# Supporting information

# Activation of donor-acceptor cyclopropanes under basic conditions. Ring opening of 2-(*p*-siloxyaryl)cyclopropane 1,1-dicarboxylates with nitro compounds and other *C*-nucleophiles

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## General experimental

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled. $CH_3CN$, $CH_2Cl_2$, DMF, and THF were distilled from $CaH_2$ prior to use. Triethylamine was distilled from $CaH_2$. Brine refers to a saturated aqueous solution of NaCl. TLC were performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV and/or anisaldehyde/$H_2SO_4$/EtOH stain and/or and or $FeCl_3$/HCl(aq.) stain and/or ninhydrine/AcOH/EtOH and/or cerium molybdate stain (Hanessian's stain) and/or chloranil/toluene stain. Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded at 300K on Bruker AM300, Fourier 300HD and Avance NEO spectrometers at the following spectrometer frequencies: 300 MHz ($^1$H NMR), 75 MHz ($^{13}$C NMR), 60 MHz ($^{29}$Si NMR). Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad), app (apparent). Peak assignments were made on the basis of COSY, HQCS and HMBC methods for selected compounds. For other compounds assignment was made by analogy.
High resolution mass spectra were acquired on Bruker micrOTOF spectrometer using electrospray ionization (ESI). Melting points were determined on a Koffler melting point apparatus and are uncorrected.

## X-ray crystallography

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu $K_\alpha$-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[s1] The structure was solved by direct methods using SHELXT [s2] and refined on $F^2$ using SHELXL-2018 [s3] in the OLEX2 program. [s4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Location of hydroxyl hydrogen atom (H3) was found from the electron density-difference map; this hydrogen atom was refined with relative isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters.

**Crystal data and structure refinement parameters for 3ae.**

| | | |
|---|---|---|
| Empirical formula | $C_{20}H_{21}NO_7$ | |
| Formula weight | 387.38 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 5.57151(5) Å | α = 90°. |
| | b = 14.07632(12) Å | β = 90°. |
| | c = 23.5481(2) Å | γ = 90°. |
| Volume | 1846.79(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.393 $g/cm^3$ | |
| Absorption coefficient | 0.891 $mm^{-1}$ | |
| F(000) | 816 | |
| Crystal size | 0.198 x 0.116 x 0.086 $mm^3$ | |
| Theta range for data collection | 3.658 to 79.994°. | |
| Index ranges | -7<=h<=7, -17<=k<=16, -30<=l<=29 | |
| Reflections collected | 24419 | |
| Independent reflections | 3993 [R(int) = 0.0322] | |
| Observed reflections | 3902 | |
| Completeness to theta = 67.684° | 100.0 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.764 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3993 / 0 / 259 | |
| Goodness-of-fit on F2 | 1.079 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0367, wR2 = 0.1001 | |
| R indices (all data) | R1 = 0.0375, wR2 = 0.1008 | |
| Absolute structure parameter | 0.5(2) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.301 and -0.191 $e.Å^{-3}$ | |

**Crystal data and structure refinement parameters for 3ag.**

| | | |
|---|---|---|
| Empirical formula | $C_{22}H_{23}NO_9$ | |
| Formula weight | 445.41 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 8.59853(9) Å | α= 90°. |
| | b = 11.65212(15) Å | β= 90°. |
| | c = 21.5751(2) Å | γ = 90°. |
| Volume | 2161.63(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.369 $g/cm^3$ | |
| Absorption coefficient | 0.907 $mm^{-1}$ | |
| F(000) | 936 | |
| Crystal size | 0.27 x 0.047 x 0.041 $mm^3$ | |
| Theta range for data collection | 4.098 to 79.892°. | |
| Index ranges | -10<=h<=8, -14<=k<=14, -27<=l<=26 | |
| Reflections collected | 13047 | |
| Independent reflections | 4408 [R(int) = 0.0310] | |
| Observed reflections | 4277 | |
| Completeness to theta = 67.684° | 100.0 % | |
| Absorption correction | Analytical | |
| Max. and min. transmission | 0.970 and 0.874 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4408 / 0 / 299 | |
| Goodness-of-fit on $F^2$ | 1.043 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0261, wR2 = 0.0654 | |
| R indices (all data) | R1 = 0.0271, wR2 = 0.0661 | |
| Absolute structure parameter | 0.10(6) | |
| Extinction coefficient | 0.0015(2) | |
| Largest diff. peak and hole | 0.178 and -0.136 $e.Å^{-3}$ | |

**Crystal data and structure refinement parameters for 3an.**

| | | |
|---|---|---|
| Empirical formula | $C_{20}H_{27}NO_9$ | |
| Formula weight | 425.42 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ | |
| Unit cell dimensions | a = 9.97285(13) Å | α = 85.062(2)°. |
| | b = 10.4324(2) Å | β = 67.0587(17)°. |
| | c = 10.6019(3) Å | γ = 89.0992(15)°. |
| Volume | 1011.82(4) Å3 | |
| Z | 2 | |
| Density (calculated) | 1.396 $g/cm^3$ | |
| Absorption coefficient | 0.934 $mm^{-1}$ | |
| F(000) | 452 | |
| Crystal size | 0.476 x 0.154 x 0.076 $mm^3$ | |
| Theta range for data collection | 4.254 to 80.218°. | |
| Index ranges | -12<=h<=10, -13<=k<=13, -13<=l<=13 | |
| Reflections collected | 29410 | |
| Independent reflections | 4376 [R(int) = 0.0313] | |
| Observed reflections | 4195 | |
| Completeness to theta = 67.684° | 99.9 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.524 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4376 / 14 / 286 | |
| Goodness-of-fit on F2 | 1.035 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0340, wR2 = 0.0897 | |
| R indices (all data) | R1 = 0.0352, wR2 = 0.0907 | |
| Extinction coefficient | 0.0031(4) | |
| Largest diff. peak and hole | 0.351 and -0.222 e.$Å^{-3}$ | |

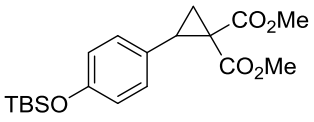
**Crystal data and structure refinement parameters for 4k.**

| | | |
|---|---|---|
| Empirical formula | $C_{19}H_{26}O_5$ | |
| Formula weight | 334.40 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | a = 10.97868(11) Å | α = 90°. |
| | b = 13.67544(13) Å | β = 99.4557(9)°. |
| | c = 12.12795(11) Å | γ = 90°. |
| Volume | 1796.13(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.237 $g/cm^3$ | |
| Absorption coefficient | 0.723 $mm^{-1}$ | |
| F(000) | 720 | |
| Crystal size | 0.161 x 0.119 x 0.081 $mm^3$ | |
| Theta range for data collection | 4.912 to 79.940°. | |
| Index ranges | -14<=h<=13, -16<=k<=17, -15<=l<=15 | |
| Reflections collected | 21043 | |
| Independent reflections | 3903 [R(int) = 0.0269] | |
| Observed reflections | 3668 | |
| Completeness to theta = 67.684° | 100.0 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.699 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3903 / 0 / 227 | |
| Goodness-of-fit on $F^2$ | 1.069 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0331, wR2 = 0.0805 | |
| R indices (all data) | R1 = 0.0349, wR2 = 0.0817 | |
| Extinction coefficient | 0.00113(19) | |
| Largest diff. peak and hole | 0.286 and -0.211 $e.Å^{-3}$ | |

**Crystal data and structure refinement parameters for 6.**

| | | |
|---|---|---|
| Empirical formula | $C_{14}H_{16}O_4$ | |
| Formula weight | 248.27 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | I2/a | |
| Unit cell dimensions | a = 20.5214(2) Å | α = 90°. |
| | b = 5.73430(5) Å | β = 97.9766(9)°. |
| | c = 22.2387(2) Å | γ = 90°. |
| Volume | 2591.64(4) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.273 $g/cm^3$ | |
| Absorption coefficient | 0.767 $mm^{-1}$ | |
| F(000) | 1056 | |
| Crystal size | 0.525 x 0.14 x 0.096 $mm^3$ | |
| Theta range for data collection | 4.014 to 80.048°. | |
| Index ranges | -26<=h<=25, -6<=k<=7, -28<=l<=28 | |
| Reflections collected | 21419 | |
| Independent reflections | 2825 [R(int) = 0.0494] | |
| Observed reflections | 2583 | |
| Completeness to theta = 67.684° | 100.0 % | |
| Absorption correction | Analytical | |
| Max. and min. transmission | 0.948 and 0.800 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2825 / 0 / 169 | |
| Goodness-of-fit on $F^2$ | 1.058 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0355, wR2 = 0.0933 | |
| R indices (all data) | R1 = 0.0384, wR2 = 0.0965 | |
| Extinction coefficient | 0.00062(10) | |
| Largest diff. peak and hole | 0.232 and -0.148 $e.Å^{-3}$ | |

List of substrates

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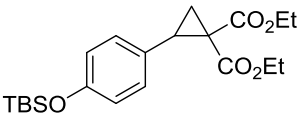


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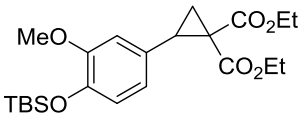


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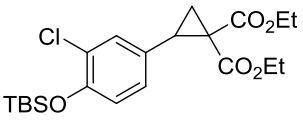


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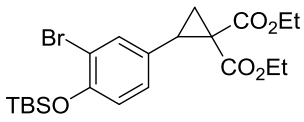


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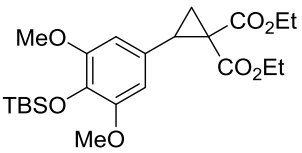


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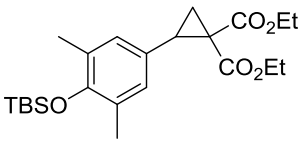


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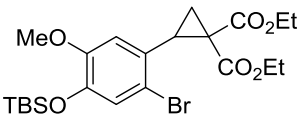


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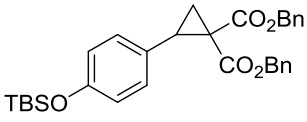


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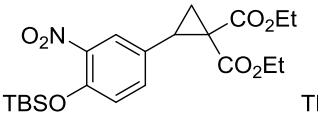


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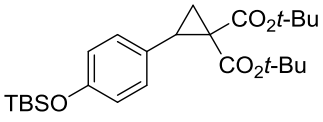


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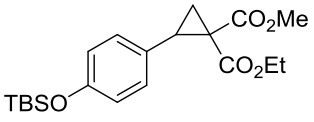


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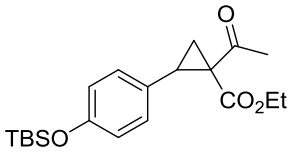


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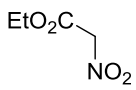


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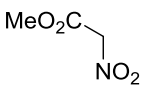


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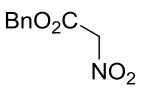


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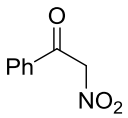


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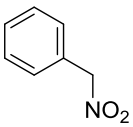


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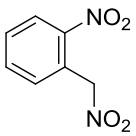


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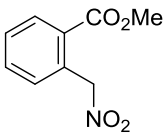


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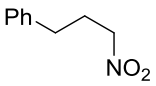


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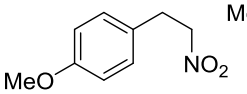


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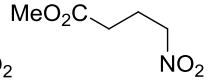


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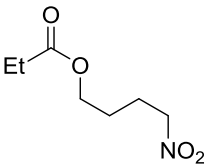


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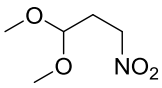


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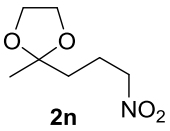


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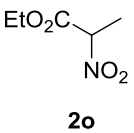
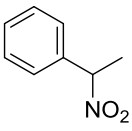
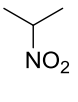


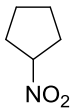

**2o**



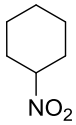

**2p**




**2q**



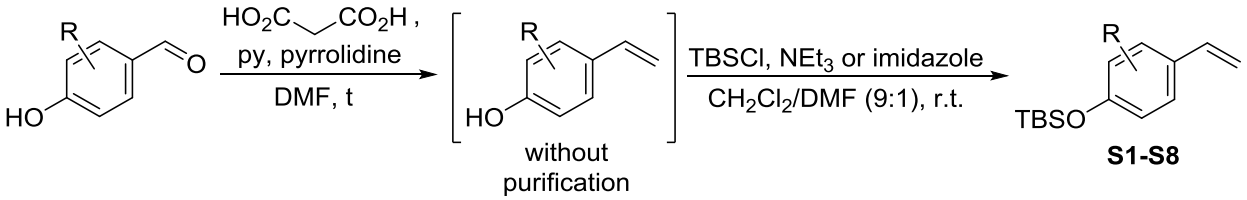

**2r**

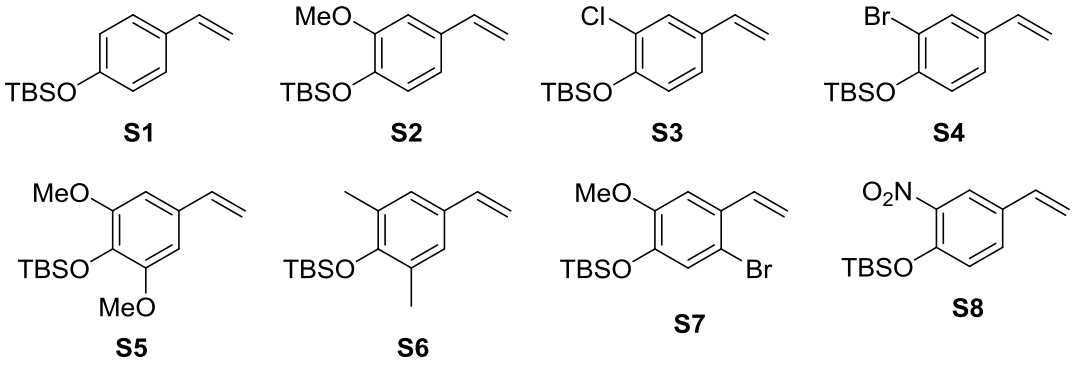



**2s**

Substrates **2a**, **2b**, **2h**, **2q**, **2s** were commercially available. Nitro compounds **2c**,[s5] **2d**,[s6] **2e**,[s7] **2f** and **2g**,[s8] **2i**,[s9] **2j**,[s10] **2k**,[s11] **2l**,[s12] **2m**,[s13] **2n**,[s14] **2o**,[s15] **2p**,[s16] **2r**,[s17] were obtained according to the literature procedures. Diazomalonates and ethyl diazoacetoacetate were obtained according to literature procedures.[s18]

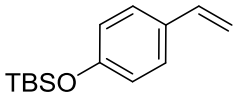
**Preparations of styrenes S1-S8**




4-Siloxystyrenes were prepared according to modified literature procedure.[s19]

***tert*-Butyldimethyl(4-vinylphenoxy)silane (S1)**



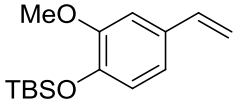

To the solution of 4-hydroxybenzaldehyde (1.22 g, 10 mmol) and malonic acid (2.08 g, 20 mmol) in DMF (16 mL) pyridine (3.2 mL, 3.13 g, 40 mmol) and pyrrolidine (0.41 mL, 0.35 g, 5.0 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then cooled to r.t. and transferred into EtOAc (70 mL) / $H_2O$ (100 mL). Aqueous layer was washed with EtOAc (70 mL) and the combined organic layers were washed with 0.5 M HCl (50 mL), brine (100 mL), dried over $Na_2SO_4$ and evaporated to obtain 1.17 g of crude 4-hydroxystyrene. (Note: crude 4-hydroxystyrenes may contain residual amounts of EtOAc and DMF. It did not affect the outcome of the next (silylation) step).

This crude 4-hydroxystyrene (1.17 g) was dissolved in $CH_2Cl_2$ (17 mL) / DMF (1.7 mL), then $NEt_3$ (2.7 mL, 1.94 g, 19.2 mmol) and TBSCl (1.64 g, 10.9 mmol) were consequently added at 0 °C under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into $CH_2Cl_2$ (40 mL) / $H_2O$ (40 mL). Aqueous layer was washed with $CH_2Cl_2$ (20 mL) and the combined organic layers were washed with brine (40 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE) to give 1.43 g (61% over two steps) of the target product **S1** as colorless oil.

$R_f$ = 0.65 (PE, UV, anisaldehyde).

NMR matched previously reported data.[s20]

***tert*-Butyl(2-methoxy-4-vinylphenoxy)dimethylsilane (S2)**

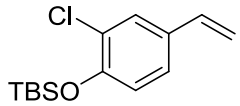



To the solution of vanilin (0.83 g, 5.44 mmol) and malonic acid (1.13 g, 10.9 mmol) in DMF (9.0 mL) pyridine (1.8 mL, 1.76 g, 22.3 mmol) and pyrrolidine (0.23 mL, 197 mg, 2.78 mmol) were consequently added. The resulting mixture was refluxed for 3.5 h, then cooled to r.t. and transferred into EtOAc (30 mL) / $H_2O$ (60 mL). Aqueous layer was washed with EtOAc (30 mL), and the combined organic layers were washed with 0.5 M HCl (20 mL), brine (60 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.82 g of crude 4-hydroxystyrene.

This crude 4-hydroxystyrene (0.82 g) was dissolved in $CH_2Cl_2$ (7.5 mL) / DMF (0.8 mL), then $NEt_3$ (1.16 mL, 0.84 g, 8.23 mmol) and TBSCl (0.71 g, 4.72 mmol) were consequently added at

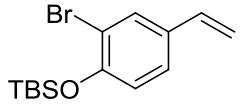
0 °C under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (70 mL) / $H_2O$ (100 mL). Organic layer was washed with brine (70 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE, then PE/EtOAc 50:1) to give 1.07 g (75% over two steps from vanilin) of the target product **S2** as light yellow oil.
$R_f$ = 0.62 (PE/EtOAc, 9:1, UV, anisaldehyde).
NMR matches previously reported data.[s21]

***tert*-Butyl(2-chloro-4-vinylphenoxy)dimethylsilane (S3)**




To the solution of 3-chloro-4-hydroxybenzaldehyde (0.47 g, 3.00 mmol) and malonic acid (0.62 g, 6.0 mmol) in DMF (5.0 mL) pyridine (1.00 mL, 0.98 g, 12.4 mmol) and pyrrolidine (0.12 mL, 103 mg, 1.45 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.53 g of crude 4-hydroxystyrene.
This crude 4-hydroxystyrene (0.53 g) was dissolved in $CH_2Cl_2$ (5.5 mL) / DMF (0.55 mL), then $NEt_3$ (0.84 mL, 0.60 g, 6.00 mmol) and TBSCl (0.52 g, 3.46 mmol) were consequently added at 0 °C under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL) and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE) to give 0.60 g (74% over two steps) of the target product **S3** as colorless oil.
$R_f$ = 0.34 (PE, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.26 (s, 6H, Me–Si), 1.06 (s, 9H, *t*-Bu), 5.20 (d, *J* = 10.9 Hz, 1H, $=CH_{2a}$), 5.64 (d, *J* = 17.6 Hz, 1H, $=CH_{2b}$), 6.62 (dd, *J* = 17.6, 10.9 Hz, 1H, =CH), 6.86 (d, *J* = 8.4 Hz, 1H, $CH_{Ar}$), 7.19 (dd, *J* = 8.4, 2.1 Hz, 1H, $CH_{Ar}$), 7.44 (d, *J* = 2.1 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.4 (Me–Si), 18.4 (C–Si), 25.7 ($\underline{Me}_3C$–Si), 113.1 ($=CH_2$), 120.7 (CH), 125.4 (CH), 125.8 ($\underline{C}_{Ar}$–Cl), 127.9 (CH), 132.1 ($C_{Ar}$), 135.3 ($CH_{Ar}$), 151.2 ($\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.5.
HRMS (ESI): *m/z* calcd. for [$C_{14}H_{21}{}^{35}ClOSi+Na^+$]: 291.0942, found: 291.0950.

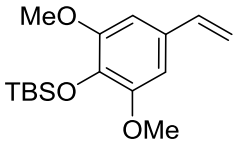
**(2-Bromo-4-vinylphenoxy)(*tert*-butyl)dimethylsilane (S4)**




To the solution of 3-bromo-4-hydroxybenzaldehyde (0.51 g, 2.54 mmol) and malonic acid (0.53 g, 5.01 mmol) in DMF (4.2 mL) pyridine (0.82 mL, 0.80 g, 10.1 mmol) and pyrrolidine (0.10 mL, 86 mg, 1.21 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.35 g of crude 4-hydroxystyrene.
This crude 4-hydroxystyrene (0.35 g) was dissolved in $CH_2Cl_2$ (3.2 mL) / DMF (0.3 mL), then $NEt_3$ (0.49 mL, 0.35 g, 3.50 mmol) and TBSCl (0.30 g, 2.00 mmol) were consequently added at 0 °C under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL), and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE) to give 0.32 g (57% over two steps) of the target product **S4** as colorless oil.

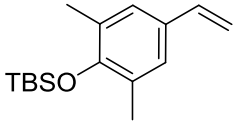
$R_f$ = 0.36 (PE, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.28 (s, 6H, Me–Si), 1.08 (s, 9H, *t*-Bu), 5.20 (dd, *J* = 10.9, 0.6 Hz, 1H, $=CH_{2a}$), 5.64 (dd, *J* = 17.6, 0.6 Hz, 1H, $=CH_{2b}$), 6.61 (dd, *J* = 17.6, 10.9 Hz, 1H, =CH), 6.85 (d, *J* = 8.4 Hz, 1H, $CH_{Ar}$), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H, $CH_{Ar}$), 7.61 (d, *J* = 2.1 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.2 (Me–Si), 18.4 (C–Si), 25.8 ($\underline{Me}_3C$–Si), 113.1 ($=CH_2$), 115.6 ($\underline{C}_{Ar}$–Br), 120.1 (CH), 126.1 (CH), 131.0 (CH), 132.3 ($C_{Ar}$), 135.1 (CH), 152.3 ($\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.3.
HRMS (ESI): *m/z* calcd. for $[C_{14}H_{21}{}^{79}BrOSi+H^+]$: 313.0618, found: 313.0619.

***tert*-Butyl(2,6-dimethoxy-4-vinylphenoxy)dimethylsilane (S5)**




To the solution of 4-hydroxy-3,5-dimethoxybenzaldehyde (0.55 g, 3.00 mmol) and malonic acid (0.62 g, 6.0 mmol) in DMF (5.0 mL) pyridine (1.00 mL, 0.98 g, 12.4 mmol) and pyrrolidine (0.12 mL, 103 mg, 1.45 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.45 g of crude 4-hydroxystyrene.
This crude 4-hydroxystyrene (0.45 g) was dissolved in $CH_2Cl_2$ (4.5 mL) / DMF (0.45 mL), then imidazole (0.34 g, 5.00 mmol) and TBSCl (0.43 g, 2.86 mmol) were consequently added at 0 °C under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL,) and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE, then PE/EtOAc 50:1) to give 0.65 g (74% over two steps) of the target product **S5** as colorless oil, that solidified upon storage in a fridge.
$R_f$ = 0.55 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 25-26 °C (EtOAc).
NMR matches previously reported data.[s21]
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, Me–Si), 1.04 (s, 9H, *t*-Bu), 3.84 (s, 6H, OMe), 5.18 (dd, *J* = 10.9, 0.7 Hz, 1H, $=CH_{2a}$), 5.64 (dd, *J* = 17.6, 0.7 Hz, 1H, $=CH_{2b}$), 6.64 (s, 2H, $CH_{Ar}$), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H, =CH).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.6 (Me–Si), 18.8 (C–Si), 25.8 ($\underline{Me}_3C$–Si), 55.8 (OMe), 103.5 (CH), 111.9 ($=CH_2$), 130.4 ($C_{Ar}$), 134.6 ($C_{Arr}$–O), 137.1 (CH), 151.7 (2×$\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.1.
HRMS (ESI): *m/z* calcd. for $[C_{16}H_{26}O_3Si+H^+]$: 295.1724, found: 295.1721.

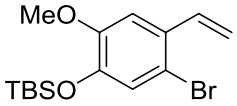
***tert*-Butyl(2,6-dimethyl-4-vinylphenoxy)dimethylsilane (S6)**




To the solution of 4-hydroxy-3,5-dimethylbenzaldehyde (0.45 g, 3.00 mmol) and malonic acid (0.62 g, 6.0 mmol) in DMF (5.0 mL) pyridine (0.97 mL, 0.95 g, 12.0 mmol) and pyrrolidine (0.12 mL, 103 mg, 1.45 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.48 g of crude 4-hydroxystyrene.

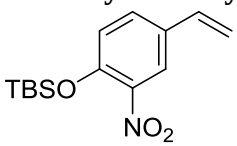
This crude 4-hydroxystyrene (0.45 g) was dissolved in $CH_2Cl_2$ (6.0 mL) / DMF (0.55 mL), then imidazole (0.40 g, 5.88 mmol) and TBSCl (0.54 g, 3.59 mmol) were consequently added at 0 °*C* under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL,) and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE) to give 0.58 g (74% over two steps) of the target product **S6** as colorless oil.
$R_f$ = 0.20 (PE, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 6H, Me–Si), 1.07 (s, 9H, *t*-Bu), 2.24 (s, 6H, Me–$C_{Ar}$), 5.13 (dd, *J* = 10.9, 0.9 Hz, 1H, =$CH_{2a}$), 5.63 (dd, *J* = 17.6, 0.9 Hz, 1H, =$CH_{2b}$), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H, =CH), 7.08 (s, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -2.9 (Me–Si), 17.9 (Me–$C_{Ar}$), 18.8 (C–Si), 26.1 ($\underline{Me}_3$C–Si), 111.5 (=$CH_2$), 126.7 (CH), 128.7 (2×$C_{Ar}$), 130.6 ($C_{Ar}$), 136.5 (CH), 152.3 ($\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 20.1.
HRMS (ESI): *m/z* calcd. for [$C_{16}H_{26}OSi+H^+$]: 263.1826, found: 263.1816.

**(5-Bromo-2-methoxy-4-vinylphenoxy)(*tert*-butyl)dimethylsilane (S7)**




To the solution of 2-bromo-4-hydroxy-5-methoxybenzaldehyde[s22] (0.46 g, 2.00 mmol) and malonic acid (0.42 g, 4.0 mmol) in DMF (3.5 mL) pyridine (0.65 mL, 0.64 g, 8.05 mmol) and pyrrolidine (83 μL, 71 mg, 1.00 mmol) were consequently added. The resulting mixture was maintained at 130 °*C* for 3 h, then cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.36 g of crude 4-hydroxystyrene.
This crude 4-hydroxystyrene (0.36 g) was dissolved in $CH_2Cl_2$ (2.9 mL) / DMF (0.30 mL), then $NEt_3$ (0.44 mL, 0.32 g, 3.14 mmol) and TBSCl (0.27 g, 1.79 mmol) were consequently added at 0 °*C* under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL,) and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE, then PE/EtOAc 50:1) to give 0.33 g (48% over two steps) of the target product **S7** as colorless oil.
$R_f$ = 0.14 (PE, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 6H, Me–Si), 1.02 (s, 9H, *t*-Bu), 3.85 (3, 3H, OMe), 5.29 (dd, *J* = 10.9, 0.9 Hz, 1H, =$CH_{2a}$), 5.640(dd, *J* = 17.4, 0.9 Hz, 1H, =$CH_{2b}$), 7.00 (dd, *J* = 17.4, 10.9 Hz, 1H, =CH), 7.03-7.06 (m, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.7 (Me–Si), 18.5 (C–Si), 25.7 ($\underline{Me}_3$C–Si), 55.6 (OMe), 109.4 (CH), 114.0 ($\underline{C}_{Ar}$–Br), 114.5 (=$CH_2$), 124.7 (CH), 130.6 ($C_{Ar}$), 135.6 (CH), 145.8 ($\underline{C}_{Ar}$–OMe), 150.7 ($\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.6.
HRMS (ESI): *m/z* calcd. for [$C_{15}H_{23}{}^{79}BrO_2Si+H^+$]: 343.0723, found: 343.0727.

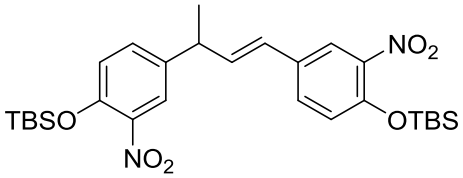
***tert*-Butyldimethyl(2-nitro-4-vinylphenoxy)silane (S8)**




To the solution of 4-hydroxy-3-nitrobenzaldehyde (0.50 g, 3.00 mmol) and malonic acid (0.62 g, 6.0 mmol) in DMF (5.0 mL) pyridine (1.00 mL, 0.98 g, 12.4 mmol) and pyrrolidine (0.12 mL, 103 mg, 1.45 mmol) were consequently added. The resulting mixture was refluxed for 3 h, then

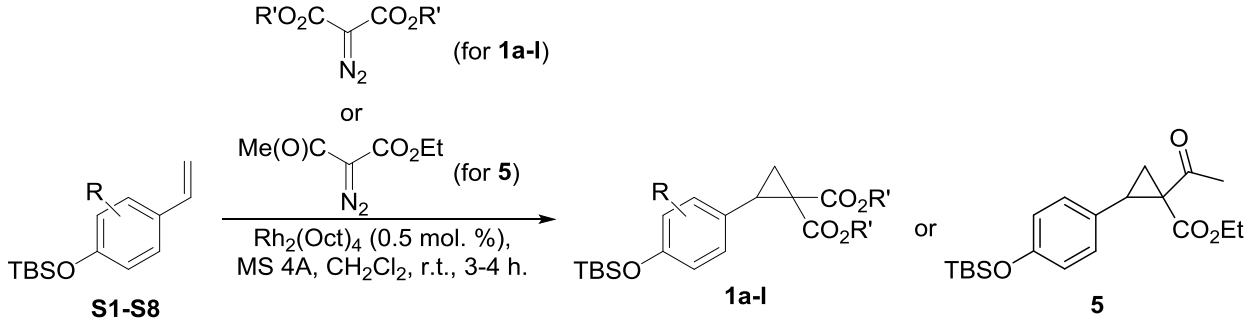
cooled to r.t. and transferred into EtOAc (20 mL) / $H_2O$ (50 mL). Aqueous layer was washed with EtOAc (20 mL), and the combined organic layers were washed with 0.5 M HCl (10 mL), brine (50 mL), dried over $Na_2SO_4$ and evaporated to obtain 0.58 g of crude 4-hydroxystyrene.
This crude 4-hydroxystyrene (0.30 g) was dissolved in $CH_2Cl_2$ (2.7 mL) / DMF (0.20 mL), then $NEt_3$ (0.42 mL, 0.30 g, 3.00 mmol) and TBSCl (0.26 g, 1.73 mmol) were consequently added at 0 °*C* under an argon atmosphere. The reaction mixture was warmed up to r.t. and left overnight, then transferred into PE (30 mL) / $H_2O$ (50 mL). Aqueous layer was washed with PE (20 mL,) and the combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (eluent: PE, then PE/EtOAc 50:1) to obtain two fractions: 252 mg of **S8** as yellow oil, 72 mg of **S8** and **S8'** mixture (ratio **S8/ S8'** = 1:1.4) and 25 mg of **S8'**. Total yield of **S8**: 271 mg (64% over two steps).
$R_f$ = 0.48 (PE/EtOAc, 9:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.28 (s, 6H, Me–Si), 1.03 (s, 9H, *t*-Bu), 5.31 (d, *J* = 10.9 Hz, 1H, $=CH_{2a}$), 5.72 (dd, *J* = 17.5 Hz, 1H, $=CH_{2b}$), 6.66 (dd, *J* = 17.5, 10.9 Hz, 1H, =CH), 6.96 (d, *J* = 8.6 Hz, 1H, $CH_{Ar}$), 7.50 (dd, *J* = 8.6, 2.3 Hz, 1H, $CH_{Ar}$), 7.84 (d, *J* = 2.3 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -4.4 (Me–Si), 18.2 (C–Si), 25.5 ($\underline{Me}_3$C–Si), 114.8 ($=CH_2$), 122.2 ($CH_{Ar}$), 123.0 (CH), 131.1 ($CH_{Ar}$), 131.2 ($C_{Ar}$), 134.3 (CH), 142.0 ($C_{Ar}$–$NO_2$), 148.7 ($\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 25.9.
HRMS (ESI): *m/z* calcd. for [$C_{14}H_{21}NO_3Si+H^+$]: 280.1363, found: 280.1373.

**(*E*)-((But-1-ene-1,3-diylbis(2-nitro-4,1-phenylene))bis(oxy))bis(tert-butyldimethylsilane) (S8')**



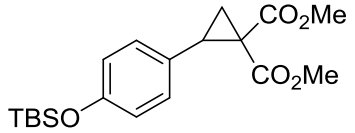

Obtained during the synthesis of **S8**. Yield: 9%.
$R_f$ = 0.42 (PE/EtOAc, 9:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.27 and 0.28 (both s, total 12H, Me–Si), 1.02 and 1.03 (both s, total 18H, *t*-Bu), 1.48 (d, *J* = 7.0 Hz, 3H, $C\underline{H}_3$–CH), 3.65 (app quint, *J* = 6.8 Hz, 1H, $CH_3$–$C\underline{H}$), 6.26 (dd, *J* = 15.9, 6.3 Hz, 1H, =CH), 6.36 (d, *J* = 15.9 Hz, 1H, =CH), 6.94 (d, *J* = 8.6 Hz, 1H, $CH_{Ar}$), 6.96 (d, *J* = 8.6 Hz, 1H, $CH_{Ar}$), 7.34 (dd, *J* = 8.6, 2.4 Hz, 1H, $CH_{Ar}$), 7.43 (dd, *J* = 8.6, 2.4 Hz, 1H, $CH_{Ar}$), 7.70 (d, *J* = 2.4 Hz, 1H, $CH_{Ar}$), 7.80 (d, *J* = 2.4 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -4.4 and -4.3 (2×Me–Si), 18.20 and 18.23 (2×C–Si), 20.9 ($\underline{Me}$–CH), 25.6 ($\underline{Me}_3$C–Si), 41.4 (Me–$\underline{C}$H), 122.2 (CH), 122.3 (CH), 122.8 (CH), 123.8 (CH), 126.9 (CH), 130.8 ($C_{Ar}$), 131.2 (CH), 132.7 (CH), 135.0 (CH), 138.2 ($C_{Ar}$), 141.8 and 142.0 (2×$C_{Ar}$–$NO_2$), 147.7 and 148.3 (2×$\underline{C}_{Ar}$–O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 25.5, 26.0.
HRMS (ESI): *m/z* calcd. for [$C_{28}H_{42}N_2O_6Si_2+NH_4^+$]: 576.2920, found: 576.2911.

**Synthesis of DAC 1 and 5.**



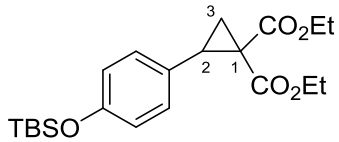

**S1-S8** **1a-l** **5**

**Dimethyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1a)**



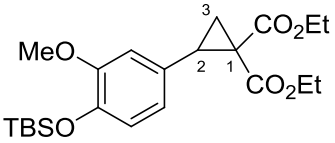

Solution of styrene **S1** (0.35 g, 1.5 mmol) and $Rh_2Oct_4$ (6 mg, 7.7 μmol) in $CH_2Cl_2$ (10 mL) was stirred with MS 4Å (0.45 g) for 10 min. In a separate vial a solution of dimethyl diazomalonate (0.28 g, 1.8 mmol, 1.2 equiv.) in $CH_2Cl_2$ (3.6 mL) was prepared. 0.9 mL of this diazomalonate solution was added dropwise (approx. 10 min) to the reaction mixture using a syringe and the resulting mixture was stirred for 0.5 h. After that the remaining part (0.27 mL) of diazomalonate solution was added dropwise (approx. 40 min) using a syringe to the reaction mixture. The reaction mixture was stirred for 2 h, filtered through Celite® and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 30:1) to give 0.46 g (85%) of the target product **1a** as white solid.
$R_f$ = 0.30 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 59-60 °C (PE/EtOAc, 10:1).
NMR matches previously reported data.[s23]

**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1b)**




DAC **1b** was obtained from styrene **S1** (183 mg, 0.78 mmol) and diethyl diazomalonate (223 mg, 0.94 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 262 mg (86%) of the target product **1b** as colorless oil.
$R_f$ = 0.29 (PE/EtOAc, 9:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 6H, Me–Si), 0.92 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 0.98 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.69 (dd, *J* = 9.2, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.14 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.17 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.86 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.16-4.33 (m, 2H, $OC\underline{H}_2CH_3$), 6.75 (d, *J* = 8.5 Hz, 1H, $CH_{Ar}$), 7.08 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.5 (Me–Si), 13.8 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.2 (C–Si), 18.9 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 31.8 (CH(2)), 37.4 (C(1)), 61.1 and 61.6 (2×$O\underline{C}H_2CH_3$), 119.8 ($CH_{Ar}$), 127.3 ($C_{Ar}$), 129.6 ($CH_{Ar}$), 155.0 ($\underline{C}_{Ar}$–O), 166.7 (C=O), 170.0 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 21.0.
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{32}O_5Si$+$Na^+$]: 415.1911, found: 415.1904.

**Diethyl 2-(4-(tert-butyldimethylsilyloxy)-3-methoxyphenyl)cyclopropane-1,1-dicarboxylate (1c)**




DAC **1c** was obtained from styrene **S2** (0.26 g, 1.00 mmol) and diethyl diazomalonate (0.22 g, 1.20 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 0.35 g (83%) of the target product **1c** as colorless oil.

$R_f$ = 0.27 (PE/EtOAc, 9:1, UV, anisaldehyde).

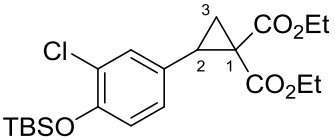
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 6H, Me–Si), 0.93 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 0.99 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.68 (dd, *J* = 9.2, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.13 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.17 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.79 (s, 3H, OMe), 3.81-3.92 (m, 2H, $OC\underline{H}_2CH_3$), 4.19-4.33 (m, 2H, $OC\underline{H}_2CH_3$), 6.65 (dd, *J* = 8.1, 2.0 Hz, 1H, $CH_{Ar}$), 6.73-6.76 (m, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.7 (Me–Si), 13.9 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.5 (C–Si), 19.0 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 32.2 (CH(2)), 37.4 (C(1)), 55.5 (OMe), 61.1 and 61.6 (2×$\underline{C}H_2CH_3$), 112.7 ($CH_{Ar}$), 120.5 ($CH_{Ar}$), 120.7 ($CH_{Ar}$), 128.0 ($C_{Ar}$), 144.4 ($\underline{C}_{Ar}$–O), 150.6 ($\underline{C}_{Ar}$–O), 166.7 (C=O), 170.0 (C=O).

$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 22.2.

HRMS (ESI): *m/z* calcd. for [$C_{22}H_{34}O_6Si$+$Na^+$]: 445.2017, found: 445.2007.

**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3-chlorophenyl)cyclopropane-1,1-dicarboxylate (1d)**




DAC **1d** was obtained from styrene **S3** (189 mg, 0.70 mmol) and diethyl diazomalonate (160 mg, 0.86 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 40:1) afforded 271 mg (91%) of the target product **1d** as colorless oil, that solidified upon storage in a fridge.

$R_f$ = 0.23 (PE/EtOAc, 9:1, UV, anisaldehyde).

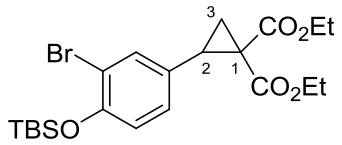
mp = 40-41 °C ($CH_2Cl_2$).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me–Si), 0.96 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.03 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.69 (dd, *J* = 9.2, 5.2 Hz, 1H, $CH_{2a}$(3)), 2.10 (dd, *J* = 7.9, 5.2 Hz, 1H, $CH_{2b}$(3)), 3.14 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.91 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.16-4.34 (m, 2H, $OC\underline{H}_2CH_3$), 6.79 (d, *J* = 8.4 Hz, 1H, $CH_{Ar}$), 6.98 (dd, *J* = 8.4, 1.9 Hz, 1H, $CH_{Ar}$), 7.23 (d, *J* = 2.1 Hz, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.4 (Me–Si), 13.9 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.3 (C–Si), 18.8 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 31.1 (CH(2)), 37.3 (C(1)), 61.2 and 61.7 (2×$\underline{C}H_2CH_3$), 120.4 ($CH_{Ar}$), 125.3 ($\underline{C}_{Ar}$–Cl), 127.7 ($CH_{Ar}$), 128.6 ($C_{Ar}$), 130.6 ($CH_{Ar}$), 150.9 ($\underline{C}_{Ar}$–O), 166.5 (C=O), 169.7 (C=O).

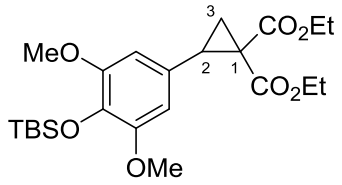
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.5.

**Diethyl 2-(3-bromo-4-(tert-butyldimethylsilyloxy)phenyl)cyclopropane-1,1-dicarboxylate (1e)**



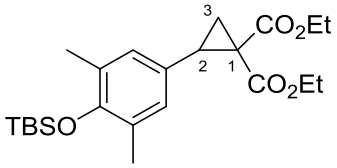

DAC **1e** was obtained from styrene **S4** (240 mg, 0.76 mmol) and diethyl diazomalonate (182 mg, 1.17 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 271 mg (*ca.* 100%) of the target product **1e** as colorless oil, that solidified upon storage in a fridge.
$R_f$ = 0.25 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 55-57 °C (EtOAc).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.23 (s, 6H, Me–Si), 0.97 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.04 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.69 (dd, *J* = 9.2, 5.2 Hz, 1H, $CH_{2a}$(3)), 2.10 (dd, *J* = 7.9, 5.2 Hz, 1H, $CH_{2b}$(3)), 3.14 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.92 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.17-4.34 (m, 2H, $OC\underline{H}_2CH_3$), 6.78 (d, *J* = 8.4 Hz, 1H, $CH_{Ar}$), 7.02 (dd, *J* = 8.4, 1.9 Hz, 1H, $CH_{Ar}$), 7.41 (d, *J* = 2.1 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.3 (Me–Si), 13.9 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.4 (C–Si), 18.8 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 31.0 (CH(2)), 37.3 (C(1)), 61.3 and 61.7 (2×$\underline{C}H_2CH_3$), 115.0 ($\underline{C}_{Ar}$–Br), 119.8 ($CH_{Ar}$), 128.4 ($CH_{Ar}$), 128.9 ($C_{Ar}$), 133.6 ($CH_{Ar}$), 151.9 ($\underline{C}_{Ar}$–O), 166.5 (C=O), 169.7 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.4.
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{31}{}^{79}BrO_5Si+Na^+$]: 471.1197, found: 471.1197.

**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (1f)**



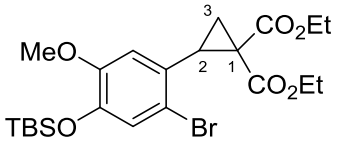

DAC **1f** was obtained from styrene **S5** (153 mg, 0.52 mmol) and diethyl diazomalonate (119 mg, 0.64 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 40:1, then 20:1) afforded 196 mg (83%) of the target product **1f** as light yellow oil, that solidified upon storage in a fridge.
$R_f$ = 0.25 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 82-83 °C (PE/EtOAc, 1:1).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6H, Me–Si), 0.95 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.00 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.68 (dd, *J* = 9.2, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.13 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.17 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.78 (s, 6H, OMe), 3.81-3.97 (m, 2H, $OC\underline{H}_2CH_3$), 4.16-4.34 (m, 2H, $OC\underline{H}_2CH_3$), 6.40 (s, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.7 (Me–Si), 13.9 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.7 (C–Si), 19.1 ($CH_2$(3)), 25.8 ($\underline{Me}_3$C–Si), 32.6 (CH(2)), 37.5 (C(1)), 55.8 (OMe), 61.1 and 61.7 (2×$O\underline{C}H_2CH_3$), 105.6 ($CH_{Ar}$), 127.1 ($C_{Ar}$), 133.7 ($C_{Ar}$), 151.3 (2×$\underline{C}_{Ar}$–O), 166.7 (C=O), 170.0 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.0.
HRMS (ESI): *m/z* calcd. for [$C_{23}H_{36}O_7Si+H^+$]: 453.2303, found: 453.2301.

**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenyl)cyclopropane-1,1-dicarboxylate (1g)**



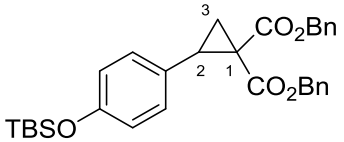

DAC **1g** was obtained from styrene **S6** (186 mg, 0.71 mmol) and diethyl diazomalonate (160 mg, 0.85 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 40:1) afforded 220 mg (74%) of the target product **1g** as colorless oil.
$R_f$ = 0.36 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 46-48 °C ($CH_2Cl_2$).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, Me–Si), 0.91 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.02 (s, 9H, *t*-Bu), 1.30 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.67 (dd, *J* = 9.2, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.11 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 2.17 (s, 6H, $C_{Ar}$–$C\underline{H}_3$), 3.11 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.81-3.97 (m, 2H, $OC\underline{H}_2CH_3$), 4.15-4.33 (m, 2H, $OC\underline{H}_2CH_3$), 6.82 (s, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -3.0 (Me–Si), 13.9 and 14.1 (2×$OCH_2C\underline{H}_3$), 17.8 ($C_{Ar}$–$\underline{Me}$), 18.8 (C–Si), 18.9 ($CH_2$(3)), 26.1 ($\underline{Me}_3$C–Si), 32.0 (CH(2)), 37.3 (C(1)), 61.0 and 61.6 (2×$O\underline{C}H_2CH_3$), 126.9 ($C_{Ar}$), 128.2 ($C_{Ar}$), 128.9 ($CH_{Ar}$), 151.4 ($\underline{C}_{Ar}$–O), 166.8 (C=O), 170.1 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 19.9.
HRMS (ESI): *m/z* calcd. for [$C_{23}H_{36}O_5Si+H^+$]: 421.2405, found: 421.2399.

**Diethyl 2-(2-bromo-4-((tert-butyldimethylsilyl)oxy)-5-methoxyphenyl)cyclopropane-1,1-dicarboxylate (1h)**




DAC **1h** was obtained from styrene **S7** (183 mg, 0.53 mmol) and diethyl diazomalonate (119 mg, 0.64 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 30:1, then 20:1) afforded 216 mg (81%) of the target product **1h** as colorless oil.
$R_f$ = 0.47 (PE/EtOAc, 3:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 and 0.14 (both s, total 6H, Me–Si), 0.92 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 0.98 (s, 9H, *t*-Bu), 1.31 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.74 (dd, *J* = 9.2, 5.2 Hz, 1H, $CH_{2a}$(3)), 2.18 (dd, *J* = 8.2, 5.2 Hz, 1H, $CH_{2b}$(3)), 3.27 (app t, *J* = 8.7 Hz, 1H, CH(2)), 3.77 (s, 3H, OMe), 3.82-3.93 (m, 2H, $OC\underline{H}_2CH_3$), 4.19-4.36 (m, 2H, $OC\underline{H}_2CH_3$), 6.56 (s, 1H, $CH_{Ar}$), 7.03 (s, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.7 (Me–Si), 13.8 and 14.2 (2×$OCH_2C\underline{H}_3$), 18.4 (C–Si), 19.1 ($CH_2$(3)), 25.6 ($\underline{Me}_3$C–Si), 33.4 (CH(2)), 36.8 (C(1)), 55.7 (OMe), 61.1 and 61.6 (2×$\underline{C}H_2CH_3$), 112.6 ($CH_{Ar}$), 117.0 ($\underline{C}_{Ar}$–Br), 124.7 ($CH_{Ar}$), 127.3 ($C_{Ar}$), 145.1 ($\underline{C}_{Ar}$–O), 149.9 ($\underline{C}_{Ar}$–O), 166.6 (C=O), 169.5 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 23.4.
HRMS (ESI): *m/z* calcd. for [$C_{22}H_{33}{}^{81}BrO_6Si+Na^+$]: 525.1103, found: 525.1099.

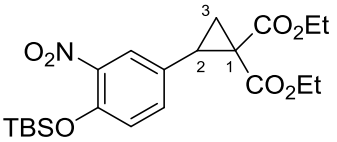
**Dibenzyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1i)**




DAC **1i** was obtained from styrene **S1** (234 mg, 1.00 mmol) and dibenzyl diazomalonate (0.37 g, 1.20 mmol) as described for **1a**. Column chromatography (eluent: PE, then PE/EtOAc, 50:1)

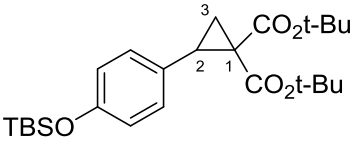
afforded 63 mg (27%) of starting styrene **S1** as colorless oil and 236 mg (47%) of target product **1i** as white solid.
$R_f$ = 0.30 (PE/EtOAc, 9:1, UV, anisaldehyde).
mp = 60-61 °C (PE/EtOAc, 1:1).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me–Si), 1.02 (s, 9H, *t*-Bu), 1.78 (dd, *J* = 9.3, 5.2 Hz, 1H, $CH_{2a}$(3)), 2.22 (dd, *J* = 8.0, 5.2 Hz, 1H, $CH_{2b}$(3)), 3.26 (app t, *J* = 8.7 Hz, 1H, CH(2)), 4.76 (d, *J* = 12.3 Hz, 1H, $CH_{2a}$(Bn)), 4.83 (d, *J* = 12.3 Hz, 1H, $CH_{2b}$(Bn)), 5.18 (d, *J* = 12.5 Hz, 1H, $CH_{2a}$(Bn)), 5.29 (d, *J* = 12.5 Hz, 1H, $CH_{2a}$(Bn)), 6.75 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.02-7.05 (m, 2H, $CH_{Ph}$), 7.09 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.24-7.38 (m, 8H, $CH_{Ph}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.3 (Me–Si), 18.3 (C–Si), 19.4 ($CH_2$(3)), 25.8 ($\underline{Me}_3$C–Si), 32.5 (CH(2)), 37.5 (C(1)), 67.2 and 67.3 (2×$\underline{C}H_2$Ph), 119.9 ($CH_{Ar}$), 127.0 ($C_{Ar}$), 128.0, 128.1, 128.2, 128.3, 128.4, and 128.6 ($CH_{Ph}$), 129.8 ($CH_{Ar}$), 135.4 and 135.6 ($C_{Ph}$), 155.2 ($\underline{C}_{Ar}$–O), 166.6 (C=O), 169.7 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 20.9.
HRMS (ESI): *m/z* calcd. for [$C_{31}H_{36}O_5Si+H^+$]: 517.2405, found: 517.2405.

**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3-nitrophenyl)cyclopropane-1,1-dicarboxylate (1j)**




DAC **1j** was obtained from styrene **S8** (146 mg, 0.52 mmol) and diethyl diazomalonate (115 mg, 0.62 mmol) as described for **1a** with following change: reaction time after addition of diazomalonate – 3 h. Column chromatography (eluent: PE/EtOAc 40:1, then 20:1) afforded 175 mg (77%) of the target product **1j** as yellow oil.
$R_f$ = 0.20 (PE/EtOAc, 9:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 6H, Me–Si), 0.98 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.00 (s, 9H, *t*-Bu), 1.32 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.74 (dd, *J* = 9.2, 5.3 Hz, 1H, $CH_{2a}$(3)), 2.13 (dd, *J* = 7.9, 5.3 Hz, 1H, $CH_{2b}$(3)), 3.18 (app t, *J* = 8.5 Hz, 1H, CH(2)), 3.85-4.01 (m, 2H, $OC\underline{H}_2CH_3$), 4.17-4.36 (m, 2H, $OC\underline{H}_2CH_3$), 6.90 (d, *J* = 8.5 Hz, 1H, $CH_{Ar}$), 7.30 (dd, *J* = 8.5, 2.4 Hz, 1H, $CH_{Ar}$), 7.68 (d, *J* = 2.4 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.4 (Me–Si), 13.8 and 14.1 (2×$OCH_2C\underline{H}_3$), 18.2 (C–Si), 18.8 ($CH_2$(3)), 25.5 ($\underline{Me}_3$C–Si), 30.6 (CH(2)), 37.3 (C(1)), 61.5 and 61.9 (2×$\underline{C}H_2CH_3$), 121.9 ($CH_{Ar}$), 125.6 ($CH_{Ar}$), 128.1 ($C_{Ar}$), 133.9 ($CH_{Ar}$), 141.6 ($C_{Ar}$–$NO_2$), 148.4 ($\underline{C}_{Ar}$–O), 166.3 (C=O), 169.4 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 26.0.
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{31}NO_7Si+H^+$]: 438.1943, found: 438.1931.

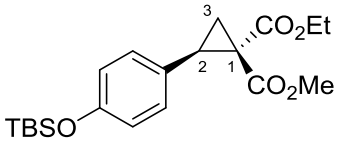
**Di-*tert*-butyl 2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1k)**




DAC **1k** was obtained from styrene **S1** (77 mg, 0.33 mmol) and di-*tert*-butyl diazomalonate (95 mg, 0.39 mmol) as described for **1a**. Column chromatography (eluent: PE, then PE/EtOAc then 50:1) afforded 24 mg (31%) of styrene **S1** and 91 mg (61%) of target product **1k** as colorless oils.
$R_f$ = 0.49 (PE/EtOAc, 9:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, Me–Si), 0.98 (s, 9H, *t*-Bu–Si), 1.14 (s, 9H, *t*-BuO), 1.51 (s, overlapped, 9H, *t*-BuO), 1.48-1.53 (m, 1H, $CH_{2a}$(3)), 1.97 (dd, *J* = 7.8, 5.0 Hz, 1H,

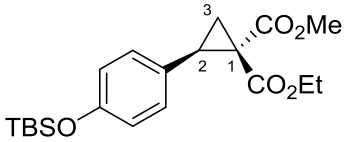
$CH_{2b}$(3)), 3.04 (app t, *J* = 8.5 Hz, 1H, CH(2)), 6.74 (d, *J* = 8.5 Hz, 1H, $CH_{Ar}$), 7.09 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.49 (Me–Si), -4.48 (Me–Si), 17.9 ($CH_2$(3)), 18.2 (C–Si), 25.7 ($\underline{Me}_3$C–Si), 27.6 ($\underline{Me}_3$C–O), 28.1 ($\underline{Me}_3$C–O), 30.5 (CH(2)), 39.2 (C(1)), 80.7 ($Me_3\underline{C}$–O), 81.6 ($Me_3\underline{C}$–O), 119.7 ($CH_{Ar}$), 127.7 ($C_{Ar}$), 129.9 ($CH_{Ar}$), 154.8 ($\underline{C}_{Ar}$–O), 166.0 (C=O), 169.4 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 20.8.
HRMS (ESI): *m/z* calcd. for [$C_{25}H_{40}O_5Si+Na^+$]: 471.2537, found: 471.2531.

**1-Ethyl 1-methyl 2-(4-(tert-butyldimethylsilyloxy)phenyl)cyclopropane-1,1-dicarboxylate (1l)**
DAC **1l** was obtained from styrene **S1** (0.29 g, 1.20 mmol) and ethyl methyl diazomalonate (0.26 g, 1.51 mmol) as described for **1a**. Column chromatography (eluent: PE/EtOAc, 30:1, then 25:1) afforded 93 mg of **1l** (dr = 20:1), 256 mg of **1l** (dr = 1:1) and 53 mg of **1l** (dr = 1:4) as colorless oils. Total yield of target product **1l**: 0.40 g. Total dr ((1*S**,2*R**)-isomer: (1*R**,2*R**)-isomer) = 1.2:1.
Relative configuration was established on the basis of $^1$H NMR assuming that anisotropic influence of aryl group shifts the signals of *cis*-$CO_2C\underline{H}_2R$ upfiled.
(1*S**,2*R**)-isomer:



(1S*,2R*)-isomer

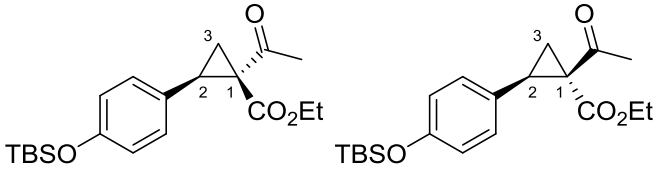
$R_f$ = 0.29 (PE/EtOAc, 1:1, UV, $FeCl_3$).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me–Si), 0.98 (s, 9H, *t*-Bu), 1.30 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.71 (dd, *J* = 9.3, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.14 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.17 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.38 (s, 3H, OMe), 4.17-4.32 (m, 2H, $OC\underline{H}_2CH_3$), 6.75 (d, *J* = 8.5 Hz, 1H, $CH_{Ar}$), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.4 (Me–Si), 14.1 ($OCH_2C\underline{H}_3$), 18.2 (C–Si), 19.1 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 32.0 (CH(2)), 37.4 (C(1)), 52.1 (OMe), 61.6 ($O\underline{C}H_2CH_3$), 119.9 ($CH_{Ar}$), 127.3 ($C_{Ar}$), 129.5 ($CH_{Ar}$), 155.0 ($\underline{C}_{Ar}$–O), 167.2 (C=O), 169.8 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 21.1.
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{30}O_5Si+H^+$]: 379.1935, found: 379.1929.
(1*R**,2*R**)-isomer:



(1R*,2R*)-isomer

$R_f$ = 0.22 (PE/EtOAc, 1:1, UV, $FeCl_3$).
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 6H, Me–Si), 0.89 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 0.98 (s, 9H, *t*-Bu), 1.71 (dd, *J* = 9.3, 5.1 Hz, 1H, $CH_{2a}$(3)), 2.16 (dd, *J* = 8.0, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.18 (app t, *J* = 8.6 Hz, 1H, CH(2)), 3.79 (s, 3H, OMe), 3.81-3.91 (m, 2H, $OC\underline{H}_2CH_3$), 6.75 (d, *J* = 8.5 Hz, 1H, $CH_{Ar}$), 7.08 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.5 (Me–Si), 13.8 ($OCH_2C\underline{H}_3$), 18.2 (C–Si), 19.0 ($CH_2$(3)), 25.7 ($\underline{Me}_3$C–Si), 32.1 (CH(2)), 37.2 (C(1)), 52.7 (OMe), 61.1 ($O\underline{C}H_2CH_3$), 119.8 ($CH_{Ar}$), 127.1 ($C_{Ar}$), 129.7 ($CH_{Ar}$), 155.0 ($\underline{C}_{Ar}$–O), 166.6 (C=O), 170.5 (C=O).
$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 21.0.
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{30}O_5Si+H^+$]: 379.1935, found: 379.1927.

**Ethyl 1-acetyl-2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1-carboxylate (5)**




(1R*,2R*)-isomer (1S*,2R*)-isomer

DAC **5** was obtained from styrene **S1** (142 mg, 0.60 mmol) and ethyl diazoacetoacetate (112 mg, 0.72 mmol) as described for **1a**. Column chromatography (eluent: PE, them PE/EtOAc, 30:1) afforded 35 mg (25%) of starting styrene **S1**, 55 mg of **5** (dr = 2.8:1) and 44 mg of **5** (dr ≈ 30:1, major (1R*,2R*)-isomer) of the target product as colorless oils. Total yield of **5**: 100 mg (46%). Total dr = 6:1.

$R_f$ = 0.20 (PE/EtOAc, 9:1, UV, anisaldehyde).

Relative configuration was assigned on the basis of $^1$H chemical shifts of MeC(O) and $CO_2Et$ groups, assuming that anisotropic effect of Ar-group shifts upfield the protons of the *cis*-located moiety.

(1*R**,2*R**)-isomer (major):

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me–Si), 0.92 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 0.98 (s, 9H, *t*-Bu), 1.73 (dd, *J* = 9.1, 4.5 Hz, 1H, $CH_{2a}$(3)), 2.20 (dd, *J* = 8.1, 4.5 Hz, 1H, $CH_{2b}$(3)), 2.47 (s, 3H, MeC(O)), 3.23 (t, *J* = 8.6 Hz, 1H, CH(2)), 3.75-3.94 (m, 2H, $OC\underline{H}_2CH_3$), 6.75 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.5 (Me–Si), 13.8 ($CH_2\underline{C}H_3$), 18.2 (C–Si), 21.7 ($CH_2$(3)), 25.7 ($\underline{Me}_3C$–Si), 29.7 and 35.4 (CH(2) and $\underline{Me}C$(O)), 44.7 (C(1)), 61.0 ($\underline{C}H_2CH_3$), 119.8 ($CH_{Ar}$), 127.5 ($C_{Ar}$), 130.0 ($CH_{Ar}$), 155.1 ($\underline{C}_{Ar}$–O), 168.3 ($CO_2$), 202.5 (C=O).

$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 21.0.

(1*S**,2*R**)-isomer (minor):

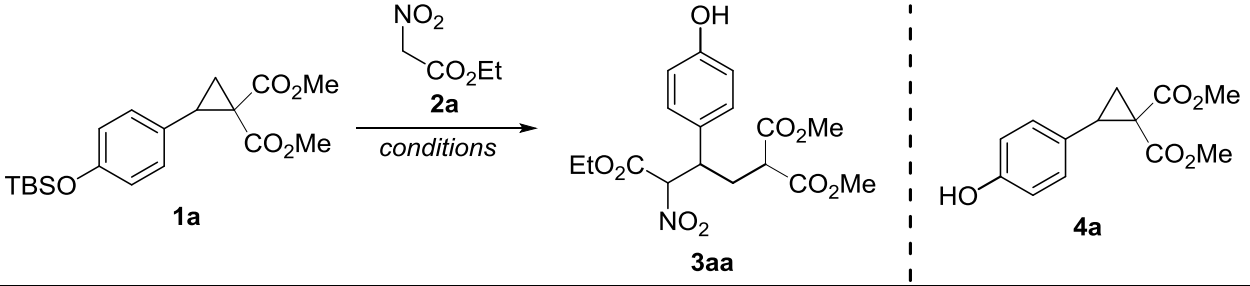
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me–Si), 0.98 (s, 9H, *t*-Bu), 1.33 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.64-1.70 (m, 1H, $CH_{2a}$(3)), 1.94 (s, 3H, MeC(O)), 2.22-2.27 (m, 1H, $CH_{2b}$(3)), 3.17-3.22 (m, 1H, CH(2)), 4.16-4.37 (m, 2H, $OC\underline{H}_2CH_3$), 6.75 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.00 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ -4.5 (Me–Si), 14.2 ($CH_2\underline{C}H_3$), 17.8 ($CH_2$(3)), 18.2 (C–Si), 25.7 ($\underline{Me}_3C$–Si), 30.2 and 34.1 (CH(2) and $\underline{Me}C$(O)), 44.4 (C(1)), 61.6 ($\underline{C}H_2CH_3$), 120.0 ($CH_{Ar}$), 126.4 ($C_{Ar}$), 129.4 ($CH_{Ar}$), 155.1 ($\underline{C}_{Ar}$–O), 170.6 ($CO_2$), 200.3 (C=O).

$^{29}$Si NMR (60 MHz, $CDCl_3$): δ 21.1.

HRMS (ESI): *m/z* calcd. for [$C_{20}H_{30}O_4Si+H^+$]: 363.1986, found: 363.1989.

**Table S1. Complete table for optimization of reaction conditions** (cf. Table 1 in the main manuscript)




1a 3aa 4a

| № | Solvent | Base (equiv.) | T, °C | Yield **3aa**, %[a] | Yield **4a**, %[a] |
|---|---|---|---|---|---|
| 1 | MeCN | - | 25 | 54 | 32 |
| 2 | MeCN | DBU (0.2) | 25 | 86 | 0 |
| 3 | MeCN | DBU (0.2) | 0 | 21 | 70 |
| 4 | MeCN | 2,6-lutidine (0.2) | 25 | 78 | 16 |
| 5 | MeCN | DIPEA (0.2) | 25 | 92 | 11 |
| 6 | MeCN | $NEt_3$ (0.2) | 25 | 85 | 0 |
| 7 | MeCN | Py (0.2) | 25 | 85 | 4 |
| 8 | MeCN | DMAP (0.2) | 25 | 93 | 4 |
| 9 | MeCN | TMG (0.2) | 25 | 87 | 5 |
| 10 | MeCN | NMM (0.2) | 25 | 93 | 0 |
| 11 | MeCN | NMM (0.1) | 25 | 92 | 4 |
| 12 | MeCN | NMM (0.5) | 25 | 90 | 5 |
| 13 | $CH_2Cl_2$ | NMM (0.2) | 25 | 89 | 0 |
| 14 | THF | NMM (0.2) | 25 | 69 | 29 |
| 15 | EtOAc | NMM (0.2) | 25 | 31 | 66 |
| 16 | Tol | NMM (0.2) | 25 | 53 | 42 |
| 17 | DMF | NMM (0.2) | 25 | 71 | 20 |
| 18 | MeCN/$H_2O$ (95:5) | NMM (0.2) | 25 | 90 | 0 |
| 19 | MeCN [b] | NMM (0.2) | 25 | 87 | 0 |
| 20[c] | MeCN | NMM (0.2) | 25 | 25 | 21 |
| 21[d] | MeCN | NMM (0.2) | 0 to 25 | 96 | 0 |

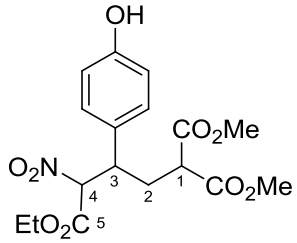
Procedure: To a 0.5 M solution of **1a** and nitro compound **2a** (1.1 equiv) base was added at the indicated temperature under an argon atmosphere, then TBAF·$3H_2O$ (1.1 equiv.) was added, and the reaction mixture was left for 1 d. Then the resulting solution was worked up and analyzed by $^1$H NMR.

[a] Determined by $^1$H NMR with an internal standard (dimethyl terephthalate); [b] MS 3Å (100 mg / 1 mL of MeCN) were added; [c] KF (2 equiv.) was used instead of TBAF·$3H_2O$; [d] A 2 M solution of TBAF·$3H_2O$ in MeCN was added dropwise at 0 °C.

**General procedure (GP) for the reactions between DAC 1 and nucleophiles. Synthesis of nitroalkylmalonates 3 and products 4,6-9**.

To the solution of DAC **1** in MeCN (1.11 ml / 1 mmol of DAC **1**) and nitro compound **2** (1.1 equiv) (for products **3,4**,**6**) or other corresponding CH-acid (1.1. equiv.) (for products **7-9**) N-methylmorpholine (0.2 equiv.) was added under an argon atmosphere. The resulting mixture was cooled to 0 °C and then a solution of TBAF·$3H_2O$ (2 M in MeCN, 1.1 equiv) was added dropwise. The reaction mixture was stirred for 5 min, warmed up to r.t. and left for 2 d, unless otherwise stated. After that it was transferred into EtOAc (20 mL) / $NH_4Cl$ (sat. aq. soln., 15 mL), organic layes was washed with $H_2O$ (15 mL), brine (20 mL), dried over $Na_2SO_4$ and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc) to give target products.

**4-Ethyl 1,1-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3aa)**




Nitromalonate **3aa** was obtained from DAC **1a** (62 mg, 0.17 mmol) and nitro compound **2a** (21 μL, 25 mg, 0.19 mmol) according to GP (reaction time – 1 d). Column chromatography (eluent: PE/EtOAc, 3:1) afforded 57 mg (87%, dr = 1:1) of the target product **3aa** as colorless oil.

$R_f$ = 0.40 (PE/EtOAc, 1:1, UV, $FeCl_3$).

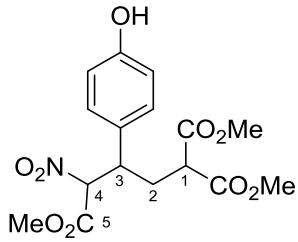
Relative configuration of stereocenters was not determined.

$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.05 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.36 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 2.20-2.46 (m, 2H, $CH_2$(2), both isomers), 3.11-3.21 (m, 1H, CH(1), both isomers), 3.62 (s, 3H, OMe, both isomers), 3.62-3.71 (m, 1H, CH(3)–Ar, both isomers), 3.81 (s, 3H, OMe, both isomers), 3.98-4.10 (m, 2H, $OC\underline{H}_2CH_3$), 4.36 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 5.26 (d, *J* = 9.8 Hz, 1H, CH(4)–$NO_2$), 5.29 (d, *J* = 10.3 Hz, 1H, CH(4)–$NO_2$), 5.29 (br s, overlapped, 1H, OH, both isomers), 6.79 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, both isomers), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.08 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): δ 13.6 and 13.9 ($CH_2\underline{C}H_3$), 30.9 and 31.3 ($CH_2$(2)), 44.0 (CH(3)–Ar), 49.3 and 49.4 (CH(1)), 52.8 and 52.9 (2×$CO_2\underline{Me}$), 63.0 and 63.5 ($O\underline{C}H_2CH_3$), 92.3 and 92.5 (CH(4)–$NO_2$), 116.0 and 116.1 ($CH_{Ar}$), 126.2 and 127.1 ($C_{Ar}$), 129.6 and 130.0 ($CH_{Ar}$), 156.1 and 156.2 ($\underline{C}_{Ar}$–OH), 163.1 and 163.2 (C(5)=O), 169.0, 169.1, 169.26, and 169.31 (all C=O).

HRMS (ESI): *m/z* calcd. for [$C_{17}H_{21}NO_9$+$NH_4^+$]: 401.1555, found: 401.1553.

**Trimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ab)**



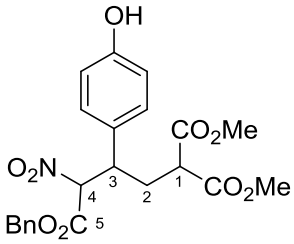

Nitromalonate **3ab** was obtained from DAC **1a** (38 mg, 0.10 mmol) and nitrocompound **2b** (11 μL, 14 mg, 0.11 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1, then 2.5:1) afforded 35 mg (92%, dr = 1:1) of the target product **3ab** as colorless oil.

$R_f$ = 0.31 (PE/EtOAc, 1:1, UV, $FeCl_3$).

Relative configuration of stereocenters was not determined.

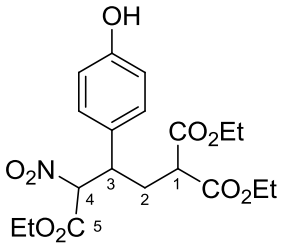
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 2.18-2.44 (m, 2H, $CH_2$(2), both isomers), 3.13-3.18 (m, 1H, CH(1)), 3.59 (s, 3H, OMe), 3.60-3.70 (m, 1H, CH(3)–Ar, both isomers), 3.62 (s, 3H, OMe, both isomers), 3.79 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.89 (s, 3H, OMe), 5.28 (d, *J* = 10.1 Hz, 1H, CH(4)–$NO_2$), 5.31 (d, *J* = 10.9 Hz, 1H, CH(4)–$NO_2$), 5.70 (br s, 1H, OH, both isomers), 6.77 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$, both isomers), 7.06 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.07 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 30.9 and 31.1 ($CH_2$(2)), 43.9 and 44.0 (CH(3)–Ar), 49.3 and 49.4 (CH(1)), 52.84, 52.85, 52.91, 52.92, 53.50, and 53.88 ($CO_2\underline{Me}$), 92.2 and 92.3 (CH(4)–$NO_2$), 116.1 ($CH_{Ar}$), 126.2 and 127.1 ($C_{Ar}$), 129.6 and 129.9 ($CH_{Ar}$), 156.0 and 156.1 ($\underline{C}_{Ar}$–OH), 163.5 and 163.7 (C(5)=O), 168.9, 169.0, 169.2, and 169.3 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{16}H_{19}NO_9$+$Na^+$]: 392.0952, found: 392.0945.

**4-Benzyl 1,1-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ac)**




Nitromalonate **3ac** was obtained from DAC **1a** (74 mg, 0.21 mmol) and nitro compound **2c** (44 mg, 0.23 mmol) according to GP (reaction time – 1 d). Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 69 mg (91%, dr = 1:1) of the target product **3ac** as colorless oil.
$R_f$ = 0.47 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): 2.15-2.45 (m, 2H, $CH_2$(2), both isomers), 3.09-3.18 (m, 1H, CH(1), both isomers), 3.55-3.71 (m, 1H, CH(3)–Ar, both isomers), 3.60 (s, overlapped, 3H, OMe, both isomers), 3.76 and 3.78 (both s, total 3H, OMe, both isomers), 4.93-5.02 (m) and 5.26-5.35 (m) (total 3H, $C\underline{H}_2$Ph and CH(4)–$NO_2$, both isomers), 5.72 (br s, 1H, OH, both isomers), 6.70 (d, *J* = 8.5 Hz, 2H) and 6.75 (d, *J* = 8.5 Hz, 1H) (total 2H, $CH_{Ar}$), 6.97-7.12 (m , 3H, $CH_{Ar}$), 7.29-7.41 (m, 4H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): 30.8 and 31.3 ($CH_2$(2)), 44.0 (CH(3)–Ar), 49.3 and 49.4 (CH(1)), 52.81, 52.87 and 52.89 (2×$CO_2\underline{Me}$), 68.6 and 68.9 ($\underline{C}H_2$Ph), 92.3 and 92.4 (CH(4)–$NO_2$), 116.1 ($CH_{Ar}$), 126.1 and 127.2 ($C_{Ar}$), 128.5, 128.6 128.75, 128.79, 128.9, 129.7 and 130.0 ($CH_{Ph}$ and $CH_{Ar}$), 133.9 and 134.1 ($C_{Ar}$), 155.95 and 156.0 ($\underline{C}_{Ar}$–OH), 162.9 and 163.1 (C(5)=O), 168.9, 169.0, 169.2 and 169.2 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{22}H_{23}NO_9$+$NH_4^+$]: 463.1711, found 463.1705.

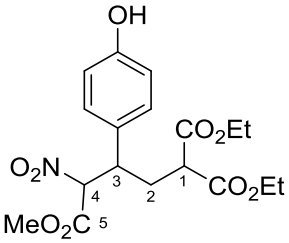
**Triethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ba)**




Nitromalonate **3ba** was obtained from DAC **1b** (43 mg, 0.11 mmol) and nitro compound **2a** (13 μL, 16 mg, 0.12 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3.5:1) afforded 40 mg (89%, dr = 1:1) of the target product **3ba** as colorless oil.
$R_f$ = 0.49 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.

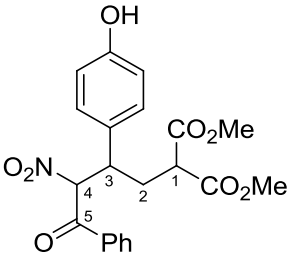
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.04 (t, *J* = 7.1 Hz), 1.20 (t, *J* = 7.1 Hz), 1.31 (t, *J* = 7.1 Hz), 1.32 (t, *J* = 7.1 Hz), and 1.35 (t, *J* = 7.1 Hz) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.17-2.43 (m, 2H, $CH_2$(2), both isomers), 3.07-3.12 (m, 1H, CH(1)), 3.60-3.71 (m, 1H, CH(3)–Ar, both isomers), 3.96-4.15 (m), 4.21-4.32 (m), and 4.35 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.26 (d, *J* = 10.1 Hz, 1H, CH(4)–$NO_2$), 5.29 (d, *J* = 10.5 Hz, 1H, CH(4)–$NO_2$), 5.73 (br s, 1H, OH), 5.77 (br s, 1H, OH), 6.76 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$, both isomers), 7.07 (d, *J* = 8.6, Hz, 2H, $CH_{Ar}$), 7.08 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.5, 13.9, 14.00 and 14.04 (all $CH_2\underline{C}H_3$), 30.8 and 31.2 ($CH_2$(2)), 43.9 (CH(3)–Ar), 49.6 and 49.7 (CH(1)), 61.9, 62.0, 63.0, and 63.4 (all $O\underline{C}H_2CH_3$), 92.4 and 92.6 (CH(4)–$NO_2$), 115.99 and 116.03 ($CH_{Ar}$), 126.2 and 127.2 ($C_{Ar}$), 129.6 and 130.0 ($CH_{Ar}$), 156.1 and 156.2 ($\underline{C}_{Ar}$–OH), 163.1 and 163.2 (C(5)=O), 168.6, 168.7, 168.9, and 169.0 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{25}NO_9$+$NH_4^+$]: 434.1422, found: 434.1422.

**1,1-Diethyl 4-methyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3bb)**




Nitromalonate **3bb** was obtained from DAC **1b** (45 mg, 0.12 mmol) and nitro compound **2b** (12 μL, 16 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 40 mg (89%, dr = 1:1) of the target product **3bb** as colorless oil.
$R_f$ = 0.47 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.20 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$, both isomers), 1.31 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$, both isomers), 2.17-2.42 (m, 2H, $CH_2$(2), both isomers), 3.07-3.13 (m, 1H, CH(1)), 3.57 (s, 3H, OMe), 3.60-3.71 (m, 1H, CH(3)–Ar, both isomers), 3.88 (s, 3H, OMe), 3.99-4.13 (m, 2H, $OC\underline{H}_2CH_3$), 3.99-4.13 (m, 2H, $OC\underline{H}_2CH_3$, both isomers), 4.20-4.31 (m, 2H, $OC\underline{H}_2CH_3$, both isomers), 5.28 (d, *J* = 10.0 Hz, 1H, CH(4)–$NO_2$), 5.32 (d, *J* = 10.6 Hz, 1H, CH(4)–$NO_2$), 5.95 (br s, 1H, OH), 6.00 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, both isomers), 7.06 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.9, 14.01 and 14.04 (all $CH_2\underline{C}H_3$), 30.8 and 31.0 ($CH_2$(2)), 43.87 and 43.93 (CH(3)–Ar), 49.6 and 49.7 (CH(1)), 53.5 and 53.8 ($CO_2\underline{Me}$), 61.9 (all $O\underline{C}H_2CH_3$), 92.3 and 92.4 (CH(4)–$NO_2$), 116.1 ($CH_{Ar}$), 126.2 and 127.2 ($C_{Ar}$), 129.6 and 129.9 ($CH_{Ar}$), 156.05 and 156.11 ($\underline{C}_{Ar}$–OH), 163.5 and 163.7 (C(5)=O), 168.6, 168.7, 168.9, and 169.0 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{18}H_{23}NO_9$+$Na^+$]: 420.1265, found: 420.1259.

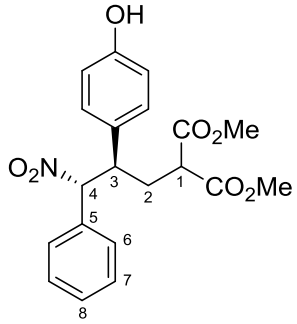
**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-4-oxo-4-phenylbutyl)malonate (3ad)**




Nitromalonate **3ad** was obtained from DAC **1a** (48 mg, 0.13 mmol) and nitro compound **2d** (24 mg, 0.15 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 45 mg (81%, dr = 1:1) of the target product **3ad** as colorless oil.
$R_f$ = 0.30 (PE/EtOAc, 1:1, UV, $FeCl_3$).

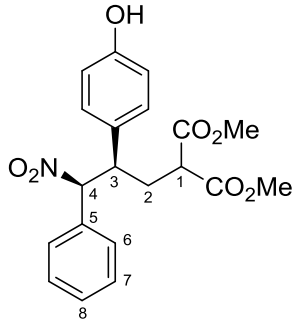
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 2.12-2.26 and 2.35-2.50 (m, 2H, $CH_2$(2), both isomers), 3.16-3.22 (m, 1H, CH(1), both isomers), 3.55 (s, 3H, OMe), 3.59 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.84-3.94 (m, 1H, CH(3)–Ar, both isomers), 5.95 (br s, 1H, OH, both isomers), 6.34 (d, *J* = 10.5 Hz, 1H, CH(4)–$NO_2$), 6.35 (d, *J* = 10.5 Hz, 1H, CH(4)–$NO_2$), 6.61 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.78 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.02 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.16 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.39 (app t, *J* = 7.7 Hz, 2H, $CH_{Ph}$), 7.52-7.57 (m, 3H, $CH_{Ph}$), 7.69 (app t, *J* = 7.4 Hz, 1H, $CH_{Ph}$), 7.77 (d, *J* = 8.3 Hz, 2H, $CH_{Ph}$), 8.10 (d, *J* = 8.3 Hz, 2H, $CH_{Ph}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$, sum of isomers): δ 31.17 and 31.24 ($CH_2$(2)), 44.10 and 44.12 (CH(3)–Ar), 49.4 and 49.6 (CH(1)), 52.77, 52.81, 52.92, and 52.96 (all OMe), 91.8 and 92.4 (CH(4)–$NO_2$), 116.00 and 116.04 ($CH_{Ar}$), 126.2 and 127.4 ($C_{Ar}$), 128.8, 128.9, 129.2, 129.3, 129.9, and 130.2 ($CH_{Ar}$ and $CH_{Ph}$), 134.5 and 135.2 ($CH_{Ph}$), 134.6 and 134.7 ($C_{Ph}$), 155.8 and 156.0 ($\underline{C}_{Ar}$–OH), 168.99, 169.04, 169.31, and 169.34 (all C=O), 187.0 and 187.8 (C(5)=O).
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{21}NO_8$+$NH_4^+$]: 433.1605, found: 433.1603.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-phenylpropyl)malonate (3ae)**
Nitromalonate **3ae** was obtained from DAC **1a** (37 mg, 0.10 mmol) and nitro compound **2e** (16 mg, 0.11 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 29 mg (73%, dr = 1.9:1) of the target product **3ae** as white powder.
$R_f$ = 0.45 (PE/EtOAc, 1:1, UV, $FeCl_3$).
mp = 155-158 °C ($CH_2Cl_2$).
Major isomer (**dimethyl 2-((2R*,3R*)-2-(4-hydroxyphenyl)-3-nitro-3-phenylpropyl)-malonate**):



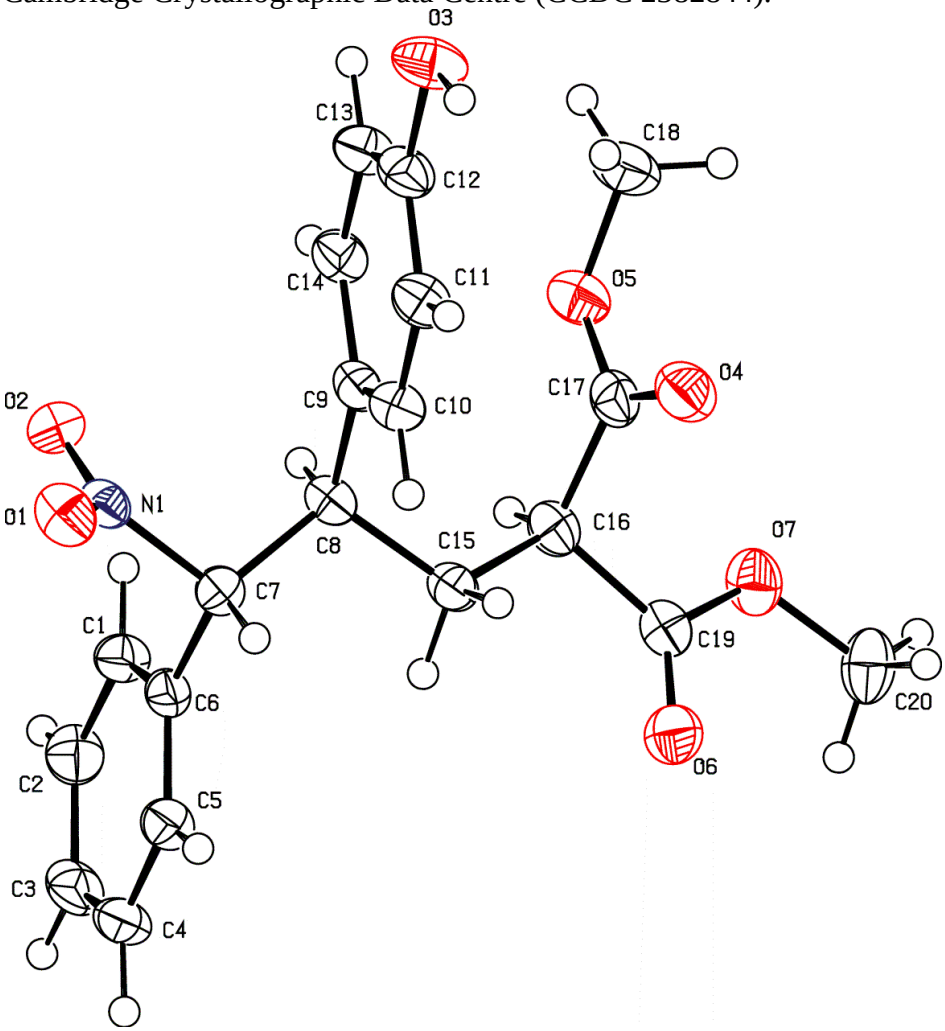

$^1$H NMR (300 MHz, COSY, acetone-$d_6$): δ 1.90 (ddd, *J* = 13.9, 11.1, 3.6 Hz, 1H, $CH_{2a}$(2)), 1.99-2.11 (m, 1H, $CH_{2b}$(2)), 3.02 (dd, *J* = 11.1, 4.0 Hz, 1H, CH(1)), 3.52 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.72-3.83 (m, 1H, CH(3)–Ar), 6.05 (d, *J* = 11.6 Hz, 1H, CH(4)–$NO_2$), 6.87 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.29 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.51-7.58 (m, 3H, $CH_{Ph}$(7) and $CH_{Ph}$(8)), 7.75-7.80 (m, 2H, $CH_{Ph}$(6)), 8.46 (s, 1H, OH).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, acetone-$d_6$): δ 31.0 ($CH_2$(2)), 46.1 (CH(3)–Ar), 49.0 (CH(1)), 51.8 ($CO_2\underline{Me}$), 51.9 ($CO_2\underline{Me}$), 96.0 (CH(4)–$NO_2$), 115.6 ($CH_{Ar}$), 128.5 ($CH_{Ph}$(6) and $C_{Ar}$), 129.2 ($CH_{Ph}$(7)), 129.6 (br, $CH_{Ar}$), 130.2 ($CH_{Ph}$(8)), 133.6 ($C_{Ph}$), 157.2 ($\underline{C}_{Ar}$–OH), 168.7 (C=O), 168.9 (C=O).

Minor isomer (**dimethyl 2-((2R*,3S*)-2-(4-hydroxyphenyl)-3-nitro-3-phenylpropyl)-malonate**):



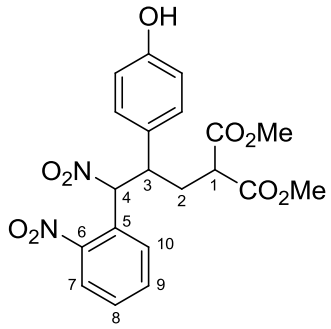

$^{1}$H NMR (300 MHz, COSY, acetone-$d_6$): δ 2.26-2.45 (m, 2H, $CH_2$(2)), 3.13 (dd, *J* = 10.2, 4.6 Hz, 1H, CH(1)), 3.57 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76-3.87 (m, 1H, CH(3)–Ar), 5.99 (d, *J* = 11.4 Hz, 1H, CH(4)–$NO_2$), 6.67 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.08 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.24-7.31 (m, 3H, $CH_{Ph}$(7) and $CH_{Ph}$(8)), 7.44-7.48 (m, 2H, $CH_{Ph}$(6)), 8.30 (s, 1H, OH).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, acetone-$d_6$): δ 32.5 ($CH_2$(2)), 46.4 (CH(3)–Ar), 49.2 (CH(1)), 51.86 ($CO_2$Me), 51.90 ($CO_2$Me), 95.7 (CH(4)–$NO_2$), 115.4 ($CH_{Ar}$), 127.1 ($C_{Ar}$), 128.5 ($CH_{Ph}$(6) and $CH_{Ph}$(7)), 129.4 ($CH_{Ph}$(8)), 130.1 ($CH_{Ar}$), 133.8 ($C_{Ph}$), 156.6 ($C_{Ar}$–OH), 168.7 (C=O), 168.9 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{21}NO_7$+$NH_4^+$]: 405.1656, found: 405.1648.

The crystallographic information for compound **3ae** (major isomer) was deposited in the Cambridge Crystallographic Data Centre (CCDC 2382844).




General view of the compound **3ae** (major isomer) in representation of atoms *via* thermal ellipsoids at 50% probability level.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-(2-nitrophenyl)propyl)malonate (3af)**




Nitromalonate **3af** was obtained from DAC **1a** (31 mg, 0.085 mmol) and nitro compound **2f** (17 mg, 0.093 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 31 mg (86%, dr = 1:1) of the target product **3af** as colorless oil, that solidified upon storage in a fridge.

$R_f$ = 0.40 (PE/EtOAc, 1:1, UV, $FeCl_3$).

mp = 120-122 °C (PE/EtOAc, 1:1)

Relative configuration of stereocenters was not determined.

$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.96 (ddd, *J* = 14.3, 11.5, 3.3 Hz, 1H, $CH_{2a}$(2), isomer-1), 2.16 (app td, *J* = 13.4, 3.4 Hz, 1H, $CH_{2b}$(2), isomer-1), 2.36-2.53 (m, 2H, $CH_2$(2), isomer-2), 3.07 (dd, *J* = 11.3, 3.5 Hz, 1H, CH(1), isomer-1), 3.16 (dd, *J* = 9.7, 5.0 Hz, 1H, CH(1), isomer-2), 3.59 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.70-3.82 (m, 1H, CH(3)–Ar, isomer-2), 3.75 (s, 3H, OMe), 3.75-3.87 (m, 1H, CH(3)–Ar, isomer-1), 3.80 (s, 3H, OMe), 5.57 (br s, 1H, OH, both isomers), 6.50 (d, *J* = 11.3 Hz, 1H, CH(4)–$NO_2$, isomer-1), 6.59 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$, isomer-2), 6.67 (d, *J* = 11.0 Hz, 1H, CH(4)–$NO_2$, isomer-2), 6.83 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$, isomer-1), 6.86 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, isomer-2), 7.19 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, isomer-1), 7.41 (app t, *J* = 7.3 Hz, 1H, CH(8), isomer-2), 7.60 (app t, *J* = 7.5 Hz, 1H, CH(9), isomer-2), 7.65 (app t, *J* = 7.3 Hz, 1H, CH(8), isomer-1), 7.73 (app d, *J* = 7.3 Hz, 1H, CH(7), isomer-2), 7.79 (app t, *J* = 7.5 Hz, 1H, CH(9), isomer-1), 7.88 (app d, *J* = 7.2 Hz, 1H, CH(10), isomer-2), 8.01 (app d, *J* = 7.3 Hz, 1H, CH(7), isomer-1), 8.08 (app d, *J* = 7.2 Hz, 1H, CH(10), isomer-1).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): δ 30.6 ($CH_2$(2), isomer-1), 32.3 ($CH_2$(2), isomer-2), 46.9 (CH(3)–Ar, isomer-1), 47.2 (CH(3)–Ar, isomer-2), 48.9 (CH(1), isomer-1), 49.4 (CH(1), isomer-2), 52.75, 52.82, and 52.85 (all $CO_2\underline{Me}$), 87.6 (CH(4)–$NO_2$, isomer-2), 89.0 (CH(4)–$NO_2$, isomer-1), 116.0 ($CH_{Ar}$, isomer-2), 116.3 ($CH_{Ar}$, isomer-1), 124.9 (CH(7), isomer-2), 125.2 (CH(7), isomer-1), 126.7 ($C_{Ar}$, isomer-2), 127.0 (C(5), isomer-1), 127.2 (C(5), isomer-2), 128.4 ($C_{Ar}$, isomer-1), 128.6 (CH(10), isomer-1), 128.9 (CH(10), isomer-2), 129.5 (br, $CH_{Ar}$, isomer-1), 129.8 ($CH_{Ar}$, isomer-2), 130.5 (CH(8), isomer-2), 131.2 (CH(8), isomer-1), 133.3 (CH(9), isomer-2), 134.0 (CH(9), isomer-1), 149.1 (CH(6)–$NO_2$, isomer-2), 150.1 (CH(6)–$NO_2$, isomer-1), 155.4 ($\underline{C}_{Ar}$–OH, isomer-2), 155.9 ($\underline{C}_{Ar}$–OH, isomer-1), 169.0, 169.1, 169.2, and 169.3 (all C=O).

HRMS (ESI): *m/z* calcd. for [$C_{20}H_{20}N_2O_9$+$NH_4^+$]: 450.1507, found: 450.1515.

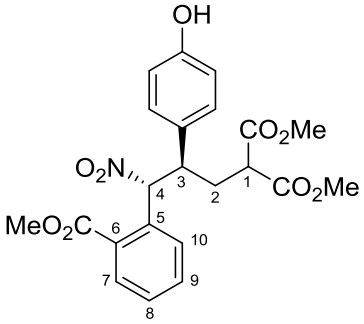
**Dimethyl 2-(2-(4-hydroxyphenyl)-3-(2-(methoxycarbonyl)phenyl)-3-nitropropyl)malonate (3ag)**

Nitromalonate **3ag** was obtained from DAC **1a** (42 mg, 0.12 mmol) and nitro compound **2g** (25 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1, then 2.5:1) afforded 23 mg (45%, dr = 2.3:1) of the target product **3ag** as colorless oil, which solidified upon storage in a fridge.

$R_f$ = 0.48 (PE/EtOAc, 1:1, UV, $FeCl_3$).

mp = 149-151 °C (PE/$CH_2Cl_2$, 10:1, for mixture of diastereomers).

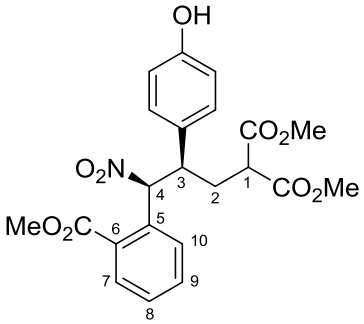
Major isomer (**dimethyl 2-((2R*,3R*)-2-(4-hydroxyphenyl)-3-(2-(methoxycarbonyl)phenyl)-3-nitropropyl)malonate**):




$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.96 (ddd, *J* = 14.1, 11.3, 3.4 Hz, 1H, $CH_{2a}$(2)), 2.16 (app td, *J* = 13.1, 3.7 Hz, 1H, $CH_{2b}$(2)), 3.04 (dd, *J* = 11.3, 3.7 Hz, 1H, CH(1)), 3.56 (s, 3H, OMe), 3.68-3.80 (m, 1H, CH(3)–Ar), 3.73 (s, 3H, OMe), 4.02 (s, 3H, OMe), 5.70 (br s, 1H, OH), 6.81 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.24 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.27 (d, *J* = 11.6 Hz, 1H, CH(4)–$NO_2$), 7.53 (app td, *J* = 7.8, 1.2 Hz, 1H, CH(8)), 7.68 (app td, *J* = 7.7, 1.4 Hz, 1H, CH(9)), 7.96 (dd, *J* = 8.0, 0.8 Hz, 1H, CH10)), 8.06 (dd, *J* = 7.9, 1.3 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 30.6 ($CH_2$(2)), 47.0 (CH(3)–Ar), 49.1 (CH(1)), 52.6, 52.7 and 52.8 (3×$CO_2$<u>Me</u>), 89.9 (CH(4)–$NO_2$), 116.0 ($CH_{Ar}$), 127.3 (CH(10)), 129.5 ($C_{Ar}$), 129.6 (br, $CH_{Ar}$), 129.8 (CH(8)), 130.5 (C(6)), 131.2 (CH(7)), 133.2 (CH(9)), 134.0 (C(5)), 155.7 (<u>C</u>$_{Ar}$–OH), 167.4 (C(6)-<u>C</u>=O), 169.2 (C=O), 169.5 (C=O).

Minor isomer (**dimethyl 2-((2R*,3S*)-2-(4-hydroxyphenyl)-3-(2-(methoxycarbonyl)phenyl)-3-nitropropyl)malonate**):

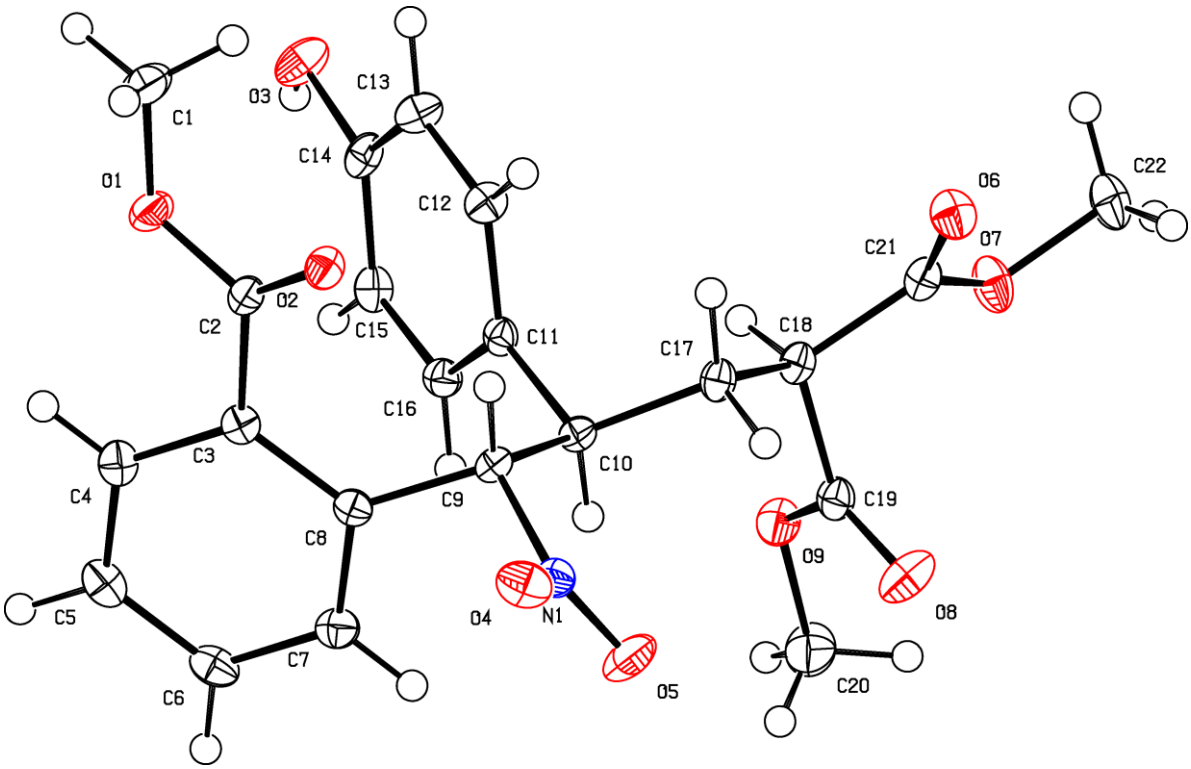



$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.37-2.52 (m, 2H, $CH_2$(2)), 3.17 (dd, *J* = 8.9, 6.0 Hz, 1H, CH(1)), 3.62 (s, 3H, OMe), 3.71-3.81 (m, 1H, CH(3)–Ar), 3.81 (s, 3H, OMe), 3.91 (s, 3H, OMe), 5.42 (br s, 1H, OH), 6.55 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.91 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.27-7.32 (m, 1H, CH(8)), 7.33 (d, *J* = 10.7 Hz, 1H, CH(4)–$NO_2$), 7.47 (app td, *J* = 7.8, 1.4 Hz, 1H, CH(9)), 7.73-7.77 (m, 1H, CH(7)), 7.75-7.79 (m, 1H, CH(10)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 32.6 ($CH_2$(2)), 47.0 (CH(3)–Ar,), 49.6 (CH(1)), 52.5, 52.7, and 52.8 (3×$CO_2$<u>Me</u>), 88.4 (CH(4)–$NO_2$), 115.5 ($CH_{Ar}$), 127.6 ($C_{Ar}$), 127.8 (CH(10)), 129.1 (CH(8)), 129.8 (C(6)), 130.1 ($CH_{Ar}$), 130.8 (CH(7)), 132.4 (CH(9)), 134.1 (C(5)), 155.1 (<u>C</u>$_{Ar}$–OH), 167.1 (C(6)-<u>C</u>=O), 169.2 (C=O), 169.3 (C=O).

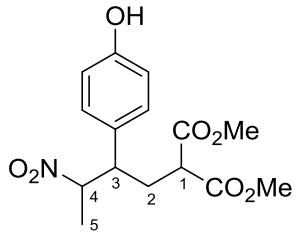
HRMS (ESI): *m/z* calcd. for [$C_{22}H_{23}NO_9$+$NH_4^+$]: 463.1711, found: 463.1723.

The crystallographic information for compound **3ag** (minor isomer) was deposited in the Cambridge Crystallographic Data Centre (CCDC 2373466).




General view of the compound **3ag** (minor isomer) in representation of atoms *via* thermal ellipsoids at 50% probability level.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitrobutyl)malonate (3ah)**




Nitromalonate **3ah** was obtained from DAC **1a** (31 mg, 0.085 mmol) and nitro compound **2h** (7 μL, 7 mg, 0.10 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 19 mg (69%, dr = 1.6:1) of the target product **3ah** as colorless oil.

$R_f$ = 0.42 (PE/EtOAc, 1:1, UV, $FeCl_3$).

Major isomer:

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.30 (d, *J* = 6.7 Hz, 3H, Me(5)), 2.20-2.30 (m, 2H, $CH_2$(2)), 3.05-3.16 (m, 2H, CH(1) and CH(3)–Ar), 3.61 (s, 3H, OMe), 3.76 (s, 3H, OMe), 4.69 (dq, *J* = 9.8, 6.7 Hz, 1H, CH(4)–$NO_2$), 5.66 (br s, 1H, OH), 6.80 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.00 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

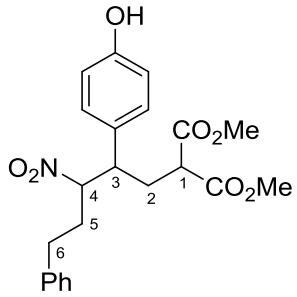
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 18.0 (Me(5)), 31.6 ($CH_2$(2)), 47.3 (CH(3)–Ar), 49.6 (CH(1)), 52.77 and 52.78 (2×OMe), 88.0 (CH(4)–$NO_2$), 116.2 ($CH_{Ar}$), 128.2 ($C_{Ar}$), 129.6 ($CH_{Ar}$), 155.7 ($\underline{C}_{Ar}$–OH), 169.1 (C=O), 169.4 (C=O).

Minor isomer:

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.65 (d, *J* = 6.6 Hz, 3H, Me(5)), 2.14 (ddd, *J* = 13.7, 12.5, 4.1 Hz, 1H, $CH_a$(2)), 2.44 (ddd, *J* = 13.7, 10.7, 3.5 Hz, 1H, $CH_{2b}$(2)), 3.05-3.16 (m, 2H, CH(1) and CH(3)–Ar), 3.65 (s, 3H, OMe), 3.78 (s, 3H, OMe), 4.75 (dq, *J* = 9.0, 6.6 Hz, 1H, CH(4)–$NO_2$), 5.66 (br s, 1H, OH), 6.77 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.00 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).

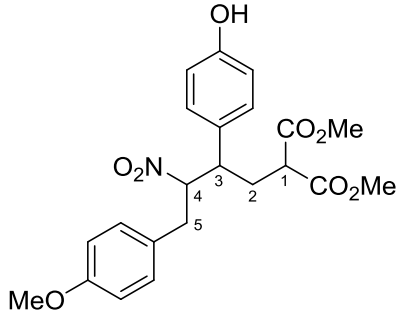
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 17.5 (Me(5)), 30.4 ($CH_2$(2)), 47.4 (CH(3)–Ar), 49.3 (CH(1)), 52.82 and 52.84 (2×OMe), 88.3 (CH(4)–$NO_2$), 115.9 ($CH_{Ar}$), 128.7 ($C_{Ar}$), 129.3 ($CH_{Ar}$), 155.7 ($\underline{C}_{Ar}$–OH), 169.3 (C=O), 169.5 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{15}H_{19}NO_7$+$NH_4^+$]: 343.1500, found: 343.1496.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-5-phenylpentyl)malonate (3ai)**




Nitromalonate **3ai** was obtained from DAC **1a** (41 mg, 0.11 mmol) and nitro compound **2i** (20 mg, 0.12 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 28 mg (60%, dr = 1.8:1) of the target product **3ai** as colorless oil.
$R_f$ = 0.48 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
Major isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.65-1.77 (m, 1H, $CH_{2a}$(5)), 2.07-2.17 (m, 1H, $CH_{2b}$(5)), 2.17-2.50 (m, 3H, $CH_2$(2) and $CH_{2a}$(6)), 2.54-2.65 (m, 1H, $CH_{2b}$(6)), 3.04-3.18 (m, 2H, CH(1) and CH(3)–Ar), 3.60 (s, 3H, OMe), 3.76 (s, 3H, OMe), 4.59 (app td, *J* = 10.7, 2.7 Hz, 1H, CH(4)–$NO_2$), 5.65 (br s, 1H, OH), 6.77 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.91 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.99-7.02 (m, 2H, $CH_{Ph}$), 7.18-7.36 (m, 3H, $CH_{Ph}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 31.8 ($CH_2$(2) and $CH_2$(6)), 33.6 ($CH_2$(5)), 46.6 (CH(3)–Ar), 49.5 (CH(1)), 52.76 and 52.78 (2×OMe), 92.5 (CH(4)–$NO_2$), 116.2 ($CH_{Ar}$), 126.4 ($CH_{Ph}$), 128.4 ($CH_{Ph}$), 128.5 ($C_{Ar}$ and $CH_{Ph}$), 129.5 ($CH_{Ar}$), 139.4 ($C_{Ph}$), 155.7 ($\underline{C}_{Ar}$–OH), 169.1 (C=O), 169.3 (C=O).
Minor isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.02-2.15 (m, 1H, $CH_{2a}$(2)), 2.27-2.41 (m, 2H, $CH_2$(5)), 2.39-2.50 (m, 1H, $CH_{2b}$(2)), 2.53-2.66 (m, 1H, $CH_{2a}$(6)), 2.67-2.77 (m, 1H, $CH_{2b}$(6)), 3.04-3.18 (m, 2H, CH(1) and CH(3)–Ar), 3.64 (s, 3H, OMe), 3.76 (s, 3H, OMe), 4.67 (app td, *J* = 9.6, 3.5 Hz, 1H, CH(4)–$NO_2$), 5.65 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.18-7.36 (m, 5H, $CH_{Ph}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 30.9 ($CH_2$(2)), 32.0 ($CH_2$(6)), 33.5 ($CH_2$(5)), 46.6 (CH(3)–Ar), 49.2 (CH(1)), 52.82 and 52.84 (2×OMe), 92.9 (CH(4)–$NO_2$), 115.9 ($CH_{Ar}$), 126.6 ($CH_{Ph}$), 128.5 ($CH_{Ph}$), 128.7 ($C_{Ar}$ and $CH_{Ph}$), 129.4 ($CH_{Ar}$), 139.6 ($C_{Ph}$), 155.7 ($\underline{C}_{Ar}$–OH), 169.2 (C=O), 169.5 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{22}H_{25}NO_7$+$NH_4^+$]: 433.1969, found: 433.1966.

**Dimethyl 2-(2-(4-hydroxyphenyl)-4-(4-methoxyphenyl)-3-nitrobutyl)malonate (3aj)**




Nitromalonate **3aj** was obtained from DAC **1a** (44 mg, 0.12 mmol) and nitro compound **2j** (24 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1, then 2.5:1) afforded 38 mg (73%, dr = 1.5:1) of the target product **3aj** as colorless oil.

$R_f$ = 0.38 (PE/EtOAc, 1:1, UV, $FeCl_3$).

Relative configuration of stereocenters was not determined.

Major isomer:

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.25-2.30 (m, 2H, $CH_2$(2)), 2.68 (dd, *J* = 14.5, 3.0 Hz, 1H, $CH_{2a}$(5)), 2.95 (dd, *J* = 14.5, 11.2 Hz, 1H, $CH_{2b}$(5)), 3.10-3.22 (m, 2H, CH(1) and CH(3)–Ar), 3.61 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.77 (s, 3H, OMe), 4.77 (app td, *J* = 11.0, 3.1 Hz, 1H, CH(4)–$NO_2$), 5.86 (br s, 1H, OH), 6.77 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.84 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.90 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.07 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 31.7 ($CH_2$(2)), 37.7 ($CH_2$(5)), 46.8 (CH(3)–Ar), 49.5 (CH(1)), 52.8 (2×$CO_2$Me), 55.2 (OMe), 95.5 (CH(4)–$NO_2$), 114.2 ($CH_{Ar}$), 116.4 ($CH_{Ar}$), 127.5 ($C_{Ar}$), 128.4 ($C_{Ar}$), 129.5 (2×$CH_{Ar}$), 155.9 ($C_{Ar}$–OH), 158.8 ($C_{Ar}$–OMe), 169.1 (C=O), 169.4 (C=O).

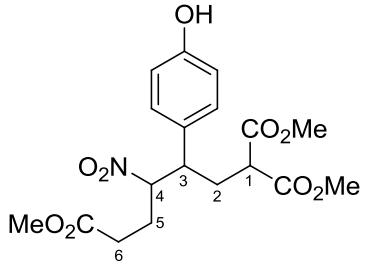
Minor isomer:

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.19-2.29 (m, 1H, $CH_{2a}$(2)), 2.57-2.67 (m, 1H, $CH_{2b}$(2)), 3.09-3.22 (m, 3H, CH(1), CH(3)–Ar, and $CH_{2a}$(5)), 3.29 (dd, *J* = 14.6, 3.6 Hz, 1H, $CH_{2b}$(5)), 3.67 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.79 (s, 3H, OMe), 4.86 (app td, *J* = 10.6, 3.8 Hz, 1H, CH(4)–$NO_2$), 5.86 (br s, 1H, OH), 6.76 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.83 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.00 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.07 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 31.1 ($CH_2$(2)), 37.1 ($CH_2$(5)), 46.7 (CH(3)–Ar), 49.3 (CH(1)), 52.87 and 52.9 (2×$CO_2$Me), 55.2 (OMe), 95.1 (CH(4)–$NO_2$), 114.3 ($CH_{Ar}$), 116.0 ($CH_{Ar}$), 127.2 ($C_{Ar}$), 128.3 ($C_{Ar}$), 129.4 ($CH_{Ar}$), 129.8 ($CH_{Ar}$), 155.8 ($C_{Ar}$–OH), 158.9 ($C_{Ar}$–OMe), 169.3 (C=O), 169.5 (C=O).

HRMS (ESI): *m/z* calcd. for [$C_{22}H_{25}NO_8$+$NH_4^+$]: 449.1918, found: 449.1915.

**Trimethyl 3-(4-hydroxyphenyl)-4-nitrohexane-1,1,6-tricarboxylate (3ak)**



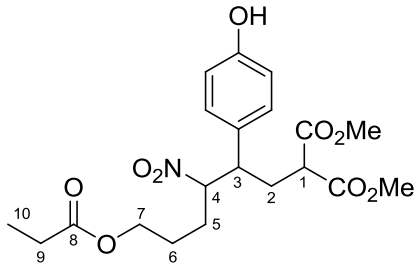

Nitromalonate **3ak** was obtained from DAC **1a** (33 mg, 0.092 mmol) and nitro compound **2k** (15 mg, 0.10 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 2.5:1) afforded 25 mg (68%, dr = 1.5:1) of the target product **3ak** as colorless oil.

$R_f$ = 0.32 (PE/EtOAc, 1:1, UV, $FeCl_3$).

Relative configuration of stereocenters was not determined.

Major isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.77-1.88 (m, 1H, $CH_{2a}$(5)), 1.95-2.07 (m, 1H, $CH_{2b}$(5)), 2.18-2.31 (m, 4H, $CH_2$(2) and $CH_2$(6)), 3.07-3.16 (m, 2H, CH(1) and CH(3)–Ar), 3.61 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.76 (s, 3H, OMe), 4.69-4.79 (m, 1H, CH(4)–$NO_2$), 5.87 (br s, 1H, OH), 6.80 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.01 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 27.2 ($CH_2$(5)), 29.8 and 31.8 ($CH_2$(2) and $CH_2$(6)), 46.7 (CH(3)–Ar), 49.4 (CH(1)), 52.0 and 52.8 (3×$CO_2$Me), 92.2 (CH(4)–$NO_2$), 116.3 ($CH_{Ar}$), 128.0 ($C_{Ar}$), 129.6 ($CH_{Ar}$), 155.9 ($C_{Ar}$–OH), 169.0 (C=O), 169.3 (C=O), 172.5 (C=O).
Minor isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.10-2.56 (m, 6H, $CH_2$(2), $CH_2$(5), and $CH_2$(6)), 3.07-3.16 (m, 2H, CH(1) and CH(3)–Ar), 3.65 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.77 (s, 3H, OMe), 4.72-4.83 (m, 1H, CH(4)–$NO_2$), 5.87 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.98 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 26.7, 29.8, and 30.8 ($CH_2$(2), $CH_2$(5), and $CH_2$(6)), 46.5 (CH(3)–Ar), 49.3 (CH(1)), 52.0, 52.80, and 52.84 (3×$CO_2$Me), 92.4 (CH(4)–$NO_2$), 116.0 ($CH_{Ar}$), 128.3 ($C_{Ar}$), 129.4 ($CH_{Ar}$), 155.8 ($C_{Ar}$–OH), 169.2 (C=O), 169.4 (C=O), 172.4 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{18}H_{23}NO_9$+$NH_4^+$]: 415.1711, found: 415.1707.

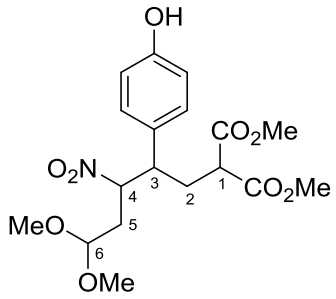
**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-6-(propionyloxy)hexyl)malonate (3al)**




Nitromalonate **3al** was obtained from DAC **1a** (41 mg, 0.12 mmol) and nitro compound **2l** (22 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1, then 2.5:1) afforded 35 mg (72%, dr = 1.6:1) of the target product **3al** as colorless oil.
$R_f$ = 0.39 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
Major isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.07 (t, *J* = 7.6 Hz, 3H, Me(10)), 1.40-1.60 (m, 3H, $CH_{2a}$(5) and $CH_2$(6)), 1.77-1.90 (m, 1H, $CH_{2b}$(5)), 2.17-2.29 (m, 2H, $CH_2$(2)), 2.25 (q, *J* = 7.6 Hz, 2H, $CH_2$(9)), 3.04-3.14 (m, 2H, CH(1) and CH(3)–Ar), 3.60 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.90-4.00 (m, 2H, $CH_2$(7)–O), 4.62 (app td, *J* = 10.5, 2.3 Hz, 1H, CH(4)–$NO_2$), 6.11 (br s, 1H, OH), 6.80 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.98 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 9.0 (Me(10)), 24.9 ($CH_2$(6)), 27.5 ($CH_2$(9)), 28.7 ($CH_2$(5)), 31.7 ($CH_2$(2)), 46.7 (CH(3)–Ar), 49.4 (CH(1)), 52.8 (2×$CO_2$Me), 62.8 ($CH_2$(7)–O), 92.9 (CH(4)–$NO_2$), 116.2 ($CH_{Ar}$), 128.1 ($C_{Ar}$), 129.5 ($CH_{Ar}$), 156.0 ($C_{Ar}$–OH), 169.0 (C=O), 169.3 (C=O), 174.7 (C(8)=O) .
Minor isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.16 (t, *J* = 7.6 Hz, 3H, Me(10)), 1.63-1.73 (m, 2H, $CH_2$(6)), 2.04-2.12 (m, 3H, $CH_{2a}$(2) and $CH_2$(5)), 2.37 (q, *J* = 7.6 Hz, 2H, $CH_2$(9)), 2.45 (ddd, *J* = 13.7, 10.9, 3.5 Hz, $CH_{2b}$(2)), 3.04-3.14 (m, 2H, CH(1) and CH(3)–Ar), 3.65 (s, 3H, OMe), 3.77 (s, 3H, OMe), 4.05-4.20 (m, 2H, $CH_2$(7)–O), 4.70 (app dt, *J* = 9.2, 7.0 Hz, 1H, CH(4)–$NO_2$), 6.06 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 9.1 (Me(10)), 25.1 ($CH_2$(6)), 27.6 ($CH_2$(9)), 28.2 ($CH_2$(5)), 30.8 ($CH_2$(2)), 46.5 (CH(3)–Ar), 49.2 (CH(1)), 52.81 and 52.84 (2×$CO_2$Me), 63.0 ($CH_2$(7)–O), 93.1 (CH(4)–$NO_2$), 116.0 ($CH_{Ar}$), 128.3 ($C_{Ar}$), 129.3 ($CH_{Ar}$), 155.9 ($C_{Ar}$–OH), 169.2 (C=O), 169.4 (C=O), 174.8 (C(8)=O) .
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{27}NO_9$+$Na^+$]: 448.1578, found: 448.1577.

**Dimethyl 2-(2-(4-hydroxyphenyl)-5,5-dimethoxy-3-nitropentyl)malonate (3am)**

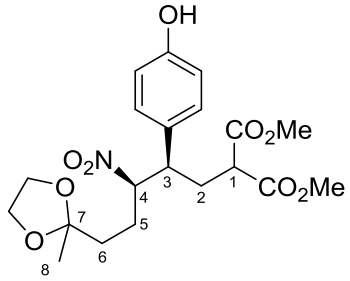



Nitromalonate **3am** was obtained from DAC **1a** (42 mg, 0.12 mmol) and nitro compound **2m** (19 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 2.5:1) afforded 35 mg (76%, dr = 2.4:1) of the target product **3am** as colorless oil.
$R_f$ = 0.35 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
Major isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.69 (ddd, *J* = 14.9, 6.9, 2.4 Hz, 1H, $CH_{2a}$(5)), 2.14-2.26 (m, 3H, $CH_{2b}$(5) and $CH_2$(2)), 3.00-3.15 (m, 2H, CH(1) and CH(3)–Ar), 3.24 (s, 6H, 2×OMe), 3.61 (s, 3H, OMe), 3.75 (s, 3H, OMe), 4.18 (dd, *J* = 6.9, 4.1 Hz, 1H, O–CH(6)–O), 4.75 (app td, *J* = 10.8, 2.4 Hz, 1H, CH(4)–$NO_2$), 6.09 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 31.4 ($CH_2$(2)), 35.3 ($CH_2$(5)), 46.7 (CH(3)–Ar), 49.5 (CH(1)), 52.8 (2×OMe), 54.0 (OMe), 54.4 (OMe), 89.2 (CH(4)–$NO_2$), 102.1 (O–CH(6)–O), 116.3 ($CH_{Ar}$), 127.9 ($C_{Ar}$), 129.5 ($CH_{Ar}$), 156.0 ($C_{Ar}$–OH), 169.0 (C=O), 169.3 (C=O).
Minor isomer:
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.11-2.23 (m, 2H, $CH_{2a}$(2) and $CH_{2a}$(5)), 2.31-2.42 (m, 1H, $CH_{2b}$(5)), 2.40-2.50 (m, 1H, $CH_{2b}$(2)), 3.00-3.15 (m, 2H, CH(1) and CH(3)–Ar), 3.33 (s, 3H, OMe), 3.35 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.76 (s, 3H, OMe), 4.32 (dd, *J* = 6.9, 3.9 Hz, 1H, O–CH(6)–O), 4.75-4.84 (m, 1H, CH(4)–$NO_2$), 5.99 (br s, 1H, OH), 6.73 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 30.7 ($CH_2$(2)), 34.7 ($CH_2$(5)), 46.7 (CH(3)–Ar), 49.3 (CH(1)), 52.8 (OMe), 52.9 (OMe), 54.1 (OMe), 54.4 (OMe), 89.2 (CH(4)–$NO_2$), 102.1 (O–CH(6)–O), 115.9 ($CH_{Ar}$), 127.9 ($C_{Ar}$), 129.5 ($CH_{Ar}$), 155.9 ($C_{Ar}$–OH), 169.2 (C=O), 169.5 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{18}H_{25}NO_9$+$NH_4^+$]: 417.1868, found: 417.1865.

**Dimethyl 2-(2-(4-hydroxyphenyl)-5-(2-methyl-1,3-dioxolan-2-yl)-3-nitropentyl)malonate (3an)**

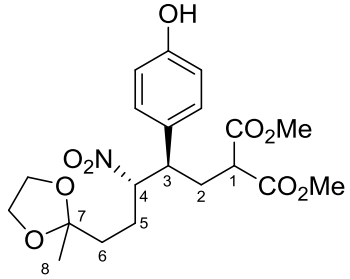
Nitromalonate **3an** was obtained from DAC **1a** (42 mg, 0.12 mmol) and nitro compound **2n** (23 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 2.5:1, then 2:1) afforded 32 mg (65%, dr = 1.9:1) of the target product **3an** as colorless oil, that solidified upon storage in a fridge.
$R_f$ = 0.38 (PE/EtOAc, 1:1, UV, $FeCl_3$).
mp = 87-89 °C and 103-106 °C ($CH_2Cl_2$) (for mixture of diastereomers).

Major isomer (**dimethyl 2-((2R*,3R*)-2-(4-hydroxyphenyl)-5-(2-methyl-1,3-dioxolan-2-yl)-3-nitropentyl)malonate**):



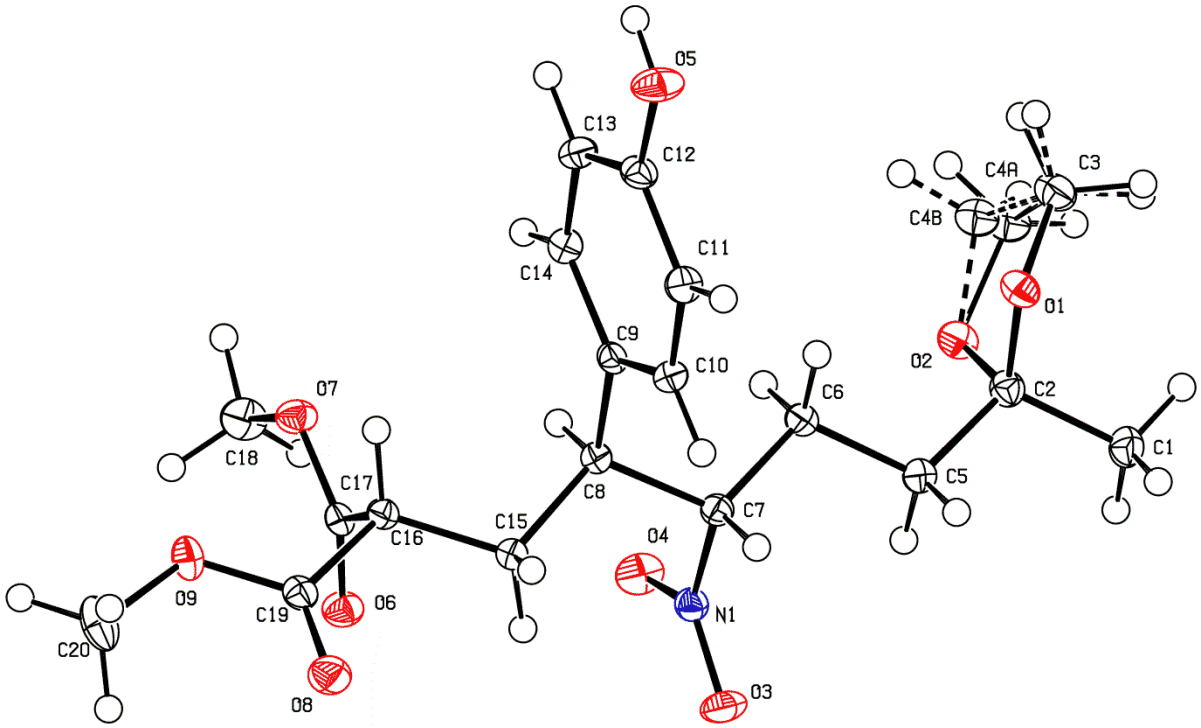

$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.17 (s, 3H, Me(8)), 1.51-1.60 (m, 3H, $CH_{2a}$(5) and $CH_2$(6)), 1.78-1.93 (m, 1H, $CH_{2b}$(5)), 2.18-2.30 (m, 2H, $CH_2$(2)), 3.01-3.11 (m, 1H, CH(3)–Ar), 3.04-3.15 (m, 1H, CH(1)), 3.60 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.72-4.00 (m, 4H, $OCH_2CH_2O$), 4.66-4.75 (m, 1H, CH(4)–$NO_2$), 6.08 (br s, 1H, OH), 6.77 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.99 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 23.8 (Me(8)), 26.8 ($CH_2$(5)), 31.7 ($CH_2$(2)), 34.5 ($CH_2$(6)), 46.8 (CH(3)–Ar), 49.5 (CH(1)), 52.8 (2×$CO_2\underline{Me}$), 64.5 and 64.6 ($OCH_2CH_2O$), 93.3 (CH(4)–$NO_2$), 109.2 (O–C(7)–O), 116.1 ($CH_{Ar}$), 128.3 ($C_{Ar}$), 129.5 ($CH_{Ar}$), 155.8 ($\underline{C}_{Ar}$–OH), 169.1 (C=O), 169.4 (C=O).

Minor isomer (**dimethyl 2-((2R*,3S*)-2-(4-hydroxyphenyl)-5-(2-methyl-1,3-dioxolan-2-yl)-3-nitropentyl)malonate**):



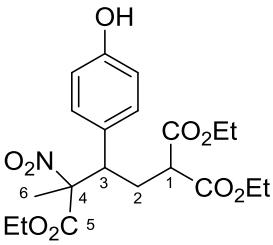

$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.32 (s, 3H, Me(8)), 1.66-1.72 (m, 2H, $CH_2$(6)), 2.07-2.16 (m, 3H, $CH_{2a}$(2) and $CH_2$(5)), 2.48 (ddd, *J* = 14.1, 10.9, 3.5 Hz, 1H, $CH_{2b}$(2)), 3.01-3.11 (m, 1H, CH(3)–Ar), 3.04-3.15 (m, 1H, CH(1)), 3.64 (s, 3H, OMe), 3.72-4.00 (m, 4H, $OCH_2CH_2O$), 3.77 (s, 3H, OMe), 4.66-4.75 (m, 1H, CH(4)–$NO_2$), 6.08 (br s, 1H, OH), 6.73 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 23.9 (Me(8)), 26.1 ($CH_2$(5)), 30.8 ($CH_2$(2)), 34.8 ($CH_2$(6)), 46.5 (CH(3)–Ar), 49.3 (CH(1)), 52.79 and 52.83 (2×$CO_2\underline{Me}$), 64.7 and 64.8 ($OCH_2CH_2O$), 93.6 (CH(4)–$NO_2$), 109.1 (O–C(7)–O), 115.9 ($CH_{Ar}$), 128.5 ($C_{Ar}$), 129.3 ($CH_{Ar}$), 155.8 ($\underline{C}_{Ar}$–OH), 169.2 (C=O), 169.5 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{27}NO_9$+$NH_4^+$]: 443.2024, found: 443.2022.

The crystallographic information for compound **3an** (major isomer) was deposited in the Cambridge Crystallographic Data Centre (CCDC 2382845).




General view of the compound **3an** (major isomer) in representation of atoms *via* thermal ellipsoids at 50% probability level.

**Triethyl 3-(4-hydroxyphenyl)-4-nitropentane-1,1,4-tricarboxylate (3bo)**




Nitromalonate **3bo** was obtained from DAC **1b** (45 mg, 0.12 mmol) and nitro compound **2o** (19 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 47 mg (96%, dr = 1:1) of the target product **3bo** as colorless oil.

$R_f$ = 0.53 (PE/EtOAc, 1:1, UV, $FeCl_3$).

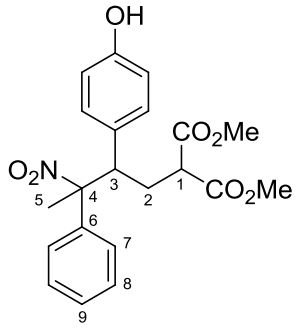
Relative configuration of stereocenters was not determined.

$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.16-1.34 (m, 9H, 3×$CH_2C\underline{H}_3$, both isomers), 1.74 (s, 3H, Me(6)), 1.75 (s, 3H, Me(6)), 2.37-2.56 (m, 2H, $CH_2$(2), both isomers), 3.05-3.13 (m, 1H, CH(1)), 3.66-3.76 (m, 1H, CH(3)–Ar, both isomers), 3.90-4.35 (m, 6H, 3×$OC\underline{H}_2CH_3$), 6.10 (br s, 1H, OH, both isomers), 6.73 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, both isomers), 7.01 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.04 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.70, 13.74, 13.86, and 14.03 (all $CH_2\underline{C}H_3$), 18.9 and 19.7 (Me(6)), 29.8 and 29.9 ($CH_2$(2)), 47.8 and 48.1 (CH(3)–Ar), 50.5 (CH(1)), 61.77, 61.78, 61.80, 63.0, and 63.1 (all $O\underline{C}H_2CH_3$), 95.9 and 96.2 (C(4)–$NO_2$), 115.76 and 115.80 ($CH_{Ar}$), 126.18 and 126.19 ($C_{Ar}$), 130.74 and 130.76 (br, $CH_{Ar}$), 156.18 and 156.24 ($\underline{C}_{Ar}$–OH), 166.3 and 166.7 (C(5)=O), 168.9, 169.2, and 169.3 (all C=O).

HRMS (ESI): *m/z* calcd. for [$C_{20}H_{27}NO_9$+$Na^+$]: 448.1578, found: 448.1567.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-phenylbutyl)malonate (3ap)**




Nitromalonate **3ap** was obtained from DAC **1a** (41 mg, 0.11 mmol) and nitro compound **2p** (19 mg, 0.12 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 41 mg (90%, dr = 1:1) of the target product **3ap** as colorless oil, that solidified upon storage in a fridge.

$R_f$ = 0.44 (PE/EtOAc, 1:1, UV, $FeCl_3$).

mp = 124-128 °C and 144-145 °C ($CH_2Cl_2$/EtOAc, 1:1, for mixture of diastereomers).

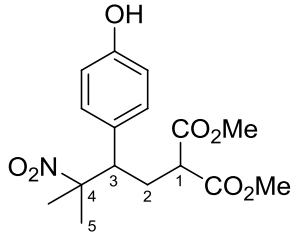
Relative configuration of stereocenters was not determined.

$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.94 (s, 3H, Me(5), isomer-2), 1.99 (s, 3H, Me(5), isomer-1), 2.02-2.10 (m, 1H, $CH_{2a}$(2), isomer-1), 2.16 (app td, *J* = 13.1, 4.0 Hz, 1H, $CH_{2b}$(2), isomer-1), 2.34 (ddd, *J* = 12.6, 10.3, 2.2 Hz, 1H, $CH_{2a}$(2), isomer-2), 2.59 (ddd, *J* = 13.8, 12.3, 4.6 Hz, 1H, $CH_{2b}$(2), isomer-2), 3.08 (dd, *J* = 10.7, 4.0 Hz, CH(1), isomer-1), 3.16 (dd, *J* = 10.2, 4.6 Hz, 1H, CH(1), isomer-2), 3.56 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.88 (dd, *J* = 12.0, 1.9 Hz, 1H, CH(3)–Ar, isomer-2), 4.15 (dd, *J* = 12.4, 3.0 Hz, 1H, CH(3)–Ar, isomer-1), 5.62 (br s, 1H, OH), 5.80 (br s, 1H, OH), 6.59 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$, isomer-2), 6.76 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$, isomer-1), 6.79 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, isomer-2), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, isomer-1), 7.14-7.19 (m, 2H, $CH_{Ph}$(7), isomer-2), 7.23-7.30 (m, 3H, $CH_{Ph}$(8) and $CH_{Ph}$(9), isomer-2), 7.41-7.49 (m, 3H, $CH_{Ph}$(8) and $CH_{Ph}$(9), isomer-1), 7.67-7.71 (m, 2H, $CH_{Ph}$(7), isomer-1).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): δ 18.5 (Me(5), isomer-1), 20.8 (Me(5), isomer-2), 29.3 ($CH_2$(2), isomer-1), 29.8 ($CH_2$(2), isomer-2), 49.8 and 49.9 (CH(1) and CH(3)–Ar, isomer-1), 50.4 and 51.1 (CH(1) and CH(3)–Ar, isomer-2), 52.67, 52.74, and 52.76 (all OMe), 96.4 (C(4)–$NO_2$, isomer-1), 97.5 (C(4)–$NO_2$, isomer-2), 115.3 ($CH_{Ar}$, isomer-2), 115.6 ($CH_{Ar}$, isomer-1), 125.3 ($CH_{Ph}$(7) , isomer-2), 126.9 ($C_{Ar}$, isomer-1), 127.0 ($CH_{Ph}$(7) , isomer-1), 127.2 ($C_{Ar}$, isomer-2), 128.5 ($CH_{Ph}$(8) , isomer-2), 128.6 ($CH_{Ph}$(9), isomer-2), 128.7 ($CH_{Ph}$(8), isomer-1), 129.5 ($CH_{Ph}$(9), isomer-1), 130.9 ($CH_{Ar}$, isomer-2), 131.5 ($CH_{Ar}$, isomer-1), 136.9 ($C_{Ph}$, isomer-1), 138.7 ($C_{Ph}$, isomer-2), 155.4 ($\underline{C}_{Ar}$–OH, isomer-2), 155.8 ($\underline{C}_{Ar}$–OH, isomer-1), 169.2, 169.4, 169.59, and 169.63 (all C=O).

HRMS (ESI): *m/z* calcd. for [$C_{21}H_{23}NO_7$+$NH_4^+$]: 419.1813, found: 419.1802.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-methyl-3-nitrobutyl)malonate (3aq)**



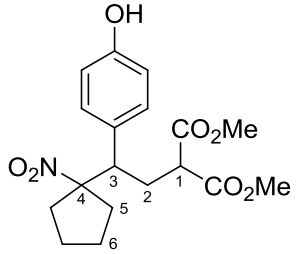

Nitromalonate **3aq** was obtained from DAC **1a** (37 mg, 0.01 mmol) and nitro compound **2q** (10 μL, 10 mg, 0.11 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 21 mg (61%) of the target product **3aq** as colorless oil, which solidified upon storage in a fridge.

$R_f$ = 0.47 (PE/EtOAc, 1:1, UV, $FeCl_3$).

mp = 76-78 °C (PE/EtOAc, 1:1).

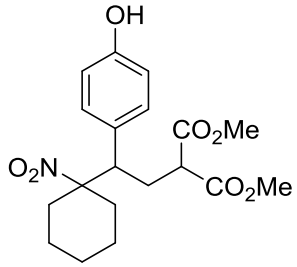
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.45 (s, 3H, $Me_a$(8)), 1.63 (s, 3H, $Me_b$(8)), 2.16-2.31 (m, 1H, $CH_{2a}$(2)), 2.35 (app td, *J* = 12.7, 4.3 Hz, 1H, $CH_{2a}$(2)), 3.09 (dd, *J* = 10.4, 4.3 Hz, 1H, CH(1)), 3.29 (dd, *J* = 12.2, 3.1 Hz, 1H), CH(3)–Ar), 3.62 (s, 3H, OMe), 3.76 (s, 3H, OMe), 5.70 (br s, 1H, OH), 6.78 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.03 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 22.6 ($Me_b$(5)), 24.8 ($Me_a$(5)), 28.9 ($CH_2$(2)), 50.0 (CH(1)), 51.1 (CH(3)–Ar), 52.75 and 52.77 (2×$CO_2$Me), 91.9 (C(4)–$NO_2$), 115.7 ($CH_{Ar}$), 127.6 ($C_{Ar}$), 130.6 ($CH_{Ar}$), 155.8 ($C_{Ar}$–OH), 169.2 (C=O), 169.6 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{16}H_{21}NO_7$+$NH_4^+$]: 357.1656, found: 357.1654.

**Dimethyl 2-(2-(4-hydroxyphenyl)-2-(1-nitrocyclopentyl)ethyl)malonate (3ar)**



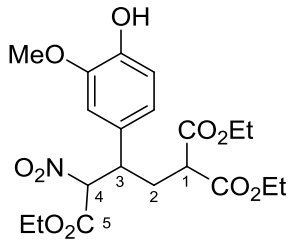

Nitromalonate **3ar** was obtained from DAC **1a** (36 mg, 0.10 mmol) and nitro compound **2r** (13 mg, 0.11 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 27 mg (75%) of the target product **3ar** as colorless oil.
$R_f$ = 0.51 (PE/EtOAc, 1:1, UV, $FeCl_3$).
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.56-1.73 (m, 4H, 2×$CH_2$), 1.82-2.00 (m, 2H, $CH_2$), 2.28-2.45 (m, 2H, $CH_2$), 2.49-2.62 (m, 2H, $CH_2$), 3.10 (dd, *J* = 10.0, 4.7 Hz, 1H, CH), 3.27 (dd, *J* = 11.5, 3.6 Hz, 1H, CH), 3.64 (s, 3H, OMe), 3.75 (s, 3H, OMe), 5.69 (br s, 1H, OH), 6.75 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.98 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 23.3 ($CH_2$), 23.5 ($CH_2$), 30.0 ($CH_2$), 34.3 ($CH_2$), 35.1 ($CH_2$), 49.6 (CH), 49.9 (CH), 52.7 and 52.8 (2×$CO_2$Me), 104.7 (C–$NO_2$), 115.7 ($CH_{Ar}$), 128.3 ($C_{Ar}$), 130.2 ($CH_{Ar}$), 155.7 ($C_{Ar}$–OH), 169.4 (C=O), 169.7 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{18}H_{23}NO_7$+$NH_4^+$]: 383.1813, found: 383.1809.

**Dimethyl 2-(2-(4-hydroxyphenyl)-2-(1-nitrocyclohexyl)ethyl)malonate (3as)**



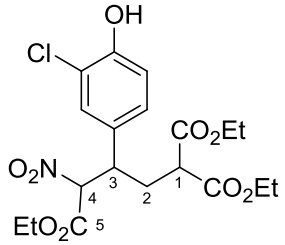

Nitromalonate **3as** was obtained from DAC **1a** (32 mg, 0.087 mmol) and nitro compound **2s** (12 μL, 13 mg, 0.10 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1) afforded 13 mg (39%) of the target product **3as** as colorless oil.
$R_f$ = 0.55 (PE/EtOAc, 1:1, UV, $FeCl_3$).
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.05-1.73 (m, 8H, 4×$CH_2$), 2.24-2.57 (m, 4H, 2×$CH_2$), 2.94-3.05 (m, 2H, 2×CH), 3.64 (s, 3H, OMe), 3.74 (s, 3H, OMe), 5.39 (br s, 1H, OH), 6.78 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 6.96 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 22.19 ($CH_2$), 22.21 ($CH_2$), 24.5 ($CH_2$), 28.5 ($CH_2$), 31.4 ($CH_2$), 32.7 ($CH_2$), 49.9 (CH), 52.2 (CH), 52.65 and 52.74 (2×$CO_2$Me), 95.1 (C–$NO_2$), 115.6 ($CH_{Ar}$), 127.9 ($C_{Ar}$), 132.1 (br, $CH_{Ar}$) 155.7 ($C_{Ar}$–OH), 169.3 (C=O), 169.6 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{25}NO_7$+$NH_4^+$]: 397.1969, found: 397.1965.

**Triethyl 3-(4-hydroxy-3-methoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ca)**




Nitromalonate **3ca** was obtained from DAC **1c** (62 mg, 0.15 mmol) and nitro compound **2a** (18 μL, 22 mg, 0.16 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3.5:1) afforded 61 mg (94%, dr = 1:1) of the target product **3ca** as slightly yellow oil.
$R_f$ = 0.51 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.04 (t, *J* = 7.1 Hz), 1.19 (t, *J* = 7.1 Hz), 1.31 (t, *J* = 7.1 Hz), and 1.36 (t, *J* = 7.1 Hz) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.15-2.41 (m, 2H, $CH_2$(2), both isomers), 3.06-3.12 (m, 1H, CH(1)), 3.59-3.70 (m, 1H, CH(3)–Ar, both isomers), 3.88 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.97-4.15 (m), 4.20-4.31 (m), and 4.35 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.28 (d, *J* = 10.1 Hz, 1H, CH(4)–$NO_2$), 5.31 (d, *J* = 10.5 Hz, 1H, CH(4)–$NO_2$), 5.67 (br s, 1H, OH), 5.69 (br s, 1H, OH), 6.68-6.74 (m, 2H, $CH_{Ar}$, both isomers), 6.87 (dd, *J* = 8.0, 1.8 Hz, 1H, $CH_{Ar}$, both isomers).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.6, 13.9, 14.05 and 14.09 (all $CH_2\underline{C}H_3$), 30.9 and 31.3 ($CH_2$(2)), 44.3 (CH(3)–Ar), 49.46 and 49.54 (CH(1)), 55.97 and 56.04 (OMe), 61.7, 62.9, and 63.4 (all $O\underline{C}H_2CH_3$), 92.3 and 92.6 (CH(4)–$NO_2$), 111.1 and 111.3 ($CH_{Ar}$), 114.85 and 114.92 ($CH_{Ar}$), 120.9 and 121.5 ($CH_{Ar}$), 126.5 and 127.5 ($C_{Ar}$), 145.7 and 145.8 ($\underline{C}_{Ar}$–O), 146.75 and 146.79 ($\underline{C}_{Ar}$–O), 162.9 and 163.1 (C(5)=O), 168.4, 468.5, 168.7, and 168.8 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{27}NO_{10}$+$NH_4^+$]: 459.1973, found: 459.1974.

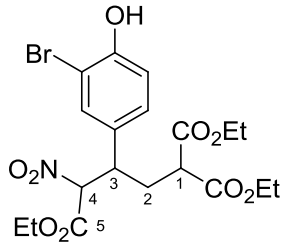
**Triethyl 3-(3-chloro-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3da)**




Nitromalonate **3da** was obtained from DAC **1d** (54 mg, 0.13 mmol) and nitro compound **2a** (15 μL, 18 mg, 0.14 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 3:1) afforded 50 mg (88%, dr = 1:1) of the target product **3da** as colorless oil.
$R_f$ = 0.45 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.06 (t, *J* = 7.2 Hz), 1.20 (t, *J* = 7.1 Hz), 1.29 (t, *J* = 7.2 Hz), and 1.34 (t, *J* = 7.2 Hz) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.11-2.44 (m, 2H, $CH_2$(2), both isomers), 3.02-3.12 (m, 1H, CH(1)), 3.58-3.72 (m, 1H, CH(3)–Ar, both isomers), 3.97-4.18 (m), 4.25 (q, *J* = 7.2 Hz), and 4.35 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.25 (d, *J* = 9.8 Hz, 1H, CH(4)–$NO_2$), 5.28 (d, *J* = 10.3 Hz, 1H, CH(4)–$NO_2$), 5.86 (br s, 1H, OH), 6.94-7.00 (m, 1H, $CH_{Ar}$, both isomers), 7.02-7.08 (m, 1H, $CH_{Ar}$, both isomers), 7.18-7.21 (m, 1H, $CH_{Ar}$, both isomers).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.6, 13.85, 13.89, 14.03 and 14.06 (all $CH_2\underline{C}H_3$), 30.7 and 31.1 ($CH_2$(2)), 43.4 (CH(3)–Ar), 49.42 and 49.49 (CH(1)), 61.8, 63.1, and 63.5 (all $O\underline{C}H_2CH_3$), 92.0 and 92.2 (CH(4)–$NO_2$), 110.5 and 110.6 ($C_{Ar}$–Br), 116.65 and 116.71 ($CH_{Ar}$), 128.5 and 129.4 ($C_{Ar}$), 129.0 and 129.5 ($CH_{Ar}$), 132.2 and 132.5 ($CH_{Ar}$), 152.5 and 152.6 ($\underline{C}_{Ar}$–O), 162.7 and 162.9 (C(5)=O), 168.2, 168.3, 168.5, and 168.6 (all C=O).

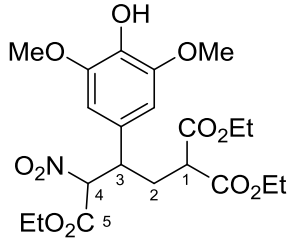
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{24}{}^{35}ClNO_9$+$Na^+$]: 468.1032, found: 468.1039.

