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† Electronic Supporting information to

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

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I. Additional experimental procedures

Computational procedure. Triplet energy of IMesH⁺BPh₄⁻ molecule and ITX were calculated by utilizing the Gaussian 03 package.^{1,2} The uB3LYP method with the 6-31G* was applied to optimize the relaxed geometries which were regularly checked.

II. Additional Figures and Tables

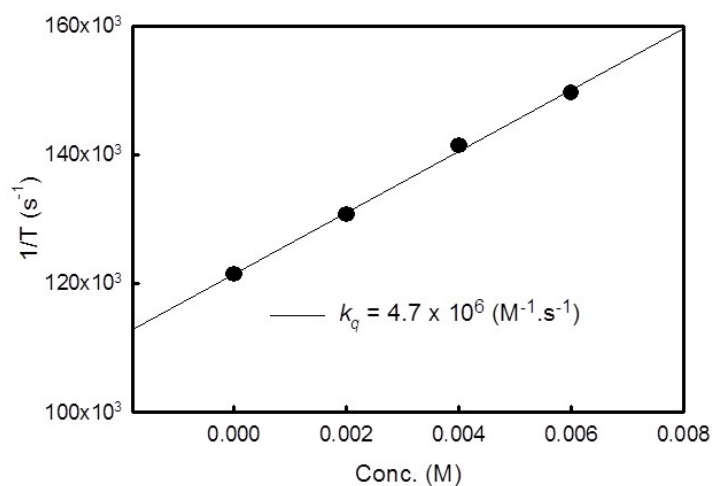


Figure S1. Stern-Volmer plot for the triplet quenching of ITX by IMesH⁺Cl⁻ monitored at 600 nm in acetonitrile ([ITX] = 10⁻⁴ M).

Method uB3LYP/6-31g*	E _{triplet} (eV)
	2.77
	3.34
	3.64

Figure S2. Triplet energy simulation of ITX, IMesH⁺ and BPh₄⁻.

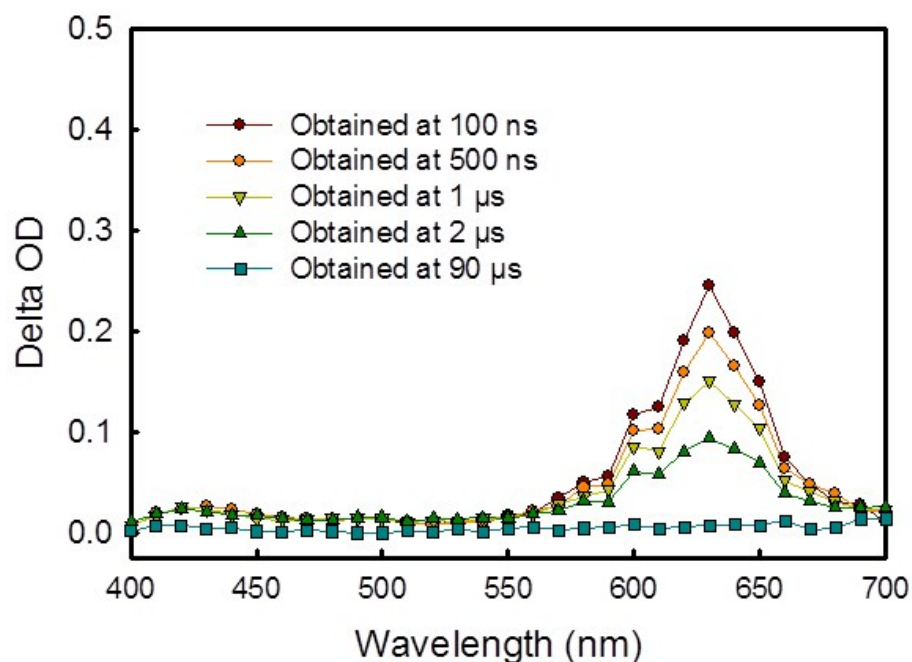


Figure S3. Transition absorption spectra of $[ITX] = 10^{-4} \text{ M}$ - $IMesH^+BPh_4^- = 6 \times 10^{-3} \text{ M}$ for 100 ns – 90 μs delay time in N_2 -saturated acetonitrile with excitation wavelength at 355 nm. OD is the optical density

