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A straight access to functionalized carbazoles by tandem reaction between indole and nitrobutadienes

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ABSTRACT

As a continuation of our research on the synthetic exploitation of the nitrobutadienic building-blocks obtained from the ring-opening of nitrothiophenes, we herein report about their reaction with the π-nucleophilic indole. Thanks to their double Michael-acceptor nature, 2,3-dinitro and 2-nitro-3-phenylsulfonyl substituted 1,3-butadienes produce poly-functionalized carbazoles through a double (inter-+intra-molecular) conjugate addition, followed by aromatization of the newly built ring. Significance is attached to the results obtained in fluorinated solvents such as trifluoroethanol, whereby a mild process, with no need for catalysis, overcomes some practical difficulties otherwise limiting the scope of the reaction. Besides the mechanistic aspects, the reaction encompasses motifs for a synthetic interest, mainly in the field of further-tunable arylcarbazoles endowed with predictable applicative properties, e.g., as fluorescent devices.

1. Introduction

In spite of aromaticity, adequately functionalized thiophenes can be effectively opened following the nucleophilic attack by a secondary amine,[1] providing a valuable access to synthetically useful, versatile, nitrobutadienic building-blocks (Scheme 1), some of which endowed with biological activity.[2] From these, during the years, we have obtained a wide collection of heterocyclic targets within metal-free overall ring-opening/ring-closing procedures characterized by a high atom economy.[3] Such targets encompass e.g., pyrroles, pyrazoles, isoxazoles and pyrazines, to cite only *N*-heterocycles, whose occurrence in biologically active molecules of both natural and synthetic origin is well-known and fosters continuing efforts in search for original preparative protocols.

Among more recent research lines in this particular field, we have investigated the behavior of some of our electrophilic building-blocks with the π-nucleophilic indole. Preliminary results have shown an intriguing variability in their reactivity, depending on the character, the number and the position of substituents on the nitrobutadienic fragment.[3d]

In particular, we reported that while model sulfides **1** and **3** (Scheme 1, Y=Z=H) react too sluggishly in $Zn(OAc)_2$-catalyzed reactions,[4] the corresponding sulfones **2** and **4** (Y=Z=H) undergo the expected indole addition to the nitrovinyl moiety, respectively producing the indole derivatives **6** and **7**, the latter as the result of a 1,4-Michael addition on the butadienic moiety (Scheme 2). More interestingly, when dinitrobutadienes **5** are reacted in the same conditions, 1,3,4- and 1,2,4-substituted carbazoles (Scheme 2, **8** and **9**, respectively) are isolated as the main products,[3d] together with minor amounts of the tetrasubstituted derivative **10**, as the final result of a double Michael addition.

The carbazole nucleus is a key structural motif present in a variety of biologically important compounds either of natural or of synthetic origin[5] endowed with e.g., antimalarial, antitumor, antiplasmodial, and antitrypanosomal activities. Besides, carbazoles have recently assumed growing importance also in the field of materials science,[6] due to their photorefractive, photoconductive, hole-transporting and light-emitting properties. Accordingly, the synthesis of carbazoles,[7,8] including naturally occurring ones, has received considerable attention and the development of green and efficient approaches to such core structure with different functional groups is a major objective in organic synthesis currently, as testified by the impressive number of publications in the field.

In consideration of the interest of the subject, it seemed worthwhile to explore more deeply the behavior of derivatives **5**, in order to better define the scope of the process and to improve its efficiency.

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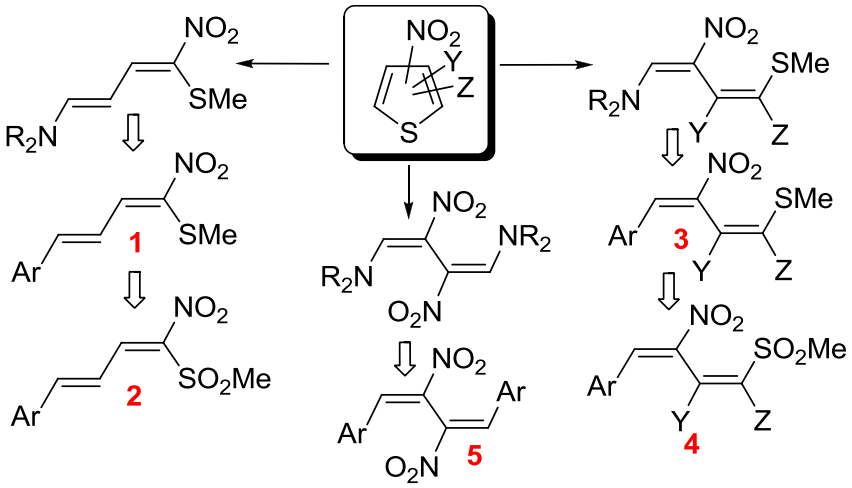
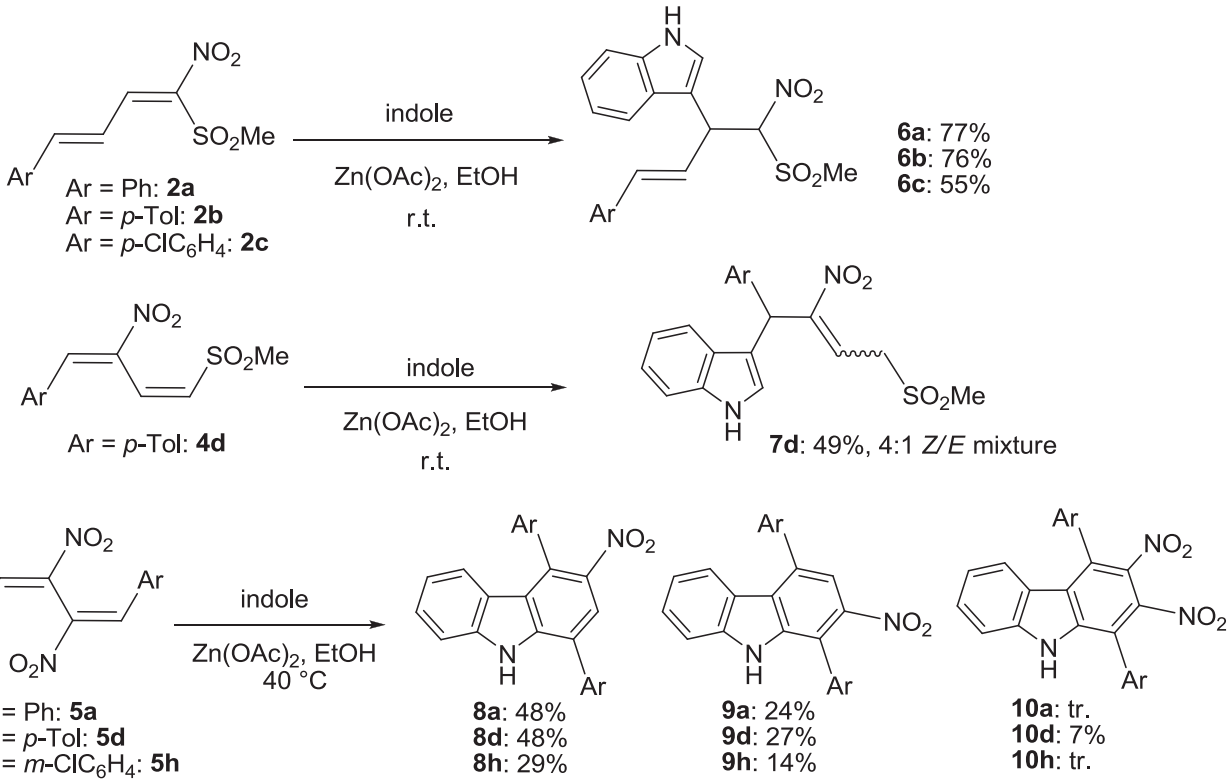


Scheme 1. Ring-opening derivatives of nitrothiophenes.



Scheme 2. Preliminary results from our previous work on the subject.[3d]

2. Results and discussion

The conditions for the reactions reported in Scheme 2 [2 equiv of indole, 1 equiv of $Zn(OAc)_2$ in EtOH, 40 °C, followed by quenching in water] have been extended to the series of 1,4-diaryl derivatives **5a**–**l**, spanning from electron-rich to electron-poor and hindered aromatic moieties, and the results are reported on the left side of Table 1.

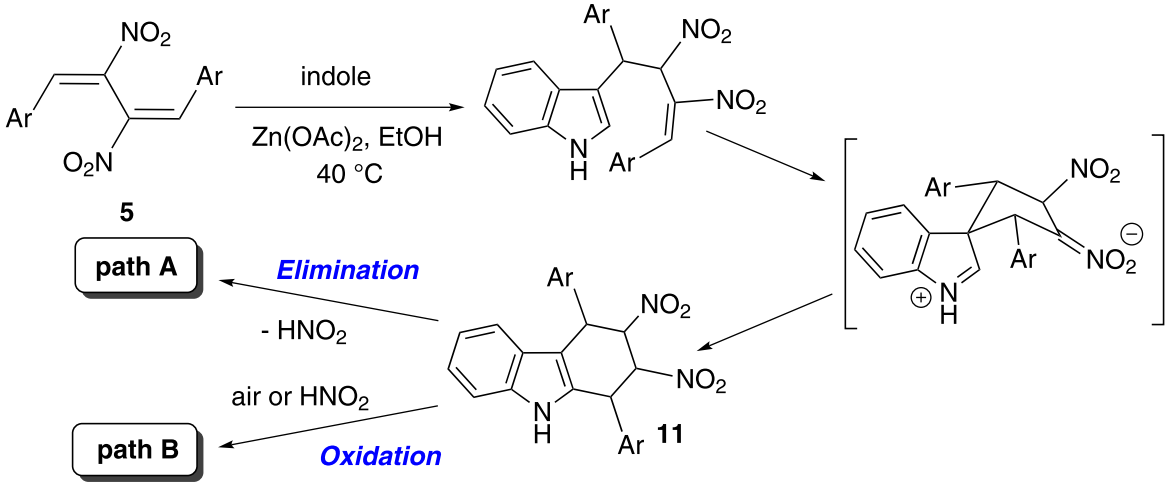
The 3-nitrocarbazole **8** is the main product in all examples, in a ratio, with respect to the 2-nitro derivative **9**, ranging from 1.5 to 2, while the 2,3-dinitrocarbazole **10** is generally present only in traces. Reactions are usually rather slow, particularly in the presence of steric hindrance (**b**, **e**, **j**) or of an electron-releasing substituent on the aryl moiety (**f**, **g**). Yields too are influenced by steric effects, as evident for **b** versus **c** and versus **d**; **h** versus **i**; **j** versus **k**. In the case of the particularly hindered mesityl derivative **5e**, not even traces of nitrocarbazoles can be observed, with total substrate recovery.

For the reaction under study we suggested[3d] a sequence of two Michael additions of indole to the nitrovinylic moieties (the first inter- and the second intra-molecular), each followed by restoration of the aromaticity of the indole ring, eventually leading to the double addition product, the tetrahydrocarbazole **11** (Scheme 3). As recently reported in similar cases,[9] the second participation of the indole nucleus could involve the same C(3) rather than the C(2) position, to generate a spiro intermediate that in acidic media can

Table 1
Results obtained in the reactions of **5a**–**l** with indole (2 equiv) and $Zn(OAc)_2$ (1 equiv) at 40 °C in EtOH, followed by water quenching, without or with an external oxidant added (see text)[a]

Entry	Substrate: Ar	Time	Yields (%)[b]				Yields (%)[b] (with DDQ)			
			8	**9**	**10**	Total	**8**	**9**	**10**	Total
1	**5a: Phenyl**	1 d	48	24	tr[c]	72	22	13	51	86
2	**5b: *o*-Tolyl**	5 d	10[d]		tr[c]	10	6[d]		7	13
3	**5c: *m*-Tolyl**	2 d	36	22	8	66	30	15	35	80
4	**5d: *p*-Tolyl**	1 d	50	30	7	87	21	10	50	81
5	**5e: Mesityl**	7 d	—	—	—	—				
6	**5f: *m*-Anisyl**	3 d	39	18	8	65	23	15	32	70
7	**5g: *p*-Anisyl**	4 d	53	20	tr[c]	73	49	20	5	74
8	**5h: *m*-Cl-Phenyl**	16 h	39	18	tr[c]	57	37	21	10	68
9	**5i: *p*-Cl-Phenyl**	16 h	45	24	tr[c]	69	33	18	18	69
10	**5j: 1-Naphthyl**	5 d	41[d]		tr[c]	41	40[d]		20	60
11	**5k: 2-Naphthyl**	4 d	58	27	tr[c]	85	55	25	11	91
12	**5l: 2-Thienyl**	2 d	46	28	tr[c]	74	32	16	29	77

[a] The oxidant was added after the reaction time indicated in the third column and left to react 2–3 h before water quenching.
[b] Yields of isolated compounds, unless otherwise indicated.
[c] tr=trace (<1%).
[d] Overall **8**+**9** yield, in a 2:1 ratio as deduced by ^{1}H NMR analysis.



Scheme 3. Proposed reaction pathways.

subsequently transform via a 1,2-migratory shift known as the Ciamician-Plancher rearrangement:[10] a possibility, which cannot be ruled out for our system.

