Electronic Supplementary Information for

Stereoretention in styrene heterodimerisation promoted by one-electron oxidants

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1. **Computational methods**

DFT calculations were performed with *Gaussian 09* rev. D.01. Geometry optimisations were carried out using the hybrid meta-GGA functional M06-2X within the unrestricted formalism using the Unrestricted Kohn-Sham (UKS) theory, with the Pople-type double-ζ split-valence basis set 6-31G(d). For the hypervalent iodine oxidant, a mixed basis set of LANL2DZ for the Iodine atom and the 6-31G(d) basis set for all other atoms was used. Minima and transition structures on the potential energy surface (PES) were confirmed as such by harmonic frequency analysis at the same level of theory. Intrinsic reaction coordinate (IRC) analyses were carried out to connect the proposed TS structures to correct minima. The eigenvalues of the spin operator $S^2$ after annihilation of spin contamination were found to range from 0.750 to 0.751 for all radical cationic structures, in agreement with the expected value of $S(S+1) = 0.75$ for a doublet wavefunction, indicating that spin contamination is not a problem for the present methodology. Single point corrections were carried out with M06-2X functional using the Karlsruhe-family polarised triple-ζ def2-TZVPP basis set.

The SMD continuum solvation model was included to account for the effect of implicit solvents acetonitrile (MeCN) and hexafluoropropanol (HFIP) on the computed Gibbs energy profile. HFIP is a versatile solvent in organic synthesis, especially in its role in stabilising radical cations and promoting single electron oxidation when combined with hypervalent iodine reagents, making its computational parametrisation within the SMD model important for general use. Since HFIP solvent is not available in the list of default/pre-defined solvents in *Gaussian 09* software, it is herein parametrised using a set of seven parameters. These include the static dielectric constant of the solvent at 25°C ($\varepsilon = 16.7$); dynamic (optical) dielectric constant – the square of the refractive index value of 1.275 at 20°C was used ($\varepsilon_{\text{Inf}} = 1.625625$); hydrogen bond acidity ($HBondAcidity = 1.96$) and basicity ($HBondBasicity = 0.00$), which are Abraham’s A and B values respectively; the surface tension of the solvent at interface ($SurfaceTensionAtInterface = 23.23$); carbon aromaticity – the fraction of aromatic carbons ($CarbonAromaticity = 0.00$) and electronegative halogenicity – the fraction of halogens ($Electronegative Halogenicity = 0.60$). These parameters were specified using the keyword “SCRF = (SMD, Solvent= Generic, Read)” in *Gaussian 09*.

All Gibbs energies were evaluated at 313.15K and were corrected for zero-point vibrational energies at the same level of theory. These values were further corrected by applying the quasi-rigid rotor harmonic oscillator (quasi-RRHO) for the vibrational entropies, as described by Grimme, using a free-rotor approximation for anharmonic vibrational modes below 100 cm$^{-1}$ and a rigid rotor harmonic oscillator approximation above this wavenumber. The free energies were further corrected using a standard concentration of 1 mol L$^{-1}$, which was used in solvation calculations. The solvent-corrected SMD(HFIP)-UM06-2X/def2-TZVPP// UM06-2X/6-31G(d) values are used for discussion.
Energy decomposition analyses were performed every three steps along the IRC up to the transition structures using the second-generation ALMO-EDA method\textsuperscript{22} implemented in Q-Chem.\textsuperscript{23} The total interaction energy was decomposed into Pauli repulsion (E\textsubscript{Pauli}), electrostatics (E\textsubscript{elec}), dispersion (E\textsubscript{disp}), charge-transfer and polarization terms (these last two are collected and reported as E\textsubscript{orb}). These calculations were performed at the M06-2X/def2-TZVP level of theory, with a (99, 590) integration grid.

Non-covalent interactions (NCIs) were analysed using NCIPLOT\textsuperscript{24} calculations. The .wfn files for NCIPLOT were generated at M06-2X/6-31G(d) level of theory. NCI indices calculated with NCIPLOT were visualised at a gradient isosurface value of \( s = 0.5 \) au. These are coloured according to the sign of the second eigenvalue (\( \lambda_2 \)) of the Laplacian of the density (\( \nabla^2 \rho \)) over the range of -0.1 (blue = attractive) to +0.1 (red = repulsive). Molecular orbitals are visualised using an isosurface value of 0.05 a.u. throughout.

Molecular structures, non-covalent interaction plots and spin density plots were visualised using PyMol software.\textsuperscript{25} Unless otherwise stated, all energy values are quoted in kcal mol\(^{-1}\) and bond distances in \( \text{Å} \).

2. Computational electrochemical potential benchmarking

To calculate the electrochemical redox potential, we need to calculate the overall Gibbs energy of reaction in solvent, \( \Delta G^o_{rxn} \) as shown in Scheme 1. One can either a) directly calculate the reaction energies within continuum solvation models, i.e., direct geometry optimisations of both neutral and radical cationic species in the solution phase, or b) construct a thermodynamic cycle by separate gas phase geometry optimisations with single point solvation energy of each species.

\[
\begin{align*}
N^+ \text{(aq)} & \quad + \quad e^- \text{(aq)} & \quad \xrightarrow{\Delta G^o_{rxn}} & \quad N \text{(aq)} \\
-N^+ \text{(g)} & \quad + \quad e^- \text{(g)} & \quad \xrightarrow{\Delta G^o_{gas}} & \quad N \text{(g)} \\
\end{align*}
\]

