# Synthesis and solution structure of 3,5-dioxopimelic acid diesters—stable 1,3,5,7-tetracarbonyl derivatives

**Stefanie Reim,[a] Dirk Michalik,*[a,b] Klaus Weisz,[c] Zhou Xiao[c] and Peter Langer*[a,b]**

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A variety of 3,5-dioxopimelic acid diesters, stable 1,3,5,7-tetracarbonyl derivatives, were prepared by catalytic condensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with methyl malonyl chloride. The keto–enol tautomerization of these compounds has been investigated by NMR spectroscopy. One keto and up to four enolic tautomers could be detected in chloroform solution and the influence of the substituents on the tautomeric equilibria has been studied.

## Introduction

A great variety of pharmacologically important natural products are biosynthetically derived from poly(β-oxo)carboxylic acids (polyketides).[1] Polyketides and related 1,3-oligocarbonyl derivatives also represent important synthetic building blocks (*e.g.* for the synthesis of polyols by stereoselective reduction).[2] An attractive synthetic approach to these compounds relies on the reaction of 1,3-dicarbonyl dianions with carboxylic acid derivatives. For example, 3,5-dioxocarboxylic acid derivatives were prepared by condensation of β-ketoester dianions[3,4] with esters, nitriles,[5,6] *N*-acyl-2-methylaziridines,[7] and Weinreb amides.[8] Harris and coworkers reported the biomimetic synthesis of various 1,3,5,7-tetracarbonyl compounds and their higher homologues based on condensations of 1,3-dicarbonyl dianions or 1,3,5-tricarbonyl trianions with esters and diesters, Weinreb amides, and salts of β-ketoesters.[9] These products are unstable and rapidly undergo an intramolecular aldol-condensation to give polyhydroxylated arenes. 3,5-Dioxopimelic acid derivatives constitute an interesting class of 1,3,5,7-tetracarbonyl compounds that have only scarcely been studied so far. Robertson and Sandrock reported the synthesis of diethyl 2,2-diethyl-3,5-dioxopimelate by the reaction of ethyl 3-chloro-3-oxo-2,2-dimethylpropionate with diethyl acetone-1,3-dicarboxylate.[10] The parent (unsubstituted) 3,5-dioxopimelates have not yet been prepared by this approach. Recently, the first approach to the parent dimethyl 3,5-dioxopimelate was reported by Kiegel and coworkers: the reaction of acetone, malonyl dichloride and ketene afforded a bis(dioxinone) that was transformed into the desired product by methanolysis (44% yield over two steps).[11] 3,5-Dioxopimelates represent potentially useful synthetic intermediates (*e.g.* for enantio- and diastereoselective hydrogenations).[11]

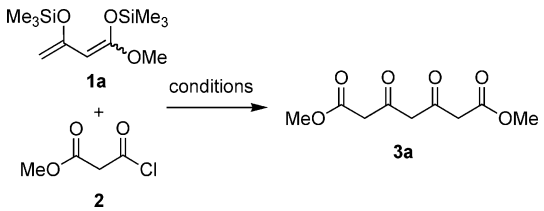
1,3-Bis(silyl enol ethers) can be regarded as electroneutral equivalents of 1,3-dicarbonyl dianions (masked dianions).[11–13] Their reaction with carboxylic acid derivatives has been studied. Chan and coworkers reported[14] the reaction of 1-methoxy-1,3-bis(trimethylsiloxy)-1,3-butadiene with acetyl chloride and with a protected β-ketoacid chloride.[15] Salicylates were prepared by the Lewis acid mediated [5 + 1] cyclization of 1-methoxy-1,3,5-tris(trimethylsiloxy)-1,3,5-hexatriene with acid chlorides and imidazolides.[16] We reported the reaction of 1,3-bis(silyl enol ethers) with various acid chlorides.[17] γ-Alkylidenebutenolides are available by the cyclization of 1,3-bis(silyl enol ethers) with oxalyl chloride[18,19] or phthaloyl chloride.[20] Recently, we reported the synthesis of 3,5-dioxopimelic acid diesters by the condensation of 1,3-bis(silyl enol ethers) with methyl malonyl chloride.[21] Herein, we report full details of these reactions, which proceed under mild conditions. With regard to our preliminary communication,[21] the synthetic protocol was significantly improved, and now provides the products in good to excellent yields. In addition, the preparative scope was considerably extended. To the best of our knowledge, the solution structure of 3,5-dioxopimelic acid diesters has not been studied in detail to date. Therefore, extensive NMR investigations of the tautomeric equilibria were carried out for the first time and the signals of all tautomers have been unambiguously assigned.

## Results and discussion

In our preliminary communication,[21] we reported that the reaction of 2.0 equiv. of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1a**) with 1.0 equiv. of methyl malonyl chloride (**2**), in the presence of 0.2 equiv. of $Me_3SiOTf$, afforded dimethyl 2,4-dioxopimelate (**3a**) in 40% yield (Table 1, entry 1). The product could be isolated in 68% yield when 0.4 equiv. of $Me_3SiOTf$ was employed (entry 2). However, the increase in the yield was outweighed by a lower degree of purity. The product was contaminated by a small amount of methyl malonic acid, which was formed by the hydrolysis of **2** and could not be separated. The yield of analytically pure product dropped to 30% (entry 3). Much to our satisfaction, analytically pure **3a** could be isolated in up to 86% yield when 3.0 equiv. of **1a** and 0.2 equiv. of $Me_3SiOTf$ were used (entry 4). The excellent yield, which proved to be reproducible, can be explained by the fact that methyl acetoacetate (formed by the hydrolysis of **1a**) can be readily separated (in contrast to hydrolyzed **2**). Interestingly, analytically pure product

[a]*Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany. E-mail: peter.langer@uni-rostock.de; Fax: 00 49 381 49864112; Tel: 0049 381 4986410*
[b]*Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany. E-mail: dirk.michalik@catalysis.de; Tel: 0049 381 4986353*
[c]*Institut für Biochemie, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Str. 4, 17487 Greifswald, Germany*

**Table 1** Optimization of the synthesis of dimethyl 2,4-dioxopimelate (**3a**)




*Reagents and conditions*: $Me_3SiOTf$, $CH_2Cl_2$, −78 → 20 °C.

| Entry | Stoichiometry: **1a**: **2** : $Me_3SiOTf$ | *n* (**2**)/mmol | *c* (**2**)/M | Yield (%) [a] |
|---|---|---|---|---|
| 1 | 2.0 : 1.0 : 0.2 | 10.0 | 0.10 | 40[b] |
| 2 | 2.0 : 1.0 : 0.4 | 6.6 | 0.07 | 68 [c] |
| 3 | 2.0 : 1.0 : 0.4 | 1.7 | 0.09 | 30 |
| 4 | 3.0 : 1.0 : 0.2 | 6.0 | 0.09 | 86 |
| 5 | 3.0 : 1.0 : 0 | 6.0 | 0.09 | 60 |
| 6 | 1.0 : 1.1 : 1.1 | 2.2 | 0.11 | 19 [c] |
| 7 | 1.0 : 1.1 : 0.4 | 3.3 | 0.11 | 0 [d] |
| 8 | 1.0 : 1.1 : 0.4 | 11.0 | 0.11 | 0 [d] |
| 9 | 1.0 : 2.0 : 0.8 | 4.0 | 0.20 | 0 [d] |

[a] Isolated yields of analytically pure **3a**. [b] See ref. 21. [c] Product contains a small amount of hydrolyzed **2**. [d] Product contains *ca.* 50% of hydrolyzed **2**.

