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An efficient cis-reduction of alkyne to alkene in the presence of a vinyl iodide: stereoselective synthesis of the C22–C31 fragment of leiodolide A

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ABSTRACT

Rapid and efficient reduction of alkyne bond in the presence of a vinyl iodide is established using freshly prepared Brown's P2-Ni as the catalyst, affording the semihydrogenated alkene products in good to excellent yields (73–91%). Based on this new method, a stereoselective synthesis of the key C22–C31 fragment of marine macrolide leiodolide A has been developed.

1. Introduction

Vinyl iodides, with well-defined geometry structures, have been widely used as important building blocks in organic natural product synthesis, owing to the valuable application of the transition-metal catalyzed cross-coupling reactions, such as Heck, Sonogashira, and Suzuki–Miyaura reactions, et al.[1,2] Efficient methods for the preparation of stereodefined vinyl iodide structures, employing as synthons in C–C bond formation, have been investigated through introducing the iodide at the very end reaction sequence.[3] Very few studies have been made regarding the stability and compatibility of vinyl iodide in functional group modification and transformation.[4] It is generally believed that vinyl iodide could not survive under most of the common reduction conditions, leading to the corresponding olefin or saturated carbon–carbon bond, instead. To our best knowledge, the only example of cis-reduction of propargyl alcohol bearing a vinyl iodide was reported by Parker in his synthesis of discodermolide.[4a] Herein we report the stereoselective synthesis of the C22–C31 fragment of leiodolide A employing a diastereoselective Seebach alkylation and a Brown's P2-Ni catalyzed alkyne semihydrogenation in the presence of a vinyl iodide.

Leiodolide A (Fig. 1) is a marine natural product originally isolated from the deep-water marine sponge *Leiodermatium* by Fenical and co-workers in 2006.[5] Preliminary biological testing indicated that leiodolide A exhibited significant cytotoxic activity in the NCI 60 tumor cell line assay, with enhanced activity against HL-60 leukemia and OVCAR-3 ovarian cancer cells. The promising biological activities as well as densely functionalized structures have prompted some efforts toward leiodolide synthesis.[6]

To provide sufficient material for further biological studies, as well as to assign the absolute configuration at C13, we initiated a study toward the total synthesis of leiodolide A and its derivatives. Due to the structural complexity of the leiodolide A, our

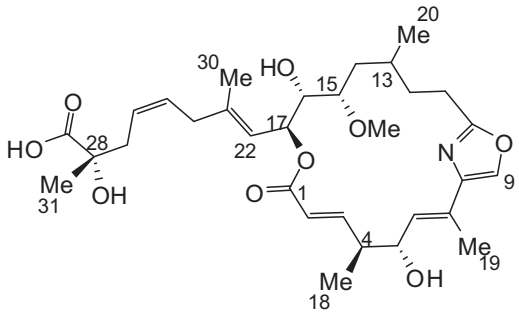

Fig. 1. Proposed structure of leiodolide A.

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synthetic approach involves the synthesis of three distinct fragments (C1–C10, C11–C17, and C22–C31) with strategic bond disconnections (Fig. 2). In this report, we describe a convenient strategy for the stereoselective synthesis of fragment C22–C31 (**3**), the α-hydroxy-α-methyl carboxylic acid side-chain, based on our new methodology. Thus, precursor **3** could be achieved via a diastereoselective alkylation of the Seebach's dioxolanone[7] **4** with a propargylic bromide **5** derived from propargyl alcohol. The key transformation in this synthetic strategy was a semihydrogenation of the C25–C26 internal acetylene.

