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Concise access toward chiral hydroxy phenylpropanoids: formal synthesis of virolongin B; kigelin; kurasoin A; 4-hydroxysattabacin, and actinopolymorphol A

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ABSTRACT

A simple, two step strategy consisting of Sharpless asymmetric dihydroxylation followed by regioselective breaking of C—O bond is utilized to target key chiral intermediates of natural products virolongin B, kigelin, kurasoin A, 4-hydroxy-sattabacin, and actinopolymorphol A. Derivatives of enantiopure hydroxy phenyl propanoids and α-hydroxy Weinreb amides are synthesized. The reductive cleavage of C—O bond in a regioselective manner is obtained using Pd/C in methanol.

β-Hydroxy phenyl propanoid unit is ubiquitous in many potent bioactive natural products. Such functionally rich phenyl propanoid units have close resemblance to monolignols and are important to biosynthesis of clinically important lignans, neolignans, and various heterolignans.[1] For example, neolignan virolongin B (**1**) was isolated from *Licaria aurea*, *Aristolochia birostris* etc. the extracts of which are known for their pronounced abortifacient, narcotic, and therapeutic properties.[2] Isocoumarin, kigelin (**2**) is a β-hydroxy propanoid unit containing natural compound showing significant activity against human pathogenic fungi (*dermatophytes*), *Microsporum canis* and *Trichophyton longifusus*.[3] Protein farnesyl transferase inhibitor, kurasoin A (**3**) was isolated from fermentation broth of *Paecilomyces* sp. FO-3684.[4]

4-Hydroxysattabacin (**4**) isolated from soil bacteria *Bacillus* sp. exhibits potent antiviral properties most notably against herpes simplex viruses type HSV 1and HSV 2.[5] Estrogen receptor dimerizing, actinopolymorphol A (**5**) was isolated from *Actinopolymorpha rutilus* (YIM 45725).[6] Neocarazostatin B (**6**) was originally discovered from the culture of *Streptomyces* sp. GP 38.[7] This bacterial carbazole can act as a free radical scavenger. It exhibits potent neuronal cell-protecting activity in case of free radical induced lipid peroxidation in rat brain cells. Lomatin (**7**) is a naturally occurring pyranocoumarin, isolated from *Lomatium nutalli* (Fig. 1).[8] All these β-hydroxy phenyl propanoid derived bioactive natural frameworks inspire synthetic chemists to develop approaches for such units in a concise and efficient manner. Studying the asymmetric synthesis of hydroxy propanoids has tremendous scope in natural product synthesis. Synthesis of such molecules requires construction of asymmetric C—O bond, which has always been of great importance in the field of synthetic organic chemistry.[9] Chiral hydroxy moieties and related derivatives form a wide range of natural compounds which prompts chemists to constantly study C—O bond forming reactions. Many literature methods are available to form C—O bond enantioselectively (Fig. 2).[10] Chiral pool and enzymatic resolution are much established methods but have their own limitations of substrate scope.[10k,l] Organocatalytic hydroxylation or use of chiral hydroxylating agents are recent enantioselective methods[10o–q] and are yet to be fully explored for natural product synthesis. Nucleophilic addition of an organo metallic reagent in the presence of a chiral ligand is a nascent and very promising method in synthesizing key building blocks of bioactive compounds[10g,h] (Fig. 2). Chiral epoxidation and asymmetric dihydroxylation (AD) are the well-documented methods for natural product synthesis[10i,j] (Fig. 2). Hence, we chose the AD and further regioselective C—O bond breaking strategy for the synthesis of natural products **1–5**. Though regioselective C—O bond breaking has good potential and scope it has been very less explored in natural product synthesis. C—O bond breaking methodologies have recently gained much attention in various other disciplines of organic chemistry. For example,

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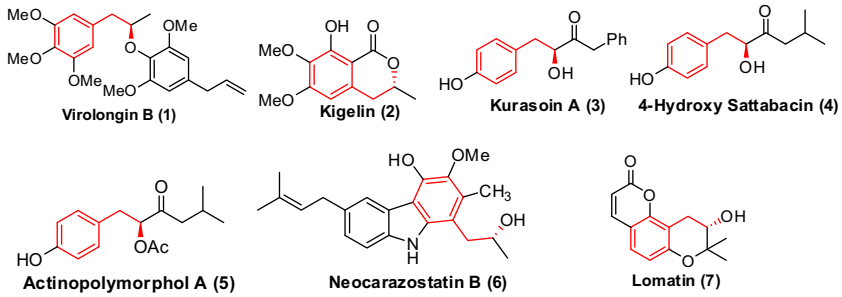


Figure 1. Representative examples of homobenzyl hydroxyl group containing chiral natural compounds.

