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 (^{1}H- and ^{13}C-) were recorded on an Bruker 250 MHz for ^{1}H and 62.5 MHz for ^{13}C; Bruker 400 MHz for ^{1}H and Varian Inova 500 (500 MHz to ^{1}H 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

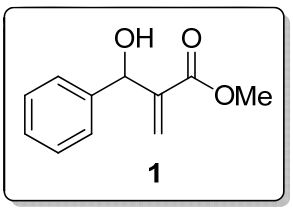
configuration ESI-QqTof with a resolution of 5,000 and 50.0 ppm accuracy in TOF mass analyzer.

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**)

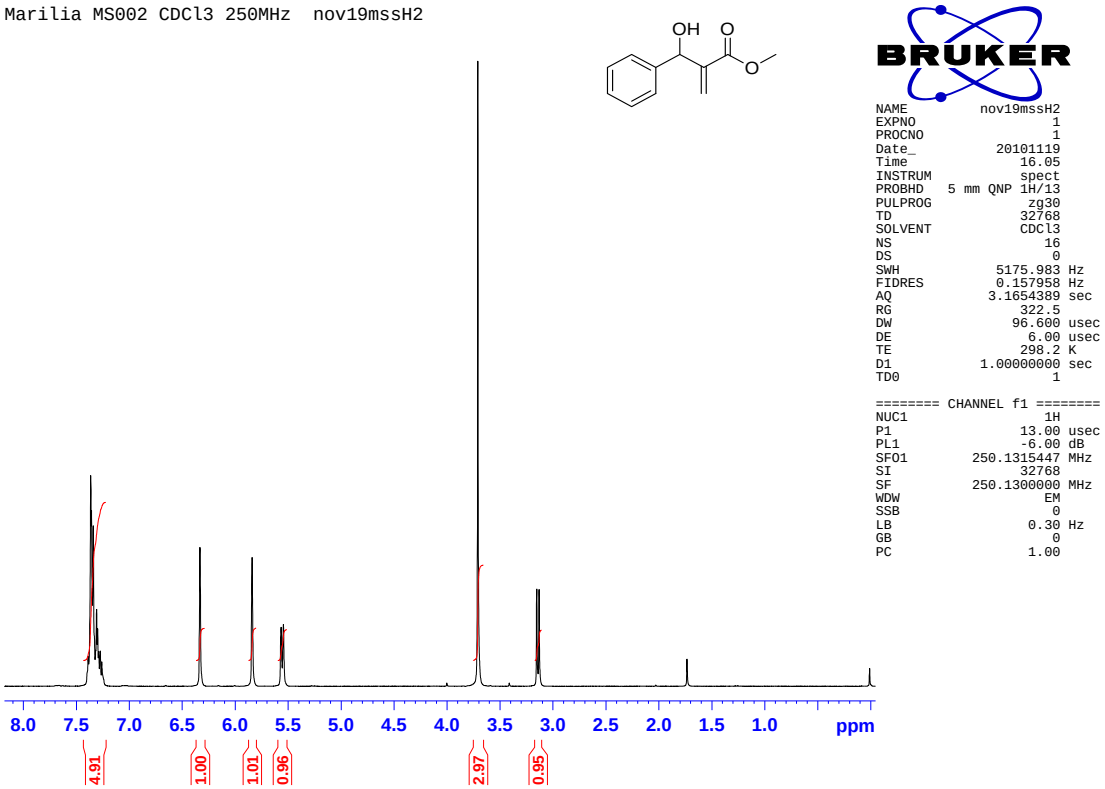
To a stirred mixture of an aldehyde (10 to 30 mmol) and acrylate (5 equiv.) was added DABCO (0.65 equivalents). The resulting mixture was stirred at room temperature. The reaction was followed by TLC. At the end the acrylate was removed under reduced pressure and the residue was dissolved in ethyl acetate (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).



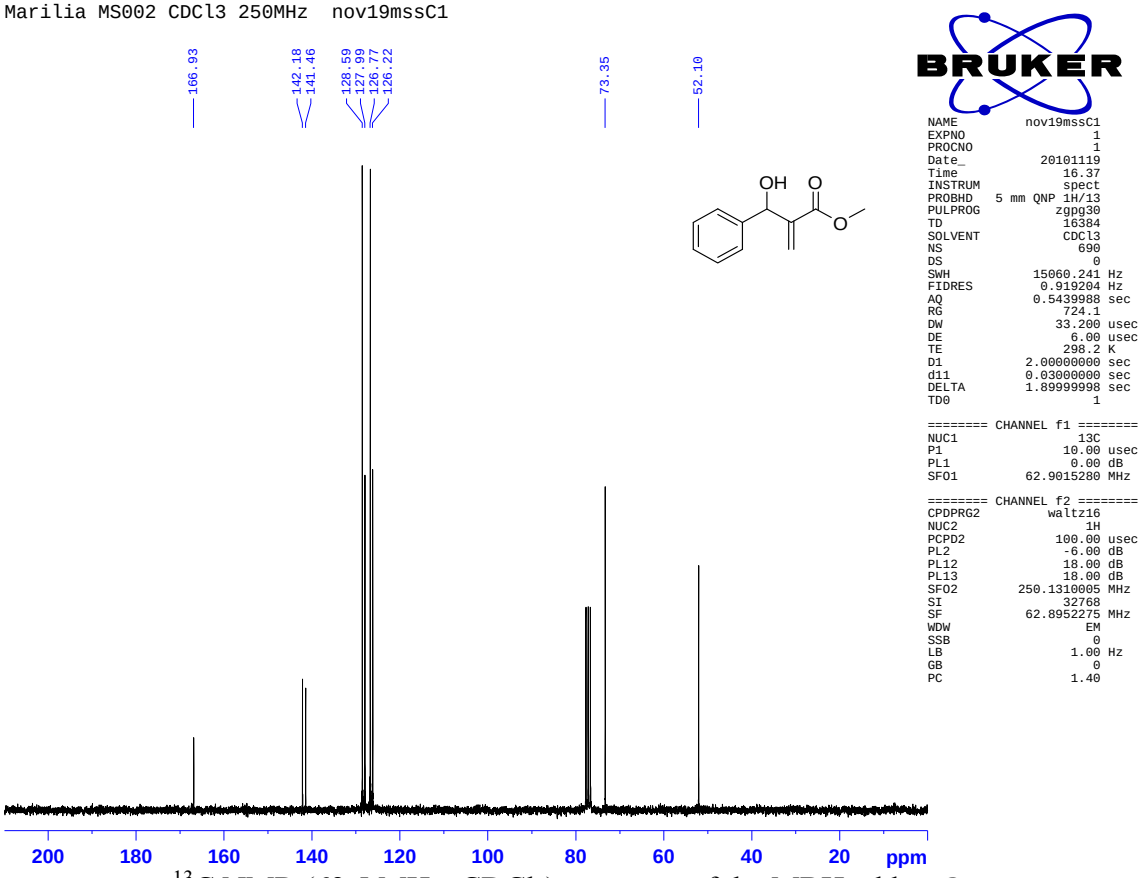
1

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

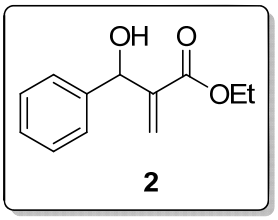
Yield: 85%, colorless oil; IR (film, ν_{max}): 3422, 2956, 1718, 1630, 1198 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 3.14 (d, ^3J = 5.5 Hz, 1H); 3.71 (t, 3H); 5.56 (d, ^3J = 5.5 Hz, 1H); 5.84 (s, 1H); 6.33 (s, 1H); 7.29-7.33 (m, 5H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.1; 73.3; 126.2; 126.8; 128; 128.6; 141.5; 142.2; 166.9. HRMS (ESI, *m/z*): Calcd. for $C_{11}H_{13}O_3$ 193.0859 $[M + H]^+$; found 193.0856.



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

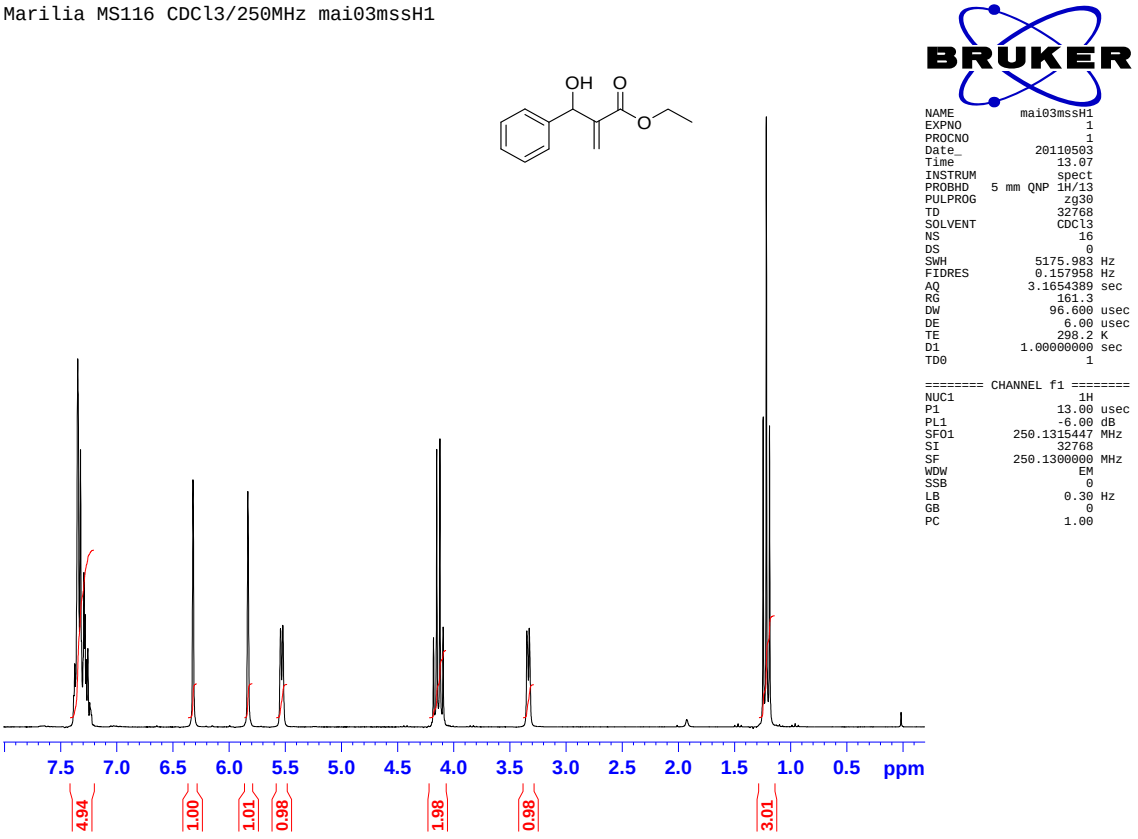


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **2**.

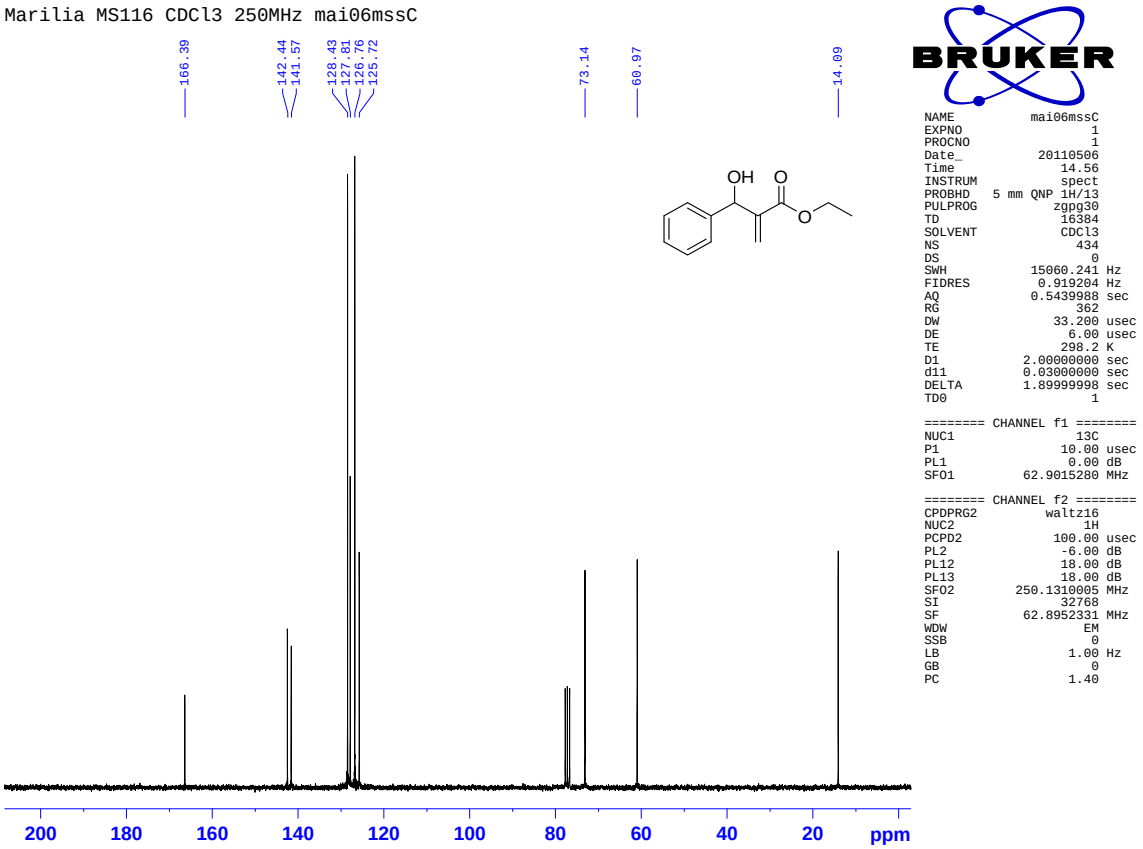


(±)-Ethyl 2-[hydroxy(phenyl)methyl]prop-2-enoate (**2**)

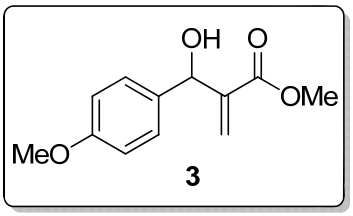
Yield: 83%, colorless oil; IR (film, ν_{max}): 3456, 3032, 2983, 2906, 1714, 1629, 1148, 1113, 864, 839 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.22 (t, ^{3}J = 7.1Hz, 3H); 3.34 (d, ^{3}J = 5.3Hz; 1H); 4.14 (q, ^{3}J = 7.13Hz, 2H); 5.53 (d, J = 5.2Hz, 1H); 5.83 (s, 1H); 6.32 (s, 1H); 7.26-7.38 (m, 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 $C_{12}H_{15}O_3$ 207.1016 $[M + H]^+$; found 207.1015.



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

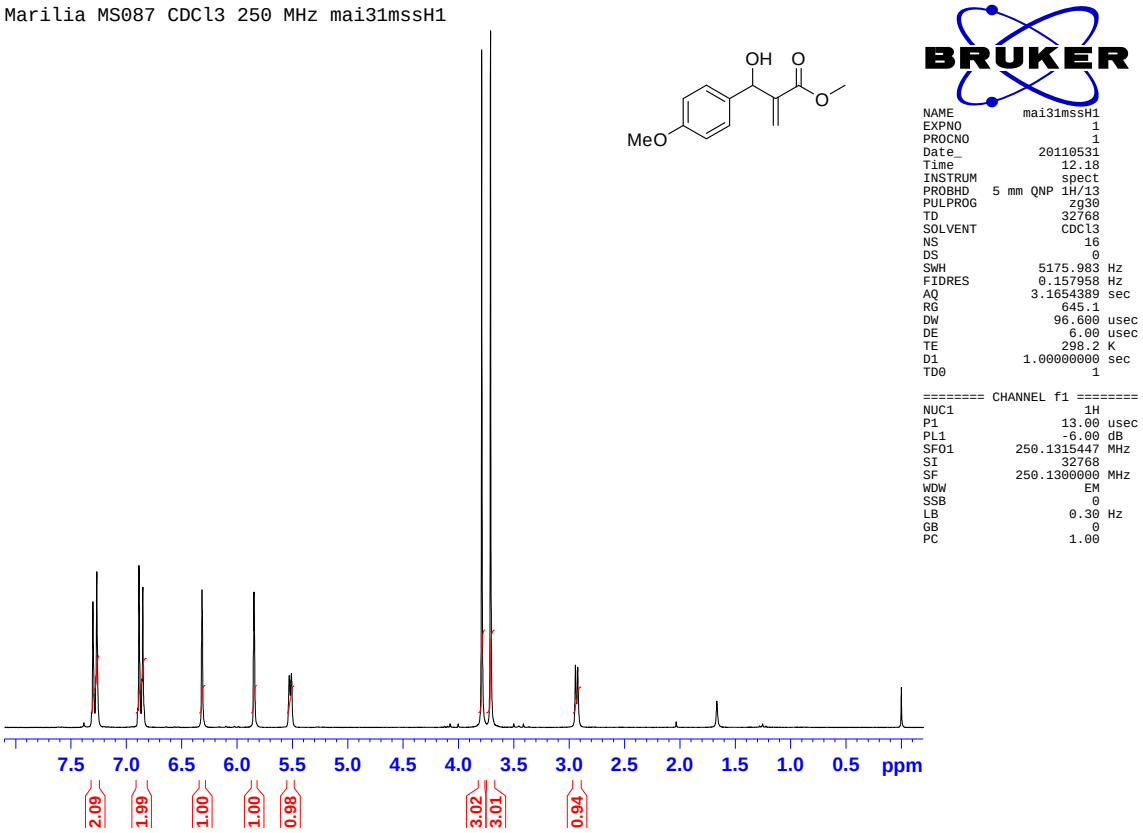


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **2**.

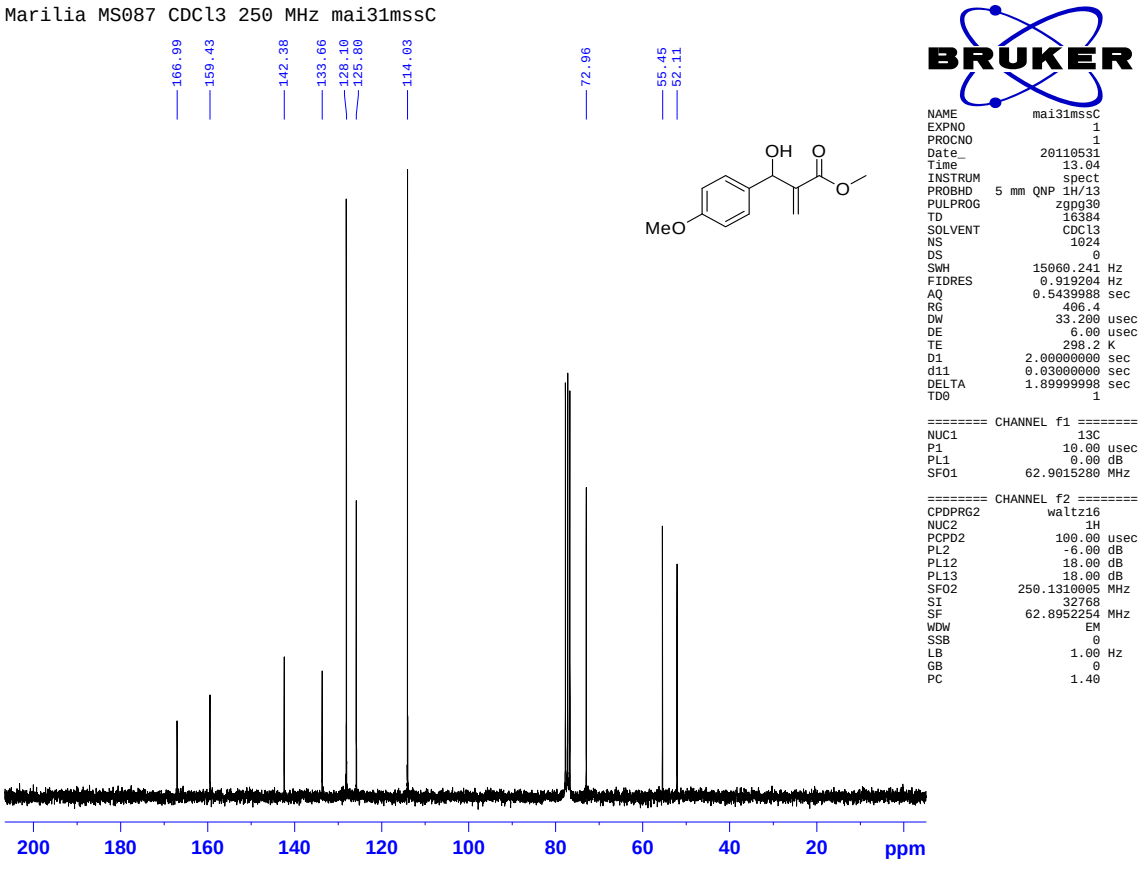


(±)-Methyl 2-[hydroxy(4-methoxyphenyl)methyl]prop-2-enoate (**3**)

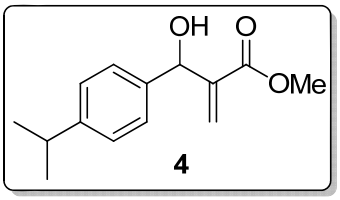
Yield: 71%, white solid, m.p. 60-63 °C; IR (KBr, ν_{max}): 3482, 2954, 2838, 1721, 1611, 1175, 1149, 830, 734 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.93 (d, ^3J = 5.2Hz, 1H); 3.71 (s, 3H); 3.79 (s, 3H); 5.52 (d, ^3J = 4.8Hz, 1H); 5.85 (s, 1H); 6.32 (s, 1H); 6.87 (d, ^3J = 8.7Hz, 2H); 7.28 (d, ^3J = 8.6Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{12}H_{15}O_4$ 223.0965 $[M + H]^+$; found 223.0963.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **3**.

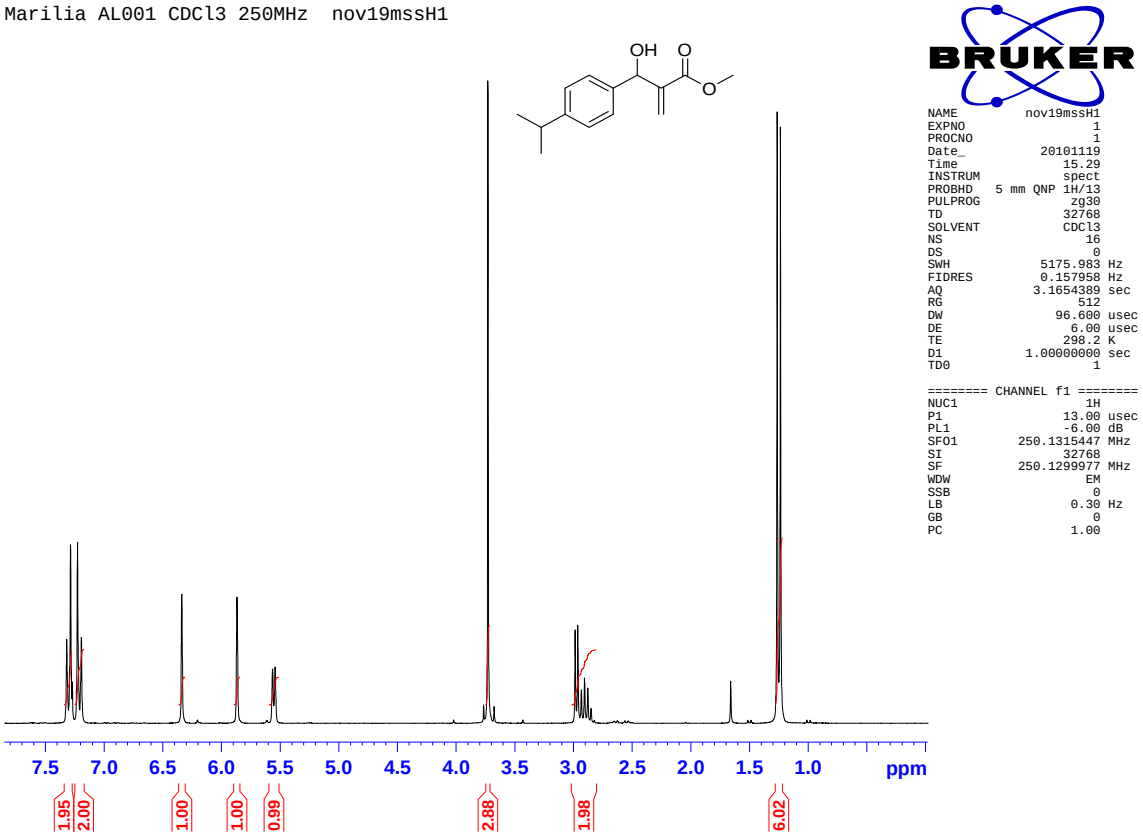


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **3**.

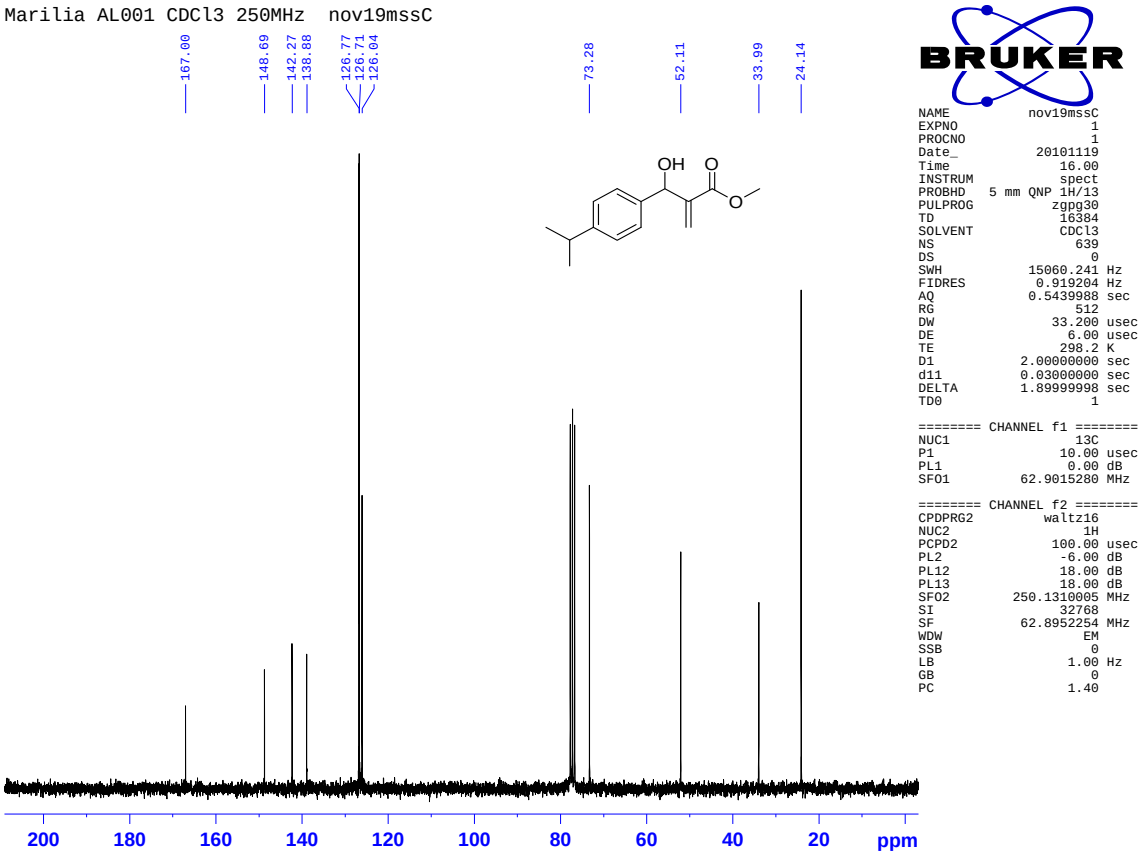


(±)-Methyl 2-{hydroxy[4-(propan-2-yl)phenyl]methyl}prop-2-enoate (**4**)

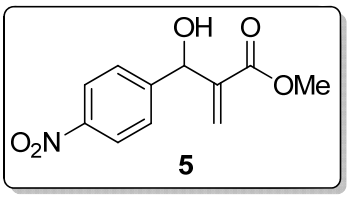
Yield: 66%, colorless oil; IR (film, ν_{max}): 3451, 2960, 2871, 1723, 1631, 1149, 822 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.25 (d, ^3J = 6.9Hz, 6H); 2.91 (m, ^3J = 6.9Hz, 1H), 2.98 (d, ^3J = 5.5Hz, 1H); 3.73 (s, 3H); 5.55 (d, ^3J = 5.4Hz, 1H); 5.87 (s, 1H); 6.34 (s, 1H); 7.21 (d, ^3J = 8.3Hz, 2H); 7.30 (d, ^3J = 8.3Hz, 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 $C_{14}H_{19}O_3$ 235.1329 $[M + H]^+$; found 235.1328.



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



^{13}C NMR (62.5 MHZ, $CDCl_3$) spectrum of the MBH adduct **4**.