\( \Delta G^o_{solv}(N^+) \quad \text{and} \quad \Delta G^o_{solv}(e^-) \)

\( \Delta G^o_{gas} \text{ and } \Delta G^o_{solv} \)

**Scheme S1.** Computation of redox potential for the reduction of a radical cation to its neutral form.

We use a thermodynamic cycle here to express \( \Delta G^o_{rxn} \) in terms of the free energy of reaction in gas phase, \( \Delta G^o_{gas} \) and the free energies of solvation, \( \Delta G^o_{solv} \) of the reacting species as shown.\textsuperscript{26,27} Since the differences in the redox potentials obtained from both direct and thermodynamic cycle methods are very small when solvent-induced geometry changes are small (for example, no change in protonation state upon solvation),\textsuperscript{26} we adopt the thermodynamic cycle approach here.
In our calculations, the gas phase energy change, $\Delta G_{\text{gas}}^{0}$, is further refined by calculating the single point energy in gas-phase at a larger basis set (def2-TZVPP) for improved accuracy.\textsuperscript{26} The reduction potentials calculated here are \textit{adiabatic} reduction potentials (ARP) since the energy is taken from each optimised species, i.e.,

$$\text{ARP} = E(\text{optimised neutral}) - E(\text{optimised radical cation}).$$  \hspace{1cm} (1)

We then have

$$\Delta G_{\text{rxn}}^{0} = -\Delta G_{\text{solv}}^{0}(N^{\bullet^{+}}) - \Delta G_{\text{solv}}^{0}(e^{-}) + \Delta G_{\text{gas}}^{0}(N^{\bullet^{+}}) + \Delta G_{\text{solv}}^{0}(N)$$ \hspace{1cm} (2)

The reduction potential of the reaction is then given by

$$E_{\text{cell}} = -\frac{\Delta G_{\text{rxn}}^{0}}{nF} - E_{\text{SHE}}$$ \hspace{1cm} (3)

We need not consider the free energy of solvation of the electron as their contribution cancels out when we consider the full reaction against experimentally measured values.\textsuperscript{27}

To decide on the best functional for the present study, we did a benchmarking study on the reduction potential of our substrates \textit{trans}-anethole 1\textsuperscript{a} and \textit{trans}-β-methylstyrene 1\textsuperscript{b} in MeCN solvent using a number of functionals. The results are given in Table S1, which shows that M06-2X functional gives the best agreement (smallest mean unsigned error) with the experimental redox potential values amongst 8 functionals tested. This is in agreement with a study of both experimental and computational electrochemical potentials for over 180 organic substrates where M06-2X functional gives an R\textsuperscript{2} value of 0.97 for the correlation between the experimental and calculated redox potentials.\textsuperscript{28} We used M06-2X for all subsequent DFT calculations.

|       | Exp\textsuperscript{a} | B3LYP | B3LYP-D3 | B97D | CAM-B3LYP | M06-2X | revPBE | TPSS-D3 | 09B97X-D |
|-------|-------------------------|-------|----------|------|-----------|--------|--------|---------|----------|
| 1\textsuperscript{a} | 1.484 | 1.184 | 1.183 | 0.975 | 1.289 | 1.388 | 1.162 | 1.006 | 1.203 |
| 1\textsuperscript{b} | 1.984 | 1.621 | 1.587 | 1.430 | 1.709 | 1.815 | 1.604 | 1.461 | 1.635 |

\textsuperscript{a}Values are taken from ref.\textsuperscript{28} where potentials are reported against standard calomel electrode in MeCN solvent (1.24V for 1\textsuperscript{a} and 1.74V for 1\textsuperscript{b}). These values are converted to be relative to SHE using conversion constants (+0.244V) in ref.\textsuperscript{29} and then reported herein. For computational studies, a value of $E_{\text{SHE}} = 4.28V$ in SMD model is used.\textsuperscript{26,27,30}

\textbf{Table S1} Computed reduction potentials of \textit{trans}-anethole 1\textsuperscript{a} and \textit{trans}-β-methylstyrene 1\textsuperscript{b} in MeCN solvent using a variety of functionals. All values are in V.
2.1 Conformational considerations for Dess-Martin periodinane (DMP), hexafluoroisopropanol (HFIP) and DMP-HFIP complex

For Dess-Martin periodinane (DMP), the reported X-ray crystal structure\textsuperscript{31} was used as the initial guess for DFT geometry optimization. For the structure of HFIP, 3 possible conformers were known to exist: antiperiplanar, synclinal and gauche.\textsuperscript{32,33} These were separated optimised using DFT and the lowest energy conformer in the gas-phase, the antiperiplanar form, which agrees with experimental observations, is used. We explored the conformations of the DMP-HFIP complex by placing the HFIP molecule, in turn, near one of the 3 acetates, at a distance between the furthest O-atom on acetate and the H-atom on alcohol group of HFIP of > 3 Å and subjecting the structures (both neutral and radical anionic) to DFT optimisation at M06-2X/GENECP(LANL2DZ for I and 6-31+G(d) for others) and then correct for solvent effect at SMD(solvent)-M06-2X/def2-TZVPP level of theory. We then compared the resultant energies of the conformers to establish the ones with lowest energy in either MeCN or HFIP solvent for the neutral and radical anionic species. All the conformers found in this way were shown in Fig. S1. The lowest energy conformers were used for the computation of redox potential of DMP-HFIP complex.

