

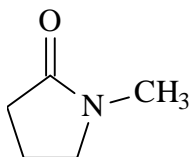
# CHAPTER 3 EXPERIMENTAL

## 3.1 Materials

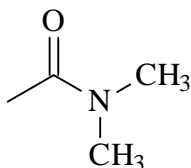
Solvent, monomer and reagent purity were obviously all important factors for the synthesis of high molecular weight polyimides. Therefore, purification of these materials was rigorous. Pure, anhydrous solvents were assured by distillation, either under vacuum or nitrogen, from a flask containing the solvent and a dehydrating agent. The glassware, monomers and reagents were also carefully purified and dried before use.

### 3.1.1 Solvents

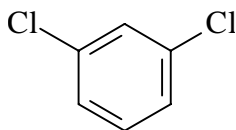
1-Methyl-2-Pyrrolidinone (NMP: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 205°C/760mmHg, 82°C/10mmHg).



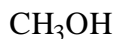
N,N-Dimethylacetamide (DMAc: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 163-165°C/760mmHg).



o-Dichlorobenzene (*o*-DCB: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 180°C/760mmHg).



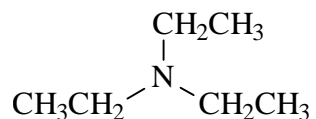
Methanol (Fisher Scientific) was received as an HPLC grade solvent and was used without further purification (b.p. 64.7°C/760mmHg).



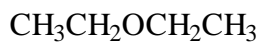
Ethanol (100%, AAPER Alcohol and Chemical) was used as received (b.p. 78.5°C/760mmHg).



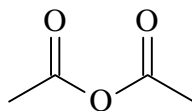
Triethylamine (TEA or  $\text{NEt}_3$ : Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under nitrogen (b.p. 88.8°C/760mmHg).



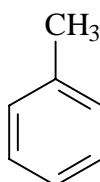
Diethyl Ether ( $\text{OEt}_2$ : Anhydrous, Mallinckrodt) was used as received (b.p. 34.6°C/760mmHg).



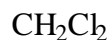
Acetic Anhydride (Aldrich) was stirred over calcium hydride for at least 12 hours prior to distillation under vacuum (~5 torr) (b.p. 138-140°C/760mmHg).



Toluene (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 110.6°C/760mmHg).



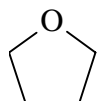
Dichloromethane (Aldrich) was used as received (b.p. 40°C/760mmHg).



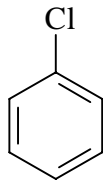
Chloroform (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 61-62°C/760mmHg).



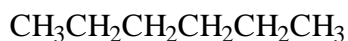
Tetrahydrofuran (THF: EM Science) was used as received (b.p. 76°C/760mmHg).



Chlorobenzene (Fisher Scientific) was received as a laboratory grade solvent and was used without further purification (b.p. 132°C/760mmHg).



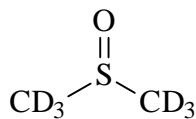
Hexane (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 69°C/760mmHg).



Deuterated Chloroform ( $\text{CDCl}_3$ ; Cambridge Isotope Laboratories) was dehydrated over molecular sieves or alumina powder prior to use (b.p. 61°C/760mmHg).



Deuterated Dimethyl Sulfoxide ( $\text{DMSO-d}_6$ ; Cambridge Isotope Laboratories) was dehydrated over molecular sieves or alumina powder prior to use (b.p. 55°C/5mmHg).



### 3.1.2 Monomer Purification

#### 3.1.2.1 Diamines

#### 1,3-Phenylenediamine (*m*-PDA)

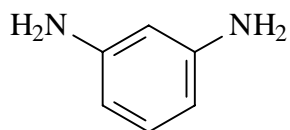
Supplier: Aldrich

Empirical Formula:  $C_6H_8N_2$

Molecular Weight (g/mole): 108.14

m.p., °C: 66

Structure:



Purification: *m*-PDA was sublimed under vacuum (~5 torr) at ~65°C. *m*-PDA is photo- and air-sensitive and must be stored under vacuum and away from light.

**5(6)-Amino-1-(4-aminophenyl)-1,3,3-trimethylindane** (diaminophenylindane or DAPI)

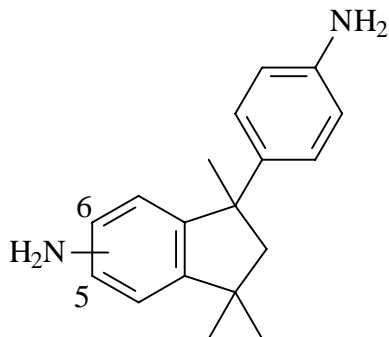
Supplier: Ciba

Empirical Formula:  $C_{18}H_{22}N_2$

Molecular Weight (g/mole): 266.39

m.p., °C: 78-112

Structure: Equimolar mixture of C-5 and C-6 isomers as determined by HPLC.



Purification: DAPI was dried under vacuum (~5 torr) at ~50°C for more than 12 hours prior to use.

**9,9-Bis(4-aminophenyl) fluorene (FDA)**

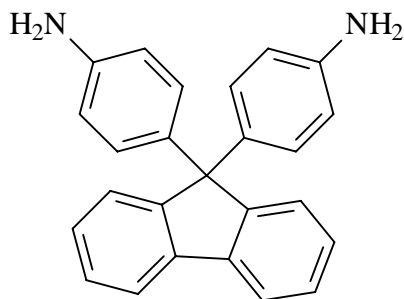
Supplier: Kennedy and Klim

Empirical Formula:  $C_{25}H_{20}N_2$

Molecular Weight (g/mole): 348.16

m.p., °C: 235-237

Structure:



Purification: Monomer grade FDA was obtained and dried at ~75°C under vacuum (~5 torr) for at least 12 hours.

**3,7-Diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)**

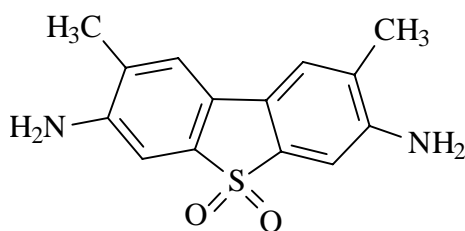
Supplier: Chriskev

Empirical Formula:  $C_{14}H_{14}O_2N_2S$

Molecular Weight (g/mole): 274.34

m.p., °C: 360 (dec.)

Structure:



Purification: Monomer grade DDBT was obtained and dried at  $\sim 50^{\circ}\text{C}$  under vacuum ( $\sim 5$  torr) for at least 12 hours.

**2,2-Bis(3-amino-4-methylphenyl)-hexafluoropropane (Bis-AT-AF)**

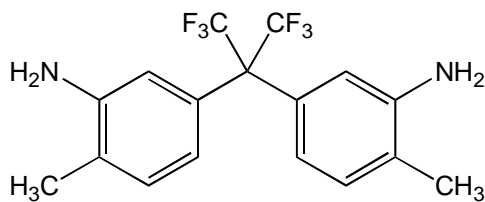
Supplier: Chriskev

Empirical Formula:  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{F}_6$

Molecular Weight (g/mole): 364

m.p.,  $^{\circ}\text{C}$ : 105-106

Structure:



Purification: Monomer grade BisATAF was obtained and dried at  $\sim 50^{\circ}\text{C}$  under vacuum ( $\sim 5$  torr) for at least 12 hours.

**2,2-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (Bis-AP-AF)**

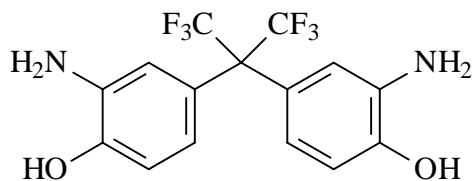
Supplier: Chriskev

Empirical Formula:  $C_{15}H_{12}O_2N_2F_6$

Molecular Weight (g/mole): 366

m.p., °C: 240-243

Structure:



Purification: BisAPAF was recrystallized from ethanol. To a 500ml 3-neck flask equipped with a mechanical stirrer, nitrogen inlet/outlet and a condenser, 100g of BisAPAF was added along with 150ml of ethanol. The solution became homogeneous at reflux. To this solution,  $CHCl_3$  was added until it became slightly turbid (~150ml). Upon cooling, the BisAPAF precipitated as a fine white powder which was filtered, washed with  $CHCl_3$  and dried under vacuum (~5 torr) at 100°C for 24 hours (~87% yield).

### **3,3'-Dihydroxy-4,4'-diamino-biphenyl (HAB)**

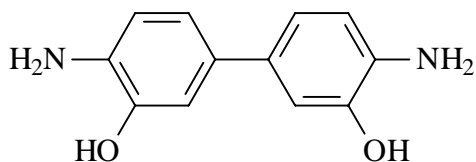
Supplier: Chriskev

Empirical Formula:  $C_{12}H_{12}O_2N_2$

Molecular Weight (g/mole): 216.2

m.p., °C: 295-296

Structure:

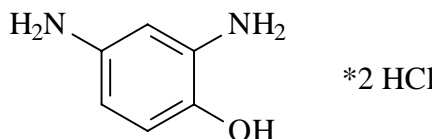




Purification: Monomer grade HAB was obtained and dried at ~50°C under vacuum (~5 torr) for at least 12 hours.

**2,4-Diaminophenol dihydrochloride (DAP)**

Supplier: Aldrich  
Empirical Formula: C<sub>6</sub>H<sub>10</sub>ON<sub>2</sub>Cl<sub>2</sub>  
Molecular Weight (g/mole): 197.07  
m.p., °C: 222 (dec.)  
Structure:



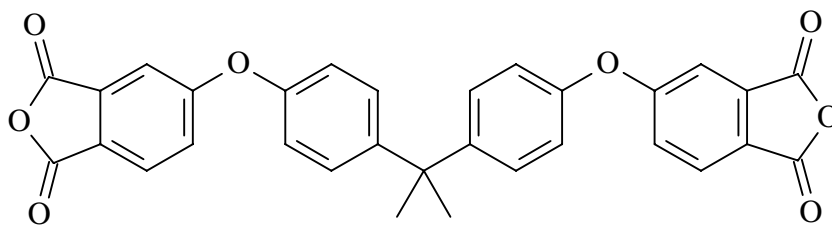
Purification: DAP was received as light pink flake of 98% purity. It was found to be monomer grade (≥99.9%) after drying for it yielded high molecular weight polyimides. DAP was dried at room temperature under vacuum (~5 torr) for at least 12 hours.

*3.1.2.2 Dianhydrides*

**2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bisphenol-A dianhydride or BPADA)**

Supplier: General Electric Company  
Empirical Formula: C<sub>31</sub>H<sub>21</sub>O<sub>8</sub>  
Molecular Weight (g/mole): 520.49  
m.p., °C: 191-193

Structure:

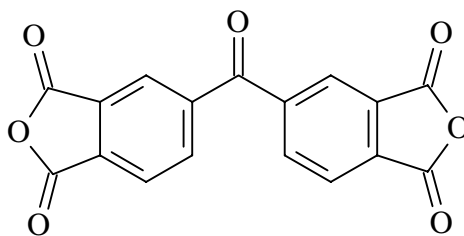


Purification: BPADA was recrystallized from a mixture of toluene and acetic anhydride. To a 1L 3-neck round bottom flask equipped with a mechanical stirrer, condenser and nitrogen inlet, 100g of BPADA, 500g of toluene and 50g of acetic anhydride was added. The mixture was heated to reflux yielding a homogeneous mixture. The mixture was allowed to cool overnight. The resulting solid BPADA was filtered and returned to the round bottom flask to which 500g of toluene and 10g of acetic anhydride was added. Again, this mixture became homogeneous at reflux and upon cooling afforded crystals of BPADA. The whole procedure was repeated again and yielded purified BPADA in about 70% yield (m.p. 191-193°C).

### 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA)

Supplier: Allco  
Empirical Formula:  $C_{17}H_6O_7$   
Molecular Weight (g/mole): 322.23  
m.p., °C: 224-226

Structure:



Purification: BTDA was obtained as a fine white powder and was dried under vacuum (~5 torr) at ~180°C for at least 12 hours prior to use.

**3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA)**

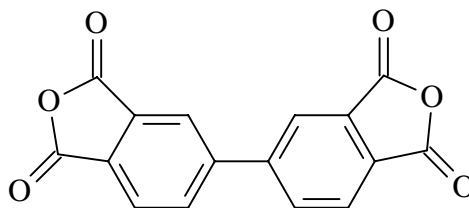
Supplier: Chriskev

Empirical Formula:  $C_{16}H_6O_6$

Molecular Weight (g/mole): 294.00

m.p., °C: 300

Structure:



Purification: Polymer grade BPDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

**1,2,4,5-Benzenetetracarboxylic dianhydride (PMDA)**

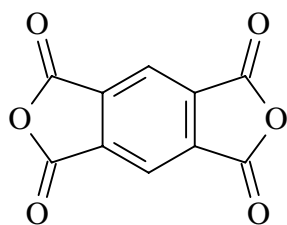
Supplier: Allco

Empirical Formula:  $C_{10}H_2O_6$

Molecular Weight (g/mole): 218.12

m.p., °C: 286

Structure:



Purification: Polymer grade PMDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

**5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene] bis-1,3-isobenzene-furandione (6FDA)**

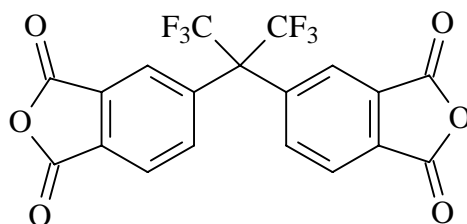
Supplier: Hoechst Celanese Corporation

Empirical Formula: C<sub>19</sub>H<sub>6</sub>F<sub>6</sub>O<sub>6</sub>

Molecular Weight (g/mole): 444.00

m.p., °C: 247

Structure:



Purification: Polymer grade 6FDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

**4,4'-Bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (biphenylether dianhydride or BPEDA)**

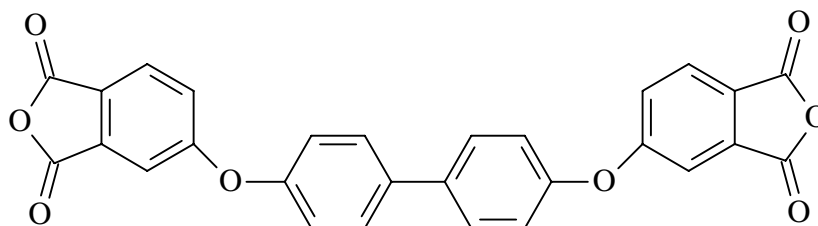
Supplier: General Electric Company

Empirical Formula:  $C_{28}H_{15}O_8$

Molecular Weight (g/mole): 478.41

m.p., °C: 294-296

Structure:



Purification: Polymer grade BPEDA was dried at  $\sim 180^\circ\text{C}$  for at least 12 hours under vacuum ( $\sim 5$  torr) prior to use.

### Diphenylsulfone dianhydride (DSDA)

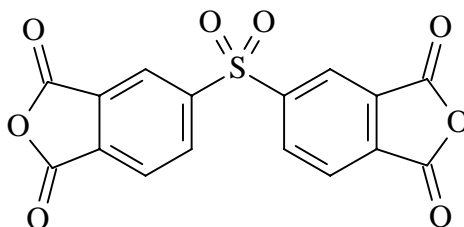
Supplier: Chriskev

Empirical Formula:  $C_{12}H_6O_8S$

Molecular Weight (g/mole): 310.24

m.p., °C: 287-288

Structure:



Purification: Polymer grade DSDA was obtained as a fine white powder and was dried at ~160°C for at least 12 hours under vacuum (~5 torr) prior to use.