**Triethyl 3-(3-bromo-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ea)**




Nitromalonate **3ea** was obtained from DAC **1e** (56 mg, 0.12 mmol) and nitro compound **2a** (15 μL, 18 mg, 0.14 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 2.5:1) afforded 38 mg (73%, dr = 1:1) of the target product **3ea** as colorless oil.
$R_f$ = 0.53 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.06 (t, *J* = 7.1 Hz), 1.20 (t, *J* = 7.1 Hz), 1.31 (t, *J* = 7.1 Hz), and 1.34 (t, *J* = 7.1 Hz) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.11-2.42 (m, 2H, $CH_2$(2), both isomers), 3.04-3.11 (m, 1H, CH(1)), 3.59-3.70 (m, 1H, CH(3)–Ar, both isomers), 3.97-4.18 (m), 4.25 (q, *J* = 7.1 Hz), and 4.34 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.25 (d, *J* = 9.8 Hz, 1H, CH(4)–$NO_2$), 5.28 (d, *J* = 10.2 Hz, 1H, CH(4)–$NO_2$), 5.82 (br s, 1H, OH), 6.95-6.99 (m, 1H, $CH_{Ar}$, both isomers), 7.07-7.11 (m, 1H, $CH_{Ar}$, both isomers), 7.33-7.34 (m, 1H, $CH_{Ar}$, both isomers).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.6, 13.85, 13.89, 14.03 and 14.06 (all $CH_2\underline{C}H_3$), 30.7 and 31.1 ($CH_2$(2)), 43.4 (CH(3)–Ar), 49.42 and 49.49 (CH(1)), 61.8, 63.1, and 63.5 (all $O\underline{C}H_2CH_3$), 92.0 and 92.2 (CH(4)–$NO_2$), 110.5 and 110.6 ($C_{Ar}$–Br), 116.65 and 116.71 ($CH_{Ar}$), 128.5 and 129.4 ($C_{Ar}$), 129.0 and 129.5 ($CH_{Ar}$), 132.2 and 132.5 ($CH_{Ar}$), 152.5 and 152.6 ($\underline{C}_{Ar}$–O), 162.7 and 162.9 (C(5)=O), 168.2, 168.3, 168.5, and 168.6 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{24}{}^{79}BrNO_9$+$NH_4^+$]: 507.0973, found: 507.0958.

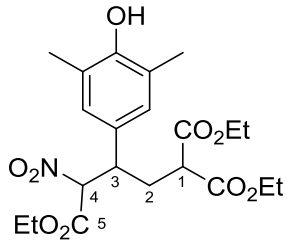
**Triethyl 3-(4-hydroxy-3,5-dimethoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3fa)**




Nitromalonate **3fa** was obtained from DAC **1f** (56 mg, 0.12 mmol) and nitro compound **2a** (15 μL, 18 mg, 0.14 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 2.5:1) afforded 45 mg (77%, dr = 1:1) of the target product **3fa** as colorless oil, that solidified upon storage in a fridge.
$R_f$ = 0.42 (PE/EtOAc, 1:1, UV, $FeCl_3$).
mp = 103-105 °C (EtOAc).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.06 (t, *J* = 7.1 Hz), 1.19 (t, *J* = 7.1 Hz), 1.31 (t, *J* = 7.2 Hz), and 1.36 (t, *J* = 7.4 Hz) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.20 (ddd, *J* = 13.6, 12.2, 4.2 Hz) and 2.27-2.43 (m) (total 2H, $CH_2$(2), both isomers), 3.05-3.15 (m, 1H, CH(1), both isomers), 3.57-3.70 (m, 1H, CH(3)–Ar, both isomers), 3.88 (s) and 3.89 (s) (total 6H, $OC\underline{H}_3$, both isomers), 3.98-4.15 (m), 4.19-4.32 (m), and 4.35 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.28 (d, *J* = 10.3 Hz, 1H, CH(4)–$NO_2$), 5.33 (d, *J* = 10.8 Hz, 1H, CH(4)–$NO_2$), 5.54 (br s) and 5.55 (br s) (total 1H, OH, both isomers), 6.42 (s, 2H, $CH_{Ar}$, both isomers).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.6, 13.9, 14.06 and 14.10 (all $CH_2\underline{C}H_3$), 30.9 and 31.3 ($CH_2$(2)), 44.8 (CH(3)–Ar), 49.4 and 49.5 (CH(1)), 56.37 and 56.42 (OMe), 61.7,

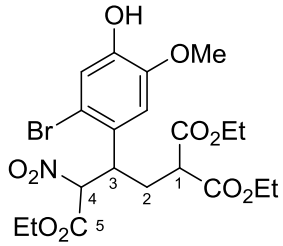
62.9, and 63.4 (all O<u>C</u>$H_2CH_3$), 92.3 and 92.5 (CH(4)–$NO_2$), 105.1 and 105.4 ($CH_{Ar}$), 125.8 and 126.8 ($C_{Ar}$), 147.3 (<u>C</u>$_{Ar}$–O, both isomers), 162.9 and 163.1 (C(5)=O), 168.4, 168.5, 168.7, and 168.8 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{29}NO_{11}$+$H^+$]: 472.1813, found: 472.1798.

**Triethyl 3-(4-hydroxy-3,5-dimethylphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ga)**




Nitromalonate **3ga** was obtained from DAC **1g** (50 mg, 0.12 mmol) and nitro compound **2a** (15 μL, 18 mg, 0.14 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 3:1) afforded 50 mg (96%, dr = 1:1) of the target product **3ga** as yellow oil.
$R_f$ = 0.62 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.02 (t, *J* = 7.1 Hz), 1.19 (t, *J* = 7.1 Hz), 1.31 (t, *J* = 7.1 Hz), and 1.36 (t, *J* = 7.2 Hz) (total 9H, all $CH_2C$<u>H</u>$_3$, both isomers), 2.10-2.24 (m, overlapped) and 2.25-2.42 (m) (total 2H, $CH_2$(2), both isomers), 2.19 and 2.20 (both s, overlapped, total 6H, $C_{Ar}$–C<u>H</u>$_3$, both isomers), 3.03-3.13 (m, 1H, CH(1), both isomers), 3.49-3.63 (m, 1H, CH(3)–Ar, both isomers), 3.95-4.15 (m), 4.25 (q, *J* = 7.1 Hz, 1H), and 4.34 (q, *J* = 7.2 Hz, 1H) (total 6H, all OC<u>H</u>$_2$$CH_3$, both isomers), 4.93 (br s) and 4.94 (br s) (total 1H, OH, both isomers), 5.25 (d, *J* = 10.1 Hz, 1H, CH(4)–$NO_2$), 5.29 (d, *J* = 10.6 Hz, 1H, CH(4)–$NO_2$), 6.78 (s, 2H, $CH_{Ar}$, both isomers).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.5, 13.87, 13.89, 14.04 and 14.08 (all $CH_2$<u>C</u>$H_3$), 15.9 and 16.0 ($C_{Ar}$–<u>Me</u>), 30.8 and 31.1 ($CH_2$(2)), 43.8 (CH(3)–Ar), 49.4 and 49.5 (CH(1)), 61.65, 61.66, 62.7, and 63.3 (all O<u>C</u>$H_2CH_3$), 92.5 and 92.7 (CH(4)–$NO_2$), 123.7 (<u>C</u>$_{Ar}$–Me, both isomers), 126.0 and 127.0 ($C_{Ar}$), 128.4 and 128.8 ($CH_{Ar}$), 152.29 and 152.34 (<u>C</u>$_{Ar}$–O), 163.0 and 163.3 (C(5)=O), 168.5, 168.6, 168.8, and 168.9 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{29}NO_9$+$NH_4^+$]: 457.2181, found: 457.2183.

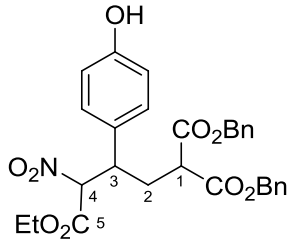
**Triethyl 3-(2-bromo-4-hydroxy-5-methoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ha)**




Nitromalonate **3ha** was obtained from DAC **1h** (61 mg, 0.12 mmol) and nitro compound **3a** (15 μL, 18 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 57 mg (90%, dr = 1.2:1) of the target product **3ha** as colorless oil.
$R_f$ = 0.45 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, COSY, $CD_3CN$, sum of isomers): δ 1.06 (t, *J* = 7.1 Hz), 1.15 (t, *J* = 7.1 Hz), 1.16 (t, *J* = 7.1 Hz), 1.24 (t, *J* = 7.1 Hz), 1.25 (t, *J* = 7.1 Hz) and 1.33 (t, *J* = 7.1 Hz) (total 9H, all $CH_2C$<u>H</u>$_3$, both isomers), 2.15-2.51 (m, 2H, $CH_2$(2), both isomers), 3.02-3.11 (m, 1H, CH(1)), 3.86 (s, 3H, OMe), 3.91-4.09 (m), 4.11-4.31 (m) and 4.36 (q, *J* = 7.1 Hz) (total 6H, all C<u>H</u>$_2$$CH_3$, both isomers), 4.17-4.30 (m, overlapped, 1H, CH(3)–Ar, both isomers), 5.61 (d, *J* = 10.5 Hz, 1H, CH(4)–$NO_2$), 5.65 (d, *J* = 10.8 Hz, 1H, CH(4)–$NO_2$), 6.90 (s) and 6.96 (s) (total 1H, $CH_{Ar}$, both isomers), 6.95 (br s, 1H, OH), 7.05 (s) and 7.08 (s) (total 1H, $CH_{Ar}$, both isomers).

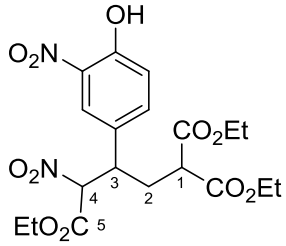
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CD_3CN$, sum of isomers): δ 12.9, 13.2, 13.4 (all $CH_2\underline{C}H_3$), 30.6 and 30.9 ($CH_2$(2)), 42.56 and 42.61 (CH(3)–Ar), 49.2 (CH(1)), 56.2 (OMe), 61.5, 61.6, 62.9 and 63.4 (all $O\underline{C}H_2CH_3$), 91.3 and 91.5 (CH(4)–$NO_2$), 111.1 and 111.9 ($CH_{Ar}$), 116.1 ($C_{Ar}$–Br), 118.8 ($CH_{Ar}$), 125.5 and 126.7 ($C_{Ar}$), 146.8 and 146.9 ($C_{Ar}$–O), 147.6 and 147.7 ($C_{Ar}$–O), 163.1 and 163.4 (C(5)=O), 168.28, 168.31 and 168.6 all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{26}{}^{79}BrNO_{10}$+$H^+$]: 520.0813, found: 520.0807.

**1,1-Dibenzyl 4-ethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ia)**




Nitromalonate **3ia** was obtained from DAC **1i** (44 mg, 0.085 mmol) and nitro compound **2a** (10 μL, 12 mg, 0.09 mmol) according to GP (reaction time – 1 d). Column chromatography (eluent: PE/EtOAc, 4:1) afforded 39 mg (87%, dr = 1:1) of the target product **3ia** as colorless oil.
$R_f$ = 0.53 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.03 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.32 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 2.21-2.50 (m, 2H, $CH_2$(2), both isomers), 3.19-3.25 (m, 1H, CH(1), both isomers), 3.60-3.72 (m, 1H, CH(3)–Ar, both isomers), 3.96-4.06 (m, 2H, $OC\underline{H}_2CH_3$), 4.32 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.95-5.07 and 5.15-5.32 (2×m, total 5H, $C\underline{H}_2$Ph and CH(4)–$NO_2$, both isomers), 5.63 (br s, 1H, OH, both isomers), 6.70 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.71 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.97 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$, both siomers), 7.18-7.39 (m, 5H, Ph, both isomers).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): δ 13.6 and 13.9 ($CH_2\underline{C}H_3$), 30.9 and 31.2 ($CH_2$(2)), 43.75 and 43.78 (CH(3)–Ar), 49.60 and 49.64 (CH(1)), 62.9 and 63.4 ($O\underline{C}H_2CH_3$), 67.5 and 67.6 (2×$CO_2\underline{C}H_2$Ph), 92.3 and 92.6 (CH(4)–$NO_2$), 116.0 and 116.1 ($CH_{Ar}$), 126.2 and 127.2 ($C_{Ar}$), 128.44, 128.45, 128.50, 128.52, 128.58, 128.61, and 128.63 (all $CH_{Ph}$), 129.6 and 130.0 ($CH_{Ar}$), 134.9 and 135.0 ($C_{Ph}$), 155.9 and 156.0 ($\underline{C}_{Ar}$–OH), 163.0 and 163.2 (C(5)=O), 168.2, 168.3, 168.5, and 168.6 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{29}H_{29}NO_9$+$Na^+$]: 558.1735, found: 558.1731.

**Triethyl 3-(4-hydroxy-3-nitrophenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ja)**

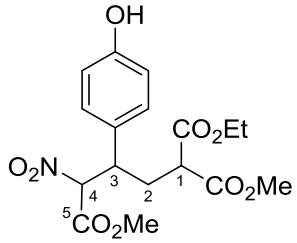



1) Nitromalonate **3ja** was obtained from DAC **1j** (53 mg, 0.12 mmol) and nitro compound **2a** (15 μL, 18 mg, 0.13 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 4:1) afforded 26 mg (67%) of DAC **4j** as yellow oil and 17 mg (30%) of the target product **3ja** as light yellow oil.
2) Nitromalonate **3ja** was obtained from DAC **1j** (40 mg, 0.09 mmol) and nitro compound **2a** (11 μL, 13 mg, 0.10 mmol) according to GP with following change: after addition of TBAF•$3H_2O$ at 0 °C reaction mixture was warmed up to r.t., stirred for 20 min and heated at 60 °C for 24 h. Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 36 mg (80%, dr = 1.1:1) of the target product **3ja** as yellow oil.

$R_f$ = 0.19 (PE/EtOAc, 3:1, UV, $FeCl_3$).

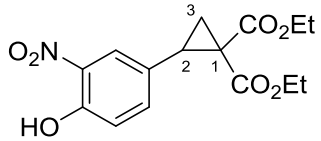
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.13 (t, *J* = 7.1 Hz), 1.21 (t, *J* = 7.1 Hz), 1.25-1.39 (m) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.23 (ddd, *J* = 14.0, 11.9, 4.6 Hz) and 2.33-2.50 (m) (total 2H, $CH_2$(2), both isomers), 2.99-3.08 (m, 1H, CH(1)), 3.69-3.83 (m, 1H, CH(3)–Ar, both isomers), 4.00-4.20 (m), 4.20-4.32 (m), and 4.37 (q, *J* = 7.1 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.31 (d, *J* = 9.4 Hz, 1H, CH(4)–$NO_2$), 5.33 (d, *J* = 10.1 Hz, 1H, CH(4)–$NO_2$), 7.18 (dd, *J* = 8.7, 3.6 Hz, 1H, $CH_{Ar}$, both isomers), 7.50 (dt, *J* = 8.7, 2.0, 1.1 Hz, 1H, $CH_{Ar}$, both isomers), 8.01 (d, *J* = 2.3 Hz, 1H, $CH_{Ar}$, both isomers), 10.6 (s, 1H. OH).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.7, 13.85, 13.90, 14.03 and 14.06 (all $CH_2\underline{C}H_3$), 30.6 and 30.9 ($CH_2$(2)), 43.3 and 43.4 (CH(3)–Ar), 49.32 and 49.36 (CH(1)), 61.9, 62.0, 63.3 and 63.7 (all $O\underline{C}H_2CH_3$), 91.5 and 91.8 (CH(4)–$NO_2$), 120.98 and 121.03 ($CH_{Ar}$), 125.1 and 125.2 ($CH_{Ar}$), 127.8 and 128.4 ($C_{Ar}$), 133.48 and 133.51 ($C_{Ar}$–$NO_2$), 137.2 and 137.8 ($CH_{Ar}$), 154.92 and 154.94 ($\underline{C}_{Ar}$–O), 162.4 and 162.6 (C(5)=O), 168.0, 168.1, 168.17, and 168.22 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{24}N_2O_{11}$+$NH_4^+$]: 474.1718, found: 474.1712.

**1-Ethyl 1,4-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3lb)**




Nitromalonate **3lb** was obtained from DAC **1l** (dr = 1:1, 65 mg, 0.17 mmol, dr = 1:1) and nitro compound **2b** (18 μL, 23 mg, 0.20 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3.5:1, then 2.5:1) afforded 60 mg (91%, dr = 1:1:1:1) of the target product **3lb** as colorless oil.
$R_f$ = 0.42 (PE/EtOAc, 1:1, UV, $FeCl_3$).
Relative configuration of stereocenters was not determined.
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.19 and 1.31 (both t, *J* = 7.1 Hz, total 3H, $CH_2C\underline{H}_3$), 2.17-2.43 (m, 2H, $CH_2$(2)), 3.10-3.16 (m, 1H, CH(1)), 3.60-3.69 (m, 1H, CH(3)–Ar), 3.57, 3.61, 3.781, 3.785, and 3.88 (all s, total 6H, OMe), 3.98-4.12 and 4.20-4.30 (both m, 2H, $OC\underline{H}_2CH_3$), 5.25-5.34 (m, 1H, CH(4)–$NO_2$), 6.14 (br s, 1H, OH, both isomers), 6.75 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.05 and 7.06 (both d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.85, 13.98 and 14.02 ($CH_2\underline{C}H_3$), 30.9 and 31.1 ($CH_2$(2)), 43.87, 43.93, and 43.99 (CH(3)–Ar), 49.48, 49.51, 49.56, and 49.60 (CH(1)), 52.8, 52.9, 53.4 and 53.9 ($CO_2\underline{Me}$), 62.04, 62.06, and 62.08 ($O\underline{C}H_2CH_3$), 92.2 and 92.4 (CH(4)–$NO_2$), 116.1 ($CH_{Ar}$), 126.1, 126.2, 127.0 and 127.1 ($C_{Ar}$), 129.6 and 129.9 ($CH_{Ar}$), 156.1 and 156.2 ($\underline{C}_{Ar}$–OH), 163.53, 163.68, and 163.70 (C(5)=O), 168.53, 168.61, 168.87, 168.91, 169.11, 169.21, 169.39, and 169.45 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{17}H_{21}NO_9$+$NH_4^+$]: 401.1555, found: 401.1556.

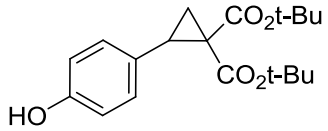
**Diethyl 2-(4-hydroxy-3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4j)**




Obtained as a side product during synthesis of nitromalonate **3ja**.
$R_f$ = 0.36 (PE/EtOAc, 3:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.32 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.75 (dd, *J* = 9.2, 5.4 Hz, 1H, $CH_{2a}$(3)), 2.14 (dd, *J* = 7.9, 5.4 Hz, 1H, $CH_{2b}$(3)), 3.19 (app t, *J* = 8.5 Hz, 1H, CH(2)), 3.84-4.04 (m, 2H, $OC\underline{H}_2CH_3$), 4.17-4.37 (m, 2H, $OC\underline{H}_2CH_3$),

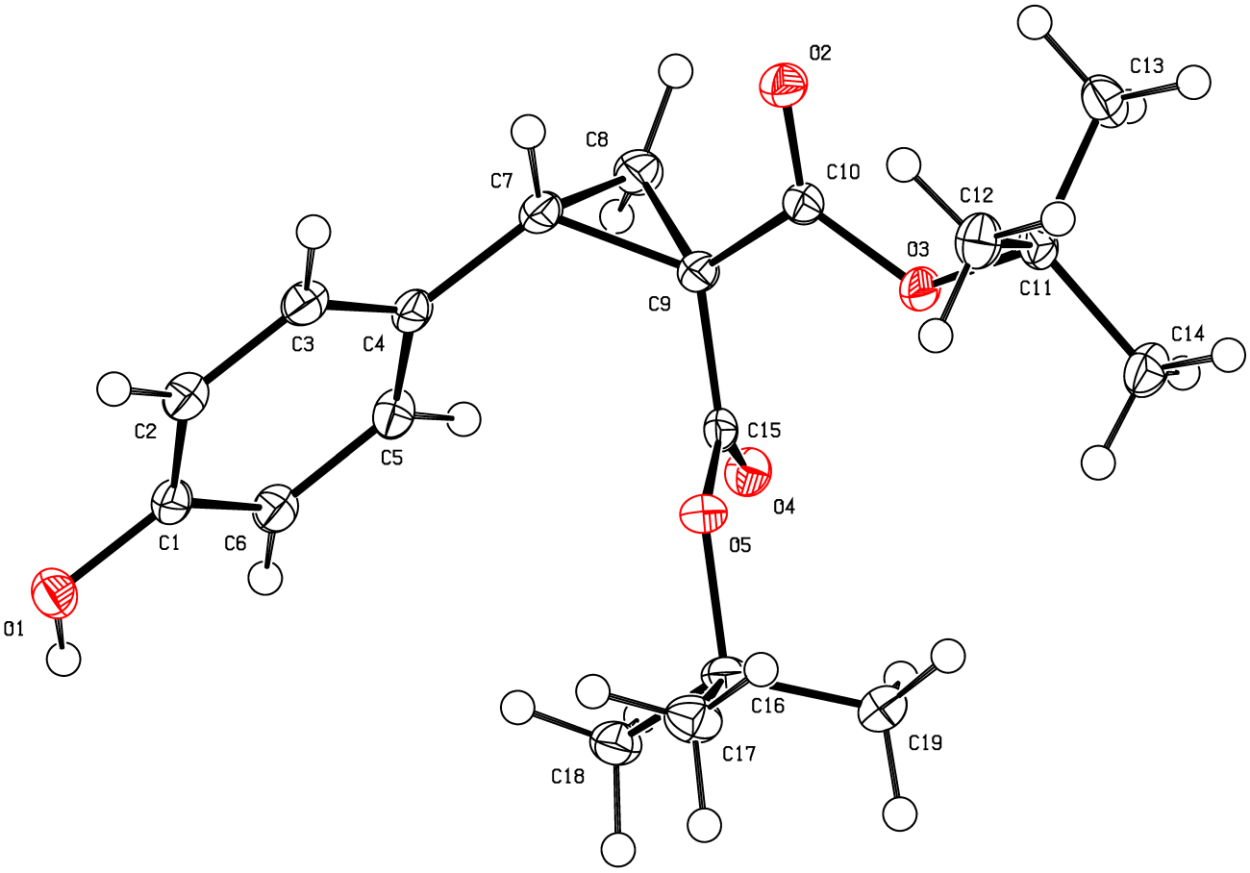
7.09 (d, $J$ = 8.7 Hz, 1H, $CH_{Ar}$), 7.49 (dd, $J$ = 8.7, 2.3 Hz, 1H, $CH_{Ar}$), 7.97 (d, $J$ = 2.3 Hz, 1H, $CH_{Ar}$), 10.52 (s, 1H, OH).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 13.9 and 14.1 (2×$OCH_2\underline{C}H_3$), 18.8 ($CH_2$(3)), 30.5 (CH(2)), 37.1 (C(1)), 61.5 and 62.0 (2×$O\underline{C}H_2CH_3$), 119.8 ($CH_{Ar}$), 124.5 ($CH_{Ar}$), 127.5 ($C_{Ar}$), 133.1 ($\underline{C}_{Ar}$–$NO_2$), 138.2 ($CH_{Ar}$), 154.3 ($\underline{C}_{Ar}$–O), 166.3 and 169.3 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{15}H_{17}NO_7$+$Na^+$]: 346.0897, found: 346.0889.

**Di-tert-butyl 2-(4-hydroxyphenyl)cyclopropane-1,1-dicarboxylate (4k)**



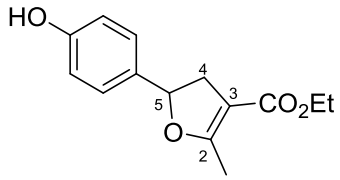

Product **4k** was obtained during the reaction of DAC **1k** (68 mg, 0.15 mmol) and nitro compound **1a** (18 μL, 22 mg, 0.16 mmol) following GP. Column chromatography (eluent: PE/EtOAc, 10:1) afforded 47 mg (94%) of the target product **4k** as white powder.
$R_f$ = 0.63 (PE/EtOAc, 1:1, UV, $FeCl_3$).
mp = 126-128 °C (PE/EtOAc, 1:1).
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 9H, *t*-Bu), 1.51 (s, overlapped, 9H, *t*-Bu), 1.48-1.54 (m, 1H, $CH_{2a}$(3)), 1.99 (dd, $J$ = 7.8, 5.1 Hz, 1H, $CH_{2b}$(3)), 3.05 (app t, $J$ = 8.5 Hz, 1H, CH(2)), 6.14 (br s, 1H, OH), 6.71 (d, $J$ = 8.5 Hz, 1H, $CH_{Ar}$), 7.08 (d, $J$ = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 18.0 ($CH_2$(3)), 27.6 ($\underline{Me}_3C$), 28.1 ($\underline{Me}_3C$), 30.7 (CH(2)), 39.1 (C(1)), 81.3 ($Me_3\underline{C}$–O), 81.9 ($Me_3\underline{C}$–O), 115.0 ($CH_{Ar}$), 126.5 ($C_{Ar}$), 130.1 ($CH_{Ar}$), 155.2 ($\underline{C}_{Ar}$–O), 166.6 (C=O), 169.6 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{26}O_5$+$Na^+$]: 357.1672, found: 357.1677.

The crystallographic information for compound **4k** was deposited in the Cambridge Crystallographic Data Centre (CCDC 2373468).




General view of the compound **4k** in representation of atoms *via* thermal ellipsoids at 50% probability level.

**Ethyl 5-(4-hydroxyphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (6)**




Product **6** was obtained during the reaction of DAC **5** (dr = 2.8: 1, 38 mg, 0.11 mmol) and nitro compound **1a** (13 μL, 16 mg, 0.12 mmol) while following GP. Column chromatography (eluent: PE/EtOAc, 9:1, then 6:1) afforded 25.5 mg (98%) of the target product **6** as colorless oil, which solidified upon storage in a fridge.

$R_f$ = 0.26 (PE/EtOAc, 3:1, UV, anisaldehyde).

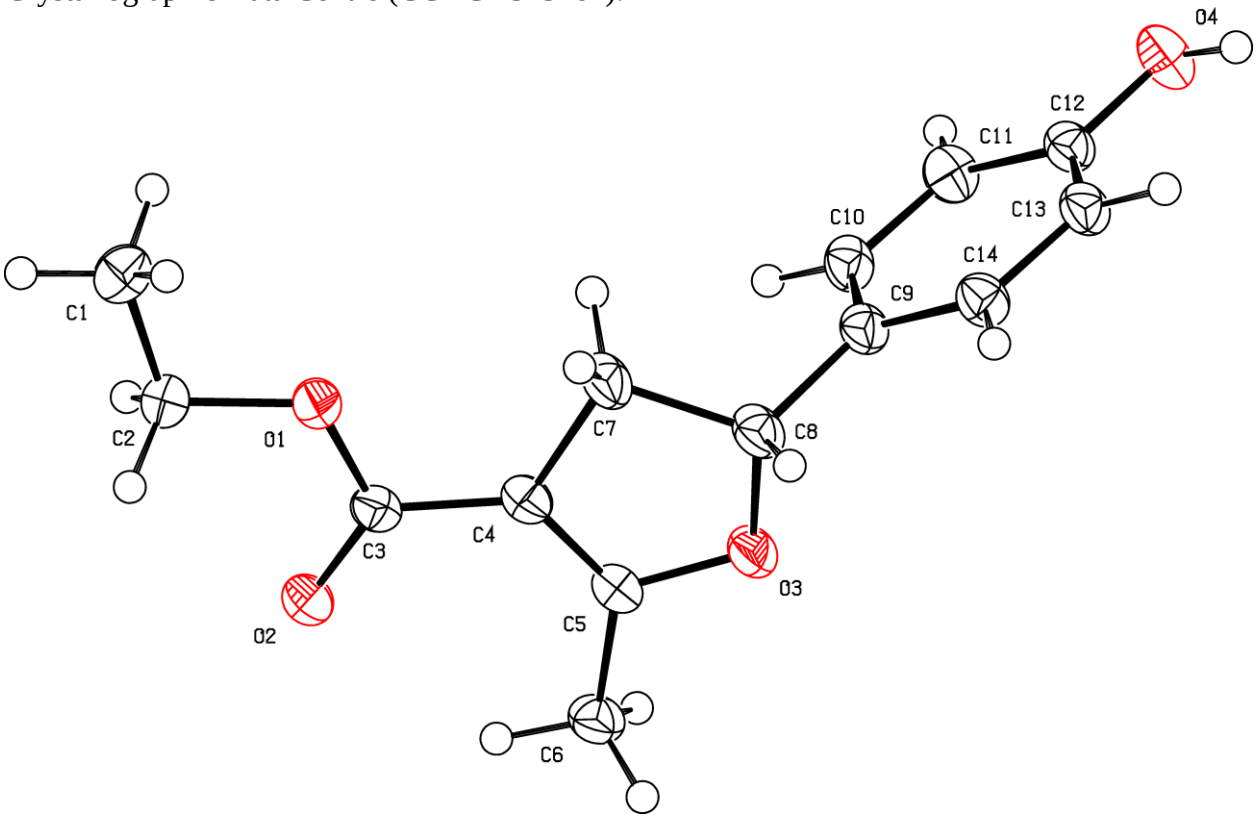
mp = 71-73 °C (PE/$CH_2Cl_2$, 1:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 2.28 (br t, *J* = 1.4 Hz, 3H, Me(2)), 2.94 (ddq, *J* = 14.5, 8.4, 1.4 Hz, 1H, $CH_{2a}$(4)), 3.31 (ddq, *J* = 14.5, 10.7, 1.4 Hz, 1H, $CH_{2b}$(4)), 4.23 (q, *J* = 7.1 Hz, 2H, $C\underline{H}_2CH_3$), 5.55 (dd, *J* = 10.7, 8.4 Hz, 1H, CH(5)), 6.32 (br s, 1H, OH), 6.86 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.22 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 14.3 and 14.4 (Me(2) and $CH_2\underline{C}H_3$), 37.6 ($CH_2$(4)), 59.9 ($\underline{C}H_2CH_3$), 83.3 (CH(5)), 101.7 (C(3)), 115.6 ($CH_{Ar}$), 127.5 ($CH_{Ar}$), 133.1 ($C_{Ar}$), 156.1 ($\underline{C}_{Ar}$–OH), 166.8 and 168.2 (C(2)–O and C=O).

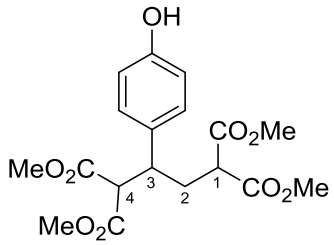
HRMS (ESI): *m/z* calcd. for [$C_{14}H_{16}O_4$+$H^+$]: 249.1121, found: 249.1128.

The crystallographic information for compound **6** was deposited in the Cambridge Crystallographic Data Centre (CCDC 2373464).




General view of the compound **6** in representation of atoms *via* thermal ellipsoids at 50% probability level.

**Tetramethyl 2-(4-hydroxyphenyl)butane-1,1,4,4-tetracarboxylate (7a)**




Malonate **7a** was obtained from DAC **1a** (39 mg, 0.11 mmol) and dimethyl malonate (14 μL, 16 mg, 0.12 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 2.5:1, then 2:1) afforded 32 mg (78%) of the target product **7a** as colorless oil.

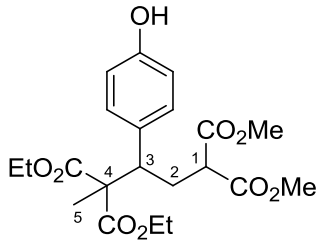
$R_f$ = 0.34 (PE/EtOAc, 1:1, UV, $FeCl_3$).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.18 (ddd, *J* = 13.6, 12.1, 4.6 Hz, 1H, $CH_{2a}$(2)), 2.36 (ddd, *J* = 13.6, 10.1, 3.3 Hz, 1H, $CH_{2b}$(2)), 3.13 (dd, *J* = 10.1, 4.6 Hz, 1H, CH(1)), 3.32 (app td, *J* = 11.7, 3.2 Hz, 1H, CH(3)–Ar), 3.46 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.66 (d, *J* = 10.6 Hz, 1H, CH(4)), 3.78 (s, 3H, OMe), 3.79 (s, 3H, OMe), 6.20 (br s, 1H, OH), 6.71 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.02 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 33.0 ($CH_2$(2)), 42.8 (CH(3)–Ar), 49.8 (CH(1)), 52.50, 52.65, 52.73, and 52.83 ($CO_2\underline{Me}$), 58. (CH(4)), 115.6 ($CH_{Ar}$), 129.5 ($CH_{Ar}$), 129.9 ($C_{Ar}$), 155.5 ($\underline{C}_{Ar}$–OH), 168.2, 168.3, 169.3, and 169.6 (all C=O).

HRMS (ESI): *m/z* calcd. for [$C_{18}H_{22}O_9$+$NH_4^+$]: 400.1602, found: 400.1602.

**4,4-Diethyl 1,1-dimethyl 3-(4-hydroxyphenyl)pentane-1,1,4,4-tetracarboxylate (7b)**




Malonate **7b** was obtained from DAC **1a** (38 mg, 0.11 mmol) and diethyl methylmalonate (20 μL, 20 mg, 0.12 mmol) according to GP (reaction time – 3 d). Column chromatography (eluent: PE/EtOAc, 2:1) afforded 15 mg (34%) of the target product **7b** as colorless oil.

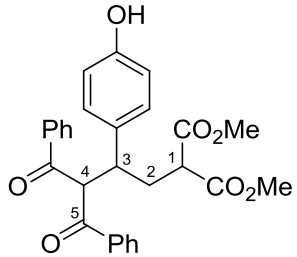
$R_f$ = 0.41 (PE/EtOAc, 1:1, UV, $FeCl_3$).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): 1.19 (t, *J* = 7.1 Hz, 1H, $CH_2C\underline{H}_3$), 1.29 (t, *J* = 7.1 Hz, 1H, $CH_2C\underline{H}_3$), 1.40 (s, 3H, Me(5)), 2.40-2.51 (m, 2H, $CH_2$(2)), 3.13 (dd, *J* = 8.2, 6.5 Hz, 1H, CH(1)), 3.38 (dd, *J* = 8.3, 6.5 Hz, 1H, CH(3)–Ar), 3.54 (s, 3H, OMe), 3.78 (s, 3H, OMe), 4.00-4.11 (m, 2H, $OCH_2CH_3$), 4.18-4.29 (m, 2H, $OCH_2CH_3$), 5.78 (br s, 1H, OH), 6.69 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.03 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, HSQC, HMBC, $CDCl_3$): 13.9 ($CH_2\underline{C}H_3$), 14.0 ($CH_2\underline{C}H_3$), 17.8 (Me(5)), 30.8 ($CH_2$(2)), 47.1 (CH(3)–Ar), 50.5 (CH(1)), 52.5 (OMe), 52.6 (OMe), 58.4 (C(4)), 61.46 ($O\underline{C}H_2CH_3$), 61.50 ($O\underline{C}H_2CH_3$), 115.2 ($CH_{Ar}$), 129.1 ($C_{Ar}$), 130.7 ($CH_{Ar}$), 155.4 ($C_{Ar}$–O), 169.6 ($CO_2$), 169.9 ($CO_2$), 171.2 ($CO_2$), 171.3 ($CO_2$).

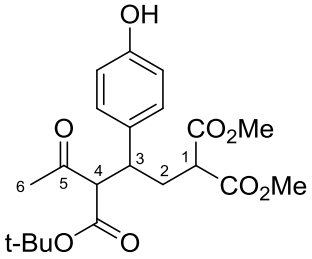
HRMS (ESI): *m/z* calcd. for [$C_{21}H_{28}O_9$+$NH_4^+$]: 442.2072, found 442.2066.

**Dimethyl 2-(3-benzoyl-2-(4-hydroxyphenyl)-4-oxo-4-phenylbutyl)malonate (7c)**

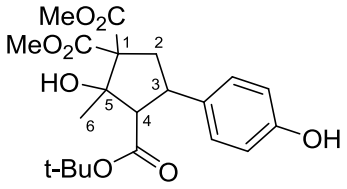


Malonate **7c** was obtained from DAC **1a** (38 mg, 0.11 mmol) and dibenzoylmethane (26 mg, 0.12 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 3:1, then 2:1) afforded 46 mg (92%) of the target product **7c** as white solid.
$R_f$ = 0.34 (PE/EtOAc, 1:1, UV, anisaldehyde).
mp = 161-163 °C (EtOAc).
$^1$H NMR (300 MHz, COSY, acetone-$d_6$): 2.25-2.45 (m, 2H, $CH_2$(2)), 3.08-3.14 (m, 1H, CH(1)), 3.51 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.83 (br t, *J* = 12.0 Hz, 1H, CH(3)–Ar), 6.24 (d, *J* = 10.2 Hz, 1H, CH(4)), 6.66 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$), 7.23 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$), 7.37 (t, *J* = 7.6 Hz, 2H, $CH_{Ph}$), 7.48-7.53 (m, 3H, $CH_{Ph}$), 7.62 (t, *J* = 7.3 Hz, 1H, $CH_{Ph}$), 7.93 (d, *J* = 7.3 Hz, 2H, $CH_{Ph}$), 8.17 (d, *J* = 7.3 Hz, 2H, $CH_{Ph}$), 8.26 (br s, 1H, OH).
$^{13}$C NMR (75 MHz, DEPT, HSQC, acetone-$d_6$): 33.0 ($CH_2$(2)), 44.1 (CH(3)–Ar), 49.7 (CH(1)), 51.68 (OMe), 51.74 (OMe), 62.3 (C(4)), 115.0 ($CH_{Ar}$), 128.5 ($CH_{Ph}$), 128.6 ($CH_{Ph}$), 128.7 ($CH_{Ph}$), 128.8 ($CH_{Ph}$), 130.2 ($CH_{Ar}$), 130.3 ($C_{Ar}$), 133.1 ($CH_{Ph}$), 133.5 ($CH_{Ph}$), 136.9 ($C_{Ph}$), 137.4 ($C_{Ph}$), 156.3 ($C_{Ar}$–O), 168.9 ($CO_2$), 169.2 ($CO_2$), 194.0 (C=O), 194.2 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{28}H_{26}O_7$+$NH_4^+$]: 492.2017, found 492.2014.

**4-tert-Butyl 1,1-dimethyl 3-(4-hydroxyphenyl)-5-oxohexane-1,1,4-tricarboxylate (7f) and 3-tert-butyl 1,1-dimethyl 2-hydroxy-4-(4-hydroxyphenyl)-2-methylcyclopentane-1,1,3-tricarboxylate (10)**




**7f**
dr ≈ 1.4:1

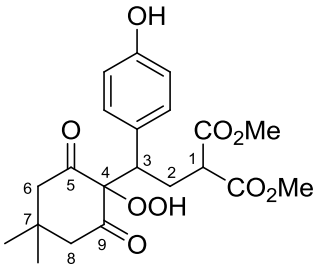



**10**

Malonate **7f** and cyclopentanol **10** were obtained from DAC **1a** (55 mg, 0.15 mmol) and *tert*-butyl acetoacetate (27 μL, 26 mg, 0.17 mmol) according to GP (reaction time – 1 d). Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 50.5 mg of the target products mixture (**7f-1** : **7f-2** : **10** = 1.2 : 1 : 1.4) and 9.5 mg of isomer **7f-2** as colorless oils. Total yield: 61 mg (95%). Relative configuration of stereocenters in **7f-1**, **7f-2**, and **10** was not determined.
$R_f$ (mixture **7f-1**+**10**) = 0.48 (PE/EtOAc, 1:1, UV, $FeCl_3$).
$R_f$ (mixture **7f-2**) = 0.30 (PE/EtOAc, 1:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, COSY, $CDCl_3$, **7f-1**): δ 1.13 (s, 9H, $CMe_3$), 1.93-2.05 (m, 1H, $CH_{2a}$(2)), 2.12-2.23 (m, 1H, $CH_{2b}$(2)), 2.31 (s, 3H, Me(6)), 3.11 (dd, *J* = 10.1, 4.3 Hz, 1H, CH(1)), 3.24-3.34 (m, 1H, CH(3)–Ar), 3.67 (d, *J* = 11.2 Hz, 1H, CH(4)), 3.56 (s, 3H, OMe), 3.80 (s, 3H, OMe), 6.31 (br s, 1H, OH), 6.71 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$), 6.99 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$).
$^1$H NMR (300 MHz, COSY, $CDCl_3$, **7f-2**): δ 1.50 (s, 9H, $CMe_3$), 1.95 (s, 3H, Me(6)), 2.06-2.18 (m, 1H, $CH_{2a}$(2)), 2.37 (app td, *J* = 10.3, 5.1 Hz, 1H, $CH_{2b}$(2)), 3.11 (dd, *J* = 10.1, 4.3 Hz, 1H, CH(1)), 3.24-3.34 (m, 1H, CH(3)–Ar), 3.57 (s, 3H, OMe), 3.73 (d, *J* = 11.0 Hz, 1H, CH(4)), 3.79 (s, 3H, OMe), 6.48 (br s, 1H, OH), 6.71 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$), 7.01 (d, *J* = 8.3 Hz, 2H, $CH_{Ar}$).
$^1$H NMR (300 MHz, COSY, $CDCl_3$, **10**): δ 1.30 (s, 9H, $CMe_3$), 1.61 (s, 3H, Me(6)), 2.16-2.26 (m, 1H, $CH_{2a}$(2)), 3.17 (dd, *J* = 14.5, 10.5 Hz, $CH_{2b}$(2)), 3.26 (d, *J* = 12.0 Hz, 1H, CH(4)), 3.69-3.77 (m, 1H, CH(3)–Ar), 3.78 (s, 6H, 2×OMe), 4.40 (s, 1H, C(5)–OH), 6.03 (br s, 1H, OH), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.18 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, **7f-1** + **7f-2** + **10**): δ 22.9 (Me(6), **10**), 27.4, 27.8, and 28.0 (C$\underline{Me}_3$, **7f-1** + **7f-2** + **10**), 28.8 (Me(6), **7f-1**), 29.7 (Me(6), **7f-2**), 33.3 ($CH_2$(2), **7f-2**), 33.6 ($CH_2$(2), **7f-1**), 40.6 ($CH_2$(2), **10**), 42.2 (CH(3)–Ar, **7f-1**), 42.5 (CH(3)–Ar, **7f-2**), 44.9 (CH(3)–Ar, **10**), 49.6 (CH(1), **7f-2**), 49.7 (CH(1), **7f-1**), 52.61, 52.66, 52.70 and 52.85 (all

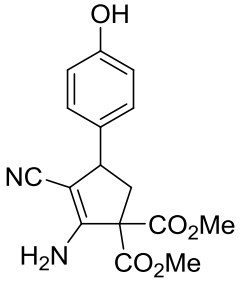
$CO_2$Me), 60.8 (CH(4), **10**), 67.4 (C(1), **10**), 67.5 (CH(4), **7f-2**), 68.2 (CH(4), **7f-1**), 81.8, 82.3, and 82.7 (all $Me_3$C–O), 83.6 (C(5)–O, **10**), 115.3, 115.4, and 115.8 (all $CH_{Ar}$), 128.8, 129.5, and 129.8 (all $CH_{Ar}$), 130.2 and 130.4 ($C_{Ar}$, **7f-1 + 7f-2**), 133.9 ($C_{Ar}$, **10**), 154.7, 155.4, and 155.5 (all $C_{Ar}$–O), 167.05, 167.12, 169.4, 169.6, 169.7, 170.5, 172.4, and 172.5 (all $CO_2$), 202.4 (C(5)=O, **7f-1**), 203.2 (C(5)=O, **7f-2**).
HRMS (ESI): *m/z* calcd. for $[C_{21}H_{28}O_8+NH_4^+]$: 426.2122, found: 426.2118.

**Dimethyl 2-(2-(1-hydroperoxy-4,4-dimethyl-2,6-dioxocyclohexyl)-2-(4-hydroxyphenyl)ethyl)malonate (8)**




Malonate **8** was obtained from DAC **1a** (38 mg, 0.11 mmol) and dimedone (16 mg, 0.12 mmol) according to GP (reaction time – 1 d). Column chromatography (eluent: EtOAc/MeOH, 40:1) afforded 41 mg (95%) of the target product **8** as white powder.
$R_f$ = 0.61 (EtOAc/MeOH, 20:1, UV, $FeCl_3$).
mp = 162-164 °C (EtOAc).
$^1$H NMR (300 MHz, COSY, acetone-$d_6$): δ 0.85 (s, 3H, Me), 1.16 (s, 3H, Me), 2.03-2.13 (m, 1H, $CH_{2a}$(2)), 2.25 (dd, *J* = 14.4, 3.4 Hz, 1H, $CH_{2a}$(6)), 2.35 (ddd, *J* = 13.9, 10.9, 2.9 Hz, 1H, $CH_{2b}$(2)), 2.50 (dd, *J* = 15.1, 3.4 Hz, 1H, $CH_{2a}$(8)), 2.94 (br d, *J* = 14.4 Hz, 1H, $CH_{2b}$(2)), 2.95 (dd, *J* = 10.9, 3.9 Hz, 1H, CH(1)), 3.06 (br d, *J* = 15.1 Hz, 1H, $CH_{2b}$(8)), 3.50 (dd, *J* = 12.3, 2.9 Hz, 1H, CH(3)–Ar), 3.56 (s, 3H, OMe), 3.68 (s, 3H, OMe), 6.75 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.12 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 8.44 (br s, 1H, OH), 10.81 (s, 1H, OH).
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, acetone-$d_6$): δ 25.4 (Me), 28.6 ($CH_2$(2)), 29.4 (Me), 30.0 (C(7)$Me_2$), 47.8 (CH(3)–Ar), 49.1 (CH(1)), 51.86 and 51.92 ($CO_2$Me), 51.9 ($CH_2$(8)), 52.9 ($CH_2$(6)), 99.9 (C(4)–OOH), 115.2 ($CH_{Ar}$), 126.1 ($C_{Ar}$), 130.8 ($CH_{Ar}$), 157.2 ($C_{Ar}$–OH), 168.9 and 169.1 ($CO_2$), 201.4 and 203.2 (C(6)=O and C(8)=O).
HRMS (ESI): *m/z* calcd. for $[C_{21}H_{26}O_9+NH_4^+]$: 440.1915, found: 440.1906.

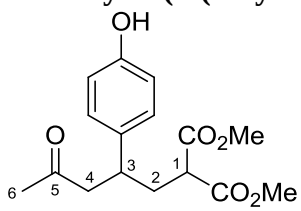
**Dimethyl 2-amino-3-cyano-4-(4-hydroxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (9)**




Cyanopentene **9** was obtained from DAC **1a** (37 mg, 0.10 mmol) and malononitrile (7.5 mg, 0.11 mmol) according to GP. Column chromatography (eluent: PE/EtOAc, 2.5:1) afforded 25 mg (78%) of the target product **9** as light yellow oil, that solidified upon storage in a fridge.
$R_f$ = 0.30 (PE/EtOAc, 1:1, UV, $FeCl_3$).
mp = 154-156 °C ($CH_2Cl_2$).
$^1$H NMR (300 MHz, $CDCl_3$): 2.27 (dd, *J* = 13.7, 7.9 Hz, 1H, $CH_{2a}$), 3.00 (dd, *J* = 13.7, 7.6 Hz, 1H, $CH_{2b}$), 3.80 (s, 3H, OMe), 3.85 (s, 3H, OMe), 4.08 (app t, *J* = 7.7 Hz, 1H, CH–Ar), 5.20 (br s, 2H, $NH_2$), 5.81 (s, 1H, OH), 6.79 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.10 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): 41.7 ($CH_2$), 46.0 (C̲H–Ar), 53.5 (OMe), 53.8 (OMe), 64.9 (C̲($CO_2Me)_2$), 84.1 (=C̲–CN), 115.7 ($CH_{Ar}$), 117.3 (CN), 128.5 ($CH_{Ar}$), 133.6 ($C_{Ar}$), 155.2 and 156.6 ($C_{Ar}$–O and =C–$NH_2$), 168.5 ($CO_2$), 169.1 ($CO_2$).
HRMS (ESI): *m/z* calcd. for [$C_{16}H_{16}N_2O_5$+$H^+$]: 317.1132, found 317.1134.

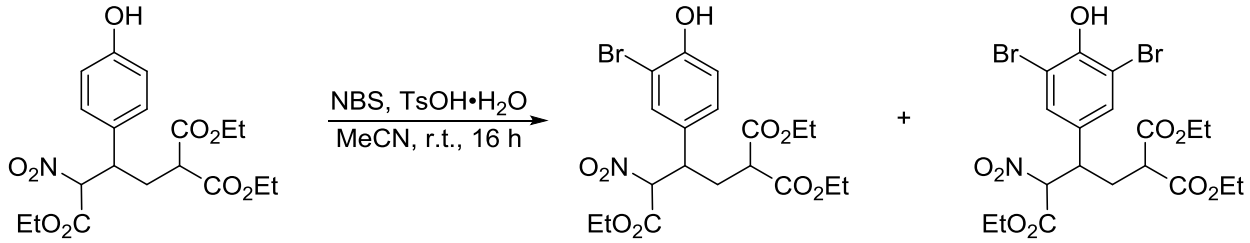
**Dimethyl 2-(2-(4-hydroxyphenyl)-4-oxopentyl)malonate (11)**




To a stirring solution of a mixture malonate **7f** and cyclopentanol **10** (**7f**/**10** = 1.6:1, 10.5 mg. 26 μmol) in $CH_2Cl_2$ (0.44 mL) TFA (50 μL, 75 mg, 0.65 mmol) was added at r.t. The reaction mixture was left overnight, diluted with EtOAc (ca. 2 mL), and evaporated at 50 °C for 0.5 h on a rotary evaporator to obtain 8.0 mg (ca. 100%) of target ketone **11** as light yellow oil.
$R_f$ = 0.28 (PE/EtOAc, 1:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, COSY, $CDCl_3$): 2.04 (s, 3H, Me(6)), 2.11 (ddd, *J* = 13.9, 11.2, 5.1, 1H, $CH_{2a}$(2)), 2.28 (ddd, *J* = 13.9, 9.7, 4.3 Hz, 1H, $CH_{2b}$(2)), 2.67-2.82 (m, 2H, $CH_2$(4)), 3.10 (dddd, *J* = 11.2, 7.6, 6.7, 4.3 Hz, 1H, CH(3)–Ar), 3.17 (dd, *J* = 9.7, 5.1 Hz, 1H, CH(1)), 3.62 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.82 (s, 1H, OH), 6.74 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.02 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, HSQC, $CDCl_3$): 30.5 (Me(6)), 35.3 ($CH_2$(2)), 38.4 (CH(3)–Ar), 49.8 (CH(1)), 50.9 ($CH_2$(4)), 52.6 (OMe), 52.7 (OMe), 115.6 ($CH_{Ar}$), 128.8 ($CH_{Ar}$), 133.6 ($C_{Ar}$), 154.8 ($C_{Ar}$–O), 169.7 ($CO_2$), 169.8 ($CO_2$), 207.6 (C(5)=O).
HRMS (ESI): *m/z* calcd. for [$C_{16}H_{20}O_6$+$H^+$]: 309.1333, found 309.1332.

**Post transformations.**

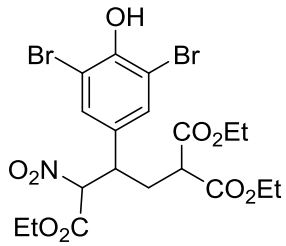
**Bromination of triethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ba)**




**3ba** **3ea**, 71% **3ma**, 17%

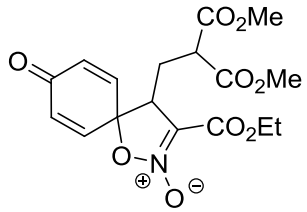
A modified literature procedure was used.[s24]
To a stirring solution of nitromalonate **3ba** (38 mg, 0.092 mmol) in MeCN (0.90 mL) TsOH·$H_2O$ (19 mg, 0.1 mmol) and NBS (19 mg, 0.1 mmol) was sequentially added at r.t. and the reaction mixture was left overnight. After that it was transferred into EtOAc (15 mL) / $Na_2S_2O_3$ (0.02 M aq. soln., 10 mL), organic layes was washed with brine (15 mL), dried over $Na_2SO_4$ and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 4:1, then 3:1) to give 9.5 mg (17%) of nitromalonate **3ma** (dr ≈ 1:1) and 32 mg (71%) of nitromalonate **3ea** (dr ≈ 1:1) as colorless oils.

**Triethyl 3-(3,5-dibromo-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ma)**



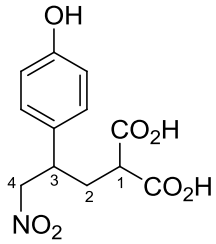
$R_f$ = 0.57 (PE/EtOAc, 1:1, UV, anisaldehyde).
$^1$H NMR (300 MHz, $CDCl_3$, sum of isomers): δ 1.12 (t, *J* = 7.1 Hz), 1.23 (t, *J* = 7.1 Hz), 1.27-1.39 (m) (total 9H, all $CH_2C\underline{H}_3$, both isomers), 2.11-2.44 (m, 2H, $CH_2$(2), both isomers), 3.02-3.12 (m, 1H, CH(1), both isomers), 3.57-3.71 (m, 1H, CH(3)–Ar, both isomers), 4.02-4.19 (m), 4.22-4.32 (m), and 4.36 (q, *J* = 7.2 Hz) (total 6H, all $OC\underline{H}_2CH_3$, both isomers), 5.24 (d, *J* = 9.7 Hz, 1H, CH(4)–$NO_2$), 5.26 (d, *J* = 10.2 Hz, 1H, CH(4)–$NO_2$), 5.98 (br s, 1H, OH), 7.34 (d, *J* = 1.13 Hz, 1H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$, sum of isomers): δ 13.7, 13.87, 13.93, 14.06 and 14.09 (all $CH_2\underline{C}H_3$), 30.6 and 31.0 ($CH_2$(2)), 43.12 and 43.14 (CH(3)–Ar), 49.3 and 49.4 (CH(1)), 61.89, 61.93, 62.3, and 63.6 (all $O\underline{C}H_2CH_3$), 91.7 and 91.9 (CH(4)–$NO_2$), 110.3 and 110.4 ($C_{Ar}$–Br), 129.8 and 130.6 ($C_{Ar}$), 132.0 and 132.3 ($CH_{Ar}$), 149.65 and 149.67 ($\underline{C}_{Ar}$–O), 162.5 and 162.7 (C(5)=O), 168.1, 168.2, 168.28, and 168.34 (all C=O).
HRMS (ESI): *m/z* calcd. for [$C_{19}H_{23}{}^{79}Br_2NO_9$+$NH_4^+$]: 587.0059, found: 587.0060.

**3-(Ethoxycarbonyl)-4-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl)-8-oxo-1-oxa-2-azaspiro[4.5]deca-2,6,9-triene 2-oxide (13)**



To a stirring solution of nitromalonate **3aa** (39 mg, 0.10 mmol) in $CH_2Cl_2$ (2.0 mL) PIFA (47 mg, 0.11 mmol) was added at 0 °C. The resulting mixture turned dark blue and was slowly warmed up to r.t. and left for 1 h. After the completion of reaction (TLC monitoring) the blue-green solution turned dark yellow. $NaHCO_3$ (sat. aq. soln., 0.5 mL) was added to the reaction mixture, after that it was stirred for 5 min and transferred into EtOAc (15 mL) / $H_2O$ (10 mL). Organic layer was washed with brine (15 mL), dried over $Na_2SO_4$ and evaporated. The residue was redissolved in toluene (app. 0.3 mL) and precipitated with PE (app. 1.0 mL) to obtain 30 mg (78%) of target product.
$^1$H NMR (300 MHz, COSY, $CDCl_3$): 1.38 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 2.31 (ddd, *J* = 14.5, 8.2, 6.3 Hz, 1H, $CH_{2a}$), 2.46 (app dt, *J* = 13.9, 6.8 Hz, 1H, $CH_{2b}$), 3.60-3.78 (m, 2H, 2×CH), 3.75 (s, 6H, 2×OMe), 4.37 (q, *J* = 7.1 Hz, 2H, $OCH_2CH_3$), 6.36 (d, *J* = 9.8 Hz, 1H, =CH), 6.48 (d, *J* = 10.0 Hz, 1H, =CH), 6.95-7.02 (m, 2H, 2× =CH).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): 14..0 ($CH_2\underline{C}H_3$), 28.2 ($CH_2$), 48.87 and 48.91 (2×CH), 53.00 and 53.02 (2×OMe), 62.6 ($O\underline{C}H_2CH_3$), 77.7 (C–O), 110.5 (C=N), 130.0 (=CH), 132.8 (=CH), 139.2 (=CH), 142.8 (=CH), 158.5 ($\underline{C}O_2$Et), 168.6 ($\underline{C}O_2$Me), 168.7 ($\underline{C}O_2$Me), 183.6 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{17}H_{19}NO_9$+$NH_4^+$]: 399.1398, found 399.1403.

**2-(2-(4-Hydroxyphenyl)-3-nitropropyl)malonic acid (14)**




Prepared according to modified literature procedure.[s25]

To a solution of nitromalonate **3aa** (76 mg, 0.20 mmol) in THF (2.0 mL) a solution of LiOH ( 38 mg, 1.60 mmol) in $H_2O$ (2.0 mL) was added at r.t. with stirring. The reaction mixture was left overnight, concentrated in vacuum and diluted with EtOAc (5 mL). The aqueous layer was acidified to pH<2 with 1M HCl (2 ml). The resulting mixture was extracted with EtOAc (10 ml), then combined organic layer was washed with brine (20 mL), dried over $Na_2SO_4$ and evaporated to give 54 mg (96%) of crude acid **14** as light yellow oil, which was used in the next step without additional purification. If necessary, the residue was triturated with PE to give white powder.

$R_f$ = 0.30 (EtOAc/MeOH, 20:1, UV, $FeCl_3$).

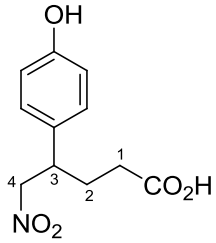
mp = 155-156 °C (dec.) (PE/EtOAc, 1:1).

$^1$H NMR (300 MHz, COSY, acetone-$d_6$): δ 2.16-2.37 (m, 2H, $CH_2$), 3.12 (dd, *J* = 10.1, 4.5 Hz, 1H, C<u>H</u>$(COOH)_2$), 3.45-3.60 (m, 1H, CH–Ar), 4.77 (dd, *J* = 12.4, 9.3 Hz, 1H, $CH_{2a}$–$NO_2$), 4.89 (dd, *J* = 12.5, 6.4 Hz, 1H, $CH_{2b}$–$NO_2$), 6.84 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$), 7.18 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$). OH protons are not visible due to broadening and exchange.

$^{13}$C NMR (75 MHz, HSQC, acetone-$d_6$): δ 32.2 ($CH_2$), 41.6 (CH–Ar), 48.8 (<u>C</u>H$(COOH)_2$), 80.5 ($CH_2$–$NO_2$), 115.7 ($CH_{Ar}$), 129.0 ($CH_{Ar}$), 129.3 ($C_{Ar}$), 157.0 ($C_{Ar}$–OH), 169.8 (COOH), 169.9 (COOH).

HRMS (ESI): *m/z* calcd. for [$C_{12}H_{13}NO_7$+$Na^+$]: 306.0584, found: 306.0577.

**4-(4-Hydroxyphenyl)-5-nitropentanoic acid (15)**




A solution of crude acid **14** (26 mg, 92 μmol) in DMF (0.9 mL) was heated at 120 °C for 4 h under an argon atmosphere. After that the reaction mixture was diluted with EtOAc (5 ml) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc/MeOH, 1:1:0.1) to give 17 mg (77%) of the target product **15** as light yellow oil, that solidified upon storage in a fridge.

mp = 128-129 °C (PE/EtOAc, 1:1).

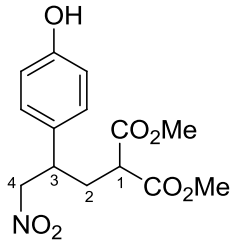
$R_f$ = 0.16 (PE/EtOAc/MeOH, 1:1:0.1, UV, $FeCl_3$).

$^1$H NMR (300 MHz, COSY, acetone-$d_6$): δ 1.83-2.03 (m, 2H, $CH_2$), 2.18-2.24 (m, 2H, $CH_2$), 3.43-3.51 (m, 1H, CH–Ar), 4.73 (dd, *J* = 12.5, 9.1 Hz, 1H, $CH_{2a}$–$NO_2$), 4.84 (dd, *J* = 12.5, 6.6 Hz, 1H, $CH_{2b}$–$NO_2$), 6.83 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.16 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 8.42 (br s, 1H, OH).

$^{13}$C NMR (75 MHz, DEPT, HSQC, acetone-$d_6$): δ 28.2 ($CH_2$), 30.7 ($CH_2$), 42.9 (CH–Ar), 80.6 ($CH_2$–$NO_2$), 115.6 ($CH_{Ar}$), 128.8 ($CH_{Ar}$), 129.9 ($C_{Ar}$), 156.8 ($C_{Ar}$–OH), 173.2 (COOH).

HRMS (ESI): *m/z* calcd. for [$C_{11}H_{13}NO_5$+$NH_4^+$]: 257.1132, found: 257.1140.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitropropyl)malonate (16)**




To a solution of nitromalonate **3ac** (53 mg, 0.12 mmol) in MeOH (2.4 mL) in a Schlenk tube 10 wt. % Pd/C (3.6 mg, 3 μmol) was added at -15 °C ($CaCl_2$-$H_2O$ cooling bath). The tube was evacuated and backfilled with $H_2$ from balloon 5 times. Then the mixture was vigorously stirred for 1 h () at the same temperature under $H_2$ atmosphere (balloon), filtered and concentrated in vacuum. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 3:1, then 2.5:1) to give 32 mg (85%) of the target product **16** as colorless oil.

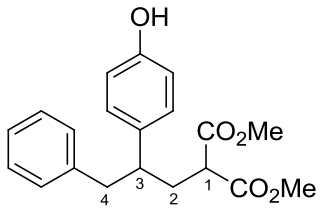
$R_f$ = 0.36 (PE/EtOAc, 1:1, UV, $FeCl_3$).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.21 (ddd, *J* = 13.9, 11.5, 4.9 Hz, 1H, $CH_{2a}$(2)), 2.36 (ddd, *J* = 13.9, 9.9, 4.1 Hz, 1H, $CH_{2b}$(2)), 3.20 (dd, *J* = 9.9, 4.9 Hz, 1H, CH(1)), 3.45 (app dtd, *J* = 11.5, 7.7, 4.1 Hz, 1H, CH(3)–Ar), 3.64 (s, 3H, OMe), 3.78 (s, 3H, OMe), 4.50-4.62 (m, 2H, $CH_2$(4)–$NO_2$), 5.53 (br s, 1H, OH), 6.79 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.05 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 32.0 ($CH_2$(2)), 41.5 (CH(3)–Ar), 49.3 (CH(1)), 52.8 (OMe), 52.9 (OMe), 80.6 ($CH_2$–$NO_2$), 116.1 ($CH_{Ar}$), 128.9 ($C_{Ar}$), 129.0 ($CH_{Ar}$), 155.6 ($C_{Ar}$–OH), 169.2 ($CO_2$), 169.3 ($CO_2$).

HRMS (ESI): *m/z* calcd. for [$C_{14}H_{17}NO_7$+$NH_4^+$]: 329.1343, found 329.1345.

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-phenylpropyl)malonate** (**17)**




To a solution of nitromalonate **3ae** (30 mg, 77 μmol) in MeOH (1.4 mL) in a Schlenk tube 20 wt. % $Pd(OH)_2$/C (5 mg, 7 μmol) was added at r.t. under an argon atmosphere. The tube was evacuated and backfilled with $H_2$ from balloon 5 times. Reaction mixture was vigorously stirred at 55 °C under $H_2$ atmosphere (balloon) for 5 h. Then the resulting mixture was cooled to r.t, filtered through Celite® and concentrated in vacuum. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 3:1) to give 18 mg (75%) of the target product **17** as colorless oil.

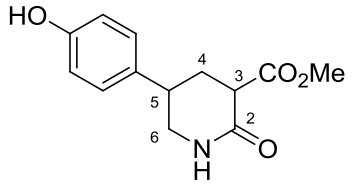
$R_f$ = 0.48 (PE/EtOAc, 1:1, anisaldehyde, *Hanessian stain*).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.17 (ddd, *J* = 13.9, 10.6, 5.0 Hz, 1H, $CH_{2a}$(2)), 2.37 (ddd, *J* = 13.9, 10.1, 3.9 Hz, 1H, $CH_{2b}$(2)), 2.76-2.85 (m, 1H, CH(3)–Ar), 2.85-2.92 (m, 2H, $CH_2$(4)), 3.20 (dd, *J* = 10.0, 4.9 Hz, 1H, CH(1)), 3.62 (s, 3H, OMe), 3.70 (s, 3H, OMe), 5.24 (br s, 1H, OH), 6.74 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 6.95 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.00-7.04 (m, 2H, $CH_{Ph}$), 7.12-7.24 (m, 3H, $CH_{Ph}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 34.7 ($CH_2$(2)), 43.9 ($CH_2$(4)), 44.9 (CH(3)–Ar), 50.0 (CH(1)), 52.5 (OMe), 52.6 (OMe), 115.4 ($CH_{Ar}$), 126.0 ($CH_{Ph}$), 128.1 ($CH_{Ph}$), 129.0 and 129.1 ($CH_{Ar}$ and $CH_{Ph}$), 134.6 ($C_{Ar}$), 139.8 ($C_{Ph}$), 154.4 ($C_{Ar}$–OH), 169.8 ($CO_2$), 170.1 ($CO_2$).

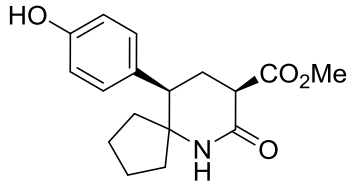
HRMS (ESI): *m/z* calcd. for [$C_{20}H_{22}O_5$+$H^+$]: 343.1540, found: 343.1533.

**Methyl 5-(4-hydroxyphenyl)-2-oxopiperidine-3-carboxylate (18)**

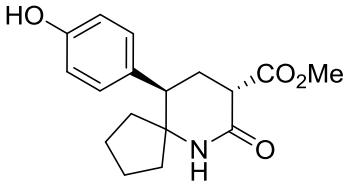



1) To a solution of nitromalonate **3ac** (47 mg, 0.11 mmol) in MeOH (2.0 mL) in a Schlenk tube 10 wt. % Pd/C (3.3 mg, 3 μmol) was added at -15 °C ($CaCl_2$-$H_2O$ cooling bath). The tube was evacuated and backfilled with $H_2$ from balloon 5 times. Reaction mixture was vigorously stirred for 1 h at the same temperature under $H_2$ atmosphere (balloon). Then the resulting mixture was warmed up to r.t. and MeOH (2 mL) and 10 wt. % Pd/C (2.0 mg, 2 μmol) were consequently added. The tube was evacuated and backfilled with $H_2$ from balloon 5 times and the resulting mixture was vigorously stirred for 3 h at 45 °C under $H_2$ atmosphere (balloon). The mixute was was cooled to r.t., filtered through Celite® and concentrated in vacuum. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: EtOAc, then EtOAc/MeOH 20:1) to give 18 mg (72%) of the target product **18** as white solid.
2) To a stirred solution of nitromalonate **16** (31 mg, 0.10 mmol) in MeOH (2.0 mL) Zn powder (median 6-9 μm) (130 mg, 2.00 mmol) and AcOH (0.11 mL, 116 mg, 1.93 mmol) were consequently added under an argon atmosphere. Reaction mixture was vigorously stirred for 16 h at r.t. and transferred into $CH_2Cl_2$ (15 mL) / $H_2O$ (20 mL). The aqueous layer was washed with $CH_2Cl_2$ (15 mL), and the combined organic layers were washed with $NaHCO_3$ (sat. aq., 10 mL), brine (20 mL), dried over $Na_2SO_4$ and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: EtOAc, then EtOAc/MeOH 20:1) to give 16 mg (66%) of the target product **18** as colorless oil.
dr = 1.4:1. Relative configuration of stereocenters was not determined.
$R_f$ = 0.20 (EtOAc, UV, ninhydrine).
$^1$H NMR (300 MHz, COSY, $CD_3OD$, sum of isomers): δ 2.18-2.38 (m, total 2H, $CH_2$(4)), 3.00-3.12 (m) and 3.14-3.25 (m) (total 1H, CH(5)), 3.28-3.52 (m, 2H, $CH_2$–N), 3.36-3.66 (m, 1H, CH(3)), 3.756 (s) and 3.763 (s) (total 3H, OMe), 6.77 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.12 (d, *J* = 8.5 Hz) and 7.14 (d, *J* = 8.5 Hz) (total 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CD_3OD$, sum of isomers): δ 30.9 ($CH_2$(5), min), 31.7 ($CH_2$(5), maj), 35.0 (CH(5)–Ar, min), 37.8 (CH(5)–Ar, maj), 47.8 ($CH_2$(6)–N, min), 48.3 ($CH_2$(6)–N, maj), 51.5 (OMe, min), 51.6 (maj), 115.1 ($CH_{Ar}$, maj + min), 127.7 ($CH_{Ar}$, maj + min), 131.85 ($C_{Ar}$, min), 191.91 ($C_{Ar}$, maj), 156.16 ($C_{Ar}$–O, min), 156.23 ($C_{Ar}$–O, maj), 168.6, 168.7, 171.4, and 171.6 (all C=O). CH(3) can not unambiguously identified due to overlapping with solvent ($CD_3OD$) signals.
HRMS (ESI): *m/z* calcd. for [$C_{13}H_{15}NO_4$+$H^+$]: 250.1074, found 250.1079.

**Methyl 10-(4-hydroxyphenyl)-7-oxo-6-azaspiro[4.5]decane-8-carboxylate (19)**




(8*R**,10*R**)-

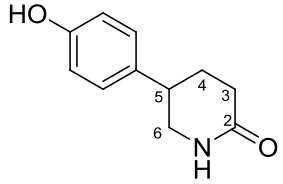



(8*S**,10*R**)-

To a stirred solution of nitromalonate **3ar** (113 mg, 0.31 mmol) in MeOH (6.0 mL) Zn powder (median 6-9 μm) (0.40 g, 6.20 mmol) and AcOH (0.35 mL, 0.37 g, 6.12 mmol) were consequently added under an argon atmosphere. Reaction mixture was vigorously stirred for 16 h at r.t. and transferred into $CH_2Cl_2$ (20 mL) / $H_2O$ (30 mL). Then TMEDA (0.23 mL, 178 mg, 1.54 mmol) was added and the resulting mixture was vigorously stirred. The aqueous layer was separated, mixed with $NaHSO_4$ (0.5 M in $H_2O$, 10 mL) and washed with EtOAc (3×20 mL). The combined organic layers were washed with brine (30 mL), dried over $Na_2SO_4$ and evaporated.

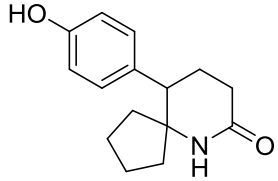
Then crude amine was dissolved in MeOH (0.60 mL), $K_2CO_3$ (20 mg, 0.15 mmol) was added, and the reaction mixture was stirred for 2 h at r.t. (TLC monitoring). Then AcOH (17 μL, 18 mg, 0.30 mmol) was added, the mixture was stirred for 10 min and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 1:1, then 1:3) to give 74 mg (79%) of the target product **19** as colorless oil.
$R_f$ = 0.38 (EtOAc, UV, ninhydrine).
(8*R**,10*R**) (major isomer) / (8*S**,10*R**) (minor isomer) = 1.1 : 1 ($^1$H NMR).
$^1$H NMR (300 MHz, COSY, $CDCl_3$, sum of isomers): δ 1.32-1.89 (m, 8H, 4×$CH_2$, both isomers), 2.20 (ddd, *J* = 13.2, 6.9, 2.5 Hz, 1H, C$H_{2a}$–CH–$CO_2$Me, maj), 2.29-2.36 (m, 1H, C$H_{2a}$–CH–$CO_2$Me, min), 2.45 (ddd, *J* = 13.6, 6.7, 3.6 Hz, 1H, C$H_{2b}$–CH–$CO_2$Me, min), 2.66 (app q, *J* = 13.1 Hz, 1H, C$H_{2b}$–CH–$CO_2$Me, maj), 3.04 (dd, *J* = 13.2, 2.5 Hz, 1H, CH–Ar, maj), 3.14 (dd, *J* = 8.2, 3.6 Hz, 1H, CH–Ar, min), 3.53 (app t, *J* = 6.9 Hz, 1H, CH–$CO_2$Me, min), 3.61 (dd, *J* = 11.7, 6.9 Hz, 1H, CH–$CO_2$Me, maj), 3.74 (s, 3H, $CO_2$Me, min), 3.79 (s, 3H, $CO_2$Me, min), 6.52 (br s, 1H, NH, maj), 6.76 (br s, 1H, NH, min), 6.81 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, min), 6.83 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, maj), 7.07 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$, both isomers). Signals of OH are not visible due to broadening.
Characteristic NOESY interactions:
Major isomer: CH–Ar / C$H_{2b}$–CH–$CO_2$Me; CH–Ar / CH–$CO_2$Me; CH–$CO_2$Me / C$H_{2a}$–CH–$CO_2$Me; CH– CH–Ar / C$H_{2a}$–CH–$CO_2$Me.
Minor isomer: $CH_{Ar}$ / CH–$CO_2$Me; $CH_{Ar}$ / C$H_{2a}$–CH–$CO_2$Me; CH–$CO_2$Me / C$H_{2a}$–CH–$CO_2$Me; CH–Ar / C$H_2$–CH–$CO_2$Me.
$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, sum of isomers): δ 22.1, 22.5, 22.8, and 23.0 (all $CH_2$, both isomers), 29.3 (C$H_2$–CH–$CO_2$Me, maj), 29.7 (C$H_2$–CH–$CO_2$Me, min), 34.4, 35.9, 37.7, and 40.5 (all $CH_2$, both isomers), 44.3 (CH–Ar, min), 45.5 (CH–Ar, maj), 46.2 (CH–$CO_2$Me, min), 49.4 (CH–$CO_2$Me, maj), 52.7 ($CO_2$Me, both isomers), 67.3 (C–N, min), 67.8 (C–N, min), 115.2 and 115.4 ($CH_{Ar}$), 130.1 ($CH_{Ar}$, maj), 130.4 ($C_{Ar}$, maj), 130.6 ($CH_{Ar}$, min), 131.2 ($C_{Ar}$, min), 155.56 and 155.64 ($C_{Ar}$–O, both isomers), 167.6 (C(O)–NH, maj), 168.1 (C(O)–NH, maj), 171.0 ($CO_2$Me, maj), 171.3 ($CO_2$Me, min).
HRMS (ESI): *m/z* calcd. for [$C_{17}H_{21}NO_4$+$H^+$]: 304.1543, found: 304.1550.

**5-(4-Hydroxyphenyl)piperidin-2-one (20)**




To the solution of piperidone **18** (29 mg, 0.11 mmol) in *N*,*N*-dimethylacetamide (1.0 mL) NaBr (23 mg, 0.22 mmol) and $H_2O$ (20 μL, 20 mg, 1.11 mmol) were consequently added. The resulting mixture was evacuated and backfilled with argon twice and gently refluxed under an argon atmosphere for 4 h. Then the reaction mixute was cooled to r.t, diluted with EtOAC (*ca.* 5 mL) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: EtOAc, then EtOAc/MeOH 20:1) to give 16 mg (76%) of the target product **20** as white solid.
$R_f$ = 0.15 (EtOAc, UV, ninhydrin).
mp = 268-270 °C (MeOH).
$^1$H NMR (300 MHz, COSY, $CD_3OD$): δ 1.99-2.13 (m, 2H, $CH_2$(4)), 2.43-2.51 (m, 2H, $CH_2$(3)), 2.93-3.03 (CH(5)–Ar), 3.27 (app d, *J* = 12.2 Hz, 1H, $CH_{2a}$(6)–N), 3.41 (dd, *J* = 11.7, 5.3 Hz, 1H, $CH_{2b}$(6)–N), 6.76 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.13 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).
$^{13}$C NMR (75 MHz, DEPT, HSQC, $CD_3OD$): δ 27.5 ($CH_2$(4)), 30.5 ($CH_2$(3)), 38.3 (CH(5)–Ar), 48.2 ($CH_2$(6)–N), 115.0 ($CH_{Ar}$), 127.6 ($CH_{Ar}$), 132.8 ($C_{Ar}$), 156.0 ($C_{Ar}$–O), 173.3 (C=O).
HRMS (ESI): *m/z* calcd. for [$C_{11}H_{13}NO_2$+$H^+$]: 192.1019, found 192.1028.

**10-(4-Hydroxyphenyl)-6-azaspiro[4.5]decan-7-one (21)**



To the solution of piperidone **19** (32 mg, 0.11 mmol) in *N*,*N*-dimethylacetamide (1.0 mL) NaBr (23 mg, 0.22 mmol) and $H_2O$ (20 μL, 20 mg, 1.11 mmol) were consequently added. The resulting mixture was evacuated and backfilled with argon twice and gently refluxed under an argon atmosphere for 3.5 h. Then the reaction mixute was cooled to r.t, diluted with EtOAc (*ca.* 5 mL) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: EtOAc, then EtOAc/MeOH 20:1) to give 25 mg (90%) of the target product **21** as white solid.

$R_f$ = 0.26 (EtOAc, UV, chloranil).

mp = 156-158°C ($CDCl_3$).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.51-1.73 (m, 3H) and 1.75-1.98 (m, 6H), (all $CH_2$ and $C\underline{H}_{2a}CH_2C(O)$), 2.22-2.54 ($C\underline{H}_{2b}CH_2C(O)$ and $CH_2C(O)$), 2.85-2.90 (m, 1H, CH–Ar), 6.76 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.12 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 8.83 (br s, 1H) and 9.23 (br s, 1H) (NH and OH).

$^{13}$C NMR (75 MHz, HSQC, HMBC, $CDCl_3$): δ 23.7 ($CH_2$), 23.9 ($CH_2$), 25.7 ($\underline{C}H_2CH_2C(O)$), 27.0 ($\underline{C}H_2C(O)$), 36.8 ($CH_2$), 42.9 ($CH_2$), 46.3 (CH–Ar), 66.5 (C–N), 114.8 ($CH_{Ar}$), 129.7 ($CH_{Ar}$), 131.8 ($C_{Ar}$), 156.0 ($C_{Ar}$–O), 174.6 (C=O).

HRMS (ESI): *m/z* calcd. for [$C_{15}H_{19}NO_2$+$H^+$]: 246.1489, found 246.1494.

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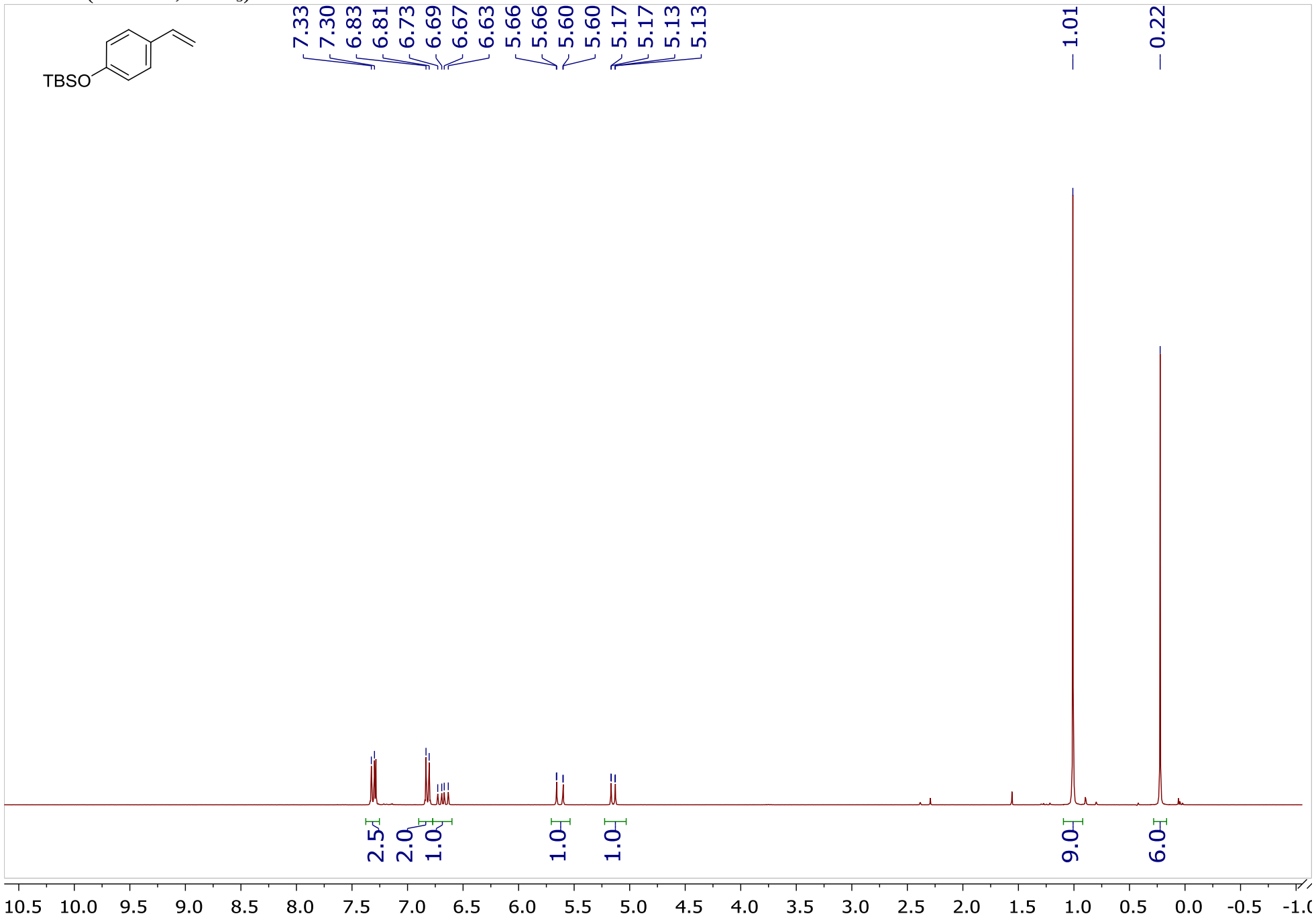
s25. Q. Wang, J. Gong, Y. Liu, Y. Wang and Z. Zhou, *Tetrahe*dr*on* 2014, **70**, 8168-8173.

# Copies of NMR spectra

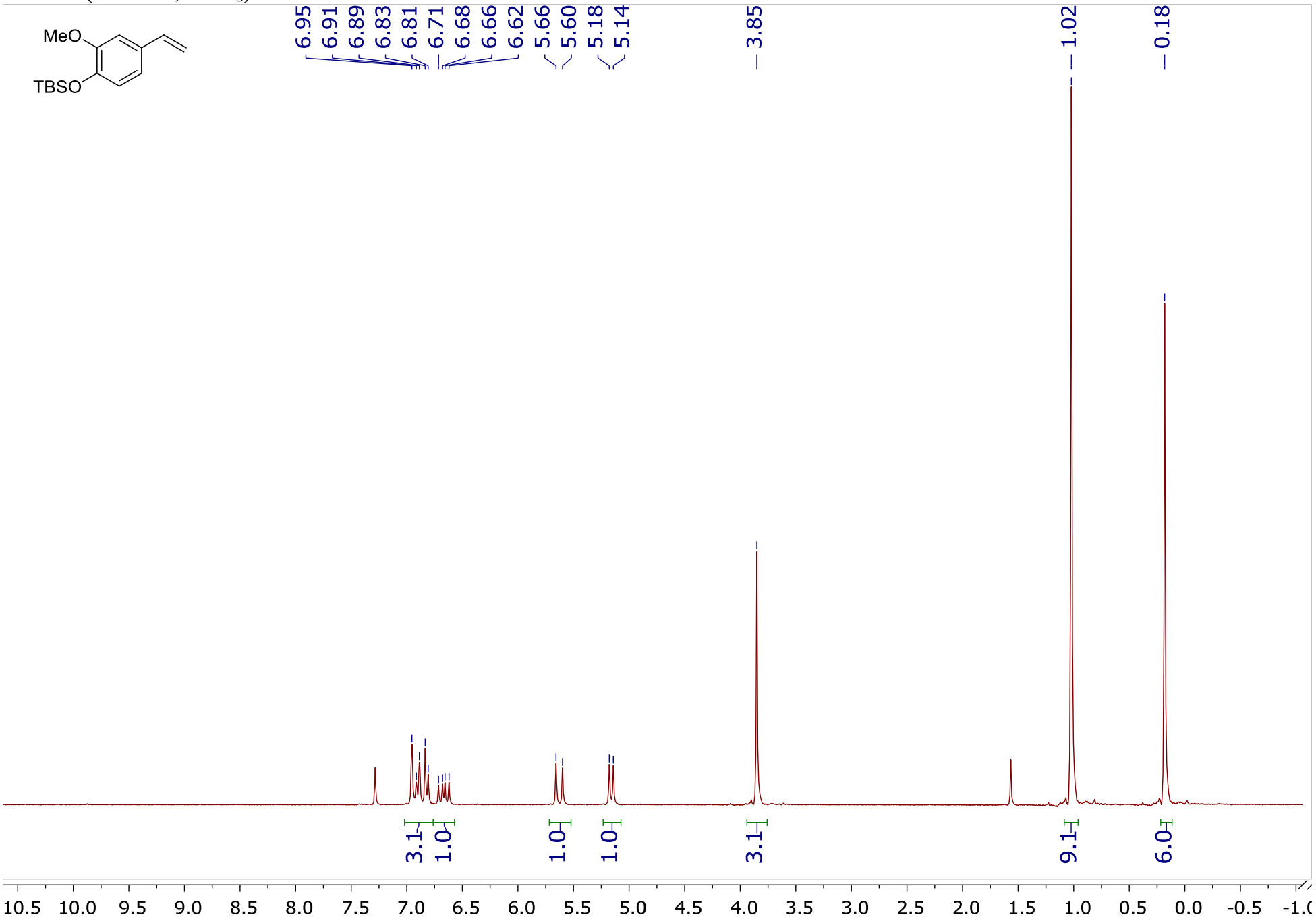
***tert*-Butyldimethyl(4-vinylphenoxy)silane (S1)**

$^1$H NMR (300 MHz, $CDCl_3$)



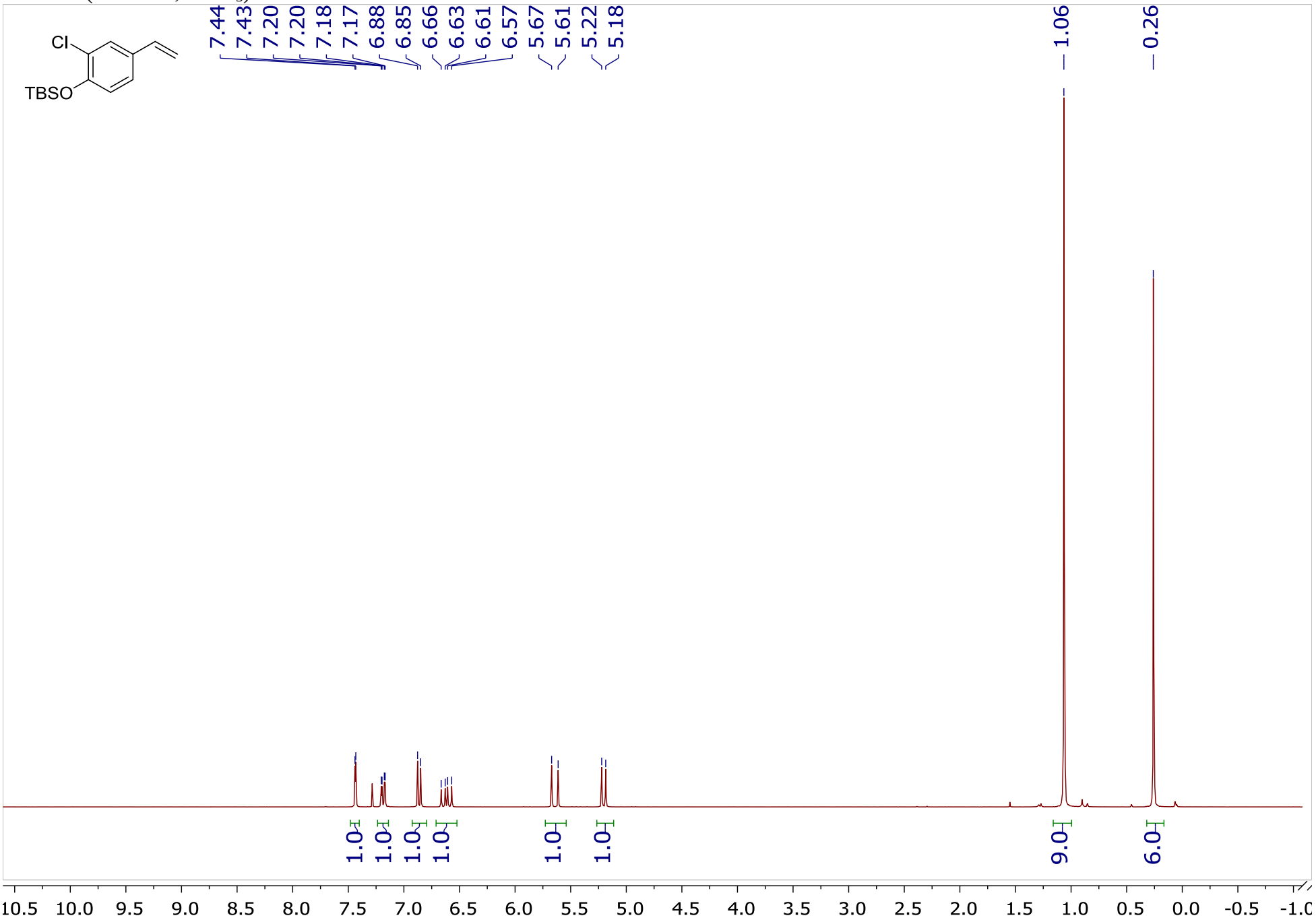
***tert*-Butyl(2-methoxy-4-vinylphenoxy)dimethylsilane (S2)**

$^1$H NMR (300 MHz, $CDCl_3$)

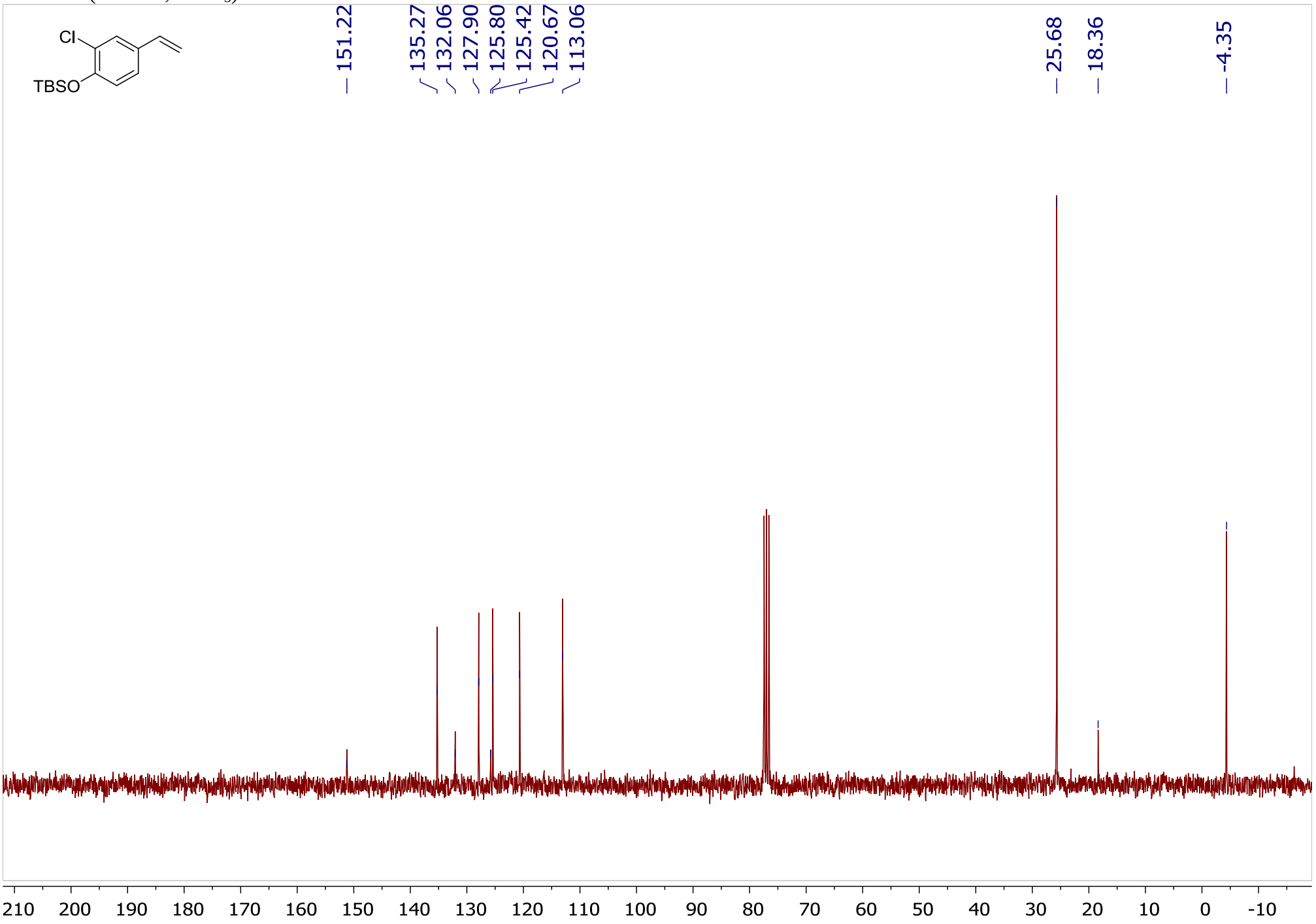


***tert*-Butyl(2-chloro-4-vinylphenoxy)dimethylsilane (S3)**

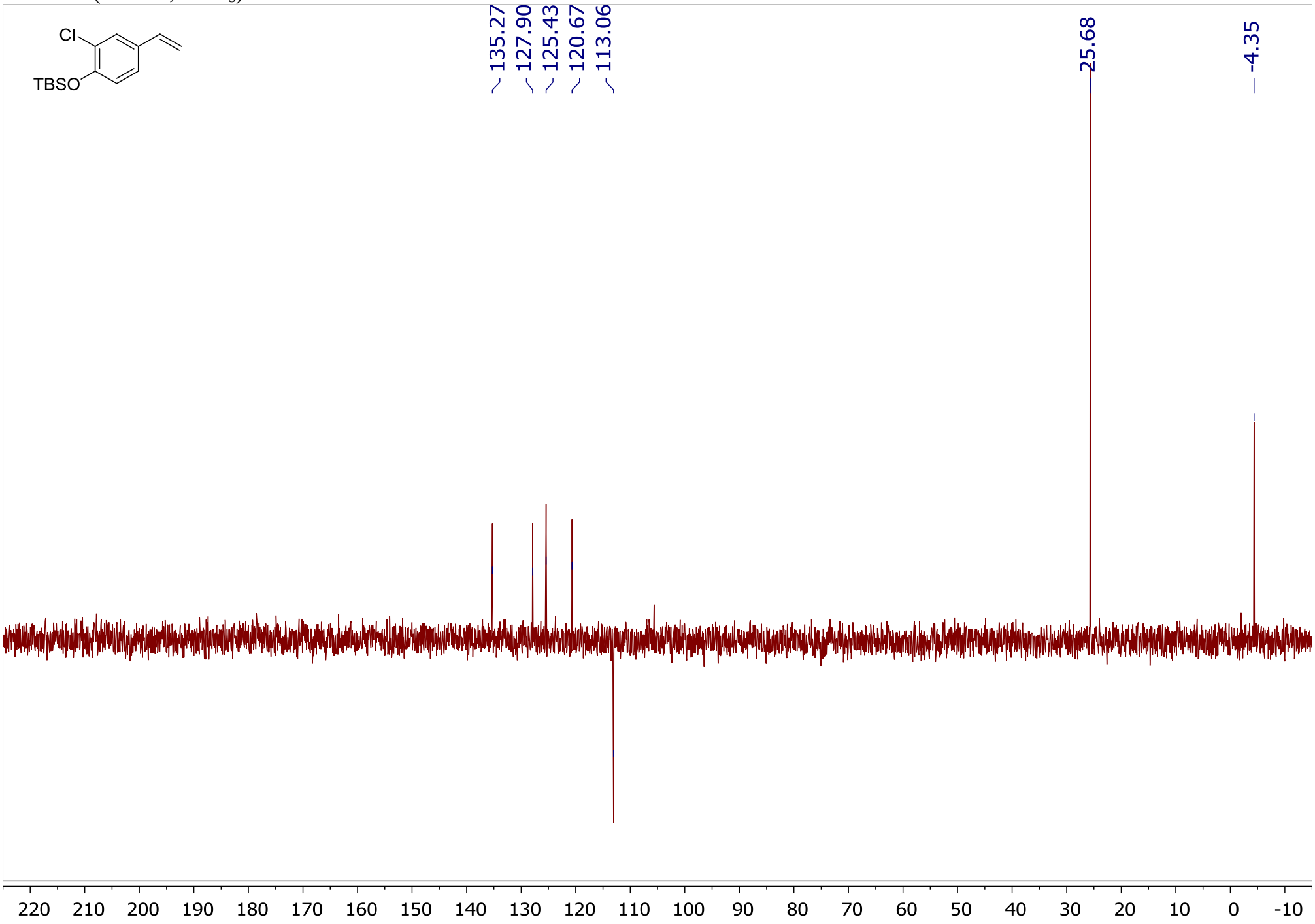
$^1$H NMR (300 MHz, $CDCl_3$)



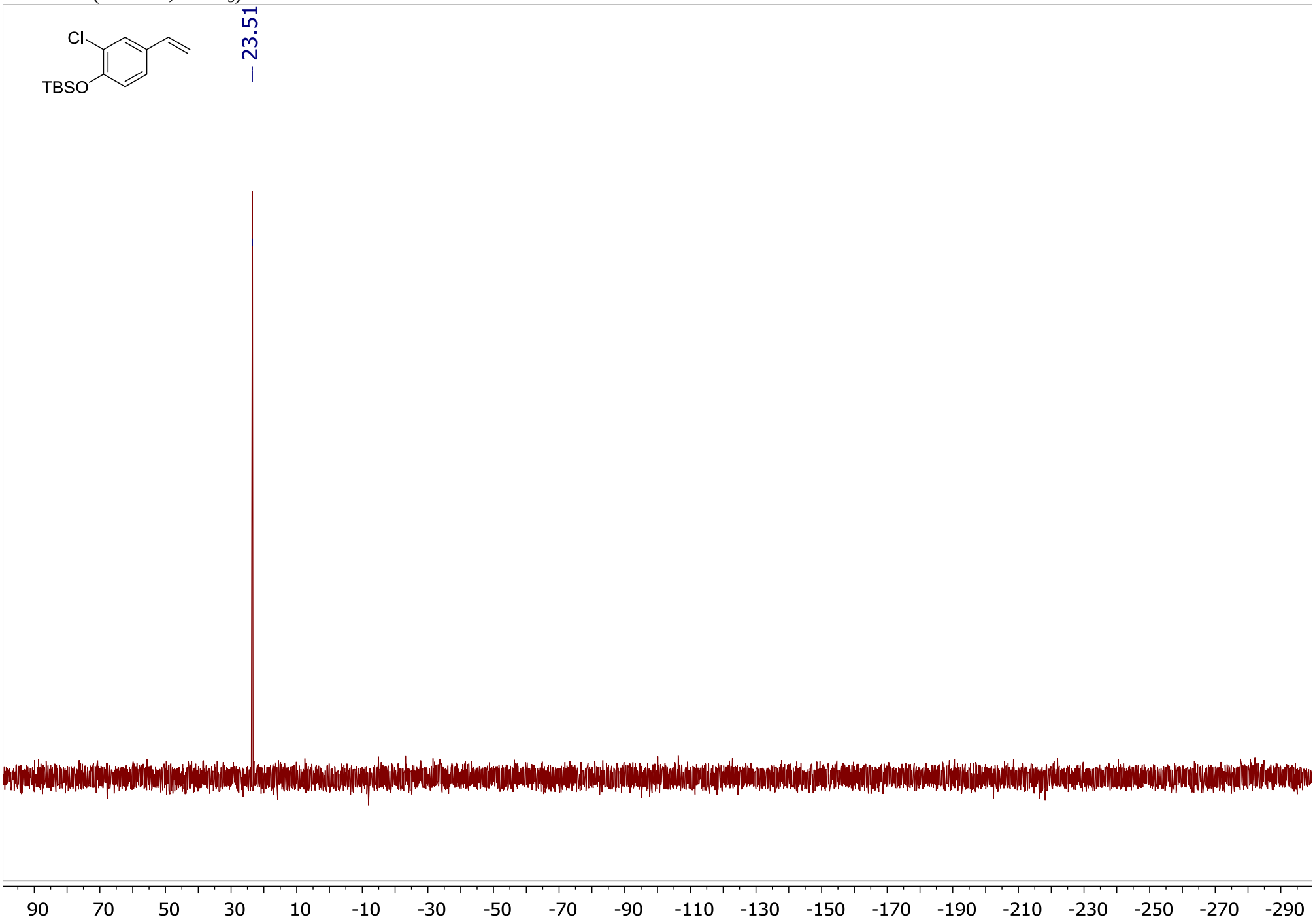
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

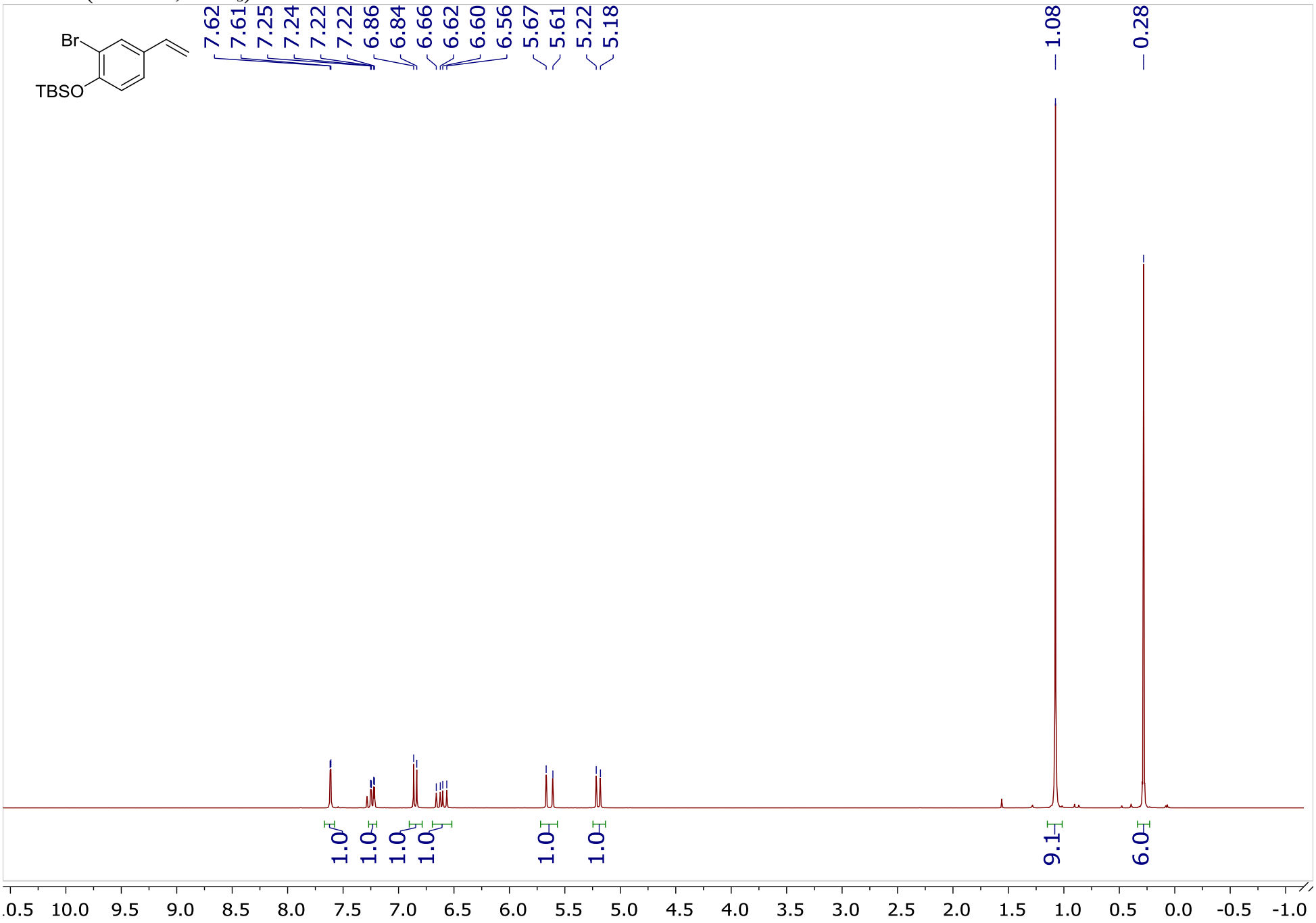


$^{29}$Si NMR (60 MHz, $CDCl_3$)

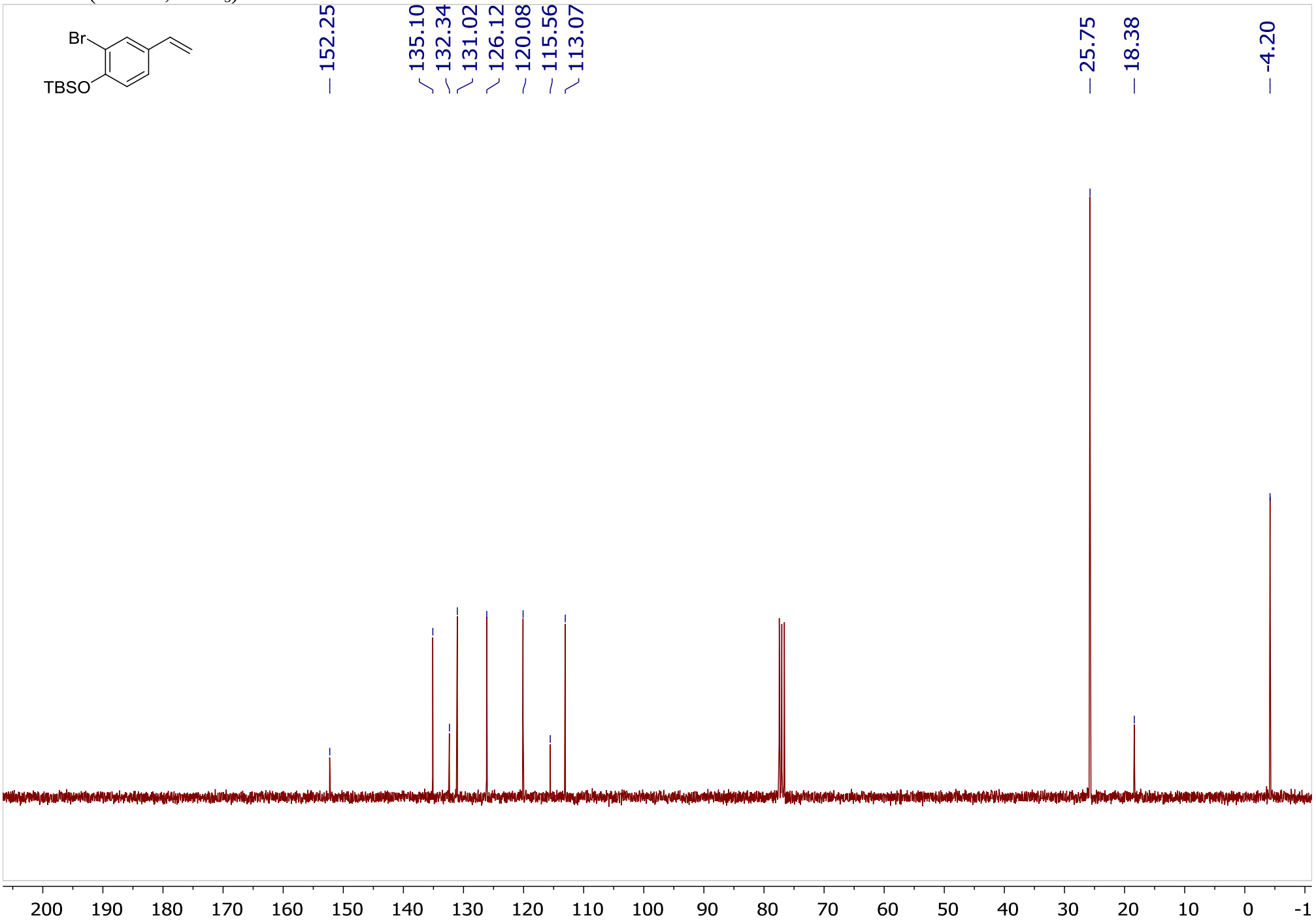


**(2-Bromo-4-vinylphenoxy)(*tert*-butyl)dimethylsilane (S4)**

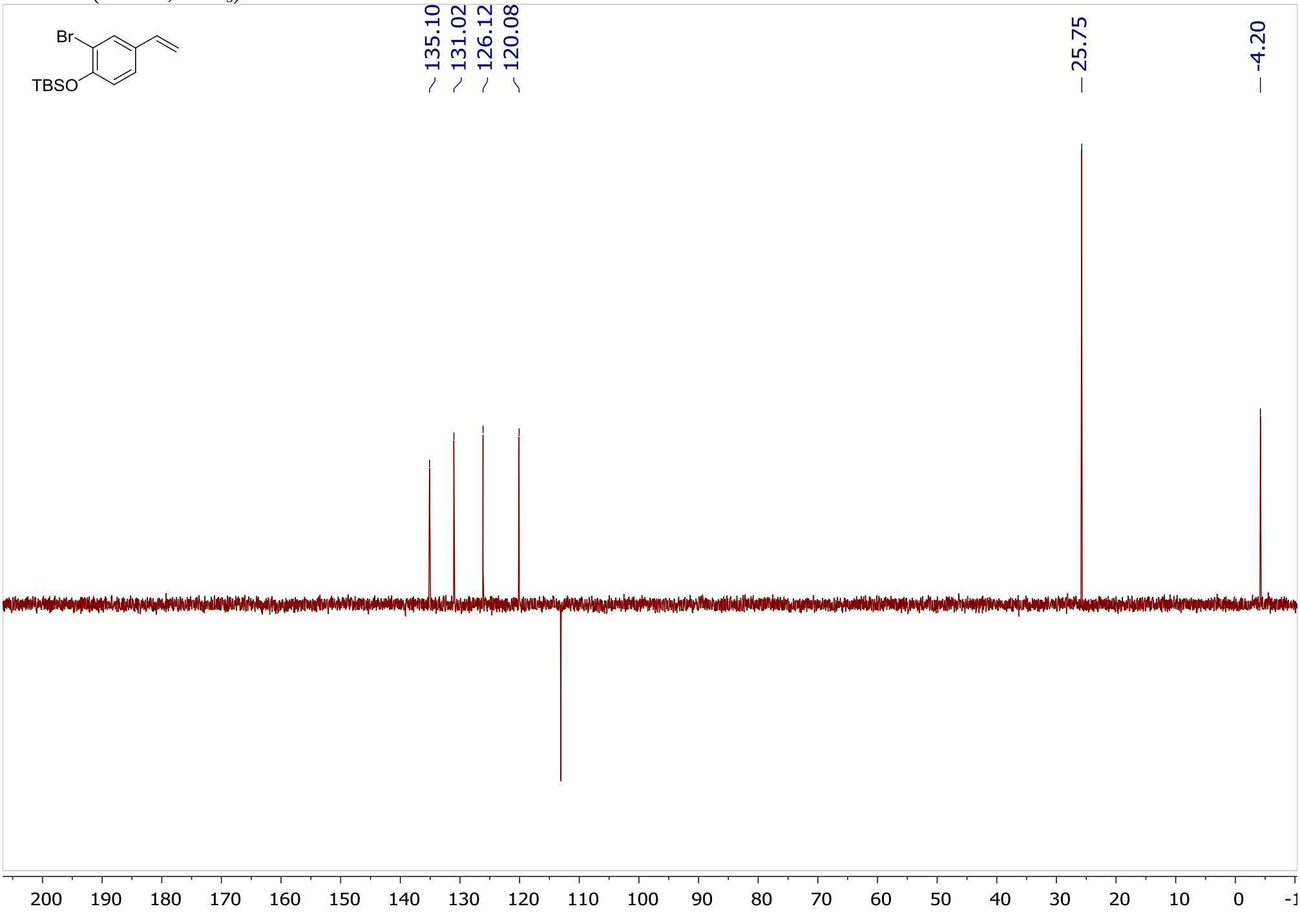
$^1$H NMR (300 MHz, $CDCl_3$)



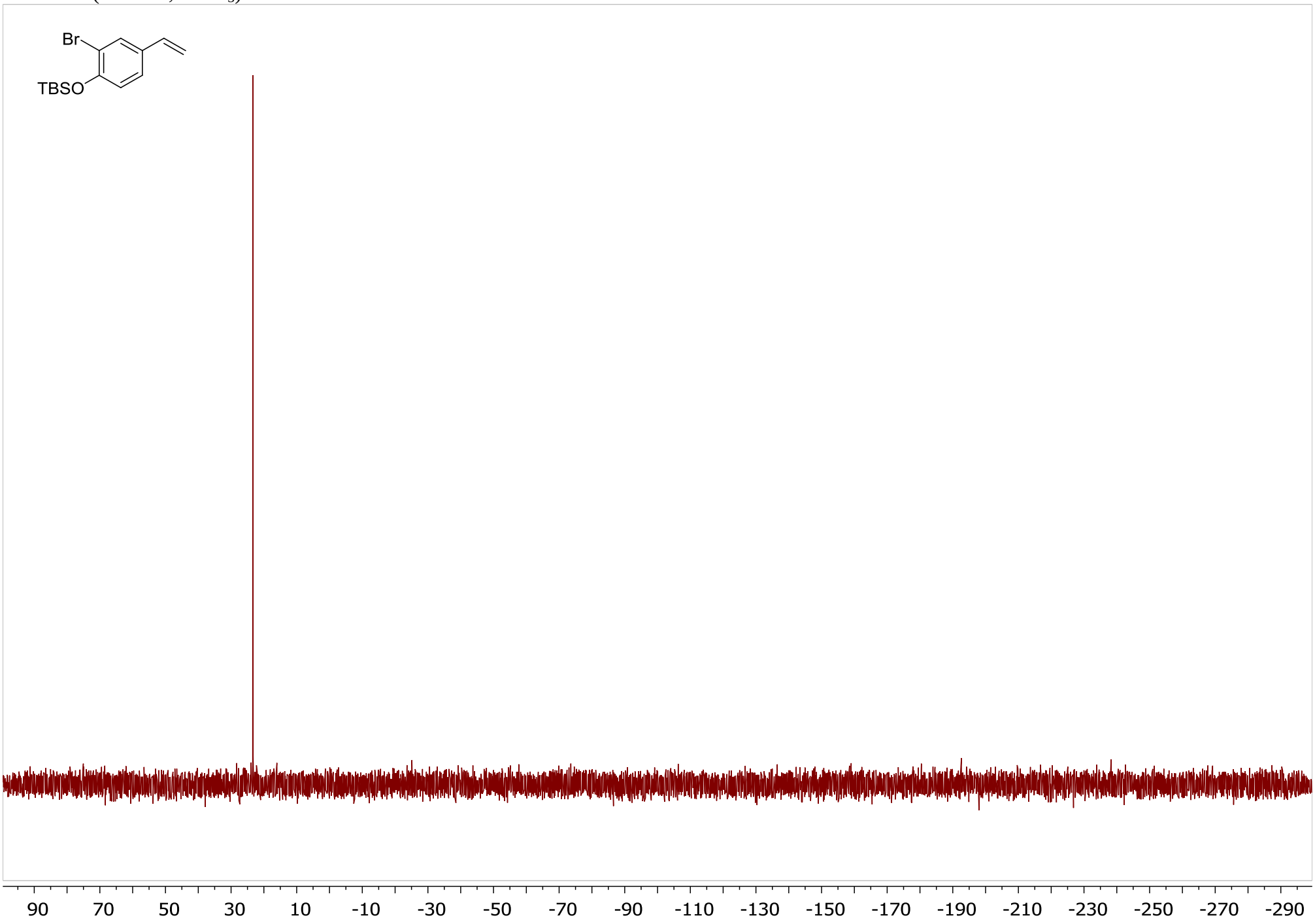
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

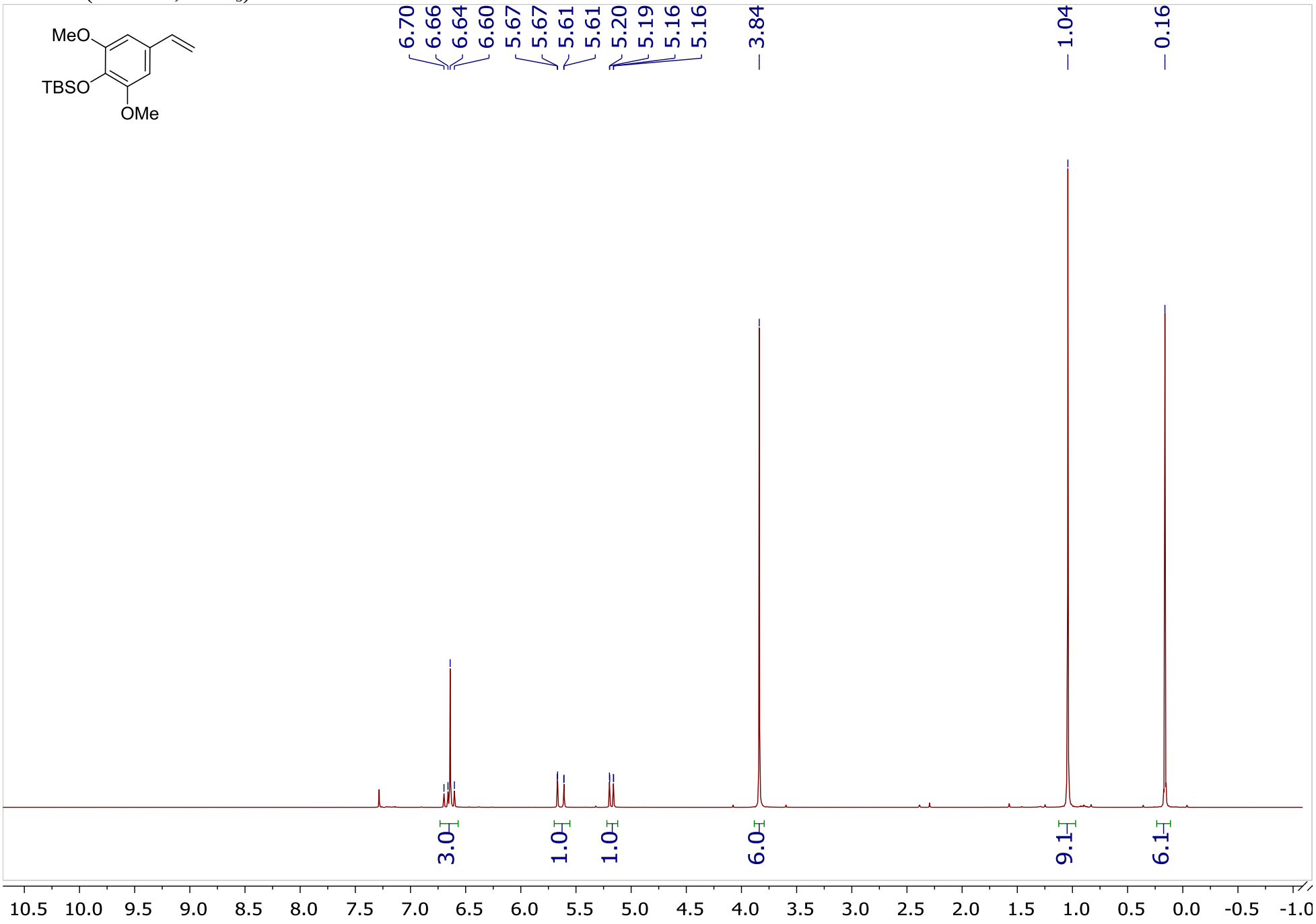


$^{29}$Si NMR (60 MHz, $CDCl_3$)

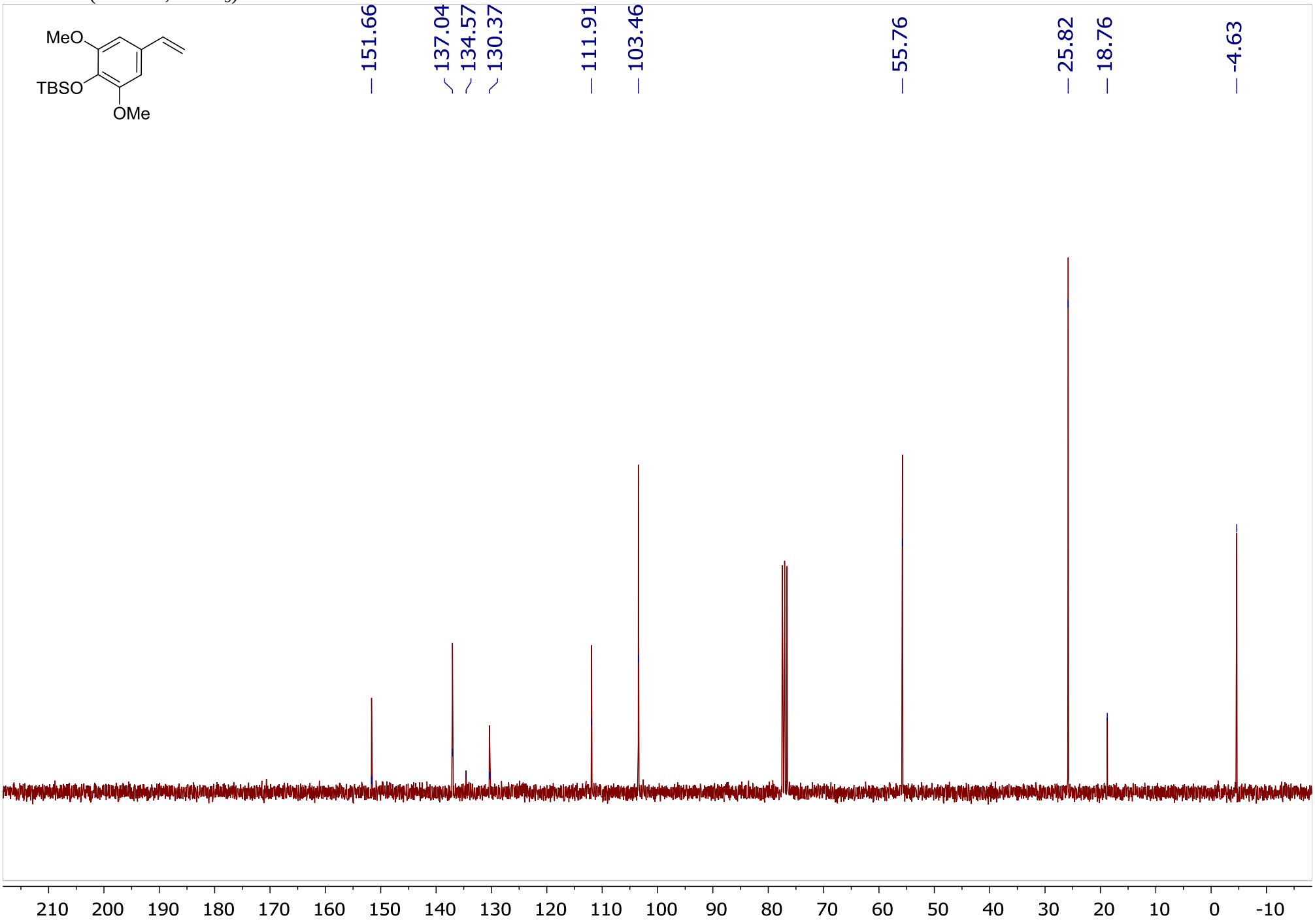


***tert*-Butyl(2,6-dimethoxy-4-vinylphenoxy)dimethylsilane (S5)**

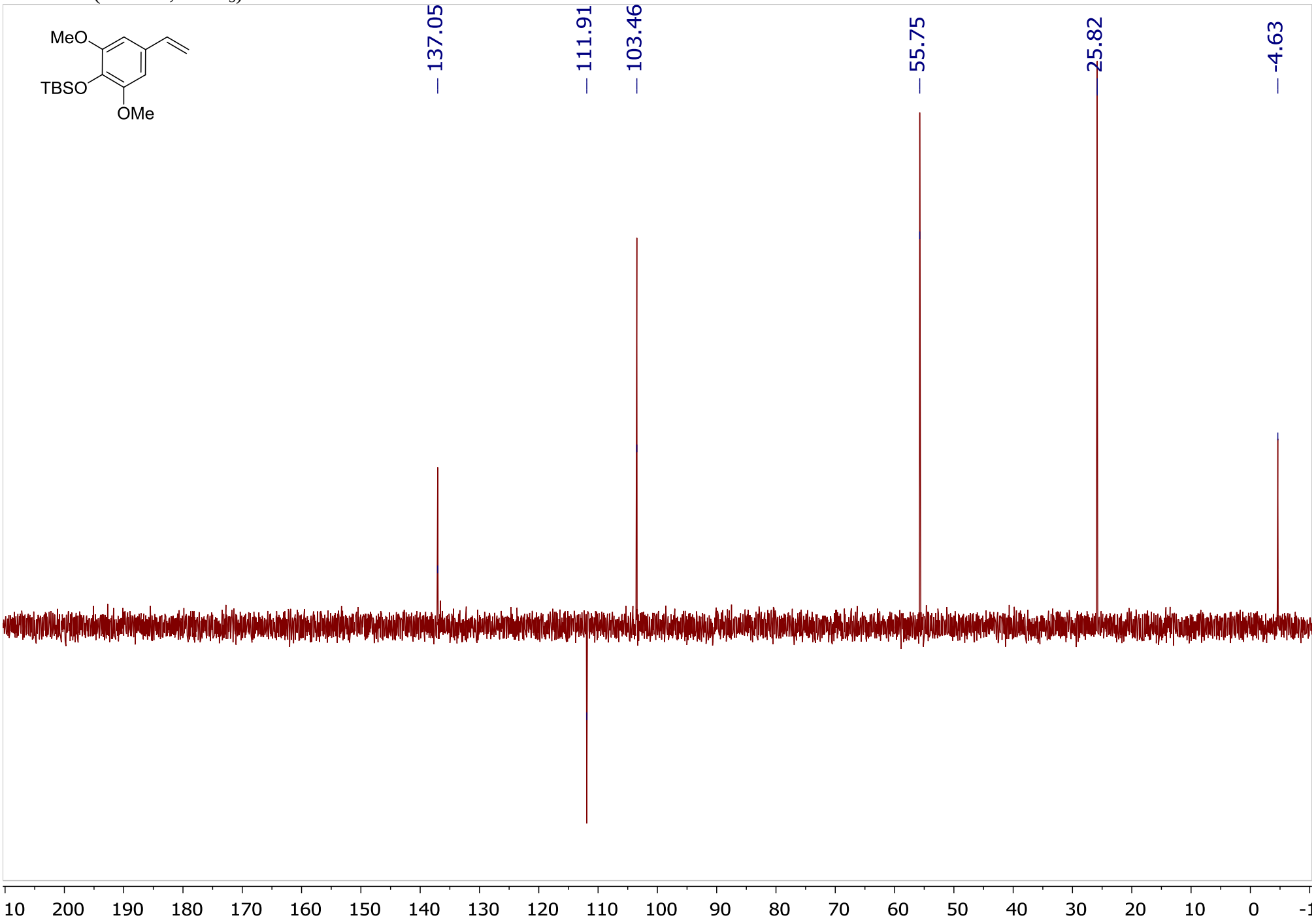
$^1$H NMR (300 MHz, $CDCl_3$)



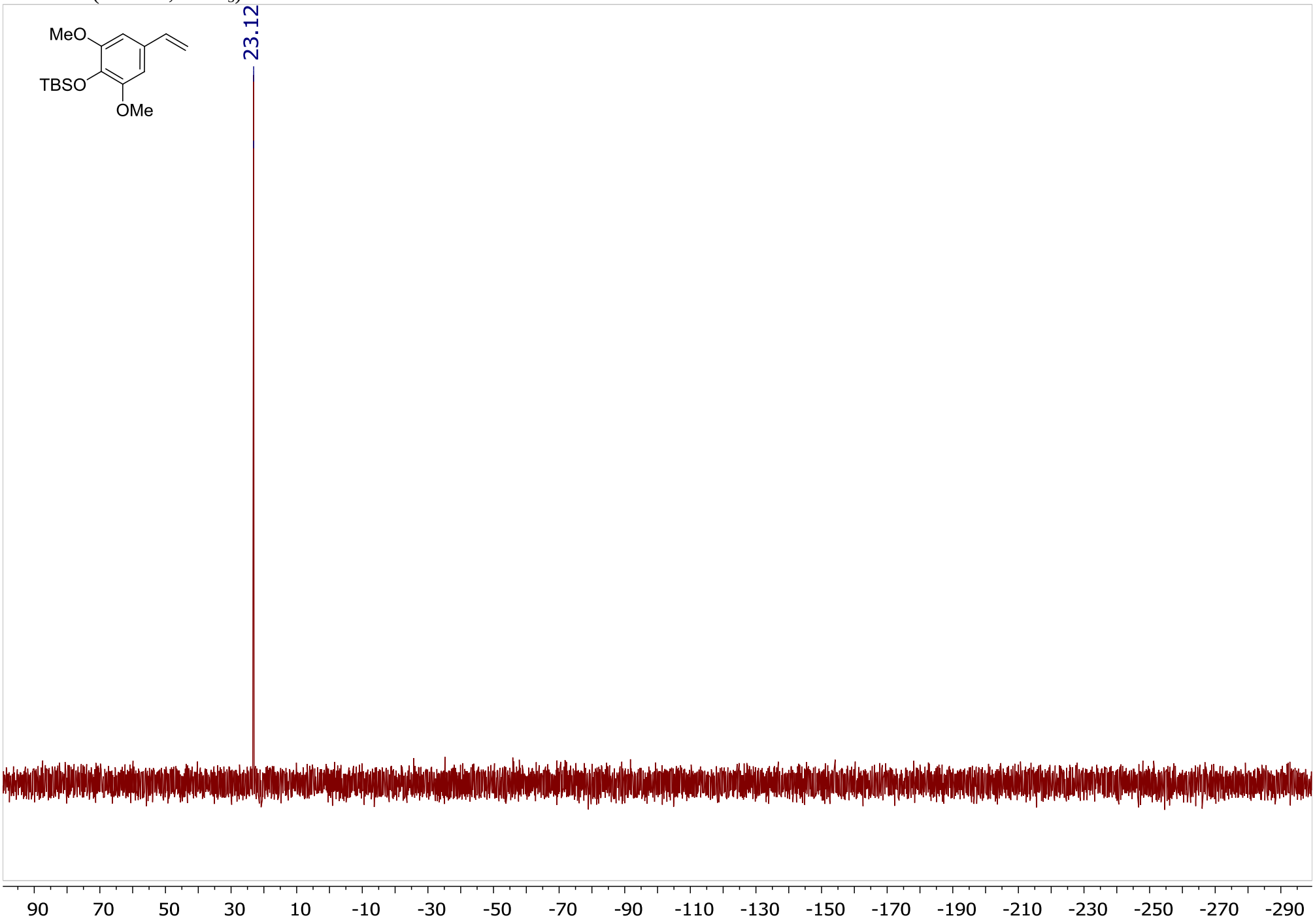
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

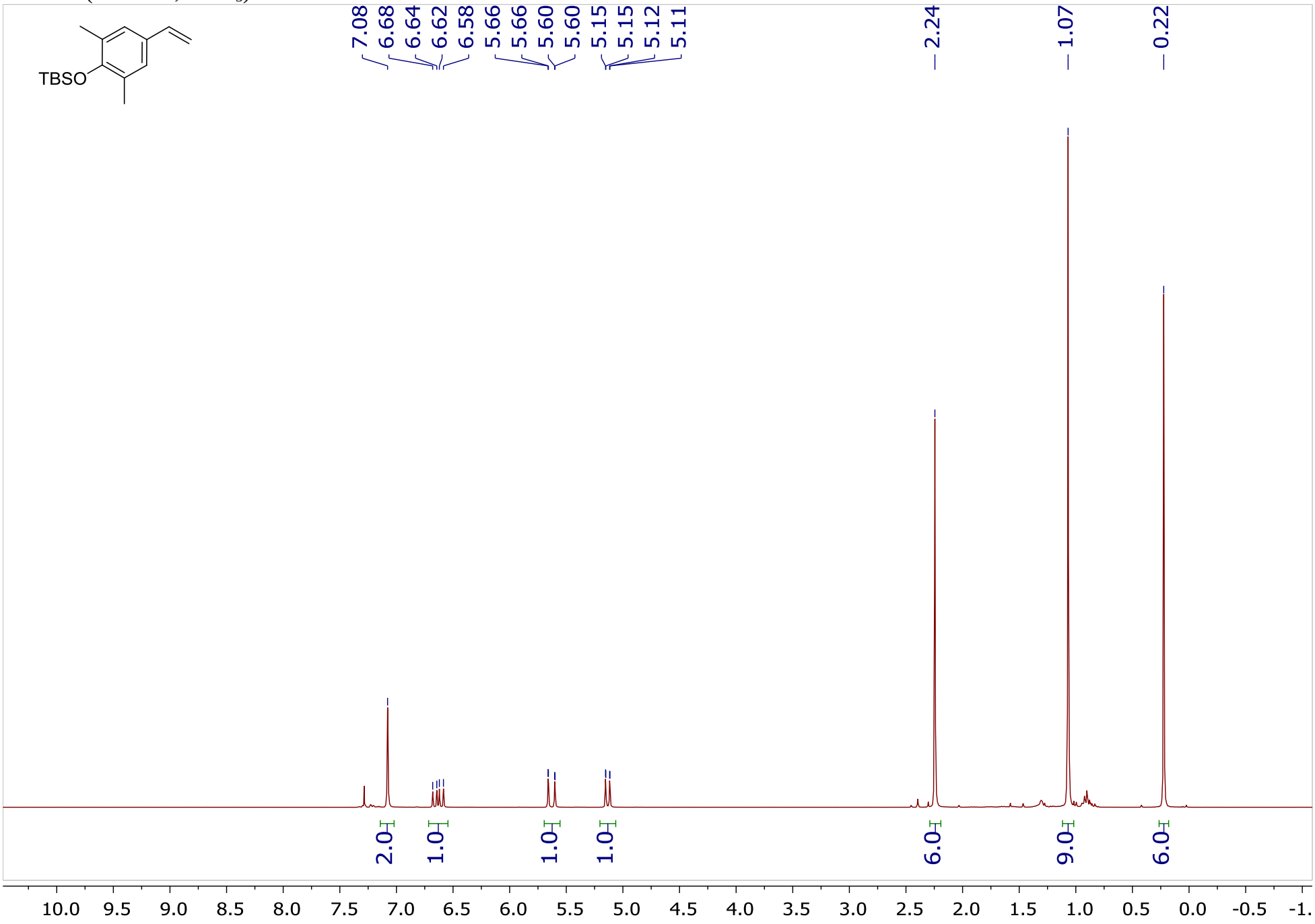


$^{29}$Si NMR (60 MHz, $CDCl_3$)

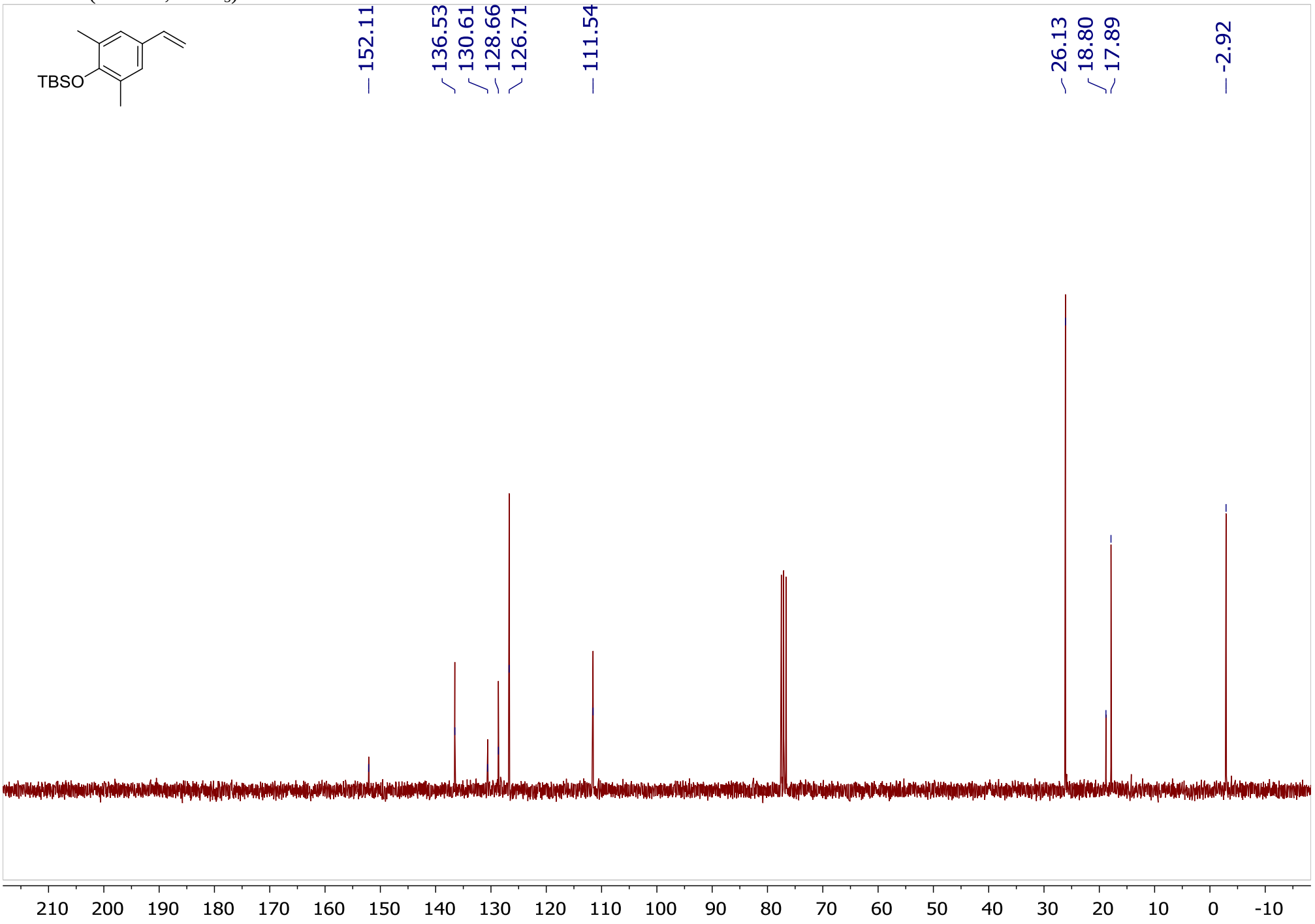


***tert*-Butyl(2,6-dimethyl-4-vinylphenoxy)dimethylsilane (S6)**

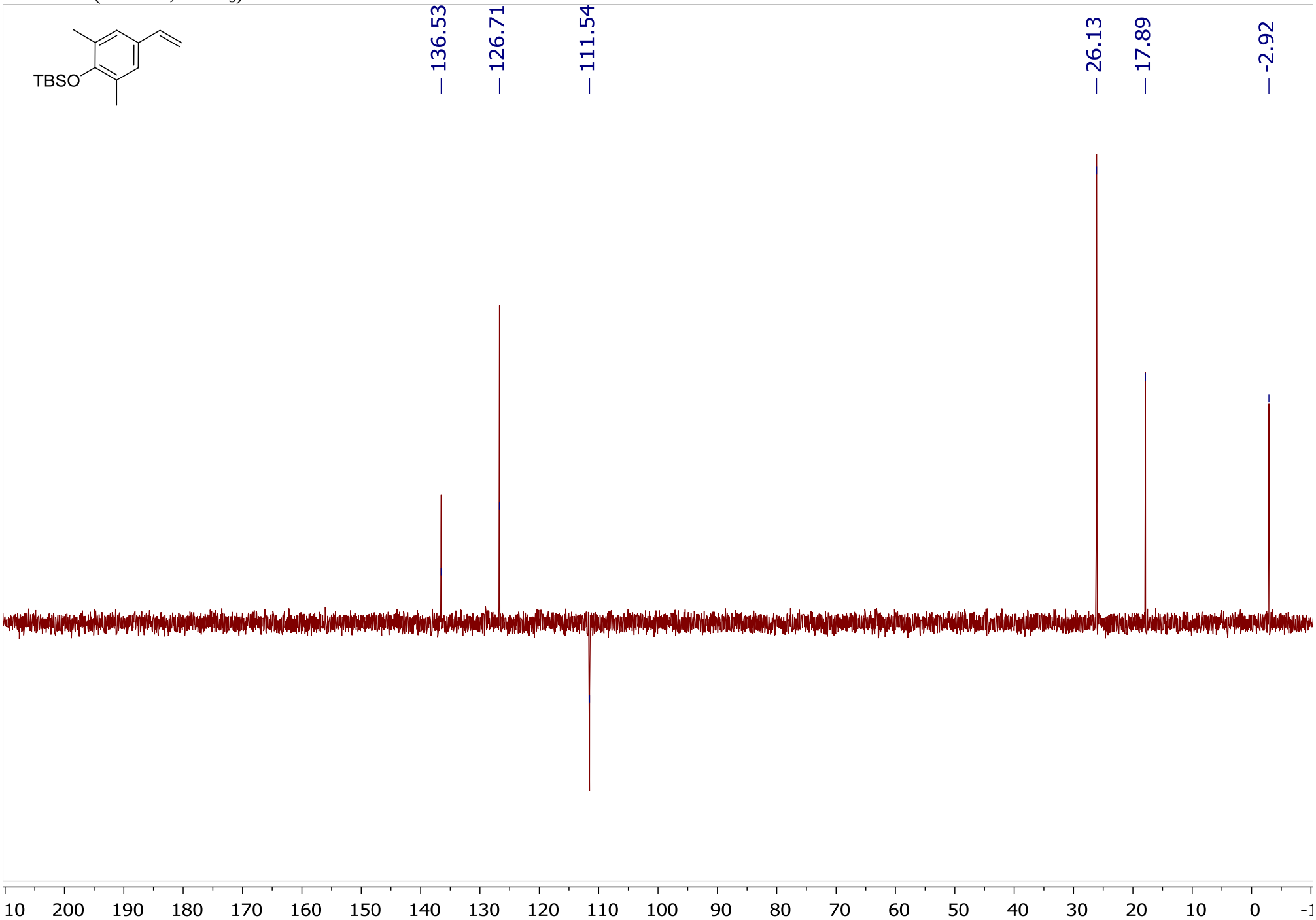
$^1$H NMR (300 MHz, $CDCl_3$)



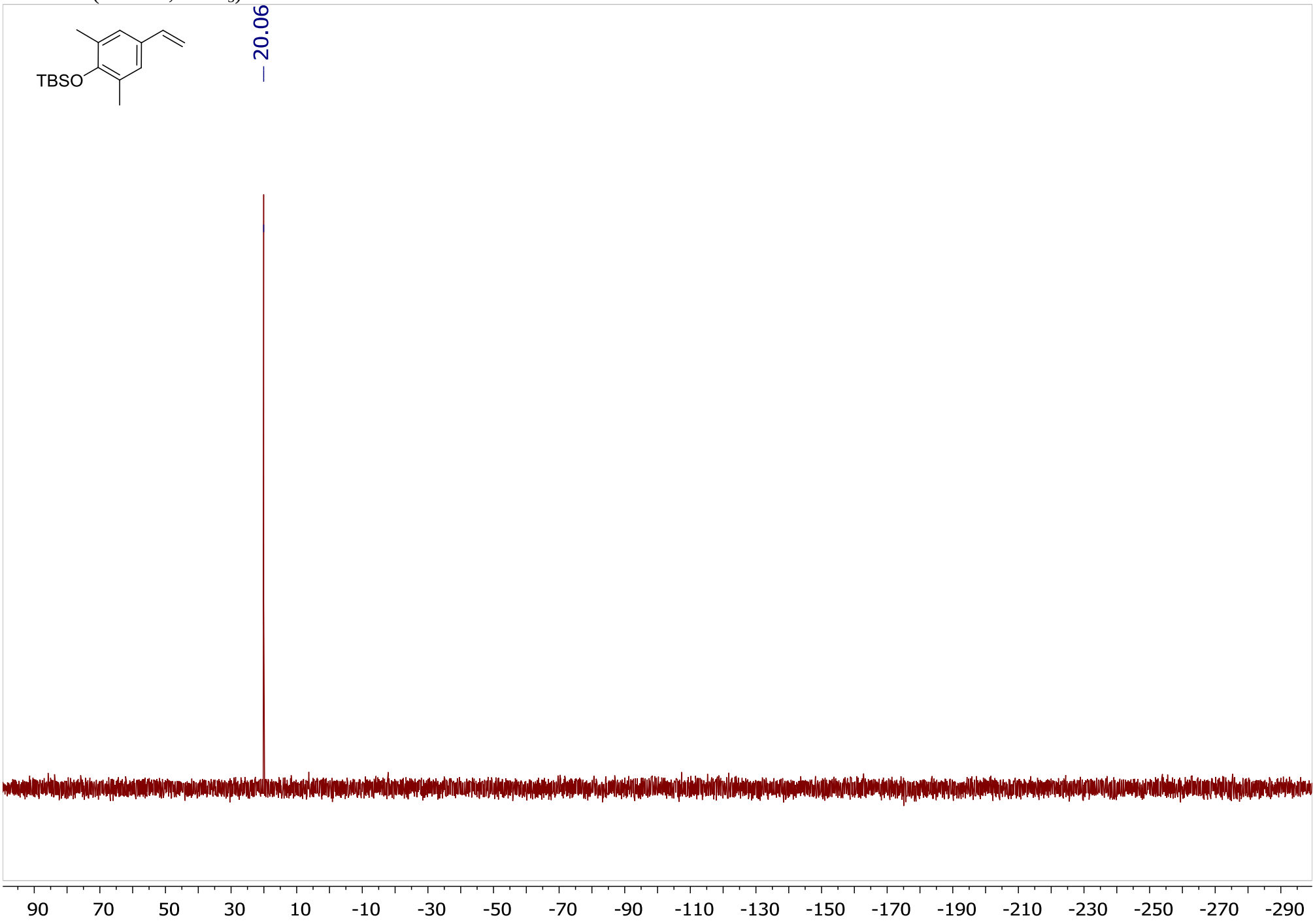
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

