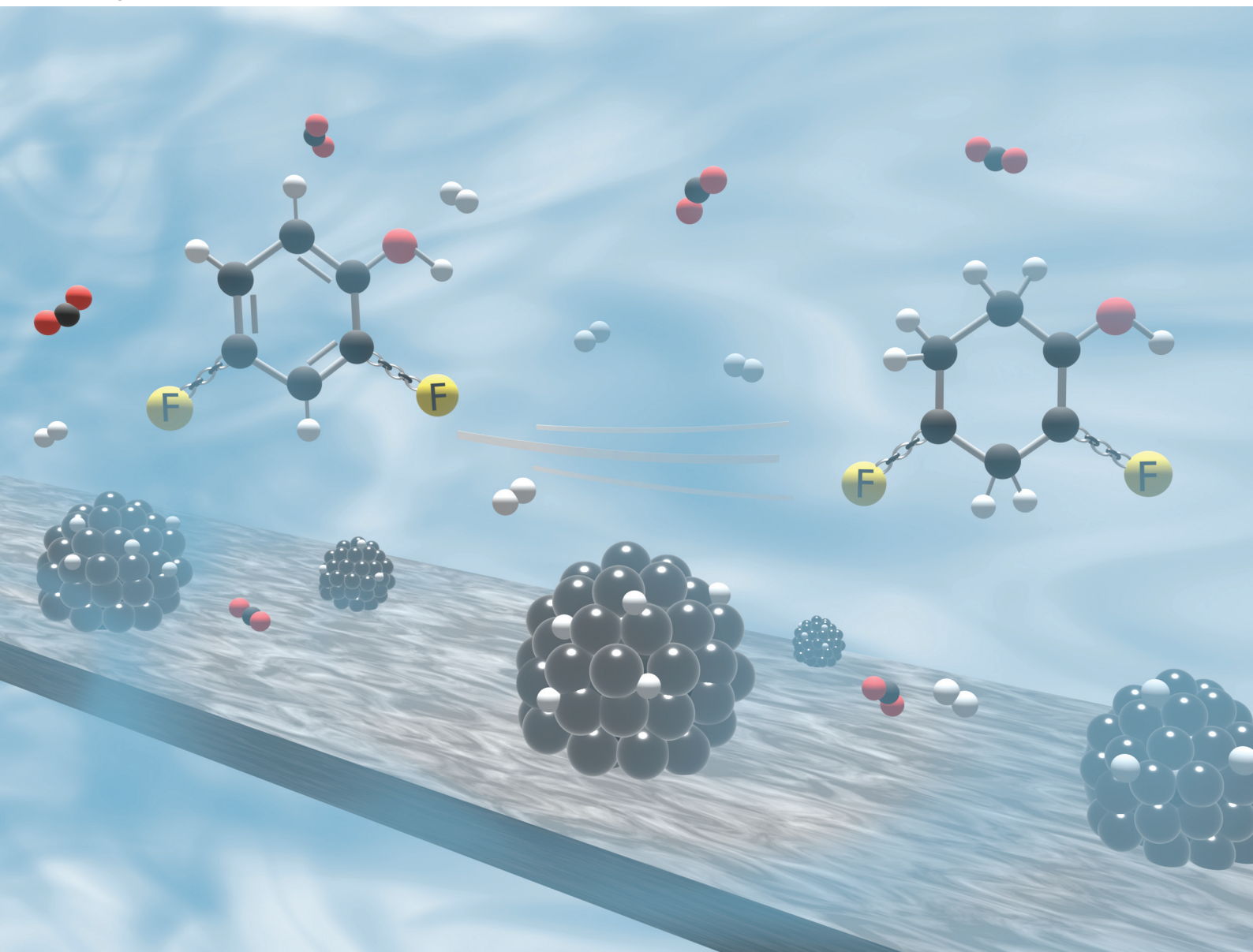


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## COMMUNICATION

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# Supercritical carbon dioxide as reaction medium for selective hydrogenation of fluorinated arenes†

