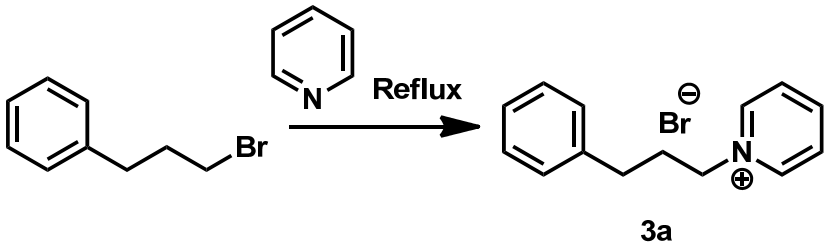
Diols and anions can control the cation-π interaction of a pyridinium boronic acid with a phenyl group connected *via* a Leonard linker

Yan-Jun Huang, Yun-Bao Jiang, Steven D. Bull, John S. Fossey and Tony D. James

Synthetic Procedure:



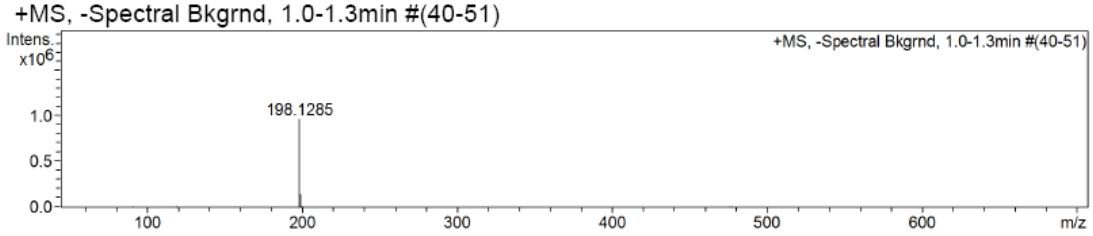
3a

In a small vial of pyridine (3 mL) was added 1-Bromo-3-Phenylpropane (0.99 g, 5 mmol) and was allowed to reflux 24 hours. The pyridine was removed and the mixture placed under high vacuum to give desired product **3a** as an oil (1.39 g, quant).

ESI-MS (m/z): [M+] calculated for $C_{14}H_{16}N$, 198.13; Found 198.13

Sample-ID	NPhPY	Submitter	Yanjun Huang
Analysis Name	NPhPY_251065_57_01_19651.d	Supervisor	Tony James
Method used	Confirm Formula Positive 50to500 loop inj.m	Acquisition Date	21/12/2009 12:14:06
Ionisation Mode	positive electrospray (ESI)		

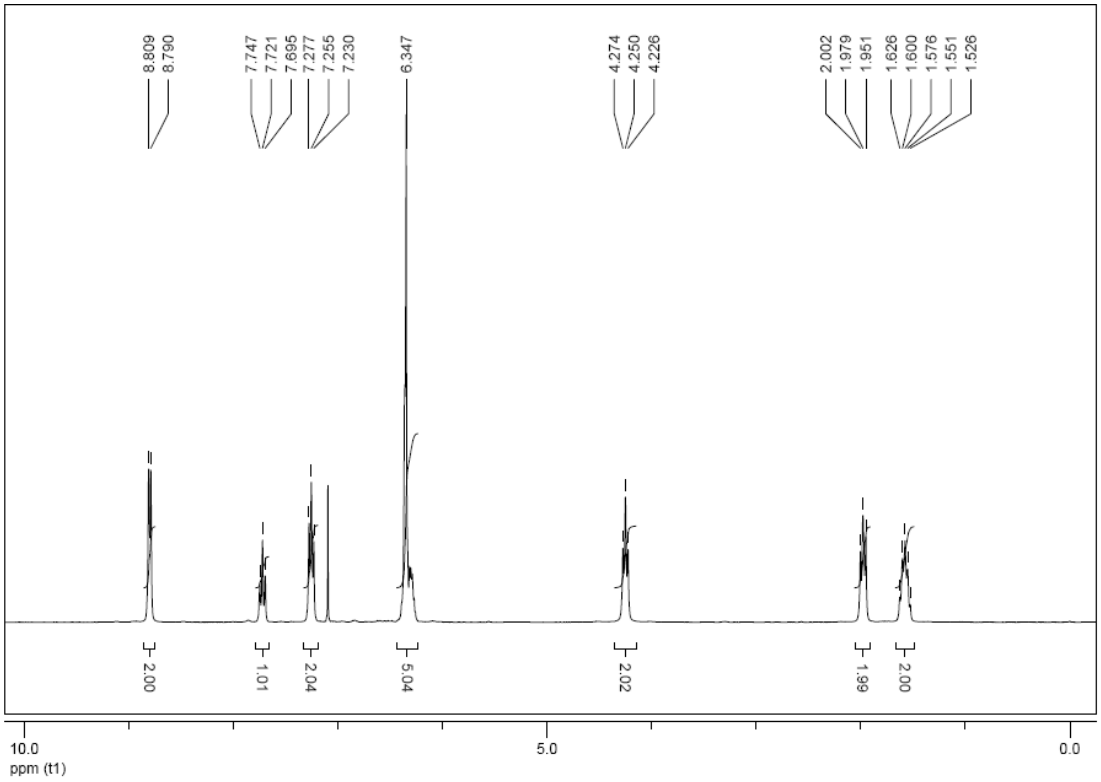
+MS, -Spectral Bkgrnd, 1.0-1.3min #(40-51)



