

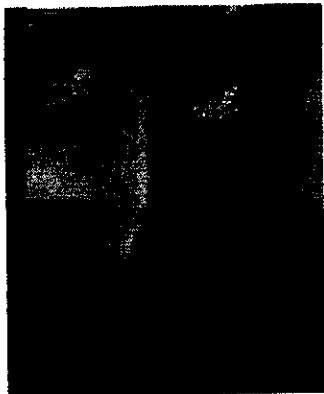
9.26.09

Baran Group Meeting

Perfume Chemistry

Elena Petricci

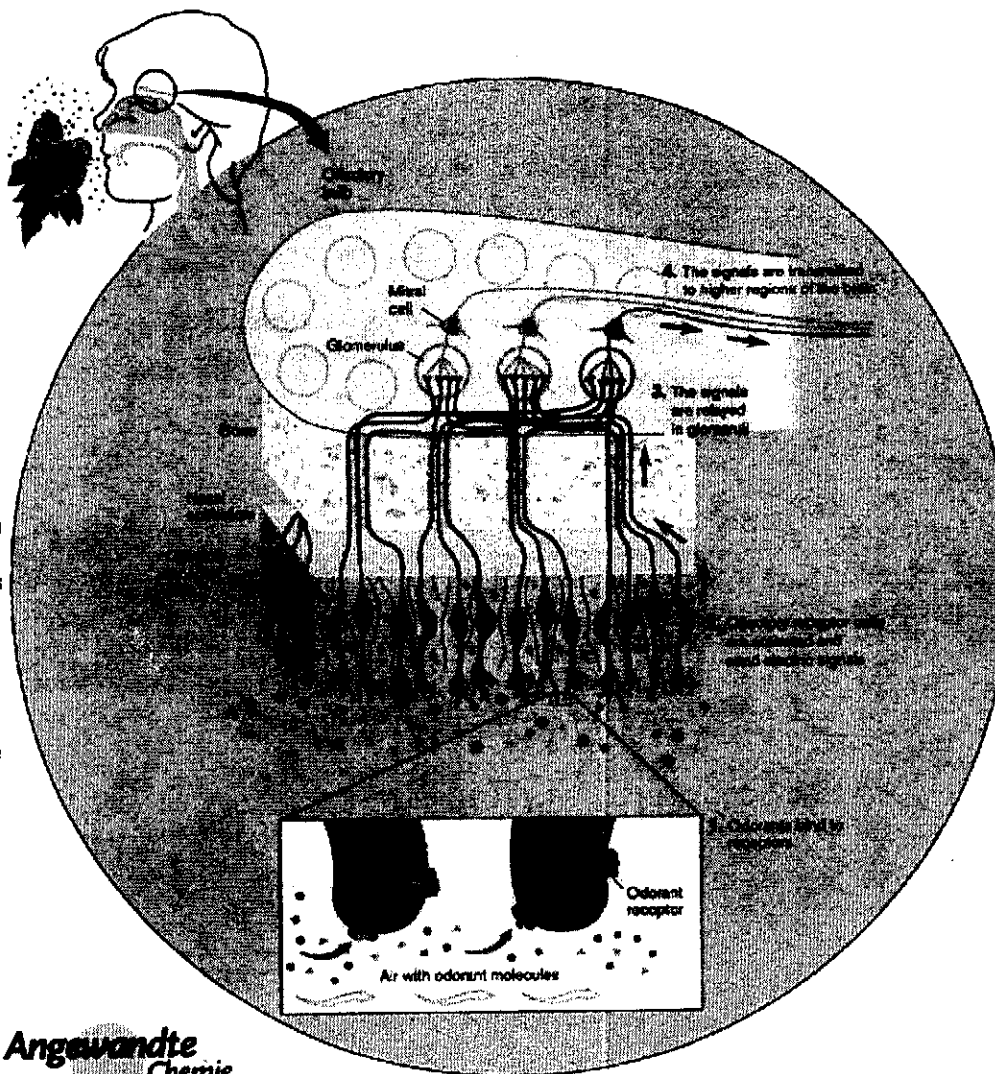
2004 Nobel Prize in Medicine and Physiology: Richard Axel, Linda B. Buck



R. Magritte (1937)

"The problem of how the brain represents the external world is not only a central theme in art but is at the very core of philosophy, psychology, and neuroscience. We are interested in how the chemosensory world is represented in the brain. All organisms have evolved a mechanism to recognize sensory information in the environment and transmit this information to the brain where it then must be processed to create an internal representation of the external world. There are many ways for organisms to probe the external world : some smell it, others listen to it, many see it. Each species therefore lives in its own unique sensory world of which other species may be partially or totally unaware."

Odorant Receptors and the Organization of the Olfactory System

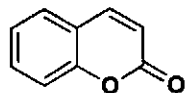


500 odorant receptors
 large number of receptors
 each capable of recognizing a
 small number of odorous
 ligands

Angewandte
Chemie

Axel ACIE 2005, 44, 6110

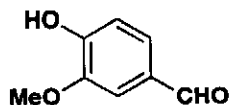
Buck ACIE 2005, 44, 6128



Cumarine (1868)

sweet, gingerbread

Fougère Royale (Houbigant, 1882)



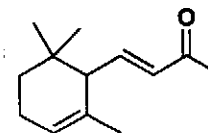
Vanillin (1876)

sweet, vanilla
Jicky (Guerlain, 1889)



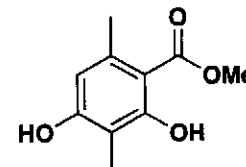
lauryl aldehyde (1880)

aldehydic, fatty, orange
Chanel N°5 (Chanel, 1921)



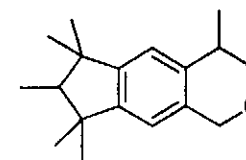
α-ionone (1898)

Floral, violet, woody
L'Original (Coty, 1906)



Evernyl (1898)

woody, moss
Egoïste Platinum
(Chanel, 1993)

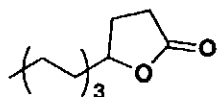


dihydromyrcenol (1960)

hesperidic, floral,
fresh
Cool Water
(Davidoff 1988)

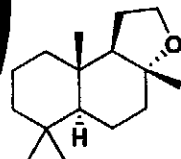
Galaxolide (1967)

musky
Trésor (C. Dior 1988)



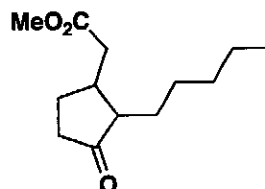
γ-undecalactone (1908)

Fruit, peach
Mutsouko (Guerlin, 1919)



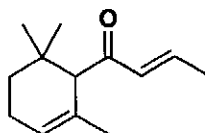
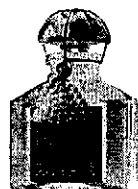
Ambrox (1950)

ambery
Drakkar Noir
(G. Laroche, 1982)



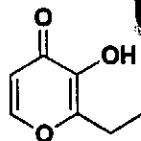
Hedione (1960)

floral, jasmine
Eau Sauvage
(C. Dior 1966)



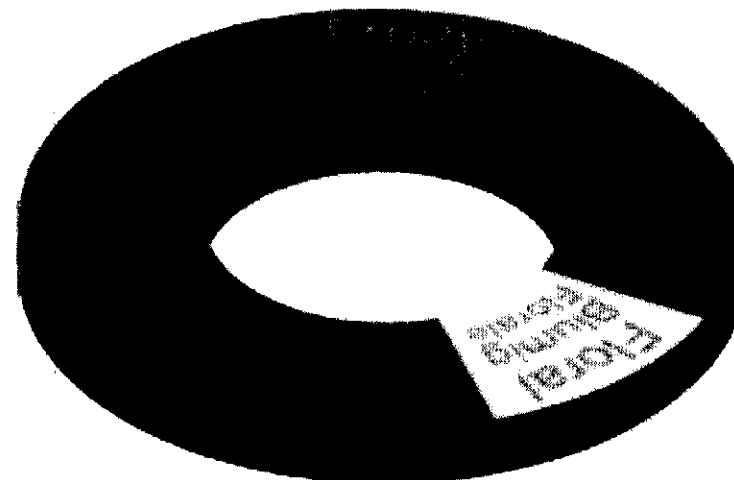
α-damascone (1969)

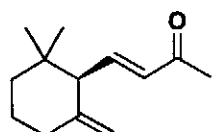
Floral, rosy, fruity
Nahéma (Guerlin, 1979)



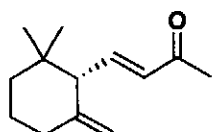
ethyl maltol(1969)

sweet, caramel, candy
Angel (T. Mugler, 1992)

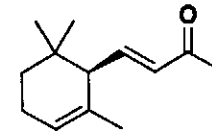




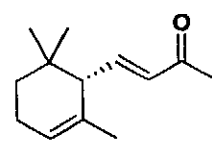
(-)- γ -ionone
Weak green, fruity, pineapple-like odor with metallic aspects



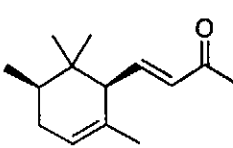
(+)- γ -ionone
Linear, very pleasant, floral, green, woody odor with a very natural violet tonality



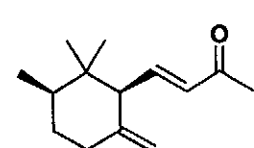
(+)- α -ionone
Linear woody, floral odor with an additional honey aspect



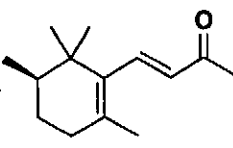
(-)- α -ionone
Floral, woody with an additional honey aspect. More powerful than the (*R*)-isomer



(+)-*cis*- α -ionone



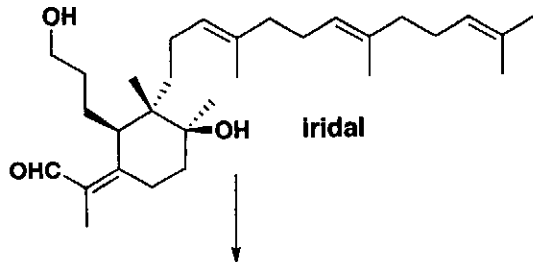
(+)-*cis*- γ -ionone



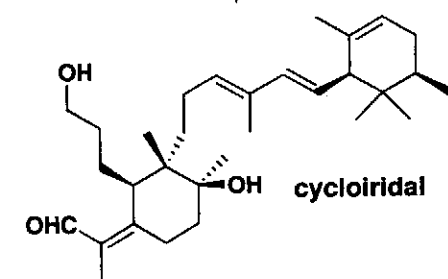
(+)- β -ionone

Brenna *Chem. Soc. Rev.* 2008, 37, 2443

Marnier *Helv. Chim. Acta* 1988, 71, 1331

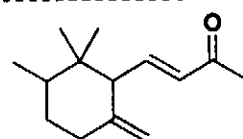


Iridal

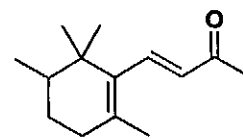


cycloiridal

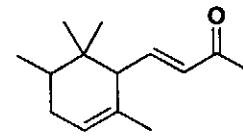
oxidative degradation



γ -ionone

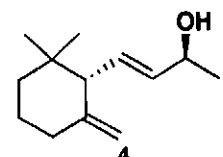
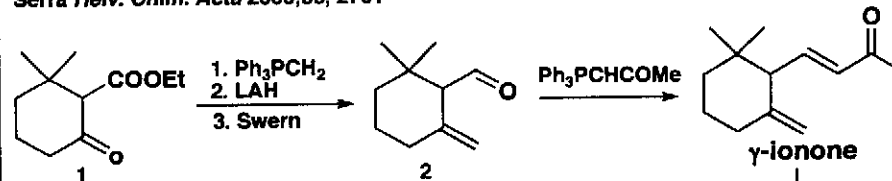


