Table of contents

1. General methods

1. General Information for materials and instruments

Chemical reagents were purchased from Sigma-Aldrich, Acros Organics or Alfa Aesar. All are used as received in absence of any specifications.

Glassware was dried over-night in an oven at 160 °C and reactions were carried out under an argon inert atmosphere.

Reactions were monitored by GC/MS analysis on an Agilent 6892N equipped with a 12 m × 0.20 mm dimethylpolysiloxane capillary column linked to a Model 5973N Mass selective detector with 70 eV ionisation energy (EIMS) and/or TLC analysis on aluminium sheets precoated (0.25 mm) silica gel F_{254} plates. Visualization was performed by a 254 nm UV lamp and stained with iodized silica, an ethanolic solution of (2,4-dinitrophenyl)hydrazine or potassium permanganate. Frontal retention values R_f have been mentioned

Organic solutions were concentrated under reduced pressure on a Heidolph Laborota 4000 rotary evaporator.

Chromatographic purifications of products were accomplished using forced-flow chromatography on Merck Geduran 40-63 µm silica gel with the appropriated solvent.

Enantiomeric excess *ee* was determined either by High Pressure Liquid Chromatography (HPLC) analysis using a Waters 2998 Photodiode Array Detector using the appropriate chiral column and the corresponding eluent as noted for each product, or by optical rotation measurements on a Perkin-Elmer model 241 polarimeter with $[\alpha]_D$ rotation values reported in degree and concentration in g/100 mL at 23 °C.

Using a Bruker Avance spectrometer, ^{1}H and ^{13}C NMR spectra were recorded respectively at 400 MHz and 100 MHz in $CDCl_3$ or DMSO-d^6. Chemical shifts were reported as δ, in parts per million (ppm), relative to the signal of the solvent.[S1] Coupling constant (*J*) are measured in hertz (Hz). The abbreviations s, d, dd, t, td, q, and m, stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, doublet of triplets, quartet, multiplet respectively. Various 2D techniques and DEPT experiments were used to establish the structures and to assign the signals.

High Resolution Mass Spectroscopy (HRMS) was performed on pure samples checked by NMR or GC/MS analysis.

UV–Visible spectra were taken on an Uvikon spectrophotometer model 941 using 1 cm quartz cuvettes.

2. Preparation of the imidazolidinones organocatalysts

The 2,2,3-trimethylimidazolidin-4-one trifluoromethanesulfonic acid salt are used for the racemic synthesis.

The (2*R*,5*S*)-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one trifluoromethanesulfonic acid salt **1** is the chiral catalyst used for this work.

The organocatalyst were prepared according to a procedure described in the literature[S2-S4]

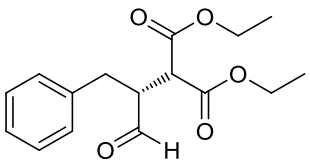
3. General procedure for the enantioselective α-alkylation of aldehydes

An overnight oven dried Pyrex glass vial was equipped with a septum and a dried magnetic stir bar. Rose Bengal (0.0025 mmol, 0.005 equiv), (2*R*,5*S*)-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one trifluoromethanesulfonic acid salt **1** (0.075 mmol, 0.15 equiv), LiCl (0.050 mmol, 0.10 equiv) and the corresponding bromide **3** (0.50 mmol, 1.0 equiv) were added successively. After purging the container with argon for 1 min, anhydrous DMSO or DMF (0.5 M, 1 mL) was added followed by starting aldehyde **2** (1.0 mmol, 2.0 equiv) and 2,6-lutidine (1.0 mmol, 2.0 equiv). Then the stirred solution was degassed for 10 min under argon bubbling and the mixture was placed 2 cm from the 24 W 6500 K 1425 lm fluorescent light source for irradiation until the complete conversion of the bromide (monitored by TLC and/or GC/MS analysis). Then 10 mL of water were added and the resulting solution was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography using the appropriate solvent to afford the desired alkylation product **4**.

The first determination of the yield was performed by ^{1}H NMR analysis after addition of butadiene sulfone used as an internal standard.

(2*R*,5*S*)-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one trifluoromethanesulfonic acid salt **1** was used as the chiral organocatalyst. The *ee* was determined by HPLC analysis : the racemic α-alkylation product was synthesized using the same general procedure using the pyrrolidinium trifluoromethanesulfonic acid salt (0.2 equiv) or 2,2,3-trimethylimidazolidin-4-one trifluoromethanesulfonic acid salt (0.2 equiv) instead of the chiral catalyst.

2. Experimental data



(*R*)-diethyl 2-(1-oxo-3-phenylpropan-2-yl)malonate
Chemical Formula: $C_{16}H_{20}O_5$
Molecular Weight: 292.33

According to the general procedure described above, Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.075 mmol, 24 mg), LiCl (0.050 mmol, 2.1 mg), diethyl bromomalonate **3a** (0.50 mmol, 84 µL) hydrocinnamaldehyde **2a** (1.0 mmol, 132 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMSO (0.5 M, 1 mL) afforded the α-alkylation product **4a** after 2 h. Purification by flash chromatography using cyclohexane/EtOAc (95/5) as the eluent led to 131 mg (89% yield, 82% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 218 nm using a Chiralcel® column OJ (250 mm × 4.6 mm, 10 µm) with an isocratic elution (hexane/isopropanol : 85/15, flow = 0.7 mL.min^{-1}) ; t_R((*S*)-isomer) = 16.9 min, t_R((*R*)-isomer) = 19.9 min. The analytical data (^{1}H NMR and ^{13}C NMR) are in accordance with those of the literature.

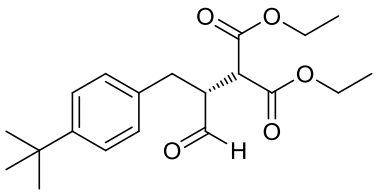
Rf (cyclohexane/EtOAc : 85/15) = 0.40

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H, C**H**O), 7.25-7.10 (m, 5H, Ar**H**), 4.16-4.14 (m, 4H, 2 × $CO_2C\mathbf{H_2}CH_3$), 3.60 (d, *J* = 7.0 Hz, 1H, C**H**$(CO_2Et)_2$), 3.32-3.28 (m, 1H, HCOC**H**), 3.05 (dd, *J* = 7.5, 14.2 Hz, 1H, C$\mathbf{H_2}$Ph), 2.75 (dd, *J* = 7.3, 14.2 Hz, 1H, C$\mathbf{H_2}$Ph), 1.19 (t, *J* = 7.1 Hz, 6H, 2 × $CO_2CH_2C\mathbf{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2 (**C**HO), 168.0 (2 × **C**$O_2CH_2CH_3$), 137.5 (**Ar**H), 129.2 (**Ar**H), 128.9 (**Ar**H), 127.0 (**Ar**H), 62.0 (2 × $CO_2\mathbf{C}H_2CH_3$), 51.9 (HCO**C**H), 51.5 (**C**H$(CO_2Et)_2$), 33.2 (**C**H_2Ph), 14.1 (2 × $CO_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 5.72 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 1.94 min

EIMS *m/z* 293 ([M+1]$^+$, 1%), 264 (8), 247 (2), 217 (2), 201 (29),173 (39), 160 (100), 145 (41), 133 (90), 115 (49), 91 (65)



(*R*)-diethyl 2-(1-(4-(*tert*-butyl)phenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: $C_{20}H_{28}O_5$
Molecular Weight: 348.43

According to the general procedure described above, Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.075 mmol, 24 mg), LiCl (0.050 mmol, 2.1 mg), diethyl bromomalonate **3a** (0.50 mmol, 84 µL) *para-tert*-butylhydrocinnamaldehyde **2b** (1.0 mmol, 101 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMSO (0.5 M, 1 mL) afforded the α-alkylation product **4b** after 3 h. Purification by flash chromatography using cyclohexane/EtOAc (95/5 to 9/1) as the eluent led to 89 mg (51% yield, 83% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 218 nm using a Chiralpak® column IC (250 mm × 4.6 mm, 5 µm) with an isocratic elution (hexane/isopropanol : 70/30, flow = 0.8 mL.min^{-1}) ; t_R((*S*)-isomer) = 20.7 min, t_R((*R*)-isomer) = 22.9 min.

Rf (cyclohexane/EtOAc : 85/15) = 0.51

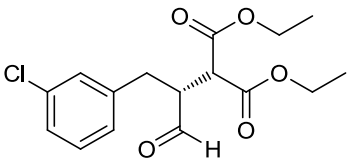
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H, C**H**O), 7.25 (d, *J* = 8.2 Hz, 2H, *m*-Ar**H**) , 7.04 (d, *J* = 8.2 Hz, 2H, *ortho*-Ar**H**), 4.20-4.08 (m, 4H, 2 × $CO_2C\mathbf{H_2}CH_3$), 3.62 (d, *J* = 7.2 Hz, 1H, C**H**$(CO_2Et)_2$), 3.36-3.25 (m, 1H, HCOC**H**), 3.02 (dd, *J* = 14.3, 7.4 Hz, 1H, C$\mathbf{H_2}$Ph), 2.73 (dd, *J* = 14.3, 7.3 Hz, 1H, C$\mathbf{H_2}$Ph), 1.23 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 6H, 2 × $CO_2CH_2C\mathbf{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5 (**C**HO), 168.2 and 168.1 (2 × **C**$O_2CH_2CH_3$), 149.9 (*para*-**Ar**H), 134.3 (*ipso*-**Ar**H), 128.9 (*ortho*-**Ar**H), 125.8 (*m*-**Ar**H), 62.1 (2 × $CO_2\mathbf{C}H_2CH_3$), 52.0 (HCO**C**H), 51.6 (**C**H$(CO_2Et)_2$), 34.6 (**C**$(CH_3)_3$), 32.8(HCOCH**C**H_2), 31.5 (C(**C**$H_3)_3$), 14.3 and 14.2 (2 × $CO_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 6.83 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 3.62 min

EIMS *m/z* 333 ([M-15]$^+$, 1%), 320 (3), 304 (1), 257 (6), 247 (5), 231 (6), 213 (3), 201 (8), 189 (100), 173 (39), 160 (45), 145 (26), 131 (26), 115 (36), 105 (7), 91 (10), 57 (30)

HRMS (EI+) exact mass calculated for [M+Na]$^+$ ($C_{16}H_{20}O_5Na$) requires m/z 371.18286, found m/z 371.18336



(*R*)-diethyl 2-(1-(3-chlorophenyl)-3-oxopropan-2-yl)malonate

Chemical Formula: $C_{16}H_{19}ClO_5$

Molecular Weight: 326.77

According to the general procedure Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.10 mmol, 32 mg), diethyl bromomalonate **3a** (0.50 mmol, 84 µL), *m*-chlorohydrocinnamaldehyde **2c** (1.0 mmol, 148 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMF (0.5 M, 1 mL) afforded the α-alkylation product **4c** after 2 h 30. Purification by flash chromatography using cyclohexane/EtOAc (95/5) as the eluent led to 147 mg (90% yield, 82% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 220 nm using a Chiralcel® column OD-H_3 (250 mm × 4.6 mm, 5 µm) with an isocratic elution (hexane/isopropanol : 94/6, flow = 0.6 mL.min^{-1}) ; t_R((*S*)-isomer) = 15.6 min, t_R((*R*)-isomer) = 16.9 min.

