

Supporting Information for:

# Capture and Release of Singlet Oxygen in Coordination-Driven Self-Assembled Organoplatinum(II) Metallacycles

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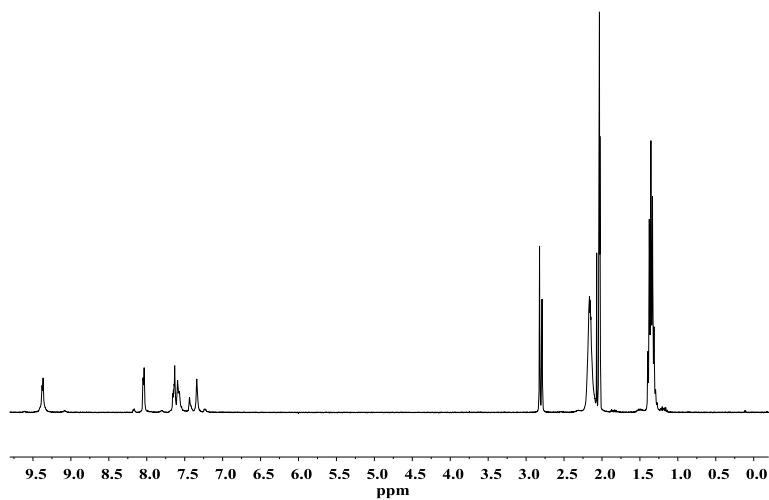
linker@uni-potsdam.de

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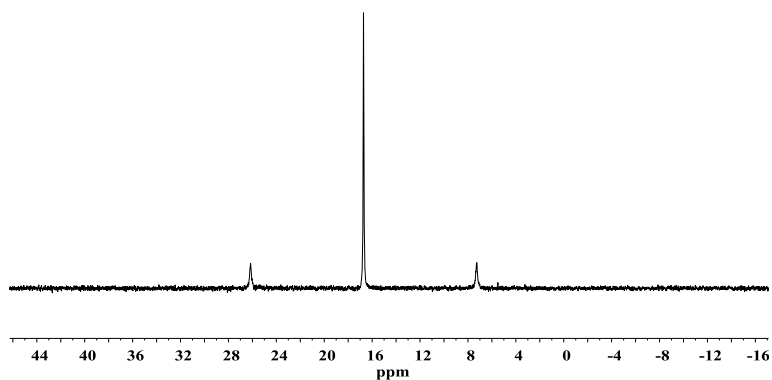
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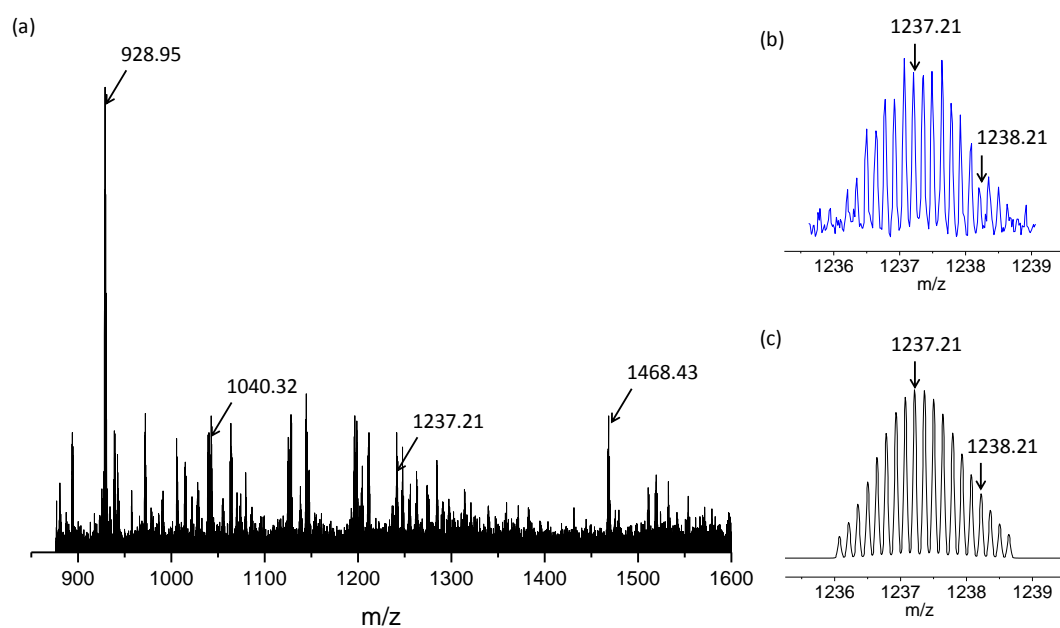
## 1. Experimental Characterization Data



