

Asymmetric Autocatalysis Triggered by Carbon Isotope ($^{13}\text{C}/^{12}\text{C}$) Chirality

Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
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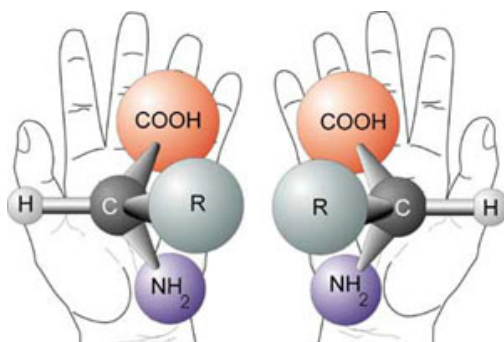
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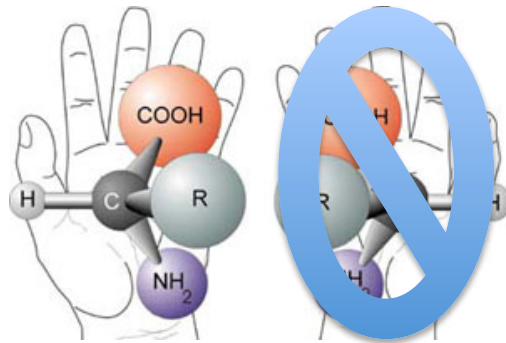
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The Homochirality Remains a Puzzle...



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All the 20 natural amino acids are left-handed.

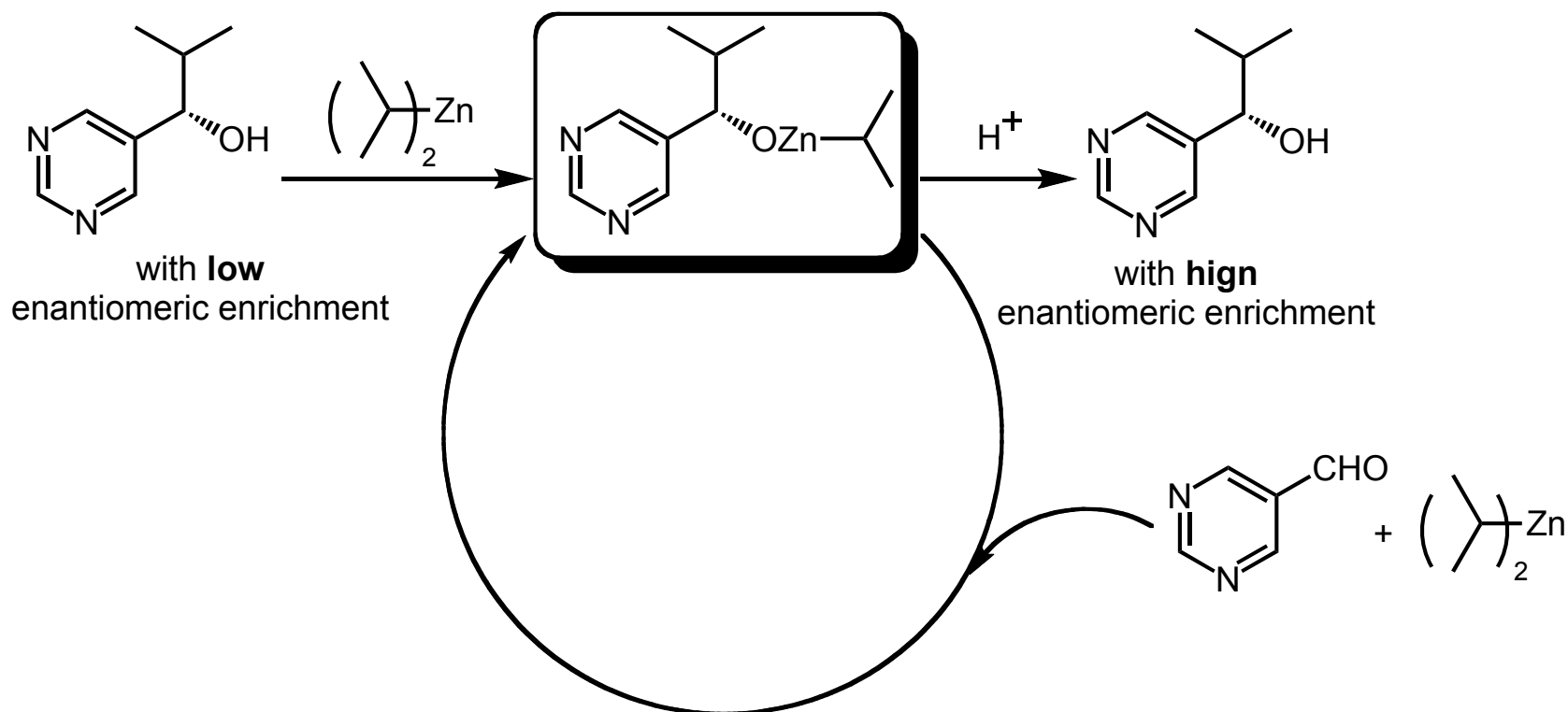
A proposed theory to explain the origin of the homochirality:

1st step Shattering the mirror: Absolute Asymmetric Synthesis

2nd step Propagating the imbalance: Asymmetric Autocatalysis

Blackmond, D. G. PNAS, 2004, 101, 5732-5736.

Asymmetric Autocatalysis and Its Implications for the Chemical Origin of Life



Soai, K.; Shibata, T.; Morioka, H.; Choji, K. *Nature*, **1995**, 378, 767-768.

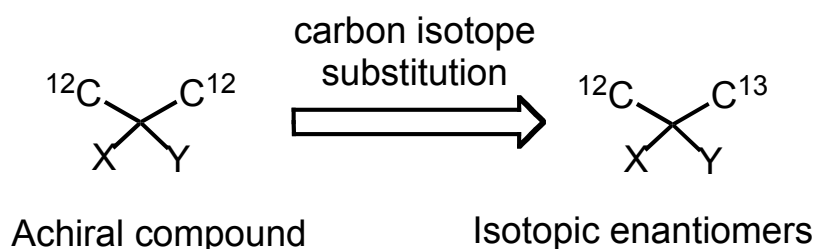
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Generation of Chirality by Carbon Isotope Substitution



Problem:

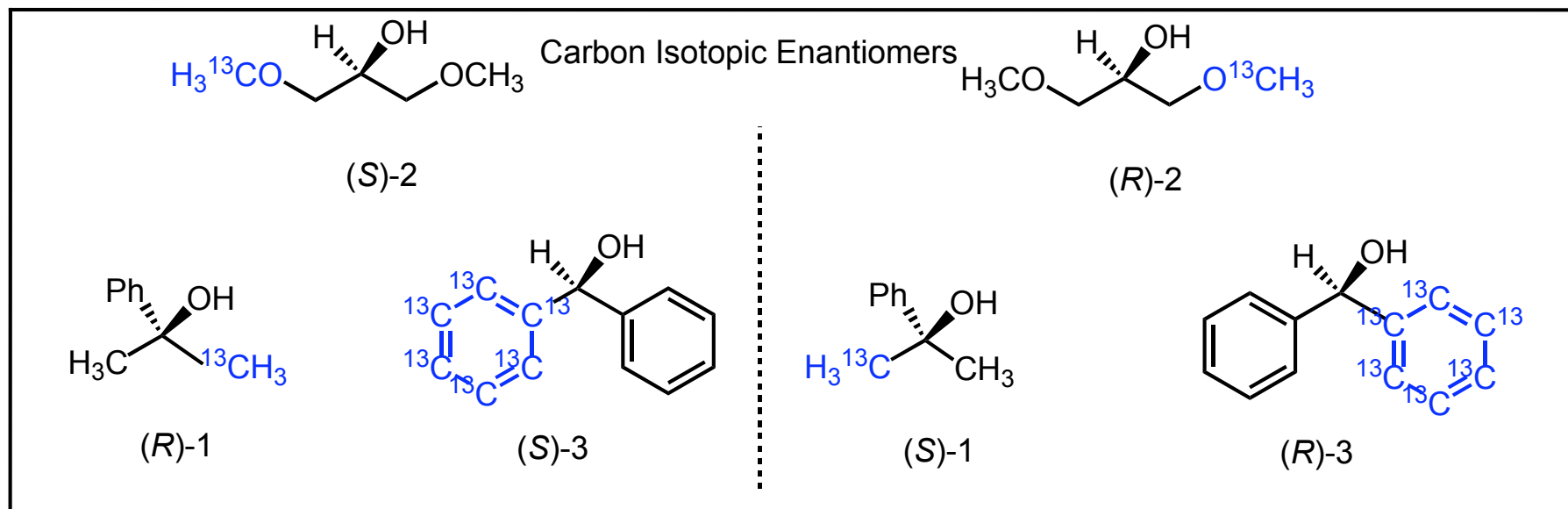
Experimentally inaccessible: very small difference between ^{13}C and ^{12}C

