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Iodine-Catalyzed Highly Diastereoselective Synthesis of *trans*-2,6-Disubstituted-3,4-Dihydropyrans: Application to Concise Construction of C28–C37 Bicyclic Core of (+)-Sorangicin A

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Abstract: A novel iodine-catalyzed highly diastereoselective synthesis of *trans*-2,6-disubstituted-3,4-dihydropyrans have been achieved from δ-hydroxy α,β-unsaturated aldehydes by treating with allyltrimethyl silane in THF at room temperature with good to excellent yields. This methodology has been successfully implemented for a concise asymmetric synthesis of C28–C37 dioxabicyclo[3.2.1]octane ring system of (+)-sorangicin A in 8 steps with 21% overall yield.

Keywords: asymmetric synthesis · iodine · oxygen heterocycles · sorangicin A

Introduction

Heterocyclic compounds are broadly distributed in nature, and constitute an integral component of several polyketides, adding a significant degree of conformational rigidity in natural products and thus likely to be critical to the pharmacophore of biological activity. Among them, 2,6-disubstituted dihydropyrans, are probably one of the most common structural motifs spread across various natural products, from simple glucose to structurally complex secondary metabolites such as luminaolide;[1] leucascandrolide A;[2] aspergillide A, B, and C;[3] misakinolides;[4] phorboxazole;[5] laulimalide;[6] swinholides;[7] scytophycins;[8] and even more elaborated architectures present in polytoxins, maitotoxins, and other marine derived natural products[9] (see also Figure 1. compounds **1**–**7**). 2,6-Disubstituted dihydropyrans are also synthetically useful intermediates in the preparation of polysubstituted tetrahydropyran ring system such as those found in the pseudomonic acid.[10] Due to the remarkable rich array of functionalities and chiral centers that these heterocycles can incorporate, their stereoselective synthesis has become a continuous challenge for synthetic organic chemists. Several approaches have been reported for the preparation of dihydropyrans and among them varied methodologies include electrophile-initiated alkylation of glycals,[11] hetero-Diels–Alder cycloadditions,[12] ring-closing metathesis,[13] Prins cyclizations,[14] metal halide induced cyclization,[15] and an intramolecular silyl-modified Sakurai reaction (ISMS).[16]

Many of these methods require long reaction times, stoichiometric use of expensive reagents, harsh reaction conditions, and some time gives poor yield and selectivity. To avoid the above limitations, we have to search for a catalyst with high catalytic activity, easy availability, short reaction time, environment friendly and simple work-up procedure. Molecular iodine[17] attracted our attention as recently it has attained considerable importance in organic synthesis because of low cost, nontoxic nature, ready availability, environment-friendly, easy handling, high efficiency for various organic transformations to the corresponding products in excellent yields with high diastereoselctivity. Since it has been used as a mild Lewis acid[18] catalyst for the activation of carbonyl compounds, including acetalization reactions, we envisaged that iodine could catalyze the reaction for the formation of 2,6-disubstituted-3,4-dihydropyrans starting from δ-hydroxy α,β-unsaturated aldehydes.

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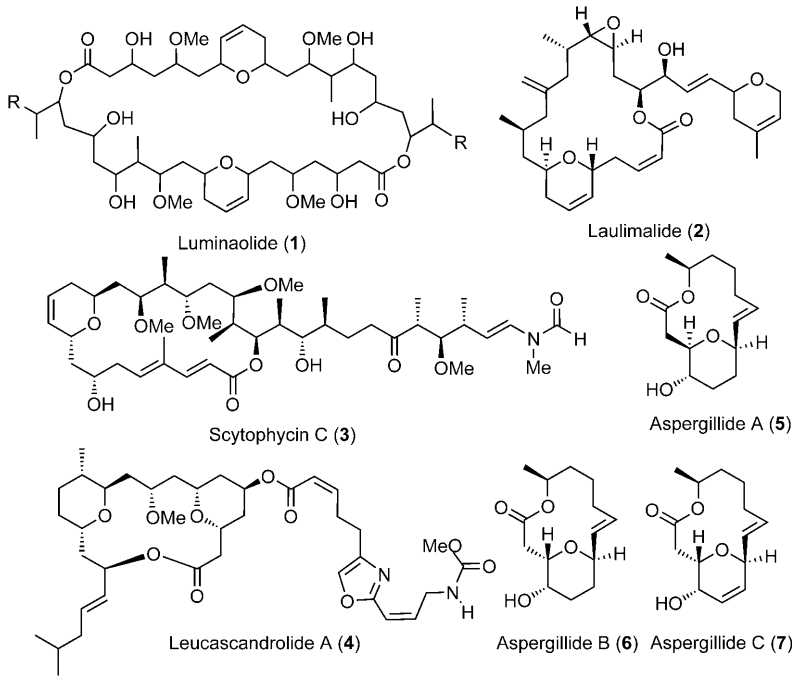
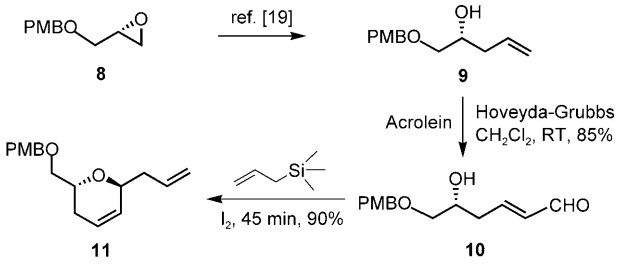


Figure 1. A few natural products bearing 2,6-disubstituted-3,4-dihydropyran moiety.

