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Supporting Information

Addition of Electron Rich Aromatics to Azafullerenium Carbocation. A Stepwise Electrophilic Substitution Mechanism.

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Experimental Section

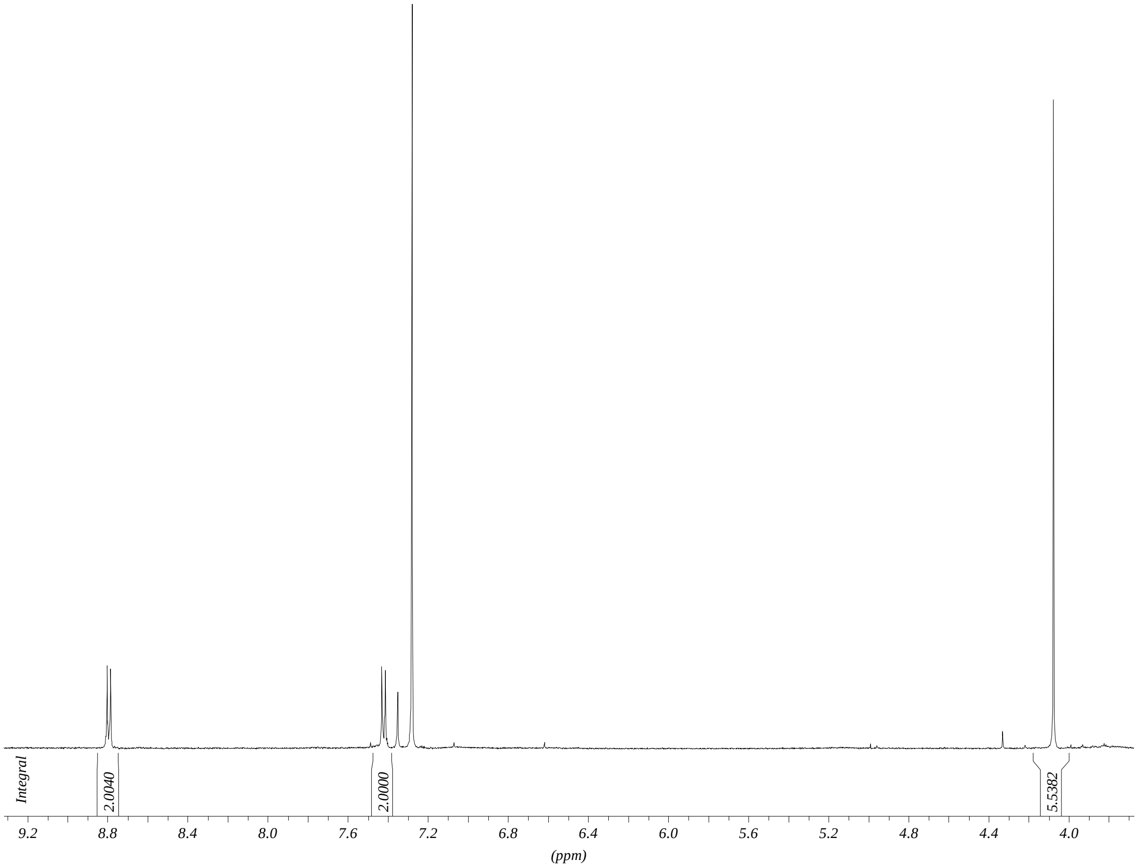
General Considerations. Azafullerene dimmer was prepared according to the literature procedure (ref 1). ^{1}H NMR spectra were recorded on a Bruker AMX-500 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si, by using the residual solvent peak as internal standard. ^{1}H NMR spectra of all azafullerene adducts were obtained in CS_2-$CDCl_3$ (2/1). HPLC analyses have been carried out on a Separon C_{18} reverse phase column with detection at 326 nm. A mixture of toluene/acetonitrile (55/45) was used as eluent at 1 ml/min flow rate. Isomeric purities were determined by ^{1}H NMR and GC-MS on a Supelco (SPB-5, 30mX0.25mm) capillary column and a Shimatzu GC-MS-QP5050 CI mass detector.

General Procedure for the Determination of the Intermolecular isotope effects. A mixture of $(C_{59}N)_2$ and a 100-fold excess of the equimolar quantities **3-*d*$_0$** and **3-*d*$_5$** as well as **4-*d*$_0$** and **4-*d*$_5$** and **4-*d*$_0$** and **4-*d*$_3$**, in separate experiments, were dissolved in 1,2-dichlorobenzene HPLC grade, together with a 20-fold excess of toluene-*p*-sulfonic acid. The reaction mixture was then heated at 130^{o}C, while a constant air stream was maintained over the solution, for about one hour (all reactions were monitored by HPLC). After the reaction was cooled down to room temperature, a 100-fold excess of triethylamine was added. Finally, 1,2-dichlorobenzene was distilled from the reaction mixture, under reduced pressure at 57^{o}C, and the remaining crude product was washed and centrifuged three to five times with acetonitrile HPLC grade. The isotope effects were determined by the integration of the appropriate product proton signals from the crude product mixtures.

