SYNTHESIS OF 2-PYRONES BRIDGED AT THE 3- AND 6-POSITIONS
BY RING-CLOSING METATHESIS

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Abstract –Synthesis of 4-hydroxy-2-pyrones bridged at the 3- and 6-positions by ring-closing metathesis was studied. The reaction of 6-(9-decenyl)-4-methoxy-3-(10-undecenoyl)pyran-2-one (6b) by the first generation ruthenium catalyst (7) gave 3,6-bridged 2-pyrone (10b) in 62% yield. The reaction of 3-(6-heptenoyl)-6-(5-hexenyl)-4-methoxypyran-2-one (6a) (n = 4) under the same conditions afforded the 3,6-bridged 2-pyrone (10a) in 6% yield together with considerable amounts of intermolecular metathesis products.

INTRODUCTION
The design and synthesis of cyclophanes, macrocycles containing aromatic or heteroaromatic groups, is a fascinating branch of organic chemistry.1,2 Previously, we reported a convenient synthesis of cyclophane (B) by intramolecular [4+2] cycloaddition of bis(acylketene) (A).3 The heterophane (B) having relatively short bridge (m = 7~10) showed planar chirality due to the restricted rotation of pyrone ring. We have demonstrated that enantiomerically pure B serve as a new optical resolution reagent.4 We have also shown that B serves as excellent intermediates for 2,6-pyridinophanes.5 In the recent years, increasing attention has been directed toward the synthesis of medium and large rings including cyclophanes using metal-catalyzed ring-closing metathesis.6 Here we report the synthesis of heterophane (B) by ring-closing metathesis of pyrone derivative (C) catalyzed by ruthenium alkylidene complexes (Scheme 1).
RESULTS AND DISCUSSION

The substrates for ring-closing metathesis were synthesized by [4+2] cycloaddition of acylketene. Meldrum’s acid was condensed with 6-heptenoic chloride (1a) and 10-undecenoic chloride (1b) by Yonemitsu method\(^7\) to produce the corresponding acylated Meldrum’s acids (2a) and (2b). These compounds were transformed into 6-(\(\square\)-alkenyl)-1,3-dioxin-4-ones (3a) and (3b) in refluxing toluene.\(^8\) Heating 3a and 3b in refluxing chlorobenzene generated acylketenes (4a) and (4b), which \textit{in situ} underwent intermolecular cycloaddition to produce 4-hydroxy-2-pyrone derivatives (5a) (54\%) and (5b) (78\%), respectively.\(^9,10\) Heating sodium salts of (5a) or (5b) with dimethyl sulfate in HMPA\(^11\) gave the methyl ether (6a) or (6b) (Scheme 2).

First, we examined ring-closing metathesis of 4-hydroxy compound (5b) (n = 8) because the reaction with ruthenium alkylidene catalysts has functional group tolerance\(^6,12\) and the 4-hydroxy hydorogen is strongly hydrogen bonded to acyl oxygen. The reaction was conducted in dichloromethane (3 mmol) under the first-generation catalyst 7 or the second-generation catalyst 8. The results are summarized in Table 1. When the reaction was conducted under catalyst (7) (5 or 10 mol\%), the desired heterophane (9b) was obtained in 13~18% yields together with starting 5b (10~12\%, Entries 1~3). The reaction of higher
concentration (20 mmol) gave lower yield of 9b (Entry 4). Use of catalyst (8) resulted in the formation of rather complex mixture, from which 9b was isolated in 7% yield (Entry 5). Compound (9b) was obtained as an inseparable mixture of E- and Z-isomers at the alkenylene bridge as indicated by ¹H- and ¹³C-NMR spectroscopic studies. For example, hydroxy protons appeared at 16.9 and 17.0 ppm in 7 : 3 ratio in the ¹H-NMR spectra. The geometry of the major component is not clear.

