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Supporting information

A New Surface-Bound Molecular Switch Based On The Photochromic Dimethyldihydropyrene With Light-Driven Release Of Singlet Oxygen Properties

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1. Methods and experimental procedure

^{1}H NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer in CD_3CN. Chemical shifts (ppm) are referenced to residual solvent peaks. Mass spectrometry analyses and high-resolution mass spectrometry analyses (ESI positive mode) were carried out at the DCM mass spectrometry facility with an Esquirre 3000 Plus (Bruker Daltonics) and ESI-QTof (XEVO G2-S QTof – WATERS), respectively. Absorption spectra were recorded using either a Varian Cary 50 Scan or a Varian Cary 300 UV-visible spectrophotometer equipped with a temperature controller unit.

Electrochemical measurements were conducted in a standard one-compartment, three-electrode electrochemical cell using a Bio-logic SP300 potentiostat. Investigations were carried out in anhydrous CH_3CN or CH_2Cl_2 containing tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte. An automatic ohmic drop compensation procedure was systematically implemented prior to recording CV data. CH-instrument vitreous carbon (Ø=3 mm) working electrodes were polished with 1 μm diamond paste before each recording. A CH instrument Ag^+/Ag electrode was used as a reference. A platinum wire was used as the counter electrode. The reference electrode was calibrated with respect to the formal potential of the Ferrocenium/Ferrocene (Fc^+/Fc) couple in CH_3CN + tetra-*n*-butylammonium perchlorate (0.1 M), which was estimated as + 0.07 V under our experimental conditions.

X-ray photoelectron spectroscopy measurements were performed using a Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al Kα (hν = 1486.6 eV) 200 W X-ray source. The X-ray spot size was 500 μm. The samples were stuck on sample holders using conductive double-sided adhesive tape and pumped overnight in the fast entry lock at ~ 5×10–8 mbar prior to transfer to the analysis chamber. The pass energy was set at 100 and 40 eV for the survey and the narrow scans, respectively. Data acquisition and processing were achieved with the Avantage software, version 4.67. Spectral calibration was determined by setting the main C(1s) component at 285 eV. Atomic percentages have been determined using this software and taking into account photoemission cross sections, analyzer transmission, and variation of electron mean free paths with kinetic energy.

The surface topography was determined by atomic force microscopy (AFM) under ambient air. The topographical features of the sample surfaces were scanned using an AFM soft tapping with Picoplus mode (Molecular Imaging Scientec, les Ulis, France). The tapping mode was performed using a sharp silicon cantilever [Tap150Al-G by Budget Sensor (Sofia, Bulgaria) with Aluminium Reflex Coating]. The cantilever was recorded with a resonance frequency of 150 kHz and a stiffness constant of 5 N m^{-1}. The RMS roughness values of the scans were calculated using the Gwyddion 2.19 program covered by GNU General Public License.

EPR spectra were obtained using a EMX Bruker spectrometer equipped with a X-band ER4102ST Bruker cavity. Singlet oxygen trapping experiments were carried out by EPR using 4-oxo-2,2,6,6-tetramethyl-4-piperidone hydrochloride (4-oxo-TMP). A self-assembled monolayer (SAM) of $\mathbf{3_c^+}$**/ITO** (0.8 cm^2) was dipped into a solution of 4-oxo-TMP (1M, CH_3CN, 3mL). The surface was then irradiated (λ>630nm, 10 min) under air and converted into $\mathbf{3_oO_2^+}$**/ITO**. The sample was then heated in the absence of light to release singlet oxygen. EPR spectra were recorded at the beginning and at the end of the experiment.

All purchased chemicals and solvents were used as received except THF and diethyl ether that were distillated over sodium/benzophenone under argon. 2,7-di-tert-butyl-4-pyridyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (DHP-Py) was synthesized following previously reported procedures.[2]

Synthesis of ***2***$_c^+$*:* 40 mg of **1**$_c$ (0.095 mmol) were dissolved in 20 mL of degassed CH_2Cl_2. 1.5 mL of $I(CH_2)_2CH_3$ (15.3 mmol) were then added and the solution was refluxed for two hours under inert atmosphere. After cooling the mixture to room temperature, the solvent was evaporated under reduced pressure and the residue was then dissolved in 2 mL of methanol. It was reprecipitated by addition of 40 mL of pentane. The precipitate (iodide salt) was filtered off, washed with diethyl ether. The product was then subjected to an anion exchange procedure using an ion-exchange resin loaded with BF_4^- to afford to ***2***$_c^+$, BF_4^- isolated as a red powder (yield 75%).

FTIR (cm^{-1}): 3648, 2950, 1634, 1596, 1514, 1460, 1383, 1360, 1345, 1232, 1218, 1175, 1058. ^{1}H NMR (400 MHz, CD_3CN) δ(ppm) : 8.80 (s, 1H), 8.79 (d, J = 5.2 Hz, 2H), 8.77 (d, J = 3.1 Hz, 2H), 8.75 (s, 1H), 8.66 (d, J = 7.9 Hz, 1H), 8.64 (s, 1H), 8.62 (d, J = 7.8 Hz, 1H), 8.47 (d, J = 6.7 Hz, 2H), 4.58 (t, J = 7.4 Hz, 2H), 2.18 – 2.16 (m, 1H), 2.12 (d, J = 7.3 Hz, 1H), 1.70 (s, 9H), 1.66 (s, 9H), 1.10 (t, J = 7.4 Hz, 3H), -3.84 (s, 3H), -3.89 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ (ppm): 150.07, 148.38, 144.56, 139.88, 138.07, 137.13, 134.63, 130.40, 128.16, 126.00, 125.07, 124.63, 124.14, 123.01, 118.97, 63.32, 37.16, 36.78, 32.04, 31.87, 31.44, 30.32, 25.40, 15.46, 15.02, 10.81. Mass (m/z): calcd: 464.3 [M-BF_4^-], found: 464.5. Exact mass [M-BF_4^-] calc.: 464.3317, found: 464.3321.

