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SCIENTIFIC REPORT

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Visit Period: 15.07.2007-11.10.2007

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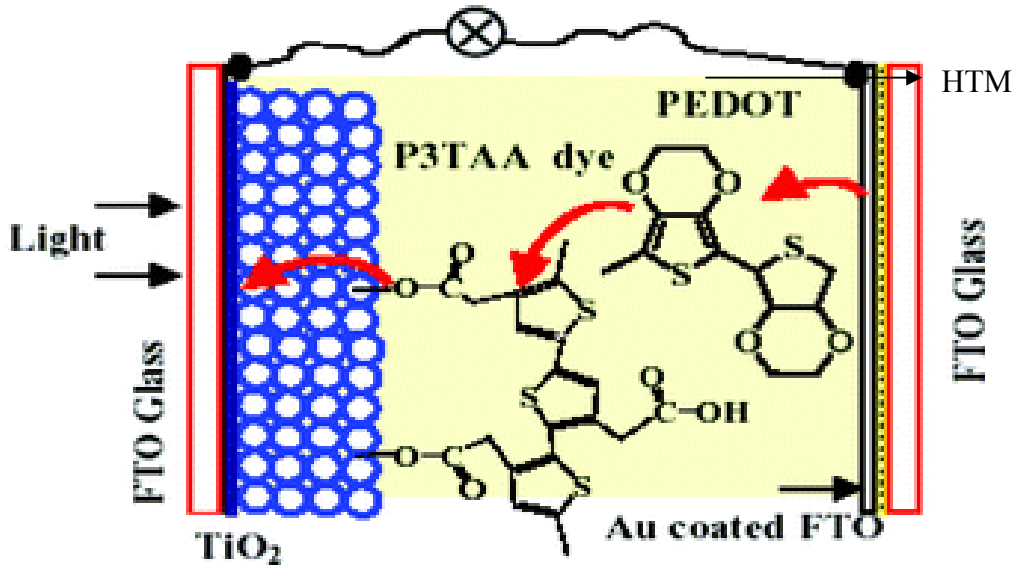
Introduction

Unlike conventional p-n junction solar cells, a dye sensitized solar cell (DSC) employs a dye-sensitized nanocrystalline porous semiconductor metal oxide infiltrated by a hole transporting matrix or liquid electrolyte. Light absorption by the sensitizer (S) is followed by injection of an electron into the conduction band of the oxide. The dye is regenerated from the resulting oxidized state (S^+) by electron donation from a redox mediator present in the electrolyte. So far the I^- / I_3^- has almost exclusively been used as redox couple reaching a conversion efficiency of over 11 % in standard global AM 1.5 solar light under standard conditions.[1]

A drawback of the I^- / I_3^- system is the mismatch between its redox potential (0.4 V vs. NHE) and that of the sensitizer (ca. 1 V versus NHE) resulting in an excessive driving force of 0.6 eV for the dye regeneration process. Because the energy loss

incurred during dye regeneration is one of the main factors limiting the performance of current dye sensitized solar cells, the search for alternative redox couples with a more positive redox potential than I^- / I_3^- is a current research topic of high priority. Reversible mediators such as ferrocene/ferrocenium yield a low photo-voltage and small photocurrents due to the rapid back reaction of injected electrons with the Fe(III) species.[2, 3] Co(II) complexes show an impressive efficiency of 8% at low light intensity but their performance drops markedly under full sun illumination.[4,5] A combination of two mediators, operating in series to regenerate the dye and transport the positive charges to the counter electrode has recently produced interesting results. [6] However to date, the solar to electric power conversion efficiency achieved with all these systems in full AM 1.5 sun light still remains well below 5%.



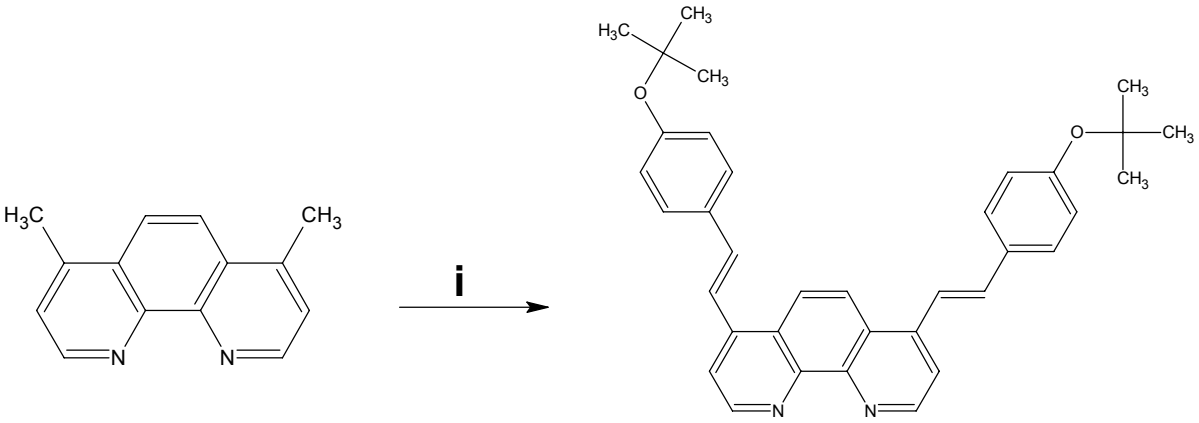
Solid State Solar Cells

In this study, we planned to synthesize some organic molecules for solid state dye sensitized organic solar cells. During the project work, methyl purine, 4-Chloro TEMPO, TEMPO Potassium Salt, TEMPO Sodium Salt, Phenoxazine Sodium Salt and Phenoxazine Potassium Salt were synthesized and structural analysis were carried out with ^{1}H-NMR and ^{13}C- NMR spectra. Four different synthetic route were

used to synthesize Phenoxazine Potassium Salt. Structural analysis and experimental details were given below.

Experiments and Analysis

Synthesis of Phenatroline with 4-t-butoxy-benzaldehyde



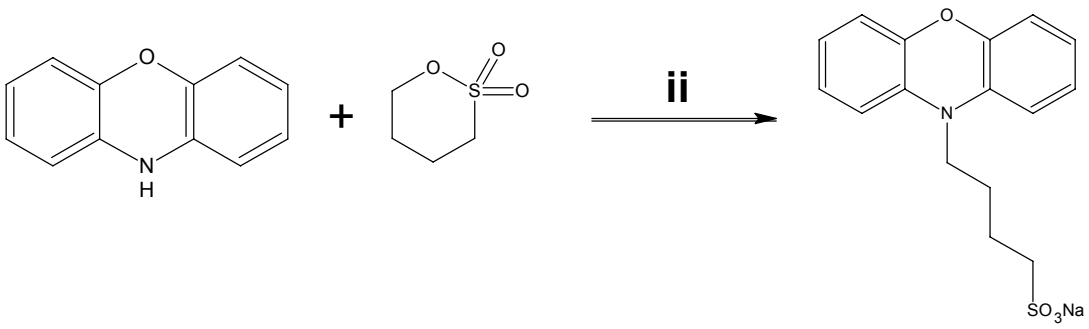
i: 4-Tert-Butoxy-Benzaldehyde, K-tBuO, DMF

	M_W(g)	M(mol)	m(g)	V(ml)
4,7-dimethly-1,10-Phenantroline	208	0.002	0.4	-
4-Tert-Butoxy-Benzaldehyde	178	0.0049	0.873	-
DMF	-	-	-	20
K-tBuO	112	0.0078	0.873	-

Procedure:

Solid tert-BuOK (0.873 g, 0.0078mol) was added to a solution of 4,7-dimethyl-1,10-phenantroline (0.4 g, 0.002mol) and 4-tert-butoxybenzaldeyde (0.873 g, 0.0049mol) in anhydrous DMF (20ml). The resulting mixture was stirred 24 h at room temperature under argon. The solvent evaporated, and methanol (200ml) was added. The insoluble solid was filtered on a sintered crucible and recrysallized from hot acetic acid, filtered, and washed with methanol to obtain brown product. NMR results showed that the reaction was unsuccessful.

Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate sodium salt



ii:NaH, DMF

	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine	183	0.0049	0.9	-
1,4-butane sultone	136	0.05	0.669	-
NaH	24	0.0089	0.2142	-
DMF	-	-	-	20

Procedure:

Solid NaH (0.2142 g, 0.0089 mol) was added in small portions into a solution of phenoxazine (0.9 g, 0.0049 mol) in dry DMF (20 ml). After the generation of hydrogen gas subsided, the reaction mixture was stirred at room temperature for 50 min, and then 1,4-butane sultone (0.669 g, 0.05 mol) was introduced into the reaction through the septum via a syringe. The resulting mixture was subsequently stirred at room temperature for 20 h, diluted with CH_2Cl_2 (15 ml), and filtered to give a pale pink powder. The crude product was dissolved in a minimum amount of methanol and precipitated out with EtOAc. The precipitate was filtered and washed with EtOAc to give the desired product phenoxazine sodium salt (0.84 g, 93%). NMR results showed that the reaction was successful

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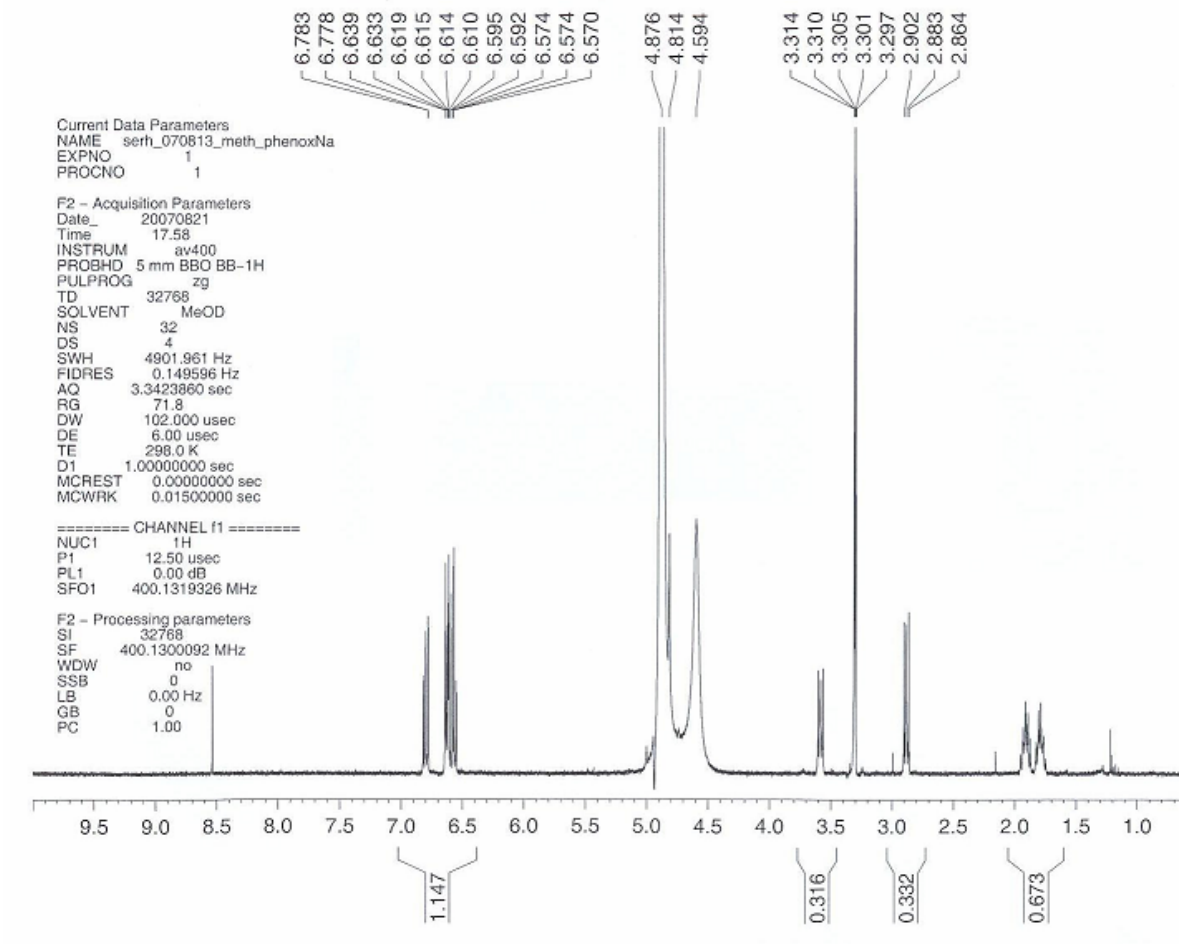
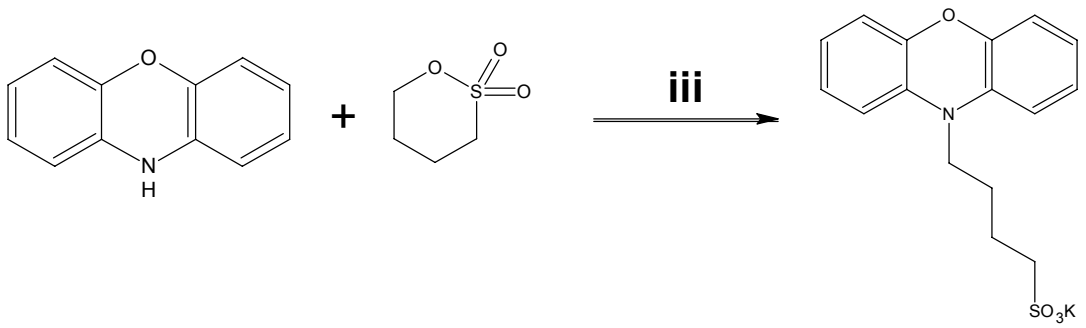


Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate potassium salt



iii:K-tBuO, DMF

	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine	183	0,0027	0,500	-
1,4-butane sultone	136	0,0027	0,372	-
K-tBuO	112	0,0028	0,315	-
DMF	-	-	-	15

Procedure:

