

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 ^{13}C -) were recorded on an Bruker 250 MHz for ^1H and 62.5 MHz for ^{13}C ; Bruker 400 MHz for ^1H and Varian Inova 500 (500 MHz to ^1H and 125 MHz for ^{13}C). Chemical shifts (δ) were expressed in ppm using deuterated chloroform (CDCl_3) and acetone- D_6 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

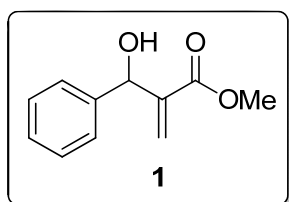
configuration ESI-QqTof with a resolution of 5,000 and 50.0 ppm accuracy in TOF mass analyzer.

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**)

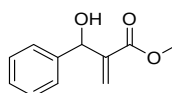
To a stirred mixture of an aldehyde (10 to 30 mmol) and acrylate (5 equiv.) was added DABCO (0.65 equivalents). The resulting mixture was stirred at room temperature. The reaction was followed by TLC. At the end the acrylate was removed under reduced pressure and the residue was dissolved in ethyl acetate (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, ν_{max}): 3422, 2956, 1718, 1630, 1198 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 3.14 (d, $^3J = 5.5$ Hz, 1H); 3.71 (t, 3H); 5.56 (d, $^3J = 5.5$ Hz, 1H); 5.84 (s, 1H); 6.33 (s, 1H); 7.29-7.33 (m, 5H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 52.1; 73.3; 126.2; 126.8; 128; 128.6; 141.5; 142.2; 166.9. HRMS (ESI, m/z): Calcd. for $\text{C}_{11}\text{H}_{13}\text{O}_3$ 193.0859 $[\text{M} + \text{H}]^+$; found 193.0856.

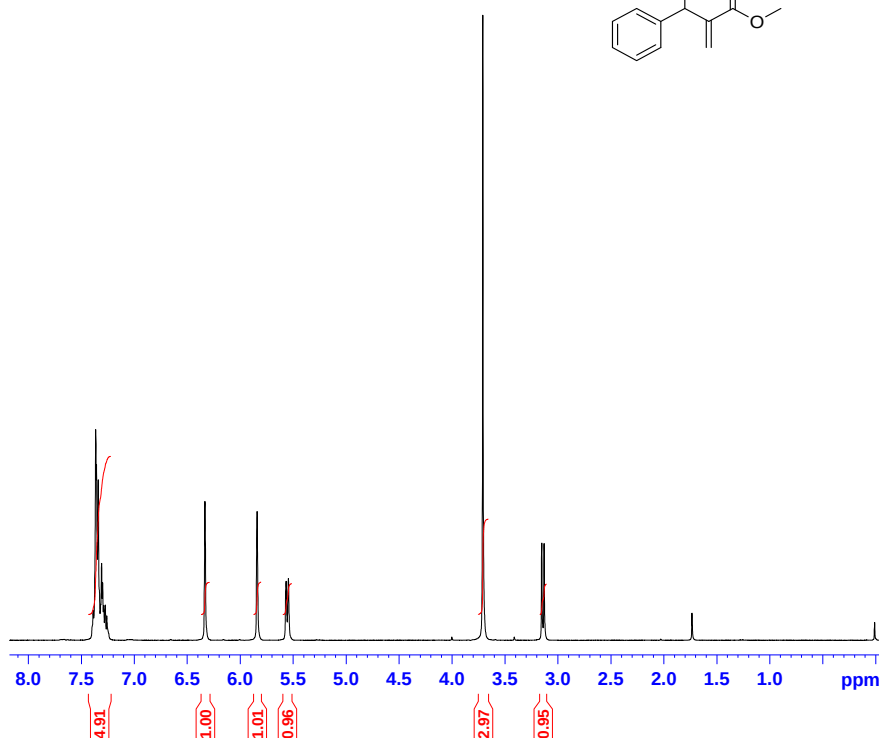
Marilia MS002 CDCl₃ 250MHz nov19mssH2



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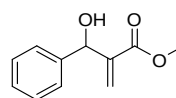
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PROCNO 1
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FIDRES 0.157958 Hz
AQ 3.1654389 sec
RG 322.5
DW 96.600 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

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¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 1.

Marilia MS002 CDCl₃ 250MHz nov19mssC1

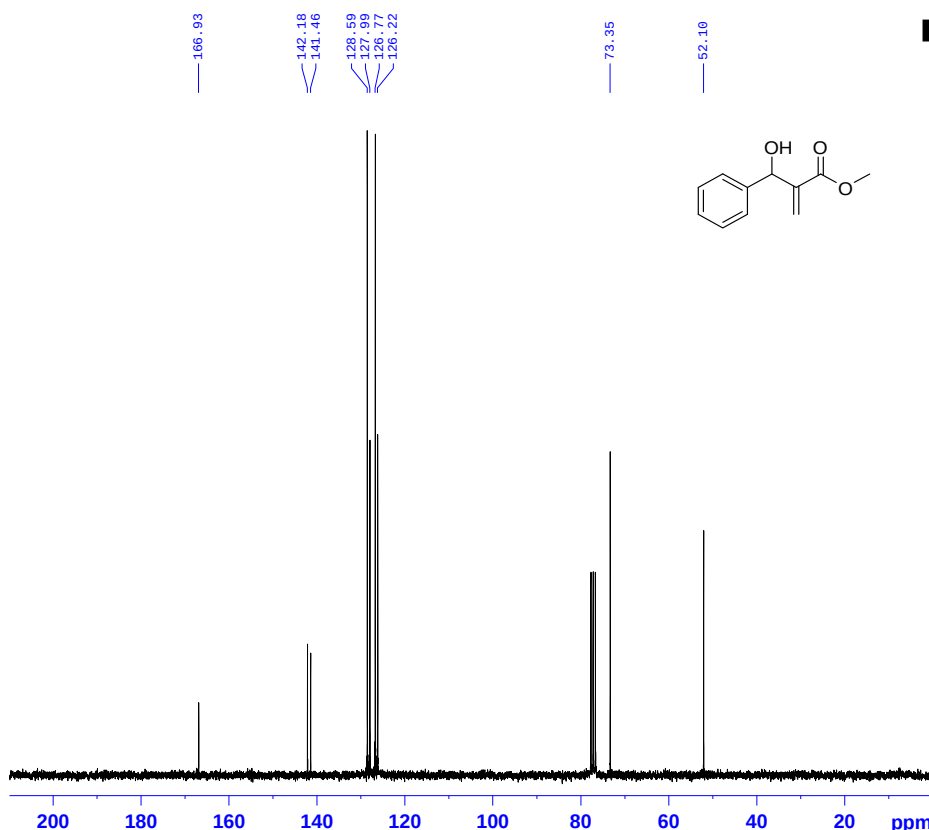


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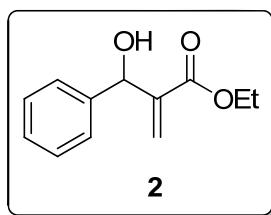
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SOLVENT CDCl3
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FIDRES 0.919204 Hz
AQ 0.5439988 sec
RG 724.1
DW 33.200 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

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PCPD2 100.00 usec
PL2 -6.00 dB
PL12 18.00 dB
PL13 18.00 dB
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LB 1.00 Hz
GB 0
PC 1.40
    
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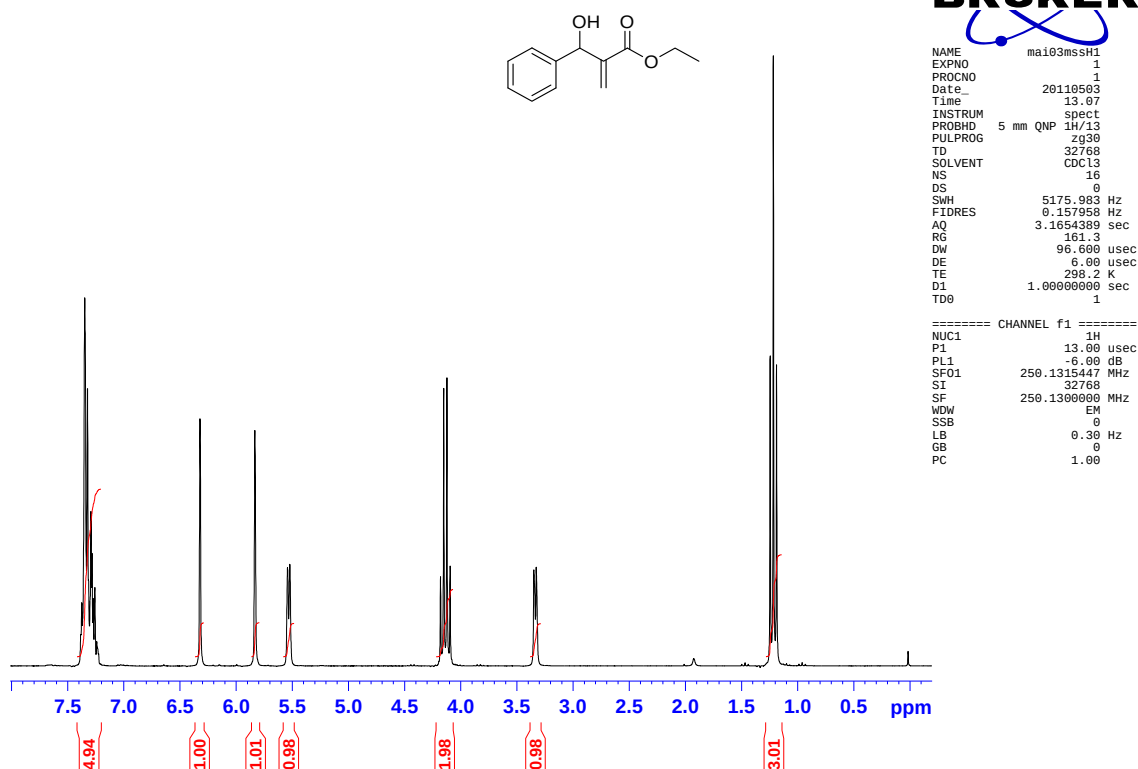
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct 2.



(±)-Ethyl 2-[hydroxy(phenyl)methyl]prop-2-enoate (**2**)

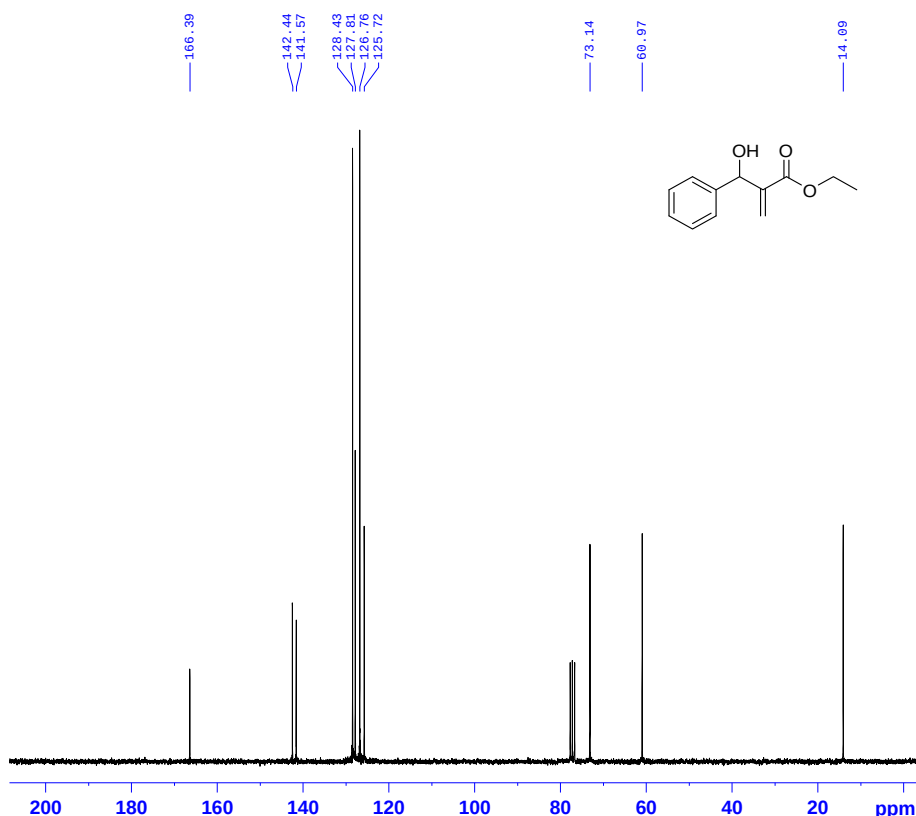
Yield: 83%, colorless oil; IR (film, ν_{max}): 3456, 3032, 2983, 2906, 1714, 1629, 1148, 1113, 864, 839 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 1.22 (t, $^3J = 7.1\text{Hz}$, 3H); 3.34 (d, $^3J = 5.3\text{Hz}$; 1H); 4.14 (q, $^3J = 7.13\text{Hz}$, 2H); 5.53 (d, $J = 5.2\text{Hz}$, 1H); 5.83 (s, 1H); 6.32 (s, 1H); 7.26-7.38 (m, 5H). ^{13}C NMR (62.5 MHz, CDCl_3): 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 $\text{C}_{12}\text{H}_{15}\text{O}_3$ 207.1016 [$\text{M} + \text{H}$] $^+$; found 207.1015.

Marilia MS116 CDCl_3 /250MHz mai03mssH1



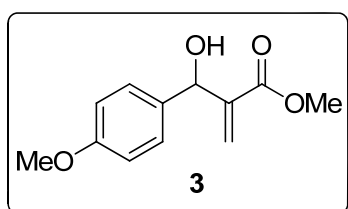
^1H NMR (250 MHz, CDCl_3) spectrum of the MBH adduct **2**.

Marilia MS116 CDCl₃ 250MHz mai06mssc



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PROCNO	1
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SWH	15060.241 Hz
FIDRES	0.919204 Hz
AQ	0.5439988 sec
RG	362
DW	33.200 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
d11	0.03000000 sec
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TD0	1
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NUC2	1H
PCPD2	100.00 usec
PL2	-6.00 dB
PL12	18.00 dB
PL13	18.00 dB
SFO2	250.1310005 MHz
SF	62.8952331 MHz
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GB	0
PC	1.40

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

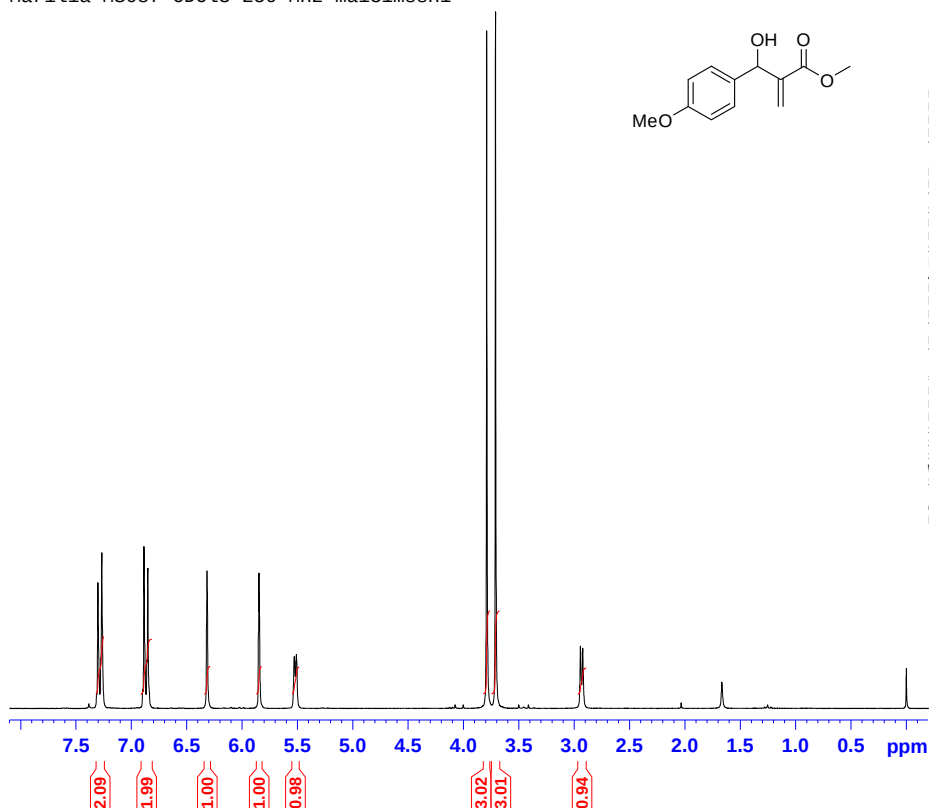


(±)-Methyl 2-[hydroxy(4-methoxyphenyl)methyl]prop-2-enoate (**3**)

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

¹H NMR (250 MHz, CDCl₃): δ 2.93 (d, ³*J* = 5.2 Hz, 1H); 3.71 (s, 3H); 3.79 (s, 3H); 5.52 (d, ³*J* = 4.8 Hz, 1H); 5.85 (s, 1H); 6.32 (s, 1H); 6.87 (d, ³*J* = 8.7 Hz, 2H); 7.28 (d, ³*J* = 8.6 Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 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 C₁₂H₁₅O₄ 223.0965 [M + H]⁺; found 223.0963.

Marilia MS087 CDCl₃ 250 MHz mai31mssH1



BRUKER

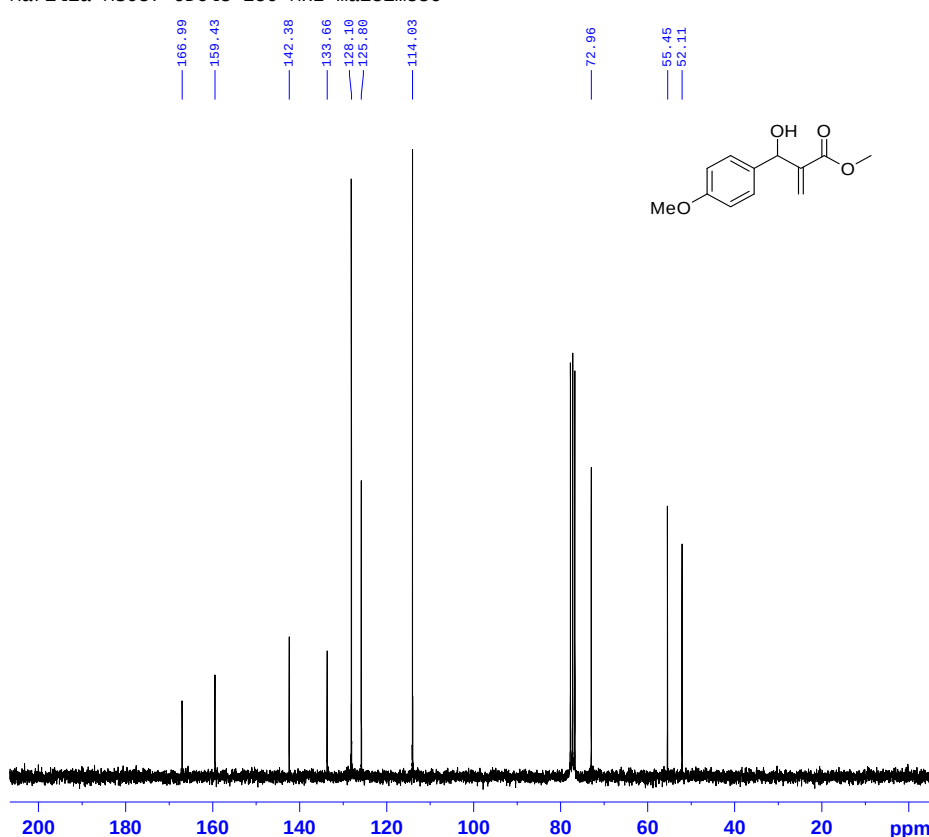
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FIDRES     0.157958 Hz
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RG         645.1
DW         96.600 usec
DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

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SSB         0
LB         0.30 Hz
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PC         1.00
    
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¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 3.

Marilia MS087 CDCl₃ 250 MHz mai31mssc



BRUKER

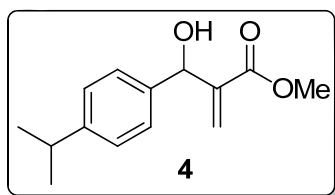
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FIDRES     0.919204 Hz
AQ         0.5439988 sec
RG         406.4
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0        1

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PCPD2      100.00 usec
PL2        -6.00 dB
PL12       18.00 dB
PL13       18.00 dB
SF02       250.1310005 MHz
SI         32768
SF         62.8952254 MHz
WDW         EM
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LB         1.00 Hz
GB         0
PC         1.40
    
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¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct 3.

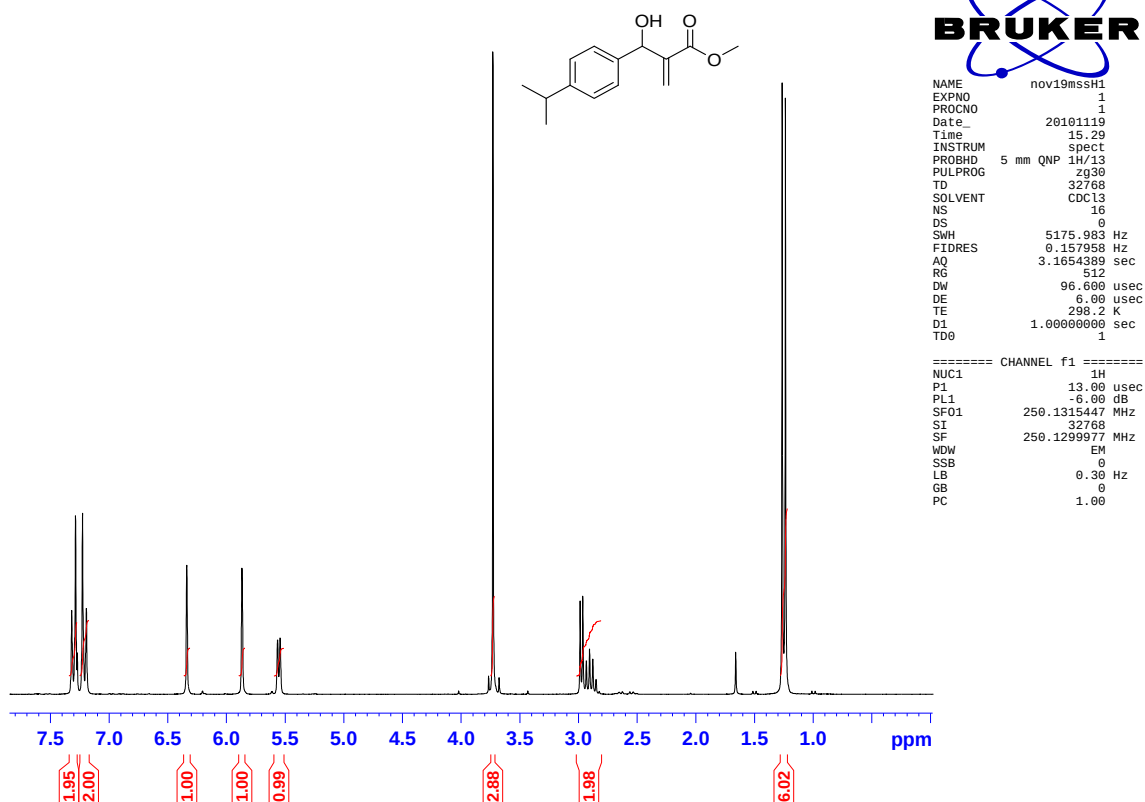


(±)-Methyl 2-{hydroxy[4-(propan-2-yl)phenyl]methyl}prop-2-enoate (**4**)

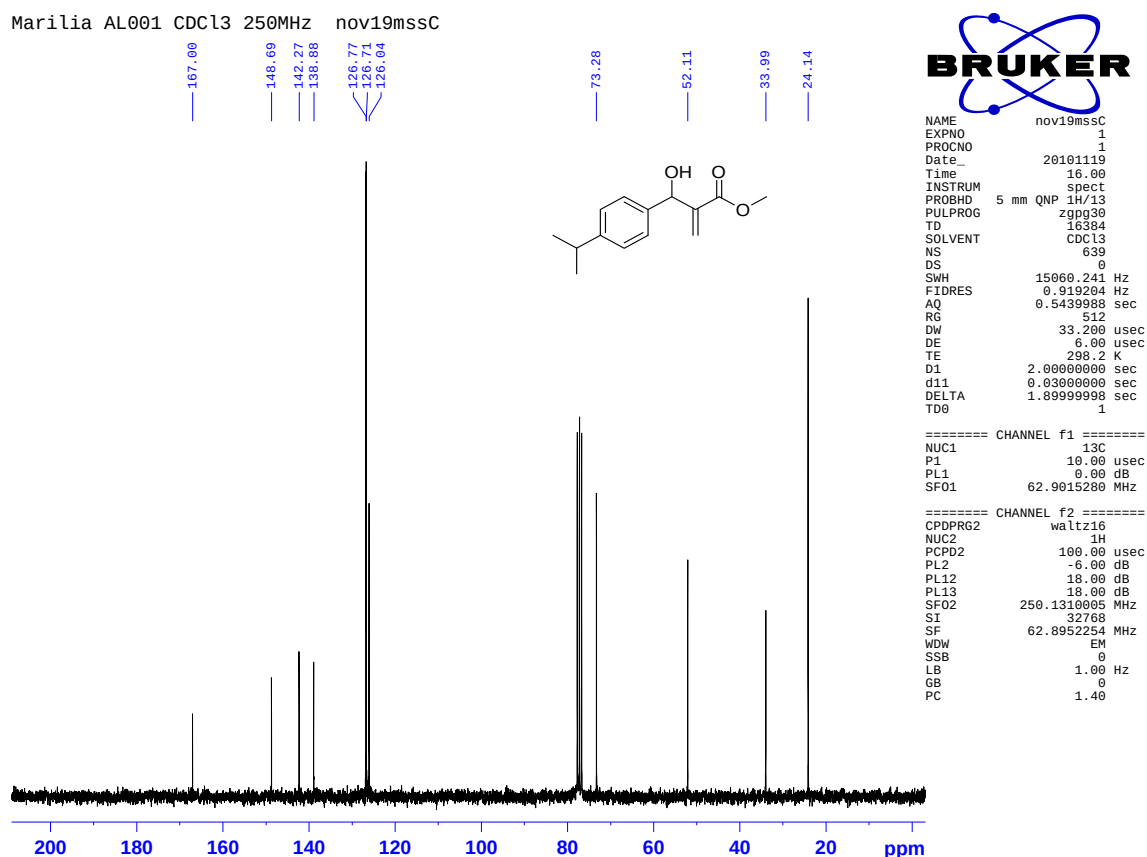
Yield: 66%, colorless oil; IR (film, $\nu_{\max}$): 3451, 2960, 2871, 1723, 1631, 1149, 822 cm^{-1} . ^1H NMR (250 MHz,

CDCl_3): δ 1.25 (d, $^3J = 6.9\text{Hz}$, 6H); 2.91 (m, $^3J = 6.9\text{Hz}$, 1H), 2.98 (d, $^3J = 5.5\text{Hz}$, 1H); 3.73 (s, 3H); 5.55 (d, $^3J = 5.4\text{Hz}$, 1H); 5.87 (s, 1H); 6.34 (s, 1H); 7.21 (d, $^3J = 8.3\text{Hz}$, 2H); 7.30 (d, $^3J = 8.3\text{Hz}$, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 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 $\text{C}_{14}\text{H}_{19}\text{O}_3$ 235.1329 $[\text{M} + \text{H}]^+$; found 235.1328.

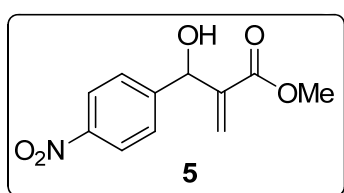
Marilia AL001 CDCl_3 250MHz nov19mssH1



^1H NMR (250 MHz, CDCl_3) spectrum of the MBH adduct **4**.



¹³C NMR (62.5 MHz, CDCl₃) 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^{1,2}; IR (KBr, $\nu_{\max}$): 3230, 2995, 1723, 1633, 1503, 1331, 1154, 1050 cm⁻¹. ¹H

NMR (250 MHz, CDCl₃): δ 3.35 (d, ³J = 6.2Hz, 1H); 3.75 (s, 3H); 5.63 (d, ³J = 6.0Hz, 1H); 5.88 (s, 1H); 6.40 (s, 1H); 7.57 (d, ³J = 8.6Hz; 2H); 8.20 (d, ³J = 8.8Hz; 2H). ¹³C

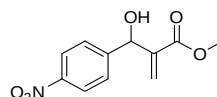
NMR (62.5 MHz, CDCl₃): δ 52.4; 72.9; 123.8; 127.5; 127.5; 141.2; 147.7; 148.8; 166.6.

HRMS (ESI, m/z): Calcd. for C₁₁H₁₂NO₅ 238.0710 [M + H]⁺; found 238.0709.

¹ Cai, J; Zhou, Z.; Zhao, G.; Tang, C. *Org. Lett.*, **2002**, 4723; Coelho, F.; Almeida, W. P.; Veronese, D.; Mateus, C. R.; Lopes, E. C. S.; Rossi, R. C.; Silveira, G. P. C.; Pavam, C. H. *Tetrahedron* **2002**, 58, 7437.

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.