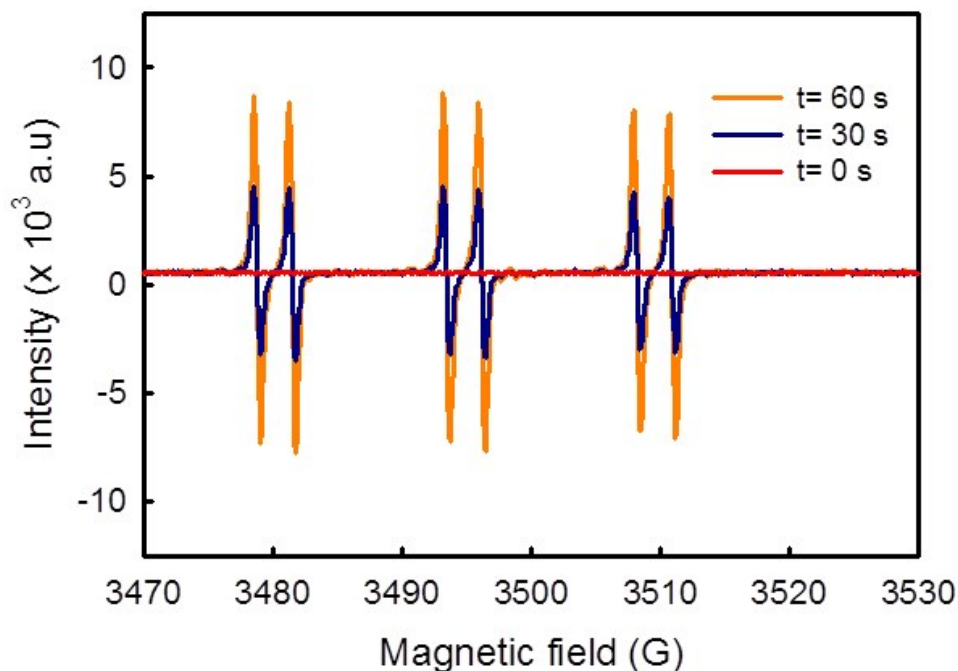


Figure S4. EPR spectra of Ph-PBN radical from a solution ITX – $IMesH^+BPh_4^-$ – PBN in acetonitrile after exposure under LED 365 nm at given time (concentration: $[ITX] = 5 \times 10^{-3} \text{ M}$, $[IMesH^+BPh_4^-] = 1.5 \times 10^{-2} \text{ M}$ and $[PBN] = 3 \times 10^{-3} \text{ M}$, respectively).