Next, ring-closing metathesis of 4-methoxy compound (6b) was studied. Heating 6b with catalyst (7) in dichloromethane afforded heterophane (10b) in 62% yield proving that the free 4-hydroxy group causes the low efficiency for formation of 9b from 5b. Heterophane (10b) was obtained as an inseparable mixture of E- and Z-isomers. The ratio of geometrical isomers was again 7 : 3 as indicated by the ¹³C-NMR spectrum, though the geometry of the major component is not clear.

The results prompted us to study the ring-closing of 6a to heterophane (10a) that is expected to show planar chirality owing to the short alkenylene bridge. However, the reaction of (6a) under the same conditions as for (6b) gave rise to a rather complex mixture. Purification by chromatography afforded heterophane (10a) only in 6% yield as an inseparable mixture of E- and Z-isomers. Considerable amounts of oily products (11) (8%) and (12) (25%) were obtained from this reaction. These products are assigned to intermolecular metathesis products. ¹H-NMR spectroscopic studies indicated that both of these are mixtures of E,Z-isomers and regioisomers. As the regioisomers, head-to-tail, head-to-head, and tail-to-tail products are possible. In Scheme 4, only head-to-tail products (11) and (12) are shown.
The results show clearly that efficiency for ring-closing metathesis is much dependent upon the bridge length of products. Heterophane (10b) having long bridge is formed in satisfactory yield, while 10a having short bridge are formed in low yield. It should be noted that intramolecular cycloaddition of bis(acylketene) (A) to produce heterophane (B) (m = 10) proceeds highly efficiently.\(^3\)

Finally, we examined conversion of 10b to heterophane of type (B). Hydrogenation of 10b with 5% Pd-C gave heterophane (13) as a sole product in 85% yield. Treatment of 13 with bromotrimethylsilane at room temperature afforded 4-hydroxy compound (14)\(^5\) in 87% yield (Scheme 5).

CONCLUSION

Synthesis of 4-hydroxy-2-pyrone bridged at the 3- and 6-positions by ring-closing metathesis was studied. The key compound (5) for this ring-closing was readily synthesized by intermolecular [4+2] cycloaddition of alkenoylketene. Ring-closing metathesis of 4-hydroxy compound (5b) under ruthenium catalyst (7) afforded heterophane (9b) in low yield, while that of and 4-methoxy compound (6b) produced...
the corresponding heterophane (10b) in satisfactory yield. Compound (10b) was successfully transformed into 3,6-bridged 4-hydroxy-2-pyrone (14). The reaction of 4-methoxy compound (6a) having short \-alkenyl groups resulted in low yield of heterophane (10a) due to the preferential formation of intermolecular metathesis products, indicating a limitation of this useful cyclization method in strained heterophane synthesis.

EXPERIMENTAL

General. Melting points were determined with a Yazawa Micro Melting Point Apparatus without correction. \(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded on a JEOL JNM-GSX 270, 400 or 500 spectrometers with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO FT/IR-8000 spectrophotometer. MS spectra were recorded on a JEOL JMS-700 Mstation spectrometer by using m-nitrobenzyl alcohol matrix. Column chromatography was done with Silica Gel 60 N (Kanto Chemical Co., Inc.). Preparative thin layer chromatography (PTLC) was done on Merck Silica Gel 60 F\(_{254}\). The ratios of solvent mixtures for chromatography are shown as volume/volume. Ruthenium alkylidene complexes (7) and (8) were purchased from Aldrich Chemical Company, Inc.

6-(5-HEXENYL)-2,2-DIMETHYL-1,3-DIOXIN-4-ONE (3A)

