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63

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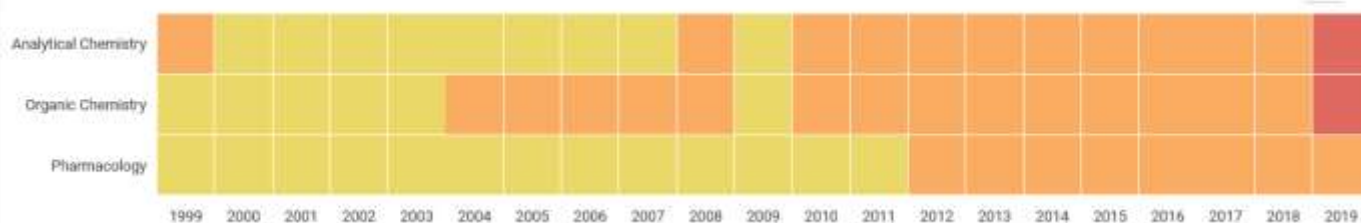
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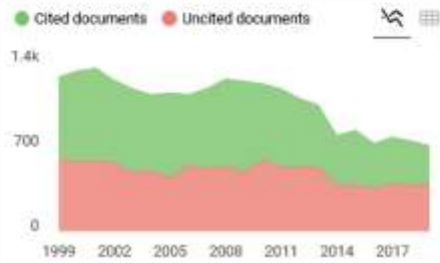
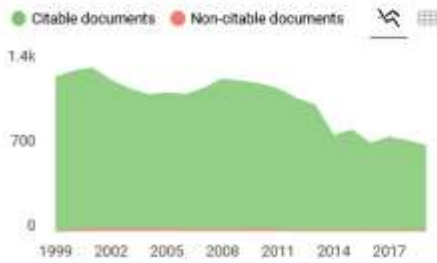
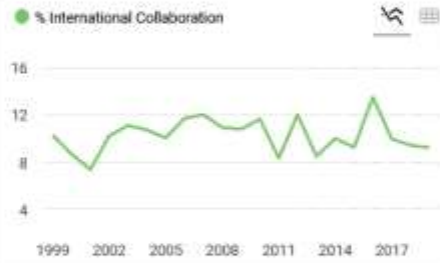
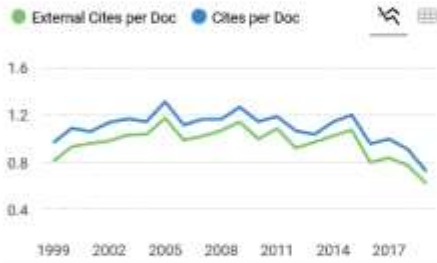
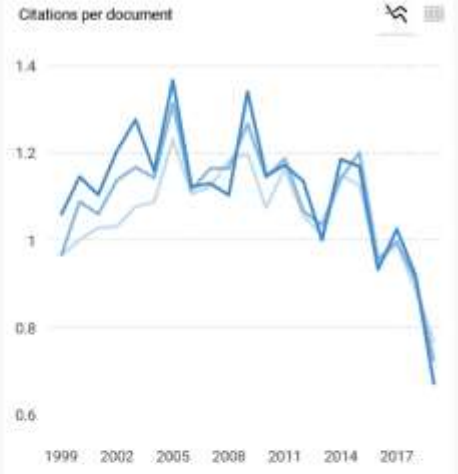
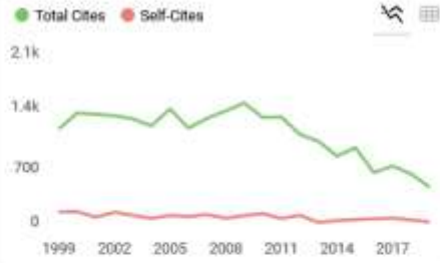
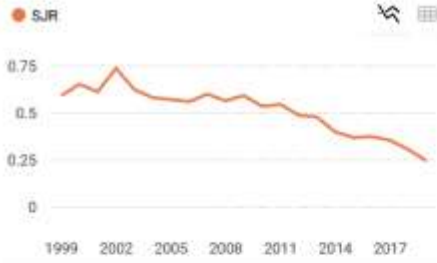
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■ CELEBRATION OF PROFESSOR ISAO KUWAJIMA

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- 1 **Preface to Heterocycles Issue**  
**Honoring the 77th Birthday of Professor Isao Kuwajima**  
Eiichi Nakamura\*

- 
- 3 **Preface to Heterocycles Issue**  
**Honoring the 77th Birthday of Professor Isao Kuwajima**  
Keiji Tanino\*
- 

■ CURRICULUM VITAE

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- 6 **Curriculum Vitae**  
Isao Kuwajima\*
- 
-

■ PUBLICATIONS

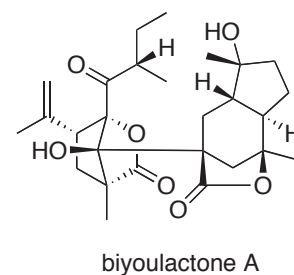
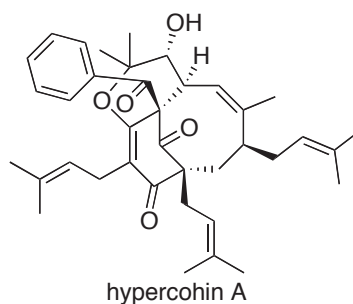
7 List of Publication

Isao Kuwajima\*

■ REVIEWS

23 Prenylated Acylphloroglucinols and Meroterpenoids from *Hypericum* Plants

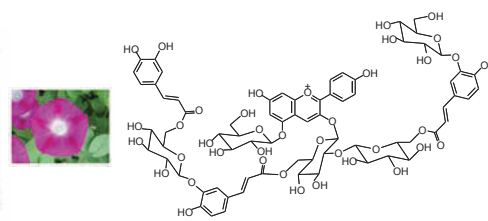
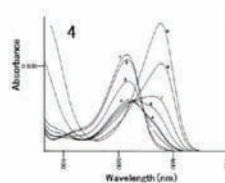
Naonobu Tanaka and Jun'ichi Kobayashi\*



Prenylated Phloroglucinol    Meroterpenoid    *Hypericum* Plant

41 Light Absorption Spectral Patterns of Intact Garden Flowers in Relation to the Flower Colors and Anthocyanin Pigments

Norio Saito, Fumi Tatsuzawa,\* and Toshio Honda



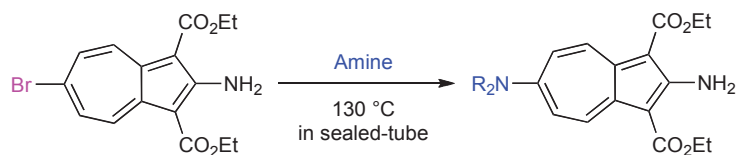
Electronic spectra of ipomoea red anthocyanin 1

Anthocyanin Pigment    Intra- and Intermolecular Co-pigmentation    Self Association    Light Absorption Spectral Pattern    Flower Color

## ■ COMMUNICATIONS

**85 Synthesis of 2,6-Diaminoazulenes by the  $S_NAr$  Reaction with Cyclic Amines**

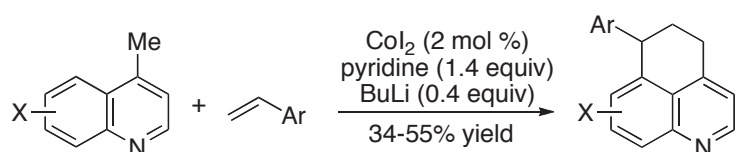
Taku Shoji,\* Yuki Fujiwara, Akifumi Maruyama, Mitsuhsa Maruyama, Shunji Ito, Masafumi Yasunami (the late), Ryuji Yokoyama, and Noboru Morita



Azulene    Amination    Aromatic Nucleophilic Substitution

**89 Cobalt-Catalyzed C5-Selective C-H Functionalization of 4-Me-Quinolines with Styrenes: An Approach to 5,6-Dihydro-4*H*-benzo[*d*h]quinolines**

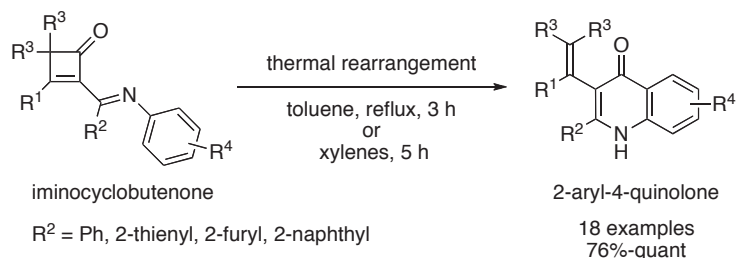
Shohei Yamamoto, Shigeki Matsunaga,\* and Motomu Kanai\*



C-H Functionalization    Cobalt Catalyst    Quinoline    Transition Metal Catalysis    Synthetic Method

**97 2-Aryl-4-quinolone Synthesis Using the Thermal Rearrangement of Iminocyclobutenones**

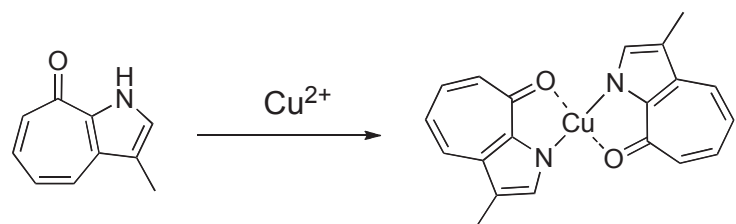
Iwao Hachiya, Keiichi Yokoyama, Akinori Ito, and Makoto Shimizu\*



4-Quinolone    Iminocyclobutenone    Thermal Rearrangement    Alkynyl Imine    Conjugate Addition Reaction

**104 Crystal Structures of 3-Methylpyrrolo[2,3-*b*]tropone and Its Copper(II) Complex**

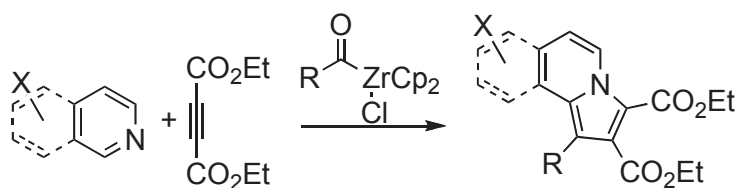
Kanji Kubo,\* Taisuke Matsumoto, Keiko Ideta, and Akira Mori



