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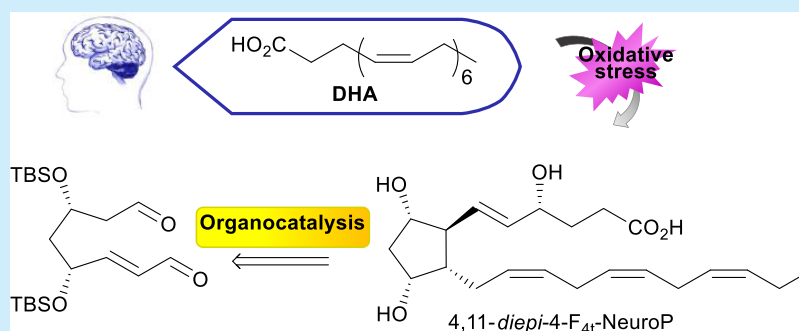
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Total Synthesis of a Docosaehaenoic Acid Prostanoid Using an Intramolecular Organocatalytic Michael Reaction of a Formyl-Enal Derivative

Johanna Revol-Cavalier, Valérie Bultel-Poncé, Alexandre Guy, Thierry Durand, Camille Oger,* and Jean-Marie Galano*



ABSTRACT: The total synthesis of a docosaehaenoic-acid-derived prostaglandin, 4,11-*diepi*-4-F_{4t}-neuroprostane, featuring a complex lateral chain was achieved for the first time. A novel prostaglandin cyclopentane skeleton obtained via an intramolecular highly selective organocatalytic Michael sequence of a formyl-enal derivative allowed the desired and exclusive thermodynamic trans configuration of the lipidic lateral chains.

Prostaglandins (PGs) remain a souvenir of organic chemists, being forever embedded in the art of total synthesis thanks to the pioneering work of E. J. Corey¹ and many other great chemists.² For biochemists and biologists, the same holds true, as PGs remain the most studied oxygenated polyunsaturated fatty acid (PUFA) metabolites.³ The PGs fulfill a considerable number of research fields due to their original biosynthesis by cyclooxygenase enzymes (COXs),⁴ their biological actions as hormone-like compounds,⁵ their use as biomarkers of human diseases, and, finally, their therapeutic applications as drugs (synthetically modified or not) for human or animals.⁶

In 1990 Morrow and coworkers discovered that autoxidation of phospholipidic arachidonic acid can also generate racemic PGF_{2α} together with its C8 isomer named 15-F_{2t}-isoprostane (Figure 1a).^{7,8} Docosaehaenoic acid (DHA) also autoxidizes into isoprostane structures (named neuroprostanes) and PGs, whereas interestingly, no known enzyme can produce PGs from DHA.⁹ Our group recently codiscovered the potent biological activity of 4-F_{4t}-neuroprostane (4-F_{4t}-NeuroP), a DHA-derived isoprostane (Figure 1b) that protects the *in vitro* and *in vivo* post-translational modifications of the ryanodine receptor under oxidative conditions.¹⁰

This unprecedented biological activity for an organic compound makes it a formidable antiarrhythmic compound

and a potential unique drug for ventilator-induced diaphragmatic dysfunction (VIDD).¹¹ Thus because DHA PGs were never investigated nor synthesized in the past, this prompted us to synthesize one 4-F_{4t}-NeuroP counterparts, the 4,11-*diepi*-4-F_{4t}-neuroprostane **1**, to further evaluate the biological and analytical relevancies of unstudied PGs. Recent synthetic efforts in the synthesis of PG revealed the pertinent use of organocatalysis to construct advanced five-membered ring prostanoid skeleton intermediates. Aggarwal and coworkers developed a one-flask access to a key bicyclic enal intermediate ready for lateral chain introduction by the 1,4 addition of vinylcuprates or copper acetylide derivatives and Wittig reactions.¹² Hayashi and coworkers also reported powerful organocatalytic cascade sequences for PG core skeletons,¹³ even to the point of establishing one side chain in the process.¹⁴ Novel synthetic methodologies were also applied for side-chain introduction, such as Baran decarboxylative alkenylation with an organozinc-derived olefin for both vinyl and allyl side chains in a recent

