

**Electronic Supplementary Information: part 2**

**Photoactivatable HNO-releasing Compounds Using the retro-Diels-Alder Reaction**

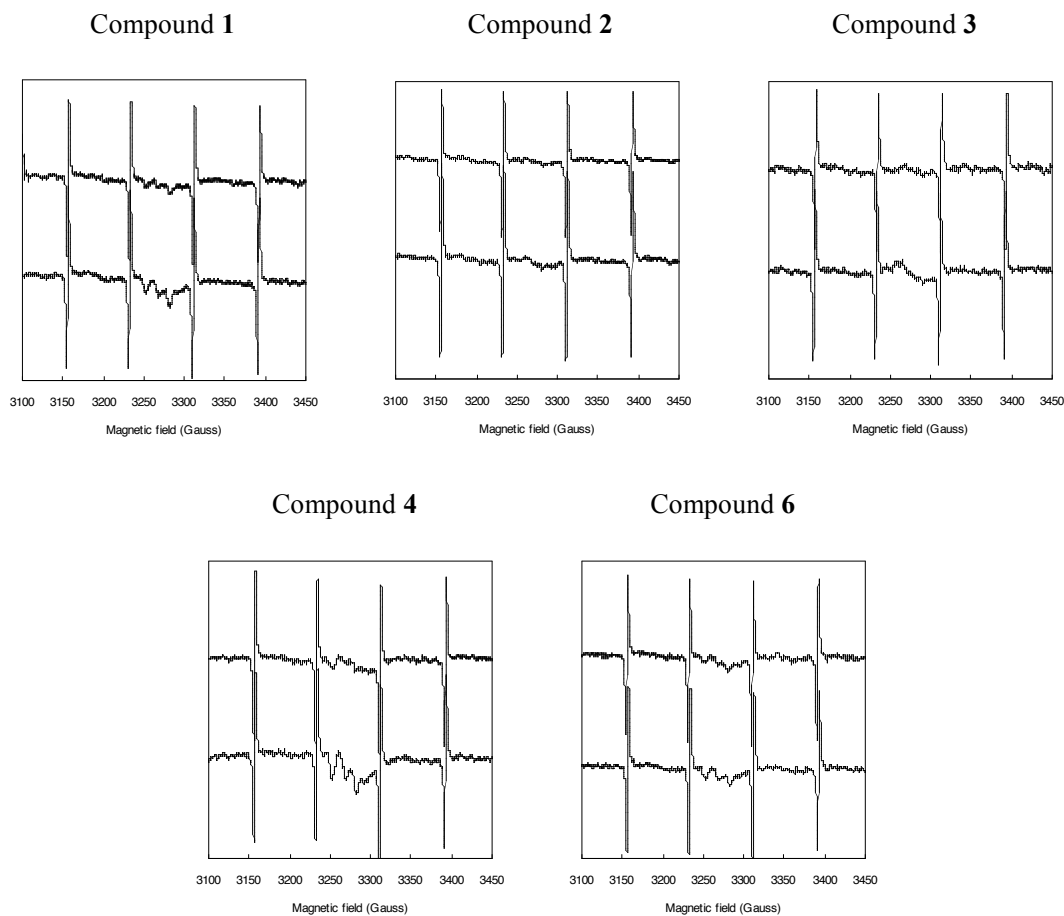
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**<Analysis 2>**

**EPR Measurement of Ferrous Nitrosyl Complex Formed from HNO and Hemin.** A solution of hemin (10 mM, 50  $\mu$ L) in DMSO was diluted with DMSO (845  $\mu$ L) and milli Q water (100  $\mu$ L). To the mixture was added a solution of donor (10 mM, 5  $\mu$ L) in DMSO. The resulted mixture (1000  $\mu$ L) as a sample for EPR studies were photoirradiated or not for 10 min at room temperature. The solution was transferred to an EPR tube and frozen in liquid nitrogen (77 K). EPR spectra were taken on a JES-RE2X spectrometer (JEOL Co. Ltd., Tokyo, Japan). The measurement conditions were follows; microwave power, 10 mW; frequency, 9.145 GHz; field, 336.5 mT; sweep width, 40 mT; sweep time, 1 min; modulation width, 0.63 mT; gain, 500; and time constant; 0.03 s.



**Figure S3.** EPR spectra of cycloadducts (1–6) in DMSO/water (9:1) with hemin. Spectra were measured either under dark conditions (top), or under photoirradiation (bottom) in the presence of manganese as an external standard.

**Detection of N<sub>2</sub>O by Gas Chromatography.** A solution of donor (1.5 μmol) in DMSO (2700 μL) and milli Q water (300 μL) was placed in a 4-mL cuvette sealed with a rubber septum. For HNO scavenging experiments, 2-mercaptoethanol (1.05 μL) was added to the solution. Every 10 min for 30 min, aliquots of the reaction headspace (50 μL) was injected onto a Shimadzu GC-2010 gas chromatograph equipped with a mass spectrometer (QP2010) and a Rt-QPLOT column (0.32 mm × 15 m) expanded by 15-m inactivated fused silica tube (total 30 m). The GC injector was operated with a split ratio of 0.1 at 200 °C. The carrier gas (He) was set at a flow rate of 2.2 mL/min. The GC oven was held at 35 °C. MS interface was set to 280 °C.

**Table S1.** N<sub>2</sub>O formation.

compounds	conditions		N <sub>2</sub> O formation <sup>a</sup> (μmol)		
	hν	2-ME <sup>b</sup>	10 min	20 min	30 min
Angeli's salt	-	-	0.254	0.424	0.533
	-	-	0.203	0.373	0.472
<b>1</b>	+	-	0.261	0.484	0.594
	+	+	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>c</sup>
	-	-	N.D. <sup>c</sup>	0.025	0.067
<b>2</b>	+	-	N.D. <sup>c</sup>	0.059	0.064
	+	+	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>c</sup>
	-	-	0.200	0.318	0.433
<b>4</b>	+	-	0.173	0.320	0.424
	+	+	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>c</sup>

<sup>a</sup> Calculation based on Angeli's salt (1.5 μmol) decomposition according to Hughes and Wimbeldon.<sup>3</sup> <sup>b</sup> 2-Mercaptoethanol (10 equiv.) <sup>c</sup> N<sub>2</sub>O was not detected.

(3) Hughes, M. N.; Wimbeldon, P. E. *J. Chem. Soc. Dalton Trans.* **1976**, 703–707.