| Neutral DMP-HFIP complex | DMP-HFIP-c1-n | DMP-HFIP-c2-n | DMP-HFIP-c3-n |
|--------------------------|---------------|---------------|---------------|
| ΔΔG = 0.0 (1.2)          | 0.7 (0.0)     | 2.2 (3.1)     |

| Radical anionic DMP-HFIP complex | DMP-HFIP-c1-ra | DMP-HFIP-c2-ra | DMP-HFIP-c3-ra |
|----------------------------------|---------------|---------------|---------------|
| ΔΔG = 0.0 (0.0)                  | 3.4 (0.6)     | 4.6 (7.3)     |
3. Reaction P1 (trans-anethole + trans-β-methylstyrene)

For complete conformational sampling of all the TSs involved in the first C–C bond formation, once a TS is found (for example ts1 in Fig. S2), we rotate one of the reactant, say t-anethole along the forming C–C bond by 120° (since there are 3 groups on each carbon atom involved in the C–C bond formation), and carry out TS search. For the example of ts1, we were able to find ts1-c2 and ts1-c3 in this way. Similarly, ts1’, ts1’-c2 and ts1’-c3 are found for the syn-addition.

|      | ts1   | ts1-c2 | ts1-c3   |
|------|-------|--------|----------|
|      | 13.5‡ (18.2‡) | 15.7‡ (18.4‡) | 15.7‡ (21.2‡) |
| r = 2.09 Å | r = 2.15 Å | r = 2.04 Å |
|      | ts1-c4 | ts2    | ts1’     |
|      | 18.3‡ (21.4‡) | 13.0‡ (16.2‡) | 14.6‡ (17.6‡) |
Fig. S2. Conformations of all TSs for the reaction between trans-anethole and trans-β-methylstyrene (P1). Distances of the first C–C bond formation (r) is given. Gibbs energies are given in kcal mol$^{-1}$. Values are for HFIP solvent with values for MeCN solvent given in brackets.
| ts1     | ts1’    |
|---------|---------|
| ![Spin density plots](image1) | ![Spin density plots](image2) |

| ts1-g1  | ts1-g2  |
|---------|---------|
| ![Spin density plots](image3) | ![Spin density plots](image4) |

**Fig. S3.** Spin density plots (at an isovalue of 0.02 a.u.) and the Mulliken spin density values of radical cationic TSs in reaction P1.

| ts1     | ts1’    |
|---------|---------|
| ![NCI plots](image5) | ![NCI plots](image6) |

| ts1-g1  | ts1-g2  |
|---------|---------|
| ![NCI plots](image7) | ![NCI plots](image8) |

**Fig. S4.** NCI plots for head-to-head and head-to-tail first C–C bond formations TSs in reaction P1.

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The distortion-interaction\textsuperscript{34,35}/activation strain (DI-AS) model\textsuperscript{35–38} was applied to understand the steric and electronic factors controlling the selectivity of cyclobutene formation. To further break down the electronic contributions and understand the contributions of the interaction energy in terms of nature of chemical bonds, we applied the energy decomposition analysis (EDA) to the TSs for the formation of cyclobutanes. EDA breaks down the interaction energy into repulsive exchange energy due to Pauli’s principle, $E_{\text{Pauli}}$, the (semi-)classical electrostatic interaction energy between the charge densities of the fragments, $E_{\text{elec}}$, the orbital interaction energies between the fragments as the TS occurs, $E_{\text{orb}}$, and the dispersion energy between the fragments $E_{\text{disp}}$. Fig. S5 to Fig. S8 shows the individual DI-AS energy and the EDA analysis for key TSs in reaction P1.

**Fig. S5.** Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1 (anti-addition) in reaction P1.
**Fig. S6.** Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1\(^{\dagger}\) (syn-addition) in reaction P1.
Fig. S7. Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1-g1 in reaction P1.
**Fig. S8.** Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1-g2 in reaction P1.
In Fig. S9 to Fig. S11, we do a pairwise comparison (between the major product and the other products) of the individual contributions to the interaction energy governing the selectivity in the TSs in reaction P1. Legend for the plots follow those in Fig. 3 in the main text.

**Fig. S9.** Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1 (star marker) and ts1′ (square marker) in reaction P1.
Fig. S10. Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1 (star marker) and ts1-g1 (full circle marker) in reaction P1.
**Fig. S11.** Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts1 (star marker) and ts1-\textbf{g2} (cross marker) in reaction P1.
4. Reaction P2 (trans-anethole + cis-β-methylstyrene)

Conformational sampling of all the TSs involved in the first C–C bond formation for this pathway were done in a similar fashion as described for reaction P1 in section 3.

|        | ts6   | ts6-c2 | ts7   |
|--------|-------|--------|-------|
| E (kcal/mol) | 19.3‡ (22.7‡) | 21.2‡ (24.6‡) | 17.4‡ (21.1‡) |
| r (Å)  | 2.09  | 2.12   | 1.58  |

|        | ts6'   | ts6'-c2 | ts6'-c2 |
|--------|--------|---------|---------|
| E (kcal/mol) | 16.1‡ (21.7‡) | 20.1‡ (22.9‡) | 21.1‡ (23.6‡) |
| r (Å)  | 2.07  | 2.13   | 1.97  |

|        | ts6-g1 | ts6-g1-c2 |
|--------|--------|-----------|
| E (kcal/mol) | 17.4‡ (20.3‡) | 21.3‡ (25.0‡) | 26.5‡ (29.9‡) |
| r (Å)  | 1.58  | 1.94   | 1.81  |

|        | ts6-g2 | ts6-g2-c2 |
|--------|--------|-----------|
| E (kcal/mol) | 22.6‡ (27.1‡) | 23.6‡ (26.9‡) |
Fig. S12. Conformations of all TSs for the reaction between trans-anethole and cis-β-methylstyrene (P2). Distances of the first C–C bond formation (r) is given. Gibbs energies are given in kcal mol⁻¹. Values are for HFIP solvent with values for MeCN solvent given in brackets.