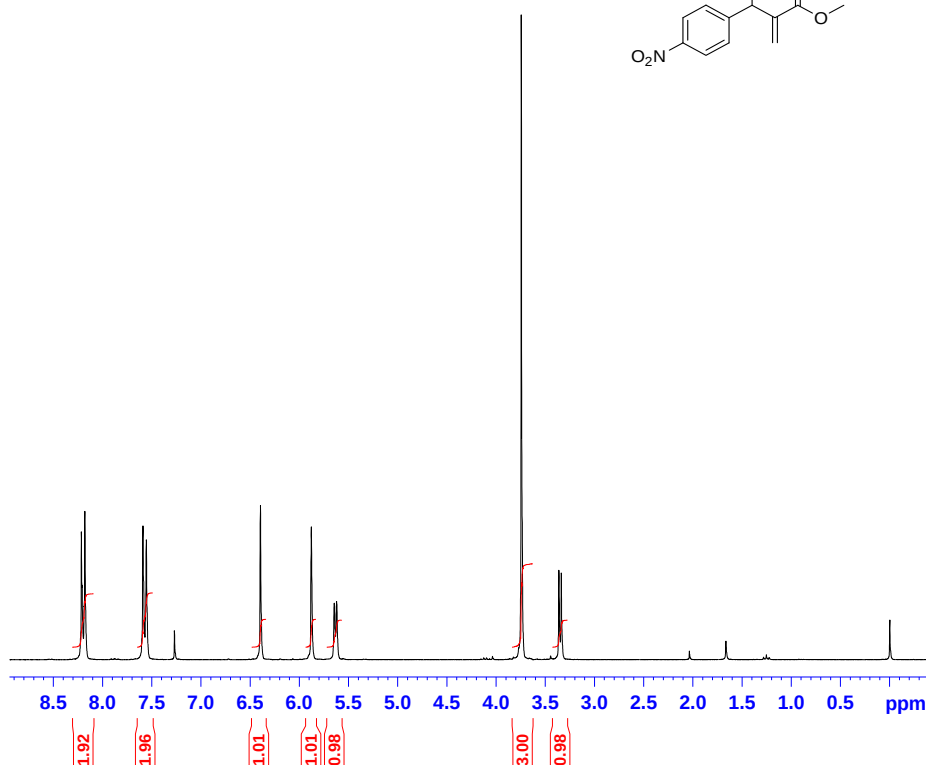
Marilia MS016 CDCl₃/ 250 MHz ago27mssH



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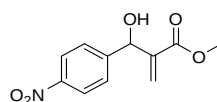
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SWH        5175.983 Hz
FIDRES     0.157059 Hz
AQ         3.1654389 sec
RG         812.7
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DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
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PL1        -6.00 dB
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SI         32768
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WDW        EM
SSB        0
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¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 5.

Marilia MS016 CDCl₃/ 250 MHz ago27mssC

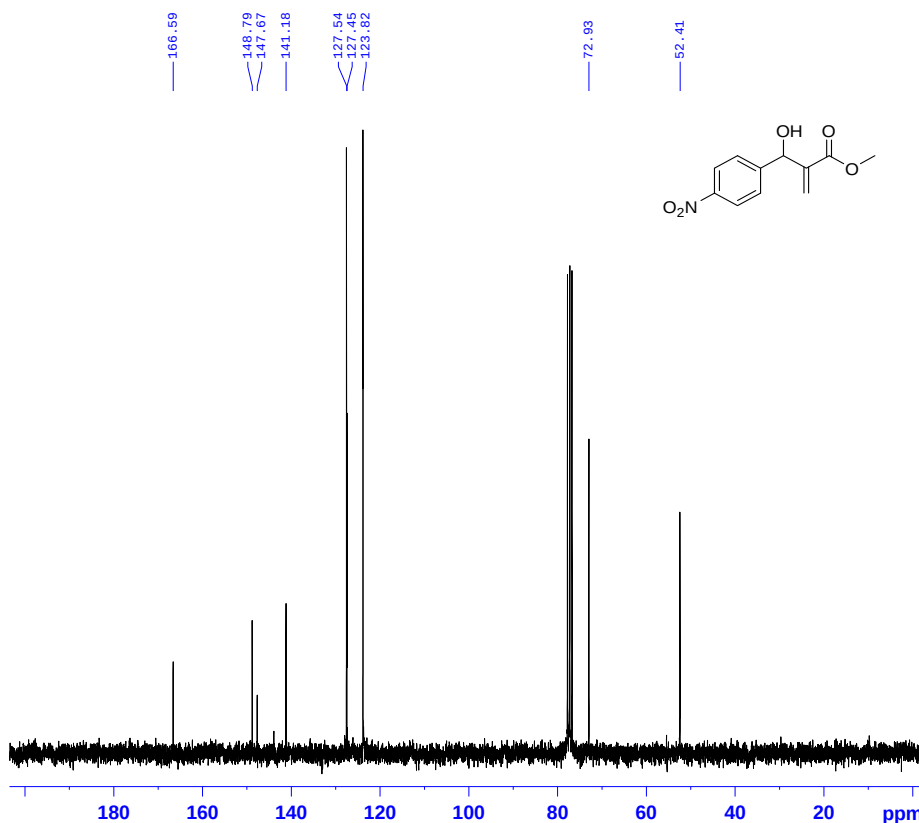


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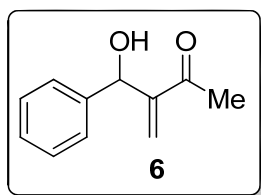
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SWH        15060.241 Hz
FIDRES     0.919204 Hz
AQ         0.5439983 sec
RG         456.1
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0        1

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PL1        0.00 dB
SF01       62.9015280 MHz

===== CHANNEL f2 =====
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NUC2       1H
PCPD2      100.00 usec
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PL13       18.00 dB
SF02       250.1310005 MHz
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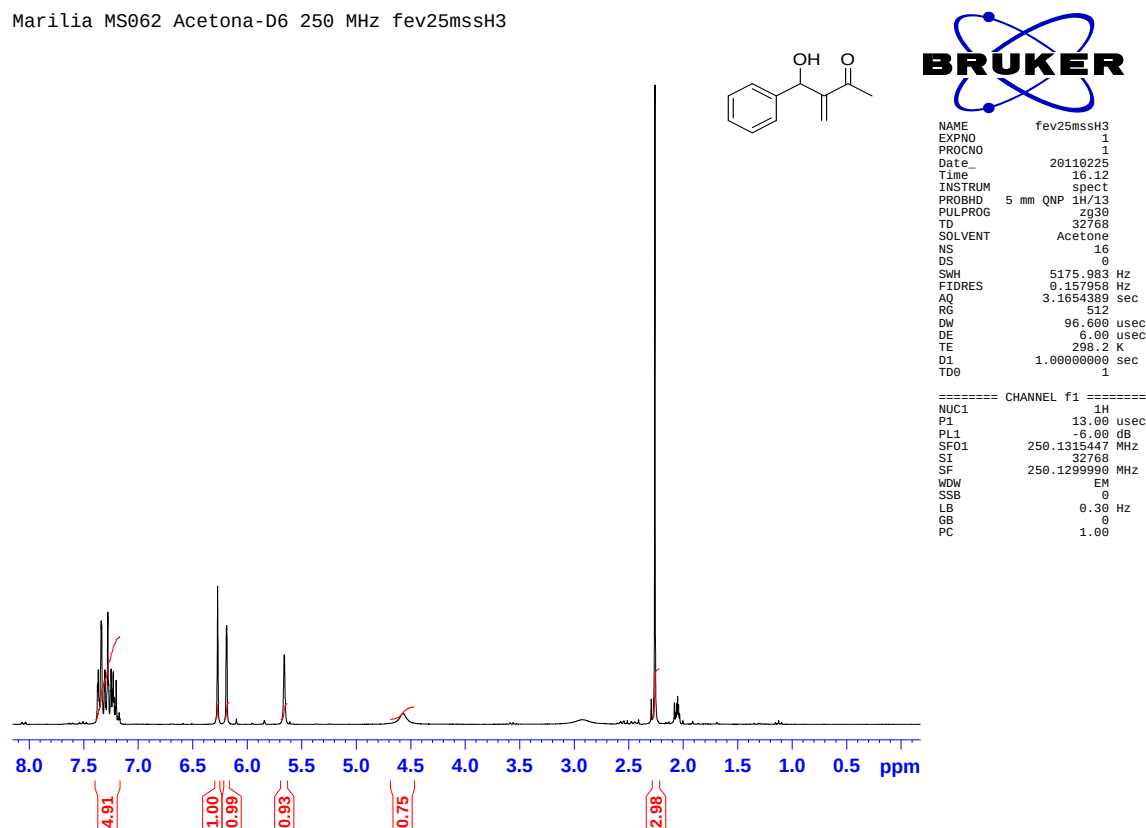
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct 5.



(±)-3-[Hydroxy(phenyl)methyl]but-3-en-2-one (**6**)

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

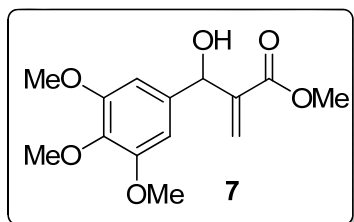
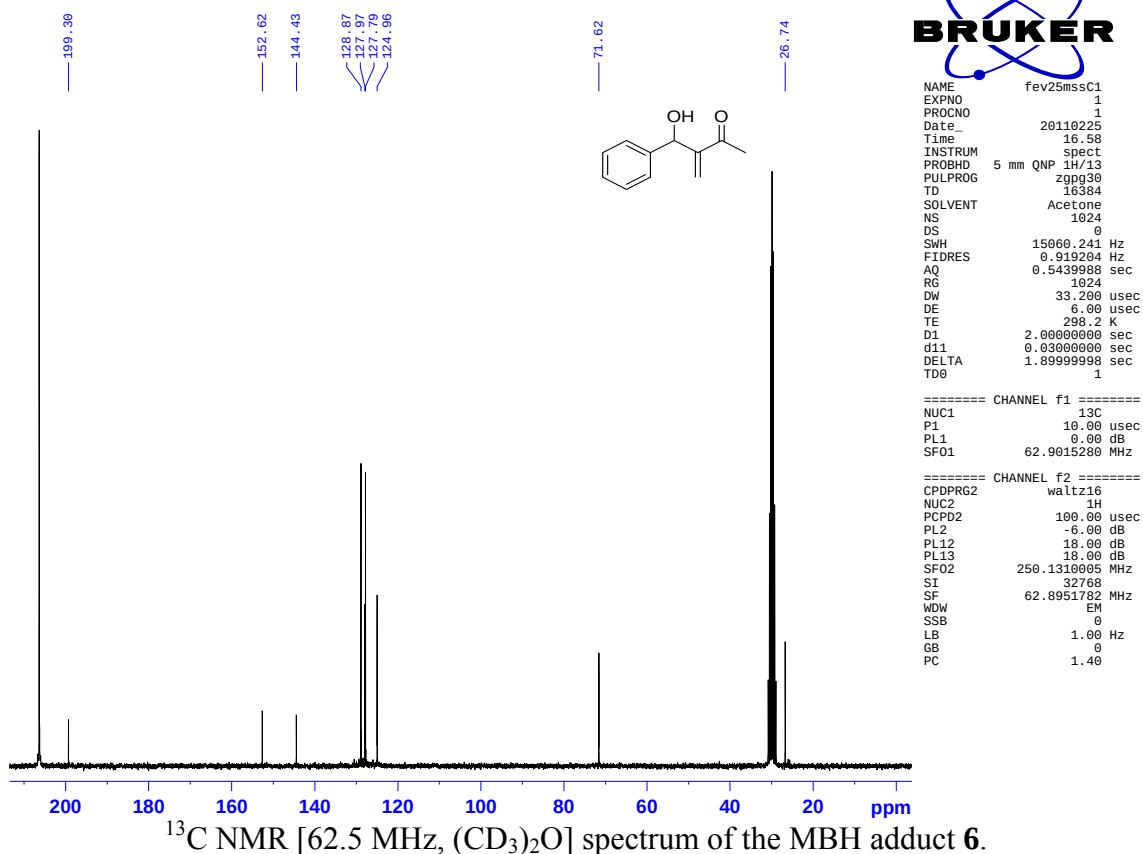
Marilia MS062 Acetona-D6 250 MHz fev25mssH3



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

³ This MBH reaction was performed with only 2 equivalents of methylvinylketone, since this acrylate is prone to polymerization.

Marilia MS062 Acetona-D6 250 MHz fev25mssC1



(±)-Methyl

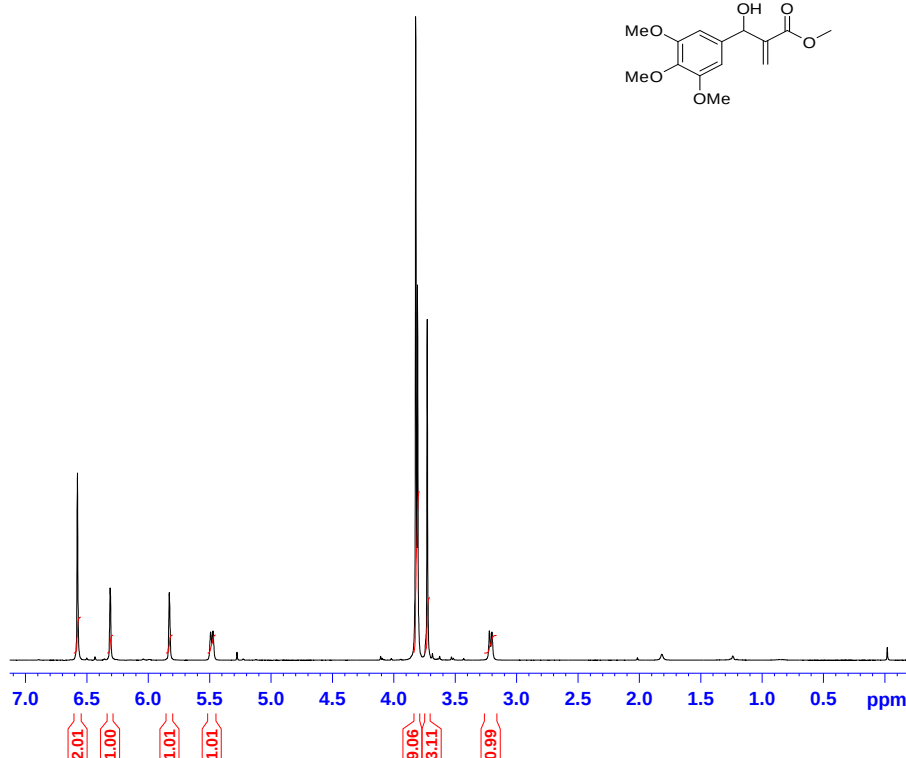
2-[hydroxy(3,4,5-

trimethoxyphenyl)methyl]prop-2-enoate (**7**)

Yield: 71%, yellow oil; IR (film, ν_{max}): 3488, 2942, 2839, 1721, 1593, 1233, 1127 cm^{-1} . ¹H NMR (250 MHz, CDCl₃): δ 3.21 (d, ³J = 5.2 Hz, 1H); 3.73 (s, 3H); 3.81 (s,

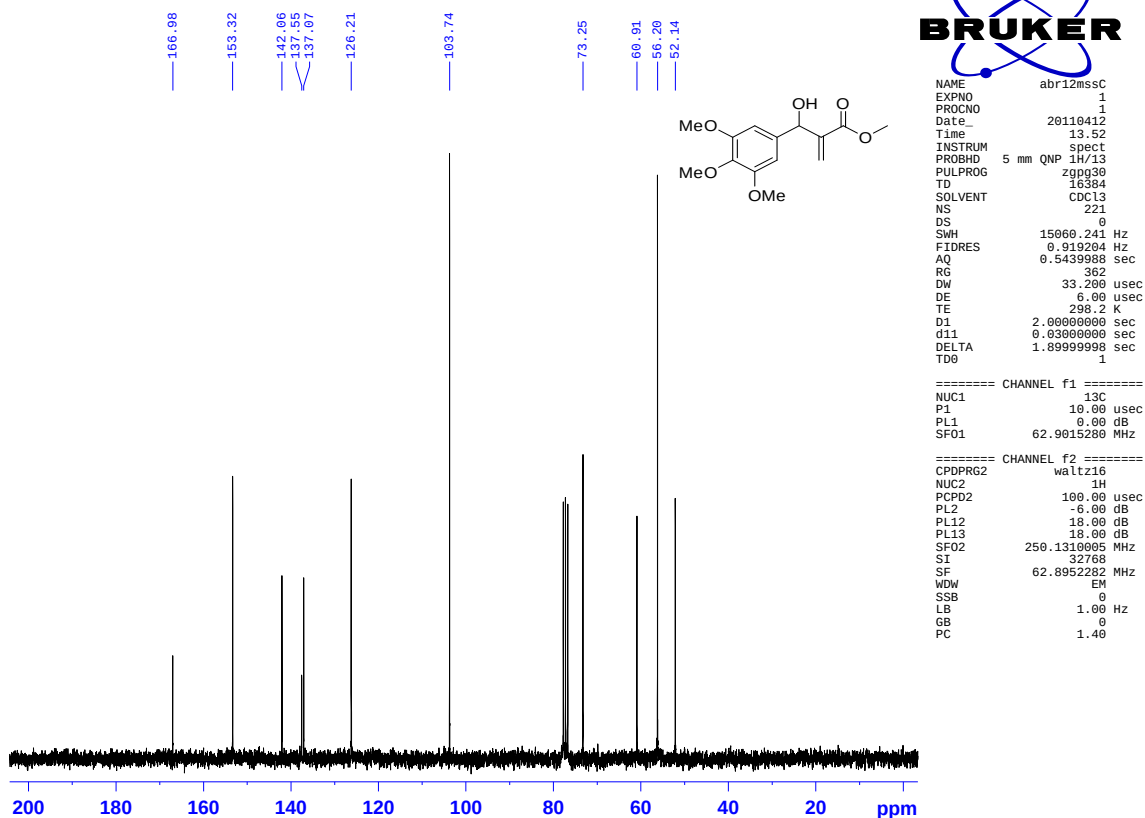
3H); 3.82 (s, 6H); 5.48 (d, ³J = 4.8 Hz, 1H); 5.83 (s, 1H); 6.31 (s, 1H); 6.58 (s, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 52.1; 56.2; 60.9; 73.3; 103.7; 126.2; 137.1; 137.6; 142.1; 153.3; 167.0. HRMS (ESI, *m/z*): Calcd. for C₁₄H₁₉O₆ 283.1176 [M + H]⁺; found 283.1173.

Marilia MS095 CDCl₃ 250MHz abr12mssH2

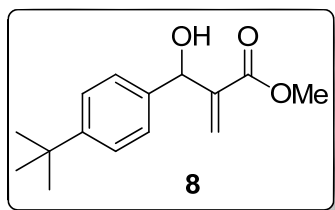


¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct 7.

Marilia MS095 CDCl₃ 250MHz abr12mssC



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct 7.

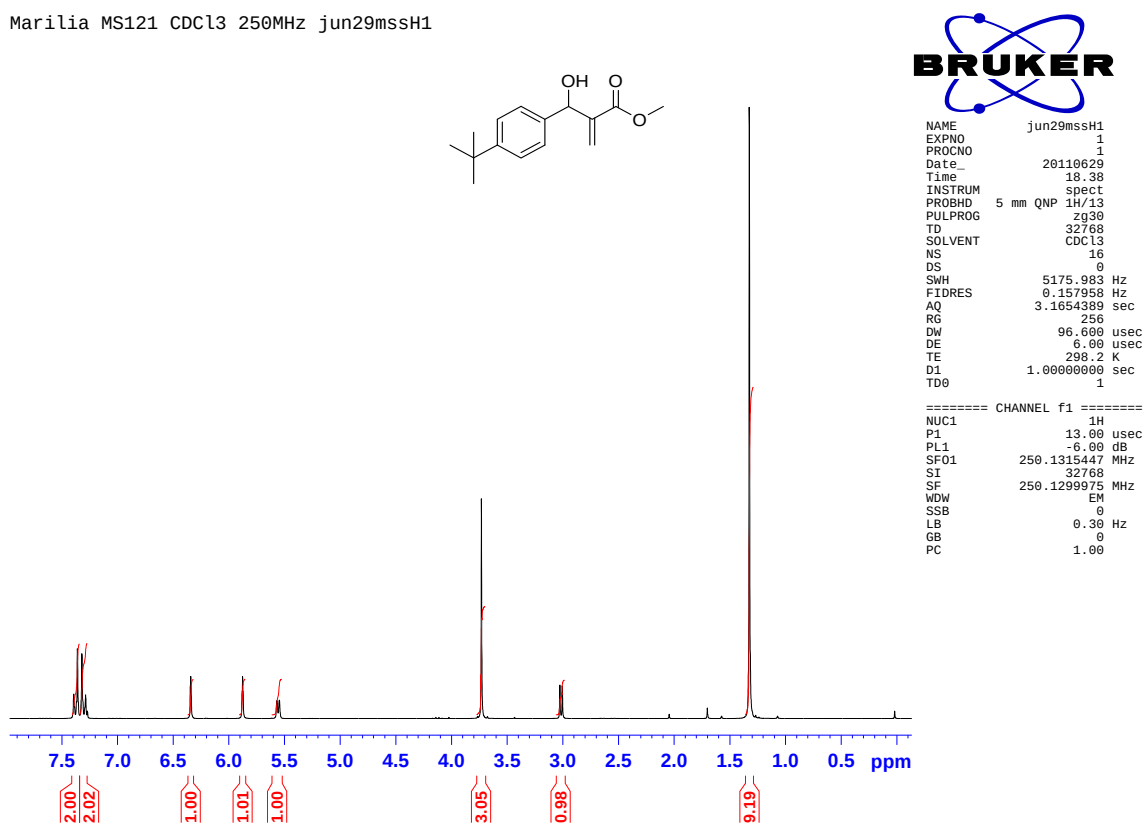


(±)-Methyl 2-[(4-*tert*-butylphenyl)(hydroxy)methyl]prop-2-enoate (**8**)

Yield: 77%, white solid, m.p. 64-66 °C; IR (KBr, $\nu_{\max}$): 3454, 2962, 2905, 2869, 1723, 1630, 1270, 1149, 1042, 854 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 1.32 (s, 9H); 3.02

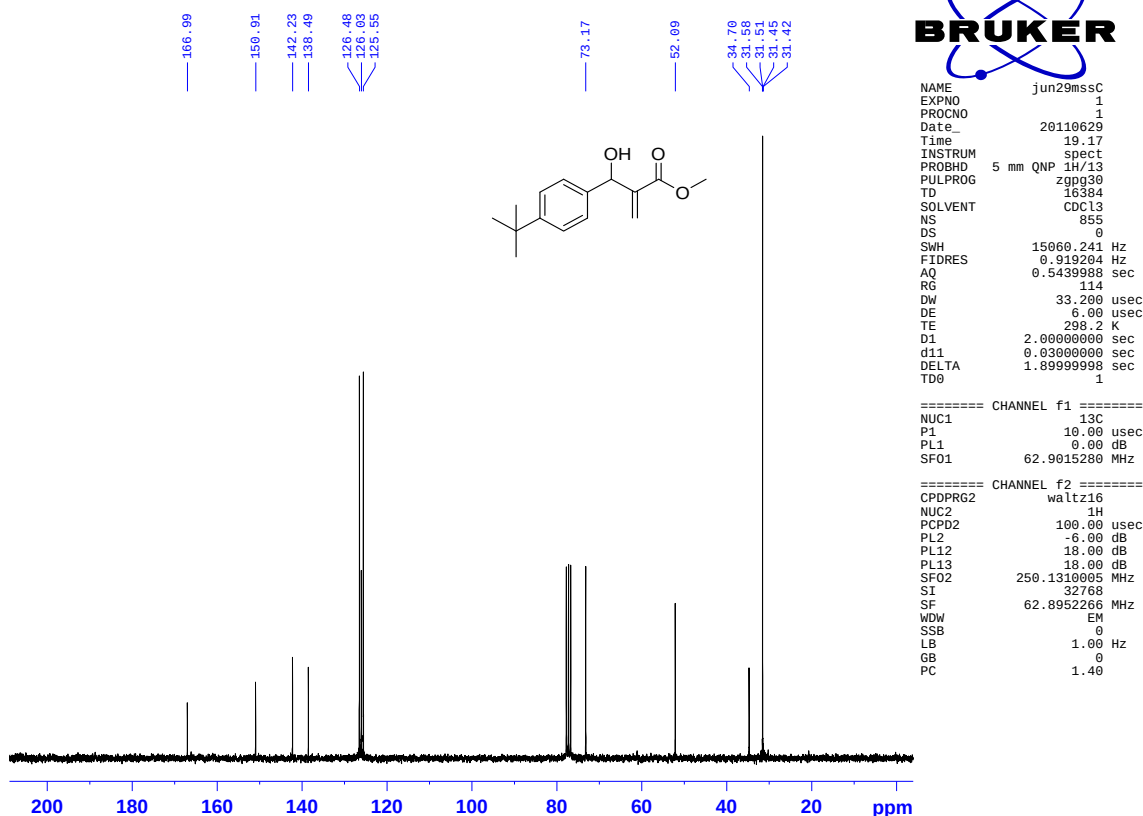
(d, $^3J = 5.5\text{Hz}$, 1H); 3.73 (s, 3H); 5.56 (d, $^3J = 5.4\text{Hz}$, 1H); 5.88 (s, 1H); 6.34 (s, 1H); 7.30 (d, $^3J = 8.5\text{Hz}$, 2H); 7.38 (d, $^3J = 8.5\text{Hz}$, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 31.2; 34.7; 52.09; 125.6; 126.0; 126.5; 138.5; 142.2; 150.9; 167.0. HRMS (ESI, m/z): Calcd. for $\text{C}_{15}\text{H}_{21}\text{O}_3$ 249.1485 $[\text{M} + \text{H}]^+$; found 249.1484.

Marilia MS121 CDCl_3 250MHz jun29mssH1

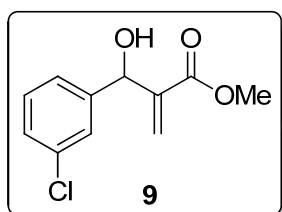


^1H NMR (250 MHz, CDCl_3) spectrum of the MBH adduct **8**.

Marilia MS121 CDCl₃ 250MHz jun29mssC



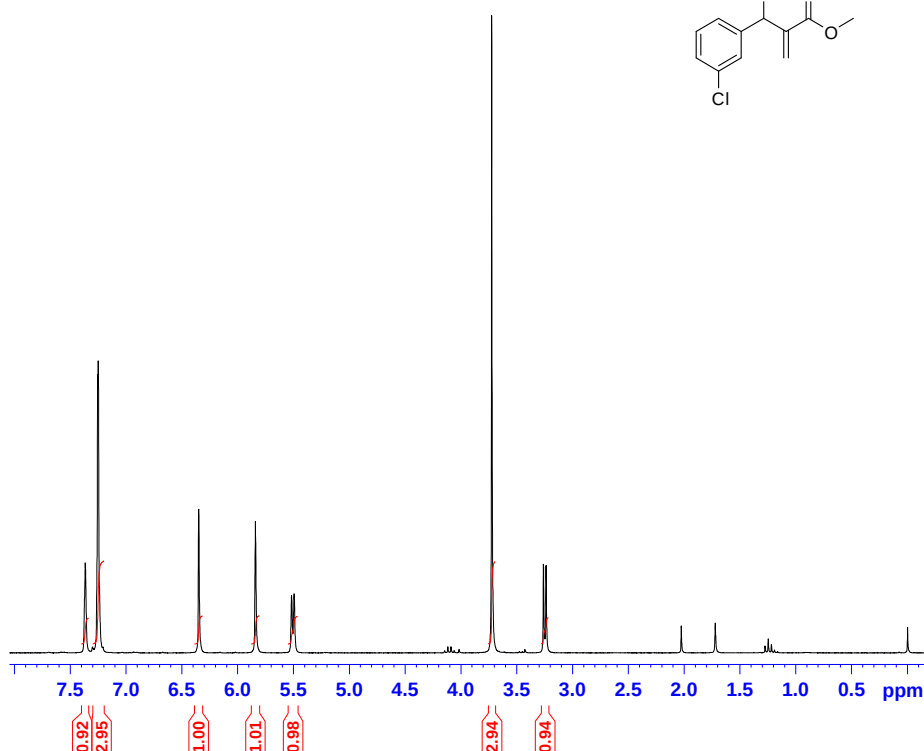
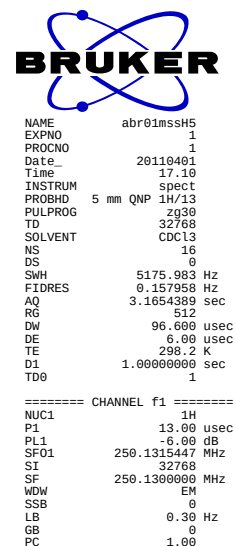
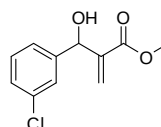
¹H NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct **8**.