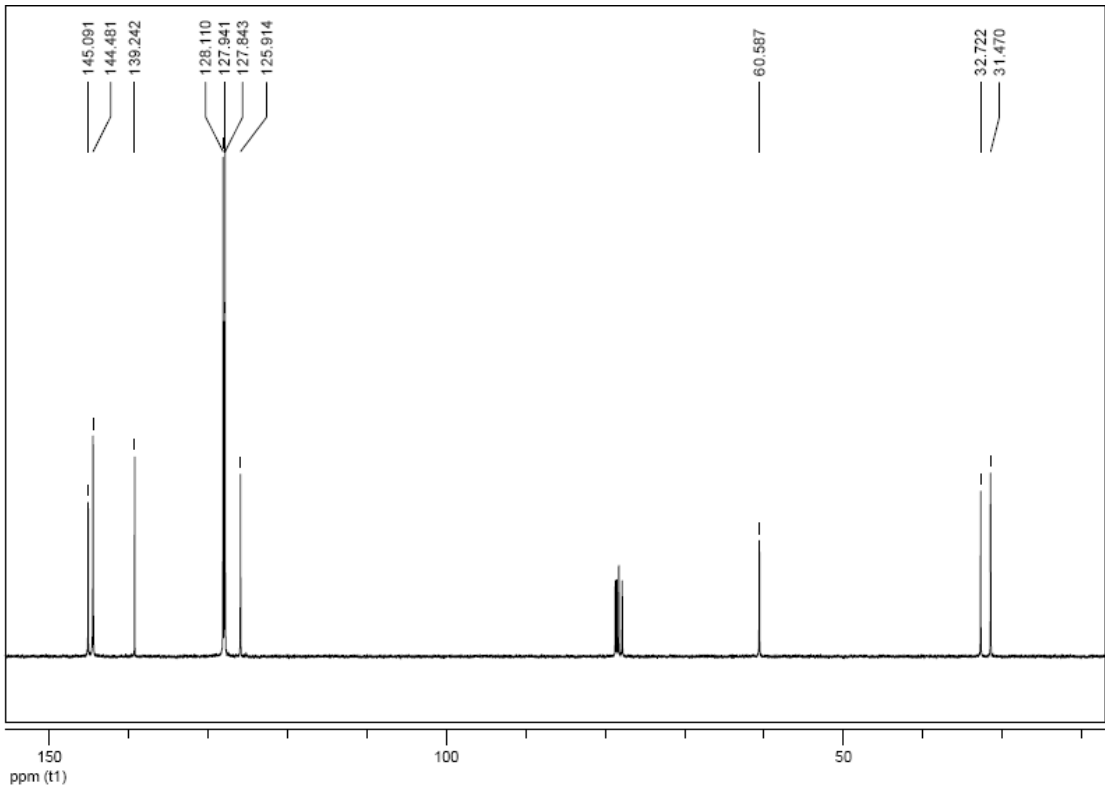
#	m/z	I	I %	Area	S/N
1	91.0545	4889	0.5	81	4970.3
2	119.0873	3769	0.4	70	2553.3
3	170.0968	1106	0.1	24	41.0
4	198.1285	959992	100.0	30944	12852.6
5	199.1314	135363	14.1	3843	1793.3
6	200.1354	7452	0.8	218	101.0
7	475.1741	3866	0.4	212	195.1
8	476.1773	1085	0.1	61	56.4
9	477.1721	3729	0.4	217	200.1
10	478.1763	1055	0.1	60	58.5

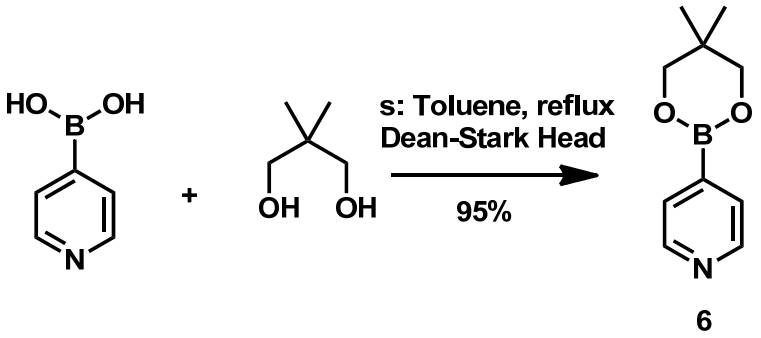
NMR

^{1}H NMR (300 MHz, Chloroform-d) δ 8.809 (d, 2H, *J*=5.7Hz), 7.747 (t, 1H, *J*=7.8Hz), 7.277 (t, 2H, *J*=7.2Hz), 6.347 (m, 5H), 4.274 (t, 2H, *J*=7.2Hz), 2.002 (t, 2H, *J*=7.5Hz), 1.576 (m, 2H)



