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Electric-Field-Assisted Organic Synthesis: A New Frontier in Reactivity Control

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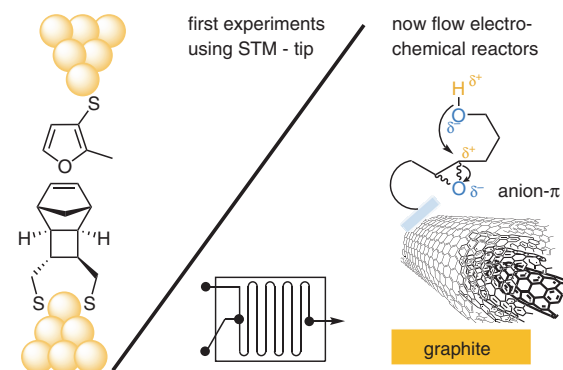
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Abstract The application of oriented external electric fields (OEEFs) to modulate chemical reactivity—termed electric field catalysis—is emerging as a powerful strategy in synthetic chemistry. Inspired by nature’s use of internal fields in enzymatic systems, this approach offers the potential to control reaction pathways, improve selectivity, and reduce energy input. While the theoretical foundations are robust, practical implementation remains challenging, particularly due to difficulties in generating stable, precisely oriented fields at the molecular scale. Recent advances, however, are addressing these obstacles. Notably, the use of multiwalled carbon nanotubes (MWCNTs), owing to their nanoscale architecture, electrical conductivity, and chemical robustness, has enabled the creation of electromicrofluidic devices capable of delivering localised electric fields with high spatial precision. Collaborative efforts, including those by the Matile group and our own, demonstrate the viability of these platforms in catalysis. These developments mark a significant step toward the broader adoption of electric-field-assisted synthesis in organic chemistry.

Key words catalysis, electromicrofluidic devices, molecular transformations, multiwalled carbon nanotubes, oriented electric fields

The emerging concept of using oriented external electric fields (OEEFs) to accelerate and steer the movement of electrons during chemical reactions is rapidly gaining traction as a transformative tool in synthetic chemistry. This approach, also referred to as *electric field catalysis*, is

grounded in strong theoretical foundations¹ and is inspired by nature’s own use of electric fields in enzymatic catalysis.² The ability to modulate reaction pathways and enhance selectivity or efficiency by applying electric fields promises to redefine how chemists design and build molecules, potentially reducing energy demands and enabling unprecedented control over molecular transformations.

Despite its compelling potential, the practical implementation of electric field catalysis has remained elusive. Mainly technical challenges, for example delivering stable and precisely oriented fields at the molecular scale, and integrating such control into routine synthetic workflows, have slowed development in this area. Nevertheless, several pioneering studies have laid important groundwork, demonstrating proof-of-concept systems and innovative strategies for field-induced catalysis.³ These early efforts have provided critical insights, though widespread adoption has been hindered by limitations in materials, device architecture, and field stability under the applied reaction conditions.

Control over the charge translocation during molecular transformations with oriented external electric fields appears highly attractive for organic synthesis. Recently, several research groups have identified a promising path forward by leveraging the unique properties of multiwalled carbon nanotubes (MWCNTs),⁴ which offer high electrical conductivity, nanoscale dimensions, and chemical stability. The group of Matile (Geneva) and our own have integrated such MWCNTs into electromicrofluidic devices;⁵ these structures present a viable platform for generating and controlling localised electric fields with the precision required for catalysis. This realisation opens new avenues for addressing longstanding barriers and brings the prospect of routine electric-field-assisted synthesis closer to reality.

Herein we show most of the recent developments in carrying out chemical reactions in electric fields and the current developments of using electric fields for reaction control.

Biosketches



Huw Chadwick studied chemistry at Cardiff University and earned his BSc in 2021. He then went on to achieve his master's degree in medicinal chemistry in 2023 from Cardiff Uni-

versity after working with Dr. Louis Luk developing site-specific protein-labelling techniques. In late 2023 he joined Prof. Thomas Wirth's group at Cardiff University, where his

doctoral research focuses on the modification of electrodes for tuneable catalysis.



Georgia Cocking studied chemistry at Cardiff University and received her MChem degree in 2025 for her project on

modifying the surface of carbon felt electrodes for electrochemical reactions. She is currently studying for her PhD in

the group of Prof. Thomas Wirth, focusing on the development of alternative synthetic, sustainable methodologies.



Johannes Westphäling studied chemistry at the RWTH Aachen University in Aachen, Germany, where he completed his MSc degree in early 2024. During this time, he conducted short research stays at the Institute of Chemical Research of

Catalonia (ICIQ) in Tarragona, Spain, and the Korea Advanced Institute of Science and Technology (KAIST)/Institute for Basic Science, Center for Catalytic Hydrocarbon Functionalisations (IBS-CCHF) in Daejeon, South Korea. He joined the group of

Prof. Mu-Hyun Baik at KAIST/IBS-CCHF for his PhD studies, where his current research is focusing on computational chemistry and electro-inductive effects.