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The selective hydrogenation of fluorinated arenes with polar functionalities is achieved, opening a versatile pathway for the production of valuable substituted fluorocyclohexane derivatives from readily available substrates. The use of supercritical carbon dioxide (scCO<sub>2</sub>) as a hydrophobic and green solvent in combination with Rh nanoparticles immobilized on molecularly modified silica as catalysts favours hydrogenation over hydrodefluorination. The approach compares favourably in terms of green chemistry metrics relative to traditional synthetic routes as exemplified for the useful building block 4-fluorocyclohexan-1-ol.

## Introduction

Fluorinated cyclohexanes are of great interest for the chemical industry where they are used as building blocks for the production of various materials,<sup>1</sup> agrochemicals,<sup>2</sup> and pharmaceuticals.<sup>3,4</sup> To access these motifs, the selective hydrogenation of widely accessible fluorinated arenes<sup>5</sup> is emerging as an attractive alternative to direct alkane fluorination methods that typically require several steps, the use of hazardous chemicals, and that are poorly atom economical (Fig. 1a).<sup>6</sup> The broad application of the hydrogenation strategy relies, however, on the development of catalytic systems capable of hydrogenating fluorinated arenes while limiting the competing and parallel hydrodefluorination, which remains a great challenge.<sup>7–11</sup> Recently, several groups, including ours,

reported catalytic systems composed of Rh-based molecular complexes<sup>12</sup> or nanoparticles<sup>13,14</sup> showing good activity and selectivity for the hydrogenation of a range of fluorinated arenes to the corresponding fluorinated cyclohexane derivatives (Fig. 1b). The studies evidenced that the hydrophobicity of the environment of the active metal sites – as controlled by ligands, supports, and the reaction media – was especially important to limit hydrodefluorination. For example, Glorius *et al.* reported the use of a Rh-carbene pre-catalyst for the selective hydrogenation of various fluorinated arenes to *cis*-fluorocycloalkanes in presence of SiO<sub>2</sub> or molecular sieves with hexane as a non-polar solvent.<sup>12,13</sup> Following our organo-metallic approach to multifunctional catalytic systems,<sup>15</sup> we showed that the selectivity of rhodium nanoparticles (NPs) could be significantly improved by immobilizing them on silica with a hydrophobic molecularly modified surface

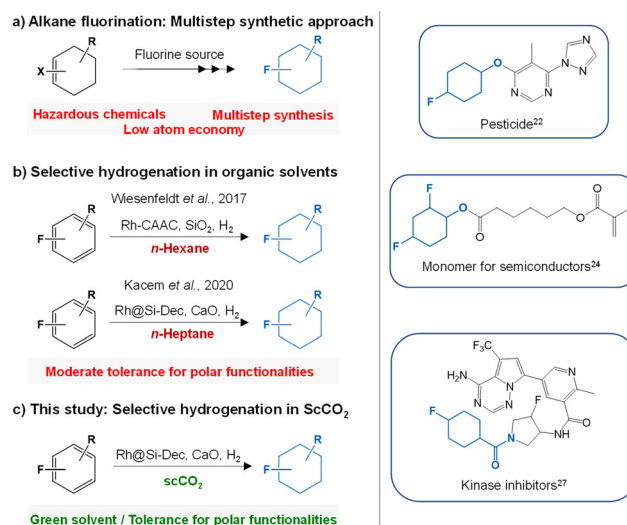


Fig. 1 Synthetic strategies for the production of fluorinated cycloalkane derivatives, and examples of applications.

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(MMS).<sup>14</sup> In particular, materials composed of Rh NPs on SiO<sub>2</sub> functionalized with decyl triethoxysilane (Rh@Si-Dec) proved highly effective when used in *n*-heptane as solvent together with CaO as HF scavenger. A range of fluorinated cyclohexane derivatives was accessed in high selectivity and yields (70–92%), with excellent catalyst stability and recyclability.

