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Enantioselective total synthesis of (+)-sarcandralactone A

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ABSTRACT

An enantioselective total synthesis of the lindenane sesquiterpene (+)-sarcandralactone A has been accomplished for the first time. The synthesis features a SeO_2-mediated [2,3]-sigmatropic rearrangement for the facile construction of the tertiary allylic alcohol as a single diastereoisomer.

1. Introduction

The plants of the Chloranthaceae family are rich sources of lindenane sesquiterpenoids and oligomers, which have attracted considerable interest due to the diverse structures and significant biological activities, such as antifungal, cytotoxicity, and inhibition of cell adhesion expression.[1] Considering the promising bioactivity and the structural complexity, a couple of synthetic efforts toward the syntheses of these compounds have been reported.[2] For example, Liu and co-workers have disclosed a racemic total synthesis of chloranthalactone A employing Hodgson cyclopropanation to construct the congested cis-, trans-3/5/6 tricyclic skeleton.[2d] Then, an asymmetric total synthesis of chloranthalactone F, along with shizukanolide, chloranthalactone A, and lindenene, was accomplished in our group,[2f] which was highlighted by a hydroxyl-directed cyclopropanation and a cascade oxidative lactonization. As a continued work on the synthetic studies of this family terpenoids of, we describe herein the efforts on the total synthesis of sarcandralactone A (**1**), which was isolated from the plant *Sarcandra glabra* by Yue's group in 2010.[3] Based on the previous work in our group, the retrosynthetic analysis is shown in Scheme 1. Horner–Wadsworth–Emmons olefination and oxidative lactonization would afford the unsaturated lactone moiety, and subsequent unusual SeO_2-mediated [2,3]-sigmatropic rearrangement[4] could deliver the tertiary allylic alcohol at C5 (Scheme 1).

2. Results and discussion

In our previous work,[2f] the Horner–Wadsworth–Emmons olefination at C7 (Scheme 1) with a low stereoselectivity in the presence of the exocyclic methylene part at C4 to give a mixture of unsaturated esters. To improve the stereoselectivity of the olefination, a substrate-controlled strategy was proposed. In considering of taking full advantage of the structural characters, introduction of the bulky group through functionalization of the exocyclic methylene would be beneficial to favorites the formation of the desired (*E*)-isomer. Practically, as outlined in Scheme 2, starting from the available intermediate ketal **3**, hydroboration[5] of the exocyclic methylene with 9-BBN followed by oxidation in the presence of $NaOH/H_2O_2$ afforded the primary alcohol **5** in 95% yield as a single stereoisomer. The excellent diastereoselectivity might be ascribed to the steric hindrance from the congested cyclopentane. Subsequent protecting group transformation for the synthesis of naked ketone **7** was achieved by way of hydroxyl ketone **6**. Upon treatment of alcohol **5** with $FeCl_3 \cdot SiO_2$ led to the hydroxyl ketone **6** in a 97% yield with no trace of any dehydrated byproducts. Under the condition of TBSCl/imidazole/DMF, silylation of the resulting primary alcohol proceeded smoothly to give ketone **7** in quantitative yield, the absolute configuration of which was determined by extensive nuclear magnetic resonance experiments and the correlation between the C6–H and the silylmethane was observed in the NOE experiment.[6] Now the stage was set up to construct the tetrasubstituted double bond. As expected, olefination of ketone **7** with triethyl phosphate derivate **8**[7] in the presence of NaH (60% in oil) in THF at 50 °C delivered the mixed esters in 99% yield with