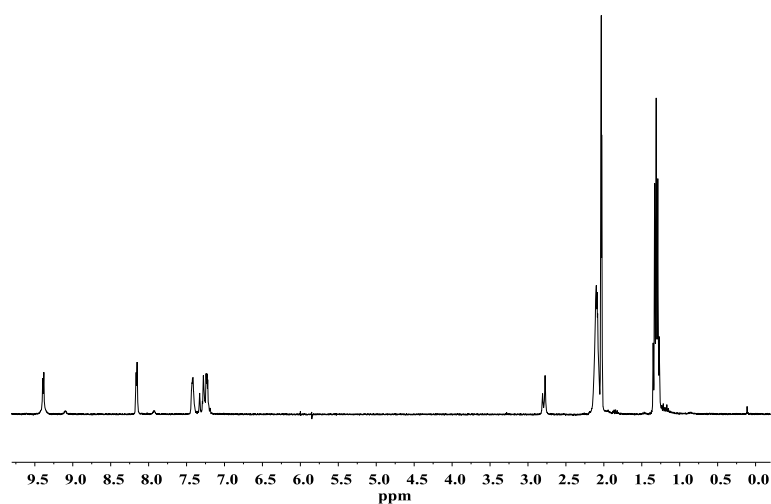
**Figure S1.**  $^1\text{H}$  NMR spectrum of **4** in Acetone- $\text{d}_6$  at 295 K.



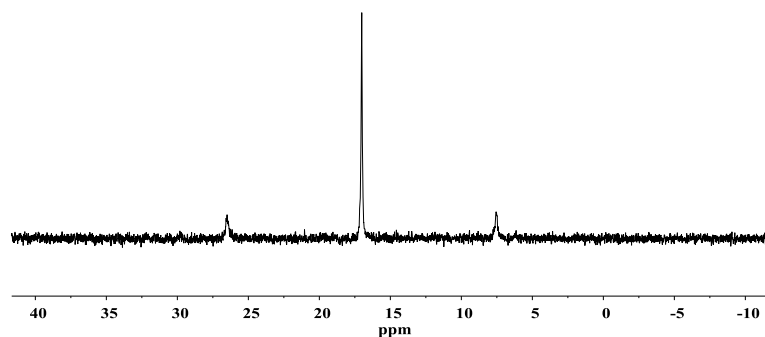
**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** in Acetone- $\text{d}_6$  at 295 K.



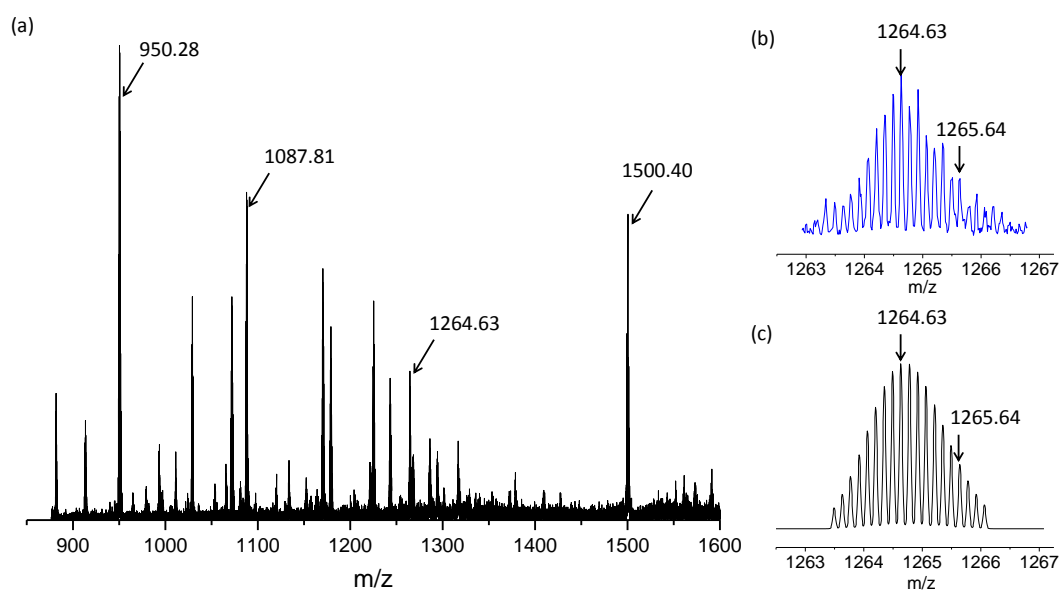
**Figure S3.** ESI-TOF-MS data for **4**. (a) ESI-TOF-MS full spectrum. (b) experimental data (upper, blue) and (c) predicted isotope distribution (below, black) of  $[\mathbf{M} - 7\text{OTf}]^{7+}$ .