Rebecca Melen studied for her undergraduate and PhD degrees at the University of Cambridge, completing her PhD in 2012 with Prof. Dominic Wright. Following postdoctoral stud-

ies with Prof. Douglas Stephan in Toronto and with Prof. Lutz Gade in Heidelberg, she took up a position at Cardiff University in 2014, where she is now a professor in inorganic chemis-

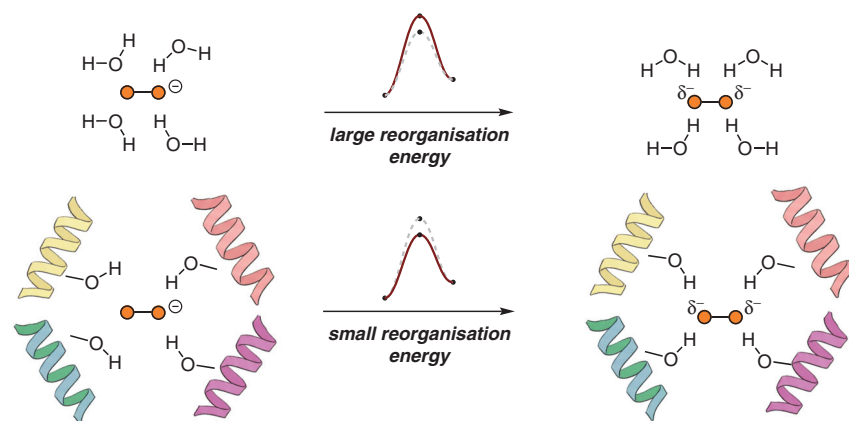
try. Her research interests lie in main group chemistry and the applications of main group Lewis acids in synthesis and catalysis.



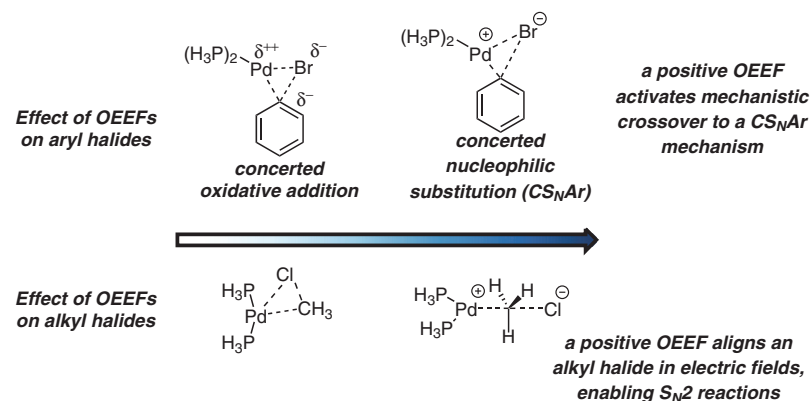
Thomas Wirth is professor of organic chemistry at Cardiff University. He received his PhD in 1992 after studying chemistry at Bonn and the Technical University of Berlin. After a

postdoctoral stay at Kyoto University as a JSPS fellow, he worked independently at the University of Basel before taking up his current position at Cardiff University in 2000. His main

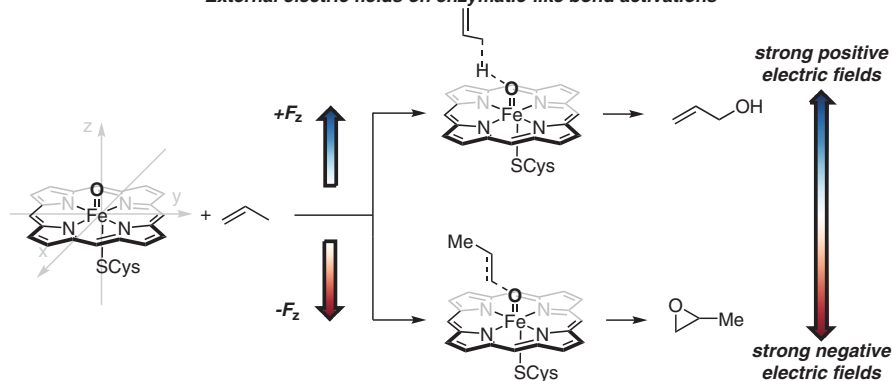
interests of research concern stereoselective electrophilic reactions, oxidative transformations with hypervalent iodine reagents and flow chemistry performed in microreactors.

