Supplementary Information for

Multiphase enantioselective Kharasch–Sosnovsky allylic oxidation based on neoteric solvents and ditopic copper complexes

Luis Aldea, José I. García* and José A. Mayoral

Instituto de Síntesis Química y Catálisis Homogénea, CSIC-Univ. de Zaragoza, Calle Pedro Cerbuna, 12. E-50009 Zaragoza, Spain
mail: ji.garcia@csic.es; Fax : +34 976762077; Tel : +34 976762271

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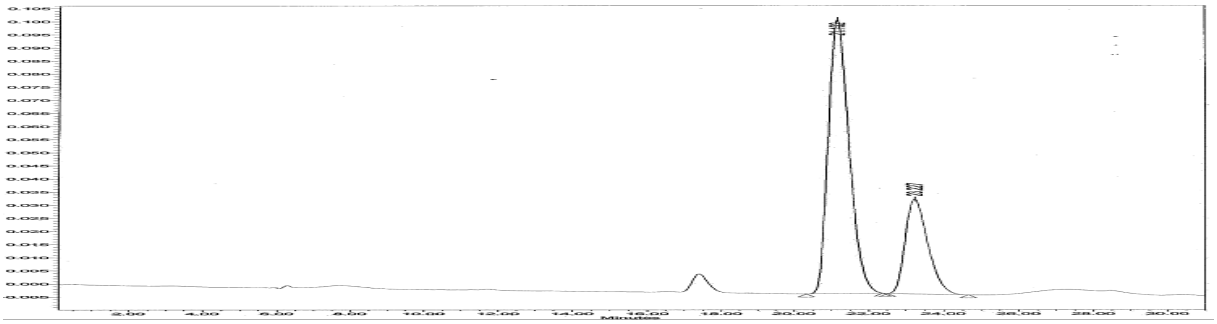
Chromatographic analyses of the reaction of cyclohexene and cycloheptene with tert-butyl perbenzoate, catalyzed by copper complexes

Reactions were monitored by gas chromatography. FID from Hewlett-Packard 5890II; cross-linked methyl silicone column: 25 m × 0.2 mm × 0.33 μm; helium as carrier gas. 20 psi; injector temperature: 230 ºC; detector temperature: 250 ºC; oven program: 65 ºC (3 min), 25 ºC min^{-1} to 250 ºC (3 min);retention times:

- *n*-decane 6.1 min.
- *tert*-butyl perbenzoate 8.1 min.
- 2-cyclohexenyl benzoate 11.2 min.
- 2-cycloheptenyl benzoate (**2c**) 11.2 min.

Enantioselectivities were determined by HPLC on a Waters Alliance Chromatograph with a PDA detector (λ = 220 nm). (*S*)-enantiomer was the major product in all cases.

2-Cyclohexenyl 1-benzoate: CHIRALCEL OJ (DAICEL) column, 0.46 cm x 25 cm, *n*-hexane; 0.80 mL min^{-1}; retention times: (*S*)-isomer 21.2 min, (*R*)-isomer 23.2 min.



2-Cycloheptenyl 1-benzoate: CHIRALCEL OJ (DAICEL) column, 0.46 cm x 25 cm, *n*-hexane; 0.35 mL min^{-1}; retention times: (*R*)-isomer 27.8 min, (*S*)-isomer 30.0 min.

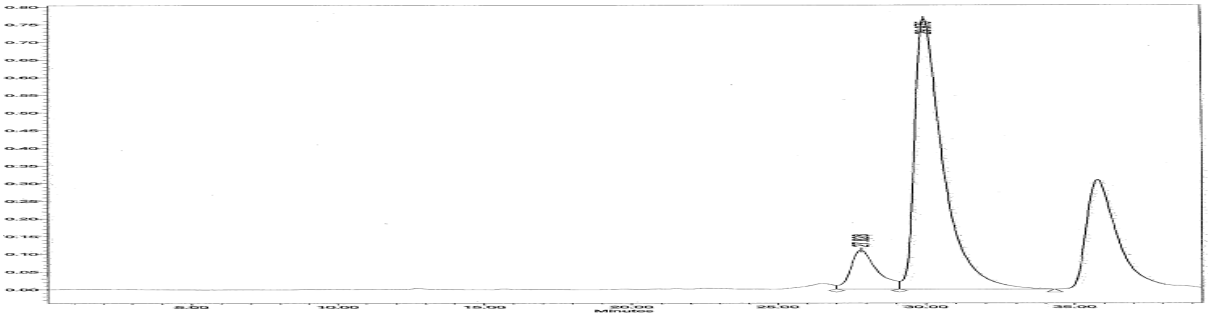


Table S1 Results obtained from the allylic oxidation of cyclohexene in BTFEP, using the ^{i}Pr-click-DAX-$CuPF_6$ complex as catalyst. Deactivation experiments. Before the fourth run, the catalytic phase is divided into two equal aliquots.

Run	Yield (%)	%ee
1	65	83
2	67	74
3	63	65
4	64	45
4*	69	68
5*	68	65
6*	64	68

*After addition of 15% fresh ligand.

Table S2 Results obtained from the allylic oxidation of cyclohexene in [BMIM][PF_6], using the ^{i}Pr-AzaBox- and ^{i}Pr-PyBox-CuCl complexes as catalyst.

Ligand	Run	Time (days)	Yield (%)	%ee
	1	2	5	8
^{i}PrAzaBox	2	2	13	11
	3	2	22	42
	4[a]	2	77	45
	5	2	3	7
	1	2	73	57
^{i}PrPyBox	2	2	47	48
	3	2	21	9
	1	2	26	33
^{i}PrAzaBox[b]	2	4	82	40
	3	5	56	33

[a] After addition of phenylhidrazine. [b] Phenylhydrazine is added in each reaction.