Fluorescent Dyes |Hot Paper|

# Evaluation of Anisole-Substituted Boron Difluoride Formazanate Complexes for Fluorescence Cell Imaging

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**Abstract:** Evaluation of three subclasses of boron difluoride formazanate complexes bearing *o*-, *m*-, and *p*-anisole *N*-aryl substituents (Ar) as readily accessible alternatives to boron dipyrromethene (BODIPY) dyes for cell imaging applications is described. While the wavelengths of maximum absorption  $(\lambda_{max})$  and emission  $(\lambda_{em})$  observed for each subclass of complexes, which differed by their carbon-bound substituents (R), were similar, the emission quantum yields for **7a**-**c** (R = cyano) were enhanced relative to **8a**-**c** (R=nitro) and **9ac** (R=phenyl). Complexes **7a**-**c** and **8a**-**c** were also significantly easier to reduce electrochemically to their radical anion and dianion forms compared to **9a**-**c**. Within each subclass, the *o*-substituted derivatives were more difficult to

# Introduction

Boron difluoride (BF<sub>2</sub>) chelates of N-donor ligands are among the most widely studied classes of molecular materials due to their unique, tunable, and potentially useful absorption, emission, and electrochemical properties.<sup>[1,2]</sup> These compounds, including the ubiquitous boron dipyrromethanes (BODIPYs) **1**,<sup>[3]</sup> have shown utility as sensors,<sup>[4,5]</sup> as efficient electrochemiluminescence luminophores,<sup>[6,7]</sup> as the functional component of organic electronics,<sup>[8]</sup> in photodynamic therapy,<sup>[9,10]</sup> and perhaps, most commonly, as fluorescence cell imaging agents.<sup>[11,12]</sup> Despite their widespread use in a broad range of applications,

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201502821. reduce, had shorter  $\lambda_{max}$  and  $\lambda_{em}$ , and lower emission quantum yields than the *p*-substituted analogues as a result of sterically driven twisting of the *N*-aryl substituents and a decrease in the degree of  $\pi$ -conjugation. The *m*-substituted complexes were the least difficult to reduce and possessed intermediate  $\lambda_{max}$ ,  $\lambda_{em}$ , and quantum yields. The complexes studied also exhibited large Stokes shifts (82–152 nm, 2143–5483 cm<sup>-1</sup>). Finally, the utility of complex **7 c** (Ar = *p*-anisole, R = cyano), which can be prepared for just a few dollars per gram, for fluorescence cell imaging was demonstrated. The use of **7 c** and 4',6-diamino-2-phenylindole (DAPI) allowed for simultaneous imaging of the cytoplasm and nucleus of mouse fibroblast cells.

further development of the chemistry of many BF<sub>2</sub> complexes has often been limited by their challenging syntheses and/or substantial cost. For example, a few milligrams of commercially available BODIPYs for cell imaging applications will often cost several hundred US dollars. Considering these factors, there remains a significant need for readily accessible molecular materials with similar or improved properties compared to BODIPYs that may be prepared by relatively simple, low-cost synthetic pathways.

BF<sub>2</sub> formazanate complexes meet these criteria and offer the ability to tune spectroscopic and electrochemical properties through structural variation.<sup>[13]</sup> The parent formazans **2**,<sup>[14]</sup> known primarily for their use in cell viability assays,<sup>[15]</sup> are typically prepared using aryl diazonium coupling reactions in aqueous media. They exist in three different conformations (i.e., "closed", "open", or "linear") depending on the carbonbound substituent (R) present.<sup>[14a,16]</sup> In recent years, the coordination chemistry of formazanate ligands **3** has received significant attention due to the rich spectroscopic and redox properties exhibited by the resulting complexes.<sup>[17,18]</sup> However, their utility in practical applications such as cell imaging has not been demonstrated.

Herein, taking inspiration from the biocompatibility of formazans, we present a study designed to evaluate a series of anisole-substituted  $BF_2$  formazanate complexes (Ar = o-anisole, *m*-anisole, *p*-anisole; R = cyano, nitro, phenyl) in an effort to showcase their utility as fluorescence cell imaging agents.

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Table 1.         Substituents           mazanate complexes	for formazans <b>4a–d</b> , <b>5a–c</b> , and <b>6</b> <b>7a–d</b> , <b>8a–c</b> , and <b>9a–c</b> .	<b>5a–c</b> and $BF_2$ for-	
Compound	Ar	R	
4a/7a	o-anisole	cyano	
4 b/7 b	<i>m</i> -anisole	cyano	
4 c/7 c	<i>p</i> -anisole	cyano	
4 d/7 d	o-ethylbenzene	cyano	
5 a/8 a	<i>o</i> -anisole	nitro	
5 b/8 b	<i>m</i> -anisole	nitro	
5 c/8 c	<i>p</i> -anisole	nitro	
6a/9a	o-anisole	phenyl	
6 b/9 b	<i>m</i> -anisole	phenyl	
6c/9c	<i>p</i> -anisole	phenyl	

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## **Results and Discussion**

#### Synthesis

Anisole-substituted formazans 4a-c, 5a-c, and 6a-c were prepared by adapting established procedures for the coupling of aryl diazonium salts and activated methylenes such as cyanoacetic acid, nitromethane, and phenylpyruvic acid in yields ranging from 18–90%.<sup>[16, 19]</sup> It is worth noting that the variability in reaction yields relates mainly to the unpredictable stability of the aryl diazonium salts involved.<sup>[20]</sup> 3-Cyanoformazans 4b-d exist primarily in the "open" conformation in solution due to the presence of a linear carbon-bound cyano substituent and were identified by their characteristic orange color (wavelength of maximum absorption ( $\lambda_{max}$ ): 419–453 nm) and the chemical shift of the <sup>1</sup>H NMR resonance originating from their NH protons ( $\delta = 11.75 - 12.89$  ppm). All other formazans produced during this study exist in the more common "closed" conformation in solution and exhibit characteristic NH resonances in their <sup>1</sup>H NMR spectra between 13.91 and 15.56 ppm and  $\lambda_{max}$  values between 448 and 530 nm in their UV/Vis absorption spectra.

 $BF_2$  formazanate complexes **7 a–d**, **8 a–c**, and **9 a–c** were prepared by heating the appropriate formazan in toluene with an excess of triethylamine and boron trifluoride diethyl etherate (Scheme 1, Table 1, Figure S1–S36, Supporting Information). The isolated yields for the complexes ranged from 15–91%



Scheme 1. General synthetic approach for the synthesis of BF<sub>2</sub> formazanate complexes **7 b**-**d** (a) and BF<sub>2</sub> formazanate complexes **7 a**, **8 a**-**c**, and **9 a**-**c** (b). See Table 1 for a detailed list of substituents.

and were highly dependent on the purification methods employed. All new BF<sub>2</sub> formazanate complexes were fully characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy, UV/Vis absorption and emission spectroscopy, IR spectroscopy, and HRMS. The formation of the BF<sub>2</sub> complexes was accompanied by the disappearance of the NH resonance in their <sup>1</sup>H NMR spectra, and the appearance of a 1:2:1 triplet and a 1:1:1:1 quartet in their <sup>11</sup>B and <sup>19</sup>F NMR spectra, respectively. With the exception of **7a** (Ar = o-anisole, R = cyano), the BF<sub>2</sub> complexes were stable towards hydrolysis. In the presence of 10 equivalents of water, complex 7a slowly hydrolyzed to re-form the parent formazan 4a (4% degradation after 48 h, 8% degradation after 96 h). By comparison, complex 7d (Ar = o-ethylbenzene, R = cyano) was indefinitely stable towards hydrolysis under the same conditions. Based on this comparison, we conclude that the hydrolysis of 7a is not driven by steric interactions alone, but rather that the lone pairs on oxygen likely play an important role in the decomposition pathway. Furthermore, the presence of the linear carbon-bound cyano substituent in 7 a may facilitate its decomposition as it potentially allows for "open" and "linear" ligand arrangements to be accessed. Similar ligand orientations are less likely for reaction intermediates derived from complexes 8a and 9a, which possess nonlinear nitro and phenyl carbon-bound substituents.

#### X-ray crystallography

Single crystals of complexes **7a** and **7b** suitable for X-ray diffraction studies were grown by slow evaporation of saturated dichloromethane solutions in a sealed vessel containing hexanes. In the solid-state **7a** and **7b** exist in "dragonfly" conformations with the nitrogen–nitrogen and carbon–nitrogen bond lengths of the formazanate ligand backbone falling between those typically associated with single and double bonds of the same atoms (Figure 1, Table 2).<sup>[21]</sup> The *N*-aryl substituents are bent out of plane relative to the N<sub>4</sub> backbone of the formazanate ligands by an average torsion angle of 61.2 and 47.7° for **7a** and **7b**, respectively. The boron atoms reside 0.54 and 0.50 Å out of the N<sub>4</sub> plane in the structures of **7a** and **7b**.