| ts6   | ts6'  |
|-------|-------|
| ![Image](image1.png) | ![Image](image2.png) |
| ts6-g1 | ts6-g2 |
| ![Image](image3.png) | ![Image](image4.png) |

Fig. S13. Spin density plots (at an isovalue of 0.02 a.u.) and the Mulliken spin density values of radical cationic TSs for the reaction between trans-anethole and cis-β-methylstyrene.
| ts6   | ts6′  |
|-------|-------|
| ![ts6](image1) | ![ts6′](image2) |
| ts6-g1 | ts6-g2 |
| ![ts6-g1](image3) | ![ts6-g2](image4) |

Fig. S14. NCI plots for head-to-head and head-to-tail first C–C bond formations TSs in reaction P2.
Fig. S15. The activation strain or distortion-interaction analyses applied to transition structures for both head-to-head (ts6 and ts6') and head-to-tail (ts6-g1 and ts6-g2) first C–C bond formation TSs. All energies are calculated at UM062X/def2TZVPP//UM062X/6-31G(d) and used without any further corrections.
Similar DI-AS/EDA results for the key TSs are shown in Fig. S16 to Fig. S19.

Fig. S16. Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6 (anti-addition) in reaction P2.
Fig. S17. Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6' (syn-addition) in reaction P2.
Fig. S18. Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6-g1 in reaction P2.
**Fig. S19.** Distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6-g2 in reaction P2.

The comparison between the major product and the other products of the individual contributions to the interaction energy governing the selectivity in the TSs in reaction P2 is shown in Fig. S20 to Fig. S22. Legend for the plots follow those in Fig. S15.
Fig. S20. Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6* (square marker) and ts6' (star marker) in reaction P2.
Fig. S21. Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6' (square marker) and ts6-g1 (full circle marker) in reaction P2. The dominant difference in the interaction comes from the charge transfer term (RHS) which is ~ 5 kcal mol\(^{-1}\) at around 2.07 Å (note the large y-axis scale that makes this less obvious).
Fig. S22. Comparison of the distortion interaction-action strain model (DI-AS) and absolutely-localized molecular orbitals energy decomposition analysis (ALMO-EDA) for ts6' (square marker) and ts6-g2 (cross marker) in reaction P2. The dominant difference in the interaction comes from the charge transfer term (RHS) which is ~ 5.5 kcal mol\(^{-1}\) at around 2.07 Å (note the large y-axis scale that makes this less obvious).
5. Estimate of electron transfer barrier

The Marcus-Hush\textsuperscript{39-42} theory is used to relate quantitatively the rate of electron transfer ($k_{ET}$) to the Gibbs energy of a reaction ($\Delta G_r$). In this framework, molecules involved in the electron transfer (ET) are treated as spheres and the solvent is treated as a continuum. Parabolic energy curves are used to represent the states of reactants and products. It is further assumed that the two parabolas have the same curvature. Within the diabatic representation (where the coupling between the two potential energy surfaces is due to electronic terms), the TS for the electron transfer (ET) occurs at where the two parabolas cross (Scheme S2).

![Scheme S2](image)

**Scheme S2.** Schematic representation of Marcus-Hush theory using parabolic Gibbs energy curves of the reactants and products.

With these, the activation energy of the ET, $\Delta G_{ET}^\ddagger$, is given by

$$\Delta G_{ET}^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{\Delta G_r}{\lambda} \right)$$

(4)

where $\Delta G_r$ is the free energy change of the reaction, in our case for the reduction of radical cation ($A^{+\cdot}$) by a neutral species (B), this is given by

$$A^{+\cdot} + B \longrightarrow A + B^{+\cdot}$$

$$\Delta G_r = G(A) + G(B^{+\cdot}) - G(A^{+\cdot}) + G(B)$$

(5)
\( \lambda \) is the reorganisation energy, which is defined as the energy required to distort the reactant molecules and the surrounding solvent shell to that of the product in its equilibrium (Scheme S2).

The rate of electron transfer, \( k_{ET} \), is then related to the activation energy of the ET, \( \Delta G_{ET}^\ddagger \), via an Arrhenius-like expression:

\[
k_{ET} = Ae^{-\Delta G^\ddagger / RT}
\]  

(6)

The reorganisation energy is composed of two parts, the internal reorganisation energy, \( \lambda_i \), and external polarisation, \( \lambda_o \), i.e., \( \lambda = \lambda_i + \lambda_o \). The former term \( \lambda_i \) describes the energy associated with geometry changes when going from the reactant to the product state; the latter term \( \lambda_o \) describes the energy change due to the polarisation/reorganisation in the surrounding (solvent) molecules due to the ET process.