β -ionone

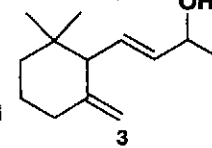


α -ionone

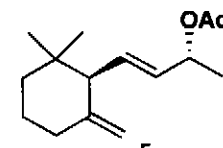
Serra *Helv. Chim. Acta* 2000, 83, 2761



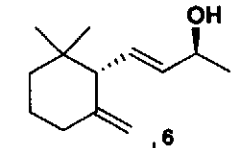
1. PNB-Cl
2. cryst.
3. KOH, MeOH



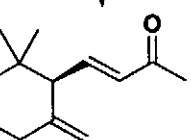
Lipase PS
vinyl acetate



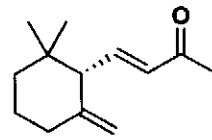
OAc



OH

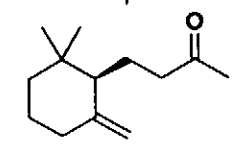


(-)- γ -ionone



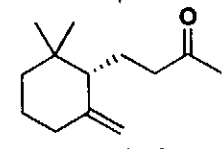
(+)- γ -ionone

Bu₃SnH
(PPh₃)₂PdCl₂



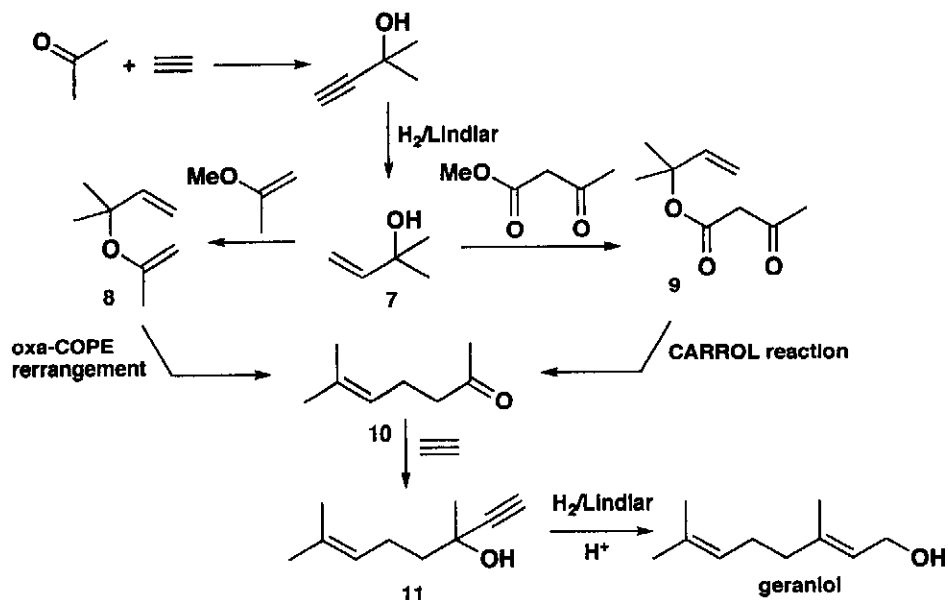
(-)- γ -dihydroionone

Bu₃SnH
(PPh₃)₂PdCl₂

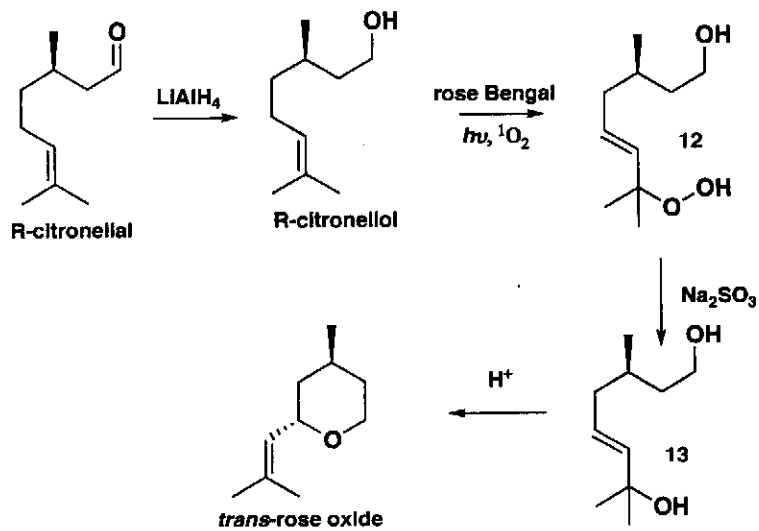


(+)- γ -dihydroionone

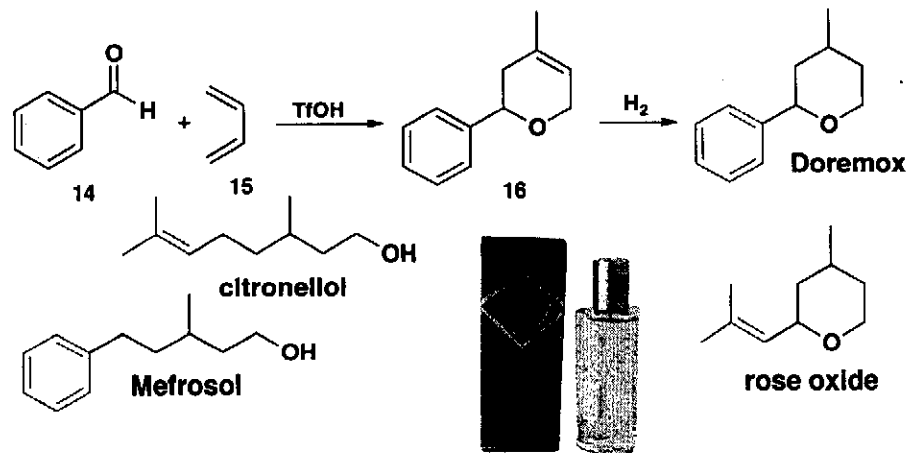
Industrial preparation of monoterpenes



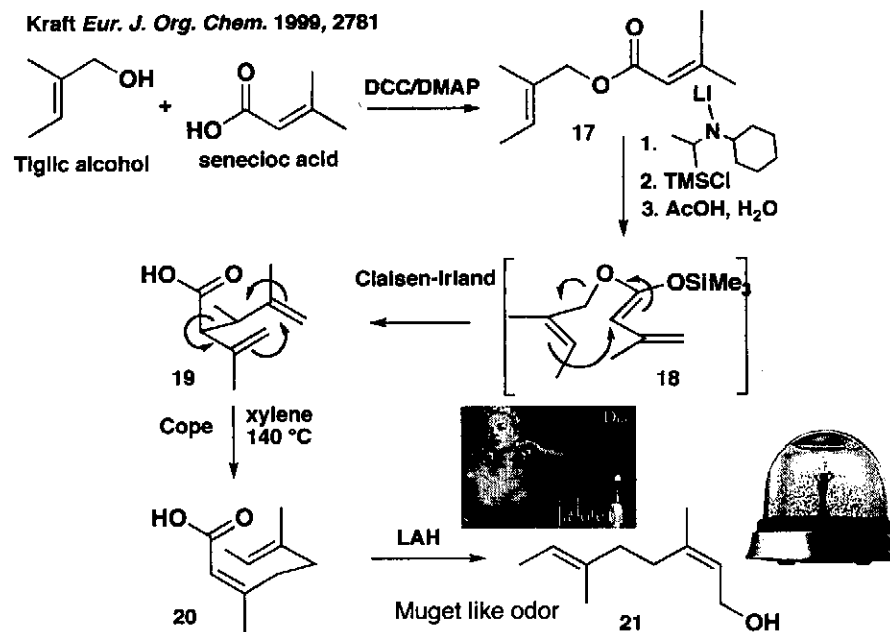
Schenk G. O. *Angew. Chem.* 1961, 73, 578



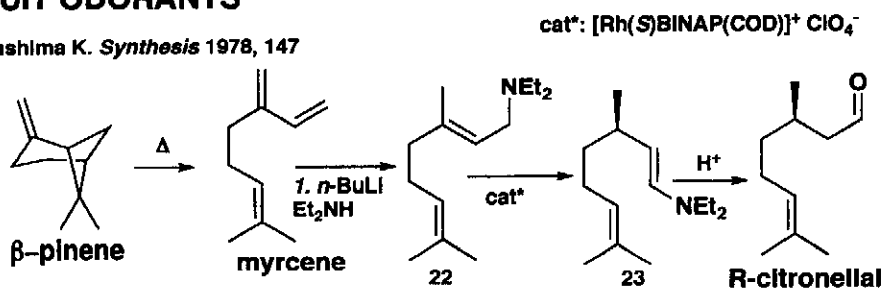
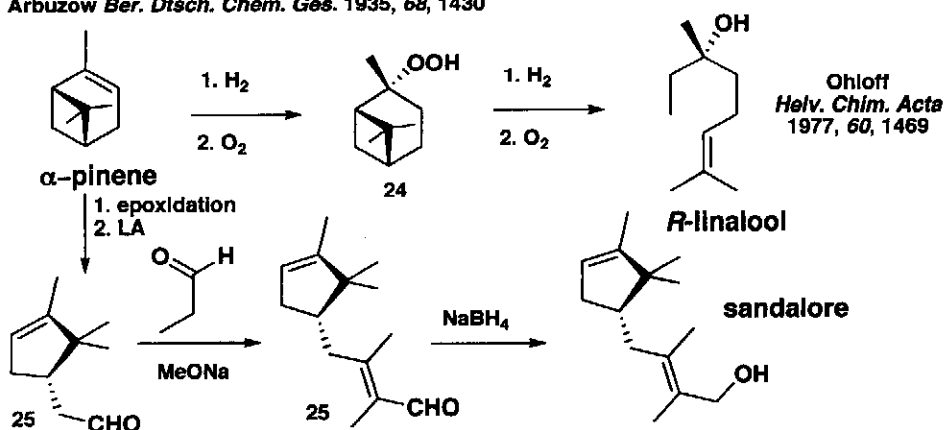
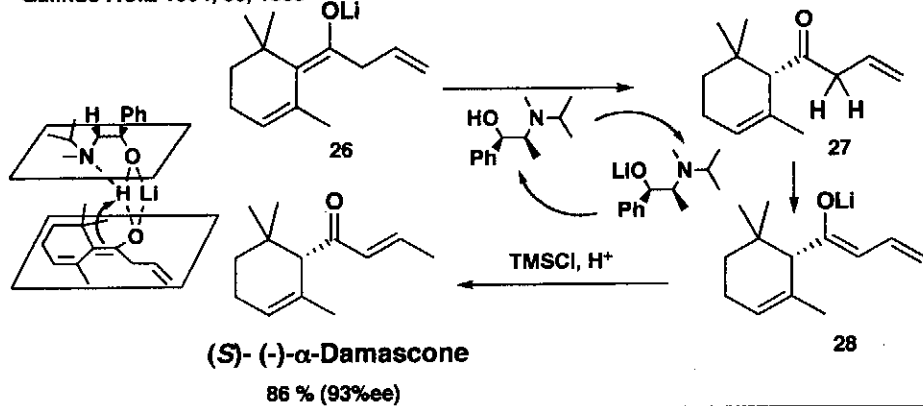
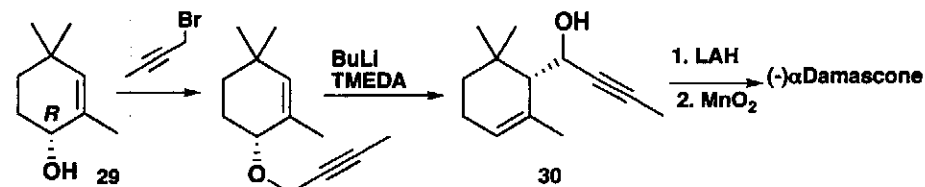
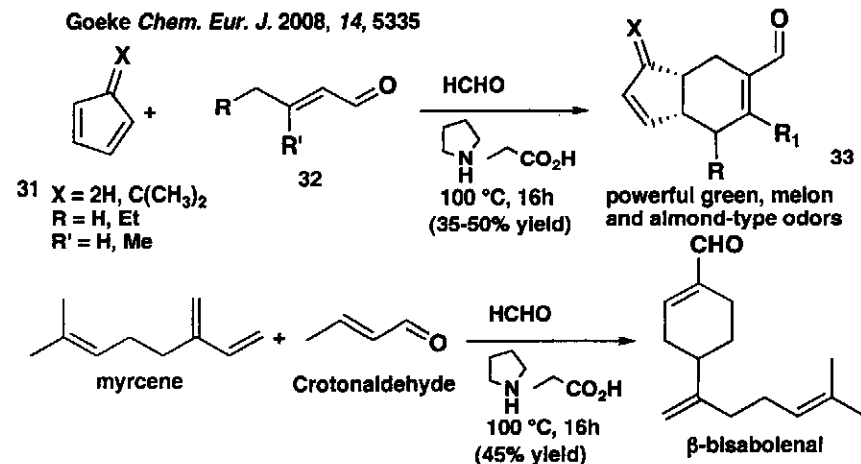
Krivda EP 581052