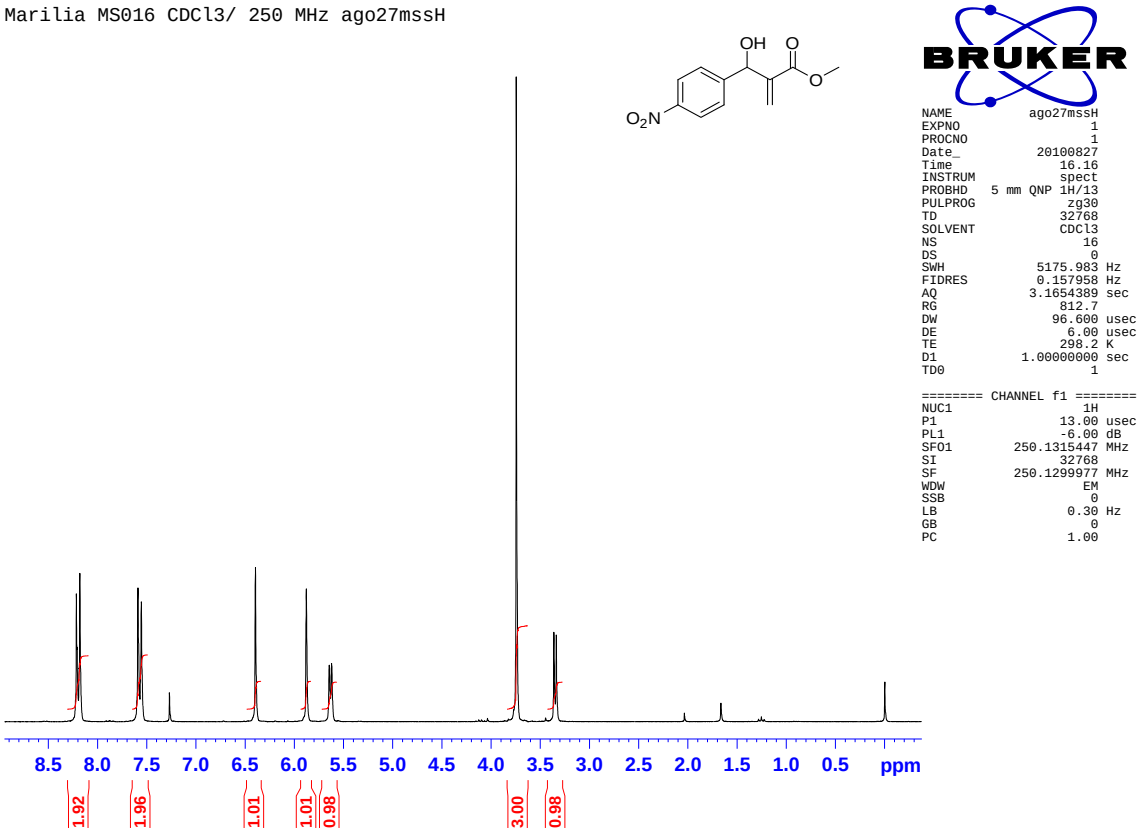


(±)-Methyl 2-[hydroxy(4-nitrophenyl)methyl]prop-2-enoate (**5**)

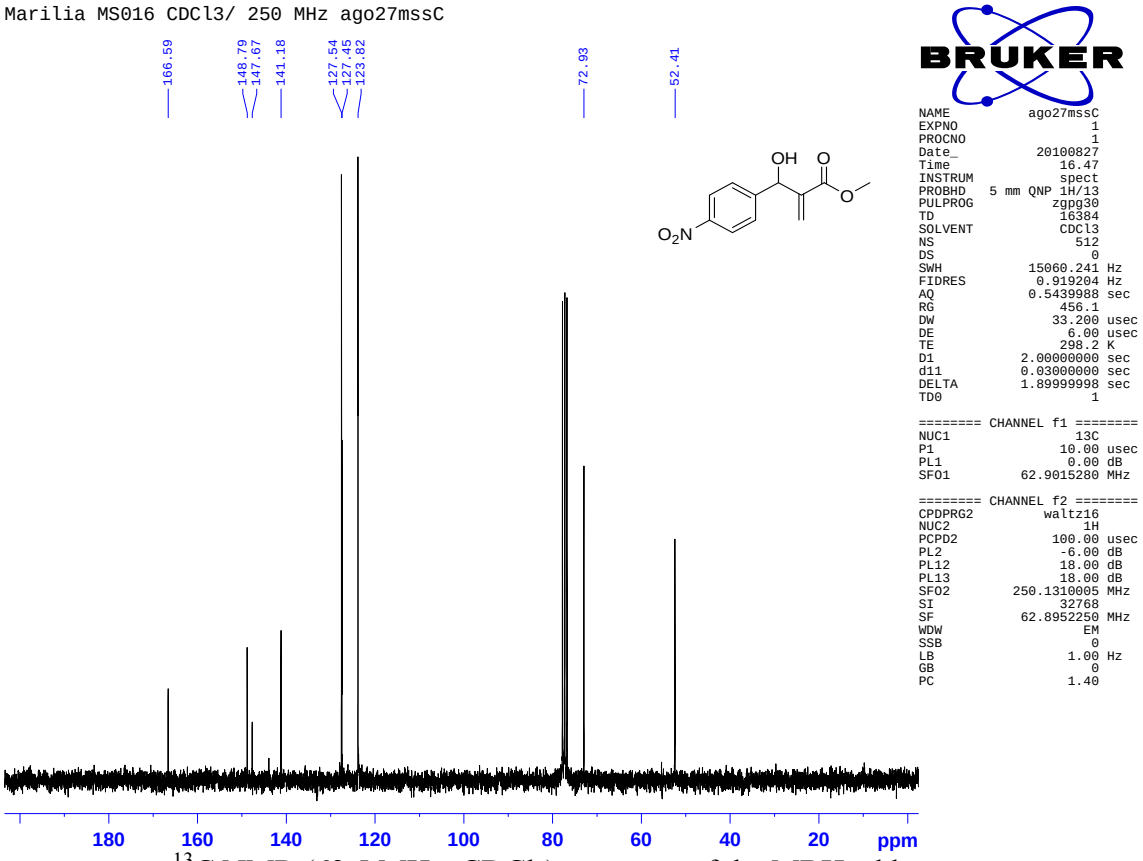
Yield: 90%, yellow solid, m.p. 71-73ºC[1,2]; IR (KBr, ν_{max}): 3230, 2995, 1723, 1633, 1503, 1331, 1154, 1050 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 3.35 (d, ^3J = 6.2Hz, 1H); 3.75 (s, 3H); 5.63 (d, ^3J = 6.0Hz, 1H); 5.88 (s, 1H); 6.40 (s, 1H); 7.57 (d, ^3J = 8.6Hz; 2H); 8.20 (d, ^3J = 8.8Hz; 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{11}H_{12}NO_5$ 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.

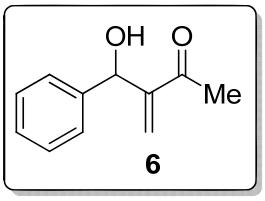
[2] Adduct **6** was purified by crystallization. To the crude product was added a tiny amount of ethyla cetate. The mixture was refluxed until the product was completely dissolved. After that a ew drops of hexane were added until the solution becomes cloudy. The mixture was placed in the refrigerator for crystallization. After 5 days at 8 ° C the crystallization was complete.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **5**.

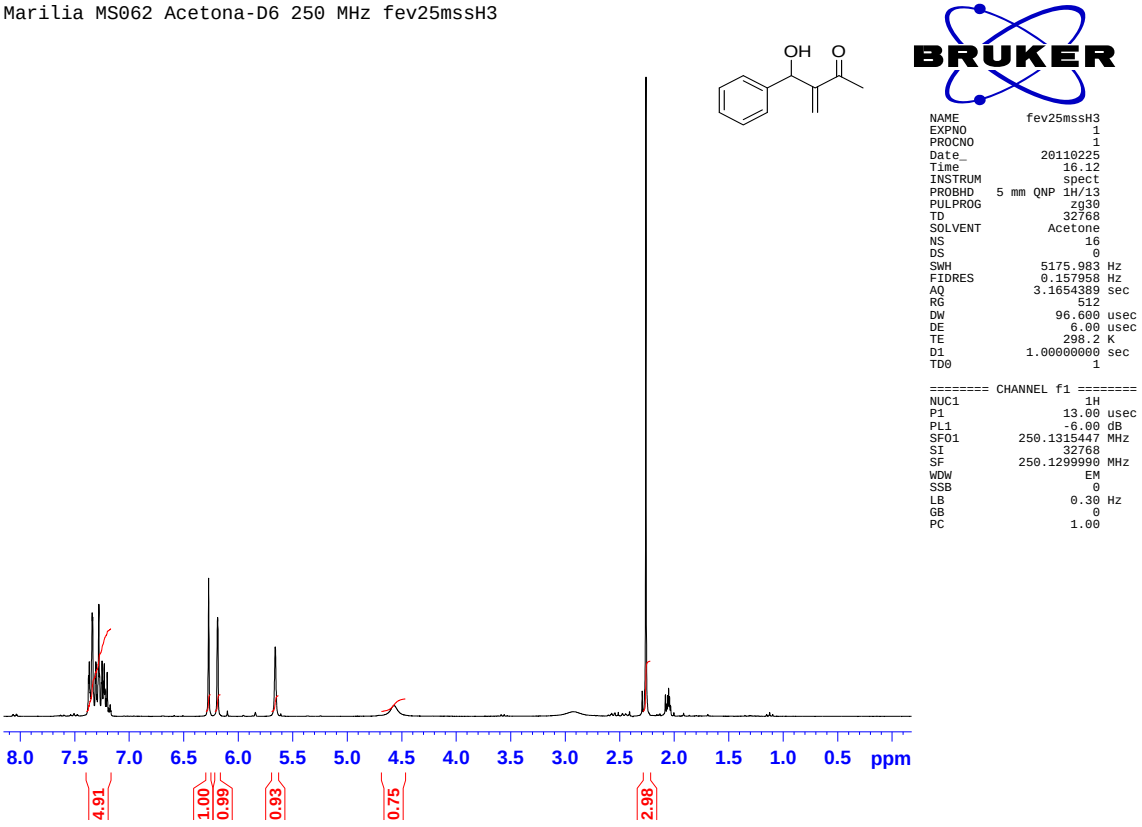


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **5**.



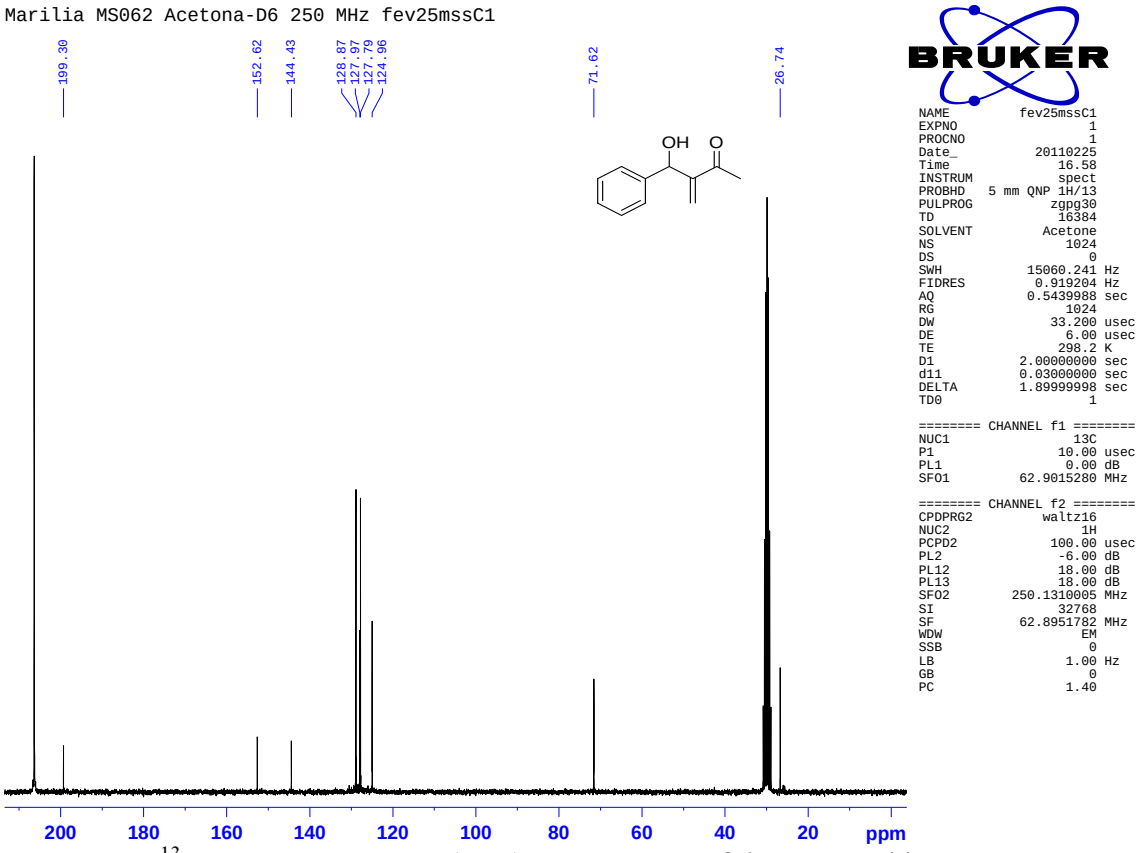
(±)-3-[Hydroxy(phenyl)methyl]but-3-en-2-one (**6**)

Yield: 62%,[3] slightly brown oil; IR (film, ν_{max}): 3423, 3063, 3031, 1673, 1192, 841 cm^{-1}. ^{1}H NMR [250 MHz, $(CD_3)_2O$]: 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, $(CD_3)_2O$]: 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 $C_{11}H_{13}O_2$ 177.0910 [M + H]$^+$; found 177.0909.

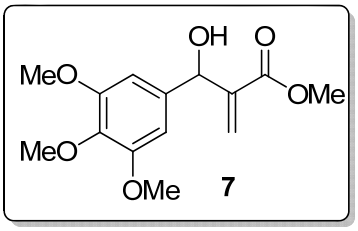


^{1}H NMR [250 MHz, $(CD_3)_2O$)] spectrum of the MBH adduct **6**.

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

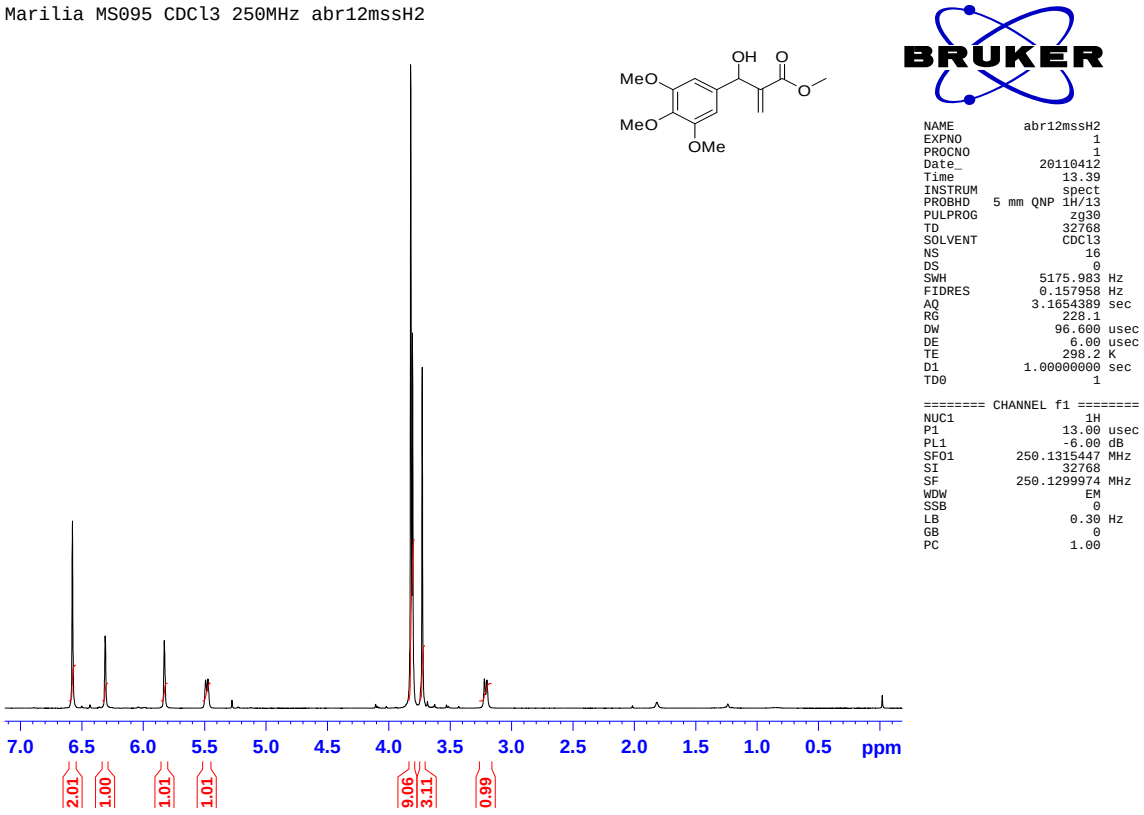


^{13}C NMR [62.5 MHz, $(CD_3)_2O$] spectrum of the MBH adduct **6**.

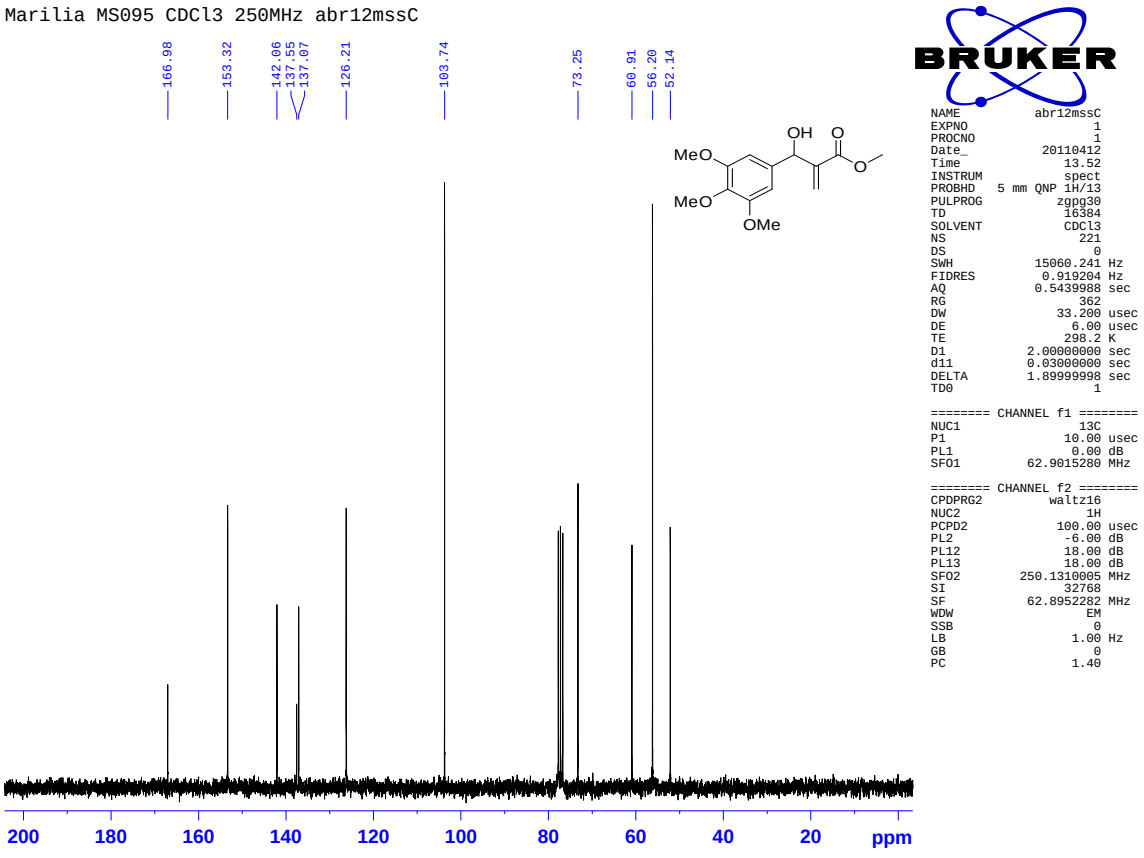


(±)-Methyl 2-[hydroxy(3,4,5-trimethoxyphenyl)methyl]prop-2-enoate (**7**)

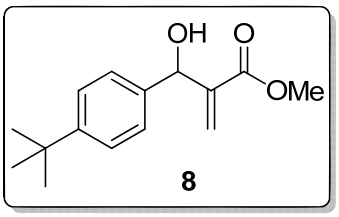
Yield: 71%, yellow oil; IR (film, ν_{max}): 3488, 2942, 2839, 1721, 1593, 1233, 1127 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.21 (d, ^3J = 5.2Hz, 1H); 3.73 (s, 3H); 3.81 (s, 3H); 3.82 (s, 6H); 5.48 (d, ^3J = 4.8Hz, 1H); 5.83 (s, 1H); 6.31 (s, 1H); 6.58 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.1; 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.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **7**.

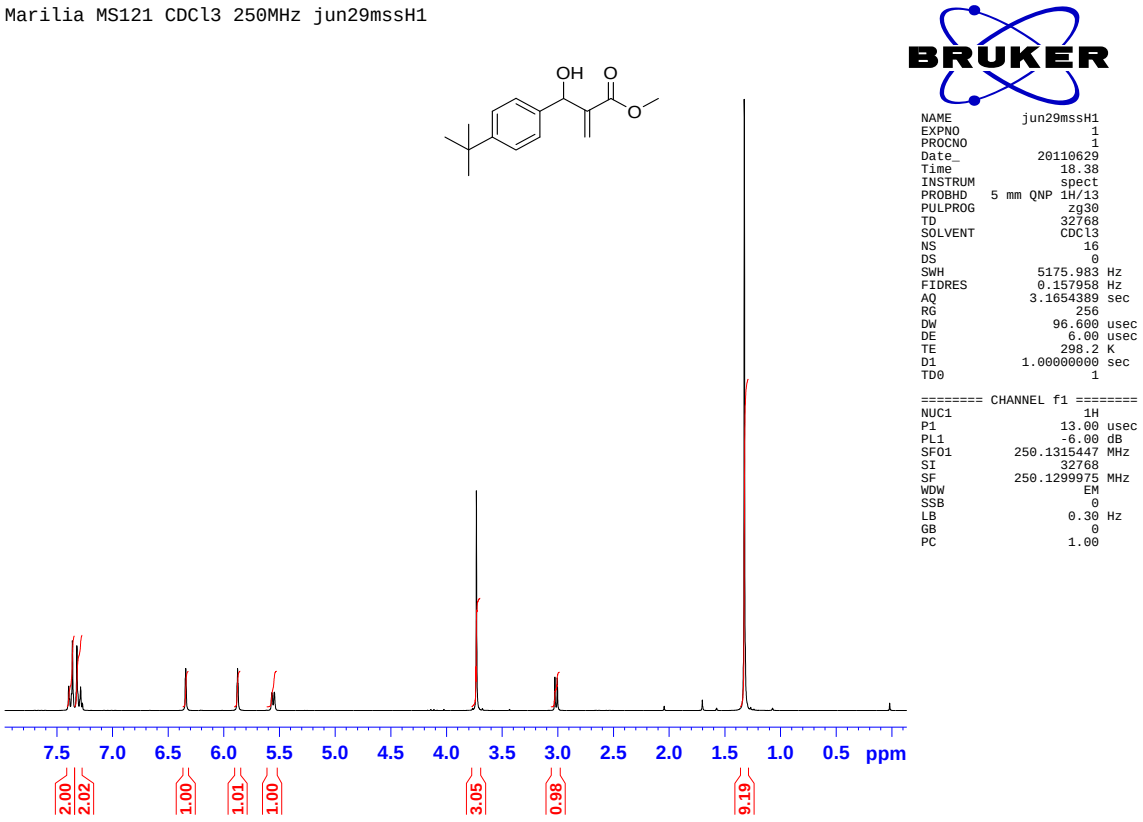


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **7**.

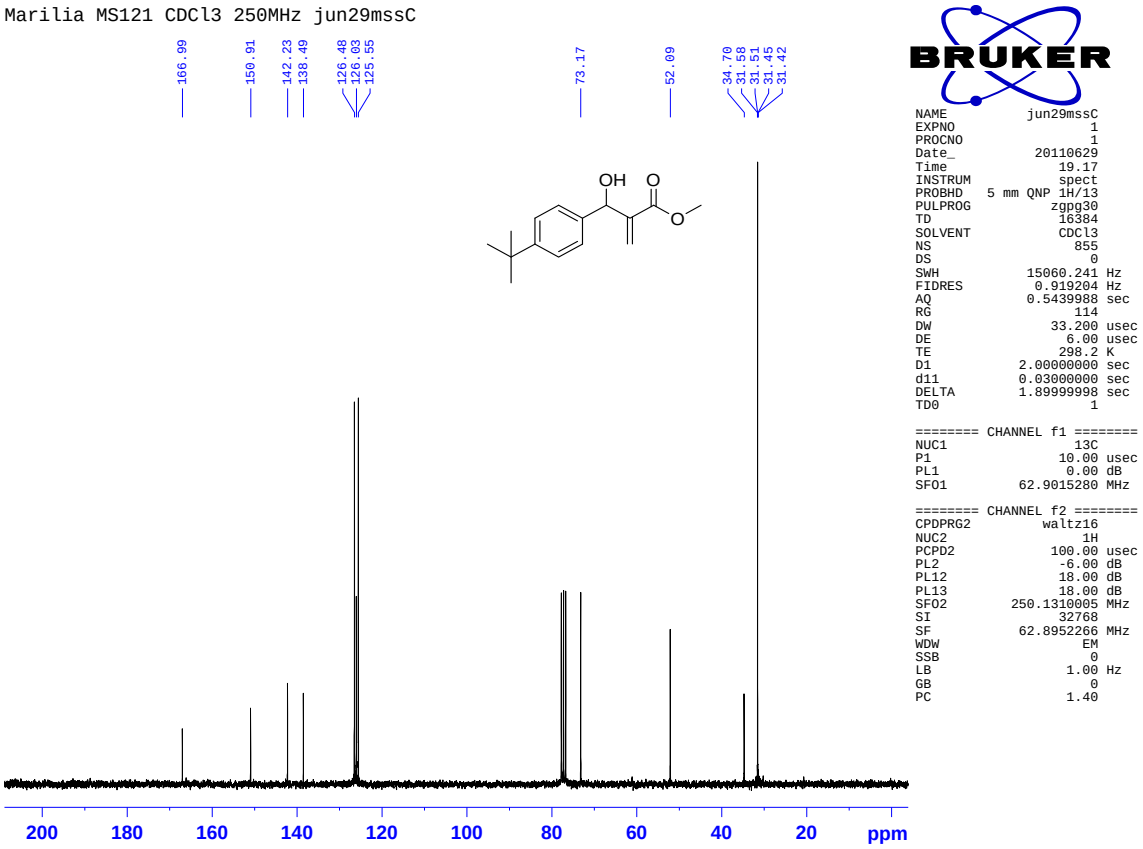


(±)-Methyl 2-[(4-*tert*-butylphenyl)(hydroxy)methyl]prop-2-enoate (**8**)

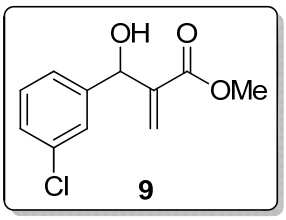
Yield: 77%, white solid, m.p. 64-66 °C; IR (KBr, ν_{max}): 3454, 2962, 2905, 2869, 1723, 1630, 1270, 1149, 1042, 854 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32 (s, 9H); 3.02 (d, ^{3}J = 5.5Hz, 1H); 3.73 (s, 3H); 5.56 (d, ^{3}J = 5.4Hz, 1H); 5.88 (s, 1H); 6.34 (s, 1H); 7.30 (d, ^{3}J = 8.5Hz, 2H); 7.38 (d, ^{3}J = 8.5Hz, 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 $C_{15}H_{21}O_3$ 249.1485 $[M + H]^+$; found 249.1484.



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

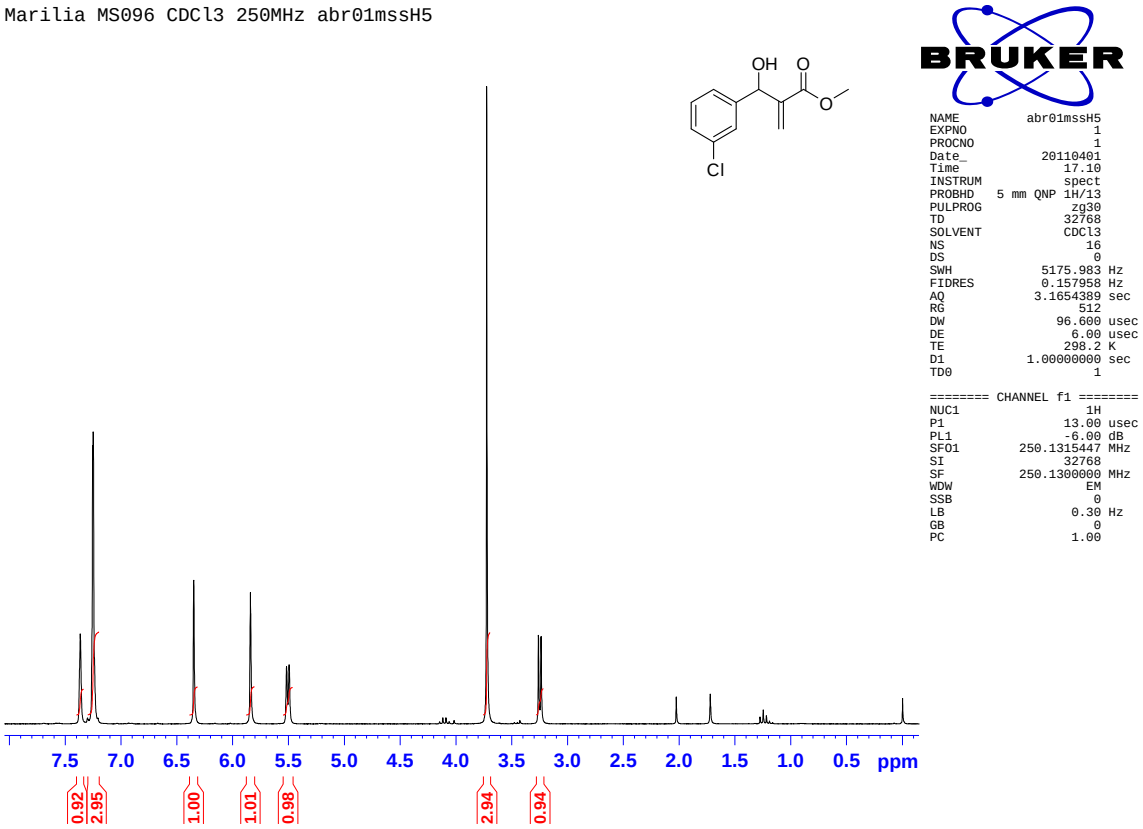


^{1}H NMR (62.5 MHz, $CDCl_3$) spectrum of the MBH adduct **8**.

