## **Supporting Information**

## Electrophilic Aromatic Substitution: New Insights into an Old Class of Reactions

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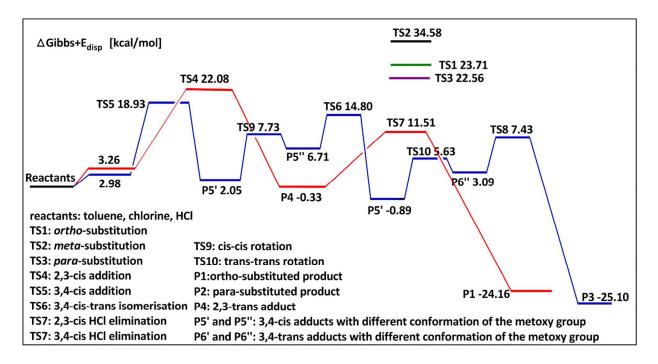
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**Figure S1.** Computed potential free energy surface (PES) for anisole- $Cl_2$  reactions, catalyzed by HCl, in simulated  $CCl_4$  solution at B2-PLYP+D3/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p). Cis-trans isomerization and elimination transition states, leading to formation of *m*-substituted product are not included.

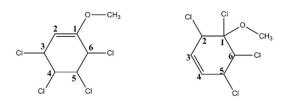
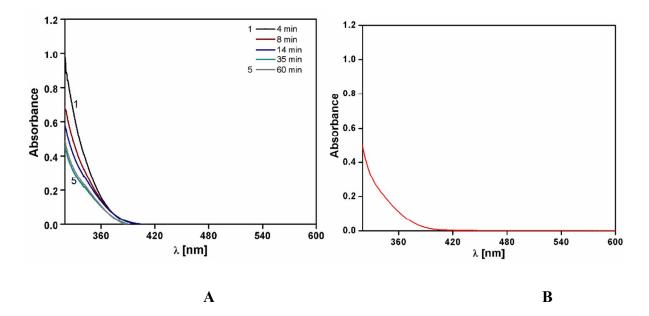
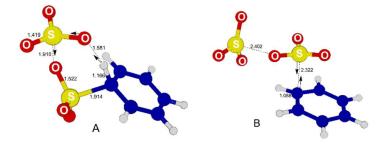


Figure S2. Addition products formed during anisole chlorination.



**Figure S3.** (A) UV spectra of the reaction mixture for benzene nitration with mixed acid in 1:1  $HNO_3:H_2SO_4$ ) in the 300 – 600 nm region; (B) Spectrum of neat nitrobenzene in the 300 – 600 nm region. All spectra are recorded at 25 °C.



**Figure S4.** M06-2X/6-311+G(2d,2p) structures of the transition state for the concerted  $S_EAr$  sulfonation of benzene with two SO<sub>3</sub> molecules in isolation (**A**) and for the stepwise process (**B**) in CH<sub>3</sub>NO<sub>2</sub>.

## **Cartesian coordinates**

The Cartesian coordinates of the optimized structures discussed in the text can be found in the Supporting Information files of the following publications:

Anisole chlorination: SI to Ref. 15.

Toluene chlorination: SI to Ref. 16.

Benzene bromination: SI to Ref. 17.

Benzene nitration: SI to Ref. 18.

Benzene sulfonation: SI to Ref. 19.