Supporting Information

Stereoselective Synthesis of Conjugated $\alpha$-$Z/e$ and $\alpha$-$Z/Z$ Dienoic acids.

Kinetic torquoselectivity versus thermodynamic control

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1- General Experimental Conditions

Unless otherwise noted, reactions were carried out under argon atmosphere with magnetic stirring in redistilled solvents when necessary. Reagents and chemicals were purchased from commercial sources and used as received. Merck 60F254 silica gel was used for thin-layer chromatography (TLC) and Merck Geduran SI 60 Å silica gel 60 (40-63 μM) was used for flash column chromatography. IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer. NMR \(^1\)H, \(^{13}\)C spectra were recorded at 400 and 100 MHz, respectively, using a Bruker AVANCE 400 spectrometer equipped with a BBFO probe. Some NMR \(^1\)H, \(^{13}\)C spectra were recorded at 75 or 62.5 MHz using a Bruker AVANCE 300 or 250. Chemical shifts are reported in ppm, using, for \(^1\)H and \(^{13}\)C, solvent residual peak as internal standard references. Coupling constants (\(J\)) are given in Hertz (Hz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). High resolution mass spectra (HRMS) were recorded on a LTQ-Orbitrap Mass Spectrometer [Thermo Scientific].

2- General Procedure for the Preparation of Carboxylates 3:
TMSCl (120 μL, 1 mmol) was added under argon to a solution of methylcoumalate (154 mg, 1 mmol) in dry THF (10 mL) at 0°C and the resulting mixture was stirred for 15 minutes. Then Grignard reagent (1.2 equiv.) was added dropwise, and the mixture was stirred for 15 minutes. The mixture was evaporated to get the anion.

4-Methoxycarbonyl-hepta-2,4,6-trienoic acid anion 3a/3a’ (ratio 3a/3a’: 60/40)

\(\text{H}_a\) \(\text{H}_b\) \(\text{H}_c\) \(\text{H}_d\) \(\text{H}_a'\) \(\text{H}_b'\) \(\text{H}_c'\) \(\text{H}_d'\)

\(\text{CO}_2\text{MgBr}\) 

\(3a\) 

\(\text{CO}_2\text{MgBr}\) 

\(3a'\)

\(^1\)H NMR (400 MHz, MeOD) \(\delta\) (ppm): 3.72 (3H, s, OCH\(_3\)) 5.46-5.65 (2H, m, He, He’) 5.87 (0.4H, d, \(J = 12\) Hz, Ha), 6.05 (0.6H, d, \(J = 12\) Hz, Ha’), 6.47 (0.6H, d, \(J = 12\) Hz, Hb), 6.58 (0.4H, d, \(J = 12\) Hz, Hb’), 6.61-6.70 (1H, He, Hd’), 6.99-7.09 (1H, m, He’, Hd).
4-Methoxycarbonyl-hexa-2,4-dienoic acid anion 3i

\[
\begin{align*}
\text{H}_b & \equiv \text{H}_a \\
\text{CO}_2\text{MgBr} & \\
\text{H}_c & \equiv \text{CO}_2\text{Me}
\end{align*}
\]

\[3i\]

\(^1\)H NMR (250 MHz, MeOD) \(\delta\) (ppm): 1.80 (3H, d, \(J = 7.2\) Hz, Me), 3.35 (3H, s, CO\(_2\)H), 6.02 (1H, d, \(J = 12\) Hz, Ha) 6.43 (1H, dd, \(J = 12.0, 1.2\) Hz, Hb), 6.75 (1H, qd, \(J = 7.2, 1.2\) Hz, Hc).

3- General Procedure for the Preparation of Carboxylic Acids 4:
To a solution of methyl coumalate (2 mmol, 308 mg) in dry THF (20 mL) at 0 °C, under argon atmosphere, trimethylsilyl chloride (2 mmol, 0.25 mL) was added slowly. After 15 minutes stirring, Grignard reagent (1-2 equiv.) was added dropwise and the resulting solution was further stirred for 1-2 hr. Then, the reaction was quenched with saturated aq. sodium bicarbonate solution and washed with dichloromethane. The aqueous layer, containing the product as its sodium salt, was then acidified by adding dilute HCl and product was extracted with dichloromethane. The organic layers were pooled, dried over anhydrous MgSO\(_4\) and evaporated to afford the pure product.