These values are substantially larger than the torsion angles of 18.3 and 37.1° and boron displacements of 0.13 and 0.34 Å observed for the two crystallographically independent forms of



**Figure 1.** Solid-state structures of complexes **7 a** (a) and **7 b** (b). Anisotropic displacement ellipsoids are shown at 50% probability and hydrogen atoms have been omitted for clarity.

	7 a	7 b	7	<b>c</b> <sup>[a]</sup>
N1-N2	1.3040(16)	1.2987(6)	1.307(2)	1.2987(6)
N3-N4	1.3038(16)	-	1.304(2)	_
C1-N2	1.3404(19)	1.3443(5)	1.340(3)	1.3443(5)
C1–N4	1.3438(18)	-	1.335(3)	_
N1-N2-C1	116.09(11)	116.42(4)	116.75(18)	116.42(4)
N1-B1-N3	101.99(10)	-	106.85(17)	-
N1-B1-N1′	-	102.63(5)	-	102.63(5)
N2-C1-N4	126.85(12)	-	130.0(2)	_
N2'-C1-N2	-	127.22(6)	-	127.22(6)
boron displacement <sup>[b]</sup>	0.54	0.50	0.13	0.50
dihedral angles <sup>[c]</sup>	62.0, 60.5	47.7, 47.7	15.3, 21.4	47.7, 47.7

**7**c.<sup>[13b]</sup> Initially, we were tempted to rationalize these trends through steric arguments, whereby interactions between the *o*-, and to a lesser extent, *m*-methoxy groups and the fluorine atoms may lead to twisting of the *N*-aryl substituents relative to the formazanate backbone. While this interpretation appears to hold true for **7a** (Ar=*o*-anisole, R=cyano), the large torsion angles observed for **7b** (Ar=*m*-anisole, R=cyano) likely arise due to crystal packing effects including slipped  $\pi$ -stacking interactions (Figure S37, Supporting Information). This conclusion is further corroborated by the fact that the methoxy substituents are *anti* to the BF<sub>2</sub> moiety in the solid-state structure of **7b**.

#### **Cyclic voltammetry**

The electrochemical properties of  $BF_2$  complexes **7** a–c were studied using cyclic voltammetry (Figure 2 and Figure S38, Supporting Information, Table 3). Each complex underwent two reversible one-electron reductions to form the corresponding ligand-centered radical anion and dianion (Scheme 2),



**Figure 2.** Cyclic voltammograms for BF<sub>2</sub> formazanate complexes **7a** (Ar = *o*-anisole, R=cyano), **7b** (Ar=*m*-anisole, R=cyano), and **7c** (Ar=*p*-anisole, R=cyano) recorded in dry, degassed acetonitrile containing ~1 mm analyte and 0.1 m  $nBu_aNPF_6$  at a scan rate of 100 mV s<sup>-1</sup>



Scheme 2. Electrochemical reduction of  $BF_2$  formazanate complexes 7a, 7b, and 7c (Ar = *o*-anisole, *m*-anisole, or *p*-anisole).

while **7c** was the only complex in the series that was oxidized (irreversibly) within the electrochemical window offered by acetonitrile.

We have previously shown that electron-donating N-aryl substituents render BF<sub>2</sub> formazanate complexes more difficult to reduce than the phenyl-substituted analogues, and that the opposite is true for complexes bearing electron-withdrawing substituents.  $^{\left[ 13b,c\right] }$  In the present study, the interpretation is slightly more complex as both steric and electronic effects must be considered. Complexes 7a and 7c possess anisole substituents with o- and p-substitution patterns, which potentially allow for resonance donation of oxygen lone pairs leading to extended  $\pi$ -conjugation of the formazanate framework. The *m*-substituted complex **7b** is not resonance delocalized, and should therefore possess properties purely associated with the inductive electron-withdrawing character of the methoxy group. Indeed, 7b is the easiest complex to reduce within the series ( $E_{\text{red 1}}^{\circ} = -0.50 \text{ V}$ ;  $E_{\text{red 2}}^{\circ} = -1.62 \text{ V}$  vs. ferrocene/ferrocenium). The o-substituted complex 7a was observed to be more difficult to reduce ( $E_{red 1}^{\circ} = -0.73$  V;  $E_{red 2}^{\circ} = -1.88$  V) than the p-



$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Table 3. Solution characterization data for BF2 complexes 7 a-d, 8a-c, and 9a-c.									
R=cyano         7a (Ar=o-anisole)         THF         456         10100         590         0.03         134         4981           CH <sub>2</sub> (J,         466         15500         589         0.04         123         4481         -0.73         -1.88           Tb (ar=m-anisole)         THF         510         20000         639         0.01         129         9358           CH <sub>2</sub> (J,         517         18500         637         0.03         120         3644         -0.50         -1.82           CH <sub>2</sub> (J,         517         18500         637         0.03         120         3644         -0.50         -1.82           CH <sub>2</sub> (J,         517         18500         637         0.03         133         100         300         -1.82           CH <sub>2</sub> (J,         558         35300         661         0.65         103         2793         -0.68         -1.82           CH <sub>4</sub> (A)         558         35300         662         0.02         129         5236         -1.83           ThF         433         14300         562         0.02         133         5468         -0.71         -1.83           ThF         436         14000         562 <td></td> <td>Solvent</td> <td><math>\lambda_{\max}</math> [nm]</td> <td><math>\varepsilon \ [\mathrm{M}^{-1} \ \mathrm{cm}^{-1}]</math></td> <td><math>\lambda_{ m em}</math> [nm]</td> <td><math>\Phi_{\rm f}^{\rm [\dot{a}]}</math></td> <td><math>v_{\rm ST}</math> [nm]</td> <td><math>v_{\rm ST}~[{\rm cm^{-1}}]</math></td> <td>E<sup>°</sup><sub>red 1</sub><sup>(b)</sup> [V]</td> <td><i>E</i><sup>°</sup><sub>red 2</sub><sup>[b]</sup> [V]</td>		Solvent	$\lambda_{\max}$ [nm]	$\varepsilon \ [\mathrm{M}^{-1} \ \mathrm{cm}^{-1}]$	$\lambda_{ m em}$ [nm]	$\Phi_{\rm f}^{\rm [\dot{a}]}$	$v_{\rm ST}$ [nm]	$v_{\rm ST}~[{\rm cm^{-1}}]$	E <sup>°</sup> <sub>red 1</sub> <sup>(b)</sup> [V]	<i>E</i> <sup>°</sup> <sub>red 2</sub> <sup>[b]</sup> [V]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	R = cyano									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 a (Ar = o-anisole)	THF	456	10100	590	0.03	134	4981		
toluene         467         16000         592         0.05         125         4521           7 b (Ar = m-anisole)         THF         510         20000         639         0.01         129         3958           CH <sub>2</sub> (2)         517         18500         637         0.03         120         3644         -0.50         -1.62           Toluene         525         21100         635         0.13         110         3300         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         1.62         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         1.62         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         - <td></td> <td>CH<sub>2</sub>Cl<sub>2</sub></td> <td>466</td> <td>15500</td> <td>589</td> <td>0.04</td> <td>123</td> <td>4481</td> <td>-0.73</td> <td>-1.88</td>		CH <sub>2</sub> Cl <sub>2</sub>	466	15500	589	0.04	123	4481	-0.73	-1.88
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		toluene	467	16000	592	0.05	125	4521		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<b>7 b</b> (Ar = <i>m</i> -anisole)	THF	510	20 000	639	0.01	129	3958		
f cluene         525         21100         635         0.13         110         3300           7 cl <sup>13b</sup> (Ar=p-anisole)         THF         556         33 400         662         0.46         106         280           7 d (Ar=o-ethylbenzene)         THF         556         33 400         662         0.67         84         2239           7 d (Ar=o-ethylbenzene)         THF         433         12000         562         0.01         129         5301           6 (Ar=0-ethylbenzene)         THF         433         12000         562         0.02         131         5408         -0.66         -1.82           6 (Ar=o-anisole)         THF         456         5900         608         0.03         152         5483           8 (Ar=o-anisole)         THF         456         5900         608         0.03         152         5483           8 (Ar=m-anisole)         THF         512         17700         656         <0.01         144         4287           8 (Ar=m-anisole)         THF         512         17700         656         <0.01         140         4209         -0.43         -1.14           8 (Ar=m-anisole)         THF         512         2770		$CH_2CI_2$	517	18500	637	0.03	120	3644	-0.50	-1.62
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		toluene	525	21100	635	0.13	110	3300		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$7 c^{[13b]}$ (Ar = p-anisole)	THF	556	33 400	662	0.46	106	2880		
folgene         572         42700         656         0.77         84         2239           7d (Ar=o-ethylbenzene)         THF         433         12000         562         0.01         129         5301           (H2,Cl2         431         14300         562         0.02         131         5408         -0.66         -1.86           R=nitro         333         4768         -0.61         -1.86         -0.61         -1.86           R=nitro         THF         456         5900         608         0.03         152         5483           R=nitro		CH <sub>2</sub> Cl <sub>2</sub>	558	35 300	661	0.65	103	2793	-0.68	-1.82
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		toluene	572	42700	656	0.77	84	2239		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<b>7 d</b> (Ar <i>=o</i> -ethylbenzene)	THF	433	12000	562	0.01	129	5301		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-	CH,Cl,	431	14300	562	0.02	131	5408	-0.66	-1.86
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		toluene	436	14000	565	0.02	129	5236		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	R = nitro									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8 a (Ar = o-anisole)	THF	456	5900	608	0.03	152	5483		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$CH_2CI_2$	466	7100	599	0.03	133	4768	-0.71	-1.83
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		toluene	468	7500	603	0.05	135	4784		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	8 b (Ar = <i>m</i> -anisole)	THF	512	17700	656	< 0.01	144	4287		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$CH_2CI_2$	511	18300	651	< 0.01	140	4209	-0.43	-1.54
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		toluene	533	18400	644	0.04	111	3234		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<b>8 c</b> (Ar = <i>p</i> -anisole)	THF	559	26700	667	0.17	108	2897		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	-	CH <sub>2</sub> Cl <sub>2</sub>	564	20100	665	0.24	101	2693	-0.60	-1.72
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		toluene	572	23600	661	0.33	82	2143		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	R = phenyl									
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9a (Ar = o-anisole)	THF	459	18900	592	< 0.01	133	4895		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		$CH_2CI_2$	464	21 600	588	0.01	124	4545	-1.09	-1.97
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		toluene	467	18800	596	< 0.01	129	4635		
CH <sub>2</sub> Cl <sub>2</sub> 521         25000         644         0.025         123         3666         -0.81         -1.87           toluene         530         22900         644         0.012         114         3340         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -	<b>9 b</b> (Ar = <i>m</i> -anisole)	THF	520	25000	643	< 0.01	123	3679		
toluene         530         22 900         644         0.012         114         3340           9 c (Ar=p-anisole)         THF         548         23 400         672         0.019         124         3367           C H <sub>2</sub> Cl <sub>2</sub> 545         29 300         670         0.063         125         3423         -0.94         -1.93		CH <sub>2</sub> Cl <sub>2</sub>	521	25000	644	0.025	123	3666	-0.81	-1.87
9 c (Ar = p-anisole)         THF         548         23 400         672         0.019         124         3367           CH <sub>2</sub> Cl <sub>2</sub> 545         29 300         670         0.063         125         3423         -0.94         -1.93		toluene	530	22900	644	0.012	114	3340		
CH <sub>2</sub> Cl <sub>2</sub> 545 29300 670 0.063 125 3423 -0.94 -1.93	<b>9</b> c (Ar = <i>p</i> -anisole)	THF	548	23 400	672	0.019	124	3367		
	-	CH <sub>2</sub> Cl <sub>2</sub>	545	29300	670	0.063	125	3423	-0.94	-1.93
toluene 551 25500 672 0.028 121 3268		toluene	551	25 500	672	0.028	121	3268		