Kraft *Eur. J. Org. Chem.* 1999, 2781



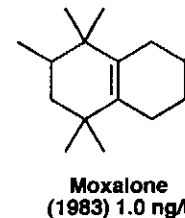
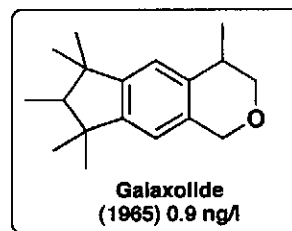
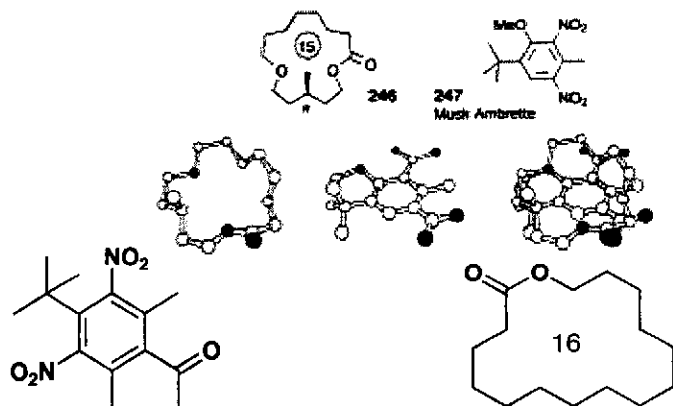
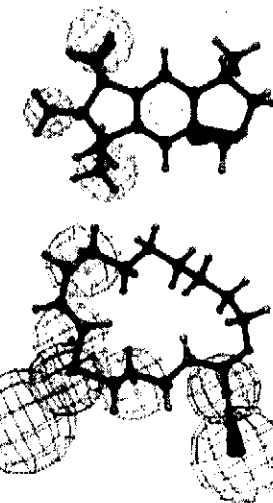
FRUIT ODORANTS

Kawashima K. *Synthesis* 1978, 147Arbuzow *Ber. Dtsch. Chem. Ges.* 1935, 68, 1430Galindo *ACIE* 1994, 33, 1888Moll *Synlett* 1995, 1097Goetze *Chem. Eur. J.* 2008, 14, 5335

MUSKS

The first is a hydrogen-bond acceptor symmetrically flanked at a distance of $6.7 \pm 0.5 \text{ \AA}$ by two hydrophobic binding pockets that are $2.5 \pm 0.5 \text{ \AA}$ apart from each other. The second feature consists of two hydrophobic groups within a distance of $5.5 \pm 0.5 \text{ \AA}$ to each other.

Beruser *New J. Chem.* 1991, 15, 307



MUSK KETONE
(1894) 0.1 ng/l

Exaltone (1927)
2.1 ng/l

Galaxolide
(1965) 0.9 ng/l

Moxalone
(1983) 1.0 ng/l

discover by Baur
searching for new
explosives
(97 \$/Kg)

Introduced at the
exorbitant price
of 49,000 \$/Kg

Big problem in
term of
biodegradability

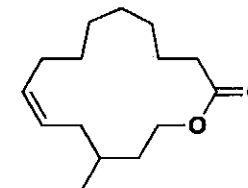
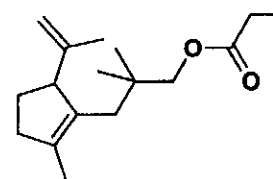
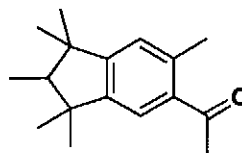
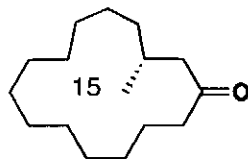


(-)-(3R)-muscone
(1926) 4.5 ng/l

Phantolide
(1952) 6.7 ng/l

Cyclomusk
(1977)

Nirvanolide
(2001) 0.1 ng/l

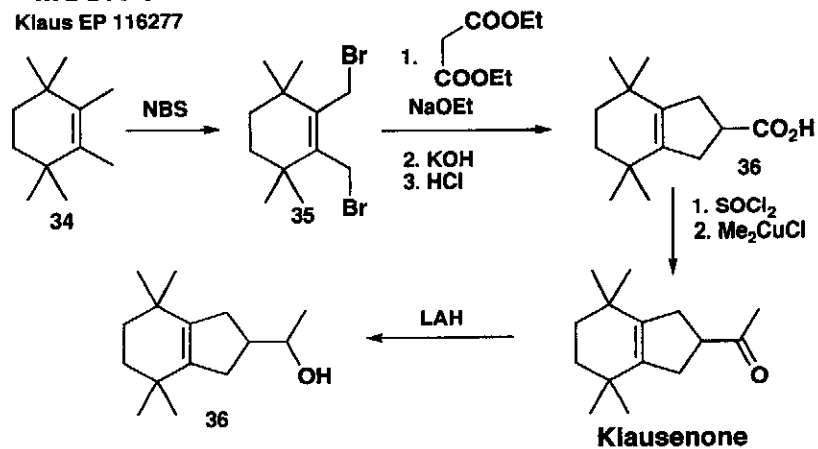


Natural musk containing muskone: 292,000 \$/Kg

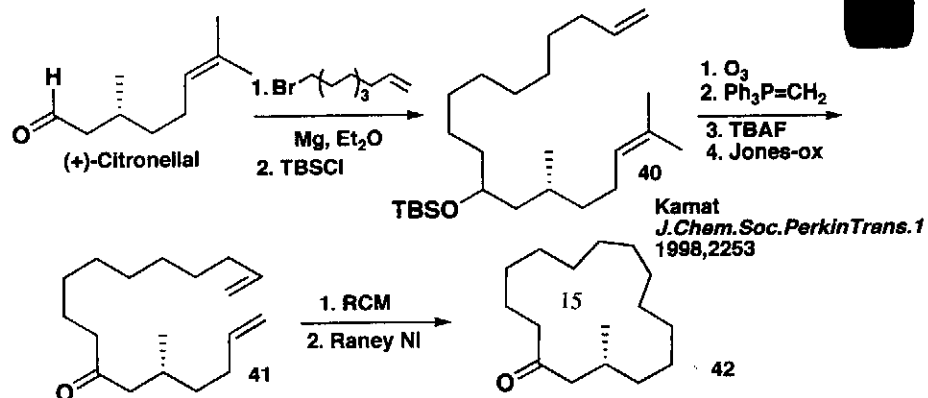
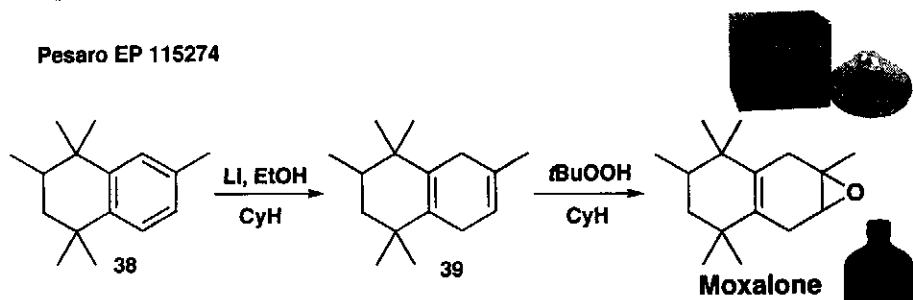
price in MS