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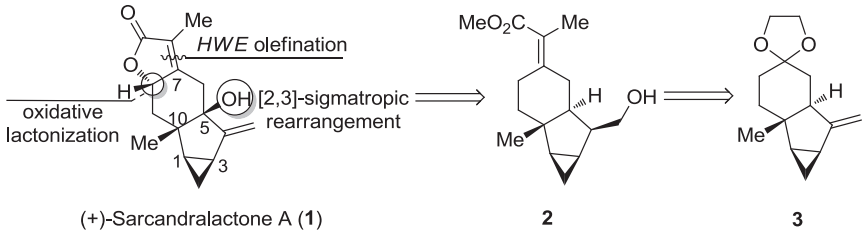
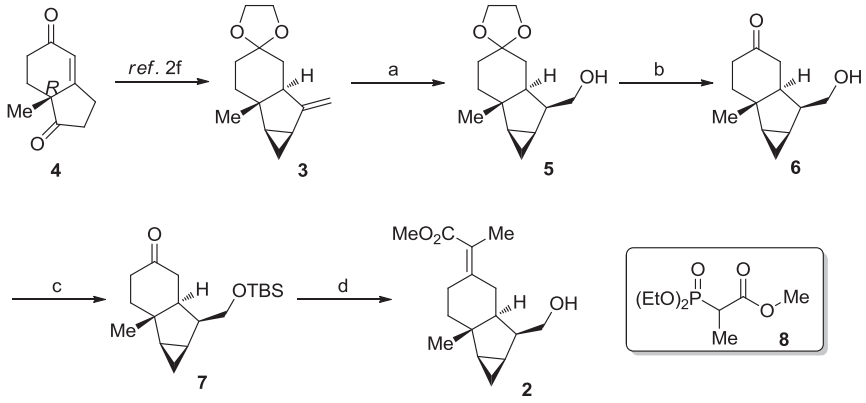


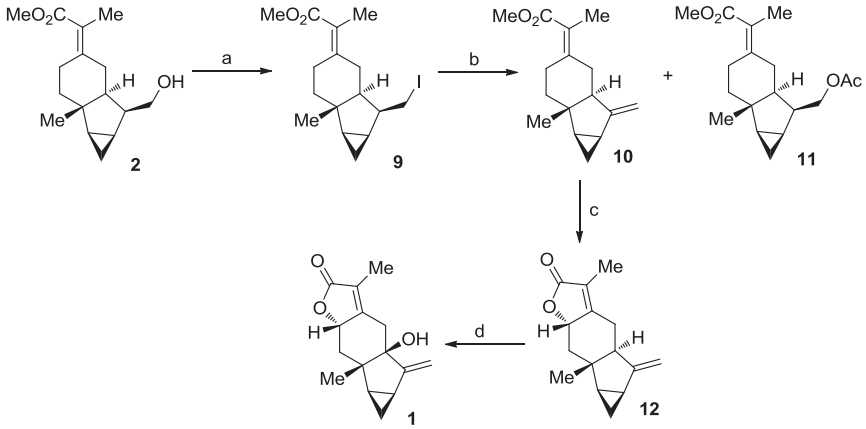
Scheme 1. Retrosynthetic analysis of (+)-sarcandralactone A.



Scheme 2. Reagents and conditions: (a) 9-BBN (0.5 M in THF), THF, 0 °C to rt; then NaOH (aq), H_2O_2 (30%), rt, 95%; (b) $FeCl_3{\cdot}SiO_2$, acetone, rt, 97%; (c) TBSCl, imidazole, DMF, rt, quant.; (d) **8**, NaH (60% in mineral oil), THF; then TBAF (1.0 M in THF), THF, 85%. 9-BBN=9-borabicyclo[3.3.1]nonane, TBSCl=*tert*-butyldimethylsilyl chloride, DMF=dimethylformamide, TBAF=tetra-*n*-butylammonium fluorine, THF=tetrahydrofuran.

a good stereoselectivity in a ratio of 7:1 in favor of the (*E*)-isomer. Subsequent removal of the TBS-group by treating with TBAF solution at room temperature provided the alcohol **2** in an 85% yield, which could be separated by flash column chromatography on silica gel. It is noteworthy that the temperature was pivotal to the full conversion of the starting material and the high yield of the desired product for that some unidentified byproducts were observed in the refluxing system. Additionally, further investigation on the Horner–Wadsworth–Emmons olefination with other derivated phosphate esters (^{i}Pr or Me) led to no obvious enhancement of the stereoselectivity. Also, exchange of the protecting group with TBDPSCl gave low yield (<50%) in the process of olefination with most starting material recovered.

