Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information

A Dormant BODIPY-Acrolein Singlet Oxygen Photosensitizer Activated upon Adduct Formation with Cysteine Residues

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This section includes:

Partition Coefficient Determination.

Partition coefficients of the BODIPY dyes were determined by the HPLC method.[1-3] An isocratic elution of water and acetonitrile (30:70) was used. The retention factor, k was determined from Equation S1 where t_R was the retention time of compound and t_0 was determined from injection of the unretained compound, formamide (t_0 = ~0.14 min). A standard curve was constructed according to Equation S2 from the following compounds: benzene (log P= 2.1), toluene (log P = 2.7), naphthalene (log P = 3.3), anthracene (log P = 4.4), pyrene (log P = 4.88), hexachlorobenzene (log P = 6.18) and 1,3,5-tri-*tert*-butylbenzne (log P = 7.6). A new standard curve was measured for each unknown sample. The average partition coefficients of the BODIPY dyes are given in Table S1, the errors correspond to the standard error of three triplicate measurements.

$$\boldsymbol{k = (t_R - t_0)/t_0} \qquad \textbf{(S1)}$$

$$\boldsymbol{\log(k) = a * \log(P) + b} \qquad \textbf{(S2)}$$

Table S1. Partition Coefficients of the BODIPY Dyes Measured by HPLC.

Compound	Log P
BromoAcroB	5.00 ± 0.03
Br_2BEt	6.48 ± 0.03
AcroB	2.83 ± 0.03
H_2BEt	4.01 ± 0.03

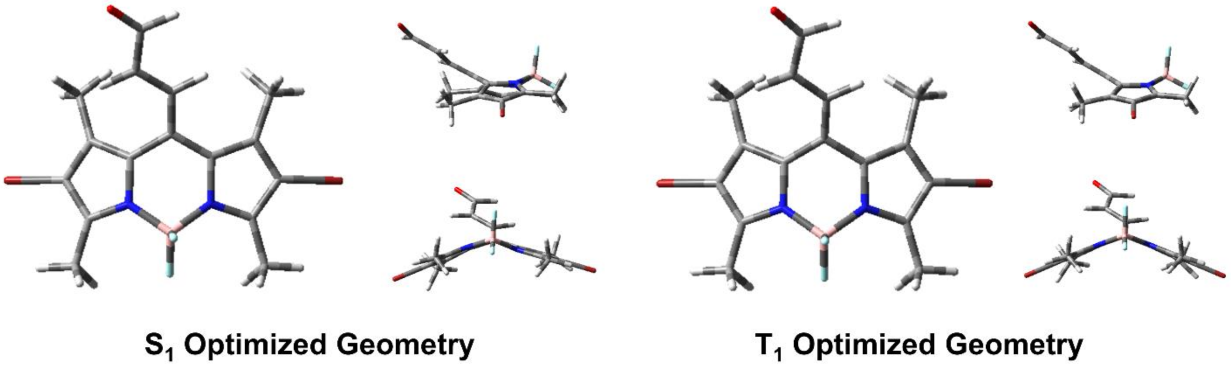


Figure S1. TD-DFT-optimized geometries of **BromoAcroB** computed for S1 (left) and T1 (right) at the B3LYP/6-31G(d) with an applied polarizable continuum model solvation of acetonitrile.

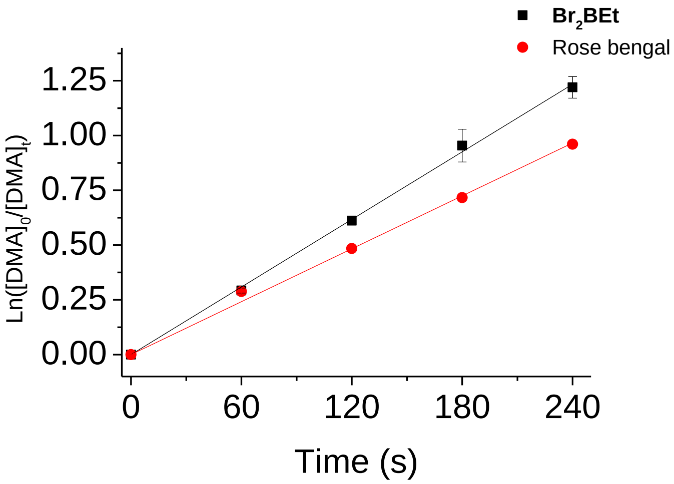


Figure S2. Pseudo first-order kinetic data of the consumption of dimethyl anthracene by photosensitized singlet oxygen by **Br$_2$BEt** and Rose Bengal ($\Phi_\Delta = 0.54$)[4] in air equilibrated acetonitrile.[5] Error bars correspond to the standard deviate of three samples.