[a] Quantum yields were determined according to a published protocol<sup>[22a]</sup> using ruthenium tris(bipyridine) hexafluorophosphate as a relative standard<sup>[22b]</sup> and corrected for wavelength-dependent detector sensitivity (Figure S41, Supporting Information). [b] Cyclic voltammograms were recorded in dry, degassed acetonitrile containing ~1 mm analyte and 0.1 m  $nBu_4NPF_6$  at a scan rate of 100 mV s<sup>-1</sup> and internally referenced relative to the ferrocene/ferrocenium redox couple.

substituted complex 7 c ( $E_{red 1}^{\circ} = -0.68$  V;  $E_{red 2}^{\circ} = -1.82$  V). We attribute this behavior to twisting of the o-anisole substituents relative to the formazanate backbone in 7a in solution. This twisting, which is consistent with the solid-state structure described above, limits the degree of  $\pi$  conjugation of the formazanate framework. The reduced degree of  $\pi$ -conjugation results in destabilization of the LUMO, and, in turn, renders 7 a more difficult to reduce than the  $\pi$ -conjugated complex **7**c. This argument is supported by DFT studies that showed the LUMO orbital of closely related complexes to include both the formazanate backbone and *N*-aryl substituents.<sup>[13b,d]</sup> To confirm that the effect of the substituent pattern on the electrochemical properties of anisole-substituted BF2 formazanate complexes was general, cyclic voltammograms were also collected for 8a-c (R=nitro) and 9a-c (R=phenyl) (Figure S39 and S40, Supporting Information, Table 3). Nitro-substituted complexes 8a-c were slightly easier to reduce than the corresponding cyano-substituted complexes due to the strong electron-withdrawing nature of the nitro group, while phenyl-substituted complexes 9a-c were much more difficult to reduce due to the absence of a strongly electron-withdrawing carbon-bound substituent on the formazanate backbone. For each series, the *m*-substituted complexes were the easiest to reduce and the *o*-substituted complexes were more difficult to reduce than the *p*-analogues, confirming that the trend discussed above is general.

#### UV/Vis absorption and emission spectroscopy

The UV/Vis absorption and emission spectra for BF<sub>2</sub> complexes **7 a–c** (R = cyano) are shown in Figure 3 and the data summarized in Table 3. Each of the complexes is strongly absorbing within the visible region of the electromagnetic spectrum with wavelengths of maximum absorption ( $\lambda_{max}$ ) ranging from 467 to 572 nm and molar extinction coefficients ( $\varepsilon$ ) ranging from 16000 to 42700 m<sup>-1</sup> cm<sup>-1</sup> in toluene. The low-energy absorption maxima for a similar set of complexes was shown by time-dependent DFT to involve primarily the HOMO–LUMO transition.<sup>[13d]</sup> The same series of compounds exhibited wavelengths of maximum emission ( $\lambda_{em}$ ) ranging from 592 to 656 nm and



**Figure 3.** UV/Vis absorption spectra (a) and emission spectra (b) for BF<sub>2</sub> formazanate complexes **7a** (Ar=*o*-anisole, R=cyano), **7b** (Ar=*m*-anisole, R=cyano), and **7c** (Ar=*p*-anisole, R=cyano) recorded for degassed 10  $\mu$ m toluene solutions.

quantum yields ( $\Phi_{\rm f}$ ) ranging from 0.05 to 0.77. As a result of the twisted conformation adopted by the N-aryl substituents, and the reduced degree of  $\pi$ -conjugation that results, the *o*substituted complex **7a** had the lowest values of  $\lambda_{max}$ (467 nm),  $\varepsilon$  (16000  $\mu^{-1}$  cm<sup>-1</sup>),  $\lambda_{\rm em}$  (592 nm), and  $\Phi_{\rm f}$  (0.05). Conversely, p-substituted complex 7c possessed properties consistent with extended  $\pi$ -conjugation arising from the relatively coplanar orientation of the N-aryl substituents and the formazanate backbone ( $\lambda_{max}$  = 572 nm;  $\varepsilon$  = 42 700  $M^{-1}$  cm<sup>-1</sup>;  $\lambda_{em}$  = 656 nm; and  $\Phi_{\rm f}$  = 0.77). The spectroscopic characteristics of the *m*-substituted analogue **7b** fall between those observed for 7a and 7c and are dictated by the presence of the inductively electron-withdrawing methoxy group ( $\lambda_{max} = 525 \text{ nm}$ ;  $\varepsilon =$ 21100  $M^{-1}$  cm<sup>-1</sup>;  $\lambda_{em} = 635$  nm; and  $\Phi_f = 0.13$ ). Complex **7 d**, which has o-ethylbenzene N-aryl substituents, has  $\lambda_{max} =$ 436 nm and  $\varepsilon = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ , confirming that the twisted structure postulated for 7 a is not unique to anisole-substituted compounds, and is driven by steric interactions (Figure S42, Supporting Information). The spectroscopic properties observed for complexes 8a-c (R=nitro) and 9a-c (R=phenyl) were closely related to those of 7 a-c, further demonstrating the generality of the trend observed (Figures S43 and S44, Supporting Information). However, it must be noted that the emission quantum yields calculated for 8a-c and 9a-c, were lower than those calculated for 7a-c. In particular, 9a-c are weakly emissive, likely as a result of nonradiative decay pathways associated with the carbon-bound phenyl substituent. Each of the anisole-substituted BF<sub>2</sub> complexes reported in this study exhibited large Stokes shifts ( $v_{ST}$ ) ranging from 82 to 152 nm (2143–5483 cm<sup>-1</sup>). This key characteristic of BF<sub>2</sub> formazanate complexes is of significant importance to their potential use as fluorescence cell imaging agents, in which photon reabsorption greatly limits emission intensity.

#### Cell imaging

Based on our evaluation of the anisole-substituted  $BF_2$  formazanate complexes described above, we concluded that complex **7c**, which can be prepared in two straightforward synthetic steps involving minimal bench time for just a few dollars per gram, was an excellent candidate for fluorescence cellimaging studies. To this end, the uptake of complex **7c** into fibroblast cells was investigated (Figure 4).



**Figure 4.** Confocal fluorescence micrographs of mouse fibroblast cells stained with  $BF_2$  formazanate complex **7 c** and DAPI. Images (a) and (b) were visualized with excitation at 559 nm and emission collected between 625–725 nm. Images (c) and (d) are an overlay of images (a) and (b) with those obtained from excitation at 405 nm and emission collected between 425–475 nm.