A solution of 6-heptenoyl chloride (1a) (0.94 g, 7.3 mmol) in dichloromethane (10 mL) was added dropwise to a stirred solution of Meldrum’s acid (1.1 g, 7.3 mmol) and pyridine (1.7 g, 22 mmol) in dichloromethane (10 mL) under ice-cooling over 15 min. The mixture was stirred for 1 h under ice-cooling and then for 1 h at rt. The mixture was acidified with 10% hydrochloric acid and extracted with ether. The organic layer was washed with 10% hydrochloric acid and then with brine. The organic layer was dried over anhydrous MgSO\(_4\) and concentrated under reduced pressure to give crude (2a) as yellow crystals. A solution of the crude (2a) in dry toluene (100 mL) and dry acetone (0.3 mL) was heated under reflux for 1 h. The solution was evaporated in vacuo and the residue was purified by silica gel column chromatography using hexane-ethyl acetate (10 : 1) to give (3a)\(^{13}\) as a colorless oil [613 mg, 40% from (1a)]. MS (FAB) \(m/z\): 211 (M\(^{+}\)+1). IR (neat) \(\nu\): 2934, 1726, 1632 cm\(^{-1}\). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 1.42-1.48 (2H, m), 1.53-1.61 (2H, m), 1.68 (6H, s), 2.05-2.10 (2H, m), 2.22 (2H, t, \(J = 7.5\) Hz), 4.96-5.04 (2H, m), 5.23 (1H, s), 5.73-5.82 (1H, m). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta\): 25.1, 25.2, 28.2, 33.3, 33.5, 93.2, 106.3, 115.0, 138.1, 161.5, 172.0.

6-(9-Decenyl)-2,2-dimethyl-1,3-dioxin-4-one (3b)

Following the procedure given for preparation of (3a), 10-undecenoyl chloride (1b) (1.8 g, 10 mmol) was condensed with Meldrum’s acid to give crude (2b). Heating (2b) in toluene gave (3b) as a colorless oil [1.3 g, 50% from (1b)]. HRMS (FAB) Calcd for C\(_{16}\)H\(_{27}\)O\(_3\) (M\(^{+}\)+1) 267.1960. Found 267.1927. IR (neat)
\[ \nu : 2926, 1728, 1634 \text{ cm}^{-1} \]. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ : 1.29-1.40 (10H, m), 1.51-1.57 (2H, m), 1.68 (6H, s), 2.02-2.06 (2H, m), 2.21 (2H, t, $J = 7.7$ Hz), 4.93 (1H, dd, $J = 9.1, 1.5$ Hz), 4.99 (1H, dd, $J = 17.1, 1.5$ Hz), 5.23 (1H, s), 5.77-5.85 (1H, m). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ : 25.1, 25.8, 28.9, 29.0, 29.1, 29.2, 29.3, 33.7, 33.8, 93.1, 106.3, 114.3, 139.1, 161.5, 172.2, 209.5.

### 3-(6-HEPTENOYL)-6-(5-HEXENYL)-4-HYDROXYPYRAN-2-ONE (5A)

A solution of (3a) (480 mg, 2.3 mmol) in dry chlorobenzene (5 mL) was refluxed for 4 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane-ethyl acetate, 10:1) to give 5a (187 mg, 54%) as colorless solid. Recrystallization from hexane gave prisms of mp 33$^\circ$C. HRMS (FAB) Calcd for C$_{18}$H$_{25}$O$_4$ (M$^+$+1) 305.1753. Found 305.1746. MS (FAB) $m/z$: 305 (M$^+$+1). IR (neat) $\nu$: 2932, 1740, 1638 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.43-1.52 (4H, m), 1.65-1.74 (4H, m), 2.04-2.13 (4H, m), 2.49 (2H, t, $J = 7.6$ Hz), 3.08 (2H, t, $J = 7.3$ Hz), 4.93-5.04 (4H, m), 5.74-5.85 (2H, m), 5.91 (1H, s), 16.8 (1H, s). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$: 23.5, 25.8, 28.2, 28.5, 33.3, 33.6, 34.2, 41.6, 99.7, 100.9, 114.7, 115.2, 138.0, 138.6, 161.2, 172.4, 181.3, 207.9.