Solid K-tBuO (0.315 g, 0.0028 mol) was added in small portions into a solution of phenoxazine (0.5 g, 0.0027 mol) in dry DMF (15 ml). After the generation of hydrogen gas subsided, the reaction mixture was stirred at room temperature for 50 min, and then 1,4-butane sultone (0.372 g, 0.0027 mol) was introduced into the reaction through the septum via a syringe. The resulting mixture was subsequently stirred at room temperature for 22 h, diluted with CH_2Cl_2 (10 ml), and filtered to give a pale brown powder. The crude product was dissolved in a minimum amount of methanol and precipitated out with EtOAc. The precipitate was filtered and washed with EtOAc to give the desired product phenoxazine potasium salt (0.48 g, 96%). NMR results showed that the reaction was successful

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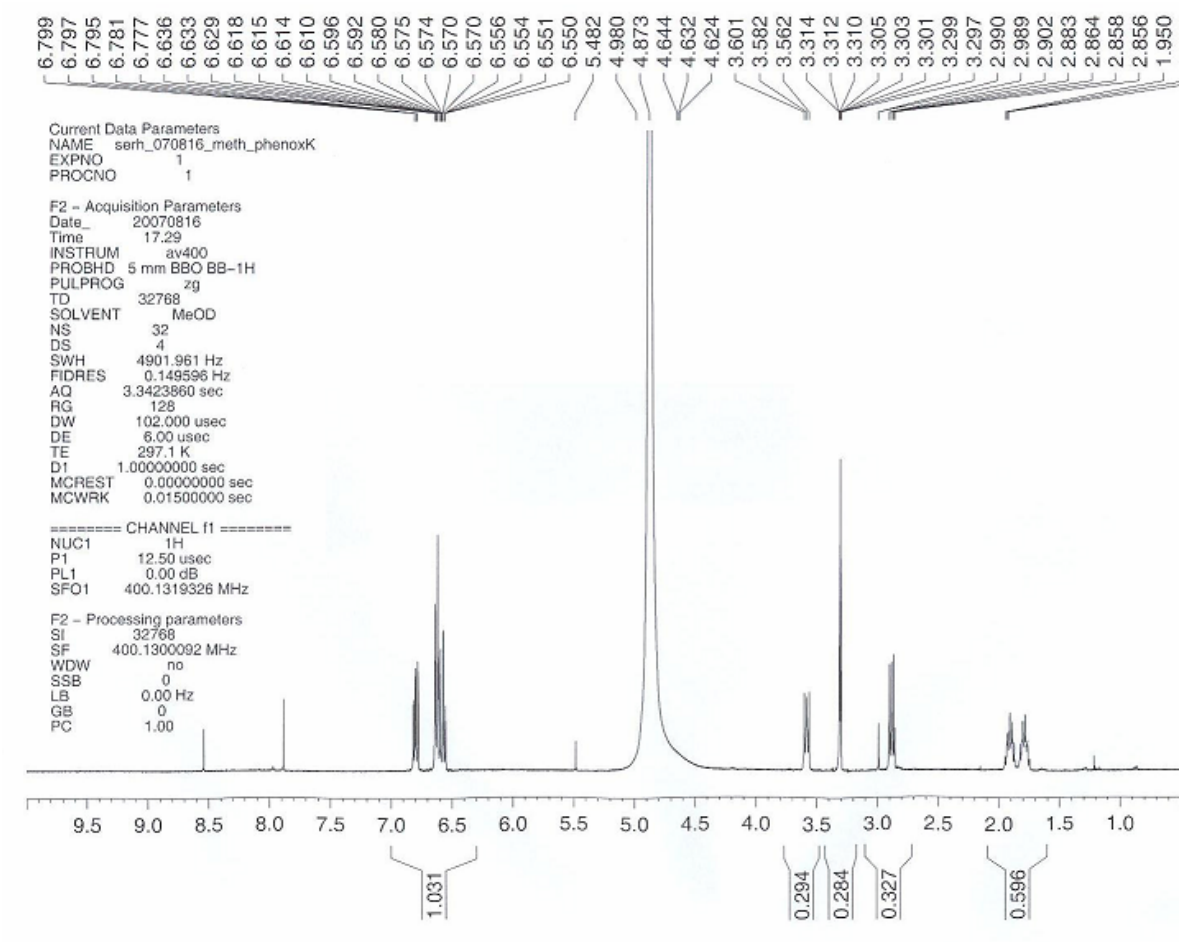
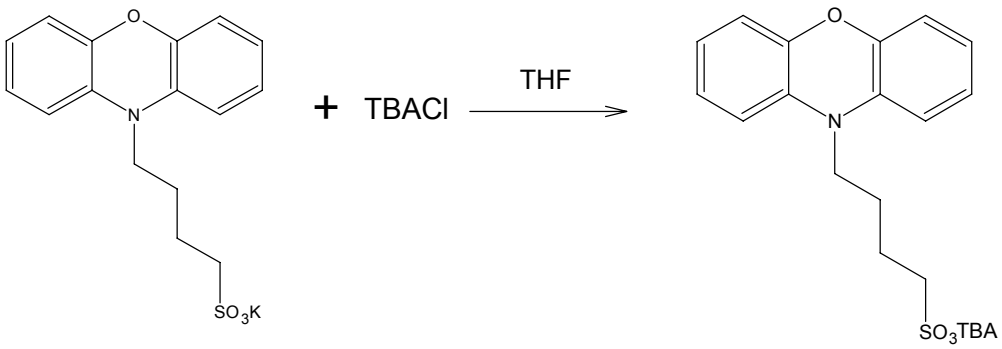


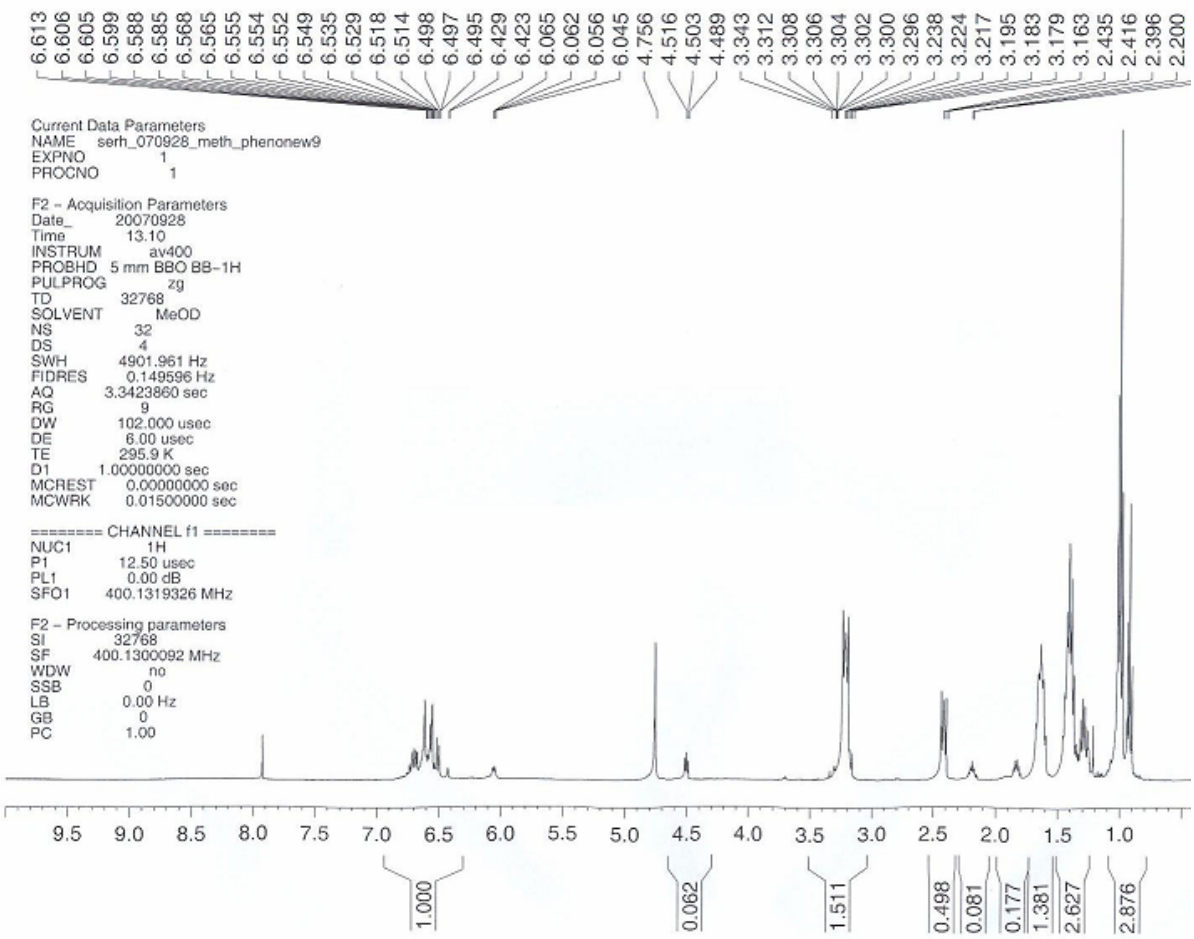
Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate tetrabutylammonium(TBA) salt-1