Rf (cyclohexane/EtOAc : 85/15) = 0.24

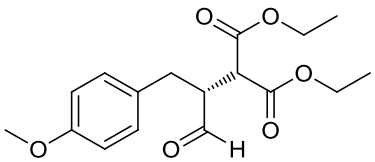
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H, C**H**O), 7.26-7.14 (m, 3H, Ar**H**), 7.26-7.09 (m, 1H, Ar**H**), 4.23 (q, 2H, *J* = 7.1 Hz, $CO_2C\mathbf{H_2}CH_3$), 4.22 (q, 2H, *J* = 7.1 Hz, $CO_2C\mathbf{H_2}CH_3$), 3.68 (d, *J* = 6.8 Hz, 1H, C**H**$(CO_2Et)_2$), 3.37 (td, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, HCOC**H**), 3.14 (dd, *J* = 7.2, 14.2 Hz, 1H, C$\mathbf{H_2}$Ph), 2.82 (dd, *J* = 7.2, 14.2 Hz, 1H, C$\mathbf{H_2}$Ph), 1.30 (t, *J* = 7.1 Hz, 6H, 2 × $CO_2CH_2C\mathbf{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5 (**C**HO), 167.9 and 167.8 (2 × **C**$O_2CH_2CH_3$), 139.7 (*ipso*-**Ar**CH_2), 134.5 (*m*-**Ar**Cl), 130.1 (*m*-**Ar**H), 129.3 (*ortho*-**Ar**H(**C**Cl)), 127.4 (*para*-**Ar**H), 127.2 (*ortho*-**Ar**H), 62.1 (2 × $CO_2\mathbf{C}H_2CH_3$), 51.6 (HCO**C**H), 51.3 (**C**H$(CO_2Et)_2$), 32.7 (**C**H_2Ph), 14.0 (2 × $CO_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 5.79 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 2.87 min

EIMS *m/z* 298 ([M-28]$^+$, 5%), 281 (1), 251 (1), 235 (17), 225 (13), 179 (22), 173 (35), 160 (100), 144 (23), 133 (32), 125 (44), 115 (46), 99 (14), 89 (15)

HRMS (EI+) exact mass calculated for [M+Na]$^+$ ($C_{16}H_{20}O_5Na$) requires m/z 349.08132, found m/z 349.08172



(*R*)-diethyl 2-(1-(4-methoxyphenyl)-3-oxopropan-2-yl)malonate

Chemical Formula: $C_{17}H_{22}O_6$

Molecular Weight: 322.35

According to the general procedure Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.10 mmol, 32 mg), diethyl bromomalonate **3a** (0.50 mmol, 84µL), *para*-methoxyhydrocinnamaldehyde **2d** (1.0 mmol, 160 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMF (0.5 M, 1 mL) afforded the α-alkylation product **4d** after 1 h 30. Purification by flash chromatography using cyclohexane/EtOAc (95/5) as the eluent led to 153 mg (94% yield, 80% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 226 nm using a Chiralcel® column OJ (250 mm × 4.6 mm, 10 µm) with an isocratic elution (hexane/isopropanol : 65/35, flow = 0.7 mL.min^{-1}) ; t_R((*S*)-isomer) = 14.7 min, t_R((*R*)-isomer) = 18.9 min.

Rf (cyclohexane/EtOAc : 85/15) = 0.32

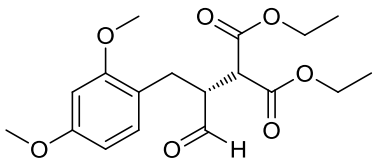
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, *J* = 0.7 Hz, 1H, C**H**O), 7.11-7.07 (m, 2H, Ar**H**), 6.85-6.81 (m, 1H, Ar**H**), 4.22-4.16 (m, 4H, 2 × $CO_2C\mathbf{H_2}CH_3$), 3.77 (s, 3H, OC$\mathbf{H}_3$), 3.66 (d, *J* = 7.9 Hz, 1H, C**H**$(CO_2Et)_2$), 3.38-3.31 (m, 1H, HCOC**H**), 3.04 (dd, *J* = 7.5, 14.3 Hz, 1H, C$\mathbf{H_2}$Ph), 2.78 (dd, *J* = 7.5, 14.3 Hz, 1H, C$\mathbf{H_2}$Ph), 1.28 (m, 6H, 2 × $CO_2CH_2C\mathbf{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4 (**C**HO), 168.2 and 168.0 (2 × **C**$O_2CH_2CH_3$), 158.6 (*para*-**Ar**OCH_3), 130.2 (*ipso*-**Ar**CH_2), 129.3 (*m*-**Ar**H), 114.2 (*ortho*-**Ar**H), 62.0 (2 × $CO_2\mathbf{C}H_2CH_3$), 55.3 (O**C**H_3), 52.1 (HCO**C**H), 51.5 (**C**H$(CO_2Et)_2$), 33.4 (**C**H_2Ph), 14.1 (2 × $CO_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 6.04 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 3.14 min

EIMS *m/z* 322 ([M]$^+$, 3%), 278 (2), 247 (1), 231 (6), 175 (5), 163 (92), 147 (17), 131 (20), 121 (100), 108 (14), 91 (8), 78 (8)

HRMS (EI+) exact mass calculated for [M+Na]$^+$ ($C_{16}H_{20}O_5Na$) requires m/z 345.13086, found m/z 345.13112



(*R*)-diethyl 2-(1-(2,4-dimethoxyphenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: $C_{18}H_{24}O_7$
Molecular Weight: 352.38

According to the general procedure described above, Rose Bengal (0.00125 mmol, 1.25 mg), the imidazolidinone catalyst **1** (0.050 mmol, 16 mg), diethyl bromomalonate **3a** (0.25 mmol, 42 µL) *ortho,para*-dimethoxyhydrocinnamaldehyde **2e** (0.5 mmol, 92 µL) and 2,6-lutidine (0.5 mmol, 57 µL) in DMF (0.5 M, 0.5 mL) afforded the α-alkylation product **4e** after 4 h. Purification by flash chromatography using cyclohexane/EtOAc (95/5 to 9/1) as the eluent led to 45 mg (51% yield, 83% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 218 nm using a Chiralcel® column OJ (250 mm × 4.6 mm, 10 µm) with an isocratic elution (hexane/ethanol : 85/15, flow = 0.5 mL.min^{-1}) ; t_R((*S*)-isomer) = 24.8 min, t_R((*R*)-isomer) = 27.4 min.

Rf (cyclohexane/EtOAc : 85/15) = 0.27

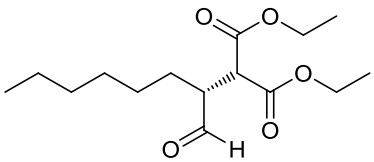
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H, C**H**O), 6.97 (d, *J* = 8.1 Hz, 1H, *ortho*-Ar**H**) , 6.9-7.1 (m, 2H, *m*,-Ar**H**), 4.33-4.02 (m, 4H, 2 × $CO_2C\mathbf{H_2}CH_3$), 3.77 (s, 1H, OC$\mathbf{H}_3$), 3.76 (s, 1H, OC$\mathbf{H}_3$), 3.59 (d, *J* = 7.5 Hz, 1H, C**H**$(CO_2Et)_2$), 3.43-3.34 (m, 1H, HCOC**H**), 3.05 (dd, *J* = 14.0, 7.3 Hz, 1H, C$\mathbf{H_2}$Ph), 2.80 (dd, *J* = 14.0, 6.9 Hz, 1H, C$\mathbf{H_2}$Ph), 1.25 (t, 3H, $CO_2CH_2C\mathbf{H_3}$), 1.24 (t, 3H, $CO_2CH_2C\mathbf{H_3}$)

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7 (**C**HO), 168.3 and 168.2 (2 × **C**$O_2CH_2CH_3$), 160.19 (*ortho*-**Ar**OCH_3) and 158.40 (*para*-**Ar**OCH_3), 131.5 (*ortho*-**Ar**H), 117.8 (*ipso*-**Ar**CH_2), 104.2 (*m*-**Ar**H), 98.6 (*m*-**Ar**H), 61.8 (2 × $CO_2\mathbf{C}H_2CH_3$), 55.4 and 55.2 (2 × O**C**H_3), 51.6 (HCO**C**H), 50.7 (**C**H$(CO_2Et)_2$), 27.6 (HCOCH**C**H_2), 14.1 (2 × $CO_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 7.18 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 4.19 min

EIMS *m/z* 352 ([M]$^+$, 3%), 221 (3), 205 (2), 192 (47), 177 (7), 161 (21), 151 (100), 138 (26), 121 (19), 103 (1), 91 (7)

HRMS (EI+) exact mass calculated for [M+Na]$^+$ ($C_{16}H_{20}O_5Na$) requires m/z 375.14142, found m/z 375.14175



(*R*)-diethyl 2-(1-oxooctan-2-yl)malonate
Chemical Formula: $C_{15}H_{26}O_5$
Molecular Weight: 286.36

According to the general procedure Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.075 mmol, 24 mg), diethyl bromomalonate **3a** (0.50 mmol, 84 µL), octanal **2f** (1.0 mmol, 156 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMSO (0.5 M, 1mL) afforded the α-alkylation **4f** product after 5 h. Purification by flash chromatography using cyclohexane/EtOAc (95/5) as the eluent led to 126 mg (88% yield, 80% ee) of the title compound as a colorless oil. The *ee* was determined by the measure of the optical rotation $[\alpha]_D^{23}$ = +50.4 (c = 0.94, CH_2Cl_2) compared to the literature value ($[\alpha]_D^{23}$ = +63.0).[S5] The analytical data (^{1}H NMR and ^{13}C NMR) are in accordance with those of the literature.

