

## Supporting Information

### **Boron complexes of thiazole-bridged 1,5-bidentate nitrogen ligands: synthesis and acid-responsive photophysical properties**

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Photophysical properties of 1,5-bidentate nitrogen ligands (**Tz**) and boron complexes (**BF<sub>2</sub>Tz**).

Table S1 Photophysical properties of **Tz**.

Thiazole	Solvent	Toluene	CHCl <sub>3</sub>
<b>Tz 1</b>	$\lambda_{\text{abs}}$ (nm)	377 398	373 404
	$\log \epsilon$	4.37 4.37	4.28 4.28
	-----		
<b>Tz 2</b>	$\lambda_{\text{abs}}$ (nm)	372 399 (s)	370 404
	$\log \epsilon$	4.29 4.26	4.12 4.12
	-----		
<b>Tz 3</b>	$\lambda_{\text{abs}}$ (nm)	371 404 (s)	369 403
	$\log \epsilon$	4.36 4.30	4.18 4.16
	-----		
<b>Tz 4</b>	$\lambda_{\text{abs}}$ (nm)	374 398	367 <b>411</b>
	$\log \epsilon$	4.56 4.56	4.13 4.12
	-----		

conc. = 10<sup>-5</sup> M

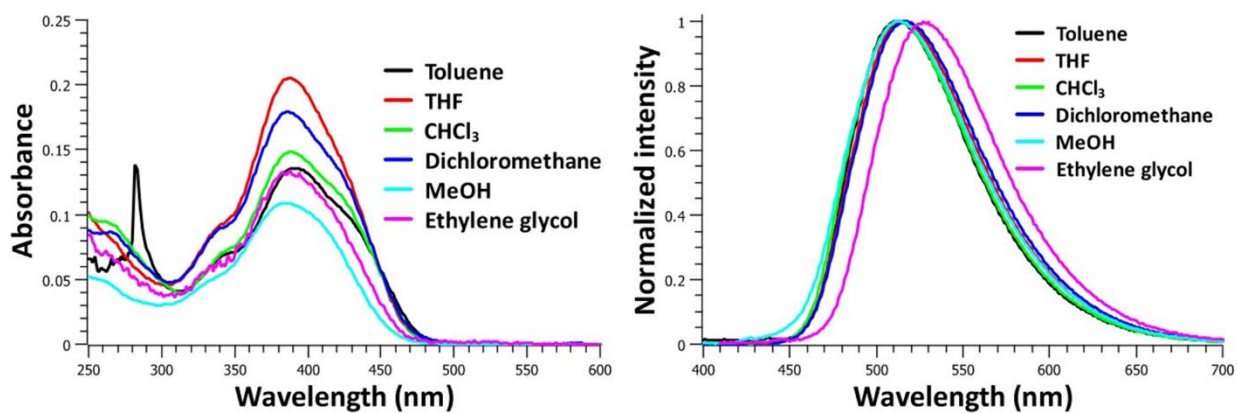
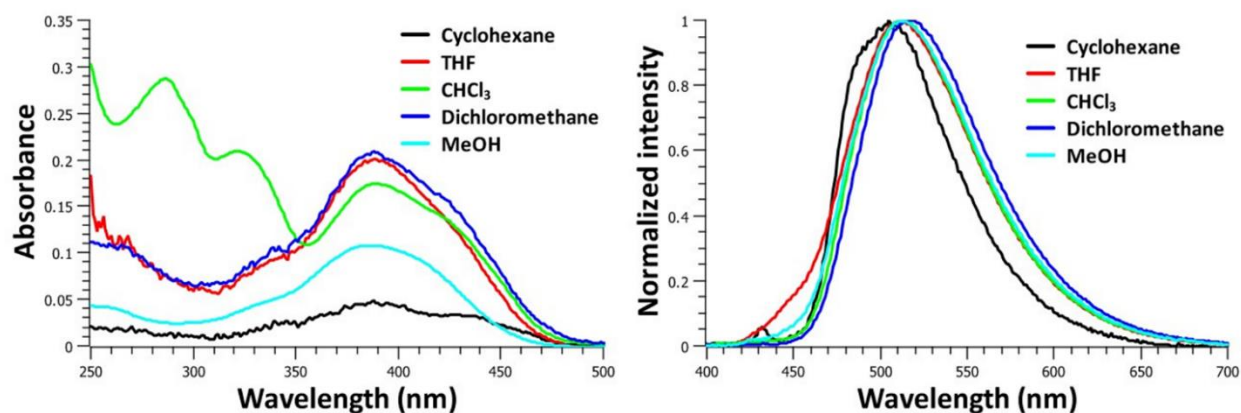


Fig. S1 Absorption (left) and emission (right) of **BF<sub>2</sub>Tz 1**.

Table S2 Photophysical properties of **BF<sub>2</sub>Tz 1**.

Solvent	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
toluene	391	385	513	[6082] (122)	0.12
THF	388	381	514	[6317] (126)	0.28
CHCl <sub>3</sub>	388	381	513	[6280] (125)	0.28
CH <sub>2</sub> Cl <sub>2</sub>	386	379	518	[6601] (132)	0.48
MeOH	385	377	513	[6480] (128)	0.28
ethylene glycol	388	381	513	[6280] (125)	0.49

<sup>a</sup> Excited at  $\lambda_{\text{max}}$ <sup>b</sup> Absolute fluorescence quantum yieldconc. = 10<sup>-5</sup> MFig. S2 Absorption (left) and emission (right) of **BF<sub>2</sub>Tz 2**.Table S3 Photophysical properties of **BF<sub>2</sub>Tz 2**.

Solvent	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
Cyclohexane	388	7.58	505	5971 [117]	0.08
THF	389	7.58	511	6137 [122]	0.23
CHCl <sub>3</sub>	389	7.58	512	6175 [123]	0.37
CH <sub>2</sub> Cl <sub>2</sub>	388	7.58	518	6468 [130]	0.23
MeOH	386	7.58	511	6337 [125]	0.32

<sup>a</sup> Excited at  $\lambda_{\text{max}}$ <sup>b</sup> Absolute fluorescence quantum yieldconc. = 10<sup>-5</sup> M

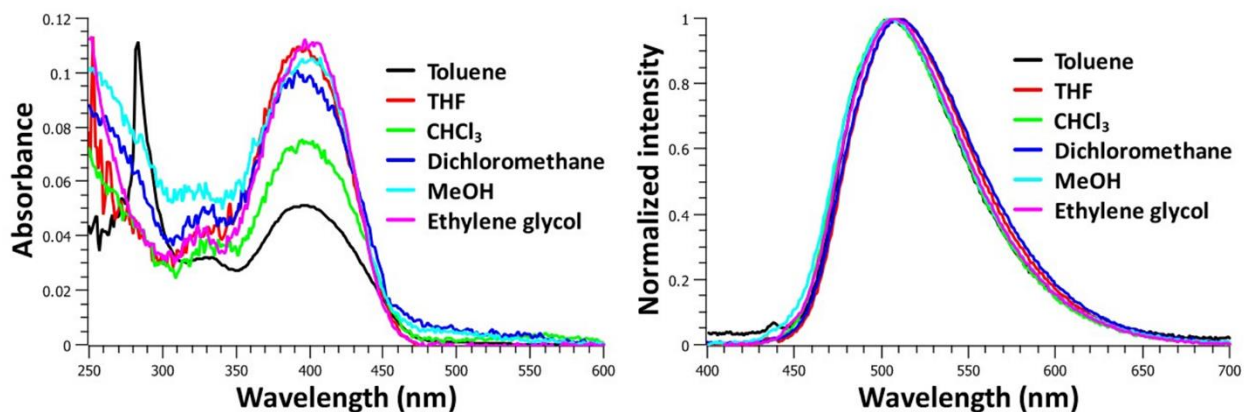


Fig. S3 Absorption (left) and emission(left) spectra of **BF<sub>2</sub>Tz 3**.

Table S4 Photophysical properties of **BF<sub>2</sub>Tz 3**.