As supported by indirect experimental evidence (for instance, the occurrence that carbazoles **8**–**10** cannot be detected in the reaction mixture by either TLC or ^{1}H NMR analysis before quenching), we suppose that **11**, possibly stabilized, in EtOH, by the coordination of the nitro groups with $Zn(OAc)_2$, can effectively evolve to **8**–**10** only after water addition and complex disruption due to the increased medium polarity.

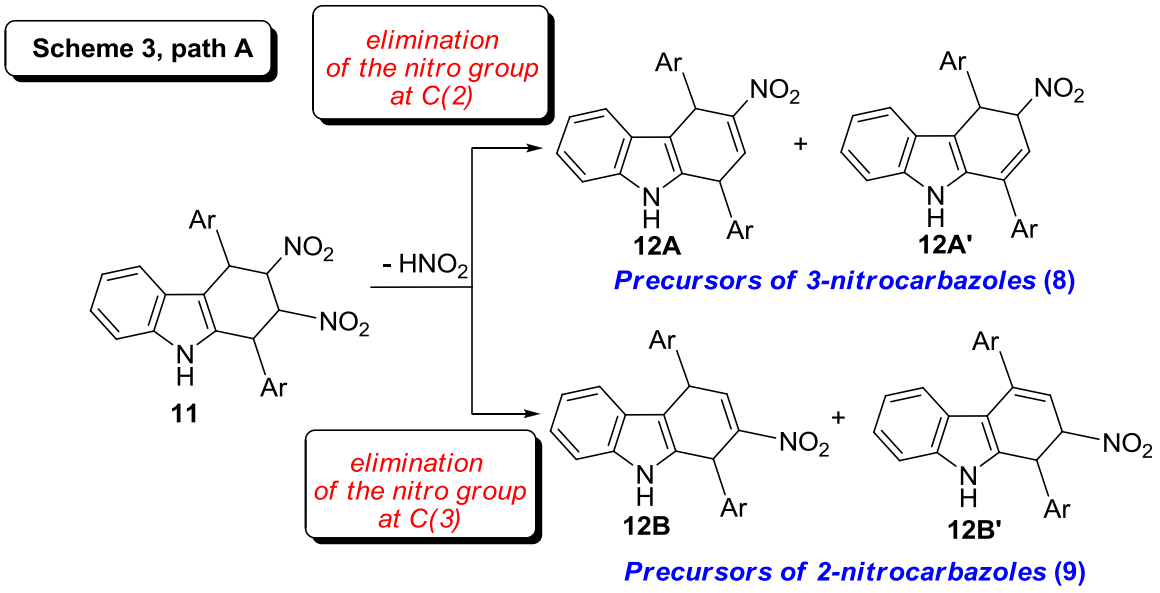
On the grounds of the structure of the isolated products and of the tetrahydrocarbazole **11**, two competitive pathways are conceivable for the latter, namely HNO_2 elimination (**path A**) and oxidation (**path B**) (Scheme 3).

As a matter of fact, the elimination of nitrous acid from **11** (an occurrence already observed in similar systems of ours,[3n] characterized by two nitro groups on adjacent sp^3 carbon atoms) followed by aromatization via oxidation either by air or by the just released nitrous acid (as an endogenous oxidizing agent) would well justify the formation of nitrocarbazoles **8** and **9**. Furthermore, it should be remarked that it could occur, for each of the two nitro groups on **11**, at the expense of either of the two adjacent protons, thus generating, at least in principle, two couples of isomers (Scheme 4).

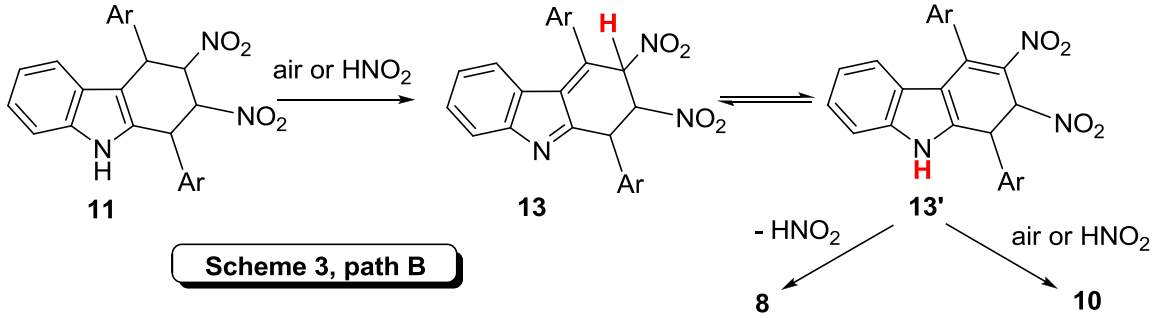
While **12A** and **12B**, characterized by an 'isolated' double bond, would presumably have a very similar stability and hence probability to be formed, **12B′** would be more effectively resonance-stabilized than **12A′** thanks to a direct conjugation between the newly formed double bond and the pyrrole nitrogen. Overall, then, the dihydrocarbazole with a nitro group at C(2), and the 2-nitrocarbazole **9** produced, should be more easily formed: an outcome, which is in contrast with the experimental evidence of a ca. 2: 1 ratio in favor of **8** throughout.

A rationalization can possibly be found within **path B** of Scheme 3. Scheme 5 portrays a conceivable sequence for the oxidative decay of intermediate **11** (accomplished, here again, by the nitrous acid released along **path A** or by air) where **13′** is formed, possibly via **13**. From **13′**, further oxidation would lead to dinitrocarbazole **10** while elimination would furnish to the 3-nitrocarbazole derivative **8** an additional chance to form.

On the grounds of the oxidative steps involved in proposed mechanism, we considered that the addition of an external oxidant could possibly increase the yield of the dinitrocarbazoles **10**, which can only arise via two successive oxidations from the tetrahydrocarbazole **11**. However, again due to the well-known sensitivity of indole to oxidants, the timing for the introduction of DDQ had to be properly evaluated.[11] Thus, we chose to add the oxidant (3 equiv) after the disappearance of the butadiene **5** (by TLC) and before quenching with water (Table 1). The choice implicitly assumed that *a)* the intramolecular process leading to **11** is fast, compared with the intermolecular initial addition, and that *b)* most of the



Scheme 4. Hypothesized dihydrocarbazoles along the way to **8** and **9**.



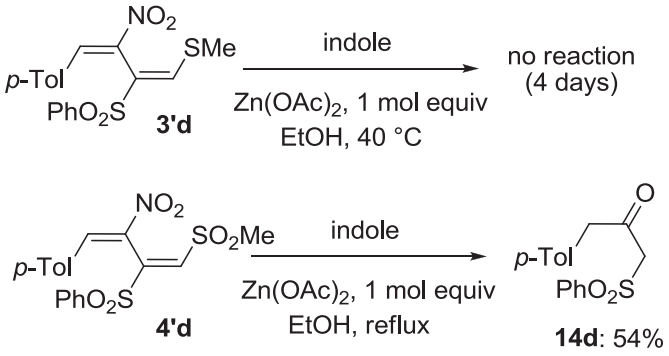
Scheme 5. Proposed route to **8** and **10** via initial oxidation of **11**.

intermediate **11** still survives (most likely as a stabilized complex: see above) prior to quenching. As a matter of fact, working-up the reactions 2–3 h after the addition of DDQ afforded the data reported on the right side of Table 1: the effect of DDQ, monitored by the increase in the yield of **10** and appreciable throughout, is of practical significance only in a few cases (**a** and **d**, where **10** becomes the main product, and, to a lower extent, **c**, **f** and **l**). Other oxidants (nitrous acid itself, MCPBA or iodine) were also investigated, with meagre overall results and, furthermore, the additional drawback of more complex final mixtures.

It is noteworthy that, even when the effect on the yield of **10** is more pronounced, the **8** to **9** ratio is scarcely altered, the former always prevailing by a factor of ca. 2: one must then admit that the access to **8** through the oxidation+elimination sequence of **path B** (Scheme 5) is still competitive.

Besides the nitro group, Michael-type additions to vinyl moieties can be effectively activated also by e.g., the sulfonyl group.[12] Both derivatives **2** and **4** (Scheme 1), though, possess a methylsulfonyl group which is not correctly positioned for a double-Michael addition and, accordingly, our preliminary results describe the formation of open-chain addition products (Scheme 2).

Nonetheless, within the nitrobutadienes of the general structures **3** and **4** of Scheme 1, the ring-opening of 3-nitro-4-(phenylsulfonyl)thiophene and further elaboration smoothly lead to derivatives such as **3′** and **4′** (Scheme 6), whose functionalization pattern, although unsymmetrical, more tightly resembles that of **5**, allowing to foresee a similar behavior. Thus, parallel experiments were realized to test the reactivity of **3′d** and **4′d**, initially employing the same conditions as those adopted for **5**, e.g., EtOH in the presence of 1 equiv of $Zn(OAc)_2$ (Scheme 6).



Scheme 6. Results of reaction with indole of **3′d** and **4′d**.

Surprisingly enough, sulfide **3′d** was recovered unchanged after prolonged reaction times. Even more surprisingly, also **4′d** proved to be unreactive, possibly due to its low solubility in the reaction medium at 40–50 °C. By heating the reaction mixture at reflux, however, only the unexpected **14d** was isolated in moderate yields,

whose structure does not include the indole moiety and is most likely the result of a Nef reaction, within a more complex process also encompassing a retro-Knoevenagel-like step. No further investigation in this direction was performed.

In the attempt to drive the reaction towards the desired double-Michael process, a number of experimental conditions reported in the literature for the conjugate addition to the nitrovinylic moiety have been tested: iodine in diethyl ether,[13] montmorillonite,[14] CF_3CH_2OH (hereinafter TFE) in dichloromethane.[15] As a partial success was achieved only in the last case (Table 2, entry 1), we eventually turned our attention to the employment of TFE as solvent, without any added catalyst or promoter. The use of fluorinated alcohols [TFE or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP)] in organic reactions has been the subject of many recent studies,[16] as such solvents often allow reactions that usually require metal catalysts. Their unique properties (high hydrogen-bonding donor ability, low nucleophilicity, high ionizing power, lower pK_a than alcohols) make them suitable for e.g., Friedel–Crafts reactions, Diels–Alder (and others) cycloadditions, oxidations and isomerizations. Easier isolation of products and convenient, eco-friendly recycling of the solvent are further advantages of such media.

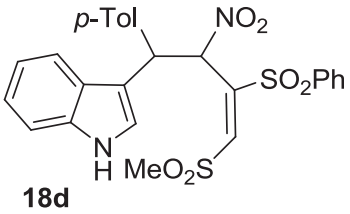
Table 2
Optimization of experimental conditions for the Scheme 7 reaction on **4′d** (Ar=*p*-Tol)

Entry	Solvent	Indole (equiv)	T (°C)	Time (h)	Yields (%)[a]				
					15d	**16d**	**17d**	**18d**	Total
1	TFE/CH_2Cl_2 1:1	2	40	24	11	tr[b]	tr[b]	59	70[c]
				48	39	tr[b]	tr[b]	49	88
2	TFE	2	40	24	38	40	6		84
3	TFE	2	50	24	40	40	10		90
4	TFE	2	60	24	32	43	10		85
5	TFE	4	60	7	27	40	8		75
6	TFE	4	80	4	13	47	9		69

[a] Yields of isolated compounds.
[b] tr=trace (<1%).
[c] Unreacted substrate also observed.

On these grounds, as the process under study possibly involves the just-cited kinds of reactions, we treated substrate **4′d** with indole (2 equiv) in TFE at 50 °C; after 24 h, the final reaction mixture was analyzed to reveal the presence of three different carbazole derivatives (Scheme 7, compounds **15**–**17**).

Different experimental conditions (Table 2) were also tried, in the attempt to reduce times, improve yields and possibly modify products distribution. Unfortunately, neither the variation of the initial amount of indole (a larger excess making the reaction faster but somewhat less clean: cf. entries 4 and 5) nor that of temperature (whose increase has a definite negative effect on the yield of **15d**) proved to be effective. On the other hand, interestingly enough, the less-polar medium of entry 1 (Table 2) leads to the isolation of the unstable open-chain mono-addition product **18d** (Chart 1), whose yield decreases to the advantage mainly of carbazole **15d** at prolonged reaction times.



18d

Chart 1.

The relatively 'soft' conditions of entry 3 were thus applied to a series of substrates **4′**, obtaining the results reported in Table 3. It should be observed that, due to the modest solubility of substrates, the initial reactant concentration is in general necessarily low, possibly justifying the rather long reaction time needed.