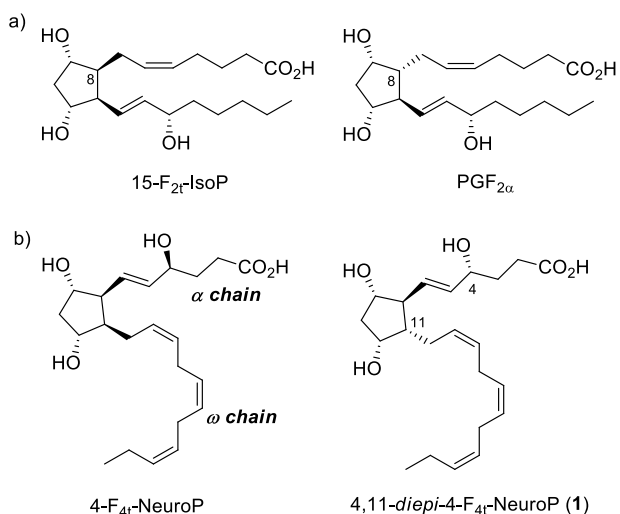
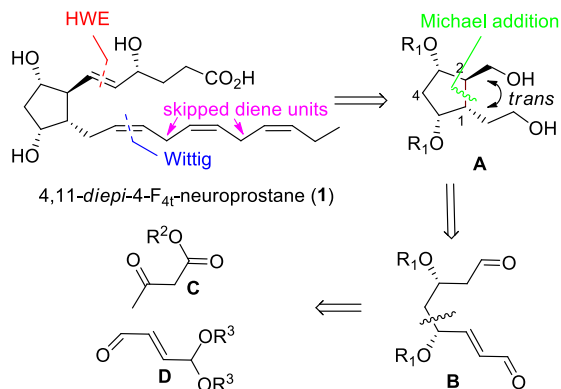


Figure 1. (a) PGF_{2α} and its C8 epimer (15-F_{2t}-IsoP). (b) Structures of 4-F_{4t}-neuroprostane and 4,11-diepi-4-F_{4t}-neuroprostane (1). By definition, the α chain in PGs has to be presented on top.

synthesis of PGF_{2α}.¹⁵ Stereoretentive cross-metathesis also proved successful for prostanooid synthesis to introduce Z-alkene side chains with excellent geometric control.¹⁶

However, one particular feature of PGs derived from complex PUFAs (e.g., DHA) compared with the well-known PGF_{2α} is the inherent sensitivity of skipped diene units (ω-chain in 1) (Scheme 1). Precursors of such side chains cannot

Scheme 1. Retrosynthesis of 4,11-diepi-4-F_{4t}-NeuroP 1

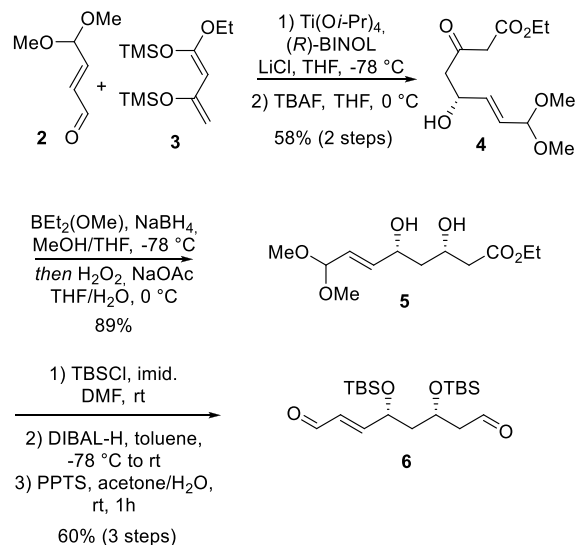


accommodate cuprate or organozinc preparation, and cross-metathesis with an advanced acyclic 1,4-diene precursor cannot be accomplished without the formation of the favored 1,4-cyclohexadiene product. The Corey lactone, famously known for PG synthesis, could seem ideally suited for 1; however, its lactone functionality may temper this idea. Indeed, the Wittig reaction conditions for the skipped diene unit of 1 are not compatible with such a lactol unit (lactol-aldehyde equilibrium not favored) because of the very low temperature required for this sensitive phosphonium-ylide reagent. The alternative would be a four-step sequence to convert the protected lactol and release the aldehyde functionality. This conundrum was observed and solved during our effort in the synthesis of 4-F_{4t}-NeuroP (epimer of 1)^{17a} with the help of a 1,5-pentadiol unit such as A (albeit with a 1,2-cis configuration) together with a novel regioselective enzymatic monoprotection.^{17b} Structure A can thus be the perfect

