

Computational Study on the Boundary Between the Concerted and Stepwise Mechanism of Bimolecular S_NAr Reactions

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1. Experimental Procedures

1.1. Software

The software used was Gaussian09^[1] (both Revisions A.02 or D.01 were used) in combination with GaussView 5.0.9^[2] for all calculations.

1.2. Methods

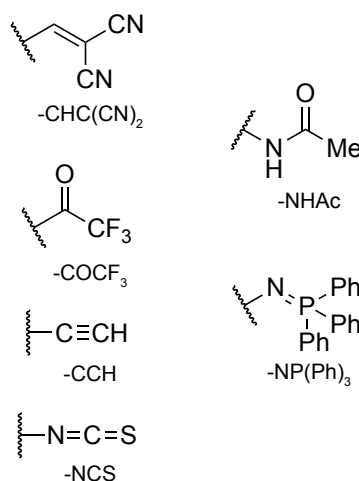
The DFT methods employed the functional as specified in combination with Pople triple- ζ basis set 6-311++G(d,p)^[3-6] for all atoms up to the atomic number Z=18. For larger atoms (these mainly applied to counter cations K⁺, Rb⁺ and Cs⁺ and the halogen atoms bromine and iodine) the appropriate MWB relativistic pseudo-potential and associated basis set was used.^[7] Solvation effects were accounted for by the solvent reaction field method using the conductor-like polarisable continuum model (CPCM) unless mentioned otherwise.^[8,9]

1.3. The Applied σ_p^- Scale

The σ_p^- values were taken from the landmark review by Hansch et al.^[10] A selection of *para*-substituents and their associated σ_p^- constants that are used in this chapter are listed in Table SI-1-1 below. The less commonly encountered structures are drawn out next to the table.

Table SI-1-1 σ_p^- Values

Entry	<i>para</i> -Substituent -R	σ_p^-
1	-NO	1.63
2	-NO ₂	1.27
3	-CHC(CN) ₂	1.20
4	-COCF ₃	1.09
5	-CN	1.00
6	-COMe	0.84
7	-CO ₂ Me	0.75
8	-CF ₃	0.65
9	-CCH	0.53
10	-NCS	0.34
11	-Cl	0.19
12	-H	0.00
13	-Me	-0.17
14	-OMe	-0.26
15	-NHAc	-0.46
16	-NP(Ph) ₃	-0.77



1.4. General Procedure

For all S_NAr reactions reported in this chapter the rate limiting transition state ('TS1') was optimised. The transition state geometry was then displaced by 0.05 units along the imaginary vibration mode in both directions. The geometries obtained in this way served as input structure for the optimisation (keyword: opt=calcfc) towards the substrate complex ('SC') and the product complex ('PC') or Meisenheimer intermediate ('MI'), respectively. Based on whether the optimisation converged directly to the product complex or to a Meisenheimer intermediate the example was classified as concerted or as stepwise, respectively. This procedure was validated as detailed in Section 2.1. If a Meisenheimer intermediate was found, the second transition state ('TS2') leading to the final product was identified for representative examples as specified.

2. Results

In this chapter a detailed descriptions is given of how the results discussed in the paper were obtained. Further, additional results are presented and discussed. The log files can be found in the accompanying archive under DOI: [10.15129/254ecae8-9c72-4bb9-9319-b16eada94f9c](https://doi.org/10.15129/254ecae8-9c72-4bb9-9319-b16eada94f9c). To help efficiently retrieve a file of interest, a list of all log files is given in Chapter 3. The structure of Chapter 3 mirrors the structure of this chapter.

2.1. Computational Model

Benchmarking DFT Functionals

All log files of the calculations presented in this section are listed in Table SI-3-1 (page 25).

The computational model was chosen and validated by comparing the performance of a variety of DFT functionals against the results of a high-level wavefunction-based method for a test-set of S_NAr reactions. A satisfactorily well performing functional was identified for the further study of S_NAr reaction mechanisms.

The S_NAr reaction shown in Figure SI-1 was used as a test case to identify a DFT functional that would predict the mechanistic turning point on the Hammett σ_p^- scale reliably (Figure 4-2). To establish a benchmark result the energy profiles of the four model reactions were calculated with the second-order Møller-Plesset perturbation theory method MP2. MP2 is a wave-function based method and was the most reliable method that was affordable in terms of computational resources (memory requirements and time) for the studied system (number of atoms, electrons, and size of the basis set). The method predicted a sharp turning point for the S_NAr mechanism from stepwise to concerted with $\tau_p^- = 0.92 \pm 0.08$. Importantly, the result was the same if either basis set, 6-311++G(d,p) or aug-cc-pVTZ, was used.

A number of DFT functionals was then applied to the same S_NAr model reactions. For all DFT calculations the 6-311++G(d,p) basis set was used. In Figure 4-2 the DFT functionals were clustered into four groups: hybrid functionals based on Becke's three parameter and/or Lee-Yang-Parr functional, members from the Minnesota family, representatives of the Perdew-Burke-Ernzerhof functional class, and methods derived from Becke's B97 functional.

None of the tested DFT methods was able to reproduce the MP2 result exactly and to predict the same mechanistic turning point. Most functionals, however, gave a result that was satisfactorily close to the MP2 result. Three functionals predicted a mechanistic turning point that was two increments or more ($\Delta\tau_p^- \geq 0.22$) away from the MP2 turning point. Importantly, from the investigated functionals, the widely used functional B3LYP with D3-dispersion correction - B3LYP-D3(BJ), as used, for example, by Jacobsen et al.^[11] - and the M06-2X functionals were among the worst-performing ones.

Four functionals were not able to predict the mechanistic turning point as sharply as the MP2 method, i.e. they produced an alternating pattern of concerted and stepwise mechanisms as the electronic nature of the *para*-substituent changes. These were the BHandHLYP, M06, PBE0-D3(BJ) and ω B97 functionals. These were consequently ruled out as suitable functionals for the following study.

As an additional measure of the performance of the DFT functionals, their ability to correctly reproduce

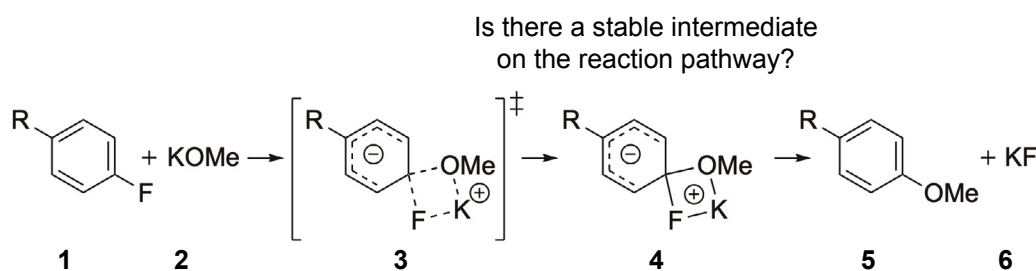
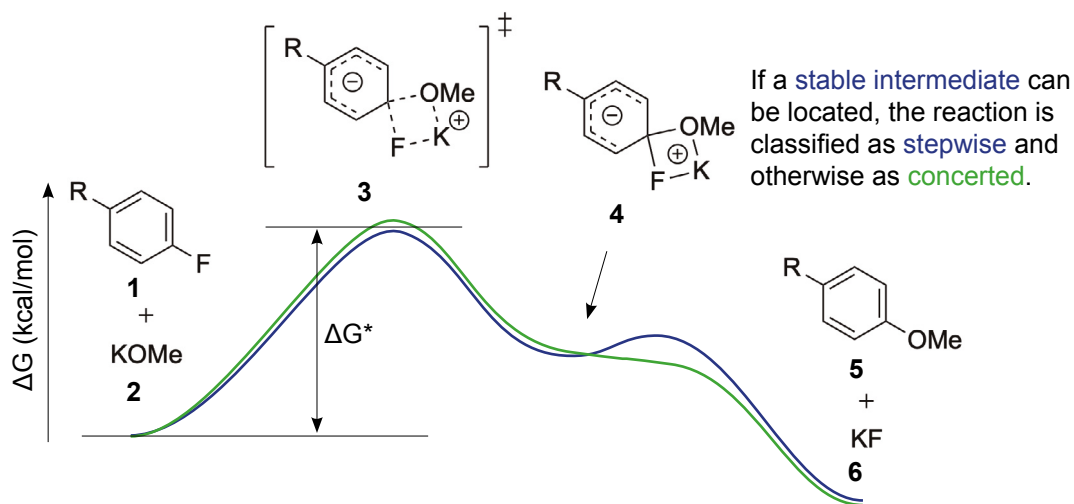


Figure SI-1 Four S_NAr reactions ($R = -COCF_3, -CN, -COMe, -CO_2Me$) were selected to benchmark DFT functionals against the results obtained with a high-level wave-function based method.



Method		MP2		B3 and LYP				Minnesota				PBE		B97					
		MP2[a]	MP2	B3PW91	B3LYP	B3LYP-D3(BJ)	CAM-B3LYP	BHandHLYP	M06L	M06	M06-2X	M11	PBE0	PBE0-D3(BJ)	HSE1PBE	B97D	ωB97	ωB97X	ωB97XD
-R	σ_p^-																		
-NO ₂	1.27				s	s													
-COCF ₃	1.09	s	s	s	s	c	s	s	s	s	s	s	s	s	c	s	s	s	s
-CN	1.00	s	s	c	c	c	c	c	c	s	c	c	c	c	c	c	c	c	c
-COMe	0.84	c	c	c	c	c	s	c	s	s	c	c	s	c	c	s	c	c	c
-CO ₂ Me	0.75	c	c	c	c	c	c	c	c	s	c	c	c	c	c	c	c	c	c
-CF ₃	0.65									c									
-CCH	0.53									c									
Result (Y/N)				✓	✓	✗	✓	✗	✓	✗	✗	✓	✓	✗	✓	✗	✗	✗	✓

Figure SI-2 The mechanistic transition point on the Hammett σ_p^- scale was calculated with a number of different methods in order to identify a suitable DFT functional. For all tested methods, the 6-311++G(d,p) basis set and cpcm solvent model for DMF was used, unless mentioned otherwise. 's' stands for 'stepwise S_NAr mechanism', 'c' stands for 'concerted S_NAr mechanism'. [a] The aug-cc-pVTZ basis set was used.

the activation energy of the rate limiting step was investigated. As reference values, the MP2/aug-cc-pVTZ results were taken. The results are shown in Figure SI-3 and Table SI-2-1. The MP2 method with the smaller 6-311++G(d,p) basis set still gave a result that is reasonably close to the MP2/aug-cc-pVTZ result. The B3 and LYP-based assembly of functionals in general seriously overestimated the activation energy. Only when dispersion correction was included [B3LYP-D3(BJ)] was a close reproduction of the MP2 reference results achieved. The members of the Minnesota functional family all underestimated the activation energy. The M06-2X functional showed a standard deviation close to 2 kcal/mol, while the range-separated hybrid functional M11 showed a standard deviation of less than 1 kcal/mol. The functionals in the PBE0 and B97 group all showed good to excellent performance.

In conclusion, from the nine DFT functionals that were found to predict the mechanistic turning point τ satisfactorily well (see Figure SI-2), four also gave a good prediction of the rate limiting energy barrier with a standard deviation of < 2 kcal/mol. Overall, the M11 and ω B97XD functionals were the two top-runners and the more modern M11 functional was selected for the further study.

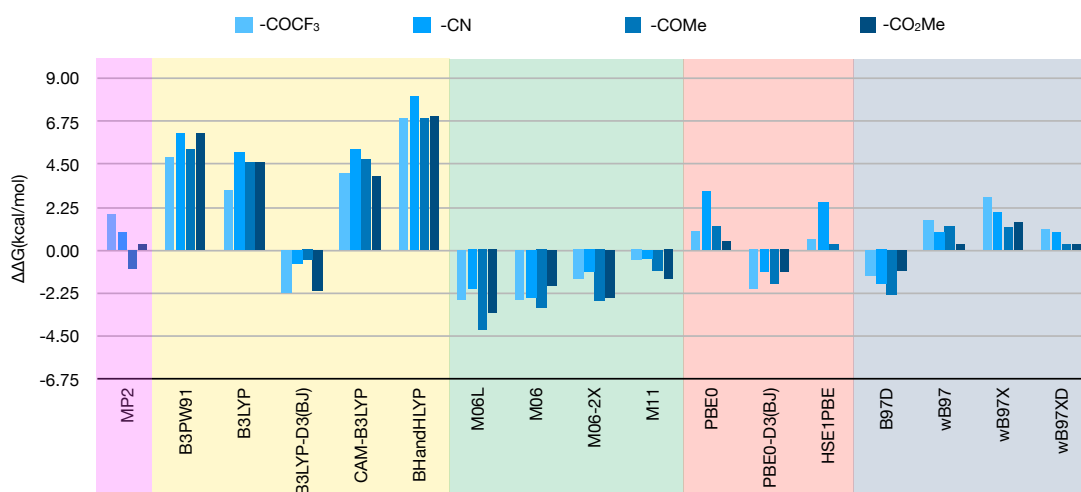


Figure SI-3 The activation energy of the rate limiting step of the S_NAr reaction from Figure SI-2 has been calculated by different DFT methods. For all tested methods the 6-311++G(d,p) basis set and cpcm solvent model for DMF was used. The deviation of these results from the MP2/aug-cc-pVTZ reference calculation is shown.

Table SI-2-1 Statistical Evaluation of the Functional Performance

Method	STD	MSD	MAD	Absolute Max. Deviation
ω B97XD	0.74	0.64	0.64	1.09
M11	0.96	-0.85	0.85	1.49
ω B97	1.11	1.00	1.00	1.56
MP2 ^[a]	1.17	0.53	1.02	1.89
HSE1PBE	1.31	0.85	0.85	2.55
PBE0-D3(BJ)	1.58	-1.53	1.53	2.04
B3LYP-D3(BJ)	1.59	-1.38	1.38	2.19
B97D	1.67	-1.59	1.59	2.31
PBE0	1.75	1.46	1.46	3.05
ω B97X	1.97	1.87	1.87	2.78
M06-2X	2.03	-1.93	1.93	2.63
M06	2.52	-2.48	2.48	3.01
M06L	3.09	-2.99	2.99	4.13
B3LYP	4.41	4.35	4.35	5.15
CAM-B3LYP	4.53	4.50	4.50	5.29
B3PW91	5.64	5.61	5.61	6.15
BHandHLYP	7.25	7.23	7.23	8.10

The table gives a more detailed analysis of the results shown Figure SI-3 in STD: standard deviation; MSD: mean signed deviation; MAD: mean absolute deviation. The functionals are colour-coded according to their ability to predict the mechanistic turning point τ satisfactorily (see Figure SI-2). [a] The same basis set - 6-311++G(d,p) - was used as for the DFT methods.

Validating the Procedure

The log files of the calculations presented in this section are included in Table SI-3-1 (page 25).

The method to test for the presence of a Meisenheimer intermediate so far was to start an optimisation from the transition state geometry that was slightly distorted along the imaginary mode. The optimisation can either converge to a Meisenheimer intermediate or directly to the product complex. Although experience showed that this method is able to detect very shallow local minima on the potential energy surface, it was necessary to establish its validity for the situation at hand. The question of particular concern was whether this method might fail to detect very fleeting Meisenheimer intermediates.

The mechanistic classification based on the M11 functional from Figure SI-2 was expanded by one example and validated by internal reaction coordinate (IRC) scans (Table SI-2-2). For the three reactions that were found to follow a concerted mechanism, the second transition state (elimination of the fluoride leaving group) was identified. IRC scans were performed starting from the rate limiting transition states. For the stepwise reaction with $-R = -\text{COCF}_3$ the IRC scan identified the Meisenheimer intermediate as a local minimum on the potential energy surface. This is in accordance with the initial classification of this example as a stepwise $\text{S}_{\text{N}}\text{Ar}$ reaction. Also, for the three concerted reactions where no intermediate was detected during the optimisation of the transition state structure towards the product complex, an IRC scan was performed. In the case of the reaction with $-R = -\text{CN}$ and $-R = -\text{COMe}$, the IRC scan located an intermediate that apparently corresponds to a Meisenheimer intermediate. A frequency calculation identified the intermediate structure for the $-R = -\text{CN}$ example as a true minimum. This was not the case for the structure with $-R = -\text{COMe}$ (imaginary modes were found in the frequency calculation). Any attempt to identify a transition state for the expulsion of the fluoride leaving group from these two hypothetical intermediate structures failed. Bond scans were performed with a step size of 0.00125 Å to search for a candidate structure for the transition state, but no maxima along the expected reaction coordinate were found in either case. Hence,

Table SI-2-2 Validation of the Method for the Classification of the Reaction Mechanism

$-R$	σ_{p}^-	Mechanism ^[a]	Int1 ^[b]	IRC ^[c]	TS2 ^[d] (kcal/mol)
$-\text{NO}_2$	1.27	stepwise	yes	-	1.61
$-\text{CHC}(\text{CN})_2$	1.20	stepwise	yes	-	3.01
$-\text{COCF}_3$	1.09	stepwise	yes	MI	1.37
$-\text{CN}$	1.00	concerted	no	MI	not found ^[f]
$-\text{COMe}$	0.84	concerted	no	(MI) ^[e]	not found ^[f]
$-\text{CO}_2\text{Me}$	0.75	concerted	no	PC	-

[a] As classified in Figure SI-2.

[b] The result is 'yes' if the optimisation from the transition state structure converged to a Meisenheimer intermediate and 'no' if it converged directly to the product complex.

[c] An internal reaction coordinate (IRC) scan was performed, starting from the rate limiting transition state TS1 in forward and reverse direction, until a stationary point was found. The result is 'MI' if a stationary point was found that corresponds to a Meisenheimer intermediate and 'PC' if the scan ran in the forward direction directly to the product complex.

[d] The energy barrier of the second transition state is given relative to the Meisenheimer intermediate.

[e] Imaginary modes were found in a frequency calculation for the stationary point structure identified by the IRC.

[f] Bond scans were performed with a step size of 0.00125 Å to search for a candidate structure for the transition state, but no maxima along the expected reaction coordinate were found.

the stationary points found by the IRC scan for these two examples are better described as inflection points rather than as true local minima on the potential energy surface. For the example with $-R = -CO_2Me$, the result from the IRC scan is in agreement with the initial classification of the reaction.

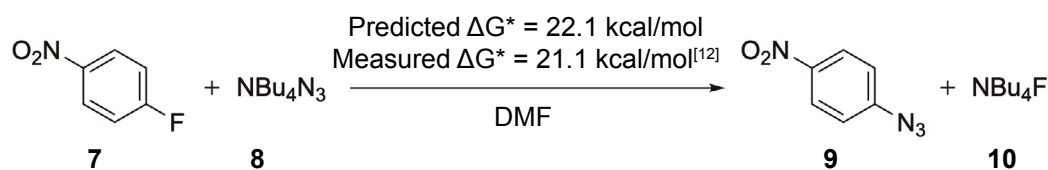
It can be concluded that the approach of optimising a transition state geometry towards the product complex is a sufficiently sensitive method for finding Meisenheimer intermediates. The method has the advantage over IRC scans that it is computationally more effective and does not falsely classify very flat regions on the potential energy surface as intermediates. Indeed, the results from the IRC scans demonstrated that the potential energy surface of S_NAr reactions close to the mechanistic turning point is - not surprisingly - very flat.

Comparison to Experiments

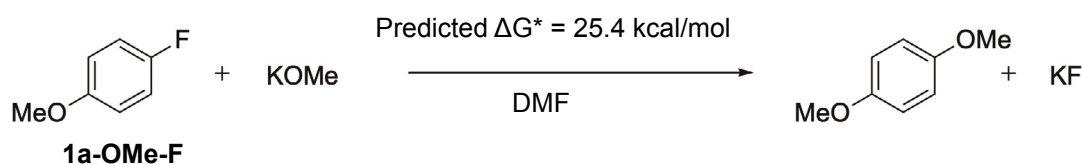
All log files of the calculations presented in this section are listed in Table SI-3-2 (page 30).

In addition to benchmarking the DFT functionals against the results from high-level ab initio calculations (i.e. the MP2 results), their predictions were compared with experimental data. First, the activation energy as calculated by the M11/6-311++G(d,p)/cpcm method was compared to the activation energy measured experimentally for one example^[12a] (Scheme SI-1). The predicted activation energy deviated by only 1 kcal/mol from the experimental^[12a] value. Similarly, we calculated the activation energy of the S_NAr reaction between potassium methoxide and *para*-methoxyfluorobenzene (Scheme SI-2).^[12b] The activation energy found of 25.4 kcal/mol appears to be in agreement with the finding that the reaction required elevated temperatures to proceed efficiently.^[12b] These results give additional confidence in the DFT method. However, it is not the accurate determination of barrier heights that is crucial for the study ahead, but the correct prediction of the existence or absence of a Meisenheimer intermediate in the reaction pathway.

There is very limited purely experimental - and at the same time convincing - evidence for concerted S_NAr mechanisms in the literature. Williams et al. made the most substantial contribution to the field in this respect.^[13-16] Therefore it was an obvious step to calculate energy profiles for some of the reactions, which Williams et al. suggested to proceed via a concerted mechanism. The displacement of phenolates **15** from a triazine-derivative **11** with amine nucleophiles **12**^[15] was chosen as a reference case (Table SI-2-3). In apparent contradiction to the claim of these reactions to be concerted,^[15] a Meisenheimer intermediate was identified for all examined cases. The energy of the Meisenheimer intermediate (MI) is given with respect to the substrate complex formed between **11** and **12**. The transition state energies are given with respect to the Meisenheimer intermediate and are of major concern for the following discussion.

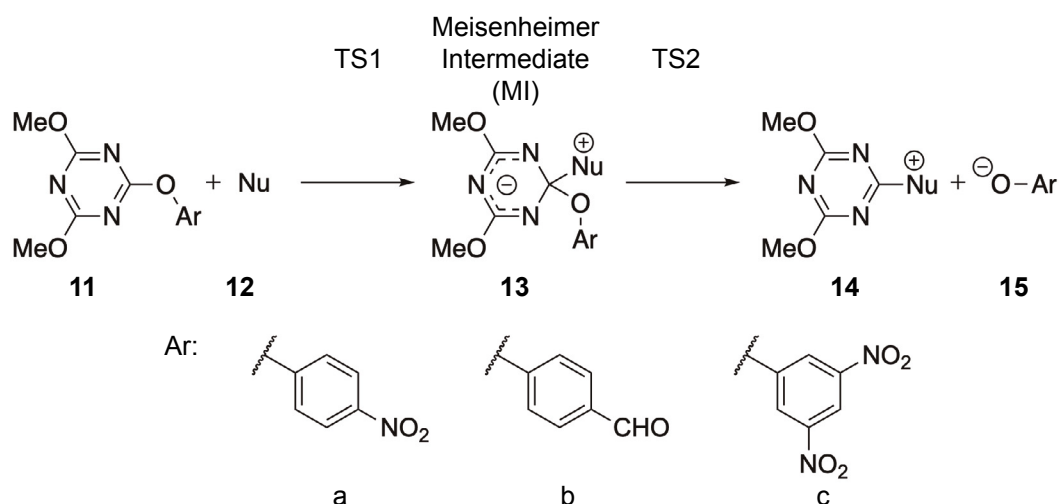


Scheme SI-1 Comparison of predicted and measured activation energy. The mechanism was found to be stepwise. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).



Scheme SI-2 Computation of the activation energy for another literature S_NAr reaction. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

Table SI-2-3 Energy profiles for S_NAr reactions where experimental evidence suggests a concerted mechanism.^[a]



Entry	Nu	Ar	TS1 w.r.t. MI (kcal/mol) ^[b]	MI ^[c] (kcal/mol)	TS2 w.r.t. MI (kcal/mol) ^[b]
1	DMAP	a	1.90	14.5	1.15
2	DMAP ^[d]	a	2.85	16.6	2.24
3	DMAP	b	2.19	15.0	1.89
4	DMAP	c	4.06	12.3	0.25
5	Morpholine ^[e]	a	1.31	11.7	6.38
6	Morpholine ^[e]	a	1.95	11.0	5.05

[a] Level of theory: M11/6-311++G(d,p)/cpcm(H₂O).

[b] Measured with respect to the Meisenheimer intermediate.

[c] Measured with respect to the substrate complex.

[d] Four explicit molecules of water were included in the calculation.

[e] The energy profiles with two different attack angles of the nucleophile were modelled for the same reaction.

The reaction was performed in an aqueous solvent system of water-dioxane 9:1.^[15] There are no parameters available to model this solvent system directly. As a reasonable approximation, the solvent model for water was chosen in the calculation.

The displacement of phenolate **15a** with DMAP as the nucleophile showed a kinetically very short-lived Meisenheimer intermediate **13a** (Entry 1). The relative barrier for the expulsion of the phenolate leaving group **15a** equals 1.15 kcal/mol. To assess the effect of explicit solvation, four water molecules were included in the calculation of the energy profile of this reaction (Entry 2). The effect of these additional molecules on the energy profile was moderate. The relative energy of the Meisenheimer intermediate slightly increased. Also, the intermediate became slightly more stable with an energy barrier for the expulsion of the leaving group **15a** being 2.24 kcal/mol instead of 1.15 kcal/mol. This result shows that explicit solvation does not have a critical effect on the energy profile of this reaction.

Only moderate changes in the energy profile were observed with the two other phenolate leaving groups **15b** and **15c** (Entries 3 and 4). When going from DMAP to the morpholine nucleophile, the rate limiting step changed from the addition of the nucleophile (TS1) to the expulsion of the leaving group (TS2) (Entries 5 and 6). Still, the kinetic stability of the Meisenheimer intermediate was very low. The energy barrier is less than 2 kcal/mol for the decay of this intermediate to the substrate complex.

The computational results stand in apparent contradiction to the interpretation of the kinetic studies that were performed by Williams et al. for this class of S_NAr reactions.^[15] Closer inspection of the computational results showed, however, that in the majority of cases the relative stability of the Meisenheimer intermediate is lower than 2 kcal/mol - thus below the typically accepted threshold of chemical accuracy.^[17] In that sense, the computational results support the interpretation of Williams' kinetic data. Following conventional experimental approaches, these S_NAr reactions appear to proceed via a concerted mechanism. With computational tools, however, it is possible to detect much shallower minima on the potential energy surface than with conventional experiments. Thereby, a reaction that appears to be concerted in the experiment can correctly be revealed to exhibit fleeting intermediates along its path.

2.2. Initial Studies

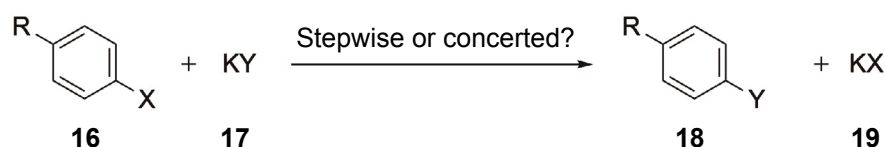
To gain a broad overview of the two mechanistic domains, three classes of S_NAr reactions were investigated. These are the halide displacement with potassium methoxide (Figure 1 in the main text), halide-halide exchange reactions (Table SI-2-4) and the analogous chalcogen-chalcogen exchange reactions (Table SI-2-5). The log files of these calculations can be found in Table SI-3-4 (page 32), Table SI-3-5 (page 34), and Table SI-3-6 (page 35), respectively.

In the halide displacement with potassium methoxide in Figure 1, only for the fluoride series was the mechanistic turning point identified, with $\tau_p^- = 1.05$. For the displacement of chloride, bromide and iodide the mechanistic turning point could not be identified. These reactions all showed a concerted energy profile even with the most electron-withdrawing *para*-nitroso substituent that was included in the σ_p^- scale.

A similar picture was obtained for the halide exchange reactions (Table SI-2-4). Only for the fluoride identity reaction was a mechanistic turning point identified ($\tau_p^- = 0.59$). For all other combinations of halides, a concerted energy profile was observed even for the examples with the *para*-nitroso substituent. Obviously the mechanistic turning point for these reaction series lies beyond the applied σ_p^- scale.

An analogous study to the halide exchange reactions was performed for the chalcogenide exchange reactions (Table SI-2-5). The nucleophilic displacement of the chalcogen residue in the substrate **20** by the potassium chalcogenide nucleophile **21** served as a model system. In contrast to the halide exchange reaction, the mechanistic turning point for most of the chalcogen exchange reactions actually fell onto the applied σ_p^- scale. Clearly, the chalcogen-chalcogen exchange reactions have a much more pronounced tendency to proceed via a stepwise mechanism. In fact, the identity reaction of methoxide proceeded via

Table SI-2-4 Halogen-Halogen Exchange Reactions



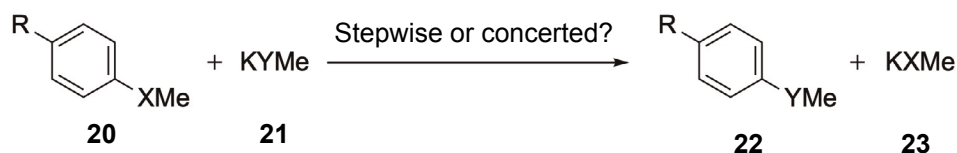
τ_p^- values for the halogen-halogen exchange reactions

	-X	-F	-Cl	-Br	-I
KY					
KF		0.59 ^[a]	>1.63 ^[b]	>1.63	>1.63
KCl			>1.63	>1.63	>1.63
KBr				>1.63	>1.63
KI					>1.63

[a] The S_NAr reaction mechanism changes from stepwise to concerted when going from the *para*-substituent $-\text{CF}_3$ ($\sigma_p^- = 0.65$) to $-\text{CCH}$ ($\sigma_p^- = 0.53$).

