

Supporting Information

Experimental Section

a. Photosensitization of 2-methyl 2-butene

A catalytic amount of bisazafullerene ($C_{59}N_2$) (0.5mgr, 0.34×10^{-3} mmol) or hydroazafullerene (0.25mgr, 0.34×10^{-3} mmol) dissolved in benzene-d₆ (1ml) was added to 2-methyl 2-butene (10mgr, 0.14mmol). A stream of pure oxygen was passed through and the mixture was subsequently irradiated with a UV lamp equipped with a Kapton filter (cut-off wavelength <400nm) for 20 minutes to give in both cases almost quantitatively an equimolar mixture of hydroperoxides **1** and **2**.

For **1**: ¹H NMR (500MHz, benzene-d₆, δ ppm): 1.03(d, $J=7.1$ Hz, 3H), 1.59(s, 3H), 4.28(q, $J=7.1$ Hz, 1H), 4.79(d, $J=1$ Hz, 1H), 4.88(d, $J=1$ Hz, 1H).

For **2**: ¹H NMR (500MHz, benzene-d₆, δ ppm): 1.16(s, 6H), 4.92(dd, $J_1=0.9$ Hz, $J_2=10.7$ Hz, 1H), 5.03(dd, $J_1=0.9$ Hz, $J_2=17.6$ Hz, 1H), 5.81(dd, $J_1=10.7$ Hz, $J_2=17.6$ Hz, 1H).

b. Photosensitization of α - terpinene

A catalytic amount of bisazafullerene ($C_{59}N_2$) (1mgr, 0.069×10^{-2} mmol) or hydroazafullerene (0.5mgr, 0.069×10^{-2} mmol) dissolved in benzene-d₆ (1ml) was added to α - terpinene (10mgr, 0.07mmol). A stream of pure oxygen was passed through and the mixture was subsequently irradiated with a UV lamp equipped with a Kapton filter (cut-off wavelength <400nm) for 30 minutes to give ascaridole **3** in 80% yield.

¹H NMR (500MHz, benzene-d₆, δ ppm): 0.97(d, $J=7.1$ Hz, 6H), 1.08(s, 3H), 1.12-1.25(m, 2H), 1.82(sep, $J=6.8$ Hz, 1H), 1.63-1.88(m, 2H), 6.08(d, $J=8.5$ Hz, 1H), 6.17(d, $J=8.5$ Hz, 1H).