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Formal Homoiodo Allylsilane Annulations: Dual Total Syntheses of (±)-Hirsutene and (±)-Capnellene

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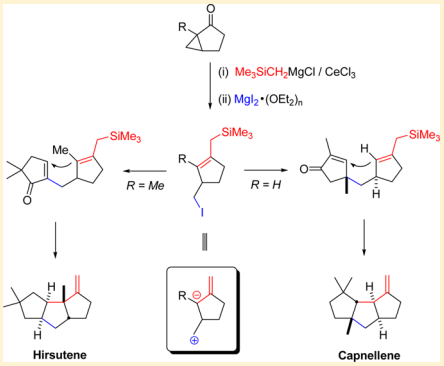
Supporting Information

ABSTRACT: Dual total syntheses of (±)-hirsutene and (±)-capnellene, two typical linear triquinane sesquiterpenes, were achieved via a formal [3 + 2] annulation strategy, as illustrated schematically. Cyclic homoiodo allylsilanes were employed as key bifunctional synthons in the synthesis, which were readily prepared from the corresponding cyclopropanated cyclopentenones. A formal [3 + 3] annulation approach for the elaboration of the bicyclic framework of the Eudesmane sesquiterpenoids based on this type of synthon was also developed.



INTRODUCTION

Hirsutene (**1**) and capnellene (**2**) are two representative members of the linearly fused triquinane sesquiterpene family (Figure 1). The inspiring molecular architectures of **1** and **2** have captured the imagination of synthetic chemists for several decades, as evidenced by the flourishing novel strategies and methodologies for their total syntheses.[1−4]

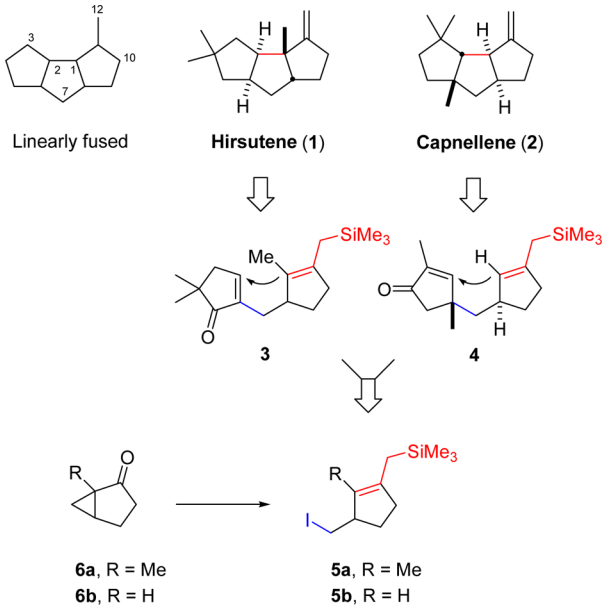


Figure 1. Formal homoiodo allylsilane annulation strategy toward the linear triquinane sesquiterpenes.

Our own interest in the total synthesis of **1** and **2** via a unified annulation strategy[2] shown in Figure 1 stemmed from our previous methodological development for the synthesis of cyclic homoiodo allylsilanes **5a** and **5b** as bifunctional synthons from the corresponding cyclopropanated cyclopentenone derivatives **6a** and **6b**, respectively.[5] The intramolecular Hosomi−Sakurai type cyclization of enone allylsilanes **3** and **4** would establish the triquinone skeleton of **1** and **2**, respectively. Cyclization precursors **3** and **4** can be prepared by alkylation of homoiodo allylsilanes **5a** and **5b** with the respective enolates of the substituted cyclopentenones. This Article describes the detailed experimental results of these studies.

RESULTS AND DISCUSSION

The total synthesis of (±)-hirsutene (**1**) commenced from cyclopentenone derivatives **6a**[6] and **8**[7] and is outlined in Scheme 1. Homoiodo allylsilane **5a** (along with chromatographically inseparable cyclohexenyl iodosilane **7a**), prepared from **6a** according to a two-step sequence previously developed in our laboratory[5] in 68% overall yield (with a ratio of 2:1 determined by GC), was alkylated with the lithium enolate of 5,5-dimethylcyclopentenone (**8**) in a solvent mixture of THF and HMPA. The purification of the crude product by standard silica gel chromatography furnished desired α-alkylation product **3** in 30% yield. It is worth noting that the presence of HMPA in the solvent mixture is critical for direct α-alkylation of enone **8** in modest yield. Alternative protocols[8] for

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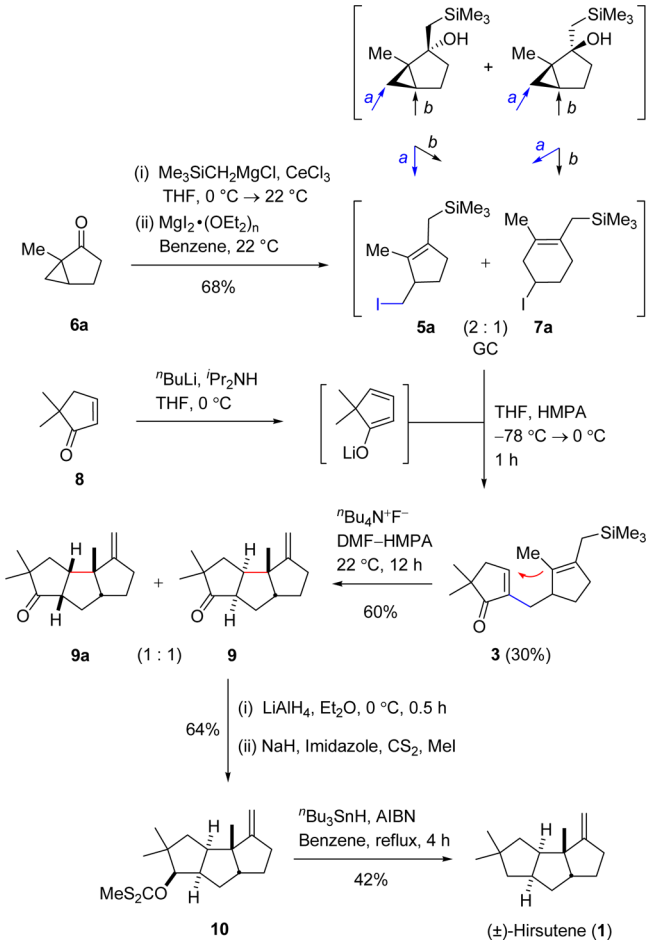
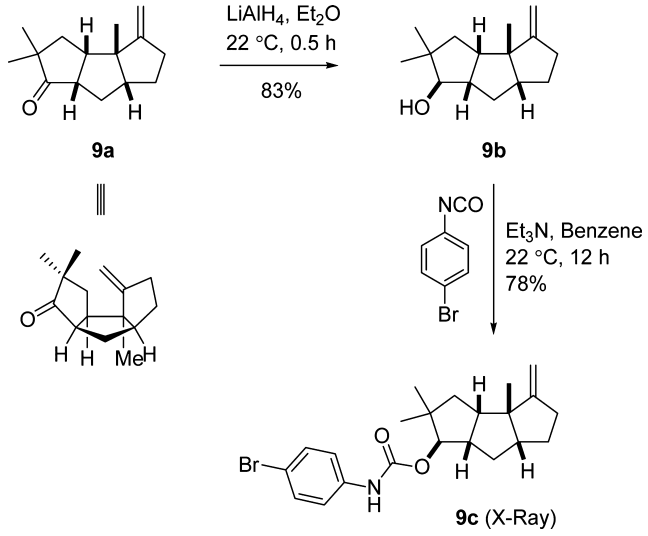
Scheme 1