4-Allylidene-pent-2-enedioic acid 5-methyl ester 4a'/4a

Ratio 4a'/4a: 90:10

\[
\begin{align*}
\text{HO}_2\text{C} & \equiv \text{MeO}_2\text{C} \\
\text{H}_a & \equiv \text{H}_b \\
\text{H}_c & \equiv \text{H}_d \\
\text{H}_e & \equiv \text{H}_f \\
\text{H}_g & \equiv \text{H}_h
\end{align*}
\]

\[4a\]

IR (KBr) \(\nu_{\text{max}}\): cm\(^{-1}\): 2953, 1701, 1436, 1193. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.77 (3H, s, OCH\(_3\)) 5.51-5.67 (2H, m, H\(_c\) & H\(_e\)) 5.86 (0.9H, d, \(J = 12.2\) Hz, H\(_a\)) 6.06 (0.1H, d, \(J = 11.7\) Hz, H\(_d\)) 6.50 (0.1H, d, \(J = 11.7\) Hz, H\(_b\)) 6.60 (0.9H, d, \(J = 12.2\) Hz, H\(_b\)) 6.64 (0.9H, d, \(J = 6.2\) Hz, H\(_d\)) 6.85 (0.1H, dd, \(J = 12.0, 7, 1\) Hz, H\(_c\)) 7.02-7.23 (1H, m, H\(_c\) & H\(_d\)) 10.43 (1H, br. s, CO\(_2\)H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 51.8 (OCH\(_3\)) 52.2 (OCH\(_3\)) 119.7 (CH) 123.6 (CH) 127.1 (CH\(_2\)) 127.2 (CH\(_2\)) 128.0 (C(CO\(_2\)Me)) 129.1 (C(CO\(_2\)Me)) 131.8 (CH) 132.9 (CH) 138.7 (CH)
141.0 (CH) 142.7 (CH) 144.6 (CH) 166.0 (CO) 166.70 (CO) 170.3 (CO) 170.7 (CO). HRMS (ES+): for (M^+Na) C_{10}H_{12}O_{4}Na, calcd. 205.04713, found 205.04712.

4-Propenylidene-pent-2-enedioic acid 5-methyl ester 4b/4b’

Ratio 4a’ (2 diastereoisomers)/4a (2 diastereoisomers): 50:50

IR (KBr) ν_{max}: cm^{-1}: 2952, 1692, 1630, 1435, 1235. ^1H NMR (250 MHz, CDCl₃) δ (ppm): 1.75 (3H, (4X) m, CH₃), 3.72 (0.75H, s, OCH₃), 3.74 (2.25H, s, OCH₃), 5.83 (0.5H, dd, J = 10.0, 7.5 Hz CH) 6.26-6.01 (1.75H, m, CH), 6.73-6.63 (2H, m, CH) 6.87 (0.25H, d, J = 11.7 Hz, H₆), 7.03 (0.25H, d, J = 10.0, Hz, CH), 7.57 (0.25H, d, J = 10.0, Hz, CH). ^13C NMR (100 MHz, CDCl₃) δ (ppm): 13.72 (CH₃), 14.06 (CH₃), 18.97 (CH₃), 19.01 (CH₃), 51.48 (OCH₃), 51.55 (OCH₃), 51.87 (OCH₃), 51.94 (OCH₃), 118.41 (CH), 118.69 (CH), 122.92 (CH), 123.25 (CH), 124.29 (CH), 125.29 (CH), 126.70 (C(CO₂Me)), 126.96 (CH), 128.00 (C(CO₂Me)), 128.00 (C(CO₂Me)), 129.1 (C(CO₂Me)) 128.16 (CH), 135.28 (CH), 137.41 (CH), 138.56 (CH), 138.58 (CH), 138.71 (CH), 141.38 (CH), 141.43 (CH), 142.00 (CH), 142.99 (CH), 143.03 (CH), 143.30 (CH), 170.67 (CO), 170.74 (CO), 171.01 (CO), 171.10 (CO). HRMS (ES+): for (M^+Na) C_{10}H_{12}O_{4}Na, calcd. 219.06278, found 219.06283.

