Supporting Information
Cryogenic Photolysis of Activated Bleomycin to Ferric Bleomycin

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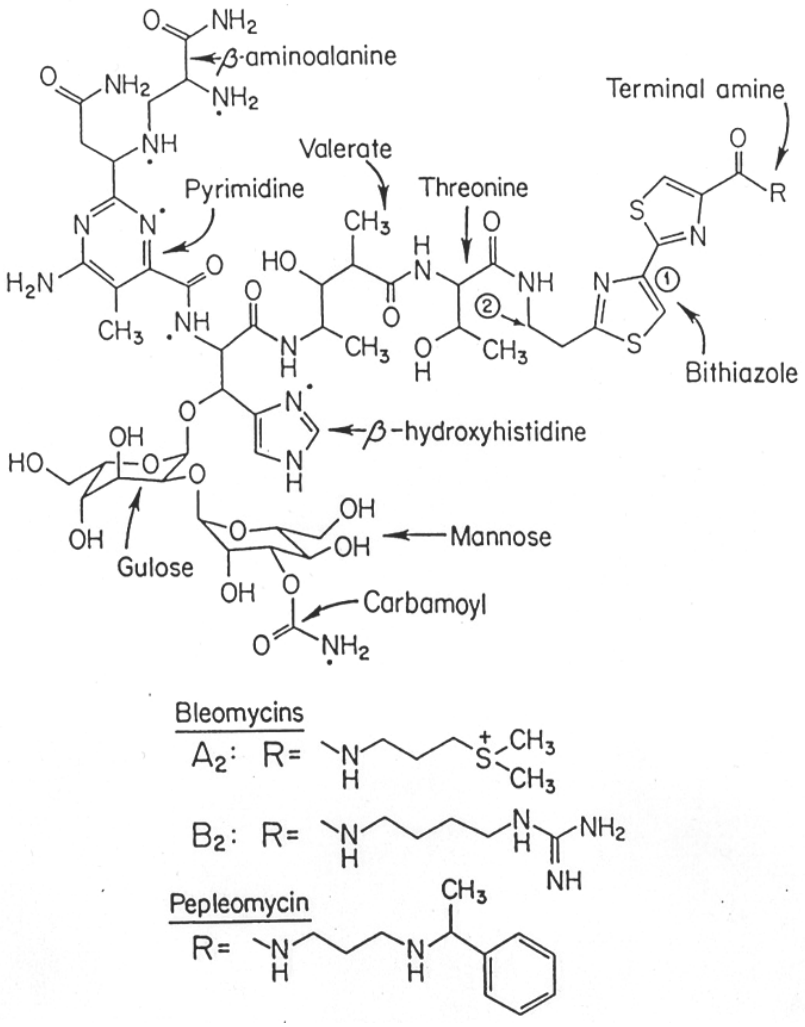

Structure 1S. The structure of bleomycin (BLM) as determined in the 1970s by H. Umezawa and colleagues,[1] who discovered this *Streptomyces* antibiotic family and its widely-utilized anti-tumor properties. The *bullets* indicate nitrogenous metal-ligands. Individual bleomycins have different terminal R groups.