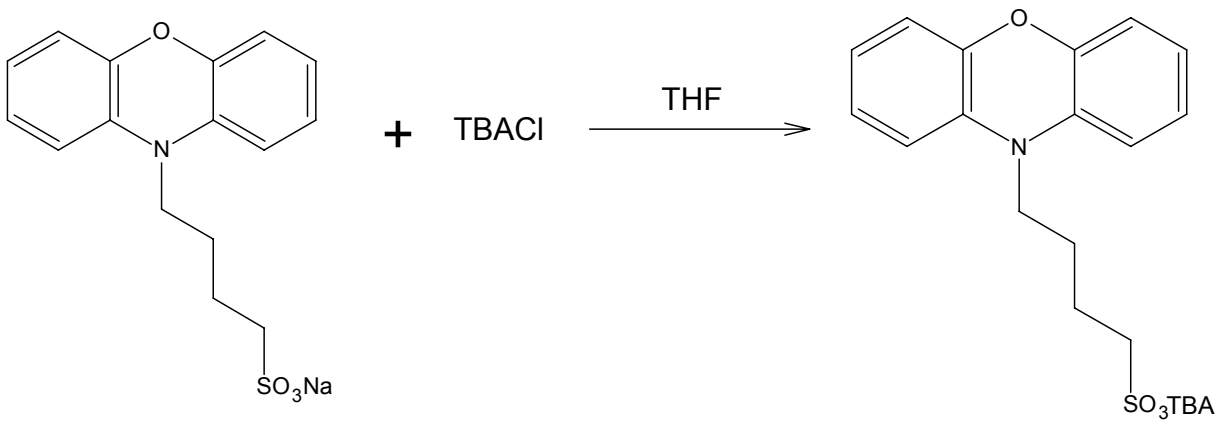
	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine potassium salt	357	0,0022	0,75	-
TBACl	277	0,0022	0,58	-
THF	-	-	-	30

Procedure:

A mixture of phenoxazine potassium salt (0.75 g, 0.0022mol) in THF (30mL) was stirred at room temperature for 24 h. Then, TBACl (0.58 g, 0.0022mol) was added in small portions during 1 h. The mixture was vigorously stirred under argon atmosphere for 24 h. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of methanol and product was recrystallized from Et_2O. The precipitate was filtered and gave the desired product phenoxazine TBA salt. NMR results showed that the reaction was unsuccessful.



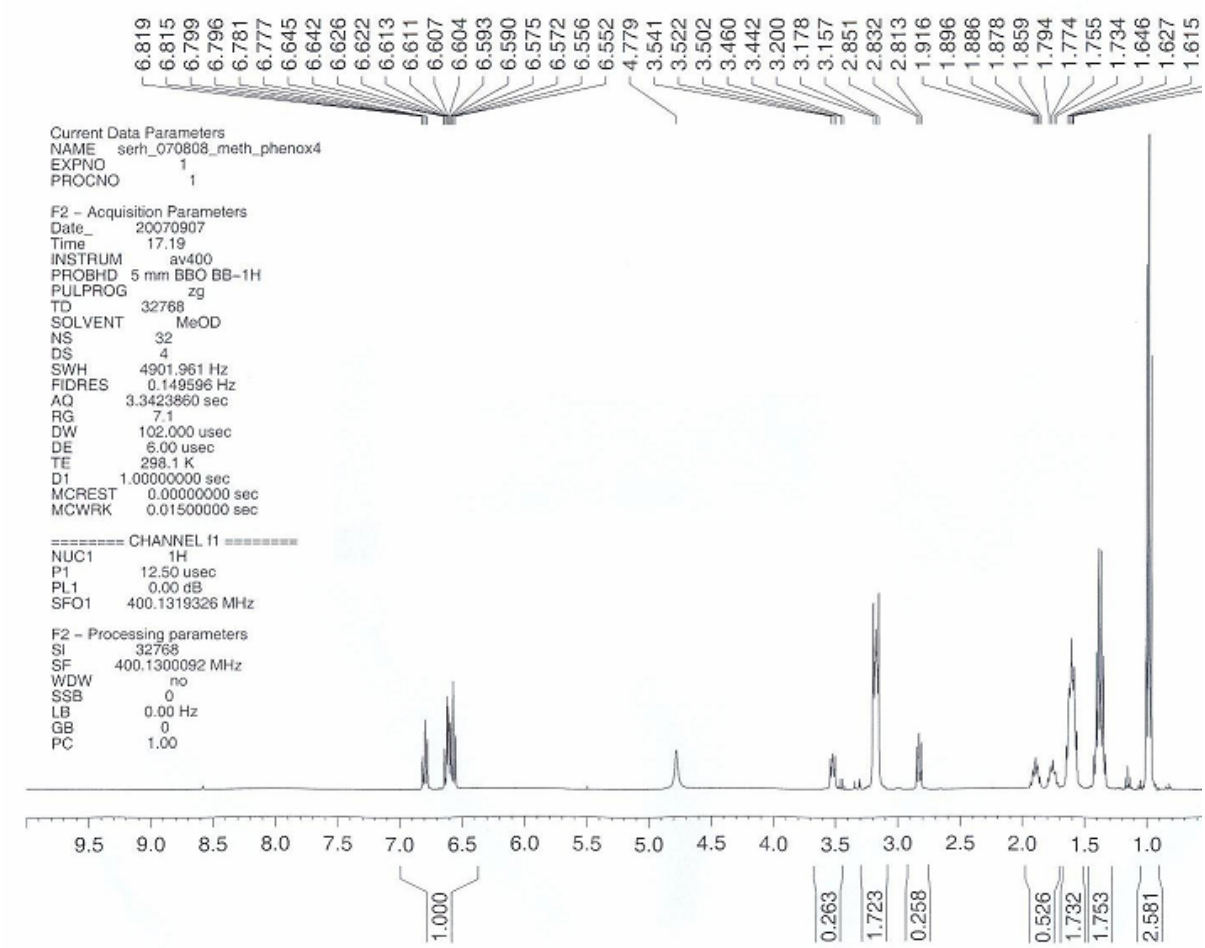
Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate tetrabutylammonium(TBA) salt-2