Mouse fibroblast cells were incubated with **7 c** for one hour, and after washing and fixing, were imaged by confocal fluorescence microscopy. The fluorescence images demonstrated that **7 c** was internalized by the fibroblast cells (Figure 4a, b). As a result of the low-energy ( $\lambda_{em} \sim 660$  nm) emission of **7 c**, this dye proved to be well suited for orthogonal imaging applications. We explored this potential by co-staining cells with the nuclear dye 4',6-diamidino-2-phenylindole (DAPI), and demonstrated that **7 c** and DAPI could be used to image the cell cytoplasm and nucleus simultaneously (Figure 4c, d). During the course of these studies, we frequently observed punctate



staining, which could be due to the dye being localized in either the endoplasmic reticulum and/or vesicles. Aggregation of the dye could be another possible explanation for the punctate appearance. However, we were able to rule out aggregation induced emission enhancement by adding water to THF solutions of **7 c**, and demonstrating that emission intensity decreases as the volume fraction of water is increased and aggregates begin to form (Figure S45, Supporting Information). We therefore conclude that the punctate staining is due to high local concentration of **7 c** rather than aggregation.

### Conclusion

We have systematically evaluated a library of o-, m-, and p-anisole-substituted BF<sub>2</sub> formazanate complexes, and, for the first time, demonstrated their potential as readily accessible fluorescence imaging agents. The substitution pattern for each subset of complexes (R = cyano, nitro, and phenyl) was shown to have a dramatic effect on their electrochemical and spectroscopic properties. In each case, the o-substituted complexes were the most difficult to reduce electrochemically, had the shortest  $\lambda_{max}$  and  $\lambda_{em}$ , and possessed low emission quantum yields due to limited  $\pi$ -conjugation of the formazanate framework. By comparison, the *p*-substituted analogues were slightly easier to reduce electrochemically, had dramatically redshifted  $\lambda_{\max}$  and  $\lambda_{em}$ , and significantly enhanced emission quantum yields (up to 0.77). Each of these traits were consistent with extended  $\pi$ -conjugation between the formazanate backbone and the N-aryl substituents. The spectroscopic properties of the msubstituted complexes, which were the easiest to reduce, were intermediate between those of the o- and p- complexes, due to the absence of resonance delocalization of the oxygen lone pairs and the inductive electron-withdrawing nature of the methoxy groups. Based on our evaluation, we were able to identify complex **7c** (Ar = p-anisole, R = cyano) as a strong candidate for use in fluorescence cell imaging applications. We subsequently demonstrated its efficacy as a fluorescent dye for orthogonal imaging of the cytoplasm (complex 7 c) and nucleus (DAPI) of mouse fibroblast cells. Our future work in this area will expand on these results and focus on cell imaging applications involving disease-targeting BF<sub>2</sub> formazanate dyes.

# **Experimental Section**

#### **General considerations**

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagents were purchased from Sigma–Aldrich or Alfa Aesar and used as received. Solvents were purchased from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under an inert (nitrogen) atmosphere containing 4 Å molecular sieves. The synthesis and characterization of compounds **4c** and **7c** have been reported previously.<sup>[13b]</sup> NMR spectra were recorded on 400 MHz (<sup>1</sup>H: 399.8 MHz, <sup>11</sup>B: 128.3 MHz, <sup>19</sup>F: 376.1 MHz) or 600 MHz (<sup>1</sup>H: 599.5 MHz, <sup>13</sup>C: 150.8 MHz) Varian INOVA spectrometers. <sup>1</sup>H NMR spectra were referenced to residual CHCl<sub>3</sub> ( $\delta$ =7.27 ppm) or (CD<sub>3</sub>)(CD<sub>2</sub>H)SO ( $\delta$ =

2.50 ppm) and <sup>13</sup>C NMR spectra were referenced to  $CDCI_3$  ( $\delta =$ 77.0 ppm) or [D<sub>6</sub>]DMSO ( $\delta$  = 39.5 ppm). <sup>11</sup>B spectra were referenced to  $BF_3 \cdot OEt_2$  at  $\delta = 0.00$  ppm, and  ${}^{19}F$  spectra were referenced to CFCl<sub>3</sub> at  $\delta$ 0.00 ppm. MS data were recorded in positive-ion mode using a high-resolution Finnigan MAT 8200 spectrometer using electron impact ionization. UV/Vis spectra were recorded using a Cary 300 Scan instrument. Molar extinction coefficients were determined from the slope of a plot of absorbance against concentration using four solutions with known concentrations ranging between 10 and 100 µм. IR spectra were recorded on a KBr disk using a Bruker Vector 33 FTIR spectrometer. Emission spectra were obtained using a Photon Technology International QM-4 SE spectrofluorometer. Excitation wavelengths were chosen based on absorption maxima from the respective UV/Vis spectrum in the same solvent. Quantum yields were calculated relative to ruthenium tris(bipyridine) hexafluorophosphate by methods described by Fery-Forgues and co-workers.<sup>[22]</sup>

#### **Electrochemical methods**

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a silver pseudo reference electrode, glassy carbon working electrode, and platinum counter electrode. Experiments were run at 100 mV s<sup>-1</sup> scan rate in degassed acetonitrile solutions of the analyte (~1 mM) and electrolyte (0.1 M tetrabutylammonium hexafluorophosphate). Cyclic voltammograms were referenced relative to the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.

#### X-ray crystallography methods

Single crystals of **7a** and **7b** were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. X-ray diffraction measurements for **7a** were made on a Nonius KappaCCD Apex2 and measurements for **7b** were made using Bruker a Kappa Axis Apex2 diffractometer. Both compounds were measured at a temperature of 110 K. The data collection strategy was a number of  $\omega$  and  $\phi$  scans which collected data over a range of angles,  $2\theta$ . The frame integration was performed using SAINT.<sup>[23]</sup> The resulting raw data was scaled and absorption corrected using a multiscan averaging of symmetry equivalent data using SADABS.<sup>[24]</sup>

The structures were solved by using a dual space methodology using the SHELXT program.<sup>[25]</sup> All nonhydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the SHELXL-2014 program from the SHELXTL program package.<sup>[26]</sup> See Table 4 for crystallographic data collection and refinement details.

CCDC-1413166 and -1413167 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Cell imaging protocols

A stock solution of  $BF_2$  formazanate complex **7 c** in DMSO (10  $\mu$ M) was prepared and subsequently diluted with Dulbecco's modified Eagle's medium (DMEM) to obtain final concentrations of 0.5  $\mu$ M of

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Table 4. X-ray diffraction data collection and refinement details for 7 a and 7 b.				
	7 a	7 b		
chemical formula	$C_{16}H_{14}BF_2N_5O_2$	$C_{16}H_{14}BF_2N_5O_2$		
<i>FW</i> [g mol <sup>-1</sup> ]	357.13	357.13		
crystal dimensions	0.411×0.149×0.104	0.384×0.324×0.246		
[mm]				
crystal habit	red needle	purple prism		
crystal system	monoclinic	monoclinic		
space group	P2 <sub>1</sub> /c	C2/m		
T [K]	110	110		
a [Å]	9.784(2)	13.349(3)		
b [Å]	18.259(5)	16.206(3)		
c [Å]	10.150(2)	8.1753(19)		
α [°]	90	90		
β [°]	111.382(6)	112.872(10)		
γ [°]	90	90		
V [ų]	1688.4(7)	1629.6(6)		
Ζ	4	4		
$ ho$ [g cm $^{-3}$ ]	1.405	1.456		
λ [Å]	1.54178 (Cu <sub>Kα</sub> )	0.71073 (Mo <sub>Kα</sub> )		
$\mu$ [cm <sup>-1</sup> ]	0.938	0.114		
diffractometer type	Nonius KappaCCD	Bruker Kappa Axis		
	Apex2	Apex2		
R <sub>merge</sub>	0.0380	0.0272		
$R_1 [I > 2\sigma(I)]$	0.0305	0.0387		
$\omega R_2 [l > 2\sigma(l)]$	0.0731	0.1127		
$R_1$ (all data)	0.0376	0.0509		
$\omega R_2$ (all data)	0.0768	0.1210		
GOF	1.054	1.058		
$R_{1} = \Sigma ( F_{o}  -  F_{c} ) / \Sigma F_{o}; \qquad \omega R_{2} = [\Sigma (\omega (F_{o}^{2} - F_{c}^{2})^{2}) / \Sigma (\omega F_{o}^{4})]^{\frac{1}{2}}; \qquad GOF = [\Sigma (\omega (F_{o}^{2} - F_{c}^{2})^{2}) / (\text{no. of reflns.} - \text{no. of params.})]^{\frac{1}{2}}$				

dye. Mouse fibroblast C3H/10T1/2 cells (ATCC, Manassas, VA) were released from the tissue culture flask by trypsinization and seeded onto cover slips in a 12-well tissue culture plate at an approximate cell density of 50000 cells per well. The cells were incubated overnight in DMEM containing 10% fetal bovine serum (FBS) at 37 °C in a 5% CO<sub>2</sub> atmosphere. The serum containing DMEM in each well was removed and replaced with serum free DMEM containing a concentration of 0.5  $\mu$ M of dye and incubated at 37 °C for 1 h. The cells were then washed three times with phosphate buffer saline (PBS), fixed with 4% paraformaldehyde and mounted onto slides containing Pro-Long Antifade mounting medium with DAPI. Images were then obtained using an Olympus FluoView FV 1000 confocal microscope.