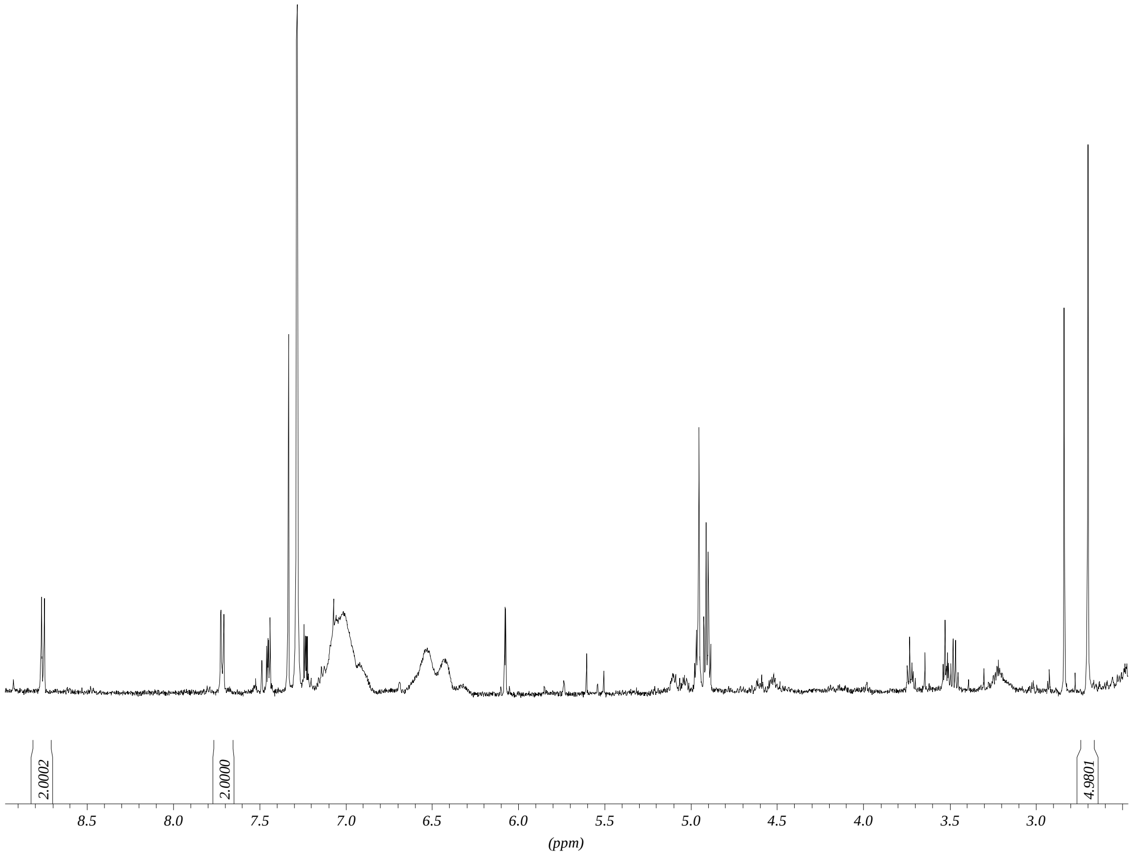
Preparation of Anisole-d_5 (3-d_5). Phenol-d_6 (1.23 g, 12.28 mmol) was dissolved in 12 ml of dry DMF, under N_2 atmosphere. After the reaction mixture was cooled at 0 ^{o}C, NaH 60% in paraffin oil (589 mg, 14.74 mmol) was added. The mixture was stirred at room temperature for 30 min and quenched at 0 ^{o}C by addition of 1.54 ml CH_3I. Following the stirring of the solution at room temperature for 30 min, Et_2O (60 ml) was added. The reaction mixture was washed three times with brine, dried over $MgSO_4$ and concentrated to afford **3-d_5** (1.28 g, 92%). Anisole-d_5 was further purified by distillation under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.99, 129.43 (t, *J*=25 Hz), 120.62 (t, *J*=24 Hz), 114.00 (t, *J*=24 Hz), 55.55; MS, m/z (relative abundance): 113(M^+, 100), 98(17), 83(76), 70(77), 54(31).

