Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Room-Temperature Nucleophilic Aromatic Fluorination: Experimental and Theoretical Studies**

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Preparation of TBAF: In a nitrogen glove box with cooling trap, TBACN (10.66 g, 37.7 mmol) was dissolved in 15 mL anhydrous THF in a 100 mL beaker. The solution was cooled to -55 ºC and hexafluorobenzene (1.3 mL, 11.2 mmol) was added slowly with stirring. Upon completion of the addition, the solution was allowed to warm gradually to –15 ºC (4 h). The mixture was subsequently cooled to –65 ºC, and filtered (vacuum) through a fritted disk. The solid was washed (2 x 4 mL) with cold (-65 ºC) THF. (The salt was not allowed to warm above –35 ºC during the isolation procedures.) The solvent was removed under reduced pressure to yield 5.9 g (60%) TBAF isolated as a colorless solid, which was stored in a –35 ºC freezer. ^{1}H NMR ($(CD_3)_2SO$) δ 3.23 (8H, m), 1.56 (8H, m), 1.28 (8H, sext, J = 7.31 Hz), 0.86 (12H, t, J = 7.31 Hz); ^{19}F NMR ($(CD_3)_2SO$) δ -72.6 ppm (s); ^{13}C NMR ($(CD_3)_2SO$) δ: 57.5, 23.1, 19.2, 13.5 ppm.

Product yields reported in Tables 1, 2 and 3 were determined by ^{1}H and ^{19}F NMR spectroscopy in small-scale reactions. All final products are characterized by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. All fluorination reactions were performed at room temperature (20±1 ºC) in anhydrous DMSO. An example of a larger scale fluorination is given below.

4-Fluorobenzonitrile: At room temperature (20±1 ºC), 0.59 g (4.0 mmol) 4-nitrobenzonitrile was added to a stirred DMSO solution of TBAF (1.24 g, 4.8 mmol). The initially colorless solution changed to purple immediately. After 30 minutes, the sample was quenched with 10 mL aqueous HCl (1 M) and extracted with CH_2Cl_2 (2x10 mL). The combined organic layers were washed with water (4x10 mL), 5% Na_2CO_3 aqueous (3x10 mL) and again water (3x10 mL). The CH_2Cl_2 solution was dried over Na_2SO_4. The resulting solution was fractionally distilled under reduced pressure to give 0.33 g (69%) 4-fluorobenzonitrile. The ^{1}H, ^{19}F, ^{13}C NMR, and mass spectra were identical with those of an authentic sample.

Computational Studies: All calculations were performed on a 128 node computer at the University of Nebraska-Lincoln computing facility. The Gaussian-view 03W interface and Gaussian-03[1] programs were used for the calculations. Optimized geometry data and transition state search energy profiles for all six fluorodenitration reactions are provided in the supporting information.

1. Additional calculational results include: a) TS search energy profiles, b) solvation energies, c) free energies in solution, d) activation free energies in solution, e) potential energy profiles in various solvents.
2. Optimized geometries include: a) reactants and products, b) reaction side minima and transition states.
3. NMR data (^{1}H, ^{19}F, and ^{13}C NMR).

1. Additional calculation results. Geometry optimizations and frequency calculations of all species were computed by DFT at the B3LYP/6-311G++(d,p) level. Solvation energies were calculated by PCM.

1. a) TS search energy profiles of fluorination of *p*-substituted nitrobenzene in gas phase

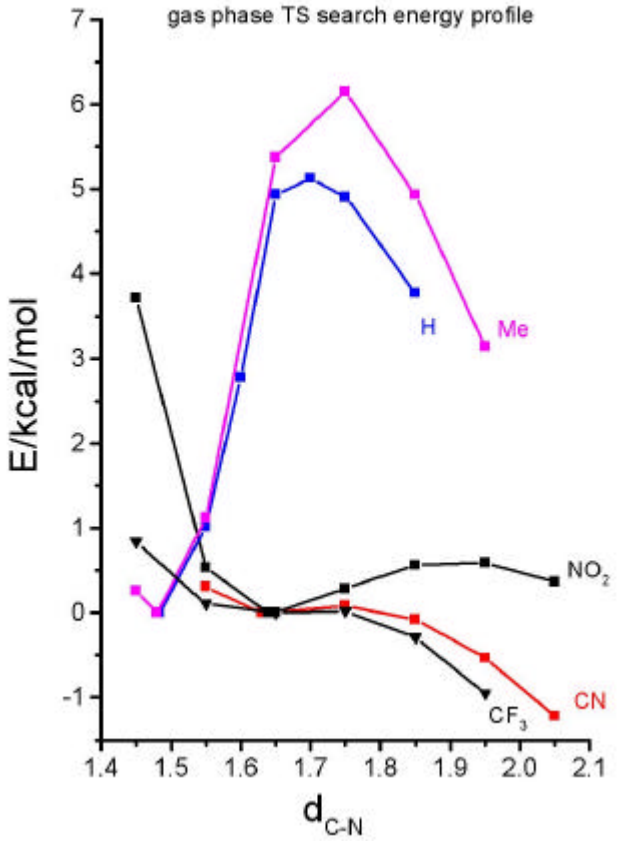

Figure S-1. Relative energy profiles of TS search for gas phase fluorination of para-substituted nitrobenzene which are shown in Scheme 2 in the text. The RM energy for all reactions was set to zero to highlight the relative energy differences at the TS.