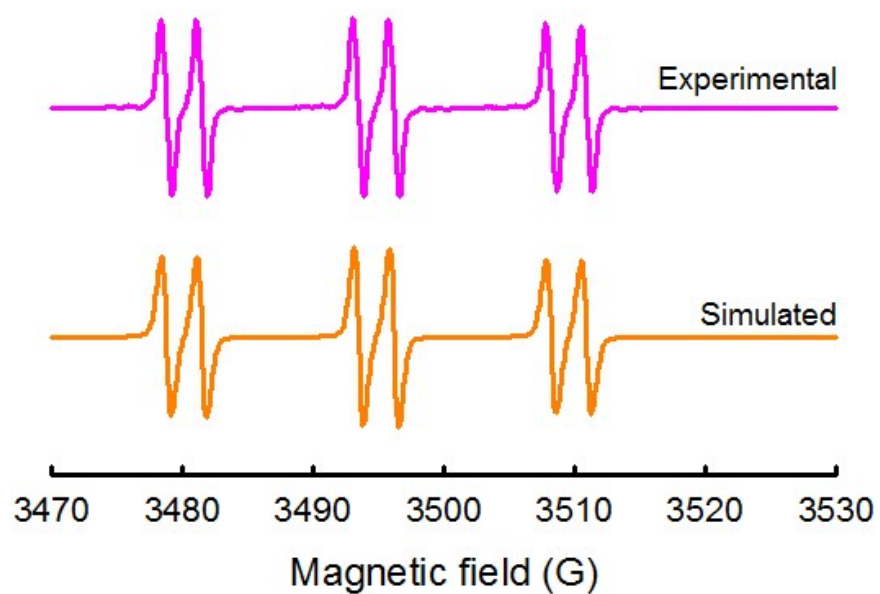


Figure S5. EPR spectra of Ph-PBN radical from a solution ITX – IMesH⁺BPh₄⁻ – PBN in acetonitrile after exposing under LED 365 nm for 60 s (concentration: [ITX] = 5×10^{-3} M, [IMesH⁺BPh₄⁻] = 1.5×10^{-2} M and [PBN] = 3×10^{-3} M, respectively).

