Supporting Information

Computational Study on the Boundary Between the Concerted and Stepwise Mechanism of Bimolecular $S_N$Ar Reactions

Simon Rohrbach, John A. Murphy* and Tell Tuttle*
*John.Murphy@strath.ac.uk
*tell.tuttle@strath.ac.uk
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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 \(\sigma_p^-\) Scale

The \(\sigma_p^-\) values were taken from the landmark review by Hansch et al.\(^10\) A selection of para-substituents and their associated \(\sigma_p^-\) 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 \(\sigma_p^-\) Values

| Entry | para-Substituent -R | \(\sigma_p^-\) |
|-------|---------------------|---------|
| 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\(_N\)Ar 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 description 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. 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 $S_N$Ar reactions. A satisfactorily well performing functional was identified for the further study of $S_N$Ar reaction mechanisms.

The $S_N$Ar 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 $\sigma_p$ 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 $S_N$Ar 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 $S_N$Ar 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.\cite{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 $\omega$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

Is there a stable intermediate on the reaction pathway?

Figure SI-1 Four $S_N$Ar reactions ($R = $-COCF$_3$, -CN, -COMe, -CO$_2$Me) were selected to benchmark DFT functionals against the results obtained with a high-level wave-function based method.
The mechanistic transition point on the Hammett $\sigma_p^-$ 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 $S_{\text{N}}Ar$ mechanism’, ‘c’ stands for ‘concerted $S_{\text{N}}Ar$ mechanism’. [a] The aug-cc-pVTZ basis set was used.

If a stable intermediate can be located, the reaction is classified as stepwise and otherwise as concerted.

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 $\tau$ 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 $\omega$B97XD functionals were the two top-runners and the more modern M11 functional was selected for the further study.

**Figure SI-2** The mechanistic transition point on the Hammett $\sigma_p^-$ 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 $S_{\text{N}}Ar$ mechanism’, ‘c’ stands for ‘concerted $S_{\text{N}}Ar$ mechanism’. [a] The aug-cc-pVTZ basis set was used.
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 |
|-------------|------|------|------|-------------------------|
| $\omega$B97XD | 0.74 | 0.64 | 0.64 | 1.09                    |
| M11         | 0.96 | -0.85| 0.85 | 1.49                    |
| $\omega$B97 | 1.11 | 1.00 | 1.00 | 1.56                    |
| MP2*       | 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                    |
| $\omega$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 $\tau$ 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 \(-R = -\text{COF}_3\) 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 $S_NAr$ 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,

| \(-R\)          | $\sigma_p$ | Mechanism\[^a^\] | Int1\[^b^\] | IRC\[^c^\] | TS2\[^d^\] (kcal/mol) |
|-----------------|------------|------------------|-------------|------------|------------------------|
| \(-\text{NO}_2\) | 1.27       | stepwise         | yes         | -          | 1.61                   |
| \(-\text{CHC(CN)}_2\) | 1.20       | stepwise         | yes         | -          | 3.01                   |
| \(-\text{COF}_3\) | 1.09       | stepwise         | yes         | MI         | 1.37                   |
| \(-\text{CN}\)   | 1.00       | concerted        | no          | MI         | not found\[^e^\]       |
| \(-\text{COMe}\) | 0.84       | concerted        | no          | (MI)\[^f^\] | 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 \(-R = -\text{CO}_2\text{Me}\), 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 \(S\text{N}_\text{Ar}\) 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\(^{[12,10]}\) (Scheme SI-1). The predicted activation energy deviated by only 1 kcal/mol from the experimental\(^{[12]}\) value. Similarly, we calculated the activation energy of the \(S\text{N}_\text{Ar}\) reaction between potassium methoxide and \(\text{para}\)-methoxyfluorobenzene (Scheme SI-2).\(^{[12,10]}\) 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.\(^{[12,10]}\) 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 \(S\text{N}_\text{Ar}\) 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 \(S\text{N}_\text{Ar}\) reaction. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).
The reaction was performed in an aqueous solvent system of water-dioxane 9:1. 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.

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

| Entry | Nu       | Ar | TS1 w.r.t. MI (kcal/mol)^[b] | MI w.r.t. MI (kcal/mol)^[c] | 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^[d] | a | 1.31                        | 11.7                        | 6.38                        |
| 6     | Morpholine^[d] | a | 1.95                        | 11.0                        | 5.05                        |

[a] Level of theory: M11/6-311++G(d,p)/cpcm(H_2O).
[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 computational results stand in apparent contradiction to the interpretation of the kinetic studies that were performed by Williams et al. for this class of $S_N$Ar reactions.\textsuperscript{[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.\textsuperscript{[17]} In that sense, the computational results support the interpretation of Williams' kinetic data. Following conventional experimental approaches, these $S_N$Ar 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 $S_N$Ar 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 \textit{para}-nitroso substituent that was included in the $\sigma_p^-$ 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 \textit{para}-nitroso substituent. Obviously the mechanistic turning point for these reaction series lies beyond the applied $\sigma_p^-$ 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 $\sigma_p^-$ 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

| KY   | -X | -F | -Cl | -Br | -I |
|------|----|----|-----|-----|----|
| KF   | 0.59\textsuperscript{[a]} | >1.63\textsuperscript{[b]} | >1.63 | >1.63 | |
| KCl  | >1.63 | >1.63 | >1.63 | >1.63 | |
| KBr  | >1.63 | >1.63 | >1.63 | |
| KI   |     |     |     |     | >1.63 |

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

\textsuperscript{[b]} The \textit{para}-nitroso substituent marks the upper limit ($\sigma_p^- = 1.63$) of the applied $\sigma_p^-$ 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\textsubscript{N}Ar reaction (i.e. the value of $\tau^-$ 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 $\tau^-$ 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\textsubscript{N}Ar 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 $\tau^-$. The addition of a second molecule of DMF led to a significant blurring of the mechanistic turning point, which manifests in an increase of $\Delta\sigma^-$ from 0.05 to 0.22. Also, the value $\tau^-$ decreased slightly by 0.18 units. However, since the mechanistic turning point is no longer sharp, it is not clear whether this decrease of $\tau^-$ 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 $\tau^-$. 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.

| $\tau^-$ values for the chalcogen-chalcogen exchange reactions | \(\text{KYMe}^{-}\text{XMe}^{-}\) | \(\text{KYMe}^{-}\text{OMe}^{-}\) | \(\text{KYMe}^{-}\text{SMe}^{-}\) | \(\text{KYMe}^{-}\text{SeMe}^{-}\) |
|---|---|---|---|---|
| KOMe | $<-0.77$\textsuperscript{[a]} | 0.27 | 0.64 |
| KSMe | 0.31 | 0.92 |
| KSeMe | | 0.70 |

[a] The para-triphenylphosphinimine [-NP(Ph)\textsubscript{3}] substituent marks the lower limit ($\sigma^p = -0.77$) of the applied $\sigma^p$-scale.

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Table SI-2-5 Chalcogen Exchange Reactions

![Chemical structure](Image)
2.4. Effect of the Nucleophile

In Figure 3 in the main text it became apparent that the series of $S_{N}Ar$ reactions with nucleophile $2e-K$

![Diagram showing $S_{N}Ar$ reaction between $R-F$ and $K-OMe$ leading to $R-OMe$ and $K-F$.]

**Figure SI-5** Transition state for the $S_{N}Ar$ reaction between $580$ ($R = NO_2$) 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 $R = NO_2$) 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$_N$Ar Pathway**

During the reviewing process it was pointed out that the highly activated substrates $1a-R-F$ with $R = NO$, NO$_2$ 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$_N$Ar 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$_N$Ar 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$_N$Ar pathway (Entry 5). The log files for the SET calculations are listed in Table SI-3-10 (page 43).

| Entry | Nucleophile | R in 1a-R-F | $\Delta G_{S_N Ar}$ (kcal/mol)$^a$ | $\Delta G^*_{S_N Ar}$ (kcal/mol) | $\Delta G_{SET}$ (kcal/mol) | $\Delta G^*_{SET}$ (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$_N$Ar product.
Figure SI-6 The mechanistic turning point was investigated for the $S_N$Ar 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 $S_N$Ar 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, $\tau_p^-$ 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 $\tau_p^-$ 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 $\tau_p^-$ with an average $\tau_p^-$ of 0.77 ± 0.10. The nucleophile 2d, in contrast, massively deviated from this average value. In fact, the $S_N$Ar reaction with this nucleophile favoured a stepwise $S_N$Ar reaction even with electron-donating substituents such as para-methyl or para-NHAc residues. Presumably, $\pi$-$\pi$-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 $\tau_p^-$. 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 $\tau_p^-$ 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 ($R = CHC(CN)_2, COCF_3$ 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 $S_N$Ar 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 $S_N$Ar 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 | $\Delta G$ $S_N$Ar (kcal/mol)$^a$ | $\Delta G^*$ $S_N$Ar (kcal/mol) | $\Delta G$ Deprotonation (kcal/mol) | $\Delta p\text{Ka}$$^{[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 $\Delta p\text{Ka}$ values were calculated according to $\Delta p\text{Ka} = \Delta G/RT$ 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.
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 $\tau_p$. This allows us to investigate steric effects by choosing a bulky and a slim nucleophile. Any significant difference in $\tau_p$ 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 $\tau_p$ remains constant throughout this series. With the sterically more bulky nucleophile $2d$-$K$, the situation is different. While there is no difference in $\tau_p$ between $2c$-$K$ and $2d$-$K$ for the substrates $1a-F$ and $30$, the value of $\tau_p$ sharply decreases for the reaction of $2d$-$K$ when a second ortho-methyl group is present as in...
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\textsubscript{N}Ar 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 \( \tau_p \) 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\textsubscript{N}Ar 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\textsubscript{N}Ar 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\textsubscript{N}Ar 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\textsubscript{N}Ar 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\textsubscript{N}Ar 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 \( \text{ca. 0.4 Å}^{[18]} \) 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 \( \Delta G^* \) show a good \( (R^2 > 0.9) \) correlation vs the Hammett substitution constant \( \sigma_p \) 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 \( \Delta G^\circ \) 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 \( \Delta G^\circ \) shows no significant correlation with the Hammett \( \sigma_p \) constant, in contrast to \( \Delta G^* \).
Figure SI-9 Geometry change of the transition state structure vs. the Hammett substitution constant $\sigma_p^-$ 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 $\Delta G^*$ vs. the Hammett substitution constant $\sigma_p$ for the displacement of fluoride from the phenyl fluoride series $1a-R-F$ by the nucleophiles $2b-K$ (x), $2d-K$ (Δ), $2e-K$ (+) and $2f-K$ (o). Level of theory: M11/6-311++G(d,p)/cpcm(DMF).

