Preparation and Characterization of Arylor Heteroaryl(3-indolyl)methylium o-Benzenedisulfonimides

Preparation and characterization of aryl or heteroaryl(3-indolyl)methylium *o*-benzenedisulfonimides

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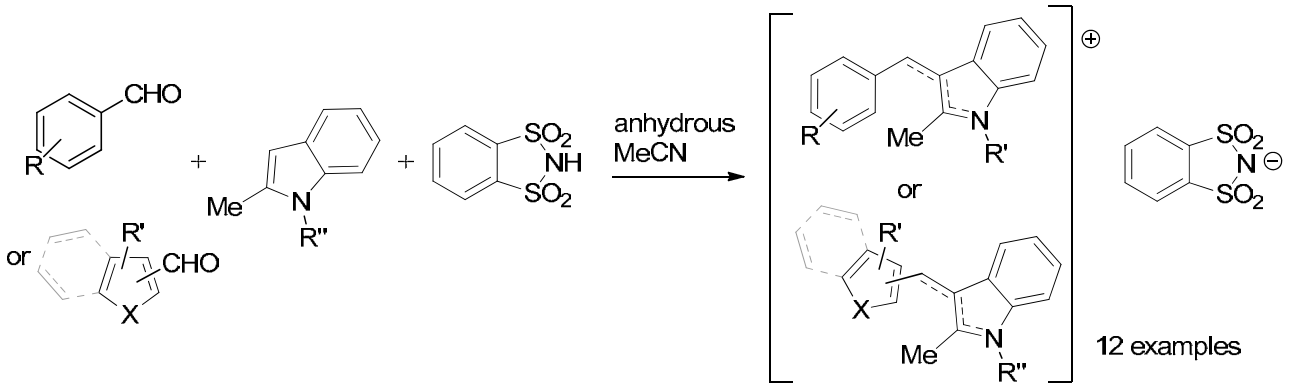


ABSTRACT

An initial study has been accomplished into the synthetic feasibility of the preparation of diarylcarbenium salt *via* the direct coupling of aryl (or heteroaryl) aldehydes and arenes (or heteroaryl analogues) in the presence of a strong organic Brønsted acid. A number of stabilized aryl or heteroaryl(3-indolyl)carbenium ions, never previously prepared in the solid state, have been isolated in excellent yields as highly stable *o*-benzenedisulfonimide salts and have been fully characterized. Their purity has been proven by spectroscopic methods and chemical reduction with $NaBH_4$. An X-ray crystal structure analysis has been performed on one of the products: an azafulvenium species was shown to be the exclusive structure in the solid state.

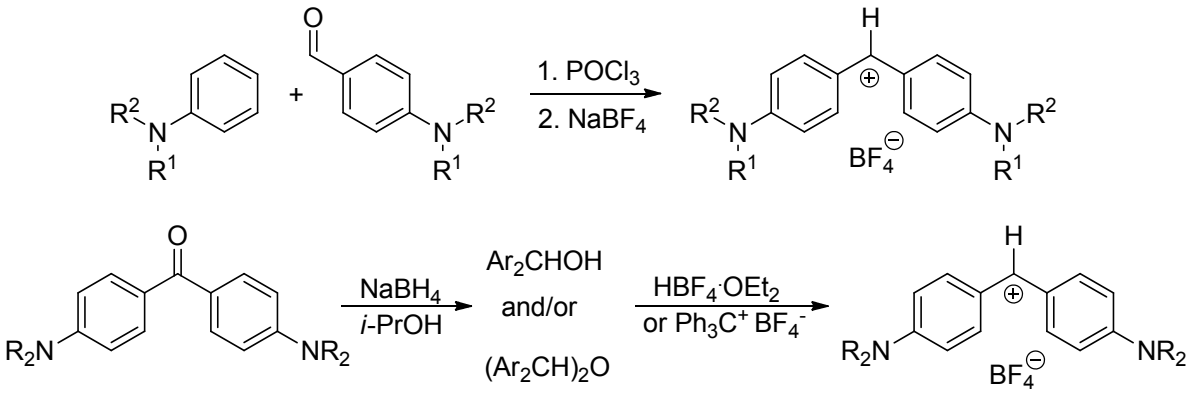
INTRODUCTION

The significance of carbocations as intermediates in organic chemistry has long been recognized and, after initial reports dealing with stable carbocations, namely trityl cations, several persistent types of these species have been thoroughly studied, normally at low temperature and in superacidic systems.[1] These cations are usually obtained in the presence of a nucleophile which should trap these normally unstable intermediates immediately after their formation.

Diarylmethyl (benzhydrylium) carbocations have been the subject of both mechanistic and preparative studies into their use as versatile intermediates for aryl substituted compound synthesis. Some of these are stable enough to be spectroscopically studied and have often been generated *in situ* via the ionization of the corresponding dibenzylic alcohols[2] or halides[3] in superacidic medium and generally at low temperature (–70 °C). Other methods for the *in situ* generation of carbocations which are useful for solvolytic studies include laser flash induced photolysis of suitable precursors,[4] and benzhydryl ester or halide solvolysis.[5] DDQ mediated oxidative reaction conditions via benzylic carbon-hydrogen activation[6] and oxidative diarylmethane C–H bond dissociation using anodic oxidation (cation pool method)[7] have been used to produce *in situ* stabilized benzylic carbocations which were immediately reacted with nucleophiles. The latter method enables carbocations to be produced as tetrafluoroborates and accumulated at –78 °C before nucleophile addition.

Their reactivity as reference electrophiles towards a variety of nucleophiles has been investigated to a considerable extent. In particular, extensive electrophilicity and nucleophilicity reference scales for the characterization of an high number of these diarylmethyl cationic electrophiles and a large variety of neutral π-, n- and σ-nucleophiles or carbanions have been reported by Mayr *et al*.[8] Stable symmetric and asymmetric diarylcarbenium salts have been prepared and their reaction rates with various nucleophiles have been studied using conventional UV-vis spectroscopy or stopped–flow methods. Benzhydrylium ions, in most cases symmetric, have been prepared and isolated as tetrafluoroborates using a number of synthetic pathways: a) the phosphorus oxychloride promoted coupling of arenes and carbaldehydes, followed by treatment with aqueous $NaBF_4$ (no reaction details reported),[9a] b) the treatment of benzhydryl alcohols with tritylium tetrafluoroborate[9a] or $HBF_4.Et_2O$ (two examples characterized)[9a,b,c] and c) the treatment of benzhydryl ethers with $HBF_4.Et_2O$ (two examples characterized) (Scheme 1).[9a,b]

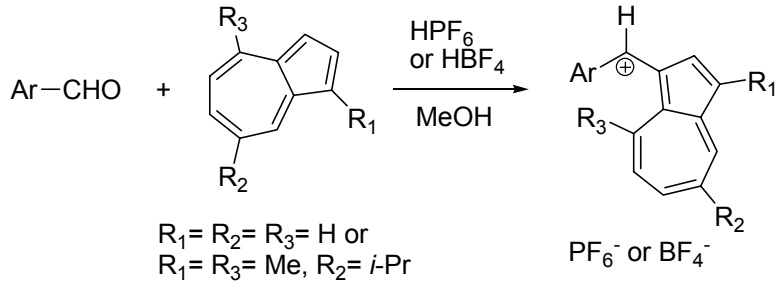
Scheme 1. Benzhydrylium tetrafluoroborate syntheses



More often than not they have been generated in situ generally as either tetrafluoroborates (as above) or alternatively, as tetrachloroborates[10] or triflates[11] after treatment with BCl_3 or TMSOTf, respectively, in DCM solution at low temperatures from suitable starting reagents (chlorides, acetates or OTMS derivatives). However, very few have been documented particularly well as far

as detailed reaction conditions for their preparation and conversions, accurate spectroscopic characterization and other chemical properties are concerned.
Finally, mono- and dicarbenium ions stabilized by expanded π-electron systems and possessing a 3-guaiazulenyl (or azulen-1-yl) group have recently been synthesized in high yields via the reaction of guaiazulene (or azulene) with aryl aldehydes (activated benzaldehydes, five-membered heteroaryl aldehyde, dicarbaldehydes, all-*trans*-retinal and *trans*-cinnamaldehyde) in the presence of hexafluorophosphoric (or tetrafluoroboric acid) in methanol (or other solvent) at 25 °C (Scheme 2). Crystal structures, spectroscopic, electrochemical and chemical properties have been discussed with a view to a comparative study.[12]
In this article we report the full details of our studies on the synthesis, structure characterization and stability of new nonsymmetric diarylmethylium ions isolated as stable *o*-benzenedisulfonimide salts, which are ready to use and have a long shelf-life.