(±)-Methyl 2-[(3-chlorophenyl)(hydroxy)methyl]prop-2-enoate
(**9**)

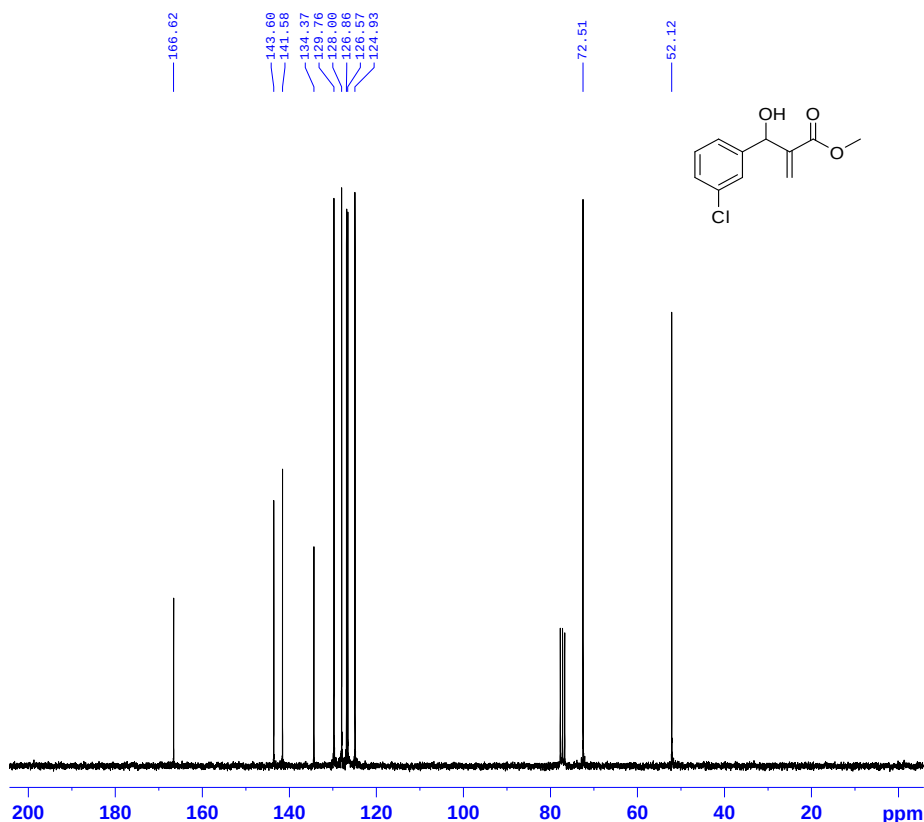
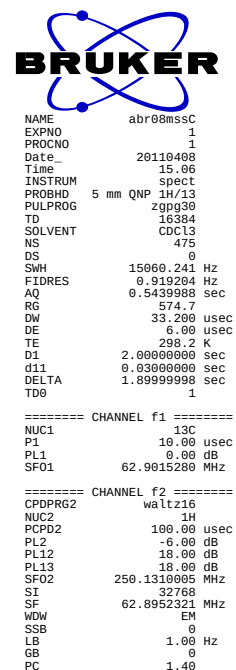
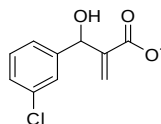
Yield: 80%, colorless oil; IR (film, ν_{max}): 3451, 2953, 1717, 1630, 1152, 884 cm⁻¹; ¹H NMR (250 MHz, CDCl₃): δ 3.25 (d, ³J = 5.8 Hz, 1H); 3.72 (s, 3H); 5.51 (d, ³J = 5.7 Hz, 1H); 5.84 (s, 1H); 5.85 (s, 1H); 7.25 (s, 3H); 7.37 (s, 1H). ¹³C NMR (62.5 MHz, CDCl₃): δ 52.1; 72.5; 124.9; 126.6; 126.9; 128.0; 129.8; 134.4; 141.6; 143.6; 166.6. HRMS (ESI, m/z): Calcd. for C₁₁H₁₂ClO₃ 227.0469 [M + H]⁺; found 227.0468.

Marilia MS096 CDCl₃ 250MHz abr01mssH5

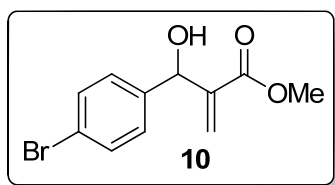


¹H NMR (250 MHz, CDCl₃) spectrum of the MBH adduct **9**.

Marilia MS096 CDCl₃ 250MHz abr08mssc



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct **9**.

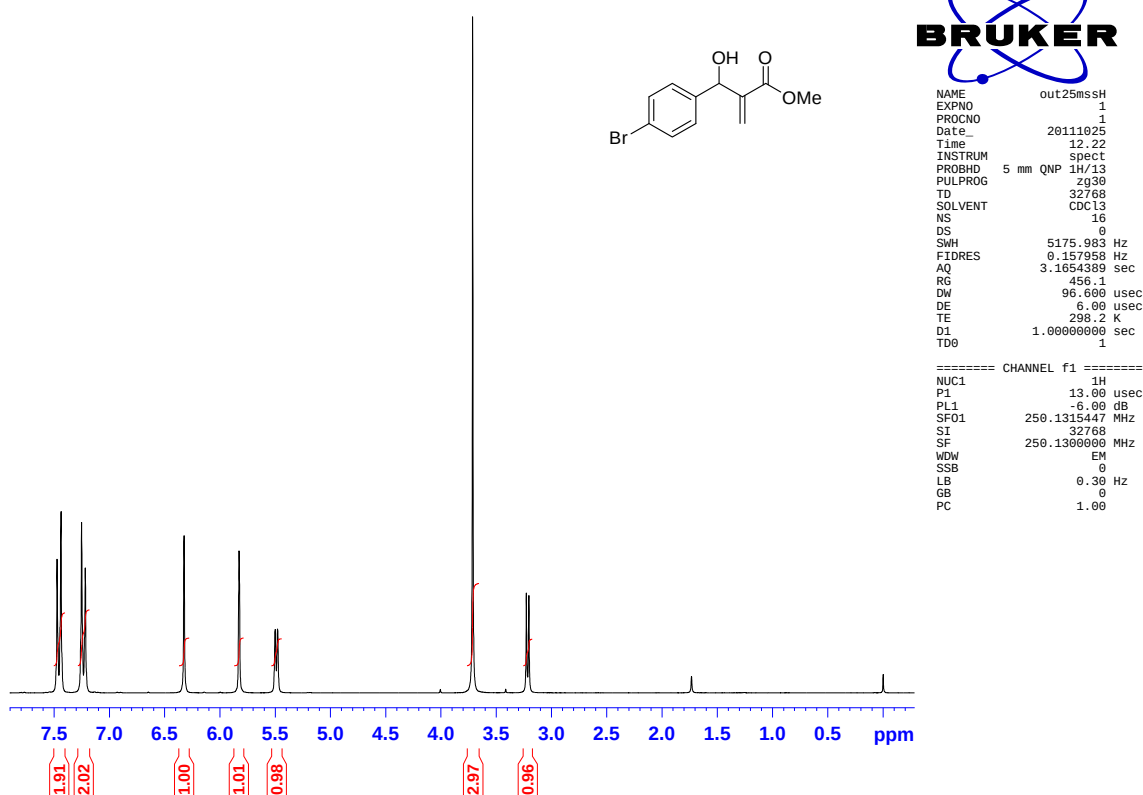


(±)-Methyl 2-[(4-bromophenyl)(hydroxy)methyl]prop-2-enoate (**10**)

Yield: 75%, white solid, m.p. 63-66 °C; IR (KBr, $\nu_{\max}$): 3342; 2959; 1717; 1635, 1274, 1160, 812 cm^{-1} . ^1H NMR

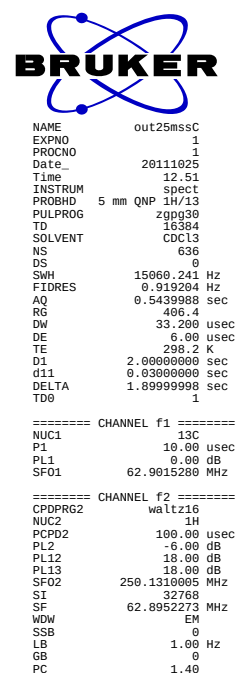
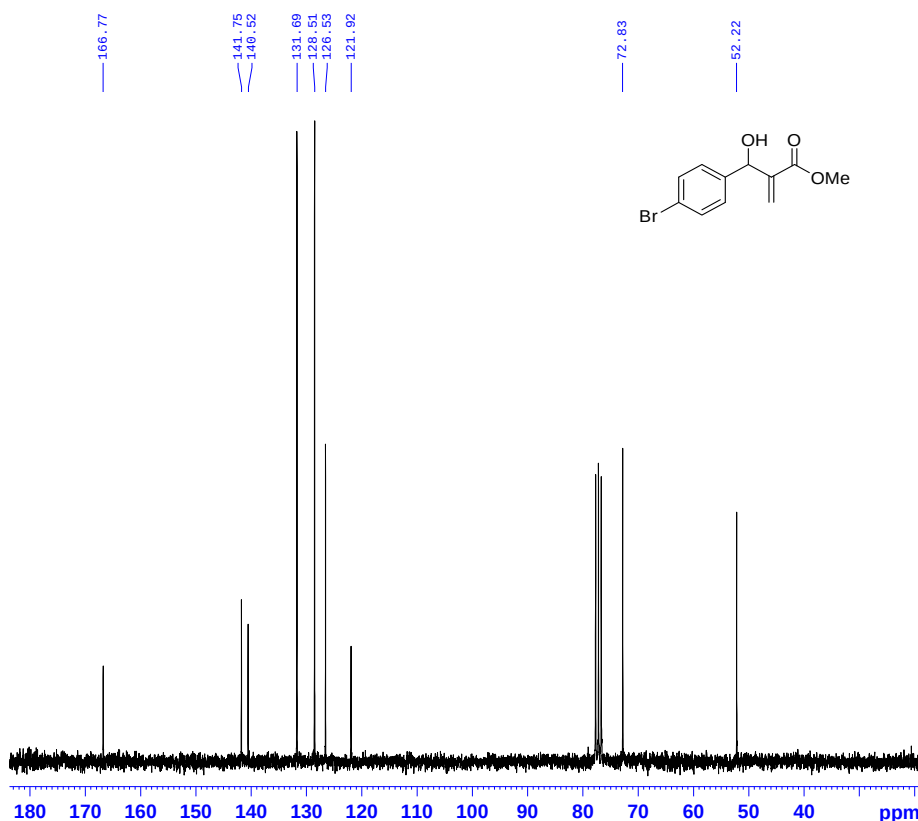
(250 MHz, CDCl_3): δ 3.22 (d, $^3J = 5.7$ Hz, 1H); 3.71 (s, 3H); 5.49 (d, $^3J = 5.6$ Hz, 1H); 5.83 (s, 1H); 6.33 (s, 1H); 7.24 (d, $^3J = 8.4$ Hz, 2H); 7.46 (d, $^3J = 8.4$ Hz, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 52.2; 72.8; 121.9; 126.5; 128.5; 131.7; 140.5; 141.7; 166.8. HRMS (ESI, m/z): Calcd. for $\text{C}_{11}\text{H}_{12}\text{BrO}_3$ 270.9964 $[\text{M} + \text{H}]^+$; found 270.9961.

Marilia ADTBr CDCl_3 250MHz out25mssH

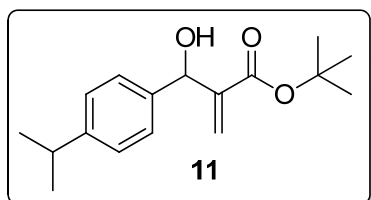


^1H NMR (250 MHz, CDCl_3) spectrum of the MBH adduct **10**.

Marilia ADTBr CDCl₃ 250MHz out25mssc



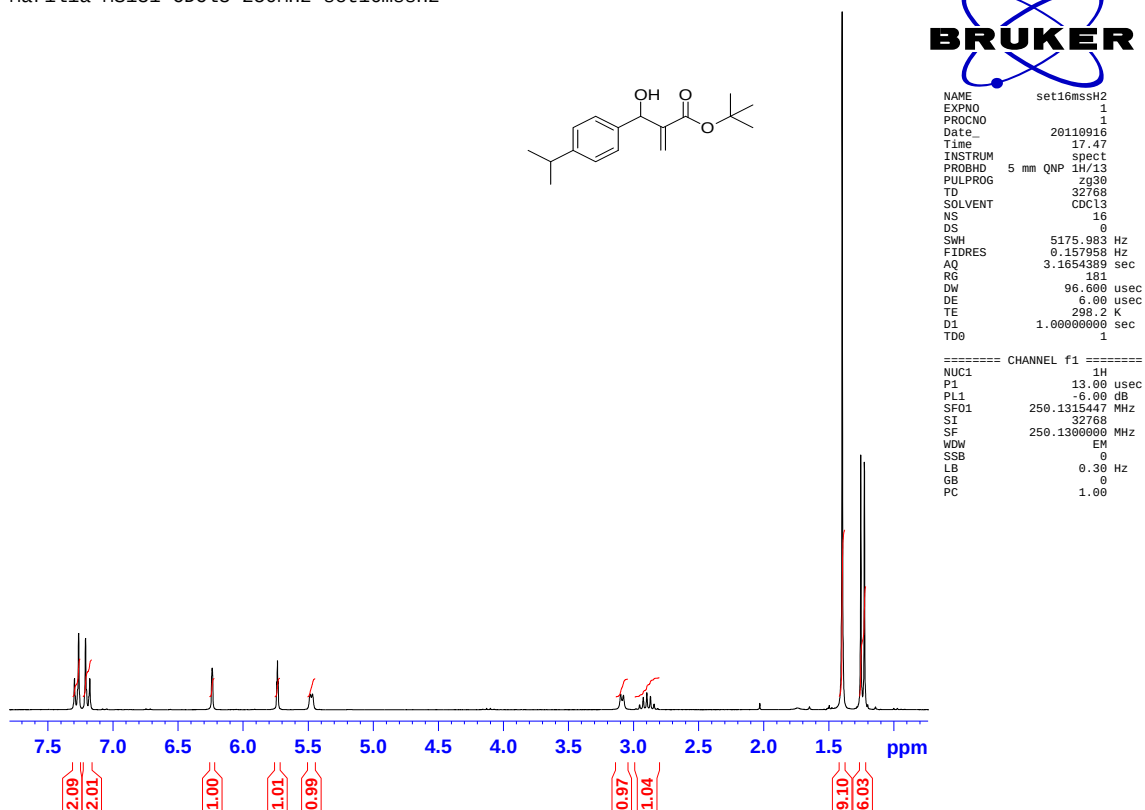
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the MBH adduct **10**.



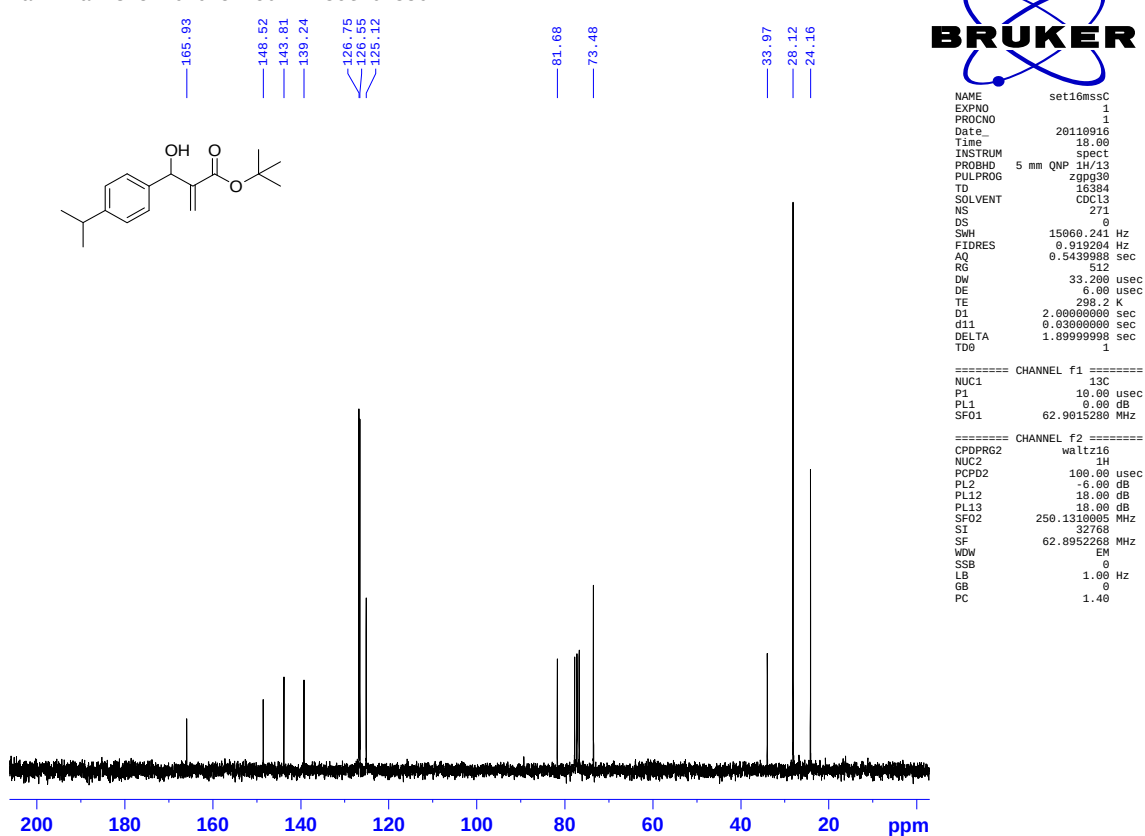
tert-Butyl 2-{hydroxy[4-(propan-2-yl)phenyl]methyl}prop-2-enoate (**11**)

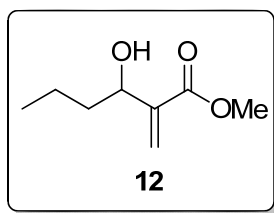
Yield: 52%, yellow tinged oil; IR (film, ν_{max}): 3441, 2962, 2931, 1716, 1630, 1150, 893, cm^{-1} . ¹H NMR (250 MHz, CDCl₃): δ 1.24 (d, $^3J = 6.9$ Hz, 3H); 1.40 (s, 9H); 2.90 (m, 1H); 3.09 (d, $^3J = 5.4$ Hz, 1H); 5.48 (d, $^3J = 4.4$ Hz, 1H); 5.74 (t, 1H); 6.24 (s, 1H); 7.19 (d, $^3J = 8.2$ Hz, 2H); 7.28 (d, $^3J = 8.3$ Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 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 C₁₇H₂₃O₂ 259.1698 [M + H]⁺; found 259.1667.

Marilia MS131 CDCl₃ 250MHz set16mssH2



Marilia MS131 CDCl₃ 250MHz set16mssc

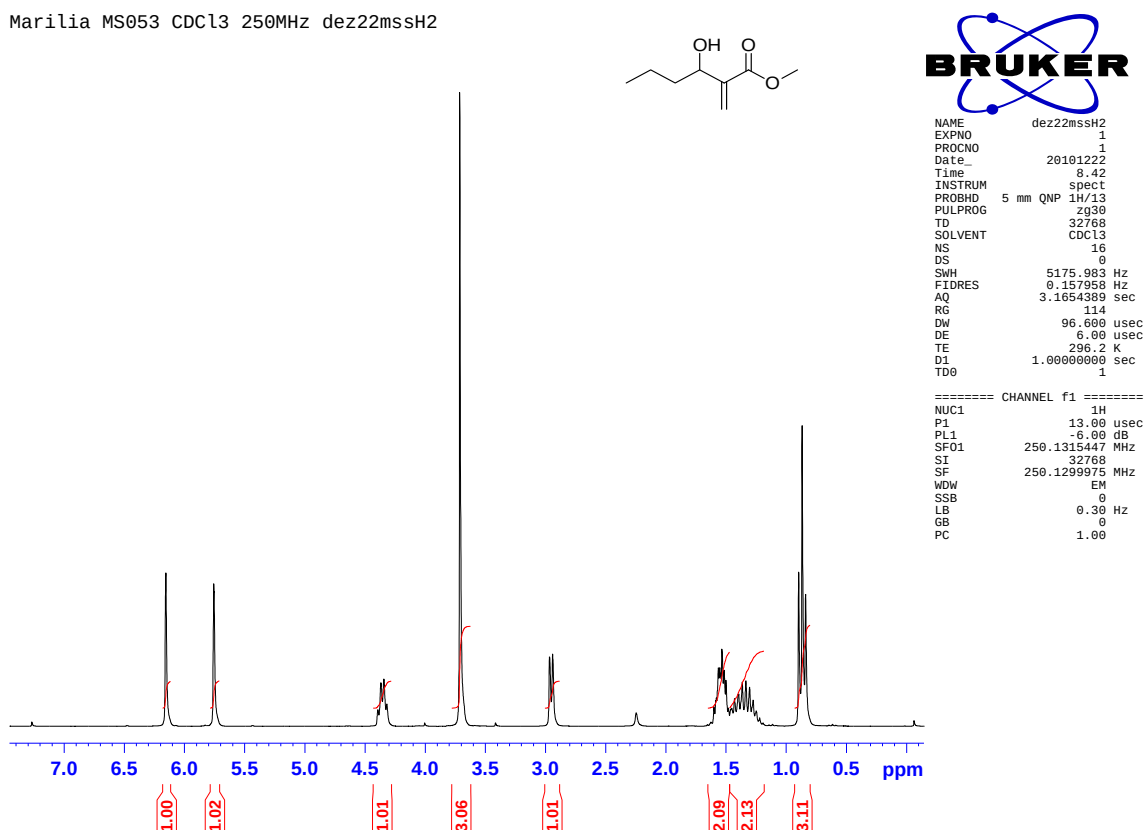




(±)-Methyl 3-hydroxy-2-methylidenehexanoate (**12**)

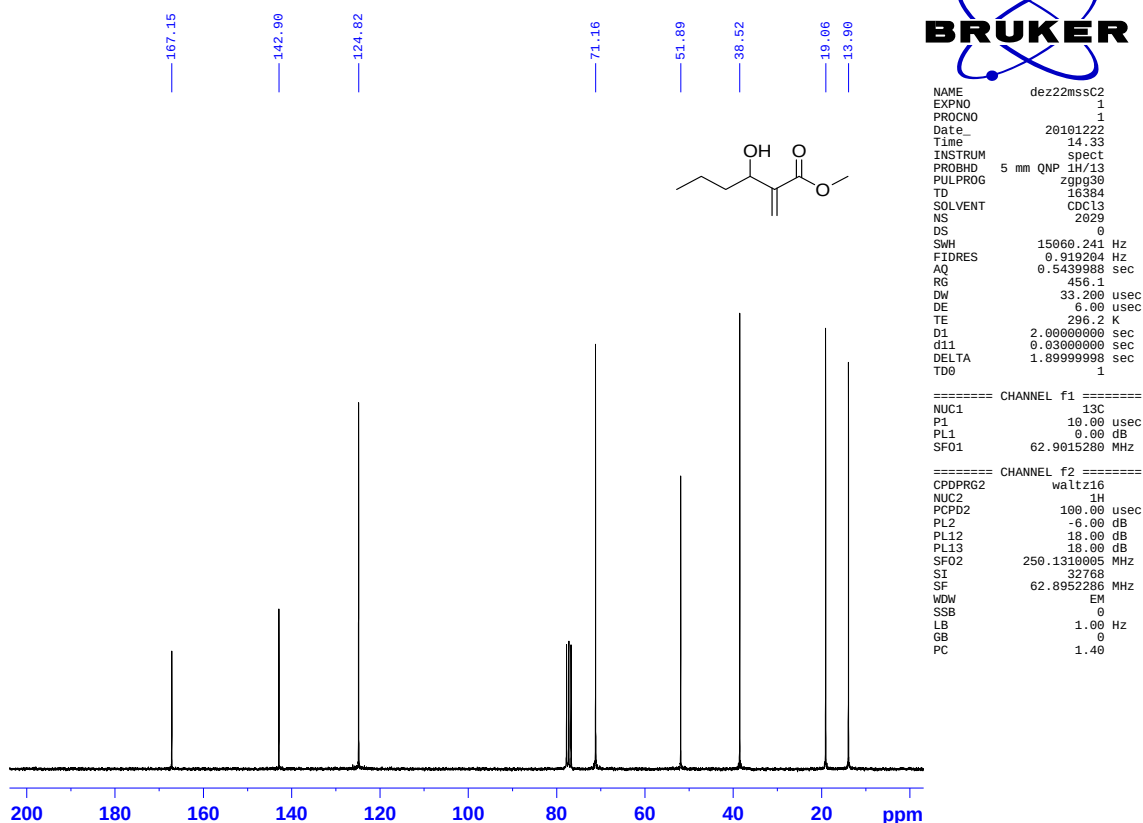
Yield: 95%, colorless oil; IR (film, $\nu_{\max}$): 3427, 2959, 2874, 1720, 1631, 1440, 1290, 1111 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 0.87 (t, $^3J = 7.2\text{Hz}$, 3H); 1.34 (m, 2H); 1.54 (m, 2H); 2.95 (d, $^3J = 6.3\text{Hz}$, 1H); 3.71 (t, 3H); 4.36 (q, $^3J = 6.4\text{Hz}$, 1H); 5.76 (s, 1H), 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 $\text{C}_8\text{H}_{15}\text{O}_3$ 159.1016 $[\text{M} + \text{H}]^+$; found 159.1017.

Marilia MS053 CDCl_3 250MHz dez22mssH2



^1H NMR (250 MHz, CDCl_3) spectrum of the MBH adduct **12**.

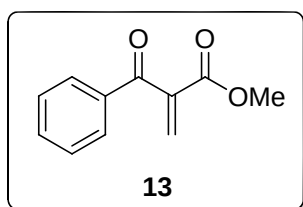
Marilia MS053 CDCl₃ 250MHz dez22mssC2



¹³C NMR (62.5 MHz, CDCl₃) 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

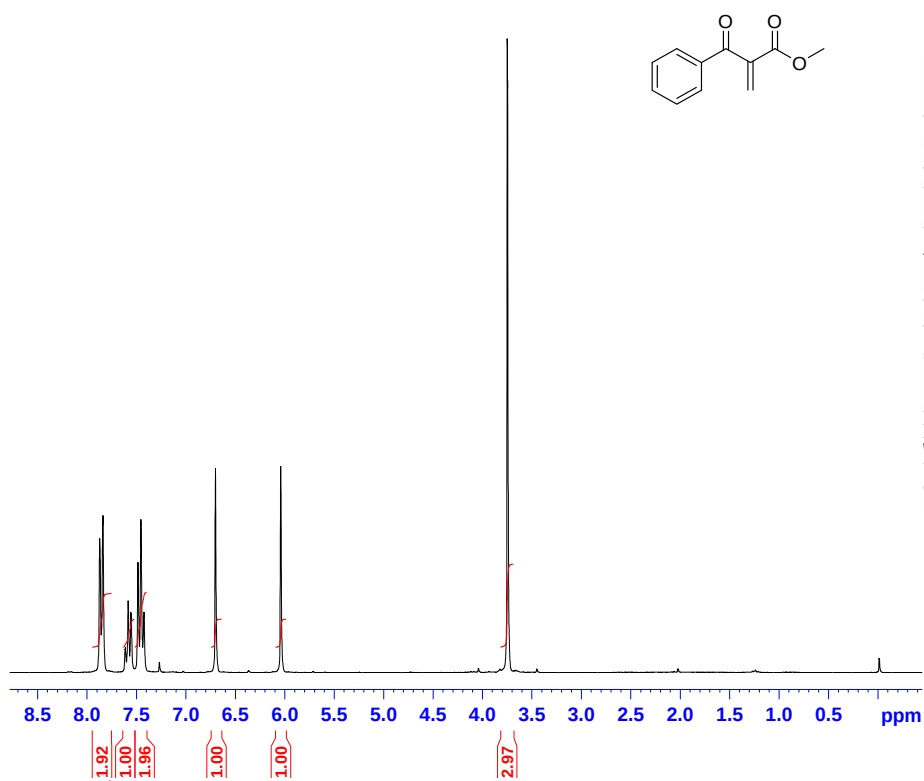


Methyl 2-benzoylprop-2-enoate (**13**)

Yield: 90%, yellow oil; IR (film, $\nu_{\max}$): 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 C₁₁H₁₁O₃ 191.0703 [M + H]⁺; found 191.0701.

⁴ When ethyl acetate was used as solvent 3.0 equivalents of IBX was required.