Figure SI-11 Correlation of the activation energy $\Delta G^*$ vs. the Hammett substitution constant $\sigma_p$ for the displacement of fluoride from the naphthly fluoride series $1b-R-F$ 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-12 Correlation of the activation energy $\Delta G^*$ vs. the Hammett substitution constant $\sigma^-$ for the displacement of fluoride from the 2-pyridyl fluoride series 1d-R-F by the nucleophiles 2a-K ($\times$), 2b-K ($\Delta$), 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 $\Delta G^*$ and $\Delta G^\circ$ vs. the Hammett substitution constant $\sigma^-$ for the displacement of fluoride from the phenyl fluoride series 1a-R-F by the nucleophiles 2c-K. Level of theory: M11/6-311++G(d,p)/cpcm(DMF).
**Figure SI-14** Correlation of the activation energy $\Delta G^*$ and $\Delta G^\circ$ vs. the Hammett substitution constant $\sigma^*$ 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 $\Delta G^*$ and $\Delta G^\circ$ vs. the Hammett substitution constant $\sigma^*$ 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 $S_N$Ar Mechanism of Substrates with a Simple Descriptor

As illustrated in Figure 6 in the main text, the $S_N$Ar 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](image)

**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.

| Entry | Method (fold- | -R (sub folder | Reaction Coordinate | File name |
|-------|---------------|---------------|---------------------|------------|
|       | er name)      | name) name)   |                     |            |
| 1     | MP2           | -COCF<sub>3</sub> | SC                 | TS_COCF3_MP2_aug-cc-pVTZ_back_trial3.log |
| 2     | "             | -COCF<sub>3</sub> | TS1                | TS_COCF3_MP2_aug-cc-pVTZ_trial3_freq.log |
| 3     | "             | -COCF<sub>3</sub> | MI                 | TS_COCF3_MP2_aug-cc-pVTZ_forward_freq.log |
| 4     | "             | -CN            | SC                 | TS_CN_MP2-aug-cc-pVTZ_back_trial2.log |
| 5     | "             | -CN            | TS                 | TS_CN_MP2-aug-cc-pVTZ |
| 6     | "             | -CN            | MI                 | TS_CN_MP2-aug-cc-pVTZ_forward_trial5.log |
| 7     | "             | -COMe          | SC                 | TS_COMe_MP2-aug-cc-pVTZ_back.log |
| 8     | "             | -COMe          | TS                 | TS_COMe_MP2-aug-cc-pVTZ_trial5_step13_freq.log |
| 9     | "             | -COMe          | PC                 | TS_COMe_MP2-aug-cc-pVTZ_forward_trial7_freq.log |
| 10    | "             | -COMe          | TS                 | TS_COMe_MP2-aug-cc-pVTZ_forward_trial7_freq.log |
| 11    | "             | -COMe          | TS                 | TS_COMe_MP2-aug-cc-pVTZ_forward_trial7_freq.log |
| 12    | "             | -CO<sub>2</sub>Me | SC                 | TS_CO2Me_MP2-aug-cc-pVTZ_back.log |
| 13    | MP2           | -COCF<sub>3</sub> | SC                 | TS_COCF3_MP2_6311++Gdp_back_trial2.log |
| 14    | "             | -COCF<sub>3</sub> | TS1                | TS_COCF3_MP2_6311++Gdp_trial4.log |
| 15    | "             | -COCF<sub>3</sub> | MI                 | TS_COCF3_MP2_6311++Gdp_forward.log |
| 16    | "             | -CN            | SC                 | TS_CN_MP2-6311++Gdp_back.log |
| 17    | "             | -CN            | TS                 | TS_CN_MP2-6311++Gdp_trial3.log |
| 18    | "             | -CN            | MI                 | TS_CN_MP2-6311++Gdp_forward.log |
| 19    | "             | -COMe          | SC                 | TS_COMe_MP2-6311++Gdp_back_trial10_freq.log |
| 20    | "             | -COMe          | TS                 | TS_COMe_MP2-6311++Gdp_trial4_freq.log |
| 21    | "             | -COMe          | PC                 | TS_COMe_MP2-6311++Gdp_forward_trial2.log |
| 22    | "             | -COMe          | SC                 | TS_CO2Me_MP2_6311++Gdp_back.log |
| 23    | "             | -COMe          | TS                 | TS_CO2Me_MP2_6311++Gdp_trial3.log |
| 24    | "             | -COMe          | PC                 | TS_CO2Me_MP2_6311++Gdp_forward_trial3.log |
| 25    | B3PW91        | -COCF<sub>3</sub> | SC                 | TS_COCF3_B3PW91_6-311++Gdp_back_trial3.log |
| 26    | "             | -COCF<sub>3</sub> | TS1                | TS_COCF3_B3PW91_6-311++Gdp.log |
| 27    | "             | -COCF<sub>3</sub> | 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 |
| 30    | "             | -CN            | PC                 | TS_CN_B3PW91_6-311++Gdp_forward_trial2.log |
| 31    | "             | -COMe          | SC                 | TS_COMe_B3PW91_6-311++Gdp_back_trial5.log |
| 32    | "             | -COMe          | TS                 | TS_COMe_B3PW91_6-311++Gdp_forward_trial3.log |
| 33    | "             | -COMe          | PC                 | TS_COMe_B3PW91_6-311++Gdp_forward_trial3.log |
| 34    | "             | -COMe          | SC                 | TS_CO2Me_B3PW91_6-311++Gdp_back_trial4.log |
| 35    | "             | -COMe          | TS                 | TS_CO2Me_B3PW91_6-311++Gdp.log |
| 36    | "             | -COMe          | PC                 | TS_CO2Me_B3PW91_6-311++Gdp_forward_trial2_freq.log |
| 37    | B3LYP         | -NO2           | SC                 | TS_NO2_F_MeO_B3LYP_back_trial4.log |
| 38    | "             | -NO2           | TS1                | TS_NO2_F_MeO_B3LYP_trial2.log |
| 39    | "             | -NO2           | MI                 | TS_NO2_F_MeO_B3LYP_forward.log |
| Entry | Method (folder name) | -R (sub folder name) | Reaction Coordinate | File name |
|-------|---------------------|---------------------|--------------------|-----------|
| 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_forward.log |
| 54    | "                   | -NO2               | MI                 | TS_NO2_F_MeO_B3LYP-D3BJ_forward_trial5.log |
| 55    | "                   | -COCF\(_3\)        | SC                 | TS_COCF3_B3LYP-D3BJ-6311++Gdp_back_trial4.log |
| 56    | "                   | -COCF\(_3\)        | TS1                | TS_COCF3_B3LYP-D3BJ-6311++Gdp_trial.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    | "                   | -COMe              | SC                 | TS_COMe_B3LYP-D3BJ-6311++Gdp_back_trial5.log |
| 65    | "                   | -COMe              | TS                 | TS_COMe_B3LYP-D3BJ-6311++Gdp_forward_trial2.log |
| 66    | "                   | -COMe              | PC                 | TS_COMe_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 |
| 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 (fold-er name) | -R (sub folder name) | Reaction Coordinate | 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   | "                   | -COCF$_3$          | TS1                 | TS_COCF3_M06L-6311++Gdp_trial2.log |
| 101   | "                   | -COMe              | TS                  | TS_COMe_M06L-6311++Gdp_trial3.log |
| 102   | "                   | -COMe              | PC                  | TS_COMe_M06L-6311++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   | "                   | -COMe              | SC                  | TS_COMe_M06-6311++Gdp_back_trial3.log |
| 113   | "                   | -COMe              | TS                  | TS_COMe_M06-6311++Gdp.log |
| 114   | "                   | -COMe              | PC                  | TS_COMe_M06-6311++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   | "                   | -COMe              | SC                  | TS_COMe_M062X-6311++Gdp_back.log |
| 125   | "                   | -COMe              | TS                  | TS_COMe_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_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   | "                   | -CH(CN)$_2$        | SC                  | TS_KOMe_CHCCCN2_F_M11_6-311++Gdp_back_trial4.log |
| 139   | "                   | -CH(CN)$_2$        | TS1                 | TS_KOMe_CHCCCN2_F_M11_6-311++Gdp.log |
| Entry | Method\(^a\) (fold-er 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.forward2.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.forward3.log |
| 148   | "                           | -COCF\(_3\)         | IRC+                    | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.log |
|       |                             |                     |                         | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.forward.log |
|       |                             |                     |                         | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.forward4.log |
|       |                             |                     |                         | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.forward5.log |
|       |                             |                     |                         | IRC_TS1_reverse_COCF3_M11_6-311++Gdp.forward6.log |
| 149   | "                           | -COCF\(_3\)         | IRC-                    | IRC_TS1_forward_COCF3_M11_6-311++Gdp.log |
|       |                             |                     |                         | IRC_TS1_forward_COCF3_M11_6-311++Gdp.forward2.log |
|       |                             |                     |                         | IRC_TS1_forward_COCF3_M11_6-311++Gdp.forward3.log |
| 150   | "                           | -CN                   | SC                      | TS_CN_M11_6-311++Gdp.forward3.log |
| 151   | "                           | -CN                   | TS                      | TS_CN_M11_6-311++Gdp.forward3.log |
| 152   | "                           | -CN                   | PC                      | TS_CN_M11_6-311++Gdp.forward3.log |
| 153   | "                           | -CN                   | IRC+                    | IRC_CN_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CN_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CN_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CN_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CN_M11_6-311++Gdp.forward3.log |
| 154   | "                           | -CN                   | IRC-                    | IRC_CN_M11_6-311++Gdp.forward3.log |
| 155   | "                           | -CN                   | Freq                    | Intermediate_by_IRC_reverse_CN_M11_6-311++Gdp.forward3.log |
| 156   | "                           | -CN                   | BS                      | BS2_CN_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | BS2_CN_M11_6-311++Gdp.forward3.log |
| 157   | "                           | -COMe                 | SC                      | TS_COMe_M11_6-311++Gdp.forward3.log |
| 158   | "                           | -COMe                 | TS                      | TS_COMe_M11_6-311++Gdp.forward3.log |
| 159   | "                           | -COMe                 | PC                      | TS_COMe_M11_6-311++Gdp.forward3.log |
| 160   | "                           | -COMe                 | IRC+                    | IRC_COMe_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_COMe_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_COMe_M11_6-311++Gdp.forward3.log |
| 161   | "                           | -COMe                 | IRC-                    | IRC_COMe_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_COMe_M11_6-311++Gdp.forward3.log |
| 162   | "                           | -COMe                 | Freq                    | Intermediate_by_IRC_reverse_COMe_M11_6-311++Gdp.forward3.log |
| 163   | "                           | -COMe                 | BS                      | BS2_COMe_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | BS2_COMe_M11_6-311++Gdp.forward3.log |
| 164   | "                           | -CO\(_2\)Me          | SC                      | TS_CO2Me_M11_6-311++Gdp.forward3.log |
| 165   | "                           | -CO\(_2\)Me          | TS                      | TS_CO2Me_M11_6-311++Gdp.forward3.log |
| 166   | "                           | -CO\(_2\)Me          | PC                      | TS_CO2Me_M11_6-311++Gdp.forward3.log |
| 167   | "                           | -CO\(_2\)Me          | IRC+                    | IRC_CO2Me_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CO2Me_M11_6-311++Gdp.forward3.log |
|       |                             |                     |                         | IRC_CO2Me_M11_6-311++Gdp.forward3.log |
| 168   | "                           | -CO\(_2\)Me          | IRC-                    | IRC_CO2Me_M11_6-311++Gdp.forward3.log |
| 169   | PBE0                        | -COCF\(_3\)         | SC                      | TS_COCF3_PBE0-6311++Gdp.forward4.log |
| 170   | "                           | -COCF\(_3\)         | TS1                     | TS_COCF3_PBE0-6311++Gdp.forward4.log |
| 171   | "                           | -COCF\(_3\)         | MI                      | TS_COCF3_PBE0-6311++Gdp.forward4.log |
| 172   | "                           | -CN                   | SC                      | TS_CN_PBE0-6311++Gdp.forward3.log |
| 173   | "                           | -CN                   | TS                      | TS_CN_PBE0-6311++Gdp.forward3.log |
| 174   | "                           | -CN                   | PC                      | TS_CN_PBE0-6311++Gdp.forward3.log |
| 175   | "                           | -COMe                 | SC                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| 176   | "                           | -COMe                 | TS                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| 177   | "                           | -COMe                 | PC                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| 178   | "                           | -COMe                 | SC                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| 179   | "                           | -COMe                 | TS                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| 180   | "                           | -COMe                 | PC                      | TS_COMe_PBE0-6311++Gdp.forward3.log |
| Entry | Method<sup>a</sup> (fold-er name) | -R (sub folder name) | Reaction Coordinate<sup>b</sup> | File name |
|-------|-----------------------------------|---------------------|------------------------------|-----------|
| 181   | PBE0-D3-BJ                        | -COCF<sub>3</sub>   | SC                           | TS_COCF3_PBE0-D3BJ_6311++Gdp_back_trial3.log |
| 182   | "                                 | -COCF<sub>3</sub>   | TS1                          | TS_COCF3_PBE0-D3BJ_6311++Gdp.log |
| 183   | "                                 | -COCF<sub>3</sub>   | 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<sub>2</sub>Me  | SC                           | TS_CO2Me_PBE0-D3BJ_6-311++Gdp_back_trial4.log |
| 191   | "                                 | -CO<sub>2</sub>Me  | TS                           | TS_CO2Me_PBE0-D3BJ_6-311++Gdp_forward_trial2.log |
| 192   | "                                 | -CO<sub>2</sub>Me  | PC                           | TS_CO2Me_PBE0-D3BJ_6-311++Gdp_forward_trial3.log |
| 193   | HSE1PBE                           | -COCF<sub>3</sub>   | SC                           | TS_COCF3_HSE1PBE_6-311++Gdp_back_trial4.log |
| 194   | "                                 | -COCF<sub>3</sub>   | TS1                          | TS_COCF3_HSE1PBE_6-311++Gdp.log |
| 195   | "                                 | -COCF<sub>3</sub>   | MI                           | TS_COCF3_HSE1PBE_6-311++Gdp_forward.log |
| 196   | "                                 | -CN                | SC                           | TS_HSE1PBE_6-311++Gdp_back_trial2.log |
| 197   | "                                 | -CN                | TS                           | TS_HSE1PBE_6-311++Gdp.log |
| 198   | "                                 | -CN                | PC                           | TS_HSE1PBE_6-311++Gdp_forward_trial3.log |
| 199   | "                                 | -COMe              | SC                           | TS_COMe_HSE1PBE_6-311++Gdp_back_trial2.log |
| 200   | "                                 | -COMe              | TS                           | TS_COMe_HSE1PBE_6-311++Gdp_forward_trial2.log |
| 201   | "                                 | -COMe              | PC                           | TS_COMe_HSE1PBE_6-311++Gdp_forward_trial2.log |
| 202   | "                                 | -CO<sub>2</sub>Me  | SC                           | TS_CO2Me_HSE1PBE_6-311++Gdp_back_trial2.log |
| 203   | "                                 | -CO<sub>2</sub>Me  | TS                           | TS_CO2Me_HSE1PBE_6-311++Gdp_forward_trial2.log |
| 204   | "                                 | -CO<sub>2</sub>Me  | PC                           | TS_CO2Me_HSE1PBE_6-311++Gdp_forward_trial2.log |
| 205   | B97D                              | -COCF<sub>3</sub>   | SC                           | TS_COCF3_B97D_6-311++Gdp_back_trial5.log |
| 206   | "                                 | -COCF<sub>3</sub>   | TS1                          | TS_COCF3_B97D_6-311++Gdp_trial2_freq.log |
| 207   | "                                 | -COCF<sub>3</sub>   | 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<sub>2</sub>Me  | SC                           | TS_CO2Me_B97D_6-311++Gdp_back_trial2.log |
| 215   | "                                 | -CO<sub>2</sub>Me  | TS                           | TS_CO2Me_B97D_6-311++Gdp.log |
| 216   | "                                 | -CO<sub>2</sub>Me  | PC                           | TS_CO2Me_B97D_6-311++Gdp_forward_trial2.log |
| 217   | wB97                              | -COCF<sub>3</sub>   | SC                           | TS_COCF3_wB97-6-311++Gdp_back_trial3.log |
| 218   | "                                 | -COCF<sub>3</sub>   | TS1                          | TS_COCF3_wB97-6-311++Gdp.log |
| 219   | "                                 | -COCF<sub>3</sub>   | 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<sub>2</sub>Me  | SC                           | TS_CO2Me_wB97_6-311++Gdp_back_trial4.log |
| 227   | "                                 | -CO<sub>2</sub>Me  | TS                           | TS_CO2Me_wB97_6-311++Gdp.log |
| 228   | "                                 | -CO<sub>2</sub>Me  | PC                           | TS_CO2Me_wB97_6-311++Gdp_forward_trial2.log |
| 229   | wB97X                             | -COCF<sub>3</sub>   | SC                           | TS_COCF3_wB97X-6-311++Gdp_back_trial4.log |
| 230   | "                                 | -COCF<sub>3</sub>   | TS1                          | TS_COCF3_wB97X-6-311++Gdp.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_N2Ar 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_N2Ar reaction coordinate. 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 form 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 |
Structure and Comment

5 Conformational change of MI

7 Expulsion of fluoride leaving group.

8 Fluoride anion and 8

9 Fluoride anion

11 Fluoride anion

12 1a-OMe-F

14 Substrate complex

15 TS

16 Product complex

17 1,4-Dimethoxybenzene

18 KF

[b] The reaction coordinate is indicated by the following abbreviations. SC: substrate complex; TSx: xth transition state; MIy: 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 |
| 4     |                                   | TS2                    | TS_DMAP_4-NO2-PhO_forward.log |
| 5     |                                   | SC                     | TS_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 |
| 9     |                                   | TS2                    | TS_DMAP_4-NO2-PhO_4_water_trial2.log |
| 10    |                                   | SC                     | TS_DMAP_4-NO2-PhO_4_water_forward.log |
| 11    | 3 (DMAP-b)                        | PC                     | TS_DMAP_4-COH-PhO_back.log |
| 12    |                                   | MI                     | TS_DMAP_4-COH-PhO_forward.log |
| 13    |                                   | TS2                    | TS_DMAP_4-COH-PhO_forward.log |
| 14    |                                   | SC                     | TS_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 |
| 18    |                                   | TS2                    | TS_DMAP_3-5-di-NO2-PhO_forward.log |
| 19    |                                   | SC                     | TS_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_forward.log |
| 22    |                                   | MI                     | TS_Morpholine_4-NO2-PhO_forward.log |
| 23    |                                   | TS2                    | TS2_Morpholine_4-NO2-PhO_forward.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 |
[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.

| 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    |                                   | PC                     | TS2_Morpholine_4-NO2-PhO_var2 Forward_trial2.log |