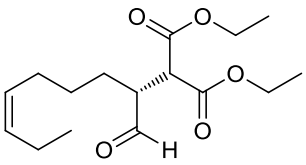
Rf (cyclohexane/EtOAc : 85/15) = 0.52

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 1.1 Hz, 1H, C**H**O), 4.25-4.15 (m, 4H, 2 × $CO_2C\mathbf{H_2}CH_3$), 3.72 (d, *J* = 8.6 Hz, 1H, C**H**$(CO_2Et)_2$), 3.10-3.07 (m, 1H, HCOC**H**), 1.60-1.56 (m, 1H, HCOCHC$\mathbf{H}_2$), 1.71-1.64 (m, 1H, HCOCHC$\mathbf{H}_2$), 1.32-1.18 (m, 14H, $HCOCHCH_2(C\mathbf{H}_2)_4$, 2 × $CO_2CH_2C\mathbf{H}_3$), 0.87-0.84 (m, 3H, $CH_2CH_2C\mathbf{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7 (**C**HO), 168.3 and 168.2 (2 × $\mathbf{C}O_2CH_2CH_3$), 62.0 and 61.9 (2 × $CO_2\mathbf{C}H_2CH_3$), 51.9 (**C**H$(CO_2Et)_2$), 50.4 (HCO**C**H), 31.6, 29.4, 26.6 and 22.6 ($HCOCHCH_2(\mathbf{C}H_2)4$), 27.2 (HCOCH**C**$H_2$), 14.1 (2 × $CO_2CH_2\mathbf{C}H_3$), 14.1 ($CH_2CH_2\mathbf{C}H_3$)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 4.73 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 1.48 min

EIMS *m/z* 258 ($[M-28]^+$, 1%), 241 (11), 202 (3), 195 (17), 185 (34), 173 (100), 166 (19), 157 (32), 141 (11), 127 (23), 99 (17), 73 (29), 55 (34)



(*R*,*Z*)-diethyl 2-(1-oxonon-6-en-2-yl)malonate
Chemical Formula: $C_{16}H_{26}O_5$
Molecular Weight: 298.37

According to the general procedure Rose Bengal (0.0025 mmol, 2.5 mg), the imidazolidinone catalyst **1** (0.10 mmol, 32 mg), diethyl bromomalonate **3a** (0.50 mmol, 84 µL), (*Z*)-non-6-enal **2g** (1.0 mmol, 165 µL) and 2,6-lutidine (1.0 mmol, 115 µL) in DMF (0.5 M, 1mL) afforded the α-alkylation product **4g** after 22 h. Purification by flash chromatography using cyclohexane/EtOAc (95/5 to 80/20) as the eluent led to 84 mg (56% yield, 85% ee) of the title compound as a colorless oil. The *ee* was determined by chiral HPLC analyses at 215 nm using a Chiralpak® column IC (250 mm × 4.6 mm, 5 µm) with an isocratic elution (hexane/isopropanol : 80/20, flow = 0.6 mL.min^{-1}) ; t_R((*S*)-isomer) = 14.8 min, t_R((*R*)-isomer) = 16.5 min. The analytical data (^{1}H NMR and ^{13}C NMR) are in accordance with those of the literature.

Rf (cyclohexane/EtOAc : 85/15) = 0.47

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 1.1 Hz, 1H, C**H**O), 5.41-5.30 (m, 1H, CH_2C**H**$CHCH_2CH_3$), 5.28-5.18 (m, 1H, CH_2CHC**H**CH_2CH_3), 4.24-4.13 (m, 4H, 2 × CO_2C**H**$_2CH_3$), 3.71 (d, *J* = 8.6 Hz, 1H, C**H**$(CO_2Et)_2$), 3.13-3.03 (m, 1H, HCOC**H**), 2.07 – 1.94 (m, 4H, C**H**$_2CHCHC$**H**$_2$), 1.76 – 1.51 (m, 2H, $HCOCHC$**H**$_2$), 1.51 – 1.29 (m, 2H, $HCOCHCH_2C$**H**$_2$), 1.29-1.19 (m, 6H, 2 × CO_2CH_2**C**H_3), 0.92 (t, *J* = 7.5 Hz, 3H, $CHCH_2C$**H**$_3$)

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5 (**C**HO), 168.2 and 168.1 (2 × **C**$O_2CH_2CH_3$), 132.6 (CH_2**C**$HCHCH_2CH_3$), 127.9 (CH_2CH**C**HCH_2CH_3), 61.9 (2 × CO_2**C**H_2CH_3), 51.8 (**C**H$(CO_2Et)_2$, 50.22 (HCO**C**H), 27.0 (**C**$H_2CHCHCH_2CH_3$), 26.6 and 26.6 (**C**H_2**C**H_2CH_2CHCH), 20.6 ($CHCH$**C**H_2CH_3), 14.3 ($CHCHCH_2$**C**H_3), 14.1 and 14.0 (2 × CO_2CH_2**C**H_3)

GC (100 °C 1 min, 25 °C/min, 300 °C) t_R (α-alkylation product) = 5.03 min, t_R (starting bromide) = 2.41 min, t_R (starting aldehyde) = 2.06 min

EIMS *m/z* 270 ([M-28]$^+$, 1%), 269 (2), 223 (8), 206 (41), 177 (37), 161 (48), 150 (13), 133 (29), 120 (100), 109 (30), 95 (15), 81 (36), 67 (31), 55 (31)

3. The photosensitizers properties

1. Absorbance in the visible domain

The UV/VIS spectra of the sensitizers were recorded in DMF. Solutions were prepared at 10^{-5} M.

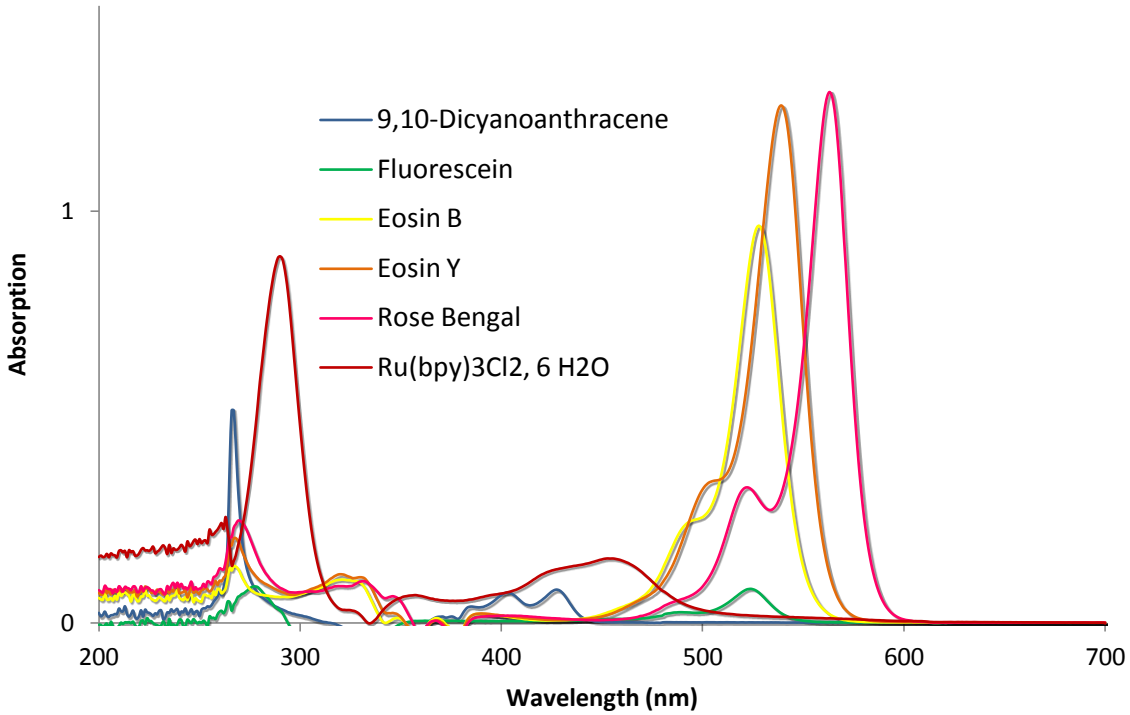


Figure S1. Absorption spectra of the main photosensitizers used for the screening studies

Table S1. Spectral properties of the main photosensitizers in the visible domain (values in DMF at 10^{-5} M)

Nature of Sensitizer	Sensitizers	λ_{max} (nm)	ε (L.mol^{-1}.cm^{-1})
Aromatic polycycles	Anthracene	381 (375[S6])*	10000
	9,10-Dicyanoanthracene (DCA)	434 (433[S6])*	11000
	Naphtalene	315 (311[S6])*	4000
	1,4-Dicyanonaphtalene (DCN)	367 (359[S6])*	8000
Xanthene derivatives	Fluoresceine	524 (450[S9])*	7000
	Eosin B	530 (528[S11])*	95000
	Eosin Y	542 (539[S9])*	121000
	Rose Bengal	563 (549[S12])*	126000
Metal complex	$Ru(bpy)_3Cl_2$	455 (452[S6])*	15000

( )* λ_{max} literature values reported in CH_3CN

2. Redox properties of the sensitizers

The suggested "light-part" mechanism is comparable to the well-known reductive quenching cycle of a photosensitizer[S7] also proposed by MacMillan[S8] and Zeitler[S9] where :

- a strong oxidant S* enables the one electron oxidation of a sacrificial enamine (to initiate the photoredox catalysis) and the oxidation of the α-amino radical species.
- a strong reductant $S^{\bullet-}$ (the semi-reduced form of the sensitizer) enables the one electron reduction of the alkyle halide into radical.

