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Supporting Materials

Table S1. Natural abundances (A_N, %) and mass ratios (m_R, %) of elements in the Soai reaction. [m] = atomic units, (a.u.). $m_R = [(m_{heavier} - m_{lightest})/m_{lightest}] \times 100$ (%).

Isotope Pair	m_R	$A_{N,heavier}$
$^1H/^2D$	99.84	0.015
$^{12}C/^{13}C$	8.36	1.11
$^{14}N/^{15}N$	7.12	0.37
$^{16}O/^{17}O$	6.31	0.037
$^{16}O/^{18}O$	12.57	0.204
$^{64}Zn/^{66}Zn$	3.12	27.81
$^{64}Zn/^{67}Zn$	4.69	4.11
$^{64}Zn/^{68}Zn$	6.25	18.57
$^{64}Zn/^{70}Zn$	9.38	0.62

Natural abundances of the lightest isotopes: $A_{N,\,lightest}$ (%), ^1H 99.985; ^{13}C 98.89; ^{14}N 99.63; ^{16}O 99.759; ^{64}Zn 48.89.

1. Supporting Materials 1

The number of possible isotopomers was calculated considering only ^1H, ^2H (D), ^{12}C and ^{13}C, while ^{14}C and ^3H were disregarded because of very low abundances. Thus in *one* methyl group C generates two cases, while the distribution of H might be H_3, H_2D, HD_2 and D_3 yielding 4 cases, thus for one methyl group we have 2 × 4 = 8 cases. Not considering the isotopes of the central carbon, we obtain different substitution for *all 3 methyl groups* in 8 × 7 × 6 = 336 cases, but because of the equivalence of the methyl groups this should be devided by 3 giving 336/3 = 112. (If the isotopes of the central carbon are regarded, we get obviously the double of this number: 224, but since this C atom does not influence the chirality of the *tert*-Bu group we used in our additional calculations the value of 112.)

2. Supporting Materials 2

The Pars–Mills equation [1,2]

The distribution of R (or S) is a binomial distribution with n, p = 0.5 parameters. This could be approximated, if n is "sufficiently large" with a normal distribution, characterized by $m = np$ and $\sigma = \frac{\sqrt{n}}{2}$ parameters, and one obtains

$$P\left(R > \frac{1+u}{2}n\right) = 1 - \Phi\left(u\sqrt{n}\right)$$

where Φ is the distribution function of the standard normal distribution. Consequently:

$$P\left(\left|\frac{R-S}{R+S}\right| > u\right) = 2\left[1 - \Phi\left(u\sqrt{n}\right)\right]$$

which is equivalent to:

$$P\left(\left|\frac{R-S}{R+S}\right| < u\right) = 2\Phi\left(u\sqrt{n}\right) - 1$$

The values of Φ can be obtained from tables (e.g., Microsoft Excel). Thus for the case where the probability (P) is expected to be ≥50% confidence one obtains Φ(0.675) = 3/4 and thus

$P\left(\left|\frac{R-S}{R+S}\right| > \frac{0.675}{\sqrt{n}}\right) = \frac{1}{2}$ which is equivalent to the Pars–Mills formula $e.e._{50\%} = \frac{0.675}{\sqrt{n}}$ or $= \frac{67.5}{\sqrt{n}}(\%)$. Narrowing the confidence range to 5%, one obtains Φ(1.96) = 0.975 thus: $P\left(\left|\frac{R-S}{R+S}\right| > \frac{1.96}{\sqrt{n}}\right) = 0.05$ which yields an analogous formula:

$$e.e._{5\%} = \frac{1.96}{\sqrt{n}} \text{ or } = \frac{196}{\sqrt{n}}(\%)$$

This latter operation shows qualitatively that if the confidence range is lowered from 50% to 5% one obtains approximately 3-fold higher *e.e.* values, or in the other words to obtain 3-fold higher *e.e.* than *e.e.*50% the confidence decreases by a factor of 10.

3. Supporting Materials 3

Control calculation of the probabilities of achiral and chiral structures in compound **S-E4**

3.1. Case (a)

Probability of asymmetric (chiral) Zn-boud *i*-Pr groups: 0.045215;
Probability of symmetric (achiral) C-bound *i*-Pr groups: 0.93380;
Thus, the probability of the 2,064,384 structures under (a): 0.045215 × 0.93380 = **0.04222 ≈ 4.2%**.

3.2. Case (b)

Probability of the symmetric (achiral) Zn-bound *i*-Pr groups: 0.954785;
Probability of the asymmetric (chiral) C-bound *i*-Pr groups: 0.06620;
Thus the probability of the 4,161,536 structures under (b): 0.954785 × 0.06620 = **0.06320 ≈ 6.3%**.

3.3. Case (c)

Probability of the asymmetric (chiral) Zn-bound *i*-Pr groups: 0.045215;
Probability of the asymmetric (chiral) C-bound *i*-Pr groups: 0.06620;
Thus the probability of the 262,176,768 structures under (c): 0.045215 × 0.06620 = **0.00300 ≈ 0.3%**.

Consequently, the probability of *all chiral structues* is the sum of these probabilities: 0.04222 + 0.06620 + 0.00300 = **0.10842 ≈ 10.8%** equal to the value deduced in the main text.

