

## *Electronic Supplementary Information*

### **Towards sustainable synthesis of pyren-1-yl azoliums via electrochemical oxidative C–N coupling**

Guillaume de Robillard,<sup>a</sup> Oumayma Makni,<sup>a</sup> H el ene Cattey,<sup>a</sup> Jacques Andrieu<sup>a,\*</sup> and Charles H. Devillers<sup>a,\*</sup>

<sup>a</sup> ICMUB UMR6302, CNRS, Univ. Bourgogne Franche-Comt e, F-21000 Dijon, France.

Fax: +33 380396065; Tel: +33 380399125

E-mail: [charles.devillers@u-bourgogne.fr](mailto:charles.devillers@u-bourgogne.fr); [jacques.andrieu@u-bourgogne.fr](mailto:jacques.andrieu@u-bourgogne.fr)

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## 1. Reagents and instrumentation

Tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) was synthesized according to the following method. Typically, in a 500 mL Erlenmeyer flask, 84.28 g of tetrafluoroboric acid, HBF<sub>4</sub> (Sigma Aldrich, 48% in H<sub>2</sub>O) was mixed with 193.84 g of a solution of tetraethylammonium hydroxide, TEOH (Alfa Aesar, 35% in H<sub>2</sub>O). The reaction mixture was continuously stirred under an air atmosphere. Then, the white precipitate formed after cooling the flask in an ice bucket was isolated by filtration on a Buchner funnel. Finally, the residue was crystallized from MeOH (Carlo Erba, RPE, 99.9%) under reflux, cooled in a freezer at -18 °C, filtered on a Buchner funnel and dried at 110 °C in the stove for at least two days before use. CH<sub>3</sub>CN (SDS, Carlo Erba, HPLC gradient 99.9%) was distilled from CaH<sub>2</sub> under Ar, unless otherwise noted. Et<sub>2</sub>O (Sigma Aldrich, 99.5%, with BHT stabilizer), HBF<sub>4</sub>·Et<sub>2</sub>O (Sigma-Aldrich), 1-methylbenzimidazole (Alfa-Aesar, 99 %) and 1-methyl-1,2,4-triazole (Alfa-Aesar, 99 %) were used as received. 1-methylimidazole (Fluka puriss, 99 %) and benzothiazole (Alfa-Aesar, 97 %) were distilled before utilization.

NMR spectra were recorded using a BRUKER 500 MHz Avance II or 300 MHz Bruker Avance III NanoBay spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard.

Mass spectra were obtained using a Bruker Micro-ToF Q instrument in ESI mode.

Elemental analyses were performed on an Analyzer CHNS/O Thermo Electron Flash EA 1112 Series.

UV/Vis absorption spectra were recorded using a Varian Cary UV/Vis spectrophotometer 50 scan using quartz cells (Hellma). In the spectroelectrochemical experiments, a UV/Vis immersion probe (Hellma, *l* = 2 mm) was connected through a fiber optic to the same spectrophotometer.

Emission spectra were recorded on a JASCO FP8500 spectrofluorometer in a 10 mm path-length quartz cuvette (Starna) containing 1 mL of a solution of 1.25×10<sup>-5</sup> M of azolium compound in acetonitrile. Measurement parameters were common for each measured compound: λ<sub>ex</sub> = 341 nm, λ<sub>em</sub> = 360–600 nm, Ex and Em slits = 5 nm, 1 nm pitch, 1 s response, scan speed = 500 nm·min<sup>-1</sup>) at 20 °C.

## 2. Electrochemistry

Unless stated otherwise, all manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen free argon at room temperature (*T* = 20 °C ± 3 °C). The supporting electrolyte (tetraethylammonium tetrafluoroborate) was degassed under vacuum before use and then dissolved to a concentration of 0.1 M. Voltammetric analyses were carried out in a standard three-electrode cell, with an Autolab PGSTAT 302 N potentiostat, connected to an interfaced computer that employed Electrochemistry Nova software. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum wire. For all voltammetric measurements, the working electrode was a platinum electrode disk (*Ø* = 1 mm). In these conditions, when operating in acetonitrile (0.1 M TEABF<sub>4</sub>), the formal potential for the ferrocene (+/0) couple was found to be +0.40 V vs. SCE.

Electrolyses were performed in a cell with one or two compartments separated with glass frits of medium porosity with an Amel 552 potentiostat/galvanostat coupled with an Amel 721 electronic integrator. A platinum wire spiral (*l* = 50 cm, *Ø* = 1 mm) was used as the working electrode, a platinum wire spiral (*l* = 50 cm, *Ø* = 1 mm) as the counter electrode and a saturated calomel electrode as the reference electrode.

### 3. Synthesis and characterization of pyren-1-yl azoliums

#### 3.1. General procedure for the formation of pyren-1-yl azoliums

Electrolyses were carried out under an argon atmosphere in 30 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), nucleophile (3.75 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (0.260 mL, 1.89 mmol) in a two compartment cell under vigorous stirring at room temperature ( $T = 20\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ ) and at controlled potential. Electrolyses were stopped after an uptake of 2.35-3.0 F per mol of pyrene. After evaporation of the solvent up to a volume of *ca.* 2 mL, the precipitate obtained by addition of water (100 mL) was washed with 20 mL of Et<sub>2</sub>O and dried under vacuum.

#### 3.2. Synthesis of 1-methyl-3-(pyren-1-yl)-1*H*-imidazol-3-ium tetrafluoroborate (1<sup>+</sup>,BF<sub>4</sub><sup>-</sup>)

*Entry 2, 3, 5, Table 1*

Electrolysis was performed in a two compartment cell under stirring, argon atmosphere, at room temperature, in 30 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), 1-methylimidazole (7.53 mmol, 3.76 mmol, 2.51 mmol for entries 2, 3 and 5, respectively) and HBF<sub>4</sub>·Et<sub>2</sub>O (1.89 mmol for entries 2 and 3, 1.25 mmol for entry 5). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 3.25, 2.35, 2.00 F per mol of pyrene, respectively, the solution was concentrated up to a volume of *ca.* 2 mL and 100 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (20 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (0.425 g, 1.15 mmol, 91.8%, 0.425 g, 1.15 mmol, 91.8%, 0.345 g, 0.93 mmol, 74.5%, respectively).

*Entry 4, Table 1*

Electrolysis was performed in a two compartment cell under stirring, at room temperature, under an initial air atmosphere, in 30 mL of acetonitrile (HPLC grade) containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), 1-methylimidazole (0.3 mL, 3.76 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (0.26 mL, 1.89 mmol). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 3.25 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 2 mL and 100 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (20 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (0.388 g, 1.05 mmol, 83.9%).

*Entry 6, Table 1*

Electrolysis was performed in a two compartment cell under stirring, under Ar, at room temperature, in 165 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (3.500 g, 17.3 mmol), 1-methylimidazole (4.15 mL, 52.1 mmol) and HBF<sub>4</sub>(Et<sub>2</sub>O) (3.6 mL, 26.2 mmol). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 2.05 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 10 mL and 200 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (50 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (6.105 g, 16.49 mmol, 95.3%).

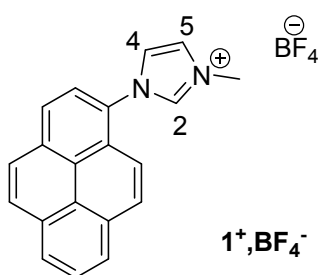
*Entry 7, Table 1*

Electrolysis was performed in a one compartment cell (galvanostatic conditions, without reference electrode) under stirring, under Ar, at room temperature, in 20 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (4.045 g, 20.0 mmol), 1-methylimidazole (4.78 mL, 60.0 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (4.12 mL, 30.0 mmol). The applied current was 50 mA. The

electrolysis was stopped after an uptake of 2.05 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 10 mL and 200 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (50 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (6.384 g, 17.25 mmol, 86.2%).

*Entry 8, Table 1*

Electrolysis was performed in a one compartment cell (galvanostatic conditions, without reference electrode) under stirring, under Ar, at room temperature, in 20 mL of acetonitrile containing pyrene (4.045 g, 20.0 mmol), 1-methylimidazole (4.78 mL, 60.0 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (4.12 mL, 30.0 mmol). The applied current was 50 mA. The electrolysis was stopped after an uptake of 2.05 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 10 mL and 200 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (50 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (5.930 g, 16.02 mmol, 80.1%).



**1-methyl-3-(pyren-1-yl)-1H-imidazol-3-ium tetrafluoroborate (1<sup>+</sup>,BF<sub>4</sub><sup>-</sup>).** Elemental analysis: Found: C, 64.88; H, 4.11; N, 7.61. Calc. for C<sub>15</sub>H<sub>20</sub>BF<sub>4</sub>N<sub>2</sub>: C, 64.90; H, 4.08; N, 7.57; λ<sub>max</sub> (CH<sub>3</sub>CN)/nm (log ε) 233 (4.62), 242 (4.76), 265 (4.36), 275 (4.58), 314 (4.01), 326 (4.36), 341 (4.51); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, 298 K) δ (ppm) 9.74 (1H, s, H2), 8.54 (1H, d, J = 8.2 Hz, Hpyrene), 8.50 (1H, br d, J = 2.9 Hz, Hpyrene), 8.47 (1H, br d, J = 3.0 Hz, Hpyrene), 8.42 (1H, d, J = 9.3 Hz, Hpyrene), 8.38 (2H, dd, J = 9.0 Hz, 7.6 Hz, Hpyrene), 8.30 (1H, t, J = 1.8 Hz, H4), 8.30 (1H, d, J = 8.1 Hz, Hpyrene), 8.23 (1H, t, J = 7.6 Hz, Hpyrene), 8.12 (1H, t, J = 1.7 Hz, H5), 7.92 (1H, d, J = 9.2 Hz, Hpyrene), 4.08 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz, 298 K) δ (ppm) 138.7 (C2), 132.2, 130.6, 130.1, 130.1, 129.3, 128.0, 127.3, 127.0, 126.9, 126.5, 125.7, 125.1, 124.9 (C4), 124.4, 124.2 (C5), 123.9, 123.1, 120.2, 36.3 (CH<sub>3</sub>); HRMS (ESI-MS) m/z calcd. For C<sub>20</sub>H<sub>16</sub>N<sub>2</sub> [M]<sup>+</sup>: 283.12298, found: 283.12195.