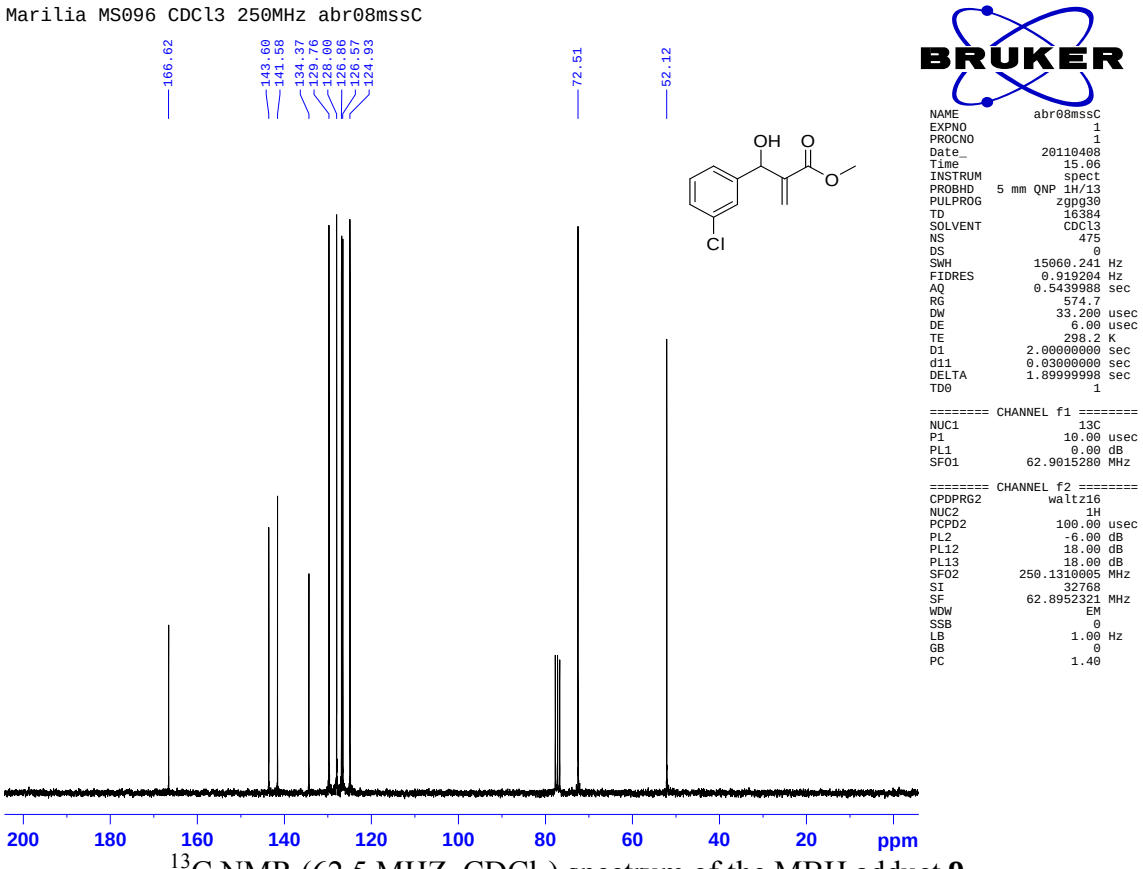


(±)-Methyl 2-[(3-chlorophenyl)(hydroxy)methyl]prop-2-enoate (**9**)

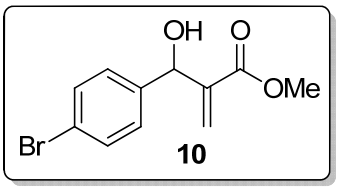
Yield: 80%, colorless oil; IR (film, ν_{max}): 3451, 2953, 1717, 1630, 1152, 884 cm^{-1}.; ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.25 (d, ^{3}J = 5.8Hz, 1H); 3.72 (s, 3H); 5.51 (d, ^{3}J = 5.7Hz, 1H); 5.84 (s,1H); 5.85 (s, 1H); 7.25 (s, 3H); 7.37 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.1; 72.5; 124.9; 126.6; 126.9; 128.0; 129.8; 134.4; 141.6; 143.6; 166.6. HRMS (ESI, *m/z*): Calcd. for $C_{11}H_{12}ClO_3$ 227.0469 $[M + H]^+$; found 227.0468.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **9**.

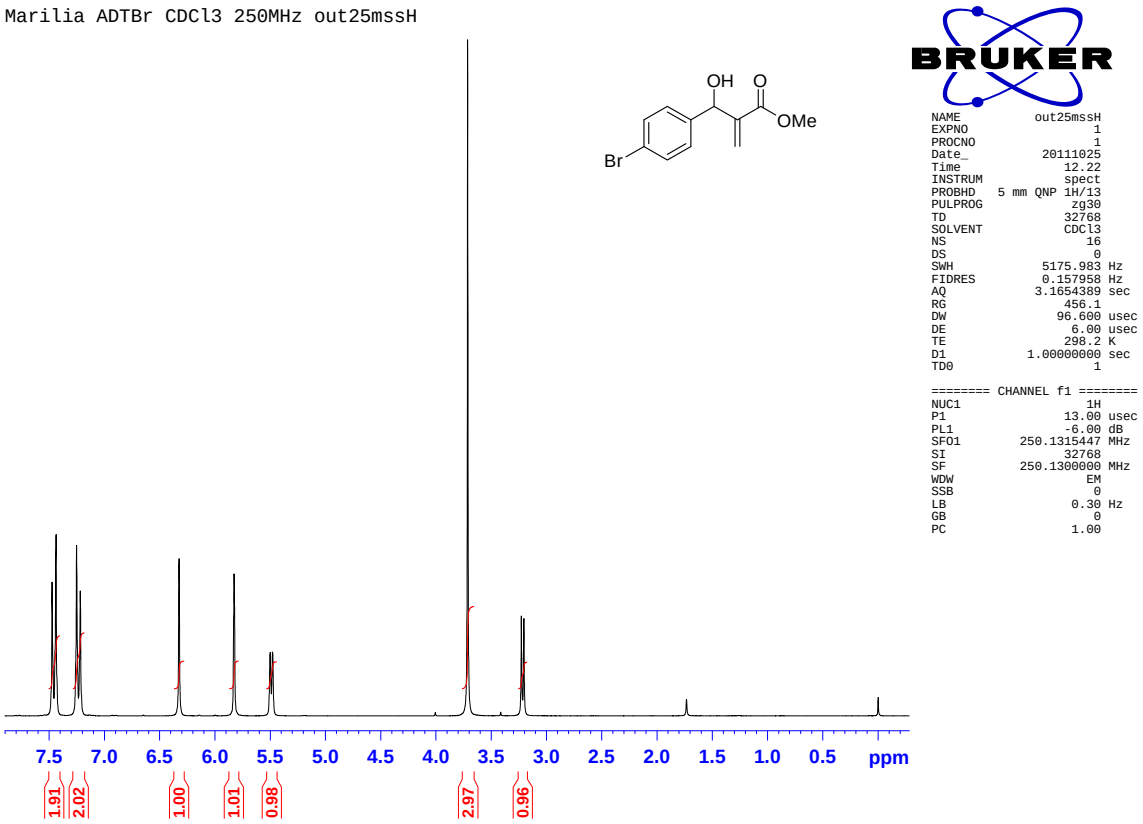


^{13}C NMR (62.5 MHZ, $CDCl_3$) spectrum of the MBH adduct **9**.

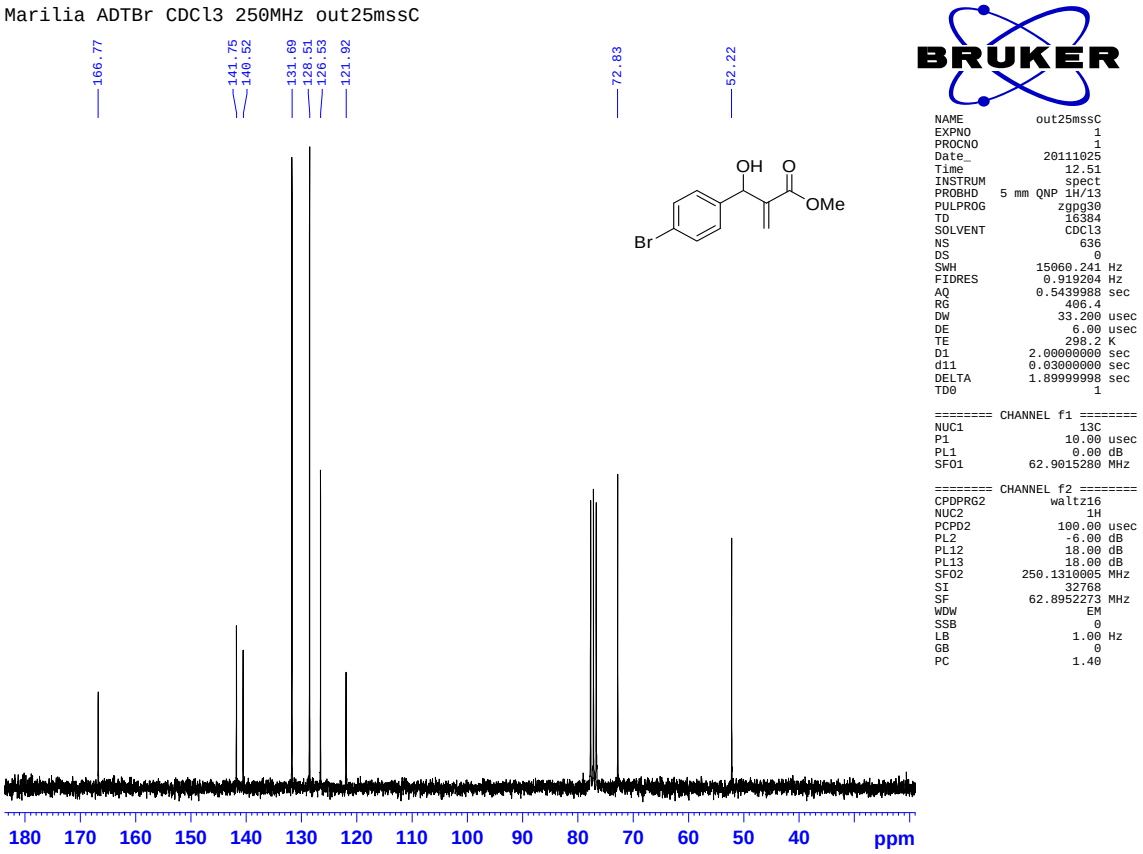


(±)-Methyl 2-[(4-bromophenyl)(hydroxy)methyl]prop-2-enoate (**10**)

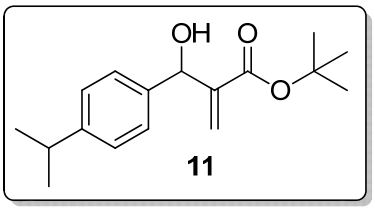
Yield: 75%, white solid, m.p. 63-66 ºC; IR (KBr, ν_{max}): 3342; 2959; 1717; 1635, 1274, 1160, 812 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.22 (d, ^{3}J = 5.7 Hz, 1H); 3.71 (s, 3H); 5.49 (d, , ^{3}J = 5.6 Hz, 1H); 5.83 (s, 1H); 6.33 (s, 1H); 7.24 (d, ^{3}J = 8.4 Hz, 2H); 7.46 (d, ^{3}J = 8.4 Hz, 2H). ^{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 $C_{11}H_{12}BrO_3$ 270.9964 $[M + H]^+$; found 270.9961.



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

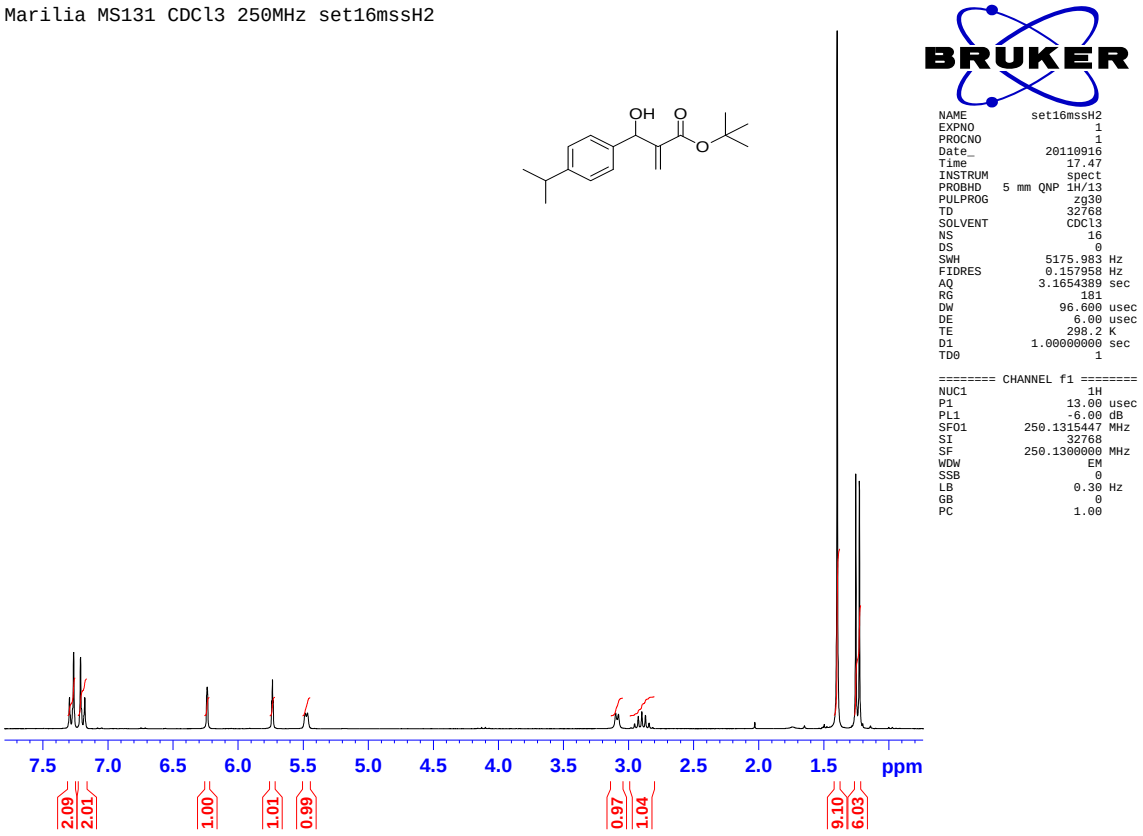


^{13}C NMR (62.5 MHZ, $CDCl_3$) spectrum of the MBH adduct **10**.

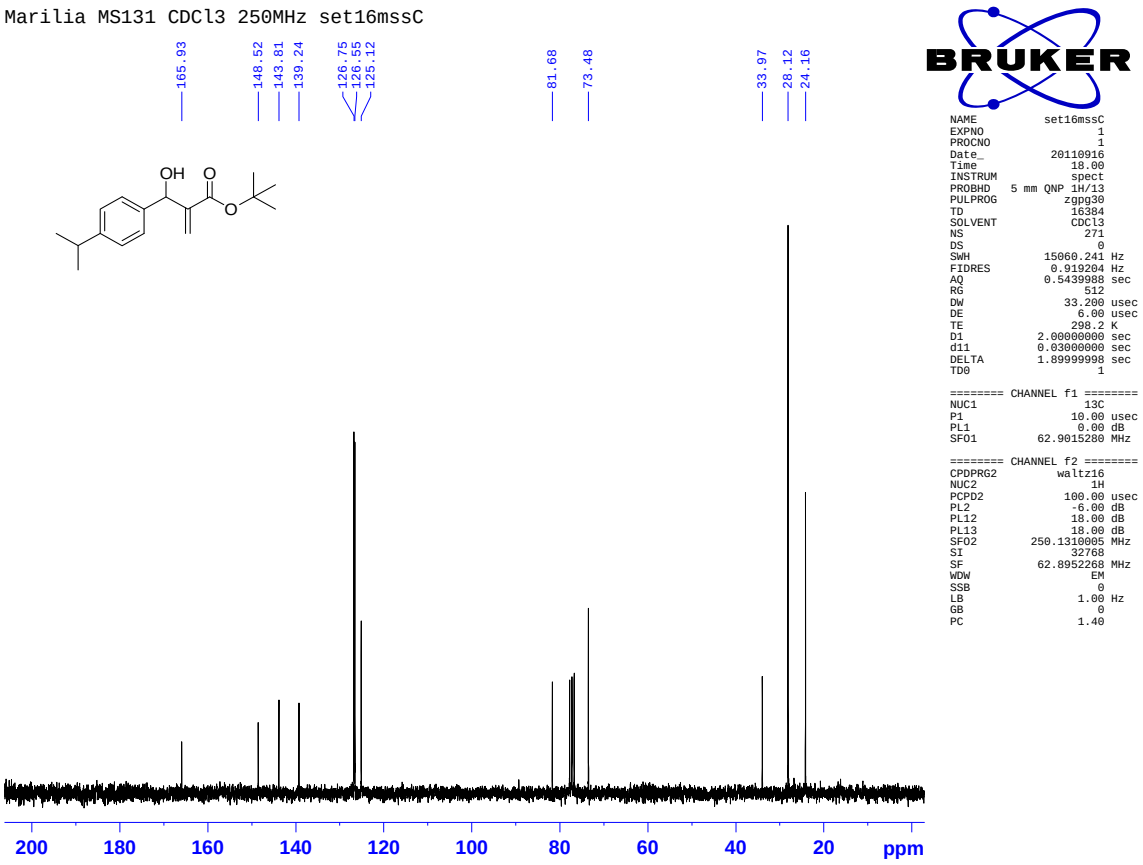


tert-Butyl 2-{hydroxy[4-(propan-2-yl)phenyl]methyl}prop-2-enoate (**11**)

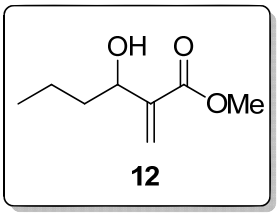
Yield: 52%, yellow tinged oil; IR (film, ν_{max}): 3441, 2962, 2931, 1716, 1630, 1150, 893, cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 (d, ^3J = 6.9 Hz, 3H); 1.40 (s, 9H); 2.90 (m, 1H); 3.09 (d, ^3J = 5.4 Hz, 1H); 5.48 (d, ^3J = 4.4 Hz, 1H); 5.74 (t, 1H); 6.24 (s, 1H); 7.19 (d, ^3J = 8.2 Hz, 2H); 7.28 (d, ^3J = 8.3 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{17}H_{23}O_2$ 259.1698 $[M + H]^+$; found 259.1667.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **11**.

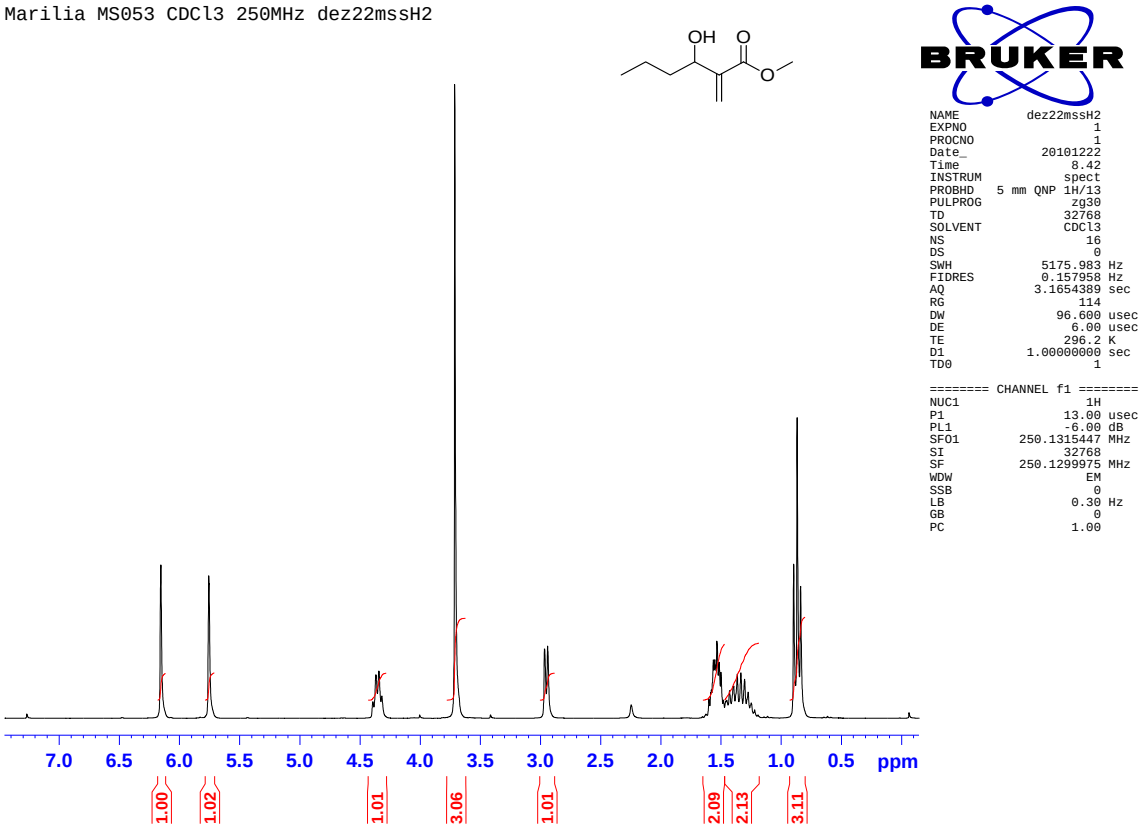


^{13}C NMR (62.5 MHZ, $CDCl_3$) spectrum of the MBH adduct **11**.

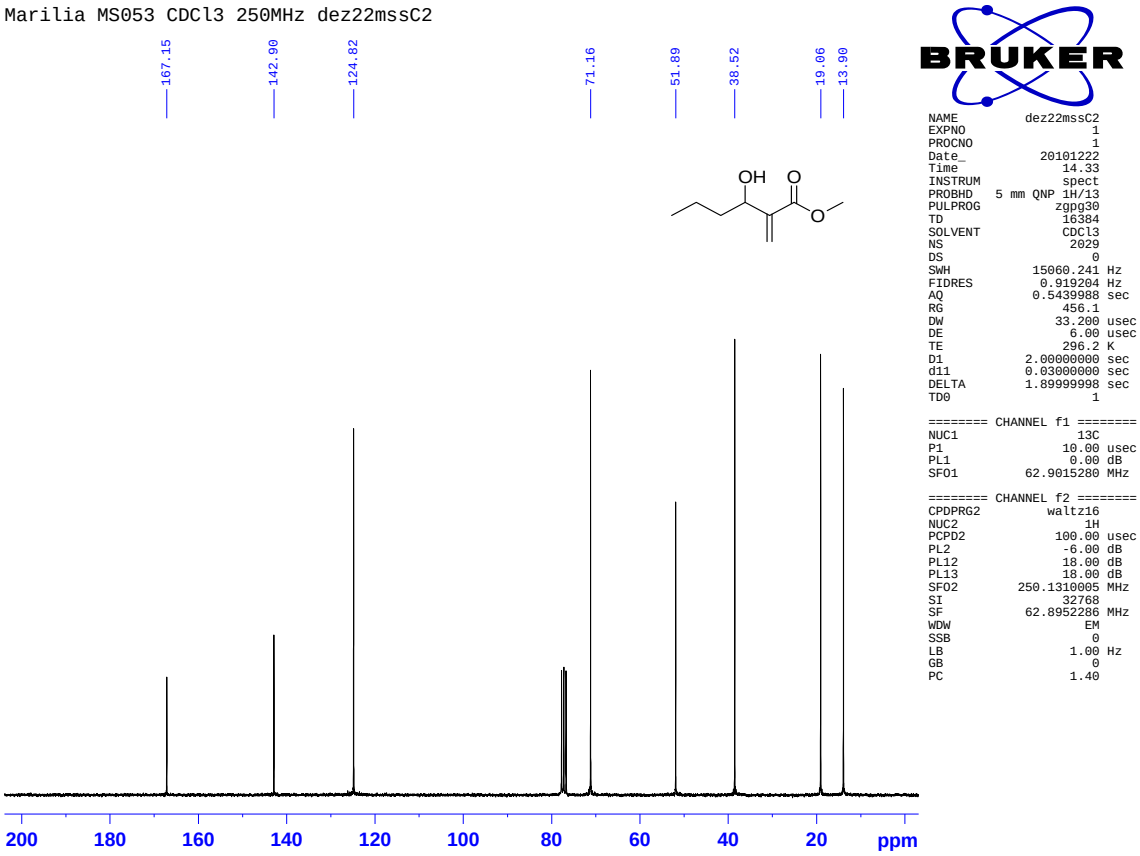


(±)-Methyl 3-hydroxy-2-methylidenehexanoate (**12**)

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 $C_8H_{15}O_3$ 159.1016 $[M + H]^+$; found 159.1017.



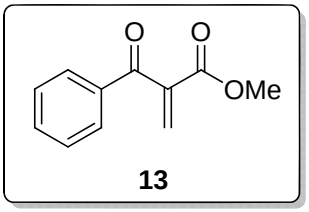
^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the MBH adduct **12**.



^{13}C NMR (62.5 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]

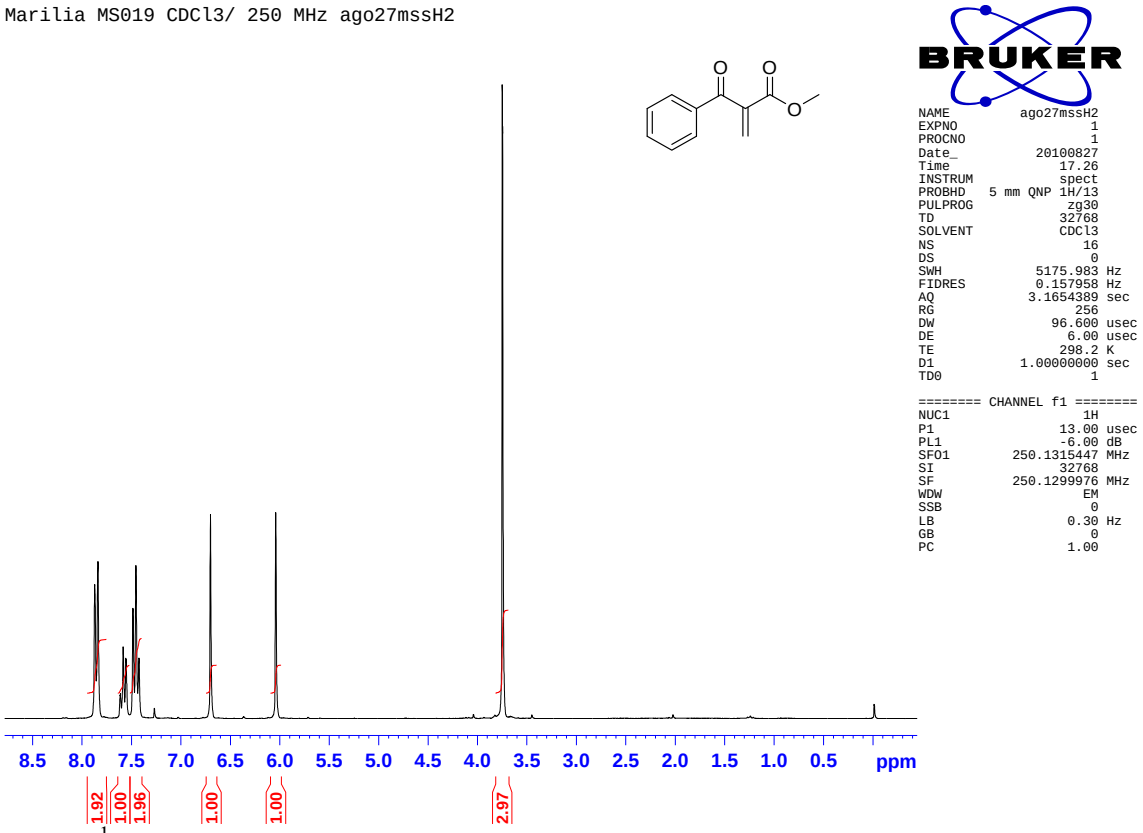


13

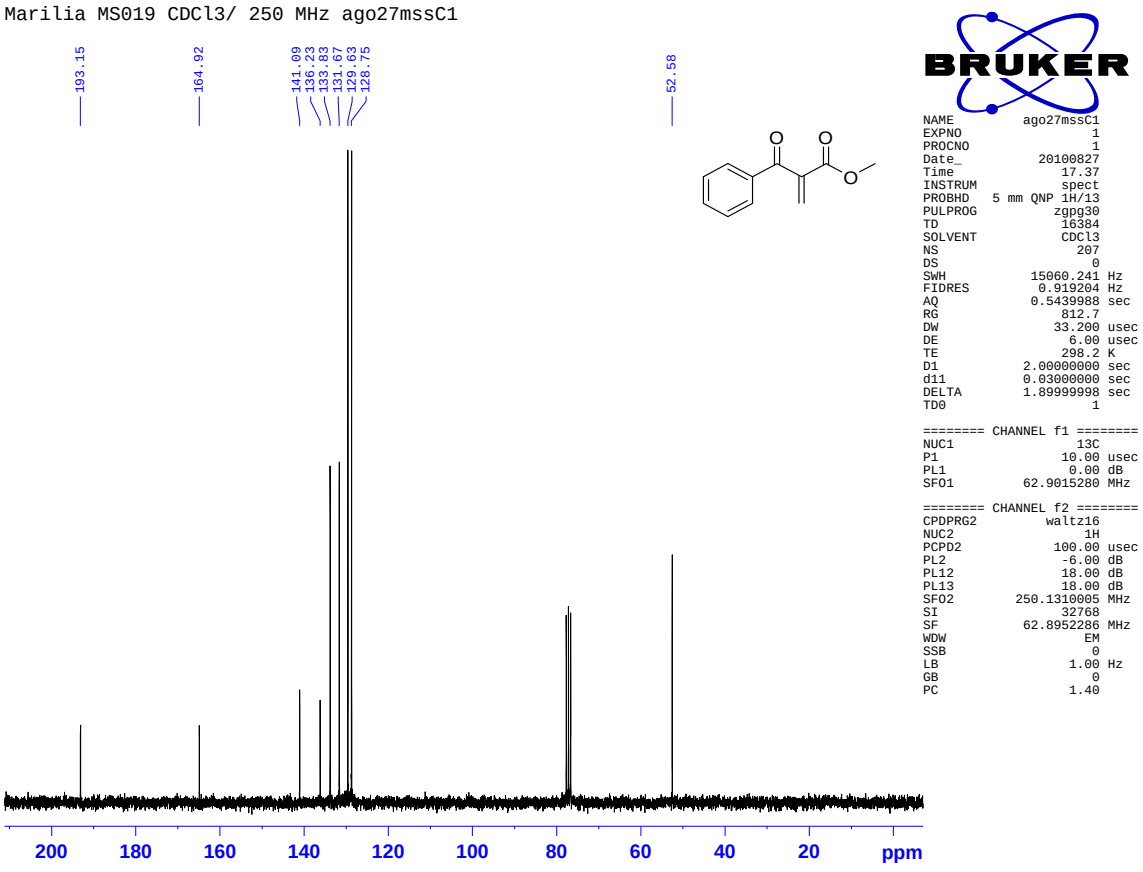
Methyl 2-benzoylprop-2-enoate (**13**)

Yield: 90%, yellow oil; IR (film, ν_{max}): 3004, 2954, 1732, 1675, 1449, 817, 807 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 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). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{11}H_{11}O_3$ 191.0703 $[M + H]^+$; found 191.0701.