Herein, we report our research on the use of iodine as a catalyst for the construction of *trans*-2,6-disubstituted-3,4-dihydropyran under neutral reaction conditions and demonstrated the application of this protocol for a concise synthesis of C28–C37 bicyclic ether core of (+)-sorangicin A.

Results and Discussion

Initially, we investigated the effect of 5 mol% iodine on the conversion of **10**, which was prepared in two steps[19,20] starting from **8** (via intermediate **9**) in good yield, with allyltrimethyl silane in CH_3CN at room temperature to obtain **11**. After 12 h at room temperature, the reaction afforded the expected *trans*-2,6-disubstituted-3,4-dihydropyran **11** in 42% yield (Scheme 1). The ^1H and ^{13}C NMR of the product revealed a single diastereomer. The stereochemistry of the product **11** was assigned by comparing the ^1H NMR data with known tetrahydropyran derivatives as well as NOE experiments. No *cis*-diastereomer was detected in the ^1H NMR spectrum of the crude product obtained from the C-allylation of δ-hydroxy α,β-unsaturated aldehydes. The reaction was incomplete even after 48 h of stirring at room temperature. To optimize the reaction conditions, screening was performed on several parameters, such as solvents, temperature, and catalyst concentration. Initially, the reaction was performed in different solvent systems (CH_2Cl_2, TBME, THF) at room temperature with 5 mol% of iodine; THF was found to be superior to other solvents. Next, the reaction was examined carefully under reflux conditions which led to an intractable mixture of products. The experiment was also conducted carefully under the influence of different concentrations of the catalyst at room temperature with THF as solvent. The use of 10 mol% molecular iodine (based on δ-hydroxy α,β-unsaturated aldehyde) gave the best result with a yield of 90% after 45 min of reaction. Increasing the iodine concentrations did not help in improving the yield and reduction of reaction time. However, no reaction was observed in absence of iodine even after a long time (48 h).

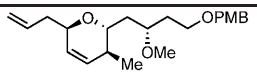
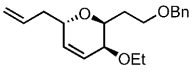
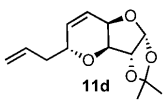
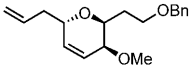
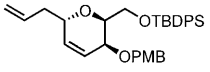
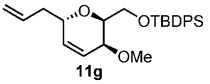
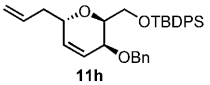
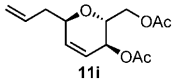
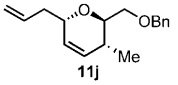
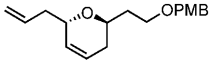


Scheme 1. Synthesis of 2,6-disubstituted-3,4-dihydropyran moiety using iodine as catalyst.

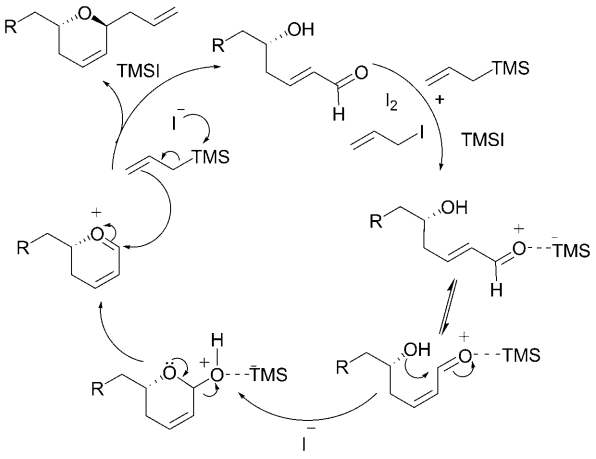
To investigate the scope and generality of the present method, a diverse range of hydroxyl–enals with different protecting groups afforded corresponding *trans*-2,6-disubstituted-3,4-dihydropyrans in good to excellent yields (Table 1). The formation of compound **11i** was reported earlier by Isobe et al.[21a] and Danishefsky et al.[21b] by means of the Hosomi–Sakurai reaction affording a mixture of α and β-isomers in 16:1 ratio. In our case we obtained exclusively one isomer, which was confirmed by spectral and analytical data. It is worth mentioning here that almost all the protecting groups were compatible to the reaction conditions.

To explain the formation of the *trans*-2,6-disubstituted-3,4-dihydropyran following catalytic pathways, we postulated that the product was generated with activation of aldehyde by in-situ formation of TMSI and subsequent formation of an oxonium intermediate in which the stereoelectronic and/or steric factors dictate the direction of the incoming nucleophile (Scheme 2). To test the viability of the proposed reaction pathways, we conceived that the reaction of a δ-hydroxy α,β-unsaturated aldehyde in presence of catalytic amount of trimethylsilyliodide (TMSI) should generate the corresponding *trans*-2,6-disubstituted-3,4-dihydropyran. Pleasingly, when 10 mol% of TMSI was added instead of molecular iodine at room temperature, the reaction com-

Table 1. Iodine-catalyzed synthesis of *trans*-2,6-disubstituted-3,4-dihydropyrans.