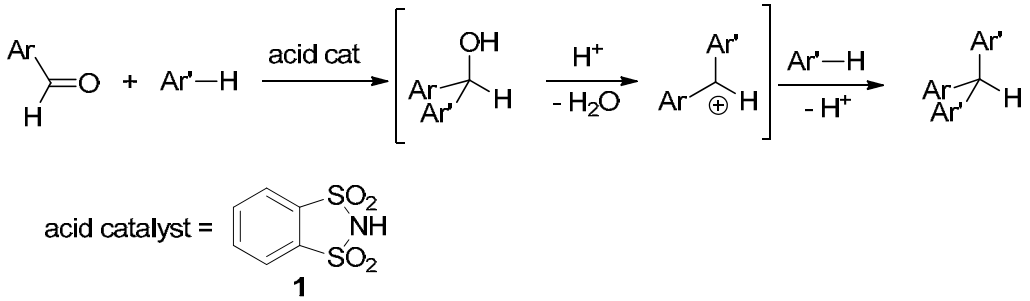
Scheme 2. Syntheses of carbenium salts stabilized by a 1-azulenyl or a 3-(guaiazulenyl) group



RESULTS AND DISCUSSION

In a previous paper, we reported a simple and efficient method for the preparation of symmetric triarylmethanes (TRAMs), from activated aryl aldehydes and activated arenes, using a multistep Friedel–Crafts hydroxyalkylation in the presence of catalytic amounts of a strong Brønsted acid, namely the *o*-benzenedisulfonimide (**1**, OBS) (Scheme 3).[13] Following a well-established mechanism pathway, the diarylmethanol produced in the first step dehydrates immediately to a diarylcarbenium ion, which reacts with a second molecule of the aromatic compound giving rise to a TRAM derivative. The synthetic procedure was extended to the synthesis of bis- and trisindolylmethanes (3,3'-BIMs and 3,3',3"-TIMs) by means of an indole reaction with aryl aldehydes or 3-formylindole, respectively, in the presence of **1** as the catalyst.

Scheme 3. Triarylmethane synthesis catalyzed by *o*-benzenedisulfonimide (1)

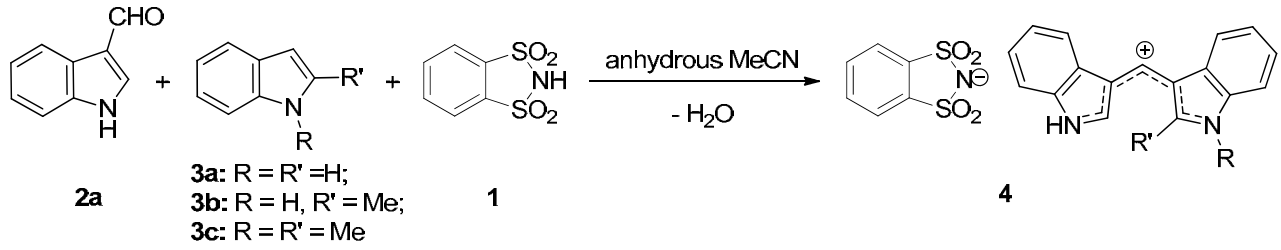


Encouraged by the good results, we decided to study the reaction mechanism further, with an eye to preparing, isolating and characterizing the carbocation intermediates. From a literature survey, we

found that 3-formylindole, heated in diluted sulfuric acid, has been reported to form urorosein salt,[14] which is very stable in the presence of strong acids at pH < 1.[15] The corresponding perchlorate was isolated in high yield from 3-formylindole and indole in hot MeOH, but no characterization was reported.[16] Some substituted phenyl(2-methyl-3H-indolylidene)methanes have been prepared and isolated as hydrochlorides (or hydrogenosulfates) from aromatic aldehydes and 2-methylindole in HCl saturated ethanol.[17] More stable bisindolylmethylium tetrafluoroborates[18a] or perchlorates[18b] have been prepared. The former have been synthesized by reacting 3-formylindole with 2-substituted indoles, whilst the latter have been isolated, together with the corresponding TIMs, from the reaction of 2-substituted indoles with 1,2-disubstituted-3-formylindoles in MeCN or from trisindolylmethane acidic cleavage in chloroform. In fact trisindolylmethanes are known to be readily cleaved by acids and give rise to resonance stabilized ammonium ions,[19] while symmetric and asymmetric TIMs have often been isolated as a mixture from the reaction of 3-formylindoles with substituted indoles in the presence of different acid catalysts.[20] Except for these few literature reports,[12,17,18] no systematic studies into the synthetic feasibility of diarylcarbenium salt synthesis and isolation *via* the direct coupling of aryl (or heteroaryl) aldehydes and arenes (or heteroarenes) have been carried out.

Following literature suggestions, 3-formylindole (**2a**) was chosen as the model aldehyde. In an initial investigation, it was reacted with indole derivatives **3** in the presence of acid **1**, in an 1.2:1:1.2 ratio in anhydrous MeCN (Scheme 4). In this reaction it was expected that *o*-benzenedisulfonimide would provide a counteranion of well-known stabilizing power.[21] We were aiming to isolate the intermediate salt **4**, which is highly stabilized by the resonance delocalization of the positive charge on both indole moieties.

Scheme 4. Synthesis of *o*-benzenedisulfonimide salts 4 starting from 3-formylindole



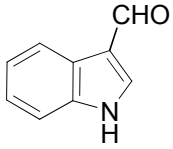
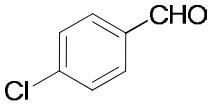
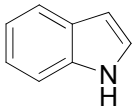
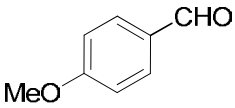
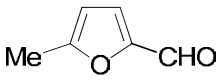
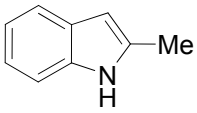
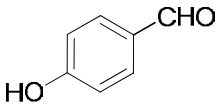
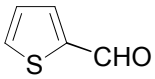
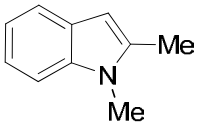
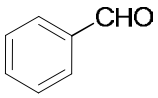
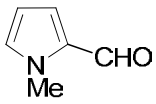
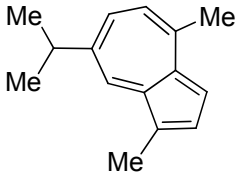
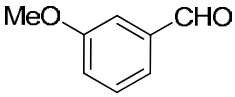
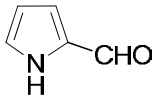
Initial trials to react 3-formylindole **2a** and unsubstituted indole (R = R'= H, **3a**) in the presence of **1** in MeCN furnished tar powders as the predominant products along with a small amount of red solid product, the ratio of which was independent of the dilution of the reaction mixture or of the reagent addition order. The black powder was probably the acid-catalyzed polymerization product of indole moieties through 2,3 linkages, as largely reported in literature.[22]

Then, 3-formylindole was reacted with 2-methylindole (R = H, R' = Me, **3b**). Here the methyl group in 2 should prevent acid-catalyzed polymerization. A solution of **3b** in anhydrous MeCN was added to a solution of **2a** and **1** in the same solvent at room temperature. The reaction was run with nearly equimolar amounts of all reagents (1: 1.2 : 1.2 molar ratio, respectively) and, after stirring for a few minutes, the separation of a brilliant red solid was observed. The solid was gathered on a büchner funnel, washed with small portions of anhydrous Et_2O and characterized by NMR, mass spectrometry and elemental analysis.

Gratifyingly, (3-indolyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (**4a**) was isolated in a 96% yield (Table 1, entry 1). Salt **4a** was further purified by means of its recrystallization from MeCN–Et_2O, and stored as a stable red powder at low temperature for long periods without significant loss of purity (^1H and ^{13}C NMR).

The synthetic procedure was then applied to a number of aromatic and heteroaromatic aldehydes and activated aromatic compounds. The structures of all tested reagents and the reaction results are reported in Reagent Chart 1 and in Table 1, respectively.

Reagent Chart 1

	Aldehydes **2**			Aromatic substrates **3** and **6**	
2a		**2f**		**3a**	
2b		**2g**		**3b**	
2c		**2h**		**3c**	
2d		**2i**		**6**	
2e		**2j**			

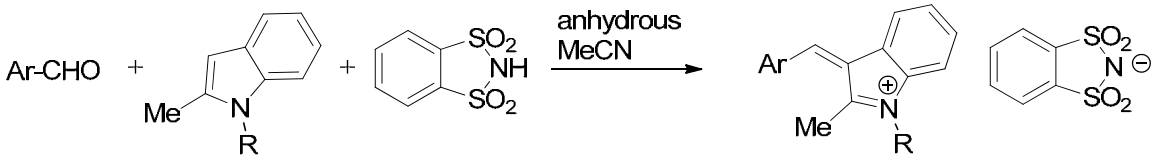
The reactions of these aldehydes with 2-methylindole (**3b**) gave salts containing a single indole moiety. Following the above optimized preparative conditions, reactions of the electron-donating group substituted benzaldehydes **2b** and **2c** and 2-methylindole furnished the *o*-benzenedisulfonimide salts salts **4b** and **4c** which were isolated in high yields (Table 1, entries 2 and 3) and fully characterized. In general, it was necessary to add anhydrous Et_2O to complete salt precipitation.