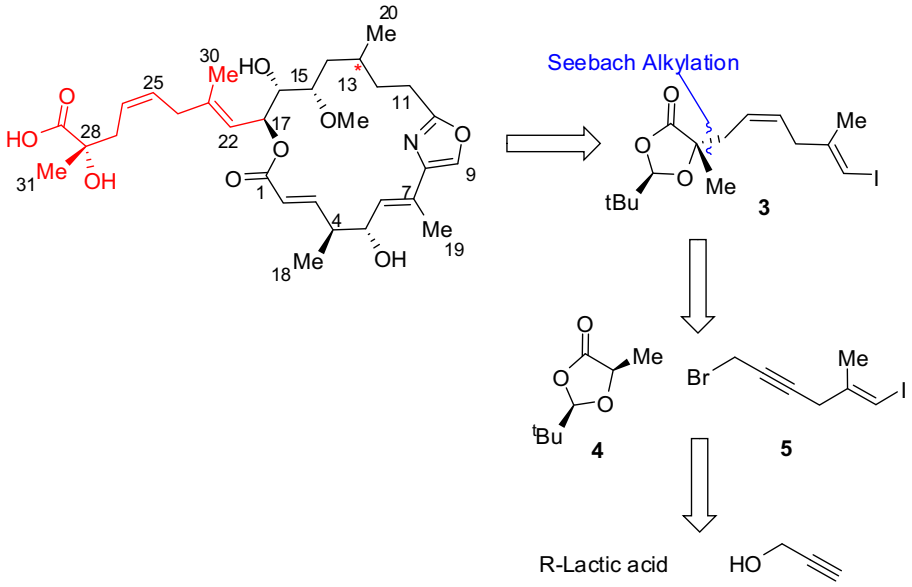


Fig. 2. Retrosynthetic analysis of leiodolide A (**1**).

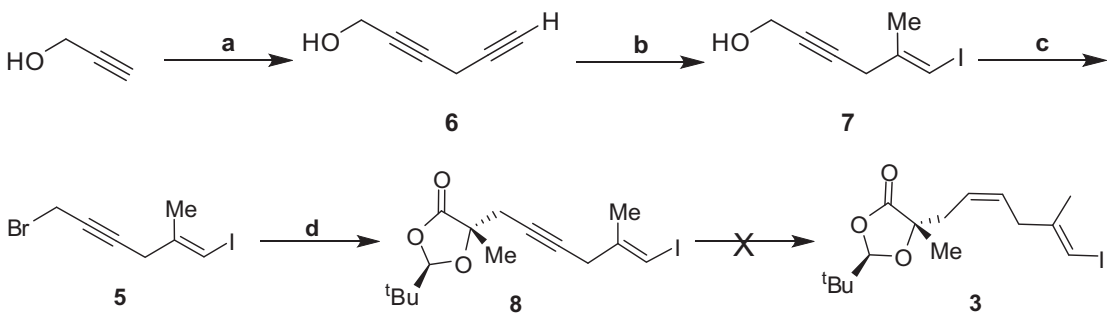
2. Results and discussion

The synthesis of the fragment C22–C31 of leiodolide A is outlined in Scheme 1. The diyne **6**[8] was prepared in a moderate yield by means of copper-mediated cross-coupling reaction between the commercially available propargyl alcohol and propargyl bromide.[9] Selective carboalumination of the terminal alkyne followed by quenching with iodine afforded vinyl iodide **7** as a single isomer in 65% yield.[10] The hydroxyl group of **7** was converted into the bromide **5** with PPh_3/CBr_4 in dichloromethane. Subsequent treatment of Seebach's (*R*)-lactic acid-derived dioxolanone **4** with LDA at −90 °C followed by the addition of propargyl bromide **5** furnished compound **8** in 85% yield and greater than 20:1 dr according to the crude NMR.[7] The absolute stereochemistry of the newly formed quaternary carbon was assigned as (*S*)-configuration based on literature precedent.[7a]

With the efficient access to vinyl iodide **8**, we next examined the semihydrogenation of triple bond under Lindlar reduction condition.[11] However, the envisaged partial hydrogenation of the alkyne **8** in the presence of vinyl iodide, turned out to be more difficult than we expected. Exposure of **8** to hydrogen gas in the presence of Lindlar catalyst with or without quinoline only resulted in the recovery of most starting material and some decomposition of the substrate due to hydrogenolysis of the vinyl iodide.