### 6-(9-Decenyl)-4-hydroxy-3-(10-undecenoyl)pyran-2-one (5b)

Following the procedure given for preparation of 5a, compound (3b) (1.2 g, 4.5 mmol) was heated to give 5b (730 mg, 78%) as a white solid. Recrystallization from hexane gave needles of mp 63$^\circ$C. HRMS (FAB) Calcd for C$_{26}$H$_{41}$O$_4$ (M$^+$+1) 417.3005. Found 417.2966. MS (FAB) $m/z$: 417 (M+1). IR (neat) $\nu$: 2920, 1740, 1638 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.23-1.38 (20H, m), 1.60-1.70 (4H, m), 2.00-2.05 (4H, m), 2.46 (2H, t, $J = 7.5$ Hz), 3.05 (2H, t, $J = 7.5$ Hz), 4.91-4.93 (2H, m), 4.96-5.00 (2H, m), 5.75-5.84 (2H, m), 5.90 (1H, s), 16.8 (1H, s). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$: 24.0, 26.4, 28.9, 29.0, 29.1, 29.2, 29.9, 29.4, 29.5, 33.8, 33.9, 34.4, 40.2, 99.7, 100.8, 114.2, 114.3, 139.2, 139.3, 161.2, 172.6, 181.4, 208.1.

### 3-(6-Heptenoyl)-6-(5-hexenyl)-4-methoxypyran-2-one (6a)

To a stirred solution of (5a) (150 mg, 0.49 mmol) in anhydrous hexamethylphosphoric triamide (2.7 mL), sodium hydride (60% in mineral oil, 23.6 mg, 0.59 mmol) was added at rt under argon atmosphere and the mixture was stirred for 2 h at rt. Dimethyl sulfate (74 mg, 0.59 mmol) was added to the mixture and the whole was stirred for 2 h at 60$^\circ$C. The reaction mixture was diluted with diethyl ether, washed with 5% hydrochloric acid and then with brine. The organic layer was dried over MgSO$_4$ and then the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 10:1) to give 6a as yellow oil (102 mg, 65%). HRMS (FAB) Calcd for C$_{19}$H$_{27}$O$_4$ (M$^+$+1)}
319.1909. Found 319.1902. MS (FAB) m/z: 319 (M⁺+1). IR (neat) ν: 2932, 1715, 1655 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ: 1.38-1.50 (4H, m), 1.62-1.72 (4H, m), 2.03-2.11 (4H, m), 2.53 (2H, t, J = 7.7 Hz), 2.82 (2H, t, J = 7.3 Hz), 3.92 (3H, s), 4.91-5.04 (4H, m), 5.73-5.84 (2H, m), 6.10 (1H, s). ¹³C-NMR (126 MHz, CDCl₃) δ: 23.5, 26.3, 28.2, 28.5, 33.3, 33.7, 34.5, 43.5, 57.2, 94.4, 105.8, 114.5, 115.2, 138.1, 138.8, 162.0, 169.5, 169.8, 200.2.

6-(9-Decenyl)-4-methoxy-3-(10-undecenoyl)pyran-2-one (6b)
Following the procedure given for preparation of 6a, 5b (470 mg, 1.1 mmol) was methylated to give (6b) (437 mg, 90%) as yellow oil. HRMS (FAB) Calcd for C₂₇H₄₃O₄ (M⁺+1) 431.3161. Found 431.3173. MS (FAB) m/z: 431 (M⁺+1). IR (neat) ν: 2924, 1713 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ: 1.28-1.36 (20H, m), 1.59-1.68 (4H, m), 1.99-2.05 (4H, m), 2.50 (2H, t, J = 7.5 Hz), 2.81 (2H, t, J = 7.5 Hz), 3.90 (3H, s), 4.89-4.99 (4H, m), 5.75-5.83 (2H, m), 6.04 (1H, s). ¹³C-NMR (126 MHz, CDCl₃) δ: 24.0, 27.0, 28.9, 29.0, 29.1, 29.2, 29.2, 29.3, 29.4, 29.5, 33.8, 33.9, 43.7, 57.1, 94.3, 105.8, 114.2, 114.3, 139.2, 139.3, 162.0, 169.4, 170.0, 200.4.

