SUPPORT INFORMATION

Oxidizing Morita-Baylis-Hillman adducts towards vicinal tricarbonyl compounds

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1. GENERAL INFORMATION

Aldehydes used as substrate for the Morita-Baylis-Hillman reactions are commercial and were purchased from specialized chemical companies. The other reagents were obtained from specialist suppliers and used without pre-treatment.

The Morita-Baylis-Hillman reactions were performed in ultrasound system 1000W and 25 KHz.

Compounds were purified by flash (70-230 mesh) or normal (230-400 mesh) silica gel column chromatography. The reactions were monitored by thin layer chromatography (TLC) using as developing system a 5% solution of ammonium phosphomolybdate in ethanol or sulfuric vanillin and UV lamp.

The NMR spectra (1H- and 13C-) were recorded on an Bruker 250 MHz for 1H and 62.5 MHz for 13C; Bruker 400 MHz for 1H and Varian Inova 500 (500 MHz to 1H and 125 MHz for 13C). Chemical shifts (δ) were expressed in ppm using deuterated chloroform (CDCl3) and acetone-D6 as internal standard. When necessary other deuterated solvents were used to record the spectra. Coupling constants (J) were expressed in Hz.

The multiplicities of the hydrogen peaks were indicated following the convention: s (singlet), d (doublet), dd (double doublet), ddd (double doublet of doublet), t (triplet), dt (double triplet), br (broad singlet), q (quartet), m (multiplet).

The absorption spectra in the infrared region (IR) were obtained in FT-IR spectrophotometer Bomem MB series, model B100, with the frequencies expressed in cm⁻¹, and the samples applied to a cell of NaCl or KBr pellets. The mass spectra of high resolution were obtained on a device Micromass (Manchester, UK) Q-Tof instrument.
configuration ESI-QqToF with a resolution of 5,000 and 50.0 ppm accuracy in TOF mass analyzer.

Melting points were obtained using an Electrothermal equipment model 9100 and were not corrected. Compounds were named according to IUPAC rules using the program MarvinSketch 5.5.0.1.

**EXPERIMENTAL GENERAL PROCEDURES**

2.1. Preparation of the Morita-Baylis-Hillman adducts (1-12)

To a stirred mixture of an aldehyde (10 to 30 mmol) and acrylate (5 equiv.) was added DABCO (0.65 equivalents). The resulting mixture was stirred at room temperature. The reaction was followed by TLC. At the end the acrylate was removed under reduced pressure and the residue was dissolved in ethyl acetate (50 mL). The organic phase was washed with distilled water (2 x 50 mL), brine (50 mL) and dried over anhydrous sodium sulfate, filtered and concentrated. The crude product was purified by silica gel column chromatography (eluent: a mixture of ethyl acetate : hexane ranging from 15:85 to 50:50 v/v).

(±)-Methyl 2-[hydroxy(phenyl)methyl]prop-2-enoate (1)

Yield: 85%, colorless oil; IR (film, \( \nu_{\text{max}} \)): 3422, 2956, 1718, 1630, 1198 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 3.14 (d, \(^3\)J = 5.5 Hz, 1H); 3.71 (t, 3H); 5.56 (d, \(^3\)J = 5.5 Hz, 1H); 5.84 (s, 1H); 6.33 (s, 1H); 7.29-7.33 (m, 5H). \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 52.1; 73.3; 126.2; 126.8; 128; 128.6; 141.5; 142.2; 166.9. HRMS (ESI, \( m/z \)): Calcd. for C\(_{11}\)H\(_{13}\)O\(_3\) 193.0859 [M + H]\(^+\); found 193.0856.
**1H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 1.**

Marilia MS002 CDC13 250MHz nov19mssH2

**13C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct 2.**

Marilia MS002 CDC13 250MHz nov19mssC1
(±)-Ethyl 2-[hydroxy(phenyl)methyl]prop-2-enoate (2)
Yield: 83%, colorless oil; IR (film, νmax): 3456, 3032, 2983, 2906, 1714, 1629, 1148, 1113, 864, 839 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 1.22 (t, 3J = 7.1Hz, 3H); 3.34 (d, 3J = 5.3Hz; 1H); 4.14 (q, 3J = 7.13Hz, 2H); 5.53 (d, J = 5.2Hz, 1H); 5.83 (s, 1H); 6.32 (s, 1H); 7.26-7.38 (m, 5H). ¹³C NMR (62.5 MHz, CDCl₃): δ 14.1; 61.0; 73.1; 125.7; 126.8; 127.8; 128.4; 141.6; 142.4; 166.4. HRMS (ESI, m/z): Calcd. for C₁₂H₁₅O₃ 207.1016 [M + H]+; found 207.1015.

Marilia MS116 CDCl₃/250MHz mai03mssH1

¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 2.
13C NMR (62.5 MHz, CDCl3) spectrum of the MBH adduct 2.

(±)-Methyl 2-[hydroxy(4-methoxyphenyl)methyl]prop-2-enoate (3)

Yield: 71%, white solid, m.p. 60-63 °C; IR (KBr, \( \nu_{\text{max}} \)): 3482, 2954, 2838, 1721, 1611, 1175, 1149, 830, 734 cm\(^{-1}\).