	Product[a]	Solvent	*t* [min]	Yield [%][b]
1	 **11b**	THF	45	96
2	 **11c**	THF	30	88
3	 **11d**	THF	60	94
4	 **11e**	THF	30	93
5	 **11f**	THF	45	84
6	 **11g**	THF	40	91
7	 **11h**	THF	45	90
8	 **11i**	THF	30	87
9	 **11j**	THF	45	90
10	 **11k**	THF	30	92

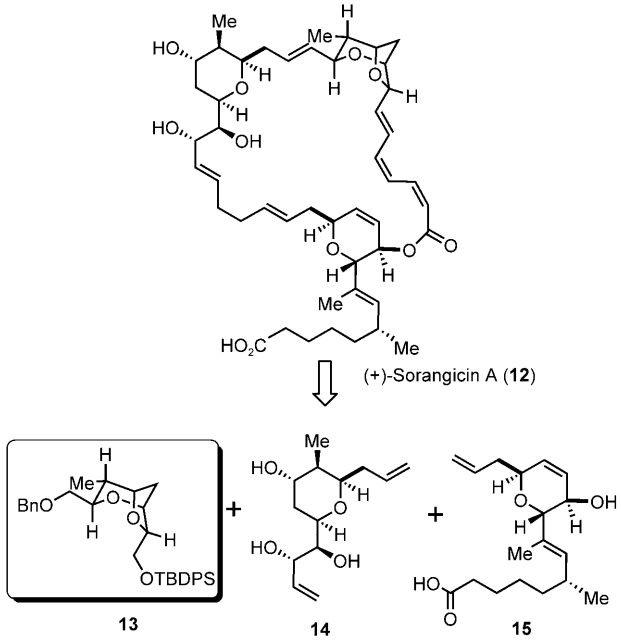
[a] Single diastereomeric product was confirmed by ^{1}H and ^{13}C NMR spectroscopy. [b] Isolated yields after purification on silica gel.



Scheme 2. Possible catalytic pathways for the formation of the product.

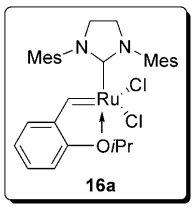
pleted in 10 min, which strongly supported our proposed mechanism. Other reagents such as NaI/TMSCl[22] and *N*-iodosuccinimide (NIS)[23] failed to produce the desired product.

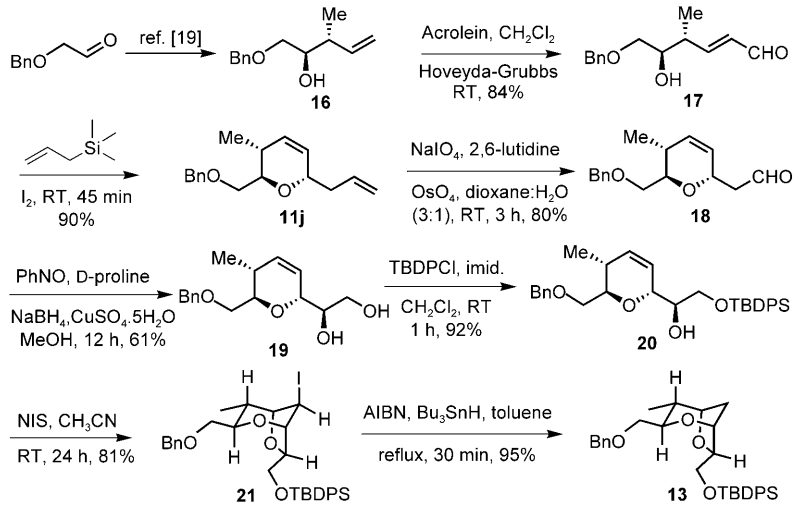
To demonstrate the applicability and generality of our method to complex biologically active natural products syntheses, we were interested in targeting the C28–C37 bicyclic ether core **13** of marine macrolactone (+)-sorangicin A (**12**).[24] The first elegant synthesis of the novel C28–C37 bicyclic ether fragment of **12** was achieved by Smith et al.[24e] and later on by Crimmins et al.[24c] As shown in Scheme 3, we envisioned that **13** would be synthesized from **11j**, which in turn could be prepared from δ-hydroxy α,β-unsaturated aldehyde **17**. Compound **17** could be achieved starting commercially available benzyloxyacetaldehyde.



Scheme 3. Retrosynthetic analysis of (+)-sorangicin A.

We initiated the synthesis of **13** with a known secondary alcohol **16**, which was obtained through asymmetric crotylation of commercially available benzyloxyacetaldehyde in 96% *ee* under conditions originally developed by Brown and Bhat.[25] In order to obtain the unsaturated aldehyde **17**, a cross-metathesis (CM)[20] between **16** and acrolein (6.0 equiv) was achieved using Hoveyda–Grubbs catalyst **16a** (10 mol%) in CH_2Cl_2 at room temperature for 24 h afforded the required aldehyde **17** in 84% yield (Scheme 4). On treatment of **17** with 10 mol% molecular iodine in THF at room temperature gave the *trans*-2,6-disubstituted-3,4-dihydropyran **11j** in 90% yield. One-step conversion of terminal olefin to aldehyde **18** was achieved by modified dihydroxylation followed by oxidative cleavage of the diol in 80% yield over two steps.[26]





Scheme 4. Synthesis of C28-C37 fragment of (+)-sorangicin A.

Table 2. Iodo-etherification under different reaction conditions.

