
Supporting Information

Synthetic Methods

Figure S-1. ^1H -NMR of 1,6- and 1,8-ANP.

Figure S-2. Absorption spectra in 1:1 acetonitrile: water, red: 1,6-ANP; blue: dG^{1,6-ANP}; purple: 10mer with 1,6-ANP adduct.

Figure S-3. Absorption spectra in 1:1 acetonitrile: water, red: 1,8-ANP; green: dG^{1,8-ANP}; blue: 10mer with 1,8-ANP adduct.

Synthetic Methods:

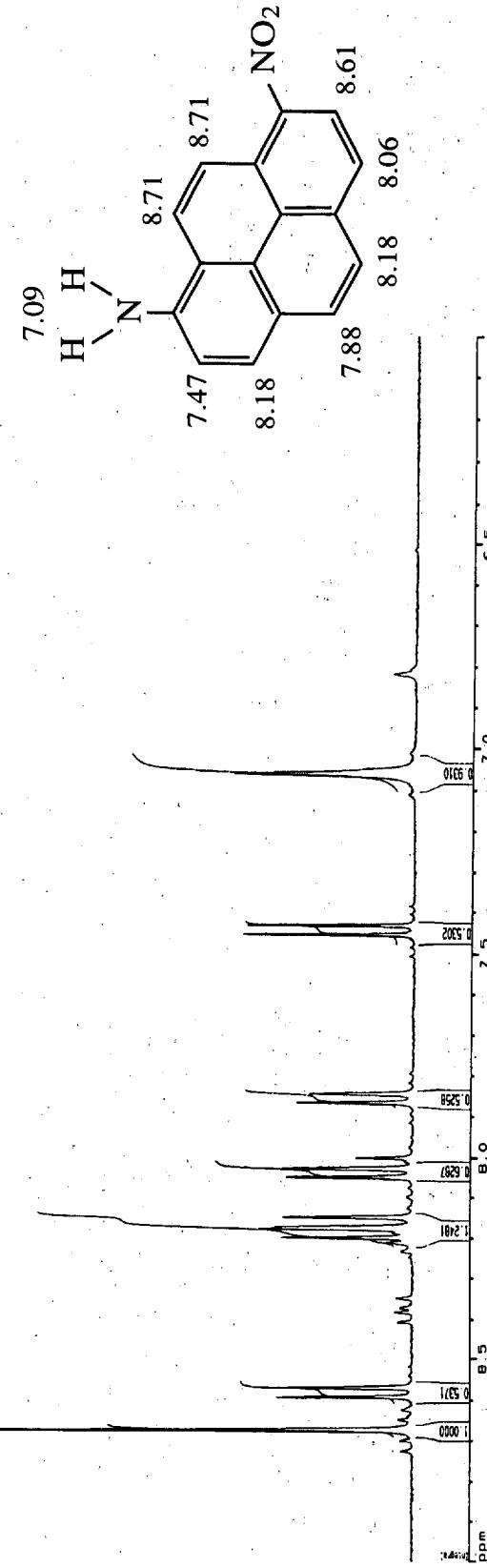
Nitration of bromopyrene. Six hundred mg of bromopyrene was allowed to react with 400 μ L of concentrated nitric acid in 5 mL glacial acetic acid with stirring at room temperature overnight. The reaction mixture was partitioned between methylene chloride and saturated aqueous sodium bicarbonate. The organic layer was concentrated and run through a silica gel column (2.5 cm x 10.0 cm, eluent, 1:1 benzene: hexane) to remove any starting material. GC-MS analysis of the reaction mixture revealed three peaks in a ratio of 2: 2: 1, corresponding to the mass of bromonitropyrene (m/z 325, 327) (total yield 78%). Separation of the bromonitropyrenes in this mixture was found to be relatively inefficient and laborious. The mixture of bromonitropyrenes, therefore, was used for the subsequent Pd-catalyzed coupling and cleavage.

