# **Supporting Information**

## Organocatalytic carbon dioxide fixation to epoxides by perfluorinated 1,3,5-triols catalysts

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## **General information**

NMR spectra were recorded on a Bruker AC 300 (300 MHz), a Bruker AC 400 (400 MHz) and a Bruker 500 (500 MHz) spectrometer. Chemical shifts are given in ppm, using as internal standards the residual CHCl<sub>3</sub> signal for <sup>1</sup>H NMR ( $\delta$  = 7.26) and the deuterated solvent signal for <sup>13</sup>C NMR ( $\delta$  = 77.0). Data for <sup>13</sup>C NMR are reported as follows: chemical shift (multiplicity). Data for <sup>1</sup>H NMR are reported as follows: chemical shift (multiplicity). Data for <sup>1</sup>H NMR are reported as follows: chemical shift (multiplicity) for a graduate the solution of the standard standards in the standard sta

All epoxides and TBAI were commercially available and were used as received.

Organocatalysts (cat1, 2, 3 and 4) were prepared using methods previously described.1

Chiral GC analysis were performed on a HP 4890 using 6 bar argon as vector. Column: 25m/0,25 mm. Chromatogram analyzed with ChromNav software.

### **Experimental section**

#### General procedure:

Organocatalyst (0.005 mmol) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, styrene epoxide (0.1 mmol) was added under  $CO_2$  atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 30 °C or 80 °C. After 6 h, the mixture was left at room temperature for 10 minutes and was dissolved in CDCl<sub>3</sub>.



<sup>1</sup> a) A. Quintard, J. Rodriguez, ACS Catal. <b>2017</b> , 7, 5513; b) C. Sperandio, G. Quintard, JV. Naubron, M.
Giorgi, M. Yemloul, JL. Parrain, J. Rodriguez, A. Quintard, Chem. Eur. J. 2019, 25, 15098; c) C. Sperandio,
J. Rodriguez, A. Quintard, Chem. Sci. DOI :10.1039/C9SC05196A.

80

25/75

20/80

15/85

1

2

3

#### Scope of the epoxide opening:



#### Compound 2a:



cat2 (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, styrene epoxide (0.1 mmol, 11 µL) was added under CO2 atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 12 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 78% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 4.34 (dd, J = 7.84, 0.76 Hz, 1*H*), 4.81 (t, J = 8.40 Hz, 1*H*), 5.69 (t, J = 8.00

Hz, 1H), 7.45-7.36 (m, 5H). Datas are in agreement with the literature.<sup>2</sup>

#### Compound 2b:



cat2 (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, propylene oxide (0.1 mmol, 7 µL) was added under CO<sub>2</sub> atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 24 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 84% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 1.50 (d, J = 6.6 Hz, 3H), 4.03 (dd, J = 7.2, 8.4 Hz, 1H), 4.55 (dd, J = 7.8, 8.4 Hz, 1H),

4.83–4.88 (m, 1*H*).

Datas are in agreement with the literature.<sup>3</sup>

#### Compound 2c:



cat2 (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, 2-oxiranylmethanol (0.1 mmol, 7 µL) was added under CO<sub>2</sub> atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 24 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 3.65 (brs, OH), 3.72 (dd, J = 3.5, 12.7 Hz, 1H), 4.04 (dd, J = 3.2, 12.9 Hz, 1H), 4.4-4.5 (m, 2H), 4.8-4.9 (m, 1H).

Datas are in agreement with the literature.<sup>4</sup>

#### Compound 2d:



cat2 (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, 1.2-Epoxy-3-phenoxypropane (0.1 mmol, 14 µL) was added under CO<sub>2</sub> atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 24 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.32 (t, *J* = 8.36 Hz, 2*H*), 7.03 (t, *J* = 7.36 Hz,

1*H*), 6.92 (d, *J* = 7.96 Hz, 2*H*), 5.07-5.02 (m, 1*H*), 4.62 (t, *J* = 8.48 Hz, 1*H*), 4.54 (dd, *J* = 5.88, 2.52 Hz, 1*H*), 4.25 (dd, *J* = 6.76, 3.88 Hz, 1*H*), 4.14 (dd, *J* = 7.12, 3.52 Hz, 1*H*). Datas are in agreement with the literature.<sup>5</sup>

#### Compound 2e:



cat2 (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, epichlorohydrin (0.1 mmol, 8 µL) was added under CO2 atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 12 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 79% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.78–3.70 (m, 2*H*), 4.41 (t, *J* = 8.0 Hz, 1*H*), 4.57 (t, *J* = 8.0 Hz, 1*H*),

<sup>&</sup>lt;sup>2</sup> Y-D. Li, D-X. Cui, J-C. Zhu, P. Huang, Z. Tian, Y-Y. Jia, P-A. Wang, Green Chem. 10.1039/C9GC02058F. <sup>3</sup> Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai, Org. Lett. 2010, 12, 5728.

