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Synthesis of Bench-Stable Diarylmethylium Tetrafluoroborates

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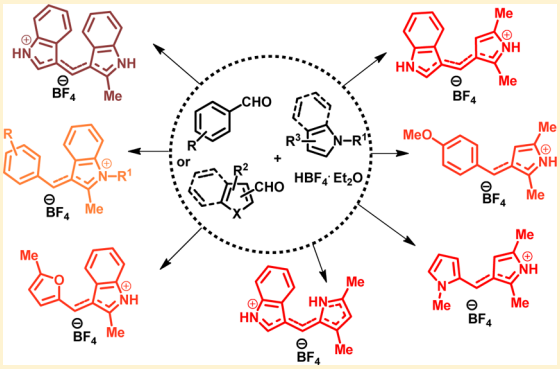
Supporting Information

ABSTRACT: A representative number of bench-stable nonsymmetric diarylcarbenium tetrafluoroborates have been isolated via the direct coupling of aryl (or heteroaryl) aldehydes and *N*-heteroarenes and fully characterized. They have proven to be highly stable in the presence of both EDG and EWG substituents. An (*E*)-iminium vinylogous substructure has been shown as the common cation scaffold by X-ray analysis and by NOE determination.



The importance of carbocations as intermediates in organic chemistry does not need to be pointed out. Persistent types of these species can be formed, normally at low temperature in superacidic systems,[1] and immediately reacted with suitable nucleophiles. Diarylmethyl carbocations, stable enough to be spectroscopically studied, are often generated *in situ* via diarylmethanols[2] or halides[3] ionization, the laser flash induced photolysis of suitable precursors,[4] benzhydryl ester or halide solvolysis,[5] DDQ-mediated oxidation, benzylic carbon−hydrogen activation,[6] and oxidative diarylmethane C−H bond dissociation using anodic oxidation.[7]

A large number of symmetric and nonsymmetric diarylcarbenium salts have been studied by Mayr's research group as reference electrophiles toward a variety of neutral π-, n-, and σ-nucleophiles or carbanion nucleophiles, leading to extensive electrophilicity and nucleophilicity scales.[8] Benzhydrylium tetrafluoroborates have been prepared, but fully characterized, in few cases;[9] they have more often been generated and reacted *in situ* as tetrafluoroborates, tetrachloroborates,[10] or triflates.[11]

Meanwhile, Takekuma's group has reported a class of mono- and dicarbenium hexafluorophosphates (or tetrafluoroborates) stabilized by the 3-guaiazulenyl group.[12]

Finally, we have reported a nonsymmetric diarylmethylium salt synthesis via the direct coupling of aryl (or heteroaryl) aldehydes and *N*-heteroarenes, which have been recently employed in a direct organocatalyzed asymmetric alkylation of aldehydes.[13] Diarylmethylium *o*-benzenedisulfonimides, which bear 2-methylindole or 1,2-dimethylindole, were isolated as stable and long shelf life salts; the counteranion was chosen because of its well-known non-nucleophilic character.[14] Only electron-rich aldehydes gave positive results, and it was not possible to replace the indole ring with the pyrrole one.

Intrigued by the reasons behind such stabilities and in order to find new stable structures of these normally highly reactive intermediates, we examined the role of the anion and then, once it was possible to replace it with an economically convenient analogue, took the cationic scaffold into consideration. We herein report the synthesis and structural characterization of new nonsymmetric diarylmethylium tetrafluoroborates **3a−l** (Table 1), ready to use and with long shelf lives. We believe that the presence of the widespread indolyl (or pyrrolyl) moiety, the high stability, and easy preparation procedure make them a tool of great synthetic relevance in organic chemistry (notably, enantioselective unsymmetrical triarylmethanes synthesis,[15] α-alkylation of carbonyl compounds,[16] 2,3-disubstituted indoline synthesis,[17] intramolecular tandem reactions,[18] aza-ene reactions,[19] normally achieved via *in situ* generated carbenium ions).

In order to examine anion relevance, we initially tested the reaction between the electron-rich 4-methoxybenzaldehyde (**1a**) and 2-methylindole (**2a**) in the presence of a tetrafluoroboric acid diethyl ether complex, widely used in organic synthesis as a source of a non-nucleophilic and quite air-stable anion. The indole substitution in position 2 prevents its acid-catalyzed polymerization through 2,3 linkages.[20]

We applied optimized conditions;[13] a solution of **2a** in anhydrous MeCN was added dropwise to a solution of **1a** and

