† Electronic Supporting information to

Photoreduction of Triplet Thioxanthone Derivative by Azolium Tetraphenylborate: A Way to Photogenerate N-Heterocyclic Carbenes

Thi Kim Hoang Trinh, a,b Fabrice Morlet-Savary, a,b Julien Pinaud, c Patrick Lacroix-Desmazes, c Corine Reibel, c Rémi Métivier, d Arnaud Brosseau, d Valérie Héroguez, e Cécile Joyeux, f Didier Le Nouen, f Abraham Chemtob * a,b

Table of contents

I. ADDITIONAL EXPERIMENTAL PROCEDURES .................................................................................................. 2
II. ADDITIONAL FIGURES AND TABLES ........................................................................................................... 2
III. REFERENCES ................................................................................................................................................. 8
IV. AUTHORS’ CONTRIBUTION ........................................................................................................................... 8

---

*a* Institut de Science des Matériaux de Mulhouse, IS2M UMR 7361 CNRS, Université de Haute-Alsace, Mulhouse, France.

*b* Université de Strasbourg, Strasbourg, France.

*c* ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France.

*d* Laboratoire PPSM, ENS Cachan, CNRS, Université Paris-Saclay, 94235, Cachan, France.

*e* Université de Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France.

*f* Laboratoire d’Innovation Moléculaire et Applications, LIMA, Université de Haute-Alsace, France.
I. Additional experimental procedures

Computational procedure. Triplet energy of IMesH\(^+\)BPh\(_4^-\) molecule and ITX were calculated by utilizing the Gaussian 03 package.\(^1\) The uB3LYP method with the 6-31G\(^*\) was applied to optimize the relaxed geometries which were regularly checked.

II. Additional Figures and Tables

![Graph](image1)

**Figure S1.** Stern-Volmer plot for the triplet quenching of ITX by IMesH\(^+\)Cl\(^-\) monitored at 600 nm in acetonitrile ([ITX] = 10\(^{-4}\) M).

<table>
<thead>
<tr>
<th>Method uB3LYP/6-31G(^*)</th>
<th>(E_{\text{triplet}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Compound Image]</td>
<td>2.77</td>
</tr>
<tr>
<td>![Compound Image]</td>
<td>3.34</td>
</tr>
<tr>
<td>![Compound Image]</td>
<td>3.64</td>
</tr>
</tbody>
</table>

**Figure S2.** Triplet energy simulation of ITX, IMesH\(^+\) and BPh\(_4^-\)
**Figure S3.** Transition absorption spectra of $[\text{ITX}] = 10^{-4} \text{ M} - \text{IMesH}^+\text{BPh}_4^- = 6 \times 10^{-3} \text{ M}$ for 100 ns – 90 µs delay time in N$_2$-saturated acetonitrile with excitation wavelength at 355 nm. OD is the optical density.

**Figure S4.** EPR spectra of Ph–PBN radical from a solution ITX – IMesH$^+$BPh$_4^-$ – PBN in acetonitrile after exposure under LED 365 nm at given time (concentration: $[\text{ITX}] = 5 \times 10^{-3} \text{ M}$, $[\text{IMesH}^+\text{BPh}_4^-] = 1.5 \times 10^{-2} \text{ M}$ and $[\text{PBN}] = 3 \times 10^{-3} \text{ M}$, respectively).
Figure S5. EPR spectra of Ph–PBN radical from a solution ITX – IMesH\textsuperscript{+}BPh\textsubscript{4}\textsuperscript{−} – PBN in acetonitrile after exposing under LED 365 nm for 60 s (concentration: [ITX] = 5 × 10\textsuperscript{-3} M, [IMesH\textsuperscript{+}BPh\textsubscript{4}\textsuperscript{−}] = 1.5 × 10\textsuperscript{2} M and [PBN] = 3 × 10\textsuperscript{-3} M, respectively).
Figure S6. (a) $^1$H-NMR spectrum of as-irradiated solution $[\text{ITX}] = 0.07 \text{ M} - [\text{IMesH}^+\text{BPh}_4^-] = 0.21 \text{ M}$ in ACN-$d_3$ after addition of CS$_2$ and (b) $^{13}$C- NMR characterization in DMSO-$d_6$ of the red precipitate after addition of CS$_2$. A substantial change in $^1$H-NMR is the emergence of protons H$_{e'}$ ($\delta = 2.36$ ppm) and protons H$_{d'}$ ($\delta = 2.31$ ppm), which are attributed to methylene protons of mesityl moieties from IMes–CS$_2$ adduct, and the shift towards to the original resonance of protons H$_e$ and H$_d$ of unreacted IMesh$^+\text{BPh}_4^-$. Moreover, all the characteristic peaks of the red precipitate in $^{13}$C-NMR are in agreement with a pure IMes–CS$_2$ adduct.$^3$
**Figure S7.** $^1$H- NMR spectra in THF-$d_8$ of: (a) IMesH$^+$BPh$_4^-$, (b) IMes, (c) the mixture of IMesH$^+$BPh$_4^-$ and IMes (9/1 equiv.), and (d) irradiated ITX – IMesH$^+$BPh$_4^-$ (1/1 equiv.).