intermediate for our synthesis. This useful intermediate would arise from the formyl enal system B following a rare organocatalytic intramolecular Michael addition.^{18–20} An asymmetric aldol reaction between synthons C and D should provide the requisite 1,3-hydroxy unit.²¹

Our endeavor started with the synthesis of the dimethylacetal of fumaraldehyde 2,²² following an inexpensive slightly modified protocol, from dimethoxyfuran in two steps on a large scale (51% yield) (Scheme 2).²³ Implementation of the

Scheme 2. Asymmetric Synthesis of Formyl-Enal Derivative 6

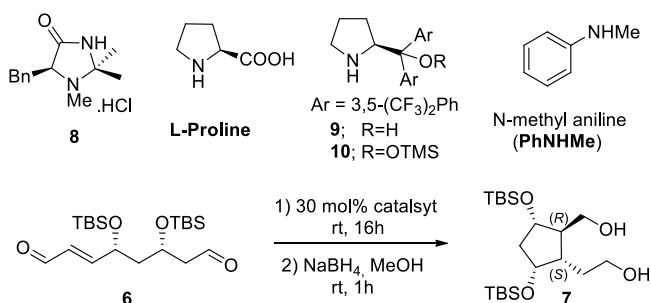


1,3-oxygenation pattern relies on an asymmetric vinylogous Mukaiyama reaction.²¹ We previously observed that the use of another dienolate partner than Chan's diene 3 proved to be problematic at the cleavage of the 1,3-dioxin-4-one-derivative; therefore, we turned to the Ramesh protocol²⁴ using the chiral titanium(IV)–1,1'-binaphtho complex (20% loading) followed by TBAF deprotection of the trimethylsilyl ether to give the requisite δ-hydroxy-β-ketoester 4 in 58% yield (over two steps) with 92% ee.²³ Diethyl methoxyborane treatment followed by the successive addition of sodium borohydride at –78 °C provided the *syn*-diol 5 in 89% yield with high selectivity (*de* = 90%).²⁵

The protection of the alcohols as their TBS-ethers was followed by the chemoselective DIBAL-H reduction of the carboxylic ester moiety prior to the acetal deprotection, which relieves the formyl-enal Michael substrate 6 and permits the chromatographic removal of the undesired anti-isomer in 60% yield over three steps.

The intramolecular organocatalyzed Michael addition investigations are described in Table 1, and because the resulting bis-aldehyde could be unstable, the crude reaction mixture was treated with NaBH₄ to isolate the corresponding diol. The intramolecular C–C bond formation of formyl-enal derivatives was originally demonstrated with the stoichiometric use of achiral or chiral amines by the Schreiber group in 1986.¹⁸ Later, List and coworkers described an enantioselective organocatalytic version on a naked substrate.¹⁹ Finally, the MacMillan group showed diastereoselective modulation depending on the solvent and enantiomer of the organocatalyst used.²⁰

Table 1. Effect of the Catalyst and the Solvent in the Organocatalyzed Michael Addition



entry	catalyst	solvent	results and isolated yield(s) of 7 ^a
1	8 or <i>ent</i> - 8	CHCl ₃	degradation
2	L-proline	CHCl ₃	(34, 34 ^b)
3	D-proline	CHCl ₃	(36, 34 ^b)
4	L-proline	DMSO	(27, 28 ^b)
5	L-proline	CH ₃ CN	(32, 30 ^b)
6	L-proline	MeOH	(16, 18 ^b)
7	L-proline	<i>i</i> -Pr ₂ O	(38)
8	L-proline	MTBE	(42)
9	L-proline	Et ₂ O	(51)
10	L-proline	THF	(55, ^c 42 ^b)
11	L-proline	THF	(56 ^{c,d})
12	9 or <i>ent</i> - 9	THF	reduced SM
13	10 or <i>ent</i> - 10	THF	reduced SM
14	PhNHMe	CHCl ₃	reduced SM
15	trifluoroacetic acid	THF	reduced SM