Scheme 2



indirect alkylation of derivatives of 5,5-dimethylcyclopentenone (**8**) are less efficient. The intramolecular cyclization[9] of allylsilane **3** mediated by TBAF[10] in a solvent mixture of DMF and HMPA at ambient temperature led to the production of an equal amount of *cis-anti-cis* triquinone derivative **9** and *cis-syn-cis* triquinone derivative[11] **9a** in 60% overall yield, which were readily separated by flash silica gel chromatography. The stereostructure of **9a** was confirmed unambiguously by the X-ray crystallography of corresponding carbamate derivative **9c** (Scheme 2).[12] The reductive deoxygenation of triquinone derivative **9** by a standard Barton–McCombie procedure[2e,13] via corresponding xanthate **10** gave (±)-hirsutene (**1**), which was identical spectroscopically to previous reports.[2]

The detailed synthesis sequence for (±)-capnellene (**2**) commenced from cyclopentenone derivatives **6b**[6] and **11**[14] and is depicted in Scheme 3. Homoiodo allylsilane **5b** (along with chromatographically inseparable cyclohexenyl iodosilane **7b**), prepared from **6b** via the standard procedures as aforementioned in 65% overall yield (with a ratio of 2.3:1 determined by GC), was alkylated with the lithium enolate of 3-ethoxy-2,5-dimethylcyclopentenone (**11**) smoothly to afford desired allylsilane **12**[15] in 70% yield as a chromatographically inseparable mixture of diastereomers. The hydride reduction of **12** with DIBAL-H followed by aqueous workup (hydrolysis) furnished desired cyclization precursor **4**[15a] in 82% yield. The cyclization of allylsilane **4** was conducted in CH_2Cl_2 at −78 °C by brief exposure to freshly distilled $TiCl_4$.[16] After aqueous workup and silica gel chromatographic purification, triquinone derivative **13** was obtained as the sole isolated product in 42% yield. It is notable that diastereomer **4***β* is unreactive under the $TiCl_4$-mediated conditions, presumably because of the unfavorable overlapping conformation (Scheme 3, diastereomer **4***α* exhibits a favorable off-set conformation instead).[16d] The methylation[17] of triquinone **13** according to a known procedure gave triquinone derivative **14** in good yield. The standard reductive deoxygenation[2e,13] of compound **14** via the aforementioned procedures produced (±)-capnellene (**2**), which was identical spectroscopically to previous reports.[3e,f]

In sharp contrast, the TBAF-mediated cyclization[10,16d] of **4** resulted in the formation of protodesilylated[10b,c] enone derivative **16a** (38% yield) and *cis-syn-cis* triquinone derivative **16b**[10] in 45% yield after silica gel chromatographic purification (Scheme 4). Interestingly, the TBAF-mediated cyclization of allylsilane **4** prefers the diastereomer **4***β* instead.

We have previously prepared via an analogous procedure cyclic homoiodo allylsilane **18** from readily available (+)-carvone derivative **17**.[5] Facile coupling of **18** with methyl acrylate was effectively mediated by a Ni(0)–pyridine complex (in situ generated via Zn reduction)[18] to afford allylsilane **19** in 80% yield (Scheme 5). The hydride reduction of the ester function of **19** with DIBAL-H in toluene gave corresponding aldehyde **20** smoothly. Exposure of **20** to freshly distilled $SnCl_4$ in a chlorinated solvent (CH_2Cl_2 or $ClCH_2CH_2Cl$) at temperatures below −78 °C furnished epimeric bicyclic alcohol products **21a** and **21b** in good yield.[19] Oxidation of **21a** or **21b** with PCC in CH_2Cl_2 led to identical bicyclic ketone **22** with yield of 95%, which bears the typical ring framework of the Eudesmane sesquiterpene.[20] Interestingly, cyclization mediated by $SnCl_4$ at −20 °C afforded the sole product **21a** in 61% isolated yield.[19a]

The hydride reduction of bicyclic ketone **22** with $LiAlH_4$ in Et_2O at 0 °C gave kinetically favorable product **21a** in 92% yield (whose skeletal and stereostructure were established unambiguously by X-ray crystallography of a dihydroxylation derivative **23a**) (Scheme 6).[12]

■ CONCLUSIONS

We have demonstrated in this Article that readily accessible cyclic homoiodo allylsilanes **5a**, **5b**, and **18** could be employed as useful synthons for a formal [3 + 2] or [3 + 3] annulation in

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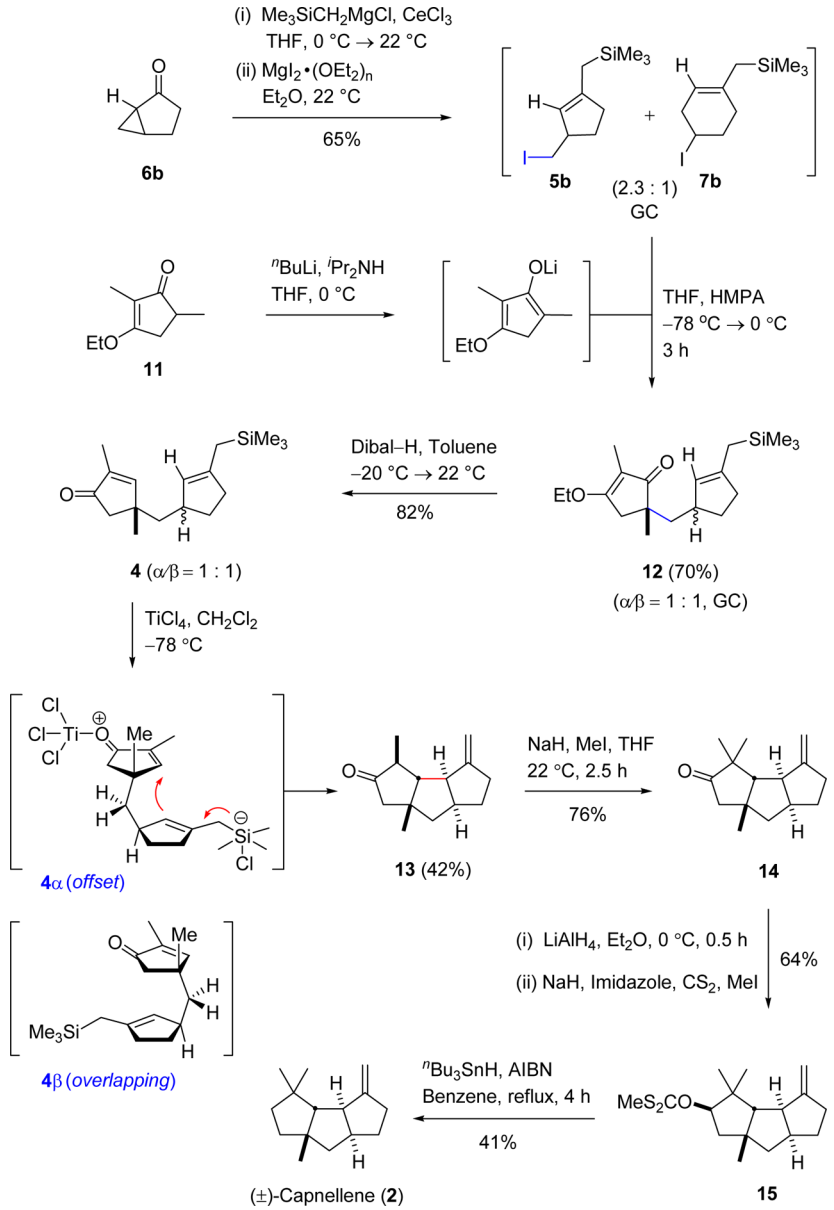
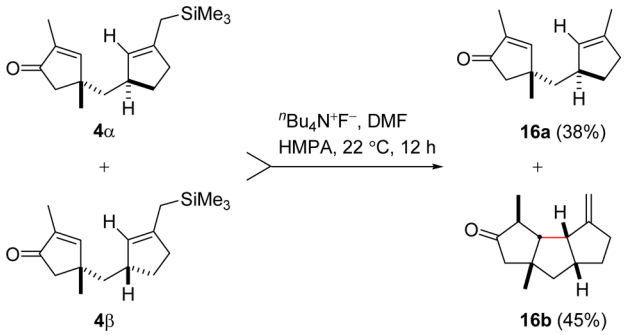
Scheme 3



