632

BF3•Et2O Promoted Sulfuration of Steroidal Sapogenins

$$AcO$$
 $H_2S, BF_3 \cdot Et_2O$
 DCM
 AcO
 $2a$

The reaction between steroidal sapogenins and hydrogen sulfide catalyzed by BF₃•Et₂O is described. The thiodiosgenin and thiotigogenin comprising a sulfur atom on the F ring have been synthesized under this mild reaction conditions.

Jun Wang,* Jingjing Wu, Weisheng Tian*

637

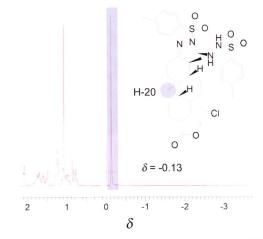
A Formal Synthesis of Betamethasone

Shasha Wang, Yong Shi,* Weisheng Tian*

A formal synthesis of betamethasone from pregnane-3β,16β,20S-triol is described. Key transformations are a bromination-acetylation of triol, an $S_{\rm N}2$ reaction of the resulting C16 α -bromide with dimethylcopperlithium to get the required C16 β -methyl group, and a double hydroxylation to prepare the dihydroxyacetone side chain.

643

Methyl Group in Isocopalane Derivative Showed an Unusual Negative 1H **NMR Chemical Shift**



An unusual negative ¹H NMR chemical shift of methyl group in condensation product of isocopalane diterpenoid with p-toluenesulfonyl hydrazide was discovered. 2D NMR, computational studies and single-crystal X-ray diffraction analysis were used to determine the real conformation.

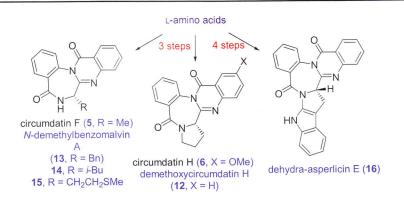
Xiong Xiao, Tiangi Chen, Fengfeng Zhang, Jiagao Cheng, Peiying Wu,* Jiangmeng Ren,* Bubing Zeng*

FULL PAPERS

646

Low-Valent Titanium-Mediated Enantioselective Synthesis of Quinazolinone Alkaloids Circumdatins F, H, and **Analogs**

Shi-Peng Luo, Hui Geng, Yu Wang, Pei-Qiang Huang*



655

Towards Reaction Control: An Expeditious Access to Racemic 5-Substituted Tetramates and 5-Substituted Tetramic Acids from Malimides

Pei-Qiang Huang,* Wei Ou, Jian-Liang Ye A versatile and divergent two-step transformation of malimides to racemic tetramates and tetramic acids is described. The method consists of Grignard reagent addition with malimides, and concentrated HCl-promoted chemoselective transformations of the latter

663

Synthesis of C1—C9 Domain of the Nominal Didemnaketal A

Shunji Zhang, Yong Shi,* Weisheng Tian*

Herein we describe a synthesis of C1-C9 domain **2** of the proposed structure of didemnaketal A, a natural product with important bioactivities, from potassium (2R,4R)-2,5-dihydroxy-4-methylpentanoate **5**. Sharpless asymmetric dihydroxylation introduced the chiral vicinal diol and chelation-controlled allylation established another chiral OH.

669

Semisynthesis of Azedarachol from Pregnanetriol, a Degradative Product of Tigogenin

Dongshan Zhang, Yong Shi,* Weisheng Tian*

Described herein is a semisynthesis of azedarachol from pregnanetriol, which featured a symbiotic elimination/deprotection process, an oxidation/reduction procedure for reversing C20 configuration, and a dehydration-dihydroxylation process to introduce 2,3-cis-diol. This synthesis also discloses some interesting selectivities of 16,20-diol unit.

674

Syntheses of (R)- and (S)-3-Methylheptanoic Acids

Shunji Zhang, Yong Shi,* Weisheng Tian*

Both enantiomers of 3-methylheptanoic acid have been synthesized from chiral methyl molecules which were derived from (R)-4-methyl- δ -valerolactone (5). A wide variety of chiral 3-methyl alkanoic acids can also be synthesized by the methods described herein.

CONTENT

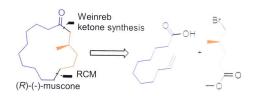
679

An Efficient Synthesis of (+)-Subersic Acid

Jing Wang, Peiqiang Wang, Jue Li, Peiying Wu,* Jiangmeng Ren,* Bubing Zeng* A seven-step synthetic route was developed to synthesize (+)-subersic acid from (-)-Sclareol. The cross coupling of the diterpene with the arene fragment using the arylation of allylic acetate followed by β -acetoxy elimination type Heck reaction was acted as the key reaction.

683

Synthesis of (R)-(-)-Muscone from (R)-5-Bromo-4-methylpentanoate: A Chiron Approach



Junwei Shen, Yong Shi,* Weisheng Tian*

Using methyl (R)-5-bromo-4-methylpentanoate, we have accomplished a synthesis of (R)-muscone, a natural macrocyclic musk, based on chiral pool strategy.