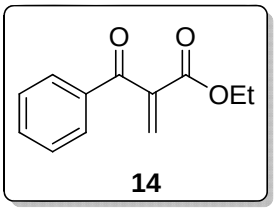
[4] When ethyl acetate was used as solvent 3.0 equivalents of IBX was required.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **13**.

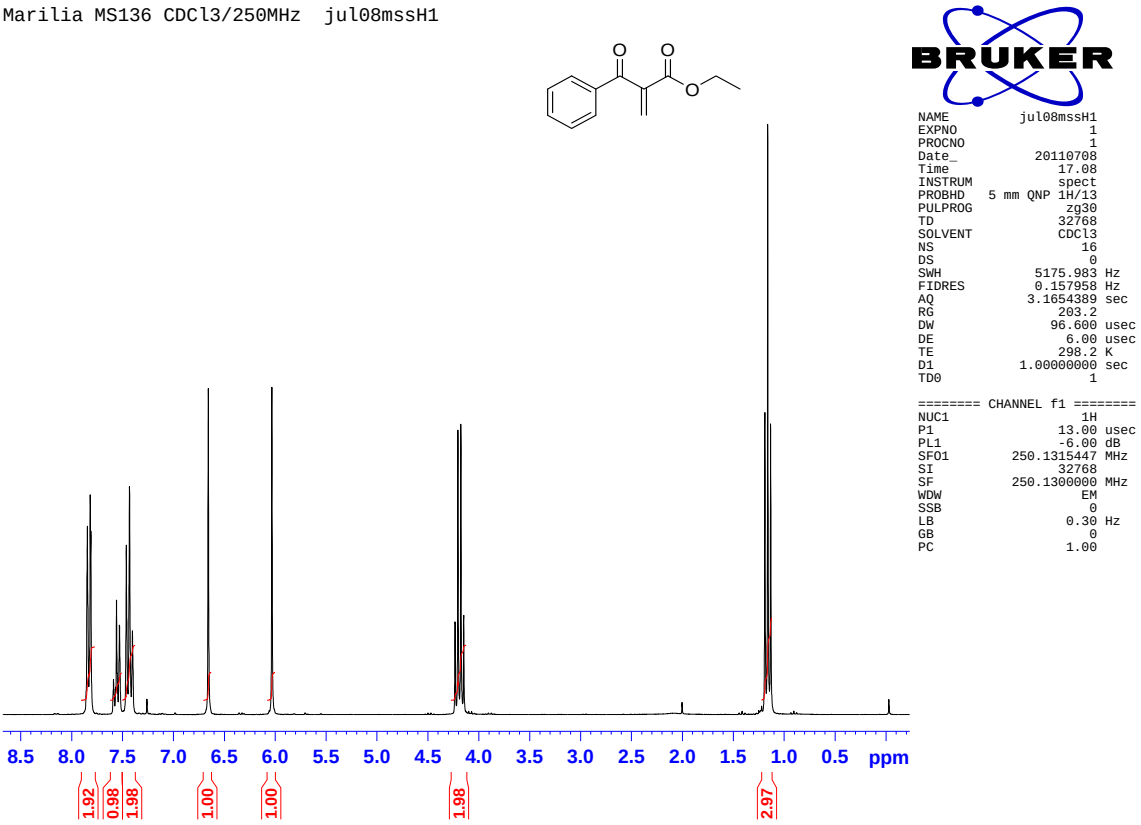


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **13**.

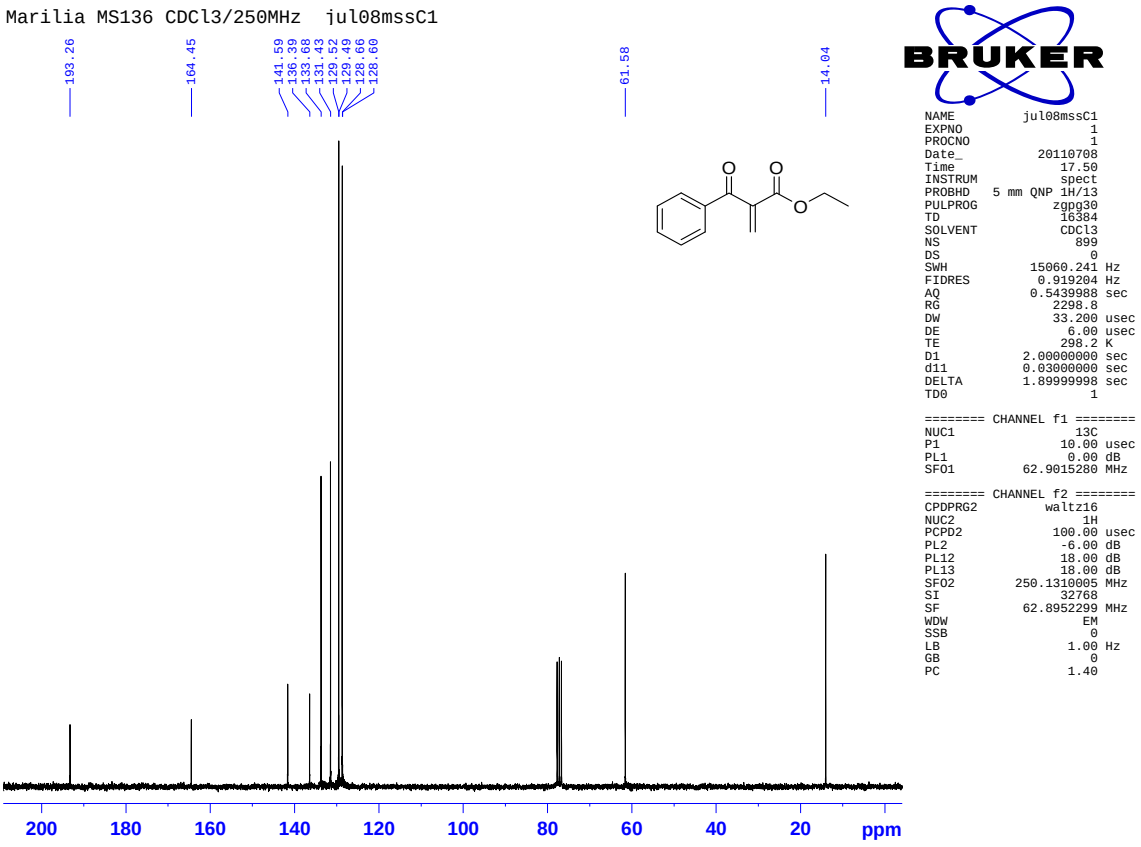


Ethyl 2-benzoylprop-2-enoate (**14**)

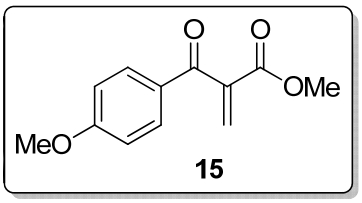
Yield: >95%, colorless oil; IR (film, ν_{max}): 3062, 2983, 1729, 1679, 1597, 1237, 1153 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.17 (t, ^{3}J = 7.1Hz, 3H); 4.20 (q, ^{3}J =7.1Hz, 2H); 6.04 (s, 1H); 6.67 (s, 1H); 7.71-7.47 (m, 2H); 7.54-7.60 (m,1H); 7.82-7.86 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{12}H_{13}O_3$ 205.0864 $[M + H]^+$; found 205.0892.



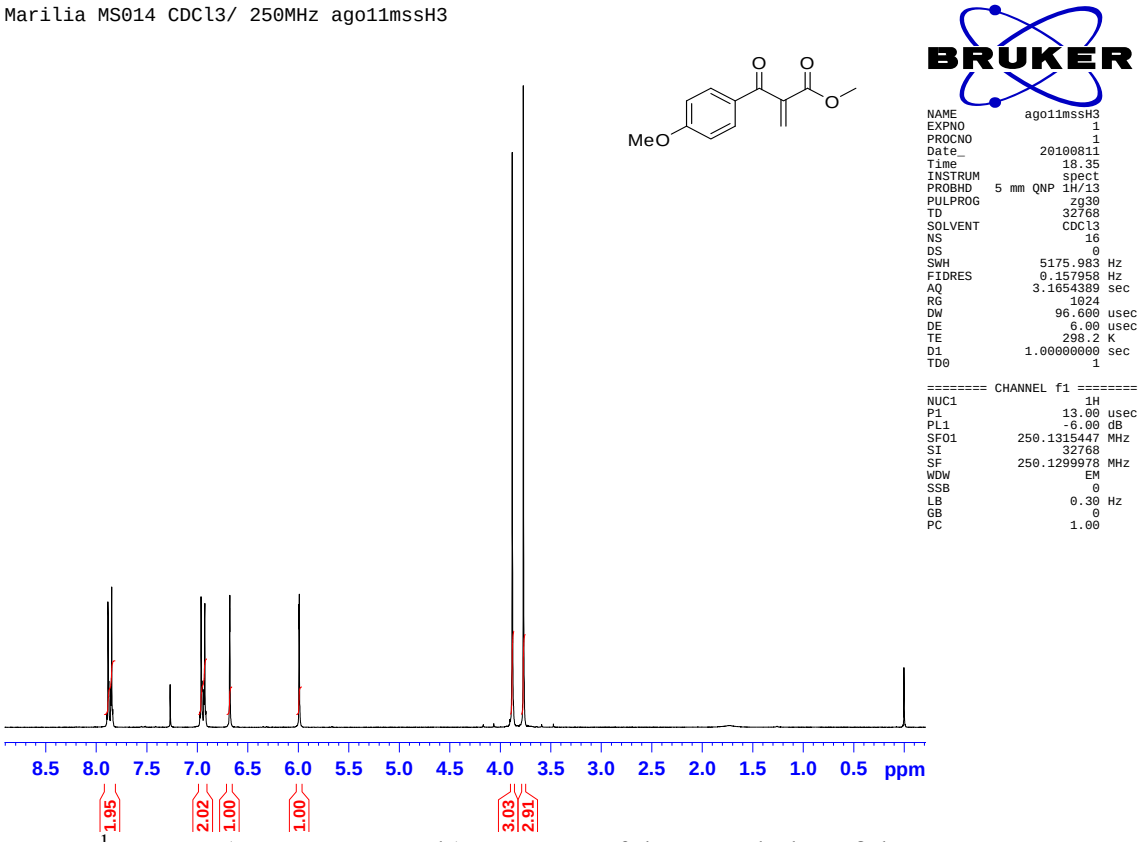
^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **14**.



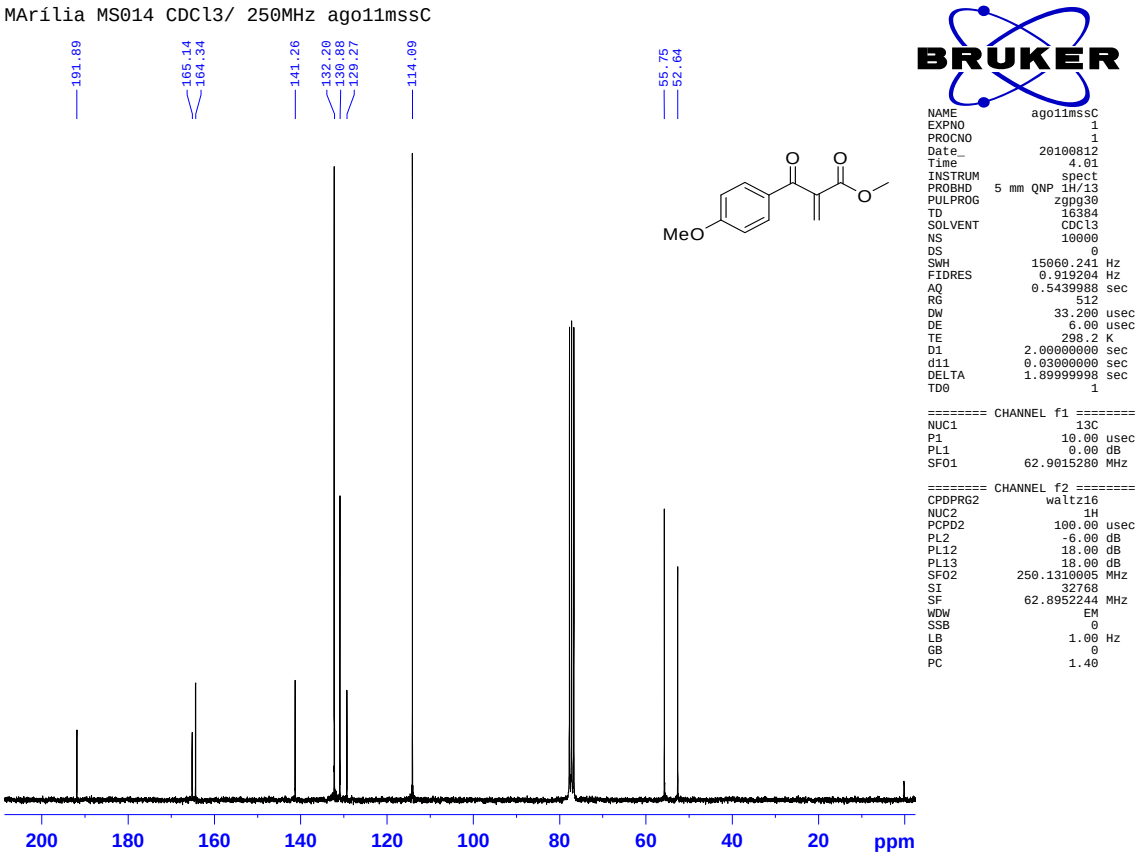
^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **14**.



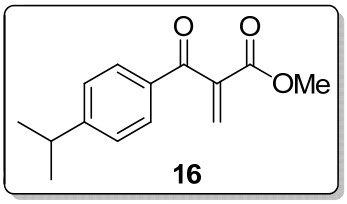
Ethyl 2-[(4-methoxyphenyl)carbonyl]prop-2-enoate (**15**) Yield: 94%, yellow oil; IR (film, ν_{max}): 2954, 2842, 1729, 1666, 1599, 1262, 1152, 847 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.77 (s, 3H); 3.88 (s, 3H); 5.99 (d, ^3J = 0.8Hz, 2H); 6.68 (d, ^3J = 0.7Hz, 2H); 6.95 (d, ^3J = 9.0Hz, 2H); 7.87 (d,^3J = 9.0Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{12}H_{13}O_4$ 221.0814 $[M + H]^+$; found 221.0830.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **15**.

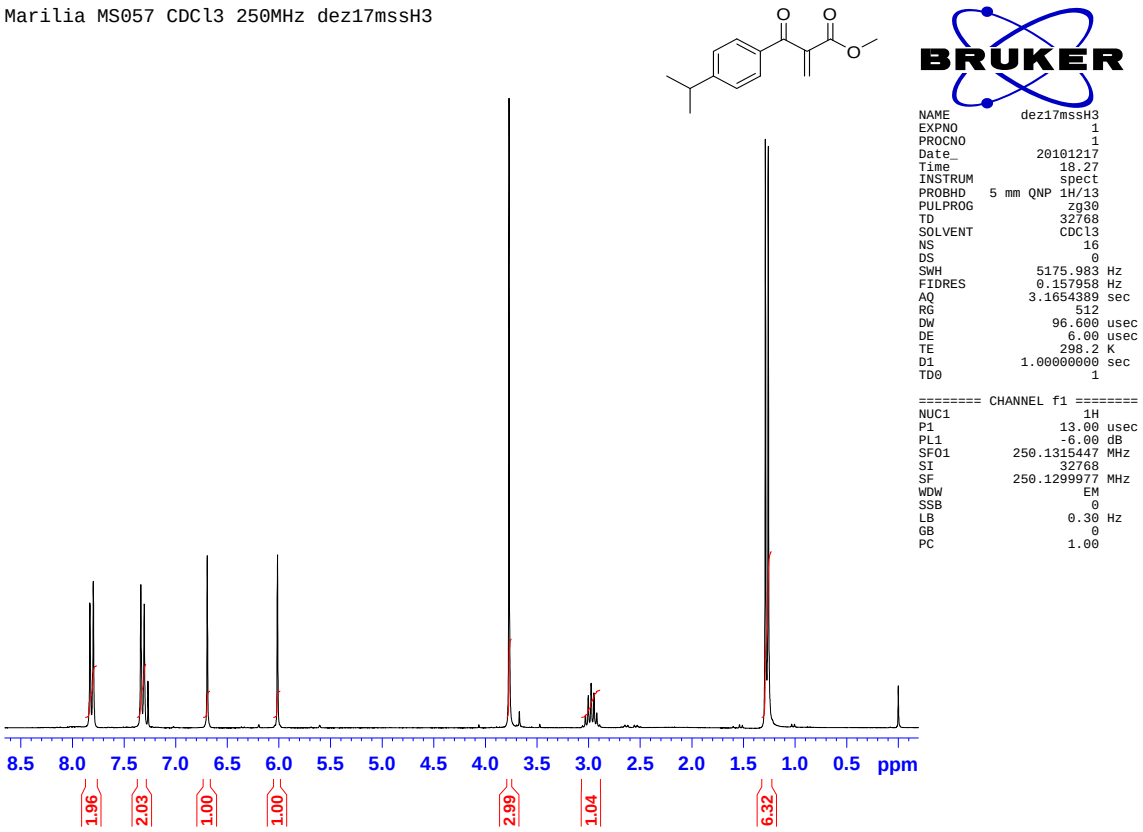


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **15**.

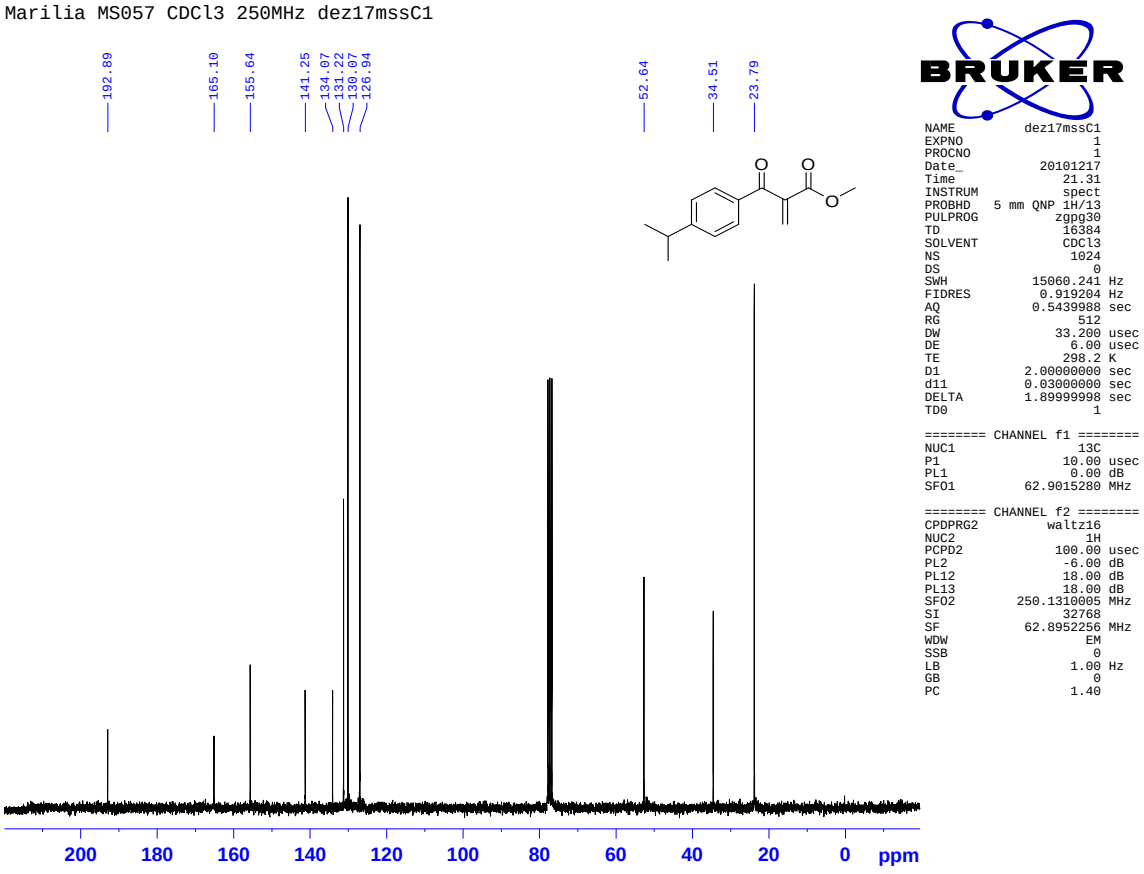


Methyl 2-{[4-(propan-2-yl)phenyl]carbonyl}prop-2-enoate (**16**)

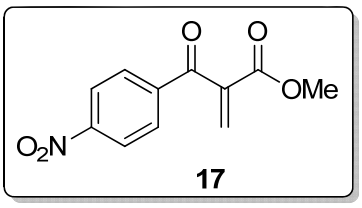
Yield: >95%, yellow oil; IR (film, ν_{max}): 2962, 2873, 1731, 1673, 1604, 1144, 852 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (d, ^{3}J = 6.9Hz, 6H); 2.98 (m, ^{3}J = 6.9Hz, 1H); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 73.2 (d, ^{3}J = 8.2Hz, 2H); 7.82 (d, ^{3}J = 8.3Hz, 2H); ^{13}C NMR (62.5 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 $C_{14}H_{17}O_3$ 233.1178 $[M + H]^+$; found 233.1200.



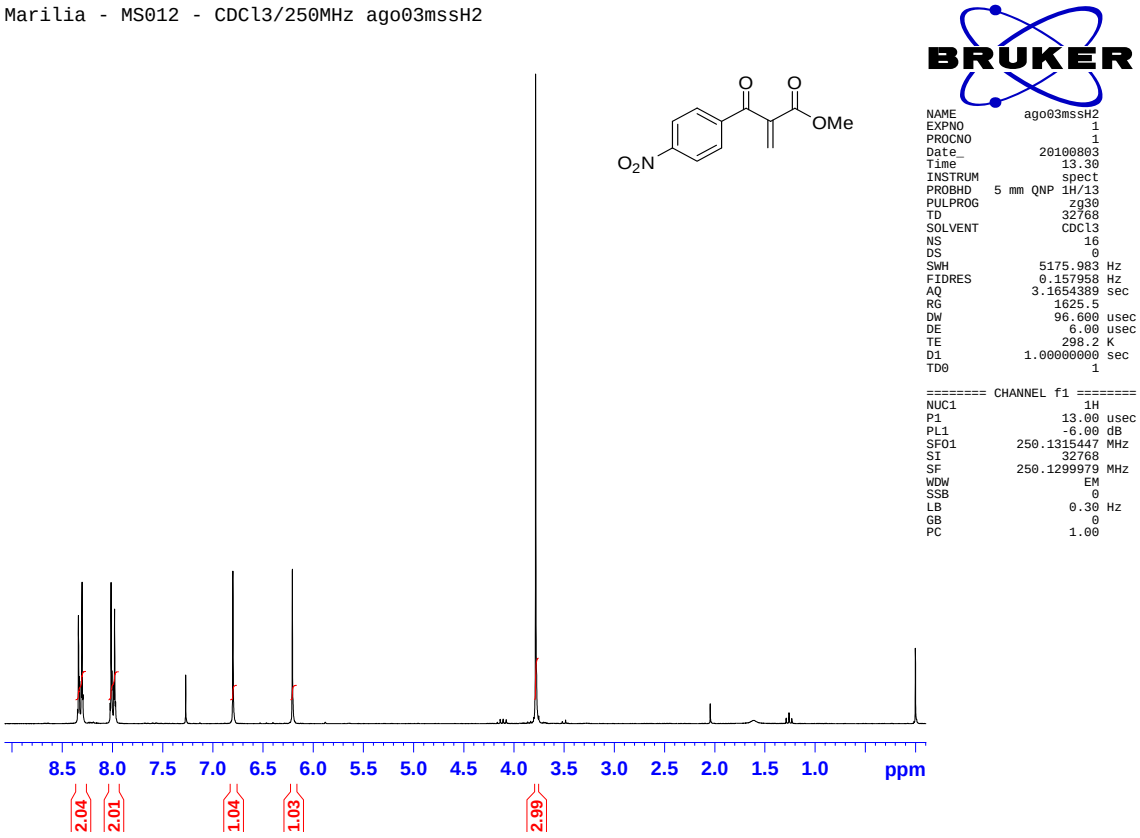
^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **16**.



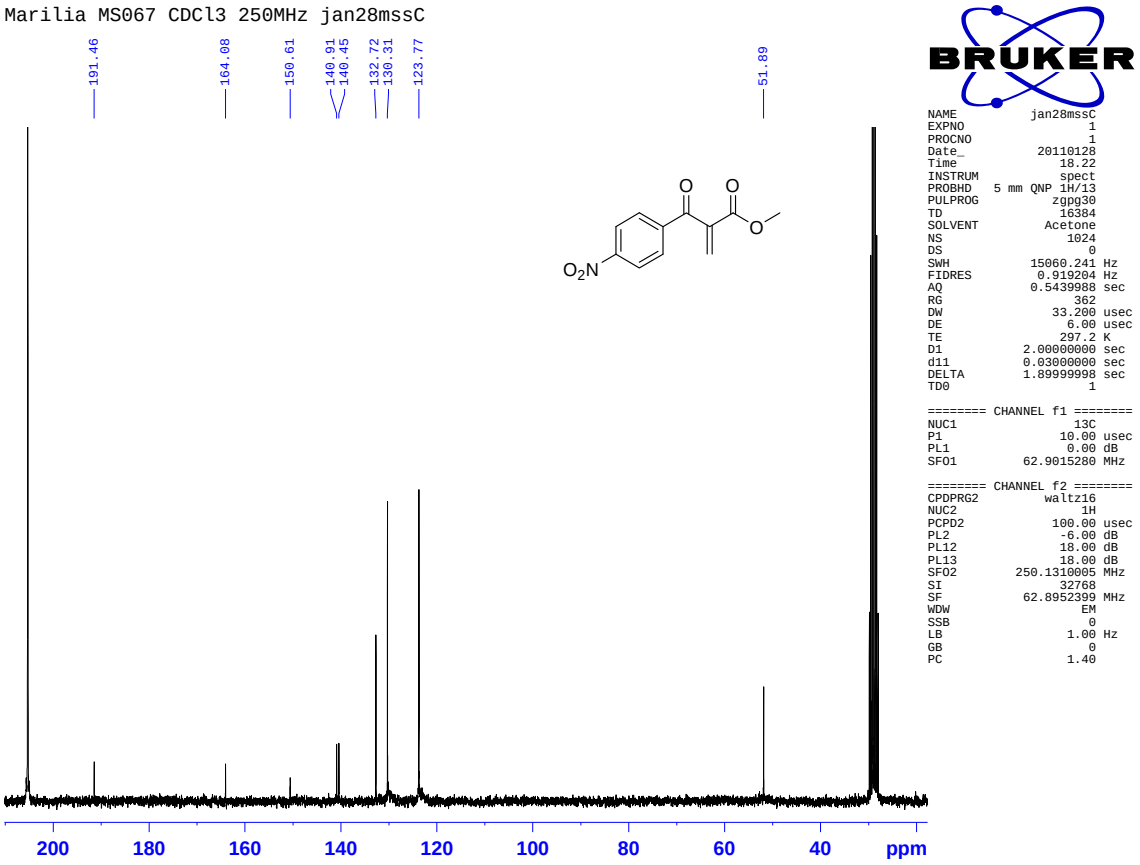
^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **16**.



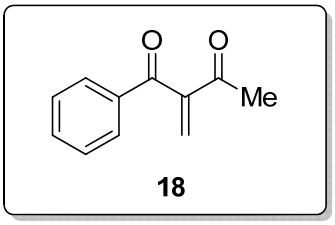
Methyl 2-[(4-nitrophenyl)carbonyl]prop-2-enoate (**17**) Yield: 90%, yellow solid; IR (KBr, ν_{max}): 2955, 1737, 1690, 1604, 1525, 1240, 702 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.78 (s, 3H); 6.21 (s, 1H); 6.80 (s, 1H); 8.00 (d, ^3J = 9.0Hz, 2H); 8.32 (d, ^3J = 9.0Hz, 2H). ^{13}C NMR [62.5 MHz, $(CD_3)_2O$]: 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 $C_{11}H_{10}NO_5$ 236.0559 $[M + H]^+$; found 236.0579.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **17**.