4-Prop-2’-methylidene-pent-2-enedioic acid 5-methyl ester 4c/4c’.

Ratio 4c (2 diastereoisomers)/4c’ (2 diastereoisomers): 70:30

IR (KBr) ν_{max}: cm^{-1}: 2954, 1707, 1625, 1436, 1259, 1242, 1199. ^1H NMR (400 MHz, CDCl₃) δ (ppm): 1.55 (t, J = 1.6 Hz, 0.9 H, CH₃), 1.59 (d, J = 7.2 Hz, 2.1 H, CH₃), 1.81-1.77 (m, 0.9 H,
CH$_3$)$_3$, 1.83 (t, $J = 1.2$ Hz, CH$_3$), 3.68 (s, 0.9 H, OCH$_3$), 3.71 (s, 2.1 H, OCH$_3$), 5.66 (dd, $J = 6.0$, 13.2 Hz, 0.7 H, H$_d$), 5.86-5.78 (m, 0.3 H, H$_d'$), 5.96 (dd, $J = 1.2$, 12.0 Hz, 1 H, 0.7 H$_a$ & 0.3 H$_a'$), 6.75 (dd, $J = 2.0$, 12.0 Hz, 0.7 H, H$_b$), 6.89 (dd, $J = 1.6$, 11.6 Hz, 0.3 H, H$_b'$), 7.29 (s, 0.7 H, H$_c$), 7.12 (s, 0.3 H, H$_c'$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 14.6 (CH$_3$), 15.1 (CH$_3$), 16.0 (CH$_3$), 23.0 (CH$_3$), 51.9 (OCH$_3$), 52.0 (OCH$_3$), 121.8 (CH), 131.7 (CH), 122.0 (CH), 125.4 (C), 128.0 (C), 131.5 (C), 133.0 (C), 136.1 (CH), 140.6 (CH), 140.8 (CH), 140.9 (CH), 145.8 (CH), 167.5 (CO), 167.6 (CO), 171.2 (CO), 171.3 (CO). HRMS (ES+): for (M$^+$+Na) C$_{11}$H$_{14}$O$_4$Na, calcd. 233.0784, found 233.0785.

4-Prop-2-ynylidene-pent-2-enedioic acid 5-methyl ester 4d/4d'.

Ratio 4d'/4d' (Z,Z)/(Z,E): 50:50

IR (KBr) $\nu_{max}$: cm$^{-1}$: 2959, 2162,1685,1433. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 3.71 (0.5H, d, $J = 2.7$ Hz, H$_d$) 3.70 (0.5H, dd, $J = 2.4$, 0.6 Hz, H$_d'$) 3.75 (1.5H, s, OCH$_3$) 3.79 (1.5H, s, OCH$_3$) 5.96 (0.5H, dd, $J = 12.3$, 0.6 Hz, H$_a$) 6.09 (0.5H, dd, $J = 11.7$, 0.9 Hz, H$_a'$) 6.15-6.20 (0.5H, m, H$_c$) 6.61-6.73 (1H, m, 0.5 H$_b$ &0.5H$_b'$) 6.96 (0.5H, ddd, $J = 12.0$, 1.8, 0.6 Hz, H$_b$) 8.0-9.5 (1H, br. S, COOH). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 52.1 (OCH$_3$), 52.5 (OCH$_3$), 79.2 (C), 79.5 (C), 91.2 (C), 92.7 (C), 115.1 (CH), 121.1 (CH), 121.8 (CH), 121.9 (CH), 124.0 (CH), 138.0 (CH), 140.3 (C), 140.5 (C), 140.6 (CH), 165.0 (CO), 165.5 (CO), 170.3 (CO), 170.7 (CO). HRMS (ES+): for (M$^+$+Na) C$_9$H$_9$O$_4$Na, calcd. 203.03147, found 203.03148.
4-But-2-ynylidene-pent-2-enedioic acid 5-methyl ester 4e/4e’.