With the pure primary-(*E*) alcohol **2** in hand, we turned our attention to the reconstruction of the exocyclic methylene (Scheme 3). Experimentally, transformation of alcohol **2** to the corresponding alkene **10** proved challenging due to the congested circumstance posed by the cyclopentane and the labile cyclopropane. Efforts such as direct dehydration in the presence of Brønsted acid or Burgess reagent[8] or Martin Sulfurane dehydration reagent[9] resulted in no reaction or ring-opened products. To surmount this obstacle, another strategy based on the E2-type reaction was tried. Initial studies indicated that S_N2-type reaction predominated in the dehydrated process with trace desired product in the protected substrates (Ts– or Ms–). Luckily, alkene **10** was finally obtained in 75% yield by way of iodide **9**, which underwent the E2 β-elimination in the presence of KOAc, giving a superior overall yield in comparison with the previous pathway. Also, the concomitantly formed byproduct **11** could be recycled to give the primary alcohol **2** using K_2CO_3 in methanol in quantitative yield at room temperature. Next, the pivotal oxidative lactonization for the total synthesis of shizukanolide A (**12**) was reevaluated. Inspired by the absorbing effect of Celite in the workup of PCC oxidation,[10] Celite solid was added into the generated CrO_3dmp (dmp=3,5-dimethylpyrazole)



Scheme 3. Reagents and conditions: (a) I_2, imidazole, PPh_3, DCM, 98%; (b) KOAc, DMF, 80 °C, 75% **10** and 23% **11**; (c) CrO_3, 3,5-dimethylpyrazole, Celite, DCM, 0 °C to reflux, 37% **12** and 45% **10** was recovered; (d) SeO_2, dioxane, 80 °C, 95%. DCM=dichloromethane.

complex[11] system before refluxing in a preheated (50 °C) oil bath. Thus, the cascade reaction product **12** was obtained uneventfully in 37% yield as a single isomer along with 45% of starting material recovered. However, addition of an acid-scavenger (KOAc, Na_2CO_3, or molecular sieves, etc.) gave no improvement of yield. With an efficient route to shizukanolide (**12**) secured, the time had come to address the next task, namely, the issue of the tertiary hydroxyl introduction at C5. Initial efforts with some radical reactions resulted in no desired product expect for some ring-opened byproducts.

Considering the multiple allylic positions in the substrate **12**, some mild oxidants were then screened. To our delight, under optimized conditions, the allylic hydroxyl could be introduced by SeO_2[12] in 95% yield with complete stereoselectivity and chemoselectivity to afford **1**. We proposed an uncommon [2,3]-sigmatropic rearrangement mediated by SeO_2 to explain the excellent selectivity (Fig. 1). Probably due to the relative thermodynamical instability of the trans-5/6 fused ring system,[13] hydrogen abstraction from the trans-face at C5 was preferred over other allylic positions to give the C=C bond migrated intermediate **14**, which would then undergo a [2,3]-sigmatropic rearrangement to provide the more stable *cis*-product **1**. The absolute configuration of sarcandralactone A was confirmed by X-ray crystallographic analysis (Fig. 1).[6] Besides, all spectral data of synthetic material were identical to the reported.[3]

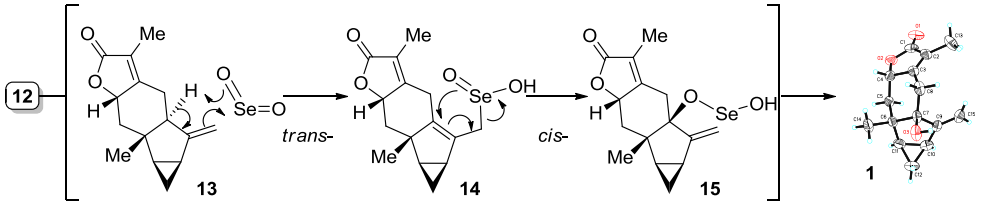


Fig. 1. Proposed a [2,3]-sigmatropic rearrangement mediated by SeO_2.