Solvent	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
toluene	397	386	507	[5465] (110)	0.23
THF	393	385	511	[5875] (118)	0.27
CHCl <sub>3</sub>	395	389	504	[5475] (109)	0.36
CH <sub>2</sub> Cl <sub>2</sub>	392	385	509	[5863] (117)	0.49
MeOH	401	386	505	[5135] (104)	0.34
ethylene glycol	397	395	508	[5503] (111)	0.29

<sup>a</sup> Excited at  $\lambda_{\text{max}}$

<sup>b</sup> Absolute fluorescence quantum yield

conc. = 10<sup>-5</sup> M

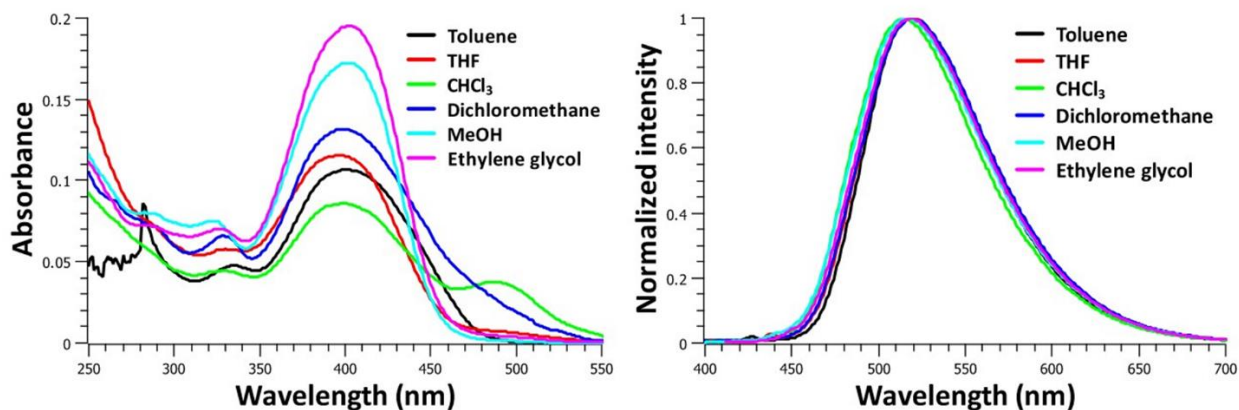


Fig. S4 Absorption (left) and emission (left) properties of **BF<sub>2</sub>Tz 4**.

Table S5 Photophysical properties of **BF<sub>2</sub>Tz 4**.

Solvent	$\lambda_{\text{abs}}$ (nm)	$\log \varepsilon$	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
toluene	399	4.02	377	518	[5757] (119)	0.09
THF	398	4.06	387	517	[5783] (119)	0.20
CHCl <sub>3</sub>	<b>398</b> 484 (s)	4.11	392	516	[5745] (118)	0.12
CH <sub>2</sub> Cl <sub>2</sub>	398	4.11	385	519	[5857] (121)	0.07
MeOH	402	4.23	389	515	[5458] (113)	0.06
ethylene glycol	403	4.29	396	519	[5546] (116)	0.07

<sup>a</sup> Excited at  $\lambda_{\text{max}}$     <sup>b</sup> Absolute fluorescence quantum yield    conc. = 10<sup>-5</sup> M

Halochromic properties of **BF<sub>2</sub>Tz 4** upon the addition of acids.Table S6 Photophysical properties of **BF<sub>2</sub>Tz 4** upon addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

Equivalent	$\lambda_{\text{abs}}$ (nm)	$\log \varepsilon$	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
0	402	3.77	377	<b>518</b>	[5570] (116)	0.12
0.1	402	3.77	377	<b>519</b>	[5607] (117)	0.12
0.2	403	3.76	376	<b>522</b>	[5656] (119)	0.12
0.4	<b>403</b> 474	4.25	425	<b>527</b>	[2121] (53)	0.09
0.6	402 477	4.57	457	<b>544</b>	[2582] (67)	0.07
0.8	403 478	4.67	467	<b>546</b>	[2605] (68)	0.06
1	402 478	4.68	468	<b>546</b>	[2605] (68)	0.08

<sup>a</sup> Excited at  $\lambda_{\text{max}}$     <sup>b</sup> Absolute fluorescence quantum yield    conc. = 10<sup>-5</sup> M in toluene

Table S7 Photophysical properties of **BF<sub>2</sub>Tz 4** upon addition of TfOH.

Equivalent	$\lambda_{\text{abs}}$ (nm)	$\log \epsilon$	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
0	398	3.22	397	<b>515</b>	[5708] (117)	0.12
0.2	398	3.20	400	<b>519</b>	[5857] (121)	0.03
0.4	<b>398</b> 452 (s)	3.13	447	<b>518</b>	[5820] (120)	0.04
0.6	466	3.20	471	<b>552</b>	[3343] (86)	0.01
0.8	469	3.23	473	<b>554</b>	[3271] (85)	0.01
1	469	3.28	474	<b>562</b>	[3528] (93)	0.03

<sup>a</sup> Excited at  $\lambda_{\text{max}}$     <sup>b</sup> Absolute fluorescence quantum yield    conc. = 10<sup>-5</sup> M in toluene

Table S8 Photophysical properties of **BF<sub>2</sub>Tz 4** upon addition of TFA.

Equivalent	$\lambda_{\text{abs}}$ (nm)	$\log \epsilon$	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
0	<b>404</b>	3.37	400	<b>514</b>	[5297] (110)	0.23
1	<b>404</b>	3.36	398	<b>519</b>	[5484] (115)	0.22
2	<b>418</b>	3.36	409	<b>518</b>	[4618] (100)	0.19
4	428	3.37	432	<b>524</b>	[4280] (96)	0.13
6	428	3.36	434	<b>531</b>	[4532] (103)	0.13
8	434	3.36	432	<b>530</b>	[4173] (96)	0.15
10	435	3.35	437	<b>534</b>	[4261] (99)	0.12
20	451	3.37	439	<b>535</b>	[3481] (84)	0.11
40	451	3.38	452	<b>541</b>	[3688] (90)	0.07
80	455	3.38	452	<b>537</b>	[3356] (82)	0.07
100	458	3.37	457	<b>543</b>	[3417] (85)	0.07

<sup>a</sup> Excited at  $\lambda_{\text{max}}$     <sup>b</sup> Absolute fluorescence quantum yield    conc. = 10<sup>-5</sup> M in toluene

## Halochromic properties of **BF<sub>2</sub>Tz 3** upon the addition of acids

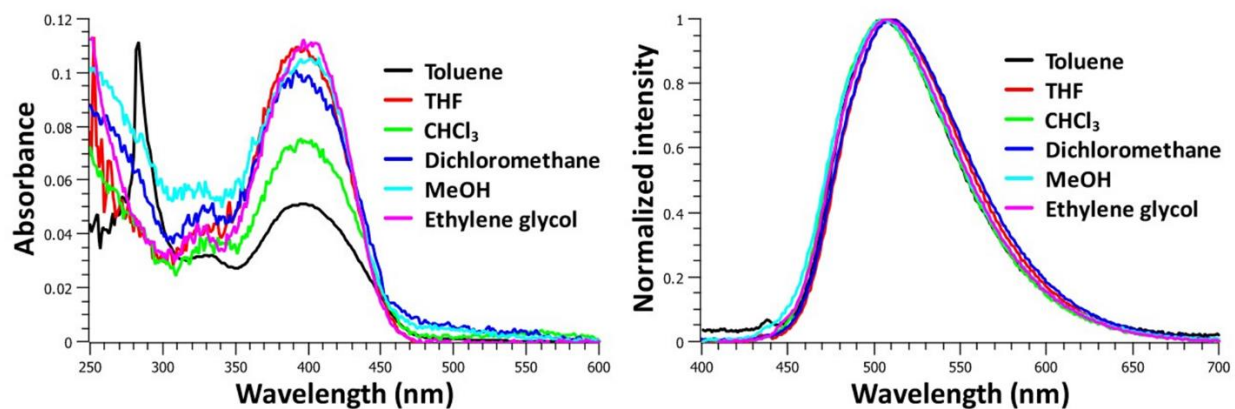


Fig. S5 Absorption (left) and emission (left) properties of **BF<sub>2</sub>Tz 3** upon addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

Table S9 Photophysical properties of **BF<sub>2</sub>Tz 3** upon addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

