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Synthetic approach to *cis* and *trans*-decalins via Diels—Alder reaction and ring-closing metathesis as key steps: further extension to dioxapropellane derivative by ring-closing metathesis

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ABSTRACT

9,10-Substituted *cis* and *trans*-decalins were synthesized by a simple route using the Diels–Alder reaction and ring-closing metathesis (RCM) as key steps. Later, the *cis*-decalin system has been extended to 3,8-dioxa[8.4.4]propellane derivative by RCM sequence as a key step.

1. Introduction

Many natural products contain an *ortho*-condensed system as part of their molecular framework.[1] To this end, decalin and hydrindane systems that appear more frequently have received considerable attention. For example the *trans*-decalin system is present in steroid and terpenoid natural products, such as drimanes, clerodanes, and abietanes.[1a] The *cis*-decalin containing diterpene agelasine-A, shows an antimicrobial activity and inhibits the activity of the enzyme Na, K-ATPase.[2] Similarly, branimycin acts as antibiotic[3] (Fig. 1).

Therefore, design of *cis* and *trans*-decalin frames is a challenging task and more specifically bridge functionalized decalins are more difficult to prepare. Although the Diels–Alder (DA) reaction is the most common route for the synthesis of decalin derivatives, other routes are also available.[1,4] Recently, Snapper and Shizuka reported the synthesis of *cis*-decalin derivatives by two-step process involving allylation and RCM,[5] and Mehta has used the RCM strategy for the synthesis of decalin based sesquiterpenoids.[6] To prepare decalin based systems, Enev et al. had reported the synthesis of branimycin antibiotics containing *cis*-decalin frame by employing RCM strategy.[7] Philips and Minger reported a tandem metathesis approach for the synthesis of decalins and hydrindanes.[8] Here, we devised a simple synthetic approach to *cis* and *trans*-decalin derivatives using allylation and metathesis[9] as key steps. Further, utilization of RCM delivers the dioxapropellane system.

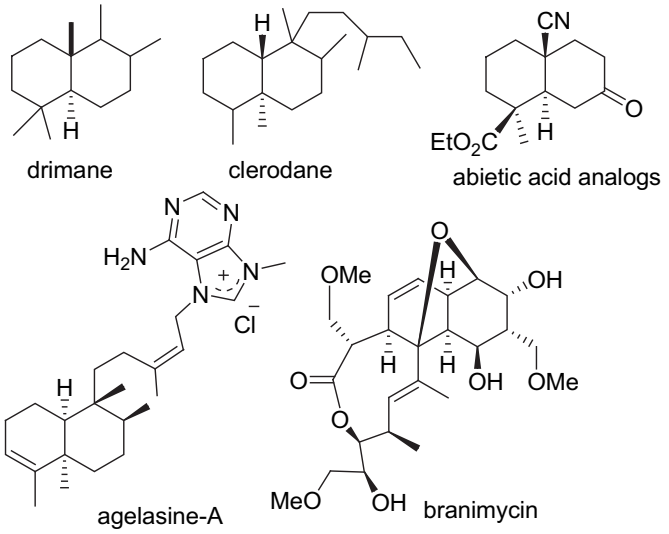

Fig. 1. Decalin based natural products.

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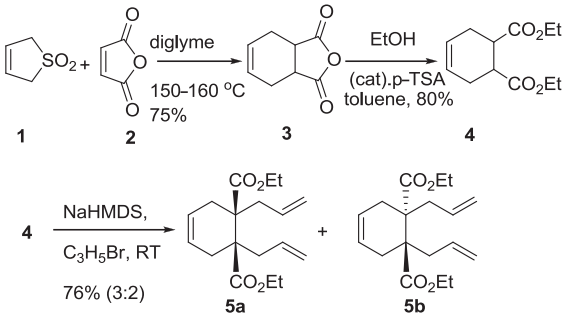
Carbocylic and heterocyclic-based propellanes are important structural units present in many natural and non-natural targets.[10] Ginsburg and Wiberg had reviewed various aspects of small and medium ring propellane derivatives.[11] Koskinen group had reviewed the literature of natural products containing propellane ring systems.[12]

2. Results and discussion

To design propellane derivatives, *cis*-decalin diester was identified as a key intermediate. To this end, the DA reaction of sulfolene (**1**) and dimethyl acetylenedicarboxylate (DMAD) under heating in toluene or sealed tube condition was attempted. To our surprise the DA reaction failed to give the required adduct. Next, an alternate DA route involving diethyl maleate and sulfolene (**1**) was attempted. Unfortunately this route also did not deliver the required DA adduct.