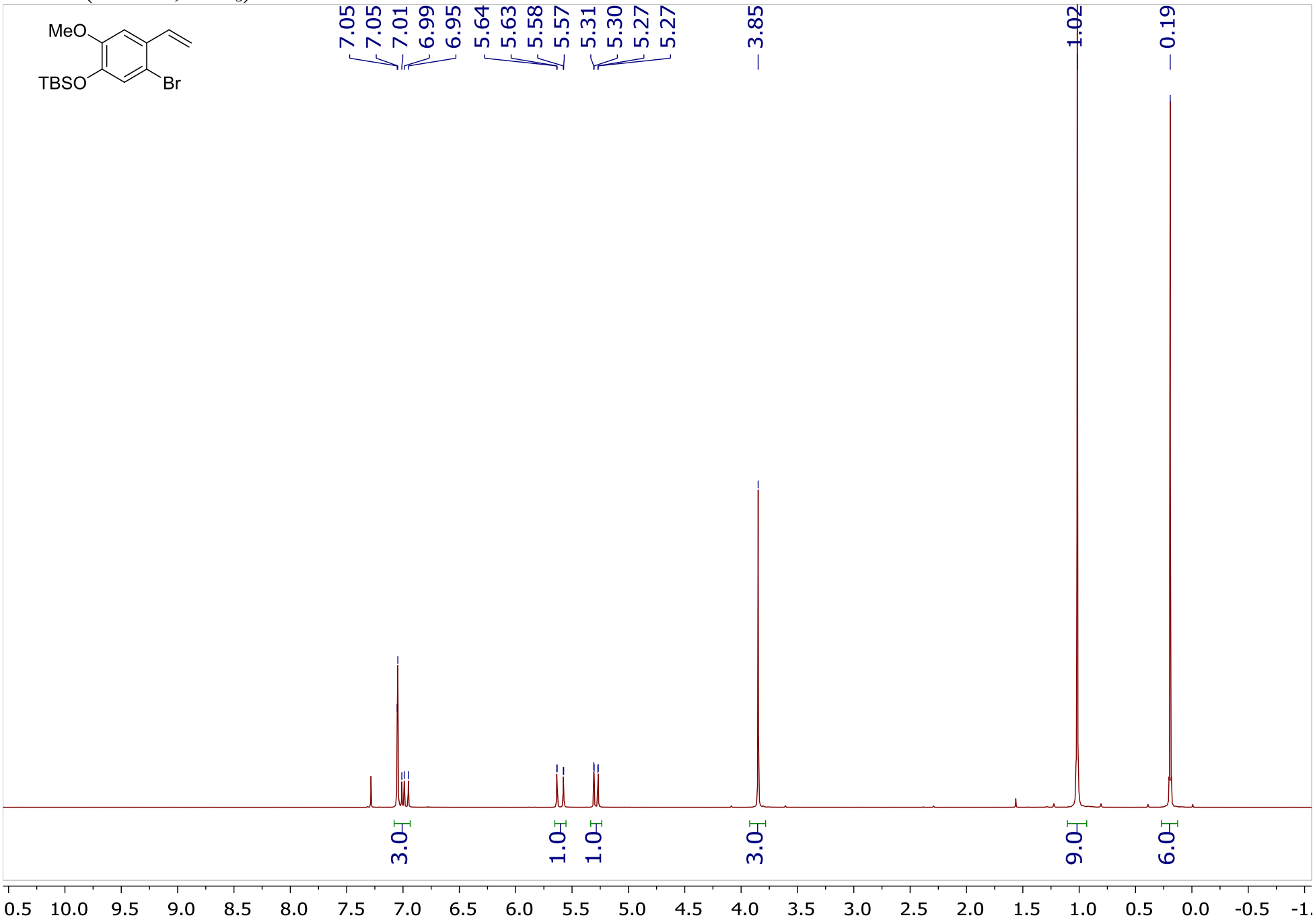


$^{29}$Si NMR (60 MHz, $CDCl_3$)

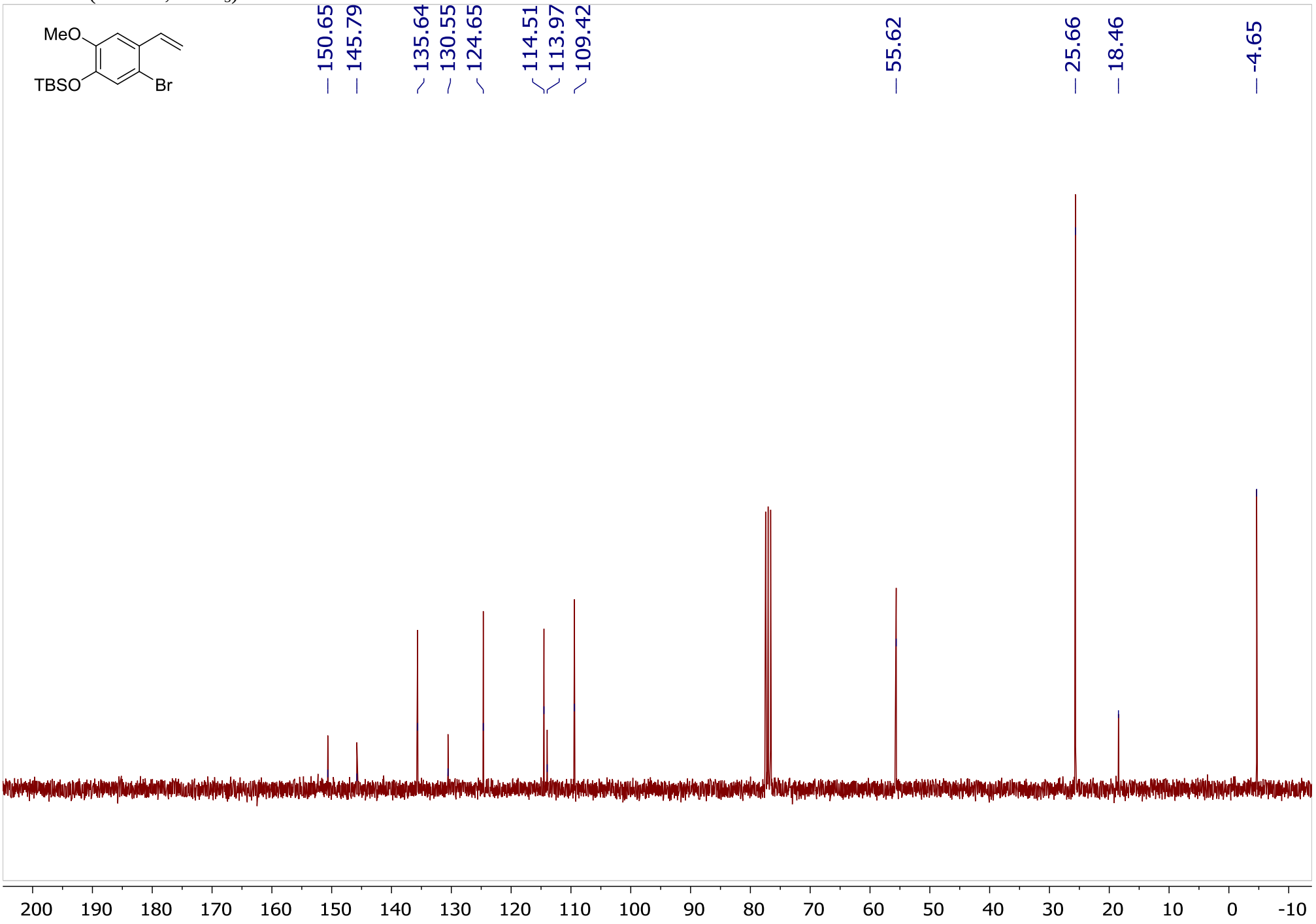


**(5-Bromo-2-methoxy-4-vinylphenoxy)(*tert*-butyl)dimethylsilane (S7)**

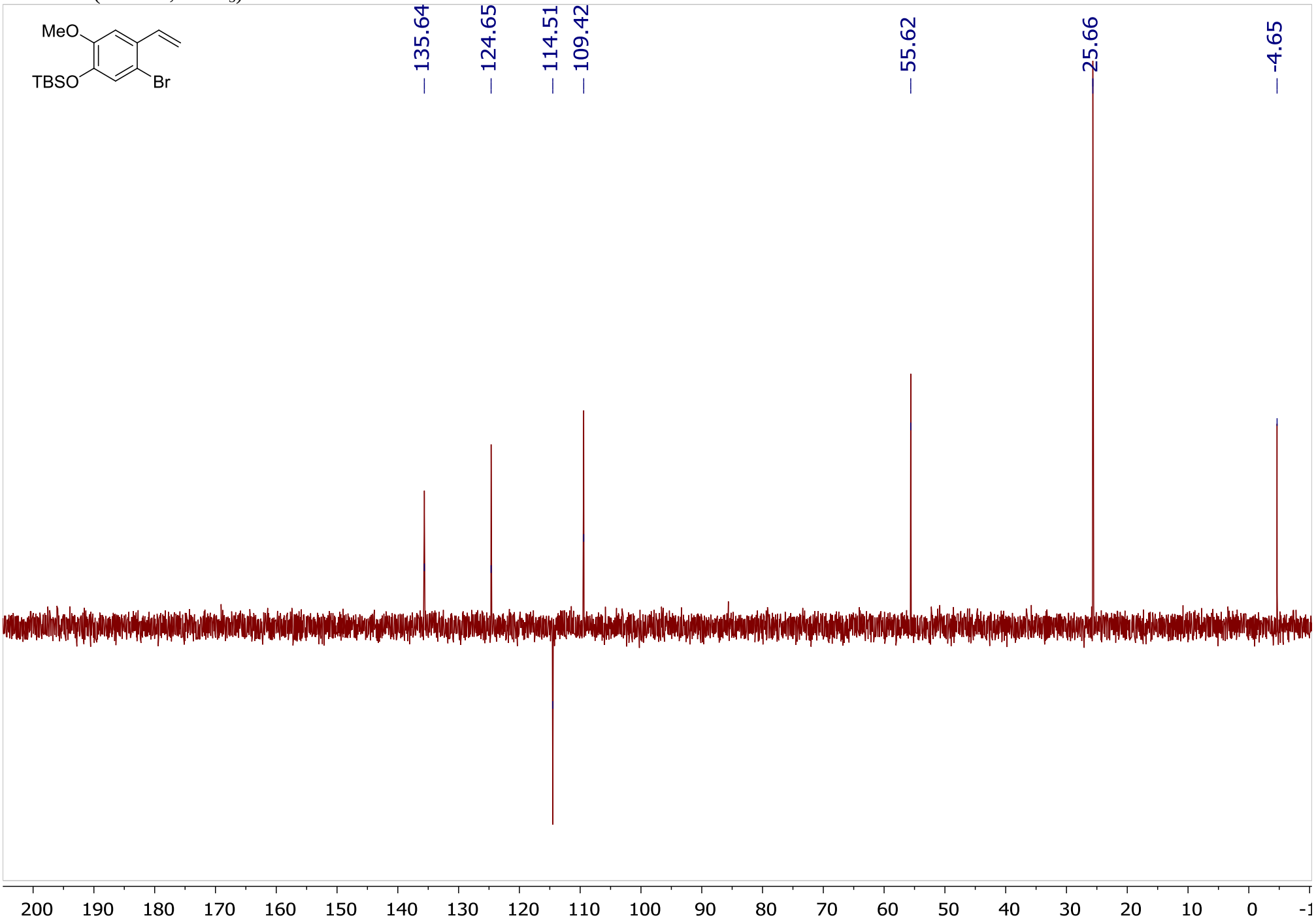
$^1$H NMR (300 MHz, $CDCl_3$)



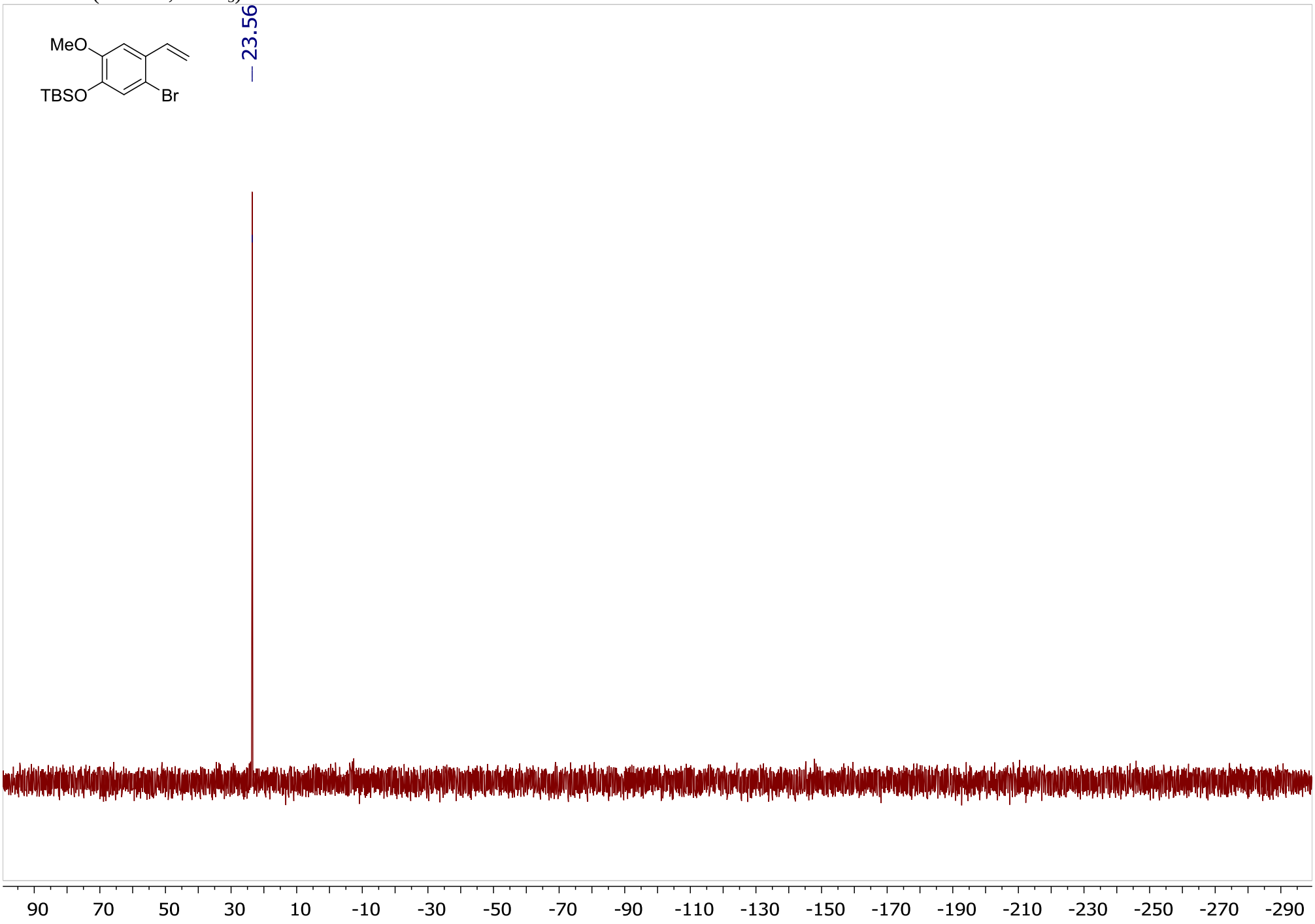
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

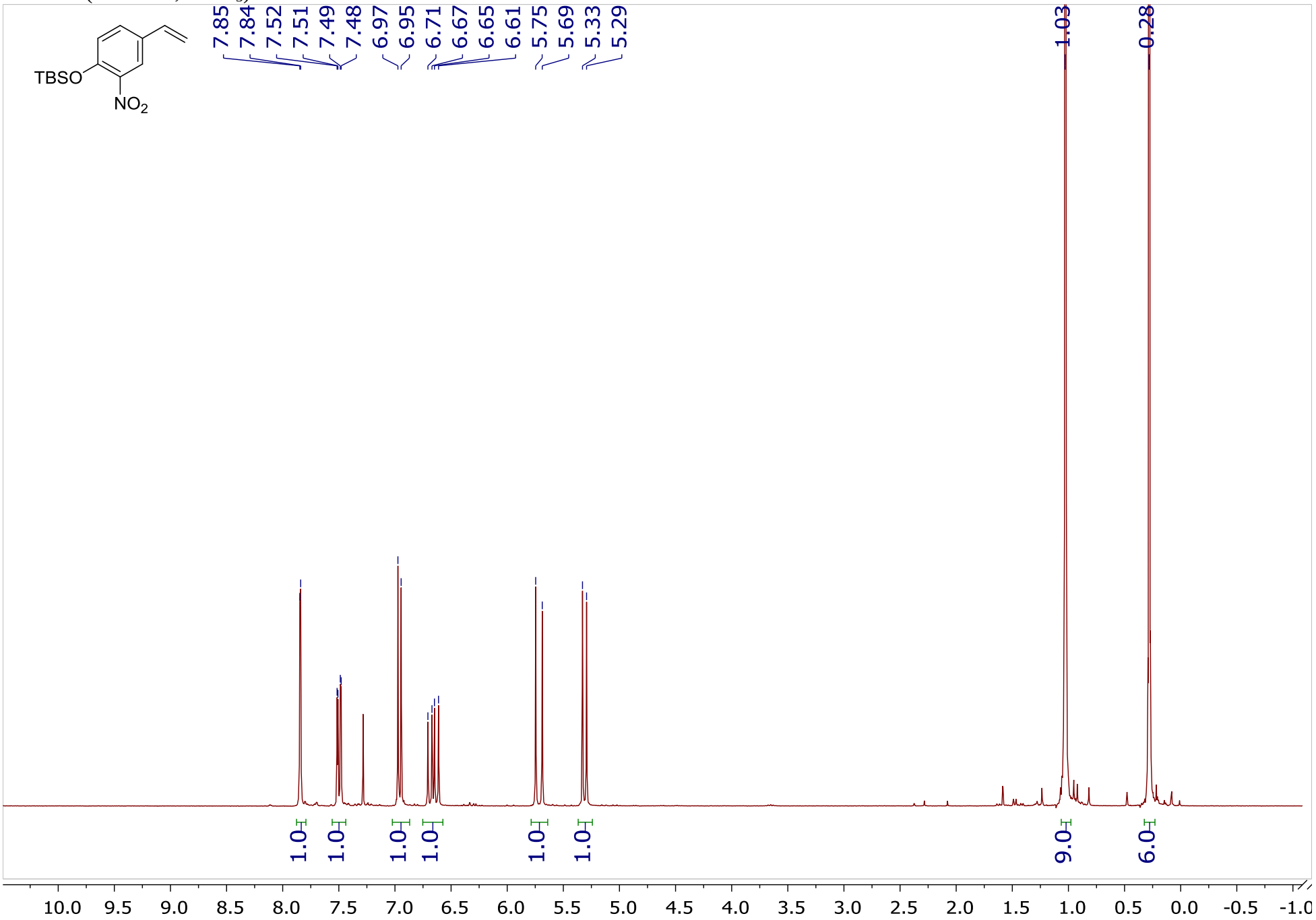


$^{29}$Si NMR (60 MHz, $CDCl_3$)

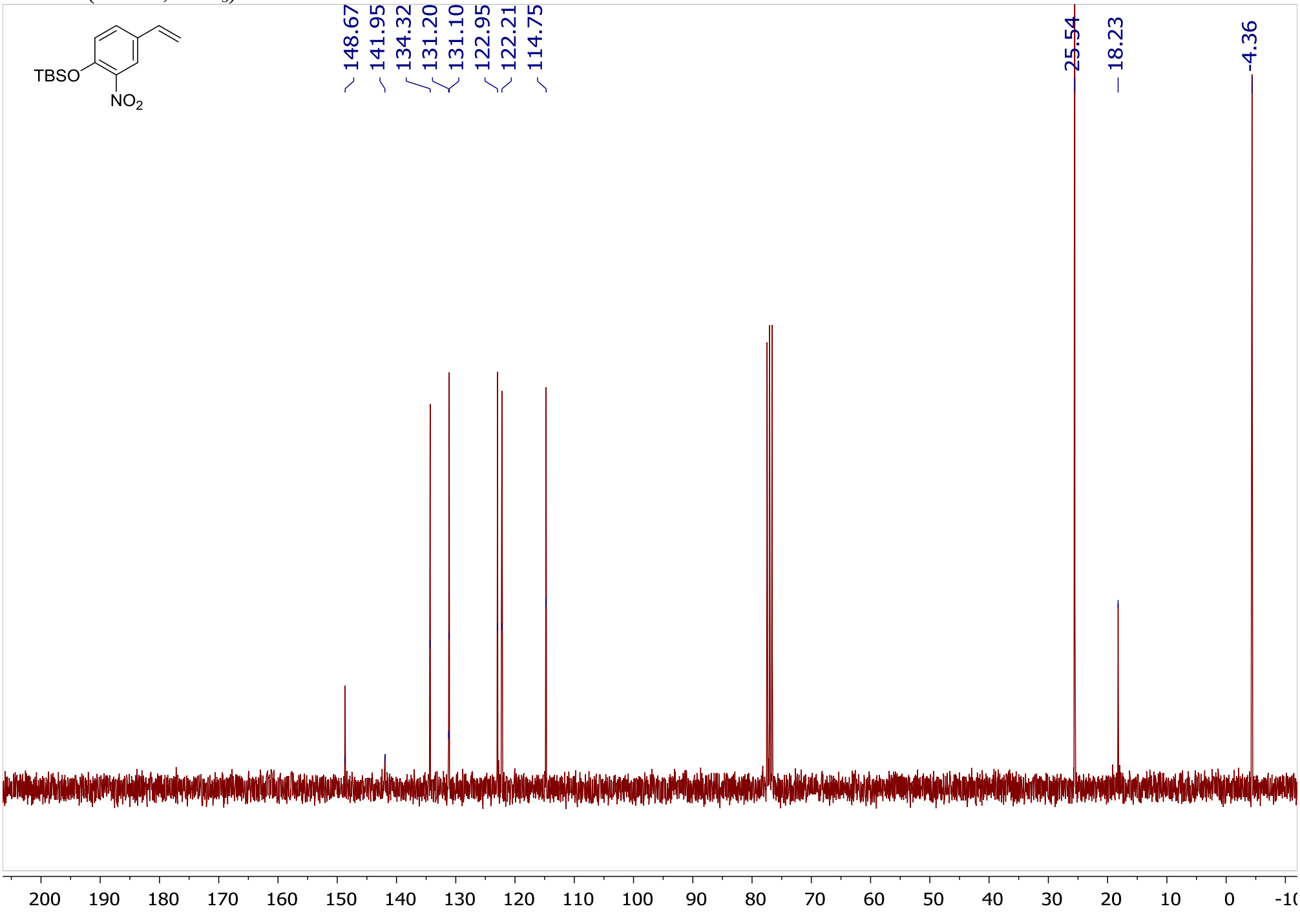


***tert*-Butyldimethyl(2-nitro-4-vinylphenoxy)silane (S8)**

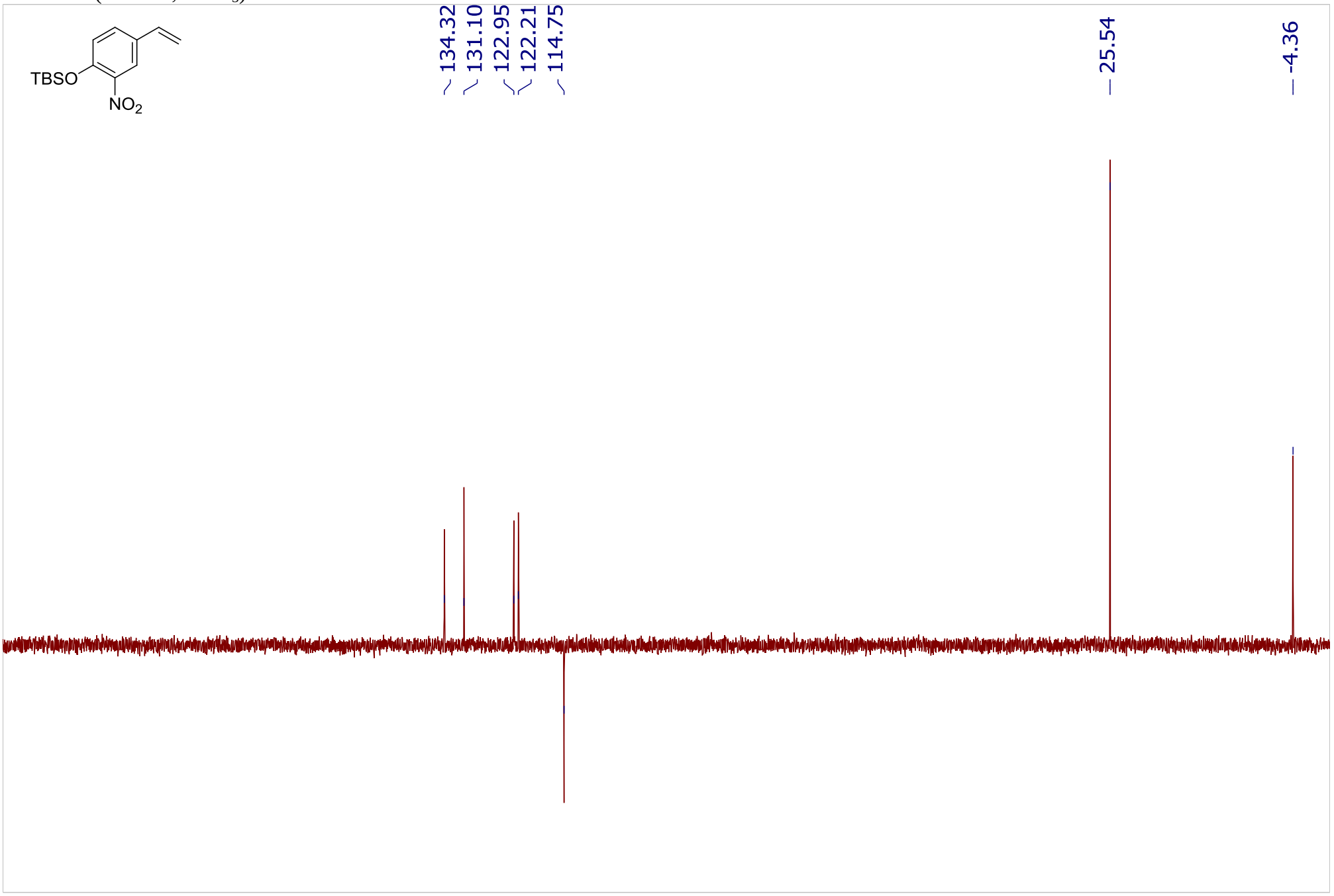
$^1$H NMR (300 MHz, $CDCl_3$)



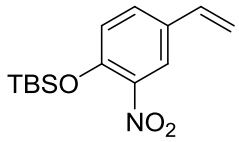
$^{13}$C NMR (75 MHz, $CDCl_3$)

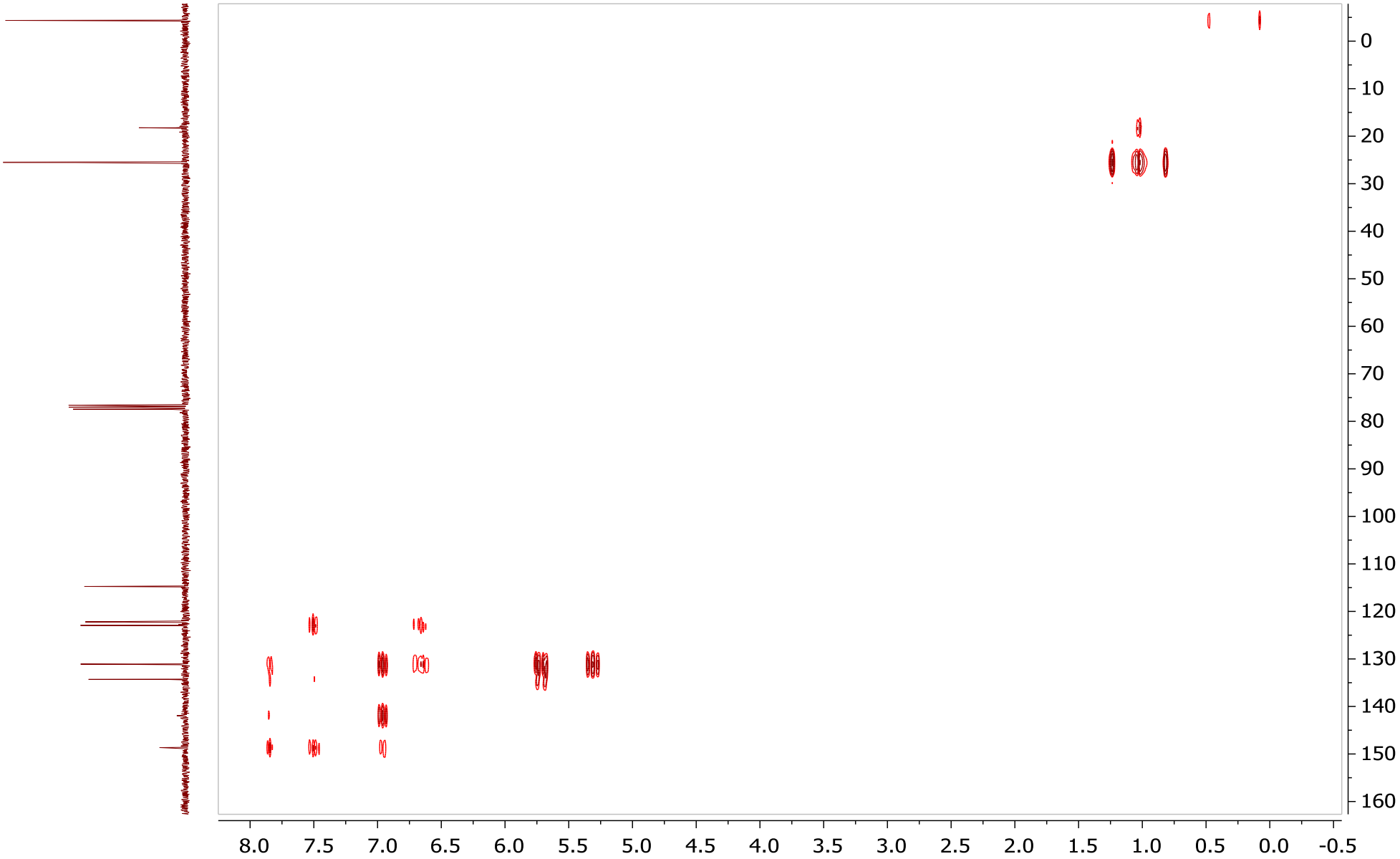


$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{13}$C HMBC


TBSO
NO2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120
130
140
150
160
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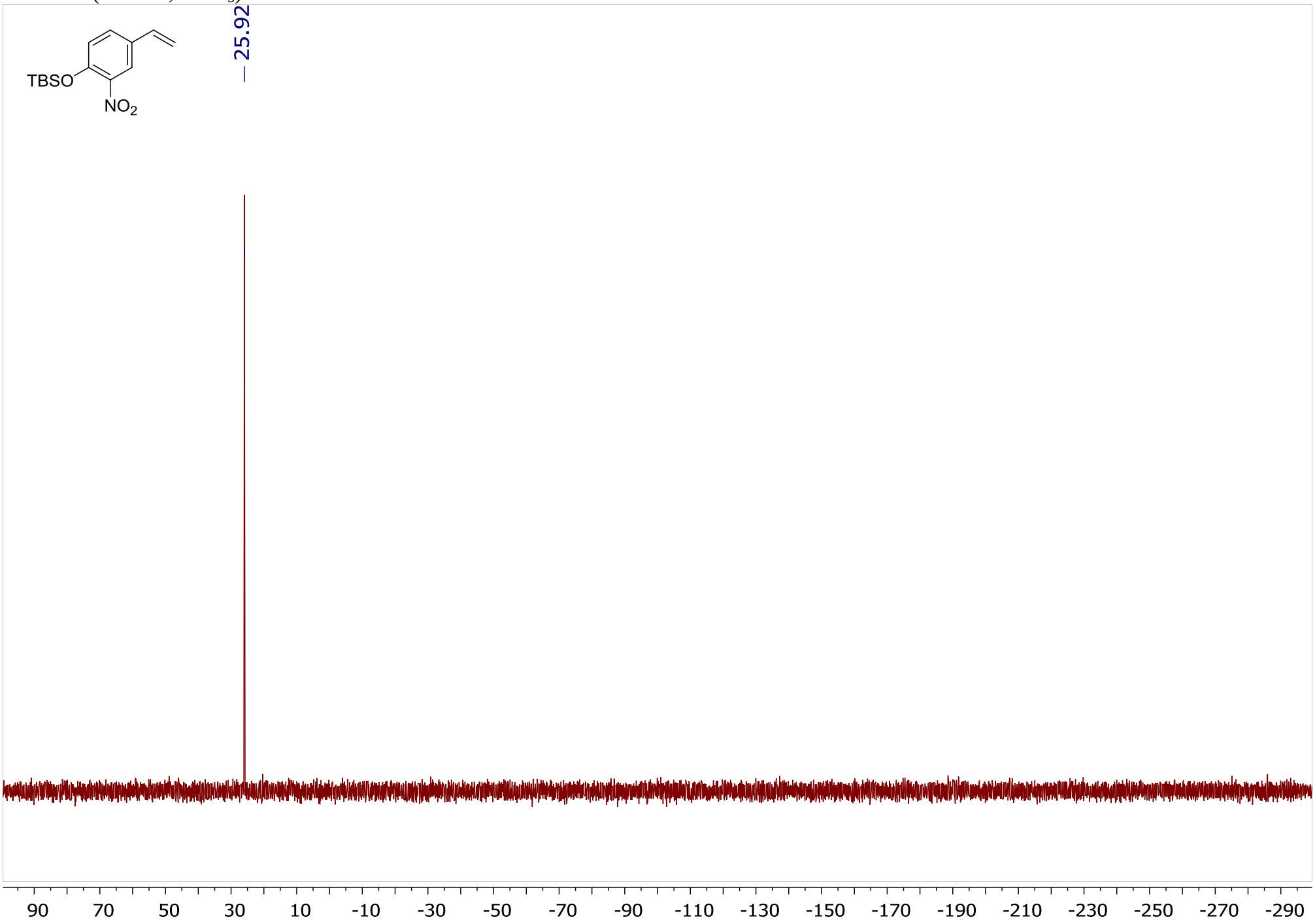
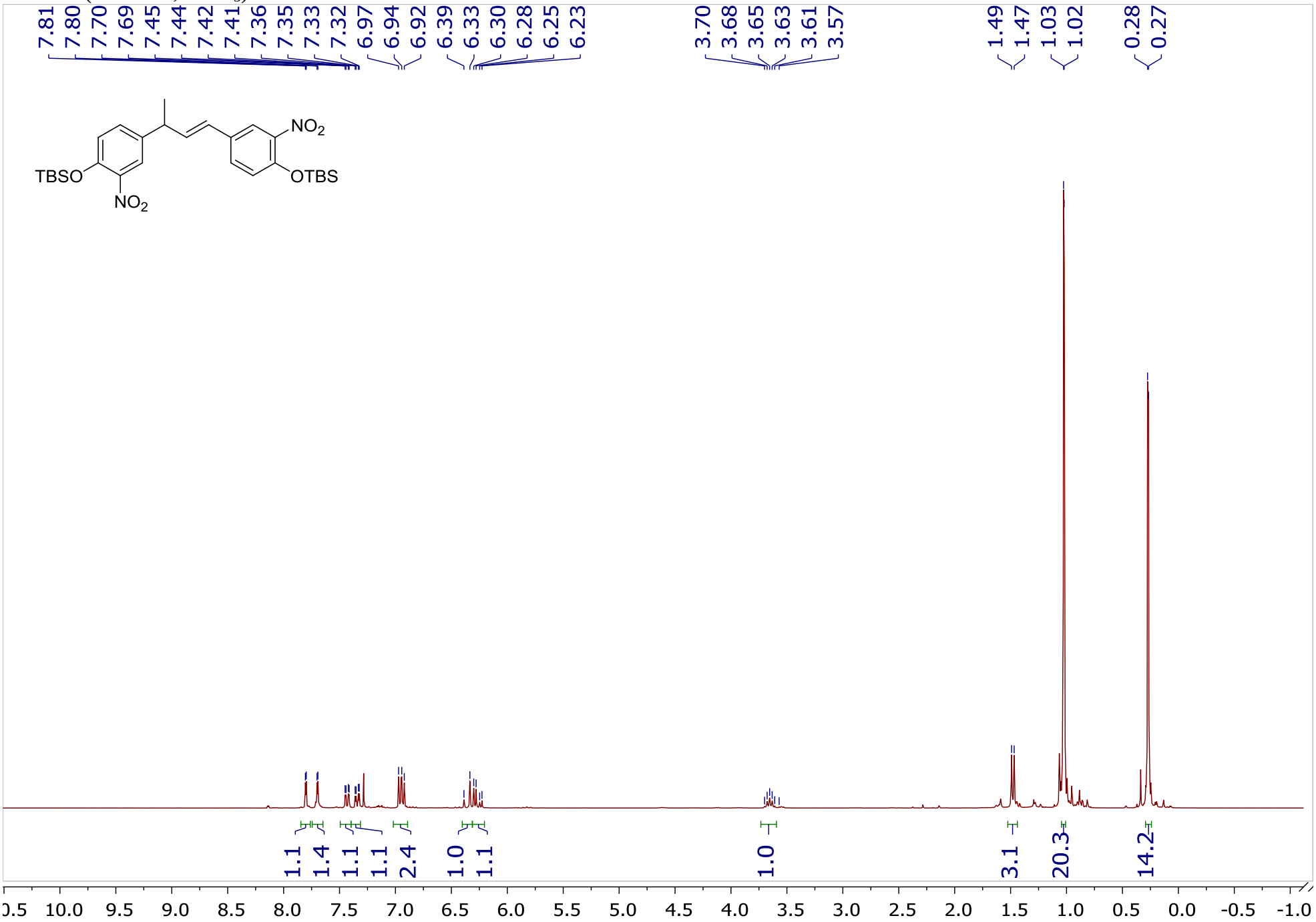
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

$^{29}$Si NMR (60 MHz, $CDCl_3$)

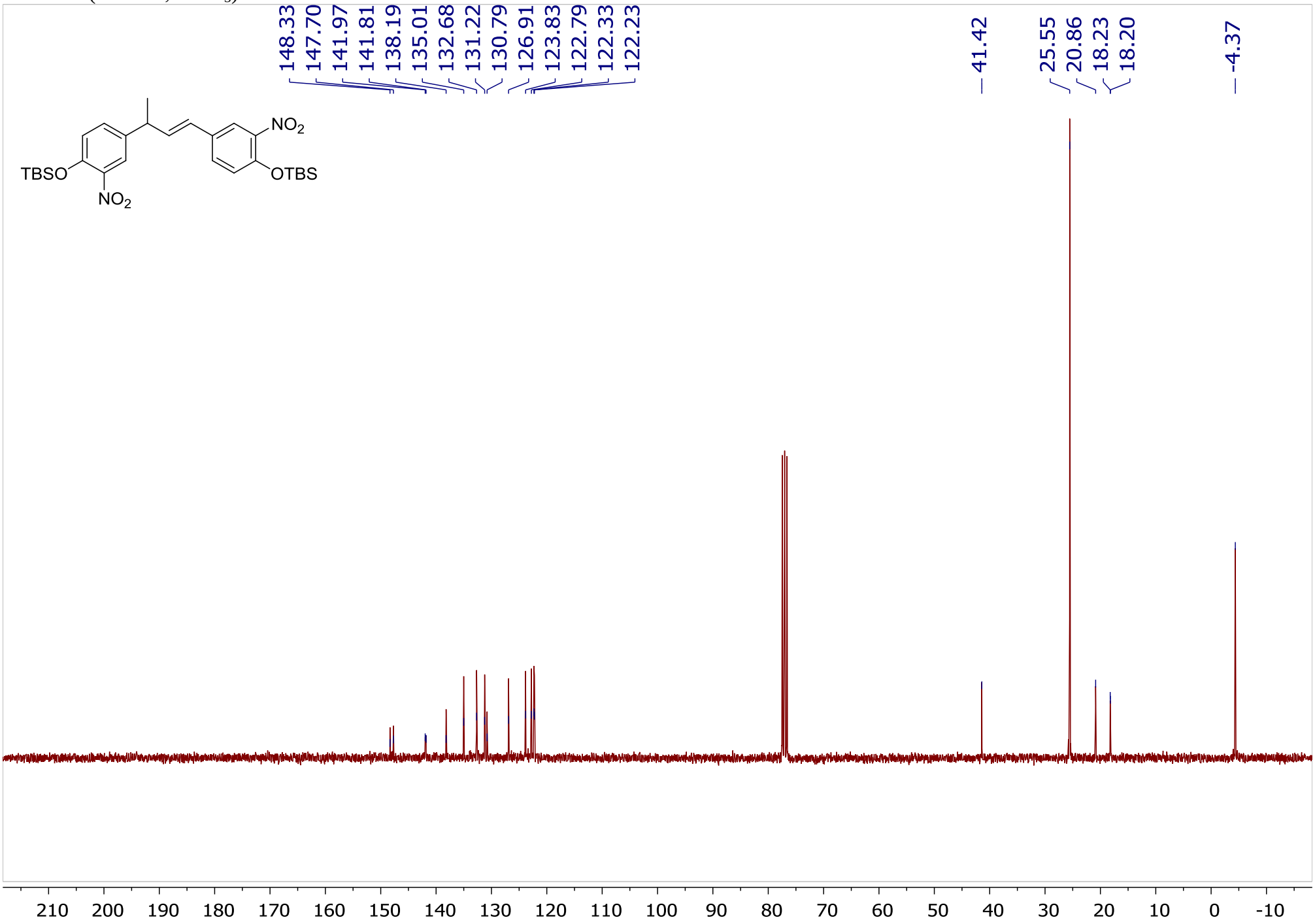


**(*E*)-((But-1-ene-1,3-diylbis(2-nitro-4,1-phenylene))bis(oxy))bis(tert-butyldimethylsilane) (S8')**

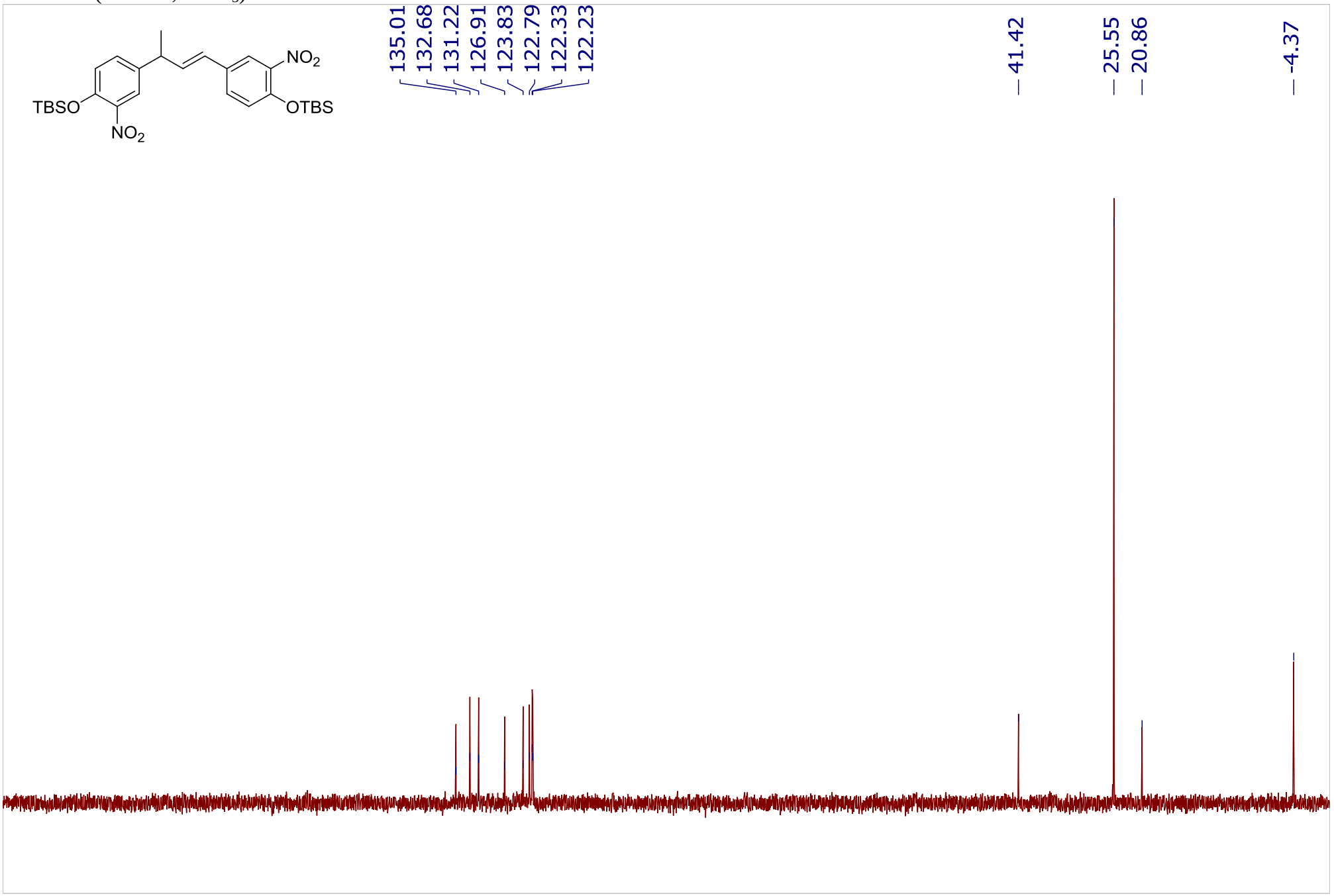
$^1$H NMR (300 MHz, $CDCl_3$)



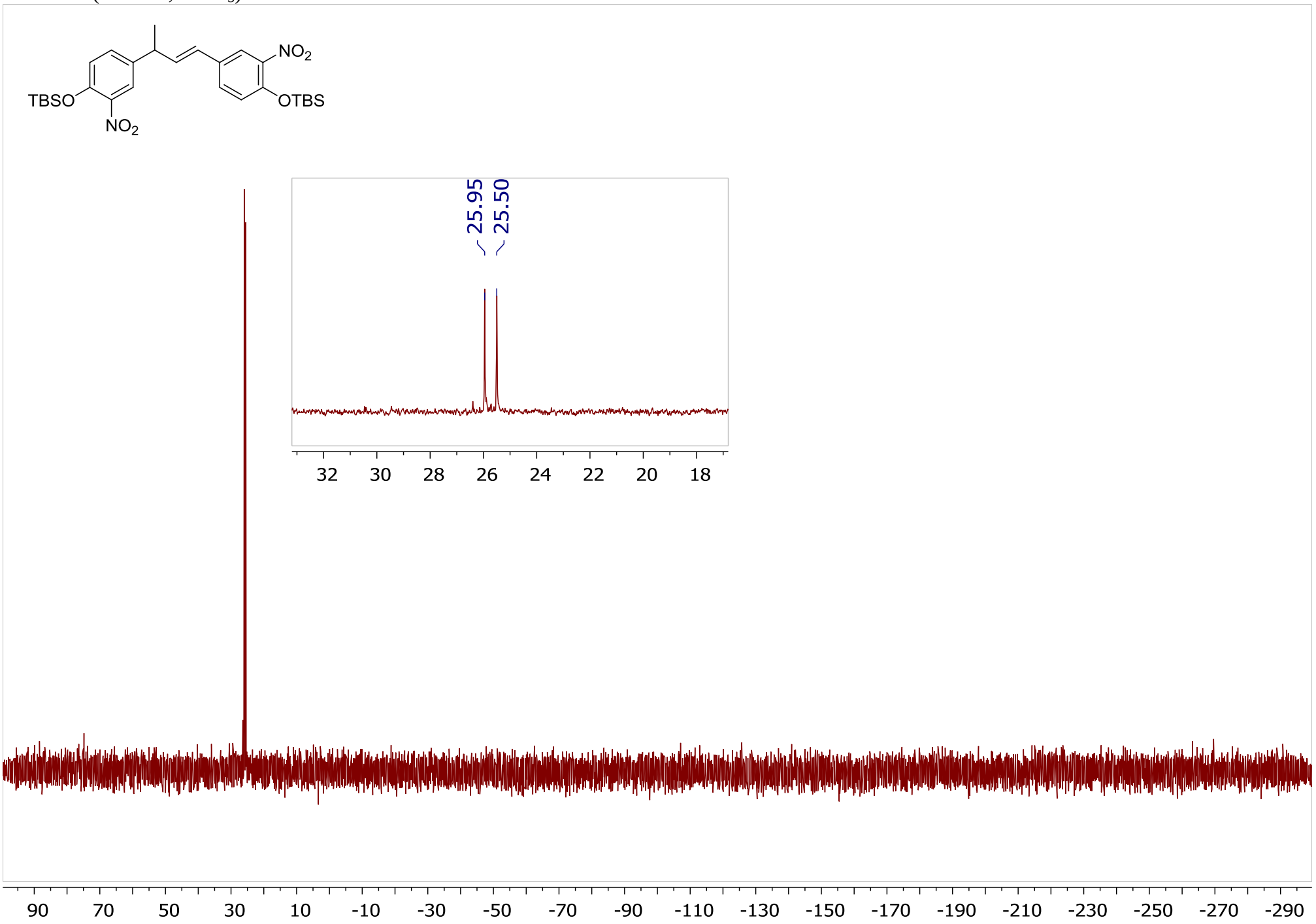
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

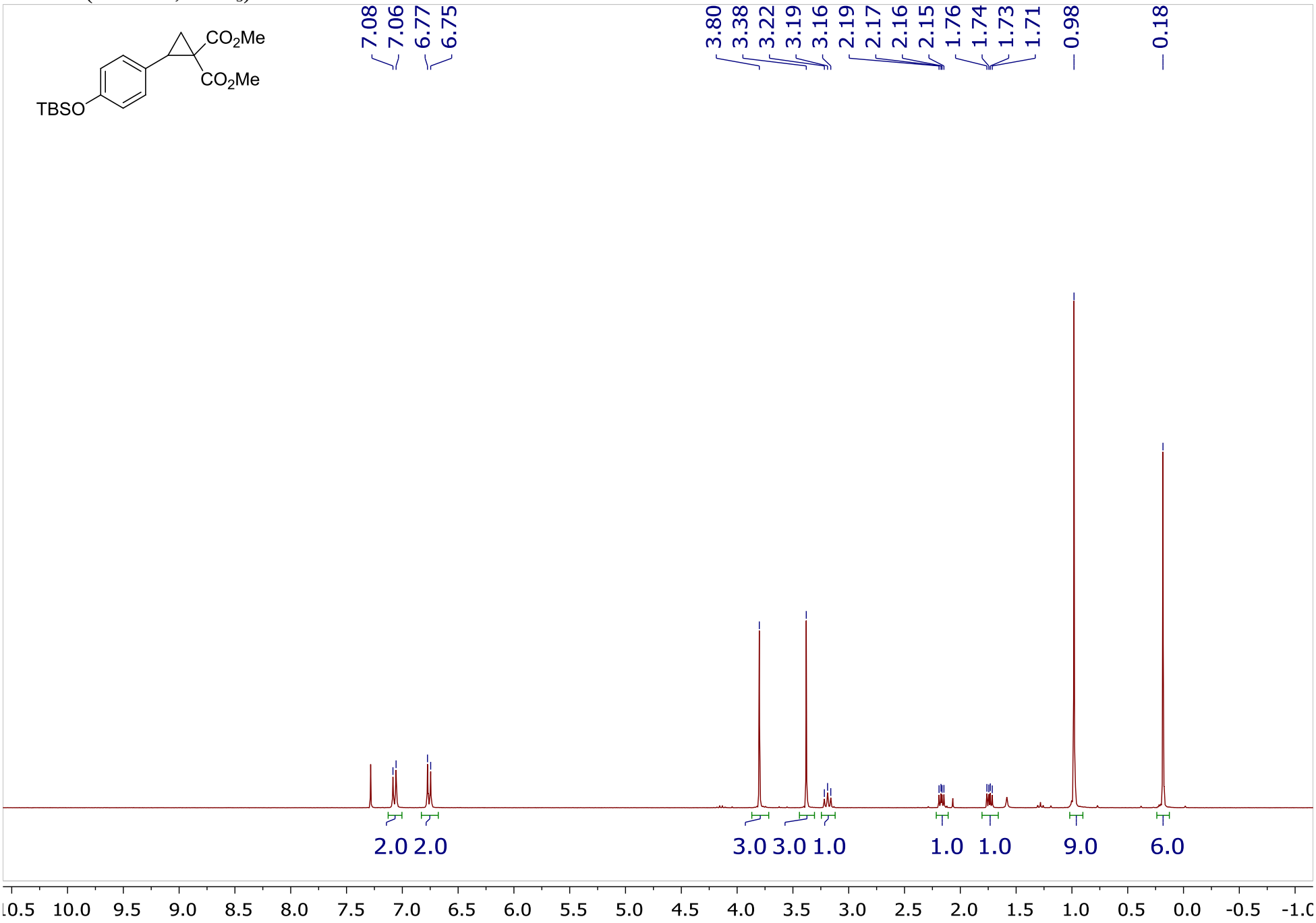


$^{29}$Si NMR (60 MHz, $CDCl_3$)



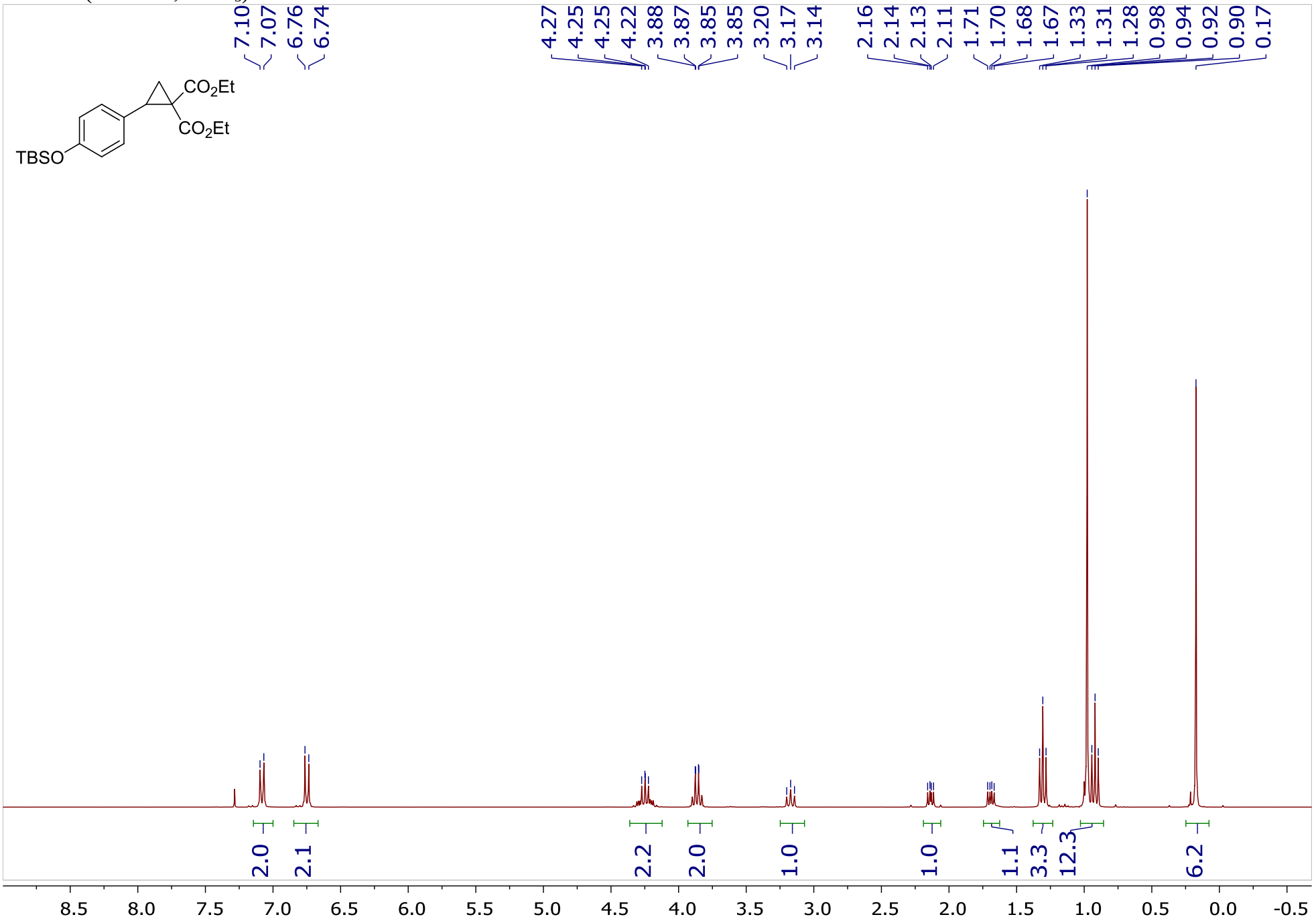
**Dimethyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1a)**

$^1$H NMR (300 MHz, $CDCl_3$)

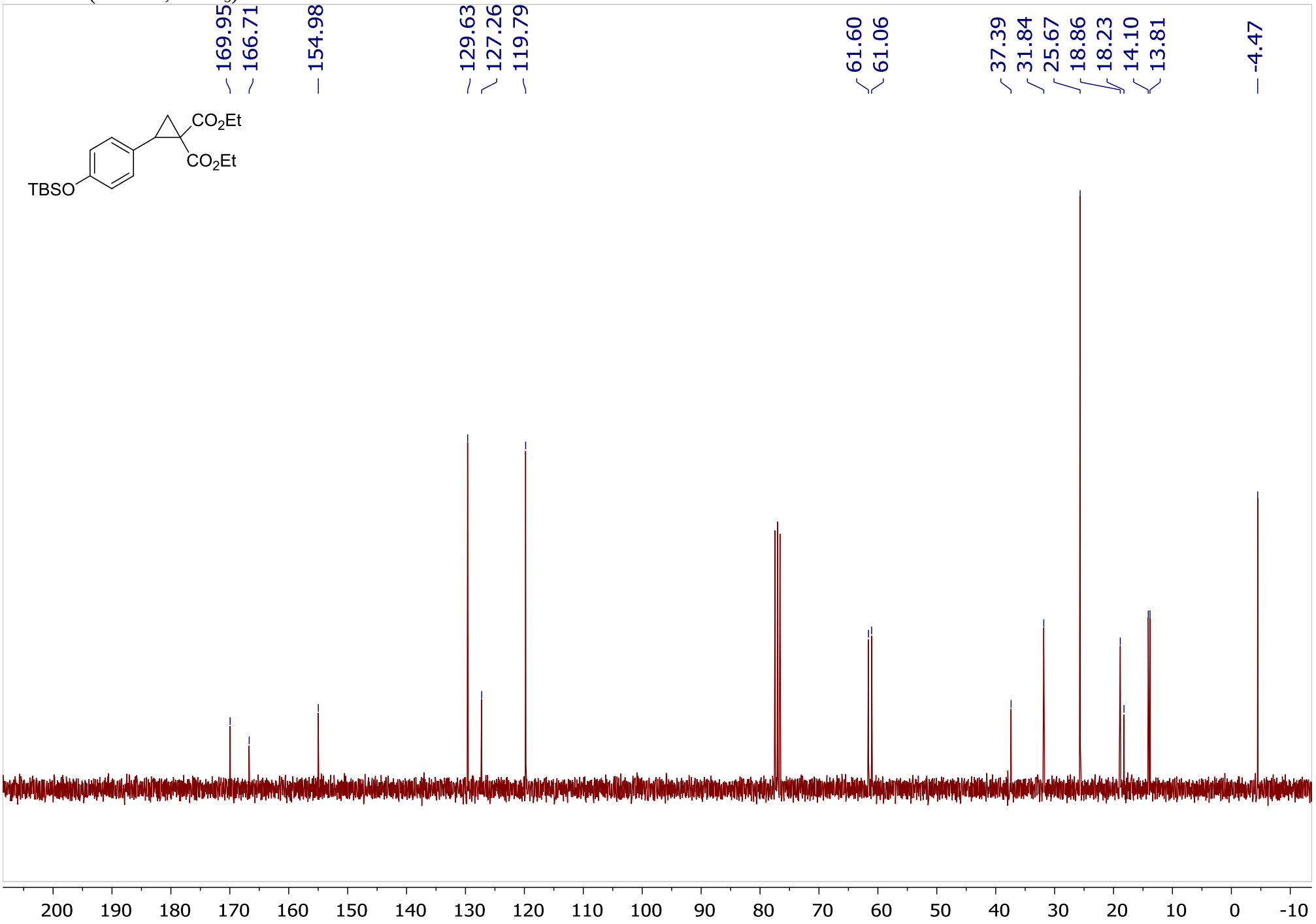


**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1b)**

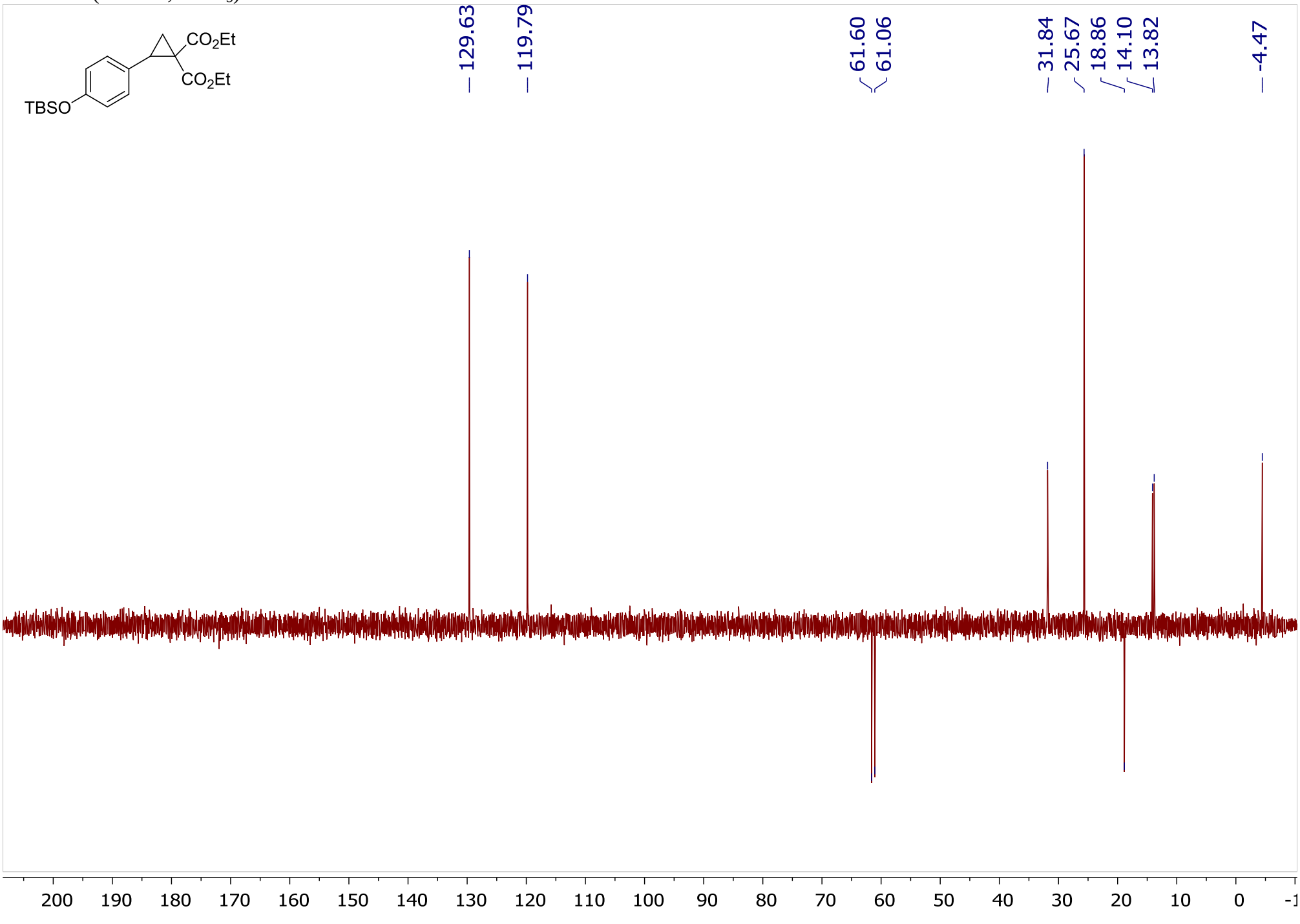
$^1$H NMR (300 MHz, $CDCl_3$)



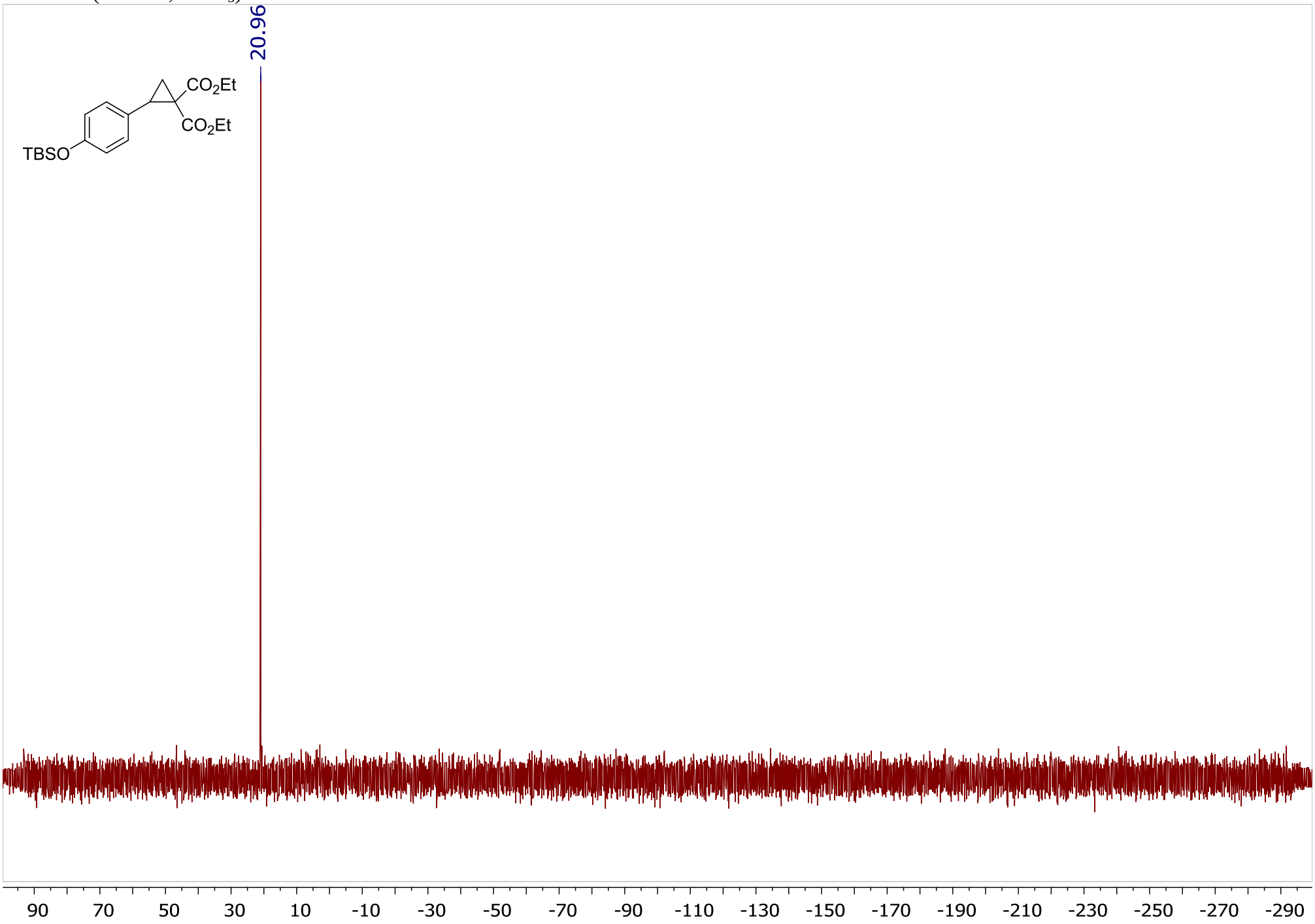
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

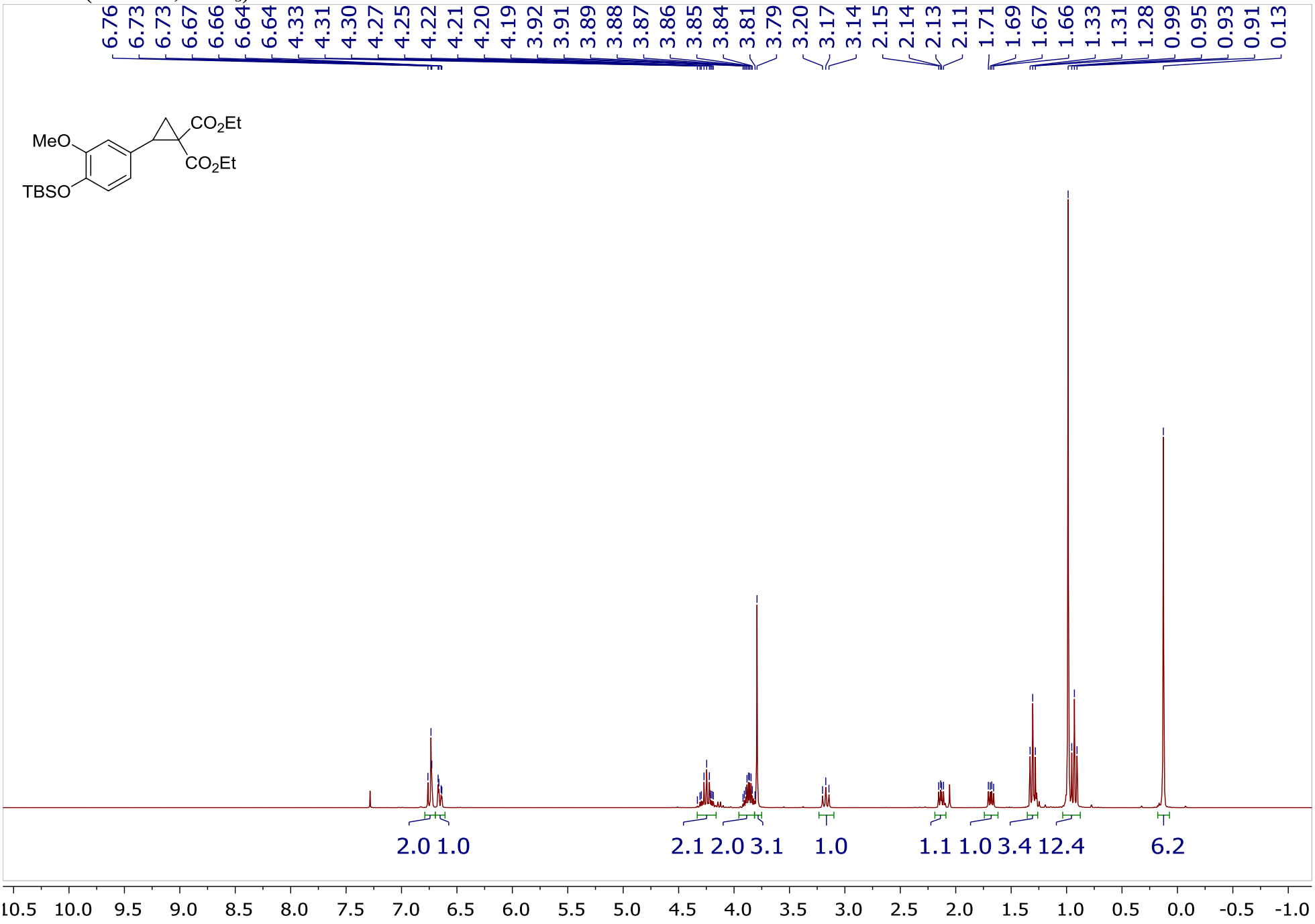


$^{29}$Si NMR (60 MHz, $CDCl_3$)

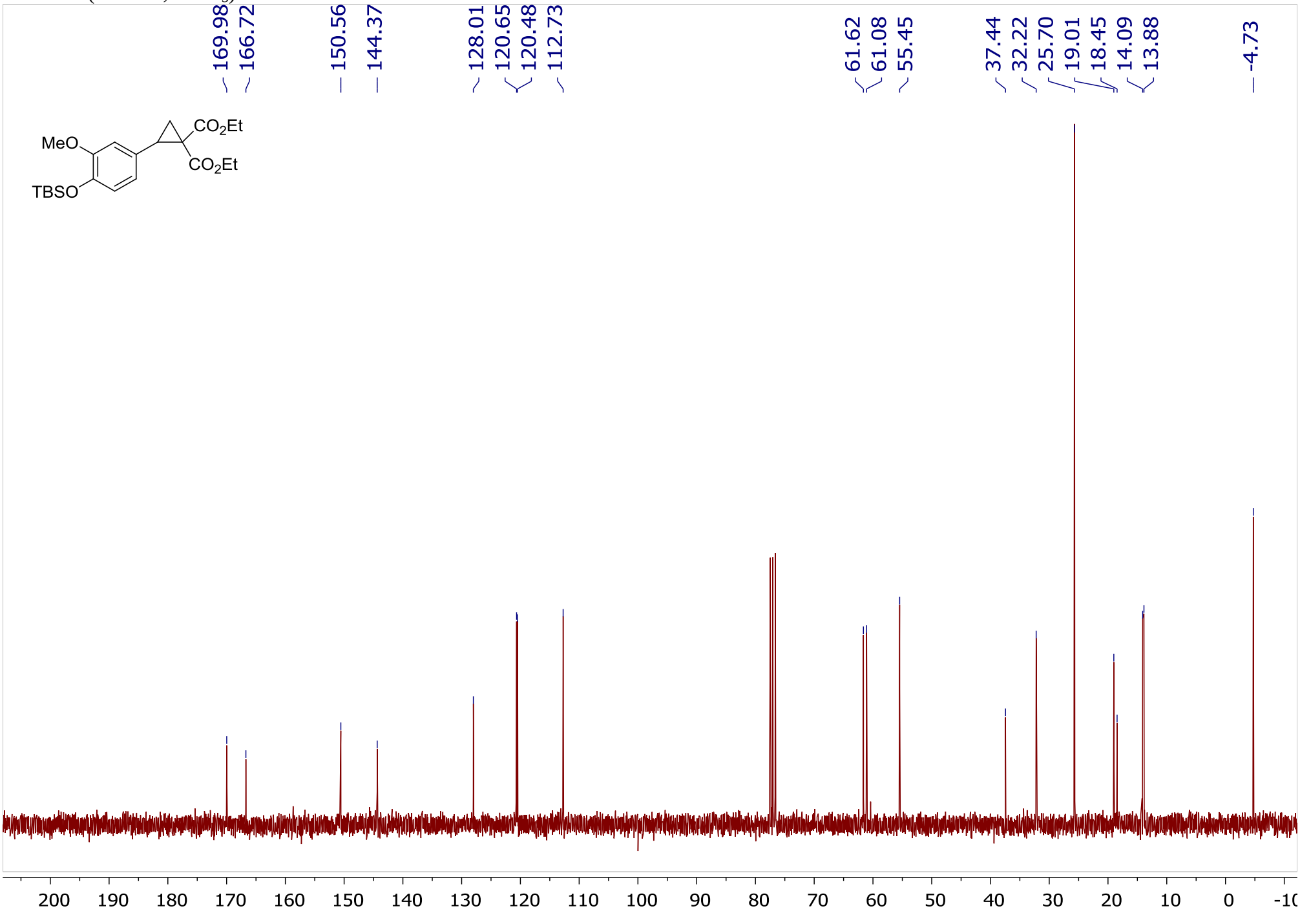


**Diethyl 2-(4-(tert-butyldimethylsilyloxy)-3-methoxyphenyl)cyclopropane-1,1-dicarboxylate (1c)**

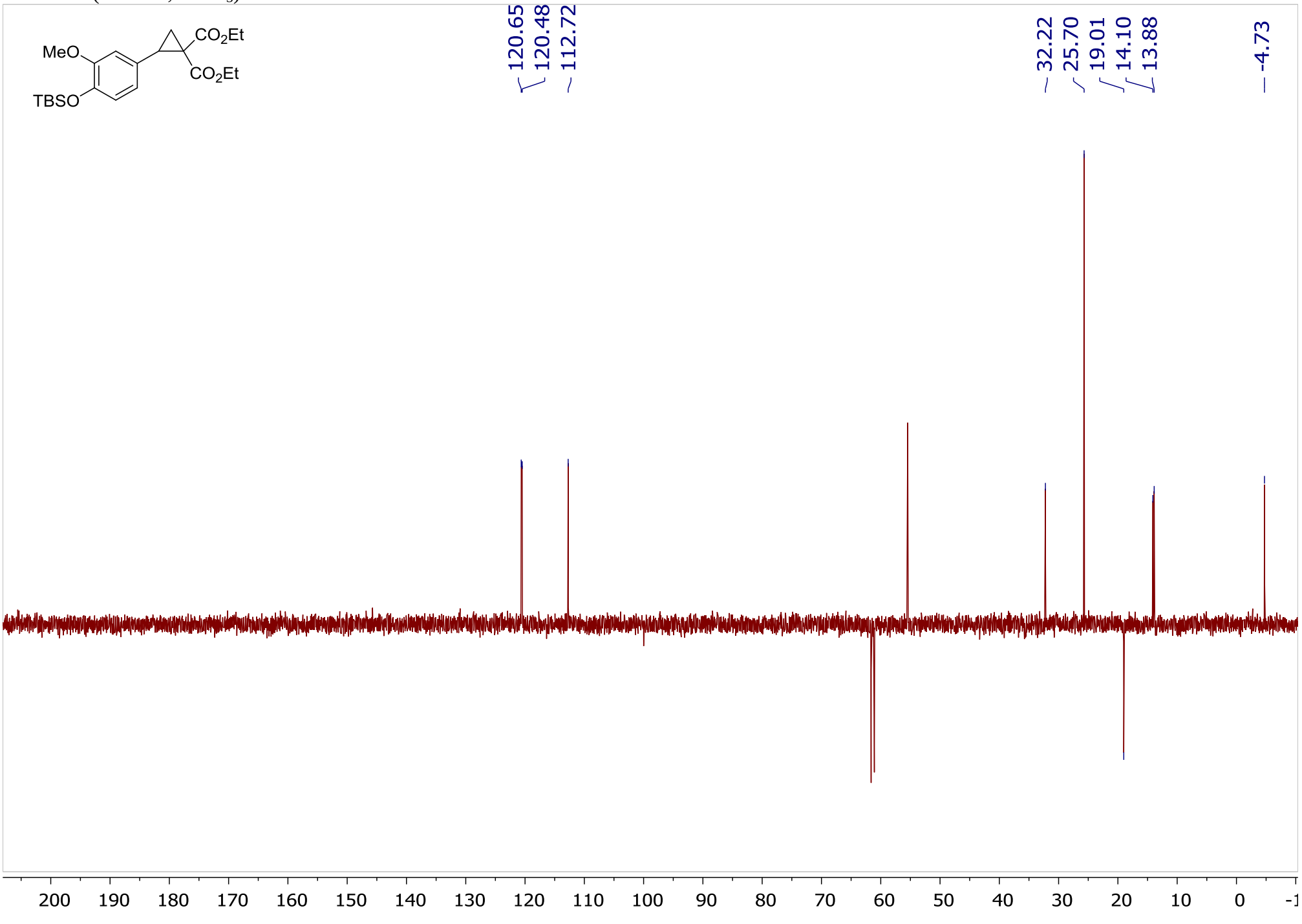
$^1$H NMR (300 MHz, $CDCl_3$)



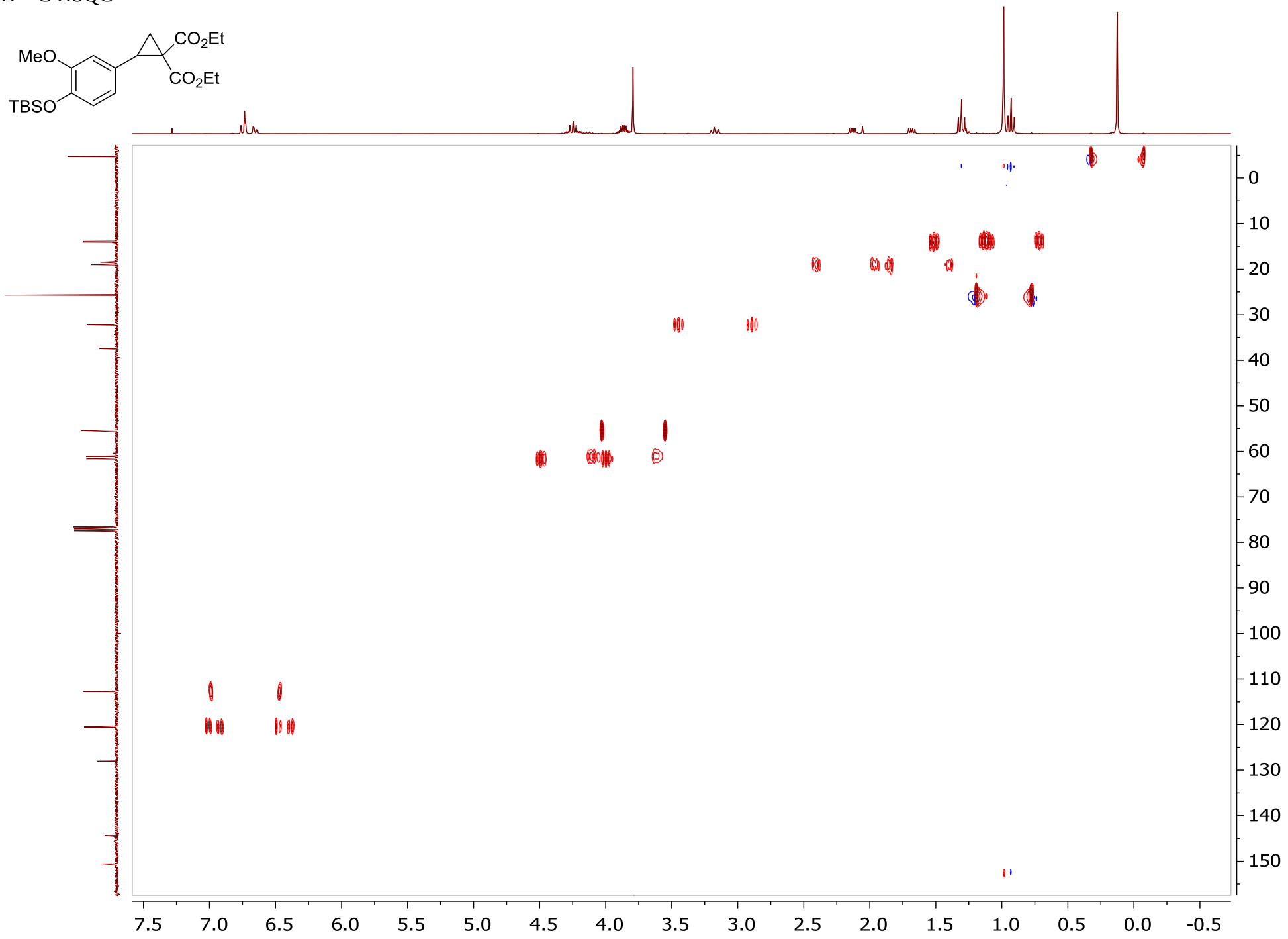
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}H$-$^{13}C$ HSQC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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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1.5
1.0
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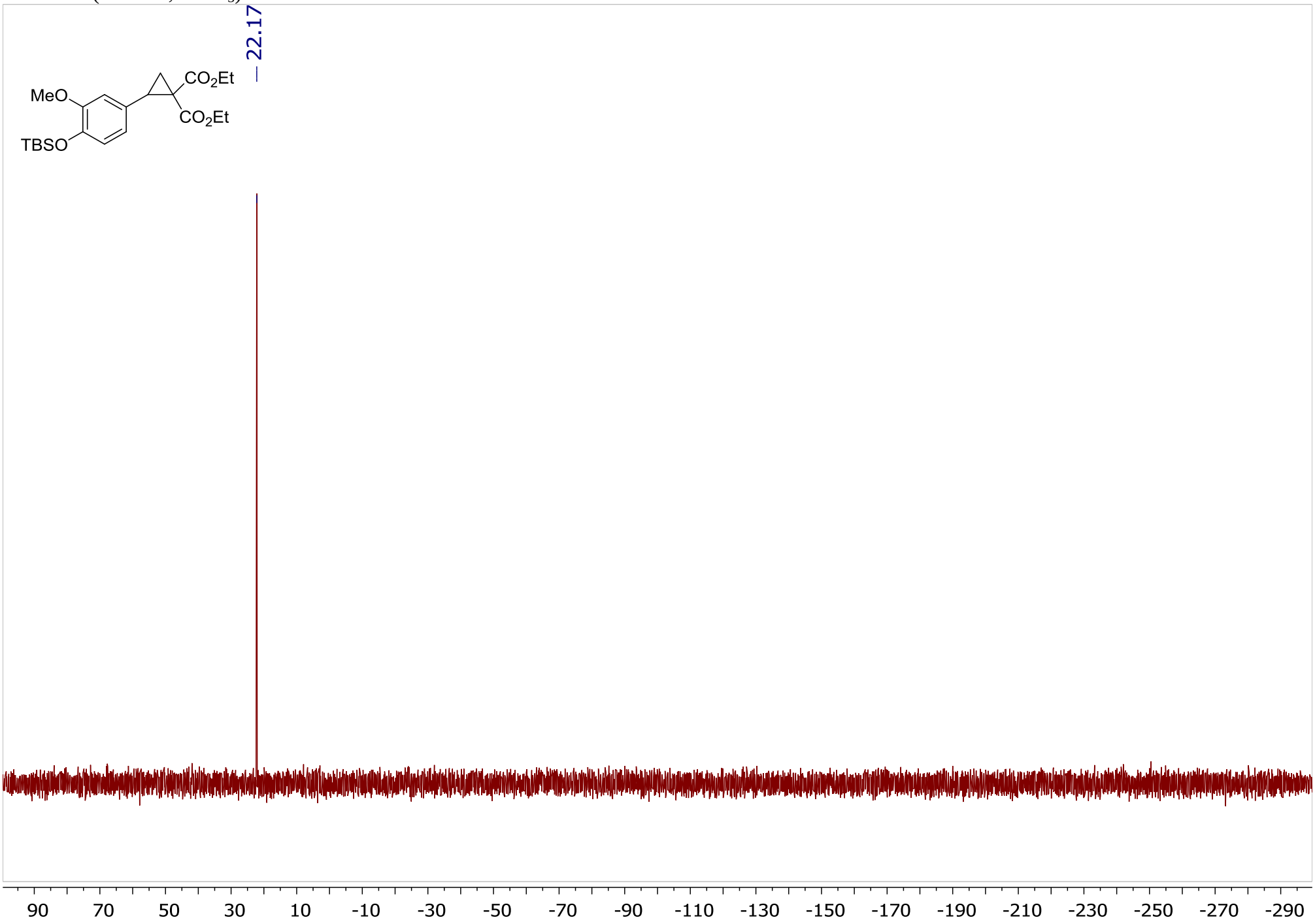
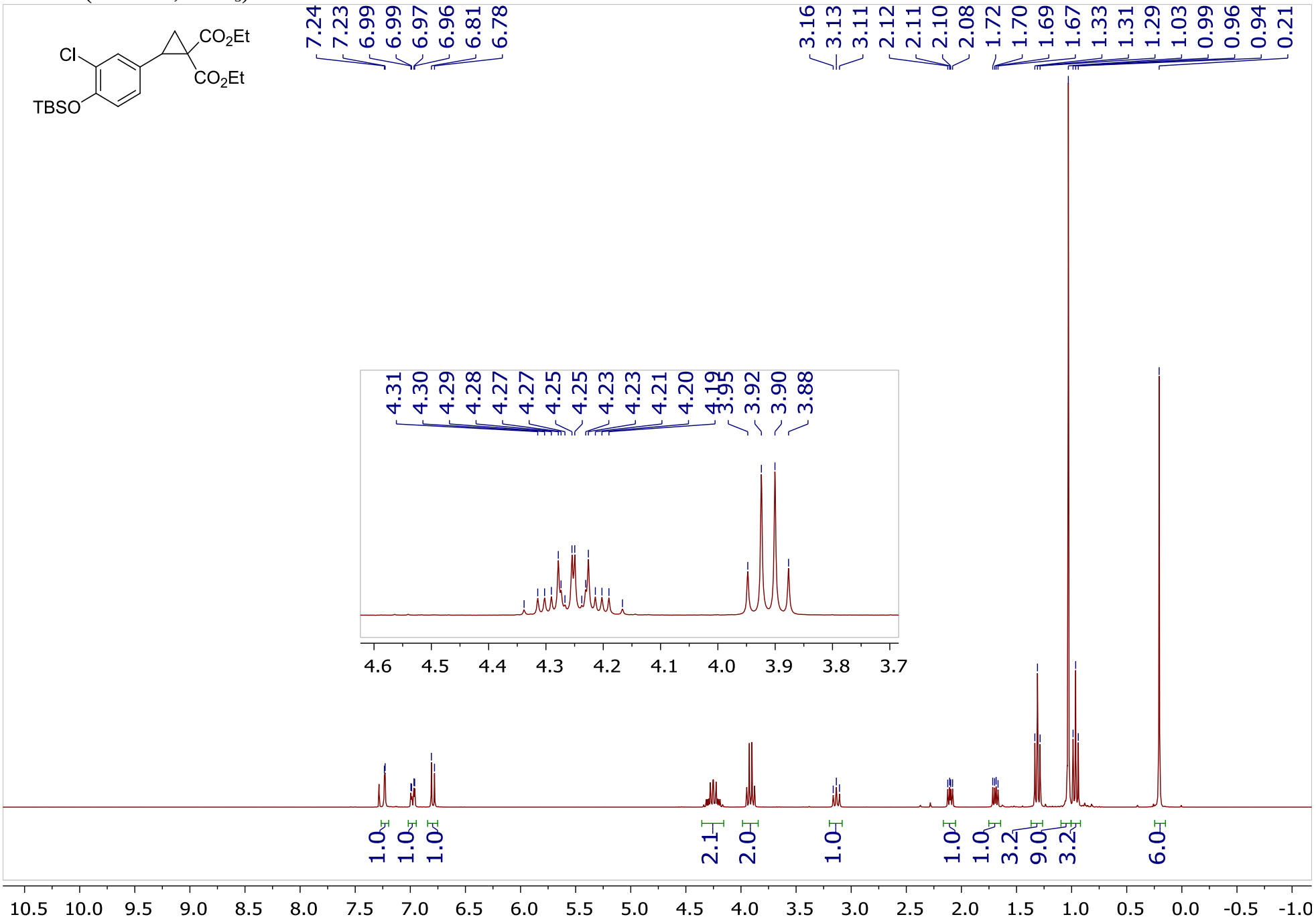
-0.5

$^{29}$Si NMR (60 MHz, $CDCl_3$)

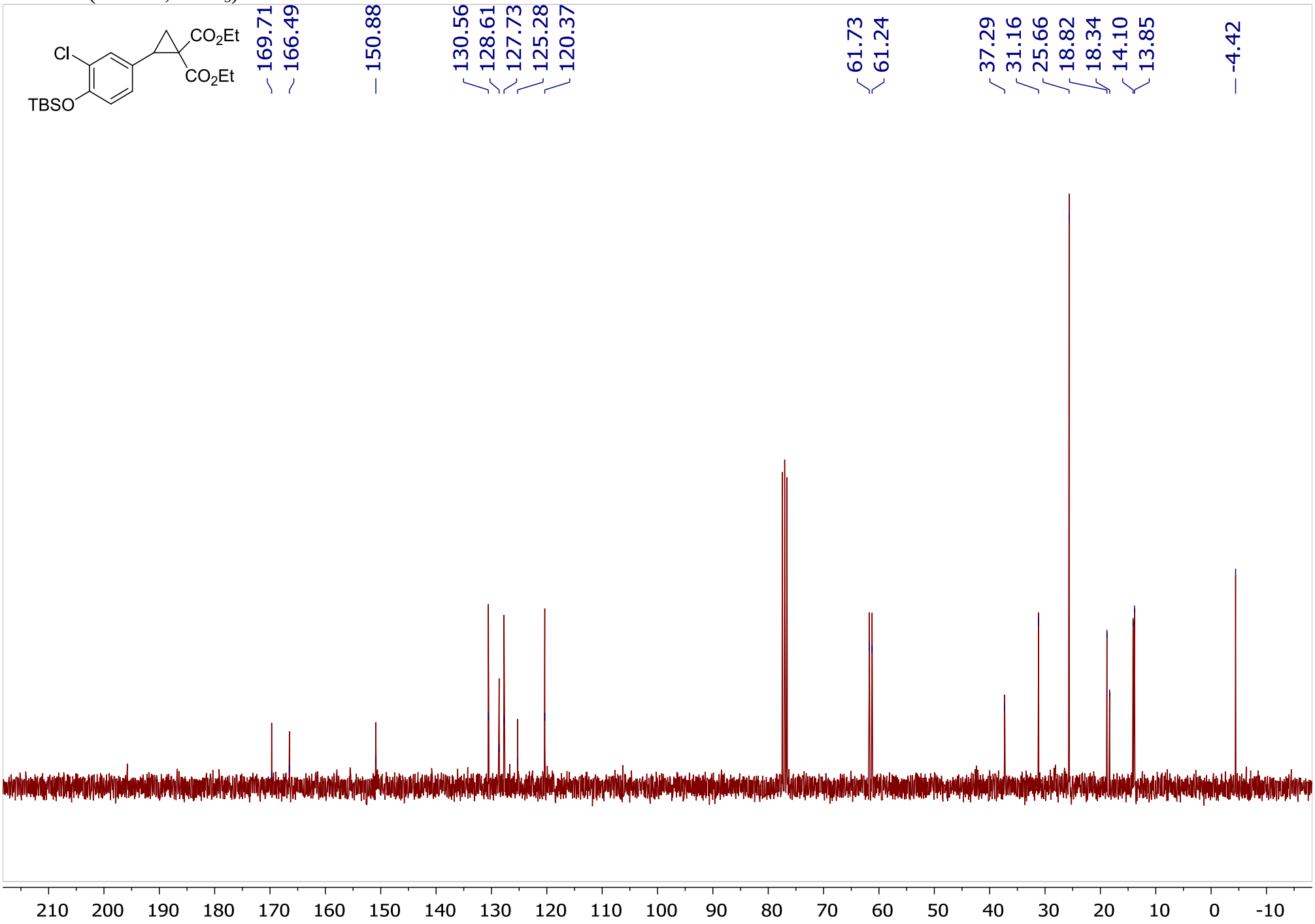


**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3-chlorophenyl)cyclopropane-1,1-dicarboxylate (1d)**

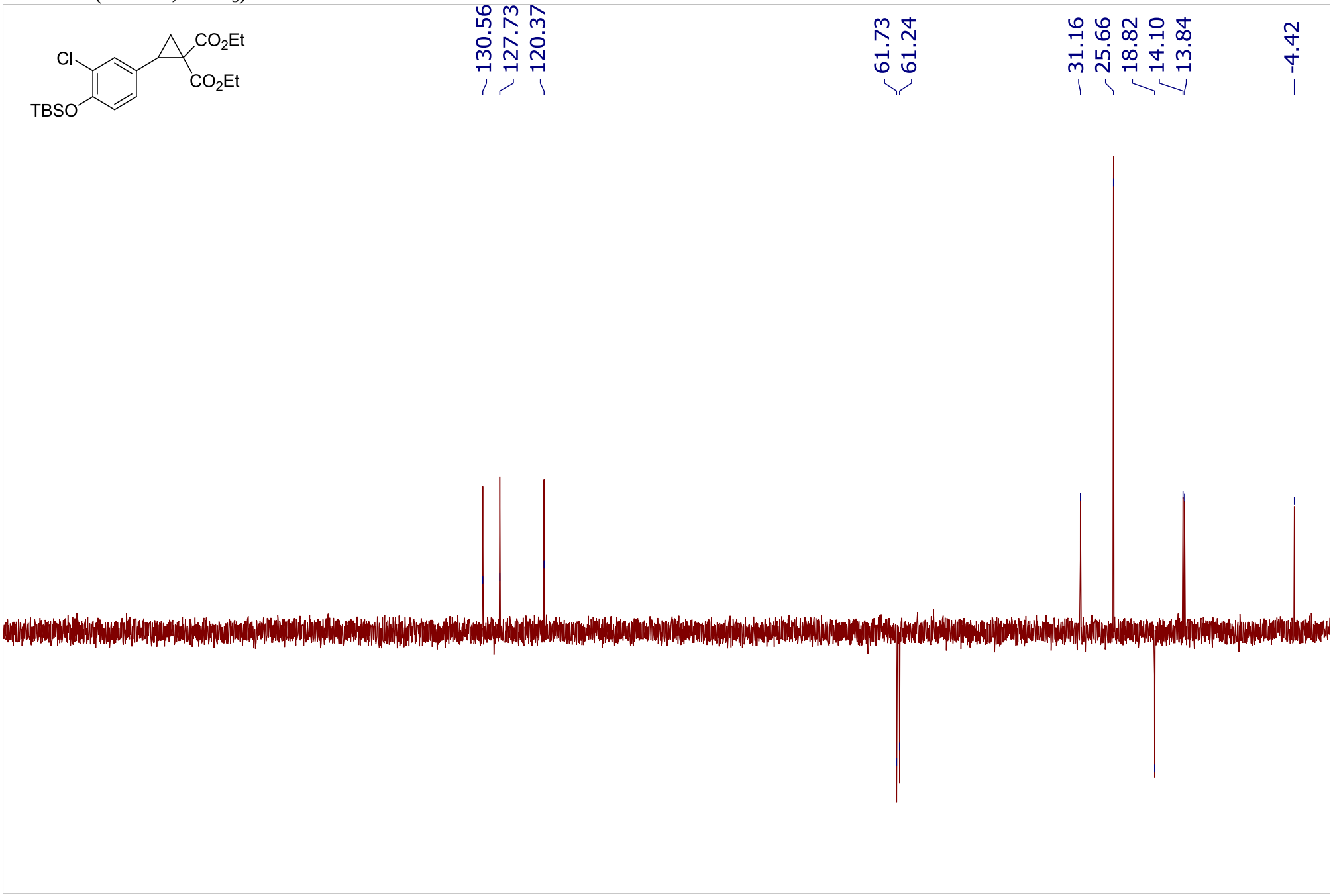
$^1$H NMR (300 MHz, $CDCl_3$)



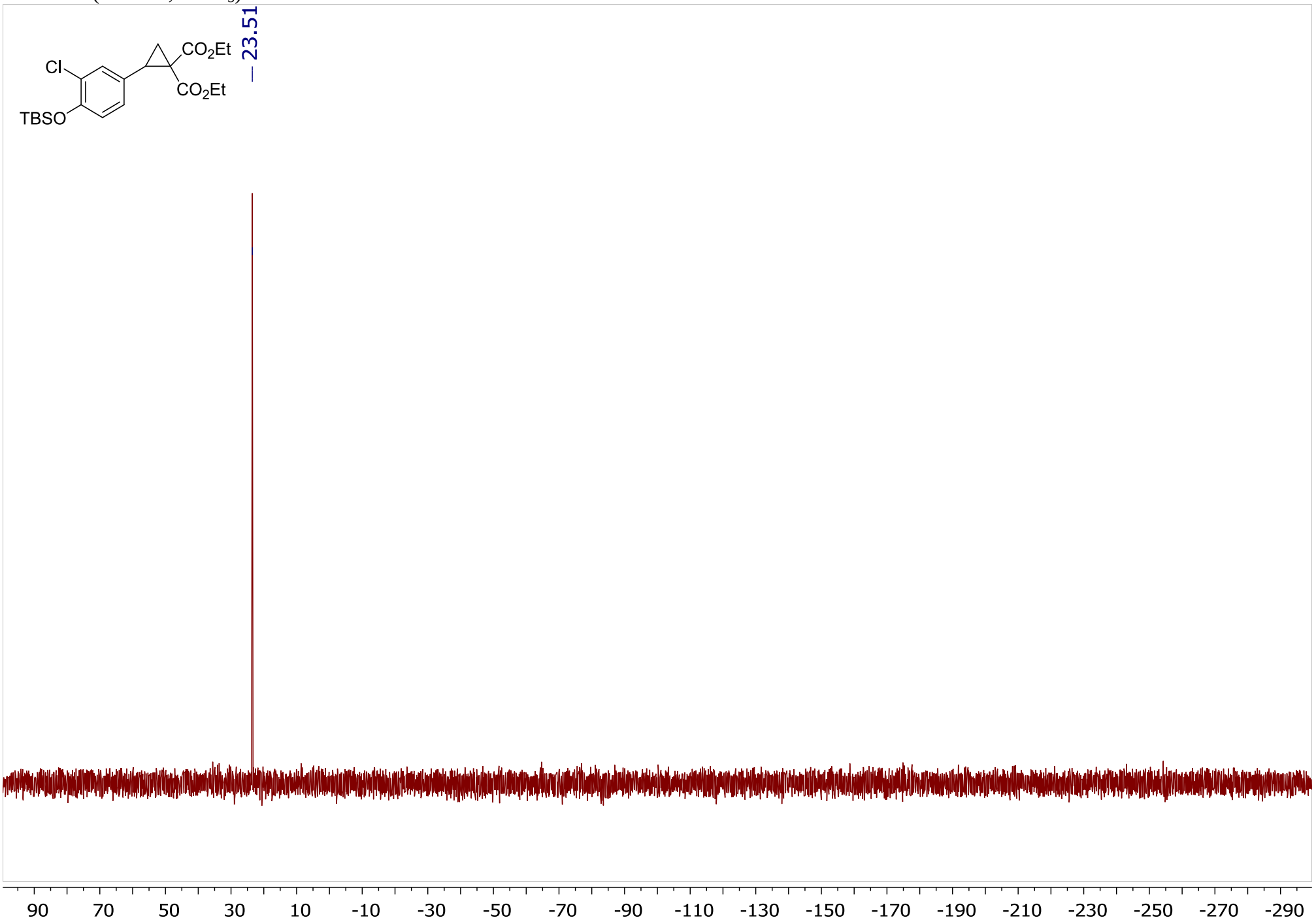
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

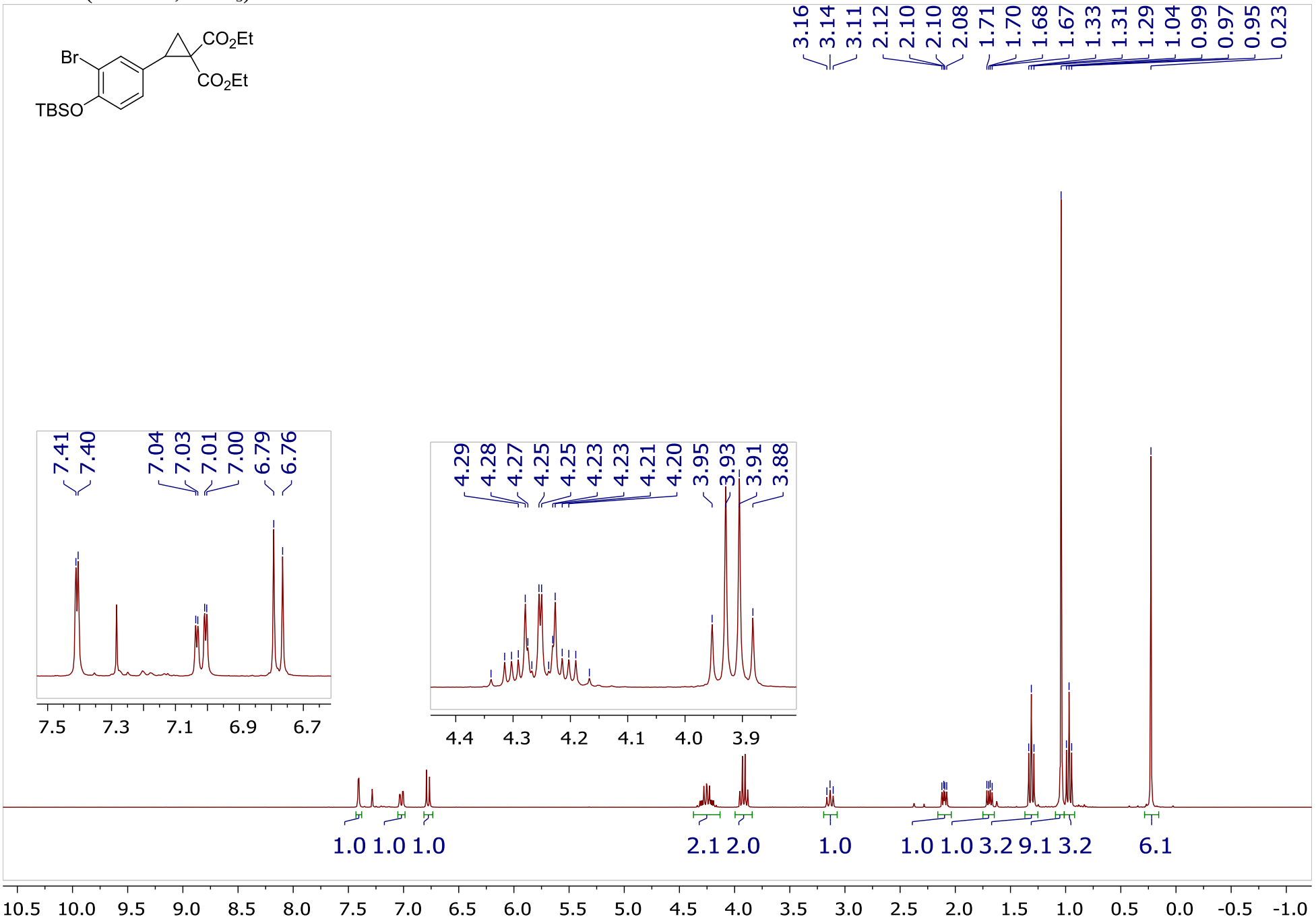


$^{29}$Si NMR (60 MHz, $CDCl_3$)

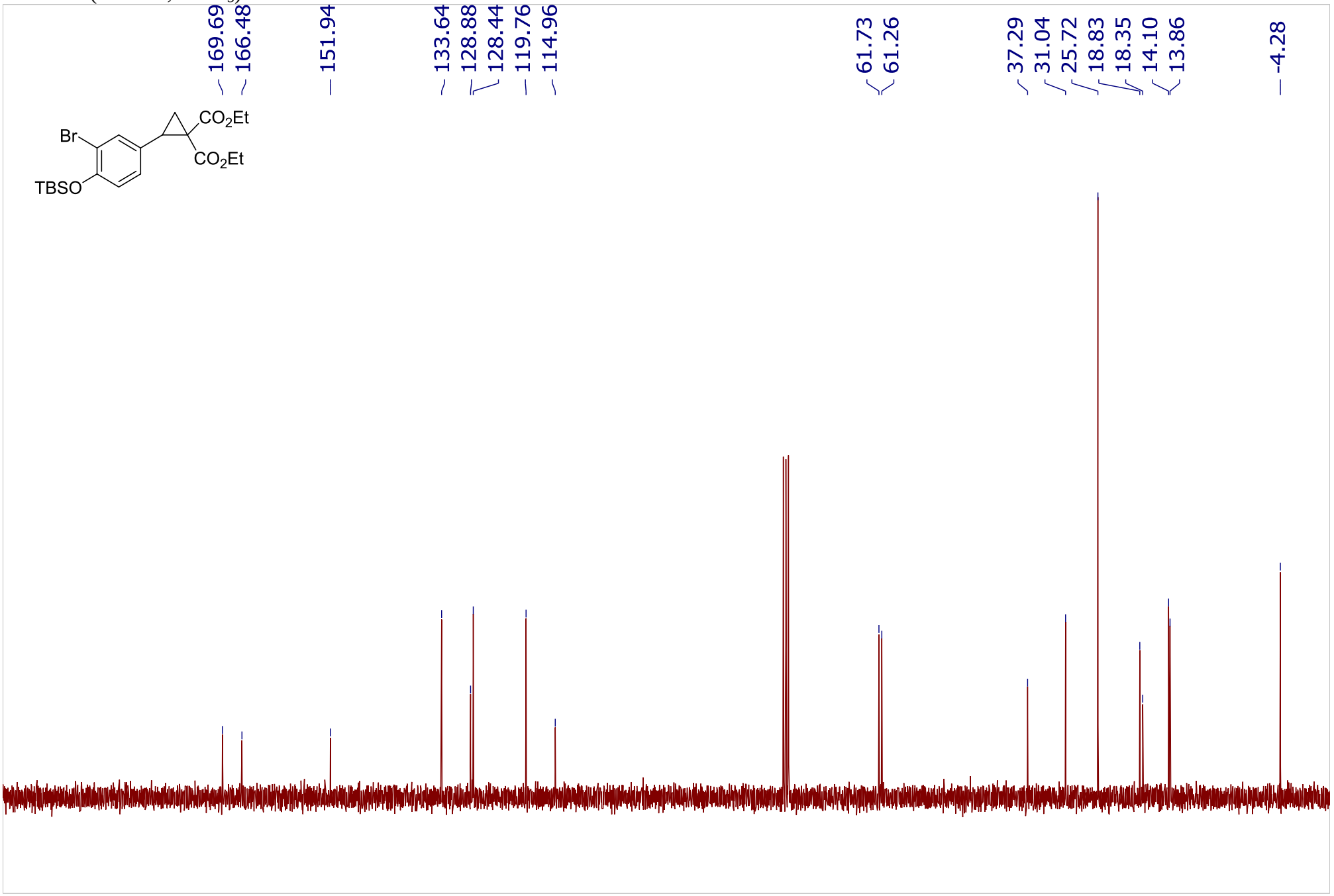


**Diethyl 2-(3-bromo-4-(tert-butyldimethylsilyloxy)phenyl)cyclopropane-1,1-dicarboxylate (1e)**

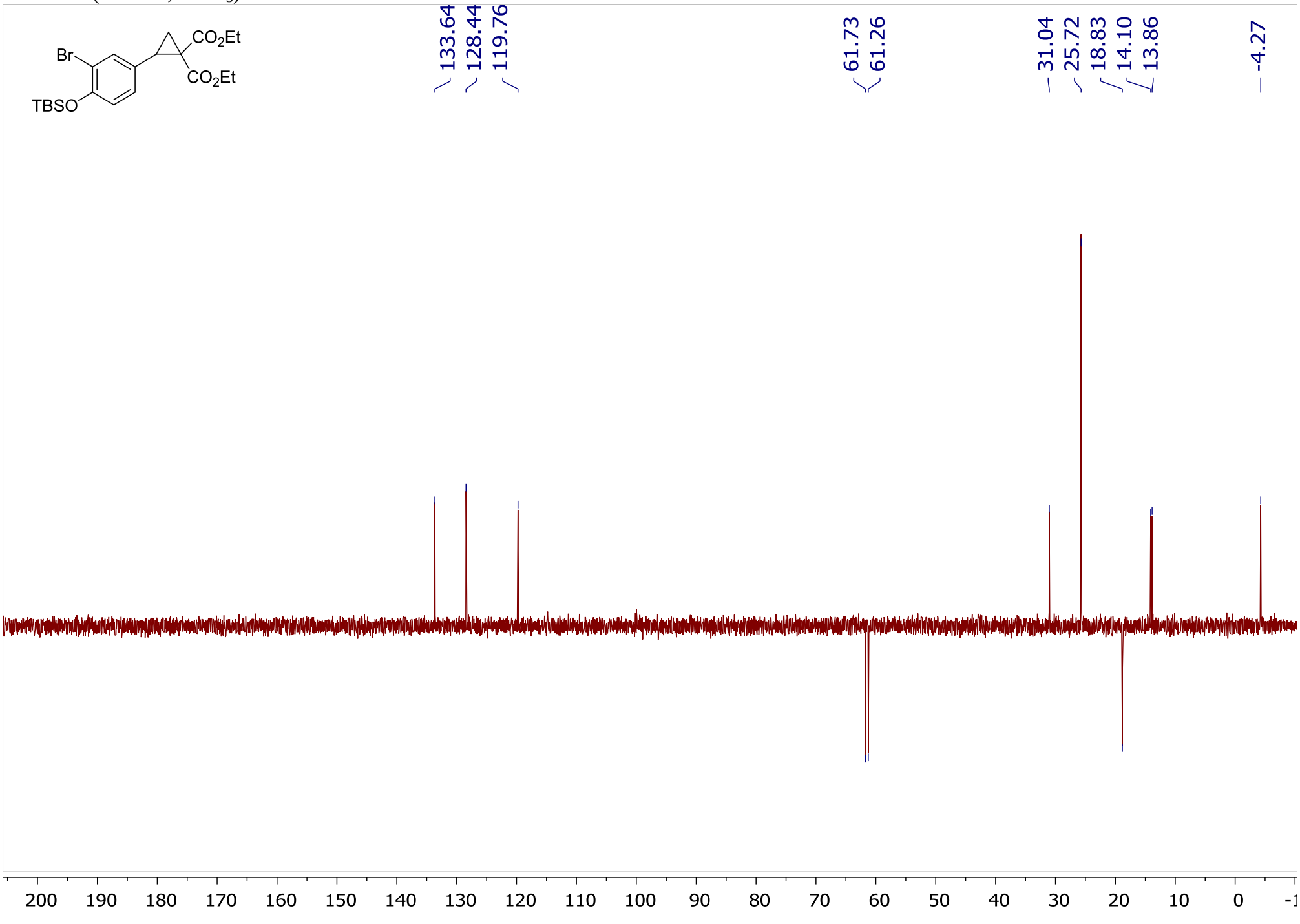
$^1$H NMR (300 MHz, $CDCl_3$)



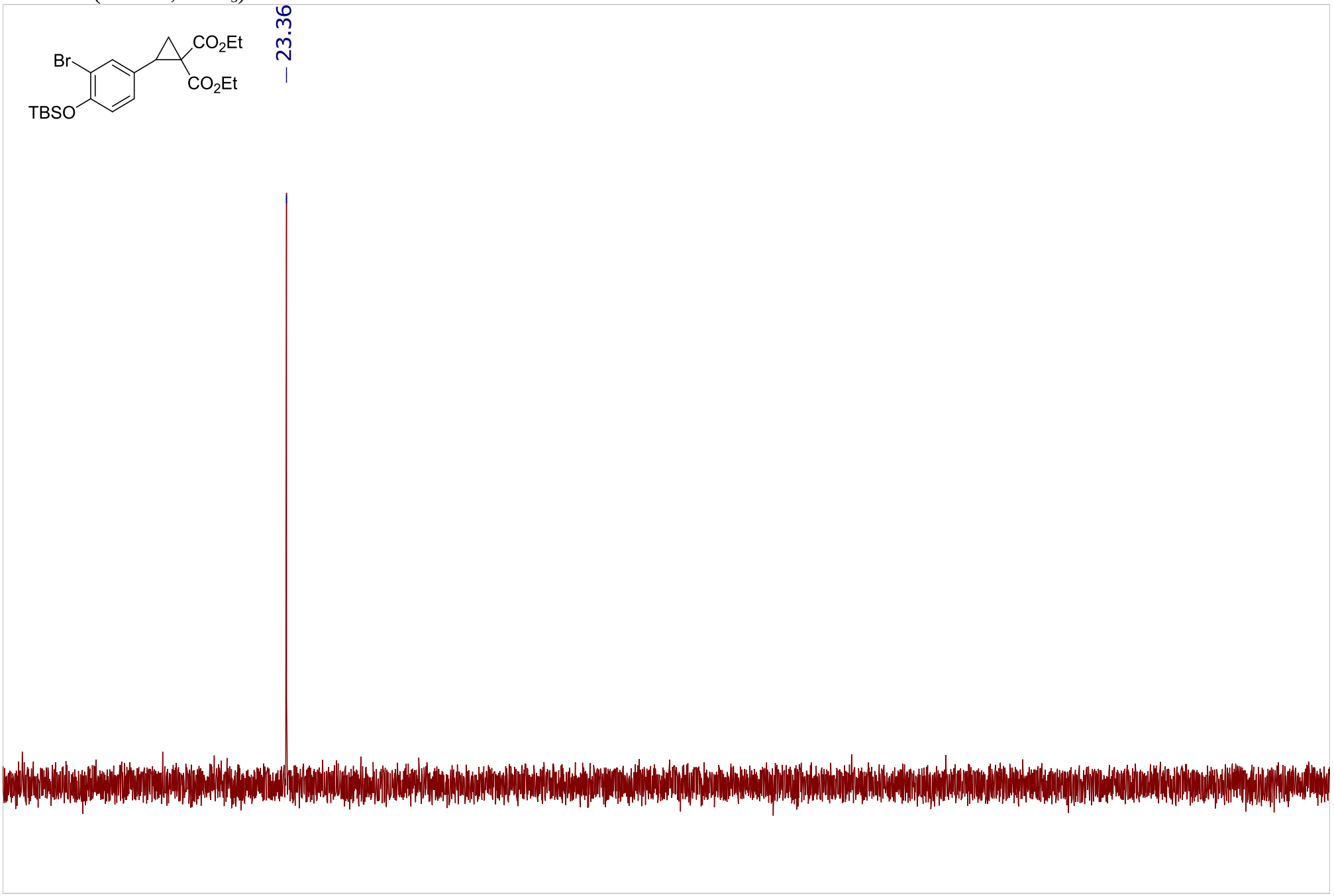
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

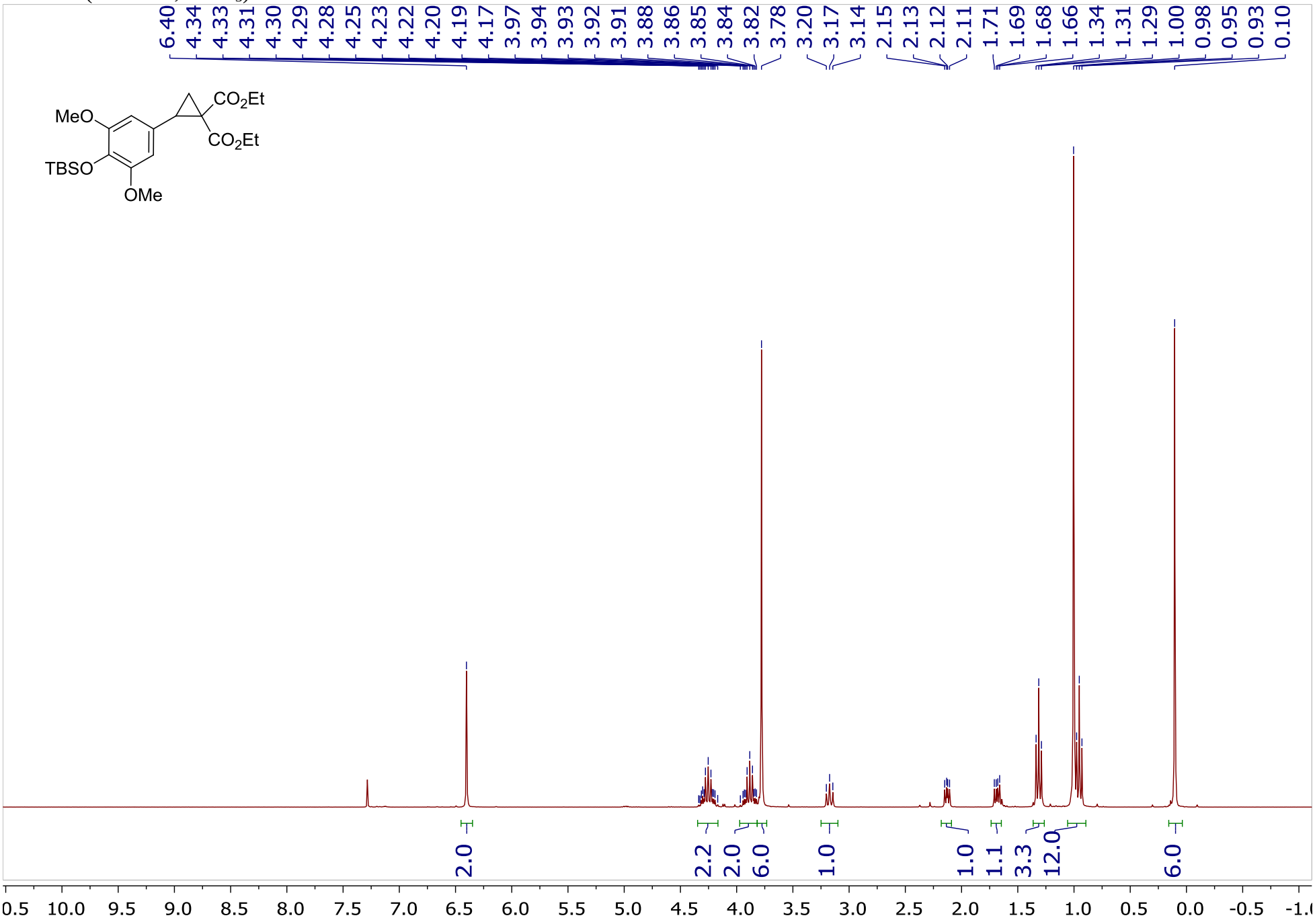


$^{29}$Si NMR (60 MHz, $CDCl_3$)

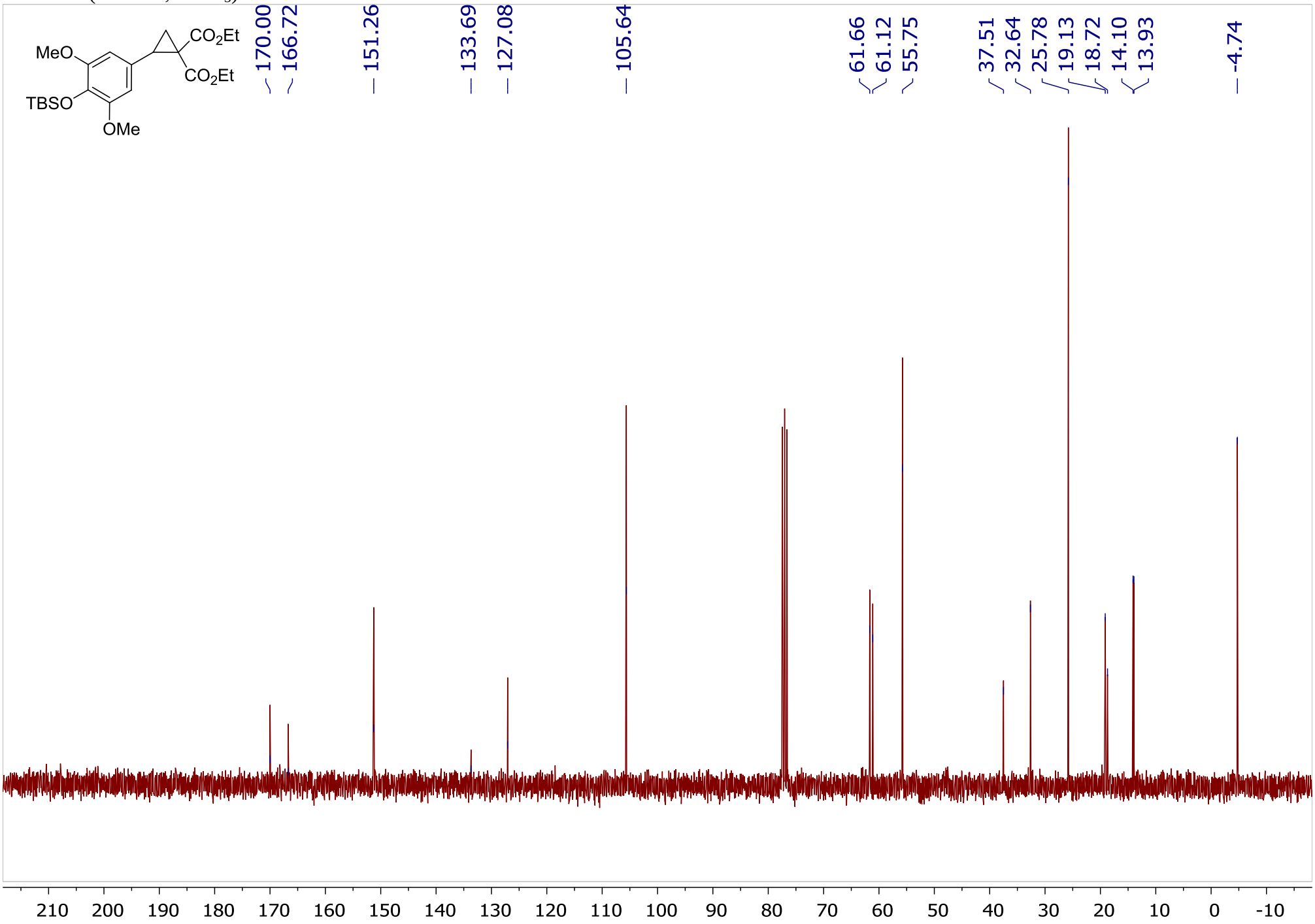


**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (1f)**

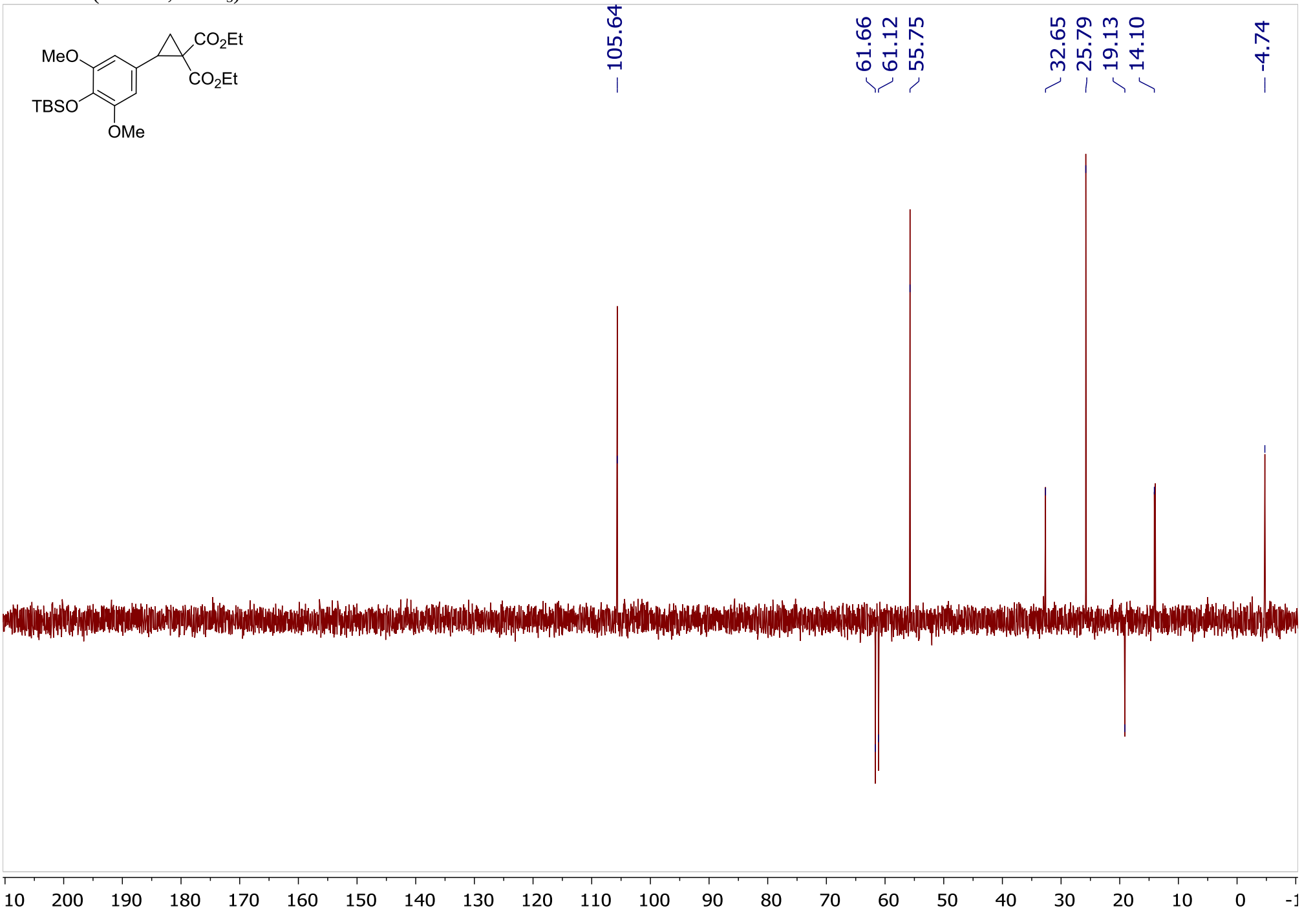
$^1$H NMR (300 MHz, $CDCl_3$)



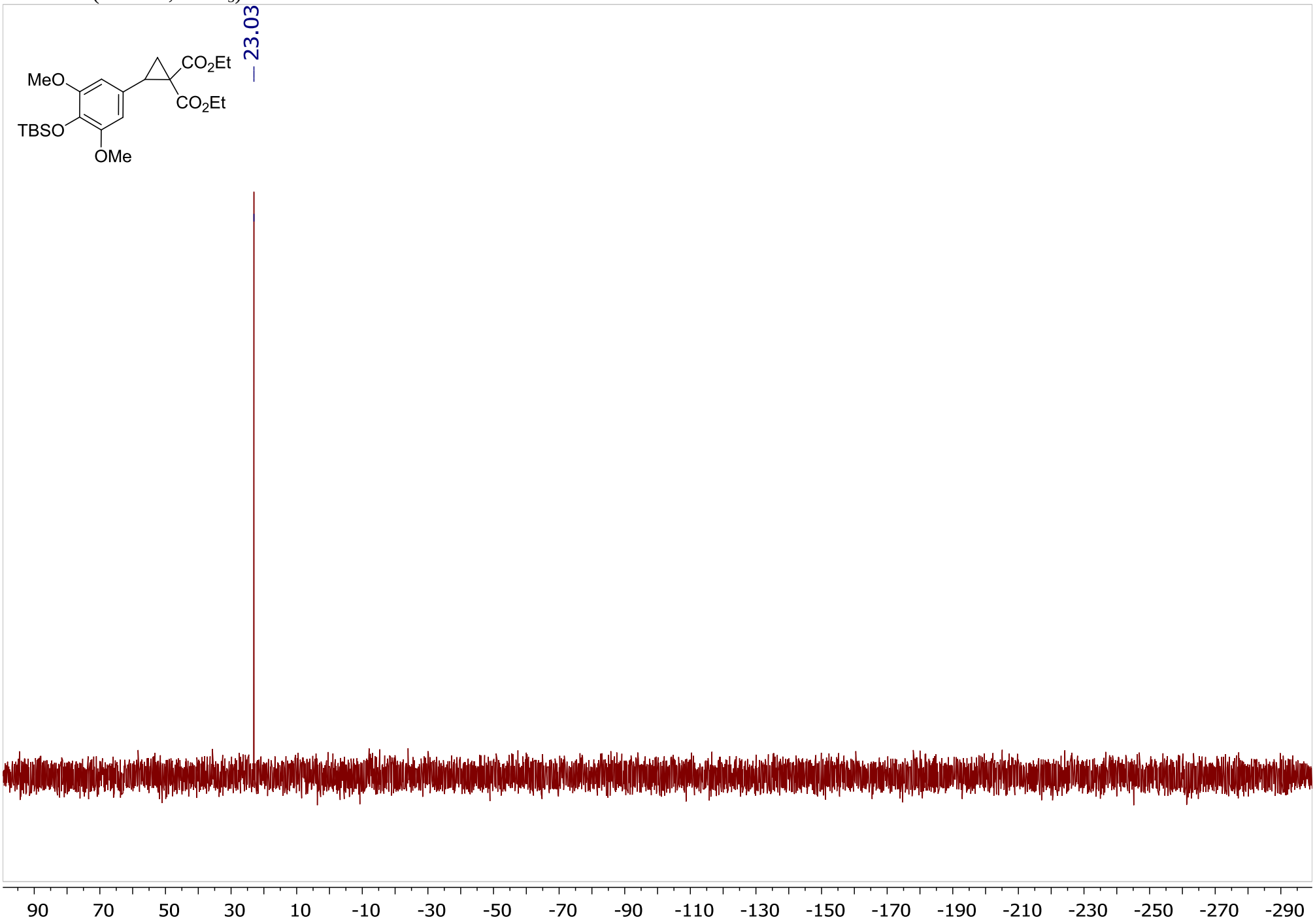
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

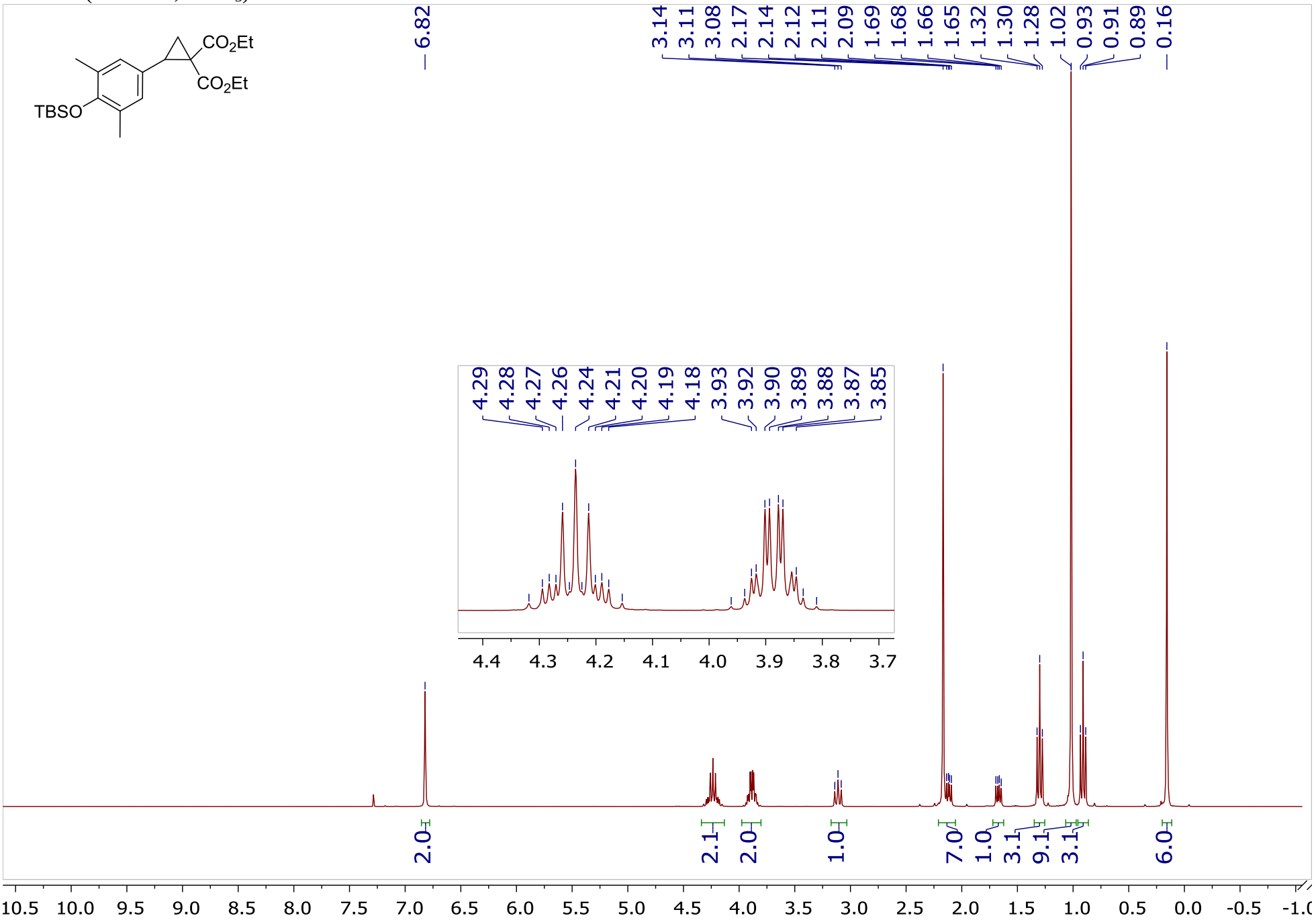


$^{29}$Si NMR (60 MHz, $CDCl_3$)

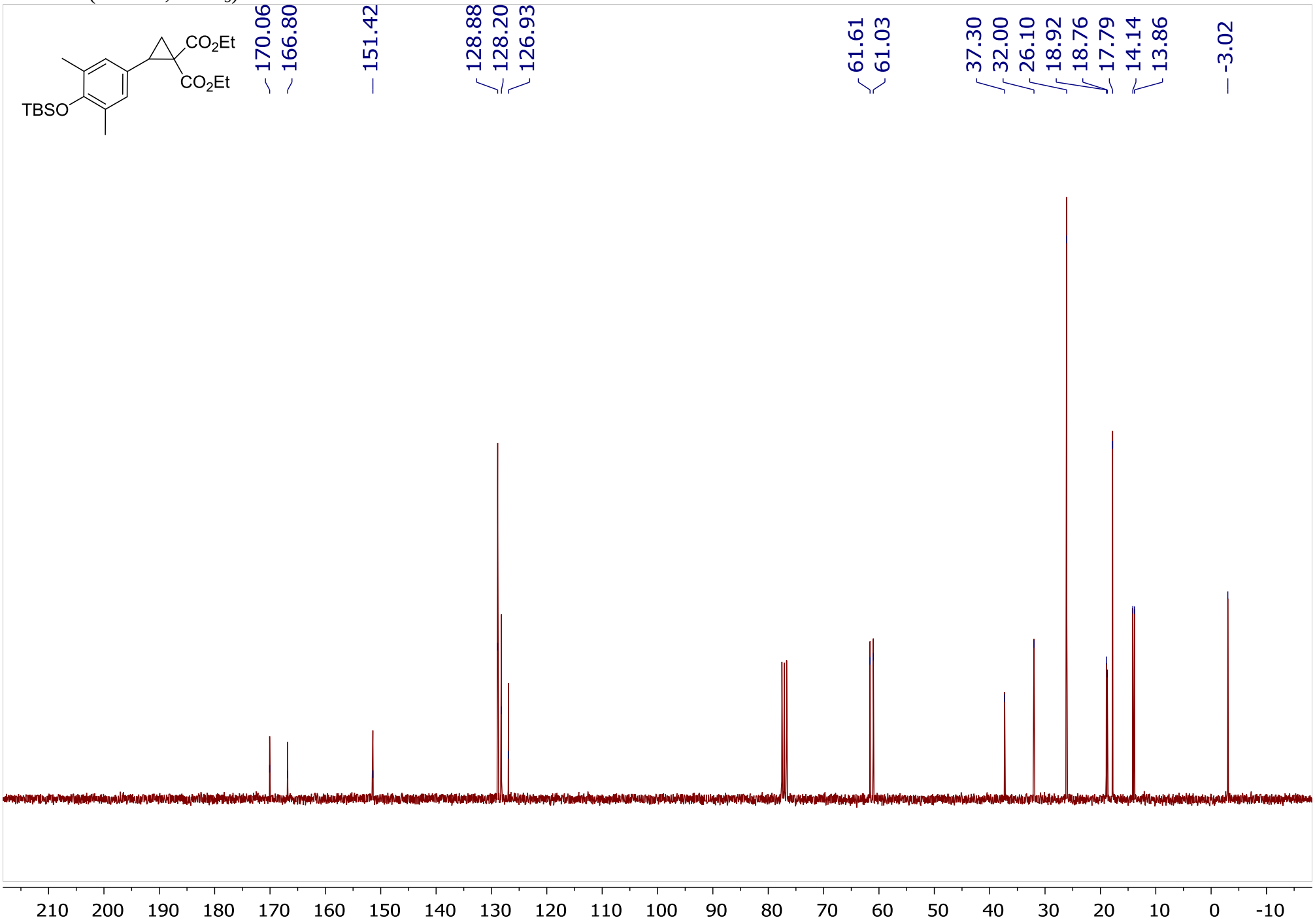


**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenyl)cyclopropane-1,1-dicarboxylate (1g)**

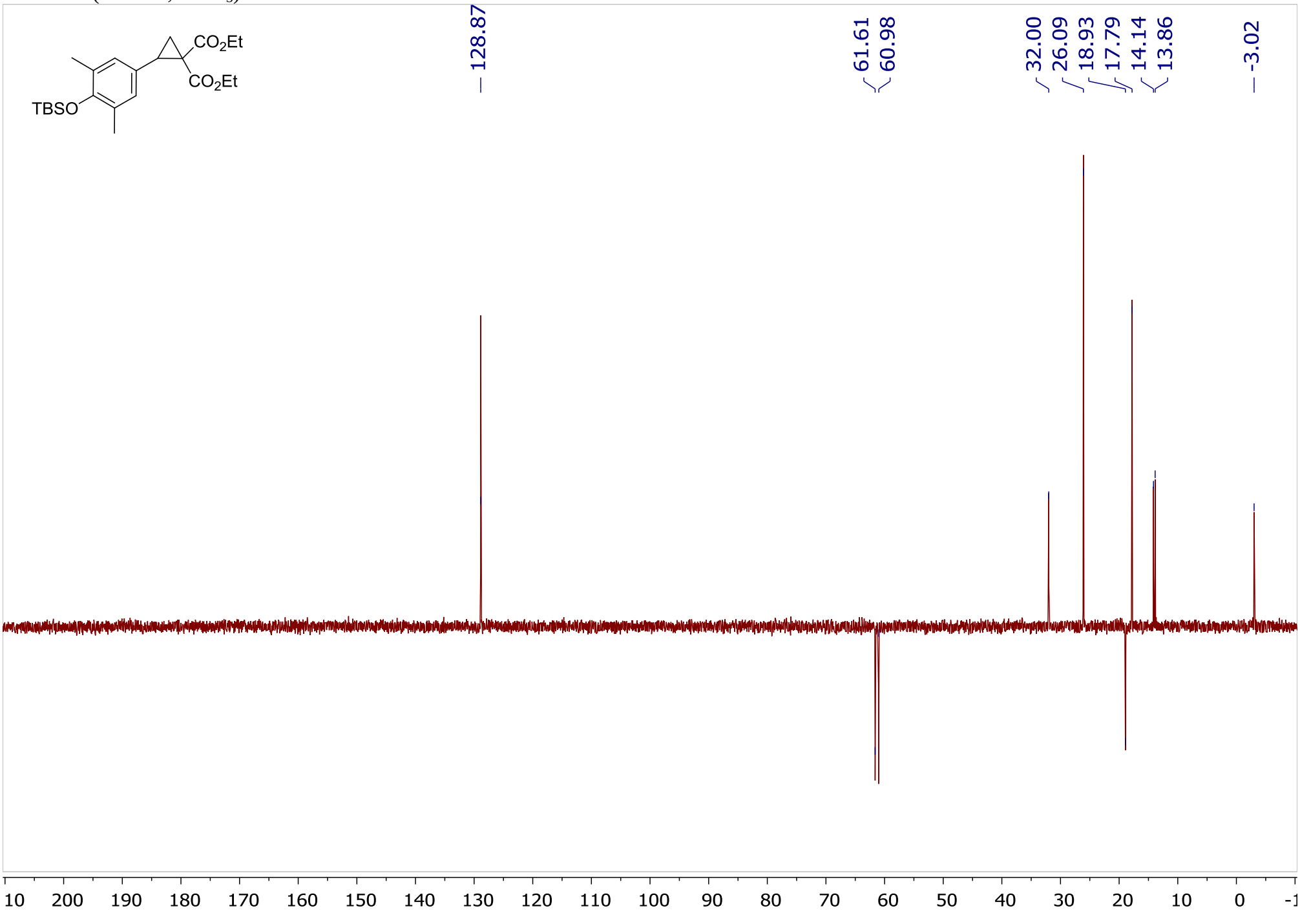
$^1$H NMR (300 MHz, $CDCl_3$)