**Figure S8.** GC trace of photoproducts obtained from the photolysis media of ITX – IMesH$^+$BPh$_4^-$ after 5 min of irradiation ([ITX] = $5 \times 10^{-4}$ M and [IMesH$^+$BPh$_4^-$] = $1.5 \times 10^{-3}$ M).
**Figure S9.** $^{11}$B-NMR spectra of photolysis of $[\text{ITX}] = 0.03 \, \text{M} - [\text{BPh}_3] = 0.03 \, \text{M}$ in THF-$d_8$: (a) prior UV exposure, and (b) after exposure for 10 min (LED 365 nm, 65 mW. cm$^{-2}$).

**Figure S10.** $^{11}$B-NMR spectra in THF-$d_8$: (a) IMesH$^+\text{BPH}_4^- – \text{IMes}$, (b) IMesH$^+\text{BPH}_4^- – \text{IMes} – \text{BPH}_3$ ($[\text{IMes}] = 0.01 \, \text{M}$, $[\text{IMesH}^+\text{BPH}_4^-] = 0.03 \, \text{M}$, $[\text{BPH}_3] = 0.01 \, \text{M}$). A white precipitation is formed immediately after the introduction of $\text{BPH}_3$ into the mixture IMesH$^+\text{BPH}_4^- – \text{IMes}$. It is attributed to the formation of IMes – BPH$_3$ adduct.
Table S1. Identification of photoproducts by GC-MS after the photolysis course of ITX-IMesH$^+$BPh$_4^-$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>EI-MS: m/z (relative abundance)</th>
<th>Molar mass (g mol$^{-1}$)</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>22.065</td>
<td>63 (7), 76 (15), 89 (2), 102 (4), 115 (5), 128 (6), 153 (40), 154 (100)</td>
<td>154</td>
<td><img src="image" alt="Biphenyl" /></td>
</tr>
<tr>
<td>Isopropylthioxanthone</td>
<td>39.186</td>
<td>65 (4), 75 (5), 91 (14), 105 (15), 135 (11), 147 (16), 165 (25), 178 (6), 191 (12), 197 (40), 223 (38), 225 (85), 240 (100)</td>
<td>240</td>
<td><img src="image" alt="Isopropylthioxanthone" /></td>
</tr>
<tr>
<td>ITX</td>
<td>42.790</td>
<td>50 (3), 69 (4), 77 (5), 89 (3), 105 (6), 139 (9), 152 (6), 165 (5), 178 (6), 196 (11), 210 (7), 224 (7), 239 (100), 254 (54)</td>
<td>254</td>
<td><img src="image" alt="ITX" /></td>
</tr>
</tbody>
</table>

### III. References


### IV. Authors' contribution

- **Thi Kim Hoang Trinh** has performed most of the experiments described in the study. Additionally, she has written this manuscript. Degree of contribution: lead.
- **Fabrice Morlet-Savary** has supervised some ESR measurements. Degree of contribution: equal.
Julien Pinaud has conceived the idea of photolatent N-heterocyclic carbenes from tetraphenylborate imidazolium salts. Additionally, he has equally contributed (with Abraham Chemtob and Valérie Héroguez) in the acquisition of the financial support for the project leading to this publication and has managed project coordination. Degree of contribution: lead.

Patrick Lacroix-Desmazes has been involved in planning of this project. He has contributed to the interpretation of results. He has also provided critical feedback and help in the manuscript drafting. Degree of contribution: equal.

Corine Reibel has supervised ERS measurements. Degree of contribution: supporting.

Rémi Métilier and Arnaud Brosseau have both arranged the laser flash photolysis experiments presented in the paper.

Valérie Héroguez has conceived the idea of in-situ generation of photolatent NHC. She has provided expertise on ROMP and equally contributed (with Abraham Chemtob and Julien Pinaud) in the acquisition of the financial support for the project leading to this publication. Degree of contribution: lead.

Cécile Joyeux has provided expertise in the analyses by gas chromatography-mass spectrometry.

Didier Le-Nouen has provided help in the analysis by $^{11}$B NMR spectroscopy.

Abraham Chemtob has provided guidance to Thi Kim Hoang Trinh (PhD student) for conducting all the experiments and equally contributed (with Julien Pinaud and Valérie Héroguez) in the acquisition of the financial support for the project leading to this publication. Finally, Abraham took the lead in writing the manuscript. Degree of contribution: lead.