### 3.1.3 Endcap Purification

#### Phthalic anhydride (PA)

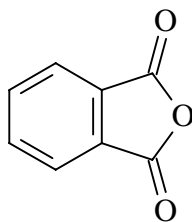
Supplier: Aldrich

Empirical Formula: C<sub>8</sub>H<sub>4</sub>O<sub>3</sub>

Molecular Weight (g/mole): 148.12

m.p., °C: 134

Structure:



Purification: PA was purified by vacuum (~5 torr) sublimation at ~120°C.

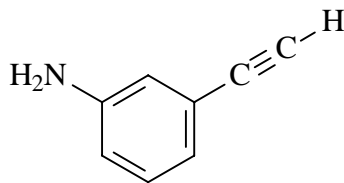
#### 3-Ethynyl aniline (*m*-aminophenyl acetylene or *m*-APA)

Supplier: Acros

Empirical Formula: C<sub>8</sub>H<sub>7</sub>N

Molecular Weight (g/mole): 117.15

Structure:



Purification: *m*-APA was distilled at ~90°C and 50 millitorr prior to use.

***m*-Aminophenol (*m*-AP)**

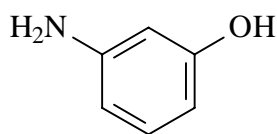
Supplier: Aldrich

Empirical Formula: C<sub>6</sub>H<sub>7</sub>ON

Molecular Weight (g/mole): 109.13

m.p., °C: 124-126

Structure:



Purification: *m*-AP was purified by vacuum sublimation (3X).

**3.1.4 Epoxy Resins**

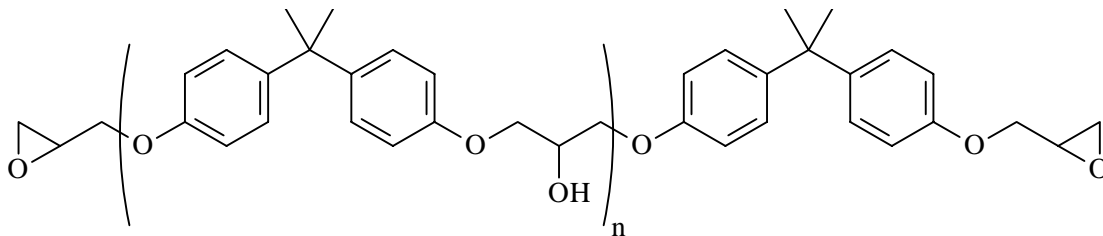
Epoxy equivalent weight (EEW) is reported for the following commercial epoxy resins. EEW was determined by titration methods and is the grams of resin required to supply 1 mole of epoxide rings.

**Bisphenol A epoxy resin (EPON 828)**

Supplier: Shell

EEW(g resin/mole epoxide): 188.65

Structure:



Purification: EPON 828 was used as received without further purification.

### **Tetraglycidyl bis-(p-aminophenyl) methane (MY721)**

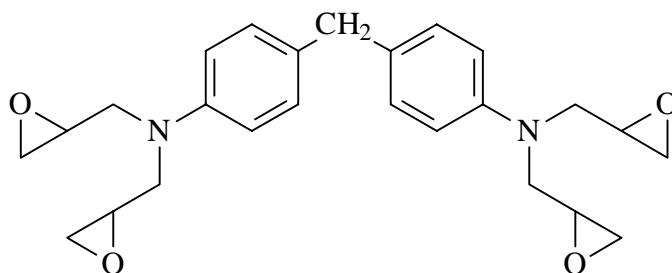
Supplier: Ciba Polymers

Empirical Formula:  $C_{25}H_{30}O_4N_2$

Molecular Weight: 435.82

EEW(g resin/mole epoxide): 112.3

Nominal Structure:



Purification: MY721 was used as received without further purification.

## **3.2 Monomer Synthesis**

### **3.2.1 Reagents**

#### **$\alpha$ -Methylstyrene ( $\alpha$ -MS)**

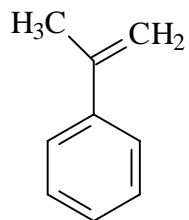
Supplier: Aldrich

Empirical Formula:  $C_9H_{10}$

Molecular Weight (g/mole): 118.18



Structure:



Purification:  $\alpha$ -MS was deinhibited (*p*-tert-butylcatechol) with basic alumina immediately prior to use.

### Sulfuric Acid

Supplier: Mallinckrodt, 96.2%

Empirical Formula: H<sub>2</sub>SO<sub>4</sub>

Molecular Weight (g/mole): 98.07

Purification: Used as received

### Nitric Acid

Supplier: Fisher, 69.5%

Empirical Formula: HNO<sub>3</sub>

Molecular Weight (g/mole): 63.01

Purification: Used as received

### Hydrazine Monohydrate

Supplier: Acros, 99%

Empirical Formula: H<sub>6</sub>N<sub>2</sub>O

Molecular Weight (g/mole): 50.06

b.p., °C: 113.5/760mmHg

Structure:



Purification: Used as received

**Palladium on Activated Carbon (Pd/C)**

Supplier: Aldrich

Empirical Formula: Pd 10%, +C

Purification: Used as received

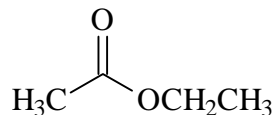
**Ethylacetate (EtOAc)**

Supplier: Mallinckrodt, 99.6%

Empirical Formula: C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>

Molecular Weight (g/mole): 90.09

Structure:



Purification: Used as received

**Magnesium Sulfate, Anhydrous**

Supplier: Mallinckrodt, Reagent Grade

Empirical Formula: MgSO<sub>4</sub>

Molecular Weight (g/mole): 120.37

Purification: Used as received

### **Basic Alumina, Activated**

Supplier: Aldrich, Standard Grade

Empirical Formula:  $\text{Al}_2\text{O}_3$

Purification: Used as received

### **Sodium Bicarbonate**

Supplier: EM Science

Empirical Formula:  $\text{NaHCO}_3$

Molecular Weight (g/mole): 84.01

Purification: Used as received

### **4,4'-Isopropylidenediphenol (bisphenol-A)**

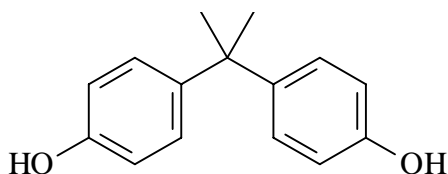
Supplier: Dow Chemical

Empirical Formula:  $\text{C}_{15}\text{H}_{16}\text{O}_2$

Molecular Weight (g/mole): 228.29

m.p., °C: 158-159

Structure:



Purification: Bisphenol A was purified by recrystallization from toluene (Bisphenol A: toluene/ 1:5.3).

### **Sodium Hydroxide**

Supplier: Mallinckrodt, Pellets, 99.4%

Empirical Formula:  $\text{NaOH}$

Molecular Weight (g/mole): 40.00

Purification: Used as received

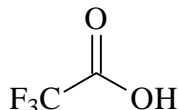
### Trifluoroacetic Acid (TFAA)

Supplier: Fisher, Reagent Grade

Empirical Formula:  $C_2HO_2F_3$

Molecular Weight (g/mole): 114.02

Structure:



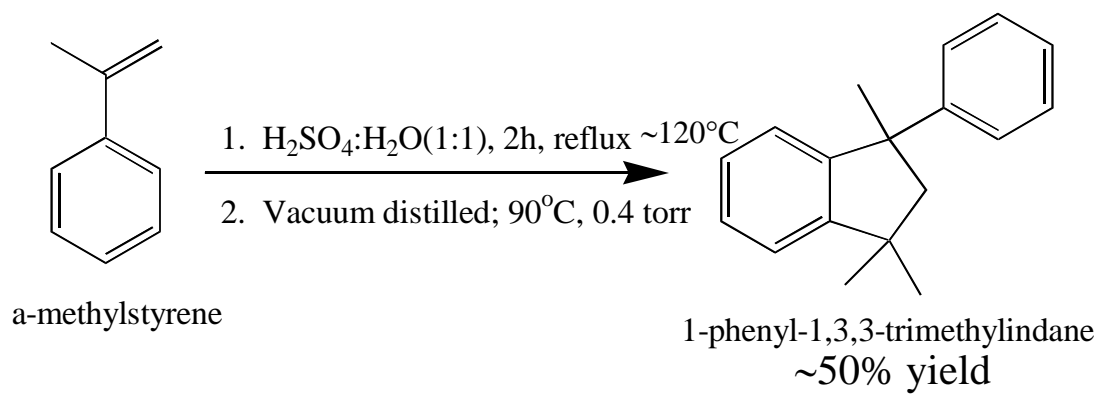
Purification: Used as received

### 3.2.2 Synthetic Procedure

#### 3.2.2.1 Synthesis of 1-phenyl-1,3,3-trimethylindane (phenylindane)-Scheme 3.2.2.1.1

*Following a procedure similar to Maier et al.<sup>269</sup>*

Catechol, a self-polymerization inhibitor, was removed from  $\alpha$ -methylstyrene ( $\alpha$ -MS) by filtration through basic alumina. Deinhibited  $\alpha$ -MS (150ml) was added to a 2L flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet/outlet. To this, a previously mixed acid solution consisting of 480ml  $H_2SO_4$  and 600ml  $H_2O$  was added slowly to the  $\alpha$ -MS. This mixture was then refluxed ( $\sim 120^\circ C$ ) for 2 hours, followed by the addition of 300ml  $H_2SO_4$  and continuation of reflux for an additional 18 hours. At this point the reaction mixture was cooled to room temperature and 400ml  $H_2O$  was added. The organic layer, which contained the phenylindane, was then washed with 5%  $NaHCO_3$ . The organics containing the phenylindane was then vacuum distilled ( $90^\circ C$ , 0.4 torr).



Scheme 3.2.2.1.1 Synthesis of 1-phenyl-1,3,3-trimethylindane from  $\alpha$ -methylstyrene

yield=50%. Appearance: white solid, m.p. 50-51°C (lit. 50-52°C); Elemental Analysis: found (expected), C: 90.81 (91.47), H: 8.47 (8.53); NMR assignments, Figures 3.2.2.1.1, 3.2.2.1.2 and 3.2.2.1.3; IR spectra, Figure 3.2.2.1.4.

### 3.2.2.2 *Synthesis of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (dinitrophenylindane or DNPI) (Scheme 3.2.2.2.1)*

*Following a procedure similar to Bateman et al.:<sup>270</sup>*

To a 250ml 3-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet, 20g of phenylindane was dissolved in 60ml of CHCl<sub>3</sub>. The flask was then placed into an ice bath at 0-5°C. A previously mixed solution containing 33ml H<sub>2</sub>SO<sub>4</sub> and 14.5ml HNO<sub>3</sub> (1.95 equivalents) was then added dropwise to the phenylindane/CHCl<sub>3</sub> over a 2 hour period while maintaining a solution temperature of 0-5°C. The reaction temperature (0-5°C) was maintained for an additional 4 hours before allowing the solution to increase to room temperature. The organic layer was then separated. The acid layer was washed with CHCl<sub>3</sub>, and combined with the organic layer. The organics were neutralized with 5% NaHCO<sub>3</sub> and dried with MgSO<sub>4</sub>. The CHCl<sub>3</sub> was removed from the DNPI using a rotoevaporator, thereby yielding a viscous yellow liquid, which, when triturated in hexane, afforded a light yellow powder. yield=70%. m.p. 110-126°C (lit. 109-125°C); Infrared Analysis: 1343cm<sup>-1</sup> (NO<sub>2</sub>-assymmetric stretch) and 1518cm<sup>-1</sup>; Elemental Analysis: found (expected), C: 66.17 (66.25), H: 5.47 (5.56), N: 8.47 (8.58), O: 19.57 (19.61); NMR assignments, Figures 3.2.2.2.1 and 3.2.2.2.2; IR spectra, Figure 3.2.2.1.4.

### 3.2.2.3 *Synthesis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (diaminophenylindane or DAPI) (Scheme 3.2.2.2.1)*

*Following a procedure similar to Zhuang's:<sup>131</sup>*

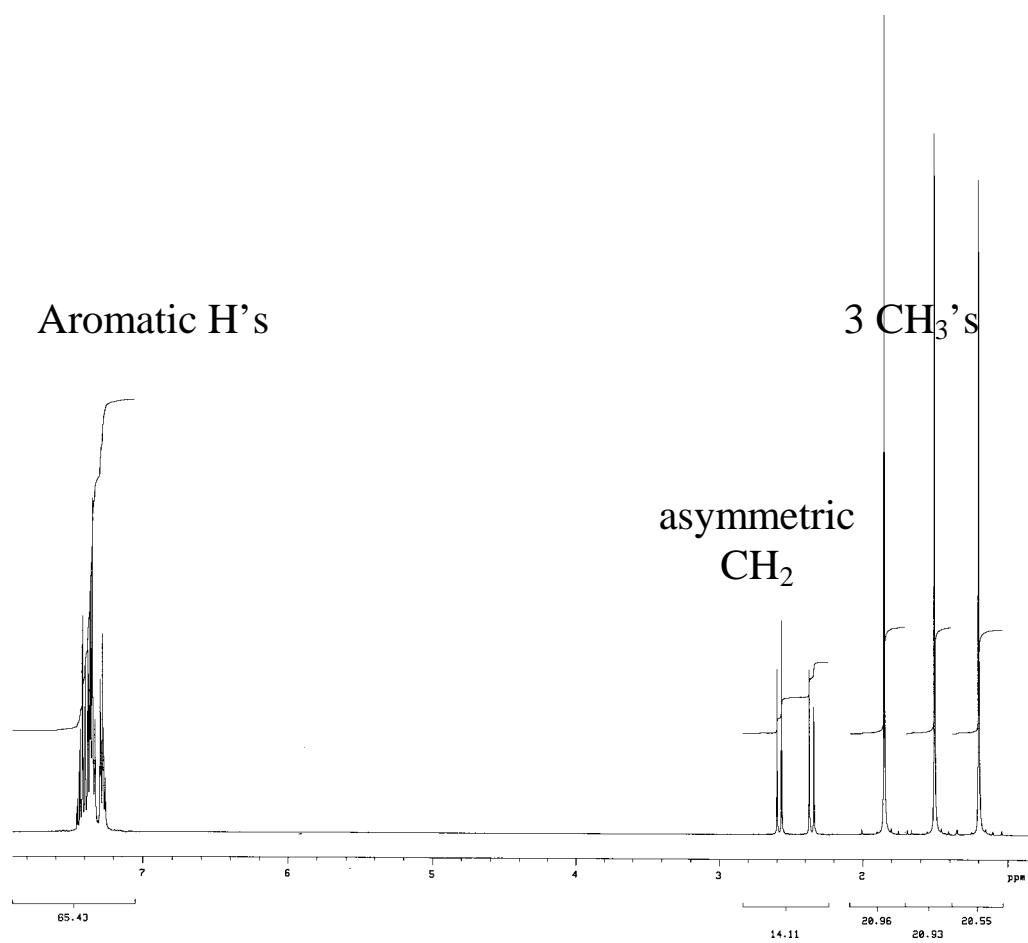
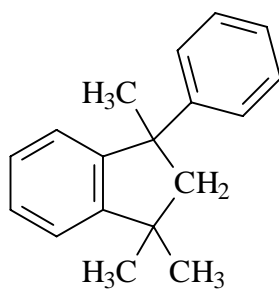