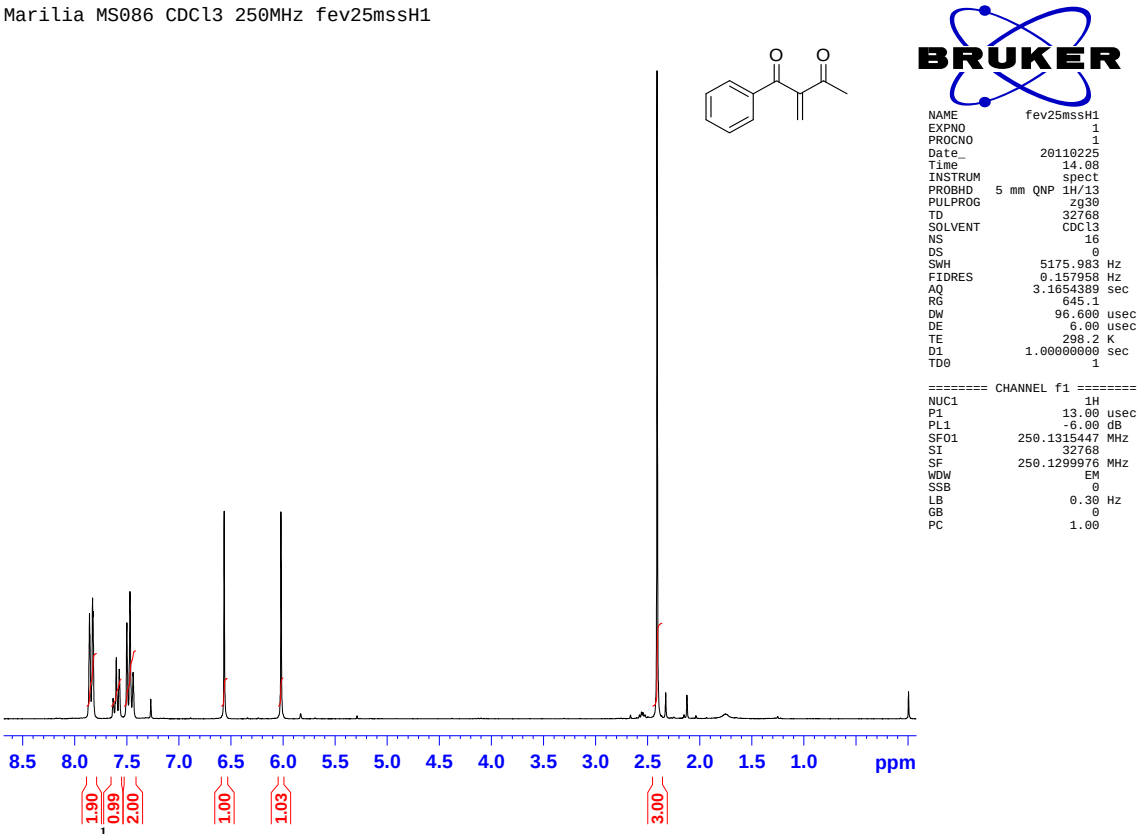


^{13}C NMR [62.5 MHZ, $(CD_3)_2O$] spectrum of the α-methylene-β-ketoester **17**.

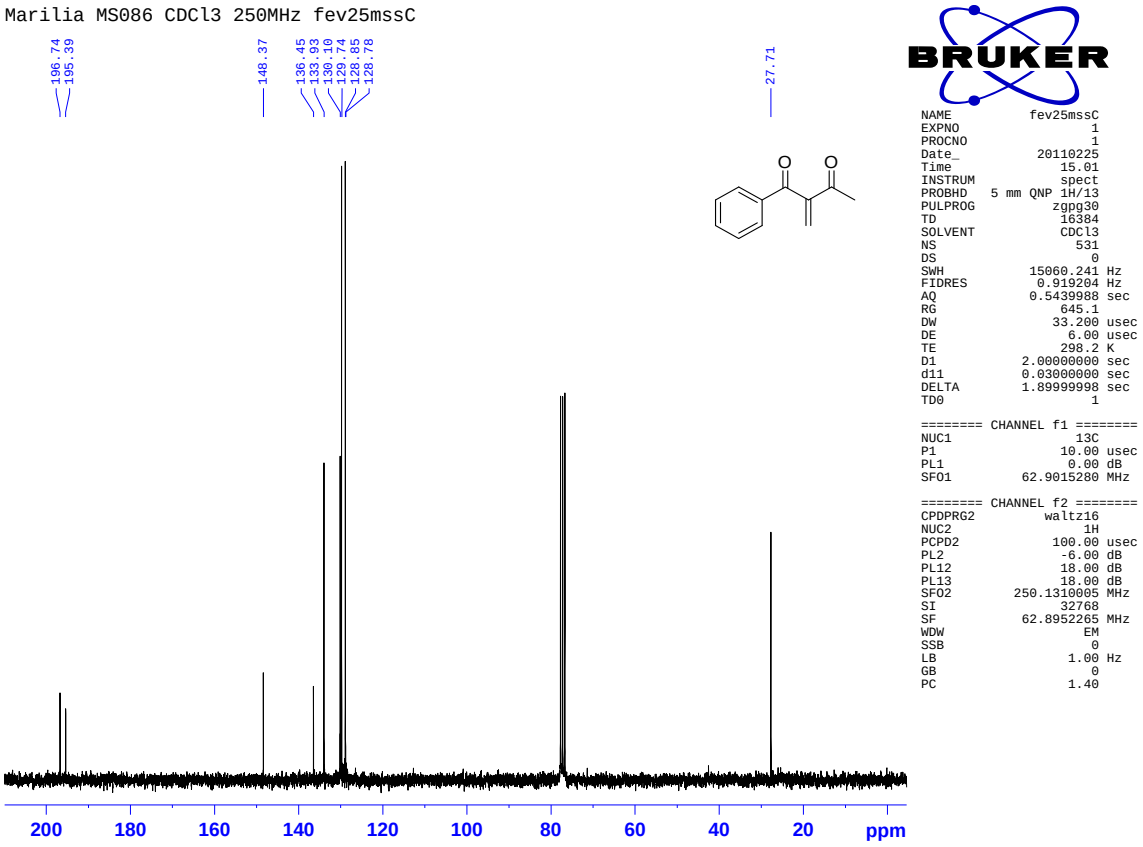


2-Methylidene-1-phenylbutane-1,3-dione (**18**)

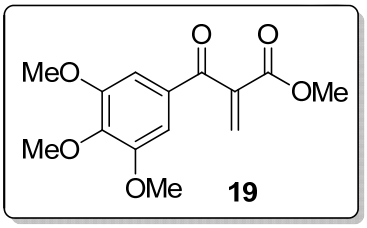
Yield: 93%, yellow oil; IR (film, ν_{max}): 3065, 2930, 1671, 1597, 1232, 1123 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.41 (s, 3H); 6.02 (s, 1H); 6.57 (s, 1H); 7.47 (m, ^{3}J = 7.2Hz, 2H); 7.60 (m, ^{3}J = 7.2Hz, 1H); 7.84 (m, ^{3}J = 7.1Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 27.7; 128.8; 128.9; 129.7; 130.1; 133.9; 136.5; 148.4; 195.4; 196.7. HRMS (ESI, *m/z*): Calcd. for $C_{11}H_{10}O_2Na$ 197.0578 $[M + Na]^+$; found *m/z* 197.0619.



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

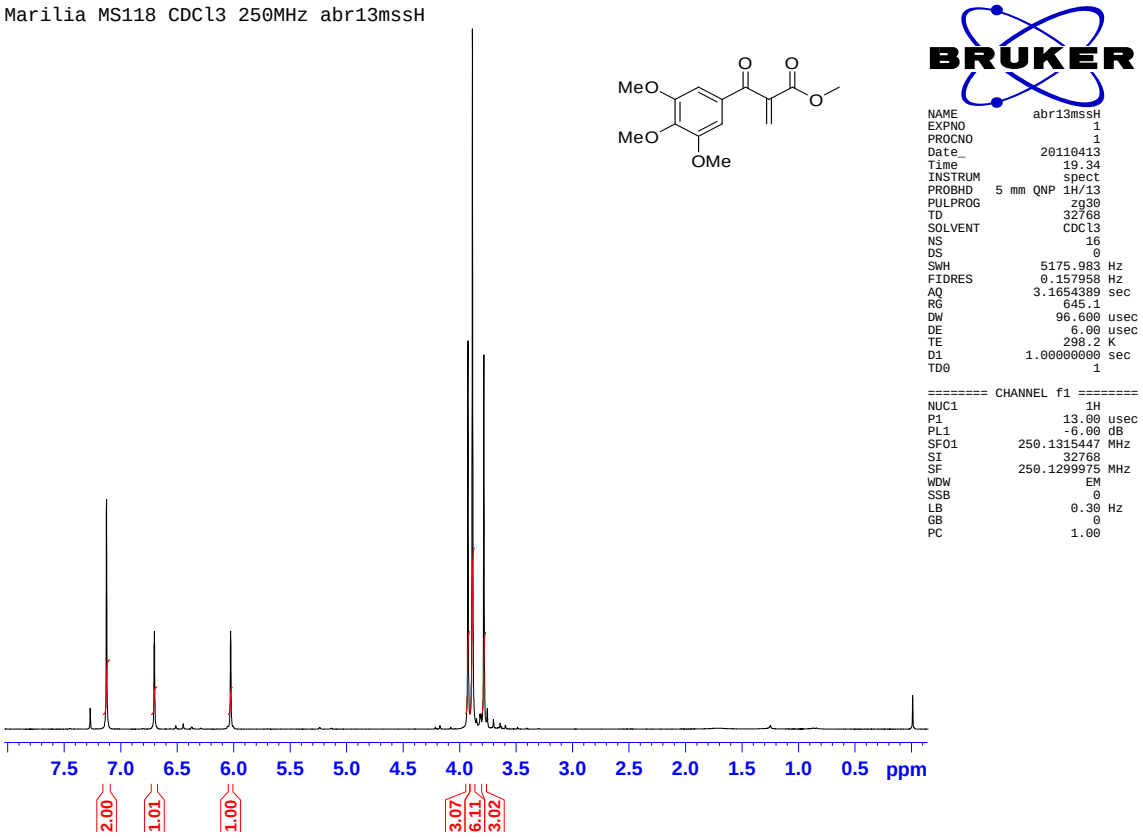


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **18**.

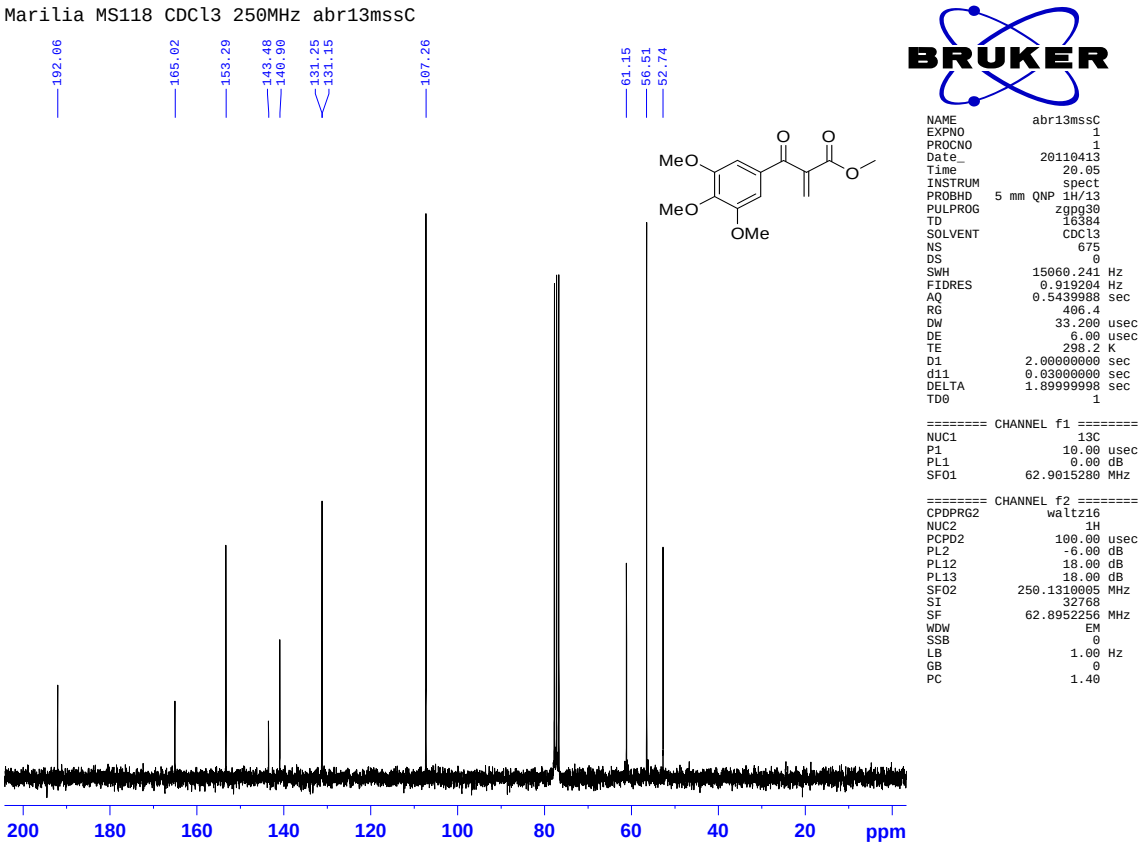


Methyl 2-[(3,4,5-trimethoxyphenyl)carbonyl]prop-2-enoate (**19**)

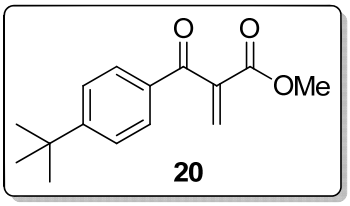
Yield: >95%, colorless oil; IR (film, ν_{max}): 2959, 2840, 1723, 1665, 1584, 1416, 1129 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.79 (s, 3H); 3.89 (s, 6H); 3.93 (s, 3H); 6.03 (s, 1H); 6.70(s, 1H); 7.13 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.7; 56.5; 61.2; 107.3; 131.2; 131.3; 140.9; 143.5; 153.3; 165.0; 192.1. HRMS (ESI, *m/z*): Calcd. for $C_{14}H_{17}O_6$ 281.1086 $[M + H]^+$; found 281.1025.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **19**.

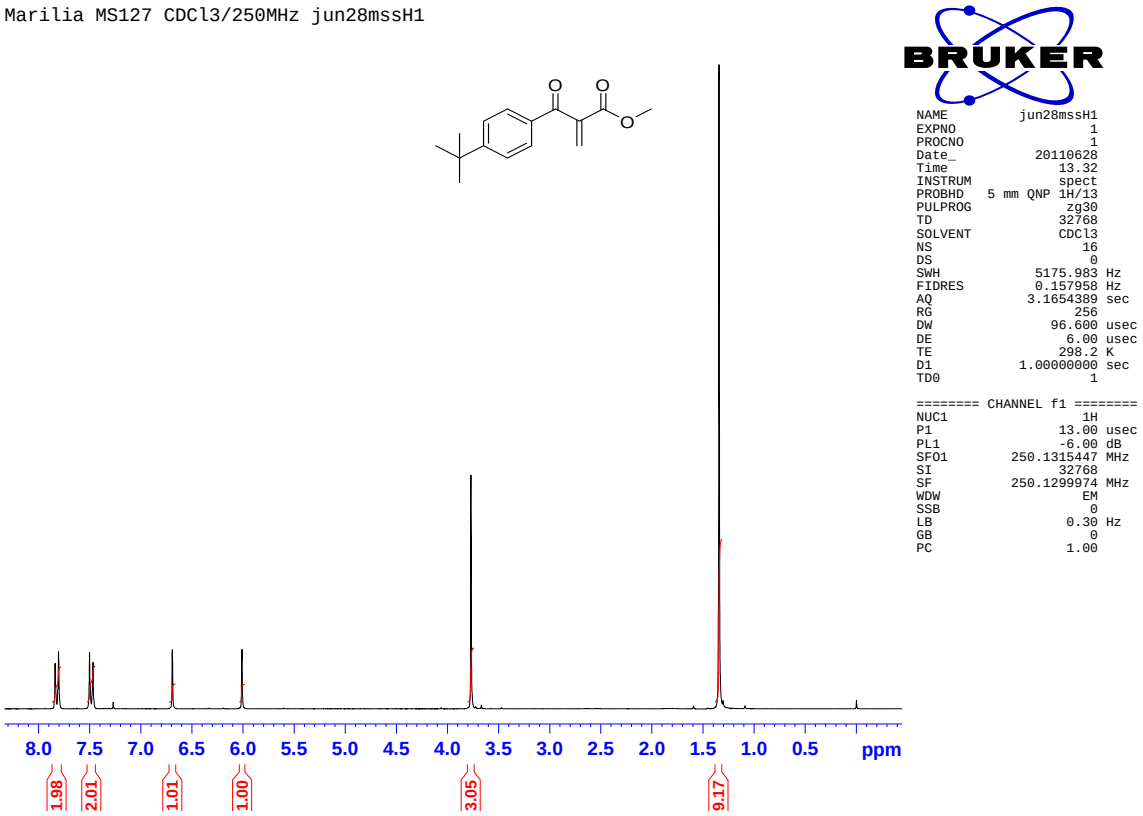


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **19**.

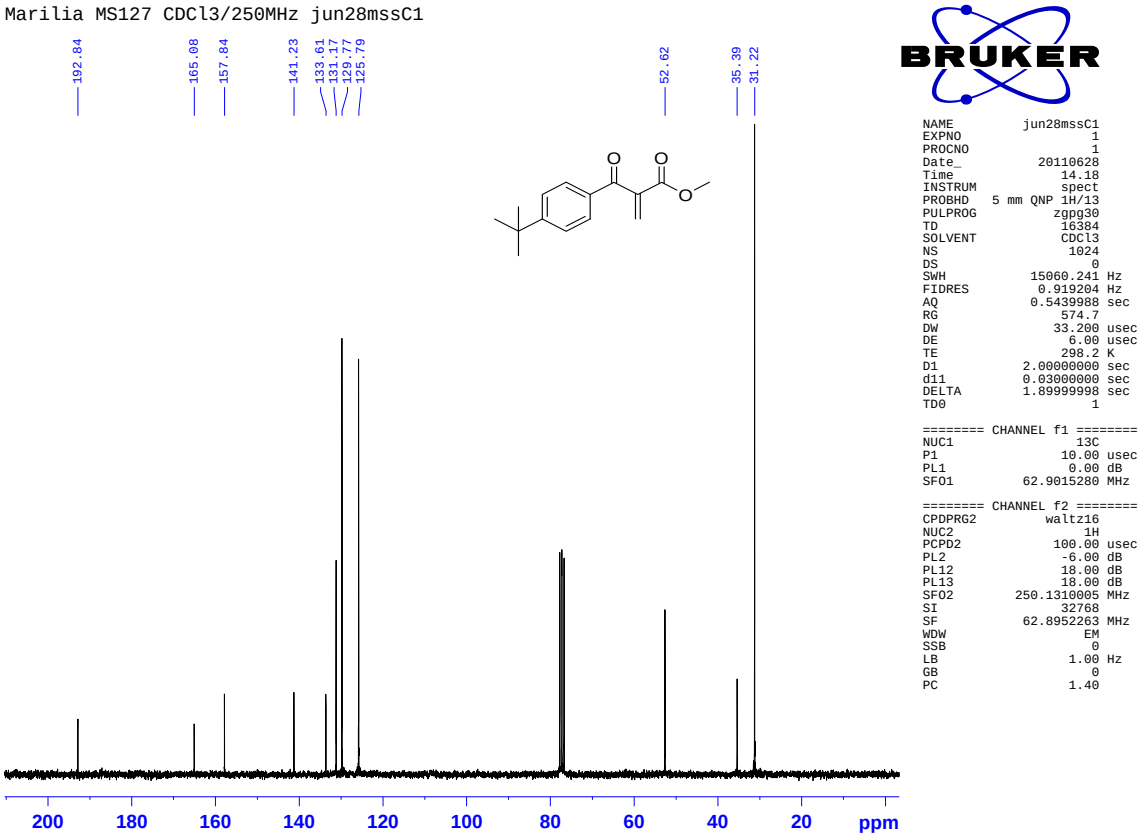


Methyl 2-[(4-*tert*-butylphenyl)carbonyl]prop-2-enoate (**20**)

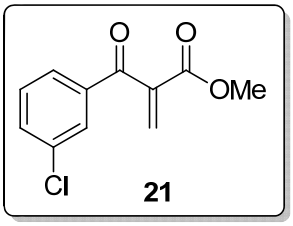
Yield: >95%, yellow solid, m.p. 42-44 ºC; IR (KBr, ν_{max}): 2963, 2906, 2871, 1731, 1673, 1603, 1239, 1156, 1145, 852 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35 (s, 9H); 3.77 (s, 3H); 6.01 (s, 1H); 6.69 (s, 1H); 7.48 (d, ^{3}J = 8.6Hz, 2H); 7.82 (d, ^{3}J = 8.6 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{15}H_{19}O_3$ 247.1334 $[M + H]^+$; found *m/z* 247.1342.



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

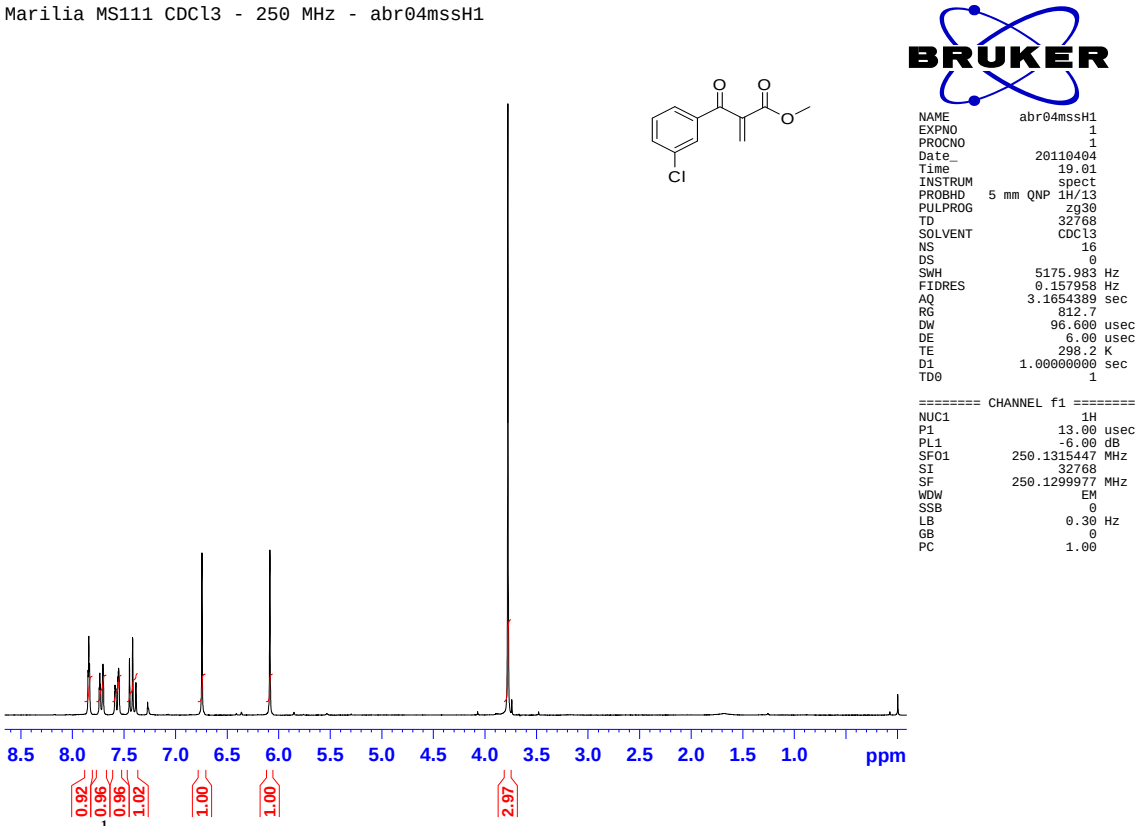


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **20**.

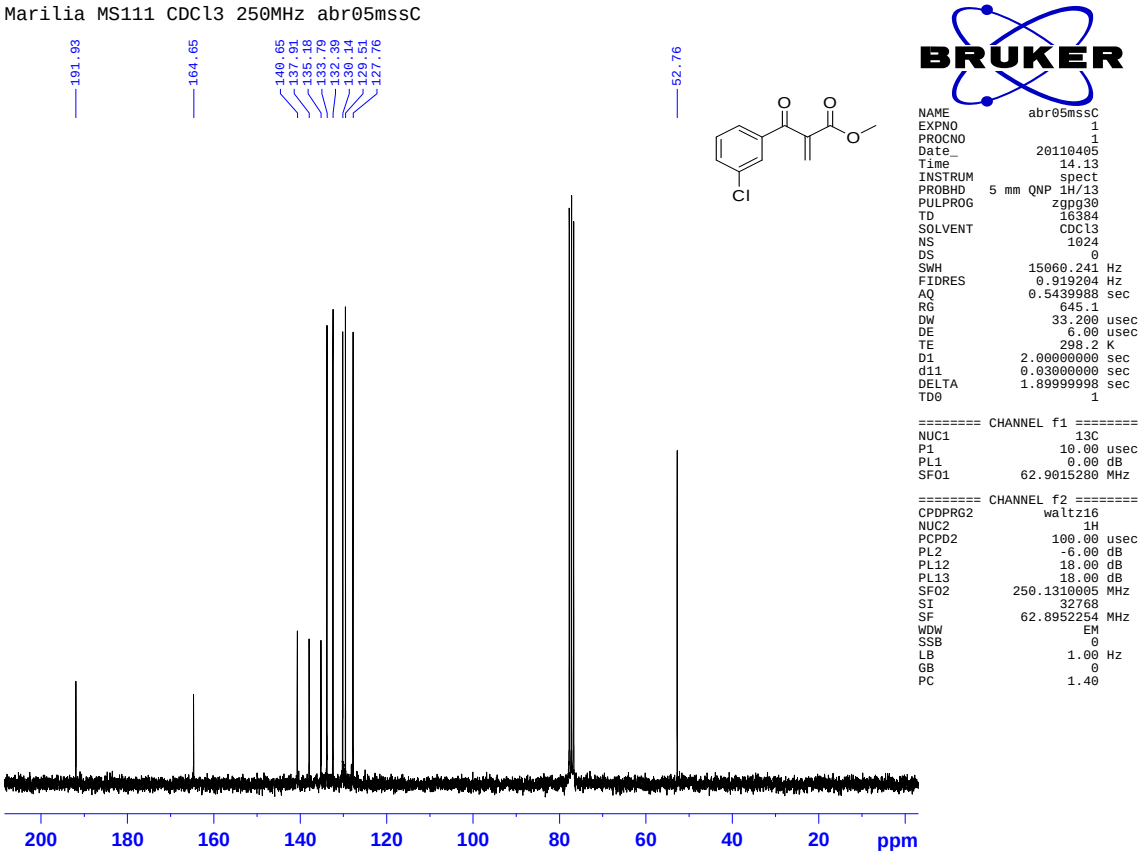


Methyl 2-[(3-chlorophenyl)carbonyl]prop-2-enoate (**21**)

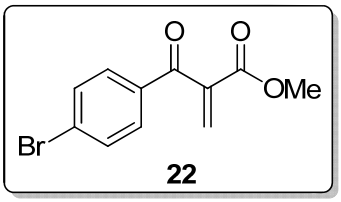
Yield: 98%, yellow tinged oil; IR (film, ν_{max}): 2954, 1737, 1690, 1591, 1238, 898 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.78 (s, 3H); 6.09 (s, 1H); 6.74 (s, 1H); 7.41 (t, ^3J =7.8Hz, 1H); 7.57 (ddd, ^3J = 1.1Hz; 2.0Hz and 8.0Hz); 7.72 (dt, ^3J = 1.5 and 7.7Hz); 7.84 (t, ^3J = 1.7Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 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 $C_{11}H_{10}ClO_3$ 225.0318 $[M + H]^+$; Found *m/z* 225.0346.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **21**.

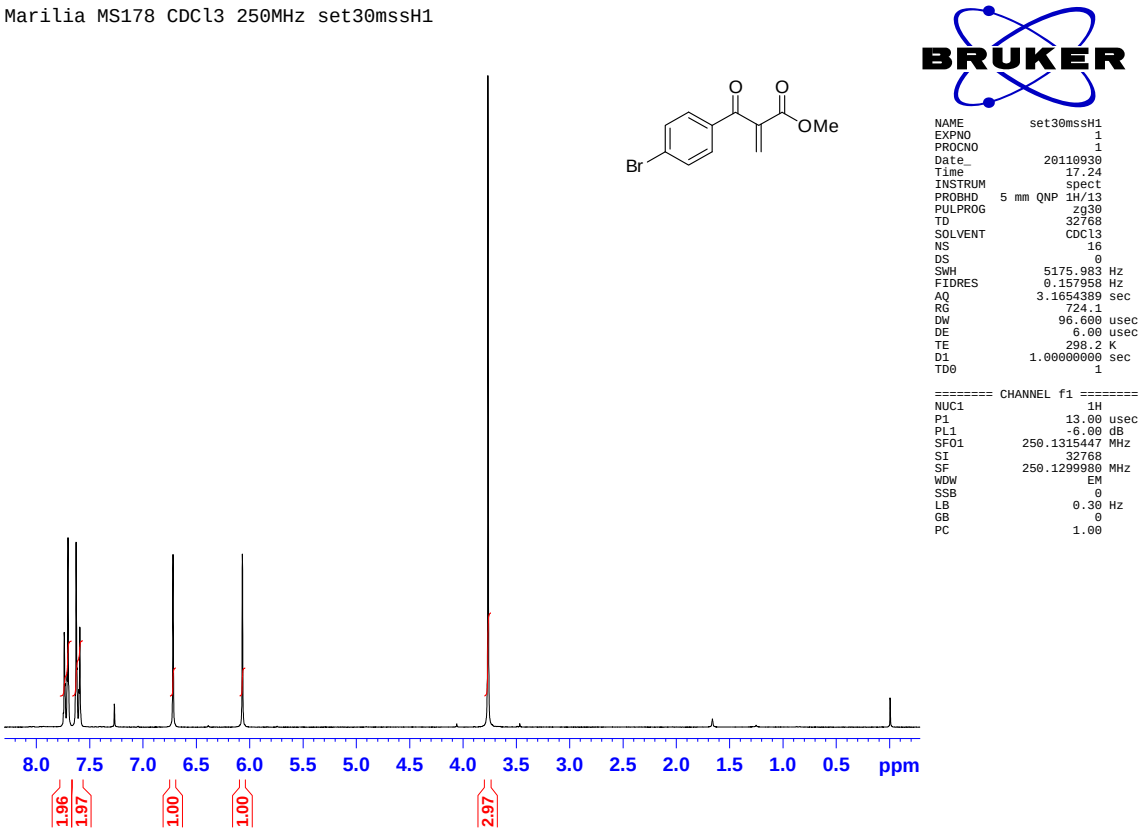


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **21**.