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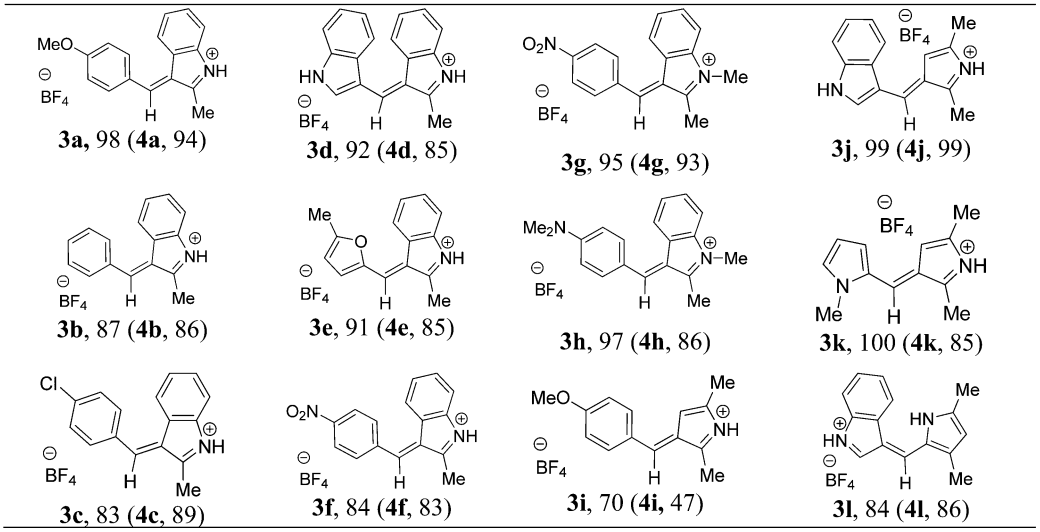
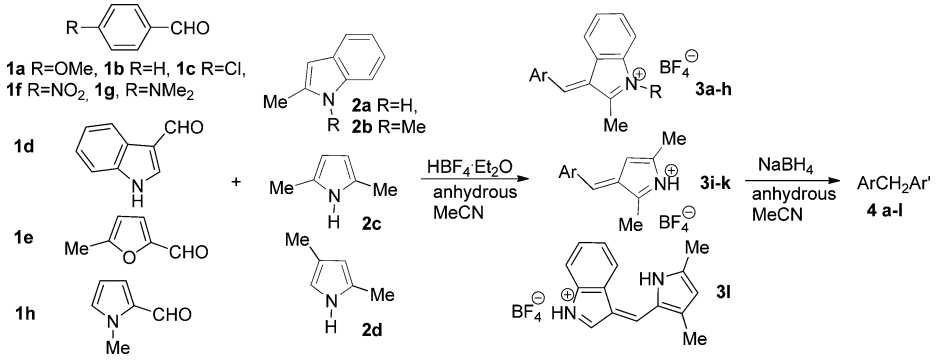
Table 1. Diarylmethylium Tetrafluoroborates 3a–l and Diarylmethane 4a–l Yields

tetrafluoroborates **3**, yield%[a,b] (diarylmethanes **4**, yield%)[c,d]



[a]Reaction conditions: molar ratio **1**:**2**:HBF_4Et_2O = 1.2:1:1.2; anhydrous MeCN, rt. [b]Yields refer to pure solid isolated products. [c]Reaction conditions: molar ratio **3**:$NaBH_4$ = 1:1; anhydrous MeCN, rt. [d]Yields refer to purified products (column chromatography; eluent:PE/EE 6/4).

Scheme 1. Synthesis of Salts 3a–l



$HBF_4{\cdot}Et_2O$ in the same solvent (molar ratio **1a**:**2a**:$HBF_4{\cdot}Et_2O$ = 1.2:1:1.2), at rt in an open vessel. The immediate formation of a bright red-colored solution and then the separation of a red precipitate indicated the reaction success. Product **3a** was isolated in 95% yield as an easily handled, bench-stable, long-life solid salt; the structure and purity were confirmed by spectroscopic methods, elemental analysis, and chemical reduction with $NaBH_4$ in anhydrous MeCN to diarylmethane **4a** in 94% yield.

In order to explore its applicability, we tested the reaction between less stabilized aryl and heteroaryl aldehydes with 2-methylindole (**2a**) or 1,2-dimethylindole (**2b**) (Scheme 1).

Unsubstituted benzaldehyde (**1b**), electron-poor 4-chlorobenzaldehyde (**1c**), heteroaromatic indol-3-carbaldehyde (**1d**), and acid-sensitive 5-methylfuran-2-carbaldehyde (**1e**) were reacted with **2a**. Aryl 2-methyl-3-indolylmethylium tetrafluoroborates **3b–e** were isolated in higher yields than the corresponding *o*-benzenedisulfonimide salts.

These results confirmed that the benzhydryl carbocation, which is the intermediate in a Friedel–Crafts hydroxyalkylation reaction,[21] can be isolated from the reaction mixture as a bench-stable salt with the counteranion of the tetrafluoroboric acid, a cheap commercially available reagent and, therefore, an economic alternative to the *o*-benzenedisulfonimide.[14]

Encouraged by these positive results, we tested the reaction on the very electron-poor 4-nitrobenzaldehyde (**1f**). We were gratified by successful reactions with indoles **2a** and **2b**: salts **3f** and **3g** were isolated in high yield and purity. Quite surprisingly, aldehyde **1f** did not give positive results in the presence of the *o*-benzenedisulfonimide.[13,21] Although we are not currently able to account for these contrasting results, we found that the solvent can be crucial for the successful nucleophilic reaction of stabilized carbenium ion.[13] Reactivity vs stability of the obtained intermediates probably controls this reaction, in which the insoluble carbenium ion salt separates from the reaction mixture driving the reaction to completion.