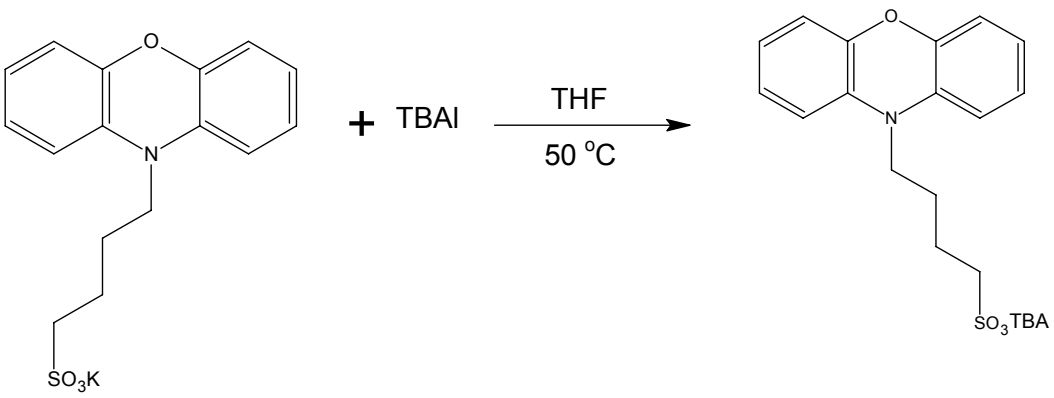
	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine sodium salt	341	0,0035	1,200	-
TBACl	277	0,0036	0,974	-
THF				45

Procedure:

A mixture of phenoxazine sodium salt (1.2 g, 0.0035mol) in THF (45mL) was stirred at room temperature for 24 h. Then, TBACl (0.974 g, 0.0036mol) was added in small portions during 1 h. The mixture was vigorously stirred under argon atmosphere for 24 h. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of $CHCl_3$ and product was recrystallized from Et_2O. The precipitate was filtered and gave the desired product phenoxazine TBA salt. NMR results showed that the reaction was unsuccessful.



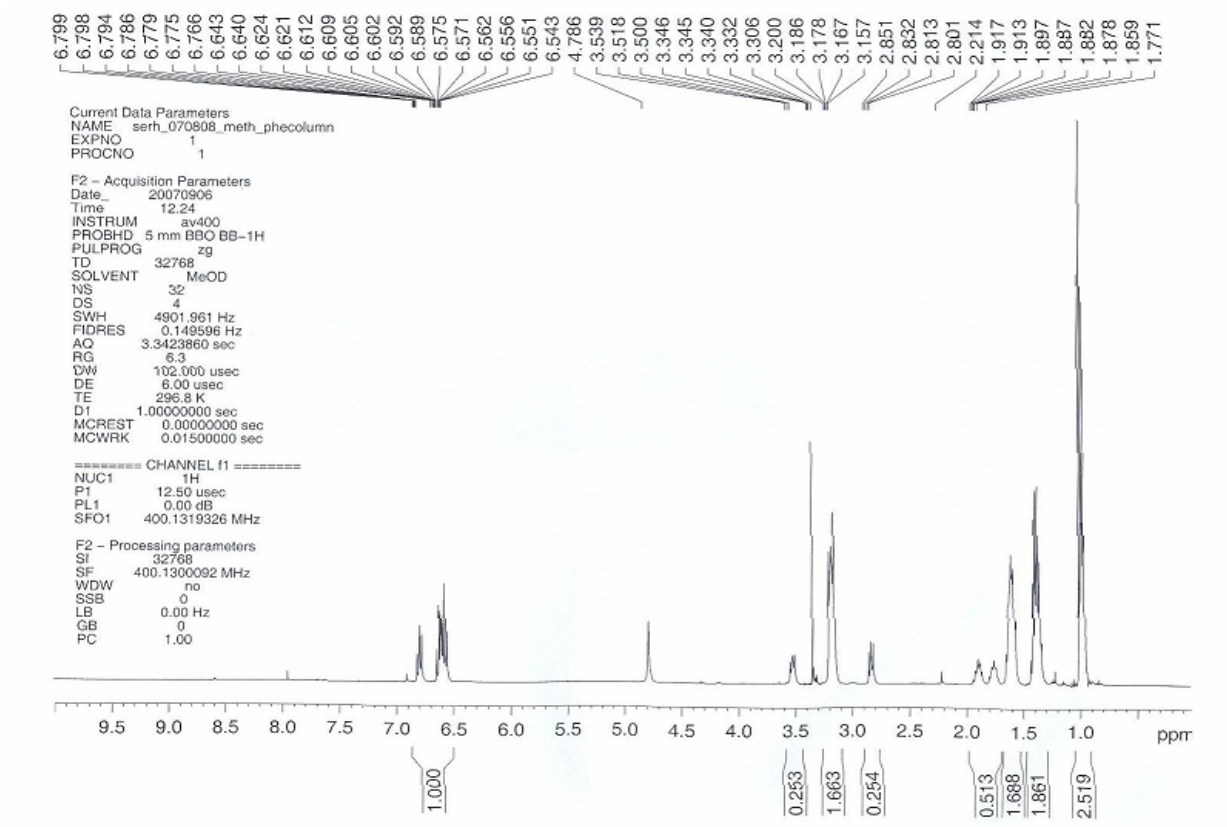
Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate tetrabutylammonium(TBA) salt-3



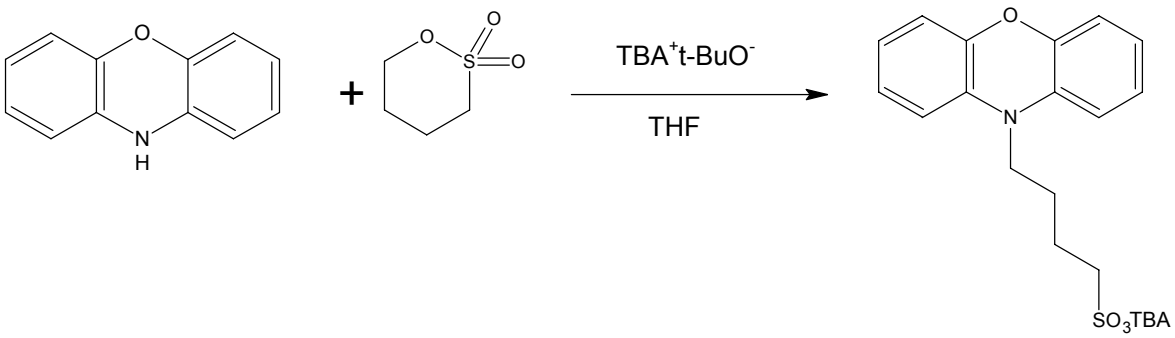
	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine salt	357	0,0014	0,50	-
TBAI	369	0,0014	0,52	-
THF	-	-	-	30

Procedure:

A mixture of phenoxazine potassium salt (0.5 g, 0.0014mol) in THF (30mL) was stirred 50 ^{o}C temperature for 24 h. Then, TBAI (0.52 g, 0.0014mol) was added in small portions during 1 h. The mixture was vigorously stirred under argon atmosphere for 24 h. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of CH_2Cl_2 and product was recrystallized from Et_2O. The precipitate was filtered and gave the desired product phenoxazine TBA salt. NMR results showed that the reaction was unsuccessful.