Potential values were picked up from several publication and calculated if necessary with the triplet excited states energies values following the relation : $E_{(S^*/S^{\bullet-})} = E_{(S/S^{\bullet-})} + E_{S^*}$

Table S2. Redox properties of the sensitizers with the intersystem conversion quantum yield

Sensitizers	$E^t(S^*/S^{\bullet-})$	$E^0(S/S^{\bullet-})$	Φ_{ISC}
DCA	0.92[S6]	-0.89[S6]	
Anthracene	-0.08[S6]	-1.93[S6]	0.72[S6]
DCN	0.35[S6]	-2.29[S6]	
Naphtalene	1.13[S6]	-1.28[S6]	0.80,[S6] 0.71[S6]
Fluoresceine	0.70[S10]	-1.22[S10]	0.021[S10]
Eosin B	0.78[S11]	-1.27[S11]	
Eosin Y	0.79[S10]	-1.06[S10]	0.64[S10]
Rose Bengal	0.81[S10] ; 0.88[S11]	-0.98[S10] ; -1.06[S11]	0,98[S11]
$Ru(bpy)_3Cl_2$	0.77[S6]	-1.35[S6]	

According to the excellent quantum yield Φ_{ISC} of Rose Bengal, it is evident that the excited state implied in the mechanism is the more stable triplet state.

We also speculated that in line with the transition spin laws (which could be extended to electron transfers) a back electron transfer could be thermodynamically favorable for singlet excited species. Therefore, a more stable triplet state (high intersystem crossing coupling) will promote the mechanism described avoiding the back electron transfer.

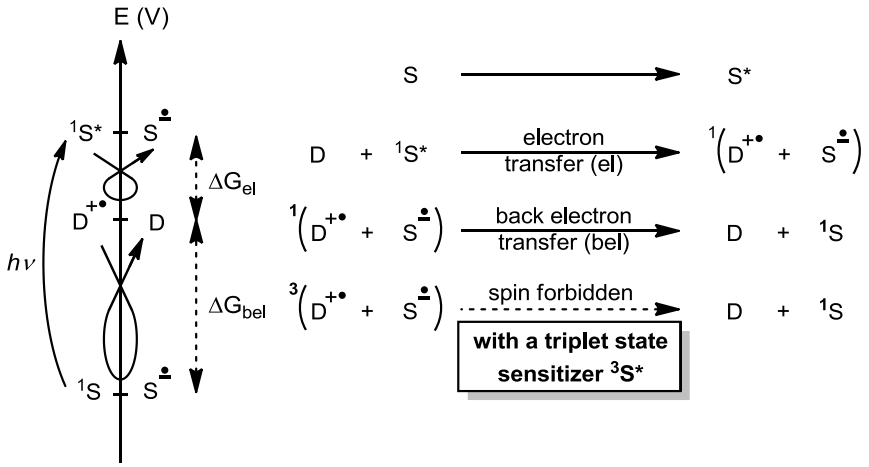


Figure S2. Effect of a triplet excited state sensitizer on a back electron transfer

4. Emission quenching experiments

Emission intensities were recorded using an F2500 Hitachi fluorescence spectrophotometer equipped with a monochromatic light monitoring with ratio calculation. All Rose Bengal solutions were excited at 563 nm and the emission intensity was observed at 578 nm. Following a general procedure, the appropriate amount of quencher was added to a 2.54 mM (mild concentration) solution of Rose Bengal prepared in DMF in a 1.0 cm quartz cuvette. The resulted mixture was diluted 2000 times to get an absorbance of RB about 0.1 at 563 nm. After degassing the sample under argon bubbling for 2 min, the fluorescence spectrum was recorded to get the emission intensities I^0 and I respectively in the absence and in the presence of quencher.

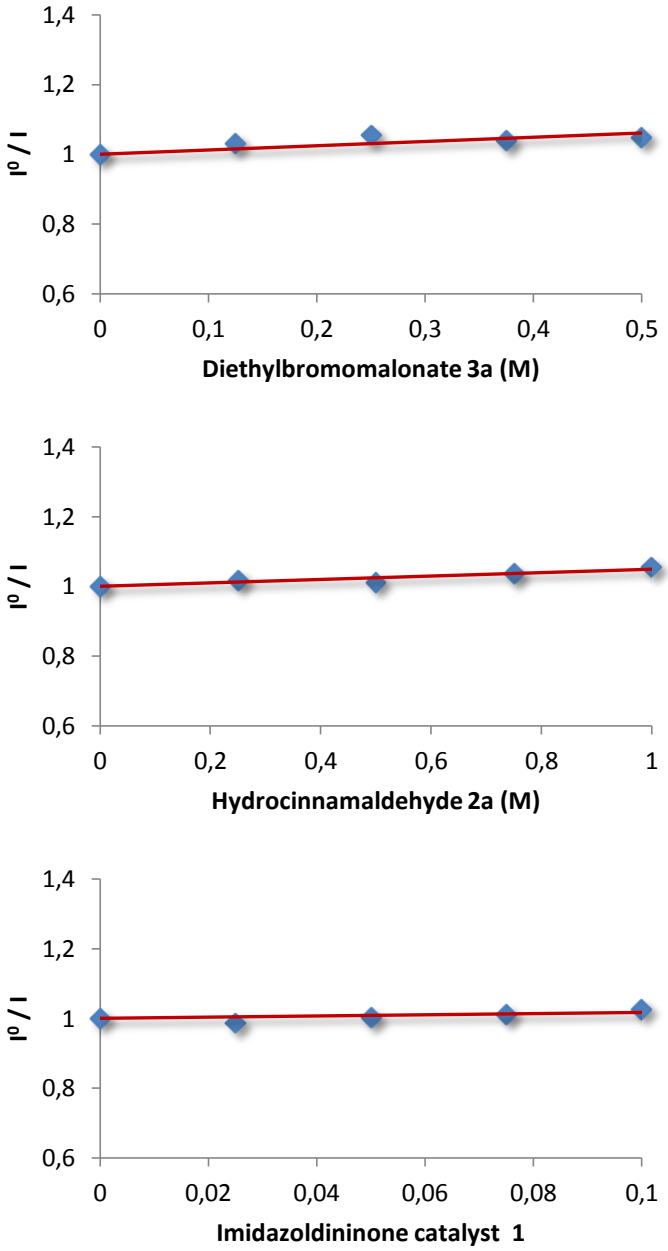


Figure S3: Rose Bengal emission quenching by the bromo compound 3a, the aldehyde 2a and catalyst 1

5. References

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S12 T. Shimidzu, T. Iyoda, Y. Koide, *J. Am. Chem. Soc.* **1985**, *107*, 35-41.

6. NMR Spectra and chiral HPLC analysis

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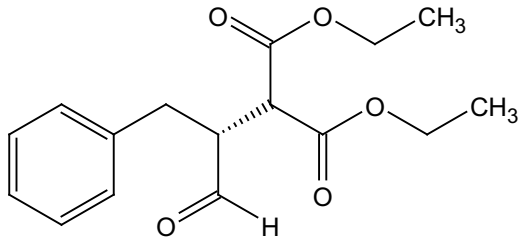
2 Spectrometer Frequency	400.13
3 Nucleus	1H



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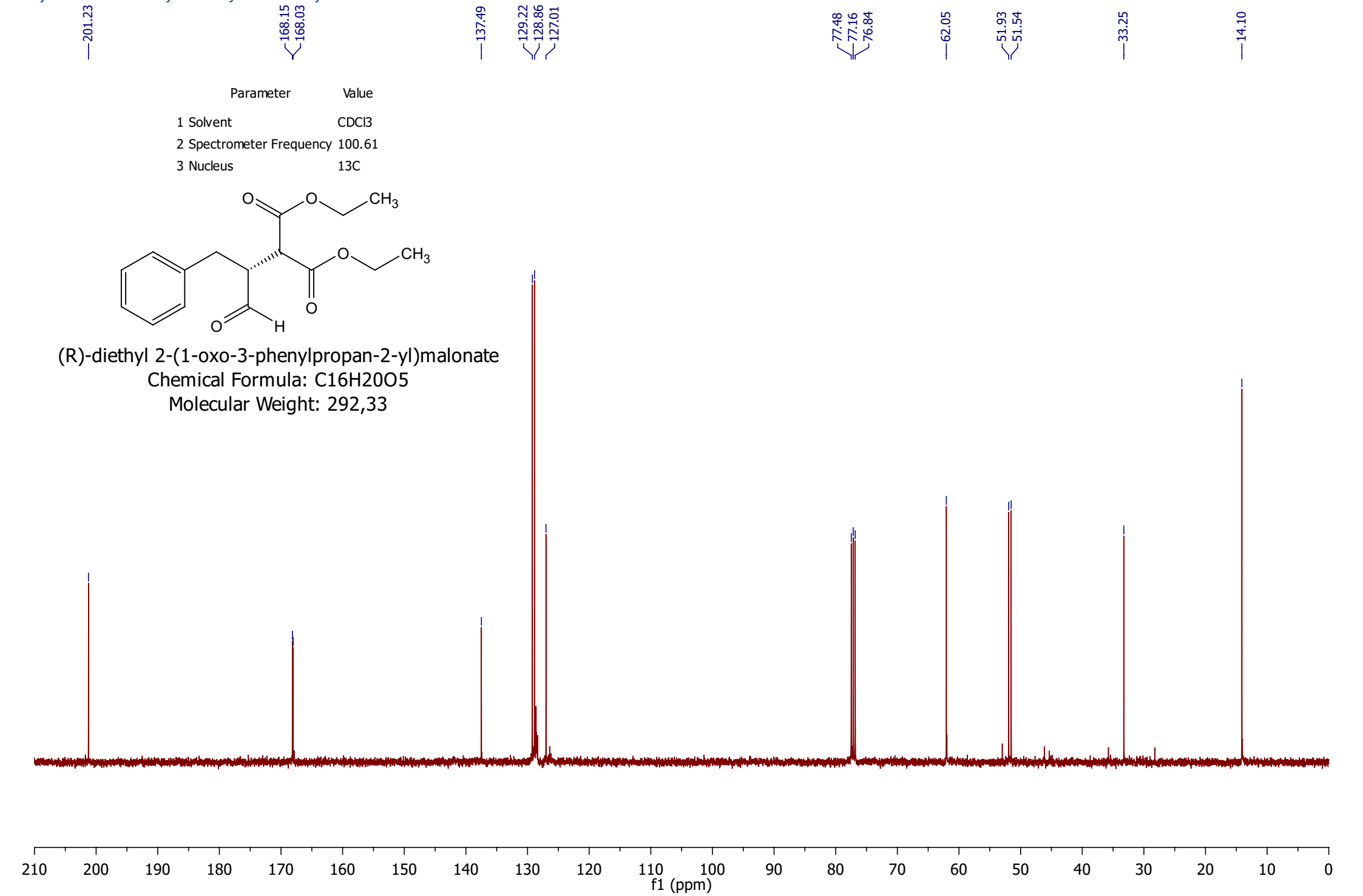
Chemical Formula: C16H20O5
Molecular Weight: 292,33