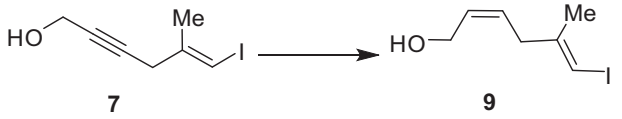
To circumvent this problem, we chose the more easily available alcohol **7** as a suitable model compound, and its semihydrogenation was investigated under a variety of different reaction conditions (Table 1).

Treatment of **7** with 1 atm of hydrogen gas in the presence of Lindlar catalyst with a catalytic amount of quinoline in ethyl acetate or methanol resulted in the recovery of starting material (entries 1 and 2). Attempts to semi-reduce the triple bond in the absence of quinoline also failed and only returned alcohol **7** (entries 3 and 4). Literature searching revealed that the reduction of propargyl alcohol to *cis*-allylic alcohol, in the presence of a vinyl iodide, could be carried out at H_2 atmosphere using $Pd/CaCO_3$ in hexane.[4a] To our depressing, hydrogenation under this condition, or at H_2 pressures as high as 4 atm, also resulted in the recovered starting material



Scheme 1. Attempted synthesis of compound **3**: (a) propargyl bromide, Et_3N, CuI, DMF, Et_2O, 54%; (b) $ZrCp_2Cl_2$, $AlMe_3$, DCM, room temperature, then I_2, Et_2O, 0 °C, 65%; (c) CBr_4, PPh_3, DCM, 0 °C, 89%; (d) **4**, LDA, THF, −90 °C, 10 min, then **5**, −78 °C, 2 h, 85%.

Table 1
Screening the semihydrogenation conditions of alkyne in the presence of vinyl iodide



7 9

Entry	Conditions	Product	Yield (%)
1	Lindlar catalyst,[b] quinoline, ethyl acetate, H_2 (1 atm), 5 h	—	ND[c]
2	Lindlar catalyst, quinoline, methanol, H_2 (1 atm), 5 h	—	ND
3	Lindlar catalyst, ethyl acetate, H_2 (1 atm), 5 h	—	ND
4	Lindlar catalyst, methanol, H_2 (1 atm), 5 h	—	ND
5	Pd/$CaCO_3$, hexane, H_2 (1 atm), 10 h	—	ND
6	Pd/$CaCO_3$, hexane, H_2 (4 atm), 10 h	—	ND
7	Zn,[d] MeOH/H_2O, 30 °C, 4 h	—	ND
8	Zn, 1,2-dibromoethane, EtOH, reflux, 4 h	—	ND
9	P2-Ni,[e] EtOH, H_2 (1 atm), 10 h	**9**	42[a]
10	P2-Ni,[f] EtOH, H_2 (1 atm), 4 min	**9**	77[a]

[a] Isolated yield.
[b] Approximately 5% Pd/$CaCO_3$, poisoned with lead.
[c] No desired product.
[d] The Zn dust was activated by stirring it in a 0.1 M HCl solution for ca. 15 min.
[e] $Ni(OAc)_2 \cdot 4H_2O$ (0.5 equiv), $NaBH_4$ (0.5 equiv), and ethylenediamine (0.2 equiv) were used at room temperature.
[f] $Ni(OAc)_2 \cdot 4H_2O$ (3.0 equiv), $NaBH_4$ (3.0 equiv), and ethylenediamine (1.2 equiv) were used at room temperature.

(entries 5 and 6). We felt that the conventional methods using poisoned heterogeneous Pd-catalysts may not work for this semihydrogenation. So we turned our efforts to other metal catalysts, such as activated zinc in methanol/H_2O[12a] or Zn/$BrCH_2CH_2Br$ system,[12b] but failed to generate the desired products (entries 7 and 8).