[b] The *para*-nitroso substituent marks the upper limit ($\sigma_p^- = 1.63$) of the applied σ_p^- scale.

Table SI-2-5 Chalcogen Exchange Reactions



τ_p^- values for the chalcogen-chalcogen exchange reactions

	-XMe	-OMe	-SMe	-SeMe
KYMe				
KOMe		<-0.77 ^[a]	0.27	0.64
KSMe			0.31	0.92
KSeMe				0.70

[a] The *para*-triphenylphosphinimine [-NP(Ph)₃] substituent marks the lower limit ($\sigma_p^- = -0.77$) of the applied σ_p^- scale.

a Meisenheimer intermediate even for the most electron-donating *para*-substituent that was investigated. With increasing atomic number of the chalcogens, the identity reaction showed a decreased tendency to proceed via a stepwise S_NAr reaction (i.e. the value of τ_p^- increases from <-0.77 for methoxide, to 0.31 for methanethiolate, to 0.70 for methaneselenolate). Likewise, the tendency of the displacement reaction of a methane chalcogenide by potassium methoxide to follow a stepwise mechanism decreases with increasing atomic number of the displaced chalcogenide (i.e. the value of τ_p^- increases from <-0.77 for methoxide, to 0.27 for methanethiolate, to 0.64 for methaneselenolate).

Clearly, a concerted mechanism is favoured for the chalcogen exchange reaction by the participation of larger (i.e. softer) chalcogens. The analogous statement holds true for the halide exchange reaction. The halides chloride, bromide and iodide all strongly favour a concerted mechanism, either in the halide exchange reaction or in an exchange reaction with potassium methoxide. Only for the S_NAr reactions involving fluoride was a stepwise energy profile found to have significant importance.

2.3. Counter-Cation and Explicit Solvent Effects

The ability of the alkali counter cation to coordinate to the leaving fluoride anion can have an effect on the mechanistic turning point as became apparent from Figure 2 in the main text and the corresponding discussion. The log files of these calculations are listed in Table SI-3-7 (page 37). In order to refine the understanding of coordination effects, explicit solvent molecules were added to the computational model as ligands of the alkali metal cation (Figure SI-4). It was assumed that the ability of the counter cation to coordinate the fluoride leaving group may decrease if its coordination sphere gets increasingly saturated with other ligands. It was found that the addition of one explicit solvent molecule in the model system did not evoke any shift in τ_p^- . The addition of a second molecule of DMF led to a significant blurring of the mechanistic turning point, which manifests in an increase of $\Delta\sigma_p^-$ from 0.05 to 0.22. Also, the value τ_p^- decreased slightly by 0.18 units. However, since the mechanistic turning point is no longer sharp, it is not clear whether this decrease of τ_p^- is actually significant. The log files of these calculations are listed in Table SI-3-8 (page 40).

Overall, including explicit solvent molecules did not produce a dramatically different prediction of the mechanistic turning point. A similar observation has already been made previously (Table SI-2-3 Entry 1 vs 2). Hence, relatively weakly coordinating ligands of the alkali metal cation do not seem to have a significant effect on the mechanistic turning point τ_p^- . This result also has practical implications. It suggests that relying on the implicit solvation model alone is a reasonable - and computationally much more effective - approximation.

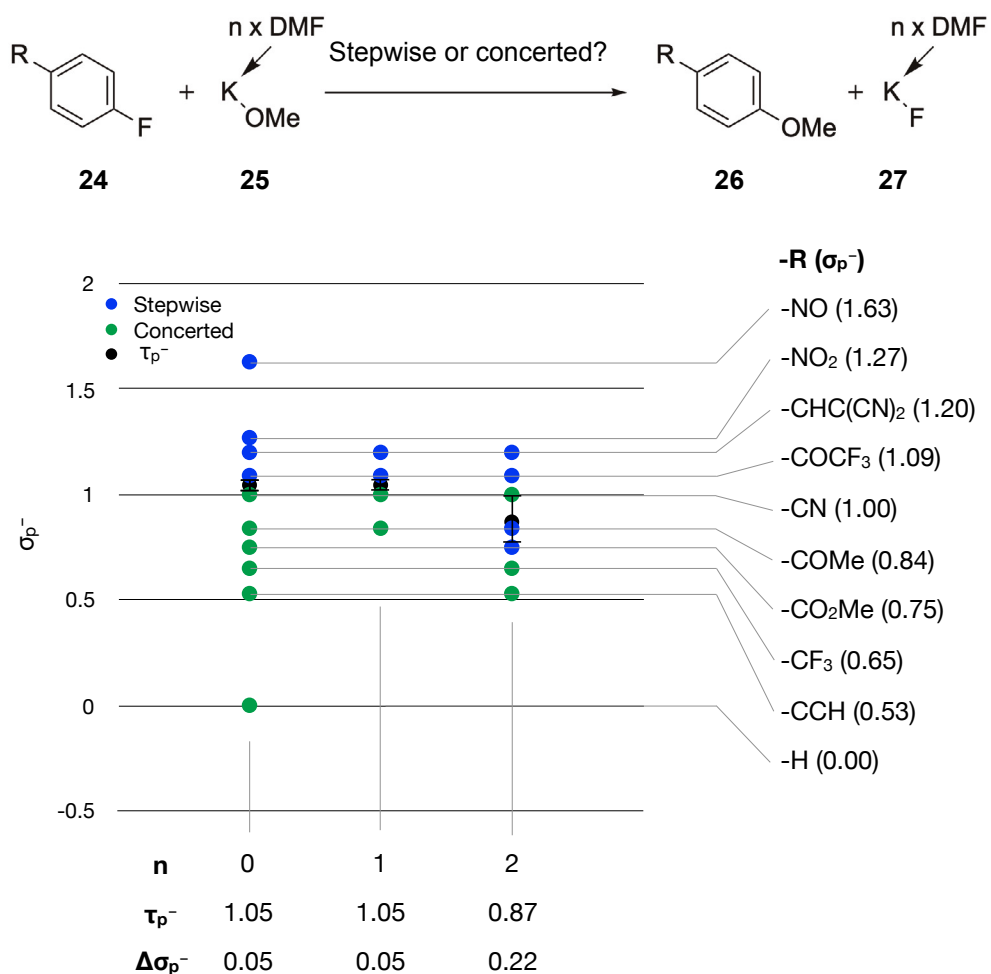


Figure SI-4 The effect of including explicit DMF solvent molecules coordinating to potassium on the mechanistic turning point was investigated for the displacement of fluoride with potassium methoxide. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

2.4. Effect of the Nucleophile

In Figure 3 in the main text it became apparent that the series of S_NAr reactions with nucleophile **2e-K**

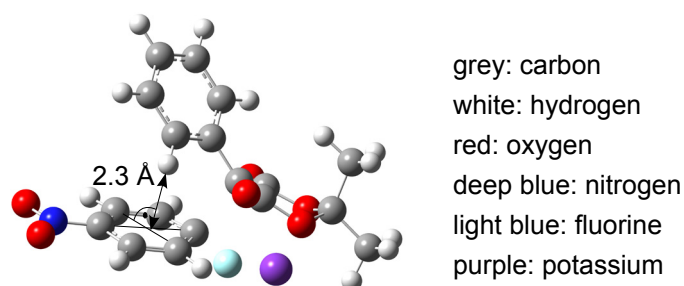


Figure SI-5 Transition state for the S_NAr reaction between **580** (R = NO₂) and the nucleophile **601e**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

favours a concerted mechanism more ($\tau_p^- = 1.36$) than the other investigated reaction series ($\tau_p^- = 1.05$). The log files of these calculations are listed in Table SI-3-9 (page 41). Closer inspection of the geometries of the rate limiting transition states including nucleophile **2e-K** showed that steric repulsion may be at the heart of this pronounced tendency to follow a concerted mechanism (Figure SI-5). One of the hydrogen atoms of the phenyl group of the nucleophile approaches the plane of the aromatic system of **1a-R-F** (here shown for R = NO₂) as closely as 2.3 Å in the transition state. This steric clash makes a Meisenheimer intermediate less energetically favourable and pushes the reaction towards a concerted pathway.

The SN(ET)Ar Pathway as an Alternative to the Bimolecular S_NAr Pathway

During the reviewing process it was pointed out that the highly activated substrates **1a-R-F** with R = NO, NO₂ and CHC(CN)₂ may react with the nucleophiles **2b-K**, **2d-K**, **2e-K** and **2f-K** alternatively via an SN(ET)Ar process. Along this reaction coordinate, first an electron would be transferred from the nucleophile to the electrophile in a single electron transfer (SET) step. In order to judge the accessibility of the SN(ET)Ar pathway the Gibbs free energy was calculated for the initial SET and compared to the energy profile of the S_NAr reaction. For isolated examples, also the activation energy of the SET was calculated according to the modified Nelsen-four-point method.^[19] The results are summarised in Table SI-2-6 below.

For most of the examples the Gibbs free energy of the SET exceeds the activation energy of the S_NAr pathway. Thus, it was possible to rule out a SN(ET)Ar pathway without further investigation. Only for the example of the Meldrum's acid derivative as the nucleophile **2d-K**, a SET was more favourable than the S_NAr pathway (Entry 5). The log files for the SET calculations are listed in Table SI-3-10 (page 43).

Table SI-2-6 The SN(ET)Ar pathway as an alternative to the bimolecular S_NAr pathway

Entry	Nucleophile	R in 1a-R-F	ΔG S _N Ar (kcal/mol) ^[a]	ΔG^* S _N Ar (kcal/mol)	ΔG SET (kcal/mol)	ΔG^* SET (kcal/mol)
1	2b-K	NO	-0.588	11.9	15.8	-
2	"	NO ₂	3.52	13.9	26.1	-
3	"	CHC(CN) ₂	-0.558	11.9	25.0	-
4	2d-K	CHC(CN) ₂	6.18	22.1	45.2	-
5	2e-K	NO	21.7	27.9	16.0	16.2
6	"	CHC(CN) ₂	22.2	28.2	36.5	-
7	2f-K	CHC(CN) ₂	-11.7	12.9	13.4	-

[a] For the formation of the Meisenheimer intermediate.

[b] For the formation of the S_NAr product.

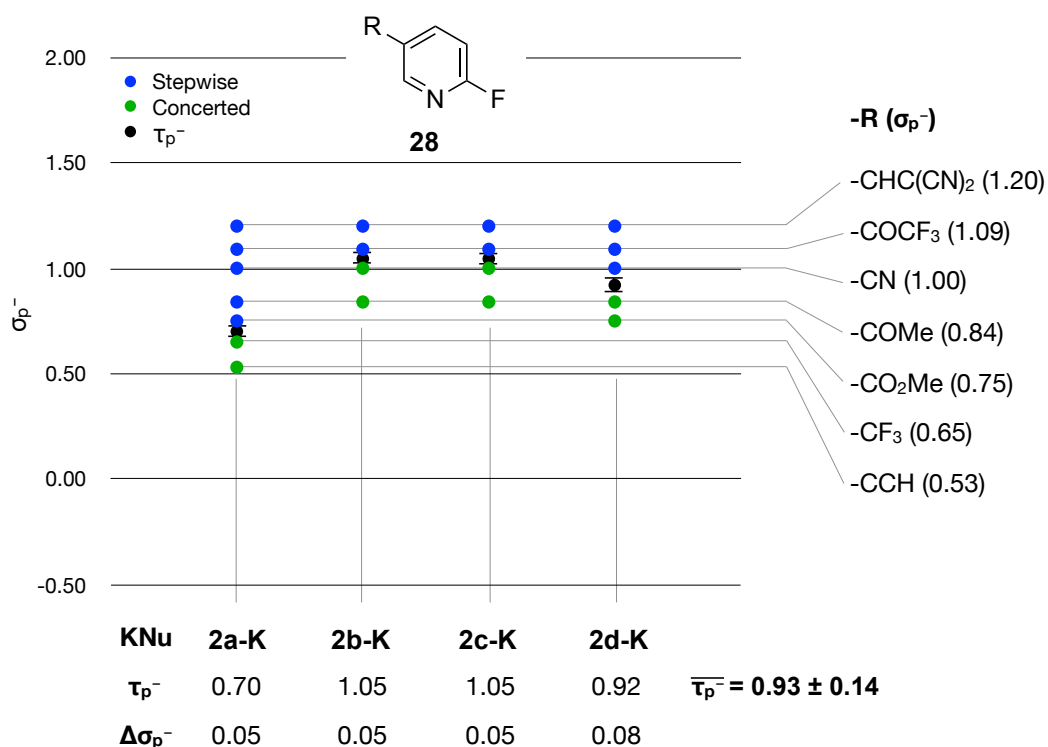


Figure SI-6 The mechanistic turning point was investigated for the S_NAr reaction of several different nucleophiles and 4-substituted 2-fluoropyridine **603**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

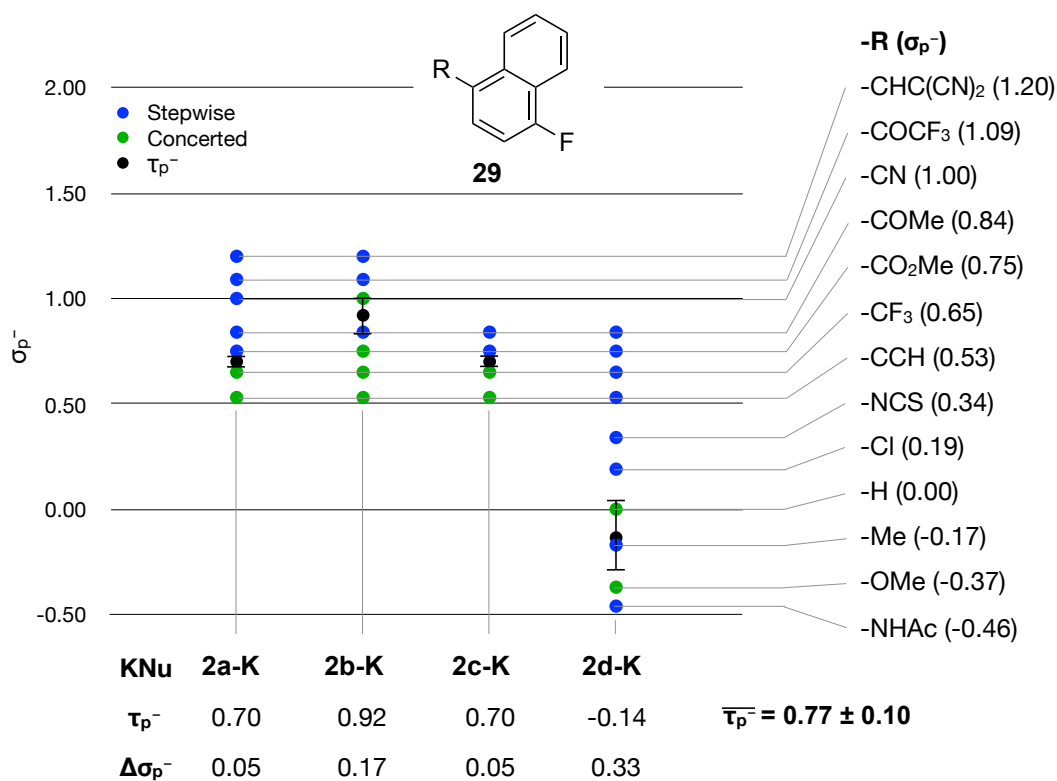


Figure SI-7 The mechanistic turning point was investigated for the S_NAr reaction of several different nucleophiles and 4-substituted 1-fluoronaphthalene **604**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

Additional Reactions of Aryl Fluorides and Various Nucleophiles

The observation that a number of very different nucleophiles showed the same mechanistic turning point was surprising. In order to investigate whether this observation is general, τ_p^- was calculated for two additional aromatic systems - **28** and **29** - and the nucleophiles **2a - d** (Figure SI-6 and Figure SI-7). For the pyridine series **28**, the variation of τ_p^- among the four nucleophiles **2a - d** was somewhat larger than in the benzene series. The average was slightly lower with a value of 0.93 ± 0.14 . The log files of these calculations are listed in Table SI-3-11 (page 43). For the naphthalene series **29**, the three nucleophiles **2a - c** showed a similar value of τ_p^- with an average τ_p^- of 0.77 ± 0.10 . The nucleophile **2d**, in contrast, massively deviated from this average value. In fact, the S_NAr reaction with this nucleophile favoured a stepwise S_NAr reaction even with electron-donating substituents such as *para*-methyl or *para*-NHAc residues. Presumably, π - π -stacking interactions or steric effects between the nucleophile and the aromatic system lead to this pronounced difference to the other nucleophiles. Therefore the reaction series of **2d** with **29** was regarded as an anomaly and not included in the calculation of τ_p^- . The log files of these calculations are listed in Table SI-3-13 (page 45).

With the exception of the reactions between **2d** and **29** it can be noted that there is relatively little variation between different nucleophiles attacking the same aromatic substrate, i.e. the observation made for the system **1a-R-F** was essentially reproduced with **28** and **29**. The mechanistic turning point does not seem to depend on the nucleophile strongly, i.e. the value τ_p^- is mainly characteristic for the aromatic system (with a fluoride leaving group).

Potential Deprotonation of 2-Pyridyl Substrates by Potassium Methoxide

For the 2-fluoropyridyl series **1d-R-F** with the three most electron-withdrawing *para*-substituents in the series (R = CHC(CN)₂, COCF₃ and CN) one may expect that the deprotonation at position 3 may be accessible with the highly basic potassium methoxide nucleophile **2a-K**. This would initiate a reaction sequence leading to an alkyne intermediate. The deprotonation could lead to the expulsion of fluoride and the subsequent addition of the nucleophile to the alkyne intermediate would give the same product as the S_NAr reaction. To elucidate the accessibility of such an alternative mechanism, the energetic profile of the initial deprotonation was investigated. The results are summarised in Table SI-2-7 below.

The deprotonation for all three examples is significantly endergonic by >10 kcal/mol. The activation energy for the S_NAr pathway, in contrast, is very low with <3 kcal/mol (calculated with respect to the substrate complex and not the isolated species). Moreover, the formation of the Meisenheimer intermediate is strongly exergonic. Thus, it can be safely concluded that deprotonation is not a competing reaction pathway for these cases. The log files of these calculations are listed in Table SI-3-12 (page 45).

Table SI-2-7 Deprotonation of 2-Fluoropyridyl Substrates by Potassium Methoxide

Entry	R in 1d-R-F	ΔG_{S_NAr} (kcal/mol) ^[a]	$\Delta G^*_{S_NAr}$ (kcal/mol)	$\Delta G_{\text{Deprotonation}}$ (kcal/mol)	ΔpKa ^[b]
1	CHC(CN) ₂	-23.6	1.82	11.2	18.9
2	COCF ₃	-20.8	1.73	11.3	19.0
3	CN	-16.3	2.89	10.6	17.8

[a] For the formation of the Meisenheimer intermediate.

[b] The ΔpKa values were calculated according to $\Delta pKa = \Delta G/RT$ where R is the ideal gas constant with the value 1.987 kcal/mol/K and T is the temperature in Kelvin and was set to 298.15 K.

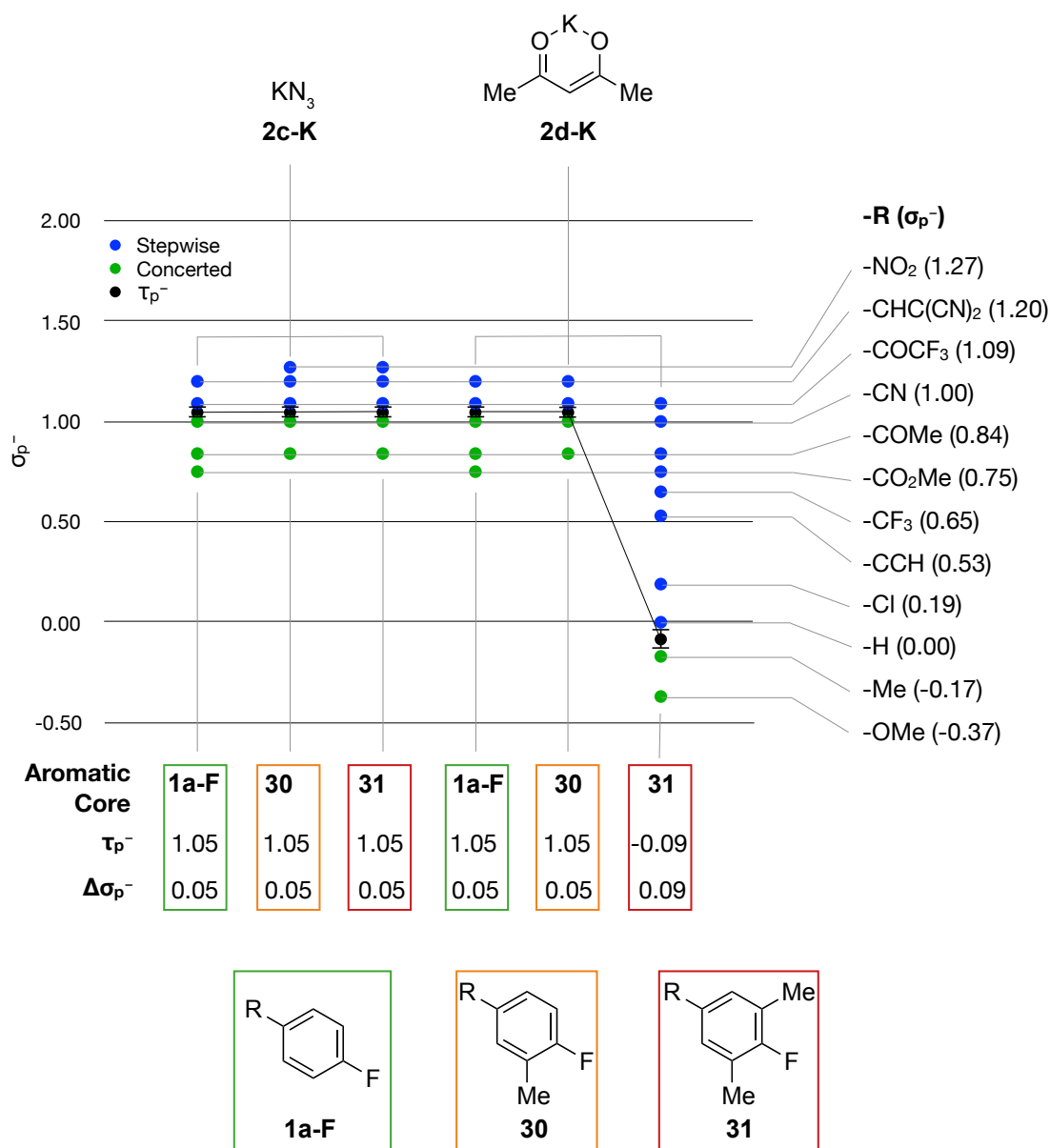


Figure SI-8 Steric effects on the S_NAr mechanistic turning point were investigated by comparing a slim with a bulky nucleophile. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

Steric Effects

For two cases so far, indication was found that, in addition to the electronic characteristics of the system, steric effects may influence the mechanistic turning point (see Figure SI-6 3 in the main text and Figure SI-7). From the above discussion, it also follows that the electronic nature of nucleophiles does not have a significant effect on τ_p^- . This allows us to investigate steric effects by choosing a bulky and a slim nucleophile. Any significant difference in τ_p^- between these two nucleophiles for the attack at the same series of substrates can then be attributed to steric effects.

Such a comparison was made for the nucleophiles **2c-K** and **2d-K** based on the aromatic substrates **1a-F**, **30** and **31** (Figure SI-8). When going from **1a-F** to **30** to **31**, the small nucleophile **2c-K** does not show any response to the increasing steric bulk and slightly more electron-rich aromatic core. The value τ_p^- remains constant throughout this series. With the sterically more bulky nucleophile **2d-K**, the situation is different. While there is no difference in τ_p^- between **2c-K** and **2d-K** for the substrates **1a-F** and **30**, the value of τ_p^- sharply decreases for the reaction of **2d-K** when a second *ortho*-methyl group is present as in

31. The log files of these calculations are listed in Table SI-3-14 (page 47).

This result shows that steric bulk on the aromatic system can force the S_NAr reaction to follow a stepwise mechanism even if a concerted reaction profile would be expected based on the electronic nature of the substrate. As follows from the combination of the nucleophile **2d-K** and the aromatic system **31**, the steric bias on the mechanism can be massive. The introduction of the second methyl group induced a larger change in τ_p^- than did the expansion of the aromatic core from benzene to anthracene, for example (Figure 4 in the main text). While changes of the electronic nature of the aromatic system affect the S_NAr reaction of various nucleophiles approximately equally, steric changes affect mainly bulky nucleophiles like **2d-K**.

2.5. Effect of the Aryl Fluoride Electrophile

As illustrated in Figure 4 in the main text, both, an additional fused ring and a nitrogen atom in the ring, help to stabilise the negative charge that accumulates on the aromatic system during the addition of the nucleophile. The better the aromatic core on its own is able to stabilise this negative charge, the less the stabilisation of a (potential) Meisenheimer intermediate depends on the electron-withdrawing nature of the *para*-substituent. The log files of these calculations are listed in Table SI-3-15 (page 49).

The electron affinity of a given aromatic system can be used to estimate whether a S_NAr displacement of the fluoride substituent proceeds via a concerted or stepwise mechanism as shown in Figure 5 in the main text. The log files of these calculations are listed in Table SI-3-16 (page 50).

2.6. S_NAr Mechanism and the Hammett Correlation

As has been seen in Figure 6 in the main text, there does not seem to be a connection between the slope of the Hammett correlation and the mechanistic preference of an S_NAr reaction series.

To further investigate what information about the overall reaction mechanism is contained in the structure of the rate-limiting transition state, the changes in the geometry of the rate-limiting transition states of the S_NAr displacement for the series **1a-R-X** (for X = F, Cl) with potassium methoxide was analysed (Figure SI-9). It can be seen that the investigated distances and angles change in a very similar way between the two series (i.e. the slopes of the correlations of the four investigated parameters are nearly the same). Further, also the absolute values of d_1 , a_1 and a_2 are very similar (as expected, there is a large difference in the distance d_2 between the two series, which reflects the length difference {ca. 0.4 Å}^[18] between the carbon-fluorine and the carbon-chlorine bond). Again, the change of mechanism from stepwise to concerted is not reflected in the change of any of the investigated parameters. The log files for these calculations can be found in Table SI-3-7 (page 37).

For most examples the calculated ΔG^\ddagger show a good ($R^2 > 0.9$) correlation vs the Hammett substitution constant σ_p^- as can be seen from the examples in Figure SI-10, Figure SI-11, and Figure SI-12. The R^2 value is typically >0.9 . Only in two instances the values deviated noticeably from a linear correlation - in the case of the reaction between the Meldrum's acid derivative nucleophile **2e-K** and the fluoro aryl series **1a-R-F** (marked as '+' in Figure SI-10) and in the reaction between potassium methoxide and the 2-fluoro pyridyl series **1d-R-F** (marked as 'x' in Figure SI-12). In the former case the deviation may be explained through the interference of steric interactions as discussed in Section 2.4 and illustrated in Figure SI-5. The log files for these calculations can be found in Table SI-3-9 (page 41), Table SI-3-13 (page 45) and Table SI-3-11 (page 43), respectively.

For three examples, also the overall free energy ΔG° was analysed in detail (series **2c-K**, **2d-K** and **2e-K** in Figure SI-13, Figure SI-14 and Figure SI-15, respectively). It was found that ΔG° shows no significant correlation with the Hammett σ_p^- constant, in contrast to ΔG^\ddagger .