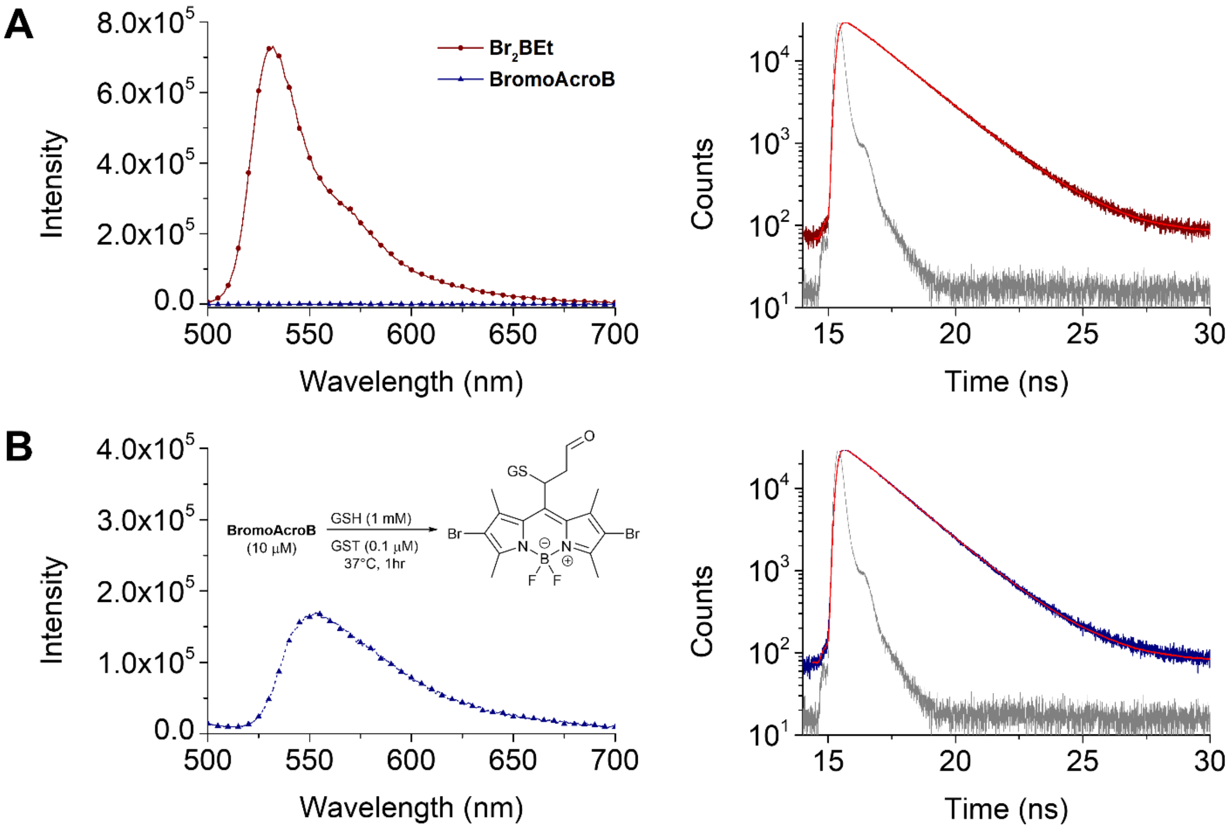