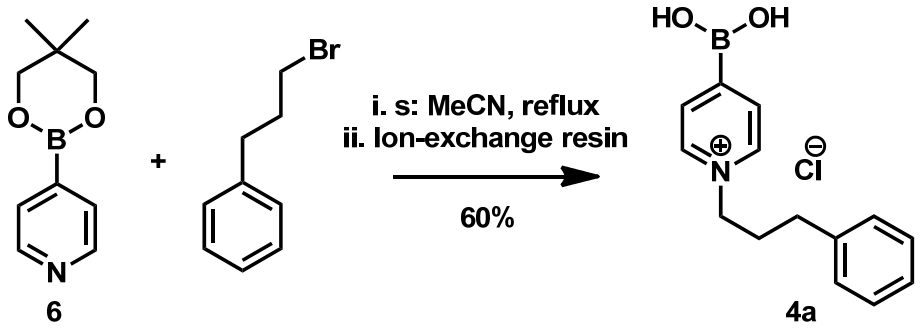
^{13}C NMR (300 MHz, Chloroform-d) δ 145.091, 144.481, 139.242, 128.110, 127.941, 127.843, 125.914, 60.587, 32.722, 31.470





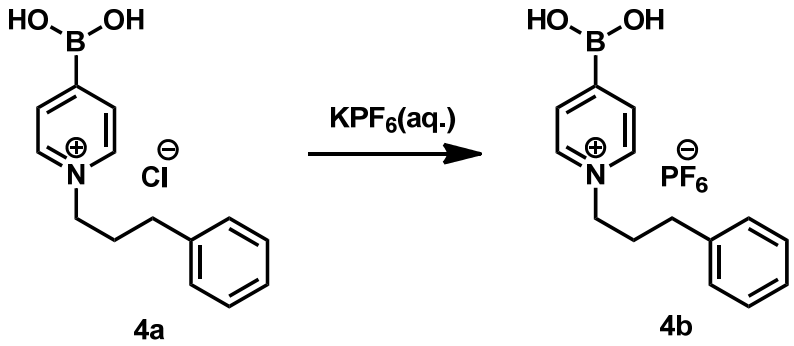
6

4-Pyridineboronic Acid (1.23g, 10mmol) and 2, 2-dimethyl-1, 3-propanediol (1.04 g, 10 mmol) were mixed in toluene (150 mL). A Dean-Stark head was fitted and the reaction mixture was heated under reflux for 3 h. The mixture was allowed to cool to room temperature. The solution as washed with water (3 x 50 mL), then dried over sodium sulfate and filtered. The volatile was removed and resulting white solid placed under high vacuum to yield 4-(5, 5-dimethyl-1, 3, 2-dioxanborinan-2-yl)pyridine **6**. (1.72 g, 90%)



6 4a

A mixture of compound **1** (192 mg, 1.0 mmol) and 1-bromo-3-phenylpropane (396 mg, 2.0 mmol) in acetonitrile (4 mL) were heated at reflux for 48 h under N_2. After removal of acetonittrile the mixture was stirred in mixed solvent (acetone: H_2O=9: 1) for 12 hours. After deprotection of the boronic acid the mixture was treated with ion-exchange resin column, 0.5 mol L^{-1} HCl-MeOH as eluent to give **4a** as chloride salt, which was recrystalised from MeOH/THF to give **4a** as a solid. (167 mg, 60%).



4a 4b

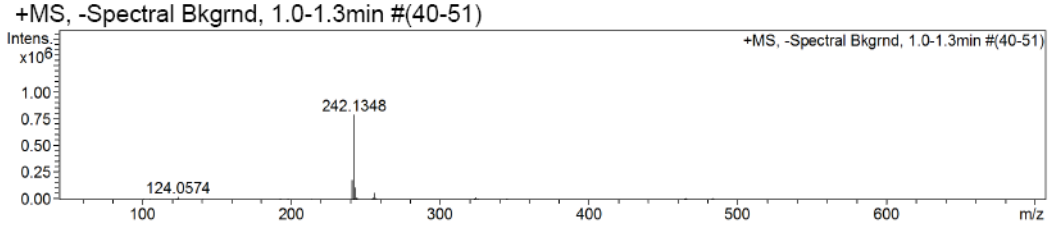
During the dropwise addition of aqueous saturated KPF_6 solution into methanol solution of **4a** (100 mg, 0.36 mmol), a precipitate formed. After washing the precipitate with cold water several times, **4b** was obtained as white solid (132 mg, 95%)

ESI-MS (m/z): [M+] calculated for $C_{14}H_{17}NO_2B$, 242.13; Found 242.13.