However, despite these promising advances, fluorinated arenes possessing polar functional groups (*i.e.* –OH, –COOH, –COOR, *etc.*) proved to be challenging substrates, and the corresponding fluorinated cyclohexane derivatives, while being key building blocks, remained so far inaccessible through this route.

In this context, we report here the use of supercritical carbon dioxide (scCO<sub>2</sub>) as reaction medium to replace commonly used organic solvents (*i.e.* hexane, heptane) in the hydrogenation of fluorinated arenes (Fig. 1c). ScCO<sub>2</sub> is non-flammable and non-toxic, and has a “generally recognized as safe (GRAS)” status in food processing.<sup>16,17</sup> It was selected here for its environmental properties<sup>18</sup> as well as for its hydrophobicity and capacity to solubilize fluorinated compounds,<sup>19,20</sup> features of great importance for this transformation. Using the selective hydrogenation of 4-fluorophenol to 4-fluorocyclo-

hexan-1-ol as model reaction, the potential of scCO<sub>2</sub> as a reaction solvent was explored through a systematic comparison of the hydrogenation performance of Rh@Si-Dec in scCO<sub>2</sub> and in heptane. This approach was then extended to a broad range of fluorinated arenes with polar functionalities, providing access to fluorinated cyclohexane derivatives that were so far out of reach through hydrogenation.

## Results and discussion

The synthesis of the Rh@Si-Dec (Fig. 2) catalyst was achieved following a previously reported procedure.<sup>14</sup> In brief, the preparation of the molecularly functionalized silica supports (Si-Dec) was accomplished through the condensation of commercial decyltriethoxysilanes on dehydroxylated SiO<sub>2</sub> (see ESI† for full synthetic and characterization details). The immobilization of Rh NPs on the support was accomplished through the wet impregnation of Si-Dec with a solution of [Rh(allyl)<sub>3</sub>] followed by reduction of the dried powder under an atmosphere of H<sub>2</sub> (50 bar) at 100 °C for 18 h. The resulting Rh@Si-Dec material was characterized by N<sub>2</sub> adsorption experiments, giving a BET surface area of 316 m<sup>2</sup> g<sup>−1</sup>, slightly lower than for the starting SiO<sub>2</sub> (332 m<sup>2</sup> g<sup>−1</sup>) as expected due to the chemisorption of the decyltriethoxysilane groups. The chemisorption of the decyl chains by silanization was demonstrated by <sup>29</sup>Si solid state NMR in a previous study.<sup>14</sup> The Rh loading (0.9 wt%) determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on Rh@Si-Dec was found well in agreement with the theoretical value (1 wt%). Scanning Transmission Electron Microscopy with High Angle Annular Dark Field (STEM-HAADF) evidenced the formation of small and well dispersed nanoparticles with an average size of 1.0 (±0.1) nm (Fig. 2b).

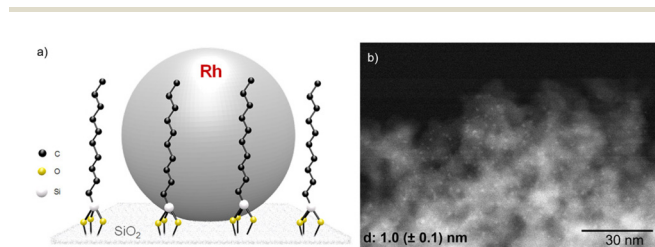


Fig. 2 (a) Schematic representation and (b) STEM-HAADF image of the Rh@Si-Dec catalyst.