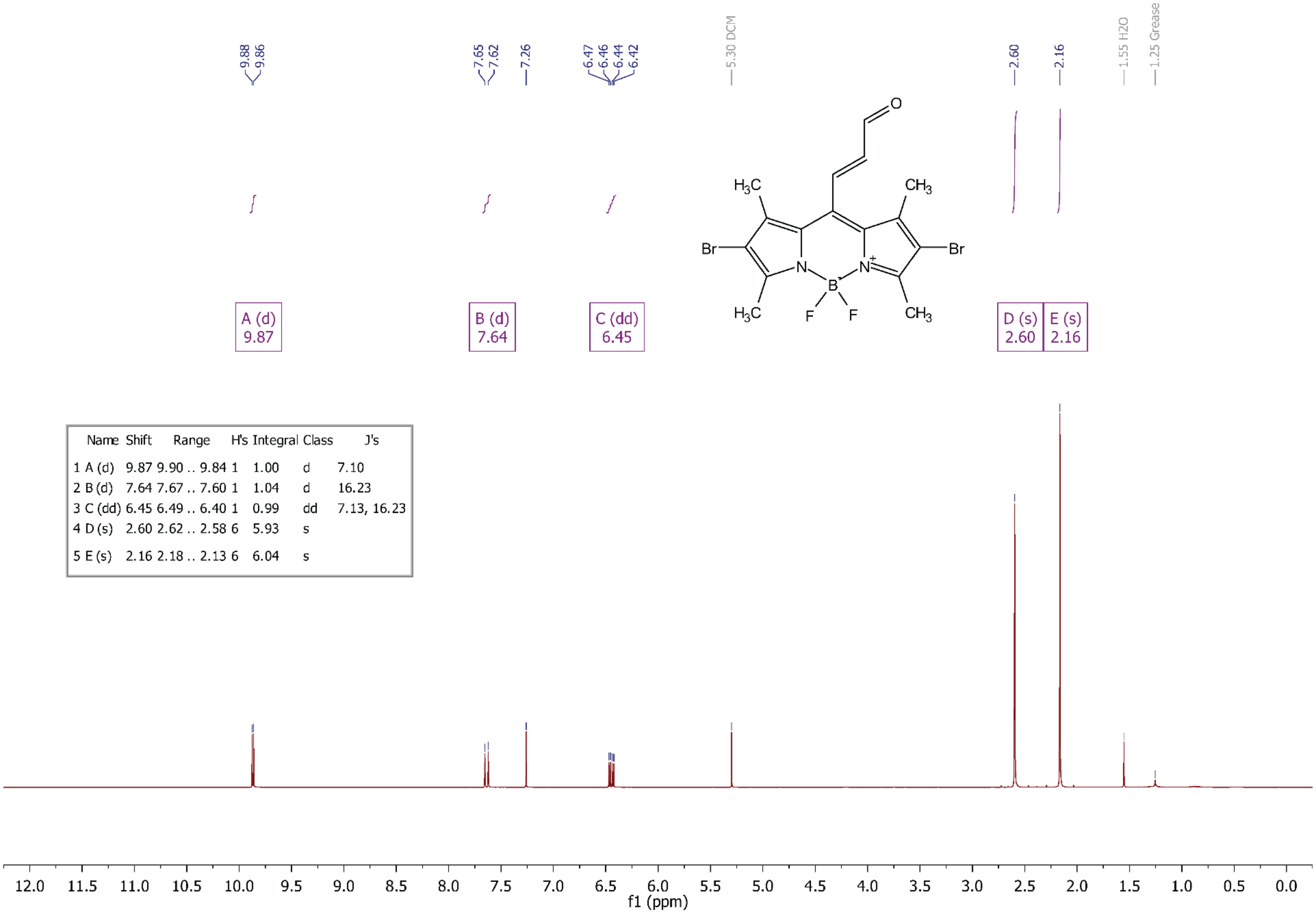
