, s, H3), 6.50 (1 H, d, H8, *J* = 8.4 Hz), 7.30 (13 H, m, arom.), 7.49 (2 H, d, arom-S, *J* = 8.2 Hz), 7.71 (1 H, d, H5, *J* = 2.0 Hz). − MS (CI^+) *m*/*z* (rel. int.) 450 (M+H, 85%), 478 (M+29, 8), 328 (M−123+1, 9).

1,2,3,4-Tetrahydro-2,2-diphenyl-6-(*p*-tolylsulphanyl)-1*H*-quinolin-4-one (20): IR (Nujol): ṽ = 3310 (NH), 1660 (C=O), 1600, 1450. − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 2.29 (3 H, s, Ar-CH_3), 3.38 (2 H, s, H3), 5.21 (1 H, br. s, NH), 6.71 (1 H, d, H8, *J* = 8.4 Hz), 7.03 (2 H, d, arom-S, *J* = 8.4 Hz), 7.13 (2 H, d, arom-S, *J* = 8.4 Hz), 7.30 (11 H, m, arom.), 7.84 (1 H, d, H5, *J* = 2.0 Hz). − MS (EI^+) *m*/*z* (rel. int.) 421 (M^+, 100%), 344 (M−77, 91), 299 (M−122, 13). − HRMS calcd. for $C_{28}H_{23}NOS$ 421.1500, found 421.1507.

4-Ethoxy-1,2-dihydro-2,2-diphenyl-5-(*p*-tolylsulphonyl)quinoline (12y/1c): IR (Nujol): ṽ = 3320 (NH), 1590, 1450, 1290 and 1135 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.42 (3 H, t, CH_2CH_3, *J* = 7.0 Hz), 2.37 (3 H, s, Ar-CH_3) − 3.93 (2 H, q, CH_2CH_3, *J* = 7.0 Hz), 4.78 (1 H, br. s, NH), 4.98 (1 H, d, H3, *J* = 1.8 Hz), 6.49 (1 H, d, H8, *J* = 8.5 Hz), 7.30 (12 H, m, arom.), 7.56 (1 H, dd, H7, J_1 = 8.5, J_2 = 2.2 Hz), 7.78 (2 H, d, arom-S, *J* = 8.1 Hz), 7.96 (1 H, d, H5, *J* = 2.2 Hz). − MS (CI^+) *m*/*z* (rel. int.) 482 (M+H, 100%), 510 (M+29, 17), 329 (M−154+1, 2).

4-Ethoxy-1,2-dihydro-2,2-diphenyl-5-(*p*-tolylsulphonyloxy)quinoline (12z/1c): IR (Nujol): ṽ = 3360 (NH), 1635, 1460, 1370 and 1150 (SO_3). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.33 (3 H, t, CH_2CH_3, *J* = 7.0 Hz), 2.43 (3 H, s, Ar-CH_3) − 3.89 (2 H, q, CH_2CH_3, *J* = 7.0 Hz), 4.37 (1 H, br. s, NH), 4.95 (1 H, s, H3), 6.33 (1 H, d, H8, *J* = 8.7 Hz), 6.60 (1 H, dd, H7, J_1 = 8.7, J_2 = 2.7 Hz), 6.99 (1 H, d, H5, *J* = 2.7 Hz), 7.30 (12 H, m, arom.), 7.71 (2 H, d, arom-S, *J* = 8.2 Hz). − MS (EI^+) *m*/*z* (rel. int.) 497 (M^+, 4%), 420 (M−77, 100), 342 (M−155, 7), 326 (M−155−16, 1). − HRMS calcd. for $C_{30}H_{27}NO_4S$ 497.1661, found 497.1668.

4-Ethoxy-1,2-dihydro-2,2-diphenyl-7-(*p*-tolylsulphonyl)quinoline (13y/1c): IR (DRIFT): ṽ = 3365 (NH), 1718, 1595, 1491, 1290 and 1110 (SO_2). − ^{1}H-NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.41 (3 H, t, CH_2CH_3, *J* = 7.0 Hz), 2.28 (3 H, s, Ar-CH_3) − 3.95 (2 H, q, CH_2CH_3, *J* = 7.0 Hz), 4.95 (1 H, d, H3, *J* = 1.8 Hz), 5.58 (1 H, s, NH), 6.62 (1 H, t, H6, *J* = 7.4 Hz), 6.93 (4 H, s, arom-S), 7.17 (10 H, m, arom.), 7.35 (1 H, dd, H7, J_1 = 7.7, J_2 = 1.6 Hz), 7.50 (1 H, d, H5, *J* = 7.7, 1.3 Hz). − MS (EI^+) *m*/*z* (rel. int.) 481 (M^+, 5%), 326 (M−155, 23), 268 (100). − HRMS calcd. for $C_{30}H_{27}NO_4S$ 497.1661, found 497.1669.

AM1 Calculations: The structure of compound **5** was optimised, and a conformational search performed varying all the rateable bonds present in the molecule always using AM1 Hamiltonian[27] at UHF level (Unrestricted Hartree−Fock) for open-shell systems and a statistical algorithm. The UHF computation is used for studying chemical reactions involving bond breaking. A Scheme, introduced in Monte Carlo Multiple Minimum, or MCMM method,[28] called *usage directed* was used. The enthalpy change for the homolytic cleavage of the R−X bond in an organic molecule (RX) (Equation 3), under standard conditions, is described in Equation 4:

$$RX \rightarrow R^\bullet + X^\bullet \quad (3)$$

$$\Delta H^\circ_{reac.} = \Delta H^\circ_F(R^\bullet) + \Delta H^\circ_F(X^\bullet) - \Delta H^\circ_F(RX) = BDE_{(R-X)} \quad (4)$$

In order to calculate the heat of formation of all the chemical species involved, the AM1 Hamiltonian (UHF level) was used. The bond dissociation energies were then obtained according to Equation 3.

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