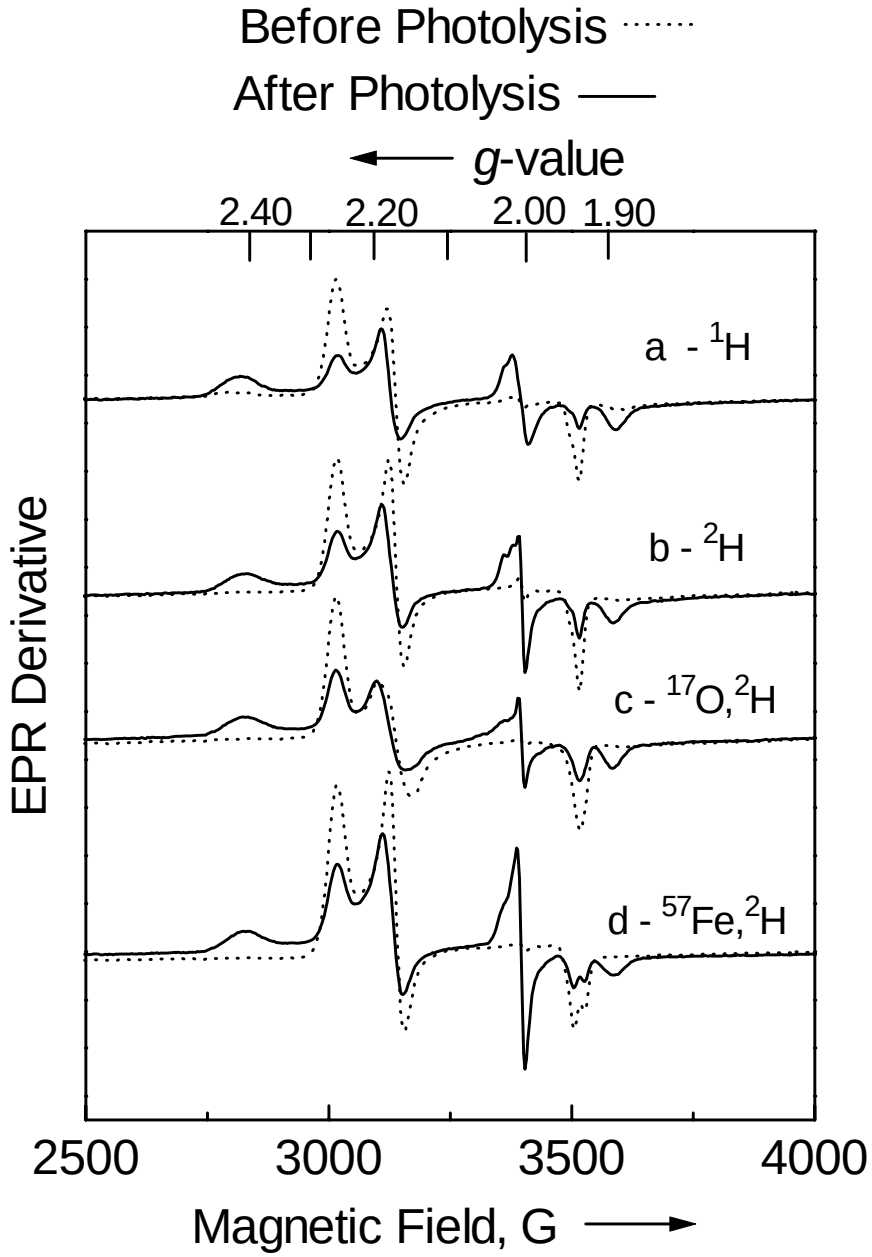

Figure 1S. Effects of ^{1}H, ^{2}H, ^{17}O, and ^{57}Fe spin isotopes on EPR spectra of ABLM cryophotoproducts. ABLM samples are shown: prior to (dotted lines) and after (solid lines) a partial (20 min) photolysis. Samples were prepared with either: (**a**) natural abundance constituents (^{1}H), (**b**) perdeuterated solvents (^{2}H), (**c**) perdeuterated solvents and $^{17}O_2$, or (**d**) perdeuterated solvents and ^{57}Fe. The ^{1}H and ^{2}H samples were 200 μL samples and the ^{17}O and ^{57}Fe were 60 μl samples of 1 mM ABLM. Both types of samples received radiation of 300 einsteins/mol of ABLM. EPR spectroscopic conditions were as in Figure 1 in the main body of the text.