Equivalent	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
0	<b>380</b>	392	<b>505</b>	[6513] (125)	0.15
0.1	382 <b>459</b>	481	<b>541</b>	[3302] (82)	0.21
0.2	<b>461</b>	479	<b>538</b>	[3104] (77)	0.17
0.4	<b>470</b>	480	<b>538</b>	[2689] (68)	0.26
0.6	<b>472</b>	479	<b>538</b>	[2599] (66)	0.21
0.8	<b>474</b>	480	<b>538</b>	[2509] (64)	0.27
1	<b>478</b>	480	<b>541</b>	[2436] (63)	0.24

conc. = 10<sup>-5</sup> in toluene



## Photophysical properties of **BF<sub>2</sub>Tz** in a solid state

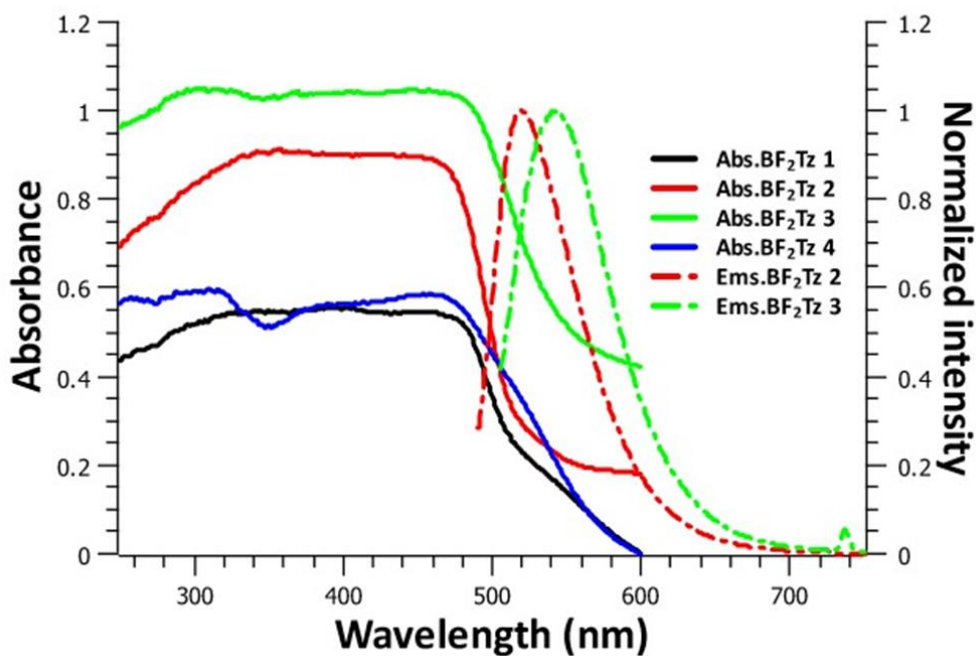


Fig. S6 Absorption and emission spectra of **BF<sub>2</sub>Tz 2** and **BF<sub>2</sub>Tz 3** in a solid state.

Table S10 Photophysical properties of **BF<sub>2</sub>Tz** in a solid state.

Thiazole	$\lambda_{\text{abs}}$ (nm)	$\log \epsilon$	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\nu_{\text{ss}}$ [cm <sup>-1</sup> ] (nm)	$\Phi_{\text{F}}$ <sup>b</sup>
<b>BF<sub>2</sub>Tz 1</b>	472	-	-	-	-	-
<b>BF<sub>2</sub>Tz 2</b>	463	-	481	520	[2367] (57)	0.08
<b>BF<sub>2</sub>Tz 3</b>	474	-	491	541	[2612] (67)	0.11
<b>BF<sub>2</sub>Tz 4</b>	<b>468</b>	-	-	-	-	-

<sup>a</sup>Excited in  $\lambda_{\text{max}}$  <sup>b</sup>Absolute fluorescence of quantum yield

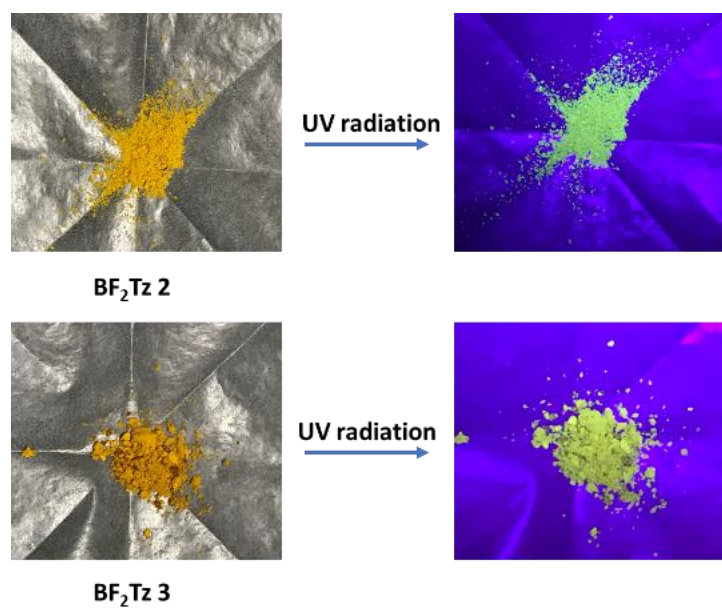


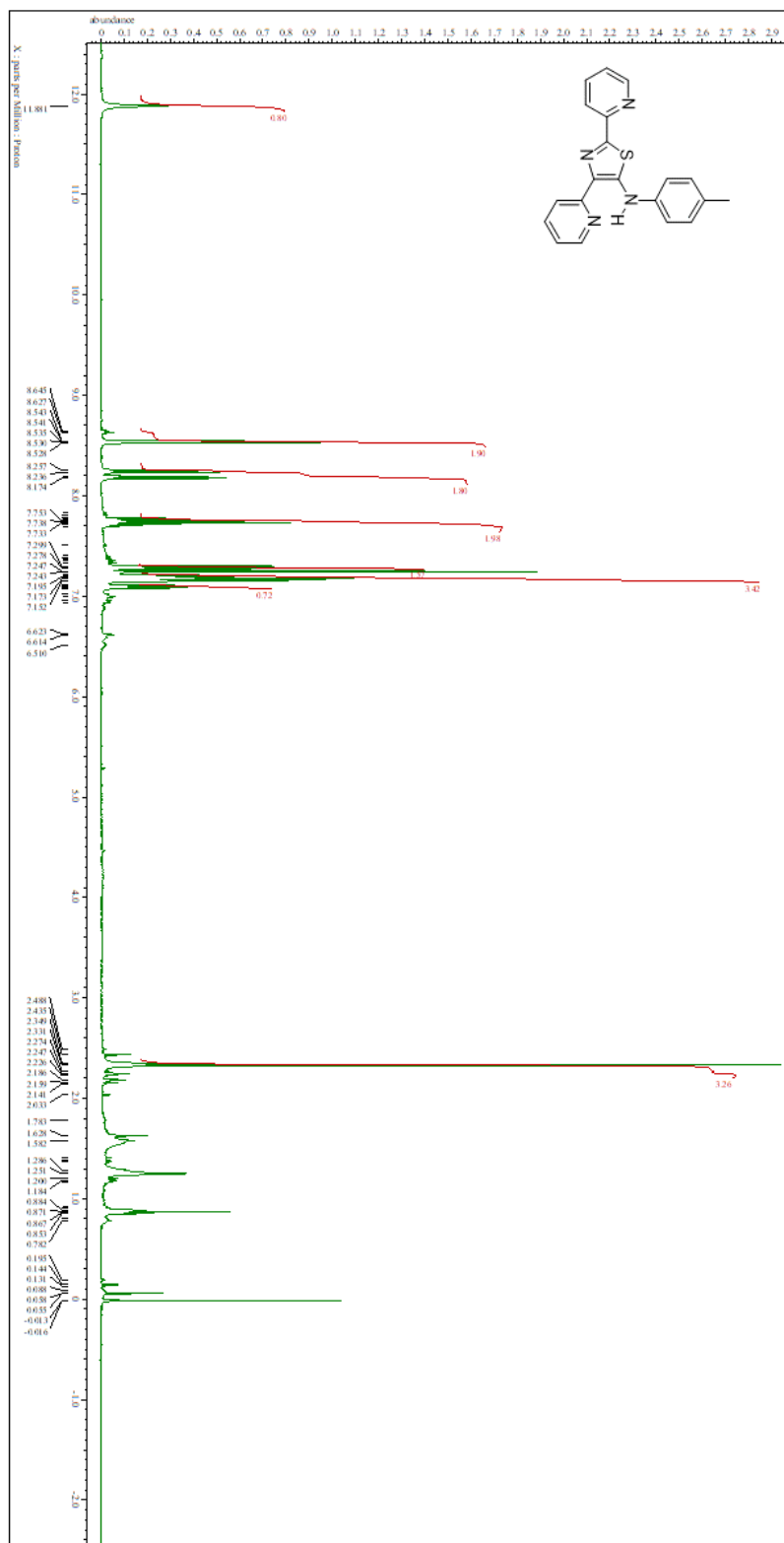
Fig. S7 Emission of **BF<sub>2</sub>Tz 2** and **BF<sub>2</sub>Tz 3** in a solid state.