Synthesis of **3**$_c^+$: 40 mg of **1**$_c$ (0.095 mmol) were dissolved in 9 mL of degassed acetonitrile. 0.5 mL of $I(CH_2)_3Si(OCH_3)_3$ (2.3 mmol) was then rapidly added and the solution was refluxed for two hours under inert atmosphere. Upon cooling the mixture to room temperature, the solvent was evaporated under reduced pressure. The residue was then dissolved in 2 mL of CH_2Cl_2 and reprecipitated by addition of 40 ml of pentane. The product was then subjected to an anion exchange procedure using an ion-exchange resin (Amberlite

IRA-93) loaded with HBF_4 to afford the targeted pyridinium salt, isolated as a red powder (yield 50%).

FTIR (cm^{-1}): 3432, 2962, 2364, 1634, 1515, 1462, 1208, 1064. ^1H NMR (400 MHz, CD_2Cl_2) δ 9.28 (d, J = 6.5 Hz, 2H), 8.75 (d, J = 9.5 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 8.60 (q, J = 7.9 Hz, 2H), 8.58 (s, 1H), 8.49 (d, J = 6.3 Hz, 2H), 4.95 (t, J = 3.7 Hz, 2H), 3.63 (s, 9H), 2.32 (dd, J = 15.3, 7.6 Hz, 2H), 1.71 (s, 9H), 1.67 (s, 9H), 0.86 (m, 2H), -3.79 (s, 3H), -3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ (ppm) 150.85, 149.79, 146.59, 146.44, 137.51, 136.99, 136.32, 133.05, 131.67, 126.14, 124.12, 123.45, 121.72, 121.50, 121.35, 119.29, 36.32, 36.13, 32.06, 31.95, 30.26, 29.78, 27.07, 14.95, 14.54. Mass (m/z): calcd: 584.4 [$M-BF_4^-$], found: 584.4. Exact mass [$M-BF_4^-$] calc.: 584.3560, found: 584.3558.

Self-assembled Monolayer Preparation: Indium doped tin oxide (ITO) coated glass slides with 25-30 Ω surface resistivity and deposed on a glass of 1.1mm were purchased from Solems (France). The ITO substrates were cleaned following the procedure described by Rovira *et al.*[1] Once the substrate cleaned, the monolayer is formed by immersing the ITO surface during 12 hours in a 1mM solution of $\mathbf{3_c}^+$ in acetonitrile. The substrate is rinsed thoroughly with acetonitrile before use.

Irradiation procedure: The solutions were irradiated in UV-visible quartz cells or NMR tubes. The concentration used for UV-visible spectroscopy and NMR experiments were comprised between 2 x 10^{-5} M and 3 x 10^{-3} M. The visible irradiations for making the isomerization of the "closed" $\mathbf{2_c}^+$ isomer to its corresponding "open" $\mathbf{2_o}^+$ were carried out with a Xe-Hg lamp, using a 630 nm cut-off filter. The samples were placed at 8°C in a cooling bath in order to limit the reverse thermal reaction. Samples were placed at a distance of 15 cm of the visible lamp.

The conversion between the different species were investigated from UV-visible and NMR experiments. Intermediate spectra were recorded at different times depending on the isomerization process rates. The molar ratio between the different species was determined by ^{1}H-NMR from the characteristic resonance peak relative integration of the N$^+$-CH_3 subunits in the different compounds.

2. Calculation of the surface coverage of $\mathbf{3_c^+}$ from CV and UV/Vis-spectroscopy experiments

The surface coverage has been estimated by integration of the voltammetric wave according to:

$\Gamma = Q/(nFA)$

where Γ is the surface coverage, n is the number of electron involved in the process, F is the faraday constant, A is the area of electrode and Q the total charge. From the anodic wave at 0.01 V.s^{-1}, we estimated that the surface coverage is $(2.4 \pm 0.3) \cdot 10^{-10}$ mol.cm^{-2} .

The surface coverage has been also estimated by UV-visible spectroscopy from the absorbance of the SAM using,

$A = \varepsilon \, \Gamma$

where A is the absorbance of the SAM , ε is the molar extinction coefficient of the compound $\mathbf{3_c}$ in solution, and Γ is the surface coverage. From absorbance we estimated that the surface coverage of SAM of $\mathbf{3_c}$ is around $2 \cdot 10^{-10} \pm 6 \cdot 10^{-11}$ mol.cm^{-2}.

3. Mass spectrum of a solution of 2oO_2^+.

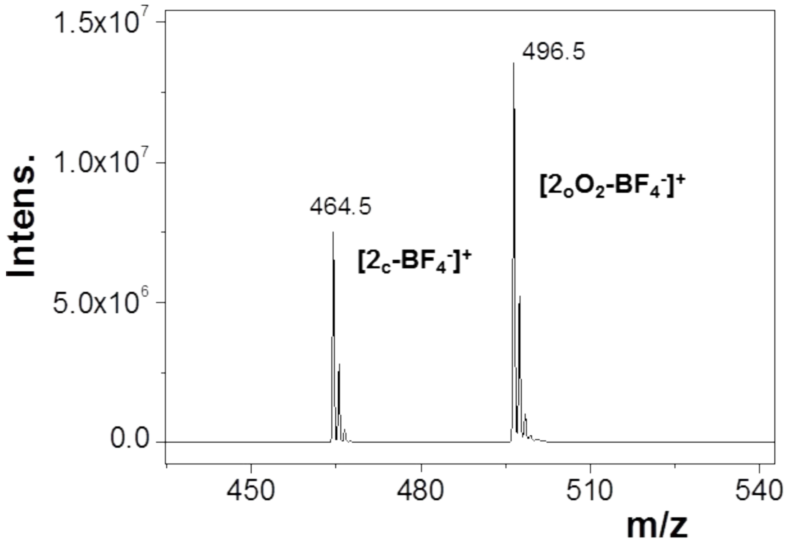


Figure ESI 1: Experimental electrospray ionization mass spectra of a solution of $\mathbf{2_oO_2}^+$ in CH_3CN. Because of the thermal back reaction, the presence of $\mathbf{2_c}^+$ is also detected.