In our estimation of the ET barriers, we assume that the geometry change upon electron transfer is small such that we can ignore the internal reorganisation energy (\( \lambda_i = 0 \)). Thus, \( \lambda = \lambda_o \). Using Marcus equation, the solvent reorganisation energy is given by\textsuperscript{39-42}

\[
\lambda_o = (\Delta e)^2 \cdot \left[ \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right] \cdot \left[ \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right]
\]

\[
= (322 \text{ kcal mol}^{-1}) \left[ \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right] \cdot \left[ \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right]
\]

(7)

where \( \Delta e \) is the amount of charge transferred, \( a_1 \) and \( a_2 \) are the radii of the molecules involved (A and B in Equation 5), \( R \) is the distance between their centres, \( \epsilon_{op} \) is the optical/dynamic dielectric constant (\( \epsilon_{op} = 1.625625 \)) and \( \epsilon \) is the static dielectric constant of the solvent (\( \epsilon = 16.7 \)) (see values of HFIP solvent in the Computational Methods section). Hence, by calculating the molecular radii of the molecules (using Gaussian “volume” keyword and the recommended \( a_0 \) value) involved in an electron transfer process, we are able to estimate the barrier of such a process using the Marcus-Hush theory outlined above (Tables S2–4).

| structure     | \( t \)-anethole | int3 | int3' | int8 | int8' |
|---------------|------------------|------|-------|------|-------|
| Recommended \( a_0 \)/Å | 4.69             | 4.95 | 5.40  | 5.39 | 5.12  |

Table S2. Computed recommended radii of structures involved in the electron transfer step in the reduction of radical cationic cyclobutyl ring to the neutral cyclobutyl ring by neutral \( t \)-anethole.

The rate of electron transfer decreases exponentially with increasing separation between the species involved in the transfer due to the Arrhenius-like dependence of the rate equation on the barrier of ET (Eq. (6)). In Eq. (7), \( R \) is the distance between the centres of the two species. We investigated the dependence of the activation barrier of ET on the separation of molecules, \( d \). The distance between two molecular centres \( R \) and the separation of the molecules \( d \) are related via
\[ R = a_1 + a_2 + d \]  

(8)

where \( a_1 \) and \( a_2 \) are the radii of the molecules involved (Scheme S3).

\[ R = a_1 + a_2 + d \]

![Diagram of intermolecular separation](image)

**Scheme S3.** Relation between the intermolecular separation \( d \) and the separation between two centres \( R \) that is used in Eq. (7).

Tables S3 and S4 are the computed values of \( \lambda \) and \( \Delta G_{ET}^\ddagger \) in HFIP and in MeCN solvent, respectively. The corresponding plots showing the dependence of \( \Delta G_{ET}^\ddagger \) on the intermolecular separation \( d \) is given in Fig. S23 and S24 respectively. Using an average intermolecular separation of 3.0 Å (c.f. intermolecular separation of 3.1Å in liquid water), we estimate that the barriers for ET in HFIP solvent is on the order of 1–3 kcal mol\(^{-1}\), whereas that in MeCN is on the order of 0–2 kcal mol\(^{-1}\).

| Separation | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) |
|------------|-------------------------------|----------------------|-------------------------------|----------------------|-------------------------------|----------------------|
| \( d / \text{Å} \) | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) | \( \lambda / \text{kcal mol}^{-1} \) | \( \Delta G_{ET}^\ddagger / \text{kcal mol}^{-1} \) |
| 0.00       | 18.6                          | 1.6                  | 17.9                          | 1.6                  | 17.9                          | 0.4                  |
| 0.25       | 19.0                          | 1.8                  | 18.3                          | 1.7                  | 18.3                          | 0.5                  |
| 0.50       | 19.5                          | 1.9                  | 18.7                          | 1.8                  | 18.7                          | 0.6                  |
| 0.75       | 19.9                          | 2.0                  | 19.1                          | 1.9                  | 19.1                          | 0.7                  |
| 1.00       | 20.3                          | 2.1                  | 19.5                          | 2.0                  | 19.5                          | 0.8                  |
| 1.25       | 20.7                          | 2.2                  | 19.8                          | 2.1                  | 19.9                          | 0.9                  |

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Table S3. Computed solvent reorganisation energy $\lambda$ and electron transfer barriers $\Delta G_{ET}^{\dagger}$ for the reduction of radical cationic cyclobutyl rings to their neutral form by $t$-anethole in HFIP solvent. Optical dielectric constant ($\epsilon_{op} = 1.625625$) and static dielectric constant ($\epsilon = 16.7$) of the solvent HFIP were used in Eq. (7). $a_1 = 4.69$ Å is the radius of $t$-anethole; $a_2$ is the radius of radical cationic cyclobutyl ring ($a_2$(int3) = 4.95 Å; $a_2$(int3') = 5.40 Å; $a_2$(int8) = 5.39 Å; $a_2$(int8') = 5.12 Å as in Table S2). $R = a_1 + a_2 + d$ is the total separation between the centres of the species involved in ET (Scheme S3).