Pd-catalyzed coupling and cleavage. $\text{Pd}(\text{OAc})_2$ (10 mg), BINAP (50 mg), Cs_2CO_3 (810 mg), and 360 μ L benzophenone imine were added to a round bottom flask containing 500 mg of the mixture of bromonitropyrenes dissolved in freshly distilled THF. The reaction mixture was refluxed under nitrogen. TLC monitoring showed that the reaction was complete in 16 h. The flask was cooled to room temperature and 5% (v/v) 2.0 M HCl was added. After 5 min at ambient temperature, the reaction mixture was filtered and concentrated *in vacuo*. The mixture was dry loaded on to a silica gel column (4.5 cm x 25.0 cm) and separated with benzene: ethyl acetate (5:1) as eluent. The R_f values for the 1,8- and 1,6-ANP isomers are 0.64 and 0.47 respectively. These two products were present in approximately equal amounts. The slowest eluting 1,3 isomer band (R_f = 0.35) was not isolated. Total yields of 80% and 95% for the coupling and cleavage, respectively, were determined by reverse phase HPLC analysis.

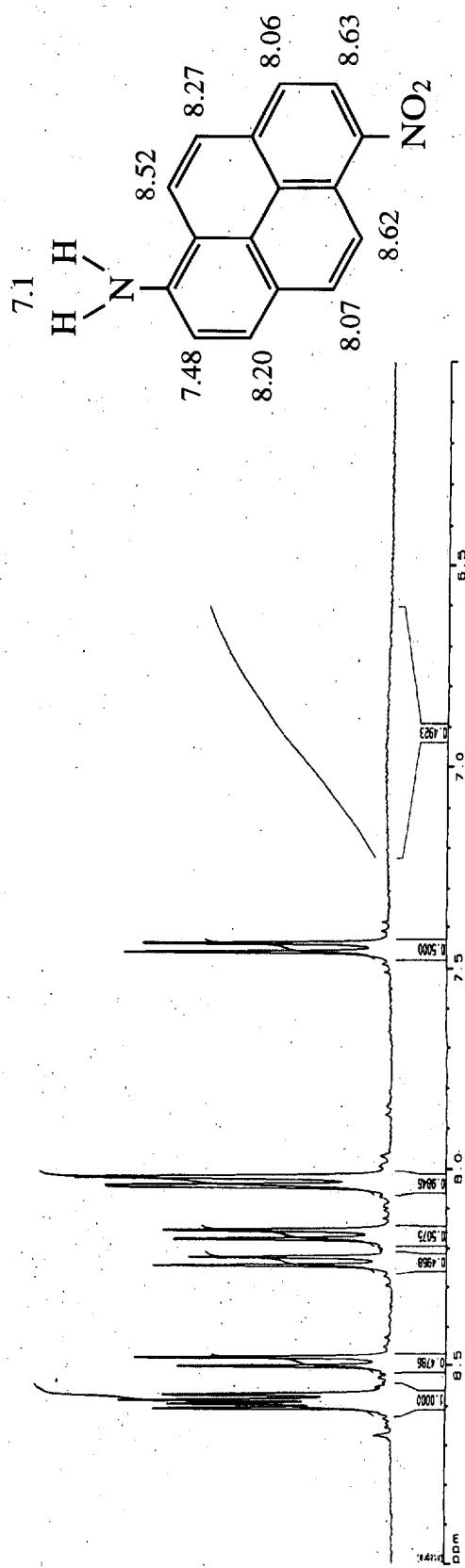
[Attempts to separate and fully characterize the products of the coupling reaction prior to addition of HCl were unsuccessful. However, FAB-MS analysis revealed a mass corresponding to the predicted benzophenone imine product ($M+1$, 427).]