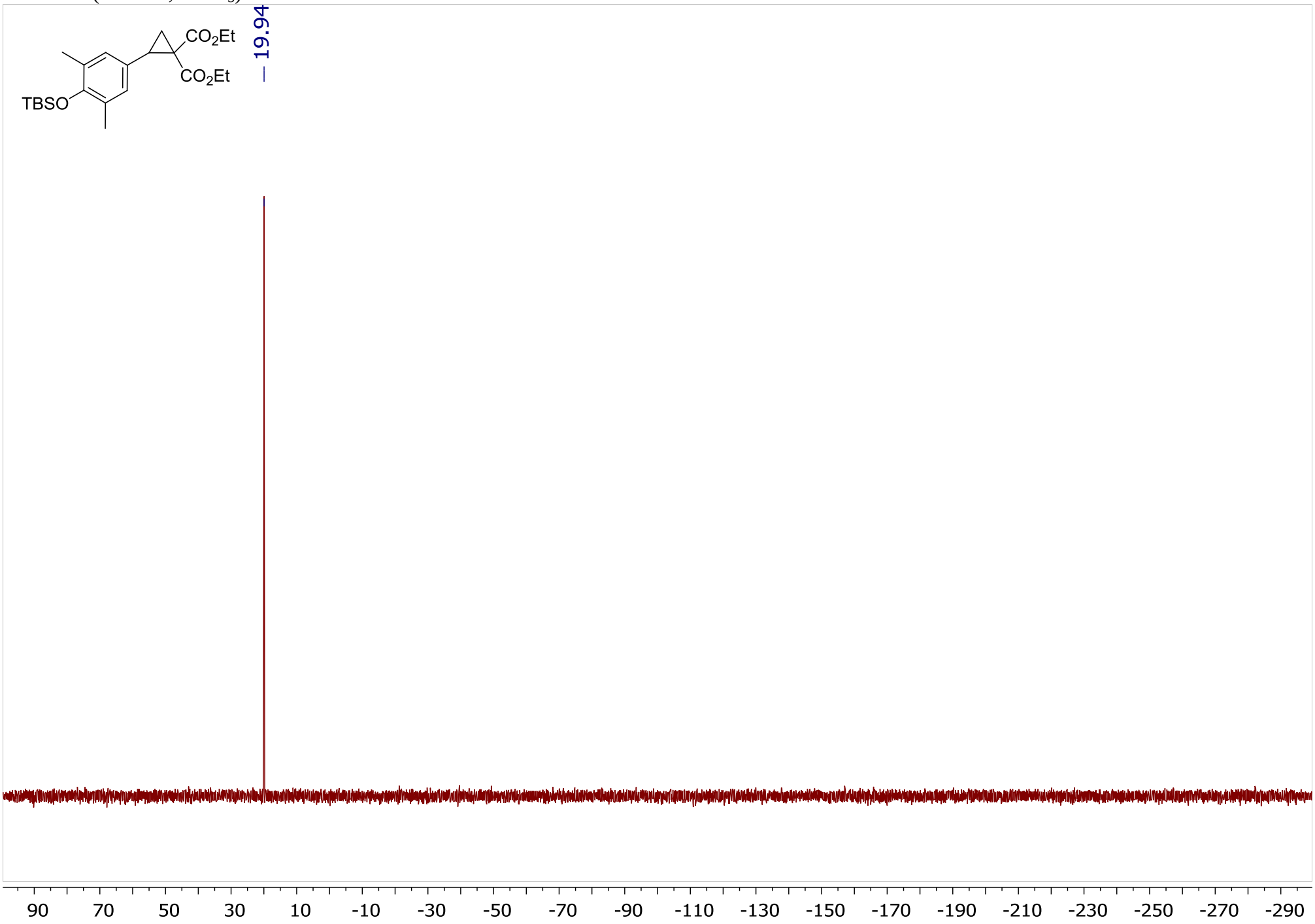
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

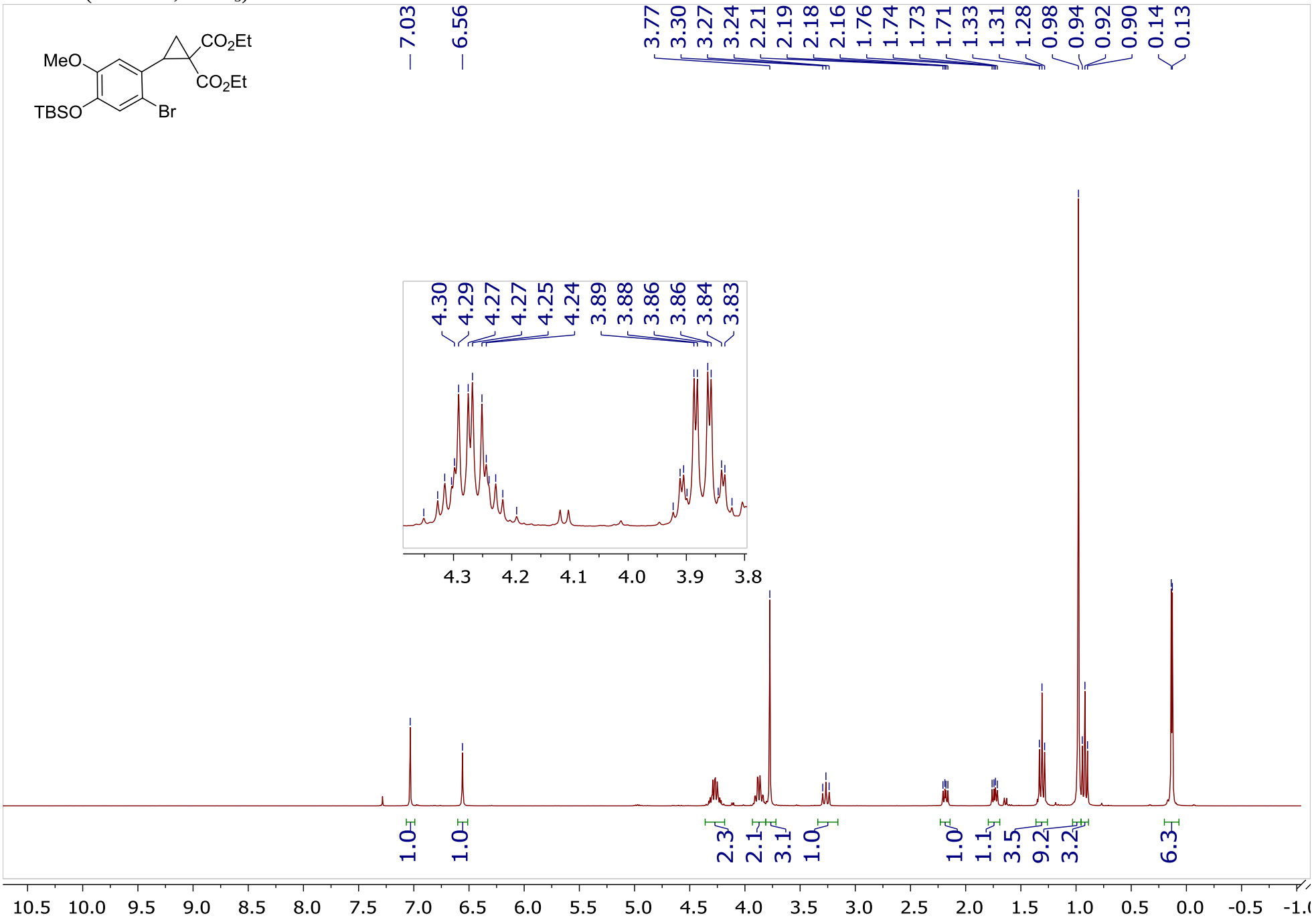


$^{29}$Si NMR (60 MHz, $CDCl_3$)

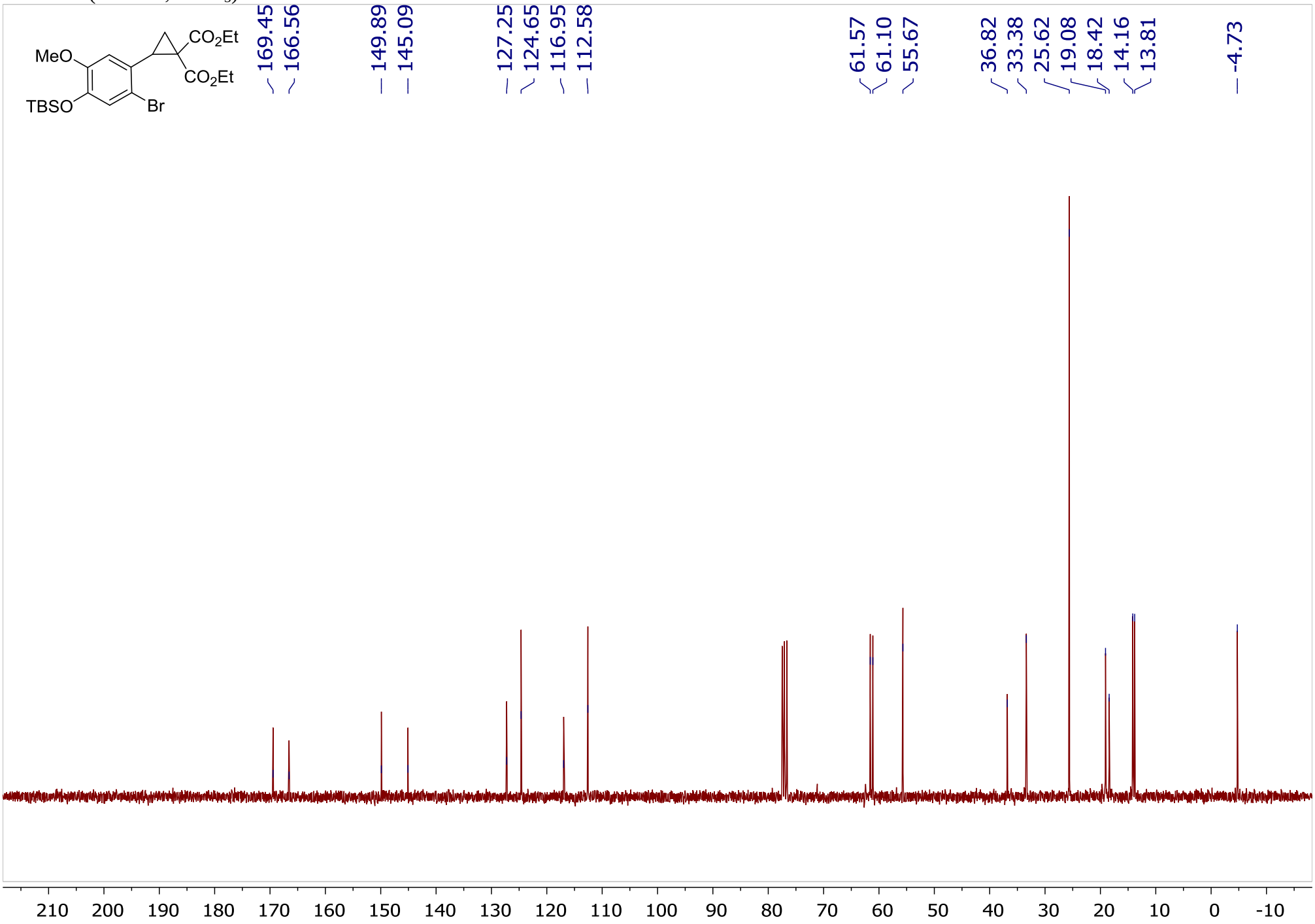


**Diethyl 2-(2-bromo-4-((tert-butyldimethylsilyl)oxy)-5-methoxyphenyl)cyclopropane-1,1-dicarboxylate (1h)**

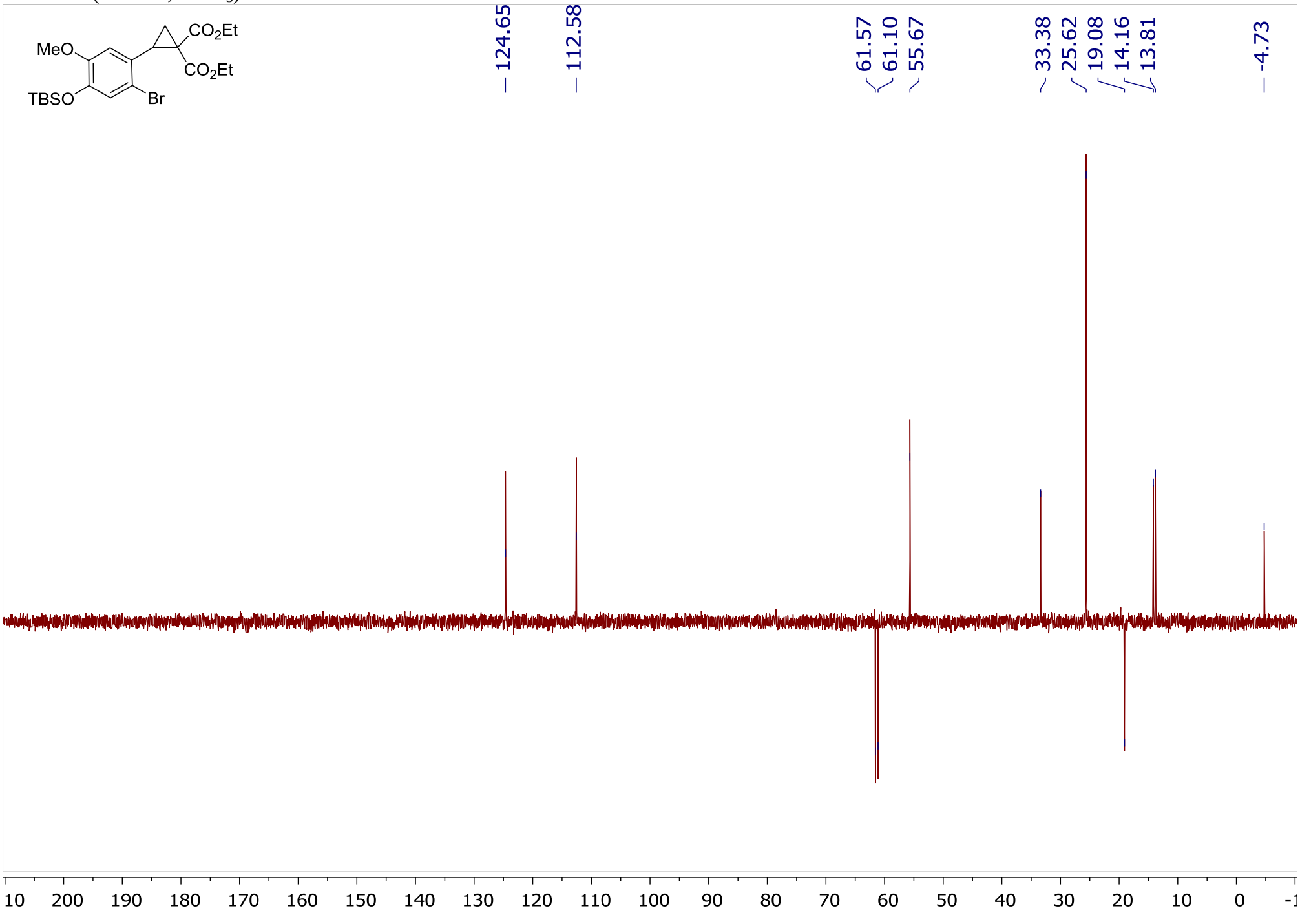
$^1$H NMR (300 MHz, $CDCl_3$)



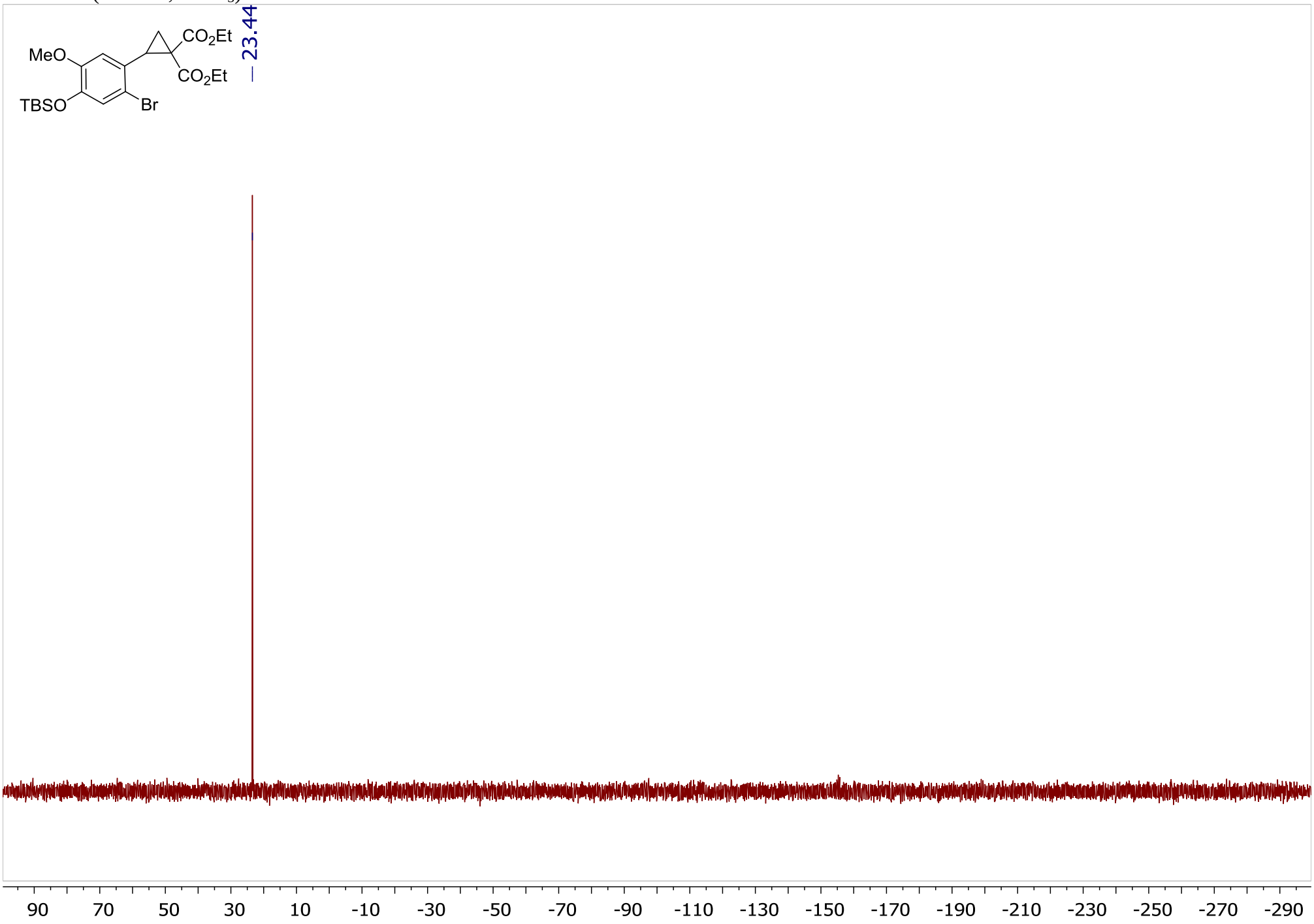
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

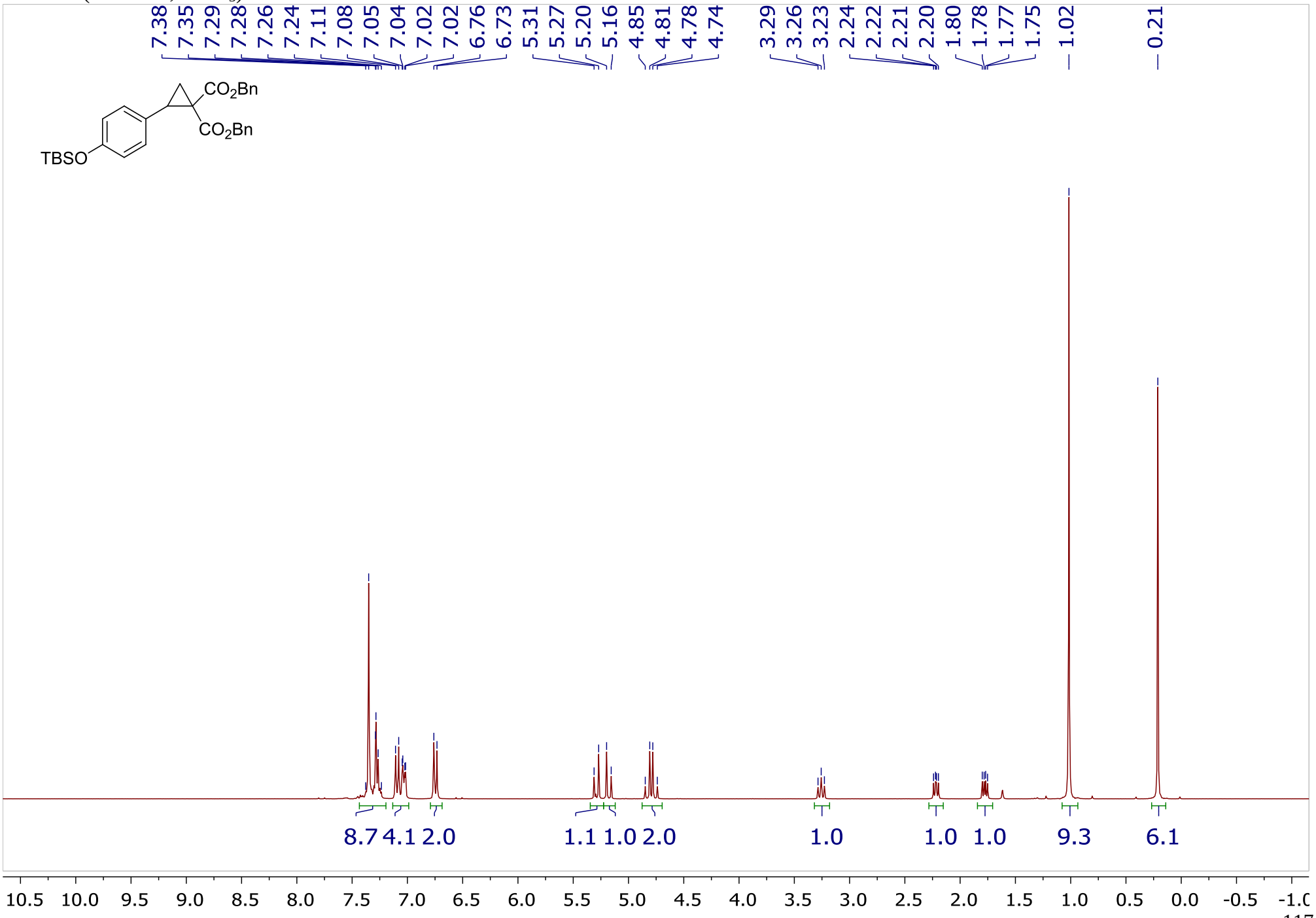


$^{29}$Si NMR (60 MHz, $CDCl_3$)

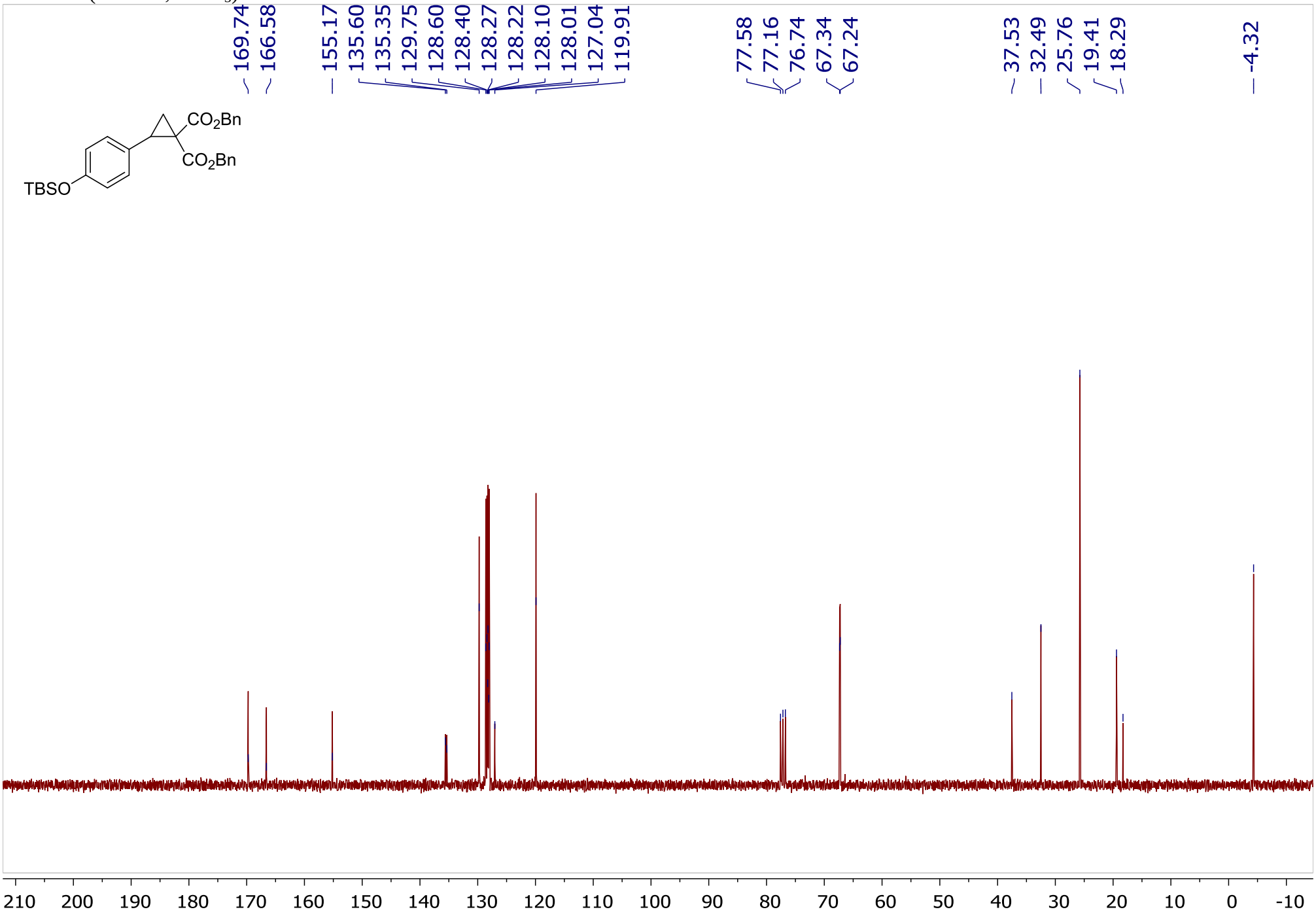


**Dibenzyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1i)**

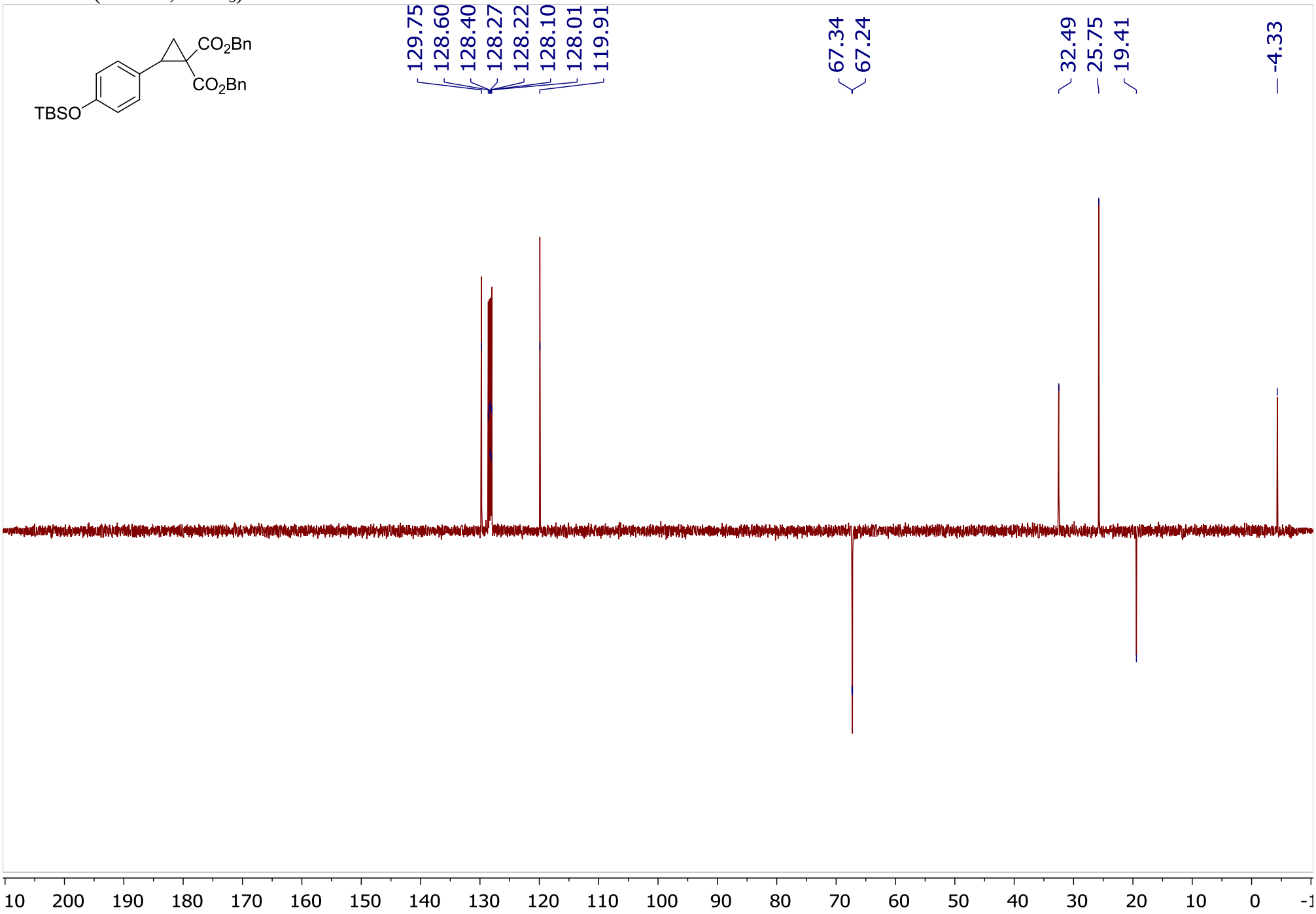
$^1$H NMR (300 MHz, $CDCl_3$)



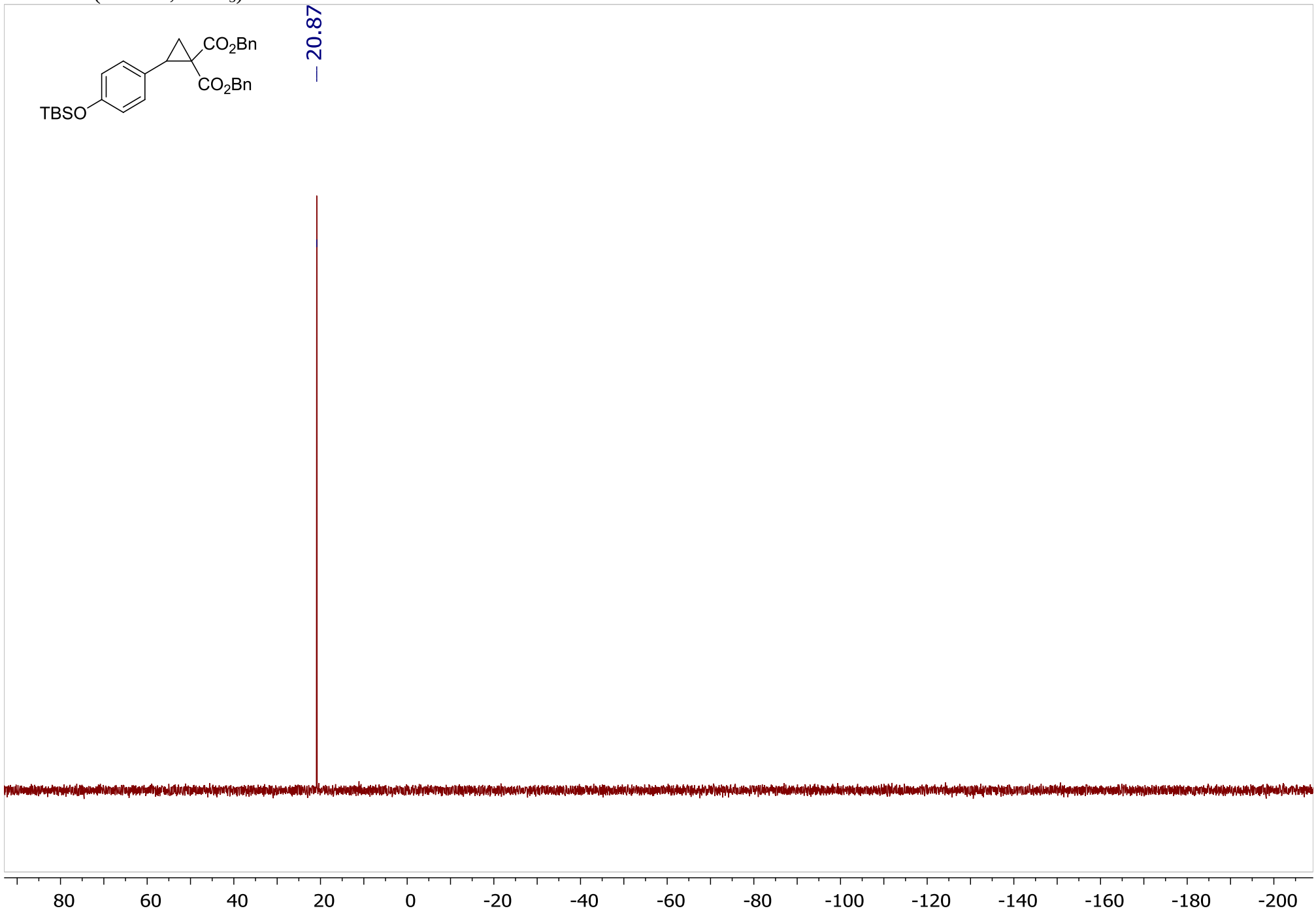
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

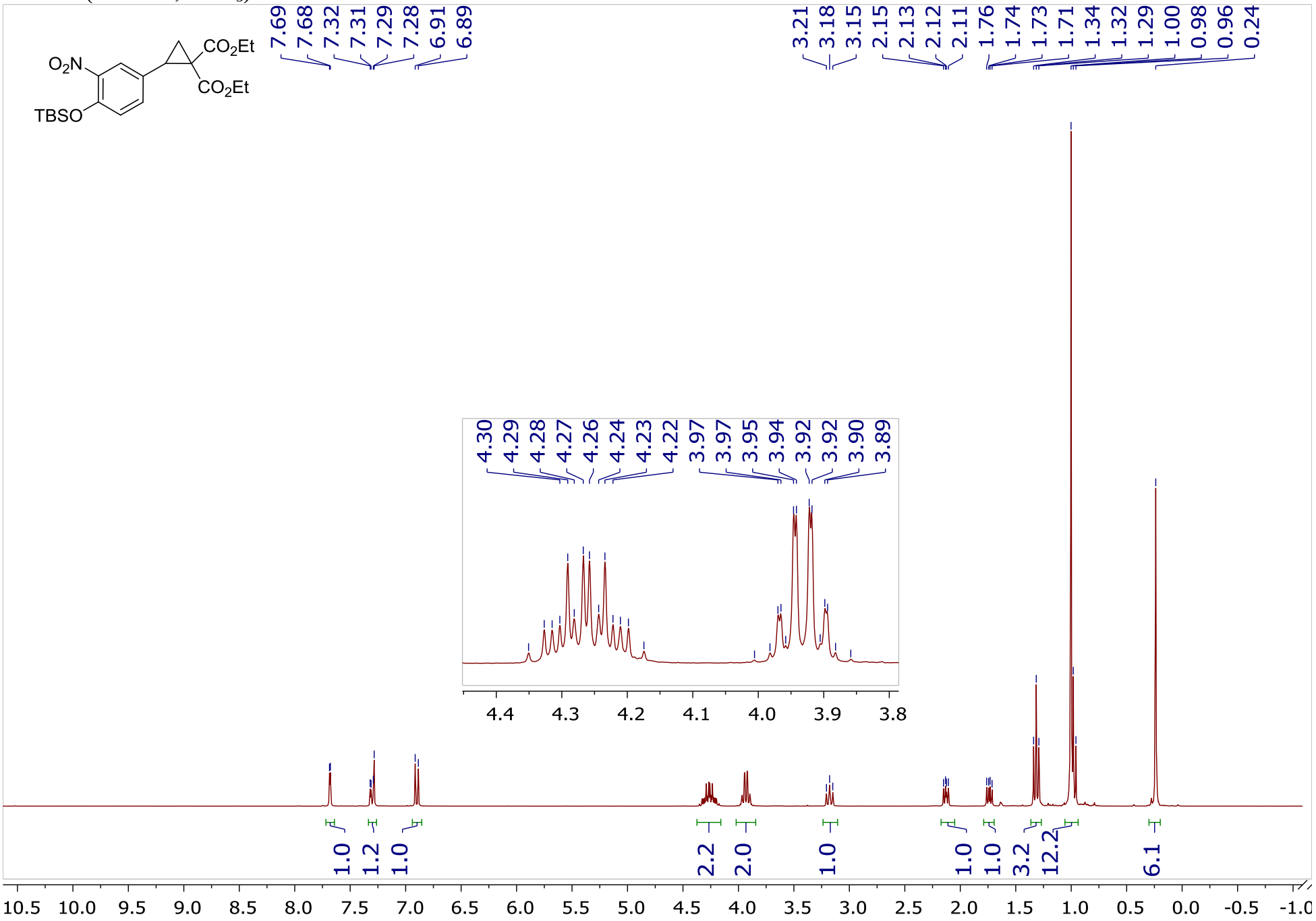


$^{29}$Si NMR (60 MHz, $CDCl_3$)

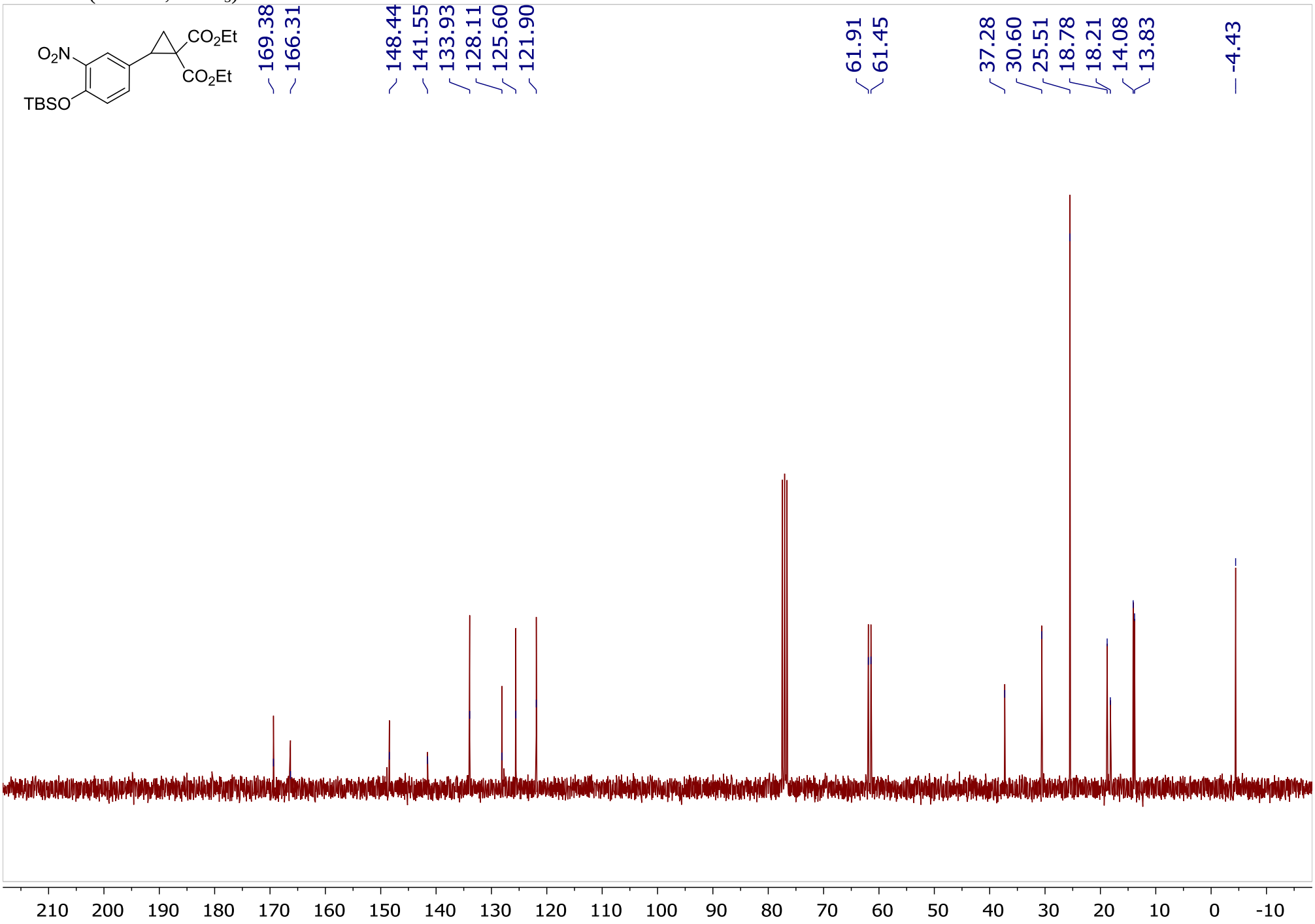


**Diethyl 2-(4-((tert-butyldimethylsilyl)oxy)-3-nitrophenyl)cyclopropane-1,1-dicarboxylate (1j)**

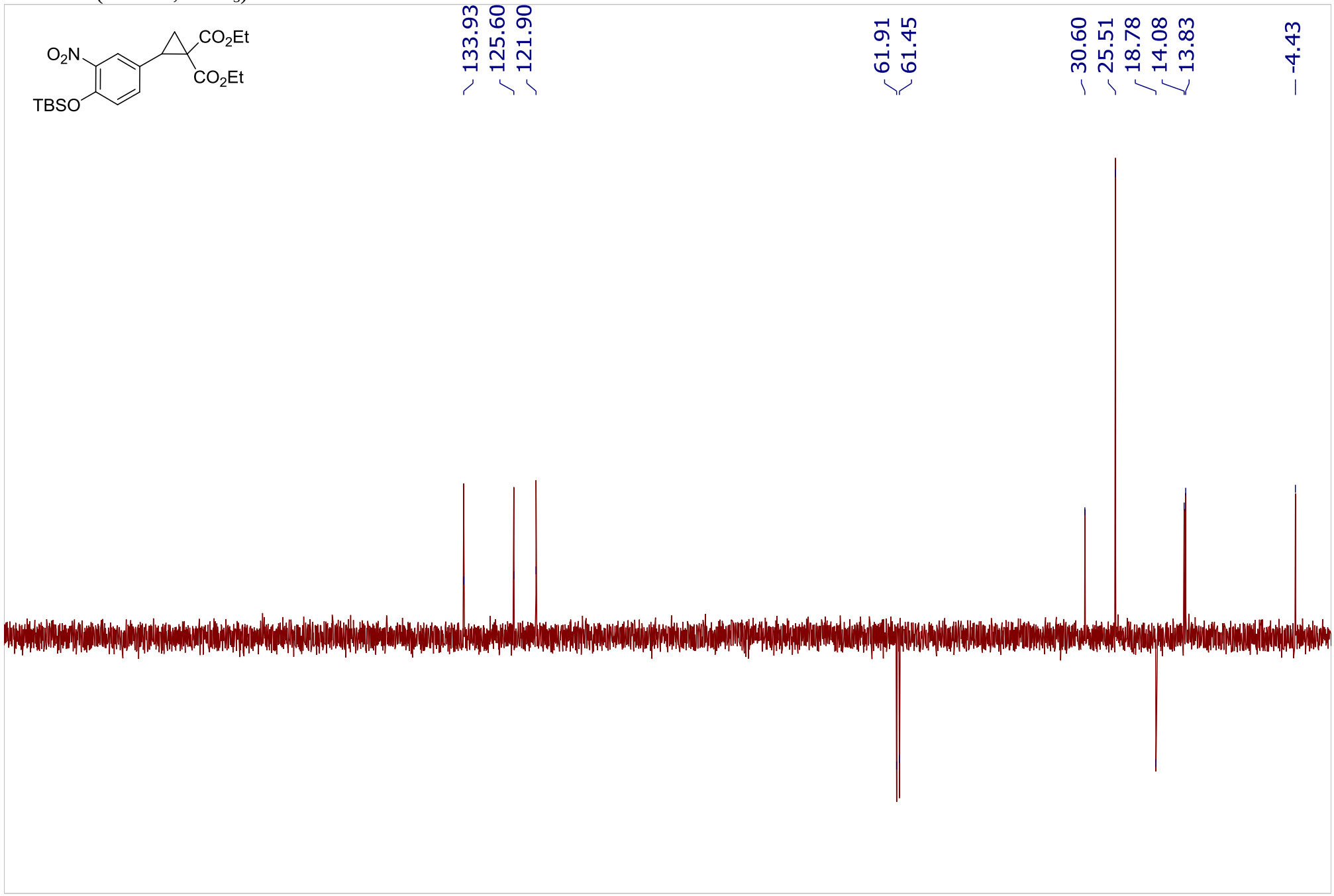
$^1$H NMR (300 MHz, $CDCl_3$)



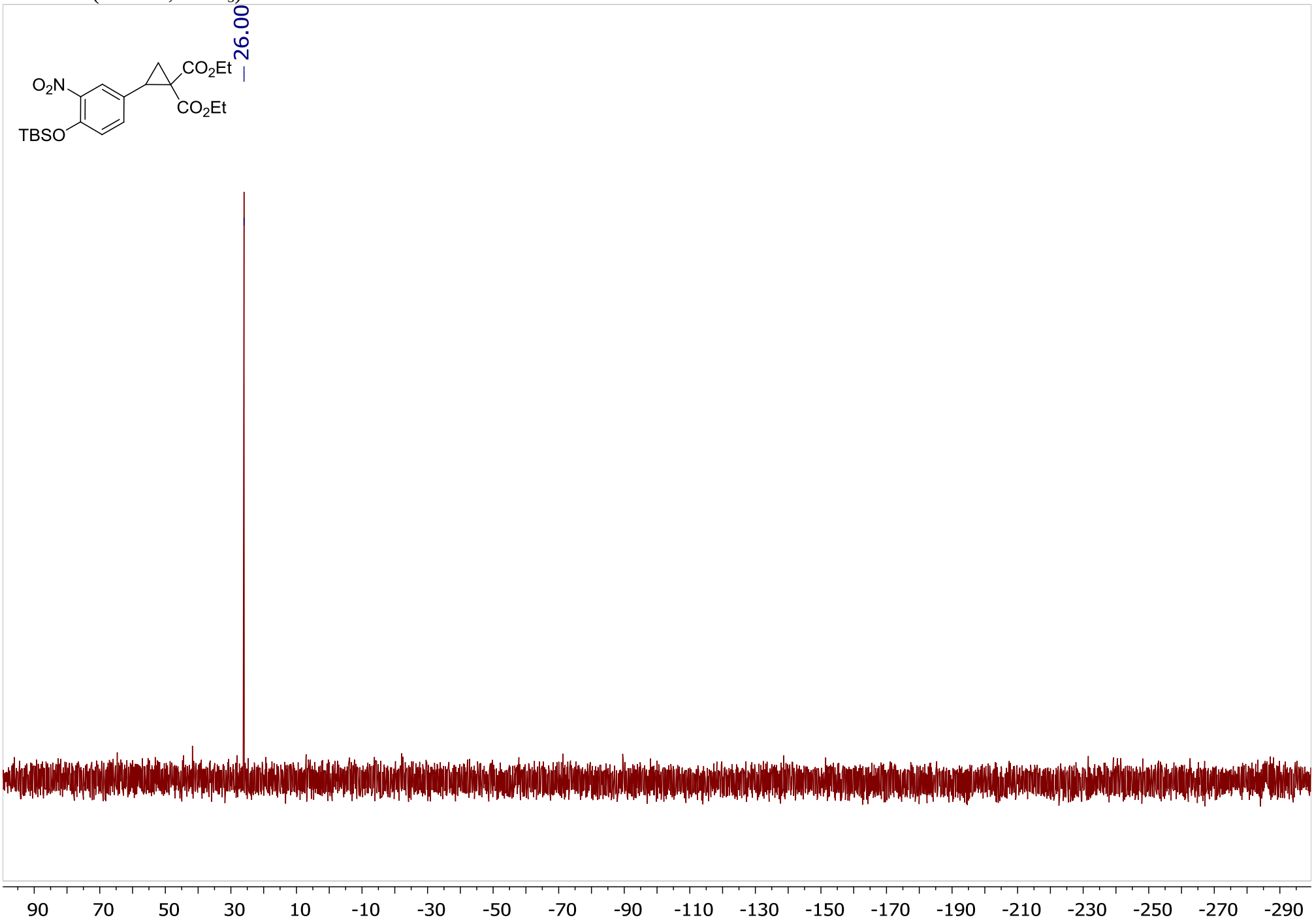
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

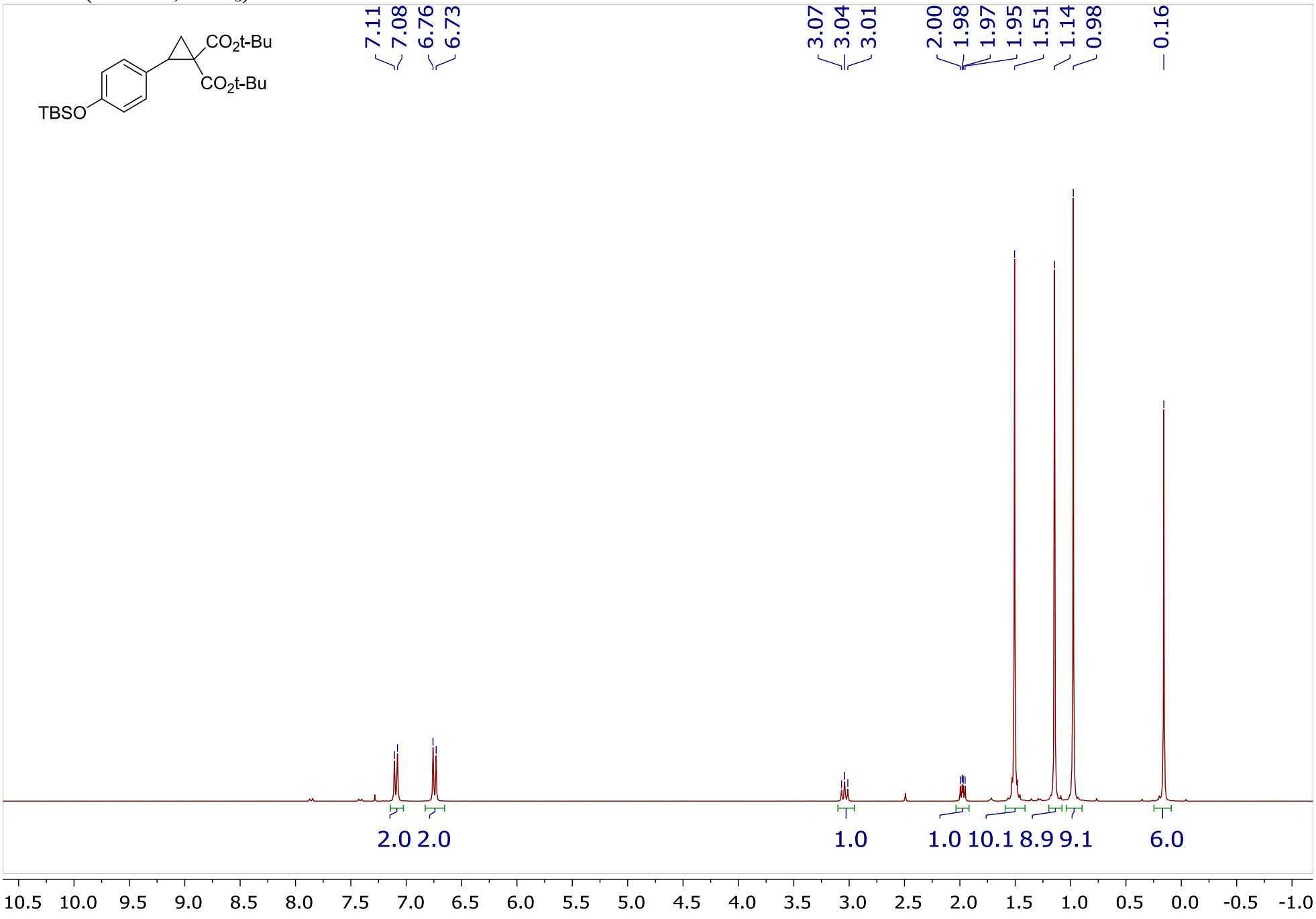


$^{29}$Si NMR (60 MHz, $CDCl_3$)

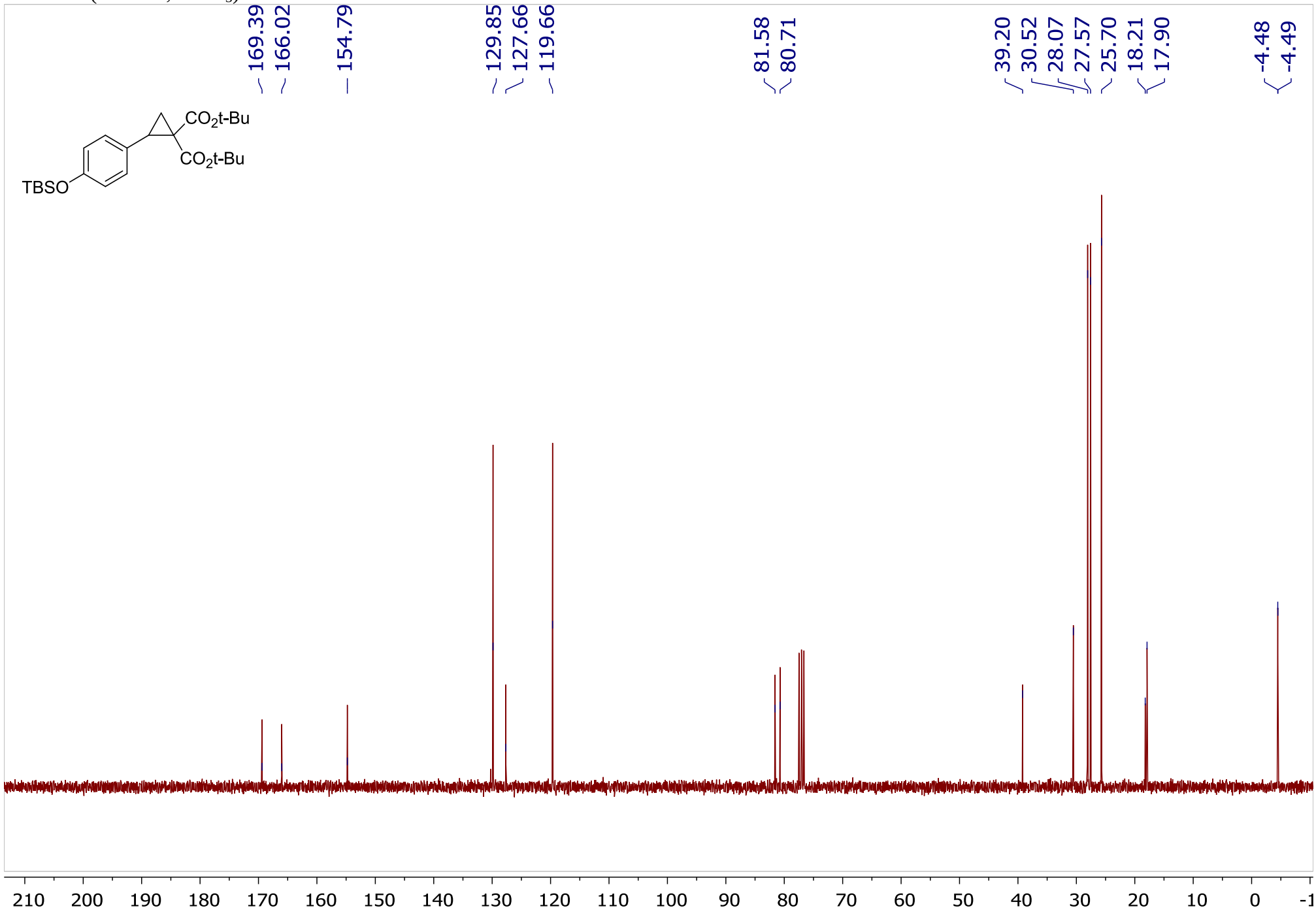


**Di-*tert*-butyl 2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)cyclopropane-1,1-dicarboxylate (1k)**

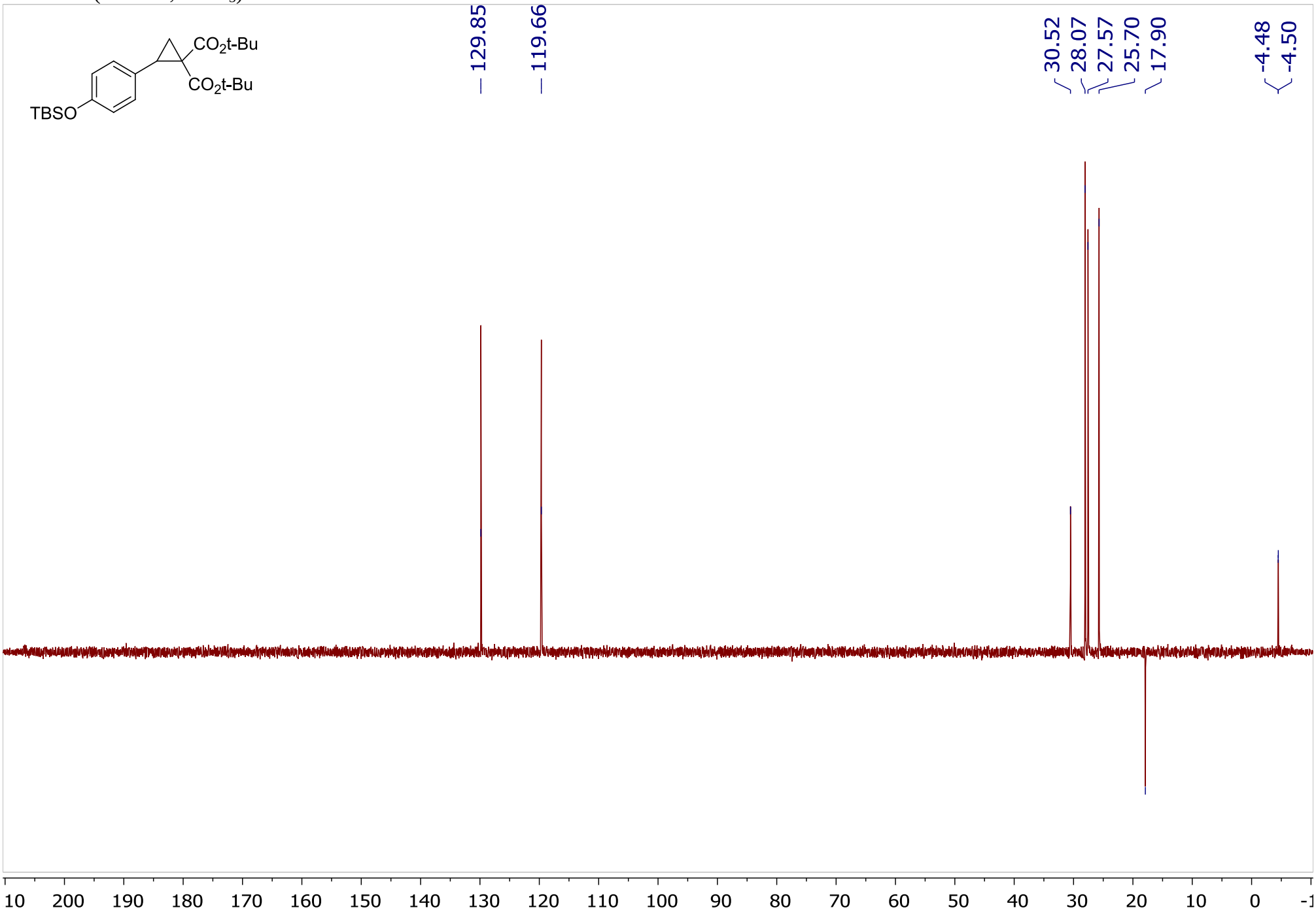
$^1$H NMR (300 MHz, $CDCl_3$)



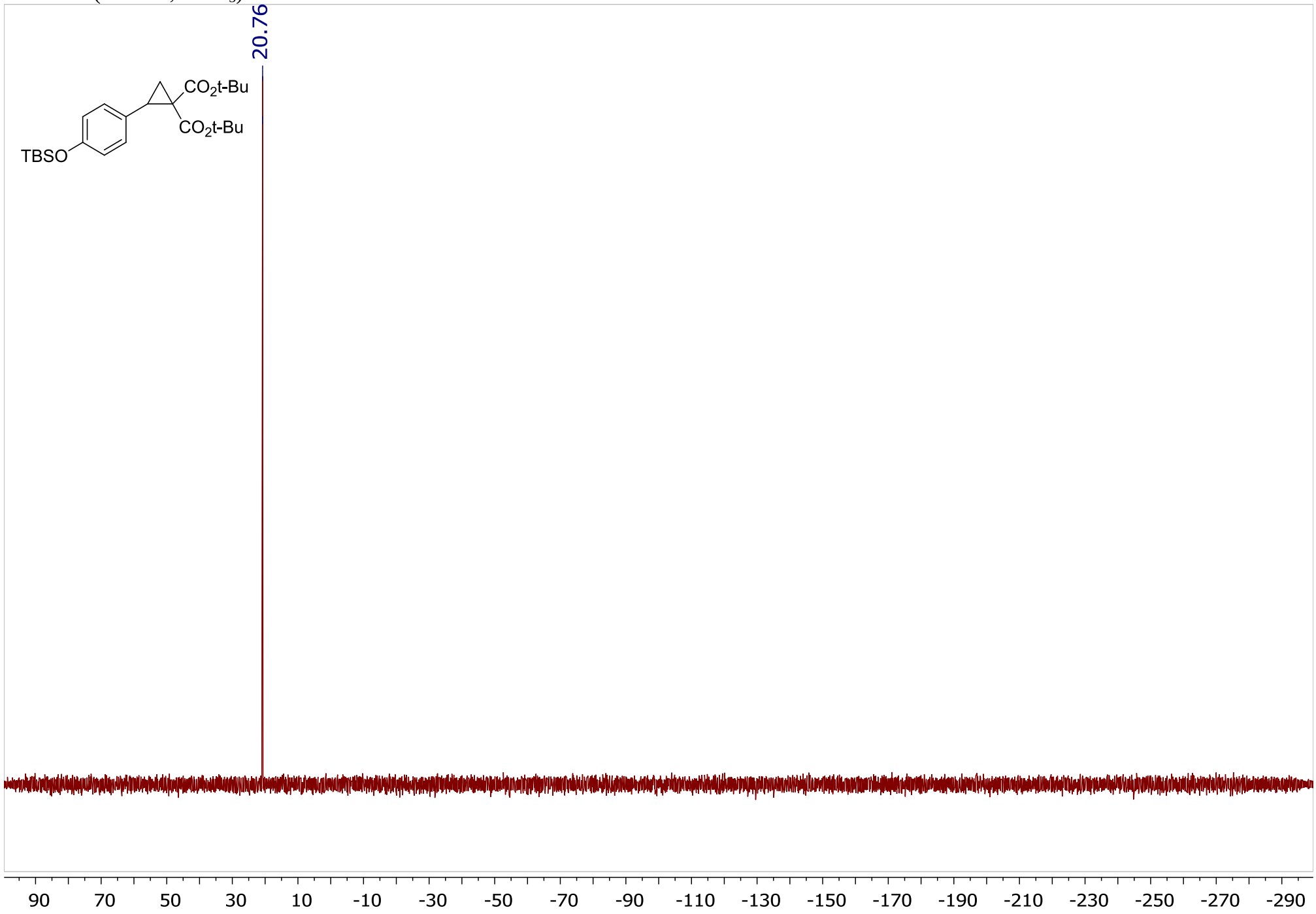
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

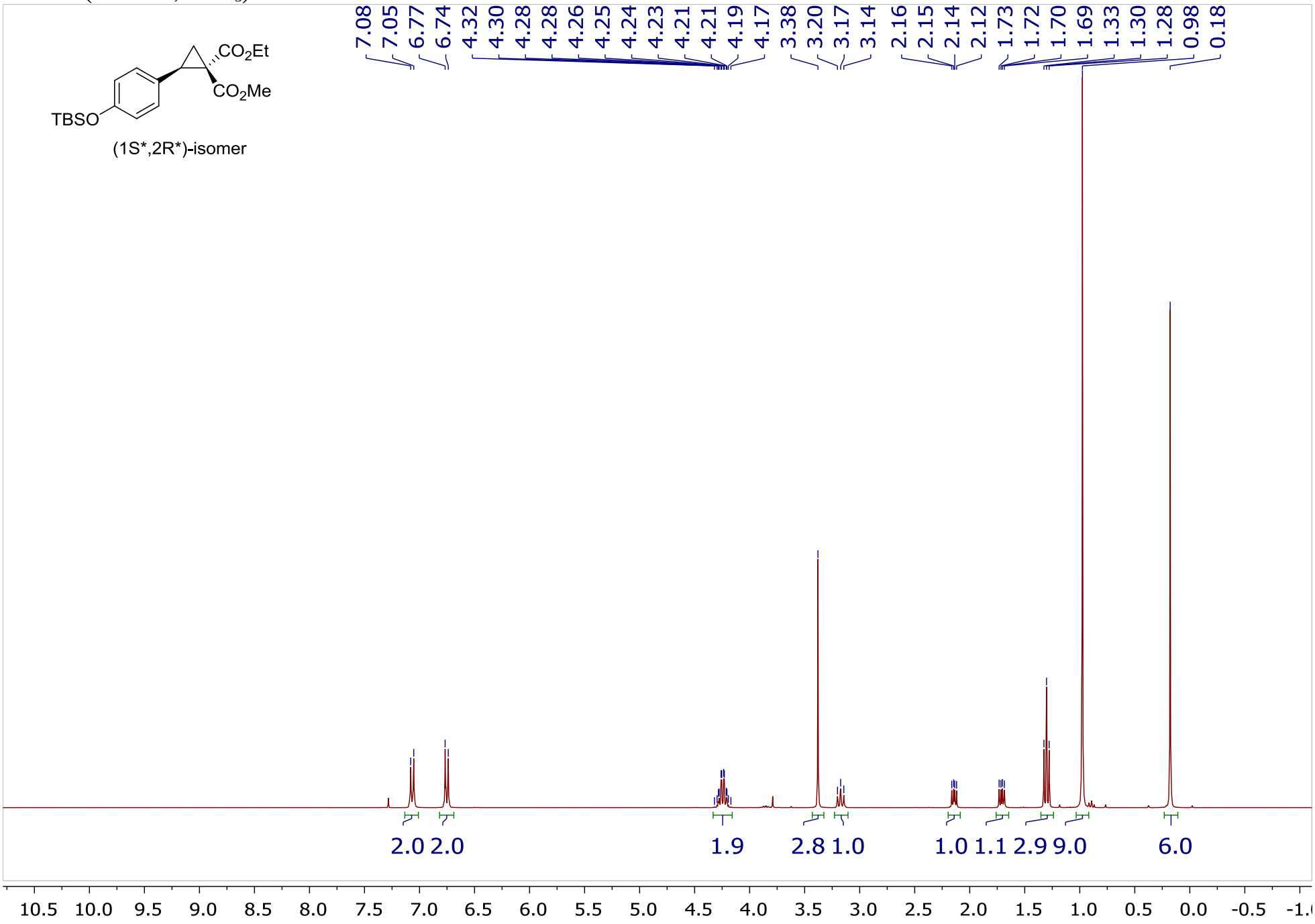


$^{29}$Si NMR (60 MHz, $CDCl_3$)

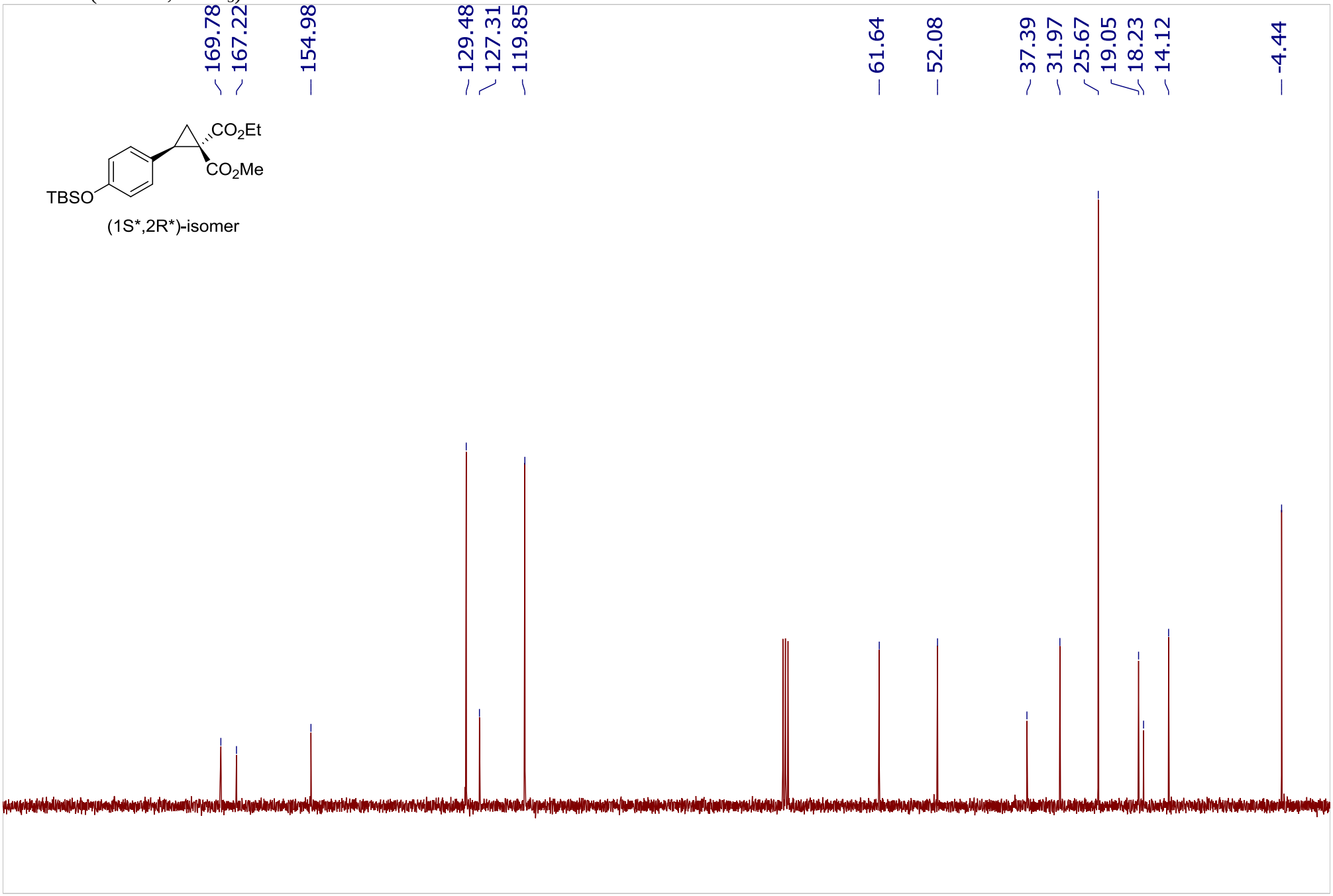


**1-Ethyl 1-methyl 2-(4-(tert-butyldimethylsilyloxy)phenyl)cyclopropane-1,1-dicarboxylate (1l)**, (1*S**,2*R**)-isomer

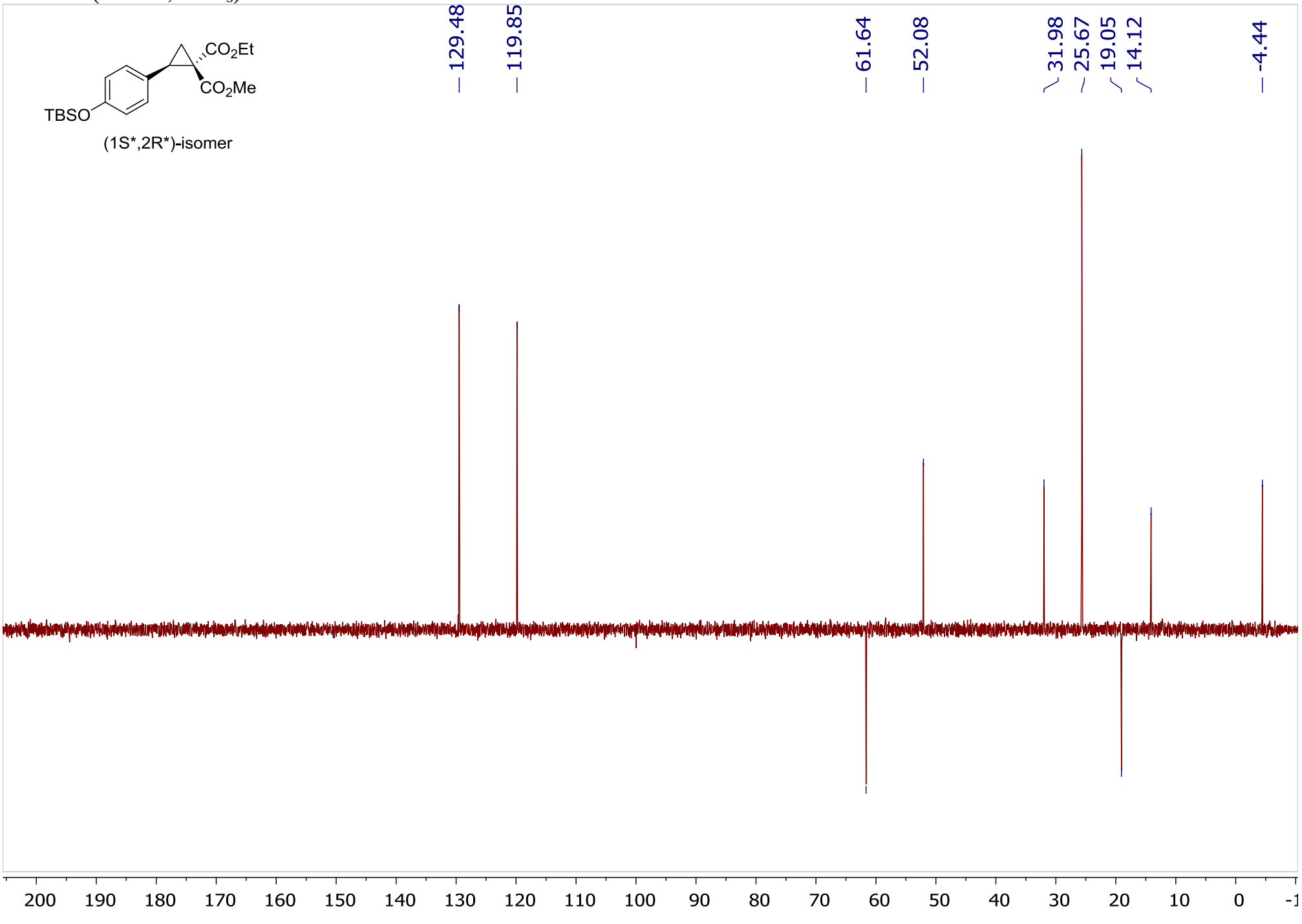
$^1$H NMR (300 MHz, $CDCl_3$)



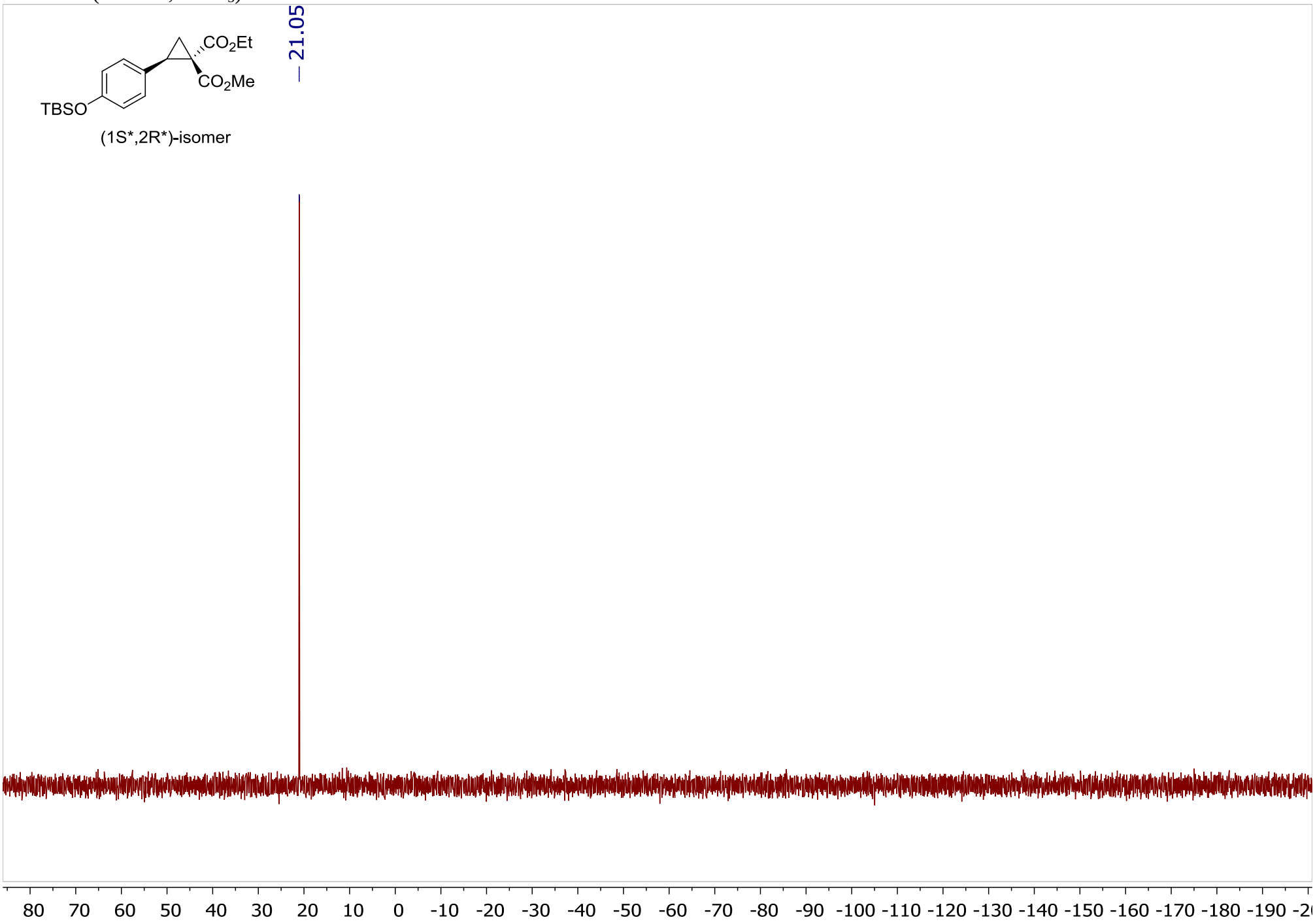
$^{13}$C NMR (75 MHz, $CDCl_3$)



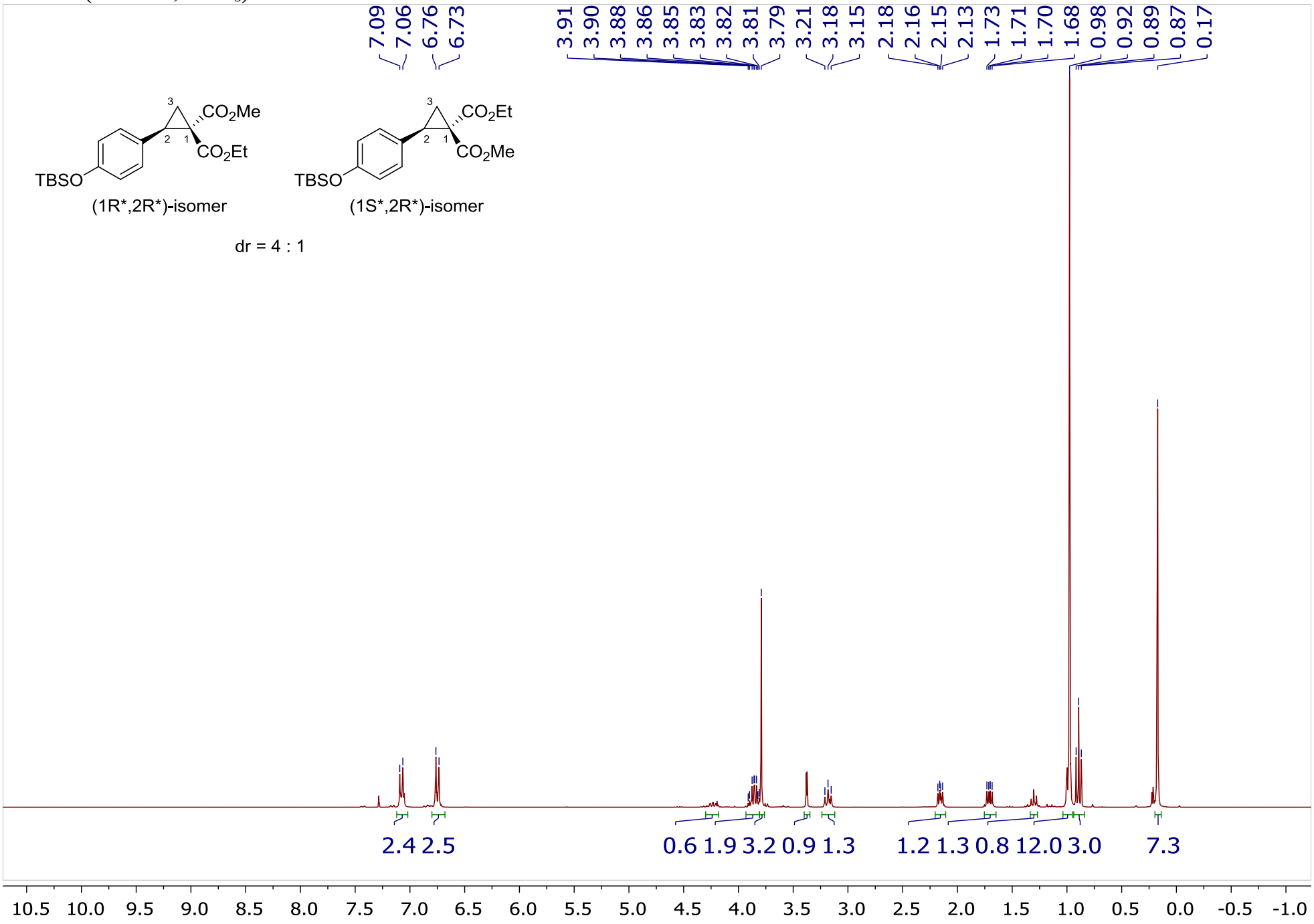
$^{13}$C DEPT (75 MHz, $CDCl_3$)



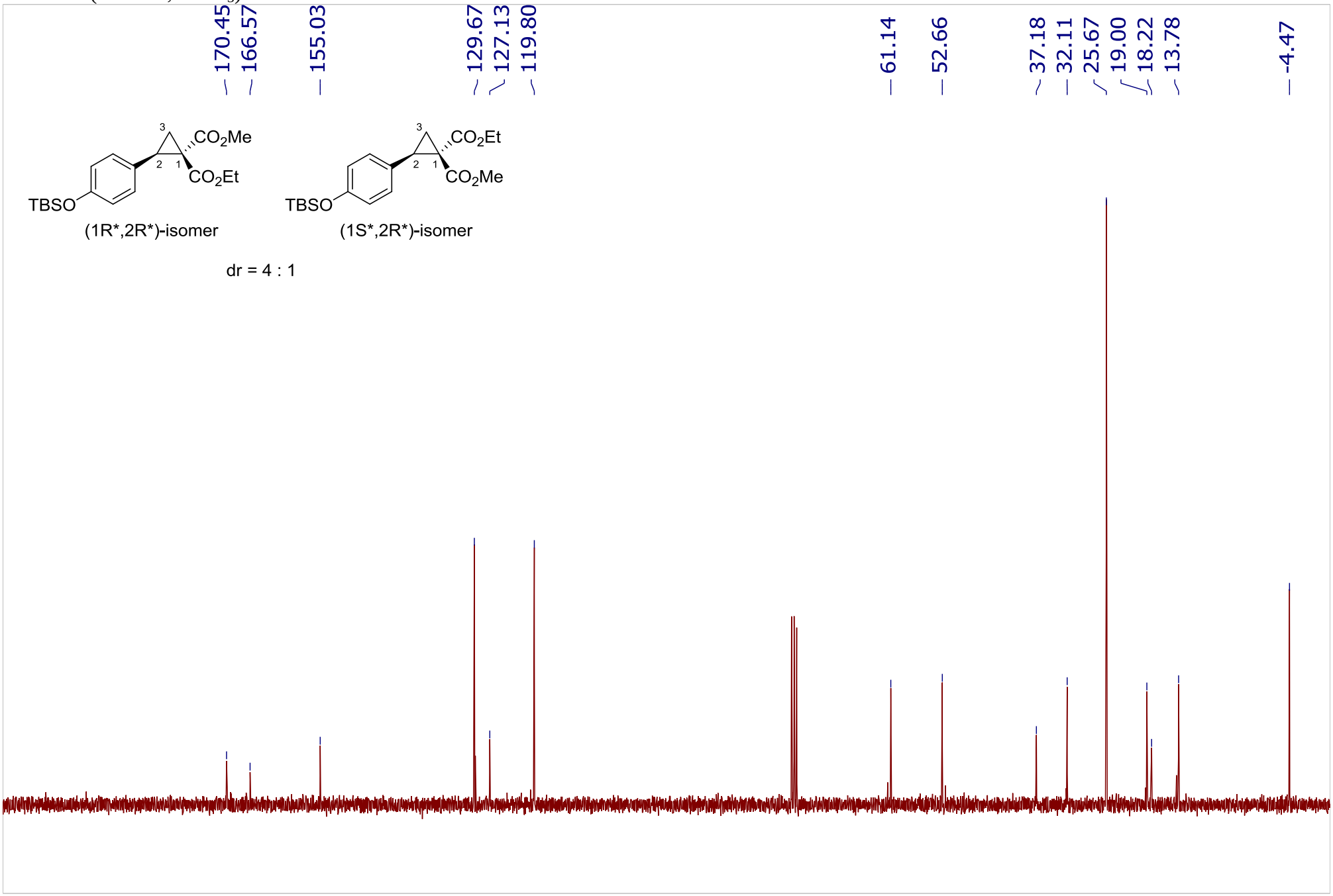
$^{29}$Si NMR (60 MHz, $CDCl_3$)



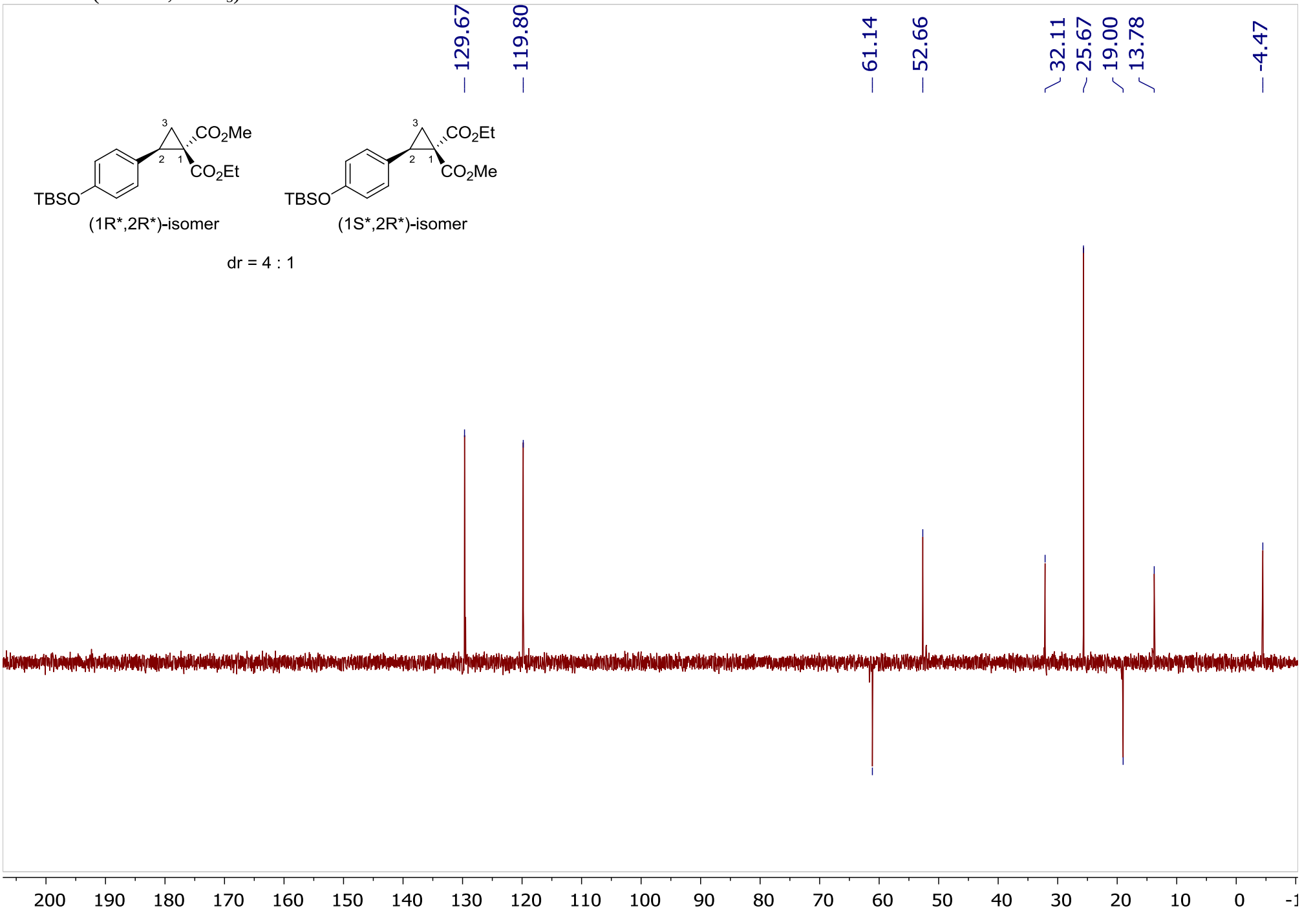
**1-Ethyl 1-methyl 2-(4-(tert-butyldimethylsilyloxy)phenyl)cyclopropane-1,1-dicarboxylate (1l)**, dr ((1*R**,2*R**)-isomer : (1*S**,2*R**)-isomer) = 4:1
$^1$H NMR (300 MHz, $CDCl_3$)



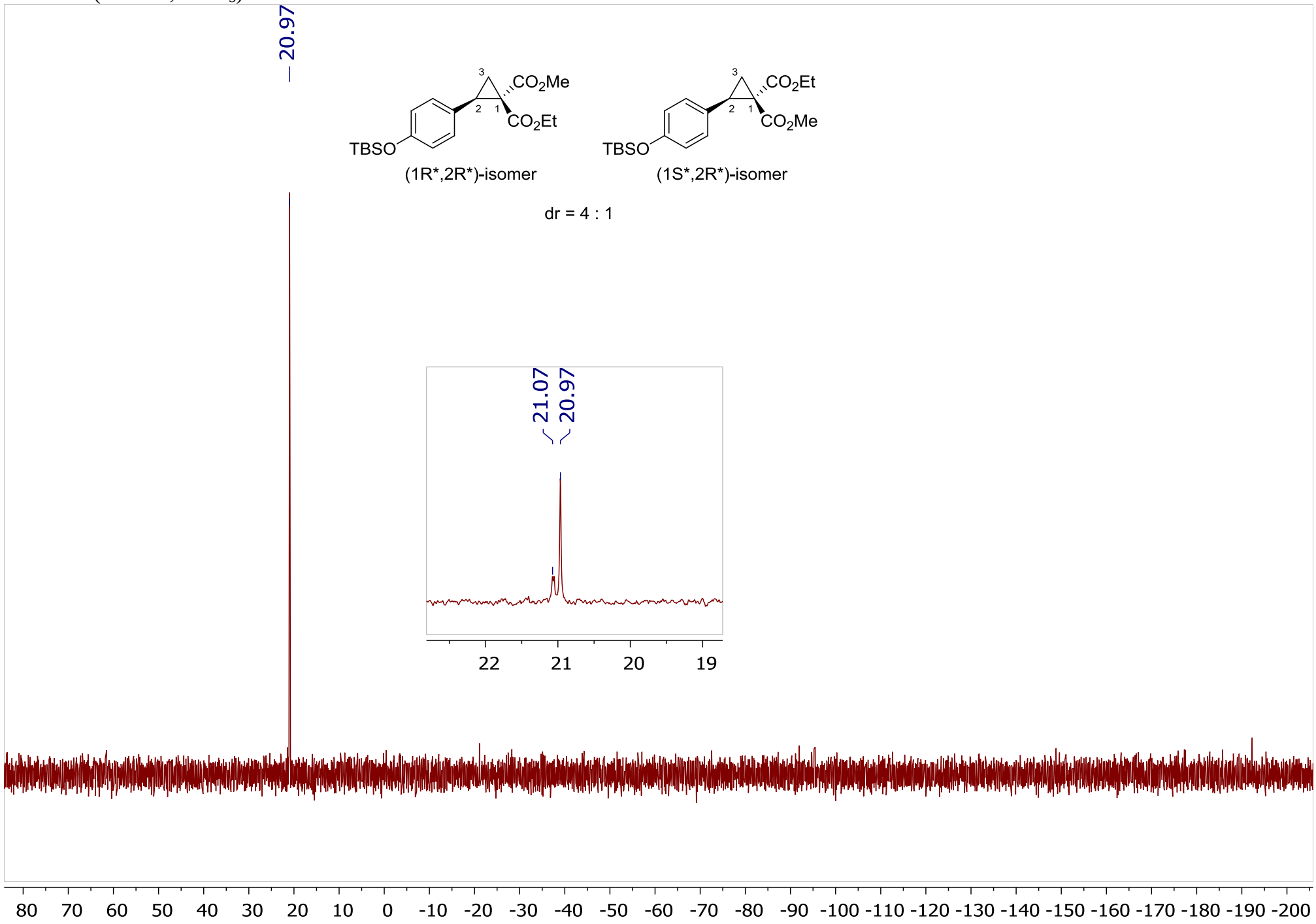
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

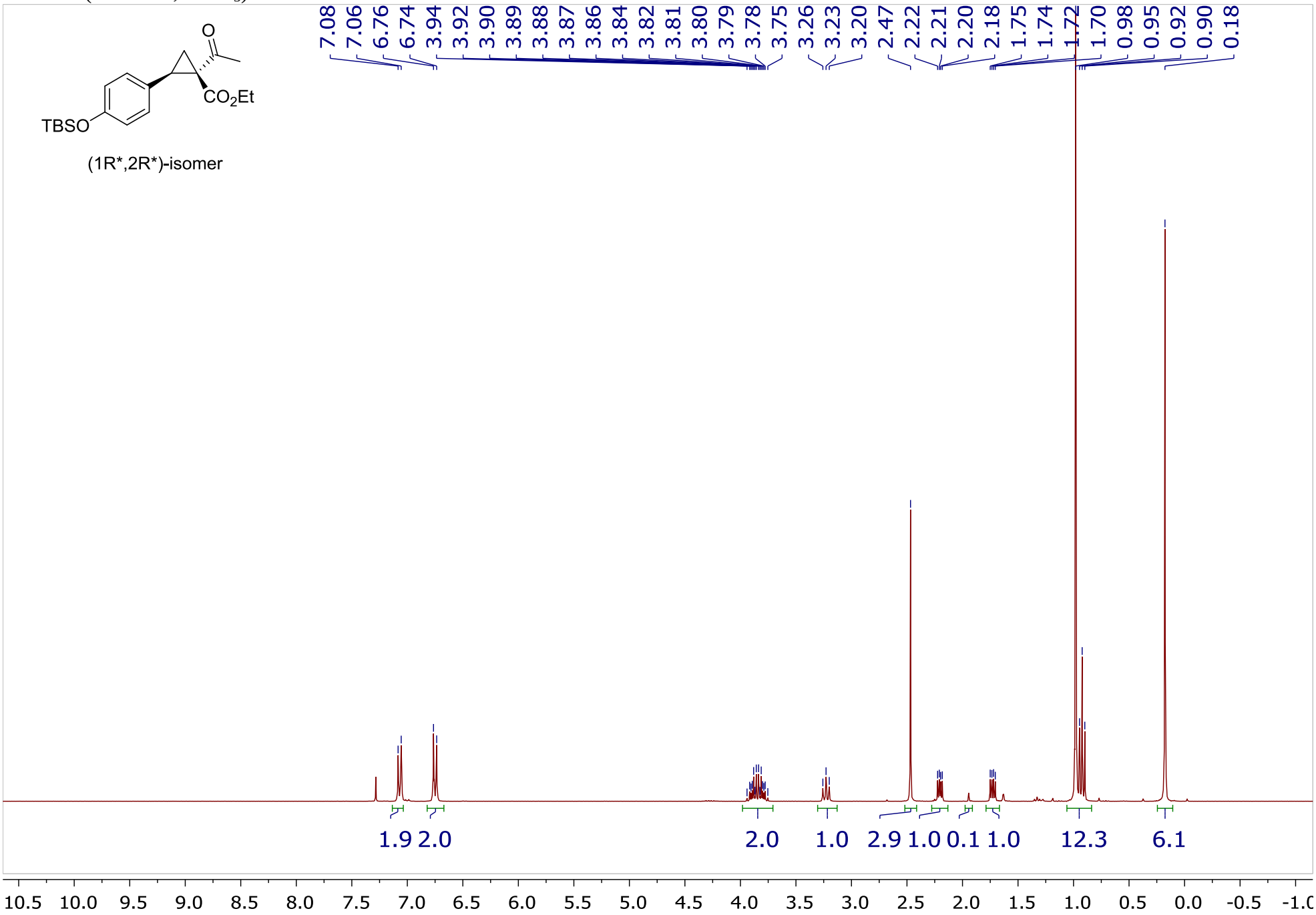


$^{29}$Si NMR (60 MHz, $CDCl_3$)

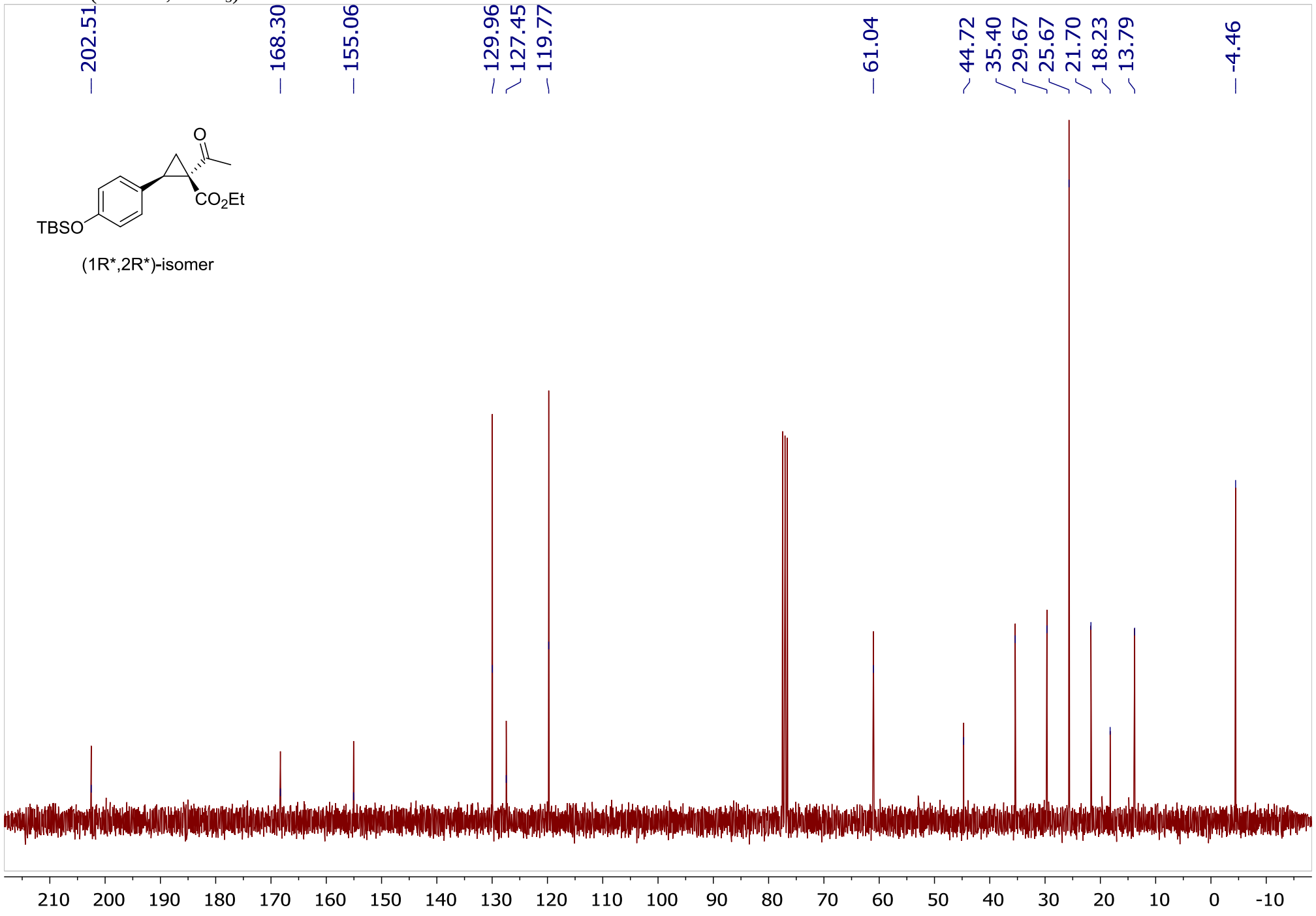


**Ethyl 1-acetyl-2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1-carboxylate (5)**, (1*R**,2*R**)-isomer

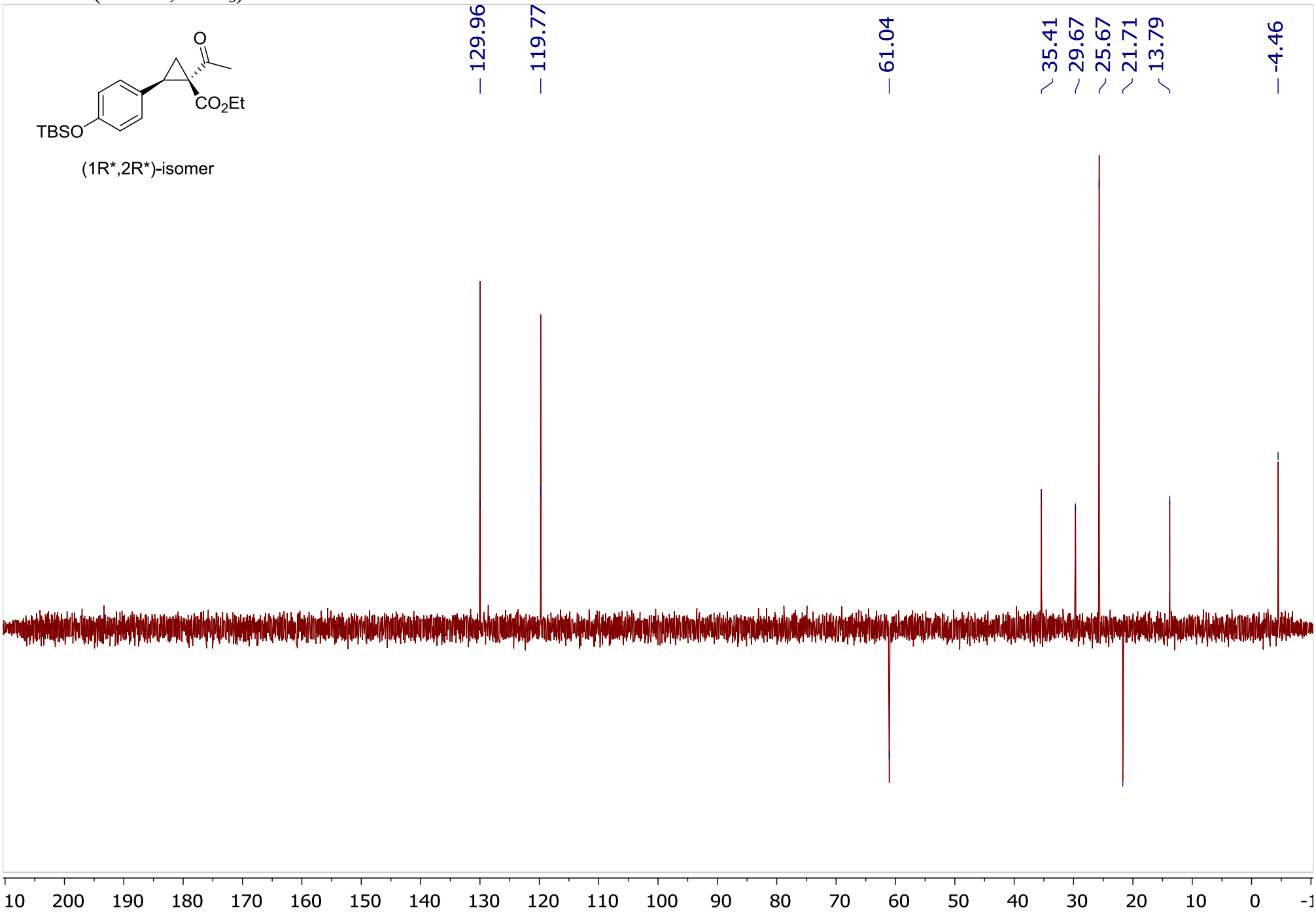
$^1$H NMR (300 MHz, $CDCl_3$)



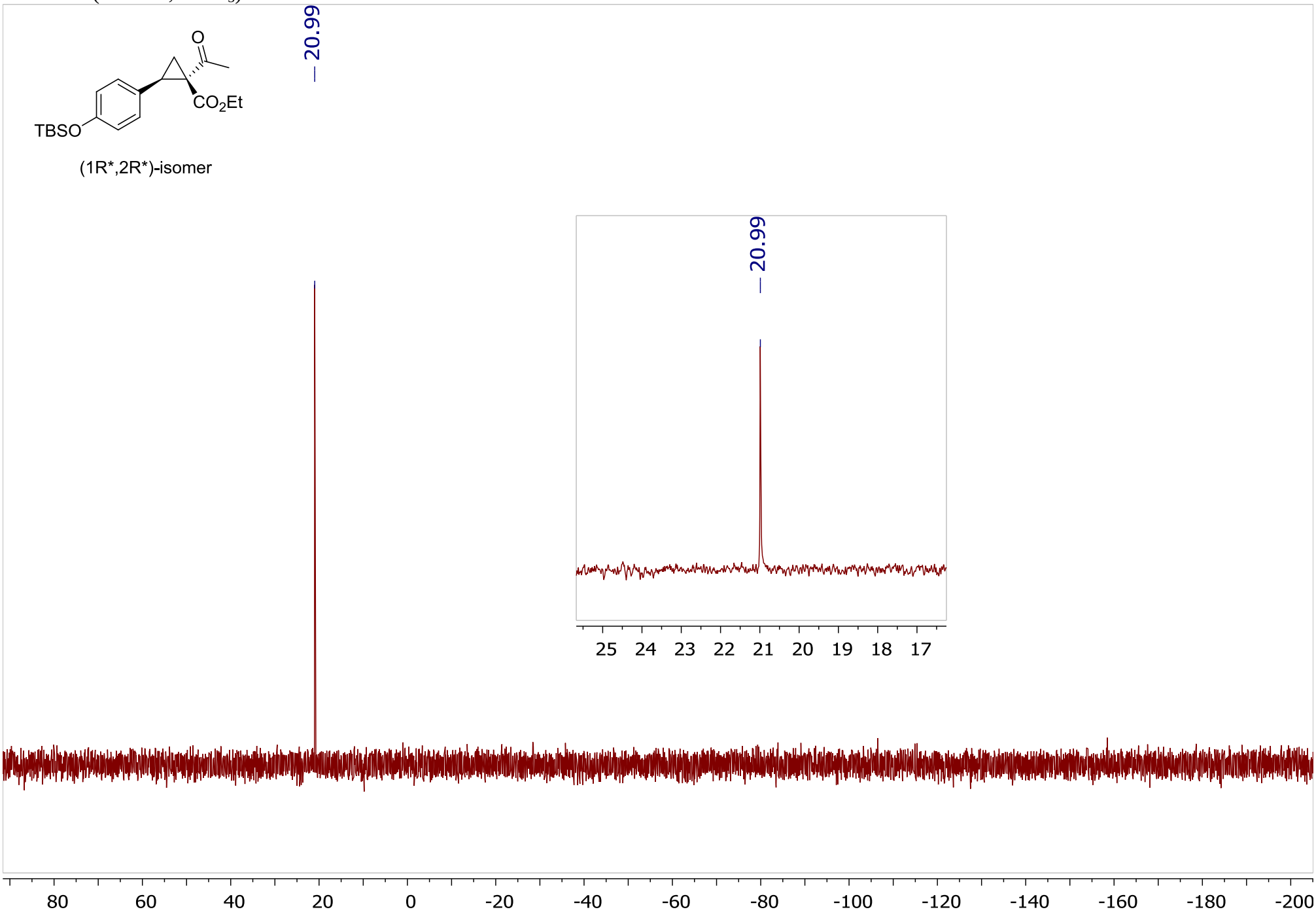
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

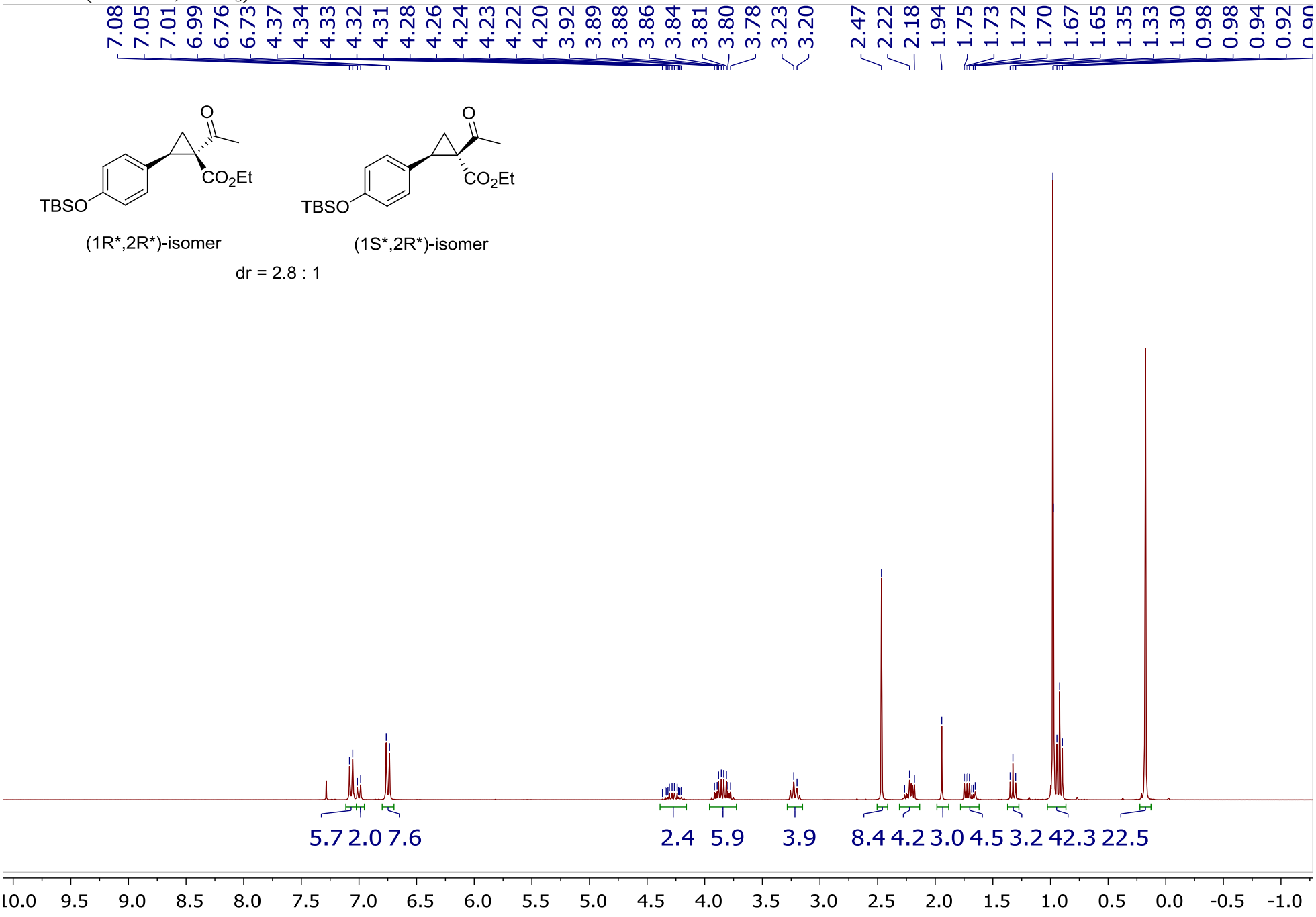


$^{29}$Si NMR (60 MHz, $CDCl_3$)

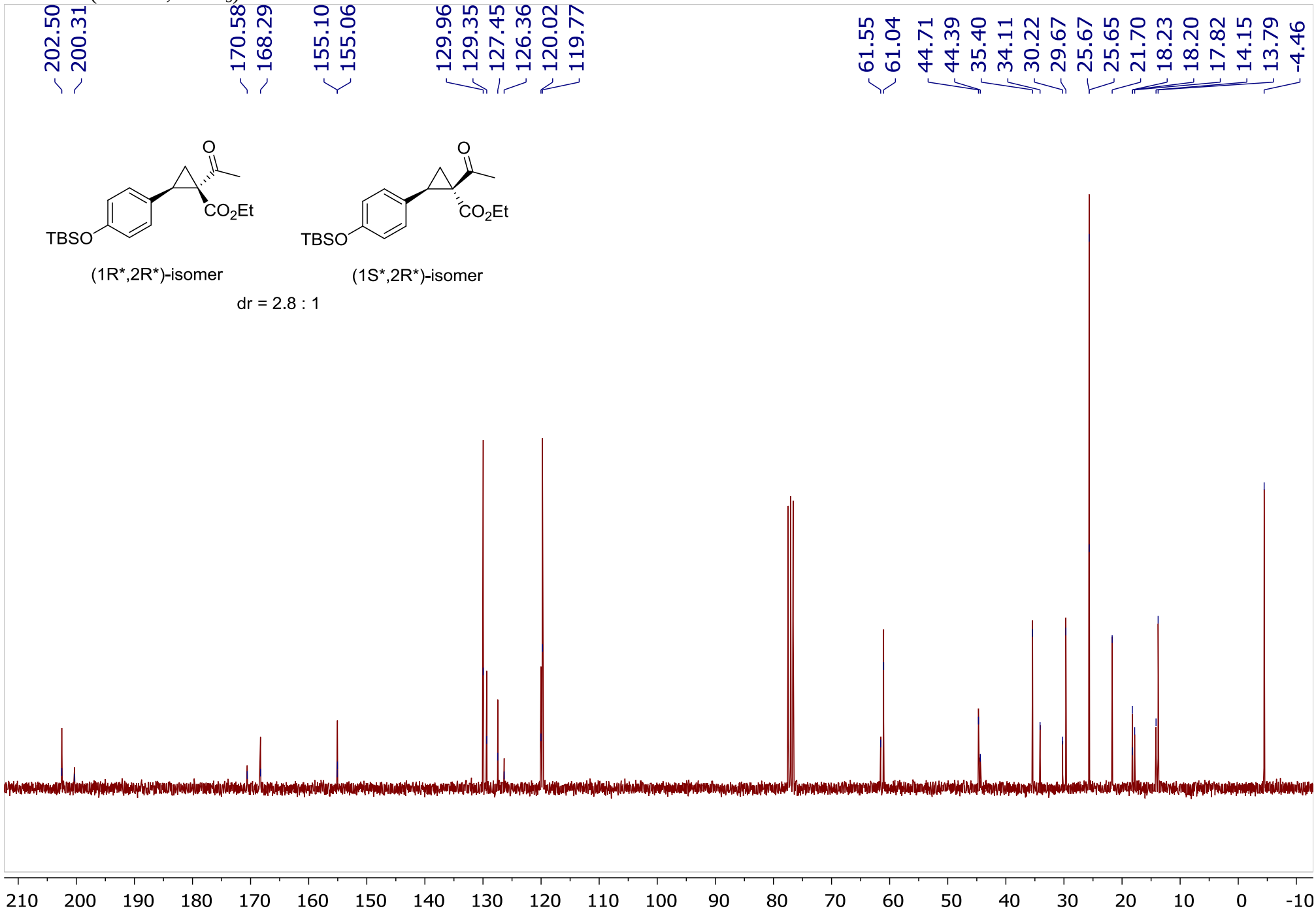


**Ethyl 1-acetyl-2-(4-((tert-butyldimethylsilyl)oxy)phenyl)cyclopropane-1-carboxylate (5)**, dr ((1*R**,2*R**)-isomer : (1*S**,2*R**)-isomer) = 2.8:1

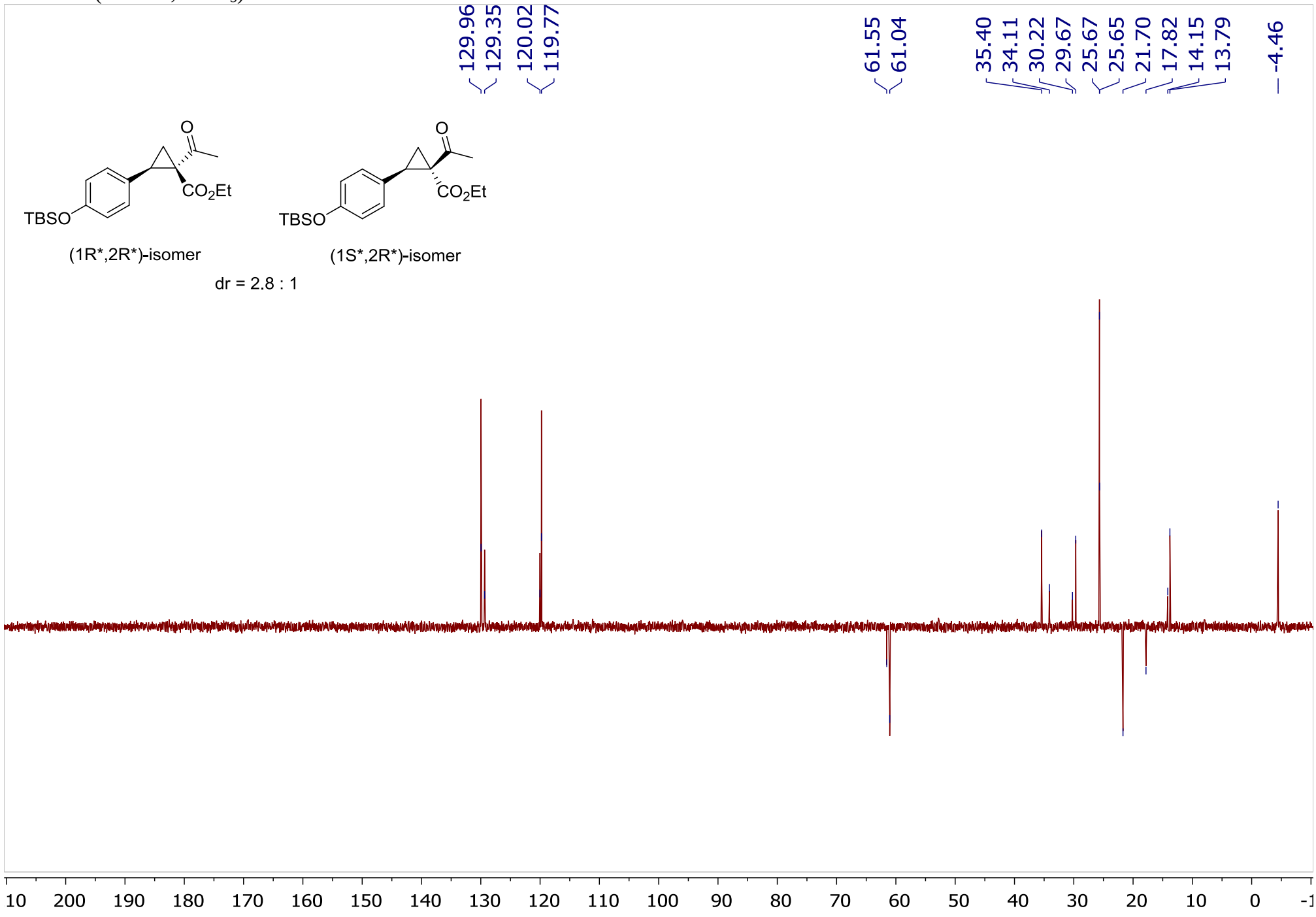
$^1$H NMR (300 MHz, $CDCl_3$)



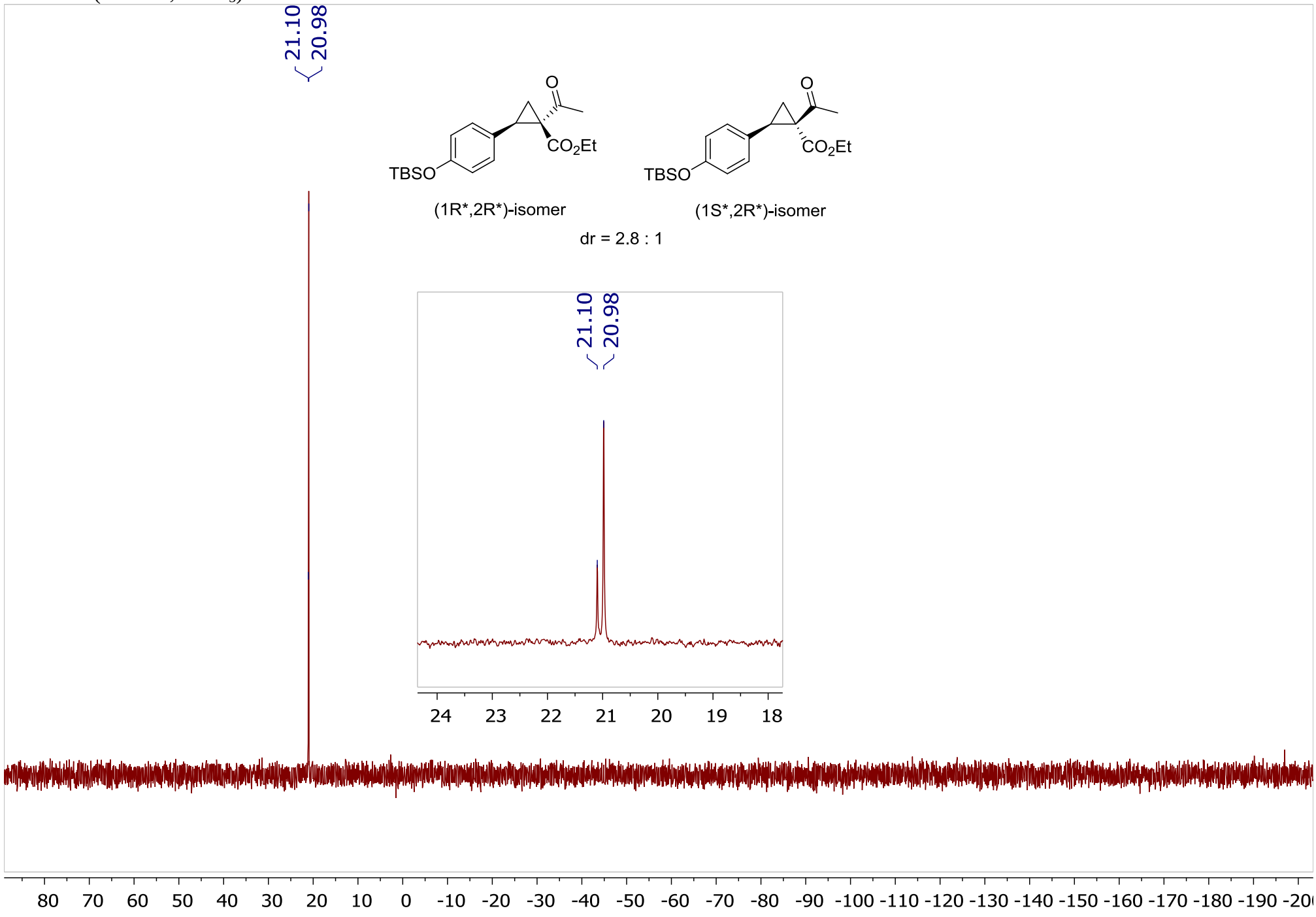
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)

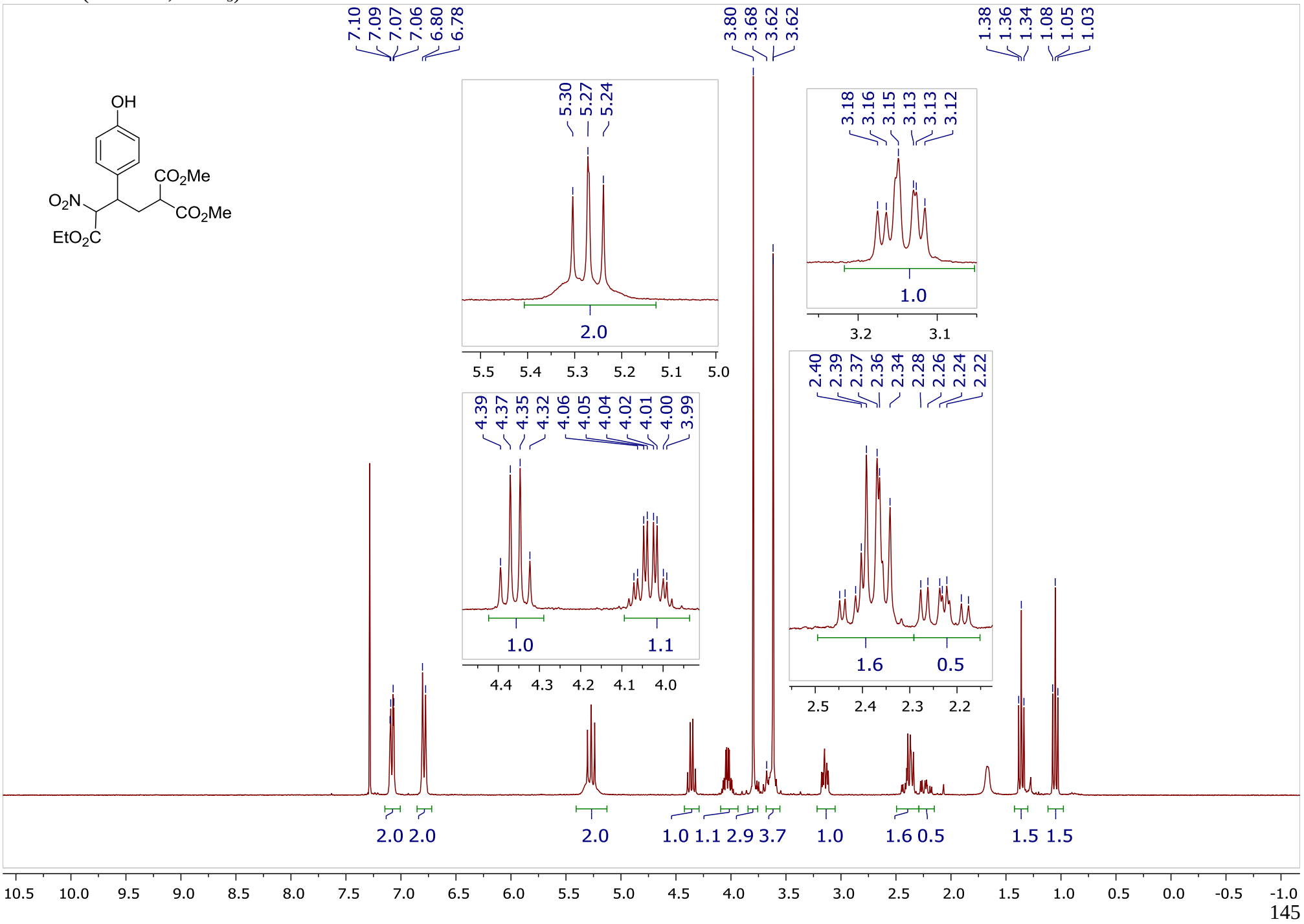


$^{29}$Si NMR (60 MHz, $CDCl_3$)

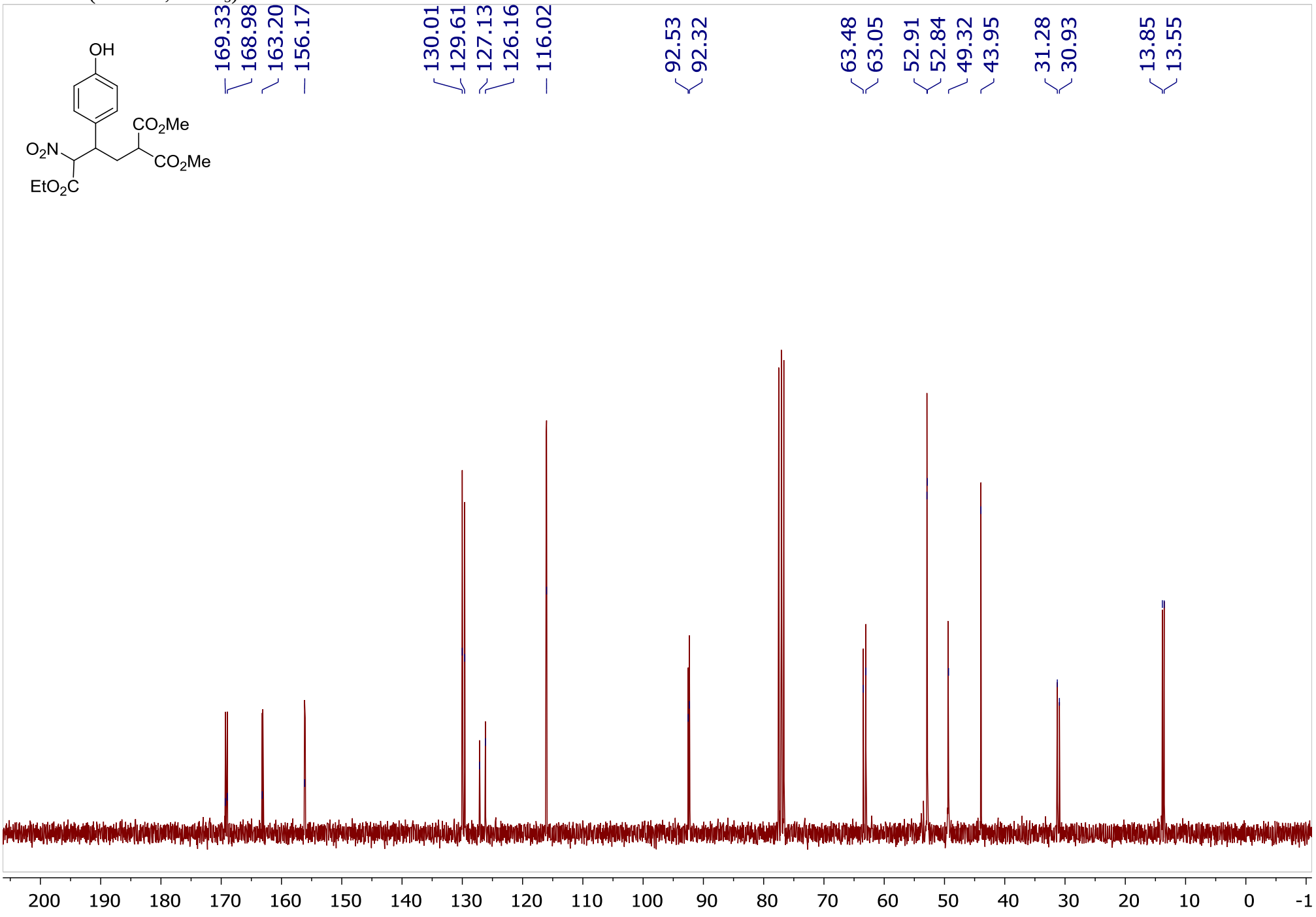


**4-Ethyl 1,1-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3aa)**, dr = 1:1

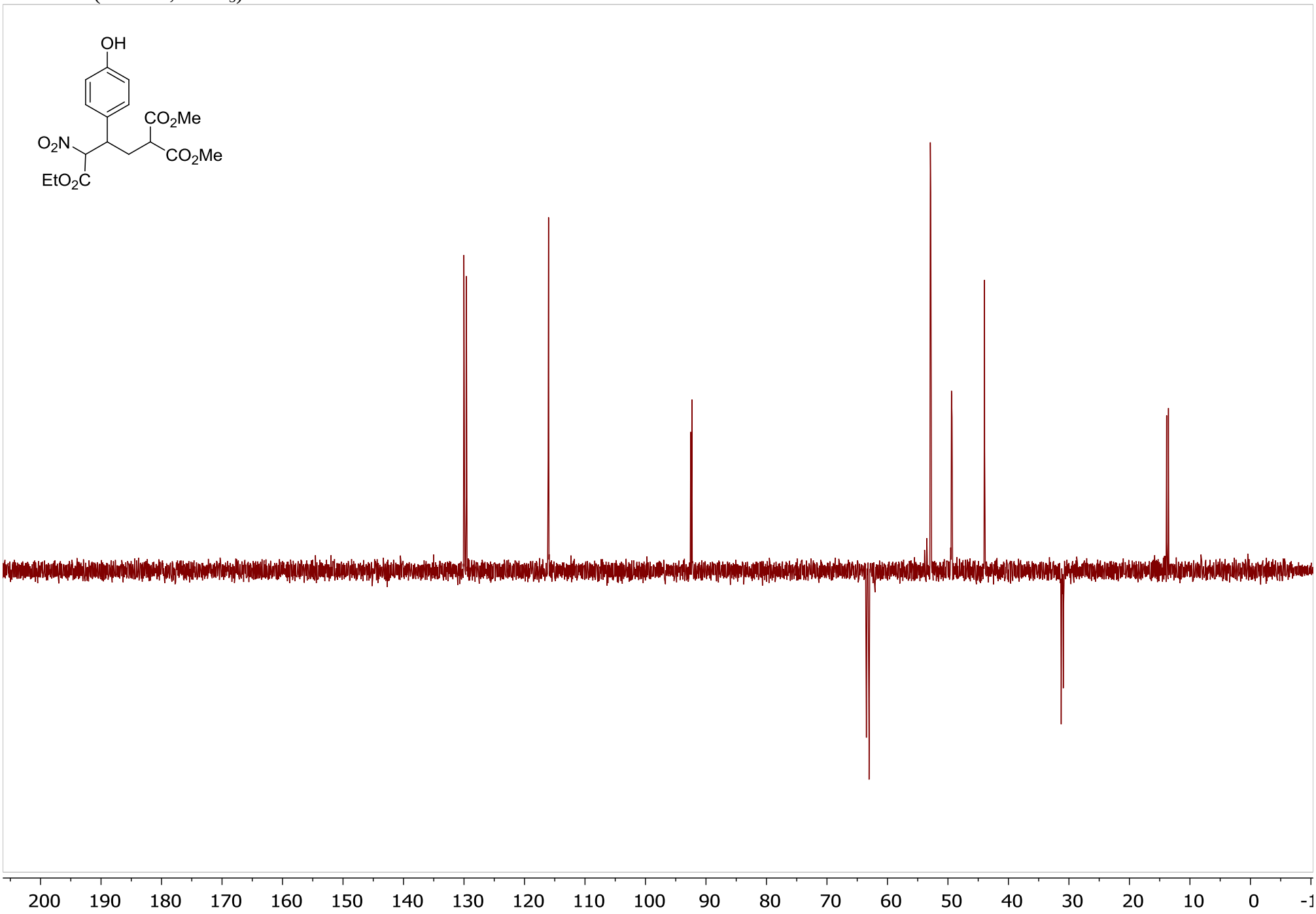
$^1$H NMR (300 MHz, $CDCl_3$)



