Synthesis of Novel Bifunctional Michael Acceptors

Laura Mediavilla Urbaneja[a] and Norbert Krause*[a]

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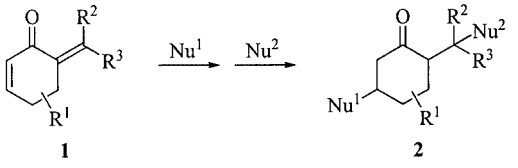
The conjugated dienones **1a**, **1c**–**e**, and **1g** were synthesized by aldol reaction of cyclohex-2-enones **3** with aldehydes or ketones and subsequent elimination. Whereas the acetone adducts could be converted into the desired products **1a/g** by treatment with $CeCl_3 \cdot 7H_2O$/NaI, the dienones **1c**–**e** were obtained by Appel bromination and dehydrobromination with triethylamine.

Introduction

The Michael addition belongs to the classical tools for the formation of carbon−carbon and carbon−heteroatom bonds. The recent development of various efficient protocols for catalytic enantioselective Michael additions has broadened the scope of this transformation considerably.[1] These methods, however, are usually applied to simple, unsubstituted substrates like cyclohex-2-enone and only scarcely to more elaborate Michael acceptors.[2] In this respect, conjugated dienones of type **1** are particularly interesting since sequential 1,4-addition reactions of two nucleophiles to the endocyclic and exocyclic acceptor system of these bifunctional Michael acceptors might give rise to the formation of richly functionalized cyclohexanones **2** with up to three stereogenic centers (Scheme 1).

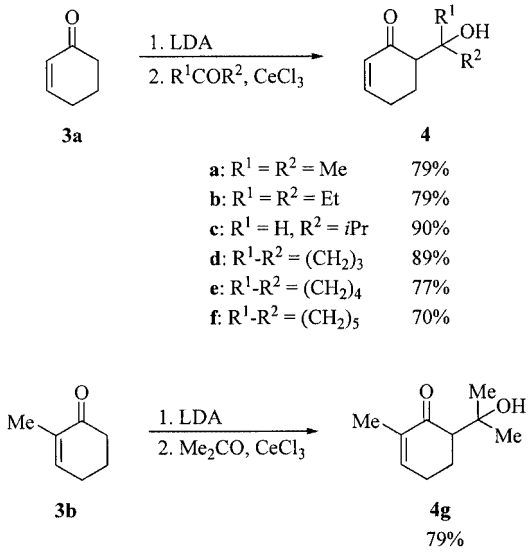


Scheme 1. Sequential Michael additions of two nucleophiles to dienones **1**

So far, only isolated reports on the synthesis of Michael acceptors **1** have appeared. These were synthesized by selenoxide elimination,[3] photochemical isomerization,[4] or aldol reactions.[5] The lack of general methods may be due to the tendency of the exocyclic C−C double bond to isomerize to a thermodynamically more favorable position. In this communication, we describe an efficient general method for the synthesis of dienones **1** which relies upon carefully controlled conditions for the elimination of aldol addition products.

Results and Discussion

The aldol addition of the lithium enolate of cyclohex-2-enone (**3a**) to acetone was reported by Marcantoni et al.[6] to proceed smoothly if the latter is activated by anhydrous cerium trichloride. We have found that this method can be expanded to various cyclic and acyclic ketones, as well as to isobutyraldehyde, to furnish the desired aldols **4a**−**f** with chemical yields ranging from 70 to 90% (Scheme 2). Similarly, 2-methylcyclohex-2-enone (**3b**) was converted into the adduct **4g** with 79% yield.