Scheme 4



organic synthesis (Figure 2), as exemplified here in a short and convergent total synthesis of (±)-hirsutene and (±)-capnellene. The total synthesis of (±)-hirsutene (**1**) was achieved in 8 steps from 2-methyl cyclopentenone in an overall yield of ca. 1.5%, and the total synthesis of (±)-capnellene (**2**) was achieved in 10 steps from cyclopentenone in an overall yield of ca. 2.8%. Eudesmane sesquiterpene framework (e.g., **21a**) was established in 5 steps from (+)-carvone in an overall yield of ca. 20%. The features of this synthesis approach include the facile incorporation of an angular substituent (e.g., methyl) and the versatile allylsilane cyclization mode and reaction conditions.[21]

■ EXPERIMENTAL SECTION

General Procedures. For product purification by flash column chromatography, silica gel (200−300 mesh) and light petroleum ether (bp 60−90 °C) were used unless otherwise noted. All solvents were purified and dried by standard techniques and distilled prior to use. Other commercially available reagents were used as received without further purification unless otherwise indicated. All organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate. All moisture-sensitive reactions were carried out under an atmosphere of nitrogen in glassware that was flame-dried under vacuum. ^{1}H and ^{13}C NMR spectra were recorded on a 300, 400, or 600 MHz spectrometer with TMS as the internal reference and $CDCl_3$ as the solvent unless otherwise indicated. IR spectra were recorded on an FT-IR

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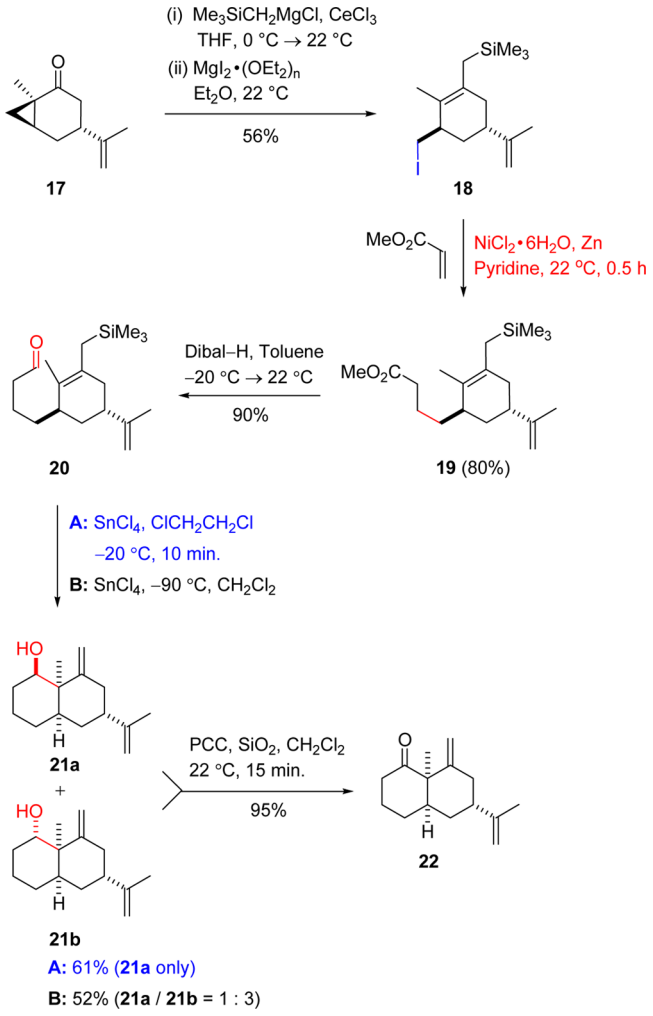
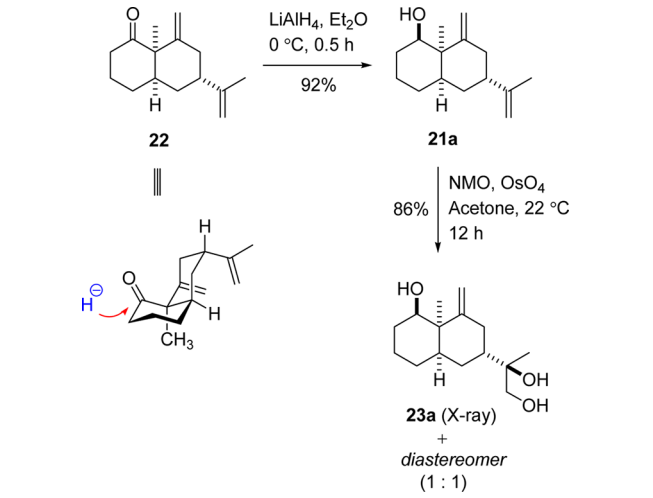
Scheme 5



Scheme 6



spectrometer as liquid film, and the data are reported in reciprocal centimeters (cm^{-1}). HRMS were determined on a FT-ICR spectrometer. For liquid secondary ion mass spectrometry (LSIMS), a Cs^+ ion beam (2 mA) was employed at 10 000 V, and the analytical-cell vacuum was 2×10^{-9} mbar. Melting points were measured on a hot stage and are uncorrected.

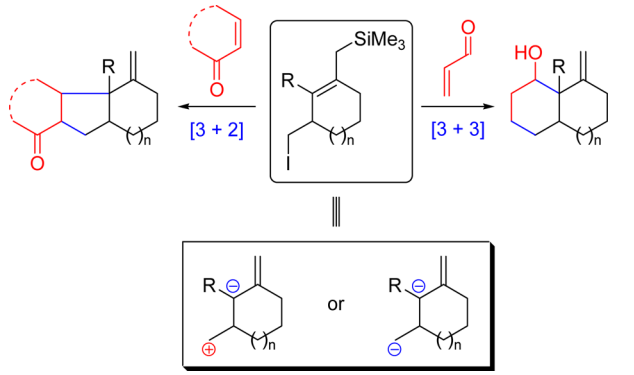


Figure 2. Homoiodo allylsilane annulation synthons.

General Procedure for the Preparation of Homoiodo Allylsilanes from Cyclopropyl Ketones. (1) Freshly dried (1 mmHg at 150 °C for 7 h from the heptahydrate) $CeCl_3$ (815 mg, 3.30 mmol) was suspended in 10 mL of anhydrous THF, and the mixture was stirred vigorously for 2 h at room temperature. The resultant solution was cooled to 0 °C by an ice bath, and a stock solution of (trimethylsilyl)methylmagnesium chloride in diethyl ether (1.0 M, 3.3 mL, 3.30 mmol) was added dropwise at the same temperature. After the mixture was stirred for 1 h at 0 °C, cyclopropyl ketone[6] (2.00 mmol) in 3 mL of THF was added, and the resulting mixture was warmed gradually to room temperature. When the consumption of the starting ketone was complete (monitored by TLC), the reaction mixture was cooled to 0 °C and quenched with water (1 mL). The organic layer was separated, and the aqueous phase was extracted with diethyl ether. The organic layers were washed with water and brine and dried ($MgSO_4$). The solvent was evaporated carefully in vacuo at 0 °C to give the cyclopropyl carbinol adduct as a yellowish oil.

(2) The crude cyclopropyl carbinol was taken in anhydrous diethyl ether (10 mL) under a nitrogen atmosphere, the mixture was stirred at 0 °C, and a freshly prepared $MgI_2 \cdot Et_2O$ (3.00 mmol, 0.25 M) solution mixture in Et_2O–benzene (1:1) was added dropwise. The resulting mixture was stirred for 10–15 min at 0 °C, quenched with saturated $NaHCO_3$, and extracted with diethyl ether. The organic extract was washed with a 10% sodium thiosulfate solution, water, and brine and dried ($MgSO_4$). The solvent was evaporated in vacuo to give an oily residue, which was purified by flash silica gel chromatography, eluting with a mixture of diethyl ether–petroleum ether (bp 30–60 °C) to afford the homoiodo allylsilane product as a colorless oil.