24-Hydroxy-22-oxabicyclo[19.2.2]pentacosa-1(24),11,21(25)-triene-2,23-dione (9b)
General procedure: To a solution of ruthenium alkylidene catalyst (7) (2.8 mg, 5 mol%) in dry dichloromethane (11 mL) was added dropwise a solution of 5b (30 mg, 0.07 mmol) in dichloromethane (9 mL) over 2 h. The solution was stirred for 12 h at room temperature and then refluxed for 6 h. Solvent was evaporated and the residue was purified by PTLC (hexane-ethyl acetate, 10 : 1) to give starting (5b) (3.6 mg, 12%) and E/Z-mixture of 9b (4.9 mg, 18%) as a colorless oil. HRMS (FAB) Calcd for C₂₄H₃₇O₄ (M⁺+1) 389.2692. Found 389.2694. MS (FAB) m/z: 389 (M⁺+1). IR (neat) ν: 2926, 1724, 1636 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ: 1.26-1.38 (18H, m), 1.52-1.72 (6H, m), 1.90-2.00 (4H, m), 2.51 (2H, t, J = 6.1 Hz), 3.07 (2H, t, J = 7.0 Hz), 5.30-5.38 (2H, m), 5.93 (1H, s), 16.9 (0.7H, s), 17.0 (0.3H, s). ¹³C-NMR (126 MHz, CDCl₃) δ: 24.3, 25.5, 26.0, 26.2, 26.8, 27.0, 27.8, 27.9, 28.0, 28.1, 28.1, 28.4, 28.4, 28.7, 28.7, 28.8, 28.9, 28.9, 29.2, 29.4, 29.5, 32.0, 32.4, 34.3, 40.7, 99.6, 101.5, 101.7, 130.0, 130.1, 130.3, 130.7, 161.0, 172.7, 181.4, 181.6, 208.7, 209.1.

16-Methoxy-14-oxabicyclo[11.2.2]heptadeca-1(16),7,13(17)-triene-2,15-dione (10a)
Following the general procedure, 6a (70 mg, 0.22 mmol) was added to a solution of catalyst (7) (9.1 mg, 5 mol%). The solution was stirred for 12 h at rt and then heated under reflux for 6 h. Purification by PTLC (hexane-ethyl acetate, 2 : 1) gave unreacted 6a (11 mg, 15%), mixture of E/Z-10a (4.1 mg, 6%), (11) (5.1 mg, 8%), and cyclic dimer (12) (16.2 mg, 25%).
E/Z-(10a): HRMS (FAB) Calcd for C\textsubscript{17}H\textsubscript{23}O\textsubscript{4} (M\textsuperscript{+}+1) 291.1596. Found 291.1604. MS (FAB) m/z: 291 (M\textsuperscript{+}+1). IR (neat) \nu: 2922, 1736, 1661 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \delta: 1.32-1.41 (4H, m), 1.71-1.79 (4H, m), 1.92-1.96 (4H, m), 2.47-2.50 (2H, m), 2.61-2.63 (2H, m), 3.88 (3H, s), 5.28-5.32 (2H, m), 6.12 (1H, s). \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3}) \delta: 22.5, 22.7, 22.8, 27.2, 27.6, 29.8, 30.0, 30.1, 31.8, 32.0, 33.6, 52.8, 96.2, 114.9, 122.2, 131.3, 131.6, 165.6, 167.7, 168.0, 173.2, 175.0, 176.0, 201.3.

11: colorless oil. HRMS (FAB) Calcd for C\textsubscript{36}H\textsubscript{49}O\textsubscript{8} (M\textsuperscript{+}+1) 609.3427. Found 609.3415. MS (FAB) m/z: 609 (M\textsuperscript{+}+1). IR (neat) \nu: 2930, 1717, 1655 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \delta: 1.38-1.48 (8H, m), 1.62-1.72 (8H, m), 2.00-2.12 (8H, m), 2.50-2.54 (4H, m), 2.79-2.85 (4H, m), 3.91 (6H, s), 4.91-5.04 (4H, m), 5.36-5.40 (2H, m), 5.74-5.84 (2H, m), 6.04 (1H, s), 6.05 (1H, s).