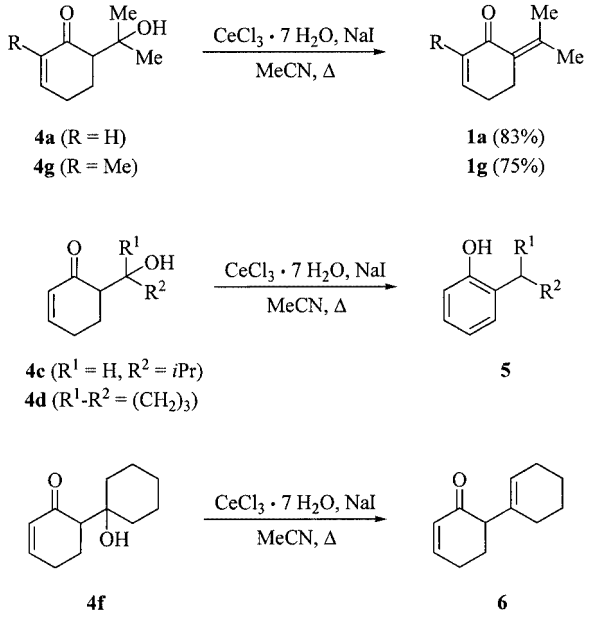


Scheme 2. $CeCl_3$-mediated aldol reaction of cyclohexenones **3**

For the dehydration of the aldol adducts **4** to the desired conjugated dienones of type **1**, we initially employed the

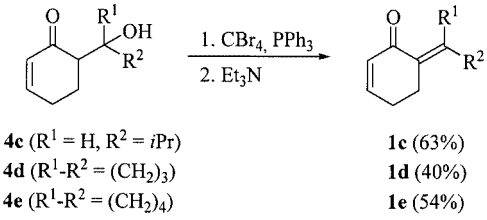
[a] Organic Chemistry II, University of Dortmund,
44221 Dortmund, Germany
Fax: +49 231/755-3884
E-mail: norbert.krause@uni-dortmund.de

conditions used by Marcantoni et al.[6] for the preparation 2-alkylidenecycloalkanes, i.e., heating with $CeCl_3 \cdot 7H_2O$ and sodium iodide in acetonitrile. Indeed, the acetone adducts **4a** and **4g** produced the desired dienones **1a** and **1g**, respectively, with good chemical yield (Scheme 3). No traces of non-conjugated or aromatic isomers could be found. In contrast to this, the aldols **4c** and **4d** furnished phenols **5** under these conditions, whereas cyclohexanone adduct **4f** gave only the non-conjugated dienone **6**. In the case of the aldols **4b** and **4e**, mixtures of regioisomers of type **1** and **6** were obtained which could not be separated.



Scheme 3. Dehydration of aldol adducts **4** with $CeCl_3 \cdot 7H_2O$/NaI

The latter findings seem to indicate a high tendency towards double bond isomerization even under very mild acidic conditions. Consequently, we turned our attention towards basic elimination conditions which required the transformation of the hydroxy group of aldols **4** into a good leaving group. Since the mesylation of tertiary alcohols is rather difficult, we decided to use Appel's conditions[7] for the conversion into the corresponding bromides. Thus, treatment of adduct **4c** with equimolar amounts of carbon tetrabromide and triphenylphosphane resulted in a clean conversion into the bromide which was subjected without isolation to the dehydrobromination with triethylamine (Scheme 4). Much to our delight, the desired conjugated dienone **1c** was obtained with 63% yield, and no traces of non-conjugated or aromatic isomerization products were found. In a similar fashion, the ketone adducts **4d** and **4e** were converted into the dienones **1d/e** with yields of 40 and 54%, respectively. Only the substrates **4b** and **4f** again afforded mixtures of conjugated and non-conjugated products under the basic elimination conditions. With various dienones **1** at hand, we are now in the process of examining their use as bifunctional Michael acceptors according to Scheme 1.



Scheme 4. Elimination of aldol adducts **4c**−**e** under Appel conditions

Conclusion

The conjugated dienones **1a**, **1c**−**e**, and **1g**, which are of interest as bifunctional Michael acceptors, were synthesized by aldol reaction of cyclohexenones **3** with aldehydes or ketones and subsequent regioselective elimination. Whereas the acetone adducts could be converted into the desired products **1a/g** by treatment with cerium(III) chloride heptahydrate/sodium iodide, the dienones **1c**−**e** were obtained in a one-pot reaction by Appel bromination and dehydrobromination with triethylamine.