Table 3
Results obtained in the reactions of **4′** with indole in TFE at 50 °C

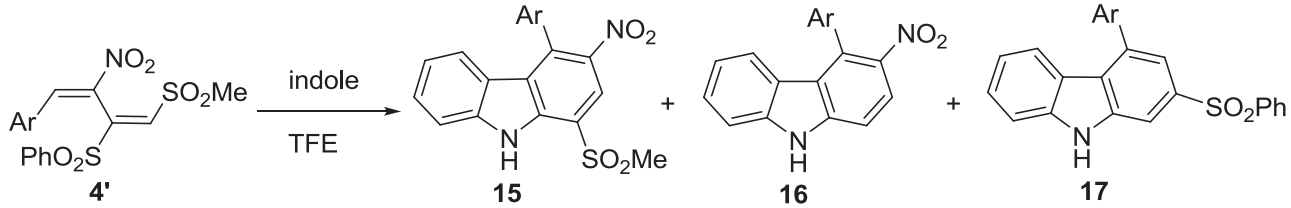
Entry	Substrate: Ar	Time (h)	Yields (%)[a]			
			15	**16**	**17**	Total
1	**4′ a: Phenyl**[b]	24	51	31	10[c]	92
2	**4′ d: *p*-Tolyl**[b]	24	40	40	10[c]	90
3	**4′ g: *p*-Anisyl**[b]	48	53	29	11[c]	93
4	**4′ i: *p*-Cl-Phenyl**	48	63	30	6[c]	99
5	**4′ j: 1-Naphthyl**	48	46	14	tr[b,d]	60
6	**4′ l: 2-Thienyl**	48	61	20	11	92

[a] Yields of isolated compounds, unless otherwise indicated.
[b] Interestingly enough, when the reactions are performed in HFIP (24 h, rt), a different distribution of products is observed: from **4′ a**, **15a**: 13%, **16a**: 57%, **17a**: 9%; from **4′ d**, **15d**: 36%, **16d**: 55%, **17d**: 9%; from **4′ g**, **15g**: 21%, **16g**: 72%, **17g**: 4%.
[c] Obtained as a mixture with the corresponding **15**.
[d] tr=trace (<1%).

Notably, the tri-substituted carbazole **15** (whose structure was unequivocally ascertained thanks to a single-crystal X-ray analysis on **15d**, Fig. 1) turns out to be the main product throughout, followed by carbazole **16**: the latter becoming prevalent when HFIP is used as solvent (see footnote *b* of Table 3).

The **15**:**16**:**17** yield ratio is almost the same along the series, evidencing that the effect of the aryl moiety is not significant. It appears reasonable that, starting from the intermediate **19**, **15** and **16** arise from a common precursor, possibly the dihydrocarbazole **20** (Scheme 8), the first by air oxidation and the second by $MeSO_2H$ elimination. Thus, **15** is the result of an elimination (of benzensulfinic acid)/aromatization process, and **16** of two consecutive sulfinic acid eliminations.

As far as compound **17** is concerned, it could share with the other two carbazole derivatives the intermediate **19**, from which it would form thanks to two consecutive eliminations (of nitrous and methanesulfinic acids), or possibly take origin directly from **18**, through an addition-elimination process (a vinylic S_N), followed by elimination of nitrous acid.



4' **15** **16** **17**

4'd: Ar = *p*-Tol **15d**: 40% **16d**: 40% **17d**: 10%

Scheme 7. Carbazole derivatives from the reaction of **4′d** with indole in TFE.

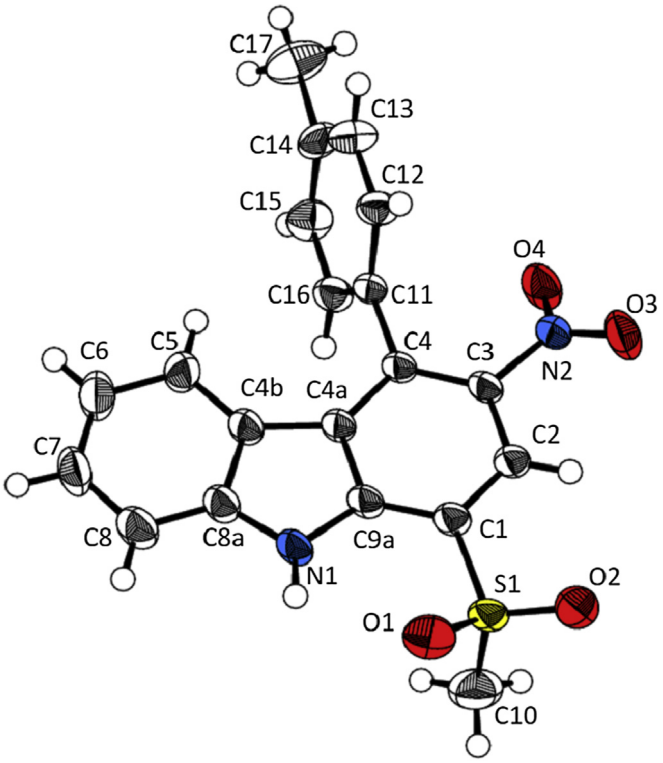
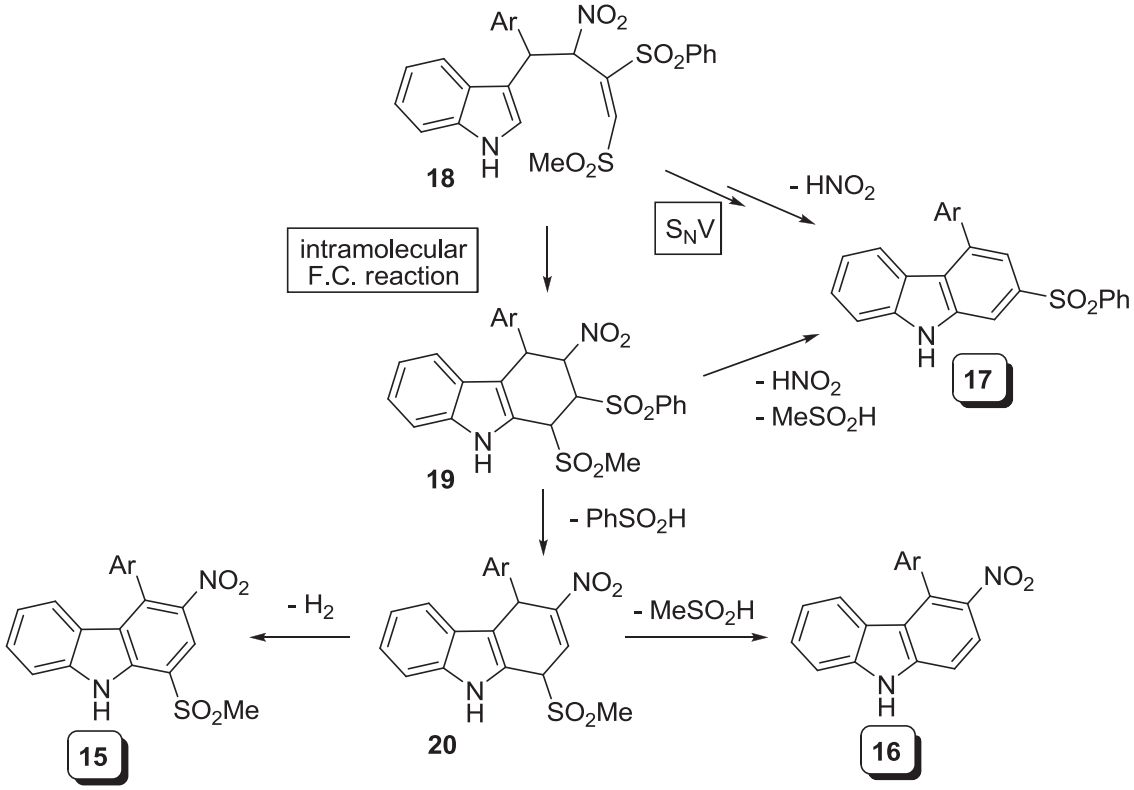


Fig. 1. ORTEP of **15d**.

It should be noted that, due to the very low quantities obtained, always as mixtures with the corresponding product **15**, it was not possible to isolate and fully characterize compounds **17** (but for **17l**). For this compound, an HSQC spectrum allowed to ascertain the pattern of substitution as a 2-phenylsulfonyl-4-thienyl- rather than 1-thienyl-3-phenylsulfonyl derivative, an alternative that could have not been in principle excluded.

The undeniable efficacy of TFE as the reaction medium for the reactions described on substrates **4′** urged us to ascertain its effect also on dinitrobutadienes **5**: the latter were thus treated with 2 equiv of indole in TFE and, at the end of the reaction (as judged by TLC/NMR disappearance of the substrate), the solvent was easily removed and the crude analyzed. The results for the reactions on substrates **5a**–**l** are reported in Table 4 (left). We were pleasantly surprised discovering that in these conditions not only the reactions are notably faster, but the dinitrocarbazole **10** becomes the main product throughout. This outcome, quite rewarding from the practical/synthetic point of view, must be considered together with the concurrent interesting evidence that 3-nitrocarbazoles **8** are now secondary with respect to 2-nitrocarbazoles **9**, whose yields are in general only barely decreased with respect to those observed in the original conditions (cf. Table 1, left). One must then admit that *a)* as hypothesized above, **9** is more easily formed than **8** within **path A** (see Scheme 4 and relevant observations in the text), *b)* the decreased yield of **8** should be essentially ascribed to a depletion of its formation via elimination from **13′** to the advantage of **10** (see Scheme 5), and *c)* the still competitive **path A** most likely provides the endogenous oxidant for **path B**.

Further confirmation of the advanced mechanistic hypotheses was indirectly obtained when adding DDQ as an external oxidant after disappearance of the substrate: the obtained results, reported on the right side of Table 4, show a modest improvement in the yield of **10** (the increase never amounting to more than 12%), the yields of the two mono-nitrated products remaining almost unchanged. It can be deduced that most of **11** evolves spontaneously in the reaction medium, and the late-added oxidant intercepts only the amount of **11** not yet evolved. Accordingly, a somewhat lower increase is observed for the anisyl derivatives, namely the more prone to undergo a 'spontaneous' oxidation.



Scheme 8. A hypothesized pathway to compounds **15**–**17**.

Table 4
Results obtained in the reactions of **5a**–**l** with indole in TFE, without or with an external oxidant added (see text)[a]

Entry	Substrate: Ar	Time	Yields (%)[b]				Yields (%)[b] (with DDQ)			
			8	**9**	**10**	Total	**8**	**9**	**10**	Total
1	**5a: Phenyl**	4 h	14	30	39	83	12	27	51	90
2	**5b: *o*-Tolyl**	4 d	11[c]		12	23	7[c]		14	21
3	**5c: *m*-Tolyl**	1 d	10	23	37	70	8	20	49	77
4	**5d: *p*-Tolyl**[d]	4 h	13	27	48	88	12	25	56	93
5	**5e: Mesityl**	7 d	—	—	—	—				
6	**5f: *m*-Anisyl**	2 d	6	14	53	73	5	14	57	76
7	**5g: *p*-Anisyl**	2 d	7	15	57	79	8	15	58	81
8	**5h: *m*-Cl-Phenyl**	16 h	8	13	50	71	9	18	55	82
9	**5i: *p*-Cl-Phenyl**	16 h	12	21	40	73	10	17	49	76
10	**5j: 1-Naphthyl**	3d	30[c]		29	59	30[c]		39	76
11	**5k: 2-Naphthyl**	2 d	18	30	39	87	15	26	48	89
12	**5l: 2-Thienyl**	1 d	11	18	51	80	10	15	57	82

[a] The oxidant was added after the reaction time indicated in the third column and left to react 2–3 h before work-up.
[b] Yields of isolated compounds, unless otherwise indicated.
[c] Overall **8** + **9** yield, in a 1:2 ratio as deduced by 1H NMR analysis.
[d] The reaction in HFIP (24 h, rt) produced the following mixture: 8d 20%, 9d 40%; 10d 20%.

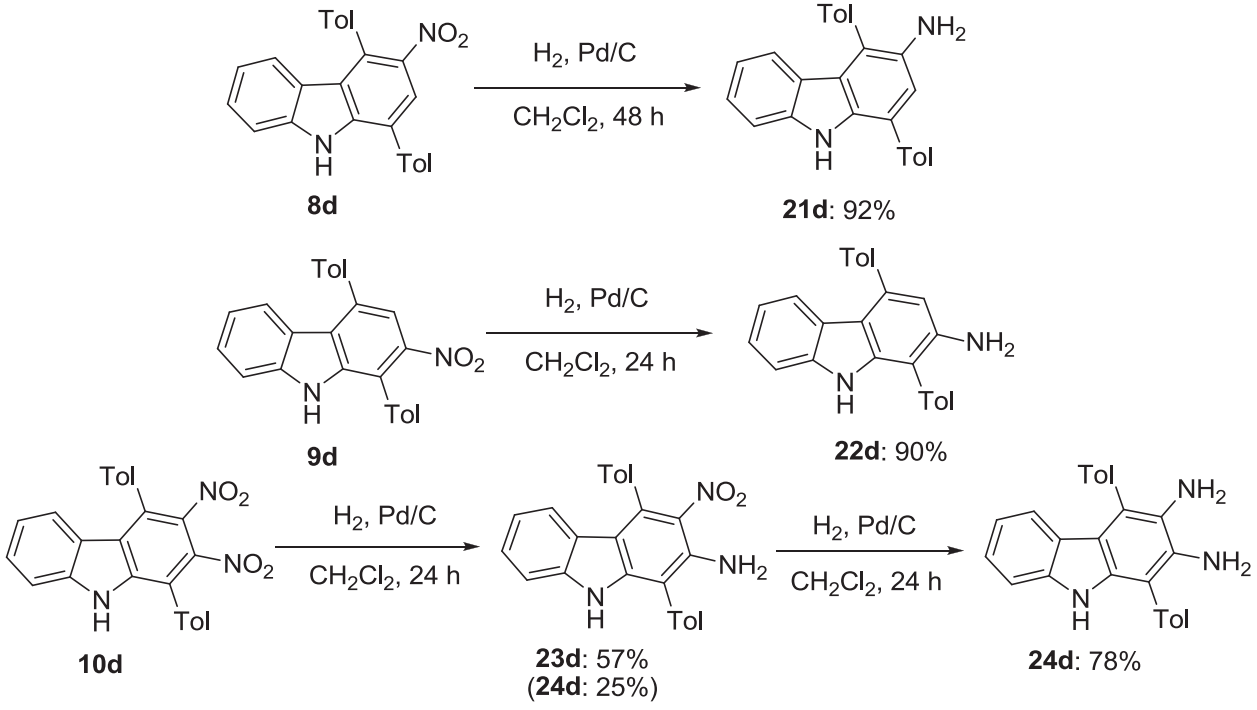
Even if the system could probably be further improved, it should be said that, with the exception of hindered substrates, these last conditions bring to 50–60% yields of the dinitro derivatives **10** throughout: a satisfactory result, especially when considering the multi-step nature of the process.