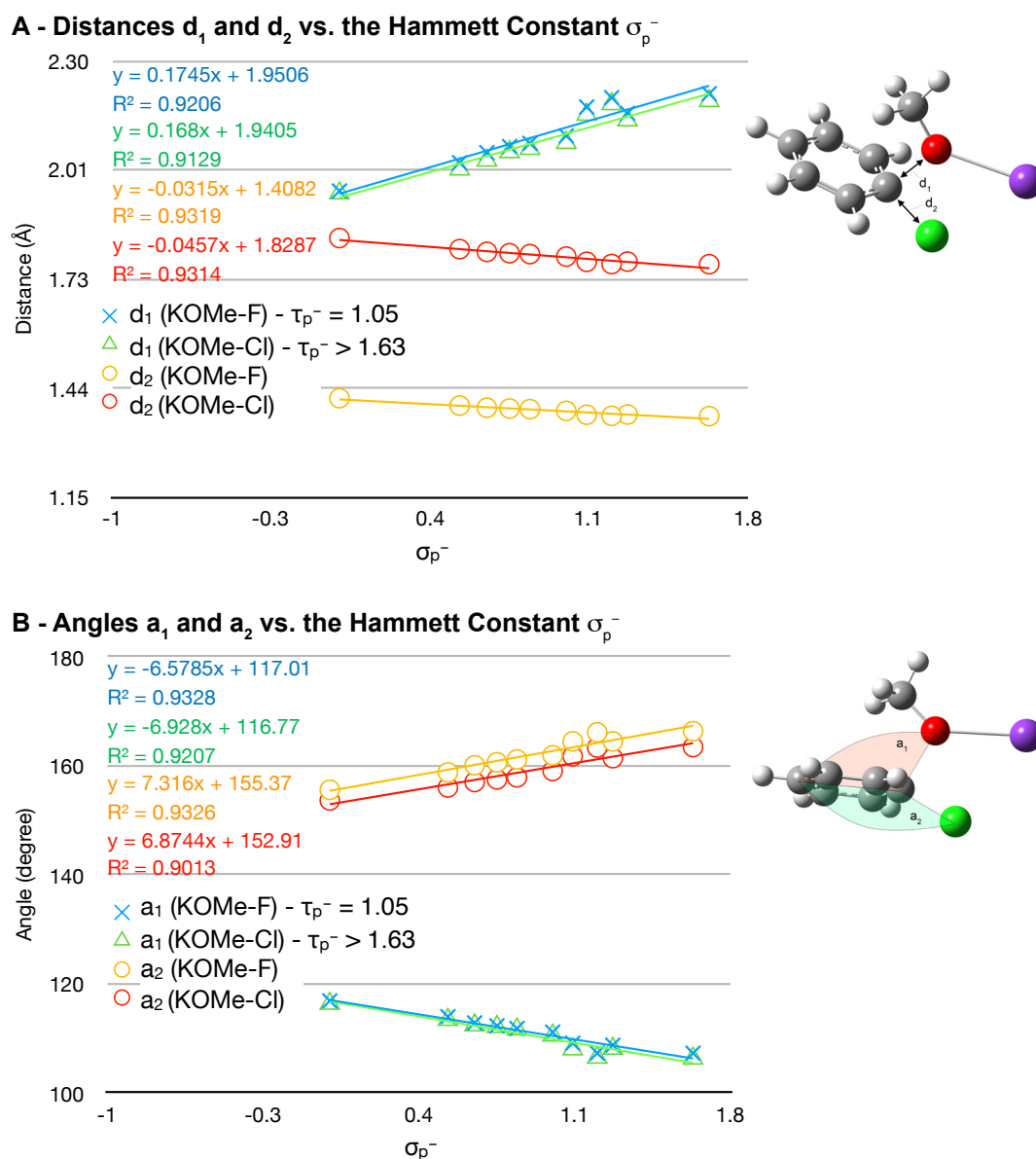


Figure SI-9 Geometry change of the transition state structure vs. the Hammett substitution constant σ_p^- for the displacement of fluoride and chloride with potassium methoxide in the series **1a-R-X**. The distances and angles, which are measured, are illustrated based on the chloride example **1a-R-Cl** with R = H. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

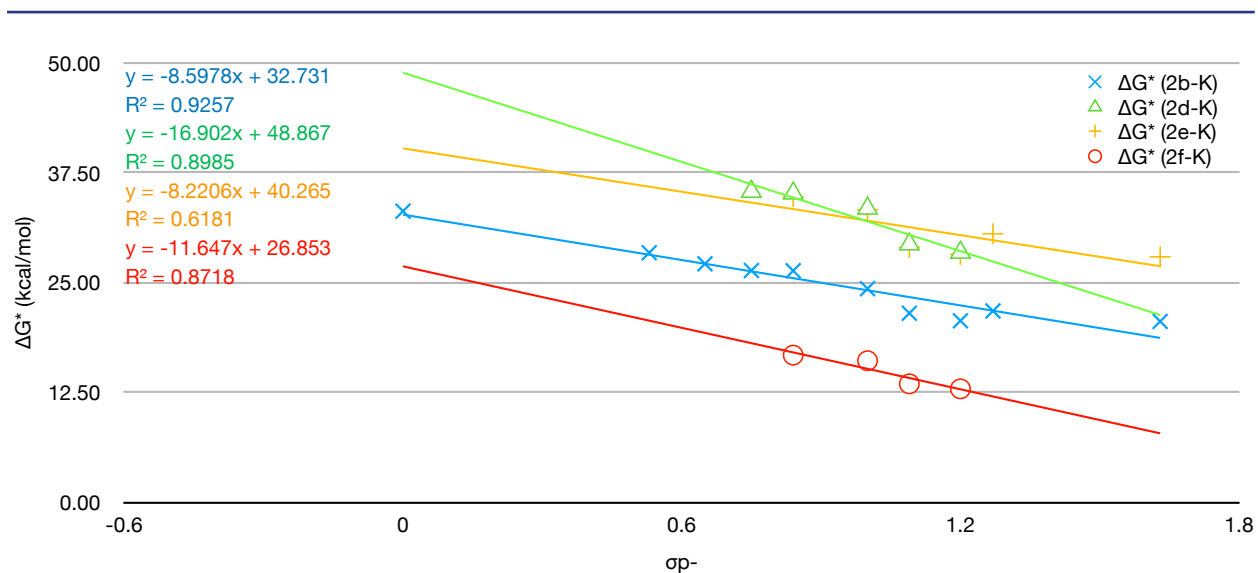


Figure SI-10 Correlation of the activation energy ΔG^* vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the phenyl fluoride series **1a-R-F** by the nucleophiles **2b-K** (x), **2d-K** (△), **2e-K** (+) and **2f-K** (o). Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

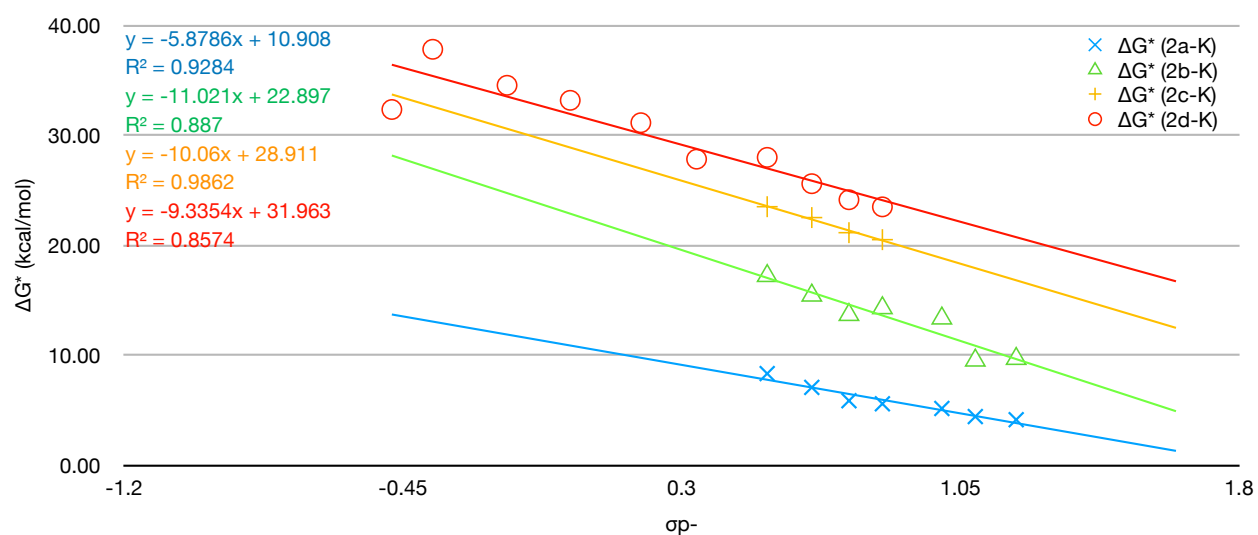


Figure SI-11 Correlation of the activation energy ΔG^* vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the naphthyl fluoride series **1b-R-F** by the nucleophiles **2a-K** (x), **2b-K** (△), **2c-K** (+) and **2d-K** (o). Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

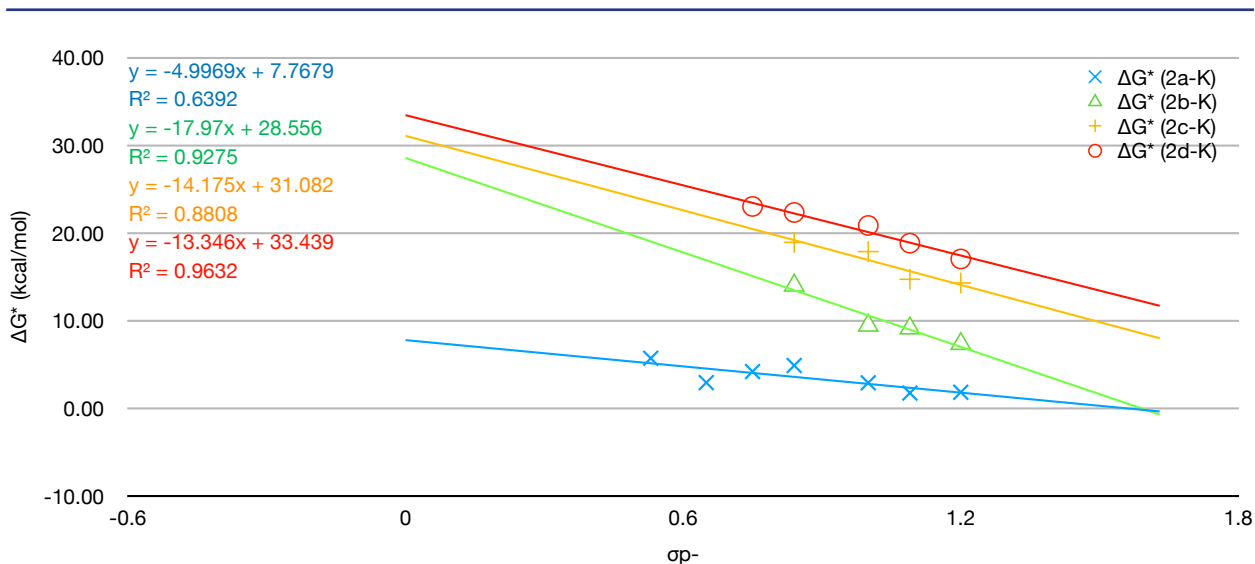


Figure SI-12 Correlation of the activation energy ΔG^* vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the 2-pyridyl fluoride series **1d-R-F** by the nucleophiles **2a-K** (x), **2b-K** (Δ), **2c-K** (+) and **2d-K** (o). Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

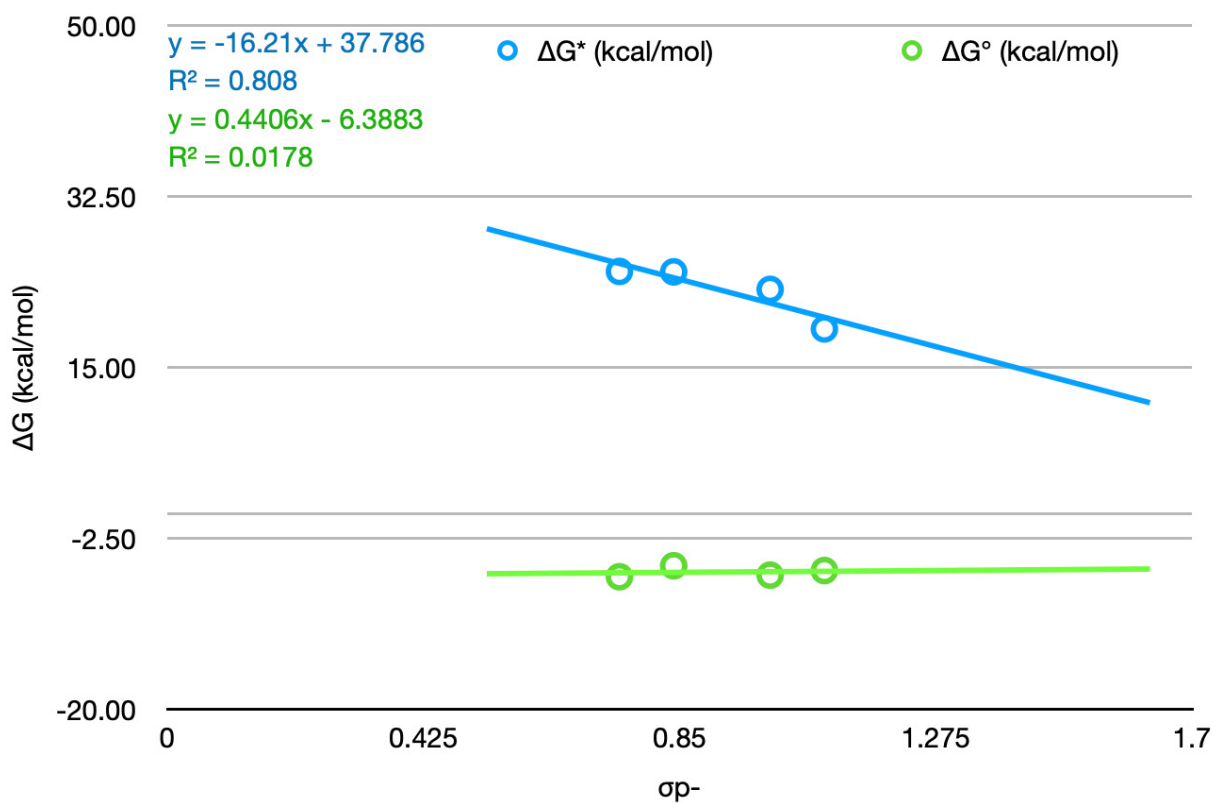


Figure SI-13 Correlation of the activation energy ΔG^* and ΔG° vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the phenyl fluoride series **1a-R-F** by the nucleophile **2c-K**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

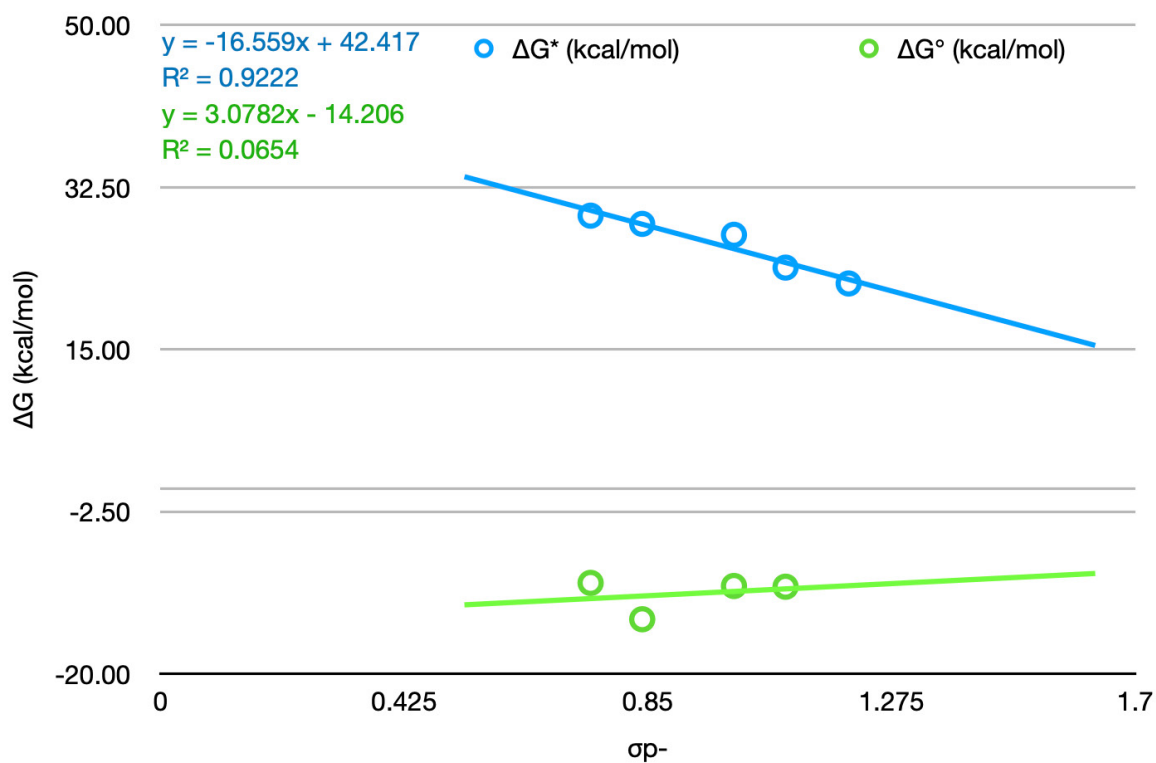


Figure SI-14 Correlation of the activation energy ΔG^* and ΔG° vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the phenyl fluoride series **1a-R-F** by the nucleophiles **2d-K**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

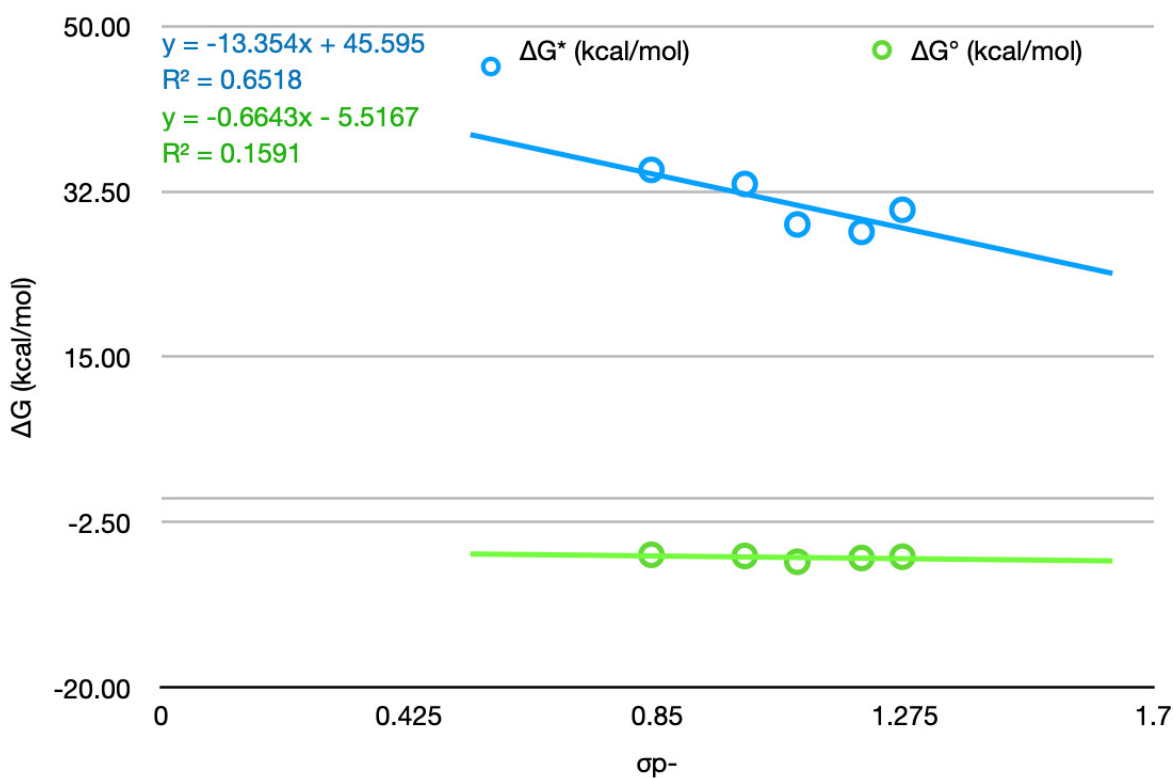


Figure SI-15 Correlation of the activation energy ΔG^* and ΔG° vs. the Hammett substitution constant σ_p^- for the displacement of fluoride from the phenyl fluoride series **1a-R-F** by the nucleophiles **2e-K**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

2.7. Predicting the S_NAr Mechanism of Substrates with a Simple Descriptor

As illustrated in Figure 6 in the main text, the S_NAr mechanism a given aryl fluoride would follow, can be predicted based on its gas-phase electron affinity (EA). Alternatively descriptors to the EA were investigated. The Mulliken charge (Figure SI-16), the ATP charge (Figure SI-17) and the 1s-orbital energy level (Figure SI-18) of the carbon atom at which the substitution takes place were investigated as atom-centred descriptors. None of these measures would serve as a suitable descriptor.

Further, the ionisation potential (IP) (Figure SI-19) and the HOMO-LUMO gap (Figure SI-20) were investigated for a subset of examples. Neither of these measures would give a suitable descriptor. The log files for these calculations can be found in the accompanying data set.

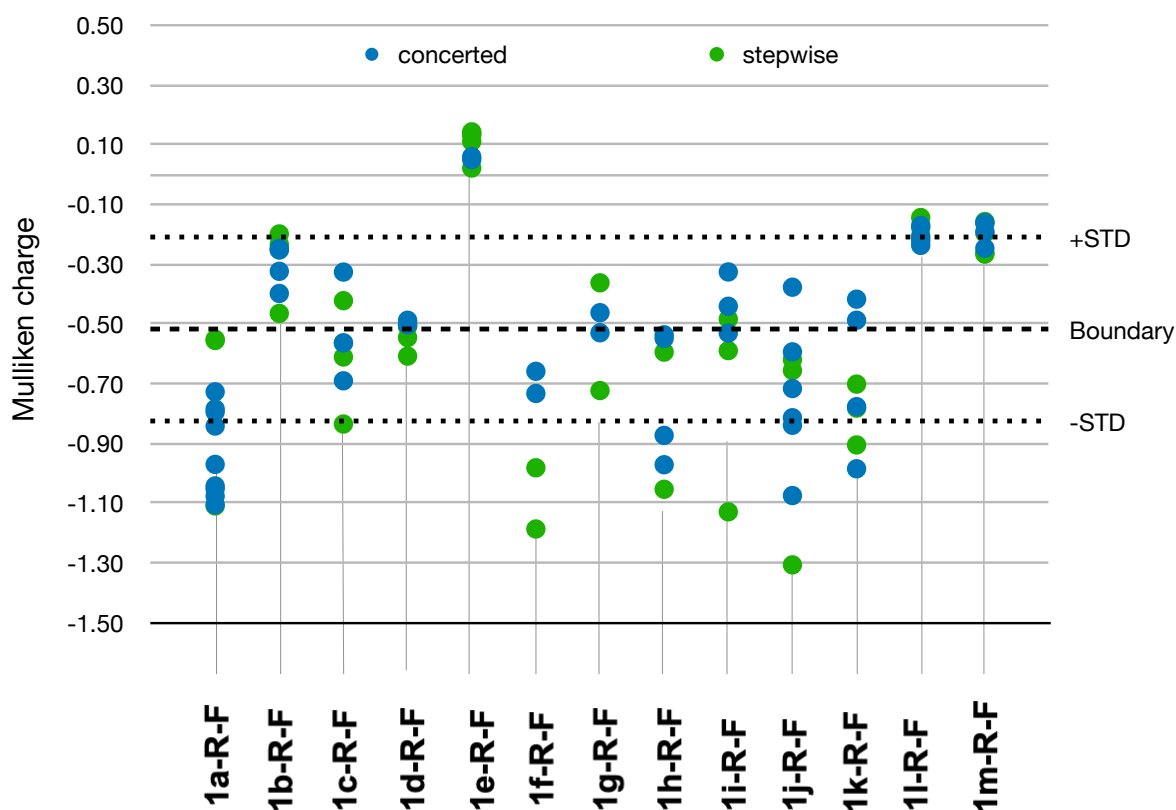


Figure SI-16 Mulliken charge of the carbon-atom at which the substitution occurs for the series **1a-R-F** to **1m-R-F**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

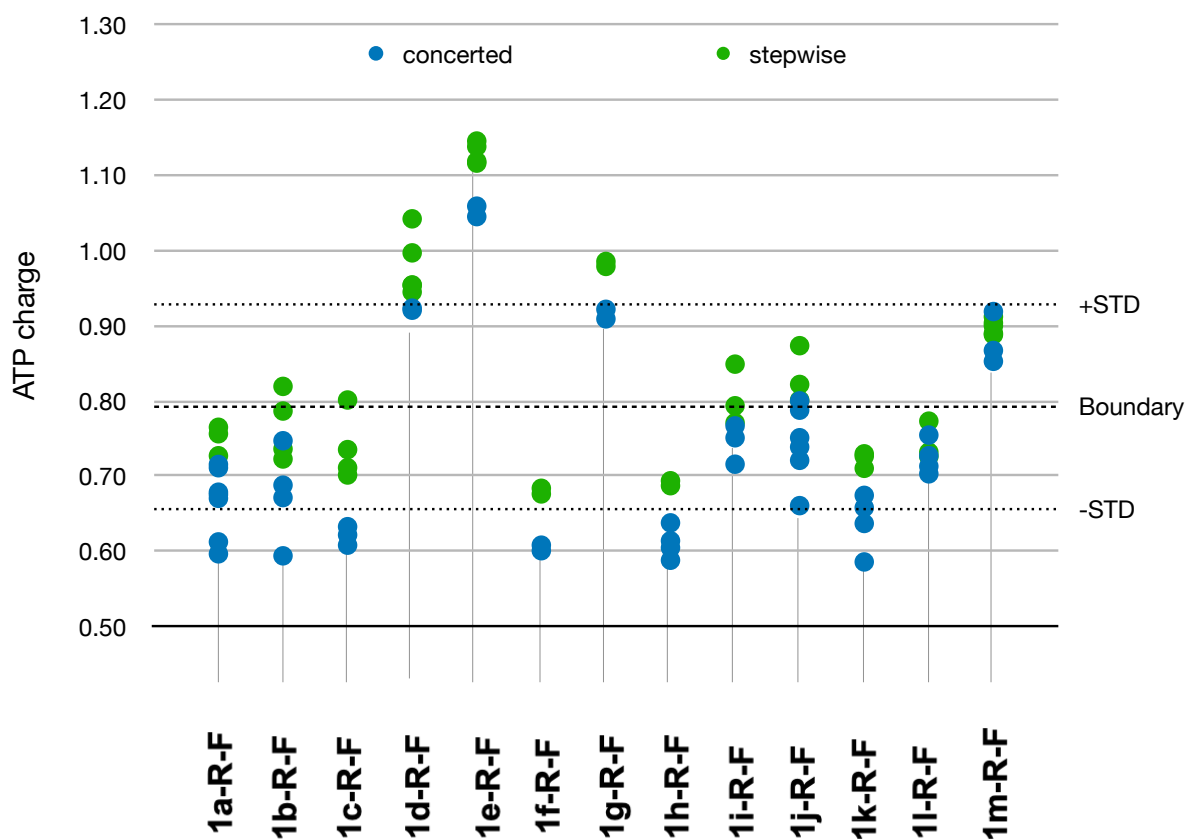


Figure SI-17 ATP charge of the carbon-atom at which the substitution occurs for the series **1a-R-F** to **1m-R-F**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

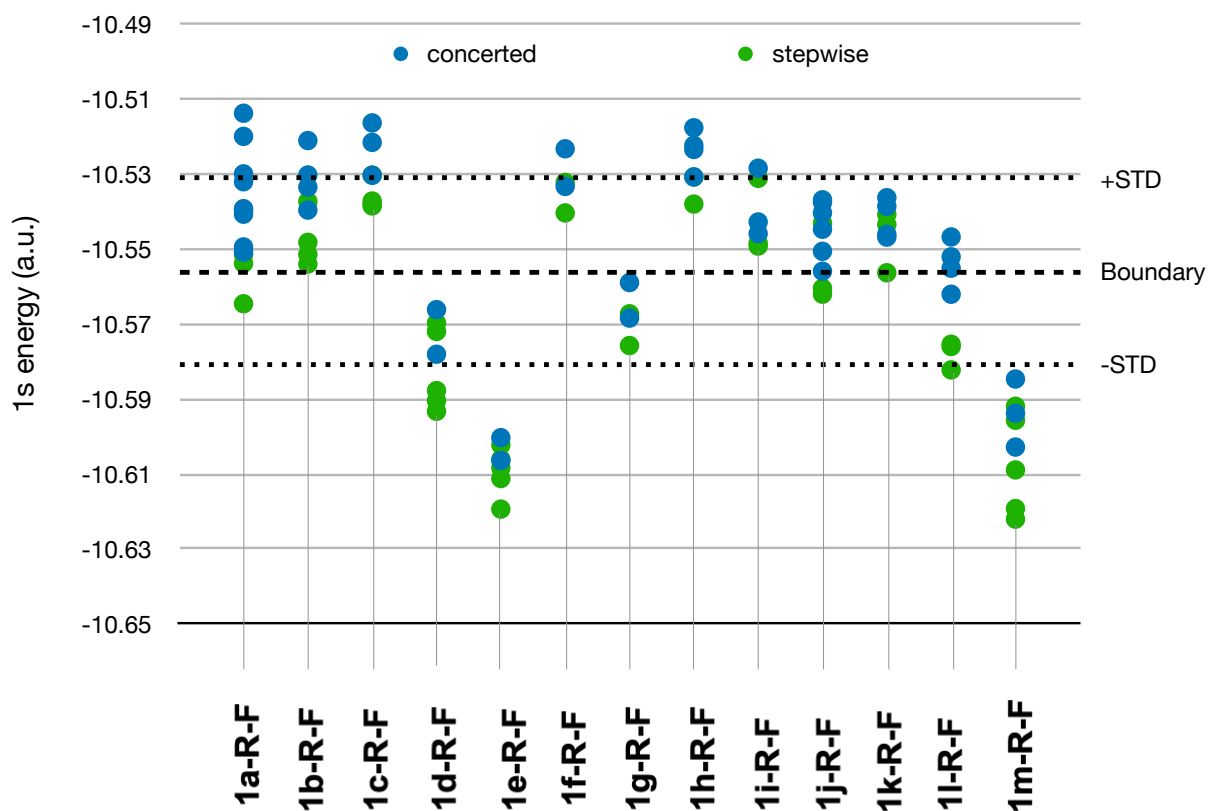


Figure SI-18 1s energy level of the carbon-atom at which the substitution occurs for the series **1a-R-F** to **1m-R-F**. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