Experimental Section

General Remarks: All reactions were carried out under an argon atmosphere using oven-dried glassware. THF was distilled from sodium benzophenone ketyl, toluene was distilled from sodium, dichloromethane, triethylamine, and diisopropylamine were distilled from CaH_2, and acetone was distilled from P_2O_5. All solvents were used immediately or stored under an argon atmosphere. Solvents for flash chromatography (pentane, cyclohexane, and ethyl acetate) were distilled before use. Cyclohex-2-enone, pentan-3-one, isobutyraldehyde, cyclohexanone, and cyclopentanone were distilled prior to use. 2-Methylcyclohex-2-enone was prepared according to ref.[8] All other commercially available starting materials were used without further purification. Column chromatography was carried out with Macherey−Nagel silica gel 60 (230−400 mesh). ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX-400 or DRX-500 spectrometer at room temperature in $CDCl_3$ or C_6D_6 as solvent. Chemicals shifts were determined relative to the residual solvent peaks ($CHCl_3$: $\delta = 7.26$ for protons, $\delta = 77.0$ for carbon atoms. C_6H_6: $\delta = 7.16$ for protons, $\delta = 128.0$ for carbon atoms). The polarization in DEPT experiments is designated with + (CH, CH_3), − (CH_2), or × ($C_{quat.}$). IR spectra were obtained with a Bruker IFS66 FT-IR spectrometer using thin films between NaCl plates. Mass spectra, high-resolution mass spectra (HRMS), and fast atom bombardment mass spectra (FAB) were measured with a Jeol SX102A spectrometer.

General Procedure for the Synthesis of Aldol Adducts 4: $CeCl_3 \cdot 7H_2O$ was dried at 140 °C/0.1 mbar for 2 h and was then suspended in dry THF at 0 °C (ice-water bath) under vigorous stirring. The white suspension was allowed to stir overnight at room temperature. After cooling to −80 °C, a THF solution of the carbonyl compound was added, and the suspension was stirred at −80 °C for 1 h. In a separate flask, a solution of LDA in THF was prepared by adding *n*BuLi to diisopropylamine in THF at 0 °C. After stirring for 20 min at this temperature, it was cooled to −80 °C, and the

enone **3** in THF was added. The mixture was stirred at −80 °C for 30 min and then added via cannula to the white suspension. The resulting orange-red suspension was stirred at −80 °C until TLC control showed full consumption of starting material (approx. 1−2 h.). The reaction mixture was then hydrolyzed with a satd. NH_4Cl solution. The organic layer was separated and concentrated in vacuo. The aqueous layer was washed three times with diethyl ether, and the combined organic layers were washed with water and brine, dried with $MgSO_4$, and the solvent was evaporated. Flash column chromatography on silica gel (cyclohexane/ethyl acetate, 6:4) afforded the aldol adduct **4**.

6-(1-Hydroxy-1-methylethyl)cyclohex-2-enone (4a):[6] From $CeCl_3$ (13.9 g, 56.4 mmol) in THF (200 mL), acetone (3.20 g, 55.1 mmol) in THF (5 mL), diisopropylamine (5.06 g, 50.0 mmol) in THF (50 mL), *n*BuLi (20.4 mL, 50.0 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 4.00 g, 41.6 mmol) in THF (5 mL); yield: 5.10 g (79%) of **4a** as a colorless oil.