4. Singlet oxygen production by irradiated 2_c^+ solution followed by trapping ESR experiments.

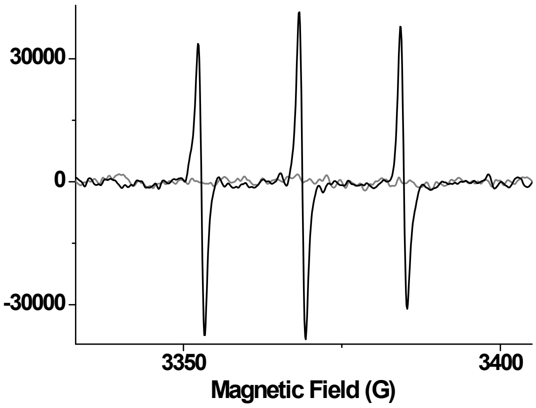


Figure ESI 2. EPR spectra of nitroxide radical generated from 4-oxo-TMP. 1M solution of 4-oxo-TMP was mixed with 44μM of $\mathbf{2_c}^+$. The solution was then irradiated (λ>630nm, 10 min) under air and converted into $\mathbf{2_o}^+$(grey). The sample was then heated in the absence of light to release singlet oxygen (black).

5. XPS spectra

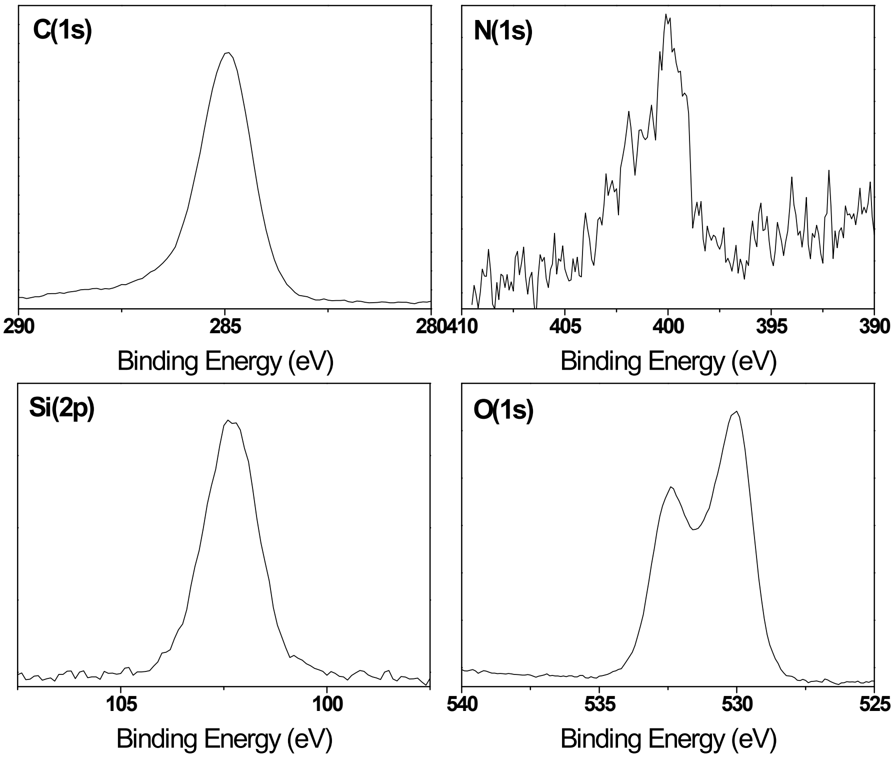


Figure ESI 3. High resolution XPS spectra of the C(1s), N(1s), Si(2p) and O(1s) bands of **3_c^+/ITO**.

6. ^{1}H and ^{13}C NMR spectrum

Figure ESI 4 represents the ^{1}H NMR spectrum of $\mathbf{2_c}$.

Figure ESI 5 represents the ^{13}C NMR spectrum of $\mathbf{2_c}$.

Figure ESI 6 and 7 represents the ^{1}H NMR spectrum of $\mathbf{2_oO_2{}^+}$. As explain in the main text, the irradiation of $\mathbf{2_c}$ leads to the formation of two endoperoxide isomers, $\mathbf{2_oO_2{}^+{}_a}$ and $\mathbf{2_oO_2{}^+{}_b}$, here we show the integration of signals for the two isomers independently.

Figure ESI 8 compares the ^{1}H NMR spectrum of $\mathbf{2_c{}^+}$ before irradiation, $\mathbf{2_oO_2{}^+}$(a) and $\mathbf{2_c{}^+}$ (c) after UV back reaction.