1. b) Solvation energies of reactants, transition states, and products

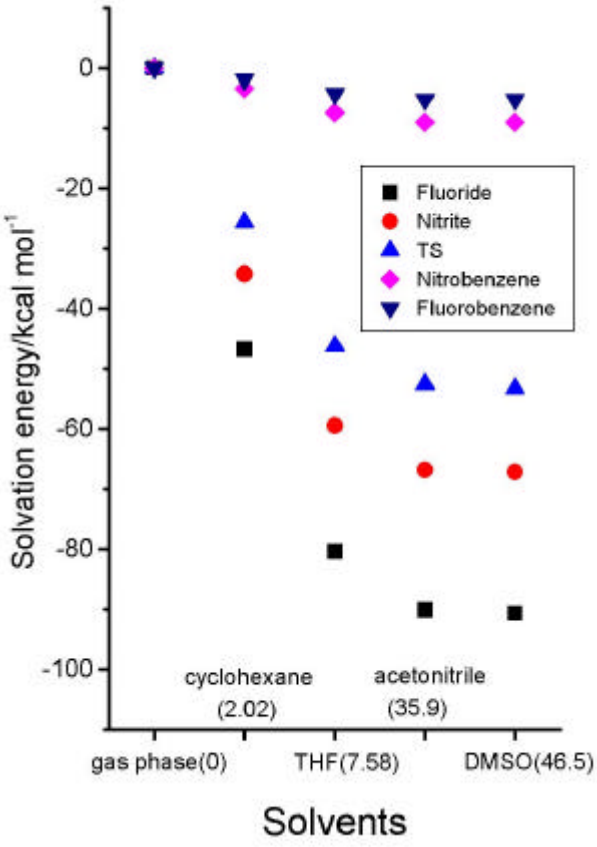

Figure S-2. Solvation free energies (ΔG^{o}) of reactants, transition states and products of nitrobenzene fluorination at 298.15 ºK.

1. c) Solvent effects on ΔG^{o}

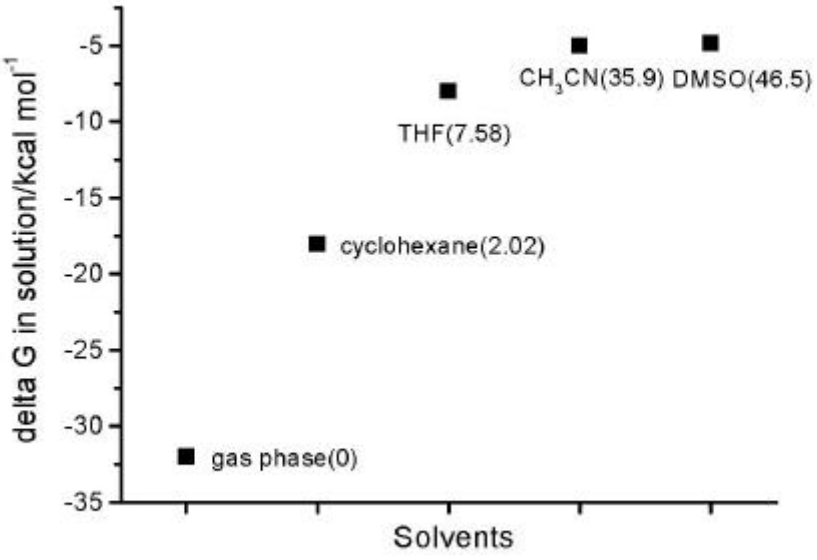

Figure S-3. ΔG^{o} for nitrobenzene fluorination in various aprotic solvents.

1. d) Solvent effects on $\Delta G^{\ddagger}$

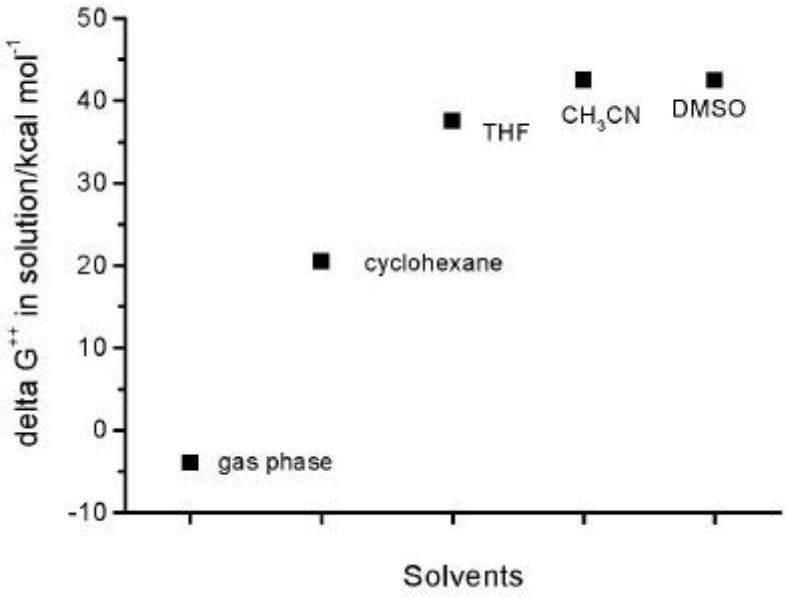

Figure S-4. Activation free energy of nitrobenzene fluorination in various aprotic solvents.