1H NMR (250 MHz, CDCl3): \( \delta \) 2.93 (d, \( ^3J = 5.2Hz, 1H \)); 3.71 (s, 3H); 3.79 (s, 3H); 5.52 (d, \( ^3J = 4.8Hz, 1H \)); 5.85 (s, 1H); 6.32 (s, 1H); 6.87 (d, \( ^3J = 8.7Hz, 2H \)); 7.28 (d, \( ^3J = 8.6Hz, 2H \)). 13C NMR (62.5 MHz, CDCl3): \( \delta \) 52.1; 55.5; 73.0; 114.0; 125.8; 128.1; 133.7; 142.4; 159.4; 170.0. HRMS (ESI, \( m/z \)): Calcd. for C\(_{12}\)H\(_{15}\)O\(_4\) 223.0965 [M + H]\(^+\); found 223.0963.
$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the MBH adduct 3.

$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the MBH adduct 3.
(±)-Methyl 2-{hydroxy[4-(propan-2-yl)phenyl]methyl}prop-2-enoate (4)

Yield: 66%, colorless oil; IR (film, $\nu_{\text{max}}$): 3451, 2960, 2871, 1723, 1631, 1149, 822 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 1.25 (d, $^3J = 6.9$ Hz, 6H); 2.91 (m, $^3J = 6.9$ Hz, 1H); 2.98 (d, $^3J = 5.5$ Hz, 1H); 3.73 (s, 3H); 5.55 (d, $^3J = 5.4$ Hz, 1H); 5.87 (s, 1H); 6.34 (s, 1H); 7.21 (d, $^3J = 8.3$ Hz, 2H); 7.30 (d, $^3J = 8.3$ Hz, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 24.1; 34.0; 52.1; 73.3; 126.0; 126.7; 126.8; 138.9; 142.3; 148.7; 167.0. HRMS (ESI, $m/z$): Calcd. for C$_{14}$H$_{19}$O$_3$ 235.1329 [M + H]$^+$; found 235.1328.

$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the MBH adduct 4.
(±)-Methyl 2-[hydroxy(4-nitrophenyl)methyl]prop-2-enoate (5)

Yield: 90%, yellow solid, m.p. 71–73°C; IR (KBr, ν_max): 3230, 2995, 1723, 1633, 1503, 1331, 1154, 1050 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 3.35 (d, J = 6.2 Hz, 1H); 3.75 (s, 3H); 5.63 (d, J = 6.0 Hz, 1H); 5.88 (s, 1H); 6.40 (s, 1H); 7.57 (d, J = 8.6 Hz; 2H); 8.20 (d, J = 8.8 Hz; 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 52.4; 72.9; 123.8; 127.5; 127.5; 141.2; 147.7; 148.8; 166.6. HRMS (ESI, m/z): Calcd. for C₁₁H₁₂NO₅ 238.0710 [M + H]⁺; found 238.0709.


² Adduct 6 was purified by crystallization. To the crude product was added a tiny amount of ethyl acetate. The mixture was refluxed until the product was completely dissolved. After that a few drops of hexane were added until the solution becomes cloudy. The mixture was placed in the refrigerator for crystallization. After 5 days at 8 °C the crystallization was complete.
The 1H NMR (250 MHz, CDCl3) spectrum of the MBH adduct 5.

The 13C NMR (62.5 MHz, CDCl3) spectrum of the MBH adduct 5.
(±)-3-[Hydroxy(phenyl)methyl]but-3-en-2-one (6)

Yield: 62%, slightly brown oil; IR (film, \( \nu_{\text{max}} \)):
3423, 3063, 3031, 1673, 1192, 841 cm\(^{-1}\). \(^1\)H NMR [250 MHz, (CD\(_3\))\(_2\)O]: \( \delta \)
2.26 (s, 3H); 4.57 (bs, 1H); 5.66 (s, 1H); 6.19 (s, 1H); 6.27 (s, 1H); 7.18-7.38 (m, 5H). \(^1\)C NMR [62.5 MHz, (CD\(_3\))\(_2\)O]: \( \delta \) 26.7; 71.6; 125.0; 127.8; 128.0; 128.9; 144.4; 152.6; 199.3. HRMS (ESI, \( m/z \)): Calcd. for C\(_{11}\)H\(_{13}\)O\(_2\) 177.0910 [M + H]\(^+\); found 177.0909.

Marilia MS062 Acetona-D6 250 MHz fev25mssH3

\(^1\)H NMR [250 MHz, (CD\(_3\))\(_2\)O] spectrum of the MBH adduct 6.

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\(^3\) This MBH reaction was performed with only 2 equivalents of methylvinylketone, since this acrylate is prone to polymerization.
(±)-Methyl 2-[hydroxy(3,4,5-trimethoxyphenyl)methyl]prop-2-enolate (7)

Yield: 71%, yellow oil; IR (film, ν\text{max}): 3488, 2942, 2839, 1721, 1593, 1233, 1127 cm\(^{-1}\). 1H NMR (250 MHz, CDCl\(_3\)): δ 3.21 (d, J = 5.2 Hz, 1H); 3.73 (s, 3H); 3.81 (s, 3H); 3.82 (s, 6H); 5.48 (d, J = 4.8 Hz, 1H); 5.83 (s, 1H); 6.31 (s, 1H); 6.58 (s, 2H). 13C NMR (62.5 MHz, CDCl\(_3\)): δ 52.1; 56.2; 60.9; 73.3; 103.7; 126.2; 137.1; 137.6; 142.1; 153.3; 167.0. HRMS (ESI, m/z): Calcd. for C\(_{14}\)H\(_{19}\)O\(_6\) 283.1176 [M + H]\(^+\); found 283.1173.
1H NMR (250 MHz, CDCl3) spectrum of the MBH adduct 7.