2.1. *cis* and *trans*-Diallylated compounds 5a,b

Subsequently, maleic anhydride (**2**) was reacted with sulfolene (**1**) in diglyme at 150–160 °C to generate the known cyclohexene derivative **3**.[13] Ethanolysis of **3** under *p*-TSA conditions using known procedure gave the diester **4**.[14] Allylation of the dianion generated from **4** gave the *cis* and *trans*-diallylated product (**5a** and **5b**) in 3:2 ratio (Scheme 1). These diastereoisomers were separated by silica-gel column chromatography.



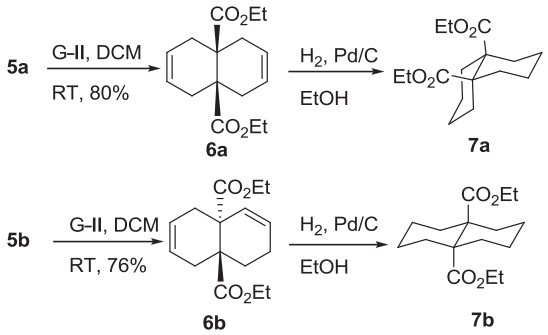
Scheme 1. Preparation of *cis* and *trans*-diallylated compounds.

2.2. *cis* and *trans*-Decalins by RCM

Both *cis*- and *trans*-diallyl derivatives **5a** and **5b** gave the expected RCM products **6a** and **6b** in good yields upon exposure to Grubbs' second generation catalyst at rt. It is interesting to note that the *trans*-diallyl derivative **5b** gave the double bond isomerized product **6b** under these conditions.[15] Further, hydrogenation of these RCM products with Pd/C gave the *cis* and *trans*-decalin derivative **7a** and **7b**, respectively (Scheme 2). The hydrogenation of *trans*-decalin derivative takes comparatively more time than *cis*-derivative. Thus we have prepared stereochemically pure *cis* and *trans*-decalin systems in 3:2 ratios by employing allylation and RCM sequence.

2.3. *cis*-Decalin diester by direct alkylation

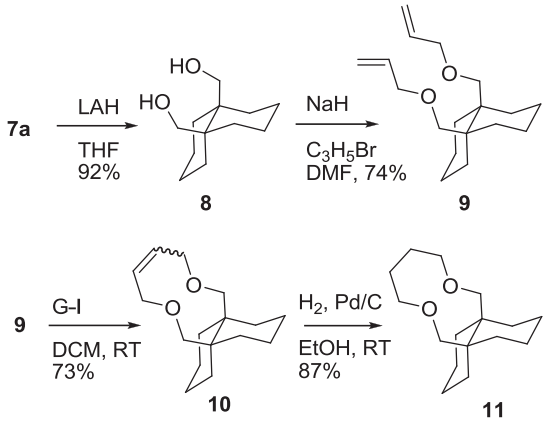
To establish the structure of *cis*-decalin derivative **7a**, its preparation by an alternate synthetic route based on literature procedure was attempted.[16] Thus, the diester **4** was alkylated with 1,4-dibromobutane using NaHMDS to generate unsaturated *cis*-decalin derivative. Subsequent catalytic hydrogenation with Pd/C in ethanol gave **7a**. The ^{1}H NMR spectral data of the compound obtained by this route is identical to that of the product obtained via metathesis (Scheme 2).



Scheme 2. Preparation of *cis* and *trans*-decalins by RCM.