Figure 3.2.2.1.1 <sup>1</sup>H NMR Spectra for 1-phenyl-1,3,3-trimethylindane

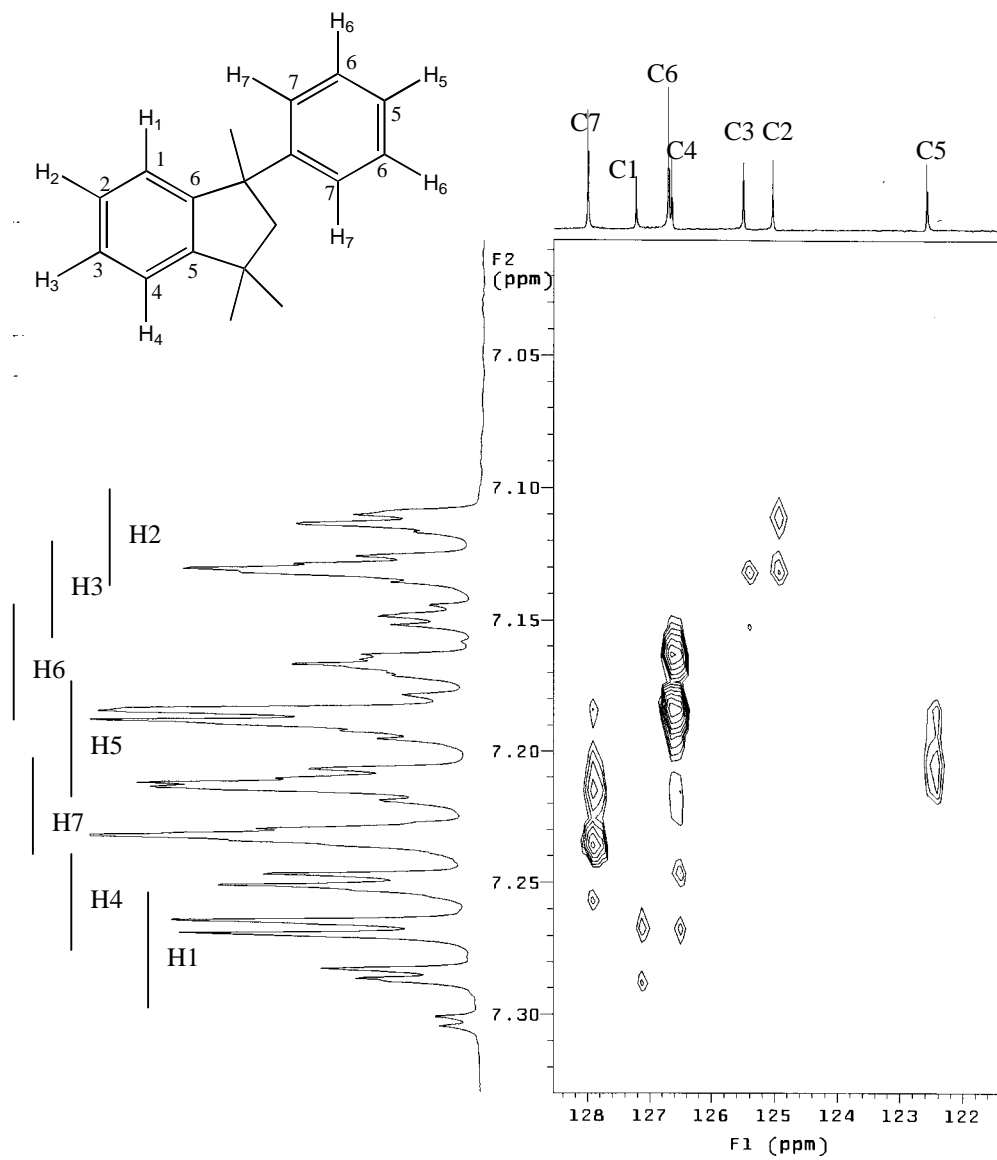


Figure 3.2.2.1.2 HMQC of 1-phenyl-1,3,3-trimethylindane



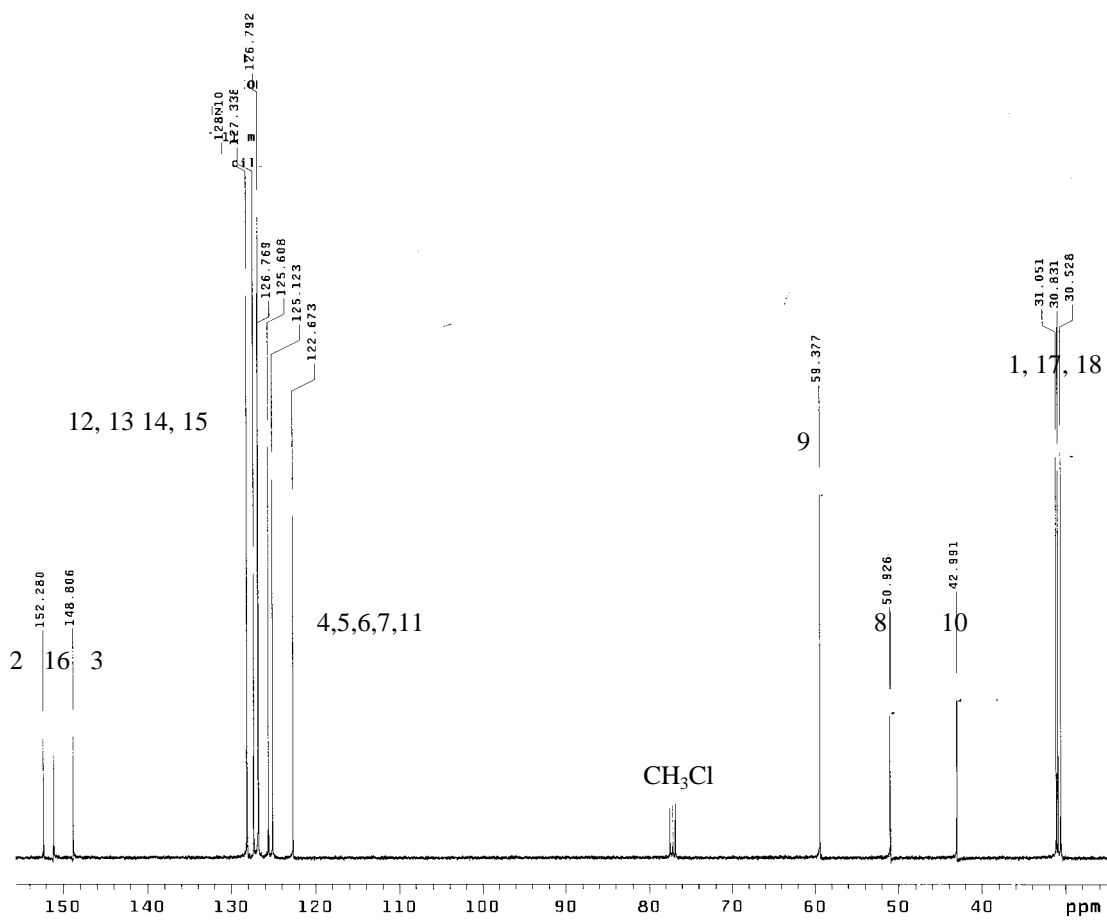
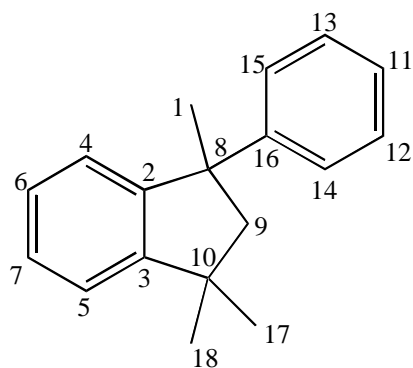


Figure 3.2.2.1.3  $^{13}\text{C}$  NMR of 1-phenyl-1,3,3-trimethylindane

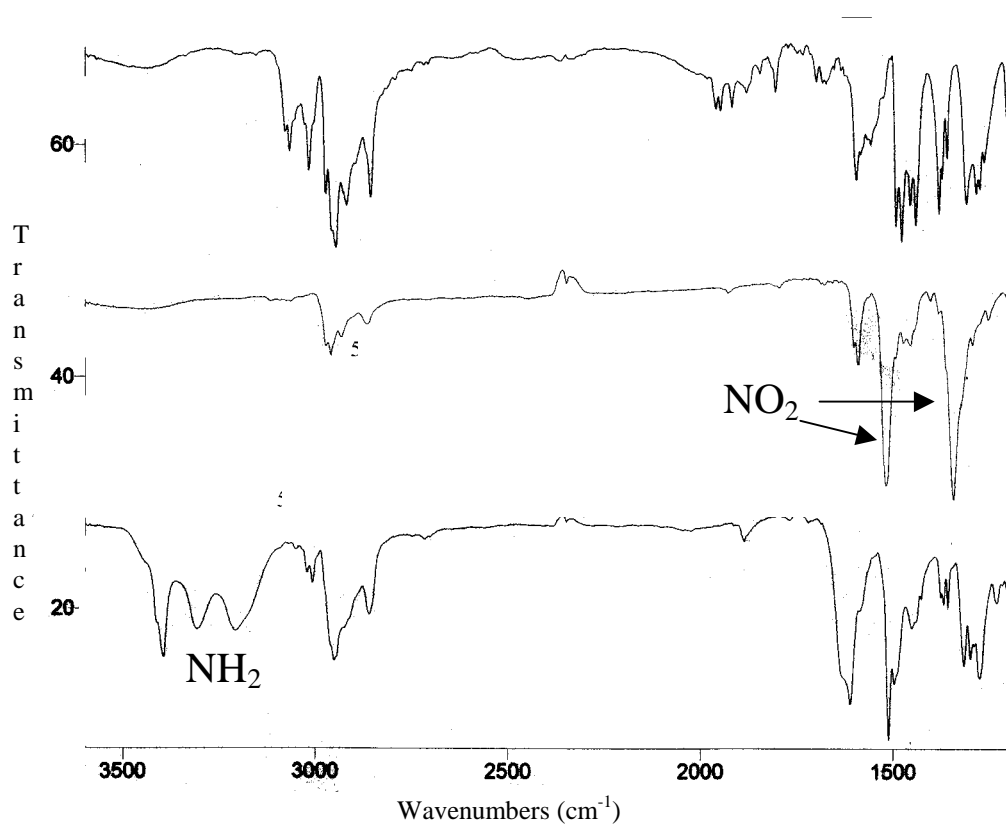
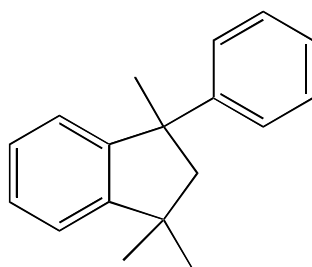
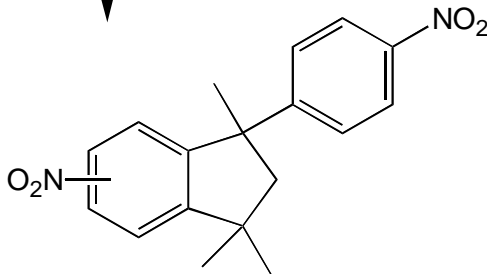


Figure 3.2.2.1.4 IR Spectra (from top to bottom) of 1-phenyl-1,3,3-trimethylindane, 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane and 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane



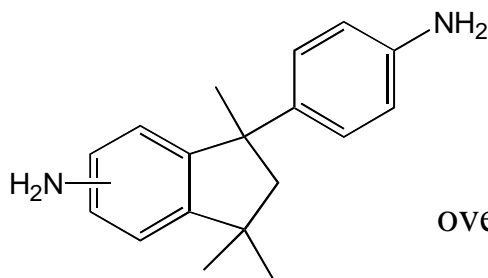
1-phenyl-1,3,3-trimethylindane

1. Dissolution in  $\text{CHCl}_3$  (25wt%)  
2.  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , 0-5C, 4h  
( $\text{CHCl}_3:\text{H}_2\text{SO}_4/2:1$ )



5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

- EtOH at reflux,  
 $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$  (9X excess),  
Pd/C



overall yield ~35%

5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane

Scheme 3.2.2.2.1 Synthesis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) from 1-phenyl-1,3,3-trimethylindane

6 & 5 Isomers, 38:62

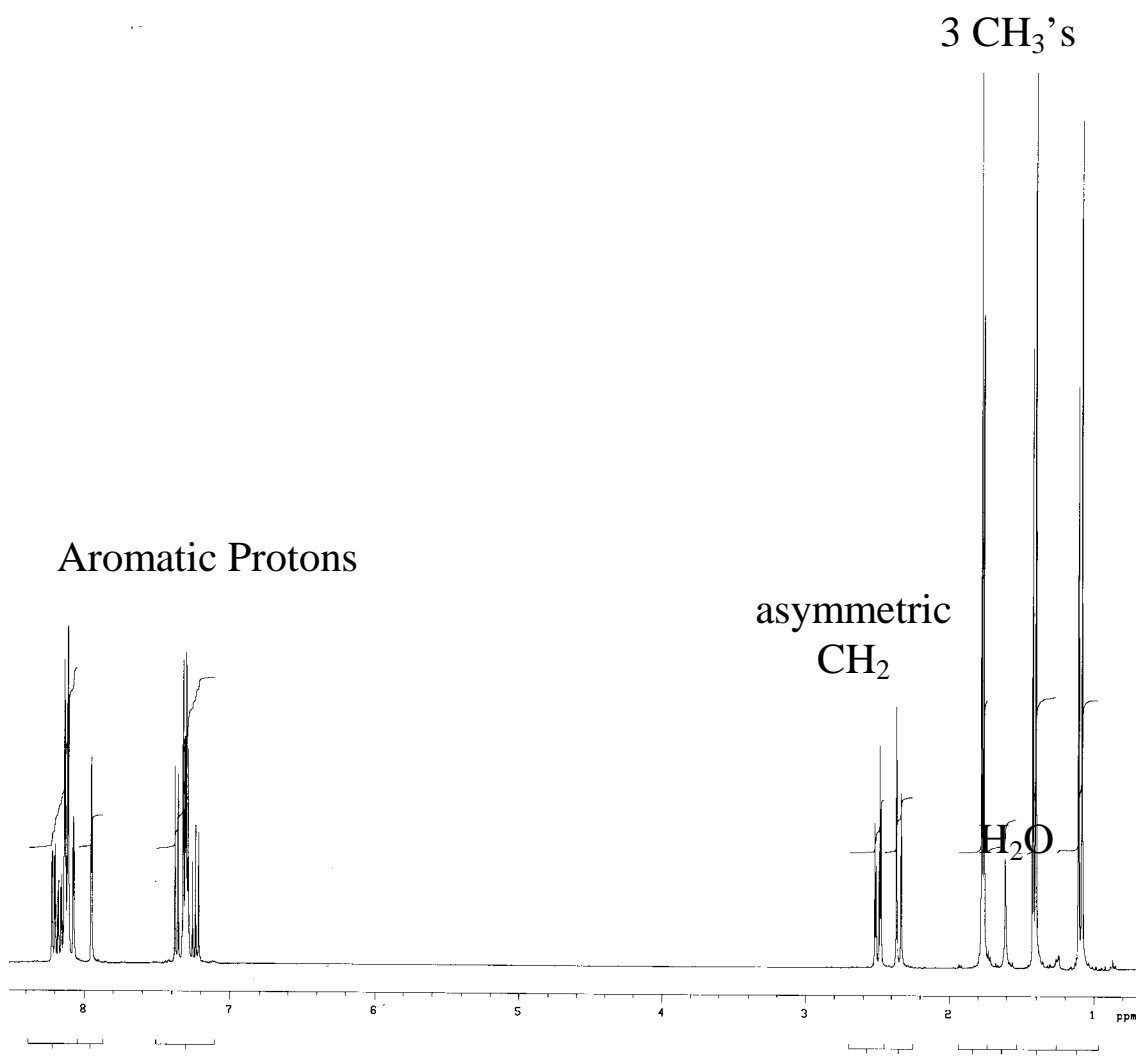
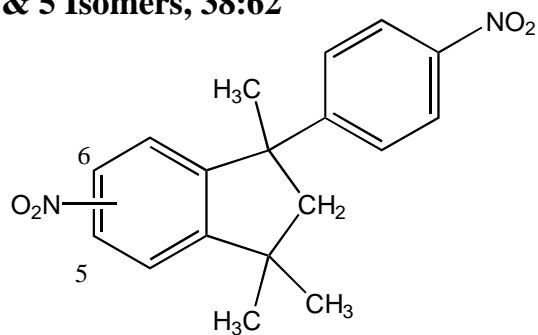