13C NMR (62.5 MHz, CDCl3) spectrum of the MBH adduct 7.
(±)-Methyl 2-[(4-tert-butylphenyl)(hydroxy)methyl]prop-2-enoate (8)

Yield: 77%, white solid, m.p. 64-66 °C; IR (KBr, νmax): 3454, 2962, 2905, 2869, 1723, 1630, 1149, 1042, 854 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 1.32 (s, 9H); 3.02 (d, ³J = 5.5Hz, 1H); 3.73 (s, 3H); 5.56 (d, ³J = 5.4Hz, 1H); 5.88 (s, 1H); 6.34 (s, 1H); 7.30 (d, ³J = 8.5Hz, 2H); 7.38 (d, ³J = 8.5Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 31.2; 34.7; 52.09; 125.6; 126.0; 126.5; 138.5; 142.2; 150.9; 167.0. HRMS (ESI, m/z): Calcd. for C₁₅H₂₁O₃ 249.1485 [M + H]⁺; found 249.1484.

Marilia MS121 CDCl3 250MHz jun29mssh1

¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 8.
(±)-Methyl 2-[(3-chlorophenyl)(hydroxy)methyl]prop-2-enoate (9)

Yield: 80%, colorless oil; IR (film, $\nu_{\text{max}}$): 3451, 2953, 1717, 1630, 1152, 884 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 3.25 (d, $^3J = 5.8$Hz, 1H); 3.72 (s, 3H); 5.51 (d, $^3J = 5.7$Hz, 1H); 5.84 (s, 1H); 5.85 (s, 1H); 7.25 (s, 3H); 7.37 (s, 1H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 52.1; 72.5; 124.9; 126.6; 126.9; 128.0; 129.8; 134.4; 141.6; 143.6; 166.6. HRMS (ESI, m/z): Calcd. for $\text{C}_{11}\text{H}_{12}\text{ClO}_3$ 227.0469 [M + H]$^+$; found 227.0468.
$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the MBH adduct 9.

$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the MBH adduct 9.
(±)-Methyl 2-[(4-bromophenyl)(hydroxy)methyl]prop-2-enoate (10)

Yield: 75%, white solid, m.p. 63-66 °C; IR (KBr, \( \nu_{\text{max}} \)): 3342; 2959; 1717; 1635, 1274, 1160, 812 cm\(^{-1}\). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 3.22 (d, \( ^3J = 5.7 \) Hz, 1H); 3.71 (s, 3H); 5.49 (d, \( ^3J = 5.6 \) Hz, 1H); 5.83 (s, 1H); 6.33 (s, 1H); 7.24 (d, \( ^3J = 8.4 \) Hz, 2H); 7.46 (d, \( ^3J = 8.4 \) Hz, 2H). \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 52.2; 72.8; 121.9; 126.5; 128.5; 131.7; 140.5; 141.7; 166.8. HRMS (ESI, \( m/z \)): Calcd. for C\(_{11}\)H\(_{12}\)BrO\(_3\) 270.9964 [M + H]\(^+\); found 270.9961.

\[ \text{Br} \quad \text{OH} \quad \text{O} \]

\[ \text{Me} \]

\[ 10 \]

\(^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the MBH adduct 10.
**13C NMR (62.5 MHz, CDCl3) spectrum of the MBH adduct 10.**

**tert-Butyl 2-\{hydroxy[4-(propan-2-yl)phenyl]methyl\}prop-2-enoate (11) Yield:** 52%, yellow tinged oil; IR (film, $\nu_{\max}$): 3441, 2962, 2931, 1716, 1630, 1150, 893, cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 1.24 (d, $^3J = 6.9$ Hz, 3H); 1.40 (s, 9H); 2.90 (m, 1H); 3.09 (d, $^3J = 5.4$ Hz, 1H); 5.48 (d, $^3J = 4.4$ Hz, 1H); 5.74 (t, 1H); 6.24 (s, 1H); 7.19 (d, $^3J = 8.2$ Hz, 2H); 7.28 (d, $^3J = 8.3$ Hz, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 24.2; 28.1; 34.0; 73.5; 81.7; 125.1; 126.5; 126.7; 139.2; 143.8; 148.5; 165.9. HRMS (ESI, $m/z$): Calcd. for C$_{17}$H$_{23}$O$_2$ 259.1698 [M + H]$^+$; found 259.1667.
\[ ^1H \text{ NMR (250 MHz, CDCl}_3 \text{) spectrum of the MBH adduct 11.} \]

\[ ^{13}C \text{ NMR (62.5 MHZ, CDCl}_3 \text{) spectrum of the MBH adduct 11.} \]
(±)-Methyl 3-hydroxy-2-methylidenehexanoate (12)

Yield: 95%, colorless oil; IR (film, ν_{max}): 3427, 2959, 2874, 1720, 1631, 1440, 1290, 1111 cm\(^{-1}\). \(^1\)H NMR (250 MHz, CDCl\(_3\)): δ 0.87 (t, \(^3\)J = 7.2Hz, 3H); 1.34 (m, 2H); 1.54 (m, 2H); 2.95 (d, \(^3\)J = 6.3Hz, 1H); 3.71 (t, 3H); 4.36 (q, \(^3\)J = 6.4Hz, 1H); 5.76 (s, 1H), 6.16 (s, 1H). \(^13\)C NMR (62.5 MHz, CDCl\(_3\)): δ 13.9; 19.1; 38.5; 51.9; 71.2; 124.8; 142.9; 167.6. HRMS (ESI, m/z): Calcd. for C\(_8\)H\(_{15}\)O\(_3\) 159.1016 [M + H]\(^+\); found 159.1017.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the MBH adduct 12.
2.2. Oxidation of MBH adducts: Preparation of α-methylene-β-ketoester (13-24)