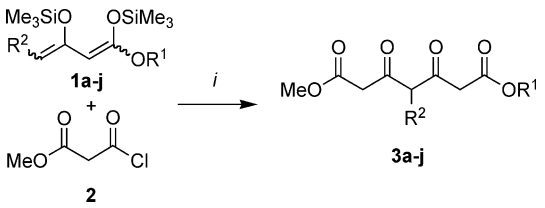
**3a** could still be isolated in 60% yield when the reaction was carried out under identical conditions, but in the *absence* of $Me_3SiOTf$ (entry 5). The reaction of **1a** (1.0 equiv.) with **2** (1.1 equiv.) and $Me_3SiOTf$ (1.1 equiv.) gave slightly impure **3a** in only 19% yield (entry 6). No product at all could be isolated when only 0.4 equiv. of $Me_3SiOTf$ (entries 7 and 8) or an excess of **2** (entry 9) were employed. This can be explained by the fact that the large amounts of hydrolyzed **2** produced could not be separated.

The reaction of **2** with 1,3-bis(silyl enol ethers) **1a–j**, following our optimized procedure (Table 1, entry 4), afforded the 3,5-dioxopimelates **3a–j** in 46–96% yield and in analytically pure form (Table 2). It is noteworthy that all products are stable and do not undergo a Dieckmann cyclization under the conditions of their formation. Products **3b** and **3i** were isolated in only 20 and 23% yield, respectively, when our original[21] protocol was applied. In contrast, products **3b** and **3i** were isolated in 84 and 77% yields, respectively, when our new protocol was employed.

Five reasonable tautomeric forms can be discussed for 3,5-dioxopimelates **3** (Scheme 1). This includes the keto and four enol forms (enol-I to enol-IV). The central 1,3-diketone moiety is enolized in the case of tautomer enol-I. The β-ketoester moiety is enolized in the case of tautomers enol-II and enol-III. These tautomers are identical for the *symmetrical* 3,5-dioxopimelates **3a–h**. Both β-ketoester moieties are enolized in the case of tautomer enol-IV.

In general, depending on the position of the proton in the intramolecular hydrogen bridge there are two enolic forms for each of tautomers enol-I, enol-II and enol-III and even four different forms of the doubly enolized enol-IV. Whereas the thermodynamic stability of the two forms should be similar for enol-I, the tautomers with an enolized keto function at C4 and/or C6 are expected to be the major contributors for enol-II, enol-III and enol-IV. The investigation of these tautomers by NMR spectroscopy is difficult due to a rapid dynamic equilibrium.[22] Even employing a low-melting freonic solvent,[23] $^1H$ NMR spectra

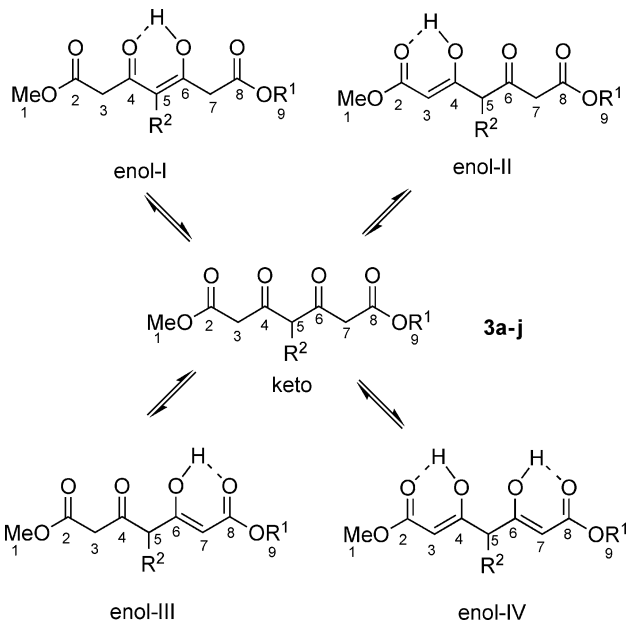
**Table 2** Synthesis of 1,3,5,7-tetracarbonyl compounds **3a–j**




*Reagents and conditions*: *i*: $Me_3SiOTf$ (0.2 equiv.), $CH_2Cl_2$, −78 → 20 °C

| **3** | $R^1$ | $R^2$ | Keto : enol-I : enol-II : enol-III : enol-IV [b] | Yield (%) [a] |
|---|---|---|---|---|
| **a** | Me | H | 25 : 70 : 4[c] : 1 | 86 |
| **b** | Me | Me | 42 : 35 : 22[c] : 1 | 84 |
| **c** | Me | Et | 49 : 16 : 33[c] : 2 | 54 |
| **d** | Me | *n*Bu | 48 : 18 : 31[c] : 2 | 63 |
| **e** | Me | *i*Bu | 52 : 15 : 31[c] : 2 | 90 |
| **f** | Me | $Cl(CH_2)_6$ | 52 : 16 : 30[c] : 2 | 62 |
| **g** | Me | Cl | 0 : 95 : 5[c] : 0 | 96 |
| **h** | Me | OMe | 30 : 58 : 11[c] : 1 | 49 |
| **i** | Et | H | 12 : 83 : 2 : 2 : 1 | 77 |
| **j** | Et | Et | 48 : 14 : 18 : 18 : 2 | 46 |

[a] Yields of isolated products. [b] Tautomeric ratio ($CDCl_3$, 300 K). [c] Enol-II and enol-III are identical.




**Scheme 1** Tautomeric forms of compounds **3**.

of **3b** acquired at temperatures as low as 173 K only exhibit a single set of signals for each of the formed tautomers, indicative of signal averaging due to a proton transfer that is still fast on the NMR chemical shift time-scale.

The results of our NMR measurements show that the populations of the keto and enol tautomers (chloroform solution) depend on the substituents located at carbon atom C-5 (for numbering, see Scheme 1). Tautomer enol-I is favoured in the case of the unsubstitued 3,5-dioxopimelates **3a** and **3i**, which is similar to the tautomerism in acetylacetone.[23] The presence of alkyl substituents and of a methoxy group at the 5-position increases the amount of the keto form at the expense of enol-I,

which can be explained by the electron donating effect of these substituents. On the other hand, the highest population of enol-I (95%) was found for the chloro-substituted 3,5-dioxopimelate **3g**, which is caused by the electron withdrawing effect of the chlorine atom. The fraction of enol-II (and enol-III for the unsymmetrical derivative **3j**) is increased as well in the case of alkyl-substituted 3,5-dioxopimelates. The amount of tautomer enol-IV, which was generally detected only in minor quantities (<2%), seems not to depend on the substituents.