Table 1 Hydrogenation of 4-fluorophenol using Rh@Si-Dec in different media

|   |                   |        |                                               |                   |        | Y (%)  |        |        |        |       |        |
|---|-------------------|--------|-----------------------------------------------|-------------------|--------|--------|--------|--------|--------|-------|--------|
| # | Solvent           | T (°C) | CO <sub>2</sub> density (g mL <sup>−1</sup> ) | t (h)             | X (%)  | 1a     | 1b     | 1c     | 1d     | 1e    | 1f     |
| 1 | None              | 80     | —                                             | 1                 | 97     | 19     | 78     | 0      | 0      | 0     | 0      |
| 2 | <i>n</i> -Heptane | 80     | —                                             | 1                 | >99    | 24 ± 1 | 63 ± 3 | 0      | 0      | 2 ± 1 | 11 ± 1 |
| 3 | scCO <sub>2</sub> | 80     | 0.5                                           | 1                 | 99 ± 1 | 55 ± 7 | 27 ± 4 | 8 ± 3  | 10 ± 3 | 0     | 0      |
| 4 | scCO <sub>2</sub> | 30     | 0.8                                           | 24                | 22     | 4      | 4      | 4      | 10     | 0     | 0      |
| 5 | scCO <sub>2</sub> | 80     | 0.5                                           | 0.25 <sup>a</sup> | 96 ± 3 | 50 ± 1 | 24 ± 2 | 11 ± 1 | 11 ± 1 | 0     | 0      |
| 6 | scCO <sub>2</sub> | 80     | 0.61                                          | 1                 | >99    | 58 ± 3 | 23 ± 1 | 10 ± 1 | 9 ± 2  | 0     | 0      |
| 7 | scCO <sub>2</sub> | 80     | 0.75                                          | 1                 | >99    | 61 ± 4 | 22 ± 1 | 10 ± 1 | 5 ± 1  | 0     | 0      |
| 8 | scCO <sub>2</sub> | 50     | 0.5                                           | 1                 | 95 ± 5 | 51 ± 2 | 25 ± 2 | 8 ± 1  | 10 ± 2 | 0     | 0      |
| 9 | scCO <sub>2</sub> | 120    | 0.5                                           | 1                 | >99    | 58 ± 3 | 34 ± 4 | 4 ± 2  | 9 ± 9  | 0     | 0      |

Reaction conditions: Catalyst (5 mg, 0.0005 mmol Rh), 4-fluorophenol (22.4 mg, 0.2 mmol, 400 eq.), *n*-heptane (750 mg, ≈1 mL) or scCO<sub>2</sub> (0.5 g mL<sup>−1</sup>, ≈12.5 g), CaO (7 mg), 500 rpm. <sup>a</sup> Time required to reach the indicated temperature. X = conversion, Y = yield, determined by GC-FID using tetradecane as internal standard.



The hydrogenation of 4-fluorophenol (**1**) was selected as model reaction for the catalytic study as this transformation has so far not been successfully achieved, and the corresponding 4-fluorocyclohexan-1-ol (**1a**) is an important building block for the production of pharmaceuticals,<sup>21</sup> agrochemicals<sup>22</sup> and functional materials such as resins.<sup>23</sup> The catalytic performances of Rh@Si-Dec using heptane or scCO<sub>2</sub> as solvents were systematically compared under a standard set of reaction conditions (see details in ESI†). The substrate-to-metal ratio was adjusted to 400:1 and small amounts of CaO were added to trap potentially formed HF. The reactors were pressurized with H<sub>2</sub> to 55 bar at room temperature and the reaction mixtures were agitated with a magnetic stir bar at 500 rpm for 1 h at a temperature of 80 °C. Reactions in heptane were performed using 1 mL of solvent in a 10 mL stainless steel autoclave. The experiments using scCO<sub>2</sub> were carried out in a 30 mL autoclave at a density of 0.5 g mL<sup>-1</sup> as determined by weighing in the corresponding amount of CO<sub>2</sub> (Fig. S1†). The solubility of substrate **1** in scCO<sub>2</sub> and in the mixture of scCO<sub>2</sub> + H<sub>2</sub> under the reaction conditions was confirmed by visual inspection using a window-equipped high-pressure reactor (Fig. S2†). No change in the physical state of the catalyst (fine powder) could be observed under supercritical conditions.