To a stirred solution of a MBH adduct (0.5 to 3 mmol) in acetonitrile (final concentration: 0.14 mol/L) was added o-iodoxybenzoic acid (IBX, 1.5 equivalents). The resulting mixture was stirred at 70 °C and the evolution of the reaction was monitored by TLC. At the end, the mixture was cooled to room temperature, filtered and the solvent was removed under reduced pressure. The residue was pure enough to be used in the next step and no further purification was needed.4

Methyl 2-benzoyleprop-2-enoate (13)

Yield: 90%, yellow oil; IR (film, νmax): 3004, 2954, 1732, 1675, 1449, 817, 807 cm⁻¹. ¹H NMR (250 MHz, CDCl3): δ 3.75 (s, 3H); 6.04 (s, 1H); 6.70 (s, 1H); 7.42-7.49 (m, 2H); 7.55-7.62 (m, 1H); 7.86 (d, 2H). ¹³C NMR (62.5 MHz, CDCl3): δ 55.6; 128.8; 129.6; 131.7; 133.8; 136.2; 141.1; 164.9; 193.2. HRMS (ESI, m/z): Calcd. for C₁₁H₁₀O₃ 191.0703 [M + H]⁺; found 191.0701.

4 When ethyl acetate was used as solvent 3.0 equivalents of IBX was required.
1H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 13.

13C NMR (62.5 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 13.
Ethyl 2-benzoylprop-2-enoate (14)

Yield: >95%, colorless oil; IR (film, ν_max): 3062, 2983, 1729, 1679, 1597, 1237, 1153 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 1.17 (t, 3J = 7.1Hz, 3H); 4.20 (q, 3J = 7.1Hz, 2H); 6.04 (s, 1H); 6.67 (s, 1H); 7.17-7.47 (m, 2H); 7.54-7.60 (m, 1H); 7.82-7.86 (m, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 14.0; 61.6; 112.6; 127.7; 129.5; 137.1; 136.4; 141.6; 164.5; 193.3. HRMS (ESI, m/z): Calcd. for C₁₂H₁₃O₃ 205.0864 [M + H]⁺; found 205.0892.
$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the α-methylene-β-ketoester 14.

Ethyl 2-[(4-methoxyphenyl)carbonyl]prop-2-enoate (15)
Yield: 94%, yellow oil; IR (film, $\nu_{\text{max}}$): 2954, 2842, 1729, 1666, 1599, 1262, 1152, 847 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 3.77 (s, 3H); 3.88 (s, 3H); 5.99 (d, $^3J = 0.8$Hz, 2H); 6.68 (d, $^3J = 0.7$Hz, 2H); 6.95 (d, $^3J = 9.0$Hz, 2H); 7.87 (d, $^3J = 9.0$Hz, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 52.6; 55.8; 114.1; 129.3; 130.9; 132.2; 141.3; 164.3; 165.1; 191.9. HRMS (ESI, $m/z$): Calcd for C$^{12}$H$_{13}$O$_4$ 221.0814 [M + H]$^+$; found 221.0830.
**1H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 15.**

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**13C NMR (62.5 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 15.**

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Methyl 2-\{4-(propan-2-yl)phenyl\}carbonyl\}prop-2-enoate (16)

Yield: >95%, yellow oil; IR (film, \(\nu_{\text{max}}\)): 2962, 2873, 1731, 1673, 1604, 1144, 852 \text{ cm}^{-1}; \(^1\)H NMR (250 MHz, CDCl\(_3\)):\(\delta\) 1.27 (d, \(J = 6.9\text{Hz}, 6\text{H}\)); 2.98 (m, \(J = 6.9\text{Hz}, 1\text{H}\)); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 73.2 (d, \(J = 8.2\text{Hz}, 2\text{H}\)); 7.82 (d, \(J = 8.3\text{Hz}, 2\text{H}\)); \(^1\)C NMR (62.5 MHz, CDCl\(_3\)):\(\delta\) 23.8; 34.5; 52.6; 127.0; 130.1; 131.2; 134.1; 141.3; 155.6; 165.1; 192.9. HRMS (ESI, \(m/z\)): Calcd. for C\(_{14}\)H\(_{17}\)O\(_3\) 233.1178 [M + H]\(^{+}\); found 233.1200.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the \(\alpha\)-methylene-\(\beta\)-ketoester 16.
Methyl 2-[(4-nitrophenyl)carbonyl]prop-2-enoate (17)

Yield: 90%, yellow solid; IR (KBr, \( \nu_{\text{max}} \)): 2955, 1737, 1690, 1604, 1525, 1240, 702 cm\(^{-1}\). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 3.78 (s, 3H); 6.21 (s, 1H); 6.80 (s, 1H); 8.00 (d, \( J = 9.0\) Hz, 2H); 8.32 (d, \( J = 9.0\) Hz, 2H). \(^{13}\)C NMR [62.5 MHz, (CD\(_3\))\(_2\)O]: \( \delta \) 51.9; 123.8; 130.3; 132.7; 140.5; 140.9; 150.6; 164.1; 191.5. HRMS (ESI, \( m/z \)): Calcd. for C\(_{11}\)H\(_{10}\)NO\(_5\) 236.0559 [M + H]\(^+\); found 236.0579.