Electrostatic preorganisation in enzymes as the origin of their catalytic power

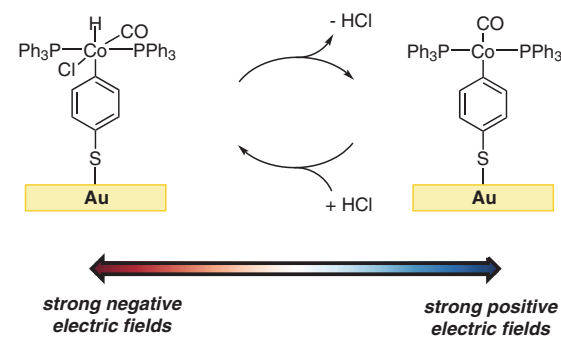
Key references: (6a) Warshel, *J. Mol. Biol.* **1976**, 103, 227. (6b) Warshel, *Chem. Rev.* **2006**, 106, 3210. (6c) Warshel, *J. Biol. Chem.* **1998**, 273, 27035.

Oriented external electric fields (OEEFs) in organometallic chemistry

Key references: (6d) Joy, *J. Am. Chem. Soc.* **2020**, 142, 3836. (6e) Shaik, *J. Am. Chem. Soc.* **2020**, 142, 12551.

External electric fields on enzymatic-like bond activations

Key references: (6f) Shaik, *J. Am. Chem. Soc.* **2004**, 126, 11746. (1a) Shaik, *ACS Phys. Chem. Au* **2024**, 4, 191.

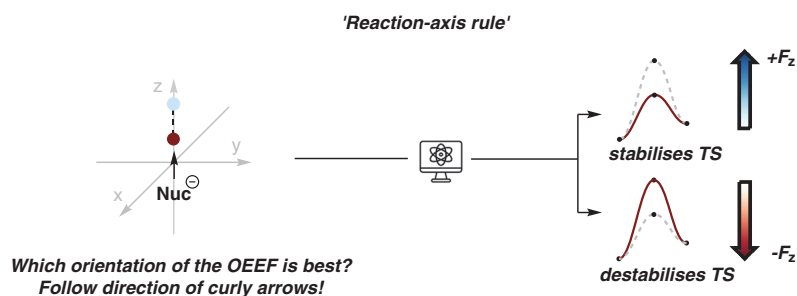
Field-switchable oxidative addition and reductive elimination

Key reference: (6g) Long, *J. Phys. Chem. Lett.* **2025**, 16, 2881.

Key Features:

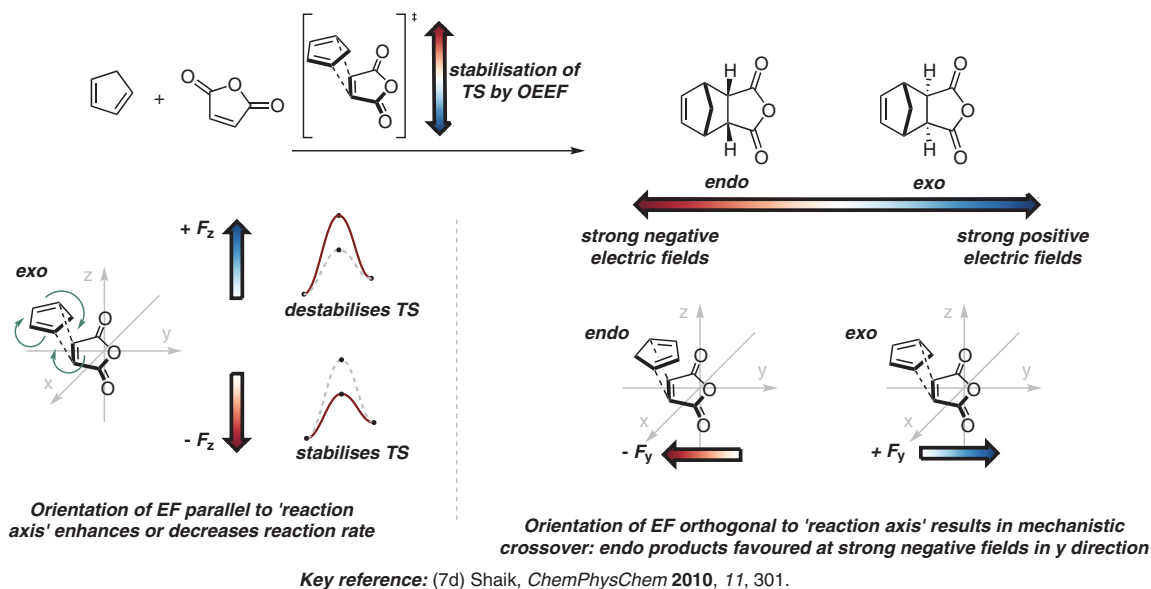
- Electrostatic catalysis has its origin in biological systems.
- The effect of enzymatic catalysis has been attributed to an electrostatic preorganisation of substrates in the active site of enzymes, stabilising developing charges in the transition states.
- The effect of external electric fields on enzymatic-like bond activations have been investigated by DFT calculations, with the group of Shaik making incredible contributions to this field.
- Investigations of the oxidative addition of aryl halides and alkyl halides have been carried out.
- These investigations highlight a mechanistic crossover when electric fields are applied, or field-switchable oxidative addition or reductive elimination of HCl to a cobalt complex.