After considerable experimentation, to our delight, the partial reduction was finally achieved and afforded the clean cis-reductive product in moderate yield (42%) with 0.5 equiv of Brown's P2-Ni catalyst,[13] which is generated in situ by reduction of nickel acetate with sodium borohydride in anhydrous ethanol. It is worth noting that the loading amount of P2-Ni catalyst is critical to the reaction. If the amount was less than 1.0 equiv, the yield could not be improved significantly even at prolonged reaction time. By adding over 2.5 equiv of catalyst, we observed the good yields (72–77%) and shorten reaction time (2–10 min) during screening the suitable reaction conditions. The reaction conditions were eventually optimized and set to 3.0 equiv freshly prepared P2-Ni as the catalyst, anhydrous ethanol as the solvent, and the reaction could proceed at room temperature.

To investigate the reaction scope, we further expanded the method to other substrates under the optimized conditions (Table 2). As expected, TBS and Bz groups were compatible to the reaction conditions, and partial hydrogenation of the protected propargyl alcohols **10** and **12**, in the presence of vinyl iodide, was achieved with excellent selectivity and high yields (entries 2 and 3). It was found that electron-donating substituent (TBS) at the hydroxyl group favored product formation, whereas an electron-withdrawing group (Bz) hindered product formation and took much longer reaction time. In addition, the terminal alkyne **14** could be reduced to the terminal alkene **15** in good yield (entry 4). The disubstituted vinyl iodide **16** also provided the corresponding alkene **17** in 81% yield (entry 5). It is interesting to note that, for the 1,4-diyne **18**, terminal alkene intermediate **19** could be trapped cleanly under our partial reduction conditions (entry 6), whereas, 1,4-diene **20** was generated with much longer reaction time (entry 7). Entries 6 and 7 also suggest the possibility of selectively obtaining terminal alkene for partial reduction of diyne by using Brown's P2-Ni as the catalyst. To our delight, the reaction proceeded smoothly to afford the designed product even in a large scale (entry 1, **7**→**9**, 1.0 mmol) and no over-reduction product was observed.[14] Finally, the partial reduction of the alkyne **8** under optimized conditions, in 3 min, accomplished the synthesis of the target fragment C22–C31 **3** in 79% yield (entry 8). In all cases studied here, the *cis*-olefins were formed cleanly without any detectable over-reduction products. The current results clearly demonstrate the potential usage of this method to structurally related natural product synthesis.

3. Conclusion

A practical method for the cis-reduction of alkyne to alkene has been developed employing Brown's P2-Ni as the catalyst. This new approach allows the presence of vinyl iodide in the reduction substrates. Based on this finding, a successful stereoselective synthesis of the key C22–C31 fragment of the marine macrolide leiodolide A has been achieved in five steps from propargyl alcohol with 21% overall yield. The completion of natural leiodolide A synthesis is currently underway in our laboratory.

4. Experimental section

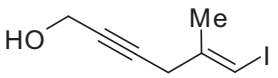
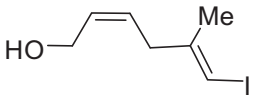
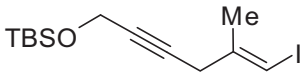
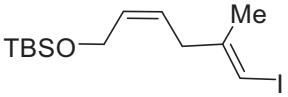
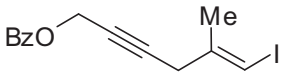
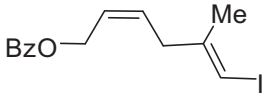
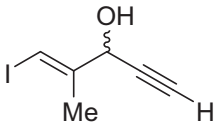
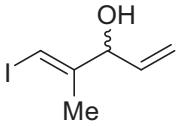
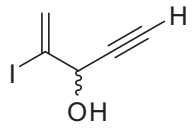
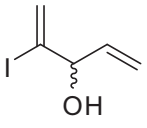
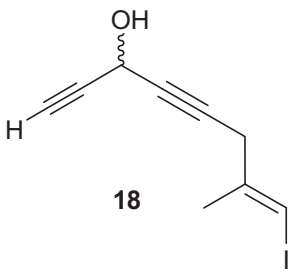
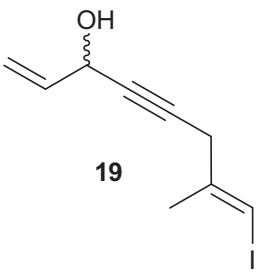
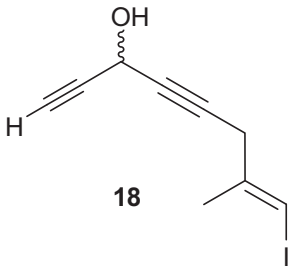
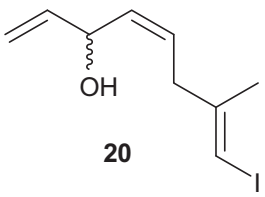
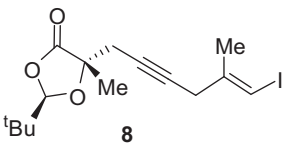
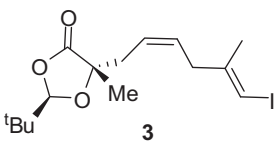
4.1. General experimental