The assignments of the signals of the tautomeric forms of 3,5-dioxopimelates **3a–j** were based on the intensities, chemical shifts and couplings, as well as proton–carbon chemical shift correlations (HSQC, HETCOR and HMBC spectra). Not all signals could be extracted, due to signal overlapping or intensities that were too low. However, some typical characteristics can be stated: the OH signal of tautomer enol-I generally appears at much lower fields than the OH signals of the other enol forms (Fig. 1). This can be explained by the fact that two keto groups are included in the chelate ring of enol-I, whereas in the case of the other enol tautomers one ester group is included, which possesses less of a proton acceptor effect.

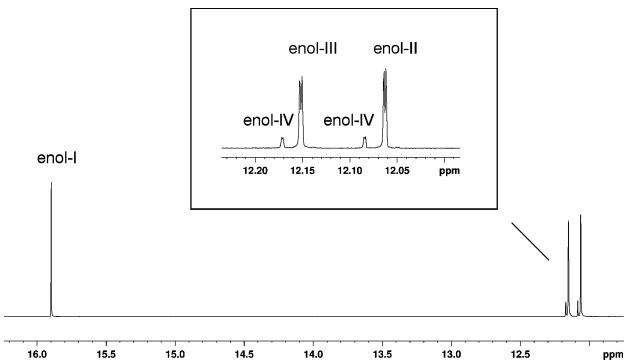



**Fig. 1** $^{1}$H NMR spectrum (500 MHz) of **3j** (region of enolic OH) in $CDCl_3$ at 300 K.

In the case of the unsymmetrical 3,5-dioxopimelates **3i** and **3j**, tautomers enol-II and enol-III are not identical anymore and separate OH signals are thus detected. Two different OH signals are also observed for enol-IV. For some of the unsubstituted 3,5-dioxopimelates **3**, doublets were observed for the OH signals of enol-II, enol-III, and enol-IV, due to coupling with the proton H-5 over four bonds ($^{4}J_{OH,CH} \leq 1$ Hz). Furthermore, in the HMBC spectra typical cross peaks could be observed for the OH protons with carbon atoms C-3, C-4, and C-5. The keto–enol tautomers can also be well recognized by the characteristic signals in the C=O and C–OH regions of the $^{13}$C NMR spectra, as given for **3j** in Fig. 2.

## Conclusions

In conclusion, a variety of 3,5-dioxopimelates were prepared in good to very good yields by a new and efficient catalytic condensation of 1,3-bis(silyl enol ethers) with methyl malonyl chloride. The reactions are convenient to carry out and the products are not readily available by other methods. The 3,5-dioxopimelates exist as mixtures of keto and various enol tautomers, which were analyzed in detail by modern NMR techniques. The population

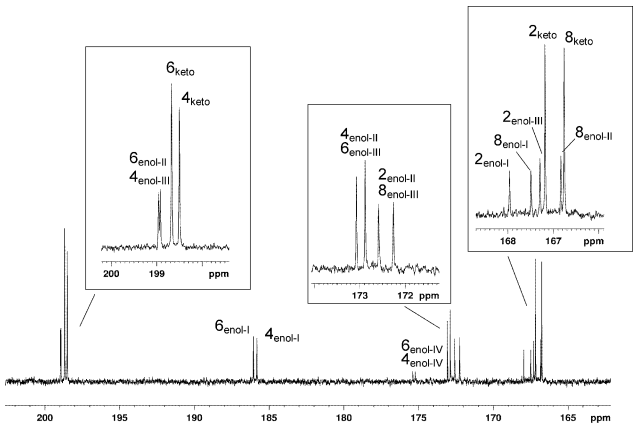



**Fig. 2** $^{13}$C NMR spectrum (125.8 MHz) of **3j** (region of C=O and C–OH) in $CDCl_3$ at 300 K.

of the keto and enol tautomers is dependent upon the substituents located at carbon atom C-5 (numbering according to Scheme 1) of the 1,3,5,7-tetracarbonyl compounds.

## Experimental section

$^{1}$H NMR spectra (300.13 and 500.13 MHz, respectively) and $^{13}$C NMR spectra (75.5 and 125.8 MHz, respectively) were recorded on Bruker spectrometers AVANCE 300 and AVANCE 500. The chemical shifts were referenced to solvent signals ($CDCl_3$: $\delta$ $^{1}$H = 7.25, $\delta$ $^{13}$C = 77.0). The NMR signals were assigned by DEPT and two-dimensional $^{1}$H,$^{1}$H COSY and $^{1}$H,$^{13}$C correlation spectra (HSQC, HETCOR, HMBC) using standard pulse sequences (standard Bruker software). Not all signals are listed. The assignments follow the atom numbering given in Scheme 1.

**Typical procedure for the synthesis of 3,5-dioxopimelates (3a–j).** To a $CH_2Cl_2$ solution (70 mL) of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (4.689 g, 18.0 mmol) were added **2** (0.819 g, 6.0 mmol, 0.64 mL) and TMSOTf (0.267 g, 1.2 mmol, 0.22 mL) at −78 °C under an argon atmosphere. The solution was allowed to warm to 20 °C over 6 h and was stirred at this temperature for 12 h. To the solution was added a saturated aqueous solution of $NH_4Cl$ (30 mL), the organic and the aqueous layer were separated and the latter was extracted with diethyl ether (3 × 30 mL). The combined organic layers were extracted with a saturated aqueous solution of NaCl, dried ($Na_2SO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (silica gel, *n*-heptane–EtOAc = 3 : 1) to give **3a** as a yellow oil (1.120 g, 86%).

**3,5-Dioxopimelic acid dimethyl ester (3a).** $^{1}$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 25 : 70 : 4 : 1): **keto**: $\delta$ = 3.88 (s, 2H, H-5); 3.73 (s, 6H, H-1,9); 3.56 (s, 4H, H-3,7); **enol-I**: $\delta$ = 14.77 (s, 1H, OH); 5.73 (s, 1H, H-5); 3.74 (s, 6H, H-1,9); 3.36 (s, 4H, H-3,7); **enol-II**: $\delta$ = 12.03 (s, 1H, OH); 5.12 (s, 1H, H-3); 3.74 (s, 3H, H-1); 3.71 (s, 3H, H-9); 3.57 (s, 2H, H-7); **enol-IV**: $\delta$ = 12.01 (s, OH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 196.3 (C-4,6); 167.2 (C-2,8); 56.2 (C-5); 52.5 (C-1,9); 49.0 (C-3,7); **enol-I**: $\delta$ = 185.8 (C-4,6); 167.6 (C-2,8); 101.0 (C-5); 52.5 (C-1,9); 44.3 (C-3,7); **enol-II**: $\delta$ = 196.5 (C-6); 167.1 (C-8); 92.6 (C-3); 52.5 (C-9); 51.5 (C-1), 48.4 (C-7). IR (neat, cm$^{-1}$): $\nu$ = 3004 (w), 2957 (m), 2849 (w), 1743 (br, s), 1630 (s), 1605 (s), 1438 (s), 1409 (m), 1332 (s),

1264 (br, s), 1158 (s), 1016 (m). MS (EI, 70 eV): $m/z$ (%) = 216 ($M^+$, 3), 184 (37), 152 (37), 143 (91), 116 (25), 101 (100). Anal. calcd for $C_9H_{12}O_6$ (216.19): C, 50.00; H, 5.59. Found: C, 50.07; H, 5.65.