\(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) spectrum of the \( \alpha \)-methylene-\( \beta \)-ketoester 16.
**1H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 17.**

**13C NMR [62.5 MHZ, (CD₃)₂O] spectrum of the α-methylene-β-ketoester 17.**
2-Methylidene-1-phenylbutane-1,3-dione (18)

Yield: 93%, yellow oil; IR (film, \( \nu_{\text{max}} \)): 3065, 2930, 1671, 1597, 1232, 1123 cm\(^{-1}\); \( ^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 2.41 (s, 3H); 6.02 (s, 1H); 6.57 (s, 1H); 7.47 (m, \( ^3J = 7.2\) Hz, 2H); 7.60 (m, \( ^3J = 7.2\) Hz, 1H); 7.84 (m, \( ^3J = 7.1\) Hz, 1H); \( ^{13}\)C NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) 27.7; 128.8; 128.9; 129.7; 130.1; 133.9; 136.5; 148.4; 195.4; 196.7. HRMS (ESI, \( m/z \)): Calcd. for C\(_{11}\)H\(_{10}\)O\(_2\)Na 197.0578 [M + Na]\(^+\); found \( m/z \) 197.0619.

\( ^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the \( \alpha \)-methylene-\( \beta \)-ketoester 18.
**13C NMR (62.5 MHz, CDCl3) spectrum of the α-methylene-β-ketoester 18.**

Methyl 2-[(3,4,5-trimethoxyphenyl)carbonyl]prop-2-enoate (19)

Yield: >95%, colorless oil; IR (film, \( \nu_{\text{max}} \)): 2959, 2840, 1723, 1665, 1584, 1416, 1129 cm\(^{-1}\). \( ^1\)H NMR (250 MHz, CDCl3): \( \delta \) 3.79 (s, 3H); 3.89 (s, 6H); 3.93 (s, 3H); 6.03 (s, 1H); 6.70 (s, 1H); 7.13 (s, 2H). \( ^13\)C NMR (62.5 MHz, CDCl3): \( \delta \) 52.7; 56.5; 61.2; 107.3; 131.2; 131.3; 140.9; 143.5; 153.3; 165.0; 192.1. HRMS (ESI, \( m/z \)): Calcd. for C\(_{14}\)H\(_{17}\)O\(_6\) 281.1086 [M + H]\(^+\); found 281.1025.
$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 19.

$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 19.
Methyl 2-[(4-tert-butylphenyl)carbonyl]prop-2-enoate (20)

Yield: >95%, yellow solid, m.p. 42-44 °C; IR (KBr, νmax): 2963, 2906, 2871, 1731, 1673, 1603, 1239, 1156, 1145, 852 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 1.35 (s, 9H); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 7.48 (d, J = 8.6Hz, 2H); 7.82 (d, J = 8.6 Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 31.2; 35.4; 125.8; 129.8; 131.2; 133.6; 141.2; 157.8; 165.1; 192.8. HRMS (ESI, m/z): Calcd for C₁₅H₁₉O₃ 247.1334 [M + H]⁺; found m/z 247.1342.

¹H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 20.
Methyl 2-[(3-chlorophenyl)carbonyl]prop-2-enolate (21)

Yield: 98%, yellow tinged oil; IR (film, ν_max): 2954, 1737, 1690, 1591, 1238, 898 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 3.78 (s, 3H); 6.09 (s, 1H); 6.74 (s, 1H); 7.41 (t, 3J = 7.8Hz, 1H); 7.57 (ddd, 3J = 1.1Hz; 2.0Hz and 8.0Hz); 7.72 (dt, 3J = 1.5 and 7.7Hz); 7.84 (t, 3J = 1.7Hz, 1H). ¹³C NMR (62.5 MHz, CDCl₃): δ 52.8; 127.8; 129.5; 130.1; 132.4; 133.8; 135.2; 137.9; 140.7; 164.7; 191.9. HRMS (ESI, m/z): Caled for C₁₁H₁₀ClO₃ 225.0318 [M + H]⁺; Found m/z 225.0346.
\(^{1}H\) NMR (250 MHz, CDCl\(_3\)) spectrum of the \(\alpha\)-methylene-\(\beta\)-ketoester 21.

\(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) spectrum of the \(\alpha\)-methylene-\(\beta\)-ketoester 21.
Methyl 2-[(4-bromophenyl)carbonyl]prop-2-en-oate (22)

Yield: 95%, yellow tinged oil; IR (film, $\nu_{\text{max}}$): 2954, 1731, 1674, 1584, 1193, 816 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 3.77 (s, 3H); 6.07 (s, 1H); 6.70 (s, 1H); 7.61 (d, $^3J = 8.7$ Hz, 2H); 7.72 (d, $^3J = 8.7$ Hz, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 52.7; 129.2; 131.1; 132.2; 135.1; 140.8; 164.7; 192.2. HRMS (ESI, $m/z$): Calcd. for C$_{11}$H$_{10}$O$_3$Br 268.9813 [M + H]$^+$; found 268.9836.

$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 22.
13C NMR (62.5 MHz, CDCl3) spectrum of the α-methylene-β-ketoester 22.