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 |
| 12    |      |                | TS1                    | TS_KOMe_CHCCN2_F_M11_6-311++Gdp.log |
| 13    |      |                | MI                     | TS_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log |
| 14    |      |                | TS2                    | TS2_KOMe_CHCCN2_F_M11_6-311++Gdp.log |
| 15    |      |                | PC                     | TS2_KOMe_CHCCN2_F_M11_6-311++Gdp_forward.log |
| 16    |      | -COF3          | SC                     | TS_COF3_M11_6-311++Gdp_back_trial2_freq.log |
| 17    |      |                | TS1                    | TS_COF3_M11_6-311++Gdp.log |
| 18    |      |                | MI                     | TS_COF3_M11_6-311++Gdp_forward Frequency.log |
| 19    |      |                | TS2                    | TS2_COF3_M11_6-311++Gdp_forward_trial3.log |
| 20    |      |                | PC                     | TS2_COF3_M11_6-311++Gdp_forward_trial.log |
| 21    |      | -CN            | SC                     | TS_CN_M11_6-311++Gdp_back_trial2.log |
| 22    |      |                | TS1                    | TS_CN_M11_6-311++Gdp.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_H_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_forward_trial2.log |
| 48    | *   | "              | TS1                    | TS_KOMe_Cl_COCF3_M11_6-311++Gdp_forward_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_forward_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.

| Entry | KY-X | -R (sub folder) | Reaction Coordinate | 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_trial2.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_trial2.log |
| 11    | "    | "     | TS1 | TS_KF-F_NCS_M11_6-311++Gdp.log |
| 12    | KF-Cl| -NO   | SC | TS_KF-Cl_NO_M11_6-311++Gdp_back_trial2.log |
| 13    | "    | "     | TS1 | TS_KF-Cl_NO_M11_6-311++Gdp.log |
| 14    | "    | "     | PC | TS_KF-Cl_NO_M11_6-311++Gdp_forward_trial2.log |
| 15    | "    | -NO2  | SC | TS_KF-Cl_NO2_M11_6-311++Gdp_back_trial2.log |
| 16    | "    | "     | TS1 | TS_KF-Cl_NO2_M11_6-311++Gdp.log |
| 17    | "    | "     | PC | TS_KF-Cl_NO2_M11_6-311++Gdp_forward_trial2.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_trial2.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_forwardTrial2.log |
| 27    | "    | -NO2  | SC | TS_KF-I_NO2_M11_6-311++Gdp_back_trial2.log |
| 28    | "    | "     | TS1 | TS_KF-I_NO2_M11_6-311++Gdp.log |
| 29    | "    | "     | PC | TS_KF-I_NO2_M11_6-311++Gdp_forward_trial2.log |
| 30    | KCl-Cl| -NO  | SC | TS_KCl-Cl_NO_M11_6-311++Gdp_back_trial2.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_trial2.log |
| 34    | "    | "     | TS1 | TS_KCl-Cl_NO2_M11_6-311++Gdp.log |
| 35    | "    | "     | PC | TS_KCl-Cl_NO2_M11_6-311++Gdp_forward_trial2.log |
| 36    | KCl-Br| -NO  | SC | TS_KCl-Br_NO_M11_6-311++Gdp_back_trial2.log |
| 37    | "    | "     | TS1 | TS_KCl-Br_NO_M11_6-311++Gdp.log |
| 38    | "    | "     | PC | TS_KCl-Br_NO_M11_6-311++Gdp_forward_trial2.log |
| 39    | "    | -NO2  | SC | TS_KCl-Br_NO2_M11_6-311++Gdp_back_trial2.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 |
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     | KOMe-OMe | -NHAc           | TS1                      | TS_KOMe-OMe_NHCOMe_M11_6-311++Gdp_forward |
| 3     | KOMe-OMe | -NPh3           | MI                       | TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_forward |
| 4     | KOMe-OMe | -NPh3           | TS1                      | TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_forward |
| 5     | KOMe-OMe | -NPh3           | MI                       | TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_forward |
| 6     | KOMe-OMe | -NPh3           | TS2                      | TS_KOMe-OMe_NPPh3_M11_6-311++Gdp_forward |
| 7     | KOMe-OMe | -CCH            | MI                       | TS_KOMe-OMe_CCH_M11_6-311++Gdp_back |
| 8     | KOMe-OMe | -CCH            | TS1                      | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 9     | KOMe-OMe | -CCH            | MI                       | TS_KOMe-OMe_CCH_M11_6-311++Gdp_back |
| 10    | KOMe-OMe | -CCH            | TS2                      | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 11    | KOMe-OMe | -CCH            | PC                       | TS2_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 12    | KOMe-OMe | -CCH            | TS1                      | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 13    | KOMe-OMe | -CCH            | MI                       | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 14    | KOMe-OMe | -CCH            | PC                       | TS2_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 15    | KOMe-OMe | -CCH            | TS1                      | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 16    | KOMe-OMe | -CCH            | PC                       | TS2_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 17    | KOMe-OMe | -CCH            | TS1                      | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |
| 18    | KOMe-OMe | -CCH            | MI                       | TS_KOMe-OMe_CCH_M11_6-311++Gdp_forward |