**4-Methyl-3,5-dioxopimelic acid dimethyl ester (3b).** Starting with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-pentadiene (2.471 g, 9.0 mmol), **2** (0.410 g, 3.0 mmol, 0.32 mL) and TMSOTf (0.133 g, 0.6 mmol, 0.11 mL) in $CH_2Cl_2$ (36 mL), **3b** was isolated as a yellow oil (0.578 g, 84%). $^1$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 42 : 35 : 22 : 1): **keto**: $\delta$ = 4.04 (q, $^3J$ = 7.3 Hz, 1H, H-5); 3.72 (s, 6H, H-1,9); 3.57, 3.54 ($q_{AB}$, $^2J$ = 16.0 Hz, 4H, H-3,7); 1.35 (d, $^3J$ = 7.3 Hz, 3H, Me); **enol-I**: $\delta$ = 15.67 (s, 1H, OH); 3.73 (s, 6H, H-1,9); 3.48 (s, 4H, H-3,7); 1.83 (s, 3H, Me); **enol-II**: $\delta$ = 12.07 (d, $^4J$ = 0.6 Hz, 1H, OH); 5.12 (s, 1H, H-3); 3.74 (s, 3H, H-1); 3.71 (s, 3H, H-9); 3.62, 3.54 ($q_{AB}$, $^2J$ = 16.0 Hz, 2H, H-7); 3.45 (q, $^3J$ = 7.3 Hz, 1H, H-5); 1.31 (d, $^3J$ = 7.3 Hz, 3H, Me); **enol-IV**: $\delta$ = 12.05 (d, $^4J$ = 0.6 Hz, 2H, OH); 5.13 (br s, 2H, H-3,7); 3.10 (q, $^3J$ = 7.2 Hz, 1H, H-5). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 199.3 (C-4,6); 167.3 (C-2,8); 59.6 (C-5); 52.4 (C-1,9); 47.3 (C-3,7); 12.3 (Me); **enol-I**: $\delta$ = 185.4 (C-4,6); 167.8 (C-2,8); 106.2 (C-5); 52.5 (C-1,9); 42.7 (C-3,7); 13.2 (Me); **enol-II**: $\delta$ = 199.2 (C-6); 174.3 (C-4); 172.6 (C-2); 167.3 (C-8); 90.8 (C-3); 52.3 (C-5); 52.3 (C-9); 51.5 (C-1); 47.3 (C-7); 12.4 (Me); **enol-IV**: $\delta$ = 176.2 (C-4,6); 172.9 (C-2,8); 89.6 (C-3,7); 51.3 (C-1,9). IR (neat, cm$^{-1}$): $\nu$ = 2994 (br, w), 2957 (m), 2849 (w), 1746 (br, s), 1627 (m), 1438 (s), 1405 (m), 1329 (s), 1258 (br, s), 1162 (s), 1043 (m), 1006 (m). MS (EI, 70 eV): $m/z$ (%) = 230 ($M^+$, 1), 198 (21), 167 (22), 166 (32), 157 (23), 130 (99), 115 (31), 101 (100). HRMS (EI): calcd for $C_{10}H_{14}O_6$ ($M^+$) 230.07849, found 230.078470. Anal. calcd for $C_{10}H_{14}O_6$ (230.21): C, 52.17; H, 6.13. Found: C, 52.16; H, 6.14.

**4-Ethyl-3,5-dioxopimelic acid dimethyl ester (3c).** Starting with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-hexadiene (2.597 g, 9.0 mmol), **2** (0.410 g, 3.0 mmol, 0.32 mL) and TMSOTf (0.133 g, 0.6 mmol, 0.11 mL) in $CH_2Cl_2$ (36 mL), **3c** was isolated as a yellow oil (0.395 g, 54%). $^1$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 49 : 16 : 33 : 2): **keto**: $\delta$ = 3.89 (t, $^3J$ = 7.0 Hz, 1H, H-5); 3.71 (s, 6H, H-1,9); 3.54, 3.51 ($q_{AB}$, $^2J$ = 16.4 Hz, 4H, H-3,7); 1.89 ('quint.', $^3J$ = 7.5 Hz, $^3J$ = 7.0 Hz, 2H, $CH_2CH_3$); 0.91 (t, $^3J$ = 7.5 Hz, 3H, $CH_2CH_3$); **enol-I**: $\delta$ = 15.88 (s, 1H, OH); 3.73 (s, 6H, H-1,9); 3.48 (s, 4H, H-3,7); 2.24 (q, $^3J$ = 7.5 Hz, 2H, $CH_2CH_3$); 1.04 (t, $^3J$ = 7.5 Hz, 3H, $CH_2CH_3$); **enol-II**: $\delta$ = 12.06 (d, $^4J$ = 0.8 Hz, 1H, OH); 5.11 (s, 1H, H-3); 3.72 (s, 3H, H-1); 3.70 (s, 3H, H-9); 3.59, 3.51 ($q_{AB}$, $^2J$ = 16.0 Hz, 2H, H-7); 3.21 (br t, 1H, H-5); 1.95–1.70 (m, 2H, $CH_2CH_3$); 0.90 (t, $^3J$ = 7.5 Hz, 3H, $CH_2CH_3$); **enol-IV**: $\delta$ = 12.08 (s, 2H, OH); 5.14 (s, 2H, H-3,7). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 198.5 (C-4,6); 167.1 (C-2,8); 67.6 (C-5); 52.4 (C-1,9); 47.7 (C-3,7); 21.6 ($CH_2CH_3$); 11.8 ($CH_2CH_3$); **enol-I**: $\delta$ = 185.8 (C-4,6); 167.9 (C-2,8); 112.8 (C-5); 52.5 (C-1,9); 41.9 (C-3,7); 20.1 ($CH_2CH_3$); 14.9 ($CH_2CH_3$); **enol-II**: $\delta$ = 198.8 (C-6); 173.0 (C-4); 172.5 (C-2); 167.2 (C-8); 91.8 (C-3); 60.1 (C-5); 52.3 (C-9); 51.4 (C-1); 47.4 (C-7); 21.4 ($CH_2CH_3$); 11.5 ($CH_2CH_3$); **enol-IV**: $\delta$ = 175.3 (C-4,6); 172.8 (C-2,8); 90.4 (C-3,7); 51.3 (C-1,9); 22.6 ($CH_2CH_3$). IR (neat, cm$^{-1}$): $\nu$ = 2958 (m), 2881 (w), 1748 (br, s), 1654 (m), 1626 (m), 1438 (s), 1404 (m), 1325 (s), 1249 (br, s), 1160 (s), 1081 (w), 1057 (w), 1011 (m). MS (CI, isobutane): $m/z$ (%) = 245 ([M + 1]$^+$, 100). Anal. calcd for $C_{11}H_{16}O_6$ (244.24): C, 54.09; H, 6.60. Found: C, 53.98; H, 6.63.