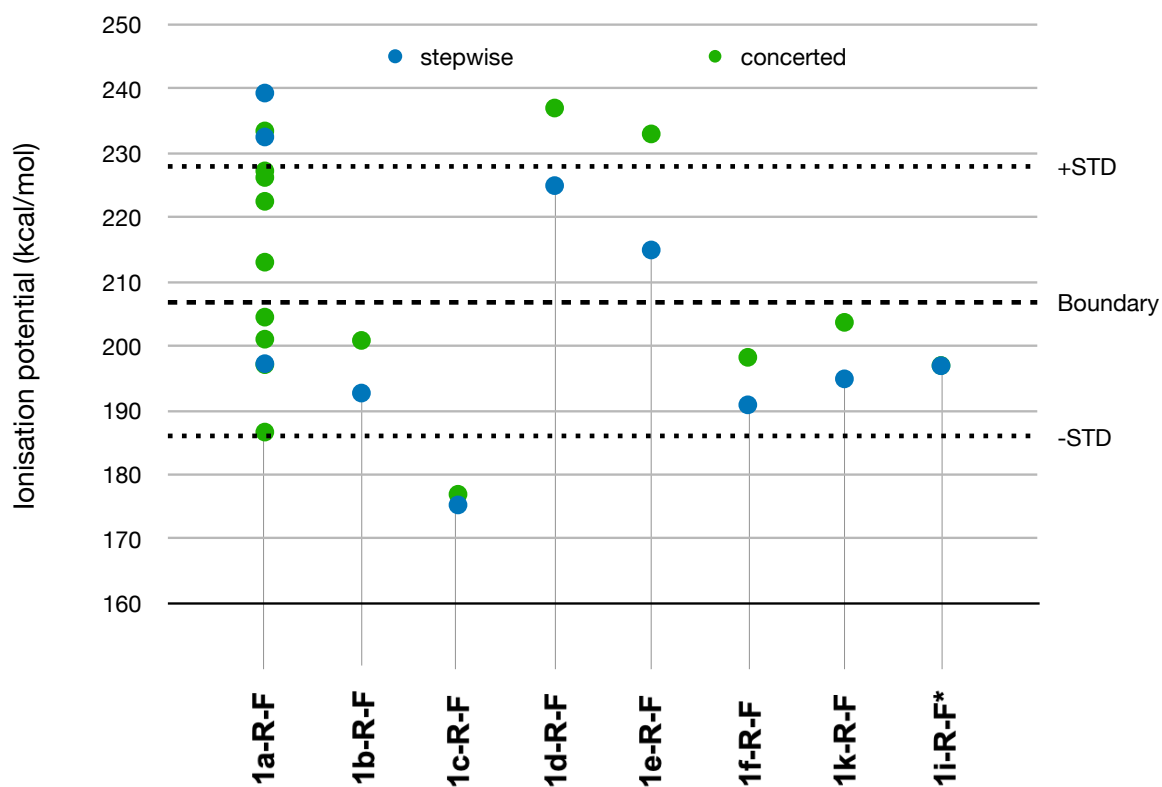


Figure SI-19 The ionisation potential of the series **1a-R-F** to **1f-R-F** and **1k-R-F** and **1i-R-F*** was calculated. *) The NH-indole analogues were considered instead of the N-Me-indole series. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

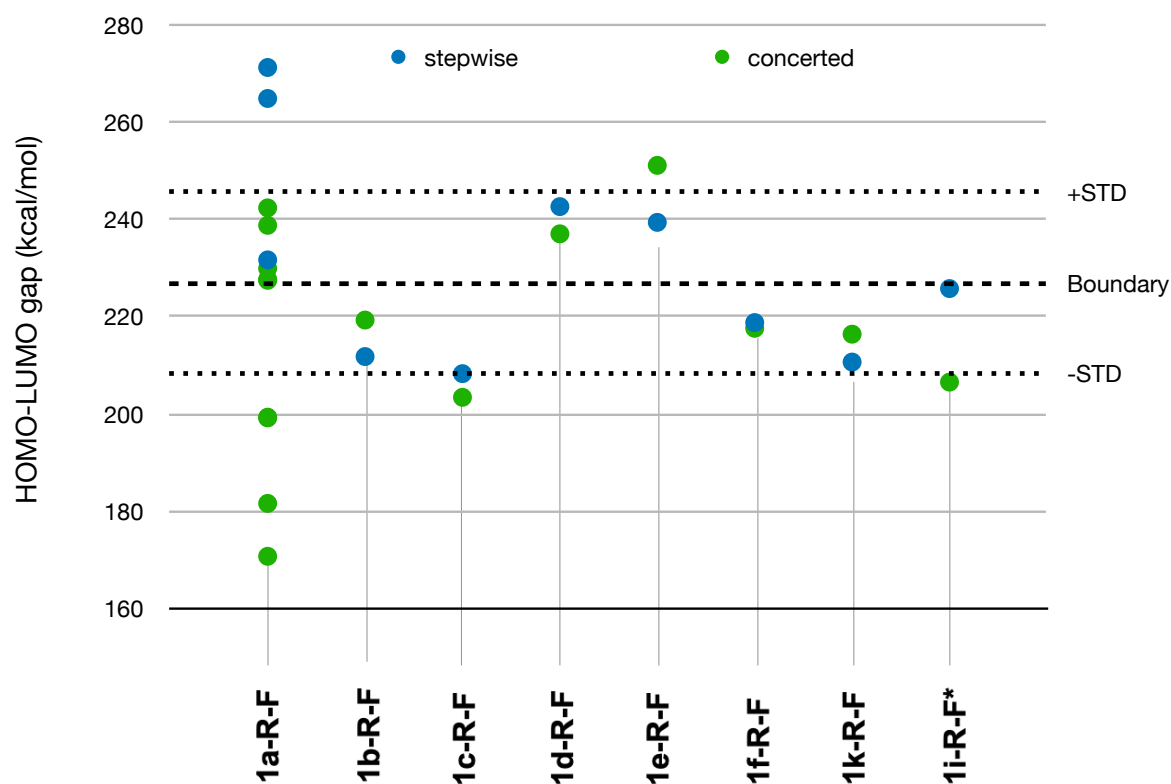


Figure SI-20 The HOMO-LUMO gap of the series **1a-R-F** to **1f-R-F** and **1k-R-F** and **1i-R-F*** was calculated. *) The NH-indole analogues were considered instead of the N-Me-indole series. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

3. Log File Archive

3.1. Computational Model

Benchmarking DFT Functionals

The names of the .log files of the calculations used to compile Figure SI-2, Figure SI-3, Table SI-2-1 and Table SI-2-2 are systematically listed below in Table SI-3-1.

Table SI-3-1

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4	"	-CN	SC	TS_CN_MP2-aug-cc-pVTZ_back_trial2.log
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6	"	-CN	MI	TS_CN_MP2-aug-cc-pVTZ_forward_trial5.log
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9	"	-COMe	PC	TS_COMe_MP2-aug-cc-pVTZ_forward_trial7_freq.log
10	"	-CO ₂ Me	SC	TS_CO2Me_MP2-aug-cc-pVTZ_back.log
11	"	-CO ₂ Me	TS	TS_CO2Me_MP2_aug-cc-pVTZ.log
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24	"	-CO ₂ Me	PC	TS_CO2Me_MP2_6311++Gdp_forward_trial3.log
25	B3PW91	-COCF ₃	SC	TS_COCF3_B3PW91_6-311++Gdp_back_trial3.log
26	"	-COCF ₃	TS1	TS_COCF3_B3PW91_6-311++Gdp.log
27	"	-COCF ₃	MI	TS_COCF3_B3PW91_6-311++Gdp_forward.log
28	"	-CN	SC	TS_CN_B3PW91_6-311++Gdp_back_trial3_freq.log
29	"	-CN	TS	TS_CN_B3PW91_6-311++Gdp.log
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33	"	-COMe	PC	TS_COMe_B3PW91_6-311++Gdp_forward_trial3.log
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36	"	-CO ₂ Me	PC	TS_CO2Me_B3PW91_6-311++Gdp_forward_trial2_freq.log
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40	"	-COCF ₃	SC	TS_COCF3_B3LYP-6311++Gdp_back_trial4.log
41	"	-COCF ₃	TS1	TS_COCF3_B3LYP-6311++Gdp.log
42	"	-COCF ₃	MI	TS_COCF3_B3LYP-6311++Gdp_forward.log
43	"	-CN	SC	TS_CN_B3LYP-6311++Gdp_back_trial3.log
44	"	-CN	TS	TS_CN_B3LYP-6311++Gdp.log
45	"	-CN	PC	TS_CN_B3LYP-6311++Gdp_forward_trial2.log
46	"	-COMe	SC	TS_COMe_B3LYP-6311++Gdp_back_trial4.log
47	"	-COMe	TS	TS_COMe_B3LYP-6311++Gdp_trial2_freq.log
48	"	-COMe	PC	TS_COMe_B3LYP-6311++Gdp_forward_trial2.log
49	"	-CO ₂ Me	SC	TS_CO2Me_B3LYP_6-311++Gdp_back_trial5.log
50	"	-CO ₂ Me	TS	TS_CO2Me_B3LYP_6-311++Gdp.log
51	"	-CO ₂ Me	PC	TS_CO2Me_B3LYP_6-311++Gdp_forward_trial3.log
52	B3LYP_D3-BJ	-NO2	SC	TS_NO2_F_MeO_B3LYP-D3BJ_back_trial5.log
53	"	-NO2	TS1	TS_NO2_F_MeO_B3LYP-D3BJ.log
54	"	-NO2	MI	TS_NO2_F_MeO_B3LYP-D3BJ_forward.log
55	"	-COCF ₃	SC	TS_COCF3_B3LYP-D3BJ-6311++Gdp_back_trial4.log
56	"	-COCF ₃	TS1	TS_COCF3_B3LYP-D3BJ-6311++Gdp_trial4.log
57	"	-COCF ₃	PC	TS_COCF3_B3LYP-D3BJ-6311++Gdp_forward_trial2.log
58	"	-CN	SC	TS_CN_B3LYP-D3BJ-6311++Gdp_back_trial3.log
59	"	-CN	TS	TS_CN_B3LYP-D3BJ-6311++Gdp.log
60	"	-CN	MI	TS_CN_B3LYP-D3BJ-6311++Gdp_forward_trial3.log
61	"	-COMe	SC	TS_COMe_B3LYP-D3BJ-6311++Gdp_back_trial2.log
62	"	-COMe	TS	TS_COMe_B3LYP-D3BJ-6311++Gdp_trial5.log
63	"	-COMe	PC	TS_COMe_B3LYP-D3BJ-6311++Gdp_forward_trial2.log
64	"	-CO ₂ Me	SC	TS_CO2Me_B3LYP-D3BJ-6311++Gdp_back_trial5.log
65	"	-CO ₂ Me	TS	TS_CO2Me_B3LYP-D3BJ-6311++Gdp.log
66	"	-CO ₂ Me	PC	TS_CO2Me_B3LYP-D3BJ-6311++Gdp_forward_trial2_freq.log
67	CAM-B3LYP	-COCF ₃	SC	TS_COCF3_CAM-B3LYP-6311++Gdp_back_trial2.log
68	"	-COCF ₃	TS1	TS_COCF3_CAM-B3LYP-6311++Gdp
69	"	-COCF ₃	MI	TS_COCF3_CAM-B3LYP-6311++Gdp_forward.log
70	"	-CN	SC	TS_CN_CAM-B3LYP-6311++Gdp_back_trial4.log
71	"	-CN	TS	TS_CN_CAM-B3LYP-6311++Gdp.log
72	"	-CN	PC	TS_CN_CAM-B3LYP-6311++Gdp_forward_trial2.log
73	"	-COMe	SC	TS_COMe_CAM-B3LYP-6311++Gdp_back_trial4.log
74	"	-COMe	TS	TS_COMe_CAM-B3LYP-6311++Gdp_trial2.log
75	"	-COMe	PC	TS_COMe_CAM-B3LYP-6311++Gdp_forward_trial2.log
76	"	-CO ₂ Me	SC	TS_CO2Me_CAM-B3LYP_6-311++Gdp_back.log
77	"	-CO ₂ Me	TS	TS_CO2Me_CAM-B3LYP_6-311++Gdp.log
78	"	-CO ₂ Me	PC	TS_CO2Me_CAM-B3LYP_6-311++Gdp_forward_trial2.log
79	BHandHLYP	-COCF ₃	SC	TS_COCF3_BHandHLYP_6-311++Gdp_back_trial2_freq.log
80	"	-COCF ₃	TS1	TS_COCF3_BHandHLYP-6-311++Gdp.log
81	"	-COCF ₃	MI	TS_COCF3_BHandHLYP-6-311++Gdp_forward.log
82	"	-CN	SC	TS_CN_BHandHLYP_6-311++Gdp_back_trial3_freq.log
83	"	-CN	TS	TS_CN_BHandHLYP-6-311++Gdp.log
84	"	-CN	PC	TS_CN_BHandHLYP-6-311++Gdp_forward_trial3.log
85	"	-COMe	SC	TS_COMe_BHandHLYP_6-311++Gdp_back_trial2_freq.log
86	"	-COMe	TS	TS_COMe_BHandHLYP_6-311++Gdp_trial2_freq.log
87	"	-COMe	MI	TS_COMe_BHandHLYP_6-311++Gdp_forward.log
88	"	-CO ₂ Me	SC	TS_CO2Me_BHandHLYP_6-311++Gdp_back_trial3_freq.log
89	"	-CO ₂ Me	TS	TS_CO2Me_BHandHLYP_6-311++Gdp.log

Entry	Method ^[a] (folder name)	-R (sub folder name)	Reaction Coordinate ^[b]	File name
90	"	-CO ₂ Me	PC	TS_CO2Me_BHandHLYP_6-311++Gdp_forward_trial2.log
91	M06L	-COCF ₃	SC	TS_COCF3_M06L-6311++Gdp_back_trial2.log
92	"	-COCF ₃	TS1	TS_COCF3_M06L-6311++Gdp.log
93	"	-COCF ₃	MI	TS_COCF3_M06L-6311++Gdp_forward.log
94	"	-CN	SC	TS_CN_M06L-6311++Gdp_back_trial2.log
95	"	-CN	TS	TS_CN_M06L-6311++Gdp.log
96	"	-CN	PC	TS_CN_M06L-6311++Gdp_forward_trial2.log
97	"	-COMe	SC	TS_COMe_M06L-6311++Gdp_back_trial4.log
98	"	-COMe	TS	TS_COMe_M06L-6311++Gdp.log
99	"	-COMe	PC	TS_COMe_M06L-6311++Gdp_forward.log
100	"	-CO ₂ Me	SC	TS_CO2Me_M06L_6-311++Gdp_back_trial3.log
101	"	-CO ₂ Me	TS	TS_CO2Me_M06L_6-311++Gdp.log
102	"	-CO ₂ Me	PC	TS_CO2Me_M06L_6-311++Gdp_forward.log
103	M06	-COCF ₃	SC	TS_COCF3_M06-6311++Gdp_back.log
104	"	-COCF ₃	TS1	TS_COCF3_M06-6311++Gdp_trial2.log
105	"	-COCF ₃	MI	TS_COCF3_M06-6311++Gdp_forward.log
106	"	-CN	SC	TS_CN_M06-6311++Gdp_back_trial2.log
107	"	-CN	TS	TS_CN_M06-6311++Gdp.log
108	"	-CN	PC	TS_CN_M06-6311++Gdp_forward_trial2.log
109	"	-COMe	SC	TS_COMe_M06-6311++Gdp_back_trial4.log
110	"	-COMe	TS	TS_COMe_M06-6311++Gdp_trial2_freq.log
111	"	-COMe	MI	TS_COMe_M06-6311++Gdp_forward.log
112	"	-CO ₂ Me	SC	TS_CO2Me_M06_6-311++Gdp_back_trial3.log
113	"	-CO ₂ Me	TS	TS_CO2Me_M06_6-311++Gdp.log
114	"	-CO ₂ Me	PC	TS_CO2Me_M06_6-311++Gdp_forward_trial3.log
115	M06	-COCF ₃	SC	TS_COCF3_M062X-6311++Gdp_back_trial5.log
116	"	-COCF ₃	TS1	TS_COCF3_M062X-6311++Gdp.log
117	"	-COCF ₃	MI	TS_COCF3_M062X-6311++Gdp_forward.log
118	"	-CN	SC	TS_CN_M062X-6311++Gdp_back.log
119	"	-CN	TS	TS_CN_M062X-6311++Gdp_trial3.log
120	"	-CN	MI	TS_CN_M062X-6311++Gdp_forward_trial2.log
121	"	-COMe	SC	TS_COMe_M062X-6311++Gdp_back_trial3.log
122	"	-COMe	TS	TS_COMe_M062X-6311++Gdp_trial2.log
123	"	-COMe	MI	TS_COMe_M062X-6311++Gdp_forward.log
124	"	-CO ₂ Me	SC	TS_CO2Me_M062X-6311++Gdp_back.log
125	"	-CO ₂ Me	TS	TS_CO2Me_M062X-6311++Gdp.log
126	"	-CO ₂ Me	MI	TS_CO2Me_M062X-6311++Gdp_forward.log
127	"	-CF ₃	SC	TS_CF3_M062X-6311++Gdp_back_trial14.log
128	"	-CF ₃	TS	TS_CF3_M062X-6311++Gdp_trial2.log
129	"	-CF ₃	PC	TS_CF3_M062X-6311++Gdp_forward_trial3.log
130	"	-CCH	SC	TS_CCH_F_MeO_M062X-6311++Gdp_back.log
131	"	-CCH	TS	TS_CCH_F_MeO_M062X-6311++Gdp.log
132	"	-CCH	PC	TS_CCH_F_MeO_M062X-6311++Gdp_forward.log
133	M11	-NO ₂	SC	TS_KOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
134	"	-NO ₂	TS1	TS_KOMe_NO2_F_M11_6-311++Gdp.log
135	"	-NO ₂	MI	TS_KOMe_NO2_F_M11_6-311++Gdp_forward_trial2.log
136	"	-NO ₂	TS2	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial8.log
137	"	-NO ₂	PC	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial2.log
138	"	-CHC(CN) ₂	SC	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_back_trial4.log
139	"	-CHC(CN) ₂	TS1	TS_KOMe_CHCCN2_F_M11_6-311++Gdp.log

Entry	Method ^[a] (folder name)	-R (sub folder name)	Reaction Coordinate ^[b]	File name
140	"	-CHC(CN) ₂	MI	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
141	"	-CHC(CN) ₂	TS2	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp.log
142	"	-CHC(CN) ₂	PC	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
143	"	-COCF ₃	SC	TS_COCF3_M11_6-311++Gdp_back_trial2_freq.log
144	"	-COCF ₃	TS1	TS_COCF3_M11_6-311++Gdp.log
145	"	-COCF ₃	MI	TS_COCF3_M11_6-311++Gdp_forward.log
146	"	-COCF ₃	TS2	TS2_COCF3_M11_6-311++Gdp.log
147	"	-COCF ₃	PC	TS2_COCF3_M11_6-311++Gdp_forward_trial3.log
148	"	-COCF ₃	IRC+	IRC_TS1_reverse_COCF3_M11_6-311++Gdp.log IRC_TS1_reverse_COCF3_M11_6-311++Gdp_trial2.log IRC_TS1_reverse_COCF3_M11_6-311++Gdp_trial3.log IRC_TS1_reverse_COCF3_M11_6-311++Gdp_trial4.log IRC_TS1_reverse_COCF3_M11_6-311++Gdp_trial5.log IRC_TS1_reverse_COCF3_M11_6-311++Gdp_trial6.log
149	"	-COCF ₃	IRC-	IRC_TS1_forward_COCF3_M11_6-311++Gdp.log IRC_TS1_forward_COCF3_M11_6-311++Gdp_trial2.log IRC_TS1_forward_COCF3_M11_6-311++Gdp_trial3.log
150	"	-CN	SC	TS_CN_M11_6-311++Gdp_back_trial2.log
151	"	-CN	TS	TS_CN_M11_6-311++Gdp.log
152	"	-CN	PC	TS_CN_M11_6-311++Gdp_forward.log
153	"	-CN	IRC+	IRC_CN_M11_6-311++Gdp_reverse.log IRC_CN_M11_6-311++Gdp_reverse_trial2.log IRC_CN_M11_6-311++Gdp_reverse_trial3.log IRC_CN_M11_6-311++Gdp_reverse_trial4.log
154	"	-CN	IRC-	IRC_CN_M11_6-311++Gdp_forward.log
155	"	-CN	Freq	Intermediate_by_IRC_reverse_CN_M11_6-311++Gdp.log
156	"	-CN	BS	BS2_CN_M11_6-311++Gdp.log BS2_CN_M11_6-311++Gdp_high_res.log
157	"	-COMe	SC	TS_COMe_M11_6-311++Gdp_back_trial2_freq.log
158	"	-COMe	TS	TS_COMe_M11_6-311++Gdp_trial3.log
159	"	-COMe	PC	TS_COMe_M11_6-311++Gdp_forward_trial2.log
160	"	-COMe	IRC+	IRC_COMe_M11_6-311++Gdp_reverse.log IRC_COMe_M11_6-311++Gdp_reverse_trial2.log
161	"	-COMe	IRC-	IRC_COMe_M11_6-311++Gdp_forward.log IRC_COMe_M11_6-311++Gdp_forward_trial2.log
162	"	-COMe	Freq	Intermediate_by_IRC_reverse_COMe_M11_6-311++Gdp.log
163	"	-COMe	BS	BS2_COMe_M11_6-311++Gdp.log BS2_COMe_M11_6-311++Gdp_high_res.log
164	"	-CO ₂ Me	SC	TS_CO2Me_M11_6-311++Gdp_back_trial2.log
165	"	-CO ₂ Me	TS	TS_CO2Me_M11_6-311++Gdp.log
166	"	-CO ₂ Me	PC	TS_CO2Me_M11_6-311++Gdp_forward_trial2.log
167	"	-CO ₂ Me	IRC+	IRC_CO2Me_M11_6-311++Gdp_reverse.log IRC_CO2Me_M11_6-311++Gdp_reverse_trial2.log
168	"	-CO ₂ Me	IRC-	IRC_CO2Me_M11_6-311++Gdp_forward.log
169	PBE0	-COCF ₃	SC	TS_COCF3_PBE0-6311++Gdp_back_trial4.log
170	"	-COCF ₃	TS1	TS_COCF3_PBE0-6311++Gdp.log
171	"	-COCF ₃	MI	TS_COCF3_PBE0-6311++Gdp_forward.log
172	"	-CN	SC	TS_CN_PBE0-6311++Gdp_back_trial3.log
173	"	-CN	TS	TS_CN_PBE0-6311++Gdp_trial2.log
174	"	-CN	PC	TS_CN_PBE0-6311++Gdp_forward_trial3.log
175	"	-COMe	SC	TS_COMe_PBE0-6311++Gdp_back_trial4.log
176	"	-COMe	TS	TS_COMe_PBE0-6311++Gdp_trial2_freq.log
177	"	-COMe	PC	TS_COMe_PBE0-6311++Gdp_forward_trial2.log
178	"	-CO ₂ Me	SC	TS_CO2Me_PBE0_6-311++Gdp_back_trial2.log
179	"	-CO ₂ Me	TS	TS_CO2Me_PBE0_6-311++Gdp_trial4.log
180	"	-CO ₂ Me	PC	TS_CO2Me_PBE0_6-311++Gdp_forward_trial3.log

Entry	Method ^[a] (folder name)	-R (sub folder name)	Reaction Coordinate ^[b]	File name
181	PBE0_D3-BJ	-COCF ₃	SC	TS_COCF3_PBE0-D3BJ_6311++Gdp_back_trial3.log
182	"	-COCF ₃	TS1	TS_COCF3_PBE0-D3BJ_6311++Gdp.log
183	"	-COCF ₃	MI	TS_COCF3_PBE0-D3BJ_6311++Gdp_forward.log
184	"	-CN	SC	TS_CN_PBE0-D3BJ_6311++Gdp_back_trial2.log
185	"	-CN	TS	TS_CN_PBE0-D3BJ_6311++Gdp.log
186	"	-CN	PC	TS_CN_PBE0-D3BJ_6311++Gdp_forward_trial2.log
187	"	-COMe	SC	TS_COMe_PBE0-D3BJ_6311++Gdp_back_trial4.log
188	"	-COMe	TS	TS_COMe_PBE0-D3BJ_6311++Gdp_trial2.log
189	"	-COMe	PC	TS_COMe_PBE0-D3BJ_6311++Gdp_back_trial4.log
190	"	-CO ₂ Me	SC	TS_CO2Me_PBE0-D3BJ_6-311++Gdp_back_trial4.log
191	"	-CO ₂ Me	TS	TS_CO2Me_PBE0-D3BJ_6-311++Gdp.log
192	"	-CO ₂ Me	PC	TS_CO2Me_PBE0-D3BJ_6-311++Gdp_forward_trial3.log
193	HSE1PBE	-COCF ₃	SC	TS_COCF3_HSEH1PBE_6-311++Gdp_back_trial4.log
194	"	-COCF ₃	TS1	TS_COCF3_HSEH1PBE_6-311++Gdp.log
195	"	-COCF ₃	MI	TS_COCF3_HSEH1PBE_6-311++Gdp_forward.log
196	"	-CN	SC	TS_HSEH1PBE_6-311++Gdp_back_trial2.log
197	"	-CN	TS	TS_HSEH1PBE_6-311++Gdp.log
198	"	-CN	PC	TS_HSEH1PBE_6-311++Gdp_forward_trial3.log
199	"	-COMe	SC	TS_COMe_HSEH1PBE_6-311++Gdp_back_trial2.log
200	"	-COMe	TS	TS_COMe_HSEH1PBE_6-311++Gdp.log
201	"	-COMe	PC	TS_COMe_HSEH1PBE_6-311++Gdp_forward_trial2.log
202	"	-CO ₂ Me	SC	TS_CO2Me_HSEH1PBE_6-311++Gdp_back_trial2.log
203	"	-CO ₂ Me	TS	TS_CO2Me_HSEH1PBE_6-311++Gdp.log
204	"	-CO ₂ Me	PC	TS_CO2Me_HSEH1PBE_6-311++Gdp_forward_trial2.log
205	B97D	-COCF ₃	SC	TS_COCF3_B97D_6-311++Gdp_back_trial5.log
206	"	-COCF ₃	TS1	TS_COCF3_B97D_6-311++Gdp_trial2_freq.log
207	"	-COCF ₃	PC	TS_COCF3_B97D-6-311++Gdp_forward_trial2.log
208	"	-CN	SC	TS_CN_B97D_6-311++Gdp_back_trial2.log
209	"	-CN	TS	TS_CN_B97D_6-311++Gdp.log
210	"	-CN	PC	TS_CN_B97D_6-311++Gdp_forward_trial2.log
211	"	-COMe	SC	TS_COMe_B97D_6-311++Gdp_back_trial2.log
212	"	-COMe	TS	TS_COMe_B97D_6-311++Gdp.log
213	"	-COMe	PC	TS_COMe_B97D_6-311++Gdp_forward_trial2.log
214	"	-CO ₂ Me	SC	TS_CO2Me_B97D_6-311++Gdp_back_trial2.log
215	"	-CO ₂ Me	TS	TS_CO2Me_B97D_6-311++Gdp.log
216	"	-CO ₂ Me	PC	TS_CO2Me_B97D_6-311++Gdp_forward_trial2.log
217	wB97	-COCF ₃	SC	TS_COCF3_wB97-6-311++Gdp_back.log
218	"	-COCF ₃	TS1	TS_COCF3_wB97-6-311++Gdp.log
219	"	-COCF ₃	MI	TS_COCF3_wB97-6-311++Gdp_forward.log
220	"	-CN	SC	TS_CN_wB97_6-311++Gdp_back_trial2_freq.log
221	"	-CN	TS	TS_CN_wB97_6-311++Gdp.log
222	"	-CN	PC	TS_CN_wB97_6-311++Gdp_forward_trial2.log
223	"	-COMe	SC	TS_COMe_wB97_6-311++Gdp_back_trial7.log
224	"	-COMe	TS	TS_COMe_wB97_6-311++Gdp.log
225	"	-COMe	MI	TS_COMe_wB97_6-311++Gdp_forward.log
226	"	-CO ₂ Me	SC	TS_CO2Me_wB97_6-311++Gdp_back_trial4.log
227	"	-CO ₂ Me	TS	TS_CO2Me_wB97_6-311++Gdp.log
228	"	-CO ₂ Me	PC	TS_CO2Me_wB97_6-311++Gdp_forward_trial2.log
229	wB97X	-COCF ₃	SC	TS_COCF3_wB97X-6-311++Gdp_back_trial4.log
230	"	-COCF ₃	TS1	TS_COCF3_wB97X-6-311++Gdp.log

Entry	Method ^[a] (folder name)	-R (sub folder name)	Reaction Coordinate ^[b]	File name
231	"	-COCF ₃	MI	TS_COCF3_wB97X-6-311++Gdp_forward.log
232	"	-CN	SC	TS_CN_wB97X_6-311++Gdp_back_trial2.log
233	"	-CN	TS	TS_CN_wB97X_6-311++Gdp.log
234	"	-CN	PC	TS_CN_wB97X_6-311++Gdp_forward_trial2.log
235	"	-COMe	SC	TS_COMe_wB97X_6-311++Gdp_back_trial2.log
236	"	-COMe	TS	TS_COMe_wB97X_6-311++Gdp.log
237	"	-COMe	PC	TS_COMe_wB97X_6-311++Gdp_forward_trial3.log
238	"	-CO ₂ Me	SC	TS_CO2Me_wB97X_6-311++Gdp_back_trial2.log
239	"	-CO ₂ Me	TS	TS_CO2Me_wB97X_6-311++Gdp.log
240	"	-CO ₂ Me	PC	TS_CO2Me_wB97X_6-311++Gdp_forward.log
241	wB97XD	-COCF ₃	SC	TS_COCF3_wB97XD-6-311++Gdp_back_trial4.log
242	"	-COCF ₃	TS1	TS_COCF3_wB97XD-6-311++Gdp.log
243	"	-COCF ₃	MI	TS_COCF3_wB97XD-6-311++Gdp_forward.log
244	"	-CN	SC	TS_CN_wB97XD-6-311++Gdp_back_trial2.log
245	"	-CN	TS	TS_CN_wB97XD-6-311++Gdp.log
246	"	-CN	PC	TS_CN_wB97XD-6-311++Gdp_forward.log
247	"	-COMe	SC	TS_COMe_wB97XD_6-311++Gdp_back_trial4.log
248	"	-COMe	TS	TS_COMe_wB97XD_6-311++Gdp.log
249	"	-COMe	PC	TS_COMe_wB97XD_6-311++Gdp_forward_trial2.log
250	"	-CO ₂ Me	SC	TS_CO2Me_wB97XD_6-311++Gdp_back_trial3_freq.log
251	"	-CO ₂ Me	TS	TS_CO2Me_wB97XD_6-311++Gdp.log
252	"	-CO ₂ Me	PC	TS_CO2Me_wB97XD_6-311++Gdp_forward_trial2.log

[a] The 6-311++G(d,p) basis set was used unless mentioned otherwise. [b] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex. Alternatively the type of calculation is stated using the following abbreviation. IRC+: internal reaction coordinate scan towards the products; IRC-: internal reaction coordinate scan towards the substrates; BS: bond scan; Freq: single point frequency calculation.