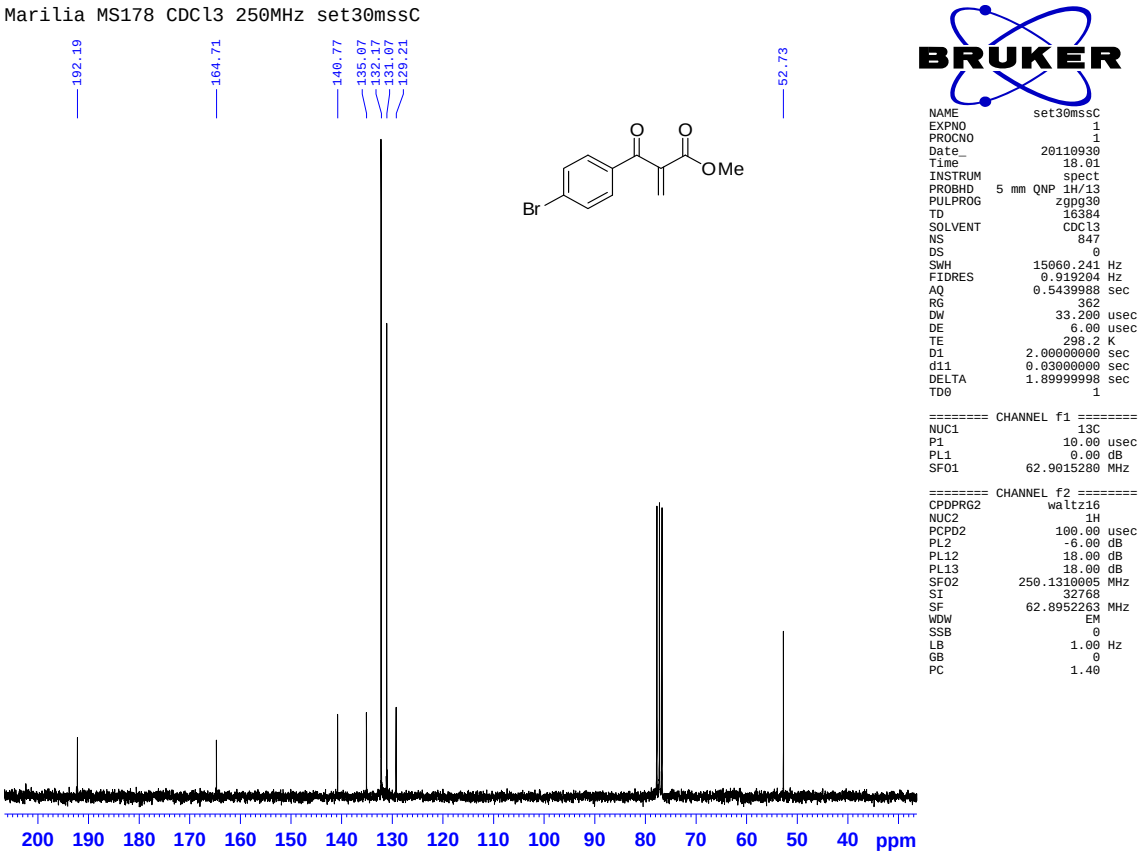


Methyl 2-[(4-bromophenyl)carbonyl]prop-2-enoate (**22**)

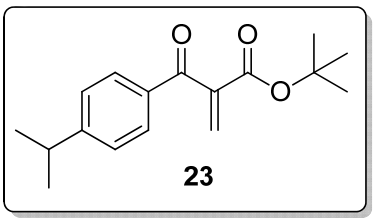
Yield: 95%, yellow tinged oil; IR (film, ν_{max}): 2954, 1731, 1674, 1584, 1193, 816 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.77 (s,3H); 6.07 (s, 1H); 6.70 (s, 1H); 7.61 (d, ^{3}J = 8.7 Hz, 2H); 7.72 (d, ^{3}J = 8.7 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.7; 129.2; 131.1; 132.2; 135.1; 140.8; 164.7; 192.2. HRMS (ESI, *m/z*): Calcd. for $C_{11}H_{10}O_3Br$ 268.9813 $[M + H]^+$; found 268.9836.



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

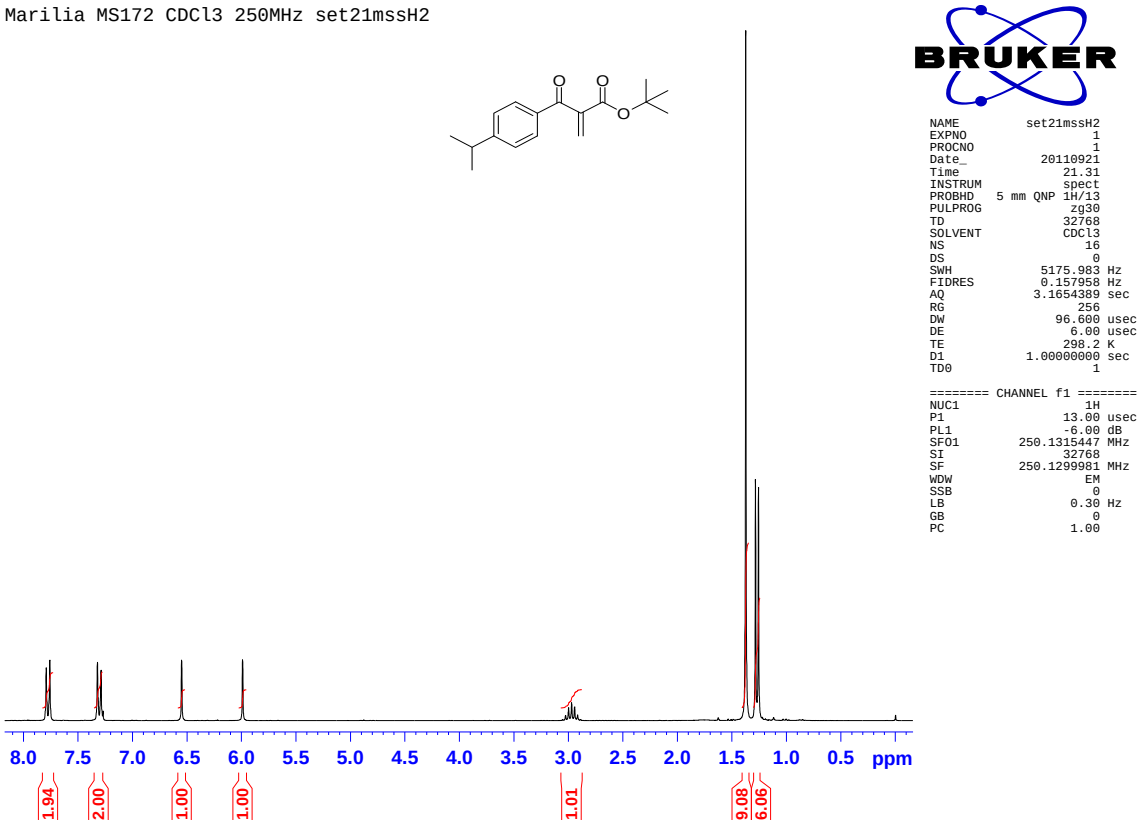


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **22**.

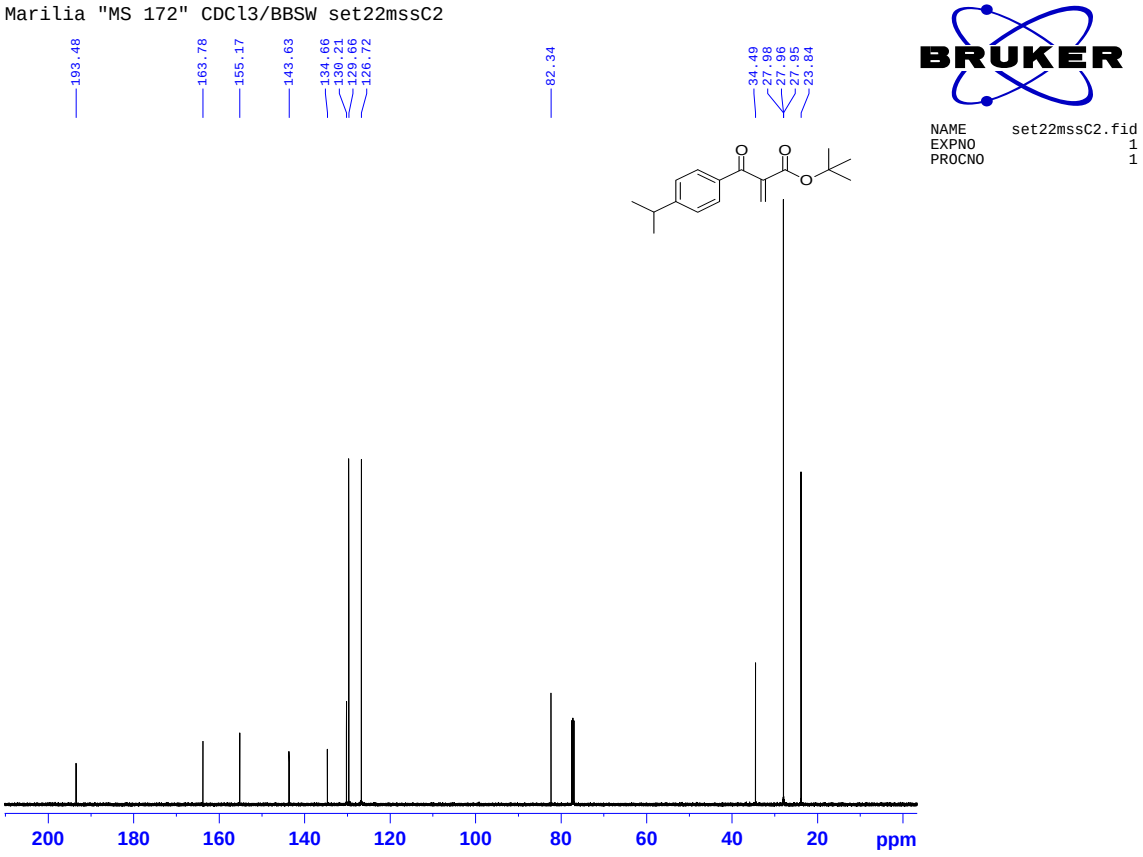


tert-Butyl 2-{[4-(propan-2-yl)phenyl]carbonyl}prop-2-enoate (**23**)

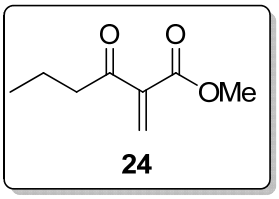
Yield: >95%, yellow tinged oil; IR (film, ν_{max}): 2965, 2933, 2873, 1724, 1674, 1570, 1149, 1055, 847 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (d, ^3J = 6.9 Hz, 6H); 1.37 (s, 9H); 2.97 (m, 1H); 5.99 (s, 1H); 6.55 (s, 1H); 7.30 (d, ^3J = 8.3 Hz, 2H); 7.77 (d, ^3J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{17}H_{22}O_3Na$ 297.1467 $[M + H]^+$; found 297.1505.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **23**.

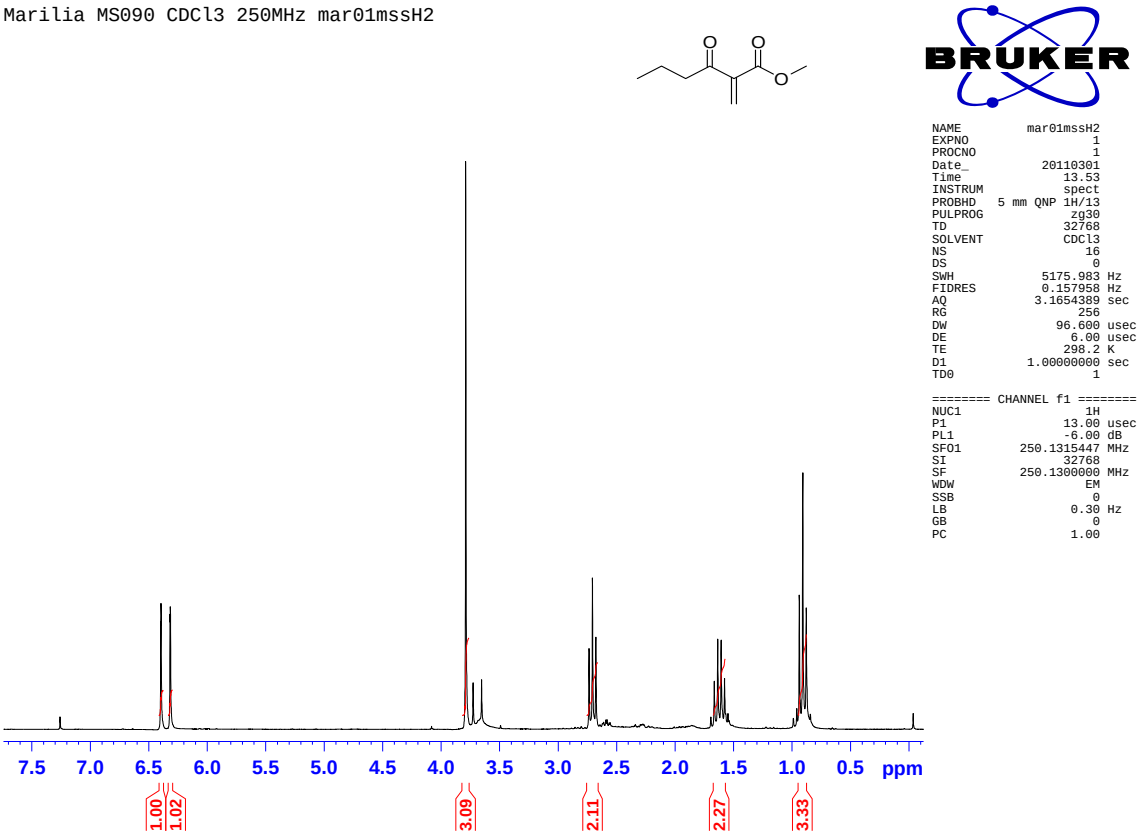


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **23**.

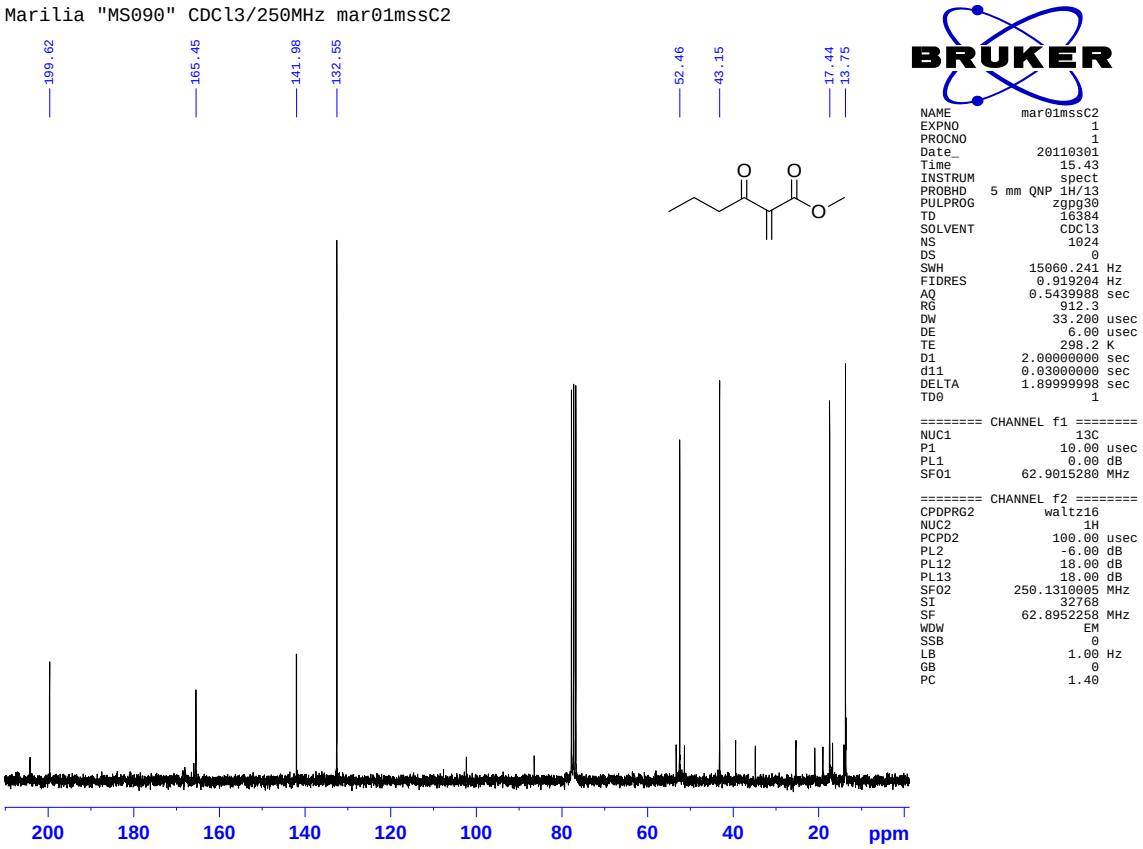


Methyl 2-methylidene-3-oxohexanoate (**24**)

Yield: 73%, colorless oil; IR (film, ν_{max}): 2962, 2876, 1750, 1714, 1630, 1435, 1269, 1096 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91 (t, ^{3}J = 7.4Hz, 3H); 1.62 (m, ^{3}J = 7.4Hz, 2H); 2.71 (t, ^{3}J = 7.3Hz, 2H); 3.79 (s, 3H); 6.32 (d, ^{3}J = 0.8Hz, 1H); 6.40 (d, ^{3}J = 0.8Hz, 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 $(C_8H_{13}O_3)_2H$ 313.1652 $[M + H]^+$; found 313.1682



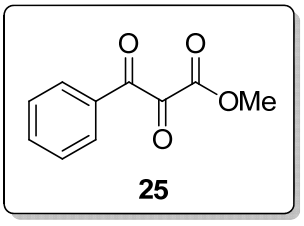
^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the α-methylene-β-ketoester **24**.



^{13}C NMR (62.5 MHz, $CDCl_3$) 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 O_2 and O_3 – 0.3-0.5% of O_3), 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).

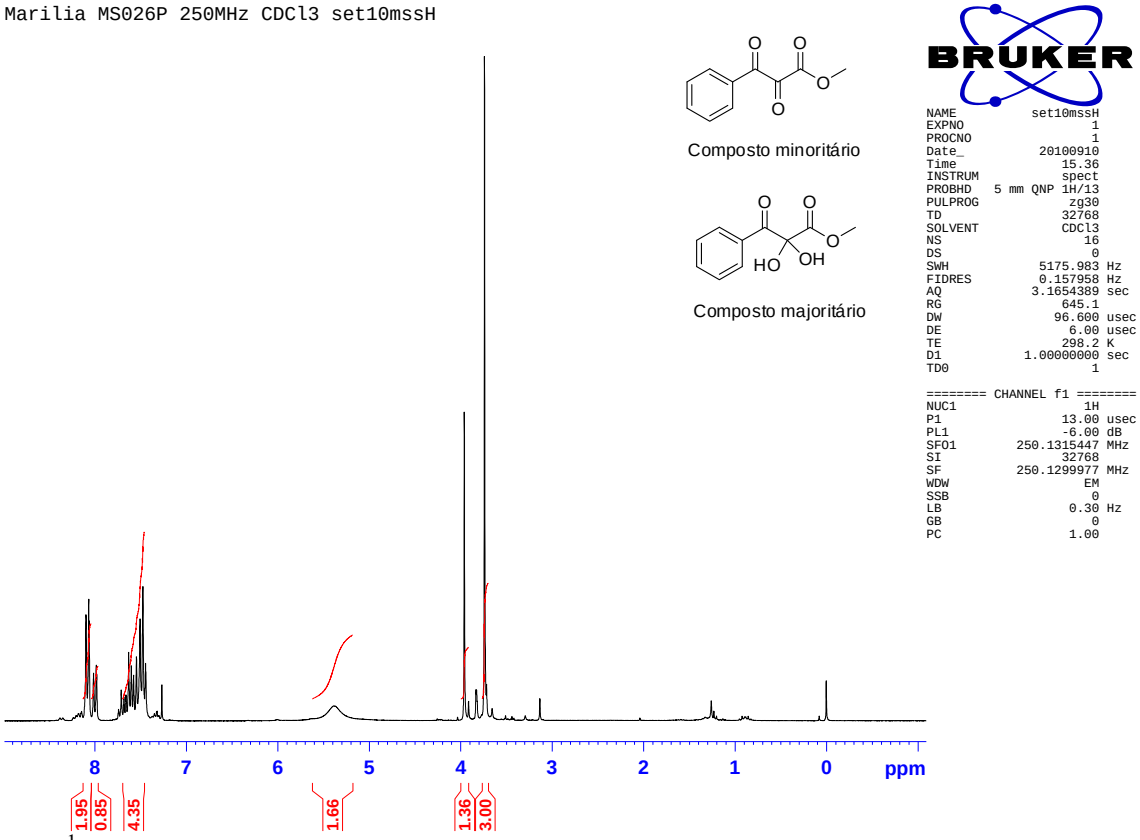


25

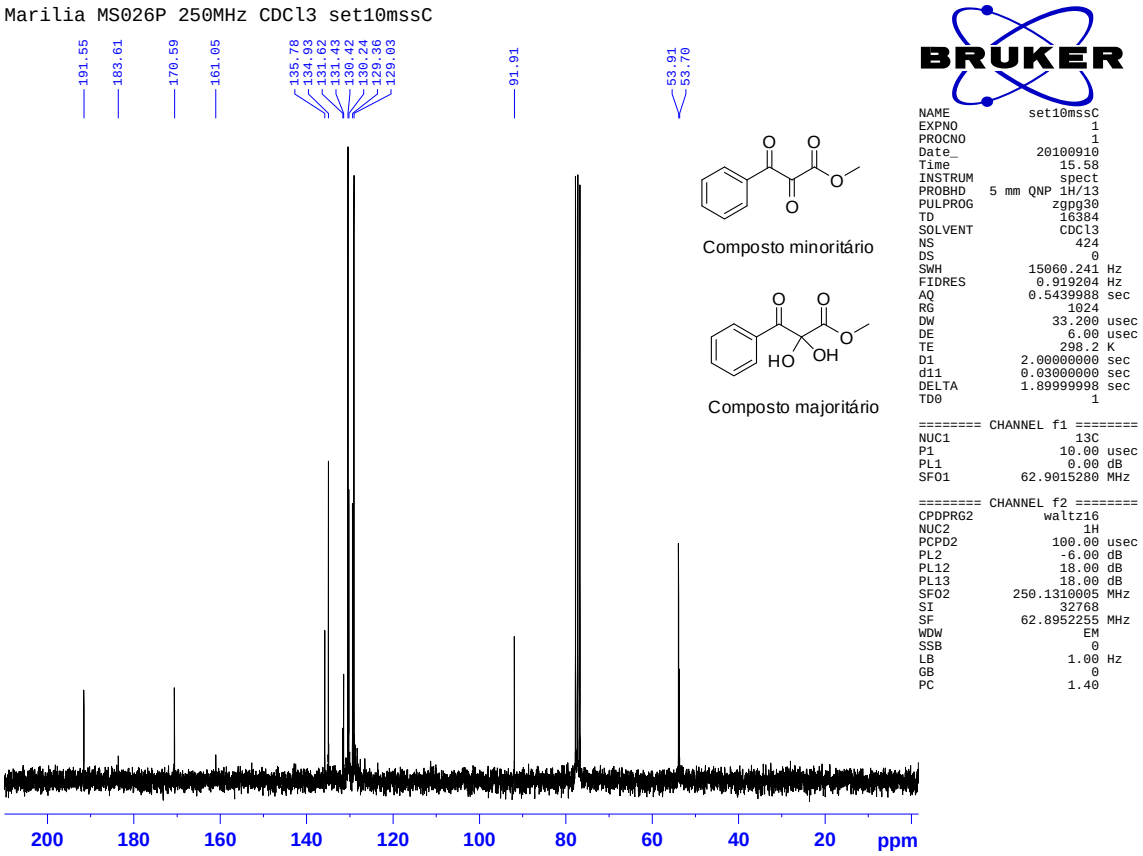
Methyl 2,3-dioxo-3-phenylpropanoate (**25**)

Yield: 78%, yellow oil; IR (film, ν_{max}): 3426, 2958, 1755, 1696, 1598, 1131, 911 cm^{-1}. Mixture 4:9 (tricarbonyl and hydrate form) - ^{1}H NMR (250 MHz, $CDCl_3$): *Tricarbonyl*

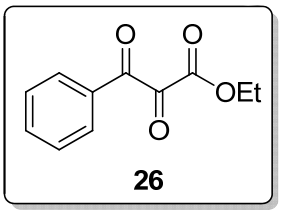
compound: δ 4.0 (s, 3H); 7.5-7.7 (m, 3H), 9.0-8.0 (m, 2H). *Hydrate*: δ 3.74 (s, 3H); 5.40 (br, 2H); 7.5-7.7 (m, 3H); 8.10 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$) - *Tricarbonyl compound*: δ 53.7; 129.4; 130.2; 131.6; 135.8; 161.1; 183.6. *Hydrate*: δ 53.9; 91.9; 129.0; 130.4; 131.4; 134.9; 170.6; 191.6. HRMS (ESI, *m/z*): Calcd for *m/z* $C_{10}H_9O_4$ 193.0500 $[M + H]^+$; found *m/z* 193.0487.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the vicinal tricarbonyl compound **25**.



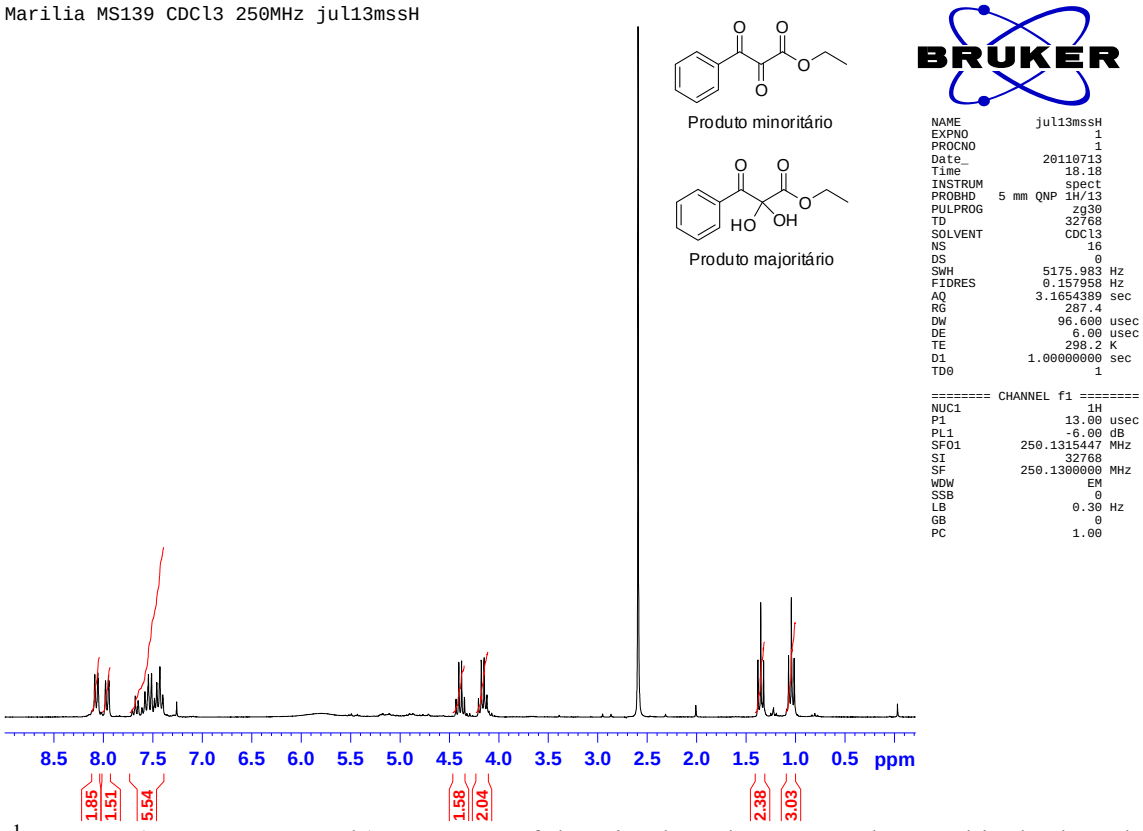
^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the vicinal tricarbonyl compound **25**.