| $\lambda$ | 1.50 | 2.00 | 2.25 | 2.50 | 2.75 | 3.00 | 3.25 | 3.50 | 3.75 | 4.00 | 4.25 | 4.50 | 4.75 | 5.00 | 5.25 | 5.50 | 5.75 | 6.00 |
|-----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 21.1      | 21.4 | 21.8 | 22.1 | 22.4 | 22.7 | 23.0 | 23.3 | 23.5 | 23.8 | 24.0 | 24.2 | 24.5 | 24.7 | 24.9 | 25.1 | 25.3 | 25.5 | 25.7 |
| 2.3       | 2.4  | 2.4  | 2.5  | 2.6  | 2.7  | 2.7  | 2.8  | 2.9  | 2.9  | 3.0  | 3.1  | 3.1  | 3.2  | 3.2  | 3.3  | 3.4  | 3.4  | 3.4  |
| 20.2      | 20.5 | 20.8 | 21.1 | 21.4 | 21.7 | 22.0 | 22.2 | 22.5 | 22.7 | 22.9 | 23.1 | 23.4 | 23.6 | 23.8 | 24.0 | 24.1 | 24.3 | 24.5 |
| 2.1       | 2.2  | 2.3  | 2.4  | 2.5  | 2.7  | 2.7  | 2.8  | 3.0  | 3.0  | 3.1  | 3.1  | 3.1  | 3.2  | 3.2  | 3.3  | 3.3  | 3.4  | 3.4  |
| 20.2      | 20.5 | 20.8 | 21.1 | 21.4 | 21.7 | 22.0 | 22.2 | 22.5 | 22.7 | 22.9 | 23.1 | 23.4 | 23.6 | 23.8 | 24.0 | 24.1 | 24.3 | 24.5 |
| 1.0       | 20.7 | 1.1  | 1.2  | 1.3  | 1.6  | 1.6  | 1.7  | 1.8  | 1.8  | 1.9  | 1.7  | 1.8  | 1.8  | 1.9  | 1.9  | 2.0  | 2.0  | 2.1  |
| 2.2       |      | 1.8  | 1.9  | 2.0  | 2.1  | 2.2  | 2.3  | 2.3  | 2.4  | 2.5  | 2.5  | 2.6  | 2.6  | 2.7  | 2.7  | 2.8  | 2.8  | 2.9  |
| Separation d/Å | int3  λ / kcal mol⁻¹ | Δ\(\text{CT}\) / kcal mol⁻¹ | int3'  λ / kcal mol⁻¹ | Δ\(\text{CT}\) / kcal mol⁻¹ | Int8  λ / kcal mol⁻¹ | Δ\(\text{G}_\text{r}\) / kcal mol⁻¹ | Int8' λ / kcal mol⁻¹ | Δ\(\text{CT}\) / kcal mol⁻¹ |
|---------------|----------------------|-----------------------------|----------------------|-----------------------------|----------------------|-----------------------------|----------------------|-----------------------------|
| 0.00          | 17.8                 | 0.6                         | 17.2                 | 0.3                         | 17.2                 | -0.8                        | 17.6                 | 0.0                         |
| 0.25          | 18.3                 | 0.7                         | 17.6                 | 0.4                         | 17.6                 | -0.7                        | 18.0                 | 0.1                         |
| 0.50          | 18.7                 | 0.8                         | 18.0                 | 0.5                         | 18.0                 | -0.6                        | 18.4                 | 0.2                         |
| 0.75          | 19.1                 | 0.9                         | 18.4                 | 0.6                         | 18.4                 | -0.5                        | 18.8                 | 0.3                         |
| 1.00          | 19.5                 | 1.0                         | 18.7                 | 0.7                         | 18.7                 | -0.4                        | 19.2                 | 0.4                         |
| 1.25          | 19.9                 | 1.1                         | 19.0                 | 0.8                         | 19.1                 | -0.3                        | 19.5                 | 0.5                         |
| 1.50          | 20.2                 | 1.2                         | 19.4                 | 0.9                         | 19.4                 | -0.3                        | 19.9                 | 0.6                         |
| 1.75          | 20.6                 | 1.3                         | 19.7                 | 0.9                         | 19.7                 | -0.2                        | 20.2                 | 0.7                         |
| 2.00          | 20.9                 | 1.3                         | 20.0                 | 1.0                         | 20.0                 | -0.1                        | 20.5                 | 0.7                         |
| 2.25          | 21.2                 | 1.4                         | 20.3                 | 1.1                         | 20.3                 | 0.0                         | 20.8                 | 0.8                         |
| 2.50          | 21.5                 | 1.5                         | 20.6                 | 1.2                         | 20.6                 | 0.0                         | 21.1                 | 0.9                         |
| 2.75          | 21.8                 | 1.6                         | 20.8                 | 1.2                         | 20.8                 | 0.1                         | 21.4                 | 0.9                         |
| 3.00          | 22.1                 | 1.6                         | 21.1                 | 1.3                         | 21.1                 | 0.2                         | 21.7                 | 1.0                         |
| 3.25          | 22.3                 | 1.7                         | 21.3                 | 1.4                         | 21.3                 | 0.2                         | 21.9                 | 1.1                         |
| 3.50          | 22.6                 | 1.8                         | 21.6                 | 1.4                         | 21.6                 | 0.3                         | 22.2                 | 1.1                         |
| 3.75          | 22.8                 | 1.8                         | 21.8                 | 1.5                         | 21.8                 | 0.4                         | 22.4                 | 1.2                         |
| 4.00          | 23.0                 | 1.9                         | 22.0                 | 1.5                         | 22.0                 | 0.4                         | 22.6                 | 1.3                         |
| 4.25          | 23.3                 | 1.9                         | 22.2                 | 1.6                         | 22.2                 | 0.5                         | 22.8                 | 1.3                         |
| 4.50          | 23.5                 | 2.0                         | 22.4                 | 1.6                         | 22.4                 | 0.5                         | 23.1                 | 1.4                         |
Table S4. Computed solvent reorganisation energy $\lambda$ and electron transfer barriers $\Delta G_{ET}^\ddagger$ for the reduction of radical cationic cyclobutyl rings to their neutral form by $t$-anethole in MeCN solvent. Optical dielectric constant, which is the square of the refractive index of acetonitrile 1.33934$^{43}$ ($\varepsilon_{\text{op}} = 1.79$) and static dielectric constant ($\varepsilon = 38.8)^{43}$ of the solvent MeCB were used in Eq. (7). $a_1 = 4.69$ Å is the radius of $t$-anethole; $a_2$ is the radius of radical cationic cyclobutyl ring ($a_2$ (int3) = 4.95 Å; $a_2$ (int3') = 5.40 Å; $a_2$ (int8) = 5.39 Å; $a_2$ (int8') = 5.12 Å as in Table S2). $R = a_1 + a_2 + d$ is the total separation between the centres of the species involved in ET (Scheme S3).