[^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.
| Entry | KYMe-XMe | -R (sub folder) | Reaction Coordinate | 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    | "        | "              | 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    | KSMe-SMe | -C6F5           | SC                  | TS_KSMe-SMe_C6F5_M11_6-311++Gdp_back.log |
| 39    | "        | "              | TS1                 | TS_KSMe-SMe_C6F5_M11_6-311++Gdp_trial2.log |
| 40    | "        | "              | MI                  | TS_KSMe-SMe_C6F5_M11_6-311++Gdp_forward.log |
| 41    | "        | -NCS            | SC                  | TS_KSMe-SMe_NCS_M11_6-311++Gdp_back.log |
| 42    | "        | "              | TS1                 | TS_KSMe-SMe_NCS_M11_6-311++Gdp.log |
| 43    | "        | "              | MI                  | TS_KSMe-SMe_NCS_M11_6-311++Gdp_forward.log |
| 44    | "        | -I              | SC                  | TS_KSMe-SMe_I_M11_6-311++Gdp_back.log |
| 45    | "        | "              | TS1                 | TS_KSMe-SMe_I_M11_6-311++Gdp.log |
| 46    | "        | "              | PC                  | TS_KSMe-SMe_I_M11_6-311++Gdp_forward.log |
| 47    | "        | -Cl             | SC                  | TS_KSMe-SMe_Cl_M11_6-311++Gdp_back.sh |
| 48    | "        | "              | TS1                 | TS_KSMe-SMe_Cl_M11_6-311++Gdp.log |
| 49    | "        | "              | PC                  | TS_KSMe-SMe_Cl_M11_6-311++Gdp_forward.log |
| 50    | KSMe-SeMe | -CHCCN2         | SC                  | TS_KSMe-SMe_CHCCN2_M11_6-311++Gdp_back.log |
| 51    | "        | "              | TS1                 | TS_KSMe-SMe_CHCCN2_M11_6-311++Gdp.log |
| 52    | "        | "              | MI                  | TS_KSMe-SMe_CHCCN2_M11_6-311++Gdp_forward.log |
| 53    | "        | -COCF3          | SC                  | TS_KSMe-SMe_COCF3_M11_6-311++Gdp_back.log |
| 54    | "        | "              | TS1                 | TS_KSMe-SMe_COCF3_M11_6-311++Gdp.log |
| 55    | "        | "              | MI                  | TS_KSMe-SMe_COCF3_M11_6-311++Gdp_forward.log |
| 56    | "        | -CN             | SC                  | TS_KSMe-SeMe_CN_M11_6-311++Gdp_back.log |
| 57    | "        | "              | TS1                 | TS_KSMe-SeMe_CN_M11_6-311++Gdp_forward.log |
| 58    | "        | "              | PC                  | TS_KSMe-SeMe_CN_M11_6-311++Gdp_forward_trial2.log |
| 59    | "        | -COMe           | SC                  | TS_KSMe-SeMe_COMe_M11_6-311++Gdp_forward.log |
| 60    | "        | "              | TS1                 | TS_KSMe-SeMe_COMe_M11_6-311++Gdp_forward_trial2.log |
| 61    | "        | "              | PC                  | TS_KSMe-SeMe_COMe_M11_6-311++Gdp_forward.log |
| 62    | KSeMe-SeMe | -CO2Me          | SC                  | TS_KSeMe-SeMe_CO2Me_M11_6-311++Gdp_back.log |
| 63    | "        | "              | TS1                 | TS_KSeMe-SeMe_CO2Me_M11_6-311++Gdp.log |
| 64    | "        | "              | MI                  | TS_KSeMe-SeMe_CO2Me_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 |
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_forward.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_forward.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_forward.log |
| 12    |                     |                 | PC TS_LiOMe_COCF3_M11_6-311++Gdp_forward_trial2.log |
| 13    |                     | -CN             | SC TS_LiOMe_CN_M11_6-311++Gdp_back_trial2.log |
| 14    |                     |                 | TS1 TS_LiOMe_CN_M11_6-311++Gdp_forward.log |
| 15    |                     | -COMe           | SC TS_LiOMe_COMe_M11_6-311++Gdp_forward_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_forward.log |
| 26    |                     |                 | MI TS_NaOMe_CHCCN2_F_M11_6-311++Gdp_forward_trial4.log |
| 27    |                     | -COCF3          | SC TS_NaOMe_COCF3_M11_6-311++Gdp_back_trial4.log |
| 28    |                     |                 | TS1 TS_NaOMe_COCF3_M11_6-311++Gdp_forward.log |
| 29    |                     |                 | MI TS_NaOMe_COCF3_M11_6-311++Gdp_forward_trial4.log |
| 30    |                     | -CN             | SC TS_NaOMe_CN_M11_6-311++Gdp_back_trial3.log |
| 31    |                     |                 | TS1 TS_NaOMe_CN_M11_6-311++Gdp_forward.log |
| 32    |                     |                 | PC TS_NaOMe_CN_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.
| Entry | Metal M (sub folder) | -R (sub folder) | Reaction Coordinate | 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_trial2.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_trial2.log |
| 41    | "                   | MI             | TS_KOme_NO_F_M11_6-311++Gdp_forward.log |
| 42    | "                   | "              | TS2                 | TS2_KOme_NO_F_M11_6-311++Gdp_trial8.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_trial2.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_forward_trial2.log |
| 49    | "                   | -CHCC2         | SC                  | TS_KOme_CHCC2_F_M11_6-311++Gdp_back_trial4.log |
| 50    | "                   | "              | TS1                 | TS_KOme_CHCC2_F_M11_6-311++Gdp_trial2.log |
| 51    | "                   | MI             | TS_KOme_CHCC2_F_M11_6-311++Gdp_forward Trial2.log |
| 52    | "                   | "              | TS2                 | TS2_KOme_CHCC2_F_M11_6-311++Gdp_trial2.log |
| 53    | "                   | "              | PC                  | TS2_KOme_CHCC2_F_M11_6-311++Gdp_forward_trial2.log |
| 54    | "                   | -COCF3         | SC                  | TS_COCF3_M11_6-311++Gdp_back_trial2_freq.log |
| 55    | "                   | "              | TS1                 | TS_COCF3_M11_6-311++Gdp_trial2.log |
| 56    | "                   | "              | MI                  | TS_COCF3_M11_6-311++Gdp_forward_trial2.log |
| 57    | "                   | "              | TS2                 | TS2_CO2Me_NO2_F_M11_6-311++Gdp_trial8.log |
| 58    | "                   | "              | PC                  | TS2_CO2Me_NO2_F_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_trial2.log |
| 61    | "                   | "              | PC                  | TS_CN_M11_6-311++Gdp_forward_trial2.log |
| 62    | "                   | -COMe          | SC                  | TS_CO2Me_M11_6-311++Gdp_back_trial2_freq.log |
| 63    | "                   | "              | TS1                 | TS_CO2Me_M11_6-311++Gdp_trial3.log |
| 64    | "                   | "              | PC                  | TS_CO2Me_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_trial2.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_trial2.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_trial2.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_trial2.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_trial2.log |
| 78    | "                   | "              | TS1                 | TS_RbOMe_NO_F_M11_6-311++Gdp_trial2.log |
| 79    | "                   | "              | MI                  | TS_RbOMe_NO_F_M11_6-311++Gdp_forward_trial2.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_trial5.log |
| 82    | "                   | MI             | TS1                 | TS_RbOMe_NO2_F_M11_6-311++Gdp_forward_trial2.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    | "                   | Ml            | 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    | "                   | Ml            | 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            | 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    | "                   | Ml            | 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   | "                   | "             | TS1                      | TS_RbOMe_CCH_F_M11_6-311++Gdp_back.log |
| 102   | "                   | "             | PC                       | TS_RbOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 103   | "                   | "             | TS1                      | 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_forward_trial2.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   | "                   | Ml            | MI                       | TS_CsOMe_NO_F_M11_6-311++Gdp_forward_trial2.log |
| 110   | "                   | "             | MC                       | TS_CsOMe_NO2_F_M11_6-311++Gdp_back_trial2.log |
| 111   | "                   | "             | TS1                      | TS_CsOMe_NO2_F_M11_6-311++Gdp_forward_trial2.log |
| 112   | "                   | "             | MI                       | TS_CsOMe_NO2_F_M11_6-311++Gdp_forward_trial2.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_forward_trial2.log |
| 115   | "                   | Ml            | MI                       | TS_CsOMe_CHCCN2_F_M11_6-311++Gdp_forward_trial2.log |
| 116   | "                   | -COCF3        | SC                       | TS_CsOMe_COCF3_M11_6-311++Gdp_back_trial3.log |
| 117   | "                   | "             | TS1                      | TS_CsOMe_COCF3_M11_6-311++Gdp_forward_trial3.log |
| 118   | "                   | "             | MI                       | TS_CsOMe_COCF3_M11_6-311++Gdp_forward_trial3.log |
| 119   | "                   | "             | MC                       | TS_CsOMe_COCF3_M11_6-311++Gdp_forward_trial3.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_forward_trial3.freq.log |
| 124   | "                   | "             | MI                       | TS_CsOMe_COMe_M11_6-311++Gdp_forward_trial3.freq.log |
| 125   | "                   | -CO2Me        | SC                       | TS_CsOMe_CO2Me_M11_6-311++Gdp_back.log |
| 126   | "                   | "             | TS1                      | TS_CsOMe_CO2Me_M11_6-311++Gdp_forward.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_forward.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_forward.log |
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 | Metal M (sub folder) | -R (sub folder) | Reaction Coordinate\[a\] | File name |
|-------|----------------------|----------------|--------------------------|-----------|
| 133   | -CHCCN2             | SC             | TS_KOMe_F_CHCCN2_1_DMF_M11_6-311++Gdp_back.log |
| 134   | -H                  | SC             | TS_KOMe_F_H_F_M11_6-311++Gdp_back.log |
| 135   |                      | TS1            | TS_KOMe_F_H_F_M11_6-311++Gdp_back.log |
| 136   |                      | PC             | TS_KOMe_F_H_F_M11_6-311++Gdp_forward_trial2.log |
| 137   | none                | COCF3          | TS_OMe_COCF3_M11_6-311++Gdp_forward_trial2.log |
| 138   |                      | TS1            | TS_OMe_COCF3_M11_6-311++Gdp_forward.log |
| 139   |                      | MI             | TS_OMe_COCF3_M11_6-311++Gdp_forward_trial2.log |
| 140   | -CN                 | SC             | TS_OMe_CN_M11_6-311++Gdp_forward_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_forward_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_forward_trial2.log |
| 148   |                      | MI             | TS_OMe_CO2Me_M11_6-311++Gdp_forward_trial2.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_forward_trial2.log |
| 151   |                      | MI             | TS_OMe_CF3_M11_6-311++Gdp_forward_trial2.log |