As an example of applicative developments, fluorescent carbazole derivatives can be simply obtained by reduction of the nitro group (a well-known fluorescence quencher) in nitrocarbazoles.[17] Thus, by catalytic hydrogenation of compound **8d** (Scheme 9) the corresponding 3-aminocarbazole derivative **21d** was obtained in high yields (92%) within 48 h, while compound **9d** was likewise satisfactorily (90%) reduced to **22** within a shorter time (24 h). The more facile reduction of the 2-nitro versus the 3-nitro group has been attributed to the involvement of the latter within a vinylogous nitroenaminic moiety.[18] Consistently, when the same reaction conditions were applied to **10d**, after 24 h the reaction mixture contained the 1,4-diaryl-2-amino-3-nitrocarbazole **23d** as the major product (57%) together with minor quantities (25%) of the diaminocarbazole **24d**. After the addition of some fresh catalyst, supplementary 24 h of hydrogenation produced the diamine in 78% yields. The classical Zn/HCl, Sn/HCl and $SnCl_2 \cdot 2H_2O$ systems were also tested, with no significant modification of relative yields and, on the other hand, similar or lower overall yields and/or longer reaction times.

The fluorescence of **21d** is clearly demonstrated by the spectra reported in Fig. 2.

3. Conclusions

Altogether, the results herein represent a further significant breakthrough of our nitrobutadienic building blocks into the field of *N*-heterocyclic synthesis. In particular, a new, one-pot procedure is illustrated, which, through a sequence of inter- and intramolecular steps and a final aromatization, builds-up a functionalized benzene



Scheme 9. Results of hydrogenation on compounds **8d**–**10d**.

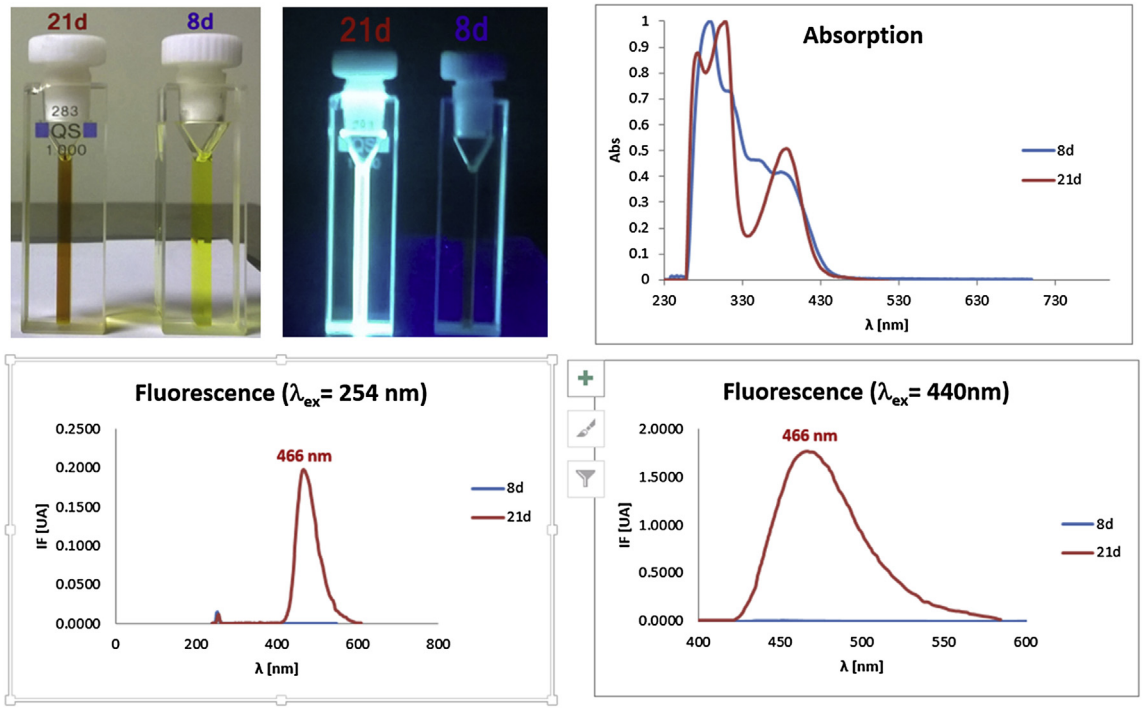


Fig. 2. Absorption spectra of compounds **8d** and **21d**.

ring onto an indole precursor, giving access to interesting carbazole derivatives. On both **4′** (Scheme 1, **4**: Z=H, Y=SO_2Ph) and **5** (which, for electronic reasons, have proved to be most suited among other nitrobutadienes: cf. Scheme 1), the process is actually characterized by the formation of mixtures of carbazoles, originating by means of competitive pathways whereby elimination and/or oxidation processes eventually lead to full aromatization of the newly condensed heterocycle.

As a matter of fact, two sets of competition are operative herein, namely *i*) elimination versus oxidation (by air, endogenous nitrous acid, or a purposely added oxidant) and, *ii*) within elimination, cleavage of different leaving groups (NO_2, $PhSO_2$, $MeSO_2$), or of identical leaving groups from different positions.

Thus, as far as the latter competition is concerned, it should be noticed that the poly-functionality of our dienes, which is essential for the hypothesized Michael-type addition (Scheme 3) and/or vinylic substitution sequence (Scheme 8), on the other hand represents, in some way, a drawback whenever it is not possible to identify operative conditions, which would perform a fully selective process leading to one or the other of the reported products. A practical significance is nonetheless guaranteed herein by the occurrence that a satisfactory product selectivity (at least allowing to easily isolate the main product) can be reached indeed by a choice of the reaction conditions. Thus, as far as reactions on the symmetrical dinitrobutadiene **5** are concerned, two sets of conditions provide preferential access to the 3-nitroderivative **8** [$Zn(OAc)_2$, EtOH, 40 °C, then water quenching: see Table 1] or to the 2,3-dinitroderivative **10** [TFE, 50 °C, then DDQ: see Table 4]. On the other hand, as far as the unsymmetrical **4′** system is concerned, the use of TFE at 50 °C is the only practicable set of conditions among those tested, leading to a 40–60% yield of the trisubstituted carbazole **15** throughout. Needless to say, when possible, the use of TFE represents a clean (the solvent can be recovered by distillation at the end of the reaction), metal-free, atom-economic and operationally simple process.

Finally, the nitro group that characterizes all of the obtained derivatives can be further modified, e.g., by reduction to amine or, according to Cadogan reaction,[19] to obtain new, more complex, angular, polycyclic derivatives.

4. Experimental section

4.1. Materials and methods

^1H NMR and ^{13}C NMR spectra were recorded with a Varian Mercury 300 Plus spectrometer, at 300 and 75 MHz, respectively; chemical shifts (TMS as internal reference) are reported as δ values (ppm). Gas chromatography–mass spectrometry (GC–MS) was performed on HP 5890/5971 (EI 70 eV) system equipped with a HP-1 MS capillary column (12 m×0.2 mm i.d×0.33 μm). High-resolution mass spectra (HRMS) were obtained with a Agilent MSD TOF mass spectrometer, and recorded in positive ion mode with an electrospray (ESI) source. Melting points were determined with a Büchi 535 apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum 65 FTIR and wave numbers are reported in cm^{-1}. Absorption spectra were recorded using a Perkin Elmer Lambda9 UV/VIS/NIR Spectrophotometer, while Fluorescence spectra were recorded (at the excitation wavelengths of 254 nm and 440 nm) with the Perkin Elmer MPF-44A Fluorescence Spectrophotometer, and were normalized using Rhodamine B in PMMA as reference standard. Petroleum ether and light petroleum refer to the fractions with bp 40–60 °C and 80–100 °C, respectively. Silica gel 230–400 mesh was used for column chromatography, all solvents being distilled before use. Tetrahydrofuran (THF) was purified by standard methods and distilled over potassium benzophenone ketyl before use. All other commercially available reagents were used as received. 4-Chlorophenylmagnesium bromide, 3-methylphenylmagnesium chloride, and 3-methoxyphenylmagnesium bromide were commercial THF or Et_2O solutions titrated just before use.

Compounds **3′** and **4′a**,**d**,**g**,**j**,**l** have been already described,[20] while **3′i** and **4′i** are new compounds, prepared according to the same procedure, in 83% and 48% yield, respectively.

*4.1.1. (E,E)-1-(4-Chlorophenyl)-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (**3′i**).* Yellow solid, mp 141–142 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.54 (3H, s), 7.27–7.33 (2H, m), 7.38–7.47 (4H, m), 7.50–7.57 (1H, m), 7.78–7.85 (2H, m), 8.24 (1H, s), 8.27 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 17.7, 110.0, 125.3, 128.2, 129.2, 129.3, 131.9, 133.7, 138.3, 139.5, 139.6, 139.7, 156.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1646, 1589, 1550, 1524, 1489, 1446, 1405, 1315, 1306, 1284, 1210, 1144, 1083, 1046, 1012. HRMS (ESI) *m/z* calcd $[M+NH_4]^+$ $C_{17}H_{18}ClN_2O_4S_2$ 413.0391 found 413.0390.

*4.1.2. (E,E)-1-(4-Chlorophenyl)-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (**4′i**).* Yellow solid, mp 209–210 °C (ethanol). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 3.30 (3H, s), 7.32–7.38 (2H, m), 7.43–7.53 (4H, m), 7.62–7.70 (1H, m), 7.71–7.83 (2H, m), 8.55 (1H, s), 8.67 (1H, s). ^{13}C NMR (DMSO-d_6, 75 MHz): δ (ppm) 47.4, 133.2, 134.2, 135.0, 137.9, 140.5, 141.5, 142.0, 142.4, 144.9, 147.2, 150.8 (two isochronous carbons). IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1661, 1586, 1527, 1448, 1334, 1322, 1309, 1285, 1214, 1165, 1156, 1145, 1093, 1088, 1041, 1013. HRMS (ESI) *m/z* calcd $[M+NH_4]^+$ $C_{17}H_{18}ClN_2O_6S_2$ 445.0289, found 445.0291.

Compounds **5a**,[1b] **b**,[1c] **d**,[1c] **e**,[21] **g**,[1c] **h**,[1c] **i**,[3b] **j**,[1c] **k**,[22] **l**,[1c] have been already described, while **5c** and **5f** are new compounds, prepared according to a reported procedure,[1b] in 89% and 93% yield, respectively.

*4.1.3. (1E,3E)-1,4-Bis(3-methylphenyl)-2,3-dinitro-1,3-butadiene (**5c**).* Yellow solid, mp 96–97 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.28 (6H, s), 7.14–7.24 (8H, m), 8.45 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.4, 127.4, 129.4, 129.7, 131.5, 133.3, 139.3, 140.1, 141.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1670, 1619, 1601, 1582, 1517, 1314, 1245, 1176, 1164, 1095, 1058. HRMS (ESI) *m/z* calcd $[M+NH_4]^+$ $C_{18}H_{20}N_3O_4$ 342.1448, found 342.1450.

*4.1.4. (1E,3E)-1,4-Bis(3-methoxyphenyl)-2,3-dinitro-1,3-butadiene (**5f**).* Yellow solid, mp 105–106 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.72 (6H, s), 6.86 (2H, t, *J* 2.1 Hz), 6.92–7.01 (4H, m), 7.26 (2H, dd, *J* 8.2, 7.7 Hz), 8.45 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.6, 115.4, 118.7, 123.3, 130.7, 131.1, 140.6, 141.6, 160.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 1694, 1586, 1537, 1489, 1457, 1432, 1288, 1038. HRMS (ESI) *m/z* calcd $[M+NH_4]^+$ $C_{18}H_{20}N_3O_6$ 374.1347, found 374.1349.

4.2. General procedure for the reaction of dinitrobutadienes 5 with indole in EtOH

To a stirred suspension of **5** (0.5 mmol) in ethanol (8 mL) at 40 °C, indole (1.1 mmol) and zinc acetate (0.5 mmol) were added. The mixture was stirred at 40 °C for the time necessary to ensure completion of reaction, then poured into water and extracted with dichloromethane; the organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate (10:1) to give **8**, **9** and **10**.

For experiments performed with the oxidant, DDQ (3 equiv) was added after the ascertained reaction time before the aqueous quenching, and the mixture kept under magnetic stirring at 40 °C for additional 2–3 h.