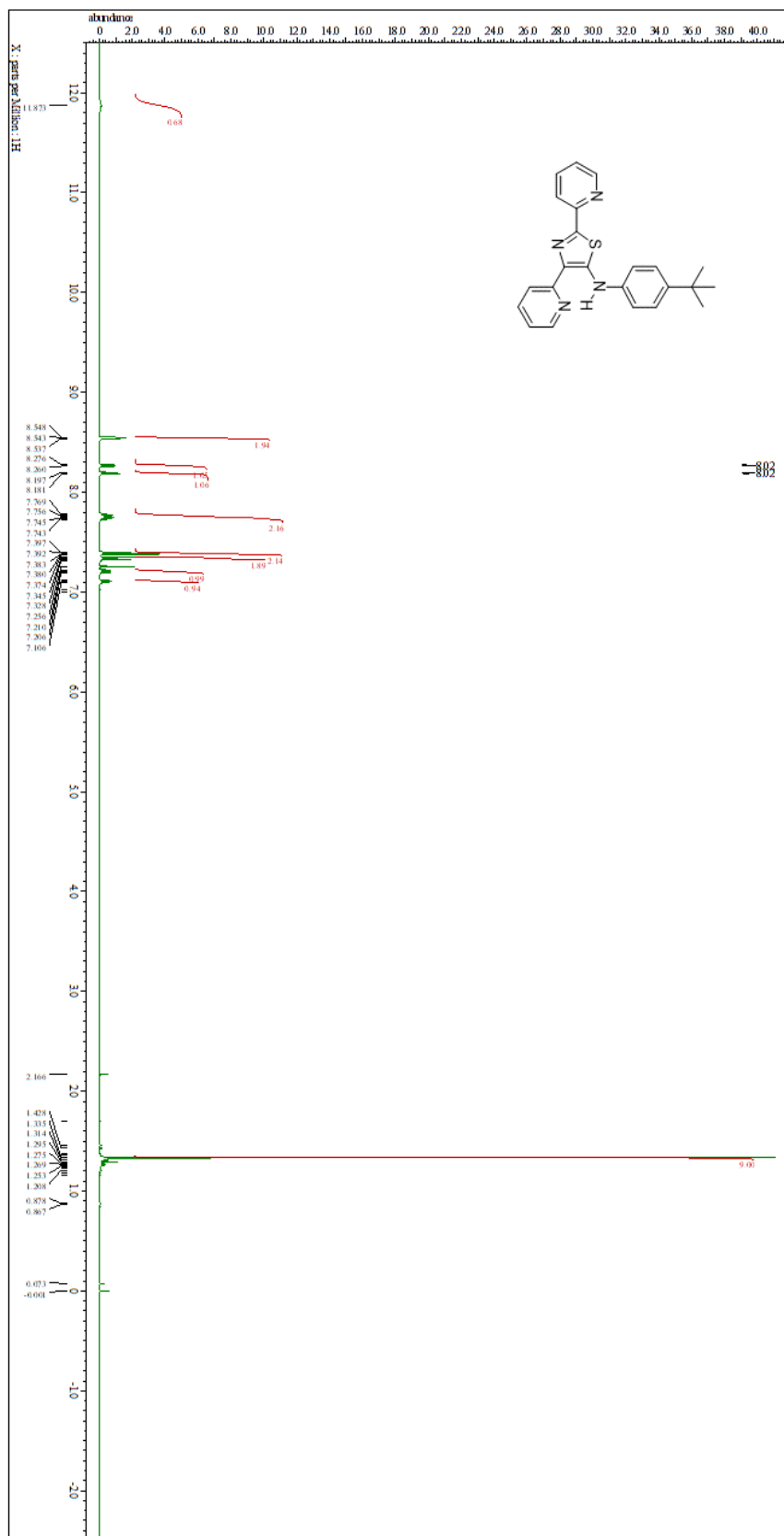
## X-ray crystallography data of **BF<sub>2</sub>Tz 1**.

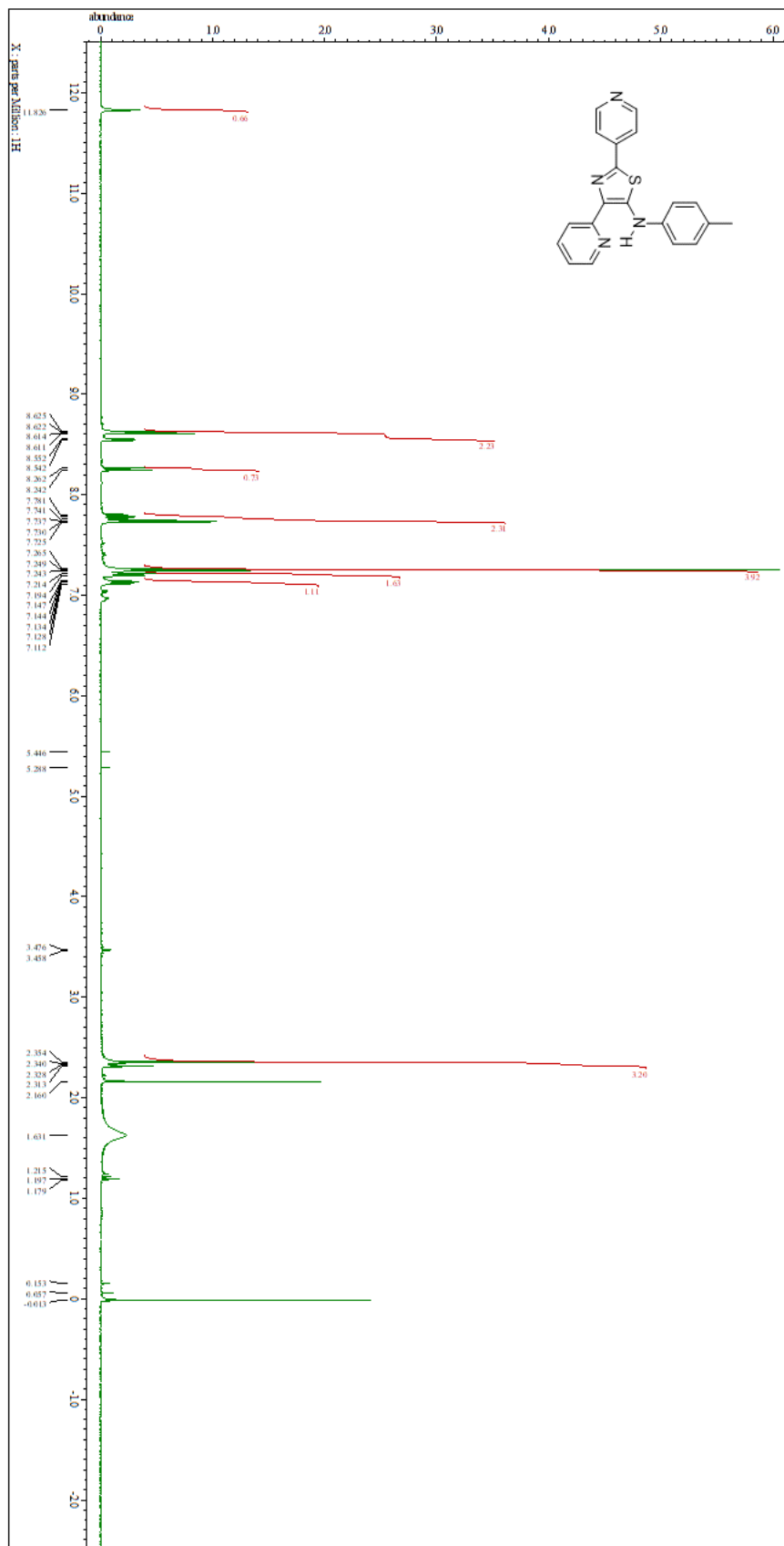
Table S11 X-ray crystallography data of **BF<sub>2</sub>Tz 1**.