With the aim of confirming the synthetic procedure relevance and of understanding the need for the indole, we took the 4-(*N*,*N*-dimethylamino)phenyl scaffold into consideration, as it is a well-known stabilizing group in benzhydrylium ions.[9] First, we reacted 4-(*N*,*N*-dimethylamino)benzaldehyde (**1g**) with 1,2-dimethylindole (**2b**): tetrafluoroborate **3h** was isolated in a 97% yield. Next, we tested the reaction protocol between **1g** and electron-rich arenes, other than indole (e.g., 1,2,4-trimethoxybenzene and 2-methylfuran), and between aldehyde **1a** with *N*,*N*-dimethylaniline, but, in both cases, without success. This confirmed the decisive role played by the indole moiety in the stabilization of the carbenium ion.

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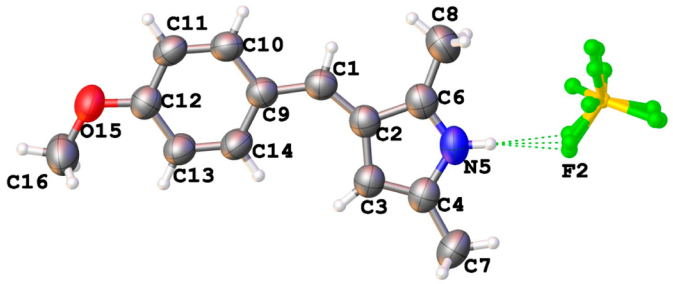

Bonds	Lengths (Å)	Bonds	Lengths (Å)
C1-C2	1.376(5)	C9-C10	1.402(5)
C1-C9	1.427(5)	C9-C14	1.410(4)
C2-C3	1.441(5)	C10-C11	1.366(5)
C2-C6	1.448(5)	C11-C12	1.398(5)
C3-C4	1.352(5)	C12-C13	1.399(5)
C4-N5	1.406(5)	C12-O15	1.349(4)
C4-C7	1.481(5)	C13-C14	1.367(5)
N5-C6	1.317(5)	O15-C16	1.429(5)
C6-C8	1.476(5)		

Figure 1. Asymmetric unit of compound **3i** with atom labeling (displacement ellipsoids for all but hydrogen and fluorine atoms are drawn at 50% probability) and relevant cation bond distances.

The X-ray analysis of one of the aforementioned benzhydrylium salts, namely, 4-methoxyphenyl(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide, showed that the cation charge is mainly localized on the nitrogen atom in an azafulvenium (iminium vinylogous) species, further stabilized by H-bonds between indole and the counteranion.[13] We, therefore, decided to substitute the indole nucleus with the pyrrole one, despite its well-known acid sensitivity.

The reaction of 4-methoxybenzaldehyde (**1a**) with 2,5-dimethylpyrrole (**2c**) under the conditions optimized for indole gave the tetrafluoroborate **3i** in 70% yield. Although **3i** was obtained in a slightly lower yield than the corresponding indolyl salt **3a**, it confirmed our hypothesis on the stabilizing role of the vinylogous iminium substructure.

In order to validate the synthetic procedure, we then tested other reactions of **2c**. The reaction with benzaldehyde (**1b**) only furnished traces of the product, as confirmed by the GC−MS analysis of the crude reaction mixture obtained via chemical reduction of the scarce solid. Changes in the reaction conditions with respect to acid amount and nature (HBF_4 and *o*-benzenedisulfonimide) and dilution gave the same unsatisfactory results. Differently to results obtained with **2a**, the halogen's mesomeric effect did not prevail over the inductive one in the reaction of **1c** with **2c**; the expected salt was not isolated. A dark solid was isolated from the reaction with aldehyde **1g**, but the chemical reduction furnished only traces of diarylmethane. Similarly, aldehyde **1e** did not give the expected salt; the carbocation is probably too unstable because of the strong electron-withdrawing substituent effect. Positive results were, however, obtained when reacting aldehyde **1d**: **3j** was isolated in high yield and purity. Furthermore, we carried out the reaction of **2c** with 1-methylpyrrol-2-carbaldehyde (**1h**) in order to obtain a dipyrrolylmethane core, which is of central importance in chemical and biological research areas. Quite unexpectedly, the tetrafluoroborate **3k** was obtained in a very high yield and purity.

Finally, we tested the reaction between 2,4-dimethylpyrrole (**2d**) and selected aldehydes (**1a**, **1d**, and **1g**). Only **1d** afforded the tetrafluoroborate **3l** in good yield and purity, whereas **1a** was ineffective and **1g** gave a dark solid, which, by reduction, furnished only traces of diarylmethane.

All the deeply colored salts proved to be stable to air and moisture, storable at low temperatures for long periods, and ready to use. Their identity and purity were confirmed by means of $NaBH_4$ chemical reduction in anhydrous MeCN; diarylmethanes **4a**−**l** were obtained in yields ranging from 83 to 99% (the single exception was **4i**; changes in reducing agent and solvent amounts were inefficient).

In the light of these results, we can infer that, in the presence of an azole moiety (whether isolated or benzene-fused), nonsymmetric diarylcarbenium ions can be easily isolated as tetrafluoroborates via direct coupling between aryl/heteroaryl aldehydes and *N*-heteroarenes.