MUSK ODORANTS

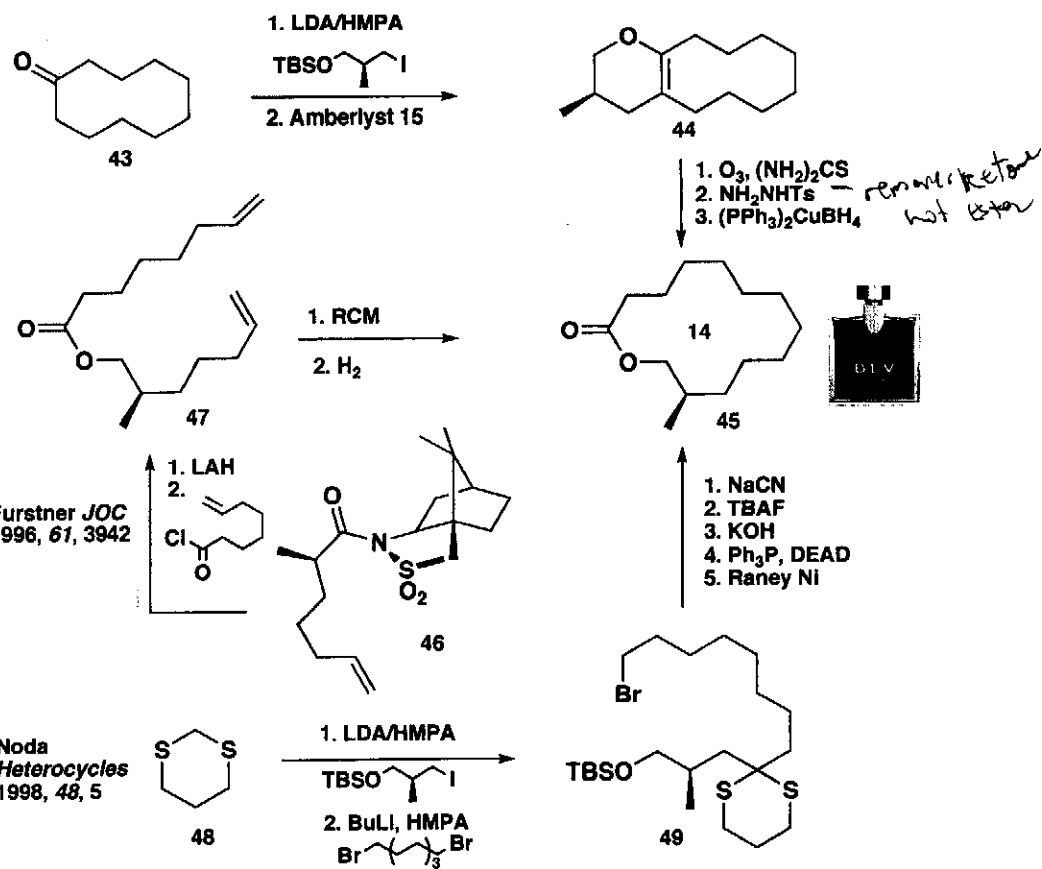
Klaus EP 116277



Pesaro EP 115274



Tochermann Liebigs Ann. Chem. 1994, 1161

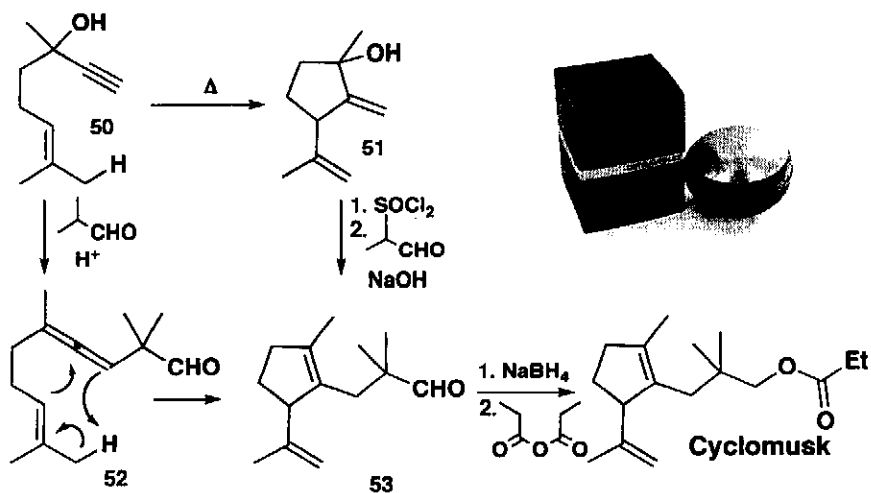
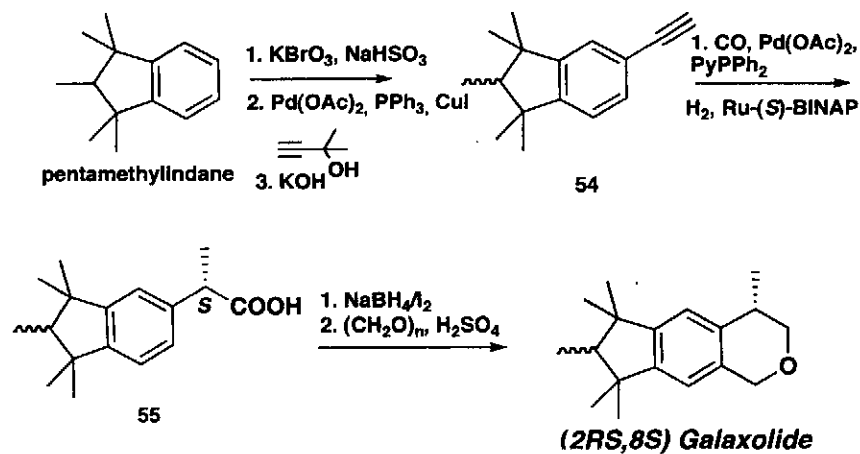
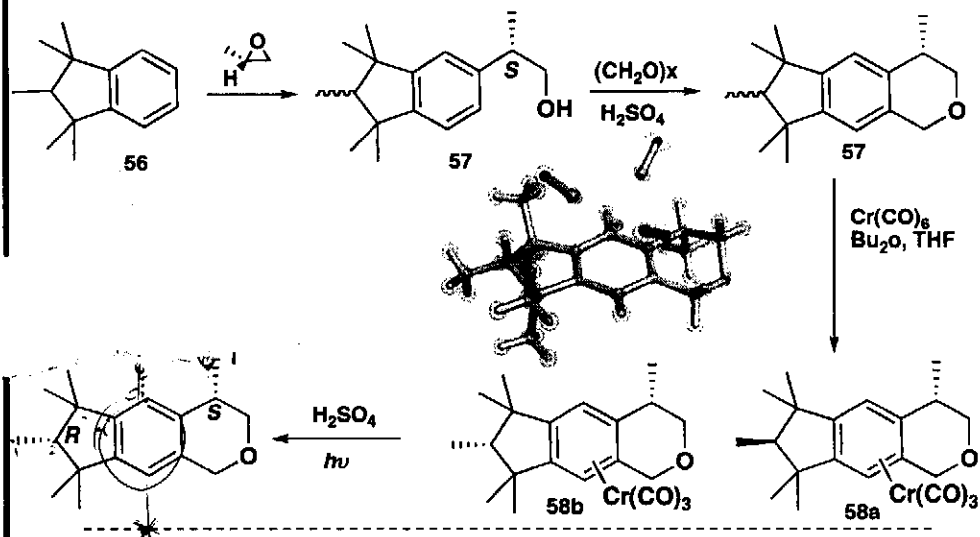
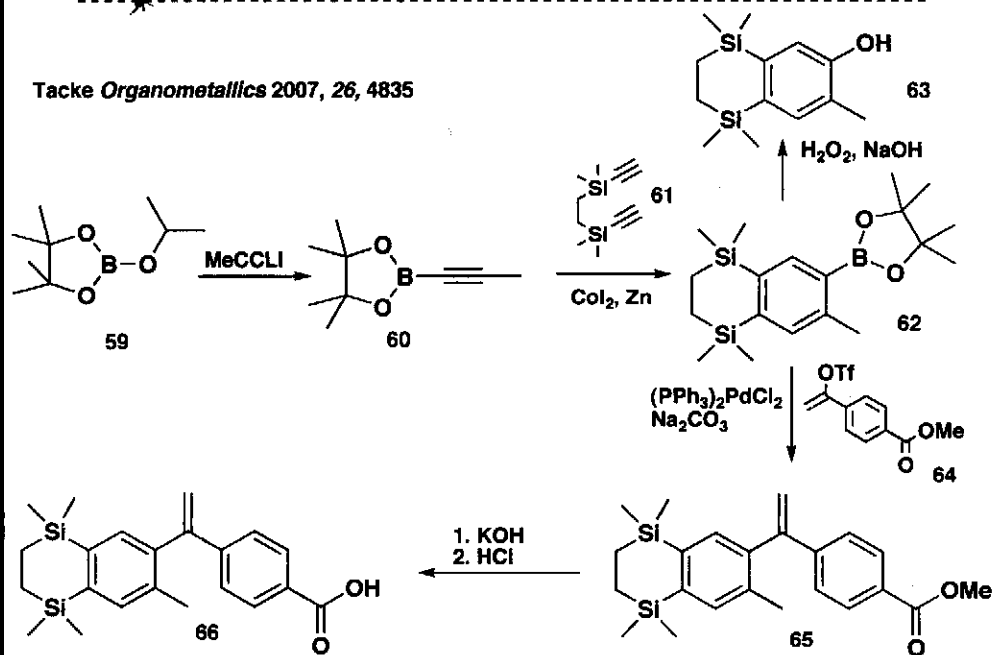


Furstner JOC 1996, 61, 3942

Noda Heterocycles 1998, 48, 5

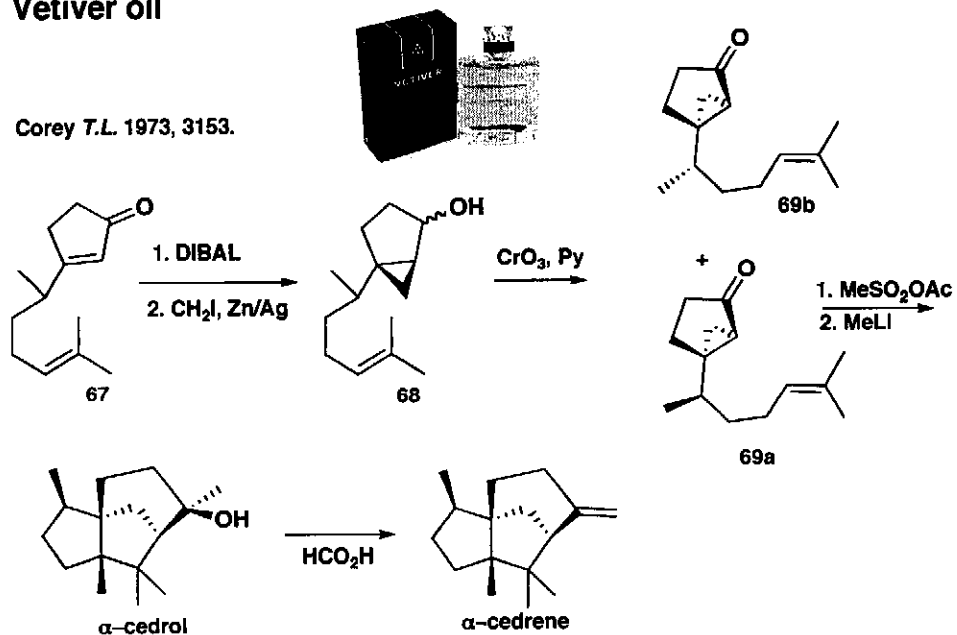


Hoffmann DE 2559433

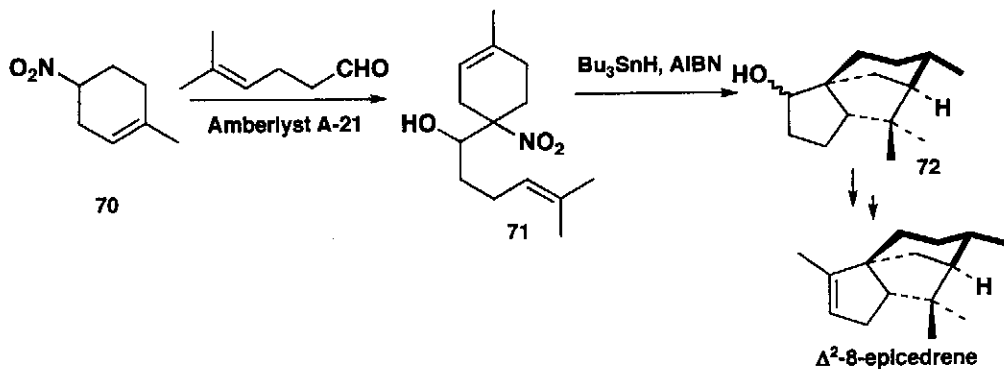
Scrivanti *Tetrahedron Asymm.* 2001, 13, 2193Frater *Helv. Chim. Acta* 1999, 82, 1656Tacke *Organometallics* 2007, 26, 4835

Vetiver oil

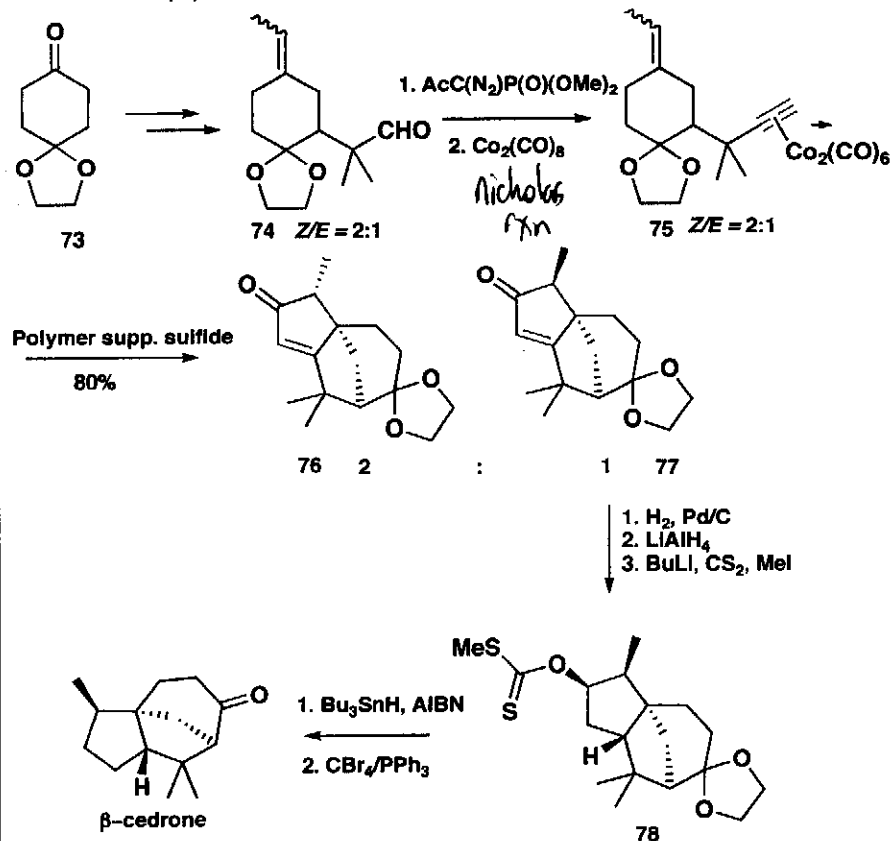
Corey T.L. 1973, 3153.