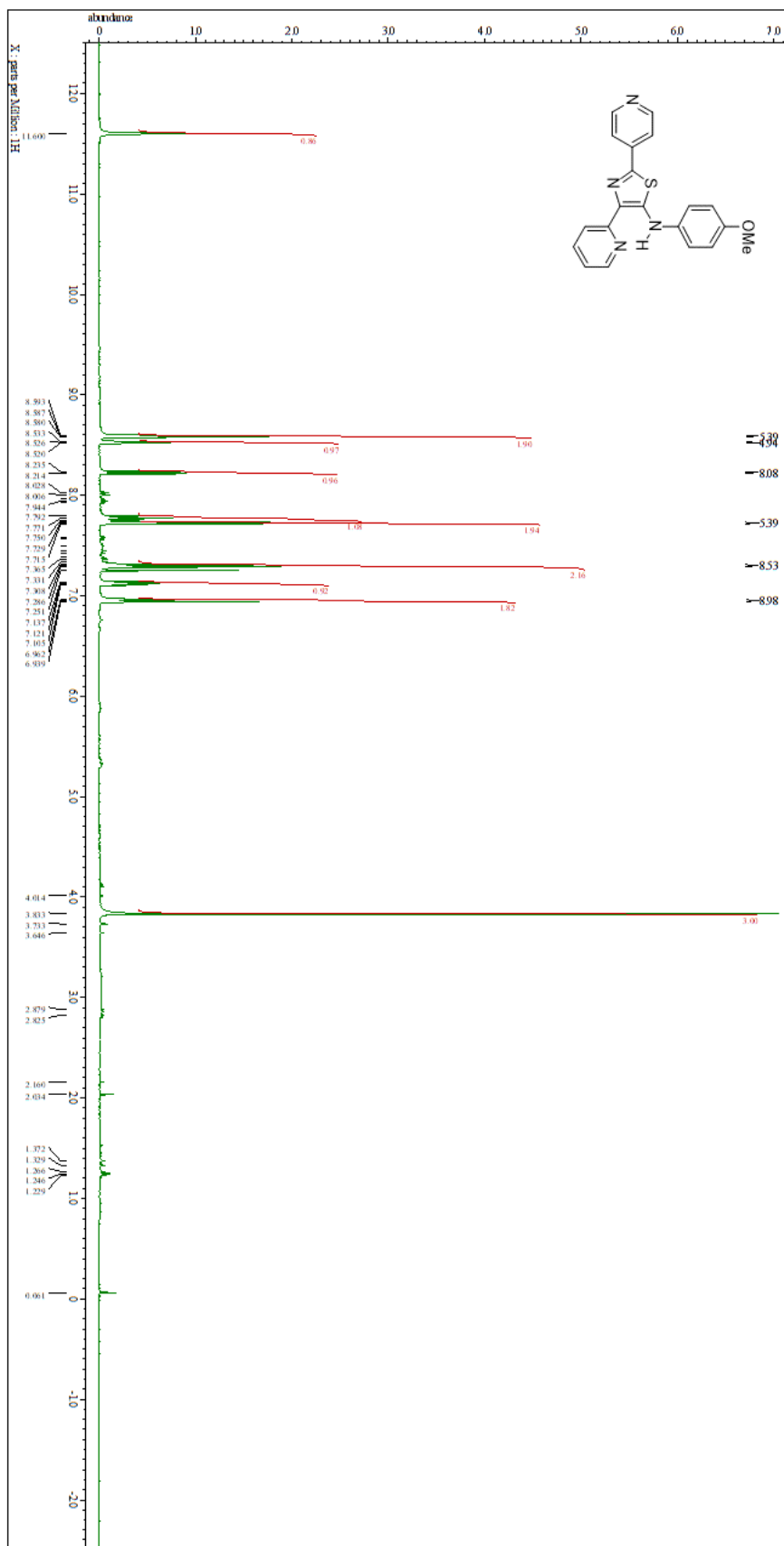
Crystal data	
Chemical formula	C <sub>20</sub> H <sub>15</sub> BF <sub>2</sub> N <sub>4</sub> S
<i>M<sub>r</sub></i>	392.23
Crystal system, space group	Triclinic, <i>P</i> <sup>-</sup> 1
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.9896 (2), 9.2646 (3), 13.4601 (4)
<i>a</i> , <i>b</i> , <i>g</i> (°)	105.166 (3), 96.037 (2), 108.811 (3)
<i>V</i> (Å <sup>3</sup> )	890.46 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> <sub>α</sub>
<i>m</i> (mm <sup>-1</sup> )	0.22
Crystal size (mm)	0.20 × 0.17 × 0.14
Data collection	
Diffractometer	Rigaku Mercury CCD (2x2 bin mode)
Absorption correction	Numerical
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.913, 0.942
No. of measured, independent and observed [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )] reflections	8310, 4063, 2984
<i>R<sub>int</sub></i>	0.016
( <i>sin</i> <i>q</i> / <i>l</i> ) <sub>max</sub> (Å <sup>-1</sup> )	0.650
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 <i>s</i> ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.042, 0.115, 1.04
No. of reflections	4063
No. of parameters	254
H-atom treatment	H-atom parameters constrained
<i>D</i> <sub>ρmax</sub> , <i>D</i> <sub>ρmin</sub> (e Å <sup>-3</sup> )	0.21, -0.18

$^1\text{H}$  and  $^{13}\text{C}$  NMR charts for **Tz** and **BF<sub>2</sub>Tz**.