Marilia MS019 CDCl₃/ 250 MHz ago27mssH2



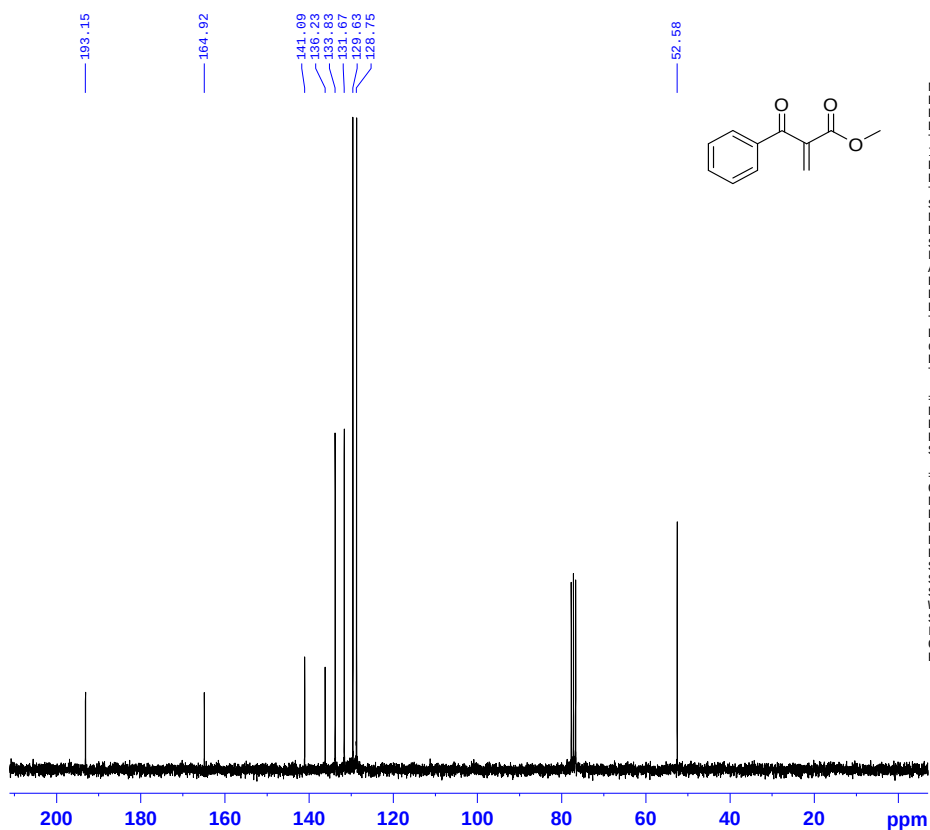
BRUKER

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EXPNO     1
PROCNO    1
Date_     20100827
Time      17.26
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        5175.983 Hz
FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         256
DW         96.600 usec
DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
D0         1

===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        -6.00 dB
SF01       250.1315447 MHz
SI         32768
SF         250.1299976 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
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Marilia MS019 CDCl₃/ 250 MHz ago27mssC1



BRUKER

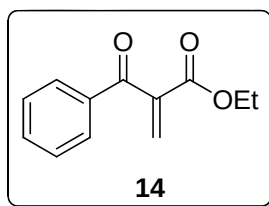
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NAME      ago27mssC1
EXPNO     1
PROCNO    1
Date_     20100827
Time      17.37
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         16384
SOLVENT   CDCl3
NS         207
DS         0
SWH        15060.241 Hz
FIDRES     0.919204 Hz
AQ         0.5439988 sec
RG         812.7
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999999 sec
D0         1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1         0.00 dB
SF01       62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        -6.00 dB
PL12       18.00 dB
PL13       18.00 dB
SF02       250.1310005 MHz
SI         32768
SF         62.8952286 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

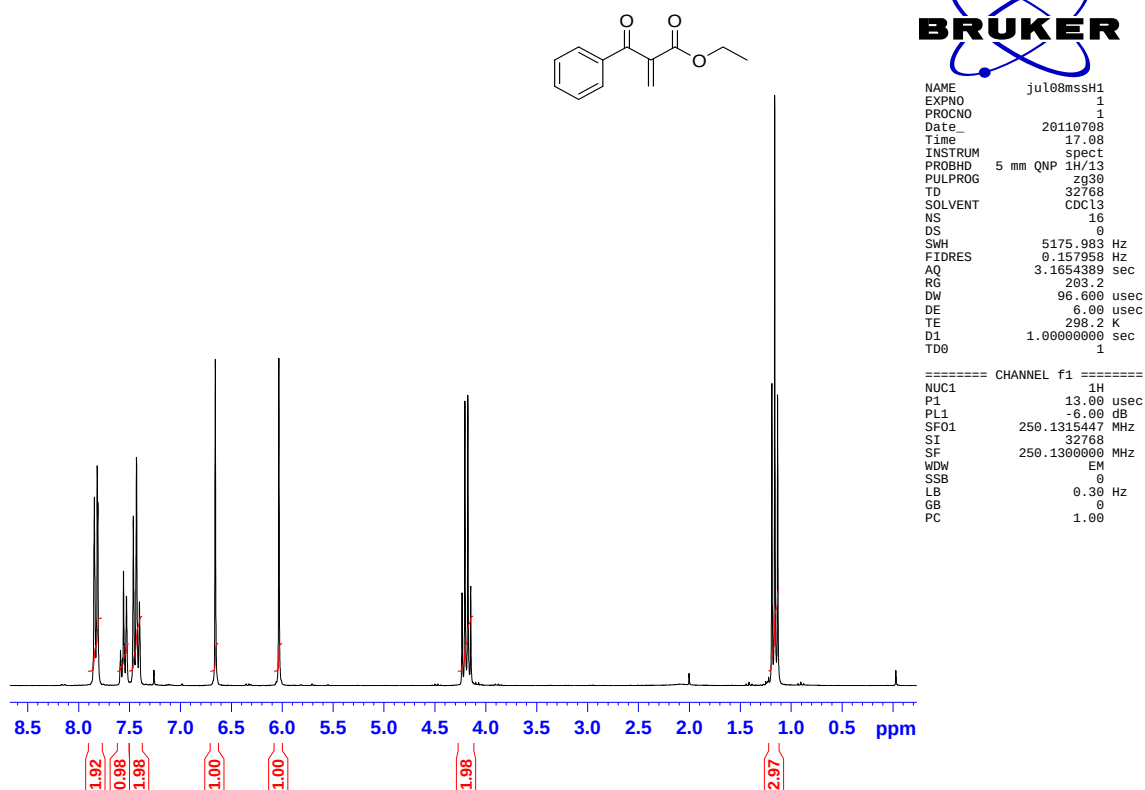
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **13**.



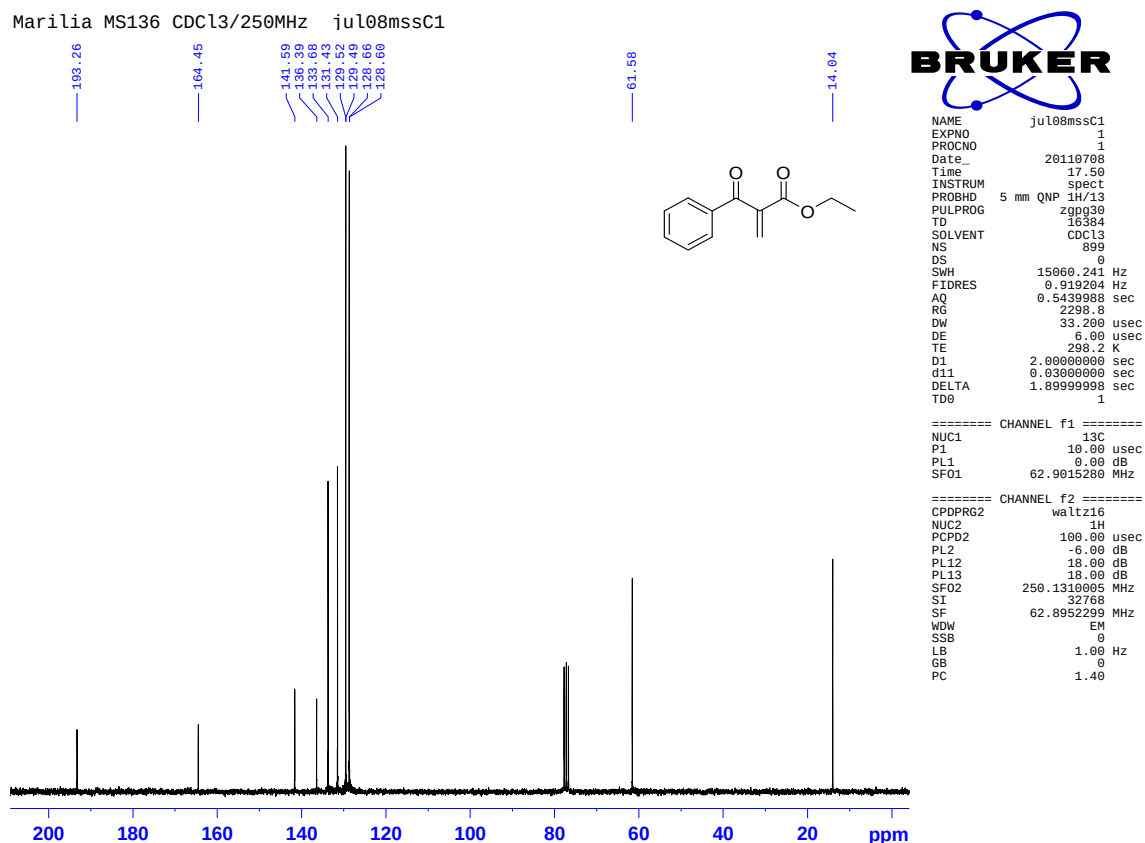
Ethyl 2-benzoylprop-2-enoate (14)

Yield: >95%, colorless oil; IR (film, $\nu_{\max}$): 3062, 2983, 1729, 1679, 1597, 1237, 1153 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 1.17 (t, $^3J = 7.1\text{Hz}$, 3H); 4.20 (q, $^3J = 7.1\text{Hz}$, 2H); 6.04 (s, 1H); 6.67 (s, 1H); 7.71-7.47 (m, 2H); 7.54-7.60 (m, 1H); 7.82-7.86 (m, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 14.0; 61.6; 128.6; 128.7; 129.5; 129.5; 131.4; 133.7; 136.4; 141.6; 164.5; 193.3. HRMS (ESI, m/z): Calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_3$ 205.0864 $[\text{M} + \text{H}]^+$; found 205.0892.

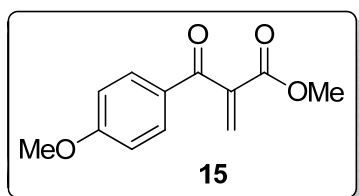
Marilia MS136 $\text{CDCl}_3/250\text{MHz}$ jul08mssH1



^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **14**.



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **14**.

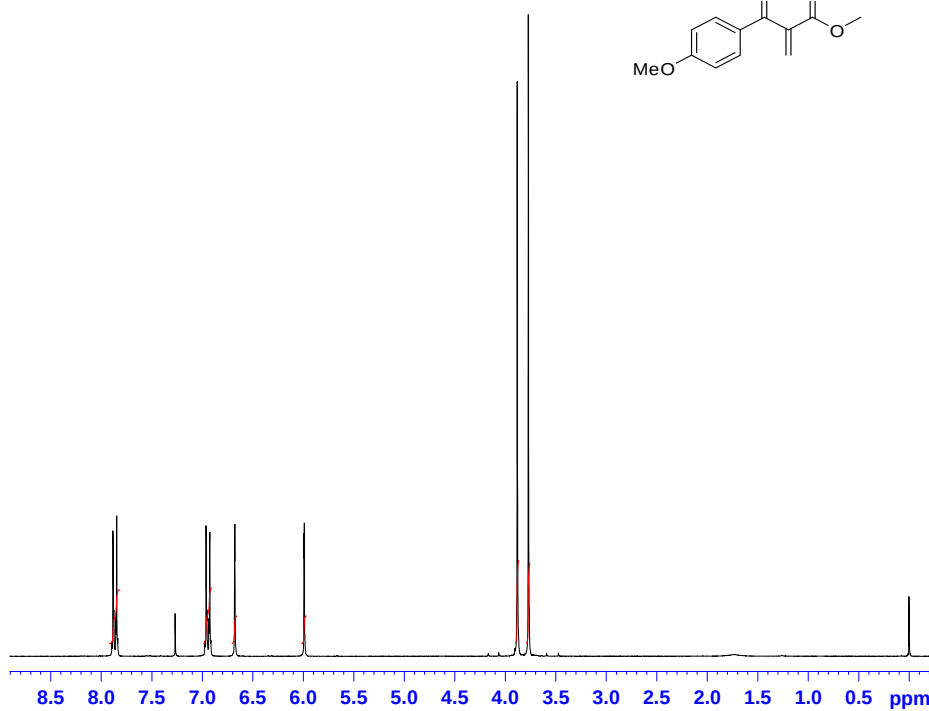


Ethyl 2-[(4-methoxyphenyl)carbonyl]prop-2-enoate (**15**)

Yield: 94%, yellow oil; IR (film, ν_{max}): 2954, 2842, 1729, 1666, 1599, 1262, 1152, 847 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 3.77 (s, 3H); 3.88 (s, 3H); 5.99 (d, ³*J* = 0.8Hz,

2H); 6.68 (d, ³*J* = 0.7Hz, 2H); 6.95 (d, ³*J* = 9.0Hz, 2H); 7.87 (d, ³*J* = 9.0Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ 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 C₁₂H₁₃O₄ 221.0814 [M + H]⁺; found 221.0830.

Marilia MS014 CDCl₃/ 250MHz ago11mssH3



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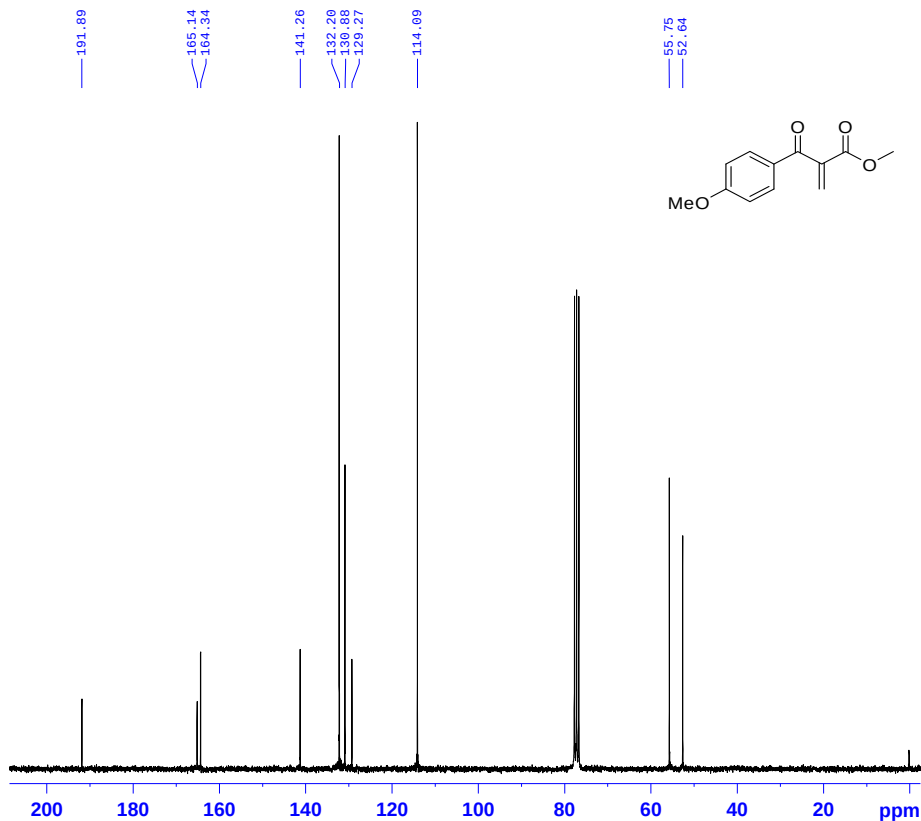
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EXPNO     1
PROCNO    1
Date_     20100811
Time      18.35
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        5175.983 Hz
FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         1024
DW         96.600 usec
DE         6.00 usec
TE         298.2 K
D1         1.0000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        -6.00 dB
SF01       250.1315447 MHz
SI         32768
SF         250.1299978 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester 15.

Marilia MS014 CDCl₃/ 250MHz ago11mssC



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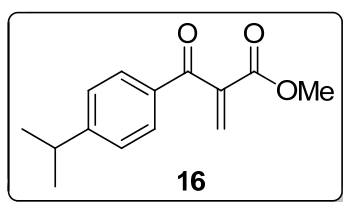
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EXPNO     1
PROCNO    1
Date_     20100812
Time      4.01
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         16384
SOLVENT   CDCl3
NS         10000
DS         0
SWH        15060.241 Hz
FIDRES     0.919204 Hz
AQ         0.5439988 sec
RG         512
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.0000000 sec
d11        0.0300000 sec
DELTA     1.8999999 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        0.00 dB
SF01       62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     100.00 usec
PL2        -6.00 dB
PL12       18.00 dB
PL13       18.00 dB
SF02       250.1310005 MHz
SI         32768
SF         62.8952244 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

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

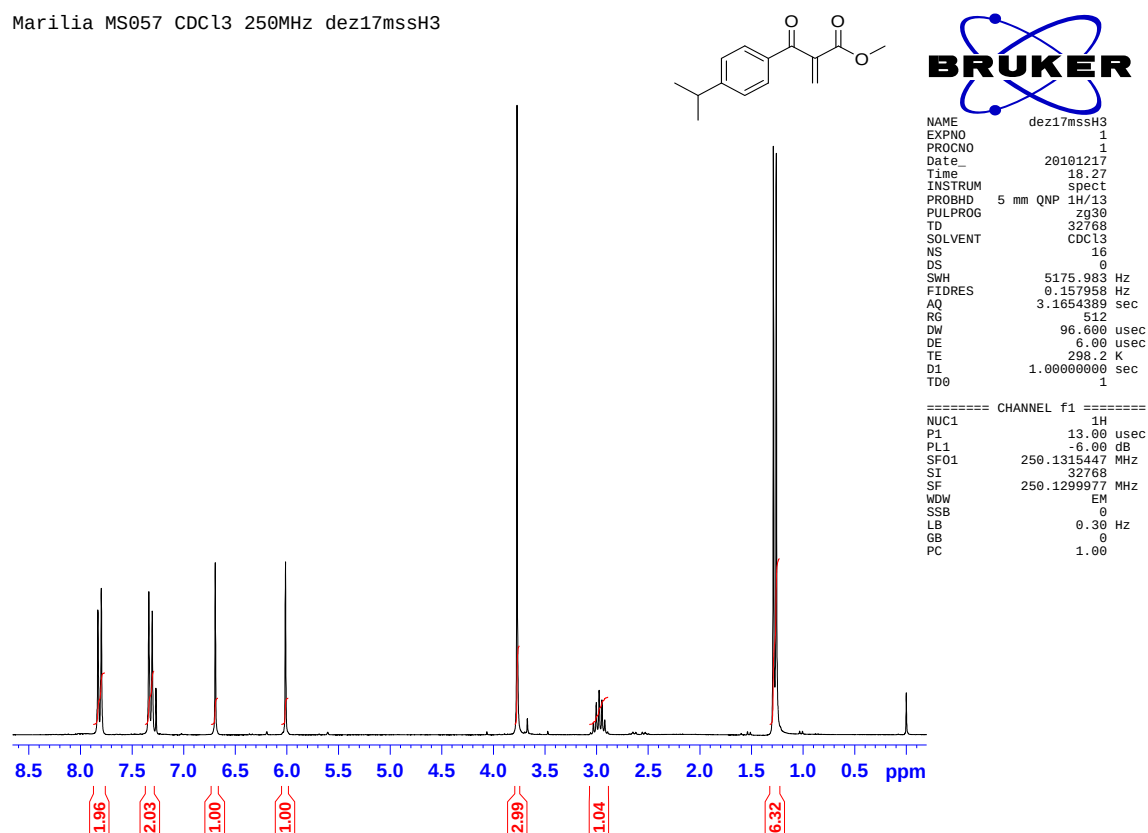


Methyl 2-{[4-(propan-2-yl)phenyl]carbonyl}prop-2-enoate (**16**)

Yield: >95%, yellow oil; IR (film, $\nu_{\max}$): 2962, 2873, 1731, 1673, 1604, 1144, 852 cm^{-1} ; ^1H NMR (250 MHz,

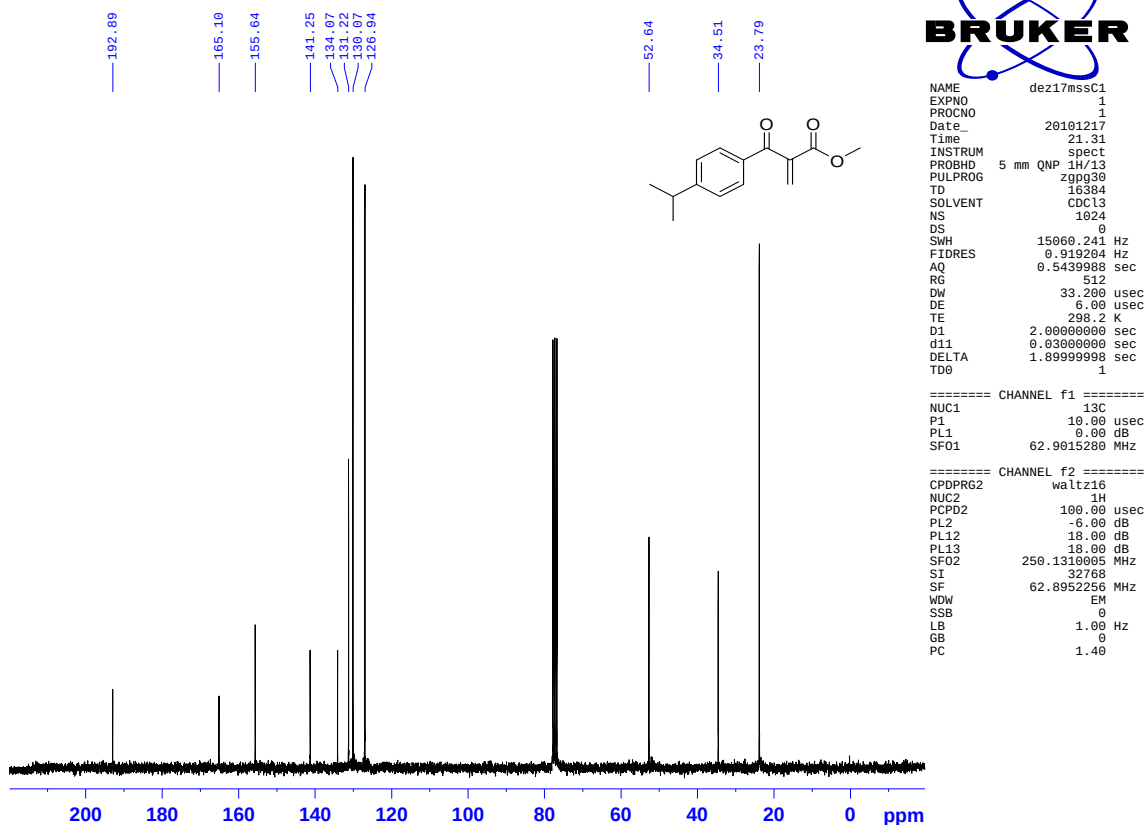
CDCl_3): δ 1.27 (d, $^3J = 6.9\text{Hz}$, 6H); 2.98 (m, $^3J = 6.9\text{Hz}$, 1H); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 73.2 (d, $^3J = 8.2\text{Hz}$, 2H); 7.82 (d, $^3J = 8.3\text{Hz}$, 2H); ^{13}C NMR (62.5 MHz, CDCl_3): δ 23.8; 34.5; 52.6; 127.0; 130.1; 131.2; 134.1; 141.3; 155.6; 165.1; 192.9. HRMS (ESI, m/z): Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_3$ 233.1178 $[\text{M} + \text{H}]^+$; found 233.1200.

Marilia MS057 CDCl_3 250MHz dez17mssH3

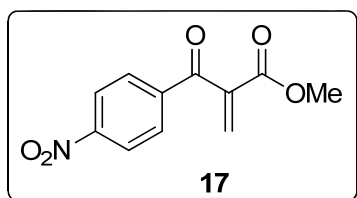


^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **16**.

Marilia MS057 CDCl3 250MHz dez17mssC1



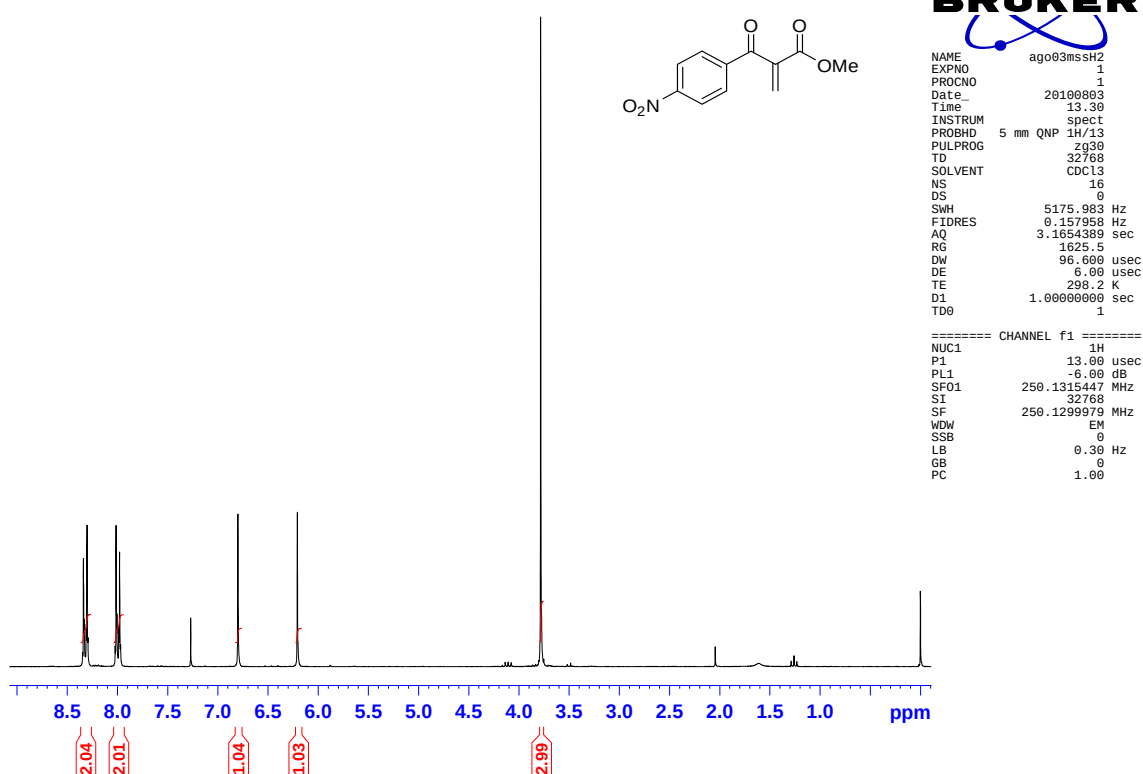
^{13}C NMR (62.5 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **16**.



Methyl 2-[(4-nitrophenyl)carbonyl]prop-2-enoate (**17**)

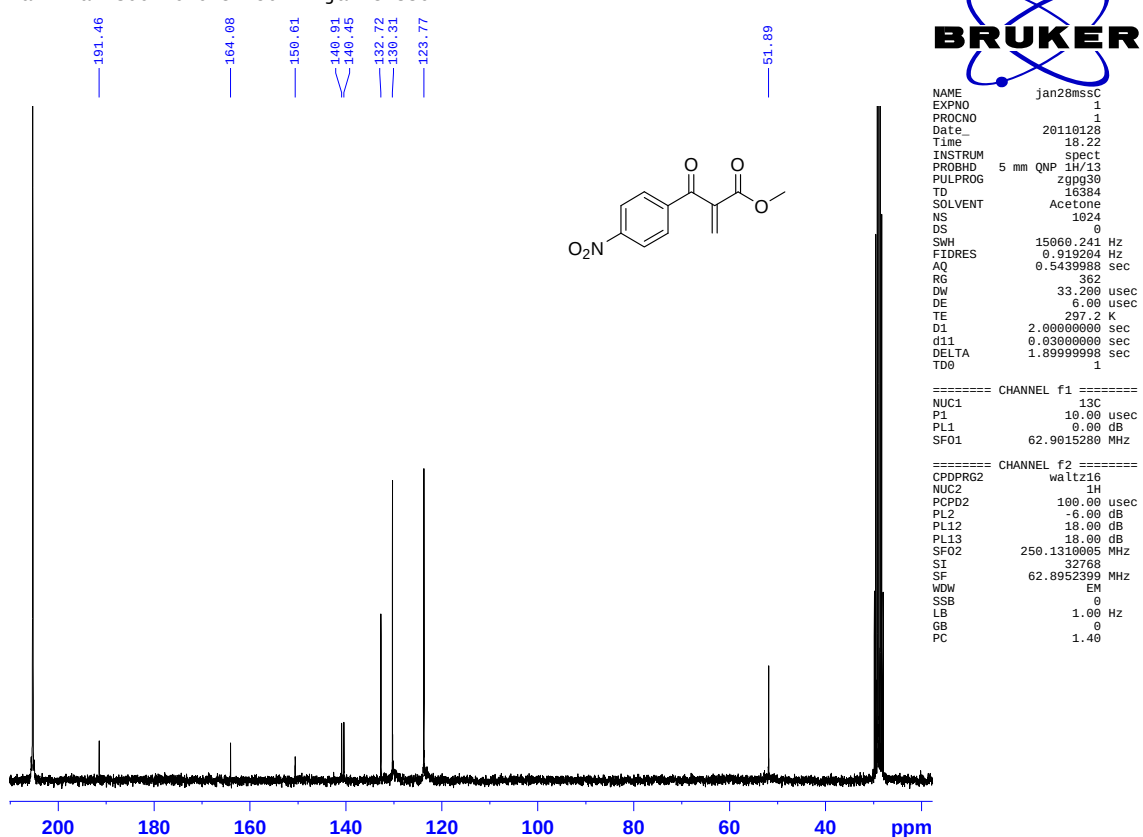
Yield: 90%, yellow solid; IR (KBr, ν_{max}): 2955, 1737, 1690, 1604, 1525, 1240, 702 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 3.78 (s, 3H); 6.21 (s, 1H); 6.80 (s, 1H); 8.00 (d, $^3J = 9.0\text{Hz}$, 2H); 8.32 (d, $^3J = 9.0\text{Hz}$, 2H). ^{13}C NMR [62.5 MHz, $(\text{CD}_3)_2\text{O}$]: δ 51.9; 123.8; 130.3; 132.7; 140.5; 140.9; 150.6; 164.1; 191.5. HRMS (ESI, m/z): Calcd. for $\text{C}_{11}\text{H}_{10}\text{NO}_5$ 236.0559 $[\text{M} + \text{H}]^+$; found 236.0579.

Marilia - MS012 - CDCl₃/250MHz ago03mssH2

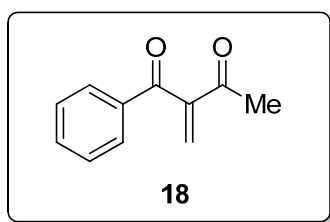


¹H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester **17**.