**4-Butyl-3,5-dioxopimelic acid dimethyl ester (3d).** Starting with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-octadiene (0.760 g, 2.4 mmol), **2** (0.109 g, 0.8 mmol, 0.09 mL) and TMSOTf (0.036 g, 0.16 mmol, 0.03 mL) in $CH_2Cl_2$ (10 mL), **3d** was isolated as a yellow oil (0.137 g, 63%). $^1$H NMR (300 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 48 : 18 : 31 : 2): **keto**: $\delta$ = 3.95 (t, $^3J$ = 7.0 Hz, 1H, H-5); 3.72 (s, 6H, H-1,9); 3.56, 3.52 ($q_{AB}$, $^2J$ = 16.0 Hz, 4H, H-3,7); 1.90–1.70 (m), 1.40–1.20 (m) ($CH_{2\,(keto,enol)}$); 0.95–0.85 (m, $CH_{3\,(keto,enol)}$); **enol-I**: $\delta$ = 15.93 (s, 1H, OH); 3.74 (s, 6H, H-1,9); 3.49 (s, 4H, H-3,7); 2.22–2.14 (m, 2H, $CH_2$); 1.40–1.20 (m) ($CH_{2\,(keto,enol)}$); 0.95–0.85 (m, $CH_{3\,(keto,enol)}$); **enol-II**: $\delta$ = 12.08 (s, 1H, OH); 5.12 (s, 1H, H-3); 3.74 (s, 3H, H-1); 3.71 (s, 3H, H-9); 3.61, 3.53 ($q_{AB}$, $^2J$ = 16.0 Hz, 2H, H-7); 3.29 (dd, $^3J$ = 8.2 Hz, $^3J$ = 6.5 Hz, 1H, H-5); 1.90–1.70 (m), 1.40–1.20 (m) ($CH_{2\,(keto,enol)}$); 0.95–0.85 (m, $CH_{3\,(keto,enol)}$); **enol-IV**: $\delta$ = 12.08 (s, 2H, OH); 5.16 (s, 2H, H-3,7). $^{13}$C NMR (75.5 MHz, $CDCl_3$): **keto**: $\delta$ = 198.5 (C-4,6); 167.2 (C-2,8); 66.3 (C-5); 52.4 (C-1,9); 47.7 (C-3,7); 29.5, 28.0, 22.4 ($CH_2$); 13.6 ($CH_3$); **enol-I**: $\delta$ = 185.9 (C-4,6); 167.9 (C-2,8); 111.6 (C-5); 52.5 (C-1,9); 42.0 (C-3,7); 32.9, 26.7, 22.6 ($CH_2$); 13.7 ($CH_3$); **enol-II**: $\delta$ = 198.9 (C-6); 173.2 (C-4); 172.6 (C-2); 167.3 (C-8); 91.7 (C-3); 58.6 (C-5); 52.3 (C-9); 51.5 (C-1); 47.4 (C-7); 29.1, 27.8, 22.4 ($CH_2$); 13.7 ($CH_2CH_3$); **enol-IV**: $\delta$ = 90.3 (C-3,7); 51.3 (C-1,9). IR (neat, cm$^{-1}$): $\nu$ = 2958 (s), 2935 (m), 2874 (w), 1749 (br, s), 1656 (m), 1626 (m), 1438 (s), 1404 (m), 1325 (s), 1244 (br, s), 1158 (s), 1094 (w), 1016 (m). MS (EI, 70 eV): $m/z$ (%) = 272 ($M^+$, 1), 184 (31), 165 (30), 143 (25), 129 (100), 116 (65), 101 (72). Anal. calcd for $C_{13}H_{20}O_6$ (272.29): C, 57.34; H, 7.40. Found: C, 57.40; H, 7.48.

**4-Isobutyl-3,5-dioxopimelic acid dimethyl ester (3e).** Starting with 1-methoxy-6-methyl-1,3-bis(trimethylsilyloxy)-1,3-heptadiene (0.950 g, 3.0 mmol), **2** (0.137 g, 1.0 mmol, 0.11 mL) and TMSOTf (0.044 g, 0.2 mmol, 0.04 mL) in $CH_2Cl_2$ (12 mL), **3e** was isolated as a yellow oil (0.245 g, 90%). $^1$H NMR (300 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 52 : 15 : 31 : 2): **keto**: $\delta$ = 4.06 (t, $^3J$ = 7.0 Hz, 1H, H-5); 3.72 (s, 6H, H-1,9); 3.56, 3.52 ($q_{AB}$, $^2J$ = 16.0 Hz, 4H, H-3,7); 1.75–1.45 (m, $CH_2CH(CH_3)_{2\,(keto,enol)}$, $CH(CH_3)_{2\,(keto,enol)}$); 0.98–0.80 (m, $CH_{3\,(keto,enol)}$); **enol-I**: $\delta$ = 16.15 (s, 1H, OH); 3.74 (s, 6H, H-1,9); 3.51 (s, 4H, H-3,7); 2.10 (d, $^3J$ = 7.4 Hz, 2H, $CH_2CH(CH_3)_2$); 1.75–1.45 (m, $CH_2CH(CH_3)_{2\,(keto,enol)}$, $CH(CH_3)_{2\,(keto,enol)}$); 0.98–0.80 (m, $CH_{3\,(keto,enol)}$); **enol-II**: $\delta$ = 12.10 (d, $^4J$ = 1.0 Hz, 1H, OH); 5.13 (s, 1H, H-3); 3.74 (s, 3H, H-1); 3.71 (s, 3H, H-9); 3.62, 3.53 ($q_{AB}$, $^2J$ = 16.0 Hz, 2H, H-7); 3.41 (m, 1H, H-5); 1.75–1.45 (m, $CH_2CH(CH_3)_{2\,(keto,enol)}$, $CH(CH_3)_{2\,(keto,enol)}$); 0.98–0.80 (m, $CH_{3\,(keto,enol)}$); **enol-IV**: $\delta$ = 12.11 (d, $^4J$ = 1.0 Hz, 2H, OH); 5.16 (s, 2H, H-3,7). $^{13}$C NMR (75.5 MHz, $CDCl_3$): **keto**: $\delta$ = 198.4 (C-4,6); 167.1 (C-2,8); 64.7 (C-5); 52.4 (C-1,9); 47.6 (C-3,7); 36.8, 35.5 ($CH_2CH(CH_3)_{2\,(keto,enol)}$); 26.3 ($CH(CH_3)_2$); 22.7, 22.2, 22.0, 21.9 ($CH_{3\,(keto,enol)}$); **enol-I**: $\delta$ = 186.5 (C-4,6); 167.9 (C-2,8); 110.5 (C-5); 52.4 (C-1,9); 42.2 (C-3,7); 36.8, 35.5 ($CH_2CH(CH_3)_{2\,(keto,enol)}$); 29.9 ($CH(CH_3)_2$); 22.7, 22.2, 22.0, 21.9 ($CH_{3\,(keto,enol)}$); **enol-II**: $\delta$ = 198.9 (C-6); 173.3 (C-4); 172.5 (C-2); 167.2 (C-8); 91.7 (C-3); 56.6 (C-5); 52.3 (C-9); 51.5 (C-1); 47.3 (C-7); 36.8, 35.5 ($CH_2CH(CH_3)_{2\,(keto,enol)}$); 25.5 ($CH(CH_3)_2$); 22.7, 22.2, 22.0, 21.9 ($CH_{3\,(keto,enol)}$); **enol-IV**: $\delta$ = 90.2 (C-3,7); 51.3 (C-1,9). IR (neat, cm$^{-1}$): $\nu$ = 2957 (s), 2872 (w), 1751 (s), 1718 (s), 1653 (w), 1629 (w), 1560 (w), 1438 (m), 1409 (w), 1368 (w), 1319 (m), 1243 (m), 1158 (m), 1093 (w), 1073 (w), 1012 (w). MS

(CI, isobutane): $m/z$ (%) = 273 ([M + 1]$^+$, 100). Anal. calcd for $C_{13}H_{20}O_6$ (272.29): C, 57.34; H, 7.40. Found: C, 57.46; H, 7.44.