Confirmation of Expected Formula

Sample-ID	NPhPYBA01	Submitter	Yanjun Huang
Analysis Name	NPhPYBA01_152322_31_01_12327.d	Supervisor	Tony James
Method used	Confirm Formula Positive 50to500 loop inj.m	Acquisition Date	22/12/2008 14:49:28
Ionisation Mode	positive electrospray (ESI)		

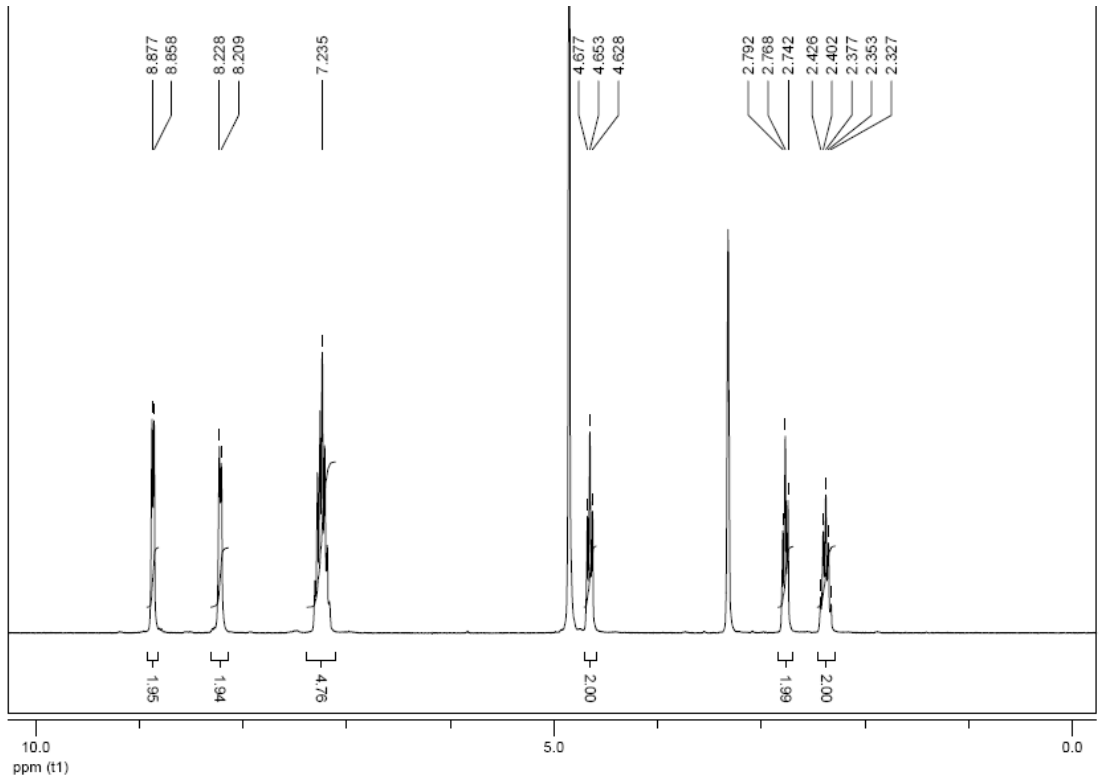
+MS, -Spectral Bkgrnd, 1.0-1.3min #(40-51)



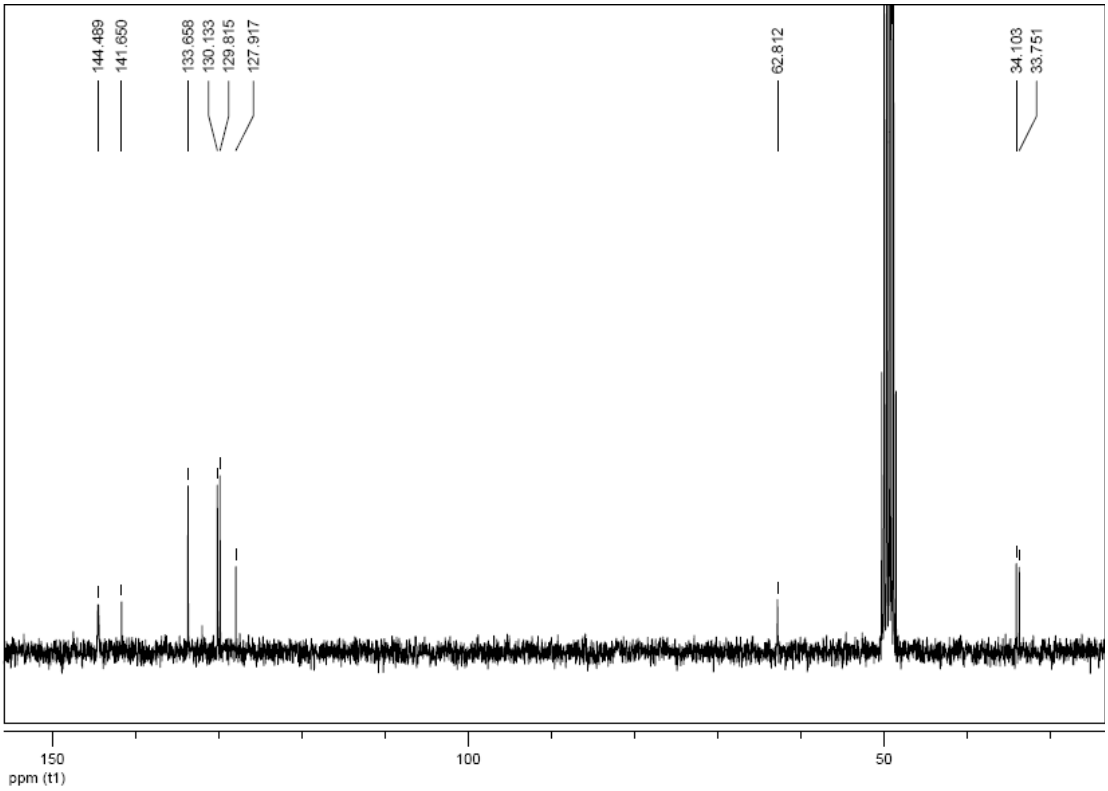
#	m/z	I	I %	Area	S/N
1	124.0574	19072	2.4	408	418.0
2	241.1384	174696	22.3	7159	2111.0
3	242.1348	783403	100.0	34078	9388.4
4	243.1378	109324	14.0	4425	1306.9
5	244.1408	10031	1.3	399	121.4
6	255.1557	13000	1.7	612	182.7
7	256.1511	58290	7.4	2629	831.2
8	257.1533	9137	1.2	409	132.2
9	324.2134	11991	1.5	670	634.6
10	483.2621	9344	1.2	633	926.8