| 152   | -CCH                | SC             | TS_OMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 153   |                      | TS1            | TS_OMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 154   |                      | PC             | TS_OMe_CCH_F_M11_6-311++Gdp_forward_trial3.log |
| 155   |                      | -H             | TS_OMe_H_F_M11_6-311++Gdp_forward_trial2.log |
| 156   |                      | TS1            | TS_OMe_H_F_M11_6-311++Gdp_forward_trial2.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.
| 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_forward2_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_trial2.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_trial2.log |
| 29    | "             | "              | PC                     | TS_KOMe-F_CF3_2_DMF_M11_6-311++Gdp_forward2_trial2.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_trial2.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_KOMe-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_trial2.log |
| 12    | "               | "              | MI                     | TS_KSMe-F_COCF3_M11-6-311++Gdp_forward_trial2.log |
| 13    | "               | "              | TS2                    | 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_KOMe-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_trial2.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            | 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.freq.log |
| 26    | "               | -CCH            | TS_KSMe-F_CCH_M11-6-311++Gdp_back_trial2.freq.log TS_KSMe-F_CCH_M11-6-311++Gdp_back_trial2.freq.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              | 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         | TS_KN3-F_CHCCN2_M11-6-311++Gdp_back_trial4.log |
| 33    | "               | TS1             | TS_KN3-F_CHCCN2_M11-6-311++Gdp_forward.log |
| 34    | "               | MI              | TS_KN3-F_CHCCN2_M11-6-311++Gdp_forward.log |
| 35    | "               | -COCF3          | 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.freq.log |
| 39    | "               | PC              | TS2_KN3-F_COCF3_M11-6311++Gdp_forward.log |
| 40    | "               | TS1             | TS_KN3-F_CN_M11-6311++Gdp_back.log |
| 41    | "               | PC              | TS_KN3-F_CN_M11-6311++Gdp.log |
| 42    | "               | TS1             | TS_KN3-F_CN_M11-6311++Gdp_forward_trial2.log |
| 43    | "               | -COMe           | TS_KN3-F_COMe_M11-6311++Gdp_forward_trial2.log |
| 44    | "               | TS1             | TS_KN3-F_COMe_M11-6311++Gdp.freq.log |
| 45    | "               | PC              | TS_KN3-F_COMe_M11-6311++Gdp_back_trial3.log |
| 46    | "               | TS1             | TS_KN3-F_COMe_M11-6311++Gdp.freq.log |
| 47    | "               | TS1             | TS_KN3-F_COMe_M11-6311++Gdp.freq.log |
| 48    | "               | PC              | TS_KN3-F_COMe_M11-6311++Gdp_forward_trial2.log |
| 49    | 601d (Kacac)    | -CHCCN2         | TS_Kacac-F_CHCCN2_M11-6-311++Gdp_back.log |
| 50    | "               | TS1             | TS_Kacac-F_CHCCN2_M11-6-311++Gdp.log |
| 51    | "               | PC              | TS_Kacac-F_CHCCN2_M11-6-311++Gdp_forward_trial2.log |
| 52    | "               | -COCF3          | TS_Kacac-F_COCF3_M11-6-311++Gdp.back.log |
| 53    | "               | TS1             | TS_Kacac-F_COCF3_M11-6-311++Gdp.freq.log |
| 54    | "               | MI              | TS_Kacac-F_COCF3_M11-6-311++Gdp_forward.log |
| 55    | "               | TS2             | TS2_Kacac-F_COCF3_M11-6-311++Gdp.freq.log |
| 56    | "               | PC              | TS2_Kacac-F_COCF3_M11-6-311++Gdp_forward.freq.log |
| 57    | "               | TS1             | 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_trial2.log |
| 60    | "               | -COMe           | TS_Kacac-F_COMe_M11-6-311++Gdp_forward_trial2.log |
| 61    | "               | TS1             | TS_Kacac-F_COMe_M11-6-311++Gdp.freq.log |
| 62    | "               | PC              | TS_Kacac-F_COMe_M11-6-311++Gdp_forward_trial2.log |
| 63    | "               | -CO2Me          | TS_Kacac-F_CO2Me_M11-6-311++Gdp.forward_trial2.log |
| 64    | "               | TS1             | TS_Kacac-F_CO2Me_M11-6-311++Gdp.back_trial2.log |
| 65    | "               | PC              | TS_Kacac-F_CO2Me_M11-6-311++Gdp_forward_trial2.log |
| 66    | 601e (KMelder)  | -NO             | TS_KMelder-F_NO2_M11-6-311++Gdp_forward_freq.log |
| 67    | "               | TS1             | TS_KMelder-F_NO2_M11-6-311++Gdp.log |
| 68    | "               | MI              | TS_KMelder-F_NO2_M11-6-311++Gdp_forward.log |
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     |                        | NO₂        | triplet                | KSMe_NO2_substrate_complex_triplet.log |
| 3     |                        | CHCCN₂     | triplet                | KSCMe_CHCCN2_substrate_complex_triplet.log |
| 4     | 2d-K                    | CHCCN₂     | 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     |                        | CHCCN₂     | triplet                | KMeldrum_CHCCN2_substrate_complex_triplet.log |
| 9     | 2f-K                    | CHCCN₂     | 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[s] | File name |
|-------|------------------|----------------|------------------------|-----------|
| 2     | "                | "              | TS1                    | TS_KOMe-F_CHCCN2_2Pyr_M11-6311++Gdp.log |
| 3     | "                | MI             | MI                     | TS_KOMe-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log |
| 4     | "                | -COCF3         | TS1                    | TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_back.log |
| 5     | "                | MI             | TS1                    | TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 6     | "                | -CN            | TS1                    | TS_KOMe-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 7     | "                | TS1            | TS1                    | TS_KOMe-F_CN_2Pyr_M11-6311++Gdp.log |
| 8     | "                | MI             | MI                     | TS_KOMe-F_CN_2Pyr_M11-6311++Gdp_forward.log |
| 9     | "                | -COMe          | TS1                    | TS_KOMe-F_COMe_2Pyr_M11-6311++Gdp_back.log |
| 10    | "                | MI             | MI                     | TS_KOMe-F_COMe_2Pyr_M11-6311++Gdp_forward_trial5.log |
| 11    | "                | -CO2Me         | TS1                    | TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp_back_trial2.log |
| 12    | "                | MI             | TS1                    | TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 13    | "                | MI             | TS1                    | TS_KOMe-F_CO2Me_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 14    | "                | -CF3           | TS1                    | TS_KOMe-F_CF3_2Pyr_M11-6311++Gdp_back.log |
| 15    | "                | PC             | TS1                    | TS_KOMe-F_CF3_2Pyr_M11-6311++Gdp_forward.log |
| 16    | "                | -CCH           | TS1                    | TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_back_trial2.log |
| 17    | "                | TS1            | TS1                    | TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp.log |
| 18    | "                | PC             | TS1                    | TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_forward.log |
| 19    | "                | TS1            | TS1                    | TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_forward_trial5.log |
| 20    | "                | PC             | TS1                    | TS_KOMe-F_CCH_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 21    | KSMe             | -CHCCN2        | TS1                    | TS_KSMe-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log |
| 22    | "                | TS1            | TS1                    | TS_KSMe-F_CHCCN2_2Pyr_M11-6311++Gdp.log |
| 23    | "                | MI             | TS1                    | TS_KSMe-F_CHCCN2_2Pyr_M11-6311++Gdp_forward.log |
| 24    | "                | -COCF3         | TS1                    | TS_KSMe-F_COCF3_2Pyr_M11-6311++Gdp_back.log |
| 25    | "                | MI             | TS1                    | TS_KSMe-F_COCF3_2Pyr_M11-6311++Gdp_trial3.log |
| 26    | "                | MI             | TS1                    | TS_KSMe-F_COCF3_2Pyr_M11-6311++Gdp_forward_trial5.log |
| 27    | "                | TS1            | TS1                    | TS_KSMe-F_CN_2Pyr_M11-6311++Gdp_back.log |
| 28    | "                | PC             | TS1                    | TS_KSMe-F_CN_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 29    | "                | PC             | TS1                    | TS_KSMe-F_CN_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 30    | "                | -COMe          | TS1                    | TS_KSMe-F_COMe_2Pyr_M11-6311++Gdp_back.log |
| 31    | "                | TS1            | TS1                    | TS_KSMe-F_COMe_2Pyr_M11-6311++Gdp.log |
| 32    | "                | PC             | TS1                    | TS_KSMe-F_COMe_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 33    | KN3              | -CHCCN2        | TS1                    | TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log |
| 34    | "                | TS1            | TS1                    | TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_trial2.log |
| 35    | "                | MI             | TS1                    | TS_KN3-F_CHCCN2_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 36    | "                | -COCF3         | TS1                    | TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp_back.log |
| 37    | "                | TS1            | TS1                    | TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp.log |
| 38    | "                | MI             | TS1                    | TS_KN3-F_COCF3_2Pyr_M11-6311++Gdp_forward.log |
| 39    | "                | PC             | TS1                    | TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 40    | "                | TS1            | TS1                    | TS_KN3-F_CN_2Pyr_M11-6311++Gdp_trial2.log |
| 41    | "                | PC             | TS1                    | TS_KN3-F_CN_2Pyr_M11-6311++Gdp_forward_trial2.log |
| 42    | "                | -COMe          | TS1                    | TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_back_trial2.log |
| 43    | "                | PC             | TS1                    | TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_forward.log |
| 44    | "                | PC             | TS1                    | TS_KN3-F_COMe_2Pyr_M11-6311++Gdp_forward_trial3.log |
| 45    | "                | PC             | TS1                    | TS_KN3-F_CO2Me_2Pyr_M11-6311++Gdp.log |
| 46    | "                | PC             | TS1                    | TS_KN3-F_CO2Me_2Pyr_M11-6311++Gdp_forward.log |
| 47    | "                | TS1            | TS1                    | TS_Kacac-F_CHCCN2_2Pyr_M11-6311++Gdp_back.log |
| 48    | "                | TS1            | TS1                    | TS_Kacac-F_CHCCN2_2Pyr_M11-6311++Gdp.log |