6-(1-Hydroxy-1-ethylpropyl)cyclohex-2-enone (4b): From $CeCl_3$ (10.3 g, 41.8 mmol) in THF (150 mL), pentan-3-one (3.57 g, 41.5 mmol) in THF (5 mL), diisopropylamine (3.79 g, 37.5 mmol) in THF (50 mL), *n*BuLi (15.3 mL, 37.5 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 3.00 g, 31.2 mmol) in THF (5 mL); yield: 4.50 g (79%) of **4b** as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.27 (m, 1 H, 3-H), 5.81 (dd, J = 1.5, 10.0 Hz, 1 H, 2-H), 4.96 (d, J = 1.8 Hz, 1 H, OH), 2.35 (dd, J = 4.5, 13.8 Hz, 1 H, 6-H), 1.68−1.60 (m, 4 H), 1.42−1.35 (m, 1 H), 1.29−1.17 (m, 2 H), 1.20−1.10 (m, 1 H), 0.96 (t, J = 7.3 Hz, 3 H, 3′-H), 0.93 (t, J = 7.3 Hz, 3 H, 3′-H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 204.5 (×, C-1), 150.2 (+, C-3), 130.9 (+, C-2), 75.9 (×, C-1′), 51.8 (+, C-6), 29.7, 28.9, 26.1, 24.6 (−, C-4, C-5, C-2′), 8.0, 7.7 (+, C-3′) ppm. IR: $\tilde{\nu}$ = 3460, 3026, 2966, 1654 cm^{-1}. EI-MS: *m*/*z* (%) = 182 (0.4) [M$^+$], 153 (93), 135 (9), 96 (100), 57 (99), 29 (19). HR-FAB-MS: calcd. for $C_{10}H_{18}NaO_2$ [M + Na]: 205.1204; found 205.1200.

6-(1-Hydroxy-2-methylpropyl)cyclohex-2-enone (4c):[9] From $CeCl_3$ (20.6 g, 83.6 mmol) in THF (300 mL), isobutyraldehyde (5.86 g, 81.3 mmol) in THF (5 mL), diisopropylamine (7.59 g, 75.0 mmol) in THF (100 mL), *n*BuLi (30.6 mL, 75.0 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 6.00 g, 62.4 mmol) in THF (5 mL); yield: 9.50 g (90%) of **4c** as a colorless oil.

6-(1-Hydroxycyclobutyl)cyclohex-2-enone (4d): From $CeCl_3$ (4.50 g, 18.3 mmol) in THF (75 mL), cyclobutanone (1.14 g, 16.3 mmol) in THF (5 mL), diisopropylamine (1.64 g, 16.2 mmol) in THF (25 mL), *n*BuLi (6.6 mL, 16.2 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 1.30 g, 13.5 mmol) in THF (5 mL); yield: 2.00 g (89%) of **4d** as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.21 (m, 1 H, 3-H), 5.83 (m, 1 H, 2-H), 3.70 (s, 1 H, OH), 2.30 (m, 1 H), 2.23−2.10 (m, 3 H), 1.95−1.84 (m, 2 H), 1.73−1.54 (m, 4 H), 1.40 (m, 1 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 201.8 (×, C-1), 149.9 (+, C-3), 130.4 (+, C-2), 76.5 (×, C-1′), 54.4 (+, C-6), 35.3, 32.9 (−, C-2′), 26.1, 23.9 (−, C-4, C-5), 13.8 (−, C-3′) ppm. IR: $\tilde{\nu}$ = 3465, 3031, 2937, 1665 cm^{-1}. EI-MS: *m*/*z* (%) = 166 (44) [M$^+$], 96 (68), 68 (36), 58 (60), 43 (100). HR-FAB-MS: calcd. for $C_{10}H_{15}O_2$ [M + H]: 167.1072; found 167.1056.

6-(1-Hydroxycyclopentyl)cyclohex-2-en-1-one (4e): From $CeCl_3$ (9.20 g, 37.3 mmol) in THF (150 mL), cyclopentanone (3.80 g, 45.2 mmol) in THF (5 mL), diisopropylamine (3.79 g, 37.5 mmol) in THF (50 mL), *n*BuLi (15.3 mL, 37.5 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 3.00 g, 31.2 mmol) in THF (5 mL); yield: 4.35 g (77%) of **4e** as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.20 (m, 1 H, 3-H), 5.83 (td, J = 2.0, 9.8 Hz, 1 H, 2-H), 3.82 (s, 1 H, OH), 2.20 (dd, J = 4.5, 13.5 Hz, 1 H), 2.04−1.78 (m, 4 H), 1.72−1.38 (m, 7 H), 1.34−1.22 (m, 1 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 202.7 (×, C-1), 149.6 (+, C-3), 130.5 (+, C-2), 82.5 (×, C-1′), 55.0 (+, C-6), 39.2, 36.7 (−, C-2′), 26.2, 25.5, 24.6, 24.2 (−, C-4, C-5, C-3′) ppm. IR: $\tilde{\nu}$ = 3480, 3032, 2957, 1663 cm^{-1}. EI-MS: *m*/*z* (%) = 180 (10) [M$^+$], 162 (13), 138 (27), 123 (22), 96 (100), 55 (32). HR-EI-MS: calcd. for $C_{11}H_{16}O_2$: 180.1150; found 180.1153.