4.3. General procedure for the reaction of dinitrobutadienes 5 with indole in TFE

Indole (1.1 mmol) was added to a stirred suspension of **5** (0.5 mmol) in TFE (8 mL) at 50 °C. The mixture was stirred at 50 °C for the time necessary to ensure completion of reaction (TLC), and then the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate (10:1) to give **8**, **9** and **10**.

For experiments performed with the oxidant, DDQ (3 equiv) was added after the ascertained reaction time, and the mixture kept under magnetic stirring at 50 °C for additional 2 h.

*4.3.1. 1,4-Diphenyl-3-nitro-9H-carbazole (**8a**).*[3d] Yellow solid, mp 175–176 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.62 (1H, d, *J* 8.1 Hz), 6.96 (1H, ddd, *J* 8.2, 6.4, 1.8 Hz), 7.33–7.68 (10H, m), 7.68–7.78 (2H, m), 8.22 (1H, s), 8.65 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.2, 120.8, 122.2, 122.9, 123.2, 123.7, 124.3, 127.2, 128.4, 128.5, 128.8, 128.9, 129.1, 129.8, 132.5, 136.7, 136.8, 139.3, 140.5, 141.8. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{24}H_{17}N_2O_2$ 365.1285, found 365.1280.

*4.3.2. 1,4-Diphenyl-2-nitro-9H-carbazole (**9a**).*[3d] Yellow solid, mp 196–197 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.05 (1H, t, *J* 7.4 Hz), 7.33–7.73 (13H, m), 7.82 (1H, s), 8.16 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.1, 117.2, 119.4, 120.3, 122.2, 123.4, 124.1, 127.8, 128.6, 128.8, 128.9, 129.2, 129.6, 129.9, 134.1, 137.2, 139.2, 141.4, 145.2, 165.4. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{24}H_{17}N_2O_2$ 365.1285, found 365.1289.

*4.3.3. 2,3-Dinitro-1,4-diphenyl-9H-carbazole (**10a**).* Yellow solid, mp 293–294 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.80 (1H, d, *J* 8.2 Hz), 7.03 (1H, ddt, *J* 7.9, 6.1, 1.8 Hz), 7.37–7.76 (12H, m), 8.40 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 6.60 (1H, d, *J* 8.1 Hz), 7.02 (1H, t, *J* 7.7 Hz), 7.47 (1H, t, *J* 7.8 Hz), 7.53–7.70 (11H, m), 12.03 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.7, 119.0, 121.7, 122.8, 123.3, 128.6, 129.0, 129.0, 129.1, 129.3, 129.4, 129.7, 130.0, 130.1, 130.1, 131.2, 131.4, 133.5, 137.8, 141.4. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{24}H_{16}N_3O_4$ 410.1135, found 410.1129.

*4.3.4. 1,4-Bis(2-methylphenyl)-3-nitro-9H-carbazole (**8b**) and 1,4-Bis(2-methylphenyl)-2-nitro-9H-carbazole (**9b**).* Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.45 (3H of **9b**, s), 2.44 (3H of **8b**, s), 2.47 (3H of **9b**, s), 2.50 (3H of **8b**, s), 6.97 (1H of **8b**, ddd, *J* 8.2, 6.3, 1.9 Hz), 7.03 (1H of **9b**, t, *J* 7.0 Hz), 7.25–7.65 (11H of **9b**+11H of **8b**), 7.78 (1H of **9b**, s), 8.16 (1H of **9b**, s), 8.18 (1H of **8b**, s), 8.62 (1H of **8b**, s). (**8b**) HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1594. (**9b**) HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1595.

*4.3.5. 1,4-Bis(2-methylphenyl)-2,3-dinitro-9H-carbazole (**10b**).* Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.37 (3H, s), 2.40 (3H, s), 6.87 (1H, d, *J* 8.0 Hz), 7.02 (1H, td, *J* 7.5, 1.5 Hz), 7.24–7.56 (10H, m), 8.45 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 19.7, 19.8, 111.4, 119.5, 120.2, 121.5, 121.5, 122.4, 126.4, 126.5, 127.5, 127.8, 129.5, 129.9, 130.1, 130.1, 130.3, 130.8, 134.4, 134.6, 135.4, 135.9, 139.0, 139.2, 140.7, 142.7. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{20}N_3O_4$ 438.1448, found 438.1446.

*4.3.6. 1,4-Bis(3-methylphenyl)-3-nitro-9H-carbazole (**8c**).* Yellow solid; mp 110–111 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.45 (3H, s), 2.51 (3H, s), 6.67 (1H, d, *J* 8.1 Hz), 6.97 (1H, ddd, *J* 8.2, 6.5, 1.8 Hz), 7.27 (1H, d, *J* 5.4 Hz), 7.29–7.44 (5H, m), 7.41–7.56 (4H, m), 8.19 (1H, s), 8.64 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.7, 21.8, 111.2, 120.8, 122.2, 123.0, 123.1, 123.9, 124.4, 125.5, 125.5, 127.1, 128.9, 128.9, 129.1, 129.3, 129.6, 129.6, 132.6, 136.6, 136.8, 138.7, 139.4, 139.7, 140.5, 141.9 HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1594.

*4.3.7. 1,4-Bis(3-methylphenyl)-2-nitro-9H-carbazole (**9c**).* Yellow solid; mp 164–165 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.46 (3H, s), 2.48 (3H, s), 7.04 (1H, ddd, *J* 8.3, 6.4, 1.8 Hz), 7.26–7.43 (6H, m), 7.43–7.50 (3H, m), 7.56 (2H, d, *J*

8.1 Hz), 7.79 (1H, s), 8.17 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.7, 21.7, 111.1, 117.1, 119.4, 120.3, 122.3, 123.5, 124.1, 125.9, 126.3, 127.6, 128.7, 129.3, 129.4 (two isochronous carbons), 129.6, 129.9, 134.0, 137.3, 138.6, 138.7, 139.2, 139.3, 141.4, 145.2 HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1592.

*4.3.8. 1,4-Bis(3-methylphenyl)-2,3-dinitro-9H-carbazole (**10c**).* Yellow solid; mp 228–229 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.45 (3H, s), 2.47 (3H, s), 6.83 (1H, d, *J* 8.2 Hz), 7.04 (1H, ddd, *J* 8.2, 6.0, 2.1 Hz), 7.27–7.55 (10H, m), 8.48 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.8, 21.8, 111.7, 119.1, 121.6, 122.8, 122.8, 123.4, 126.1, 126.1, 128.5, 129.2, 129.4, 129.5, 129.9, 130.4, 130.9, 131.1, 131.5, 132.2, 133.4, 137.0, 137.8, 139.1, 139.9, 141.4. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{20}N_3O_4$ 438.1448, found 438.1451.

*4.3.9. 1,4-Bis(4-methylphenyl)-3-nitro-9H-carbazole (**8d**).*[3d] Yellow solid; mp 213–214 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.49 (3H, s), 2.53 (3H, s), 6.74 (1H, d, *J* 8.1 Hz), 6.98 (1H, ddd, *J* 8.3, 6.0, 2.1 Hz), 7.29–7.47 (8H, m), 7.62 (2H, d, *J* 8.1 Hz), 8.16 (1H, s), 8.60 (1H, br s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.46 (3H, s), 2.49 (3H, s), 6.55 (1H, d, *J* 8.0 Hz), 6.92 (1H, t, *J* 7.4 Hz), 7.32 (2H, d, *J* 8.0 Hz), 7.35 (1H, m part. overlapped with the previous), 7.42 (2H, d, *J* 8.0 Hz), 7.46 (2H, d, *J* 7.9 Hz), 7.59 (1H, d, *J* 8.1 Hz), 7.69 (2H, d, *J* 8.0 Hz), 8.06 (1H, s), 11.81 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.6, 21.8, 111.2, 120.8, 122.2, 123.1, 123.2, 124.0, 124.3, 127.2, 128.4, 128.5, 129.9, 130.6, 132.5, 133.6, 134.0, 138.1, 138.9, 139.4, 140.5, 142.2. GC–MS *m*/*z* 392. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1597.

*4.3.10. 1,4-Bis(4-methylphenyl)-2-nitro-9H-carbazole (**9d**).*[3d] Yellow solid; mp 124–125 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.50 (3H, s), 2.52 (3H, s), 7.05 (1H, t, *J* 7.1 Hz), 7.33–7.45 (8H, m), 7.52–7.64 (3H, m), 7.77 (1H, s), 8.16 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.45 (3H, s), 2.47 (3H, s), 7.01 (1H, t, *J* 7.7 Hz), 7.35–7.49 (8H, m), 7.53–7.61 (4H, m), 11.29 (1H, s). ^{13}C NMR (CDCl3, 75 MHz): δ (ppm) 21.6 (two isochronous carbons), 111.1, 117.1, 119.2, 120.2, 122.3, 123.5, 124.0, 127.6, 128.8, 129.1, 129.6, 130.3, 131.0, 136.3, 137.1, 138.4, 138.7, 138.8, 141.4, 145.4. GC–MS *m*/*z* 392. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_2$ 393.1598, found 393.1594.

*4.3.11. 1,4-Bis(4-methylphenyl)-2,3-dinitro-9H-carbazole (**10d**).*[3d] Yellow solid; mp 267–268 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.49 (3H, s), 2.52 (3H, s), 6.90 (1H, d, *J* 8.1 Hz), 7.05 (1H, td, *J* 7.4, 1.6 Hz), 7.25–7.58 (10H, m), 8.40 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.47 (3H, s), 2.50 (3H, s), 6.71 (1H, d, *J* 8.5 Hz), 7.04 (1H, t, *J* 7.7 Hz), 7.39–7.53 (9H, m), 7.61 (1H, d, *J* 8.3 Hz), 11.97 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.6, 21.7, 111.5, 118.9, 121.4, 122.8, 122.8, 123.3, 128.1, 128.4, 128.7, 128.8, 130.0, 130.4, 130.6, 131.3, 137.2, 137.7, 139.5, 140.1, 140.7, 141.3. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{20}N_3O_4$ 438.1448, found 438.1442.

*4.3.12. 1,4-Bis(3-methoxyphenyl)-3-nitro-9H-carbazole (**8f**).* Yellow solid; mp 173–174 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.85 (3H, s), 3.93 (3H, s), 6.74 (1H, d, *J* 8.1 Hz), 6.95–7.14 (5H, m), 7.17–7.33 (1H, m), 7.35–7.44 (2H, m), 7.45–7.62 (3H, m), 8.22 (1H, s), 8.69 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.6, 56.2, 111.4, 113.4, 113.7, 113.9, 114.1, 121.5, 121.5, 122.4, 123.9, 124.9, 125.1, 125.2, 126.1, 129.4, 129.5, 129.7, 130.8, 131.5, 137.1, 137.3, 139.2, 146.8, 160.0, 160.5. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_4$ 425.1496, found 425.1492.

*4.3.13. 1,4-Bis(3-methoxyphenyl)-2-nitro-9H-carbazole (**9f**).* Yellow solid; mp 164–165 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.87 (3H, s), 3.88 (3H, s), 7.00–7.12 (4H, m), 7.17–7.30 (3H, m), 7.37–7.44 (2H, m), 7.46–7.53 (2H, m), 7.55–7.62 (1H, m), 7.81 (1H, s), 8.23 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.6, 56.0, 111.4, 113.3, 113.8, 114.1, 114.2, 114.7, 118.0, 121.4, 121.5, 122.3, 123.0, 126.1, 129.1, 129.5, 130.7, 132.9, 133.1, 133.9, 135.5, 138.0, 138.8, 143.5, 159.9, 160.7. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_4$ 425.1496, found 425.1493.

*4.3.14. 1,4-Bis(3-methoxyphenyl)-2,3-dinitro-9H-carbazole (**10f**).* Yellow solid; mp 217–218 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.85 (3H, s), 3.86 (3H, s), 6.90 (1H, d, *J* 8.1 Hz), 7.00–7.16 (7H, m), 7.45 (2H, dd, *J* 6.1, 1.3 Hz), 7.51 (2H, ddd, *J* 8.4, 7.6, 3.3 Hz), 8.55 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.5, 55.6, 111.4, 113.8, 113.9, 114.1, 114.1, 115.5, 121.5, 121.5, 122.4, 124.3, 125.0, 126.3, 129.2, 129.5, 130.3, 130.8, 135.9, 136.8, 137.0, 139.2, 142.7, 147.2, 160.1, 160.7. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{20}N_3O_6$ 470.1347, found 470.1342.

*4.3.15. 1,4-Bis(4-methoxyphenyl)-3-nitro-9H-carbazole (**8g**).* Yellow solid; mp 183–184 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.92 (3H, s), 3.94 (3H, s), 6.79 (1H, d, *J* 8.1 Hz), 6.99 (1H, ddd, *J* 8.1, 6.2, 2.0 Hz), 7.12 (4H, ddd, *J* 10.5, 6.3, 2.3 Hz), 7.31–7.47 (4H, m), 7.65 (2H, d, *J* 8.7 Hz), 8.12 (1H, s), 8.65 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.5, 55.6, 111.2, 114.5, 115.2, 120.7, 121.9, 123.0, 123.4, 123.9, 124.0, 127.1, 128.6, 129.1, 129.7, 129.7, 131.7, 139.4, 140.5, 142.4, 159.6, 160.0. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_4$ 425.1496, found 425.1495.