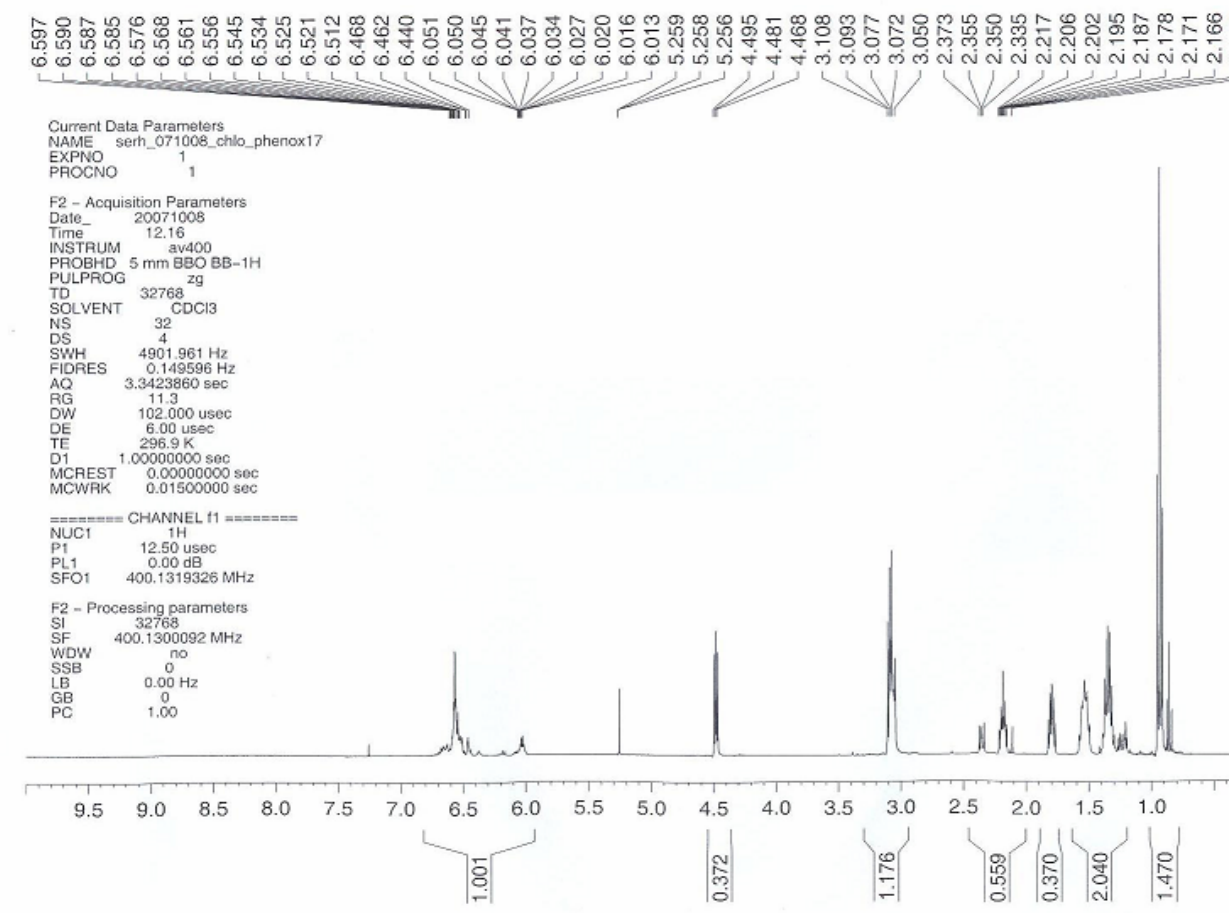
Synthesis of 4-(10H-phenoxazin-10-yl)butane-1-sulfonate tetrabutylammonium(TBA) salt-4



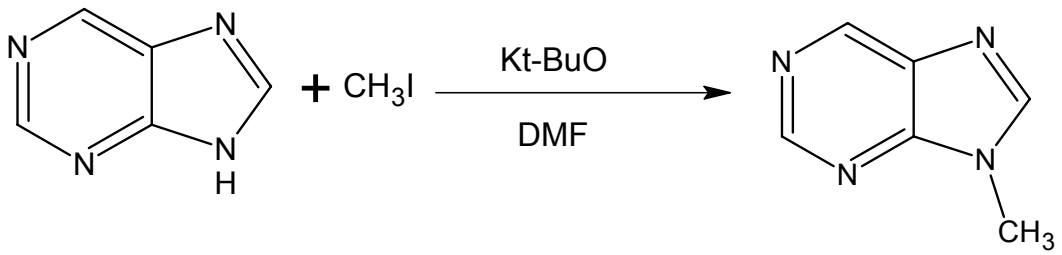
	M_W(g)	M(mol)	m(g)	V(ml)
Phenoxazine	183	0,0027	0,5	-
1,4-butane sultone	136	0,0027	0,372	-
$TBA^+t\text{-}BuO^-$	315	0,0028	0,315	-
THF	-	-	-	23

Procedure:

To a solution of phenoxazine(0.5 g, 0.0027mol) in anhydrous THF (23 ml) was added $TBA^+t\text{-}BuO^-$(0.315 g, 0.0028 mol) and the resulting slurry stirred for 50 min at room temperature. 1,4-butane sultone (0.372 g, 0.0027 mol) was then added and stirred for 24 h at room temperature. The solvent was removed under reduced pressure and methanol (5ml) was added to dissolve the solid. The organic mixture was recrystallized from CH_2Cl_2 (7ml). After filtration of the organic mixture, dark brown oil was obtained. NMR results showed that the reaction was successful