# Representative procedure for the preparation of formazans 4a, 4b, and 4d

**Formazan 4a (Ar**<sub>1</sub> = **Ar**<sub>5</sub> = *o*-anisole, **R**<sub>3</sub> = **CN**): In air, cyanoacetic acid (2.40 g, 28.2 mmol) and sodium hydroxide (11.4 g, 285 mmol) were dissolved in deionized water (140 mL). The resulting colorless solution was cooled to 0 °C and stirred for 2 h. In a separate flask, *o*-anisidine (6.92 g, 56.2 mmol) was combined with concentrated hydrochloric acid (14.0 mL, 168 mmol) in deionized water (55 mL) and stirred for 1.5 h at 0 °C. A solution of sodium nitrite (5.83 g, 84.5 mmol) in deionized water (17 mL) was cooled to 0 °C in an ice bath for 1.5 h before it was added dropwise to the *o*-anisidine solution over a 25 min period. The resulting yellow/brown diazonium salt solution was stirred for 1 h at 0 °C before it was added to the alkaline cyanoacetic acid solution. Upon addition, the solution turned blood red and a precipitate of the same color formed. The

mixture was left to warm slowly with stirring for 18 h before the solid was isolated by vacuum filtration. The filtrate was neutralized with  $1 \,\text{M}$  HCl (ca. 150 mL), extracted into dichloromethane (3  $\times$ 150 mL), washed with deionized water (3×150 mL), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated in vacuo to afford a red solid. The crude solids were combined and purified by flash column chromatography (dichloromethane, neutral alumina) and recrystallized from a saturated methanolic solution to afford formazan 4a as red needles. Yield: 6.10 g, 70%; m.p. 136-138°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta = 13.91$  (s, 1 H, NH), 7.78 (d,  ${}^{3}J_{HH} = 8$  Hz, 2 H, aryl CH), 7.34-7.31 (m, 2H, aryl CH), 7.06-7.02 (m, 4H, aryl CH), 4.00 ppm (s, 6H, OCH<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta = 152.5$ , 136.1, 130.0, 121.4, 116.5, 116.5, 116.1, 112.0, 56.1 ppm; FTIR (KBr):  $\tilde{\nu} =$  3074 (m), 3027 (m), 2970 (m), 2944 (m), 2840 (m), 2224 (s), 1584 (s), 1485 (s), 1482 (s), 1258 (s), 1024 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max} = 448 \text{ nm}$  ( $\epsilon = 19700 \text{ M}^{-1} \text{ cm}^{-1}$ ); MS (El = + ve mode): exact mass calculated for [C<sub>16</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>]<sup>+</sup>: 309.1226; exact mass found: 309.1238; difference: + 3.9 ppm.

Formazan 4b ( $Ar_1 = Ar_5 = m$ -anisole,  $R_3 = CN$ ): From 3.41 g (27.7 mmol) of m-anisidine. Yield: 0.751 g, 18% of a dark-red microcrystalline solid; m.p. 132-134°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): open isomer (major, 75%):  $\delta = 12.89$  (s, 1 H, N*H*), 7.37 (t,  ${}^{3}J_{HH} = 8$  Hz, 2 H, aryl CH), 7.22-7.21 (m, 2H, aryl CH), 7.19-7.17 (m, 2H, aryl CH), 6.92 (dd, <sup>3</sup>J<sub>HH</sub> = 8, <sup>4</sup>J<sub>HH</sub> = 3 Hz, 2 H, aryl CH), 3.89 ppm (s, 6 H, OCH<sub>3</sub>); linear isomer (minor, 25%):  $\delta = 9.14$  (s, 1H, NH), 7.53 (d,  ${}^{3}J_{HH} = 8$  Hz, 1H, aryl CH), 7.43-7.40 (m, 3H, aryl CH), 7.33-7.30 (m, 1H, aryl CH), 7.07-7.06 (m, 1 H, aryl CH), 7.02 (m, 1 H, aryl CH), 6.74-6.73 (m, 1 H, aryl CH), 3.89 (s, 3H, OCH<sub>3</sub>), 3.88 ppm (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta = 161.0$ , 160.8, 160.4, 153.2, 147.5, 142.0, 130.5, 130.3, 130.3, 129.9, 125.1, 119.2, 117.7, 115.7, 114.4, 113.0, 111.2, 108.0, 107.9, 105.6, 103.5, 100.9, 55.6 ppm (br); FTIR (KBr):  $\tilde{\nu} =$  3276 (m), 3086 (m), 3008 (m), 2960 (m), 2839 (m), 2227 (s), 1609 (s), 1535 (s), 1496 (s), 1412 (m), 1240 (s), 1150 (m), 1044 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max}$  432 nm ( $\epsilon$  = 20150 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI = +ve mode): exact mass calculated for  $[C_{16}H_{15}N_5O_2]^+$ : 309.1226; exact mass found: 309.1221; difference: -1.6 ppm.

Formazan 4d (Ar<sub>1</sub> = Ar<sub>5</sub> = o-ethylbenzene, R<sub>3</sub> = CN): From 2.96 g (24.4 mmol) of 2-ethylaniline. Yield: 0.322 g, 9% of a dark-red powder; m.p. 89-91 °C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): open isomer (major, 81%):  $\delta = 11.75$  (s, 1H, NH), 7.67–7.65 (m, 2H, aryl CH), 7.34–7.31 (m, 6H, aryl CH), 2.97 (q, <sup>3</sup>J<sub>HH</sub>=8Hz, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.35 ppm (m, 6H, CH<sub>2</sub>CH<sub>3</sub>); linear isomer (minor, 29%):  $\delta$  = 9.17 (s, 1H, NH), 7.77 (d, <sup>3</sup>J<sub>HH</sub>=8 Hz, 1H, aryl CH), 7.72 (m, 1H, aryl CH), 7.44 (m, 2H, aryl CH), 7.40 (m, 2H, aryl CH), 7.30-7.28 (m, 1H, aryl CH), 7.15 (m, 1 H, CH), 3.18 (q,  ${}^{3}J_{HH} = 8$  Hz, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 2.80 (q, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.39 ppm (m, 6 H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta = 149.3$ , 145.3, 144.2, 138.1, 137.8, 132.3, 131.9, 130.0, 129.6, 129.5, 129.1, 129.0, 127.6, 127.4, 127.2, 126.5, 124.8, 115.6, 115.5, 115.4, 113.3, 108.0, 24.7, 24.2, 23.5, 16.3, 15.0, 13.8 ppm; FTIR (KBr):  $\tilde{\nu} =$  3338 (m), 3077 (m), 2973 (m), 2936 (m), 2878 (m), 2227 (m), 1589 (m), 1529 (s), 1457 (m), 1276 (m), 1201 (m), 1157 (m), 1060 cm<sup>-1</sup> (w); UV/Vis (toluene):  $\lambda_{max}$  419 nm ( $\varepsilon$  = 25,500  $M^{-1}$  cm<sup>-1</sup>); MS (El = +ve mode): exact mass calculated for [C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>]<sup>+</sup>: 305.1640; exact mass found: 305.1639; difference: -0.3 ppm.

# Representative procedure for the preparation of formazans 5 ${\rm a}$ and 5 ${\rm b}$

**Formazan 5 a**  $(Ar_1 = Ar_5 = o\text{-anisole}, R_3 = NO_2)$ : The following procedure was adapted from a protocol developed by von Eschwege and co-workers.<sup>[19b]</sup> In air, *o*-anisidine (3.63 g, 29.5 mmol) was added to deionized water (28 mL) containing concentrated hydro-

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chloric acid (16.0 mL, 192 mmol). The mixture was cooled to  $-10\,^{\circ}$ C in an acetone/ice bath and stirred for 1 h. In a separate flask, sodium nitrite (3.22 g, 46.7 mmol) was dissolved in deionized water (9.20 mL) and cooled to  $-10^{\circ}$ C in an acetone/ice bath for 30 min. The sodium nitrite solution was added to the o-anisidine mixture dropwise over the course of 30 min. The resulting yellow/ brown diazonium salt solution was then added to a flask containing sodium acetate (28.5 g, 347 mmol), glacial acetic acid (29.0 mL), and deionized water (14 mL) and stirred at room temperature for 5 min. Nitromethane (8.98 g, 7.97 mL, 147 mmol) was then added and the solution was stirred for 1 h before deionized water (1.60 L) was added. The solution was stirred for an additional 30 min and vacuum filtered to afford a red solid. The filtrate was extracted into dichloromethane (3×250 mL), washed with deionized water (4× 200 mL), dried over MgSO<sub>4</sub>, gravity filtered and concentrated in vacuo to afford a dark-red solid. The crude solids were combined and purified by flash column chromatography (dichloromethane, neutral alumina) to afford formazan 5a as a dark-red microcrystalline solid. Yield: 4.01 g, 82%; m.p. 176-178°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta = 14.87$  (s, 1 H, NH), 7.97–7.95 (m, 2 H, aryl CH), 7.38–7.35 (m, 2H, aryl CH), 7.08-7.05 (m, 2H, aryl CH), 7.04-7.03 (m, 2H, aryl CH), 4.02 ppm (s, 6 H, OCH<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta =$ 153.0, 136.2, 130.8, 121.6, 117.0, 112.0, 56.1 ppm; FTIR (KBr):  $\tilde{\nu} =$ 3057 (m), 2990 (m), 1660 (m), 1578 (s), 1423 (m), 1267 (m), 897 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  472 nm ( $\varepsilon = 8000 \text{ M}^{-1} \text{ cm}^{-1}$ ); MS (EI = +ve mode): exact mass calculated for  $[C_{15}H_{15}N_5O_4]^+$ : 329.1124; exact mass found: 329.1121; difference: -0.9 ppm.

