Supplementary Material (ESI) for Chemical Communication

Syntheses and Characterization of Polymer-Supported Organotrifluoroborates: Applications in Radioiodination Reactions

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General comments: All glassware was dried in an oven at 120 ^{o}C and flushed with dry argon prior to use. All solvents and chemicals were purchased from commercial sources and used as received. Dowex 1-X 10 (Bio.Rad Laboratories, 100-200 mesh, chloride form. Control number, MM06170). DI water (Barnstead E-pure) was used in all solution preparation and reactions. Potassium organotrifluoroborates were prepared from organoboronic acids or esters according to the reported procedures or obtained from commercial sources. ^{11}B and ^{13}C solid-state NMR spectroscopy was performed on a Varian INOVA 400 MHz solid state NMR. IR spectroscopy was carried out using a Nicolet 6700 FT/IR with a continuum microscope. UV/vis spectroscopy was performed using an Evolution 600 UV-vis. The pH value of the solutions was measured using an Accumet Basic pH Meter. No-carrier-added Na^{123}I (in 0.1% aqueous NaOH) was purchased from MDS Nordion, Inc.

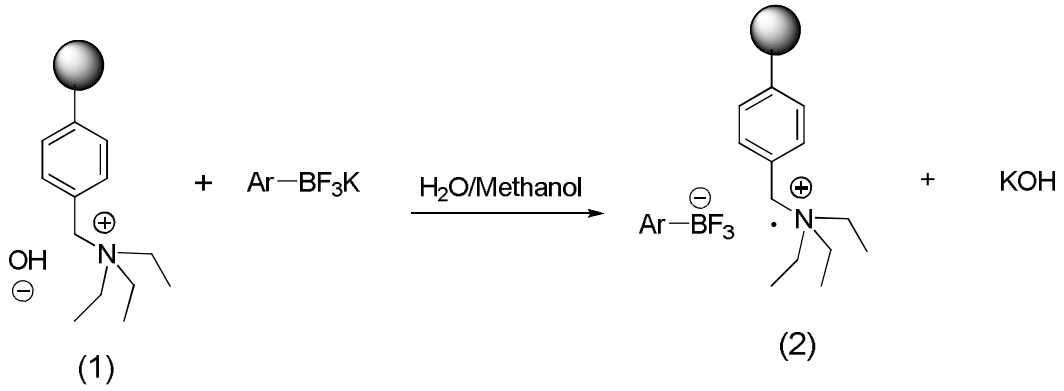
1. Preparation of the Dowex resin bearing quaternary ammonium hydroxide moieties through chloride-hydroxide anion exchange

Dowex 1-X 10 (10 grams) was washed sequentially with 1 *N* aqueous HCl (3 x 40 mL), 1 *N* aqueous NaOH (3 x 40 mL), water (100 mL) of water and then dried overnight prior to use.

[When aqueous $AgNO_3$ is added to the second (NaOH) wash, a white precipitate (AgCl) forms, confirming that chloride-hydroxide anion exchange occurred]

2. Synthesis of Dowex-supported 2-naphthylenyltrifluoroborate salt

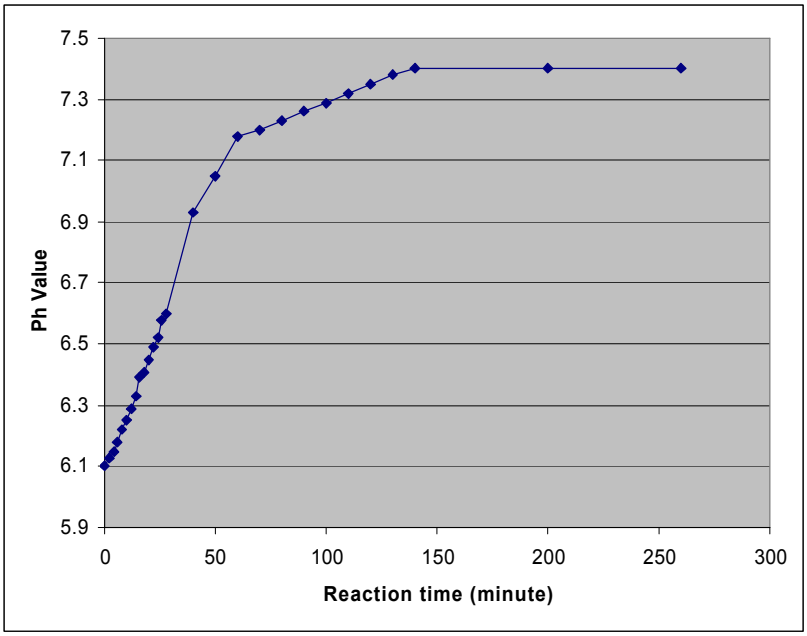
To a suspension of the base form of the Dowex resin (1 g) in H_2O (10 mL), a solution of 2-naphthylenyltrifluoroborate (1 mmol) in MeOH (10 mL) was added in one portion. The pH of the reaction mixture was then monitored.