	Reagent[a]	Solvent	T	t [h]	Yield [%][b]
1	I_2	CH_2Cl_2	RT	72	10
2	I_2	THF	RT	72	11
3	I_2	CH_3CN	RT	72	15
4	I_2	CH_2Cl_2	reflux	2	decomp
5	I_2	THF	reflux	1	decomp
6	I_2	CH_3CN	reflux	1	decomp
7	I_2, $NaHCO_3$	CH_2Cl_2	RT	72	15
8	I_2, $NaHCO_3$	THF	RT	72	18
9	I_2, $NaHCO_3$	CH_3CN	RT	72	28
10	NIS	CH_2Cl_2	RT	24	21
11	NIS	THF	RT	24	34
12	NIS	CH_3CN	RT	24	81
13	NIS	PMHS	RT	24	0
14	PhSeCl, DIEA	THF	−78 °C	12	0

[a] Stoichiometric amount was taken. [b] Isolated yields after purification on silica gel.

Direct catalytic asymmetric α-aminoxylation of the resulting aldehyde by using enantiopure proline as the catalyst and nitrosobenzene as the oxygen source and in situ reduction gave the 1,2-diol **19** in 61% yield over three steps.[27]

Selective protection of the primary hydroxyl group as its *tert*-butyldiphenylsilyl (TBDPS) ether yielded **20** in 92% yield. The C36 stereogenic center was confirmed by modified Mosher's method.[28] Treatment of **20** with different iodine source (Table 2) gave unsatisfactory results except with NIS/CH_3CN,[29] which furnished the corresponding iodo-ether derivative **21** as a single regio-isomer in excellent yield (95%). De-iodination was achieved smoothly by treatment of **21** with Bu_3SnH and azobisisobutyronitrile (AIBN) in toluene under reflux conditions to obtain **13** in 94% yield.[30] The product was confirmed by ^1H, ^{13}C NMR and HRMS data. The stereochemistry of the advanced intermediate was ascertained by NOE experiments.

Conclusion

In conclusion, we have described an efficient protocol for the synthesis of *trans*-2,6-disubstituted-3,4-dihydropyran, which is an essential core for a number of complex natural products, from δ-hydroxy α,β-unsaturated aldehyde and allyltrimethylsilane in a highly regio- and stereoselective manner. We have also demonstrated the broad scope of the protocol to the construction of C28–C37 fragment of (+)-sorangicin A in 8 steps with 21% overall yield. Further applications and extensions of the methodology are currently ongoing in our laboratory and will be reported in due time.

Experimental Section

General methods: Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in an oven/flame-dried glassware. All anhydrous solvents were distilled prior to use: THF, toluene, and *tert*-butyl methyl ether from Na and benzophenone; CH_2Cl_2, DMSO from CaH_2; MeOH from Mg cake. Commercial reagents were used without purification. Column chromatography was carried out by using Spectrochem silica gel (60–120 mesh). Specific optical rotations $[\alpha]_D$ are given in 10^{-1} °cm^2g^{-1}. Infrared spectra were recorded in $CHCl_3$/neat (as mentioned) and reported in cm^{-1}. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and coupling constants (J) are reported in Hz. The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

General procedure for iodo cyclization: Iodine (0.1 mmol) was added to a stirred solution of δ-hydroxyl α,β-unsaturated aldehyde (1.0 mmol) and allyltrimethyl silane (2.0 mmol) in THF (3 mL) at 0 °C and allowed to come to room temperature. After completion of the reaction (as indicated by TLC; 30–60 min), the reaction mixture was quenched with saturated solution of $NaHSO_3$ (3 mL). The reaction mixture was extracted with *tert*-butyl methyl ether (TBME) (2 × 10 mL), combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a pale yellow oil, which was purified by silica gel column chromatography using 2–5% ethyl acetate/hexane as eluent to obtain 84–96% of isolated yield of the cyclized product.

Data for 11: $[\alpha]_D^{25} = +103$ (c 0.33 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu} = 3450$, 2922, 2853, 1640, 1613, 1512, 1461, 1363, 1300, 1247, 1177, 1090, 1036, 913, 821, 772, 709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.27$ (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.94–5.79 (m, 2H), 5.72 (m, 1H), 5.15–5.03 (m, 2H), 4.51 (q, J = 11.7, 15.3 Hz, 2H), 4.24 (m, 1H), 3.96 (m, 1H), 3.80 (s, 1H), 3.55 (m, 1H), 3.45 (m, 1H), 2.45 (m, 1H), 2.28 (m, 1H), 2.05–1.98 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 156.0$, 134.8, 129.2, 129.1, 123.8, 116.9, 113.7, 130.5, 73.0, 72.2, 72.3, 67.2, 55.2, 38.9, 27.1 ppm; ESI-HRMS: m/z calcd for $C_{17}H_{22}O_3$ $[M+Na]^+$: 297.1466; found: 297.1465.