Troponoid    Pyrrolo[2,3-*b*]tropone    Cu(II) Complex    Crystal Structure    X-Ray Analysis

**108 Three-Component Synthesis of Indolizines from Azaaromatic-Acetylenedicarboxylate Zwitterions with Acylzirconocene Chloride Complexes**

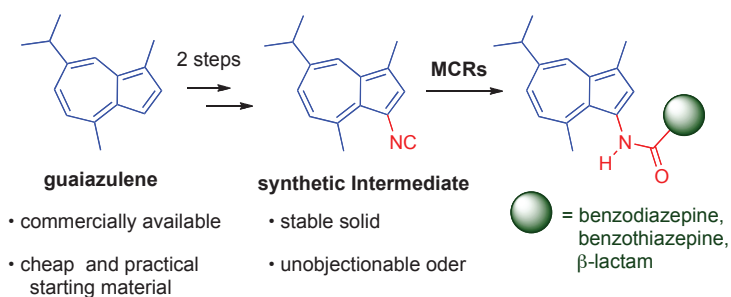
Akio Saito,\* Naoki Yamashita, Kohei Sudo, and Yuji Hanzawa



Acylzirconocene Chloride    Azaaromatic Compound    Nucleophilic Addition    Three-Component Synthesis    Zwitterion

**113 Facile Synthesis of Guaiazulene-Heterocycle Hybrids via Ugi Multicomponent Reactions**

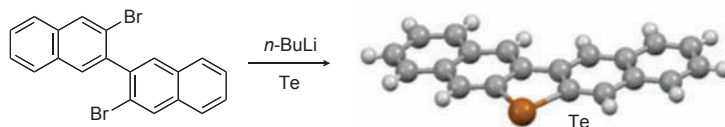
Naoko Takenaga,\* Koh Fukazawa, Miki Maruko, and Koichi Sato\*



Guaiazulene    Isocyanide    Multicomponent Reaction    Ugi Reaction

**121 Synthesis and Structural Characterization of a Novel Organotellurium Compound: Dinaphtho[2,3-*b*;2',3'-*d'*]-tellurophene**

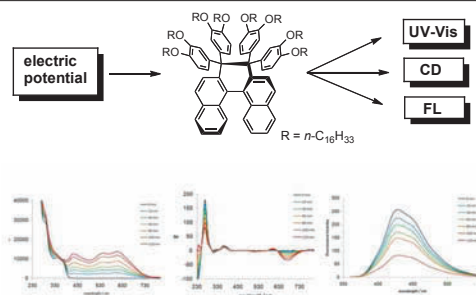
Mio Matsumura, Atsuya Muranaka, Naoki Kakusawa, Jyoji Kurita, Daisuke Hashizume, Masanobu Uchiyama,\* and Shuji Yasuike\*



Dinaphthotellurophene    Tellurium    Planar Structure    Group 16 Element    HOMO-LUMO Gap

**126 Three-Way Output Molecular Response System Based on Tetrakis(3,4-dialkoxyphenyl)-3,4-dihydro[5]helicenes: Perturbation of Properties by Long Alkyl Chains**

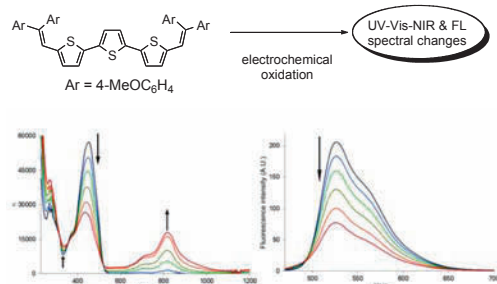
Yusuke Ishigaki, Satoshige Yoshida, Hidetoshi Kawai, Ryo Katoono, Kenshu Fujiwara, Takanori Fukushima, and Takanori Suzuki\*



Redox System    Electrochromism    Long Alkyl Chain    Circular Dichroism    Dihydroxepin

**136 Bis(diarylethenyl)thiophene, -bithiophene, and -terthiophene: A New Series of Violen-Cyanine Hybrid-Type Electron Donors**

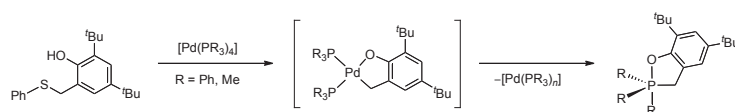
Yusuke Ishigaki, Hidetoshi Kawai, Ryo Katoono, Kenshu Fujiwara, and Takanori Suzuki\*



Electron Donor    Redox System    Electrochromism    NIR    Fluorescence

**144 Palladium(0)-Mediated C-S and O-H Bonds Cleavage Reaction in 2-Hydroxybenzyl Phenyl Sulfide: Formations of Oxyphosphorane and 1,2-Oxapalladacycle**

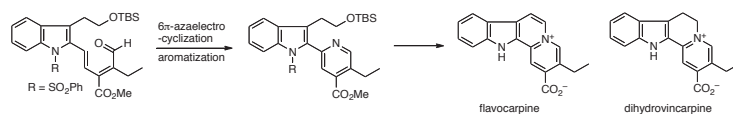
Norio Nakata, Noriyuki Furukawa, Hiroki Kobayashi, Izuru Suzuki, and Akihiko Ishii\*



Oxyphosphorane    Oxapalladacycle

**150 Total Syntheses of Zwitterionic Indole Alkaloids, Flavocarpine and Dihydrovincarpine, by Extended Method for Substituted Pyridine Synthesis through Azaelectrocyclization**

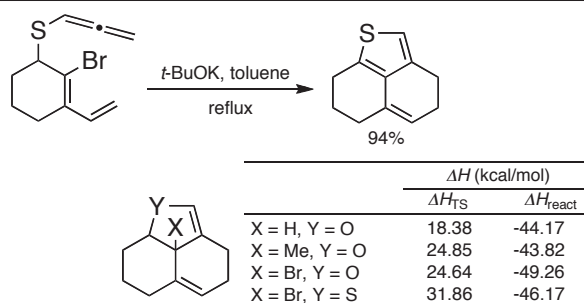
Yoshikatsu Hirose, Hiroshi Tsuchikawa,  
Toyoharu Kobayashi,\* and Shigeo Katsumura\*



Total Synthesis    Zwitterionic Indole Alkaloid    Substituted Pyridine    Azaelectrocyclization

**157 Tandem [4+2] Cycloaddition/Aromatization Sequence of Allenyl 2-Bromo-3-vinylcyclohex-2-enyl Thioether to Naphtho[1,8-*bc*]thiophene**

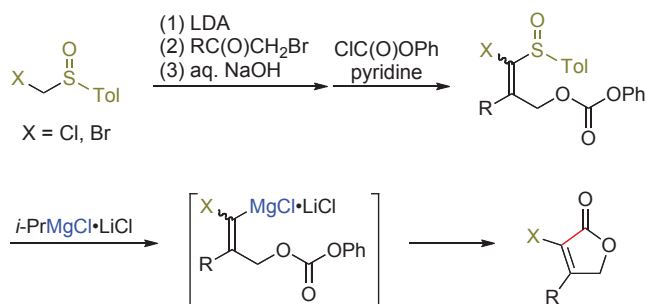
Noriyuki Hatae,\* Aiichirou Kaji, Chiaki Okada, and Eiko Toyota



Naphtho[1,8-*bc*]thiophene    Tandem [4+2] Cycloaddition/Aromatization    Density Functional Study

**163 Synthesis of  $\alpha$ -Halobutenolides Using the Nucleophilicity of Magnesium Alkylidene Carbenoids**

Tsutomu Kimura,\* Kazuki Fukuda, Gaku Kashiwamura, and Tsuyoshi Satoh\*

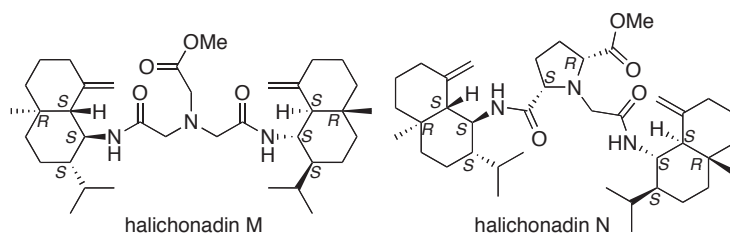


$\alpha$ -Halobutenolide    3-Halofuran-2(5*H*)-one    Cyclization Reaction    Magnesium Alkylidene Carbenoid    Nucleophilicity

■ PAPERS

**173 Halichonadins M-Q, Sesquiterpenes from an Okinawan Marine Sponge *Halichondria* sp.**

Naonobu Tanaka, Shohei Suto, Miki Asai, Taishi Kusama,  
Azusa Takahashi-Nakaguchi, Tohru Gonoj, Jane Fromont,  
and Jun'ichi Kobayashi\*

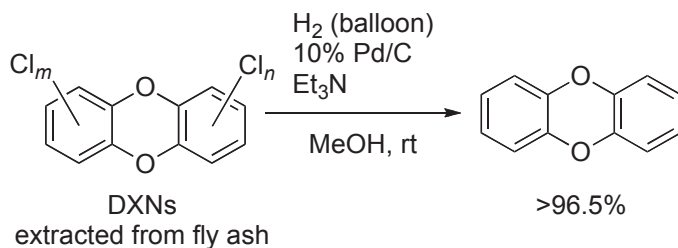


Marine Sponge    *Halichondria* sp.    Sesquiterpene    Halichonadins M-Q



**186 Pd/C-Catalyzed Hydrodechlorination of Dioxins from Fly Ash under Ambient Pressure and Temperature**

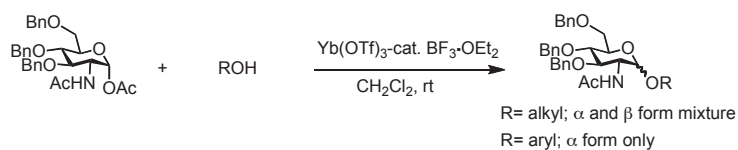
Yasunari Monguchi,\* Akiko Ido, Miki Niikawa, Nobuharu Nagatsu, Ryosuke Mizukoshi, Hisamitsu Nagase, and Hironao Sajiki\*



Hydrodechlorination Reaction    Palladium on Carbon    Dioxin    Fly Ash    Degradation

**198 Formation of 2-Acetamido-2-deoxy-D-glucopyranosidic Linkages via Glycosidation Using a Combination of Two Lewis Acids**