Marilia MS067 CDCl₃ 250MHz jan28mssC



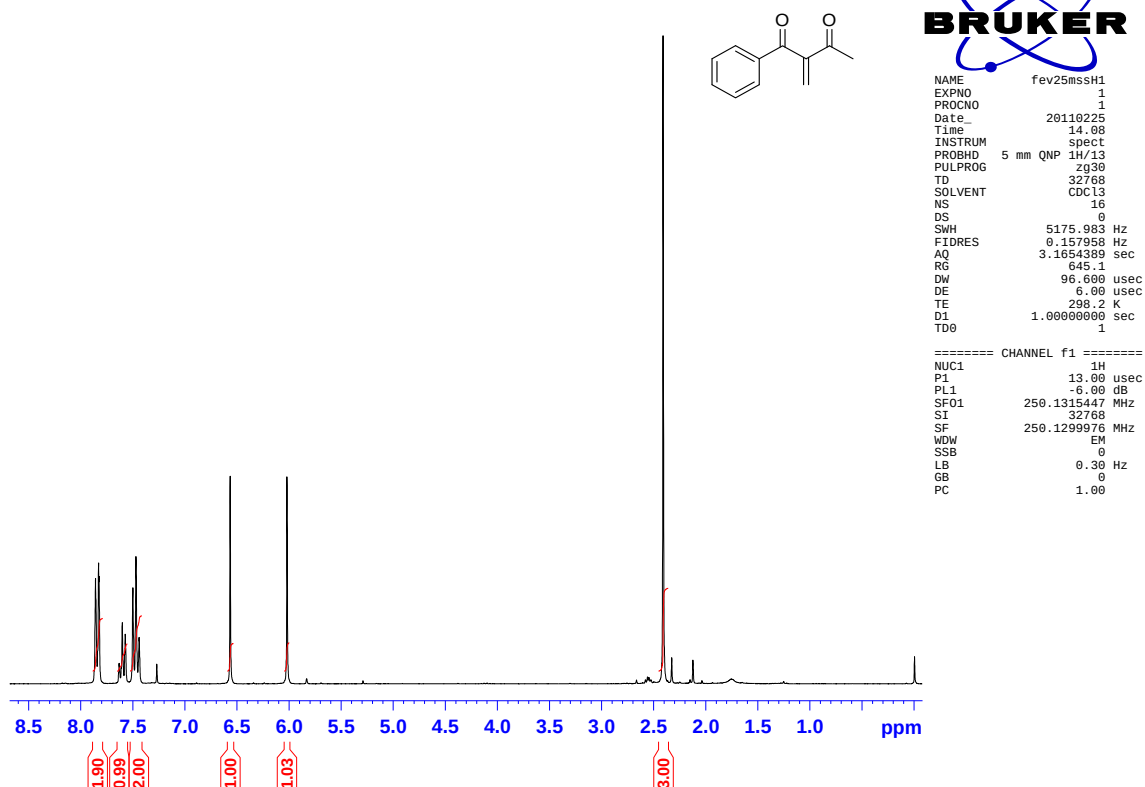
¹³C NMR [62.5 MHz, (CD₃)₂O] spectrum of the α-methylene-β-ketoester **17**.



2-Methylidene-1-phenylbutane-1,3-dione (18)

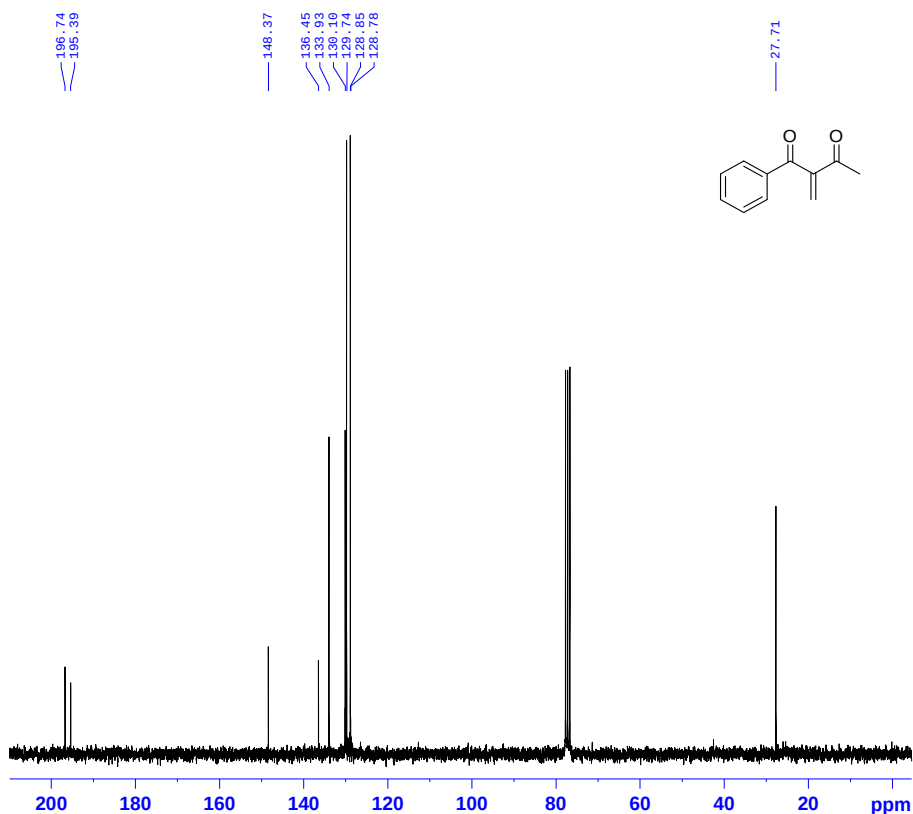
Yield: 93%, yellow oil; IR (film, $\nu_{\max}$): 3065, 2930, 1671, 1597, 1232, 1123 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 2.41 (s, 3H); 6.02 (s, 1H); 6.57 (s, 1H); 7.47 (m, $^3J = 7.2\text{Hz}$, 2H); 7.60 (m, $^3J = 7.2\text{Hz}$, 1H); 7.84 (m, $^3J = 7.1\text{Hz}$, 1H); ^{13}C NMR (62.5 MHz, CDCl_3): δ 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 $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Na}$ 197.0578 $[\text{M} + \text{Na}]^+$; found m/z 197.0619.

Marilia MS086 CDCl_3 250MHz fev25mssh1



^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **18**.

Marilia MS086 CDCl3 250MHz fev25mssC



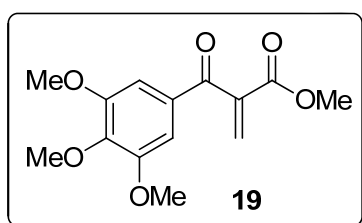
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NAME fev25mssC
EXPNO 1
PROCNO 1
Date_ 20110225
Time 15.01
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 16384
SOLVENT CDCl3
NS 531
DS 0
SWH 15060.241 Hz
FIDRES 0.919204 Hz
AQ 0.5439088 sec
RG 645.1
DW 33.200 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.00 dB
SFO1 62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 250.1310005 MHz
SI 32768
SF 62.8952265 MHz
WDW EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

^{13}C NMR (62.5 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **18**.

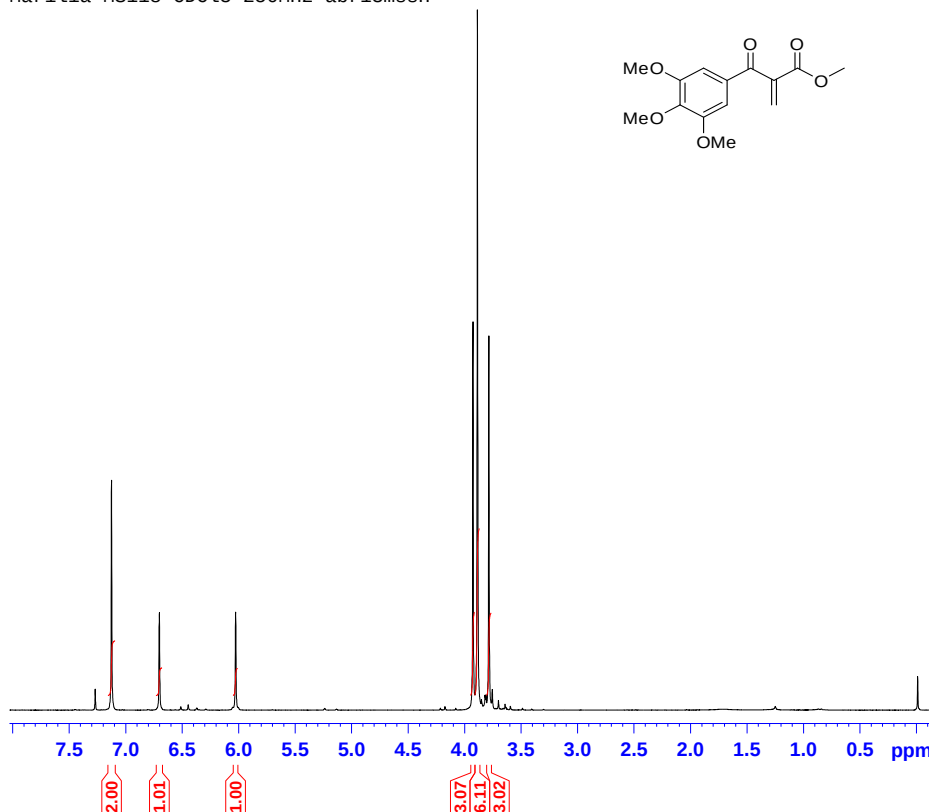


Methyl 2-[(3,4,5-trimethoxyphenyl)carbonyl]prop-2-enoate (**19**)

Yield: >95%, colorless oil; IR (film, ν_{max}): 2959, 2840, 1723, 1665, 1584, 1416, 1129 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 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, CDCl_3): δ 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 $\text{C}_{14}\text{H}_{17}\text{O}_6$ 281.1086 $[\text{M} + \text{H}]^+$; found 281.1025.

Marilia MS118 CDCl₃ 250MHz abr13mssH



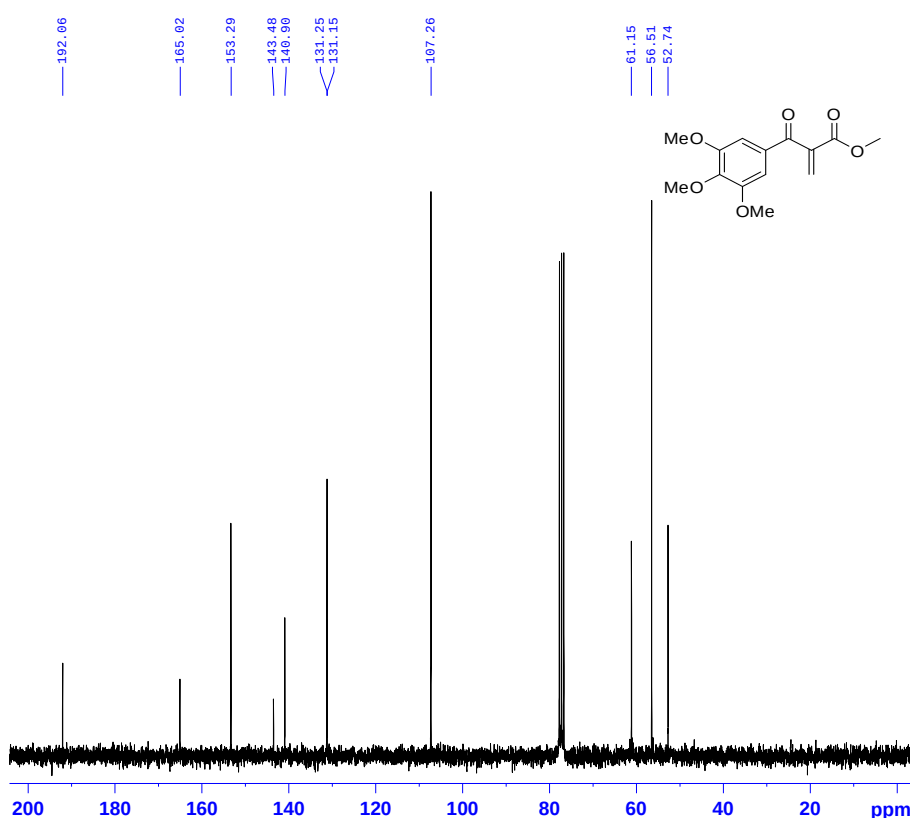
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NAME      abr13mssH
EXPNO     1
PROCNO    1
Date_     20110413
Time      19.34
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        5175.983 Hz
FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         645.1
DW         96.680 usec
DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        -6.00 dB
SF01       250.1315447 MHz
SI         32768
SF         250.1299975 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹H NMR (250 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **19**.

Marilia MS118 CDCl₃ 250MHz abr13mssC



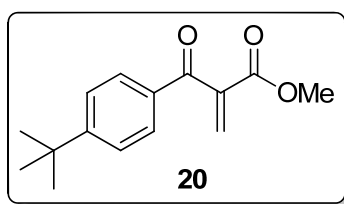
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NAME      abr13mssC
EXPNO     1
PROCNO    1
Date_     20110413
Time      20.05
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         16384
SOLVENT   CDCl3
NS         675
DS         0
SWH        15060.241 Hz
FIDRES     0.919204 Hz
AQ         0.5439988 sec
RG         406.4
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.00000000 sec
D11        0.03000000 sec
DELTA      1.89999998 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1         0.00 dB
SF01       62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        -6.00 dB
PL12       18.00 dB
PL13       18.00 dB
SF02       250.1310005 MHz
SI         32768
SF         62.8952256 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **19**.

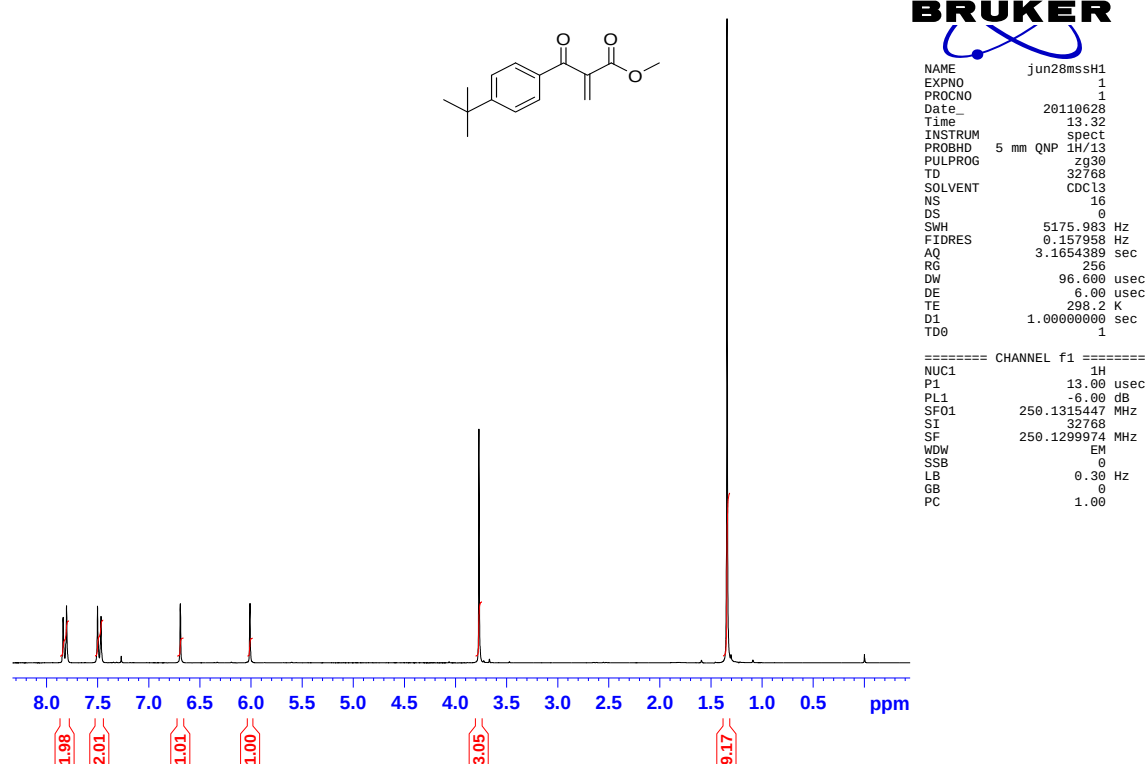


Methyl 2-[(4-*tert*-butylphenyl)carbonyl]prop-2-enoate
(**20**)

Yield: >95%, yellow solid, m.p. 42-44 °C; IR (KBr, ν_{max}):
2963, 2906, 2871, 1731, 1673, 1603, 1239, 1156, 1145,

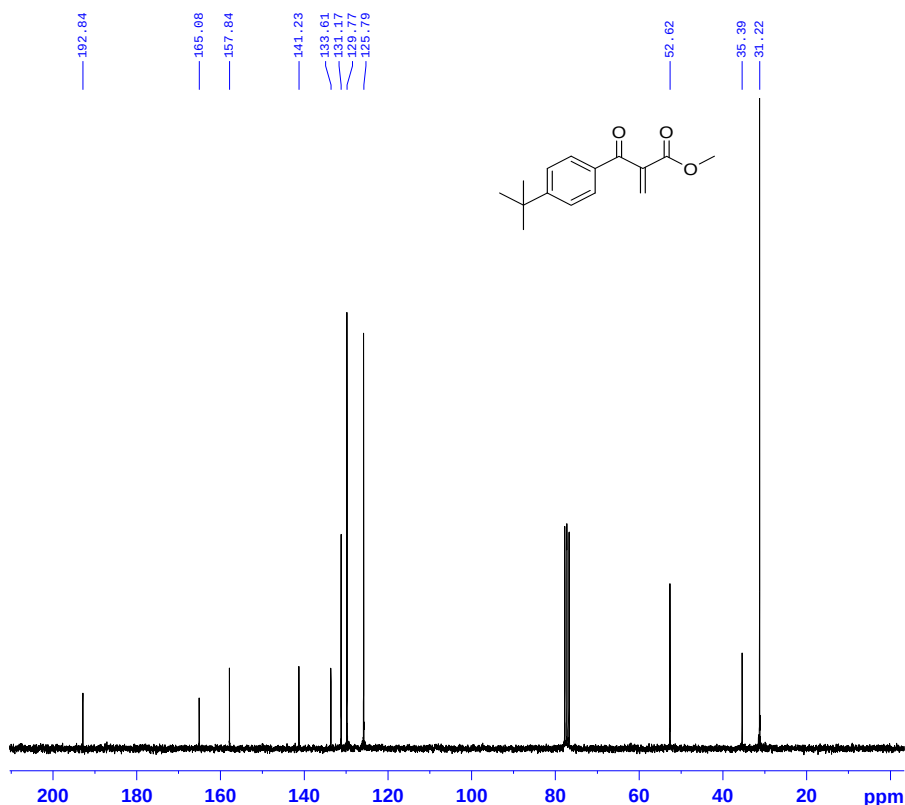
852 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 1.35 (s, 9H); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 7.48 (d, $^3J = 8.6\text{Hz}$, 2H); 7.82 (d, $^3J = 8.6\text{ Hz}$, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 31.2; 35.4; 125.8; 129.8; 131.2; 133.6; 141.2; 157.8; 165.1; 192.8. HRMS (ESI, m/z): Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3$ 247.1334 $[\text{M} + \text{H}]^+$; found m/z 247.1342.

Marilia MS127 $\text{CDCl}_3/250\text{MHz}$ jun28mssH1



^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **20**.

Marilia MS127 CDCl₃/250MHz jun28mssC1



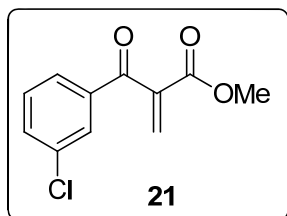
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NAME          jun28mssC1
EXPNO         1
PROCNO        1
Date_         20110628
Time          14.18
INSTRUM       spect
PROBHD        5 mm QNP 1H/13
PULPROG       zgpg30
TD            16384
SOLVENT       CDCl3
NS            1024
DS            0
SWH           15060.241 Hz
FIDRES        0.919204 Hz
AQ            0.5439988 sec
RG            574.7
DW            33.200 usec
DE            6.00 usec
TE            298.2 K
D1            2.0000000 sec
d11           0.0300000 sec
DELTA         1.8999999 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
PL1           0.00 dB
SF01          62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         100.00 usec
PL2           -6.00 dB
PL12          19.00 dB
PL13          18.00 dB
SF02          250.1310005 MHz
SI            32768
SF            62.8952263 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester **20**.

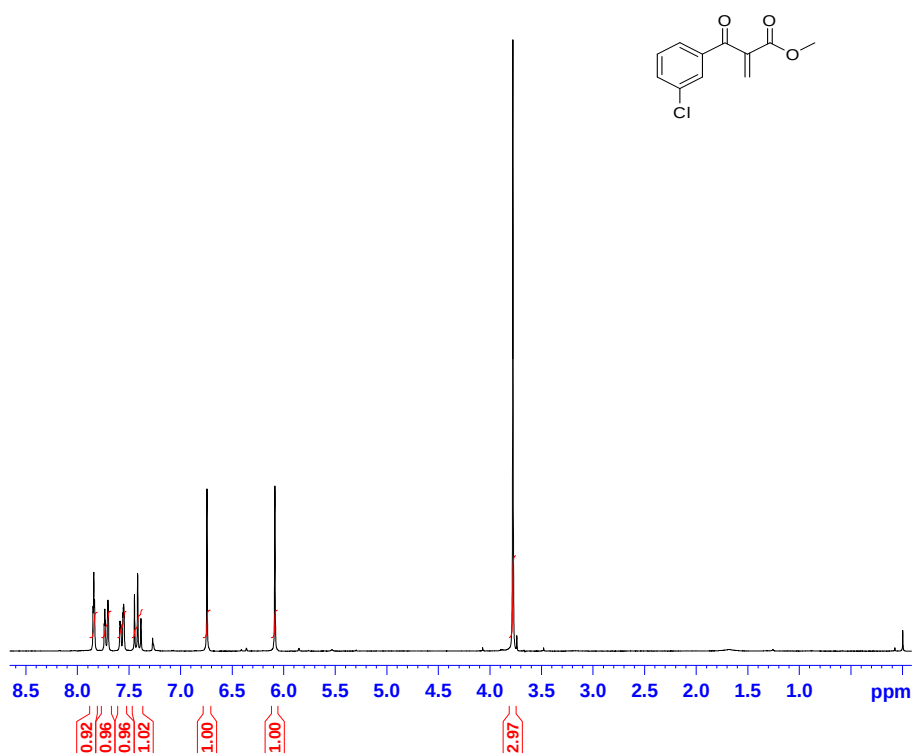


Methyl 2-[(3-chlorophenyl)carbonyl]prop-2-enoate (**21**)

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 =

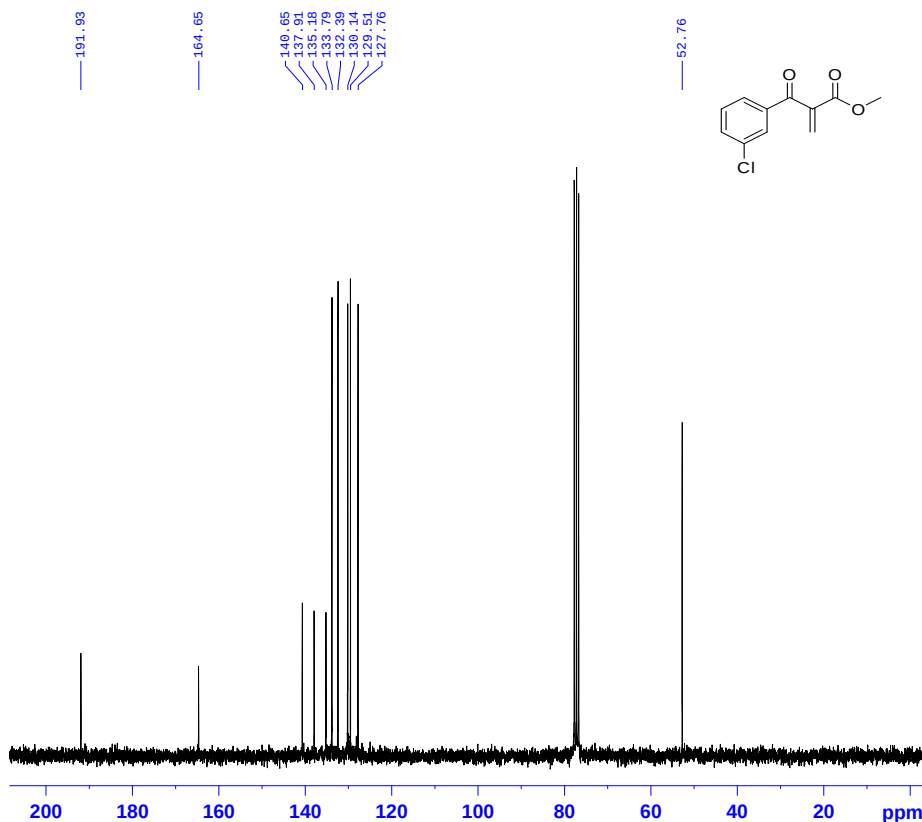
1.5 and 7.7Hz); 7.84 (t, ³J = 1.7Hz, 1H). ¹³C NMR (62.5 MHz, CDCl₃): δ 52.8; 127.8; 129.5; 130.1; 132.4; 133.8; 135.2; 137.9; 140.7; 164.7; 191.9. HRMS (ESI, m/z): Calcd for C₁₁H₁₀ClO₃ 225.0318 [M + H]⁺; Found m/z 225.0346.

Marilia MS111 CDCl₃ - 250 MHz - abr04mssh1



¹H NMR (250 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **21**.

