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Vinylthiylation of Octafluorotoluene and its Derivatives

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Vinylthiolation of Octafluorotoluene and its Derivatives

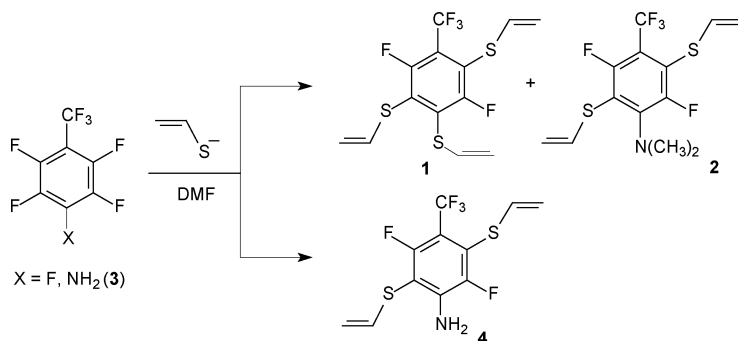
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1,2,5-Tri(vinylthio)-4-trifluoromethyl-3,6-difluorobenzene (**1**) and 1-dimethylamino-2,5-di(vinylthio)-4-trifluoromethyl-3,6-difluorobenzene (**2**) were obtained in 13 and 73% yields, respectively, by the reaction of octafluorotoluene with a three-fold excess of the ethenethiolate anion (which can readily be generated from divinylsulfide under the action of sodium in liquid ammonia) at 10–20°C in DMF (which is used instead of liquid ammonia). The compound **2** is formed as a result of transamidation with dimethylformamide (Scheme).

The interaction of 1-amino-4-trifluoromethyl-2,3,5,6-tetrafluorobenzene (**3**) with the ethenethiolate anion in DMF at 10–20°C affords 1-amino-2,5-di(vinylthio)-4-trifluoromethyl-3,6-difluorobenzene (**4**) in 18% yield (Scheme).



SCHEME

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Therefore we have shown that when perfluorobenzenes contain an electron-withdrawing substituent (CF_3), solvents (NH_3 , DMF) also act as reactants, posing strong competition to the ethenethiolate anion in nucleophilic substitution reactions. These results allow the targeted synthesis of polyfunctional perfluorobenzenes.