2.4. Synthesis of 3,8-dioxa[8.4.4]propellane by RCM

Having prepared both the *cis* and *trans*-decalin derivatives **7a** and **7b**, we focused our attention toward the synthesis of 3,8-dioxapropellane derivative. To this end, diester **7a** was reduced with LAH to deliver the diol **8**. The preparation of this diol **8** is known in the literature from the reduction of 9,10-decalin anhydride by LAH.[17] O-Allylation of the diol **8** with allyl bromide in DMF gave the *cis*-9,10-bis(allyloxymethyl)decalin (**9**) in good yield. RCM of diallyl derivative **9** with the Grubbs' first generation catalyst afforded the tricyclic system **10** as a *cis*–*trans* olefinic mixture,[18] which on hydrogenation gave the saturated dioxapropellane derivative **11** (Scheme 3).



Scheme 3. Preparation of 3,8-dioxa[8.4.4]propellane.

3. Conclusion

A simple route for the synthesis of *cis* and *trans*-decalin derivatives has been developed by utilizing DA reaction and RCM sequence as key steps. One of these decalin systems was found to be useful to prepare dioxapropellane system via the RCM approach.

4. Experimental section

4.1. General procedures

All the reactions were monitored by employing TLC technique using appropriate solvent system for development. Reactions

involving oxygen sensitive reagents or catalysts were performed in degassed solvents. Dry tetrahydrofuran (THF) was obtained by distillation over sodium benzophenone ketyl freshly prior to use. Dichloromethane was distilled over P_2O_5. Magnesium sulfate/sodium sulfate were dried in an oven at 130 °C for 1 day before use. All the solvent extracts were washed successively with water, brine (saturated sodium chloride solution) and dried over anhydrous magnesium sulfate/sodium sulfate, and concentrated at reduced pressure on rotary evaporator. Yields reported are isolated yields of the products after purification by column chromatography. All the commercial grade reagents were used without further purification. Infrared (IR) spectra for solid samples were recorded as KBr pellets and liquid samples as their film between CsCl plates. Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were generally recorded on 400 MHz or 300 MHz spectrometers. Carbon Nuclear Magnetic Resonance (^{13}C NMR) spectra were recorded on 100 MHz or 75 MHz spectrometer. NMR samples were generally made in chloroform-*d* solvent and chemical shifts were reported in δ scale using tetramethylsilane (TMS) as an internal standard. The standard abbreviation s, d, t, q and m, refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Coupling constants (*J*) are reported in Hertz. Analytical thin-layer chromatography (TLC) was performed on (10×5 cm) glass plates coated with silica gel (containing 13% calcium sulfate as a binder). Silica gel is coated on glass plates using 'Sandwich Technique.' In this process, two equally sized clean glass plates are immersed in uniformly stirred silica gel suspension in an organic solvent (usually ethyl acetate). Only the exposed surface of the plate is thus coated with silica gel. The solvent evaporates readily leaving a thin-layer of silica gel and then the plate is ready for the use. Visualization of the spots on TLC plates was achieved either by exposure to iodine vapors or UV light. The products were purified by silica gel (100–200 mesh) column chromatography.

*4.1.1. Diethyl 1,2-diallylcyclohex-4-ene-1,2-dicarboxylate (**5a**,**b**).* To a cooled solution (at 0 °C) of diethyl tetrahydropthalate (**4**) (250 mg, 1.35 mmol) in THF (10 mL) was added NaHMDS (1 M solution in hexane) (4 mL, 4 mmol) in drop-wise manner. After half an hour the solution became red in color. Allyl bromide (0.46 mL, 5.43 mmol) was added slowly at 0 °C. After completion of the reaction (TLC monitoring, 10 h), the reaction mixture was quenched with aqueous saturated NH_4Cl solution (2 mL) and the solvent was evaporated under reduced pressure. The residue was partitioned between water (50 mL) and ether (25 mL). The aqueous portion was extracted with ether (3×25 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the resulting residue was purified by a silica-gel column chromatography (3% ethyl acetate/petroleum ether) to gave *cis* and *trans* **5a** (189 mg) and **5b** (126 mg), respectively, in 3:2 ratio as a thick pale yellow liquid. The overall yield is 76%.