Figure 1 The influence of OEEFs in enzyme and organometallic catalysis⁶

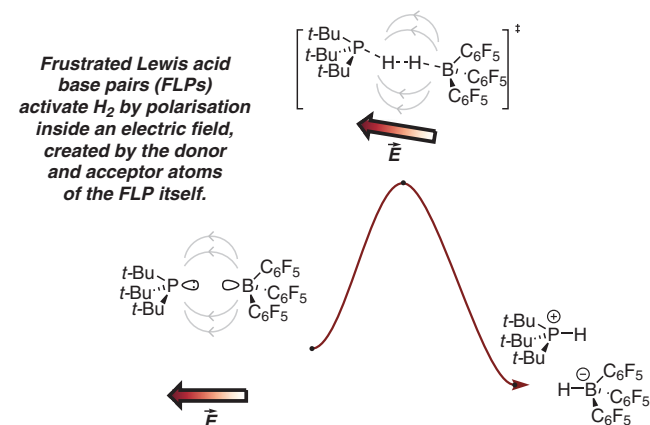


Key references: (7a) Shaik, *Chem. Soc. Rev.* **2018**, 47, 5125. (7b) Shaik, *Nat. Chem.* **2016**, 8, 1091.

The effect of OEEF on Diels–Alder reactions

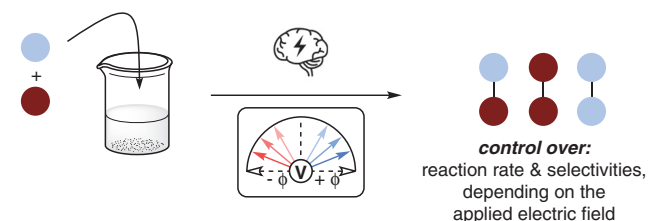


Electric fields in frustrated Lewis acid base pairs



Key reference: (7c) Grimme, *Angew. Chem. Int. Ed.* **2010**, 49, 1402.