The intermediacy of vinylogous iminium species in reaction mechanisms involving indole substructures (alkylideneindoleninium ions) has often been recognized in cases such as direct coupling,[22] DDQ-based 3-arylmethylindole dehydrogenation,[23] and suitable leaving group elimination (hydroxyl, sulfonamide, halides), for example, in the (1*H*-3-indolyl)(aryl)methanols acid dehydration[24] or acid-catalyzed *N*-tosyl-3-indolylbenzylamines treatment.[25] Sometimes, the presence of vinylogous iminium intermediates has been demonstrated using spectroscopic methods.[26] The chemistry of alkylideneindoleninium ions and alkylideneindolenines has been recently reviewed.[27]

In most salts **3**, the positive charge can be delocalized by resonance to both diarylcarbenium rings. As previously reported, X-ray analysis of 4-methoxyphenyl(2-methyl-3-indolyl)methylium *o*-benzenedisulfonimide clearly showed an almost planar cation, the two planar aromatic moieties form an angle of 31°, and the positive charge is localized on the nitrogen atom in a highly extended conjugated scaffold. A X-ray analysis was needed to confirm our initial hypothesis on the feasibility of indole ring substitution in the new salts. Therefore, X-ray diffraction analysis was performed on salt **3i**, which was chosen in order to compare present and previous results.[12,13]

The asymmetric unit of **3i** and some relevant bond distances of the diarylmethylium ion are reported in Figure 1.

The diarylmethylium moiety is completely planar (mean deviation from planarity = 0.055 Å), suggesting wide electron density delocalization throughout the whole molecule. However, typical double bond distances are located at the C1−C2, C3−C4, and N5−C6 bonds. Furthermore, although the BF_4^- ion is disordered in three positions, its distance from the N5−H5 fragment is sufficiently short (1.971 Å av.) to hypothesize that the positive charge is localized on the N5 atom, confirming the major significance of a vinylogous iminium resonance structure. Moreover, the positive charge is slightly transferred to the oxygen atom of the *p*-anisyl group in a quinoid structure. This is demonstrated by the planarity of the entire cation and by the C12−O15 bond distance, which is shorter than a typical C−O single bond.

This fact could explain the very few tetrafluoroborates obtainable from 2,5-dimethylpyrrole (**3i**−**k**) and the single one from 2,4-dimethylpyrrole (**3l**) in comparison with the number and variety of salts from indole (**3a**−**h**). In salts **3i**−**l**, both parts of the benzhydrylium cation are involved in charge delocalization, meaning that particularly electron-rich (*p*-

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anisyl/indole/pyrrole) scaffolds are required in the aldehyde moiety.

Furthermore, an *E* configuration was shown, as previously observed.[13] This result prompted us to confirm the stereochemistry using NOE experiments (see the Supporting Information).

Different selective excitations were performed on salts **3c** and **3f**. Selective excitation of methyl protons of **3f** showed a positive NOE on the benzylic proton, while selective excitation of the phenyl ring protons in the *meta* position (with respect to NO_2) showed a positive NOE on the benzylic proton, the phenyl protons in *ortho* (with respect to NO_2) and the indole proton in position 4. Finally, selective excitation of the indole proton in 4 showed a positive NOE on the proton in 5 and on the phenyl protons in the *meta* position (with respect to NO_2). Similar behavior was observed for **3c**. Moreover, it was possible to perform a selective excitation of the benzylic proton. A positive NOE was observed on the protons in the *meta* position (with respect to Cl) and on the methyl protons. On the basis of this evidence, we can confirm that the phenyl moiety and indole ring occupy the same side of the double bond.

In summary, we have reported a simple, direct synthesis and spectral characterization of new stable, long shelf life, and ready to use diarylcarbenium tetrafluoroborates via the direct coupling of aryl or heteroaryl aldehydes and *N*-heteroarenes, where the azole ring is the crucial framework for the high stability.

EXPERIMENTAL SECTION

General Information. All reactions were conducted in open air 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 an 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 and 50 MHz, respectively; chemical shifts are given in ppm relative to $CDCl_3$. Selective excitation ^1H NMR spectra were recorded on a spectrometer at 400 MHz in a mixture of $CDCl_3$−TFA (10%), using a DPFGSE-NOE sequence with a 50 Hz "rsnob" pulse and a mixing time of 1.5 s. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ = 7.27 ppm). 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 of 40−60 °C and is abbreviated as PE. Commercially available reagents and solvents were used without purification or distillation prior to use. Room temperature (20−25 °C) is abbreviated as rt. Yields for pure (GC, GC−MS, TLC, ^1H NMR) isolated products are listed in Table 1. The structure and purity of all new products were determined by elemental analysis, ESI, ^1H, ^{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, ^1H NMR, and ^{13}C NMR) with those reported in the literature.

Crystal Analysis. Reflections were collected at room temperature on an X-ray diffractometer, with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Crystal data for $C_{14}H_{16}BNOF_4$ (M = 301.09 g/mol): orthorhombic, space group *Pbca* (No. 61), a = 13.8025(13) Å, b = 12.8183(6) Å, c = 16.7453(8) Å, V = 2962.7(3) Å^3, Z = 8, T = 295 K, μ = 0.118 mm^{-1}, D_{calc} = 1.350 g/cm^3, 6281 reflections measured (4.866 ≤ 2Θ ≤ 49.426), 2486 unique (R_{int} = 0.0387, R_{sigma} = 0.0580), which were used in all calculations. The final R_1 was 0.0889 ($I > 2\sigma(I)$), and wR_2 was 0.2891 (all data). All non-hydrogen cation atoms were anisotropically refined. The BF_4 anion is disordered between three equivalent positions with a 0.33 occupancy factor, and all of its atoms were isotropically refined. Hydrogen atom positions were calculated and refined riding on the atom connected, with U_{iso} = 1.2 or 1.5 U_{eq} of the corresponding bonded atoms. A Gaussian absorption correction was applied. Software used: CrysAlisPro[28] (collection, integration), SHELXS (structure solution and refinement),[29] and OLEX2-molecular graphics.[30] Crystal data were deposited at CSD with code CCDC 1038486.

