Electronic Supplementary Information for

Glycerol-Based Solvents as Green Reaction Media in Epoxidations with Hydrogen peroxide catalysed by bis[3,5-bis(trifluoromethyl)-diphenyl] diselenide

Héctor García-Marín,[a] John C. van der Toorn,[b] José A. Mayoral,[c] José I. García,*[a] and Isabel W. C. E. Arends*[b]

[a] *Laboratory for Organic Chemistry and Catalysis Delft University of Technology Julianalaan 136. 2628 BL Delft. Netherlands. Fax: +31 15 2784700; Tel: +31 15 2784423; E-mail: I.Arends@tnw.tudelft.nl*

[b] *Dept. Organic Chemistry, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Univ. de Zaragoza-CSIC, Pedro Cerbuna, 12, E-50009 Zaragoza, Spain. Fax:+34 976762077; Tel: +34 976762271; E-mail: jig@unizar.es*

[c] *Instituto Universitario de Catálisis Homogénea, Facultad de Ciencias, Univ. de Zaragoza, Pedro Cerbuna, 12, E-50009 Zaragoza, Spain. Fax: 976762077; Tel: 976762077; E-mail: mayoral@unizar.es.*

Content

1. Abbreviations for solvents

The abbreviations for all solvents used in this work are:

Common solvents:

trifluoroethanol	TFE
dichloromethane	DCM
n-butanol	n-BuOH
n-hexanol	n-HxOH
ethanol	EtOH
2-propanol	2-PrOH
i-propyl ether	i-Pr_2O
diethylene glycol dibutyl ether	DEGDBE
etyleneglycol dimethyl ether	EGDME
1,4-dioxane	Diox

Glycerol derivatives:

1,3-dimethoxy-2-propanol	101
1-methoxy-3-tert-butoxy-2-propanol	104t
1-n-butoxy-3-tert-butoxy-2-propanol	404t
1,3-di-n-butoxy-2-propanol	404
1,3-bis(2,2,2-trifluoroethoxy)-2-propanol	3F03F
1,3-bis(2,2,3,3,3-pentafluoropropoxy)-2-propanol	5F05F
1,3-bis(2,2,3,3,4,4,4-heptafluorobutoxy)-2-propanol	7F07F
1,2,3-trimethoxypropane	111
1,2-dimethoxy-3-isopropoxypropane	113i
1,2-dimethoxy-3-isobutoxypropane	114i
1-butoxy-2-methoxy-3-isopropoxypropane	3i14
1,2-dimethoxy-3-tert-butoxypropane	114t
1,3-di-n-butoxy-2-methoxypropane	414
1,2,3-tri-n-butoxypropane	444
1-isopropoxy-2-methoxy-3-(2,2,2-trifluoroethoxy)propane	3i13F
1-tert-butoxy-2-methoxy-3-(2,2,2-trifluoroethoxy)-propane	4t13F
1-n-butoxy-2-methoxy-3-(2,2,2-trifluoro-ethoxy)propane	413F
2-methoxy-1,3-bis(2,2,2-trifluoroethoxy)propane	3F13F

2. Data of epoxidation

In table S1 are shown variables, x_n, used to measure the rate of epoxidation of cyclooctene using different solvents.

Table S1. Results in catalytic epoxidation of cyclooctene using different solvents.

Solvent	x_1	x_2	x_3	x_4	x_5	x_6	x_7
TFE	491	40	75	94	95	97	97
5F05F	214	17	33	48	79	85	92
3F03F	155	16	29	48	77	84	98
7F07F	172	14	28	46	82	85	91
DCM	153	15	28	48	70	77	87
3F13F	130	13	23	38	57	64	78
413F	75	6	11	19	33	39	56
n-HxOH	67	6	10	18	33	39	57
3i13F	64	5	10	17	31	38	55
n-BuOH	100	1	9	17	32	38	55
4t13F	52	6	10	17	29	35	53
EtOH	51	4	8	14	26	33	49
404	46	4	8	13	25	30	47
i-PrOH	44	3	7	12	24	29	47
404t	38	3	6	9	19	24	40
114i	27	5	7	10	18	23	35
414	31	3	5	10	18	23	36
444	31	4	6	9	17	21	32
104t	47	1	5	9	17	21	34
3i14	36	3	5	8	14	18	29
i-Pr_2O	38	2	5	8	14	18	26
101	15	4	4	7	12	15	26
114t	54	2	4	8	11	14	21
DEGDBE	18	2	3	6	14	18	28
113i	24	2	4	7	11	14	23
111	21	2	4	6	11	14	21
EGDME	13	2	3	4	8	10	17
Diox	9	1	1	2	4	5	7