Spectral data for compound **5a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54–5.64 (m, 4H), 4.95–5.04 (m, 4H), 4.15–4.27 (m, 2H), 3.95–4.12 (m, 2H), 2.55–2.68 (m, 4H), 2.21 (dd, J_1=13.7 Hz, J_2=8.8 Hz, 2H), 2.08 (dd, J_1=16.7 Hz, J_2=2.7 Hz, 2H), 1.22 (t, J=7.0 Hz, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.7, 134.8, 123.9, 118.6, 60.7, 50.3, 36.0, 28.4, 14.1 ppm. IR (neat): ν_{max} 3056, 2917, 1745, 1438, 1199, 913 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{18}H_{26}O_4Na$: 329.1729; found: 329.1737.

Spectral data for compound **5b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54–5.67 (m, 4H), 5.03–5.07 (m, 4H), 4.09–4.20 (m, 4H), 2.89 (dd, J_1=13.1 Hz, J_2=6.4 Hz, 2H), 2.46 (d, J=17.4 Hz, 2H), 2.27 (dd, J_1=13.1 Hz, J_2=8.3 Hz, 2H), 2.04 (d, J=17.7 Hz, 2H), 1.25 (t, J=7.0 Hz, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.8, 133.5, 124.3, 118.5, 60.5, 50.5, 37.2, 30.0, 14.0 ppm. IR (neat): ν_{max} 3054, 2912, 1750, 1438, 1199, 911 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{18}H_{27}O_4$: 307.1909; found: 307.1899.

*4.1.2. cis-Diethyl 1,4,4a,5,8,8a-hexahydronaphthalene-4a,8a-dicarboxylate (**6a**).* To a solution of **5a** (25 mg, 0.08 mmol) in DCM (10 mL), Grubbs' second generation catalyst (3.46 mg, 5 mol %) was added under argon at rt. After completion of the reaction (TLC monitoring, 6 h), the solvent was evaporated under reduced pressure and the residue was purified by a silica-gel column chromatography (3% ethyl acetate/petroleum ether) to give **6a** (17.8 mg, 80% yield) as a thick colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.56 (s, 4H), 4.13 (q, J=7.0 Hz, 4H), 2.64 (br s, 3H), 2.38 (d, J=15.0 Hz, 5H), 1.23 (t, J=7.0 Hz, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 175.6, 124.0, 60.5, 44.4, 33.7, 14.2 ppm. IR (KBr): ν_{max}: 2856, 1768, 1438, 913 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{23}O_4$: 279.1596; found: 279.1602.

*4.1.3. trans-Diethyl 1,2,4a,5,8,8a-hexahydronaphthalene-4a,8a-dicarboxylate (**6b**).* To a solution of **5b** (55 mg, 0.18 mmol) in DCM (10 mL), Grubbs' second generation catalyst (7.6 mg, 5 mol %) was added under argon at rt. After completion of the reaction (TLC monitoring, 6 h), the solvent was evaporated under reduced pressure and the residue was purified by a silica-gel column chromatography (3% ethyl acetate/petroleum ether) to give **6b** (37 mg, 76% yield) as a thick colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58–5.68 (m, 4H), 5.01 (t, J=7.3 Hz, 1H), 4.11–4.16 (m, 1H), 3.98–4.08 (m, 2H), 2.62–2.73 (m, 6H),1.21 (t, J=7.0 Hz, 3H), 2.26 (dd, J_1=13.7 Hz, J_2=8.8 Hz, 1H), 2.12 (dd, J_1=16.8 Hz, J_2=2.7 Hz, 1H), 1.27 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 175.0, 173.7, 134.8, 125.3, 123.9, 118.6, 60.7, 60.4, 50.3, 45.5, 35.9, 34.2, 34.2, 28.4, 14.1, 14.0 ppm. IR (KBr): ν_{max}: 2848, 1758, 1442, 911 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{23}O_4$: 279.1596; found: 279.1591.

4.2. General procedure for the hydrogenation

To a solution of unsaturated diester in ethanol, 10% palladium/charcoal was added and the reaction mixture was stirred at rt for required time (monitored by NMR) under 1 atm hydrogen pressure. Then, the reaction mixture was filtered through Celite and washed with ethyl acetate (20 mL). The solvent was removed under reduced pressure and the crude product was purified by silica-gel column chromatography. Elution of the column with 5% ethyl acetate/petroleum ether gave the hydrogenated product.