^aUnless otherwise noted, the reaction was performed by employing **6** (0.13 mmol) and the organocatalyst (0.04 mmol, 30 mol %) in solvent (3 mL) at room temperature for 16 h. No full conversion was observed. The aldol product mixture was treated with NaBH₄ (0.39 mmol), and the diol was characterized. See the [Supporting Information](#) for details. ^b4 h reaction time, no full conversion, ^cFull conversion after 16 h. ^dOn a 1 g (2.5 mmol) scale at room temperature for 16 h.

List's protocol that described the almost exclusive 1,2-trans configuration of the corresponding Michael reaction adduct¹⁹ gave a complete degradation of the starting material **6** with imidazolidinone catalyst **8** or its enantiomer after 4 h (Table 1, entry 1). MacMillan's L-proline thermodynamic control protocol in CHCl₃²⁰ exclusively provided the requisite trans isomer **7** as the sole observable isomer (out of the four possible ones) in 34% yield (no full conversion after 4 or 16 h, Table 1, entry 2). Interestingly, D-proline as a catalyst afforded the same stereoisomer in a similar yield (Table 1, entry 3). Solvent screening with L-proline as the catalyst showed that highly polar solvents used by MacMillan for kinetic control (MeOH, CH₃CN, and DMSO; Table 1, entries 4–6) resulted in lower yields still with total 1,2-trans selectivity. Ether solvents proved to be more satisfactory (Table 1, entries 7–10), as the best result was observed with Et₂O and THF (Table 1, entries 9 and 10), and only THF afforded full conversion. The gram-scale investigation afforded **7** with the same yield and reaction time (56%, 16 h) (Table 1, entry 11). Possible enantiomeric enrichment during the L-proline-catalyzed Michael addition was checked by performing the reaction starting from *ent*-**6** with both L- and D-proline. *ent*-**7** was obtained with the same isolated yields (after 16 h), suggesting that no ee enrichment occurred. (This strategy was used because the ee values of **7** or other derivatives could not be obtained.) Other screened

catalysts, such as trifluoromethyl-substituted diarylprolinol **9** or TMS-derived **10** (both enantiomers) in THF, gave only the recovered starting material (Table 1, entries 12 and 13).

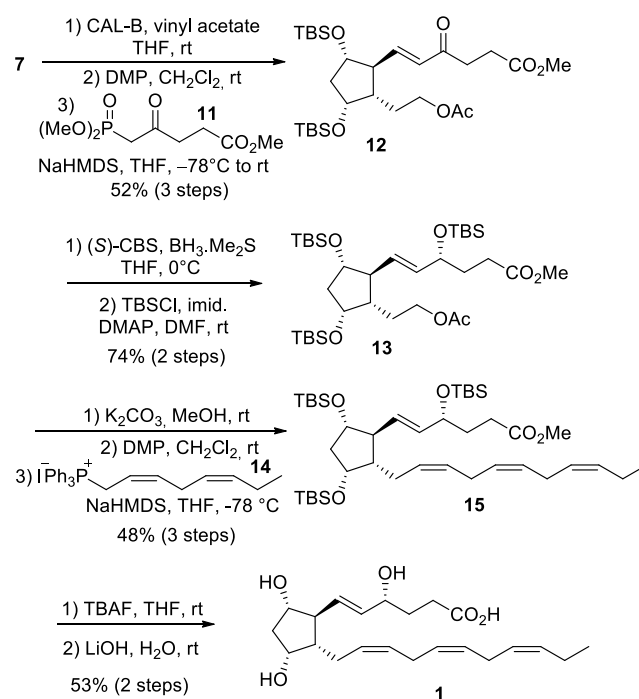
Similarly, the achiral N-methyl aniline (PhNHMe) reagent used in Schreiber's protocol¹⁸ gave no conversion (Table 1, entry 14). The efficiency of both enantiomers of proline and the poor results of other catalysts led us to consider the possibility of an acid-catalyzed mechanism, but the use of trifluoroacetic acid resulted in no conversion (Table 1, entry 15).