^{1}H NMR Spectra

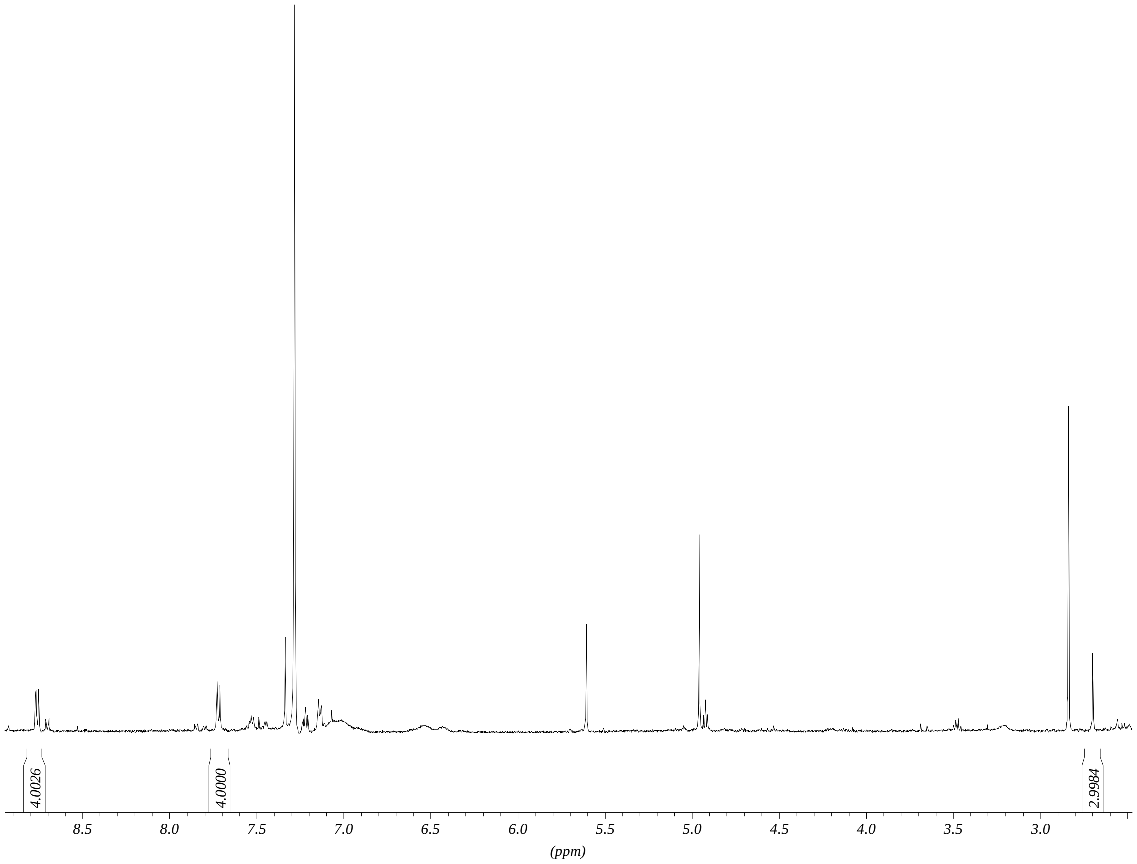
S4: Intermolecular Isotope Effect for the rection of **2** with Anisoles d_5/d_0