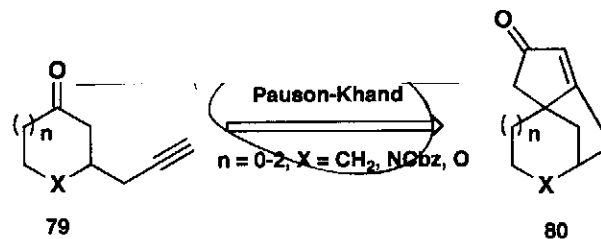
Chen T.L. 1992, 33, 1749.



Kerr O.L. 2001, 3, 2945

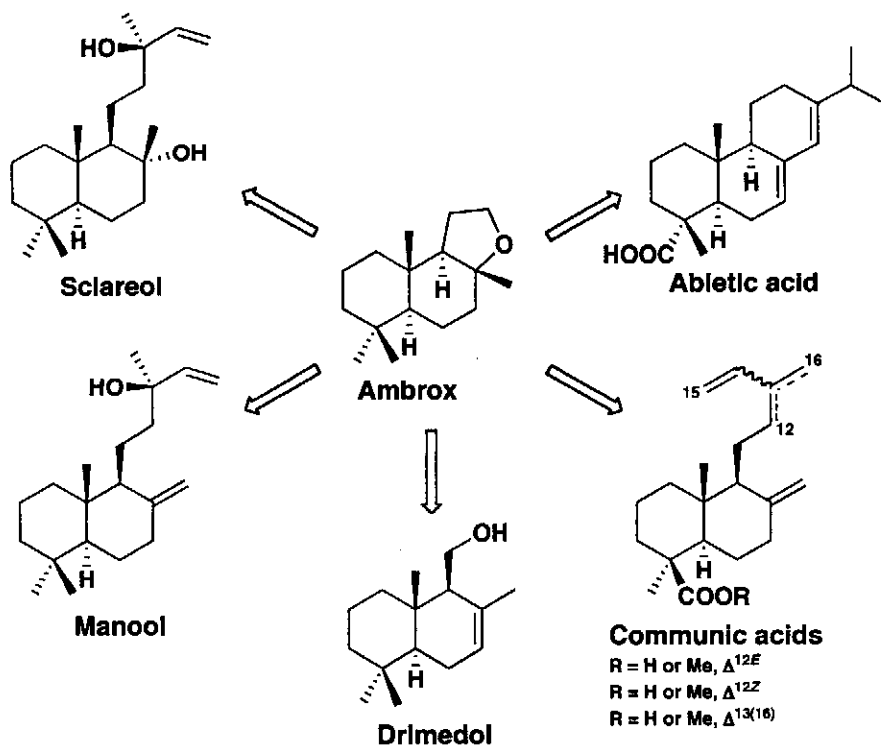


Hoshino Heterocycles 2002, 57, 1100

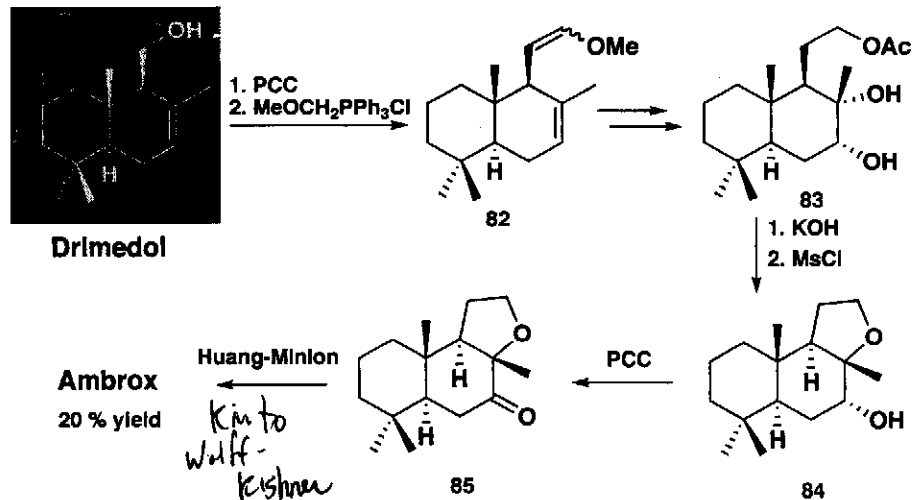




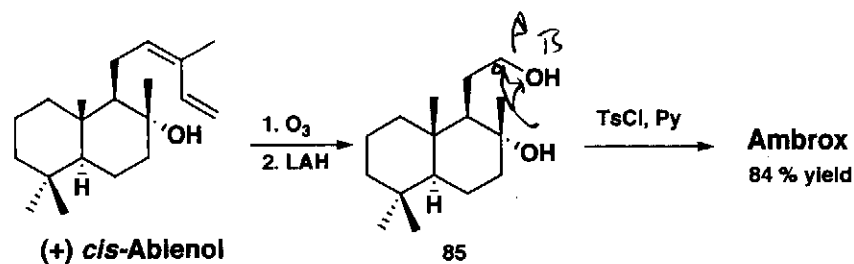
- Wood and amber odor
- Animal origin: secreted in the stomach or intestinal tract of the sperm whale and release into the sea in the form of a gray to black stonelike mass
- Ethers, ketones and cyclic ketals almost always derived from commonly occurring natural terpenes.

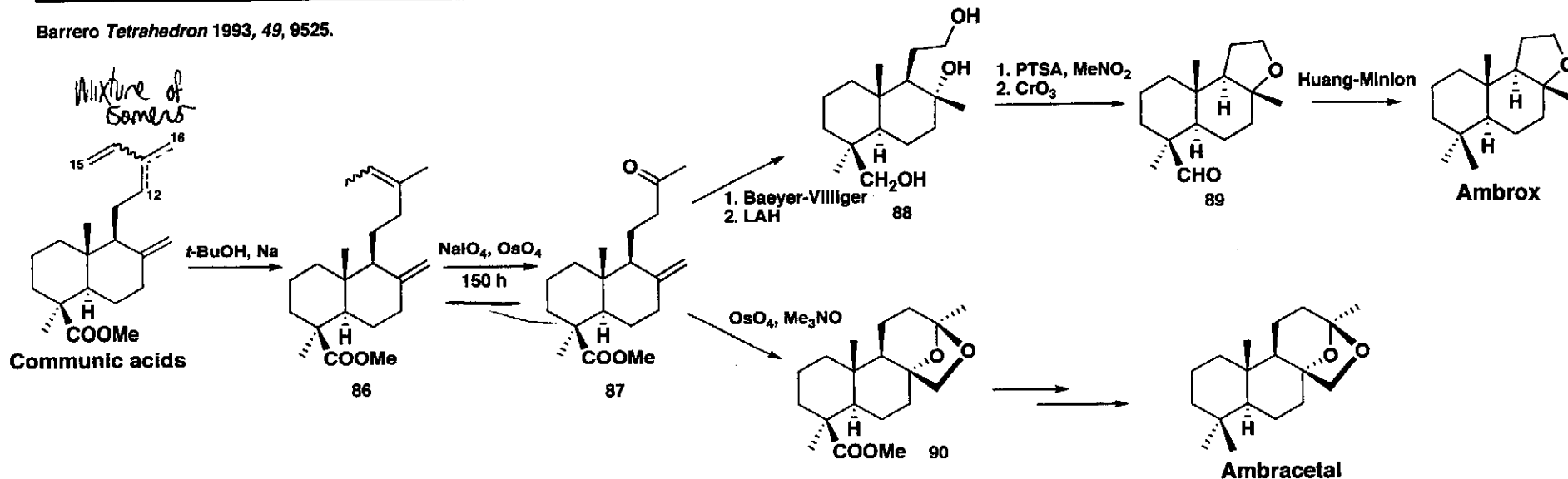
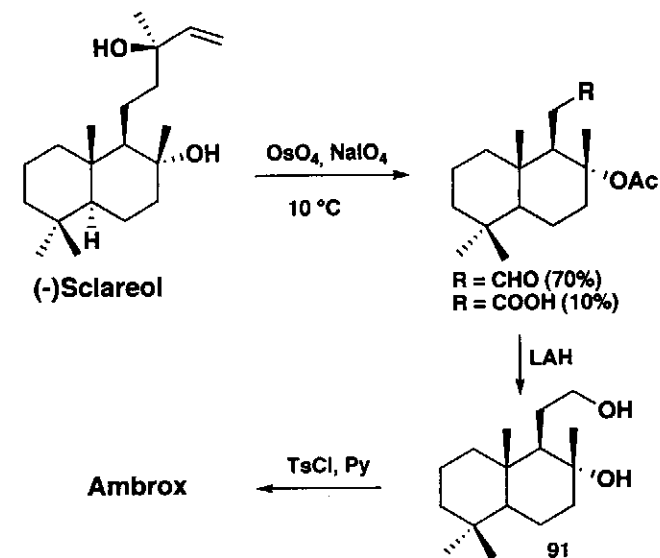
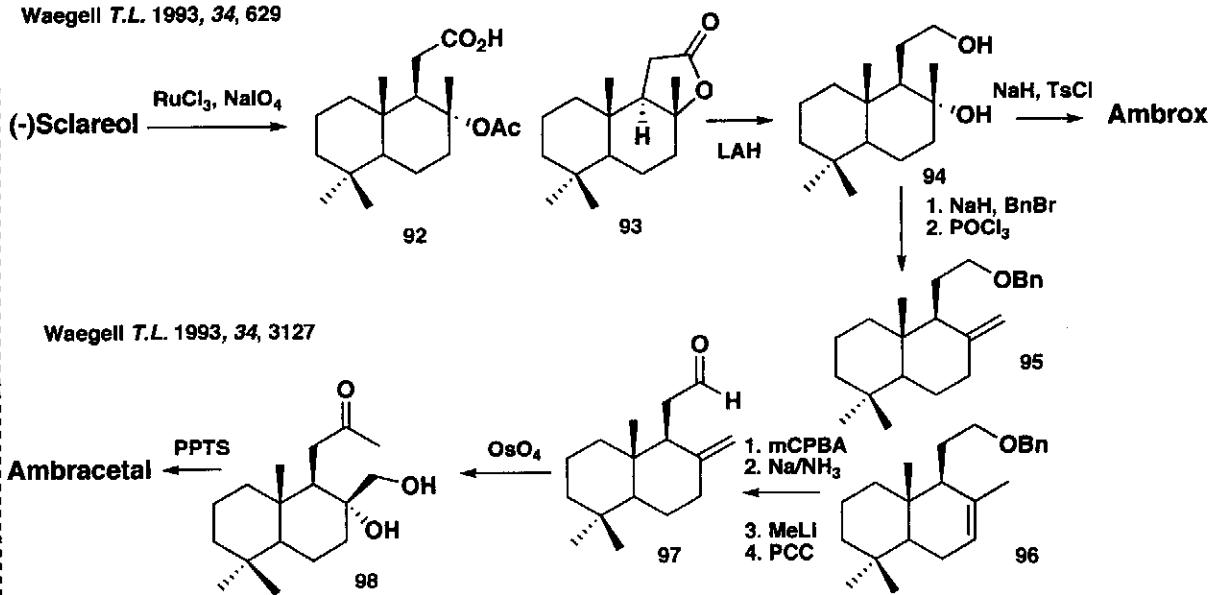