Solution:

Asymmetric Autocatalysis

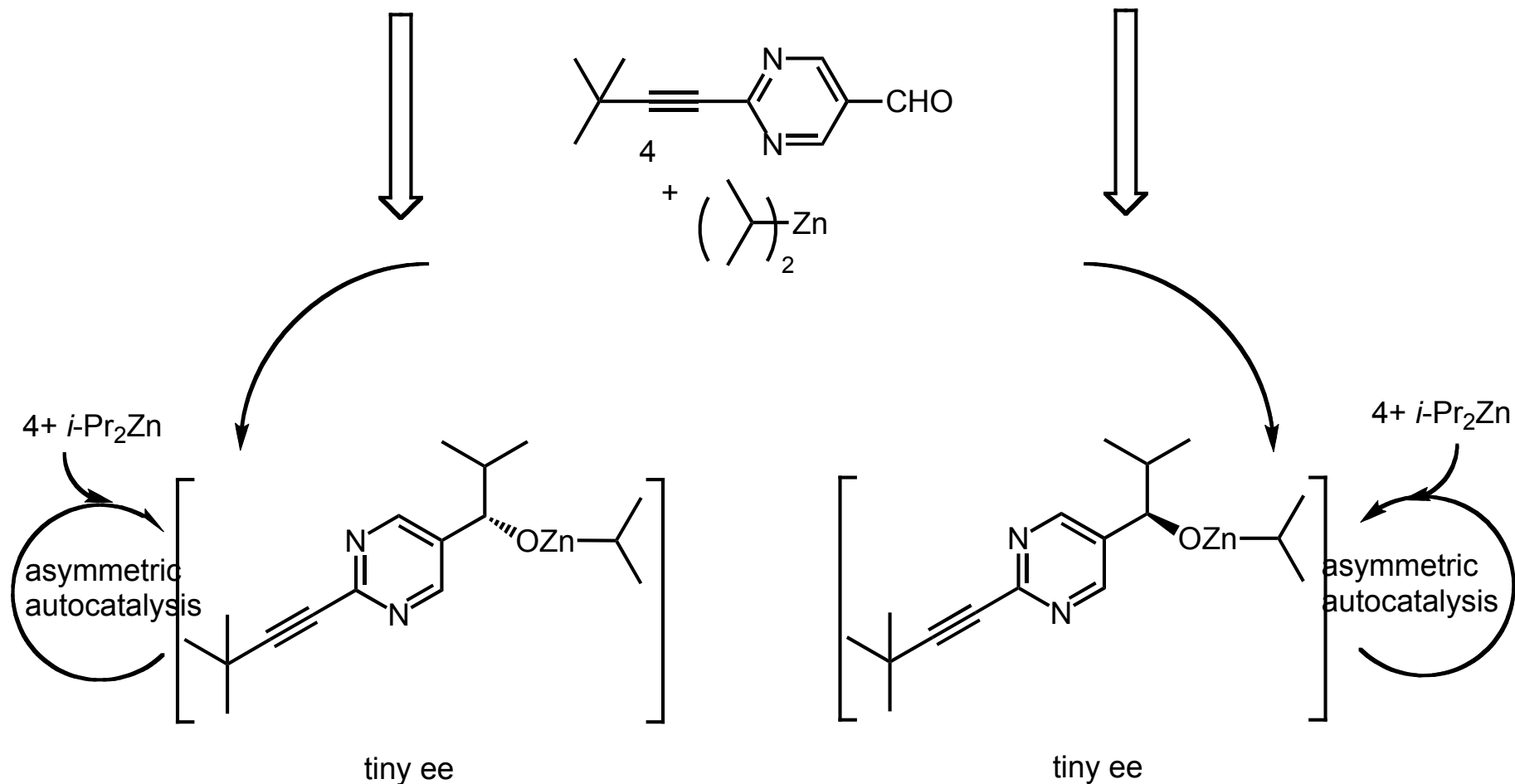
Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
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Discrimination of the Carbon Isotopic Chirality by Asymmetric Autocatalysis



