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A Simple and Efficient Strategy Towards Eleven-Membered Carbocycles via Novel Synthetic Transformations of Pentafulvenes

K. Syam Krishnan,[a] Jinesh M. Kuthanapillil,[a] Rani Rajan,[a] E. Suresh,[b] and K. V. Radhakrishnan*[a]

Dedicated to Professor Yoshinori Yamamoto, Tohoku University, Sendai on the occasion of his 65th birthday

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A novel and versatile method towards the synthesis of eleven-membered carbocycles through a three step reaction sequence from pentafulvenes is described. The [6+3] adduct of pentafulvenes with 3-oxidopyrylium betaine on selective reduction followed by ruthenium catalyzed oxidative cleavage afforded a novel eleven-membered carbocyclic triketone with a bridging ether linkage. The methodology described herein is easy to perform and delivers densely functionalized carbocycles in good yields. The procedure is noteworthy as it hardly requires an elaborated catalytic system and proceeds with high level of atom efficiency from cheap and easily available starting materials.

Introduction

The development of novel and efficient methodologies for the synthesis of eleven-membered carbocycles is an interesting challenge in synthetic organic chemistry. A number of natural products based on eleven-membered skeletons are known[1] and many new molecules[2] are being discovered. They constitute one of the important and largest groups among diterpenes. The broad distribution of these molecules[3–5] combined with their structural architecture and impressive range of biological activities sustains unabated interest in the synthesis of eleven-membered carbocycles. Some of the biologically active natural products with eleven-membered skeletons are shown in Figure 1.

A number of methodologies are known in the literature for the construction of these macrocyclic structures.[1] Mehta and co-workers reported the first enantioselective total synthesis[6] of dolabellanes through an oxy-Cope ring expansion reaction. Williams and co-workers reported the macrocyclizations through intramolecular Julia reactions,[7] followed by other approaches from the same group.[8] The intramolecular β-keto ester alkylation approach by Jenny and Borschberg,[9] tandem Cope rearrangement/McMurry-type cyclization by Takeshita and co-workers,[10] Claisen rearrangement[11] and intramolecular pinacol coupling fol-

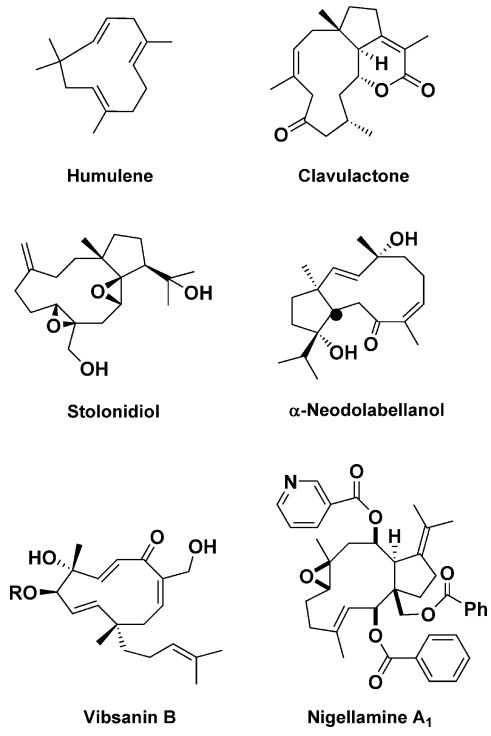

Figure 1. Biologically active natural products with eleven-membered skeleton.

[a] National Institute for Interdisciplinary Science and Technology, CSIR (Formerly Regional Research Laboratory), Trivandrum 695019, Kerala, India
Fax: +91-471-2491712
E-mail: radhupreethi@rediffmail.com
[b] Analytical Sciences Discipline, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002, Gujarat, India
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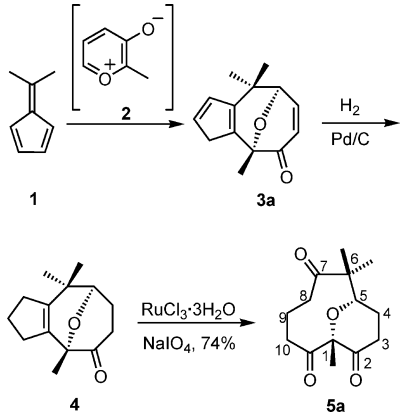
lowed by dianion accelerated oxy-Cope rearrangement[12] (Corey and Kania) and the methodologies by Luker and Whitby[13] are some of the significant strategies. Methodologies utilizing the macrocyclic ring closure via enolate alkylation[14] and intramolecular alkylation routes are also known in the literature.[15] Herein we report a novel and efficient strategy towards the synthesis of an 11 membered carbocycle with a bridging ether linkage through a cycloaddition strategy involving pentafulvenes.

