List of 10 Best Papers and Details

(Dr. Rodney A. Fernandes)

No.	Papers	Broad area
1	Jothi L. Nallasivam and Rodney A. Fernandes* J. Am. Chem. Soc. 2016, 138, 13238–13245.	Catalysis, asymmetric synthesis, π-allylpalladium, tetrahydrofuran compounds
2	Rodney A. Fernandes,* Ashvin J. Gangani and Arpita Panja <i>Org. Lett.</i> 2021, 23, 6227–6231.	New method, catalysis, π -allylpalladium, isoxazolines
3	Rodney A. Fernandes,* Sachin P. Gholap, Vijay P. Chavan, Akeel S. Saiyed and Shubhankar Bhattacharyya <i>Org. Lett.</i> 2020 , <i>22</i> , 3438–3443.	New method, carbenes, pentannulation, indanones
4	Amit Bhowmik and Rodney A. Fernandes* Org. Lett. 2019, 21, 9203–9207.	New method, oxidative cleavage, cinnamaldehydes
5	Rupesh A. Kunkalkar and Rodney A. Fernandes* Chem. Commun. 2019, 55, 2313–2316.	Lewis acid catalysis, 4- arylcoumarins, drug synthesis
6	Sachin P. Gholap, Dashrath Jangid and Rodney A. Fernandes* J. Org. Chem. 2019, 84, 3537–3551.	Bronsted acid catalysis, natural products synthesis
7	Gujjula V. Ramakrishna and Rodney A. Fernandes* Org. Lett. 2019, 21, 5827–5831.	Total synthesis of natural products, triyne
8	Rupesh A. Kunkalkar and Rodney A. Fernandes* J. Org. Chem. 2019, 84, 12216–12220	Total synthesis of natural products, protecting-group-free synthesis, polyenes
9	Sandip V. Mulay and Rodney A. Fernandes* Chem. Eur. J. 2015, 21, 4842–4852	Total synthesis of natural products, actinorhodins
10	Rodney A. Fernandes* and Vijay P. Chavan Chem. Commun. 2013, 49, 3354–3356	Total synthesis of natural products, asteriscunolide C

1] Pd-Catalyzed Site-Selective Mono Allylic Substitution and Bis-Arylation by Directed Allylic C-H Activation: Synthesis of anti- γ -(Aryl,Styryl)- β -Hydroxy Acids and Highly Substituted Tetrahydrofurans.

Jothi L. Nallasivam and Rodney A. Fernandes*

J. Am. Chem. Soc. **2016**, *138*, 13238–13245.

[Impact Factor = 15.2]

This paper describes an efficient Pd-catalyzed site-selective arylation of γ -vinyl- γ -lactone 1a by aryl boronic acids. The former has been contemplated as allyl electrophile donor for allylic arylation via π -allyl palladium using 1.5 equiv. of aryl boronic acid 2. Use 3.0 equiv. of the latter resulted in mono-arylation by allylic substitution and subsequent site-selective second arylation by directed allylic C–H activation giving stereoselectively $anti-\gamma$ -(aryl,styryl)- β -hydroxy acids. The presence of O_2 was demonstrated to be crucial for the unprecedented regio- and stereoselective directed second arylation via Pd(II) catalysis. Thus, a good synergy of dual catalysis by Pd(0) and Pd(II) was observed. This methodology was elaborated to synthesize highly substituted THFs including aryl-Hagen's gland lactone analogues via intramolecular iodoetherification. The 2,4-biaryl-THF unit synthesized is present in natural products like calyxolanes and magnosalicin.

2] Synthesis of 5-Vinyl-2-isoxazolines by Palladium-Catalyzed Intramolecular O-Allylation of Ketoximes.

Rodney A. Fernandes,* Ashvin J. Gangani and Arpita Panja Org. Lett. 2021, 23, 6227–6231.

[Impact Factor = 6.1]

In this paper we have developed an efficient method for the synthesis of 5-vinyl-2-isoxazolines via two different strategies based on Pd-catalysis. Both the methods converge to the electrophilic π -allylpalladium formed either by leaving group ionization or the more efficient allylic C-H activation. This is then attacked intramolecularly by the suitably placed oxygen nucleophile of the ketoxime giving efficiently the 5-vinyl-2-isoxazolines. Various other useful compounds were synthesized from the latter using the olefin or imine handles by functional group addition. The acid obtained is an analogous intermediate for roxifiban and ISO-I drug molecules.