**Note:** The file names are generated based on the reaction coordinates and KNu, indicating the path to the specific log file for each reaction.
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     | COCF₃   | 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 | MeOKlog |

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_back.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_forward.log |
| 5     | "                | "              | TS1                    | TS_KOMe-F_COCF3_Np_M11_6-311++Gdp_back.log |
| 6     | "                | "              | MI                     | TS_KOMe-F_COCF3_Np_M11_6-311++Gdp_forward_trial2.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_forward_trial2.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_forward_trial2.log |
| 12    | "                | "              | 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    | "               | "               | MI                     | TS_KOMe-F_CCH_Np_M11_6-311++Gdp_forward_trial2.log |
| 21    | "               | -CHCCN2         | SC                     | TS_KSMe-F_CHCCN2_Np_M11_6-311++Gdp_back.log |
| 22    | "               | "               | MI                     | TS_KSMe-F_CHCCN2_Np_M11_6-311++Gdp_forward.log |
| 23    | "               | -COCF3          | SC                     | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp_back_trial3.log |
| 24    | "               | "               | TS1                    | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp.log |
| 25    | "               | "               | MI                     | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp_forward_trial2.log |
| 26    | "               | -CN             | SC                     | TS_KSMe-F_CN_Np_M11_6-311++Gdp_back.log |
| 27    | "               | "               | MI                     | TS_KSMe-F_CN_Np_M11_6-311++Gdp_forward_trial2.log |
| 28    | "               | "               | MI                     | TS_KSMe-F_CN_Np_M11_6-311++Gdp_forward.log |
| 29    | "               | -COMe           | SC                     | TS_KSMe-F_COMe_Np_M11_6-311++Gdp_back.log |
| 30    | "               | "               | MI                     | TS_KSMe-F_COMe_Np_M11_6-311++Gdp_forward_trial2.log |
| 31    | "               | -CO2Me          | SC                     | TS_KSMe-F_CO2Me_Np_M11_6-311++Gdp_back.log |
| 32    | "               | "               | TS1                    | TS_KSMe-F_CO2Me_Np_M11_6-311++Gdp.log |
| 33    | "               | -COCF3          | SC                     | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp_back_trial3.log |
| 34    | "               | "               | TS1                    | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp.log |
| 35    | "               | "               | PC                     | TS_KSMe-F_COCF3_Np_M11_6-311++Gdp_forward_trial2.log |
| 36    | "               | -CF3            | SC                     | TS_KSMe-F_CF3_Np_M11_6-311++Gdp_back.log |
| 37    | "               | "               | TS1                    | TS_KSMe-F_CF3_Np_M11_6-311++Gdp.log |
| 38    | "               | "               | PC                     | TS_KSMe-F_CF3_Np_M11_6-311++Gdp_back.log |
| 39    | "               | -CCH            | SC                     | TS_KSMe-F_CCH_Np_M11_6-311++Gdp_back.log |
| 40    | "               | "               | TS1                    | TS_KSMe-F_CCH_Np_M11_6-311++Gdp_forward_trial2.log |
| 41    | "               | "               | PC                     | TS_KSMe-F_CCH_Np_M11_6-311++Gdp_forward.log |
| 42    | "               | -COMe           | SC                     | TS_KN3-F_COMe_Np_M11_6-311++Gdp_back.log |
| 43    | "               | "               | TS1                    | TS_KN3-F_COMe_Np_M11_6-311++Gdp_trial2.log |
| 44    | "               | "               | MI                     | TS_KN3-F_COMe_Np_M11_6-311++Gdp_forward.log |
| 45    | "               | -CO2Me          | SC                     | TS_KN3-F_CO2Me_Np_M11_6-311++Gdp_back.log |
| 46    | "               | "               | TS1                    | TS_KN3-F_CO2Me_Np_M11_6-311++Gdp.log |
| 47    | "               | -CF3            | SC                     | TS_KN3-F_CF3_Np_M11_6-311++Gdp_back.log |
| 48    | "               | "               | TS1                    | TS_KN3-F_CF3_Np_M11_6-311++Gdp_forward_trial2.log |
| 49    | "               | "               | PC                     | TS_KN3-F_CF3_Np_M11_6-311++Gdp_forward.log |
| 50    | "               | -CCH            | SC                     | TS_KN3-F_CCH_Np_M11_6-311++Gdp_back.log |
| 51    | "               | "               | TS1                    | TS_KN3-F_CCH_Np_M11_6-311++Gdp_forward_trial2.log |
| 52    | "               | "               | PC                     | TS_KN3-F_CCH_Np_M11_6-311++Gdp_forward.log |
| 53    | "               | "               | PC                     | TS_Kacac-F_COMe_Np_M11_6-311++Gdp_forward_log |
| 54    | "               | -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_forward_trial2.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_forward_trial2.log |
Steric Effects