Pentafulvenes have been the subject of great interest both from synthetic and theoretical points because they exhibit different modes of cycloadditions. In cycloadditions, pentafulvenes can participate as a 2π, 4π or 6π component and have served as excellent synthons for the synthesis of triquinanes, pyrindines etc.[16] Investigations from our own laboratory[17] have unraveled the interesting reactivity profile of fulvenes in cycloaddition reactions. Fulvenes have found extensive use as key intermediates in the synthesis of natural products such as hirsutene,[18] capnellene,[19] β-vetivone,[20] hinesol,[21] and silphinene.[22]

Results and Discussion

We have recently reported a facile [6+3] cycloaddition of pentafulvenes with 3-oxidopyrylium betaines leading to the formation of 5–8-fused oxa-bridged cyclooctanoids.[23] The [6+3] adducts obtained by the present methodology contain an α,β-unsaturated ketone, an oxa-bridge and a cyclopentadiene functionality, which makes these adducts potentially amenable to a number of synthetic transformations. In addition, depending on the type of fulvene and 3-oxidopyrylium betaine used, manipulations can also be carried out in the eight membered ring.

In the context of our general interest in utilizing pentafulvenes for the synthesis of novel molecules,[17] we decided to explore the reactivity of fulvene derived 5–8-fused oxabridged cyclooctanoids in the synthesis of biologically interesting natural products. The preliminary result of our investigation along this line is presented in this communication. Our initial studies involved the chemo selective reduction of the two disubstituted double bonds in the 5–8-fused oxabridged cyclooctanoid **3a**. The reduction of **3a** over Pd/C at 1 atm. pressure of H_2 afforded the product **4** in quantitative yield. Ruthenium based oxidative cleavage of the tetrasubstituted double bond in **4** gave the eleven-membered carbocycle **5a** in 74% yield. The reaction is illustrated in Scheme 1.



Scheme 1. Reagents and conditions a) Et_3N (1.2 equiv.), $CHCl_3$, 50 °C; b) H_2 (1 atm), Pd/C, EtOAc; c) $RuCl_3.3H_2O$ (0.1 equiv.), $NaIO_4$ (6.0 equiv.), $CH_3CN/CCl_4/H_2O$ (1:1:1).

The product was characterized by detailed spectral analysis (IR, ^1H and ^{13}C NMR and mass spectra). Unambiguous evidence for the structure and stereochemistry of the product was obtained by single-crystal X-ray analysis (Figure 2).[24]

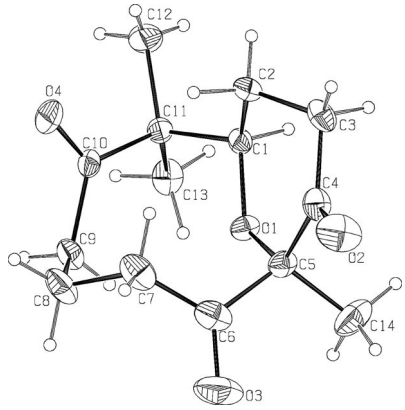
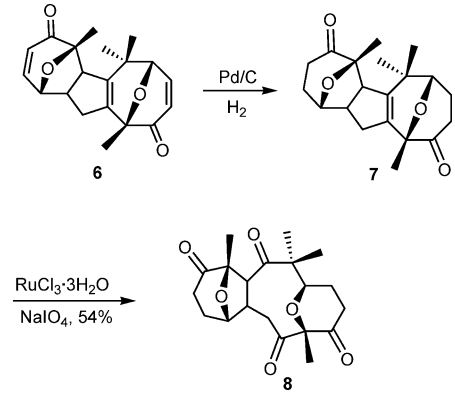


Figure 2. ORTEP plot for the crystal structure of **5a**.

To establish the generality of the transformation from **1** to **5**, a number of eleven-membered ether bridged macrocycles were synthesized from 5–8-fused cyclooctanoids in very good to excellent yields. The results of our investigations are summarized in Table 1.