Data for 11b: $[\alpha]_D^{25} = +14.2$ (c 0.8 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu} = 3482$, 2925, 2857, 1729, 1612, 1513, 1459, 1367, 1300, 1247, 1178, 1091, 1037, 914, 820, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.27$ (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.86 (m, 1H), 5.70–5.59 (m, 2H), 5.16–5.00

(m, 2H), 4.45–4.38 (m, 2H), 4.16 (m, 1H), 3.81–3.74 (m, 3H), 3.62 (m, 1H), 3.57–3.46 (m, 3H), 3.36–3.26 (m, 3H), 2.41 (m, 1H), 2.26 (m, 1H), 2.00–1.66 (m, 4H), 1.53 (m, 1H), 0.97 ppm (d, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.0$, 135.2, 131, 130.6, 129.2, 127.9, 116.7, 113.7, 74.8, 72.6, 71.5, 71.0, 66.5, 57.0, 55.2, 38.8, 38.8, 34.2, 34.0, 18.0 ppm; ESI-HRMS: m/z calcd for $C_{22}H_{32}O_4$ $[M+Na]^+$: 383.2198; found: 383.2195.

Data for 11c: $[\alpha]_D^{25}=+111$ (c 0.73 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3500$, 2922, 2853, 1641, 1455, 1365, 1104, 997, 738, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.31$–7.21 (m, 5H), 5.94–5.85 (m, 2H), 5.78 (m, 1H), 5.11–5.00 (m, 2H), 4.47 (m, 2H), 4.17 (m, 1H), 4.00 (dt, $J=3.8$, 9.8 Hz, 1H), 3.64–3.43 (m, 5H), 2.34 (m, 1H), 2.19 (m, 1H), 1.96–1.81 (m, 2H), 1.17 ppm (t, $J=6.7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 138.5, 134.7, 132.6, 128.3, 127.6, 127.5, 124.6, 116.9, 72.9, 71.5, 70.6, 68.5, 67, 64.3, 37.3, 29.9, 15.5 ppm; ESI-HRMS: m/z calcd for $C_{19}H_{26}O_3$ $[M+Na]^+$: 325.1779; found: 325.1772.

Data for 11d: $[\alpha]_D^{25}=-34.1$ (c 0.28 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3450$, 2923, 2852, 1726, 1640, 1459, 1375, 1215, 1164, 1084, 1015, 731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=6.11$–6.01 (m, 2H), 5.98 (d, $J=3.8$ Hz, 1H), 5.84 (m, 1H), 5.18–5.09 (m, 2H), 4.59 (d, $J=3.8$ Hz, 1H), 4.36 (m, 1H), 4,27 (m, 1H), 4.14 (d, $J=2.5$ Hz, 1H), 2.14 (m, 1H), 2.29 (m, 1H), 1.52 (s, 3H), 1.33 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=134.8$, 133.9, 120.7, 117.6, 111.4, 105.3, 84.7, 73.5, 72.3, 70.2, 37.0, 26.7, 26.1 ppm; ESI-HRMS: m/z calcd for $C_{13}H_{18}O_4$ $[M+Na]^+$: 261.1102; found: 261.1105.

Data for 11e: $[\alpha]_D^{25}=+90.1$ (c 0.52 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3480$, 2920, 2848, 1645, 1450, 1370, 1112, 997, 739, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.32$–7.21 (m, 5H), 5.98–5.85 (m, 2H), 5.79 (m, 1H), 5.11–5.00 (m, 2H), 4.48 (m, 2H), 4.17 (t, $J=6.0$ Hz, 1H), 4.0 (m, 1H), 3.64–3.50 (m, 3H), 3.35 (s, 3H), 2.35 (m, 1H), 2.20 (m, 1H), 1.93–1.81 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.2$, 143.7, 138.1, 133, 129.6, 128.4, 127.7, 124.4, 84, 73.2, 71.7, 67.8, 60.6, 57.6, 32.3, 14.2 ppm; ESI-HRMS: m/z calcd for $C_{18}H_{24}O_3$ $[M+Na]^+$: 288.1723; found: 325.1775.

Data for 11f: $[\alpha]_D^{25}=-23.7$ (c 0.72 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3100$, 2922, 2853, 1640, 1731, 1513, 1464, 1429, 1360, 1247, 1120, 1036, 990, 825, 770, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.71$–7.67 (m, 4H), 7.42–7.34 (m, 6H), 7.17 (d, $J=8.7$ Hz, 2H), 6.80 (d, $J=8.8$ Hz, 2H), 5.91–5.89 (m, 2H), 5.81 (m, 1H), 5.06 (m, 1H), 5.01 (m, 1H), 4.51 (q, $J=11.7$, 18.5 Hz, 2H), 4.24 (m, 1H), 3.98–3.80 (m, 3H), 3.79 (m, 3H), 2.34 (m, 1H), 2.20 (m, 1H), 1.07 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 166.8, 135.6, 135.2, 134.9, 134.5, 133.7, 129.6, 127.5, 123.6, 117.1, 72.3, 72.1, 69.7, 62.4, 56.6, 37.3, 26.9, 14.3 ppm; ESI-HRMS: m/z calcd for $C_{33}H_{40}O_4Si$ $[M+H]^+$: 528.2690; found: 528.2693.

Data for 11g: $[\alpha]_D^{25}=-24.4$ (c 1.5 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3070$, 2925, 2855, 1731, 1464, 1429, 1255, 1189, 1107, 998, 830, 740, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.73$–7.67 (m, 4H), 7.45–7.34 (m, 6H), 6.04 (m, 1H), 5.94 (m, 1H), 5.82 (m, 1H), 5.11–5.01 (m, 2H), 4.25 (m, 1H), 3.95–3.86 (m, 2H), 3.79 (m, 1H), 3.68 (m, 1H), 3.36 (s, 1H), 2.37 (m, 1H), 2.22 (m, 1H), 1.07 ppm (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=135.6$, 134.9, 134.5, 133.7, 129.6, 127.6, 123.6, 117.1, 72.3, 72.1, 69.7, 62.4, 56.6, 37.3, 26.9,19.3 ppm; ESI-HRMS: m/z calcd for $C_{26}H_{34}O_3Si$ $[M+H]^+$: 422.2275; found: 422.2279.