(1) (2)

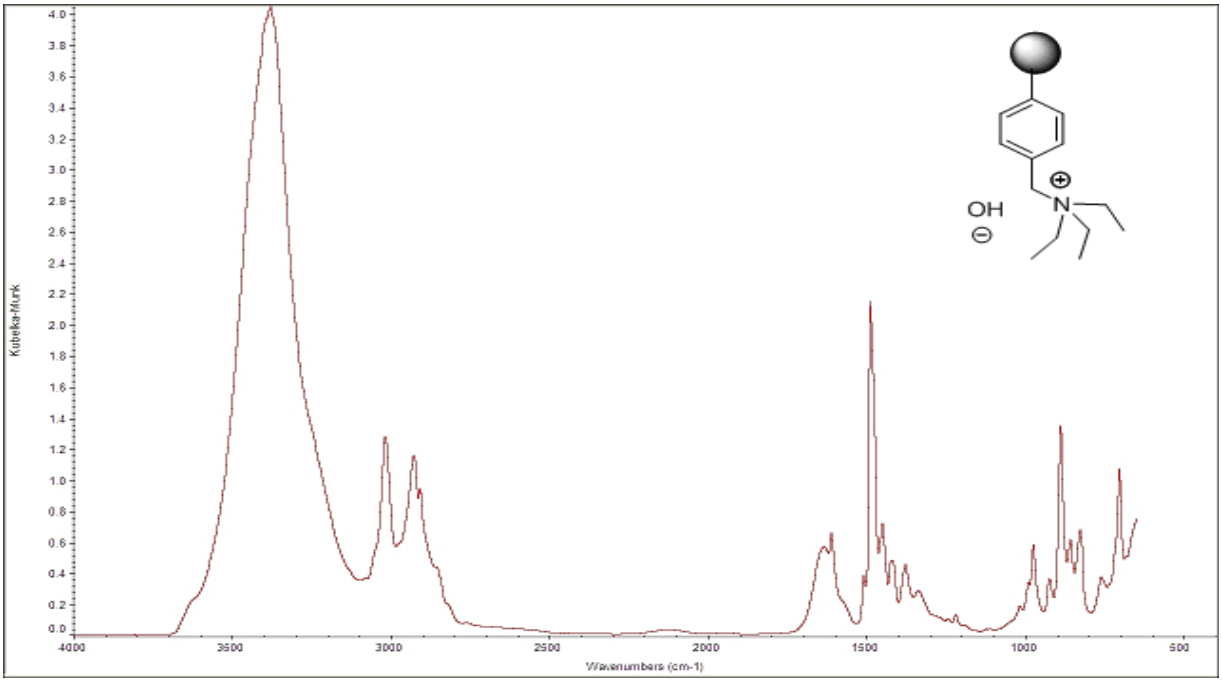
Reaction time versus pH was measured as a means of monitoring the formation of the Dowex-supported 2-naphthylenyltrifluoroborate salt. The reactions were generally complete in less than 3 hours.

Time (Min.)	PH value	Time (Min.)	PH value	Time (Min.)	PH value
0	6.1	20	6.45	90	7.26
2	6.13	22	6.49	100	7.29
4	6.15	24	6.52	110	7.32
6	6.18	26	6.58	120	7.35
8	6.22	28	6.60	130	7.38
10	6.25	40	6.93	140	7.40
12	6.29	50	7.05	200	7.40
14	6.33	60	7.18	260	7.40
16	6.39	70	7.20		
18	6.41	80	7.23		