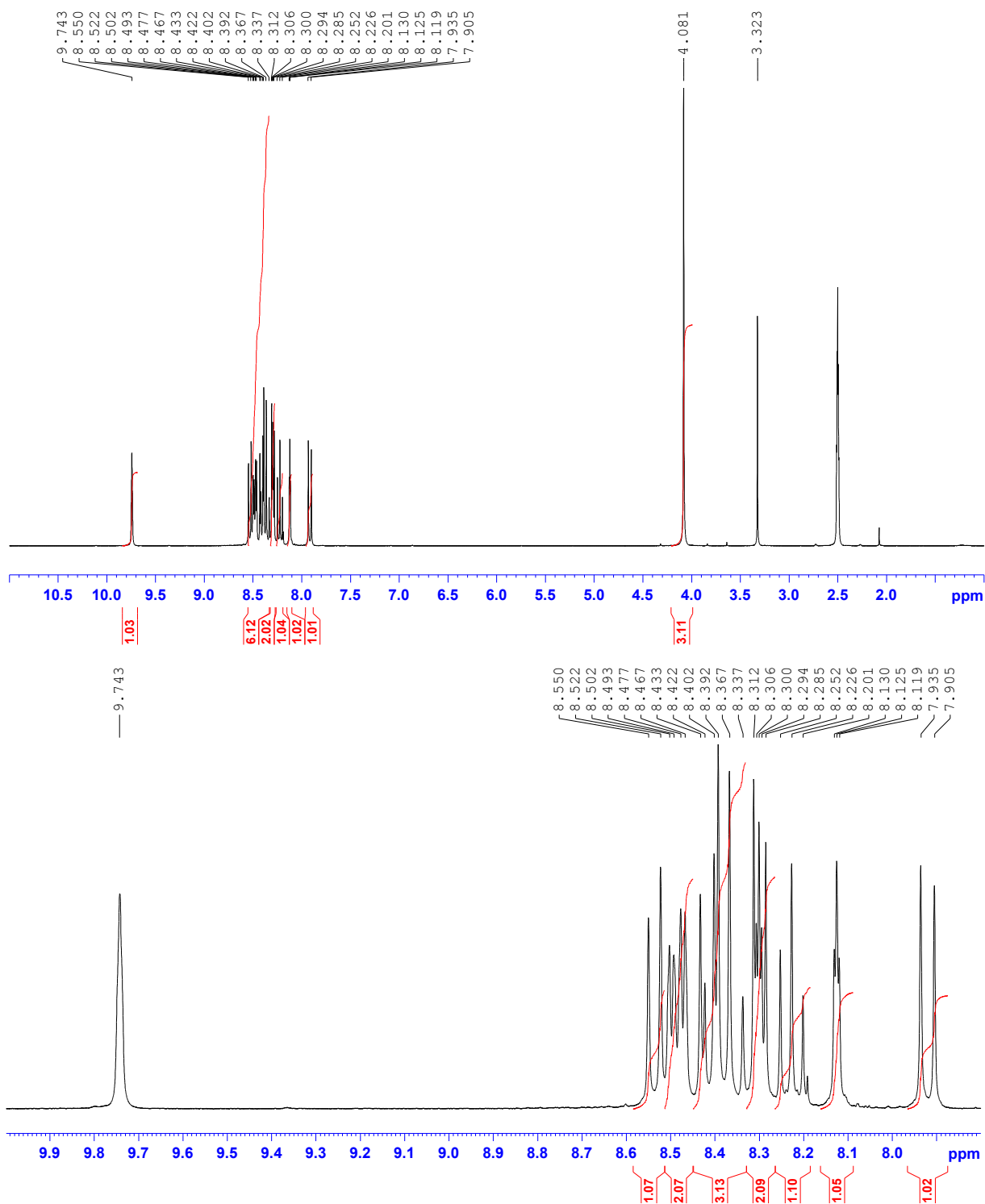


Figure S1.  $^1\text{H}$  NMR spectrum of  $1^+\text{BF}_4^-$  in  $\text{DMSO-d}_6$ , 300 MHz, 298 K.



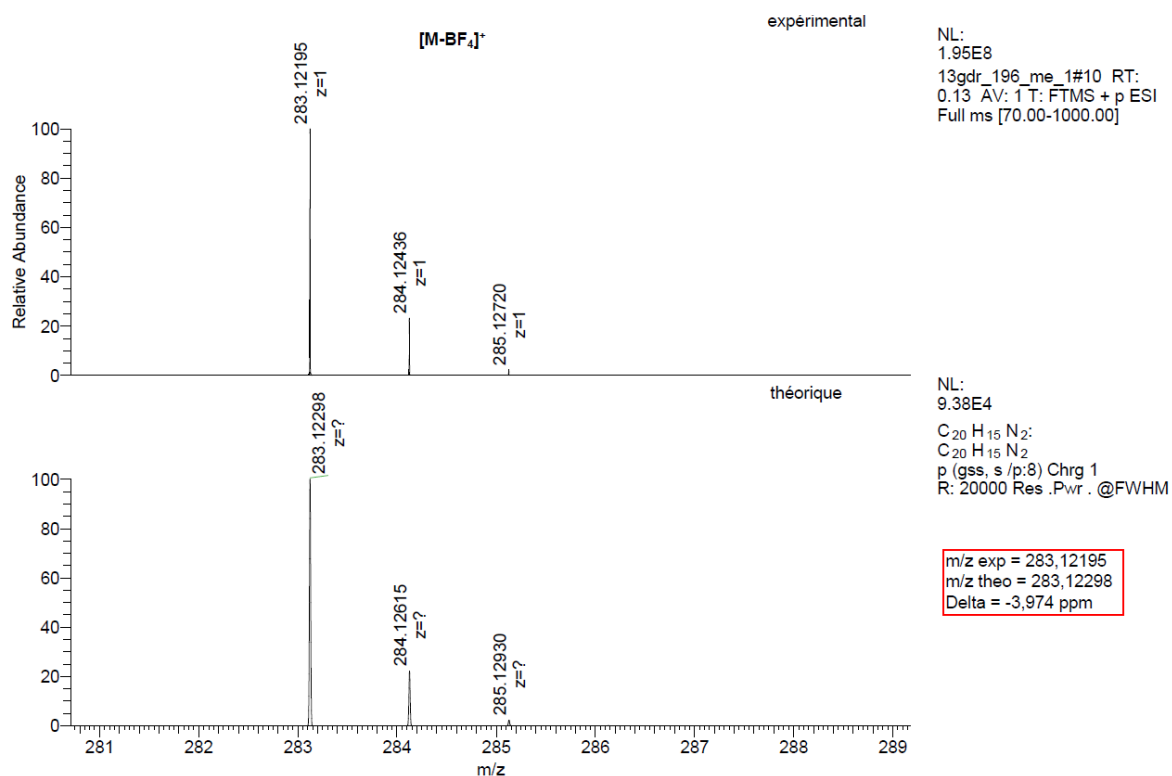
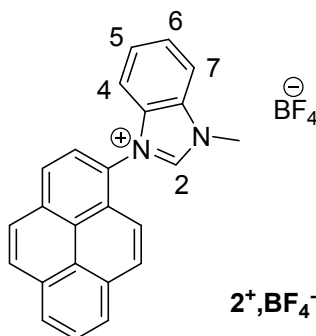


Figure S3. HRMS (ESI-MS) of  $1^+,BF_4^-$

### 3.3. Synthesis of 1-methyl-3-(pyren-1-yl)-1*H*-benzimidazol-3-ium tetrafluoroborate ( $2^+,BF_4^-$ )

Entry 9, Table 1

Electrolysis was performed in a two compartment cell under stirring, under Ar, at room temperature, in 30 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), methylimidazole (0.498 g, 3.77 mol) and HBF<sub>4</sub>·Et<sub>2</sub>O (0.26 mL, 1.89 mmol). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 2.66 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 2 mL and 100 mL of water was added. The resulting white precipitate was filtered, washed with Et<sub>2</sub>O (20 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (0.430 g, 1.02 mmol, 81.7%).