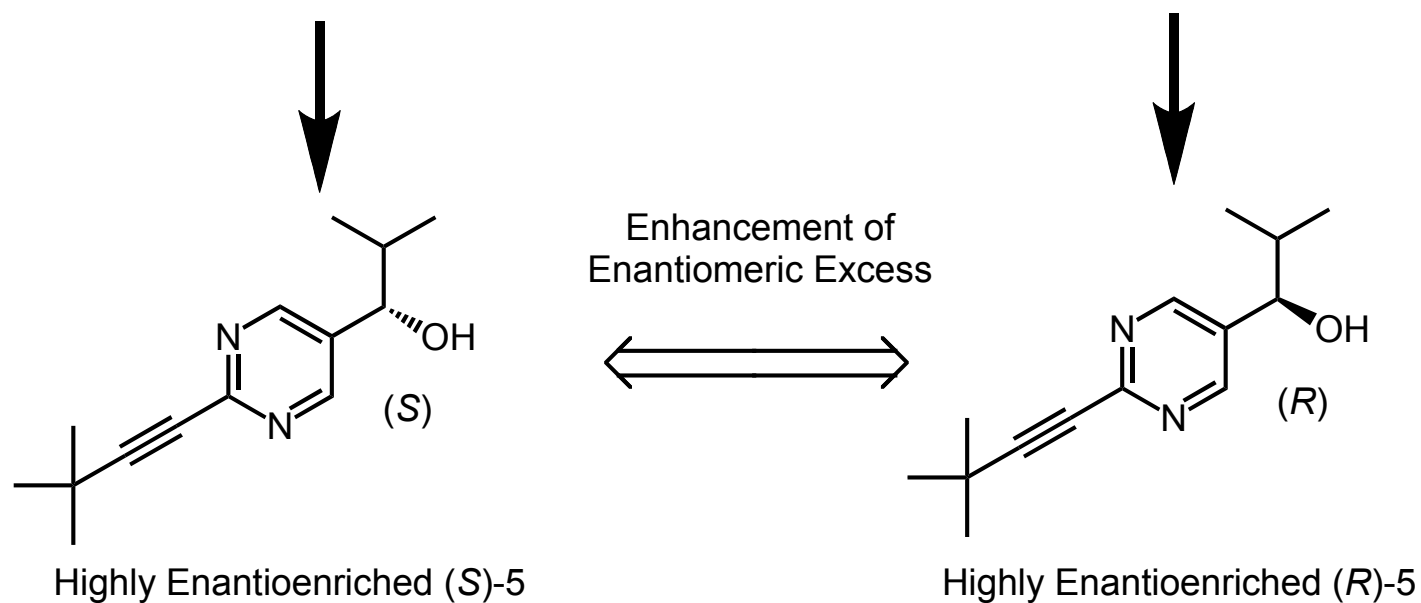
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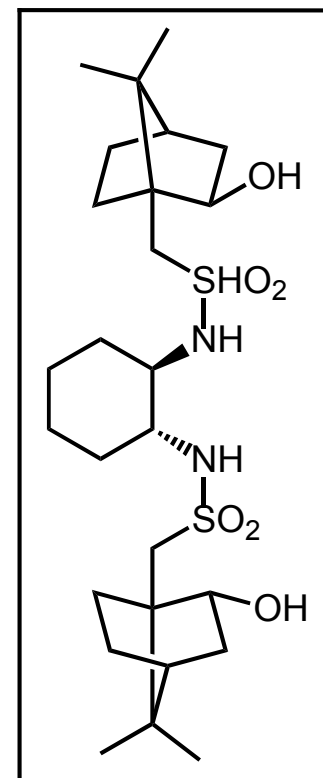
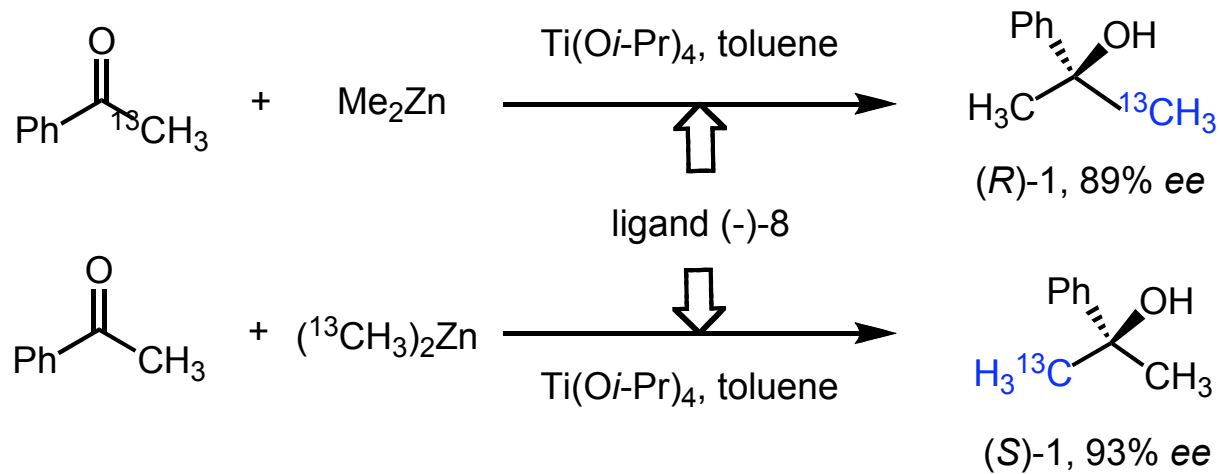