Under neat conditions in the absence of solvent, **1** was nearly fully converted after one hour, however with a very poor selectivity towards the desired product **1a** of only 20% whereas hydrodefluorination to cyclohexanol **1b** was the major pathway (78% yield, Table 1, entry 1). Using heptane as a solvent, complete conversion was reached giving a similar product mixture composed of 4-fluorocyclohexan-1-ol (**1a**, 24%), cyclohexanol (**1b**, 63%), and cyclohexane (**1f**, 11%) (Table 1, entry 2). In sharp contrast, the selectivity and yield of **1a** reached an average value of 55 ± 7% over a series of 25 experiments (see details in ESI†) in scCO<sub>2</sub> indicating that hydrogenation could be favoured over hydrodefluorination in this medium (entry 3). Other products include **1b** (27 ± 4%) and the intermediates 4-fluorocyclohexanone (**1c**, 8 ± 3%) and cyclohexanone (**1d**, 10 ± 3%). Interestingly, **1c** and **1d** were not observed in heptane. These results indicate that the use of scCO<sub>2</sub> as reaction medium has the potential to improve very significantly the selectivity of the Rh@Si-Dec catalyst for the hydrogenation of challenging fluorinated arenes as compared to non-polar hydrocarbons as solvents.

Low conversion was observed when running the reaction at 30 °C with selectivity for **1a** in a similar range as in heptane (Table 1, entry 4). Rapid hydrogenation of **1** was observed at reaction temperatures above the critical temperature of CO<sub>2</sub>, reaching already 96% conversion during the heating time (15 min) required to reach 80 °C (Table 1, entry 5). The relative selectivity of *ca.* 2:1 for **1a** over **1b** was maintained in this case. Increasing the CO<sub>2</sub> density from 0.5 to 0.61 and 0.75 g mL<sup>-1</sup> did not affect significantly the conversion nor the selectivity toward **1a** (entries 6 and 7). Thus, a CO<sub>2</sub> density of 0.5 g mL<sup>-1</sup> was selected for further investigations as it allows working under mild total pressure, far away from the technical

limitations of the reactor (*T*<sub>max</sub> = 200 °C, *p*<sub>max</sub> = 400 bar). Varying the reaction temperature around 80 °C (50 °C entry 8, 120 °C entry 9) did not improve the selectivity toward the formation of **1a**.

Furthermore, scCO<sub>2</sub> was tested with several other Rh-based catalysts possessing similar Rh NPs size (Fig. S3–S8, Tables S1 and S2†). Typically, conversion and selectivity were lower and only Rh@SiO<sub>2</sub> reached similar performance data. In order to maintain the combined effect of reaction medium and surface modification, the Rh@Si-Dec catalyst was chosen for further studies.

Motivated by these promising results, the scope of the reaction was explored by considering various fluorinated arenes bearing different functional groups (acid, ester, alcohol, phenol, ether, and amide). For all substrates, the performances of Rh@Si-Dec in heptane and scCO<sub>2</sub> were compared under optimized conditions (Table 2).

