Supporting Information: Calculation of Keq:

Based on equations 1-4 (scheme 5 in manuscript), the rate of appearance of the nitroxyl radicals dR/dt on photo-excitation of **Ru-2** in the presence of PBN can be described by equation 5.

(5) $dR/dt = K_2 \times [Ru\text{-}2(III) \cdots O_2^{-\cdot}] \times [PBN]$

At steady state, the equilibrium constant for the cage formation may be expressed as:

(6) $$K_{eq}(2) = \frac{[Ru(II)\text{-}2^{*} \cdots O_2]}{([Ru\text{-}2(II)]_0 - [[Ru\text{-}2^{*}(II) \cdots O_2]) \times ([O_2]_0 - [Ru\text{-}2^{*}(II) \cdots O_2])}$$

Since

$[Ru(II)\text{-}2]_0 = 1\text{-}2$ mM, $[O_2]_0 \sim 0.5$ mM and $[Ru(II)\text{-}2]_0 > [Ru\text{-}2^{*}(II) \cdots O_2]$

Equation (6) may be simplified to:

(7) $K_{eq}(2) = [Ru\text{-}2^{*}(II) \cdots O_2] / [Ru\text{-}2(II)]_0 \times ([O_2]_0 - [Ru\text{-}2^{*}(II) \cdots O_2])$

And re-arranged to:

(8) $[Ru\text{-}2^{*}(II) \cdots O_2] = K_{eq}(2) \times [Ru\text{-}2(II)]_0] \times [O_2]_0 / 1 + K_{eq}(2) \times [Ru\text{-}2(II)]_0]$

As $K_{eq}(2) \times [Ru\text{-}2(II)]_0 << 1$, substituting Equation (8) into Equation (5) yields:

(9) $dR/dt = K_2 \times K_{eq}(2) \times [O_2]_0 \times [PBN] \times [Ru\text{-}2(II)]_0$

Plotting dR/dt as a function of $[Ru\text{-}2(II)]_0$ we retrieved the following equation:

(a) $\tan \alpha = K_2 \times K_{eq}(2) \times [O_2]_0 \times [PBN]$

Using the K_2 value for DMPO ($K_2 = 10\ M^{-1}sec^{-1}$), the Keq is estimated as $3.1\ M^{-1}$.