Data for 11h: $[\alpha]_D^{25}=-42$ (c 0.32 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3110$, 2925, 2853, 1730, 1644, 1460, 1428, 1364, 1255, 1110, 997, 912, 831, 741, 703 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.72$–7.67 (dd, $J=1.5$, 7.7 Hz, 4H), 7.44–7.32 (m, 6H), 7.29–7.26 (m, 5H), 5.97–5.90 (m, 2H), 5.83 (m, 1H), 5.11–5.02 (m, 2H), 4.65–4.54 (q, $J=11.9$, 19.5 Hz, 2H), 4.27 (m, 1H), 4.03–3.83 (m, 4H), 2.36 (m, 1H), 2.22 (m, 1H), 1.08 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=135.6$, 135.5, 134.5, 133.4, 129.6, 129.5, 128.2, 127.7, 127.6, 127.4, 124.1, 117.1, 115.8, 72.5, 71.9, 70.9, 68.1, 62.5, 37.3, 26.9, 19.2 ppm; ESI-HRMS: m/z calcd for $C_{32}H_{38}O_3$ $[M+H]^+$: 498.2591; found: 498.2589.

Data for 11i: $[\alpha]_D^{25}=+53.5$ (c 0.9 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=2921$, 2851, 1742, 1457, 1371, 1232, 1046, 913, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=5.97$–5.77 (m, 3H), 5.18–5.09 (m, 3H), 4.28 (m, 1H), 4.22 (d, $J=6.6$ Hz, 1H), 4.16 (m, 1H), 3.96 (m, 1H), 2.47 (m, 1H), 2.33 (m, 1H), 2.09 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=170.8$, 170.4, 133.9, 132.8, 123.6, 117.5, 71.3, 69.7, 64.9, 62.8, 37.8, 21.0, 20.7 ppm; ESI-HRMS: m/z calcd for $C_{13}H_{18}O_5$ $[M+H]^+$: 254.1152; found: 254.1155.

Data for 11j: $[\alpha]_D^{25}=+6.2$ (c 0.51 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3448$, 2924, 1855, 1729, 1640, 1454, 136, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.4$–7.25 (m, 5H), 5.88 (m, 1H), 5.65 (q, $J=10.4$, 16.8 Hz, 2H), 5.15–5.04 (m, 2H), 4.59 (q, $J=12.3$, 18.9 Hz, 2H), 4.23 (m, 1H), 3.60 (d, $J=4.3$ Hz, 2H), 3.53 (m, 1H), 2.42 (m, 1H), 2.27 (m, 2H), 0.96 ppm (d, $J=7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=138.5$, 134.9, 130.7, 128.3, 128.0, 127.6, 127.5, 116.9, 74.1, 73.3, 71.7, 70.8, 38.9, 30.2, 17.9 ppm; ESI-HRMS: m/z calcd for $C_{17}H_{22}O_2$ $[M+Na]^+$: 258.16198; found: 258.16208.

Data for 11k: $[\alpha]_D^{25}=-20.4$ (c 1.9 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}=3445$, 2920, 2843, 1641, 1610, 1505, 1450, 1358, 1310, 1240, 1172, 1091, 1040, 909, 825, 770, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (d, $J=$ 8.5 Hz, 2H), 6.84 (d, $J=8.7$ Hz, 2H), 5.89–5.75 (m, 2H), 5.68 (m, 1H), 5.11–5.01 (m, 2H), 4.41 (s, 2H), 4.16 (m, 1H), 3.85 (m, 1H), 3.79 (m, 3H), 3.62–3.48 (m, 2H), 2.38 (m, 1H), 2.22 (m, 1H), 1.99–1.91 (m, 2H), 1.8–1.72 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.2$, 135.2, 130.7, 129.3, 129.2, 124.4, 116.7, 113.8, 72.7, 72.3, 66.6, 64.9, 55.2, 38.8, 35.6, 30.7 ppm; ESI-HRMS: m/z calcd for $C_{18}H_{24}O_3$ $[M+H]^+$: 288.1725; found: 288.1731.