In all cases, the selectivity and yield of fluorocyclohexane derivatives were at least as good, and often much better when using scCO<sub>2</sub> than when using heptane as solvent. The selectivity improvement in scCO<sub>2</sub> was particularly striking for multi-fluorinated substrates (**2**, **3**, **4**, **7**, and **8**), providing products **2a**, **3a**, **4a**, **7a** and **8a** in 20–78% yield (28–80% selectivity) against 2–35% yield (2–36% selectivity) in heptane. Interestingly, **2a** and **4a** can be used directly as building blocks for the synthesis of fluorine-containing polymers<sup>24</sup> and liquid crystal materials.<sup>25</sup> Methyl 2- and 4-fluorocyclohexane-1-carboxylate (**5a**, **6a**) were obtained in excellent yields from **5** and **6** in both reaction media, but with still slightly better selectivity in scCO<sub>2</sub>. With increasing numbers of fluorine substituents (**7** and **8**), the benefits of using scCO<sub>2</sub> became more obvious in line with the known compatibility of fluorinated compounds and scCO<sub>2</sub>. **7a** and **8a** are key intermediates for the synthesis of bioactive molecules,<sup>26,27</sup> and were produced in 56% and 55% yield under these conditions, respectively.

Furthermore, monofluorinated cyclohexanes with acid (**9a**), phenol (**10a**), ether (**11a**), amide (**12a**) and NBoc-protected amine (**13a**) substitutes were obtained in good yields using both solvents, with a slightly better selectivity in scCO<sub>2</sub>. To the best of our knowledge, this is the first report for the synthesis of compounds **3a**, **7a**, **8a**, **10a** and **12a** by hydrogenation of the corresponding fluorinated arenes. The structures of these products were validated by GC-MS and NMR analysis (see ESI† for details).

To stress the significance of this work, a conventional multistep preparation method of 4-fluorocyclohexan-1-ol (Fig. S9†) *via* fluorination was systematically compared to the selective hydrogenation of readily available and cheap 4-fluorophenol to fluorocyclohexan-1-ol (Fig. S10†). For the comparison, five parameters based on the green chemistry principles<sup>28</sup> were considered, *i.e.* the number of steps (Steps), the atom economy (AE), the overall reaction yield (*Y*), the hazardous nature of the reagents (Safety) and the economical aspect (Eco) (detailed description is provided in the ESI: Fig. S9–S10, Table S3†). The spider web-type graph in Fig. 3 shows that all the parameters

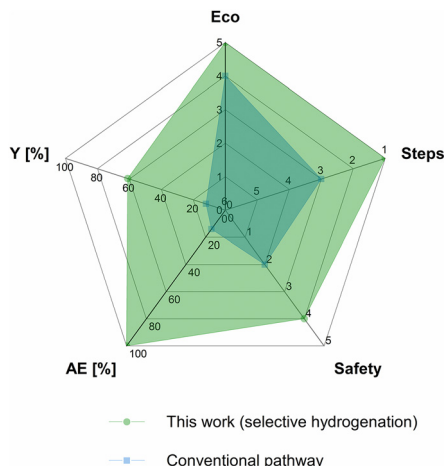


**Table 2** Hydrogenation of fluorinated arenes using Rh@Si-Dec catalyst in scCO<sub>2</sub> and heptane

| Substrate                                                                                               | Product                                                                                           | scCO <sub>2</sub> |                            |                            | Heptane      |                            |                            |
|---------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|-------------------|----------------------------|----------------------------|--------------|----------------------------|----------------------------|
|                                                                                                         |                                                                                                   | <i>X</i> (%)      | <i>S</i> <sub>xa</sub> (%) | <i>Y</i> <sub>xa</sub> (%) | <i>X</i> (%) | <i>S</i> <sub>xa</sub> (%) | <i>Y</i> <sub>xa</sub> (%) |
| <br><b>1</b>           | <br><b>1a</b>    | >99               | 55                         | 55                         | >99          | 24                         | 24                         |
| <br><b>2</b>           | <br><b>2a</b>    | 89                | 78                         | 69                         | 98           | 11                         | 11                         |
| <br><b>3</b>           | <br><b>3a</b>    | 75                | 55                         | 41                         | 76           | 7                          | 5                          |
| <br><b>4</b>           | <br><b>4a</b>    | 70                | 28                         | 20                         | 99           | 2                          | 2                          |
| <br><b>5</b>           | <br><b>5a</b>    | 97                | 80                         | 78                         | >99          | 78                         | 78                         |
| <br><b>6</b>           | <br><b>6a</b>    | 96                | 90                         | 86                         | 95           | 83                         | 79                         |
| <br><b>7</b>          | <br><b>7a</b>   | 88                | 64                         | 56                         | 96           | 36                         | 34                         |
| <br><b>8</b> [a, b]  | <br><b>8a</b>  | 72                | 76                         | 55                         | >99          | 35                         | 35                         |
| <br><b>9</b> [c]     | <br><b>9a</b>  | >99               | 80                         | 80                         | >99          | 75                         | 75                         |
| <br><b>10</b> [c, d] | <br><b>10a</b> | >99               | 79                         | 79                         | >99          | 83                         | 83                         |
| <br><b>11</b>        | <br><b>11a</b> | 82                | 84                         | 69                         | >99          | 77                         | 77                         |
| <br><b>12</b> [c, d] | <br><b>12a</b> | 99                | 47                         | 47                         | >99          | 42                         | 42                         |
| <br><b>13</b> [e]    | <br><b>13a</b> | >99               | 72                         | 72                         | >99          | 70                         | 70                         |