3] Fischer Carbene Pentannulation with Alkynes Having Adjacent Carbonate or Acyloxy Groups: Synthesis of 3-Substituted 1-Indanones.

Rodney A. Fernandes,* Sachin P. Gholap, Vijay P. Chavan, Akeel S. Saiyed and Shubhankar Bhattacharyya

Org. Lett. 2020, 22, 3438-3443.

[Impact Factor = 6.1]

This Letter discloses the Fischer carbene pentannulation with alkynes having the adjacent acyloxy or carbonate groups. Various 3-substituted 1-indanones (22 examples) have been prepared by this method. In the case of chiral enantiopure alkynes, the reaction afforded single enantiopure diastereomers. The acyloxy or carbonate carbonyl group probably coordinates with the Cr metal, retarding the CO insertion to give the ketene intermediate required for benzannulation. The diverted reaction results in an aryl ring giving an ortho attack, resulting in pentannulation leading to indanone compounds. The method has been elaborated to complete the synthesis of the core structure of 3-epi-mutisianthol.

4] Iron(III)/O₂-Mediated Regioselective Oxidative Cleavage of 1-Arylbutadienes to Cinnamaldehydes.

Amit Bhowmik and Rodney A. Fernandes*

Org. Lett. 2019, 21, 9203-9207.

[Impact Factor = 6.1]

In this paper, we have developed an efficient Fe(III)/O₂-mediated regioselective oxidative cleavage of the terminal double bond of 1-arylbutadienes to various cinnamaldehydes in good to excellent yields. The method can be executed in a simple operation under an oxygen atmosphere and aqueous media. Thus, the method holds promise in organic synthesis being environmentally benevolent and that limited procedures are available for such excellent oxidative cleavage. Bioactive substituted sinapaldehydes and anti-cancer trienone curcuminoids were synthesized as an application of this methodology.

5] Lewis Acid-Catalyzed Annulative Partial Dimerization of 3-Aryloxyacrylates to 4-Arylchroman-2-ones: Synthesis of Analogues of Tolterodine, $ROR\gamma$ Inhibitor and a GPR40 Agonist. Rupesh A. Kunkalkar and Rodney A. Fernandes*

Chem. Commun. 2019, 55, 2313-2316.

[Impact Factor = 6.2]

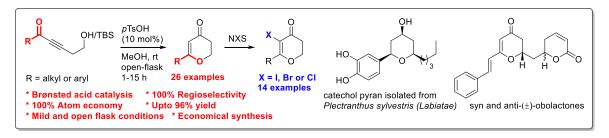
In this communication, we have developed a beguiling annulative partial dimerization/rearrangement of 3-aryloxyacrylates under Lewis-acid conditions to 4-arylchroman-2-ones (4-aryldihydrocoumarins), which are important structural motifs in many natural products. The reaction occurs through C3–O aryloxy bond cleavage, electrophilic aromatic substitution, O–C aryl-migration and lactonization. This method is important, as the addition of a phenol to an alkyl/aryl propiolate and one-step rearrangement provide 4-arylchroman-2-ones. The methodology has been elaborated to various analogues of the drug tolterodine, RORy-inhibitors and a GPR40 agonist.

6] Metal-Free Brønsted Acid-Catalyzed Rearrangement of δ -Hydroxyalkynones to 2,3-Dihydro-4H-pyran-4-ones: Total Synthesis of Obolactone and a Catechol Pyran Isolated from Plectranthus Sylvestris.