3. Conclusion

In summary, with an improved route to the shizukanolide (**12**), a *cis*-tertiary allylic alcohol was installed by an unusual [2,3]-sigmatropic rearrangement mediated by SeO_2 to accomplish the first enantioselective total synthesis of (+)-sarcandralactone A (20% overall yield in nine steps from **3**). Further studies to synthesize other lindenane sesquiterpenoids and dimmers are being actively pursued in our laboratory.

4. Experimental section

4.1. General

Experimental procedures and characterization data for selected compounds are included in this text. Additional experimental procedures, characterization data, and spectra for all new compounds can be found in the Supplementary data submitted along with this manuscript and the Supplementary data of a previous communication.[2f]

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware and monitored by TLC on precoated silica gel HSGF254 plates (Yantai Chemical Co., Ltd). Column chromatography was performed on silica gel 300–400 mesh (Yantai Chemical Co., Ltd) and eluted with hexanes and ethyl acetate mixtures. All solvents were refluxed and distilled from sodium benzophenone ketyl (THF) or CaH_2 (CH_2Cl_2, DMF). The NMR spectra (^1H: 400/500 MHz, ^{13}C: 100/125 MHz) are reported in δ units (parts per million) and J values (hertz) with Me_4Si as the internal standard. Infrared (IR) spectra are reported in wave numbers (cm^{-1}). Melting points were measured on SGW X-4 microscopic melting point apparatus. Optical rotations are reported in units of 10^{-1} deg cm^3 g^{-1}.

4.2. ((1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-1b-Methyloctahydro-1*H*-spiro[cyclopropa[*a*]indene-4,2′-[1,3]dioxolan]-6-yl)methanol (5)

To a cooled (0 °C) solution of **3** (20 mg, 0.091 mmol) in THF (10 mL) was added a solution of 9-BBN (0.5 M in THF, 1.82 mL, 0.91 mmol) drop-wise. After being warmed to room temperature and stirred for another 3 h, the mixture was again cooled to 0 °C and carefully quenched by successive addition of 3.0 M NaOH (aq) (0.15 mL, 0.45 mmol) and 30% H_2O_2 (0.15 mL). The resulting mixture was stirred for further 2 h at room temperature. The aqueous layer was extracted with Et_2O, and the combined organic phases were washed with brine, dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=3:1) to afford primary alcohol **5** (21 mg, 95%) as a colorless oil.

R_f=0.40 (Hexane/EtOAc=1:1); $[\alpha]_D^{27}$ −40.02 (*c* 0.45, $CHCl_3$); IR (film): 3338, 2921, 1077 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.96–3.86 (m, 4H), 3.80–3.72 (m, 1H), 3.66–3.58 (m, 1H), 2.00 (td, J=13.1, 3.5 Hz, 1H), 1.86–1.80 (m, 1H), 1.76–1.66 (m, 3H), 1.52–1.38 (m, 5H), 1.26–1.14 (m, 1H), 0.94–0.82 (m, 1H), 0.76–0.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.5, 65.3, 64.3, 64.1, 58.5, 46.9, 39.1, 35.8, 33.8, 32.3, 28.6, 23.0, 16.5, 15.6; LRMS (ESI): m/z 261.1 $[M+Na]^+$; HRMS (ESI): calcd for $C_{14}H_{22}O_3Na^+$ $[M+Na]^+$ 261.14666, found: 261.14732.

4.3. (1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-6-(Hydroxymethyl)-1b-methyloctahydrocyclopropa[*a*] inden-4(1b*H*)-one (6)

$FeCl_3 \cdot SiO_2$ (18 mg, 100 mg/mmol) was added in one portion to a solution of alcohol **5** (42 mg, 0.18 mmol) in acetone (10 mL). The resultant mixture was stirred at room temperature for another 3 h before being diluted with Et_2O and filtered through a thin silica gel pad. The obtained filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=5:2) to afford ketone **6** (34 mg, 97%) as a colorless oil.