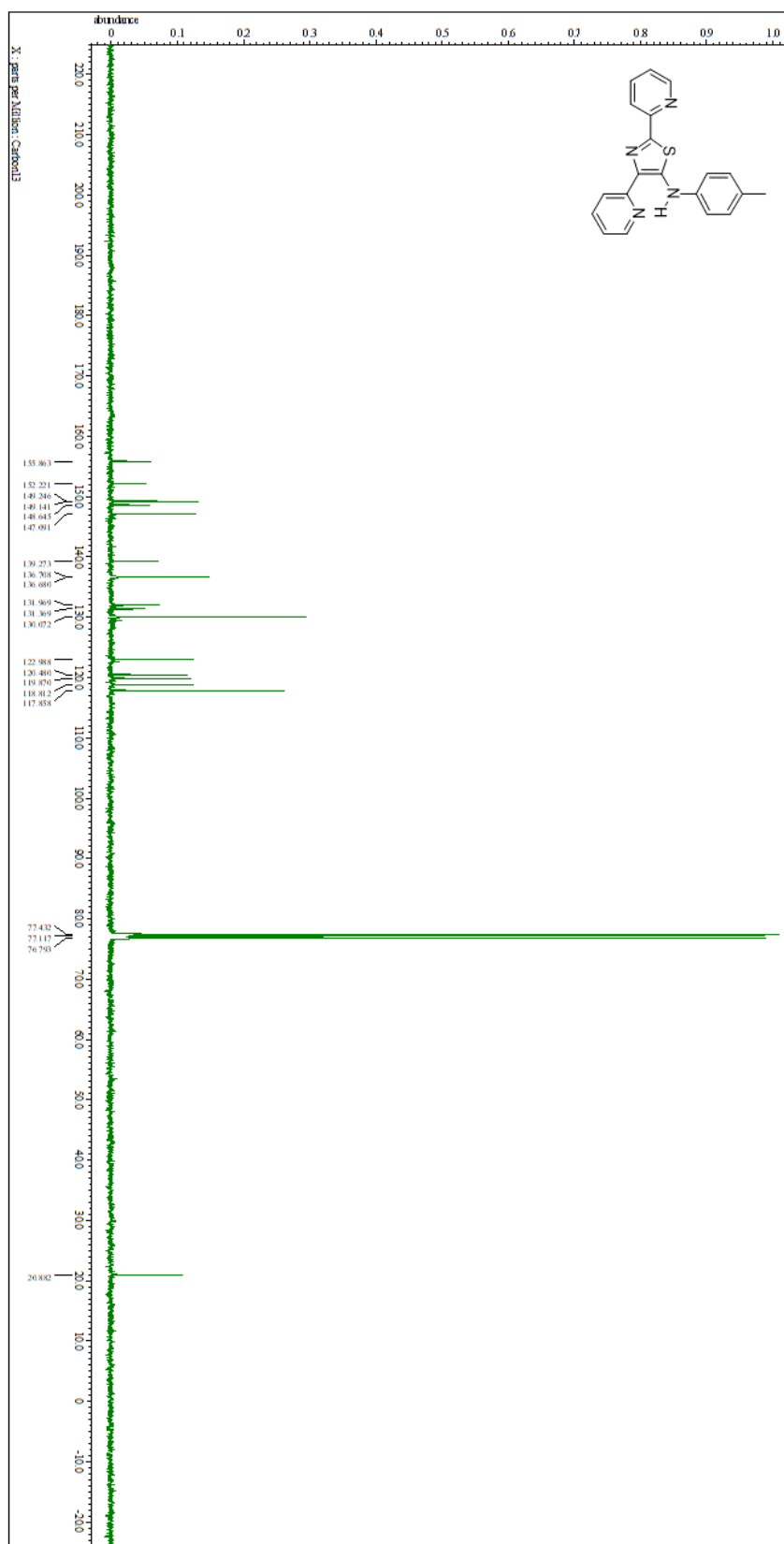




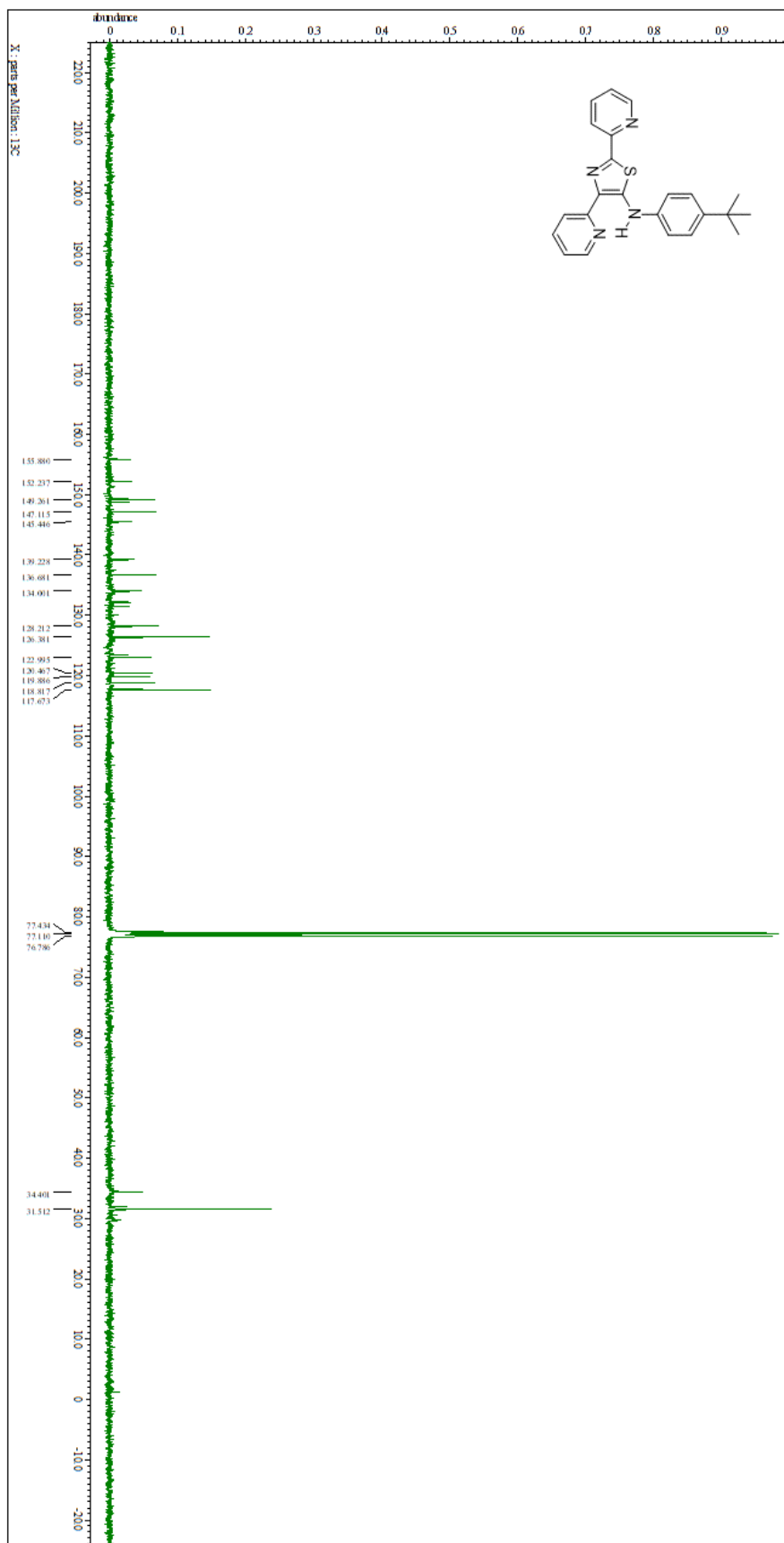


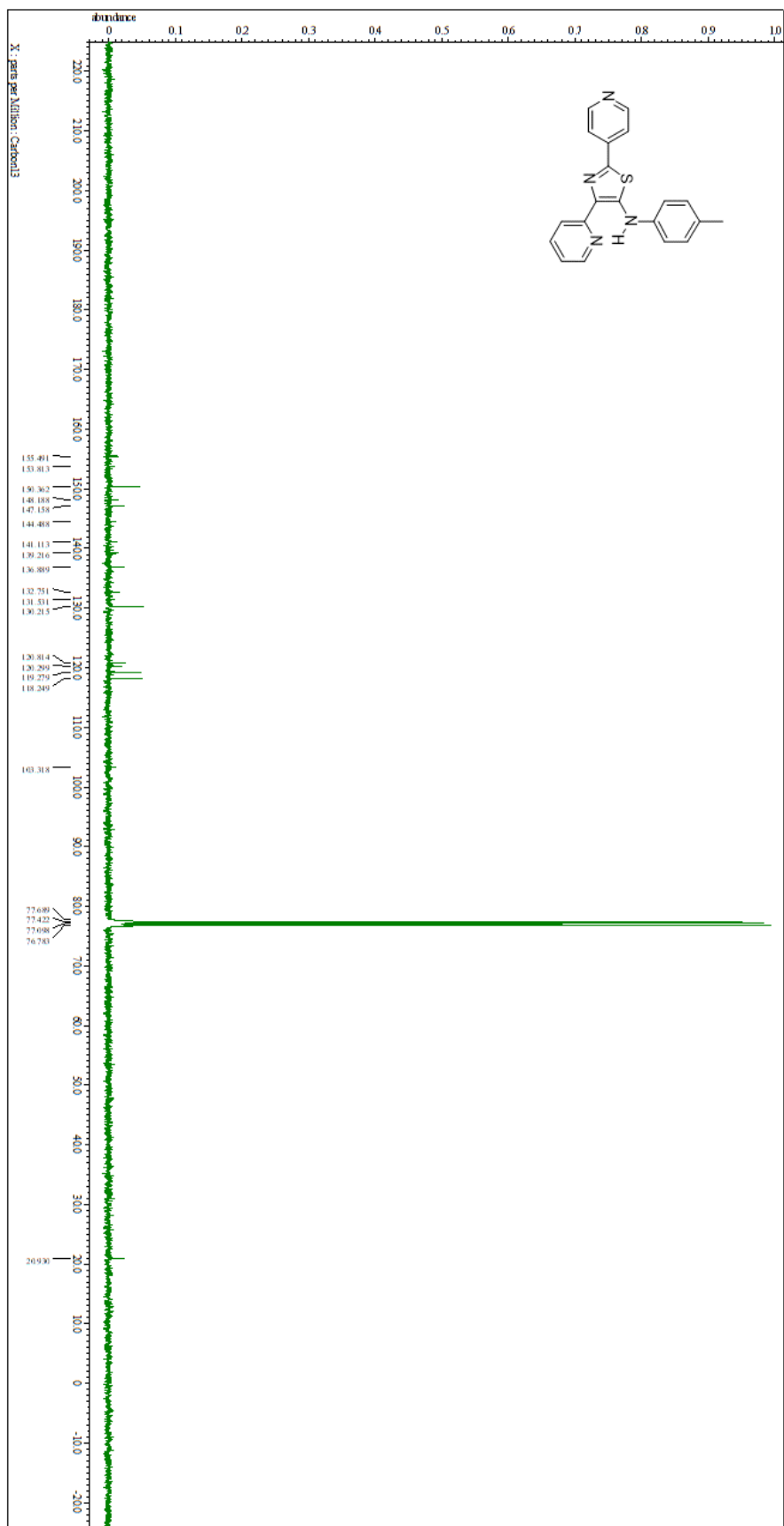


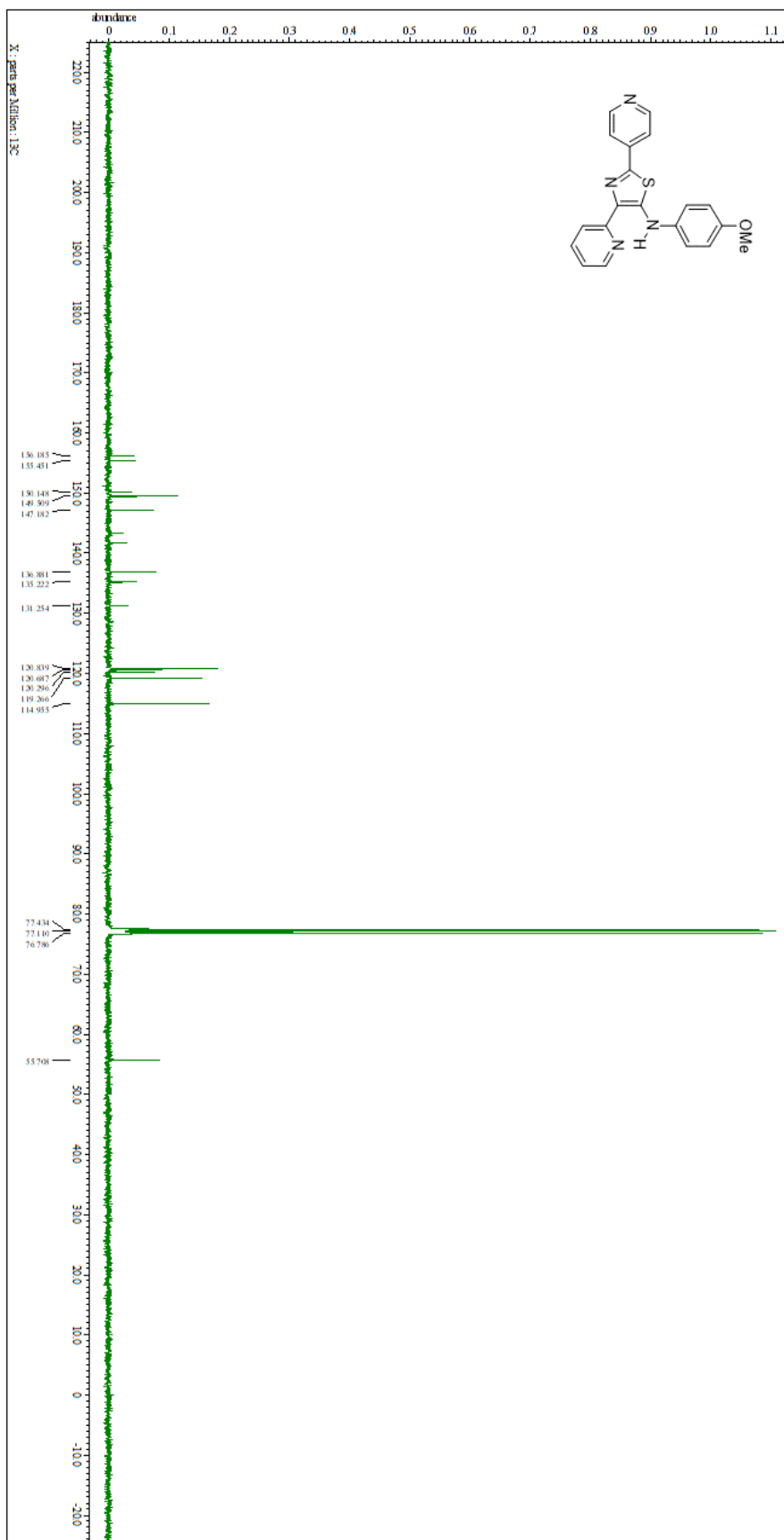