**4-(6-Chlorohexyl)-3,5-dioxopimelic acid dimethyl ester (3f).** Starting with 10-chloro-1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-decadiene (0.910 g, 2.4 mmol), **2** (0.109 g, 0.8 mmol, 0.09 mL) and TMSOTf (0.036 g, 0.16 mmol, 0.03 mL) in $CH_2Cl_2$ (10 mL), **3f** was isolated as a yellow oil (0.165 g, 62%). $^1$H NMR (300 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 52 : 16 : 30 : 2): **keto**: $\delta$ = 3.97 (t, $^3J$ = 6.9 Hz, 1H, H-5); 3.72 (s, 6H, H-1,9); 3.65–3.43 (m, H-3,7$_{(keto)}$, H-3,7$_{(enol-I)}$, H-7$_{(enol-II)}$); 1.88–1.68 (m), 1.45–1.25 (m) ((CH$_2$)$_6$Cl$_{(keto,enol)}$); **enol-I**: $\delta$ = 16.00 (s, 1H, OH); 3.74 (s, 6H, H-1,9); 3.65–3.43 (m, H-3,7$_{(keto)}$, H-3,7$_{(enol-I)}$, H-7$_{(enol-II)}$); 2.20 (m, 2H, C$H_2$(CH$_2$)$_5$Cl); 1.88–1.68 (m), 1.45–1.25 (m) ((CH$_2$)$_6$Cl$_{(keto,enol)}$); **enol-II**: $\delta$ = 12.09 (s, 1H, OH); 5.12 (s, 1H, H-3); 3.74 (s, 3H, H-1); 3.71 (s, 3H, H-9); 3.65–3.43 (m, H-3,7$_{(keto)}$, H-3,7$_{(enol-I)}$, H-7$_{(enol-II)}$); 3.30 (dd, $^3J$ = 8.0 Hz, $^3J$ = 6.5 Hz, 1H, H-5); 1.88–1.68 (m), 1.45–1.25 (m) ((CH$_2$)$_6$Cl$_{(keto,enol)}$); **enol-IV**: $\delta$ = 12.10 (s, 2H, OH); 5.15 (s, 2H, H-3,7). $^{13}$C NMR (75.5 MHz, $CDCl_3$): **keto**: $\delta$ = 198.4 (C-4,6); 167.2 (C-2,8); 66.2 (C-5); 52.5 (C-1,9); 47.7 (C-3,7); 45.0, 44.9 (CH$_2$Cl$_{(keto,enol)}$); 32.4, 32.3, 30.6, 28.8, 28.6, 28.0, 27.9, 27.2, 27.0, 26.8, 26.5, 26.4 ((*C*H$_2$)$_5$CH$_2$Cl$_{(keto,enol)}$); **enol-I**: $\delta$ = 186.0 (C-4,6); 167.9 (C-2,8); 111.5 (C-5); 52.5 (C-1,9); 45.9, 44.9 (CH$_2$Cl$_{(keto,enol)}$); 42.1 (C-3,7); 32.4, 32.3, 30.6, 28.8, 28.6, 28.0, 27.9, 27.2, 27.0, 26.8, 26.5, 26.4 ((*C*H$_2$)$_5$CH$_2$Cl$_{(keto,enol)}$); **enol-II**: $\delta$ = 198.8 (C-6); 173.0 (C-4); 172.6 (C-2); 167.3 (C-8); 91.8 (C-3); 58.5 (C-5); 52.4 (C-9); 51.5 (C-1); 47.4 (C-7); 45.0, 44.9 (CH$_2$Cl$_{(keto,enol)}$); 32.4, 32.3, 30.6, 28.8, 28.6, 28.0, 27.9, 27.2, 27.0, 26.8, 26.5, 26.4 ((*C*H$_2$)$_5$CH$_2$Cl$_{(keto,enol)}$); **enol-IV**: $\delta$ = 90.3 (C-3,7); 51.3 (C-1,9). IR (neat, cm$^{-1}$): $\nu$ = 2999 (w), 2953 (m), 2937 (m), 2860 (w), 1749 (br, s), 1653 (m), 1625 (m), 1437 (s), 1404 (m), 1324 (s), 1243 (br, s), 1159 (m), 1064 (w), 1016 (m). MS (CI, isobutane): $m/z$ (%) = 337 ([M + 1]$^+$, $^{37}$Cl, 37), 335 ([M + 1]$^+$, $^{35}$Cl, 100). Anal. calcd for $C_{15}H_{23}O_6Cl$ (334.79): C, 53.81; H, 6.92. Found: C, 53.95; H, 7.06.

**4-Chloro-3,5-dioxopimelic acid dimethyl ester (3g).** Starting with 4-chloro-1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (0.885 g, 3.0 mmol)), **2** (0.137 g, 1.0 mmol, 0.11 mL) and TMSOTf (0.044 g, 0.2 mmol, 0.04 mL) in $CH_2Cl_2$ (12 mL), **3g** was isolated as a yellow oil (0.240 g, 96%). $^1$H NMR (500 MHz, $CDCl_3$, enol-I : enol-II = 95 : 5): **enol-I**: $\delta$ = 14.65 (s, 1H, OH); 3.74 (s, 6H, H-1,9); 3.66 (s, 4H, H-3,7); **enol-II**: $\delta$ = 12.06 (s, 1H, OH); 5.45 (s, 1H, H-3); 5.34 (s, 1H, H-5); 3.74 (s, 2H, H-7). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **enol-I**: $\delta$ = 183.6 (C-4,6); 166.9 (C-2,8); 108.7 (C-5); 52.6 (C-1,9); 42.7 (C-3,7); **enol-II**: $\delta$ = 192.3 (C-6); 166.7 (C-8); 93.3 (C-3); 67.0 (C-5); 51.9 (C-1); 45.6 (C-7). IR (neat, cm$^{-1}$): $\nu$ = 3458 (br, w), 3000 (w), 2957 (m), 2850 (w), 1745 (br, s), 1621 (m), 1438 (s), 1405 (m), 1328 (s), 1259 (br, s), 1208 (s), 1173 (s), 1152 (s), 1016 (m). MS (EI, 70 eV): $m/z$ (%) = 252 (M$^+$, $^{37}$Cl, 1), 250 (M$^+$, $^{35}$Cl, 3), 186 (67), 177 (30), 158 (32), 150 (37), 101 (100). HRMS (EI): calcd for $C_9H_{11}O_6Cl$ (M$^+$, $^{35}$Cl): 250.02387, found 250.023346.