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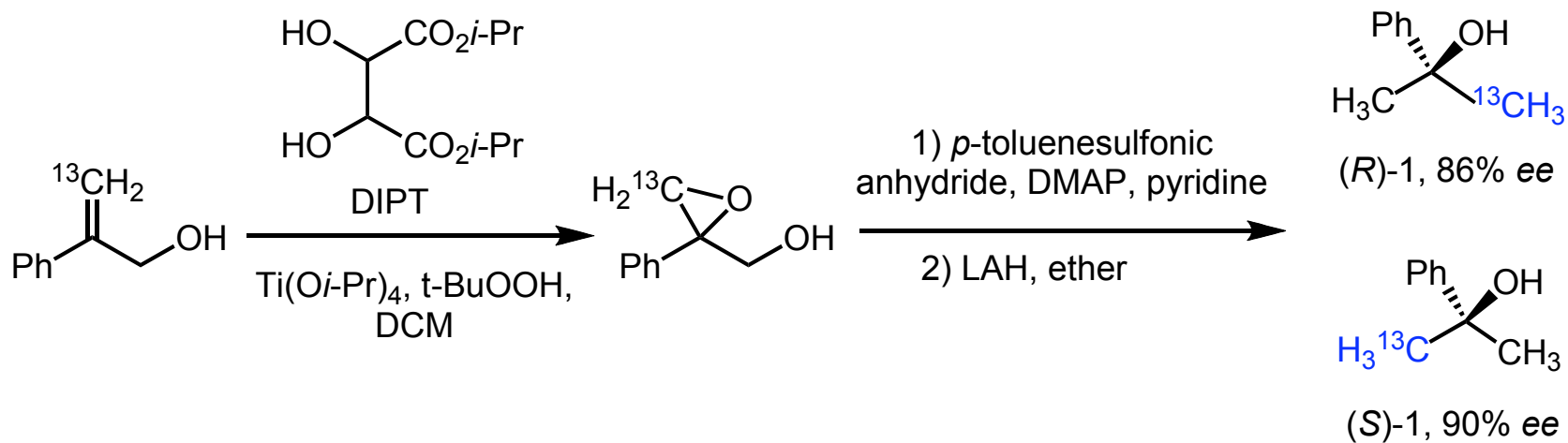
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Synthesis of Compound 1---Route 1