Marilia MS111 CDCl₃ 250MHz abr05mssc



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α -methylene- β -ketoester **21**.



```
NAME      abr04mssh1
EXPNO     1
PROCNO    1
Date_     20110404
Time      19.01
INSTRUM   spect
PROBHD    5 mm QNP
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        5175.983 Hz
FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         812.7
DW         96.600 usec
DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

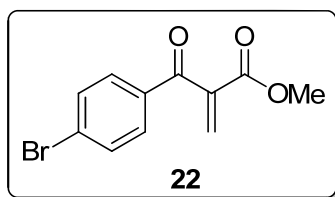
===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        -6.00 dB
SF01       250.1315447 MHz
SI         32768
SF         250.1299977 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
```



```
NAME      abr05mssc
EXPNO     1
PROCNO    1
Date_     20110405
Time      14.13
INSTRUM   spect
PROBHD    5 mm QNP
PULPROG   zgpg30
TD         16384
SOLVENT   CDCl3
NS         1024
DS         0
SWH        15060.241 Hz
FIDRES     0.919204 Hz
AQ         0.5439988 sec
RG         645.1
DW         33.200 usec
DE         6.00 usec
TE         298.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999999 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1         0.00 dB
SF01       62.9015280 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        -6.00 dB
PL12       18.00 dB
PL13       18.00 dB
SF02       250.1310005 MHz
SI         32768
SF         62.8952254 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

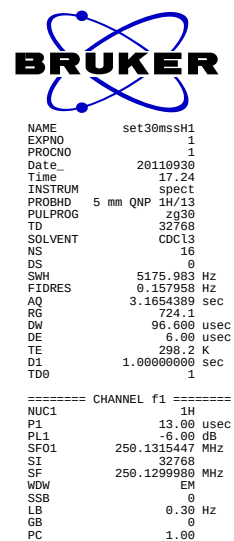
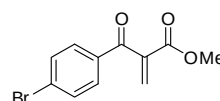
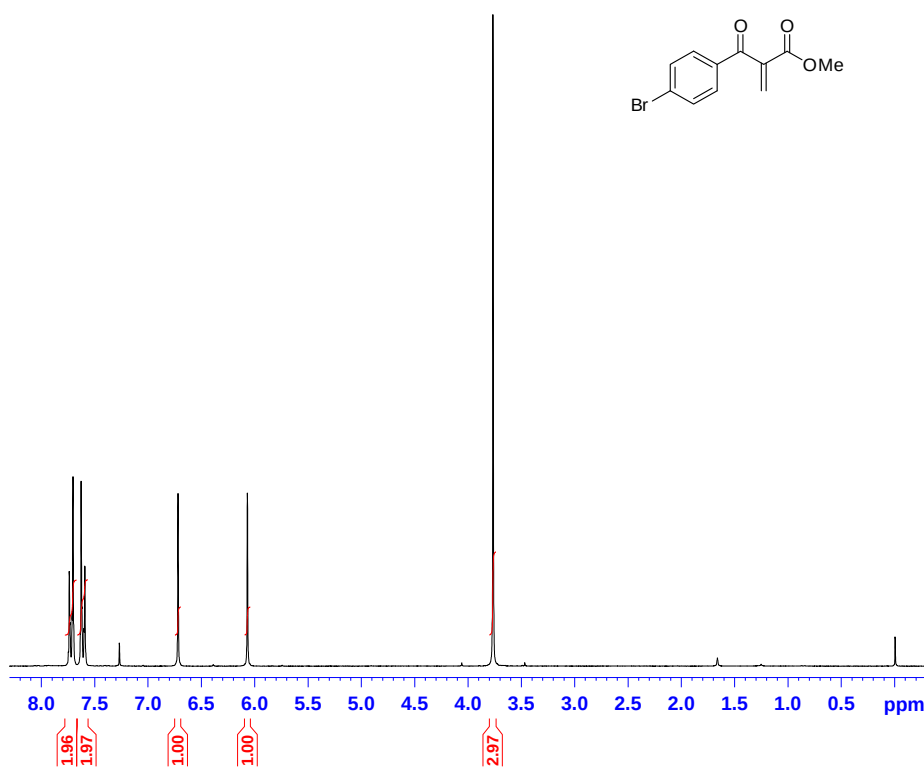


Methyl 2-[(4-bromophenyl)carbonyl]prop-2-enoate (**22**)

Yield: 95%, yellow tinged oil; IR (film, $\nu_{\max}$): 2954, 1731, 1674, 1584, 1193, 816 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 3.77 (s, 3H); 6.07 (s, 1H); 6.70 (s, 1H); 7.61 (d, $^3J = 8.7$

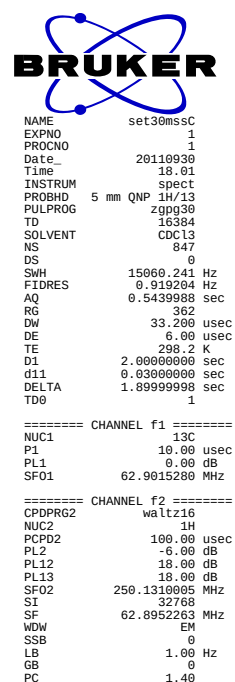
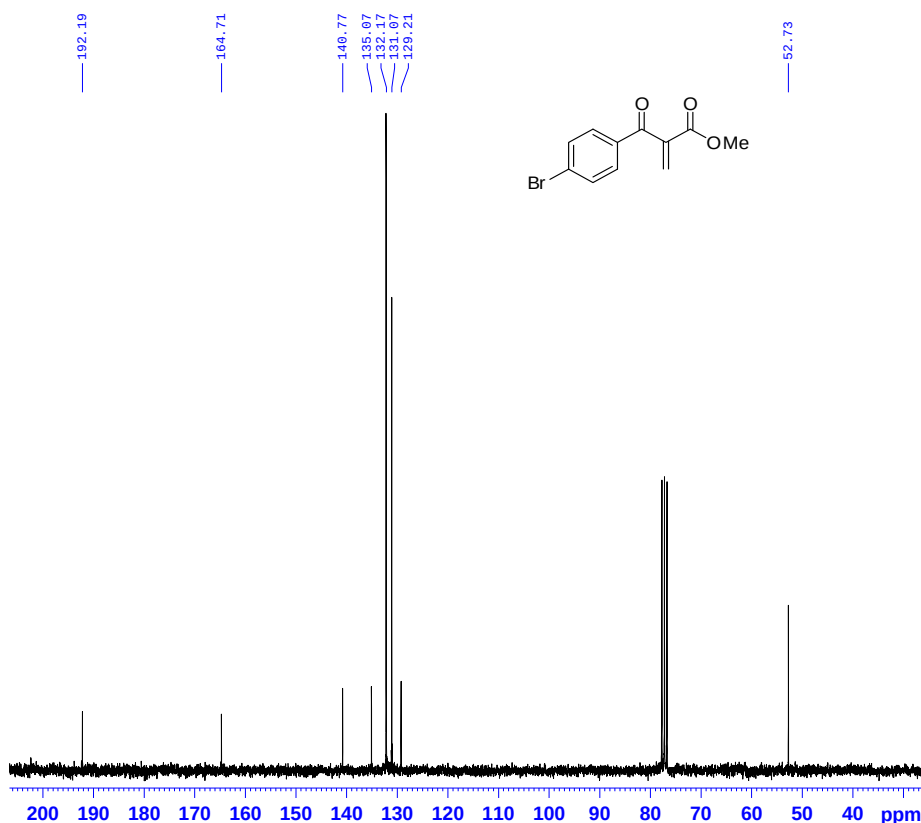
Hz, 2H); 7.72 (d, $^3J = 8.7$ Hz, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 52.7; 129.2; 131.1; 132.2; 135.1; 140.8; 164.7; 192.2. HRMS (ESI, m/z): Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_3\text{Br}$ 268.9813 $[\text{M} + \text{H}]^+$; found 268.9836.

Marilia MS178 CDCl_3 250MHz set30mssH1

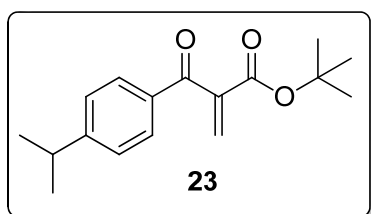


^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **22**.

Marilia MS178 CDCl₃ 250MHz set30mssc



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester **22**.



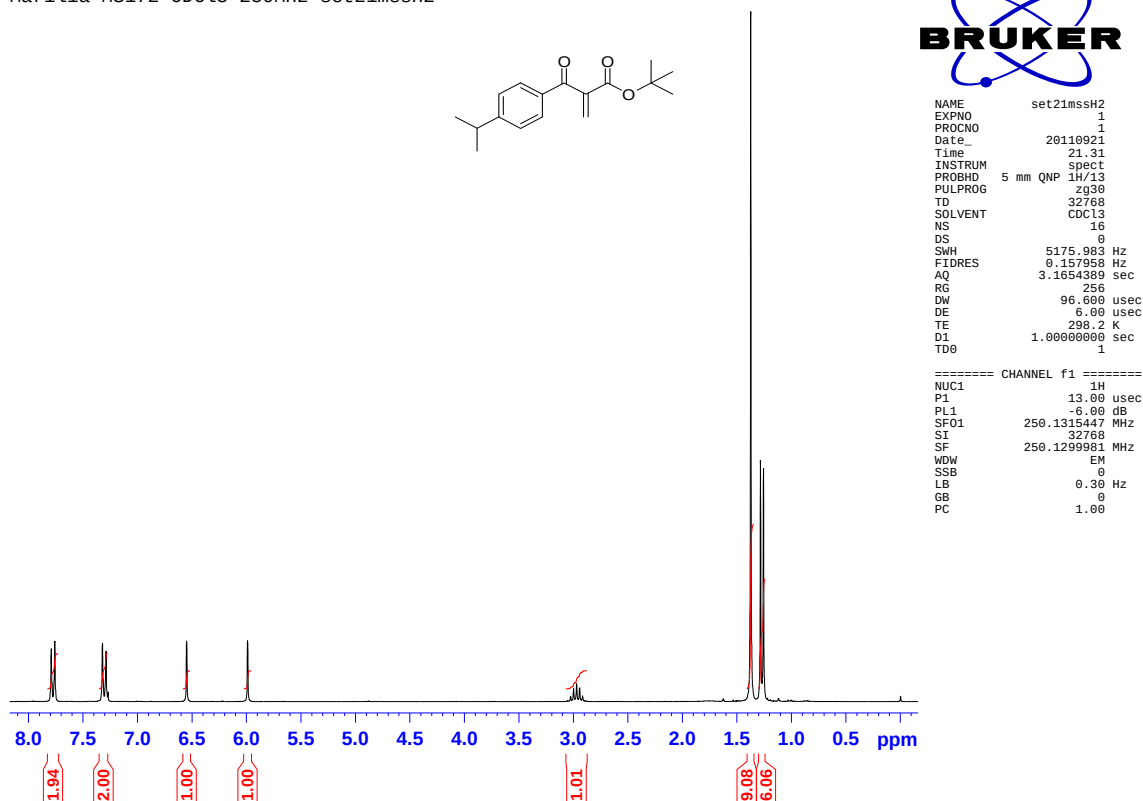
tert-Butyl 2-{[4-(propan-2-yl)phenyl]carbonyl}prop-2-enoate (**23**)

Yield: >95%, yellow tinged oil; IR (film, ν_{max}): 2965, 2933, 2873, 1724, 1674, 1570, 1149, 1055, 847 cm⁻¹. ¹H

NMR (250 MHz, CDCl₃): δ 1.27 (d, ³*J* = 6.9 Hz, 6H);

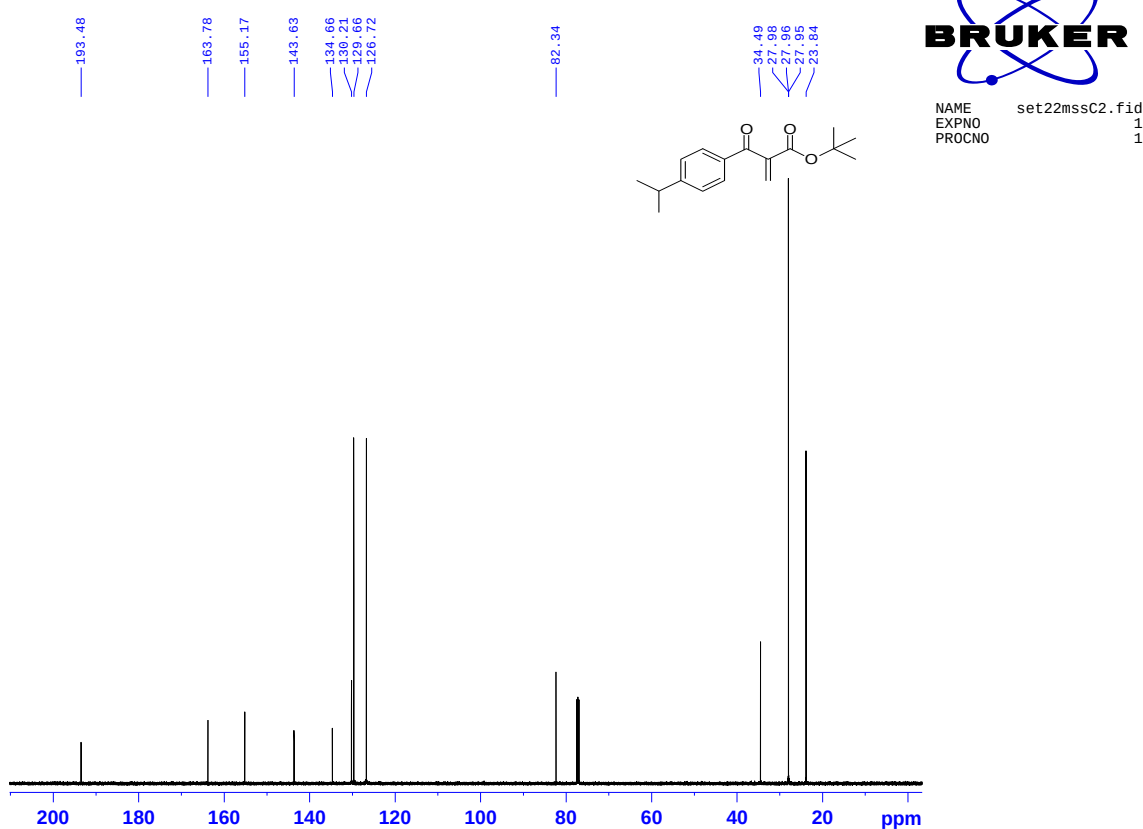
1.37 (s, 9H); 2.97 (m, 1H); 5.99 (s, 1H); 6.55 (s, 1H); 7.30 (d, ³*J* = 8.3 Hz, 2H); 7.77 (d, ³*J* = 8.3 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 23.8; 28.0; 34.5; 82.3; 126.7; 129.7; 130.2; 134.7; 143.6; 155.2; 163.8; 193.5. HRMS (ESI, *m/z*): Calcd. for C₁₇H₂₂O₃Na 297.1467 [M + H]⁺; found 297.1505.

Marilia MS172 CDCl₃ 250MHz set21mssh2

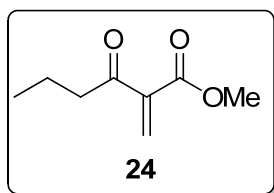


¹H NMR (250 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester **23**.

Marilia "MS 172" CDCl₃/BBSW set22mssc2



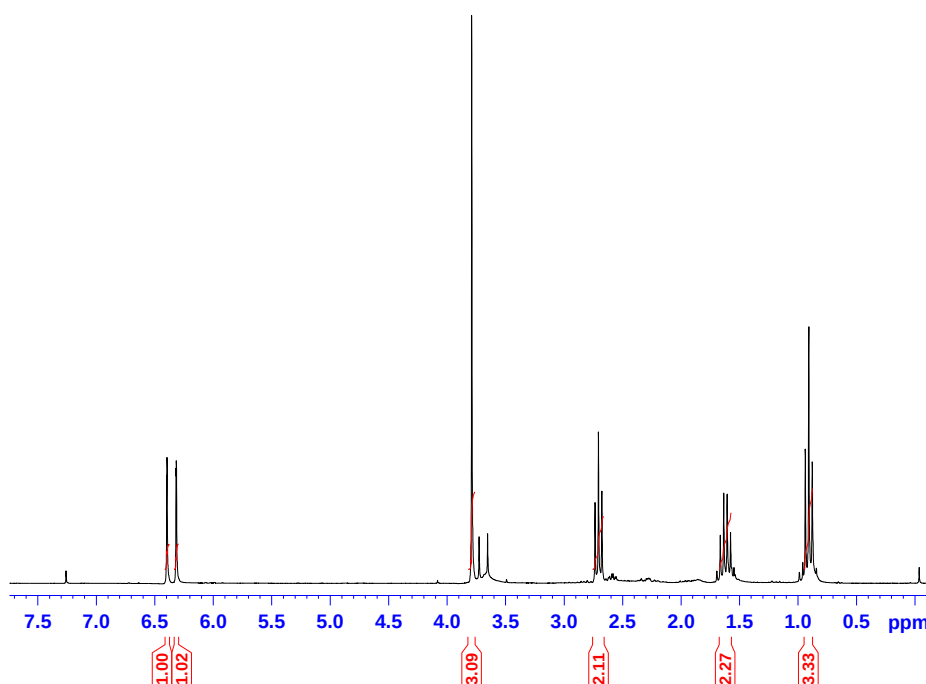
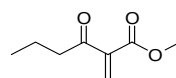
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the α-methylene-β-ketoester **23**.



Methyl 2-methylidene-3-oxohexanoate (**24**)

Yield: 73%, colorless oil; IR (film, ν_{max}): 2962, 2876, 1750, 1714, 1630, 1435, 1269, 1096 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 0.91 (t, $^3J = 7.4\text{Hz}$, 3H); 1.62 (m, $^3J = 7.4\text{Hz}$, 2H); 2.71 (t, $^3J = 7.3\text{Hz}$, 2H); 3.79 (s, 3H); 6.32 (d, $^3J = 0.8\text{Hz}$, 1H); 6.40 (d, $^3J = 0.8\text{Hz}$, 1H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 13.8; 17.4; 43.2; 52.5; 132.6; 142.0; 165.5; 199.6. HRMS (ESI, m/z): Calcd. for $(\text{C}_8\text{H}_{13}\text{O}_3)_2\text{H}$ 313.1652 $[\text{M} + \text{H}]^+$; found 313.1682

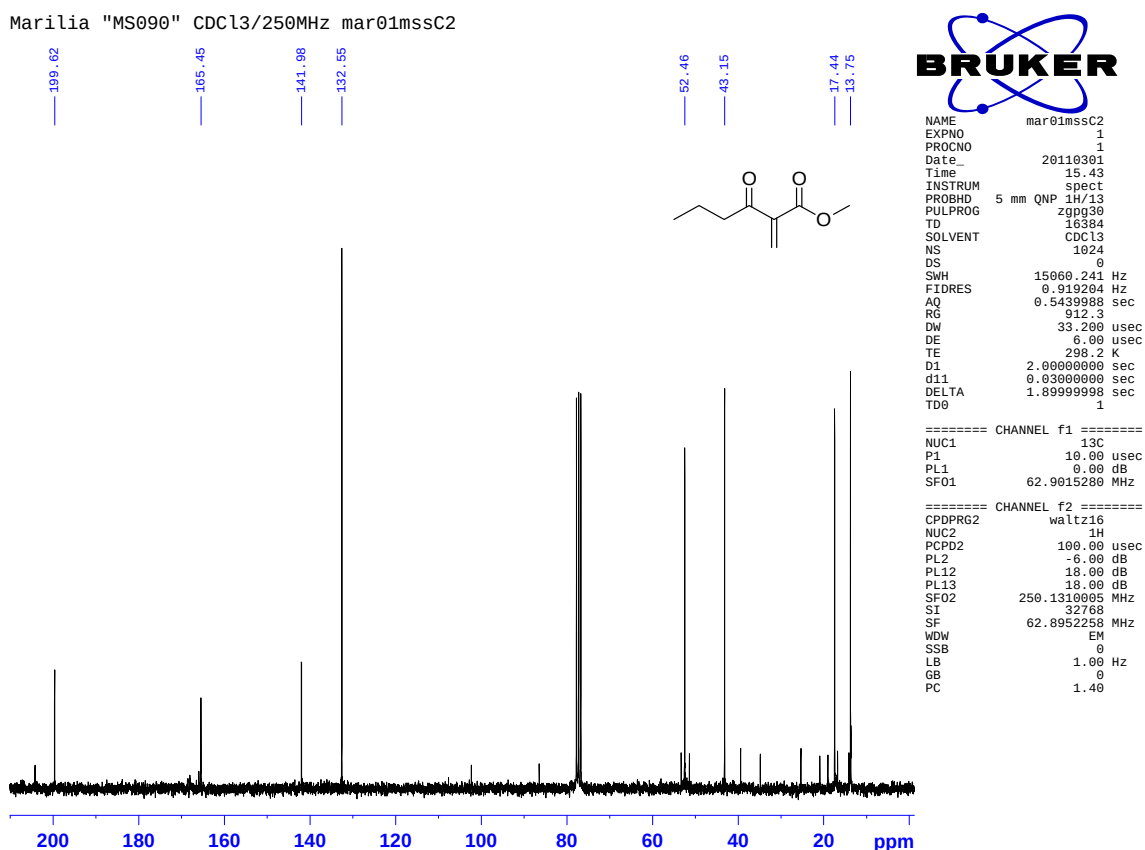
Marilia MS090 CDCl_3 250MHz mar01mssh2



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NAME      mar01mssh2
EXPNO     1
PROCNO    1
Date_     20110301
Time      13.53
INSTRUM    spect
PROBHD     5 mm QNP 1H/13
PULPROG    zg30
TD         32768
SOLVENT    CDCl3
NS         16
DS         0
SWH         5175.083 Hz
FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         256
DW         96.600 usec
DE         6.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        -6.00 dB
SF01       250.1315447 MHz
SI         32768
SF         250.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

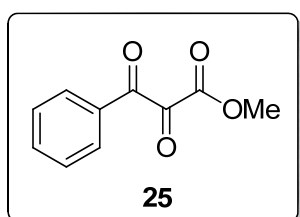
^1H NMR (250 MHz, CDCl_3) spectrum of the α -methylene- β -ketoester **24**.



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

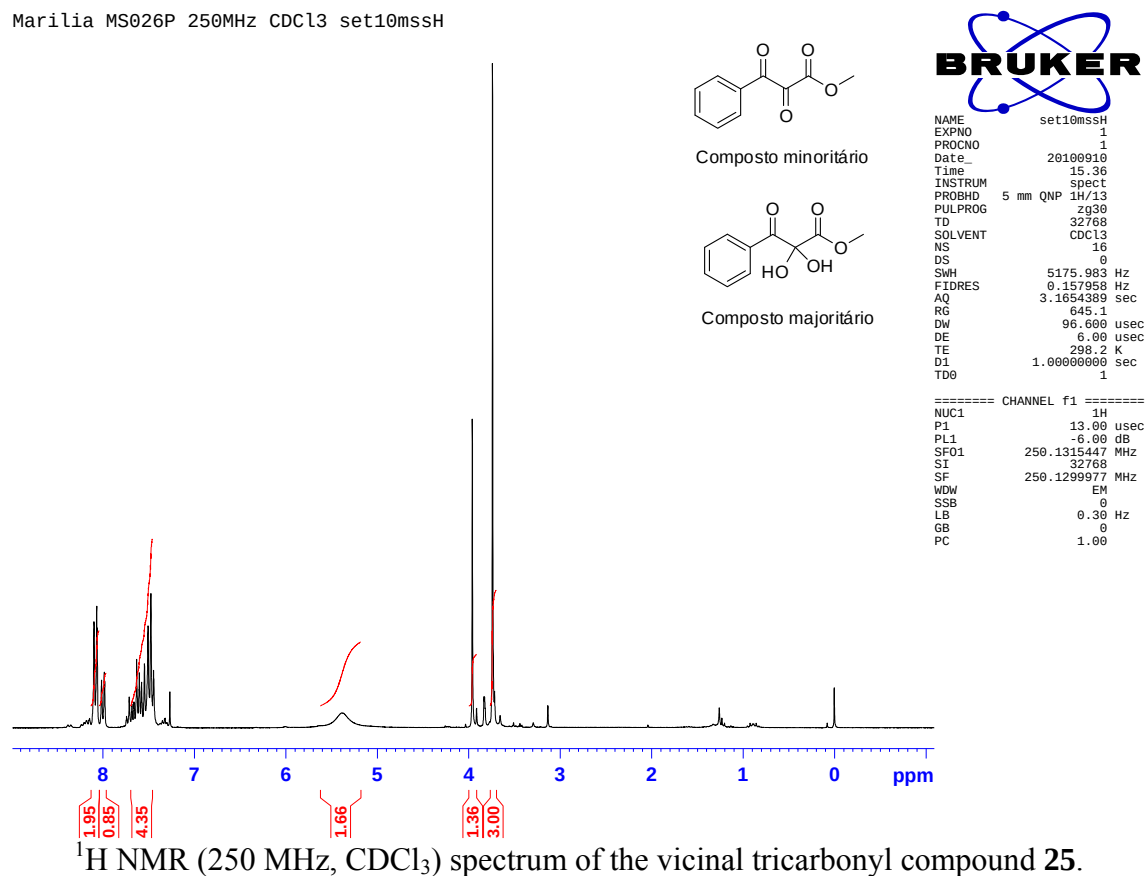


Methyl 2,3-dioxo-3-phenylpropanoate (**25**)

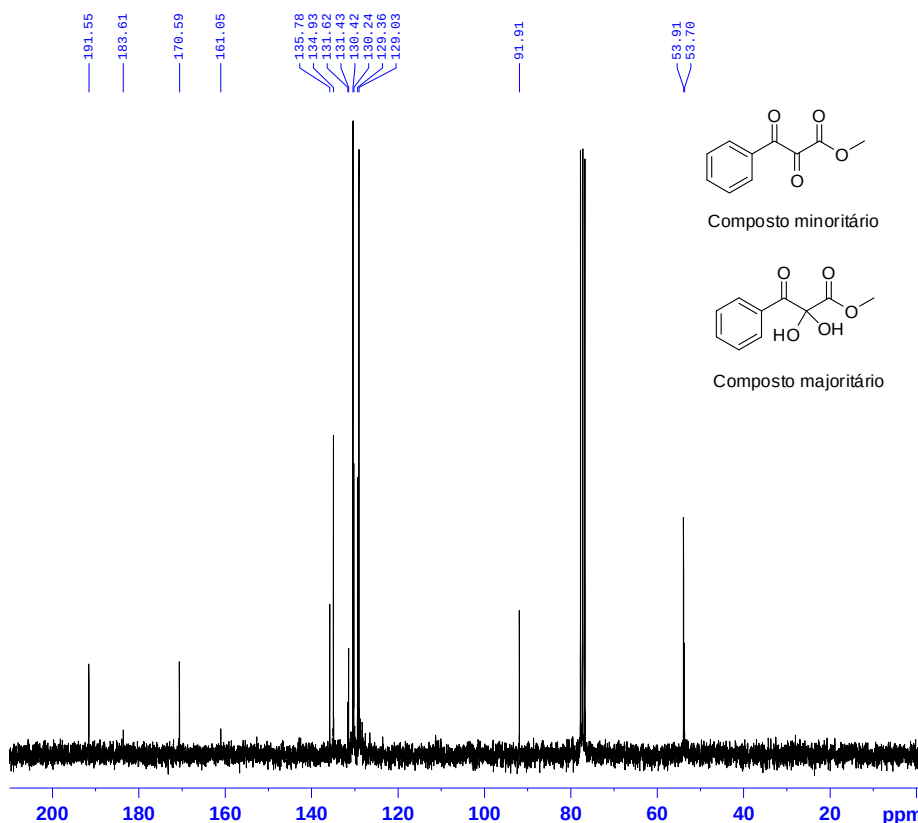
Yield: 78%, yellow oil; IR (film, ν_{max}): 3426, 2958, 1755, 1696, 1598, 1131, 911 cm⁻¹. Mixture 4:9 (tricarbonyl and hydrate form) - ¹H NMR (250 MHz, CDCl₃): *Tricarbonyl*

compound: δ 4.0 (s, 3H); 7.5-7.7 (m, 3H), 9.0-8.0 (m, 2H). *Hydrate*: δ 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*: δ 53.7; 129.4; 130.2; 131.6; 135.8; 161.1; 183.6. *Hydrate*: δ 53.9; 91.9; 129.0; 130.4; 131.4; 134.9; 170.6; 191.6. HRMS (ESI, m/z): Calcd for m/z $\text{C}_{10}\text{H}_9\text{O}_4$ 193.0500 $[\text{M} + \text{H}]^+$; found m/z 193.0487.