All reactions were performed under a nitrogen atmosphere and solvents were dried according to the established procedures ahead of use. All reagents were purchased from commercial corporations. Flash chromatography (FC) was performed using E Merck silica gel 60 (240–400 mesh). All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. Optical rotations were recorded on a polarimeter. Infrared spectra were recorded on a *Perkin–Elmer 1000* series FTIR with wave numbers expressed in cm^{-1} using samples prepared as thin films between salt plates. HRMS were measured with mass spectrometer. ^1H NMR and ^{13}C NMR were measured on 400 MHz spectrometers (NMR in $CDCl_3$ with TMS as an internal standard). Chemical shifts (δ) are given in parts per million relative to residual solvent (usually chloroform; δ 7.26 for ^1H NMR or 77.23 for proton decoupled ^{13}C NMR), and coupling constants (J) in hertz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet, whereby the prefix *app* is applied in cases where the true multiplicity is unresolved, and *br* when the signal in question is broadened.

*4.1.1. Hexa-2,5-diyn-1-ol (**6**).* To a solution of propargyl alcohol (50 mg, 0.893 mmol) in Et_2O (0.6 mL) and DMF (0.2 mL) at room temperature were added CuI (170 mg, 0.893 mmol) and Et_3N (90 mg, 0.893 mmol). After 5 min, a solution of propargyl bromide (105 mg, 0.893 mmol) in Et_2O (0.4 mL) was added, and the reaction mixture was stirred vigorously for 3.5 h. Then the mixture was treated with satd NH_4Cl solution (0.5 mL). The crude reaction mixture was filtered through a Celite pad and the organic layer was removed under reduced pressure and extracted with Et_2O (3×20 ml). The combined organic layers were washed with aqueous brine, dried over Na_2SO_4, and concentrated under vacuum. The crude was purified by FC (silica gel, hexanes/EtOAc 6:1) to give known compound **6** as a light yellow oil (45 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$) δ: 4.25 (t, J=2.0, 2H), 3.21 (dd, J=2.0, 4.8, 2H), 2.08 (t, J=2.8, 1H), 1.95 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.2, 79.1, 77.8, 69.1, 51.1, 9.6; IR (film, cm^{-1}): 3290, 2291, 2227, 2126.