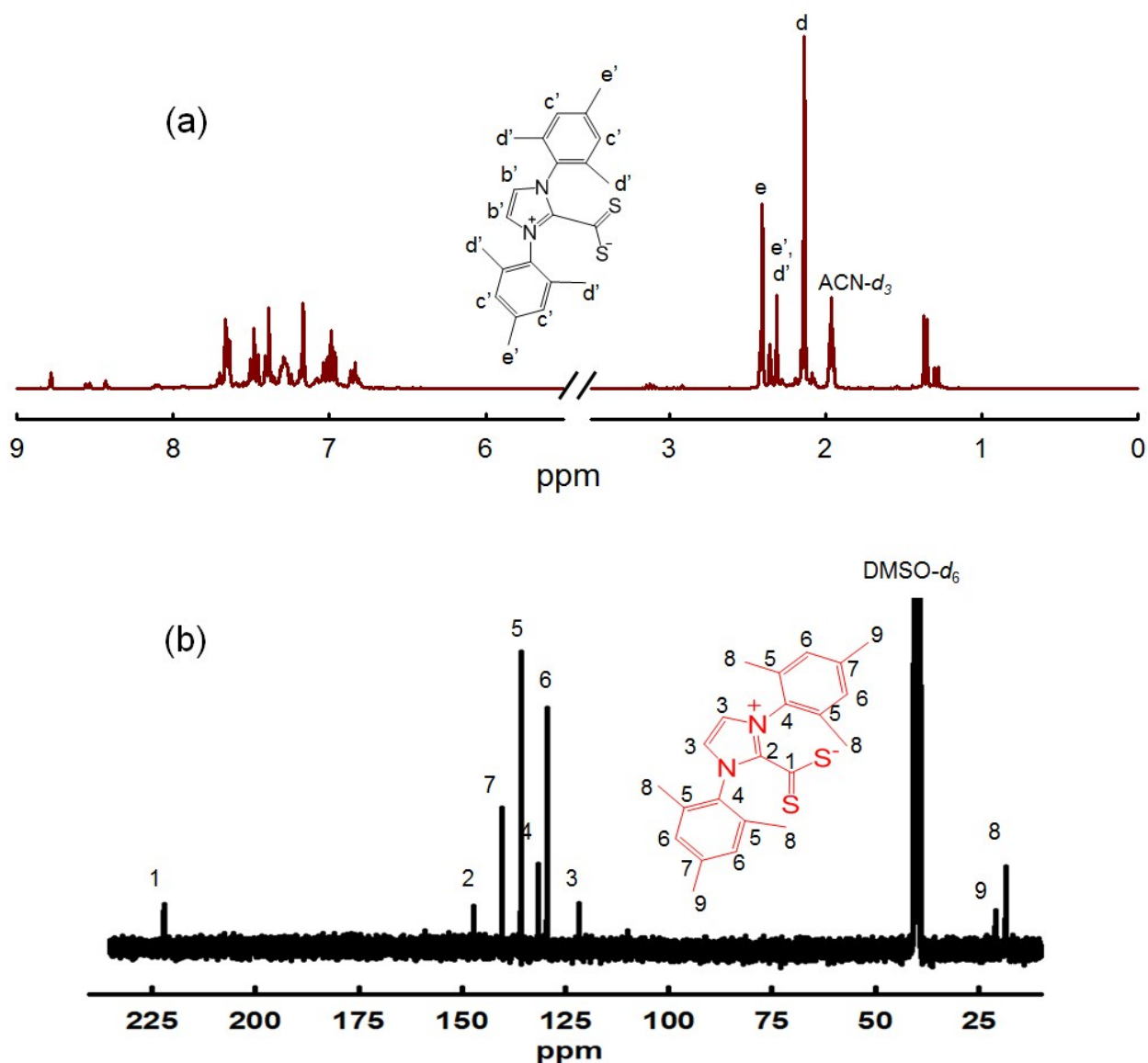


Figure S6. (a) ^1H -NMR spectrum of as-irradiated solution $[\text{ITX}] = 0.07 \text{ M}$ – $[\text{IMesH}^+\text{BPh}_4^-] = 0.21 \text{ M}$ in ACN- d_3 after addition of CS_2 and (b) ^{13}C -NMR characterization in DMSO- d_6 of the red precipitate after addition of CS_2 . A substantial change in ^1H -NMR is the emergence of protons $\text{H}_{e'}$ ($\delta = 2.36 \text{ ppm}$) and protons $\text{H}_{d'}$ ($\delta = 2.31 \text{ ppm}$), 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⁺BPh₄⁻. Moreover, all the characteristic peaks of the red precipitate in ^{13}C -NMR are in agreement with a pure IMes- CS_2 adduct.³

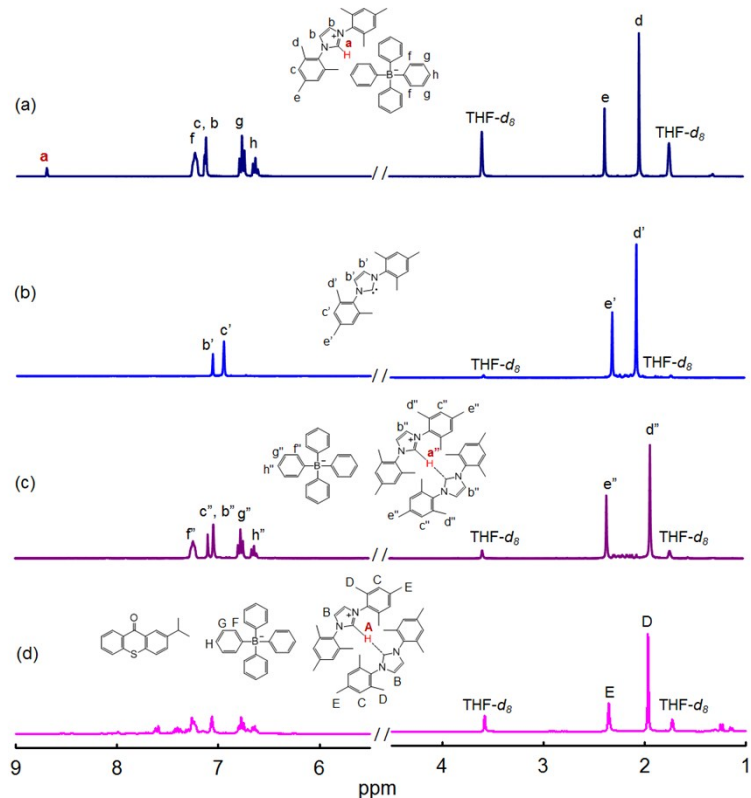


Figure S7. ^1H - NMR spectra in $\text{THF}-d_8$ of: (a) $\text{IMesH}^+\text{BPh}_4^-$, (b) IMes , (c) the mixture of $\text{IMesH}^+\text{BPh}_4^-$ and IMes (9/1 equiv.), and (d) irradiated $\text{ITX} - \text{IMesH}^+\text{BPh}_4^-$ (1/1 equiv.).