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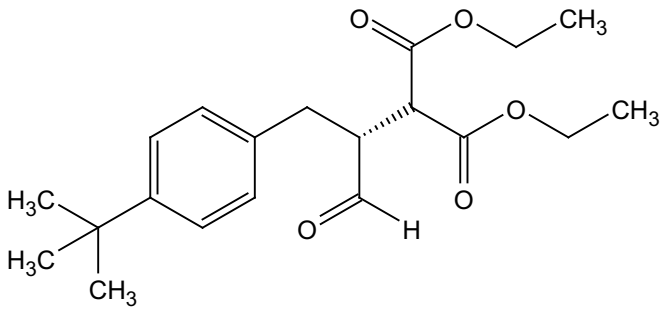

(R)-diethyl 2-(1-(4-(tert-butyl)phenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: C20H28O5
Molecular Weight: 348,43

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134.20
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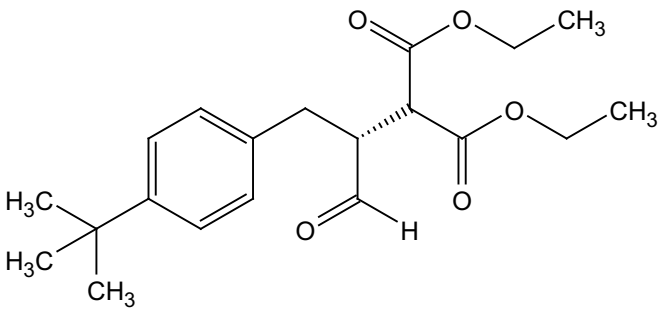

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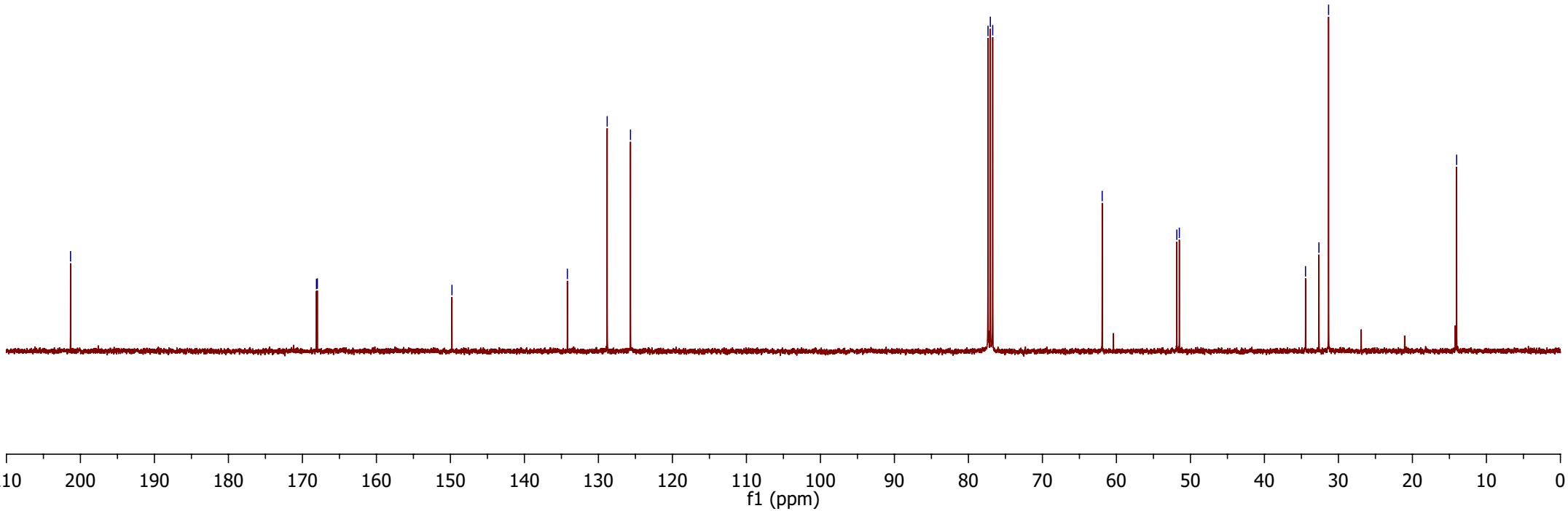

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Parameter	Value
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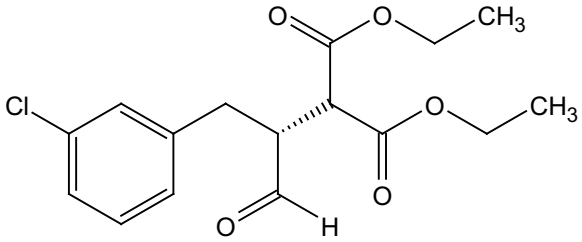
2 Spectrometer Frequency	400.13
3 Nucleus	1H



(R)-diethyl 2-(1-(3-chlorophenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: C16H19ClO5
Molecular Weight: 326,77

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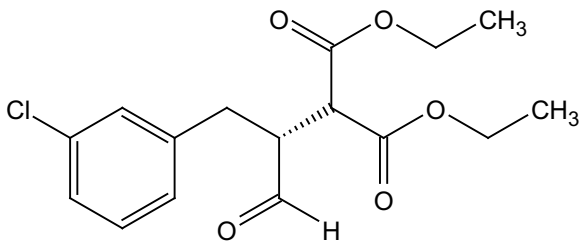

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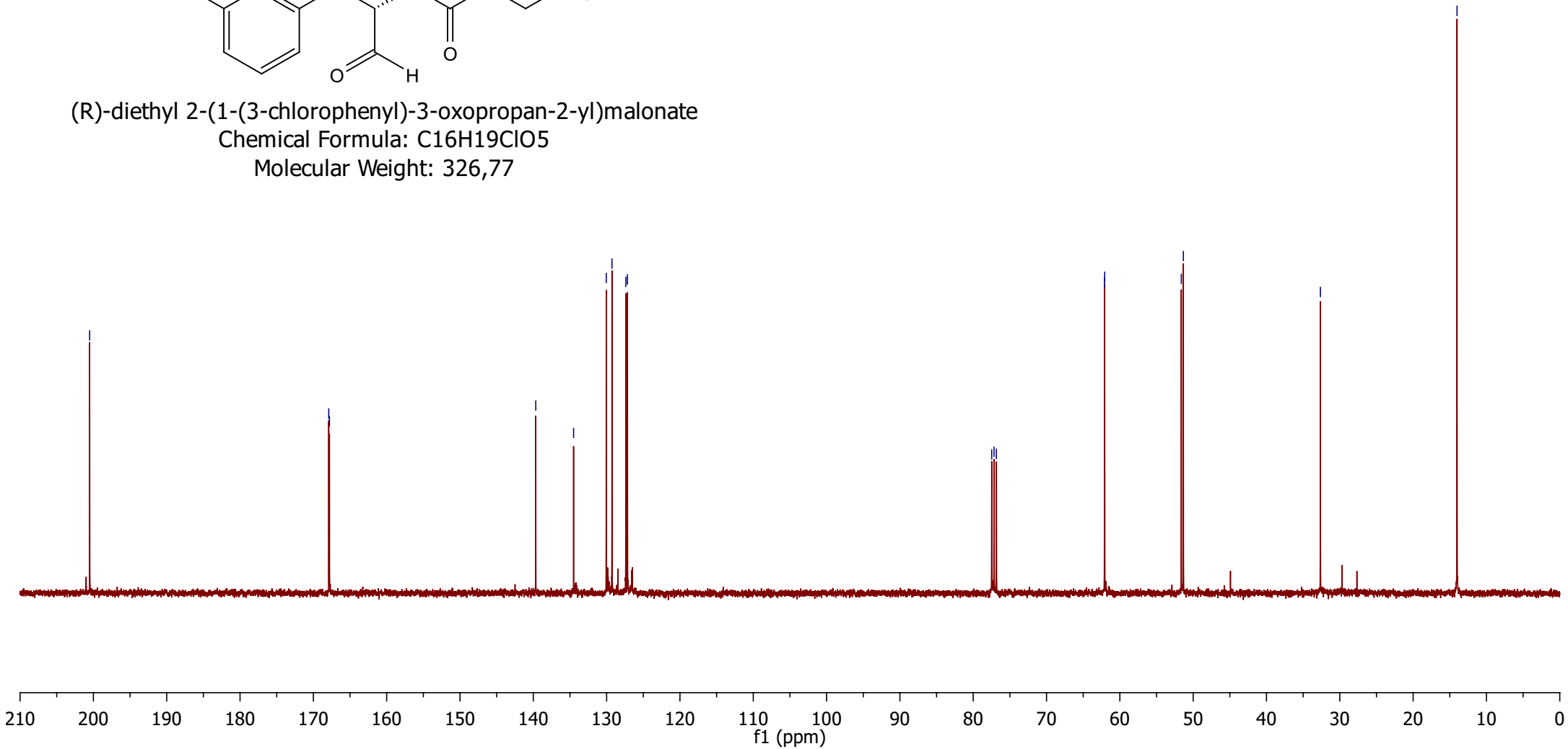