Figure ESI 4 : ^{1}H NMR spectrum of $\mathbf{2_c}^+$

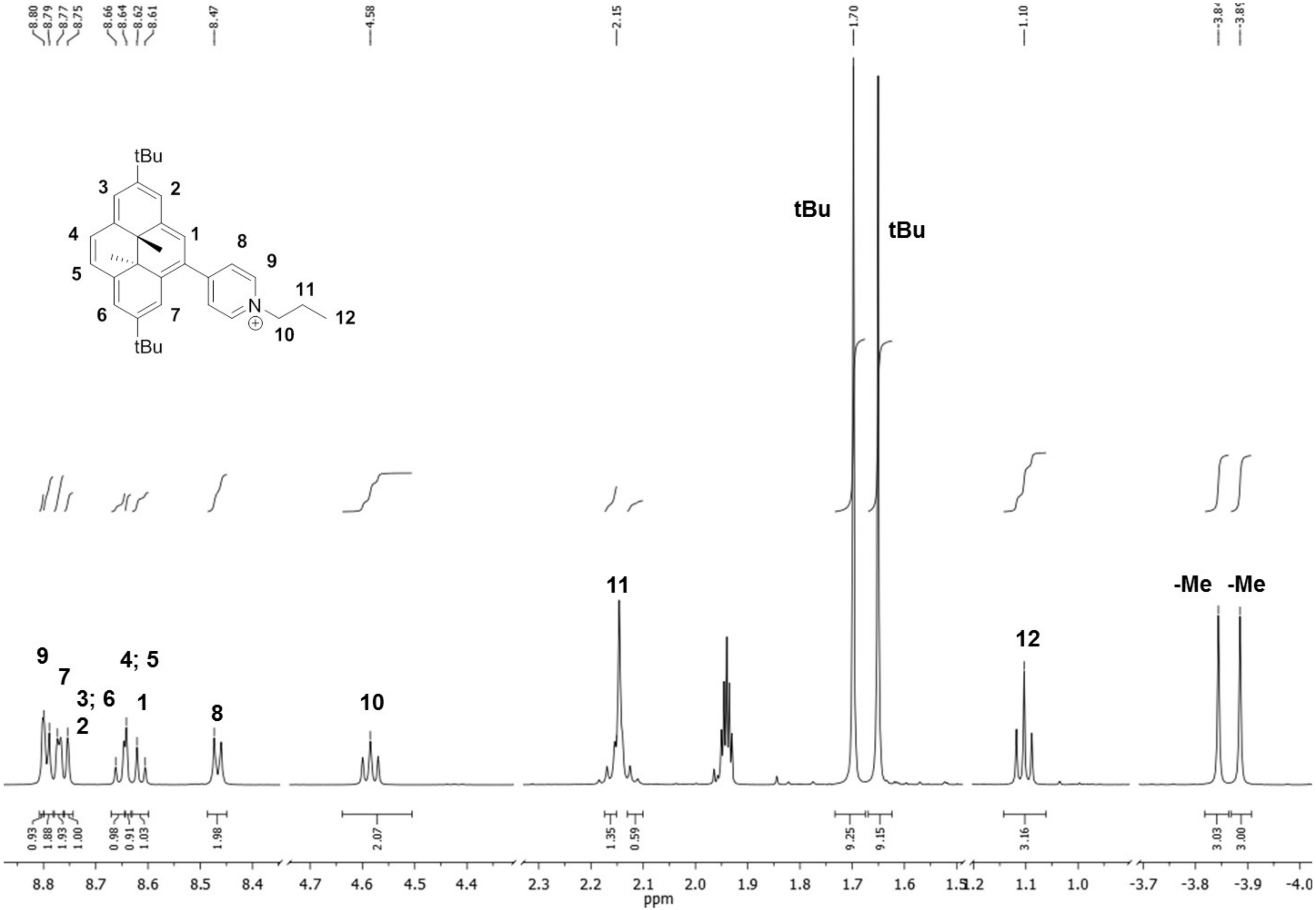


Figure ESI 5 : ^{13}C NMR spectrum of $\mathbf{2_c}^+$