**tert-Butyl 2-[(4-(propan-2-yl)phenyl)carbonyl]prop-2-enoate (23)**

Yield: >95%, yellow tinged oil; IR (film, $\nu_{max}$): 2965, 2933, 2873, 1724, 1674, 1570, 1149, 1055, 847 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl3): $\delta$ 1.27 (d, $^3J = 6.9$ Hz, 6H); 1.37 (s, 9H); 2.97 (m, 1H); 5.99 (s, 1H); 6.55 (s, 1H); 7.30 (d, $^3J = 8.3$ Hz, 2H); 7.77 (d, $^3J = 8.3$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl3): $\delta$ 23.8; 28.0; 34.5; 82.3; 126.7; 129.7; 130.2; 134.7; 143.6; 155.2; 163.8; 193.5. HRMS (ESI, m/z): Calcd. for C$_{17}$H$_{22}$O$_3$Na $^{297.1467}$ [M + H]$^+$; found 297.1505.
$^{1}$H NMR (250 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 23.

$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 23.
Methyl 2-methylidene-3-oxohexanoate (24)

Yield: 73%, colorless oil; IR (film, $\nu_{\text{max}}$): 2962, 2876, 1750, 1714, 1630, 1435, 1269, 1096 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 0.91 (t, $^3J = 7.4$Hz, 3H); 1.62 (m, $^3J = 7.4$Hz, 2H); 2.71 (t, $^3J = 7.3$Hz, 2H); 3.79 (s, 3H); 6.32 (d, $^3J = 0.8$Hz, 1H); 6.40 (d, $^3J = 0.8$Hz, 1H). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 13.8; 17.4; 43.2; 52.5; 132.6; 142.0; 165.5; 199.6. HRMS (ESI, $m/z$): Calcd. for (C$_8$H$_{13}$O$_3$)$_2$H $313.1652$ [M + H]$^+$; found 313.1682.

$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the $\alpha$-methylene-$\beta$-ketoester 24.
2.3. Preparation of the vicinal tricarbonyl compounds (VTC) (25-36)

Into a stirred solution of a 1,3-dicarbonyl (0.5 to 3.0 mmol) in methanol or dichloromethane (15 mL) was bubbled a flow of ozone (a mixture of dry O2 and O3 – 0.3-0.5% of O3), at -78 °C. The reaction progress was monitored by thin layer chromatography. The reactions took 10 to 50 minutes to be completed. At the end dimethyl sulfide (10 equivalents) was added and the resulting mixture was stirred for further 2 hours. During this time, the reaction temperature was allow to warm slowly (room temperature). The solvents were removed under reduced pressure and the residue was purified by a silica gel column chromatography (eluent: ethyl acetate: hexane (a solvent gradient was increased slowly from 10:90 to 50:50, v/v)).

Methyl 2,3-dioxo-3-phenylpropanoate (25)
Yield: 78%, yellow oil; IR (film, νmax): 3426, 2958, 1755, 1696, 1598, 1131, 911 cm⁻¹. Mixture 4:9 (tricarbonyl and hydrate form) - ¹H NMR (250 MHz, CDCl3): Tricarbonyl
compound: $\delta$ 4.0 (s, 3H); 7.5-7.7 (m, 3H), 9.0-8.0 (m, 2H). Hydrate: $\delta$ 3.74 (s, 3H); 5.40 (br, 2H); 7.5-7.7 (m, 3H); 8.10 (m, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) - Tricarbonyl compound: $\delta$ 53.7; 129.4; 130.2; 131.6; 135.8; 161.1; 183.6. Hydrate: $\delta$ 53.9; 91.9; 129.0; 130.4; 131.4; 134.9; 170.6; 191.6. HRMS (ESI, $m/z$): Calcd for $m/z$ C$_{10}$H$_9$O$_4$ 193.0500 [M + H]$^+$; found $m/z$ 193.0487.

$^{1}$H NMR (250 MHz, CDCl$_3$) spectrum of the vicinal tricarbonyl compound 25.
Ethyl 2,3-dioxo-3-phenylpropanoate (26)

Yield: >95%, greenish yellow oil; IR (film, $\nu_{\text{max}}$): 3415, 2985, 1750, 1695, 1235, 1133, 1101, 1015 cm$^{-1}$. Mixture of the vicinal tricarbonyl compound and its hydrated form (4:5) - $^1$H NMR (250 MHz, CDCl$_3$): Tricarbonyl compound: $\delta$ 1.36 (t, $^3J$ = 7.1Hz, 3H); 4.40 (q, $^3J$ = 7.1Hz, 2H); 7.41-8.10 (m, 5H). *Hydrate*: $\delta$ 1.05 (t, $^3J$ = 7.1Hz, 3H); 4.17 (q, $^3J$ = 7.1Hz, 2H); 7.41-8.10 (m, 5H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) - Tricarbonyl compound: $\delta$ 14.1; 63.4; 129.3; 130.1; 131.6; 135.7; 160.6; 183.9; 190.4. *Hydrate*: $\delta$ 13.8; 63.0; 92.1; 128.8; 130.3; 131.7; 134.6; 169.9; 192.2. HRMS (ESI, m/z): Calcd for C$_{11}$H$_{11}$O$_4$ 207.0657 [M + H]$^+$; found m/z 207.0660.
1H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound 36 and its hydrated form.