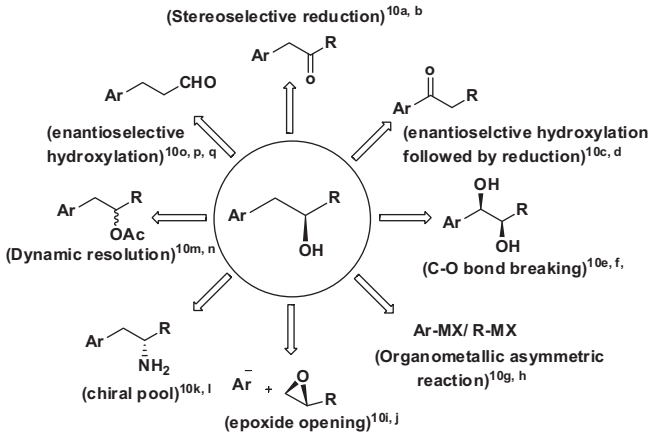


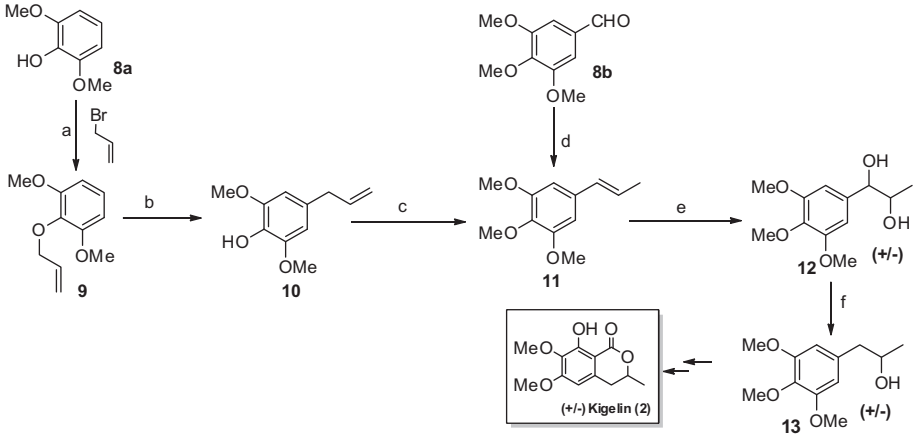
Figure 2. Enantioselective C—O bond forming reactions.

selective hydrogenolysis of C—O bonds of lignin (a polymeric material/ biomass derived from plants) to get smaller fragments/ molecules having tremendous demands in their usage as lignocellulosic biofuels.[11] Novel synthesis of chemical frameworks via targeted C—O bond scission is yet another recently explored topic in the field of synthetic organic chemistry.[12] Many catalytic systems are being optimized to selectively cleave C—O bonds in a molecule demonstrating not only the efficacy of catalytic systems but also highlighting the importance of the C—O bond breaking strategy.[13]

To realize the synthesis of the natural compound, kigelin, (**2**) we targeted synthesis of key chiral intermediate **13** and for the synthesis of key compound **13** we needed to synthesise isoelemicine **11** which was synthesized as reported in the literature.[14] Synthetic procedure commenced with the allyation of phenol **8a** to get compound **9** which on Claisen rearrangement gave the phenolic compound **10**. $PdCl_2$ mediated isomerisation of 1**0** and further methylation gave the required iso-elemicin **11**. Compound **11** was also synthesized by Grignard addition of ethyl magnesium bromide to 3,4,5-trmethoxy benzaldehyde followed by dehydration in two steps. Subsequently under the UpJohn dihydroxylation[15] conditions compound **11** afforded racemic diol **12.** Having synthesized diol compound **12** the stage was set to study the regioselective cleavage of benzylic hydroxyl group and obtain hydroxyphenyl propanoids of further synthetic application. Hydrogenolysis is always a tricky reaction and selectivity depends on the substrate reactivity hence different combination of catalysts and conditions are reported.[16] Initially we studied racemic compound **12** (Scheme 1) to study the regioselective C—O bond breaking under different conditions (Table 1).