6-(1-Hydroxycyclohexyl)cyclohex-2-enone (4f): From $CeCl_3$ (10.8 g, 43.8 mmol) in THF (100 mL), cyclohexanone (3.38 g, 34.4 mmol) in THF (5 mL), diisopropylamine (3.48 g, 34.4 mmol) in THF (50 mL), *n*BuLi (14.0 mL, 34.4 mmol, 2.45 M solution in hexane), and cyclohex-2-enone (**3a**, 3.02 g, 31.4 mmol) in THF (5 mL); yield: 4.26 g (70%) of **4f** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (m, 1 H, 3-H), 5.95 (ddd, J = 1.0, 2.5, 9.8 Hz, 1 H, 2-H), 4.50 (s, 1 H, OH), 2.45−2.30 (m, 3 H), 2.10 (m, 1 H), 1.80−1.58 (m, 5 H), 1.54−1.40 (m, 4 H), 1.30 (dt, J = 4.0, 13.0, Hz, 1 H), 1.08 (qt, J = 3.5, 13.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0 (×, C-1), 150.8 (+, C-3), 130.7 (+, C-2), 73.1 (×, C-1′), 55.9 (+, C-6), 35.4, 31.8 (−, C-2′), 26.4, 25.8, 24.6, 21.2, 21.1 (−, C-4, C-5, C-3′, C-4′) ppm. IR: $\tilde{\nu}$ = 3469, 2930, 1657 cm^{-1}. EI-MS: *m*/*z* (%) = 194 (3) [M$^+$], 176 (9), 138 (6), 96 (100), 55 (23), 41 (16). HR-EI-MS: calcd. for $C_{12}H_{18}O_2$: 194.1307; found 194.1304.

6-(1-Hydroxy-1-methylethyl)-2-methylcyclohex-2-enone (4g): From $CeCl_3$ (9.00 g, 36.5 mmol) in THF (100 mL), acetone (2.10 g, 36.2 mmol) in THF (5 mL), diisopropylamine (3.29 g, 32.5 mmol) in THF (50 mL), *n*BuLi (13.3 mL, 37.5 mmol, 2.45 M solution in hexane), and 2-methylcyclohex-2-enone (**3b**, 3.00 g, 27.2 mmol) in THF (5 mL); yield: 3.60 g (79%) of **4g** as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.06 (m, 1 H, 3-H), 5.15 (s, 1 H, OH), 2.13 (dd, J = 4.4, 14.2 Hz, 1 H), 1.70−1.63 (m, 5 H), 1.56−1.49 (m, 1 H), 1.31−1.23 (m, 1 H), 1.23 (s, 3 H), 1.18 (s, 3 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 203.6 (×, C-1), 145.5 (+, C-3), 136.2 (×, C-2), 72.2 (×, C-1′), 56.4 (+, C-6), 28.6, 25.1 (−, C-4, C-5), 25.9 (+, C-2′), 16.0 (+, 2-CH_3) ppm. IR: $\tilde{\nu}$ = 3475, 2973, 1652 cm^{-1}. EI-MS: *m*/*z* (%) = 168 (0.4) [M$^+$], 153 (12), 110 (100), 95 (56), 82 (13), 59 (24), 43 (34). HR-FAB-MS: calcd. for $C_{10}H_{17}O_2$ [M + H]: 169.1228; found 169.1230.