Figure 3.2.2.2.1 <sup>1</sup>H NMR of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

5&6 Isomers, 38:62

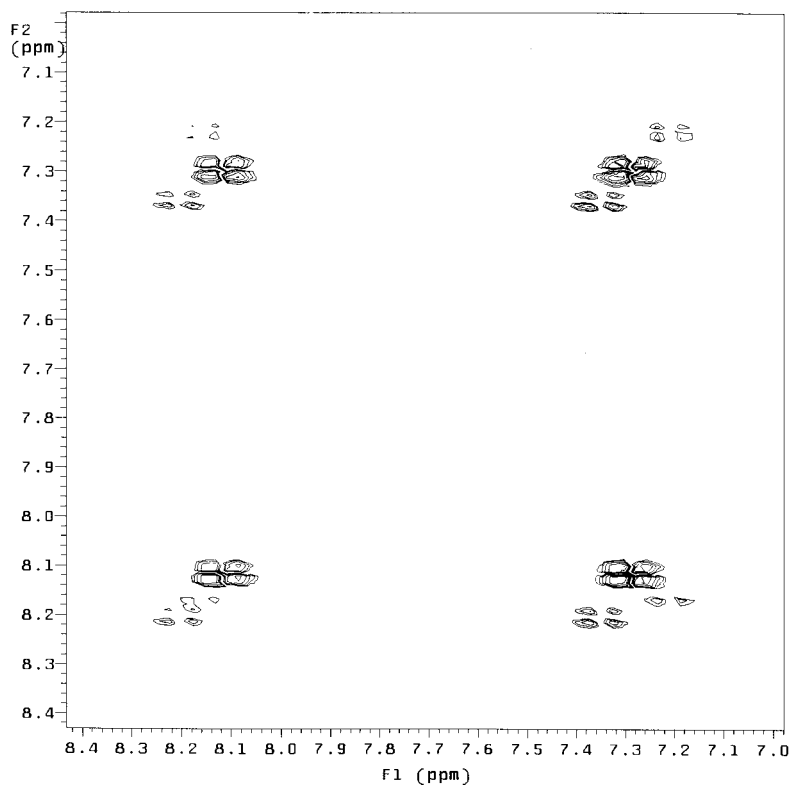
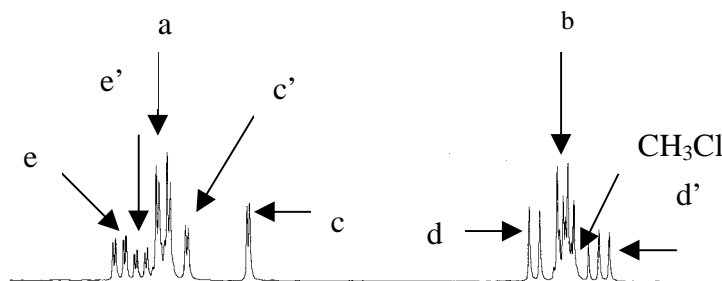
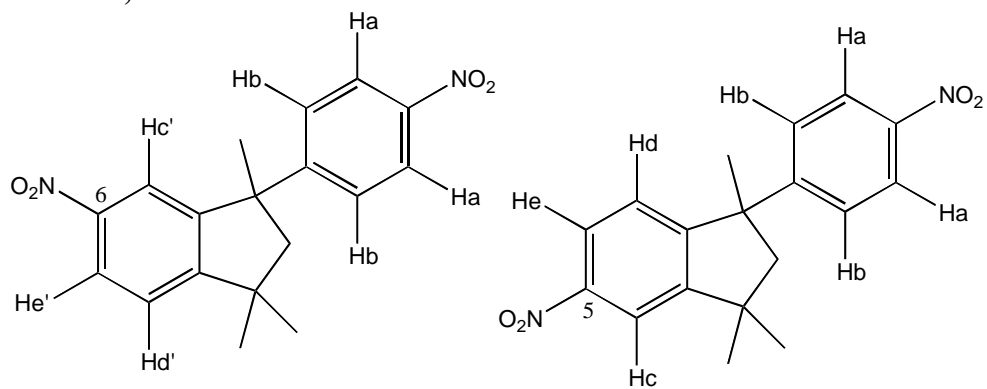


Figure 3.2.2.2.2 DQCosY of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

To a 3-neck 250ml flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet were added 3g of DNPI and 220ml ethanol and the mixture was heated to reflux. Once dissolved, 0.25g Pd/C was added followed by 12ml of hydrazine (9 molar excess), which was slowly added from a dropping funnel. After the addition, reflux was continued for 2 hours before 0.1g of Pd/C was added. Reflux was continued overnight. Activated charcoal (0.2g) was then added while maintaining reflux. After 10 minutes the reaction mixture was hot filtered through Celite. The ethanol was removed and the resulting oil was triturated in H<sub>2</sub>O to afford a white powder. Quantitative yield, m.p. 77-104°C (lit. 47-54°C); Elemental Analysis: found (expected), C: 81.06 (81.16), H: 8.41 (8.32), N: 10.35 (10.52); NMR assignments, Figures 3.2.2.3.1 and 3.2.2.3.2; Infrared Analysis: 1612cm<sup>-1</sup> (C-N) and 3207cm<sup>-1</sup>, 3307cm<sup>-1</sup> and 3393cm<sup>-1</sup> (N-H stretch) (Figure 3.2.2.1.4)

#### 3.2.2.4 *Synthesis of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (trinitrophenylindane or TNPI) (Scheme 3.2.2.4.1)*

To a 250ml 3-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet was added 5g of phenylindane dissolved in 40ml of CHCl<sub>3</sub>. The solution was then placed into an ice bath at 0-5°C and 30ml of chilled H<sub>2</sub>SO<sub>4</sub> solution was added. A previously mixed acidic solution containing 20ml H<sub>2</sub>SO<sub>4</sub> and 3.85ml HNO<sub>3</sub> (2 molar equivalents plus 1%) was then added dropwise to the solution over a 20 minute period while maintaining a solution temperature of 0-5°C. Next, the beaker containing the nitric acid was rinsed with 10ml of H<sub>2</sub>SO<sub>4</sub>. The reaction temperature (0-5°C) was maintained for an additional 4 hours. The acid layer was washed with CHCl<sub>3</sub>, which was then combined with the organic layer. The organics were made neutral with 5% NaHCO<sub>3</sub> and dried with MgSO<sub>4</sub>. The CHCl<sub>3</sub> was removed from the TNPI using a rotoevaporator yielding a viscous yellow liquid, which when triturated overnight in hexane afforded a light yellow powder. About 3.24g were recovered (50% yield), consisting of a mixture of mono-, di- and tri-substituted product. The tri-substituted isomer was readily

**6 & 5 Isomers, 43:57**

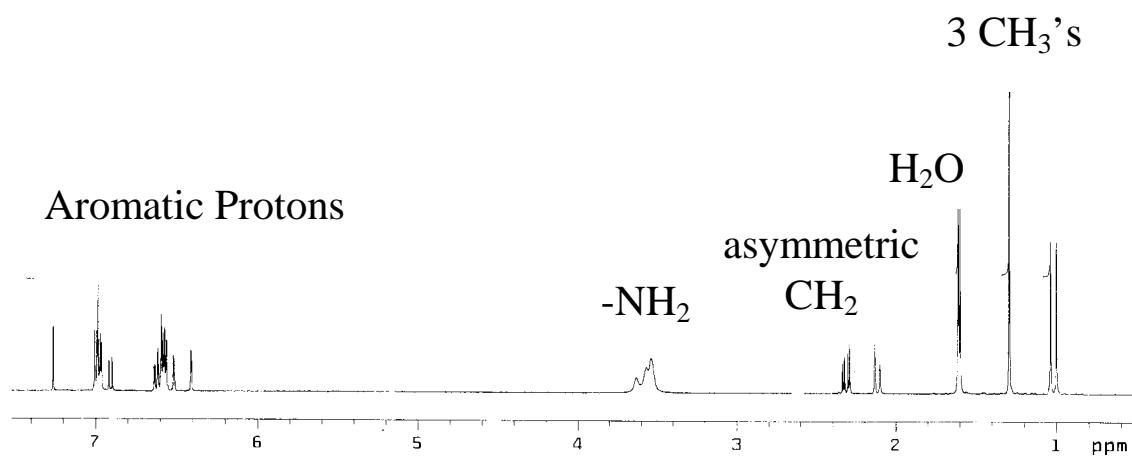
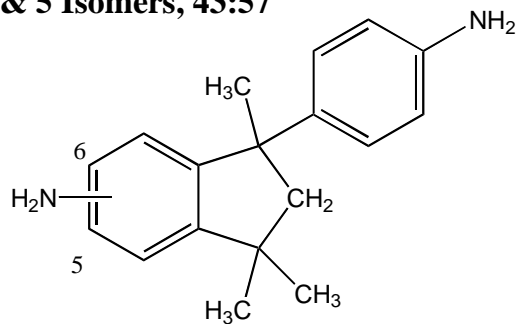


Figure 3.2.2.3.1 <sup>1</sup>H NMR of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane

5&6 Isomers, 43:57

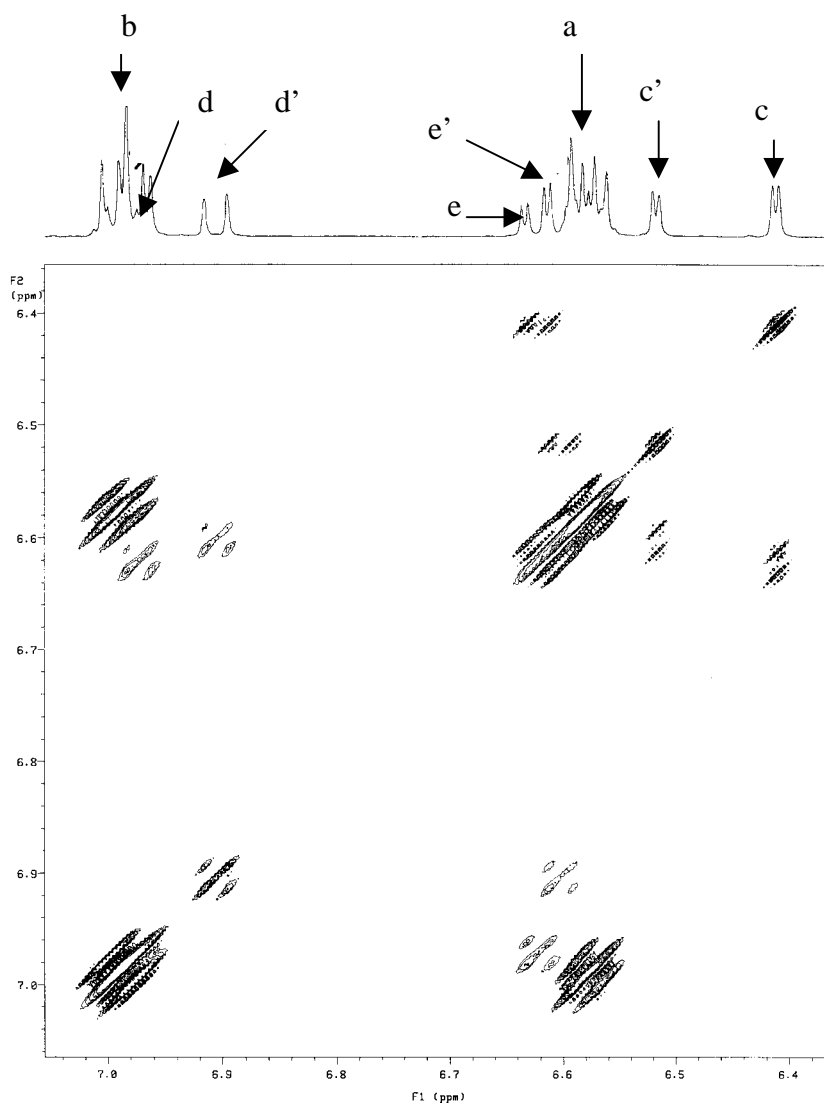
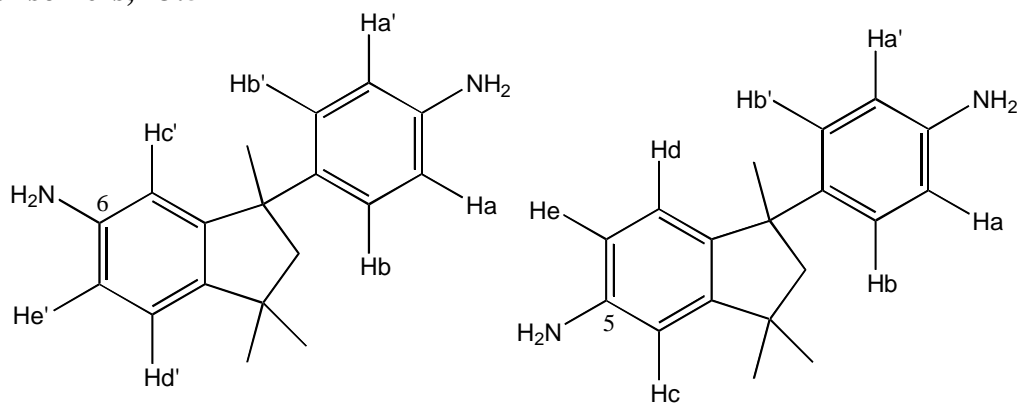
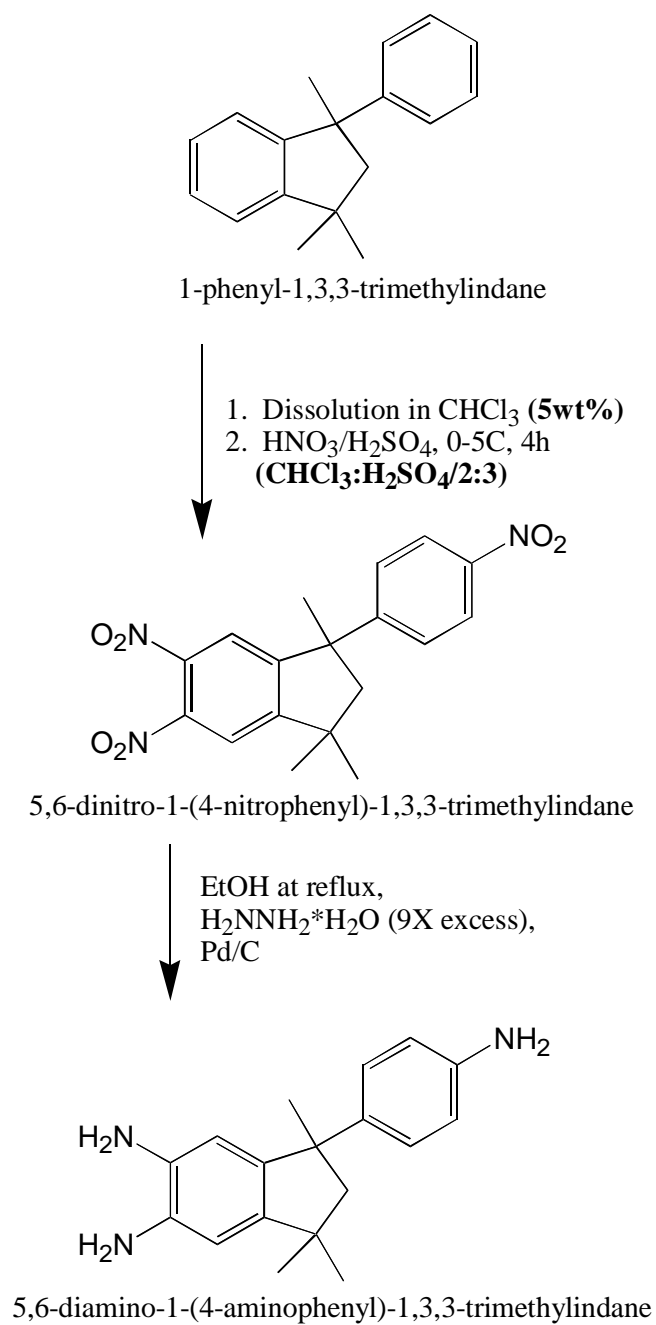


Figure 3.2.2.3.2 DQCOSY of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane





Scheme 3.2.2.4.1 Synthesis of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane (TAPI) from 1-phenyl-1,3,3-trimethylindane

recrystallized from ethanol to afford a crystalline yellow powder. m.p. 184-185°C (new compound); Elemental Analysis: found (expected), C: 57.98 (58.22), H: 4.66 (4.61), N: 11.11 (11.32), O: 25.98 (25.85); NMR assignments, Figures 3.2.2.4.1 and 3.2.2.4.2.