Proton NMR of Aminonitropyrenes

1-amino-8-nitropyrene

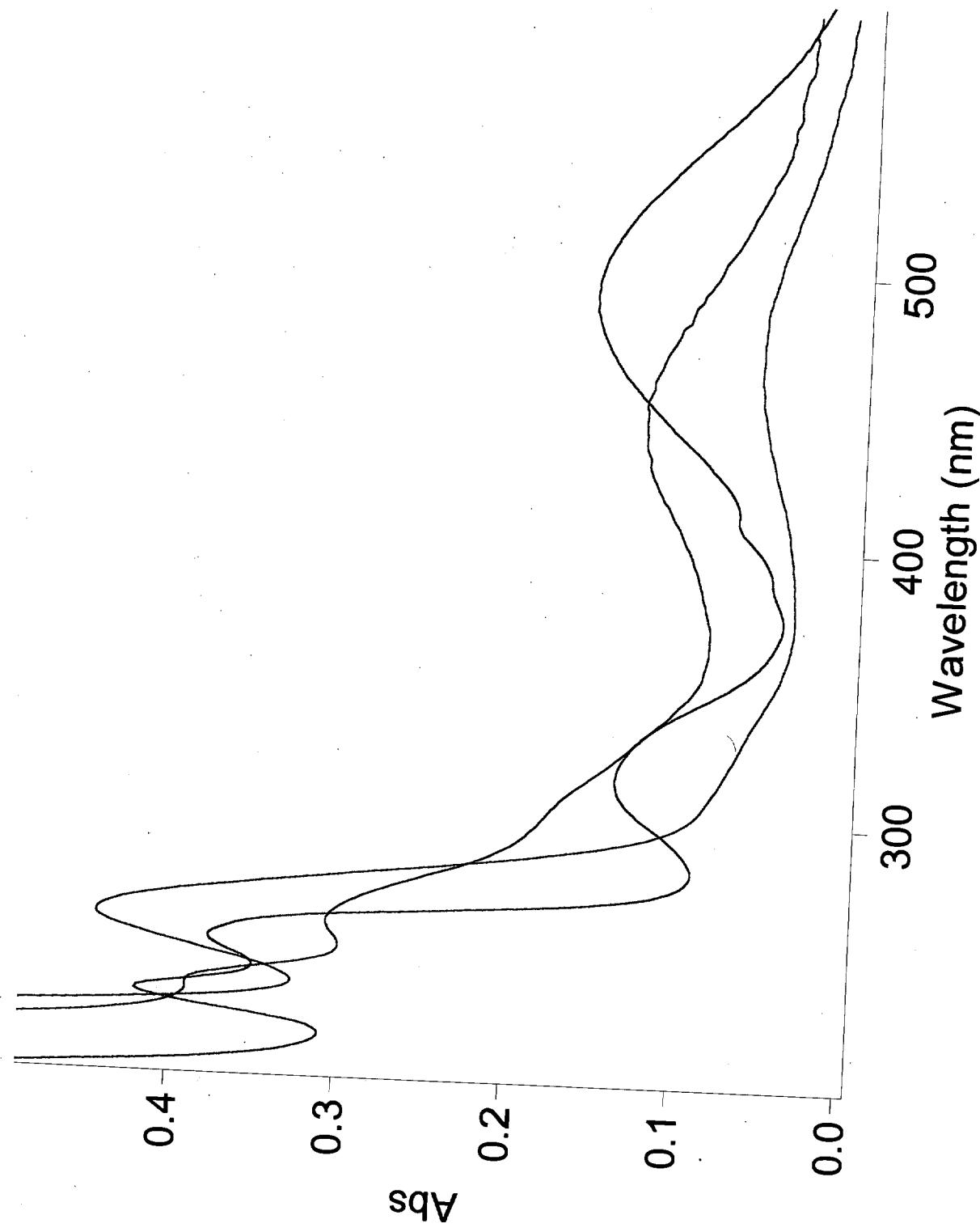


1-amino-6-nitropyrene



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Page 1 of 3



S-2