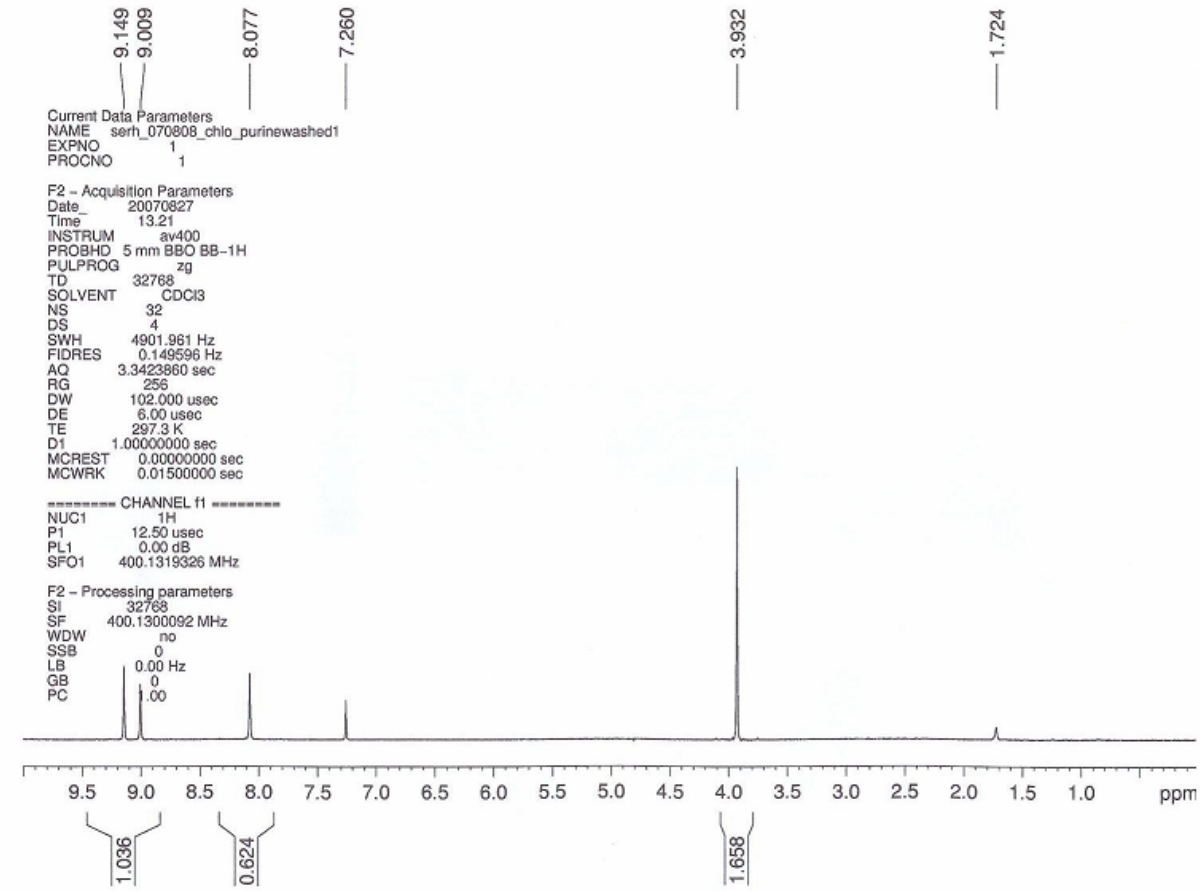
Synthesis of methyl purine



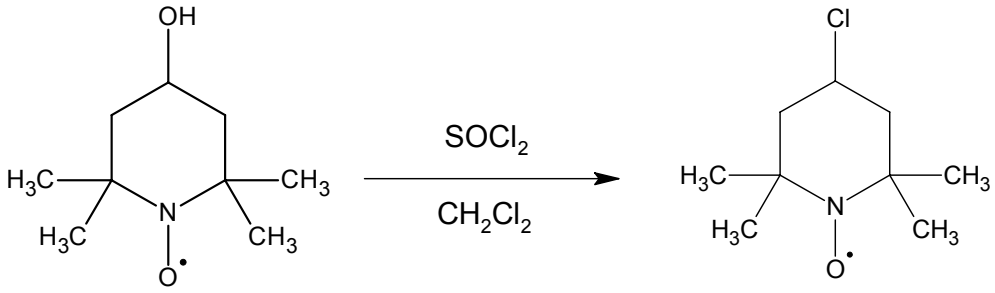
	M_W(g)	M(mol)	m(g)	V(ml)
Purine	120	0,0027	0,5	-
CH_3I	141	0,0027	0,372	-
K-tBuO	112	0,0028	0,315	-
DMF	-	-	-	15

Procedure:

A solution of purine (0.5 g, 0.0027mol) in dry DMF (10ml) was added dropwise to a suspension of K-tBuO (0.372 g, 0.0027mol) in dry DMF (3ml). This mixture was stirred for 50 min at room temperature, after which a solution of methyl iodide (0.372 g, 0.0028mol) in DMF (2ml) was added slowly. After stirring 24 h, the DMF was removed in vacuo and the crude product purified by column chromatography. (eluted with 9:1 $CHCl_3$:MeOH). NMR results showed that the reaction was successful.



Synthesis of 4-Chloro TEMPO



	M_W(g)	M(mol)	m(g)	V(ml)
TEMPO	172	0.0058	1.00	
$SOCl_2$	118,9	0.0058	0.69	
CH_2Cl_2	-	-	-	35

Procedure:

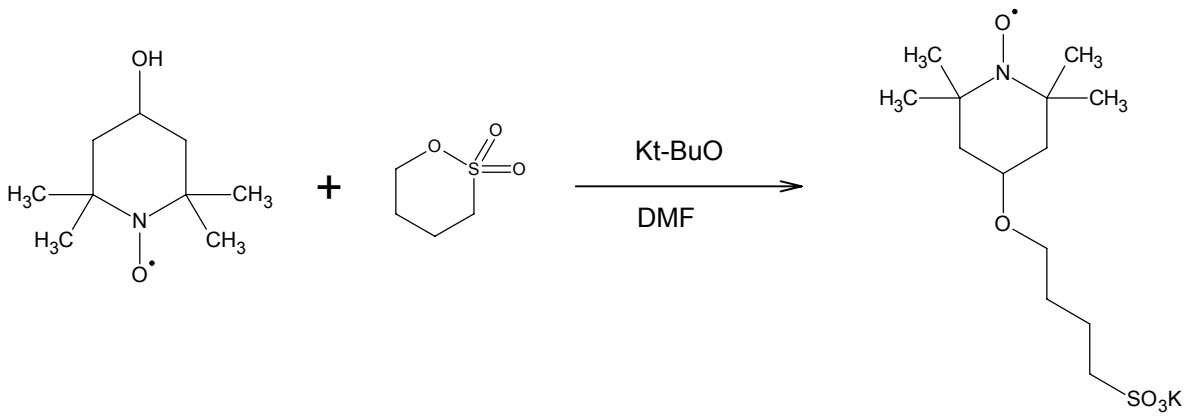
To a solution of 4-hydroxy-TEMPO (1 g, 0.0058 mol) in anhydrous CH_2Cl_2(35ml) was added Kt-BuO(0.49 g, 0.0048 mol) and the resulting slurry stirred for 45 min at room temperature. 1,4-butane sultone(0.61 g, 0.0043 mol) was then added and stirred for 6 h at room temperature. The solvent was removed under reduced pressure and methanol (30 ml) was added to dissolve the solid. The organic mixture was diluted with Et_2O (15 ml). After filtration of the organic mixture, red oil was obtained.