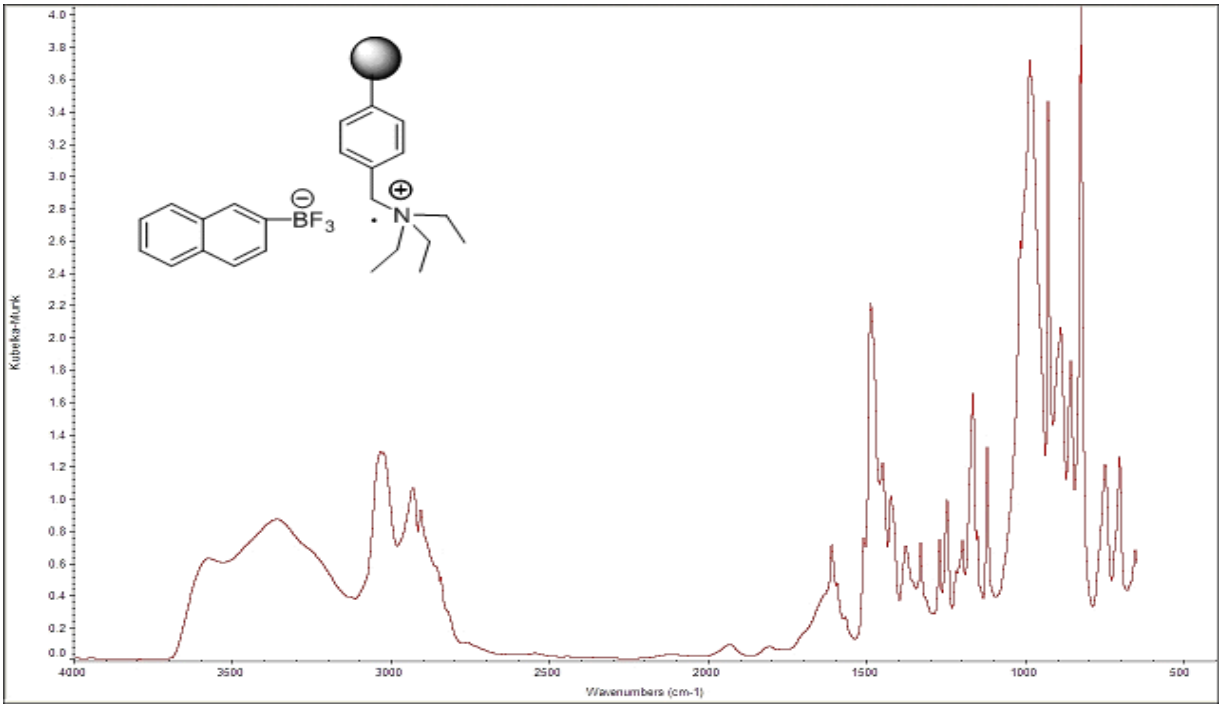


3. IR study:

A, IR spectrum of Dowex resin bearing quaternary ammonium hydroxide moieties

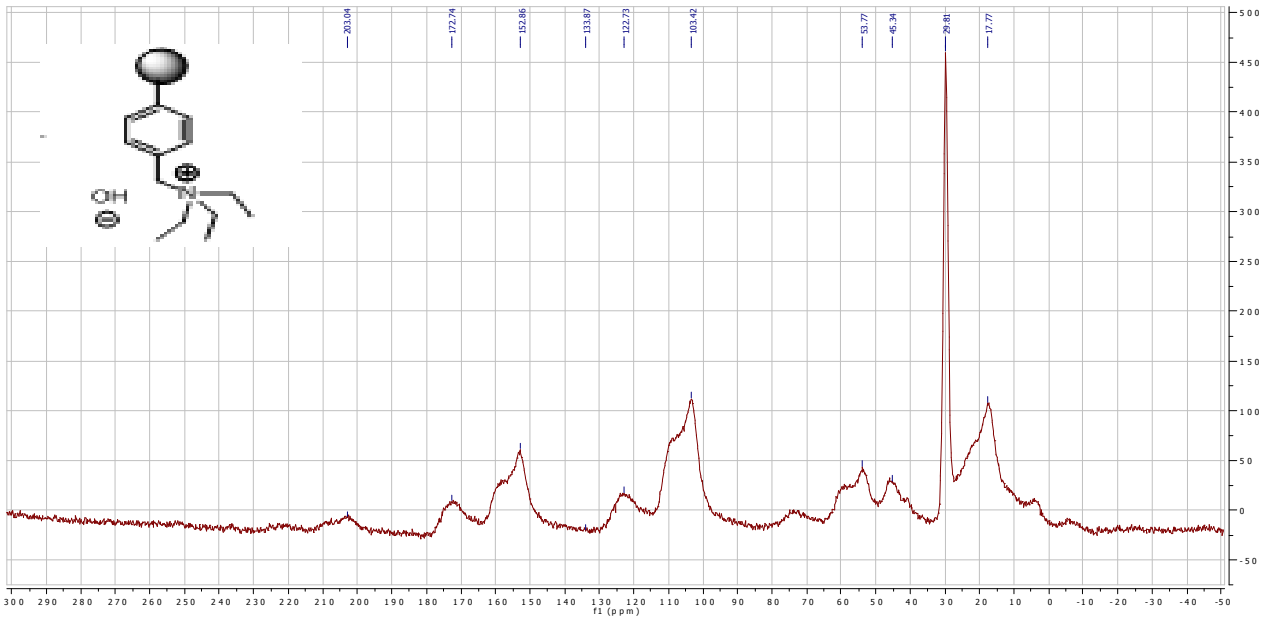


B. IR spectrum of Dowex-supported 2-naphthylenyltrifluoroborate salt