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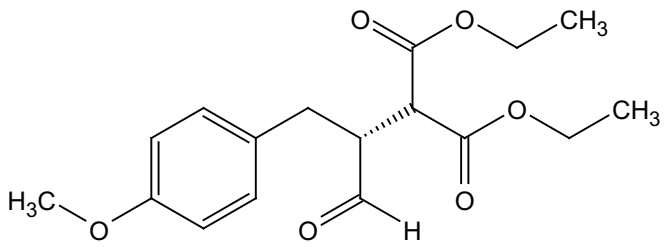

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Molecular Weight: 322,35

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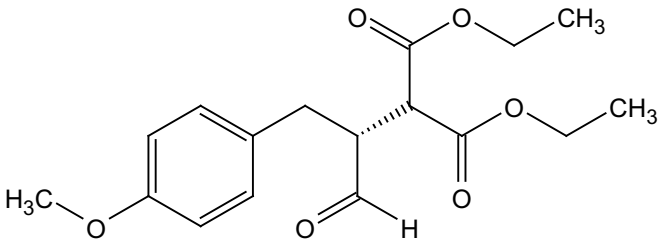

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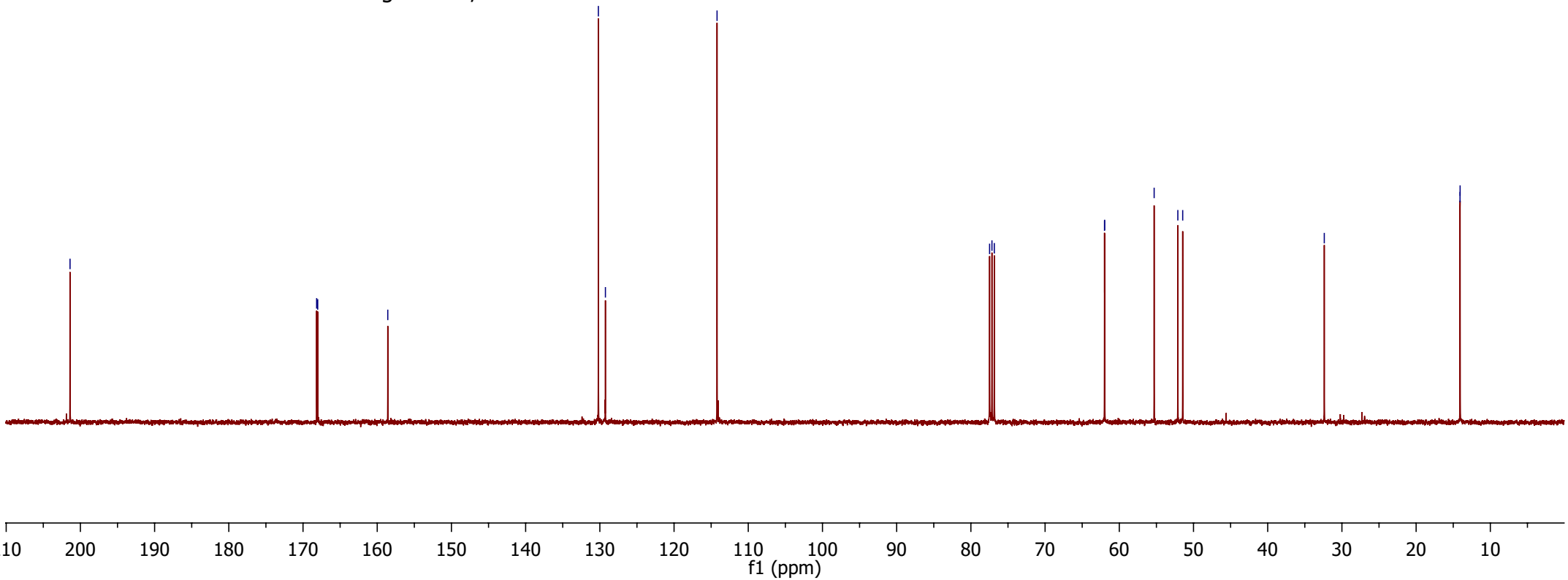

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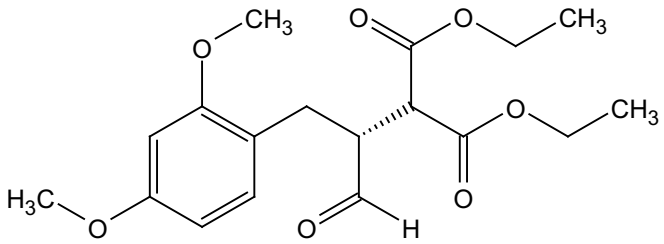

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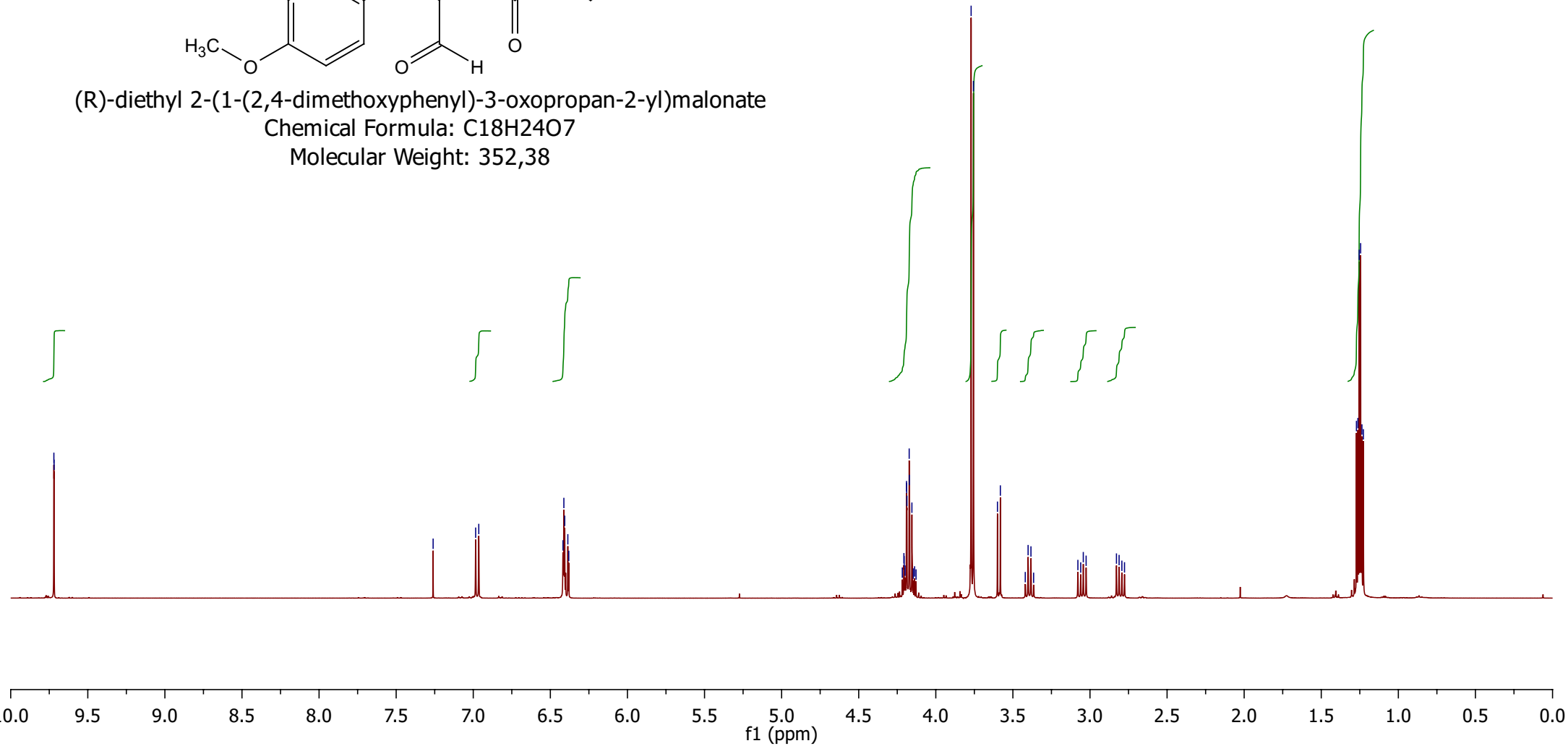
Molecular Weight: 352,38



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Parameter	Value
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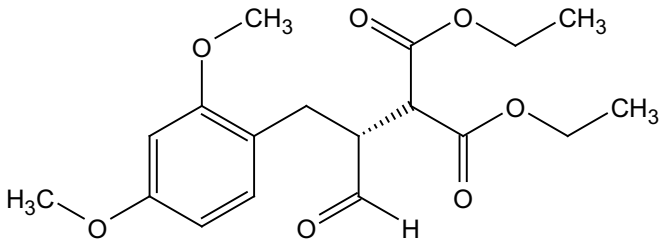