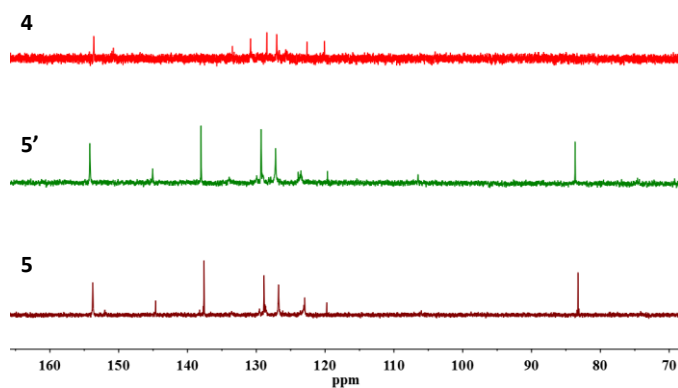
**Figure S4.** <sup>1</sup>H NMR spectrum of **5** in Acetone-*d*<sub>6</sub> at 295 K.



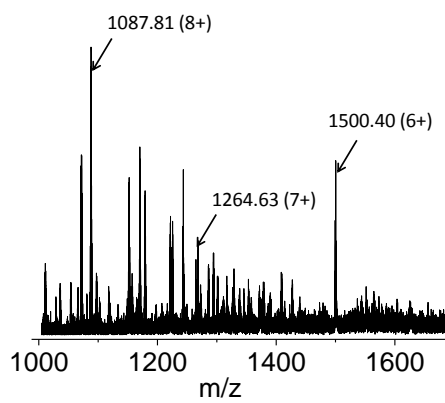
**Figure S5.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5** in Acetone- $\text{d}_6$  at 295 K.



**Figure S6.** ESI-TOF-MS data for **5**. (a) ESI-TOF-MS full spectrum. (b) experimental data (upper, blue) and (c) predicted isotope distribution (below, black) of  $[\text{M} - 7\text{OTf}]^{7+}$ .



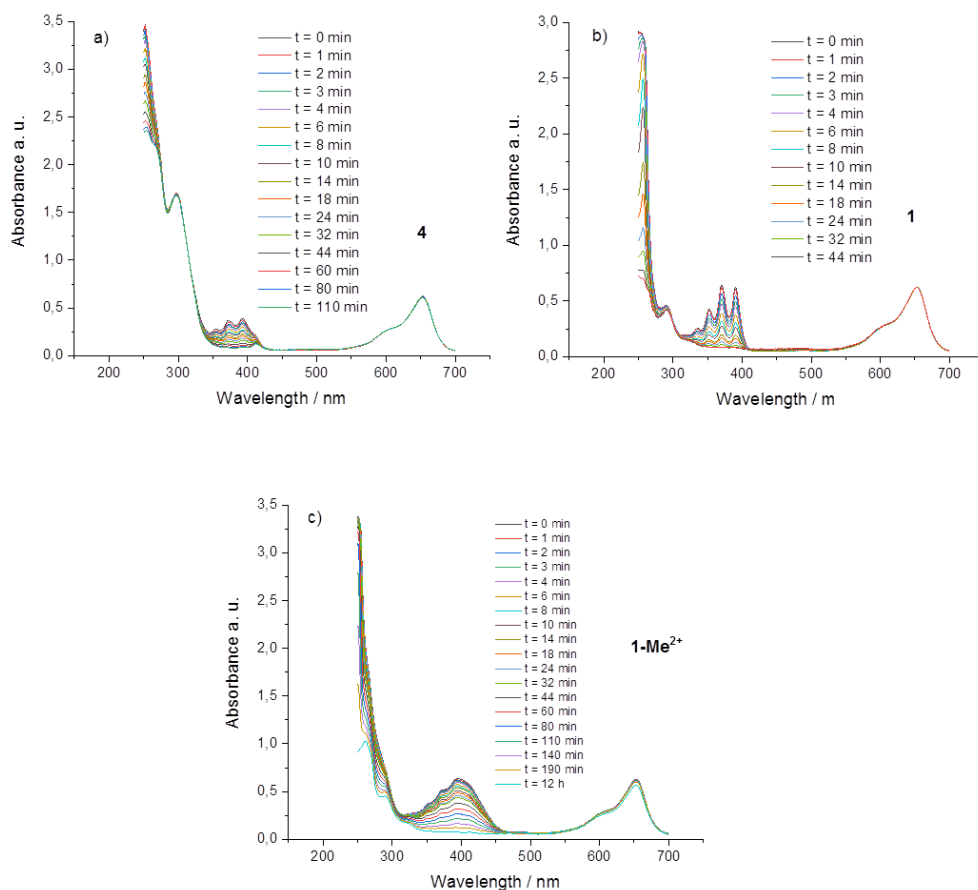
**Figure S7.** Partial  $^{13}\text{C}$  NMR (500 MHz, acetone- $\text{d}_6$ , 298 K) of complexes **4**, **5'**, **5**.