First we tried microwave assisted hydrogenolysis using $Pd(OH)_2$ /C and ammonium formate in ethylene glycol.[17] This always gave a complex mixture. Refluxing the reaction mixture with a strong hydride donor, lithium aluminum hydride (LAH) also failed to deliver the product (entry 2, Table 1).[18] Pressure hydrogenation conditions using different supported palladium catalysts such as Pd $(OH)_2$/C; Pd/C(10%) their combinations in ethanol failed to break regioselective C—O bond.[19] Acidic additives such as perchloric acid and acetic acid etc. also failed to give promising results (entry 4, Table 1).[20]

Finally changing the solvent to dry methanol and under pressure hydrogenation condition (4.5 atm), in the presence of Pd/C



Scheme 1. Reagents and conditions: (a) K_2CO_3, acetone reflux, 6 h, 98%; (b) DCB, reflux,16 h, 88%; (c) (i) $PdCl_2$ (0.1 equiv), MeOH, rt, argon, 24 h, 85%; (ii) $(CH_3)_2SO_4$, K_2CO_3, acetonitrile, 8 h, rt, 98%; (d) EtMgBr, 0 °C to rt, 2 h then PTSA toluene, heat, 55%; (e) Upjohn conditions, acetone–H_2O (1:1), OsO_4 (0.02 equiv), NMO (3 equiv), 18 h, rt, 95%; (f) 10% Pd/C (60%), H_2 (4.5 atm), MeOH, 72 h, rt, 85%.

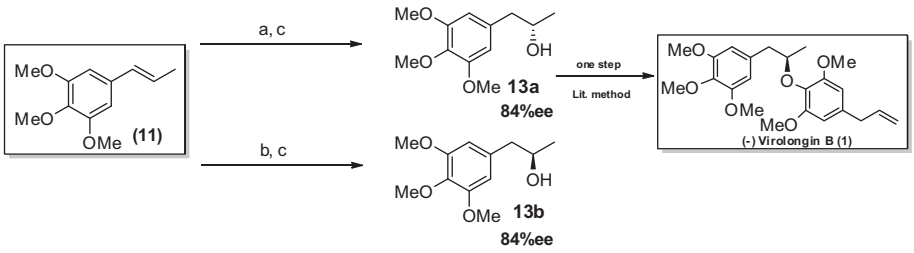
Table 1
Regioselective C—O bond breaking and optimization studies of model structure (**12**)

Entry	Reaction conditions	Remarks
1	Microwave; Ammonium formate 10% Pd/C (W/W); ethylene glycol	Mix. of compounds[a]
2	LAH, THF/Dioxane reflux	—[a]
3	$Pd(OH)_2/C$; EtOH, H_2 (4 atm)	—[a]
4	EtOH, $HClO_4$, Pd/C, H_2 (4 atm)	Mix. of compounds[b]
5	MeOH, Pd/C (0.2 W/W), H_2 (4.5 atm)	50% of **13**[a]
6	MeOH, Pd/C (0.6 W/W), H_2 (4.5 atm)	85% of **13**
7	MeOH, Pd/C (1 equiv W/W), H_2 (4.5–6 atm)	85% of **13**

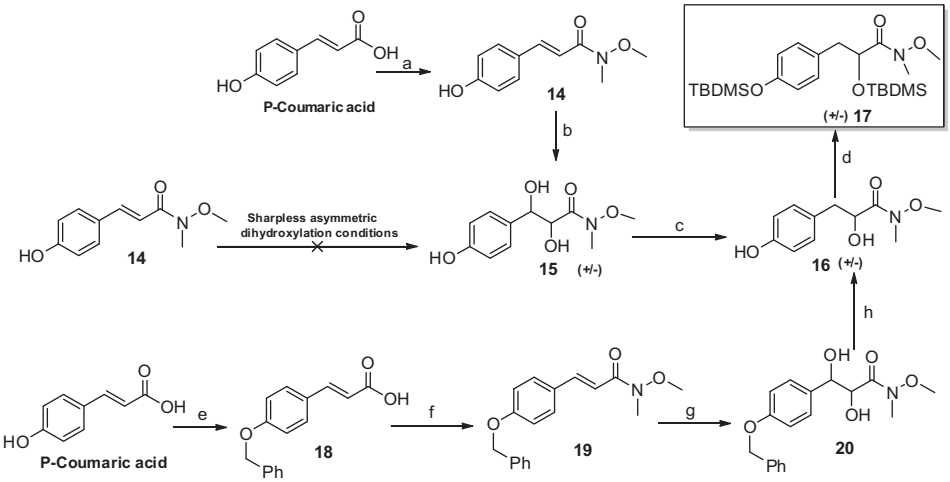
[a] The starting material was recovered.
[b] EtOAc, dioxane, acetic acid as solvents were also tried.