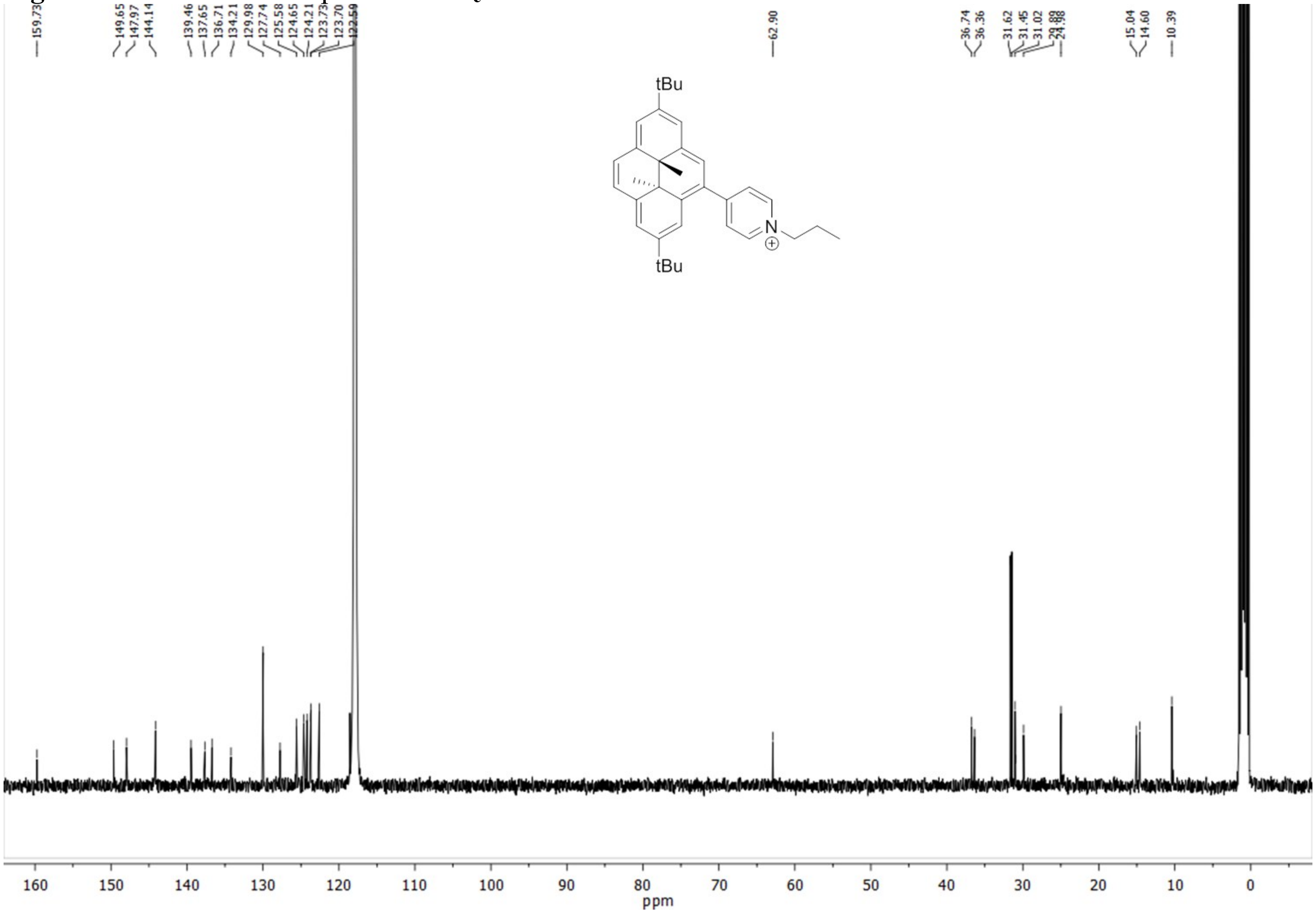


Figure ESI 6 : ^{1}H NMR spectrum of $\mathbf{2_oO_2{}^+{}_b}$

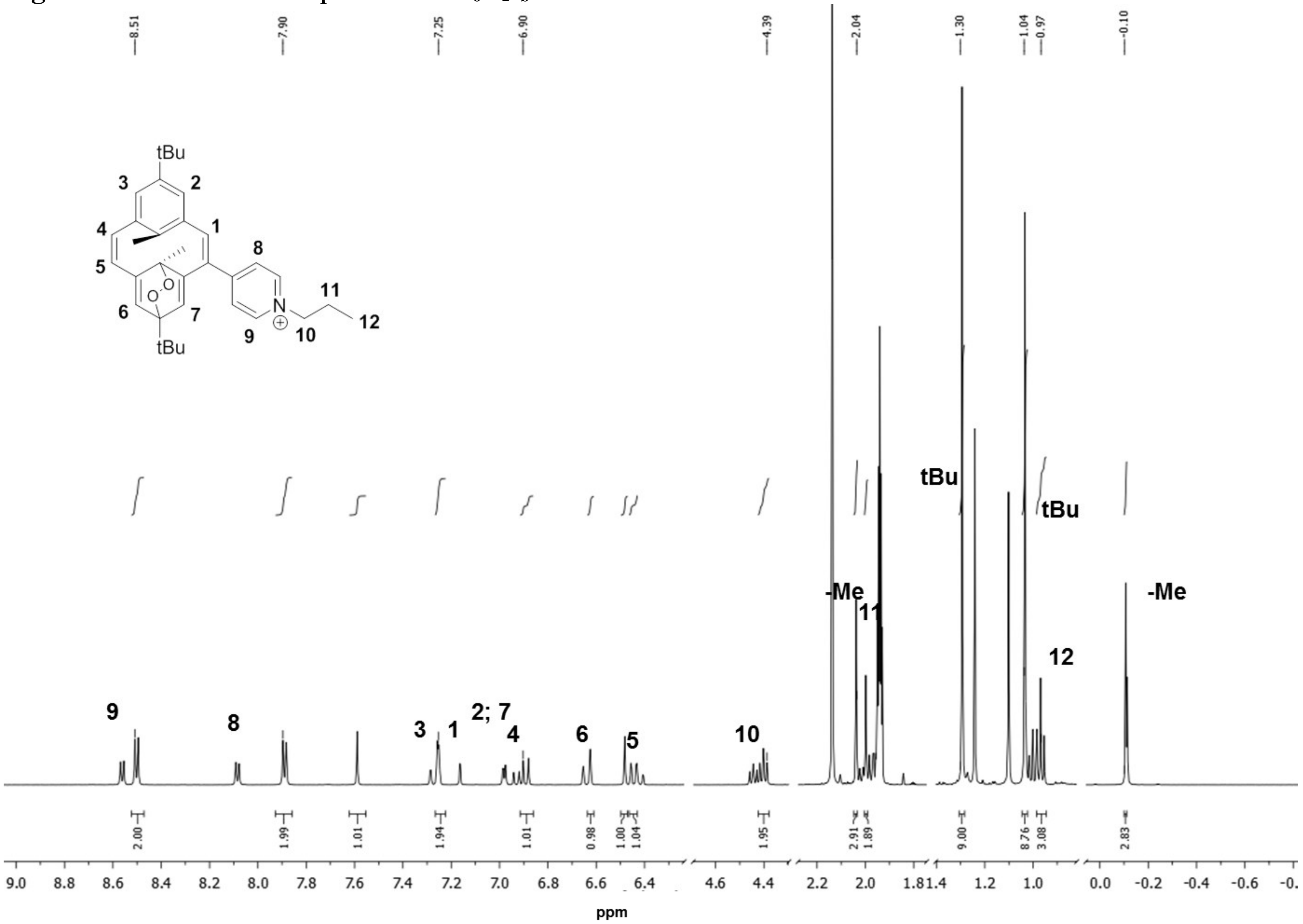