**1-methyl-3-(pyren-1-yl)-1*H*-benzimidazol-3-ium tetrafluoroborate ( $2^+,BF_4^-$ ).** Elemental analysis: Found: C, 68.70; H, 4.27; N, 6.63. Calc. for C<sub>24</sub>H<sub>17</sub>BF<sub>4</sub>N<sub>2</sub>: C, 68.60; H, 4.08; N, 6.67;  $\lambda_{max}$  (CH<sub>3</sub>CN)/nm (log  $\epsilon$ ) 234 (4.57), 242 (4.70), 265 (4.44), 276 (4.61), 315 (4.04), 327

(4.36), 342 (4.49);  $^1\text{H}$  NMR (Acetone- $\text{d}_6$ , 300 MHz, 298K)  $\delta$  (ppm) 10.08 (1H, s, H2), 8.59 (1H, d,  $J = 8.2$  Hz,  $\text{H}_{\text{pyrene}}$ ), 8.51 (1H, m,  $\text{H}_{\text{pyrene}}$ ), 8.48-8.36 (4H, m,  $\text{H}_{\text{pyrene}}$ ), 8.31 (2H, m,  $\text{H4} + \text{H}_{\text{pyrene}}$ ), 8.23 (1H, t,  $J = 7.7$  Hz,  $\text{H}_{\text{pyrene}}$ ), 7.89 (1H, m, H5), 7.83 (1H, d,  $J = 9.3$  Hz,  $\text{H}_{\text{pyrene}}$ ), 7.73 (1H, m, H6), 7.54 (1H, m, H7), 4.53 (3H, d,  $J = 0.5$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (Acetone- $\text{d}_6$ , 75 MHz, 298K)  $\delta$  (ppm) 145.0 (C2), 134.6, 134.3, 133.4, 132.1, 131.6, 131.3, 130.7, 128.7, 128.4, 128.3, 128.2, 128.1, 127.7, 126.7, 126.5, 126.3, 125.9, 124.7, 121.3, 114.9, 114.7 (C7), 34.7 ( $\text{CH}_3$ ); HRMS (ESI-MS)  $m/z$  calcd. For  $\text{C}_{24}\text{H}_{17}\text{N}_2$   $[\text{M}]^+$ : 333.13863, found: 333.13727.

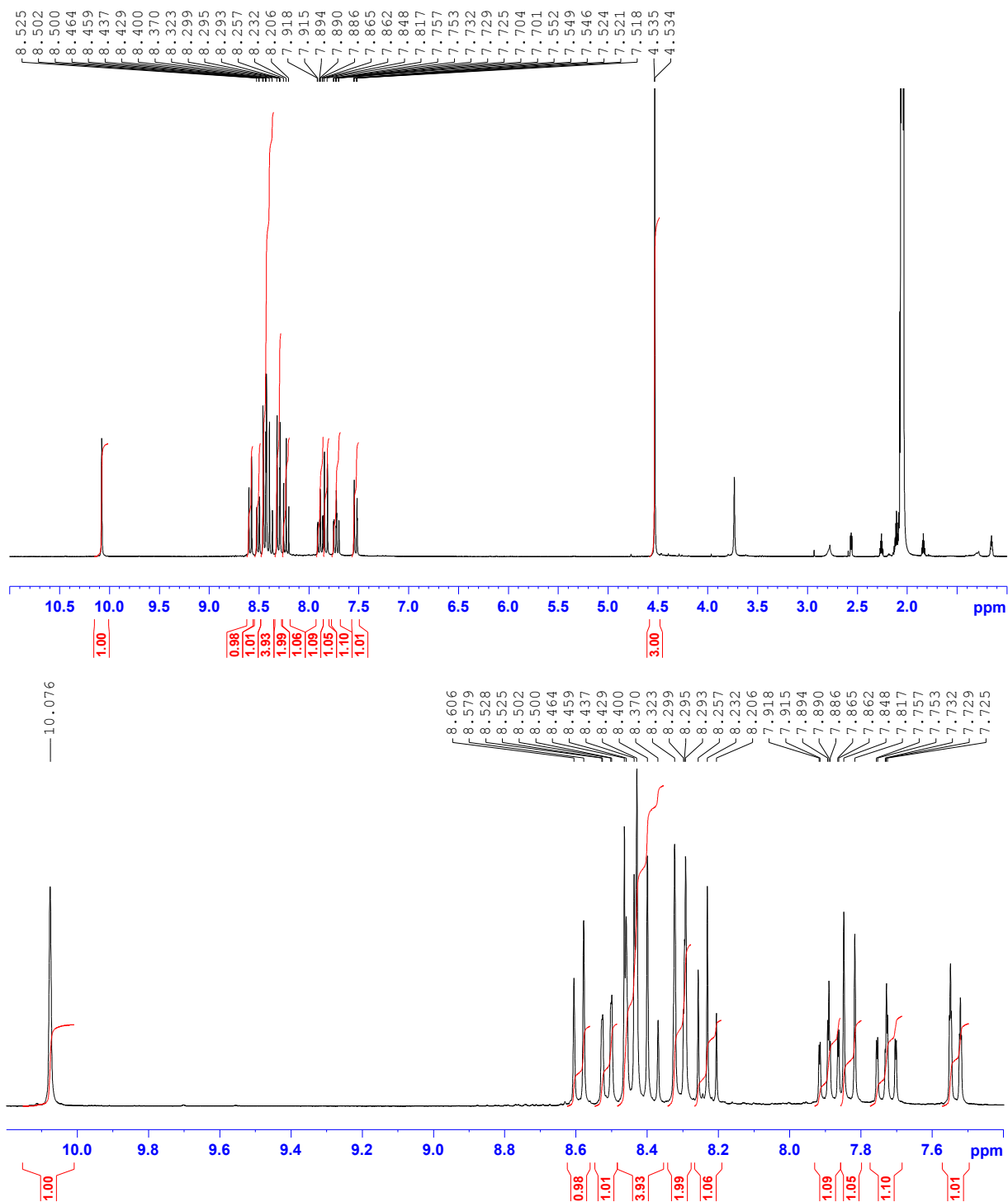


Figure S4.  $^1\text{H}$  NMR spectrum of  $2^+ \cdot \text{BF}_4^-$  in Acetone- $\text{d}_6$ , 300 MHz, 298 K.



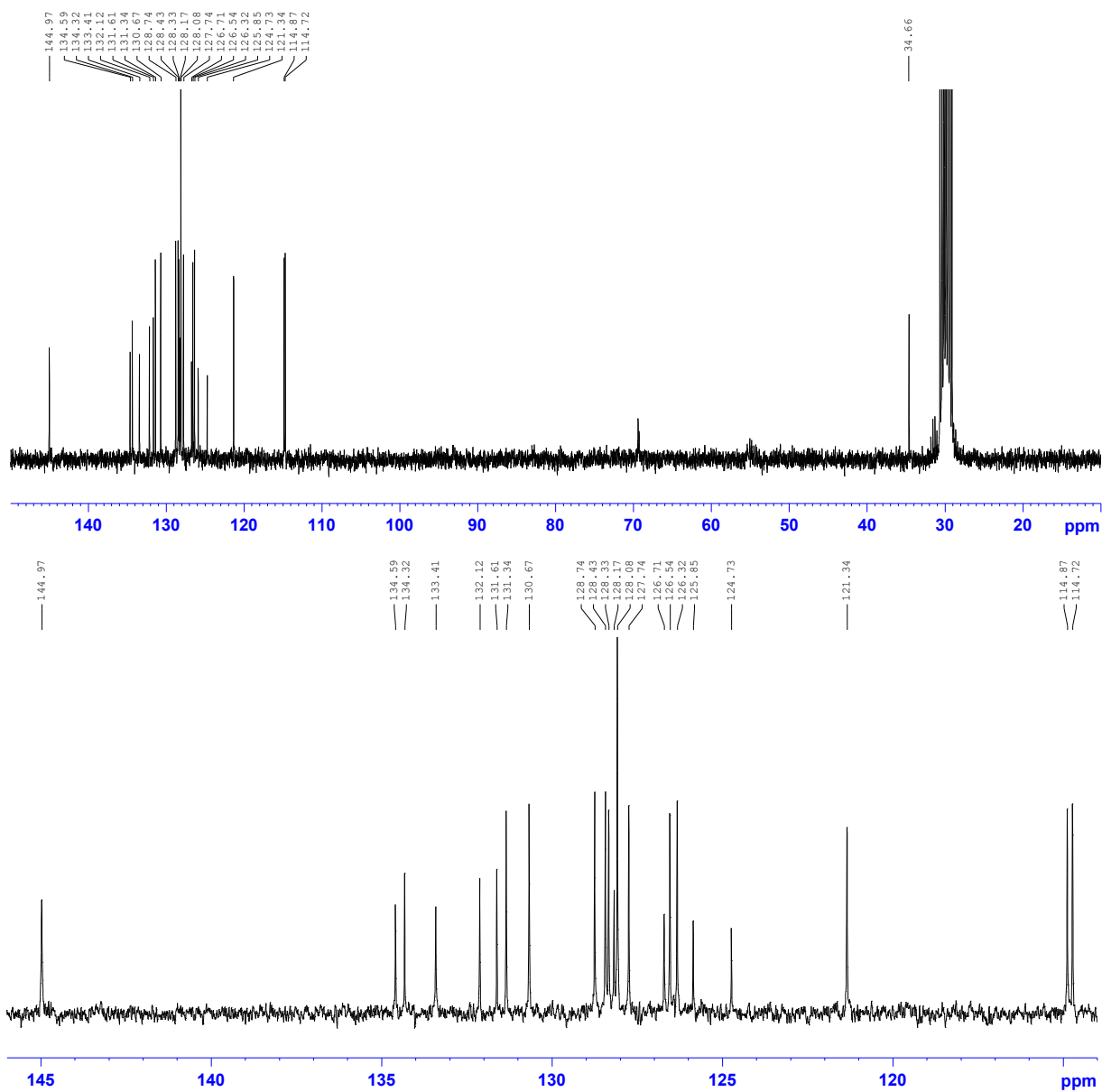


Figure S5.  $^{13}\text{C}$  NMR spectrum of  $2^+, \text{BF}_4^-$  in  $\text{Acetone-d}_6$ , 75 MHz, 298 K.