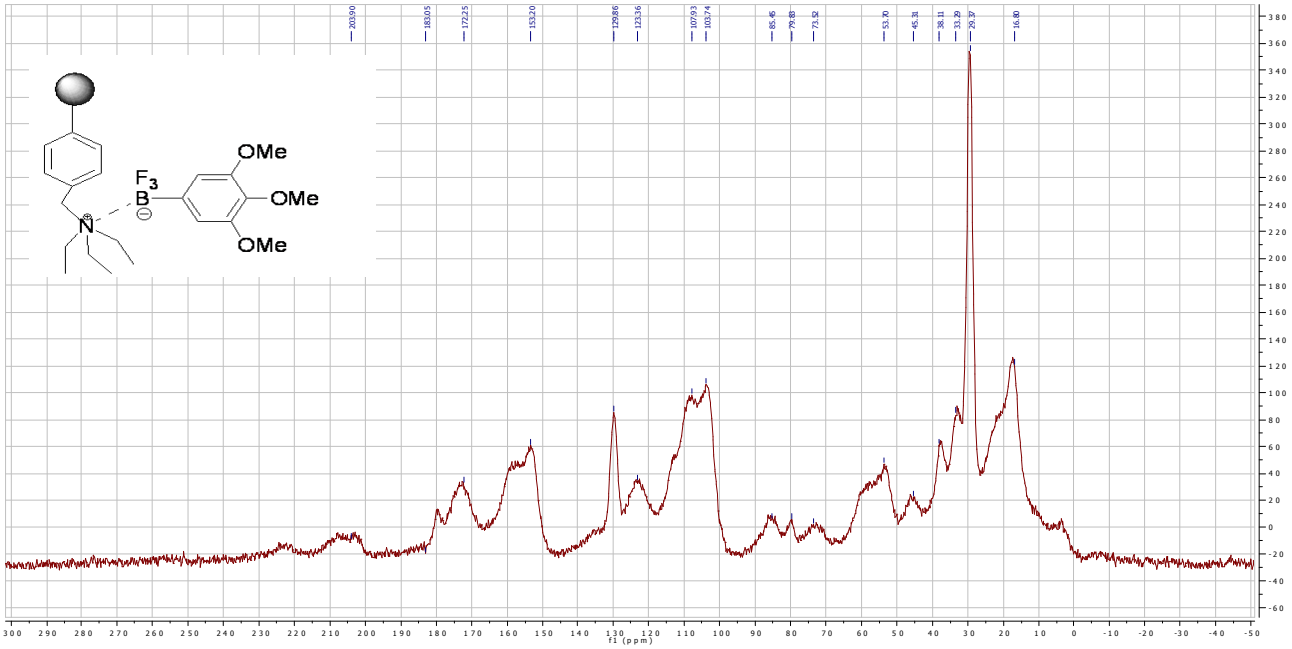


4. NMR study

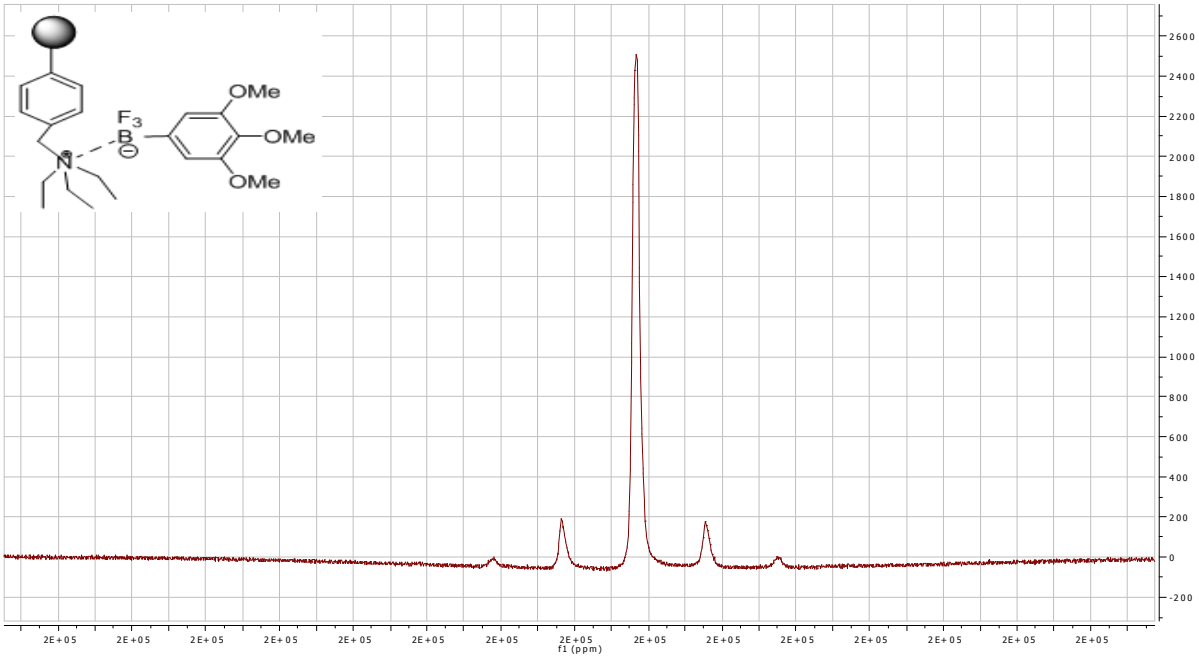
A.. Solid-state ^{13}C-NMR of Dowex resin bearing quaternary ammonium hydroxide moieties:



B. Solid-state ^{13}C-NMR study of Dowex-supported 3,4,5-trimethoxyphenyl BF_3K salt (57.8 ppm and 65.6 ppm, which confirms the presence of the OMe group in the polymer supported material)



C. Solid-state ^{11}B NMR of Dowex-supported 3,4,5-trimethoxyphenyl BF_3K salt



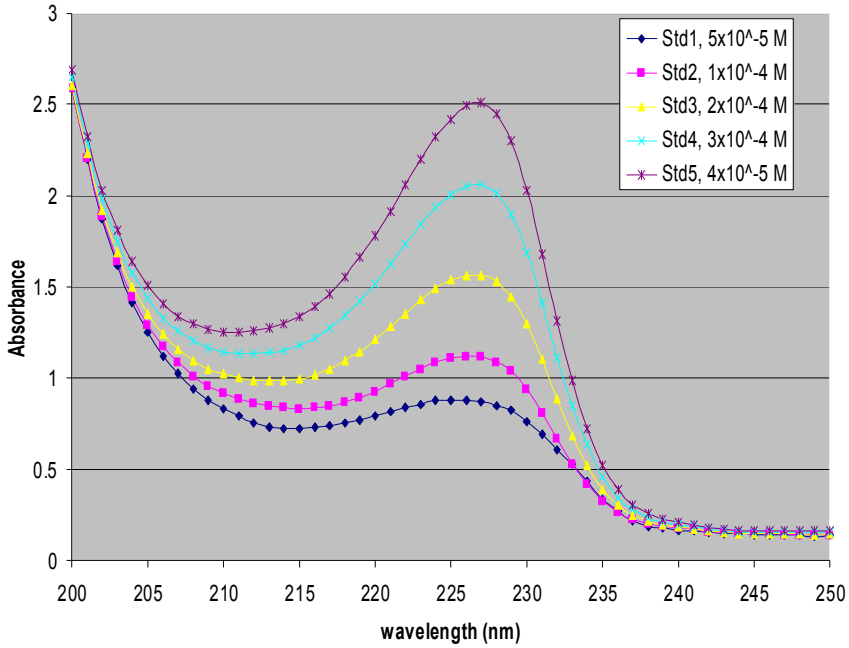
5. Determination of the maximum loading of Ar-BF_3^- on the Dowex surface through an UV/*vis* spectorsopic analysis.

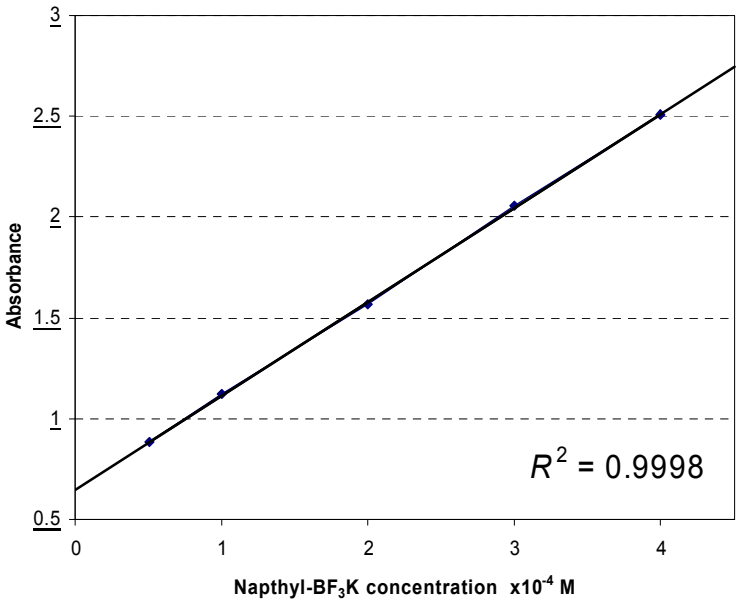
To determine the maximum loading of Ar-BF_3^- on the Dowex surface, two series of experiments were carried out using two different potassium organotrifluoroborates.