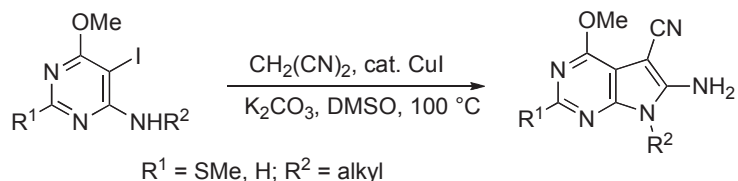
Yoshiki Oda, Masanobu Midorikawa, and Takashi Yamanoi\*



Glycosylation    Aryl Glycoside    Arbutin    4-Hydroxyphenyl 2-Acetamido-2-deoxy- $\alpha$ -D-glucopyranoside    Ytterbium Triflate

**216 Synthesis of 7-Alkyl-6-amino-7H-pyrrolo[2,3-d]-pyrimidine-6-carbonitriles by the Copper-Catalyzed Reaction of 4-(Alkylamino)-5-iodopyrimidines with Propanedinitrile**

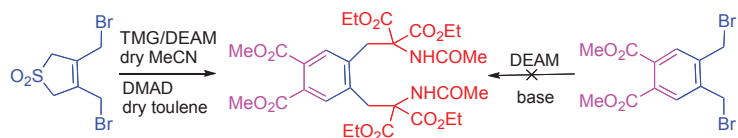
Kazuhiro Kobayashi,\* Kazuya Nakazawa, Shohei Yuba, Hidetaka Hiyoshi, and Kazuto Umezū



7H-Pyrrolo[2,3-d]pyrimidine    Amino Nitrile    Copper(I) Iodide    Coupling Reaction    Malononitrile

**226 Diversity Oriented Approach to Phenylalanine Derivatives via the Diels-Alder Reaction Involving Sulfolene Intermediates**

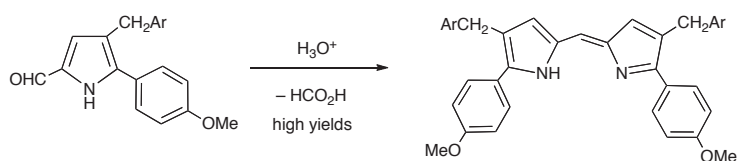
Sambasivarao Kotha\* and Vijayalakshmi Bandi



$\alpha$ -Amino Acid    Diels-Alder Reaction    Sulfolene    Diethyl Acetamidomalonate    Unusual Amino Acid

**238 Unusually Efficient Deformylative Synthesis of 1,2,8,9-Tetrasubstituted Dipyrins from 4,5-Disubstituted Pyrrole-2-carbaldehydes**

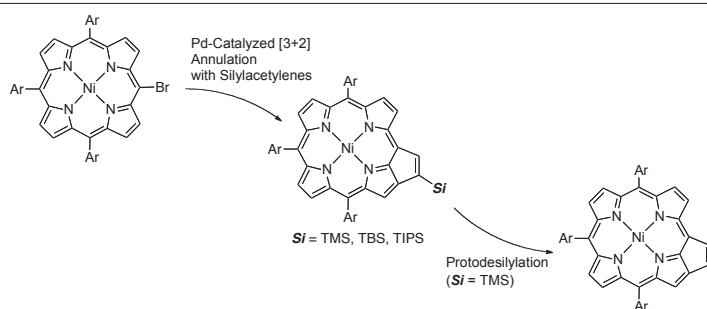
Mitsunori Oda,\* Yurie Fujiwara, Yoshimitsu Kumai, Akira Ohta, and Ryuta Miyatake



Dipyrromethene    Pyrrole    Proton Sensor    X-Ray Crystallographic Analysis    BODIPY

**252 Palladium-Catalyzed [3+2] Annulation of *meso*-Bromoporphyrin with Silylacetylenes and Desilylation of 8<sup>a</sup>-Silyl-7,8-dehydropurpurin**

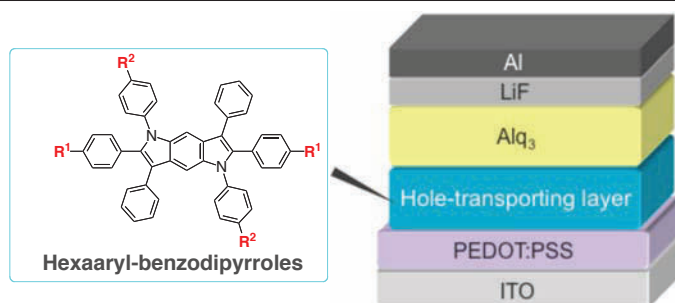
Norihito Fukui, Seiji Arai, Hiroshi Shinokubo, Hideki Yorimitsu,\* and Atsuhiko Osuka\*



Porphyrin    Dehydropurpurin    Annulation    Pd Catalyst    Antiaromatic Compound

**261 Hexaaryl-benzodipyrroles: Properties and Application as Amorphous Carrier-Transporting Materials**

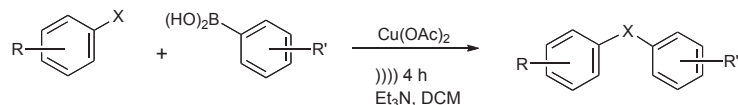
Hayato Tsuji,\* Yuki Yokoi, Shunsuke Furukawa, and Eiichi Nakamura\*



Pyrrole    Carrier Mobility    Semiconducting Material    Light-Emitting Diode

**271 Copper Mediated Formation of Carbon-Heteroatom Bonds Using Organoboron Reagents and Ultrasound**

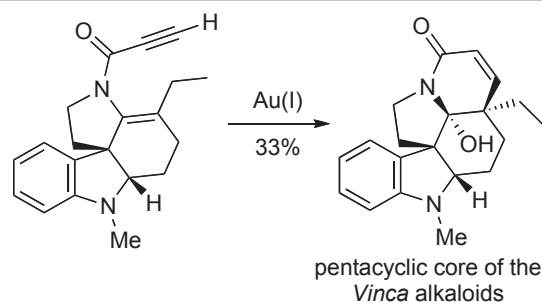
Bryan J. Musolino and George W. Kabalka\*



Heteroatom    Organoboron    Coupling Reaction    Ultrasound    Copper

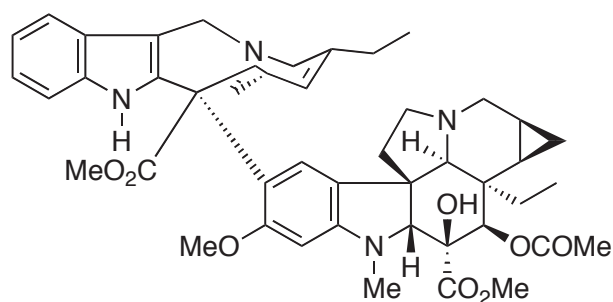
**298 ABC → ABCE/D Based Approaches to the Pentacyclic Ring System of the *Vinca* Alkaloids Using Intramolecular Hetero-[2+2]cycloaddition and Gold(I)-Catalyzed 6-*endo-dig* Cyclisation Protocols**

Lorenzo V. White, Martin G. Banwell,\* and Anthony C. Willis


*Vinca* Alkaloid    6-*endo-dig* Cyclisation    Au(I)-Catalysis    Fischer Indole Synthesis

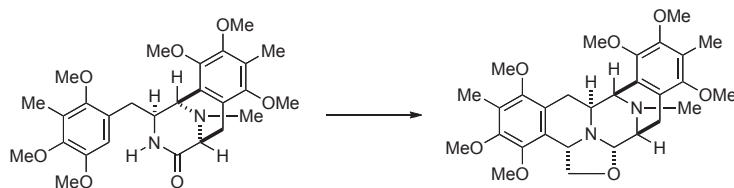
**316 Bisindole Alkaloids Condensed with a Cyclopropane Ring, Part 2. Cyclopropano-vinorelbine and Its Derivatives**

Péter Keglevich, László Hazai, Zsófia Dubrovay, Zsuzsanna Sánta, Miklós Dékány, Csaba Szántay, Jr., György Kalaus, and Csaba Szántay\*


*N*<sup>1</sup>-Formyl-cyclopropano-vinorelbine    5<sup>1</sup>-Desmethylene-cyclopropano-vinblastine    Different Tumor Cell Line    Antitumor Activity

**327 Synthetic Studies on Saframycin Antibiotics: An Improved Synthesis of Tricyclic Lactam Intermediate and Construction of the Core Ring System of Saframycin A**

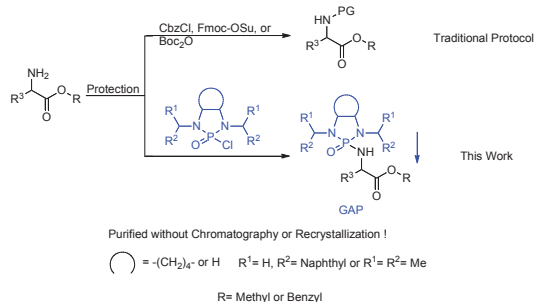
Shinya Kimura, Shintaro Kawai, Masayuki Azuma, Yoshifumi Umehara, Yu-ichi Koizumi, Masashi Yokoya, and Naoki Saito\*



Aminonitrile    Isoquinoline    Cytotoxicity    Saframycin A

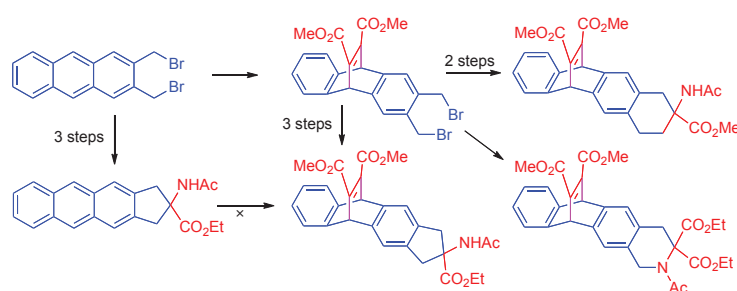
**344 Group-Assisted Purification (GAP) for Protection of Amino Acids Using *N*-Phosphonyl Functional Groups**