**Formazan 5b** (Ar<sub>1</sub>=Ar<sub>5</sub>=*m*-anisole, R<sub>3</sub>=NO<sub>2</sub>): From 2.19 g (17.8 mmol) of *m*-anisidine. Yield: 1.77 g, 60% of dark-red microcrystalline solid; m.p. 134–136 °C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): δ = 15.08 (s, 1 H, NH), 7.35 (t, <sup>3</sup>J<sub>HH</sub>=8 Hz, 2 H, aryl CH), 7.24–7.23 (m, 2H, aryl CH), 7.21–7.19 (m, 2H, aryl CH), 6.92 (dd, <sup>3</sup>J<sub>HH</sub>=8, <sup>4</sup>J<sub>HH</sub>= 2 Hz, 2 H, aryl CH), 3.85 ppm (s, 6 H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>): δ = 160.8, 147.2, 130.3, 116.4, 113.8, 103.3, 55.5 ppm; FTIR (KBr):  $\bar{\nu}$  = 3058 (m), 3018 (m), 2973 (m), 2858 (m), 1661 (m), 1610 (s) 1552 (m), 1493 (w), 1434 (w), 1360 (w), 1267 (s), 1143 (w), 1045 (w), 896 (w), 826 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max}$ =466 nm (ε = 21200 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>15</sub>H<sub>15</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 329.1124; exact mass found: 329.1118; difference: -1.8 ppm.

Preparation of Formazan 5c ( $Ar_1 = Ar_5 = p$ -anisole,  $R_3 = NO_2$ ): In air, nitromethane (1.23 g, 1.08 mL, 20.0 mmol) was combined with deionized water (150 mL), and sodium hydroxide (1.76 g, 44.0 mmol) before the mixture was cooled to 0°C in an ice bath. In a separate flask, p-anisidine (5.00 g, 41.0 mmol) and concentrated hydrochloric acid (11.1 mL, 133 mmol) were mixed with deionized water (15 mL) and cooled to  $0\,^\circ C$  in an ice bath. A cooled solution (0°C) of sodium nitrite (3.35 g, 49.0 mmol) in deionized water (10 mL) was added slowly to the amine solution. This mixture was left to stir at 0 °C for 30 min, at which time the dark-yellow diazonium salt solution was added dropwise to the nitromethane solution described above over a 10 min period. The resulting mixture was left to warm slowly with stirring for 18 h, during which time a dark-red precipitate had formed. The dark-red solid was isolated by vacuum filtration and purified by flash column chromatography (dichloromethane, neutral alumina) to afford formazan 5c as a dark-red microcrystalline solid. Yield: 6.59 g, 55%; m.p. 162-164 °C; <sup>1</sup>H NMR (599.5 MHz, [D<sub>6</sub>]DMSO):  $\delta =$  14.61 (s, 1 H, NH), 7.86 (d,  ${}^{3}J_{HH} = 8$  Hz, 4 H, aryl CH), 7.11 (d,  ${}^{3}J_{HH} = 8$  Hz, 4 H, aryl CH), 3.85 ppm (s, 6H, OCH<sub>3</sub>);  ${}^{13}C{}^{1}H{}$  NMR (150.8 MHz, [D<sub>6</sub>]DMSO):  $\delta =$ 160.5, 140.1, 121.8, 114.9, 55.7 ppm; FTIR (KBr): 3061 (m), 3018 (m), 2995 (m), 1659 (m), 1574 (w), 1428 (m), 1348 (w), 1268 (s), 1159 (w), 899 (m), 745 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  504 nm ( $\epsilon =$ 

 $18400\,\text{m}^{-1}\,\text{cm}^{-1});$  MS (EI,  $+\,\text{ve}$  mode): exact mass calculated for  $[C_{15}H_{15}N_5O_4]^+:$  329.1124; exact mass found: 329.1123; difference: -0.3 ppm.

#### Representative procedure for preparation of formazans 6a-c

Formazan 6a ( $Ar_1 = Ar_5 = o$ -anisole,  $R_3 = Ph$ ): In air, phenylpyruvic acid (1.0 g, 6.1 mmol) and sodium hydroxide (1.83 g, 45.7 mmol) were combined with deionized water (150 mL) and cooled to 0 °C in an ice bath for 30 min. In a separate flask, o-anisidine (1.50 g, 12.2 mmol) and concentrated hydrochloric acid (3.5 mL, 42 mmol) were mixed in deionized water (10 mL), and cooled to  $0\,^\circ C$  in an ice bath for 10 min. A cooled solution (0°C) of sodium nitrite (0.97 g, 14.0 mmol) in deionized water (5 mL) was added slowly to the amine solution over a 10 min period. This yellow mixture was left to stir at  $0^{\circ}$ C for 30 min, at which time it was added dropwise to the phenylpyruvic acid reaction mixture described above over a 10 min period. The resulting solution was left to warm slowly with stirring for 18 h, at which time a purple precipitate had formed. The purple solid was isolated by filtration and purified by flash column chromatography (dichloromethane, neutral alumina) to afford formazan **6a** as a purple microcrystalline solid. Yield: 1.98 g, 90%; m.p. 120–122 °C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 15.01 (s, 1 H, NH), 8.24-8.23 (m, 2 H, aryl CH), 7.98-7.97 (m, 2 H, aryl CH), 7.49-7.46 (m, 2H, aryl CH), 7.38-7.36 (m, 1H, aryl CH), 7.28-7.25 (m, 2H, aryl CH), 7.10-7.07 (m, 2H, aryl CH), 7.04-7.02 (m, 2H, aryl CH), 4.02 ppm (s, 6H, OCH<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta =$ 152.0, 142.2, 138.0, 137.9, 128.3, 128.0, 127.3, 125.8, 121.3, 115.7, 111.7, 56.0 ppm; FTIR (KBr):  $\tilde{\nu} = 3076$  (m), 3008 (m), 2915 (m), 1659 (m), 1267 (m), 1106 (s), 752 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  = 507 nm ( $\epsilon$  = 22 900 m<sup>-1</sup> cm<sup>-1</sup>); MS (El, +ve mode): exact mass calculated for [C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>: 360.1586; exact mass found: 360.1580; difference: -1.7 ppm.

Formazan 6b (Ar<sub>1</sub> = Ar<sub>5</sub> = *m*-anisole, R<sub>3</sub> = Ph): From 1.50 g (12.2 mmol) of *m*-anisidine. Yield: 1.38 g, 63% as a dark-red solid; m.p. 99–101°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 15.35 (s, 1H, NH), 8.15–8.14 (m, 2H, aryl CH), 7.48–7.46 (m, 2H, aryl CH), 7.39–7.36 (m, 3H, aryl CH), 7.31 (s, 2H, aryl CH), 7.24–7.23 (m, 2H, aryl CH), 6.87–6.85 (m, 2H, aryl CH), 3.91 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.7, 149.1, 141.0, 137.3, 130.0, 128.4, 127.6, 125.8, 113.4, 112.6, 102.9, 55.4 ppm. FTIR (KBr): 3057 (m), 2991 (m), 1660 (m), 1643 (m), 1426 (m), 1268 (s), 1103 (s), 898 (m), 745 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  = 496 nm ( $\varepsilon$  = 21600 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI, +ve mode): exact mass calculated for [C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>: 360.1586; exact mass found: 360.1584; difference: -0.6 ppm.