In order to further extend the synthetic utility of the present method, unsubstituted benzaldehyde (**2d**) and less activated 3-methoxybenzaldeheyde (**2e**) were reacted with **3b**: salts **4d** and **4e** were obtained although in lower yield (Table 1, entries 4 and 5). Then, electron-withdrawing group substituted aldehydes were tested, however, whilst salt **4f** was obtained in high yield and purity from 4-chlorobenzaldehyde (**2f**) (Table 1, entry 6), the reaction of 4-nitrobenzaldehyde gave only a little amount of black solid. Spectroscopic analyses of the isolated solid and chromatographic analyses of the complex reaction mixture proved that the reaction did not occur. Furthermore, traces of the triarylmethane product were detected.

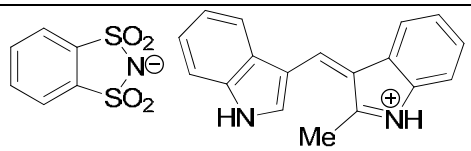
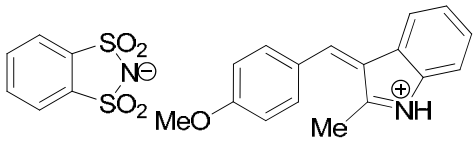
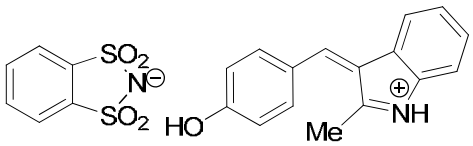
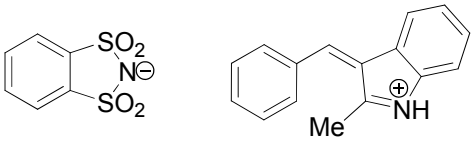
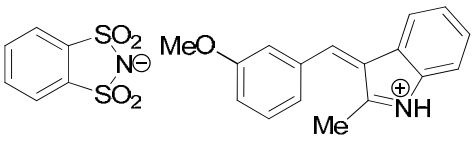
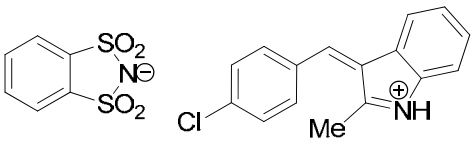
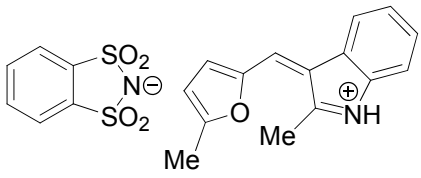
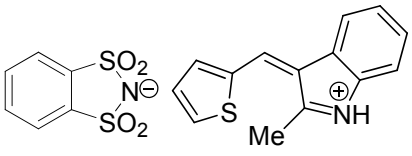
In the light of these results, we suggest that the electron-donating substituent effect of aldehydes **2b**–**c** strongly stabilizes the carbenium reaction intermediates, which could be easily isolated as *o*-benzenedisulfonimide salts. Starting from 4-nitrobenzaldehyde, the too unstable corresponding

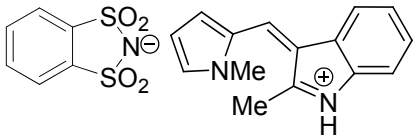
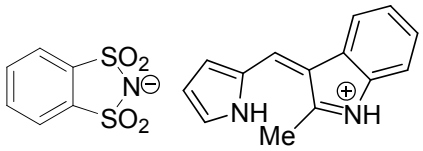
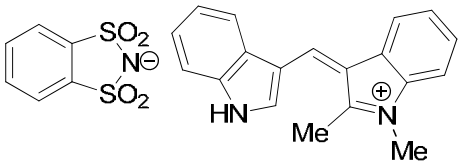
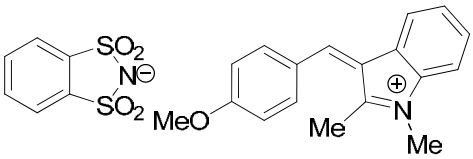
carbocation could not be isolated, owing to the strong electron-withdrawing substituent effect. Furthermore, its great reactivity has been documented in TRAM synthesis from 4-nitrobenzaldehyde and indoles in the absence of any catalyst under heating.[13,23] In the case of **2f**, the mesomeric effect of the halogen prevailed over the inductive one as demonstrated by the high yield of isolated salt **4f**. Accordingly, salts **4d** and **4e** were isolated in significantly lower yield.

Table 1: Diarylmethylium *o*-benzenedisulfonimides **4a**–l[a]



2a–j **3b–c** **1** **4a–l**

Entry	Reactants		Products **4**		**4** Yield (%)[b]
1	**2a**	**3b**	**4a**		96
2	**2b**	**3b**	**4b**		90
3	**2c**	**3b**	**4c**		91
4	**2d**	**3b**	**4d**		47
5	**2e**	**3b**	**4e**		52
6	**2f**	**3b**	**4f**		94
7	**2g**	**3b**	**4g**		97
8	**2h**	**3b**	**4h**		95

9	**2i**	**3b**	**4i**		94
10	**2j**	**3b**	**4j**		82
11	**2a**	**3c**	**4k**		96
12	**2b**	**3c**	**4l**		91

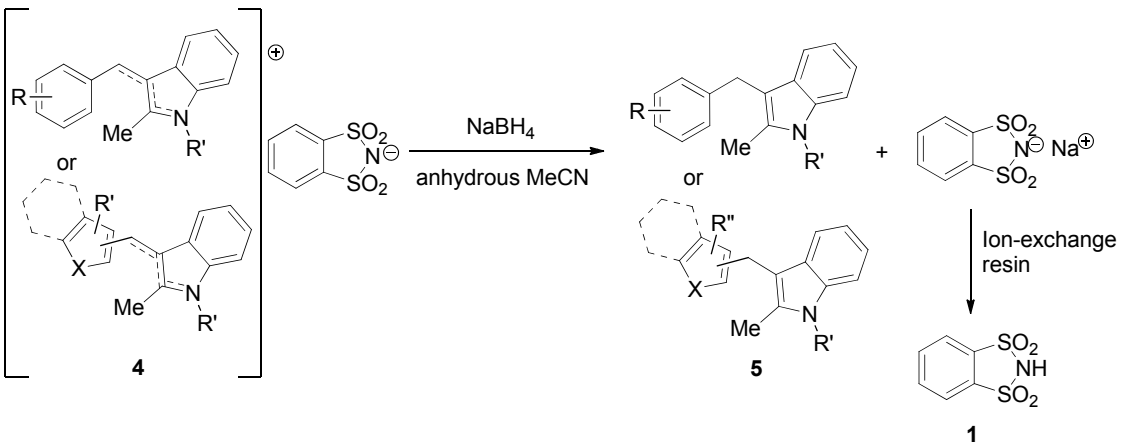
[a] Reaction conditions: **2 : 3 : 1** molar ratio = 1.2 : 1 : 1.2; anhydrous MeCN, rt.
[b] Yields refer to pure solid isolated products.

In the next phase the acid-sensitive electron-rich five-membered heteroaryl aldehydes **2g**, **2h** and **2i** were tested. The (5-methyl-2-furyl), 2-thienyl and (1-methyl-2-pyrrolyl)(2-methyl-3-indolyl)methylium salts **4g–i** were obtained in good yields (entries 7–9). In order to prevent the acid polymerization of the more acid-sensitive 2-formylpyrrole (**2j**), reaction conditions were slightly modified as follows: separate solutions of **2j** and **1** in anhydrous MeCN were simultaneously dropwise added to a solution of **3b** in the same solvent. Salt **4j** was obtained in a fairly lower yield (entry 10).

The molecular structures of salts **4b–j** were established in the same way as for salt **4a**. All of these isolated deeply colored solid salts proved to be stable to air and moisture, storable at low temperatures and ready to use.