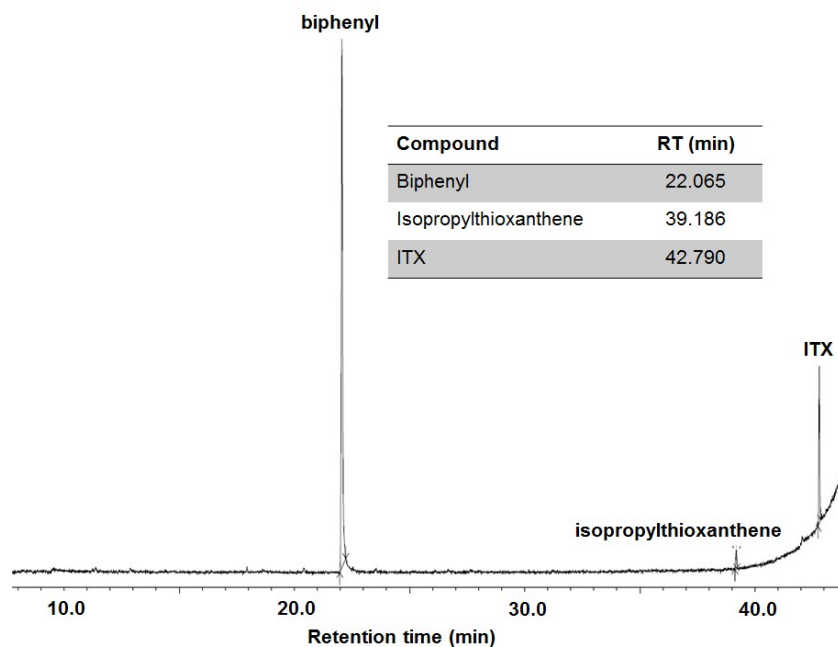


Figure S8. GC trace of photoproducts obtained from the photolysis media of $\text{ITX} - \text{IMesH}^+\text{BPh}_4^-$ after 5 min of irradiation ($[\text{ITX}] = 5 \times 10^{-4} \text{ M}$ and $[\text{IMesH}^+\text{BPh}_4^-] = 1.5 \times 10^{-3} \text{ M}$).

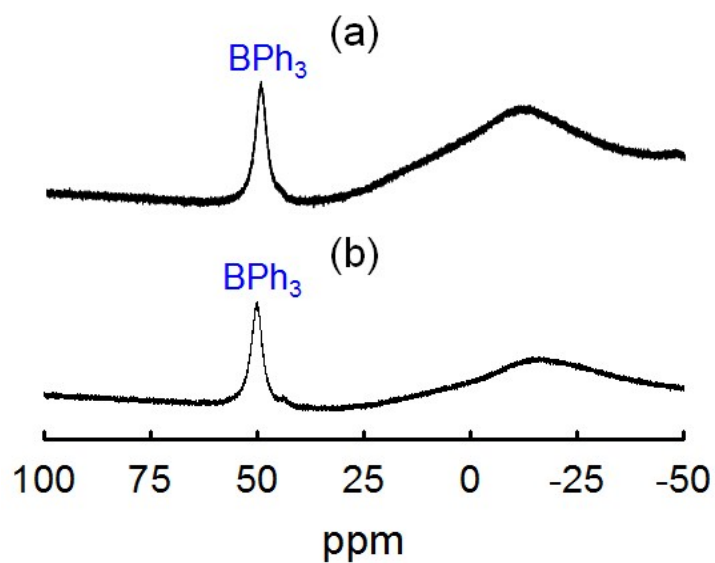


Figure S9. ^{11}B -NMR spectra of photolysis of $[\text{ITX}] = 0.03 \text{ M}$ - $[\text{BPh}_3] = 0.03 \text{ M}$ in $\text{THF-}d_8$: (a) prior UV exposure, and (b) after exposure for 10 min (LED 365 nm, 65 mW. cm^{-2}).