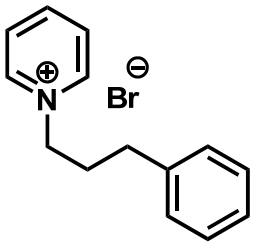
NMR

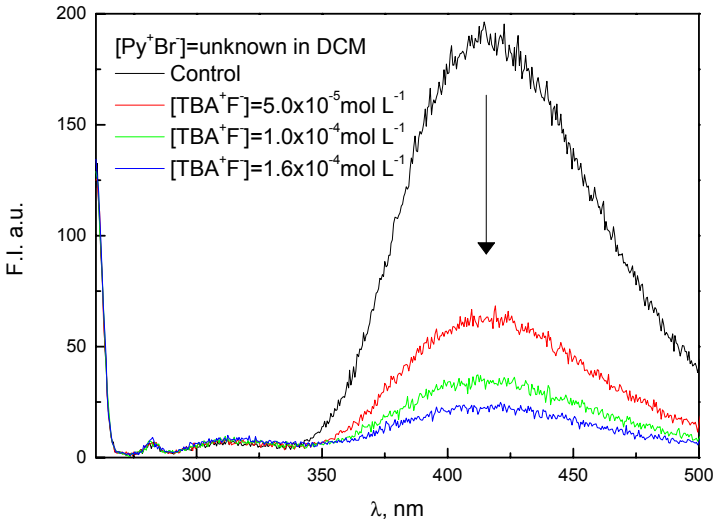
^{1}H NMR (300 MHz, Methanol-d_4) δ 8.877 (d, 2H, *J*=5.7Hz), 8.228 (d, 2H, *J*=5.7Hz), 7.235 (m, 5H), 4.653 (t, 2H, *J*=7.2Hz), 2.768 (t, 2H, *J*=7.5Hz), 2.377(m, 2H)

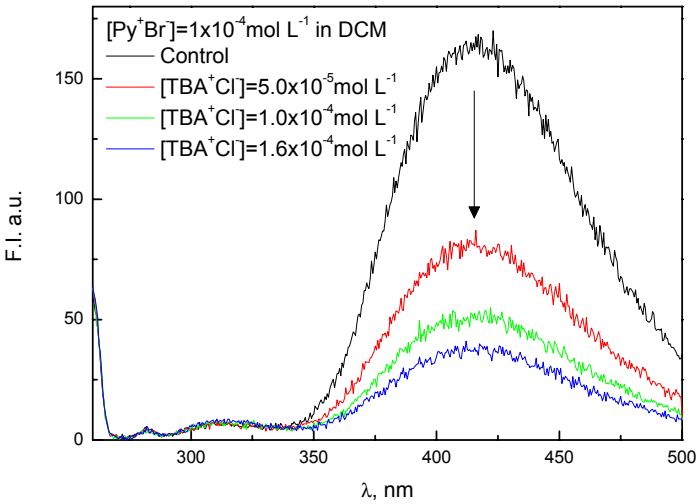


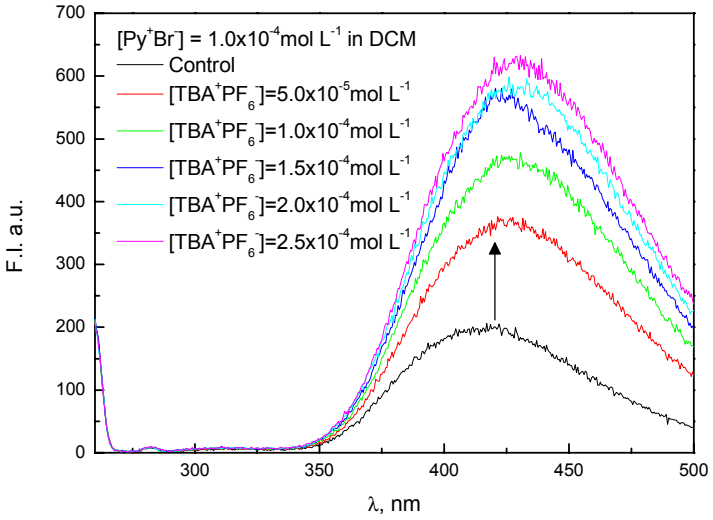
^{13}C NMR (300 MHz, Methanol-d_4) δ 144.489, 141.650, 133.658, 130.133, 129.815, 127.917, 62.812, 34.103, 33.751, one carbon was not observed due to quadropolar relaxation.