Cortés *Heterocycles* 1987, 26, 2801

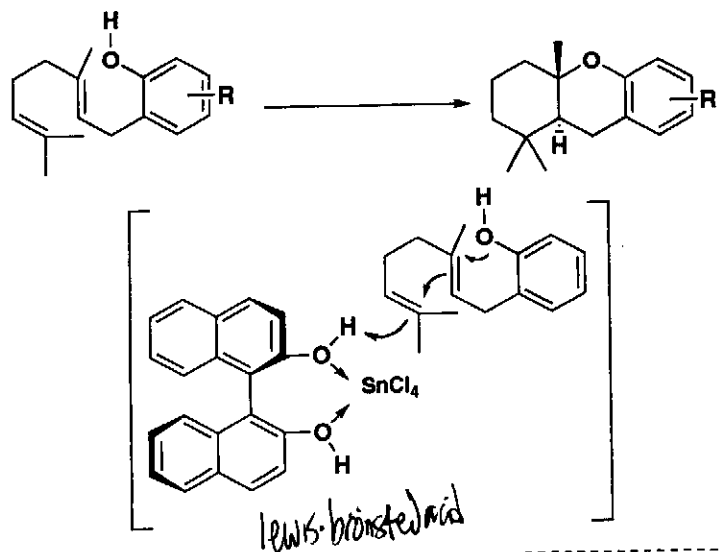


Barrero *Tetrahedron* 1993, 49, 10405

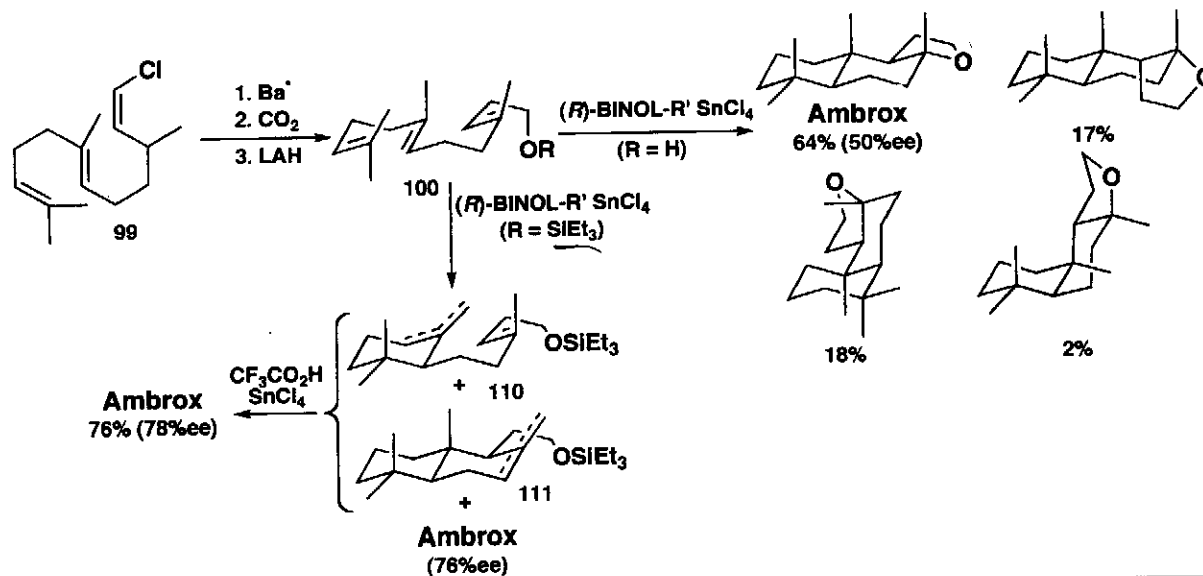
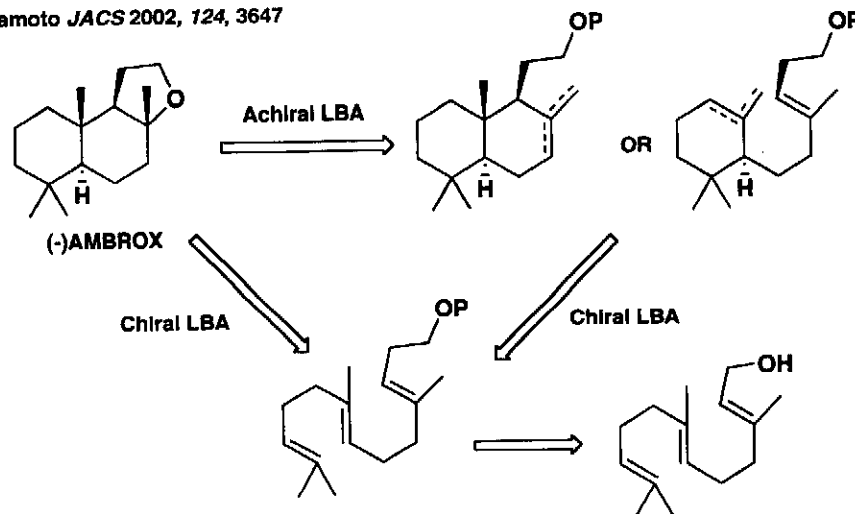


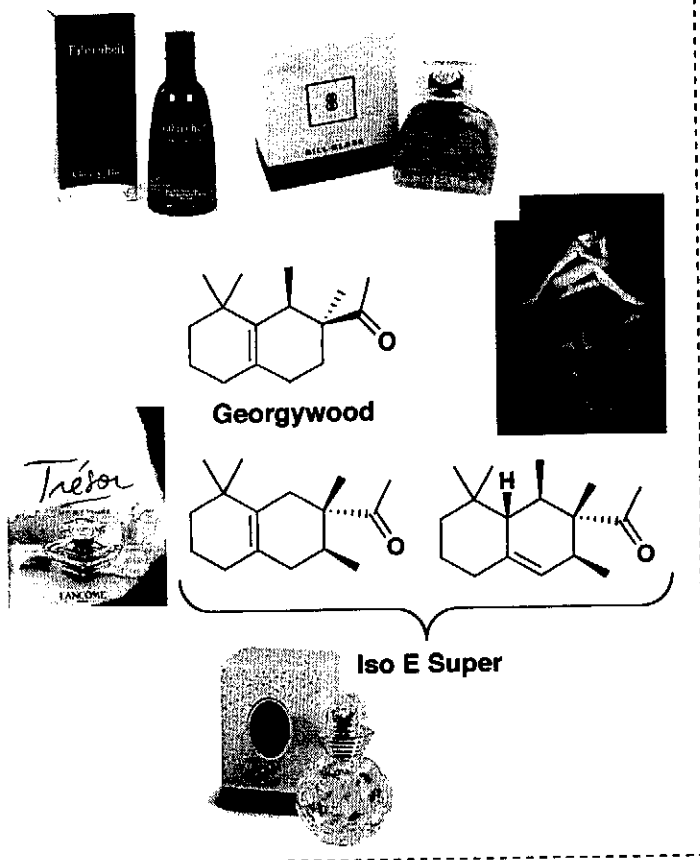
Barrero *Tetrahedron* 1993, 49, 9525.Barrero *Tetrahedron* 1993, 49, 10405Waegell *T.L.* 1993, 34, 629