Caution! *Although easily handled, isolated product* ***3k*** *was a respiratory irritant.*

General Procedures. *General Procedure for Diarylmethylium Tetrafluoroborates* ***3a–l*** *Synthesis.* A solution of aromatic compound **2** (3.0 mmol) in anhydrous MeCN (5 mL) was added dropwise at rt and under stirring to a mixture of aldehyde **1** (3.6 mmol) and tetrafluoroboric acid/ether complex (0.59 g, 3.6 mmol) in anhydrous MeCN (15 mL) in an open vessel. The deeply colored solution lightened, and a red or orange 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.

*(4-Methoxyphenyl)(2-methyl-3-indolyl)methylium Tetrafluoroborate (**3a**).* (0.99 g, 98% yield); dp 211.0 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.89 (s, 3H), 3.97 (s, 3H), 7.13 (d, J = 8.8 Hz, 2H), 7.34−7.54 (2 overlapped m, 3H), 8.02 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 7.2 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 12.8, 55.5, 114.8, 115.4 (2C), 122.4, 123.9 (q), 125.6 (q), 127.4 (q), 128.0, 129.7, 136.5 (2C), 139.5 (q), 158.3, 166.5 (q), 170.0 (q); IR ($CHCl_3$) ν_{max} 3467, 3033, 3019, 1579, 1515, 1417, 1350; exact ESI full mass: found m/z 250.26 (calcd for $C_{17}H_{16}NO^+$, m/z 250.12); Anal. Calcd for $C_{17}H_{16}BF_4NO$: C, 60.57; H, 4.78; N, 4.15. Found C, 60.35; H, 4.76; N, 4.13.

*(2-Methyl-3-indolyl)(phenyl)methylium Tetrafluoroborate (**3b**).* (0.80 g, 87% yield); dp 170.0 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.96 (s, 3H), 7.32−7.72 (m, 6H), 7.88−7.93 (m, 2H), 8.07 (d, J = 7.4 Hz, 1H), 8.53 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 13.3, 115.5, 123.1, 123.7 (q), 128.7, 129.5 (2C), 130.7, 131.0 (q), 131.8 (2C), 132.3 (q), 134.9, 140.0 (q), 158.1, 172.0 (q); IR ($CHCl_3$) ν_{max} 3470, 3018, 1714, 1612, 1572, 1459, 1339, 1231; exact ESI full mass: found m/z 220.21 (calcd for $C_{16}H_{14}N$: M^+, m/z 220.11); Anal. Calcd for $C_{16}H_{14}BF_4N$: C, 62.58; H, 4.60; N, 4.56. Found C, 62.38; H, 4.57; N, 4.53.

*(4-Chlorophenyl)(2-methyl-3-indolyl)methylium Tetrafluoroborate (**3c**).* (0.85 g, 83% yield); dp 190.0 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.96 (s, 3H), 7.30−7.50 (m, 1H), 7.52−7.64 (m, 4H), 7.87 (d, J = 8.6 Hz, 2H), 8.05 (d, J = 7.6 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 13.2, 115.5, 123.0, 123.4 (q), 128.8, 129.9 (2C), 130.6 (q), 131.0, 131.3 (q), 132.8 (2C), 140.0 (q), 141.6 (q), 156.2, 173.0 (q); IR ($CHCl_3$) ν_{max} 3025, 3018, 2401, 1521, 1420, 1207; exact ESI full mass: found m/z 254.21 (calcd for $C_{16}H_{13}ClN^+$: M^+, m/z 254.07); Anal. Calcd for $C_{16}H_{13}BClF_4N$: C, 56.27; H, 3.84; N, 4.10. Found C, 56.22; H, 3.80; N, 4.12.

*(3-Indolyl)(2-methyl-3-indolyl)methylium Tetrafluoroborate (**3d**).* (0.95 g, 92% yield); dp 200 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.82 (s, 3H), 7.35−7.53 (m, 5H), 7.58−7.70 (m, 2H), 7.86−7.90 (m, 1H), 8.64 (s, 1H), 8.65 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 12.3, 113.7 (2C), 117 (q), 120.0, 120.9 (q), 121.7, 124.2 (q), 125.1, 126.2, 126.3, 126.5 (q), 127.5, 137.3 (q), 138.1 (q), 141.2, 147.8, 162.7 (q); IR ($CHCl_3$) ν_{max} 3467, 3027, 3024, 1576, 1426, 1218, 1024; exact ESI full mass: found m/z 259.20 (calcd for $C_{18}H_{15}N_2$: M^+: m/z 259.12); Anal. Calcd for $C_{18}H_{15}BF_4N_2$: C, 62.46; H, 4.37; N, 8.09. Found C, 62.30; H, 4.35; N, 8.06.