*4.3.16. 1,4-Bis(4-methoxyphenyl)-2-nitro-9H-carbazole (**9g**).* Yellow solid; mp 172–173 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.91 (3H, s), 3.95 (3H, s), 7.06 (1H, t, *J* 1.6 Hz), 7.07–7.17 (4H, m), 7.32–7.48 (4H, m), 7.55–7.66 (3H, m), 7.74 (1H, s), 8.19 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.5, 55.6, 111.1, 114.3, 115.0, 117.1, 118.7, 120.2, 122.4, 123.4, 125.9, 127.6, 129.9, 130.2, 130.4, 131.6, 136.8, 139.0, 141.4, 145.5, 159.9, 160.0. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{21}N_2O_4$ 425.1496, found 425.1498.

*4.3.17. 1,4-Bis(4-methoxyphenyl)-2,3-dinitro-9H-carbazole (**10g**).* Yellow solid; mp 228–229 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.91 (3H, s), 3.94 (3H, s), 6.94 (1H, d, *J* 8.2 Hz), 7.05 (1H, ddd, *J* 8.3, 6.4, 1.9 Hz), 7.10 (2H, d, *J* 2.4 Hz), 7.12 (2H, d, *J* 2.5 Hz), 7.37–7.52 (6H, m), 8.44 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.2, 56.4, 111.5, 118.5, 119.7, 121.5, 122.4, 122.9, 129.0, 129.4, 130.1, 130.2, 130.4, 130.7, 130.8, 130.8, 136.1, 139.2, 140.7, 142.4, 160.8, 161.8. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{26}H_{20}N_3O_6$ 470.1347, found 470.1341.

*4.3.18. 1,4-Bis(3-chlorophenyl)-3-nitro-9H-carbazole (**8h**).*[3d] Orange solid; mp 257–258 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.67 (1H, d, *J* 8.1 Hz), 7.03 (1H, td, *J* 7.6, 2.0 Hz), 7.28–7.67 (9H, m), 7.72 (1H, m), 8.23 (1H, s), 8.66 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.2, 117.6, 119.6, 120.4, 122.2, 123.5, 124.4, 126.8 (two isochronous carbons), 126.8, 127.0, 127.0, 127.3, 127.8, 127.9, 128.1, 128.2, 128.2, 128.3, 128.5, 128.6, 129.4, 131.7, 133.3, 133.3, 133.6, 133.7, 136.7, 137.2, 139.1, 141.5, 145.2 (several signals are split, presumably due to the presence of two conformers). HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{15}Cl_2N_2O_2$ 433.0505, found 433.0502.

*4.3.19. 1,4-Bis(3-chlorophenyl)-2-nitro-9H-carbazole (**9h**).*[3d] Yellow solid; mp 207–208 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.10 (1H, ddd, *J* 8.3, 6.3, 2.1 Hz), 7.30–7.76 (11H, m), 7.84 (1H, s), 8.14 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.4, 117.2, 118.4, 120.8, 121.8, 123.3, 124.3, 127.2, 127.4, 128.2, 128.9, 129.0, 129.2, 129.3, 130.3, 130.9, 134.9, 135.4,

135.8, 135.9, 138.6, 140.8, 141.6, 144.8. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{15}Cl_2N_2O_2$ 433.0505, found 433.0501.

*4.3.20. 1,4-Bis(3-chlorophenyl)-2,3-dinitro-9H-carbazole (**10h**).* Orange solid; mp 208–209 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.83 (1H, d, *J* 8.2 Hz), 7.10 (1H, ddt, *J* 7.7, 6.1, 1.7 Hz), 7.37–7.66 (10H, m), 8.45 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.9, 117.9, 122.1, 122.4, 123.0, 123.2, 127.3, 127.3, 127.4, 129.1, 129.2, 129.3, 130.1, 130.1, 130.2, 130.6, 130.8, 131.4, 132.7, 135.1, 135.4, 136.0, 137.6, 141.5. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{14}Cl_2N_3O_4$ 478.0356, found 478.0358.

*4.3.21. 1,4-Bis(4-chlorophenyl)-3-nitro-9H-carbazole (**8i**).* Yellow solid; mp 255–256 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.71 (1H, d, *J* 7.9 Hz), 7.03 (1H, ddd, *J* 8.2, 6.2, 2.0 Hz), 7.36–7.48 (4H, m), 7.55–7.64 (4H, m), 7.68 (2H, d, *J* 8.2 Hz), 8.20 (1H, s), 8.73 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.4, 117.7, 119.4, 121.1, 122.2, 122.8, 123.4, 127.5, 129.5, 129.9 (two isochronous carbons), 130.1, 130.8, 131.5, 134.5, 135.1, 139.1, 139.3, 140.6, 141.5. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{15}Cl_2N_2O_2$ 433.0505, found 433.0501.

*4.3.22. 1,4-Bis(4-chlorophenyl)-2-nitro-9H-carbazole (**9i**).* Yellow solid; mp 222–223 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.09 (1H, ddt, *J* 7.9, 6.6, 1.2 Hz), 7.36–7.50 (3H, m), 7.50–7.69 (8H, m), 7.81 (1H, s), 8.12 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.4, 117.3, 118.6, 120.7, 122.0, 123.4, 124.3, 128.2, 129.3, 130.0, 130.4, 130.6, 132.5, 134.9, 135.2, 136.2, 137.6, 138.8, 141.6, 145.0. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{15}Cl_2N_2O_2$ 433.0505, found 433.0499.

*4.3.23. 1,4-Bis(4-chlorophenyl)-2,3-dinitro-9H-carbazole (**10i**).* Yellow solid; mp 239–240 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.87 (1H, d, *J* 8.1 Hz), 7.10 (1H, t, *J* 7.4 Hz), 7.44–7.54 (6H, m), 7.55–7.66 (4H, m), 8.38 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.8, 118.0, 119.1, 122.0, 122.4, 123.1, 128.9, 129.3, 129.7, 130.2, 130.4 (two isochronous carbons), 130.4, 130.5, 131.7, 136.0, 136.6, 137.6, 139.9, 141.4. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{24}H_{14}Cl_2N_3O_4$ 478.0356, found 478.0358.

*4.3.24. 1,4-Bis(1-naphthyl)-3-nitro-9H-carbazole (8j) and 1,4-Bis(1-naphthyl)-2-nitro-9H-carbazole (**9j**).* Yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.17 (1H of **8j**, dd, *J* 3.8, 8.1 Hz), 6.60–6.73 (1H of **9j** and 1H of **8j**, m), 7.11–7.70 (15H of **9j** and 12H of **8j**, m), 7.90–8.02 (4H of **9j** and 4H of **8j**, m), 8.14 (1H of **8j**, s), 8.35 (1H of **8j**, s). (**8j**). HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{21}N_2O_2$ 465.1598, found 465.1595. (**9j**) HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{21}N_2O_2$ 465.1598, found 465.1593.

*4.3.25. 1,4-Bis(1-naphthyl)-2,3-dinitro-9H-carbazole (**10j**).* Yellow solid; mp 253–254 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.23 (1H, d, *J* 8.1 Hz), 6.77 (1H, app. t, *J* 7.3 Hz), 7.17–7.72 (12H, m), 7.94–8.20 (4H, m), 8.47 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 119.8, 121.5, 121.5, 122.4, 123.5, 125.3, 125.6, 126.0, 126.4, 126.5, 126.9, 127.3, 127.5, 127.8 (two isochronous carbons), 127.9, 128.2, 128.4, 128.7, 130.8, 131.6, 132.1, 132.4, 133.1, 134.3, 135.0, 136.1, 139.2, 140.8, 144.1. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{20}N_3O_4$ 510.1448, found 510.1449.

*4.3.26. 1,4-Bis(2-naphthyl)-3-nitro-9H-carbazole (**8k**).* Orange solid; mp 225–226 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.62 (1H, d, *J* 8.0 Hz), 6.87 (1H, ddd, *J* 8.1, 7.0, 1.2 Hz), 7.30–7.48 (2H, m), 7.51–7.70 (5H, m), 7.81–7.96 (3H, m), 7.96–8.07 (3H, m), 8.12 (2H, dd, *J* 8.4, 5.4 Hz), 8.24 (1H, s), 8.37 (1H, s), 8.75 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.2, 120.9, 122.5, 123.0, 123.3, 123.8, 124.5, 126.2, 126.6, 126.6, 126.8, 127.1, 127.1, 127.2, 127.2, 127.7, 128.1, 128.2, 128.3, 128.5, 128.8, 129.8, 132.4, 133.2, 133.2, 133.7, 133.8, 134.1, 134.2, 139.6, 140.6, 142.2. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{21}N_2O_2$ 465.1598, found 465.1593.

*4.3.27. 1,4-Bis(2-naphthyl)-2-nitro-9H-carbazole (**9k**).* Orange solid; mp 252–253 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.99 (1H, ddd, *J* 8.2, 6.7, 1.4 Hz), 7.30–7.47 (2H, m), 7.51–7.69 (6H, m), 7.83 (1H, dd, *J* 8.3, 1.7 Hz), 7.90–8.04 (6H, m), 8.08 (2H, dd, *J* 8.4, 2.3 Hz), 8.19 (1H, m), 8.22 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.2, 117.6, 119.6, 120.4, 122.2, 123.5, 124.4, 126.8, 126.8, 127.0, 127.0, 127.3, 127.8, 127.9, 127.9, 128.1, 128.2, 128.2, 128.3, 128.5, 128.6, 129.4, 131.7, 133.3, 133.3, 133.6, 133.7, 136.7, 137.2, 139.1, 141.5, 145.2. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{21}N_2O_2$ 465.1598, found 465.1595.

*4.3.28. 1,4-Bis(2-naphthyl)-2,3-dinitro-9H-carbazole (**10k**).* Yellow solid; mp 252–253 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.78 (1H, d, *J* 8.1 Hz), 6.93 (1H, ddd, *J* 8.2, 5.4, 2.7 Hz), 7.34–7.47 (2H, m), 7.55–7.73 (7H, m), 7.86–8.14 (7H, m), 8.61 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.6, 119.1, 121.7, 122.7, 123.0, 123.3, 125.8, 126.1, 126.6, 127.0, 127.3, 127.4, 127.7, 128.1, 128.2 (two isochronous carbons), 128.5, 128.6, 128.6, 128.8, 129.1, 130.0, 130.0, 130.9, 131.1, 131.3, 133.4, 133.5, 133.6, 133.7, 138.0, 141.4. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{32}H_{20}N_3O_4$ 510.1448, found 510.1444.

*4.3.29. 1,4-Bis(2-thienyl)-3-nitro-9H-carbazole (**8l**).* Orange solid; mp 165–166 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.79 (1H, d, *J* 8.3 Hz), 7.06 (1H, ddd, *J* 8.2, 6.5, 1.7 Hz), 7.15 (1H, dd, *J* 3.5, 1.2 Hz), 7.25–7.29 (1H, m), 7.44 (2H, dd, *J* 8.4, 1.7 Hz), 7.51 (2H, ddd, *J* 5.1, 4.3, 1.2 Hz), 7.61 (1H, dd, *J* 5.1, 1.2 Hz), 8.27 (1H, s), 8.94 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.5, 119.6, 121.0, 121.5, 121.5, 122.4, 123.5, 125.0, 128.8, 129.0, 129.0, 129.2, 129.3, 130.9, 130.9, 137.4, 138.4, 139.2, 139.7, 142.2. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{20}H_{13}N_2O_2S_2$ 377.0413, found 377.0410.

*4.3.30. 1,4-Bis(2-thienyl)-2-nitro-9H-carbazole (**9l**).* Orange solid; mp 186–187 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.07 (1H, ddd, *J* 8.1, 6.9, 1.3 Hz), 7.24 (1H, dd, *J* 5.2, 3.5 Hz), 7.28 (1H, d, *J* 5.7 Hz), 7.37 (1H, dd, *J* 3.5, 1.2 Hz), 7.41 (1H, dd, *J* 6.9, 1.2 Hz), 7.46 (2H, d, *J* 4.4 Hz), 7.48 (1H, dd, *J* 5.1, 1.2 Hz), 7.56 (1H, d, *J* 7.7 Hz), 7.73 (1H, dd, *J* 7.9, 0.9 Hz), 8.67 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.4, 116.5, 117.1, 119.3, 121.4, 121.5, 122.3, 127.3, 128.8, 128.9, 129.0, 129.2, 129.2, 130.7, 131.3, 134.2, 134.4, 138.8, 140.7, 143.1. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{20}H_{13}N_2O_2S_2$ 377.0413, found 377.0416.

*4.3.31. 1,4-Bis(2-thienyl)-2,3-dinitro-9H-carbazole (**10l**).* Orange solid; mp 283–284 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.93 (1H, dt, *J* 8.3, 1.1 Hz), 7.13 (1H, ddd, *J* 8.3, 6.2, 2.0 Hz), 7.23–7.32 (3H, m), 7.34–7.38 (1H, m), 7.44–7.56 (2H, m), 7.61–7.71 (2H, m), 8.74 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 111.4, 120.1, 120.8, 121.5, 121.5, 122.4, 125.6, 125.9, 128.8 (two isochronous carbons), 129.2 (two isochronous carbons), 130.8, 133.1, 133.7, 133.9, 135.4, 137.1, 139.2, 141.3. HRMS (ESI) *m*/*z* calcd $[M+H]^+$ $C_{20}H_{12}N_3O_4S_2$ 422.0264, found 422.0260.