*3.2.2.5 Synthesis of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane (triaminophenylindane or TAPI) (Scheme 3.2.2.4.1)*

To a 3-neck 500ml flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet were added 3.85g of TNPI and 375ml ethanol, which was subsequently heated to reflux. Once dissolved, 0.15g Pd/C was added followed by 16ml hydrazine (9 molar excess), which was slowly added from a dropping funnel. After the addition, reflux was continued for 4 hours before 0.1g of Pd/C was added and refluxed overnight. Activated charcoal (0.2g) was then added while maintaining reflux. After 10 minutes the hot reaction mixture was filtered through Celite. The ethanol was removed and the resulting oil was triturated in H<sub>2</sub>O to afford a light gray powder. yield~95%. m.p. 140-142°C (new compound); Elemental Analysis: found (expected), C: 76.23 (76.83), H: 8.15 (8.24), N: 14.89 (14.93); NMR assignments, Figure 3.2.2.5.1.

*3.2.2.6 Synthesis of 4-hydroxy- $\alpha$ -methylstyrene (isopropenylphenol or IPP) (Scheme 3.2.2.6.1)<sup>272</sup>*

To a 500ml 3-neck round bottom flask equipped with a mechanical stirrer (with vacuum adapter) and a vacuum fixture with a collection flask (Figure 3.2.2.6.1) was added 250g bisphenol A and 0.87g NaOH (~0.35wt%). The reaction flask was heated under vacuum at 175°C until most of the solids had melted (bisphenol A, m.p. 156°C). The reaction temperature was increased to 220°C, while maintaining a reduced pressure of ~350mmHg, for 2 hours. This was followed by increasing the temperature to 250°C for 6 hours under a pressure of ~50mmHg. At this point, during the period of several hours, a yellow solid was observed to distill over at 125-145°C. The yield of the yellow

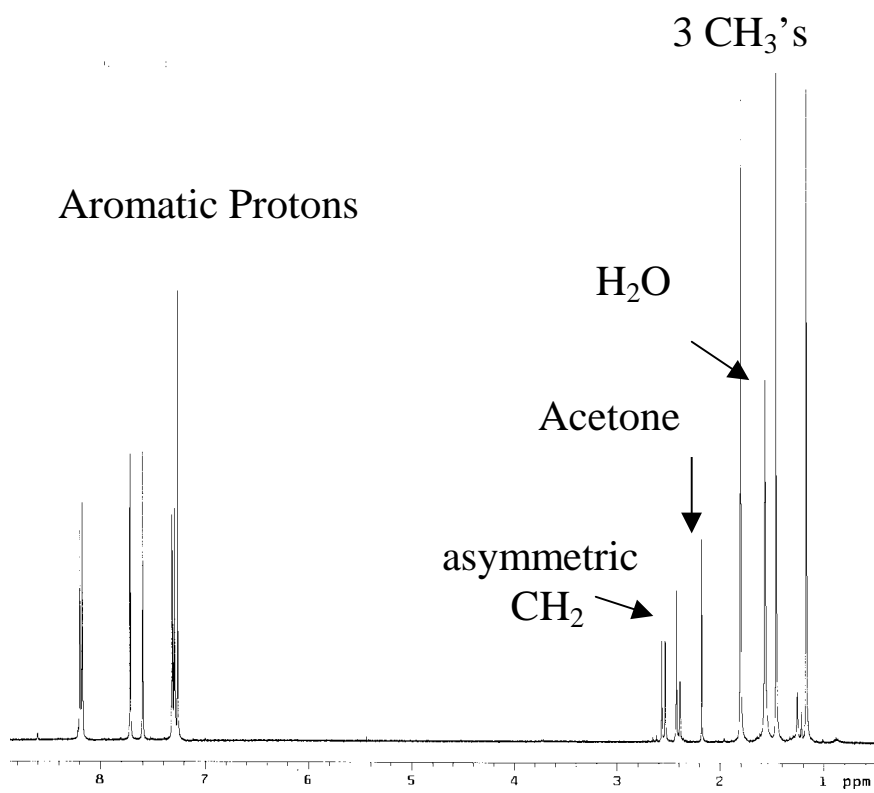
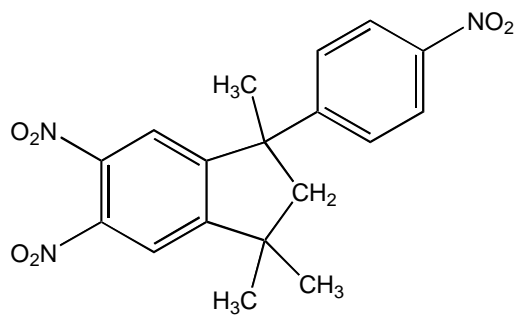


Figure 3.2.2.4.1 <sup>1</sup>H NMR of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

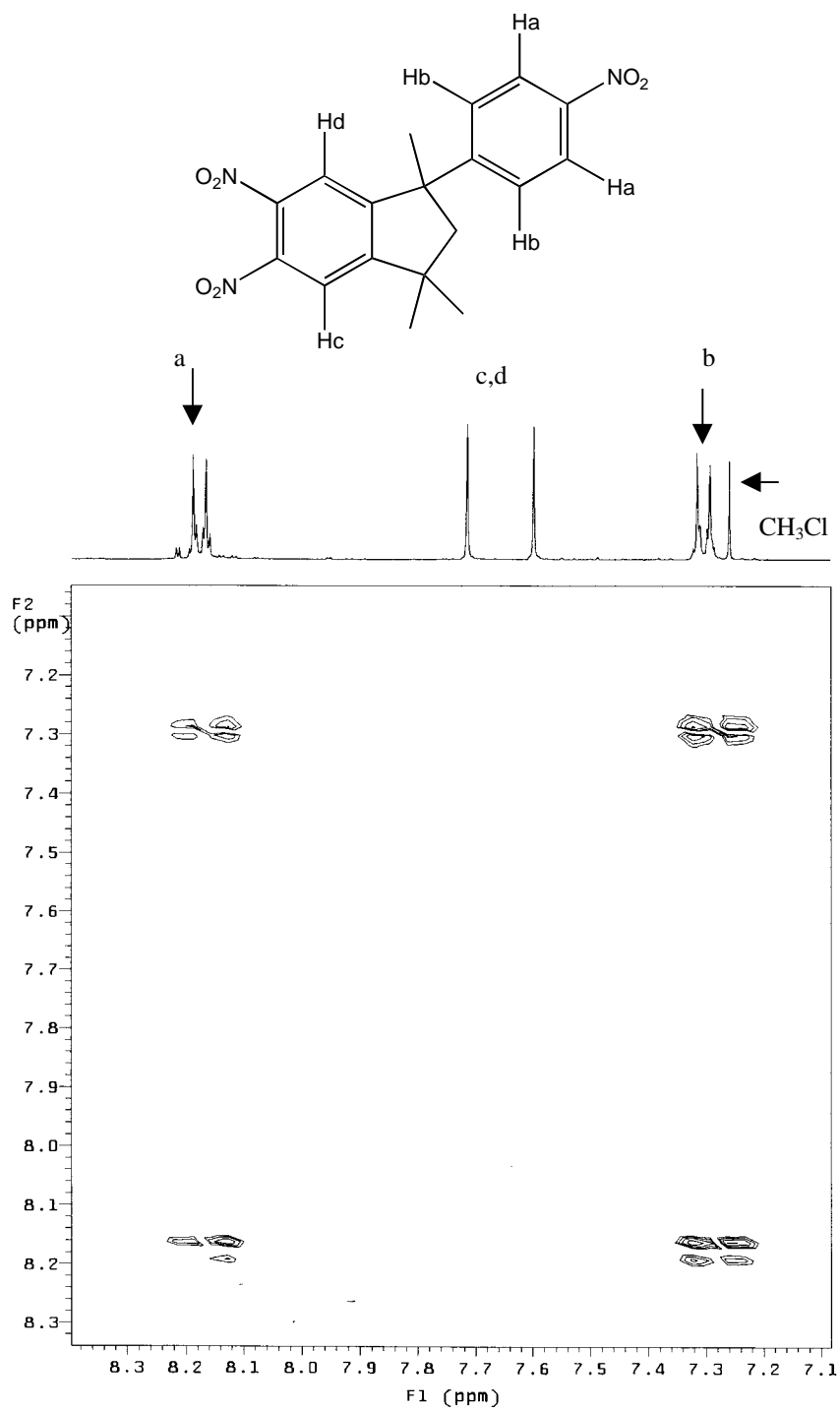


Figure 3.2.2.4.2 DQCoS of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

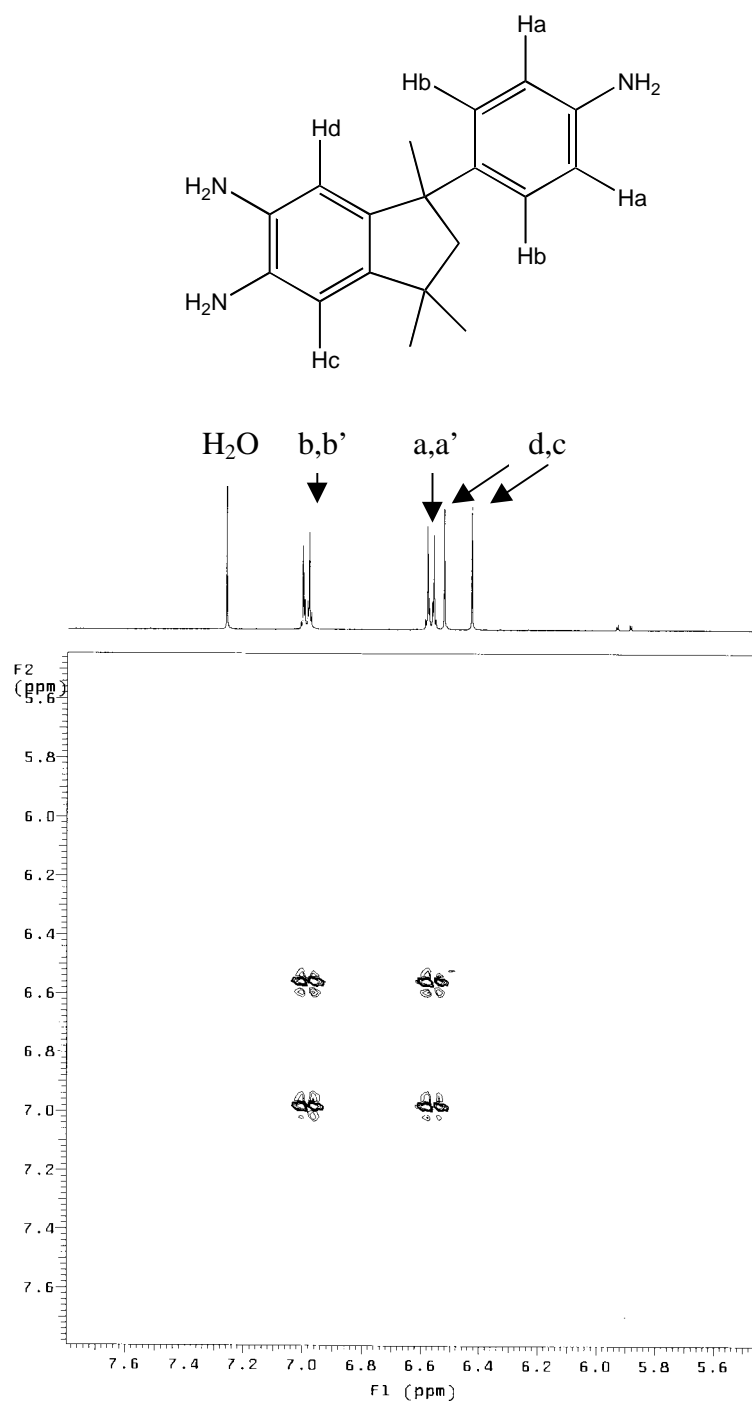
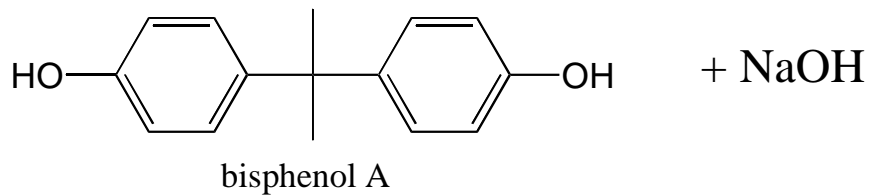
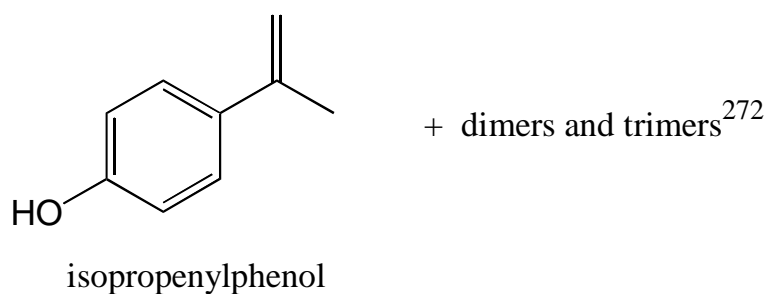


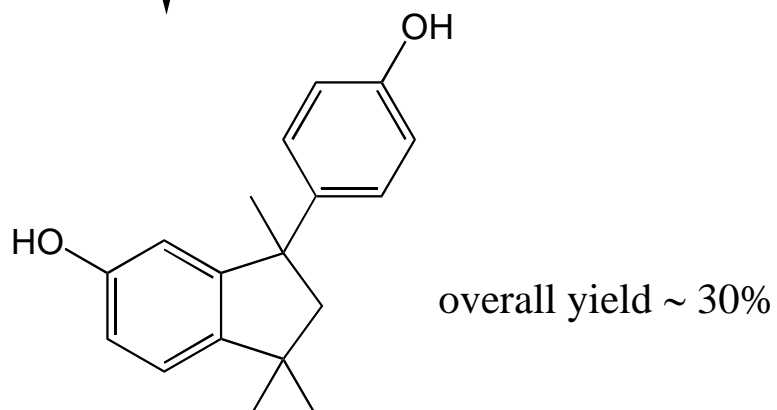
Figure 3.2.2.5.1 DQCOSY of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane



- ↓ 1. 175C until melt  
 220C, 2h, 350mmHg  
 250C, 6h, 50mmHg  
 ↓ 2. PhOH removed by distillation



↓ Trifluoroacetic Acid, R.T., 24 hours



6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane

Scheme 3.2.2.6.1 Synthesis of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI)

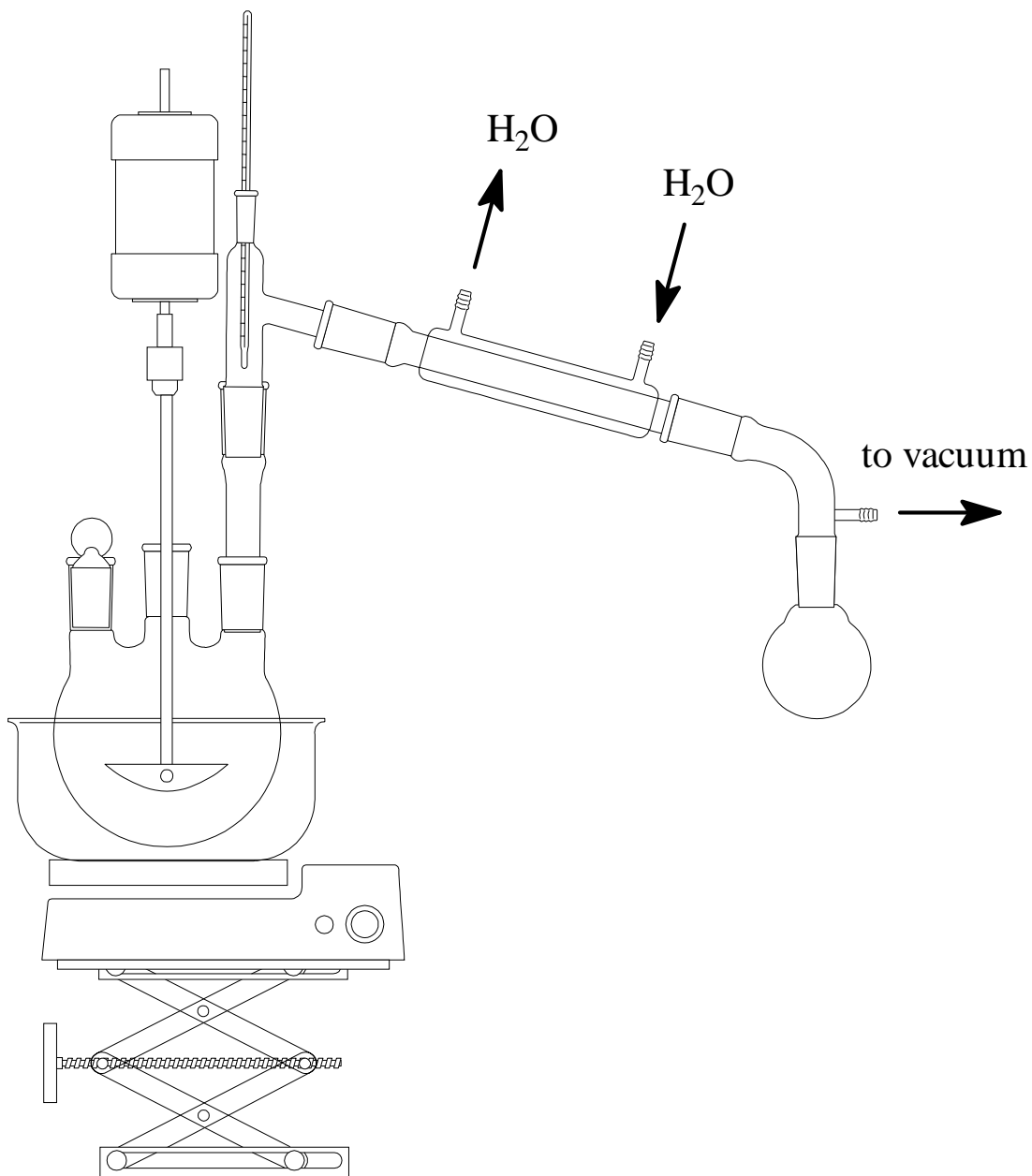


Figure 3.2.2.6.1 Reaction Apparatus for the Synthesis of 4-hydroxy- $\alpha$ -methylstyrene

solid was 180g, which was surmised to consist of phenol and isopropenylphenol (IPP).<sup>272</sup> To a 500ml flask, equipped as shown in Figure 3.2.2.6.1, 180g of the phenol/IPP mixture was added. Phenol (identified as such by <sup>1</sup>H NMR and its melting point) was removed at 90-140°C under a reduced pressure of 5 torr. Throughout this distillation the mixture became increasingly more viscous due to the removal of a low molecular weight molecule (phenol) and, more than likely, oligomerization of IPP. The resulting yellow oil was recovered in a 56g quantity and solidified at room temperature.

*3.2.2.7 Synthesis of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (dihydroxyphenylindane or DHPI) (Scheme 3.2.2.6.1)*

*Following a procedure similar to Dai's:*<sup>271</sup>

To a 500ml 3-neck flask equipped with a mechanical stirrer and a condenser were charged 56g of a mixture of IPP and IPP dimers and trimers. (Note: At room temperature the mixture is a solid. Therefore, immediately after the removal of phenol in the previous step, it was transferred while hot to the 3-neck reaction flask). To the reaction flask containing the mixture of IPP structures were slowly added ~150ml trifluoroacetic acid. This reaction mixture was held at room temperature for 24 hours. Trifluoroacetic acid (b.p. 72°C/760mmHg) was then removed under vacuum to yield a dark red, viscous solution. Once dissolved in ether, the solution was washed with 5% NaHCO<sub>3</sub>. Upon removal of the ether, the viscous residue was dissolved in toluene and triturated in hexane affording a light gray powder. Recovered yield, 41.1g (~30%). m.p. 193.5-195°C (lit. 194-195°C); Elemental analysis: found (expected); C:80.56 (80.23), H:7.51 (7.51); NMR Assignments, Figures 3.2.2.7.1 and 3.2.2.7.2.



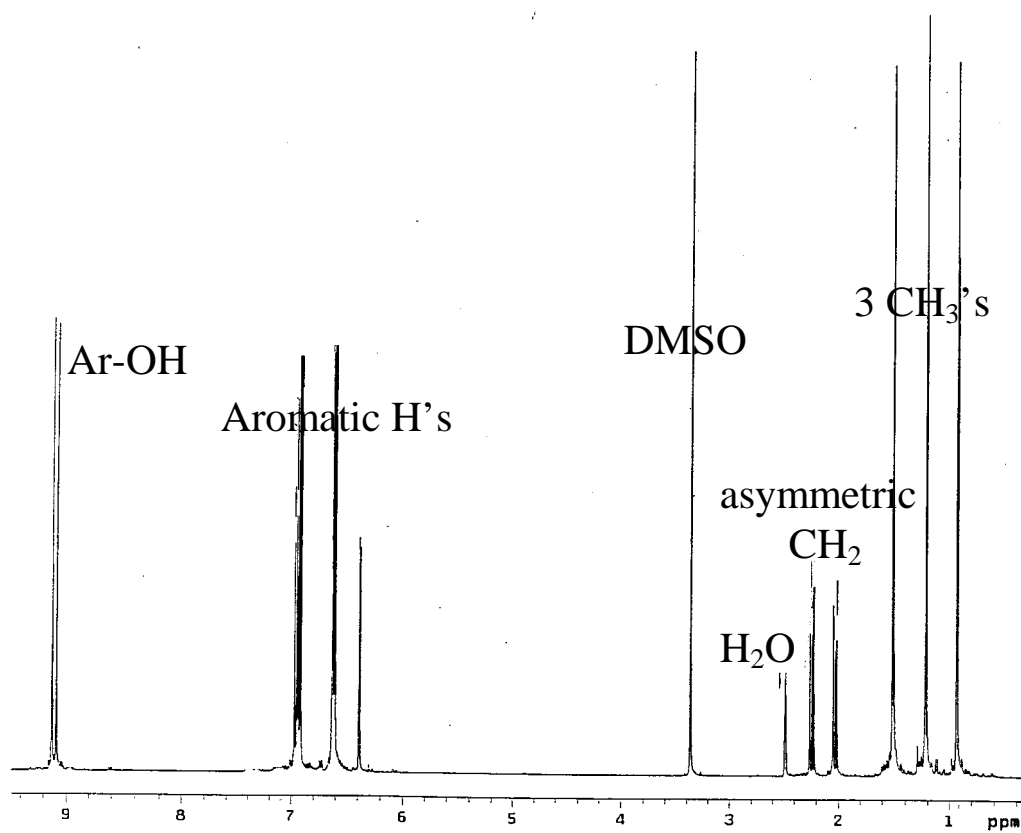
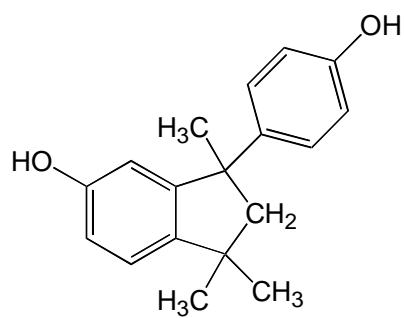


Figure 3.2.2.7.1 <sup>1</sup>H NMR of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane

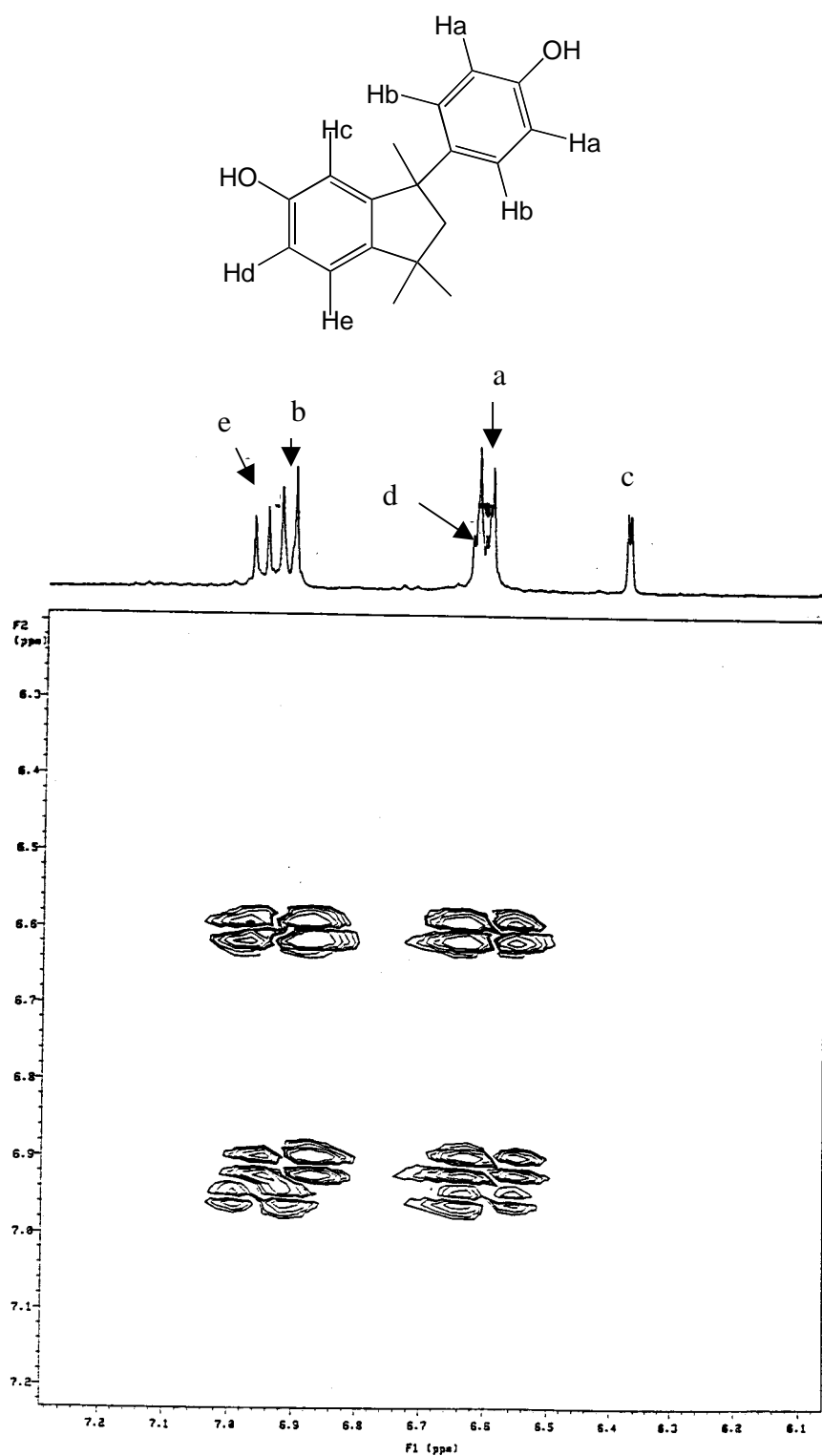


Figure 3.2.2.7.2 DQCosY of 6-hydroxy-(4-hydroxyphenyl)-1,3,3-trimethylindane

## **3.3 Characterization Methods**

### **3.3.1 Intrinsic Viscosity (IV)**

Intrinsic viscosity measurements provided a qualitative measurement of molecular weight. Measurements were conducted using a Cannon-Ubbelohde viscometer at  $25\pm 1^\circ\text{C}$  with NMP as the solvent. The reported values result from the linear extrapolation of four different sample concentrations to zero concentration.

### **3.3.2 Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC)**

GPC was conducted with a Waters GPC/ALC 150C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. Waters  $\mu$  Styragel HT3 + HT4 columns were used. The mobile phase was NMP, containing 0.02M  $\text{P}_2\text{O}_5$ . The flow rate was 1.0 mL/min, the injection volume was 200 $\mu\text{L}$ ; the experimental temperature was  $60^\circ\text{C}$ ; the polymer concentration was approximately 4 mg/mL. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. A series of polystyrene standards having narrow molecular weight distributions (Polymer Laboratory ) were employed to generate the universal calibration curve.<sup>87,88</sup>

### **3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR was used to confirm functional groups within both the monomers and polymers. Measurements were conducted on a Nicolet Impact 400 FTIR Spectrometer using either KBr pellets containing 1-5 wt% of monomer, or on thin polymeric films.

### **3.3.4 Polymer Solubility**

Polyimide solubility was determined at targeted concentrations of 10% (w/v) in a number of solvents including methylene chloride, chloroform, THF, NMP and DMAc. “Soluble” polyimides went into solution at room temperature, whereas “insoluble” polyimides precipitated out of solution after being cooled from a soluble state at higher temperatures. Visibly swollen polyimides were designated as “swelled” and partially soluble systems as “slightly swelled”.

### **3.3.5 Thermogravimetric Analysis (TGA)**

Dynamic TGA was employed to assess weight loss and thermal stability of polyimide samples using a Perkin Elmer TGA-7 Thermogravimetric Analyzer. Prior to this experiment the samples were carefully dried to remove possible solvent contribution to the reported 5% weight loss values. The typical heating rate was 10°C/minute in either nitrogen or air. Estimated error:  $\pm 10\text{wt}\%$

### **3.3.6 Differential Scanning Calorimetry (DSC)**

DSC provided information on polymer thermal transitions. Glass transition temperatures ( $T_g$ ) reported were obtained on a Perkin Elmer DSC-7 Differential Scanning Calorimeter. Scans were conducted under nitrogen at a heating rate of 10°C/min, unless otherwise stated. Second heat  $T_g$  values are reported as the midpoint of the change in slope of the baseline. Estimated error:  $\pm 3^\circ\text{C}$

### **3.3.7 Water Sorption**

Water uptake was determined on polyimide thin films dried to constant weight at 200°C and then immersed in either water at 30°C, or 50% humidity at 25°C. The films were then monitored periodically until a constant weight percent of water uptake was found.