(2*R*,3*R*)-1-(Benzyloxy)-3-methylpent-4-en-2-ol (16): *E*-2-Butene (5 mL, excess) was added through a cannula to a stirred suspension of KO*t*Bu (2.5 g, 21.85 mmol) in THF (50 mL) at −78 °C, followed by the drop wise addition of *n*BuLi (15.0 mL, 1.45 M in hexane, 21.75 mmol). The reaction suspension was slowly warmed to −45 °C stirred at this temperature for 15 min and then cooled to −78 °C. A solution of (+)-*B*-methoxydiisopinocampheylborane (7.9 g, 24.95 mmol) in diethyl ether (20 mL) was then added through a cannula over a 15 min period. Stirring was continued for 10 min and boron trifluoride diethyl ether (3.8 mL, 30.0 mmol) added, followed by addition of a pre-cooled solution of **8** (2.34 mL, 16.65 mmol) in diethyl ether (15 mL). After completion of the reaction (checked by TLC), the reaction mixture was warmed to 0 °C and quenched with 2.5 M aqueous solution of NaOH (14 mL) and aqueous solution of hydrogen peroxide (3.75 mL, 33.0 mmol). The reaction mass was refluxed for 1 h. The reaction mixture was then cooled to room temperature, the organic phase separated and washed with Na_2SO_3 (75 mL). The aqueous layer was extracted with ethyl acetate (3×50 mL), the combined organic layer dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using 6–8% ethyl acetate/hexane as eluent to obtain **16** (2.8 g, 82%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.34$–7.26 (m, 5H), 5.81 (m, 1H), 5.08–4.09 (m, 2H) 4.53 (s, 2H), 3.63 (m, 1H), 3.47 (dd, $J=3.2$, 9.4 Hz, 1H) 3.37 (dd, $J=7.5$, 9.2 Hz, 1H), 2.32 (m, 1H), 1.04 ppm (d, $J=6.7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=140.0$, 137.9, 129.5, 128.4, 127.7, 115.5, 73.5, 73.3, 72.5, 40.7, 16.1 ppm.

(4*R*,5*R*)-6-(Benzyloxy)-5-hydroxy-4-methylhex-2-enal (17): Hoveyda–Grubbs catalyst **16a** (288 mg, 0.48 mmol) and acrolein (2.80 g, 49.0 mmol) were added to a solution of **16** (1.0 g, 4.85 mmol) in CH_2Cl_2 (8 mL) and the resulting mixture was stirred at room temperature for overnight. After concentration, the crude oil was purified by flash chromatography on silica gel using 3–5% ethyl acetate: hexane to afford **17** (961 mg, 84%) as a colorless liquid.

2-[(2*S*,5*R*,6*R*)-6-(benzyloxymethyl)-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]acetaldehyde (18): 2,6-Lutidine (3.6 mL, 31.0 mmol) was added to a stirred solution of **11j** (2.0 g, 7.75 mmol) in 1,4-dioxane (25 mL). $NaIO_4$ (6.6 g, 31.0 mmol) was dissolved in distilled water (10 mL) and then added to the reaction mixture. Finally, OsO_4 (0.78 mL, 0.78 mmol, 1 M solution in toluene) was added and stirring was continued in the dark. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched with saturated aq. $NaHSO_3$ (10 mL) solution. Organic solvent was removed under reduced pressure, aqueous layer extracted with *tert*-butyl methyl ether (3×40 mL), the combined organic layer was washed with 1 N HCl (3×50 mL) to remove excess lutidine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a colorless oil, which was purified by silica gel column chromatography using 20% ethyl acetate/hexane as eluent to give aldehyde **18** (1.7 g, 80%) as a colorless liquid. $[\alpha]_D^{25}=-9.8$ (c 0.39 in $CHCl_3$);

IR (KBr, neat): $\tilde{\nu}$ = 3434, 3029, 2962, 2871, 1724, 1453, 1365, 1001 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.39–7.22 (m, 5H), 5.73–5.62 (m, 2H), 4.77 (m, 1H), 4.56 (q, J = 12.3, 14.9 Hz, 2H), 3.61–3.53 (m, 2H), 3.47 (m, 1H), 2.73 (m, 1H), 2.54 (m, 1H), 2.30 (m, 1H), 0.96 ppm (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.9, 138.1, 131.6, 128.2, 127.7, 127.5, 126.6, 74.2, 73.2, 70.2, 67.5, 47.7, 29.8, 17.7 ppm.

(*R*)-1-[(2*R*,5*R*,6i)-6-(Benzyloxymethyl)-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]ethane-1,2-diol (19): Nitrosobenzene (452 mg, 0.423 mmol) followed by D-proline (128 mg, 1.05 mmol) were added to a stirred solution of aldehyde **9** (1.1 g, 4.23 mmol) in dry DMSO (5 mL) under a nitrogen atmosphere and the resulting mixture was stirred the solution turned deep orange. Then the reaction mixture was diluted with methanol (10 mL) and cooled to 0 °C. $NaBH_4$ (160 mg, 4.23 mmol) was added in portions and further stirred for 30 min. At this stage TLC was checked which showed complete disappearance of the starting material. Methanol was removed under reduced pressure and diluted with water (30 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give deep orange syrup, which was dissolved in methanol and stirred overnight with excess $CuSO_4 \cdot 5H_2O$ at room temperature to get the desired diol compound. Again, methanol was removed, water (20 mL) added and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a yellow oil which was purified by silica gel column chromatography using 40% ethyl acetate/hexane as eluent to afford diol **19** (0.72 g, 61%) as a colorless liquid. $[\alpha]_D^{25} = -10.1$ (c 0.42 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}$ = 3421, 2923, 2854, 1724, 1454, 1455, 1099 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.28 (m, 5H), 5.73 (q, J = 10.2, 11.9 Hz, 2H), 4.61–4.54 (m, 1H), 4.20 (m, 1H), 3.85–3.48 (m, 6H), 2.2 (m, 1H), 0.96 ppm (d, J = 6.98 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.9, 128.4, 127.7, 127.7, 124.1, 75.2, 73.7, 73.4, 72.1, 70.8, 63.3, 30.2, 17.5 ppm; ESI-HRMS: m/z calcd for $C_{16}H_{23}O_4$ $[M+H]^+$: 278.15181; found: 278.15083.