# 13C NMR for spectra for Tz



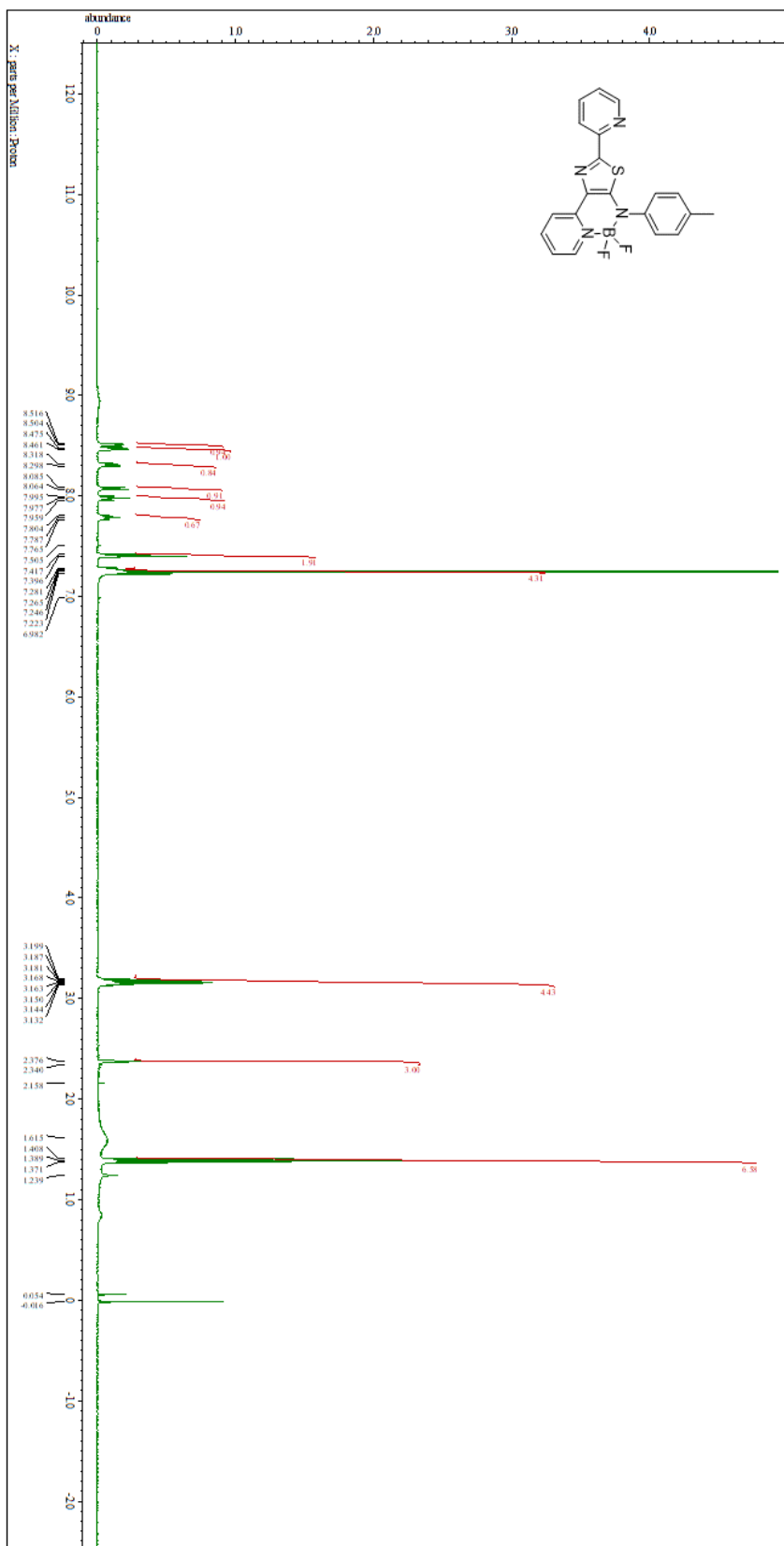


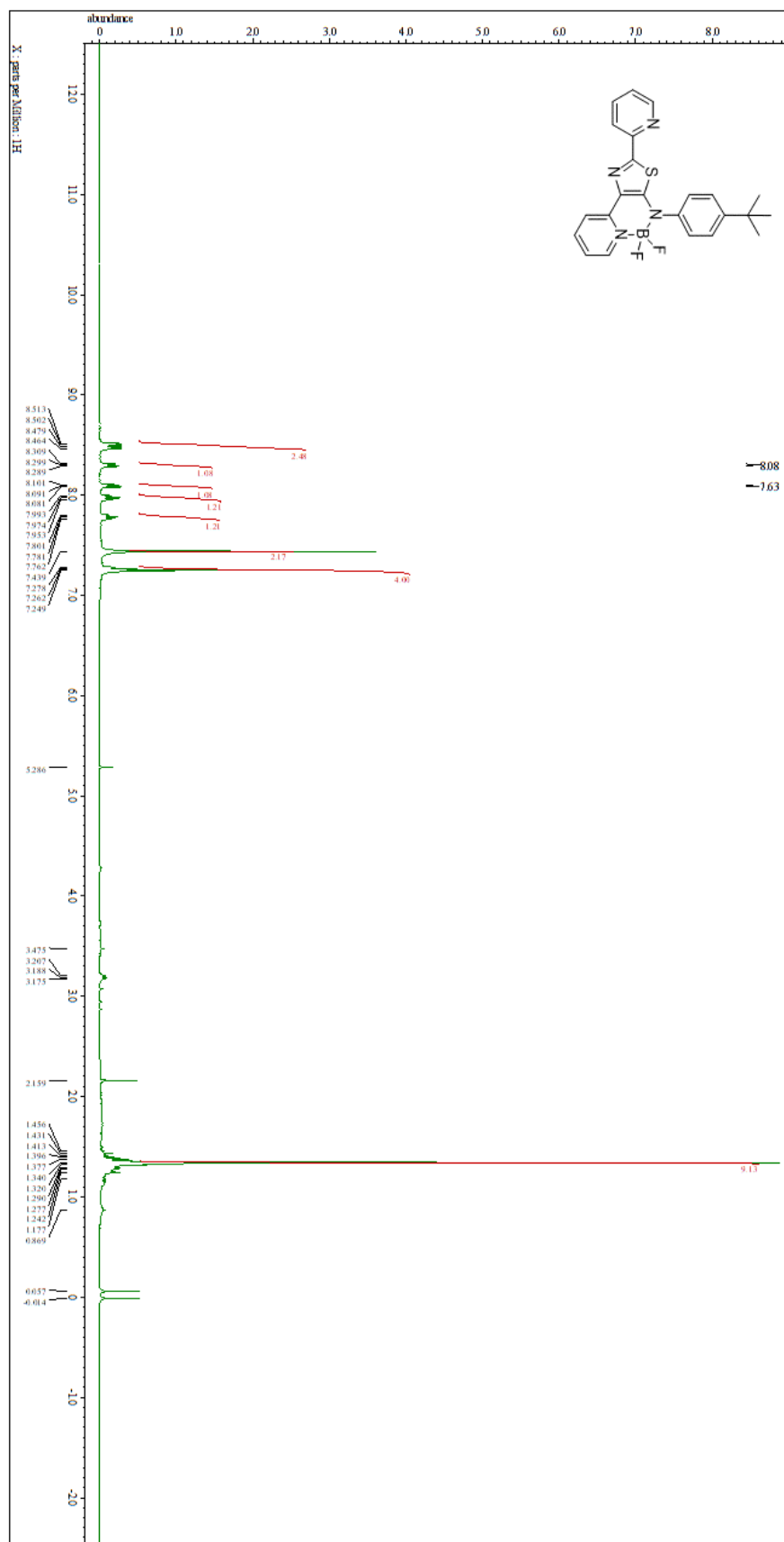


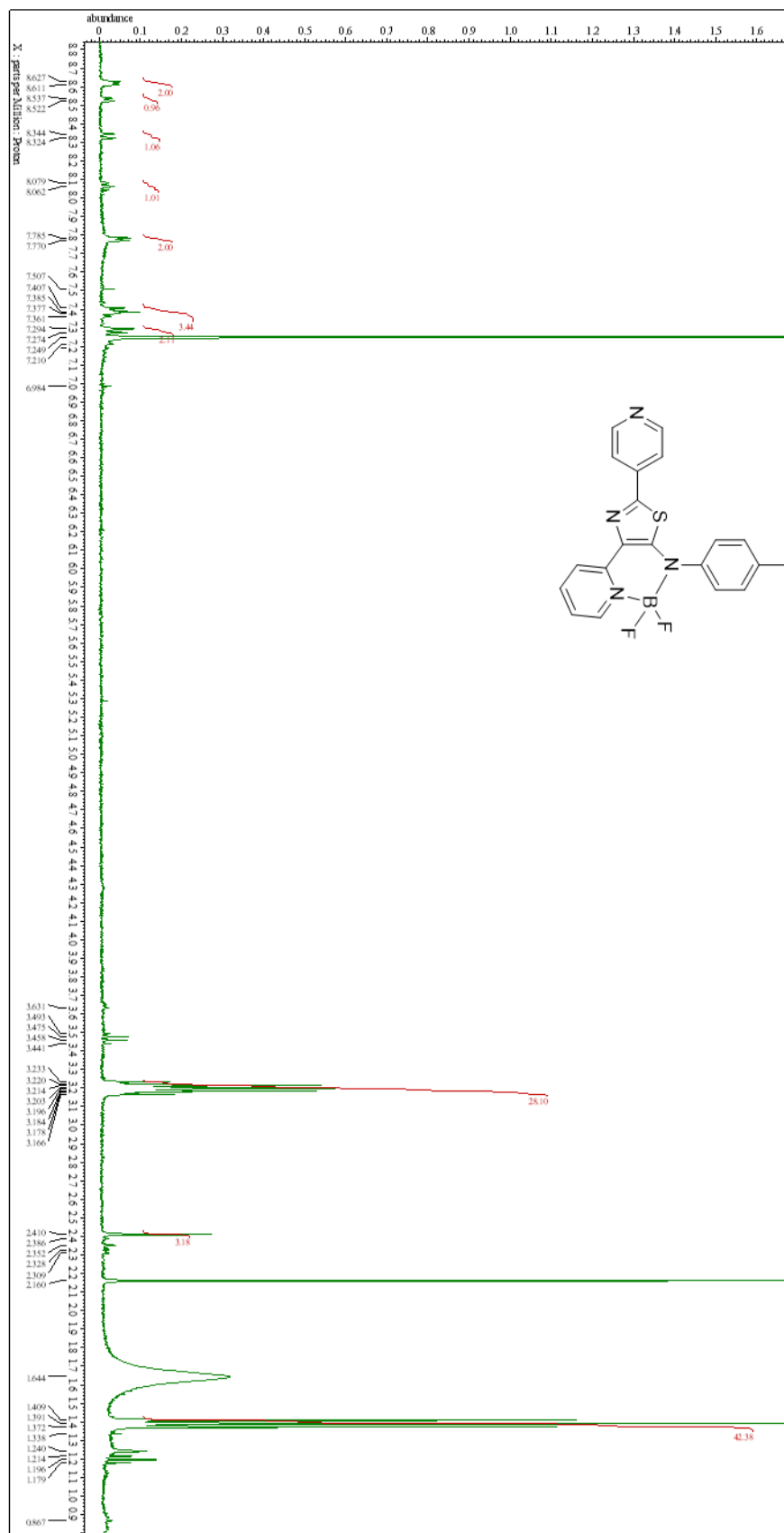