*4.1.2. (E)-6-Iodo-5-methylhex-5-en-2-yn-1-ol (**7**).* To a solution of bis(cyclopentadienyl)zirconium dichloride (565 mg, 1.934 mmol) in dry DCM (7 mL) at 0 °C was added $AlMe_3$ (6.286 mmol, 6.5 equiv) dropwise. After stirring for 45 min at room temperature, alkyne **6** (91 mg, 0.967 mmol) in DCM (1.5 ml) was added dropwise. The reaction mixture was stirred at room temperature for 30 h and then cooled to 0 °C, followed by the addition of iodide (828 mg,

Table 2
Semihydrogenation of alkynes in the presence of vinyl iodide using P2-Ni catalyst

Entry	Substrate	Product[a]	Time (min)	Yield (%)[b]
1	 **7**	 **9**	4	77
2	 **10**	 **11**	2	91
3	 **12**	 **13**	5	73[c]
4	 **14**	 **15**	2	73
5	 **16**	 **17**	5	81
6	 **18**	 **19**	3	75
7	 **18**	 **20**	>15	83
8	 **8**	 **3**	3	79

[a] Unless otherwise noted, $Ni(OAc)_2 \cdot 4H_2O$ (3.0 equiv), $NaBH_4$ (3.0 equiv), and ethylenediamine (1.2 equiv) were used at room temperature.
[b] Isolated yield. *Caution*: most compounds above need handle with care for their low boiling point.
[c] Starting material of 21% was recovered.

3.259 mmol) in dry Et_2O. The resulting mixture was allowed to warm to room temperature and stirred for 1.5 h. The reaction was quenched by the careful addition of satd $Na_2S_2O_3$ solution, and the resulting mixture was filtered through a Celite pad and the aqueous layer was extracted with DCM (3×20 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude was purified by FC (silica gel, hexanes/EtOAc 5:1) to give compound **7** as a colorless oil (148 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.26 (s, 1H), 4.28 (s, 2H), 3.10 (d, J=1.6, 2H), 1.90 (s, 3H), 1.66 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 81.9, 81.6, 77.2, 51.3, 28.6, 23.8; IR (film, cm^{-1}): 2289, 2213, 1668, 1627, 1271, 1012; EI-HRMS calcd for C_7H_9IO, 235.9698; found: 235.9701 ([M]$^+$).

*4.1.3. (E)-6-Bromo-1-iodo-2-methylhex-1-en-4-yne (**5**).* To a solution of **7** (39 mg, 0.165 mmol) and CBr_4 (72 mg, 0.215 mmol) in dry DCM (2 mL) at 0 °C under N_2 protection, was added PPh_3 (65 mg, 0.248 mmol) portionwise. After 15 min, the solution was warmed to room temperature and stirred for another 1 h. The solvent was removed in vacuum and the crude was purified by FC (silica gel, hexanes) to give compound **5** as a light yellow oil (43 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.26 (s, 1H), 3.93 (t, J=2.4, 2H), 3.12 (d, J=1.6, 2H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 83.4, 77.5, 77.2, 28.7, 23.8, 14.9; IR (film, cm^{-1}): 2233, 1632, 1208, 1130, 611, 565; EI-HRMS calcd for C_7H_8BrI, 297.8854; found: 297.8859 ([M]$^+$).

*4.1.4. (2R,5S)-2-tert-Butyl-5-((E)-6-iodo-5-methylhex-5-en-2-ynyl)-5-methyl-1,3-dioxolan-4-one (**8**).* To a solution of diisopropylamine (44 mg, 0.430 mmol) in THF (1 mL) at −60 °C was added *n*-BuLi (0.173 mL, 0.415 mmol, 2.4 M in hexanes) dropwise. The solution was warmed to −10 °C over 1 h and then recooled to −90 °C. Next, a solution of dioxolanone **4** (66 mg, 0.415 mmol) in THF (1 mL) was added slowly down the walls of the flask for precooling. The reaction mixture was stirred at −90 °C for 10 min and then the bromide **5** (40 mg, 0.134 mmol) was added dropwise. The reaction mixture was warmed slowly to −10 °C over 2 h and then quenched with satd aqueous NH_4Cl (1 mL). The aqueous layer was extracted with EtOAc (3×20 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude was purified by FC (silica gel, hexanes/EtOAc 20:1) to give compound **8** as a pale yellow oil (42 mg, 85%). $[\alpha]_D^{20}$ −10.2 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.25 (s, 1H), 5.37 (s, 1H), 3.03 (s, 2H), 2.70–2.57 (m, 2H), 1.89 (s, 3H), 1.48 (s, 3H), 0.96(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 142.0, 109.5, 79.4, 79.0, 77.2, 77.1, 34.6, 28.7, 27.8, 23.7, 23.3, 23.1; IR (film, cm^{-1}): 2964, 2218, 1799, 1694, 1632, 1485, 1175, 1146, 1077, 983; EI-HRMS calcd for $C_{15}H_{21}IO_3$, 376.0535; found: 376.0540 ([M]$^+$).