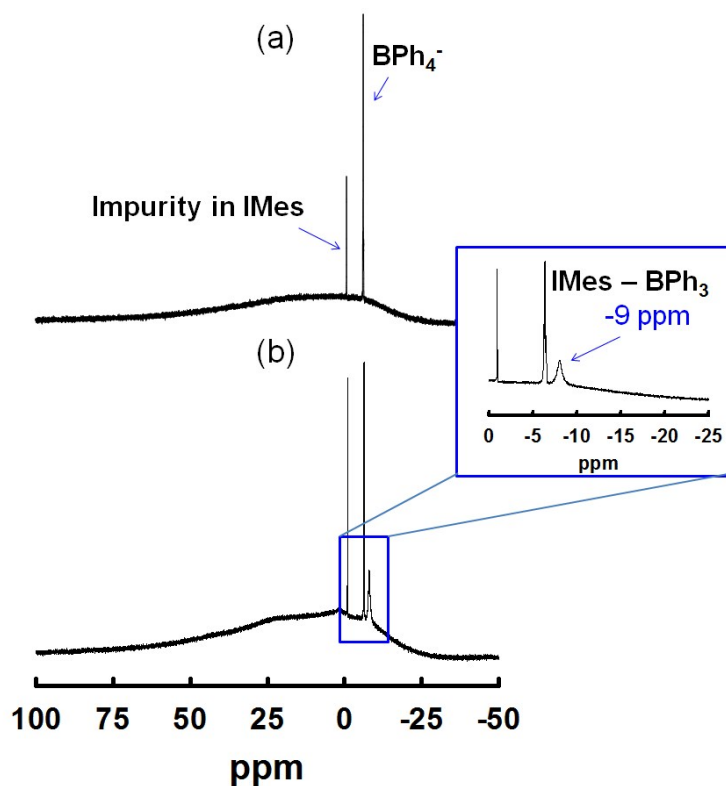
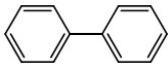
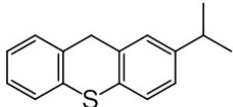
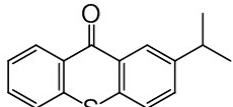


Figure S10. ^{11}B -NMR spectra in $\text{THF-}d_8$: (a) $\text{IMesH}^+\text{BPh}_4^- - \text{IMes}$, (b) $\text{IMesH}^+\text{BPh}_4^- - \text{IMes} - \text{BPh}_3$ ($[\text{IMes}] = 0.01 \text{ M}$, $[\text{IMesH}^+\text{BPh}_4^-] = 0.03 \text{ M}$, $[\text{BPh}_3] = 0.01 \text{ M}$). A white precipitation is formed immediately after the introduction of BPh_3 into the mixture $\text{IMesH}^+\text{BPh}_4^- - \text{IMes}$. It is attributed to the formation of $\text{IMes} - \text{BPh}_3$ adduct.

Table S1. Identification of photoproducts by GC-MS after the photolysis course of ITX- IMesH⁺BPh₄⁻

Compound	Retention time (min)	EI-MS: <i>m/z</i> (relative abundance)	Molar mass (g mol ⁻¹)	Chemical structure
Biphenyl	22.065	63 (7), 76 (15), 89 (2), 102 (4), 115 (5), 128 (6), 153 (40), 154 (100)	154	
Isopropylthioxanthone	39.186	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)	240	
ITX	42.790	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)	254	

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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 photolabile 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 Métivier** 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 photolabile 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.