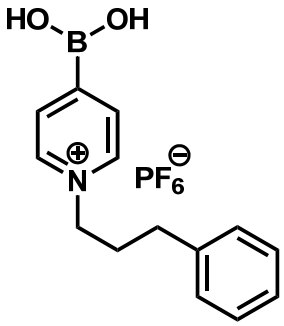


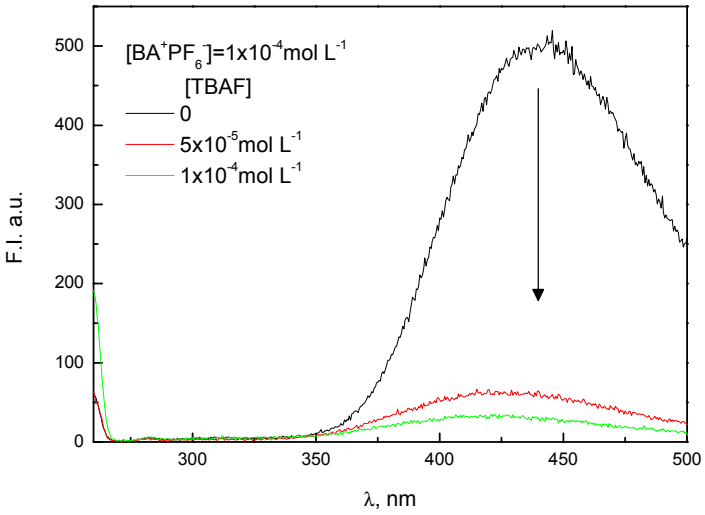

N
Br

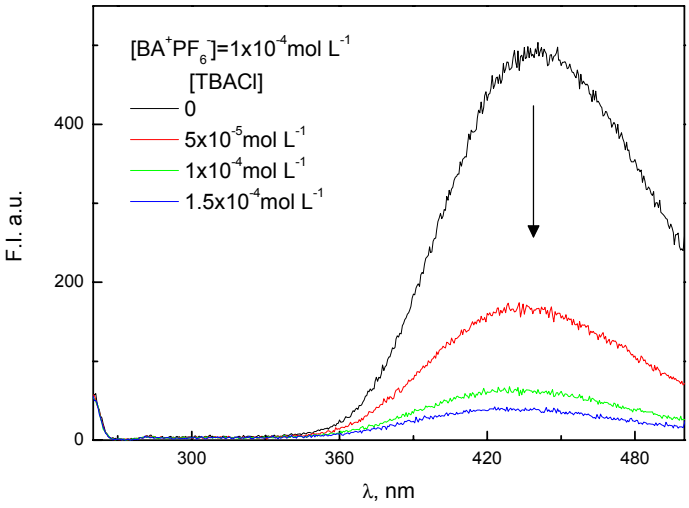

[Py+Br-]=unknown in DCM
Control
[TBA+F-]=5.0x10-5mol L-1
[TBA+F-]=1.0x10-4mol L-1
[TBA+F-]=1.6x10-4mol L-1
F.I. a.u.
λ, nm
0
50
100
150
200
300
350
400
450
500

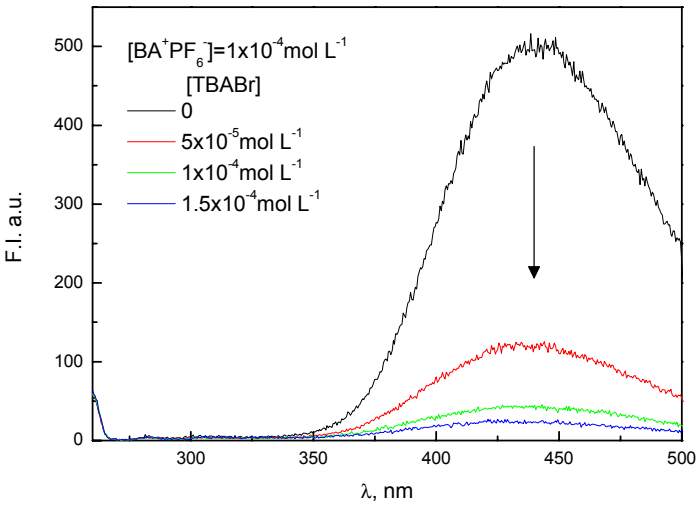

[Py+Br-]=1x10-4mol L-1 in DCM
Control
[TBA+Cl-]=5.0x10-5mol L-1
[TBA+Cl-]=1.0x10-4mol L-1
[TBA+Cl-]=1.6x10-4mol L-1
F.I. a.u.
λ, nm
0
50
100
150
300
350
400
450
500