*((3-(Iodomethyl)-2-methylcyclopent-1-en-1-yl)methyl)-trimethylsilane (**5a**) and ((4-Iodo-2-methylcyclohex-1-en-1-yl)-methyl)trimethylsilane (**7a**).* Compounds **5a** and **7a** were prepared using the above general procedure in an overall yield of 68% as a chromatographically inseparable mixture. The ratio was determined by GC–MS to be 2.0:1 (GC–MS conditions: DB-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm); flow rate = 1.0 mL/min; source temperature 250 °C; injection port 220 °C, 40 °C/3 min). Colorless oil: R_f = 0.60 (petroleum ether); IR (film) ν_{max} = 2952, 2848, 1663, 1417, 1247, 1164, 853, 841, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.49–4.48 (m, compound **7a**, 0.4H), 3.40 (dd, compound **5a**, 1H, J = 3.2, 10.0 Hz), 3.18 (dd, compound **5a**, 1H, J = 7.2, 9.6 Hz), 2.67–2.62 (m, 2H), 2.30–2.24 (m, 1H), 2.14–1.93 (m, 5H), 1.57–1.52 (m, 7H), 1.42–1.39 (m, 1.6H), 0.02 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 128.7, 126.9, 121.4, 51.3, 44.3, 36.5, 35.6, 32.8, 29.3, 28.8, 24.0, 19.8, 19.5, 16.5, 12.2, −0.5, −0.7; EI-MS (m/z) M^+ 308 (5.9%), 181 (25%), 93 (30%), 73 (100%).

*((3-(Iodomethyl)cyclopent-1-en-1-yl)methyl)trimethylsilane (**5b**) and ((4-Iodocyclohex-1-en-1-yl)methyl)trimethylsilane (**7b**).* Compounds **5b** and **7b** were prepared using the above general procedure in an overall yield of 65% as a chromatographically inseparable mixture. The ratio was determined by GC–MS spectra to be 2.3:1 (GC–MS conditions: DB-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm); flow rate =1.0 mL/min; source temperature 250 °C; injection port 220 °C, 40 °C/3 min.). Colorless oil; R_f = 0.60

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(petroleum ether); IR (film) ν_{max} = 2952, 2921, 1636, 1248, 1168, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.05 (s, compound **5b**, 1H), 5.02 (s, compound **7b**, 0.3H), 4.52−4.45 (m, compound **7b**, 0.4H), 3.19 (dd, compound **5b**, 1H, J = 6.8, 12.0 Hz), 3.10 (dd, compound **5b**, 1H, J = 9.6, 12.0 Hz), 3.00−2.98 (m, 1H), 2.80−2.61 (m, 1H), 2.31−2.17 (m, 2H), 2.13−1.98 (m, 3H), 1.57−1.49 (m, 3H), 0.03 (s, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 134.9, 124.5, 116.7, 48.3, 38.2, 36.9, 35.0, 31.5, 31.2, 29.7, 28.1, 27.9, 21.7, 15.6, −1.1, −1.3; EI−MS (m/z) M^+ 294 (1.9%), 167 (39%), 79 (35%), 73 (100%).

*5,5-Dimethyl-2-((2-methyl-3-((trimethylsilyl)methyl)cyclopent-2-en-1-yl)methyl)cyclopent-2-enone (**3**).* To a stirred mixture of diisopropylamine (0.34 mL, 2.40 mmol) in dry THF (4 mL) was added *n*-BuLi (1.6 M in hexane, 1.38 mL, 2.20 mmol) dropwise at 0 °C under N_2, and the mixture was stirred for 30 min. The resulting LDA solution was cooled to −78 °C, and a mixture of **8** (220 mg, 2.00 mmol) and HMPA (1.0 mL, 5.40 mmol) in dry THF (3 mL) was added dropwise, and the solution was stirred for 30 min. A mixture of **5a** and **7a** (2:1 (GC), 940 mg, 3.00 mmol) in 5 mL of THF was added dropwise over 10 min via syringe at −78 °C. The reaction mixture was warmed gradually to room temperature over 1 h, quenched with 1 mL of saturated aqueous NH_4Cl, and extracted with diethyl ether. The ethereal layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give compound **3** (104 mg, 30%) as a colorless oil: R_f = 0.65 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2956, 2867, 1704, 1440, 1247, 1146, 1022, 841, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 2.72 (br s, 1H), 2.49−2.42 (m, 2H), 2.21−2.11 (m, 2H), 1.96−1.85 (m, 2H), 1.55 (s, 3H), 1.49−1.47 (m, 2H), 1.34−1.26 (m, 2H), 1.12 (s, 6H), −0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.3, 154.7, 142.7, 133.6, 130.5, 47.9, 43.7, 43.0, 36.9, 29.3, 28.4, 25.2, 25.1, 19.4, 12.6, −0.8 (3C, $-Si(CH_3)_3$); HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{31}OSi$, 291.2139; found, 291.2135.

*(3aR,3bR,6aR,7aR)-2,2,3b-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-1-one (**9**) and (3aS,3bR,6aR,7aS)-2,2,3b-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-1-one (**9a**).* To a mixture of TBAF trihydrate (62 mg, 0.24 mmol) in dry DMF (3 mL) was added powdered 4 Å molecular sieves (50 mg). After stirring for 15 min, the mixture was filtered, and the resulting filtrate was transferred to a reaction vessel containing 100 mg of 4 Å molecular sieves and HMPA (0.40 mL, 2.16 mmol). After stirring for 15 min at room temperature, a solution of allylsilane **3** (63 mg, 0.22 mmol) in 1 mL of dry DMF was added to the above slurry over 30 min via a syringe pump. The reaction mixture was stirred at room temperature for 12 h, quenched with 1 mL of water, and extracted with ether. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give compounds **9** (15 mg, 30%) and **9a** (15 mg, 30%) as colorless oils, respectively. Compound **9**: R_f = 0.55 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2956, 2867, 1735, 1459, 1378, 1093, 879, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.85 (d, 1H, J = 2.4 Hz), 2.76−2.68 (m, 2H), 2.66−2.52 (m, 1H), 2.49−2.40 (m, 2H), 2.33−2.30 (m, 1H), 1.93−1.86 (m, 2H), 1.80−1.73 (m, 1H), 1.65−1.60 (m, 2H), 1.54−1.41 (m, 1H), 1.10 (s, 3H), 1.06 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 224.8, 161.5, 104.7, 57.6, 50.7, 49.2, 48.9, 47.1, 40.4, 34.5, 31.5, 28.4, 24.6, 24.3, 22.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{23}O$, 219.1743; found, 219.1746. Compound **9a**: R_f = 0.54 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2962, 2867, 1740, 1329, 1129, 1094, 912, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.94 (s, 1H), 4.65 (s, 1H), 2.49−2.35 (m, 4H), 2.22−2.09 (m, 2H), 1.73−1.70 (m, 1H), 1.56−1.42 (m, 4H), 1.12 (s, 3H), 0.98 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 223.9, 158.2, 105.8, 56.8, 55.5, 53.1, 49.5, 47.7, 41.7, 35.3, 34.0, 29.9, 29.2, 24.9, 24.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{23}O$, 219.1743; found, 219.1745.

*(1R,3aS,3bR,6aR,7aS)-2,2,3b-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-1-ol (**9b**).* To a suspension of $LiAlH_4$ (20 mg, 0.53 mmol) in dry Et_2O (1.5 mL) at 0 °C was added compound **9a** (25 mg, 0.11 mmol) in dry Et_2O (1.5 mL) under N_2. After stirring for 30 min at 0 °C, the reaction mixture was quenched with 1 mL of water and extracted with ether. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give hydroxyl olefin **9b** (18 mg, 83%) as a colorless oil: R_f = 0.31 (petroleum ether/EtOAc = 3:1); IR (film) ν_{max} = 3360, 2944, 2856, 1650, 1457, 1671, 1072, 1028, 876 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H), 4.64 (s, 1H), 3.59 (d, 1H, J = 6.4 Hz), 2.93−2.84 (m, 1H), 2.58−2.49 (m, 1H), 2.37 (t, 2H, J = 8.8 Hz), 2.25−2.18 (m, 1H), 1.78−1.70 (m, 1H), 1.69−1.57 (m, 3H), 1.33−1.22 (m, 2H), 1.15 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 105.7, 80.7, 56.0, 55.0, 54.4, 49.9, 44.7, 42.0, 34.6, 30.7, 30.0, 28.2, 27.6, 24.2; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{25}O$, 221.1900; found, 221.1903.