<sup>&</sup>lt;sup>4</sup> J. Meléndez, M. North, P. Villuendas, Chem. Commun., 2009, 2577.

<sup>&</sup>lt;sup>5</sup> Y-D. Li, D-X. Cui, J-C. Zhu, P. Huang, Z. Tian, Y-Y. Jia, P-A. Wang, *Green Chem.* DOI:10.1039/C9GC02058F.

4.98-4.92 (m, 1H). Datas are in agreement with the literature.6

#### Compound 2f:



**cat2** (0.005 mmol, 2.28 mg) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, cyclohexene oxide (0.1 mmol, 10  $\mu$ L) was added under CO<sub>2</sub> atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 80 °C. After 48 h, the mixture was left at room temperature for 10 minutes and filtered on silica gel. 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 1.40–1.46 (m, 2*H*), 1.60–1.65 (m, 2*H*), 1.88–1.92 (m, 4*H*), 4.67–4.70 (m, 2*H*). Datas are in agreement with the literature.<sup>7</sup>

#### Mechanistic studies:

**Cat2** (0.005 mmol) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, styrene oxide (0.1 mmol) was added under CO<sub>2</sub> atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 30 °C. After 2 h, the mixture was left at room temperature for 10 minutes, was dissolved in Et<sub>2</sub>O and was filtered on cotton. The ee of products were determined by GC using a chiral column.



GC enantiomeric excess determination for **2a**: cyclosil-b; 120°C for 10 min than 1°C/min until 220°C. rt1 = 49.4 min; rt2 = 50.0 min.



GC enantiomeric excess determination for **1a**: cyclosil-b;  $120^{\circ}$ C for 10 min than  $1^{\circ}$ C/min until  $220^{\circ}$ C. rt1 = 4.2 min; rt2 = 4.3 min.



**Cat2** (0.005 mmol) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, (*R*)-1 styrene oxide (0.1 mmol) was added under  $CO_2$  atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 30 °C. After 2 h, the mixture was left at room temperature for 10 minutes, was

<sup>&</sup>lt;sup>6</sup> X. Wu, C. Chen, Z. Guo, M. North, A. C. Whitwood, ACS Catal. 2019, 9, 1895.

<sup>&</sup>lt;sup>7</sup> X. Zheng, S. Luo, L. Zhang, J-P. Cheng, *Green Chem.*, **2009**, *11*, 455.

dissolved in Et<sub>2</sub>O and was filtered on cotton. The ee of products **2a** was determined by GC using a chiral column (cyclosil-b).



GC enantiomeric excess determination for **1a**: cyclosil-b;  $120^{\circ}$ C for 10 min than  $1^{\circ}$ C/min until 220°C. rt1 = 4.2 min; rt2 = 4.3 min.



	#	Peak Name	СН	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
	1	Unknown	1	4,175	624911	293691	99,422	99,298	N/A	83968	N/A	1,932	
Γ	2	Unknown	1	4,283	3634	2077	0,578	0,702	N/A	N/A	N/A	N/A	

GC enantiomeric excess determination for **2a**: cyclosil-b; 120°C for 10 min than 1°C/min until 220°C. rt1 (maj) = 49.4 min; rt2 (min) = 50.0 min.



**Cat2** (0.005 mmol) and TBAI (0.005 mmol, 1.85 mg) was added in neat flask. Then, (*R*)-1 styrene oxide (0.1 mmol) was added under  $CO_2$  atmosphere (1 atm, using a balloon) at room temperature and the reaction was stirred at 30 °C. After 12 h, the mixture was left at room temperature for 10 minutes, was dissolved in Et<sub>2</sub>O and was filtered on cotton. The ee of product **2a** was determined by GC using a chiral column (cyclosil-b).



GC enantiomeric excess determination for **2a**: cyclosil-b; 120°C for 10 min than 1°C/min until 220°C. rt1 (maj) = 49.4 min; rt2 (min) = 50.0 min.



[	#	Peak Name	СН	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
[	1	Unknown	1	48,683	285768	30042	96,509	95,943	N/A	578376	7,226	1,639	
ſ	2	Unknown	1	50,425	10337	1270	3,491	4,057	N/A	787459	N/A	1,059	

After 2 h, the mixture was left at room temperature for 10 minutes, was dissolved in  $Et_2O$  and was filtered on cotton. The ee of product **2a** was determined by GC using a chiral column (cyclosil-b).

## Spectras