Yamamoto JACS 1999, 121,4906



Yamamoto JACS 2002, 124, 3647



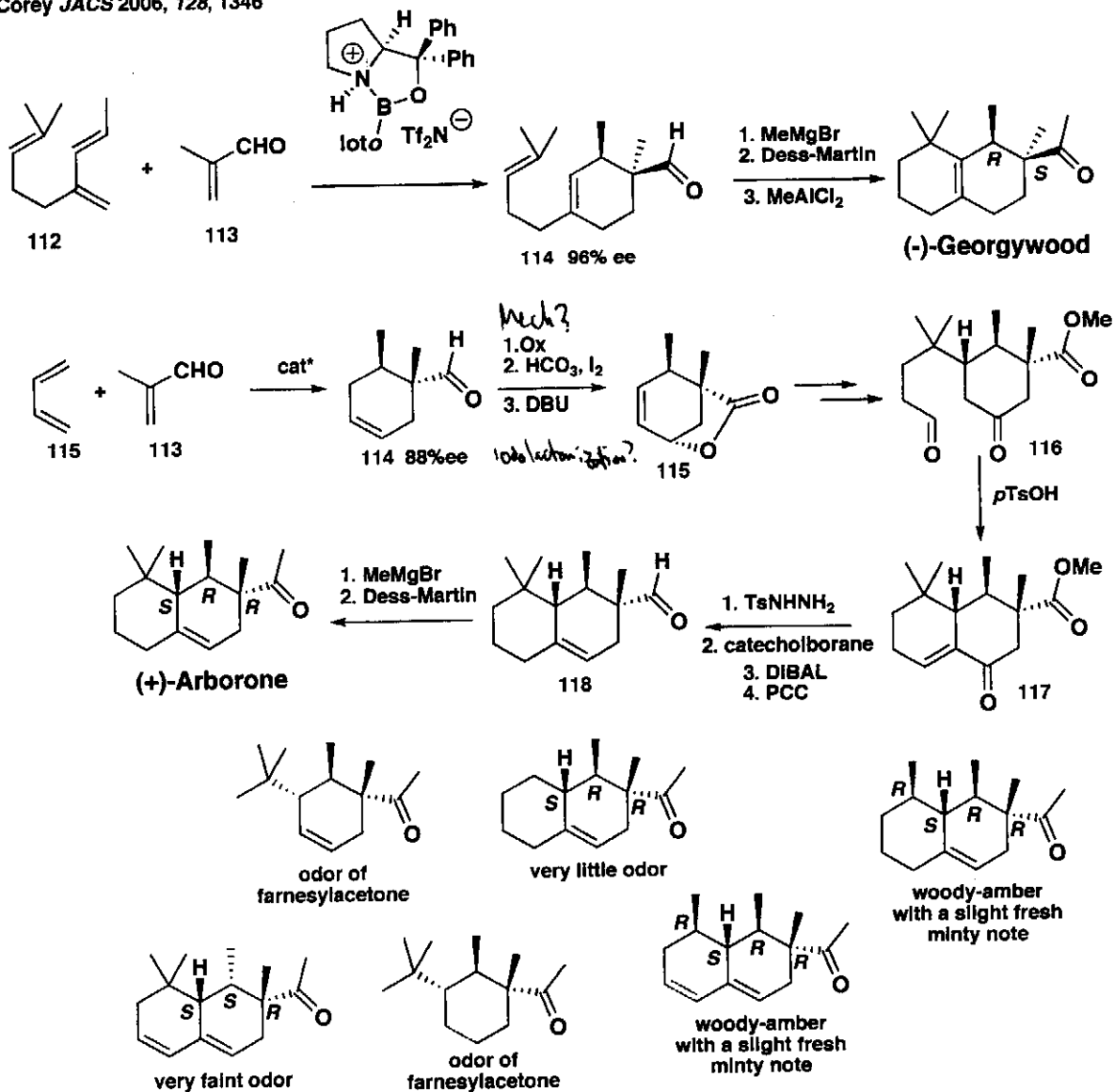


Iso E Super

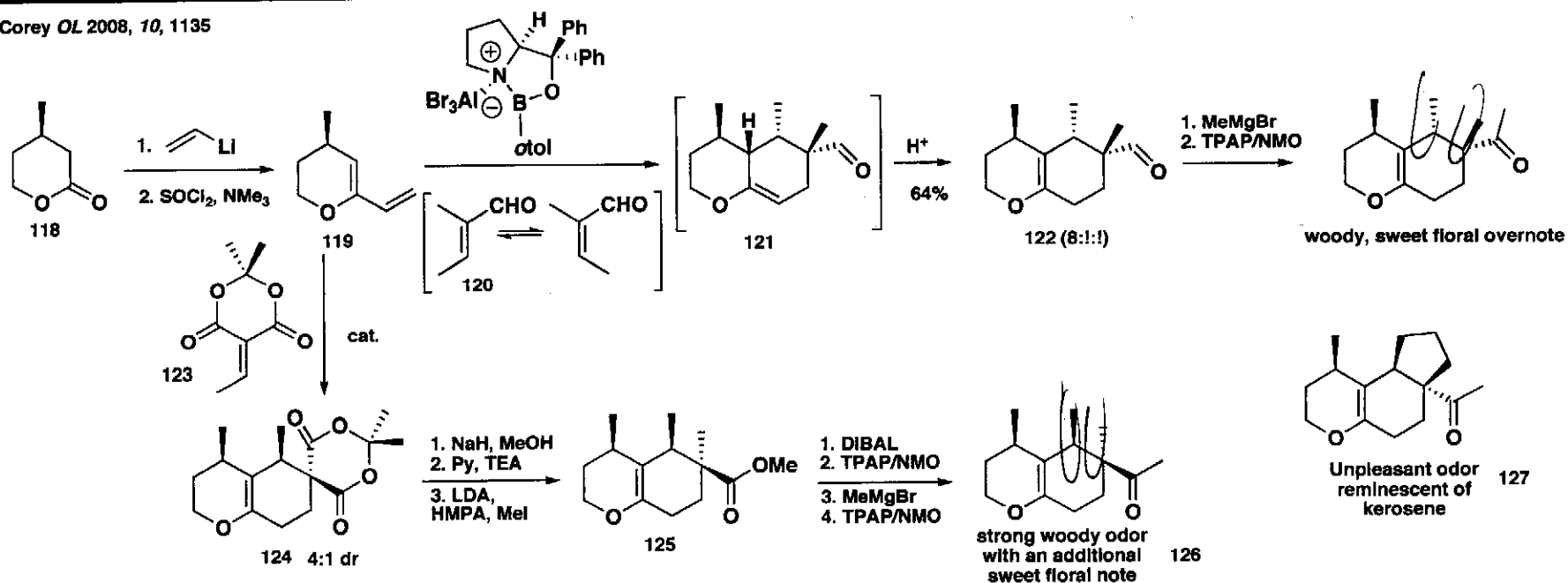
Georgywood

(+)-Arborone

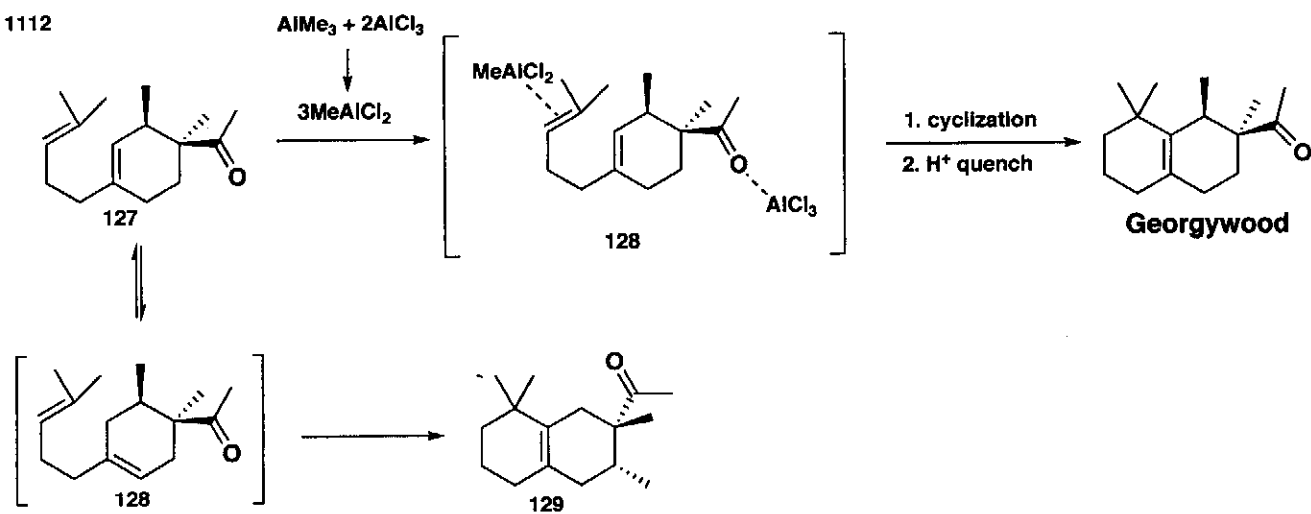
Corey JACS 2006, 128, 1346



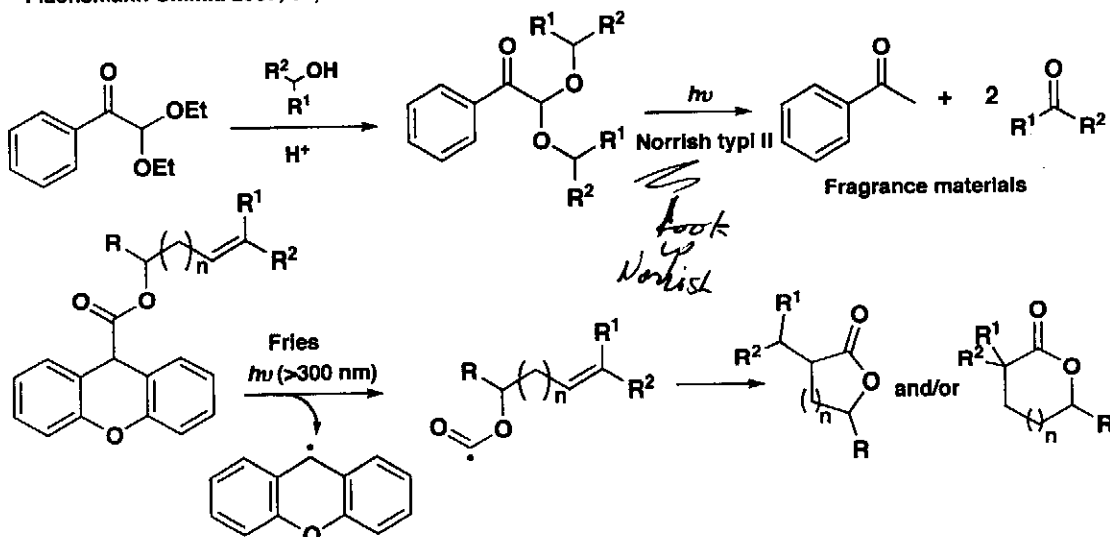
Corey *OL* 2008, 10, 1135



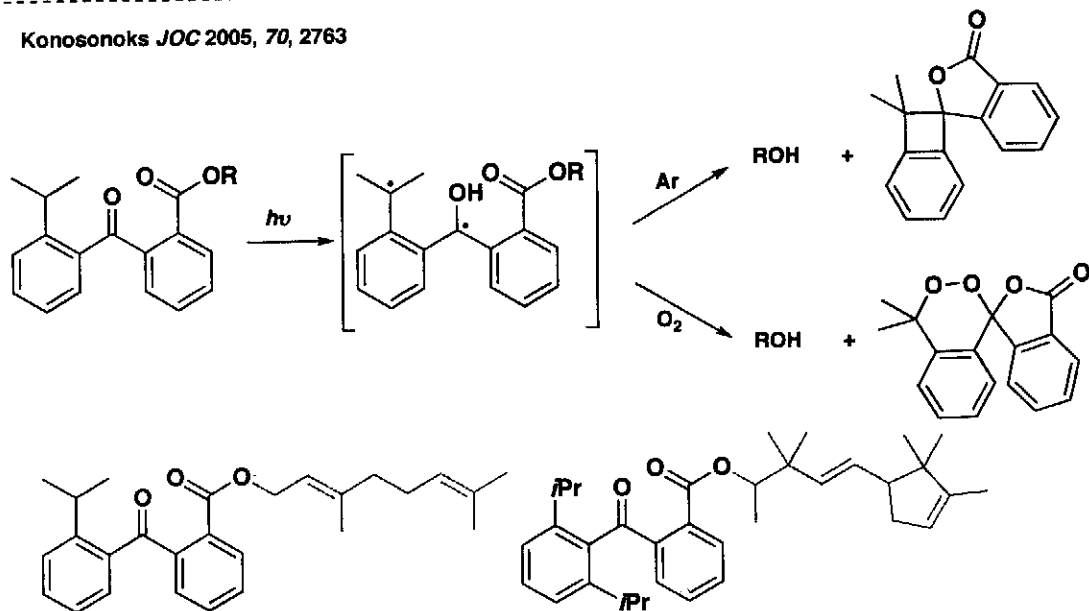
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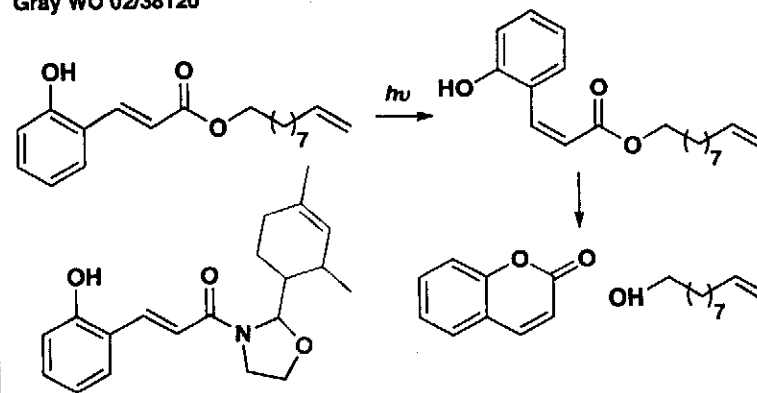
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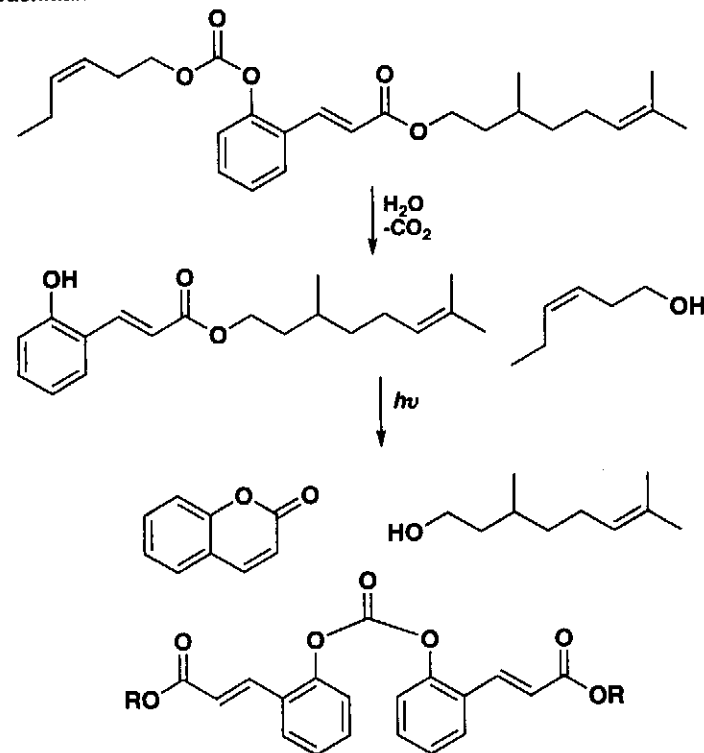
Konosonoks *JOC* 2005, 70, 2763