Validating the Procedure

The log files for the IRC scans shown in Table SI-2-2 are included in Table SI-3-1 under the method 'M11' and marked as 'IRC' in the 'Reaction Coordinate' column.

Comparison to Experiments

All files for the calculation shown in Scheme SI-1 and Scheme SI-2 are listed in Table SI-3-2 below. The activation energy of the S_NAr reaction shown in Scheme SI-1 was calculated with respect to the separated substrates. The counter cation was not included in the computational model. A minor conformational change of the Meisenheimer intermediate was detected along the S_NAr reaction coordinated. The structure 'TS2' in table Table SI-3-2 corresponds to the transition state associated with this conformational change.

All files for the calculation shown in Table SI-2-3 are listed in Table SI-3-3 below. If two files are given for the Meisenheimer intermediate (MI) it means that once the MI has been optimised starting from the first transition state (TS1) and once starting from the second transition state (TS2).

Table SI-3-2

Entry	Structure and Comment	Reaction Coordinate ^[a]	File name
1	Azide anion	-	azide.log
2	7	-	Substrate.log
3	Azide anion and 7	SC	TS_NO2_Azide_back.log
4	Addition of azide on 7	TS1	TS_NO2_Azide.log

Entry	Structure and Comment	Reaction Coordinate ^[a]	File name
5	-	MI1	TS_NO2_Azide_forward.log
6	Conformational change of MI	TS2	TS2_NO2_Azide_conformation.log
7	-	MI2	TS3_NO2_Azide_back.log
8	Expulsion of fluoride leaving group.	TS3	TS3_NO2_Azide.log
9	Fluoride anion and 8	PC	TS3_NO2_Azide_forward.log
10	8	-	Product.log
11	Fluoride anion	-	fluoride.log
12	1a-OMe-F	-	Substrate_2la_M11_6-311++Gdp.log
13	KOMe	-	KOMe.log
14	Substrate complex	SC	Substrate_complex_2la_M11_6-311++Gdp.log
15	TS	TS1	TS_2la_M11_6-311++Gdp.log
16	Product complex	PC	Product_complex_2la_M11_6-311++Gdp.log
17	1,4-Dimethoxybenzene	-	Product_2la_M11_6-311++Gdp_trial2.log
18	KF	-	KF.log

[b] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TSx: xth transition state; Mly: Meisenheimer intermediate in conformation y; PC: product complex.

Table SI-3-3

Entry	Entry in Table SI-2-3 (Sub Folder)	Reaction Coordinate ^[a]	File name
1	1 (DMAP-a)	PC	TS_DMAP_4-NO2-PhO_back_trial3.log
2	"	TS1	TS_DMAP_4-NO2-PhO_trial2.log
3	"	MI	TS_DMAP_4-NO2-PhO_forward.log TS2_DMAP_4-NO2-PhO_back.log
4	"	TS2	TS2_DMAP_4-NO2-PhO_forward.log
5	"	SC	TS2_DMAP_4-NO2-PhO_forward_trial2.log
6	2 (DMAP-a_water)	PC	TS_DMAP_4-NO2-PhO_4_water_back_trial2.log
7	"	TS1	TS_DMAP_4-NO2-PhO_4_water_trial4.log
8	"	MI	TS_DMAP_4-NO2-PhO_4_water_forward_trial2.log TS2_DMAP_4-NO2-PhO_4_water_back.log
9	"	TS2	TS2_DMAP_4-NO2-PhO_4_water_trial2.log
10	"	SC	TS2_DMAP_4-NO2-PhO_4_water_forward.log
11	3 (DMAP-b)	PC	TS_DMAP_4-COH-PhO_back.log
11	"	TS1	TS_DMAP_4-COH-PhO.log
12	"	MI	TS_DMAP_4-COH-PhO_forward.log TS2_DMAP_4-COH-PhO_back.log
13	"	TS2	TS2_DMAP_4-COH-PhO.log
14	"	SC	TS2_DMAP_4-COH-PhO_forward_trial2.log
15	4 (DMAP-c)	PC	TS_DMAP_3-5-di-NO2-PhO_back.log
16	"	TS1	TS_DMAP_3-5-di-NO2-PhO_trial2.log
17	"	MI	TS_DMAP_3-5-di-NO2-PhO_forward.log TS2_DMAP_3-5-di-NO2-PhO_back.log
18	"	TS2	TS2_DMAP_3-5-di-NO2-PhO.log
19	"	SC	TS2_DMAP_3-5-di-NO2-PhO_forward.log
20	5 (Morpholien-a_1)	PC	TS_Morpholine_4-NO2-PhO_back.log
21	"	TS1	TS_Morpholine_4-NO2-PhO.log
22	"	MI	TS_Morpholine_4-NO2-PhO_forward.log TS2_Morpholine_4-NO2-PhO_back.log
23	"	TS2	TS2_Morpholine_4-NO2-PhO.log
24	"	SC	TS2_Morpholine_4-NO2-PhO_forward.log
25	5 (Morpholien-a_1)	PC	TS_Morpholine_4-NO2-PhO_var2_back_trial3.log

Entry	Entry in Table SI-2-3 (Sub Folder)	Reaction Coordinate ^[a]	File name
26	“	TS1	TS_Morpholine_4-NO2-PhO_var2.log
27	“	MI	TS_Morpholine_4-NO2-PhO_var2_forward.log TS2_Morpholine_4-NO2-PhO_var2_back.log
28	“	TS2	TS2_Morpholine_4-NO2-PhO_var2.log
29	“	SC	TS2_Morpholine_4-NO2-PhO_var2_forward_trial2.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

3.2. Initial Studies

The calculations of this section were calculated on M11/6-311++G(d,p)/cpcm(DMF) level of theory. For each example the substrate complex ('SC'), rate limiting transition state ('TS1'), and product complex ('PC') or Meisenheimer intermediate ('MI') as appropriate, was calculated. For selected examples also the second transition ('TS2') state was calculated.

The log files for the calculations shown in Figure 1 in the main text for the displacement of the halides fluoride, chloride, bromide and iodide by potassium methoxide are listed in below in Table SI-3-4.

Table SI-3-4

Entry	X	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	F	-NO	SC	TS_KOMe_NO_F_M11_6-311++Gdp_back_trial2.log
2	“	“	TS1	TS_KOMe_NO_F_M11_6-311++Gdp.log
3	“	“	MI	TS_KOMe_NO_F_M11_6-311++Gdp_forward.log
4	“	“	TS2	TS2_KOMe_NO_F_M11_6-311++Gdp.log
5	“	“	PC	TS2_KOMe_NO_F_M11_6-311++Gdp_forward.log
6	“	-NO2	SC	TS_KOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
7	“	“	TS1	TS_KOMe_NO2_F_M11_6-311++Gdp.log
8	“	“	MI	TS_KOMe_NO2_F_M11_6-311++Gdp_forward_trial2.log
9	“	“	TS2	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial8.log
10	“	“	PC	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial2.log
11	“	-CHCCN2	SC	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_back_trial4.log
11	“	“	TS1	TS_KOMe_CHCCN2_F_M11_6-311++Gdp.log
12	“	“	MI	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
13	“	“	TS2	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp.log
14	“	“	PC	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
15	“	-COCF3	SC	TS_COCF3_M11_6-311++Gdp_back_trial2_freq.log
16	“	“	TS1	TS_COCF3_M11_6-311++Gdp.log
17	“	“	MI	TS_COCF3_M11_6-311++Gdp_forward.log
18	“	“	TS2	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial8.log
19	“	“	PC	TS2_COCF3_M11_6-311++Gdp_forward_trial3.log
20	“	-CN	SC	TS_CN_M11_6-311++Gdp_back_trial2.log
21	“	“	TS1	TS_CN_M11_6-311++Gdp.log
22	“	“	PC	TS_CN_M11_6-311++Gdp_forward.log
23	“	-COMe	SC	TS_COMe_M11_6-311++Gdp_back_trial2_freq.log
24	“	“	TS1	TS_COMe_M11_6-311++Gdp_trial3.log
25	“	“	PC	TS_COMe_M11_6-311++Gdp_forward_trial2.log
26	“	-CO2Me	SC	TS_CO2Me_M11_6-311++Gdp_back_trial2.log
27	“	“	TS1	TS_CO2Me_M11_6-311++Gdp.log
28	“	“	PC	TS_CO2Me_M11_6-311++Gdp_forward_trial2.log
29	“	-CF3	SC	TS_KOMe_CF3_F_M11_6-311++Gdp_back_trial2.log
30	“	“	TS1	TS_KOMe_CF3_F_M11_6-311++Gdp.log

Entry	X	-R (sub folder)	Reaction Coordinate ^[a]	File name
31	"	"	PC	TS_KOMe_CF3_F_M11_6-311++Gdp_forward_trial2.log
32	"	-CCH	SC	TS_KOMe_CCH_F_M11_6-311++Gdp_back_trial2.log
33	"	"	TS1	TS_KOMe_CCH_F_M11_6-311++Gdp.log
34	"	"	PC	TS_KOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log
35	"	-H	SC	TS_KOMe_H_F_M11_6-311++Gdp_back_trial2.log
36	"	"	TS1	TS_KOMe_H_F_M11_6-311++Gdp.log
37	"	"	PC	TS_KOMe_H_F_M11_6-311++Gdp_forward_trial2.log
38	Cl	-NO	SC	TS_KOMe-Cl_NO_M11_6-311++Gdp_back_trial3.log
39	"	"	TS1	TS_KOMe-Cl_NO_M11_6-311++Gdp.log
40	"	"	PC	TS_KOMe-Cl_NO_M11_6-311++Gdp_forward_trial2.log
41	"	-NO2	SC	TS_KOMe-Cl_NO2_M11_6-311++Gdp_back_trial2.log
42	"	"	TS1	TS_KOMe-Cl_NO2_M11_6-311++Gdp.log
43	"	"	PC	TS_KOMe-Cl_NO2_M11_6-311++Gdp_forward_trial2.log
44	"	-CHCCN2	SC	TS_KOMe-Cl_CHCCN2_M11_6-311++Gdp_back_trial3.log
45	"	"	TS1	TS_KOMe-Cl_CHCCN2_M11_6-311++Gdp.log
46	"	"	PC	TS_KOMe-Cl_CHCCN2_M11_6-311++Gdp_forward_trial2.log
47	"	-COCF3	SC	TS_KOMe-Cl_COCF3_M11_6-311++Gdp_back_trial4_freq.log
48	"	"	TS1	TS_KOMe-Cl_COCF3_M11_6-311++Gdp_trial4.log
49	"	"	PC	TS_KOMe-Cl_COCF3_M11_6-311++Gdp_forward_trial2.log
50	"	-CN	SC	TS_KOMe-Cl_CN_M11_6-311++Gdp_back_trial2_freq.log
51	"	"	TS1	TS_KOMe-Cl_CN_M11_6-311++Gdp.log
52	"	"	PC	TS_KOMe-Cl_CN_M11_6-311++Gdp_forward_trial3.log
53	"	-COMe	SC	TS_KOMe-Cl_COMe_M11_6-311++Gdp_back_trial2.log
54	"	"	TS1	TS_KOMe-Cl_COMe_M11_6-311++Gdp_trial2.log
55	"	"	PC	TS_KOMe-Cl_COMe_M11_6-311++Gdp_forward_trial4.log
56	"	-CO2Me	SC	TS_KOMe-Cl_CO2Me_M11_6-311++Gdp_back_trial2_freq.log
57	"	"	TS1	TS_KOMe-Cl_CO2Me_M11_6-311++Gdp.log
58	"	"	PC	TS_KOMe-Cl_CO2Me_M11_6-311++Gdp_forward_trial2.log
59	"	-CF3	SC	TS_KOMe-Cl_CF3_M11_6-311++Gdp_back_trial2.log
60	"	"	TS1	TS_KOMe-Cl_CF3_M11_6-311++Gdp.log
61	"	"	PC	TS_KOMe-Cl_CF3_M11_6-311++Gdp_forward_trial2.log
62	"	-CCH	SC	TS_KOMe-Cl_CCH_M11_6-311++Gdp_back_trial2.log
63	"	"	TS1	TS_KOMe-Cl_CCH_M11_6-311++Gdp.log
64	"	"	PC	TS_KOMe-Cl_CCH_M11_6-311++Gdp_forward_trial3.log
65	"	-H	SC	TS_KOMe-Cl_H_M11_6-311++Gdp_back_trial2.log
66	"	"	TS1	TS_KOMe-Cl_H_M11_6-311++Gdp.log
67	"	"	PC	TS_KOMe-Cl_H_M11_6-311++Gdp_forward_trial2.log
68	Br	-NO	SC	TS_KOMe-Br_NO_M11_6-311++Gdp_back.log
69	"	"	TS1	TS_KOMe-Br_NO_M11_6-311++Gdp.log
70	"	"	PC	TS_KOMe-Br_NO_M11_6-311++Gdp_forward.log
71	"	-NO2	SC	TS_KOMe-Br_NO2_M11_6-311++Gdp_back.log
72	"	"	TS1	TS_KOMe-Br_NO2_M11_6-311++Gdp.log
73	"	"	PC	TS_KOMe-Br_NO2_M11_6-311++Gdp_forward.log
74	I	-NO	SC	TS_KOMe-I_NO_M11_6-311++Gdp_back.log
75	"	"	TS1	TS_KOMe-I_NO_M11_6-311++Gdp_trial2.log
76	"	"	PC	TS_KOMe-I_NO_M11_6-311++Gdp_forward.log
77	"	-NO2	SC	TS_KOMe-I_NO2_M11_6-311++Gdp_back.log
78	"	"	TS1	TS_KOMe-I_NO2_M11_6-311++Gdp_trial2.log
79	"	"	PC	TS_KOMe-I_NO2_M11_6-311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations shown in Table SI-2-4 for the halide exchange reactions are listed in below in Table SI-3-5.

Table SI-3-5

Entry	KY-X	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	KF-F	-CO2Me	SC	TS_KF-F_CO2Me_M11_6-311++Gdp_back_trial2.log
2	"	"	TS1	TS_KF-F_CO2Me_M11_6-311++Gdp.log
3	"	"	MI	TS_KF-F_CO2Me_M11_6-311++Gdp_forward.log
4	"	-CF3	SC	TS_KF-F_CF3_M11_6-311++Gdp_back_trial2.log
5	"	"	TS1	TS_KF-F_CF3_M11_6-311++Gdp.log
6	"	"	MI	TS_KF-F_CF3_M11_6-311++Gdp_forward.log
7	"	-CCH	SC	TS_KF-F_CCH_M11_6-311++Gdp_back.log
8	"	"	TS1	TS_KF-F_CCH_M11_6-311++Gdp.log
9	"	"	PC	TS_KF-F_CCH_M11_6-311++Gdp_forward_trial2.log
10	"	-NCS	SC	TS_KF-F_NCS_M11_6-311++Gdp_back.log
11	"	"	TS1	TS_KF-F_NCS_M11_6-311++Gdp.log
11	"	"	PC	TS_KF-F_NCS_M11_6-311++Gdp_forward_trial2.log
12	KF-Cl	-NO	SC	TS_KF-Cl_NO_M11_6-311++Gdp_back.log
13	"	"	TS1	TS_KF-Cl_NO_M11_6-311++Gdp.log
14	"	"	PC	TS_KF-Cl_NO_M11_6-311++Gdp_forward.log
15	"	-NO2	SC	TS_KF-Cl_NO2_M11_6-311++Gdp_back.log
16	"	"	TS1	TS_KF-Cl_NO2_M11_6-311++Gdp.log
17	"	"	PC	TS_KF-Cl_NO2_M11_6-311++Gdp_forward.log
18	KF-Br	-NO	SC	TS_KF-Br_NO_M11_6-311++Gdp_back_trial2.log
19	"	"	TS1	TS_KF-Br_NO_M11_6-311++Gdp.log
20	"	"	PC	TS_KF-Br_NO_M11_6-311++Gdp_forward_trial2.log
21	"	-NO2	SC	TS_KF-Br_NO2_M11_6-311++Gdp_back_trial2.log
22	"	"	TS1	TS_KF-Br_NO2_M11_6-311++Gdp.log
23	"	"	PC	TS_KF-Br_NO2_M11_6-311++Gdp_forward.log
24	KF-I	-NO	SC	TS_KF-I_NO_M11_6-311++Gdp_back_trial2.log
25	"	"	TS1	TS_KF-I_NO_M11_6-311++Gdp.log
26	"	"	PC	TS_KF-I_NO_M11_6-311++Gdp_forward.log
27	"	-NO2	SC	TS_KF-I_NO2_M11_6-311++Gdp_back.log
28	"	"	TS1	TS_KF-I_NO2_M11_6-311++Gdp.log
29	"	"	PC	TS_KF-I_NO2_M11_6-311++Gdp_forward.log
30	KCl-Cl	-NO	SC	TS_KCl-Cl_NO_M11_6-311++Gdp_back.log
31	"	"	TS1	TS_KCl-Cl_NO_M11_6-311++Gdp.log
32	"	"	PC	TS_KCl-Cl_NO_M11_6-311++Gdp_forward_trial2.log
33	"	-NO2	SC	TS_KCl-Cl_NO2_M11_6-311++Gdp_back.log
34	"	"	TS1	TS_KCl-Cl_NO2_M11_6-311++Gdp.log
35	"	"	PC	TS_KCl-Cl_NO2_M11_6-311++Gdp_forward.log
36	KCl-Br	-NO	SC	TS_KCl-Br_NO_M11_6-311++Gdp_back.log
37	"	"	TS1	TS_KCl-Br_NO_M11_6-311++Gdp.log
38	"	"	PC	TS_KCl-Br_NO_M11_6-311++Gdp_forward.log
39	"	-NO2	SC	TS_KCl-Br_NO2_M11_6-311++Gdp_back.log
40	"	"	TS1	TS_KCl-Br_NO2_M11_6-311++Gdp.log
41	"	"	PC	TS_KCl-Br_NO2_M11_6-311++Gdp_forward_trial2.log
42	KCl-I	-NO	SC	TS_KCl-I_NO_M11_6-311++Gdp_back_trial2.log
43	"	"	TS1	TS_KCl-I_NO_M11_6-311++Gdp.log
44	"	"	PC	TS_KCl-I_NO_M11_6-311++Gdp_forward_trial2.log

Entry	KY-X	-R (sub folder)	Reaction Coordinate ^[a]	File name
45	"	-NO2	SC	TS_KCl-I_NO2_M11_6-311++Gdp_back.log
46	"	"	TS1	TS_KCl-I_NO2_M11_6-311++Gdp.log
47	"	"	PC	TS_KCl-I_NO2_M11_6-311++Gdp_forward_trial2.log
48	KBr-Br	-NO	SC	TS_KBr-Br_NO_M11_6-311++Gdp_back_trial3.log
49	"	"	TS1	TS_KBr-Br_NO_M11_6-311++Gdp.log
50	"	"	PC	TS_KBr-Br_NO_M11_6-311++Gdp_forward_trial2.log
51	"	-NO2	SC	TS_KBr-Br_NO2_M11_6-311++Gdp_back_trial3.log
52	"	"	TS1	TS_KBr-Br_NO2_M11_6-311++Gdp.log
53	"	"	PC	TS_KBr-Br_NO2_M11_6-311++Gdp_forward.log
54	KBr-I	-NO	SC	TS_KBr-I_NO_M11_6-311++Gdp_back_trial2.log
55	"	"	TS1	TS_KBr-I_NO_M11_6-311++Gdp.log
56	"	"	PC	TS_KBr-I_NO_M11_6-311++Gdp_forward.log
57	"	-NO2	SC	TS_KBr-I_NO2_M11_6-311++Gdp_back.log
58	"	"	TS1	TS_KBr-I_NO2_M11_6-311++Gdp.log
59	"	"	PC	TS_KBr-I_NO2_M11_6-311++Gdp_forward.log
60	KI-I	-NO	SC	TS_KI-I_NO2_M11_6-311++Gdp_back.log
61	"	"	TS1	TS_KI-I_NO2_M11_6-311++Gdp.log
62	"	"	PC	TS_KI-I_NO2_M11_6-311++Gdp_forward_trial2.log
63	"	-NO2	SC	TS_KI-I_NO2_M11_6-311++Gdp_back.log
64	"	"	TS1	TS_KI-I_NO2_M11_6-311++Gdp_forward.log
65	"	"	PC	TS_KI-I_NO2_M11_6-311++Gdp.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations shown in Table SI-2-5 for the chalcogen exchange reactions are listed in below in Table SI-3-6.

Table SI-3-6

Entry	KYMe-XMe	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	KOMe-OMe	-NHAc	SC	TS_KOMe-OMe_NHCOMe_M11_6-311++Gdp_back
2	"	"	TS1	TS_KOMe-OMe_NHCOMe_M11_6-311++Gdp.log
3	"	"	MI	TS_KOMe-OMe_NHCOMe_M11_6-311++Gdp_forward.log
4	"	-NPPh3	SC	TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_back_trial3.log
5	"	"	TS1	TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_trial2.log
6	"	"	MI	TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_forward.log
7	KOMe-SMe	-CCH	SC	TS_KOMe-SMe_CCH_M11_6-311++Gdp_back.log
8	"	"	TS1	TS_KOMe-SMe_CCH_M11_6-311++Gdp.log
9	"	"	MI	TS_KOMe-SMe_CCH_M11_6-311++Gdp_forward.log TS2_KOMe-SMe_CCH_M11_6-311++Gdp_back.log
10	"	"	TS2	TS2_KOMe-SMe_CCH_M11_6-311++Gdp.log
11	"	"	PC	TS2_KOMe-SMe_CCH_M11_6-311++Gdp_forward.log
11	"	-NCS	SC	TS_KOMe-SMe_NCS_M11_6-311++Gdp_back.log
12	"	"	TS1	TS_KOMe-SMe_NCS_M11_6-311++Gdp.log
13	"	"	MI	TS_KOMe-SMe_NCS_M11_6-311++Gdp_forward.log
14	"	-Cl	SC	TS_KOMe-SMe_Cl_M11_6-311++Gdp_back.log
15	"	"	TS1	TS_KOMe-SMe_Cl_M11_6-311++Gdp.log
16	"	"	PC	TS_KOMe-SMe_Cl_M11_6-311++Gdp_forward.log
17	"	-H	SC	TS_KOMe-SMe_H_M11_6-311++Gdp_back_trial2.log
18	"	"	TS1	TS_KOMe-SMe_H_M11_6-311++Gdp.log

Entry	KYMe-XMe	-R (sub folder)	Reaction Coordinate ^[a]	File name
19	"	"	PC	TS_KOMe-SMe_H_M11_6-311++Gdp_forward_trial3.log
20	KOMe-SeMe	-NO2	SC	TS_KOMe-SeMe_NO2_M11_6-311++Gdp_back.log
21	"	"	TS1	TS_KOMe-SeMe_NO2_M11_6-311++Gdp.log
22	"	"	MI	TS_KOMe-SeMe_NO2_M11_6-311++Gdp_forward.log
23	"	-CN	SC	TS_KOMe-SeMe_CN_M11_6-311++Gdp_back.log
24	"	"	TS1	TS_KOMe-SeMe_CN_M11_6-311++Gdp.log
25	"	"	MI	TS_KOMe-SeMe_CN_M11_6-311++Gdp_forward.log
26	"	-COMe	SC	TS_KOMe-SeMe_COMe_M11_6-311++Gdp_back.log
27	"	"	TS1	TS_KOMe-SeMe_COMe_M11_6-311++Gdp.log
28	"	"	MI	TS_KOMe-SeMe_COMe_M11_6-311++Gdp_forward.log
29	"	-CO2Me	SC	TS_KOMe-SeMe_CO2Me_M11_6-311++Gdp_back.log
30	"	"	TS1	TS_KOMe-SeMe_CO2Me_M11_6-311++Gdp_trial2.log
31	"	"	MI	TS_KOMe-SeMe_CO2Me_M11_6-311++Gdp_forward.log
32	"	-CCH	SC	TS_KOMe-SeMe_CCH_M11_6-311++Gdp_back_trial2.log
33	"	"	TS1	TS_KOMe-SeMe_CCH_M11_6-311++Gdp.log
34	"	"	PC	TS_KOMe-SeMe_CCH_M11_6-311++Gdp_forward_trial2.log
35	"	-Cl	SC	TS_KOMe-SeMe_Cl_M11_6-311++Gdp_back.log
36	"	"	TS1	TS_KOMe-SeMe_Cl_M11_6-311++Gdp.log
37	"	"	PC	TS_KOMe-SeMe_Cl_M11_6-311++Gdp_forward.log
38	KSMc-SMe	-C6F5	SC	TS_KSMc-SMe_C6F5_M11_6-311++Gdp_back.log
39	"	"	TS1	TS_KSMc-SMe_C6F5_M11_6-311++Gdp_trial2.log
40	"	"	MI	TS_KSMc-SMe_C6F5_M11_6-311++Gdp_forward.log
41	"	-NCS	SC	TS_KSMc-SMe_NCS_M11_6-311++Gdp_back.log
42	"	"	TS1	TS_KSMc-SMe_NCS_M11_6-311++Gdp.log
43	"	"	MI	TS_KSMc-SMe_NCS_M11_6-311++Gdp_forward.log
44	"	-I	SC	TS_KSMc-SMe_I_M11_6-311++Gdp_back.log
45	"	"	TS1	TS_KSMc-SMe_I_M11_6-311++Gdp.log
46	"	"	PC	TS_KSMc-SMe_I_M11_6-311++Gdp_forward.log
47	"	-Cl	SC	TS_KSMc-SMe_Cl_M11_6-311++Gdp_back.sh
48	"	"	TS1	TS_KSMc-SMe_Cl_M11_6-311++Gdp.log
49	"	"	PC	TS_KSMc-SMe_Cl_M11_6-311++Gdp_forward.log
50	KSMc-SeMe	-CHCCN2	SC	TS_KSMc-SeMe_CHCCN2_M11_6-311++Gdp_back.log
51	"	"	TS1	TS_KSMc-SeMe_CHCCN2_M11_6-311++Gdp.log
52	"	"	MI	TS_KSMc-SeMe_CHCCN2_M11_6-311++Gdp_forward.log
53	"	-COCF3	SC	TS_KSMc-SeMe_COCF3_M11_6-311++Gdp_back.log
54	"	"	TS1	TS_KSMc-SeMe_COCF3_M11_6-311++Gdp.log
55	"	"	MI	TS_KSMc-SeMe_COCF3_M11_6-311++Gdp_forward.log
56	"	-CN	SC	TS_KSMc-SeMe_CN_M11_6-311++Gdp_back.log
57	"	"	TS1	TS_KSMc-SeMe_CN_M11_6-311++Gdp_forward.log
58	"	"	PC	TS_KSMc-SeMe_CN_M11_6-311++Gdp_forward.log
59	"	-COMe	SC	TS_KSMc-SeMe_COMe_M11_6-311++Gdp_back_trial2.log
60	"	"	TS1	TS_KSMc-SeMe_COMe_M11_6-311++Gdp.log
61	"	"	PC	TS_KSMc-SeMe_COMe_M11_6-311++Gdp_forward.log
62	KSeMe-SeMe	-COMe	SC	TS_KSeMe-SeMe_COMe_M11_6-311++Gdp_back.log
63	"	"	TS1	TS_KSeMe-SeMe_COMe_M11_6-311++Gdp.log
64	"	"	MI	TS_KSeMe-SeMe_COMe_M11_6-311++Gdp_forward.log
65	"	-CO2Me	SC	TS_KSeMe-SeMe_CO2Me_M11_6-311++Gdp_back.log
66	"	"	TS1	TS_KSeMe-SeMe_CO2Me_M11_6-311++Gdp.log

Entry	KYMe-XMe	-R (sub folder)	Reaction Coordinate ^[a]	File name
67	"	"	MI	TS_KSeMe-SeMe_CO2Me_M11_6-311++Gdp_forward.log
68	"	-CF3	SC	TS_KSeMe-SeMe_CF3_M11_6-311++Gdp_back.sh
69	"	"	TS1	TS_KSeMe-SeMe_CF3_M11_6-311++Gdp.log
70	"	"	PC	TS_KSeMe-SeMe_CF3_M11_6-311++Gdp_forward_trial2.log
71	"	-CCH	SC	TS_KSeMe-SeMe_CCH_M11_6-311++Gdp_back_trial2.log
72	"	"	TS1	TS_KSeMe-SeMe_CCH_M11_6-311++Gdp.log
73	"	"	PC	TS_KSeMe-SeMe_CCH_M11_6-311++Gdp_forward_trial2.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

3.3. Counter-Cation and Explicit Solvent Effects

The log files for the calculations shown in Figure 2 in the main text investigating the effect of the counter cation on the mechanistic turning point are listed in below in Table SI-3-7.