*(5-Methyl-2-furyl)(2-methyl-3-indolyl)methylium Tetrafluoroborate (**3e**).* (0.85 g, 91% yield); dp 204 °C (anhydrous MeCN/anhydrous Et_2O); ^1H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ =

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J. Org. Chem. 2015, 80, 4791−4796

2.74 (s, 3H), 2.84 (s, 3H), 6.69 (d, J = 3.8 Hz, 1H), 7.43−7.54 (m, 3H), 7.70 (d, J = 3.8, 1H), 7.85 (s, 1H), 8.59−8.64 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 12.5, 14.5, 114.2, 115.1, 122.0 (q), 123.8 (q), 124.5, 127.3, 128.8, 134.2, 137.5, 138.8 (q), 149.9 (q), 168.0 (q), 169.4 (q); IR ($CHCl_3$) ν_{max} 3032, 3012, 1577, 1427, 1238, 1198; exact ESI full mass: found m/z 224.16 (calcd for $C_{15}H_{14}NO$: M^+, m/z 224.11); Anal. Calcd for $C_{15}H_{14}BF_4NO$: C, 57.91; H, 4.54; N, 4.50. Found C, 57.72; H, 4.52; N, 4.52.

*(2-Methyl-3-indolyl)(4-nitrophenyl)methylium Tetrafluoroborate (**3f**).* (0.89 g, 84% yield); dp 200 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 3.02 (s, 3H), 7.35−7.43 (m, 1H), 7.50−7.61 (m, 2H), 7.79 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.8, 2H), 8.44 (d, J = 8.8, 2H), 8.56 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 13.3, 116.0, 123.0 (q), 123.5, 124.3 (2C), 129.3, 131.3 (2C), 131.8, 134.3 (q), 138.4 (q), 140.4 (q), 149.5 (q), 152.9, 174.7 (q); IR ($CHCl_3$) ν_{max} 3033, 3012, 1640, 1235, 1197; exact ESI full mass: found m/z 265.07 (calcd for $C_{16}H_{13}N_2O_2$: M^+, m/z 265.10); Anal. Calcd for $C_{16}H_{13}BF_4N_2O_2$: C, 54.58; H, 3.72; N, 7.96; Found C, 54.40; H, 3.71; N, 7.98.

*(1,2-Dimethyl-3-indolyl)(4-nitrophenyl)methylium Tetrafluoroborate (**3g**).* (1.04 g, 95% yield); dp 218 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.96 (s, 3H), 4.01 (s, 3H), 7.36−7.44 (m, 1H), 7.53−7.64 (m, 2H), 7.95 (d, J = 8.8, 2H), 8.39 (d, J = 8.8, 2H), 8.56 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 12.1, 33.4, 113.8, 123.0 (q), 123.6, 124.3 (2C), 129.6, 131.2 (2C), 131.5, 133.8 (q), 138.6 (q), 143.0 (q), 149.4 (q), 152.2, 173.2 (q); IR ($CHCl_3$) ν_{max} 3032, 3012, 1534, 1238, 1198; exact ESI full mass: found m/z 279.11 (calcd for $C_{17}H_{15}N_2O_2$: M^+, m/z 279.11); Anal. Calcd for $C_{17}H_{15}BF_4N_2O_2$: C, 55.77; H, 4.13; N, 7.65; Found C, 55.69; H, 4.14; N, 7.62.

*(4-N,N-Dimethylaminophenyl)(1,2-dimethyl-3-indolyl)methylium Tetrafluoroborate (**3h**).* (1.06 g, 97% yield); dp 178 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.96 (s, 3H), 3.45 (s, 6H), 4.03 (s, 3H), 7.41−7.49 (m, 1H), 7.55−7.68 (m, 2H), 7.83 (d, J = 8.8 Hz, 1H) overlapped with 7.80−7.88 (m, 1H), 8.05 (d, J = 8.6, 2H), 8.54 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 11.7, 33.0, 47.2 (2C), 113.6, 121.2 (2C), 122.8 (q), 123.4, 129.7, 131.5, 132.9 (2C), 133.4 (q), 135.2 (q), 142.9 (q), 144.3 (q), 152.1, 172.8 (q); IR ($CHCl_3$) ν_{max} 3026, 3016, 1615, 1574, 1513, 1376, 1327, 1174; exact ESI full mass: found m/z 277.22 (calcd for $C_{19}H_{21}N_2$: M^+, m/z 277.17); Anal. Calcd for $C_{19}H_{21}BF_4N_2$: C, 62.66; H, 5.81; N, 7.69. Found C, 62.70; H, 5.79; N, 7.71.

*(2,5-Dimethyl-3-pyrrolyl)(4-methoxyphenyl)methylium Tetrafluoroborate (**3i**).* (0.63 g, 70% yield); dp 182 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.29 (s, 3H), 2.72 (s, 3H), 3.96 (s, 3H), 6.69 (br s, 1H), 7.11 (d, J = 9.0, 2H), 7.98 (d, J = 9.0, 2H), 8.19 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 11.4, 11.7, 55.6, 108.8, 116.1 (2C), 126.6 (q), 130.3 (q), 138.4 (2C), 141.6 (q), 158.5, 164.9 (q), 167.9 (q); IR ($CHCl_3$) ν_{max} 3026, 3018, 1582, 1512, 1328, 1275, 1233, 1212, 1200; exact ESI full mass: found m/z 214.15 (calcd for $C_{14}H_{16}NO$: M^+, m/z 214.12); Anal. Calcd for $C_{14}H_{16}BF_4NO$: C, 55.85; H, 5.36; N, 4.65; Found C, 55.71; H, 5.33; N, 4.66.