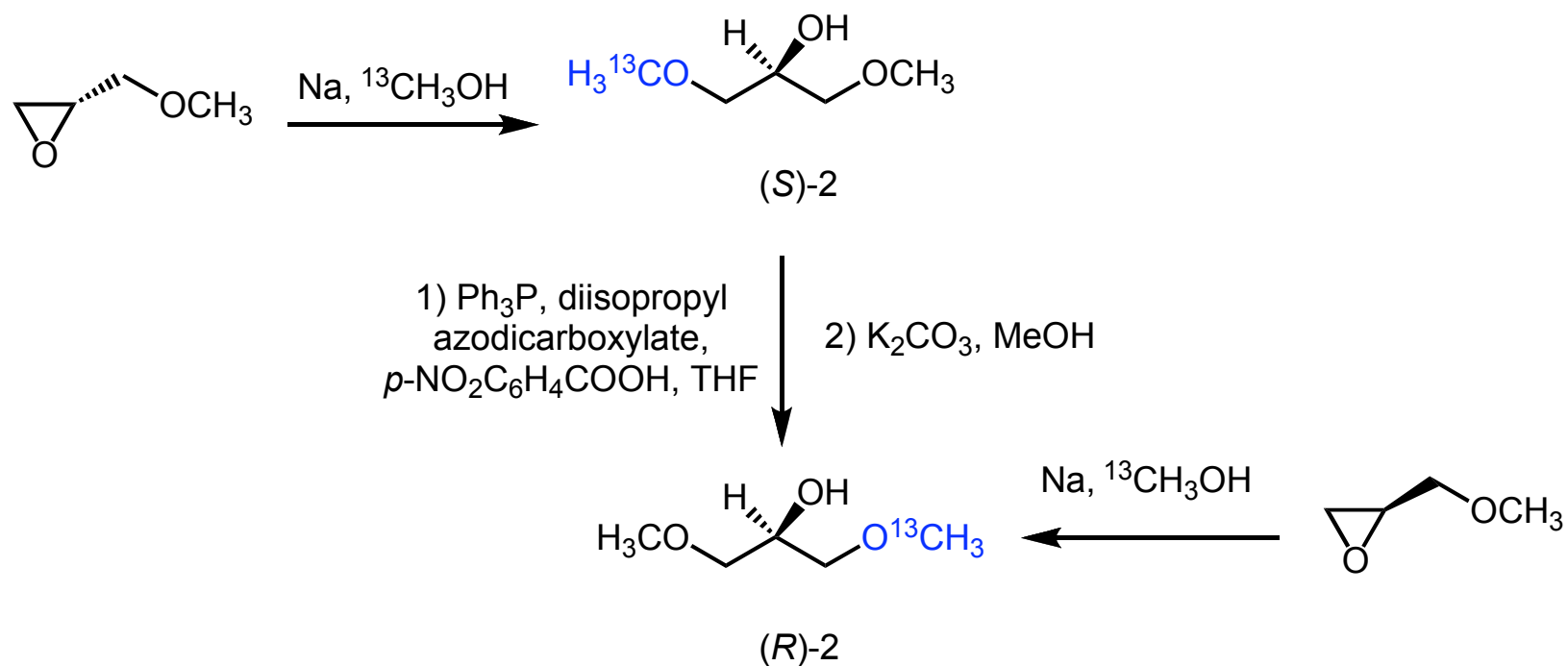
Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
Science, **2009**, 324, 492.