A.. Study *A* using potassium 2-naphthelenyltrifluoroborate:

Potassium 2-naphthelenyltrifluoroborate 234 mg (1.0 mmol) was dissolved in methanol (40 mL). The solution was carefully to a 100 mL volumetric flask. Then DI water (40 mL) was added to this solution. DI water and methanol (*v*/*v* 1:1) were added to attain a total volume of 100 mL. Afterwards, 0.25 ml, 0.5 ml, 1 ml, 1.5 ml and 2 ml of the solution was taken and placed in 5 volumetric flasks (50 ml) separately. To all of flasks co-solvent [DI water and methanol (*v*/*v* 1:1)] was added to reach the volume of 50 ml.

Five standard samples obtained were then subjected to the UV/*vis* study.

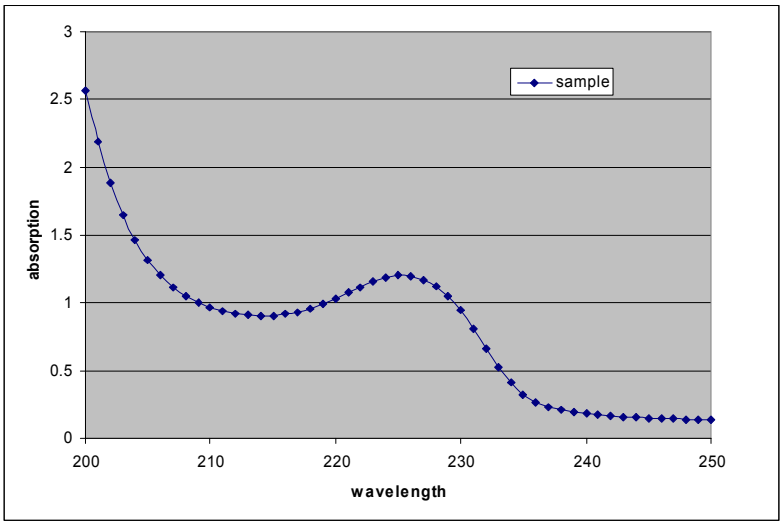




Calibration plot: **y = 0.4656x + 0.649**

Control experiment: Dowex (1.0 g) was added to potassium 2-naphthelenyltrifluoroborate (1.0 mmol) in methanol-water (*v*/*v* 1:1, 20 mL). After completion of the reaction (monitored by pH

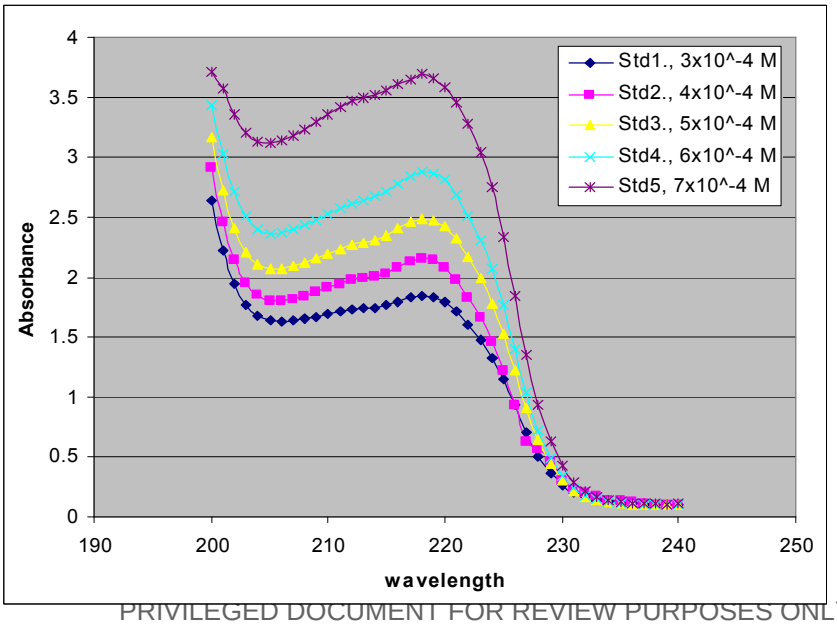
meter), the Dowex-supported aryltrifluoroborate was filtered off and washed thoroughly with methanol-water (*v*/*v* 1:1, 60 mL). The filtrate was diluted to 100 mL using 50% aqueous methanol and 200 µL of this solution was taken and again diluted to 10 mL using 50% aqueous methanol and analyzed by UV/vis spectroscopy.