Guanghui An, Cole Seifert, Hao Sun, Yi Pan, and Guigen Li\*


 Group-Assisted Purification    Phosphonyl Halide    *N*-Phosphonyl Amino Acid

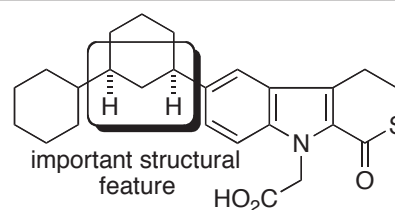
**357 Design and Synthesis of Conformationally Constrained Bicyclo[2.2.2]octane-based Unusual  $\alpha$ -Amino Acid Derivatives via the Diels–Alder Reaction**

Sambasivarao Kotha\* and Milind Meshram


 Bicyclic  $\alpha$ -Amino Acid Derivative    Anthracene Derivative     $\sigma$ -Quinodimethane    Diels-Alder Reaction    Glycine Equivalent

**372 Synthesis and Evaluations of GLP-1 Secretion and Anti-Diabetic Effect in KK $\Delta$ y Mice of New Tricyclic Compounds**

Daisuke Minehira, Daisuke Takeda, Shota Miyawaki, Atsushi Kato, Isao Adachi,\* Akira Miyazaki, Ryuta Miyatake, Masahito Umezaki, Kyoko Miura, Yoshiro Kitahara, Kenji Sugimoto, Yuji Matsuya, and Naoki Toyooka\*

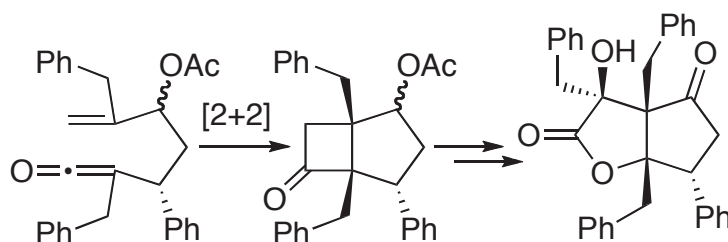


strong GLP-1 secretion and anti-diabetic properties

GLP-1 Secretion    Tricyclic Compound    Friedel-Crafts Reaction

**405 Stereoselective Approach toward Ophidilactones Based on an Intramolecular [2 + 2] Cycloaddition Reaction**

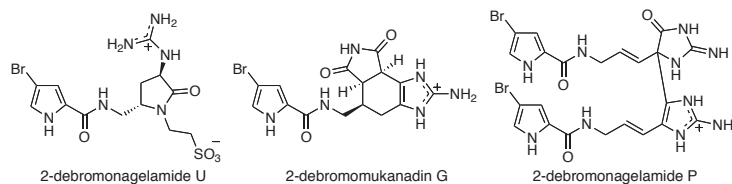
Takaaki Matsubara, Jun Ishihara, and Susumi Hatakeyama\*



Baeyer-Villiger Oxidation    [2 + 2] Cycloaddition    Ketene    Lactone    Natural Product Synthesis

**425 2-Debromonagelamide U, 2-Debromomukanadin G, and 2-Debromonagelamide P from Marine Sponge *Agelas* sp.**

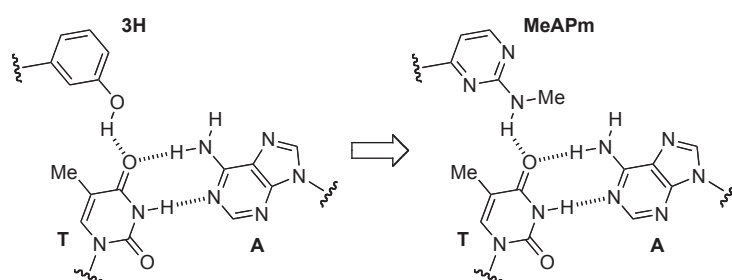
Kenta Nakamura, Taishi Kusama, Naonobu Tanaka, Kanae Sakai, Tohru Gonoi, Jane Fromont, and Jun'ichi Kobayashi\*



Bromopyrrole Alkaloid    *Agelas* sp.    2-Debromonagelamide U    2-Debromomukanadin G    2-Debromonagelamide P

**432 Base Pair Recognition Ability of 2-(Methylamino)-pyrimidin-4-yl Nucleobase in Parallel Triplex DNA**

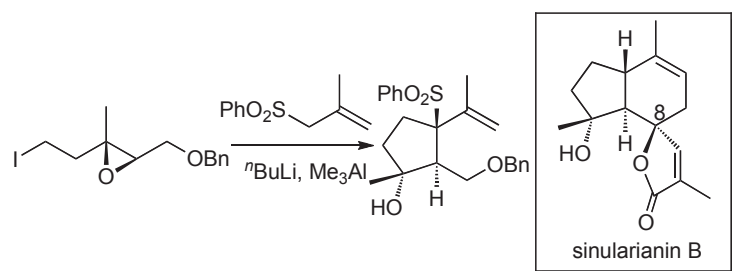
Yoshiyuki Hari,\* Satoshi Kashima, Yuya Matsuda, Akihiro Sakata, Ryutarō Takamine, Shin Ijitsu, and Satoshi Obika\*



Modified Nucleobase    Triplex DNA    Triplex-Forming Oligonucleotide

**442 Total Synthesis of Marine Sesquiterpenoid Sinularianin B and 8-*epi*-Sinularianin B**

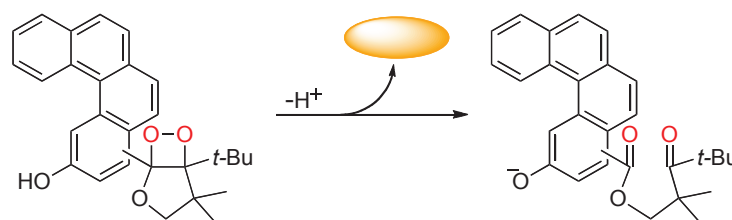
Koichiro Ota and Hiroaki Miyaoka\*



Sinularianin B    Total Synthesis    Spirolactone    One-Pot Synthesis    Natural Product

**462 Synthesis of Bicyclic Dioxetanes Bearing a Hydroxyphenanthrene or Hydroxy[4]helicene Moiety and Their Base-Induced Chemiluminescent Decomposition**

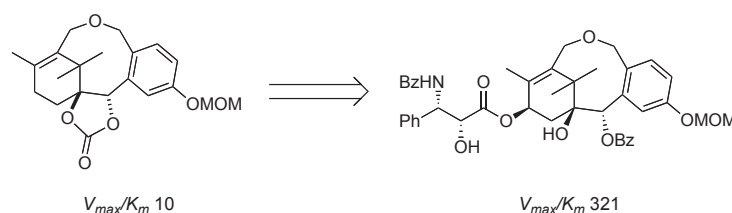
Yohei Koyama, Nobuko Watanabe, Hisako K. Ijuin, and Masakatsu Matsumoto\*



Dioxetane    Chemiluminescence    Helicene

**482 Synthesis and Biological Evaluation of C-Aromataxane Derivatives as P-Glycoprotein-Mediated Multi Drug Resistance Reversal Agents**

Takayuki Doi,\* Naoko Yamaguchi, Kosuke Ohsawa, Kazuoki Nakai, Masahito Yoshida, Kazuhiro Satake, Yuji Mitani, Hiroshi Nakagawa, Takashi Takahashi, and Toshihisa Ishikawa



$V_{max}/K_m$  10

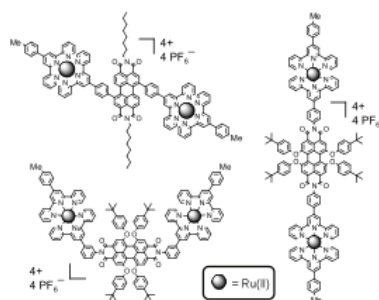
$V_{max}/K_m$  321

98% recovery of cytotoxicity of paclitaxel in the presence of 5.0  $\mu$ M **5a** (IC<sub>50</sub> 30 nM against MDR KB-G2 cells)

9-Membered Cyclic Ether    MDR Reversal Agent    Paclitaxel    P-Glycoprotein    Cytotoxicity

**502 Perylene-Based, *Bis*(terpyridine)-Ru(II) Complexes: Synthesis, Electrochemical and Photovoltaic Properties**

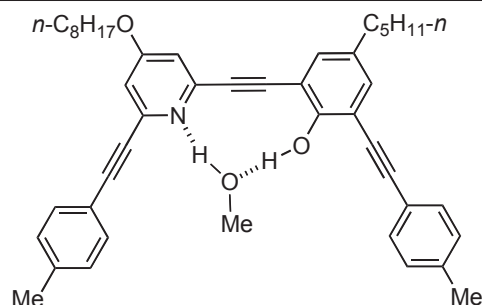
Hany El-Batal, Juan Manríquez Rocha, Perla F. Méndez, Luis A. Godínez, Kai Guo, Xiaopeng Li, Xiaocun Lu, Chrys Wesdemiotis, Charles N. Moorefield, and George R. Newkome\*



Terpyridine Perylene *Bis*(terpyridine) Complex Ruthenium

**515 A New Class of Structurally Simple and Highly Emissive Fluorophores with a Pyridine–Acetylene–Phenol Conjugate**

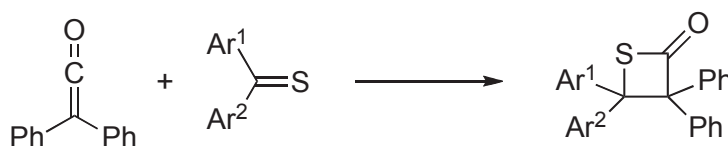
Yuki Ohishi, Hajime Abe,\* and Masahiko Inouye\*



Pyridine Phenol Hydrogen Bonding Optical Property Responsiveness to Acid and Base

**529 Thermal [2+2]-Cycloadditions of Diphenylketene with Aryl- and Hetaryl-Substituted Thioketones**

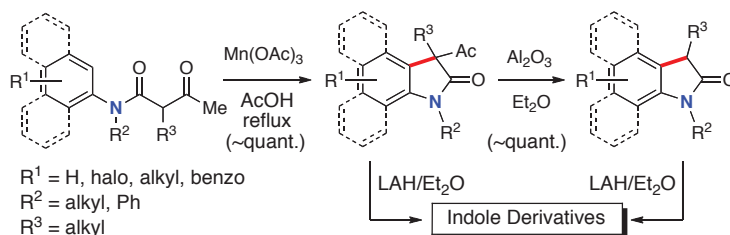
Grzegorz Młostoń,\* Katarzyna Urbaniak, Anna Szychowska, Anthony Linden, and Heinz Heimgartner\*



Cycloaddition Reaction Thioketone Diphenylketene Thietan-2-one X-Ray Crystallography