$C_9H_{17}Cl^{\bullet}$

Anal. Calcd for $C_9H_{17}Cl^{\bullet}$:C 56.69, H 8.99, N 7.35

Found: C 47.27, H 11.05, N 6.38

Synthesis of 4-[(2,2,4,4 tetrametylpiperidin-4-yl)oxy]butane-1-sulfonate potassium salt



	M_W(g)	M(mol)	m(g)	V(ml)
TEMPO	172	0.0043	0.75	
1,4-butane sultone	136	0.0043	0.61	
K-tBuO	112	0.0048	0.49	
DMF	-	-	-	20

Procedure:

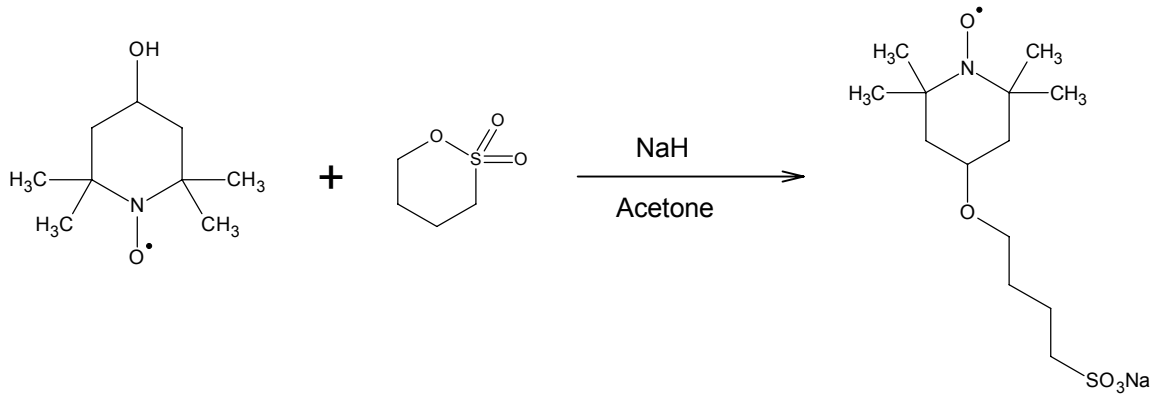
To a solution of 4-hydroxy-TEMPO (0.75 g, 0.0043 mol) in anhydrous DMF (20 ml) was added Kt-BuO(0.49 g, 0.0048 mol) and the resulting slurry stirred for 45 min at room temperature. 1,4-butane sultone (0.61 g, 0.0043 mol) was then added and stirred for 6 h at room temperature. The solvent was removed under reduced pressure and methanol (30 ml) was added to dissolve the solid. The organic mixture was diluted with Et_2O (15 ml). After filtration of the organic mixture, red oil was obtained.

$C_{13}H_{25}NKO_5S^{\bullet}$

Anal. Calcd for $C_{13}H_{25}NKO_5S^{\bullet}$: C 45.06, H 7.27, N 4.04.

Found: C 41.01, H 7.26, N 4.31

Synthesis of 4-[(2,2,4,4 tetrametylpiperidin-4-yl)oxy]butane-1-sulfonate sodium salt



	M_W(g)	M(mol)	m(g)	V(ml)
TEMPO	172	0,0052	0,900	
1,4-butane sultone	136	0,0052	0,711	
NaH	24	0,0052	0,209	
Acetone	-	-	-	25

Procedure:

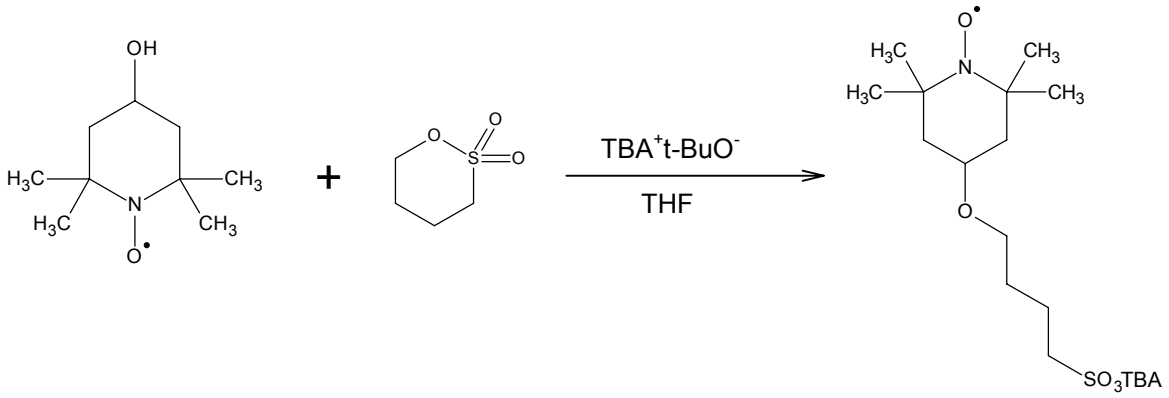
To a solution of 4-hydroxy-TEMPO (0.9 g, 0.0052 mol) in anhydrous acetone (25 ml) was added NaH (0.209 g, 0.0052 mol) and the resulting slurry stirred for 45 min at room temperature. 1,4-butane sultone (0.711 g, 0.0052 mol) was then added and stirred for 8 h at room temperature. The acetone was removed under reduced pressure and methanol (45 ml) was added to dissolve the solid. The organic mixture was diluted with Et_2O (25 ml). After filtration of the organic mixture, orange oil was obtained.

$C_{13}H_{25}NNaO_5S^{\cdot}$

Anal. Calcd for $C_{13}H_{25}NNaO_5S^{\cdot}$: C 47.26, H 7.63, N 4.24.

Found: C 48.82, H 9.901, N 4.48

Synthesis of 4-[(2,2,4,4 tetrametylpiperidin-4-yl)oxy]butane-1-sulfonate tetrabutylammonium(TBA) (uncompleted)



	M_W(g)	M(mol)	m(g)	V(ml)
TEMPO	172	0.0052	0.900	-
1,4-butane sultone	136	0.0052	0.707	-
$TBA^+t\text{-}BuO^-$	315	0.0058	1.827	-
THF	-	-	-	30

Procedure:

To a solution of 4-hydroxy-TEMPO (0.9 g, 0.0052 mol) in anhydrous THF (30 ml) was added $TBA^+t\text{-}BuO^-$(1.827 g, 0.0058 mol) and the resulting slurry stirred for 45 min at room temperature. 1,4-butane sultone (0.707 g, 0.0052 mol) was then added and stirred for 8 h at room temperature. The solvent was removed under reduced pressure and methanol (40 ml) was added to dissolve the solid. The organic mixture was diluted with Et_2O (25 ml). After filtration of the organic mixture, reddish oil was obtained.

REFERENCES

(1) (a) Nazeeruddin, M.K.; De Angelis ,F.; Fantacci ,S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Bessho, T.; Grätzel, M. *J. Am. Chem. Soc.* 2005, *127*, 16835. (b) Grätzel, M. *Chem. Lett.* 2005, *34*, 8. (c) Chiba, Y., Islam, A.; Watanabe, Y; Komiya, R.; Koide, N.; Han, L. *Japanese Journal of Appl. Phys., Part 2: Letters & Express Letters*, 2006, *45*, 24.

(2) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. R. *J. Phys. Chem. B* 2001, *105*, 1422.

(3) Gregg, B. A. *Coord. Chem. Rev*. 2004, *248*, 1215.

(4) (a) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Graetzel, M. *J. Phys. Chem. B* 2001, *105*, 10461. (b) Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J.-E.; Graetzel, M. *Chem. Eur.J.* 2003, *9*, 3756.

(5) Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc.* 2002, *124*, 11215

(6) Cazzanti, S.; Caramori, S.; Argazzi, R.; Elliott, C.M.; Bignozzi, C.A. *J. Am. Chem. Soc.* 2006, *128*, 9996.

(7) Nishide, H.; Suga, T. *Interface,* 2005, *14(4)*, 32.