Ratio 4e'/4e (Z,Z)/(Z,E): 70:30

IR (KBr) ν_max: cm⁻¹: 2950, 2213, 1723, 1685, 1609, 1436. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.06 (0.9H, d, J = 2.8 Hz, CH₃) 2.08 (2.1 H, d, J = 2.8 Hz, CH₂) 3.72 (0.9H, s, OCH₃) 3.76 (2.1H, s, OCH₂) 5.86 (0.7H, d, J = 12.0 Hz, Hₐ) 6.03 (0.3H, dd, J = 12.0, 0.8 Hz, Hₐ) 6.18 (0.7H, d, J = 2.4 Hz, Hₐ) 6.68-6.54 (1H, m, 0.3 Hₜ & 0.7 Hₖ) 6.97 (0.3H, dd, J = 12.0, 0.8 Hz, Hₗ) 11.0 (1H, br. s, COOH). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 5.2 (CH₃), 5.4 (CH₂), 51.9 (OCH₃), 52.2 (OCH₂), 76.4 (C), 76.9 (C), 101.9 (C), 102.5 (C), 120.3 (CHₐ), 123.1 (CHₐ), 123.7 (CHₕ), 124.5 (CHₕ), 137.4 (CHₖ), 137.7 (C), 138.4 (C), 141.1 (CHₖ), 165.5 (CO), 166.1 (CO), 170.9 (CO), 171.4 (CO). HRMS (ES+): for (M⁺+Na) C₁₃H₁₀O₄Na, calcd. 217.0471, found 217.0469.

4-Benzylidene-pent-2-enedioic acid 5-methyl ester 4f

IR (KBr) ν_max: cm⁻¹: 2951, 1708, 1629,1434, 1256, 1175. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.78 (s, 3 H, OCH₃), 6.17 (dd, J = 0.8, 11.6 Hz, 1 H, Hₛ), 6.89 (dd, J = 2.0, 11.6 Hz, 1 H, Hₙ), 7.45-7.35 (m, 5 H, Ph), 7.69 (d, J = 0.8 Hz, Hₜ). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 50.2 (OCH₃), 123.6 (CH), 128.4 (C), 128.5 (CH), 129.7 (CH), 130.6 (CH), 134.4 (C), 140.1 (CH), 141.4 (CH), 167.1 (CO), 171.2 (CO). HRMS (ES+): for (M⁺+Na) C₁₃H₁₂O₄Na, calcd. 255.0628, found 255.0627.
4-Thiophenyl-pent-2-enedioic acid 5-methyl ester 4g

IR (KBr) $\nu_{\text{max}}$: cm$^{-1}$: 2956, 1709, 1621,1434, 1260, 1205. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 3.75 (s, 3 H, OCH$_3$), 6.19 (dd, $J = 0.8, 11.6$ Hz, 1 H, H$_a$), 7.04 (dd, $J = 2.0, 11.6$ Hz, 1 H, H$_b$), 7.11 (dd, $J = 3.6, 5.2$ Hz, 1 H, H$_c$), 7.30 (d, $J = 4.0$ Hz, 1 H, H$_d$), 7.53 (d, $J = 5.2$ Hz, 1 H, H$_e$), 7.83 (dd, $J = 0.8, 2.0$ Hz, 1 H, H$_f$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 52.2 (OCH$_3$), 124.7 (CH$_a$), 125.0 (CH$_e$), 127.9 (C), 131.4 (CH$_d$), 133.2 (CH$_c$), 138.1 (C), 139.5 (CH$_b$), 166.7 (CO), 170.9 (CO). HRMS (ES+): for (M$^+$+Na) C$_{11}$H$_{10}$O$_4$NaS, calcd. 261.0192, found 261.0189.

4-Cyclopropyl-pent-2-enedioic acid 5-methyl ester 4h

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 0.71 (m, 2 H, H$_e$), 1.00 (m, 2 H, H$_e$), 1.65-1.48 (m, 1 H, H$_d$), 3.70 (s, 3 H, OCH$_3$), 6.05 (d, $J = 14.4$ Hz, 1 H, H$_a$), 6.23 (d, $J = 13.2$ Hz, 1 H, H$_b$), 6.92 (dd, $J = 1.5, 12.6$ Hz, 1 H, H$_b$). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 9.25 (CH$_2$), 12.8 (CH), 51.8, (OCH$_3$), 122.5 (CH), 126.1 (C), 139.0 (CH), 151.7 (CH), 166.5 (CO), 171.0 (CO). HRMS (ES+): for (M$^+$+Na) C$_{10}$H$_{12}$O$_4$Na, calcd. 219.06278, found 219.06282.