Figure ESI 7 : ¹H NMR spectrum of $\mathbf{2_oO_2{}^{+}{}_a}$

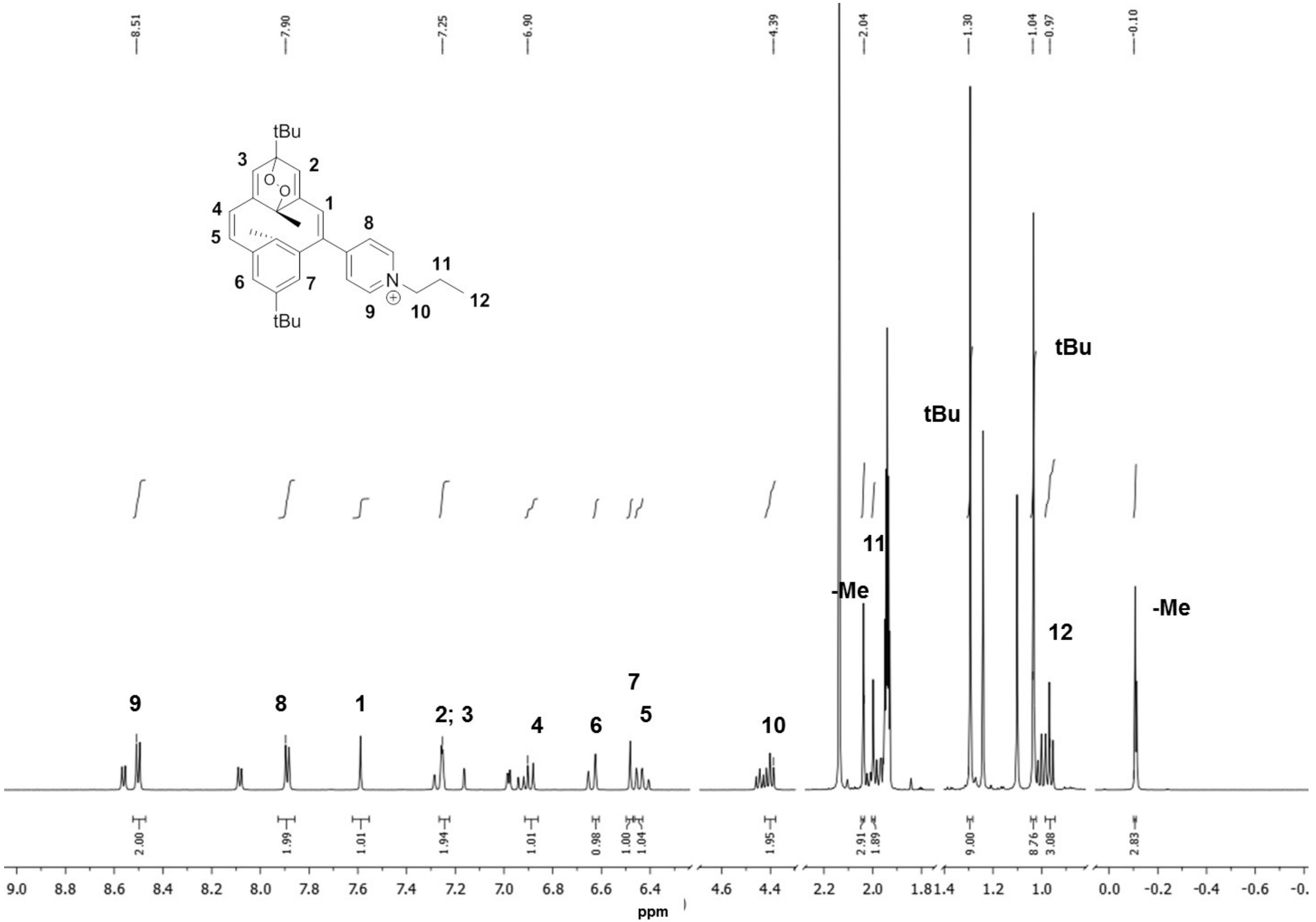
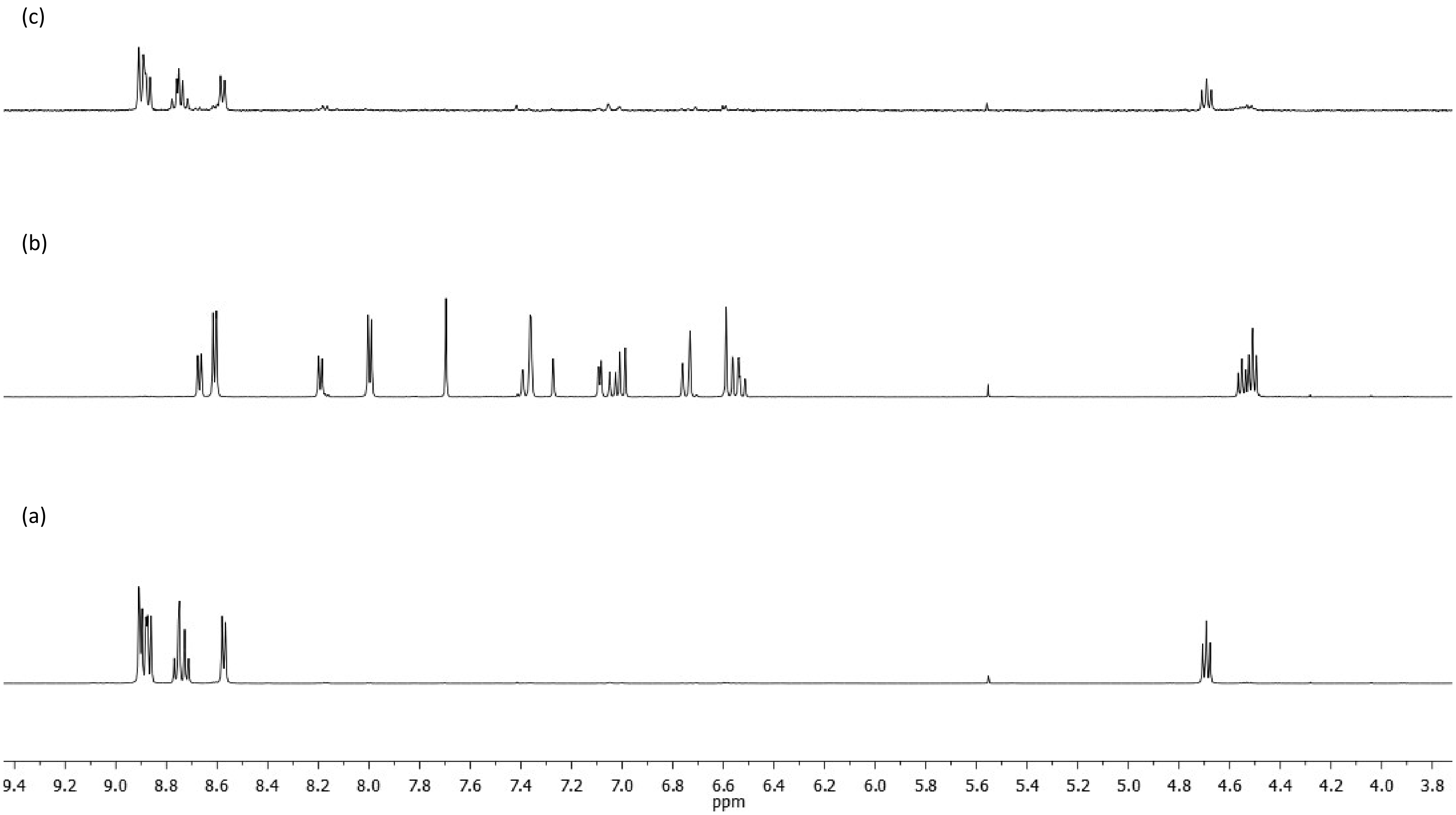