Table SI-3-7

Entry	Metal M (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	Li	-NO	SC	TS_LiOMe_NO_F_M11_6-311++Gdp_back_trial2.log
2	"	"	TS1	TS_LiOMe_NO_F_M11_6-311++Gdp.log
3	"	"	MI	TS_LiOMe_NO_F_M11_6-311++Gdp_forward.log
4	"	-NO2	SC	TS_LiOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
5	"	"	TS1	TS_LiOMe_NO2_F_M11_6-311++Gdp_trial2_freq.log
6	"	"	PC	TS_LiOMe_NO2_F_M11_6-311++Gdp_forward.log
7	"	-CHCCN2	SC	TS_LiOMe_CHCCN2_F_M11_6-311++Gdp_back_trial2.log
8	"	"	TS1	TS_LiOMe_CHCCN2_F_M11_6-311++Gdp.log
9	"	"	MI	TS_LiOMe_CHCCN2_F_M11_6-311++Gdp_forward_trial3.log
10	"	-COCF3	SC	TS_LiOMe_COCF3_M11_6-311++Gdp_back_trial2.log
11	"	"	TS1	TS_LiOMe_COCF3_M11_6-311++Gdp.log
11	"	"	PC	TS_LiOMe_COCF3_M11_6-311++Gdp_forward_trial2.log
12	"	-CN	SC	TS_LiOMe_CN_M11_6-311++Gdp_back_trial2.log
13	"	"	TS1	TS_LiOMe_CN_M11_6-311++Gdp.log
14	"	"	PC	TS_LiOMe_CN_M11_6-311++Gdp_forward_trial2.log
15	"	-COMe	SC	TS_LiOMe_COMe_M11_6-311++Gdp_back_trial2_freq.log
16	"	"	TS1	TS_LiOMe_COMe_M11_6-311++Gdp_trial2.log
17	"	"	PC	TS_LiOMe_COMe_M11_6-311++Gdp_forward.log
18	"	-CO2Me	SC	TS_LiOMe_CO2Me_M11_6-311++Gdp_back_trial3.log
19	"	"	TS1	TS_LiOMe_CO2Me_M11_6-311++Gdp_trial2_freq.log
20	"	"	PC	TS_LiOMe_CO2Me_M11_6-311++Gdp_forward_trial2.log
21	Na	-NO2	SC	TS_NaOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
22	"	"	TS1	TS_NaOMe_NO2_F_M11_6-311++Gdp_trial2_freq.log
23	"	"	MI	TS_NaOMe_NO2_F_M11_6-311++Gdp_forward.log
24	"	-CHCCN2	SC	TS_NaOMe_CHCCN2_F_M11_6-311++Gdp_back_trial3_freq.log
25	"	"	TS1	TS_NaOMe_CHCCN2_F_M11_6-311++Gdp.log
26	"	"	MI	TS_NaOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
27	"	-COCF3	SC	TS_NaOMe_COCF3_M11_6-311++Gdp_back_trial4.log
28	"	"	TS1	TS_NaOMe_COCF3_M11_6-311++Gdp.log
29	"	"	MI	TS_NaOMe_COCF3_M11_6-311++Gdp_forward.log
30	"	-CN	SC	TS_NaOMe_CN_M11_6-311++Gdp_back_trial3.log
31	"	"	TS1	TS_NaOMe_CN_M11_6-311++Gdp.log
32	"	"	PC	TS_NaOMe_CN_M11_6-311++Gdp_forward.log

Entry	Metal M (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
33	"	-COMe	SC	TS_NaOMe_COMe_M11_6-311++Gdp_back_trial3_freq.log
34	"	"	TS1	TS_NaOMe_COMe_M11_6-311++Gdp_trial3_freq.log
35	"	"	PC	TS_NaOMe_COMe_M11_6-311++Gdp_forward.log
36	"	-CO2Me	SC	TS_NaOMe_CO2Me_M11_6-311++Gdp_back.log
37	"	"	TS1	TS_NaOMe_CO2Me_M11_6-311++Gdp.log
38	"	"	PC	TS_NaOMe_CO2Me_M11_6-311++Gdp_forward.log
39	K	-NO	SC	TS_KOMe_NO_F_M11_6-311++Gdp_back_trial2.log
40	"	"	TS1	TS_KOMe_NO_F_M11_6-311++Gdp.log
41	"	"	MI	TS_KOMe_NO_F_M11_6-311++Gdp_forward.log
42	"	"	TS2	TS2_KOMe_NO_F_M11_6-311++Gdp.log
43	"	"	PC	TS2_KOMe_NO_F_M11_6-311++Gdp_forward.log
44	"	-NO2	SC	TS_KOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
45	"	"	TS1	TS_KOMe_NO2_F_M11_6-311++Gdp.log
46	"	"	MI	TS_KOMe_NO2_F_M11_6-311++Gdp_forward_trial2.log
47	"	"	TS2	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial8.log
48	"	"	PC	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial2.log
49	"	-CHCCN2	SC	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_back_trial4.log
50	"	"	TS1	TS_KOMe_CHCCN2_F_M11_6-311++Gdp.log
51	"	"	MI	TS_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
52	"	"	TS2	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp.log
53	"	"	PC	TS2_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
54	"	-COCF3	SC	TS_COCF3_M11_6-311++Gdp_back_trial2_freq.log
55	"	"	TS1	TS_COCF3_M11_6-311++Gdp.log
56	"	"	MI	TS_COCF3_M11_6-311++Gdp_forward.log
57	"	"	TS2	TS2_KOMe_NO2_F_M11_6-311++Gdp_trial8.log
58	"	"	PC	TS2_COCF3_M11_6-311++Gdp_forward_trial3.log
59	"	-CN	SC	TS_CN_M11_6-311++Gdp_back_trial2.log
60	"	"	TS1	TS_CN_M11_6-311++Gdp.log
61	"	"	PC	TS_CN_M11_6-311++Gdp_forward.log
62	"	-COMe	SC	TS_COMe_M11_6-311++Gdp_back_trial2_freq.log
63	"	"	TS1	TS_COMe_M11_6-311++Gdp_trial3.log
64	"	"	PC	TS_COMe_M11_6-311++Gdp_forward_trial2.log
65	"	-CO2Me	SC	TS_CO2Me_M11_6-311++Gdp_back_trial2.log
66	"	"	TS1	TS_CO2Me_M11_6-311++Gdp.log
67	"	"	PC	TS_CO2Me_M11_6-311++Gdp_forward_trial2.log
68	"	-CF3	SC	TS_KOMe_CF3_F_M11_6-311++Gdp_back_trial2.log
69	"	"	TS1	TS_KOMe_CF3_F_M11_6-311++Gdp.log
70	"	"	PC	TS_KOMe_CF3_F_M11_6-311++Gdp_forward_trial2.log
71	"	-CCH	SC	TS_KOMe_CCH_F_M11_6-311++Gdp_back_trial2.log
72	"	"	TS1	TS_KOMe_CCH_F_M11_6-311++Gdp.log
73	"	"	PC	TS_KOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log
74	"	-H	SC	TS_KOMe_H_F_M11_6-311++Gdp_back_trial2.log
75	"	"	TS1	TS_KOMe_H_F_M11_6-311++Gdp.log
76	"	"	PC	TS_KOMe_H_F_M11_6-311++Gdp_forward_trial2.log
77	Rb	-NO	SC	TS_RbOMe_NO_F_M11_6-311++Gdp_back.log
78	"	"	TS1	TS_RbOMe_NO_F_M11_6-311++Gdp.log
79	"	"	MI	TS_RbOMe_NO_F_M11_6-311++Gdp_forward.log
80	"	-NO2	SC	TS_RbOMe_NO2_F_M11_6-311++Gdp_back_trial5.log
81	"	"	TS1	TS_RbOMe_NO2_F_M11_6-311++Gdp.log
82	"	"	MI	TS_RbOMe_NO2_F_M11_6-311++Gdp_forward.log

Entry	Metal M (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
83	"	-CHCCN2	SC	TS_RbOMe_CHCCN2_F_M11_6-311++Gdp_back_trial8_freq_on_step23.log
84	"	"	TS1	TS_RbOMe_CHCCN2_F_M11_6-311++Gdp.log
85	"	"	MI	TS_RbOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
86	"	-COCF3	SC	TS_RbOMe_COCF3_M11_6-311++Gdp_back_trial3.log
87	"	"	TS1	TS_RbOMe_COCF3_M11_6-311++Gdp.log
88	"	"	MI	TS_RbOMe_COCF3_M11_6-311++Gdp_forward.log
89	"	-CN	SC	TS_RbOMe_CN_M11_6-311++Gdp_back_trial2.log
90	"	"	TS1	TS_RbOMe_CN_M11_6-311++Gdp.log
91	"	"	PC	TS_RbOMe_CN_M11_6-311++Gdp_forward.log
92	"	-COMe	SC	TS_RbOMe_COMe_M11_6-311++Gdp_back_trial5.log
93	"	"	TS1	TS_RbOMe_COMe_M11_6-311++Gdp_forward_trial2.log
94	"	"	MI	TS_RbOMe_COMe_M11_6-311++Gdp_forward_trial2.log
95	"	-CO2Me	SC	TS_RbOMe_CO2Me_M11_6-311++Gdp_back.log
96	"	"	TS1	TS_RbOMe_CO2Me_M11_6-311++Gdp.log
97	"	"	PC	TS_RbOMe_CO2Me_M11_6-311++Gdp_forward.log
98	"	-CF3	SC	TS_RbOMe_CF3_F_M11_6-311++Gdp_back.log
99	"	"	TS1	TS_RbOMe_CF3_F_M11_6-311++Gdp.log
100	"	"	PC	TS_RbOMe_CF3_F_M11_6-311++Gdp_forward_trial2.log
101	"	-CCH	SC	TS_RbOMe_CCH_F_M11_6-311++Gdp_back.log
102	"	"	TS1	TS_RbOMe_CCH_F_M11_6-311++Gdp.log
103	"	"	PC	TS_RbOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log
104	"	-H	SC	TS_RbOMe_H_F_M11_6-311++Gdp_back_trial2.log
105	"	"	TS1	TS_RbOMe_H_F_M11_6-311++Gdp.log
106	"	"	PC	TS_RbOMe_H_F_M11_6-311++Gdp_forward_trial2.log
107	Cs	-NO	SC	TS_CsOMe_NO_F_M11_6-311++Gdp_back.log
108	"	"	TS1	TS_CsOMe_NO_F_M11_6-311++Gdp_forward.log
109	"	"	MI	TS_CsOMe_NO_F_M11_6-311++Gdp_forward.log
110	"	-NO2	SC	TS_CsOMe_NO2_F_M11_6-311++Gdp_back_trial2.log
111	"	"	TS1	TS_CsOMe_NO2_F_M11_6-311++Gdp.log
112	"	"	MI	TS_CsOMe_NO2_F_M11_6-311++Gdp_forward.log
113	"	-CHCCN2	SC	TS_CsOMe_CHCCN2_F_M11_6-311++Gdp_back_trial2.log
114	"	"	TS1	TS_CsOMe_CHCCN2_F_M11_6-311++Gdp.log
115	"	"	MI	TS_CsOMe_CHCCN2_F_M11_6-311++Gdp_forward.log
116	"	-COCF3	SC	TS_CsOMe_COCF3_M11_6-311++Gdp_back_trial3.log
117	"	"	TS1	TS_CsOMe_COCF3_M11_6-311++Gdp.log
118	"	"	MI	TS_CsOMe_COCF3_M11_6-311++Gdp_forward.log
119	"	-CN	SC	TS_CsOMe_CN_M11_6-311++Gdp_back_trial2.log
120	"	"	TS1	TS_CsOMe_CN_M11_6-311++Gdp_forward_trial3.log
121	"	"	PC	TS_CsOMe_CN_M11_6-311++Gdp_forward_trial3.log
122	"	-COMe	SC	TS_CsOMe_COMe_M11_6-311++Gdp_back.log
123	"	"	TS1	TS_CsOMe_COMe_M11_6-311++Gdp_trial3_freq.log
124	"	"	Mi	TS_CsOMe_COMe_M11_6-311++Gdp_forward.log
125	"	-CO2Me	SC	TS_CsOMe_CO2Me_M11_6-311++Gdp_back.log
126	"	"	TS1	TS_CsOMe_CO2Me_M11_6-311++Gdp.log
127	"	"	PC	TS_CsOMe_CO2Me_M11_6-311++Gdp_forward.log
128	"	-CF3	SC	TS_CsOMe_CF3_F_M11_6-311++Gdp_back.log
129	"	"	TS1	TS_CsOMe_CF3_F_M11_6-311++Gdp.log
130	"	"	PC	TS_CsOMe_CF3_F_M11_6-311++Gdp_forward.log
131	"	-CCH	SC	TS_CsOMe_CCH_F_M11_6-311++Gdp_back.log
132	"	"	TS1	TS_CsOMe_CCH_F_M11_6-311++Gdp.log

Entry	Metal M (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
133	"	"	PC	TS_CsOMe_CCH_F_M11_6-311++Gdp_forward.log
134	"	-H	SC	TS_CsOMe_H_F_M11_6-311++Gdp_back.log
135	"	"	TS1	TS_CsOMe_H_F_M11_6-311++Gdp.log
136	"	"	PC	TS_CsOMe_H_F_M11_6-311++Gdp_forward_trial2.log
137	none	-COCF3	SC	TS_OMe_COCF3_M11_6-311++Gdp_back_trial2.log
138	"	"	TS1	TS_OMe_COCF3_M11_6-311++Gdp.log
139	"	"	MI	TS_OMe_COCF3_M11_6-311++Gdp_forward.log
140	"	-CN	SC	TS_OMe_CN_M11_6-311++Gdp_back_trial2.log
141	"	"	TS1	TS_OMe_CN_M11_6-311++Gdp.log
142	"	"	MI	TS_OMe_CN_M11_6-311++Gdp_forward.log
143	"	-COMe	SC	TS_OMe_COMe_M11_6-311++Gdp_back_trial2.log
144	"	"	TS1	TS_OMe_COMe_M11_6-311++Gdp_forward.log
145	"	"	MI	TS_OMe_COMe_M11_6-311++Gdp_forward.log
146	"	-CO2Me	SC	TS_OMe_CO2Me_M11_6-311++Gdp_back_trial4.log
147	"	"	TS1	TS_OMe_CO2Me_M11_6-311++Gdp.log
148	"	"	MI	TS_OMe_CO2Me_M11_6-311++Gdp_forward.log
149	"	-CF3	SC	TS_OMe_CF3_F_M11_6-311++Gdp_back_trial2.log
150	"	"	TS1	TS_OMe_CF3_F_M11_6-311++Gdp.log
151	"	"	MI	TS_OMe_CF3_F_M11_6-311++Gdp_forward_trial2.log
152	"	-CCH	SC	TS_OMe_CCH_F_M11_6-311++Gdp_back.log
153	"	"	TS1	TS_OMe_CCH_F_M11_6-311++Gdp.log
154	"	"	PC	TS_OMe_CCH_F_M11_6-311++Gdp_forward_trial3.log
155	"	-H	SC	TS_OMe_H_F_M11_6-311++Gdp_back.log
156	"	"	TS1	TS_OMe_H_F_M11_6-311++Gdp.log
157	"	"	PC	TS_OMe_H_F_M11_6-311++Gdp_forward_trial2.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations with explicit solvent molecules shown in Figure SI-4 are listed in below in Table SI-3-8. For the example without explicit solvation see Table SI-3-7.

Table SI-3-8

Entry	n (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	1	-CHCCN2	SC	TS_KOMe-F_CHCCN2_1_DMF_M11_6-311++Gdp_back.log
2	"	"	TS1	TS_KOMe-F_CHCCN2_1_DMF_M11_6-311++Gdp.log
3	"	"	MI	TS_KOMe-F_CHCCN2_1_DMF_M11_6-311++Gdp_forward.log
4	"	-COCF3	SC	TS_KOMe-F_COCF3_1_DMF_M11_6-311++Gdp_back.log
5	"	"	TS1	TS_KOMe-F_COCF3_1_DMF_M11_6-311++Gdp.log
6	"	"	MI	TS_KOMe-F_COCF3_1_DMF_M11_6-311++Gdp_forward.log
7	"	-CN	SC	TS_KOMe-F_CN_1_DMF_M11_6-311++Gdp_back_trial2.log
8	"	"	TS1	TS_KOMe-F_CN_1_DMF_M11_6-311++Gdp_trial2.log
9	"	"	PC	TS_KOMe-F_CN_1_DMF_M11_6-311++Gdp_forward_trial2.log
10	"	-COMe	SC	TS_KOMe-F_COMe_1_DMF_M11_6-311++Gdp_back.log
11	"	"	TS1	TS_KOMe-F_COMe_1_DMF_M11_6-311++Gdp.log
11	"	"	PC	TS_KOMe-F_COMe_1_DMF_M11_6-311++Gdp_forward_trial2.log
12	2	-CHCCN2	SC	TS_KOMe-F_CHCCN2_2_DMF_M11_6-311++Gdp_back.log
13	"	"	TS1	TS_KOMe-F_CHCCN2_2_DMF_M11_6-311++Gdp_trial2.log
14	"	"	MI	TS_KOMe-F_CHCCN2_2_DMF_M11_6-311++Gdp_forward.log

Entry	n (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
15	"	-COCF3	SC	TS_KOMe-F_COCF3_2_DMF_M11_6-311++Gdp_back.log
16	"	"	TS1	TS_KOMe-F_COCF3_2_DMF_M11_6-311++Gdp_trial2.log
17	"	"	MI	TS_KOMe-F_COCF3_2_DMF_M11_6-311++Gdp_forward.log
18	"	-CN	SC	TS_KOMe-F_CN_2_DMF_M11_6-311++Gdp_back.log
19	"	"	TS1	TS_KOMe-F_CN_2_DMF_M11_6-311++Gdp_trial4.log
20	"	"	PC	TS_KOMe-F_CN_2_DMF_M11_6-311++Gdp_forward_trial2.log
21	"	-COMe	SC	TS_KOMe-F_COMe_2_DMF_M11_6-311++Gdp_back_trial2.log
22	"	"	TS1	TS_KOMe-F_COMe_2_DMF_M11_6-311++Gdp_trial2.log
23	"	"	MI	TS_KOMe-F_COMe_2_DMF_M11_6-311++Gdp_forward.log
24	"	-CO2Me	SC	TS_KOMe-F_CO2Me_2_DMF_M11_6-311++Gdp_back_trial2.log
25	"	"	TS1	TS_KOMe-F_CO2Me_2_DMF_M11_6-311++Gdp.log
26	"	"	MI	TS_KOMe-F_CO2Me_2_DMF_M11_6-311++Gdp_forward.log
27	"	-CF3	SC	TS_KOMe-F_CF3_2_DMF_M11_6-311++Gdp_back.log
28	"	"	TS1	TS_KOMe-F_CF3_2_DMF_M11_6-311++Gdp.log
29	"	"	PC	TS_KOMe-F_CF3_2_DMF_M11_6-311++Gdp_forward.log
30	"	-CCH	SC	TS_KOMe-F_CCH_2_DMF_M11_6-311++Gdp_back.log
31	"	"	TS1	TS_KOMe-F_CCH_2_DMF_M11_6-311++Gdp.log
32	"	"	PC	TS_KOMe-F_CCH_2_DMF_M11_6-311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

3.4. Effect of the Nucleophile

The .log files for the calculations of different nucleophiles shown in Figure 3 in the main text are listed in below in Table SI-3-9. For the examples with potassium methoxide as the nucleophile see Table SI-3-7.

Table SI-3-9

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	KSMe	-NO	SC	TS_KSMe-F_NO_M11-6-311++Gdp_back_trial3.log
2	"	"	TS1	TS_KSMe-F_NO_M11-6-311++Gdp.log
3	"	"	MI	TS_KSMe-F_NO_M11-6-311++Gdp_forward_trial2.log
4	"	-NO2	SC	TS_KSMe-F_NO2_M11-6-311++Gdp_back_trial2.log
5	"	"	TS1	TS_KSMe-F_NO2_M11-6-311++Gdp.log
6	"	"	MI	TS_KSMe-F_NO2_M11-6-311++Gdp_forward_trial2.log
7	"	-CHCCN2	SC	TS_KSMe-F_CHCCN2_M11-6-311++Gdp_back_trial6.log
8	"	"	TS1	TS_KSMe-F_CHCCN2_M11-6-311++Gdp.log
9	"	"	MI	TS_KSMe-F_CHCCN2_M11-6-311++Gdp_forward_trial2.log
10	"	-COCF3	SC	TS_KSMe-F_COCF3_M11-6-311++Gdp_back_trial2.log
11	"	"	TS1	TS_KSMe-F_COCF3_M11-6-311++Gdp.log
11	"	"	MI	TS_KSMe-F_COCF3_M11-6-311++Gdp_forward_trial2.log
12	"	"	TS2	TS2_KSMe-F_COCF3_M11-6-311++Gdp.log
13	"	"	PC	TS2_KSMe-F_COCF3_M11-6-311++Gdp_forward_trial2.log
14	"	-CN	SC	TS_KSMe-F_CN_M11-6-311++Gdp_back_trial3.log
15	"	"	TS1	TS_KSMe-F_CN_M11-6-311++Gdp.log
16	"	"	PC	TS_KSMe-F_CN_M11-6-311++Gdp_forward_trial2.log
17	"	-COMe	SC	TS_KSMe-F_COMe_M11-6-311++Gdp_back_trial2.log
18	"	"	TS1	TS_KSMe-F_COMe_M11-6-311++Gdp.log
19	"	"	PC	TS_KSMe-F_COMe_M11-6-311++Gdp.log
20	"	-CO2Me	SC	TS_KSMe-F_CO2Me_M11-6-311++Gdp_back_trial2.log
21	"	"	TS1	TS_KSMe-F_CO2Me_M11-6-311++Gdp.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
22	"	"	PC	TS_KSMe-F_CO2Me_M11-6-311++Gdp_forward_trial2.log
23	"	-CF3	SC	TS_KSMe-F_CF3_M11-6-311++Gdp_back_trial3.log
24	"	"	TS1	TS_KSMe-F_CF3_M11-6-311++Gdp.log
25	"	"	PC	TS_KSMe-F_CF3_M11-6-311++Gdp_forward_trial2_freq.log TS_KSMe-F_CF3_M11-6-311++Gdp_forward_trial2.log
26	"	-CCH	SC	TS_KSMe-F_CCH_M11-6-311++Gdp_back_trial2_freq.log TS_KSMe-F_CCH_M11-6-311++Gdp_back_trial2.log
27	"	"	TS1	TS_KSMe-F_CCH_M11-6-311++Gdp.log
28	"	"	PC	TS_KSMe-F_CCH_M11-6-311++Gdp_forward_trial2.log
29	"	-H	SC	TS_NaSMe-F_H_M11-6-311++Gdp_back_trial3.log
30	"	"	TS1	TS_NaSMe-F_H_M11-6-311++Gdp.log
31	"	"	PC	TS_NaSMe-F_H_M11-6-311++Gdp_forward_trial3.log
32	KN3	-CHCCN2	SC	TS_KN3-F_CHCCN2_M11_6-311++Gdp_back_trial4.log
33	"	"	TS1	TS_KN3-F_CHCCN2_M11_6-311++Gdp.log
34	"	"	MI	TS_KN3-F_CHCCN2_M11_6-311++Gdp_forward.log
35	"	-COCF3	SC	TS_KN3-F_COCF3_M11-6311++Gdp_back.log
36	"	"	TS1	TS_KN3-F_COCF3_M11-6311++Gdp.log
37	"	"	MI	TS_KN3-F_COCF3_M11-6311++Gdp_forward.log
38	"	"	TS2	TS2_KN3-F_COCF3_M11-6311++Gdp.log
39	"	"	PC	TS2_KN3-F_COCF3_M11-6311++Gdp_forward.log
40	"	-CN	SC	TS_KN3-F_CN_M11-6311++Gdp_back.log
41	"	"	TS1	TS_KN3-F_CN_M11-6311++Gdp.log
42	"	"	PC	TS_KN3-F_CN_M11-6311++Gdp_forward_trial2.log
43	"	-COMe	SC	TS_KN3-F_COMe_M11-6311++Gdp_back_trial2.log
44	"	"	TS1	TS_KN3-F_COMe_M11-6311++Gdp.log
45	"	"	PC	TS_KN3-F_COMe_M11-6311++Gdp_forward_trial2.log
46	"	-CO2Me	SC	TS_KN3-F_CO2Me_M11-6311++Gdp_back_trial3.log
47	"	"	TS1	TS_KN3-F_CO2Me_M11-6311++Gdp.log
48	"	"	PC	TS_KN3-F_CO2Me_M11-6311++Gdp_forward.log
49	601d (Kacac)	-CHCCN2	SC	TS_Kacac-F_CHCCN2_M11_6-311++Gdp_back.log
50	"	"	TS1	TS_Kacac-F_CHCCN2_M11_6-311++Gdp.log
51	"	"	MI	TS_Kacac-F_CHCCN2_M11_6-311++Gdp_forward.log
52	"	-COCF3	SC	TS_Kacac-F_COCF3_M11_6-311++Gdp_back.log
53	"	"	TS1	TS_Kacac-F_COCF3_M11_6-311++Gdp.log
54	"	"	MI	TS_Kacac-F_COCF3_M11_6-311++Gdp_forward.log
55	"	"	TS2	TS2_Kacac-F_COCF3_M11_6-311++Gdp.log
56	"	"	PC	TS2_Kacac-F_COCF3_M11_6-311++Gdp_forward.log
57	"	-CN	SC	TS_Kacac-F_CN_M11_6-311++Gdp_back.log
58	"	"	TS1	TS_Kacac-F_CN_M11_6-311++Gdp.log
59	"	"	PC	TS_Kacac-F_CN_M11_6-311++Gdp_forward.log
60	"	-COMe	SC	TS_Kacac-F_COMe_M11_6-311++Gdp_back.log
61	"	"	TS1	TS_Kacac-F_COMe_M11_6-311++Gdp.log
62	"	"	PC	TS_Kacac-F_COMe_M11_6-311++Gdp_forward_trial2.log
63	"	-CO2Me	SC	TS_Kacac-F_CO2Me_M11_6-311++Gdp_back_trial2.log
64	"	"	TS1	TS_Kacac-F_CO2Me_M11_6-311++Gdp.log
65	"	"	PC	TS_Kacac-F_CO2Me_M11_6-311++Gdp_forward_trial2.log
66	601e (KMeldrum)	-NO	SC	TS_KMeldrum-F_NO2_M11_6-311++Gdp_back.log
67	"	"	TS1	TS_KMeldrum-F_NO2_M11_6-311++Gdp.log
68	"	"	MI	TS_KMeldrum-F_NO2_M11_6-311++Gdp_forward.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
69	"	-NO2	SC	TS_KMeldrum-F_NO2_M11_6-311++Gdp_back.log
70	"	"	TS1	TS_KMeldrum-F_NO2_M11_6-311++Gdp.log
71	"	"	MI	TS_KMeldrum-F_NO2_M11_6-311++Gdp_forward_trial3.log
72	"	-CHCCN2	SC	TS_KMeldrum-F_CHCCN2_M11_6-311++Gdp_back.log
73	"	"	TS1	TS_KMeldrum-F_CHCCN2_M11_6-311++Gdp.log
74	"	"	MI	TS_KMeldrum-F_CHCCN2_M11_6-311++Gdp_forward.log
75	"	"	TS2	TS2_KMeldrum-F_CHCCN2_M11_6-311++Gdp.log
76	"	"	PC	TS2_KMeldrum-F_CHCCN2_M11_6-311++Gdp_forward_trial2.log
77	"	-COCF3	SC	TS_KMeldrum-F_COCF3_M11_6-311++Gdp_back_trial2.log
78	"	"	TS1	TS_KMeldrum-F_COCF3_M11_6-311++Gdp.log
79	"	"	MI	TS_KMeldrum-F_COCF3_M11_6-311++Gdp_forward_trial3.log
80	"	-CN	SC	TS_KMeldrum-F_CN_M11_6-311++Gdp_back.log
81	"	"	TS1	TS_KMeldrum-F_CN_M11_6-311++Gdp.log
82	"	"	PC	TS_KMeldrum-F_CN_M11_6-311++Gdp_forward.log
83	"	-COMe	SC	TS_KMeldrum-F_COMe_M11_6-311++Gdp_back.log
84	"	"	TS1	TS_KMeldrum-F_COMe_M11_6-311++Gdp.log
85	"	"	PC	TS_KMeldrum-F_COMe_M11_6-311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations of SETs leading towards an SN(ET)Ar pathway discussed in Table SI-2-6 are listed below in Table SI-3-10. For the substrate complexes in singlet states see Table SI-3-9 above.