5). Total free energy profile

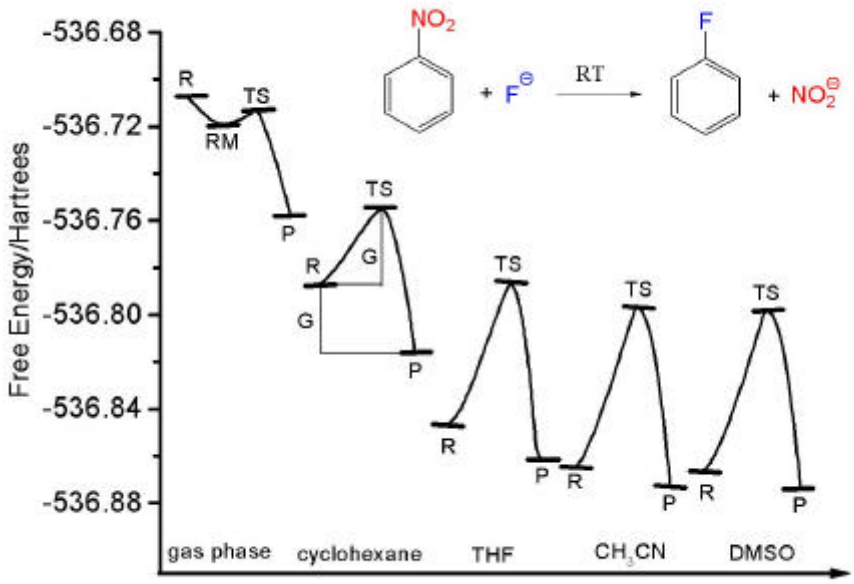

Figure S-5 Total free energy profile of nitrobenzene fluorination in various solvents. R: reactant, RM: reactant side local minima, TS: transition state, P: product.

2. Optimized geometries

2. a) Reactants

4-methylnitrobenzene

C	-1.34745200	1.20365700	-0.01067200
C	0.04200700	1.21480700	-0.00453900
C	0.71993700	0.00001500	-0.00019900
C	0.04191400	-1.21478600	-0.00408000
C	-1.34749000	-1.20356100	-0.01024600
C	-2.06480100	0.00009400	-0.01061400
H	-1.88406900	2.14608600	-0.01794700
H	0.60184600	2.13991800	-0.00613600
H	0.60171900	-2.13991700	-0.00536000
H	-1.88416900	-2.14596700	-0.01715300
N	2.19585200	-0.00002500	0.00339400
O	2.76613900	-1.08477500	0.00468900
O	2.76618500	1.08469800	0.00581900
C	-3.57190000	-0.00002600	0.01482100
H	-3.97942900	-0.88274000	-0.48225200
H	-3.93927400	-0.00572400	1.04687700
H	-3.97947600	0.88794800	-0.47267300

nitrobenzene

C	-1.82120000	-1.21025500	-0.00007600
C	-0.42987200	-1.21868500	-0.00020700
C	0.24143600	0.00000200	0.00002400
C	-0.42987600	1.21868700	0.00023500
C	-1.82120400	1.21025500	0.00006400
C	-2.51544100	-0.00000100	-0.00001500
H	-2.36245400	-2.14876900	-0.00010500
H	0.13529800	-2.14043900	-0.00038200
H	0.13529200	2.14044200	0.00042600
H	-2.36246000	2.14876800	0.00007900
N	1.72256900	0.00000000	0.00004400
O	2.29079700	1.08449100	-0.00039500
O	2.29078800	-1.08449300	0.00033900
H	-3.59938800	-0.00000400	-0.00003100

4-fluoronitrobenzene

C	-1.39205100	-1.21923100	-0.00028600
C	-0.00276400	-1.21830600	-0.00028400
C	0.67134600	0.00000000	0.00000600
C	-0.00276400	1.21830600	0.00029200
C	-1.39205100	1.21923100	0.00028700
C	-2.05724400	0.00000000	-0.00000100
H	-1.95792600	-2.14180700	-0.00052000
H	0.56041200	-2.14113000	-0.00047000
H	0.56041200	2.14113000	0.00048100

H	-1.95792700	2.14180700	0.00051800
N	2.14789700	0.00000000	0.00001000
O	2.71589600	-1.08505600	0.00072200
O	2.71589600	1.08505600	-0.00073700
F	-3.40460300	0.00000000	-0.00000500