4. Supporting Materials 4

The Pars-Mills expectable *e.e.* values for compound **S-E4,** according to approaches under cases (a), (b) and (c), with 50% confidence (*e.e.*50%).

4.1. Case (a)

Table S2. Expected enantiomeric excesses for 4.1. Case (a).

Sample Size	*e.e.*50% (%)
millimol	1.34112×10^{-8}
micromole	4.24101×10^{-7}
nanomol	1.34112×10^{-5}
picomol	4.24101×10^{-4}
femtomol	1.34112×10^{-2}

4.2. Case (b)

Table S3. Expected enantiomeric excesses for 4.2. Case (b).

Sample Size	*e.e.*$_{50\%}$ (%)
millimol	1.09615×10^{-8}
micromole	3.46633×10^{-7}
nanomol	1.09615×10^{-5}
picomol	3.46633×10^{-4}
femtomol	1.09615×10^{-2}

4.3. Case (c)

Table S4. Expected enantiomeric excesses for 4.3. Case (c).

Sample Size	*e.e.*$_{50\%}$ (%)
millimol	5.03115×10^{-8}
micromole	1.59099×10^{-6}
nanomol	5.03115×10^{-5}
picomol	1.59099×10^{-3}
femtomol	5.03115×10^{-2}

5. Supporting Materials 5

Possibilities of chiral Zn atoms in the Schiaffino-Ercolani intermediates [3] of the Soai reaction (O—chrality by four different substituents, O—hirality if the two oxygen atoms are different isotopes) [numbering of ref. [3] has been retained].

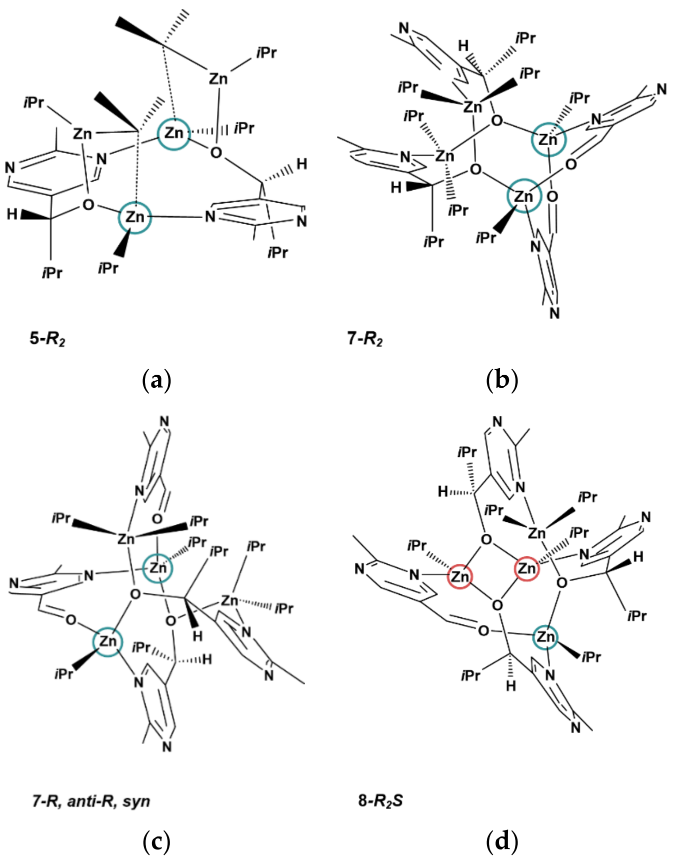
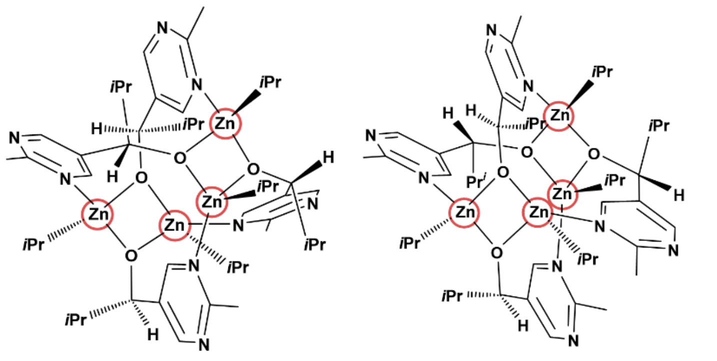


Figure S1. *Cont.*



9-R$_2$S2 (**e**)

9-R$_4$ (**f**)

Figure S1. Chirality of Zn atoms in the Schiaffino-Ercolani intermediates (see text above).

References

1. Barabás, B.; Caglioti, L.; Micskei, K.; Zucchi, C.; Pályi, G. Isotope Chirality and Asymmetric Autocatalysis: A Possible Entry to Biological Chirality. *Orig. Life Evol. Biosph.* **2008**, *38*, 317–327.
2. Mills, W.H. Some Aspects of Stereochemistry. *Chem. Ind. (London)* **1932**, 750–759.
3. Schiaffino, L.; Ercolani, G. Unraveling the Mechanism of the Soai Asymmetric Autocatalytic Reaction by First-Principles Calculations: Induction and Amplification of Chirality by Self-Assembly of Hexamolecular Complexes. *Angew. Chem. Int. Ed.* **2008**, *47*, 6832–6835.