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Suplementary Materials: Polycyclic Ketone Monooxygenase (PockeMO): A Robust Biocatalyst for the Synthesis of Optically Active Sulfoxides

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S.1. Study of the Thioanisole Concentration Effect on the PockeMO-Catalytic Properties

Thioanisole **1a** (10, 50 , 100 or 200 mM) was added to 1.0 mL Tris/HCl 50 mM (pH 8.0) containing NADPH (0.2 mM), sodium phosphite (1.0 equivalent) and PockeMO (1.0 μM). The reactions were stirred at 25, 45 or 60 ºC at 220 rpm for the times established. Once finished, the reactions were extracted with EtOAc (2 x 0.5 mL) and dried onto Na_2SO_4. The samples were directly analysed by GC/MS and HPLC in order to determine, respectively, the level of conversion, the percentage of chiral methyl phenyl sulfoxide (*R*)-**1b** and methyl phenyl sulfone **1c**, as well as the enantiomeric excesses of sulfoxide (*R*)-**1b**. Results are summarized in Table S.1.

Table S1. Enantiomeric excesses, conversions and space time yields obtained in the PockeMO-catalyzed sulfoxidation of thioanisole at different concentrations and temperatures.

[**1a**] (mM)	T (ºC)	t (h)	conversion (%)[a]	Space time yield (mmol L^{-1} h^{-1})	*ee* (*R*)-**1b** (%)
10	25	16	>97	61.9	88
50	25	16	45	140.6	89
100	25	30	13	43.3	86
200	25	48	7	29.2	85
10	45	8	>97	123.8	87
50	45	20	96	240.0	86
100	45	24	43	179.2	86
200	45	24	17	141.7	84
10	60	7	>97	138.1	82
50	60	24	92	191.7	80
100	60	24	35	145.8	80
200	60	24	11	91.7	79

[a] For all the reactions studied, the amount of sulfone **1c** was below 5%.

S.2. GC Analyses

GC Analyses were performed on a HP-5MS cross-linked methyl siloxane column (30 m × 0.25 mm × 0.25 μm, 1.0 bar N_2) and were used for the determination of the conversions and the amount of both sulfoxides **1-12b** and sulfones **1–12c** (Table S2). For all the compounds, the following program was employed: 50 ºC (5 min), 10 ºC/min, 200 ºC (3 min).

Table S2. Determination of conversions and amounts of sulfoxides and sulfones by employing GC.

Substrate	t_R (min) Sulfide	t_R (min) Sulfoxide	t_R (min) Sulfone
1	11.0	15.1	15.7

2	12.2	16.2	16.9
3	15.4	18.7	19.5
4	16.5	18.9	19.5
5	14.9	18.6	19.3
6	14.1	17.1	17.7
7	14.1	17.2	17.7
8	13.9	16.6	17.0
9	12.5	17.0	17.7
10	18.9	21.8	22.3
11	19.5	21.9	22.5
12	12.8	15.8	16.6

S.3. HPLC Analyses

For the determination of the enantiomeric excesses of compounds **1–12b** (Table S3), the following columns were employed: column A: Chiralcel OB (0.46 cm × 25 cm), column B: Chiralcel OD (0.46 cm × 25 cm) and column C: Chiralcel OJ-H (0.46 cm × 25 cm), all three from Daicel.

Table S3. Determination of enantiomeric excesses by HPLC.

Substrate	Column	Flow rate (mL min^{-1})	T (ºC)	Eluent[a]	Retention time (min)
1b	B	1.0	30	*n*-hexane-IPA 9:1	10.2 (*R*); 12.0 (*S*)
2b	B	1.0	30	*n*-hexane-IPA 95:5	12.9 (*R*); 16.5 (*S*)
3b	B	1.0	30	*n*-hexane-IPA 95:5	16.9 (*R*); 18.2 (*S*)
4b	C	1.0	30	*n*-hexane-IPA 9:1	47.1 (*R*); 52.3 (*S*)
5b	B	1.0	30	*n*-hexane-IPA 9:1	14.1 (*R*); 15.2 (*S*)
6b	A	1.0	30	*n*-hexane-IPA 9:1	13.5 (*S*); 20.7 (*R*)
7b	A	1.0	30	*n*-hexane-IPA 9:1	12.8 (*S*); 18.8 (*R*)
8b	A	1.0	30	*n*-hexane-IPA 9:1	15.4 (*S*); 22.6 (*R*)
9b	B	1.0	30	*n*-hexane-IPA 9:1	17.0 (*R*); 18.7 (*S*)
10b	B	1.0	30	*n*-hexane-IPA 95:5	26.1 (*R*); 29.0 (*S*)
11b	B	0.5	30	*n*-hexane-IPA 9:1	22.1 (*R*); 26,7 (*S*)
12b	A	0.5	30	*n*-hexane-IPA 9:1	14.7 (*S*); 17.1 (*R*)

[a] All the experiments were performed with isocratic eluent.