OEEFs as smart reagents

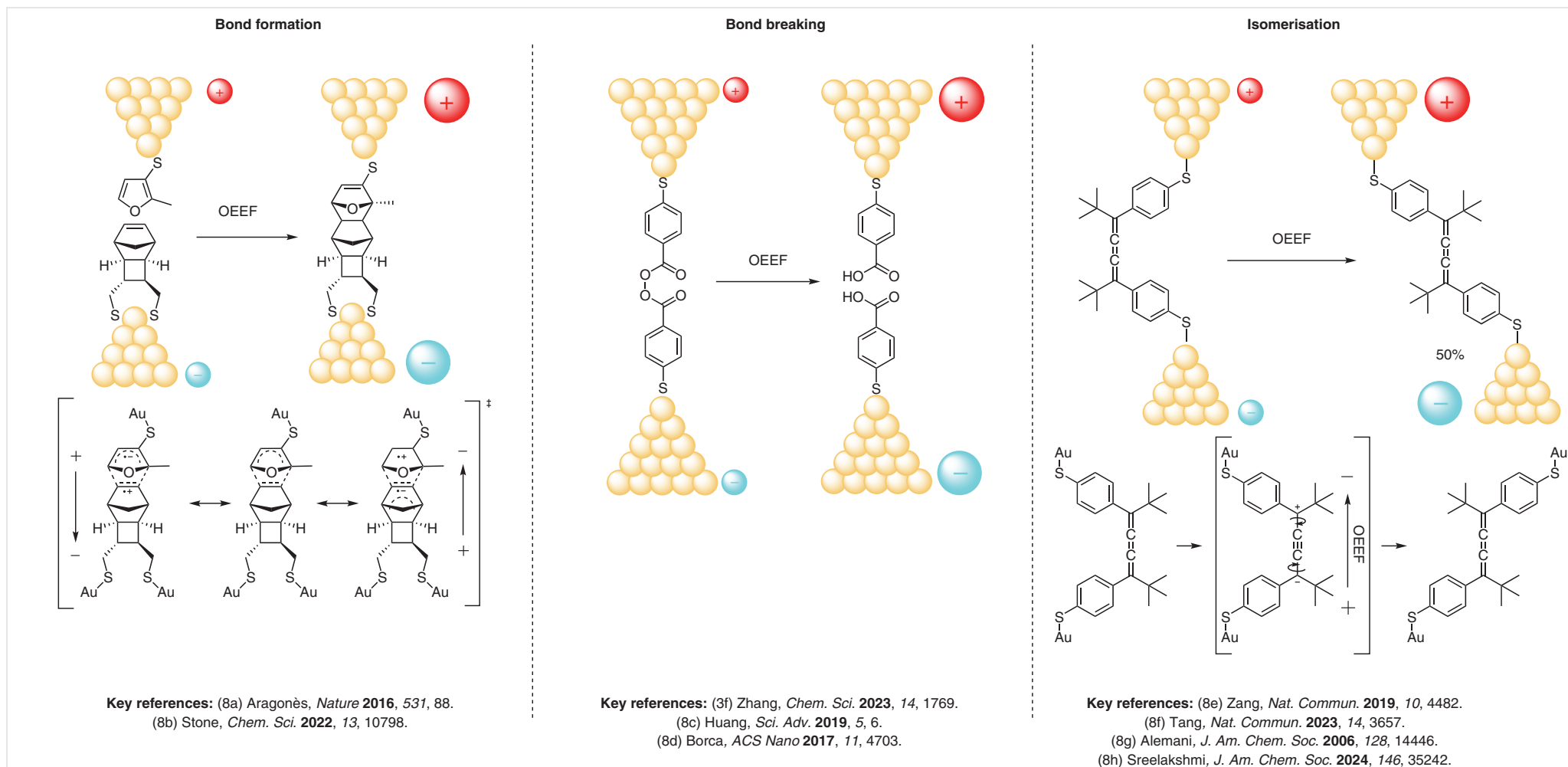


Key references: (7b) Shaik, *Nat. Chem.* **2016**, *8*, 1091.
(1a) Shaik, *ACS Phys. Chem. Au* **2024**, *4*, 191.

Key features:

- The 'reaction-axis rule' determines which orientation of the external electric field stabilises transition states most, and therefore results in the highest rate enhancement.
- With this rule, the effect of OEEFs on Diels–Alder reactions can be rationalised. Depending on the orientation of the field, not only a rate enhancement is anticipated, but also a change in the selectivity of this reaction.
- Apart from these external fields, FLPs create an electric field between the donor and acceptor atoms, resulting in the polarisation and cleavage of H₂.
- Lastly, OEEFs can be regarded as 'smart reagents': depending on the direction and magnitude of the applied field, reaction rates can be accelerated or selectivities can be changed.

Figure 2 The ‘Reaction-Axis rule’, the influence of OEEFs on Diels–Alder reactions, and a highlight of internal electric fields in FLPs⁷



Reviews: (1e) Ciampi, *Chem. Soc. Rev.* **2018**, 47, 5146. (8k) Dief, *Nat. Res.* **2023**, 56, 600. (8j) Chen, *Nat. Res.* **2023**, 8, 165.

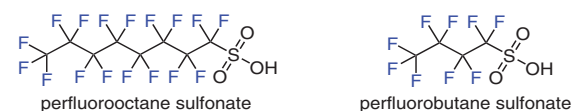
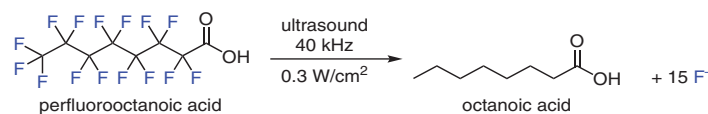
Key features:

- Reactions between STM (scanning tunneling microscopy) tips enables strong electric fields to be generated due to the small interelectrode distance.
- Electric fields between STM tips enable a broad range of reactions to take place: bond breaking, bond forming and isomerisation.
- The STM-based break junction (STM-BJ) technique enables quantification of bonds breaking, forming or isomerising.

Figure 3 Reactions in the electric field of an STM tip^{1e,3f,8}

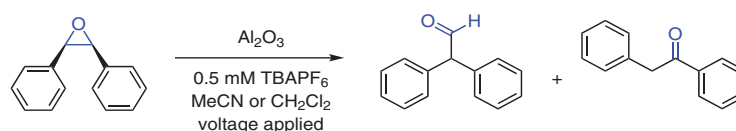
Cleaving C–F bonds in PFAS substances

interfacial electrostatic field (IEF)

Key reference: (9a) Wang, *Angew. Chem. Int. Ed.* **2024**, 63, e202402440.

Improved selectivity of an epoxide rearrangement

IEF

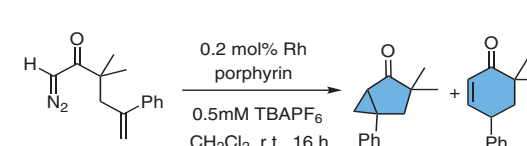


No field	1	:	4
With field	17	:	1

Key reference: (9b) Gorin, *J. Am. Chem. Soc.* **2012**, 134, 186.