*(2,5-Dimethyl-3-pyrrolyl)(3-indolyl)methylium Tetrafluoroborate (**3j**).* (0.85 g, 91% yield); dp 174 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.21 (s, 3H), 2.58 (s, 3H), 7.31−77.45 (m, 1H), 7.48−7.54 (m, 2H), 7.80−7.85 (m, 1H), 8.30 (s, 1H), 8.46 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 11.4, 11.7, 107.7, 113.8, 118.0 (q), 118.3 (q), 125.0 (q), 125.5 (2C), 126.3, 137.4 (q), 137.6 (q), 148.2 (q), 155.8 (q), 156.0 (q); IR ($CHCl_3$) ν_{max} 3025, 3014, 1580, 1334, 1295, 1225; exact ESI full mass: found m/z 213.16 (calcd for $C_{15}H_{15}N_2$: M^+, m/z 223.12); Anal. Calcd for $C_{15}H_{15}BF_4N_2$: C, 58.10; H, 4.88; N, 9.03; Found C, 58.15; H, 4.85; N, 9.00.

*(2,5-Dimethyl-3-pyrrolyl)(1-methyl-2-pyrrolyl)methylium Tetrafluoroborate (**3k**).* (0.82 g, quantitative yield); dp 208 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.21 (s, 3H), 2.56 (s, 3H), 3.88 (s, 3H), 6.63 (br s, 1H), 7.48−7.62 (m, 2H), 7.81 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 11.2, 11.7, 34.4, 117.8, 123.6 (q), 129.2, 133.2 (q), 137.8 (2C), 138.2 (q), 142.8, 156.7 (q); IR ($CHCl_3$) ν_{max} 3331, 3026, 3017, 1621, 1509, 1403, 1225, 1218, 1209; exact ESI full mass: found m/z 187.12 (calcd for $C_{12}H_{15}N_2$: M^+, m/z 187.12); Anal. Calcd for $C_{12}H_{15}BF_4N_2$: C, 52.59; H, 5.52; N, 10.22; Found C, 52.44; H, 5.50; N, 10.24.

*(3,5-Dimethyl-2-pyrrolyl)(3-indolyl)methylium Tetrafluoroborate (**3l**).* (0.78 g, 84% yield); dp 216 °C (anhydrous MeCN/anhydrous Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$−CF_3COOD): δ = 2.46 (s, 3H), 2.54 (s, 3H), 6.40 (s, 1H), 7.35−7.42 (m, 2H), 7.45−7.55 (m, 1H), 7.77−7.85 (m, 1H), 7.99 (s, 1H), 8.50 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$−CF_3COOD): δ = 11.5, 13.9, 113.2 (q), 113.4, 118.0, 120.1, 124.6, 125.8, 127.0 (q), 132.5, 133.1 (q), 136.7 (q), 137.8, 147.1 (q), 151.6 (q); IR ($CHCl_3$) ν_{max} 3032, 3012, 1583, 1237, 1198; exact ESI full mass: found m/z 213.17 (calcd for $C_{15}H_{15}N_2$: M^+, m/z 223.12); Anal. Calcd for $C_{15}H_{15}BF_4N_2$: C, 58.10; H, 4.88; N, 9.03; Found C, 58.15; H, 4.86; N, 9.04.

*General Procedure for Diarylmethylium Tetrafluoroborates **3a**−**l** Reduction.* $NaBH_4$ (1.0 mmol, 0.04 g) was added portionwise at rt and under stirring to a solution of salt **3** (1.0 mmol) in anhydrous MeCN (15 mL). The reaction was instantaneous, and the deeply 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 × 20 mL), and evaporated under reduced pressure. The crude residue was the virtually pure reduction product **4** (GC, GC−MS, ^{1}H NMR), which was, however, purified via short column chromatography (eluent PE/EE 6/4); yields of purified products are reported in Table 1. Structure and purity of products **4a**−**e** were confirmed by comparing physical and spectral data (MS, ^{1}H NMR, and ^{13}C NMR) with previously reported data;[13] yields and physical and spectroscopic data are listed below for new products **4f**−**l**.

*(4-Nitrophenyl)(2-methyl-3-indolyl)methane (**4f**).*[31] Yellow solid (0.22 g, 83% yield); mp 123.0−124.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 4.10 (s, 2H), 6.97−7.11 (m, 2H), 7.20−7.24 (m,2H), 7.29 (d, J = 8.8 Hz, 2H), 7.83 (br s, 1H), 8.03 (d, J = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6, 29.9, 108.7 (q), 110.2, 117.7, 119.4, 121.2, 123.4 (2C), 128.2 (q), 128.8 (2C), 131.8 (q), 135.1 (q), 146.0 (q), 149.3 (q); IR ($CHCl_3$) ν_{max} 3471, 3009, 2921, 1599, 1518, 1461, 1347, 1068; MS m/z (%): 266 [M^+](100), 144 (85).