*4.2.1. cis-9,10-Bis(carboethoxy)decalin (**7a**).* (Reaction time 2 days, yield 99%). Mp 44–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.12 (q, J=7.0 Hz, 4H), 2.40 (br s, 2H), 1.90 (br s, 2H), 1.80–1.25 (m, 12H), 1.23 (t, J=7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 60.1, 47.7, 31.0 (br s), 22.0, 14.3 ppm. IR (KBr): ν_{max}: 2943, 1718, 1265, 1142, 1032 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{27}O_4$: 283.1909; found: 283.1900.

*4.2.2. trans-9,10-Bis(carboethoxy)decalin (**7b**).* (Reaction time 3 days, yield 99%). Mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26–4.18 (dq, J_1=7.0 Hz, J_2=3.7 Hz, 2H), 4.06–3.98 (dq, J_1=7.0 Hz, J_2=3.7 Hz, 2H), 2.03 (m, 2H), 1.88 (m, 2H), 1.64–1.28 (m, 4H), 1.25 (t, J=7.2 Hz, 8H), 0.89 (t, J=7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 60.3, 52.0, 32.7, 26.2, 20.6, 18.5, 14.9, 14.2 ppm. IR (KBr): ν_{max}: 2963, 1715, 1265, 1140, 1033 cm^{-1}. HRMS (QTOF ES$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{27}O_4$: 283.1909; found: 283.1918.

*4.2.3. cis-9,10-Bis(hydroxymethyl)decalin (**8**).* To a suspension of LAH (862 mg, 22.69 mmol) in dry THF (30 mL), *cis*-9,10-bis(carboethoxy)decalin (**7a**) (1.6 g, 5.67 mmol) was added by dissolving in dry THF (15 mL) under nitrogen and the reaction mixture was refluxed for 7 h. After completion of the reaction (TLC monitoring), the reaction mixture was cooled to 0 °C and quenched with ethyl acetate and stirred for 30 min at rt. Then, the organic layer was

washed with water (2–3 times), brine and dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was washed with petroleum ether afforded **8** as pure white solid (1.03 g, 92%). Mp 152–156 °C. (lit. mp 152 °C and 180–182 °C).[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (br s, 2H), 3.29 (br s, 2H), 2.73 (br s, 2H), 2.15–1.40 (m, 16H) ppm. ^{13}C NMR (65.5 MHz, $CDCl_3$): δ 68.1, 39.2, 30.3, 21.6 ppm.

*4.2.4. cis-9,10-Bis(allyloxymethyl)decalin (**9**).* To a suspension of NaH (242 mg, 10.1 mmol) in DMF (25 mL), *cis*-9,10-bis(hydroxymethyl)decalin (**8**) (500 mg, 2.52 mmol) was added. Then, the reaction mixture was cooled to 0 °C and allyl bromide (917 mg, 7.57 mmol) was added dropwise. Finally, the reaction mixture was stirred at rt for 24 h and after completion of the reaction (TLC monitoring), the reaction was quenched with NH_4Cl, extracted with ethyl acetate, washed with water, brine and dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography. Elution of the column with 2% ethyl acetate/petroleum ether gave **9** (517 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94–5.84 (m, 2H), 5.28 (q, J=1.8 Hz, 1H), 5.23 (q, J=1.8 Hz, 1H), 5.15 (q, J=1.8 Hz, 1H), 5.12 (q, J=1.8 Hz, 1H), 3.92 (td, J=2.1 Hz, 1.8 Hz, 4H), 3.57 (br s, 2H), 3.20 (br s, 2H), 1.90–1.20 (m, 16H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 116.2, 74.5, 72.4, 39.0, 32.0(br s), 21.8 ppm. IR (neat): ν_{max}: 2926, 2863, 1468, 1094, 920 cm^{-1}. HRMS (QTOF ES$^+$): m/z [M+H]$^+$ calcd for $C_{18}H_{31}O_2$: 279.2324; found: 279.2318.