4-Ethylidene-pent-2-enedioic acid 5-methyl ester 4i

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ (ppm): 1.82 (3H, d, $J = 7.2$ Hz, CH$_3$), 3.71 (3H, s, OCH$_3$), 6.02 (1H, d, $J = 11.7$ Hz, H$_d$), 6.71 (1H, d, $J = 11.7$ Hz, H$_b$), 6.92 (1H, q, $J = 7.2$ Hz, H$_c$), 9.08 (1H,
br. s, CO₂H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 30.0 (CH₃), 51.8 (OCH₃), 122.8 (CH), 129.4 (C), 139.1 (CH), 142.3 (CH), 166.5 (CO), 172.1 (CO).

4-Ethyl-pent-2-enedioic acid 5-methyl ester 4j

IR (KBr) νₘₐₓ: cm⁻¹: 2954, 1708, 1432, 1349, 1258. ¹H NMR (250 MHz, CDCl₃) δ (ppm): 1.04 (t, J = 7.5 Hz, 3 H, CH₃), 2.17 (quintet, J = 7.5 Hz, 2 H, CH₂), 3.70 (s, 3 H, OCH₃), 6.01 (d, J = 12.5 Hz, 1 H, Ha), 6.85-6.75 (m, 2 H, Hₐ & Hₗ).

4-Isobutylidene-pent-2-enedioic acid 5-methyl ester 4k

¹H NMR (250 MHz, CDCl₃) δ (ppm): 1.01 (3H, d, J = 6.8 Hz, CH(CH₃)₂) 1.20 (3H, d, J = 6.4 Hz, CH(CH₃)₂) 2.52-2.62 (1H, m, CH(CH₃)₂) 3.82 (3H, s, CO₂CH₃) 6.02 (1H, d, J = 12.4 Hz, Ha) 6.63 (1H, d, J = 10.4 Hz, Hc) 6.79 (1H, dd, J = 11.6, 2.0 Hz, Cb). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 17.50 (CH₃), 20.13(CH₃), 45.13 (CH), 52.24 (CO₂CH₃), 122.92 (CH), 127.42 (C), 138.87 (CH), 151.91 (CH), 165.77 (CO₂H), 169.15 (CO₂CH₃).

4- General Procedure for the Preparation of Unsaturated Lactones 5:

To a solution of methyl coumalate (2 mmol, 308 mg) in dry THF (20 mL) at 0 °C, under argon atmosphere, trimethylsilyl chloride (2 mmol, 0.25 mL) was added slowly. After 15 minutes stirring, Grignard reagent (1-2 equiv.) was added dropwise and the resulting solution was further stirred for 1-2 hr. Then the reaction was quenched with saturated aq. sodium bicarbonate solution and extracted twice with dichloromethane. The organic layers, were dried.
over anhydrous MgSO\textsubscript{4} and avaporated under reduced pressure. The residue was chromatographed on silica gel (Ethyl acetate / cyclohexane).

2-Phenyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5f

2-Cyclopropyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5h

2-Methyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5i
\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 1.43 \ (3\text{H}, \ d, \ J = 6.4 \text{ Hz, CH}_3), \ 3.10-3.29 \ (2\text{H}, \ m, \ H_a), \ 3.71 \ (3\text{H}, \ s, \ \text{OCH}_3) \ 5.31 \ (1\text{H}, \ qt, \ J = 6.8, 2.0 \text{ Hz, H}_c) \ 6.88 \ (1\text{H}, \ dd, \ J = 5.0, 2.8 \text{ Hz, H}_b). \]^1\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 21.68 \ (\text{CH}_3), \ 30.02 \ (\text{CH}_a), \ 52.10 \ (\text{OCH}_3), \ 75.62 \ (\text{CH}_c), \ 131.60 \ (\text{C(\text{CO}_2\text{CH}_3)}), \ 132.56 \ (\text{CH}_b), \ 163.64 \ (\text{CO}), \ 167.53 \ (\text{CO}).