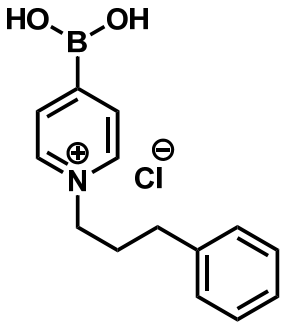

[Py+Br-] = 1.0x10-4mol L-1 in DCM
Control
[TBA+PF6-]=5.0x10-5mol L-1
[TBA+PF6-]=1.0x10-4mol L-1
[TBA+PF6-]=1.5x10-4mol L-1
[TBA+PF6-]=2.0x10-4mol L-1
[TBA+PF6-]=2.5x10-4mol L-1
F.I. a.u.
λ, nm
0
100
200
300
400
500
600
700
300
350
400
450
500

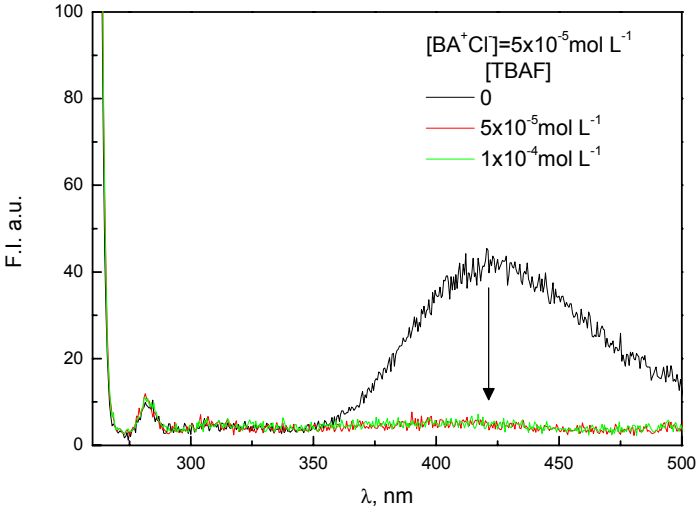

HO
B
OH
N
PF6

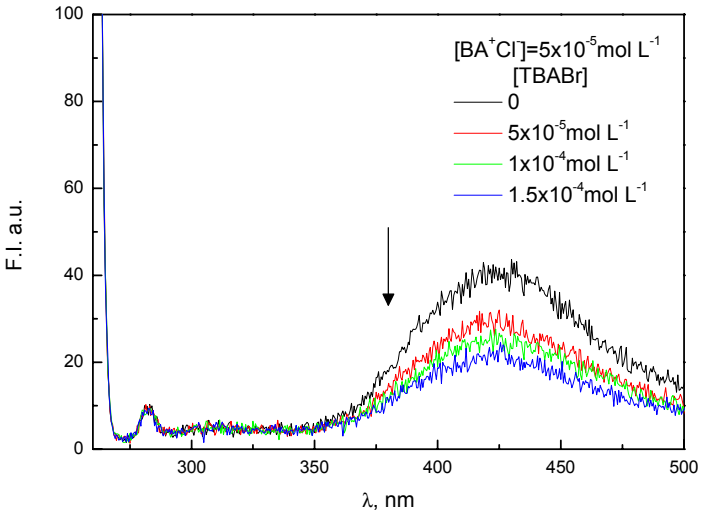

[BA+PF6-]=1x10-4mol L-1
[TBAF]
0
5x10-5mol L-1
1x10-4mol L-1
F.I. a.u.
λ, nm
0
100
200
300
400
500
300
350
400
450
500

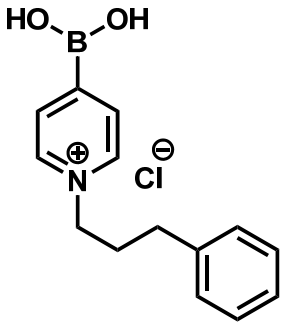

[BA+PF6-]=1x10-4mol L-1
[TBACl]
0
5x10-5mol L-1
1x10-4mol L-1
1.5x10-4mol L-1
F.I. a.u.
λ, nm
0
200
400
300
360
420
480

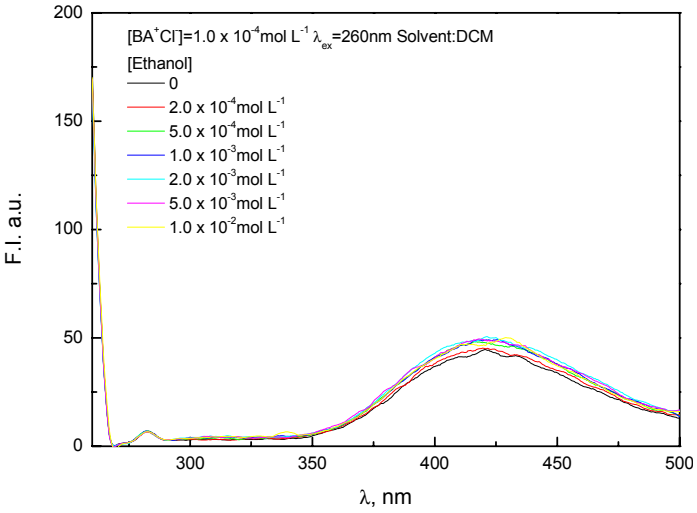

[BA+PF6-]=1x10-4mol L-1
[TBABr]
0
5x10-5mol L-1
1x10-4mol L-1
1.5x10-4mol L-1
F.I. a.u.
λ, nm
0
100
200
300
400
500
300
350
400
450
500