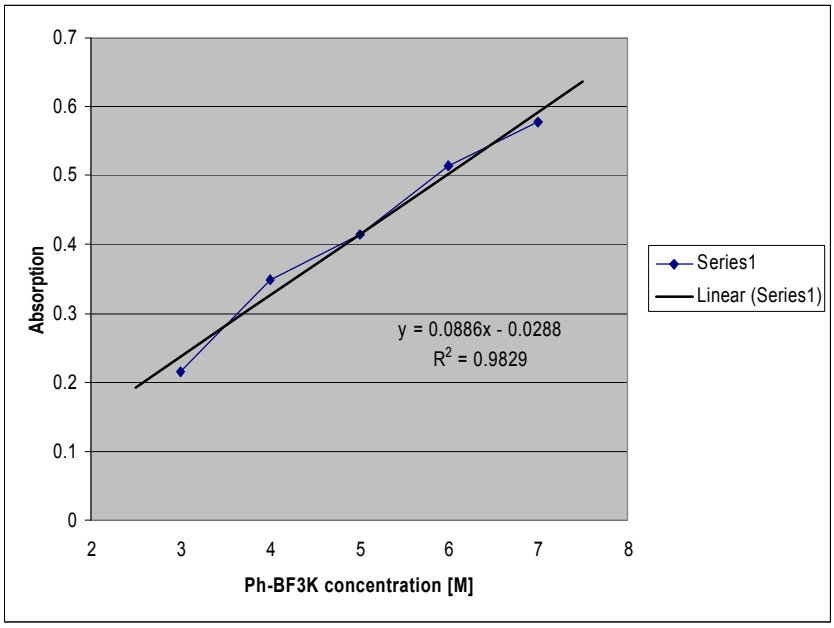


Based on the UV absorbance (1.201Å) of the diluted reaction sample, based on the calibration plot the quantity of unreacted potassium 2-naphthelenyltrifluoroborate in the original filtrate (from the control experiment) was calculated to be 0.59 mmol. Therefore, the maximum loading amount is 0.41 mmole of organotrifluoroborate per 1 g of Dowex polymer.

5b. Study *B* using phenyltrifluoroborate:

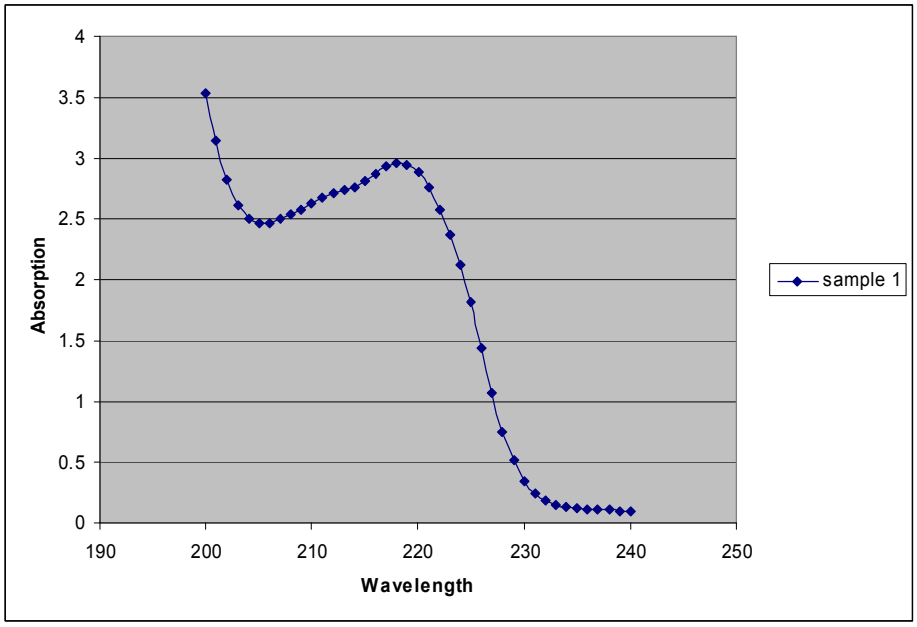
For the preparation of the five standard samples and the control experiment, see study A in 5a.