*(1R,3aS,3bR,6aR,7aS)-2,2,3b-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-1-ol (**9c**).* To a mixture of compound **9b** (20 mg, 0.09 mmol) in dry benzene (1 mL) were added 4-bromophenylisocyanate (22 mg, 0.11 mmol) and Et_3N (0.10 mL, 0.70 mmol) at 0 °C. The resulting mixture was stirred at room temperature overnight and quenched with 1 mL of water. The reaction mixture was extracted with ether, and the organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give **9c** (38 mg, 78%) as a colorless solid: R_f = 0.58 (petroleum ether/EtOAc = 10:1); mp 123−125 °C; IR (film) ν_{max} = 3320, 2957, 2867, 1735, 1459, 1379, 1129, 1094, 912, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 2H, J = 8.8 Hz), 7.29 (d, 2H, J = 8.8 Hz), 6.56 (br s, 1H), 4.96 (s, 1H), 4.65 (s, 1H), 4.62 (d, 1H, J = 6.0 Hz), 2.59−2.52 (m, 1H), 2.50−2.36 (m, 3H), 2.22−2.12 (m, 2H), 1.75−1.70 (m, 1H), 1.64−1.60 (m, 1H), 1.55−1.47 (m, 2H), 1.13 (s, 3H), 1.04 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.3, 137.2, 131.9 (2C), 127.6, 120.1, 115.7, 105.6, 83.7, 55.6, 54.8, 54.3, 49.0, 43.9, 43.1, 34.7, 31.3, 30.6, 28.1, 27.6, 24.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{29}BrNO_2$, 418.1376; found, 418.1380. X-ray crystallographic data of **9c**: $C_{22}H_{28}BrNO_2$, monoclinic, space group: Cc, a = 11.002 (4) Å, b = 24.264 (8) Å, c = 9.485 (3) Å, β = 123.324 (14) °, Z = 4, d_{calcd} = 1.313 g/cm^3, $R_1(I > 2\sigma(I))$ = 0.0633, wR_2 = 0.0766.

*(1R,3aR,3bR,6aR,7aR)-2,2,3b-Trimethyldecahydro-1H-cyclopenta[a]pentalen-1-ol (**9d**).* Compound **9d** was prepared by a procedure analogous to that for compound **9b** in 81% yield as a colorless oil: R_f = 0.31 (petroleum ether/EtOAc = 3:1); IR (film) ν_{max} = 3503, 2933, 2867, 1713, 1427, 1363, 1222, 1091, 901 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.77 (d, 1H, J = 2.4 Hz), 3.22 (d, 1H, J = 7.6 Hz), 2.61 (q, 1H, J = 9.6 Hz), 2.51−2.46 (m, 2H), 2.45−2.37 (m, 1H), 2.24−2.15 (m, 1H), 2.13−2.04 (m, 1H), 1.76−1.70 (m, 1H), 1.65−1.61 (m, 1H), 1.60−1.48 (m, 2H), 1.47−1.40 (m, 1H), 1.01 (s, 3H), 0.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 104.1, 87.8, 55.8, 50.0, 49.5, 47.6, 42.4, 41.0, 35.5, 29.9, 26.7, 25.4, 22.1, 19.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{25}O$, 221.1900; found, 221.1904.

*S-Methyl O-((1R,3aR,3bR,6aR,7aR)-2,2,3b-Trimethyldecahydro-1H-cyclopenta[a]pentalen-1-yl) Carbonodithioate (**10**).* A mixture of compound **9d** (25 mg, 0.11 mmol), NaH (18 mg, 0.75 mmol), and imidazole (2 mg, 0.03 mmol) in dry THF (2 mL) in a 10 mL three-necked flask was refluxed with stirring for 3 h under nitrogen, and a mixture of carbon disulfide (0.30 mL, 5.00 mmol) in 1 mL of THF was added dropwise. After refluxing for 45 min, methyl iodide (0.50 mL, 8.00 mmol) was added to the reaction mixture and refluxed for another 30 min. The reaction mixture was quenched with acetic acid (0.15 mL), diluted with water, and extracted with ether. The ethereal layer was washed with water, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 15:1) to give xanthate derivative **10** (28 mg, 81%) as a colorless oil: R_f = 0.70 (petroleum ether/EtOAc = 10:1); IR (film) ν_{max} = 2947, 2867, 1649, 1460, 1370, 1222, 1058, 964, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.52 (d, 1H, J = 6.4 Hz), 4.83 (s, 1H), 4.78 (d, 1H, J = 2.4 Hz), 2.74−2.69 (m, 1H), 2.58−2.52 (m, 1H), 2.54 (s, 3H), 2.49−2.44 (m, 2H), 2.20−2.16

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(m, 1H), 1.95−1.89 (m, 1H), 1.78−1.70 (m, 1H), 1.62−1.57 (m, 1H), 1.53−1.46 (m, 3H), 1.06 (s, 6H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 161.7, 104.2, 96.7, 55.7, 49.8, 49.6, 47.6, 43.9, 41.7, 35.9, 30.4, 27.3, 26.2, 22.4, 21.8, 18.8; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{27}OS_2$, 311.1498; found, 311.1504.

*(3aR,3bR,6aR,7aS)-2,2,3b-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalene (**1**).* A mixture of tri-*n*-butyltin hydride (41 mg, 0.14 mmol) and AIBN (2 mg, 0.01 mmol) in dry benzene (2 mL) was brought to 80 °C, and a mixture of xanthate **10** (15 mg, 0.05 mmol) in dry benzene (1 mL) was introduced. After refluxing for 6 h, the reaction mixture was evaporated in vacuo, and the residual oil was charged on an $AgNO_3$-impregnated silica gel column. An elution with petroleum ether removed the organotin impurities. Further elution with *n*-hexane gave hydrocarbon **1** (8 mg, 42%) as a colorless oil: R_f = 0.95 (petroleum ether); IR (film) ν_{max} = 2921, 2862, 1660, 1585, 1456, 1248, 1162, 872 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.77 (s, 1H), 2.63−2.57 (m, 1H), 2.53−2.44 (m, 3H), 2.17−2.11(m, 1H), 1.78−1.71 (m, 1H), 1.65 (ddd, 2H, J = 2.0, 8.4, 10.4 Hz), 1.48−1.40 (m, 4H), 1.29−1.19 (m, 1H), 1.05 (s, 3H), 1.04−0.98 (m, 1H), 0.92 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 103.5, 56.0, 53.5, 50.0, 49.0, 44.3, 41.9, 40.9, 38.6, 30.9, 29.7, 27.3, 26.8, 23.2.