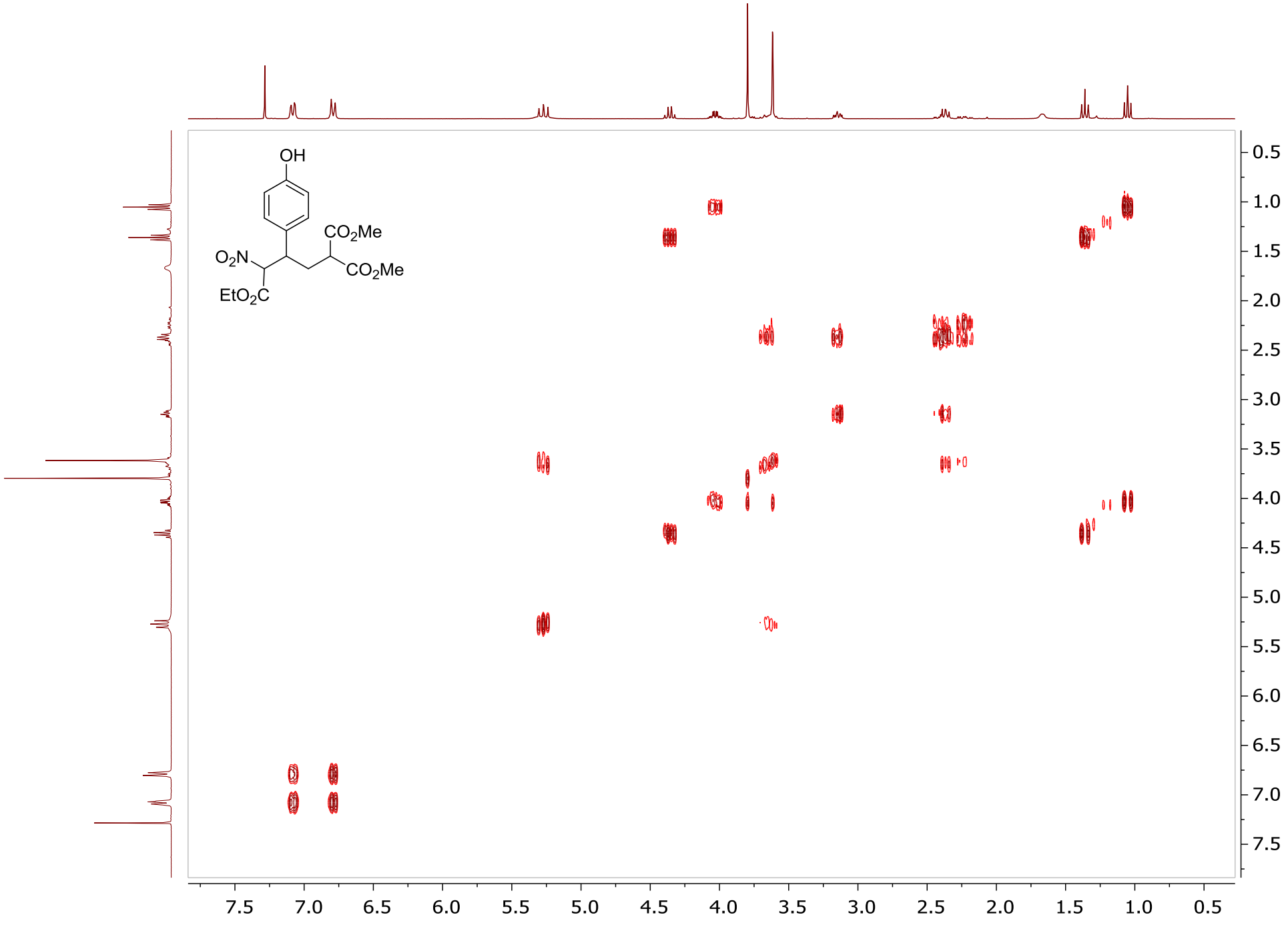
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Me
EtO2C
0.5
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1.5
2.0
2.5
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4.0
4.5
5.0
5.5
6.0
6.5
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6.5
6.0
5.5
5.0
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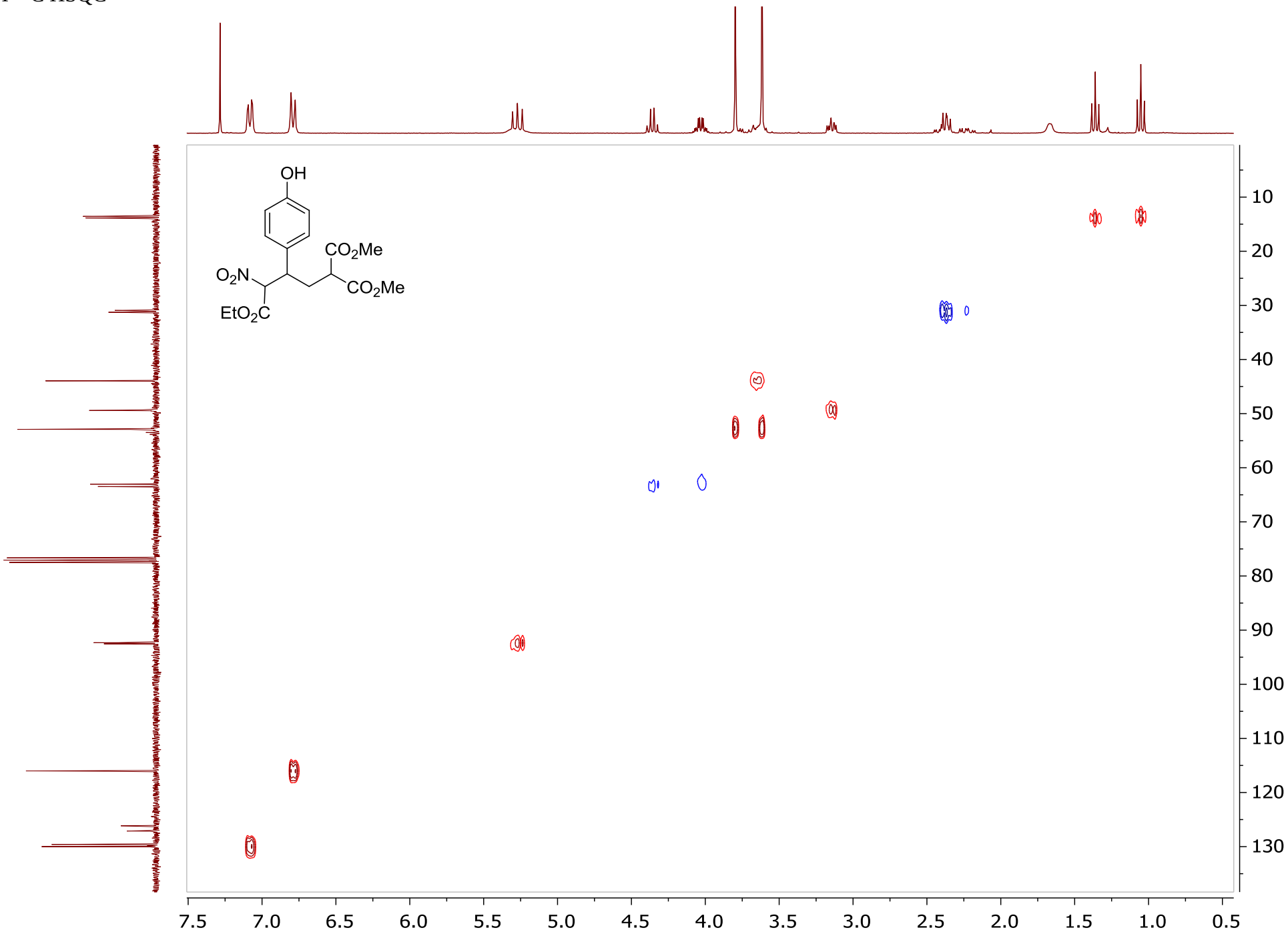
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC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O2N
CO2Me
EtO2C
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30
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70
80
90
100
110
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7.0
6.5
6.0
5.5
5.0
4.5
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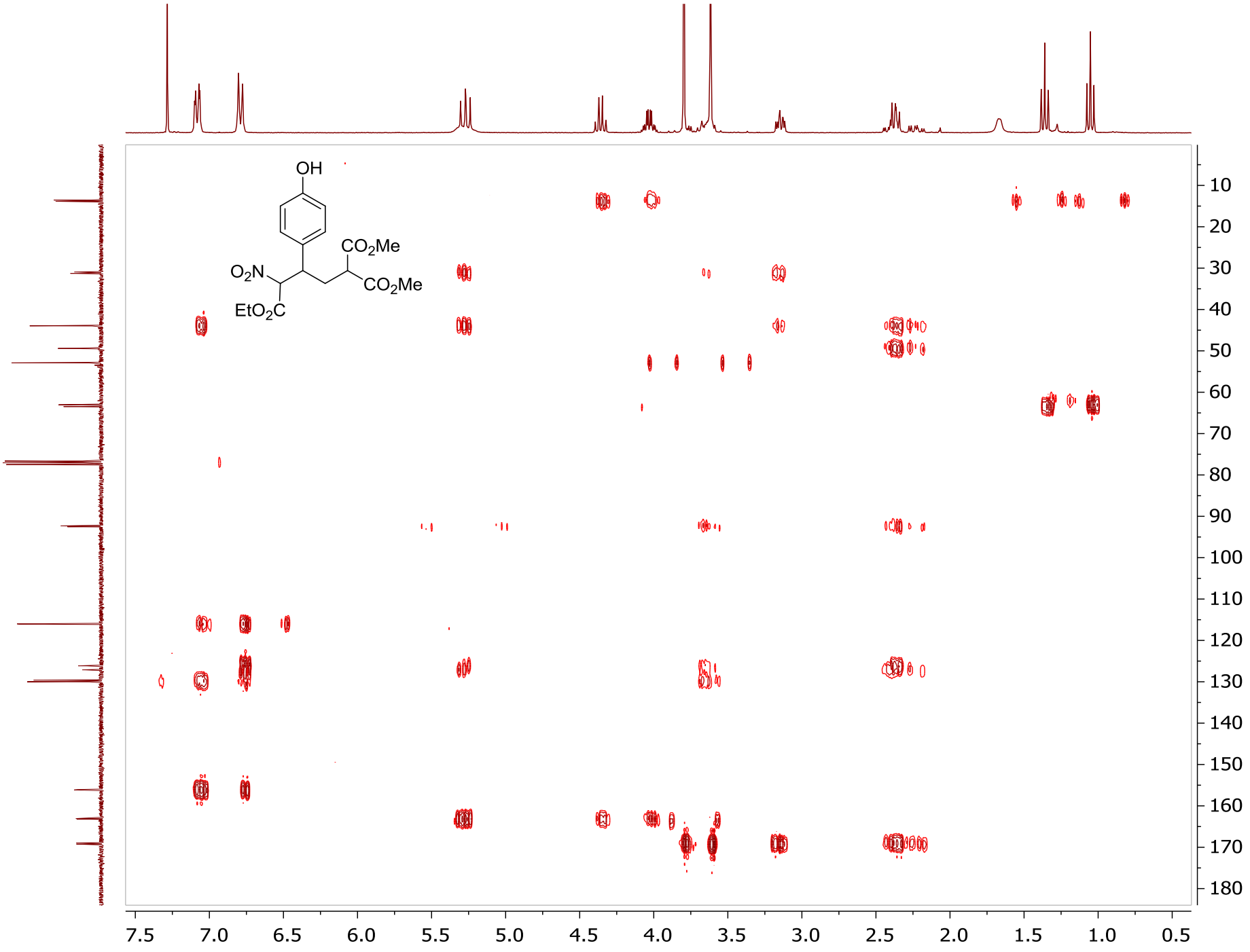
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HMBC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CO2Me
O2N
CO2Me
EtO2C
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20
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100
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180
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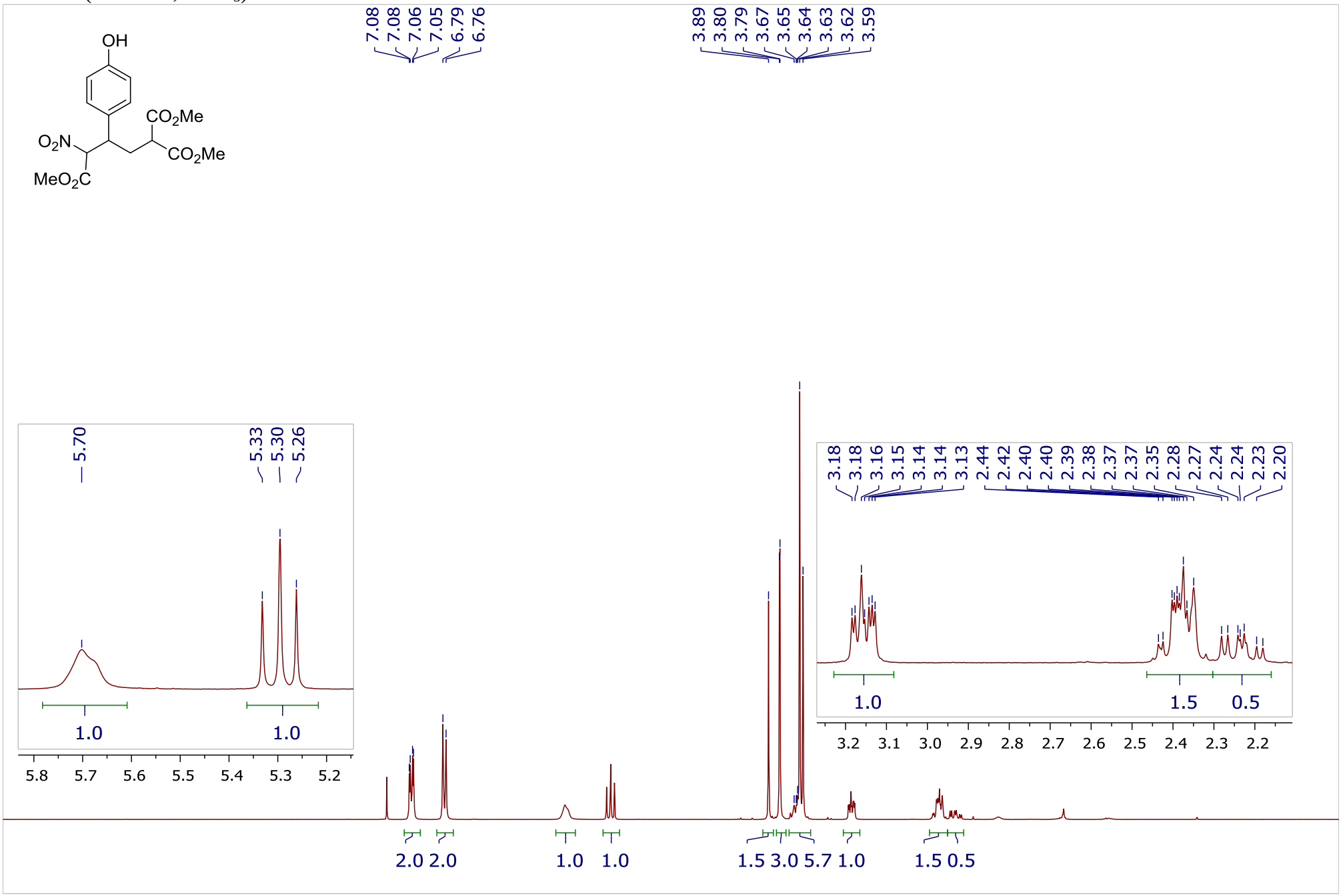
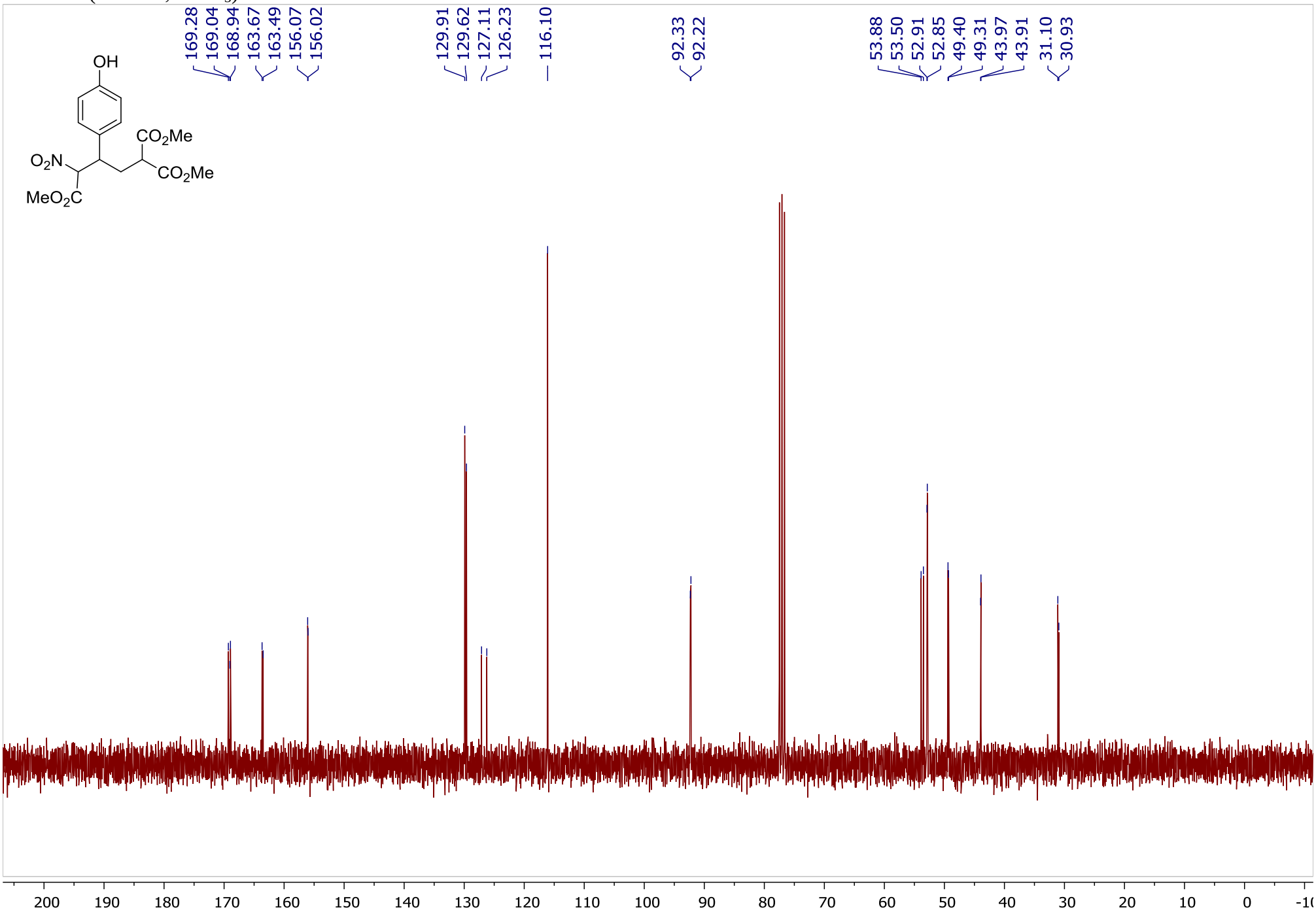
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Trimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ab)**, dr = 1:1

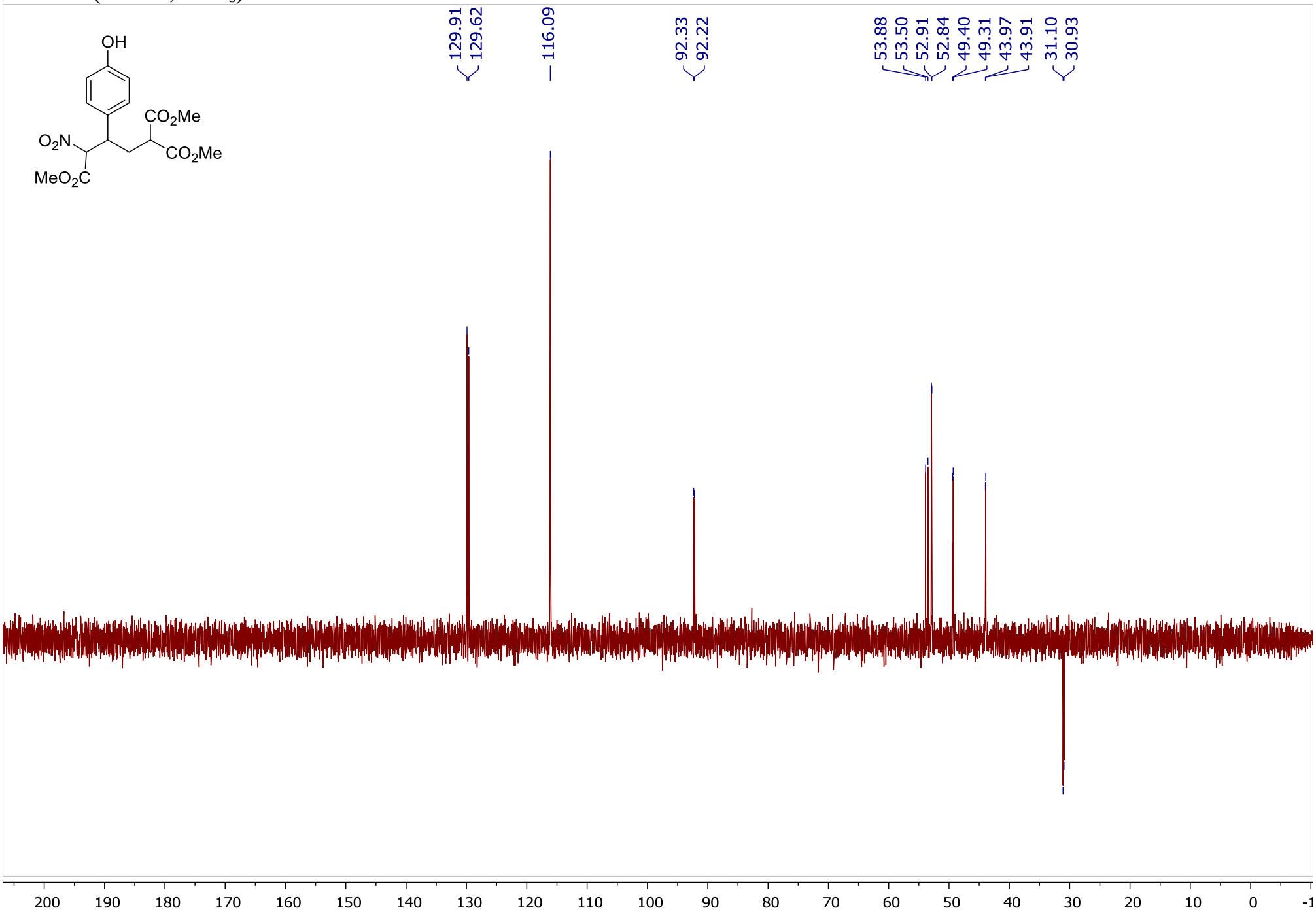
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

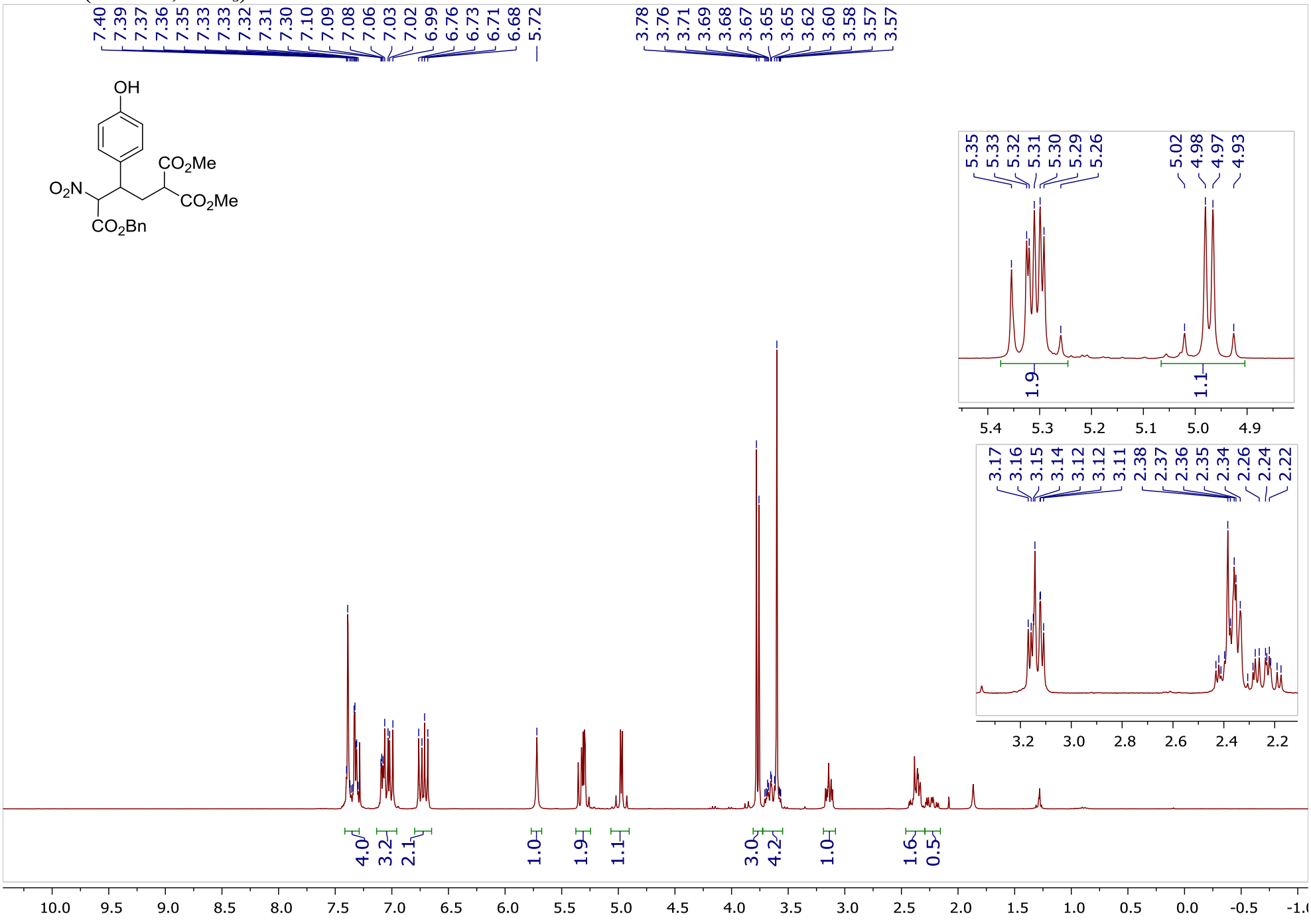


$^{13}$C DEPT (75 MHz, $CDCl_3$)

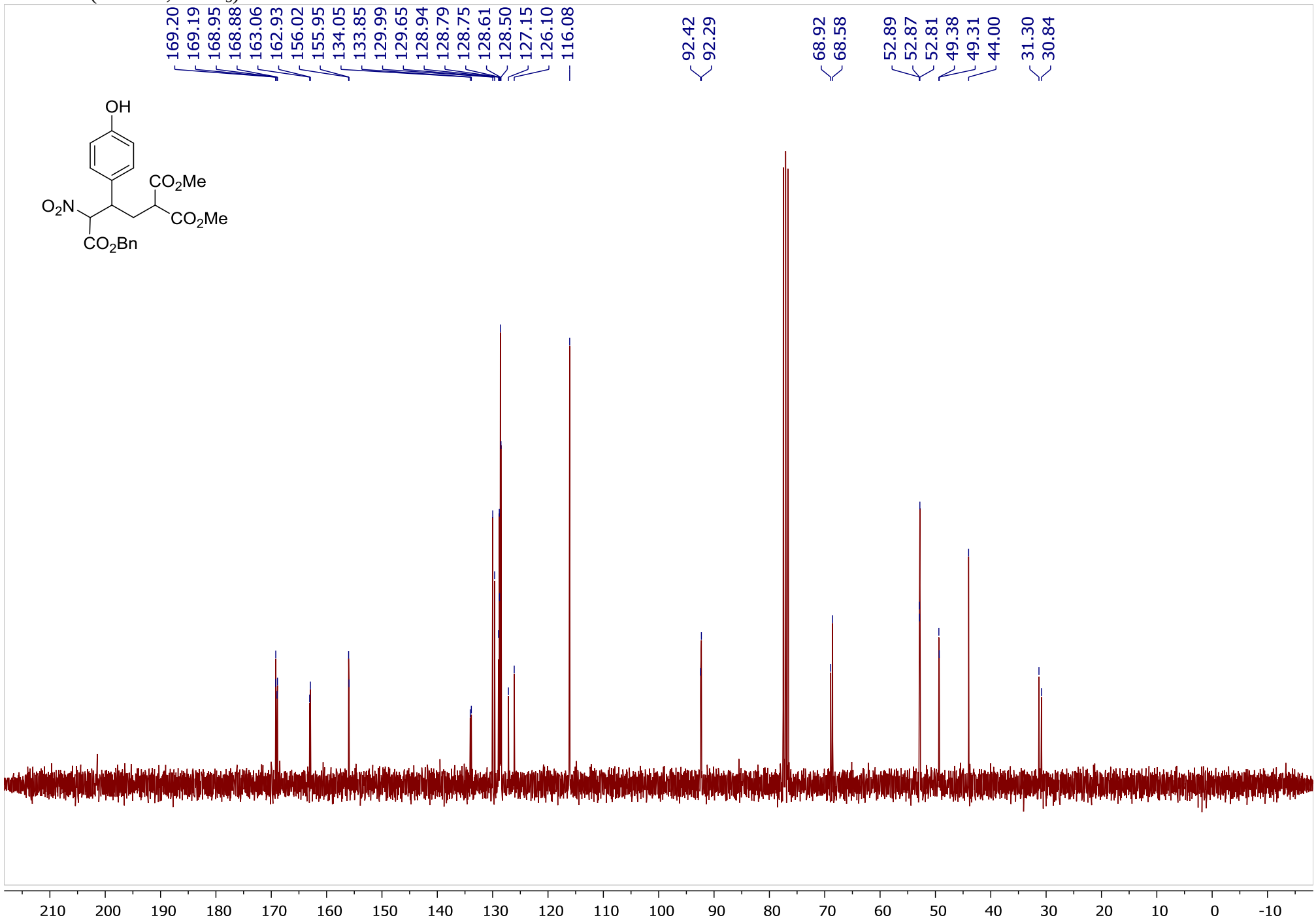


**4-Benzyl 1,1-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ac)**, dr = 1:1

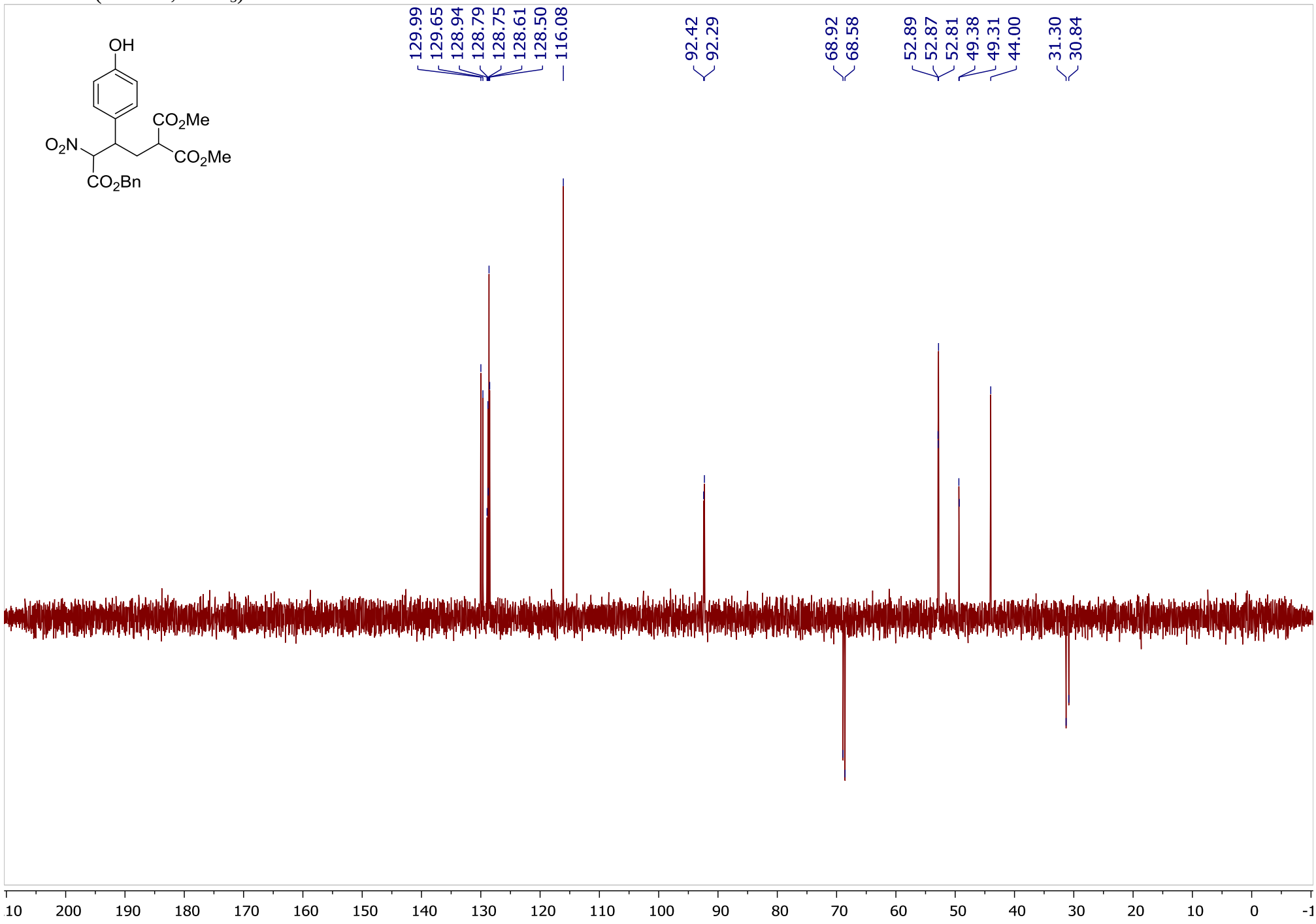
$^1$H NMR (300 MHz, $CDCl_3$)



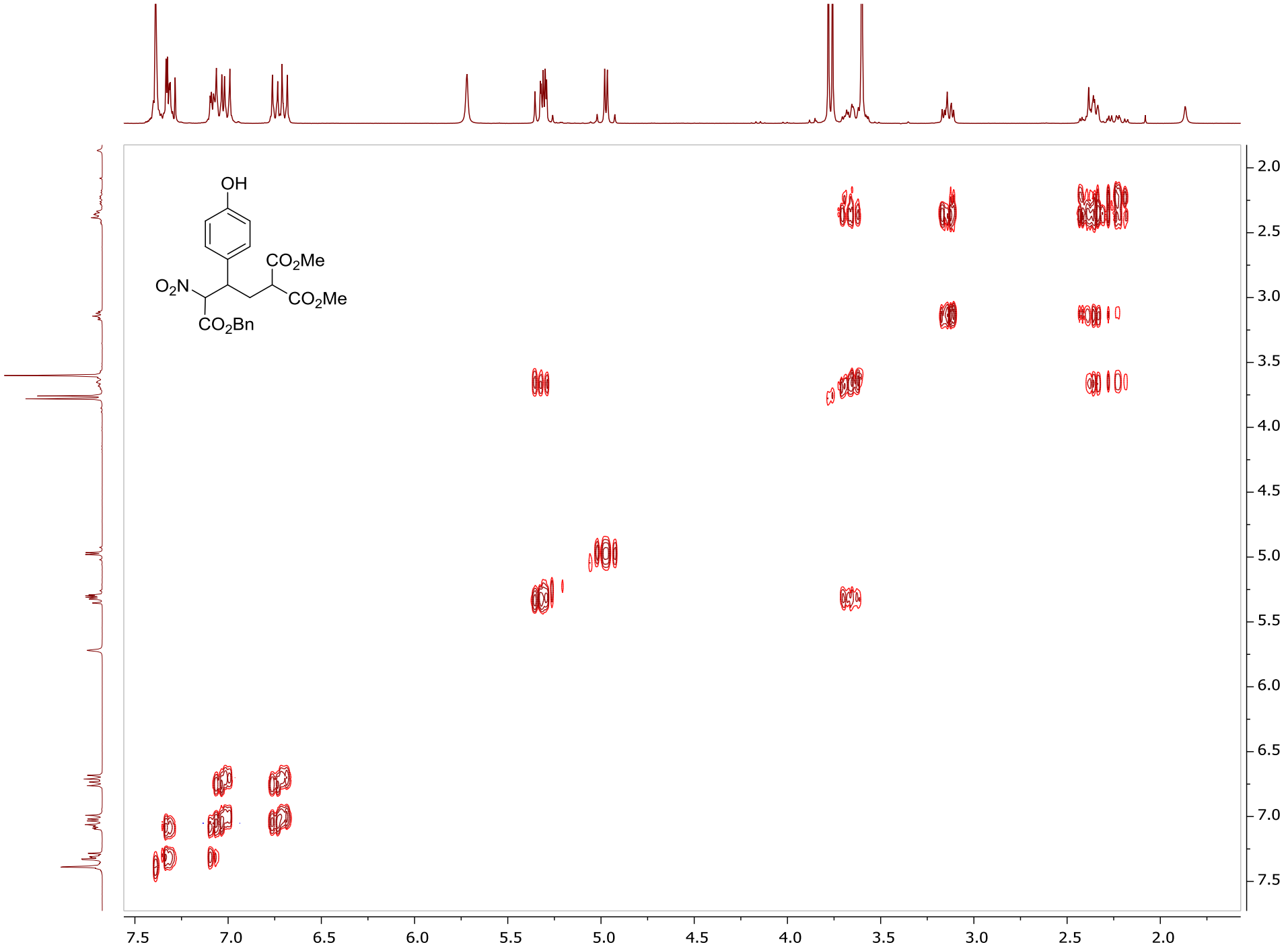
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
CO2Bn
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5.5
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7.0
7.5
7.5
7.0
6.5
6.0
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5.0
4.5
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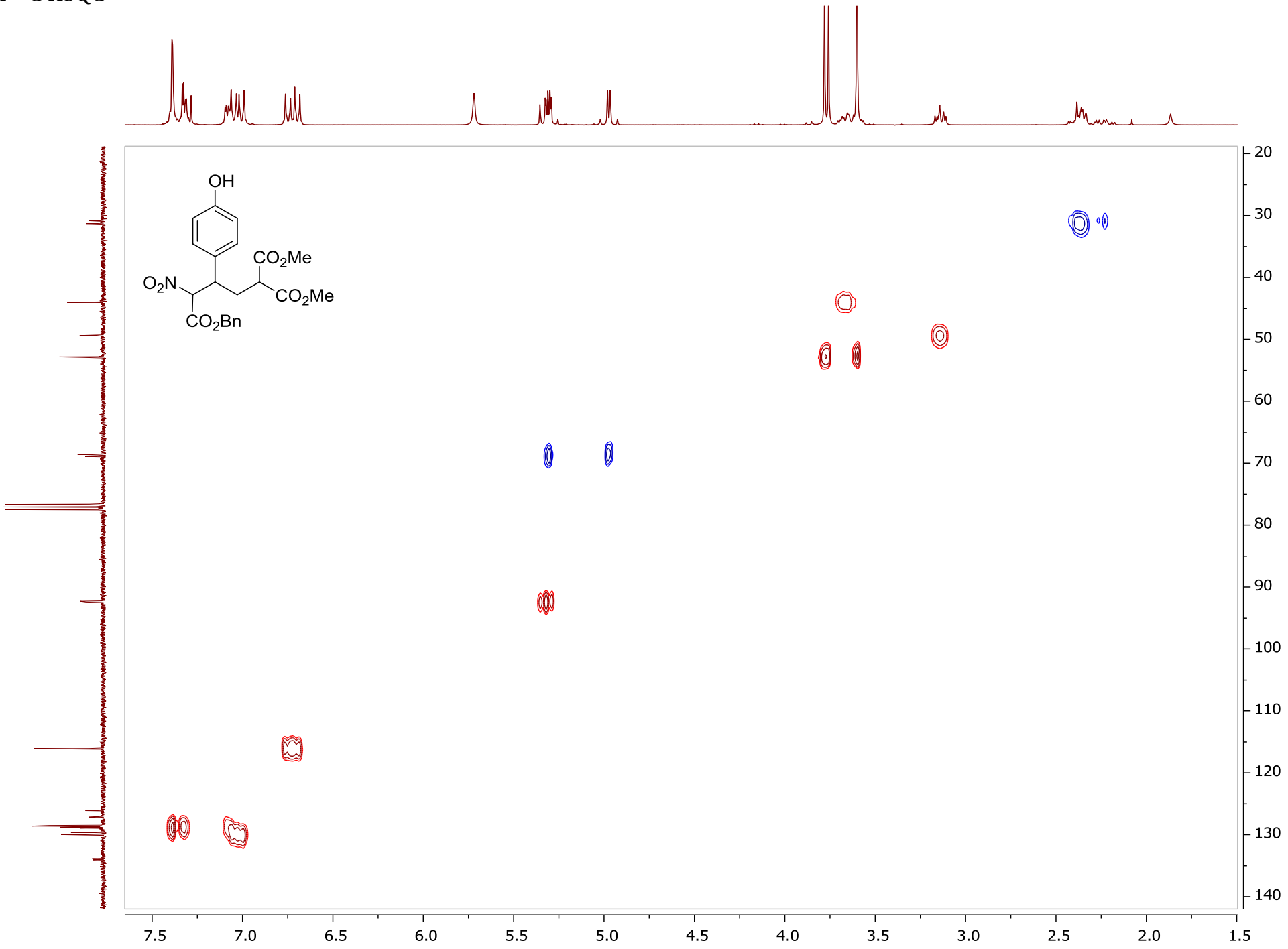
3.0
2.5
2.0

$^{1}H$-$^{13}C$ HSQC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O2N
CO2Me
CO2Bn
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30
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50
60
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80
90
100
110
120
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140
7.5
7.0
6.5
6.0
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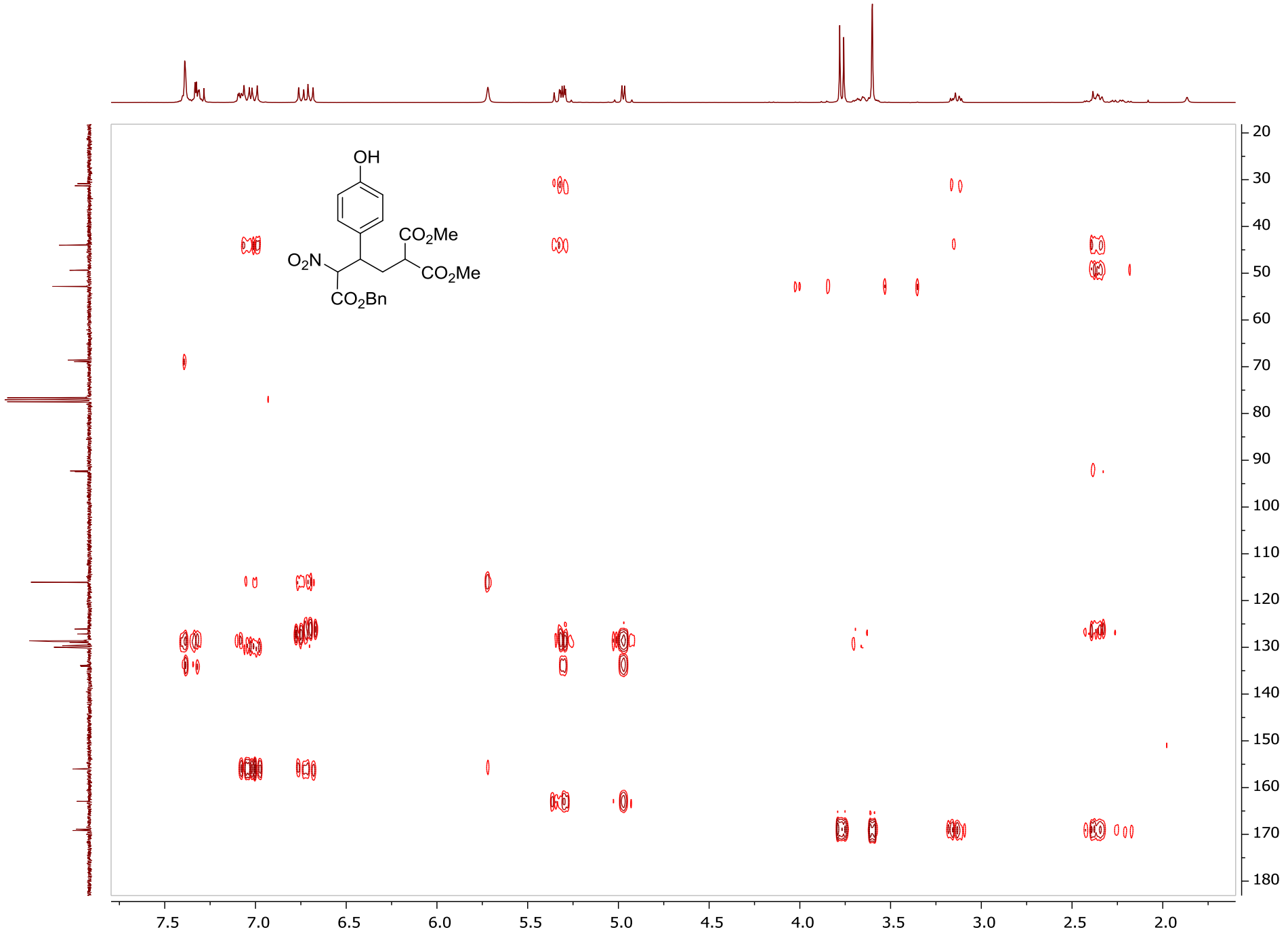
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HMBC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CO2Me
CO2Bn
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100
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120
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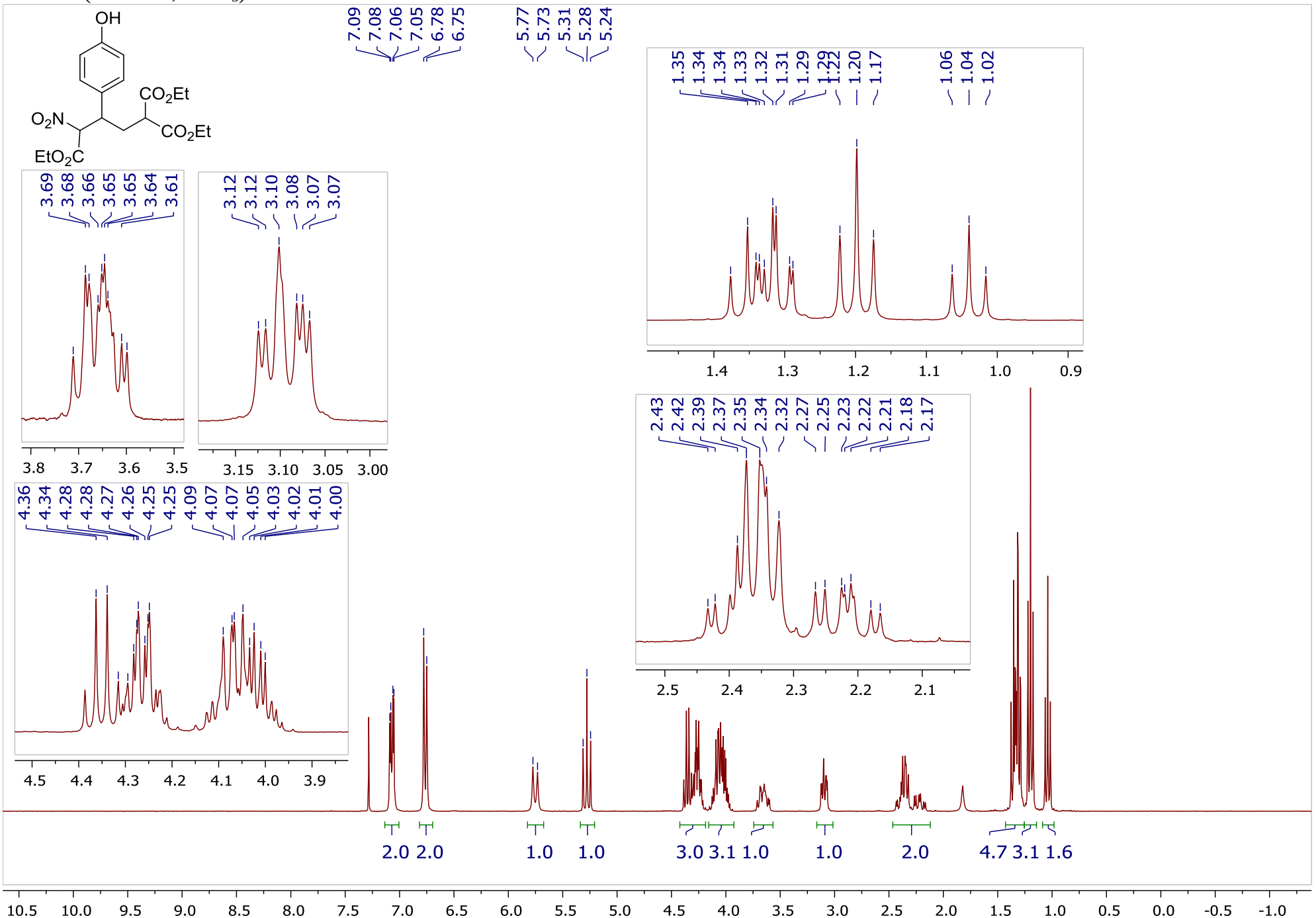
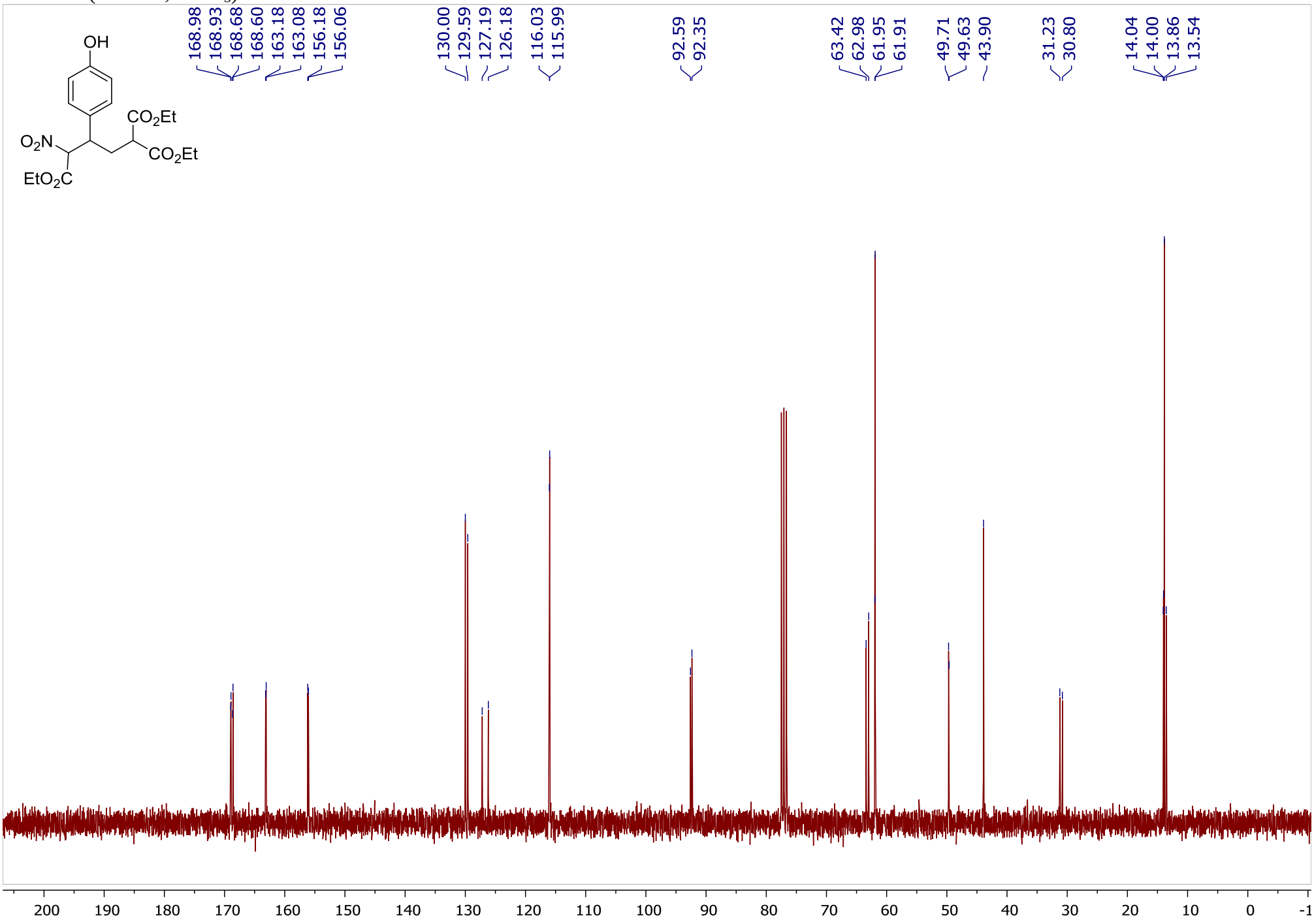
140
150
160
170
180
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

**Triethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ba)**, dr = 1:1

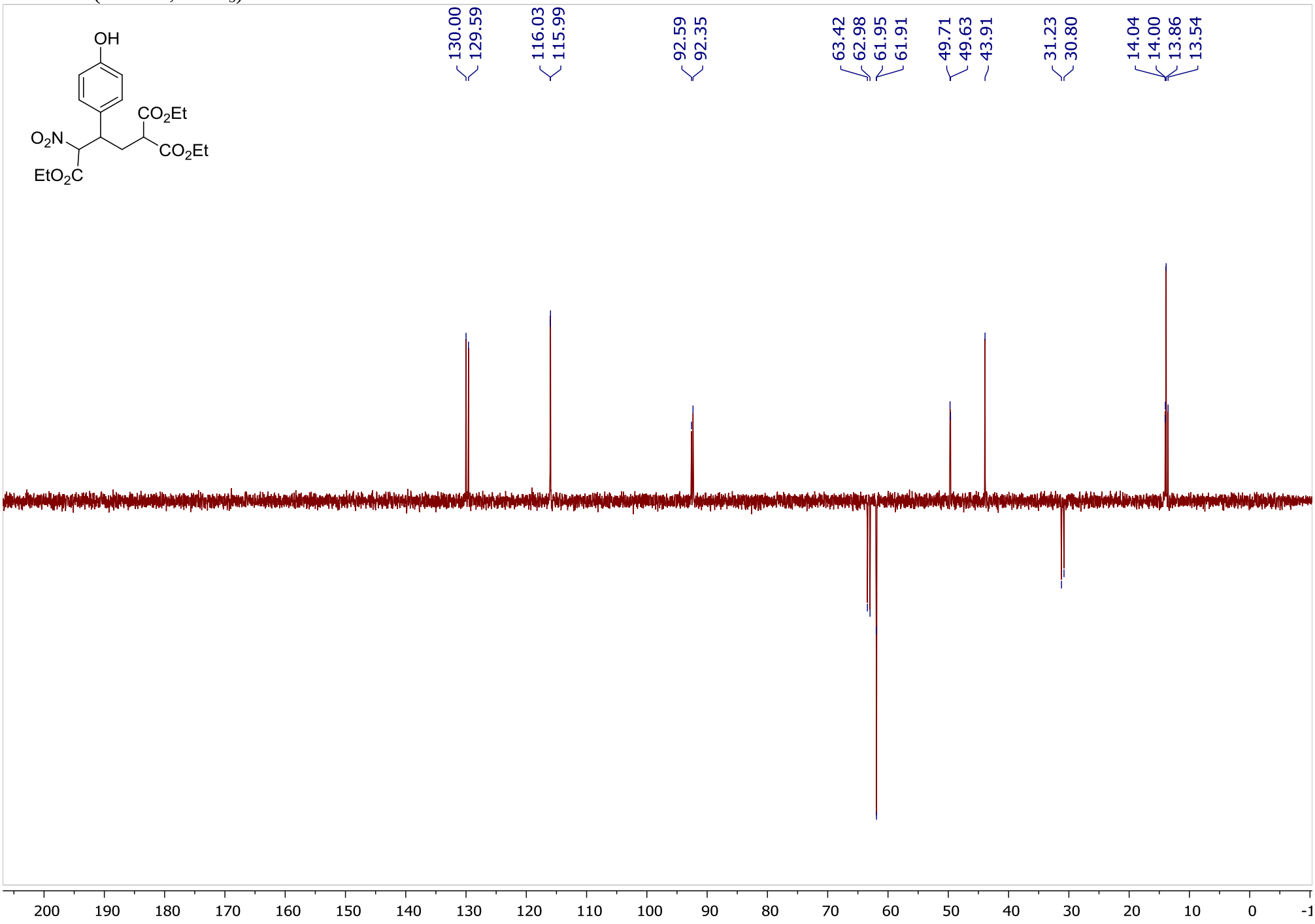
$^1$H NMR (300 MHz, $CDCl_3$)



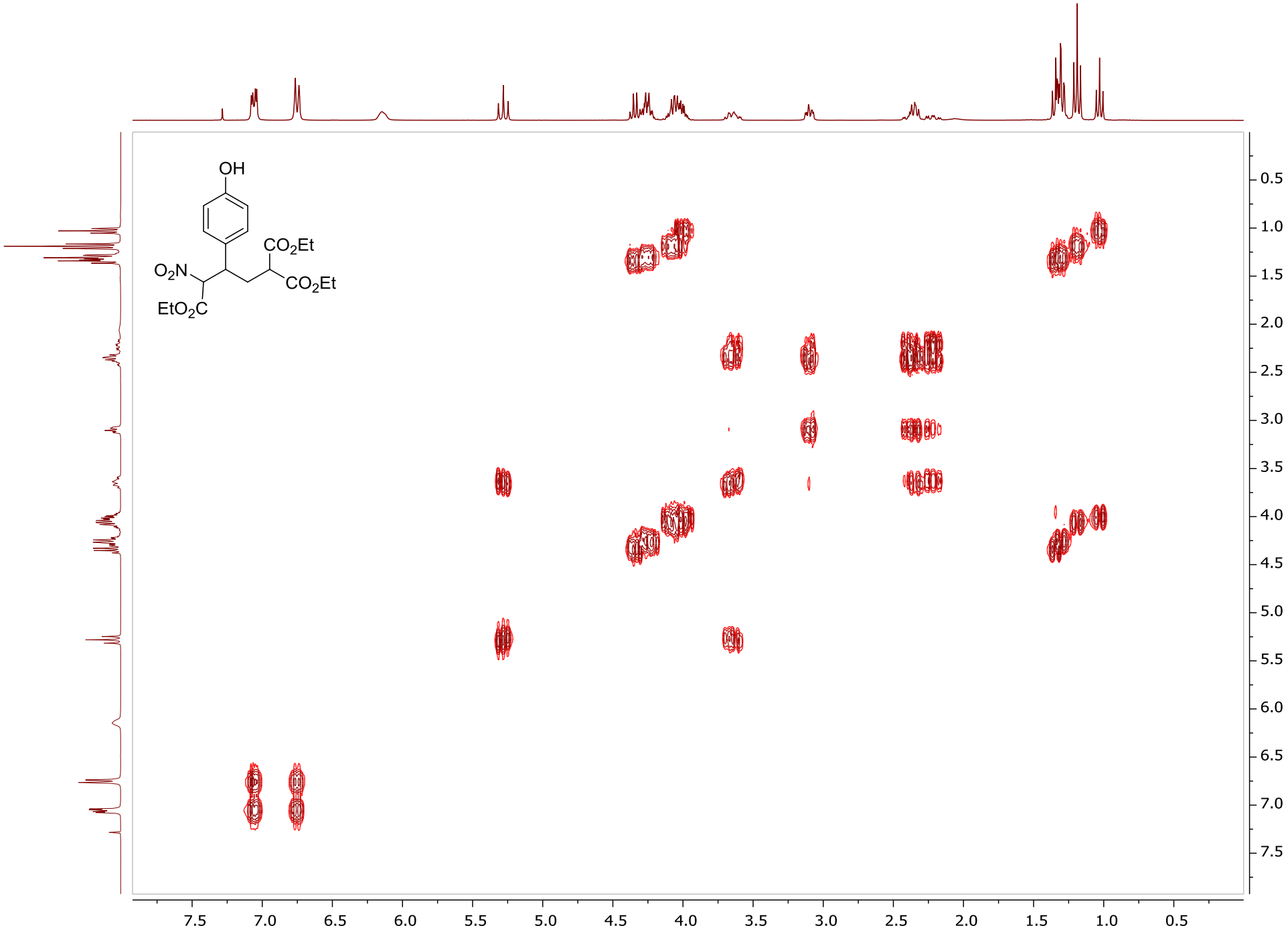
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Et
EtO2C
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1.5
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3.0
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4.0
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5.0
5.5
6.0
6.5
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6.5
6.0
5.5
5.0
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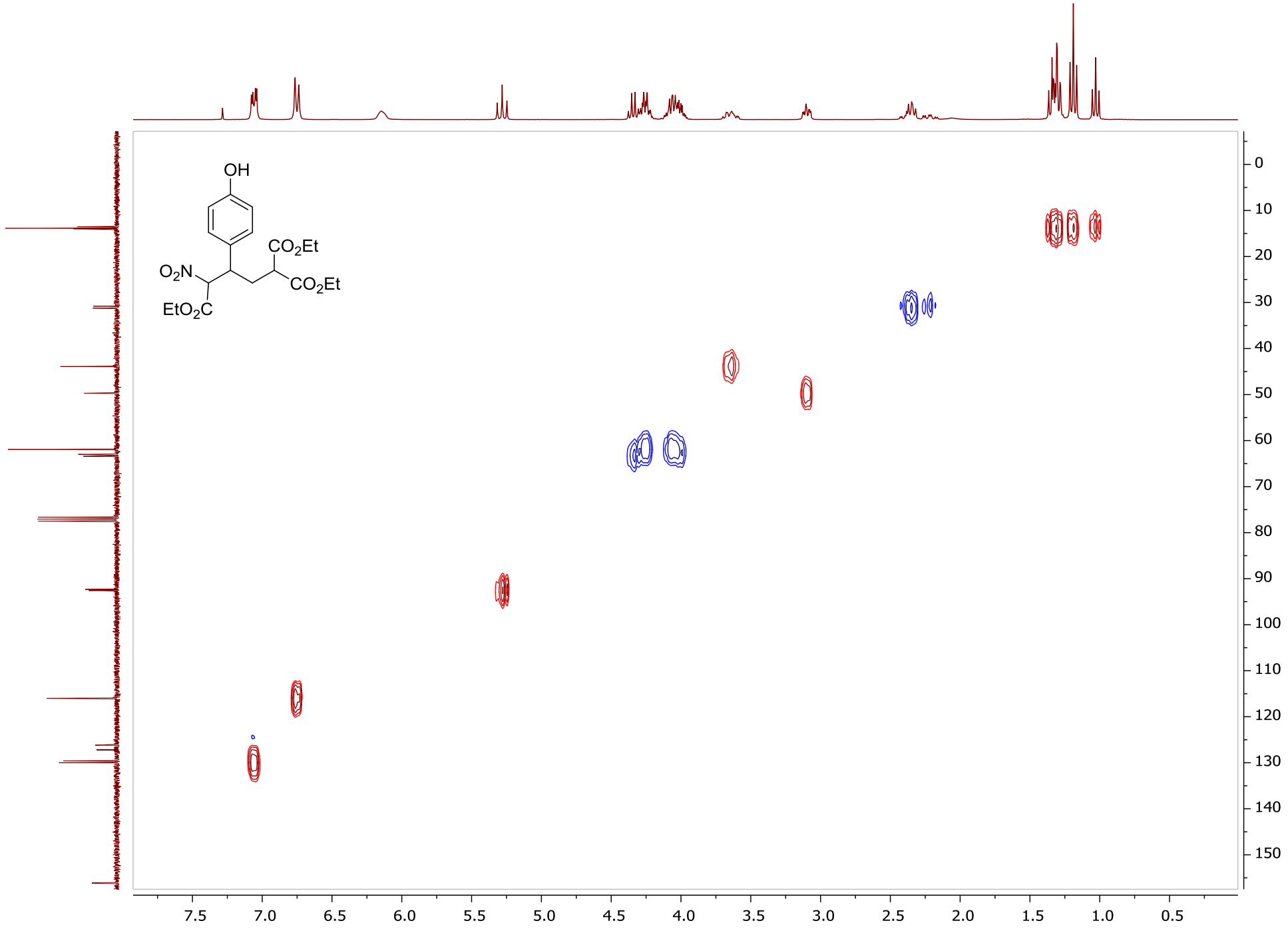
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC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EtO2C
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90
100
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140
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7.5
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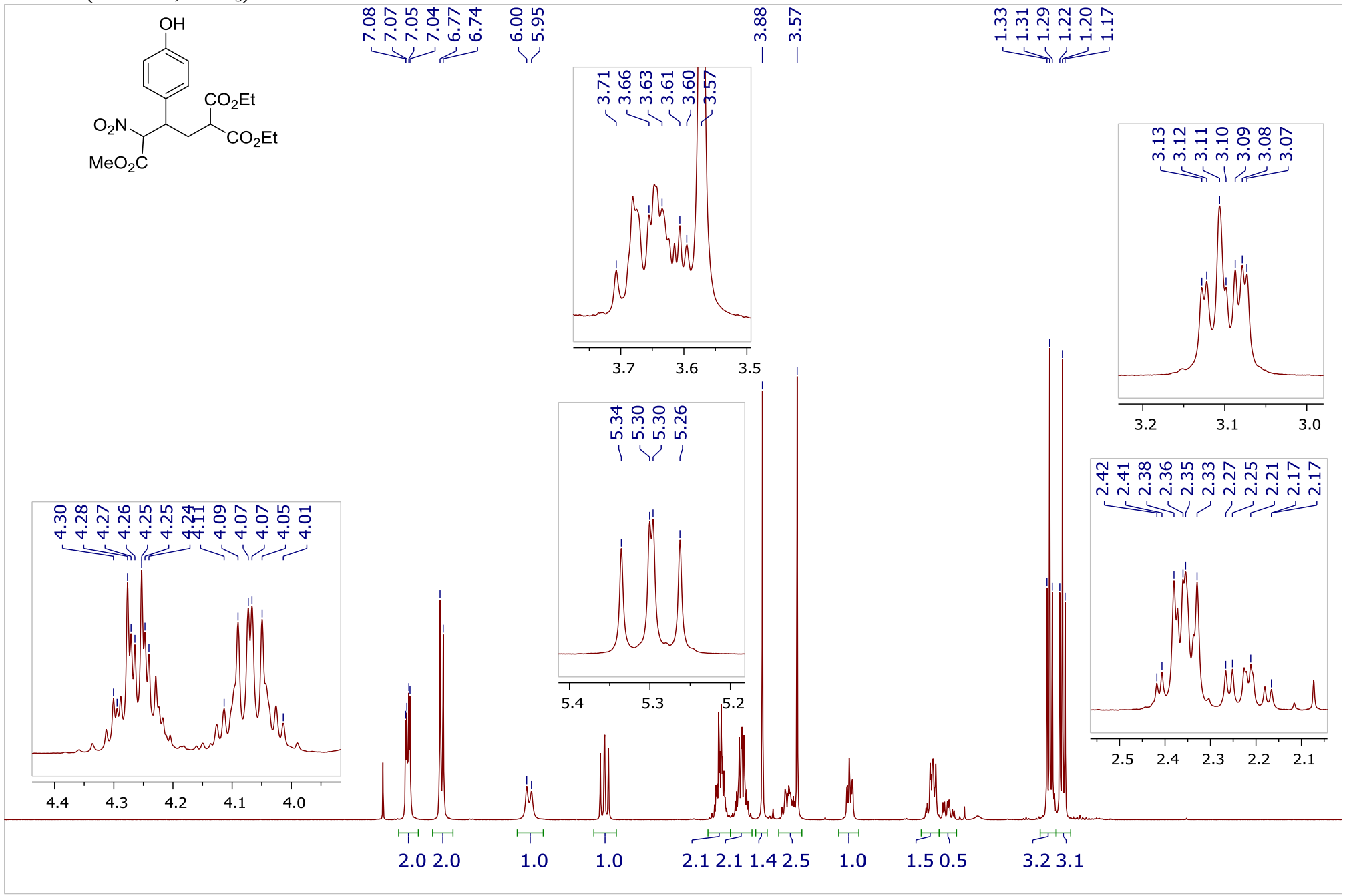
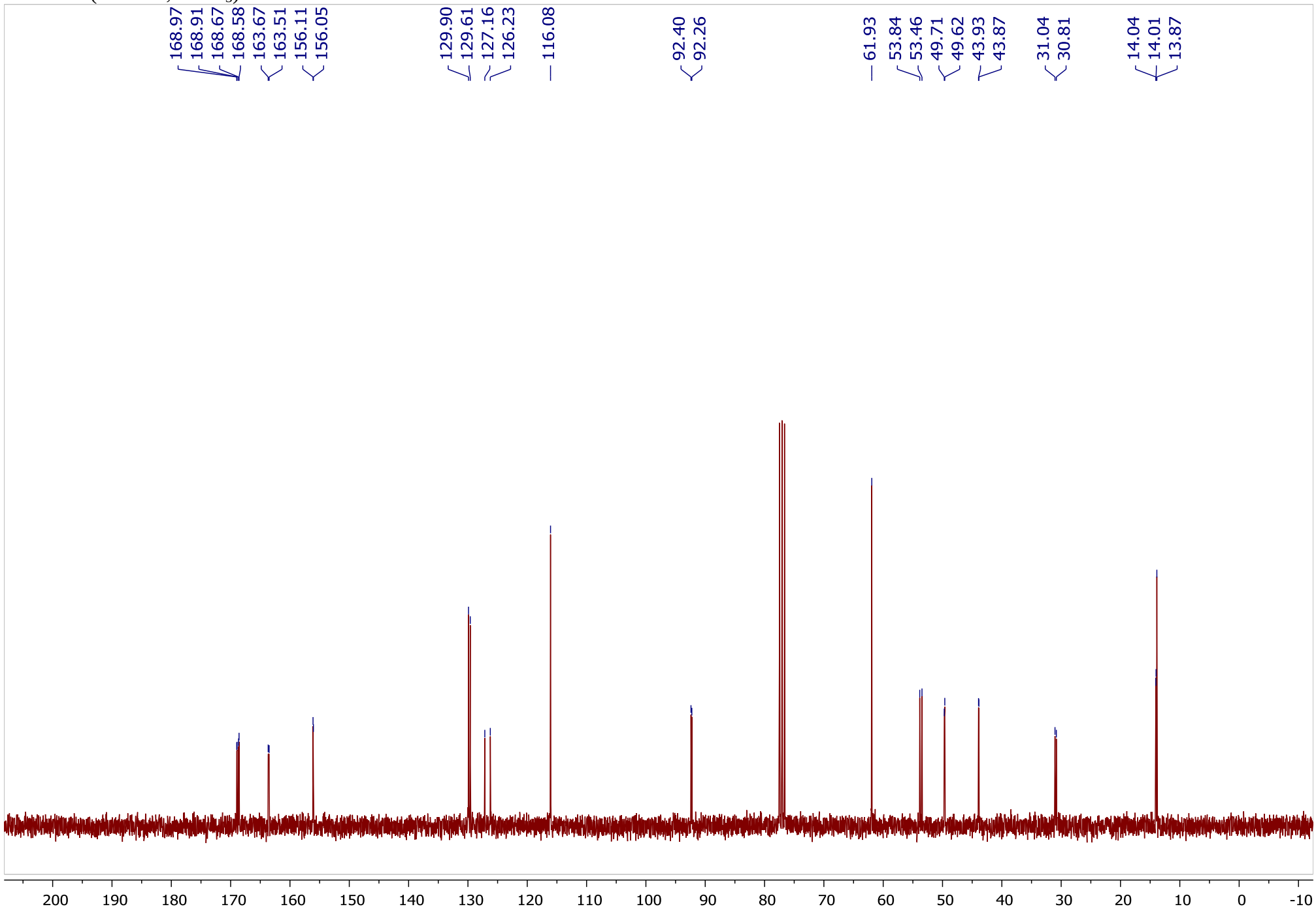
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**1,1-Diethyl 4-methyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3bb)**, dr = 1:1

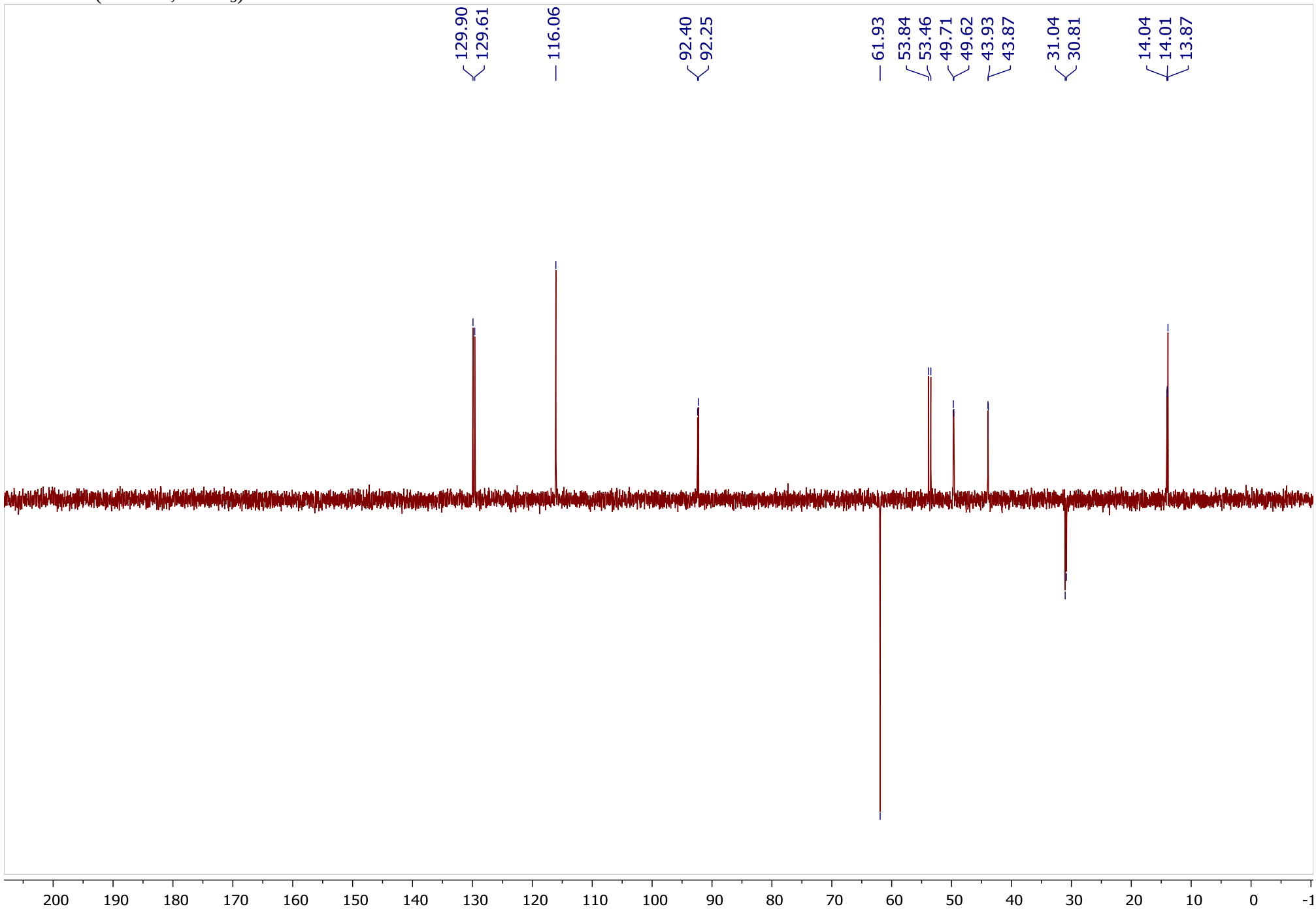
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

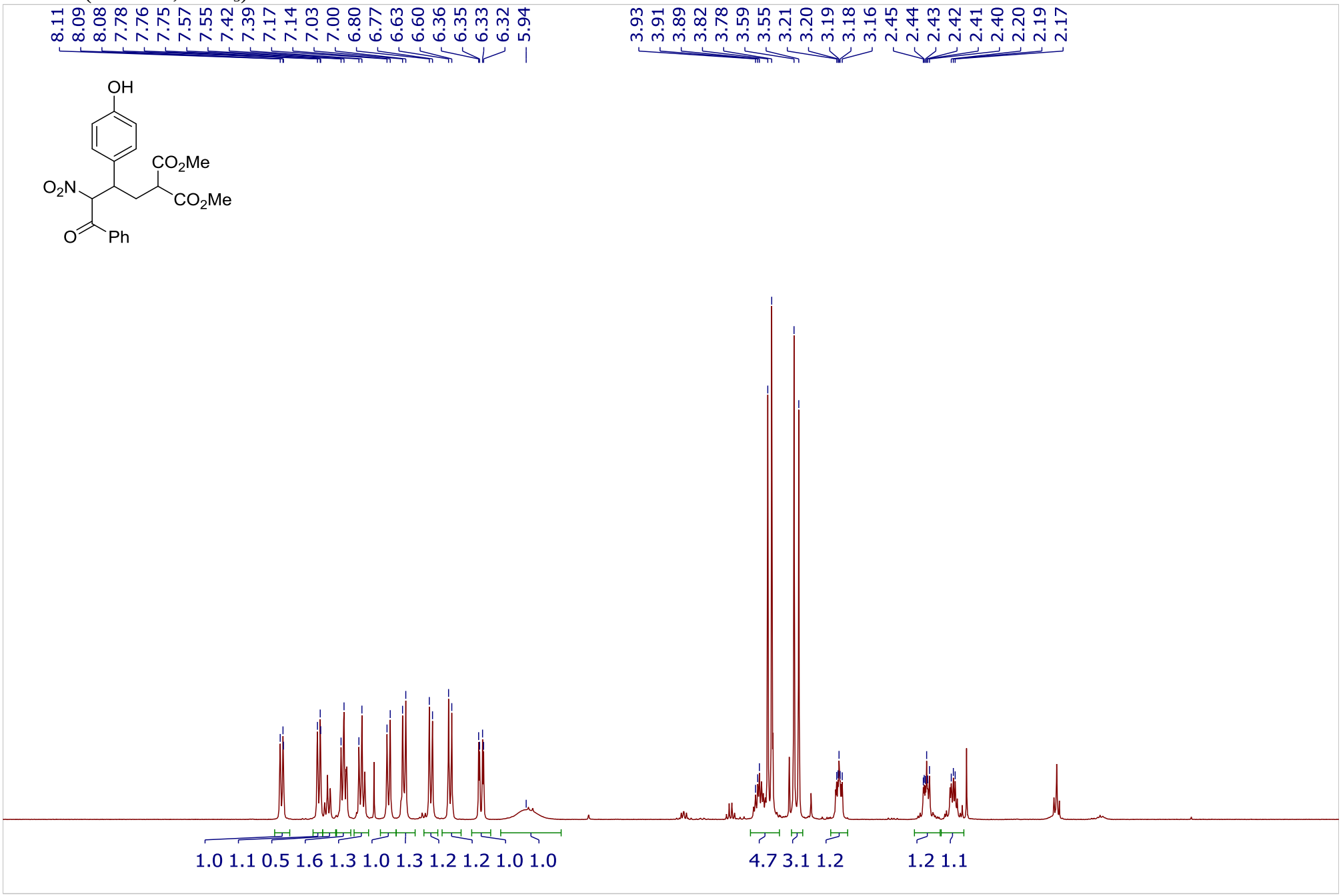


$^{13}$C DEPT (75 MHz, $CDCl_3$)

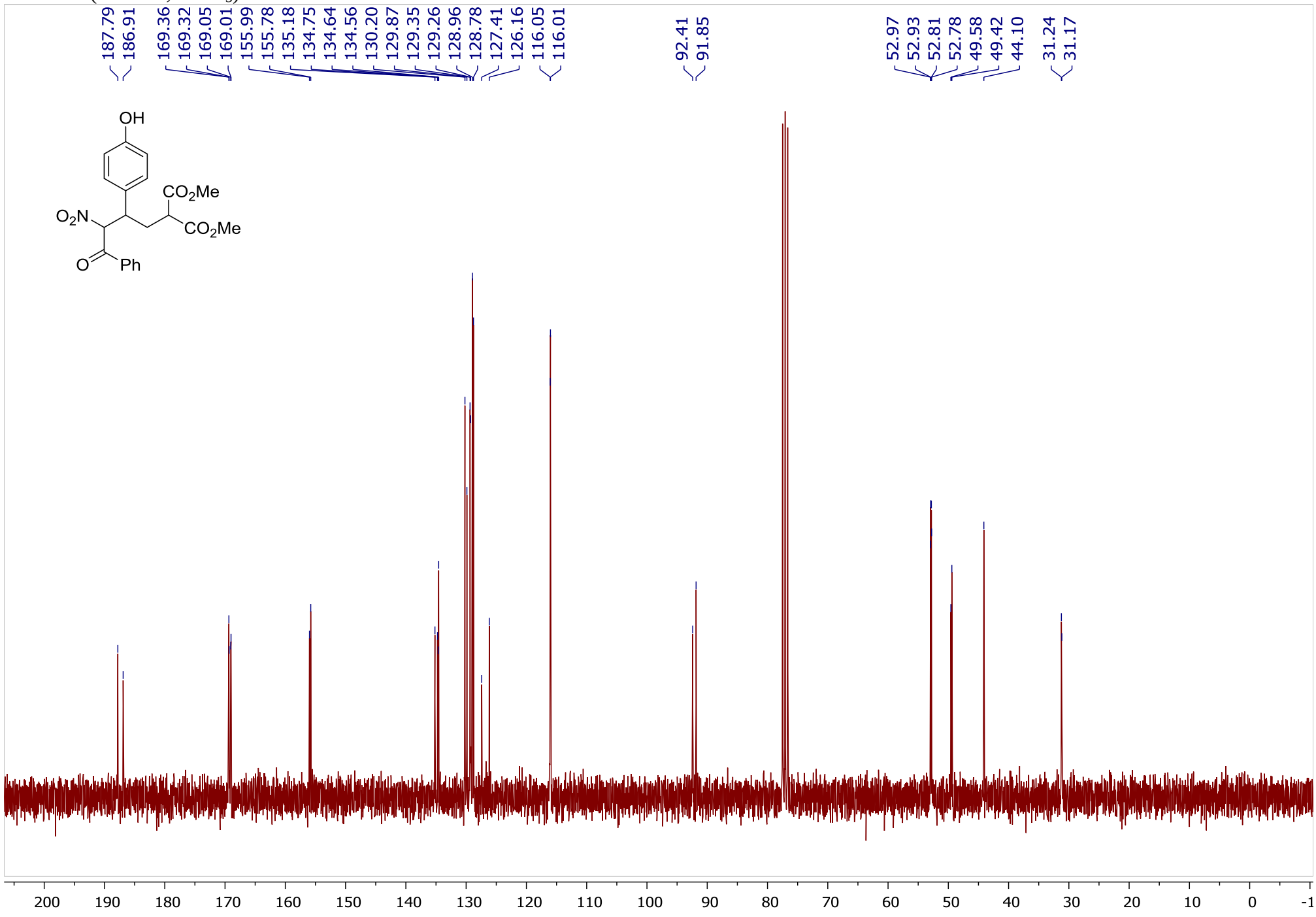


**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-4-oxo-4-phenylbutyl)malonate (3ad)**, dr = 1:1

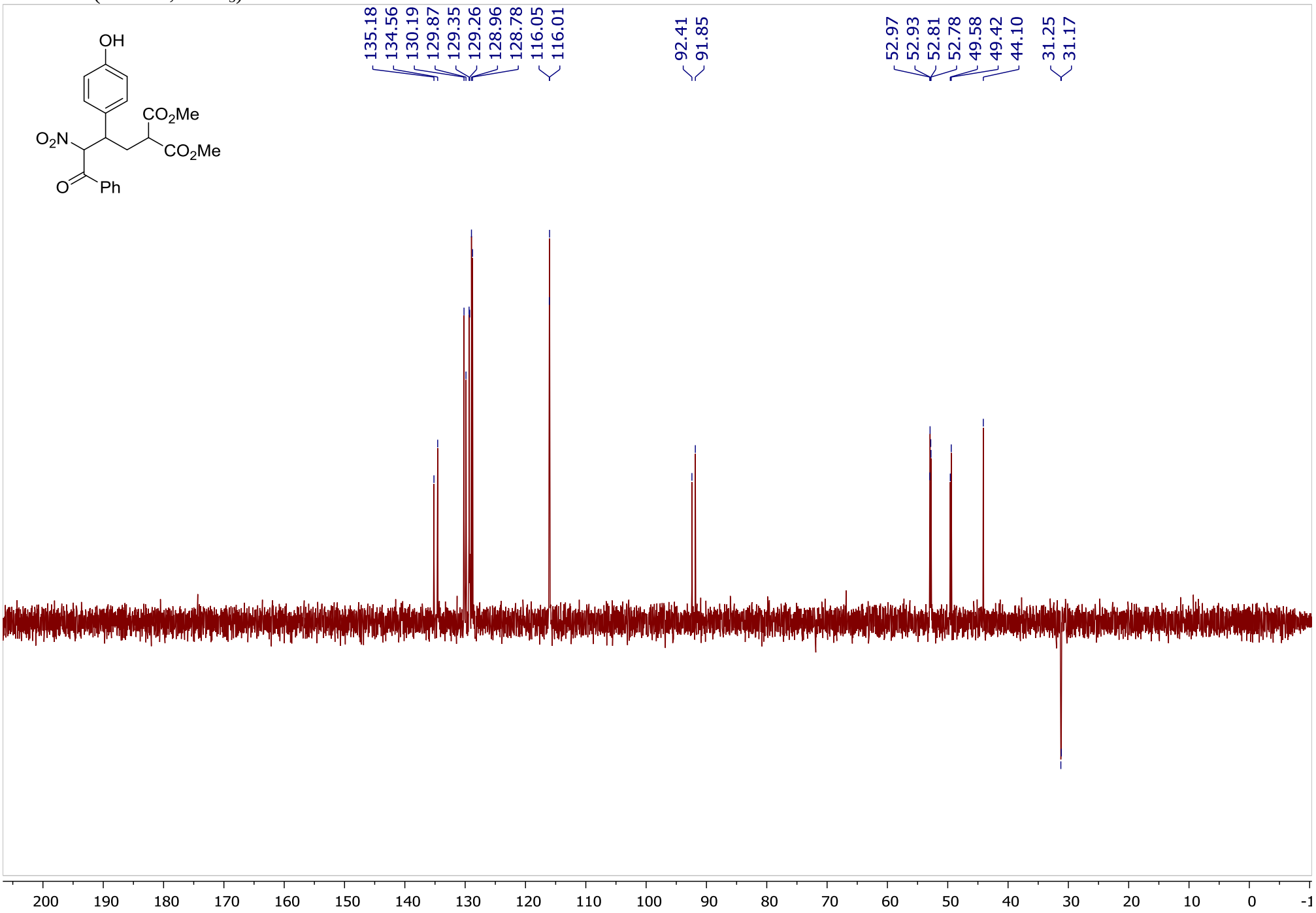
$^1$H NMR (300 MHz, $CDCl_3$)



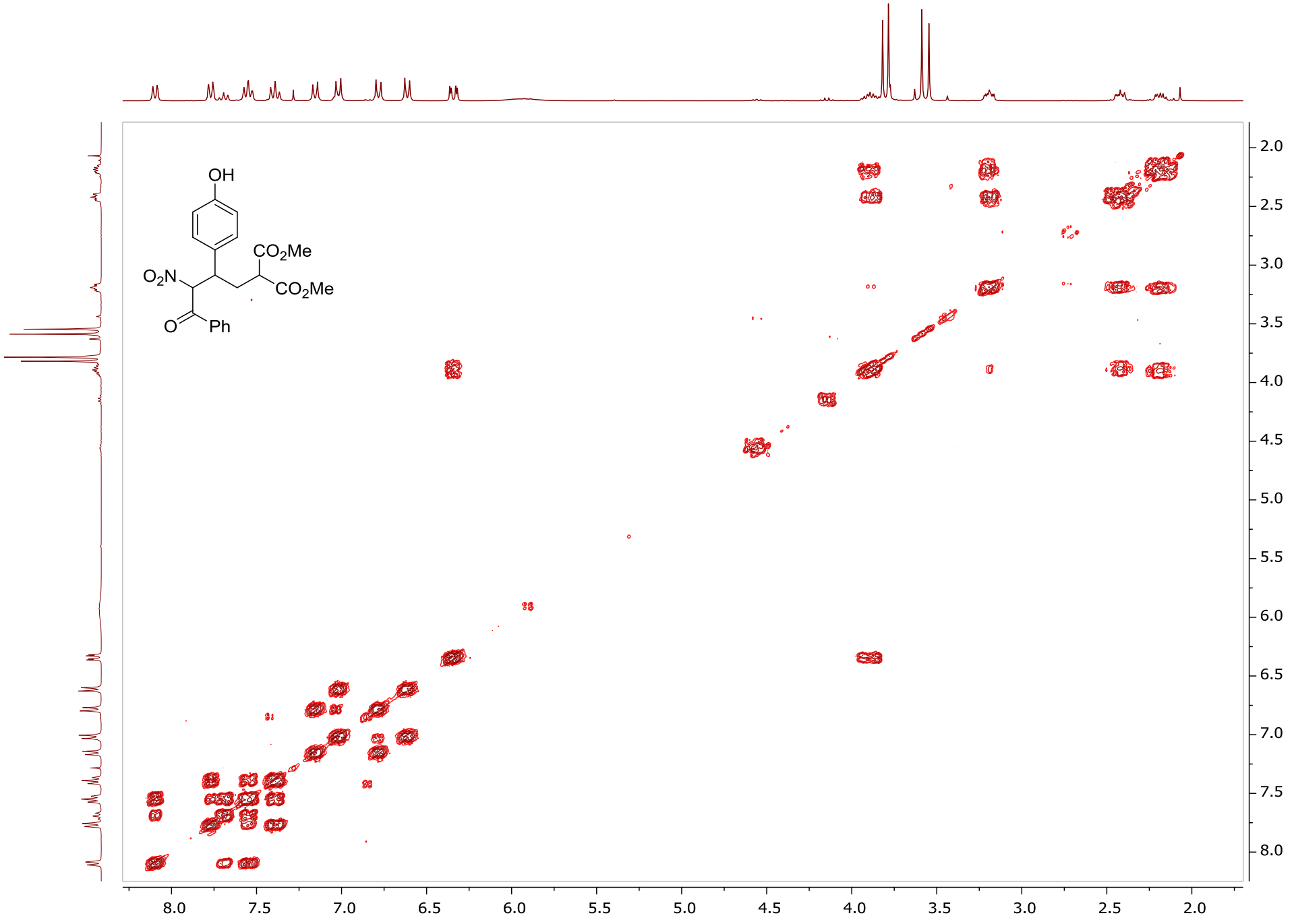
$^{13}$C NMR (75 MHz, $CDCl_3$)



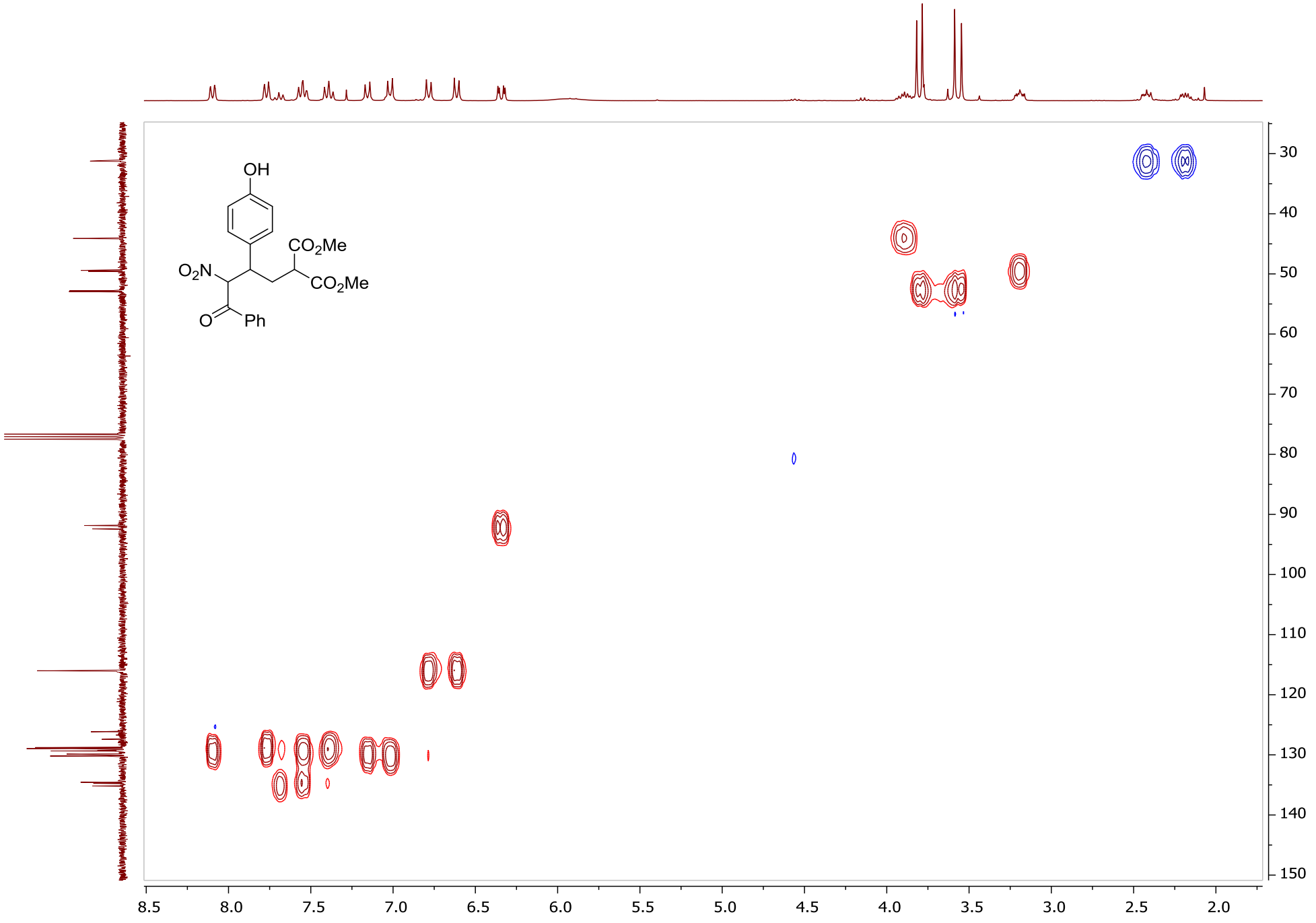
$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY



$^{1}H$-$^{13}C$ HSQC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CO2Me
O
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150
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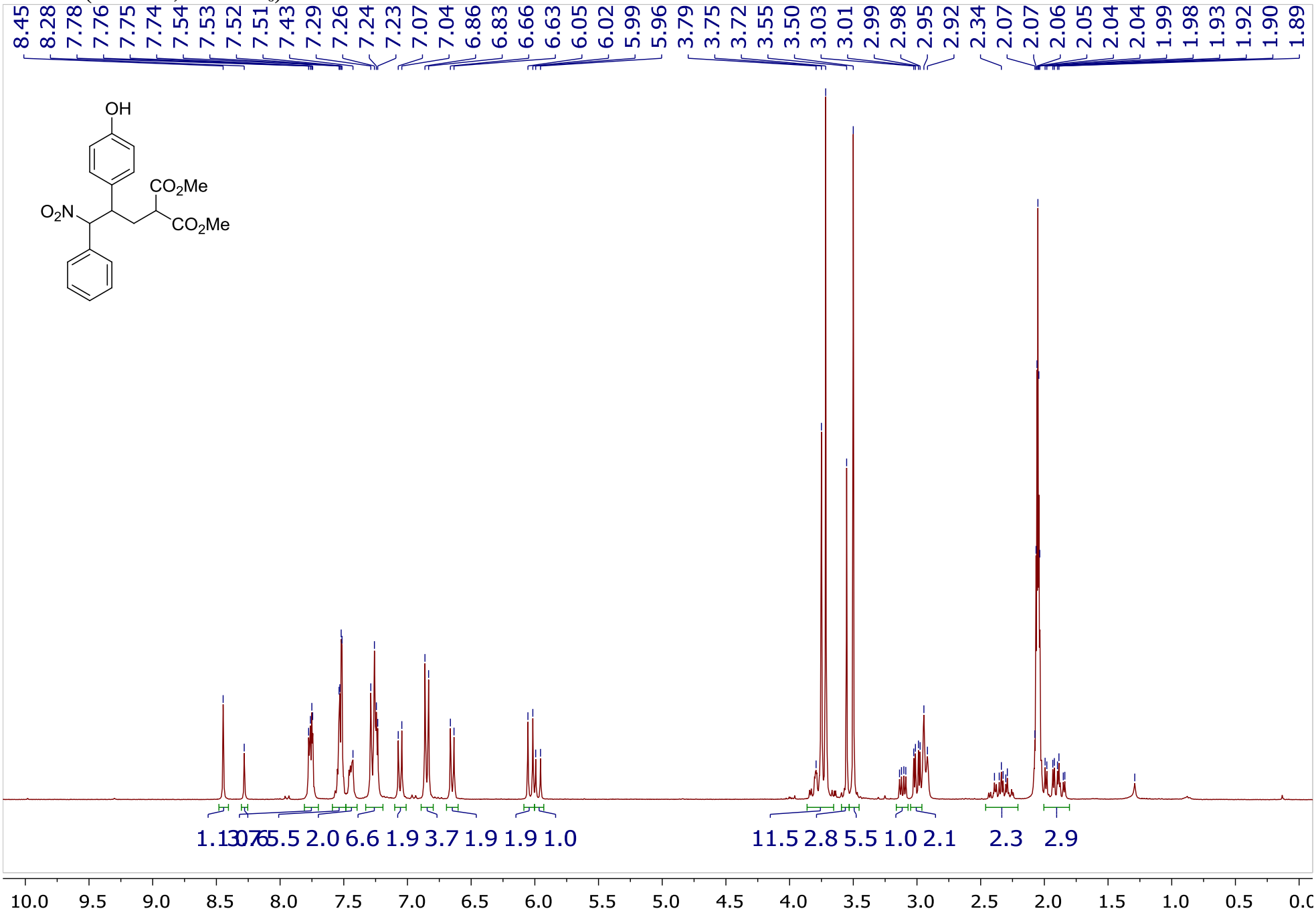
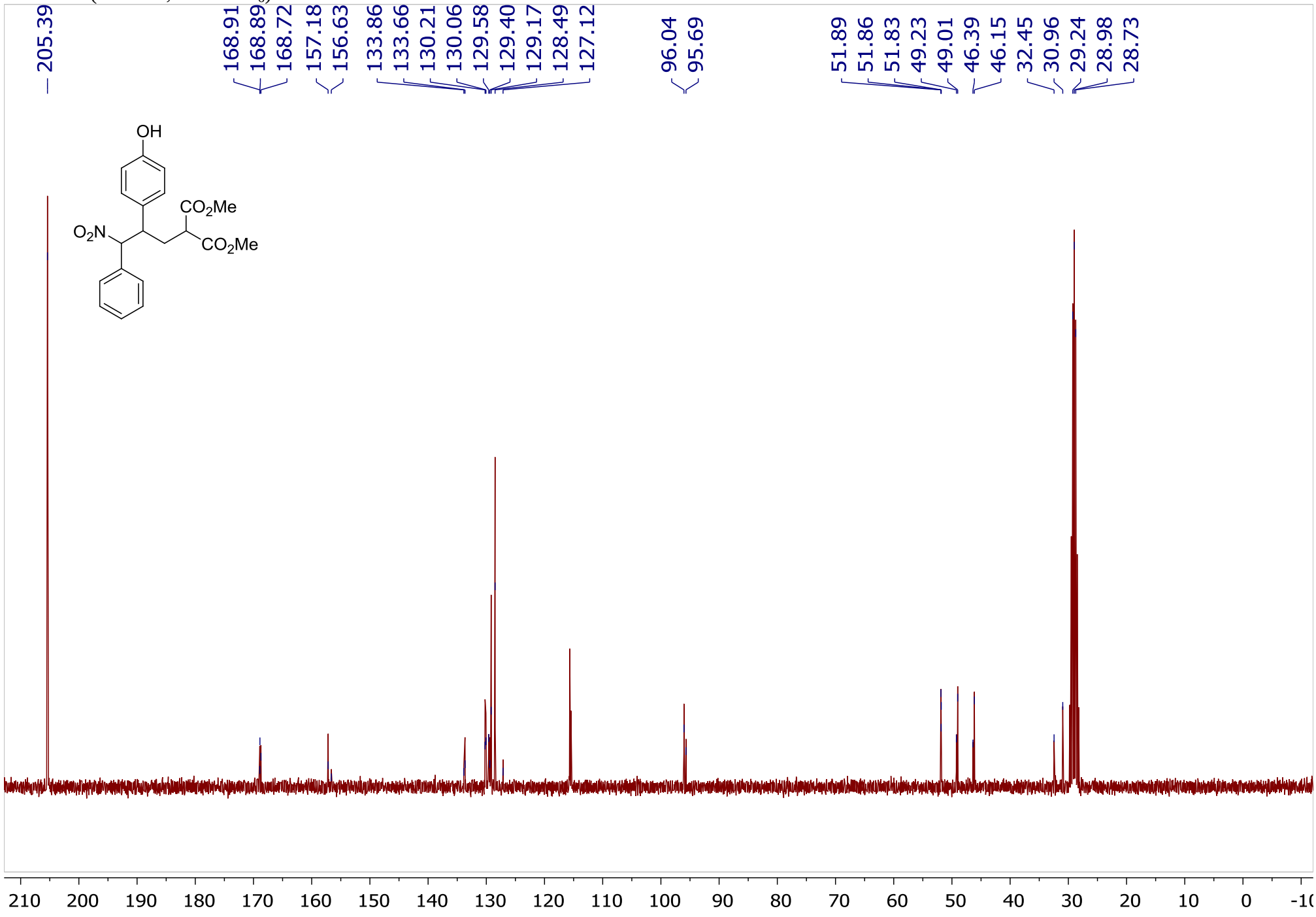
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-phenylpropyl)malonate (3ae)**, dr = 1.9:1

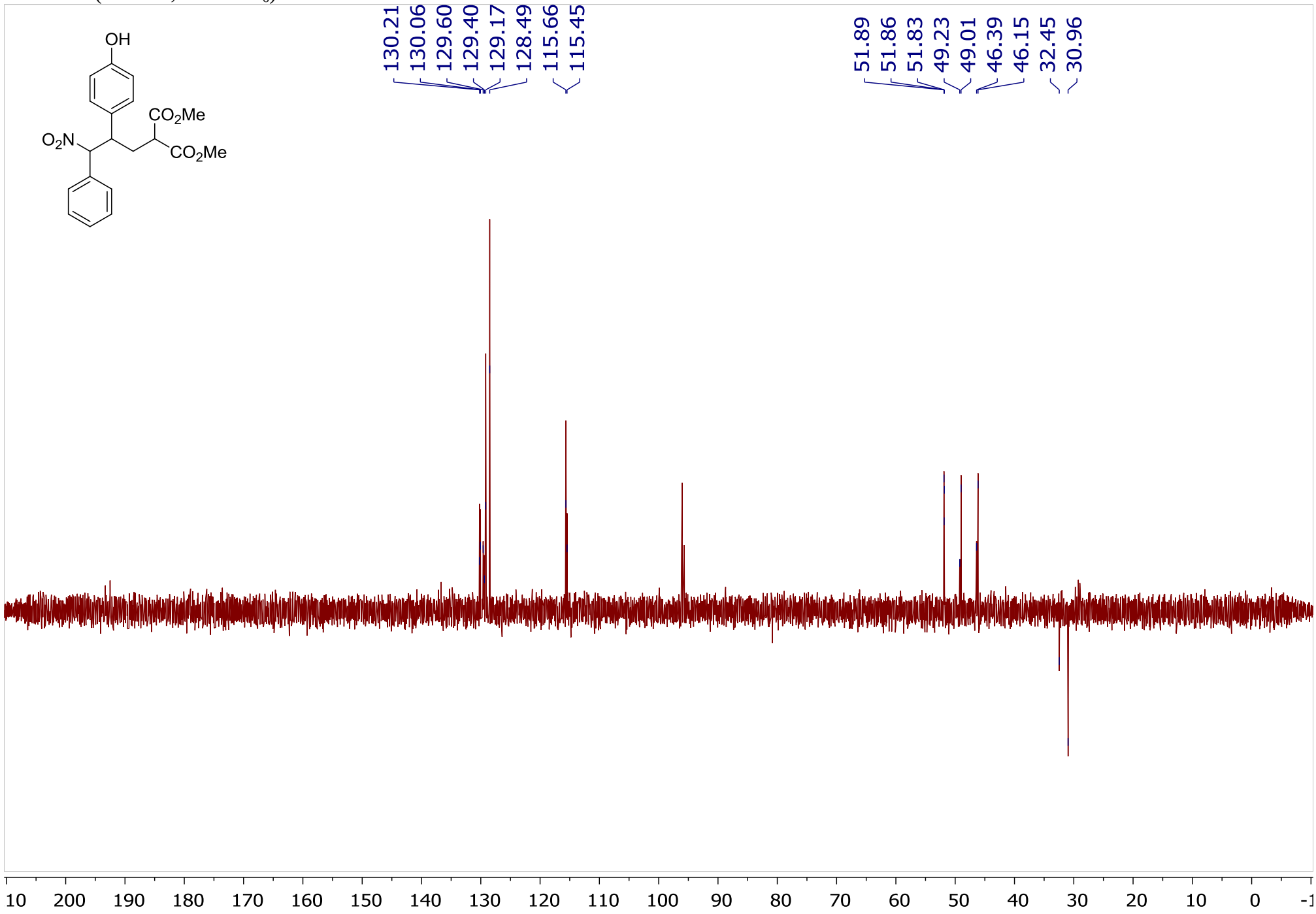
$^1$H NMR (300 MHz, acetone-$d_6$)



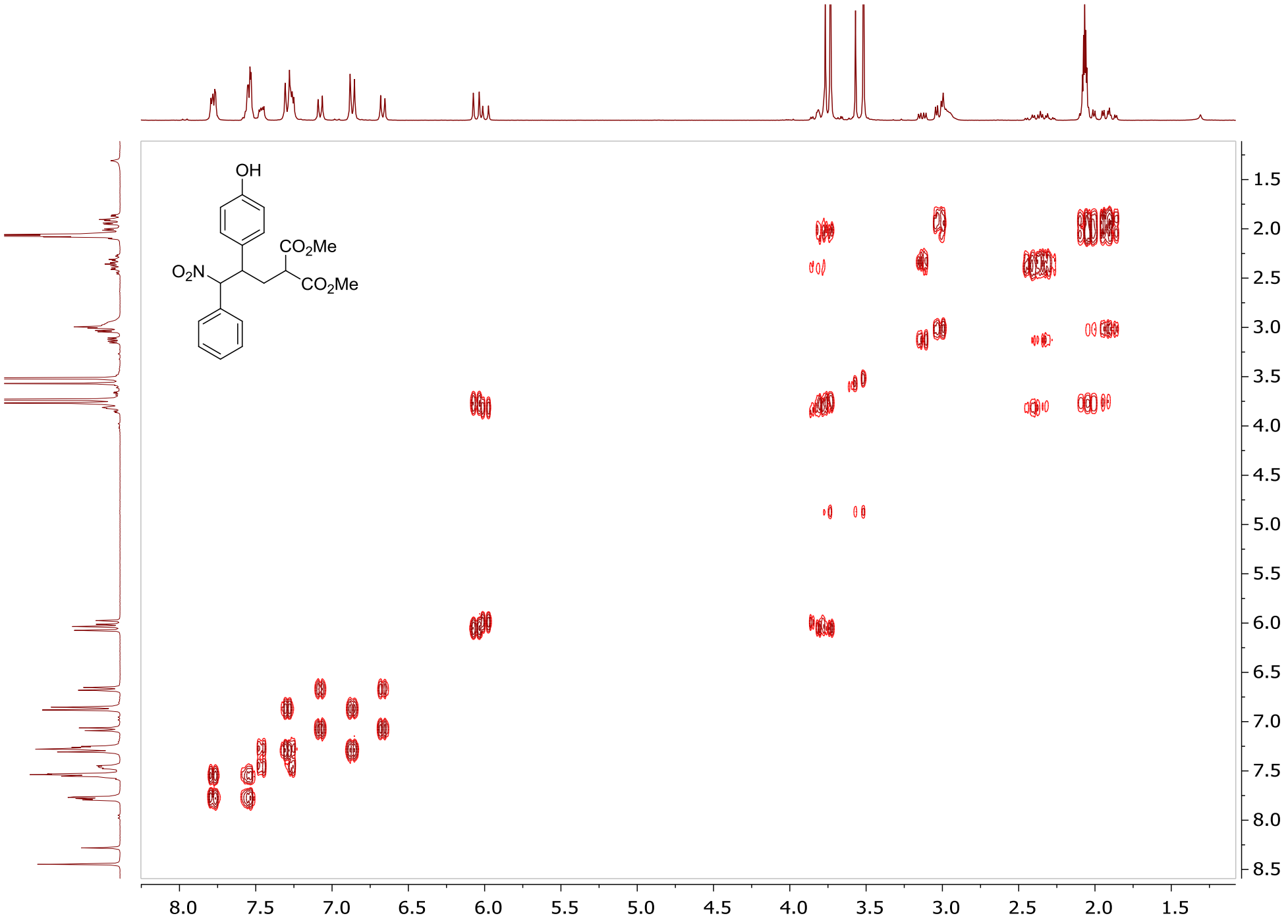
$^{13}$C NMR (75 MHz, acetone-$d_6$)



$^{13}$C DEPT (75 MHz, acetone-$d_6$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Me
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6.0
6.5
7.0
7.5
8.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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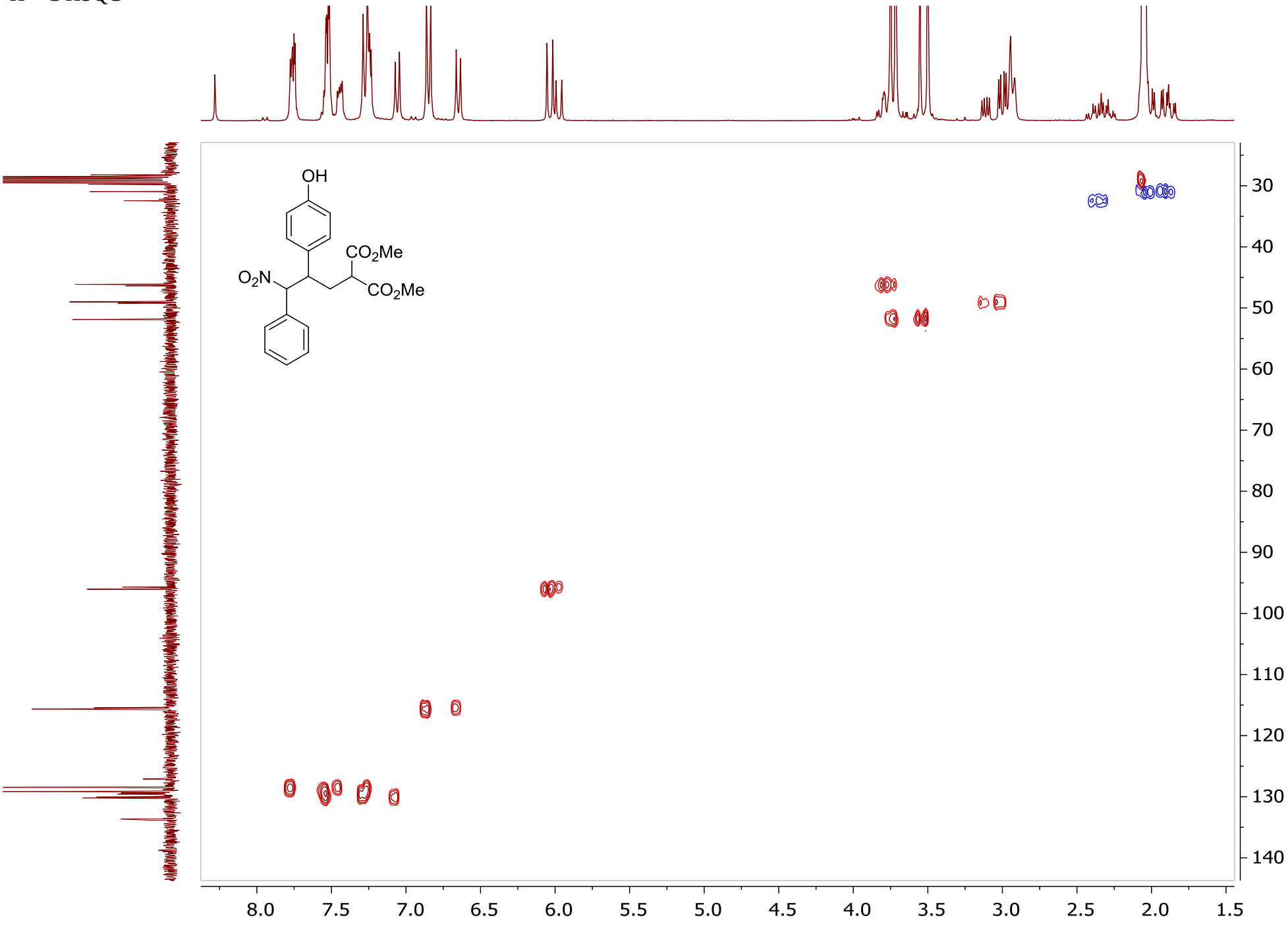
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HSQC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CO2Me
O2N
CO2Me
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40
50
60
70
80
90
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110
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130
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7.0
6.5
6.0
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4.0
3.5
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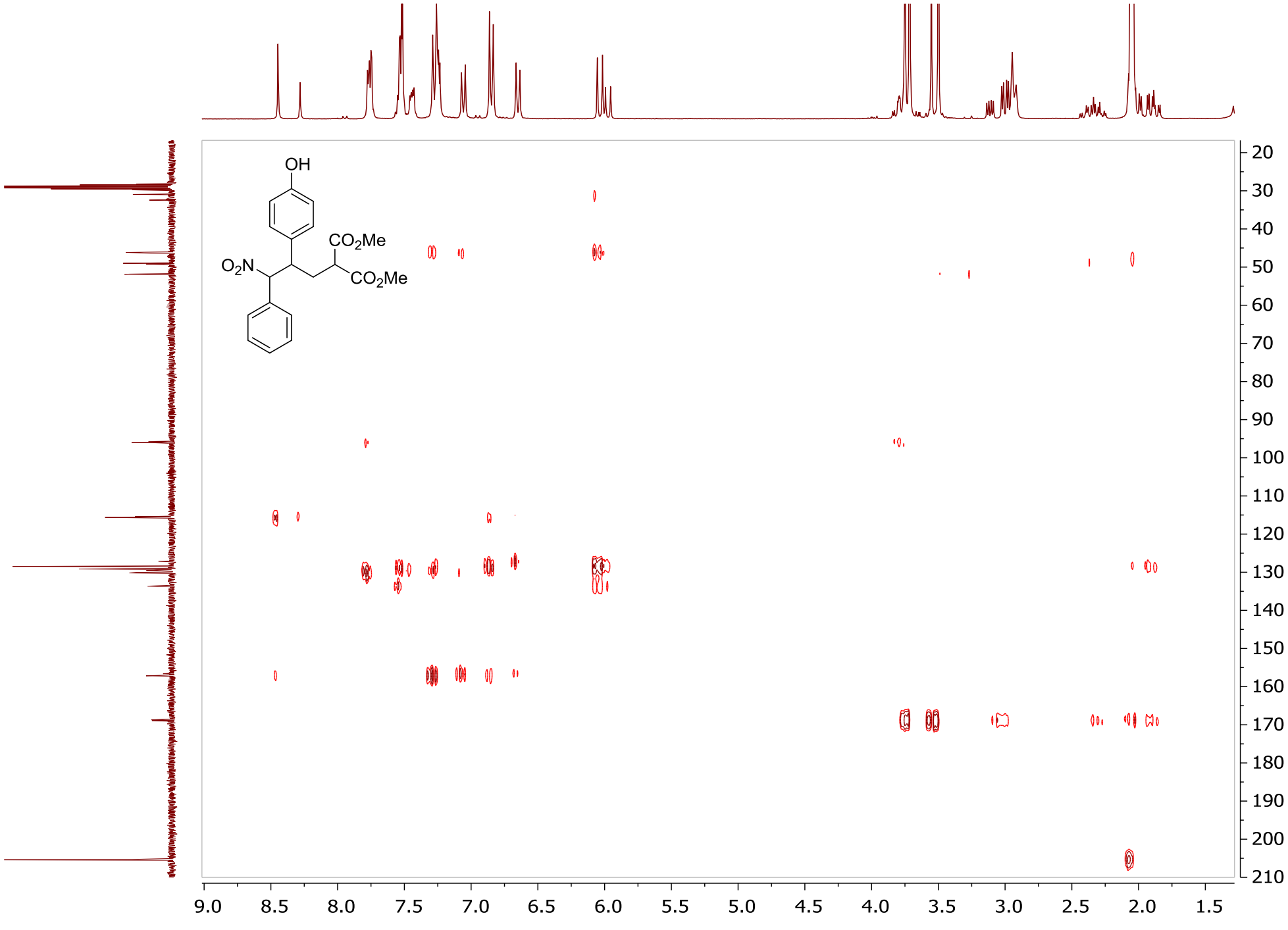
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HMBC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170
180
190
200
210
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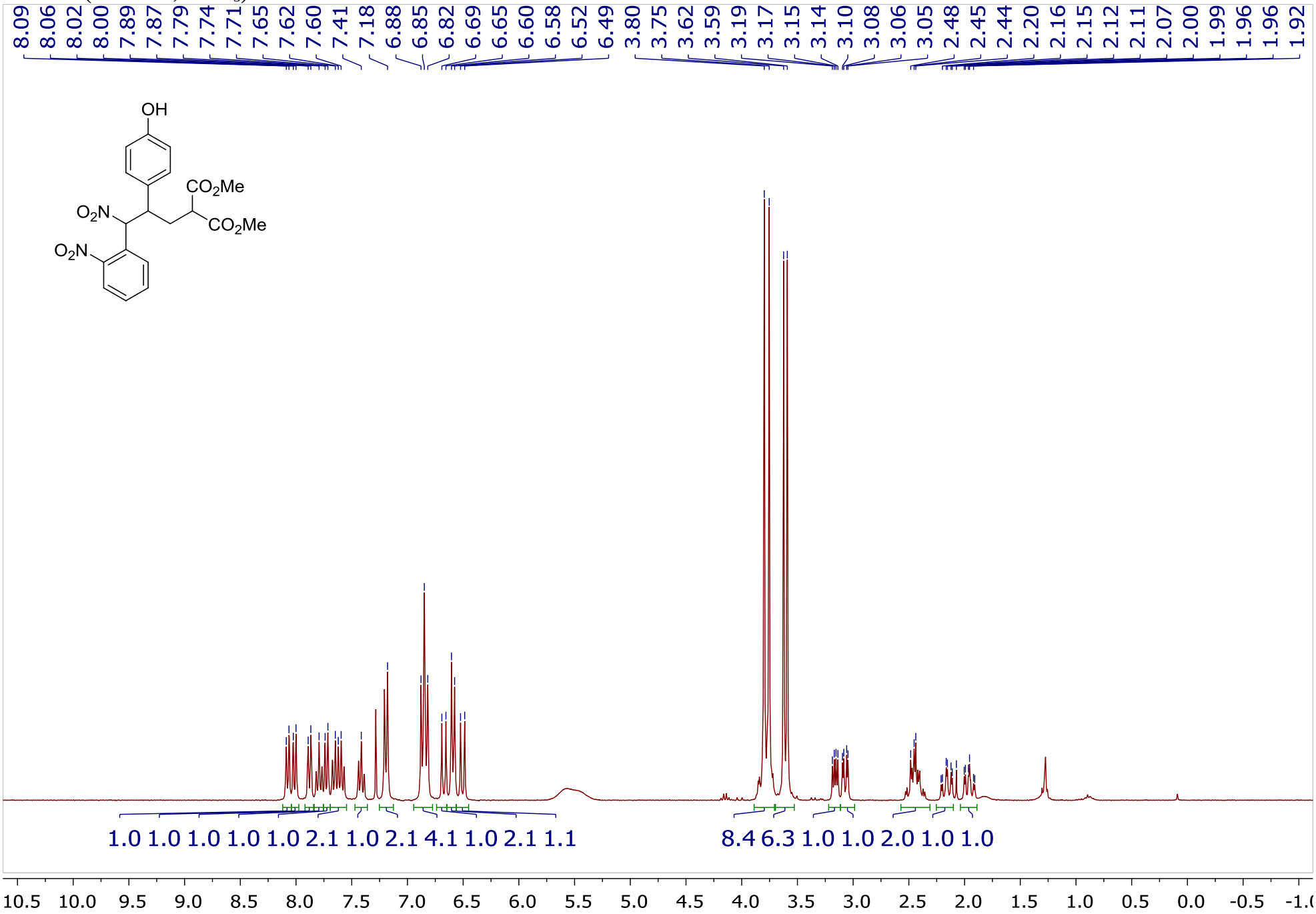
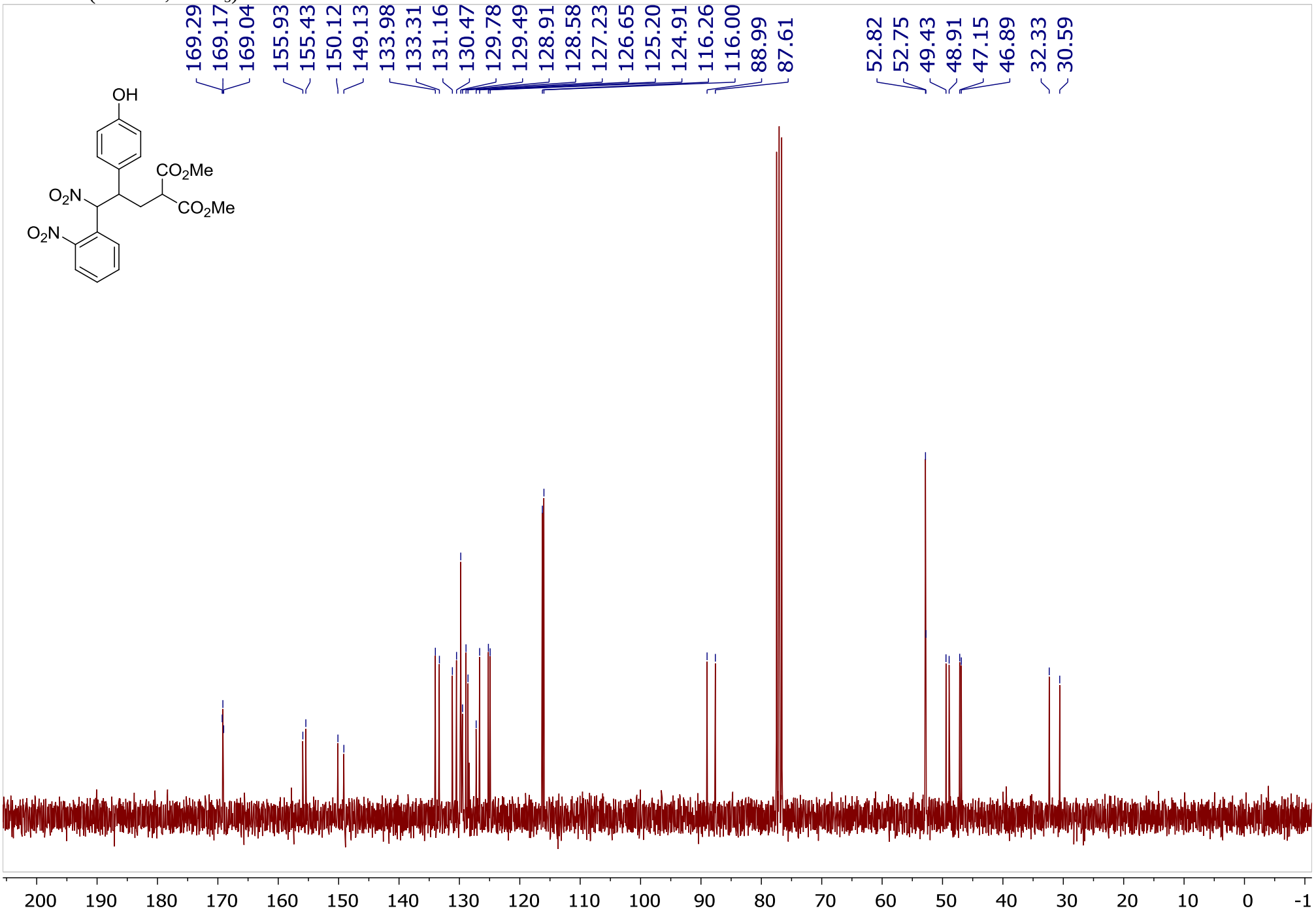
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-(2-nitrophenyl)propyl)malonate (3af)**, dr = 1:1

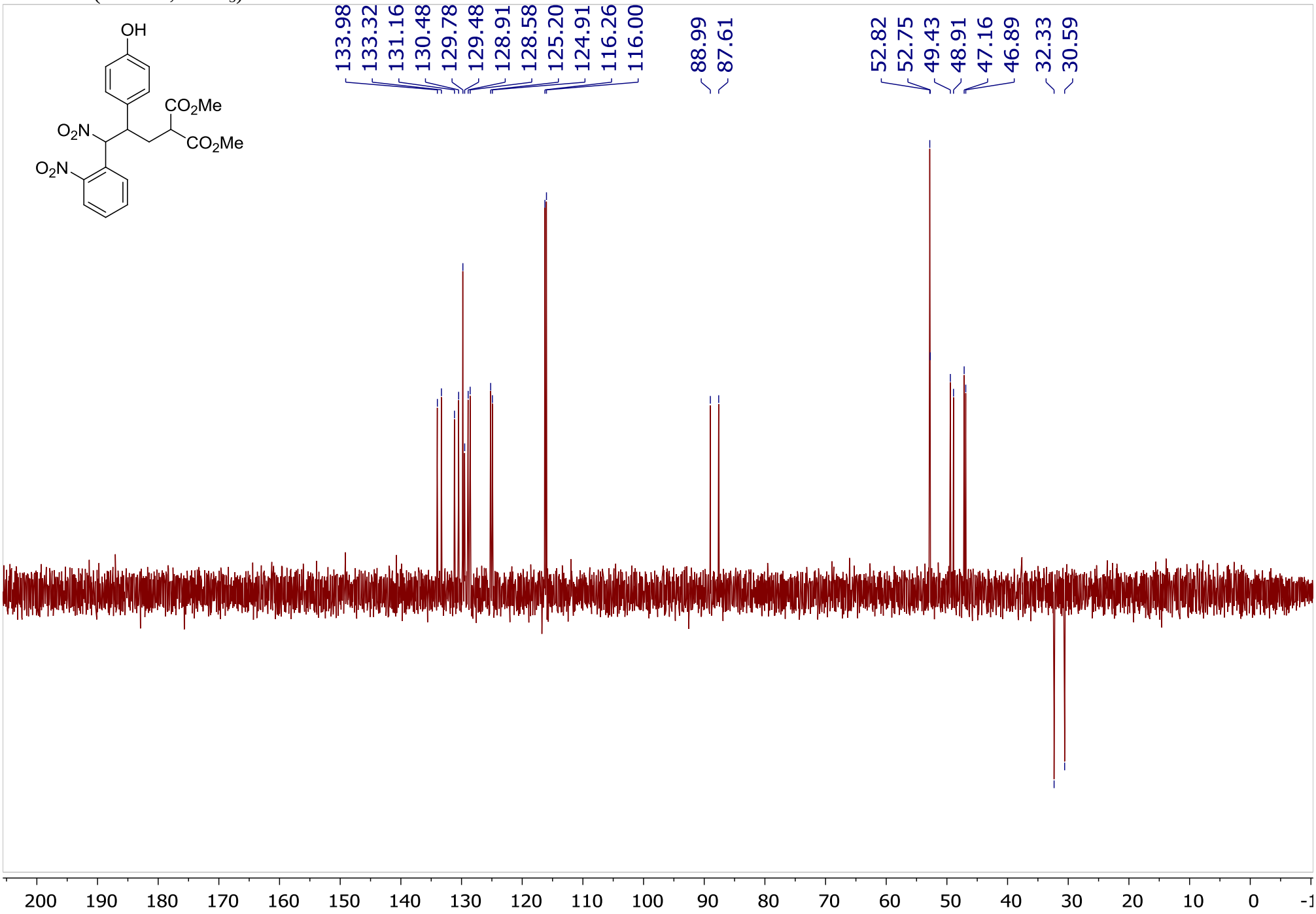
$^1$H NMR (300 MHz, $CDCl_3$)



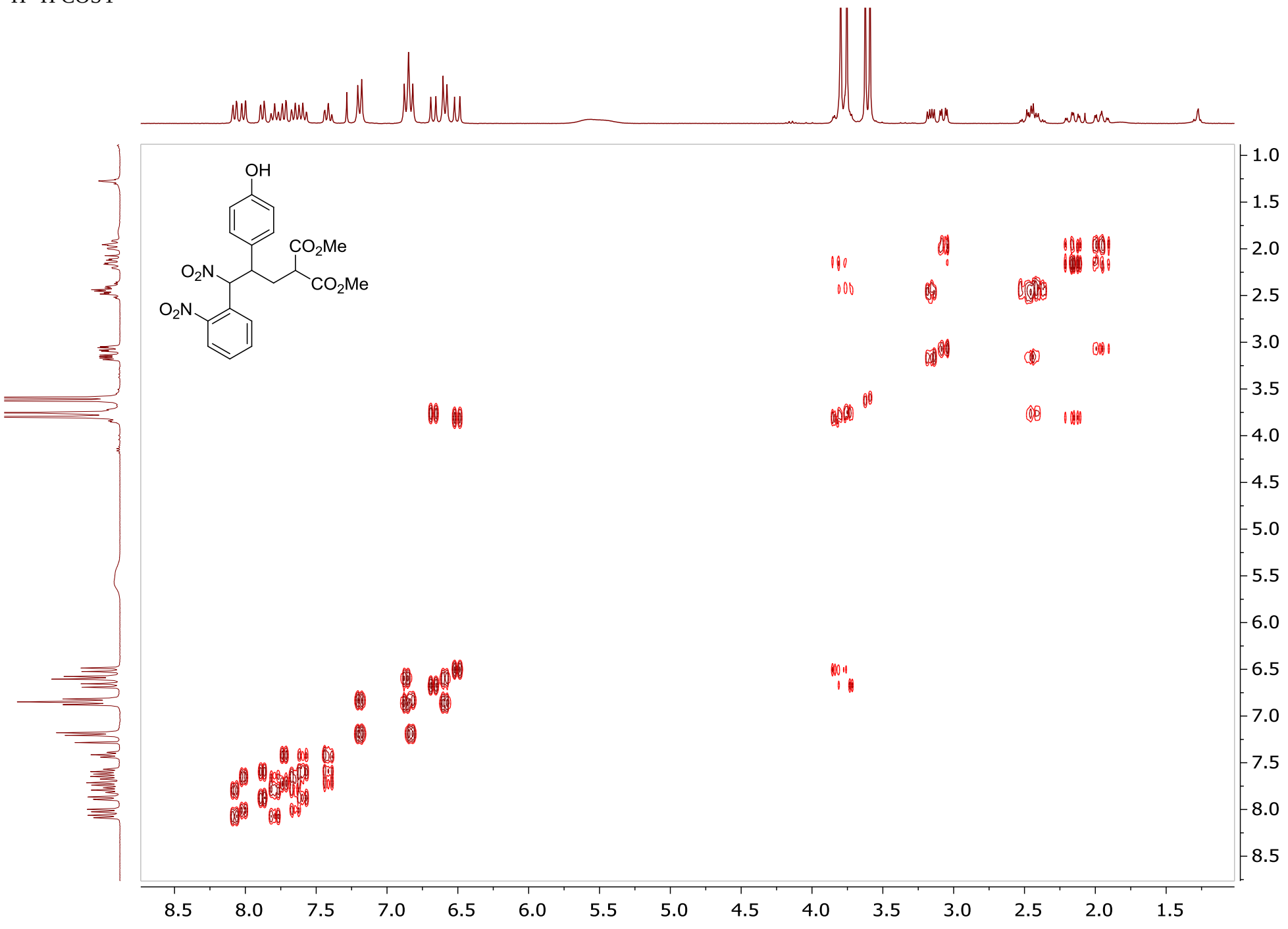
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Me
O2N
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1.5
2.0
2.5
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3.5
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4.5
5.0
5.5
6.0
6.5
7.0
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8.5
8.5
8.0
7.5
7.0
6.5
6.0
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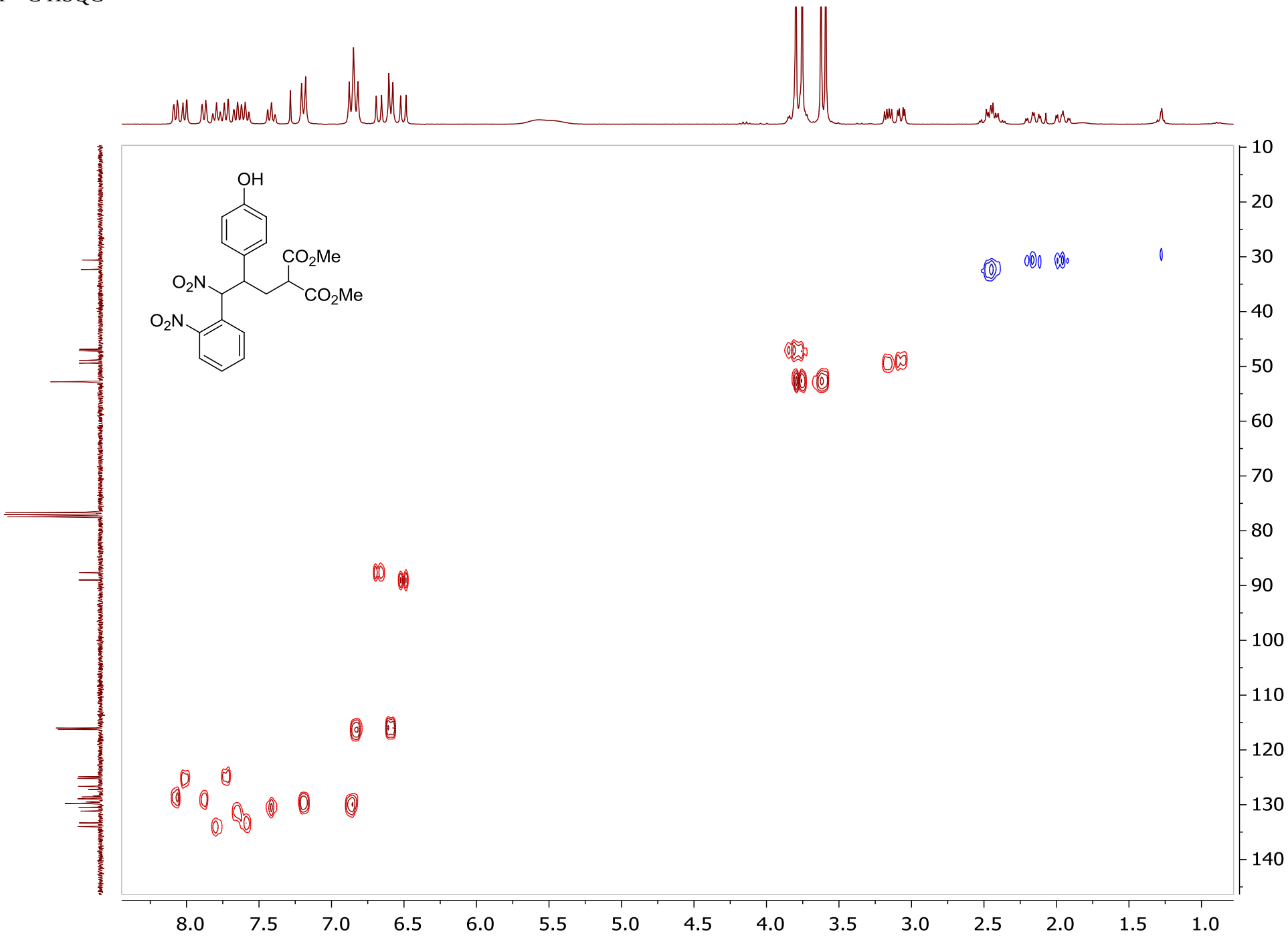
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}$H-$^{13}$C HSQC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CO2Me
O2N
CO2Me
O2N
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20
30
40
50
60
70
80
90
100
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8.0
7.5
7.0
6.5
6.0
5.5
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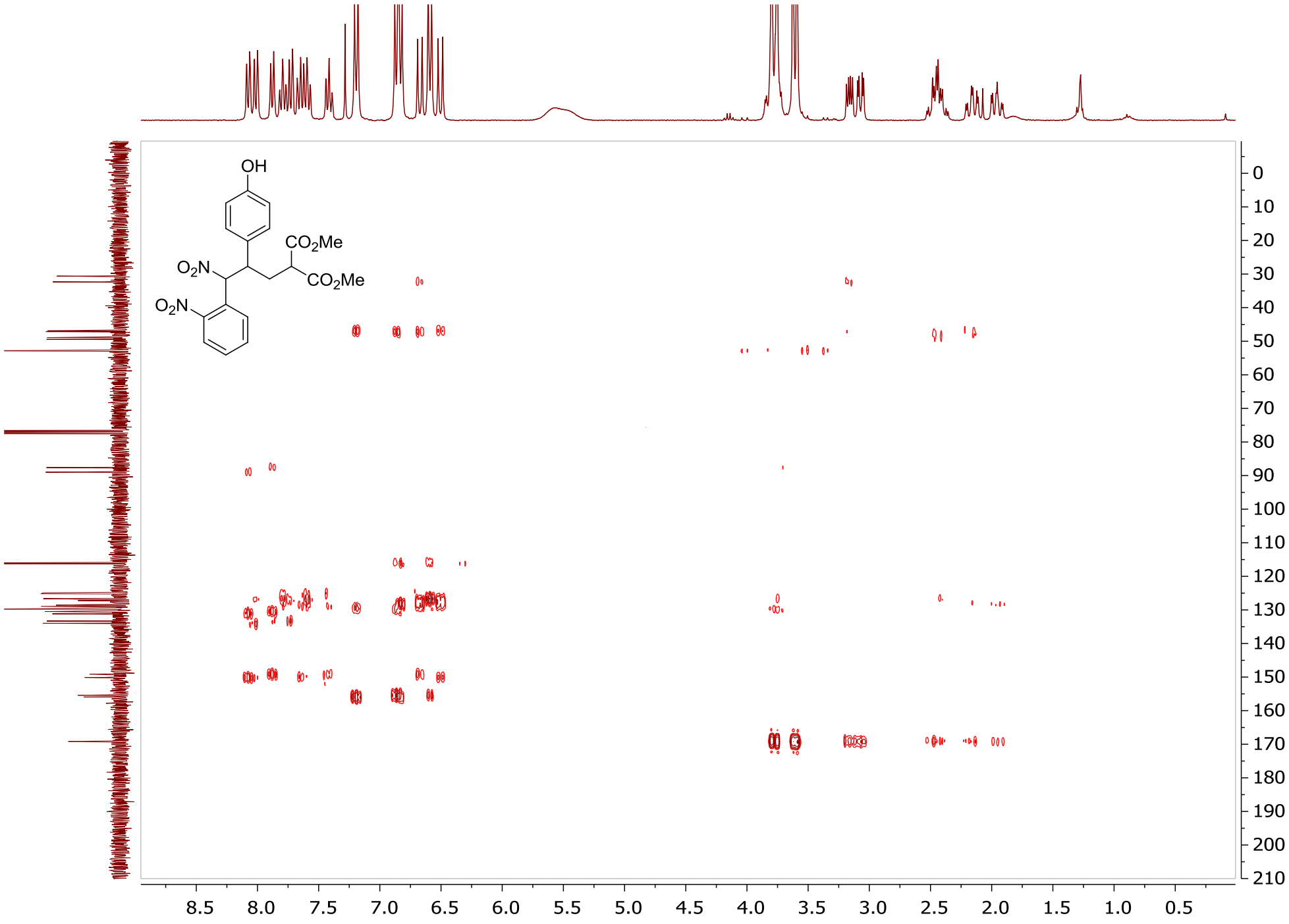
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HMBC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O2N
CO2Me
O2N
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120
130
140
150
160
170
180
190
200
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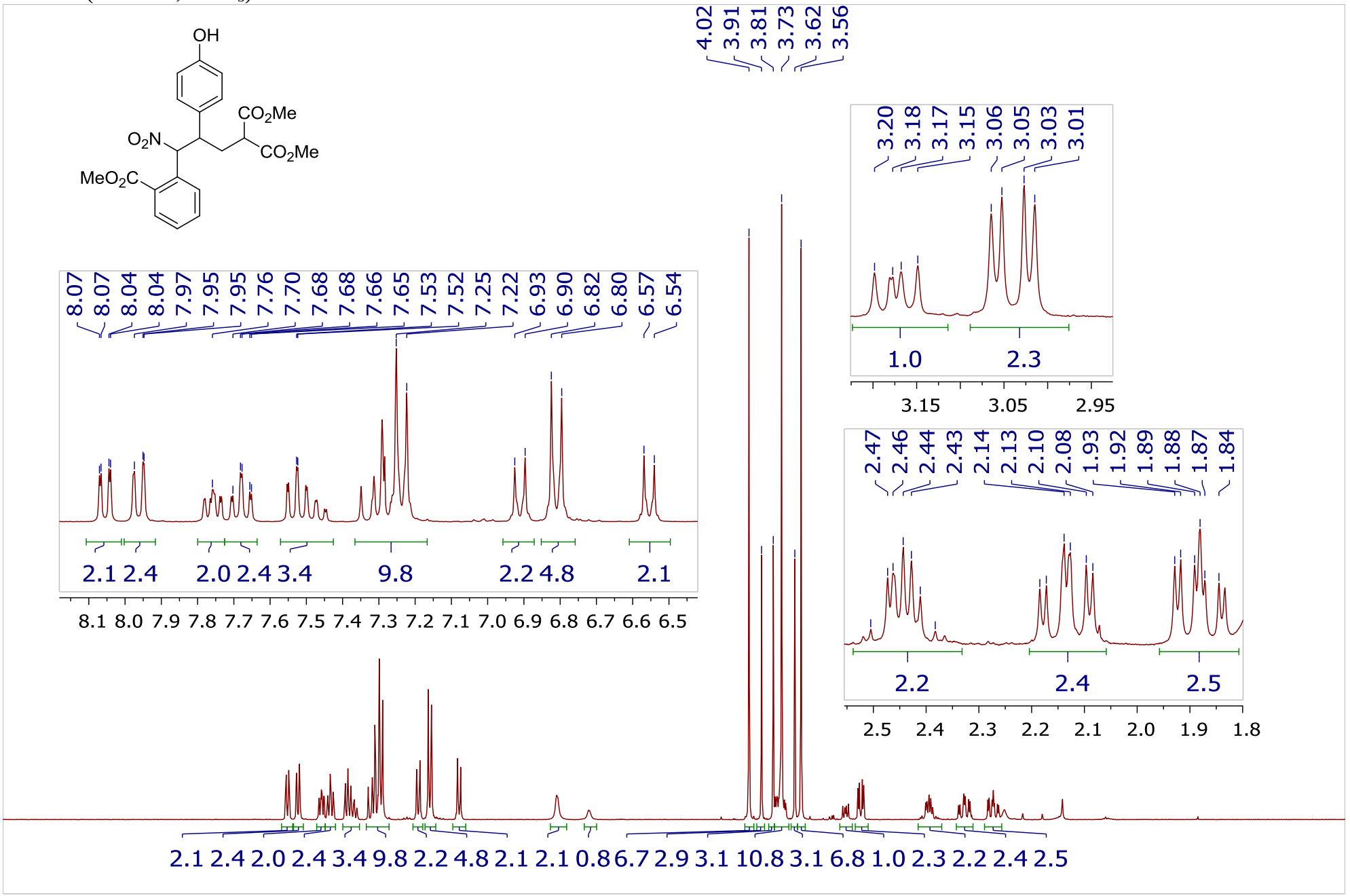
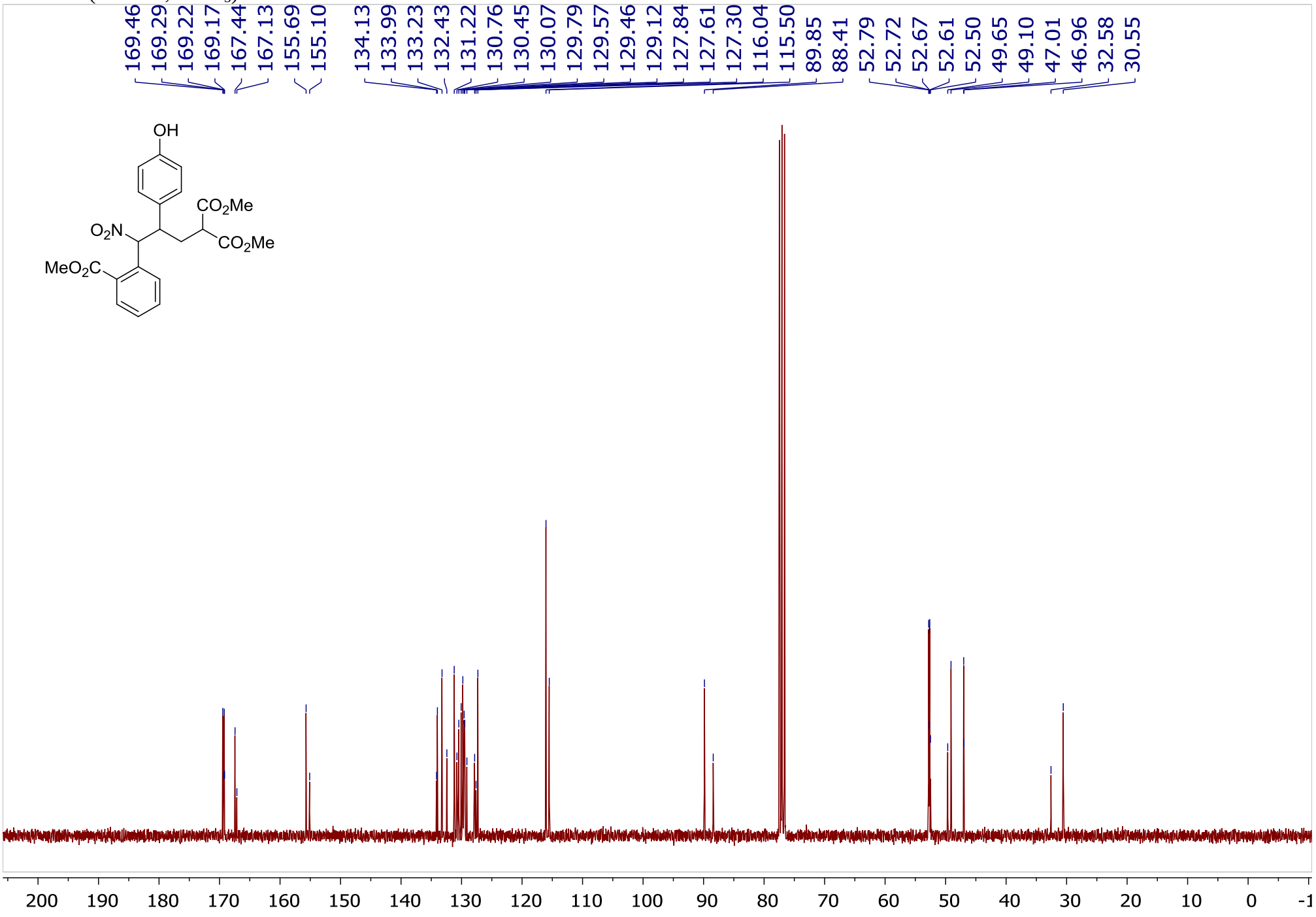
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-(2-(methoxycarbonyl)phenyl)-3-nitropropyl)malonate (3ag)**, dr = 2.3:1

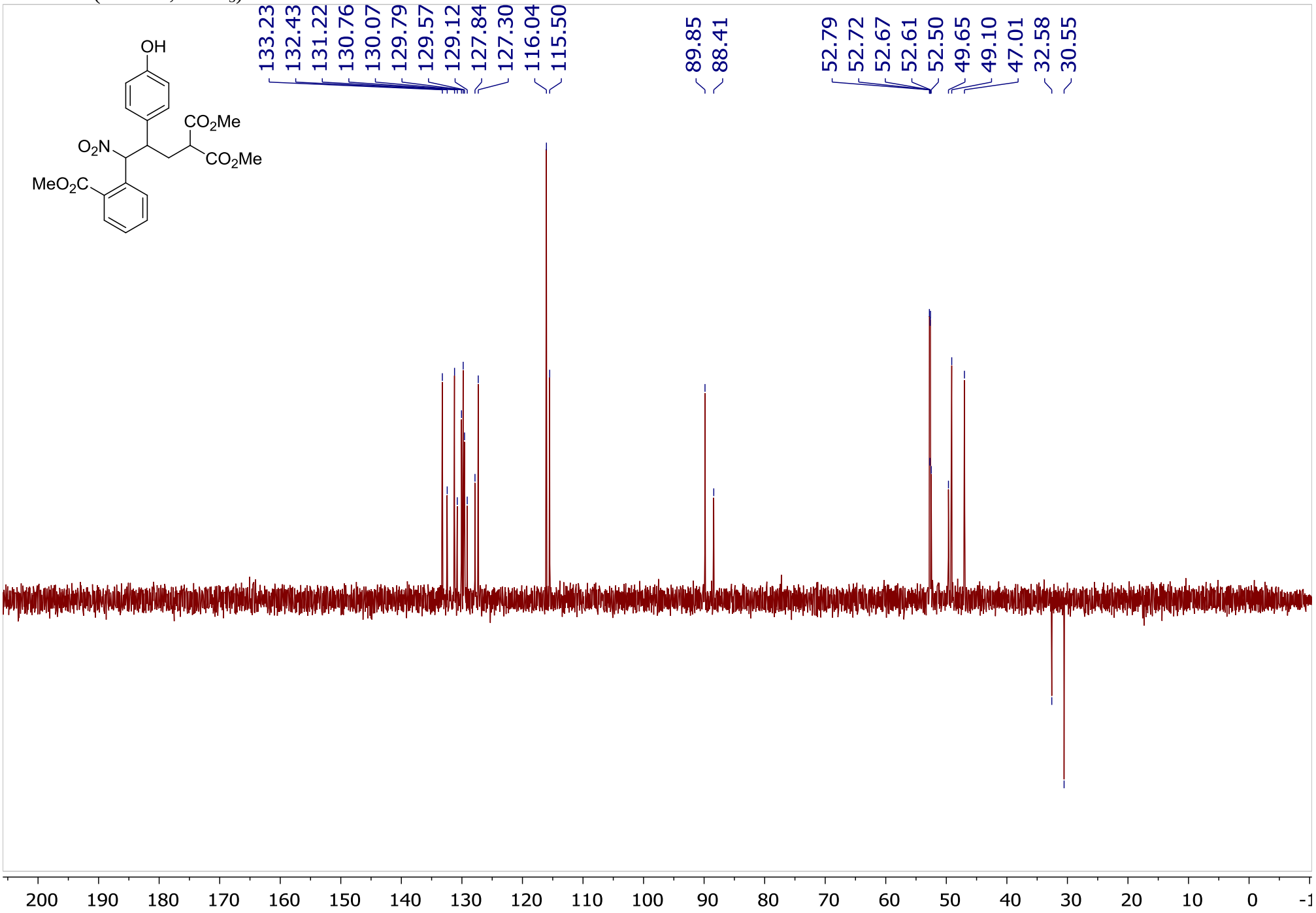
$^1$H NMR (300 MHz, $CDCl_3$)