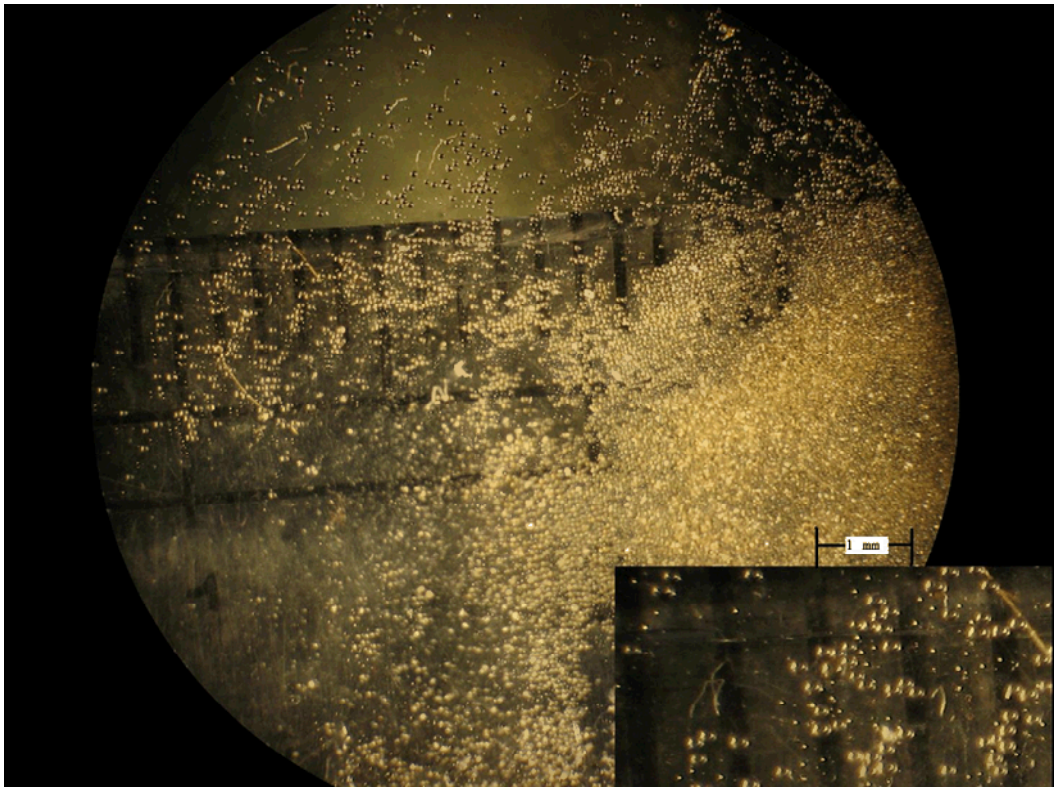
Calibration plot: **y = 0.0886x – 0.0288**

Control experiment: Dowex (1.0 g) was added to potassium 2-phenyltrifluoroborate (1.0 mmol) in methanol-water (*v*/*v* 1:1, 20 mL). After completion of the reaction (monitored by pH meter), the Dowex-supported aryltrifluoroborate was filtered off and washed thoroughly with methanol-water (*v*/*v* 1:1, 60 mL). The filtrate was diluted to 100 mL using 50% aqueous methanol and 1 mL of this solution was taken and again diluted to 10 mL using 50% aqueous methanol and analyzed by UV/vis spectroscopy.

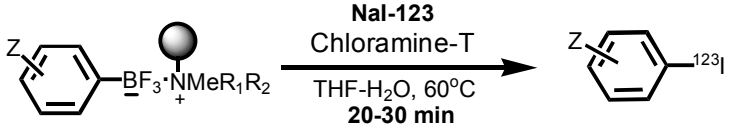


Based on the UV absorbance (0.497Å) of the diluted reaction sample and the calibration plot, the quantity of unreacted potassium phenyltrifluoroborate in the original filtrate (from the control experiment) was calculated to be 0.61 mmol. Therefore, the maximum loading amount is 0.39 mmole of organotrifluoroborate per 1 g of Dowex polymer.

6. The appearance of Dowex-supported BF_3 salts under a microscope (enlarged 70 times). The diameter of these beads are approcimately 0.1 mm.



7. Radioiodination of resin-supported $ArBF_3$ salts



A suspension of Dowex supported organotrifluoroborate (10 mg in 0.5 mL of 33% aqueous THF) was placed in a 2 mL Wheaton vial containing no-carrier-added $Na^{123}I$ (1.0 mCi in 0.1% aqueous NaOH). Chloramine-T (1.0 mg) was added to the reaction vial which was sealed and covered with aluminum foil. The reaction mixture was stirred for 20-30 min at 60 ^{o}C and then aqueous sodium thiosulfite (100 μL of a 1.0 x 10^{-4} M solution) was added to destroy residual molecular iodine. The product was extracted into hexane-ethyl acetate (v/v, 20:1, 1 mL) and then purified by passing it through a silica gel cartridge using hexanes as eluant. The total synthesis time was about 40-50 min. The radiochemical yield is shown below.