Marilia MS026P 250MHz CDCl_3 set10mssH

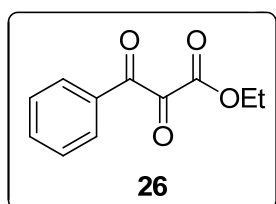


Marilia MS026P 250MHz CDCl3 set10mssc



BRUKER	
NAME	set10mssc
EXPNO	1
PROCNO	1
Date_	20100910
Time	15.58
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	16384
SOLVENT	CDCl3
NS	424
DS	0
SWH	15060.241 Hz
FIDRES	0.919204 Hz
AQ	0.5439988 sec
RG	1024
DW	33.200 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
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P1	10.00 usec
PL1	0.00 dB
SF01	62.9015280 MHz
===== CHANNEL f2 =====	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	-6.00 dB
PL12	18.00 dB
PL13	18.00 dB
SF02	250.1310005 MHz
SI	32768
SF	62.8952255 MHz
WDW	EM
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LB	1.00 Hz
GB	0
PC	1.40

¹³C NMR (62.5 MHz, CDCl₃) spectrum of the vicinal tricarbonyl compound **25**.

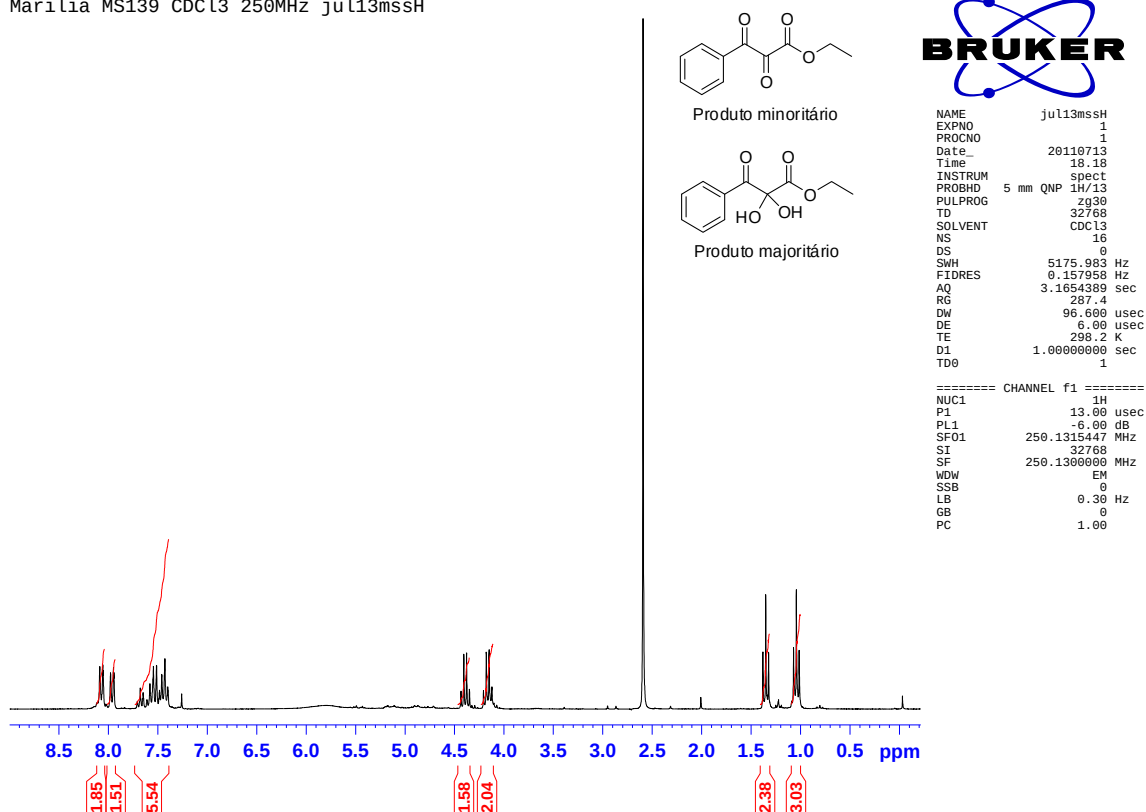


Ethyl 2,3-dioxo-3-phenylpropanoate (**26**)

Yield: >95%, greenish yellow oil; IR (film, $\nu_{\max}$): 3415, 2985, 1750, 1695, 1235, 1133, 1101, 1015 cm⁻¹. Mixture of the vicinal tricarbonyl compound and its hydrated form (4:5) - ¹H

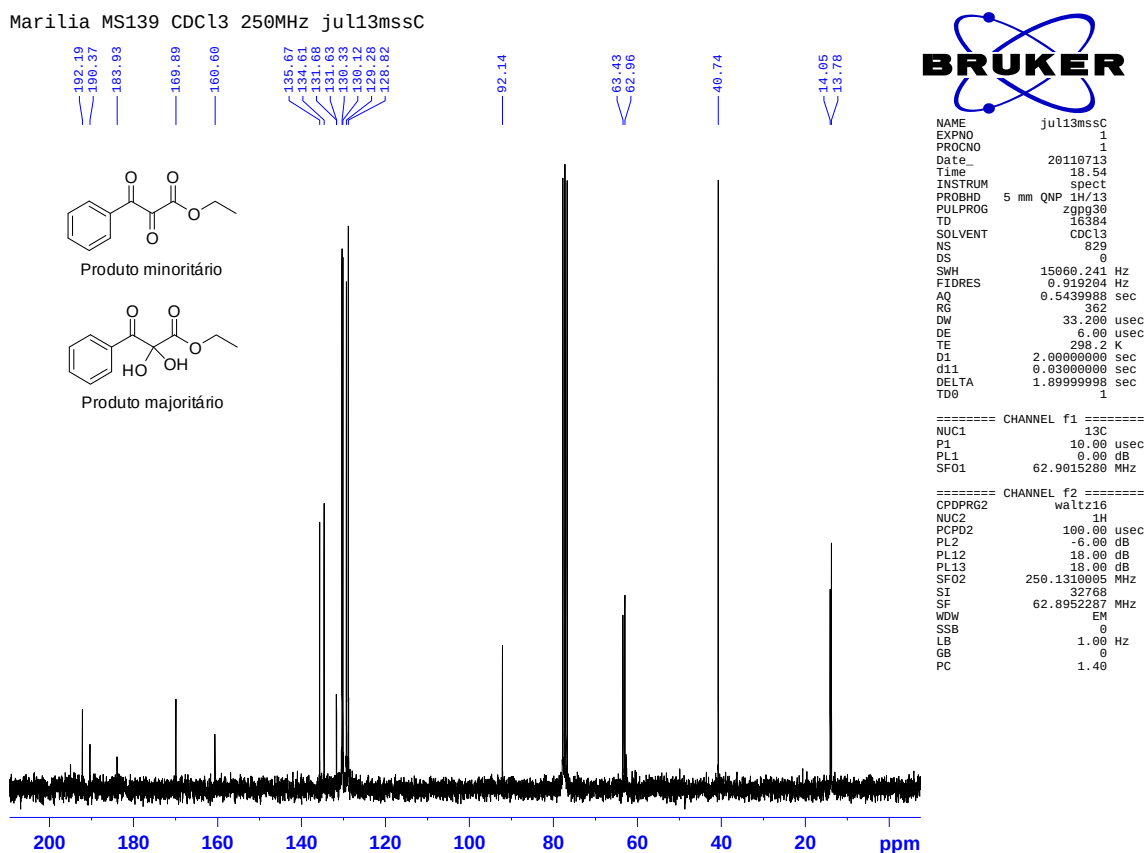
NMR (250 MHz, CDCl₃): *Tricarbonyl compound*: δ 1.36 (t, ³J = 7.1Hz, 3H); 4.40 (q, ³J = 7.1Hz, 2H); 7.41-8.10 (m, 5H). *Hydrate*: δ 1.05 (t, ³J = 7.1Hz, 3H); 4.17 (q, ³J = 7.1Hz, 2H); 7.41-8.10 (m, 5H). ¹³C NMR (62.5 MHz, CDCl₃) - *Tricarbonyl compound*: δ 14.1; 63.4; 129.3; 130.1; 131.6; 135.7; 160.6; 183.9; 190.4. *Hydrate*: δ 13.8; 63.0; 92.1; 128.8; 130.3; 131.7; 134.6; 169.9; 192.2. HRMS (ESI, m/z): Calcd for C₁₁H₁₁O₄ 207.0657 [M + H]⁺; found m/z 207.0660.

Marilia MS139 CDCl₃ 250MHz jul13mssH

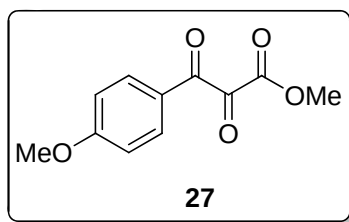


¹H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound **36** and its hydrated form.

Marilia MS139 CDCl₃ 250MHz jul13mssC



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the vicinal tricarbonyl compound **26** and its hydrated form.



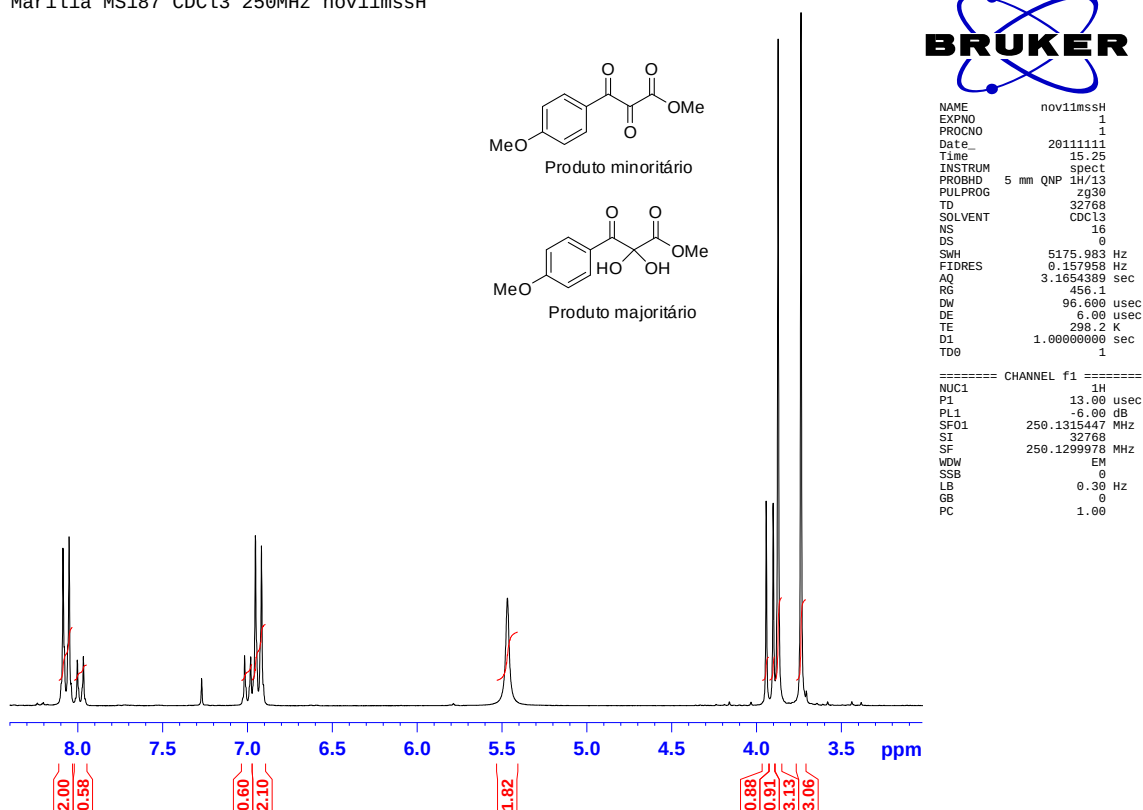
Methyl 3-(4-methoxyphenyl)-2,3-dioxopropanoate (27)

Yield: 76%, yellow tinged oil; IR (film, $\nu_{\max}$): 3407, 2954, 2844, 1747, 1682, 1602, 1254, 1175, 1128, 845 cm^{-1} .

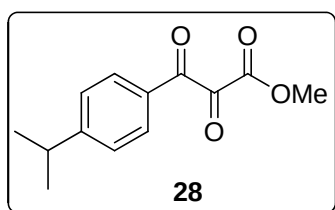
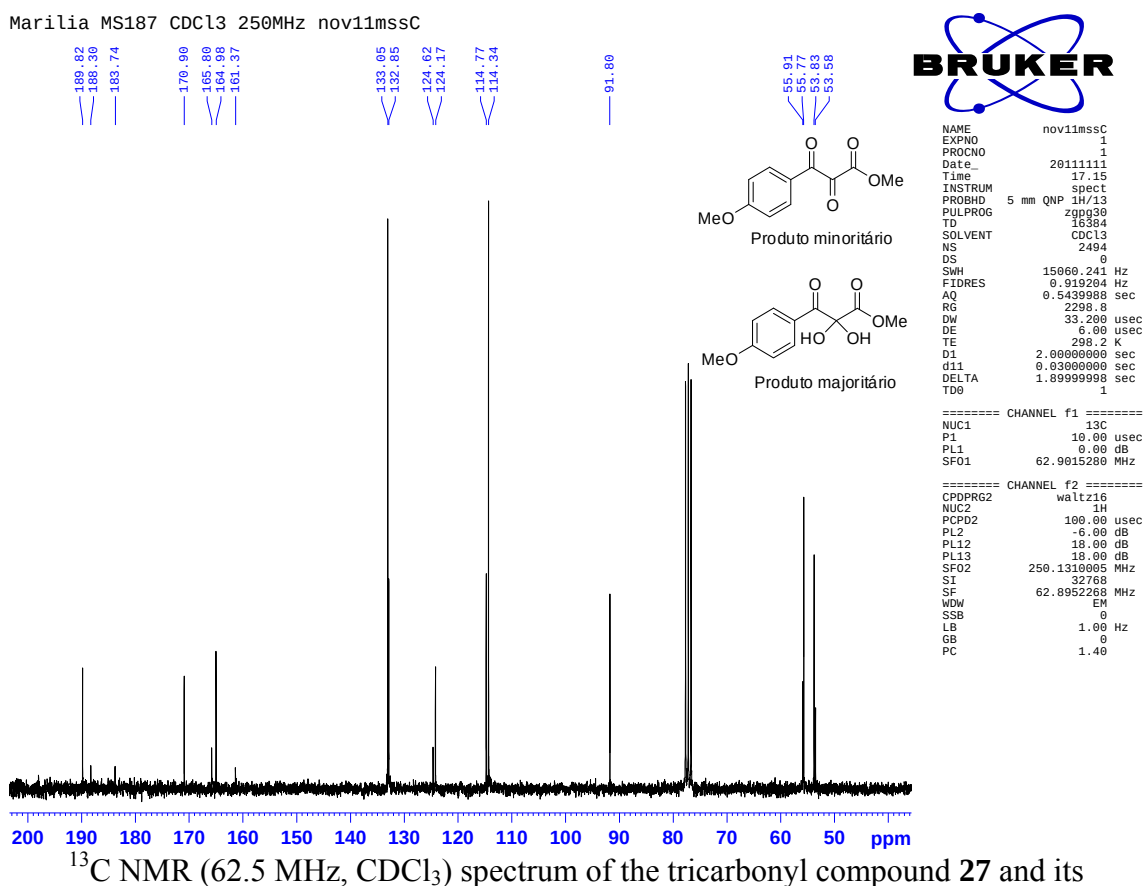
¹H NMR (250 MHz, CDCl_3):

Tricarbonyl compound: δ 3.90 (s, 3H); 3.94 (s, 3H); 7.00 (d, $^3J = 9.0\text{Hz}$, 2H); 7.98 (d, $^3J = 9.0\text{Hz}$, 2H). *Hydrate*: δ 3.74 (s, 3H); 3.98 (s, 3H); 5.47 (s, 2H); 6.94 (d, $^3J = 9.0\text{Hz}$, 2H); 8.07 (d, $^3J = 9.0\text{Hz}$, 2H). ¹³C NMR [62.5 MHz, CDCl_3]: *Tricarbonyl compound*: δ 53.6; 55.9; 91.8; 114.8; 124.6; 132.9; 161.4; 165.0; 183.7; 188.3. *Hydrate*: δ 53.8; 55.8; 91.8; 114.3; 124.2; 133.0; 165.0; 170.9; 189.8. HRMS (ESI, m/z): Calcd for $\text{C}_{11}\text{H}_{11}\text{O}_5$ m/z 223.0607 $[\text{M} + \text{H}]^+$. Found m/z 223.0678.

Marilia MS187 CDCl_3 250MHz nov11mssh



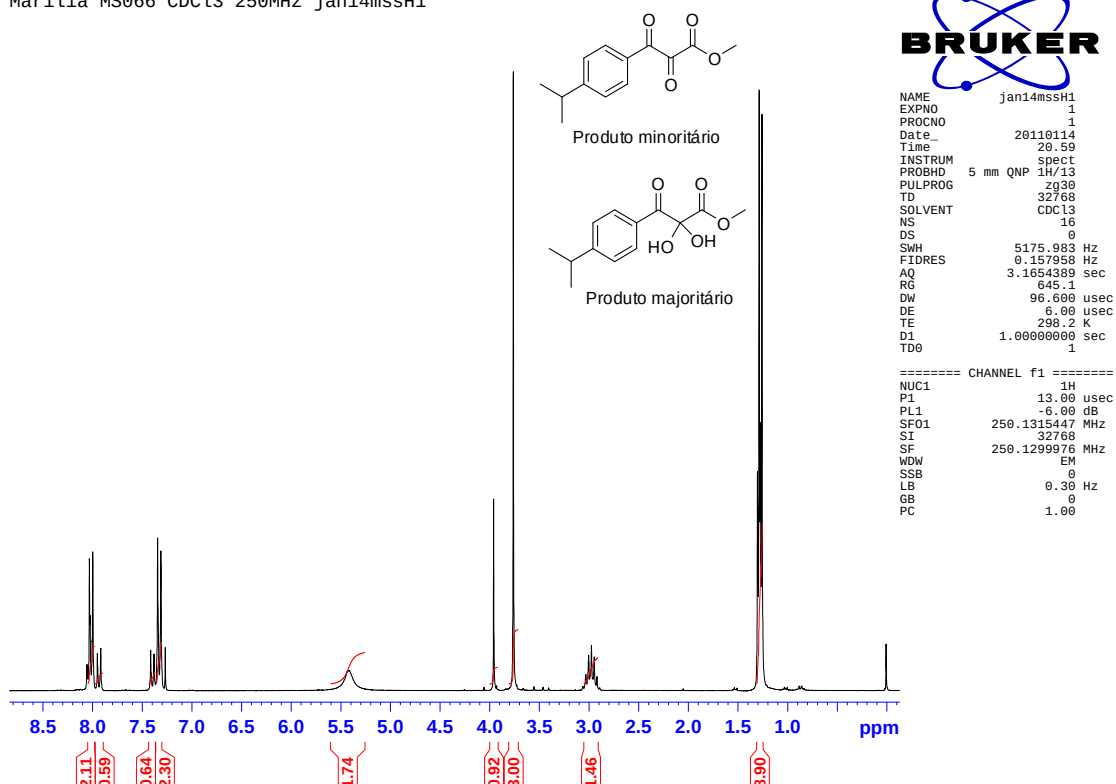
¹H NMR (250 MHz, CDCl_3) spectrum of the tricarbonyl compound **27** and its hydrated form.



Methyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (**28**)

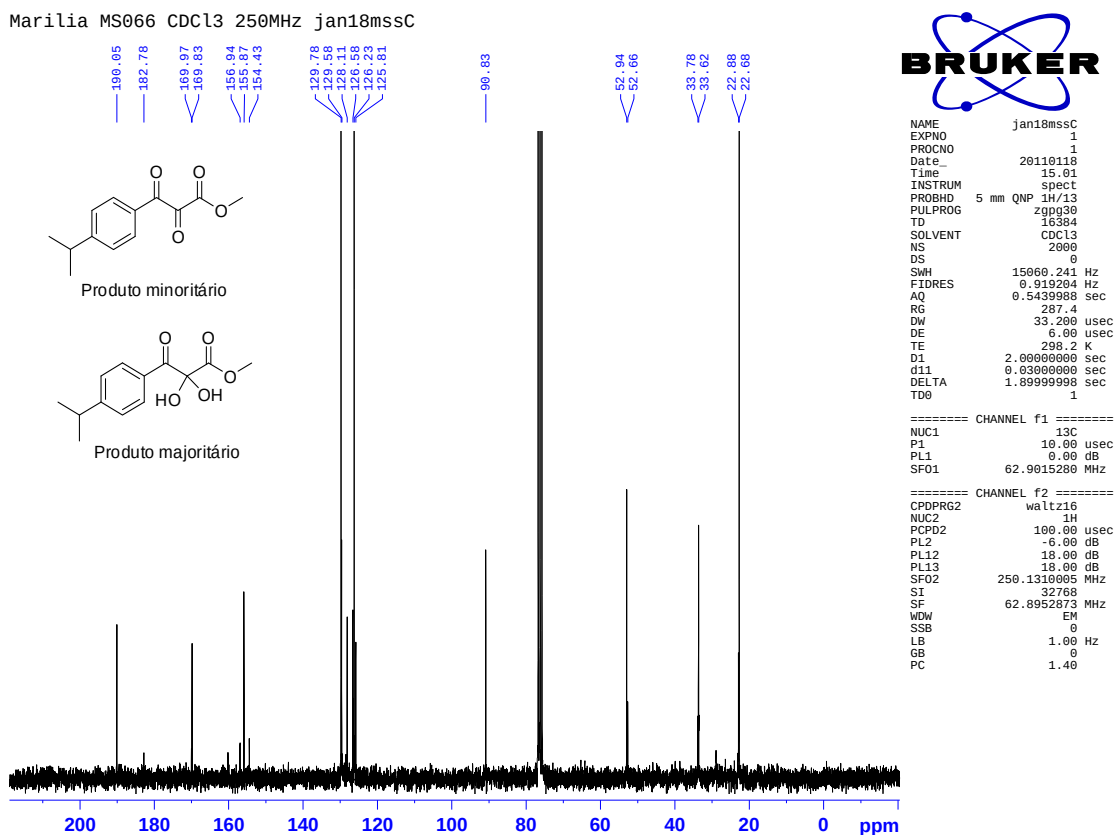
Yield: 76%, yellow oil; IR (film, ν_{max}): 3413, 2959, 2876, 1749, 1691, 1606, 1185, 854 cm⁻¹. Mixture of vicinal tricarbonyl compound and its hydrate form (1:3) - ¹H NMR (250 MHz, CDCl₃): *Tricarbonyl compound*: δ 1.29 (d, ³J = 6.9Hz, 6H); 2.98 (m, 1H); 3.96 (s, 1H); 7.40 (d, ³J = 8.3Hz, 2H); 7.93 (d, ³J = 8.4Hz, 2H). *Hydrate*: δ 1.27 (d, ³J = 6.9Hz, 6H); 2.98 (m, 1H); 3.76 (s, 1H); 5.42 (br, 2H); 7.33 (d, ³J = 8.4Hz, 2H); 8.02 (d, ³J = 8.4Hz, 2H). ¹³C NMR (62.5 MHz, CDCl₃) - *Tricarbonyl compound*: δ 22.9; 33.8; 52.7; 125.8; 126.6; 129.6; 154.4; 156.9; 170.0; 182.8. *Hydrate*: δ 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 C₁₃H₁₅O₄ m/z 235.0937 [M + H]⁺; found m/z 235.0970.

Marilia MS066 CDCl₃ 250MHz jan14mssH1

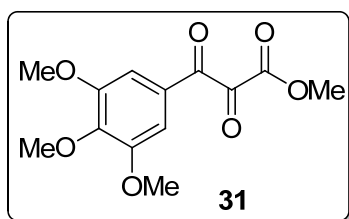


¹H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound **28** and its hydrated form.

Marilia MS066 CDCl₃ 250MHz jan18mssc



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound **28** and its hydrated form.

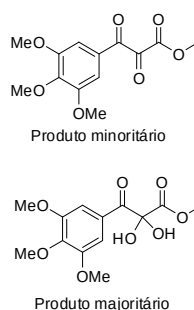
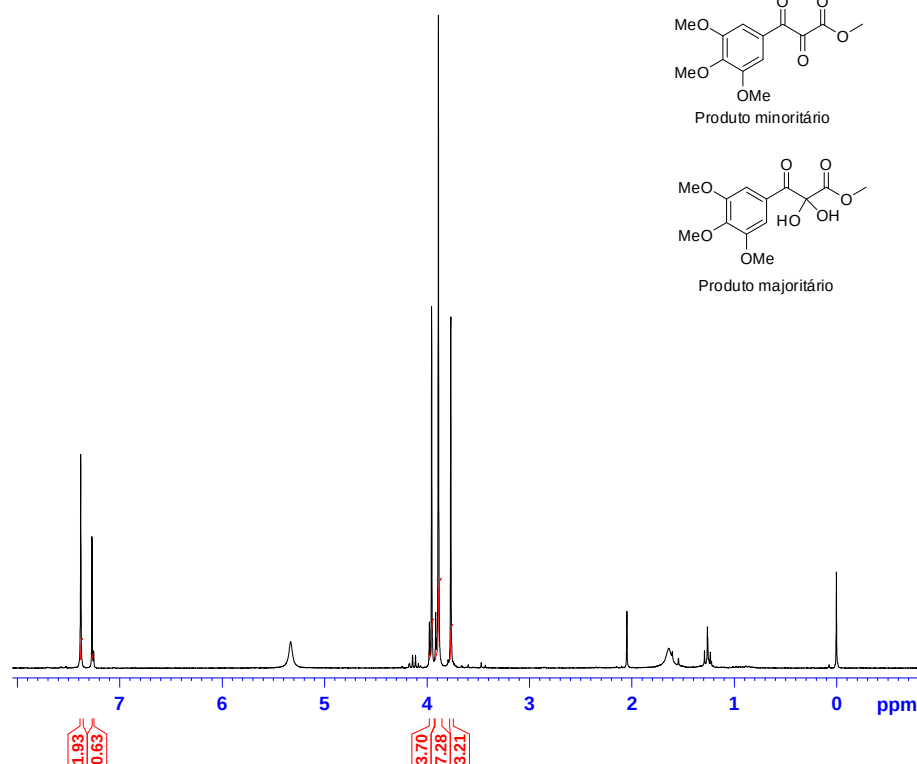


Methyl 2,3-dioxo-3-(3,4,5-trimethoxyphenyl)propanoate
(**31**)

Yield: 67%, yellow oil; IR (film, $\nu_{\max}$): 3418, 2954, 2843, 1747, 1693, 1585, 1127 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 3.79 (s, 3H); 3.91 (s, 6H); 3.97 (s, 3H); 5.35

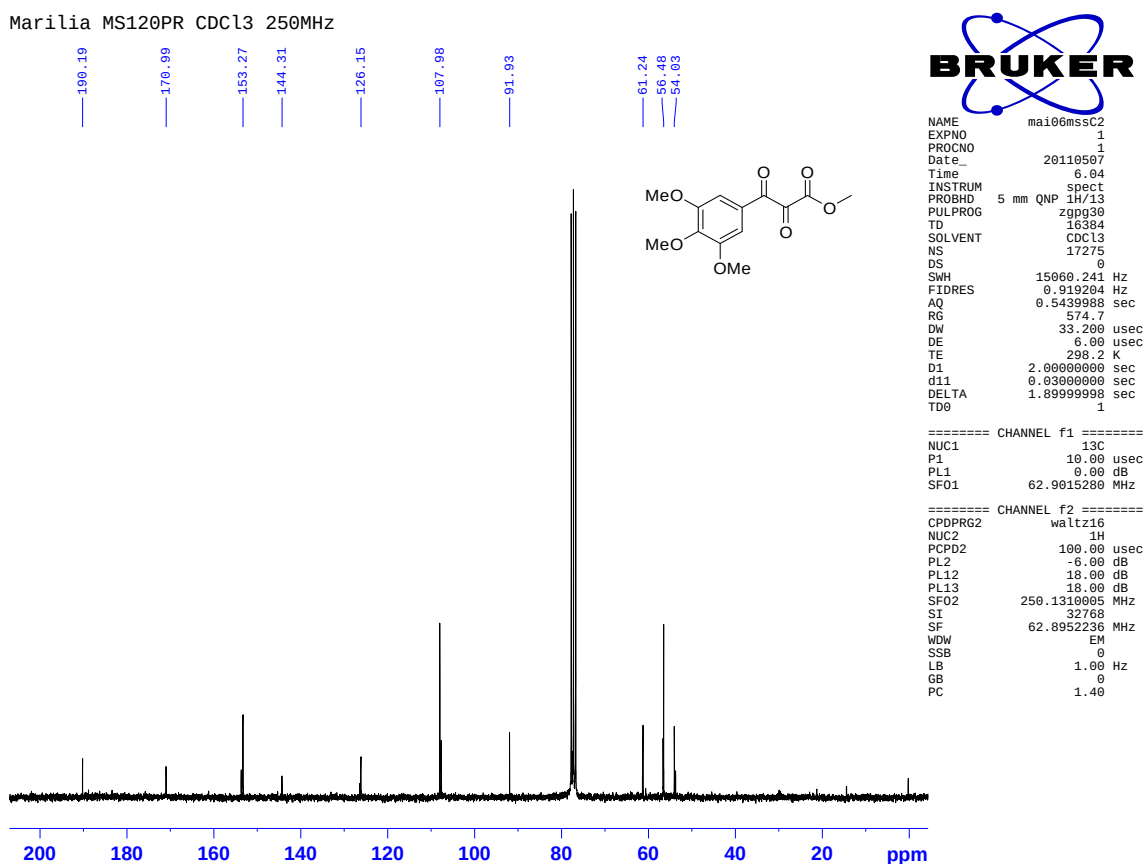
(bs, 2H); 7.40 (s, 2H); ^{13}C NMR (62.5 MHz, CDCl_3): δ 54.0; 56.5; 61.2; 91.9; 108.0; 126.2; 144.3; 153.3; 171.0; 190.2; HRMS (ESI, m/z): Calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_7$ 283.0812 [$\text{M} + \text{H}$] $^+$; found 283.0809.

Marilia MS120PR CDCl_3 250MHz mai02mssH

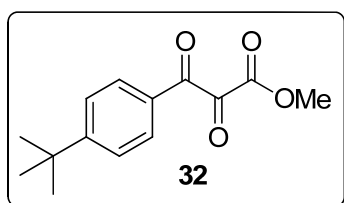


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RG	1824.6
DW	96.600 usec
DE	6.00 usec
TE	298.2 K
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TD0	1
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PL1	-6.00 dB
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SI	32768
SF	250.1299975 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^1H NMR (250 MHz, CDCl_3) spectrum of the tricarbonyl compound **31** and its hydrated form.