Table SI-3-10

Entry	Nucleophile (sub folder)	R in 1a-R-F	Reaction Coordinate ^[a]	File name
1	2b-K	NO	triplet	KSMe_NO_substrate_complex_triplet_trial2.log
2	"	NO ₂	triplet	KSMe_NO2_substrate_complex_triplet.log
3	"	CHC(CN) ₂	triplet	KSMe_CHCCN2_substrate_complex_triplet.log
4	2d-K	CHC(CN) ₂	triplet	Kacac-F_CHCCN2_substrate_complex_triplet.log
5	2e-K	NO	triplet	KMeldrum_NO_substrate_complex_triplet.log
6	"	"	triplet in singlet geom.	KMeldrum_NO_substrate_complex_triplet_in_singlet_geom.log
7	"	"	singlet in triplet geom.	KMeldrum_NO_substrate_complex_singlet_in_triplet_geom.log
8	"	CHC(CN) ₂	triplet	KMeldrum_CHCCN2_substrate_complex_triplet.log
9	2f-K	CHC(CN) ₂	triplet	KPhAc-F_CHCCN2_substrate_complex_triplet.log

[a] 'triplet': Complex of the nucleophile and electrophile was optimised as a triplet. 'triplet in singlet geom.':

A single point calculation was performed on the geometry of the singlet complex but with triplet electronic configuration. 'singlet in triplet geom.': A single point calculation was performed on the geometry of the triplet complex but with singlet electronic configuration.

The log files for the calculations of different nucleophiles with 2-fluoropyridines shown in Figure SI-6 are listed in below in Table SI-3-11.

Table SI-3-11

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	KOMe	-CHCCN2	SC	TS_KOMe-F_CHCCN2_2Pyr_M11-6311++Gdp_back_trial4.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
2	"	"	TS1	TS_KOMe-F_CHCCN2_2Pyr_M11-6311++Gdp.log
3	"	"	MI	TS_KOMe-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log
4	"	-COCF3	SC	TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_back.log
5	"	"	TS1	TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp.log
6	"	"	MI	TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial2.log
7	"	-CN	SC	TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial2.log
8	"	"	TS1	TS_KOMe-F_CN_2Pyr_M11-6311++Gdp.log
9	"	"	MI	TS_KOMe-F_CN_2Pyr_M11-6311++Gdp_forward.log
10	"	-COMe	SC	TS_KOMe-F_COMe_2Pyr_M11-6311++Gdp_back.log
11	"	"	TS1	TS_KOMe-F_COMe_2Pyr_M11-6311++Gdp_trial2.log
11	"	"	MI	TS_KOMe-F_COMe_2Pyr_M11-6311++Gdp_forward_trial5.log
12	"	-CO2Me	SC	TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp_back_trial2.log
13	"	"	TS1	TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp.log
14	"	"	MI	TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp_forward.log
15	"	-CF3	SC	TS_KOMe-F_CF3_2Pyr_M11-6311++Gdp_back.log
16	"	"	TS1	TS_KOMe-F_CF3_2Pyr_M11-6311++Gdp.log
17	"	"	PC	TS_KOMe-F_CF3_2Pyr_M11-6311++Gdp_forward.log
18	"	-CCH	SC	TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_back_trial2.log
19	"	"	TS1	TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp.log
20	"	"	PC	TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_forward.log
21	KSMc	-CHCCN2	SC	TS_KSMc-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log
22	"	"	TS1	TS_KSMc-F_CHCCN2_2Pyr_M11-6311++Gdp.log
23	"	"	MI	TS_KSMc-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log
24	"	-COCF3	SC	TS_KSMc-F_COCF3_2Pyr_M11-6311++Gdp_back.log
25	"	"	TS1	TS_KSMc-F_COCF3_2Pyr_M11-6311++Gdp_trial3.log
26	"	"	MI	TS_KSMc-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial5.log
27	"	-CN	SC	TS_KSMc-F_CN_2Pyr_M11-6311++Gdp_back.log
28	"	"	TS1	TS_KSMc-F_CN_2Pyr_M11-6311++Gdp.log
29	"	"	PC	TS_KSMc-F_CN_2Pyr_M11-6311++Gdp_forward_trial2.log
30	"	-COMe	SC	TS_KSMc-F_COMe_2Pyr_M11-6311++Gdp_back.log
31	"	"	TS1	TS_KSMc-F_COMe_2Pyr_M11-6311++Gdp.log
32	"	"	PC	TS_KSMc-F_COMe_2Pyr_M11-6311++Gdp_forward_trial2.log
33	KN3	-CHCCN2	SC	TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log
34	"	"	TS1	TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_trial2.log
35	"	"	MI	TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log
36	"	-COCF3	SC	TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp_back.log
37	"	"	TS1	TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp.log
38	"	"	MI	TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp_forward.log
39	"	-CN	SC	TS_KN3-F_CN_2Pyr_M11-6311++Gdp_back_trial2.log
40	"	"	TS1	TS_KN3-F_CN_2Pyr_M11-6311++Gdp.log
41	"	"	PC	TS_KN3-F_CN_2Pyr_M11-6311++Gdp_forward_trial2.log
42	"	-COMe	SC	TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_back_trial2.log
43	"	"	TS1	TS_KN3-F_COMe_2Pyr_M11-6311++Gdp.log
44	"	"	PC	TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_forward_trial3.log
45	"	-CO2Me	SC	TS_KN3-F_CO2Me_2Pyr_M11-6311++Gdp_back.log
46	"	"	TS1	TS_KN3-F_CO2Me_2Pyr_M11-6311++Gdp.log
47	"	"	PC	TS_KN3-F_CO2Me_2Pyr_M11-6311++Gdp_forward.log
48	601d (Kacac)	-CHCCN2	SC	TS_Kacac-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log
49	"	"	TS1	TS_Kacac-F_CHCCN2_2Pyr_M11-6311++Gdp.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
50	"	"	MI	TS_Kacac-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log
51	"	-COCF3	SC	TS_Kacac-F_COCF3_2Pyr_M11-6311++Gdp_back.log
52	"	"	TS1	TS_Kacac-F_COCF3_2Pyr_M11-6311++Gdp.log
53	"	"	MI	TS_Kacac-F_COCF3_2Pyr_M11-6311++Gdp_forward.log
54	"	-CN	SC	TS_Kacac-F_CN_2Pyr_M11-6311++Gdp_back.log
55	"	"	TS1	TS_Kacac-F_CN_2Pyr_M11-6311++Gdp.log
56	"	"	MI	TS_Kacac-F_CN_2Pyr_M11-6311++Gdp_forward.log
57	"	-COMe	SC	TS_Kacac-F_COMe_2Pyr_M11-6311++Gdp_back.log
58	"	"	TS1	TS_Kacac-F_COMe_2Pyr_M11-6311++Gdp.log
59	"	"	PC	TS_Kacac-F_COMe_2Pyr_M11-6311++Gdp_forward_trial2.log
60	"	-CO2Me	SC	TS_Kacac-F_CO2Me_2Pyr_M11-6311++Gdp_back.log
61	"	"	TS1	TS_Kacac-F_CO2Me_2Pyr_M11-6311++Gdp.log
62	"	"	PC	TS_Kacac-F_CO2Me_2Pyr_M11-6311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations of the deprotonation pathway of 2-fluoropyridyl substrates by potassium methoxide in Table SI-2-7 are listed below in Table SI-3-12.

Table SI-3-12

Entry	Subfolder	Comment	File name
1	CHC(CN) ₂	protonated form	Pyridien_F_CHCCN2_neutral.log
2	"	potassium salt	K3-Pyridine_F_CHCCN2.log
3	COCF ₃	protonated form	Pyridine_F_COCF3_neutral.log
4	"	potassium salt	K3-Pyridine_F_COCF3_trial2.log
5	CN	protonated form	Pyridine_F_CN_neutral.log
6	"	potassium salt	K3-Pyridine_F_CN.log
7	MeOX	methanol	MeOH.log
8	"	potassium methoxide	MeOK.log

The log files for the calculations of different nucleophiles with naphthalene shown in Figure SI-7 are listed in below in Table SI-3-13.

Table SI-3-13

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	KOMe	-CHCCN2	SC	TS_KOMe-F_CHCCN2_Np_M11_6-311++Gdp_back.log
2	"	"	TS1	TS_KOMe-F_CHCCN2_Np_M11_6-311++Gdp.log
3	"	"	MI	TS_KOMe-F_CHCCN2_Np_M11_6-311++Gdp_forward.log
4	"	-COCF3	SC	TS_KOMe-F_COCF3_Np_M11_6-311++Gdp_back.log
5	"	"	TS1	TS_KOMe-F_COCF3_Np_M11_6-311++Gdp.log
6	"	"	MI	TS_KOMe-F_COCF3_Np_M11_6-311++Gdp_back.log
7	"	-CN	SC	TS_KOMe-F_CN_Np_M11_6-311++Gdp_back_trial2.log
8	"	"	TS1	TS_KOMe-F_CN_Np_M11_6-311++Gdp.log
9	"	"	MI	TS_KOMe-F_CN_Np_M11_6-311++Gdp_forward.log
10	"	-COMe	SC	TS_KOMe-F_COMe_Np_M11_6-311++Gdp_back.log
11	"	"	TS1	TS_KOMe-F_COMe_Np_M11_6-311++Gdp.log
11	"	"	MI	TS_KOMe-F_COMe_Np_M11_6-311++Gdp_forward.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
12	"	-CO2Me	SC	TS_KOMe-F_CO2Me_Np_M11_6-311++Gdp_back.log
13	"	"	TS1	TS_KOMe-F_CO2Me_Np_M11_6-311++Gdp.log
14	"	"	MI	TS_KOMe-F_CO2Me_Np_M11_6-311++Gdp_forward.sh
15	"	-CF3	SC	TS_KOMe-F_CF3_Np_M11_6-311++Gdp_back_trial2.log
16	"	"	TS1	TS_KOMe-F_CF3_Np_M11_6-311++Gdp_trial2.log
17	"	"	PC	TS_KOMe-F_CF3_Np_M11_6-311++Gdp_forward_trial2.log
18	"	-CCH	SC	TS_KOMe-F_CCH_Np_M11_6-311++Gdp_back.log
19	"	"	TS1	TS_KOMe-F_CCH_Np_M11_6-311++Gdp.log
20	"	"	PC	TS_KOMe-F_CCH_Np_M11_6-311++Gdp_forward.log
21	KSMc	-CHCCN2	SC	TS_KSMc-F_CHCCN2_Np_M11-6-311++Gdp_back.log
22	"	"	TS1	TS_KSMc-F_CHCCN2_Np_M11-6-311++Gdp.log
23	"	"	MI	TS_KSMc-F_CHCCN2_Np_M11-6-311++Gdp_forward.log
24	"	-COCF3	SC	TS_KSMc-F_COCF3_Np_M11-6-311++Gdp_back_trial3.log
25	"	"	TS1	TS_KSMc-F_COCF3_Np_M11-6-311++Gdp.log
26	"	"	MI	TS_KSMc-F_COCF3_Np_M11-6-311++Gdp_forward_trial2.log
27	"	-CN	SC	TS_KSMc-F_CN_Np_M11-6-311++Gdp_back.log
28	"	"	TS1	TS_KSMc-F_CN_Np_M11-6-311++Gdp.log
29	"	"	PC	TS_KSMc-F_CN_Np_M11-6-311++Gdp_forward_trial3.log
30	"	-COMe	SC	TS_KSMc-F_COMe_Np_M11-6-311++Gdp_back.log
31	"	"	TS1	TS_KSMc-F_COMe_Np_M11-6-311++Gdp.log
32	"	"	MI	TS_KSMc-F_COMe_Np_M11-6-311++Gdp_forward.log
33	"	-CO2Me	SC	TS_KSMc-F_CO2Me_Np_M11-6-311++Gdp_back.log
34	"	"	TS1	TS_KSMc-F_CO2Me_Np_M11-6-311++Gdp_forward.log
35	"	"	PC	TS_KSMc-F_CO2Me_Np_M11-6-311++Gdp_forward.log
36	"	-CF3	SC	TS_KSMc-F_CF3_Np_M11-6-311++Gdp_back.log
37	"	"	TS1	TS_KSMc-F_CF3_Np_M11-6-311++Gdp.log
38	"	"	PC	TS_KSMc-F_CF3_Np_M11-6-311++Gdp_back.log
39	"	-CCH	SC	TS_KSMc-F_CCH_Np_M11-6-311++Gdp_back.log
40	"	"	TS1	TS_KSMc-F_CCH_Np_M11-6-311++Gdp.log
41	"	"	PC	TS_KSMc-F_CCH_Np_M11-6-311++Gdp_forward_trial2.log
42	KN3	-COMe	SC	TS_KN3-F_COMe_Np_M11-6311++Gdp_back.log
43	"	"	TS1	TS_KN3-F_COMe_Np_M11-6311++Gdp_trial2.log
44	"	"	MI	TS_KN3-F_COMe_Np_M11-6311++Gdp_forward.log
45	"	-CO2Me	SC	TS_KN3-F_CO2Me_Np_M11-6311++Gdp_back.log
46	"	"	TS1	TS_KN3-F_CO2Me_Np_M11-6311++Gdp.log
47	"	"	PC	TS_KN3-F_CO2Me_Np_M11-6311++Gdp_forward.log
48	"	-CF3	SC	TS_KN3-F_CF3_Np_M11-6311++Gdp_back.log
49	"	"	TS1	TS_KN3-F_CF3_Np_M11-6311++Gdp.log
50	"	"	PC	TS_KN3-F_CF3_Np_M11-6311++Gdp_forward.log
51	"	-CCH	SC	TS_KN3-F_CCH_Np_M11-6311++Gdp_back.log
52	"	"	TS1	TS_KN3-F_CCH_Np_M11-6311++Gdp.log
53	"	"	PC	TS_KN3-F_CCH_Np_M11-6311++Gdp_forward.log
54	601d (Kacac)	-COMe	SC	TS_Kacac-F_COMe_Np_M11_6-311++Gdp_back_trial3.log
55	"	"	TS1	TS_Kacac-F_COMe_Np_M11_6-311++Gdp.log
56	"	"	MI	TS_Kacac-F_COMe_Np_M11_6-311++Gdp_forward.log
57	"	-CO2Me	SC	TS_Kacac-F_CO2Me_Np_M11_6-311++Gdp_back.log
58	"	"	TS1	TS_Kacac-F_CO2Me_Np_M11_6-311++Gdp.log
59	"	"	MI	TS_Kacac-F_CO2Me_Np_M11_6-311++Gdp_forward.log
60	"	-CF3	SC	TS_Kacac-F_CF3_Np_M11_6-311++Gdp_back.log
61	"	"	TS1	TS_Kacac-F_CF3_Np_M11_6-311++Gdp.log

Entry	KNu (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
62	"	"	MI	TS_Kacac-F_CF3_Np_M11_6-311++Gdp_forward.log
63	"	-CCH	SC	TS_Kacac-F_CCH_Np_M11_6-311++Gdp_back.log
64	"	"	TS1	TS_Kacac-F_CCH_Np_M11_6-311++Gdp.log
65	"	"	MI	TS_Kacac-F_CCH_Np_M11_6-311++Gdp_forward.log
66	"	-NCS	SC	TS_Kacac-F_NCS_Np_M11_6-311++Gdp_back.log
67	"	"	TS1	TS_Kacac-F_NCS_Np_M11_6-311++Gdp.log
68	"	"	MI	TS_Kacac-F_NCS_Np_M11_6-311++Gdp_forward.log
69	"	-Cl	SC	TS_Kacac-F_Cl_Np_M11_6-311++Gdp_back.log
70	"	"	TS1	TS_Kacac-F_Cl_Np_M11_6-311++Gdp.log
71	"	"	MI	TS_Kacac-F_Cl_Np_M11_6-311++Gdp_forward.log
72	"	-H	SC	TS_Kacac-F_H_Np_M11_6-311++Gdp_back.log
73	"	"	TS1	TS_Kacac-F_H_Np_M11_6-311++Gdp_trial2.log
74	"	"	PC	TS_Kacac-F_H_Np_M11_6-311++Gdp_forward.log
75	"	-Me	SC	TS_Kacac-F_Me_Np_M11_6-311++Gdp_back.log
76	"	"	TS1	TS_Kacac-F_Me_Np_M11_6-311++Gdp.log
77	"	"	MI	TS_Kacac-F_Me_Np_M11_6-311++Gdp_forward.log
78	"	-OMe	SC	TS_Kacac-F_OMe_Np_M11_6-311++Gdp_back.log
79	"	"	TS1	TS_Kacac-F_OMe_Np_M11_6-311++Gdp.log
80	"	"	PC	TS_Kacac-F_OMe_Np_M11_6-311++Gdp_forward.log
81	"	-NHAc	SC	TS_Kacac-F_NHAc_Np_M11_6-311++Gdp_back.log
82	"	"	TS1	TS_Kacac-F_NHAc_Np_M11_6-311++Gdp.log
83	"	"	MI	TS_Kacac-F_NHAc_Np_M11_6-311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

Steric Effects

The log files for the calculations shown in Figure SI-8 are listed in below in Table SI-3-14. For the examples with the aromatic system **1a-F** see Table SI-3-7.

Table SI-3-14

Entry	KNu/Ar (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	2c-K (Me)	-NO2	SC	TS_KN3-F_NO2_ortho-Me_M11-6311++Gdp_back_trial2.log
2	"	"	TS1	TS_KN3-F_NO2_ortho-Me_M11-6311++Gdp.log
3	"	"	MI	TS_KN3-F_NO2_ortho-Me_M11-6311++Gdp_forward_trial3.log
4	"	-CHCCN2	SC	TS_KN3-F_CHCCN2_ortho-Me_M11_6-311++Gdp_back_trial2.log
5	"	"	TS1	TS_KN3-F_CHCCN2_ortho-Me_M11_6-311++Gdp.log
6	"	"	MI	TS_KN3-F_CHCCN2_ortho-Me_M11_6-311++Gdp_forward.log
7	"	-COCF3	SC	TS_KN3-F_COCF3_ortho-Me_M11-6311++Gdp_back_trial2.log
8	"	"	TS1	TS_KN3-F_COCF3_ortho-Me_M11-6311++Gdp.log
9	"	"	MI	TS_KN3-F_COCF3_ortho-Me_M11-6311++Gdp_forward.log
10	"	-CN	SC	TS_KN3-F_CN_ortho-Me_M11-6311++Gdp_back_trial7.log
11	"	"	TS1	TS_KN3-F_CN_ortho-Me_M11-6311++Gdp.log
11	"	"	PC	TS_KN3-F_CN_ortho-Me_M11-6311++Gdp_forward.log
12	"	-COMe	SC	TS_KN3-F_COMe_ortho-Me_M11-6311++Gdp_back_trial3.log
13	"	"	TS1	TS_KN3-F_COMe_ortho-Me_M11-6311++Gdp.log
14	"	"	PC	TS_KN3-F_COMe_ortho-Me_M11-6311++Gdp_forward.log
15	2c-K (di-Me)	-NO2	SC	TS_KN3-F_NO2_ortho-di-Me_M11-6311++Gdp_back.log
16	"	"	TS1	TS_KN3-F_NO2_ortho-di-Me_M11-6311++Gdp.log
17	"	"	MI	TS_KN3-F_NO2_ortho-di-Me_M11-6311++Gdp_forward.log

Entry	KNu/Ar (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
18	"	-CHCCN2	SC	TS_KN3-F_CHCCN2_ortho-di-Me_M11_6-311++Gdp_back.log
19	"	"	TS1	TS_KN3-F_CHCCN2_ortho-di-Me_M11_6-311++Gdp.log
20	"	"	MI	TS_KN3-F_CHCCN2_ortho-di-Me_M11_6-311++Gdp_forward_trial2.log
21	"	-COCF3	SC	TS_KN3-F_COCF3_ortho-di-Me_M11-6311++Gdp_back.log
22	"	"	TS1	TS_KN3-F_COCF3_ortho-di-Me_M11-6311++Gdp.log
23	"	"	MI	TS_KN3-F_COCF3_ortho-di-Me_M11-6311++Gdp_forward_trial2.log
24	"	-CN	SC	TS_KN3-F_CN_ortho-di-Me_M11-6311++Gdp_back.log
25	"	"	TS1	TS_KN3-F_CN_ortho-di-Me_M11-6311++Gdp.log
26	"	"	PC	TS_KN3-F_CN_ortho-di-Me_M11-6311++Gdp_forward.log
27	"	-COMe	SC	TS_KN3-F_COMe_ortho-di-Me_M11-6311++Gdp_back_trial2.log
28	"	"	TS1	TS_KN3-F_COMe_ortho-di-Me_M11-6311++Gdp.log
29	"	"	PC	TS_KN3-F_COMe_ortho-di-Me_M11-6311++Gdp_forward.log
30	2d-K (Me)	-CHCCN2	SC	TS_Kacac-F_CHCCN2_ortho-Me_M11_6-311++Gdp_back.log
31	"	"	TS1	TS_Kacac-F_CHCCN2_ortho-Me_M11_6-311++Gdp.log
32	"	"	MI	TS_Kacac-F_CHCCN2_ortho-Me_M11_6-311++Gdp_forward.log
33	"	-COCF3	SC	TS_Kacac-F_COCF3_ortho-Me_M11_6-311++Gdp_back.log
34	"	"	TS1	TS_Kacac-F_COCF3_ortho-Me_M11_6-311++Gdp.log
35	"	"	MI	TS_Kacac-F_COCF3_ortho-Me_M11_6-311++Gdp_forward.log
36	"	-CN	SC	TS_Kacac-F_ortho-Me_CN_M11_6-311++Gdp_back.log
37	"	"	TS1	TS_Kacac-F_ortho-Me_CN_M11_6-311++Gdp.log
38	"	"	PC	TS_Kacac-F_ortho-Me_CN_M11_6-311++Gdp_forward.log
39	"	-COMe	SC	TS_Kacac-F_COMe_ortho-Me_M11_6-311++Gdp_back.log
40	"	"	TS1	TS_Kacac-F_COMe_ortho-Me_M11_6-311++Gdp.log
41	"	"	PC	TS_Kacac-F_COMe_ortho-Me_M11_6-311++Gdp_forward_trial2.log
42	2d-K (di-Me)	-COCF3	SC	TS_Kacac-F_COCF3_ortho-di-Me_M11_6-311++Gdp_back.log
43	"	"	TS1	TS_Kacac-F_COCF3_ortho-di-Me_M11_6-311++Gdp_forward.log
44	"	"	MI	TS_Kacac-F_COCF3_ortho-di-Me_M11_6-311++Gdp_forward.log
45	"	-CN	SC	TS_Kacac-F_ortho-di-Me_CN_M11_6-311++Gdp_back.log
46	"	"	TS1	TS_Kacac-F_ortho-di-Me_CN_M11_6-311++Gdp.log
47	"	"	MI	TS_Kacac-F_ortho-di-Me_CN_M11_6-311++Gdp_forward.log
48	"	-COMe	SC	TS_Kacac-F_COMe_ortho-di-Me_M11_6-311++Gdp_back.log
49	"	"	TS1	TS_Kacac-F_COMe_ortho-di-Me_M11_6-311++Gdp.log
50	"	"	Mi	TS_Kacac-F_COMe_ortho-di-Me_M11_6-311++Gdp_forward.log
51	"	-CO2Me	SC	TS_Kacac-F_CO2Me_ortho-di-Me_M11_6-311++Gdp_back.log
52	"	"	TS1	TS_Kacac-F_CO2Me_ortho-di-Me_M11_6-311++Gdp.log
53	"	"	MI	TS_Kacac-F_CO2Me_ortho-di-Me_M11_6-311++Gdp_forward.log
54	"	-CF3	SC	TS_Kacac-F_CF3_ortho-di-Me_M11_6-311++Gdp_back.log
55	"	"	TS1	TS_Kacac-F_CF3_ortho-di-Me_M11_6-311++Gdp.log
56	"	"	MI	TS_Kacac-F_CF3_ortho-di-Me_M11_6-311++Gdp_forward.log
57	"	-CCH	SC	TS_Kacac-F_CCH_ortho-di-Me_M11_6-311++Gdp_back.log
58	"	"	TS1	TS_Kacac-F_CCH_ortho-di-Me_M11_6-311++Gdp.log
59	"	"	MI	TS_Kacac-F_CCH_ortho-di-Me_M11_6-311++Gdp_forward.log
60	"	-NCS	SC	TS_Kacac-F_NCS_ortho-di-Me_M11_6-311++Gdp_back.log
61	"	"	TS1	TS_Kacac-F_NCS_ortho-di-Me_M11_6-311++Gdp.log
62	"	"	MI	TS_Kacac-F_NCS_ortho-di-Me_M11_6-311++Gdp_forward.log
63	"	-Cl	SC	TS_Kacac-F_Cl_ortho-di-Me_M11_6-311++Gdp_back.log
64	"	"	TS1	TS_Kacac-F_Cl_ortho-di-Me_M11_6-311++Gdp.log
65	"	"	MI	TS_Kacac-F_Cl_ortho-di-Me_M11_6-311++Gdp_forward.log
66	"	-H	SC	TS_Kacac-F_H_ortho-di-Me_M11_6-311++Gdp_back.log
67	"	"	TS1	TS_Kacac-F_H_ortho-di-Me_M11_6-311++Gdp.log

Entry	KNu/Ar (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
68	"	"	MI	TS_Kacac-F_H_ortho-di-Me_M11_6-311++Gdp_forward.log
69	"	-Me	SC	TS_Kacac-F_Me_ortho-di-Me_M11_6-311++Gdp_back.log
70	"	"	TS1	TS_Kacac-F_Me_ortho-di-Me_M11_6-311++Gdp.log
71	"	"	PC	TS_Kacac-F_Me_ortho-di-Me_M11_6-311++Gdp_forward.log
72	"	-OMe	SC	TS_Kacac-F_OMe_ortho-di-Me_M11_6-311++Gdp_back.log
73	"	"	TS1	TS_Kacac-F_OMe_ortho-di-Me_M11_6-311++Gdp.log
74	"	"	PC	TS_Kacac-F_OMe_ortho-di-Me_M11_6-311++Gdp_forward_trial2.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

3.5. Effect of the Aryl Fluoride Electrophile

The log files for the calculations of different aromatic systems with the potassium methoxide nucleophile shown in Figure 4 in the main text are listed in below in Table SI-3-15. For the examples with the aromatic systems **1a-R-F**, **1d-R-F** and **1b-R-F** see Table SI-3-7, Table SI-3-11 and Table SI-3-13, respectively.

Table SI-3-15

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	Pyrimidine	-COMe	SC	TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp_back.log
2	"	"	TS1	TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp.log
3	"	"	MI	TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp_forward.log
4	"	-CO2Me	SC	TS_KOMe-F_CO2Me_Pyrm_M11-6311++Gdp_back.log
5	"	"	TS1	TS_KOMe-F_CO2Me_Pyrm_M11-6311++Gdp.log
6	"	"	MI	TS_KOMe-F_CO2Me_Pyrm_M11-6311++Gdp_forward.log
7	"	-CF3	SC	TS_KOMe-F_CF3_Pyrm_M11-6311++Gdp_back.log
8	"	"	TS1	TS_KOMe-F_CF3_Pyrm_M11-6311++Gdp.log
9	"	"	MI	TS_KOMe-F_CF3_Pyrm_M11-6311++Gdp_back.log
10	"	-CCH	SC	TS_KOMe-F_CCH_Pyrm_M11-6311++Gdp_back.log
11	"	"	TS1	TS_KOMe-F_CCH_Pyrm_M11-6311++Gdp.log
11	"	"	MI	TS_KOMe-F_CCH_Pyrm_M11-6311++Gdp_forward.log
12	"	-NCS	SC	TS_KOMe-F_NCS_Pyrm_M11-6311++Gdp_back.log
13	"	"	TS1	TS_KOMe-F_NCS_Pyrm_M11-6311++Gdp.log
14	"	"	MI	TS_KOMe-F_NCS_Pyrm_M11-6311++Gdp_forward.log
15	"	-H	SC	TS_KOMe-F_H_Pyrm_M11-6311++Gdp_back_trial2.log
16	"	"	TS1	TS_KOMe-F_H_Pyrm_M11-6311++Gdp.log
17	"	"	PC	TS_KOMe-F_H_Pyrm_M11-6311++Gdp_forward_trial2.log
18	"	-Me	SC	TS_KOMe-F_Me_Pyrm_M11-6311++Gdp_back.log
19	"	"	TS1	TS_KOMe-F_Me_Pyrm_M11-6311++Gdp_trial2.log
20	"	"	PC	TS_KOMe-F_Me_Pyrm_M11-6311++Gdp_forward.log
21	Anthracene	-CO2Me	SC	TS_KOMe-F_CO2Me_Ant_M11_6-311++Gdp_back.log
22	"	"	TS1	TS_KOMe-F_CO2Me_Ant_M11_6-311++Gdp.log
23	"	"	MI	TS_KOMe-F_CO2Me_Ant_M11_6-311++Gdp_back.log
24	"	-CF3	SC	TS_KOMe-F_CF3_Ant_M11_6-311++Gdp_back.log
25	"	"	TS1	TS_KOMe-F_CF3_Ant_M11_6-311++Gdp_trial4.log
26	"	"	MI	TS_KOMe-F_CF3_Ant_M11_6-311++Gdp_forward.log
27	"	-CCH	SC	TS_KOMe-F_CCH_Ant_M11_6-311++Gdp_back.log
28	"	"	TS1	TS_KOMe-F_CCH_Ant_M11_6-311++Gdp.log
29	"	"	MI	TS_KOMe-F_CCH_Ant_M11_6-311++Gdp_forward.log
30	"	-NCS	SC	TS_KOMe-F_NCS_Ant_M11_6-311++Gdp_back.log
31	"	"	TS1	TS_KOMe-F_NCS_Ant_M11_6-311++Gdp.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
32	"	"	MI	TS_KOMe-F_NCS_Ant_M11_6-311++Gdp_forward.log
33	"	-H	SC	TS_KOMe-F_H_Ant_M11_6-311++Gdp_back.log
34	"	"	TS1	TS_KOMe-F_H_Ant_M11_6-311++Gdp.log
35	"	"	PC	TS_KOMe-F_H_Ant_M11_6-311++Gdp_forward_trial2.log
36	"	-Me	SC	TS_KOMe-F_Me_Ant_M11_6-311++Gdp_back.log
37	"	"	TS1	TS_KOMe-F_Me_Ant_M11_6-311++Gdp.log
38	"	"	PC	TS_KOMe-F_Me_Ant_M11_6-311++Gdp_forward.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex.