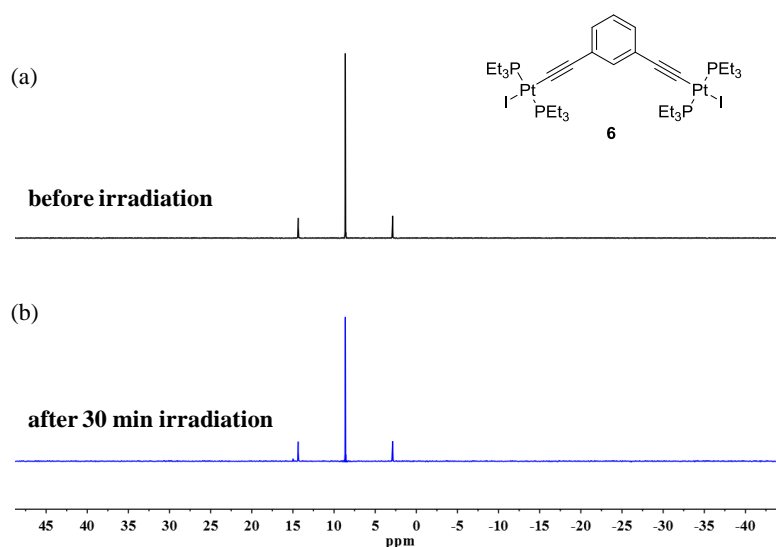
**Figure S8.** ESI-TOF-MS data for **5'**.

## 2. Photooxygenations monitored by UV/vis spectroscopy.

For the comparative study of the kinetics of complex **4**, ligand **1** and cationic species  $1\text{-Me}^{2+}$ , 10 mL of a mother-solution of methylene blue in  $\text{CD}_3\text{OD}$  was prepared, where an absorbance maximum at 660 nm was adjusted to  $\sim 0.8$ . This solution was then distributed over three quartz cuvettes, to which the three compounds were added from corresponding stock solutions. The concentration of all three compounds was  $5 \times 10^{-5} \text{ M}$ . After the first UV/vis spectra were recorded, each sample was irradiated with LED light (660 nm, 3 W per sample) and a spectrum measured thereafter. For the decay curves in the main text the  $\lambda_{\text{max}}$  values of 392 nm (**4**), 390 nm (**1**) and 395 nm ( $1\text{-Me}^{2+}$ ) were taken.



**Figure S9.** UV/vis absorbance spectra of solutions ( $5 \times 10^{-5} \text{ M}$ ) of a) complex **4**; b) ligand **1**; and c) the cationic species  $1\text{-Me}^{2+}$  in the presence of the sensitizer methylene blue ( $5 \times 10^{-6} \text{ M}$ ) in methanol- $\text{d}_4$  during irradiation.