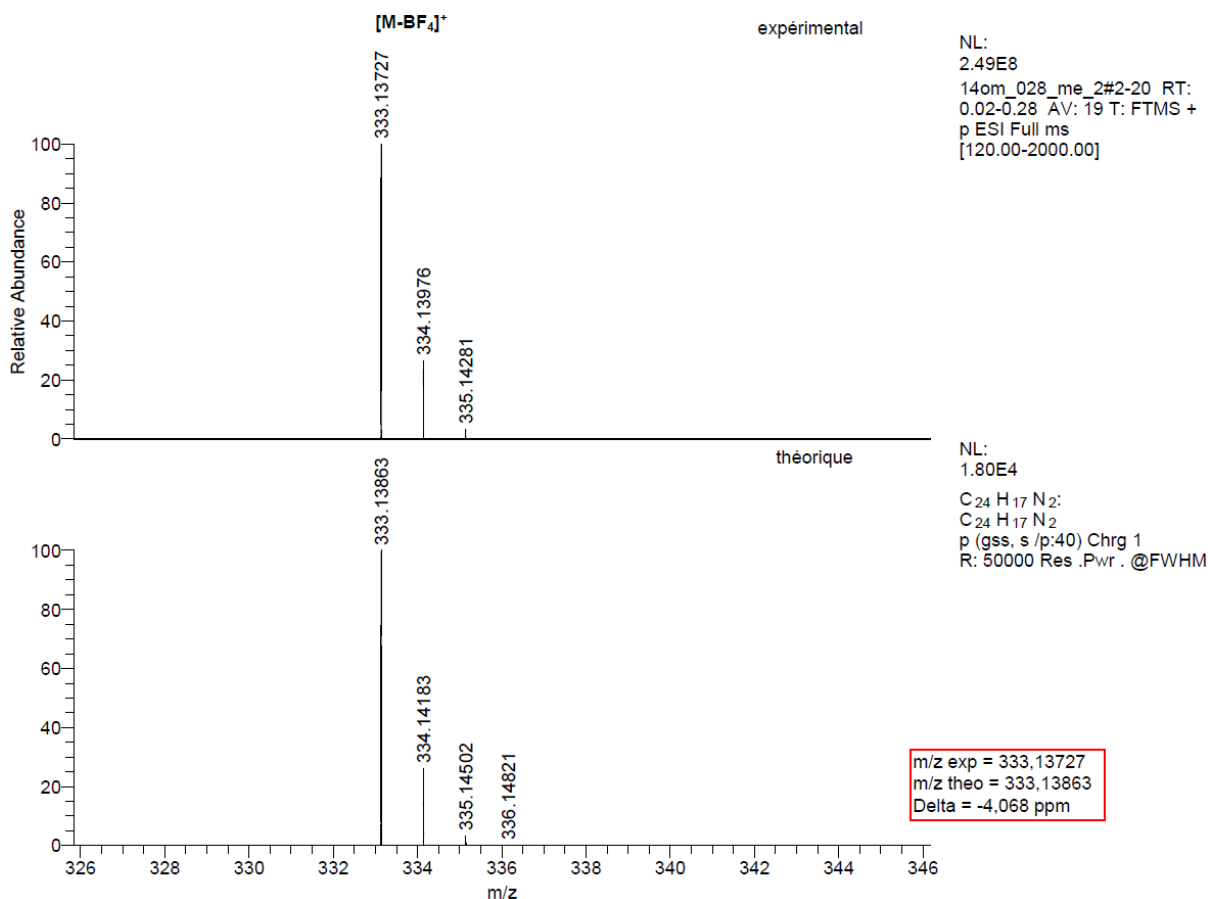
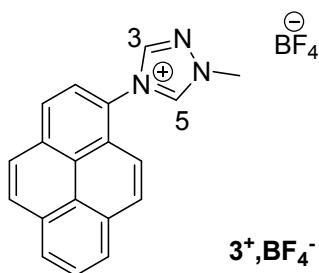


Figure S6. HRMS (ESI-MS) of  $2^+, \text{BF}_4^-$

### 3.4. Synthesis of 1-methyl-4-(pyren-1-yl)-1*H*-1,2,4-triazol-4-ium tetrafluoroborate ( $3^+, \text{BF}_4^-$ )

Entry 10, Table 1

Electrolysis was performed in a two compartment cell under stirring, under Ar, at room temperature, in 30 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), 1-methyl-1,2,4-triazole (0.285 mL, 3.77 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (0.260 mL, 1.89 mmol). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 2.55 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 2 mL and 100 mL of water was added. The slightly yellow precipitate was filtered, washed with Et<sub>2</sub>O (20 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (0.407 g, 1.10 mmol, 87.8%).



1-methyl-4-(pyren-1-yl)-1*H*-1,2,4-triazol-4-ium tetrafluoroborate ( $3^+, \text{BF}_4^-$ ). Elemental

analysis: Found: C, 61.71; H, 3.80; N, 11.18. Calc. for  $C_{19}H_{14}BF_4N_3$ : C, 61.49; H, 3.80; N, 11.32;  $\lambda_{max}$  (CH<sub>3</sub>CN)/nm (log  $\epsilon$ ) 233 (4.58), 242 (4.73), 265 (4.34), 275 (4.55), 314 (4.00), 327 (4.34), 342 (4.49);  $^1H$  NMR (DMSO-d<sub>6</sub>, 300 MHz, 298K)  $\delta$  (ppm) 10.75 (1H, s, H5), 9.79 (1H, s, H3), 8.58 (1H, d,  $J = 8.2$  Hz, H<sub>pyrene</sub>), 8.55-8.42 (4H, m, H<sub>pyrene</sub>), 8.40-8.34 (2H, m, H<sub>pyrene</sub>), 8.25 (1H, t,  $J = 7.7$  Hz, H<sub>pyrene</sub>), 8.07 (1H, d,  $J = 9.3$  Hz, H<sub>pyrene</sub>), 4.29 (3H, s, CH<sub>3</sub>);  $^{13}C$  NMR (DMSO-d<sub>6</sub>, 75 MHz, 298K)  $\delta$  (ppm) 145.5 (C3), 144.5 (C5), 132.6, 130.6, 130.3, 130.0, 129.6, 127.4, 127.1, 127.0, 126.7, 125.7, 125.1, 124.8, 124.6, 123.8, 122.9, 120.2, 39.1 (CH<sub>3</sub>); HRMS (ESI-MS)  $m/z$  calcd. For  $C_{19}H_{14}N_3$  [M]<sup>+</sup>: 284.11822, found: 284.11741.

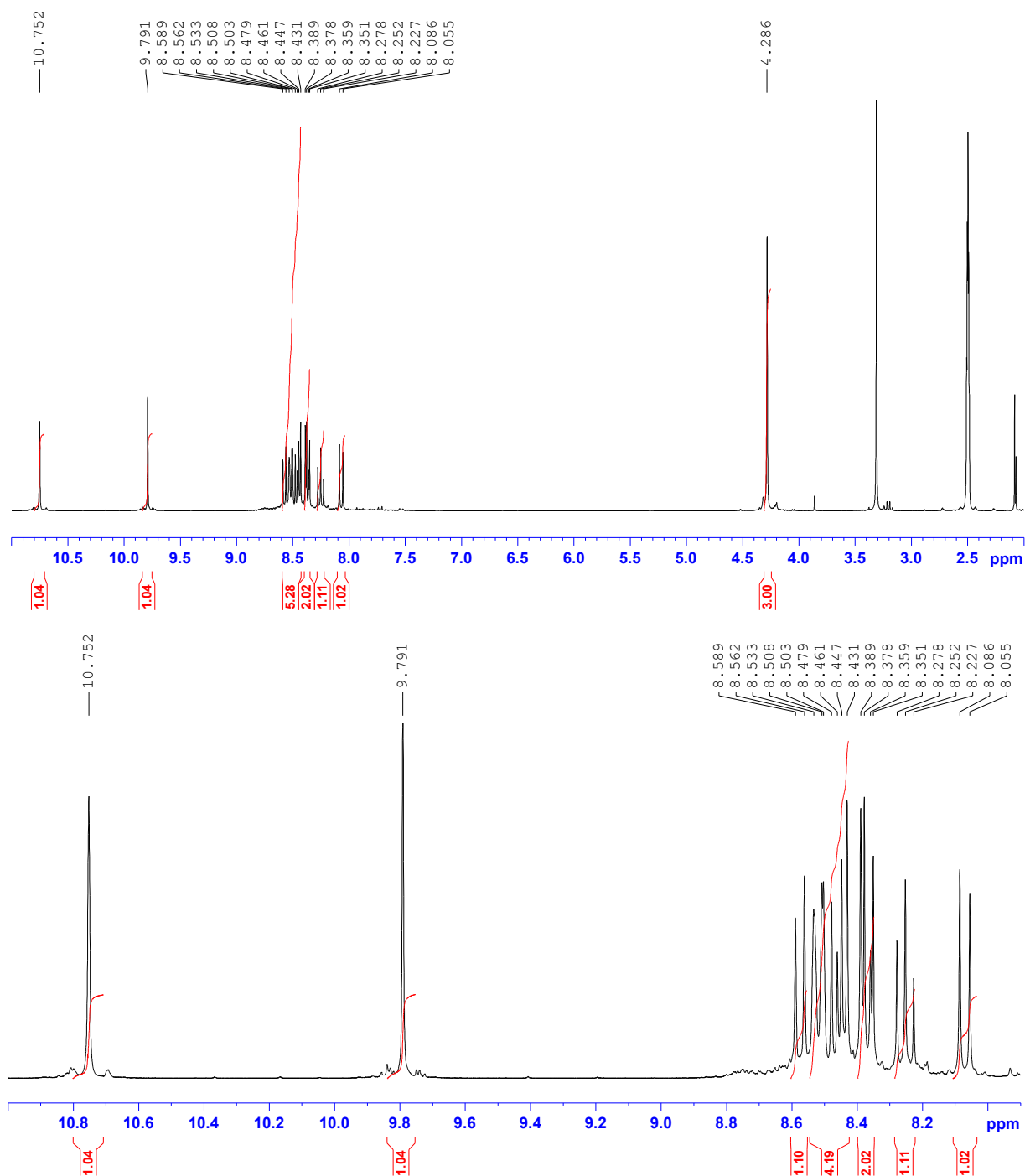


Figure S7.  $^1H$  NMR spectrum of  $3^+, BF_4^-$  in DMSO-d<sub>6</sub>, 300 MHz, 298 K.