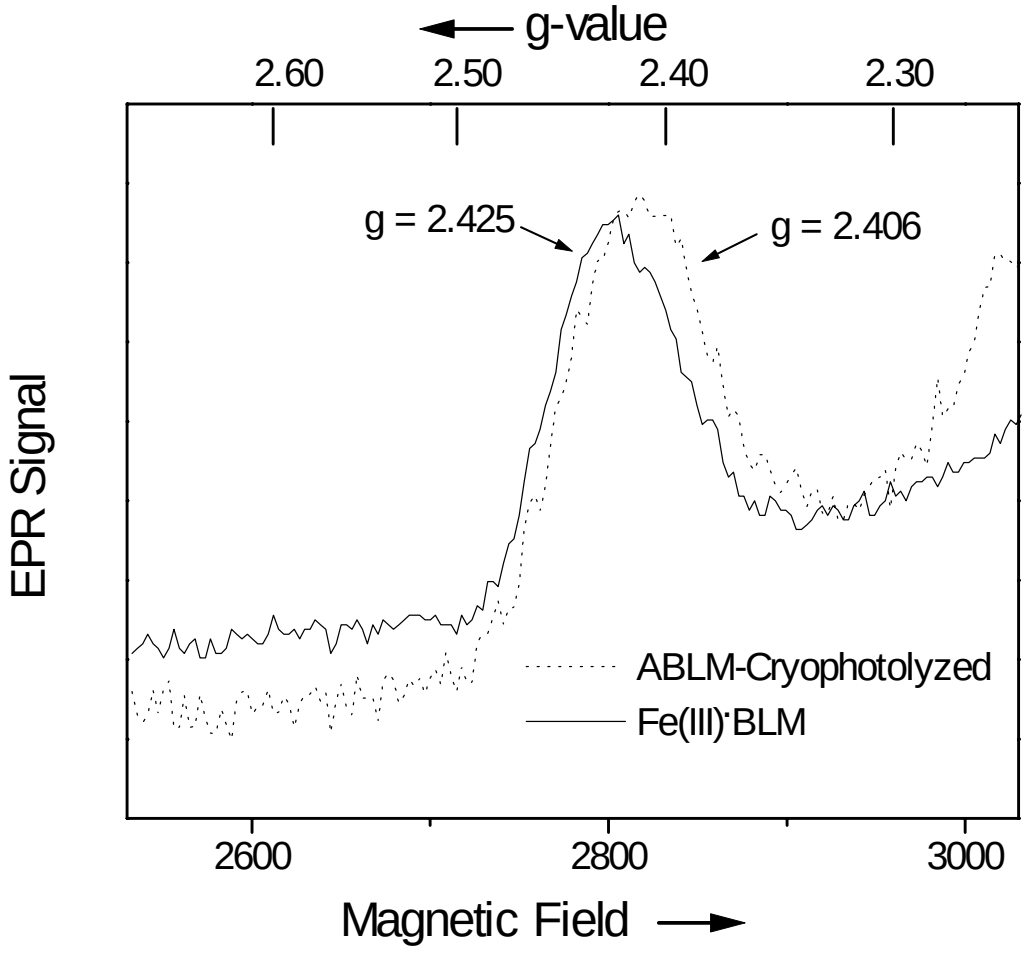

Figure 2S. Comparison of Fe(III)•BLM spectra near g_1. The product was created by cryophotolysis or *de novo* at room temperature by addition of Fe(III) to BLM in HEPES buffer. EPR conditions for taking these spectra were as in Figure 1 in the main body of the text.

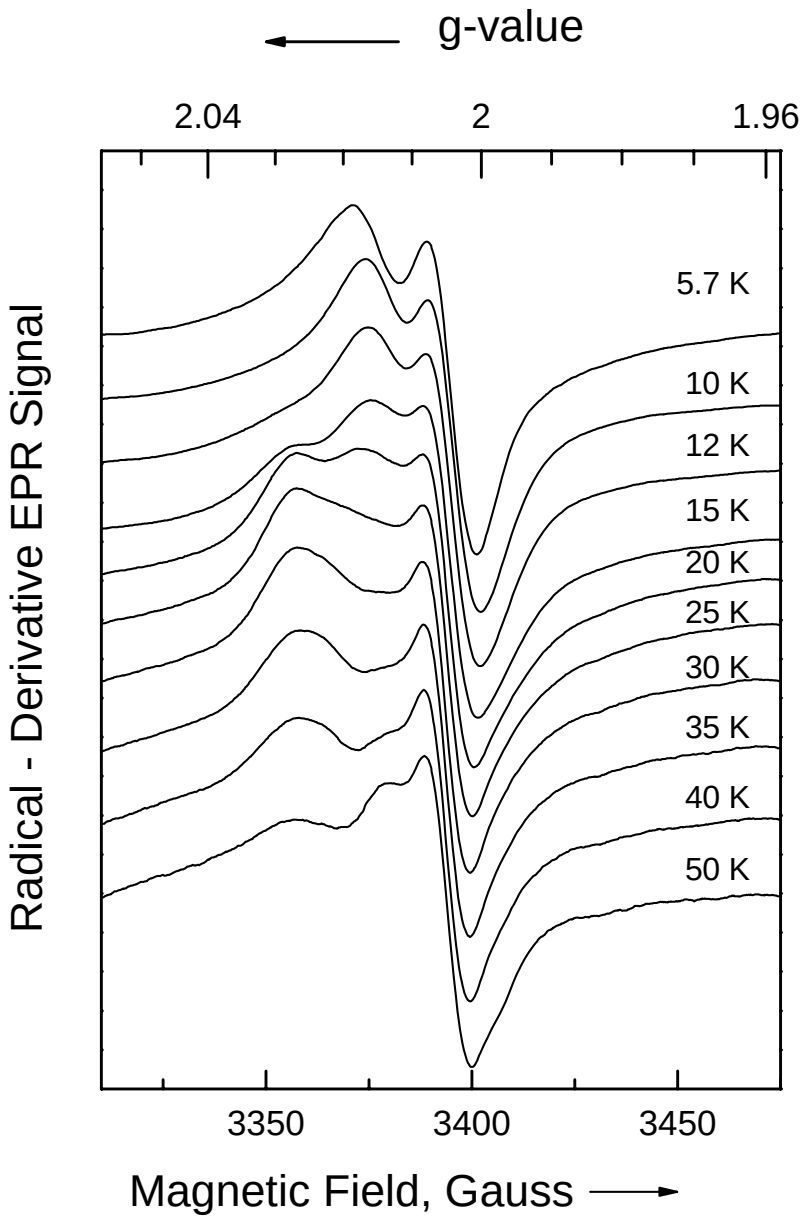

Figure 3S. Temperature-dependent interconversions of the photolyzed ABLM radical. This sample, in perdeuterated solvent, was also used for Figure 4 in the main body of the text. These temperature dependent changes are fully reversible in the 6-50 K range. These spectra were obtained at 3 G modulation, 200 s total signal accumulation over the field range shown, 20 mW power, ν_{EPR} = 9.52 GHz.