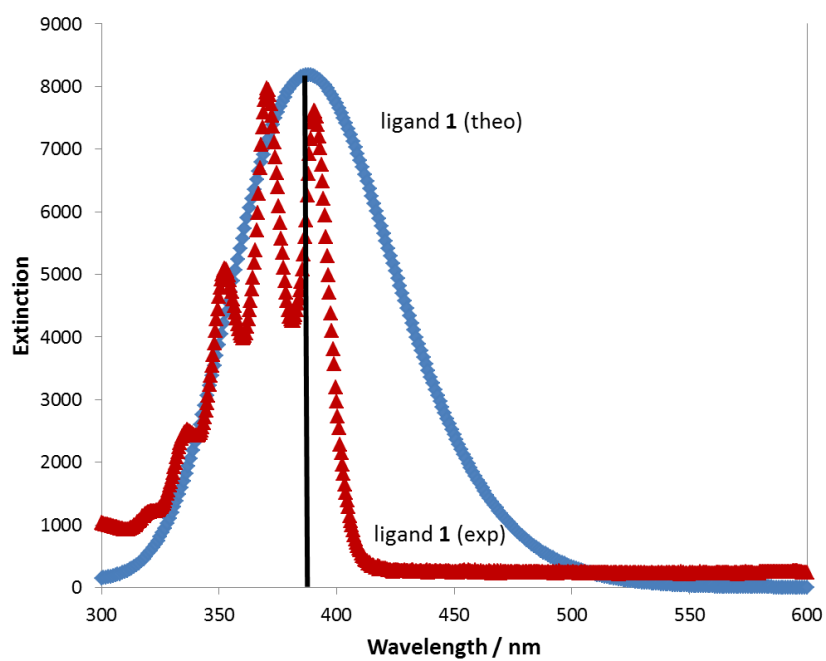
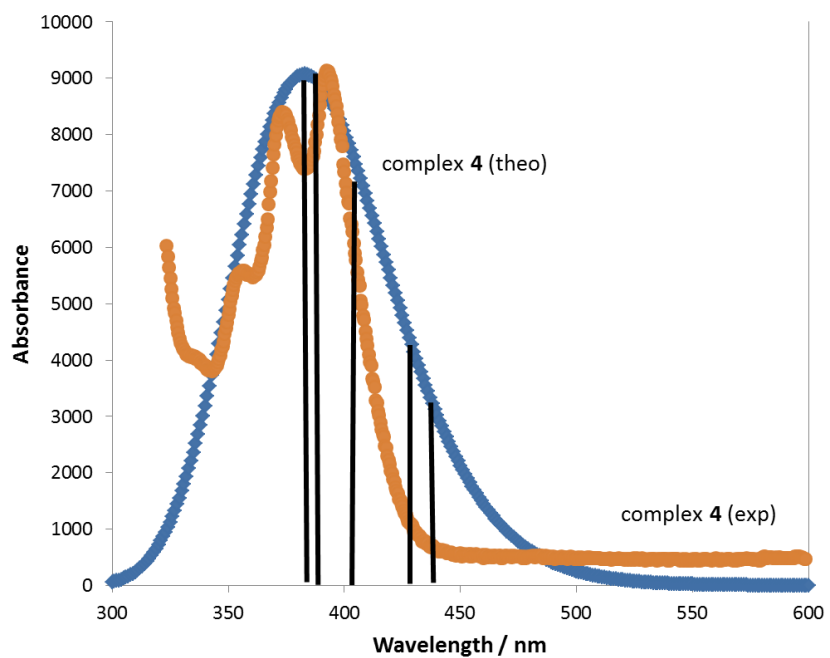


**Figure S10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{CD}_2\text{Cl}_2$  at 295 K. (a) before irradiation, (b) after 30 min irradiation.

### 3. Theoretical calculation results

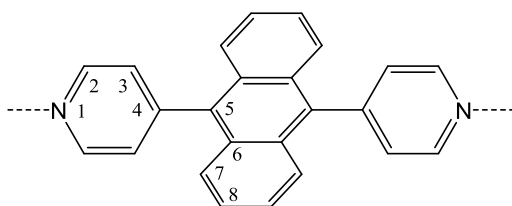
**Table S1.** TDDFT results of the ground state of complex **6** (transitions with  $f < 0.01$  are not shown).