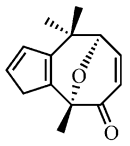
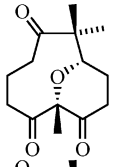
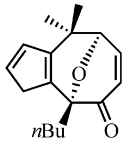
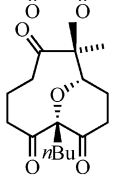
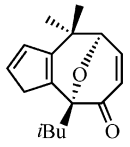
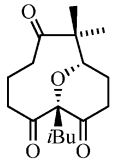
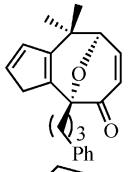
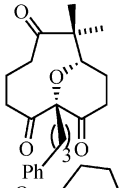
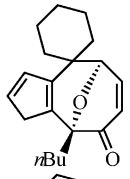
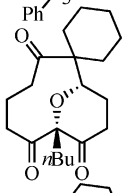
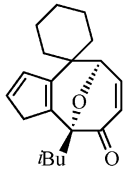
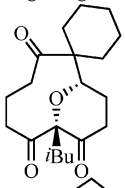
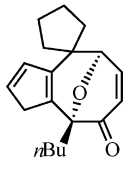
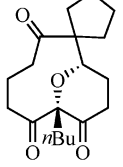
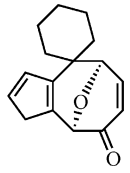
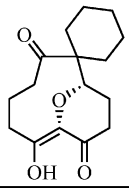
We have also carried out similar transformation of the 7–5–8-fused oxabridged molecule[23c] **6** leading to the macrocycle **8** in 54% yield (Scheme 2).



Scheme 2. Reagents and conditions a) H_2 (1 atm),Pd/C (b) $RuCl_3·3H_2O$ (0.1 equiv.), $NaIO_4$ (6.0 equiv.), $CH_3CN/CCl_4/H_2O$ (1:1:1).

The product, an eleven-membered carbocyclic triketone with an ether bridge has a cyclic β-diketone as a part of the molecule, hence the keto functionalities of the molecule can be selectively functionalized towards 11-membered carbocycles of interest. The cyclic β-diketone with a C–O bond

Table 1. Synthesis of eleven-membered carbocycles. [a] Reaction conditions: (a) H_2 (1 atm), Pd/C (b) $RuCl_3 \cdot 3H_2O$ (0.1 equiv.), $NaIO_4$ (6.0 equiv.), $CH_3CN/CCl_4/H_2O$ (1:1:1).

Entry	Substrate	Product	% Yield
1	 **3a**	 **5a**	74
2	 **3b**	 **5b**	70
3	 **3c**	 **5c**	59
4	 **3d**	 **5d**	60
5	 **3e**	 **5e**	50
6	 **3f**	 **5f**	80
7	 **3g**	 **5g**	67
8	 **3h**	 **5h**	60[a]

[a] Product was isolated in the enol form.

on the α-carbon can be effectively utilized towards the synthesis of pyrazoles,[25] isoxazoles,[26] triazole[27] and a number of bicyclic or polycondensed heterocycles of pharmaceutical importance. In addition to the above properties, 1,3-diketones are key structural units in many chelating ligands for lanthanide and transition metals.[28]

Conclusions

In conclusion, we have unraveled a novel and versatile method towards the synthesis of eleven-membered carbocycles through a three step reaction sequence from pentafulvenes. The methodology described herein is easy to carry out and delivers densely functionalized carbocycles in good yields, without employing any elaborated catalytic system. The novel eleven-membered triketones, obtained by the present methodology offer many possibilities of downstream chemistry. We believe that this methodology will find use in the synthesis of a number of diterpenoids having the eleven-membered carbocyclic skeleton.

Experimental Section

General Methods: All reactions were conducted in oven-dried glassware. Solvents used for the experiments were distilled and dried as specified. All reactions were monitored by TLC (Silica gel 60 F254, 0.25 mm, Merck), visualization was effected with UV and/or by staining with Enholm yellow solution. Chromatography refers to open column chromatography on silica gel (100–200 mesh). NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Bruker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer; absorptions are reported in cm^{-1}. Mass spectra were recorded under EI/HRMS or FAB/LRMS using JEOL JMS 600H mass spectrometer.