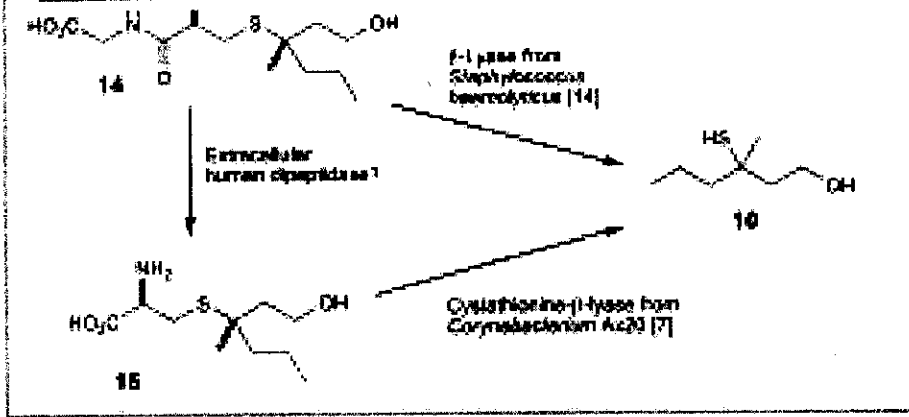
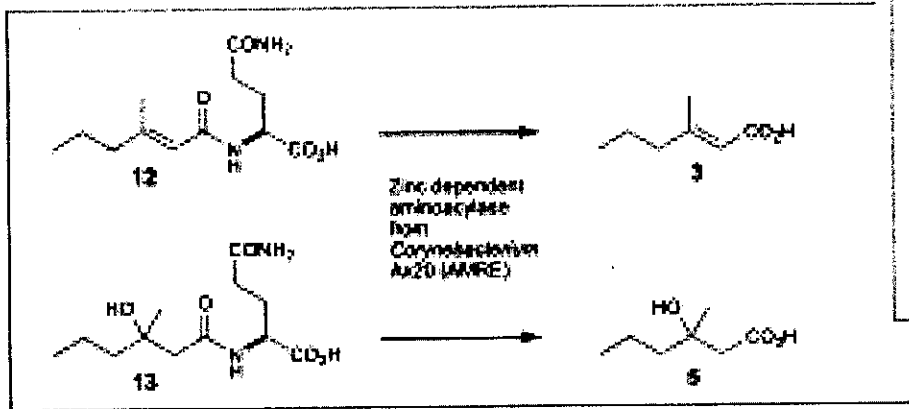
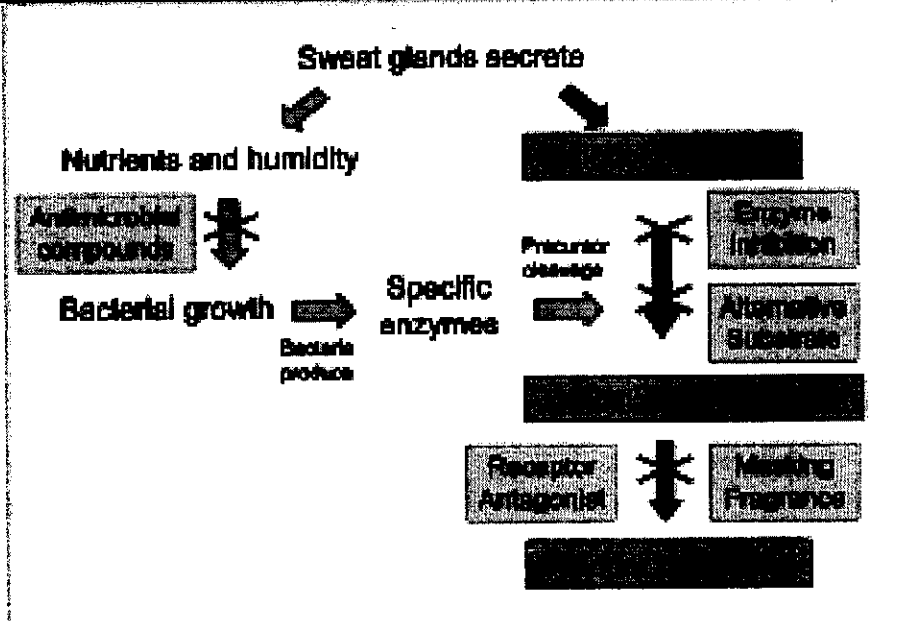
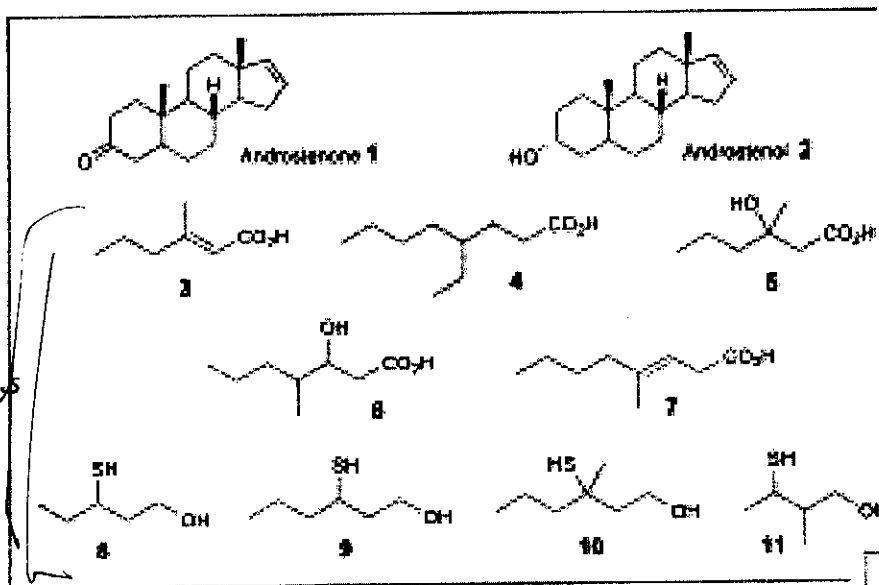
Gray WO 02/38120

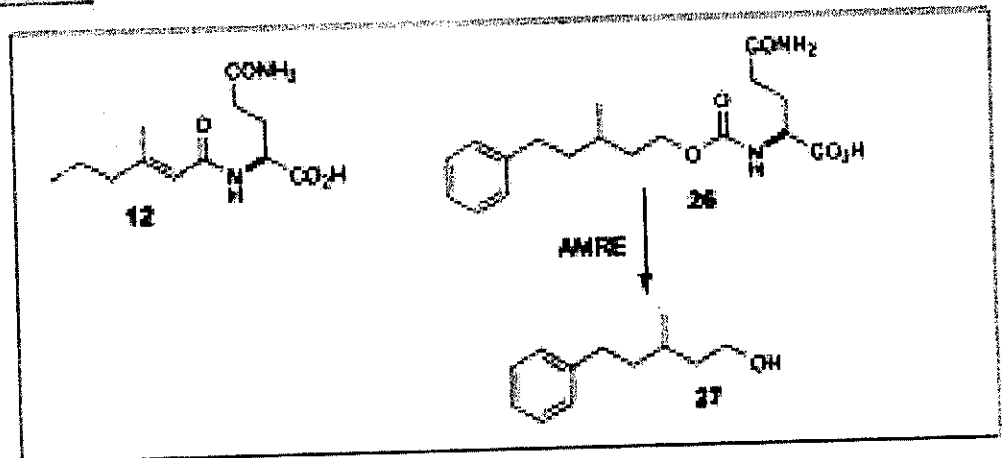
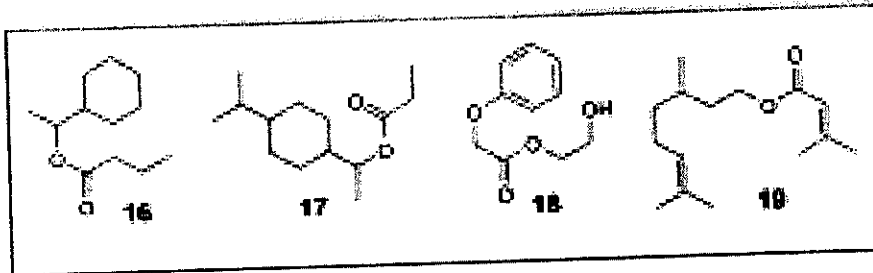


Bachmann WO 2005/077881



body
odor





Scheme 3: Release of phenoxanal 27 from precursor 26 [34], in analogy to the release of sweat acid 3 from natural precursor 12 (Scheme 1)

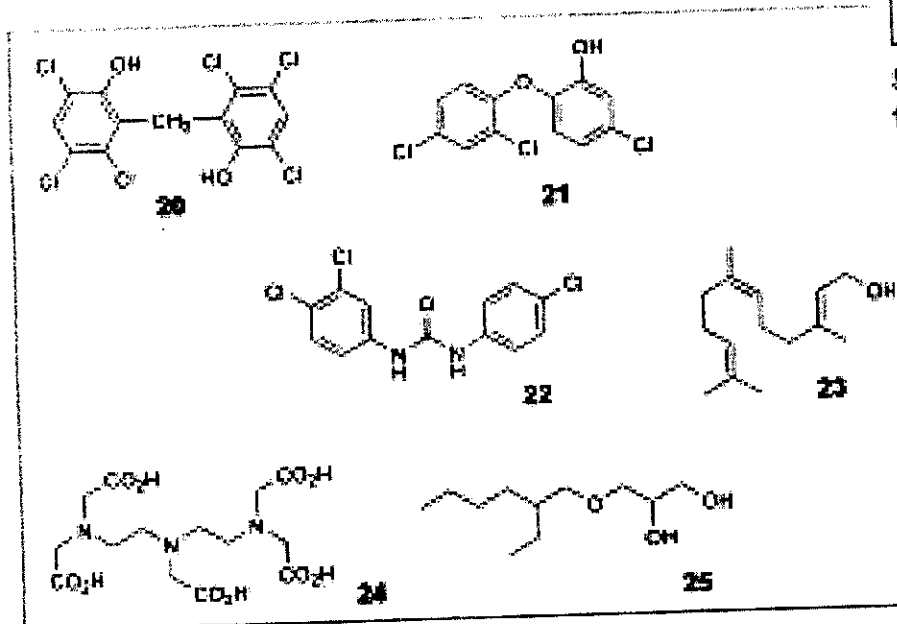


Fig. 4. Some classical and new antibacterial deodorant ingredients

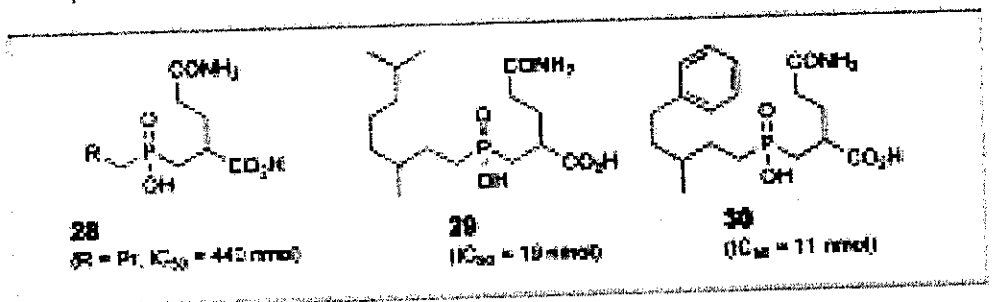


Fig. 6. First and second generation AMRE Inhibitors

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