4-(trifluoromethyl)nitrobenzene

C	-0.33478100	1.21334500	-0.02680200
C	1.05520100	1.21799600	-0.01316000
C	1.72492500	0.00009000	-0.00505800
C	1.05477500	-1.21767200	-0.01295600
C	-0.33511700	-1.21254200	-0.02664900
C	-1.02540900	0.00055700	-0.03568900
H	-0.87839900	2.14905800	-0.03954800
H	1.61827200	2.14079000	-0.01039800
H	1.61756900	-2.14063300	-0.01005800
H	-0.87899500	-2.14814700	-0.03925800
N	3.20927000	-0.00014800	0.00731900
O	3.77365100	1.08484400	0.01270800
O	3.77329500	-1.08532900	0.01224200
C	-2.53392900	0.00013700	0.00014300
F	-2.99582000	-0.01065000	1.27396200
F	-3.05470300	-1.08271900	-0.61432400
F	-3.05535500	1.09252300	-0.59636400

4-cyanonitrobenzene

C	-1.08341500	-1.21710900	-0.00018600
C	0.30476300	-1.21883500	-0.00016300
C	0.97437300	0.00000400	0.00000600
C	0.30476100	1.21884200	0.00017200
C	-1.08341800	1.21711200	0.00018900
C	-1.78136000	0.00000100	0.00000000
H	-1.63047200	-2.15108300	-0.00031900
H	0.86882300	-2.14112200	-0.00029700
H	0.86881800	2.14113000	0.00030900
H	-1.63047700	2.15108500	0.00032000
N	2.45855600	0.00000000	0.00001000
O	3.02209100	-1.08534800	0.00044400
O	3.02210800	1.08534000	-0.00046100
C	-3.21304300	-0.00000100	-0.00000300
N	-4.36802100	-0.00000300	-0.00000500

1,4-dinitrobenzene

C	0.69483200	1.22023700	0.00019700
C	-0.69484000	1.22023600	0.00023300
C	-1.36244400	0.00000000	0.00000200
C	-0.69483800	-1.22023600	-0.00022400
C	0.69483400	-1.22023500	-0.00017900
C	1.36244100	0.00000200	0.00001000

H	1.25937300	2.14204700	0.00034800
H	-1.25938400	2.14204400	0.00038600
H	-1.25938100	-2.14204500	-0.00038100
H	1.25937700	-2.14204300	-0.00032600
N	-2.84880900	0.00000000	-0.00000300
O	-3.41112100	-1.08531300	0.00030000
O	-3.41111900	1.08531400	-0.00031300
N	2.84880700	0.00000000	0.00001600
O	3.41113200	1.08530700	-0.00023900
O	3.41112400	-1.08531000	0.00020700

2. b) Products

4-methylfluorobenzene

C	-0.64092000	1.19970300	-0.01002600
C	0.75281100	1.21162300	-0.00151100
C	1.42379300	0.00000500	0.00376900
C	0.75272700	-1.21161900	-0.00151100
C	-0.64095400	-1.19964300	-0.01002800
C	-1.36117300	0.00006800	-0.01082900
H	-1.17483000	2.14426000	-0.01782900
H	1.31317200	2.13839900	-0.00326000
H	1.31306400	-2.13841000	-0.00326100
H	-1.17490700	-2.14418400	-0.01782500
F	2.78204500	-0.00005900	0.00831200
C	-2.87127100	-0.00001700	0.01279800
H	-3.27762200	-0.88110300	-0.48920600
H	-3.24982700	-0.00528000	1.04080700
H	-3.27753000	0.88613500	-0.48021900

fluorobenzene

C	-1.13429300	-1.20679400	0.00000000
C	0.26000500	-1.21588100	0.00000000
C	0.92584900	0.00000000	-0.00000200
C	0.26000500	1.21588100	0.00000000
C	-1.13429200	1.20679400	0.00000000
C	-1.83323100	0.00000000	0.00000000
H	-1.67282000	-2.14748100	0.00000200
H	0.82607200	-2.13901400	-0.00000100
H	0.82607300	2.13901400	0.00000000
H	-1.67282000	2.14748100	0.00000200
F	2.28288400	0.00000000	0.00000100
H	-2.91671300	0.00000000	0.00000000

1,4-difluorobenzene

C	0.69688200	1.21489400	0.00000100
C	-0.69688200	1.21489400	0.00000000
C	-1.36508200	0.00000000	0.00000000
C	-0.69688100	-1.21489400	0.00000000

C	0.69688100	-1.21489400	0.00000100
C	1.36508200	0.00000000	0.00000300
H	1.25949200	2.13975600	0.00000000
H	-1.25949200	2.13975600	-0.00000100
H	-1.25949200	-2.13975600	-0.00000100
H	1.25949100	-2.13975600	0.00000000
F	-2.72101500	0.00000000	-0.00000100
F	2.72101500	0.00000000	-0.00000300

4-fluorobenzotrifluoride

C	0.34081300	1.21067500	-0.02376400
C	1.73177200	1.21601300	-0.00593900
C	2.39836000	-0.00005700	0.00374900
C	1.73124100	-1.21593200	-0.00591500
C	0.34037700	-1.21001700	-0.02379100
C	-0.35453600	0.00051600	-0.03584900
H	-0.20077500	2.14790000	-0.03731500
H	2.29554800	2.14003500	-0.00223800
H	2.29467700	-2.14016100	-0.00218600
H	-0.20154200	-2.14709400	-0.03736900
F	3.74891800	-0.00038200	0.01912000
C	-1.85753800	0.00017400	-0.00181200
F	-2.33599800	-0.01079300	1.26927400
F	-2.38241000	-1.08355700	-0.61784800
F	-2.38282500	1.09374100	-0.59954200