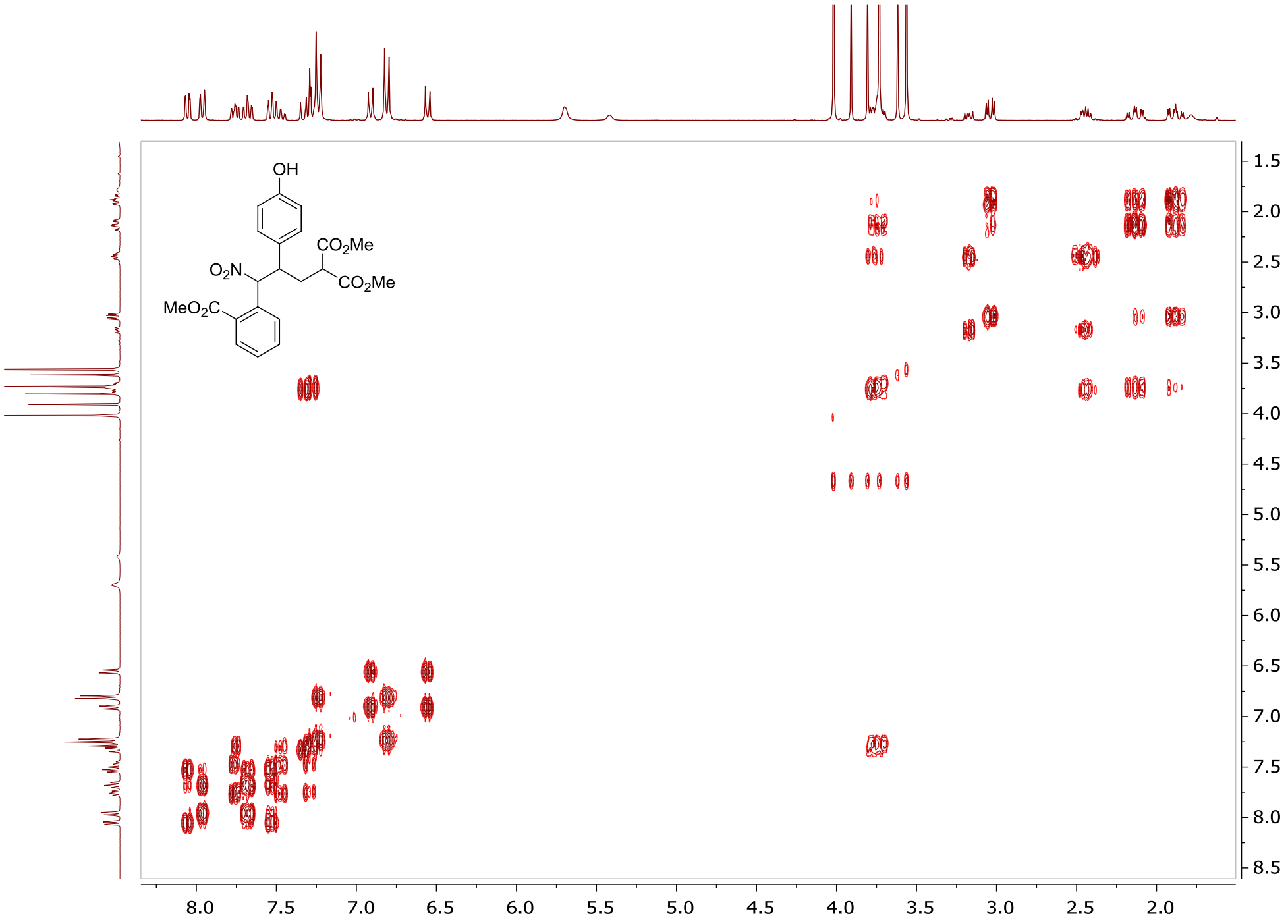
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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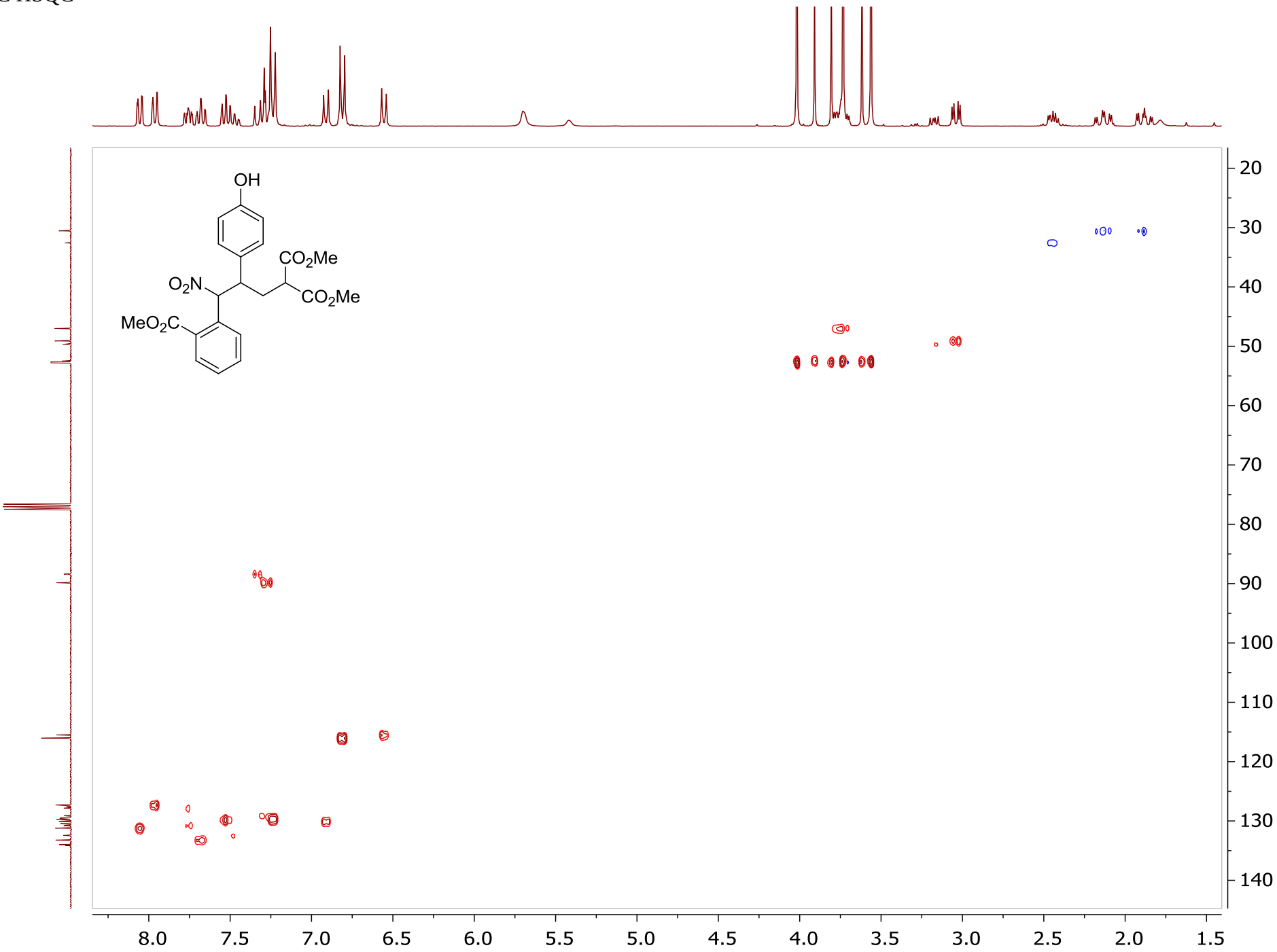
CO2Me
O2N
CO2Me
MeO2C
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

$^{1}H$-$^{13}C$ HSQC


OH
CO2Me
O2N
CO2Me
MeO2C
20
30
40
50
60
70
80
90
100
110
120
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140
8.0
7.5
7.0
6.5
6.0
5.5
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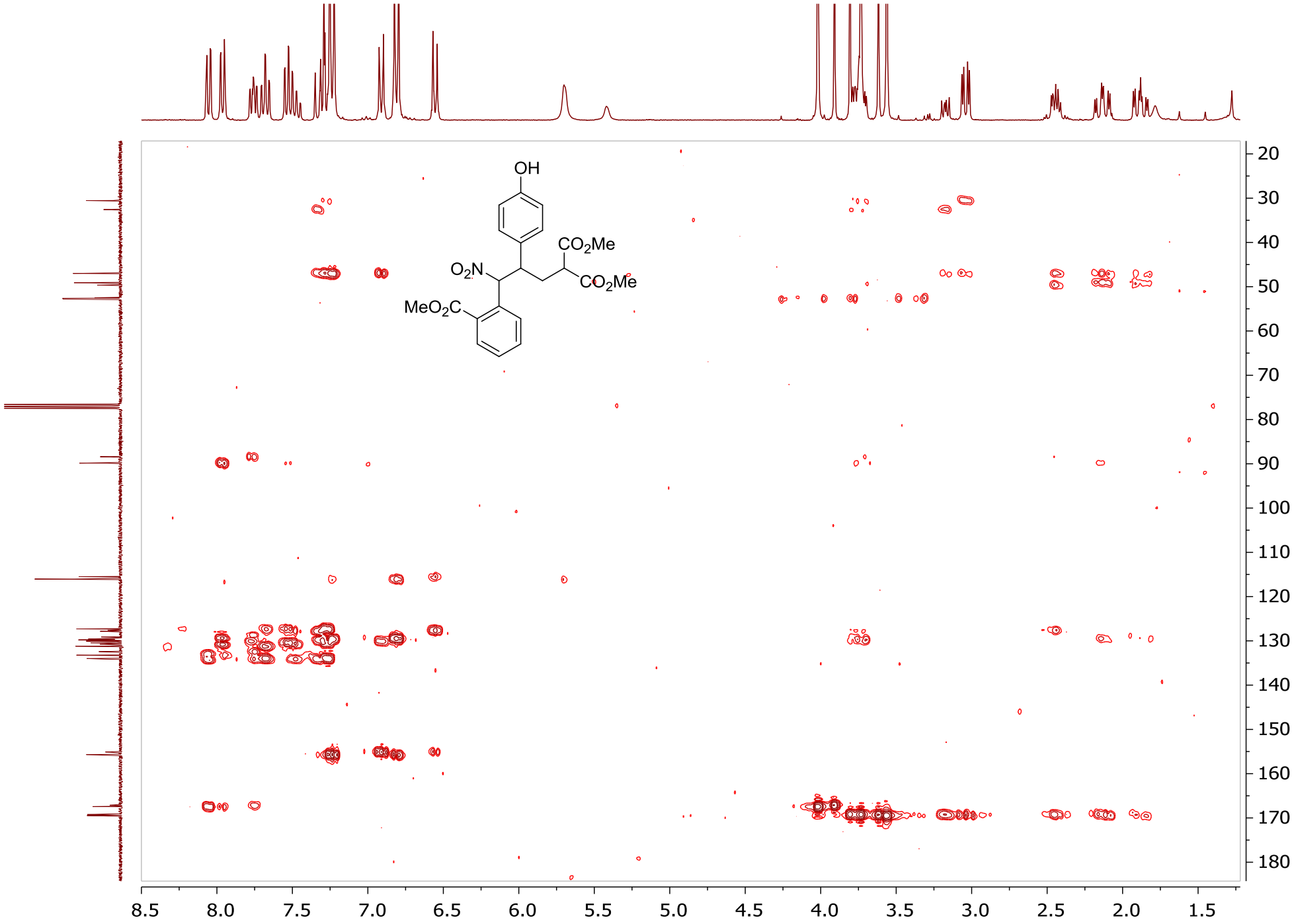
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HMBC


OH
$CO_2Me$
$O_2N$
$CO_2Me$
$MeO_2C$
20
30
40
50
60
70
80
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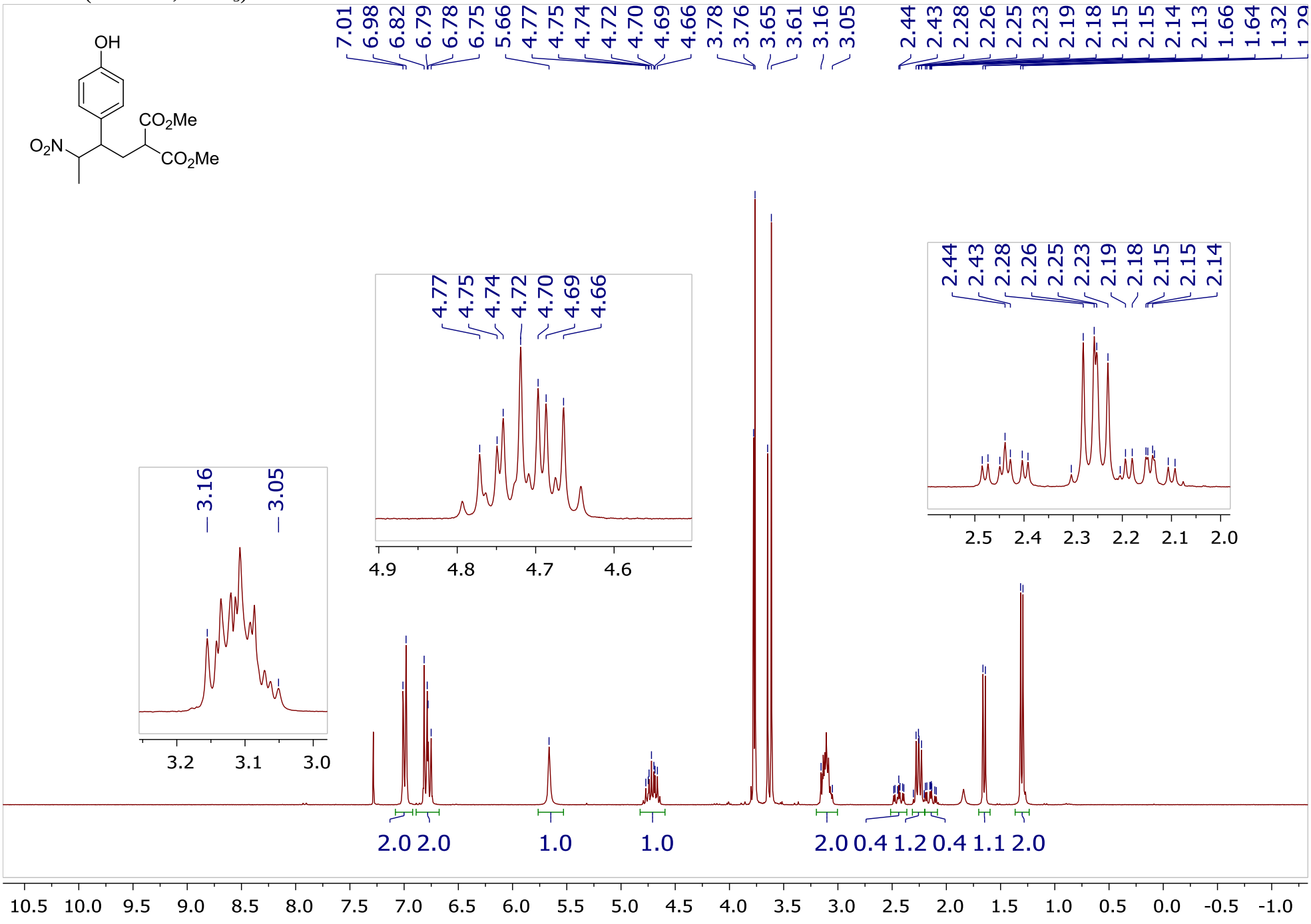
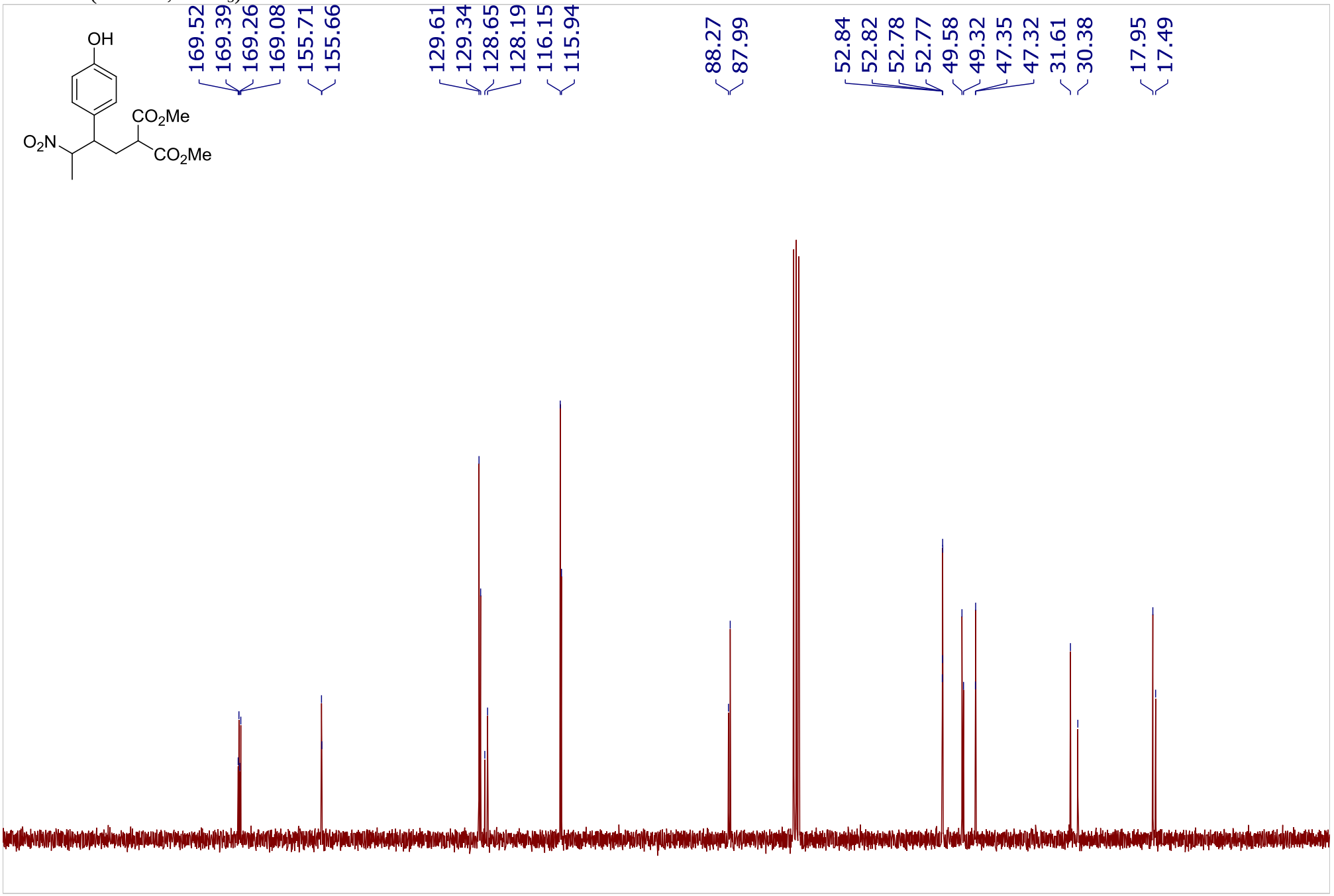
100
110
120
130
140
150
160
170
180
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitrobutyl)malonate (3ah)**, dr = 1.6:1

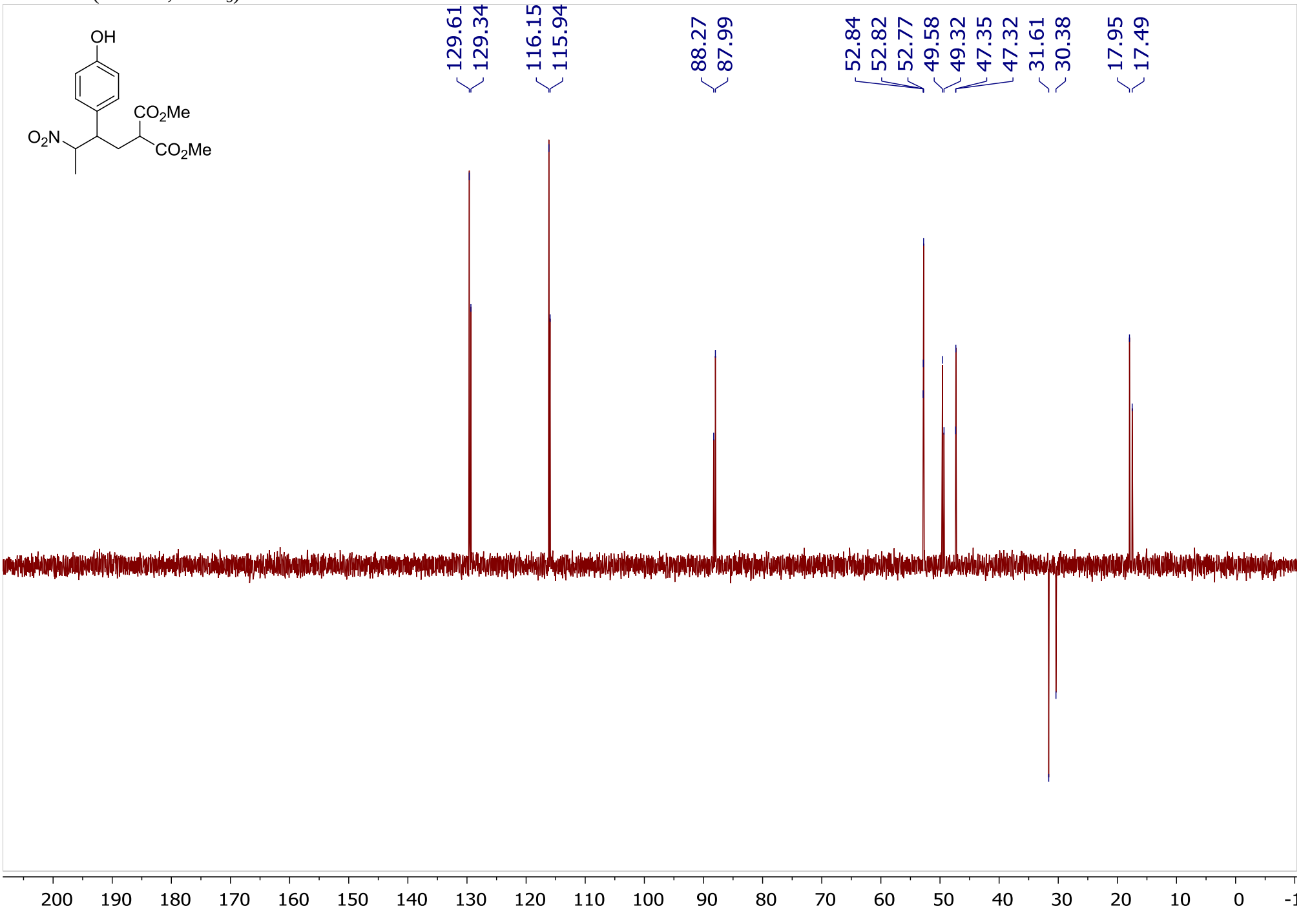
$^1$H NMR (300 MHz, $CDCl_3$)



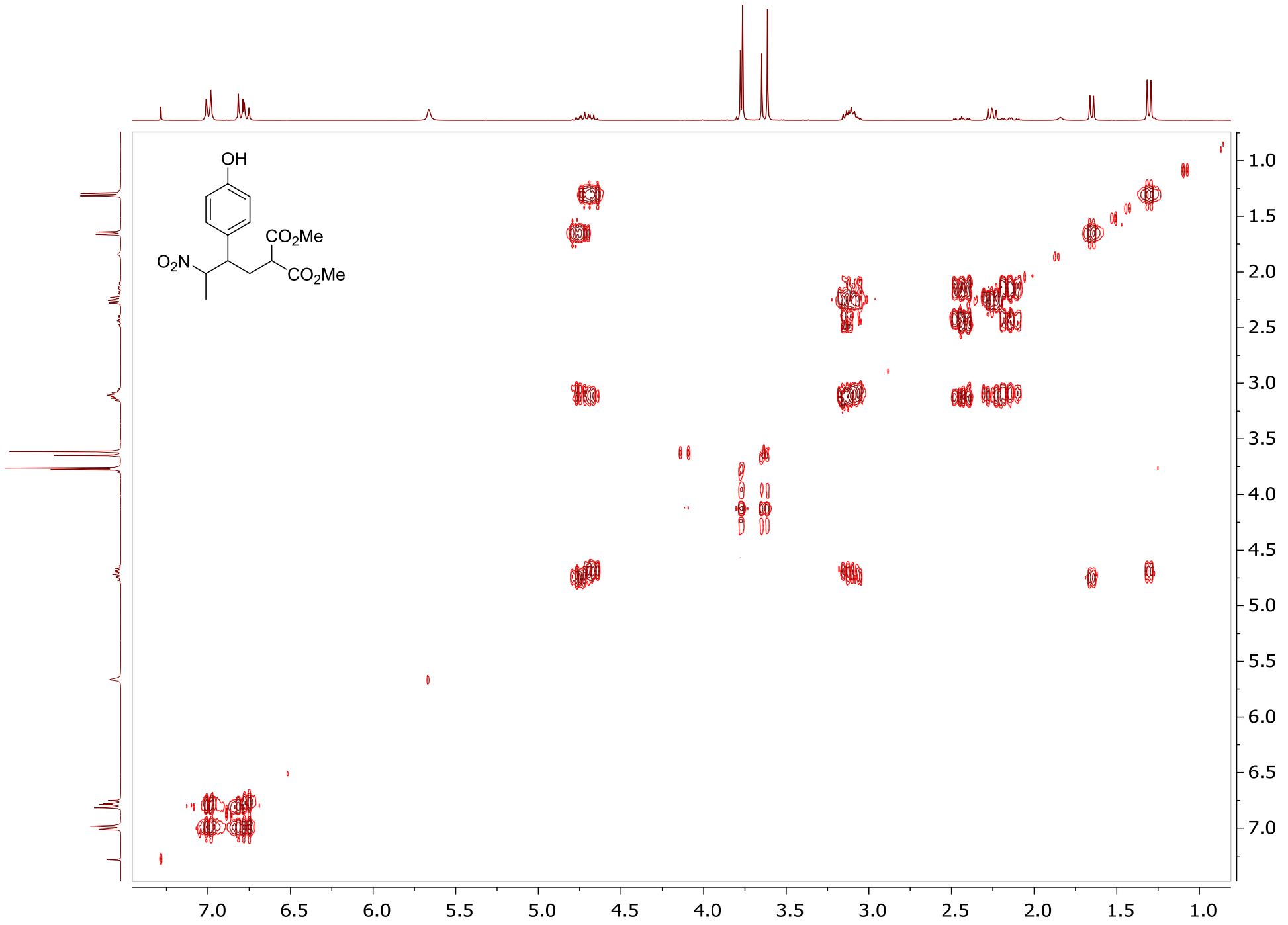
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
O2N
CO2Me
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1.5
2.0
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3.5
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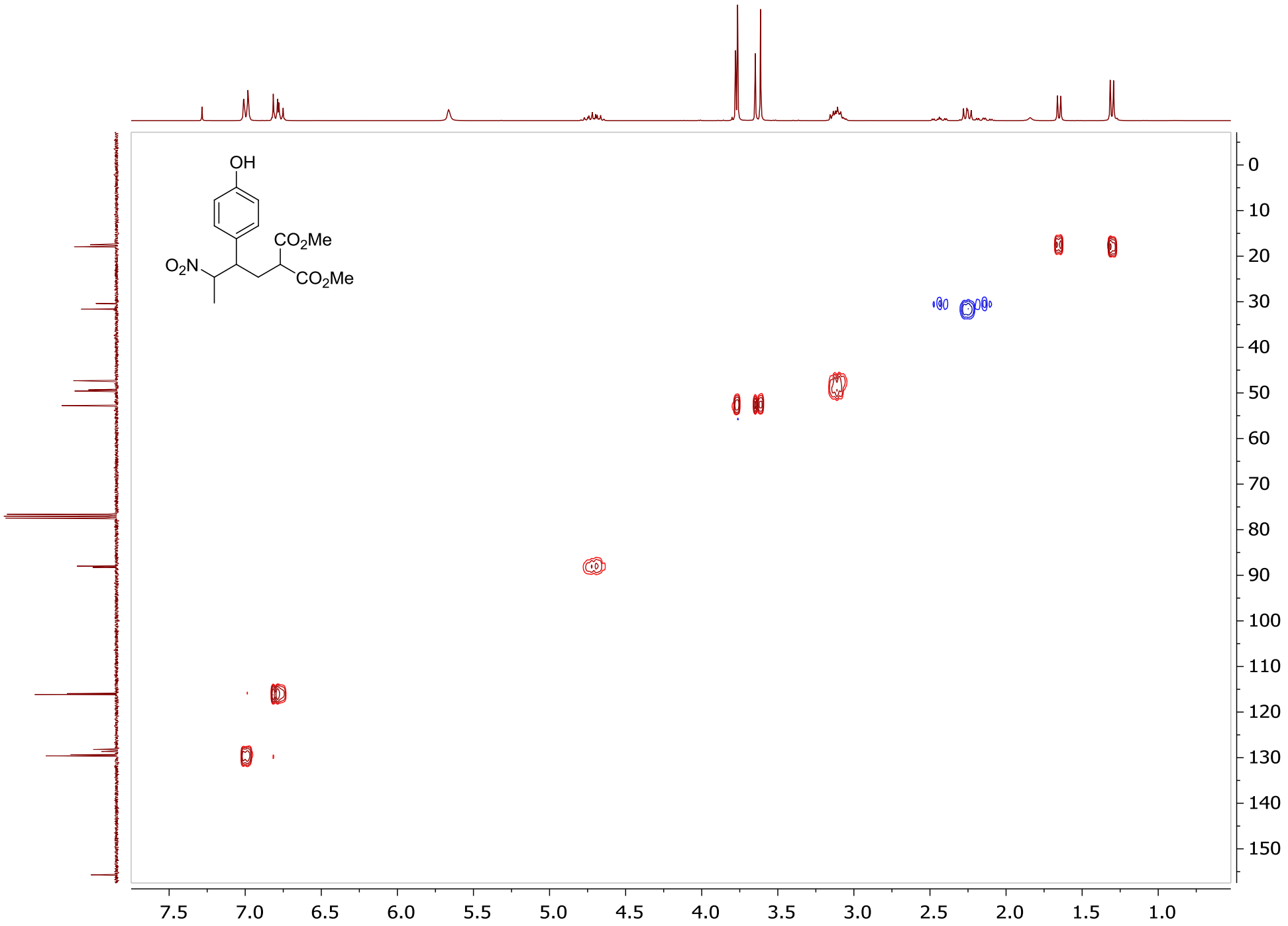
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HSQC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CO2Me
O2N
CO2Me
0
10
20
30
40
50
60
70
80
90
100
110
120
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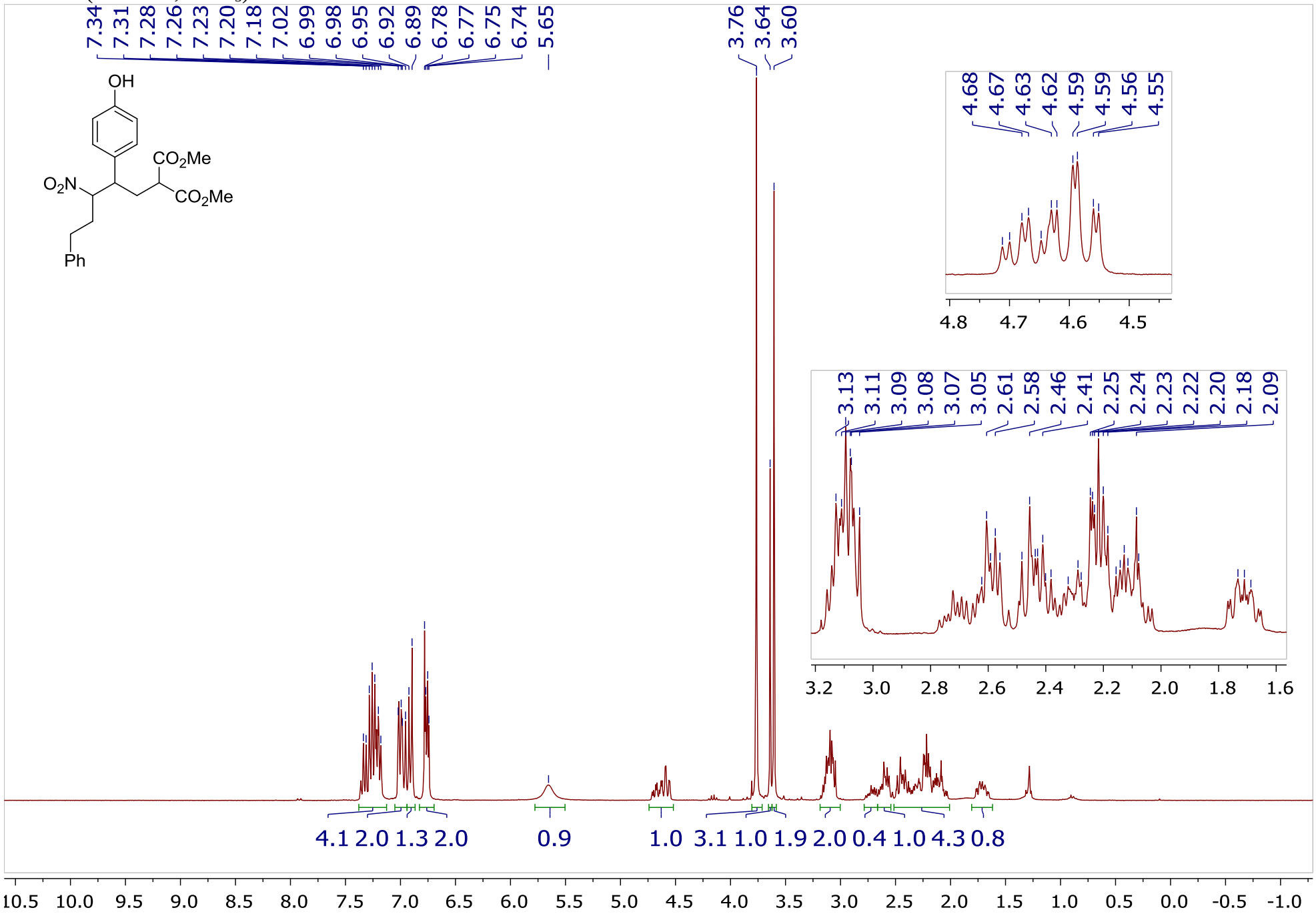
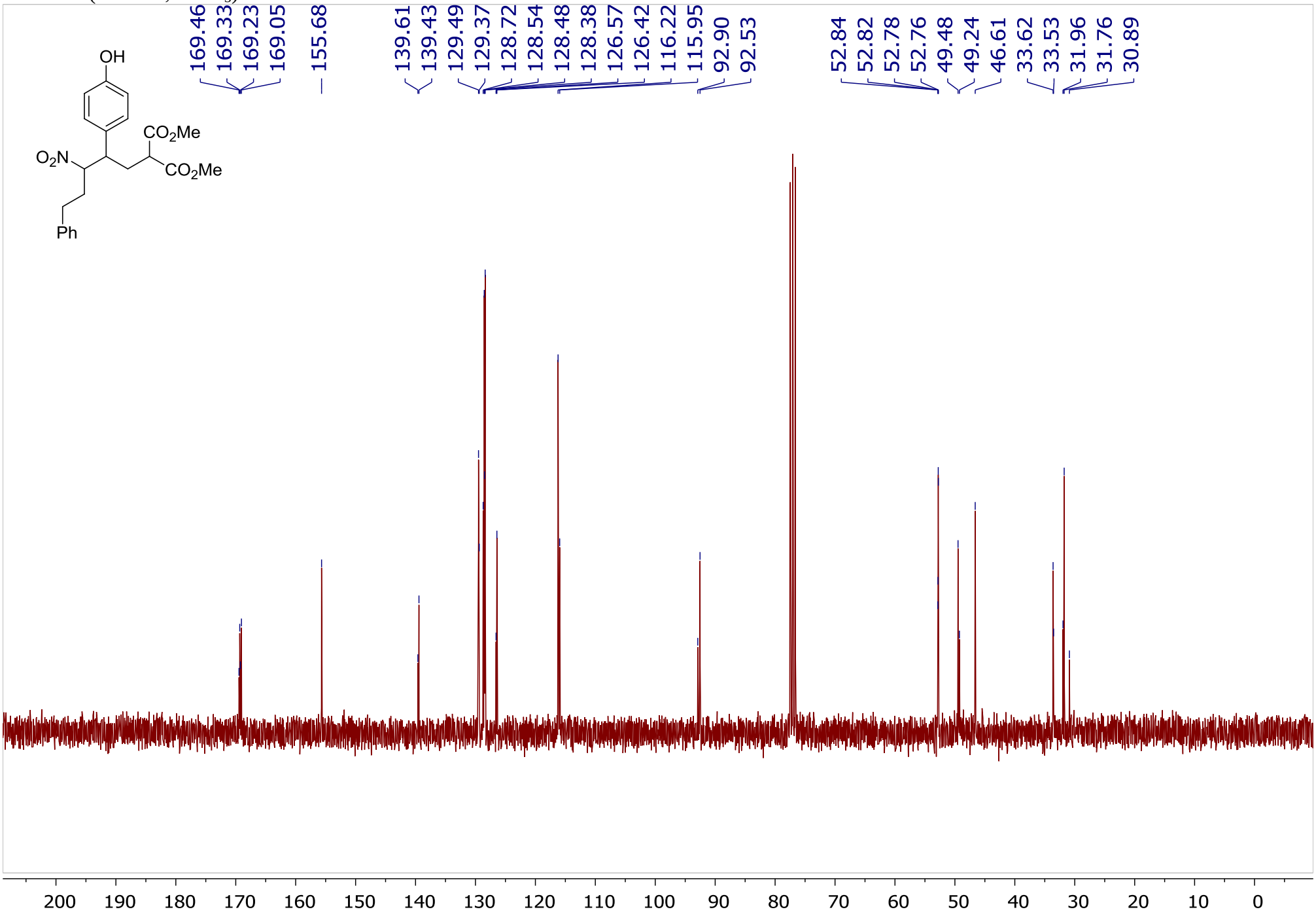
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-5-phenylpentyl)malonate (3ai)**, dr = 1.8:1

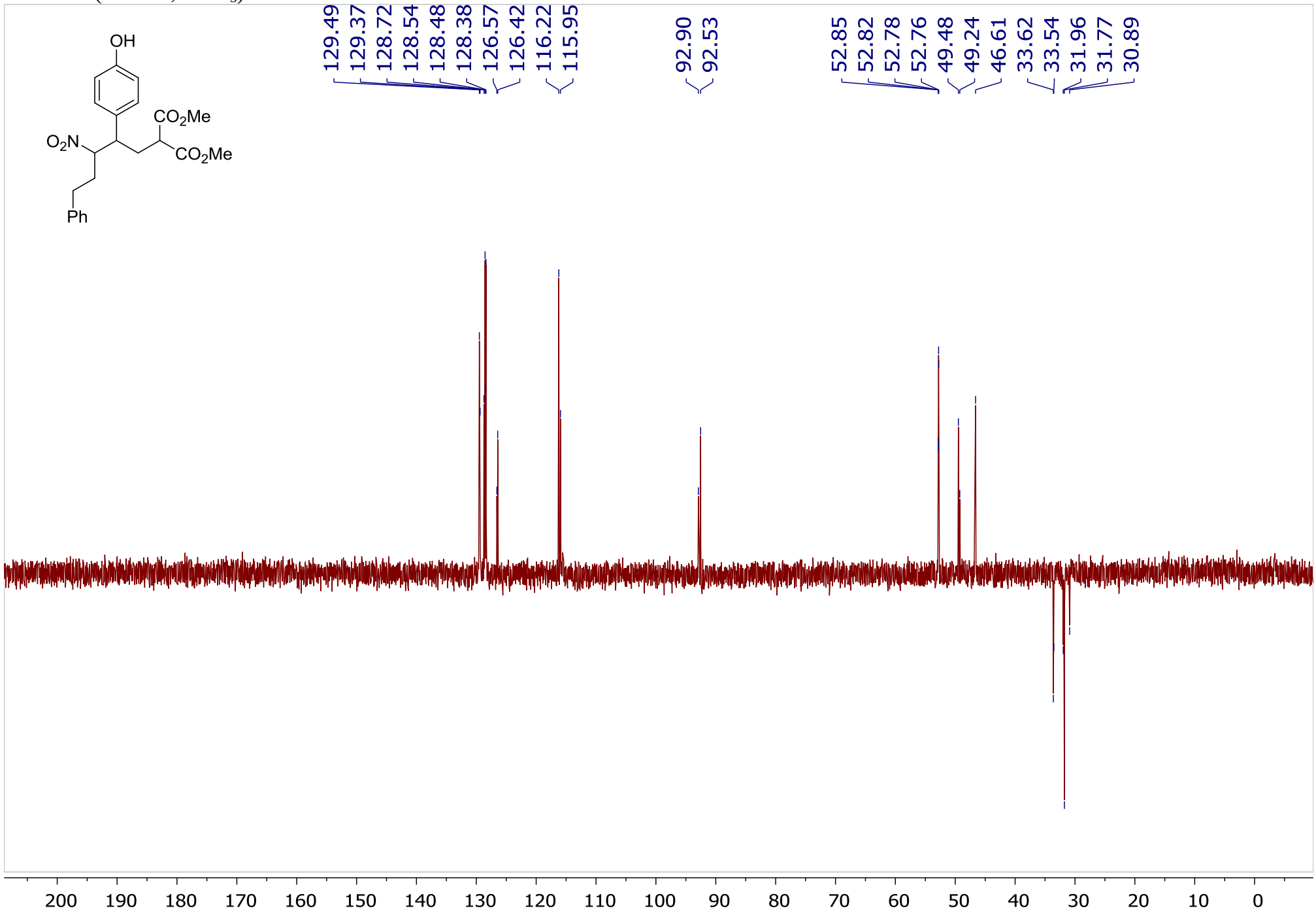
$^1$H NMR (300 MHz, $CDCl_3$)



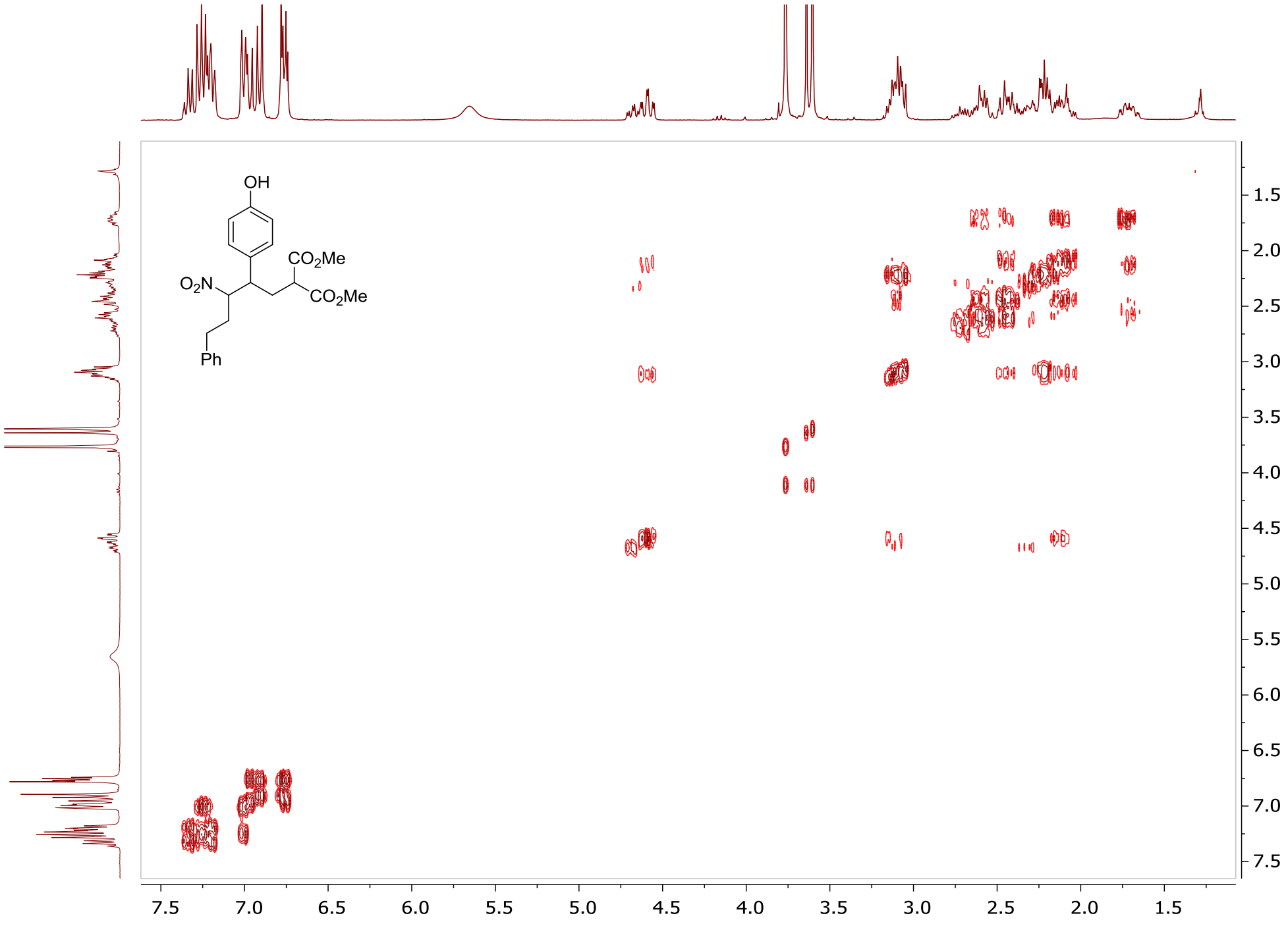
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Me
Ph
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3.0
3.5
4.0
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5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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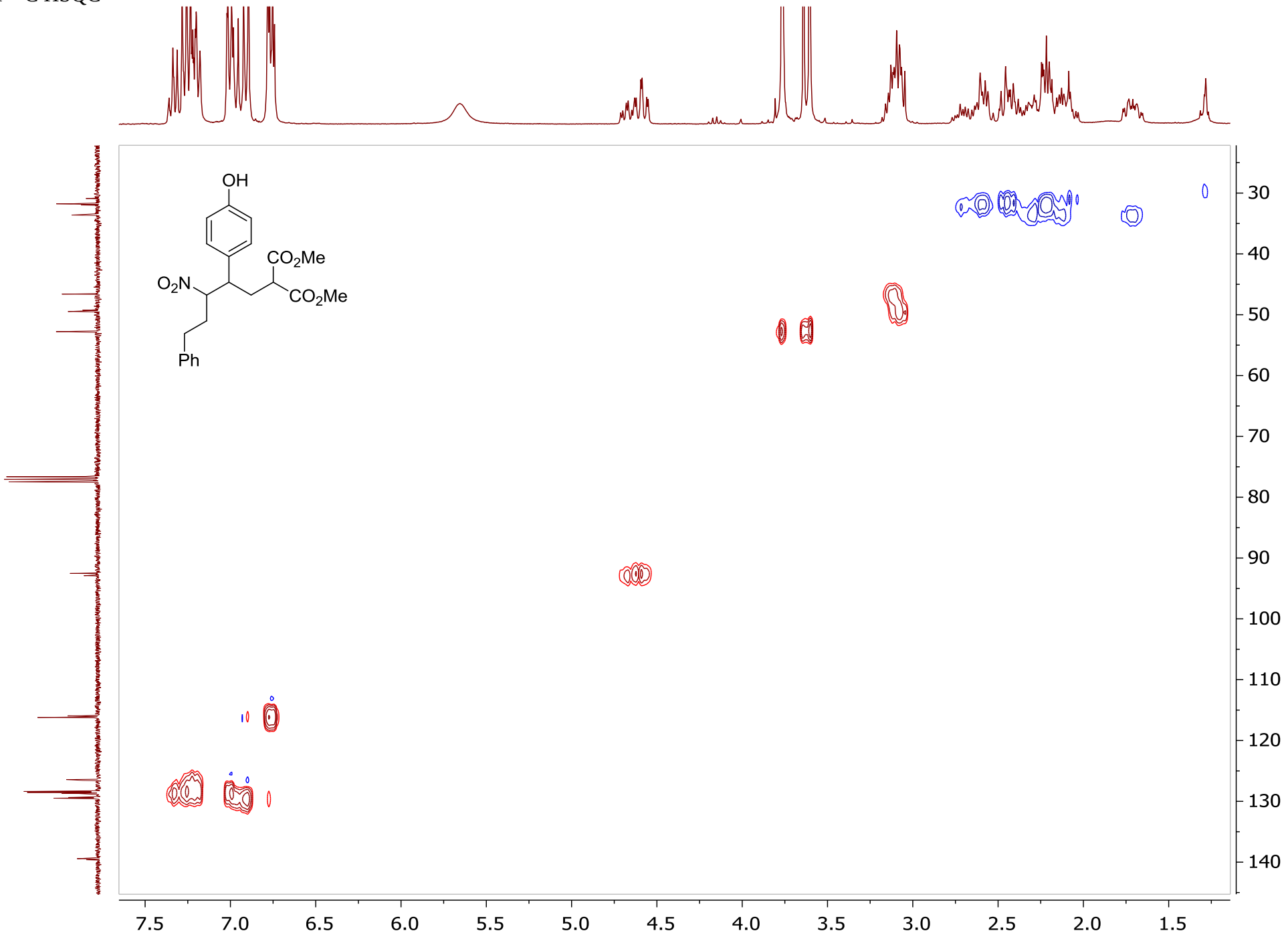
2.0
1.5

$^{1}H$-$^{13}C$ HSQC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O2N
CO2Me
Ph
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50
60
70
80
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100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
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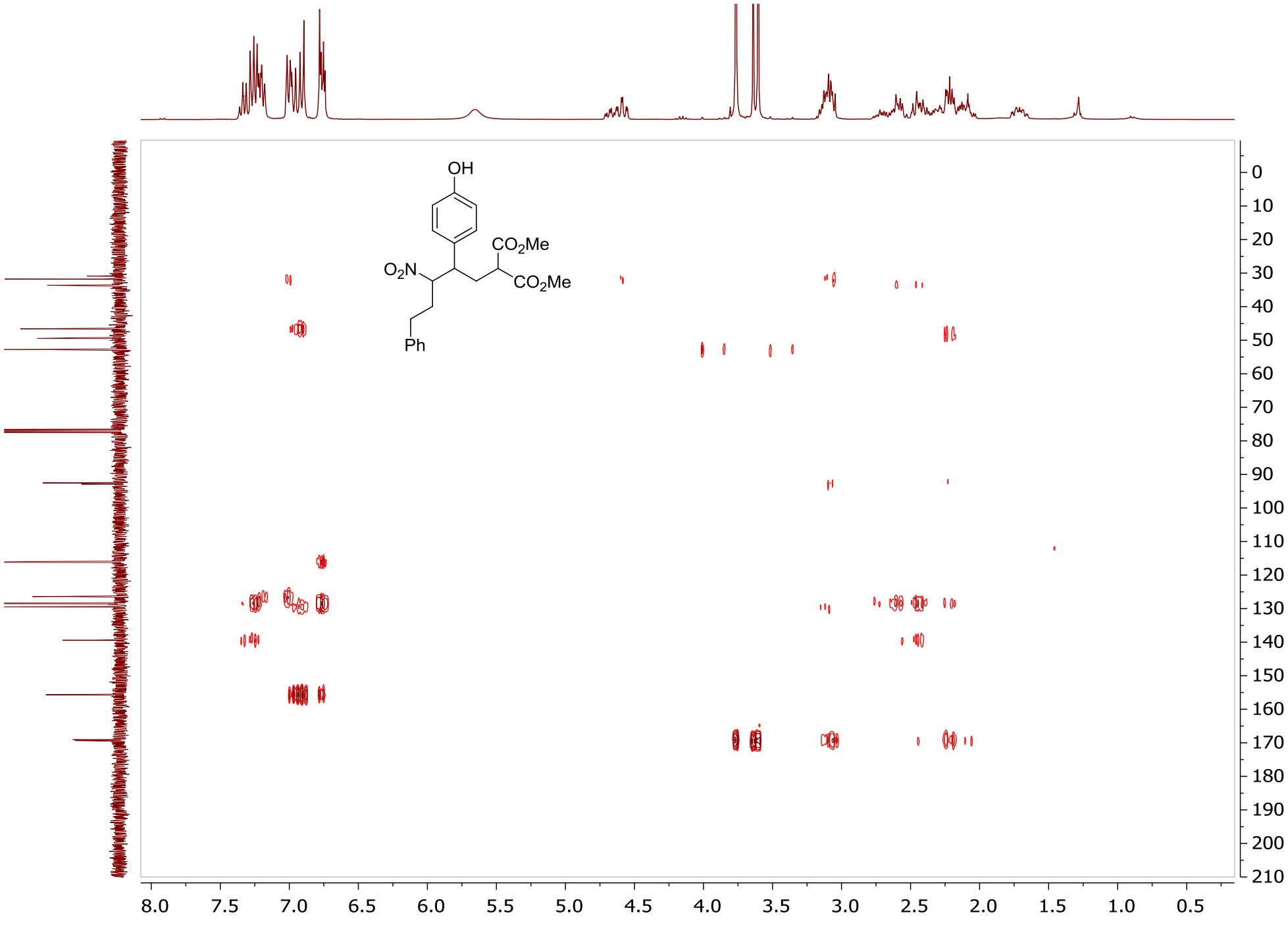
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HMBC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O2N
CO2Me
Ph
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130
140
150
160
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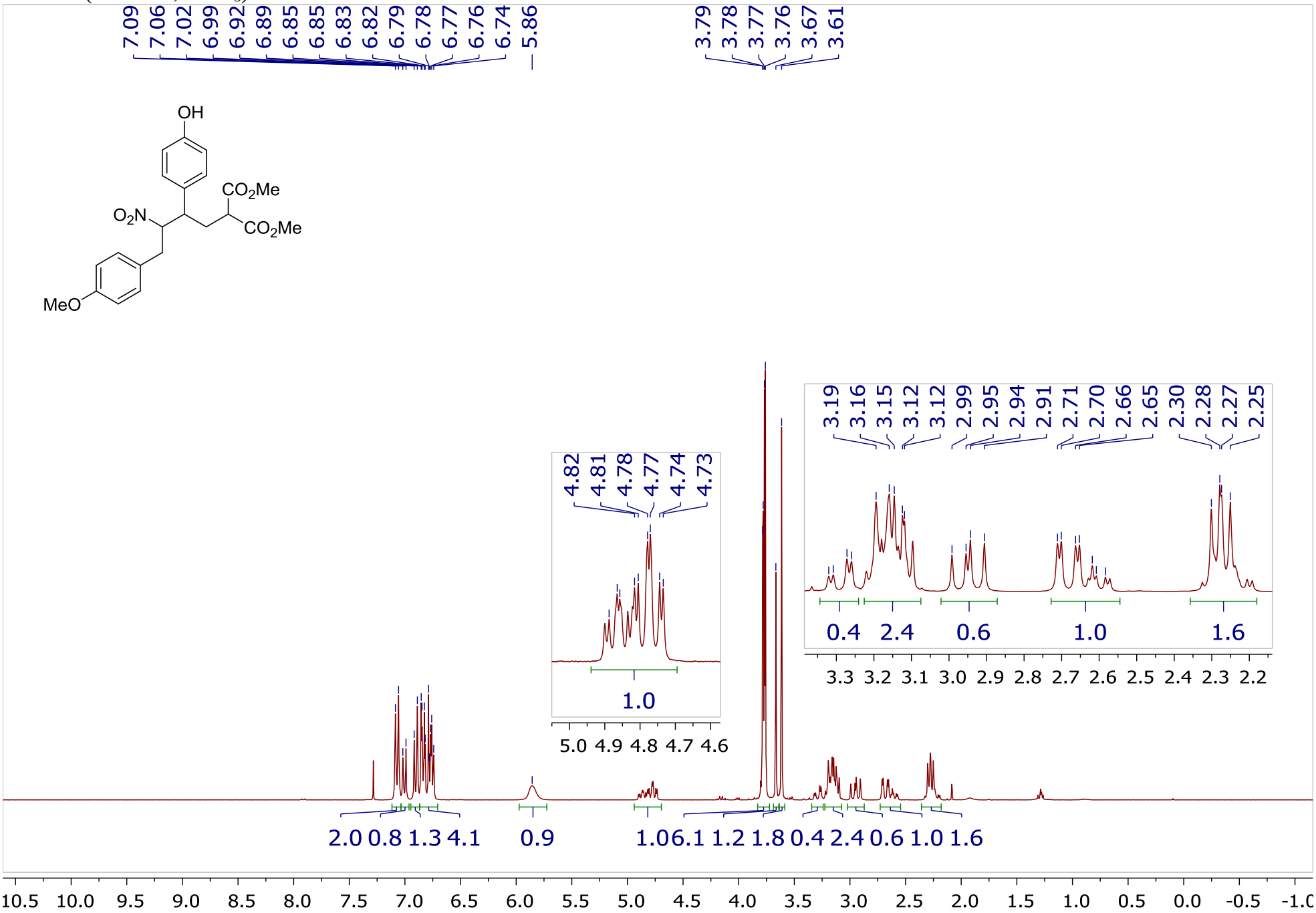
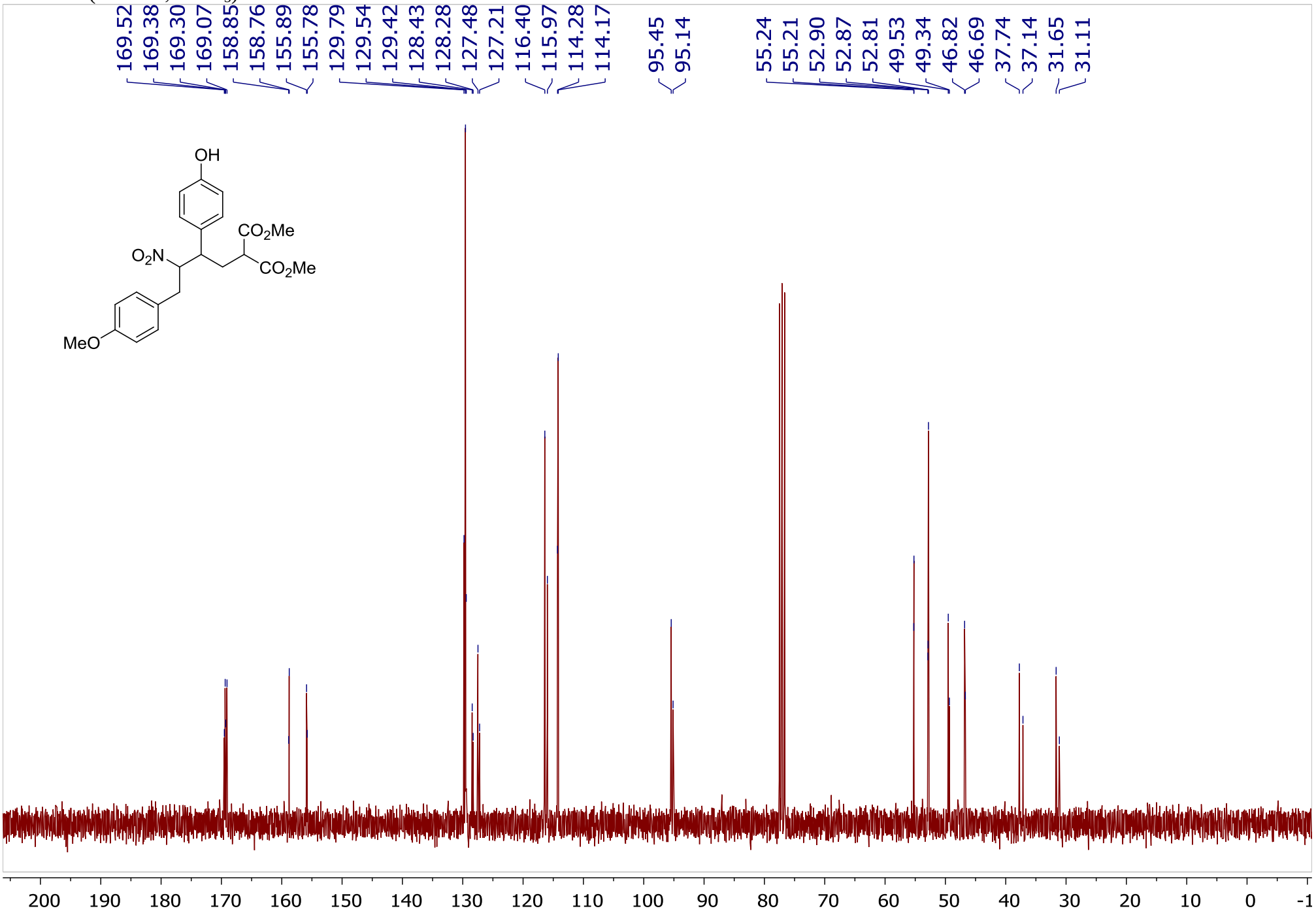
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-4-(4-methoxyphenyl)-3-nitrobutyl)malonate (3aj)**, dr = 1.5:1

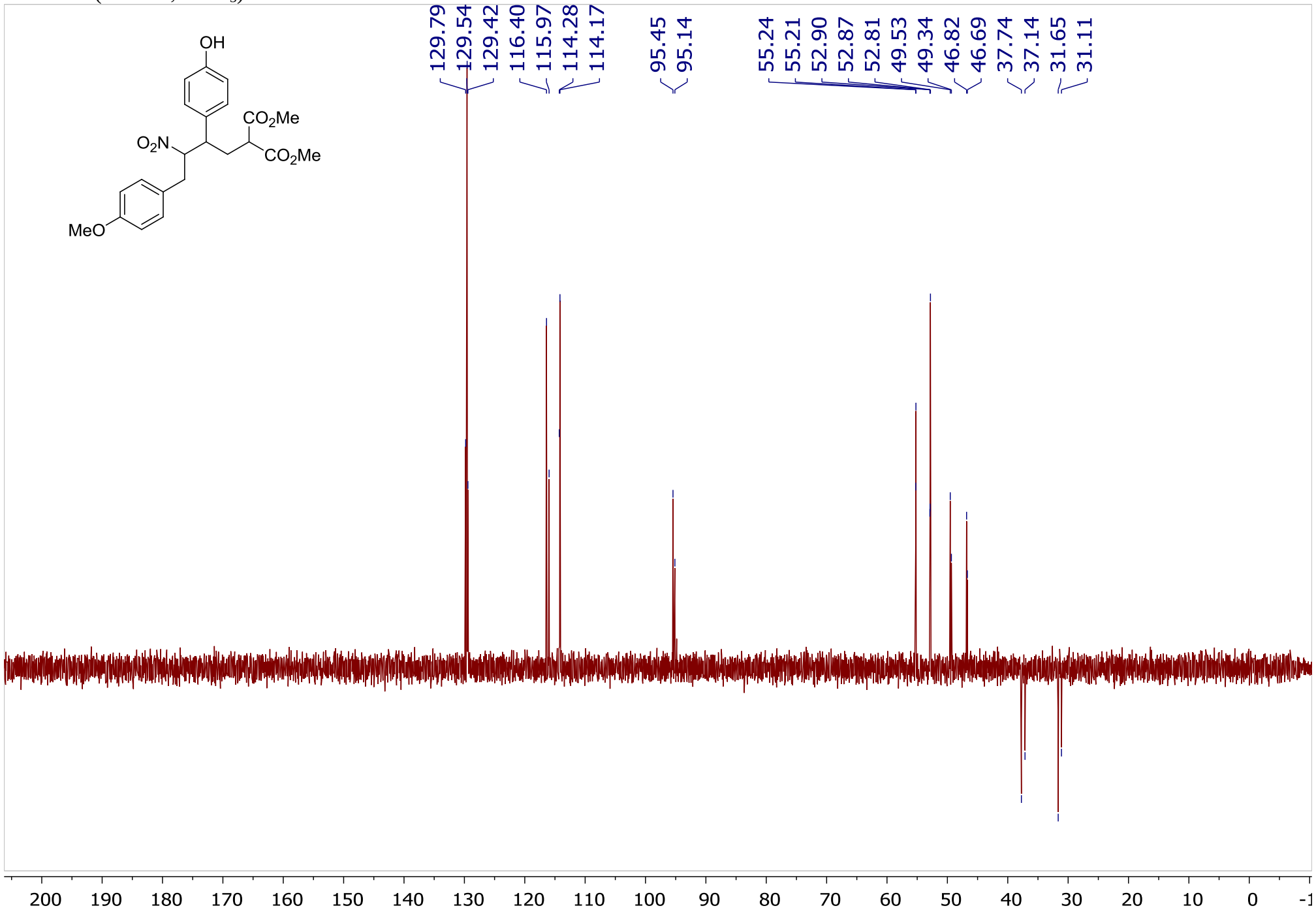
$^1$H NMR (300 MHz, $CDCl_3$)



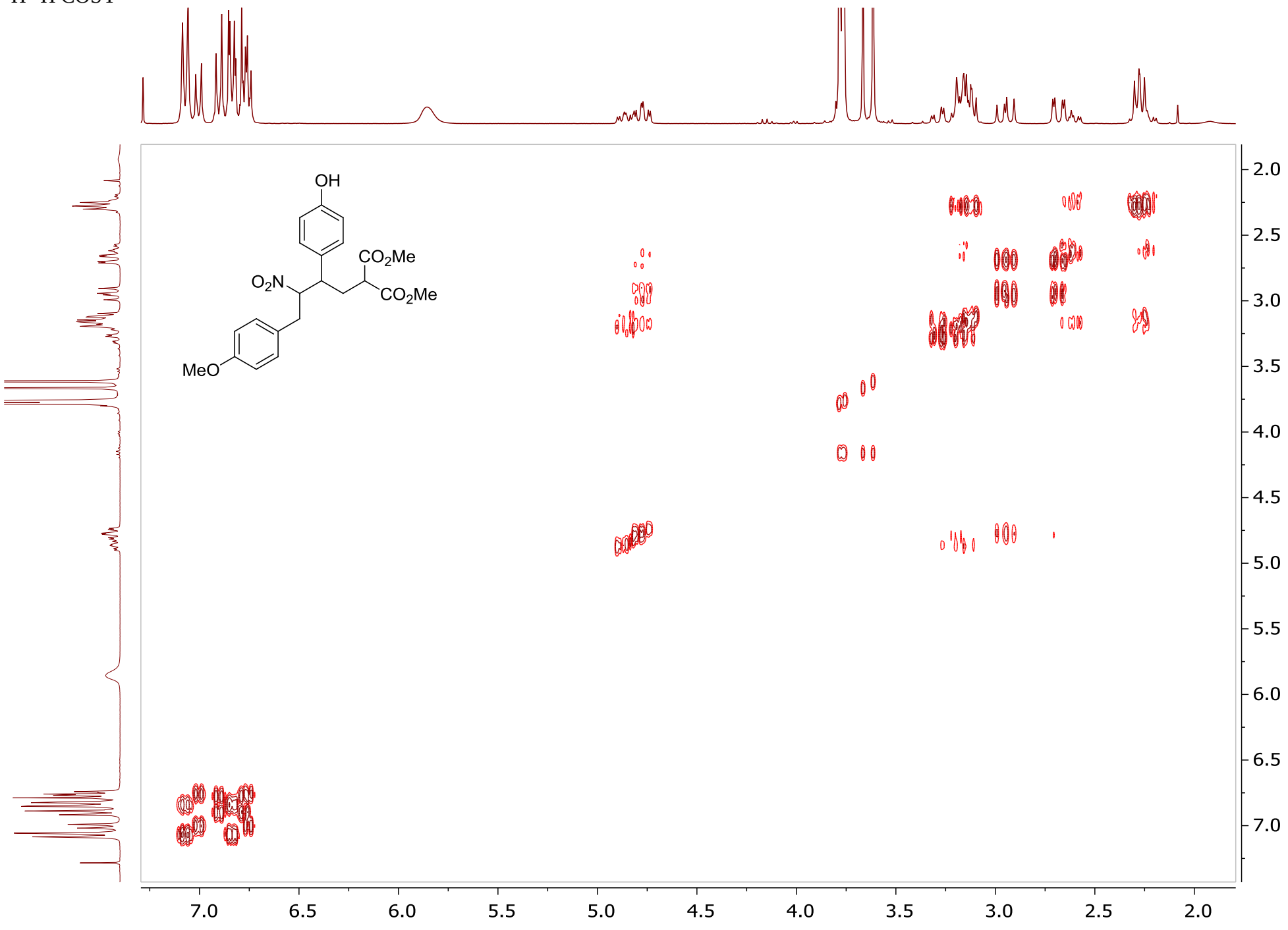
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
O2N
CO2Me
MeO
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
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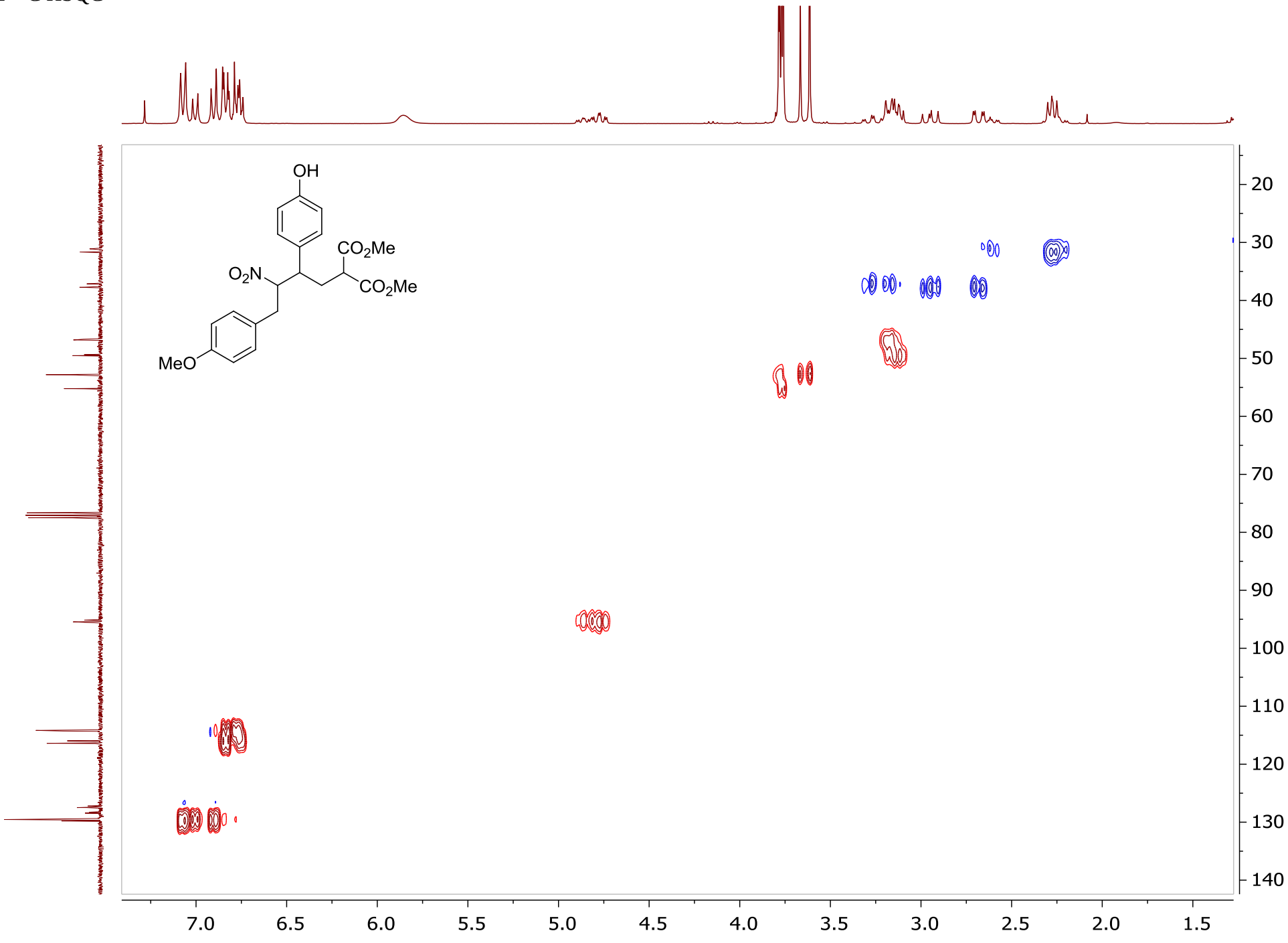
4.5
4.0
3.5
3.0
2.5
2.0

$^{1}H$-$^{13}C$ HSQC


OH
CO2Me
O2N
CO2Me
MeO
20
30
40
50
60
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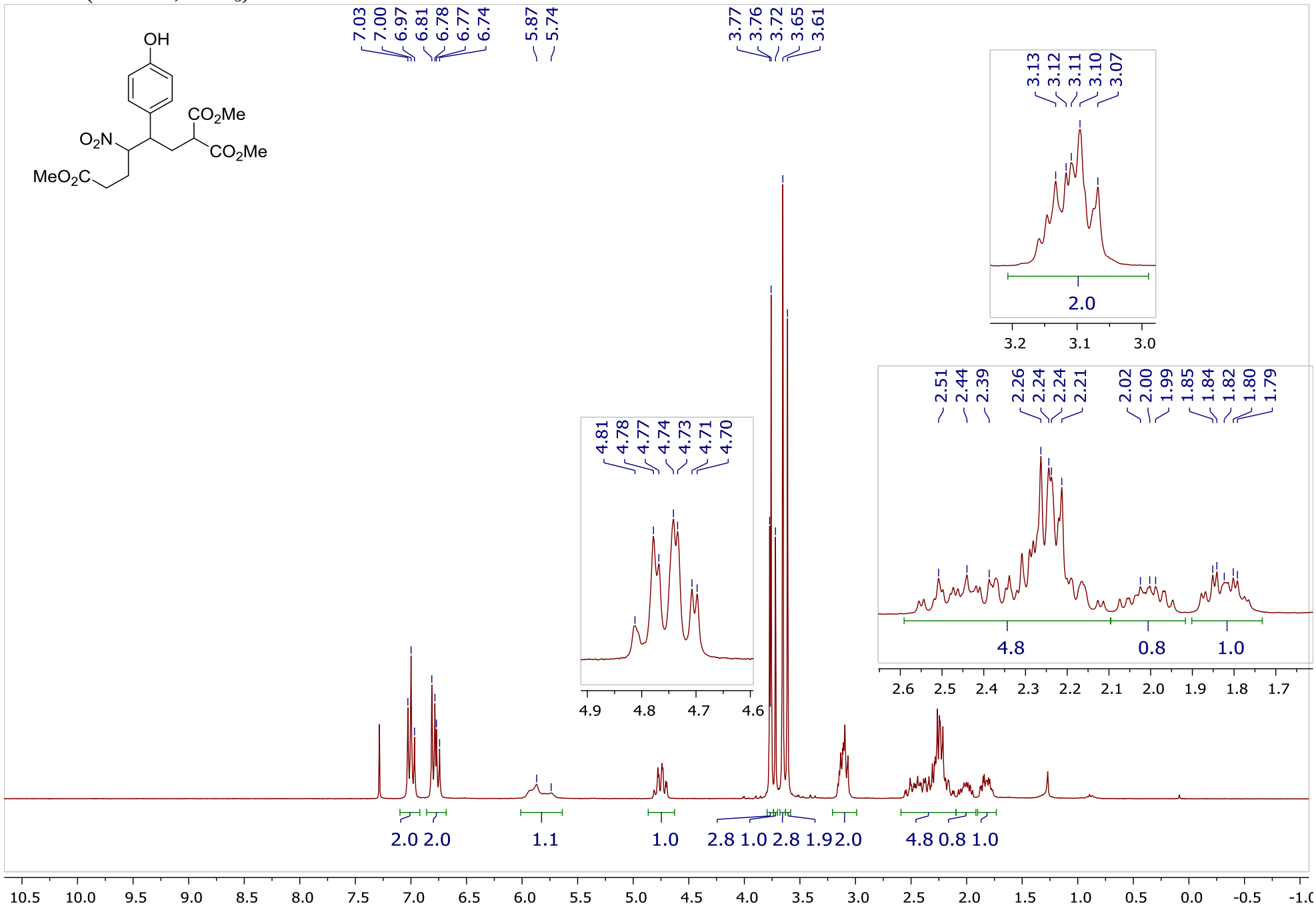
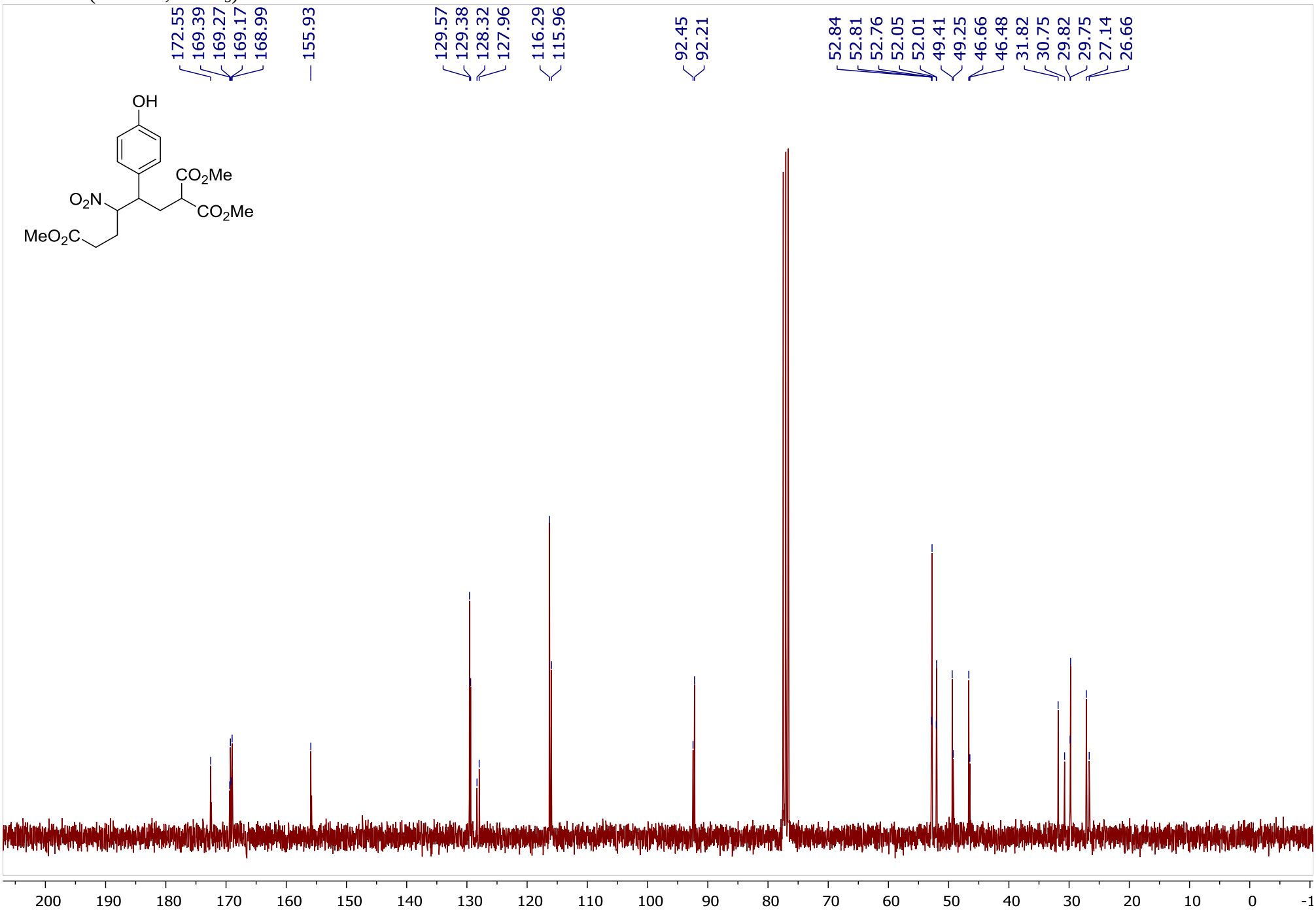
80
90
100
110
120
130
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

**Trimethyl 3-(4-hydroxyphenyl)-4-nitrohexane-1,1,6-tricarboxylate (3ak)**, dr = 1.5:1

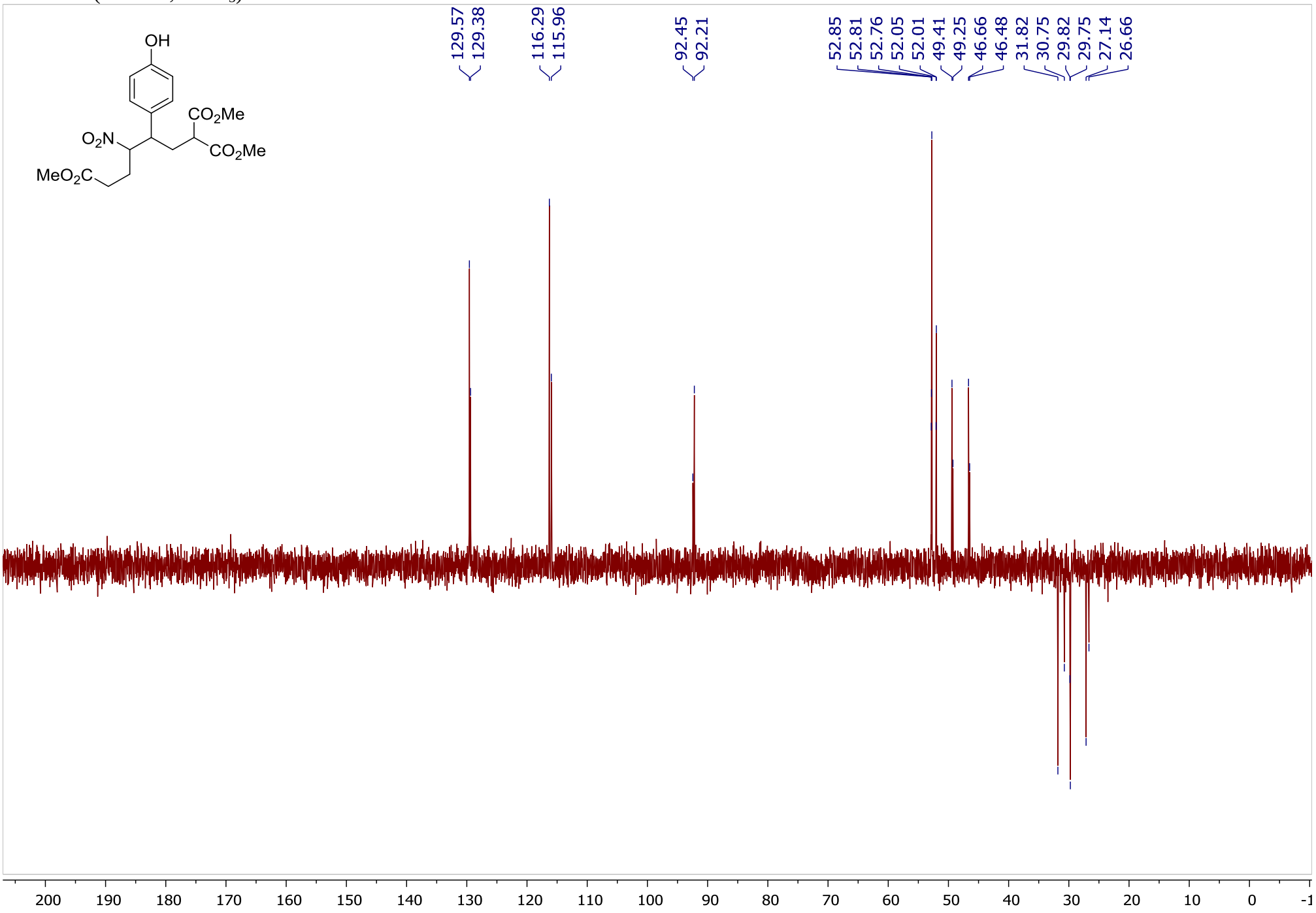
$^1$H NMR (300 MHz, $CDCl_3$)



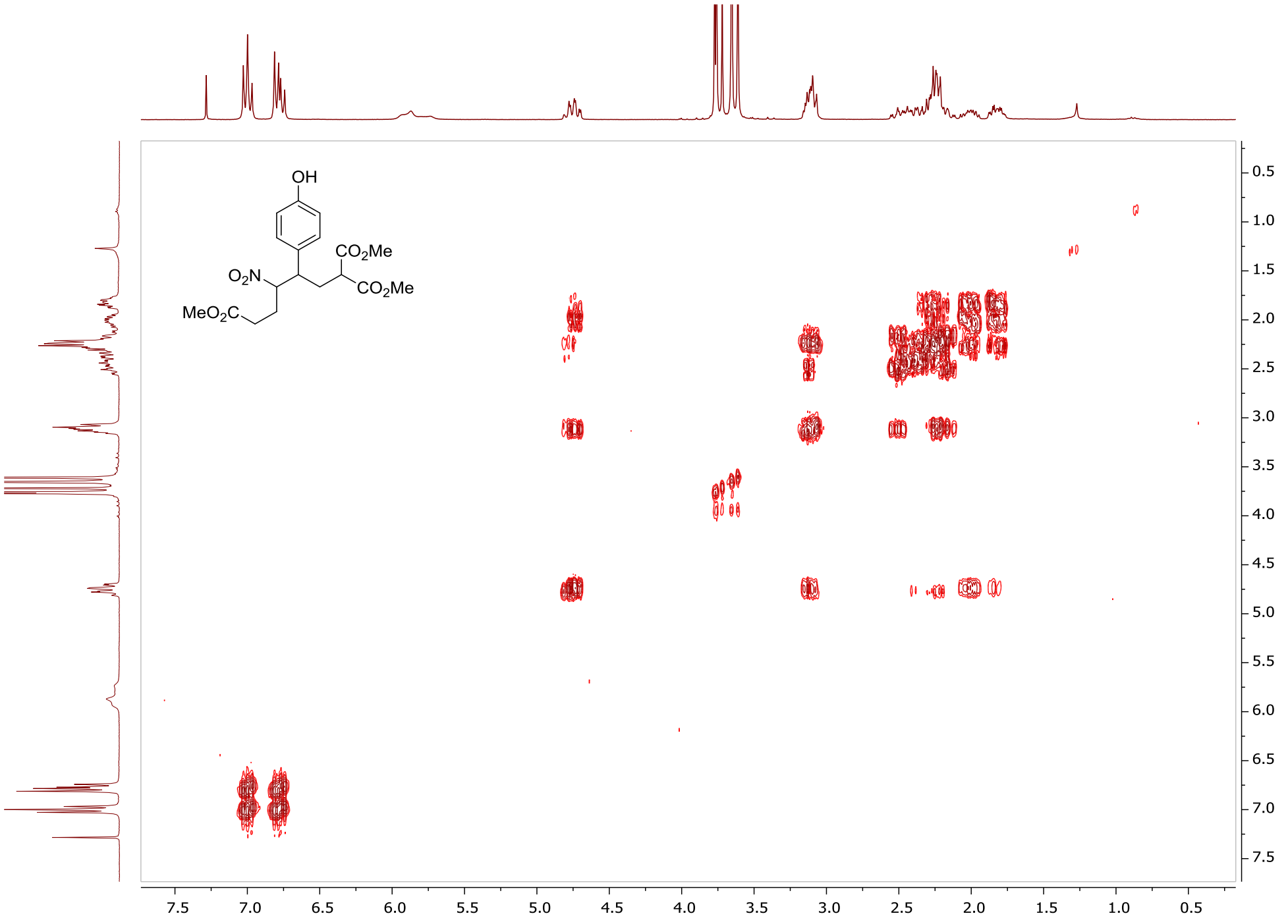
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
O2N
CO2Me
MeO2C
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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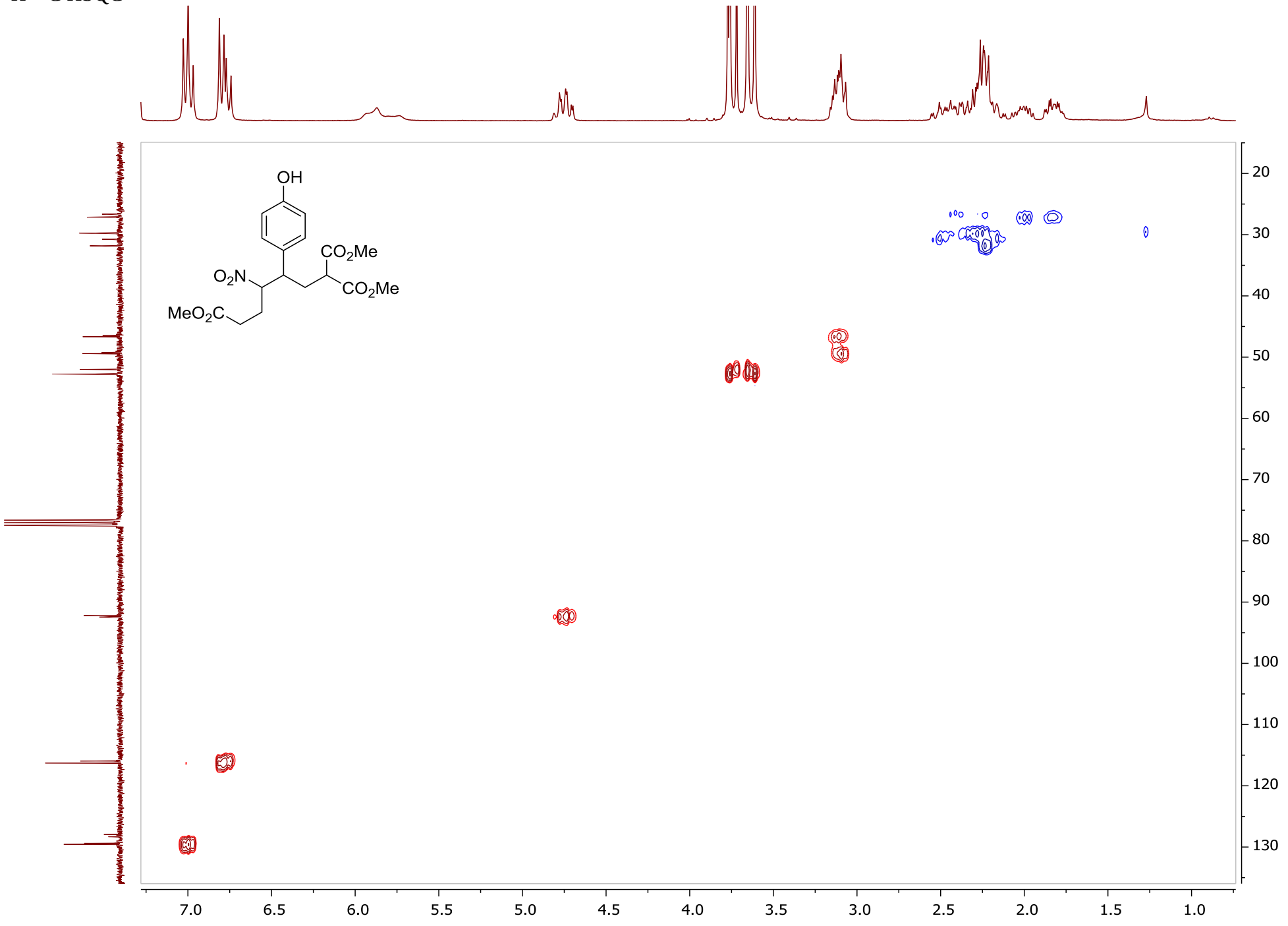
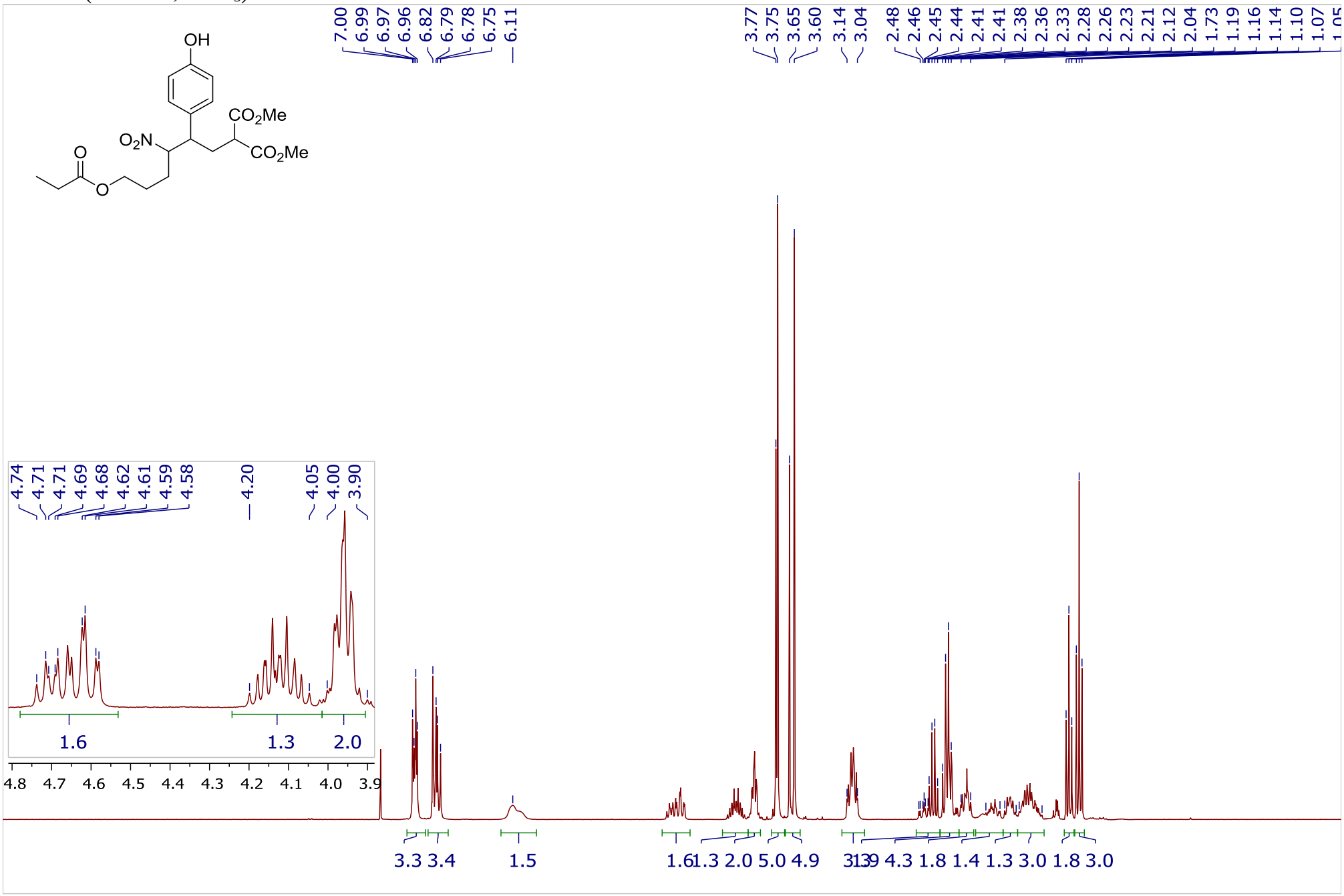
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC

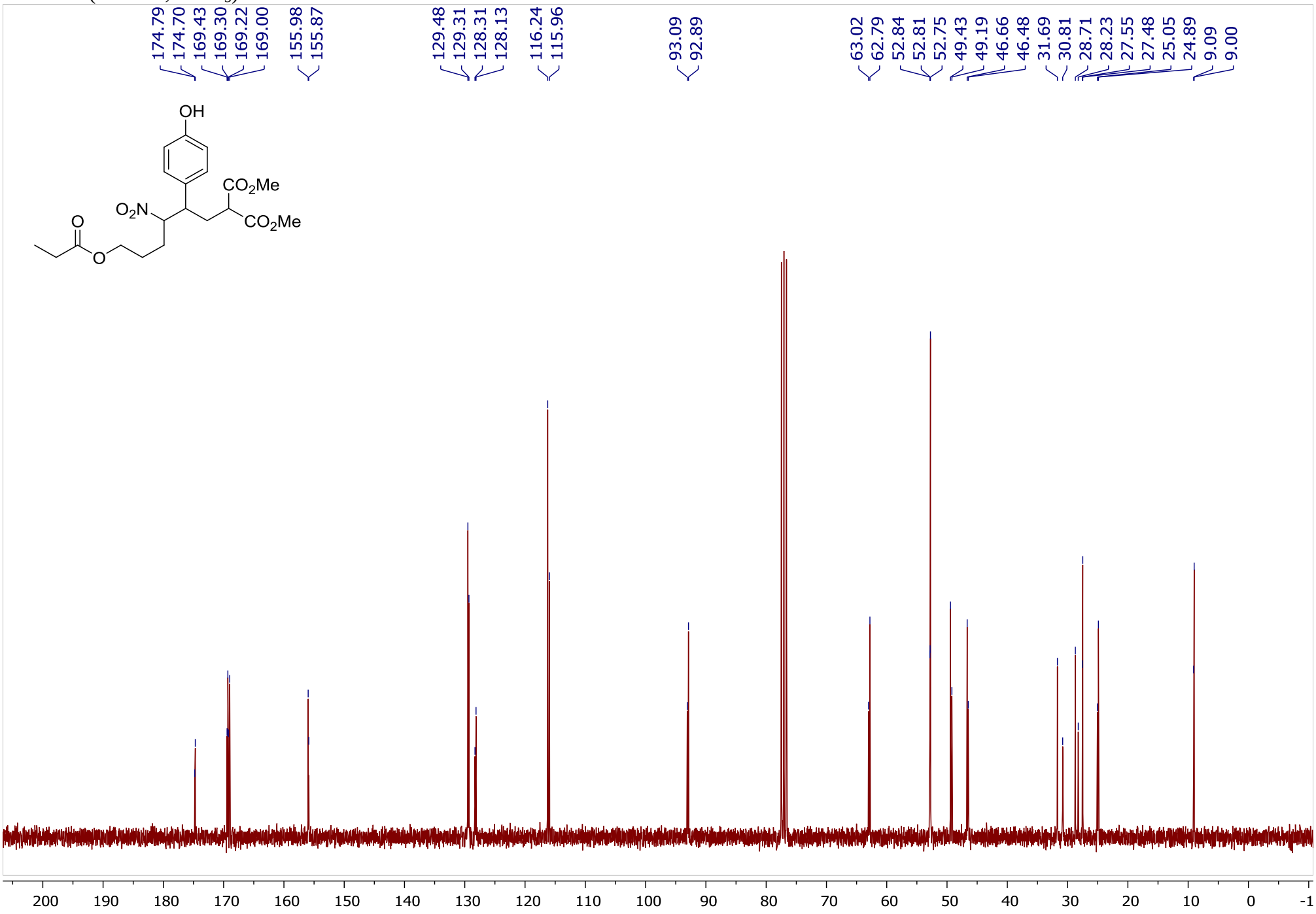

OH
CO2Me
O2N
CO2Me
MeO2C
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-6-(propionyloxy)hexyl)malonate (3al)**, dr = 1.6:1

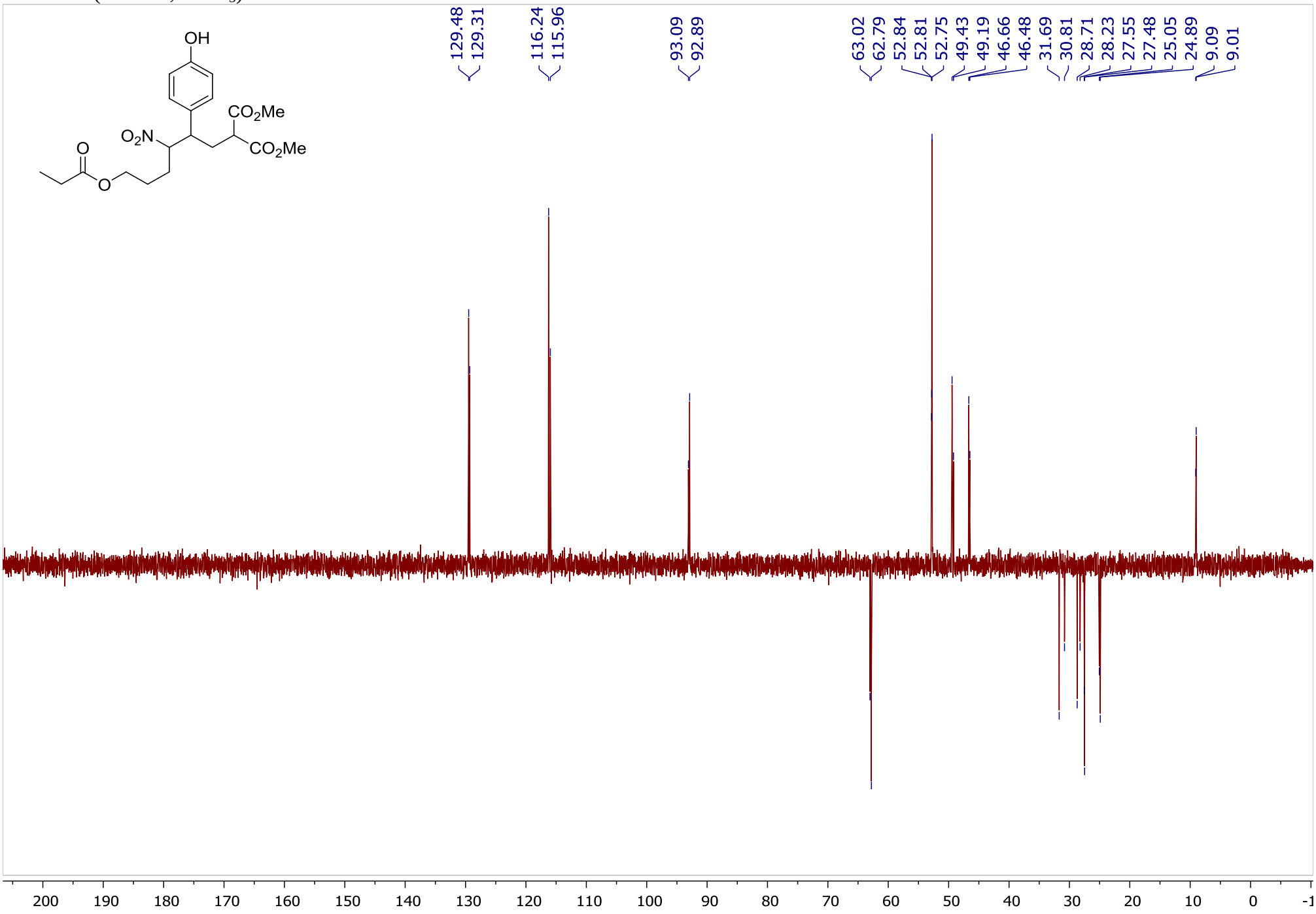
$^1$H NMR (300 MHz, $CDCl_3$)



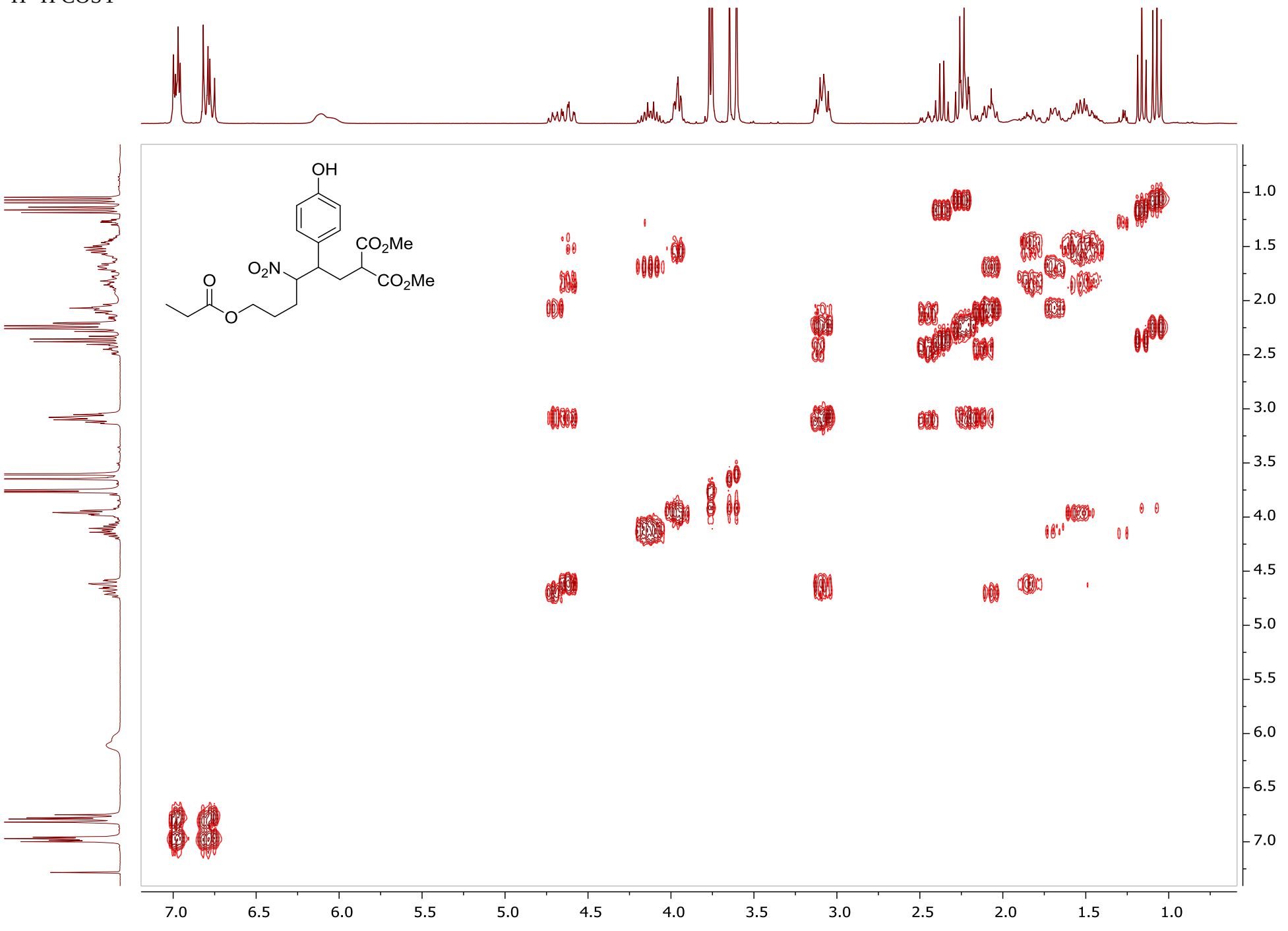
$^{13}$C NMR (75 MHz, $CDCl_3$)



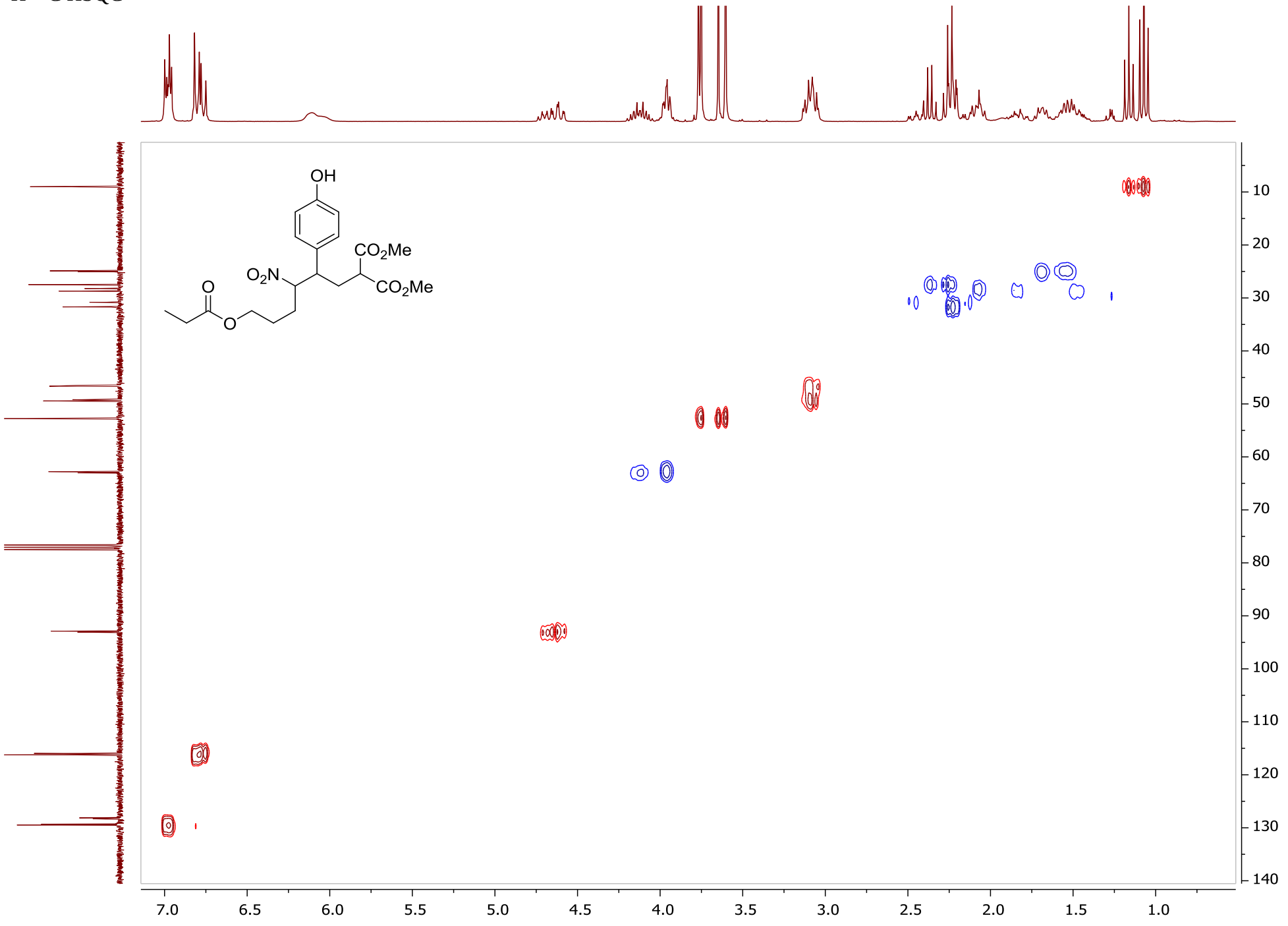
$^{13}$C DEPT (75 MHz, $CDCl_3$)



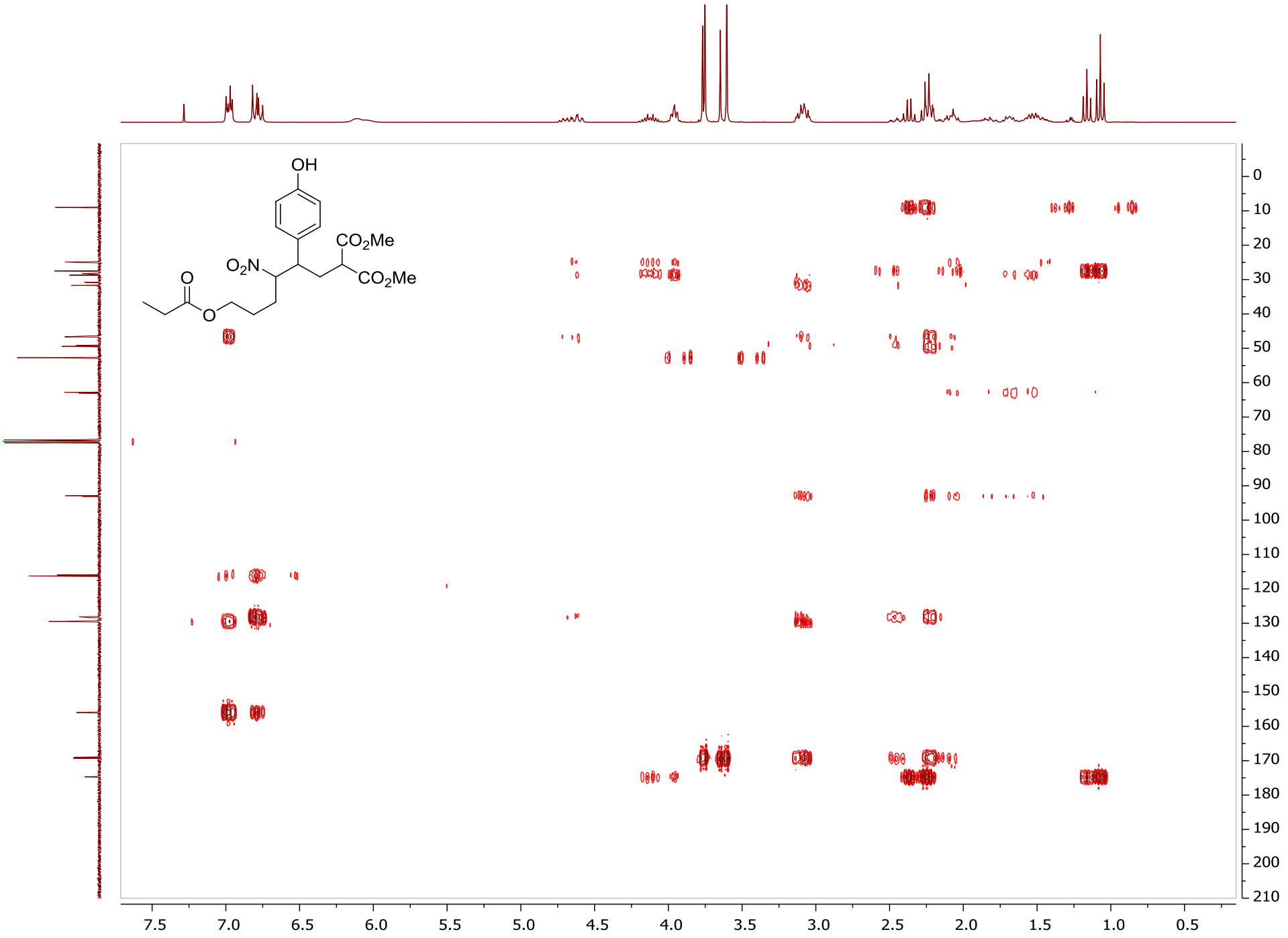
$^{1}$H-$^{1}$H COSY


OH
CO2Me
O2N
CO2Me
O
O
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HSQC


OH
CO2Me
O2N
CO2Me
O
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HMBC


OH
CO2Me
O2N
CO2Me
O
O
0
10
20
30
40
50
60
70
80
90
100
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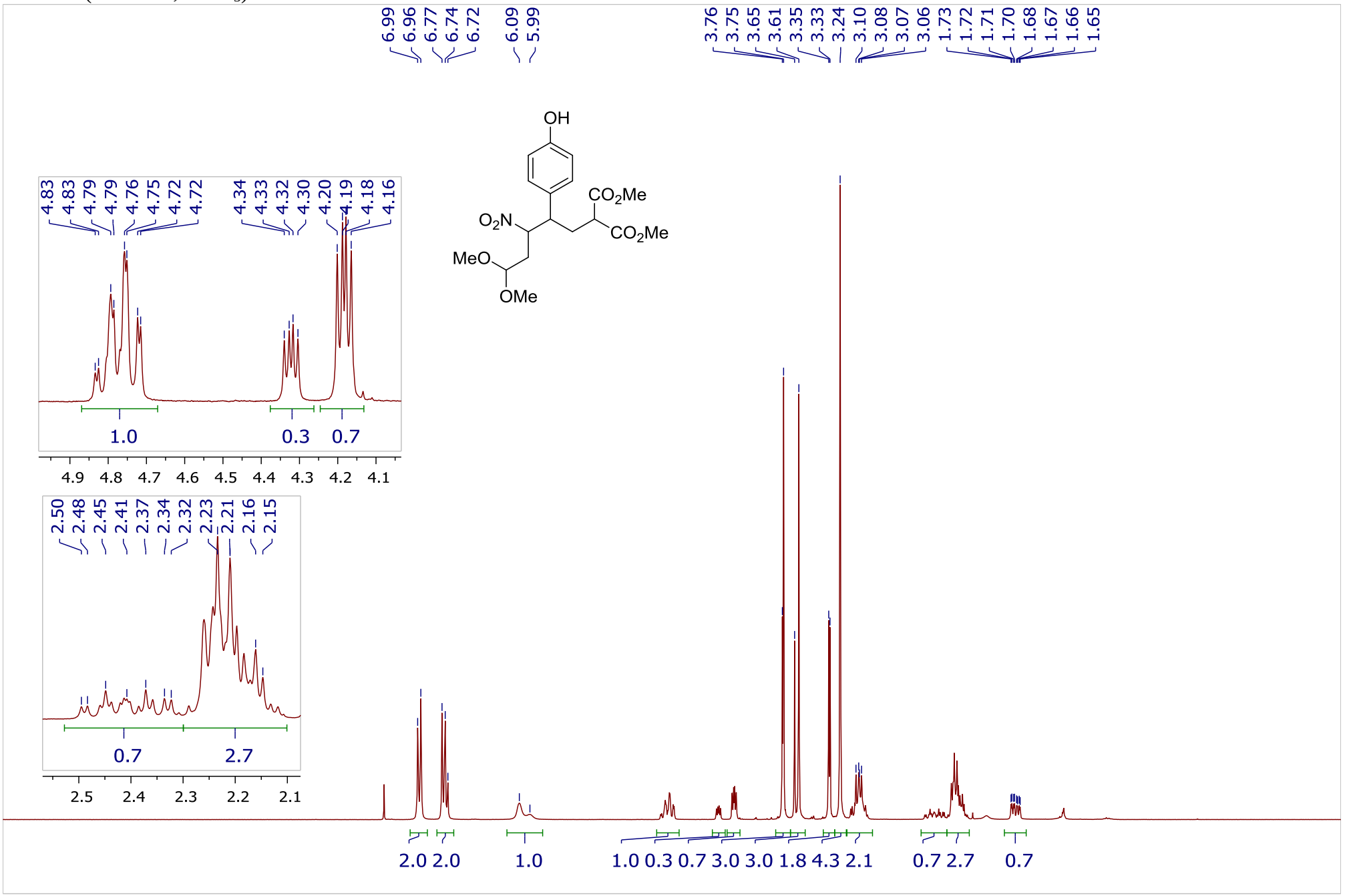
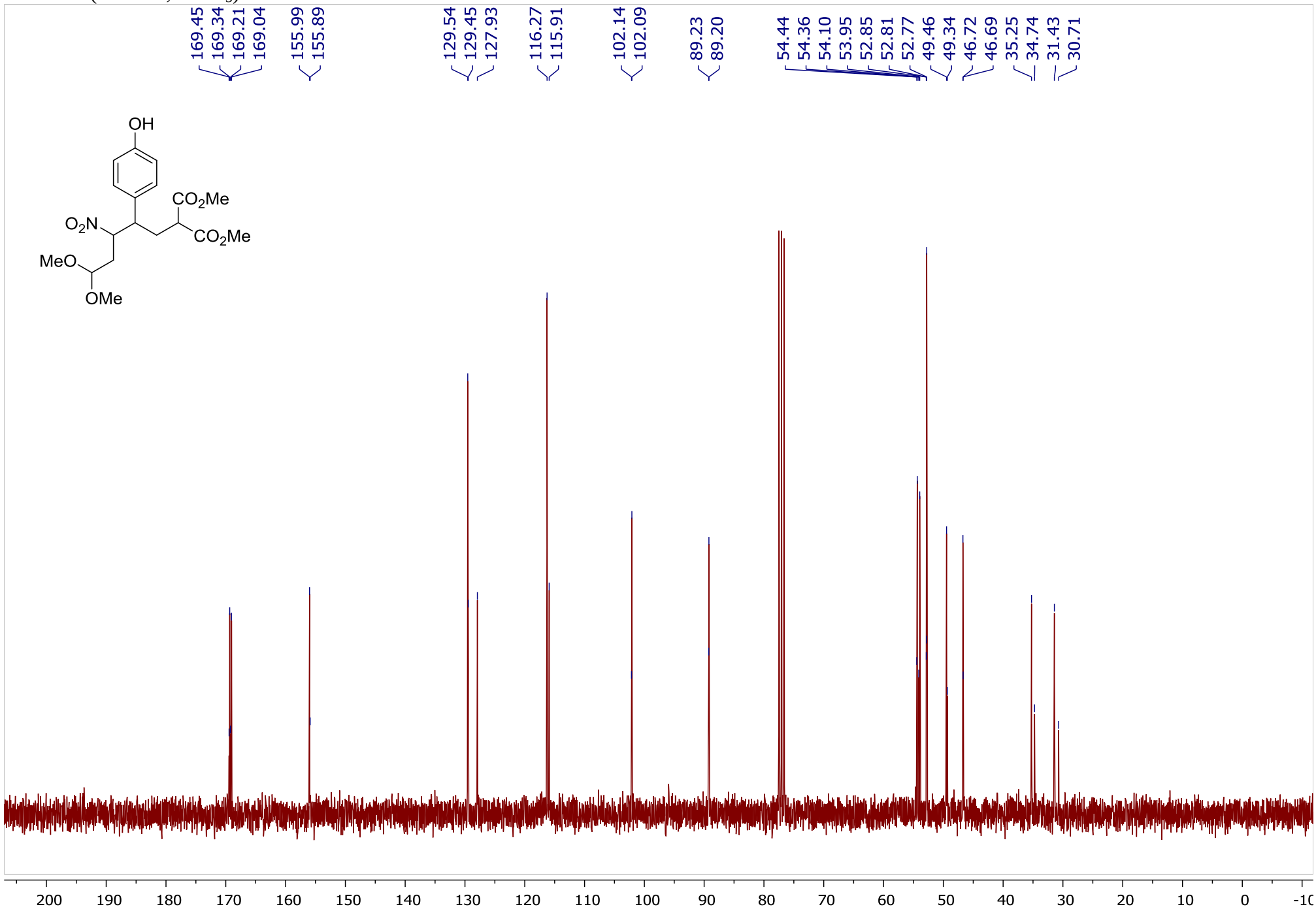
130
140
150
160
170
180
190
200
210
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-5,5-dimethoxy-3-nitropentyl)malonate (3am)**, dr = 2.4:1

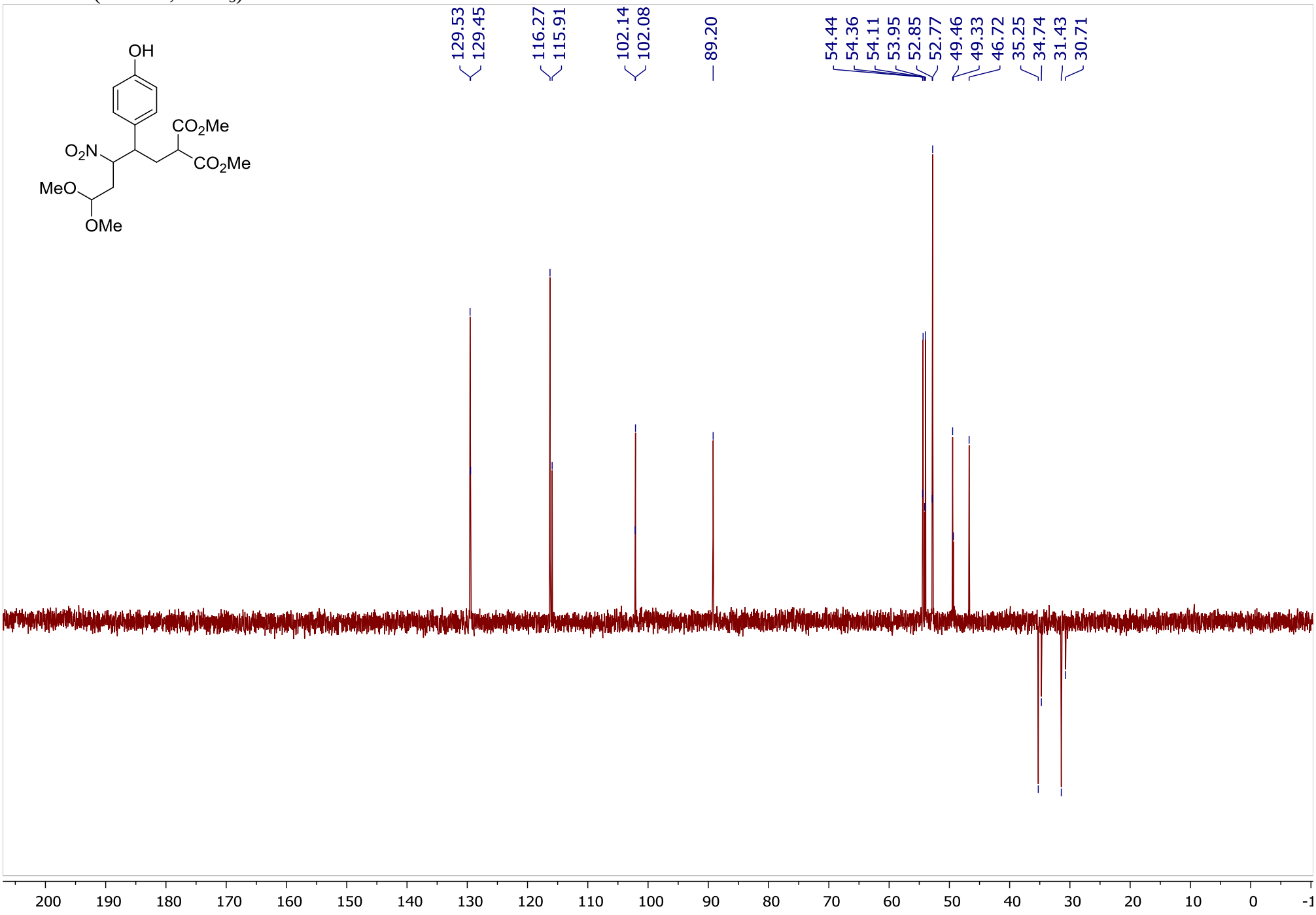
$^1$H NMR (300 MHz, $CDCl_3$)



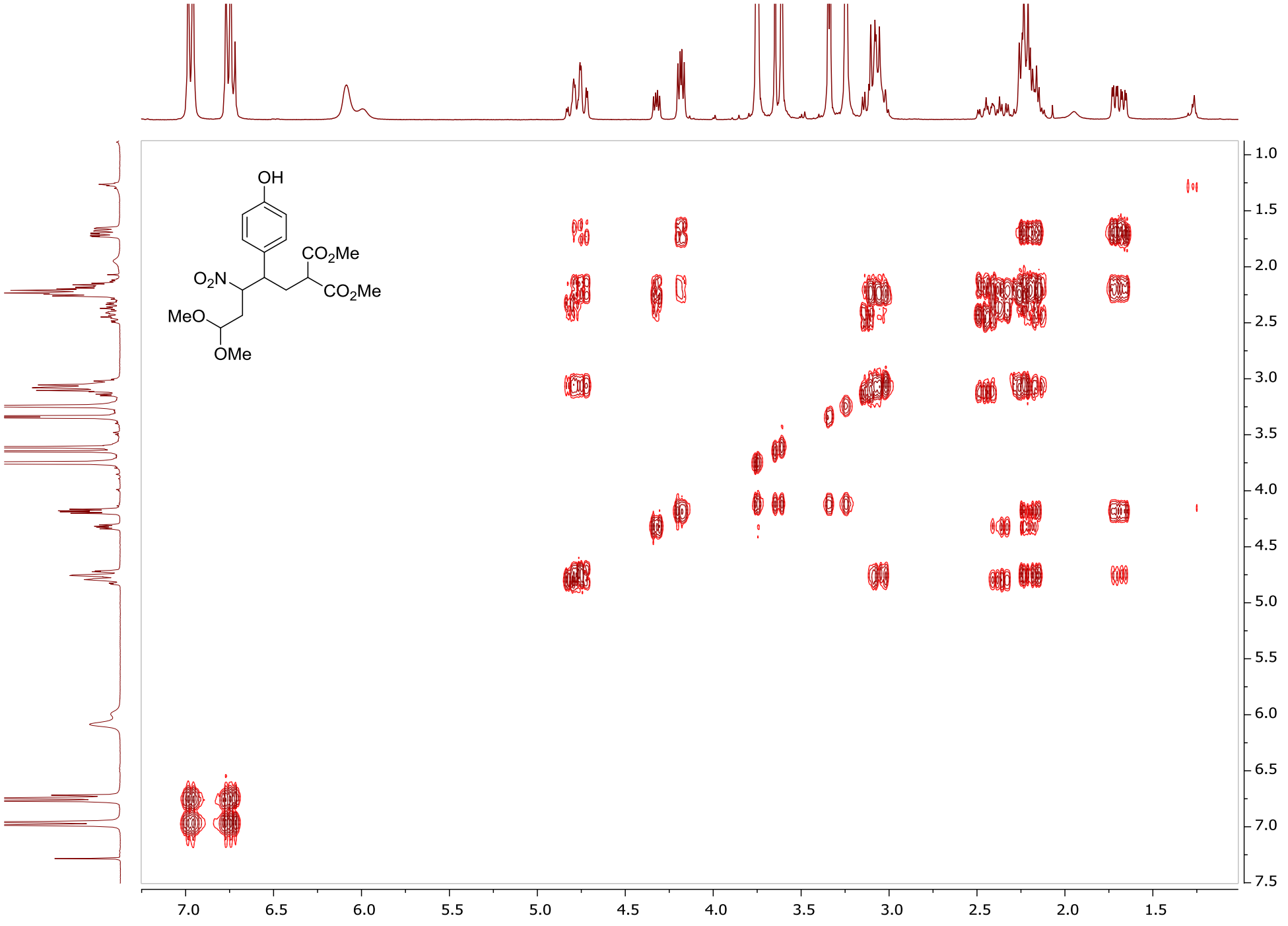
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY


OH
CO2Me
O2N
CO2Me
MeO
OMe
1.0
1.5
2.0
2.5
3.0
3.5
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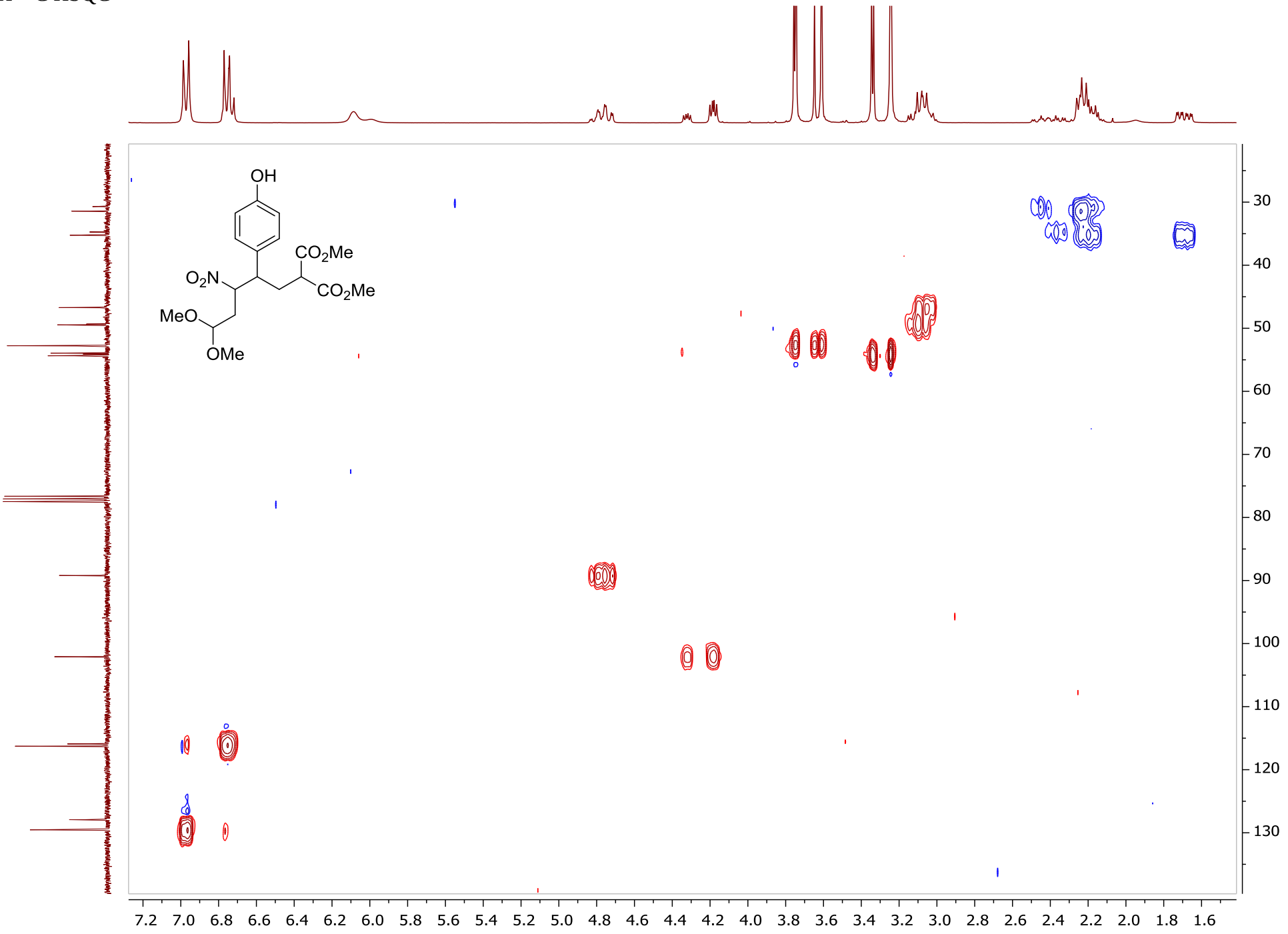
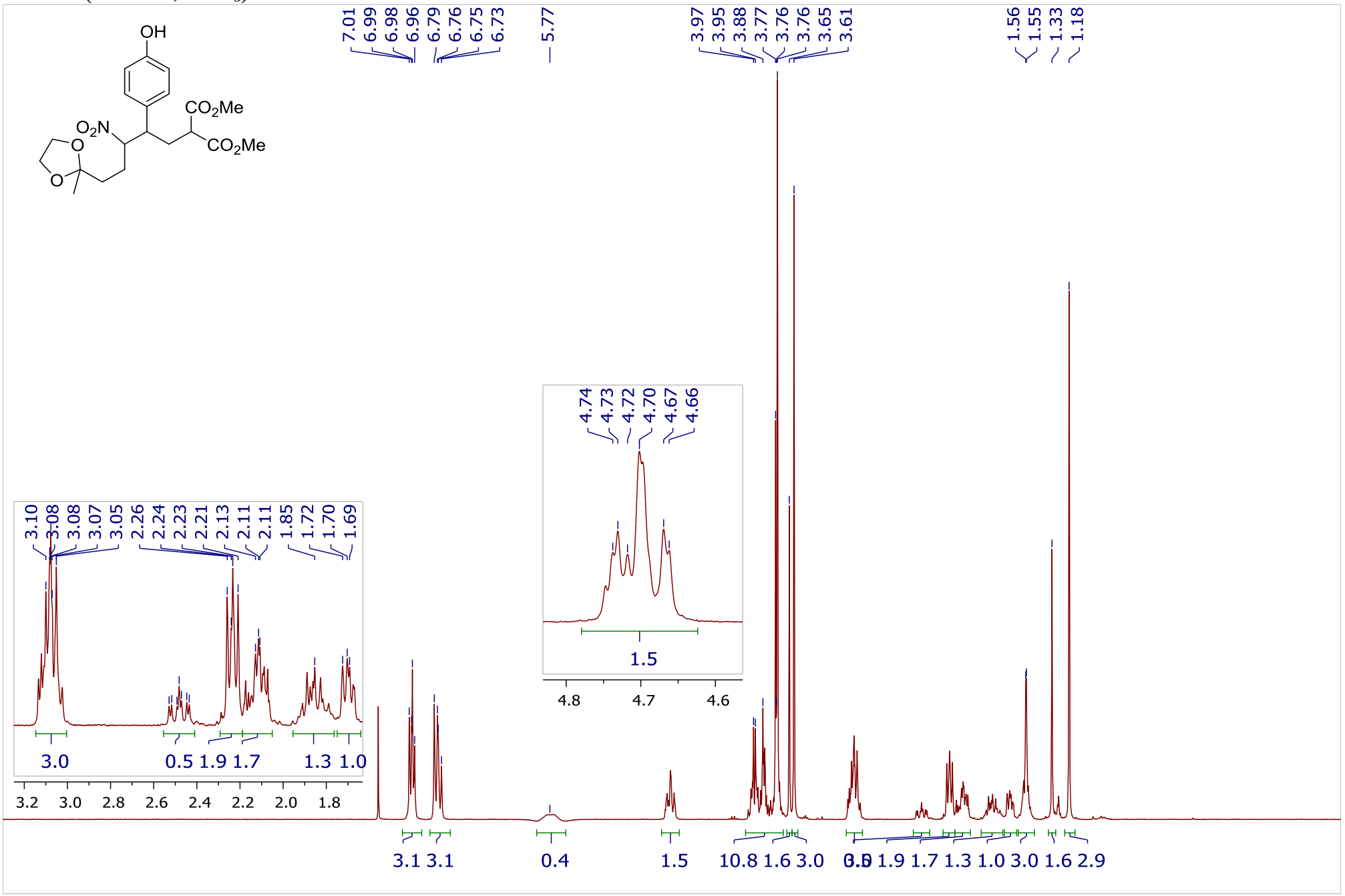
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}$H-$^{13}$C HSQC

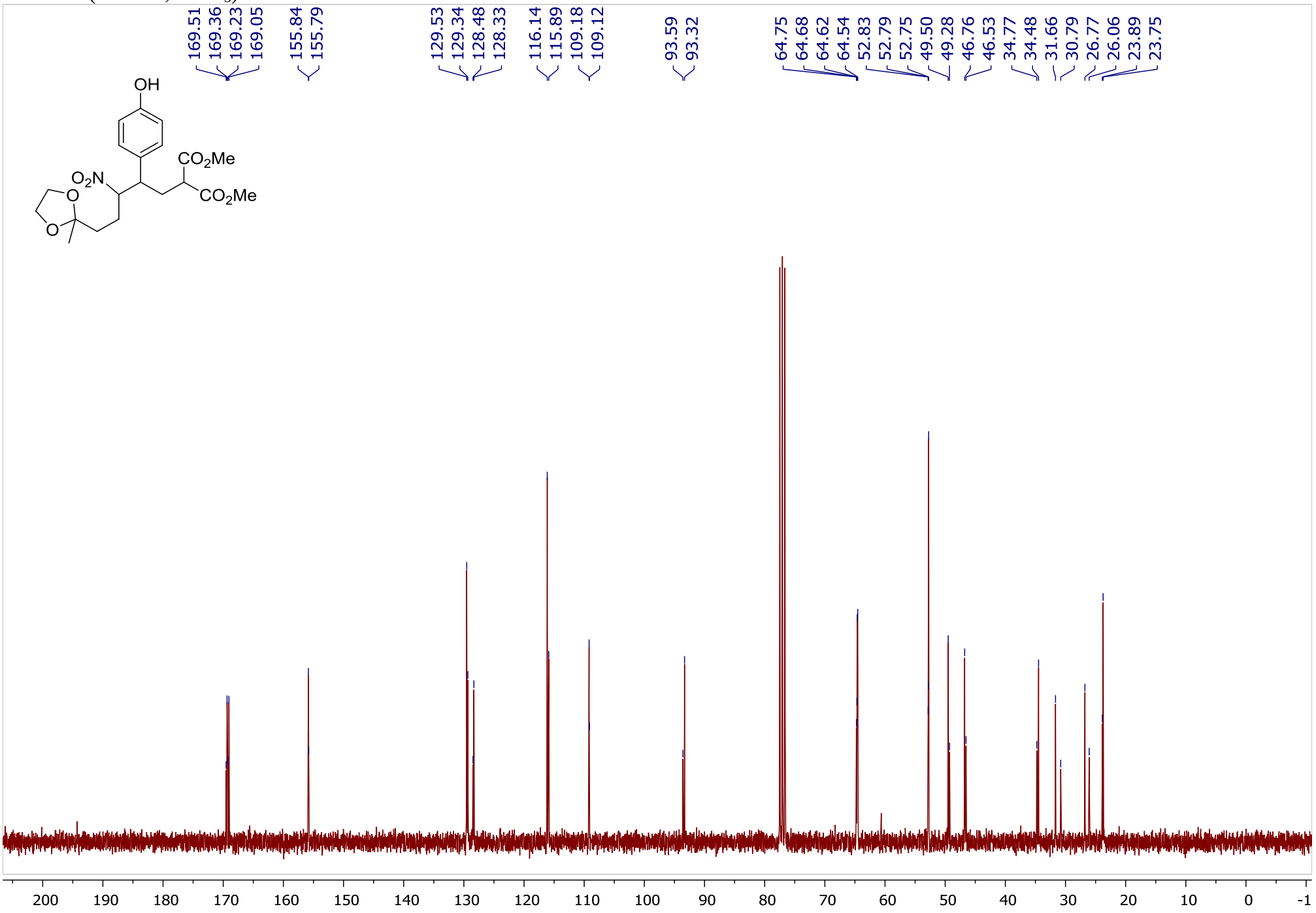

OH
CO2Me
O2N
CO2Me
MeO
OMe
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
30 40 50 60 70 80 90 100 110 120 130

**Dimethyl 2-(2-(4-hydroxyphenyl)-5-(2-methyl-1,3-dioxolan-2-yl)-3-nitropentyl)malonate (3an)**, dr = 1.9:1

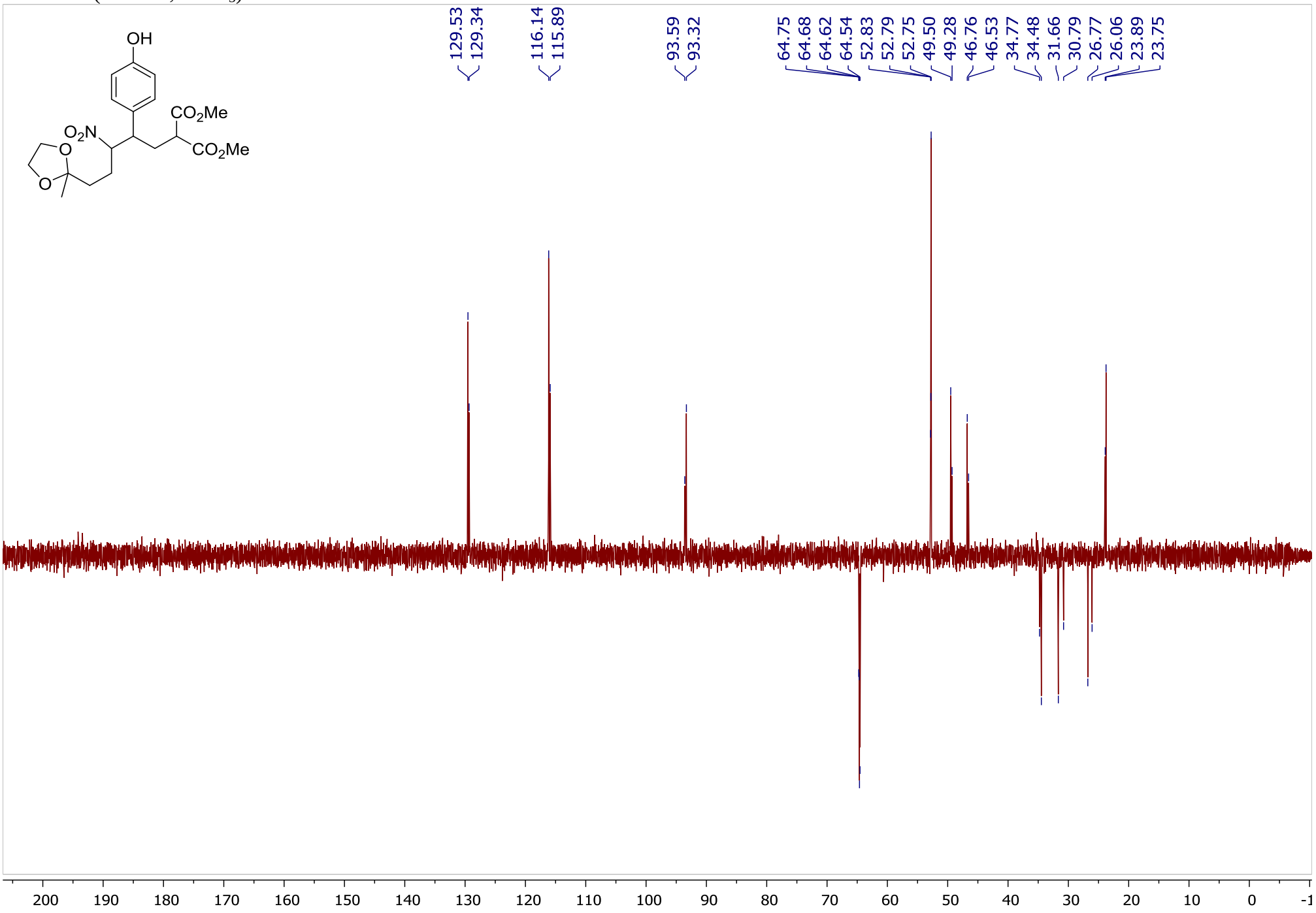
$^1$H NMR (300 MHz, $CDCl_3$)



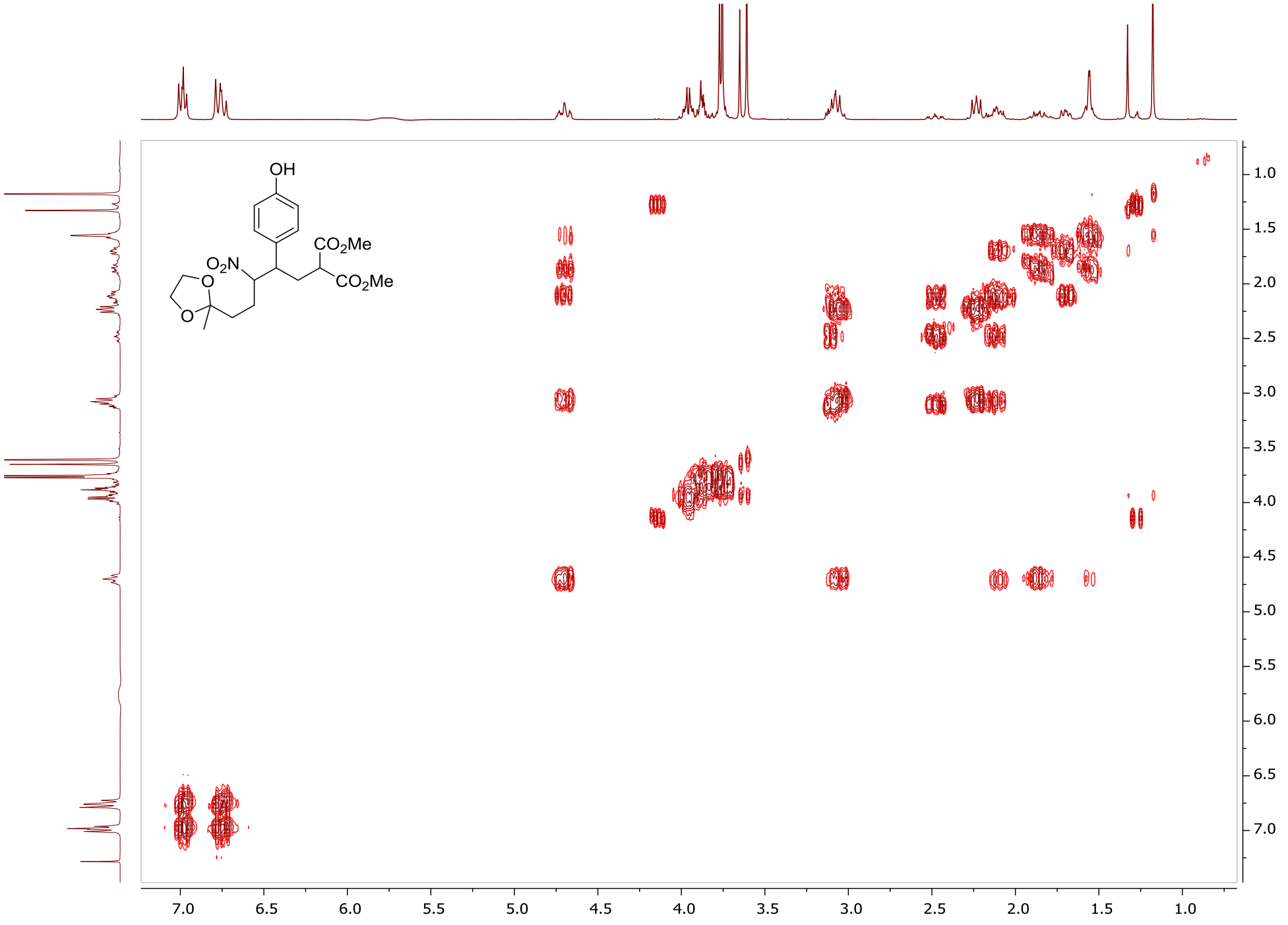
$^{13}$C NMR (75 MHz, $CDCl_3$)