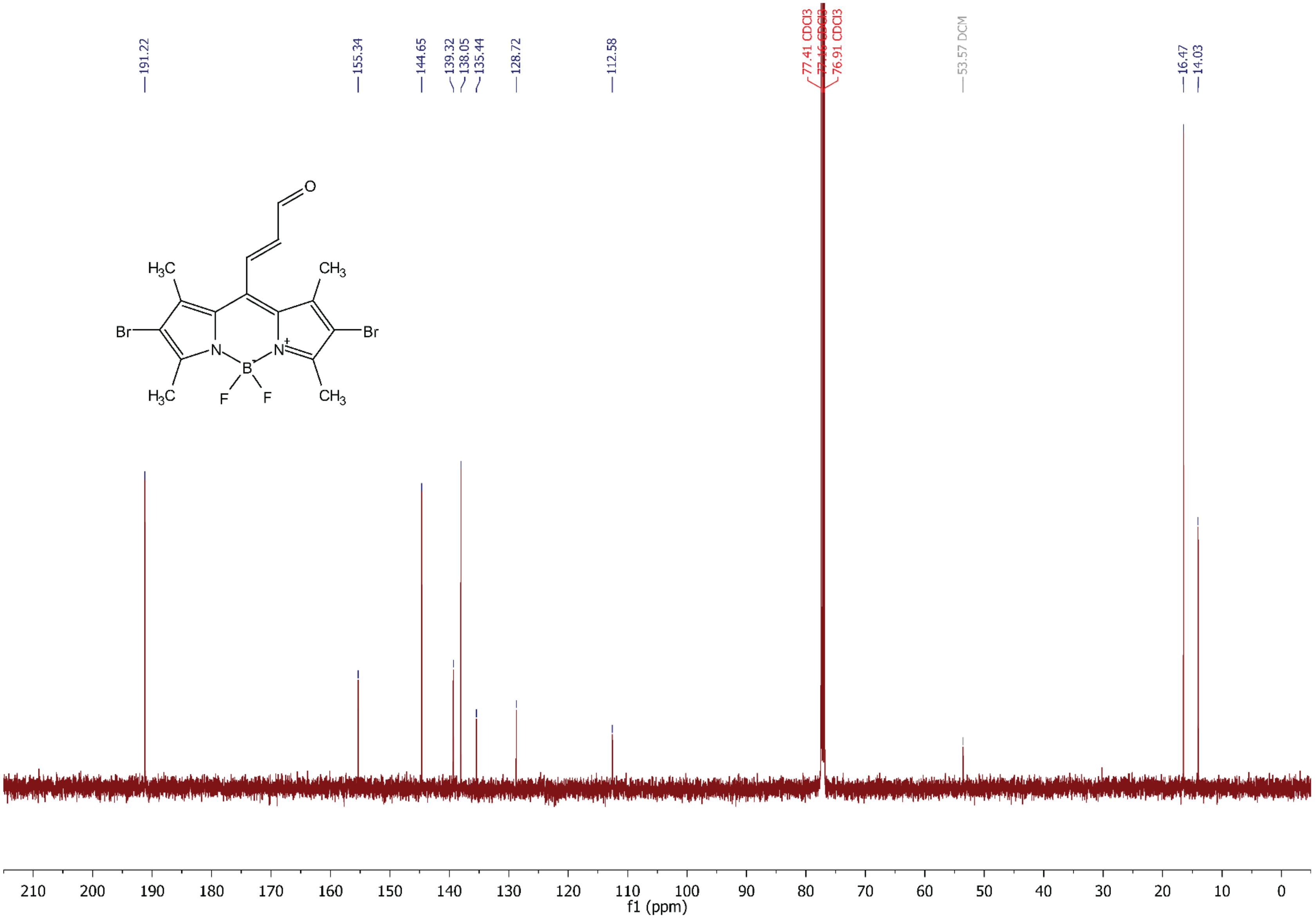