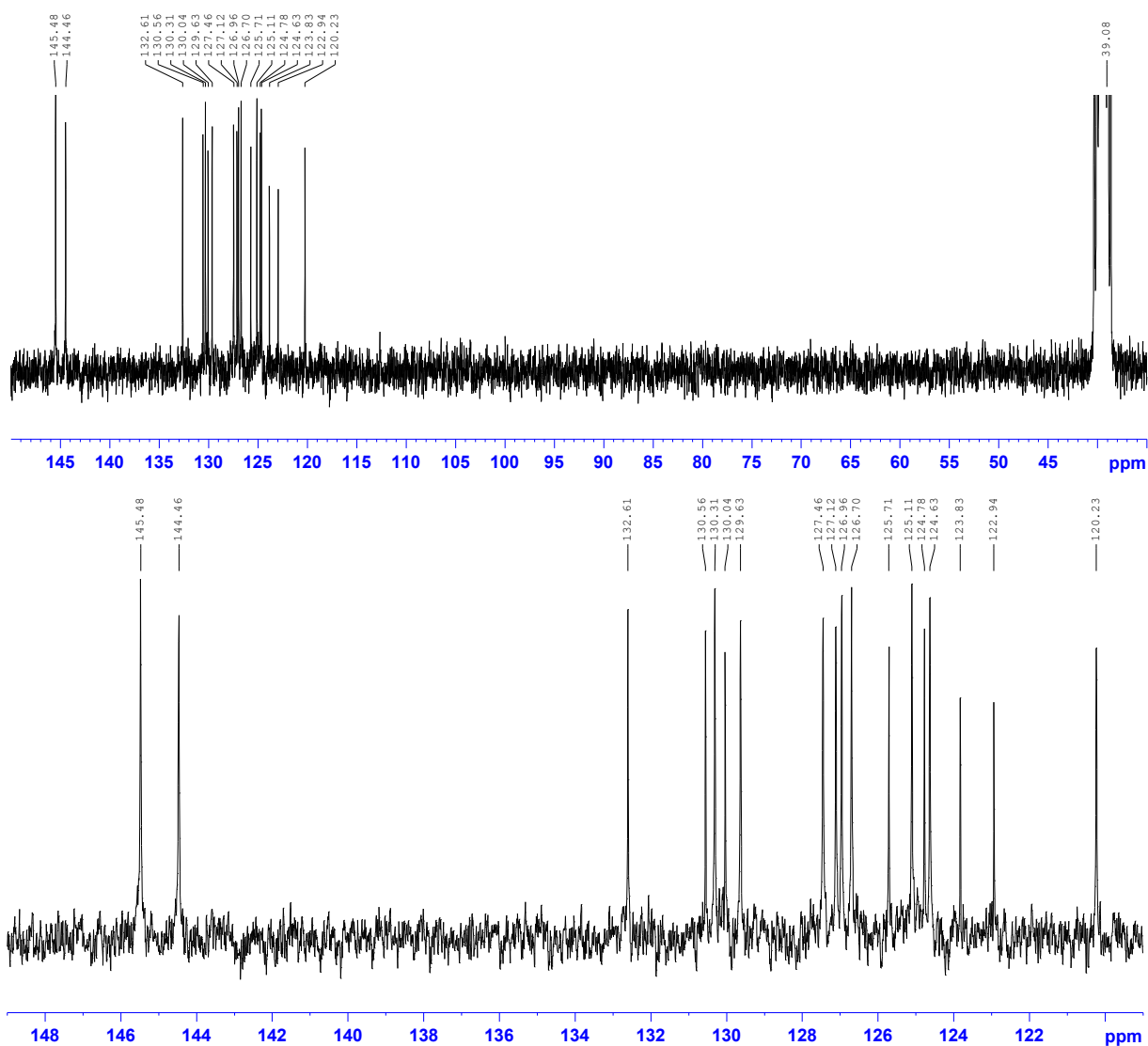


Figure S8.  $^{13}\text{C}$  NMR spectrum of  $3^+\text{BF}_4^-$  in  $\text{DMSO-d}_6$ , 75 MHz, 298 K.

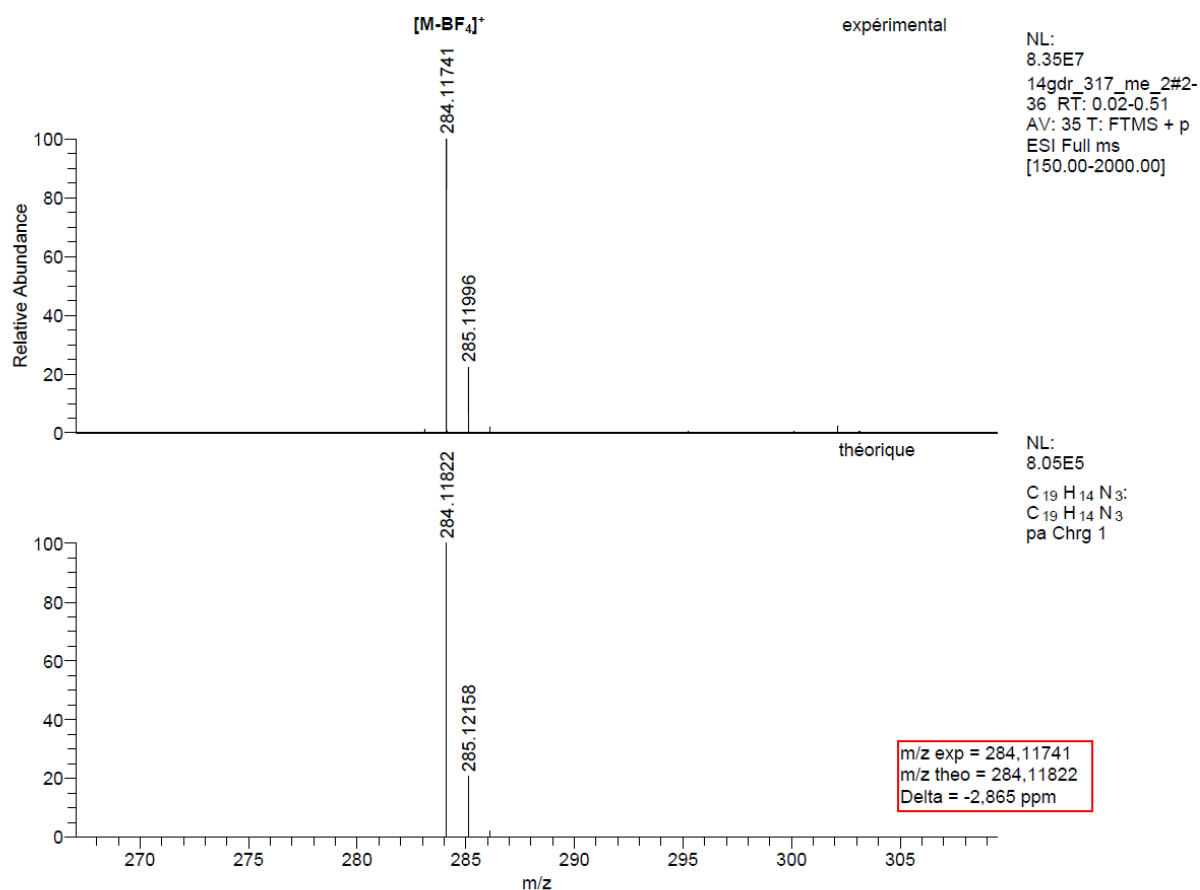
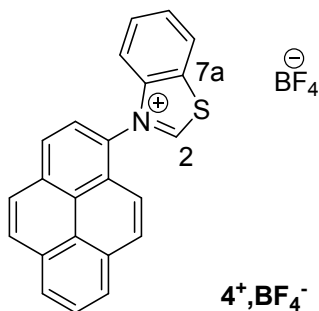