Reaction conditions: Rh@Si-Dec (5 mg, 0.0005 mmol Rh), substrate (0.2 mmol), scCO<sub>2</sub> (0.5 g mL<sup>-1</sup>, ≈12.5 g), CaO (7 mg for monofluoroalkene, 14 mg for difluoroalkene and 21 mg for trifluoroalkene), 55 bar H<sub>2</sub>, 80 °C, 1 h, 500 rpm. <sup>a</sup> 20 mg Rh@Si-Dec. <sup>b</sup> 120 °C. <sup>c</sup> Substrate (0.1 mmol). <sup>d</sup> 10 mg Rh@Si-Dec. <sup>e</sup> 2 h.





**Fig. 3** Spider web-type graph representing the comparison based on green chemistry metrics between the preparation of 4-fluorocyclohexan-1-ol via conventional multistep fluorination, and the hydrogenation approach proposed in this work.

are clearly in favour of the hydrogenation route proposed here, in particular considering atom economy, safety, and yield.

## Conclusion

The reactivity of a molecularly modified Rh@Si-Dec catalyst was explored for the selective hydrogenation of fluorinated arenes using  $\text{scCO}_2$  as a green solvent, and compared to the use of *n*-heptane. The use of  $\text{scCO}_2$  generally favoured hydrogenation over hydrodefluorination, thus improving very significantly the selectivity of the reaction in a number of synthetically important applications. This improvement was particularly striking for substrates bearing polar functionalities (e.g. 4-fluorophenol) as well as multiple fluorine substituents (e.g. difluorophenol, difluorophenylacetate, etc.). As a result, a wide range of fluorinated arenes could be hydrogenated using Rh@Si-Dec in  $\text{scCO}_2$ , giving highly valuable fluorocyclohexane derivatives in moderate to high yields in one step. This strategy was shown to be potentially more efficient and sustainable than conventional multistep fluorination approaches, paving the way towards the production of valuable fluorinated building blocks directly via catalytic hydrogenation of widely available fluorinated arenes.

## Author contributions

S. Kacem, A. Bordet and W. Leitner proposed the project. N. Theyssen, A. Bordet and W. Leitner co-supervised the project. S. Kacem prepared the catalytic material and performed the activity tests in heptane, while Y. X. Qiao performed the experiments in supercritical  $\text{CO}_2$ . C. Wirtz performed all the NMR measurements and made full analysis. All