$S_n$	$\lambda/\text{nm}$	$f$	transitions and their coefficients
1	442	0.082	HOMO→LUMO (0.359)
			HOMO→LUMO+1 (0.504)
			HOMO→LUMO+2 (0.339)
3	431	0.037	HOMO→LUMO (-0.318)
			HOMO→LUMO+1 (0.485)
			HOMO→LUMO+2 (-0.389)
5	401	0.033	HOMO-1→LUMO (0.368)
			HOMO-1→LUMO+1 (0.597)
9	383	0.224	HOMO-1→LUMO (0.592)
			HOMO-1→LUMO+1 (-0.371)



**Figure S11.** Theoretical and experimental UV/vis spectra of the ligand 1 and the complexes 5 and 6.





	<b>1</b>	<b>6</b>	<b>1-Me<sup>2+</sup></b>
N1	-0.405	-0.448	-0.364
C2	0.181	0.268	0.355
C3	-0.009	0.034	0.042
C4	0.018	0.014	0.049
C5	-0.070	-0.076	-0.057
C6	0.106	0.121	0.119
C7	-0.051	-0.064	-0.058
C8	0.001	0.031	0.058

**Figure S12.** Mulliken charge populations ( $Q/e$ ) of the ligand **1**, complex **6** and the cationic species **1-Me<sup>2+</sup>**.

#### 4. Singlet oxygen trapping experiments

To determine the amount of  $^1\text{O}_2$ , three trapping experiments with the trap DPBF were performed. For each run the EPO was mixed with the trap in a 10 mL glass flask and dissolved in 2 mL toluene- $d_8$ . From each solution an aliquot of 50  $\mu\text{L}$  was taken, diluted to 4 mL and the DPBF absorbance at 416 nm was measured giving  $A_{416_{\text{before}}}$ . The solutions were subjected to three cycles of freeze-pump-and-thaw in order to remove atmospheric oxygen and then sealed with a stopper. The flasks were kept overnight at a temperature of 100  $^\circ\text{C}$ . The solutions were transferred to a flask and diluted to 5 mL, then 125  $\mu\text{L}$  were taken and diluted to 4 mL to measure the DPBF absorbance giving  $A_{416_{\text{after}}}$ . The difference between the absorbances of these two spectra allows to calculate the amount of DPBF, which reacted with  $^1\text{O}_2$ :

$$n(\text{DPBF}_{\text{oxidized}}) = (A_{416_{\text{before}}} - A_{416_{\text{after}}}) / A_{416_{\text{before}}} * n(\text{DPBF}_{\text{total}})$$

The percentage of  $^1\text{O}_2$  generated per EPO gives :  $\phi(^1\text{O}_2) = n(\text{DPBF}_{\text{oxidized}}) / n(\text{EPO})$ .

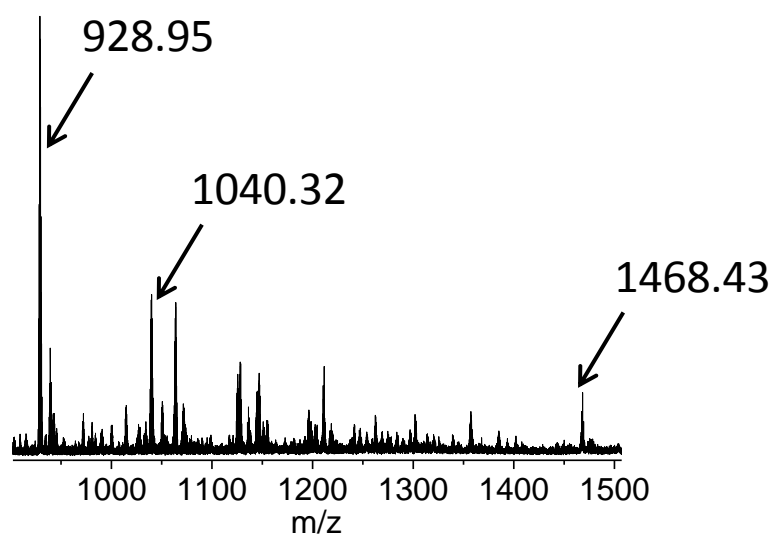
Note that  $n(\text{EPO}) = 1/6 n(5)$

The results are summarized in Table S2:

Table S2. Summary of the results of the transfer experiments using the trap DBPF

run	$n(\text{EPO})/\text{mol}$	$n(\text{DPBF}_{\text{total}})/\text{mol}$	$n(\text{DPBF}_{\text{oxidized}})$	$\phi(^1\text{O}_2)$
1	$1.99 \times 10^{-6}$	$1.03 \times 10^{-5}$	$5.58 \times 10^{-7}$	0.28
2	$3.85 \times 10^{-6}$	$8.8 \times 10^{-6}$	$1.08 \times 10^{-6}$	0.28
3	$6.22 \times 10^{-6}$	$8.9 \times 10^{-6}$	$1.64 \times 10^{-6}$	0.27

## 5. ESI-TOF-MS Spectra



**Figure S13.** ESI-TOF-MS data for 4'.