Synthesis of Compound 1---Route 2



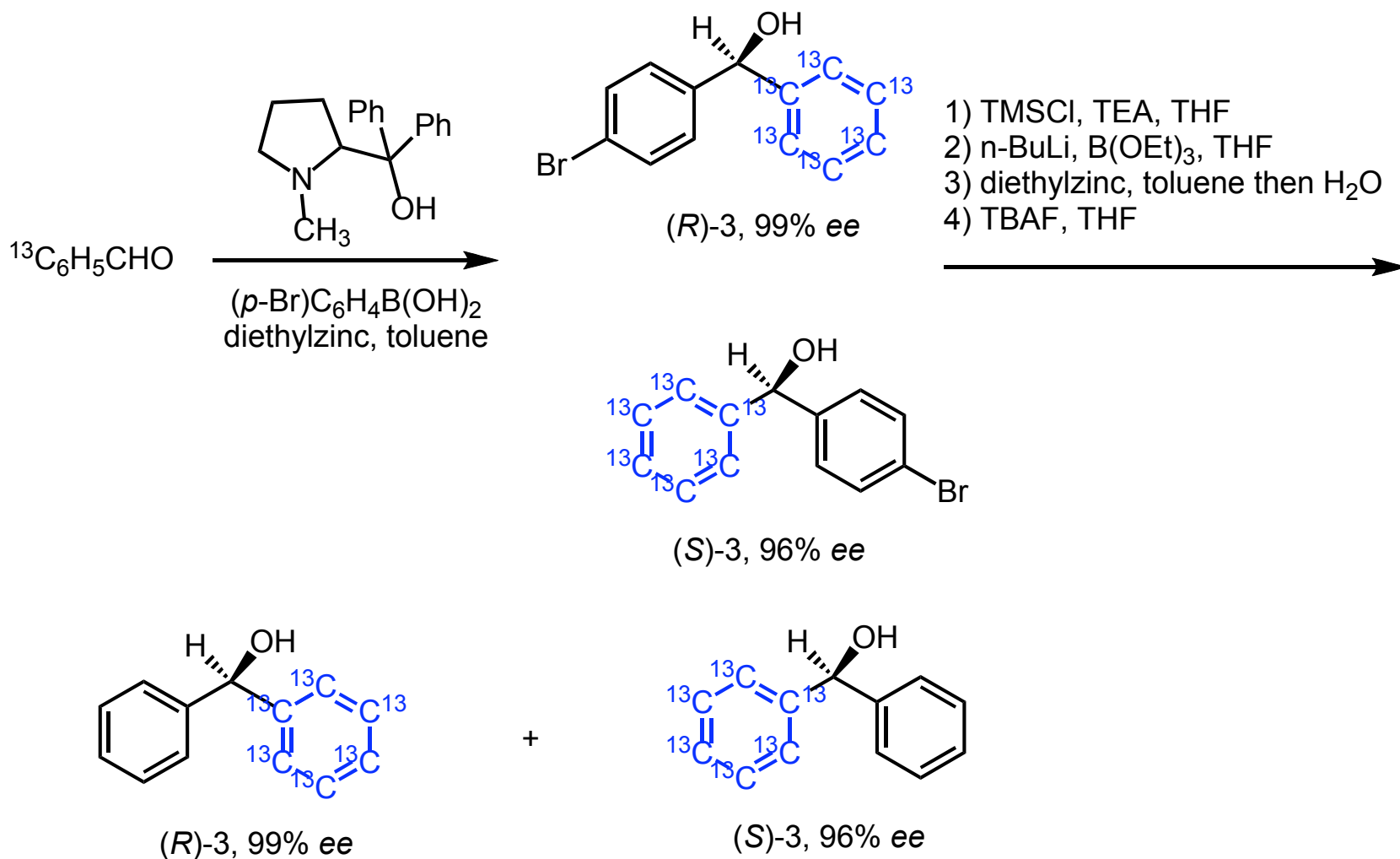
Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
Science, **2009**, 324, 492.

Synthesis of Compound 2



Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
Science, **2009**, 324, 492.

Synthesis of Compound 3



Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K.
Science, **2009**, 324, 492.

Chiral Discrimination of the Isotopic Carbons Using Compound 1 from Route 1

Entry	Chiral alcohol	Isolated yield	ee	configuration
1	(<i>R</i>)-1 (89% ee)	94	92	<i>S</i>
2	(<i>S</i>)-1 (93% ee)	95	96	<i>R</i>
3	(<i>R</i>)-1 (89% ee)	80	88	<i>S</i>
4	(<i>S</i>)-1 (93% ee)	94	96	<i>R</i>
5	(<i>R</i>)-1 (89% ee)	96	88	<i>S</i>
6	(<i>S</i>)-1 (93% ee)	97	94	<i>R</i>
7	(<i>R</i>)-1 (89% ee)	ND	93	<i>S</i>
8	(<i>S</i>)-1 (93% ee)	92	93	<i>R</i>

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Chiral Discrimination of the Isotopic Carbons Using Compound 1 from Route 2

Entry	Chiral alcohol	Isolated yield	ee	configuration
1	(<i>R</i>)-1 (86% ee)	94	94	<i>S</i>
2	(<i>S</i>)-1 (86% ee)	87	95	<i>R</i>
3	(<i>R</i>)-1 (86% ee)	93	94	<i>S</i>
4	(<i>S</i>)-1 (90% ee)	98	93	<i>R</i>
5	(<i>R</i>)-1 (86% ee)	85	92	<i>S</i>
6	(<i>S</i>)-1 (84% ee)	93	88	<i>R</i>
7	(<i>R</i>)-1 (86% ee)	88	89	<i>S</i>
8	(<i>S</i>)-1 (90% ee)	93	90	<i>R</i>

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Wine Time



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