*4.3.32. 1-(4-Methylphenyl)-3-(phenylsulfonyl)propan-2-one (**14d**).* White solid; mp 87–88 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.33 (3H, s), 3.93 (2H, s), 4.15 (2H, s), 6.97–7.11 (2H, m), 7.11–7.20 (2H, m), 7.49–7.68 (2H, m), 7.62–7.77 (1H, m), 7.82–7.98 (2H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.3, 50.8, 65.6, 76.8, 77.3, 77.7, 128.6, 129.4, 129.6, 129.7, 130.0, 134.6, 137.6, 138.8, 196.2. GC–MS: Rt 5.43, *m*/*z* 288(12)

[M+•], 147(100), 141(15), 105(87), 77(50). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{16}H_{17}O_3S$ 289.0893, found 289.0892.

4.4. General procedure for the reaction of nitrobutadienes 4′ with indole in TFE

Indole (0.25 mmol) was added to a stirred suspension of **4′** (0.123 mmol) in TFE (6 mL) at 50 °C. The mixture was stirred at 50 °C for the time necessary to ensure completion of reaction (see Table 3), and then the solvent was removed under reduced pressure. The residue was purified by column chromatography using petroleum ether/ethyl acetate (10:1) to give **15**, **16** and **17**. Compounds **17** (minor) are usually in mixture with **15** (major): it is usually possible to obtain by crystallization only **15** as pure samples. Only in the case of Ar=thienyl, compound **17l** could be isolated and fully characterized.

*4.4.1. (E)-3-(4-(Methylsulfonyl)-2-nitro-3-(phenylsulfonyl)-1-(p-tolyl)but-3-en-1-yl)-1H-indole (**18d**).* Unstable intermediate isolated as an oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.17 (3H, s), 3.14 (3H, s), 4.63 (1H, d, *J* 14.7 Hz), 4.87 (1H, d, *J* 14.7 Hz), 6.47 (1H, s), 6.91–6.99 (5H, m), 7.03–7.08 (2H, m), 7.15 (1H, d, *J* 3.0 Hz), 7.17 (1H, d, *J* 2.9 Hz), 7.18–7.37 (3H, m), 7.76–7.92 (2H, m), 7.93 (1H, s).

*4.4.2. 1-Methylsulfonyl-3-nitro-4-phenyl-9H-carbazole (**15a**).* Yellow solid, mp 242–243 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.31 (3H, s), 6.61 (1H, d, *J* 8.2 Hz), 6.93–7.13 (1H, m), 7.35–7.43 (2H, m), 7.45–7.52 (1H, m), 7.53–7.64 (4H, m), 8.69 (1H, s), 10.04 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 45.0, 111.9, 119.9, 121.8, 122.4, 122.5, 122.9, 125.7, 127.6, 128.5, 128.9, 129.2, 135.1, 137.6, 138.2, 140.7, 140.8. GC–MS: Rt 6.01, *m/z* 366(100) [M+•], 257(54), 241(88), 240(71), 107(38). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{19}H_{15}N_2O_4S$ 367.0747, found 367.0752.

*4.4.3. 3-Nitro-4-phenyl-9H-carbazole (**16a**).* Yellow solid, mp 158–159 °C (dichloromethane/petroleum ether). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.60 (1H, d, *J* 8.1 Hz), 6.96 (1H, t, *J* 7.4 Hz), 7.31–7.52 (5H, m), 7.52–7.71 (3H, m), 8.21 (1H, d, *J* 8.9 Hz), 8.58 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 109.6, 111.0, 120.5, 122.7, 123.3, 127.0, 128.1, 128.2, 128.9, 130.9, 133.5, 136.7, 140.5, 141.2, 141.4 (two isochronous carbons). GC–MS: Rt 4.56, *m/z* 288(100) [M+•], 241(78), 240(35), 106(31). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{18}H_{13}N_2O_2$ 289.0972, found 289.0967.

*4.4.4. 4-Phenyl-2-phenylsulfonyl-9H-carbazole (**17a**).* Isolated by chromatographic column as a mixture with **15a**: only a few signals in the ^{1}H NMR spectrum can be assigned with confidence: ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.97–8.04 (2H, m), 8.10 (1H, d, *J* 1.6 Hz), 8.61 (1H, s). GC–MS: Rt 11.40, *m/z* 383(100) [M+•], 241(99), 230(63), 128(35), 77(98). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{24}H_{18}NO_2S$ 384.1053, found 384.1055.

*4.4.5. 4-(4-Methylphenyl)-1-methylsulfonyl-3-nitro-9H-carbazole (**15d**).* Yellow solid, mp 250–252 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.53 (3H, s), 3.29 (3H, s), 6.73 (1H, d, *J* 8.1 Hz), 6.97–7.18 (1H, m), 7.28 (2H, d, *J* 8.0 Hz), 7.40 (2H, d, *J* 8.0 Hz), 7.45–7.57 (2H, m), 8.63 (1H, s), 9.98 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.6, 45.0, 111.8, 119.7, 121.7, 122.4, 122.5, 123.0, 125.7, 127.5, 128.4, 129.9, 131.9, 137.5, 138.4, 138.8, 140.7, 141.2. GC–MS: Rt 12.15, *m/z* 380(100) [M+•], 271(33), 254(59), 113(32). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{20}H_{17}N_2O_4S$ 381.0904, found 381.0907.

*4.4.6. 4-(4-Methylphenyl)-3-nitro-9H-carbazole (**16d**).* Yellow solid, mp 211–212 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.51 (3H, s), 6.90–7.06 (1H, m), 6.98 (1H, ddd, *J* 8.2, 6.7, 1.6 Hz), 7.19–7.52 (7H, m), 8.17 (1H, d, *J* 8.9 Hz), 8.59 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.5, 109.4, 110.9, 120.5, 122.7, 122.8, 123.4, 126.9, 128.0, 129.6, 133.5, 133.6, 137.9, 140.5, 141.3, 141.6 (two isochronous carbons). GC–MS: Rt 9.84, *m/z* 302(100) [M+•], 257(31), 254(31), 241(35). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{19}H_{15}N_2O_2$ 303.1128, found 303.1133.

*4.4.7. 4-(4-Methylphenyl)-1-phenylsulfonyl-9H-carbazole (**17d**).* Isolated by chromatographic column as a mixture with **15d**: only a few signals in the ^{1}H NMR spectrum can be assigned with confidence: ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.95–8.04 (2H, m), 8.07 (1H, d, *J* 1.6 Hz), 8.57 (1H, s). GC–MS: Rt 17.18, *m/z* 397(100) [M+•], 281(18), 241(38), 78(41), 64(34). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{25}H_{20}NO_2S$ 398.1209, found 398.1205.

*4.4.8. 1-Methylsulfonyl-4-(4-methoxyphenyl)-3-nitro-9H-carbazole (**15g**).* Yellow solid, mp 251–252 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.30 (3H, s), 3.95 (3H, s), 6.80 (1H, d, *J* 8.1 Hz), 7.07 (1H, t, *J* 7.6 Hz), 7.12 (2H, d, *J* 8.7 Hz), 7.31 (2H, d, *J* 8.7 Hz), 7.49 (1H, t, *J* 7.5 Hz), 7.56 (1H, d, *J* 8.1 Hz), 8.62 (1H, s), 10.02 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 45.0, 55.4, 111.9, 114.6, 119.7, 121.7, 122.3, 122.5, 123.0, 126.0, 126.8, 128.4, 129.1, 137.4, 138.0, 140.7, 141.4, 160.0. GC–MS: Rt 7.70, *m/z* 396(66) [M+•], 228(70), 114(61), 100(100). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{20}H_{17}N_2O_5S$ 397.0853, found 397.0854.

*4.4.9. 4-(4-Methoxyphenyl)-3-nitro-9H-carbazole (**16g**).* Yellow solid, mp 170–171 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.94 (3H, s), 6.77 (1H, d, *J* 8.0 Hz), 6.99 (1H, ddd, *J* 8.2, 6.7, 1.5 Hz), 7.06–7.15 (2H, m), 7.28–7.50 (5H, m), 8.15 (1H, d, *J* 8.9 Hz), 8.52 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 55.4, 109.4, 110.9, 114.4, 120.5, 122.6, 122.8, 123.0, 123.4, 127.0, 128.5, 129.4, 133.1, 140.4, 141.2, 141.9, 159.5. GC–MS: Rt 5.46, *m/z* 318(96) [M+•], 258(40), 228(74), 114(100), 100(60). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{19}H_{15}N_2O_3$ 319.1077, found 319.1076.

*4.4.10. 4-(4-Methoxyphenyl)-2-phenylsulfonyl-9H-carbazole (**17g**).* Isolated by chromatographic column as a mixture with **15g**: only a few signals in the ^{1}H NMR spectrum can be assigned with confidence: ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.97–8.03 (1H, m), 8.05 (1H, d, *J* 1.6 Hz), 8.30 (1H, s). GC–MS: Rt 21.18, *m/z* 413(100) [M+•], 281(29), 228(35), 110(27), 96(35), 77(61), 64(67). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{25}H_{20}NO_3S$ 414.1158, found 414.1153.

*4.4.11. 4-(4-Chlorophenyl)-1-methylsulfonyl-3-nitro-9H-carbazole (**15i**).* Yellow solid, mp 236–238 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.30 (3H, s), 6.70 (1H, d, *J* 8.1 Hz), 7.09 (1H, ddd, *J* 8.2, 6.8, 1.4 Hz), 7.31–7.43 (2H, m), 7.45–7.74 (4H, m), 8.69 (1H, s), 10.04 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 45.0, 112.0, 120.2, 122.0, 122.2, 122.5, 122.7, 125.6, 128.7, 129.2, 129.6, 133.5, 135.1, 136.9, 137.6, 140.8 (two isochronous carbons). GC–MS: Rt 11.42, *m/z* 400(100) [M+•], 370(41), 275(32), 256(38), 240(45), 100(19). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{19}H_{14}ClN_2O_4S$ 401.0357, found 401.0352.

*4.4.12. 4-(4-Chlorophenyl)-3-nitro-9H-carbazole (**16i**).* Yellow solid, mp 221–223 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.69 (1H, d, *J* 8.0 Hz), 7.02 (1H, ddd, *J* 8.2, 6.5, 1.7 Hz), 7.30–7.41 (2H, m), 7.38–7.46 (2H, m), 7.49 (1H, d, *J* 9.0 Hz), 7.52–7.58 (2H, m), 8.22 (1H, d, *J* 9.0 Hz), 8.62 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 109.9, 111.1, 120.8, 122.5, 122.8, 123.0, 127.2, 128.8, 129.2, 129.7, 132.2, 134.2, 135.2, 140.5, 141.2, 141.4. GC–MS: Rt 9.45, *m/z* 322(100) [M+•], 292(85), 257(58), 241(77), 114(54), 106(52), 96(48). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{18}H_{12}ClN_2O_2$ 323.0582, found 323.0580.

*4.4.13. 4-(4-Chlorophenyl)-2-phenylsulfonyl-9H-carbazole (**17i**).* Isolated by chromatographic column as a mixture with **15i**: only a few signals in the ^{1}H NMR spectrum can be assigned with

confidence: ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.96–8.04 (1H, m), 8.11 (1H, d, *J* 1.5 Hz), 8.61 (1H, s). GC–MS: Rt 20.93, *m/z* 417(13) [M+•], 264(40), 241(91), 213(22), 158(17), 77(100). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{24}H_{17}ClNO_2S$ 418.0663, found 418.0660.

*4.4.14. 1-Methylsulfonyl-4-(1-naphthyl)-3-nitro-9H-carbazole (**15j**).* Yellow solid, mp 254–255 °C (ethanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.37 (3H, s), 6.12 (1H, d, *J* 8.0 Hz), 6.82 (1H, ddd, *J* 8.2, 7.1, 1.0 Hz), 7.27–7.32 (2H, m), 7.36–7.46 (2H, m), 7.48–7.56 (2H, m), 7.66 (1H, dd, *J* 8.3, 7.1 Hz), 8.02 (1H, d, *J* 8.2 Hz), 8.10 (1H, d, *J* 8.2 Hz), 8.83 (1H, s), 10.03 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 45.1, 111.7, 120.2, 121.9, 122.2, 122.7, 122.8, 124.5, 125.2, 125.7, 126.3, 126.5, 127.0, 128.4, 128.7, 129.3, 130.9, 132.8, 133.6, 137.0, 137.7, 140.7, 141.4. GC–MS: Rt 13.64, *m/z* 416(57) [M+•], 308(26), 291(100), 146(46), 131(28). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{23}H_{17}N_2O_4S$ 417.0904, found 417.0900.

*4.4.15. 4-(1-Naphthyl)-3-nitro-9H-carbazole (**16j**).* Yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.10 (1H, d, *J* 8.1 Hz), 6.74 (1H, ddd, *J* 8.2, 7.2, 1.1 Hz), 7.33–7.38 (1H, m), 7.41 (1H, dt, *J* 8.4, 1.0 Hz), 7.44–7.51 (2H, m), 7.53 (1H, dd, *J* 5.7, 3.3 Hz), 7.58 (1H, d, *J* 8.9 Hz), 7.63 (1H, dd, *J* 8.3, 7.0 Hz), 7.71 (1H, dd, *J* 5.7, 3.3 Hz), 7.99 (1H, d, *J* 8.2 Hz), 8.06 (1H, d, *J* 8.4 Hz), 8.36 (1H, d, *J* 8.9 Hz), 8.58 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 109.8, 110.8, 120.7, 122.6, 123.0, 125.0, 125.4, 125.8, 126.2, 126.6, 127.0, 128.4, 128.6, 128.8, 130.9, 131.6, 132.4, 133.6, 134.5, 140.4, 141.5, 167.8. GC–MS: Rt 10.84, *m/z* 338(100) [M+•], 309(49), 292(76), 146(65), 131(46). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{22}H_{15}N_2O_2$ 339.1128, found 339.1126.