Sachin P. Gholap, Dashrath Jangid and Rodney A. Fernandes*

J. Org. Chem. 2019, 84, 3537-3551.

[Impact Factor = 4.8]



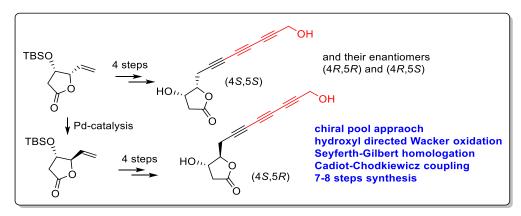
This paper describes a simple, metal-free and cost-effective pTsOH-catalyzed intramolecular rearrangement of δ -hydroxyalkynones to substituted 2,3-dihydro-4H-pyran-4-ones. The rearrangement occurs regioselectively under mild and open-air conditions. The scope has been illustrated by synthesizing several mono- and disubstituted-2,3-dihydro-4H-pyran-4-ones in up to 96% yield with 100% atom economy. A regioselective and chemoselective vinylic halogenation has also been achieved on the synthesized dihydropyranones. Further application of this rearrangement in the total synthesis of syn/anti-(\pm)-obolactones and a catechol pyran isolated from Plectranthus sylvestris (Labiatae) has been demonstrated.

7] Total Synthesis of the Sensitive Triyne Natural Product (4S,5S)-4,8-Dihydroxy-3,4-dihydrovernoniyne and All of Its Stereoisomers.

Gujjula V. Ramakrishna and Rodney A. Fernandes*

Org. Lett. 2019, 21, 5827-5831.

[Impact Factor = 6.1]



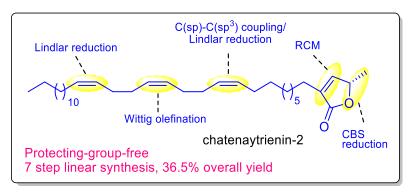
In this Letter, we have described an efficient and concise strategy for the total synthesis of (4S,5S)-4,8-dihydroxy-3,4-dihydrovernoniyne in seven steps from L-mannonic- γ -lactone in 16.7% overall yield. We have also achieved the synthesis of all other stereoisomers, having the (4S,5R), (4R,5R), and (4R,5S) configurations. The synthesis involved an efficient conversion of chiral pool materials in a one-pot two-step process into γ -vinyl- β -hydroxy- γ -lactones, hydroxyl-directed Wacker oxidation, Seyferth–Gilbert alkyne formation, and Cadiot–Chodkiewicz coupling. The synthesis also confirmed the revised structure earlier considered for the natural isolate and that it should have the (4S,5S) configuration.

8] Protecting-Group-Free Total Synthesis of Chatenaytrienin-2.

Rupesh A. Kunkalkar and Rodney A. Fernandes*

J. Org. Chem. 2019, 84, 12216-12220

[Impact Factor = 4.8]



In this paper we have executed an efficient, convergent and protecting-group-free first total synthesis of chatenaytrienin-2 using ring-closing metathesis, (*Z*)-selective Wittig olefination, C(sp)-C(sp³) Sonogashira coupling, and Lindlar reduction as key steps. The synthesis is completed in 7 linear steps with 36.5% overall yield. The strategy is flexible that the synthesis of other chatenaytrienins now has been achieved by varying the alkyl chain carbons in the materials used.

9] Synthetic Studies on Actinorhodin and γ -Actinorhodin: Synthesis of Deoxyactinorhodin and Deoxy- γ -Actinorhodin/Crisamicin A Isomer.

Sandip V. Mulay and Rodney A. Fernandes*

Chem. Eur. J. 2015, 21, 4842-4852

[Impact Factor = 5.2]

An efficient and remarkable bidirectional Dötz benzannulation and oxa-Pictet-Spengler reaction based strategy toward the synthesis of actinorhodin and γ -actinorhodin has been explored. This work has resulted in the synthesis of deoxyactinorhodin and deoxy- γ -actinorhodin. The latter is a regioisomer of crisamicin A (which has 10,10'-dihydroxy groups).

10] A 12-Membered to a Strained 11-Membered Ring: First Stereoselective Total Synthesis of (–)-Asteriscunolide C.

Rodney A. Fernandes* and Vijay P. Chavan

Chem. Commun. 2013, 49, 3354-3356

[Impact Factor = 6.2]

In this communication, the first stereoselective total synthesis of (–)-asteriscunolide C has been accomplished in twelve steps and 16% overall yield. The sequence of intramolecular HWE-olefination and penultimate 12-membered to strained 11-membered ring synthesis was achieved using RCM reaction. The only chiral centre in the molecule was derived from the chiral pool material D-pantolactone. Although, RCM reaction failed to deliver asteriscunolide D, the strategy can be readily adopted towards the synthesis of other members like asteriscunolide A and B through *Z*-selective Wittig olefination in the initial stages.