as a catalyst could dramatically improve the outcome without usage of strong acidic conditions giving us 50% of the expected compound. NMR data of the compound obtained after purification was exactly matching with the literature reports.[21] With these initial results we further optimized the conditions and noted that increasing loading of catalyst increased the yield to 80–85%. Increasing the catalyst loading further neither could accelerate the reaction nor improve the yield of the expected compound (entry 7, Table 1). With these encouraging results for the regioselective C—O bond breaking method, we decided to complete the asymmetric version of the same sequence. Simply traversing the dihydroxylation reaction under Sharpless asymmetric conditions yielded both alpha, $[\alpha]^{26.7} = +11.47$ (c 1.9, $CHCl_3$); 90% ee and beta, $[\alpha]^{26.6} = -12.09$ (c 1.8, $CHCl_3$) as chiral dihydroxy compounds using Sharpless ligands $(DHQ)_2PHAL$ and $(DHQD)_2PHAL$ respectively (Scheme 2). Regioselective C—O bond breaking of chiral diols under optimized conditions resulted in synthesis of both the enantiomers of hydroxy phenyl propanoid derivative **13a**, 84% ee, $[\alpha]^{24.4} = +11.38$ (c 0.9, $CHCl_3$); matching with the reported optical rotation $[\alpha]^{20} = +20.8$ (c 0.8, $CHCl_3$) and **13b,** 84% ee, $[\alpha]^{26.6} = -11.14$ (c 0.8, $CHCl_3$). ^1H, ^{13}C NMR, and optical rotations were in well accordance to the compound reported in the literature. Compound **13** constitutes a formal access to synthesis of dihydroisocoumarin based natural compound kigelin, an active ingredient of skin creams and lotions.[22] Asymmetric synthesis of the same can be accomplished using chiral intermediate **13b** and from chiral compound **13a** synthesis of a neolignan, virolongin B, (**1**) natural compound exhibiting wide range of bioactivity and other pharmacoproperties is known in the literature.[23]

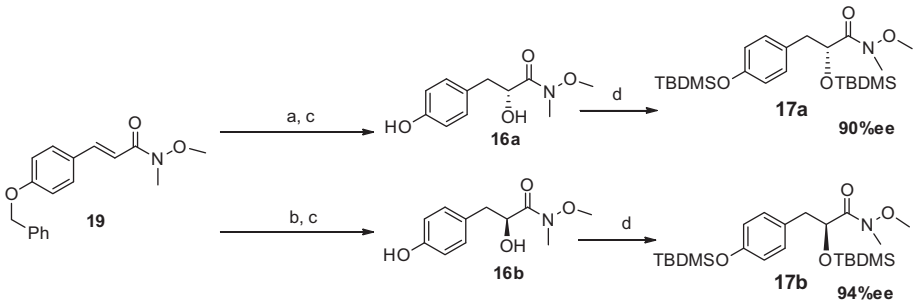
Scope of the method was then successfully extended to more challenging and tricky scaffolds, α,β unsaturated Weinreb amide derivatives to synthesize chiral α-hydroxy Weinreb amides (Scheme 3). Synthesis commenced with commercially available *p*-coumaric acid which was converted to Weinreb amide **14** by EDC coupling followed by UpJohn dihydroxylation to get a water soluble phenolic dihydroxy compound **15** which upon regioselective C—O bond breaking yielded **16** in racemic form. However, the phenolic Weinreb amide **14** failed to give the corresponding chiral diols under Sharpless conditions and we attributed this outcome to the fact that phenolic core of the compound may be following unwanted oxidation reactions in the presence of K_3Fe



Scheme 2. Reagents and conditions: (a) $(DHQ)_2PHAL$ (0.05 equiv), OsO_4 (0.02 equiv; (2% aq), $K_3Fe(CN)_6$ (3 equiv), K_2CO_3 (3 equiv), ^{t}Butanol–H_2O (1:1), 18 h, rt, 90%.; (b) $(DHQD)_2PHAL$ (0.05 equiv), OsO_4 (0.02 equiv), $K_3Fe(CN)_6$ (3 equiv), K_2CO_3 (3 equiv), ^{t}Butanol–H_2O (1:1), 18 h, rt, 90%; (c) 10% Pd/C (60%), H_2 (4.5 atm), MeOH, 72 h, rt, 85%.