**540 Mn(III)-Based Oxidative Cyclization of *N*-Aryl-3-oxobutanamides. Facile Synthesis and Transformation of Substituted Oxindoles**

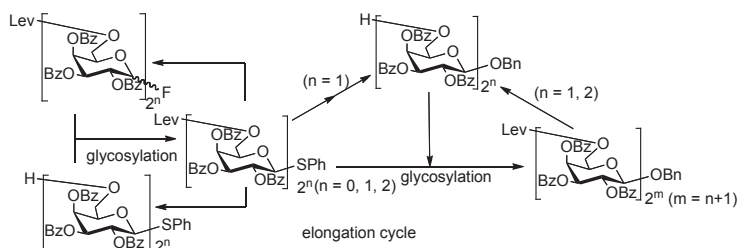
Nobutaka Kikue, Tetsuya Takahashi, and Hiroshi Nishino\*



*N*-Aryl-3-oxobutanamide 3-Acetylindolin-2-one 1*H*-Indole Oxidation Cyclization

**563 Synthesis of Model Compounds Related to Linear  $\beta$ -D-(1 $\rightarrow$ 6)-Galactosyl Side-Chains of Polysaccharides from *Astragalus mongholicus* Bunge**

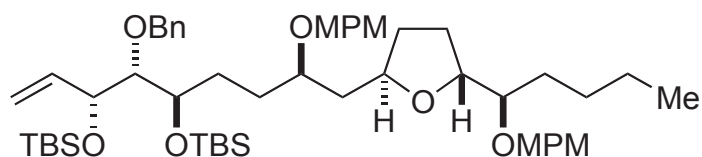
Noriyasu Hada, Ryo Shimura, Kyoko Hakamata, Hiroaki Kiyohara, Haruki Yamada, Tadahiro Takeda, and Fumiyuki Kiuchi\*



$\beta$ (1 $\rightarrow$ 6)-Oligogalactan *Astragalus mongholicus*

**579 Studies toward the Total Synthesis of Amphidinolide N: Stereocontrolled Synthesis of the C13–C29 Segment**

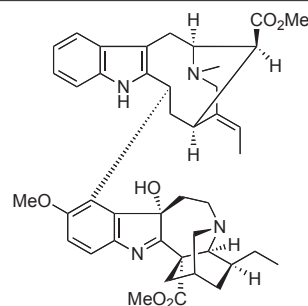
Makoto Sasaki,\* Yuki Kawashima, and Haruhiko Fuwa



Amphidinolide N    Marine Dinoflagellate    Macrolide    Total Synthesis

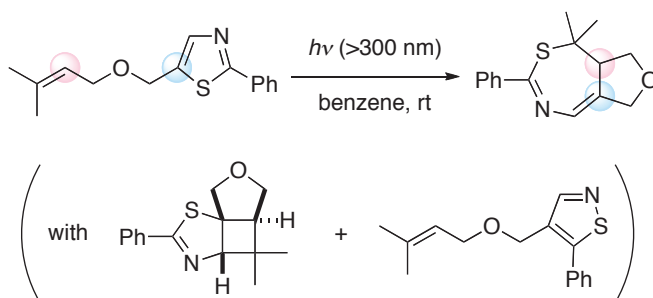
**SHORT PAPERS**
**601 A New Indole Alkaloid from *Voacanga grandifolia***

Azusa Haseo, Alfarius Eko Nugroho, Yusuke Hirasawa, Toshio Kaneda, Osamu Shirota, Abdul Rahman, Idha Kusumawati, Noor Cholies Zaini, and Hiroshi Morita\*


 Bisindole Alkaloid    Voacalgine F    *Voacanga grandifolia*    Structure Elucidation

**607 Novel Intramolecular Cyclization-Skeletal Reorganization of 2-Arylthiazoles under Photoirradiation**

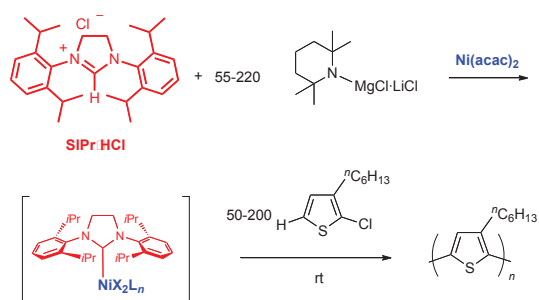
Noriyoshi Arai,\* Moe Mizota, and Takeshi Ohkuma\*



Photoreaction    Cyclization    Skeletal Reorganization    Thiazole    Thiazepine

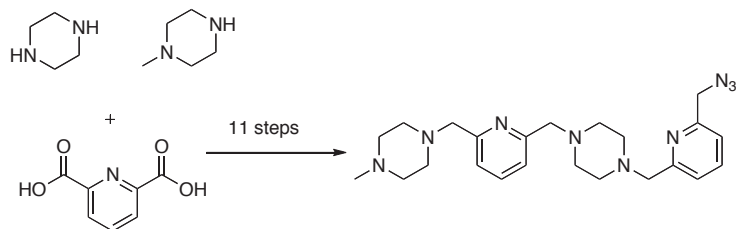
**617 Studies on the Effect of *N*-Heterocyclic Carbene as a Ligand for Nickel(II)-Catalyzed Polymerization of Thiophenes**

Atsunori Mori,\* Makoto Fujio, and Shunsuke Tamba


*N*-Heterocyclic Carbene    Nickel Catalyst    Thiophene    Polythiophene    Acetylacetonate

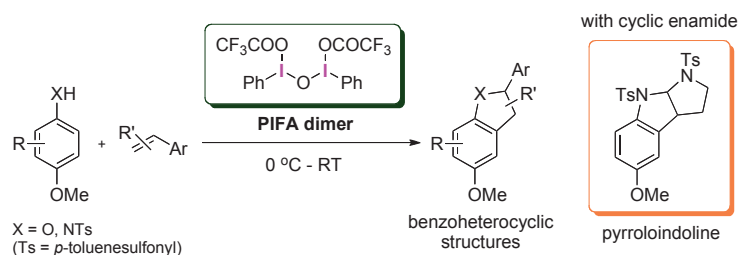
**625 Synthesis of Unprotected CH<sub>2</sub>-Skipped Piperazine-Pyridine Alternating Cycles with Azide End-group**

Andi Kipper, Indrek Kalvet, Kaido Tämm, Lauri Sikk, Peeter Burk, Kuldar Kõiv, and Uno Mäeorg\*


 CH<sub>2</sub>-Skipped Heterocycle    Pyridine-Piperidine Alternating Cycle    Organic Synthesis

**631 Phenol and Aniline Oxidative Coupling with Alkenes by Using Hypervalent Iodine Dimer for the Rapid Access to Dihydrobenzofurans and Indolines**

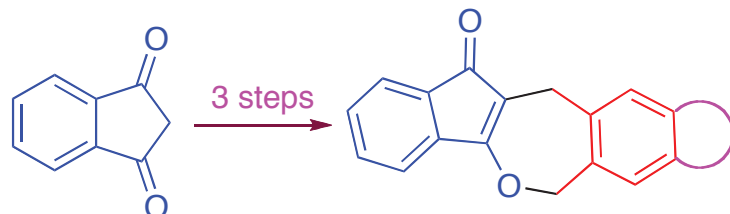
Toshifumi Dohi, Yosuke Toyoda, Tomofumi Nakae, Daichi Koseki, Hiroko Kubo, Tohru Kamitanaka, and Yasuyuki Kita\*



Hypervalent Iodine    C-C Coupling Reaction    Oxidation    Cyclization    Benzoheterocycle

**645 Diversity Oriented Approach to Oxepine Derivatives: Further Expansion *via* Diels-Alder Reaction**

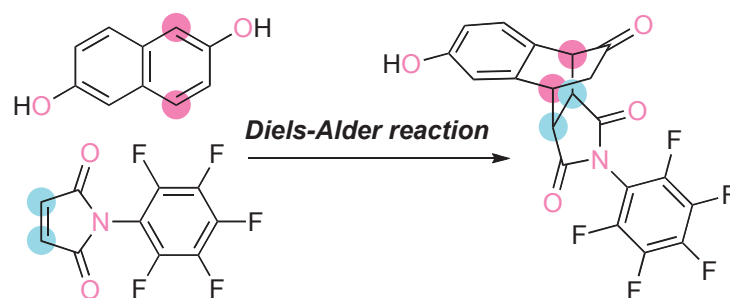
Sambasivarao Kotha\* and Rashid Ali



Oxepine    Diels-Alder Reaction    Rongalite    Sultine    Alkylation Reaction

**659 *N*-(2,3,4,5,6-Pentafluorophenyl)maleimide as a Powerful Dienophile in Dearomatizing Diels-Alder Reactions**

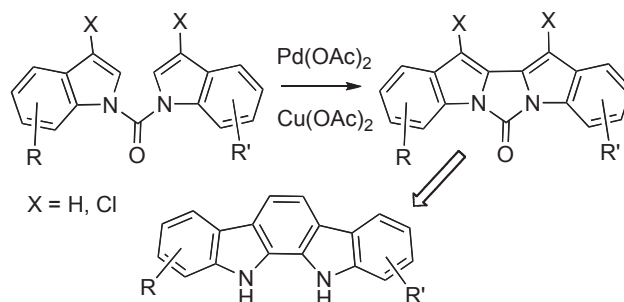
Koichi Hagiwara, Masafumi Iwatsu, Daisuke Urabe, and Masayuki Inoue\*



Diels-Alder Reaction    Dearomatization    Carbocycle    Quaternary Carbon    Total Synthesis

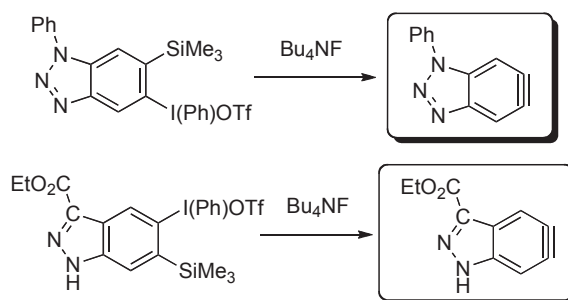
**673 Pd-Catalyzed Intramolecular Oxidative Coupling Reaction of 1,1'-Carbonyldiindoles**

Takumi Abe and Minoru Ishikura\*


 2,2'-Biindolyl    Pd-Catalyzed Coupling Reaction    Indolo[2,3-*b*]carbazole    Tjipanzole