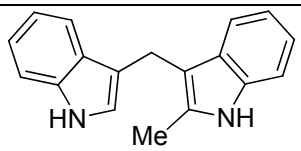
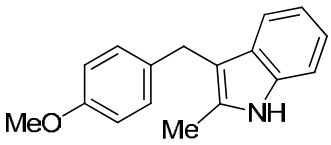
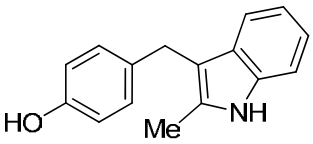
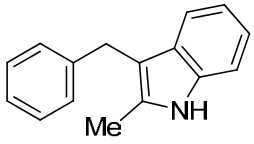
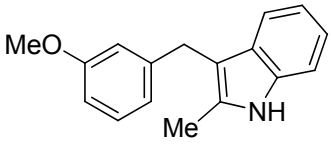
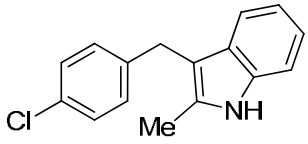
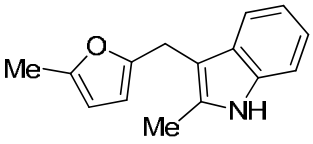
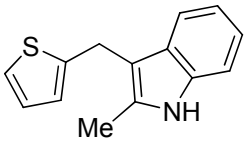
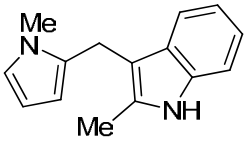
The identity and purity of salts **4** were confirmed by means of $NaBH_4$ chemical reduction in anhydrous MeCN. The aryl(2-methyl-3-indolyl)methanes **5a–j** were obtained in yields ranging from 80 to 96%. (Scheme 5; Table 2). As in the case of the parent salt yields, reduction products including a pyrrole moiety were obtained in modest yields (Table 2, entries 8 and 9).

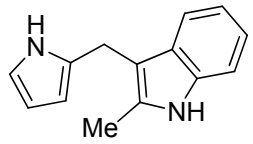
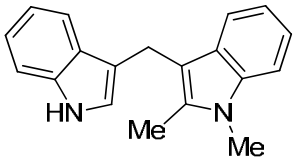
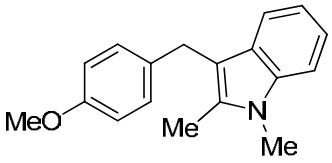
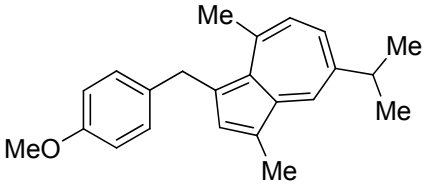
Scheme 5. Reduction of salts 4 to diarylmethanes 5.



The scope of carbocation synthesis by direct coupling reaction between aldehydes and arenes was further tested by reacting carbonyl derivatives **2a** and **2b** with 1,2-dimethylindole (**3c**) as the nucleophile. Diarylmethylium salts **4k** and **4l** were analogously isolated in high yields (Table 1, entries 11 and 12) and their purity was proven by spectroscopic methods and by chemical reduction to diarylmethanes **5k** and **5l** as described above (Table 2, entries 11 and 12).

Table 2 Diarylmethanes **5a**–**m**[a]

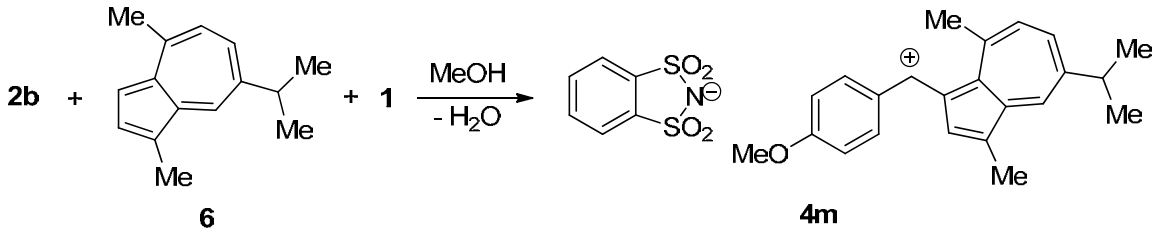
entry	*o*-benzenedisulfonimide salts **4**	Diarylmethanes **5**		**5** Yield (%)[b]
1	**4a**	**5a**		92
2	**4b**	**5b**		93
3	**4c**	**5c**		90
4	**4d**	**5d**		99
5	**4e**	**5e**		80
6	**4f**	**5f**		90
7	**4g**	**5g**		91
8	**4h**	**5h**		88
9	**4i**	**5i**		68

10	**4j**	**5j**		67
11	**4k**	**5k**		96
12	**4l**	**5l**		86
13	**4m**	**5m**		94

[a] Reaction conditions: $NaBH_4$, anhydrous MeCN, rt.
[b] Yields refer to isolated products purified by column chromatography.

In Takekuma's papers,[12] benzhydryl hexafluorophosphates bearing a 3-guaiazulenyl group and an activated aryl or five-membered heteroaryl group were prepared in MeOH at 25 °C. Our efforts directed to obtain (3-guaiazulenyl)(4-methoxyphenyl)methylium *o*-benzenedisulfonimide (**4m**) from **2b** and guaiazulene (**6**) in the presence of OBS and according to our conditions in MeCN at rt, gave the expected salt in a low 25% yield, whilst a yield of 99% was obtained when the reaction was carried out in MeOH (Scheme 6). Salt identity and purity were confirmed by spectroscopic analyses and by reduction to diarylmethane **5m** with $NaBH_4$ (Table 2, entry 13).

Scheme 6. Synthesis of salt 4m



Interestingly, (4-methoxyphenyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (**4b**) could not be prepared in MeOH. These results suggest that the choice of the solvent is crucial and it must consider the nature of the involved nucleophile; however**, f**urther studies are in progress.
OBS was easily recoverable after the work-up of the aqueous reaction mixture and it was recycled for use in other syntheses after rapid elution on a Dowex ion–exchange resin, thus confirming the economic and ecological advantages that have already been reported.[13]
Then, the reactivity of aldehydes **2a,b,g,i** with activated aromatic nucleophiles (1,2,4-trimethoxybenzene, 2-methylfuran, 1-methylpyrrole and 2,5-dimethylpyrrole) was studied in the presence of OBS in the same molar ratios as above. Unfortunately, either no reaction or very complex reaction mixtures were obtained, although in some cases the corresponding TRAMs were

achieved in good yields under stronger reaction conditions (see for example reaction of **2b** with 1,2,4-trimethoxybenzene or 2-methylfuran).[13]
In the light of these results, it can be inferred that, according to the experimental conditions here described, one indole moiety is needed to stabilize the secondary diarylcarbenium ions like the guaiazulenyl group in Takekuma's work.[12] Furthermore, it should be noted that the indole ring cannot be replaced by the pyrrole ring.
In salts **4**, the diarylcarbenium ion can be stabilized by positive charge resonance delocalization both onto the phenyl and the indole rings. For example, salt **4b** can be described by the more stable resonance structures I, II and III (Figure 1).

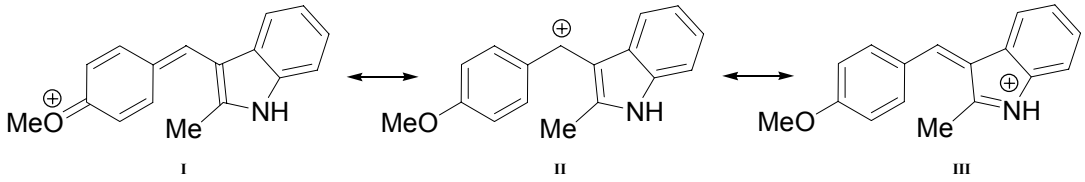


Figure 1. Resonance structures for salt 4b

In order to understand the indole stabilization effect and fully characterize the structure of benzhydryl cations, X-ray analysis of salt **4b** was carried out.
The molecular structure of **4b** is shown in Fig.2.

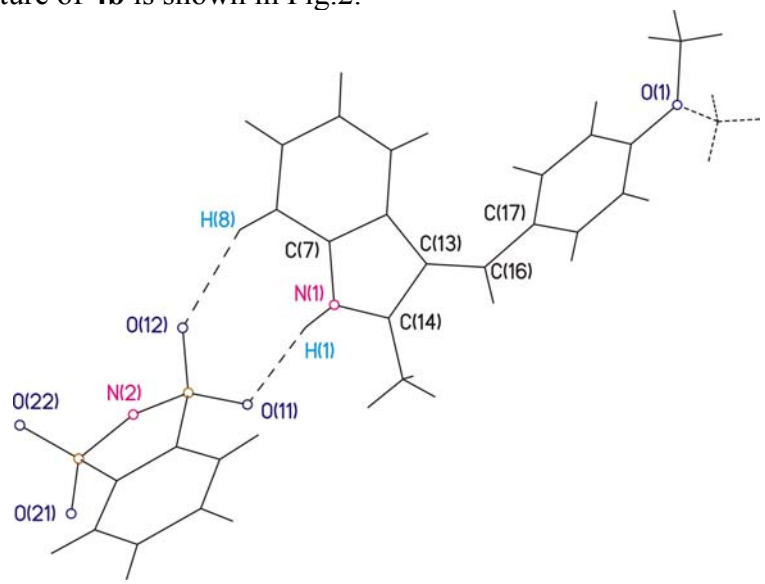


Figure 2. Anion and cation of salt **4b** $[C_6H_4NO_4S_2][C_{17}H_{16}NO]$. Relevant bond lengths(Å) with e.s.d.'s: S(1)-O(12) 1.4348(15), S(1)-O(11) 1.4386(15), S(1)-N(2) 1.555(2), S(2)-O(21) 1.4189(17), S(2)-O(22) 1.4193(17), S(2)-N(2) 1.583(2), N(1)-C(14) 1.306(3), N(1)-C(7) 1.404(3), C(13)-C(16) 1.358(3), C(13)-C(14) 1.447(3), C(16)-C(17) 1.440(3). Methyls attached to O(1) are disordered.