24-Methoxy-22-oxabicyclo[19.2.2]pentacosa-1(24),11,21(25)-triene-2,23-dione (10b)
Following the general procedure, a solution of 6b (30 mg, 0.07 mmol) was added to a solution of catalyst (7) (2.8 mg, 5 mol%) over 2 h. The solution was stirred for 12 h at rt and then heated under reflux for 6 h. Purification by PTLC (hexane-ethyl acetate, 5:1) provided unreacted 6b (2.0 mg, 7%) and 10b (17.4 mg, 62%) as colorless oil. 10b: HRMS (FAB) Calcd for C\textsubscript{25}H\textsubscript{39}O\textsubscript{4} (M\textsuperscript{+}+1) 403.2848. Found 403.2834. MS (FAB) m/z: 403 (M\textsuperscript{+}+1). IR (neat) \nu: 2922, 1736, 1665 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \delta: 1.23-1.35 (18H, m), 1.58-1.77 (6H, m), 1.94-2.00 (4H, m), 2.54-2.57 (2H, m), 2.81-2.84 (2H, m), 3.93 (3H, s), 5.35-5.37 (2H, m), 6.06 (1H, s). \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3}) \delta: 22.8, 26.8, 26.9, 27.8, 28.0, 28.2, 28.4, 28.9, 29.0, 29.1, 29.4, 29.5, 29.8, 31.0, 31.7, 31.8, 31.9, 32.0, 33.3, 52.9, 96.5, 100.0, 109.0, 114.0, 124.5, 131.0, 165.2, 168.2, 168.9, 176.0, 184.0, 207.0.

24-Methoxy-22-oxabicyclo[19.2.2]pentacosa-1(24),11,21(25)-triene-2,23-dione (10b) (10b)

Compound (10b) (120 mg, 0.3 mmol) was hydrogenated with 5% Pd-C (35 mg) under atmospheric pressure in ethanol (8.5 mL) at rt for 3 h. The catalyst was filtered off and the filtrate was evaporated. Purification of the residue by PTLC gave 13 (103 mg, 85%). HRMS (FAB) Calcd for C\textsubscript{25}H\textsubscript{41}O\textsubscript{4} (M\textsuperscript{+}+1) 405.3005. Found 405.2972. MS (FAB) m/z: 405 (M\textsuperscript{+}+1). IR (neat) \nu: 2922, 1692 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \delta: 1.22-1.31 (28H, m), 1.57 (1H, t, J = 7.5 Hz), 1.60 (1H, t, J = 6.9 Hz), 1.70-1.72 (2H, m), 2.53 (2H, t, J = 6.7 Hz), 2.78 (2H, t, J = 7.4 Hz), 3.91 (3H, s), 6.05 (1H, s). \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3})
\[ \delta : 24.6, 26.3, 28.0, 28.3, 28.4, 28.5, 28.6, 28.7, 28.8, 28.8, 28.9, 29.2, 34.5, 43.5, 57.2, 94.7, 105.3, 162.0, 169.5, 170.1, 201.1. \]

**24-Hydroxy-22-oxabicyclo[19.2.2]pentacosane-1(24),21(25)-diene-2,23-dione (14)**

Bromotrimethylsilane (46 mg, 0.3 mmol) was added to a solution of 13 (25 mg, 0.06 mmol) in dry dichloromethane (1.5 mL) under ice cooling. The mixture was stirred for 3 h at rt. Water was added to the reaction mixture and the whole was extracted with ether. The organic layer was washed with brine, dried over MgSO\(_4\), and concentrated. Purification of the residue by PTLC (hexane-ethyl acetate, 5 : 1) gave 14 (21 mg, 87\%) as a colorless oil. \(^1\)H-NMR (270 MHz, CDCl\(_3\)) \[ \delta : 1.21-1.35 (26H, m), 1.40 (2H, m), 1.69 (4H, m), 2.51 (2H, t, \( J = 6.4 \) Hz), 3.06 (2H, t, \( J = 7.2 \) Hz), 5.92 (1H, s), 16.96 (1H, s). \] This compound was identified by the comparison of the \(^1\)H-NMR spectrum with that of an authentic sample.\(^5\)

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