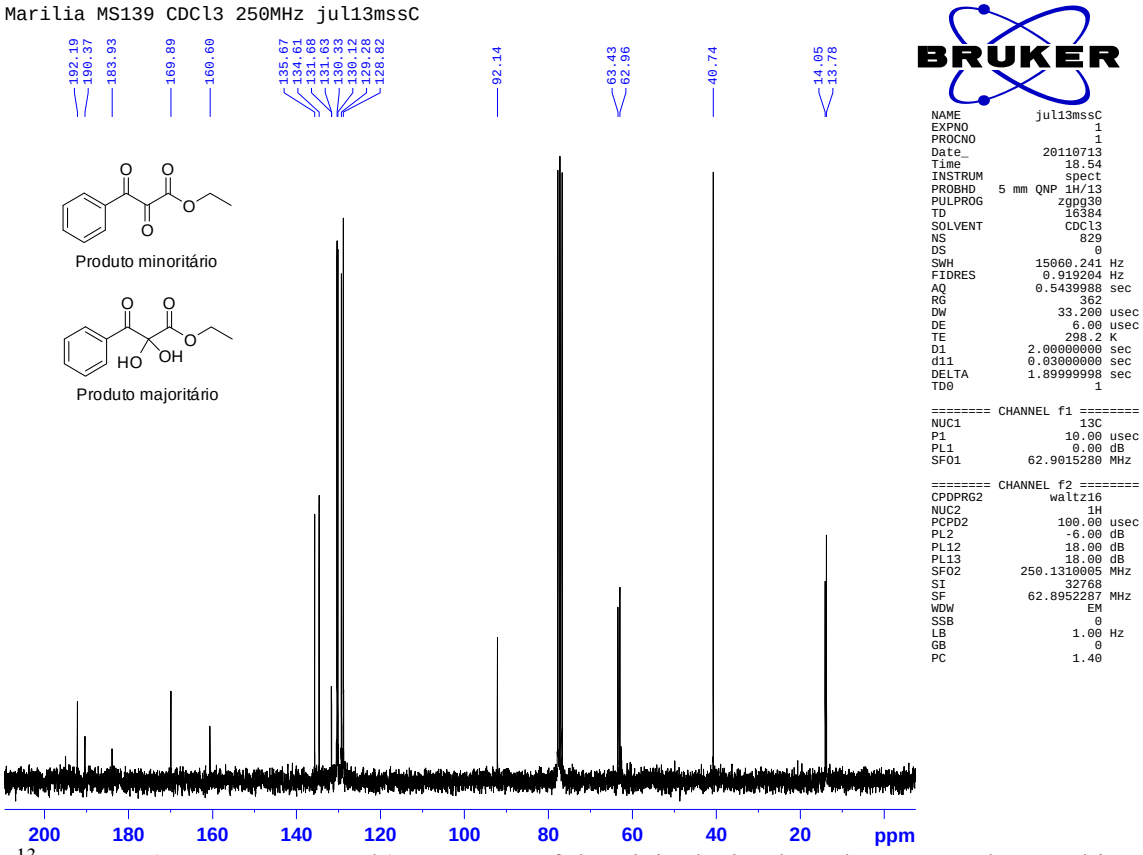
26

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

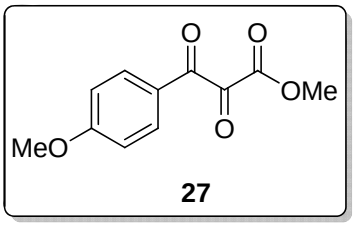
Yield: >95%, greenish yellow oil; IR (film, ν_{max}): 3415, 2985, 1750, 1695, 1235, 1133, 1101, 1015 cm^{-1}. Mixture of the vicinal tricarbonyl compound and its hydrated form (4:5) - ^{1}H NMR (250 MHz, $CDCl_3$): *Tricarbonyl compound*: δ 1.36 (t, ^3J = 7.1Hz, 3H); 4.40 (q, ^3J = 7.1Hz, 2H); 7.41-8.10 (m, 5H). *Hydrate*: δ 1.05 (t, ^3J = 7.1Hz, 3H); 4.17 (q, ^3J = 7.1Hz, 2H); 7.41-8.10 (m, 5H). ^{13}C NMR (62.5 MHz, $CDCl_3$) - *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 $C_{11}H_{11}O_4$ 207.0657 $[M + H]^+$; found *m/z* 207.0660.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **36** and its hydrated form.



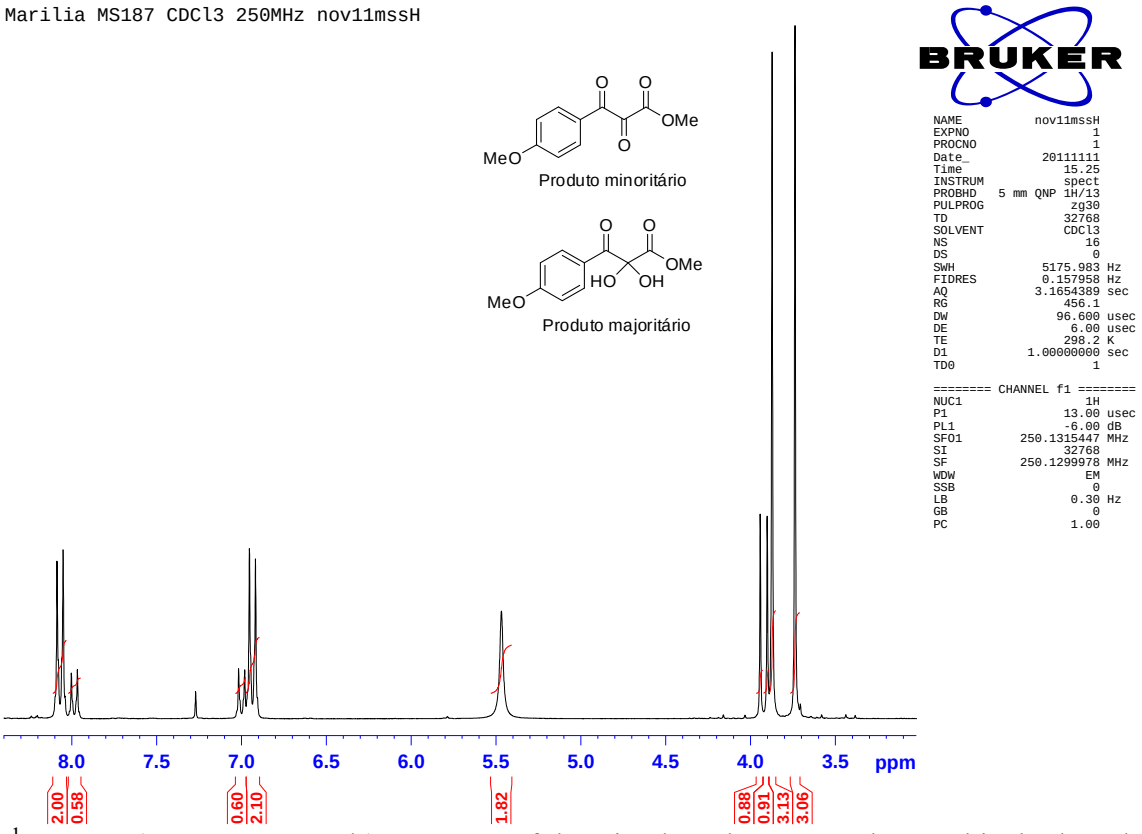
^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the vicinal tricarbonyl compound **26** and its hydrated form.



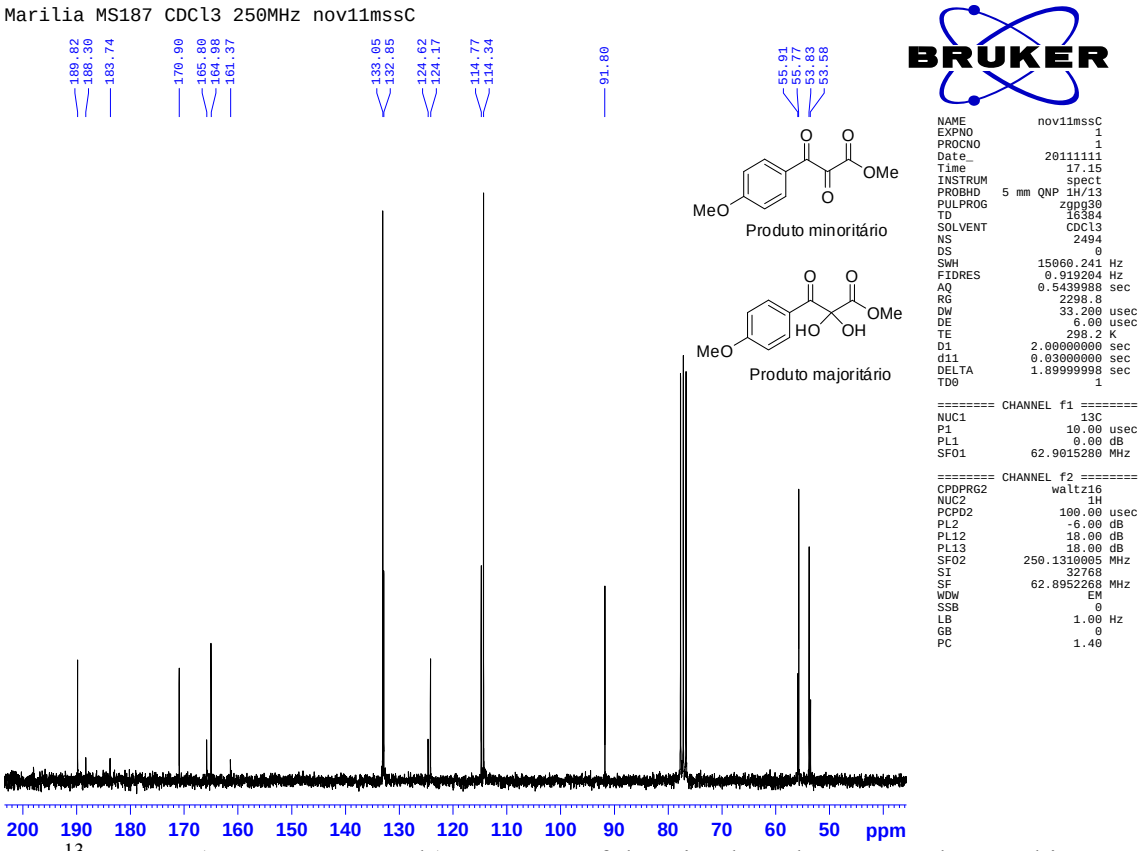
27

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

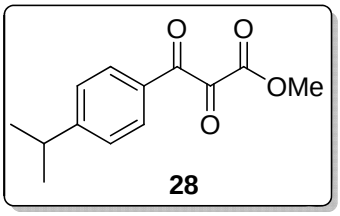
Yield: 76%, yellow tinged oil; IR (film, ν_{max}): 3407, 2954, 2844, 1747, 1682, 1602, 1254, 1175, 1128, 845 cm^{-1}. Mixture of the vicinal tricarbonyl compound and its hydrated form (1:3). ^{1}H NMR (250 MHz, $CDCl_3$): *Tricarbonyl compound*: δ 3.90 (s, 3H); 3.94 (s, 3H); 7.00 (d, ^{3}J = 9.0Hz, 2H); 7.98 (d, ^{3}J = 9.0Hz, 2H). *Hydrate*: δ 3.74 (s, 3H); 3.98 (s, 3H); 5.47 (s, 2H); 6.94 (d, ^{3}J = 9.0Hz, 2H); 8.07 (d, ^{3}J = 9.0Hz, 2H). ^{13}C 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 $C_{11}H_{11}O_5$ *m/z* 223.0607 $[M + H]^+$. Found *m/z* 223.0678.



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

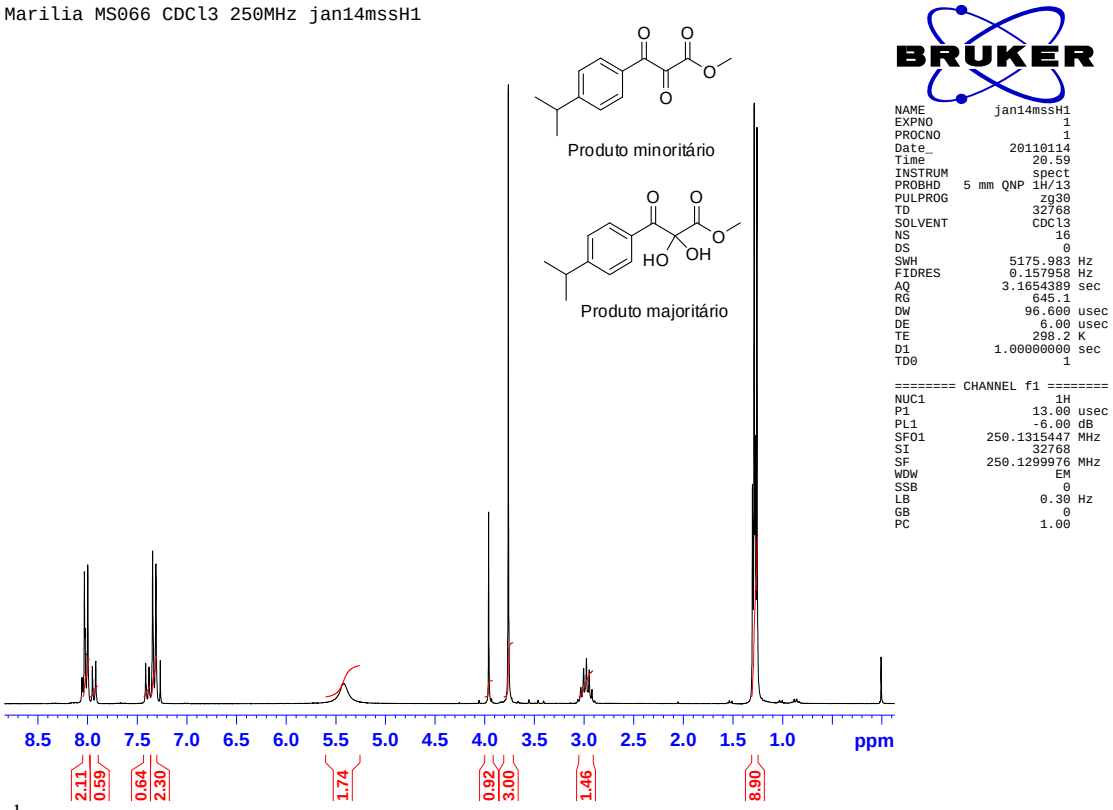


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **27** and its hydrated form.

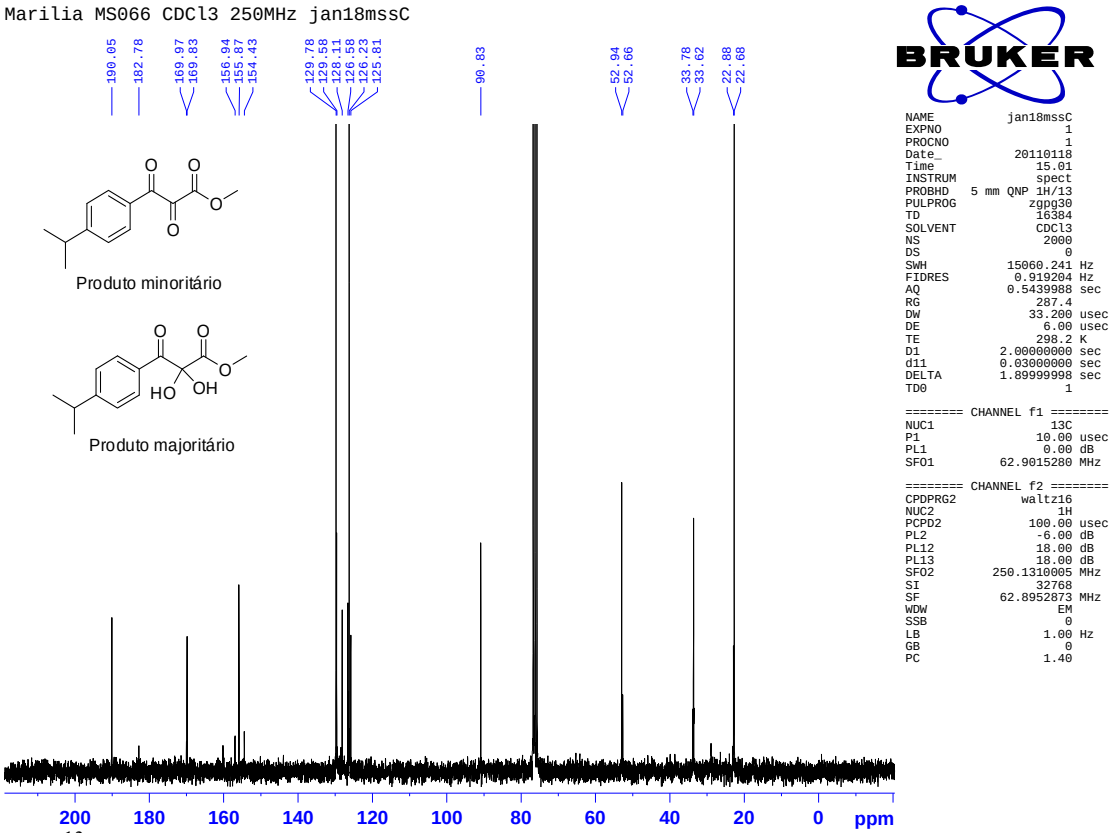


Methyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (**28**)

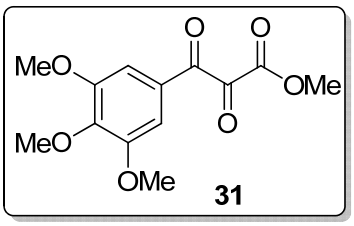
Yield: 76%, yellow oil; IR (film, ν_{max}): 3413, 2959, 2876, 1749, 1691, 1606, 1185, 854 cm^{-1}. Mixture of vicinal tricarbonyl compound and its hydrate form (1:3) - ^{1}H NMR (250 MHz, $CDCl_3$): *Tricarbonyl compound*: δ 1.29 (d, ^3J = 6.9Hz, 6H); 2.98 (m, 1H); 3.96 (s, 1H); 7.40 (d, ^3J = 8.3Hz, 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). ^{13}C NMR (62.5 MHz, $CDCl_3$) - *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 $C_{13}H_{15}O_4$ *m/z* 235.0937 $[M + H]^+$; found *m/z* 235.0970.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **28** and its hydrated form.

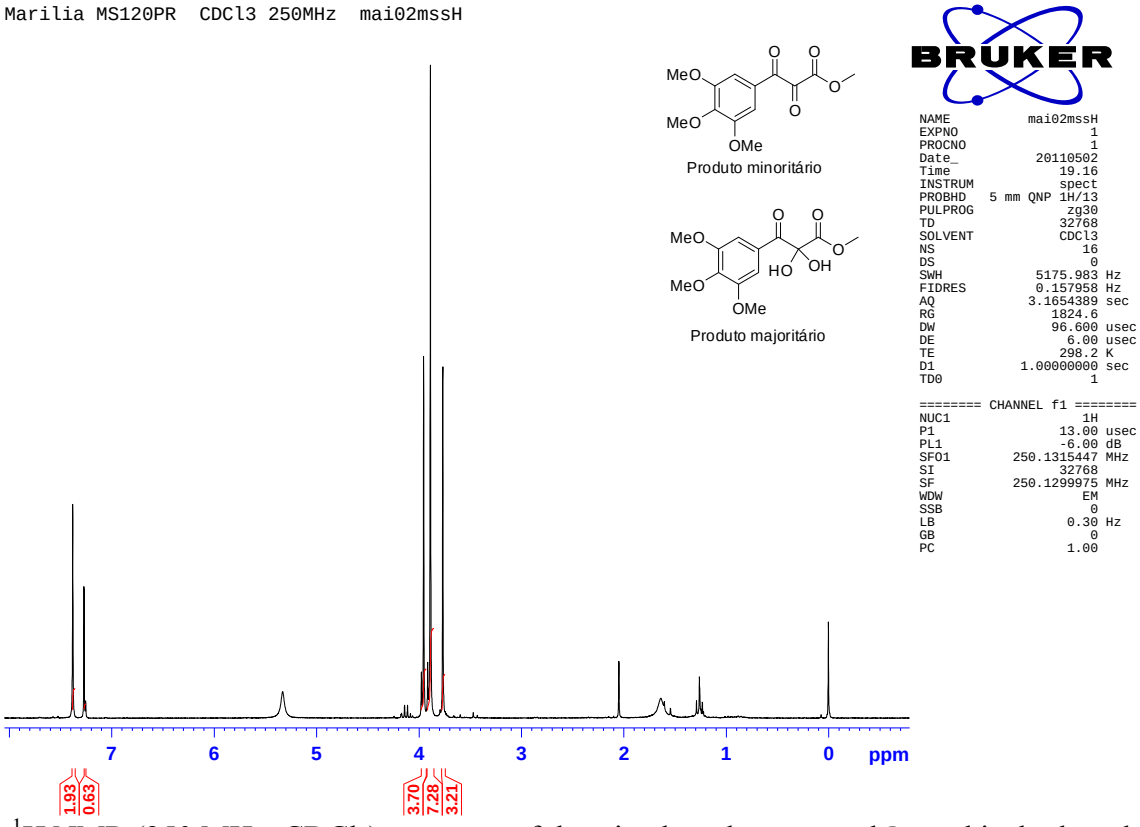


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **28** and its hydrated form.

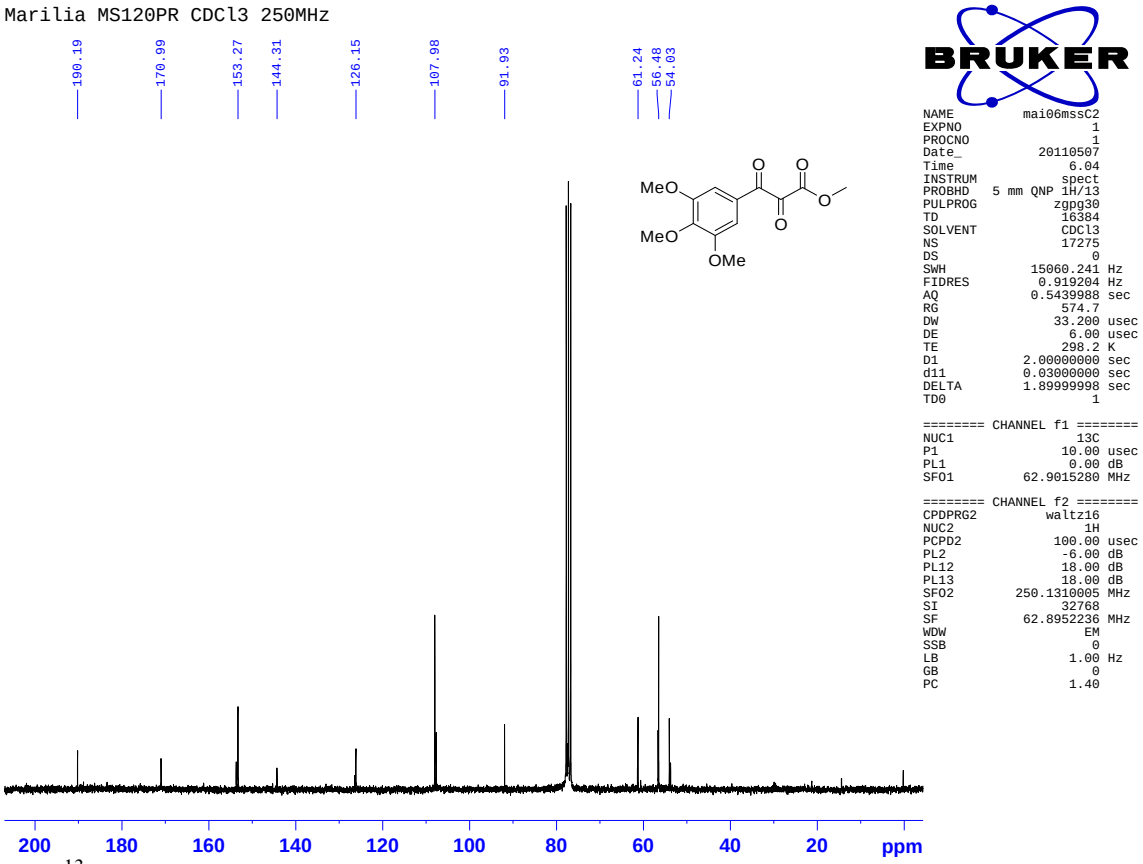


Methyl 2,3-dioxo-3-(3,4,5-trimethoxyphenyl)propanoate (**31**)

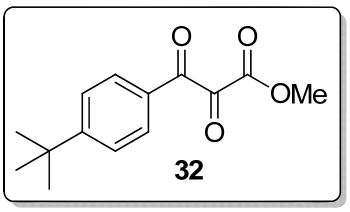
Yield: 67%, yellow oil; IR (film, ν_{max}): 3418, 2954, 2843, 1747, 1693, 1585, 1127 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.79 (s, 3H); 3.91 (s, 6H); 3.97 (s, 3H); 5.35 (bs, 2H); 7.40 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 54.0; 56.5; 61.2; 91.9; 108.0; 126.2; 144.3; 153.3; 171.0; 190.2; HRMS (ESI, *m/z*): Calcd. for $C_{13}H_{15}O_7$ 283.0812 $[M + H]^+$; found 283.0809.



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

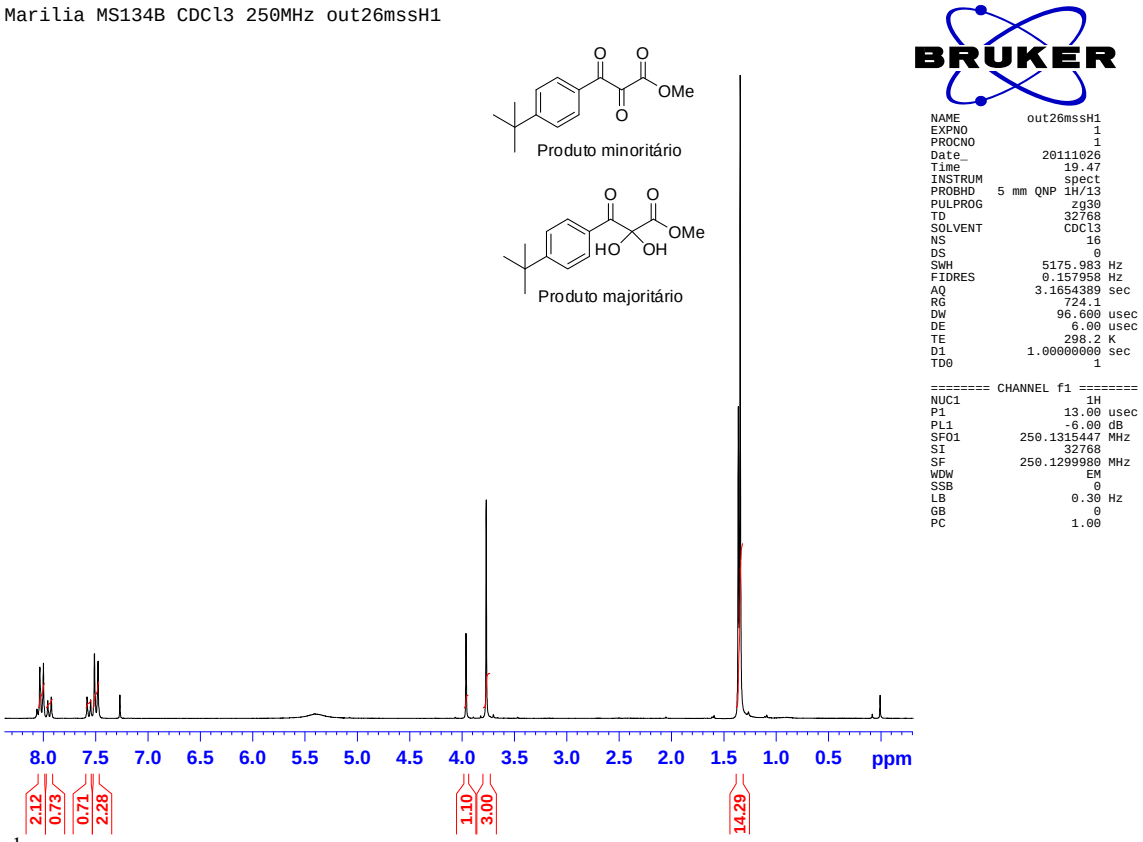


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **31** and its hydrated form.