R_f=0.35 (Hexane/EtOAc=1:1); $[\alpha]_D^{24}$ −23.42 (*c* 0.65, $CHCl_3$); IR (film): 3420, 2923, 1700, 1419, 1201, 1039, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.76–3.55 (m, 2H), 248–2.40 (m, 2H), 2.28–2.22 (m, 1H), 2.16–2.08 (m, 1H), 2.04–1.88 (m, 3H), 1.60–1.50 (m, 1H), 1.34–1.18 (m, 3H), 0.90–0.70 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 64.4, 58.8, 47.6, 40.6, 39.0, 38.0, 36.7, 28.3, 23.1, 16.4, 16.2; LRMS (EI): m/z 194 $[M]^+$; HRMS (EI): calcd for $C_{12}H_{18}O_2^+$ $[M]^+$ 194.1307, found: 194.1303.

4.4. (1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-6-(((*tert*-Butyldimethylsilyl)oxy) methyl)-1b-methyloctahydrocyclopropa[*a*]inden-4(1b*H*)-one (7)

To a stirred solution of alcohol **6** (120 mg, 0.62 mmol) in dried DMF (12 mL) were successively added imidazole (105 mg,

1.55 mmol) and TBSCl (193 mg, 1.24 mmol). After being stirred for another 2 h for full conversion, the mixture was quenched by water. The mixture was diluted with Et_2O and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=50:1) to afford silyl ether **7** (190 mg, 99%) as a colorless oil.

R_f=0.60 (Hexane/EtOAc=10:1); $[\alpha]_D^{24}$ −109.59 (*c* 2.0, $CHCl_3$); IR (film): 2926, 2855, 1715, 1464, 1257, 1098, 836, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (d, *J*=5.8 Hz, 1H), 2.47–2.41 (m, 2H), 2.33–2.29 (m, 1H), 2.15–2.10 (m, 2H), 1.98–1.86 (m, 2H), 1.56–1.48 (m, 1H), 1.36–1.16 (m, 2H), 0.90–0.86 (m, 12H), 0.84–0.79 (m, 1H), 0.76–0.69 (m, 1H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 64.9, 59.4, 47.8, 41.0, 39.2, 38.1, 36.8, 28.2, 25.9, 23.0, 18.3, 16.3, 16.2, −5.38, −5.40; LRMS (ESI): *m*/*z* 331.2 $[M+Na]^+$; HRMS (ESI): calcd for $C_{18}H_{32}O_2SiNa^+$ $[M+Na]^+$ 331.20693, found: 331.20728.

4.5. (*E*)-Methyl 2-((1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-6-(hydroxymethyl)-1b-methyloctahydro cyclopropa[*a*]inden-4(1b*H*)-ylidene) propanoate (2)

To a cooled (0 °C) solution of NaH (60% in mineral oil, 214 mg, 5.36 mmol) in THF (20 mL) was added triethyl phosphate derivate **8** slowly. After being stirred at room temperature for 1 h, a solution of **7** (165 mg, 0.54 mmol) in THF (3 mL) was added in one portion to the above mixture. The resultant system was heated in an oil bath at 50 °C for another 6 h. After cooling to room temperature, the mixture was quenched by brine. The aqueous was extracted with Et_2O and dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=80:1) to provide a mixture ester in a ratio of 7:1, which determined by crude ^1H NMR and GC–MS.

To a solution of the above mixture in THF (20 mL) was added a solution of TBAF (1.0 M in THF, 1.08 mL, 1.08 mmol) in one portion. The resultant mixture was stirred for another 4 h at room temperature and quenched with H_2O. The aqueous phase was separated and extracted with Et_2O. The combined organic phases were dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=120:1) to provide ester **2** (132 mg, 85%) as a colorless oil.