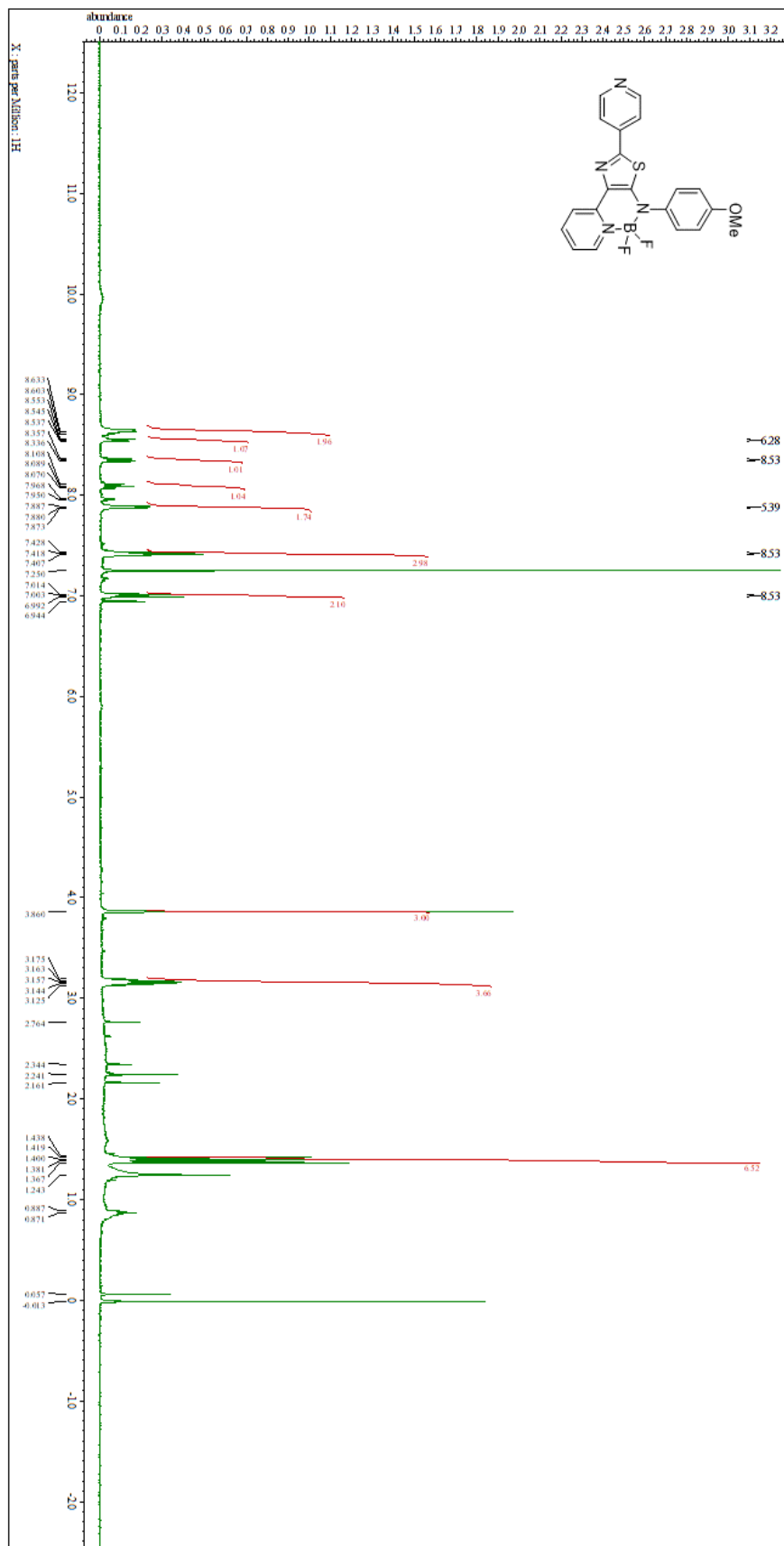


# 1H NMR of Boron complex (BF<sub>2</sub>Tz)









# $^{13}\text{C}$ NMR of Boron complex (BF<sub>2</sub>Tz)