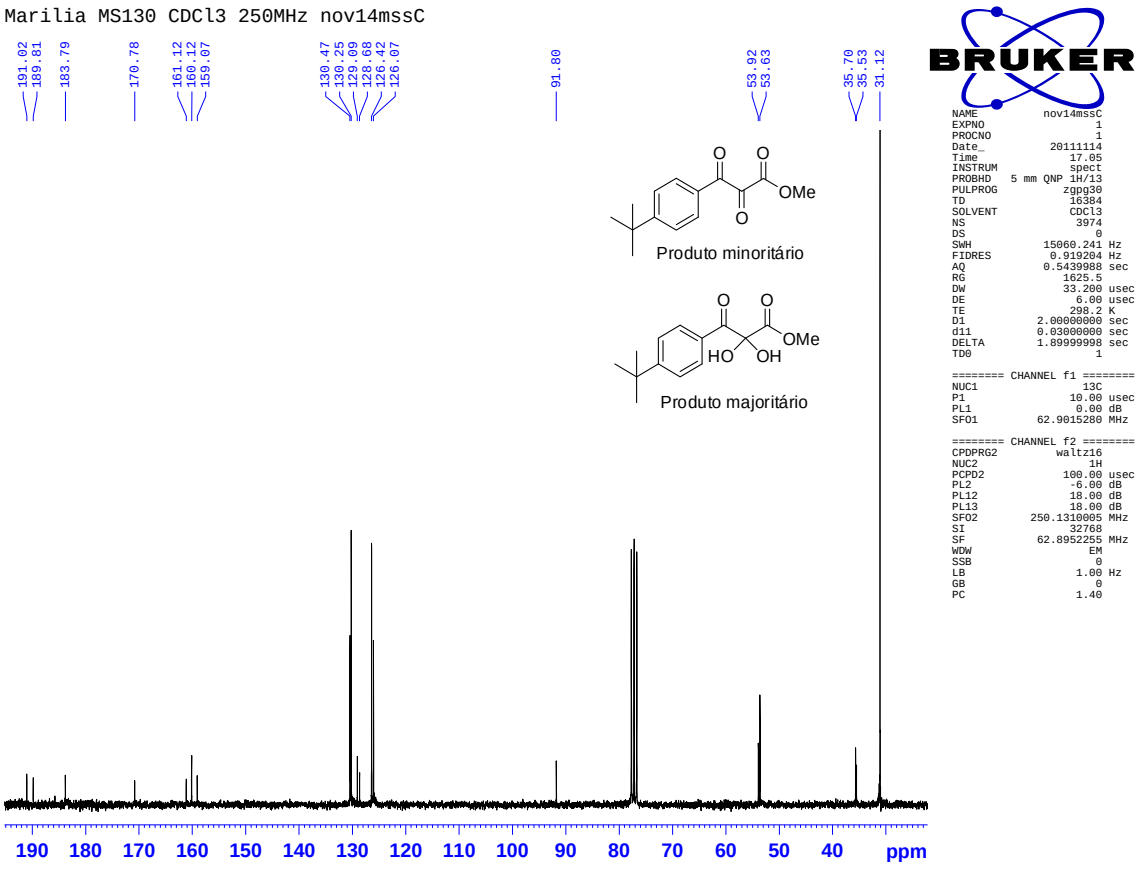


Methyl 3-(4-*tert*-butylphenyl)-2,3-dioxopropanoate (**32**)

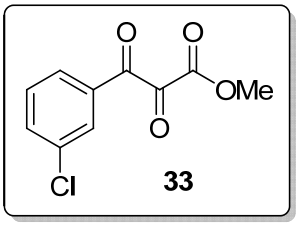
Yield: >95%; white solid, m.p. 56-59 ºC; IR (KBr, ν_{max}): 3416, 2962, 1748, 1688, 1604, 1250, 1127 cm^{-1}. Mixture of the tricarbonyl compound and its hydrate (1:3): ^{1}H NMR (250 MHz, $CDCl_3$) - *Tricarbonyl compound*: δ 1.35 (s, 9H); 3.95 (s, 3H); 7.56 (d, ^3J = 8.5 Hz, 2H); 7.93 (d, ^3J = 8.5 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 ^{13}C (62.5 MHz, $CDCl_3$): *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 $C_{14}H_{17}O_4$ *m/z* 249.1127 $[M + H]^+$; found *m/z* 249.1104



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **32** and its hydrated form.

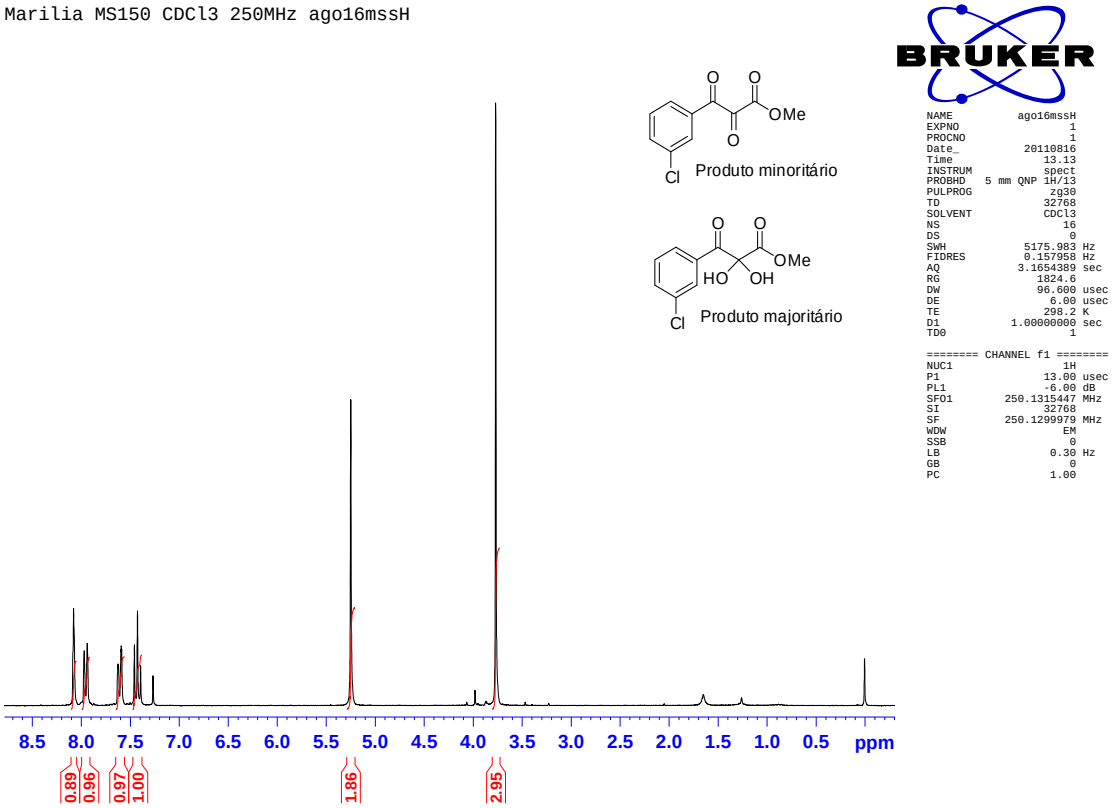


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **32** and its hydrated form.

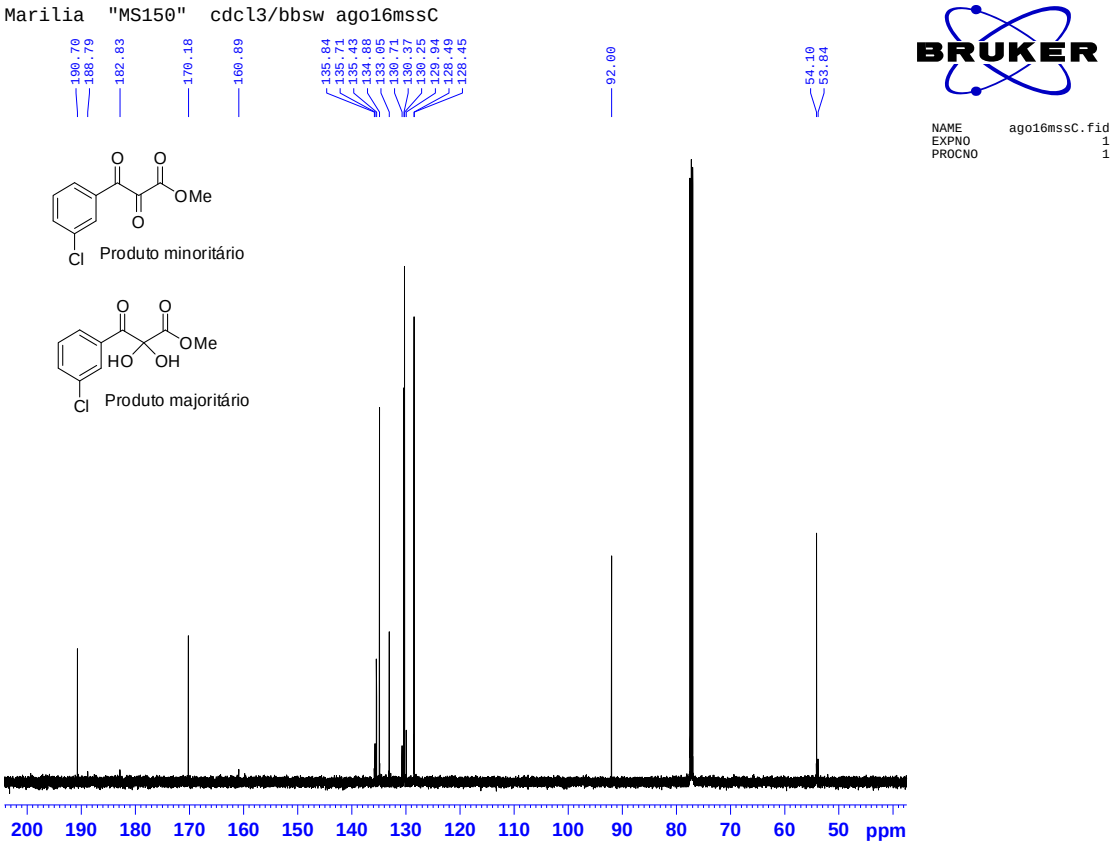


Methyl 3-(3-chlorophenyl)-2,3-dioxopropanoate (**33**)

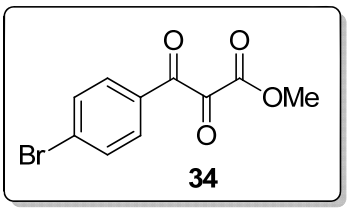
Yield: 65%, yellow tinged solid, m.p. 66-67ºC. IR (KBr, ν_{max}): 3468, 3421, 3073, 2959, 1755, 1743, 1701, 1110, 912 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.77 (s, 3H); 5.25 (s, 2H); 7.43 (t, ^3J = 8.0 Hz, 1H); 7.61 (dt, ^3J = 1.0 Hz, ^3J = 8.0 Hz, 1H); 7.96 (d, ^3J = 7.9 Hz, 1H); 8.08 (s, 1H). 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 $C_{14}H_{17}O_3$ 227.0111 $[M + H]^+$; Found *m/z* 227.0189.



^{1}H NMR(250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **33** and its hydrated form

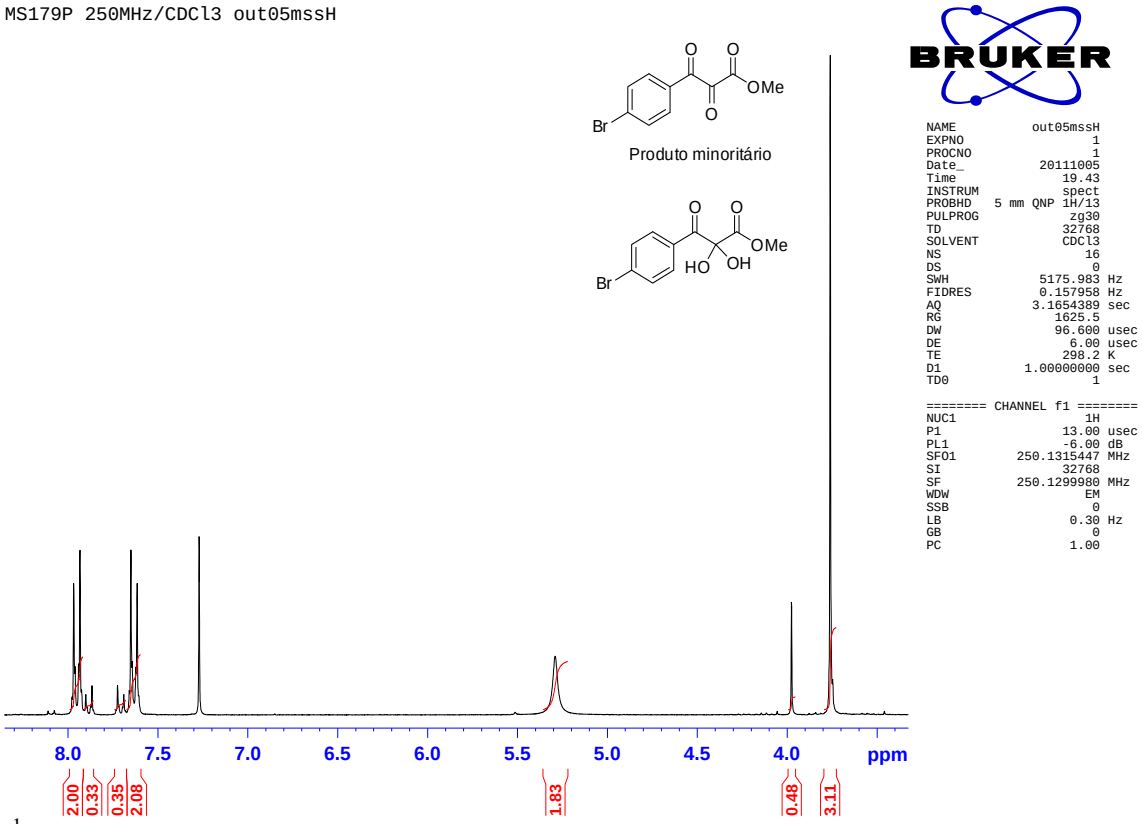


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **33** and its hydrated form

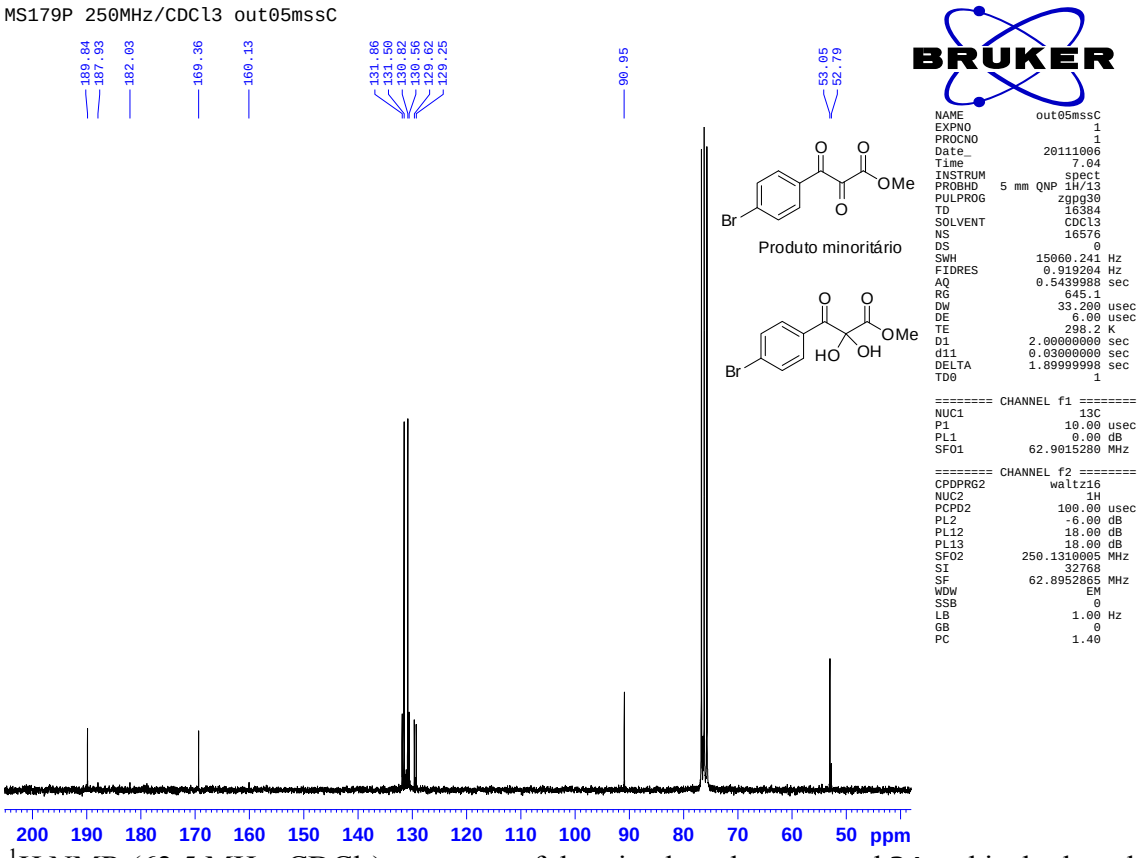


Methyl 3-(4-bromophenyl)-2,3-dioxopropanoate (**34**)

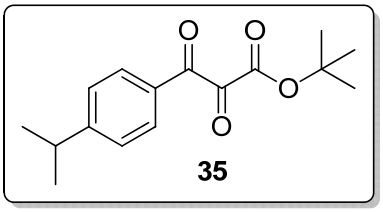
Yield: 75%, white solid, m.p. 99-100 ºC; IR (KBr, ν_{max}): 3421, 1756, 1738, 1694, 1585, 1133, 803 cm^{-1}. Mixture of tricarbonyl compound and hydrate (1:6) ^{1}H NMR (250 MHz, $CDCl_3$) - *Tricarbonyl compound*: δ 3.97 (s, 3H); 7.70 (d, ^3J = 8.7 Hz, 2H); 7.88 (d, ^3J = 8.7 Hz, 2H). *Hydrate:* δ 3.75 (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 $C_{10}H_8BrO_4$ 270.9600 $[M + H]^+$; found 270.9591



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **34** and its hydrated form.

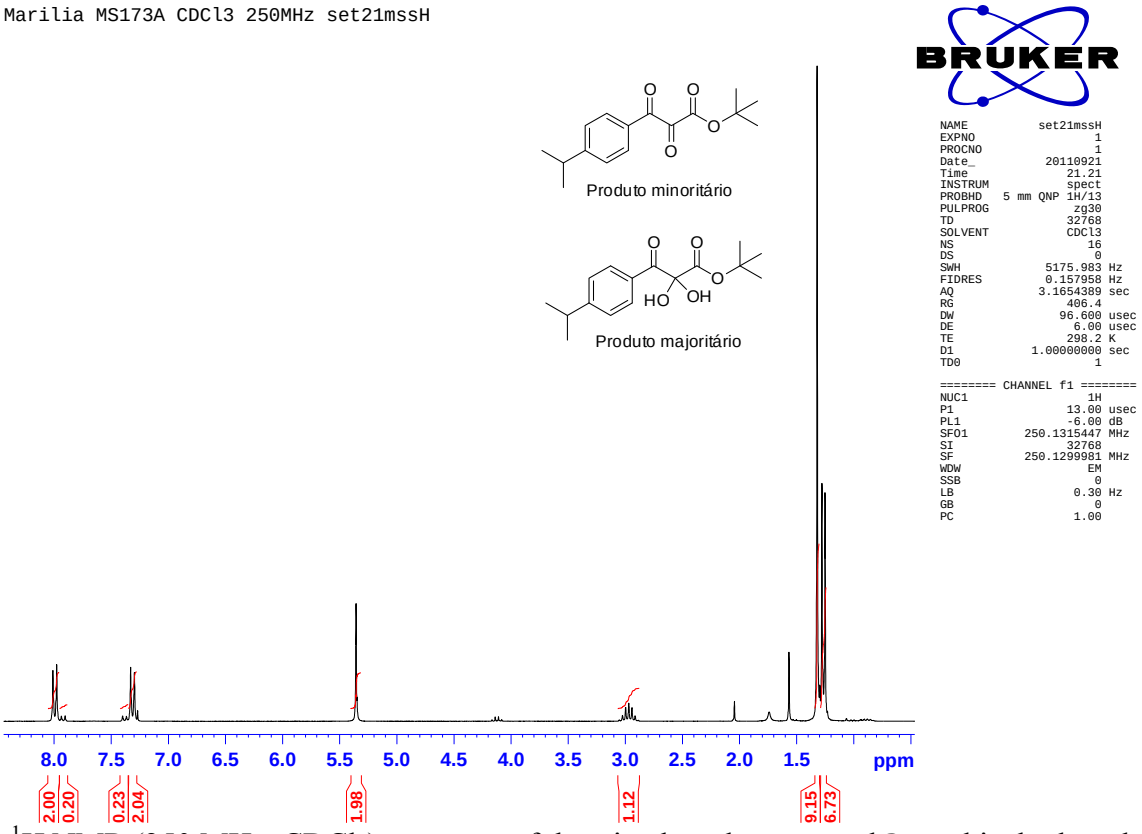


^{1}H NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **34** and its hydrated form.

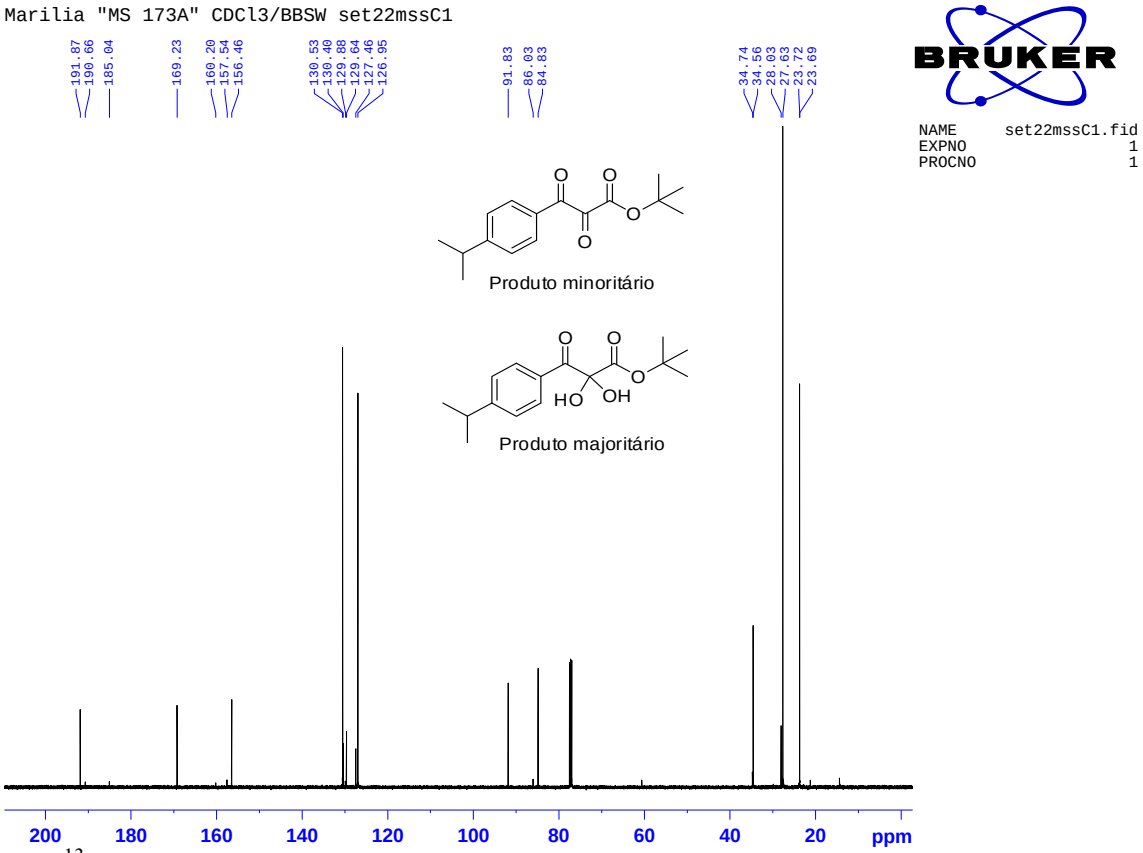


tert-Butyl 2,3-dioxo-3-[4-(propan-2-yl)phenyl]propanoate (**35**)

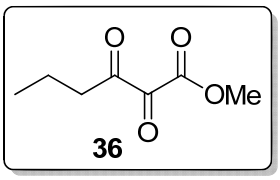
Yield: 61%, yellow tinged oil; IR (film, ν_{max}): 3432, 2965, 2933, 2873, 1738, 1692, 1606, 1571, 1128, 851 cm^{-1}. Mixture tricarbonyl compound and its hydrated form (1:10). ^{1}H NMR (250 MHz, $CDCl_3$) - *Tricarbonyl compound*: δ 7.38 (d, ^{3}J = 8.3 Hz, 2H); 7.92 (d, ^{3}J = 8.3 Hz, 2H). *Hydrate*: δ 1.26 (d, ^{3}J = 6.9 Hz, 6H); 1.32 (s, 9H); 2.97 (m, 1H); 5.36 (s, 2H); 7.31 (d, ^{3}J = 8.4 Hz, 2H); 7.99 (d, ^{3}J = 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 $C_{16}H_{21}O_4$ 277.1434 $[M + H]^+$; found 277.1430.



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

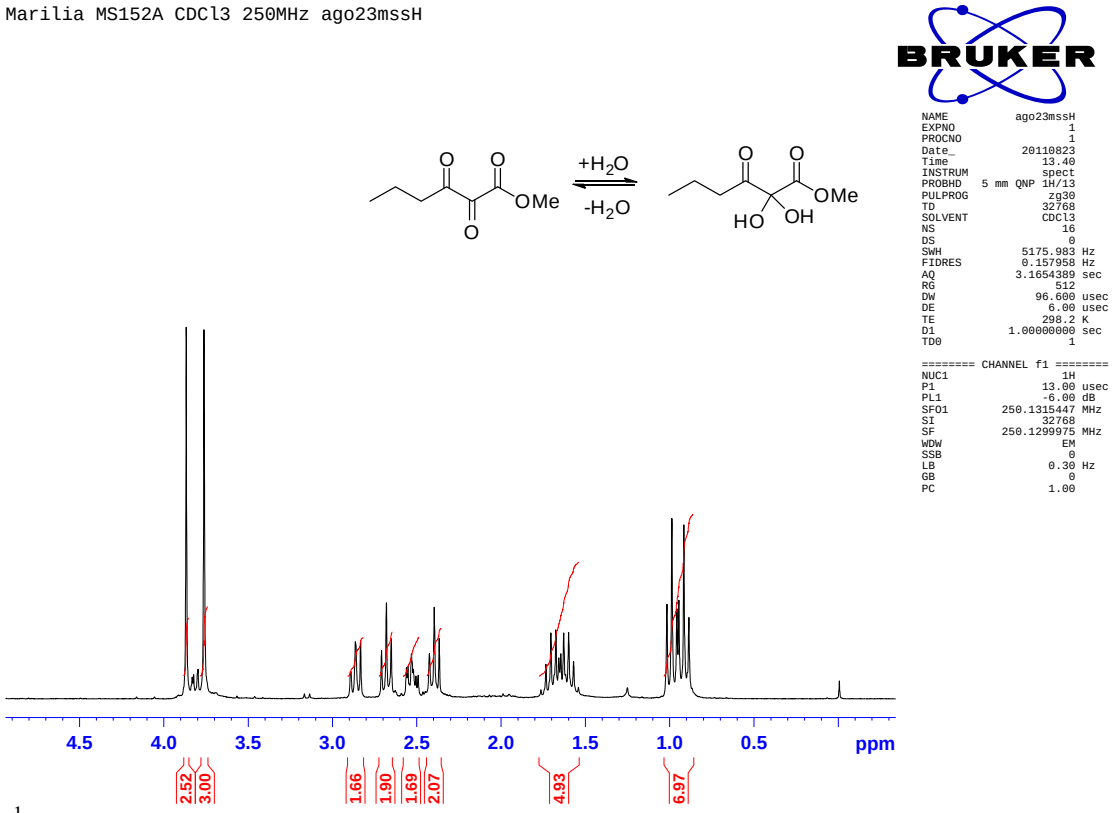


^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **35** and its hydrated form.

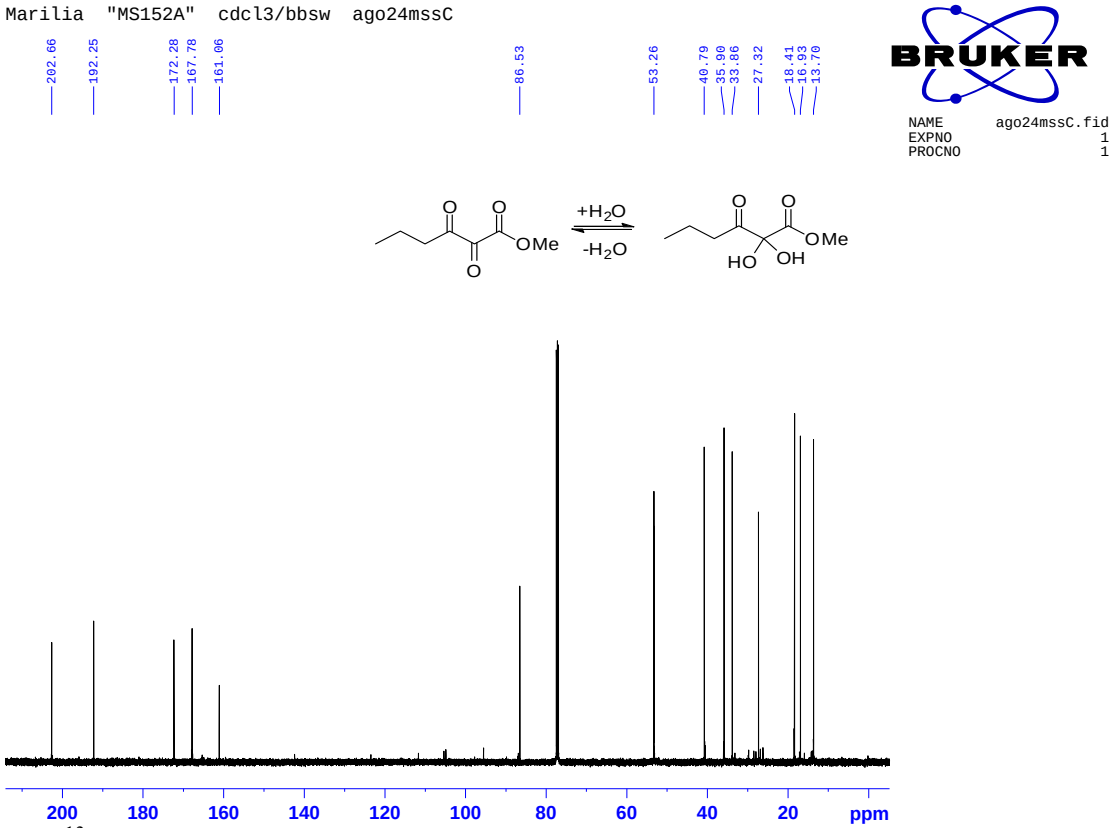


Methyl 2,3-dioxohexanoate (**36**)

Yield: 22%, colorless oil; IR (film, ν_{max}): 3420, 2962, 2876, 1750, 1714 cm^{-1}. Mixture tricarbonyl compound and hydrate (1:1). ^{1}H NMR (250 MHz, $CDCl_3$): 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). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_7H_{11}O_4$ 159.0652 $[M + H]^+$; found 159.0650.



^{1}H NMR (250 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **36** and its hydrated form.



^{13}C NMR (62.5 MHz, $CDCl_3$) spectrum of the tricarbonyl compound **36** and its hydrated form.