General Procedure for the Synthesis of Eleven-Membered Carbocycles 5: The cycloadduct **3** (1.0 equiv.) was dissolved in anhydrous ethyl acetate. 5 mol-% of Pd/C (10% on carbon) was added and the reaction mixture was stirred under 1 atm pressure of H_2 at room temp. for 6 h. After the completion of the reaction as indicated by TLC, the reaction mixture was filtered through a pad of celite. The solvent was removed under reduced pressure and the residue was dissolved in a 1:1 mixture of CH_3CN and CCl_4 (10 mL). Sodium periodate (6.0 equiv.) was added to the solution and the mixture was stirred. A solution of ruthenium trichloride (0.1 equiv.) in water (10 mL) was added in one portion, and vigorous stirring was continued for 5 h. The reaction mixture was diluted with water (10 mL) and was extracted with CH_2Cl_2 (3 × 20 mL) and filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the residue was subjected to chromatography on a silica gel (100–200 mesh) column using ethyl acetate/hexanes mixture as eluent afforded the product in good yield.

Compound 5a: Following the general experimental procedure, the cycloadduct **3a** (100 mg, 0.4612 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (592 mg, 2.7672 mmol) and ruthenium trichloride (10 mg, 0.0461 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5a** as a pale yellow solid (86 mg, 74%). M.p. 62–64 °C. R_f = 0.58 (30% EtOAc/hexanes). IR (KBr): $\tilde{\nu}_{max}$ = 2958, 2929, 2871, 1735, 1699, 1474, 1446, 1366, 1226, 1095, 1046, 1007 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.96 (dd, J_1 = 4.6, J_2 = 12.4 Hz, 1 H), 3.03–2.94 (m, 1 H), 2.66–2.58 (m, 2 H), 2.36–2.32 (m, 1 H), 2.19–2.03 (m, 6 H), 1.52 (s, 3 H), 1.38 (s, 3 H), 1.03 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.6, 207.2, 206.8, 86.5, 82.7, 52.2, 37.9, 37.3, 35.1, 23.8, 22.9, 22.4, 21.1, 20.6 ppm. HRMS (EI): for $C_{14}H_{20}O_4$, calcd. (M^+): 252.1346, found (M + 1): 253.1362.

Compound 5b: Following the general experimental procedure, the cycloadduct **3b** (100 mg, 0.3971 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (509 mg, 2.3826 mmol) and ruthenium trichloride (8 mg, 0.0397 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5b** as a colourless viscous liquid (82 mg, 70%). R_f = 0.68 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2960, 2868, 1732, 1695, 1455, 1368, 1223, 1197, 1103, 1061 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.98 (dd, J_1 = 4.2, J_2 = 12.5 Hz, 1 H), 3.03–2.95 (m, 1 H), 2.67–2.52 (m, 2 H), 2.24 2.02 (m, 9 H), 1.69–1.66 (m, 2 H), 1.54 (s, 3 H), 1.33–1.26 (m, 2 H), 1.03 (s, 3 H), 0.90 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.8, 206.8, 205.6, 89.9, 83.2, 52.4, 38.0, 37.9, 37.8, 37.0, 34.8, 25.8, 24.0, 23.5, 22.9, 21.1, 14.2 ppm. HRMS (EI) for $C_{17}H_{26}O_4$, calcd. (M^+): 294.1831, found (M + 1): 295.1767.

Compound 5c: Following the general experimental procedure, the cycloadduct **3c** (100 mg, 0.3971 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (509 mg, 2.3826 mmol) and ruthenium trichloride (8 mg, 0.0397 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5c** as a colourless viscous liquid (69 mg, 59%). R_f = 0.67 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2959, 2858, 1732, 1699, 1455, 1385, 1367, 1196, 1105, 1064, 1015 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.99 (dd, J_1 = 4.2, J_2 = 12.6 Hz, 1 H), 2.96–2.89 (m, 1 H), 2.71–2.64 (m, 2 H), 2.35–2.04 (m, 8 H), 1.91–1.85 (m, 1 H), 1.75–1.62 (m, 4 H), 1.04 (s, 3 H), 0.97 (d, J = 6.6 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.8, 207.0, 206.7, 90.4, 83.1, 52.4, 42.2, 37.9, 37.6, 36.8, 24.6, 24.4, 24.1, 24.0, 23.4, 22.6, 21.2 ppm. HRMS (EI) for $C_{17}H_{26}O_4$, calcd. (M^+): 294.1831, found (M + 1): 295.1857.