Scheme 3. Reagents and condition: (a) EDC·HCl (1.1 equiv), N,O-dimethyl hydrochloride (1.3 equiv), Hunig's base (3.5 equiv), HOBT (1.1 equiv), DMF, 48 h, rt, 70%; (b) Upjohn conditions, acetone–H_2O (1:1), OsO_4 (0.02 equiv), NMO (3 equiv), 72 h, rt, 80%; (c) 10% Pd/C (60%), H_2 (4.5 atm), MeOH, 110 h, rt, 65%.; (d) TBDMSCl (2.1 equiv), imidazole (2.5 equiv), DMF, 18 h, rt, 90%; (e) Benzyl bromide (2.1 equiv), NaOH (5 equiv), EtOH–H_2O (1:1), reflux, 36 h, followed by acidic-work-up, 95%; (f) EDC·HCl (1.1 equiv), *N,O*-dimethylhydroxylamine hydrochloride (1.3 equiv), Hunig base (3.5 equiv), HOBT (1.1 equiv), DMF, 56 h, rt, 85%; (g) Upjohn conditions, acetone–H_2O (1:1), OsO_4 (0.02 equiv), NMO (3 equiv), 48 h, rt, 90%; (h) 10% Pd/C (60%), H_2 (4.5 atm), MeOH, 110 h, rt, 75%.



Scheme 4. Reagents and conditions: (a) $(DHQ)_2PHAL$ (0.05 equiv), OsO_4 (0.02 equiv), $K_3Fe(CN)_6$ (3 equiv), K_2CO_3 (3 equiv), THF–^{t}Butanol–H_2O (1:2:2), 18 h, rt, 90%; (b) $(DHQD)_2PHAL$ (0.05 equiv), OsO_4 (0.02 equiv), $K_3Fe(CN)_6$ (3 equiv), K_2CO_3 (3 equiv), THF–^{t}Butanol–H_2O (1:2:2), 18 h, rt, 90%; (c) 10% Pd/C (60%), H_2 (4.5 atm), MeOH, 110 h, rt, 75%.; (d) TBDMSCl (2.1 equiv), imidazole (2.5 equiv), DMF, 18 h, rt, 90%.

$(CN)_6$ which is used as an oxidizing agent in the reaction. Therefore we decided to protect the phenolic hydroxyl of Weinreb amide compound **14** by a benzyl group which could be later knocked under the optimized late stage hydrogenolysis step (C—O bond breaking) along with the targeted benzylic hydroxyl group to give compound **16** in one step. After protection and EDC mediated coupling the α,β unsaturated Weinreb amide **19** (Scheme 4) gave diol **20** under Upjohn conditions as well as corresponding chiral diols were synthesized in a smooth manner using Sharpless asymmetric dihydroxylation.

Chiral alpha diol, 98% ee, $[\alpha]^{25} = -1.8$ (*c* 0.8, MeOH) and beta diol, 98% ee, $[\alpha]^{25.4} = +1.89$ (*c* 0.74, MeOH) conveniently underwent regioselective C—O bond breaking slowly (110 h) without much affecting the enantioselectivities and hence gave us both the enantiomers of α-hydroxy Weireb amide **16a** and **16b**; which were characterized as their silyl ethers **17a**, 90% ee, $[\alpha]^{24.5} = +3.59$ (*c* 2.0, $CHCl_3$) and **17b**, 94% ee, $[\alpha]^{24} = -1.33$ (*c* 0.9, $CHCl_3$). Selective hydrogenolysis of diols of Weinreb amides are not known in the literature and this is the first report wherein such derivatives are utilized in order to access chiral enantiomers of α-hydroxy Weinreb amide. Corresponding beta enantiomer, **17b** of α-hydroxy Weinreb amide gives formal access to three key bioactive natural products such as potent antitumor compound, kurasoin A (**3**);[24] antiviral compound 4**-** Hydroxy sattabacin (**4**) (HSV 1 and HSV 2);[25] and also recently isolated actinopolymorphol A (**5**) a new class of natural products not previously known to modulate estrogen receptor function and hence implicated in cancer chemoprevention.[26]

In conclusion, a simple and effective regioselective C—O bond breaking method is studied for its application in the field of synthesis of β-hydroxy phenyl propanoid containing natural products. We have synthesized key chiral intermediates derivatives of chiral hydroxy phenyl propanoids and also α-hydroxy Weinreb amide derivatives to formally access five different bioactive natural compounds. We envision that the scope of the present regioselective C—O bond breaking method can also be extended to other competitive aromatic scaffolds, such as chromans and carbazole derivatives to target enantioselective synthesis of lomatin and neocarazostatin B (Fig 1) respectively.

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Supplementary data

Supplementary data (detailed experimental procedure, characterization of the products and copies of spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.06.070.

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