**681 Generation and Reactions of Heteroaromatic Arynes Using Hypervalent Iodine Compounds**

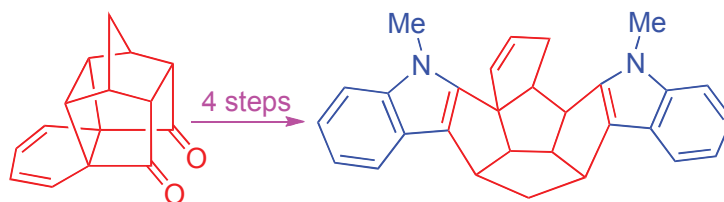
Keisuke Gondo, Juzo Oyamada, and Tsugio Kitamura\*



Heteroaromatic Aryne    Hypervalent Iodine    Didehydrobenzotriazole    Didehydroindazole    Polycyclic Heteroaromatic Compound

**690 Design of Aza-Polyquinanes *via* Fischer Indole Cyclization under Green Conditions**

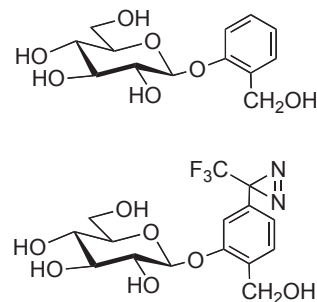
Sambasivarao Kotha\* and Ajay Kumar Chinnam



Fischer Indole Synthesis    Polyquinane    Low Melting Mixture    Caged Compound    Diels-Alder Reaction

**698 Synthesis of Photoreactive Diaziriny Salicin Derivative to Elucidate Functional Analysis of the Bitter Taste Receptor**

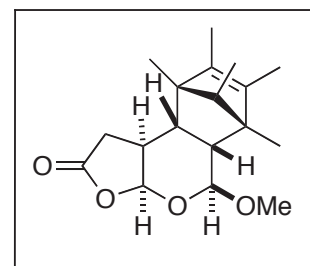
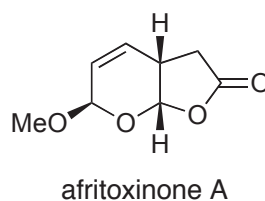
Munenori Sakurai, Takuma Yoshida, Lei Wang, Yuta Murai, Katsuyoshi Masuda, Yasuko Sakihama, Yasuyuki Hashidoko, Yasumaru Hatanaka, and Makoto Hashimoto\*



Diazirine    Photoaffinity Label    Salicin    Bitter Taste    Glucosidation

**706 Synthetic Study of Afritoxinone A: Stereoselective Construction of Furopyranone Moiety**

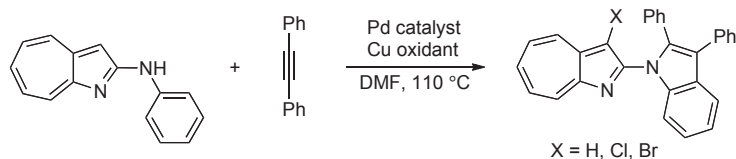
Hideki Abe, Toshihiro Yoshie, Takumi Wagatsuma, Toyoharu Kobayashi, and Hisanaka Ito\*



Afrifoxinone A    Dihydrofuropyranone    Stereoselective 1,4-Addition Reaction    Acetalization

**715 The Cycloaddition of 2-Phenylamino-1-azaazulene with Diphenylacetylene Using Palladium Catalytic Systems**

Hiroyuki Fujii,\* Shigeki Oka, Ippei Nakamura, Yu Kawai, Reiko Ikeda, Takeo Konakahara, and Noritaka Abe

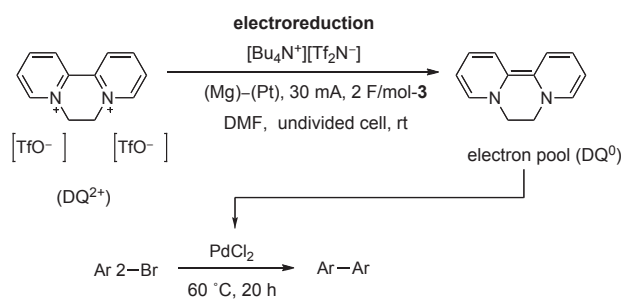


1-Azaazulene    Cycloaddition Reaction    Indole



723 **Diquat Triflate, a Precursor of Organic Reductant**

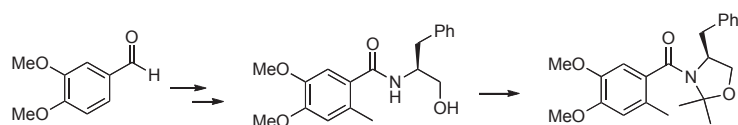
Manabu Kuroboshi,\* Takashi Kondo, and Hideo Tanaka



Electroreduction    Diquat    Organic Reductant    Homo-Coupling Reaction    Biaryl

730 **Synthesis and Crystal Structure of (4*S*)-4-Benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine**

Maria Chrzanowska,\* Zofia Meissner,  
Joanna M. Chrzanowska, and Andrzej K. Gzella



Chiral Auxiliary    Chiral Oxazolidine    8-Oxoberbine    Oxidation of Aromatic Aldehyde    X-Ray Analysis

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 645 Ali, Rashid  
 344 An, Guanghui  
 607 Arai, Noriyoshi  
 252 Arai, Seiji  
 173 Asai, Miki  
 327 Azuma, Masayuki  
 226 Bandi, Vijayalakshmi  
 298 Banwell, Martin G.  
 625 Burk, Peeter  
 690 Chinnam, Ajay Kumar  
 730 Chrzanowska, Joanna M.  
 730 Chrzanowska, Maria  
 316 Dékány, Miklós  
 631 Dohi, Toshifumi  
 482 Doi, Takayuki  
 316 Dubrovay, Zsófia  
 502 El-Batal, Hany  
 173, 425 Fromont, Jane  
 715 Fujii, Hiroyuki  
 617 Fujio, Makoto  
 126, 136 Fujiwara, Kenshu  
 85 Fujiwara, Yuki  
 238 Fujiwara, Yurie  
 113 Fukazawa, Koh  
 163 Fukuda, Kazuki  
 252 Fukui, Norihito  
 126 Fukushima, Takanori  
 144 Furukawa, Noriyuki  
 261 Furukawa, Shunsuke  
 579 Fuwa, Haruhiko  
 502 Godínez, Luis A.  
 681 Gondo, Keisuke  
 173, 425 Gonoï, Tohru  
 502 Guo, Kai  
 730 Gzella, Andrzej K.  
 97 Hachiya, Iwao  
 563 Hada, Noriyasu  
 659 Hagiwara, Koichi  
 563 Hakamata, Kyoko  
 108 Hanzawa, Yuji  
 432 Hari, Yoshiyuki  
 601 Haseo, Azusa  
 698 Hashidoko, Yasuyuki  
 698 Hashimoto, Makoto  
 121 Hashizume, Daisuke  
 157 Hatae, Noriyuki  
 405 Hatakeyama, Susumi  
 698 Hatanaka, Yasumaru  
 316 Hazai, László  
 529 Heimgartner, Heinz  
 601 Hirasawa, Yusuke  
 150 Hirose, Yoshikatsu  
 216 Hiyoshi, Hidetaka  
 41 Honda, Toshio  
 104 Ideta, Keiko  
 186 Ido, Akiko  
 432 Ijitsu, Shin  
 462 Ijuin, Hisako K.  
 715 Ikeda, Reiko  
 659 Inoue, Masayuki  
 515 Inouye, Masahiko  
 126, 136 Ishigaki, Yusuke  
 405 Ishihara, Jun  
 144 Ishii, Akihiko  
 482 Ishikawa, Toshihisa  
 673 Ishikura, Minoru  
 97 Ito, Akinori  
 706 Ito, Hisanaka  
 85 Ito, Shunji  
 659 Iwatsu, Masafumi  
 271 Kabalka, George W.  
 157 Kaji, Aiichirou  
 121 Kakusawa, Naoki  
 316 Kalaus, György  
 625 Kalvet, Indrek  
 631 Kamitanaka, Tohru  
 89 Kanai, Motomu  
 601 Kaneda, Toshio  
 432 Kashima, Satoshi  
 163 Kashiwamura, Gaku  
 372 Kato, Atsushi  
 126, 136 Katoono, Ryo  
 150 Katsumura, Shigeo  
 126, 136 Kawai, Hidetoshi  
 327 Kawai, Shintaro  
 715 Kawai, Yu  
 579 Kawashima, Yuki  
 316 Keglevich, Péter  
 540 Kikue, Nobutaka  
 327 Kimura, Shinya  
 163 Kimura, Tsutomu  
 625 Kipper, Andi  
 631 Kita, Yasuyuki  
 372 Kitahara, Yoshiro  
 681 Kitamura, Tsugio  
 563 Kiuchi, Fumiyuki  
 563 Kiyohara, Hiroaki  
 144 Kobayashi, Hiroki  
 23, 173, 425 Kobayashi, Jun'ichi  
 216 Kobayashi, Kazuhiro  
 150, 706 Kobayashi, Toyoharu  
 625 Kõiv, Kuldar  
 327 Koizumi, Yu-ichi