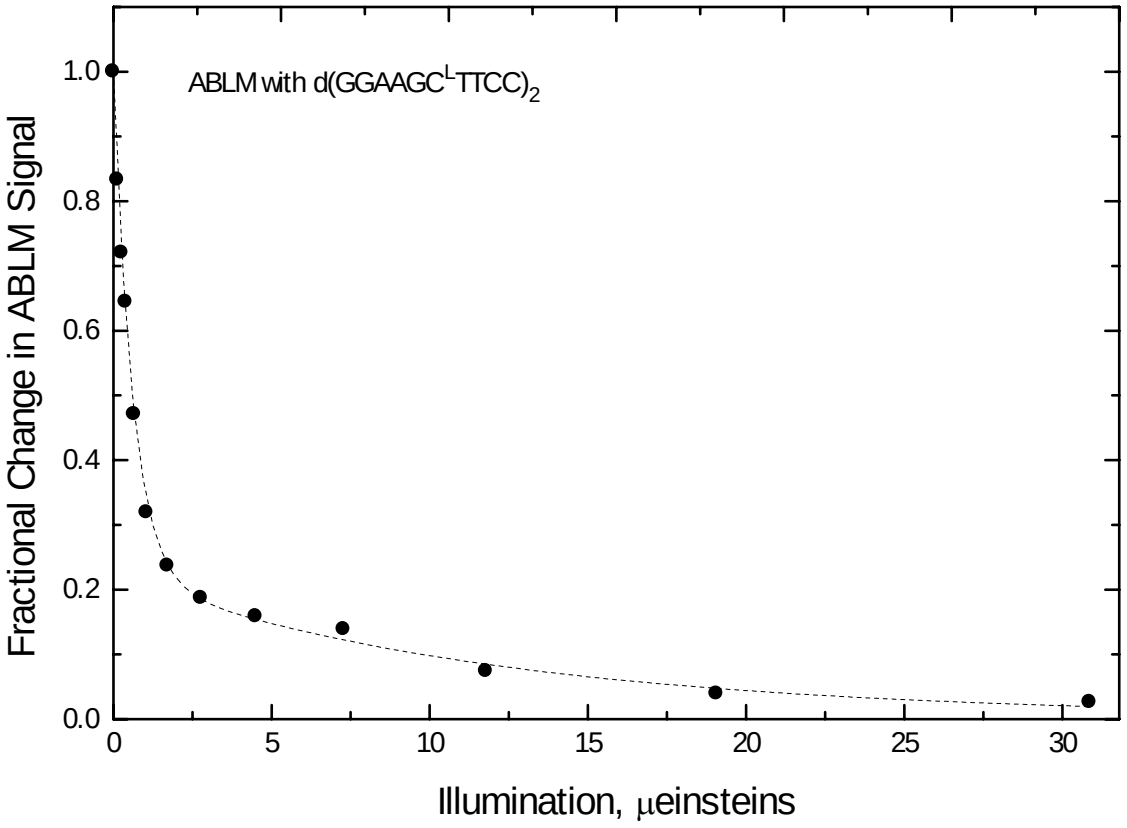

Figure 4S. Course of ABLM cryophotolysis in the presence of d(GGAAGC^{L}TTCC)$_2$, which has a 2′O-,4′-methylenylcytidine (C^{L}) not cleaved by ABLM under ambient conditions The percentage change in the ABLM signal was estimated from the g = 1.94 derivative, measured at 15 K with 2 mW microwave power and 6 G modulation. Concentrations of Fe-BLM and d(GGAAGC^{L}TTCC)$_2$ were 1 mM in a 60 μL sample.

Table 1S. Effect of a 2′O-,4′-methylenylcytidine (C^L) on DNA Cleavage

Oligonucleotide	Base propenal yield *(μM)*[a]
$d(GGAAGCTTCC)_2$	14.3
$d(GGAAGC^LTTCC)_2$	<0.1
both	15.9

[a]Samples (75 μL) contained 0.11 mM bleomycin, 0.11 mM oligonucleotide duplex (each), 20 mM sodium phosphate buffer, pH 7.8, and 0.10 mM Fe(II), added last. Run 1 h at 0 °C, to completion, incubation mixtures then received 725 μL TBA for base propenal assay.

Reference

(1) Takita, T.; Muraoka, Y.; Nakatani, T.; Fujii, A.; Umezawa, Y.; Naganawa, H.; Umizawa, H. *J. Antibiot. (Tokyo)* **1978**, *31*, 801.