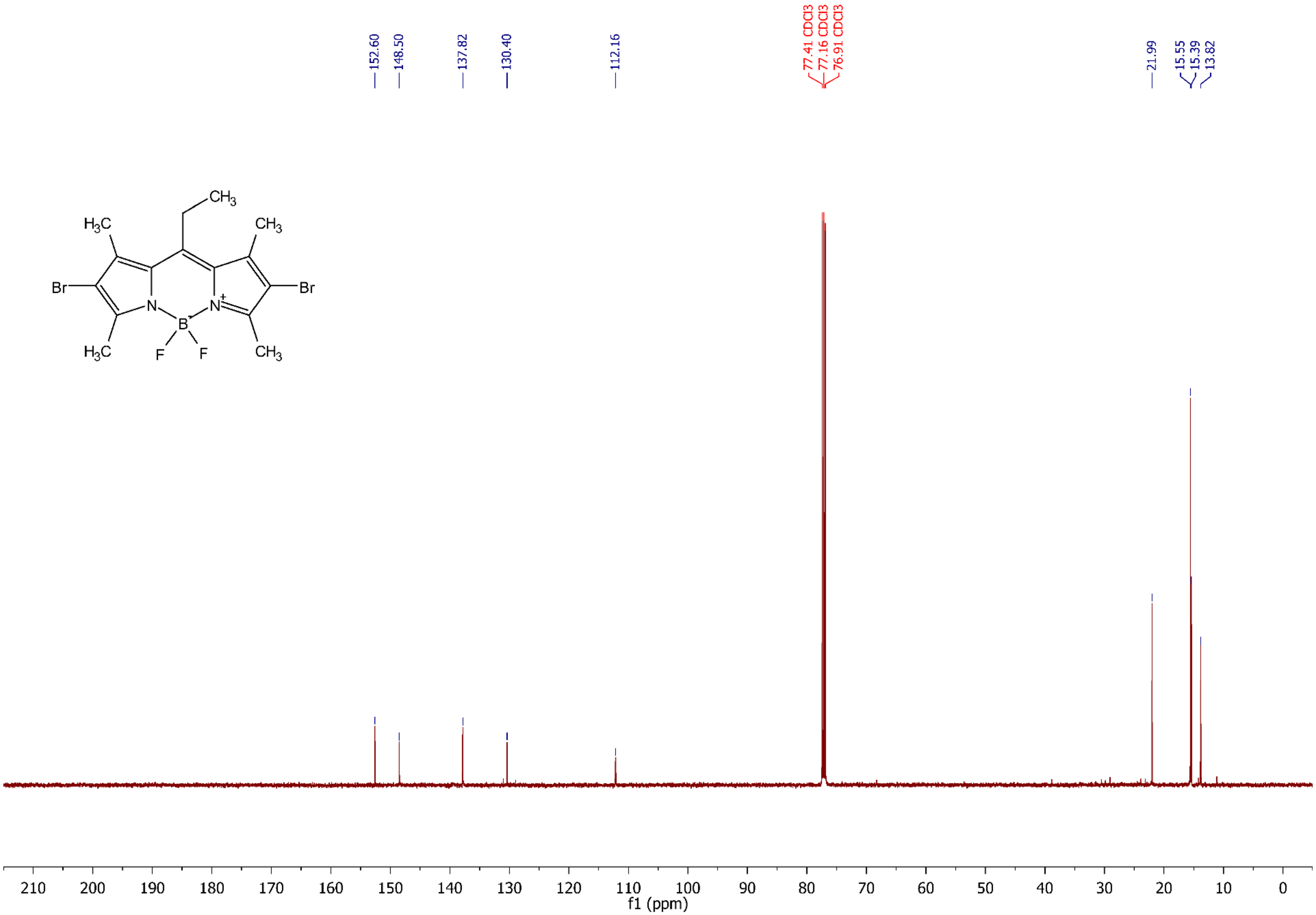