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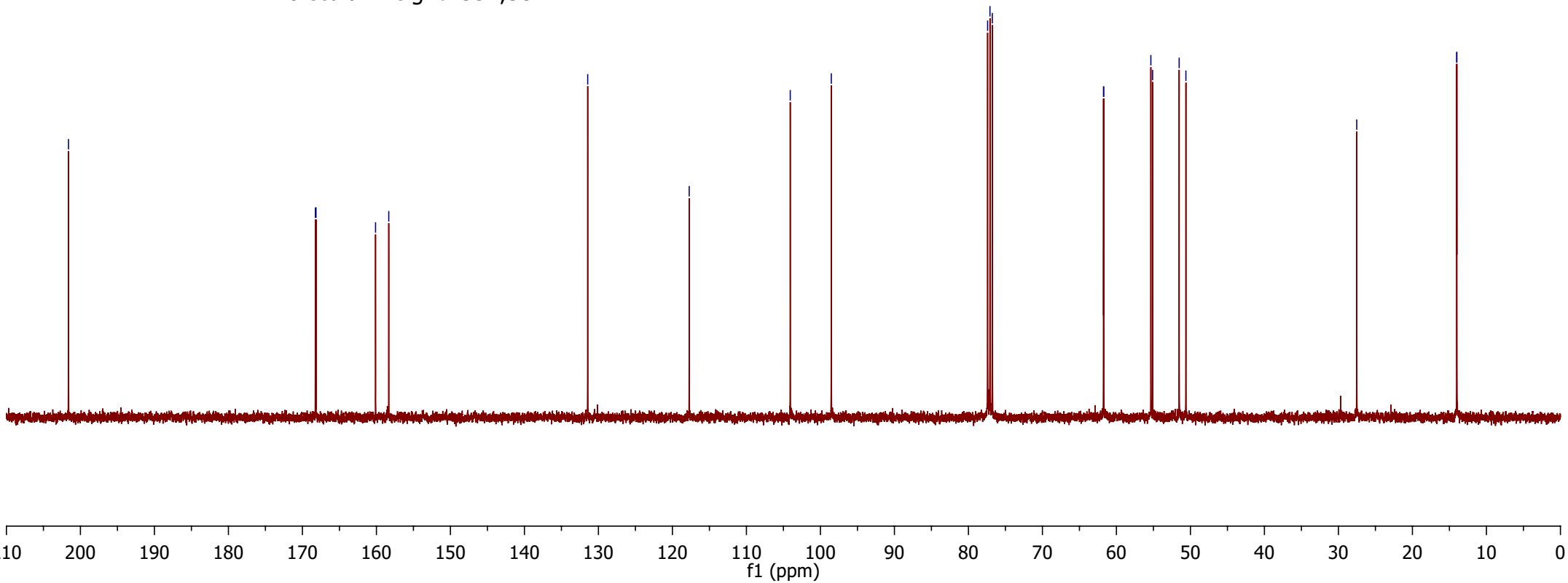

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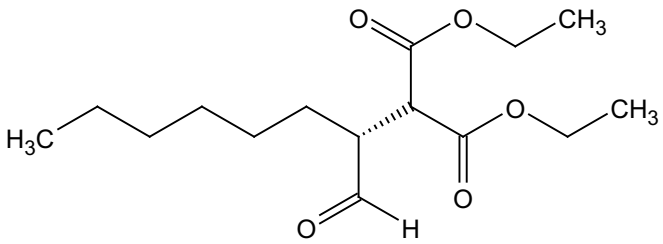

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Chemical Formula: C15H26O5
Molecular Weight: 286,36

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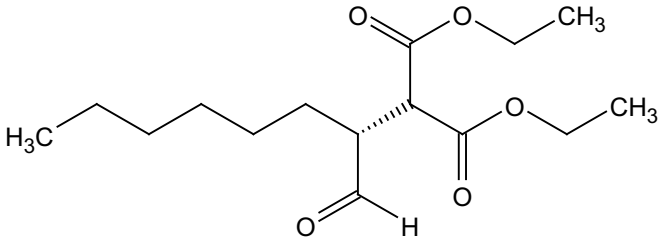

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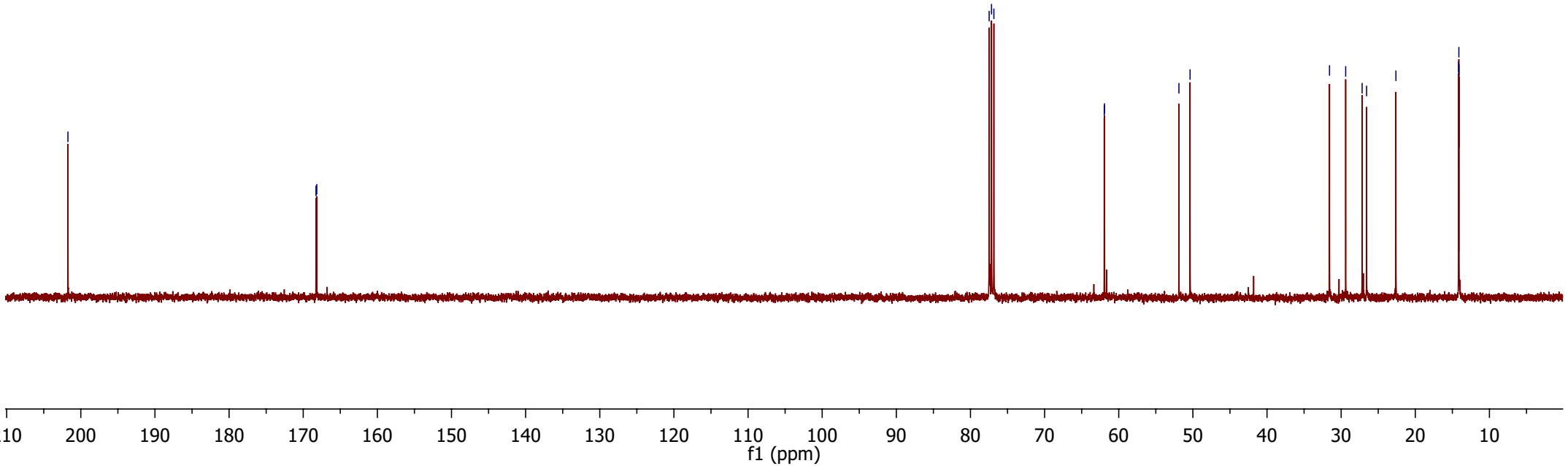

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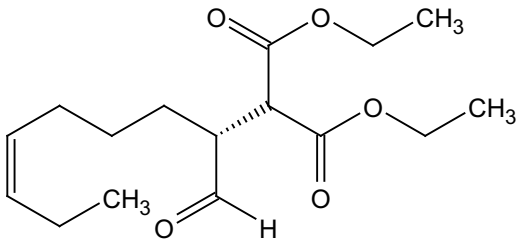

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Molecular Weight: 298,37

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Parameter	Value
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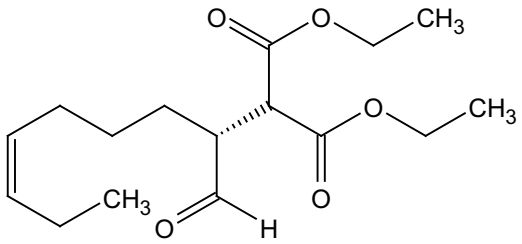
2 Spectrometer Frequency	100.61
3 Nucleus	13C



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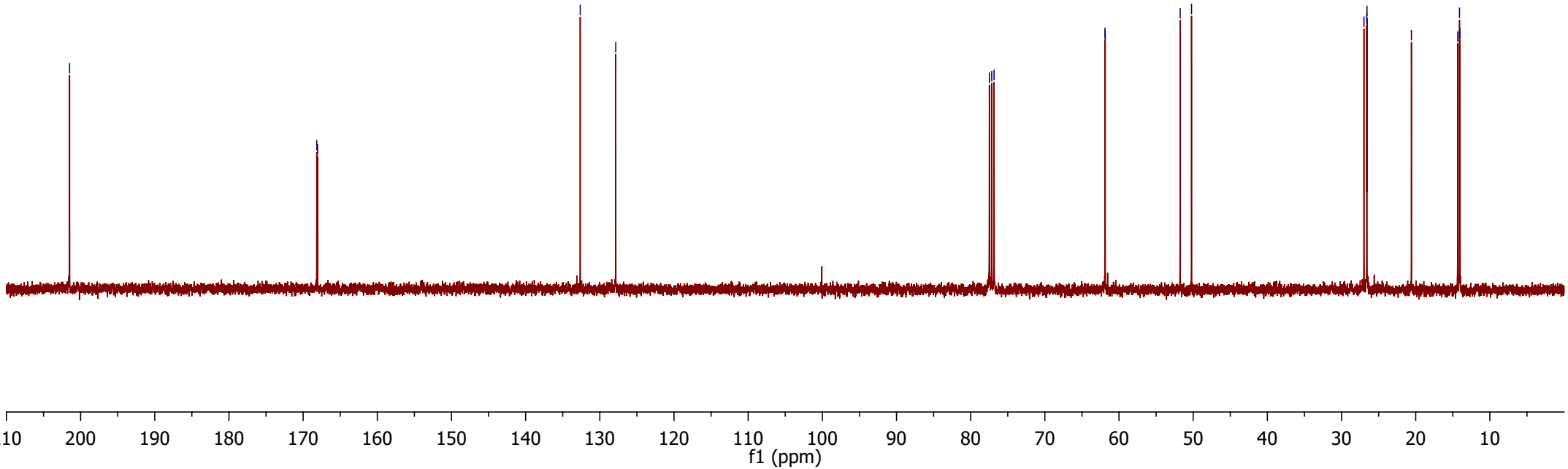
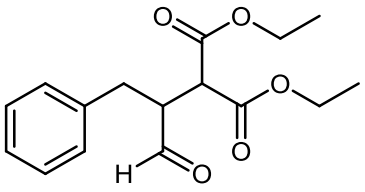
Chemical Formula: C16H26O5
Molecular Weight: 298,37