*(5R)-3-Ethoxy-2,5-dimethyl-5-((3-((trimethylsilyl)methyl)-cyclopent-2-en-1-yl)methyl)cyclopent-2-enone (**12**).* To a stirred solution of diisopropylamine (0.34 mL, 2.40 mmol) in dry THF (4 mL) was added *n*-BuLi (1.6 M in hexane, 1.38 mL, 2.20 mmol) at 0 °C under N_2, and the mixture was stirred for 30 min. The resulting LDA solution was cooled to −78 °C, and a mixture of compound **11** (308 mg, 2.00 mmol) and HMPA (1.0 mL, 5.41 mmol) in dry THF (4 mL) was added dropwise. After stirring for 30 min at −78 °C, a mixture of compounds **5b** and **7b** (2.3:1 (GC), 470 mg, 1.60 mmol) in 3 mL of THF was added over 10 min. The reaction mixture was warmed to room temperature over 3 h and quenched with 1 mL of saturated aqueous NH_4Cl. The mixture was extracted with 100 mL of EtOAc, and the organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give compound **12** (250 mg, 70%) as a colorless oil. The diastereoisomeric ratio of compound **12** was determined by GC−MS spectra to be 1:1 (GC−MS conditions: DB-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm); flow rate = 1.0 mL/min; source temperature 250 °C; injection port 220 °C, 15 °C/min): R_f = 0.51 (petroleum ether/EtOAc = 4:1); IR (film) ν_{max} = 2953, 2921, 1690, 1637, 1382, 1336, 1246, 1011, 847 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (s, 0.5H, α isomer), 4.92 (s, 0.5H, β isomer), 4.19−4.16 (m, 2H), 2.66 and 2.33 (ABq, each 1H, J = 17.2 Hz), 2.61−2.51 (m, 1H), 2.14−2.05 (m, 4H), 1.61 (s, 3H), 1.48 (s, 2H), 1.53−1.42 (m, 2H), 1.39−1.35 (m, 3H), 1.10 (s, 3H), −0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 210.0, 181.4, 181.3, 141.8, 141.5, 126.7, 126.5, 114.2, 113.7, 65.0, 46.9, 46.7, 44.9, 44.6, 42.2, 42.2, 39.6, 39.1, 37.2, 37.1, 33.1, 32.5, 25.0, 24.0, 21.4, 21.3, 15.3, 6.2, 6.1, −1.4, −1.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{33}O_2Si$, 321.2244; found, 321.2245.

*(4R)-2,4-Dimethyl-4-((3-((trimethylsilyl)methyl)cyclopent-2-en-1-yl)methyl)cyclopent-2-enone (**4**).* To a mixture of **12** (110 mg, 0.34 mmol) in 2 mL of toluene at −20 °C was added dropwise DIBAL-H (1.2 M in *n*-hexane, 0.57 mL, 0.68 mmol). After stirring for 30 min, the reaction mixture was quenched with 0.5 mL of water and extracted with ether. The ethereal layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give compound **4** (78 mg, 82%) as a colorless oil: R_f = 0.62 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2954, 2920, 1708, 1248, 848 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, 0.5H, J = 1.2 Hz, α isomer), 7.06 (d, 0.5H, J = 1.2 Hz, β isomer), 4.96 (s, 1H, α/β = 1:1), 2.59−2.56 (m, 1H), 2.41 and 2.17 (ABq, each 1H, J = 18.8 Hz, O═C—CH_2−), 2.15−1.94 (m, 3H), 1.74 (s, 3H), 1.71−1.64 (m, 1H), 1.55−1.45 (m, 2H), 1.53 (s, 2H), 1.45−1.31 (m, 2H), 1.18 (s, 3H), −0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 167.6, 167.4, 142.0, 141.9, 139.1, 139.0, 126.7, 126.5, 48.8, 48.6, 48.1, 47.9, 42.4, 42.3, 37.3, 37.1, 33.6, 33.3, 27.4, 27.0, 21.4, 9.9, 9.9, −1.3, −1.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{29}OSi$, 277.1982; found, 277.1986.

*(3S,3aS,3bS,6aS,7aR)-3,7a-Dimethyl-4-methyleneoctahydro-1H-cyclopenta[a]pentalen-2(3bH)-one (**13**).* To a mixture of compound **4** (55 mg, 0.20 mmol) in dry CH_2Cl_2 (2 mL) was added titanium tetrachloride (1.0 M in CH_2Cl_2, 0.30 mL, 0.30 mmol) at −78 °C under N_2. After stirring for 1 min at −78 °C, the reaction mixture was quenched with 0.5 mL of saturated aqueous $NaHCO_3$. The reaction mixture was extracted with ether (20 mL), and the organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to give compound **13** (20 mg, 42%) as a colorless oil: R_f = 0.53 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2933, 2866, 1739, 1655, 1455, 1376, 1182, 880 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.69 (s, 1H), 2.68−2.55 (m, 2H), 2.48−2.38 (m, 1H), 2.28−2.22 (m, 1H), 2.08−2.04 (m, 1H), 2.07 (s, 2H), 1.98−1.94 (m, 1H), 1.77−1.67 (m, 2H), 1.52−1.49 (m, 1H), 1.38−1.33 (m, 1H), 1.18 (s, 3H), 1.15 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.6, 157.7, 105.4, 60.3, 49.4, 48.0, 47.4, 47.3, 46.2, 42.7, 33.0, 30.4, 26.6, 11.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{21}O$, 205.1587; found, 205.1582.

*(3aR,3bS,6aS,7aR)-3,3,7a-Trimethyl-4-methyleneoctahydro-1H-cyclopenta[a]pentalen-2(3bH)-one (**14**).* To a suspension of NaH (4.8 mg, 0.20 mmol) in dry THF (1 mL) was added a solution of compound **13** (33 mg, 0.16 mmol) in dry THF (1 mL) at room temperature. After stirring for 30 min, methyl iodide (0.23 mL, 3.75 mmol) in THF (1 mL) was added to the reaction mixture. The reaction mixture was stirred for 2 h and quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to give compound **14** (25 mg, 76%) as a colorless oil: R_f = 0.58 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2943, 2868, 1737, 1653, 1454, 1380, 877 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.77 (d, 1H, J = 1.6 Hz), 2.82 (br d, 1H, J = 8.0 Hz), 2.61−2.46 (m, 2H), 2.39−2.33 (m, 1H), 2.31 and 2.23 (ABq, each 1H, J = 18.4 Hz), 2.03 (d, 1H, J = 3.6 Hz), 1.84−1.71 (m, 2H), 1.57−1.50 (m, 1H), 1.38 (dd, 1H, J = 9.6, 13.2 Hz), 1.26 (s, 3H), 1.90 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 223.9, 158.2, 105.4, 66.3, 51.5, 49.8, 49.2, 46.8, 46.4, 43.5, 32.1, 30.0, 29.3, 28.3, 23.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{23}O$, 219.1743; found, 219.1740.

*(2R,3aR,3bS,6aS,7aR)-3,3,7a-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-2-ol (**14a**).* Compound **14a** was prepared by a procedure analogous to that of compound **9b** in 82% yield as a colorless oil: R_f = 0.31 (petroleum ether/EtOAc = 3:1); IR (film) ν_{max} = 3360, 2944, 2865, 1650, 1457, 1371, 1073, 1028, 876 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 1H), 4.77 (s, 1H), 3.77 (dd, 1H, J = 6.4, 10.0 Hz), 2.71−2.68 (m, 2H), 2.50−2.44 (m, 1H), 2.40−2.37 (m, 1H), 1.91−1.78 (m, 3H), 1.69−1.50 (m, 2H), 1.34−1.21 (m, 2H), 1.11 (s, 3H), 1.07 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 105.1, 80.9, 68.3, 51.5, 48.3, 48.2, 47.5, 46.3, 44.5, 32.6, 31.8, 29.7, 28.5, 17.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{25}O$, 221.1900; found, 221.1905.

*S-Methyl O-((2R,3aR,3bS,6aS,7aR)-3,3,7a-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalen-2-yl) Carbonodithioate (**15**).* Compound **15** was prepared by a procedure analogous to that of compound **10** as a colorless oil (79%): R_f = 0.71 (petroleum ether/EtOAc = 10:1); IR (film) ν_{max} = 2949, 2866, 1650, 1454, 1221, 1057, 963, 877 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (t, 1H, J = 6.4 Hz), 4.92 (d, 1H, J = 1.6 Hz), 4.78 (d, 1H, J = 1.6 Hz), 2.87−2.85 (m, 1H), 2.76−2.71 (m, 1H), 2.56 (s, 3H), 2.52−2.48 (m, 1H), 2.41−2.38 (m, 1H), 2.17−2.12 (m, 1H), 1.86−1.73 (m, 4H), 1.56−1.50 (m, 1H), 1.31−1.27 (m, 1H), 1.25 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 158.6, 105.4, 92.7, 68.5, 52.0, 49.7, 48.4, 45.7, 45.6, 45.0, 32.5, 31.8, 29.4, 29.2, 20.3, 18.8; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{27}OS_2$, 311.1498; found, 311.1502.