Figure S3. (A) Emission spectra of 1 µM solutions of **BromoAcroB** (blue triangles) and **Br$_2$BEt** (red circles) in acetonitrile. (B) Emission spectrum of **BromoAcroB** following activation by reaction with glutathione (GSH), catalyzed by glutathione-S-transferase (GST) in phosphate buffer saline. Right panels: Corresponding time-resolved emission decays and fittings. Instrument response is shown in gray.

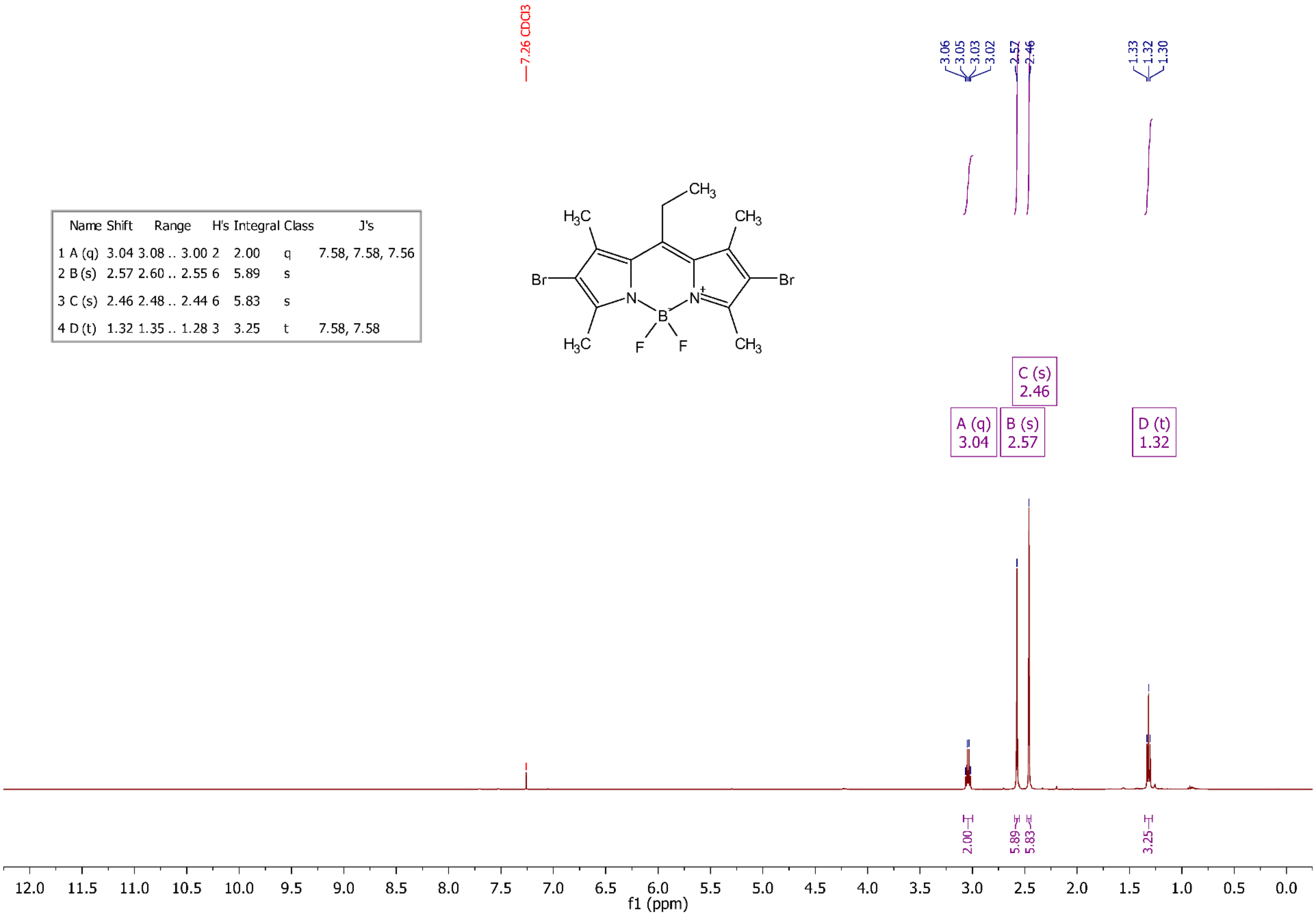


	Name	Shift	Range	H's	Integral	Class	J's
1	A (d)	9.87	9.90 .. 9.84	1	1.00	d	7.10
2	B (d)	7.64	7.67 .. 7.60	1	1.04	d	16.23
3	C (dd)	6.45	6.49 .. 6.40	1	0.99	dd	7.13, 16.23
4	D (s)	2.60	2.62 .. 2.58	6	5.93	s	
5	E (s)	2.16	2.18 .. 2.13	6	6.04	s	


191.22
155.34
144.65
139.32
138.05
135.44
128.72
112.58
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
53.57 DCM
16.47
14.03
O
H3C
CH3
Br
Br
N
N+
B-
F
F
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


152.60
148.50
137.82
130.40
112.16
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.99
15.55
15.39
13.82
CH3
H3C
CH3
Br
Br
N
N+
B-
F
F
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

	Name	Shift	Range	H's	Integral	Class	J's
1	A (q)	3.04	3.08 .. 3.00	2	2.00	q	7.58, 7.58, 7.56
2	B (s)	2.57	2.60 .. 2.55	6	5.89	s	
3	C (s)	2.46	2.48 .. 2.44	6	5.83	s	
4	D (t)	1.32	1.35 .. 1.28	3	3.25	t	7.58, 7.58



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