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

| 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    | "                | "               | MI                      | TS_Kacac-F_Cl_Np_M11_6-311++Gdp_forward.log |
| 71    | "                | "               | SC                      | 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_forward.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_forward.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_forward.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.
| Entry | KNu/Ar (sub folder) | -R (sub folder) | Reaction Coordinate\(\text{a}\) | 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_forward.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_M11-6311++Gdp_back.log |
| 34    | "                   | "              | TS1               | TS_Kacac-F_COCF3_ortho-Me_M11-6311++Gdp.log |
| 35    | "                   | "              | Mi                | TS_Kacac-F_COCF3_ortho-Me_M11-6311++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_forward.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_forward.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_forward.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_forward.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_forward.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_forward.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_forward.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_forward.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_forward.log |
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.

| Entry | Aromatic system (sub folder) | -R (sub folder) | Reaction Coordinate[a] | File name |
|-------|-----------------------------|----------------|------------------------|-----------|
| 68    | Pyrimidine                  | -COMe          | MI                     | TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp_back.log |
| 69    |                             | -Me            | TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp_back.log |
| 70    |                             | -OMe           | TS_KOMe-F_COMe_Pyrm_M11-6311++Gdp_back.log |
| 71    | Anthracene                  | -CO2Me         | MI                     | TS_KOMe-F_CO2Me_Ant_M11_6-311++Gdp_back.log |
| 72    |                             | -CF3           | MI                     | TS_KOMe-F_CF3_Ant_M11_6-311++Gdp_back.log |
| 73    |                             | -CCH           | MI                     | TS_KOMe-F_CCH_Ant_M11_6-311++Gdp_back.log |
| 74    |                             | -NCS           | MI                     | TS_KOMe-F_NCS_Ant_M11_6-311++Gdp_back.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 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     |                             | -NO            | radical-anion           | EA_Benzene_NO-F_rad-anion.log |
| 3     |                             | -NO2           | neutral                 | EA_Benzene_NO2-F_neutral.log |
| 4     |                             | -NO2           | radical-anion           | EA_Benzene_NO2-F_rad-anion.log |
| 5     |                             | -COCF3         | neutral                 | EA_Benzene_COCF3-F_neutral.log |
| 6     |                             | -COCF3         | radical-anion           | EA_Benzene_COCF3-F_rad-anion.log |
| 7     |                             | -CN            | neutral                 | EA_Benzene_CN-F_neutral.log |
| 8     |                             | -CN            | radical-anion           | EA_Benzene_CN-F_rad-anion.log |
| 9     |                             | -COMe          | neutral                 | EA_Benzene_COMe-F_neutral.log |
| 10    |                             | -COMe          | radical-anion           | EA_Benzene_COMe-F_rad-anion.log |
| 11    |                             | -CO2Me         | neutral                 | EA_Benzene_CO2Me-F_neutral.log |
| 12    |                             | -CO2Me         | radical-anion           | EA_Benzene_CO2Me-F_rad-anion.log |
| 13    |                             | -CF3           | neutral                 | EA_Benzene_CF3-F_neutral.log |
| 14    |                             | -CF3           | radical-anion           | EA_Benzene_CF3-F_rad-anion_trial2.log |
| 15    |                             | -CCH           | neutral                 | EA_Benzene_CCH-F_neutral.log |
| 16    |                             | -CCH           | radical-anion           | EA_Benzene_CCH-F_rad-anion_trial2.log |
| 17    |                             | -NCS           | neutral                 | EA_Benzene_NCS-F_neutral.log |
| 18    |                             | -NCS           | radical-anion           | EA_Benzene_NCS-F_rad-anion_trial2.log |
| 19    |                             | -Cl            | neutral                 | EA_Benzene_Cl-F_neutral.log |
| 20    |                             | -Cl            | radical-anion           | EA_Benzene_Cl-F_rad-anion.log |
| 21    |                             | -H             | neutral                 | EA_Benzene_H-F_neutral.log |
| 22    |                             | -H             | radical-anion           | EA_Benzene_H-F_rad-anion.log |
| 23    |                             | -Me            | neutral                 | EA_Benzene_Me-F_neutral.log |
| 24    | 1b-R-F (Naphthalene)        | -CHCCN2        | neutral                 | EA_Naphthalene_CHCCN2_neutral_pop.log |
| 25    |                             | -CHCCN2        | radical-anion           | EA_Naphthalene_CHCCN2_rad-anion.log |
| 26    |                             | -COCF3         | neutral                 | EA_Naphthalene_COCF3-F_rad-anion_trial2.log |
| 27    |                             | -COCF3         | radical-anion           | EA_Naphthalene_COCF3-F_rad-anion_trial2.log |
| 28    |                             | -CN            | neutral                 | EA_Naphthalene_CN-F_neutral_pop.log |