authors discussed the results and edited the manuscript before submission.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 M. Hird, *Chem. Soc. Rev.*, 2007, **36**, 2070–2095.
- 2 T. Fujiwara and D. O'Hagan, *J. Fluor. Chem.*, 2014, **167**, 16–29.
- 3 J. Wang, M. Sanchez-Rosello, J. L. Acena, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432–2506.
- 4 G. Backfisch, M. Bakker, G. Blaich, W. Braje, K. Drescher, T. Erhard, A. Haupt, C. Hoft, A. Kling, V. Lakics, H. Mack, F. Oellien, R. Peter, F. Pohlki and A. L. Relo, US20190062305A1, 2019.
- 5 D. E. Yerien, S. Bonesi and A. Postigo, *Org. Biomol. Chem.*, 2016, **14**, 8398–8427.
- 6 R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell Publishing Ltd, Oxford, 2004.
- 7 H. Yang, H. Gao and R. J. Angelici, *Organometallics*, 1999, **18**, 2285–2287.
- 8 G. Haufe, S. Pietz, D. Wölker and R. Fröhlich, *Eur. J. Org. Chem.*, 2003, 2166–2175.
- 9 K. J. Stanger and R. J. Angelici, *J. Mol. Catal. A: Chem.*, 2004, **207**, 59–68.
- 10 M. P. Wiesenfeldt, Z. Nairoukh, T. Dalton and F. Glorius, *Angew. Chem., Int. Ed.*, 2019, **58**, 10460–10476.
- 11 T. Charvillat, P. Bernardelli, M. Daumas, X. Pannecoucke, V. Ferey and T. Besset, *Chem. Soc. Rev.*, 2021, **50**, 8178–8192.
- 12 M. P. Wiesenfeldt, Z. Nairoukh, W. Li and F. Glorius, *Science*, 2017, **357**, 908–912.
- 13 D. Moock, M. P. Wiesenfeldt, M. Freitag, S. Muratsugu, S. Ikemoto, R. Knitsch, J. Schneidewind, W. Baumann, A. H. Schäfer, A. Timmer, M. Tada, M. R. Hansen and F. Glorius, *ACS Catal.*, 2020, **10**, 6309–6317.



- 14 S. Kacem, M. Emondts, A. Bordet and W. Leitner, *Catal. Sci. Technol.*, 2020, **10**, 8120–8126.
- 15 A. Bordet and W. Leitner, *Acc. Chem. Res.*, 2021, **54**, 2144–2157.
- 16 J. R. Hyde, P. Licence, D. Carter and M. Poliakoff, *Appl. Catal., A*, 2001, **222**, 119–131.
- 17 P. Licence, J. Ke, M. Sokolova, S. K. Ross and M. Poliakoff, *Green Chem.*, 2003, **5**, 99–104.
- 18 W. Leitner, *Acc. Chem. Res.*, 2002, **35**, 746–756.
- 19 D. A. Newman, T. A. Hoefling, R. R. Beitle, E. J. Beckman and R. M. Enick, *J. Supercrit. Fluids*, 1993, **6**, 205–210.
- 20 P. G. Jessop and W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, 1999.
- 21 C. Qi, H. Tsui, Q. Zeng, Z. Yang and X. Zhang, WO2020/238900A1, 2020.
- 22 Y. Nokura, H. Ikegami, H. Tomioka and D. Takaoka, WO2012/050237A1, 2012.
- 23 T. Masuyama, S. Yamamoto and K. Ichikawa, JP2020015900A, 2020.
- 24 T. Arai and T. Itokazu, JP2009197184A, 2009.
- 25 D. Xue, C. Dong and G. Renwei, CN103627405, 2012.
- 26 R. Shimono, D. Matsuda, S. Masuda and S. Yamamoto, JP2018199623A, 2018.
- 27 S. H. Watterson, M. Andappan Murugaiah Subbaiah, C. D. Dzierba, H. Gong, J. M. Guernon, J. Guo, A. C. Hart, G. Luo, J. E. Macor, W. J. Pitts, J. Shi, B. L. Venables, C. A. Weigelt, Y.-J. Wu, Z. B. Zheng, S.-Y. Sit and J. Chen, WO2019US14918, 2019.
- 28 P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312.