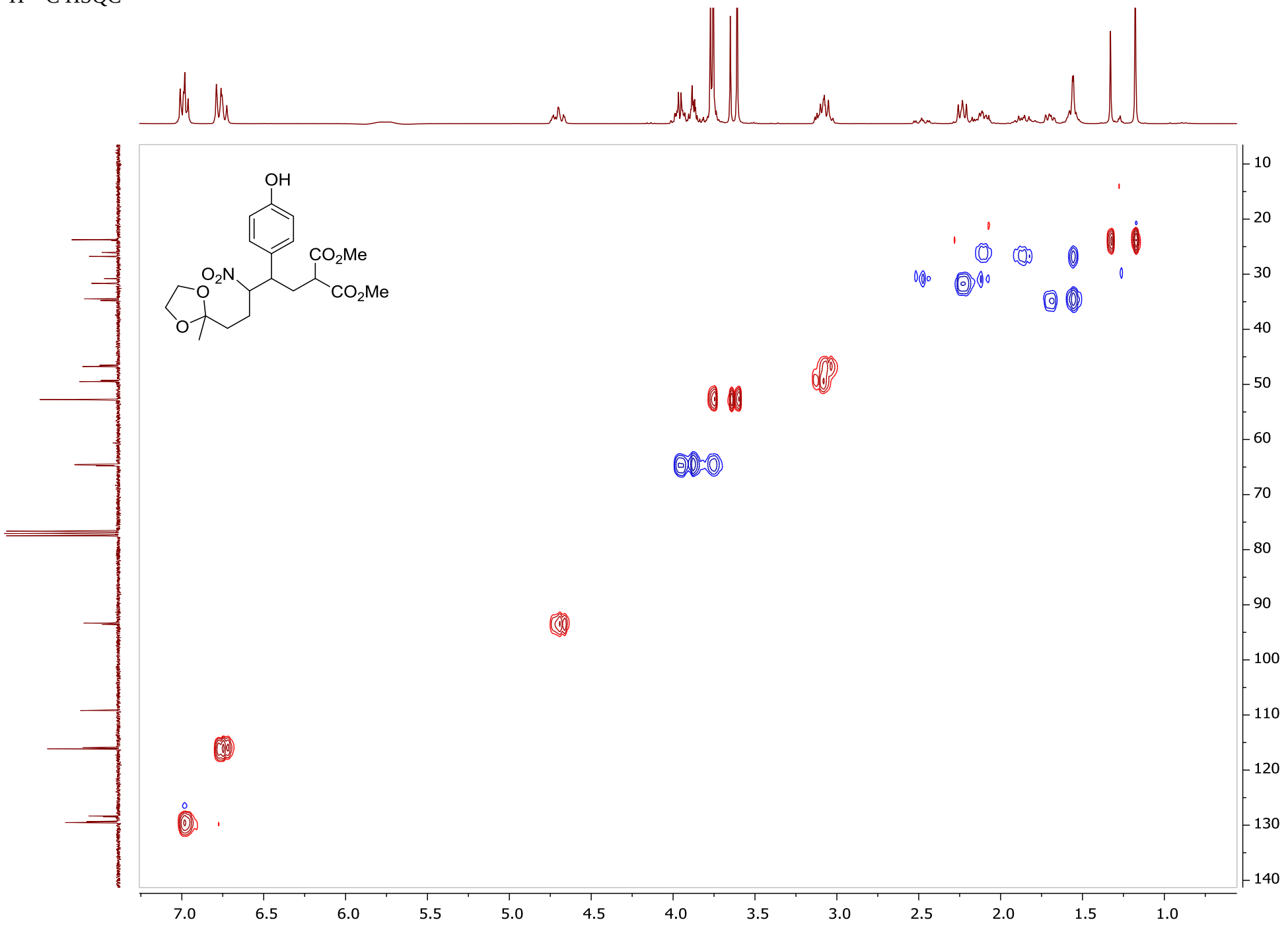
$^{13}$C DEPT (75 MHz, $CDCl_3$)



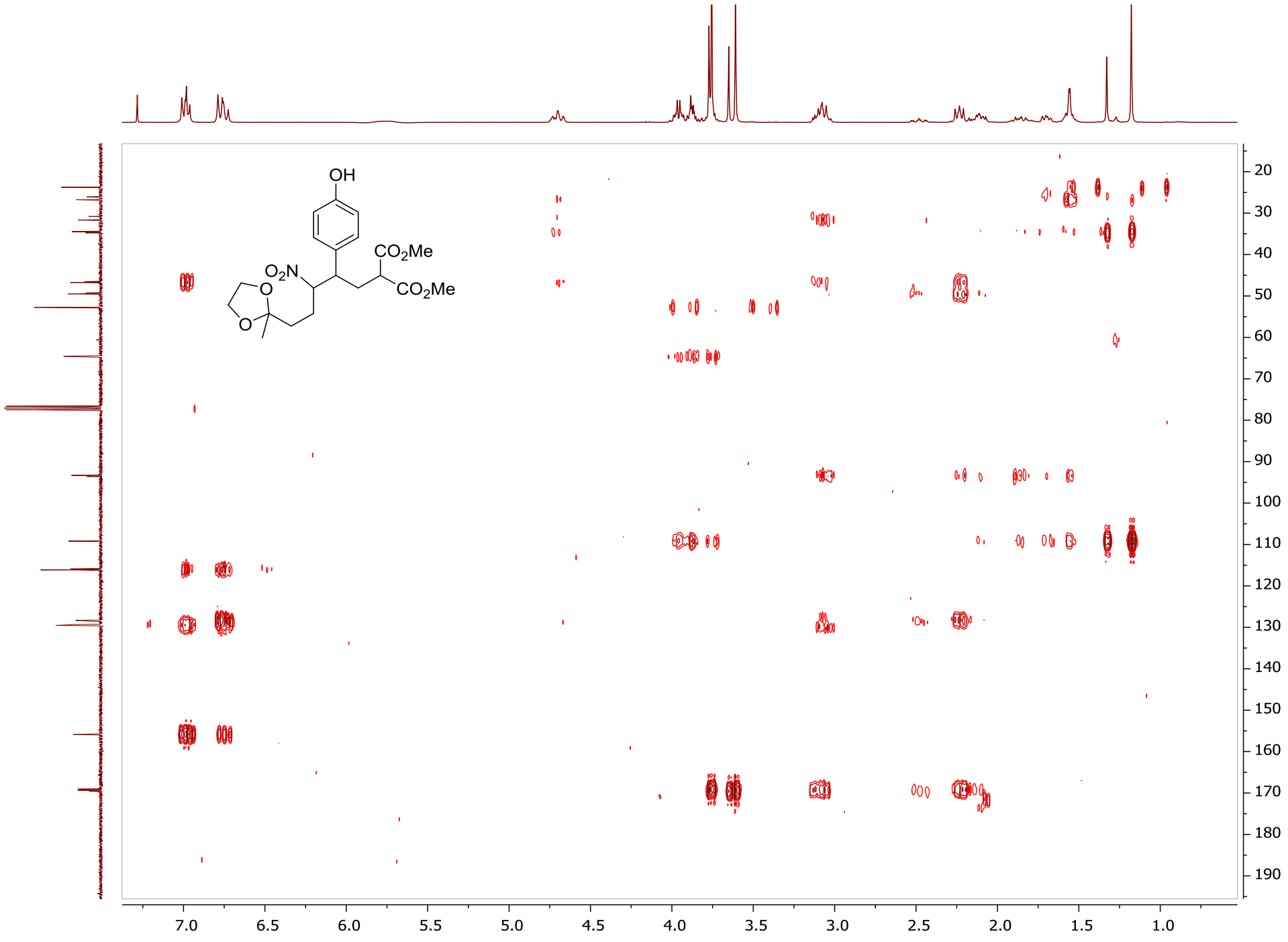
$^{1}$H-$^{1}$H COSY



$^{1}H$-$^{13}C$ HSQC

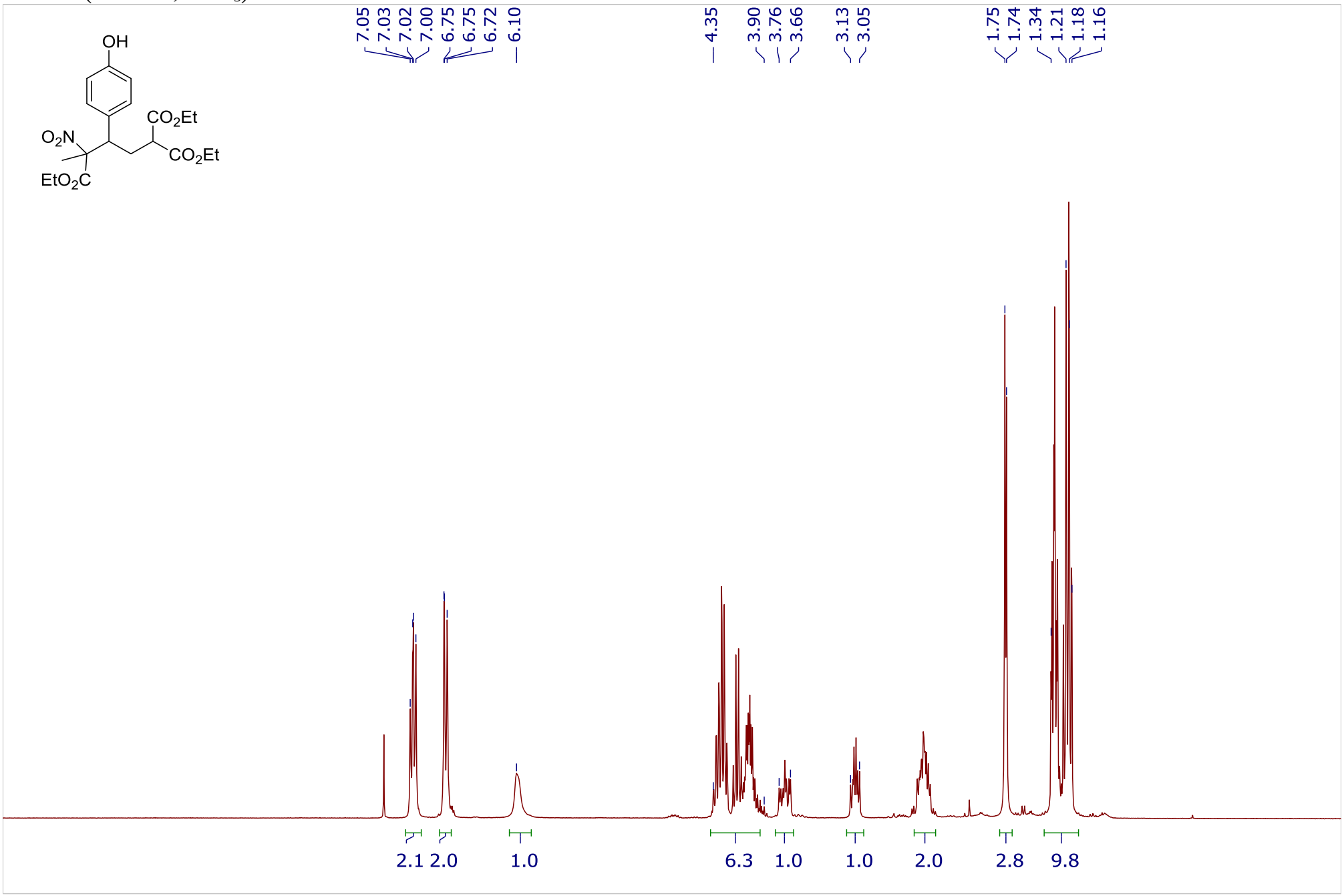

OH
$CO_2Me$
$O_2N$
O
$CO_2Me$
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HMBC

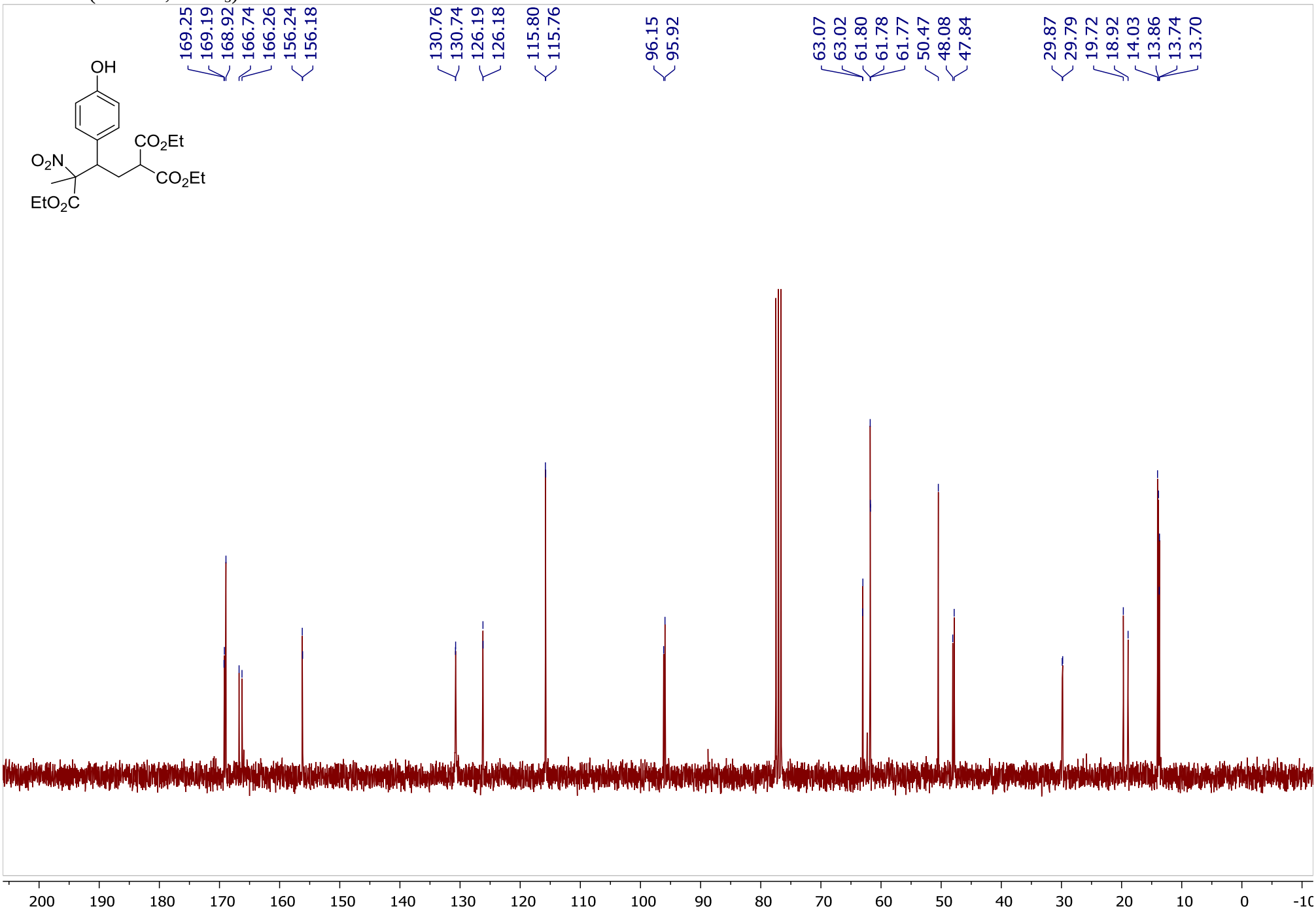

OH
$CO_2Me$
$O_2N$
O
O
$CO_2Me$
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**Triethyl 3-(4-hydroxyphenyl)-4-nitropentane-1,1,4-tricarboxylate (3bo)**, dr = 1:1

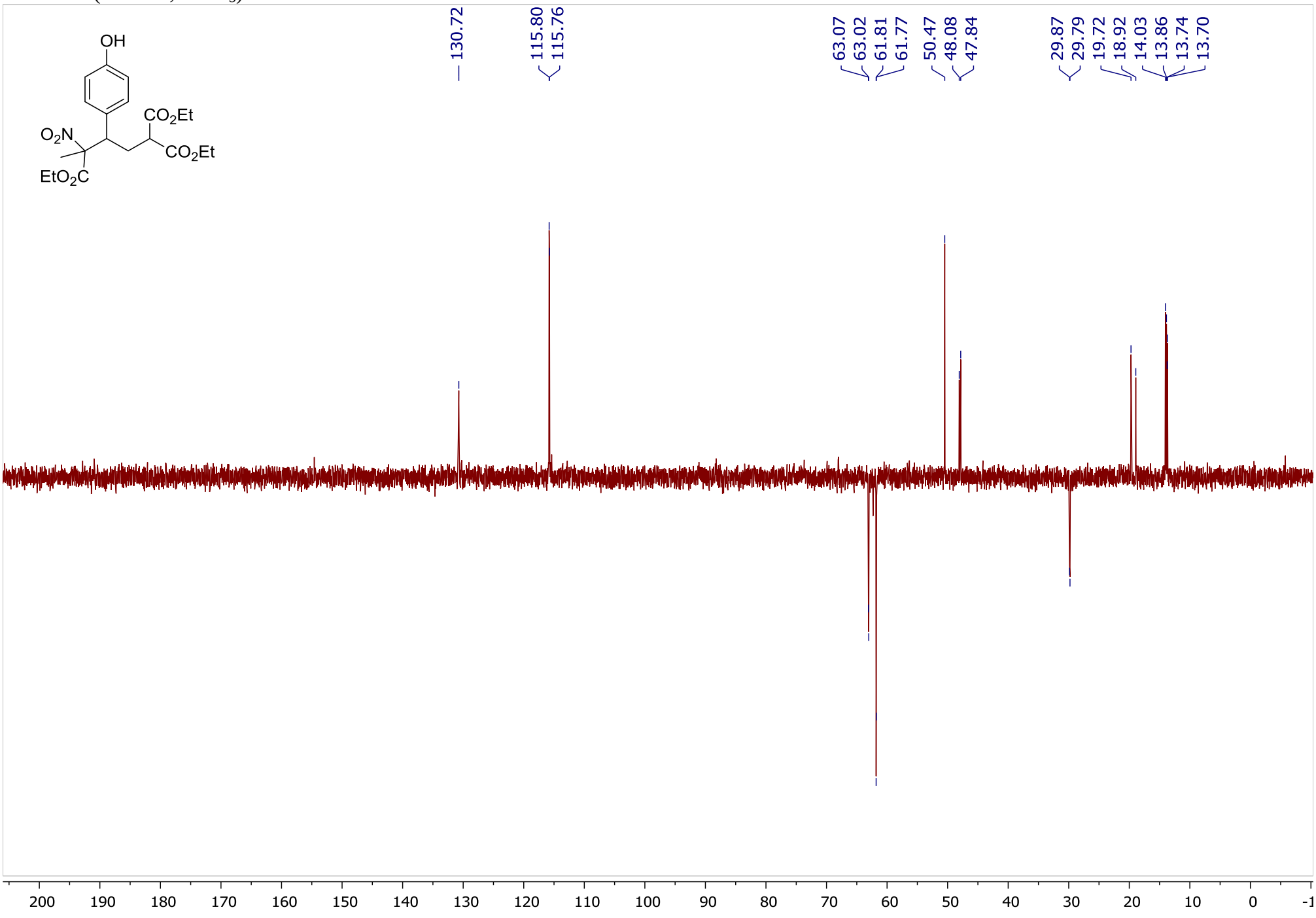
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

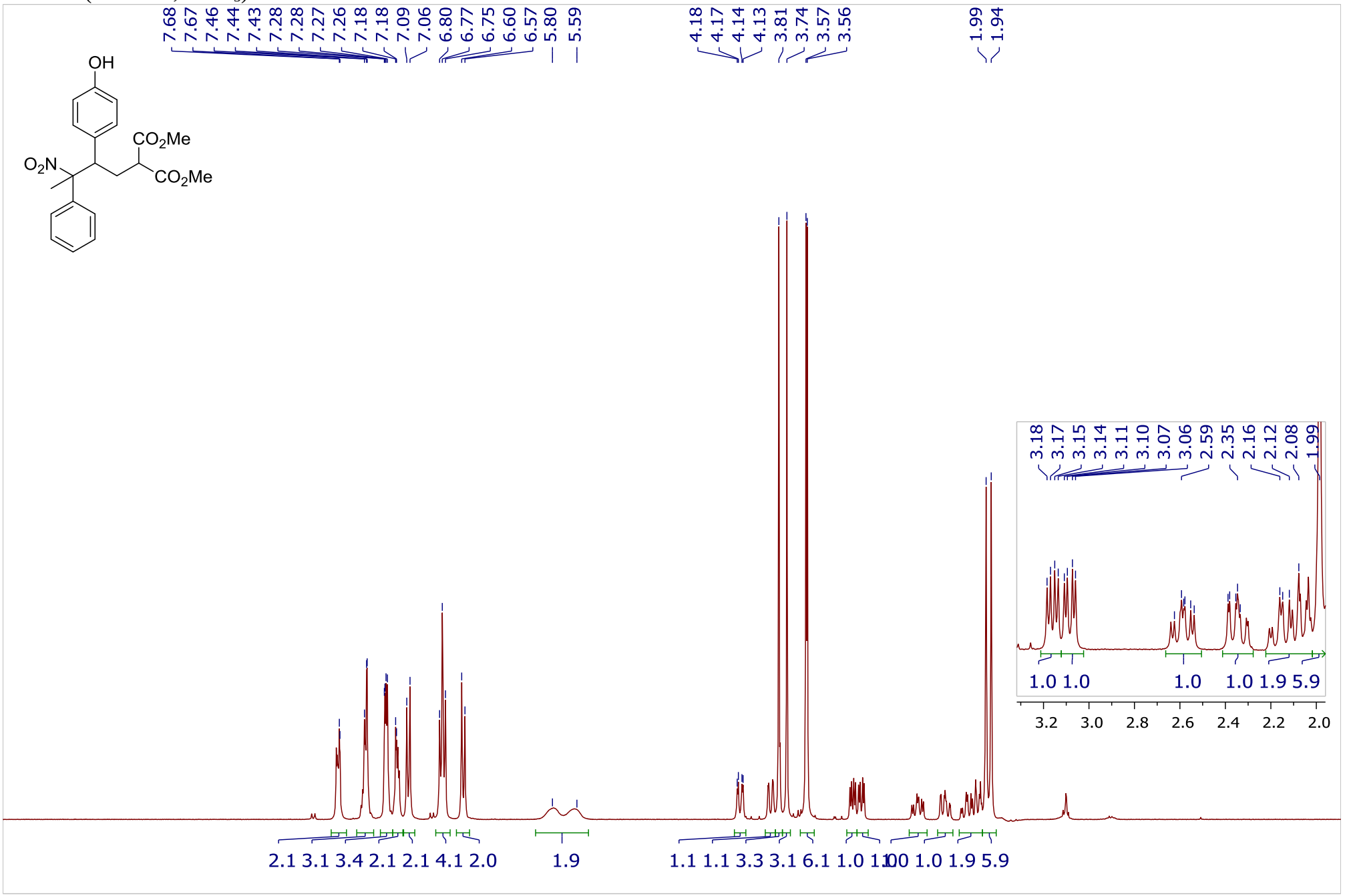


$^{13}$C DEPT (75 MHz, $CDCl_3$)

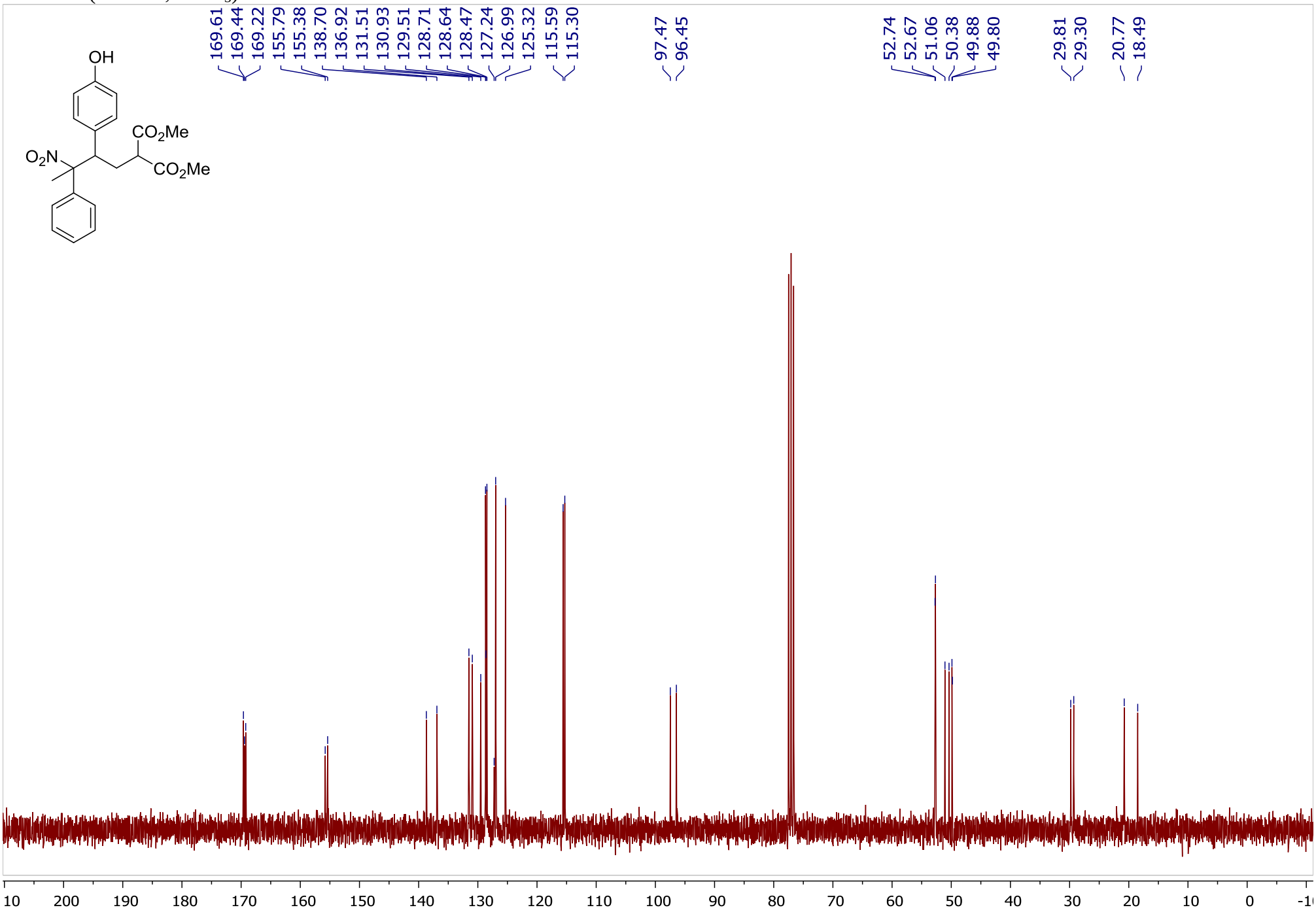


**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitro-3-phenylbutyl)malonate (3ap)**, dr = 1:1

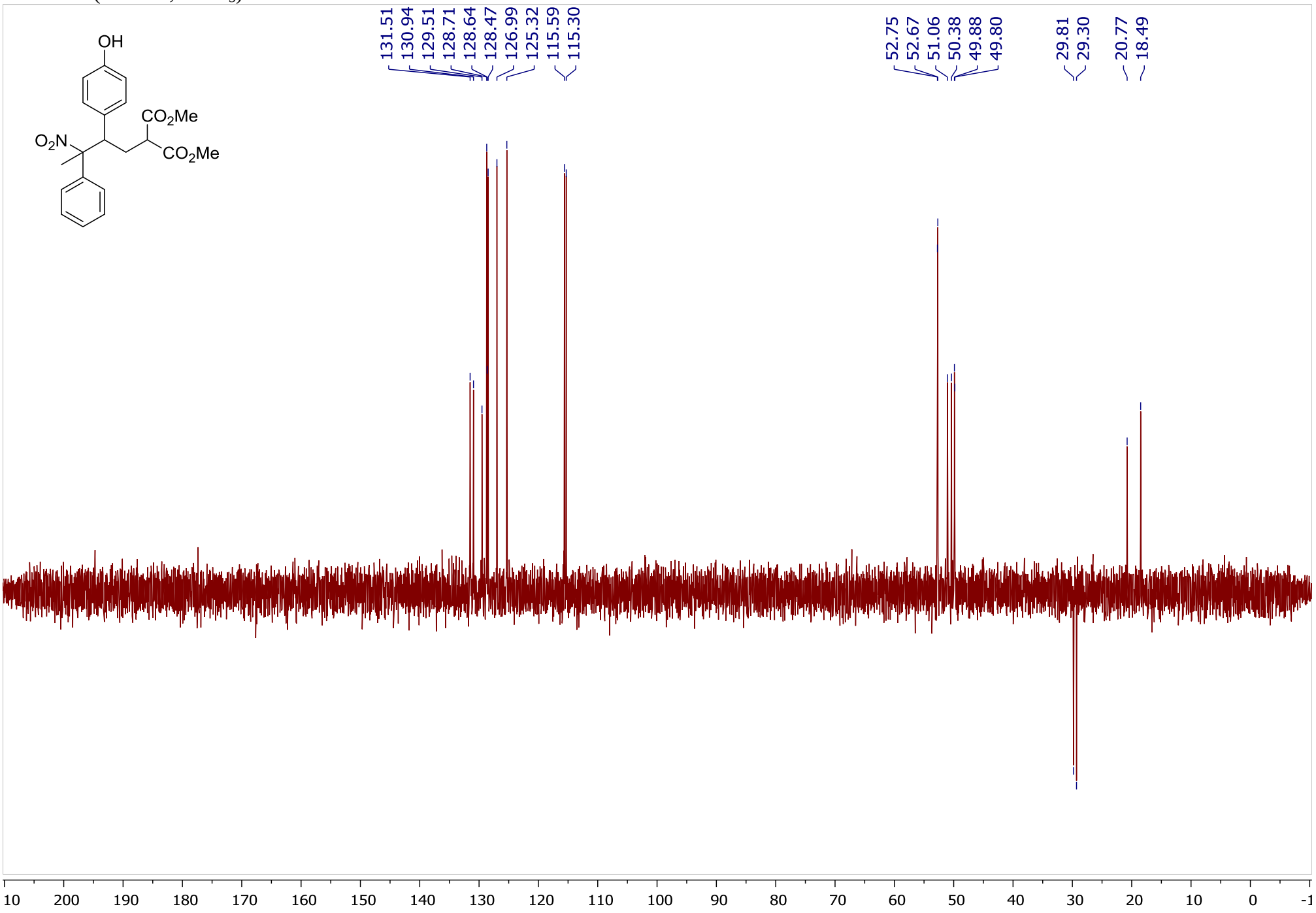
$^1$H NMR (300 MHz, $CDCl_3$)



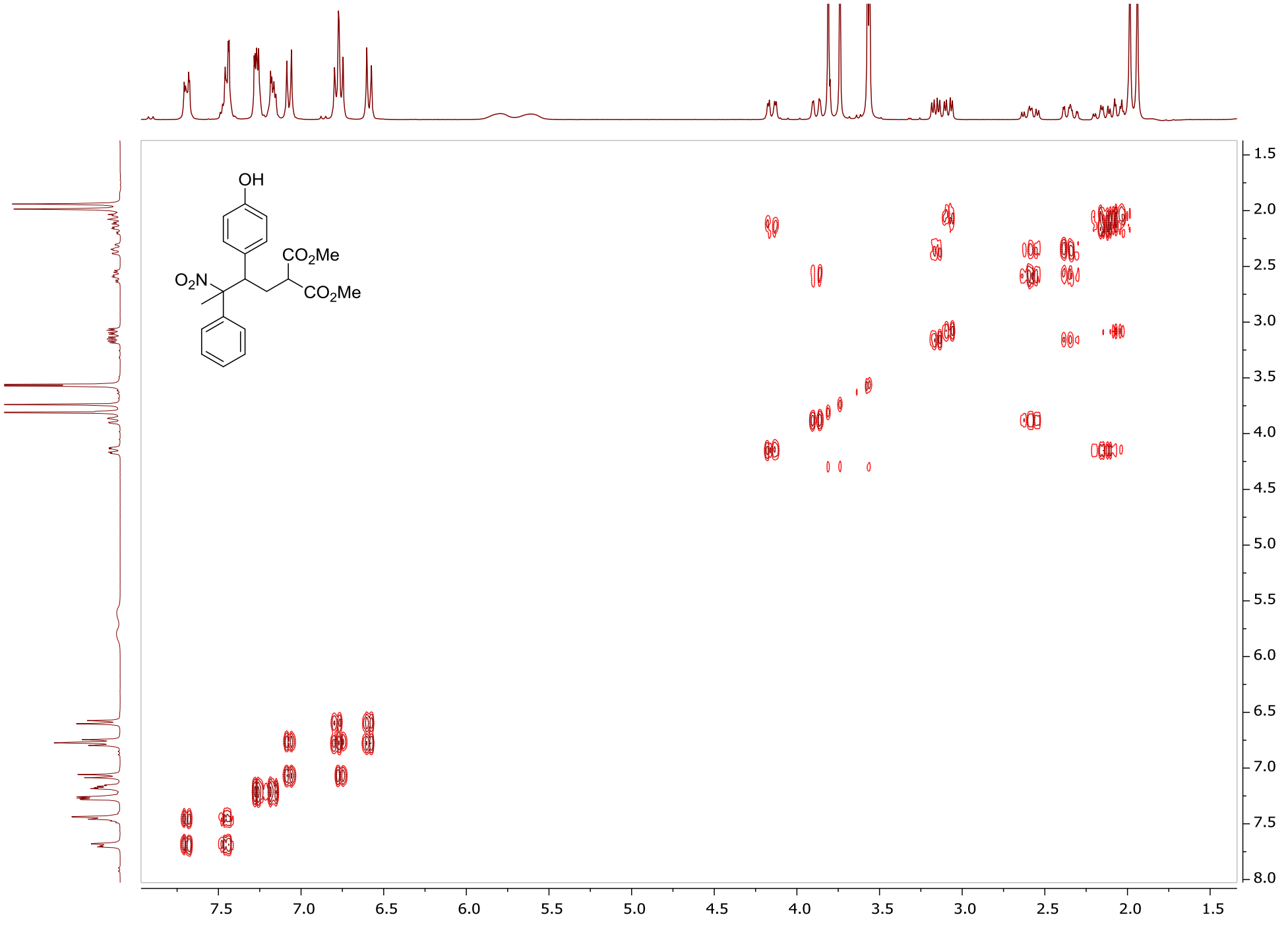
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY


OH
CO2Me
O2N
CO2Me
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
7.5
7.0
6.5
6.0
5.5
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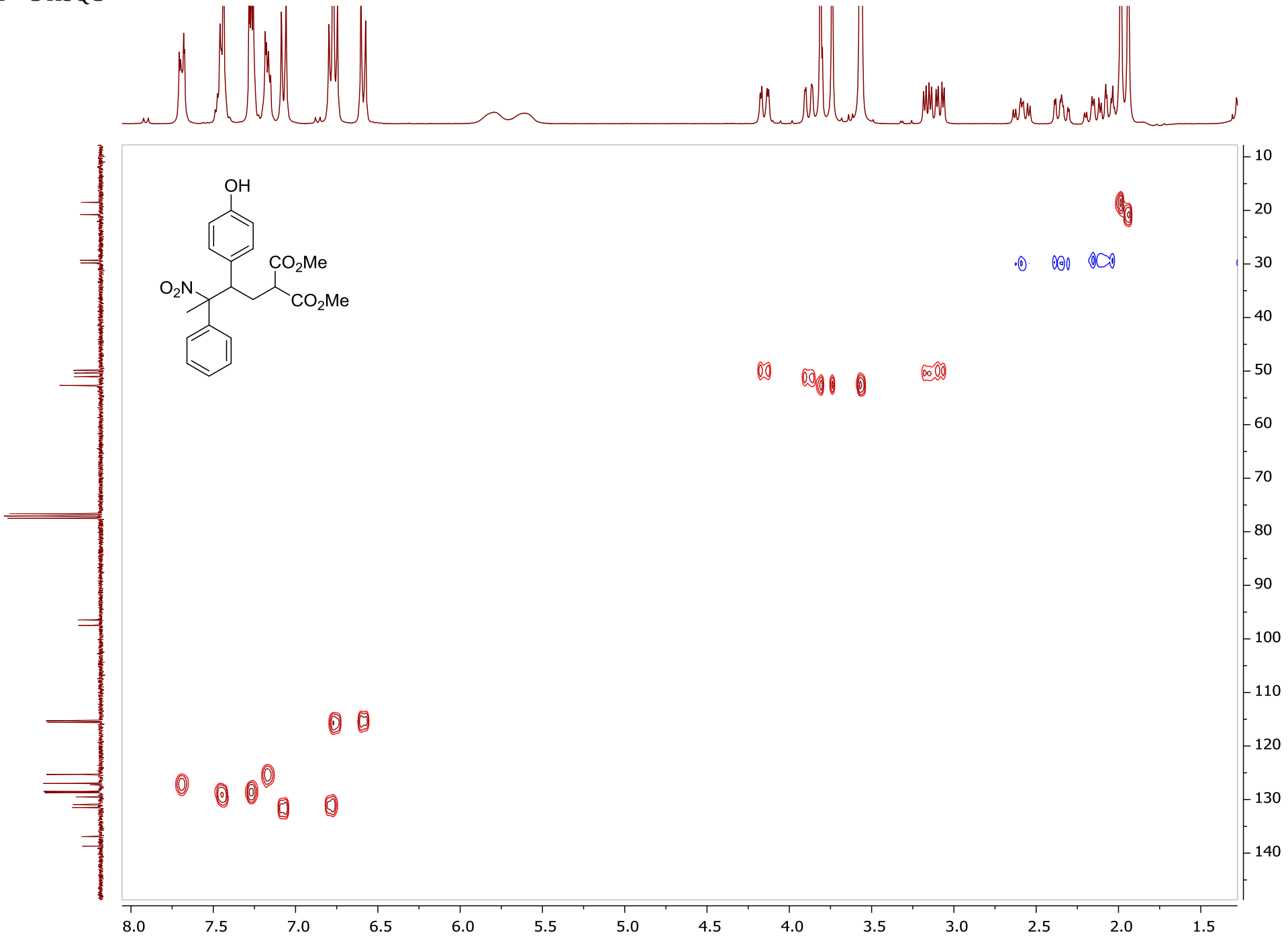
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HSQC


OH
CO2Me
O2N
CO2Me
10
20
30
40
50
60
70
80
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100
110
120
130
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8.0
7.5
7.0
6.5
6.0
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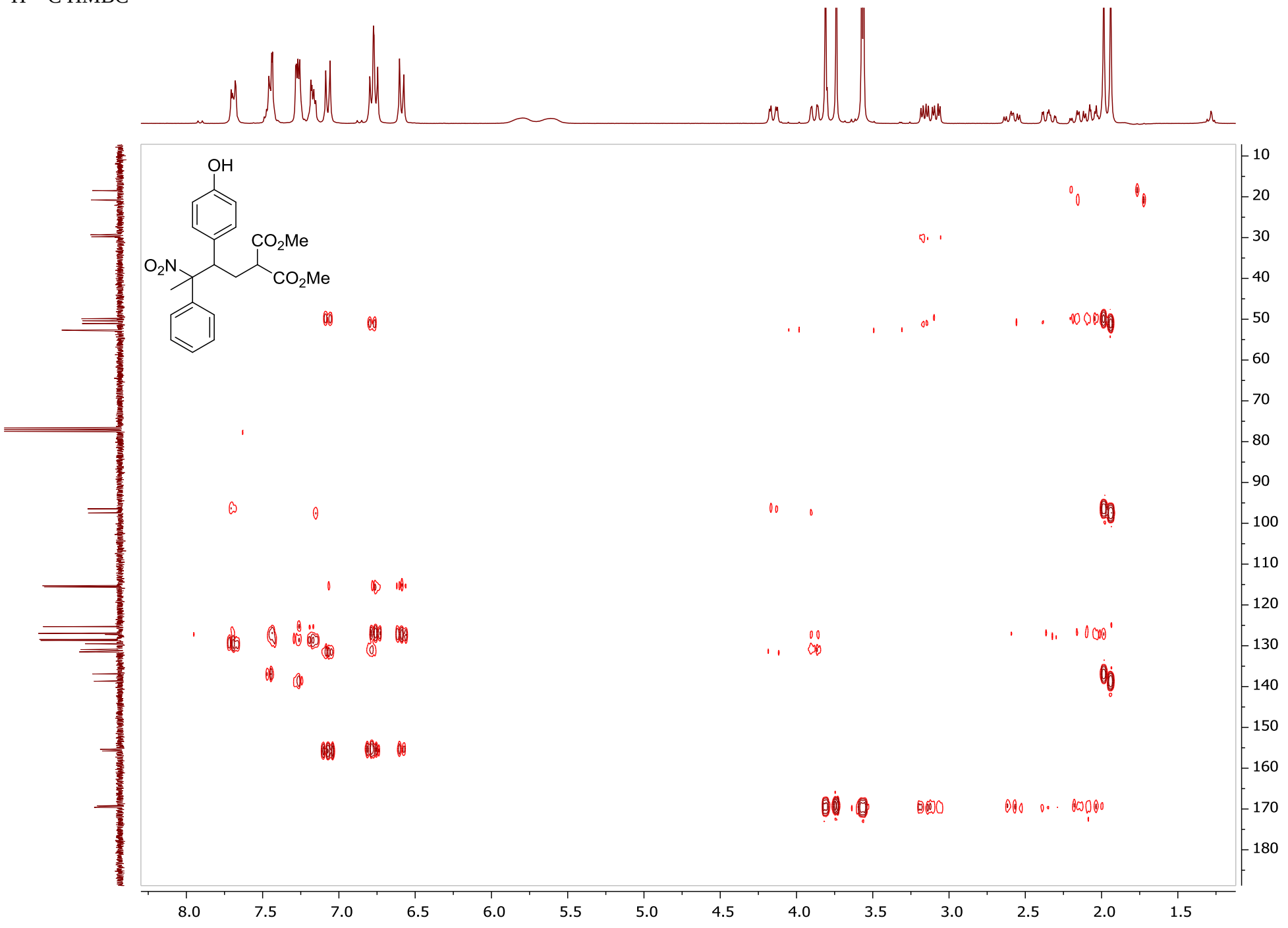
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HMBC


OH
CO2Me
O2N
CO2Me
10
20
30
40
50
60
70
80
90
100
110
120
130
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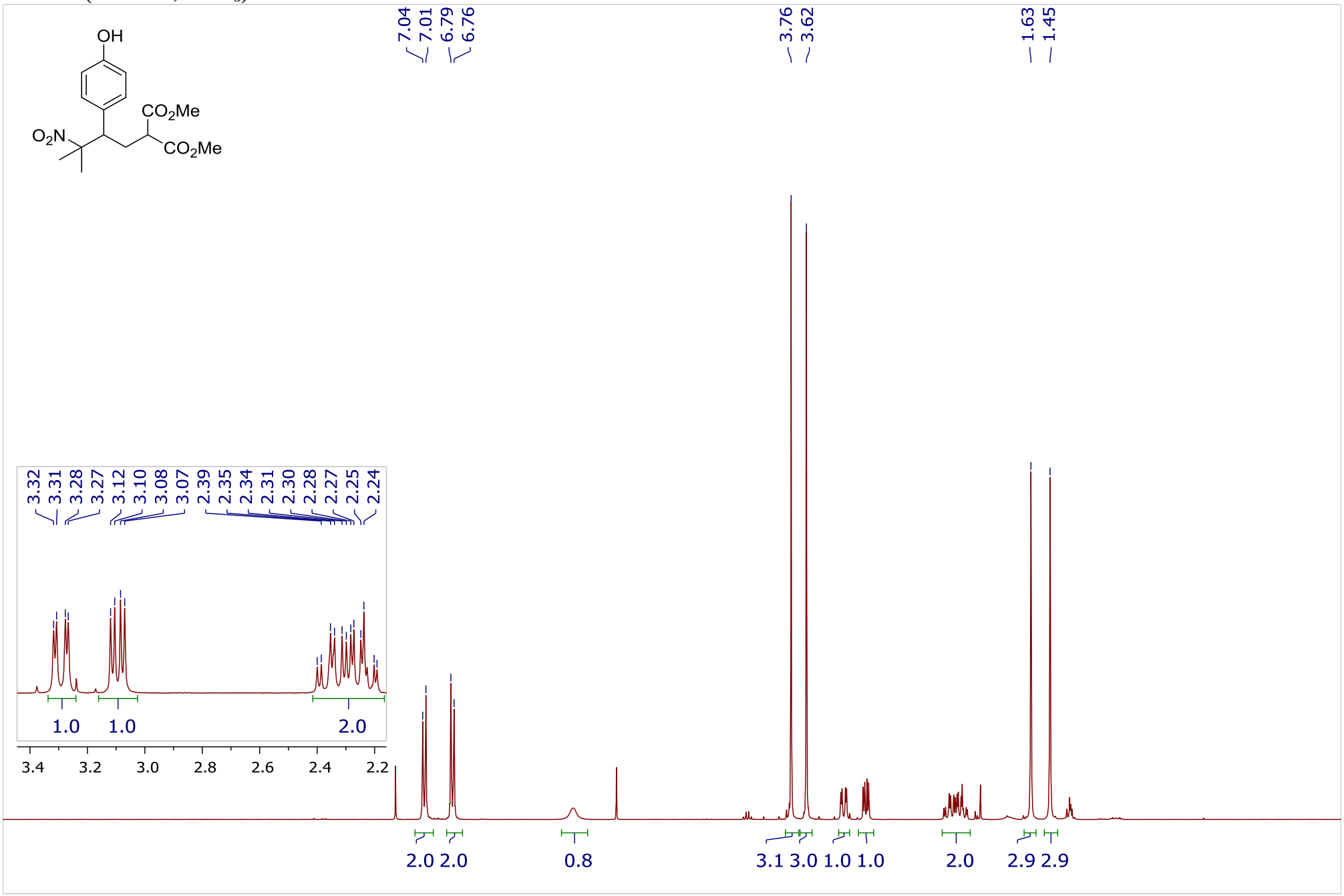
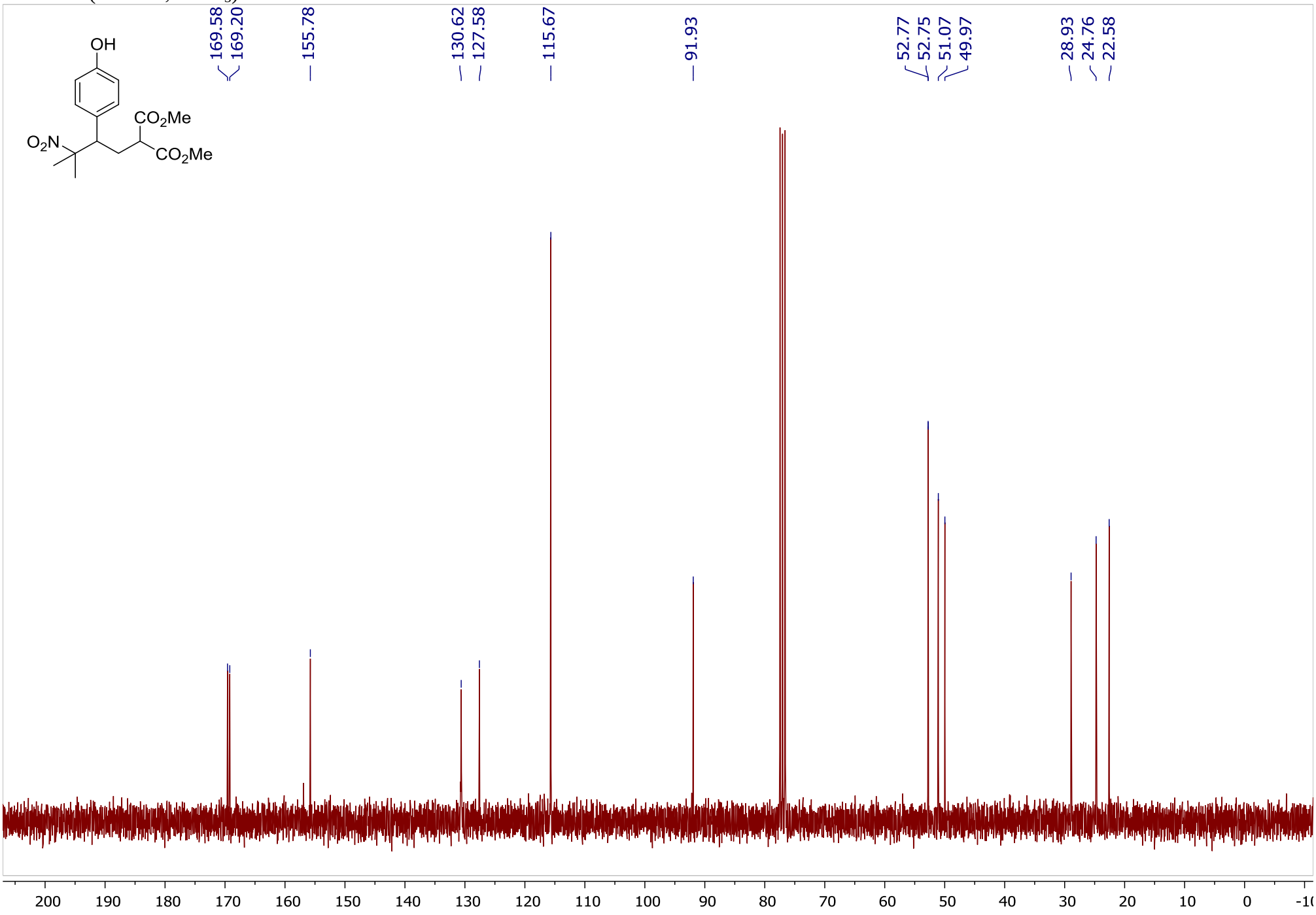
150
160
170
180
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-methyl-3-nitrobutyl)malonate (3aq)**

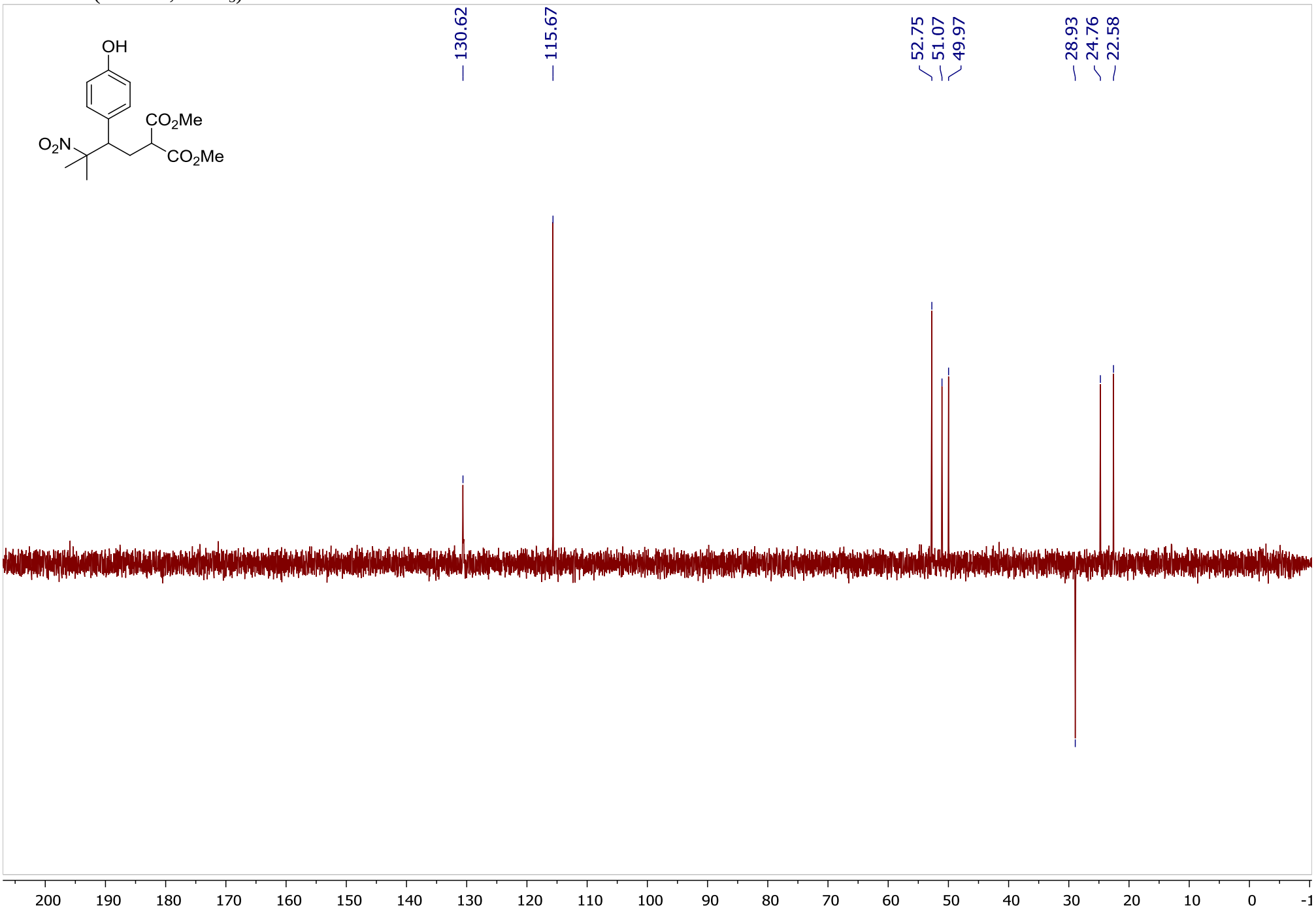
$^1$H NMR (300 MHz, $CDCl_3$)



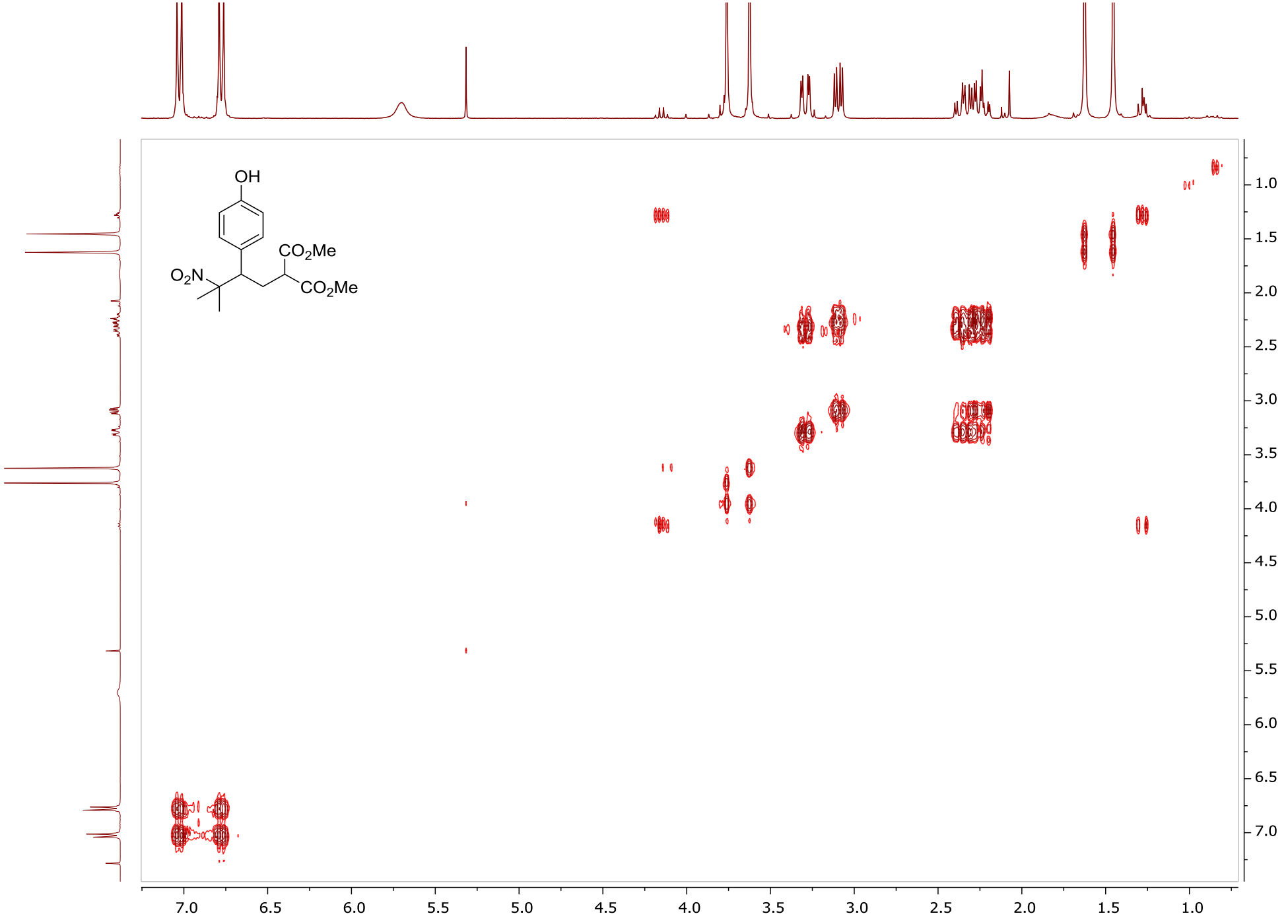
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
O2N
CO2Me
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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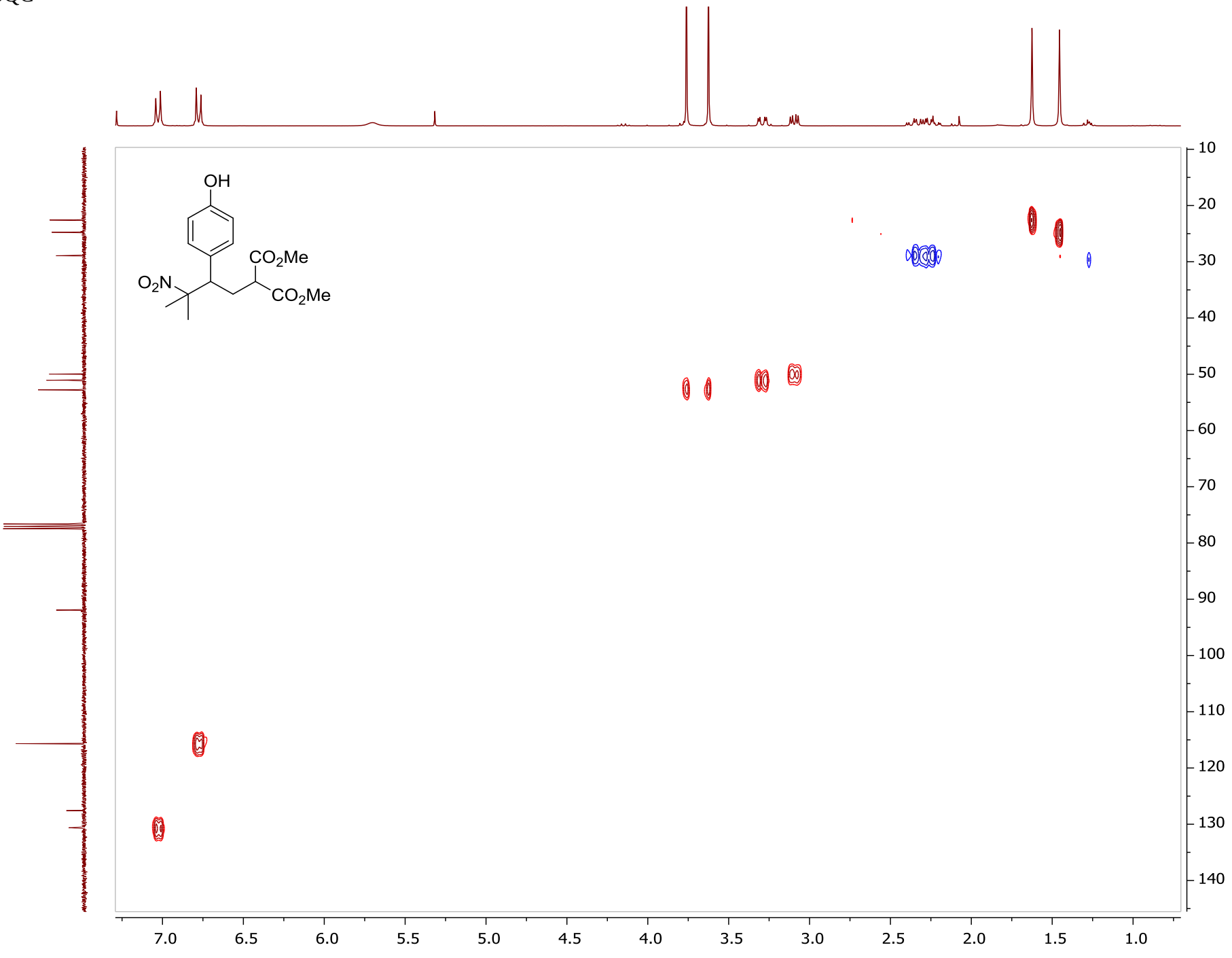
1.0

$^{1}H$-$^{13}C$ HSQC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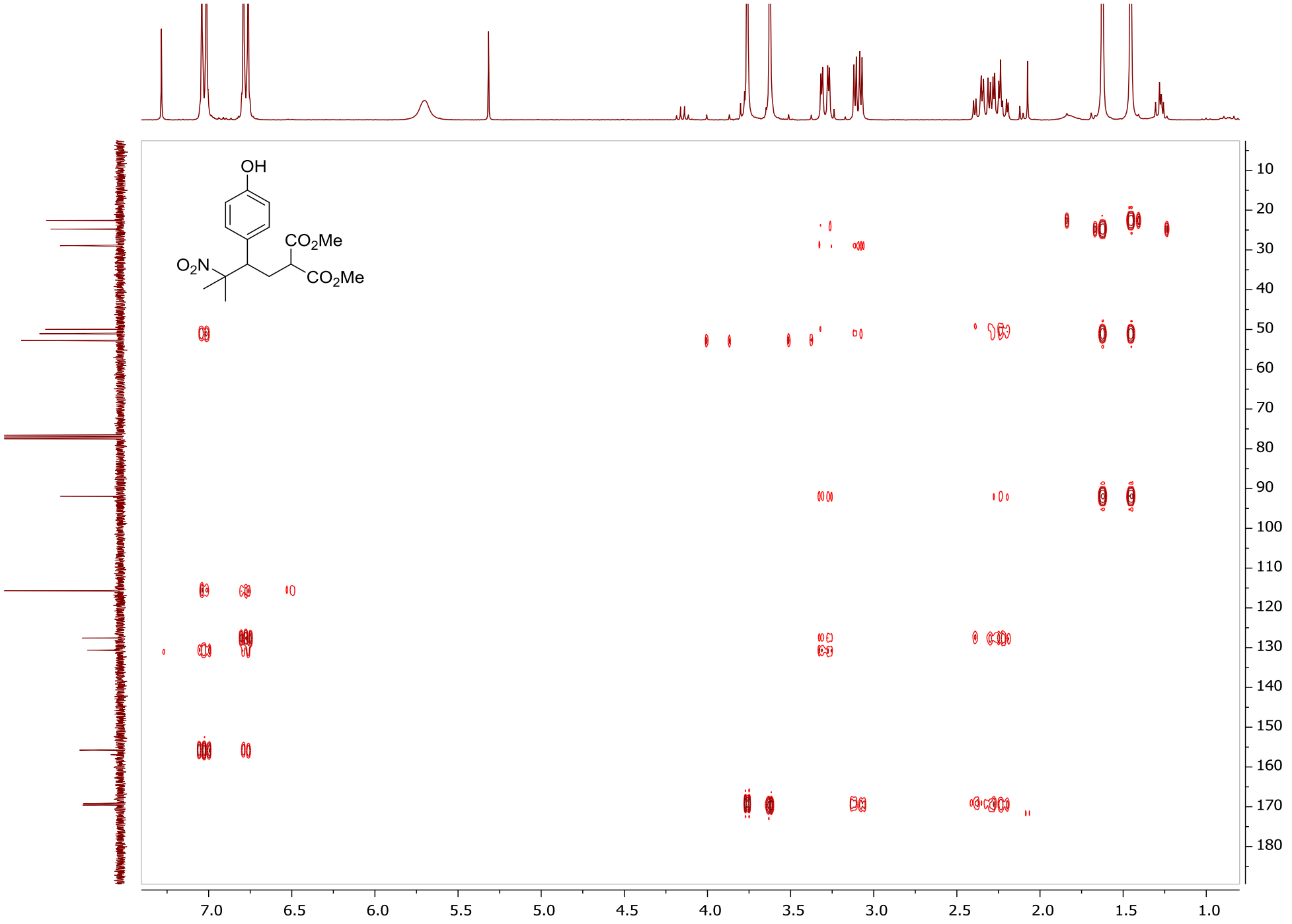
1.0

$^{1}H$-$^{13}C$ HMBC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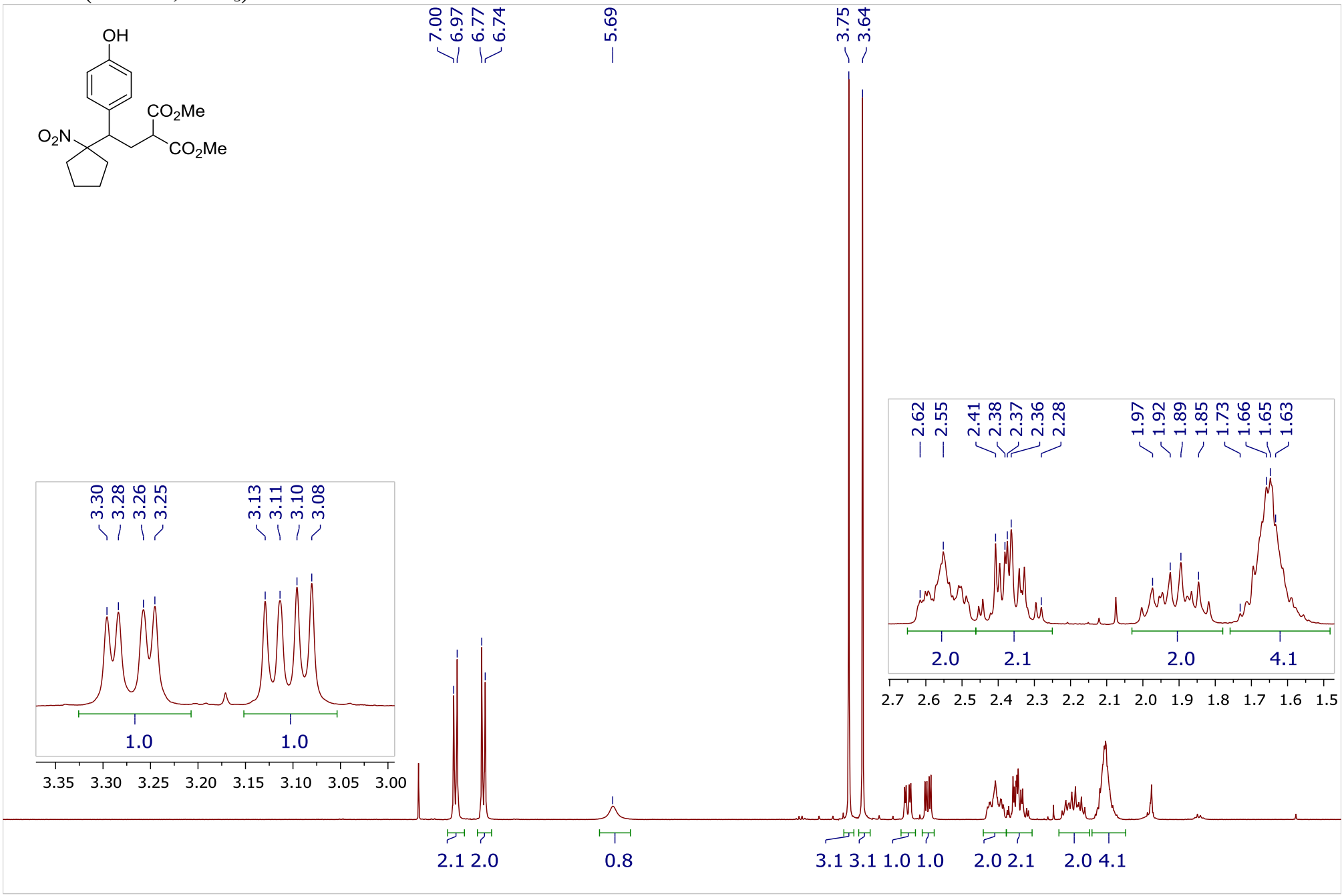
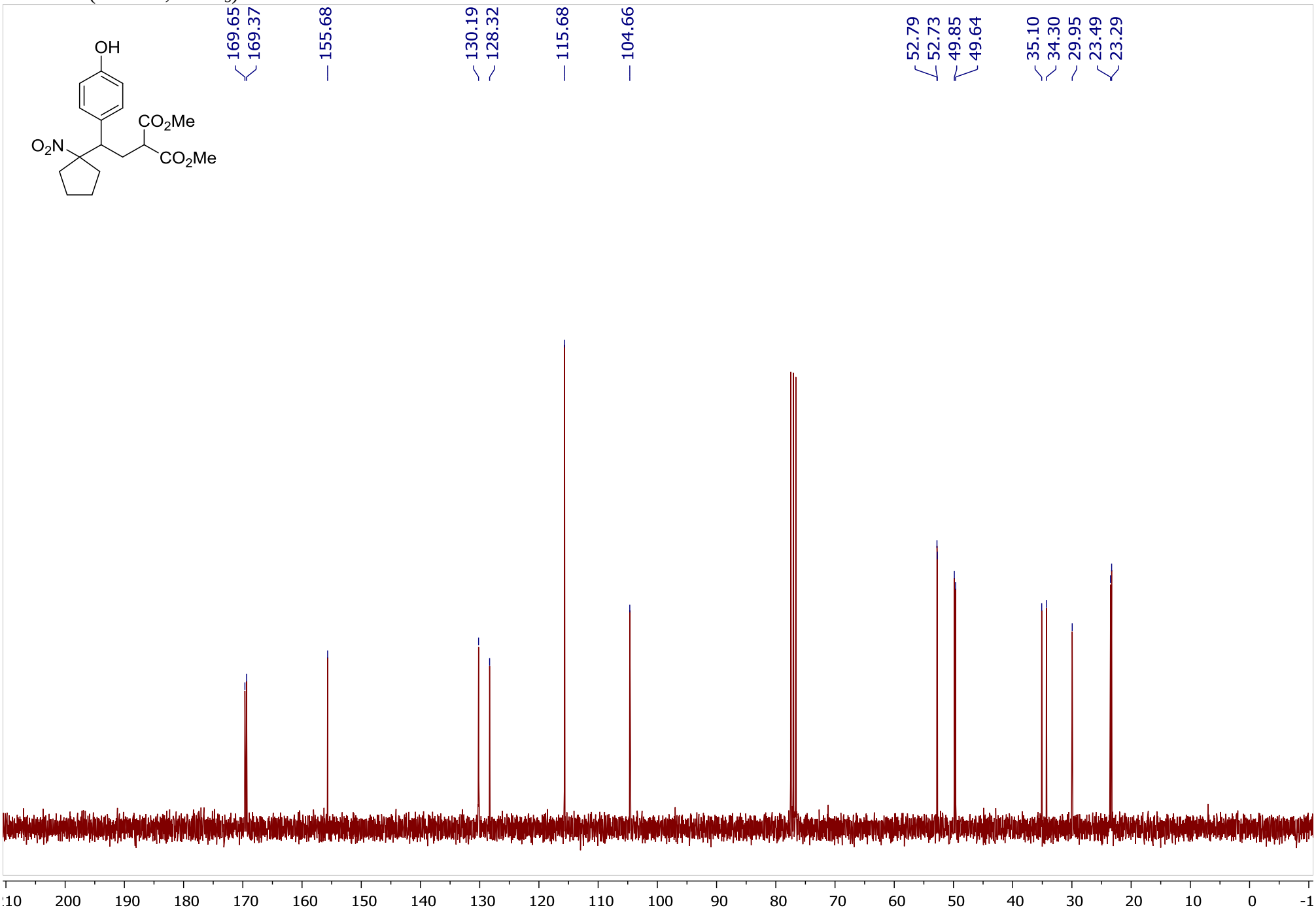
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**Dimethyl 2-(2-(4-hydroxyphenyl)-2-(1-nitrocyclopentyl)ethyl)malonate (3ar)**

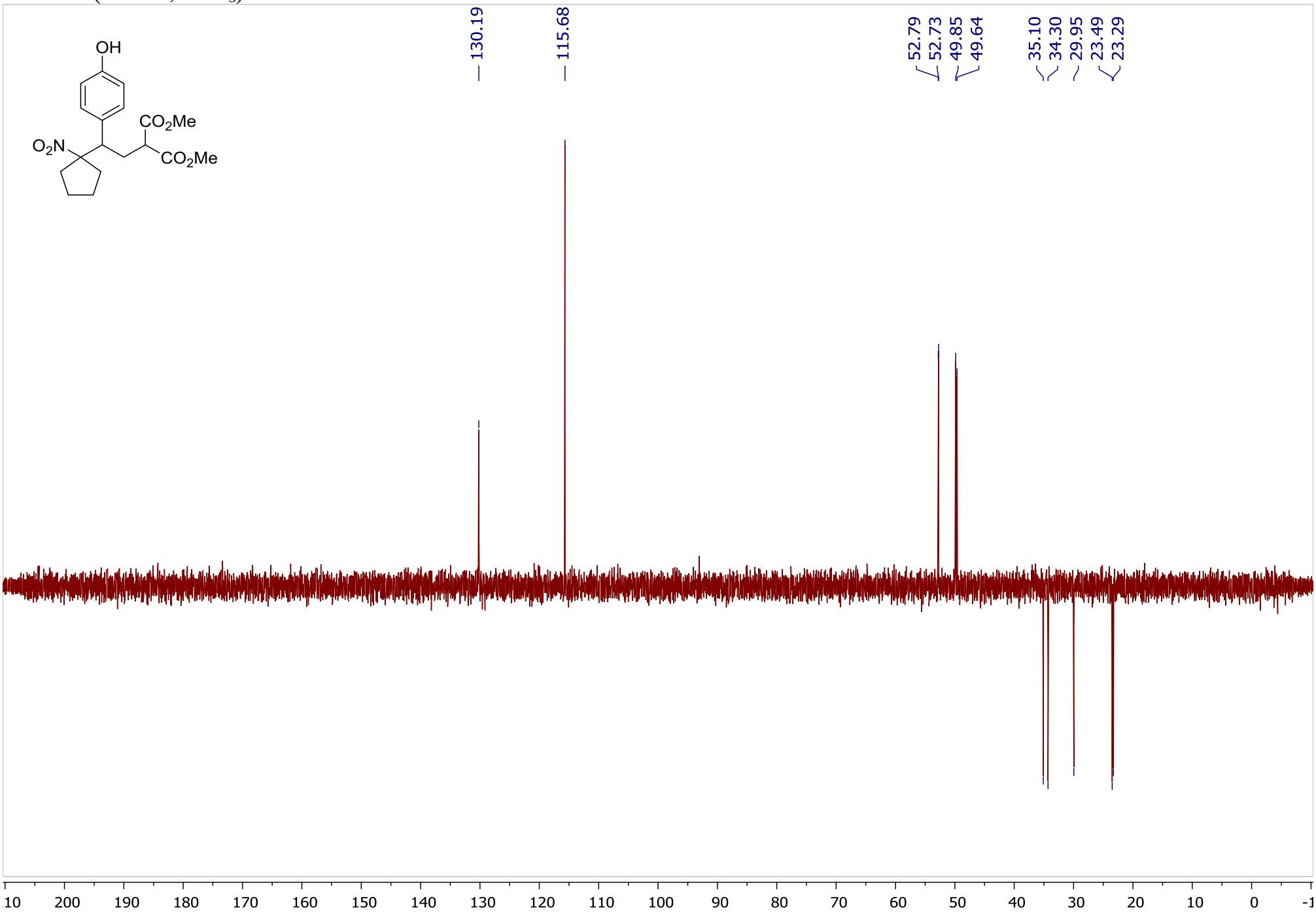
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

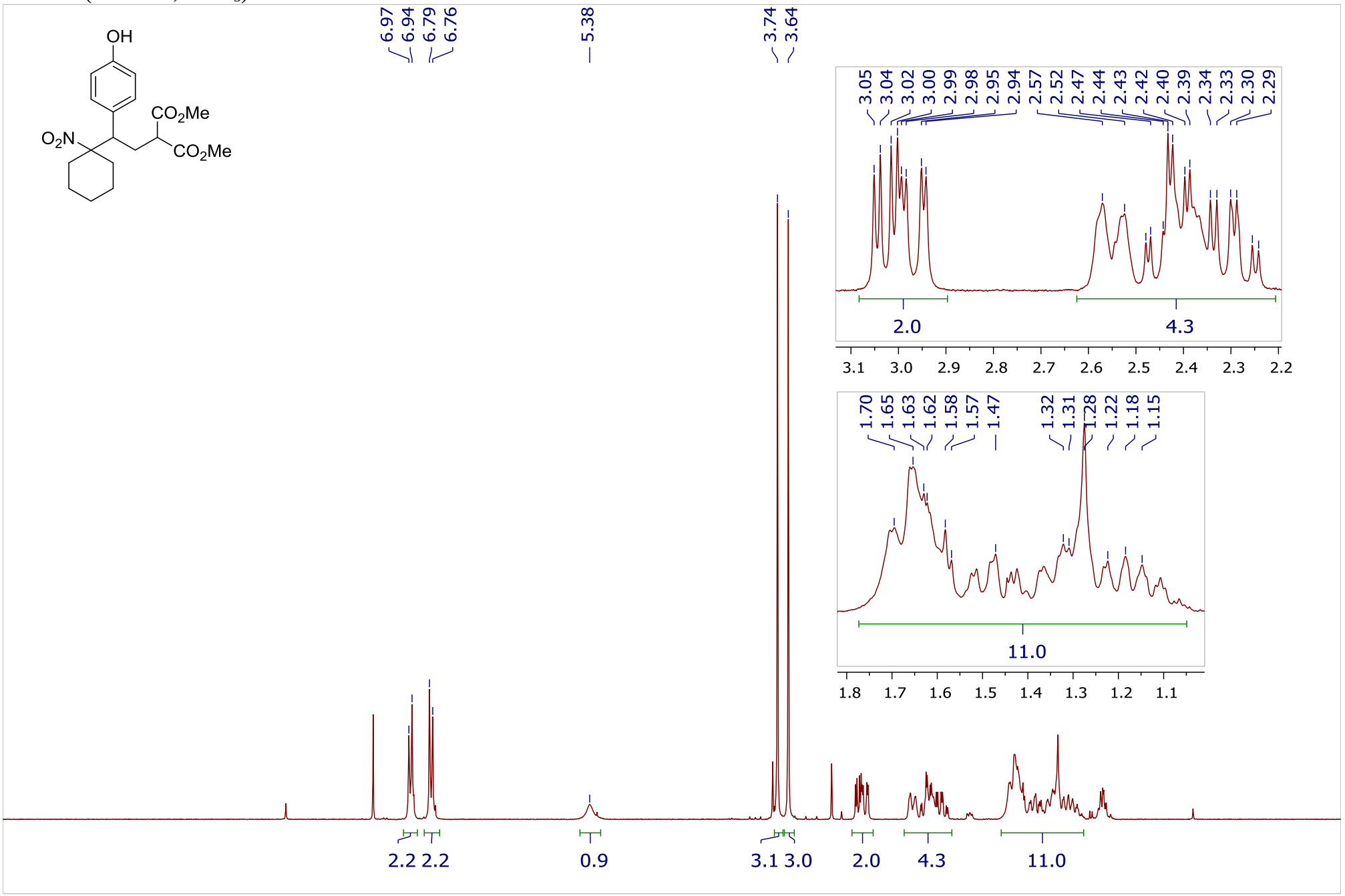


$^{13}$C DEPT (75 MHz, $CDCl_3$)

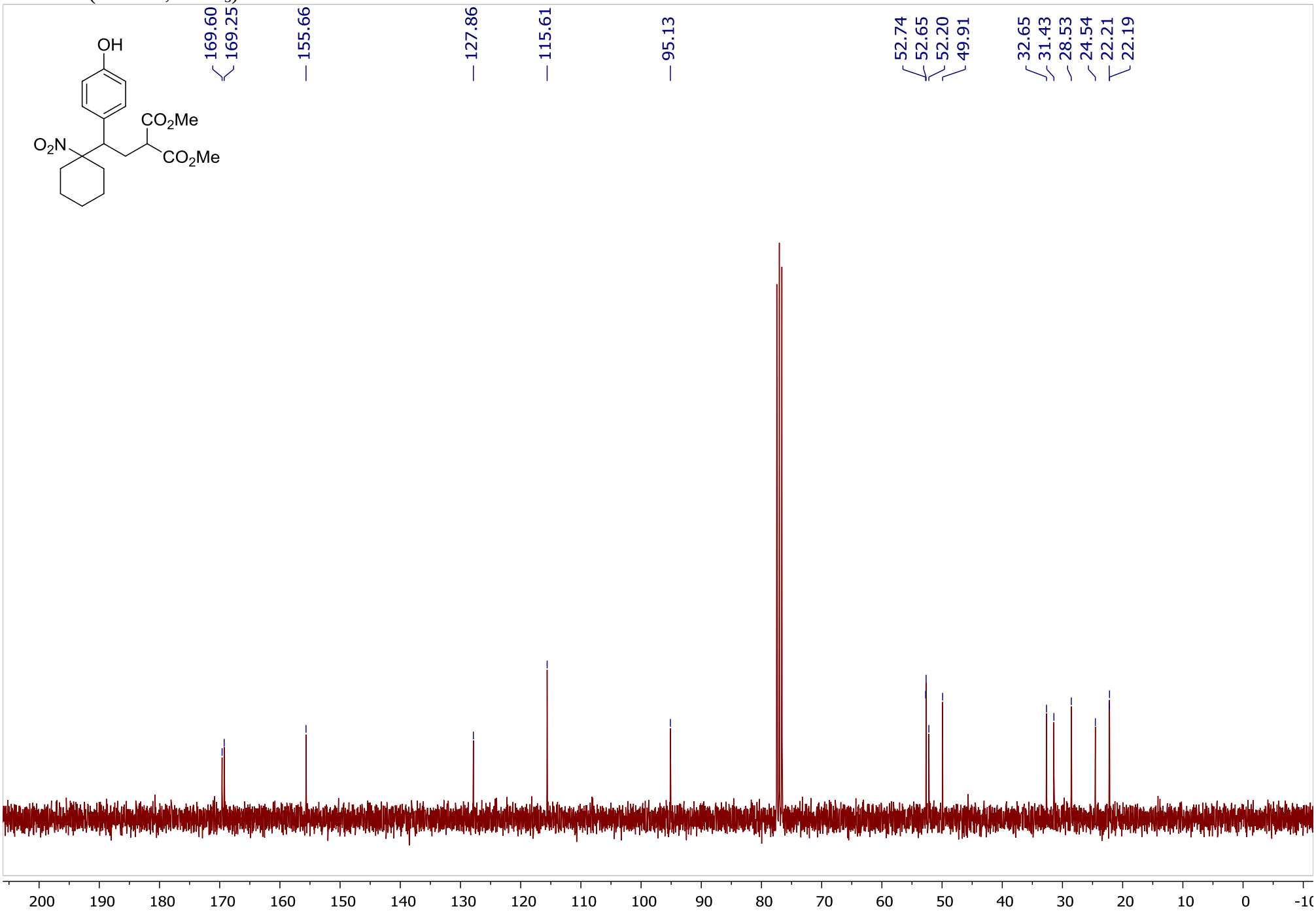


**Dimethyl 2-(2-(4-hydroxyphenyl)-2-(1-nitrocyclohexyl)ethyl)malonate (3as)**

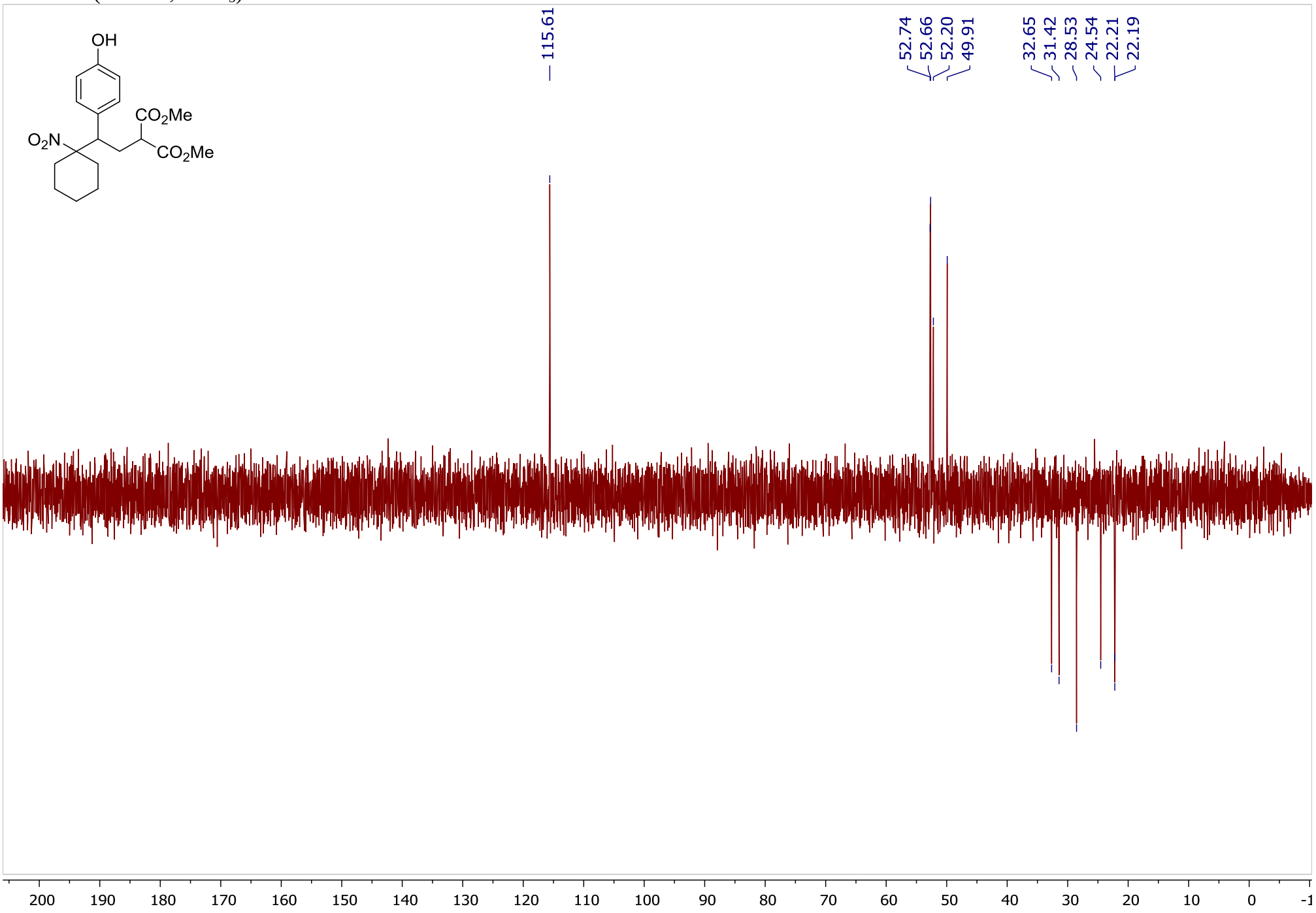
$^1$H NMR (300 MHz, $CDCl_3$)



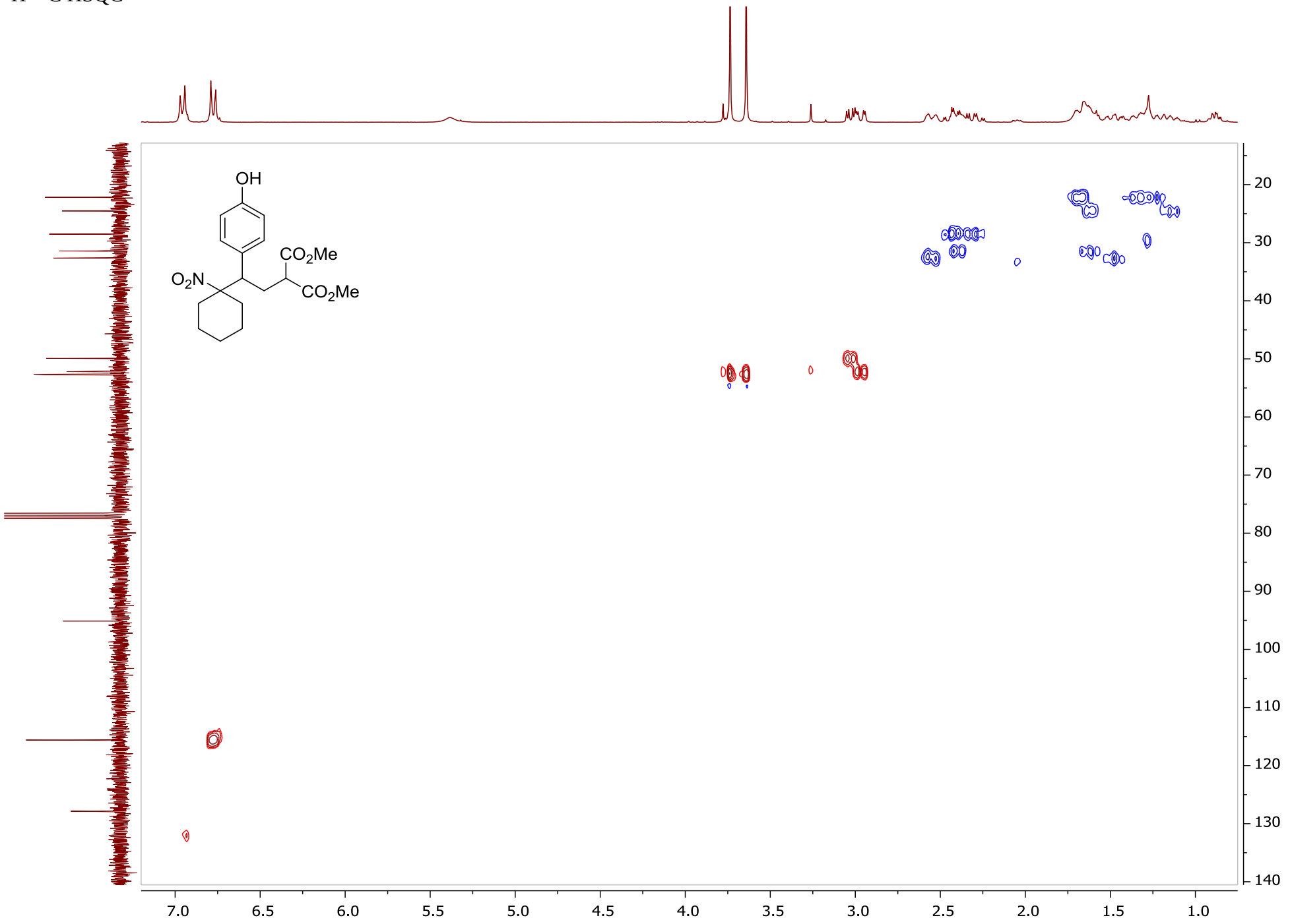
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}H$-$^{13}C$ HSQC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5.5
5.0
4.5
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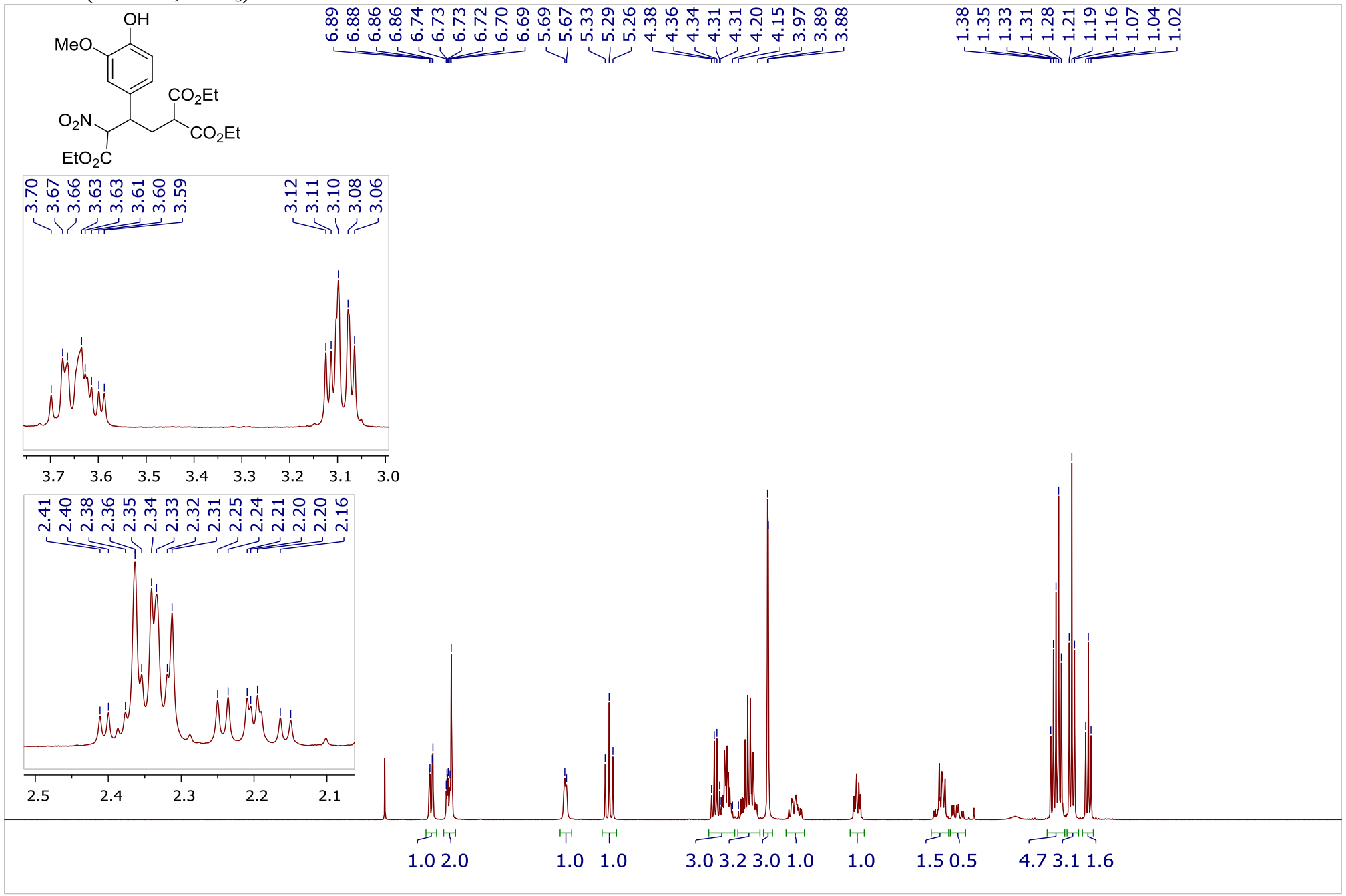
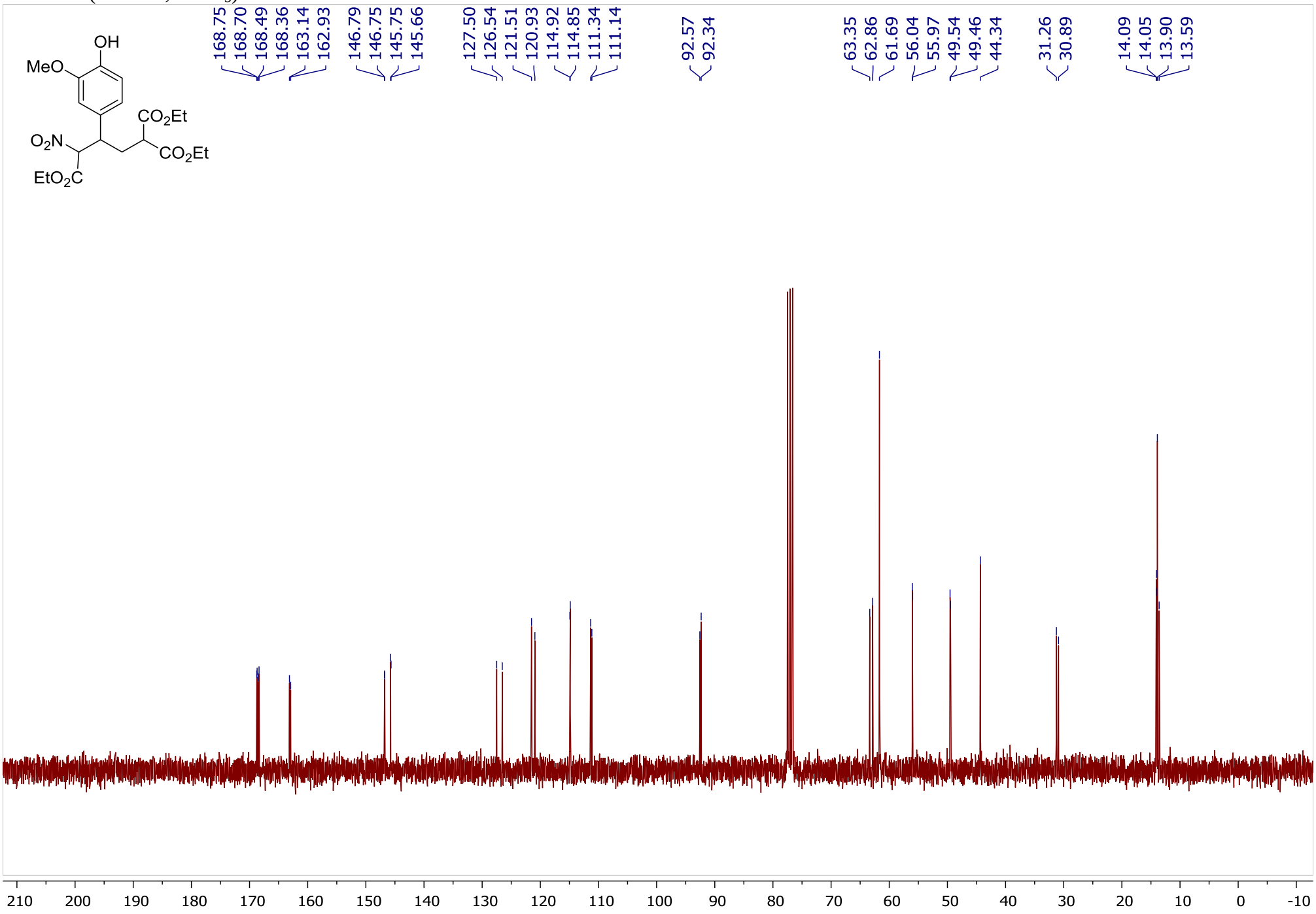
2.5
2.0
1.5
1.0

**Triethyl 3-(4-hydroxy-3-methoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ca)**, dr = 1:1

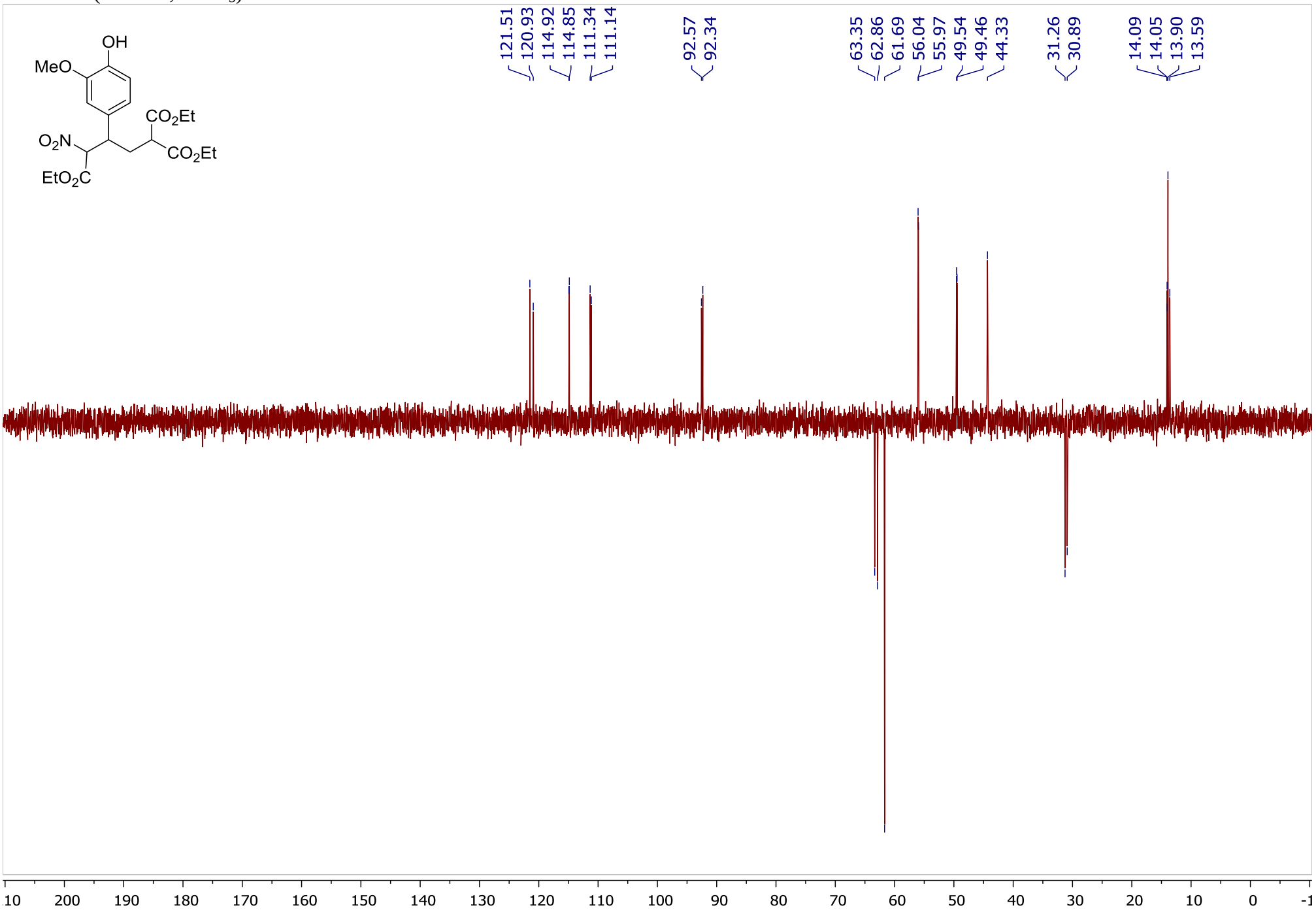
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

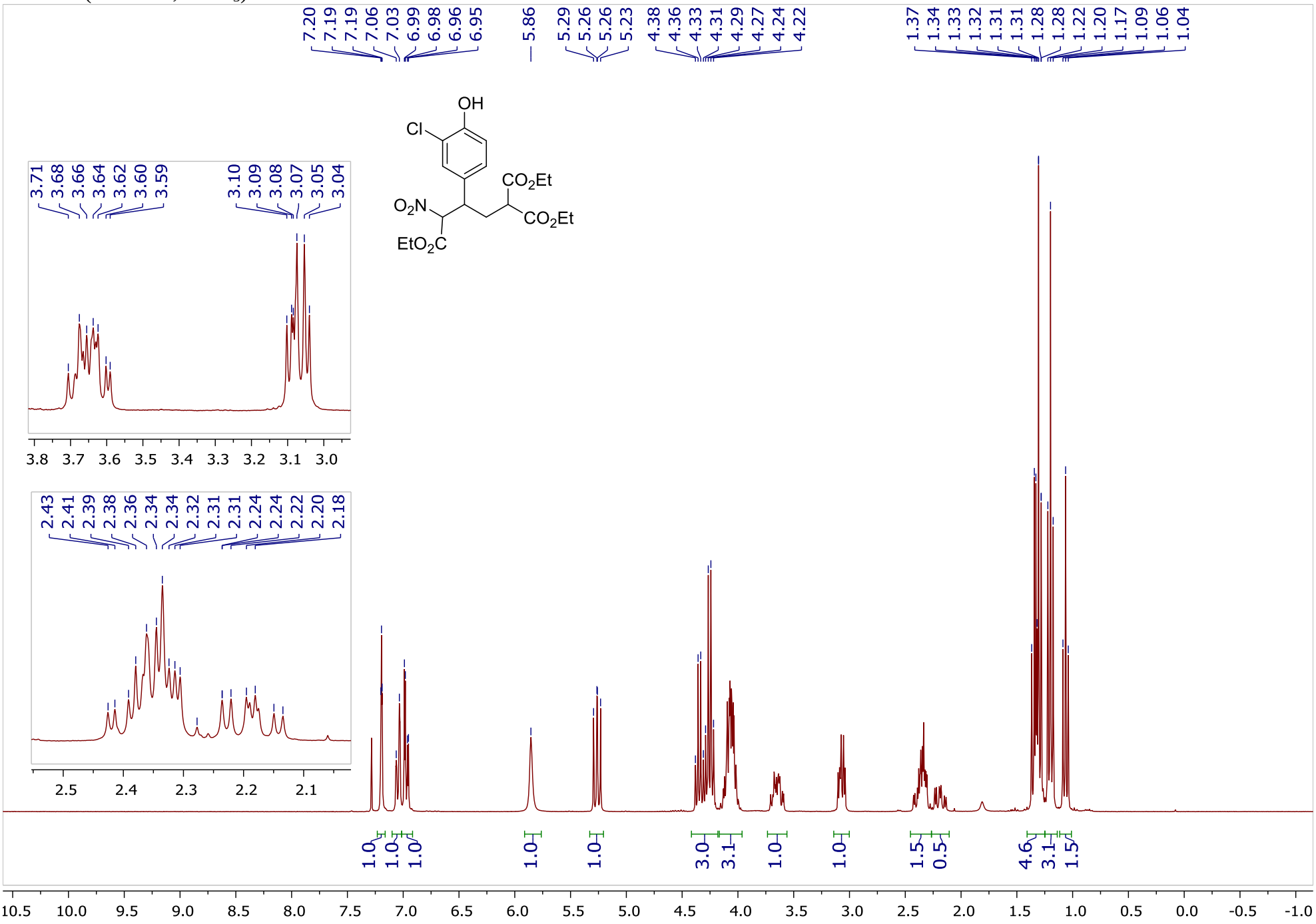


$^{13}$C DEPT (75 MHz, $CDCl_3$)

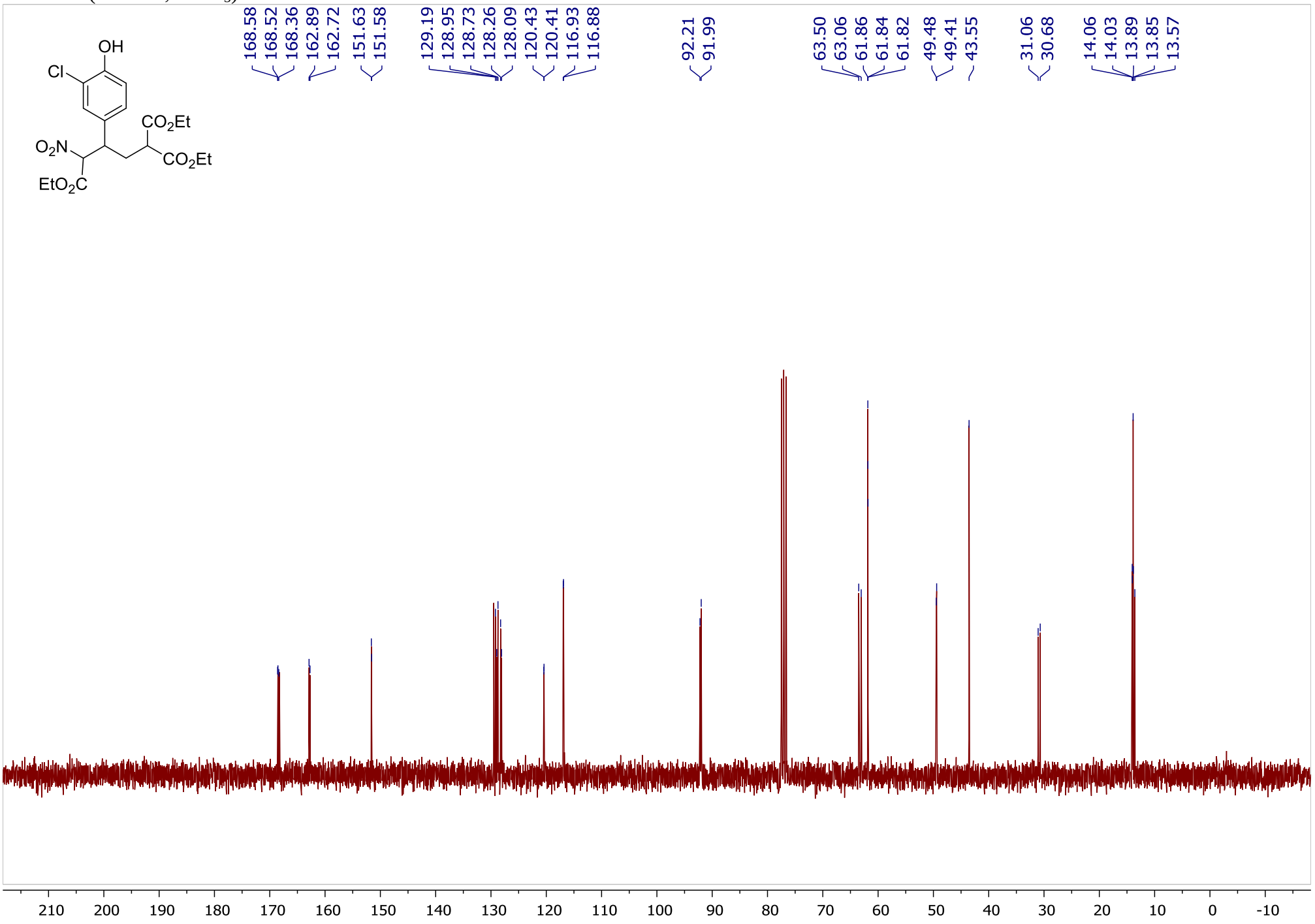


**Triethyl 3-(3-chloro-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3da)**, dr = 1:1

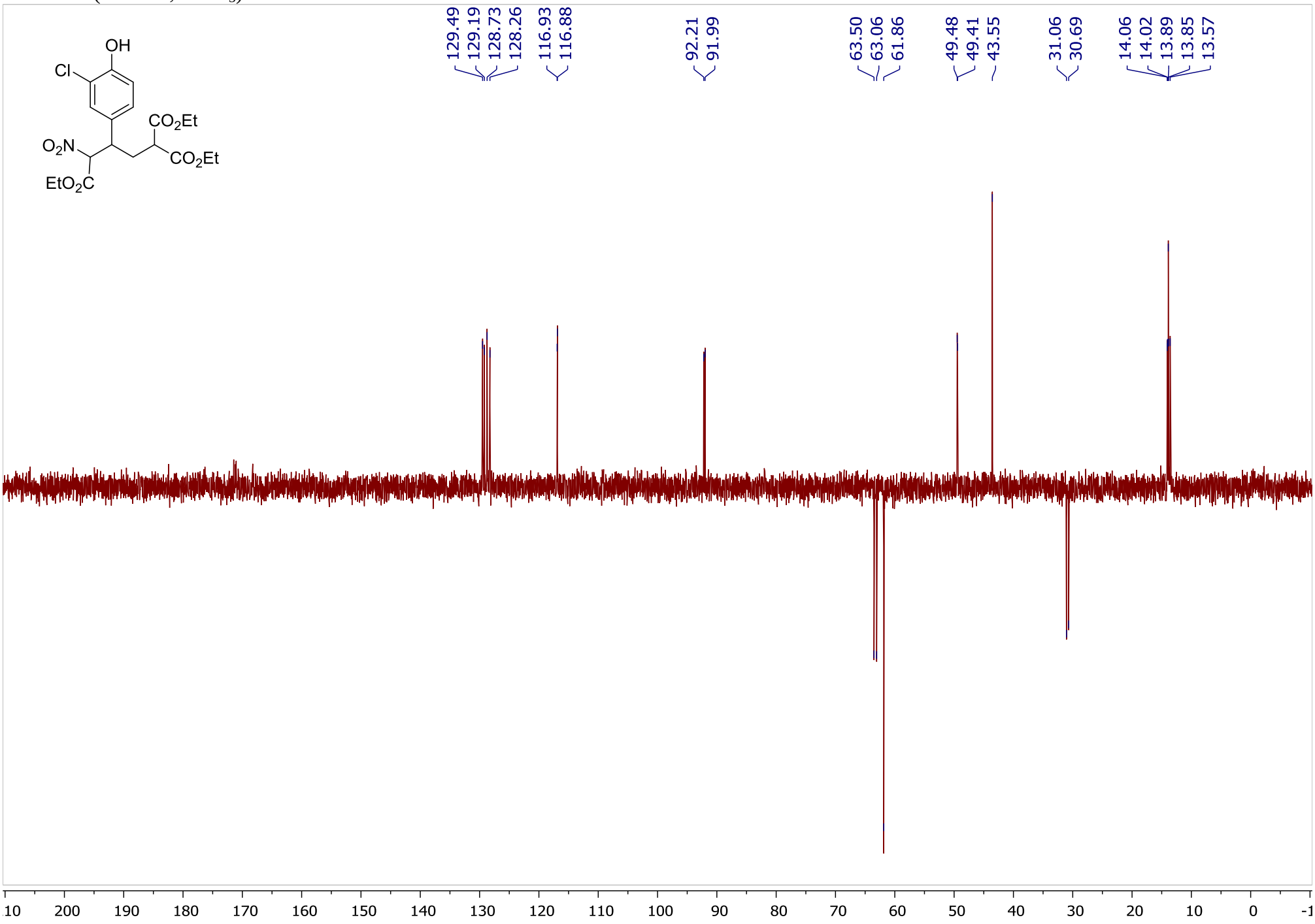
$^1$H NMR (300 MHz, $CDCl_3$)



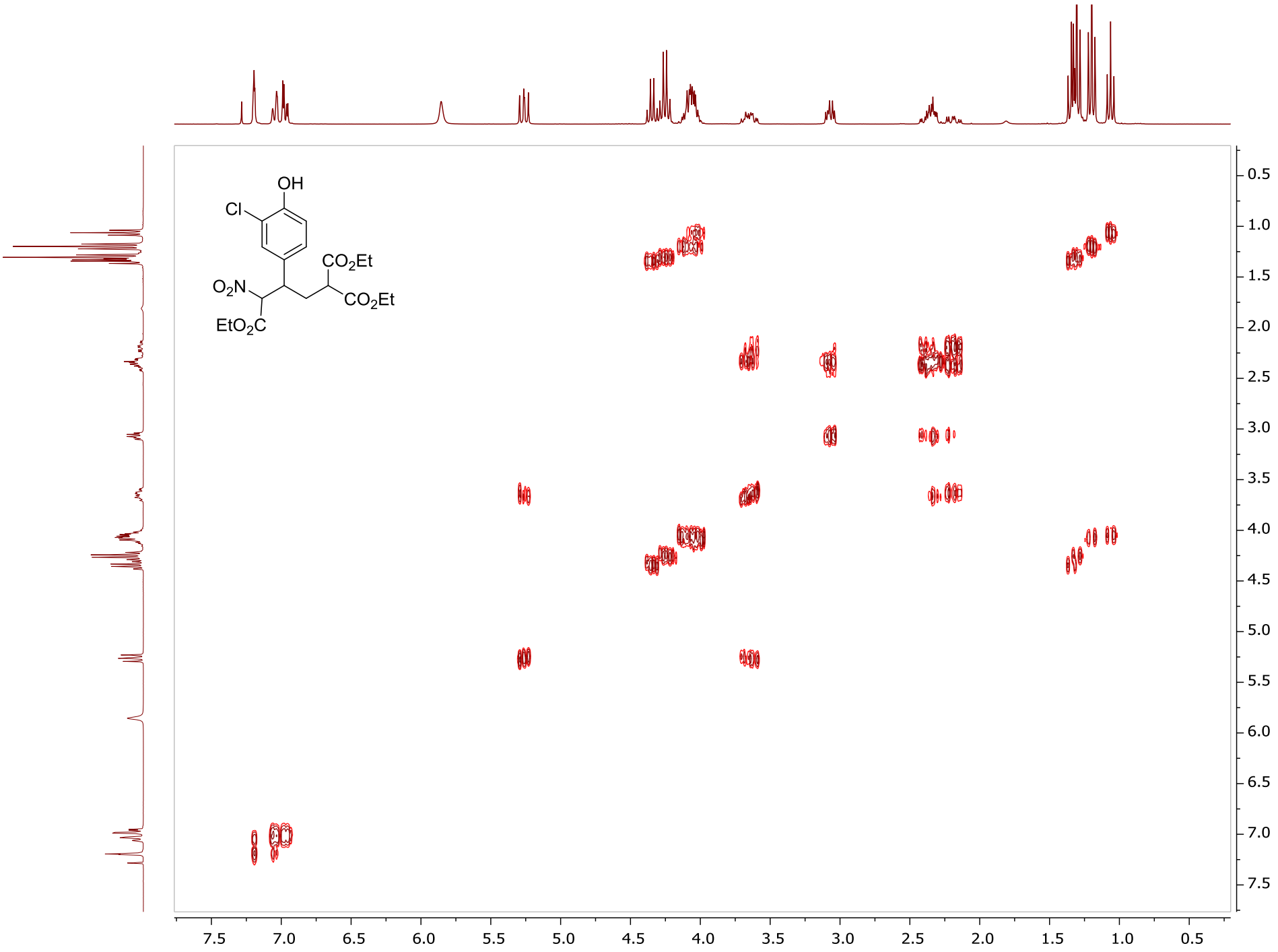
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Et
EtO2C
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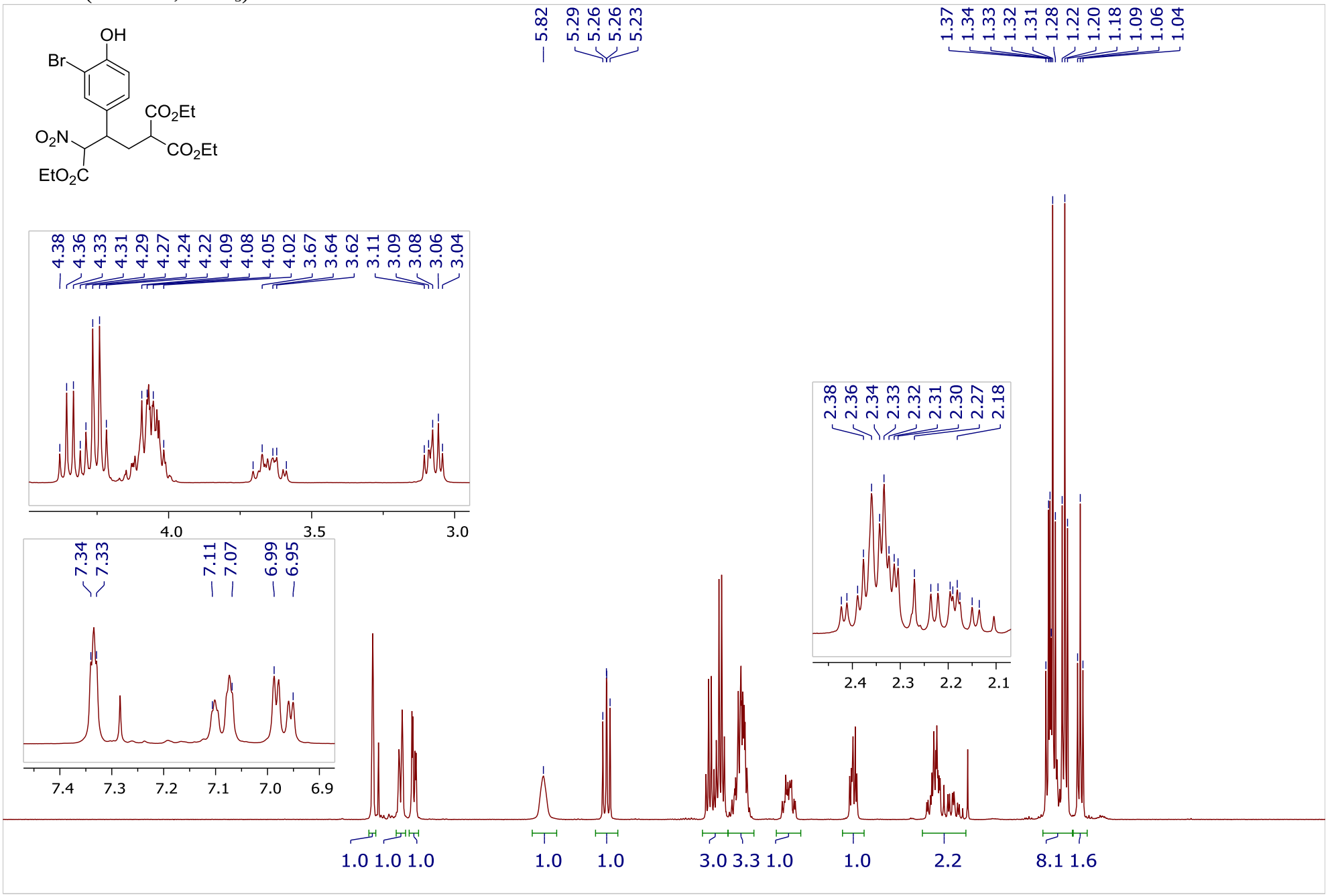
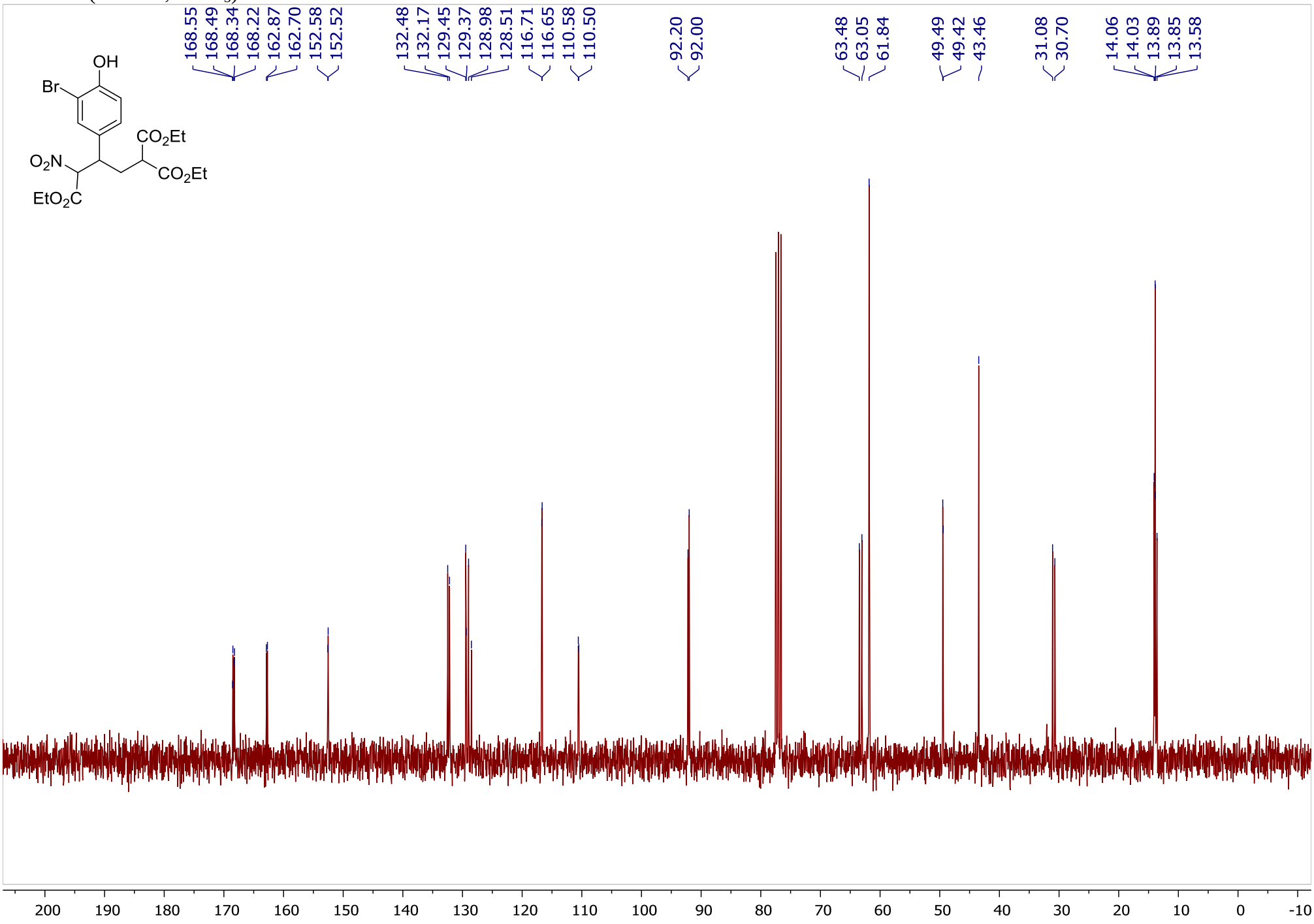
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Triethyl 3-(3-bromo-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ea)**, dr = 1:1

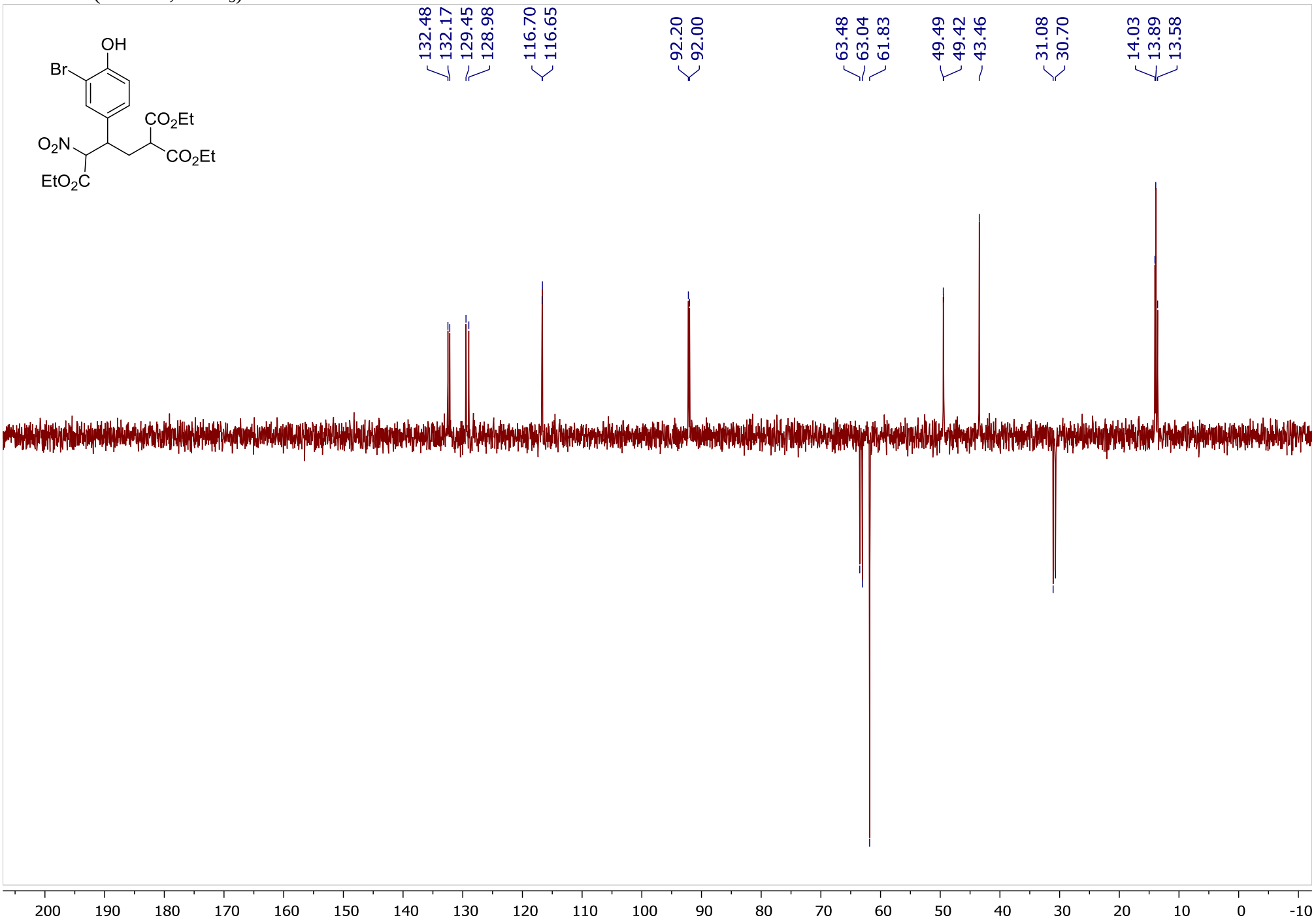
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

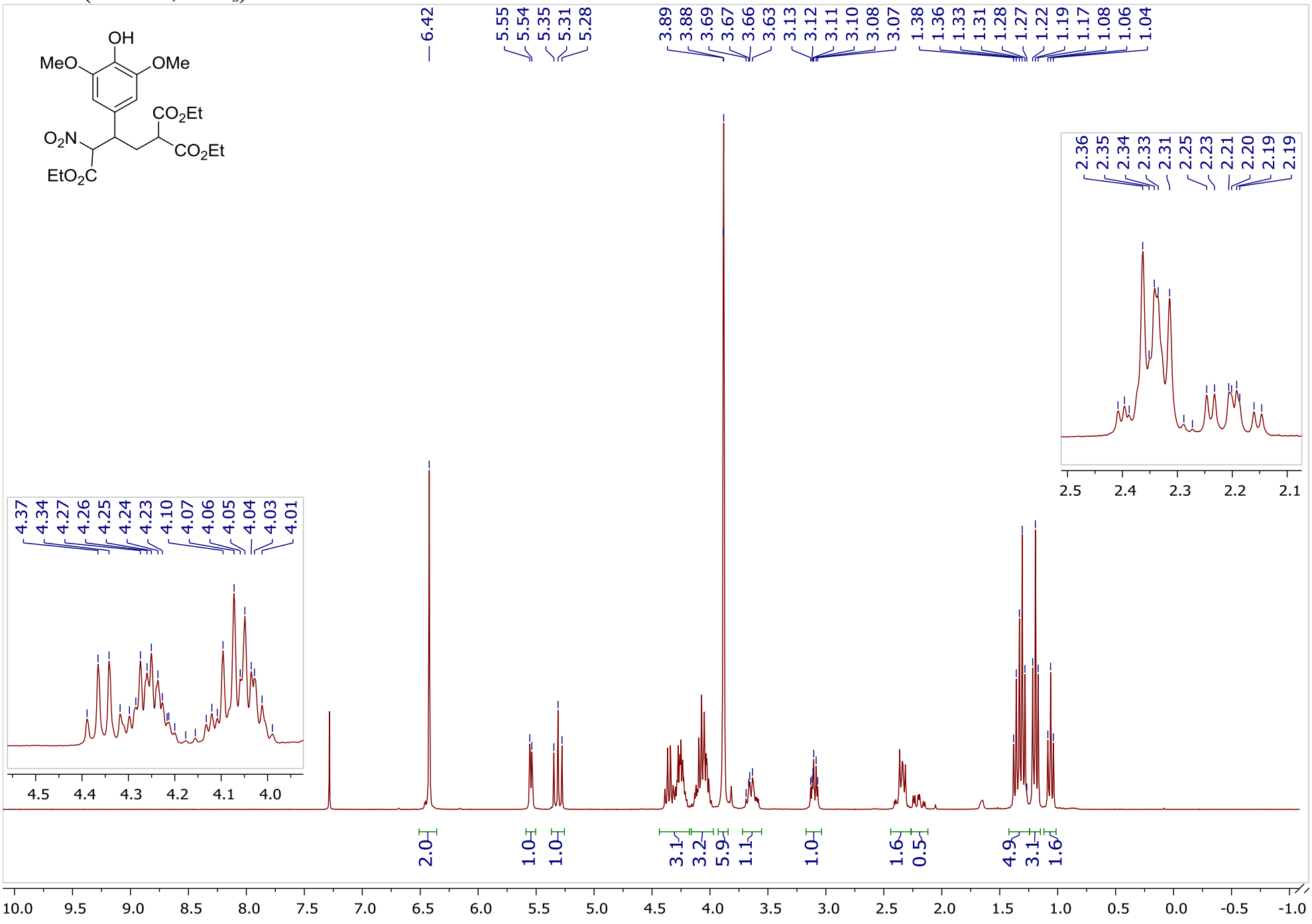


$^{13}$C DEPT (75 MHz, $CDCl_3$)

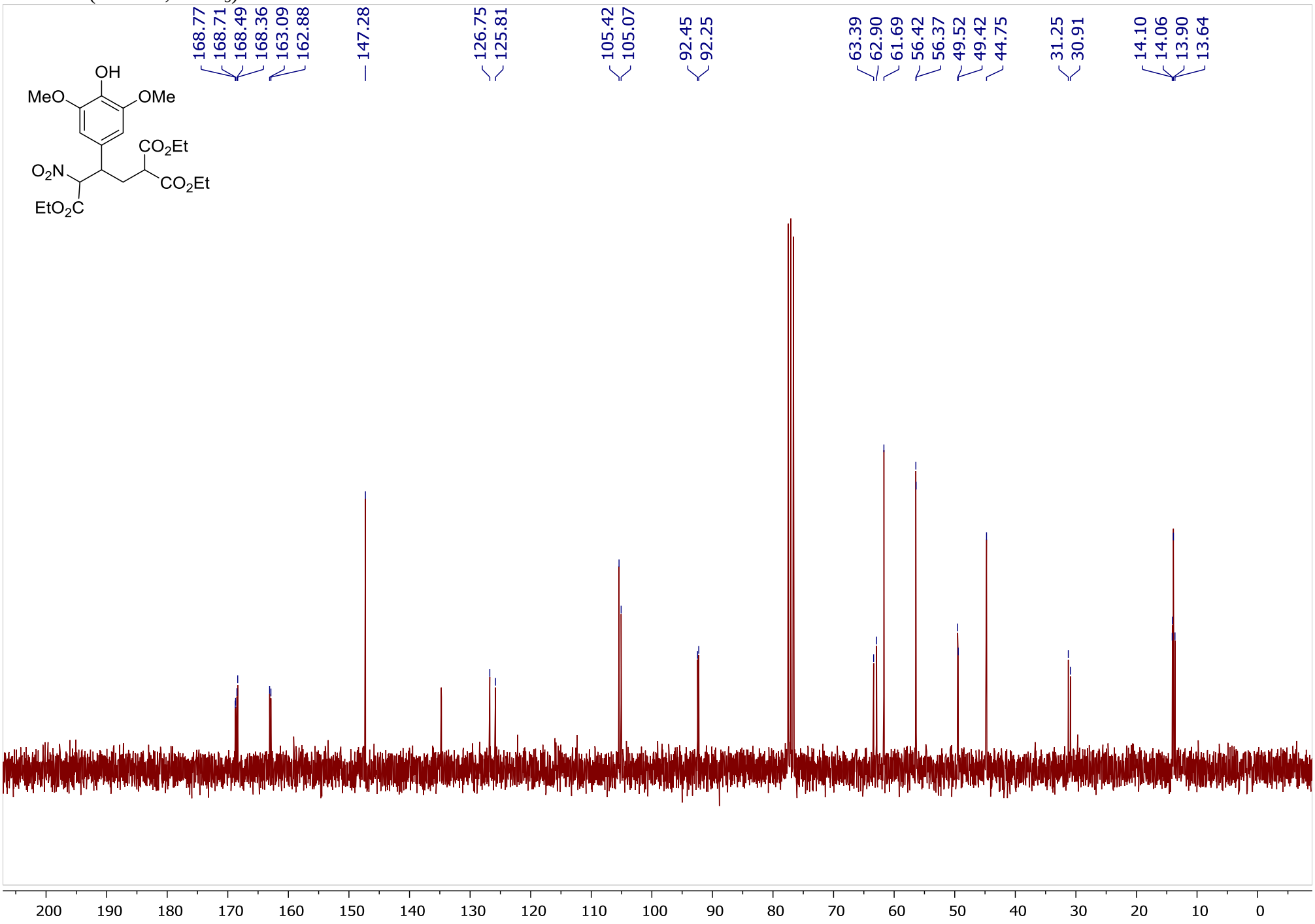


**Triethyl 3-(4-hydroxy-3,5-dimethoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3fa)**, dr = 1:1

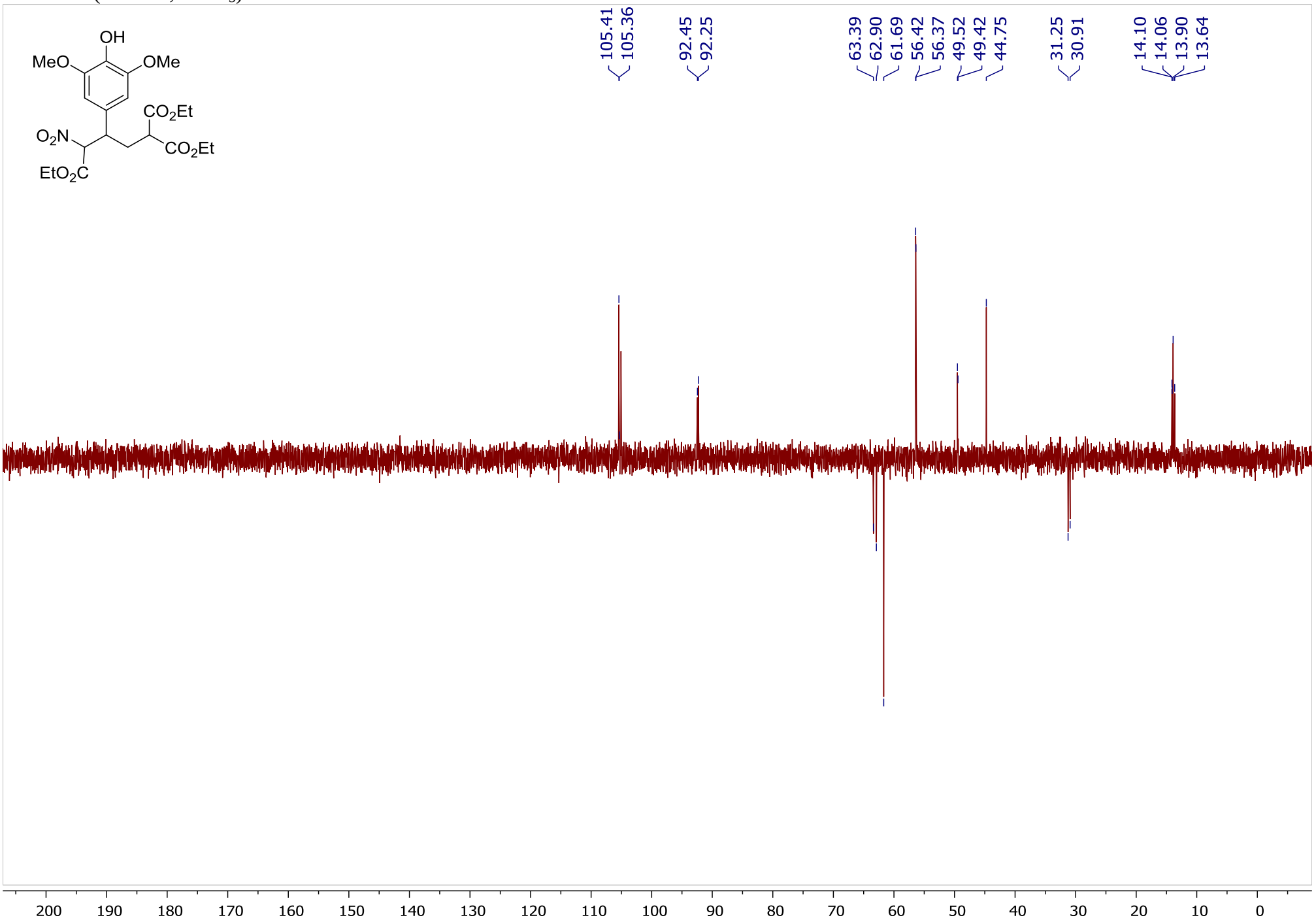
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

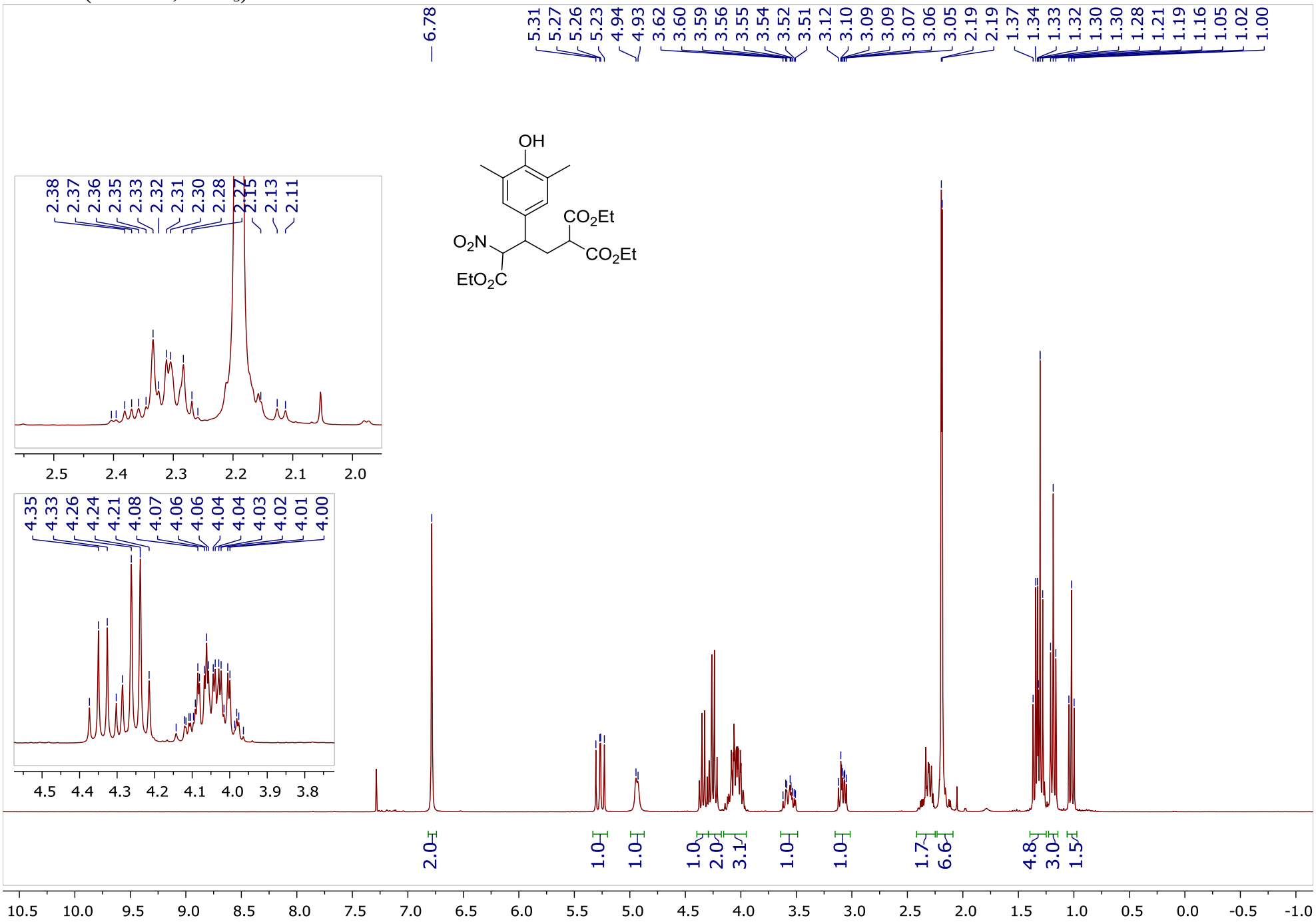


$^{13}$C DEPT (75 MHz, $CDCl_3$)