4-fluorobenzonitrile

C	-0.36165400	1.21431500	0.00000100
C	1.02745300	1.21719500	0.00000100
C	1.69397500	-0.00000100	0.00000200
C	1.02744800	-1.21719500	0.00000100
C	-0.36165800	-1.21431100	0.00000100
C	-1.06455500	0.00000500	-0.00000100
H	-0.90676600	2.14979400	0.00000000
H	1.59217300	2.14069500	0.00000000
H	1.59216600	-2.14069500	0.00000000
H	-0.90677500	-2.14978600	0.00000000
F	3.04303300	-0.00000500	-0.00000100
C	-2.49504300	0.00000400	-0.00000100
N	-3.65055500	-0.00000600	0.00000000

4-fluoronitrobenzene (see in reactants)

nitrite ion

N	0.00000000	0.00000000	0.00000000
O	1.19934100	0.00000000	0.00000000
O	-0.65695600	1.00340300	0.00000000

2. c) Optimized geometries of reactant side local minima (RM) and transition state (TS) in gas phase RM of 4-methylnitrobenzene fluorination

C	-0.14049400	1.20916700	-0.15932700
C	-1.52982200	1.19868300	-0.11852300
C	-2.25249600	0.00000200	-0.08986400
C	-1.52982000	-1.19867900	-0.11854000
C	-0.14049400	-1.20916100	-0.15934400
C	0.54946100	0.00000400	-0.13941200
H	0.42277600	2.13097400	-0.16796600
H	-2.06487700	2.14468400	-0.10695400
H	-2.06487400	-2.14468100	-0.10698200
H	0.42277800	-2.13096600	-0.16799200
F	1.51175800	-0.00003000	1.91380000
N	2.00611800	0.00000600	-0.40182800
O	2.55895700	1.08230500	-0.57724000
O	2.55895400	-1.08228800	-0.57727300
C	-3.76070700	0.00000000	0.00022600
H	-4.19043700	-0.88443100	-0.48020700
H	-4.10064400	-0.00010100	1.04354700
H	-4.19042700	0.88452600	-0.48003700

TS for 4-methylnitrobenzene fluorination

C	0.13148200	-1.21330000	0.27153700
C	1.49005400	-1.19001700	-0.00560900
C	2.21813400	0.00000700	-0.15058000
C	1.49006600	1.19002100	-0.00558000
C	0.13148100	1.21331200	0.27155900
C	-0.60448800	0.00001100	0.43962300
H	-0.40571600	-2.14914600	0.35736100
H	2.00512500	-2.14331800	-0.11649300
H	2.00515100	2.14331600	-0.11644100
H	-0.40570700	2.14916400	0.35738600
F	-1.42645800	-0.00001500	1.72311400
N	-2.02812500	0.00000400	-0.49582500
O	-2.49223400	-1.07915700	-0.84756700
O	-2.49221700	1.07915700	-0.84761500
C	3.70676700	-0.00001900	-0.40697100
H	4.01457900	0.88303000	-0.97894600
H	4.30200300	-0.00157200	0.51911000
H	4.01420300	-0.88145800	-0.98164900

RM of nitrobenzene fluorination

C	0.57453500	-1.21298300	-0.14911900
C	1.96433200	-1.20509200	-0.11219400
C	2.67023000	0.00000000	-0.09027900
C	1.96433300	1.20509300	-0.11218900
C	0.57453500	1.21298400	-0.14911400
C	-0.11219800	0.00000000	-0.12615300
H	0.00687400	-2.13208000	-0.15366500

H	2.50129700	-2.14866100	-0.09898000
H	2.50129800	2.14866200	-0.09896900
H	0.00687500	2.13208100	-0.15365500
F	-1.07248300	-0.00000800	1.89816400
N	-1.56989300	0.00000200	-0.40096500
O	-2.12152800	-1.08217800	-0.57972300
O	-2.12152800	1.08218300	-0.57971700
H	3.75510400	0.00000000	-0.06164900

TS of nitrobenzene fluorination

C	-0.57565400	1.21785200	0.16815900
C	-1.90468600	1.19731400	-0.22245000
C	-2.60303200	0.00000000	-0.42753900
C	-1.90468600	-1.19731400	-0.22245100
C	-0.57565400	-1.21785300	0.16815700
C	0.14141000	0.00000000	0.39730900
H	-0.04544200	2.15086900	0.30948900
H	-2.41157100	2.14800700	-0.37378700
H	-2.41157100	-2.14800700	-0.37378800
H	-0.04544200	-2.15086900	0.30948900
F	0.83816100	0.00000000	1.75297400
N	1.63557400	0.00000000	-0.40019300
O	2.13111400	1.07911600	-0.70487000
O	2.13111500	-1.07911600	-0.70486900
H	-3.64245300	0.00000000	-0.73601900