Formazan 6c (Ar<sub>1</sub> = Ar<sub>5</sub> = *p*-anisole, R<sub>3</sub> = Ph): From 1.48 g (12.0 mmol) of *p*-anisidine. Yield: 1.69 g, 82% as a dark-red solid; m.p. 122–124°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 15.56 (s, 1 H, NH), 8.13 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2 H, aryl CH), 7.65 (d, <sup>3</sup>*J*<sub>HH</sub> = 9 Hz, 4 H, aryl CH), 7.45–7.43 (m, 2 H, aryl CH), 7.34 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 1 H, aryl CH), 6.99 (d, <sup>3</sup>*J*<sub>HH</sub> = 9 Hz, 4 H, aryl CH), 3.88 ppm (s, 6 H, OCH<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.2, 142.0, 140.6, 137.8, 128.3, 127.2, 125.6, 120.0, 114.7, 55.6 ppm; FTIR (KBr):  $\bar{\nu}$  = 3263 (br, s), 2984 (m), 2884 (w), 2794 (s), 1594 (s), 1573 (m), 1507 (s), 1495 (s), 1226 (s), 1176 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  = 530 nm ( $\varepsilon$  = 23400 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI, +ve mode): exact mass calculated for [C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>: 360.1586; exact mass found: 360.1581; difference: -1.4 ppm.

#### Representative procedure for the preparation of formazanate $BF_2$ complexes 7 a and 7 d

Formazanate BF<sub>2</sub> complex 7 a ( $Ar_1 = Ar_5 = o$ -anisole,  $R_3 = CN$ ): Formazan 4 a (0.500 g, 1.61 mmol) was dissolved in toluene (250 mL)



before triethylamine (1.45 g, 2.00 mL, 14.2 mmol) was added and the solution stirred for 30 min. Boron trifluoride diethyl etherate (3.45 g, 3.00 mL, 24.3 mmol) was then added and the solution heated to 105 °C for 36 h. During this time, the solution gradually changed color from dark-red to red/orange. The solution was cooled to 20  $^\circ\text{C}$  and deionized water (25 mL) was added to quench any remaining reactive species. The mixture was then washed with deionized water (3 $\times$ 50 mL), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated in vacuo to afford 7 a as a red/orange solid. The crude solid was purified by flash column chromatography (dichloromethane, neutral alumina) to afford 7a as a bright-orange powder. This compound hydrolyzes slowly. Analyses were performed using dry solvents. Yield: 0.353 g, 61%; m.p. 134-136°C; <sup>1</sup>H NMR (599.5 MHz, dry CDCl<sub>3</sub>):  $\delta = 7.46 - 7.43$  (m, 2 H, aryl CH), 7.30-7.28 (m, 2H, aryl CH), 7.05-7.01 (m, 4H, aryl CH), 3.91 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta = 154.8$ , 132.5, 132.4, 127.2, 120.8, 113.8, 112.8, 56.4 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$  = -1.9 ppm (t,  ${}^{1}J_{\rm BF}$  = 20 Hz);  ${}^{19}$ F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$  = -154.3 ppm (q,  ${}^{1}J_{FB} = 19 \text{ Hz}$ ); FTIR (KBr):  $\tilde{\nu} = 3072$  (m), 3017 (m), 2960 (m), 2853 (m), 2237 (s), 1605 (s), 1488 (s), 1340 (s), 1260 (s), 1195 (s), 1164 (s), 1030 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max}$  467 nm ( $\epsilon$  = 16000  $M^{-1}$  cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>16</sub>H<sub>14</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>]<sup>+</sup>: 357.1209; exact mass found: 357.1212; difference: +0.8 ppm.

Formazanate BF<sub>2</sub> complex 7 d (Ar<sub>1</sub>=Ar<sub>5</sub>=o-ethylbenzene, R<sub>3</sub> = CN): From 0.366 g (1.20 mmol) of formazan 4d. Yield: 0.095 g, 22% of dark-orange oil; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$ =7.47-7.45 (m, 2H, aryl CH), 7.42-7.39 (m, 4H, aryl CH), 7.34-7.31 (m, 2H, aryl CH), 2.65 (q, <sup>3</sup>J<sub>HH</sub>=8 Hz, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.24 ppm (t, <sup>3</sup>J<sub>HH</sub>=7 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta$ =140.9, 139.7, 131.0, 130.5, 126.6, 126.3, 113.4, 24.3, 14.9 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$ =-1.9 (t, <sup>1</sup>J<sub>BF</sub>=24 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$ =-146.9 ppm (q, <sup>1</sup>J<sub>FB</sub>=24 Hz); FTIR (KBr):  $\tilde{\nu}$ =3077 (m), 2975 (s), 2938 (s), 2879 (m), 2247 (m), 1453 (s), 1336 (s), 1217 (s), 1084 (s), 1025 (s), 970 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max}$  436 nm ( $\varepsilon$ = 14000 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>18</sub>H<sub>18</sub>BF<sub>2</sub>N<sub>8</sub>]<sup>+</sup>: 353.1623; exact mass found: 353.1626; difference: +0.8 ppm.

#### Representative procedure for the preparation of formazanate $BF_2$ complexes 7 b, 8 b,c, and 9a-c

Formazanate  $BF_2$  complex 7 b ( $Ar_1 = Ar_5 = m$ -anisole,  $R_3 = CN$ ): Formazan 4b (0.398 g, 1.28 mmol) was dissolved in toluene (175 mL) before triethylamine (0.391 g, 0.540 mL, 3.86 mmol) was added and the solution stirred for 30 min. Boron trifluoride diethyl etherate (0.92 g, 0.80 mL, 6.5 mmol) was then added and the solution heated to 80 °C for 18 h. During this time, the solution gradually changed color from dark-red to purple. The solution was cooled to 20 °C and deionized water (15 mL) was added to quench any remaining reactive species. The mixture was then washed with deionized water (3 $\times$ 50 mL), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated in vacuo to afford 7b as a purple solid. The crude solid was purified by flash column chromatography (dichloromethane, neutral alumina) and recrystallized from a saturated methanolic solution to afford **7 b** as a purple microcrystalline solid. Yield: 0.221 g, 48%; m.p. 143–145 °C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55 (d, <sup>3</sup>J<sub>HH</sub>=9 Hz, 2 H, aryl CH), 7.42–7.40 (m, 4 H, aryl CH), 7.08 (dd,  ${}^{3}J_{HH} = 8$ ,  ${}^{4}J_{HH} = 3$  Hz, 2 H, aryl CH), 3.89 ppm (s, 6 H, OCH<sub>3</sub>);  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta\!=\!$  160.4, 144.1, 130.2, 118.2, 116.0 (t,  ${}^{4}J_{CF} = 3$  Hz), 114.0, 107.6, 55.7 ppm;  ${}^{11}B$  NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta\!=\!-0.8~{
m ppm}$  (t,  ${}^1\!J_{
m BF}\!=\!31~{
m Hz}$ );  ${}^{19}{
m F}~{
m NMR}$  (376.1 MHz,  ${
m CDCI}_3$ ):  $\delta\!=$ -132.6 ppm (q,  ${}^{1}J_{FB} = 29 \text{ Hz}$ ); FTIR (KBr):  $\tilde{\nu} = 3072$  (m), 3016 (m), 2958 (m), 2850 (m), 2237 (s), 1605 (s), 1582 (s), 1487 (s), 1456 (m), 1339 (s), 1293 (m), 1260 (s), 1195 (m), 1164 (m), 1031 cm<sup>-1</sup> (s); UV/ Vis (toluene):  $\lambda_{max}$  525 nm ( $\varepsilon$ =21100 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>16</sub>H<sub>14</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>]<sup>+</sup>: 357.1209; exact mass found: 357.1198; difference: -3.1 ppm.

Formazanate BF<sub>2</sub> complex 8b (Ar<sub>1</sub>=Ar<sub>5</sub>=*m*-anisole, R<sub>3</sub>=NO<sub>2</sub>): From 0.398 g (1.21 mmol) of formazan 5b. Yield: 0.111 g, 24% of dark-purple microcrystalline solid; m.p. 78–80°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$ =7.64–7.62 (m, 2H, aryl CH), 7.52–7.50 (m, 2H, aryl CH), 7.43 (t, <sup>3</sup>J<sub>HH</sub>=8 Hz, 2H, aryl CH), 7.09 (dd, <sup>3</sup>J<sub>HH</sub>=8, <sup>4</sup>J<sub>HH</sub>=2 Hz, 2H, aryl CH), 3.90 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta$ =160.5, 144.2, 130.3, 118.5, 116.3 (<sup>4</sup>J<sub>CF</sub>=4 Hz), 108.0, 55.7 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.7 (t, <sup>1</sup>J<sub>BF</sub>= 29 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$ =-134.6 ppm (q, <sup>1</sup>J<sub>FB</sub>= 29 Hz); FTIR (KBr):  $\tilde{\nu}$ =3076 (m), 3013 (m), 2863 (m), 1658 (m), 1580 (m), 1424 (m), 1266 (m), 1095 (s), 745 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  533 nm ( $\varepsilon$ =18400 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>15</sub>H<sub>14</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 377.1107; exact mass found: 377.1104; difference: -0.8 ppm.