The configuration of compound **7** was assigned as a (1*S*,2*R*)-trans isomer thanks to NOESY experiments on its corresponding lactone and comparisons with two other known diastereoisomers of **7**.²³ The above results showed the difficulty in predicting the diastereomeric outcome of this intramolecular reaction, as we observed that compound **6** overcomes the possible chiral catalyst influence, leading to the thermodynamic stable 1,2-trans adduct encountered in the PG skeleton when MacMillan and Mangion substrate showed L- and D-proline reversed stereoinductive effects.²⁰ Moreover, the reaction may proceed through an iminium-enol, enamine-enal, or even a dual mechanism via open- or close-state transition states, and further investigations (experimental reactions and computational molecular modeling) are ongoing.

Quite surprisingly, and to the best of our knowledge, diol **7** was never considered for PG synthesis, but with this useful skeleton in hand, the first synthesis of 4,11-*diepi*-4-F_{4t}-NeuroP **1** continued.

First, the selective enzymatic acetylation of 1,5-nonsymmetrical diols developed by our group proved once again to be effective, and diol **7** was regioselectively acetylated at the less hindered alcohol (Scheme 3) with complete selectivity.^{17b} Dess–Martin oxidation of the remaining alcohol afforded the aldehyde substrate, which was directly coupled to the anion of phosphonate **11**^{17a} introducing the backbone of the α -chain of **12** in 52% yield over three steps. The remaining functionaliza-

Scheme 3. Synthesis of 4,11-*diepi*-4-F_{4t}-NeuroP **1**



tion to access intermediate **13** required the diastereomeric reduction of the enone **12**. Thus the (*S*)-CBS-2-methylloxazaborolidine strategy provided the (*R*)-alcohol product with good selectivity (*dr* = 88:12 by ¹H NMR) and was followed by TBS-ether protection in good yield (74% over two steps). The acetate cleavage of **13** under basic conditions (K₂CO₃ in MeOH) allowed the chromatographic removal of the undesired C4-(*S*)-epimer. Dess–Martin oxidation and the subsequent ω -chain introduction by a Wittig procedure with the previously described complex ylide of phosphonium salt **14**²⁶ provide **15** in 48% yield over three steps. Finally, tetra-*n*-butylammonium fluoride (TBAF)-mediated cleavage of the TBS groups led to the corresponding five-membered lactone, which was ring-opened with LiOH to provide 4,11-*diepi*-4-F_{4t}-NeuroP **1** in 53% over two steps.

Our results demonstrated the pertinence of the described organocatalytic disconnection to provide an ideally adapted Corey lactone surrogate for complex PGs in seven steps. Our approach was validated by the first total synthesis of a PG DHA-derived isomer **1**, named 4,11-*diepi*-4-F_{4t}-NeuroP, according to the isoprostane nomenclature in 17 steps from **2** and **3** in 1.6% overall yield.

Further perspectives include the development of a cascade process, as one could envisage that the known 4-hydroxy-2,6-octadienedial²⁷ would accommodate a regioselective organocatalytic oxa-Michael addition²⁸ (Jørgensen catalyst) to introduce the 1,3-*syn* diol unit followed by subsequent intramolecular cyclization (this work) to furnish a similar PG skeleton (and orthogonal protection of the 1,3-diol). Recent investigations on catalytic intramolecular conjugate additions of aldehyde-derived enamines to α,β -unsaturated esters could also promise an alternative approach to the above one-pot process where no regioselective oxa-Michael reaction would be required.²⁹

Finally, the analytical relevance of 4,11-*diepi*-4-F_{4t}-NeuroP **1** is currently being studied in our lipidomics laboratory, and its biological potential is also under scrutiny.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c02553>.

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Notes

The authors declare no competing financial interest.

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