x_1=TOF_0, x_2=Conv(5'), x_3=Conv(10'), x_4=Conv(30'), x_5=Conv(45'), x_6=Conv(60'), x_7=Conv(120')

3. Data reduction (PCA)

It is shown in figure S1 that a single y variable already contains 93% of the overall variance (indicating the high correlation between the TOF_0 and the conversions at different reaction times), so this transformed variable was subsequently used as a reactivity index for statistical analyses of solvent effects.

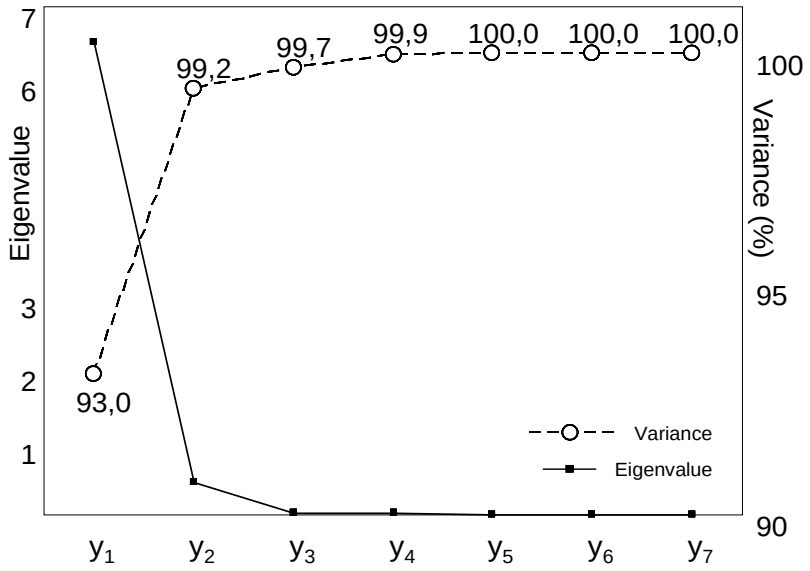

Figure S1. Cumulative variance in principal component analysis of TOF_0 and conversion values.

In table S2 are shown variables, x_n, used to measure the rate of epoxidation of cyclooctene using different solvents.

Table S2. Component matrix in principal component analysis.

	Component 1
x_1	0,953
x_2	0,962
x_3	0,974
x_4	0,995
x_5	0,974
x_6	0,967
x_7	0,924

These components are used to summarize all variables (x_n) in only one variable, which remain more than 93% of variance.

$$y_1 = 0{,}953 \cdot x_1 + 0{,}962 \cdot x_2 + 0{,}974 \cdot x_3 + 0{,}995 \cdot x_4 + 0{,}974 \cdot x_5 + 0{,}967 \cdot x_6 + 0{,}924 \cdot x_7$$

4. Variables y_1

Variables y_1 generated by a principal component analysis from data of table S1 are shown in table S3. These variables are normalized

Table S3. Results normalized in catalytic epoxidation of cyclooctene using different solvents.