RM of 4-fluoronitrobenzene fluorination

C	-0.17159700	0.15676100	-1.21251200
C	-0.28257200	1.54356400	-1.21375700
C	-0.33240000	2.21009000	0.00000000
C	-0.28257200	1.54356400	1.21375700
C	-0.17159700	0.15676100	1.21251200
C	-0.07679900	-0.52284600	0.00000000
H	-0.11171200	-0.40647700	-2.13197300
H	-0.32757900	2.10400200	-2.13993500
H	-0.32757900	2.10400200	2.13993500
H	-0.11171200	-0.40647700	2.13197300
F	2.06152900	-1.22753600	0.00000000
N	-0.17223200	-1.99967000	0.00000000
O	-0.28257200	-2.56770300	-1.08258600
O	-0.28257200	-2.56770300	1.08258600
F	-0.44924300	3.57848300	0.00000000

TS of 4-fluoronitrobenzene fluorination

C	0.29672000	-0.11124000	1.21673700
C	0.29672000	-1.50089400	1.20509600
C	0.29801000	-2.18583300	0.00000000
C	0.29672000	-1.50089400	-1.20509600
C	0.29672000	-0.11124000	-1.21673700

C	0.31306400	0.63863600	0.00000000
H	0.28226300	0.43469300	2.15059300
H	0.29467000	-2.05457700	2.13847700
H	0.29467000	-2.05457700	-2.13847700
H	0.28226300	0.43469300	-2.15059300
F	1.41007700	1.69907100	0.00000000
N	-0.88384300	1.85238400	0.00000000
O	-1.32008700	2.23611500	1.07945900
O	-1.32008700	2.23611500	-1.07945900
F	0.29733500	-3.57417700	0.00000000

RM of 4-(trifluoromethyl)nitrobenzene fluorination

C	-0.85648100	-1.22186400	0.24766900
C	0.51451900	-1.20444800	0.13995100
C	1.24242900	0.00000000	0.10018900
C	0.51451800	1.20444800	0.13995300
C	-0.85648100	1.22186400	0.24767000
C	-1.60972800	0.00000000	0.37720500
H	-1.40271900	-2.15475700	0.27352300
H	1.04453800	-2.14959100	0.08323400
H	1.04453800	2.14959100	0.08323500
H	-1.40271900	2.15475700	0.27352400
F	-2.41746900	0.00000000	1.68830300
N	-2.94104700	0.00000000	-0.52921000
O	-3.40819000	-1.07976500	-0.86582400
O	-3.40819100	1.07976500	-0.86582200
C	2.69675000	0.00000000	-0.10474000
F	3.32368900	-1.09401000	0.42627100
F	3.09915700	0.00000000	-1.43453900
F	3.32368900	1.09401100	0.42627000

TS of 4-(trifluoromethyl)nitrobenzene fluorination

C	0.85263900	-1.22266200	-0.42643600
C	-0.50984500	-1.20531900	-0.23858200
C	-1.23217800	0.00000000	-0.14258000
C	-0.50984500	1.20531900	-0.23858200
C	0.85263900	1.22266200	-0.42643500
C	1.60731900	0.00000000	-0.51642200
H	1.39509100	-2.15564600	-0.50374000
H	-1.04006600	-2.15008700	-0.17824800
H	-1.04006600	2.15008700	-0.17824600
H	1.39509100	2.15564600	-0.50373900
F	2.53042300	0.00000000	-1.65813300
N	2.89201500	0.00000000	0.61751400
O	3.30796600	-1.08006800	1.01589200
O	3.30796600	1.08006800	1.01589300
C	-2.67388600	0.00000000	0.13611500
F	-3.32770900	-1.09409900	-0.36267600
F	-3.00863300	-0.00000100	1.48399800
F	-3.32770900	1.09410000	-0.36267500

RM of 4-(trifluoromethyl)nitrobenzene fluorination

C	-0.12955000	-1.22507900	0.24873200
C	1.22914700	-1.20831600	0.06033200
C	1.96092000	0.00000000	-0.03673700
C	1.22914700	1.20831600	0.06033100
C	-0.12955100	1.22508000	0.24873300
C	-0.88229300	0.00000000	0.39972000
H	-0.67421400	-2.15762300	0.30847100
H	1.75999600	-2.15151400	-0.02233600
H	1.75999500	2.15151500	-0.02233800
H	-0.67421500	2.15762300	0.30846900
F	-1.65847800	0.00000000	1.68683100
N	-2.22684200	0.00000000	-0.52243200
O	-2.69162700	-1.08016800	-0.85960500
O	-2.69162700	1.08016700	-0.85960600
C	3.35947100	0.00000000	-0.23703200
N	4.51213400	0.00000000	-0.40107200

TS for 4-cyanonitrobenzene fluorination

C	-0.12297400	-1.22493600	0.41844300
C	1.22095200	-1.20973400	0.13933900
C	1.93974800	0.00000000	-0.01952700
C	1.22095400	1.20973000	0.13936000
C	-0.12297300	1.22493000	0.41846300
C	-0.87113000	-0.00000300	0.53444100
H	-0.66171700	-2.15623800	0.53393800
H	1.75207700	-2.15181500	0.04727700
H	1.75208000	2.15181300	0.04731300
H	-0.66171400	2.15623100	0.53397200
F	-1.76932500	-0.00001200	1.66896800
N	-2.18944300	0.00000600	-0.61299600
O	-2.60783100	-1.08032700	-1.00769600
O	-2.60781000	1.08034400	-1.00770400
C	3.32486200	0.00000100	-0.30179900
N	4.46540000	0.00000100	-0.53448000