Compound 5d: Following the general experimental procedure, the cycloadduct **3d** (100 mg, 0.3121 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (400 mg, 1.8726 mmol) and ruthenium trichloride (6 mg, 0.0312 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5d** as a colourless viscous liquid (65 mg, 60%). R_f = 0.62 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2929, 2857, 1732, 1698, 1602, 1492, 1454, 1367, 1223, 1092, 1012 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.16 (m, 5 H), 3.96 (dd, J_1 = 4.2, J_2 = 12.5 Hz, 1 H), 3.02–2.93 (m, 1 H), 2.67–2.51 (m, 4 H), 2.22–1.81 (m, 9 H), 1.77–1.72 (m, 2 H), 1.52 (s, 3 H), 1.02 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.9, 206.9, 205.9, 141.7, 128.4, 128.3, 125.9, 89.6, 83.0, 52.2, 37.7, 37.6, 36.8, 35.9, 34.4, 25.3, 23.8, 23.2, 22.5, 20.8 ppm. HRMS (EI) for $C_{22}H_{28}O_4$, calcd. (M^+): 356.1988, found (M + 1): 357.1946.

Compound 5e: Following the general experimental procedure, the cycloadduct **3e** (100 mg, 0.3351 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (430 mg, 2.0106 mmol) and ruthenium trichloride (7 mg, 0.0335 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5e** as a colourless viscous liquid (56 mg, 50%). R_f = 0.73 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2932, 2857, 1728, 1694, 1455, 1345, 1245, 1206, 1105, 1064, 1032 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.03 (dd, J_1 = 3.8, J_2 = 12.5 Hz, 1 H), 3.16–3.11 (m, 1 H), 2.98–2.88 (m, 2 H), 2.67–2.61 (m, 1 H), 2.46–2.44 (m, 1 H), 2.27–2.11 (m, 3 H), 1.90–1.52 (m, 12 H), 1.36–1.20 (m, 6 H), 0.89 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 216.7, 207.4, 205.1, 89.6, 82.6, 56.9, 48.5, 38.3, 37.9, 36.9, 34.7, 29.4, 25.7, 25.6, 23.5, 23.4, 22.9, 22.8, 22.0, 13.9 ppm. HRMS (EI) for $C_{20}H_{30}O_4$, calcd. (M^+): 334.2144, found 334.2165.

Compound 5f: Following the general experimental procedure, the cycloadduct **3f** (100 mg, 0.3351 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (430 mg, 2.0106 mmol) and ruthenium trichloride (7 mg, 0.0335 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5f** as a colourless viscous liquid (90 mg, 80%). R_f = 0.70 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2930, 2857, 1732, 1693, 1455, 1361, 1207, 1109, 1086, 1036 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.02 (dd, J_1 = 3.8, J_2 = 12.6 Hz, 1 H), 3.16–3.12 (m, 1 H), 2.91–2.87 (m, 1 H), 2.67–2.57 (m, 2 H), 2.31–2.25 (m, 3 H), 2.12–2.05 (m, 5 H), 1.94–1.88 (m, 1 H), 1.85–1.59 (m, 10 H), 0.97 (d, J = 6.4 Hz, 3 H), 0.87 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 216.6, 207.3, 205.9, 90.2, 82.6, 57.1, 42.4, 38.4, 38.2, 36.7, 34.7, 33.9, 29.8, 26.5, 25.9, 25.5, 24.5, 24.2, 24.0, 23.7 ppm. HRMS (EI) for $C_{20}H_{30}O_4$, calcd. (M^+): 334.2144, found 334.2154.

Compound 5g: Following the general experimental procedure, the cycloadduct **3g** (100 mg, 0.3516 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (451 mg, 2.1096 mmol) and ruthenium trichloride (7 mg, 0.0352 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5g** as a colourless viscous liquid (76 mg, 67%). R_f = 0.74 (30% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 2957, 2872, 1732, 1694, 1455, 1361, 1320, 1225, 1195, 1106, 1067 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.06 (dd, J_1 = 3.8, J_2 = 12.5 Hz, 1 H), 3.15–3.06 (m, 1 H), 2.67–2.60 (m, 1 H), 2.46–2.05 (m, 8 H), 1.94–1.61 (m, 8 H), 1.37–1.29 (m, 4 H), 1.22–1.03 (m, 2 H), 0.90 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 216.0, 207.4, 204.6, 89.7, 81.5, 65.1, 38.9, 38.7, 37.0, 34.8, 33.9, 30.7, 25.7, 25.1, 24.6, 23.8, 23.3, 22.9, 13.9 ppm. HRMS (EI) for $C_{19}H_{28}O_{24}$, calcd. (M^+): 320.1988, found 320.2007.