4.2. General experimental procedure for the partial hydrogenation

To a solution of nickel acetate tetrahydrate (72 mg, 0.289 mmol) in EtOH (2 mL) was added a solution of sodium borohydride (11 mg, 0.289 mmol) in EtOH (0.5 mL) quickly. The solution was stirred for 30 min and then added ethylenediamine (7.5 μL, 0.115 mmol) followed by addition of alkyne (0.096 mmol) dissolved in EtOH (0.2 mL). The reaction mixture was stirred under 1 atm of hydrogen for a few minutes (2–5 min) and then removed the hydrogen tube. The reaction was monitored by TLC. Upon transformation of the starting material, water was added. The mixture was extracted with EtOAc, and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude was purified by FC (silica gel) to give the designed product.

*4.2.1. (2Z,5E)-6-Iodo-5-methylhexa-2,5-dien-1-ol (**9**).* Compound **9** was prepared in 77% yield after purification according to the general procedure as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.95 (s, 1H), 5.75 (dt, J=6.4, J=11.2, 1H), 5.54 (dt, J=7.6, J=10.8, 1H), 4.21 (d, J=6.4, 2H), 2.97 (d, J=7.6, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 130.8, 128.5, 75.9, 58.4, 37.1, 24.1; IR (film, cm^{-1}): 3336, 2920, 2850, 1028, 766, 666; EI-HRMS calcd for $C_7H_{11}IO$, 237.9855; found: 237.9860 ([M]$^+$).

*4.2.2. tert-Butyl-(2Z,5E)-6-iodo-5-methylhexa-2,5-dienyloxy)dimethylsilane (**11**).* Compound **11** was prepared in 91% yield after purification according to the general procedure as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.93 (s, 1H), 5.66 (dt, J=6.0, J=11.2, 1H), 5.42 (dt, J=7.6, J=11.2, 1H), 4.22 (d, J=6.0, 2H), 2.93 (d, J=7.2, 2H), 1.83 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 132.0, 126.4, 75.7, 59.2, 37.3, 25.9, 24.1, 18.3, −5.2; IR (film, cm^{-1}): 2954, 2929, 2856, 1661, 1254, 1101, 776, 667; HRMS (EI) peaks and HRMS (ESI$^+$) peaks due to [M+H]$^+$ or [M+Na]$^+$ were not detected.

*4.2.3. (2Z,5E)-6-Iodo-5-methylhexa-2,5-dienyl benzoate (**13**).* Compound **13** was prepared in 73% yield (recovered 20% SM) after purification according to the general procedure as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05–8.03 (m, 2H), 7.58–7.52 (m, 1H), 7.46–7.42 (m, 2H), 6.00 (s, 1H), 5.83 (dt, J=6.8, J=11.2, 1H), 5.42 (dt, J=7.6, J=10.8, 1H), 4.87 (d, J=6.8, 2H), 3.07 (d, J=7.6, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.5, 133.0, 131.1, 130.1, 129.6, 128.4, 125.9, 76.2, 60.3, 37.3, 24.1; IR (film, cm^{-1}): 2923, 1717, 1601, 1584, 1451, 768, 711; HRMS (EI) peaks and HRMS (ESI$^+$) peaks due to [M+H]$^+$ or [M+Na]$^+$ were not detected.