R_f=0.55 (Hexane/EtOAc=2:1); $[\alpha]_D^{25}$ −96.16 (*c* 0.75, $CHCl_3$); IR (film): 3446, 3000, 2919, 1717, 1623, 1436, 1279, 1037, 779; ^1H NMR (400 MHz, $CDCl_3$) δ 3.77 (dd, *J*=10.8, 4.8 Hz, 1H), 3.71 (s, 3H), 3.64 (dd, *J*=10.8, 7.2 Hz, 1H), 2.76 (dq, *J*=16.4, 2.8 Hz, 1H), 2.57–2.45 (m, 1H), 2.39–2.28 (m, 1H), 1.84–1.72 (m, 6H), 1.68–1.58 (m, 2H), 1.54–1.46 (m, 1H), 1.33–1.23 (m, 1H), 1.22–1.13 (m, 2H), 0.82–0.77 (m, 1H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 145.9, 121.7, 65.4, 59.5, 51.3, 47.6, 39.1, 38.3, 29.1, 28.8, 27.4, 22.5, 16.6, 16.5, 15.4; LRMS (ESI): *m*/*z* 287.2 $[M+Na]^+$; HRMS (EI): calcd for $C_{16}H_{24}O_3Na^+$ $[M+Na]^+$ 287.16231, found: 287.16173.

4.6. (*E*)-Methyl 2-((1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-6-(iodomethyl)-1b-methyloctahydro cyclopropa[*a*]inden-4(1b*H*)-ylidene)propanoate (9)

To a stirred solution of **2** (35 mg, 0.13 mmol) in DCM (10 mL) at 0 °C were successively added imidazole (45 mg, 0.66 mmol), PPh_3 (174 mg, 0.66 mmol), and I_2 (168 mg, 0.66 mmol). After stirring at room temperature for 2 h, the mixture was quenched by saturated Na_2SO_3 (aq). The aqueous layer was extracted with DCM and dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=100:1) to provide iodide **9** (49 mg, 98%).

R_f=0.60 (Hexane/EtOAc=10:1); $[\alpha]_D^{26}$ −103.18 (*c* 1.0, $CHCl_3$); IR (film): 2946, 2921, 1716, 1432, 1381, 1277, 1192, 1106, 864, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.44 (dd, *J*=9.6, 3.6 Hz, 1H), 3.14 (dd, *J*=9.6, 8.4 Hz, 1H), 2.80 (dq, *J*=16.4, 2.8 Hz, 1H), 2.54–2.42 (m, 1H), 2.35–2.25 (m, 1H), 1.85–1.75 (m, 4H), 1.73–1.60 (m, 3H), 1.48–1.40 (m, 1H), 1.32–1.15 (m, 3H), 0.86–0.81 (m, 1H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 145.2, 122.0, 63.0, 51.4, 47.1, 39.8, 38.5, 28.8, 28.3, 27.3, 26.5, 16.8, 16.5, 15.5, 10.6; LRMS (ESI): *m*/*z* 397.1 $[M+Na]^+$; HRMS (ESI): calcd for $C_{16}H_{23}IO_2Na^+$ $[M+Na]^+$ 397.06404, found: 397.06479.

4.7. (*E*)-Methyl 2-((1a*R*,1b*S*,5a*S*,6a*S*)-1b-methyl-6-methyleneoctahydrocyclo propa[*a*]inden-4(1b*H*)-ylidene) propanoate (10) and (*E*)-methyl 2-((1a*R*,1b*S*,5a*S*,6*S*,6a*S*)-6-(acetoxymethyl)-1b-methyloctahydrocyclopropa[*a*]inden-4(1b*H*)-ylidene)propanoate (11)

To a stirred solution of iodide **9** (210 mg, 0.56 mmol) in DMF (15 mL) at room temperature was added KOAc (551 mg, 5.61 mmol). The resultant mixture was stirred in a preheated (80 °C) oil bath for 4 h. After cooling to room temperature, the mixture was quenched with saturated NH_4Cl (aq). The aqueous phase was extracted with Et_2O, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=100:1 to 30:1) to provide the alkene **10** (103 mg, 75%) and acetate **11** (39 mg, 23%).