13C NMR (62.5 MHz, CDCl₃) spectrum of the vicinal tricarbonyl compound 26 and its hydrated form.
Methyl 3-(4-methoxyphenyl)-2,3-dioxopropanoate (27)

Yield: 76%, yellow tinged oil; IR (film, \( \nu_{\text{max}} \)): 3407, 2954, 2844, 1747, 1682, 1602, 1254, 1175, 1128, 845 cm\(^{-1}\). Mixture of the vicinal tricarbonyl compound and its hydrated form (1:3). \(^1\)H NMR (250 MHz, CDCl\(_3\)):

**Tricarbonyl compound**: \( \delta \) 3.90 (s, 3H); 3.94 (s, 3H); 7.00 (d, \( ^3J = 9.0\)Hz, 2H); 7.98 (d, \( ^3J = 9.0\)Hz, 2H). **Hydrate**: \( \delta \) 3.74 (s, 3H); 3.98 (s, 3H); 5.47 (s, 2H); 6.94 (d, \( ^3J = 9.0\)Hz, 2H); 8.07 (d, \( ^3J = 9.0\)Hz, 2H). \(^{13}\)C NMR [62.5 MHz, CDCl\(_3\)]: **Tricarbonyl compound**: \( \delta \) 53.6; 55.9; 91.8; 114.8; 124.6; 132.9; 161.4; 165.0; 183.7; 188.3. **Hydrate**: \( \delta \) 53.8; 55.8; 91.8; 114.3; 124.2; 133.0; 165.0; 170.9; 189.8. HRMS (ESI, m/z): Calcd for C\(_{11}\)H\(_{11}\)O\(_5\) m/z 223.0607 \([\text{M} + \text{H}]^+\). Found m/z 223.0678.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the tricarbonyl compound 27 and its hydrated form.
Methyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (28)

Yield: 76%, yellow oil; IR (film, \( \nu_{\text{max}} \)): 3413, 2959, 2876, 1749, 1691, 1606, 1185, 854 cm\(^{-1}\). Mixture of vicinal tricarbonyl compound and its hydrate form (1:3) - \(^1\)H NMR (250 MHz, CDCl\(_3\)):

Tricarbonyl compound: \( \delta \) 1.29 (d, \( ^3 J = 6.9 \) Hz, 6H); 2.98 (m, 1H); 3.96 (s, 1H); 7.40 (d, \( ^3 J = 8.3 \) Hz, 2H); 7.93 (d, \( ^3 J = 8.4 \) Hz, 2H). Hydrate: \( \delta \) 1.27 (d, \( ^3 J = 6.9 \) Hz, 6H); 2.98 (m, 1H); 3.76 (s, 1H); 5.42 (br, 2H); 7.33 (d, \( ^3 J = 8.4 \) Hz, 2H); 8.02 (d, \( ^3 J = 8.4 \) Hz, 2H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) - Tricarbonyl compound: \( \delta \) 22.9; 33.8; 52.7; 125.8; 126.6; 129.6; 154.4; 156.9; 170.0; 182.8. Hydrate: \( \delta \) 22.7; 33.6; 52.9; 90.8; 126.2; 128.1; 129.8; 155.9; 169.8; 190.1. HRMS (ESI, m/z): Calcd for C\(_{13}\)H\(_{15}\)O\(_4\) m/z 235.0937 [M + H]\(^+\); found m/z 235.0970.
1H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound 28 and its hydrated form.

13C NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound 28 and its hydrated form.
Methyl 2,3-dioxo-3-(3,4,5-trimethoxyphenyl)propanoate (31)

Yield: 67%, yellow oil; IR (film, $\nu_{\text{max}}$): 3418, 2954, 2843, 1747, 1693, 1585, 1127 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 3.79 (s, 3H); 3.91 (s, 6H); 3.97 (s, 3H); 5.35 (bs, 2H); 7.40 (s, 2H); $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 54.0; 56.5; 61.2; 91.9; 108.0; 126.2; 144.3; 153.3; 171.0; 190.2; HRMS (ESI, $m/z$): Calcd. for C$_{13}$H$_{15}$O$_7$ 283.0812 [M + H]$^+$; found 283.0809.

$^1$H NMR (250 MHz, CDCl$_3$) spectrum of the tricarbonyl compound 31 and its hydrated form.
Methyl 3-(4-tert-butylphenyl)-2,3-dioxopropanoate (32)

Yield: >95%; white solid, m.p. 56-59 °C; IR (KBr, \( \nu_{\text{max}} \)):
3416, 2962, 1748, 1688, 1604, 1250, 1127 cm\(^{-1}\). Mixture of the tricarbonyl compound and its hydrate (1:3): \( ^1\)H NMR (250 MHz, CDCl\(_3\)) - Tricarbonyl compound: \( \delta \) 1.35 (s, 9H); 3.95 (s, 3H); 7.56 (d, \( ^3J = 8.5 \) Hz, 2H); 7.93 (d, \( ^3J = 8.5 \) Hz, 2H). Hydrate: \( \delta \) 1.34 (s,9H); 3.76 (s, 3H); 7.49 (d, \( ^3J = 8.6 \) Hz, 2H); 8.01 (d, \( ^3J = 8.6 \) Hz, 2H). NMR de \(^{13}\)C (62.5 MHz, CDCl\(_3\)): Tricarbonyl compound: \( \delta \) 31.1; 35.5; 53.9; 126.1; 128.7; 130.5; 160.1; 161.1; 183.8; 189.8. Hydrate: \( \delta \) 31.1; 35.7; 53.6; 91.8; 126.4; 129.1; 130.3; 159.1; 170.8; 191.0. HRMS (ESI, m/z): Calcd for C\(_{14}\)H\(_{17}\)O\(_4\) m/z 249.1127 [M + H]\(^+\); found m/z 249.1104
1H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound 32 and its hydrated form.
$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the tricarbonyl compound 32 and its hydrated form.