Table 3. The most relevant hydrogen bonds in salt **4b**.

D–H···A	D–H (Å)	H···A(Å)	D···A(Å)	D–H···A (°)
N(1)–H(1)···O(11)	0.79(2)	2.08(2)	2.842(3)	165(2)

C(8)–H(8)···O(12)	0.90(2)	2.42(2)	3.224(3)	150(1)

The values of bond distances clearly agree with the resonance structure III. In fact the C(14)–N(1)(1.306(3) Å) and C(13)–C(16)(1.357(3)Å) distances have a formal double bond character, in particular when compared with the corresponding N(1)–C(7) (1.404(3) Å) and C(16)–C(17) (1.442(3) Å) bond lengths. The presence of the positive charge on the N(1) atom is also confirmed by the interaction with the anion. As in other compounds the hydrogen bond acceptor is an oxygen atom of the anion and not the N(2) atom. In fact the shorter hydrogen bonds involve the O(11) and O(12) atoms and NH(1) and CH(8) atoms of the same molecule (see Figure 2) while the other oxygen atoms and N(2) form quite longer hydrogen bonds with different cations. Other salts, for example $[NH_4][C_6H_4(SO_2)_2]\cdot H_2O$[24] and the structurally related $[M][C_6H_4(SO_2)_2]\cdot H_2O$(M= K,Rb),[25] show the same behaviour. The hydrogen bonds are listed in table 3. The bond length and angle values correspond to strong (NH(1)···O(11)) and weak(CH(8)···O(12)) character according to the classification of Desiraju.[26] N(2), O(21) and O(22) form very weak hydrogen bonds with C–H donors and create connections between different anions and cations. The other distances and angles in the two ions correspond to those reported in the literature. The anion is roughly planar with a mean deviation from planarity of 0.053 Å. The two parts of the cation are planar with a mean deviation from planarity of 0.021–0.039 Å and they form an angle of 31°. Two features are noteworthy: the planarity of the Ph-O(1)C(23A, B) moiety and the disorder of the two C(23) methyls with same occupancy factor. The C(20)-O(1) distance of 1.352(3) Å corresponds to a Csp^2-O bond length and is quite different from the O(1)-C(23A,B) distances (1.498(4) Å av.); the methoxy group planarity and the bond lengths are in accord with similar uncharged molecules. In the light of all previous results, we can conclude that the structure of the cation salt **4b** (and, in general, of our salts) is described by the resonance structure III.

CONCLUSIONS

In summary, in this paper we have reported the results of a systematic study of diarylcarbenium ion synthesis *via* the direct coupling of aryl (or heteroaryl) aldehydes and arenes (or heteroarenes). A number of new diarylmethilium ions bearing indole rings as the crucial framework for their stability have been isolated as stable *o*-benzenedisulfonimide salts which have long shelf-lives and are ready to use. Preparing other diarylcarbenium salts in the solid state is a challenging goal. In order to explore the synthetic feasibility and utility of these salts as highly reactive intermediates in organic reactions, research is currently under way on suitable reactions with a variety of nucleophiles and reaction conditions.

EXPERIMENTAL SECTION

GENERAL INFORMATION

All the reactions were conducted in vials using analytical grade reagents, and were monitored by TLC, GC, GC-MS and NMR spectrometry. GC-MS spectra were recorded on a mass selective detector connected to a GC with a cross-linked methyl silicone capillary column. Mass spectra were recorded on a mass spectrometer equipped with ElectroSpray Ionization source (ESI). Infrared (IR) data are presented as frequency of absorption (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or $CDCl_3$–CF_3COOD on a spectrometer at 200 MHz and 50 MHz, respectively; chemical shifts are given in ppm relative to $CDCl_3$. TLC were performed on silica gel TLCPET foils GF 254, 2–25 μm, layer thickness 0.2 mm, medium pore diameter 60 Å. Plates were visualized using UV

light (254 nm). Column chromatography was carried out using SiO_2 (pore size 70 Å, 70–230 mesh). Petroleum ether refers to the fraction boiling in the range 40–60 °C and is abbreviated as PE. Commercially available reagents and solvents were used without purification or distillation prior to use. DOWEX HCR-W2 ion-exchange resin was purchased. Room temperature (20–25 °C) is abbreviated as rt. *o*-Benzenedisulfonimide (**1**) was prepared as described in literature.[21] Details for the reactions and yields for the pure (GC, GC-MS, TLC, ^{1}H NMR) isolated products are listed in Table 1 and 2. The structure and purity of all new products were determined by elemental analysis, ESI, ^{1}H, ^{13}C NMR and DEPT spectra. The structure and purity of known products were confirmed by means of comparison of their physical and spectral data (MS, ^{1}H NMR and ^{13}C NMR) with those reported in literature.

Crystal analysis. The 38528 X-ray data reflections of compound **4b** have been collected at rt (λ=MoK$_\alpha$ 0.71073 Å) on a Gemini R Ultra diffractometer.[27] Crystal data: monoclinic C2/c, with a = 26.1638(12) Å, b = 13.1605(4) Å, c = 14.4032(6) Å, β = 118.224(5)°, Z = 4, Dc= 1.424 g/cm^3, μ = 0.282 mm^{-1}, crystal size 0.036 x 0.040 x 0.06 mm. Refinement: full-matrix least-squares on F^2; non hydrogen atoms have been anisotropically refined. The methoxy group is disordered between two equivalent positions with 0.5 occupancy factor. The majority of hydrogen atoms have been located in the final Fourier-difference maps and refined with coordinates and U_{iso} free. The H atoms of methyls C(23A,B) have been calculated and refined with U_{iso} = 1.5 U_{eq} of the corresponding bonded atoms. No absorption correction has been applied owing to the small μR. Unique data / parameters 5642 /362, GOOF = 0.821, R1 = 0.0410, wR2 = 0.0817 [I>2sigma(I)]. Software used: CrysAlisPro[28] (collection, integration), SHELXTL[29] (structure solution, conventional refinement and molecular graphics). Crystal data deposited at CSD with code CCDC 857161.

General Procedures:

General procedure for diarylmethylium *o*-benzenedisulfonimides 4a–i, k–l synthesis:

A solution of the aromatic compound **3** (3.0 mmol) in anhydrous MeCN (5 mL) was added dropwise at rt and under stirring to a mixture of aldehyde **2** (3.6 mmol) and *o*-benzenedisulfonimide (**1**, 0.79 g, 3.6 mmol) in anhydrous MeCN (15 mL). The deep colored solution lightened and a red solid separated. After stirring at rt for 30 min, anhydrous Et_2O was added to complete the separation and the solid was gathered on a Buchner funnel, washed with anhydrous Et_2O and dried under reduced pressure.

(3-Indolyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4a)

(1.37 g, 96% yield); dp 198.5–199.5 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.83 (s, 3H), 7.31–7.49 (m, 5H), 7.54–7.69 (m, 2H), 7.84–7.98 (m, 5H), 8.65 (s, 1H), 8.68 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 12.9, 113.8, 120.1 (q), 120.7, 121.8, 121.8 (2C), 124.2 (q), 125.0, 126.2, 126.2, 126.5, 127.4, 134.3 (2C), 137.3 (q), 138.1 (q), 139.2 (q, 3C), 141.3, 147.4, 162.6 (q); IR ($CHCl_3$) ν_{max} 3024, 3020, 2380, 1520, 1431, 1235, 1220, 1200; exact ESI full mass: found *m/z* 259.24 (calcd for $C_{18}H_{15}N_2^+$: *m/z* 259.12); Anal. Calcd for $C_{24}H_{19}N_3O_4S_2$: C, 60.36; H, 4.01; N, 8.80; S, 13.43; Found C, 60.32; H, 4.00; N, 8.78; S, 13.39.