### 3.3.8 Polyimide Oligomer and Epoxy Resin Titrations

Non-aqueous potentiometric titrations were employed to determine the molecular weight of amine terminated polyimides and the epoxy equivalent weight (EEW) of epoxy resins using a MCI GTOS Automatic Titrator equipped with a standard calomel electrode and reference electrode.

A typical amine terminated polyimide titration was conducted as follows:

Hydrogen bromide in acetic acid was the titrant for oligomeric amine terminated polyimides. The titrant (~0.02N) was standardized with dry potassium hydrogen phthalate (KHP) immediately prior to titrating. The polymer was completely dissolved in a solvent mixture of chloroform:acetic acid (5:1, v/v) before conducting the experiment. The end-point was detected as the maximum of the first derivative for the potential versus volume of titrant used. The end-point was then used to calculate the number of reactive groups in the system. The calculated number average molecular weight values were very reproducible,  $\pm 1.0\%$  (typically 3-5 runs).

A typical epoxy resin titration was conducted as follows:

Perchloric acid with a phase transfer agent, tetramethylammonium bromide, was utilized for the titration of epoxy resins. The titrant (~0.02N) was standardized with dry potassium hydrogen phthalate (KHP) immediately prior to titrating. The epoxy resin was completely dissolved in chloroform before conducting the experiment. The end-point was detected as the maximum of the first derivative for the potential versus volume of titrant used. The end-point was then used to calculate the epoxy equivalent weight (EEW), which is the number of grams of epoxy resin per mole of reactive epoxide rings. The calculated EEW values were very reproducible,  $\pm 1.0\%$  (typically 3-5 runs).

### 3.3.9 Refractive Index (RI) Measurement

Refractive indices of thin polymer films were measured on a Metricon™ Model 2010 prism coupler thin film thickness/refractive index measurement system (633nm),

with an index accuracy of  $\pm 0.001$ , and an index resolution of  $\pm 0.0005$ . Prism type: 200-P-4.

### **3.3.10 Permeation Apparatus**

The homopolyimides used in this study were in the form of dense, planar (sheet) membranes varying in the thickness from 15-40 $\mu\text{m}$ . Films were solution cast from NMP and dried under vacuum at 200 $^{\circ}\text{C}$  for 24 hours. The solvent-free thin films were immediately used in the gas permeation device to avoid moisture uptake.

Measurement of the permeability coefficients were performed at Medal by Mr. Dean Kratzner. Figure 3.3.10.1 shows the apparatus used in this experiment. The  $\text{O}_2$  and  $\text{N}_2$  permeabilities of polymer membranes were characterized at 30 $^{\circ}\text{C}$  by a mean permeability coefficient with units of barrer (Ba).

$$1 \text{ Ba} = 10^{-10} \text{ cm (STP)/(cm}^2\text{*sec*cmHg)}$$

The experimental procedure was as follows:

The membrane was mounted in a permeation cell prior to degassing the whole apparatus. Permeant gas was then introduced on the upstream side, and the permeant pressure on the downstream side was monitored using a MKS-Baratron pressure transducer. From the known steady-state permeation rate, pressure difference across the membrane, permeable area and film thickness, the permeability coefficient was determined.

### **3.3.11 Melting Point (m.p.) Measurement**

A Lab Devices Melt-Temp II was used to determine melting points of purified compounds. Heating rate  $< 1^{\circ}/\text{min}$ .

### **3.3.12 High Performance Liquid Chromatography (HPLC)**

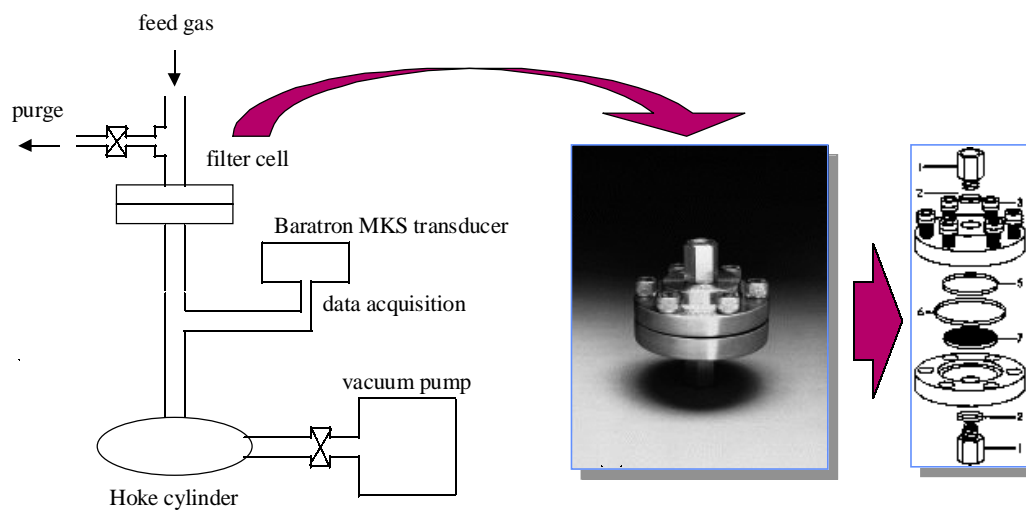


Figure 3.3.10.1 Gas Permeation Apparatus

Reversed-phase high performance liquid chromatography (HPLC) analyses were conducted on a Vista 5500 with an C-18 (octadecyl or ODS) column. Separation of the two DAPI isomers required an initial mobile phase composition of 50% acetonitrile/50% water. After 5 minutes, the schedule allowed for a gradient change to 100% acetonitrile over 20 minutes. Rate 1ml/min, UV detector (254nm).

### **3.3.13 Nuclear Magnetic Resonance (NMR) Spectroscopy**

Nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were obtained using a Varian Unity 400 Spectrometer. NMR was used primarily to determine monomer purity and to confirm molecular structure of newly synthesized monomers.



## 3.4 Polymerization Methods

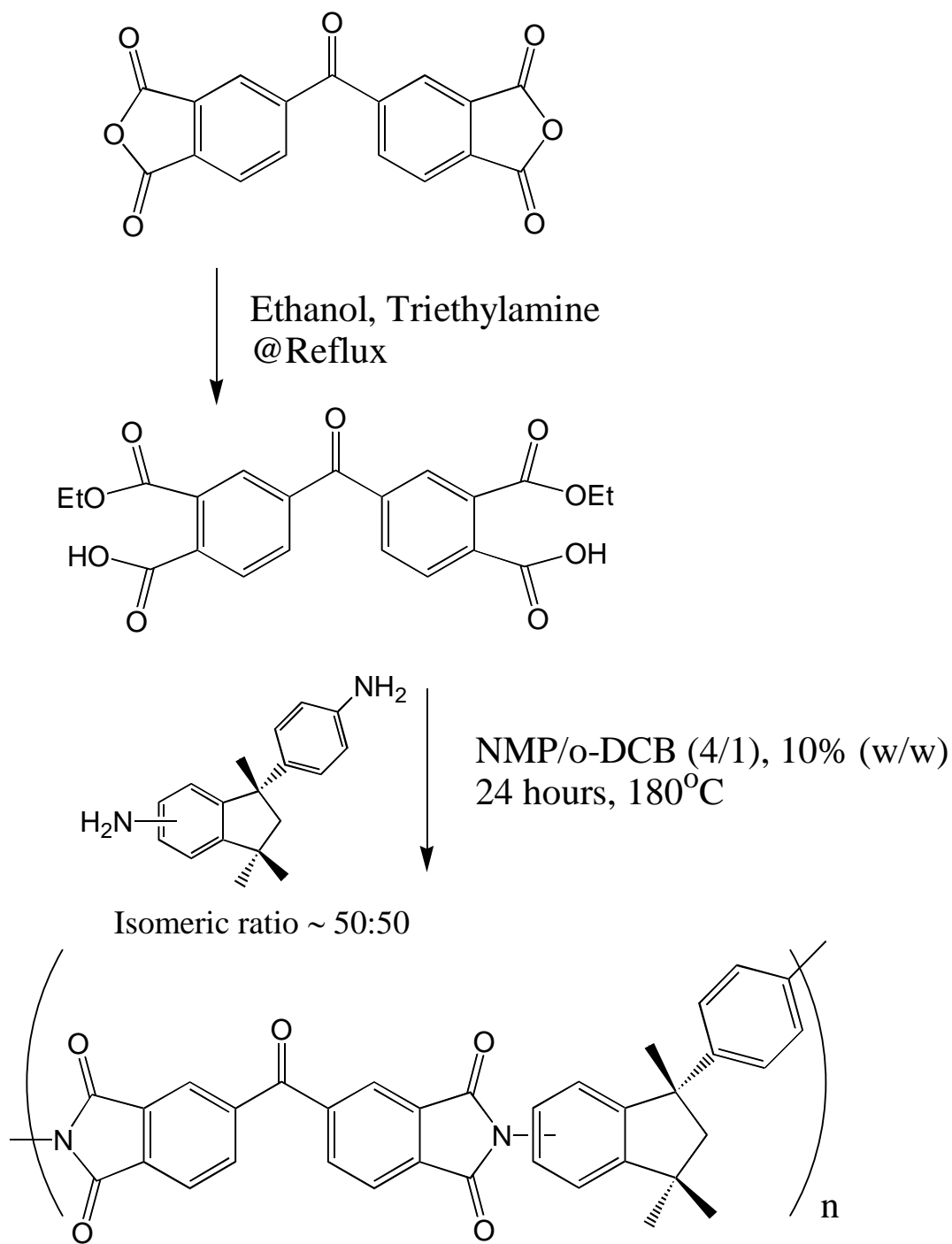
Four synthetic procedures were utilized to form high molecular weight polyimides. These were: chemical, high temperature solution, thermal and ester-acid precursor imidization. In the following sections, typical procedures are given for each of these methods.

### 3.4.1 Ester-Acid Precursor Method for the Formation of High Molecular Weight 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzofurandione (6FDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

A general scheme for all of the polymers synthesized by this method is shown in Scheme 3.4.1.1.

A typical example is as follows. To a three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a reverse Dean-Stark trap with a condenser (Figure 3.4.1.1), 2.500 g ( $5.63 \times 10^{-3}$  mol) of 6FDA was charged and rinsed in with 40ml of ethanol and 3ml triethylamine. Under refluxing conditions, the ethyl ester-acid of the dianhydride was formed. After approximately one hour, the excess ethanol and triethylamine had distilled into the trap leaving a viscous ester-acid mixture. The diamine, DAPI, was added to this mixture in an equimolar amount, 1.4997 g ( $5.63 \times 10^{-3}$  mol), and washed in with NMP/*o*-DCB (4/1) to give ten weight percent solids. The trap was drained and filled with the azeotroping solvent, *o*-DCB. The solution temperature was then raised to 180°C to obtain fully cyclized imide linkages.<sup>21</sup> Within a few minutes, distillation of ethanol and water were observed as the amic acid was formed, followed quickly by imidization.

The viscous solution was cooled after 24 hours of reaction time and precipitated into stirred methanol. The polymer solids were filtered and washed with methanol and diethylether. The resulting powder was dried under vacuum at 180°C for 24 hours.



Scheme 3.4.1.1 Ester-Acid Precursor Method for the Formation of High Molecular Weight 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