**4-Methoxy-3,5-dioxopimelic acid dimethyl ester (3h).** Starting with 1,4-dimethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (0.401 g, 1.38 mmol), **2** (0.063 g, 0.46 mmol, 0.05 mL) and TMSOTf (0.020 g, 0.09 mmol, 0.02 mL) in $CH_2Cl_2$ (6 mL), **3h** was isolated as a yellow oil (0.056 g, 49%). $^1$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-IV = 30 : 58 : 11 : 1): **keto**: $\delta$ = 4.60 (s, 1H, H-5); 3.72 (s, 6H, H-1,9); 3.64, 3.60 ($q_{AB}$, $^2J$ = 16.4 Hz, 4H, H-3,7); 3.48 (s, 3H, OMe); **enol-I**: $\delta$ = 13.40 (s, 1H, OH); 3.74 (s, 6H, H-1,9); 3.60 (s, 3H, OMe); 3.55 (s, 4H, H-3,7); **enol-II**: $\delta$ = 11.90 (s, 1H, OH); 5.37 (s, 1H, H-3); 4.25 (s, 1H, H-5); 3.75 (s, 3H, H-1); 3.72 (s, 3H, H-9); 3.43 (s, 2H, H-7); **enol-IV**: $\delta$ = 11.60 (s, OH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 197.2 (C-4,6); 167.1 (C-2,8); 92.0 (C-5); 59.2 (OMe); 52.4 (C-1,9); 45.3 (C-3,7); **enol-I**: $\delta$ = 181.0 (C-4,6); 167.8 (C-2,8); 136.8 (C-5); 62.7 (OMe); 52.5 (C-1,9); 39.9 (C-3,7); **enol-II**: $\delta$ = 198.1 (C-6); 167.2 (C-8); 96.7 (C-3); 86.0 (C-5); 58.3 (OMe); 52.4 (C-9); 51.6 (C-1). IR (neat, cm$^{-1}$): $\nu$ = 3447 (br, w), 3007 (w), 2958 (m), 2849 (w), 1732 (br, s), 1664 (m), 1640 (m), 1440 (s), 1401 (m), 1329 (s), 1268 (br, s), 1218 (s), 1178 (s), 1108 (s), 1019 (m).

**3,5-Dioxopimelic acid ethyl ester methyl ester (3i).** Starting with 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (3.294 g, 12.0 mmol), **2** (0.546 g, 4.0 mmol, 0.43 mL) and TMSOTf (0.178 g, 0.8 mmol, 0.14 mL) in $CH_2Cl_2$ (48 mL), **3i** was isolated as a yellow oil (0.709 g, 77%). $^1$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-III : enol-IV = 12 : 83 : 2 : 2 : 1): **keto**: $\delta$ = 4.15 (q, $^3J$ = 7.3 Hz, 2H, OCH$_2$); 3.86 (s, 2H, H-5); 3.70 (s, 3H, H-1); 3.54 (s, 2H), 3.52 (s, 2H) (H-3,7); 1.24 (t, $^3J$ = 7.3 Hz, CH$_2$C$H_3$); **enol-I**: $\delta$ = 14.75 (s, 1H, OH); 5.71 (s, 1H, H-5); 4.16 (q, $^3J$ = 7.3 Hz, 2H, OCH$_2$); 3.71 (s, 3H, H-1); 3.33 (s, 2H), 3.32 (s, 2H) (H-3,7); 1.24 (t, $^3J$ = 7.3 Hz, 3H, CH$_2$C$H_3$); **enol-II**, **enol-III**: $\delta$ = 12.10 (s, 1H, OH$_{(enol-II)}$); 12.00 (s, 1H, OH$_{(enol-III)}$); 5.09 (s, 2H), 5.08 (s, 2H) (H-3$_{(enol-II)}$, H-7$_{(enol-III)}$); 3.71 (s, H-1$_{(enol-II,enol-III)}$); 3.55 (s, 2H), 3.53 (s, 2H) (H-7$_{(enol-II)}$, H-3$_{(enol-III)}$); 1.25 (t, $^3J$ = 7.3 Hz, CH$_2$C$H_{3(enol-II)}$); 1.24 (t, $^3J$ = 7.3 Hz, CH$_2$C$H_{3(enol-III)}$); **enol-IV**: $\delta$ = 12.08 (s, 1H, OH); 11.99 (s, 1H, OH); 5.12 (s, 1H), 5.08 (s, 1H) (H-3,7). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 196.4 (C-6); 196.3 (C-4); 167.2 (C-2); 166.8 (C-8); 61.6 (OCH$_2$); 56.1 (C-5); 52.4 (C-1); 49.3 (C-7); 49.0 (C-3); 13.99 (CH$_2$*C*H$_3$); **enol-I**: $\delta$ = 186.0 (C-6); 185.8 (C-4); 167.6 (C-2); 167.1 (C-8); 100.9 (C-5); 61.5 (OCH$_2$); 52.5 (C-1); 44.5 (C-7); 44.3 (C-3); 14.01 (CH$_2$*C*H$_3$); **enol-II**, **enol-III**: $\delta$ = 196.7, 196.6 (C-6$_{(enol-II)}$, C-4$_{(enol-III)}$); 172.4, 172.1 (C-4$_{(enol-II)}$, C-6$_{(enol-III)}$); 169.3, 169.1 (C-2$_{(enol-II)}$, C-8$_{(enol-III)}$); 167.1, 166.6 (C-8$_{(enol-II)}$, C-2$_{(enol-III)}$); 92.8, 92.5 (C-3$_{(enol-II)}$, C-7$_{(enol-III)}$); 48.7, 48.4 (C-7$_{(enol-II)}$, C-3$_{(enol-III)}$); **enol-IV**: $\delta$ = 91.5, 91.3 (C-3,7). IR (neat, cm$^{-1}$): $\nu$ = 2985 (m), 2958 (m), 1740 (br, s), 1635 (s), 1616 (s), 1438 (s), 1369 (m), 1328 (s), 1261 (br, s), 1158 (s), 1030 (s). MS (EI, 70 eV): $m/z$ (%) = 230 (M$^+$, 4), 184 (28), 157 (57), 152 (60), 143 (87), 115 (60), 111 (35), 101 (100). Anal. calcd for $C_{10}H_{14}O_6$ (230.21): C, 52.17; H, 6.13. Found: C, 51.89; H, 6.18.