Compound 5h: Following the general experimental procedure, the cycloadduct **3h** (100 mg, 0.4127 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (529 mg, 2.4762 mmol) and ruthenium trichloride (9 mg, 0.0413 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **5h** as a pale yellow viscous liquid (69 mg, 60%). R_f = 0.43 (50% EtOAc/hexanes). IR (film): $\tilde{\nu}_{max}$ = 3313, 2924, 2855, 1709, 1682, 1455, 1388, 1262, 1215, 1118, 1089 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (br. s, 1 H), 4.41–4.36 (m, 1 H), 2.72–2.56 (m, 2 H), 2.46–2.40 (m, 2 H), 2.32 (t, J = 5.9 Hz, 2 H), 2.05–2.01 (m, 2 H), 1.71–1.66 (m, 4 H), 1.50–1.43 (m, 4 H), 1.37–1.25 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.7, 178.2,146.5, 144.1, 87.2, 50.6, 38.1, 34.4, 30.6, 28.2, 25.3, 24.7, 23.3, 22.7, 22.3, 21.8 ppm. HRMS (EI) for $C_{16}H_{22}O_4$, calcd. (M^+): 278.1518, found 278.1524.

Compound 8: Following the general experimental procedure, the cycloadduct **6** (75 mg, 0.2298 mmol) on catalytic hydrogenation and subsequent treatment with sodium periodate (295 mg, 1.3787 mmol) and ruthenium trichloride (5 mg, 0.0229 mmol) in a 1:1:1 mixture of CH_3CN, CCl_4 and water (10 mL) for 5 h at room temp. afforded the product **8** as a pale yellow solid (45 mg, 54%). M.p. 198–200 °C; R_f = 0.38 (30% EtOAc/hexanes). IR (KBr): $\tilde{\nu}_{max}$ = 2965, 2934, 1732, 1703, 1698, 1613, 1455, 1385, 1338, 1205, 1136, 1090, 1024 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.53 (t, J = 6.4 Hz, 1 H), 3.96–3.87 (m, 2 H), 3.14 (d, J = 8.0 Hz, 1 H), 2.87–2.79 (m, 1 H), 2.46–2.18 (m, 5 H), 1.94–1.88 (m, 1 H), 1.57–1.54 (m, 2 H), 1.53 (s, 3 H), 1.49 (s, 3 H), 1.38 (s, 3 H), 1.34–1.22 (m, 1 H), 1.19 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.6, 203.2, 202.8, 84.9, 82.0, 76.6, 75.1, 62.9, 50.1, 36.9, 34.0, 33.3, 29.7, 27.8, 26.6, 22.3, 20.9, 20.7, 18.5 ppm. HRMS (EI) for $C_{20}H_{26}O_6$, calcd. (M^+): 362.1729, found 362.1727.

Supporting Information (see also the footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra of all new compounds.

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[24] X-ray crystal data for **5a**. Empirical formula: $C_{14}H_{20}O_4$, formula weight: 252.30, T = 293(2) K, λ = 0.71073, crystal system: monoclinic, space group: $P2_1/c$, unit cell dimensions: a = 12.3704(15) Å, α = 90°, b = 8.9352(11) Å, β = 111.405°, c = 12.9931(17) Å, γ = 90°, V = 1337.1(3) A^3, Z = 4, density (calcd.) = 1.253 Mg/m^3, absorption coefficient: 0.091 mm^{-1}, F(000)544, crystal size: 0.392 × 0.32 × 0.27 mm, theta range for data collection: 1.77–24.99°, index ranges: $-12 \le h \le 14$, $-10 \le k \le 10$, $-15 \le l \le 11$, reflections collected: 6442, independent reflections: 2344 [R(int) = 0.0218], absorption correction, MUTISCAN SADABS refinement method, full-matrix least-squares on F^2, data/restraints/parameters: 2344/0/205, Goodness-of-fit on F^2: 1.048, final R indices [$I > 2\sigma(I)$] $R1$ = 0.0696, $wR2$ = 0.1950, R indices (all data): R_1 = 0.0823, $wR2$ = 0.2074, largest diff. peak and hole: 0.599 and –0.179 e·A^{-3}. CCDC-622537 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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