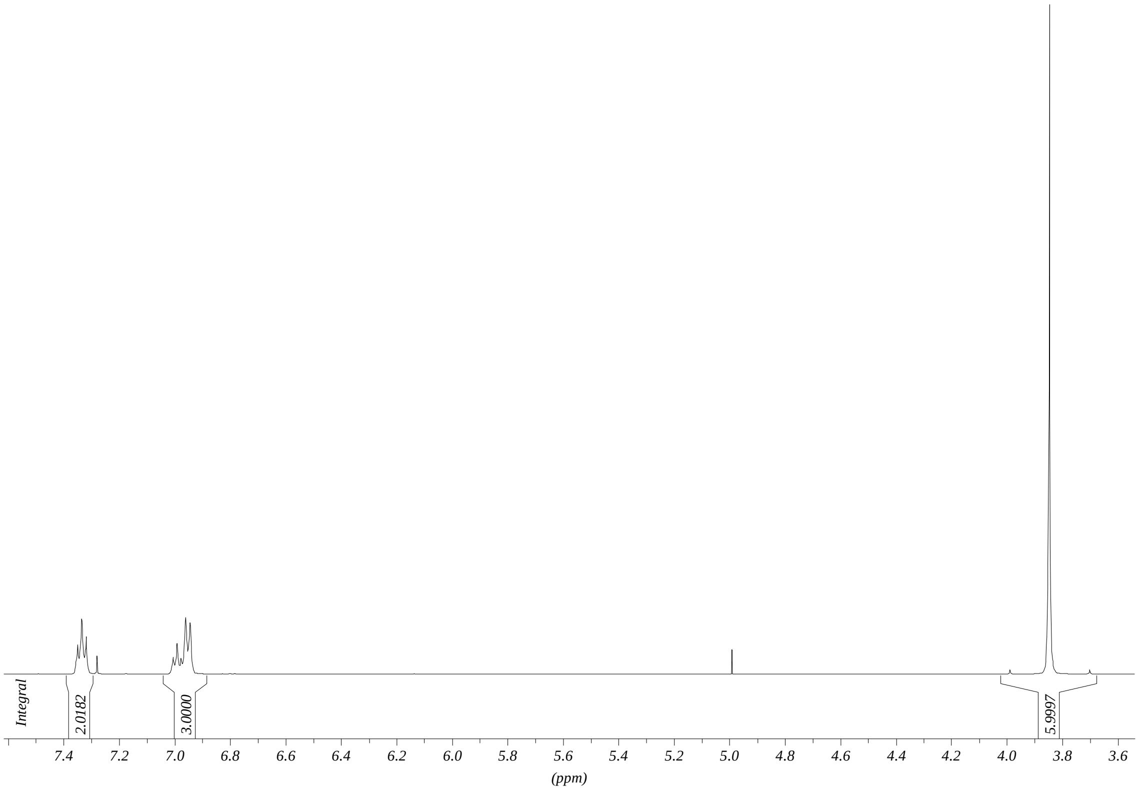
S5: Intermolecular Isotope Effect for the reaction of **2** with Toluenes d_5/d_0



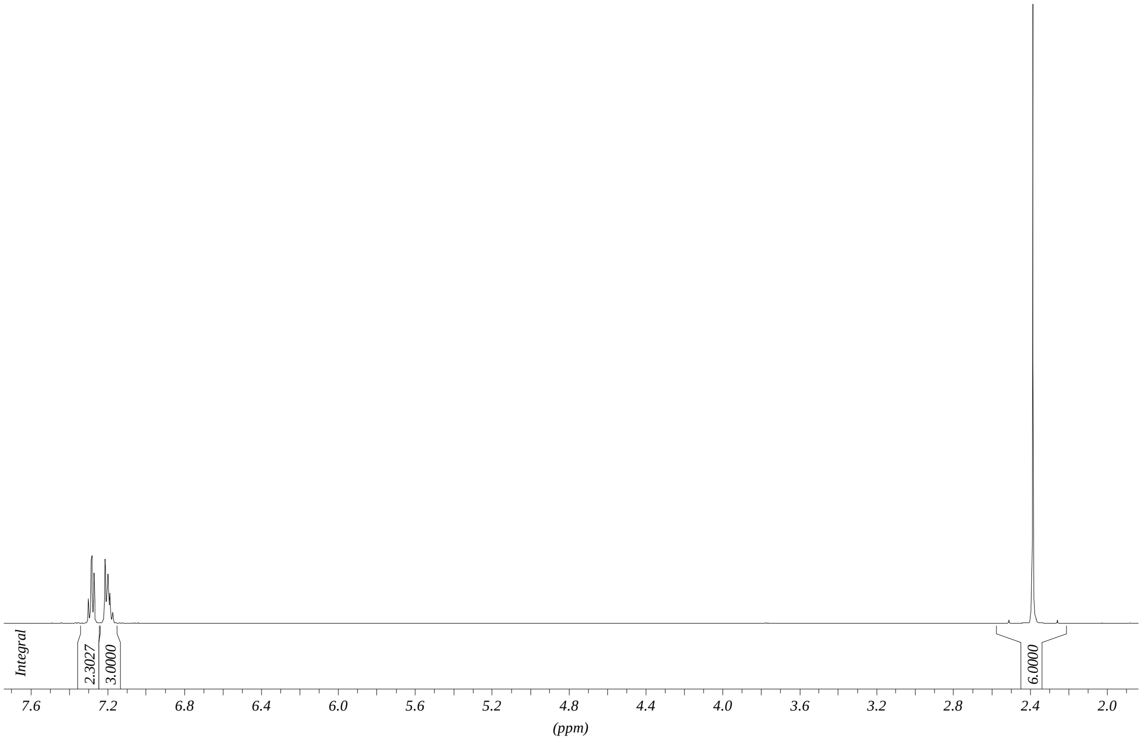
S6: Intermolecular Isotope Effect for the reaction of **2** with Toluenes d_3/d_0



S7: Equimolar Mixture of Anisoles d_5/d_0



S8: Equimolar Mixture of Toluenes d_5/d_0



S9: Equimolar Mixture of Toluenes d_3/d_0