Solvent	**y_1**
TFE	3,38
5F05F	1,59
3F03F	1,46
7F07F	1,42
DCM	1,29
3F13F	0,90
413F	0,03
n-HxOH	0,01
3i13F	-0,05
n-BuOH	-0,07
4t13F	-0,09
EtOH	-0,22
404	-0,27
i-PrOH	-0,32
404t	-0,45
114i	-0,46
414	-0,50
444	-0,52
104t	-0,55
3i14	-0,60
i-Pr_2O	-0,63
101	-0,67
114t	-0,68
DEGDBE	-0,68
113i	-0,72
111	-0,75
EGDME	-0,84
Diox	-1,01

5. Properties of solvents

Values of parameters used in correlation between the ratio of epoxidation of cyclooctene and properties of solvents used as media are shown on in table S4.

Table S4. Values of LogP, ETN, π*, β and α for solvents used

Solvent	Subgroup	logP	ET_N	π*	β	α
TFE	A	0,649	0,898	0,73	0,00	1,51
DCM	A	1,073	0,309	0,82	0,00	0,30
n-BuOH	A	0,971	0,586	0,47	0,88	0,79
n-HxOH	A	1,883	0,559	0,40	0,45	0,33
EtOH	A	-0,343	0,654	0,54	0,77	0,83
2-PrOH	A	0,368	0,546	0,48	0,95	0,76
i-Pr_2O	A	1,503	0,105	0,27	0,49	0,00
DEGDBE	A	2,446	0,2‡	0,5‡	0,4‡	0,0‡
EGDME	A	-0,080	0,231	0,53	0,41	0,00
Diox	A	-0,262	0,164	0,55	0,37	0,00
101	A	-0,591	0,50	0,65†	0,6†,‡	0,4†
104t	B	0,340	0,44	0,65†	0,6†,‡	0,4†
404t	B	1,669	0,39	0,65†	0,6†,‡	0,4†
404	A	2,066	0,45	0,65†	0,6†,‡	0,4†
3F03F	A	1,424	0,701	0,55†	0,7†,‡	0,8†
5F05F	B	2,407	0,699	0,55†	0,7†,‡	0,8†
7F07F	B	3,390	0,685	0,55†	0,7†,‡	0,8†
111	A	-0,183	0,3*	0,4†	0,4†,‡	0,0†,‡
113i	B	0,544	0,22	0,4†	0,4†,‡	0,0†,‡
114i	B	1,009	0,21	0,4†	0,4†,‡	0,0†,‡
3i14	B	1,872	0,155	0,4†	0,4†,‡	0,0†,‡
114t	B	0,749	0,214	0,4†	0,4†,‡	0,0†,‡
414	B	2,475	0,145	0,4†	0,4†,‡	0,0†,‡
444	A	3,804	0,11	0,4†	0,4†,‡	0,0†,‡
3i13F	B	1,551	0,39	0,55†	0,45†,‡	0,1†,‡
4t13F	B	1,756	0,373	0,55†	0,45†,‡	0,1†,‡
413F	B	2,154	0,385	0,55†	0,45†,‡	0,1†,‡
3F13F	A	1,832	0,553	1,0	0,5‡	0,30

† Average for a very similar subgroup of solvents. ‡ Estimated.

Values of logP for all solvents have been calculated by addition group theory.[20]

Values of ETN, π*, β have been taken from literature for common solvents,[21–25] or they have been determined by experimental measures for glycerol based solvents (preparing to be published).

Values for α have been determined based on ETN and π* values.[26]

6. References

[20] Ghose A.K., Viswanadhan V.N., Wendoloski J.J., *J. Phys. Chem.*, **1998**, *102*, 3762-3772

[21] C. Reichardt *Chem. Rev.*, **1994**, 94 (8), 2319-2358.

[22] C. Laurence, P. Nicolet, M. T. Dalati, J. L. Abboud, R. Notario, *J. Phys. Chem.*, **1994**, 98 (23), 5807-5816.

[23] M. J. Kamlet, J. L. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.*, **1983**, 48 (17), 2877-2887.

[24] M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.*, **1976**, 98 (2), 377-383.

[25] R. W. Taft, M. J. Kamlet *J. Am. Chem. Soc.*, **1976**, 98 (10), 2886-2894.

[26] Y. Marcus, *Chem. Soc. Rev.*, **1993,** *22*, 409.