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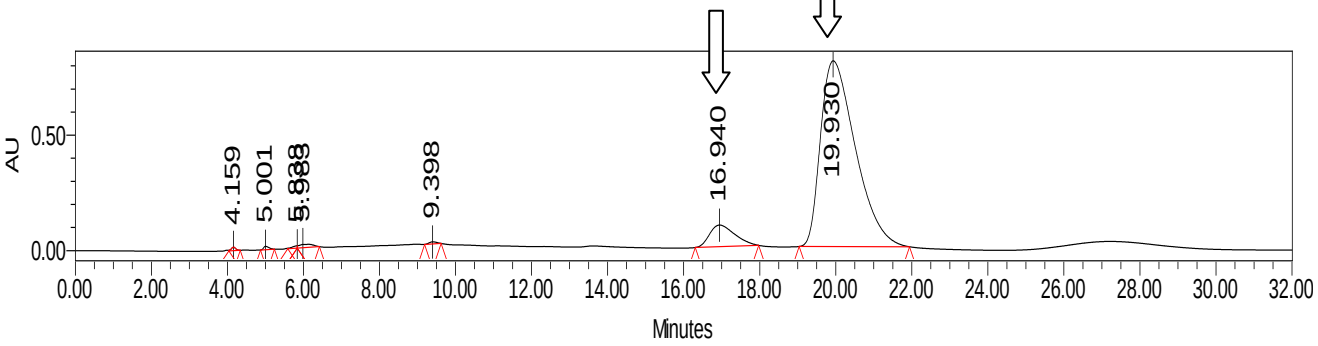
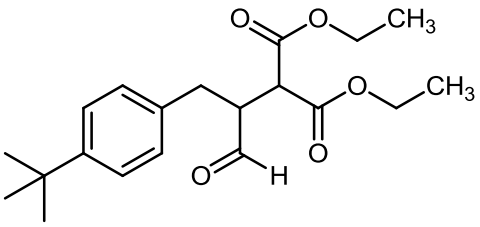
Chemical Formula: $C_{16}H_{20}O_5$

Molecular Weight: 292,33

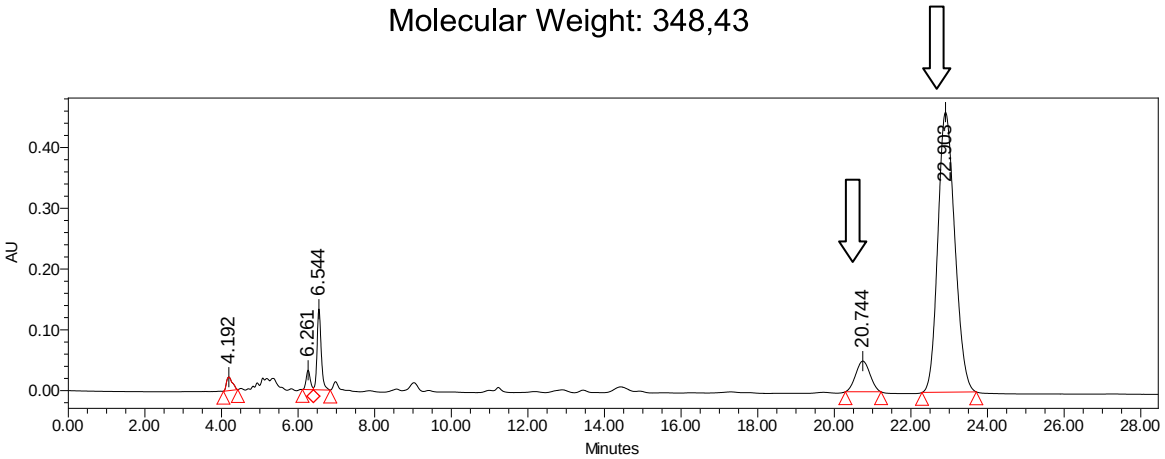


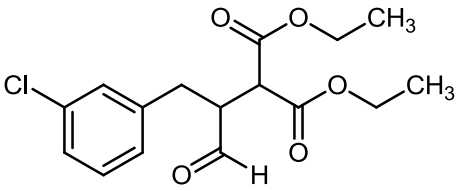


diethyl 2-(1-(4-(*tert*-butyl)phenyl)-3-oxopropan-2-yl)malonate

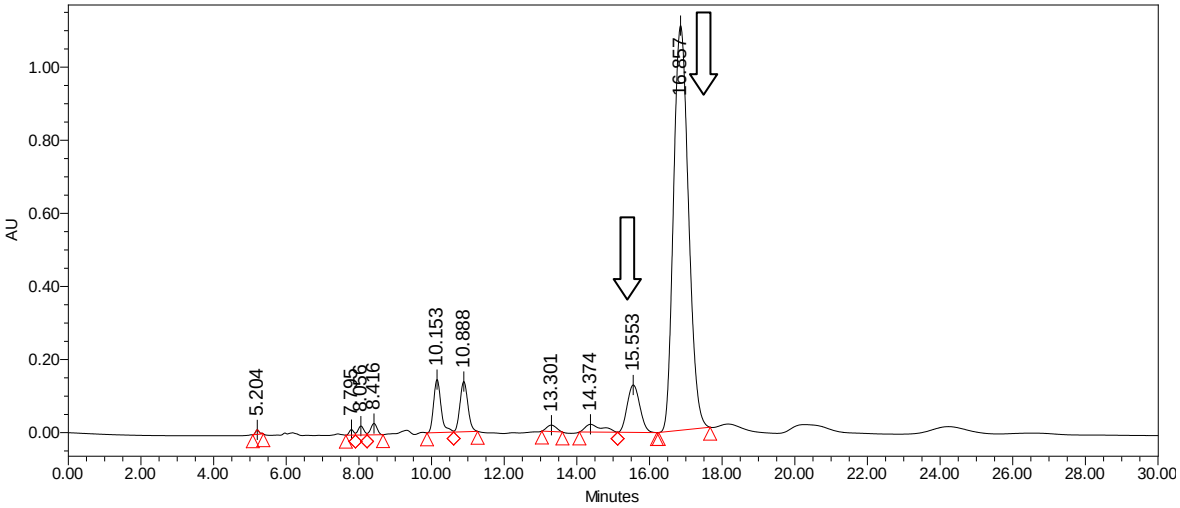
Chemical Formula: $C_{20}H_{28}O_5$

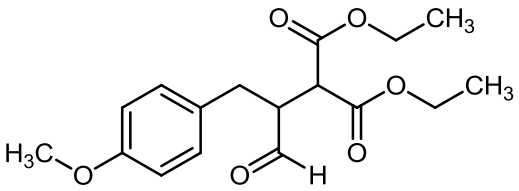
Molecular Weight: 348,43



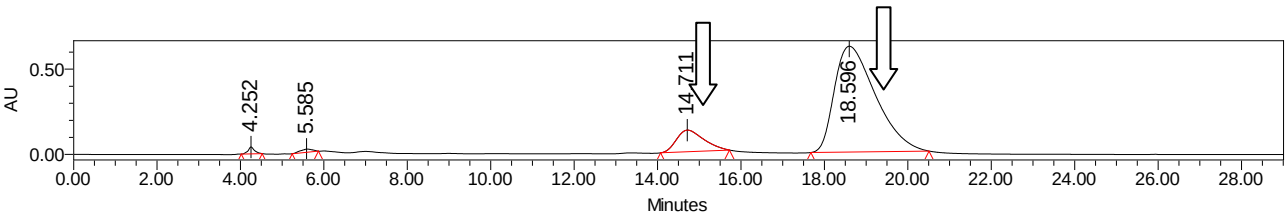


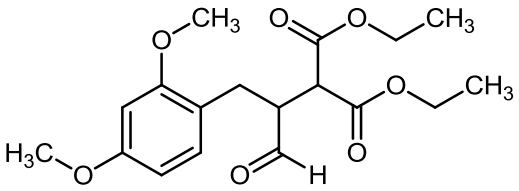
diethyl 2-(1-(3-chlorophenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: $C_{16}H_{19}ClO_5$
Molecular Weight: 326,77



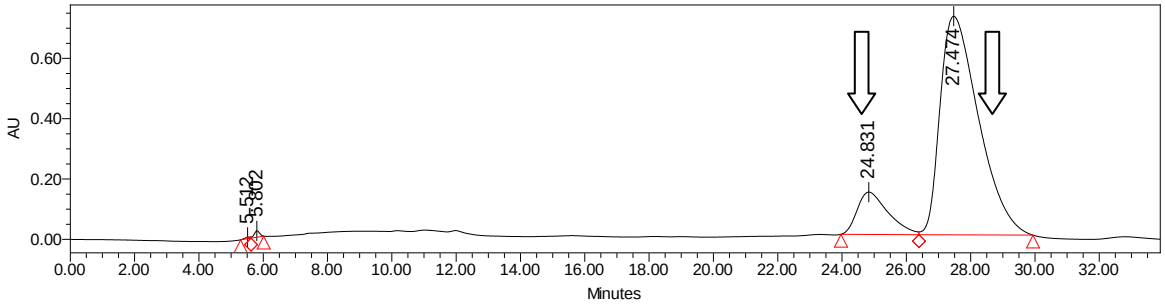


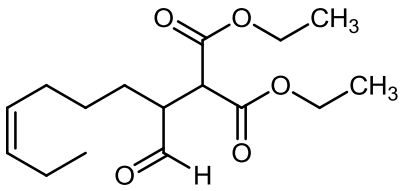
diethyl 2-(1-(4-methoxyphenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: $C_{17}H_{22}O_6$
Molecular Weight: 322,35





diethyl 2-(1-(2,4-dimethoxyphenyl)-3-oxopropan-2-yl)malonate
Chemical Formula: $C_{18}H_{24}O_7$
Molecular Weight: 352,38





(*Z*)-diethyl 2-(1-oxonon-6-en-2-yl)malonate
Chemical Formula: $C_{16}H_{26}O_5$
Molecular Weight: 298,37