Methyl 3-(3-chlorophenyl)-2,3-dioxopropanoate (33)
Yield: 65%, yellow tinged solid, m.p. 66-67°C. IR (KBr, $v_{\text{max}}$): 3468, 3421, 3073, 2959, 1755, 1743, 1701, 1110, 912 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 3.77 (s, 3H); 5.25 (s, 2H); 7.43 (t, $^3J = 8.0$ Hz, 1H); 7.61 (dt, $^3J = 1.0$ Hz, $^3J = 8.0$ Hz, 1H); 7.96 (d, $^3J = 7.9$ Hz, 1H); 8.08 (s, 1H). Mixture of the tricarbonyl compound and its hydrate (1:3) - $^{13}$C NMR (125 MHz, CDCl$_3$): **Tricarbonyl compound:** $\delta$ 53.8; 128.4; 129.9; 130.7; 135.7; 135.8; 160.9; 182.8; 188.8. **Hydrate:** $\delta$ 54.1; 92.0; 128.5; 130.2; 130.4; 133.1; 134.9; 135.4; 170.2; 190.7; HRMS (ESI, m/z): Calcd for C$_{14}$H$_{17}$O$_3$ 227.0111 [M + H]$^+$; Found m/z 227.0189.

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$^1$H NMR(250 MHz, CDCl$_3$) spectrum of the tricarbonyl compound 33 and its hydrated form.
$^{13}$C NMR (62.5 MHz, CDCl$_3$) spectrum of the tricarbonyl compound 33 and its hydrated form

Methyl 3-(4-bromophenyl)-2,3-dioxopropanoate (34)
Yield: 75%, white solid, m.p. 99-100 °C; IR (KBr, $\tilde{\nu}_{\text{max}}$): 3421, 1756, 1738, 1694, 1585, 1133, 803 cm$^{-1}$. Mixture of tricarbonyl compound and hydrate (1:6) $^1$H NMR (250 MHz, CDCl$_3$) - *Tricarbonyl compound*: $\delta$ 3.97 (s, 3H); 7.70 (d, $^3J = 8.7$ Hz, 2H); 7.88 (d, $^3J = 8.7$ Hz, 2H). *Hydrate*: $\delta$ 3.75 (s, 3H); 5.28 (br, 2H); 7.62 (d, $^3J = 8.7$ Hz, 2H); 7.94 (d, $^3J = 8.7$ Hz, 2H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) - *Tricarbonyl compound*: $\delta$ 52.8; 130.6; 131.9; 160.1; 182.0; 187.9; *Hydrate*: $\delta$ 53.1; 91.0; 129.3; 129.6; 130.8; 131.5; 169.4; 189.8. HRMS (ESI, $m/z$): Calcd. for C$_{10}$H$_8$BrO$_4$ 270.9600 [M + H]$^+$; found 270.9591
**1H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound 34 and its hydrated form.**

**1H NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound 34 and its hydrated form.**
 tert-Butyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (35)

Yield: 61%, yellow tinged oil; IR (film, \( \nu_{\text{max}} \)): 3432, 2965, 2933, 2873, 1738, 1692, 1606, 1571, 1128, 851 cm\(^{-1}\). Mixture tricarbonyl compound and its hydrated form (1:10). \(^1\)H NMR (250 MHz, CDCl\(_3\)) - *Tricarbonyl compound*: \( \delta \) 7.38 (d, \( ^3J = 8.3 \) Hz, 2H); 7.92 (d, \( ^3J = 8.3 \) Hz, 2H).

*Hydrate*: \( \delta \) 1.26 (d, \( ^3J = 6.9 \) Hz, 6H); 1.32 (s, 9H); 2.97 (m, 1H); 5.36 (s, 2H); 7.31 (d, \( ^3J = 8.4 \) Hz, 2H); 7.99 (d, \( ^3J = 8.4 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) - *Tricarbonyl compound*: \( \delta \) 23.7; 28.0; 34.7; 86.0; 127.5; 129.9; 130.4; 157.5; 160.2; 185.0; 190.7.

*Hydrate*: \( \delta \) 23.7; 27.6; 34.6; 84.8; 91.8; 127.0; 129.6; 130.5; 156.5; 169.2; 191.9. HRMS (ESI, \( m/z \)): Calcd. for C\(_{16}\)H\(_{21}\)O\(_4\) 277.1434 [M + H]\(^+\); found 277.1430.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) spectrum of the tricarbonyl compound 35 and its hydrated form.
Methyl 2,3-dioxohexanoate (36)
Yield: 22%, colorless oil; IR (film, νmax): 3420, 2962, 2876, 1750, 1714 cm⁻¹. Mixture tricarbonyl compound and hydrate (1:1). ¹H NMR (250 MHz, CDCl₃): δ 0.92 (t, ³J = 7.4Hz, 3H); 0.99 (t, ³J = 7.4Hz, 3H); 1.54-1.76 (m, 4H); 2.40 (t, 1H); 2.53 (m, 1H); 2.68 (t, 1H); 2.86 (t, 1H); 3.76 (s, 3H); 3.87 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 13.7; 16.9; 18.4; 27.3; 33.9; 40.8; 53.3; 86.5; 161.1; 167.8; 172.3; 192.3; 202.7. HRMS (ESI, m/z): Calcd. for C₇H₉O₄ 159.0652 [M + H]^+; found 159.0650.
\[ ^1H \text{NMR (250 MHz, CDCl}_3\text{) spectrum of the tricarbonyl compound 36 and its hydrated form.} \]

\[ ^{13}C \text{NMR (62.5 MHz, CDCl}_3\text{) spectrum of the tricarbonyl compound 36 and its hydrated form.} \]