*4.2.5. 3,8-Dioxa[8.4.4]octadec-5-ene (**10**).* A solution of *cis*-9,10-bis (allyloxymethyl)decalin (**9**) (150 mg, 0.54 mmol) in dry DCM (15 mL) was degassed with nitrogen for 5 min and then Grubbs first generation catalyst (5 mmol %) was added and the reaction mixture was stirred at rt for 24 h. After completion of the reaction (TLC monitoring), solvent was evaporated under vacuum and the crude product was purified by silica-gel column chromatography. Elution of the column with 2% ethyl acetate/petroleum ether gave **10** as a *cis–trans* olefinic mixture (99 mg, 73%). Mp 150–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (t, J=2.6 Hz, 2H), 3.97 (s, 4H), 3.43 (br s, 4H), 1.90–1.20 (m, 16H) ppm. ^{13}C NMR (65.5 MHz, $CDCl_3$): δ 129.6, 74.1, 71.1, 39.0, 32.0 (br s), 21.7(br s) ppm. IR (KBr): ν_{max}: 2925, 2861, 1467, 1265, 1103 cm^{-1}. HRMS (QTOF ES$^+$): m/z [M+H]$^+$ calcd for $C_{16}H_{27}O_2$: 251.2011; found: 251.2008.

*4.2.6. 3,8-Dioxa[8.4.4]propellane (**11**).* To a solution of 3,8-dioxa [8.4.4]octadec-5-ene (**10**) (50 mg, 0.20 mmol) in ethanol (10 mL), 10% palladium/charcoal was added and the reaction mixture was stirred at rt for 24 h under 1 atm hydrogen pressure. Then, the reaction mixture was filtered through Celite and washed with ethyl acetate (20 mL), after the removal of solvent under reduced pressure crude product was obtained. The crude product was purified by silica-gel column chromatography. Elution of the column with 2% ethyl acetate/petroleum ether gave **11** as a white solid (45 mg, 87%). Mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (s, 4H), 3.40 (s, 4H), 1.95–1.40 (m, 20H) ppm. ^{13}C NMR (65.5 MHz, $CDCl_3$): δ 76.5, 71.0, 39.0, 29.9(br s), 26.5, 21.9 ppm. IR (KBr): ν_{max}: 2920, 2859, 1117, 1012 cm^{-1}. HRMS (QTOF ES$^+$): m/z [M+H]$^+$ calcd for $C_{16}H_{29}O_2$: 253.2168; found: 253.2163.