¹³C NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound **31** and its hydrated form.

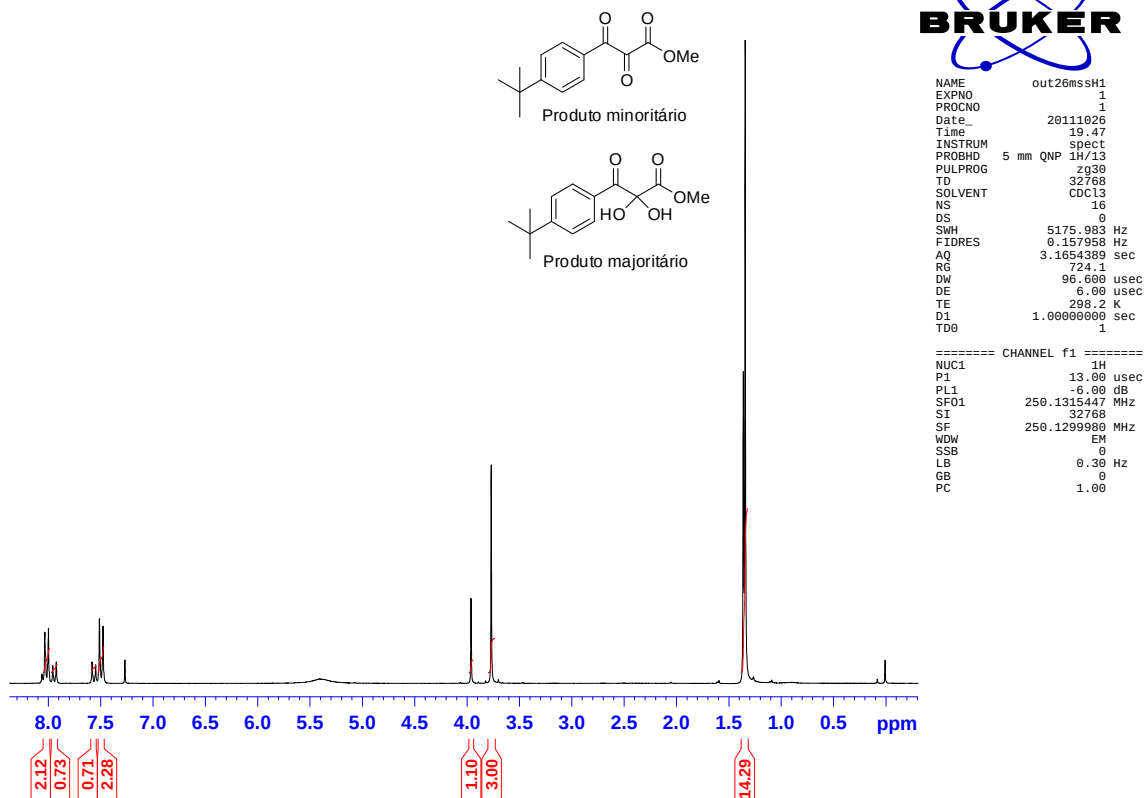


Methyl 3-(4-tert-butylphenyl)-2,3-dioxopropanoate (**32**)

Yield: >95%; white solid, m.p. 56-59 °C; IR (KBr, $\nu_{\max}$): 3416, 2962, 1748, 1688, 1604, 1250, 1127 cm⁻¹. Mixture of the tricarbonyl compound and its hydrate (1:3): ¹H

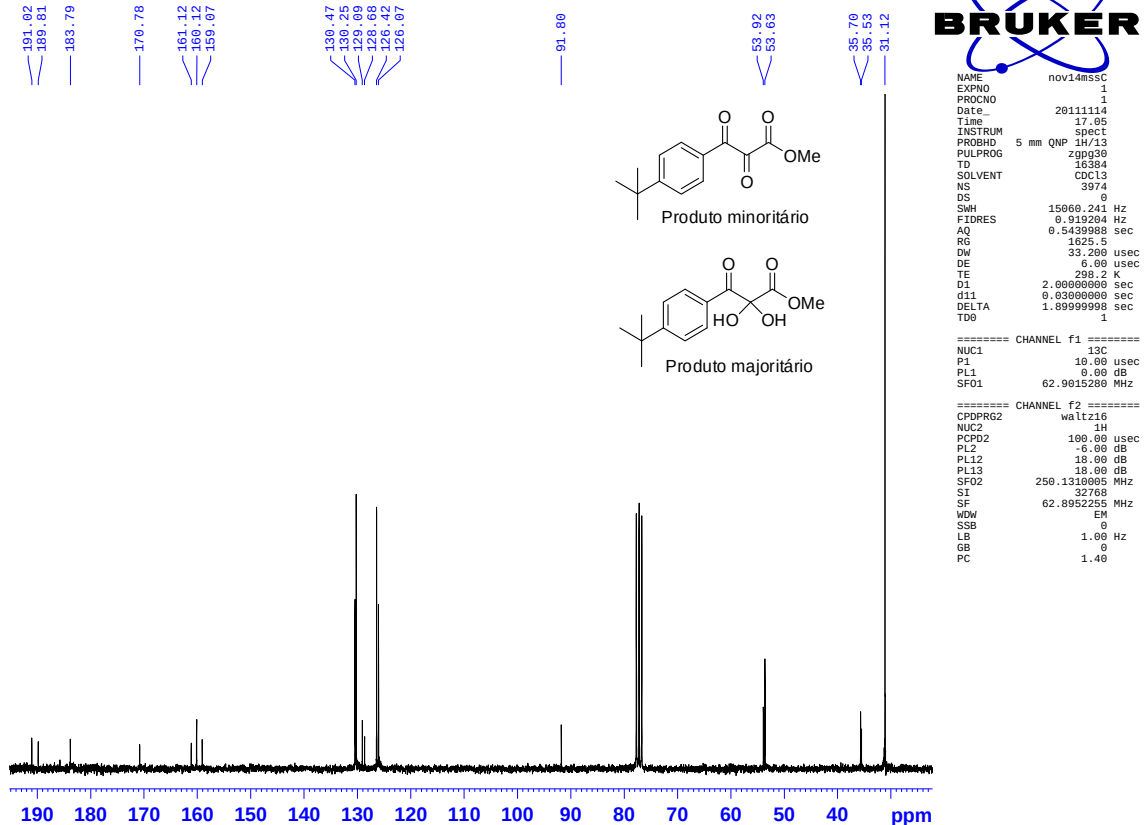
NMR (250 MHz, CDCl₃) - *Tricarbonyl compound*: δ 1.35 (s, 9H); 3.95 (s, 3H); 7.56 (d, ³J = 8.5 Hz, 2H); 7.93 (d, ³J = 8.5 Hz, 2H). *Hydrate*: δ 1.34 (s, 9H); 3.76 (s, 3H); 7.49 (d, ³J = 8.6 Hz, 2H); 8.01 (d, ³J = 8.6 Hz, 2H). NMR de ¹³C (62.5 MHz, CDCl₃): *Tricarbonyl compound*: δ 31.1; 35.5; 53.9; 126.1; 128.7; 130.5; 160.1; 161.1; 183.8; 189.8. *Hydrate*: δ 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 C₁₄H₁₇O₄ m/z 249.1127 [M + H]⁺; found m/z 249.1104

Marília MS134B CDCl₃ 250MHz out26mssH1

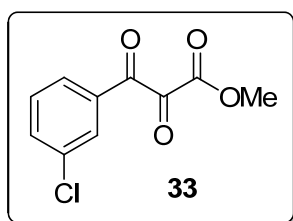


¹H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound **32** and its hydrated form.

Marília MS130 CDCl₃ 250MHz nov14mssc



^{13}C NMR (62.5 MHz, CDCl_3) spectrum of the tricarbonyl compound **32** and its hydrated form.

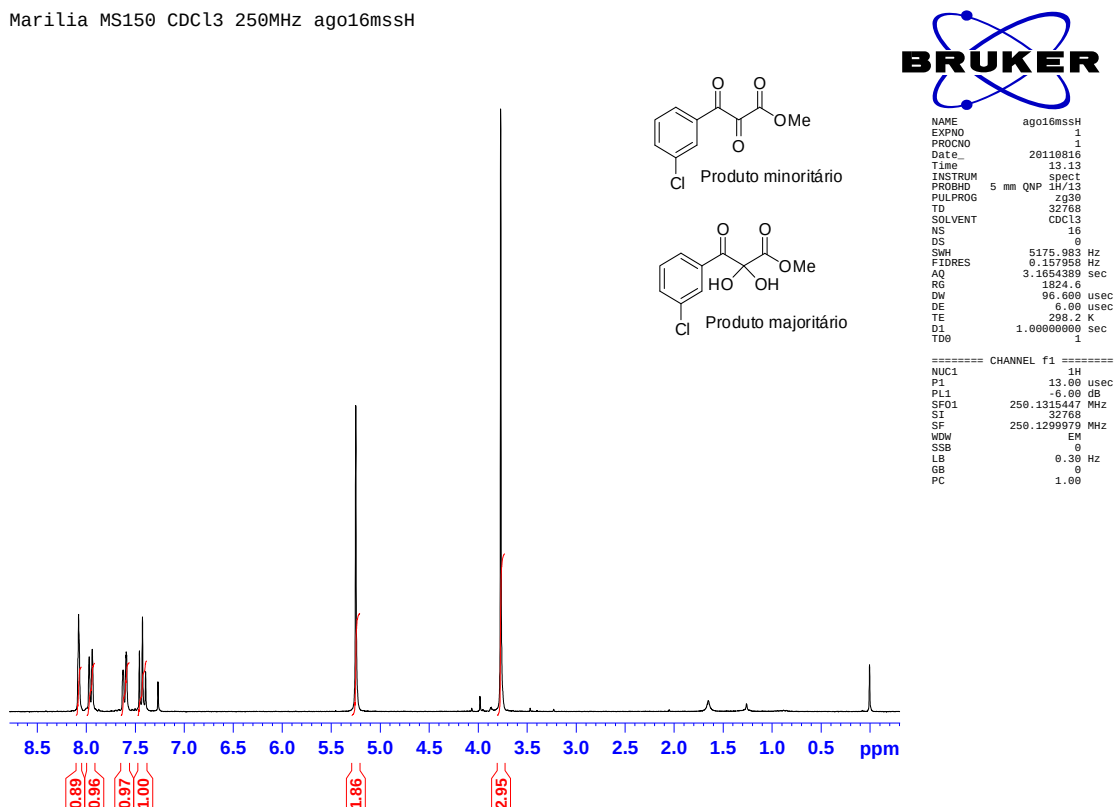


Methyl 3-(3-chlorophenyl)-2,3-dioxopropanoate (**33**)

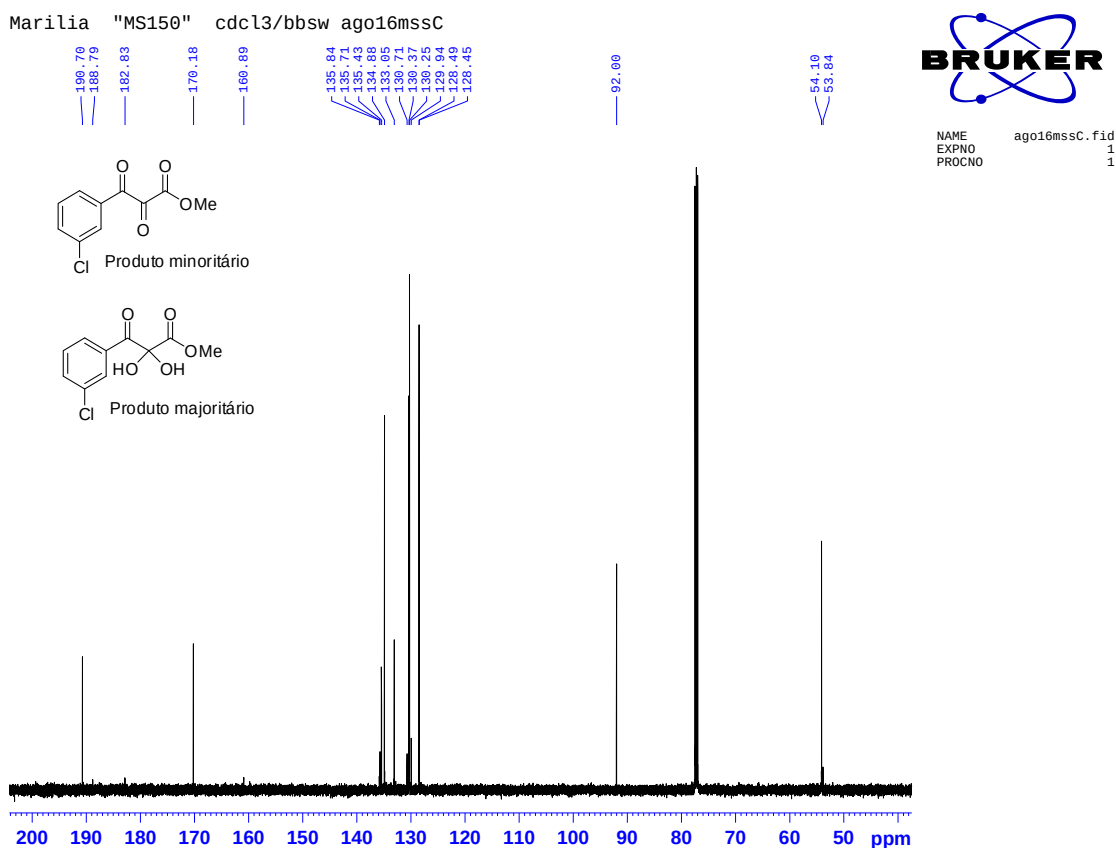
Yield: 65%, yellow tinged solid, m.p. 66-67°C. IR (KBr, ν_{max}): 3468, 3421, 3073, 2959, 1755, 1743, 1701, 1110, 912 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ 3.77 (s, 3H); 5.25 (s, 2H); 7.43 (t, $^3J = 8.0$ Hz, 1H); 7.61 (dt, $^3J = 1.0$ Hz, $^3J = 8.0$ Hz, 1H); 7.96 (d, $^3J = 7.9$ Hz, 1H); 8.08 (s, 1H). Mixture of the tricarbonyl compound and its hydrate (1:3) - ^{13}C

NMR (125 MHz, CDCl_3): *Tricarbonyl compound*: δ 53.8; 128.4; 129.9; 130.7; 135.7; 135.8; 160.9; 182.8; 188.8. *Hydrate*: δ 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 $\text{C}_{14}\text{H}_{17}\text{O}_3$ 227.0111 $[\text{M} + \text{H}]^+$; Found m/z 227.0189.

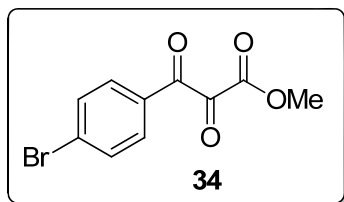
Marilia MS150 CDCl_3 250MHz ago16mssH



^1H 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

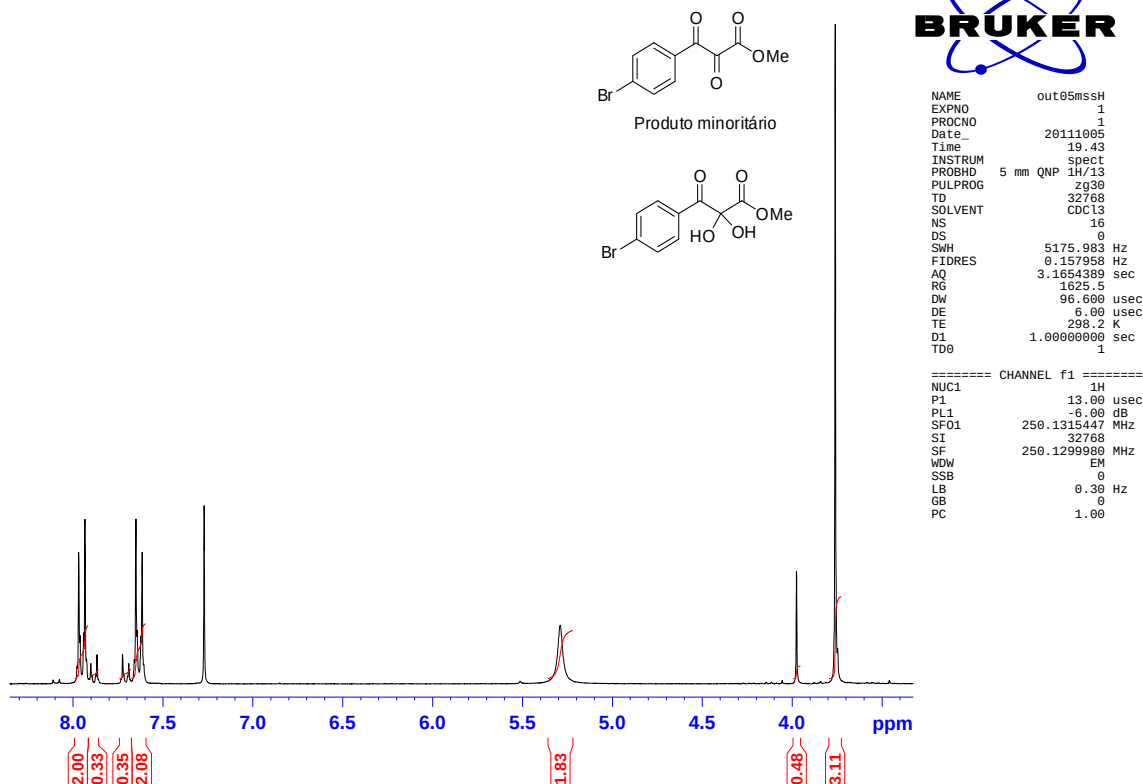


Methyl 3-(4-bromophenyl)-2,3-dioxopropanoate (**34**)

Yield: 75%, white solid, m.p. 99-100 °C; IR (KBr, ν_{max}): 3421, 1756, 1738, 1694, 1585, 1133, 803 cm^{-1} . Mixture of tricarbonyl compound and hydrate (1:6) ^1H NMR (250

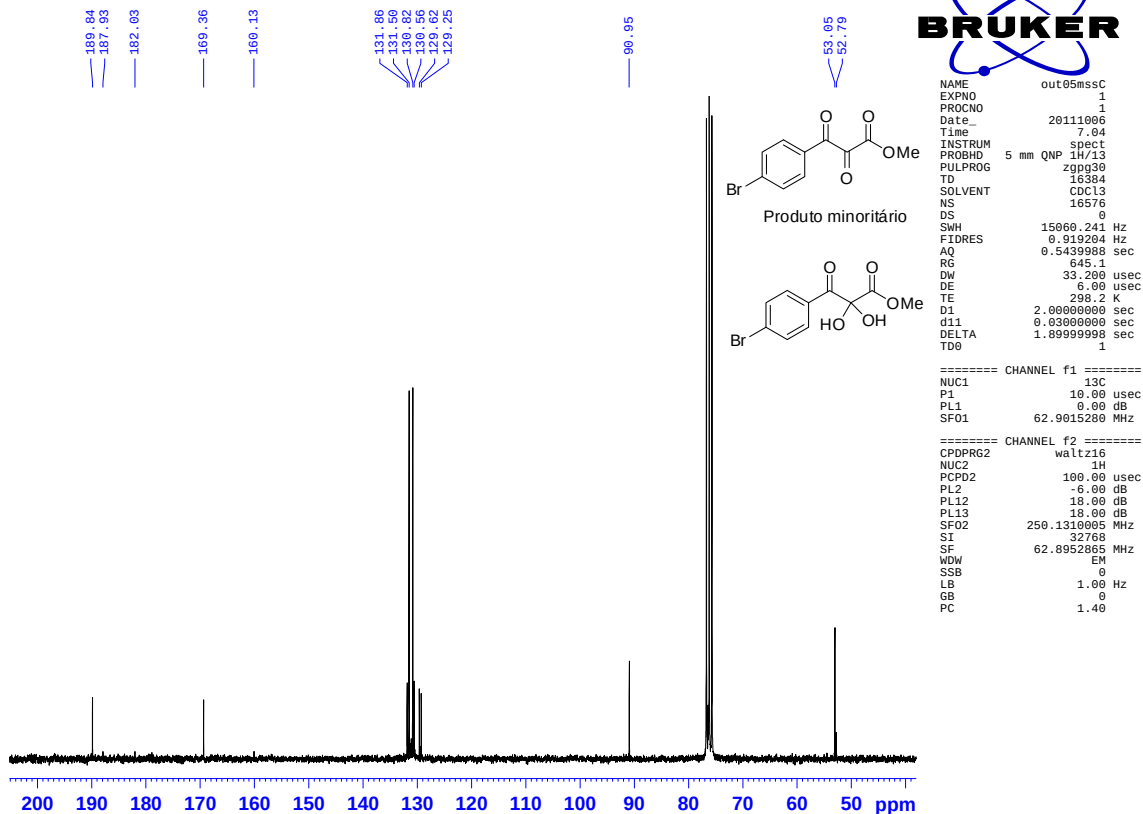
MHz, CDCl_3) - *Tricarbonyl compound*: δ 3.97 (s, 3H); 7.70 (d, $^3J = 8.7$ Hz, 2H); 7.88 (d, $^3J = 8.7$ Hz, 2H). *Hydrate*: δ 3.75 (s, 3H); 5.28 (br, 2H); 7.62 (d, $^3J = 8.7$ Hz, 2H); 7.94 (d, $^3J = 8.7$ Hz, 2H). ^{13}C NMR (62.5 MHz, CDCl_3) - *Tricarbonyl compound*: δ 52.8; 130.6; 131.9; 160.1; 182.0; 187.9; *Hydrate*: δ 53.1; 91.0; 129.3; 129.6; 130.8; 131.5; 169.4; 189.8. HRMS (ESI, m/z): Calcd. for $\text{C}_{10}\text{H}_8\text{BrO}_4$ 270.9600 $[\text{M} + \text{H}]^+$; found 270.9591

MS179P 250MHz/CDC13 out05mssH

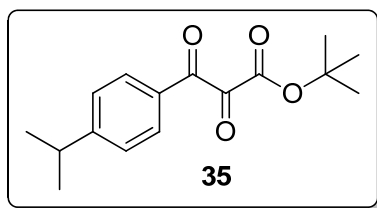


¹H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound **34** and its hydrated form.

MS179P 250MHz/CDC13 out05mssC



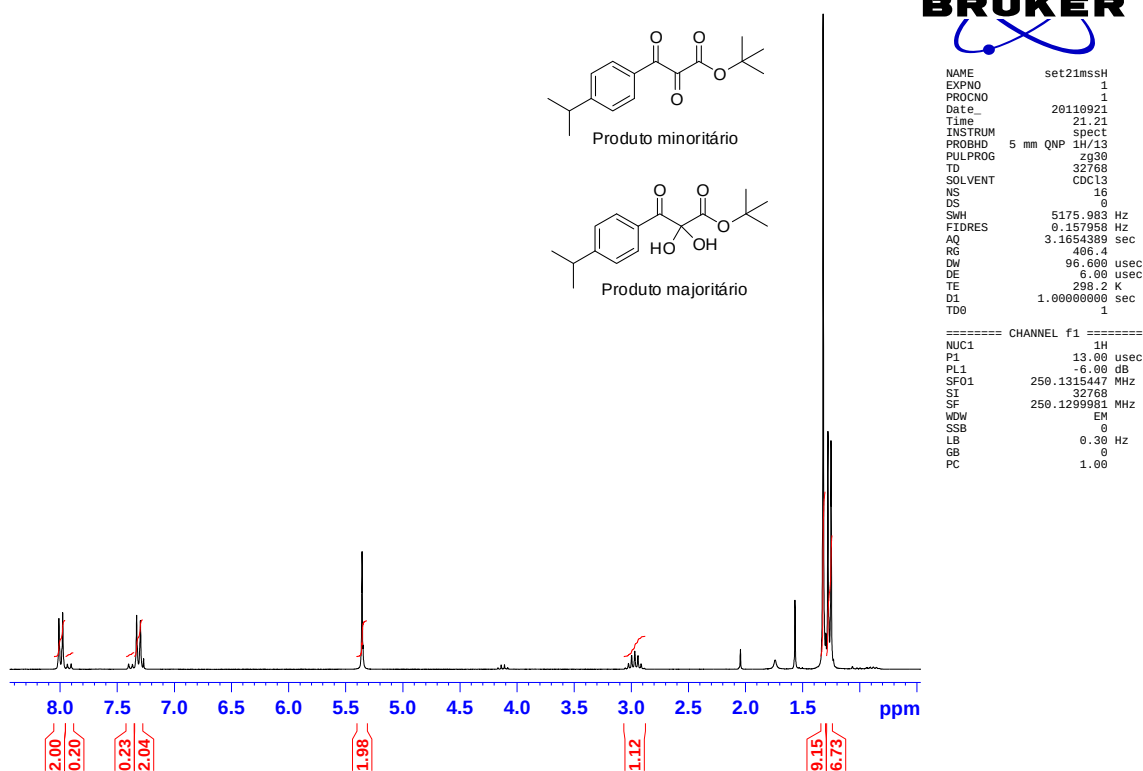
¹³C NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound **34** and its hydrated form.



tert-Butyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (**35**)

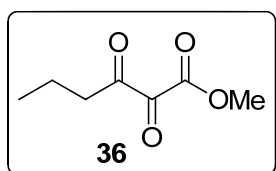
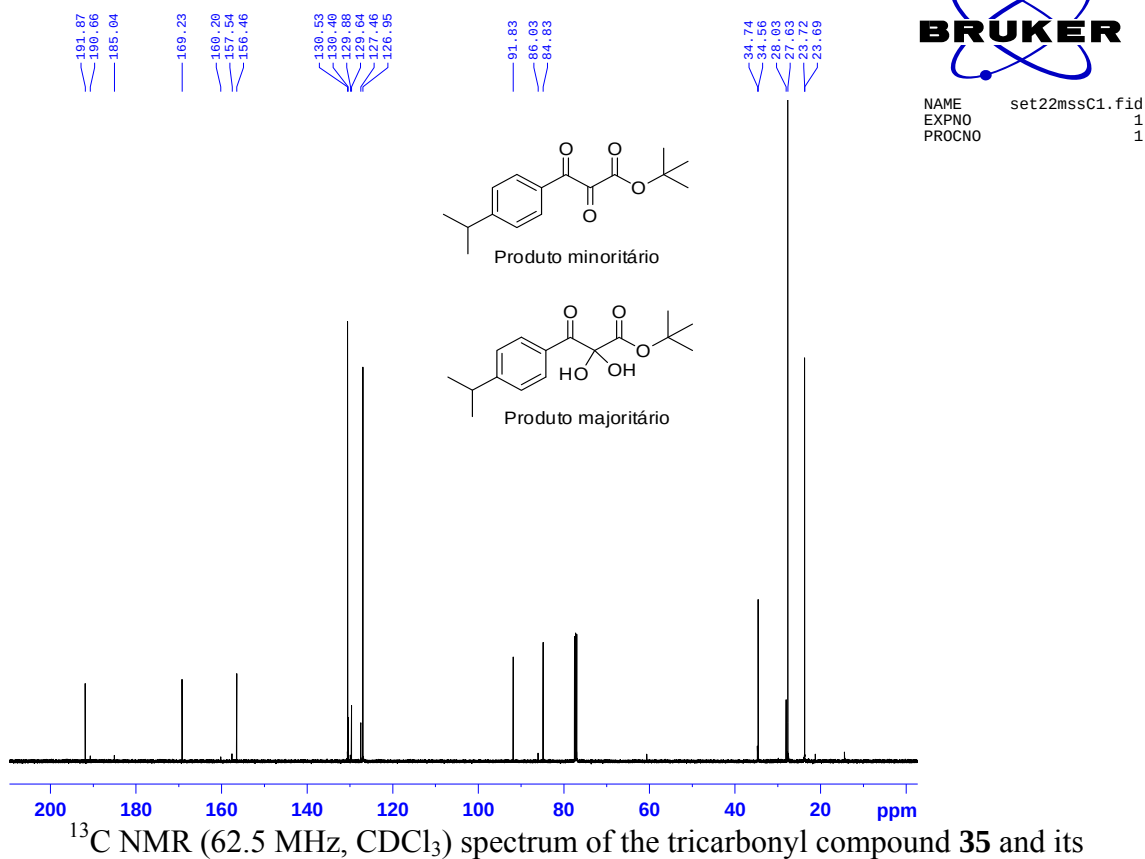
Yield: 61%, yellow tinged oil; IR (film, $\nu_{\max}$): 3432, 2965, 2933, 2873, 1738, 1692, 1606, 1571, 1128, 851 cm^{-1} . Mixture tricarbonyl compound and its hydrated form (1:10). ^1H NMR (250 MHz, CDCl_3) - *Tricarbonyl compound*: δ 7.38 (d, $^3J = 8.3$ Hz, 2H); 7.92 (d, $^3J = 8.3$ Hz, 2H). *Hydrate*: δ 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*: δ 23.7; 28.0; 34.7; 86.0; 127.5; 129.9; 130.4; 157.5; 160.2; 185.0; 190.7. *Hydrate*: δ 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 $\text{C}_{16}\text{H}_{21}\text{O}_4$ 277.1434 $[\text{M} + \text{H}]^+$; found 277.1430.

Marília MS173A CDCl_3 250MHz set21mssh



^1H NMR (250 MHz, CDCl_3) spectrum of the tricarbonyl compound **35** and its hydrated form.

Marília "MS 173A" CDCl₃/BBSW set22mssC1



Methyl 2,3-dioxohexanoate (**36**)

Yield: 22%, colorless oil; IR (film, ν_{max}): 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 C₇H₁₁O₄ 159.0652 [M + H]⁺; found 159.0650.

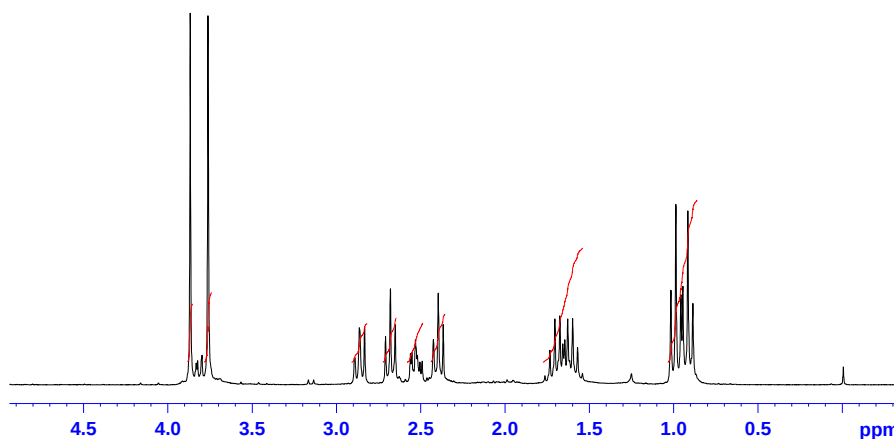
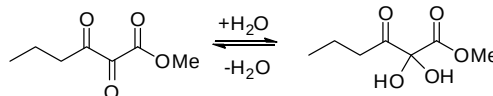
Marilia MS152A CDCl₃ 250MHz ago23mssH



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FIDRES     0.157958 Hz
AQ         3.1654389 sec
RG         512
DW         96.690 usec
DE         6.00 usec
TE         298.2 K
D1         1.0000000 sec
TD0        1

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PL1       -6.00 dB
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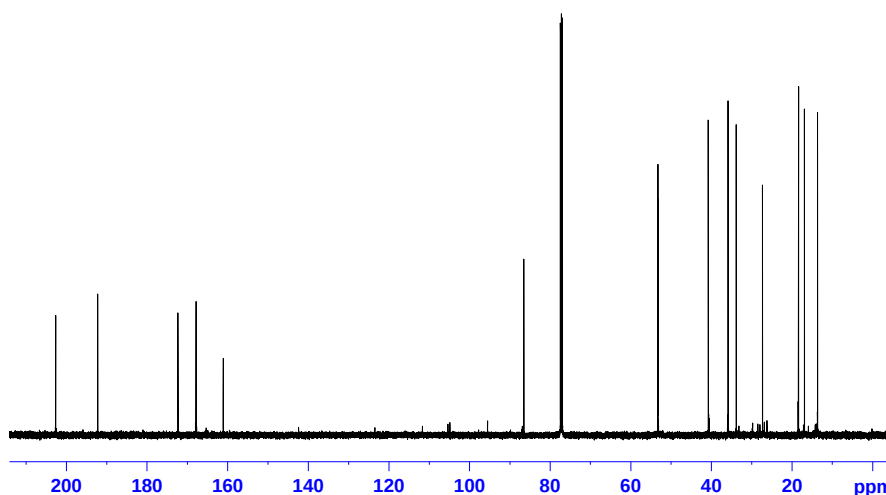
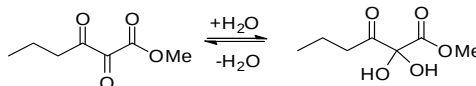
¹H NMR (250 MHz, CDCl₃) spectrum of the tricarbonyl compound **36** and its hydrated form.

Marilia "MS152A" cdcl3/bbsw ago24mssc



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NAME      ago24mssc.fid
EXPNO     1
PROCNO    1
    
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¹³C NMR (62.5 MHz, CDCl₃) spectrum of the tricarbonyl compound **36** and its hydrated form.