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*(R)-2,4-Dimethyl-4-(((S)-3-methylcyclopent-2-en-1-yl)methyl)-cyclopent-2-enone (**16a**) and (3S,3aS,3bR,6aR,7aR)-3,7a-Dimethyl-4-methyleneoctahydro-1H-cyclopenta[a]pentalen-2(3bH)-one (**16b**).* A mixture of powdered 4 Å molecular sieves (50 mg) and TBAF trihydrate (31 mg, 0.12 mmol) in dry DMF (1.5 mL) was stirred at room temperature for 15 min. The mixture was filtered, and the resulting filtrate was transferred to a reaction vessel containing 100 mg of powdered 4 Å molecular sieves and HMPA (0.20 mL, 1.07 mmol). The resulting mixture was stirred for 15 min, and a solution of allylsilane **4** (33 mg, 0.12 mmol) in dry DMF (0.50 mL) was added dropwise over 30 min via a syringe pump. The resulting mixture was stirred at room temperature for 12 h and quenched with 0.5 mL of water. The mixture was extracted with ether, and the organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to give **16a** (9 mg, 38%) and **16b** (11 mg, 45%) as colorless oils, respectively. Compound **16a**: R_f = 0.47 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2960, 2923, 1704, 1441, 1379, 1011, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, 1H, J = 1.2 Hz), 5.10 (d, 1H, J = 1.6 Hz), 2.55−2.52 (m, 1H), 2.37 and 2.13 (ABq, each 1H, J = 18.8 Hz), 2.16−2.11 (m, 1H), 2.01−1.96 (m, 1H), 1.72 (d, 3H, J = 0.8 Hz), 1.69−1.64 (m, 2H), 1.67 (s, 3H), 1.48−1.29 (m, 2H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 167.1, 140.3, 139.1, 129.2, 48.4, 47.5, 42.3, 42.3, 36.5, 33.4, 27.4, 16.5, 9.9; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{21}O$, 205.1587; found, 205.1594. Compound **16b**: R_f = 0.53 (petroleum ether/EtOAc = 8:1); IR (film) ν_{max} = 2937, 2869, 1738, 1456, 1156, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (t, 1H, J = 1.4 Hz), 4.77 (s, 1H), 3.38 (t, 1H, J = 9.2 Hz), 3.00−2.90 (m, 1H), 2.39 and 2.10 (ABq, each 1H, J = 18.8 Hz), 2.31−2.27 (m, 2H), 2.04−1.93 (m, 2H), 1.77−1.68 (m, 3H), 1.50−1.45 (m, 1H), 1.19 (s, 3H), 1.10 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 222.2, 153.0, 108.1, 59.7, 50.2, 50.0, 48.2, 46.6, 45.0, 44.8, 35.0, 30.0, 26.1, 17.2; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{21}O$, 205.1587; found, 205.1592.

*(3aS,3bS,6aS,7aS)-3,3,7a-Trimethyl-4-methylenedecahydro-1H-cyclopenta[a]pentalene (**2**).* A mixture of tri-*n*-butyltin hydride (33 mg, 0.14 mmol) and AIBN (2 mg, 0.01 mmol) in dry benzene (2 mL) was brought to 80 °C, and a mixture of xanthate **15** (15 mg, 0.05 mmol) in dry benzene (1 mL) was added. After refluxing for 6 h, the resulting mixture was evaporated in vacuo, and the residual oil was charged on an $AgNO_3$-impregnated silica gel column. An elution with petroleum ether removed the organotin impurities. Further elution with hexane provided hydrocarbon **2** (8 mg, 41%) as a colorless oil: R_f = 0.96 (petroleum ether); IR (film) ν_{max} = 2942, 2864, 1651, 1459, 1370, 876 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.78 (s, 1H), 2.66−2.64 (m, 1H), 2.57−2.44 (m, 2H), 2.38−2.36 (m, 1H), 1.71−1.65 (m, 3H), 1.68−1.61 (m, 2H), 1.56−1.47 (m, 3H), 1.46−1.42 (m, 2H), 1.22−1.19 (m, 1H), 1.15 (s, 3H), 1.08 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 104.9, 69.0, 53.3, 52.3, 47.9, 46.0, 42.3, 41.6, 40.5, 31.8, 31.5, 30.8, 29.0, 26.0.

*(((3R,5R)-3-(Iodomethyl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)trimethylsilane (**18**).* Compound **18** was prepared[5,6] from (+)-carvone in 56% yield as a colorless oil: R_f = 0.95 (petroleum ether); $[\alpha]_D^{20}$ = +45 (c = 0.8, $CHCl_3$); IR (film) ν_{max} = 2954, 2921, 1645, 1446, 1248, 847 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (d, 2H, J = 6.4 Hz), 3.47 (dq, 1H, J = 1.2, 10.0 Hz), 3.03 (t, 1H, J = 10.4 Hz), 2.36 (br d, 1H, J = 7.6 Hz), 2.19−2.14 (m, 1H), 2.19 (d, 1H, J = 13.2 Hz), 1.89−1.79 (m, 2H), 1.76 (s, 3H), 1.64 (s, 3H), 1.61 (s, 2H), 1.53−1.49 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 131.7, 122.7, 108.8, 44.3, 38.2, 36.1, 32.1, 24.3, 20.9, 18.7, 12.0, −0.5; EI−MS (m/z) M^+ 362 (2.2%), 235 (19%), 161 (11%), 73 (100%).

*Methyl-4-((1R,5R)-2-methyl-5-(prop-1-en-2-yl)-3-((trimethylsilyl)-methyl)cyclohex-2-en-1-yl) Butanoate (**19**).* To a stirred slurry of zinc dust (1.07 g, 16.50 mmol) in pyridine (5 mL) was added methyl acrylate (1.35 mL, 15.00 mmol) at room temperature. Powdered nickel(II) chloride hexahydrate (1.19 g, 5.00 mmol) was added to the above slurry mixture. The resulting suspension was brought to 50 °C and stirred for 20 min. The resulting red-brown mixture was cooled to room temperature, and halide **18** (1.81 g, 5.00 mmol) in pyridine (5 mL) was added dropwise. After stirring for 1 h, the reaction mixture was filtered with a short plug of Celite (elution with 100 mL Et_2O). The filtrate was washed with HCl (1 N), water, and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash silica gel column chromatography to give compound **19** (1.29 g, 80%) as a colorless oil: R_f = 0.58 (petroleum ether/EtOAc = 10:1); $[\alpha]_D^{20}$ = +50 (c = 2.4, $CHCl_3$); IR (film) ν_{max} = 2950, 1742, 1438, 1246, 1198, 844 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 2H), 3.66 (s, 3H), 2.37−2.29 (m, 2H), 2.24−2.17 (m, 1H), 1.92−1.83 (m, 3H), 1.80−1.68 (m, 2H), 1.75 (s, 3H), 1.58 (s, 3H), 1.59−1.50 (m, 1H), 1.53 (s, 2H), 1.48−1.38 (m, 2H), 1.35−1.24 (m, 1H), −0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 150.2, 127.9, 125.7, 108.3, 51.4, 40.8, 38.0, 36.8, 34.3, 32.4, 31.3, 24.0, 23.7, 20.7, 18.5, −0.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{35}O_2Si$, 323.2401; found, 323.2396.

*4-((1R,5R)-2-Methyl-5-(prop-1-en-2-yl)-3-((trimethylsilyl)methyl)-cyclohex-2-en-1-yl)butanal (**20**).* To a mixture of compound **19** (102 mg, 0.32 mmol) in CH_2Cl_2 (1.5 mL) was added DIBAL-H (0.29 mL, 0.34 mmol, 1.2 M in hexane) dropwise at −20 °C. After stirring for 2 h, the reaction was quenched with 0.5 mL of water and extracted with ether (100 mL). The ethereal layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. The solution was evaporated, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give aldehyde **20** (83 mg, 90%) as a colorless oil: R_f = 0.75 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +53 (c = 1.7, $CHCl_3$); IR (film) ν_{max} = 2923, 1729, 1447, 1247, 1090, 844 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, 1H, J = 1.2 Hz), 4.70 (s, 2H), 2.49−2.37 (m, 2H), 2.21−2.20 (m, 1H), 1.93−1.83 (m, 3H), 1.78−1.70 (m, 2H), 1.73 (s, 3H), 1.57−1.49 (m, 2H), 1.55 (s, 3H), 1.52 (s, 2H), 1.38−1.25 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 150.2, 128.1, 125.5, 108.4, 44.1, 40.9, 38.0, 36.9, 32.5, 31.3, 24.0, 20.8, 20.7, 18.5, −0.5; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{32}NaOSi$, 315.2115; found, 315.2117.