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References and notes

1. (a) Varner, M. A.; Grossman, R. B. *Tetrahedron* **1999**, *55*, 13867; (b) Vandewalle, M.; Clerco, P. D. *Tetrahedron* **1985**, *41*, 1767; (c) Takashi, T. *Synthesis* **2000**, 611; (d) Singh, V.; Iyer, S. R.; Pal, S. *Tetrahedron* **2005**, *61*, 9197; (e) Nakadate, S.; Nozawa, K.; Horie, H.; Fujii, Y.; Nagai, M.; Hosoe, T.; Kawai, K.-I.; Yaguchi, T.; Fukushima, K. *J. Nat. Prod.* **2007**, *70*, 1510; (f) Oguchi, T.; Watanabe, K.; Ohkubo, K.; Abe, H.; Katoh, T. *Chem.—Eur. J.* **2009**, *15*, 2826; (g) Yao, G.; Vidor, N. B.; Foss, A. P.; Chang, L. C. *J. Nat. Prod.* **2007**, *70*, 901.
2. Nakamura, H.; Wua, H.; Ohizumia, Y.; Hiratab, Y. *Tetrahedron Lett.* **1984**, *25*, 2989.
3. Mulzer, J.; Castagnolo, D.; Felzmann, W.; Marchart, S.; Pilger, C.; Enev, V. S. *Chem.—Eur. J.* **2006**, *12*, 5992.
4. Kim, W. H.; Lee, J. H.; Aussedat, B.; Danishfsky, S. J. *Tetrahedron* **2010**, *66*, 6391.
5. Shizuka, M.; Snapper, M. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 5049.
6. Mehta, G.; Kumaran, R. S. *Tetrahedron Lett.* **2003**, *44*, 7055.
7. Enev, V. S.; Drescher, M.; Mulzer, J. *Org. Lett.* **2008**, *10*, 413; (b) Marchart, S.; Mulzer, J.; Enev, V. S. *Org. Lett.* **2007**, *9*, 813; (c) Marchart, S.; Gromov, A.; Mulzer, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 2050.
8. Minger, T. L.; Phillips, A. J. *Tetrahedron Lett.* **2002**, *43*, 5357.
9. (a) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003; Vol. 1–3; (b) Grubbs, R. H.; Schrock, R. R.; Fürstner, A. *Advanced Synthesis & Catalysis, Olefin Metathesis*; Wiley-VCH: Weinheim, 2007; Vol. 349, pp 1–265; (c) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3741; (d) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748; (e) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760; (f) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490; (g) Kotha, S.; Lahiri, K. *Synlett* **2007**, 2767; (h) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117; (i) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012; (j) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243; (k) Mori, M. *J. Mol. Cat. A: Chem.* **2004**, *213*, 73; (l) Astruc, D. *New J. Chem.* **2005**, *29*, 42; (m) Kotha, S.; Mandal, K. *Chem.—Asian J.* **2008**, *4*, 354; (n) Kotha, S.; Sreenivasachary, N. *Indian J. Chem., Sect. B* **2001**, *40*, 763; (o) Casterlenas, R.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2004**, *213*, 31; (p) Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786; (q) Deshmukh, P. H.; Blechert, S. *Dalton Trans.* **2007**, 2479.
10. (a) Ginsburg, D. *Propellanes: Structure and Reactions*; Chemie, GmbH: D-6940, Weinheim, 1975; (b) Ginsburg, D. *Propellanes: Structure and Reactions (Sequel-I)*; Chemie, GmbH: D-6940, Weinheim, 1975; (c) Ginsburg, D. *Propellanes: Structure and Reactions (Sequel-II)*; Chemie, GmbH: D-6940, Weinheim, 1980; (d) Kotha, S.; Dipak, M. K. *Chem.—Eur. J.* **2006**, *12*, 4446; (e) Nguyen, T. X.; Kobayashi, Y. *J. Org. Chem.* **2008**, *73*, 5536; (f) Shi, Q. W.; Sauriol, F.; Mamer, O.; Zamir, L. O. *Chem. Commun.* **2003**, 68.
11. (a) Ginsburg, D. *Acc. Chem. Res.* **1969**, *2*, 121; (b) Ginsburg, D. *Acc. Chem. Res.* **1972**, *5*, 249; (c) Ginsburg, D. *Top. Curr. Chem.* **1987**, *137*, 1; (d) Ginsburg, D. *Acc. Chem. Res.* **1974**, *7*, 286; (e) Ginsburg, D. *Tetrahedron* **1974**, *30*, 1487; (f) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379; (g) Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229; (h) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975.
12. Pihko, A. J.; Koskinen, A. M. P. *Tetrahedron* **2005**, *61*, 8769.
13. Harwood, L. M.; Moody, C. J. *Experimental Organic Chemistry: Principles and Practice*; Blackwell Scientificlication: Victoria, 1989; 624–625.
14. Cope, A. C.; Herrick, E. C. p 304 *Organic Syntheses*; 1963; Coll. Vol. 4 Vol. 30, p 29 (1950).
15. (a) Schmidt, B. *Eur. J. Org. Chem.* **2004**, 1865 and references cited therein.
16. (a) Bilyard, K. G.; Garratt, P. J.; Hunter, R.; Lete, E. *J. Org. Chem.* **1982**, *47*, 4731; (b) Bilyard, K. G.; Garratt, P. J.; Zahler, R. *Synthesis* **1980**, 389; (c) Rae, I. D.; Serelis, A. K. *Aust. J. Chem.* **1941**, *1*, 43.
17. (a) Shea, K. J.; Greeley, A. C.; Nguyen, S.; Beauchamp, P. D.; Aue, D. H.; Witzemant, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5901; (b) Altman, J.; Babad, E.; Itzchaki, J.; Ginsburg, D. *Tetrahedron* **1966**, *22*, 279.
18. (a) Delgado, M.; Martin, J. D. *J. Org. Chem.* **1999**, *64*, 4798; (b) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792; (c) Abell, A. D.; Alexander, N. A.; Aitken, S. G.; Chen, H.; Coxon, J. M.; Jones, M. A.; McNabb, S. B.; Taylor, A. M. *J. Org. Chem.* **2009**, *74*, 4354.