- 715 Konakahara, Takeo  
 723 Kondo, Takashi  
 631 Koseki, Daichi  
 226, 357, 645, 690 Kotha, Sambasivarao  
 462 Koyama, Yohei  
 631 Kubo, Hiroko  
 104 Kubo, Kanji  
 238 Kumai, Yoshimitsu  
 121 Kurita, Jyoji  
 723 Kuroboshi, Manabu  
 173, 425 Kusama, Taishi  
 601 Kusumawati, Idha  
 6, 7 Kuwajima, Isao  
 344 Li, Guigen  
 502 Li, Xiaopeng  
 529 Linden, Anthony  
 502 Lu, Xiaocun  
 625 Mäeorg, Uno  
 113 Maruko, Miki  
 85 Maruyama, Akifumi  
 85 Maruyama, Mitsuhsa  
 698 Masuda, Katsuyoshi  
 405 Matsubara, Takaaki  
 432 Matsuda, Yuya  
 462 Matsumoto, Masakatsu  
 104 Matsumoto, Taisuke  
 121 Matsumura, Mio  
 89 Matsunaga, Shigeki  
 372 Matsuya, Yuji  
 730 Meissner, Zofia  
 502 Méndez, Perla F.  
 357 Meshram, Milind  
 198 Midorikawa, Masanobu  
 372 Minehira, Daisuke  
 482 Mitani, Yuji  
 372 Miura, Kyoko  
 442 Miyaoka, Hiroaki  
 238, 372 Miyatake, Ryuta  
 372 Miyawaki, Shota  
 372 Miyazaki, Akira  
 607 Mizota, Moe  
 186 Mizukoshi, Ryosuke  
 529 Młostoń, Grzegorz  
 186 Monguchi, Yasunari  
 502 Moorefield, Charles N.  
 104 Mori, Akira  
 617 Mori, Atsunori  
 601 Morita, Hiroshi  
 85 Morita, Noboru  
 698 Murai, Yuta  
 121 Muranaka, Atsuya  
 271 Musolino, Bryan J.  
 186 Nagase, Hisamitsu  
 186 Nagatsu, Nobuharu  
 631 Nakae, Tomofumi  
 482 Nakagawa, Hiroshi  
 482 Nakai, Kazuoki  
 1, 261 Nakamura, Eiichi  
 715 Nakamura, Ippei  
 425 Nakamura, Kenta  
 144 Nakata, Norio  
 216 Nakazawa, Kazuya  
 502 Newkome, George R.  
 186 Niikawa, Miki  
 540 Nishino, Hiroshi  
 601 Nugroho, Alfarius Eko  
 432 Obika, Satoshi  
 238 Oda, Mitsunori  
 198 Oda, Yoshiki  
 515 Ohishi, Yuki  
 607 Ohkuma, Takeshi  
 482 Ohsawa, Kosuke  
 238 Ohta, Akira  
 715 Oka, Shigeki  
 157 Okada, Chiaki  
 252 Osuka, Atsuhiko  
 442 Ota, Koichiro  
 681 Oyamada, Juzo  
 344 Pan, Yi  
 601 Rahman, Abdul  
 502 Rocha, Juan Manríquez  
 108 Saito, Akio  
 327 Saito, Naoki  
 41 Saito, Norio  
 186 Sajiki, Hironao  
 425 Sakai, Kanae  
 432 Sakata, Akihiro  
 698 Sakihama, Yasuko  
 698 Sakurai, Munenori  
 316 Sánta, Zsuzsanna  
 579 Sasaki, Makoto  
 482 Satake, Kazuhiro  
 113 Sato, Koichi  
 163 Satoh, Tsuyoshi  
 344 Seifert, Cole  
 97 Shimizu, Makoto  
 563 Shimura, Ryo  
 252 Shinokubo, Hiroshi  
 601 Shiota, Osamu  
 85 Shoji, Taku  
 625 Sikk, Lauri  
 108 Sudo, Kohei  
 372 Sugimoto, Kenji  
 344 Sun, Hao  
 173 Suto, Shohei  
 144 Suzuki, Izuru  
 126, 136 Suzuki, Takanori  
 316 Szántay, Csaba  
 316 Szántay, Jr., Csaba  
 529 Szychowska, Anna  
 482 Takahashi, Takashi  
 540 Takahashi, Tetsuya  
 173 Takahashi-Nakaguchi, Azusa  
 432 Takamine, Ryutarō  
 372 Takeda, Daisuke  
 563 Takeda, Tadahiro  
 113 Takenaga, Naoko  
 617 Tamba, Shunsuke  
 625 Tämm, Kaido  
 723 Tanaka, Hideo  
 23, 173, 425 Tanaka, Naonobu  
 3 Tanino, Keiji  
 41 Tatsuzawa, Fumi  
 631 Toyoda, Yosuke  
 372 Toyooka, Naoki  
 157 Toyota, Eiko  
 150 Tsuchikawa, Hiroshi  
 261 Tsuji, Hayato  
 121 Uchiyama, Masanobu  
 327 Umehara, Yoshifumi  
 372 Umezaki, Masahito  
 216 Umezu, Kazuto  
 659 Urabe, Daisuke  
 529 Urbaniak, Katarzyna  
 706 Wagatsuma, Takumi  
 698 Wang, Lei  
 462 Watanabe, Nobuko  
 502 Wesdemiotis, Chrys  
 298 White, Lorenzo V.  
 298 Willis, Anthony C.  
 563 Yamada, Haruki  
 482 Yamaguchi, Naoko  
 89 Yamamoto, Shohei  
 198 Yamanoi, Takashi  
 108 Yamashita, Naoki  
 121 Yasuike, Shuji  
 85 Yasunami, Masafumi  
 261 Yokoi, Yuki  
 327 Yokoya, Masashi  
 97 Yokoyama, Keiichi  
 85 Yokoyama, Ryuji  
 252 Yorimitsu, Hideki  
 482 Yoshida, Masahito  
 126 Yoshida, Satoshi  
 698 Yoshida, Takuma  
 706 Yoshie, Toshihiro  
 216 Yuba, Shohei  
 601 Zaini, Noor Cholies

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## A NEW INDOLE ALKALOID FROM *VOACANGA GRANDIFOLIA*

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and Hiroshi Morita<sup>a,\*</sup>**

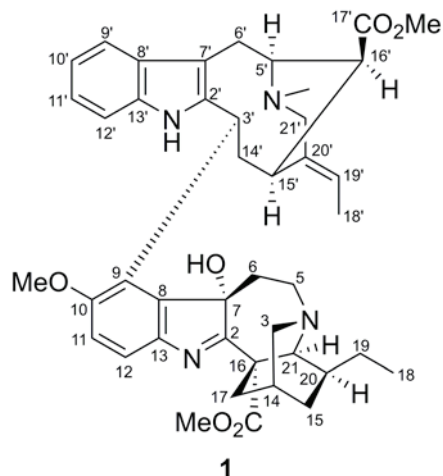
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**Abstract** – A new bisindole alkaloid, voacalgine F (**1**), has been isolated from the bark of Indonesian *Voacanga grandifolia* (Miq.) Rolfe. Its structure was elucidated on the basis of 1D and 2D-NMR data analysis.

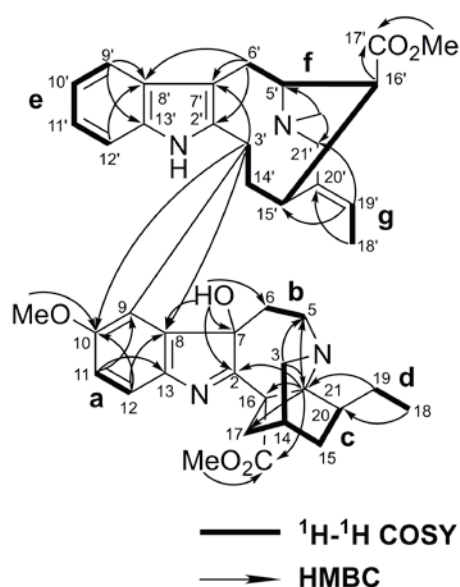
*Voacanga* is a small genus of the Apocynaceae family consisting of 12 species. Species of this genus are distributed mainly in the tropical Africa and Malaysia, and have been reported to contain vobasine, eburnane, iboga, and aspidosperma type of monoterpene indole alkaloids.<sup>1</sup> Various activities have been reported for monoterpene indole alkaloids, such as cytotoxicity,<sup>2</sup> anti-melanogenesis,<sup>3</sup> anti-plasmodial,<sup>4</sup> and vasorelaxant activities.<sup>5</sup> In the search for new bioactive compounds from tropical plants,<sup>3,5-8</sup> alkaloid constituents of *V. grandifolia* bark were investigated and a new bisindole alkaloid voacalgine F (**1**) was isolated together with voacamine,<sup>9-12</sup> voacangine,<sup>9</sup> voacanginehydroxyindolenine,<sup>13</sup> and pagicerine.<sup>14</sup> The isolation and structure elucidation of **1** are reported herein.

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<sup>†</sup>Dedicated to the celebration of the 77<sup>th</sup> birthday of Prof. Dr. Isao Kuwajima, Professor emeritus of Tokyo Institute of Technology



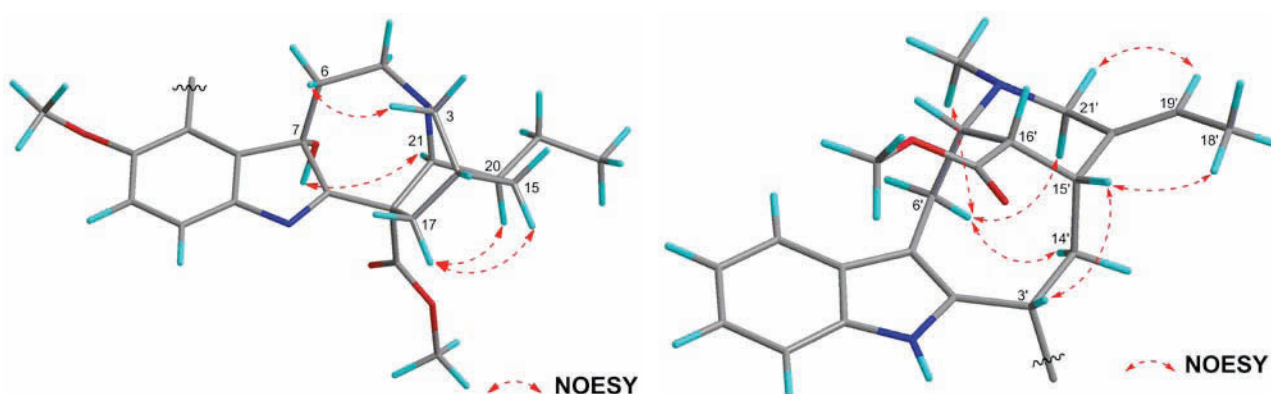
Voacalgine F (**1**) was obtained as yellow amorphous solid and the molecular formula was determined as  $C_{43}H_{52}N_4O_6$  from the HRESIMS data ( $m/z$  721.3978  $[M+H]^+$ , calcd for  $C_{43}H_{53}N_4O_6$ , 721.3965). The IR absorptions ( $3430$  and  $1720$   $cm^{-1}$ ) implied the presence of hydroxyl and carbonyl functionalities. Analysis of the  $^{13}C$ -NMR data (Table 1) showed that the chemical shift of 21 carbon signals is highly similar to the vobasine unit of voacamine, suggesting the presence of a vobasine unit in **1**. The chemical shift of the other carbon signals is highly similar to that of voacangine hydroxyindolenine, except for downfield shift of C-9. These data suggested the structure of **1** as a new vobasine-iboga type of bisindole alkaloids as shown in Figure 1.