*4.2.4. (E)-1-Iodo-2-methylpenta-1,4-dien-3-ol (**15**).* Compound **15** was prepared in 73% yield after purification according to the general procedure as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.40 (s, 1H), 5.86–5.78 (m, 1H), 5.35–5.21 (m, 2H), 4.67 (d, J=5.6, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 137.8, 116.5, 78.9, 78.2, 20.3; IR (film, cm^{-1}): 3398, 2955, 2918, 1462, 1377; EI-HRMS calcd for C6H9IO, 223.9698; found: 223.9701 ([M]$^+$).

*4.2.5. 2-Iodopenta-1,4-dien-3-ol (**17**).* Compound **17** was prepared in 81% yield after purification according to the general procedure as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.45–6.44 (m, 1H), 5.92 (d, J=1.6, 1H), 5.84 (ddd, J=5.2, J=10.4, J=15.6, 1H), 5.42 (dt, J=1.2, 17.2, 1H), 5.33 (dt, J=1.2, 10.4, 1H), 4.37 (s, 1H), 1.56 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 125.9, 117.5, 115.7, 78.5; IR (film, cm^{-1}): 3405, 3081, 2924, 2854, 1640, 1631, 1082, 1038, 990, 910; HRMS (EI) peaks and HRMS (ESI$^+$) peaks due to [M+H]$^+$ or [M+Na]$^+$ were not detected.

*4.2.6. (E)-8-Iodo-7-methylocta-1,7-dien-4-yn-3-ol (**19**).* Compound **19** was prepared in 75% yield (recovered 25% SM) after purification according to the general procedure as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.25 (s, 1H), 5.97 (ddd, J=5.2, 10.0, 15.2, 1H), 5.44 (d, J=17.2, 1H), 5.22 (d, J=10.4, 1H), 4.89 (dd, J=1.2, 3.6, 1H), 3.12 (s, 2H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.2, 116.4, 82.5, 82.2, 77.2, 63.4, 28.6, 23.8; IR (film, cm^{-1}): 3359, 3065, 2914, 2878, 2247, 2210, 1643, 1416, 1378, 928; EI-HRMS calcd for $C_9H_{11}IO$, 261.9855; found: 261.9858 ([M]$^+$).

*4.2.7. (4Z,7E)-8-Iodo-7-methylocta-1,4,7-trien-3-ol (**20**).* Compound **20** was prepared in 83% yield after purification according to the general procedure as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.96 (s, 1H), 5.89 (ddd, J=6.0, 10.4, 16.8, 1H), 5.58–5.49 (m, 2H), 5.26 (d, J=17.6, 1H), 5.14 (d, J=10.4, 1H), 4.94–4.93 (m, 1H), 3.00 (d, J=6.0, 2H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 139.2, 132.7, 128.1, 115.1, 76.1, 68.9, 37.3, 24.1; IR (film, cm^{-1}): 3364, 3066, 2964, 2878, 1642, 1619, 987, 926, 765, 669; EI-HRMS calcd for $C_9H_{13}IO$, 264.0011; found: 263.9898 ([M]$^+$).

*4.2.8. (2R,5S)-2-tert-Butyl-5-((2Z,5E)-6-iodo-5-methylhexa-2,5-dienyl)-5-methyl-1,3-dioxolan-4-one (**3**).* Compound **3** was prepared in 79% yield after purification according to the general procedure as a pale yellow oil. $[\alpha]_D^{20}$ −13.5 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ: 5.93 (s, 1H), 5.65–5.56 (m, 2H), 5.18 (s, 1H), 2.95 (d, *J*=5.2, 2H), 2.55–2.45 (m, 2H), 1.84 (s, 3H), 1.44 (s, 3H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 145.8, 130.6, 124.2, 108.8, 79.9, 75.8, 37.0, 34.6, 34.2, 24.2, 23.3, 23.0; IR (film, cm^{-1}): 2963, 1798, 1682, 1632, 1485, 1172, 1140, 1078, 983, 793, 768; EI-HRMS calcd for $C_{15}H_{23}IO_3$, 378.0692; found: 378.0697 ($[M]^+$).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.008.

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