|       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 4.75  | 23.7  | 2.1   | 22.6  | 1.7   | 22.6  | 0.6   | 23.3  | 1.4   |
| 5.00  | 23.9  | 2.1   | 22.8  | 1.7   | 22.8  | 0.6   | 23.5  | 1.5   |
| 5.25  | 24.1  | 2.2   | 23.0  | 1.8   | 23.0  | 0.7   | 23.7  | 1.5   |
| 5.50  | 24.3  | 2.2   | 23.2  | 1.8   | 23.2  | 0.7   | 23.8  | 1.6   |
| 5.75  | 24.5  | 2.2   | 23.3  | 1.9   | 23.4  | 0.7   | 24.0  | 1.6   |
| 6.00  | 24.7  | 2.3   | 23.5  | 1.9   | 23.5  | 0.8   | 24.2  | 1.6   |

Fig. S23. Computed electron transfer barriers $\Delta G_{ET}^\ddagger$ as a function of intermolecular separation $d$ in HFIP solvent plotted using data from Table S3.
Studies of both organic and inorganic systems in the gas phase revealed fast electron transfer rates close to diffusion limit. The reaction barriers are thus much smaller than that for the chemical transformations. It was also shown that the rate of electron transfer in gas phase is more than $10^4$ times faster than in solvents. We found that the ET barriers are very small (1–3 kcal mol$^{-1}$ in HFIP) for the reduction of radical cationic products to their neutral forms for the exergonic reactions. These calculations show that ET processes occur much faster than bond-forming events.

Fig. S24. Computed electron transfer barriers $\Delta G_{ET}^\dagger$ as a function of intermolecular separation $d$ in MeCN solvent plotted using data from Table S4.
6. Absolute contribution to Gibbs energies

| Structure | E/au     | ZPE/au     | H/au     | qh-G/au     | SP DFT (MeCN)       | SP DFT (HFIP)       |
|-----------|----------|------------|----------|-------------|---------------------|---------------------|
| 1a_n      | -463.275335 | 0.196779   | -463.06578 | -463.113618 | -463.47216          | -463.45545          |
| 1a_rc     | -463.009101 | 0.196496   | -462.79962 | -462.848486 | -463.26901          | -463.24939          |
| 1b_n      | -348.797531 | 0.163449   | -348.624   | -348.665962 | -348.94416          | -348.93471          |
| 1b_rc     | -348.508642 | 0.162615   | -348.33574 | -348.378687 | -348.72508          | -348.71327          |
| 2a_n      | -463.272892 | 0.197361   | -463.06308 | -463.110068 | -463.46919          | -463.45309          |
| 2a_rc     | -463.002658 | 0.197471   | -462.79254 | -462.840538 | -463.26241          | -463.24302          |
| 2b_n      | -348.79484  | 0.16385    | -348.6212  | -348.662328 | -348.9408965        | -348.9320263        |
| 2b_rc     | -348.50186  | 0.163047   | -348.32873 | -348.371138 | -348.7182068        | -348.7067152        |

Pathways for reaction P1:

| Structure | E/au     | ZPE/au     | H/au     | qh-G/au     | SP DFT (MeCN)       | SP DFT (HFIP)       |
|-----------|----------|------------|----------|-------------|---------------------|---------------------|
| int1      | -811.830601 | 0.361677   | -811.4454 | -811.51614  | -812.22251          | -812.2014           |
| ts1       | -811.8204  | 0.362952   | -811.43567 | -811.502488 | -812.20993          | -812.18829          |
| ts1-c2    | -811.819673 | 0.362972   | -811.43472 | -811.502623 | -812.2087           | -812.184            |
| ts1-c3    | -811.817037 | 0.363451   | -811.43215 | -811.498282 | -812.20593          | -812.18563          |
| ts1-c4    | -811.8155  | 0.36279    | -811.43086 | -811.4983   | -812.2041           | -812.1799           |
| int2      | -811.827989 | 0.364325   | -811.44197 | -811.50846  | -812.21797          | -812.19793          |
| int2-c2   | -811.820702 | 0.364306   | -811.43435 | -811.502244 | -812.2152           | -812.1903           |
| ts2       | -811.820847 | 0.363704   | -811.43568 | -811.502244 | -812.21374          | -812.18974          |
| int3      | -811.840226 | 0.365772   | -811.45287 | -811.519828 | -812.22781          | -812.2043           |
| int3n     | -812.112396 | 0.366062   | -811.72494 | -811.791592 | -812.44141          | -812.42075          |
| int1'     | -811.830818 | 0.361768   | -811.44565 | -811.516213 | -812.2224           | -812.2011           |
| ts1'      | -811.819644 | 0.362084   | -811.4353  | -811.503838 | -812.2087           | -812.1845           |
| int2'     | -811.828386 | 0.364445   | -811.44207 | -811.509328 | -812.2171           | -812.1934           |
| ts2'      | -811.820275 | 0.36361    | -811.43523 | -811.501806 | -812.2145           | -812.1908           |
|       | Energy 1  | Energy 2  | Energy 3  | Energy 4  | Energy 5  |
|-------|-----------|-----------|-----------|-----------|-----------|
| int3' | -811.835024 | 0.365927 | -811.44761 | -811.514395 | -812.2244 | -812.2019 |
| int3'n | -812.107687 | 0.367099 | -811.71966 | -811.784291 | -812.4374 | -812.4175 |
| ts1'-c2 | -811.819856 | 0.362392 | -811.43541 | -811.503368 | -812.2088 | -812.1851 |
| int2'-c2 | -811.826467 | 0.364267 | -811.44032 | -811.507619 | -812.2142 | -812.1906 |
| ts1'-c3 | -811.817539 | 0.363326 | -811.43235 | -811.499952 | -812.2055 | -812.1814 |
| ts2'-c2 | -811.823048 | 0.364276 | -811.4376 | -811.503233 | -812.2148 | -812.1918 |
| ts1-g1 | -811.809343 | 0.36205 | -811.42516 | -811.493286 | -812.20077 | -812.17717 |
| ts1-g1-c2 | -811.806243 | 0.361937 | -811.42217 | -811.490302 | -812.19741 | -812.17262 |
| int3-g1 | -811.831003 | 0.365911 | -811.44365 | -811.510568 | -812.22339 | -812.2003 |
| int3n-g1 | -812.10813 | 0.366794 | -811.7204 | -811.785243 | -812.43726 | -812.41714 |
| ts1-g2 | -811.807979 | 0.362206 | -811.4238 | -811.491482 | -812.19861 | -812.17524 |
| ts1-g2-c2 | -811.807962 | 0.362225 | -811.42389 | -811.490853 | -812.19733 | -812.17567 |
| int3-g2 | -811.836531 | 0.365899 | -811.44902 | -811.516229 | -812.22909 | -812.20503 |
| int3n-g2 | -812.112681 | 0.365856 | -811.72627 | -811.79125 | -812.44314 | -812.42185 |

Pathways for reaction P2:

|       | Energy 1  | Energy 2  | Energy 3  | Energy 4  | Energy 5  |
|-------|-----------|-----------|-----------|-----------|-----------|
| int6  | -811.827255 | 0.362165 | -811.44194 | -811.511825 | -812.2197 | -812.1982 |
| ts6   | -811.8138 | 0.36304 | -811.42878 | -811.496384 | -812.2023 | -812.1785 |
| int7  | -811.821458 | 0.364966 | -811.43464 | -811.501867 | -812.2103 | -812.1865 |
| ts6-c2 | -811.811556 | 0.363612 | -811.42618 | -811.493393 | -812.2 | -812.1763 |
| ts7   | -811.81425 | 0.364527 | -811.42861 | -811.494203 | -812.2074 | -812.1843 |
| int8  | -811.829942 | 0.366245 | -811.44256 | -811.508156 | -812.2191 | -812.1968 |
| int8n | -812.103398 | 0.367212 | -811.71538 | -811.779767 | -812.4319 | -812.4125 |
| int6' | -811.827223 | 0.362287 | -811.44177 | -811.51156 | -812.2202 | -812.1994 |
| ts6'  | -811.816034 | 0.363552 | -811.43102 | -811.496903 | -812.2056 | -812.1854 |
| int7' | -811.82257 | 0.364928 | -811.43621 | -811.501884 | -812.2118 | -812.192 |
| ts6'-c2 | -811.8122 | 0.363485 | -811.42696 | -811.49451 | -812.201 | -812.176 |
| ts6'-c3 | -811.8122 | 0.363485 | -811.42696 | -811.49451 | -812.201 | -812.176 |
Table S5. Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 363K) for the SET-catalysed cyclobutanation. Suffix “n” in the structure names denotes neutral species and “ra” denotes radical anionic species. Unless otherwise stated, all other species are radical cationic.

| Structure       | E/au     | ZPE/au      | qh-G/au    | SP DFT (Gas)          | SP DFT (MeCN)          | SP DFT (HFIP)          |
|-----------------|----------|-------------|------------|-----------------------|------------------------|------------------------|
| DMP_n           | -1115.8415 | 0.249938   | -1115.645008 | -1402.6497            | -1402.735629           | -1402.662437           |
| DMP_ra          | -1115.7557 | 0.252638   | -1115.554097 | -1402.5603            | -1402.591708           | -1402.510992           |
| DMP-HFIP-c1-n   | -1905.3042 | 0.319248   | -1905.047433 | -2192.4754            | -2192.50852            | -2192.435681           |
| DMP-HFIP-c2-n   | -1905.3081 | 0.319648   | -1905.051909 | -2192.4767            | -2192.509908           | -2192.433998           |
Table S6. Absolute values (in Hartrees) used for redox potential calculation. SP (gas) denotes gas-phase correction at M06-2X/def2-TZVPP level of theory. The solvent corrections are the same as before.
7. Optimised geometries

Geometries of all optimized structures (in .xyz format with their associated energy in Hartrees) are included in a separate folder named ESI_structures_xyz with an associated README file. All these data have been deposited with this Supporting Information and uploaded to Zenodo.org (DOI: 10.5281/zenodo.3946825).

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