Figure S9. HRMS (ESI-MS) of  $3^+,BF_4^-$

### 3.5. Synthesis of 3-(pyren-1-yl)-benzothiazol-3-ium tetrafluoroborate ( $4^+,BF_4^-$ )

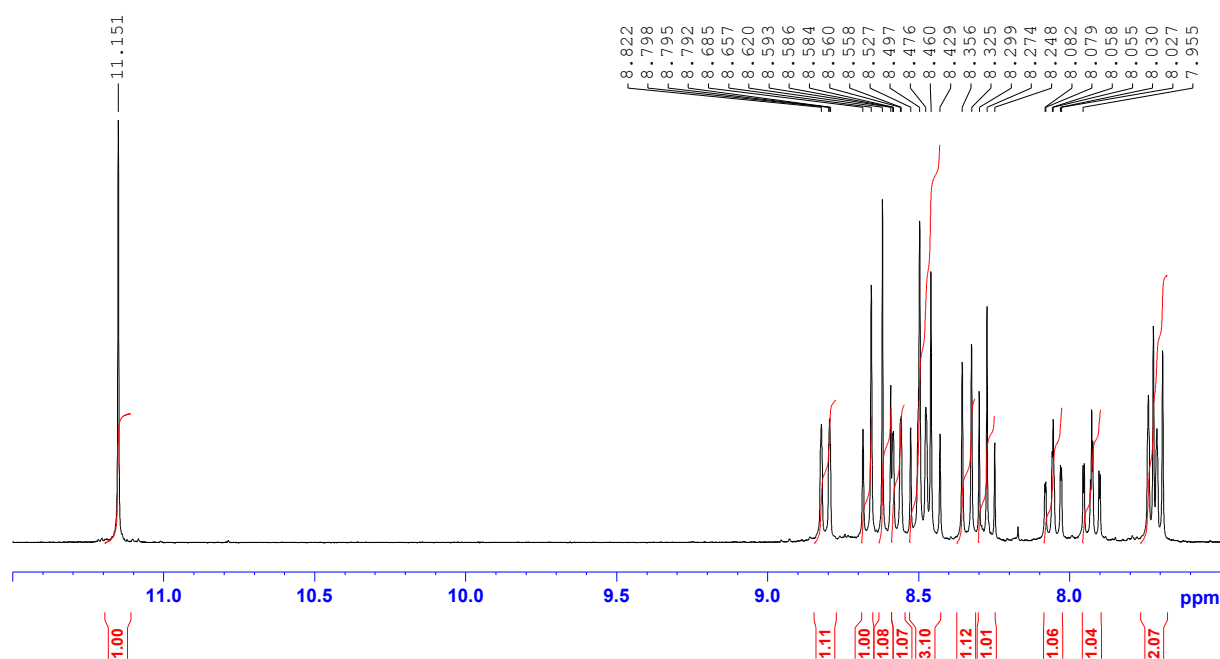
#### Entry 11, Table 1

Electrolysis was performed in a two compartment cell under sonication, under Ar, shielded from light, at room temperature, in 30 mL of acetonitrile containing 0.1 M of TEABF<sub>4</sub>, pyrene (0.253 g, 1.25 mmol), benzothiazole (0.41 mL, 3.75 mmol) and HBF<sub>4</sub>·OEt<sub>2</sub> (0.26 mL, 1.89 mmol). The applied potential was + 1.40 V/ECS. The electrolysis was stopped after an uptake of 3 F per mol of pyrene, the solution was concentrated up to a volume of *ca.* 2 mL and 100 mL of water was added. The resulting precipitate was filtered, washed with Et<sub>2</sub>O (50 mL) and dissolved in acetonitrile. After removing the solvent, the solid was dried under vacuum (0.305 g, 0.72 mmol, 57.3%).



**3-(pyren-1-yl)-benzothiazol-3-ium tetrafluoroborate (4<sup>+</sup>,BF<sub>4</sub><sup>-</sup>).**

Elemental analysis: Calc. for C<sub>23</sub>H<sub>14</sub>BF<sub>4</sub>NS: C, 65.27; H, 3.33; N, 3.31; S, 7.58; Found: C, 65.07; H, 3.37; N, 3.35; S, 7.81;  $\lambda_{\text{max}}$  (CH<sub>3</sub>CN)/nm (log  $\epsilon$ ) 234 (4.65), 242 (4.79), 266 (4.39), 276 (4.51), 314 (4.12), 328 (4.32), 342 (4.38); <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 300 MHz, 298K)  $\delta$  (ppm) 11.15 (1H, s, H2), 8.81 (1H, m, H4), 8.67 (1H, d, *J* = 8.2 Hz, H<sub>pyrene</sub>), 8.61 (1H, d, *J* = 8.2 Hz, H<sub>pyrene</sub>), 8.57 (1H, m, H<sub>pyrene</sub>), 8.53-8.42 (3H, m, H<sub>pyrene</sub>), 8.33 (1H, d, *J* = 8.9 Hz, H<sub>pyrene</sub>), 8.27 (1H, t, *J* = 7.6 Hz, H<sub>pyrene</sub>), 8.04 (1H, m, H5), 7.92 (1H, m, H6), 7.73 (1H, m, H7), 7.71 (1H, d, *J* = 9.2 Hz, H<sub>pyrene</sub>); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 125 MHz, 298K)  $\delta$  (ppm) 167.5 (C7a), 143.9 (C2), 134.9, 132.6, 132.1, 131.9, 131.8 (C6), 131.6, 131.1, 130.4 (C5), 129.4, 128.6, 128.5, 128.1, 127.8, 126.6, 126.3 (C4), 125.9, 125.8, 124.6, 120.8, 118.8; HRMS (ESI-MS) *m/z* calcd. For C<sub>23</sub>H<sub>14</sub>NS [M]<sup>+</sup>: 336.08282, found: 336.08415.



**Figure S10.** <sup>1</sup>H NMR spectrum of 4<sup>+</sup>,BF<sub>4</sub><sup>-</sup> in Acetone-d<sub>6</sub>, 500 MHz, 298 K.

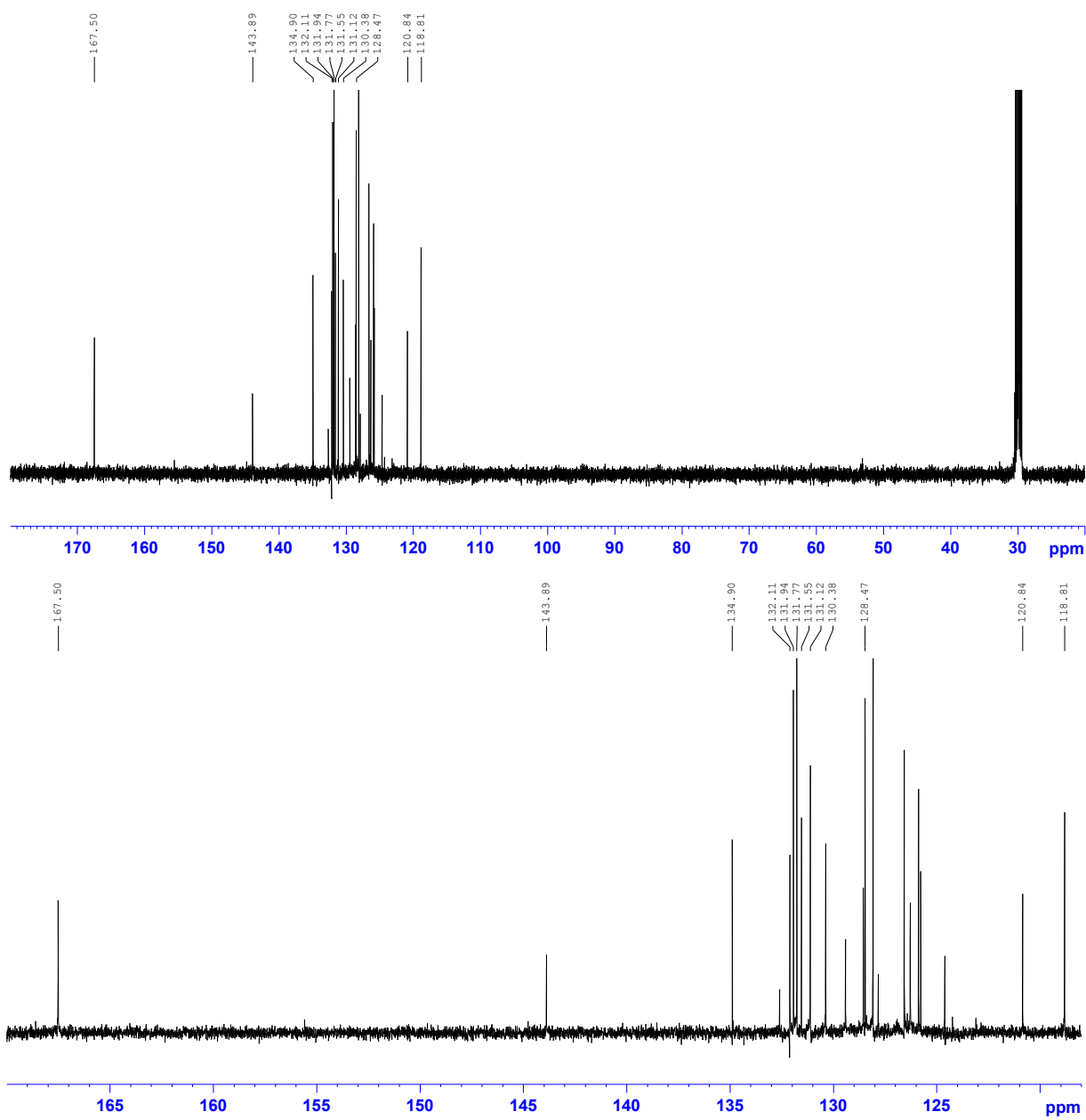
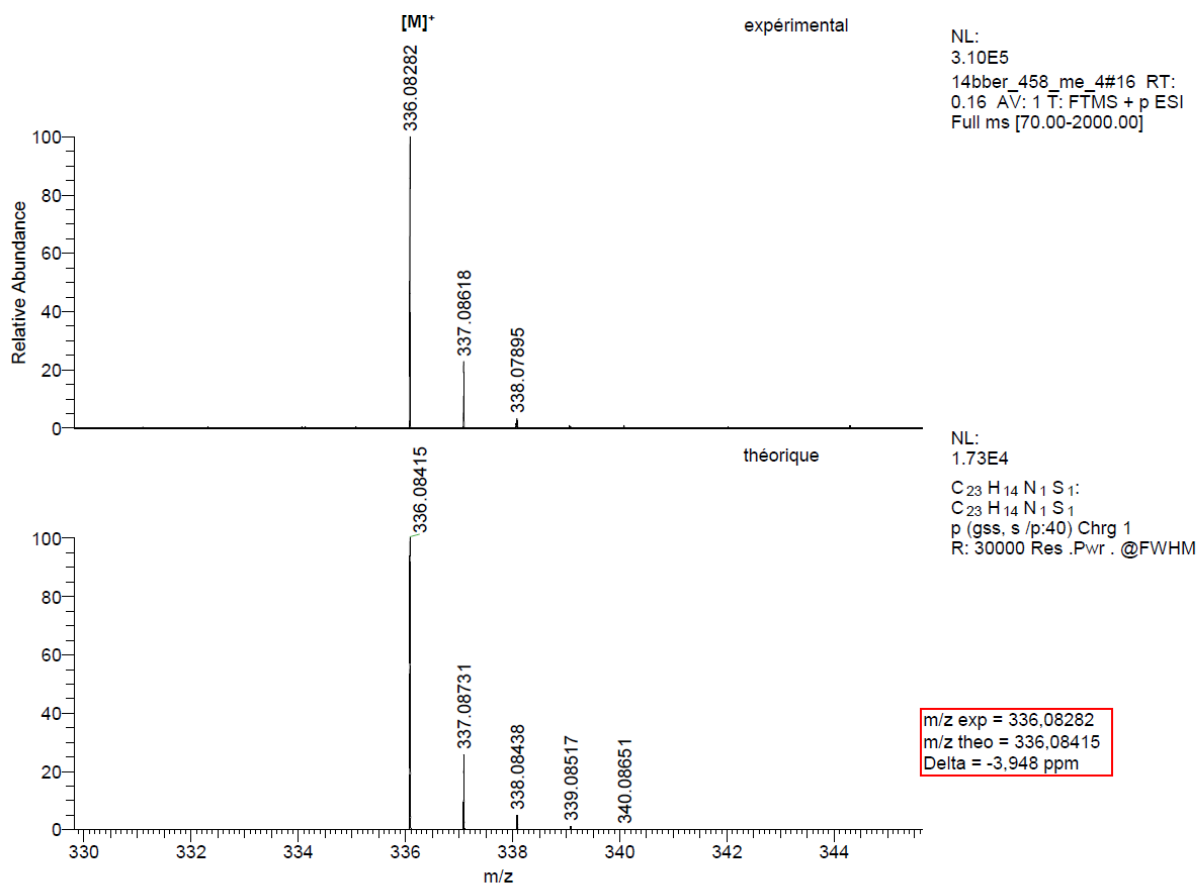