RM of 1,4-dinitrobenzene fluorination

C	0.49983300	1.23253500	0.31225700
C	-0.85280800	1.21693100	0.12422500
C	-1.56522700	0.00000000	0.02443600
C	-0.85280800	-1.21693100	0.12422300
C	0.49983300	-1.23253600	0.31225500
C	1.26004600	0.00000000	0.44166800
H	1.04677100	2.16299000	0.38085900
H	-1.40443600	2.14476500	0.04652500
H	-1.40443600	-2.14476500	0.04652100

H	1.04677100	-2.16299000	0.38085400
F	2.06385800	-0.00000200	1.67162700
N	2.55751100	0.00000100	-0.55967700
O	3.00511000	1.08057400	-0.91349300
O	3.00511200	-1.08057300	-0.91349000
N	-2.96172000	0.00000000	-0.17498800
O	-3.56530700	-1.09113100	-0.26095600
O	-3.56530700	1.09113000	-0.26095400

TS of 1,4-dinitrobenzene fluorination

C	-0.48456200	-1.22865000	0.59826400
C	0.84447500	-1.21945700	0.26551500
C	1.52993800	0.00000000	0.07613900
C	0.84447500	1.21945800	0.26551400
C	-0.48456200	1.22865000	0.59826200
C	-1.21577400	0.00000000	0.69290900
H	-1.02383600	-2.15459600	0.74832900
H	1.39447300	-2.14506500	0.15970300
H	1.39447300	2.14506600	0.15969900
H	-1.02383700	2.15459600	0.74832500
F	-2.22637700	0.00000000	1.66227700
N	-2.49135600	0.00000000	-0.72852900
O	-2.86640000	-1.08034100	-1.16932800
O	-2.86640600	1.08033800	-1.16932600
N	2.91167600	0.00000000	-0.24891400
O	3.50077400	1.08989600	-0.38780300
O	3.50077400	-1.08989600	-0.38780200

3. NMR data.

Compound 2: ^{1}H, 8.23 (1H), 8.01 (1H), 7.34 (1H), 7.17 (1H); ^{19}F, -68.2.

Compound 3: ^{1}H, 8.43 (1H), 8.21 (1H), 7.46 (1H); ^{19}F, -73.03; ^{13}C, 158.20 (d, J=233.8), 146.4 (d, J=13.47), 142.7 (d, J=1.35), 124.4 (d, J=4.38), 116.1 (d, J=34.02).

Compound 4: ^{1}H, 8.31 (1H), 7.28 (2H); ^{19}F, -69.69; ^{13}C, 161.08 (d, d, J^{1}=243.90, J^{2}=14.82), 148.01 (t, J=7.75), 107.2, (d, d, J^{1}=39.75, J^{2}=13.14).

Compound 5: ^{1}H, 8.71 (1H), 8.62 (1H), 7.84 (1H); ^{19}F, -60.62 (3F), -63.01 (1F); ^{13}C, 164.77 (d, J=242.5), 145.58 (d, q, J^{d}=16.84, J^{q}=4.04), 140.32 (d, q, J^{d}=9.77, J^{q}=3.03), 123.19 (q, J=272.17), 123.74 (q, d, J^{q}=33.01, J^{d}=2.36), 111.00 (d, J=38.40).

Compound 6 ^{1}H, 8.39 (1H), 8.23 (1H), 8.00 (1H), 7.80 (1H), 7.72 (1H), 7.52 (1H), 7.45 (1H), 4.05 (2H), 1.02 (3H); ^{19}F, -62.27; ^{13}C, 193.53 (s), 165.08 (d, J=0.34) 164.74 (d, J=243.2), 149.10 (d, J=16.51), 142.44 (d, J=9.43), 139.8 (s), 133.04 (s), 131.22 (d, J=2.69), 130.44 (s), 129.75 (s), 127.54 (s), 110.29 (d, J=37.73).

Compound 7: ^{1}H, 8.77 (1H), 8.67 (1H), 8.42 (1H); ^{19}F, -80.4; ^{13}C, 159.7 (d, J=251.3), 142.61 (d, J=3.71), 141.73 (d, J=8.1), 133.76 (d, J=36.7).

Compound 8: ^{1}H, 8.15; ^{19}F, -83.84; ^{13}C, 165.8 (d, d, J^{1}=243.53, J^{2}=5.39), 123.9 (d, d, J^{1}=46.15, J^{2}=24.0).
Compound 9: ^{1}H, 9.21 (1H), 8.80 (1H), 7.3-7.4 (5H), 5.63 (2H); ^{19}F, -73.14.

Compound 10: ^{1}H, 7.66 (1H), 7.56 (1H), 7.39 (2H), 7.21 (4H), 5.44 (2H); ^{19}F, -107.86 (s, 1F), -114.31 (m, 1F); ^{13}C, 162.21 (d, J=243.90), 154.13 (d, J=244.88), 137.7 (d, J=14.48), 133.01 (d, J=4.38), 132.64 (d, J=3.03), 130.12 (d, J=8.42), 123.08 (d, J=2.69), 122.92 (s), 119.24 (d, J=2.69), 116.13 (d, J=21.56), 111.27 (s), 45.30 (s).