The log files for the calculations used to correlate electron affinities and the mechanistic turning points shown in Figure 5 in the main text are listed in below in Table SI-3-16. For the calculation of the S_NAr reaction pathway with the aromatic systems **1a-R-F** to **1e-R-F** see Table SI-3-7 (**1a-R-F**), Table SI-3-11 (**1d-R-F**) and Table SI-3-13 (**1b-R-F**) and Table SI-3-15 (**1c-R-F** and **1e-R-F**) respectively.

Table SI-3-16

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
1	1a-R-F (Benzene)	-NO	neutral	EA_Benzene_NO-F_neutral.log
2	"	"	radical-anion	EA_Benzene_NO-F_rad-anion.log
3	"	-NO ₂	neutral	EA_Benzene_NO ₂ -F_neutral.log
4	"	"	radical-anion	EA_Benzene_NO ₂ -F_rad-anion.log
5	"	-COCF ₃	neutral	EA_Benzene_COCF ₃ -F_neutral.log
6	"	"	radical-anion	EA_Benzene_COCF ₃ -F_rad-anion.log
7	"	-CN	neutral	EA_Benzene_CN-F_neutral.log
8	"	"	radical-anion	EA_Benzene_CN-F_rad-anion.log
9	"	-COMe	neutral	EA_Benzene_COMe-F_neutral.log
10	"	"	radical-anion	EA_Benzene_COMe-F_rad-anion.log
11	"	-CO ₂ Me	neutral	EA_Benzene_CO ₂ Me-F_neutral.log
11	"	"	radical-anion	EA_Benzene_CO ₂ Me-F_rad-anion.log
12	"	-CF ₃	neutral	EA_Benzene_CF ₃ -F_neutral.log
13	"	"	radical-anion	EA_Benzene_CF ₃ -F_rad-anion_trial2.log
14	"	-CCH	neutral	EA_Benzene_CCH-F_neutral.log
15	"	"	radical-anion	EA_Benzene_CCH-F_rad-anion_trial2.log
16	"	-NCS	neutral	EA_Benzene_NCS-F_neutral.log
17	"	"	radical-anion	EA_Benzene_NCS-F_rad-anion_trial2.log
18	"	-Cl	neutral	EA_Benzene_Cl-F_neutral.log
19	"	"	radical-anion	EA_Benzene_Cl-F_rad-anion.log
20	"	-H	neutral	EA_Benzene_H-F_neutral.log
21	"	"	radical-anion	EA_Benzene_H-F_rad-anion.log
22	"	-Me	neutral	EA_Benzene_Me-F_neutral.log
23	"	"	radical-anion	EA_Benzene_Me-F_rad-anion_trial2.log
24	1b-R-F (Naphthalene)	-CHCCN ₂	neutral	EA_Naphthalene_CHCCN ₂ _neutral_pop.log
25	"	"	radical-anion	EA_Naphthalene_CHCCN ₂ _rad-anion.log
26	"	-COCF ₃	neutral	EA_Naphthalene_COCF ₃ -F_trial2_neutral_pop.log
27	"	"	radical-anion	EA_Naphthalene_COCF ₃ -F_rad-anion.log
	"	-CN	neutral	EA_Naphthalene_CN-F_neutral_pop.log
	"	"	radical-anion	EA_Naphthalene_CN-F_rad-anion.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
	"	-COMe	neutral	EA_Naphthalene_COMe-F_trial2_neutral_pop.log
	"	"	radical-anion	EA_Naphthalene_COMe-F_rad-an.log
	"	-CO2Me	neutral	EA_Naphthalene_CO2Me-F_neutral.log
	"	"	radical-anion	EA_Naphthalene_CO2Me-F_rad-anion.log
	"	-CF3	neutral	EA_Naphthalene_CF3-F_neutral.log
	"	"	radical-anion	EA_Naphthalene_CF3-F_rad-anion.log
	"	-CCH	neutral	EA_Naphthalene_CCH-F_neutral_pop.log
	"	"	radical-anion	EA_Naphthalene_CN-F_rad-anion.log
	1c-R-F (Anthracene)	-CO2Me	neutral	EA_Anthracene_CO2Me-F_neutral_pop.log
	"	"	radical-anion	EA_Anthracene_CO2Me-F_rad-anion.log
	"	-CF3	neutral	EA_Anthracene_CF3-F_neutral_pop.log
	"	"	radical-anion	EA_Anthracene_CF3-F_rad-anion.log
	"	-CCH	neutral	EA_Anthracene_CCH-F_neutral_pop.log
	"	"	radical-anion	EA_Anthracene_CCH-F_rad-anion.log
	"	-NCS	neutral	EA_Anthracene_NCS-F_neutral.log
	"	"	radical-anion	EA_Anthracene_NCS-F_rad-anion.log
28	"	-Cl	neutral	EA_Anthracene_Cl-F_neutral.log
29	"	"	radical-anion	EA_Anthracene_Cl-F_rad-anion.log
30	"	-H	neutral	EA_Anthracene_H-F_neutral_pop.log
	"	"	radical-anion	EA_Anthracene_H-F_rad-anion.log
	"	-Me	neutral	EA_Anthracene_Me-F_neutral_pop.log
	"	"	radical-anion	EA_Anthracene_Me-F_rad-anion.log
	1d-R-F (Pyridine)	-CHCCN2	neutral	EA_Pyridine_F_CHCCN2_neutral_pop.log
	"	"	radical-anion	EA_Pyridine_F_CHCCN2_rad-anion.log
	"	-COCF3	neutral	EA_Pyridine_COCF3-F_neutral_pop.log
	"	"	radical-anion	EA_Pyridine_COCF3-F_rad-anion.log
	"	-CN	neutral	EA_Pyridine_F_CN_neutral_pop.log
	"	"	radical-anion	EA_Pyridine_F_CN_rad-anion.log
	"	-COMe	neutral	EA_Pyridine_COMe-F_neutral_pop.log
	"	"	radical-anion	EA_Pyridine_COMe-F_rad-anion.log
	"	-CO2Me	neutral	EA_Pyridine_CO2Me-F_neutral.log
	"	"	radical-anion	EA_Pyridine_CO2Me-F_rad-anion.log
	"	-CF3	neutral	EA_Pyridine_CF3-F_neutral_trial2.log
	"	"	radical-anion	EA_Pyridine_CF3-F_rad-anion.log
	"	-CCH	neutral	EA_Pyridine_F_CCH_neutral_pop.log
	"	"	radical-anion	EA_Pyridine_F_CCH_rad-anion.log
	1e-R-F (Pyrimidine)	-COMe	neutral	EA_Pyrimidine_COMe-F_neutral_pop.log
	"	"	radical-anion	EA_Pyrimidine_COMe-F_rad-anion.log
31	"	-CO2Me	neutral	EA_Pyrimidine_CO2Me-F_neutral_pop.log
33	"	-CF3	neutral	EA_Pyrimidine_CF3-F_neutral_pop.log
34	"	"	radical-anion	EA_Pyrimidine_CF3-F_rad-anion.log
35	"	-CCH	neutral	EA_Pyrimidine_CCH-F_neutral_pop.log
36	"	"	radical-anion	EA_Pyrimidine_CCH-F_rad-anion.log
37	"	-NCS	neutral	EA_Pyrimidine_NCS-F_neutral.log
38	"	"	radical-anion	EA_Pyrimidine_NCS-F_rad-anion.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
39	"	-Cl	neutral	EA_Pyrimidine_Cl-F_neutral.log
	"	"	radical-anion	EA_Pyrimidine_Cl-F_rad-anion.log
	"	-H	neutral	EA_Pyrimidine_F_H_neutral_pop.log
	"	"	radical-anion	EA_Pyrimidine_F_H_rad-anion.log
	"	-Me	neutral	EA_Pyrimidine_Me-F_neutral.log
	"	"	radical-anion	EA_Pyrimidine_Me-F_rad-anion.log
	1f-R-F (Quinoline)	-CCH	neutral	EA_Quinoline_F_CCH_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	EA_Quinoline_F_CCH_M11_6-311++Gdp_rad-anion.log
	"	-NCS	neutral	EA_Quinoline_NCS-F_neutral.log
	"	"	radical-anion	EA_Quinoline_NCS-F_rad-anion.log
	"	-Cl	neutral	EA_Quinoline_Cl-F_neutral.log
	"	"	radical-anion	EA_Quinoline_Cl-F_rad-anion.log
	"	-H	neutral	EA_Quinoline_H-F_neutral_pop.log
	"	"	radical-anion	EA_Quinoline_H-F_rad-anion.log
	"	-CCH	SC	TS_KOMe-F_CCH_Quinoline_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CCH_Quinoline_M11_6-311++Gdp.log
	"	"	MI	TS_KOMe-F_CCH_Quinoline_M11_6-311++Gdp_forward.log
	"	-NCS	SC	TS_KOMe-F_NCS_Quinoline_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_NCS_Quinoline_M11_6-311++Gdp.log
	"	"	MI	TS_KOMe-F_NCS_Quinoline_M11_6-311++Gdp_forward.log
	"	-Cl	SC	TS_KOMe-F_Cl_Quinoline_M11_6-311++Gdp_back.log
40	"	"	TS1	TS_KOMe-F_Cl_Quinoline_M11_6-311++Gdp.log
41	"	"	PC	TS_KOMe-F_Cl_Quinoline_M11_6-311++Gdp_forward.log
42	"	-H	SC	TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_back.log
43	"	"	TS1	TS_KOMe-F_H_Quinoline_M11_6-311++Gdp.log
44	"	"	PC	TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_forward.log
45	1g-R-F (Isoquinoline)	-CCH	neutral	EA_Isoquinoline_F_CCH_M11_6-311++Gdp_neutral_pop.log
46	"	"	radical-anion	EA_Isoquinoline_F_CCH_M11_6-311++Gdp_rad-anion.log
47	"	-NCS	neutral	EA_Isoquinoline_F_NCS_M11_6-311++Gdp_neutral_pop.log
48	"	"	radical-anion	EA_Isoquinoline_F_NCS_M11_6-311++Gdp_rad-anion.log
49	"	-Cl	neutral	EA_Isoquinoline_F_Cl_M11_6-311++Gdp_neutral_pop.log
50	"	"	radical-anion	EA_Isoquinoline_F_Cl_M11_6-311++Gdp_rad-anion.log
51	"	-H	neutral	EA_Isoquinoline_F_H_M11_6-311++Gdp_neutral_pop.log
52	"	"	radical-anion	EA_Isoquinoline_F_H_M11_6-311++Gdp_rad-anion.log
53	"	-CCH	SC	TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp_back.log
54	"	"	TS1	TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp.log
55	"	"	MI	TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp_forward.log
	"	-NCS	SC	TS_KOMe-F_NCS_Isoquinoline_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_NCS_Isoquinoline_M11_6-311++Gdp.log
	"	"	MI	TS_KOMe-F_NCS_Isoquinoline_M11_6-311++Gdp_forward.log
	"	-Cl	SC	TS_KOMe-F_Cl_Isoquinoline_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_Cl_Isoquinoline_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_Cl_Isoquinoline_M11_6-311++Gdp_forward.log
	"	-H	SC	TS_KOMe-F_H_Isoquinoline_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_H_Isoquinoline_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_H_Isoquinoline_M11_6-311++Gdp_forward.log
	1h-R-F (Acridine)	-CCH	neutral	EA_Acridine_F_CCH_neutral_pop.log
	"	"	radical-anion	EA_Acridine_F_CCH_rad-anino.log
	"	-NCS	neutral	EA_Acridine_F_NCS_neutral_pop.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
	"	"	radical-anion	EA_Acridine_F_NCS_rad-anion.log
	"	-Cl	neutral	EA_Acridine_F_Cl_neutral_pop.log
	"	"	radical-anion	EA_Acridine_F_Cl_rad-anion.log
	"	-H	neutral	EA_Acridine_F_H_neutral_pop.log
	"	"	radical-anion	EA_Acridine_F_H_rad-anion.log
	"	-Me	neutral	EA_Acridine_F_Me_neutral_pop.log
	"	"	radical-anion	EA_Acridine_F_Me_rad-anion.log
	"	-NHAc	neutral	EA_Acridine_F_NHAc_neutral.log
	"	"	radical-anion	EA_Acridine_F_NHAc_rad-anion.log EA_Acridine_F_NHAc_trial2_neutral_pop.log
	"	-CCH	SC	TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp.log
	"	"	MI	TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward.log
	"	-NCS	SC	TS_KOMe-F_NCS_Acridine_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_NCS_Acridine_M11_6-311++Gdp.log
	"	"	MI	TS_KOMe-F_NCS_Acridine_M11_6-311++Gdp_forward.log
	"	-Cl	SC	TS_KOMe-F_Cl_Acridine_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_Cl_Acridine_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_Cl_Acridine_M11_6-311++Gdp_forward_trial4.log
	"	-H	SC	TS_KOMe-F_H_Acridine_M11_6-311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_H_Acridine_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_H_Acridine_M11_6-311++Gdp_forward.log
	"	-Me	SC	TS_KOMe-F_Me_Acridine_M11_6-311++Gdp_back_trial2.log
	"	"	TS1	TS_KOMe-F_Me_Acridine_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_Me_Acridine_M11_6-311++Gdp_forward_trial2.log
	"	-NHAc	SC	TS_KOMe-F_HNAC_Acridine_M11_6-311++Gdp_back_trial2.log
	"	"	TS1	TS_KOMe-F_HNAC_Acridine_M11_6-311++Gdp.log
	"	"	PC	TS_KOMe-F_HNAC_Acridine_M11_6-311++Gdp_forward.log
	1i-R-F (N-Me-Indole)	-NO2	neutral	EA_NMeIndole_NO2_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_NO2_F_rad-anion.log
	"	-COCF3	neutral	EA_NMeIndole_COCF3_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_COCF3_F_rad-anion.log
	"	-CN	neutral	EA_NMeIndole_CN_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_CN_F_rad-anion.log
	"	-COMe	neutral	EA_NMeIndole_COMe_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_COMe_F_rad-anion.log
	"	-CO2Me	neutral	EA_NMeIndole_CO2Me_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_CO2Me_F_rad-anion.log
	"	-CF3	neutral	EA_NMeIndole_CF3_F_neutral_pop.log
	"	"	radical-anion	EA_NMeIndole_CF3_F_rad-anion.log
	"	-NO2	SC	TS_NMeIndole_KOMe_NO2_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_NMeIndole_KOMe_NO2_F_M11_6-311++Gdp.log
	"	"	MI	TS_NMeIndole_KOMe_NO2_F_M11_6-311++Gdp_forward.log
	"	-COCF3	SC	TS_NMeIndole_KOMe_COCF3_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_NMeIndole_KOMe_COCF3_F_M11_6-311++Gdp.log
	"	"	MI	TS_NMeIndole_KOMe_COCF3_F_M11_6-311++Gdp_forward.log
	"	-CN	SC	TS_NMeIndole_KOMe_CN_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_NMeIndole_KOMe_CN_F_M11_6-311++Gdp.log
	"	"	PC	TS_NMeIndole_KOMe_CN_F_M11_6-311++Gdp_forward.log
	"	-COMe	SC	TS_NMeIndole_KOMe_COMe_F_M11_6-311++Gdp_back.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
	"	"	TS1	TS_NMeIndole_KOMe_COMe_F_M11_6-311++Gdp.log
	"	"	MI	TS_NMeIndole_KOMe_COMe_F_M11_6-311++Gdp_forward.log
	"	-CO2Me	SC	TS_NMeIndole_KOMe_CO2Me_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_NMeIndole_KOMe_CO2Me_F_M11_6-311++Gdp.log
	"	"	PC	TS_NMeIndole_KOMe_CO2Me_F_M11_6-311++Gdp_forward.log
	"	-CF3	SC	TS_NMeIndole_KOMe_CF3_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_NMeIndole_KOMe_CF3_F_M11_6-311++Gdp.log
	"	"	PC	TS_NMeIndole_KOMe_CF3_F_M11_6-311++Gdp_forward.log
	1j-R-F (Benzofuran)	-NO2	neutral	EA_Benzofuran_NO2_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_NO2_F_rad-anion.log
	"	-COCF3	neutral	EA_Benzofuran_COCF3_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_COCF3_F_rad-anion.log
	"	-CN	neutral	EA_Benzofuran_CN_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_CN_F_rad-anion.log
	"	-COMe	neutral	EA_Benzofuran_COMe_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_COMe_F_rad-anion.log
	"	-CO2Me	neutral	EA_Benzofuran_CO2Me_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_CO2Me_F_rad-anion.log
	"	-CF3	neutral	EA_Benzofuran_CF3_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_CF3_F_rad-anion.log
	"	-CCH	neutral	EA_Benzofuran_CCH_F_trial2_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_CCH_F_rad-anion.log
	"	-NCS	neutral	EA_Benzofuran_NCS_F_trial2_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_NCS_F_rad-anion.log
	"	-Cl	neutral	EA_Benzofuran_Cl_F_neutral_pop.log
	"	"	radical-anion	EA_Benzofuran_Cl_F_rad-anion.log
	"	-NO2	SC	TS_Benzofuran_KOMe_NO2_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_NO2_F_M11_6-311++Gdp.log
	"	"	MI	TS_Benzofuran_KOMe_NO2_F_M11_6-311++Gdp_forward.log
	"	-COCF3	SC	TS_Benzofuran_KOMe_COCF3_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_COCF3_F_M11_6-311++Gdp.log
	"	"	MI	TS_Benzofuran_KOMe_COCF3_F_M11_6-311++Gdp_forward.log
	"	-CN	SC	TS_Benzofuran_KOMe_CN_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_CN_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofuran_KOMe_CN_F_M11_6-311++Gdp_forward_trial2.log
	"	-COMe	SC	TS_Benzofuran_KOMe_COMe_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_COMe_F_M11_6-311++Gdp.log
	"	"	MI	TS_Benzofuran_KOMe_COMe_F_M11_6-311++Gdp_forward.log
	"	-CO2Me	SC	TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp_forward_trial2.log
	"	-CF3	SC	TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.log
	"	-CCH	SC	TS_Benzofuran_KOMe_CCH_F_M11_6-311++Gdp_back_trial2.log
	"	"	TS1	TS_Benzofuran_KOMe_CCH_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofuran_KOMe_CCH_F_M11_6-311++Gdp_forward.log
	"	-NCS	SC	TS_Benzofuran_KOMe_NCS_F_M11_6-311++Gdp_back.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
	"	"	TS1	TS_Benzofuran_KOMe_NCS_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofuran_KOMe_NCS_F_M11_6-311++Gdp_forward.log
	"	-Cl	SC	TS_Benzofurn_KOMe_Cl_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benzofurn_KOMe_Cl_F_M11_6-311++Gdp.log
	"	"	PC	TS_Benzofurn_KOMe_Cl_F_M11_6-311++Gdp_forward_trial2.log
	1k-R-F (Benzothiophene)	-CN	neutral	Benzothiophene_CN_F_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	Benzothiophene_CN_F_M11_6-311++Gdp_rad-anion.log
	"	-COMe	neutral	Benothiophene_COMe_F_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	Benothiophene_COMe_F_M11_6-311++Gdp_rad-anion.log
	"	-CO2Me	neutral	EA_Benzothiophene_CO2Me-F_neutral.log
	"	"	radical-anion	EA_Benzothiophene_CO2Me-F_rad-anion.log
	"	-CF3	neutral	EA_Benzothiophene_CF3-F_neutral.log
	"	"	radical-anion	EA_Benzothiophene_CF3-F_rad-anion.log
	"	-CCH	neutral	Benzothiophene_CCH_F_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	Benzothiophene_CCH_F_M11_6-311++Gdp_rad-anion.log
	"	-NCS	neutral	Benzothiophene_NCS_F_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	Benzothiophene_NCS_F_M11_6-311++Gdp_rad-anion.log
	"	-Cl	neutral	Benzothiophene_Cl_F_M11_6-311++Gdp_neutral_pop.log
	"	"	radical-anion	Benzothiophene_Cl_F_M11_6-311++Gdp_rad-anion.log
	"	-CN	SC	TS_Benothiophene_KOMe_CN_F_M11_6-311++Gdp_back.log
	"	"	TS1	TS_Benothiophene_KOMe_CN_F_M11_6-311++Gdp.log
56	"	"	MI	TS_Benothiophene_KOMe_CN_F_M11_6-311++Gdp_forward.log
57	"	-COMe	SC	TS_Benothiophene_KOMe_COMe_F_M11_6-311++Gdp_back.log
58	"	"	TS1	TS_Benothiophene_KOMe_COMe_F_M11_6-311++Gdp.log
59	"	"	MI	TS_Benothiophene_KOMe_COMe_F_M11_6-311++Gdp_forward.log
60	"	-CO2Me	SC	TS_Benothiophene_KOMe_CO2Me_F_M11_6-311++Gdp_back.log
61	"	"	TS1	TS_Benothiophene_KOMe_CO2Me_F_M11_6-311++Gdp.log
62	"	"	MI	TS_Benothiophene_KOMe_CO2Me_F_M11_6-311++Gdp_forward.log
63	"	-CF3	SC	TS_Benothiophene_KOMe_CF3_F_M11_6-311++Gdp_back.log
64	"	"	TS1	TS_Benothiophene_KOMe_CF3_F_M11_6-311++Gdp.log
65	"	"	PC	TS_Benothiophene_KOMe_CF3_F_M11_6-311++Gdp_forward_trial2.log
66	"	-CCH	SC	TS_Benzothiophene_KOMe_CCH_F_M11_6-311++Gdp_back.log
67	"	"	TS1	TS_Benzothiophene_KOMe_CCH_F_M11_6-311++Gdp.log
68	"	"	PC	TS_Benzothiophene_KOMe_CCH_F_M11_6-311++Gdp_forward.log
69	"	-NCS	SC	TS_Benzothiophene_KOMe_NCS_F_M11_6-311++Gdp_back.log
70	"	"	TS1	TS_Benzothiophene_KOMe_NCS_F_M11_6-311++Gdp.log
71	"	"	PC	TS_Benzothiophene_KOMe_NCS_F_M11_6-311++Gdp_forward.log
72	"	-Cl	SC	TS_Benzothiophene_KOMe_Cl_F_M11_6-311++Gdp_back.log
73	"	"	TS1	TS_Benzothiophene_KOMe_Cl_F_M11_6-311++Gdp.log
74	"	"	PC	TS_Benzothiophene_KOMe_Cl_F_M11_6-311++Gdp_forward.log
75	1l-R-F (N-Me-Pyrrole)	-NO2	neutral	EA_NMePyrrole_F_NO2_neutral_pop.log
76	"	"	radical-anion	EA_NMePyrrole_F_NO2_rad-anion.log
77	"	-CHCCN2	neutral	EA_NMePyrrole_F_CHCCN2_neutral_pop.log
78	"	"	radical-anion	EA_NMePyrrole_F_CHCCN2_rad-anion.log
79	"	-COCF3	neutral	EA_NMePyrrole_F_COCF3_neutral_pop.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
80	"	"	radical-anion	EA_NMePyrrole_F_COCF3_rad-anion.log
81	"	-CN	neutral	EA_NMePyrrole_F_CN_neutral_pop.log
82	"	"	radical-anion	EA_NMePyrrole_F_CN_rad-anion_trial2.log
83	"	-COMe	neutral	EA_NMePyrrole_F_COMe_neutral_pop.log
84	"	"	radical-anion	EA_NMePyrrole_F_COMe_rad-anion.log
85	"	-CO2Me	neutral	EA_NMePyrrole_F_CO2Me_neutral_pop.log
86	"	"	radical-anion	EA_NMePyrrole_F_CO2Me_rad-anion.log
	"	-CF3	neutral	EA_NMePyrrole_F_CF3_neutral_pop.log
	"	"	radical-anion	EA_NMePyrrole_F_CF3_rad-anion.log
	"	-NO2	SC	TS_KOMe-F_NO2_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_NO2_NMePyrrole_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_NO2_NMePyrrole_M11-6311++Gdp_forward.log
	"	-CHCCN2	SC	TS_KOMe-F_CHCCN2_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CHCCN2_NMePyrrole_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_CHCCN2_NMePyrrole_M11-6311++Gdp_forward.log
	"	-COCF3	SC	TS_KOMe-F_COCF3_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_COCF3_NMePyrrole_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_COCF3_NMePyrrole_M11-6311++Gdp_forward.log
	"	-CN	SC	TS_KOMe-F_CN_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CN_NMePyrrole_M11-6311++Gdp.log
	"	"	PC	TS_KOMe-F_CN_NMePyrrole_M11-6311++Gdp_forward_trial2.log
	"	-COMe	SC	TS_KOMe-F_COMe_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_COMe_NMePyrrole_M11-6311++Gdp_trial2.log
	"	"	PC	TS_KOMe-F_COMe_NMePyrrole_M11-6311++Gdp_forward.log
	"	-CO2Me	SC	TS_KOMe-F_CO2Me_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CO2Me_NMePyrrole_M11-6311++Gdp.log
	"	"	PC	TS_KOMe-F_CO2Me_NMePyrrole_M11-6311++Gdp_forward.log
	"	-CF3	SC	TS_KOMe-F_CF3_NMePyrrole_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CF3_NMePyrrole_M11-6311++Gdp.log
	"	"	PC	TS_KOMe-F_CF3_NMePyrrole_M11-6311++Gdp_forward_trial4.log
	1m-R-F (Furan)	-NO2	neutral	Furan_F_NO2_neutral_pop.log
	"	"	radical-anion	Furan_F_NO2_rad-anion.log
	"	-COCF3	neutral	Furan_F_COCF3_neutral_pop.log
	"	"	radical-anion	Furan_F_COCF3_rad-anion.log
	"	-CN	neutral	Furan_F_CN_neutral_pop.log
	"	"	radical-anion	Furan_F_CN_rad-anion.log
	"	-COMe	neutral	Furan_F_COMe_neutral_pop.log
	"	"	radical-anion	Furan_F_COMe_rad-anion.log
	"	-CO2Me	neutral	Furan_F_CO2Me_neutral_pop.log
	"	"	radical-anion	Furan_F_CO2Me_rad-anion.log
	"	-CF3	neutral	Furan_F_CF3_neutral_pop.log
	"	"	radical-anion	Furan_F_CF3_rad-anion_trial3.log
	"	-CCH	neutral	Furan_F_CCH_neutral_pop.log
	"	"	radical-anion	Furan_F_CCH_rad-anion.log
	"	-NCS	neutral	Furan_F_NCS_neutral_pop.log
	"	"	radical-anion	Furan_F_NCS_rad-anion.log
	"	-NO2	SC	TS_KOMe-F_NO2_Furan_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_NO2_Furan_M11-6311++Gdp_trial2.log
	"	"	MI	TS_KOMe-F_NO2_Furan_M11-6311++Gdp_forward.log
	"	-COCF3	SC	TS_KOMe-F_COCF3_Furan_M11-6311++Gdp_back.log

Entry	Aromatic system (sub folder)	-R (sub folder)	Reaction Coordinate ^[a]	File name
	"	"	TS1	TS_KOMe-F_COCF3_Furan_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_COCF3_Furan_M11-6311++Gdp_forward.log
	"	-CN	SC	TS_KOMe-F_CN_Furan_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CN_Furan_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_CN_Furan_M11-6311++Gdp_forward.log
	"	-COMe	SC	TS_KOMe-F_COMe_Furan_M11-6311++Gdp_back_trial2.log
	"	"	TS1	TS_KOMe-F_COMe_Furan_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_COMe_Furan_M11-6311++Gdp_forward.log
	"	-CO2Me	SC	TS_KOMe-F_CO2Me_Furan_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CO2Me_Furan_M11-6311++Gdp.log
	"	"	MI	TS_KOMe-F_CO2Me_Furan_M11-6311++Gdp_forward.log
	"	-CF3	SC	TS_KOMe-F_CF3_Furan_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CF3_Furan_M11-6311++Gdp.log
	"	"	PC	TS_KOMe-F_CF3_Furan_M11-6311++Gdp_forward.log
	"	-CCH	SC	TS_KOMe-F_CCH_Furan_M11-6311++Gdp_back.log
	"	"	TS1	TS_KOMe-F_CCH_Furan_M11-6311++Gdp_trial2.log
		"	PC	TS_KOMe-F_CCH_Furan_M11-6311++Gdp_forward.log
87		-NCS	SC	TS_KOMe-F_NCS_Furan_M11-6311++Gdp_back.log
		"	TS1	TS_KOMe-F_NCS_Furan_M11-6311++Gdp.log
		"	PC	TS_KOMe-F_NCS_Furan_M11-6311++Gdp_forward_trial2.log

[a] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TS1: first transition state; MI: Meisenheimer intermediate; TS2: second transition state; PC: product complex, neutral: the neutral species (used for EA calculation); radical-anion: the radical anion species (no counter cation included, used for EA calculation).

3.6. S_NAr Mechanism and the Hammett Correlation

The log files for the Hammett correlation studies shown in Figure 6, and Figure SI-9 can be found in Table SI-3-7.

4. References

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