Figure ESI 8 : ^{1}H NMR spectrum in CD$_3$CN of $\mathbf{2_c^+}$ **(a)** , $\mathbf{2_oO_2^+}$**(a)** and $\mathbf{2_c^+}$ **(c) (**after UV back reaction)



7. ^{1}H and ^{13}C NMR spectrum

Figure ESI 9 represents the ^{1}H NMR spectrum of $\mathbf{3_c}^{+}$.

Figure ESI 10 represents the ^{13}C NMR spectrum of $\mathbf{3_c}^{+}$.

Figure ESI 9 : ^{1}H NMR spectrum of $\mathbf{3_c}^+$

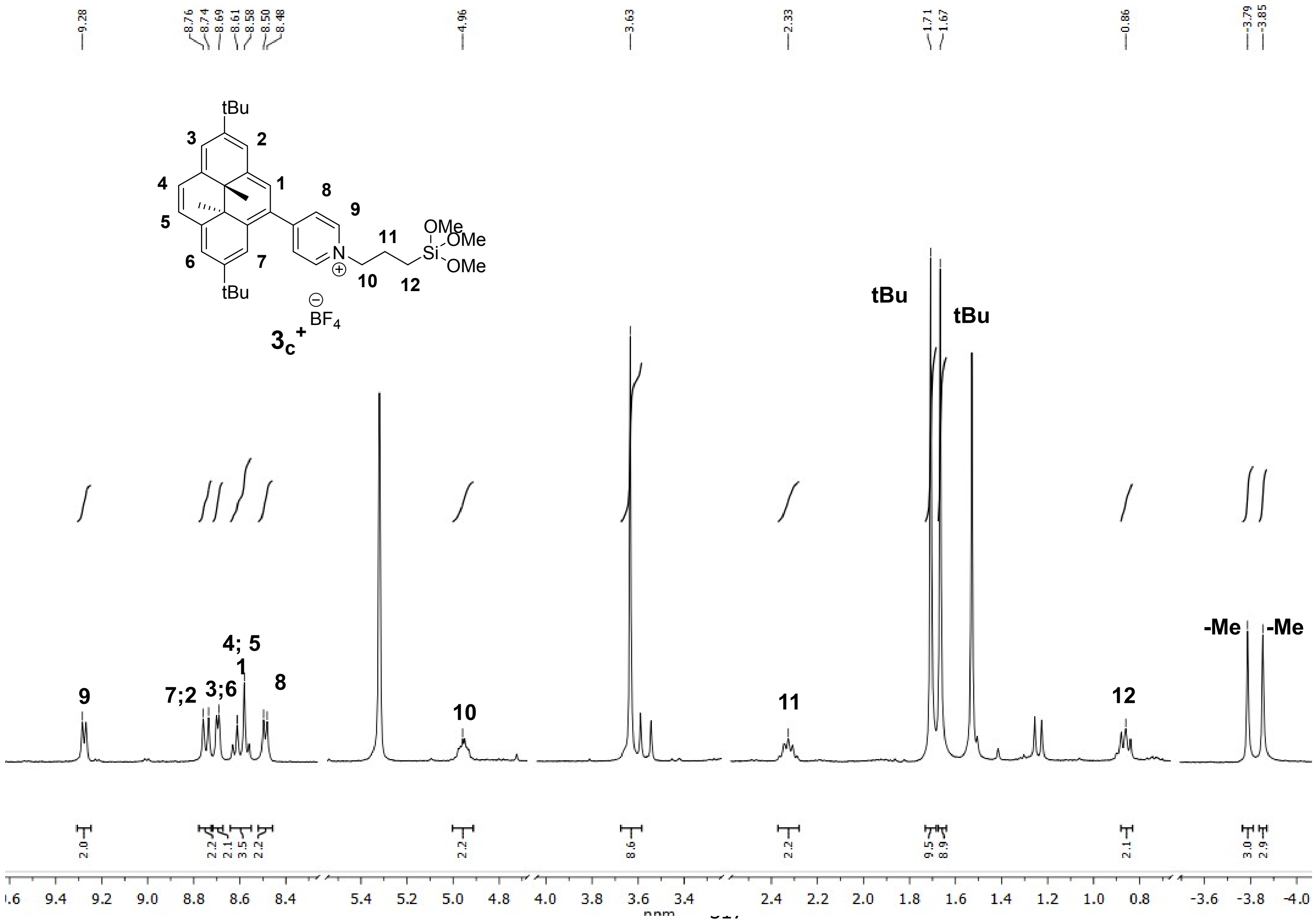