Improved selectivity of carbene chemistry

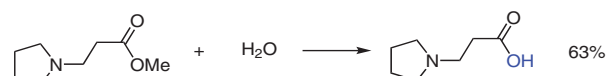
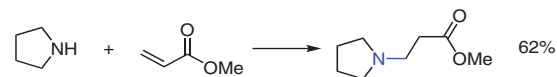
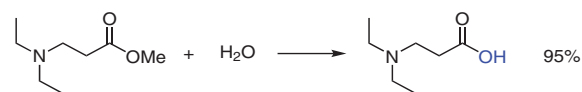
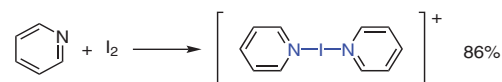
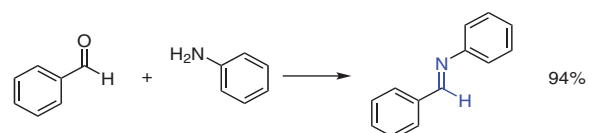
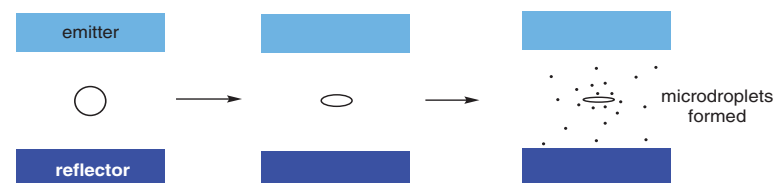
IEF



No field	10	:	1
With field max	100	:	1

Key reference: (9c) Gorin, *J. Am. Chem. Soc.* **2013**, 135, 11257.

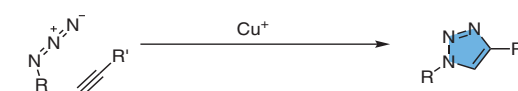
Acoustic levitation for contactless microdroplet reactions



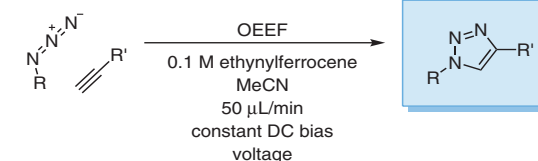
Key reference: (9d) Li, *J. Am. Chem. Soc.* **2024**, 146, 29267.
 Further references: (3g) Song, *J. Am. Chem. Soc.* **2023**, 145, 26003. (9e) Gu, *Environ. Sci. Technol.* **2024**, 58, 20277. (9f) Li, *Sep. Purif. Technol.* **2025**, 372, 133559. (9g) Tang, *J. Am. Chem. Soc.* **2025**, 147, 8289. (9h) Wang, *Nat. Commun.* **2021**, 12, 3508.

Sustainable click reactions (Huisgen cycloadditions) using a microfluidic cell

Previous work:



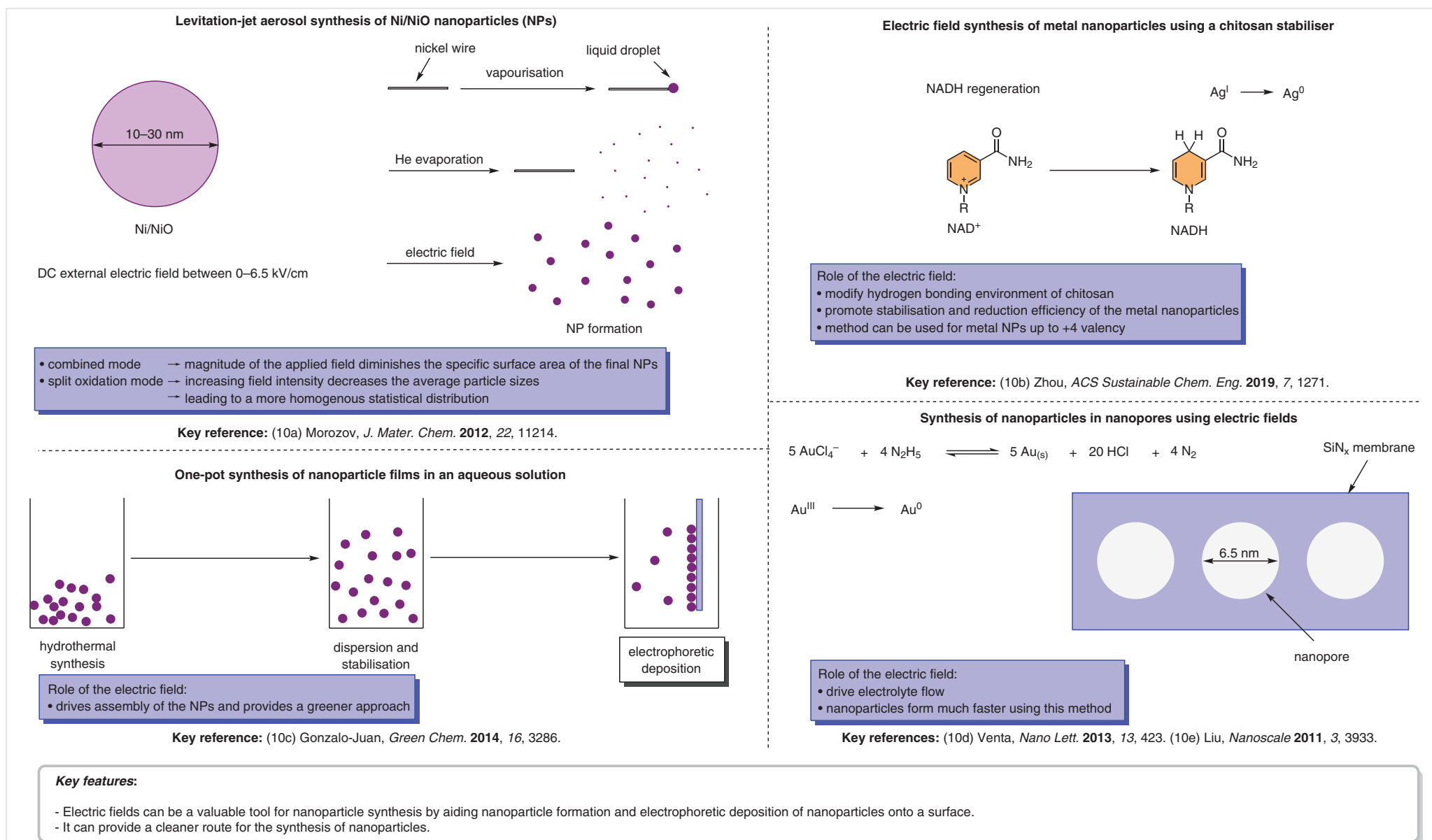
This work:

Key reference: (3c) Sevim, *Nat. Commun.* **2024**, 15, 790.

Key features:

- The use of electric fields enables the ability to change and improve the selectivity of a reaction, as shown with the epoxide rearrangement and carbene chemistry.
- It can also be used to reduce the amount of additional reagents needed for a reaction to proceed.
- It has been shown to be applicable to a variety of organic reactions.
- Investigations into its ability to treat PFAS substances have also been carried out.

Figure 4 Organic reactions assisted by electric fields^{3c,g,9}

Figure 5 Electric-field-assisted nanoparticle synthesis¹⁰

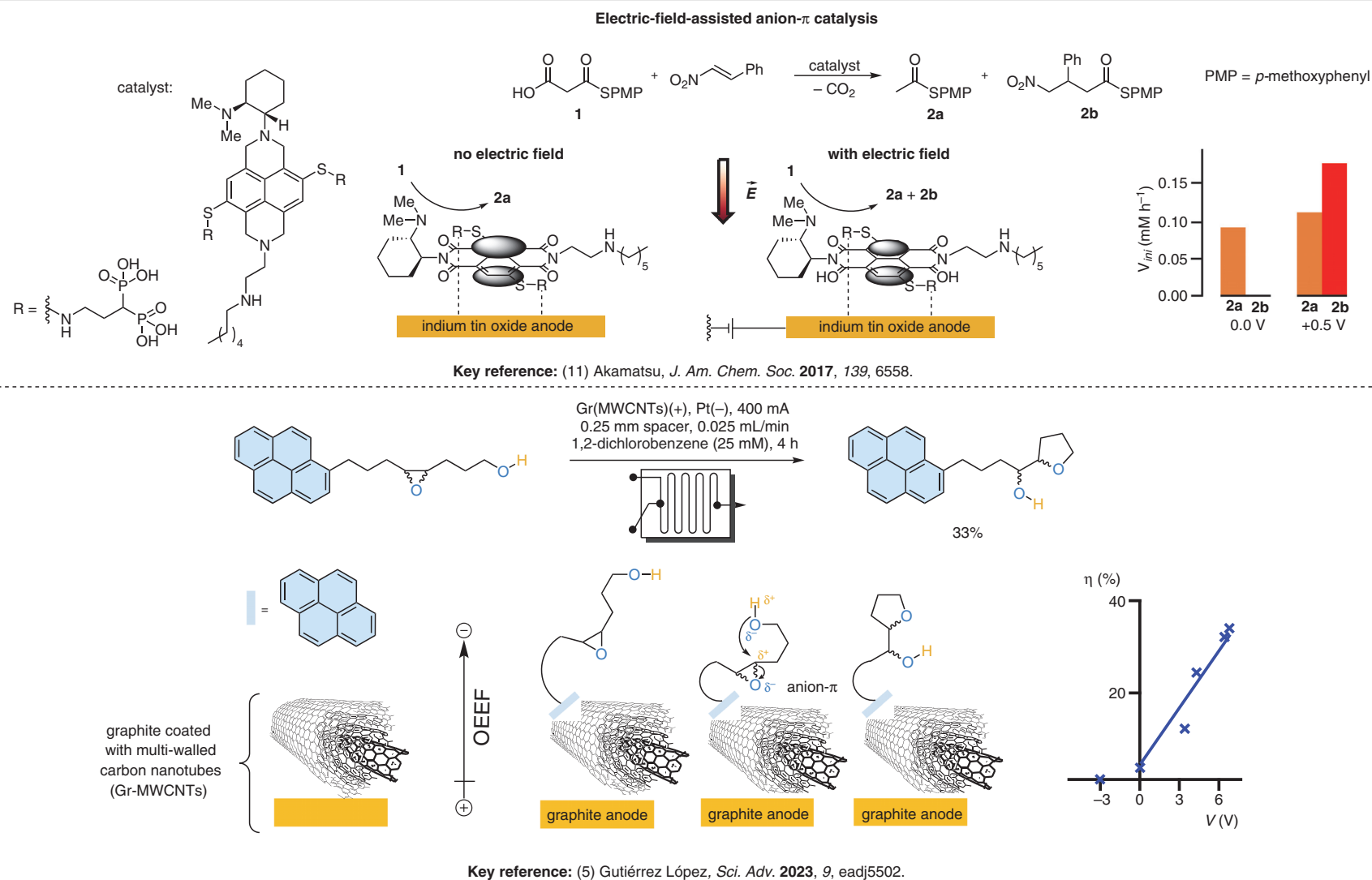
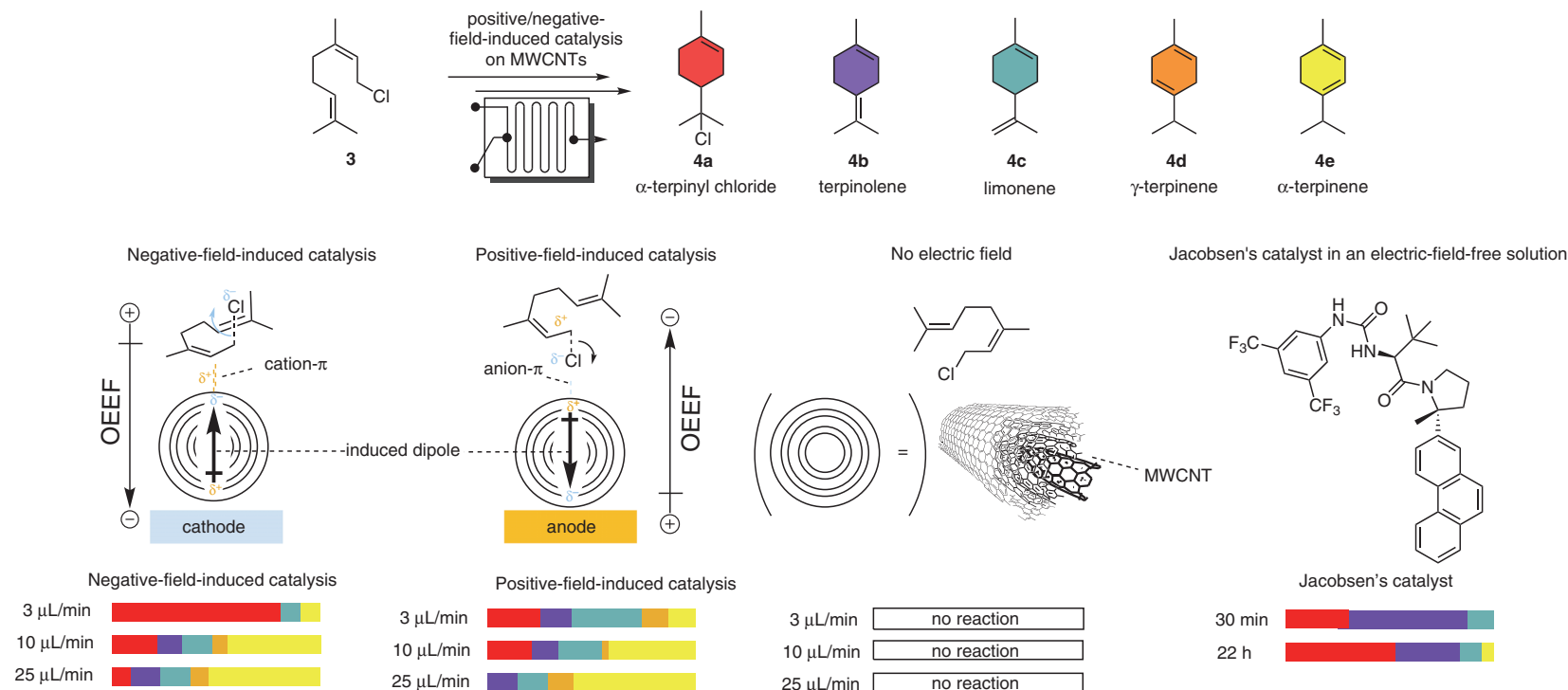


Figure 6 Examples of electric-field-assisted anion- π catalysis on modified electrodes^{5,11}

Electric-field-assisted anion/cation- π catalysis of terpene cyclisations

Key reference: Jozeliunaite, *Angew. Chem. Int. Ed.* **2024**, *64*, e202417333.

Key features:

- Electric fields enable polarisation of π -systems close to the electrode surface which create macrodipoles.
- These macrodipoles enable the stabilisation of anionic or cationic intermediates, depending on the polarisation of the electrode, catalysing the reaction.

Figure 7 Examples of electric-field-assisted anion- π and cation- π catalysis in electrochemical microfluidic devices¹²

Conflict of Interest

The authors declare no conflict of interest.

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