Compound 11: ^{1}H, 7.95 (2H), 7.50 (2H); ^{19}F, -103.4; ^{13}C, 165.0 (d, J=253.64), 135.9 (d, J=9.43), 117.7 (d, J=22.91), 108.1 (d, J=2.69), 118.4 (s).

Compound 13: ^{1}H, 7.93 (1H), 7.82 (1H), 7.55 (1H), 7.43 (1H); ^{19}F, -108.7 (m) ^{13}C, 162.8 (d, J=255.32), 136.85 (d, J=8.08), 134.5 (s), 126.2 (d, J=2.02), 117.0 (d, J=18.86), 114.2 (s), 100.36 (d, J=14.82).

Compound 14: ^{1}H, 8.58 (1H), 7.99 (1H), 8.07 (1H); ^{19}F, -106.95 (m); ^{13}C, 160.46 (d, J=255.32), 135.76 (s), 135.06 (d, J=9.09), 121.39 (d, J=18.86), 119.43 (d, J=22.91), 117.40 (s), 109.49 (d, J=3.71).

Compound 15: ^{1}H, 8.02 (1H), 7.96 (1H), 7.47 (1H); ^{19}F, -111.02 (t, J=6.88), ^{13}C, 158.35 (d, J=257.01), 136.85 (s), 133.35 (s), 127.28 (d, J=4.72), 121.18 (d, J=15.83), 113.5 (s), 102.34 (d, J=14.48).

Compound 16: ^{1}H, 7.93 (1H), 7.49 (2H); ^{19}F, -105.88 (m); ^{13}C, 162.82 (d, d, J^{1}=258.36, J^{2}=4.04), 138.13 (t, J=10.44), 113.39 (d, d, J^{1}=19.20, J^{2}=3.71), 110.0 (s), 91.36 (t, J=18.86).

Compound 17: ^{1}H, 10.22 (1H), 7.82 (1H), 7.29 (1H); ^{19}F, -115.9 (m); ^{13}C, 185.31 (t, J=4.38), 162.6 (d, d, J1=261.05, J2=6.06), 138.0 (t, J=11.45), 114.0 (t, J=11.2), 113.3 (d, d, J^{1}=24.25, J^{2}=15.16)

Compound 18: ^{1}H, 7.97 (2H), 7.36 (2H), 4.27 (2H), 1.31 (2H); ^{19}F, -106.26 (m); ^{13}C, 165.52 (d, J=250.94), 165.16 (s), 132.34 (d, J=9.77), 126.84 (d, J=2.69), 116.26 (d, J=22.23), 61.22 (s), 14.49 (s).

Compound 19 ^{1}H, 7.77 (2H), 7.68 (2H), 7.42 (2H), 7.08 (2H); ^{19}F, -107.4 (m); ^{13}C, 192.79 (s), 164.13 (d, J=250.94), 162.79 (s), 134.00 (d, J=2.69), 131.93 (d, J=9.43), 131.86 (s), 129.02 (s), 115.34 (d, J=21.89), 113.74 (s)

Compound 20: ^{1}H, 7.94 (1H), 7.82 (1H), 7.55 (1H), 7.44 (1H); ^{19}F, -108.6 (m); ^{13}C, 162.87 (d, J=255.66), 136.80 (d, J=8.76), 134.47 (s), 126.20 (d, J=3.37), 117.02 (d, J=19.20), 114.4 (s), 100.5 (d, J=15.16).

Compound 21: ^{1}H, 7.94 (1H), 7.71 (1H), 7.66~7.65 (2H); ^{19}F, -109.95 (m); ^{13}C, 162.15 (d, J=246.57), 133.25 (d, J=7.75), 129.91 (d, J=1.35), 122.17 (d, J=20.21), 120.23 (d, J=24.93), 118.08 (d, J=1.68), 113.48 (d, J=9.43)

Compound 22: ^{1}H, 8.28 (2H), 7.92 (2H); ^{19}F, -102.6 (m); ^{13}C, 166.4 (d, J=254), 144.4 (d, J=1.35), 127.0 (d, J=10.44), 118.15 (d, J=24.60).

Compound 23: ^{1}H, 7.97 (2H), 7.46 (2H); ^{19}F, -103.1 (m); ^{13}C, 165.0 (d, J=254.0), 135.9 (d, J=9.77), 118.5 (s), 117.6 (d, J=22.91), 108.3 (d, J=3.03).

Compound 24, ^{1}H, 7.81 (2H), 7.45 (2H); ^{19}F, -60.49 (s), -107.07 (m); ^{13}C, 164.73 (d, J=250.27), 128.93 (d, q, J^{d}=8.76, J^{q}=3.03), 124.39 (q, J=271.49), 125.94 (q, d, J^{q}=32.0, J^{d}=2.02), 117.46 (d, J=22.57).

Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 03 (version 6.0)*, Gaussian, Inc.; Pittsburgh, PA, **2003**