(4-Methoxyphenyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4b)

(1.26 g, 90% yield);.dp 152.0–153.0 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.89 (s, 3H), 3.96 (s, 3H), 7.11 (d, *J* = 9.0 Hz, 2H), 7.32–7.55 (2 overlapped m, 3H), 7.77–7.85 (m, 2H), 7.87–7.95 (m, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 7.0 Hz, 1H), 8.37 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.5, 55.9, 115.2, 115.4 (2C), 121.9 (2C), 122.3, 123.9 (q), 125.5 (q), 127.6 (q), 127.9, 129.8, 134.5 (2C), 136.3 (2C), 139.0 (q, 2C), 139.7 (q), 157.7, 166.2 (q), 170.1 (q); IR ($CHCl_3$) ν_{max} 3026, 3018, 2400, 1522, 1430, 1230, 1190; exact ESI full mass: found *m/z* 250.22 (calcd for $C_{17}H_{16}NO^+$, *m/z* 250.12); Anal. Calcd for $C_{23}H_{20}N_2O_5S_2$: C, 58.96; H, 4.30; N, 5.98; S 13.69. Found C, 58.90; H, 4.32; N, 5.94; S, 13.70.

(4-Hydroxyphenyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4c)

(1.24 g, 91% yield); dp 173.1–174.0 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.87 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.39–7.49 (m, 3H), 7.81–7.96 (m, 6H), 8.09 (d, *J* = 6.6 Hz, 1H), 8.32 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.3,

114.9, 117.1 (2C), 121.8 (2C), 122.4, 123.9 (q), 125.4 (q), 127.1 (q), 127.9, 129.6, 134.3 (2C), 136.8 (2C), 139.2 (q), 139.5 (q), 158.1, 163.7 (q), 169.7 (q); IR ($CHCl_3$) ν_{max} 3028, 3018, 2400, 1510, 1430, 1215, 1200; exact ESI full mass: found *m/z* 236.26 (calcd for $C_{16}H_{14}NO$: M^+, *m/z* 236.11); Anal. Calcd for $C_{22}H_{18}N_2O_5S_2$: C, 58.14; H, 3.99; N, 6.16; S, 14.11. Found C, 58.20; H, 3.90; N, 6.20; S, 14.00.

(2-Methyl-3-indolyl)(phenyl)methylium *o*-benzenedisulfonimide (4d)

(0.62 g, 47% yield); dp 143.5–145.0 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 3.00 (s, 3H), 7.32–7.72 (m, 6H), 7.79–7.95 (m, 6H), 8.05 (d, *J* =7.8 Hz, 1H), 8.47 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.6, 115.5, 122.0 (2C), 123.1, 123.7 (q), 128.6, 129.4 (2C), 130.8, 131.2 (q), 131.7 (2C), 132.3 (q), 134.5 (2C), 134.8, 138.8 (q, 2C), 140.1 (q), 157.7, 172.6 (q); IR ($CHCl_3$) ν_{max} 3028, 3018, 2405, 1521, 1423, 1231; exact ESI full mass: found *m/z* 220.24 (calcd for $C_{16}H_{14}N$: M^+, *m/z* 220.11); Anal. Calcd for $C_{22}H_{18}N_2O_4S_2$: C, 60.26; H, 4.14; N, 6.39; S, 14.62. Found C, 60.10; H, 3.98; N, 6.25; S, 14.50.

(3-Methoxyphenyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4e)

(0.73 g, 52% yield);.dp 134.5–136.20 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.96 (s, 3H), 3.92 (s, 3H), 7.20–7.33 (m, 1H), 7.38–7.58 (m, 6H), 7.83–7.98 (m, 4H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.44 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.2, 55.4, 115.3, 116.3, 120.7, 122.1 (2C), 123.4, 123.6 (q), 124.8, 128.7, 130.7, 130.9, 131.5 (q), 133.6 (q), 134.9 (2C), 138.2 (q, 2C), 157.4, 159.3(q), 172.7 (q); IR ($CHCl_3$) ν_{max} 3023, 3016, 2400, 1521, 1421, 1216; exact ESI full mass: found *m/z* 250.20 (calcd for $C_{17}H_{16}NO^+$, *m/z* 250.12); Anal. Calcd for $C_{23}H_{20}N_2O_5S_2$: C, 58.96; H, 4.30; N, 5.98; S 13.69. Found C, 58.86; H, 4.20; N, 5.90; S, 13.76.

(4-Chlorophenyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4f)

(1.33 g, 94% yield); dp 180.6–181.5 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.95 (s, 3H), 7.33–7.61 (m, 5H), 7.80–8.05 (m, 7H), 8.43 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.5, 115.5, 122.0 (2C), 123.1, 123.5 (q), 128.8, 129.9 (2C), 130.6 (q), 130.9, 131.4 (q), 132.8 (2C), 134.7 (2C), 138.6 (q), 140.1 (q), 141.6 (q), 155.9, 172.8 (q); IR ($CHCl_3$) ν_{max} 3023, 3018, 2400, 1521, 1424, 1216; exact ESI full mass: found *m/z* 254.19 (calcd for $C_{16}H_{13}ClN^+$: M^+, *m/z* 254.07); Anal. Calcd for $C_{22}H_{17}ClN_2O_4S_2$: C, 58.87; H, 3.62; Cl, 7.50; N, 5.92; S, 13.56. Found C, 58.62; H, 3.60; Cl, 7.37; N, 6.00; S, 13.42.

(5-Methyl-2-furyl)(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide (4g)

(1.29 g, 97% yield); dp 172–174 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.72 (s, 3H), 2.84 (s, 3H), 6.67 (d, *J* = 3.8 Hz, 1H), 7.43–7.52 (m, 3H), 7.65 (d, *J* = 3.8, 1H), 7.80 (s, 1H), 7.84–7.99 (m, 4H), 8.58–8.66 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.1, 15.0, 114.4, 115.2, 121.9 (2C), 122.2 (q), 123.9 (q), 124.5, 127.4, 128.9, 134.1, 134.3 (2C), 137.1, 138.9 (q), 139.1 (q, 2C), 149.8 (q), 168.2 (q), 168.9 (q); IR ($CHCl_3$) ν_{max} 3027, 3020, 2390, 1515, 1435, 1235, 1205; exact ESI full mass: found *m/z* 224.17 (calcd for $C_{15}H_{14}NO$: M^+, *m/z* 224.11); Anal. Calcd for $C_{21}H_{18}N_2O_5S_2$: C, 57.00; H, 4.10; N, 6.33; S, 14.49. Found C, 56.88; H, 4.18; N, 6.38; S, 14.41.

(2-Methyl-3-indolyl)(2-thienyl)methylium *o*-benzenedisulfonimide (4h)

(1.24 g, 95% yield); dp 159–160 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.93 (s, 3H), 7.41–7.58 (m, 4H), 7.76–7.84 (m, 2H), 7.88–7.94 (m, 2H), 8.08 (d, *J* = 4.0 Hz, 1H), 8.22 (d, *J* = 5.0 Hz, 1H), 8.46 (s, 1H) overlapped with 8.48–8.56 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.6, 115.3, 121.9 (2C), 123.0 (q), 123.4, 125.9 (q), 128.0, 129.9, 130.5, 134.4 (2C), 137.0 (q), 139.0 (q, 2C), 139.3 (q), 142.7, 145.0, 146.3, 170.9 (q); IR ($CHCl_3$) ν_{max} 3021, 3015, 2390, 1520, 1420, 1235, 1200; exact ESI full mass: found *m/z* 226.18 (calcd for $C_{14}H_{12}NS$: M^+, *m/z* 226.06); Anal. Calcd for $C_{20}H_{16}N_2O_4S_3$: C, 54.04; H, 3.63; N, 6.30; S, 21.64. Found C, 53.96; H, 3.61; N, 6.38; S, 21.55.

(2-Methyl-3-indolyl)(1-methyl-2-pyrrolyl)methylium *o*-benzenedisulfonimide (4i)

(1.24 g, 94% yield); dp 146.4–148.0 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.80 (s, 3H), 3.95 (s, 3H), 6.66 (dd, *J*= 4.8 and *J*= 2.2 Hz, 1H), 7.31–7.40

(m, 2H), 7.42–7.52 (m, 2H), 7.74–7.83 (m, 2H), 7.84–7.94 (m, 3H), 8.04 (br s, 1H), 8.14–8.22 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 12.9, 34.8, 114.1, 116.3, 119.9 (q), 121.0, 121.8 (2C), 124.1 (q), 126.4, 127.9, 128.5, 131.7 (q), 134.3 (2C), 138.2, 138.5 (q), 139.1 (q, 2C), 141.2 (q); IR ($CHCl_3$) ν_{max} 3026, 3018, 2360, 1530, 1427, 1225, 1210, 1200; exact ESI full mass: found *m/z* 223.19 (calcd for $C_{15}H_{15}N_2$: M^+, *m/z* 223.2); Anal. Calcd for $C_{21}H_{19}N_3O_4S_2$: C, 57.13; H, 4.34; N, 9.52; S, 14.52. Found C, 57.18; H, 4.31; N, 9.50; S, 14.47.