[^a]: The reaction coordinate is indicated by the following abbreviations.
| Entry | Aromatic system (sub folder) | -R (sub folder) | Reaction Coordinate | File name |
|-------|-----------------------------|----------------|---------------------|-----------|
|      |                            | -COMe          | neutral             | EA_Naphthalene_COMe-F_trial2_neutral_pop.log |
|      |                            | "             | radical-anion       | EA_Naphthalene_COMe-F_rad-anion.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_CCH-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.pop.log |
|      |                            | "             | 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 |
|      |                            | -CO2F3         | neutral             | EA_Pyridine_CO2F3-F_neutral_pop.log |
|      |                            | "             | radical-anion       | EA_Pyridine_CO2F3-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_pop.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_CI-F_neutral.log |
|       | *                            | "              | radical-anion          | EA_Pyrimidine_CI-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_pop.log |
|       | "                            | "              | radical-anion          | EA_Quinoline_NCS-F_rad-anion.log |
|       | "                            | -Cl            | neutral                | EA_Quinoline_CI-F_neutral_pop.log |
|       | “                            | radical-anion  | EA_Quinoline_CI-F_rad-anion.log |
|       | “                            | -H             | neutral                | EA_Quinoline_H-F_neutral_pop.log |
|       | “                            | radical-anion  | EA_Quinoline_H-F_rad-anion_pop.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_CI_Quinoline_M11_6-311++Gdp_back.log |
|       | 40                            | TS1            | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp.log |
|       | 41                            | "              | PC                     | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_forward.log |
|       | 42                            | "              | 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 |
|       | "                            | radical-anion  | EA_Isoquinoline_F_CCH_M11_6-311++Gdp_rad-anion.log |
|       | “                            | -NCS           | neutral                | EA_Isoquinoline_F_NCS_neutral_pop.log |
|       | “                            | radical-anion  | EA_Isoquinoline_F_NCS_rad-anion_pop.log |
|       | “                            | -Cl            | neutral                | EA_Isoquinoline_F_CI_M11_6-311++Gdp_rad-anion.log |
|       | "                            | radical-anion  | EA_Isoquinoline_F_CI_M11_6-311++Gdp_pop.log |
|       | “                            | -H             | neutral                | EA_Isoquinoline_F_H_M11_6-311++Gdp_neutral_pop.log |
|       | "                            | radical-anion  | EA_Isoquinoline_F_H_M11_6-311++Gdp_rad-anion.log |
|       | “                            | -CCH           | SC                     | TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_CCH_Isoquinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -NCS           | SC                     | TS_KOMe-F_ICI_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_ICI_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_ICI_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -Cl            | SC                     | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -CCH           | SC                     | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -Cl            | SC                     | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_CI_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -H             | SC                     | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -CCH           | SC                     | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_back.log |
|       | “                            | TS1            | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp.log |
|       | “                            | MI             | TS_KOMe-F_H_Quinoline_M11_6-311++Gdp_forward.log |
|       | “                            | -NCS           | neutral                | EA_Acridine_F_CCH_neutral_pop.log |
|       | “                            | radical-anion  | EA_Acridine_F_CCH_rad-anion.log |
|       | “                            | -NCS           | neutral                | EA_Acridine_F_NCS_neutral_pop.log |
| Entry | Aromatic system (sub folder) | -R (sub folder) | Reaction Coordinate | 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_pop.log |
|       |                             | radical-anion   | EA_Acridine_F_NHAc_rad-anion.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                          | MI              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward.log |
|       | TS1                         | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_back.log |
|       |                             | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial4.log |
|       |                             | TS1             | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       | PC                          | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       | PC                          | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_KOMe-F_CCH_Acridine_M11_6-311++Gdp_forward_trial2.log |
| 1i-R-F (N-Me-Indole) | -NO2 neutral | EA_NMeldone_NO2_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_NO2_F_rad-anion.log |
|       |                             | -COCF3 neutral  | EA_NMeldone_COCF3_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_COCF3_F_rad-anion.log |
|       |                             | -CN neutral     | EA_NMeldone_CN_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_CN_F_rad-anion.log |
|       |                             | -COMe neutral   | EA_NMeldone_COMe_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_COMe_F_rad-anion.log |
|       |                             | -CO2Me neutral  | EA_NMeldone_CO2Me_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_CO2Me_F_rad-anion.log |
|       |                             | -CF3 neutral    | EA_NMeldone_CF3_F_neutral_pop.log |
|       |                             | radical-anion   | EA_NMeldone_CF3_F_rad-anion.log |
|       | -NO2 SC                     | TS_NMeldone_KOMe_NO2_F_M11_6-311++Gdp_back.log |
|       |                             | TS1             | TS_NMeldone_KOMe_NO2_F_M11_6-311++Gdp.log |
|       | MI                          | MI              | TS_NMeldone_KOMe_NO2_F_M11_6-311++Gdp_forward.log |
|       | -COCF3 SC                   | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_back.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp.log |
|       | MI                          | MI              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1             | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | PC              | TS_NMeldone_KOMe_COCF3_F_M11_6-311++Gdp_forward_trial2.log |
| Entry | Aromatic system (sub folder) | -R (sub folder) | Reaction Coordinate\(\text{a}\) | File name |
|-------|-----------------------------|----------------|-----------------------------|-----------|
|       |                             |                | TS1                         | TS_NMelndole_KOMe_COMe_F_M11_6-311++Gdp.log |
|       |                             | MI             | TS_NMelndole_KOMe_COMe_F_M11_6-311++Gdp_forward.log |
|       | -CO2Me                      | SC             | TS_NMelndole_KOMe_CO2Me_F_M11_6-311++Gdp_back.log |
|       |                             | TS1            | TS_NMelndole_KOMe_CO2Me_F_M11_6-311++Gdp.log |
|       | -PC                         | SC             | TS_NMelndole_KOMe_CO2Me_F_M11_6-311++Gdp_back.log |
|       |                             | TS1            | TS_NMelndole_KOMe_CO2Me_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_NMelndole_KOMe_CO2Me_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_neutral_pop.log |
|       |                             | radical-anion  | EA_Benzofuran_CCH_F_rad-anion.log |
|       | -NCS                        | neutral        | EA_Benzofuran_NCS_F_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 |
|       | -M1                         | SC             | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp_back.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp.log |
|       |                             | MI             | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp_forward.log |
|       | -CN                         | 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.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 |
|       |                             | TS1            | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp_forward_trial2.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CO2Me_F_M11_6-311++Gdp.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 |
|       |                             | TS1            | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.log |
|       |                             | TS1            | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp.log |
|       |                             | PC             | TS_Benzofuran_KOMe_CF3_F_M11_6-311++Gdp_forward.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        | Benzo thiophene_CN_F_M11_6-311++Gdp_neutral_pop.log |
| "    | "                          | radical-anion  | Benzo thiophene_CN_F_M11_6-311++Gdp_rad-anion.log |
| "    | -COMe                      | neutral        | Benzo thiophene_COMe_F_M11_6-311++Gdp_neutral_pop.log |
| "    | "                          | radical-anion  | Benzo thiophene_COMe_F_M11_6-311++Gdp_rad-anion.log |
| "    | -CO2Me                     | neutral        | EA_Benzo thiophene_CO2MeF_neutral.log |
| "    | "                          | radical-anion  | EA_Benzo thiophene_CO2MeF_rad-anion.log |
| "    | -CF3                       | neutral        | EA_Benzo thiophene_CF3F_neutral.log |
| "    | "                          | radical-anion  | EA_Benzo thiophene_CF3F_rad-anion.log |
| "    | -CCH                       | neutral        | Benzo thiophene_CCH_F_M11_6-311++Gdp_neutral_pop.log |
| "    | "                          | radical-anion  | Benzo thiophene_CCH_F_M11_6-311++Gdp_rad-anion.log |
| "    | -NCS                       | neutral        | Benzo thiophene_NCS_F_M11_6-311++Gdp_neutral_pop.log |
| "    | "                          | radical-anion  | Benzo thiophene_NCS_F_M11_6-311++Gdp_rad-anion.log |
| "    | -Cl                        | neutral        | Benzo thiophene_Cl_F_M11_6-311++Gdp_neutral_pop.log |
| "    | "                          | radical-anion  | Benzo thiophene_Cl_F_M11_6-311++Gdp_rad-anion.log |
| "    | -CN                        | SC             | TS_Benzo thiophene_KOMe_CN_F_M11_6-311++Gdp_back.log |
| "    | "                          | TS1            | TS_Benzo thiophene_KOMe_CN_F_M11_6-311++Gdp_forward.log |
| 56   | "                          | MI             | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_forward.log |
| 57   | "                          | COMe           | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_back.log |
| 58   | "                          | TS1            | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_forward_trial2.log |
| 59   | "                          | MI             | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_forward.log |
| 60   | "                          | CO2Me          | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_back.log |
| 61   | "                          | TS1            | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_forward_trial2.log |
| 62   | "                          | MI             | TS_Benzo thiophene_KOMe_CO2MeF_M11_6-311++Gdp_forward.log |
| 63   | "                          | CF3            | TS_Benzo thiophene_KOMe_CF3F_M11_6-311++Gdp_forward.log |
| 64   | "                          | TS1            | TS_Benzo thiophene_KOMe_CF3F_M11_6-311++Gdp_forward_trial2.log |
| 65   | "                          | PC             | TS_Benzo thiophene_KOMe_CF3F_M11_6-311++Gdp_forward_trial2.log |
| 66   | "                          | CCH            | TS_Benzo thiophene_KOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 67   | "                          | TS1            | TS_Benzo thiophene_KOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 68   | "                          | PC             | TS_Benzo thiophene_KOMe_CCH_F_M11_6-311++Gdp_forward_trial2.log |
| 69   | "                          | NCS            | TS_Benzo thiophene_KOMe_NCS_F_M11_6-311++Gdp_forward_trial2.log |
| 70   | "                          | TS1            | TS_Benzo thiophene_KOMe_NCS_F_M11_6-311++Gdp_forward_trial2.log |
| 71   | "                          | PC             | TS_Benzo thiophene_KOMe_NCS_F_M11_6-311++Gdp_forward_trial2.log |
| 72   | "                          | TS1            | TS_Benzo thiophene_KOMe_Cl_F_M11_6-311++Gdp_forward_trial2.log |
| 73   | "                          | PC             | TS_Benzo thiophene_KOMe_Cl_F_M11_6-311++Gdp_forward_trial2.log |
| 74   | "                          | PC             | TS_Benzo thiophene_KOMe_Cl_F_M11_6-311++Gdp_forward_trial2.log |
| 75   | 11-R-F (N-Me-Pyrrole)      | -NO2           | EA_NMePyrrole_F_NO2_neutral_pop.log |
| 76   | "                          | radical-anion  | EA_NMePyrrole_F_NO2_rad-anion.log |
| 77   | "                          | CHCCN2         | EA_NMePyrrole_F_CHCCN2_neutral_pop.log |
| 78   | "                          | radical-anion  | EA_NMePyrrole_F_CHCCN2_rad-anion.log |
| 79   | "                          | COCF3          | EA_NMePyrrole_F_COFC3_neutral_pop.log |
| Entry | Aromatic system (sub folder) | -R (sub folder) | Reaction Coordinate | File name |
|-------|-----------------------------|----------------|--------------------|-----------|
| 80    | -                            | radical-anion  | EA_NMePyrrole_F_COOF3_rad-anion.log |
| 81    | -CN                         | neutral        | EA_NMePyrrole_F_CN_neutral_pop.log |
| 82    | -                            | radical-anion  | EA_NMePyrrole_F_COOMe_neutral_pop.log |
| 83    | -COMe                       | neutral        | EA_NMePyrrole_F_COOMe_rad-anion_pop.log |
| 84    | -CO2Me                      | neutral        | EA_NMePyrrole_F_CO2Me_neutral_pop.log |
| 85    | -                            | radical-anion  | EA_NMePyrrole_F_CO2Me_rad-anion.log |
| 86    | -CF3                        | neutral        | EA_NMePyrrole_F_CF3_neutral_pop.log |
|       |                             | radical-anion  | EA_NMePyrrole_F_CF3_rad-anion_pop.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_log |
|       |                             | TS1            | 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_forward.log |
|       | -CN                         | SC             | TS_KOMe_F_CN_NMePyrrole_M11-6311++Gdp_back.log |
|       |                             | TS1            | 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 |
|       | -CO2Me                      | SC             | TS_KOMe_F_CO2Me_NMePyrrole_M11-6311++Gdp_back.log |
|       |                             | TS1            | 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_forward_trial4.log |
| 1m-R-F (Furan) | -NO2                     | neutral        | Furan_F_NO2_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_NO2_rad-anion_pop.log |
|       | -COCF3                      | neutral        | Furan_F_COCF3_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_COCF3_rad-anion_pop.log |
|       | -CN                         | neutral        | Furan_F_CN_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_CN_rad-anion_pop.log |
|       | -COMe                       | neutral        | Furan_F_COMe_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_COMe_rad-anion_pop.log |
|       | -CO2Me                      | neutral        | Furan_F_CO2Me_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_CO2Me_rad-anion_pop.log |
|       | -CF3                        | neutral        | Furan_F_CF3_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_CF3_rad-anion_trial3_pop.log |
|       | -CCH                        | neutral        | Furan_F_CCH_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_CCH_rad-anion_pop.log |
|       | -NCS                        | neutral        | Furan_F_NCS_neutral_pop.log |
|       |                             | radical-anion  | Furan_F_NCS_rad-anion_pop.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_pop.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 |
|       | "                           | -CN            | 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 |
|       | "                           | "              | MI                     | TS_KOMe-F_COMe_Furan_M11-6311++Gdp.log |
|       | "                           | -CO2Me         | SC                     | TS_KOMe-F_CO2Me_Furan_M11-6311++Gdp_back.log |
|       | "                           | "              | MI                     | TS_KOMe-F_CO2Me_Furan_M11-6311++Gdp_forward.log |
| 87    | "                           | -CF3           | SC                     | TS_KOMe-F_CF3_Furan_M11-6311++Gdp_back.log |
|       | "                           | "              | PC                     | TS_KOMe-F_CF3_Furan_M11-6311++Gdp_forward.log |
|       | "                           | -CCH           | SC                     | TS_KOMe-F_CCH_Furan_M11-6311++Gdp_forward.log |
|       | "                           | "              | TS1                    | TS_KOMe-F_CCH_Furan_M11-6311++Gdp_trial2.log |
|       | "                           | "              | PC                     | TS_KOMe-F_CCH_Furan_M11-6311++Gdp_forward.log |
|       | "                           | -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. S₅Ar 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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