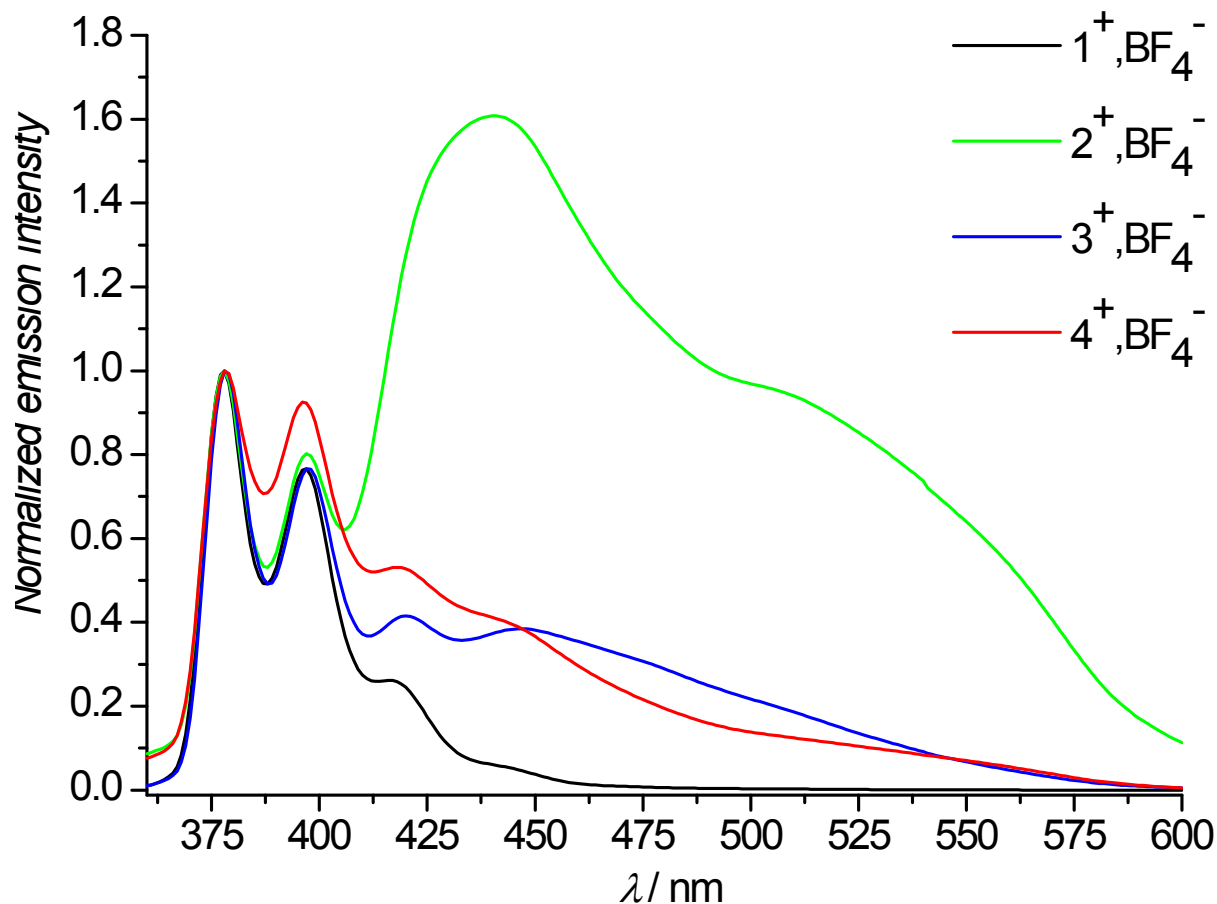
Figure S11.  $^{13}\text{C}$  NMR spectrum of  $4^+, \text{BF}_4^-$  in  $\text{Acetone-d}_6$ , 125 MHz, 298 K.



**Figure S12.** HRMS (ESI-MS) of 4<sup>+</sup>,BF<sub>4</sub><sup>-</sup>



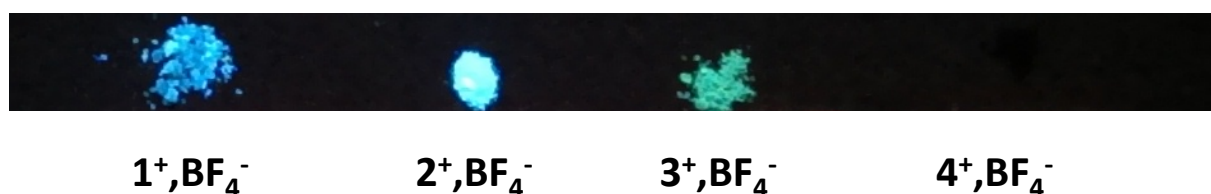
### 3.6. Fluorescence properties of azolium compounds



**Figure S13.** Normalized emission spectra of  $1^+, \text{BF}_4^-$ ,  $2^+, \text{BF}_4^-$ ,  $3^+, \text{BF}_4^-$  and  $4^+, \text{BF}_4^-$  (normalized at  $\lambda = 378$  nm, identical measurement parameters for each compound,  $\text{CH}_3\text{CN}$ ,  $C = 1.25 \times 10^{-5}$  M,  $\lambda_{\text{excitation}} = 341$  nm).

**Table S1.** Wavelengths of maxima and associated relative emission intensities for  $1^+, \text{BF}_4^-$ ,  $2^+, \text{BF}_4^-$ ,  $3^+, \text{BF}_4^-$  and  $4^+, \text{BF}_4^-$  ( $\text{CH}_3\text{CN}$ ,  $C = 1.25 \times 10^{-5}$  M,  $\lambda_{\text{excitation}} = 341$  nm, identical measurement parameters were used for each compound). The highest emission intensity (for  $1^+, \text{BF}_4^-$  at 378 nm) was arbitrarily fixed to 1.000 for an easier comparison between pyrene-based compounds.

Compound	$\lambda_{\text{max}}$ (nm) / relative emission intensity	$\lambda_{\text{max}}$ (nm) / relative emission intensity	$\lambda_{\text{max}}$ (nm) / relative emission intensity	$\lambda_{\text{max}}$ (nm) / relative emission intensity
$1^+, \text{BF}_4^-$	378 / 1.000	397 / 0.766	416 / 0.262	
$2^+, \text{BF}_4^-$	378 / 0.012	397 / 0.009	440 / 0.019	
$3^+, \text{BF}_4^-$	378 / 0.396	397 / 0.304	420 / 0.165	447 / 0.153
$4^+, \text{BF}_4^-$	378 / 0.007	396 / 0.006	418 / 0.004	



**Figure S14.** Picture taken with  $\lambda_{\text{excitation}} = 365$  nm for  $1^+, \text{BF}_4^-$ ,  $2^+, \text{BF}_4^-$ ,  $3^+, \text{BF}_4^-$  and  $4^+, \text{BF}_4^-$  in the solid state.