(2-Methyl-3-indolyl)(2-pyrrolyl)methylium *o*-benzenedisulfonimide (4j)

A solution of the aromatic compound **3b** (0.39 g; 3.0 mmol) in MeCN (10 mL) and a solution of *o*–benzenedisulfonimide (**1**, 0.79 g, 3.6 mmol) in MeCN (10 mL) were simultaneously added dropwise to a solution of the aldehyde **2g** (0.34; 3.6 mmol) in MeCN (10 mL) at rt and under stirring. The solution was deeply red colored and a black powder began to separate. After stirring at rt for 30 min, the solid was filtered off. Anhydrous Et_2O (75 mL) was added to the solution to precipitate the brown solid which was gathered on a Buchner funnel, washed thoroughly with anhydrous Et_2O and dried under reduced pressure.

(0.86 g, 67% yield); dp 166.7–167.8 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.70 (s, 3H), 6.68–6.73 (m, 1H), 7.28–7.44 (m, 3H), 7.67–7.72 (m, 2H), 7.73–7.81 (m, 2H), 7.82–7.93 (m, 2H), 8.00–8.06 (m, 1H), 8.17 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 12.9, 114.0, 118.0, 119.3 (q), 120.9, 121.8 (2C), 123.9 (q), 126.3, 127.6, 129.0, 130.8 (q, 2C), 134.2 (2C), 137.8, 138.2 (q), 139.2 (q, 2C), 141.1; IR ($CHCl_3$) ν_{max} 3026, 3018, 2415, 1515, 1425, 1225, 1211, 1200; exact ESI full mass: found *m/z* 209.20 (calcd for $C_{14}H_{13}N_2$: M^+, *m/z* 209.11); Anal. Calcd for $C_{20}H_{17}N_3O_4S_2$: C, 56.19; H, 4.01; N, 9.83; S, 15.00. Found C, 56.10; H, 3.95; N, 10.05; S, 14.90.

(1,2-Dimethyl-3-indolyl)(3-indolyl)methylium *o*-benzenedisulfonimide (4k)

(1.42 g, 96% yield); dp 194.4–195.5 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.80 (s, 3H), 3.87 (s, 3H), 7.30–7.46 (m, 5H), 7.49–7.66 (m, 2H), 7.69–7.77 (m, 2H), 7.79–7.90 (m, 3H), 8.68 (s, 1H), 8.71 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 11.9, 31.8, 111.6, 114.2, 117.5 (q), 120.1 (q), 120.6, 121.7 (2C), 122.3, 124.3 (q), 124.9, 126.2 (2C), 126.5, 127.2, 134.0 (2C), 137.7 (q), 139.5 (q, 2C), 140.2 (q, 2C), 147.6, 161.1 (q); IR ($CHCl_3$) ν_{max} 3027, 3018, 2392, 1535, 1435, 1227, 1210, 1200; exact ESI full mass: found *m/z* 273.28 (calcd for $C_{19}H_{17}N_2$: M^+, *m/z* 273.14); Anal. Calcd for $C_{25}H_{21}N_3O_4S_2$: C, 61.08; H, 4.31; N, 8.55; S, 13.05. Found C, 60.99; H, 4.31; N, 8.53; S, 13.11.

(1,2-Dimethyl-3-indolyl)(4-methoxyphenyl)methylium *o*-benzenedisulfonimide (4l)

(1.32 g, 91% yield); dp 153.1–154.2 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 2.89 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.38–7.49 (m, 1H), 7.49–7.56 (m, 2H), 7.72–7.79 (m, 2H), 7.80–7.88 (m, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 7.60 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 12.3, 32.9, 55.9, 113.0, 115.4 (2C), 121.9 (2C), 122.6, 124.0 (q), 125.6 (q), 127.2 (q), 128.4, 129.7, 134.3 (2C), 136.4 (2C), 139.0 (q), 142.0 (q), 157.6, 166.2 (q), 170.0 (q); IR ($CHCl_3$) ν_{max} 3028, 3019, 2410, 1533, 1423, 1235, 1198; exact ESI full mass: found *m/z* 264.25 (calcd for $C_{18}H_{18}NO$: M^+, *m/z* 264.14); Anal. Calcd for $C_{24}H_{22}N_2O_5S_2$: C, 59.73; H, 4.60; N, 5.81; S, 13.29. Found C, 59.71; H, 4.61; N, 5.83; S, 13.19.

(3-Guaiazulenyl)(4-methoxyphenyl)methylium *o*-benzenedisulfonimide (4m)

A solution of the compound **6** (0.20 g; 1.0 mmol) in MeOH (3 mL) was added dropwise at rt and under stirring to a mixture of aldehyde **2b** (0.16 g; 1.2 mmol) and *o*-benzenedisulfonimide (**1**, 0.26 g, 1.2 mmol) in MeOH (3 mL). The solution was deeply red colored. After stirring at rt for 120 min, anhydrous Et_2O was added to complete the separation and the red solid was gathered on a Buchner funnel, washed thoroughly with anhydrous Et_2O and dried under reduced pressure.

(0.53 g, 99% yield); dp 151.4–152.3 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$–CF_3COOD): δ = 1.42 (d, *J* = 7.0 Hz, 6H), 2.50 (s, 3H), 3.32 (s, 3H) overlapped with 3.30–3.45 (m, 1H), 3.91 (s, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.77–7.85 (m, 2H), 7.86–7.98 (2 m overlapped, 3H), 8.21 (dd, *J* = 11.2 and 2.0 Hz, 1H), 8.35 (d, *J* = 11.0 Hz, 1H), 8.43

(d, J = 2.0 Hz, 1H), 8.66 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$–CF_3COOD): δ = 13.2, 23.4 (2C), 29.2, 39.4, 55.7, 109.0 (q), 115.6 (2C), 121.9 (2C), 127.7 (q), 134.3 (2C), 136.0, 136.4 (q), 137.5, 139.1 (q, 2C), 141.3, 143.0 (2C), 147.7, 150.9, 152.2 (q), 155.3 (q), 158.6 (q), 164.4 (q), 168.3 (q); IR ($CHCl_3$) ν_{max} 3025, 3016, 2405, 1531, 1425, 1235, 1227, 1205, 1200; exact ESI full mass: found *m/z* 317.22 (calcd for $C_{23}H_{25}O$: M^+, *m/z* 317.19); Anal. Calcd for $C_{29}H_{29}NO_5S_2$: C, 65.02; H, 5.46; N, 2.61; S, 11.97. Found C, 65.05; H, 5.49; N, 2.58; S, 11.90.

General procedure for diarylmethylium *o*-benzenedisulfonimides 4a–m reduction:

$NaBH_4$ (2.0 mmol, 0.08 g) was added portionwise at rt and under stirring to a solution of the salts **4** (1.0 mmol) in anhydrous MeCN (15 mL). The reaction was instantaneous and the deep colored solution immediately faded. After stirring at rt for 10 min, the reaction mixture was treated with Et_2O/water (40 mL; 1 : 1). The organic phase was separated, washed with brine (2 x 20 ml) and evaporated under reduced pressure. The crude residue was the virtually pure reduction product **5** (GC, GC–MS, ^{1}H NMR). The eluent of the short column chromatography purification, isolated product yields and physical and spectroscopic data are listed below.

(3-Indolyl)(2-methyl-3-indolyl)methane (5a)[30]

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.24 g, 93% yield); mp 172.2–173 °C (DCM–PE) (lit. mp 131–134 °C);[30] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 4.12 (s, 2H), 6.61 (br s, 1H), 6.95–7.30 (m, 7H), 7.43 (d, J = 7.4 Hz, 1H), 7.56–7.72 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 19.8, 109.9, 110.2 (q), 110.9, 116.0, 118.4, 118.7, 118.9, 119.0, 120.7, 121.7, 121.9 (q), 127.3 (q), 128.8 (q), 131.1 (q), 135.1 (q), 136.3 (q); MS *m/z* (%): 260 [M^+](100), 245 (55), 143 (45).

(4-Methoxyphenyl)(2-methyl-3-indolyl)methane (5b)[31]

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.23 g, 93% yield); mp 116.6–117.8 °C (DCM–PE) (lit. mp 119–120 °C);[17b] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 3.92 (s, 3H), 4.32 (s, 2H), 7.08 (d, J = 8.6 Hz, 2H), 7.35–7.50 (m, 5H), 7.67 (br s, 1H), 7.72–7.85 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 29.4, 55.3, 110.7 (q), 110.8, 114.0 (2C), 118.6, 119.4, 121.1, 129.1 (q), 129.5 (2C), 132.0 (q), 134.2 (q), 135.6 (q), 157.8 (q); MS *m/z* (%): 251 [M^+](100), 236 (75), 144 (70).