2-Ethyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5j

IR (KBr) \ \nu_{\text{max}}: \ \text{cm}^{-1}: 2954, 1708, 1671, 1432, 1349, 1258, 1216, 1183. \ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 0.10 \ (t, \ J = 7.6 \text{ Hz, 3 H, CH}_3), \ 1.74 \ (m, \ 1 \text{ H, H}_d), \ 1.96 \ (m, \ 1 \text{ H, H}_d), \ 3.19 \ (\text{td, J = 2.8, 22.8 Hz, H}_a), \ 3.28 \ (\text{ddd, J = 1.6, 5.2, 22.4 Hz, H}_a), \ 3.32 \ (\text{s, 3 H, OCH}_3), \ 5.32-5.26 \ (m, \ 1 \text{ H, H}_c)7.00 \ (\text{dd, J = 2.8, 5.2 Hz, 1 H, H}_b). \ ^1\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 8.8 \ (\text{CH}_3), \ 28.7 \ (\text{CH}_2), \ 30.3 \ (\text{CH}_a), \ 52.2 \ (\text{OCH}_3), \ 80.3 \ (\text{CH}_c), \ 130.2 \ (\text{C}), \ 133.1 \ (\text{CH}_b), \ 163.8 \ (\text{CO}), \ 167.7 \ (\text{CO}). \ \text{HRMS (ES+): for (M}^+\text{+Na) C}_9\text{H}_{12}\text{O}_4\text{Na, calcd. 207.0628, found 207.0626.}

2-Isopropyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5k

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 0.87 \ (3\text{H}, \ d, \ J = 6.8 \text{ Hz, CH(CH}_3)_2), \ 1.09 \ (3\text{H}, \ d, \ J = 6.8 \text{ Hz, CH(CH}_3)_2) \ 2.09-2.17 \ (1\text{H, m, CH(\text{CH}_3)_2}) \ 3.14-3.29 \ (1\text{H, m, H}_a) \ 3.79 \ (3\text{H, s, OCH}_3) \ 5.21 \ (1\text{H, dt, J = 3.6, 2.4 Hz, H}_c) \ 7.02 \ (1\text{H, dd, J = 4.8, 2.8 Hz, H}_b). \ ^1\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ (\text{ppm}): 15.7 \ (\text{CH(\text{CH}_3)_2}), \ 19.2 \ (\text{CH(\text{CH}_3)_2}), \ 30.7 \ (\text{CH}_a), \ 34.0 \ (\text{CH(\text{CH}_3)_2}), \ 52.3 \ (\text{OCH}_3), \ 84.0 \ (\text{CH}_3), \ 129.8 \ (\text{CO}_2\text{CH}_3)), \ 133.5 \ (\text{CH}_b), \ 164.3 \ (\text{CO}_2), \ 167.9 \ (\text{CO}_2). \ \text{HRMS (ES+): for (M}^+\text{+Na) C}_{10}\text{H}_{14}\text{O}_4\text{Na, calcd. 221.0777, found 221.0784.}

Electronic Supplementary Material (ESI) for RSC Advances
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Spectre 1H routine en 8 Scan

3a

3a'

Electronic Supplementary Material (ESI) for RSC Advances
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$\text{CO}_2\text{MgBr}$

$\text{CO}_2\text{Me}$

3i
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JA-57-400/3
13C routine
decouple 1H
32 scans
JA-62-400/1

1H routine
8 scans

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JA-62-400/2

13C routine
decouple 1H
32 scans

5.17 5.36 51.85 52.27 76.84 CDCl3 77.16 Chloroform-d 77.48 CDCl3 102.51 103.87 120.34 123.09 123.68 124.52 137.38 137.75 138.36 141.11 165.49 166.09 170.90 171.39

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JA-50-400/1
1H routine
8 scans
Spectre 1H routine en 8 Scan
Spectre 13C routine en 32 Scan

$\text{CO}_2\text{Me}$

5h