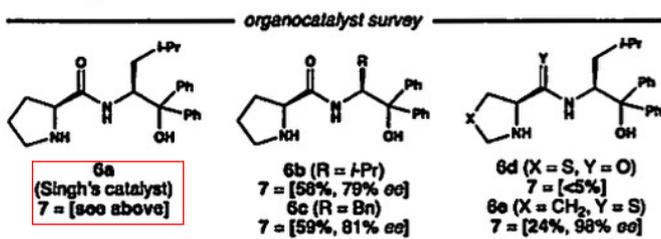
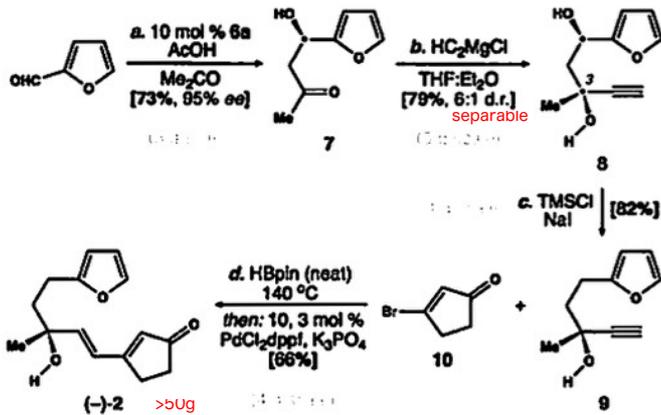


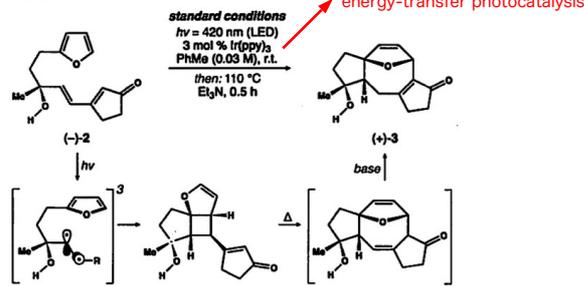
### Scheme 1. Enantioselective Synthesis of (-)-2<sup>a</sup>



<sup>a</sup>The relative stereochemistry of **8** was determined by single-crystal X-ray diffraction (CCDC 2429376).

### photocatalytic polyeneisomerization

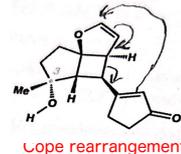
Table 1. Photocatalytic Cycloisomerization of (-)-2 to (+)-3<sup>a</sup>



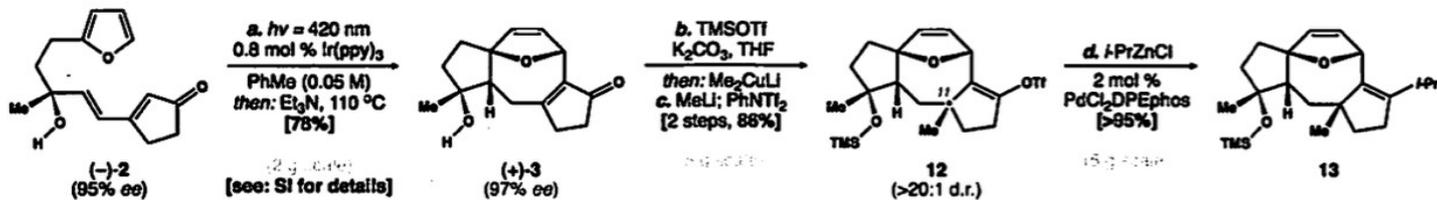
triplet-state species

entry	deviation from std. conditions	d.r. (11) <sup>b</sup>	3 (%) <sup>c</sup>
1	none	14:1	76
2	no photocatalyst	n/a	trace
3	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	13:1	50
4	Ir(dddtpy)(ppy) <sub>2</sub> PF <sub>6</sub>	14:1	66
5	[Ir(dFCF <sub>3</sub> ppy) <sub>2</sub> (dtbpy)]PF <sub>6</sub>	14:1	49
6	<i>n</i> -BuOH	2:1	trace
7	MeCN	4:1	57
8	1,4-dioxane	6:1	69
9	PhMe = 0.1 M	10:1	55
10	1 mol % Ir(ppy) <sub>3</sub>	14:1	74
11	0.5 mol % Ir(ppy) <sub>3</sub>	13:1	70

<sup>a</sup>Reactions were carried out in standard NMR tubes (O.D. = 5 mm; thin wall = 0.38 mm). <sup>b</sup>The d.r. of **11** (at C3) was determined by <sup>1</sup>H NMR in C<sub>6</sub>D<sub>6</sub>. <sup>c</sup>Reported yields of **3** were determined by NMR in C<sub>6</sub>D<sub>6</sub> using 1,3,5-trimethoxybenzene as an internal standard.



### Scheme 2. Total Synthesis of (+)-Fusicocadiene (1)<sup>a,b</sup>

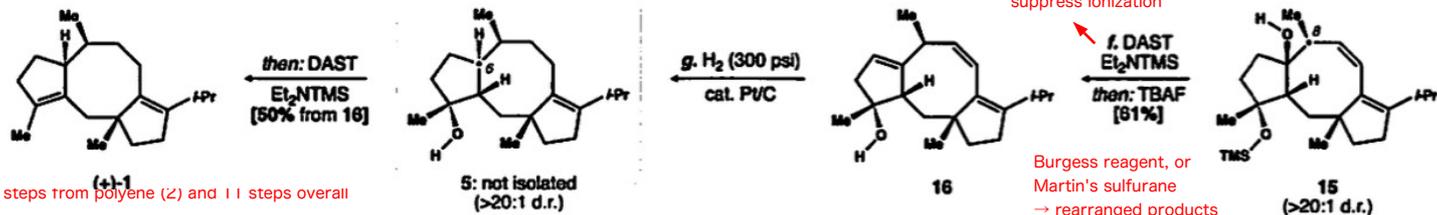


H-F-tubing spindle reactor

Cp<sub>2</sub>Ti(CH<sub>2</sub>) generated from Iebbe's

[see: Table 2]

essential



suppress ionization

Burgess reagent, or Martin's sulfuranone  $\rightarrow$  rearranged products

<sup>a</sup>Polycycle (+)-3 crystallized with increased enantiopurity (97% ee). <sup>b</sup>For (+)-1: observed  $[\alpha]_D = 21.9^\circ$  ( $c = 0.01$ , CHCl<sub>3</sub>); reported  $[\alpha]_D = 20.0^\circ$  ( $c = 0.16$ , CHCl<sub>3</sub>).

Table 2. Ring-Opening of Allylic Ether **13**<sup>a</sup>

g. H<sub>2</sub> (300 psi), cat. Pt/C

h. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

i. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

j. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

k. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

l. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

m. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

n. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

o. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

p. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

q. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

r. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

s. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

t. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

u. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

v. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

w. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

x. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

y. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

z. (-)-2 (95% ee)  $\rightarrow$  (+)-3 (97% ee)

<sup>a</sup>Reported values reflect isolated yields following purification.