6-(1-Methylethylidene)cyclohex-2-enone (1a):[4] A suspension of $CeCl_3$·7 H_2O (19.4 g, 52.1 mmol) and NaI (7.80 g, 52.0 mmol) in acetonitrile (80 mL) was stirred for 24 h under reflux. The resulting mixture was cooled to room temperature, and a solution of **4a** (2.50 g, 16.2 mmol) in acetonitrile (10 mL) was added dropwise. The reaction mixture was refluxed for 2 h; at this point, TLC control showed complete consumption of the starting material. After cooling to room temperature, the mixture was diluted with diethyl ether (200 mL), water (50 mL) was added, and the mixture was stirred for 5 min. The organic layer was separated, and the aqueous phase was washed three times with diethyl ether. The combined organic layers were washed with a satd. $Na_2S_2O_3$ solution, water and brine, and dried with Na_2SO_4. After removal of the solvent, the crude product was purified by flash column chromatography on silica gel (pentane/diethyl ether/triethylamine, 8:2:0.02), affording 1.80 g (83%) of **1a** as a pale yellow liquid.

(*E*)-6-(2-Methylpropylidene)cyclohex-2-enone (1c): A solution of CBr_4 (12.8 g, 38.6 mmol) in dry CH_2Cl_2 (10 mL) was stirred for 5 min at 0 °C, and a solution of **4c** (5.40 g, 32.1 mmol) in dry CH_2Cl_2 (10 mL) was added. The reaction mixture was stirred for 5 min at 0 °C, and then a precooled solution (0 °C) of PPh_3 (10.1 g,

38.5 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise. Stirring at 0 °C was continued for 90 min, followed by the dropwise addition of Et_3N (5.06 g, 50.0 mmol). After stirring for another 10 min at 0 °C, the major part of the solvent was removed in vacuo. The residue was poured slowly with stirring into diethyl ether (50 mL). Filtration through Celite, washing of the residue with diethyl ether, drying of the filtrate with Na_2SO_4 and removal of the solvent gave the crude product. Purification by flash column chromatography (SiO_2, pentane/diethyl ether/triethylamine, 4:1:0.02) afforded 3.02 g (63%) of **1c** as a pale yellow oil. ^{1}H NMR (500 MHz, C_6D_6): δ = 6.73 (d, J = 9.8 Hz, 1 H, 1′-H), 6.27 (td, J = 4.3, 10.0 Hz, 1 H, 3-H), 6.14 (td, J = 1.7, 10.0 Hz, 1 H, 2-H), 2.38−2.25 (m, 1 H, 2′-H), 2.21 (dt, J = 1.5, 6.3 Hz, 2 H), 1.73 (m, 2 H), 0.82 (d, J = 6.5 Hz, 6 H, 3′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 187.3 (×, C-1), 148.0 (+, C-1′), 143.7 (+, C-3), 132.7 (×, C-6), 131.3 (+, C-2), 26.9 (+, C-2′), 25.6, 25.1 (−, C-4, C-5), 22.3 (+, C-3′) ppm. IR: $\tilde{\nu}$ = 2961, 1674, 1627 cm^{-1}. EI-MS: *m*/*z* (%) = 150 (100) [M$^+$], 107 (58), 82 (60), 67 (54), 39 (97). HR-EI-MS: calcd. for $C_{10}H_{14}O$: 150.1045; found 150.1066. The *E* geometry was assigned by comparison of the chemical shift of 1′-H with that of related compounds.[10]