### 3.7. Crystal structure determination of $1^+, \text{BF}_4^-$ and $2^+, \text{BF}_4^-$ .

**Crystal Data** for  $\text{C}_{20}\text{H}_{15}\text{BF}_4\text{N}_2$  ( $M=370.15$  g/mol): orthorhombic, space group Pbc<sub>a</sub> (no. 61),  $a = 11.5582(7)$  Å,  $b = 12.3717(7)$  Å,  $c = 23.8099(18)$  Å,  $V = 3404.7(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 115.0$  K,  $\mu(\text{MoK}\alpha) = 0.115$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.444$  g/cm<sup>3</sup>, 22986 reflections measured ( $5.914^\circ \leq 2\theta \leq 54.95^\circ$ ), 3884 unique ( $R_{\text{int}} = 0.0301$ ,  $R_{\text{sigma}} = 0.0249$ ) which were used in all calculations. The final  $R_1$  was 0.0499 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1362 (all data).

**Crystal Data** for  $\text{C}_{26}\text{H}_{20}\text{BF}_4\text{N}_3$  ( $M=461.26$  g/mol): triclinic, space group P-1 (no. 2),  $a = 8.5758(6)$  Å,  $b = 10.4878(7)$  Å,  $c = 12.8368(8)$  Å,  $\alpha = 75.320(2)^\circ$ ,  $\beta = 78.092(2)^\circ$ ,  $\gamma = 74.019(2)^\circ$ ,  $V = 1062.06(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 100.0$  K,  $\mu(\text{MoK}\alpha) = 0.110$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.442$  g/cm<sup>3</sup>, 52383 reflections measured ( $5.576^\circ \leq 2\theta \leq 55.19^\circ$ ), 4913 unique ( $R_{\text{int}} = 0.0332$ ,  $R_{\text{sigma}} = 0.0167$ ) which were used in all calculations. The final  $R_1$  was 0.0379 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1019 (all data).

**Table S2.** Crystal and structure refinement data for  $1^+, \text{BF}_4^-$  and  $2^+, \text{BF}_4^-$ .

Identification Code	$1^+, \text{BF}_4^-$	$2^+, \text{BF}_4^-$
Empirical formula	$\text{C}_{20}\text{H}_{15}\text{BF}_4\text{N}_2$	$\text{C}_{26}\text{H}_{20}\text{BF}_4\text{N}_3$
Formula weight	370.15	461.26
Temperature/K	115	100
Crystal system	orthorhombic	triclinic
Space group	Pbc <sub>a</sub>	P-1
$a/\text{Å}$	11.5582(7)	8.5758(6)
$b/\text{Å}$	12.3717(7)	10.4878(7)
$c/\text{Å}$	23.8099(18)	12.8368(8)
$\alpha/^\circ$	90	75.320(2)
$\beta/^\circ$	90	78.092(2)
$\gamma/^\circ$	90	74.019(2)
Volume/Å <sup>3</sup>	3404.7(4)	1062.06(12)
$Z$	8	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.444	1.442
$\mu/\text{mm}^{-1}$	0.115	0.110
$F(000)$	1520.0	476.0
Crystal size/mm <sup>3</sup>	$0.30 \times 0.25 \times 0.10$	$0.25 \times 0.17 \times 0.13$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/ $^\circ$	5.914 to 54.95	5.576 to 55.19
Index ranges	$-15 \leq h \leq 9, -16 \leq k \leq 10, -29 \leq l \leq 30$	$-11 \leq h \leq 11, -13 \leq k \leq 13, -16 \leq l \leq 16$
Reflections collected	22986	52383
Independent reflections	3884 [ $R_{\text{int}} = 0.0301, R_{\text{sigma}} = 0.0249$ ]	4913 [ $R_{\text{int}} = 0.0332, R_{\text{sigma}} = 0.0167$ ]
Data/restraints/parameters	3884/0/273	4913/0/309
Goodness-of-fit on $F^2$	1.026	1.033
Final R indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0499, wR_2 = 0.1221$	$R_1 = 0.0379, wR_2 = 0.0933$
Final R indexes [all data]	$R_1 = 0.0714, wR_2 = 0.1362$	$R_1 = 0.0506, wR_2 = 0.1019$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.39/-0.32	0.39/-0.32
$N^\circ$ CCDC	1058690	1058691

#### 4. Atom efficiency and E factor calculations

$$\text{Atom efficiency (\%)} = \frac{M_{\text{final product}}}{\sum xM_{\text{reactant}}} \times 100$$

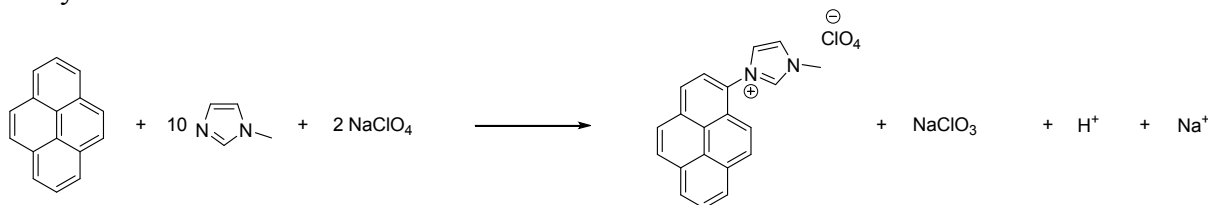
$$E \text{ factor (molar)} = EM = \frac{\sum xM_{\text{waste}}}{M_{\text{final product}}}$$

$$E \text{ factor (mass)} = Em = \frac{\sum m_{\text{reactant}} - m_{\text{final product}}}{m_{\text{final product}}}$$

entry	Reactant (xM/m)			M <sub>waste</sub> (g.mol <sup>-1</sup> )			M <sub>final product</sub> m <sub>final product</sub>	Atom efficiency (%)	E <sub>M</sub>	E <sub>m</sub>
	pyrene	nucleophile	Anion source	byproduct	excess					
					nucleophile	other				
1	202.26 g.mol <sup>-1</sup> 0.506 g	10×82.1 g.mol <sup>-1</sup> 2.053 g	2×122.44 g.mol <sup>-1</sup> 0.612 g	1.01 (H <sup>+</sup> ) 83.45 (ClO <sub>3</sub> <sup>-</sup> )	9×82.1 (MeIm)	2×22.99 (Na <sup>+</sup> )	382.8 g.mol <sup>-1</sup> 0.861 g	30	2.27	2.68
2	202.26 g.mol <sup>-1</sup> 0.253 g	6×82.1 g.mol <sup>-1</sup> 0.618 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	5×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 0.425 g	45	1.23	1.44
3	202.26 g.mol <sup>-1</sup> 0.253 g	3×82.1 g.mol <sup>-1</sup> 0.309 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	2×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 0.425 g	64	0.57	0.71
4	202.26 g.mol <sup>-1</sup> 0.253 g	3×82.1 g.mol <sup>-1</sup> 0.309 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	2×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 0.388 g	64	0.57	0.87
5	202.26 g.mol <sup>-1</sup> 0.253 g	2×82.1 g.mol <sup>-1</sup> 0.206 g	1×87.81 g.mol <sup>-1</sup> 0.110 g	2.02 (H <sub>2</sub> )	82.1 (MeIm)		370.2 g.mol <sup>-1</sup> 0.345 g	81	0.23	0.65
6	202.26 g.mol <sup>-1</sup> 3.500 g	3×82.1 g.mol <sup>-1</sup> 4.275 g	1.5×87.81 g.mol <sup>-1</sup> 2.279 g	2.02 (H <sub>2</sub> )	2×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 6.105 g	64	0.57	0.65
7	202.26 g.mol <sup>-1</sup> 4.045 g	3×82.1 g.mol <sup>-1</sup> 4.923 g	1.5×87.81 g.mol <sup>-1</sup> 2.634 g	2.02 (H <sub>2</sub> )	2×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 6.384 g	64	0.57	0.82
8	202.26 g.mol <sup>-1</sup> 4.045 g	3×82.1 g.mol <sup>-1</sup> 4.923 g	1.5×87.81 g.mol <sup>-1</sup> 2.634 g	2.02 (H <sub>2</sub> )	2×82.1 (MeIm)	0.5×87.81 (HBF <sub>4</sub> )	370.2 g.mol <sup>-1</sup> 5.93 g	64	0.57	0.96
9	202.26 g.mol <sup>-1</sup> 0.253 g	3×132.2 g.mol <sup>-1</sup> 0.498 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	2×132.2 (MeBzIm)	0.5×87.81 (HBF <sub>4</sub> )	420.2 g.mol <sup>-1</sup> 0.430 g	58	0.74	1.13
10	202.26 g.mol <sup>-1</sup> 0.253 g	3×83.1 g.mol <sup>-1</sup> 0.418 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	2×83.1 (MeTrz)	0.5×87.81 (HBF <sub>4</sub> )	371.1 g.mol <sup>-1</sup> 0.407 g	64	0.57	1.05
11	202.26 g.mol <sup>-1</sup> 0.253 g	3×135.2 g.mol <sup>-1</sup> 0.511 g	1.5×87.81 g.mol <sup>-1</sup> 0.164 g	2.02 (H <sub>2</sub> )	2×135.2 (BzThz)	0.5×87.81 (HBF <sub>4</sub> )	423.2 g.mol <sup>-1</sup> 0.305 g	57	0.75	2.04

Solvent and supporting electrolyte have been excluded from these calculations excepted if they are used as reactant.

##### Entry 1



##### Entry 2-11