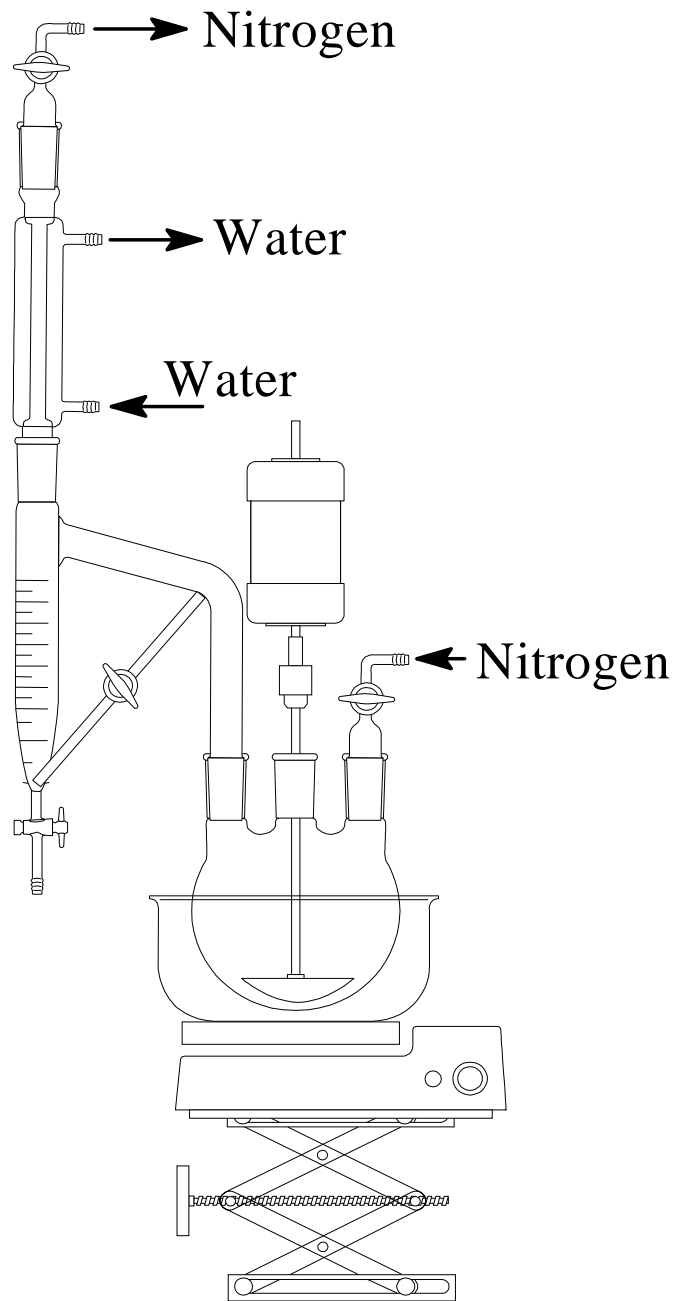


Figure 3.4.1.1 Polymerization Apparatus

### **3.4.2 Chemical Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)**

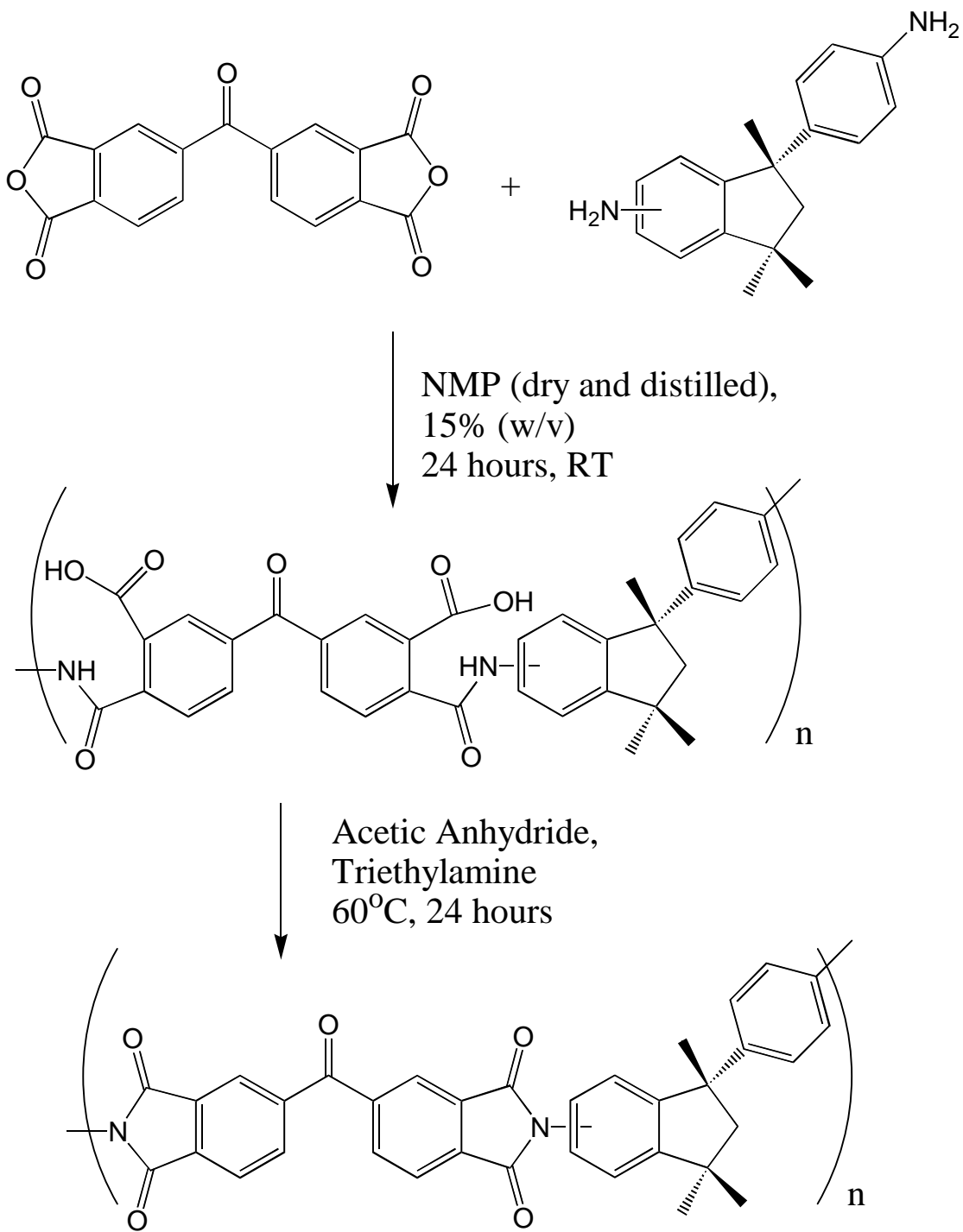
A general scheme for polyimides synthesized by the chemical imidization method is shown in Scheme 3.4.2.1.

A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a condenser (Figure 3.4.1.1), 2.1311g (8 mmol) of DAPI was added followed by 15 ml of dried and distilled NMP. Once dissolved, 2.5778g (8 mmol) of BTDA was slowly added over a 30 minute period. The purpose of slowly adding the dianhydride to the diamine was to favor the reaction of the anhydride moieties with the excess amine versus hydrolysis of anhydride by residual water. The BTDA was rinsed in with 16.4ml of NMP to give a total weight percent of 15% (w/v). The solution was stirred for 24 hours at room temperature to form the polyamic acid of DAPI and BTDA.

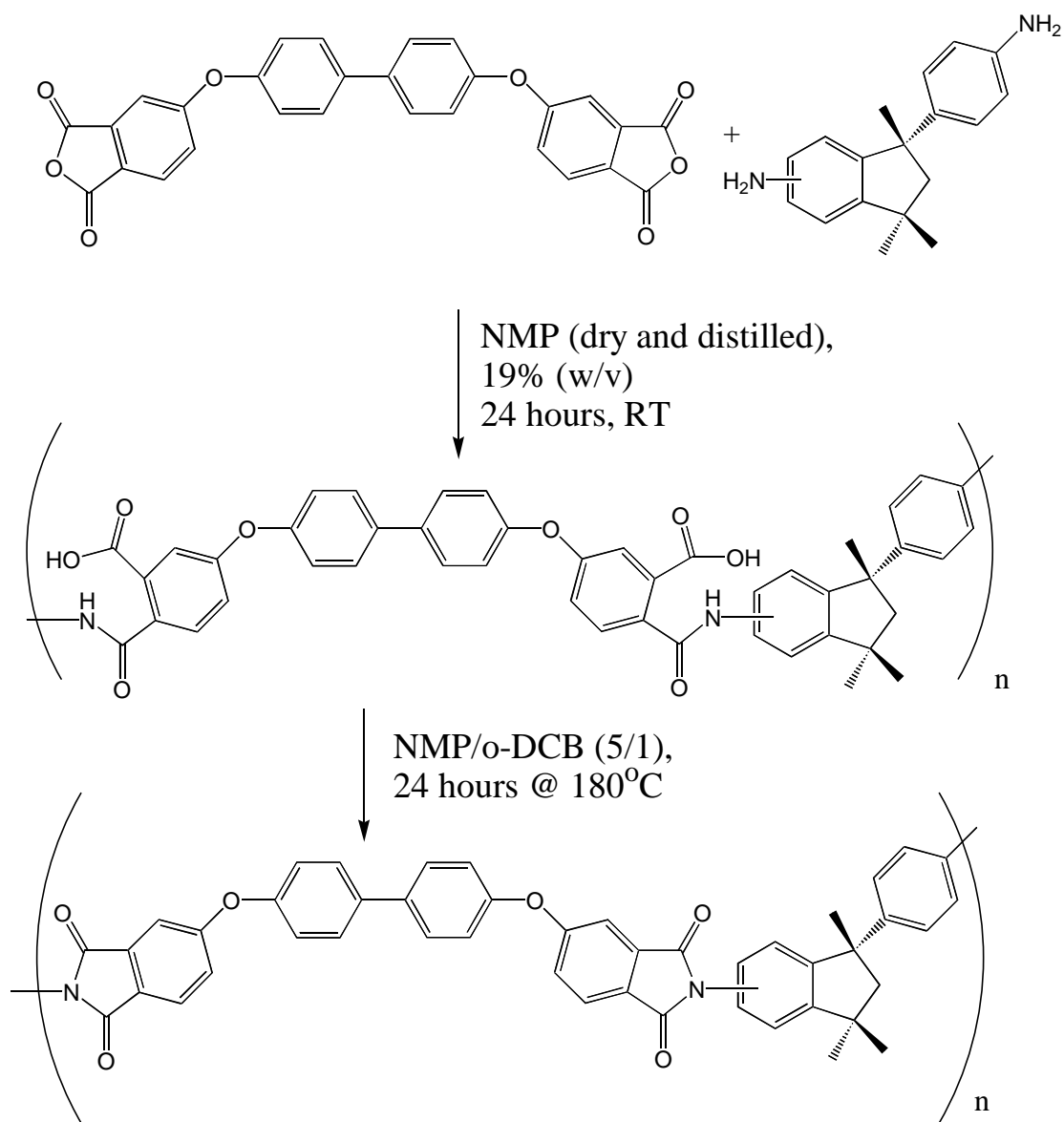
To cyclize the polyamic acid to the polyimide, 4.9ml (6 molar excess) of acetic anhydride and 4.9ml (6 molar excess) of triethylamine was added (the acetic anhydride and triethylamine were dry and distilled). The solution temperature was raised to 60°C for 24 hours before cooling and precipitating the polyimide in methanol followed by washing with diethyl ether. The resulting powder was dried under vacuum (~5 torr) at 200°C to remove residual water and solvent.

### **3.4.3 Solution Imidization of High Molecular Weight 4,4'-bis [4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPEDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)**

A general scheme for polyimides synthesized by the solution imidization route is shown in Scheme 3.4.3.1.



Scheme 3.4.2.1 Chemical Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)



Scheme 3.4.3.1 Solution Imidization of High Molecular Weight 4,4'-bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPEDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

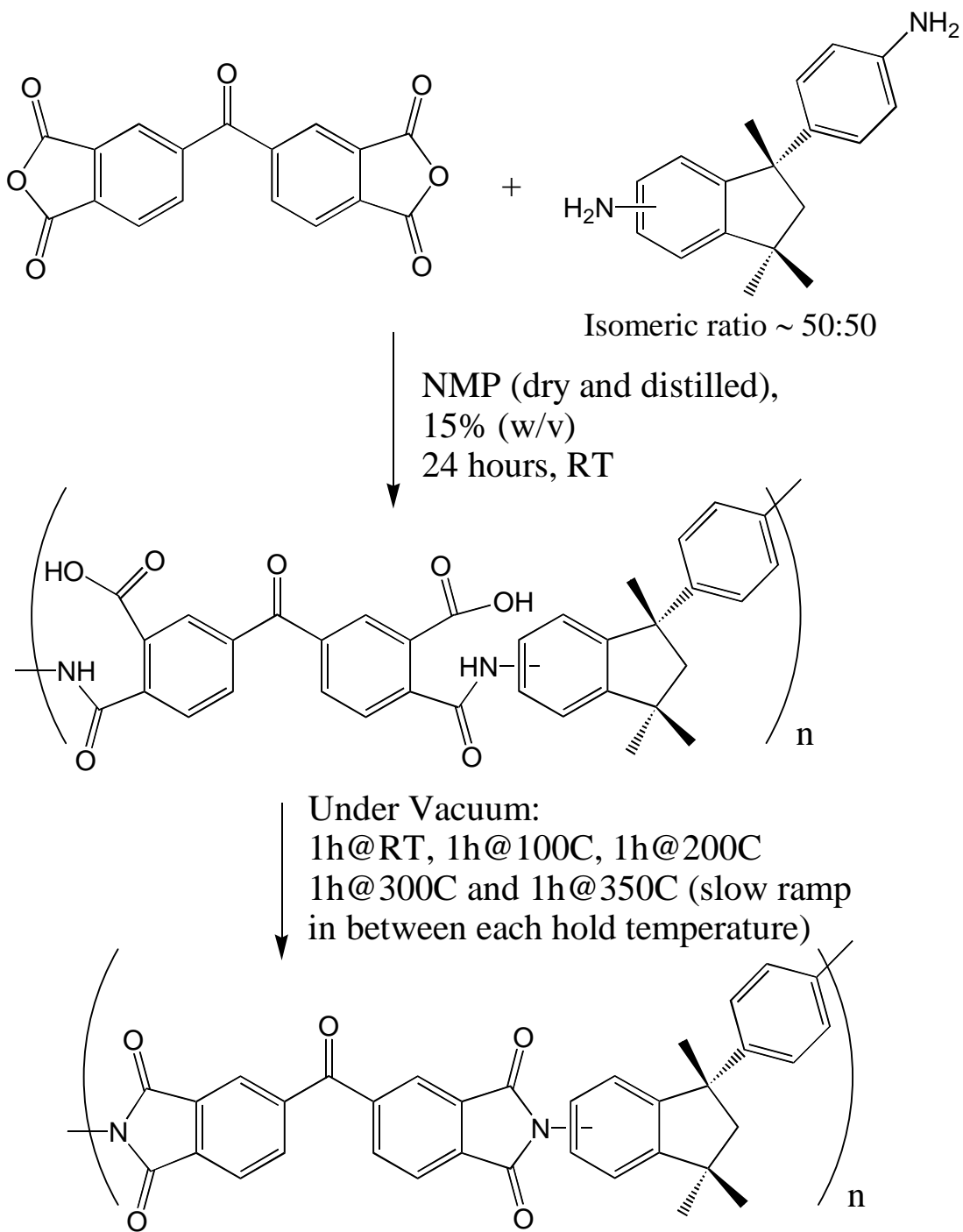
A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap with a condenser (Figure 3.4.1.1), 2.0032g (18.5 mmol) of m-PDA was added and dissolved in 25 ml of dry and distilled NMP. To this homogeneous solution, 8.8620g (0.0185 moles) of BPEDA was slowly added along with 32ml of NMP (19wt% (w/v)). After being stirred for 24 hours at room temperature, the resulting polyamic acid was thermally imidized in solution. The azeotroping solvent, dry and distilled *o*-DCB, used to facilitate the removal of water produced during the reaction was used in the following ratio: NMP:*o*-DCB/5:1. The *o*-DCB was also used to fill the reverse Dean-Stark trap to maintain a constant solvent volume inside the flask. The polyamic acid solution was thermally imidized at 180°C for 24 hours before being cooled and poured into methanol to precipitate the polymer which was subsequently washed with diethyl ether.

#### **3.4.4 Thermal Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)**

A general scheme for polyimides synthesized by the thermal imidization route is shown in Scheme 3.4.4.1.

A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap with a condenser (Figure 3.4.1.1), 0.9892g (3.7 mmol) of DAPI was added followed by 15ml of dried and distilled NMP. Once dissolved, 1.1965g (3.7 mmol) of BTDA was slowly added to the solution over a 30 minute period. The BTDA was rinsed in with 16.4ml of NMP to give a total weight percent of 15% (w/v). The solution was stirred for 24 hours at room temperature to form the polyamic acid of DAPI and BTDA.

The following thermal imidization schedule was performed on the polyamic acid cast from solution onto a glass plate: (under vacuum with slow ramping between each hold temperature) 1 hour at RT, 1h at 100°C, 1h at 200°C, 1h at 300°C and 1h at 350°C.



Scheme 3.4.4.1 Thermal Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)



The final imidization temperature depended on the  $T_g$  of the resulting polymer. As a general rule, the final imidization temperature must be  $>20^\circ\text{C}$  above  $T_g$ . Following imidization, the polyimide film was removed from the glass plate with a small addition of water. The film was then redried at  $200^\circ\text{C}$  under vacuum for more than 12 hours.

### 3.5 Synthesis of Controlled Molecular Weight Polyimide Oligomers

Controlled molecular weight polyimide oligomers were synthesized by the ester-acid method. The stoichiometry of the monomers was varied according to the Carothers Equation to achieve the various desired molecular weight oligomers.

The Carothers Equation:

$$\langle X_n \rangle = N_o / [(1/2) * (2N_o - N_o p f_{av})] = 2 / (2 - p f_{av}) = 2 / (2 - f_{av}) \quad (\text{when } p = 1)$$

where,

$\langle X_n \rangle$  = the number average degree of polymerization,

$p$  = the extent of reaction of the functional groups, and

$f_{av} = 4r/(r+1)$ ,  $r = N_A/N_B$  for AA and BB type monomers with BB as the excess component or,  $r = N_A/(N_B + N_B')$ , when  $N_B'$  of monofunctional B endcapper is used.

Reorganization yields,

$$\langle X_n \rangle = (1 + r) / (1 - r).$$

A typical polymerization procedure for an amine terminated polyimide oligomer with a number average molecular weight of 5,000 g/mole is as follows: To a 250ml 3-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a reverse Dean-Stark trap with a condenser (Figure 3.4.1.1), 14.8183 g (2.85 mmol) of BPADA was charged and rinsed in with 55ml of ethanol and 3ml of triethylamine. Under refluxing conditions, the ethyl ester-acid of the dianhydride was formed. After approximately one hour, the excess ethanol and triethylamine was distilled leaving a viscous ester-acid mixture. The diamine, *m*-PDA, was added to this mixture in the calculated stoichiometric offset amount, 3.4518 g (3.19 mmol), and washed in with NMP/*o*-DCB (5/1) to give twenty weight percent solids. The trap was drained and filled with the azeotroping solvent, *o*-DCB. The temperature was then raised to 180°C to obtain fully cyclized imide linkages.<sup>21</sup> Within a few minutes, distillation of ethanol and water was observed as the amic acid was formed, followed quickly by imidization.

The solution was cooled after 24 hours. The polymer was precipitated in stirred methanol, then was filtered and washed with methanol and diethyl ether. The resulting powder was dried under vacuum (~5 torr) at 180°C for 24 hours.