*(4-Nitrophenyl)(1,2-dimethyl-3-indolyl)methane (**4g**).* Yellow solid (0.27 g, 93% yield); mp 114.0−115.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.65 (3H), 4.14 (s, 2H), 6.95−7.08 (m, 2H), 7.10−7.28 (m, 2H), 7.29 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.2, 29.5, 30.2, 107.9 (q), 108.6, 117.7, 119.0, 120.8, 123.4 (2C), 127.3 (q), 128.7 (2C), 133.7 (q), 136.5 (q), 146.0 (q), 149.6 (q); IR ($CHCl_3$) ν_{max} 3468, 3029, 2943, 1597, 1521, 1474, 1347, 1068; MS m/z (%): 280 [M^+](100), 158 (100); Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found C, 72.70; H, 5.77; N, 9.96.

*(4-N,N-Dimethylaminophenyl)(1,2-dimethyl-3-indolyl)methane (**4h**).* Light pink solid (0.24 g, 86% yield); mp 128.0−129.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.87 (s, 6H), 3.64 (s, 3H), 4.02 (s, 2H), 6.65 (d, J = 8.6 Hz, 2H), 7.01−7.15 (m, 2H) overlapped with 7.10 (d, J = 8.8 Hz, 2H), 7.17−7.28 (m, 1H), 7.46 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.2, 29.2, 29.4, 40.8 (2C), 108.3, 110.3 (q), 112.9 (2C), 118.3, 118.6, 120.3, 127.9 (q), 128.6 (2C), 130.2 (q), 133.1 (q), 136.5 (q), 148.8 (q); IR ($CHCl_3$) ν_{max} 3467, 3029, 3022, 3011, 2943, 1614, 1519, 1473, 1236, 1198, 1066; MS m/z (%): 278 [M^+](100), 263 (100); Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06; Found C, 81.78; H, 7.95; N, 10.02.

*(2,5-Dimethyl-3-pyrrolyl)(4-methoxyphenyl)methane (**4i**).* Oil (0.10 g, 47% yield); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 2.19 (s, 3H), 3.69 (s, 2H), 3.80 (s, 3H), 5.60−5.65 (m, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.48 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.9, 12.9, 31.3, 55.1, 106.9, 113.6 (2C), 118.3 (q), 121.8 (q), 124.9 (q), 129.2 (2C), 134.9 (q), 160.4 (q); IR ($CHCl_3$) ν_{max} 3443, 3020, 3006, 2935, 1611, 1511, 1465, 1248, 1201, 1177; MS m/z (%): 215 [M^+](100), 200 (75), 108 (60). Anal. Calcd

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J. Org. Chem. 2015, 80, 4791−4796

for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51; Found C, 77.91; H, 7.95; N, 6.49.

*(2,5-Dimethyl-3-pyrrolyl)(3-indolyl)methane (**4j**).* Light brown solid (0.20 g, 91% yield); mp 113.0−114.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (s, 6H), 3.80 (s, 2H), 5.68 (br s, 1H), 6.84 (s, 1H), 7.03−7.19 (m, 2H), 7.25−7.35 (m, 2H), 7.61 (d, J = 7.2 Hz, 1H), 7.76 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.9, 12.8, 21.6, 107.1, 110.8, 117.1 (q), 117.9 (q), 118.9 (2C), 121.6 (2C), 124.7 (q), 127.4 (q), 133.7 (q), 136.3 (q); IR ($CHCl_3$) ν_{max} 3470, 3003, 2920, 1606, 1455, 1418, 1338, 1085; MS m/z (%): 224 [M^+](100), 209 (65), 107 (60); Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49; Found C, 80.15; H, 7.16; N, 12.44.

*(2,5-Dimethyl-3-pyrrolyl)(1-methyl-2-pyrrolyl)methane (**4k**).* Light brown solid (0.16 g, 85% yield); mp 84.0−85.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.09 (s, 3H), 2.15 (s, 3H), 3.48 (s, 3H), 3.61 (s, 2H), 5.54−5.58 (m, 1H), 5.80−5.85 (m, 1H), 5.98−6.10 (m, 1H), 6.48−6.53 (m, 1H), 7.26 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.7, 12.8, 23.4, 33.5, 106.1, 106.4, 106.9, 116.1 (q), 120.8, 121.6 (q), 124.8 (q), 133.0 (q); IR ($CHCl_3$) ν_{max} 3468, 3032, 2998, 1575, 1494, 1436, 1068; MS m/z (%): 188 [M^+](100), 173 (45), 107 (90); Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88; Found C, 76.40; H, 8.54; N, 14.82.

*(3,5-Dimethyl-2-pyrrolyl)(3-indolyl)methane (**4l**).* Light brown solid (0.19 g, 86% yield); mp 84.0−85.0 °C (DCM−PE); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.07 (s, 6H), 3.96 (s, 2H), 5.66 (br s, 1H), 6.91 (s, 1H), 7.03−7.17 (m, 2H), 7.32 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.90 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.8, 12.7, 21.4, 107.5, 110.9, 113.6 (q), 114.1 (q), 118.8, 119.4, 122.0, 122.1, 124.7 (q), 124.9 (q), 127.2 (q), 136.3 (q); IR ($CHCl_3$) ν_{max} 3480, 3018, 1576, 1418, 1222, 1069; MS m/z (%): 224 [M^+](100), 209 (70), 117 (45; Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49; Found C, 80.12; H, 7.20; N, 12.51.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **3a−l** and **4a−l**; selective excitation spectra for salts **3c** and **3f**; tables of full bond lengths and angles and CIF file for compound **3i**; and ORTEP and full refinement data of **3i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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