*4.4.16. 1-Methylsulfonyl-3-nitro-4-(2-thienyl)-9H-carbazole (**15l**).* Yellow solid, mp 288–289 °C (ethanol). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 3.50 (3H, s), 6.60 (1H, d, *J* 8.0 Hz), 7.09 (1H, t, *J* 7.6 Hz), 7.25 (1H, dd, *J* 3.6, 1.2 Hz), 7.34 (1H, dd, *J* 5.1, 3.5 Hz), 7.52 (1H, t, *J* 7.6 Hz), 7.81 (1H, d, *J* 8.1 Hz), 7.93 (1H, dd, *J* 5.0, 1.3 Hz), 8.57 (1H, s), 12.35 (1H, s). ^{13}C NMR (DMSO-d_6, 75 MHz): δ (ppm) 43.8, 113.7, 121.6, 121.7, 122.1, 122.2, 122.5, 126.4, 128.2, 128.4, 128.8, 129.0, 129.8, 134.5, 137.0, 141.0, 142.3. GC–MS: Rt 10.31, *m/z* 372(51) [M+•], 354(84), 342(96), 246(100), 207(80), 179(68), 87(78). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{17}H_{13}N_2O_4S_2$ 373.0311, found 373.0316.

*4.4.17. 3-Nitro-4-(2-thienyl)-9H-carbazole (**16l**).* Yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.79 (1H, d, *J* 7.9 Hz), 6.91–7.12 (2H, m), 7.14 (1H, dd, *J* 3.5, 1.2 Hz), 7.42–7.47 (2H, m), 7.51 (1H, d, *J* 8.9 Hz), 7.61 (1H, dd, *J* 5.1, 1.2 Hz), 8.18 (1H, d, *J* 8.8 Hz), 8.53 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 110.4, 111.0, 119.0, 119.9, 120.8, 122.6, 122.8, 123.0, 125.6, 127.0, 127.1, 127.4, 127.4, 135.9, 140.5, 141.0. GC–MS: Rt 8.81, *m/z* 294(70) [M+•], 276(98), 264(78), 246(69), 218(92), 165(100), 88(94). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{16}H_{11}N_2O_2S$ 295.0536, found 295.0533.

*4.4.18. 2-Phenylsulfonyl-4-(2-thienyl)-9H-carbazole (**17l**).* Yellow solid; mp 101–103 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.04–7.12 (1H, m), 7.22 (1H, dd, *J* 5.1, 3.5 Hz), 7.32 (1H, dd, *J* 3.5, 1.2 Hz), 7.42–7.59 (6H, m), 7.62–7.72 (1H, m), 7.73 (1H, d, *J* 1.6 Hz), 7.97–8.04 (2H, m), 8.11 (1H, d, *J* 1.6 Hz), 8.57 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 108.6, 109.5, 118.6, 119.3, 120.1, 121.6, 124.9, 125.9, 125.9, 126.1, 126.3, 126.3, 127.8, 129.3, 131.5, 136.2, 137.4, 138.6, 139.6, 140.5. GC–MS: Rt 31.05, *m/z* 389 (100) [M+•], 247(33), 236(27), 204(14), 77(13). HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{22}H_{16}NO_2S_2$ 390.0617, found 390.0613.

4.5. General procedure for the reduction of nitrocarbazoles 8d–10d to aminocarbazoles 21d–24d

In a two-neck round-bottom flask, the substrate dissolved in dichloromethane was added with Pd/C (100% weight equivalent), the system deaerated and kept under hydrogen atmosphere and magnetic stirring. The advancement of the reaction was checked by TLC. At the end of the reaction, the mixture was filtered, the catalyst washed with dichloromethane and the solvent removed under reduced pressure. For the reactions on **8d** and **9d** the crude was crystallized and pure **21d** and **22d** were obtained, respectively; in the case of **10d** the crude was purified by column chromatography using petroleum ether/ethyl acetate (10:1) to give **23d** and **24d**, in 57% and 25% yields, respectively.

*4.5.1. 1,4-Bis(4-methylphenyl)-9H-carbazol-3-amine (**21d**).* White solid; mp 230–231 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.47 (3H, s), 2.52 (3H, s), 3.46 (2H, s), 6.85 (1H, t, *J* 7.3 Hz), 6.93 (1H, d, *J* 7.9 Hz), 6.98 (1H, s), 7.18–7.33 (2H, m), 7.33–7.49 (6H, m), 7.61 (2H, d, *J* 7.6 Hz), 8.10 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.42 (3H, s), 2.47 (3H, s), 4.43 (2H, s), 6.65–6.78 (2H, m), 6.95 (1H, s), 7.16 (1H, ddd, *J* 8.2, 5.5, 2.8 Hz), 7.26–7.34 (2H, m), 7.35–7.46 (5H, m), 7.54–7.63 (2H, m), 10.66 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.4, 21.6, 110.5, 115.4, 118.7, 121.1, 122.4, 122.9, 123.5, 124.8, 125.4, 128.4, 130.0, 130.1, 130.3, 131.7, 134.4, 136.2, 137.4, 137.4, 137.6, 140.3. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{23}N_2$ 363.1856, found 363.1851.

*4.5.2. 1,4-Bis(4-methylphenyl)-9H-carbazol-2-amine (**22d**).* White solid; mp 231–232 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.47 (3H, s), 2.49 (3H, s), 3.85 (2H, s), 6.60 (1H, s), 6.92 (1H, t, *J* 7.0 Hz), 7.12–7.28 (2H, m), 7.33 (2H, d, *J* 7.6 Hz), 7.36–7.45 (3H, m), 7.48 (2H, d, *J* 7.6 Hz), 7.56 (2H, d, *J* 7.6 Hz), 7.80 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.43 (6H, s), 4.73 (2H, s), 6.51 (1H, s), 6.77 (1H, t, *J* 7.6 Hz), 7.07 (1H, t, *J* 7.5 Hz), 7.18 (1H, d, *J* 8.0 Hz), 7.27–7.50 (9H, m), 10.26 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.5, 21.5, 108.4, 110.0, 111.0, 113.3, 119.0, 121.3, 123.9, 124.1, 129.1, 129.2, 130.1, 130.7, 132.0, 137.23, 137.7, 137.9, 138.3, 139.5, 140.3, 141.9. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{23}N_2$ 363.1856, found 363.1858.

*4.5.3. 1,4-Bis(4-methylphenyl)-3-nitro-9H-carbazol-2-amine (**23d**).* Orange solid; mp 156–157 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.48 (3H, s), 2.49 (3H, s), 5.02 (2H, s), 6.67 (1H, dd, *J* 8.0, 1.0 Hz), 6.87 (1H, ddd, *J* 8.2, 6.7, 1.5 Hz), 7.11–7.24 (2H, m), 7.29–7.38 (4H, m), 7.39–7.48 (4H, m), 7.75 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.46 (3H, s), 2.46 (3H, s), 5.17 (2H, s), 6.43–6.52 (1H, m), 6.73–6.83 (1H, m), 7.16 (1H, td, *J* 8.1, 7.6, 1.2 Hz), 7.25–7.34 (3H, m), 7.34–7.44 (4H, m), 7.44–7.52 (2H, m), 10.68 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 21.0 (two isochronous carbons), 108.5, 111.3, 113.0, 119.1, 120.2, 123.0, 125.1, 128.3, 129.4, 130.3, 130.4, 130.5, 131.2, 133.4, 137.4, 137.6, 137.7, 140.9, 141.3, 141.5. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{22}N_3O_2$ 408.1707, found 408.1702.

*4.5.4. 1,4-Bis(4-methylphenyl)-9H-carbazol-2,3-diamine (**24d**).* White solid; mp 273–275 °C (petroleum ether/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.48 (3H, d, *J* 1.6 Hz), 2.53 (3H, d, *J* 1.9 Hz), 3.32 (4H, br s), 6.84 (1H, m), 7.13–7.37 (2H, m), 7.37–7.52 (9H, m), 8.09 (1H, s). ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 2.44 (3H, s), 2.47 (3H, s), 4.02 (4H, s), 6.49–6.69 (2H, m), 6.92–7.05 (1H, m), 7.21–7.48 (9H, m), 9.98 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 16.1, 16.3, 106.7, 108.0, 114.4, 116.0, 116.7, 117.7, 118.5, 124.1, 124.3, 124.5, 124.6, 124.9, 126.0, 126.1, 128.0, 128.9, 134.4, 134.5, 135.7, 137.4. HRMS (ESI) *m/z* calcd $[M+H]^+$ $C_{26}H_{24}N_3$ 378.1965, found 378.1961.

*4.5.5. X-ray crystallographic study of compound **15d**.* $C_{20}H_{16}N_2O_4S$, M=380.42, pale yellow prism with irregular shape and dimensions 0.30×0.40×0.55 mm. Triclinic, space group $P\bar{1}$, *a*=9.470(1) Å,

b=10.467(1) Å, c=11.679(1) Å, α=101.51(1)°, β=103.78(1)°, γ=107.65(1)°, V=1024.2(2) Å^3, Z=2, F(000)=396, d_{calcd}=1.234 g/cm^3, μ (MoKα)=0.184 mm^{-1}. Crystals were grown from ethyl acetate solution.

Intensity data were collected at 295 K on a Bruker-Nonius MACH3 diffractometer (graphite monochromated Mo Kα radiation): ω-θ scans, scan width 1.12°, minimum speed 0.96° min^{-1}, θ_{max}=29°; 5697 total measured reflections, 5383 independent reflections of which 4132 with I>4 σ(I).

The structure was solved with the SIR*2014* program,[23] with all non-hydrogen atoms clearly revealed from the first Fourier map. The refinement was accomplished by means of full-matrix least squares cycles using the SHELXL program,[24] the correct assignment of atomic species being possible on the basis of bond distances and U_{iso} values. After some cycles of anisotropic refinement of the heavier atoms, all hydrogen atoms were obtained in subsequent difference Fourier maps. Their coordinates were restrained in idealized positions, by means of AFIX43 or AFIX 137 (for methyl groups) instructions, and their isotropic displacement parameters constrained to 1.5 times the U_{eq} of the corresponding bonded atom. At convergence, however, the residuals were still rather high (R1=0.135, wR2=0.427) and six additional peaks of non-negligible electron density, with values ranging between 6.6 and ~1.0 eÅ^{-3}, appeared in the ΔF map. All residual peaks were located across the b edge of the cell, at coordinates $x\approx0.0$, $y\approx0.5$, $z\approx0.0$, namely approximately around a centre of symmetry. After some unfruitful attempts to fit the observed peaks according to the solvent molecule (AcOEt), also considering a partial molecular fragment of it, and even by trying the structure solution in the acentric space group $P1$, the presence of disordered solvent molecules has been regarded as the only plausible explanation.

In order to improve the structural model, the BYPASS procedure was applied,[25] using the SQUEEZE routine as implemented in the PLATON program.[26] According to this procedure, the diffuse electron density in the disordered areas is calculated and referred back, by means of discrete Fourier transform, to the observed structure factors; the corrected data, obtained by subtracting the contribution of the disordered solvent, are then used in the subsequent refinement of the ordered part of the structure. In the present case, the total volume of the potential solvent area in the unit cell is 185 Å^3, corresponding to a total electron count of 43. These values are compatible with the presence of 1 molecule of ethyl acetate per unit cell (V_{AcOEt}: 88 Å^3; electrons per molecule: 48), i.e., a host:-guest ratio of ~2:1.

The final indexes are: $R1$=0.048 (over 3920 reflections with $F_o>4\sigma$ F_o) and $wR2$=0.138 for 246 refined parameters and 5383 reflections, max shift/e.s.d=0.014, Goodness of fit S=1.049, $\Delta\rho_{min}$=−0.31 eÅ^{-3}, $\Delta\rho_{max}$=+0.28 eÅ^{-3}.

Fig. 1 shows the ortep diagram of the molecule with atom numbering. Bond distances and bond angles compare well with tabulated values and only one slightly short intermolecular contact, involving the terminal C17 methyl group, has been found. The molecules are linked through intermolecular N9−H9 ··· O2 hydrogen bonds (as plotted in Supplementary data, Fig. 2) [O2 in (−x, −y, −z), donor−acceptor distance d=2.903(3) Å and N9−H9−O2 angle of 159.3(1)°], giving rise to pairs, which are located at the origin of the elementary cell. As an example, the packing of the molecules is viewed in the projection along the [100] direction, where the shaded areas corresponding to the voids accessible to the disordered solvent, are also highlighted (Supplementary data, Fig. 3).

Crystallographic data (CIF file, FCF file) for the structure in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication numbers CCDC-1026522. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

Supplementary data (Spectroscopic data, copies of the ^{1}H and ^{13}C NMR spectra for all compounds; crystallographic materials, fluorescence measurements for compounds **8d** and **21d**.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.05.046.

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