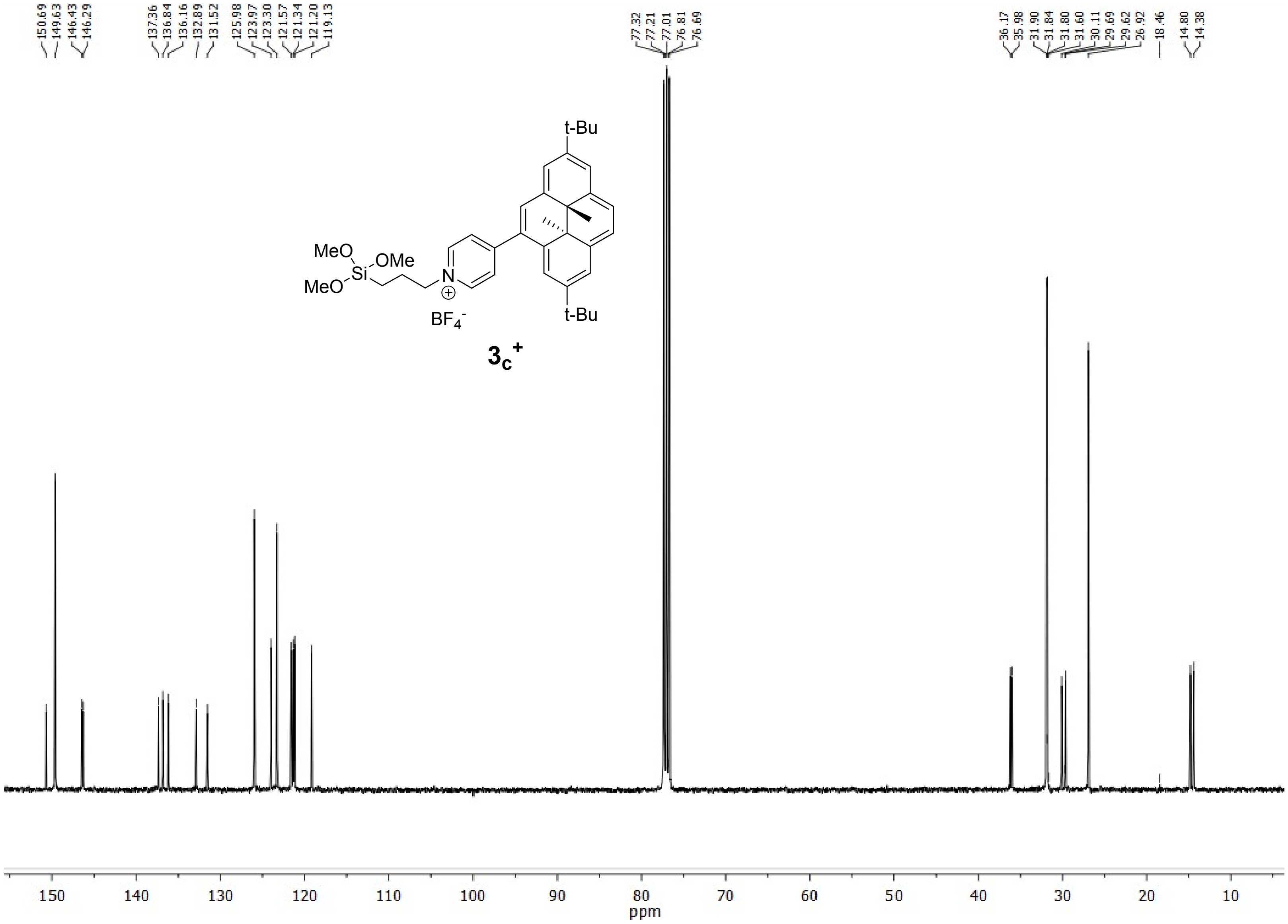


Figure ESI 10 : ^{13}C NMR spectrum of $\mathbf{3_c}^+$



8. References

[1] C. Simao, M. Mas-Torrent, J. Casado-Montenegro, F. Odon, J. Veciana, C. Rovira, *J. Am. Chem. Soc.*, **2011**, *133*, 13256.

[2] D. Roldan, S. Cobo, F. Lafolet, N. Vilà, C. Bochot, C. Bucher, E. Saint-Aman, M. Boggio-Pasqua, M. Garavelli, G. Royal, *Chem. Eur. J.*, **2015**, *21*, 455.