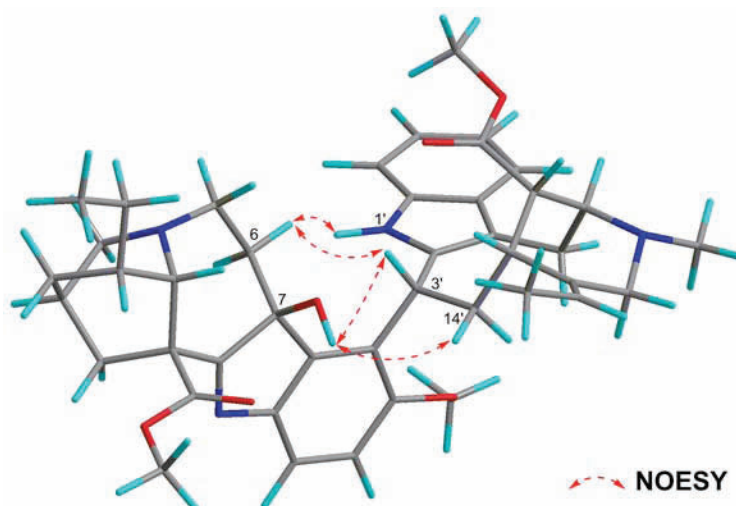
**Figure 1.** Selected 2D-NMR Correlations of **1**

The planar structure of **1** was further confirmed by 2D NMR analysis ( $^1H$ - $^1H$  COSY, HSQC and HMBC, Figure 1). Analysis of  $^1H$ - $^1H$  COSY and HSQC data revealed the presence of 7 partial structure (**a-g**).

HMBC correlations of 7-OH to C-2, C-6, C-7 and C-8, H-11 to C-9 and C-13, and H-12 to C-8 and C-10 confirmed the presence of a 7-hydroxyindolenine moiety and the connection of C-6 and C-7. HMBC cross-peaks of H<sub>3</sub>-18 to C-20 suggested the connectivity of C-19 and C-20, and the HMBC correlations of H<sub>2</sub>-3 to C-5 and C-21, H<sub>2</sub>-19 to C-21, H-21 to C-2, C-5, C-16, C-17 and a carbonyl ( $\delta_C$  174.4), and a methyl ( $\delta_H$  3.73) to  $\delta_C$  174.4 completed the structure of the iboga unit. HMBC cross-peaks of H-3' to C-7', H<sub>2</sub>-6' to C-2', C-7', and C-8', H-9' to C-8' and C-13', and H-12' to C-8' suggested the presence of an indole unit and the connectivity of partial structure **f** to the indole unit. HMBC cross-peaks of H<sub>3</sub>-18' to C-20', and H-19 to C15' and C-21' revealed the connectivity of partial structures **f**, **g**, and C-21' through C-20'. HMBC correlations of a methyl ( $\delta_H$  2.61) to C-5' and C-21' established the connections between C-5' and C-21' through a nitrogen atom, and HMBC cross-peaks of H-16' to C-17', and another methyl ( $\delta_H$  2.49) to C-17' suggested the presence of a methoxycarbonyl moiety at C-16'. Finally, the two units were confirmed to be connected by C-9 to C-3' bond by the HMBC correlations of H-3' to C-8 and C-10.



**Figure 2.** Selected NOESY Correlations of Each Indole Unit in **1**



**Figure 3.** Selected NOESY Correlations Between Two Indole Unit of **1**

The relative configuration of **1** was assigned using the  $^1\text{H}$ - $^1\text{H}$  coupling constant values,  $^1\text{H}$  NMR chemical shift and NOESY correlations. The orientation of 7-OH and H-21 was assigned as  $\alpha$  from the NOESY correlation 7-OH/H-21. The relative configuration C-14, C-16, C-20, C-21, C-3' and C-5' was assigned to be the same as in voacamine based on the NOESY correlations shown in Figure 2. The orientation of the methoxycarbonyl at C-16' was deduced from the highly shielded  $^1\text{H}$  NMR chemical shift of the methoxy group ( $\delta_{\text{H}}$  2.49), and the configuration of the C-19'-C-20' was determined to be *E* from the NOESY correlation of H-19'/H<sub>2</sub>-21'. Finally the relative configuration of the total molecule was deduced from the NOESY correlations of H-6a/NH and H-3', 7-OH/H-3' and H-14'a (Figure 3).

**Table 1.**  $^1\text{H}$  (700 MHz) &  $^{13}\text{C}$  (175 MHz) NMR Data of **1** in  $\text{CDCl}_3$

	$\delta_{\text{H}}$ (J, Hz)	$\delta_{\text{C}}$		$\delta_{\text{H}}$ (J, Hz)	$\delta_{\text{C}}$
2		187.0	2'		136.7
3	2.85 (2H, m)	48.7	3'	5.28 (1H, d, 11.9)	36.7
5a	3.15 (1H, m)	49.2	5'	4.06 (1H, m)	59.5
5b	3.79 (1H, m)		6'a	3.20 (1H, m)	19.1
6a	2.24 (1H, td, 13.2, 3.6)	33.9	6'b	3.50 (1H, m)	
6b	2.52 (1H, br. d, 13.2)		7'		110.0
7		89.9	8'		130.1
8		141.2	9'	7.53 (1H, d, 7.4)	117.4
9		130.1	10'	7.06 (1H, t, 7.4)	118.9
10		158.0	11'	7.05 (1H, t, 7.4)	121.0
11	6.68 (1H, d, 8.3)	112.6	12'	7.09 (1H, d, 7.4)	109.7
12	7.27 (1H, d, 8.3)	119.8	13'		135.3
13		145.3	14'a	1.83 (1H, m)	33.6
14	1.98 (1H, br. s)	27.0	14'b	3.13 (1H, td, 13.6, 3.8)	
15a	1.15 (1H, d, 12.0)	32.1	15'	3.80 (1H, m)	33.1
15b	1.80 (1H, d, 12.0)		16'	2.75 (1H, br. s)	47.0
16		59.1	17'		171.6
17a	2.64 (1H, m)	34.0	18'	1.64 (3H, d, 6.8)	12.4
17b	2.70 (1H, d, 13.9)		19'	5.32 (1H, q, 6.8)	118.6
18	0.89 (3H, t, 7.0)	11.6	20'		138.1
19	1.45 (2H, m)	26.4	21'a	2.92 (1H, m)	52.4
20	1.41 (1H, m)	37.7	21'b	3.78 (1H, m)	
21	3.87 (1H, br. s)	58.8	17'-OMe	2.49 (s)	50.0
$\text{CO}_2\text{Me}$		174.4	N-Me	2.61 (br. s)	42.4
$\text{CO}_2\text{Me}$	3.73 (s)	53.3	NH	7.15 (s)	
10-OMe	3.39 (s)	56.5			
7-OH	4.15 (s)				

## EXPERIMENTAL

**General Experimental Procedures.** Optical rotations were measured on a JASCO DIP-1000 automatic digital polarimeter. UV spectra were obtained on an Ultrospec 2100 pro spectrophotometer and IR



spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. High-resolution ESI MS were obtained on a LTQ Orbitrap XL (Thermo Scientific).  $^1\text{H}$  and 2D NMR spectra were recorded on a Bruker AV700 spectrometer and chemical shifts were referenced to the residual solvent peaks ( $\delta_{\text{H}}$  7.26 and  $\delta_{\text{C}}$  77.0 for chloroform-*d*). Standard pulse sequences were employed for the 2D NMR experiments.

**Plant Material.** The barks of *V. grandifolia* were collected at Purwodadi Botanical Garden, Indonesia in 2008. The botanical identification was made by Ms. Sri Wuryanti, Purwodadi Botanical Garden. A voucher specimen has been deposited in the herbarium at Purwodadi Botanical Garden, Pasuruan, Indonesia.

**Extraction and Isolation.** The dried and powdered bark of *V. grandifolia* (300 g) was extracted successively with MeOH. Part of the extract (17.0 g of 28.4 g) was dissolved in 3% aqueous tartaric acid (pH 2) and then partitioned with EtOAc. The aqueous layer was treated with saturated  $\text{Na}_2\text{CO}_3$  (aq.) to pH 9 and was partitioned successively by  $\text{CHCl}_3$  and *n*-BuOH. Part of the  $\text{CHCl}_3$  soluble materials (5.0 g of 5.10 g) was subjected to an LH-20 column ( $\text{CHCl}_3/\text{MeOH}$  1:1) to obtain 12 fractions.

Fraction 7 was fractionated by amino silica gel column chromatography (*n*-hexane/EtOAc, 1:0~1:1,  $\text{CHCl}_3/\text{MeOH}$ , 0:1~1:0) to obtain voacamine (100.8 mg, 0.032%). In addition, fraction eluted by  $\text{CHCl}_3/\text{MeOH}$  (80:1) was further separated by ODS HPLC (Inertsil ODS-3, 5  $\mu\text{m}$ , 10 x 250 mm; 35% MeCN in 0.1% aqueous  $\text{HCO}_2\text{H}$ ; flow rate 2 mL/min; UV detection at 254 nm) to obtain **1** ( $t_{\text{r}}$  30 min., 2.7 mg, 0.001%).

Fraction 11 was separated by repeated amino silica gel column chromatography (*n*-hexane/EtOAc, 1:0~1:1,  $\text{CHCl}_3/\text{MeOH}$ , 0:1~1:0) and silica gel column chromatography ( $\text{CHCl}_3/\text{MeOH}$ , 0:1~1:0) to give voacangine (23.8 mg, 0.0043%), voacanginehydroxyindolenine (12.8 mg, 0.0079%), and pagicerine (3.6 mg, 0.0012%).

Voacalgine F (**1**): yellow amorphous solid;  $[\alpha]_{\text{D}}^{22}$  -132 (*c* 1.0, MeOH); IR (KBr)  $\nu_{\text{max}}$  3430, 2940 and 1720  $\text{cm}^{-1}$ ; UV (MeOH)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 225 (23400) and 290 (9000) nm;  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (Table 1); ESIMS  $m/z$  721 ( $\text{M}+\text{H}^+$ ); HRESIMS  $m/z$  721.3978 ( $\text{M}+\text{H}^+$ ; calcd for  $\text{C}_{43}\text{H}_{53}\text{N}_4\text{O}_6$ , 721.3965).

## ACKNOWLEDGEMENTS

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