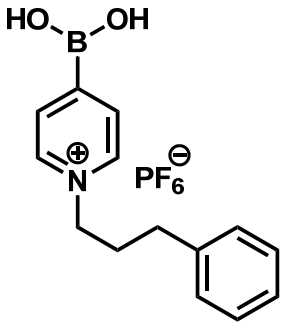

HO
B
OH
N
Cl

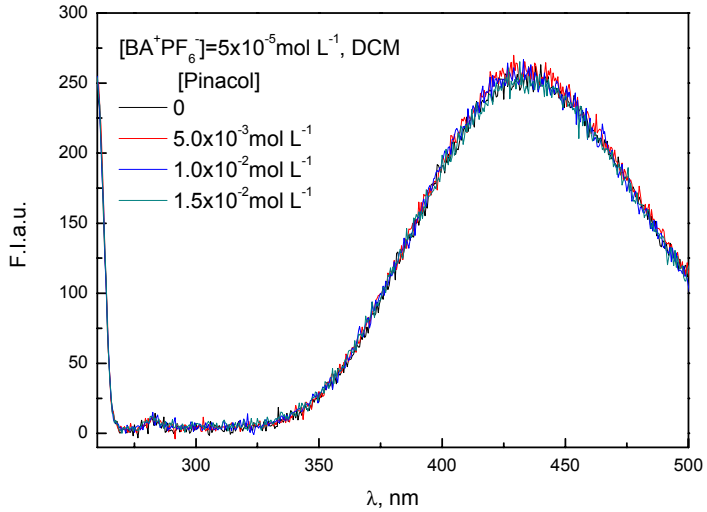

[BA+Cl-]=5x10-5mol L-1
[TBAF]
0
5x10-5mol L-1
1x10-4mol L-1
F.I. a.u.
λ, nm
0
20
40
60
80
100
300
350
400
450
500

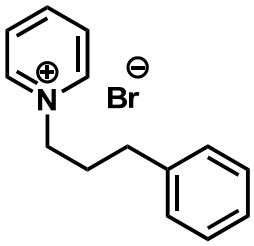

[BA+Cl-]=5x10-5mol L-1
[TBABr]
0
5x10-5mol L-1
1x10-4mol L-1
1.5x10-4mol L-1
F.I. a.u.
λ, nm
0
20
40
60
80
100
300
350
400
450
500

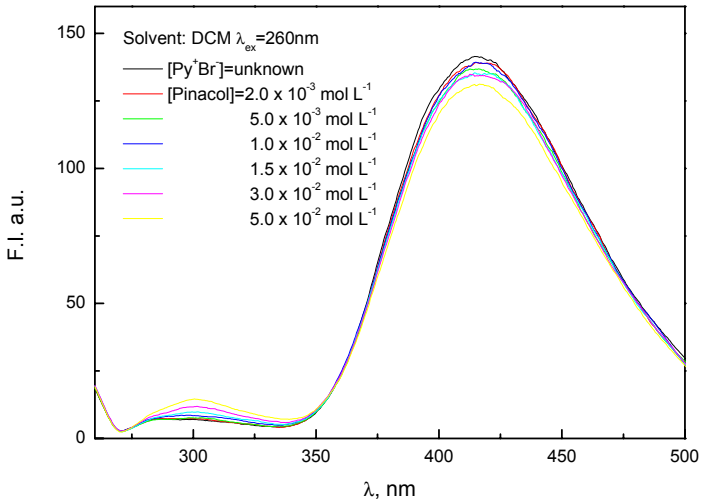

HO
B
OH
N
Cl


[BA+Cl-]=1.0 x 10-4mol L-1 λex=260nm Solvent:DCM
[Ethanol]
0
2.0 x 10-4mol L-1
5.0 x 10-4mol L-1
1.0 x 10-3mol L-1
2.0 x 10-3mol L-1
5.0 x 10-3mol L-1
1.0 x 10-2mol L-1
F.I. a.u.
λ, nm
0
50
100
150
200
300
350
400
450
500


HO
B
OH
N
PF6


[BA+PF6-]=5x10-5mol L-1, DCM
[Pinacol]
0
5.0x10-3mol L-1
1.0x10-2mol L-1
1.5x10-2mol L-1
F.I.a.u.
λ, nm
300
250
200
150
100
50
0
300
350
400
450
500





Author contributions:

JSF, SDB and TDJ conceived the idea,

JSF, Y-BJ. and TDJ planned experiments

TDJ wrote the paper

YJH carried out experiments