(*R*)-1-[(2*R*,5*R*,6*R*)-6-(Benzyloxymethyl)-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]-2-(*tert*-butyldiphenylsilyloxy)ethanol (20): Imidazole (220 mg, 3.2 mmol) and TBDPSCl (450 mg, 1.6 mmol) were added to a stirred solution of diol **19** (450 mg, 1.6 mmol) in CH_2Cl_2 (15 mL), and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with water (15 mL) and the water layer was washed with CH_2Cl_2 (2 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a colorless oil, which was purified by silica gel column chromatography with 5% ethyl acetate/hexane as eluent to yield alcohol **20** (750 mg, 92%) as a colorless liquid. $[\alpha]_D^{25} = +3.2$ (c 0.48 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}$ = 3440, 2928, 2857, 1721, 1459, 1427, 1384, 1273, 1110, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.65 (m, 4H), 7.44–7.25 (m, 11H), 5.71–5.66 (m, 2H), 4.58 (q, J = 12.1, 21.2 Hz, 2H) 4.29 (m, 1H), 3.86–3.72 (m, 3H), 3.60–3.53 (m, 2H), 2.29 (m, 1H), 1.06 (s, 9H), 0.93 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.5, 132.3, 129.6, 128.2, 127.5, 124.5, 74.7, 73.2, 72.8, 72.6, 70.5, 64.6, 30.0, 26.7, 17.5, 19.1 ppm; ESI-HRMS: m/z calcd for $C_{32}H_{40}O_4Si$ $[M+Na]^+$: 539.2593; found: 539.2610.

(1*S*,3*R*,4*S*,5*S*,7*R*,8*R*)-3-(Benzyloxymethyl)-7-ethyl-8-iodo-4-methyl-2,6-dioxabicyclo[3.2.1]octane (21): NIS (360 mg, 1.3 mmol) was added to a stirred solution of the alcohol **20** (550 mg, 1.1 mmol) in dry CH_3CN (10 mL) under a nitrogen atmosphere, and the resulting mixture was stirred in the dark for 24 h. The reaction mixture was quenched with saturated $NaHSO_3$ (5 mL). Acetonitrile was removed under reduced pressure and the water layer was washed with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a colorless oil, which was purified by silica gel column chromatography by using 3% ethyl acetate/hexane as eluent to give **21** (572 mg, 81%) as a light yellow solid. $[\alpha]_D^{25} = +2.4$ (c 0.41 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}$ = 3448, 3067, 2925, 2855, 1638, 1461, 1427, 1365, 1111, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.67 (m, 4H), 7.43–7.25 (m, 11H), 4.57 (s, 2H), 4.30–4.25 (m, 2H), 4.21 (m, 1H), 4.12 (br d, J = 5.9 Hz, 1H), 4.04 (m, 1H), 3.93 (m, 1H), 3.63 (m, 1H), 3.56–3.48 (m, 2H), 2.35 (m, 1H), 1.04 (s, 9H), 0.81 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3, 135.6, 133.1, 129.7, 128.2, 127.7, 127.6, 127.4, 80.9, 80.3, 77.1, 73.3, 71.7, 61.5, 33.3, 29.7, 26.7, 19.1, 15.8 ppm; ESI-HRMS: m/z calcd for $C_{32}H_{39}O_4SiI$ $[M+Na]^+$: 665.1560, found: 665.1571.

(1*S*,3*R*,4*S*,5*S*,7*R*,8*R*)-3-(Benzyloxymethyl)-7-ethyl-4-methyl-2,6-dioxabicyclo[3.2.1]octane (13): AIBN (5 mg) was added to a stirred solution of **21** (40 mg, 0.062 mmol) in dry toluene (3 mL), and the resulting mixture was heated under reflux under a nitrogen atmosphere. Then Bu_3SnH (0.034 mL, 0.124 mmol) was added to the reaction mixture under refluxed conditions. After completion of the reaction (monitored by TLC), toluene was removed under reduced pressure and the crude mass directly loaded on silica gel, which on purification with 5% ethyl acetate/hexane afforded **13** (31 mg, 95%) as a colorless liquid. $[\alpha]_D^{25} = -22$ (c 0.29 in $CHCl_3$); IR (KBr, neat): $\tilde{\nu}$ = 3463, 2923, 2852, 1644, 1464, 1370, 1262, 1221, 1129, 1091, 1020, 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.67 (m, 4H), 7.4–7.28 (m, 11H), 4.63–4.45 (m, 3H), 4.23 (d, J = 6.6 Hz, 1H), 4.10 (m, 1H), 4.03–3.9 (m, 2H), 3.53–3.38 (m, 3H), 2.02 (m, 1H), 1.86 (d, J = 11.5 Hz, 1H), 1.66 (m, 1H), 1.05 (s, 9H), 0.81 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.6, 133.5, 129.6, 128.3, 127.6, 127.6, 127.5, 83.4, 79.2, 77.4, 74.6, 73.2, 71.2, 61.7, 38.2, 37.1, 29.9, 26.8, 19.1, 15.7 ppm; ESI-HRMS: m/z calcd for $C_{32}H_{40}O_4Si$ $[M+Na]^+$: 534.3029; found: 534.3032.

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