6-(Cyclobutylidene)cyclohex-2-enone (1d): According to the synthesis of **1c** from CBr_4 (3.98 g, 12.0 mmol) in CH_2Cl_2 (5 mL), **4d** (1.66 g, 10.0 mmol) in CH_2Cl_2 (5 mL), PPh_3 (3.15 g, 12.0 mmol) in CH_2Cl_2 (10 mL) and Et_3N (1.52 g, 15.0 mmol); reaction time: 3 h. Yield: 600 mg (40%) of **1d** as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (td, J = 4.3, 10.0 Hz, 1 H, 3-H), 6.04 (td, J = 1.7, 10.0 Hz, 1 H, 2-H), 3.15 (m, 2 H), 2.80 (m, 2 H), 2.50 (m, 2 H), 2.33 (m, 2 H), 2.85 (pent, J = 7.8 Hz, 2 H, 3′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.9 (×, C-1), 156.9 (×, C-1′), 148.1 (+, C-3), 131.6 (+, C-2), 125.4 (×, C-6), 34.2, 30.8, 25.3, 25.3 (−, C-4, C-5, C-2′), 17.6 (−, C-3′) ppm. IR: $\tilde{\nu}$ = 3030, 2950, 1687, 1634 cm^{-1}. EI-MS: *m*/*z* (%) = 148 (100) [M$^+$], 147 (76), 133 (32), 120 (22), 105 (46), 39 (26). HR-EI-MS: calcd. for $C_{10}H_{12}O$: 148.0888; found 148.0880

6-(Cyclopentylidene)cyclohex-2-enone (1e): According to the synthesis of **1c** from CBr_4 (1.58 g, 4.8 mmol) in CH_2Cl_2 (3 mL), **4e** (650 mg, 3.6 mmol) in CH_2Cl_2 (3 mL), PPh_3 (1.25 g, 4.8 mmol) in CH_2Cl_2 (6 mL) and Et_3N (0.56 g, 5.5 mmol); reaction time: 3 h. Yield: 315 mg (54%) of **1e** as a pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.24 (td, J = 4.0, 10.0 Hz, 1 H, 3-H), 6.16 (td, J = 1.6, 10.0 Hz, 1 H, 2-H), 3.02 (m, 2 H), 2.26 (t, J = 6.5 Hz, 2 H), 2.00 (t, J = 7.3 Hz, 2 H), 1.80−1.70 (m, 2 H), 1.49 (pent, J = 7.0 Hz, 2 H), 1.37 (pent, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 188.3 (×, C-1), 157.3 (×, C-1′), 145.8 (+, C-3), 132.6 (+, C-2), 125.6 (×, C-6). 34.7, 33.0, 28.6, 27.3, 25.6, 25.5 (−, C-4, C-5, C-2′, C-3′) ppm. IR: $\tilde{\nu}$ = 3032, 2957, 1660, 1626, 1601 cm^{-1}. EI-MS: *m*/*z* (%) = 162 (100) [M$^+$], 133 (28), 105 (15), 91 (36), 79 (34), 67 (19), 39 (19). HR-EI-MS: calcd. for $C_{11}H_{14}O$: 162.1045; found 162.1046.

2-Methyl-6-(1-methylethylidene)cyclohex-2-enone (1g): As in the preparation of **1a**, refluxing of **4g** (1.50 g, 8.9 mmol) in acetonitrile (5 mL) with $CeCl_3 \cdot 7\ H_2O$ (10.7 g, 28.7 mmol) and NaI (4.32 g, 28.8 mmol) in acetonitrile (30 mL) for 12 h afforded 1.02 g (75%) of **1g** as a pale yellow liquid. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.14 (s, 1 H, 3-H), 2.30 (t, J = 6.0 Hz, 2 H), 2.16 (s, 3 H, 2′-H), 1.88 (d, J = 1.2 Hz, 3 H, 2-CH_3), 1.86−1.85 (m, 2 H), 1.50 (s, 3 H, 2′-H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 190.9 (×, C-1), 141.9 (+, C-3), 141.1, 138.1, 130.2 (×, C-2, C-6, C-1′), 28.7, 26.6 (−, C-4, C-5), 23.0, 22.1 (+, C-2′), 16.8 (+, 2-CH_3) ppm. IR: $\tilde{\nu}$ = 2922, 1660, 1624 cm^{-1}. EI-MS: *m*/*z* (%) = 150 (100) [M$^+$], 135 (21), 107 (61), 91 (26), 79 (19), 39 (18). HR-EI-MS: calcd. for $C_{10}H_{14}O$: 150.1045; found 150.1043.

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