Formazanate BF<sub>2</sub> complex 8 c (Ar<sub>1</sub> = Ar<sub>5</sub> = *p*-anisole, R<sub>3</sub> = NO<sub>2</sub>): From 1.19 g (3.60 mmol) of formazan 5 c. Yield: 0.291 g, 21% of dark-purple microcrystalline solid; m.p. 154–156°C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.99 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 4H, aryl CH), 7.01 (dd, <sup>3</sup>J<sub>HH</sub> = 9, <sup>4</sup>J<sub>HH</sub> = 2 Hz, 4H, aryl CH), 3.91 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.4, 137.0, 125.2, 114.9, 100.0, 55.8 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.7 ppm (t, <sup>1</sup>J<sub>BF</sub> = 30 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$  = -137.1 ppm (q, <sup>1</sup>J<sub>FB</sub> = 29 Hz); FTIR (KBr):  $\tilde{\nu}$  = 3058 (m), 3011 (m), 2993 (m), 1656 (m), 1580 (w), 1420 (m), 1340 (w), 1270 (s), 1151 (w), 900 (m), 745 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  579 nm ( $\varepsilon$  = 23600 м<sup>-1</sup> cm<sup>-1</sup>); MS (EI = + ve mode): exact mass calculated for [C<sub>15</sub>H<sub>14</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 377.1107; exact mass found: 377.1101; difference: -1.6 ppm.

Formazanate BF<sub>2</sub> complex 9a (Ar<sub>1</sub>=Ar<sub>5</sub>=o-anisole, R<sub>3</sub>=Ph): This complex required additional purification by flash column chromatography (toluene, silica gel). From 0.396 g (1.10 mmol) of formazan 6a. Yield: 0.212 g, 47% of an orange solid; m.p. 158-160°C; <sup>1</sup>H NMR (399.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.08–8.06 (m, 2 H, aryl CH), 7.46– 7.38 (m, 5H, aryl CH), 7.23-7.22 (m, 2H, aryl CH), 7.04-6.99 (m, 4H, aryl CH), 3.92 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 155.0, 151.5, 133.3, 133.1, 130.9, 129.2, 128.5, 127.3, 125.7,$ 120.6, 112.5, 56.3 ppm;  $^{11}{\rm B}$  NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta\!=\!-1.2$  ppm (t,  ${}^{1}J_{BF} = 19 \text{ Hz}$ );  ${}^{19}\text{F} \text{ NMR}$  (376.1 MHz, CDCl<sub>3</sub>):  $\delta = -160.6 \text{ ppm}$  (q,  ${}^{1}J_{FB} = 19$  Hz); FTIR (KBr):  $\tilde{\nu} = 3057$  (m), 2988 (m), 2967 (w), 2843 (m), 1666 (m), 1496 (s), 1441 (m), 1359 (m), 1268 (s), 1124 (s), 1050 (m), 897 (m), 745 cm  $^{-1}$  (m); UV/Vis (toluene):  $\lambda_{max} =$  467 nm ( $\epsilon =$ 18,800  $\text{m}^{-1}$  cm<sup>-1</sup>); MS (El, +ve mode): exact mass calculated for  $[\mathsf{C}_{21}\mathsf{H}_{19}\mathsf{BF}_2\mathsf{N}_4\mathsf{O}_2]^+$ : 408.1569; exact mass found: 408.1564; difference: -1.2 ppm.

Formazanate BF<sub>2</sub> complex 9 b (Ar<sub>1</sub>=Ar<sub>5</sub>=*m*-anisole, R<sub>3</sub>=Ph): From 0.613 g (1.70 mmol) of formazan 6 b. Yield: 0.621 g, 90% of a purple/red solid; m.p. 76–78 °C; <sup>1</sup>H NMR (399.8 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.14–8.13 (m, 2H, aryl CH), 7.57–7.56 (m, 2H, aryl CH), 7.52–7.49 (m, 2H, aryl CH), 7.47–7.46 (m, 3H, aryl CH), 7.41–7.39 (m, 2H, aryl CH), 7.02–7.01 (m, 2H, aryl CH), 3.89 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.1, 148.9, 145.0, 133.5, 129.8, 129.3, 128.7, 125.5, 116.1 (m), 116.0, 108.5, 55.5 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.6 ppm (t, <sup>1</sup>*J*<sub>BF</sub> = 29 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$  = -144.2 ppm (q, <sup>1</sup>*J*<sub>FB</sub> = 28 Hz); FTIR (KBr):  $\tilde{\nu}$  = 3058 (m), 2989 (m), 2900 (m), 2841 (w), 1667 (m), 1605 (m), 1494 (m), 1424 (m), 1357 (w), 1267 (s), 1119 (m), 897 (w), 745 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  = 530 nm ( $\varepsilon$  = 22900 m<sup>-1</sup> cm<sup>-1</sup>); MS (EI, +ve mode): exact mass calculated for [C<sub>21</sub>H<sub>19</sub>BF<sub>2</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>: 408.1569; exact mass found: 408.1570; difference: +0.2 ppm.

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**Formazanate BF**<sub>2</sub> **complex 9c** (**A**r<sub>1</sub>=**A**r<sub>5</sub>=*p*-anisole, **R**<sub>3</sub>=**Ph**): From 1.00 g (2.80 mmol) of formazan **6c**. Yield: 0.711 g, 62% of a dark-purple solid; m.p. 170–172 °C; <sup>1</sup>H NMR (399.8 MHz, CDCl<sub>3</sub>):  $\delta$ =8.12 (d, <sup>3</sup>J<sub>HH</sub>=7 Hz, 2H, aryl CH), 7.88 (d, <sup>3</sup>J<sub>HH</sub>=9 Hz, 4H, aryl CH), 7.49–7.41 (m, 3H, aryl CH), 6.98 (d, <sup>3</sup>J<sub>HH</sub>=9 Hz, 4H, aryl CH), 3.88 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.7, 137.6, 134.0, 128.9, 128.6, 125.4, 124.9, 114.3, 55.6 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$ =-0.4 ppm (t, <sup>1</sup>J<sub>BF</sub>=29 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta$ =-145.3 ppm (q, <sup>1</sup>J<sub>FB</sub>=29 Hz); FTIR (KBr):  $\tilde{\nu}$ = 2948 (m), 2900 (m), 2834 (m), 1641 (s), 1596 (s), 1508 (s), 1313 (m), 1249 (s), 1164 cm<sup>-1</sup> (s); UV/Vis (toluene):  $\lambda_{max}$  551 nm ( $\varepsilon$ = 25500 M<sup>-1</sup> cm<sup>-1</sup>); MS (EI, +ve mode): exact mass calculated for [C<sub>21</sub>H<sub>19</sub>BF<sub>2</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>: 408.1569; exact mass found: 408.1576; difference: + 1.7 ppm.

Preparation of formazanate  $BF_2$  complex 8a ( $Ar_1 = Ar_5 = o$ -anisole, R<sub>3</sub>=NO<sub>2</sub>): Formazan 5a (1.00 g, 3.04 mmol) was dissolved in toluene (250 mL) before triethylamine (2.82 g, 3.90 mL, 27.9 mmol) was added and the solution stirred for 30 min. Boron trifluoride diethyl etherate (6.44 g, 5.60 mL, 45.4 mmol) was added and the solution heated with stirring at 105 °C for 144 h at which time the solution was dark-purple with a blue hue on the sides of the flask. The solution was cooled to 20°C and poured directly onto a column containing neutral alumina. After the toluene solution was adsorbed onto the alumina, dichloromethane was used as the eluent. The crude product was isolated as a bright-orange solution, which was washed with deionized water (3×1.00 L). The organic layer was collected, dried over MgSO<sub>4</sub>, gravity filtered, and concentrated in vacuo to afford 8a as a red-orange solid. The crude solid was purified by flash column chromatography (toluene, neutral alumina,  $R_f = 0.33$ ) to afford **8a** as a bright orange powder. Yield: 0.163 g, 15%; m.p. 166–168 °C; <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): δ=7.47 (t,  ${}^{3}J_{HH} = 8$  Hz, 2 H, aryl CH), 7.36 (d,  ${}^{3}J_{HH} = 8$  Hz, 2 H, aryl CH), 7.06– 7.03 (m, 4H, aryl CH), 3.92 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>): δ = 155.0, 132.9, 132.7, 127.3, 120.9 (2C), 112.9, 56.5 ppm; <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$  ppm (t, <sup>1</sup>J<sub>BF</sub> = 19 Hz); <sup>19</sup>F NMR (376.1 MHz, CDCl<sub>3</sub>):  $\delta = -156.0 \text{ ppm}$  (q, <sup>1</sup> $J_{FB} =$ 18 Hz); FTIR (KBr):  $\tilde{\nu}$  = 3035 (m), 2974 (m), 2845 (m), 1660 (m), 1587 (m), 1557 (m), 1494 (m), 1332 (m), 1260 (m), 1100 (s), 1021 (m), 814 (m), 751 cm<sup>-1</sup> (m); UV/Vis (toluene):  $\lambda_{max}$  468 nm ( $\varepsilon$  = 7500  $M^{-1}$  cm<sup>-1</sup>); MS (EI = +ve mode): exact mass calculated for [C<sub>15</sub>H<sub>14</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 377.1107; exact mass found: 377.1101; difference: -1.6 ppm.

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