*(1R,4aR,6R,8aR)-8a-Methyl-8-methylene-6-(prop-1-en-2-yl)-decahydronaphthalen-1-ol (**21a**).* To a stirred mixture of aldehyde **20** (120 mg, 0.41 mmol) in 1,2-dichloroethane (1 mL) was added a stock solution of freshly distilled stannic tetrachloride (1.0 M in 1,2-dichloroethane, 0.82 mL, 0.82 mmol) dropwise at −20 °C. After stirring for 10 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, diluted with ether (100 mL), and washed with saturated $NaHCO_3$ (5 mL) and brine (5 mL). The ethereal phase was dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash silica gel column chromatography to give compound **21a** (62 mg, 61%) as a colorless oil: R_f = 0.24 (petroleum ether/EtOAc = 10:1); $[\alpha]_D^{20}$ = +15 (c = 1.0, $CHCl_3$); IR (film) ν_{max} = 3416, 2928, 1641, 1452, 1373, 1038, 906, 888 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1H), 5.02 (s, 1H), 4.71 (s, 2H), 3.50 (dd, 1H, J = 4.4, 12.0 Hz), 2.29 (d, 2H, J = 2.8 Hz), 2.23−2.00 (m, 2H), 1.87−1.79 (m, 1H), 1.79−1.71 (m, 2H), 1.75 (s, 3H), 1.60−1.54 (m, 2H), 1.51−1.45 (m, 2H), 1.34 (s, 3H), 1.27−1.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8 (2C), 111.9, 108.5, 80.7, 45.2, 43.8, 40.6, 39.4, 32.4, 30.2, 28.2, 25.1, 24.5, 20.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{24}NaO$, 243.1719; found, 243.1724.

*(1S,4aR,6R,8aR)-8a-Methyl-8-methylene-6-(prop-1-en-2-yl)-decahydronaphthalen-1-ol (**21b**).* To a stirred mixture of **20** (120 mg, 0.41 mmol) in dichloromethane (1 mL) was added dropwise a stock solution of freshly distilled stannic tetrachloride (1.0 M in dichloromethane, 0.82 mL, 0.82 mmol) at −90 °C. After stirring for 10 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, diluted with ether (100 mL), and successively washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL). The ethereal phase was dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash silica gel column chromatography to give compounds **21a** (35 mg, 13%) and **21b** (12 mg, 39%) as colorless oils. Compound **21b**: R_f = 0.24 (petroleum ether/EtOAc = 10:1); $[\alpha]_D^{20}$ = −22 (c = 0.2, $CHCl_3$); IR (film) ν_{max} = 3440, 2928, 1639, 1448, 1082, 890 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 (d, 1H, J = 0.8 Hz), 4.79 (s, 2H), 4.77 (s, 1H), 3.98 (br s, 1H), 2.47−2.43 (m, 1H), 2.37 (d, 2H, J = 11.2 Hz), 1.93−1.92 (m, 1H), 1.84−1.83 (m, 1H), 1.79−

1.69 (m, 2H), 1.72 (s, 3H), 1.68−1.56 (m, 4H), 1.49−1.46 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.5, 110.8, 110.1, 70.0, 44.1, 43.8, 40.6, 39.4, 37.0, 31.2, 28.2, 27.7, 24.5, 21.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{24}NaO$, 243.1719; found, 243.1727.

*(4aR,6R,8aR)-8a-Methyl-8-methylene-6-(prop-1-en-2-yl)-octahydronaphthalen-1(2H)-one (**22**).* To a stirred mixture of compounds **21a** and **21b** (diastereoisomers, 17 mg, 0.08 mmol) in dry DCM (1 mL) was added SiO_2 (20 mg). After stirring for 5 min, powdered PCC (30 mg, 0.14 mmol) was added in one portion to the above suspension. After stirring for 15 min, the reaction mixture was filtered through a short pad of Celite, eluting with ether. The resulting filtrate was concentrated, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 1:1) to give compound **22** (15 mg, 95%) as a colorless oil: R_f = 0.70 (petroleum ether/EtOAc = 10:1); $[\alpha]_D^{20}$ = +79 (c = 2.0, $CHCl_3$); IR (film) ν_{max} = 2934, 1705, 1640, 1453, 1373, 1235, 1112, 895 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.76 (s, 1H), 4.75 (s, 1H), 4.34 (s, 1H), 2.67 (td, 1H, J = 6.4, 14.4 Hz), 2.45−2.35 (m, 2H), 2.28−2.26 (m, 2H), 2.02−1.96 (m, 1H), 1.92−1.84 (m, 3H), 1.81 (s, 3H), 1.75−1.52 (m, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 149.1, 149.1, 111.2, 109.1, 55.9, 45.3, 40.0, 39.6, 37.3, 32.4, 28.4, 26.0, 22.0, 20.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{23}O$, 219.1743; found, 219.1748.

*(R)-2-((2R,4aR,5R,8aR)-5-Hydroxy-4a-methyl-4-methylenedecahydronaphthalen-2-yl)propane-1,2-diol (**23a**).* To a stirred mixture of compound **21a** (62 mg, 0.28 mmol) in dry acetone (2 mL) and *N*-methylmorpholine *N*-oxide (31 mg, 0.26 mmol) was added OsO_4 (5.0 mg, 0.02 mmol) in 1 mL of *i*-PrOH at 0 °C under N_2. After stirring for 2 h, the reaction mixture was quenched with 2 mL of saturated aqueous $NaHSO_3$ and extracted with ether. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The solid residue was purified by recrystallization from a solvent mixture of petroleum ether/EtOAc (2:1) to give diastereomer **23a** (15 mg, 43%) as colorless crystals: R_f = 0.15 (petroleum ether/EtOAc = 1:1); $[\alpha]_D^{20}$ = −15 (c = 0.2, $CHCl_3$); mp 136−138 °C; IR (film) ν_{max} = 3394, 2931, 2859, 1703, 1638, 1454, 1041, 908 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (s, 1H), 5.05 (s, 1H), 3.57−3.50 (m, 2H), 3.41 (dd, 1H, J = 9.0, 16.2 Hz), 2.29−2.17 (m, 2H), 2.07−1.98 (m, 1H), 1.94−1.84 (m, 1H), 1.80−1.77 (m, 2H), 1.76−1.66 (m, 2H), 1.55−1.43 (m, 1H), 1.43−1.34 (m, 2H), 1.31 (s, 3H), 1.30−1.22 (m, 1H), 1.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.2, 112.2, 80.2, 74.4, 68.4, 45.1, 43.1, 39.7, 35.2, 34.0, 30.1, 28.2, 26.9, 25.1, 20.2; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{27}O_3$, 255.1955; found, 255.1958. X-ray crystallographic data of **23a**: $C_{15}H_{26}O_3$, monoclinic, space group: $C2$, a = 19.18 (5) Å, b = 9.99 (3) Å, c = 7.58 (2) Å, β = 94.11 (3)°, Z = 4, d_{calcd} = 1.166 g/cm^3, $R_1(I > 2\sigma(I))$ = 0.0631, wR_2 = 0.3156.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for compounds **9c** and **23a**, GC−MS data for compounds **5a**, **7a**, **5b**, **7b**, and **12**, ^{1}H and ^{13}C NMR spectra for compounds **1**−**4**, **9**, **10**, **12**−**15**, **18**−**20**, **22**, **5a**, **7a**, **5b**, **7b**, **9a**−**d**, **14a**, **16a**, **16b**, **21a**, **21b**, and **23a**, and CIF files for **9c** and **23a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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