(4-Hydroxyphenyl)(2-methyl-3-indolyl)methane (5c)[32]

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.21 g, 90% yield); mp 141.8–142.6 °C (DCM–PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 3.94 (s, 2H), 6.62 (d, J = 8.4 Hz, 2H), 6.90–7.12 (m, 5H), 7.80–7.25 (m, 1H), 7.30–7.38 (m,1H), 7.73 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 29.0, 110.0, 110.7 (q), 115.0 (2C), 118.2, 119.0, 120.8, 128.7 (q), 129.1 (2C), 131.4 (q), 133.6 (q), 135.1 (q), 153.4 (q); MS *m/z* (%): 237 [M^+](100), 222 (70), 144 (85).

(2-Methyl-3-indolyl)phenylmethane (5d)[31]

Chromatographic eluent: PE–AcOEt 8:2; white solid (0.22 g, quant. yield); mp 118.5–119.2 °C (DCM–PE) (lit. mp 122–123 °C);[33] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 4.03 (s, 2H), 6.94–7.25 (m, 8H), 7.35 (d, J = 7.6 Hz, 1H), 7.73 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 29.9, 109.9, 110.4 (q), 118.2, 119.1, 120.8, 125.4, 128.1 (4C), 128.7 (q), 131.4 (q), 135.1 (q), 141.5 (q); MS *m/z* (%): 221 [M^+](100), 206 (45), 144 (90).

(3-Methoxyphenyl)(2-methyl-3-indolyl)methane (5e)[31]

Chromatographic eluent: PE–AcOEt 7:2; white solid (0.20 g, 80% yield); mp 87.5–88.2 °C (DCM–PE) (lit. mp 84–87 °C);[31] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 3.72 (s, 3H), 4.02 (s, 2H), 6.65–6.85 (m, 3H), 6.98–7.26 (m, 4H), 7.40 (d, J = 8.2 Hz, 1H), 7.68 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 30.0, 54.9, 110.0, 110.2 (q), 110.6, 114.2, 118.2, 119.1, 120.6, 120.8, 128.7 (q), 129.1, 131.5 (q), 135.1 (q), 143.3 (q), 159.5 (q); MS *m/z* (%): 251 [M^+](100), 236 (45), 144 (85).

(4-Chlorophenyl)(2-methyl-3-indolyl)methane (5f)

Chromatographic eluent: PE–AcOEt 8:2; white solid (0.23 g, 90% yield); mp 133.5–134.5 °C (DCM–PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 3.98 (s, 2H), 6.94–7.38 (m,8H), 7.72 (br

s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 29.3, 109.9(q), 110.0, 118.0, 119.2, 121.0, 128.2 (2C), 128.5 (q), 129.4 (2C), 131.1 (q), 131.5 (q), 135.1 (q), 139.9 (q); MS *m/z* (%): 255 [M^+](95), 240 (50), 144 (100); Anal. Calcd for $C_{16}H_{13}ClN$: C, 75.44; H, 5.14; Cl, 13.92; N, 5.50. Found: C, 75.55; H, 5.25; Cl, 13.80; N, 5.42.

(5-Methyl-2-furyl)(2-methyl-3-indolyl)methane (5g)

Chromatographic eluent: PE–AcOEt 8:2; viscous oil (0.22 g, 91% yield); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.31 (s, 3H), 4.04 (s, 2H), 5.78–5.88 (m, 2H), 7.10–7.20 (m, 3H), 7.45–7.58 (2 m overlapped, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.4, 13.5, 23.2, 105.9 (2C), 107.7 (q), 110.2, 118.2 119.1, 120.8, 128.5 (q), 131.8 (q), 135.1 (q), 150.3 (q), 153.1 (q); MS *m/z* (%): 225 [M^+](95), 210 (100), 182 (40); Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.77; H, 6.70; N, 6.40.

(2-Methyl-3-indolyl)(2-thienyl)methane (5h)

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.20 g, 88% yield); mp 69.4–70.2 °C (DCM – PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 4.22 (s, 2H), 6.75–6.82 (m, 1H), 6.82–6.90 (m, 1H), 7.03–7.15 (m, 3H), 7.18–7.28 (m, 1H), 7.42–7.48 (m, 1H), 7.65 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.5, 24.5, 110.3 (2C, CH and q overlapped), 118.1, 119.3, 121.0, 123.1, 124.0, 126.7, 128.3 (q), 131.6 (q), 135.1 (q), 145.5 (q); MS *m/z* (%): 227 [M^+](100), 212 (80), 144(45); Anal. Calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16; S, 14.11. Found: C, 73.79; H, 5.60; N, 6.20; S, 14.00.

(2-Methyl-3-indolyl)(1-methyl-2-pyrrolyl)methane (5i)

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.15 g, 68% yield); mp 106.6–107.6 °C (DCM –PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.44 (s, 3H), 3.93 (s, 2H), 5.74–5.80 (m, 1H), 5.96 (dd, *J* = 3.4 and *J* = 2.8 Hz, 1H), 6.47–6.52 (m, 1H), 6.94–7.10 (m, 2H), 7.17–7.25 (m, 1H), 7.27–7.35 (m, 1H), 7.68 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.5, 22.0, 33.6, 106.3, 107.2, 108.4 (q), 110.0, 118.3, 119.1, 120.8, 121.2, 128.6 (q), 131.4 (q), 131.7 (q), 135.1 (q); MS *m/z* (%):224 [M^+](100), 209 (45), 143(90); Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.19; H, 7.00; N, 12.26.

(2-Methyl-3-indolyl)(2-pyrrolyl)methane (5j)

Chromatographic eluent: PE–AcOEt 7:3; viscous oil (0.14 g, 67% yield); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 4.02 (s, 2H), 5.96–6.01 (m, 1H), 6.05–6.12 (m, 1H), 6.49–6.53 (m, 1H), 6.95–7.13 (m, 2H), 7.17–7.27 (m, 1H), 7.31–7.39 (m, 1H), 7.75 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.3, 22.3, 105.0, 108.1, 108.4 (q), 110.2, 116.1, 118.0, 119.4, 121.0, 128.6 (q), 131.2 (q), 131.9 (q), 135.1 (q); MS *m/z* (%):210 [M^+](100), 195 (45), 131(55); Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.10; H, 6.60; N, 13.24.

(1,2-Dimethyl-3-indolyl)(3-indolyl)methane (5k)[18a]

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.24 g, 86% yield); mp 139.6–141.2 °C (DCM –PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 3.64 (s, 3H), 4.15 (s, 2H), 6.60–6.64 (m, 1H), 6.93–7.06 (m, 1H), 7.07–7.18 (m, 2H), 7.19–7.28 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.62–7.69 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.2, 20.1, 29.4, 108.4, 109.4 (q), 110.9, 116.3 (q), 118.4, 118.4, 118.7, 119.0, 120.3, 121.7, 122.0, 127.3 (q), 127.9 (q), 133.1 (q), 136.4 (q), 136.5 (q); MS *m/z* (%):274 [M^+](100), 259 (80), 157(30).

(4-Methoxyphenyl)(1,2-dimethyl-3-indolyl)methane (5l)

Chromatographic eluent: PE–AcOEt 7:3; white solid (0.25 g, 94% yield); mp 94.4–95.5 °C (PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.63 (s, 3H), 3.72 (s, 3H), 4.01 (s, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H) overlapped with 6.93–7.16 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.3, 29.4, 55.1, 108.4, 110.1 (q), 113.6 (2C), 118.2, 118.7, 120.4, 127.9 (q), 129.0 (2C), 133.3 (q), 134.0 (q), 136.6 (q), 157.6 (q); MS *m/z* (%):265 [M^+](100), 250 (95), 158(75); Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.33; H, 7.20; N, 5.39.

(3-Guaiazulenyl)(4-methoxyphenyl)methane (5m)[12]

Chromatographic eluent: PE–AcOEt 8:2; blue paste (0.31 g, 96% yield);[12] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 7.2 Hz, 6H), 2.60 (s, 3H), 2.83 (s, 3H), 3.00 (sept, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 4.52 (s, 2H), 6.77 (d, *J* = 8.8 Hz, 2H overlapped with m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 11.4 and 2.0 Hz, 1H), 7.36 (s, 1H), 8.06 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.8, 24.5, 26.5, 36.2, 37.6, 55.1, 113.6 (2C), 124.0 (q), 125.9 (q), 126.1, 129.3 (2C), 132.9 (q), 133.2, 134.6, 135.3 (q), 137.6 (q), 138.7 (q), 141.0, 145.3 (q), 157.5 (q); MS *m/z* (%): 318 [M^+](100), 303 (95).

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SUPPORTING INFORMATION: ^{1}H and ^{13}C NMR spectra for compounds **4a–m** and **5a–m**; full bond lengths and angles table and CIF file for compound **4b**, ORTEP and full refinement data of **4b**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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