**4-Ethyl-3,5-dioxopimelic acid ethyl ester methyl ester (3j).** Starting with 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-hexadiene (2.723 g, 9.0 mmol), **2** (0.410 g, 3.0 mmol, 0.32 mL) and TMSOTf (0.133 g, 0.6 mmol, 0.11 mL) in $CH_2Cl_2$ (36 mL), **3j** was isolated as a yellow oil (0.356 g, 46%). $^1$H NMR (500 MHz, $CDCl_3$, keto : enol-I : enol-II : enol-III : enol-IV = 48 : 14 : 18 : 18 : 2): **keto**: $\delta$ = 4.22–4.14 (m, OCH$_{2\,(keto,enol)}$); 3.90 (t, $^3J$ = 7.0 Hz, 1H, H-5); 3.71 (s, 3H, H-1); 3.63–3.50 (m, H-3,7$_{(keto)}$, H-7$_{(enol-II)}$, H-3$_{(enol-III)}$); 1.89 ('quint', 2H, CHC$H_2$CH$_3$); 1.30–1.23 (4t, $^3J$ = 7.0 Hz, OCH$_2$C$H_{3\,(keto,enol)}$); 0.92 (t, $^3J$ = 7.5 Hz, 3H, CHCH$_2$C$H_3$); **enol-I**: $\delta$ = 15.90 (s, 1H, OH); 4.22–4.14 (m, OCH$_{2\,(keto,enol)}$); 3.74 (s, 3H), 3.73 (s, 3H) (H-1$_{(enol-I)}$, H-1$_{(enol-III)}$); 3.49 (s, 2H, H-3); 3.47 (s, 2H, H-7); 2.25 (q, $^3J$ = 7.5 Hz, 2H, CC$H_2$CH$_3$); 1.30–1.23 (4t, $^3J$ = 7.0 Hz, OCH$_2$C$H_{3\,(keto,enol)}$); 1.05 (t, $^3J$ = 7.5 Hz, 3H, CCH$_2$C$H_3$); **enol-II**: $\delta$ = 12.06 (d, $^4J$ = 1.0 Hz, 1H, OH); 5.12 (s, 1H), 5.10 (s, 1H) (H-3$_{(enol-II)}$, H-7$_{(enol-III)}$); 4.22–4.14 (m, 2H, OCH$_{2\,(keto,enol)}$); 3.70 (s, 3H, H-1); 3.63–3.50

(m, H-3,7$_{(keto)}$, H-7$_{(enol-II)}$, H-3$_{(enol-III)}$); 3.21 (m, 2H, H-5$_{(enol-II,enol-III)}$); 1.95–1.71 (m, 4H, CHC$H_2$CH$_{3\,(enol-II,enol-III)}$); 0.91 (t, $^3J$ = 7.5 Hz, 6H, CHCH$_2$C$H_{3\,(enol-II,enol-III)}$); **enol-III**: $\delta$ = 12.15 (d, $^4J$ = 1.0 Hz, 1H, OH); 5.12 (s, 1H), 5.10 (s, 1H) (H-3$_{(enol-II)}$, H-7$_{(enol-III)}$); 4.22–4.14 (m, OCH$_{2\,(keto,enol)}$); 3.74 (s, 3H), 3.73 (s, 3H) (H-1$_{(enol-I)}$, H-1$_{(enol-III)}$); 3.63–3.50 (m, H-3,7$_{(keto)}$, H-7$_{(enol-II)}$, H-3$_{(enol-III)}$); 3.21 (m, 2H, H-5$_{(enol-II,enol-III)}$); 1.95–1.71 (m, 4H, CHC$H_2$CH$_{3\,(enol-II,enol-III)}$); 0.91 (t, $^3J$ = 7.5 Hz, 6H, CHCH$_2$C$H_{3\,(enol-II,enol-III)}$); **enol-IV**: $\delta$ = 12.17 (d, $^4J$ = 0.8 Hz, 1H, OH); 12.08 (d, $^4J$ = 0.8 Hz, 1H, OH); 5.15 (s, 1H), 5.13 (s, 1H) (H-3,7); 3.72 (s, 3H, H-1). $^{13}$C NMR (125.8 MHz, $CDCl_3$): **keto**: $\delta$ = 198.7 (C-6); 198.5 (C-4); 167.2 (C-2); 166.7 (C-8); 67.7 (C-5); 61.6 (OCH$_2$); 52.4 (C-1); 48.0 (C-7); 47.7 (C-3); 21.7 (CH$C$H$_2$CH$_3$); 14.0 (OCH$_2$$C$H$_3$); 11.9 (CHCH$_2$$C$H$_3$); **enol-I**: $\delta$ = 186.0 (C-6); 185.8 (C-4); 168.0 (C-2); 167.5 (C-8); 112.8 (C-5); 61.5, 61.4 (OCH$_{2\,(enol-I,enol-II)}$); 52.5 (C-1); 42.2 (C-7); 41.9 (C-3); 20.1 ($C$CH$_2$CH$_3$); 14.9 (CCH$_2$$C$H$_3$); 14.1, 14.1, 14.0 (OCH$_2$$C$H$_{3\,(enol-I,enol-II,enol-III)}$); **enol-II**: $\delta$ = 198.9 (C-6); 173.1, 172.9 (C-4$_{(enol-II)}$, C-6$_{(enol-III)}$); 172.6, 172.3 (C-2$_{(enol-II)}$, C-8$_{(enol-III)}$); 166.8 (C-8); 91.8 (C-3); 61.5, 61.4 (OCH$_{2\,(enol-I,enol-II)}$); 60.2, 60.1 (C-5$_{(enol-II,enol-III)}$); 51.5 (C-1); 47.7 (C-7); 21.5, 21.4 (CH$C$H$_2$CH$_{3\,(enol-II,enol-III)}$); 14.1, 14.1, 14.0 (OCH$_2$$C$H$_{3\,(enol-I,enol-II,enol-III)}$); 11.6 (CHCH$_2$$C$H$_3$); **enol-III**: $\delta$ = 198.9 (C-4); 173.1, 172.9 (C-4$_{(enol-II)}$, C-6$_{(enol-III)}$); 172.6, 172.3 (C-2$_{(enol-II)}$, C-8$_{(enol-III)}$); 167.3 (C-2); 92.1 (C-7); 60.5 (OCH$_2$); 60.2, 60.1 (C-5$_{(enol-II,enol-III)}$); 52.3 (C-1); 47.5 (C-3); 21.5, 21.4 (CH$C$H$_2$CH$_{3\,(enol-II,enol-III)}$); 14.1, 14.1, 14.0 (OCH$_2$$C$H$_{3\,(enol-I,enol-II,enol-III)}$); 11.6 (CHCH$_2$$C$H$_3$); **enol-IV**: $\delta$ = 175.4, 175.2 (C-4,6); 90.6, 90.4 (C-3,7); 51.3 (C-1); 22.6 (CH$C$H$_2$CH$_3$); 14.2 (OCH$_2$$C$H$_3$). IR (neat, cm$^{-1}$): $\nu$ = 3648 (w), 3630 (w), 3447 (w), 2976 (m), 2940 (m), 2880 (w), 1747 (br, s), 1655 (m), 1626 (s), 1439 (s), 1406 (m), 1369 (m), 1322 (s), 1245 (br, s), 1159 (s), 1097 (m), 1081 (m), 1028 (s). MS (EI, 70 eV): $m/z$ (%) = 258 ($M^+$, 3), 212 (33), 180 (85), 165 (71), 158 (73), 144 (100). HRMS (EI): calcd for $C_{12}H_{18}O_6$ ($M^+$) 258.10979, found 258.109726.

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