Compound **11**: R_f=0.30 (Hexane/EtOAc=10:1); $[\alpha]_D^{25}$ −43.30 (*c* 1.1, $CHCl_3$); IR (film): 3065, 2923, 2858, 1743, 1712, 1434, 1379, 1366, 1231, 1106, 1037, 848, 792, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.21–4.09 (m, 2H), 3.71 (s, 3H), 2.78 (dq, *J*=16.4, 2.8 Hz, 1H), 2.56–2.44 (m, 1H), 2.40–2.30 (m, 1H), 2.07 (s, 3H), 1.88–1.72 (m, 5H), 1.68–1.54 (m, 3H), 1.33–1.23 (m, 1H), 1.22–1.12 (m, 2H), 0.82–0.77 (m, 1H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.7, 145.6, 121.8, 66.7, 60.2, 51.3, 44.0, 39.1, 38.3, 29.1, 28.6, 27.3, 22.5, 21.0, 16.50, 16.46, 15.4; LRMS (EI): *m*/*z* 306 $[M]^+$; HRMS (EI): calcd for $C_{18}H_{26}O_4^+$ $[M]^+$ 306.1831, found: 306.1827.

4.8. (+)-Sarcandralactone A (1)

To a cooled (0 °C) solution of alkene **10** (20 mg, 0.081 mmol) in DCM (10 mL) were successively added CrO_3 (41 mg, 0.41 mmol) and 3,5-dimethylpyrazole (78 mg, 0.82 mmol). After being stirred at 0 °C for another 1 h, to the mixture was added Celite and heated to reflux for 12 h with an oil bath. After cooling to room temperature, the mixture was filtered through a silica gel pad and washed with Et_2O. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=150:1 to 50:1 to 20:1) to afford lactone **12** (7 mg, 37%) and alkene **10** (9 mg, 45%).

The obtained lactone **12** (7 mg, 0.030 mmol) was dissolved in dried dioxane (5 mL) and added SeO_2 (13 mg, 0.12 mmol) in one portion. The resulting mixture was heated in an oil bath (80 °C) for 1 h. After cooling to room temperature, the mixture was filtered through a silica gel pad and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (Hexane/EtOAc=8:1) to afford *cis*-product alcohol **1** (7 mg, 95%).

R_f=0.35 (Hexane/EtOAc=2:1); mp=189–191 °C; $[\alpha]_D^{30}$ +139.60 (*c* 0.5, MeOH) (lit.,[3] colorless gum/solid, $[\alpha]_D^{20}$ +168 (*c* 0.1, MeOH)); IR (KBr): 3461, 2926, 1735, 1261, 1092, 1028, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (s, 1H), 4.98 (s, 1H), 4.69 (dd, *J*=12.3, 5.5 Hz, 1H), 3.18 (d, *J*=14.6 Hz, 1H), 2.42 (d, *J*=14.6 Hz, 1H), 2.34 (dd, *J*=12.8, 5.8 Hz, 1H), 1.84 (m, 1H), 1.79 (s, 3H), 1.54 (q, *J*=4.0 Hz, 1H), 1.45 (m, 1H), 1.15 (t, *J*=12.6 Hz, 1H), 0.69 (dq, *J*=8.2. 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 159.1, 153.9, 120.0, 106.4, 80.3, 77.2, 45.4,

45.1, 32.7, 31.7, 20.9, 17.2, 13.8, 8.2; LRMS (EI): m/z 246 $[M]^+$; HRMS (EI): calcd for $C_{15}H_{18}O_3{}^+$ $[M]^+$ 246.1256, found: 246.1257.

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Supplementary data

Experimental procedures and characterization data for compounds **1**, **2**, **5**, **6**, **7**, **9**, and **11** are provided. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 939621 (sarcandralactone A, **1**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk). Experimental procedures and characterization data for compounds **3**, **4**, **10**, and **12** can be found in the supplementary data of a previous communication.[2f] Supplementary data associated with this article can be found in the online version, at http://pubs.rsc.org/en/content/articlelanding/2012/cc/c2cc17882f. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.10.083.

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