## Gategory

## Mimicking Nature: Enantioselective Cationic Polyene Cyclization



Tricyclization:

9 examples up to $93 \%$ yield up to $>99.5 \%$ ee ( 0.5 mmol scale)


$\xrightarrow{\begin{array}{l}\{\mathrm{Ir}(\mathrm{cod}) \mathrm{Cl}\}_{2}(4 \mathrm{~mol} \%) \\ (\boldsymbol{R}) \text {-ligand }(16 \mathrm{~mol} \%)\end{array}}$
 DCE, 24 h, r.t.

## Selected examples:


$90 \%$ yield
$>99.5 \%$ ee


89\% yield
$99.5 \%$ ee

$71 \%$ yield
99\% ee

$>99.5 \%$ ee

## Key words

polycyclization
iridium

Significance: The biogenic isoprene rule, established in 1955 by Ruzicka, Eschenmoser, and Stork (Helv. Chim. Acta 1955, 38, 1890; J. Am. Chem. Soc. 1955, 77, 5068), stimulated biomimetic studies for the construction of polycyclic frameworks, like the steroid skeleton. Approaches based on Bronsted/Lewis acid catalysis (Yamamoto, Loh, Corey), organocatalysis (Ishihara, MacMillan, Jacobsen), and transition-metal catalysis (Takeuchi, Helmchen, Hartwig) are reported.

Comment: The authors report the development of a highly enantioselective polycyclization method using the combination of Lewis acid activation with iridium-catalyzed allylic substitution. This strategy relies on direct use of branched, racemic allylic alcohols and furnishes a diverse and unique set of carbo- and heteropolycyclic ring systems in good yield and $\geq 99 \%$ ee.


90\% yield $>99.5 \%$ ee

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[^0]:    sYNFACTS Contributors: Mark Lautens, Harald Weinstabl Synfacts 2013, 9(3), 0285 Published online: 15.02.2013
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