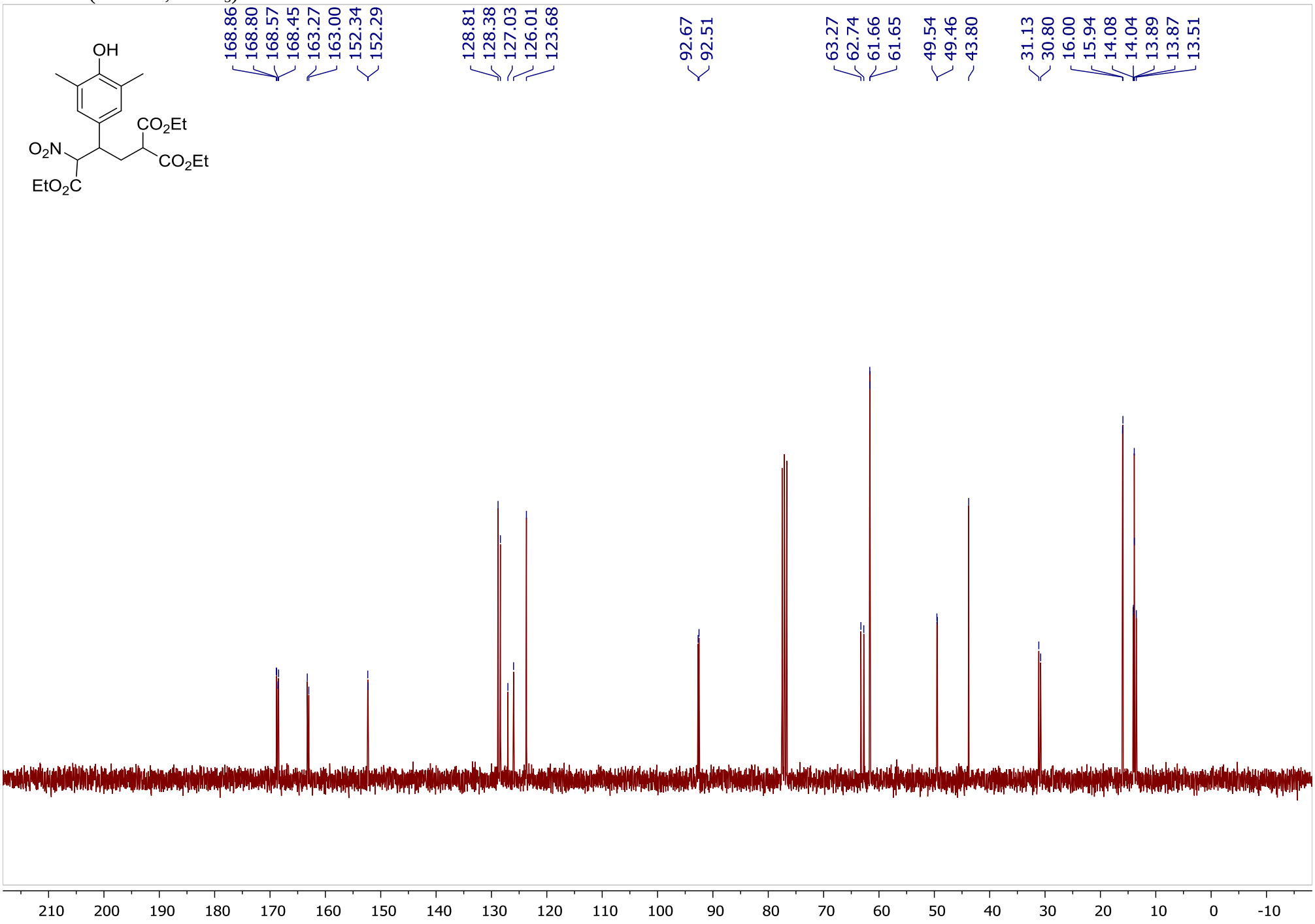


**Triethyl 3-(4-hydroxy-3,5-dimethylphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ga)**, dr = 1:1

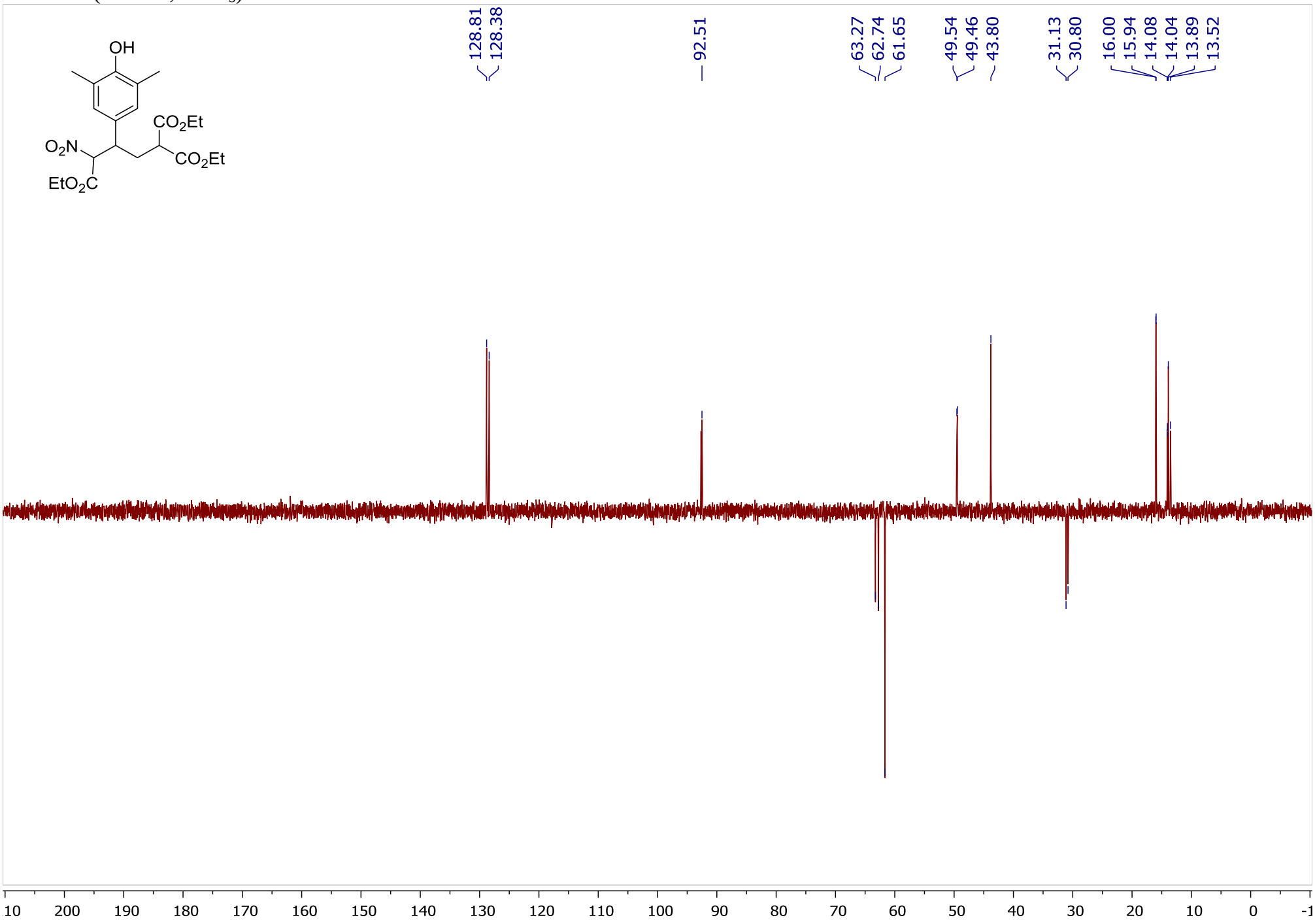
$^1$H NMR (300 MHz, $CDCl_3$)



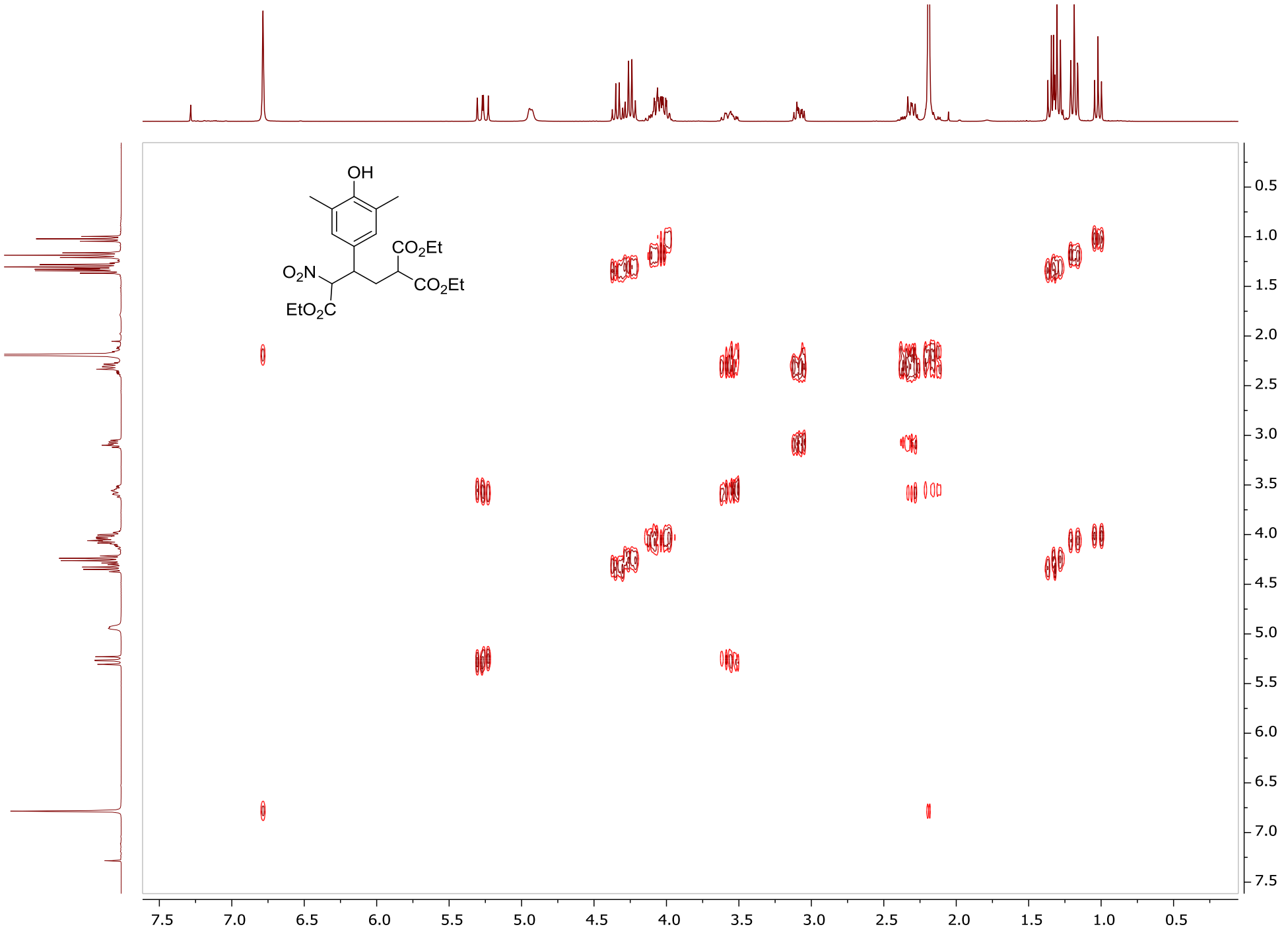
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Et
EtO2C
0.5
1.0
1.5
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3.0
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4.0
4.5
5.0
5.5
6.0
6.5
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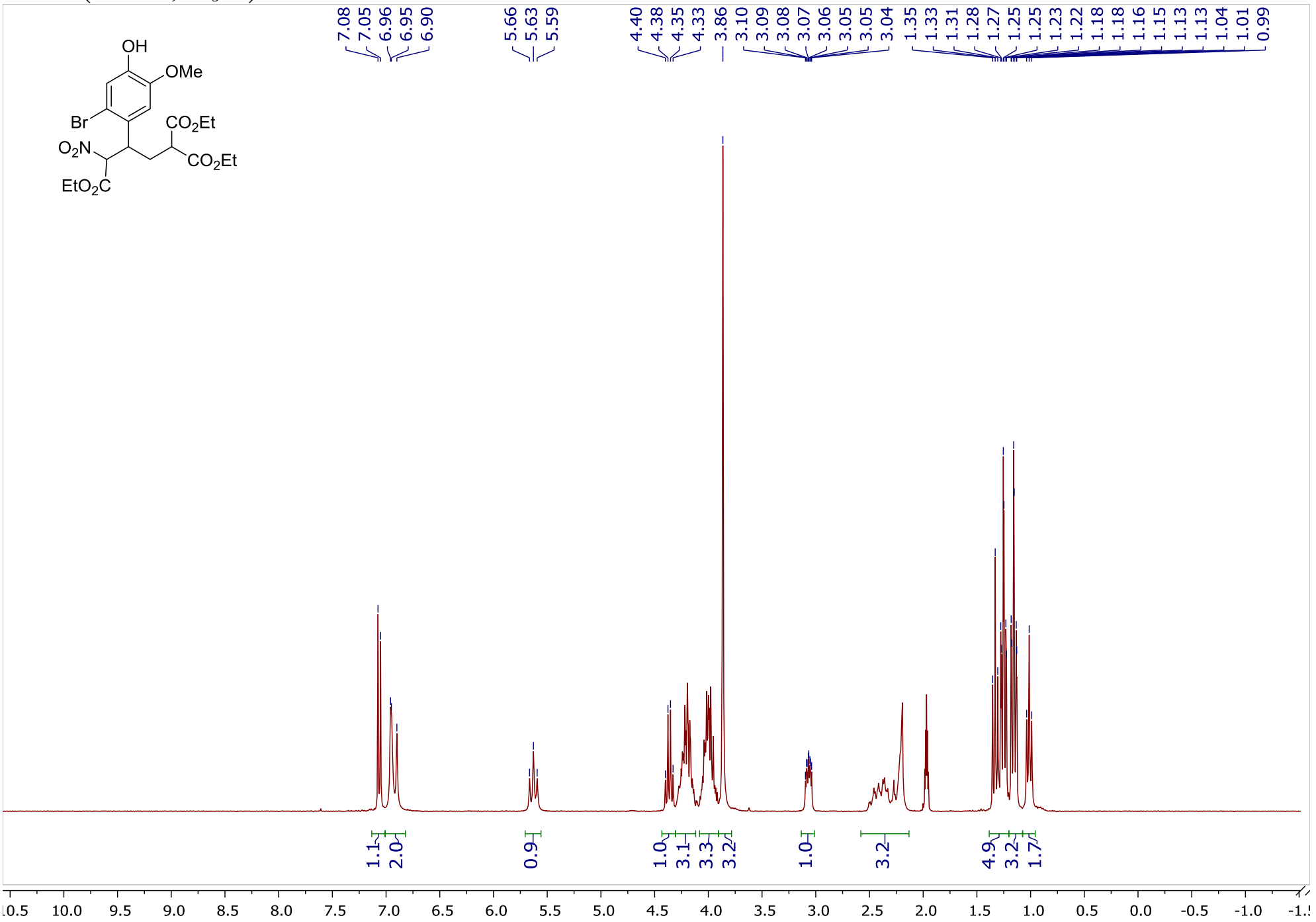
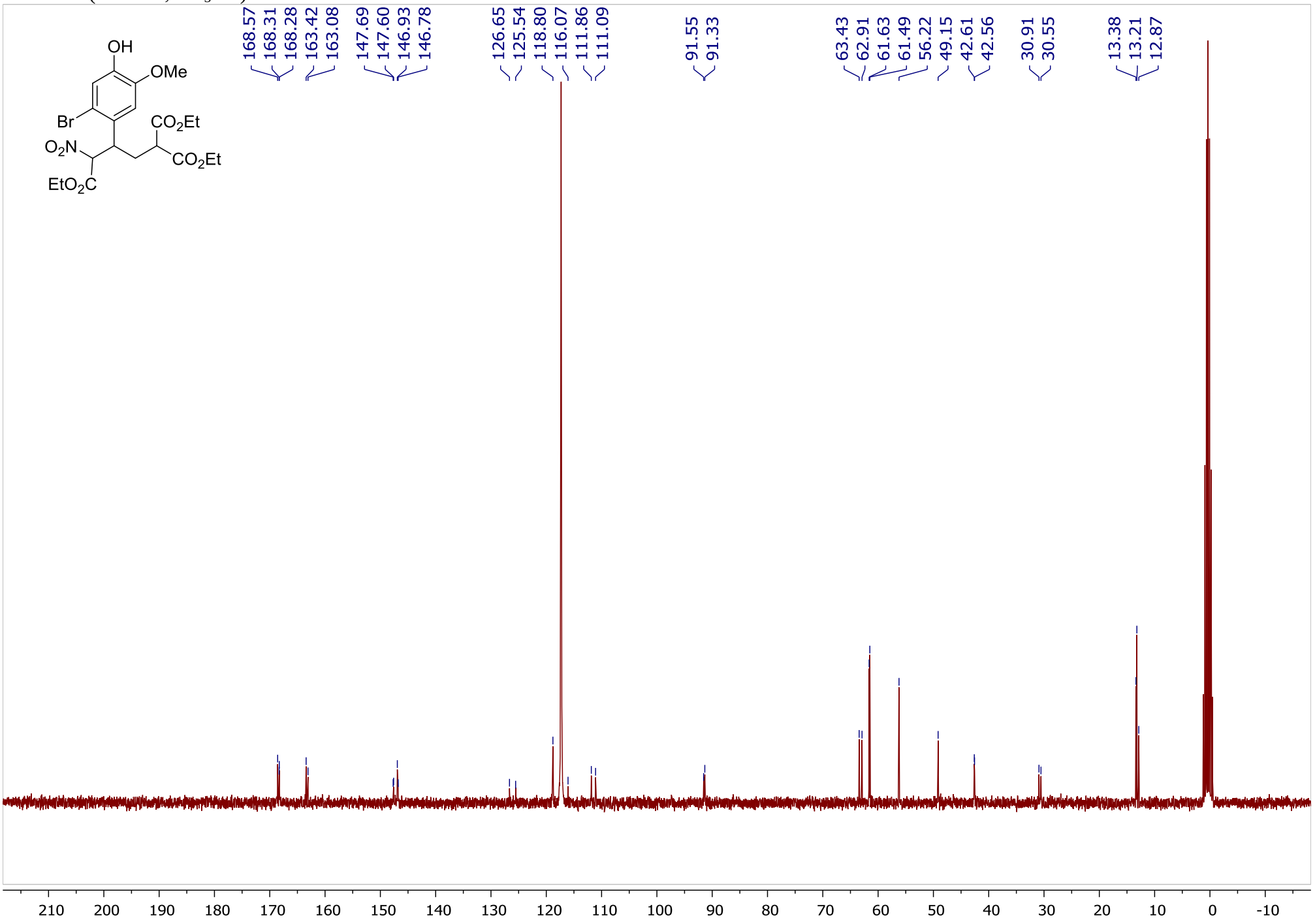
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Triethyl 3-(2-bromo-4-hydroxy-5-methoxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ha)**, dr = 1.2:1

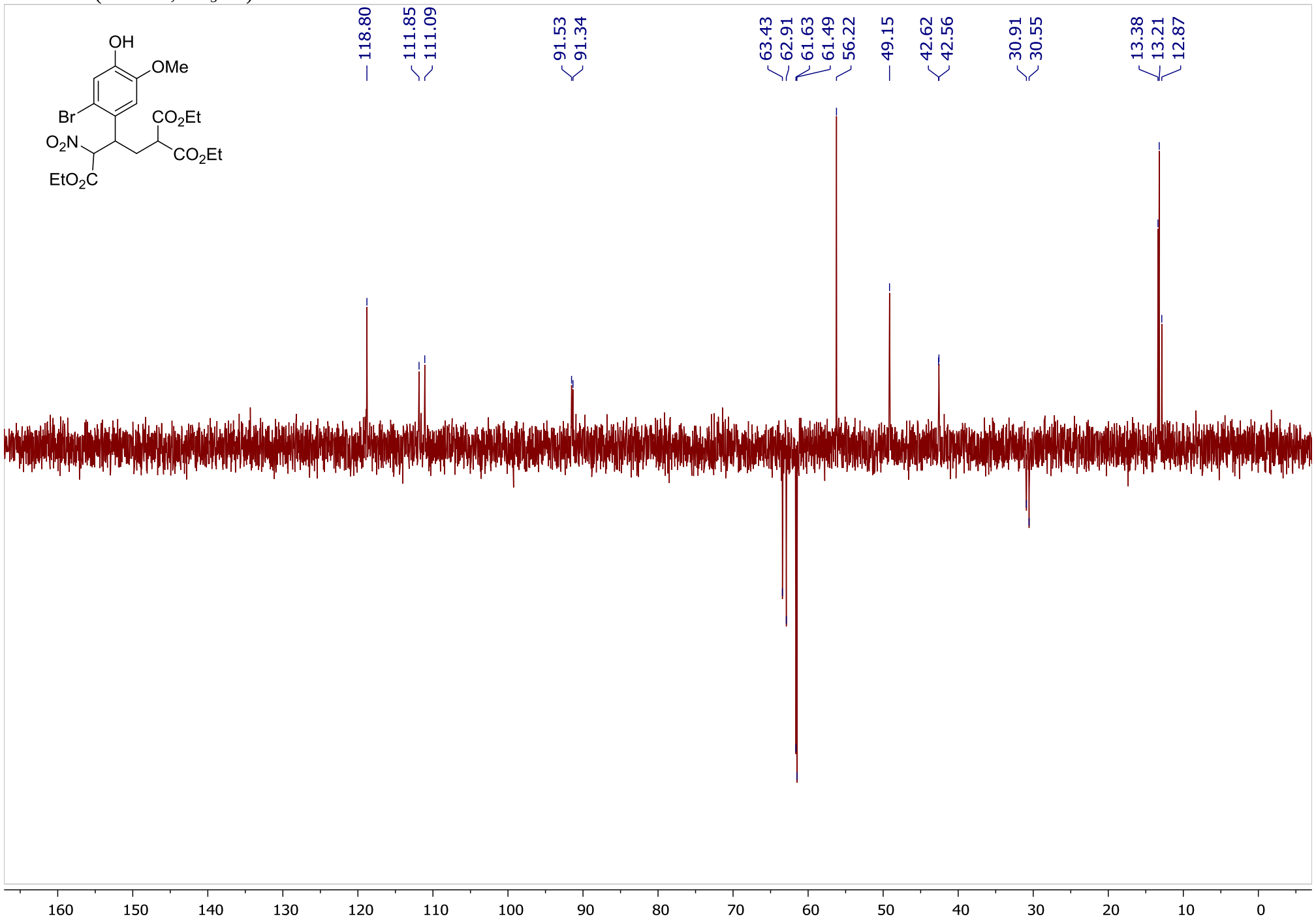
$^1$H NMR (300 MHz, $CD_3CN$)



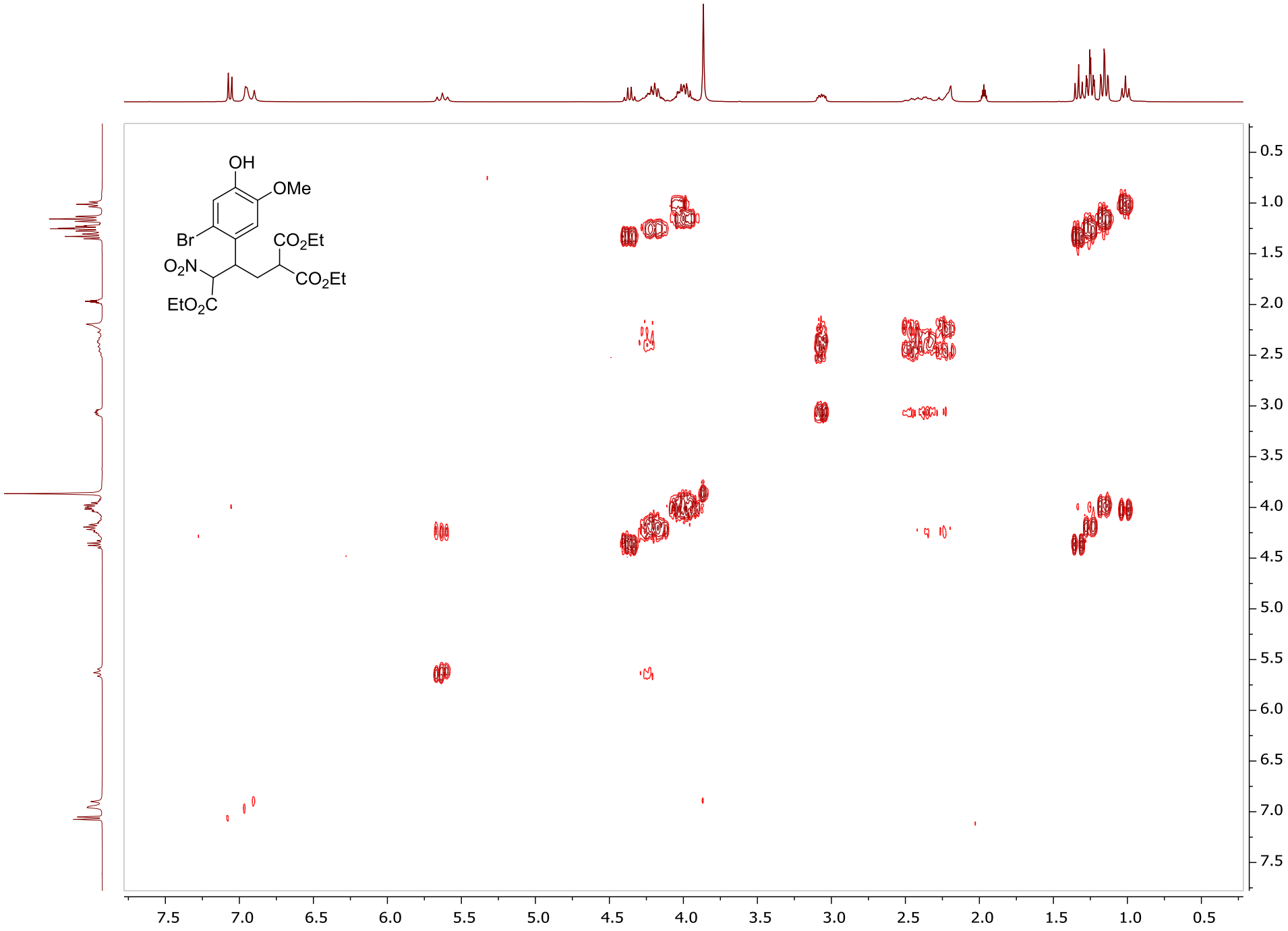
$^{13}$C NMR (75 MHz, $CD_3CN$)



$^{13}$C DEPT (75 MHz, $CD_3CN$)



$^{1}$H-$^{1}$H COSY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O2N
CO2Et
EtO2C
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3.5
4.0
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5.5
6.0
6.5
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6.5
6.0
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5.0
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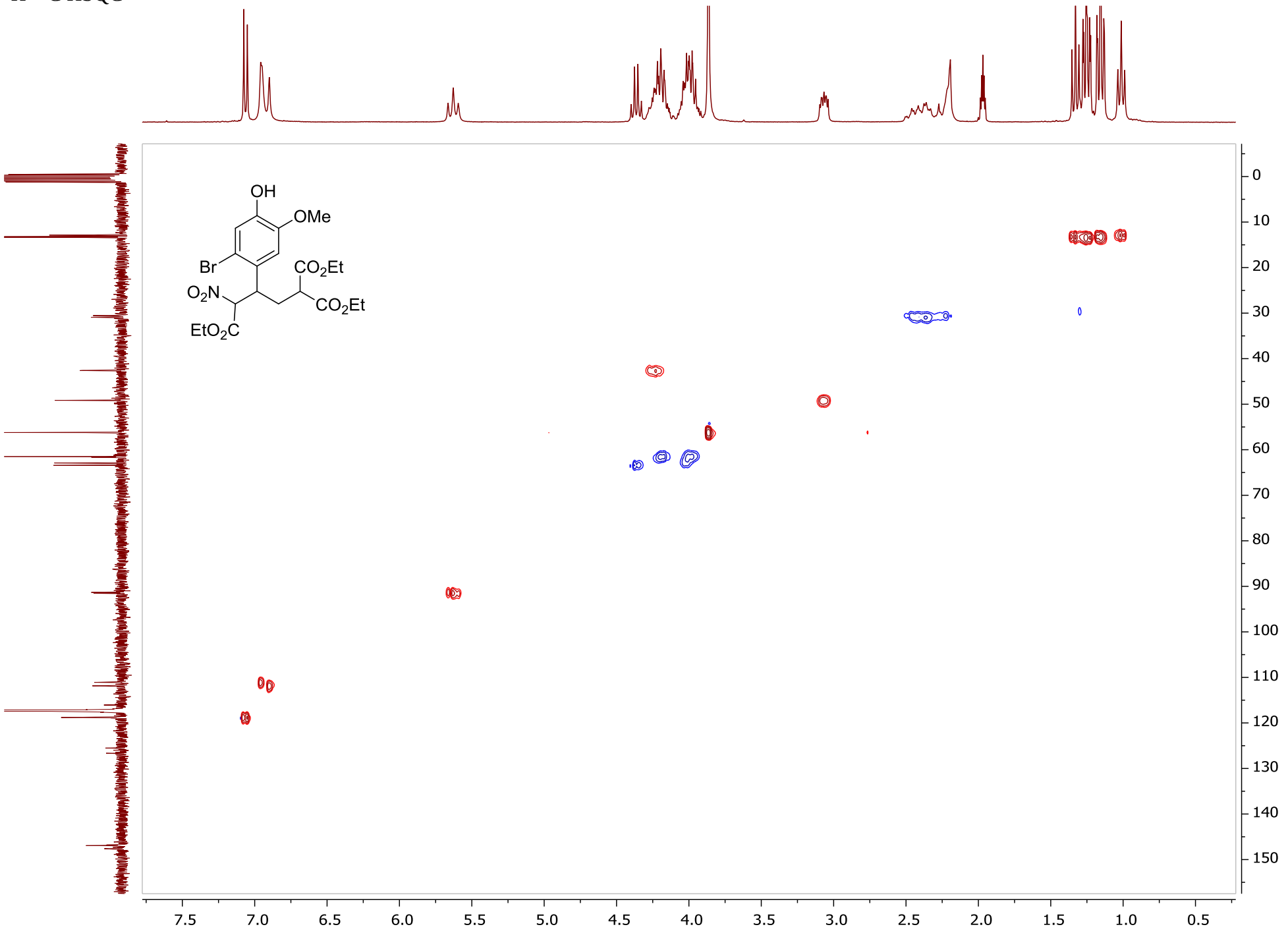
0.5

$^{1}H$-$^{13}C$ HSQC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$O_2N$
$CO_2Et$
$EtO_2C$
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5.0
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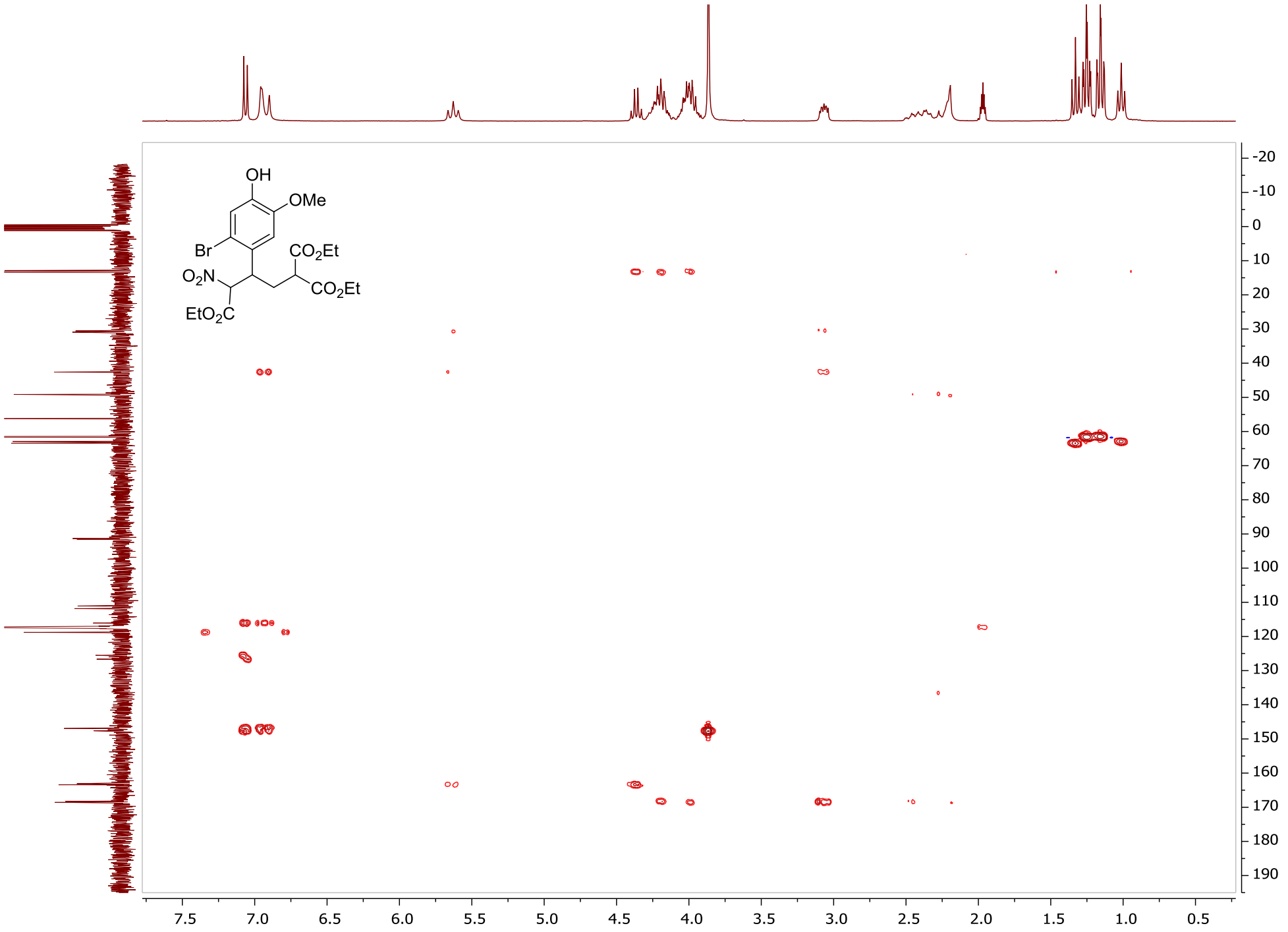
0.5

$^{1}H$-$^{13}C$ HMBC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OMe
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CO2Et
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90
100
110
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170
180
190
7.5
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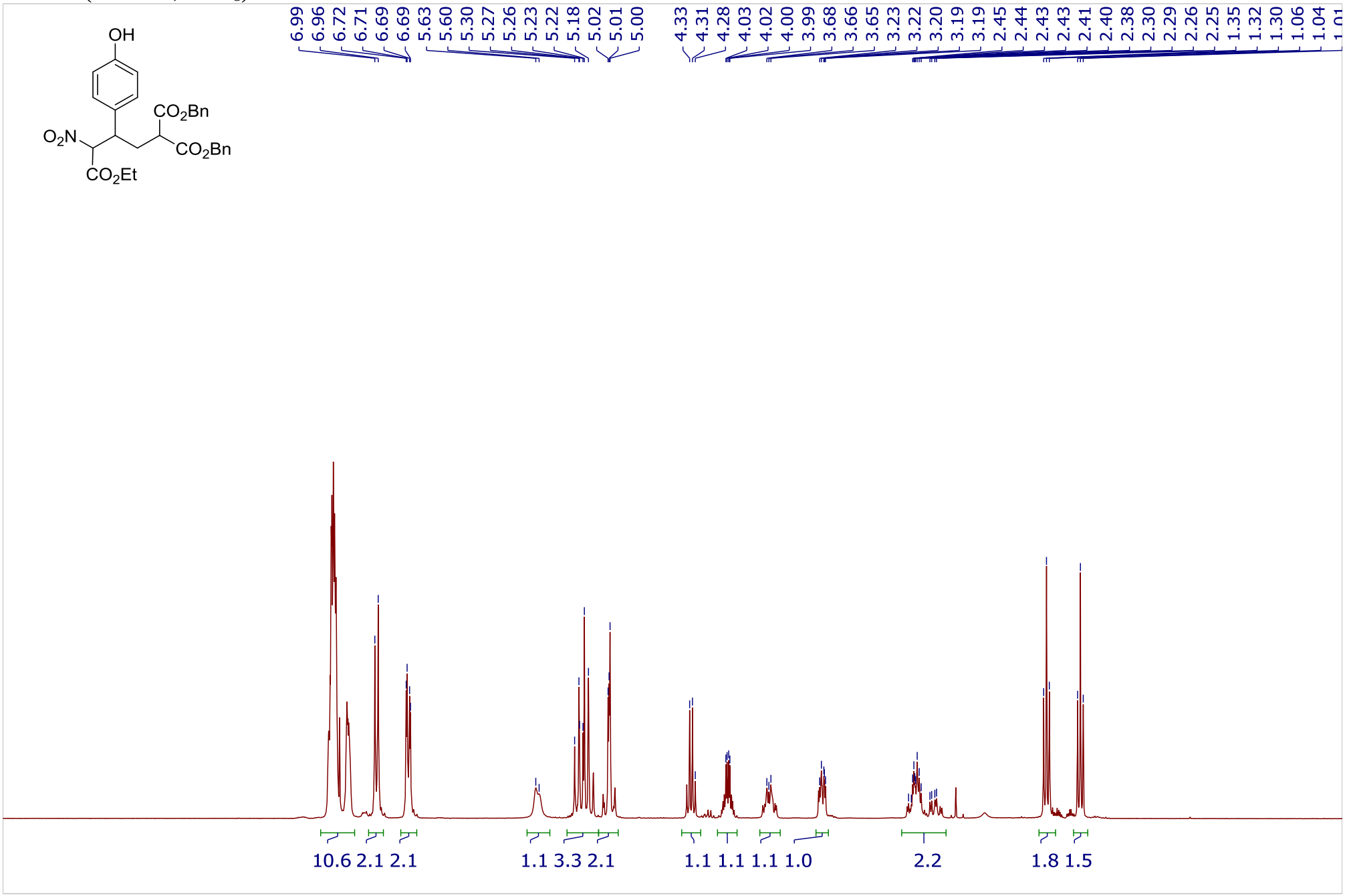
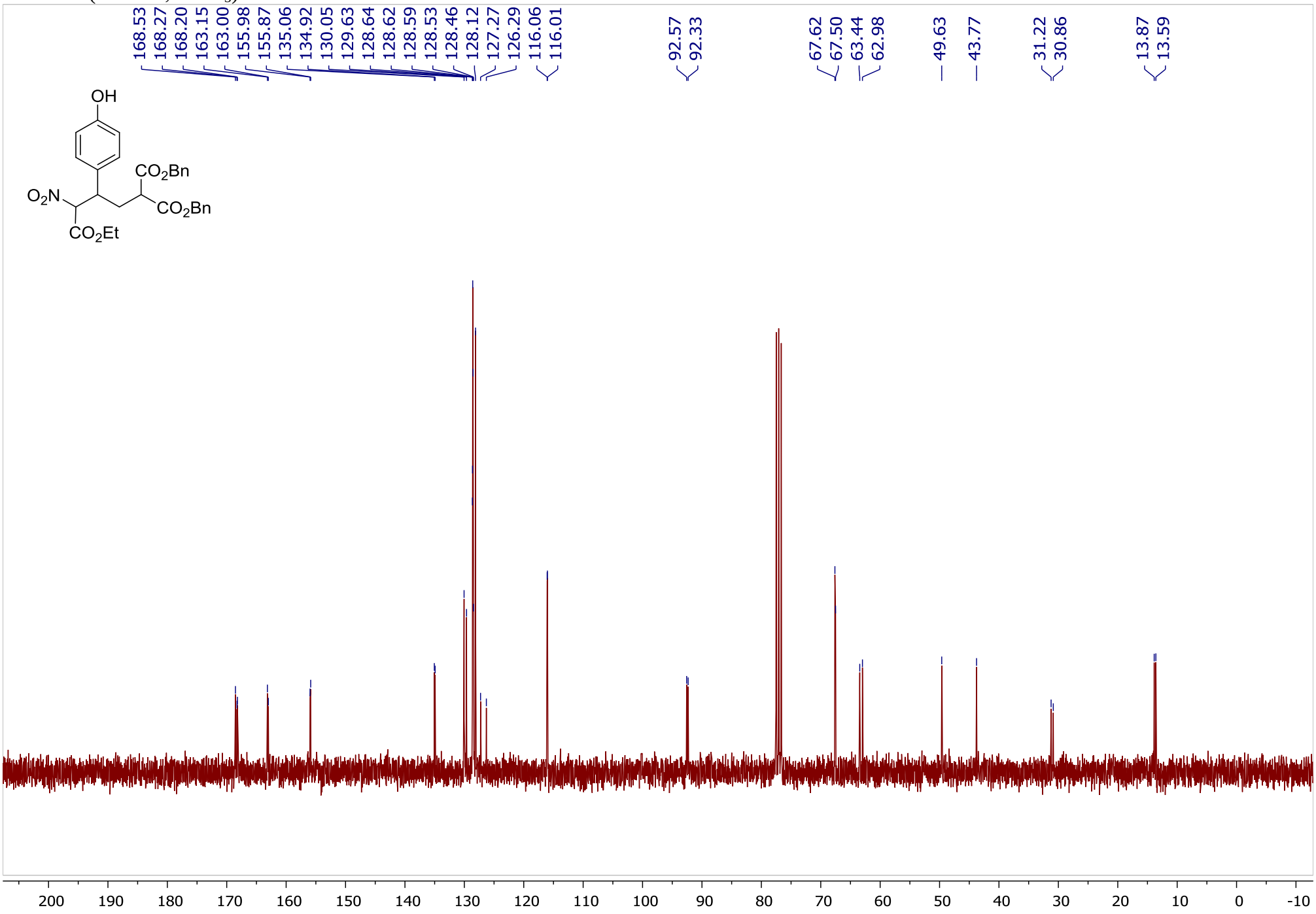
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**1,1-Dibenzyl 4-ethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ia)**, dr = 1:1

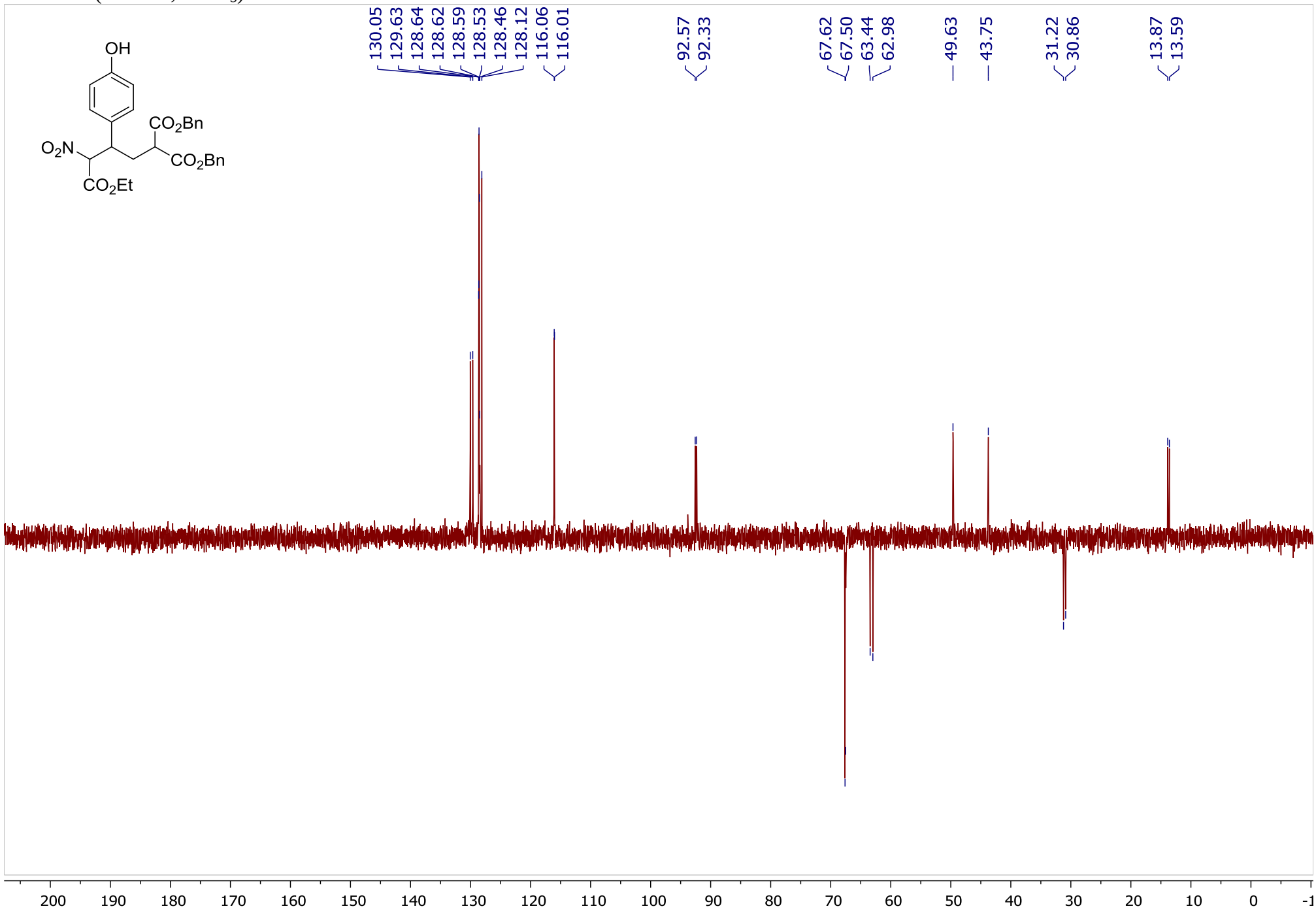
$^1$H NMR (300 MHz, $CDCl_3$)



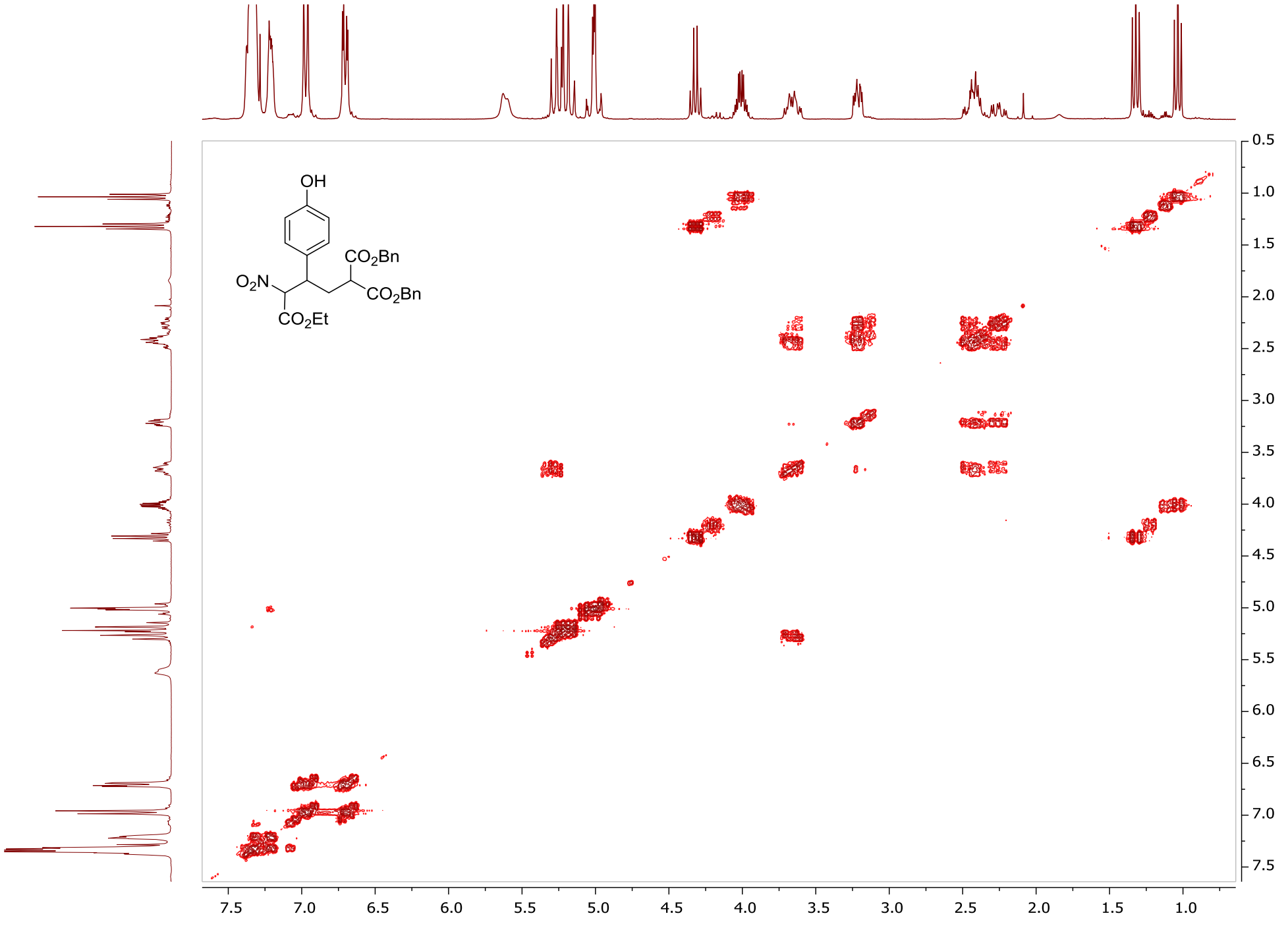
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}H$-$^{1}H$ COSY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CO2Bn
CO2Et
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7.0
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7.5
7.0
6.5
6.0
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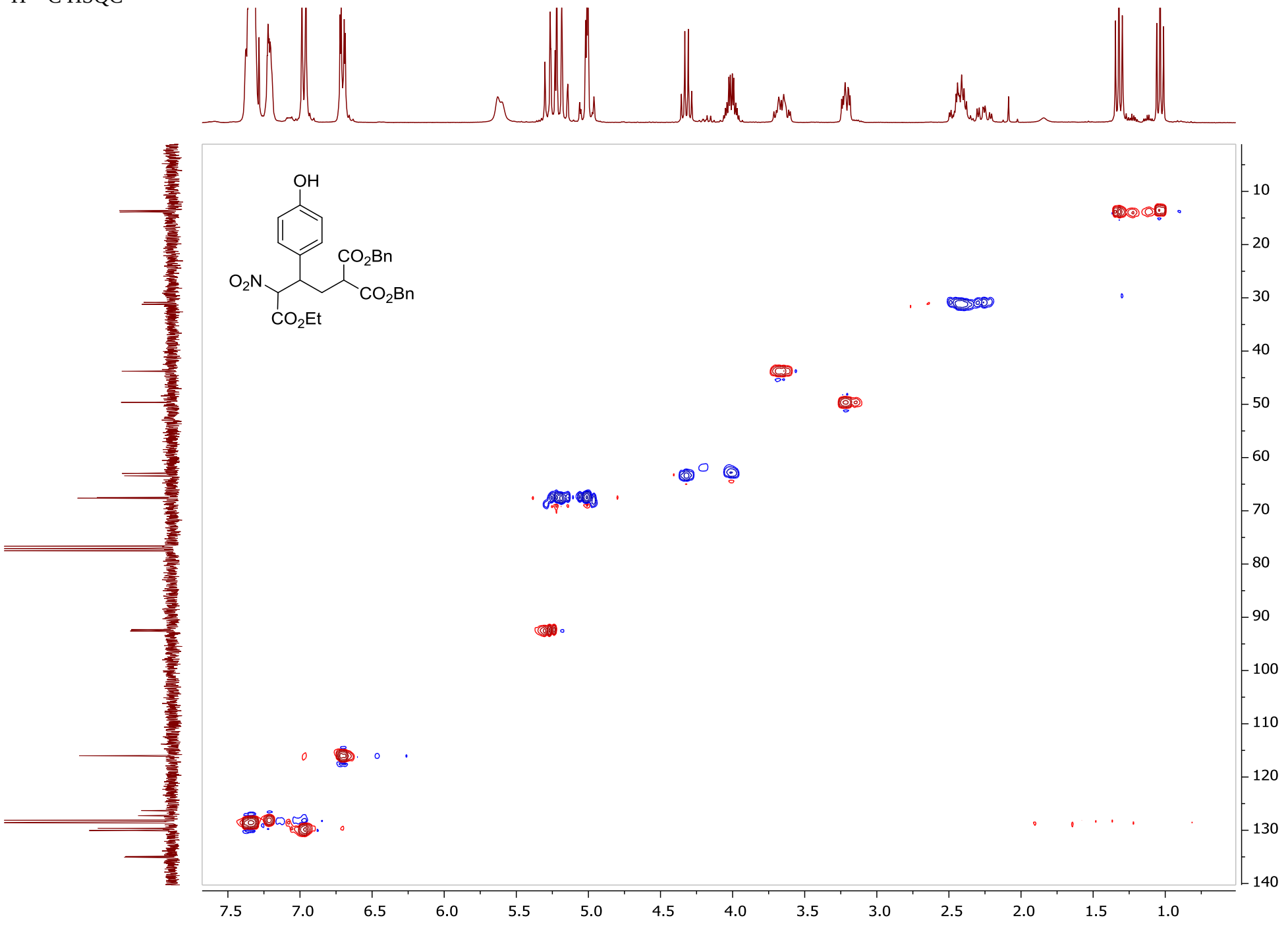
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HSQC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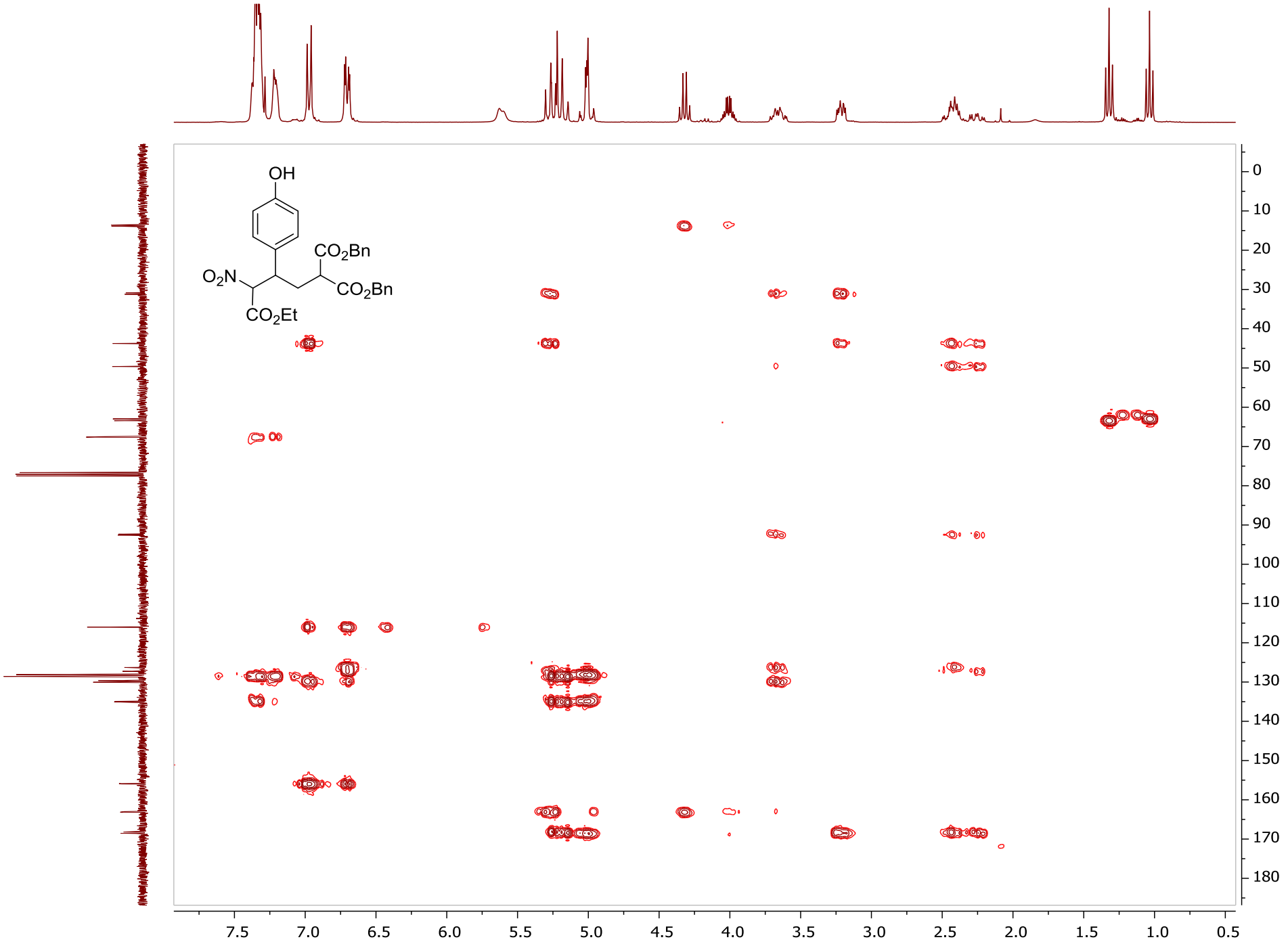
O2N
CO2Bn
CO2Et
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HMBC


OH
CO2Bn
O2N
CO2Bn
CO2Et
0
10
20
30
40
50
60
70
80
90
100
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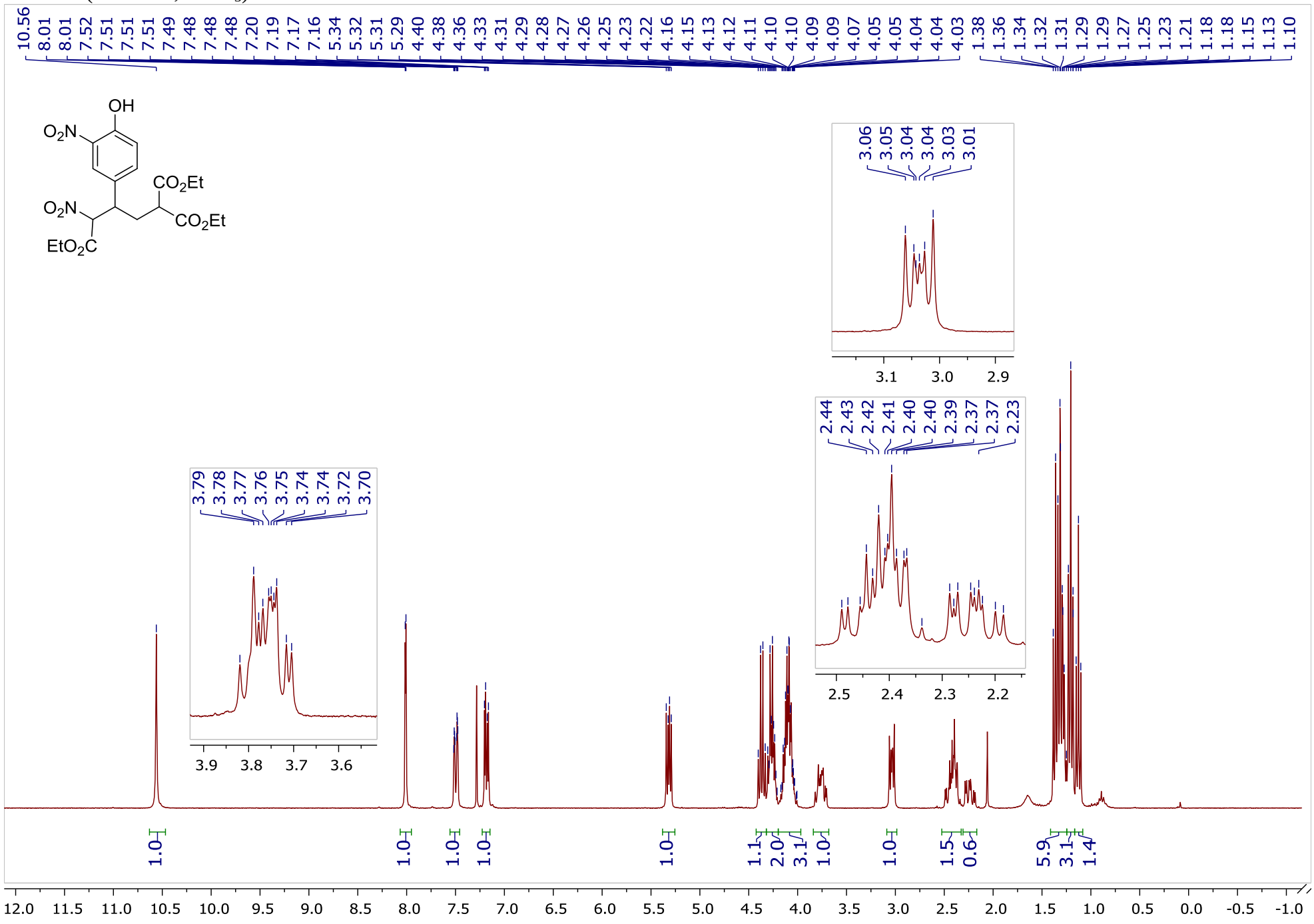
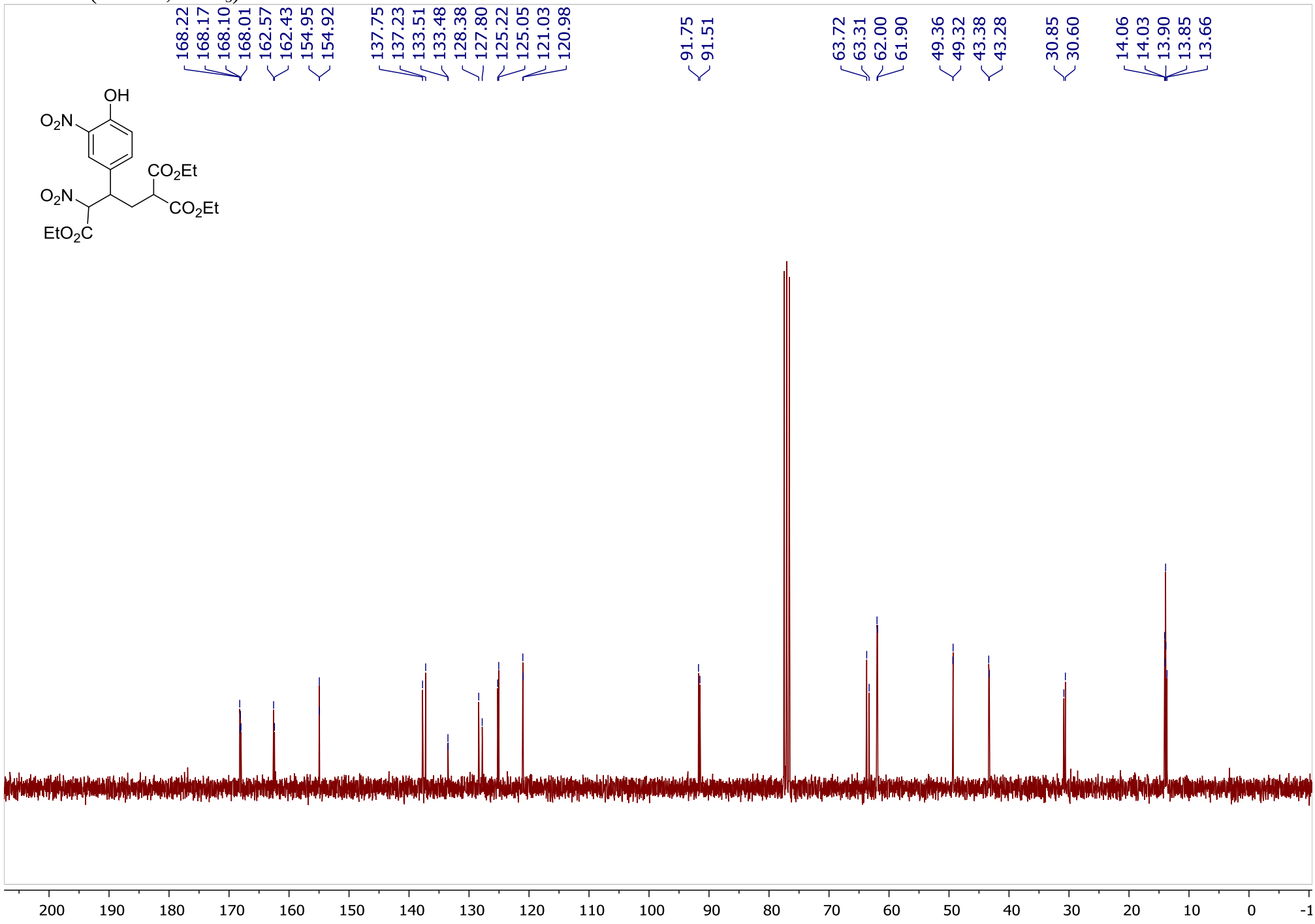
120
130
140
150
160
170
180
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Triethyl 3-(4-hydroxy-3-nitrophenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ja)**, dr = 1.1:1

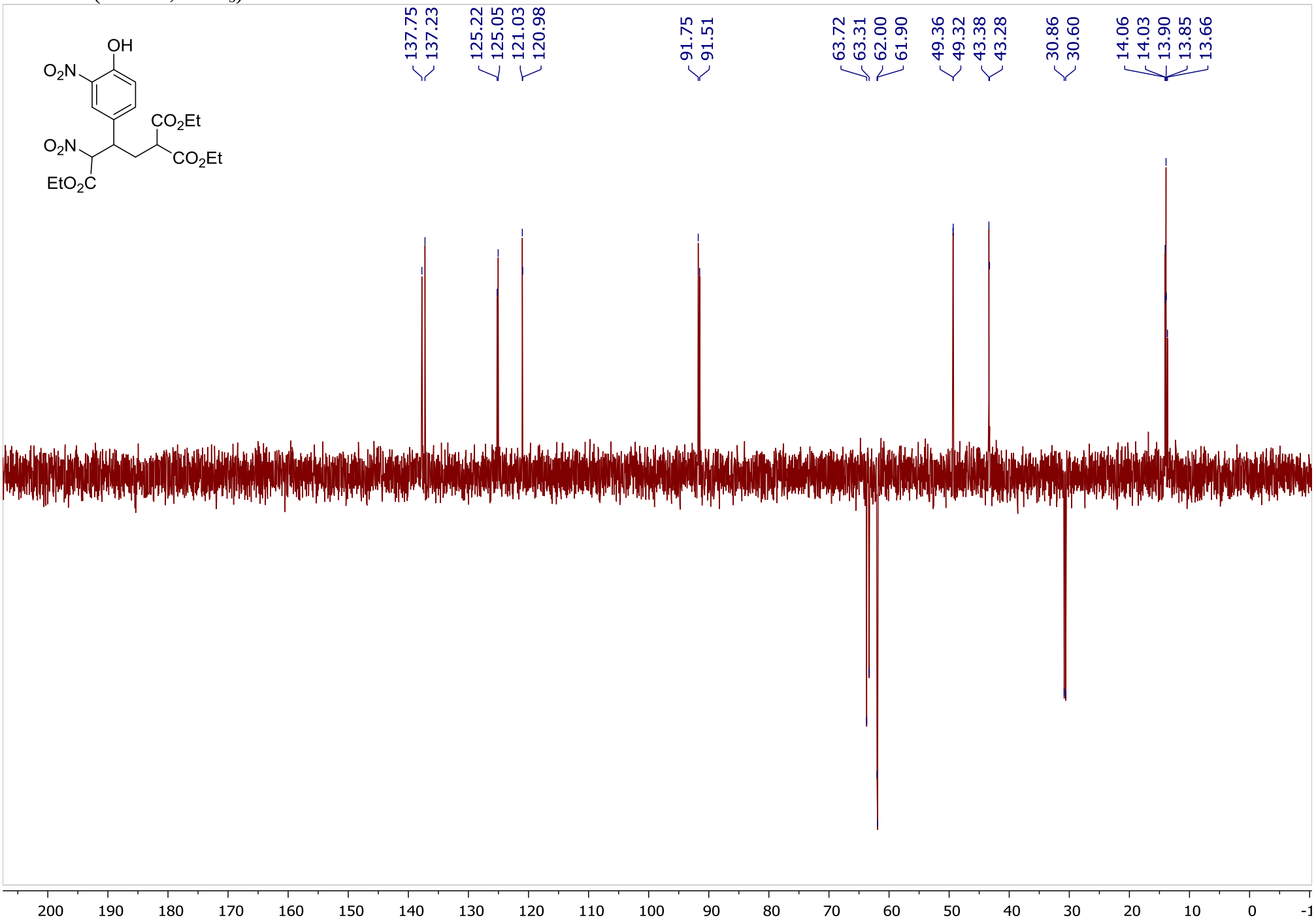
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

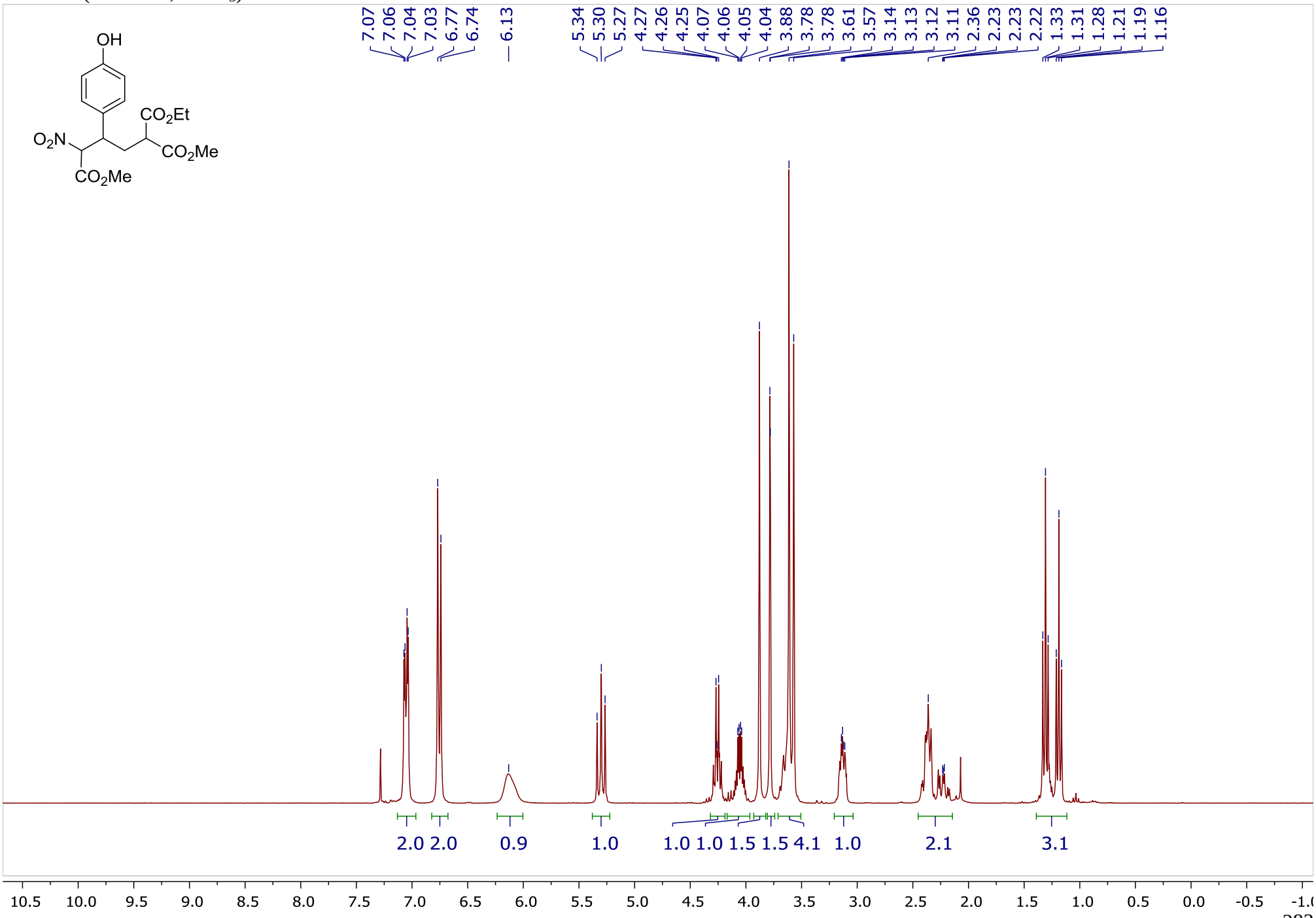


$^{13}$C DEPT (75 MHz, $CDCl_3$)

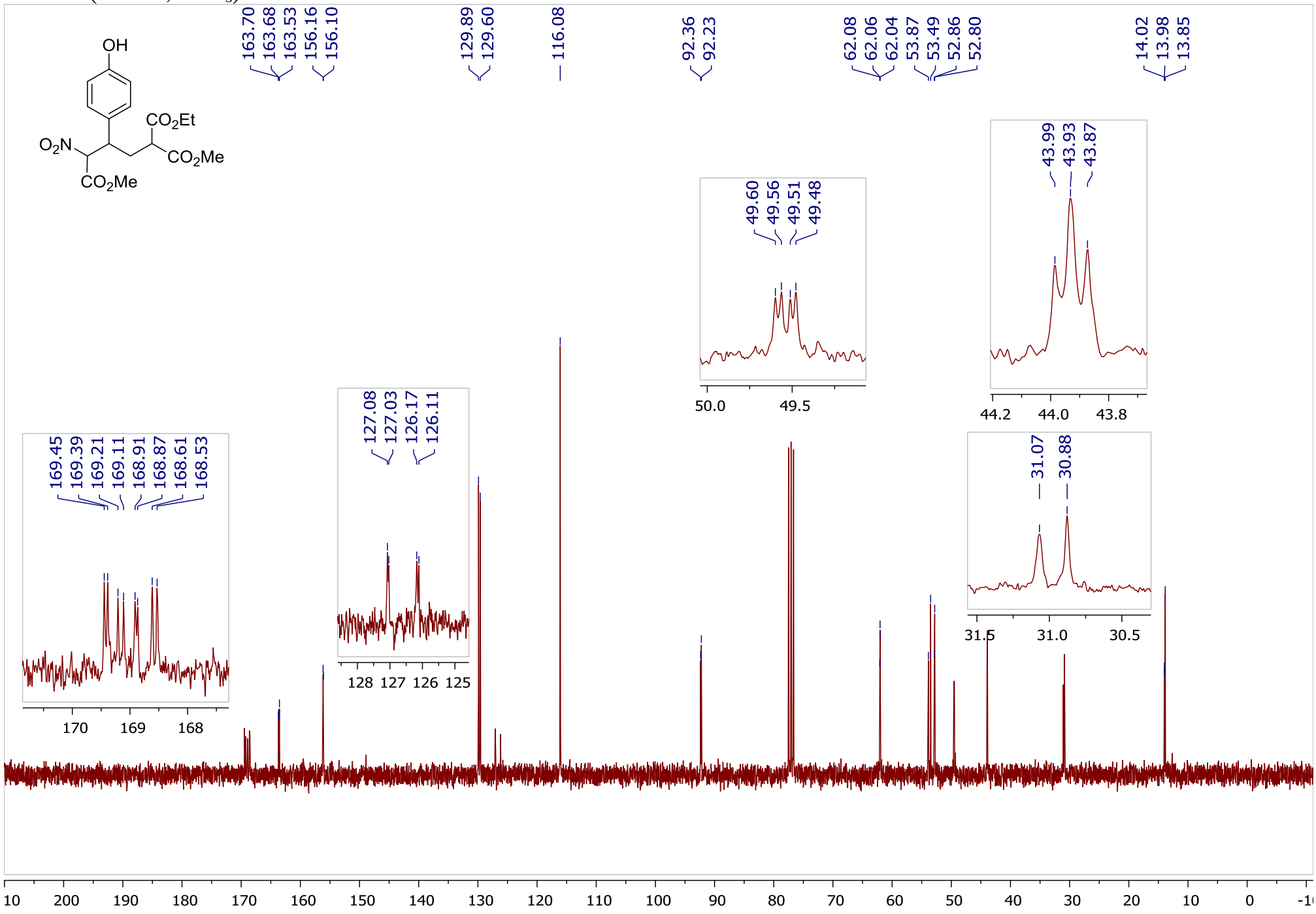


**1-Ethyl 1,4-dimethyl 3-(4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3lb)**, dr = 1:1:1:1

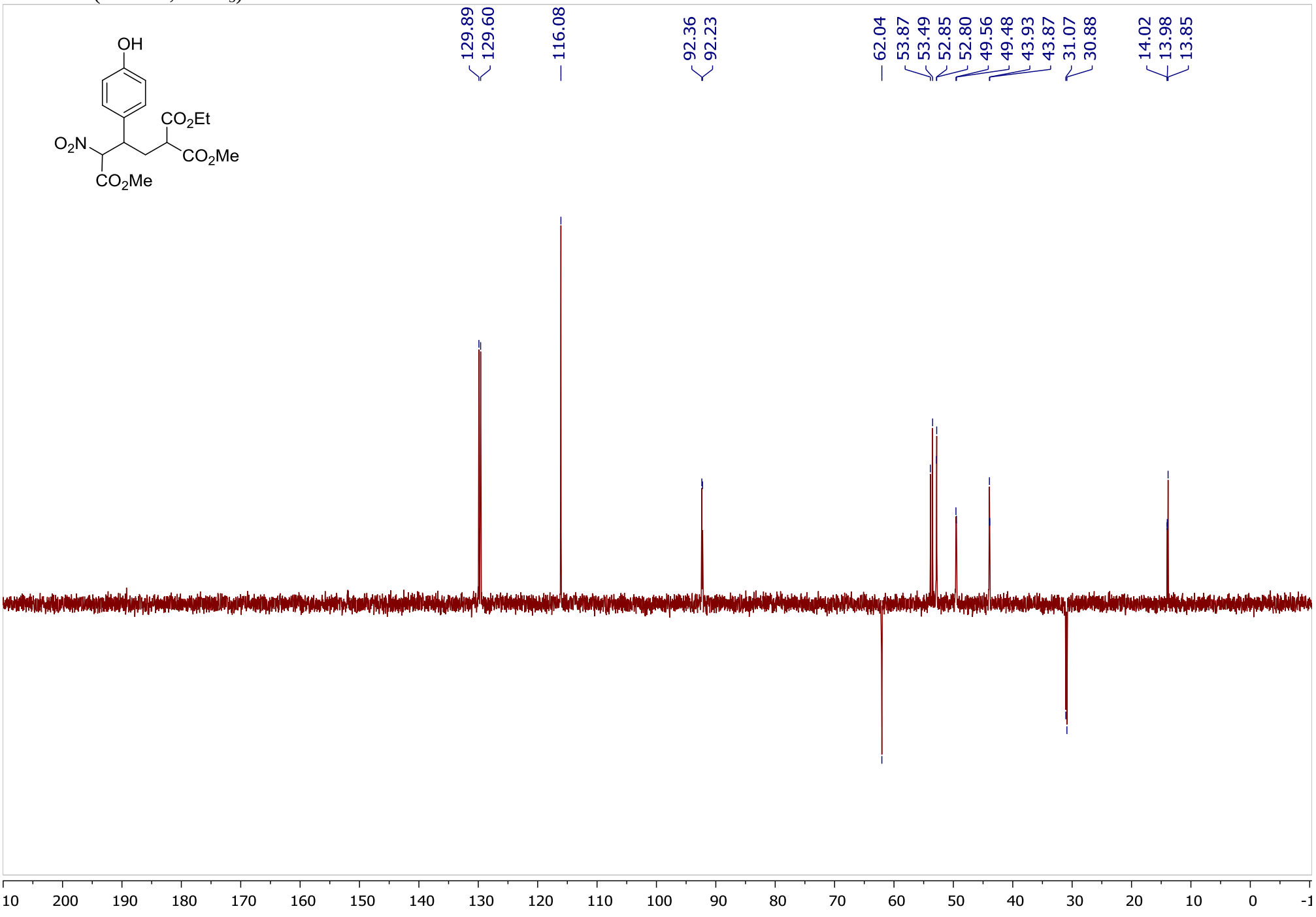
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

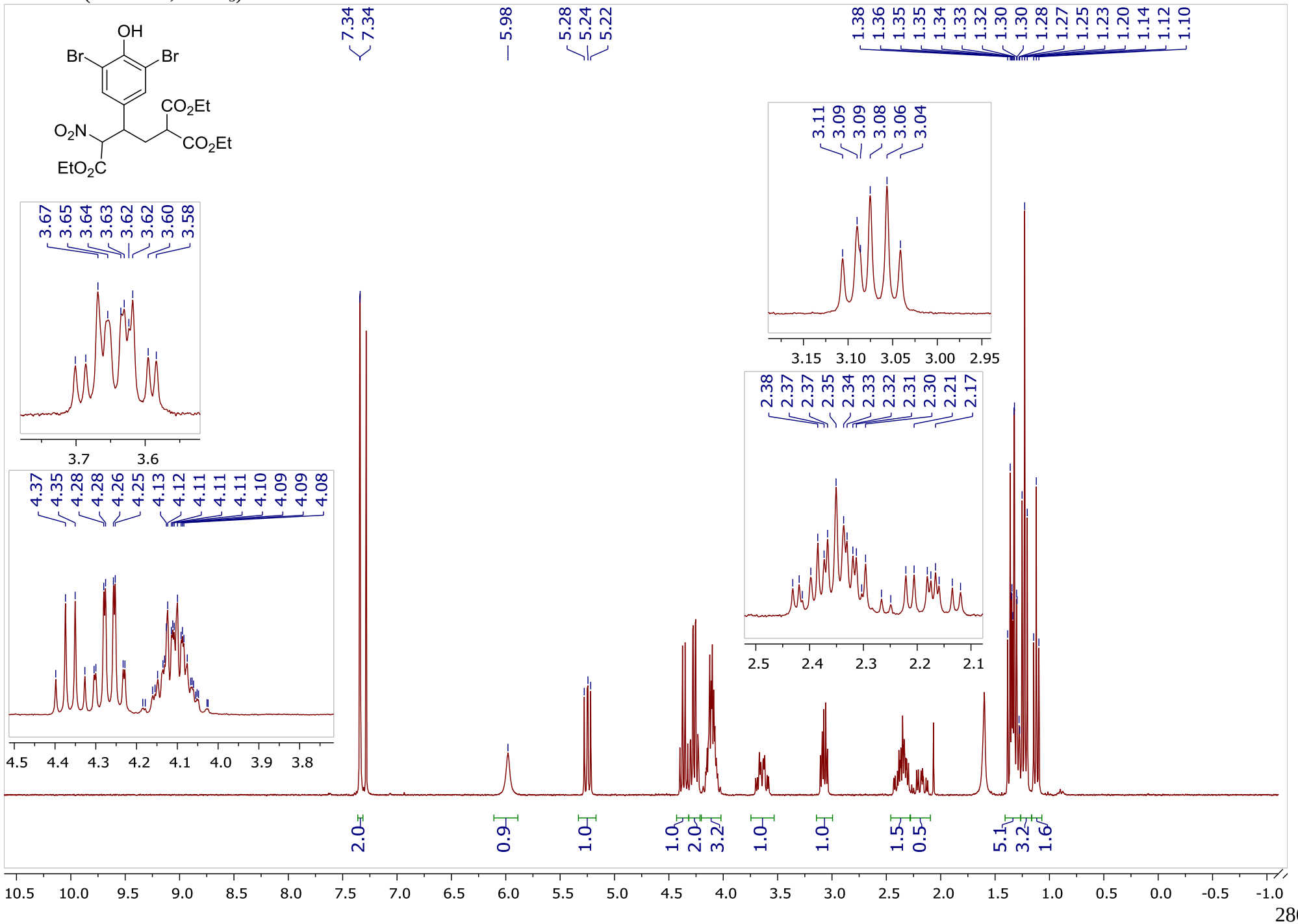


$^{13}$C DEPT (75 MHz, $CDCl_3$)

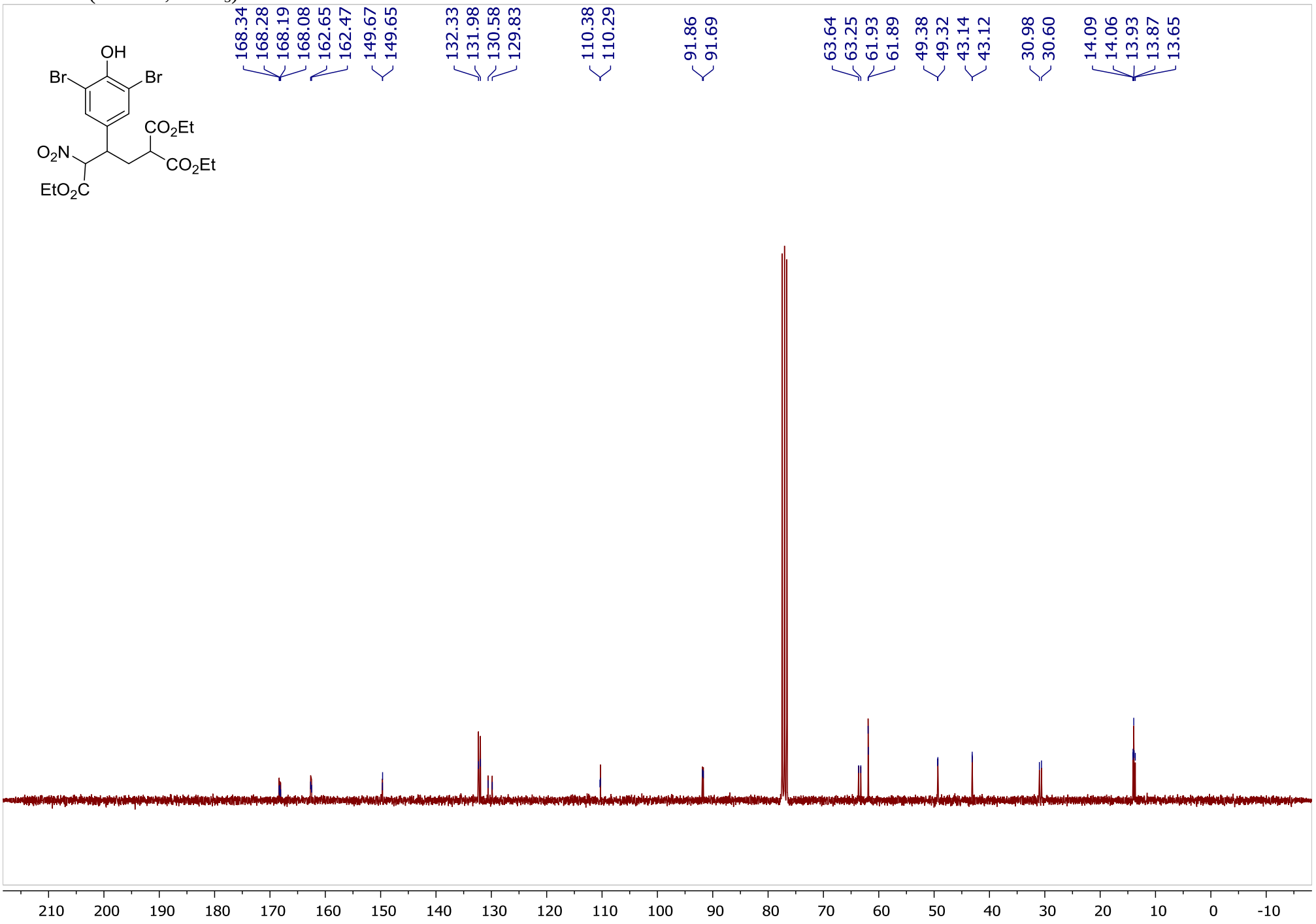


**Triethyl 3-(3,5-dibromo-4-hydroxyphenyl)-4-nitrobutane-1,1,4-tricarboxylate (3ma)**, dr = 1:1

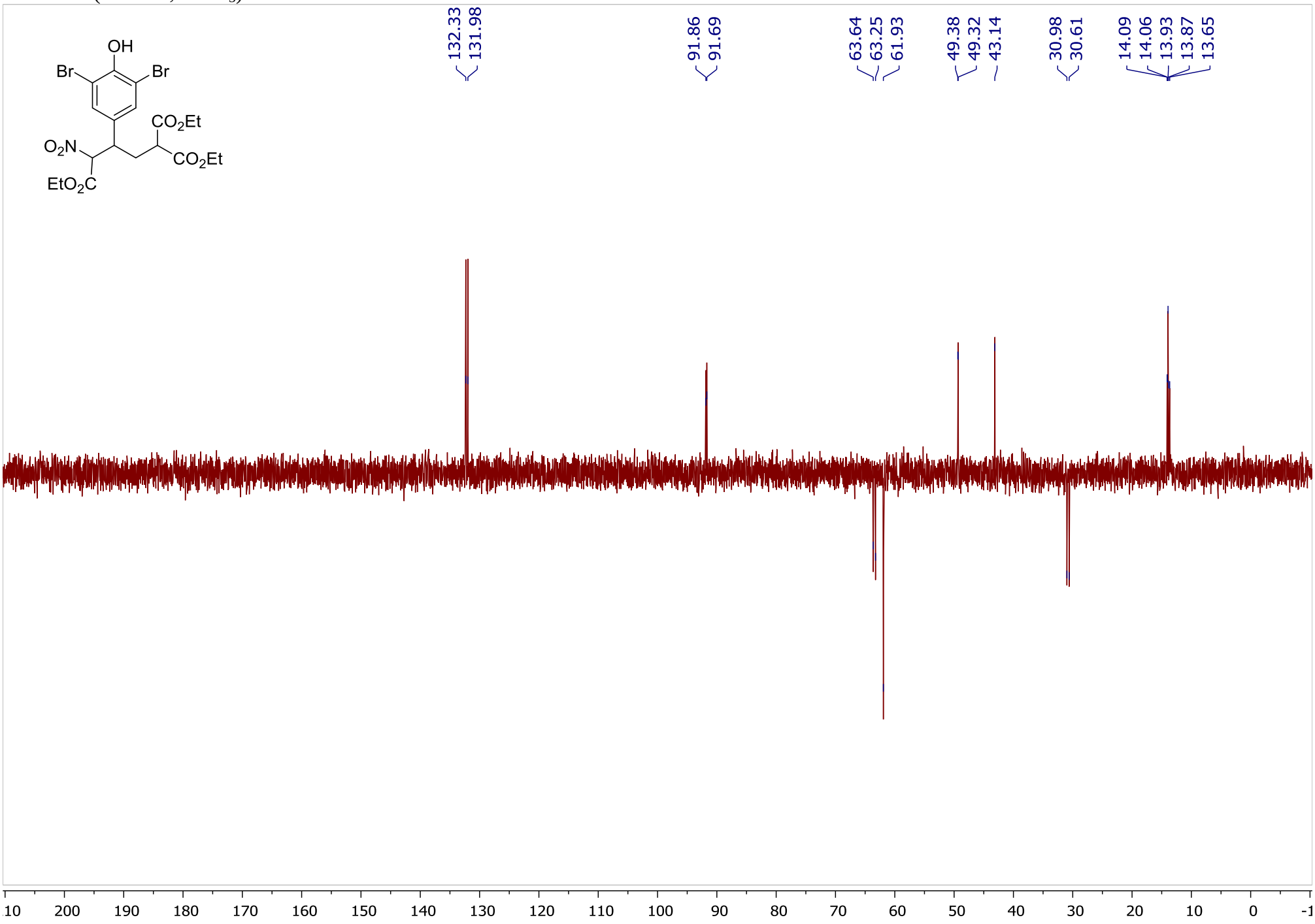
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

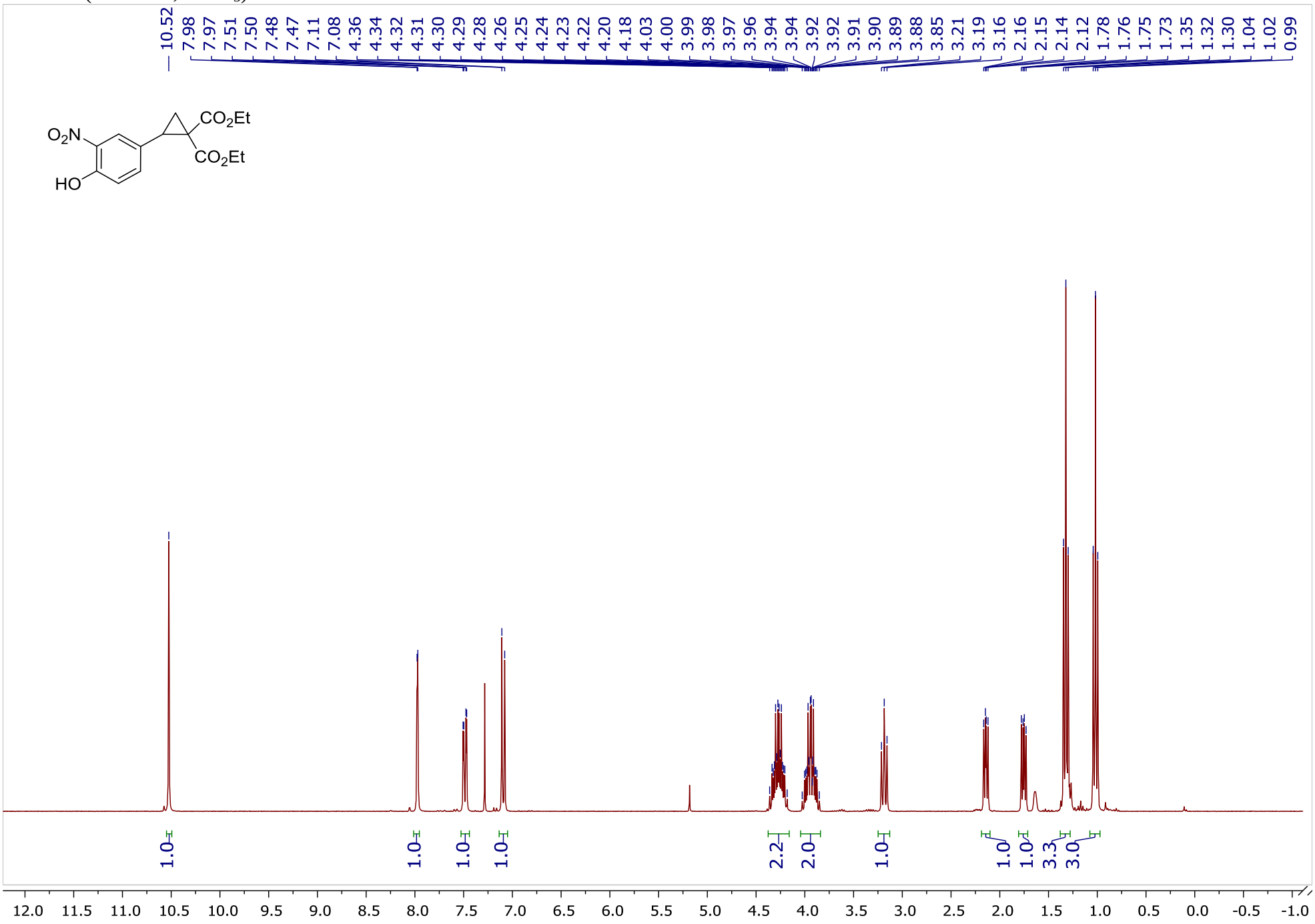


$^{13}$C DEPT (75 MHz, $CDCl_3$)

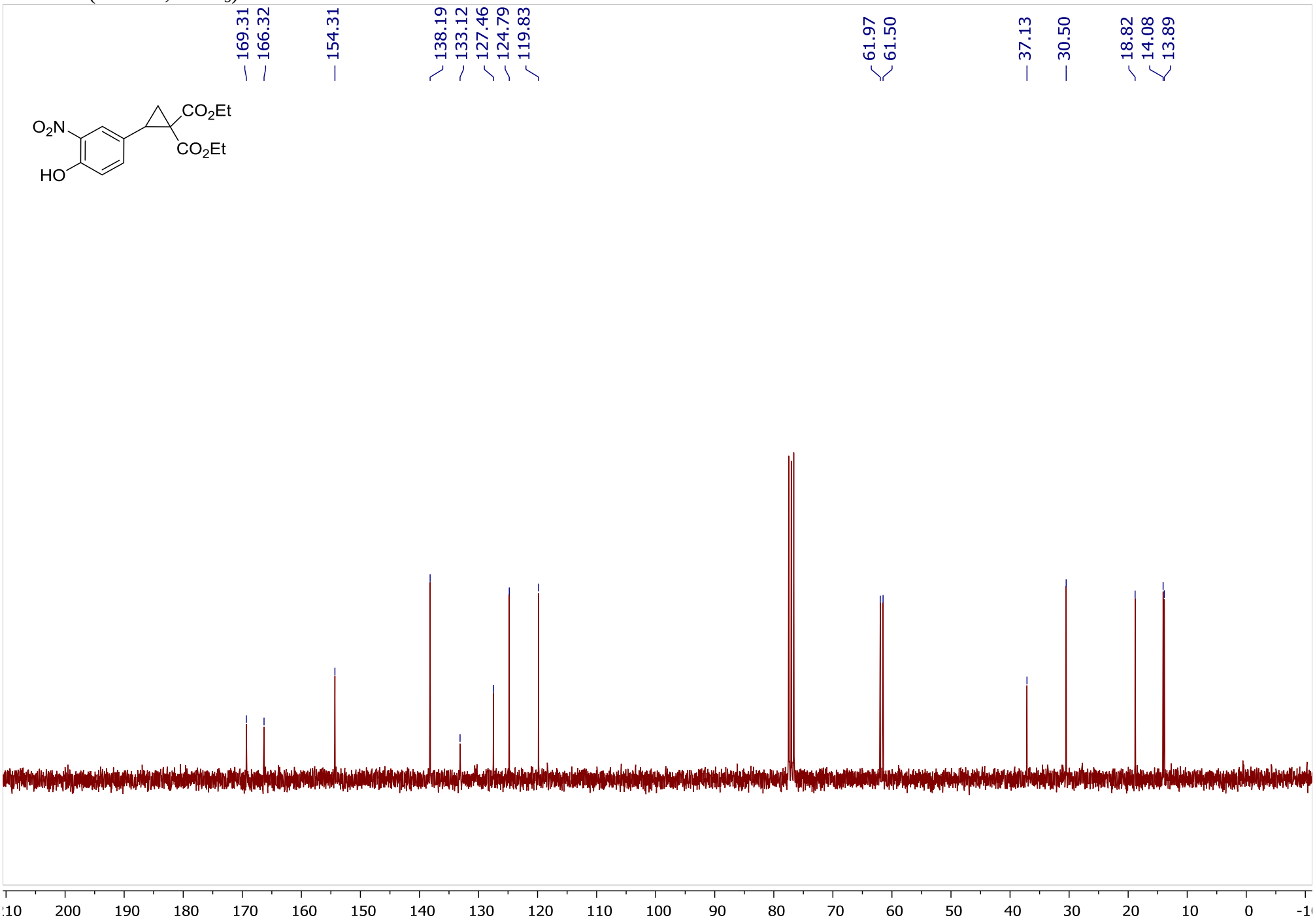


**Diethyl 2-(4-hydroxy-3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4j)**

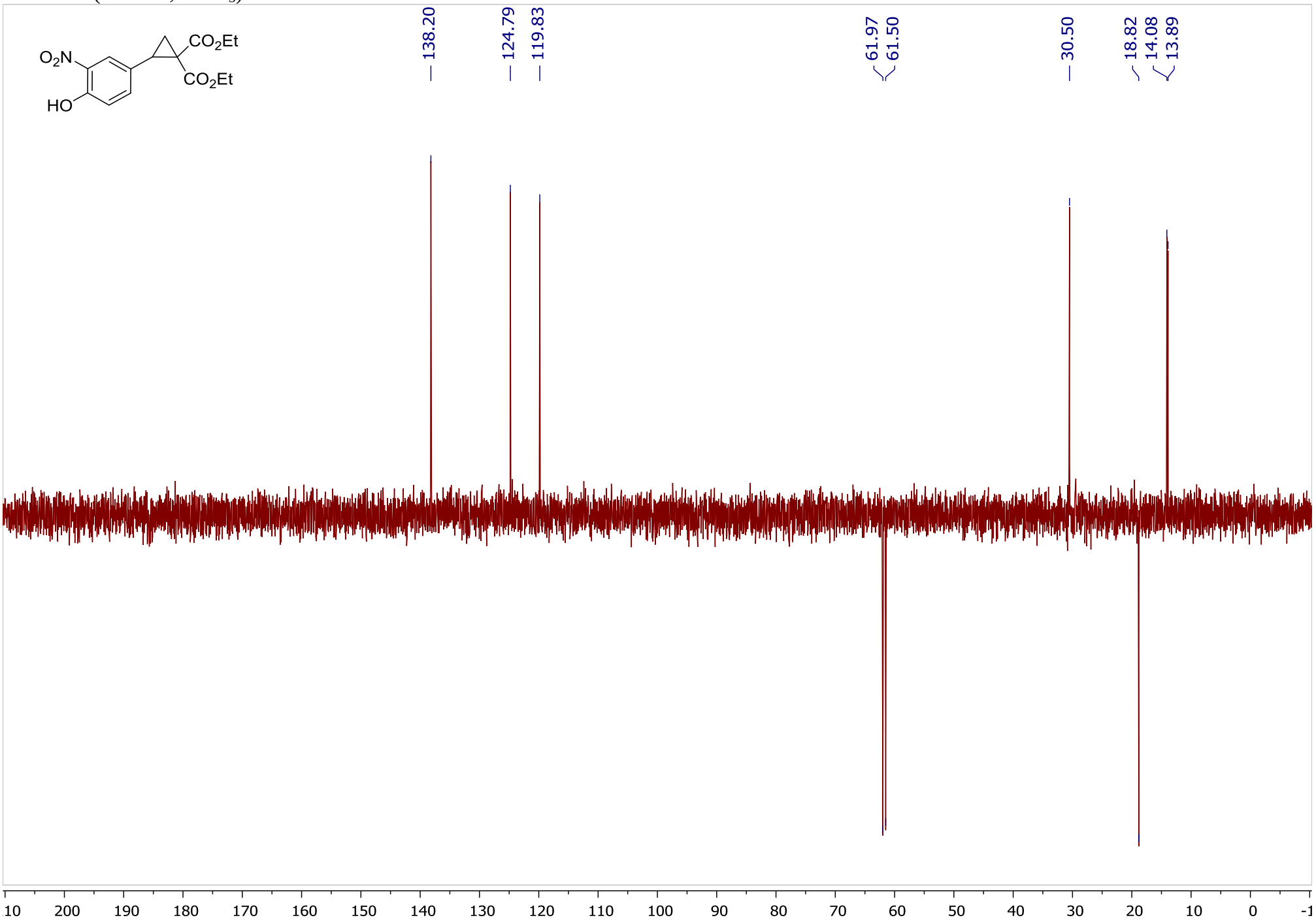
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

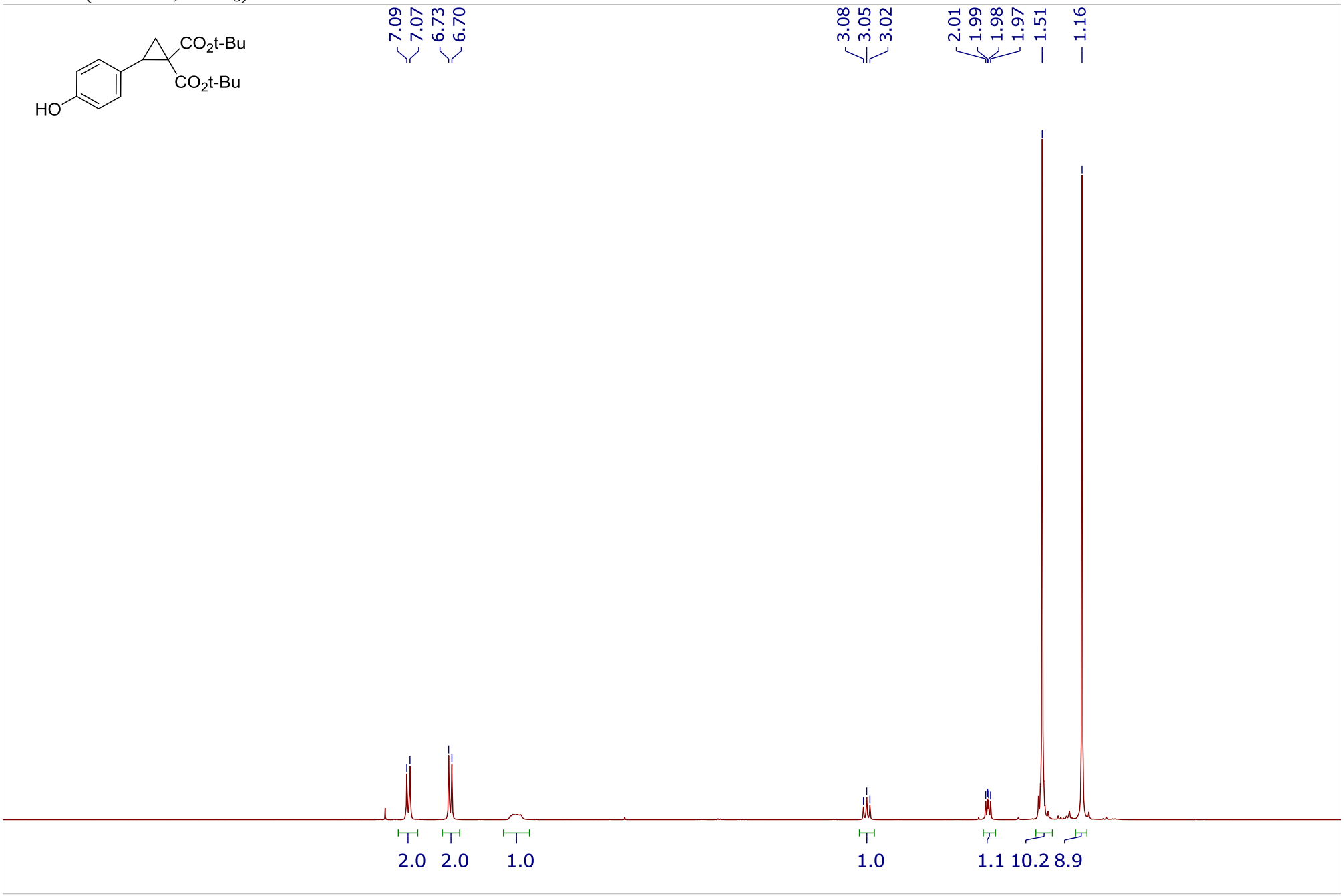


$^{13}$C DEPT (75 MHz, $CDCl_3$)

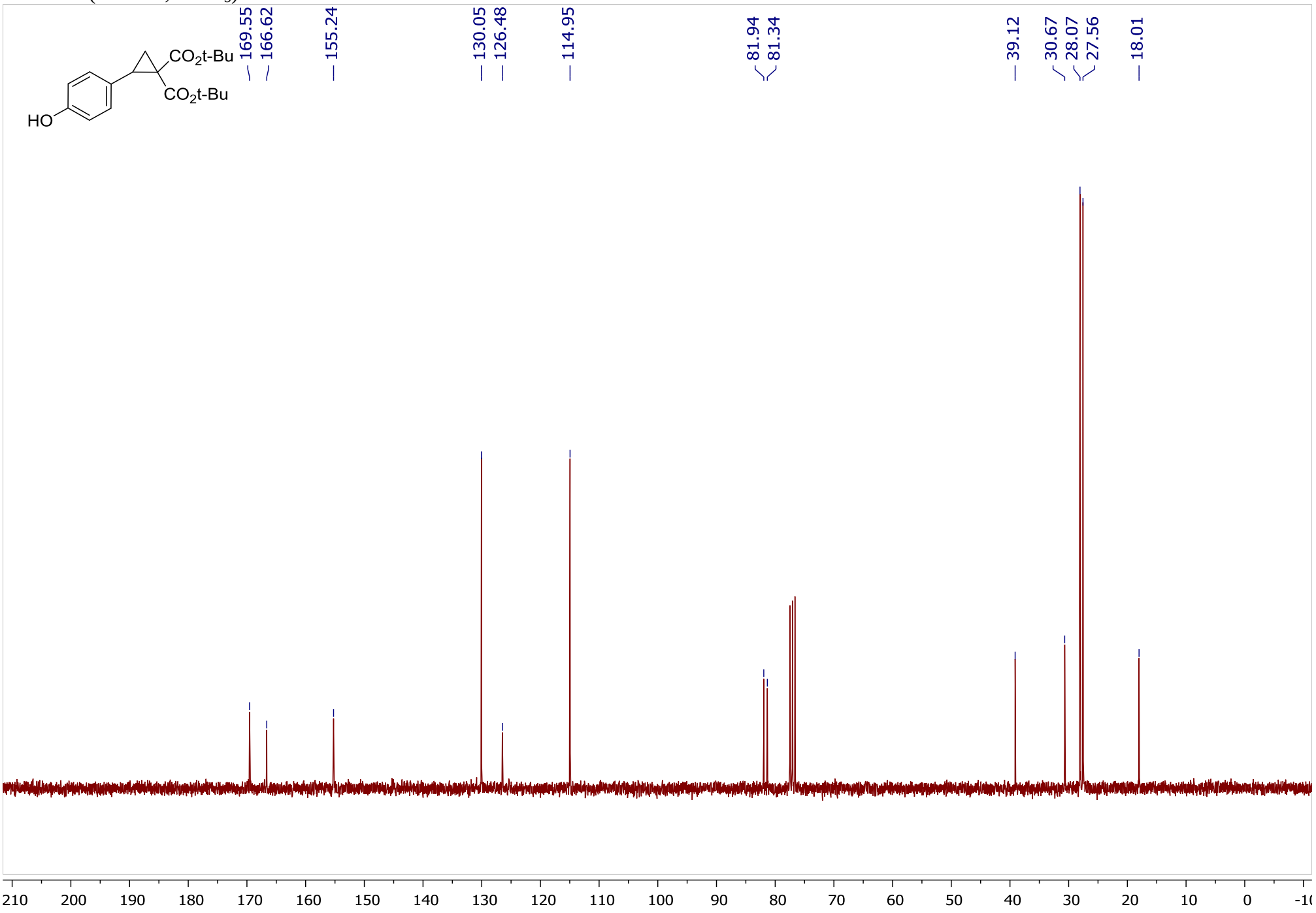


**Di-tert-butyl 2-(4-hydroxyphenyl)cyclopropane-1,1-dicarboxylate (4k)**

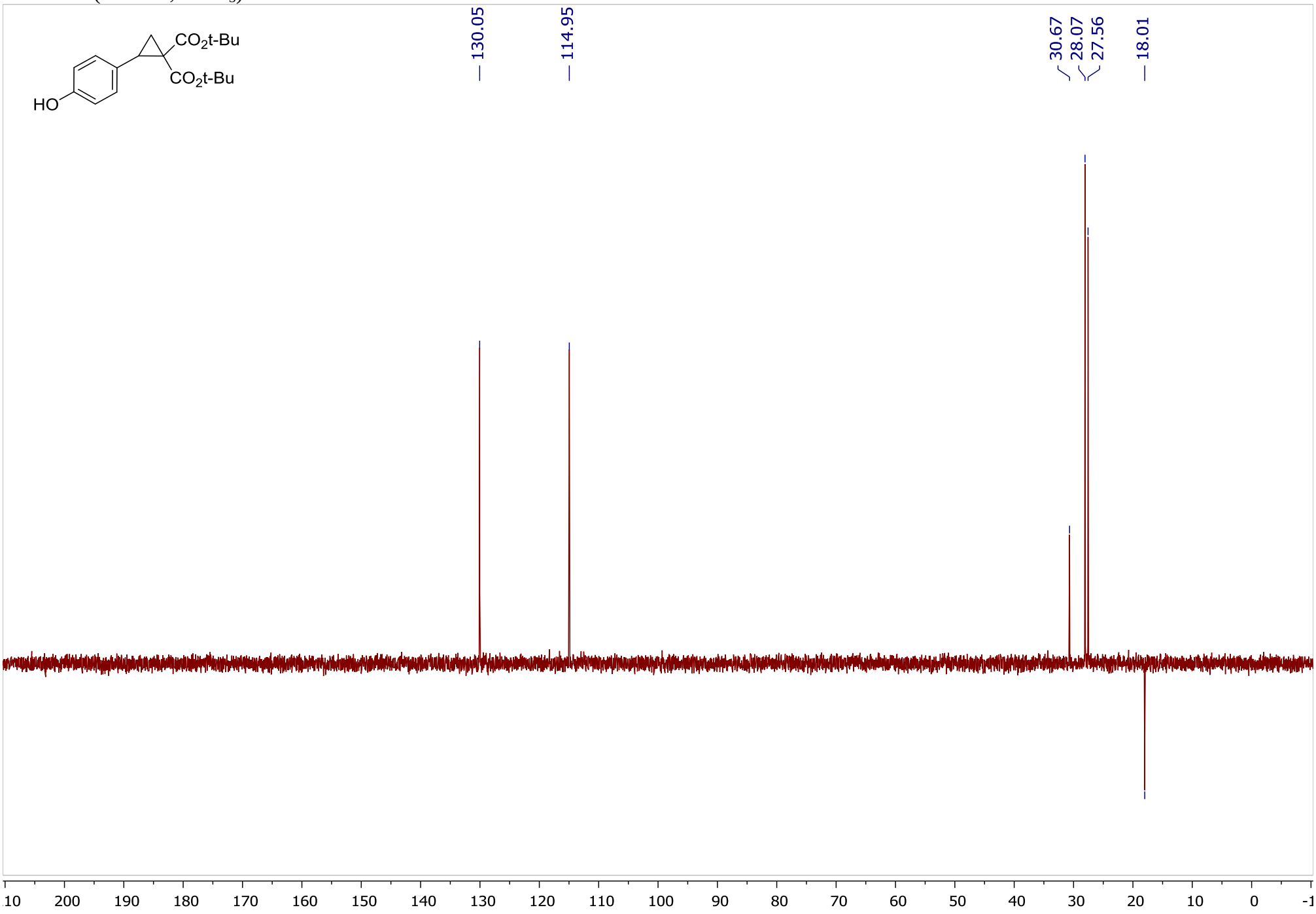
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

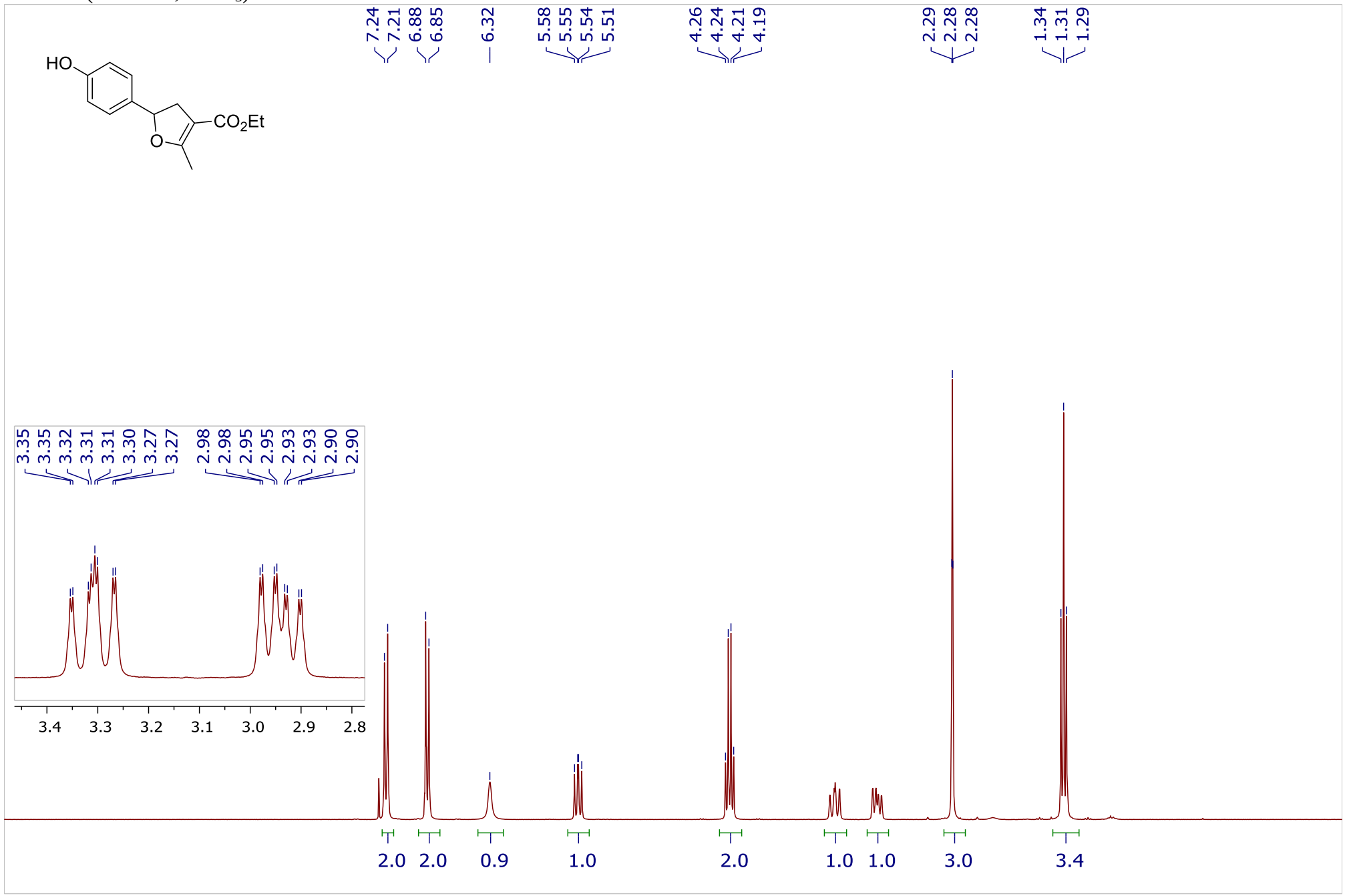


$^{13}$C DEPT (75 MHz, $CDCl_3$)

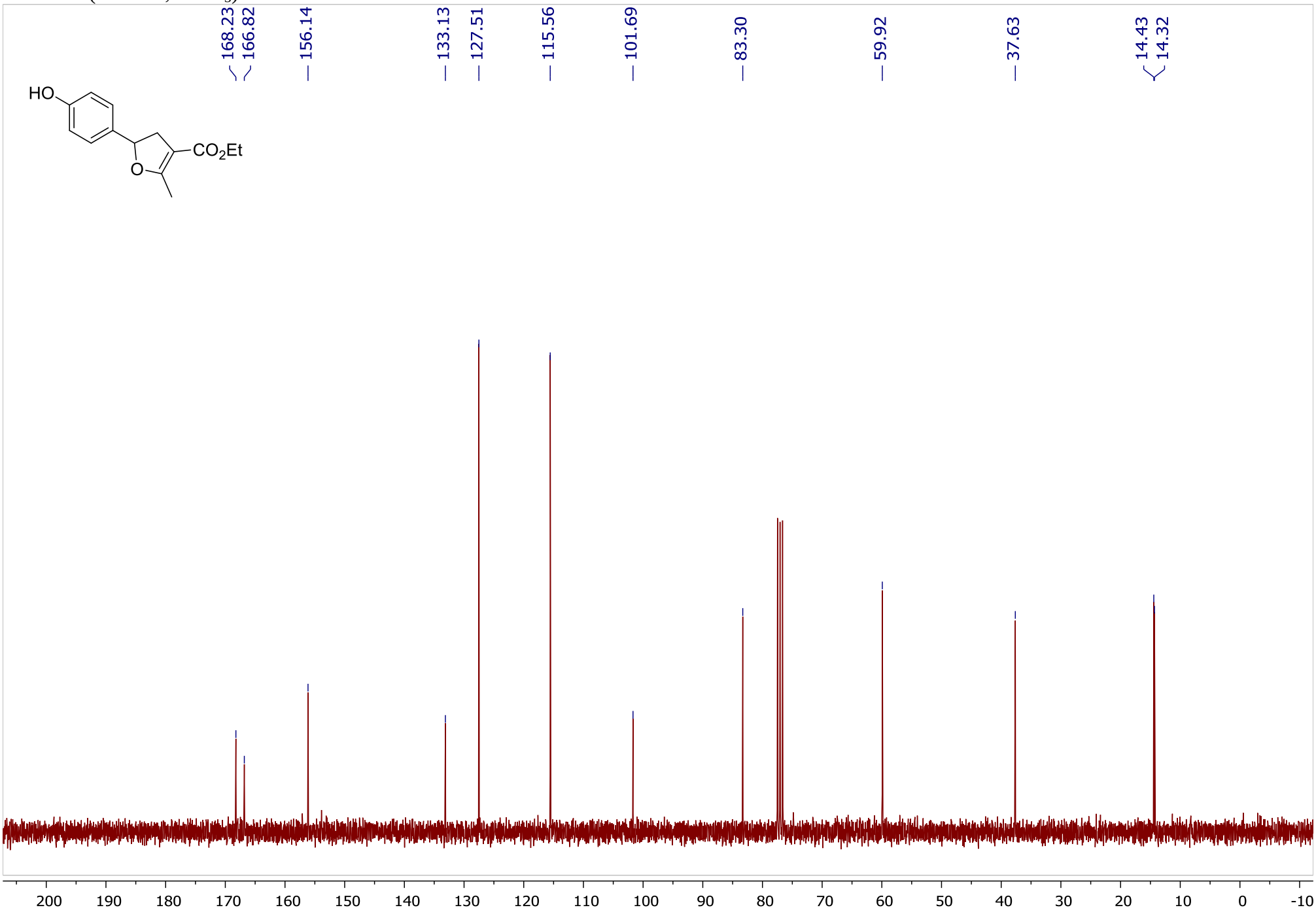


**Ethyl 5-(4-hydroxyphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (6)**

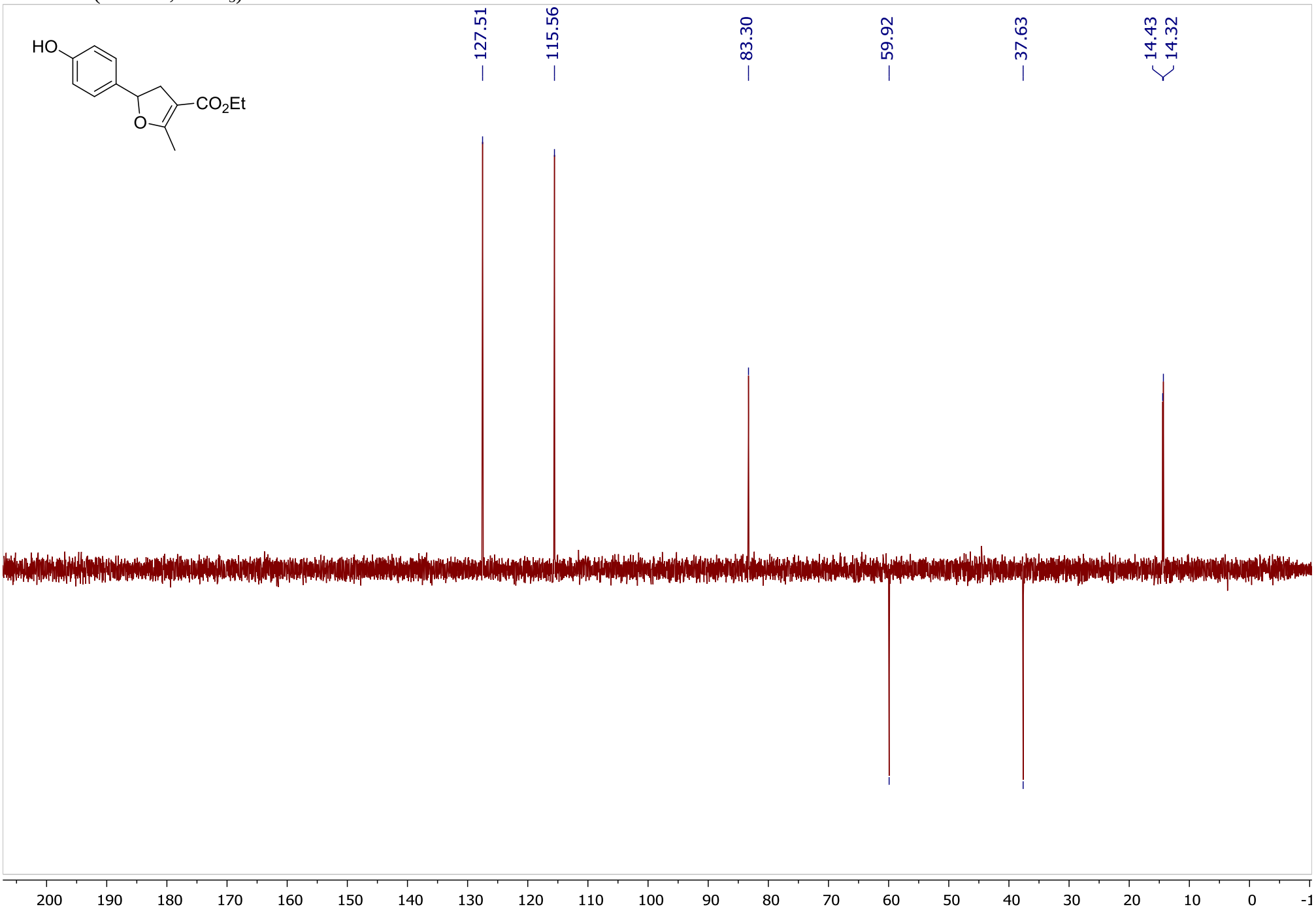
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

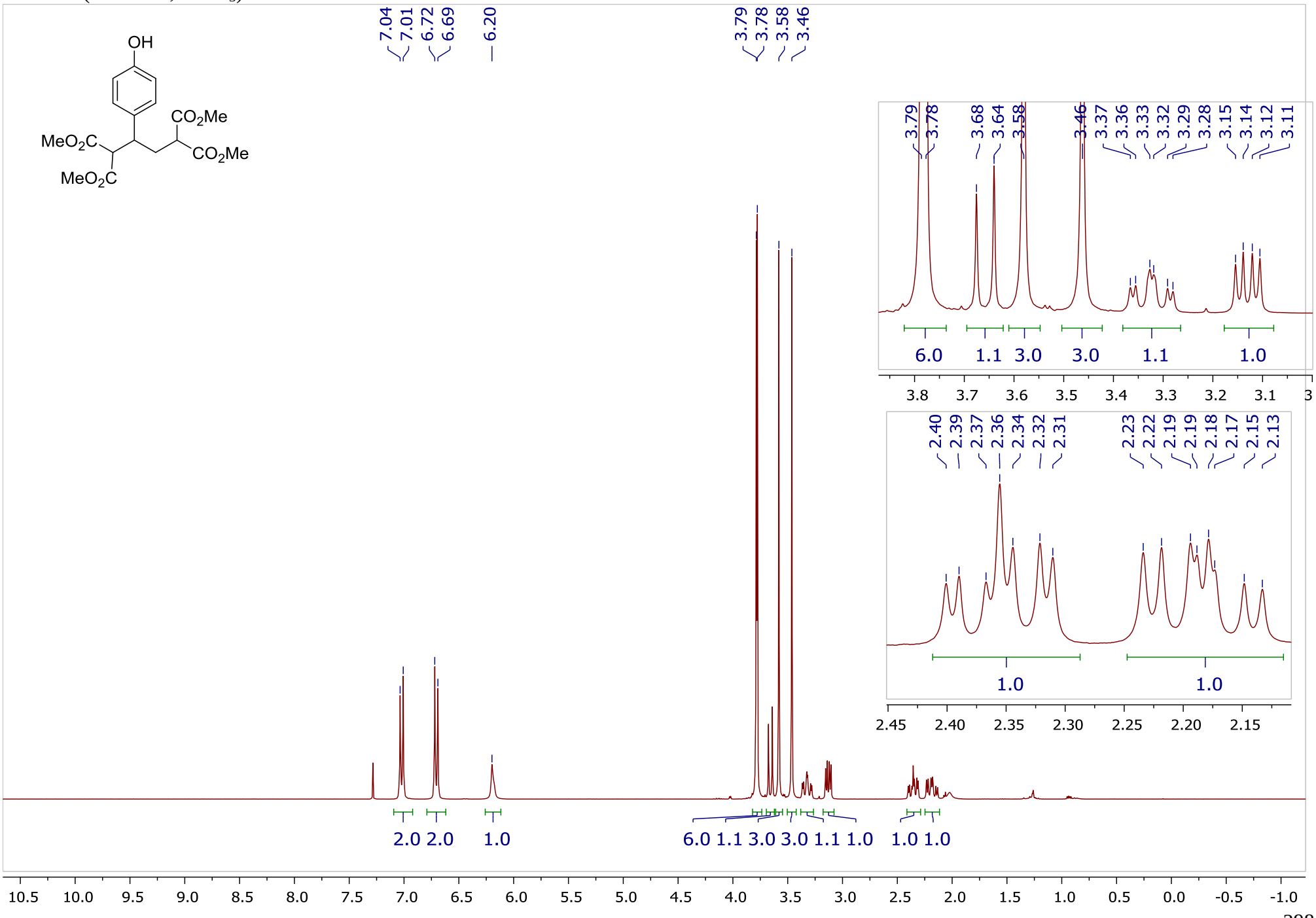


$^{13}$C DEPT (75 MHz, $CDCl_3$)

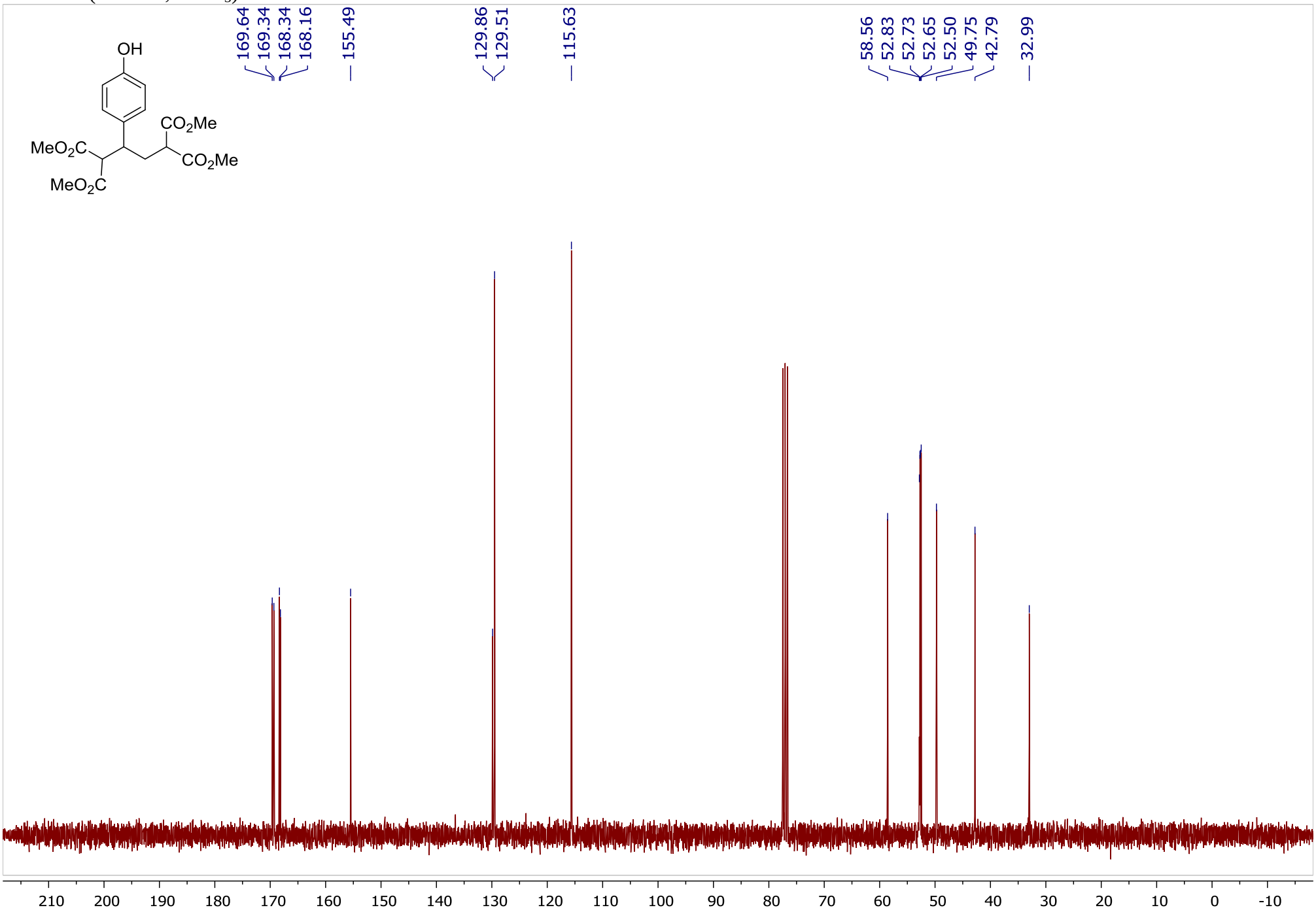


**Tetramethyl 2-(4-hydroxyphenyl)butane-1,1,4,4-tetracarboxylate (7a)**

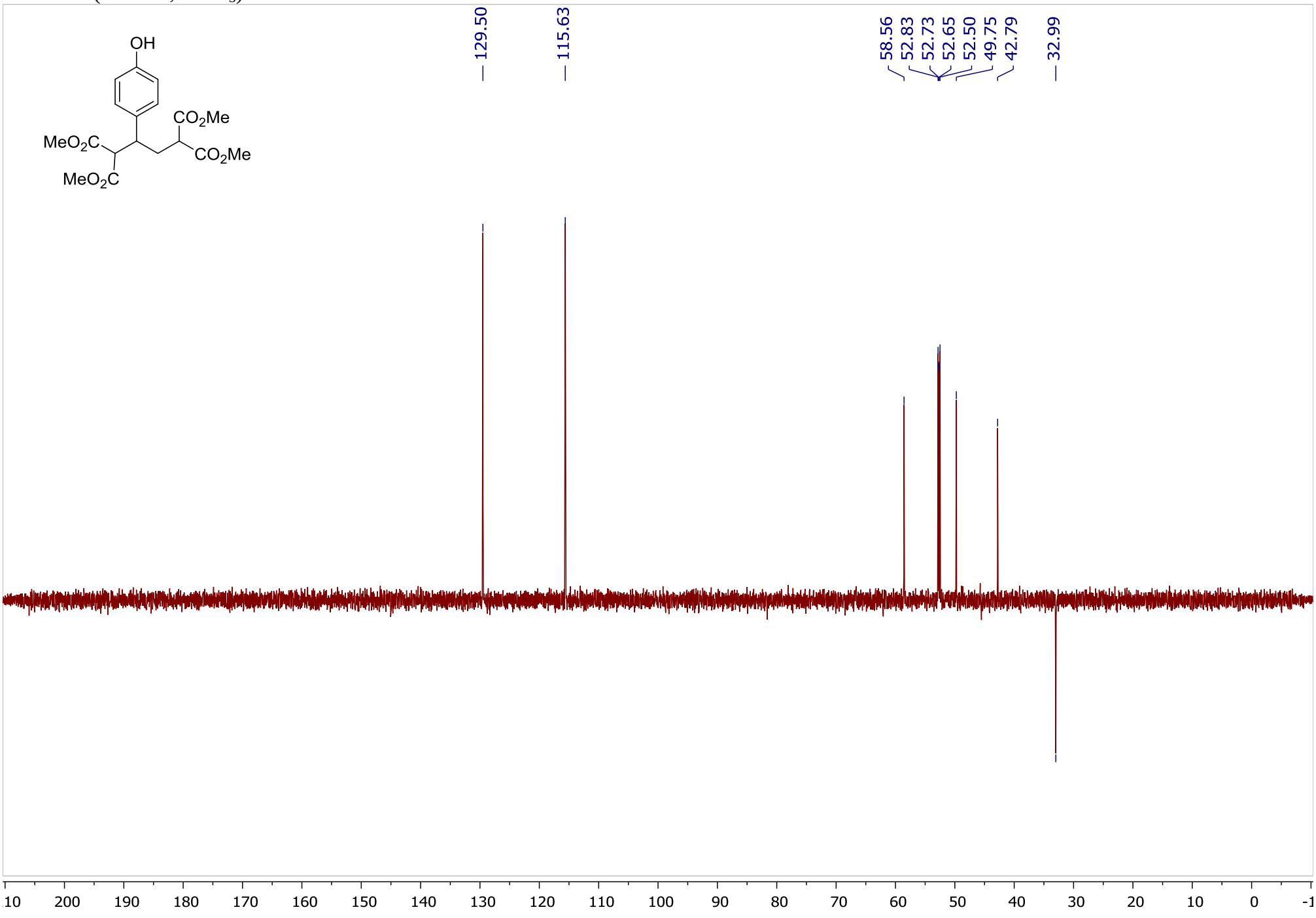
$^1$H NMR (300 MHz, $CDCl_3$)



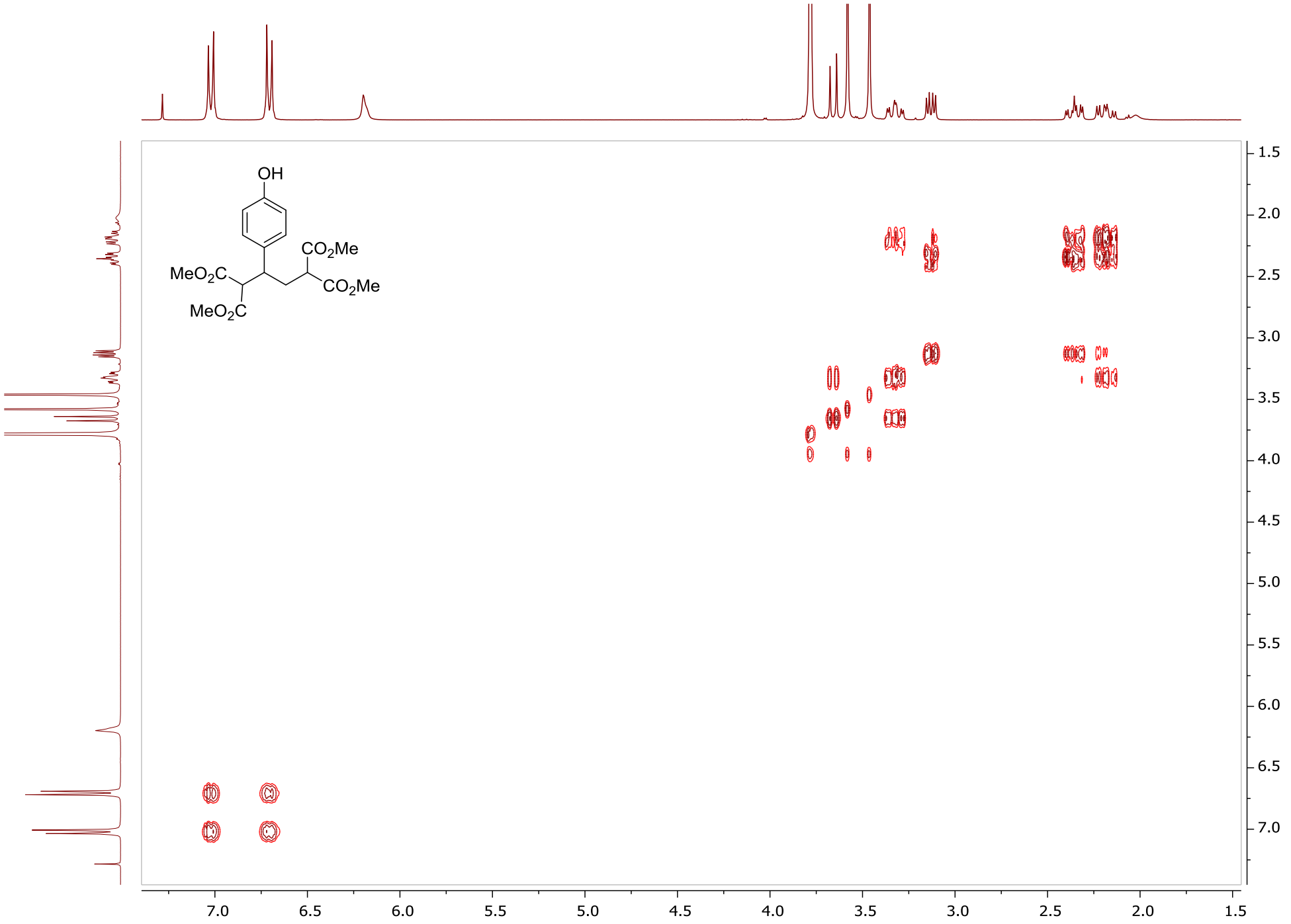
$^{13}$C NMR (75 MHz, $CDCl_3$)



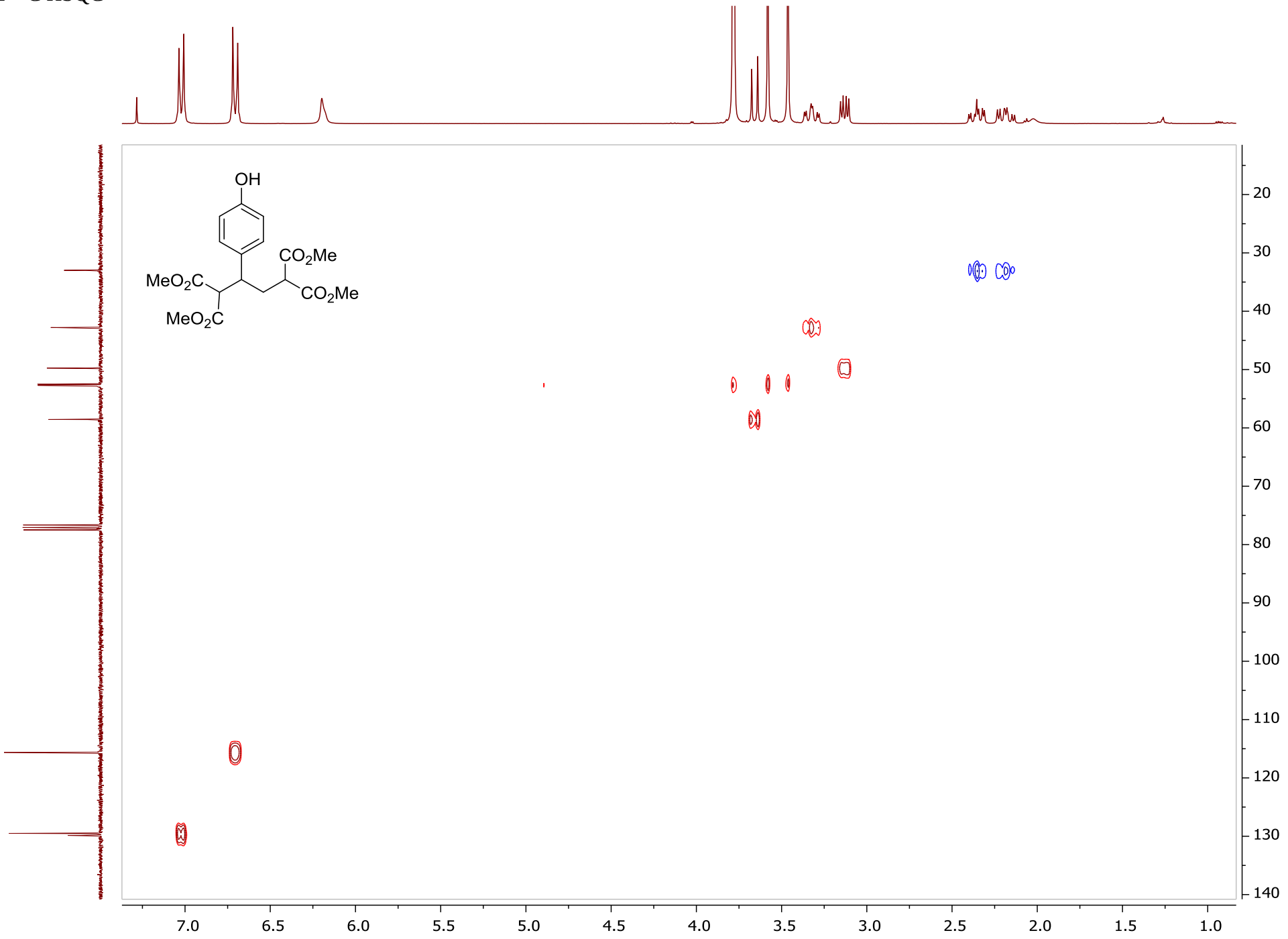
$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY

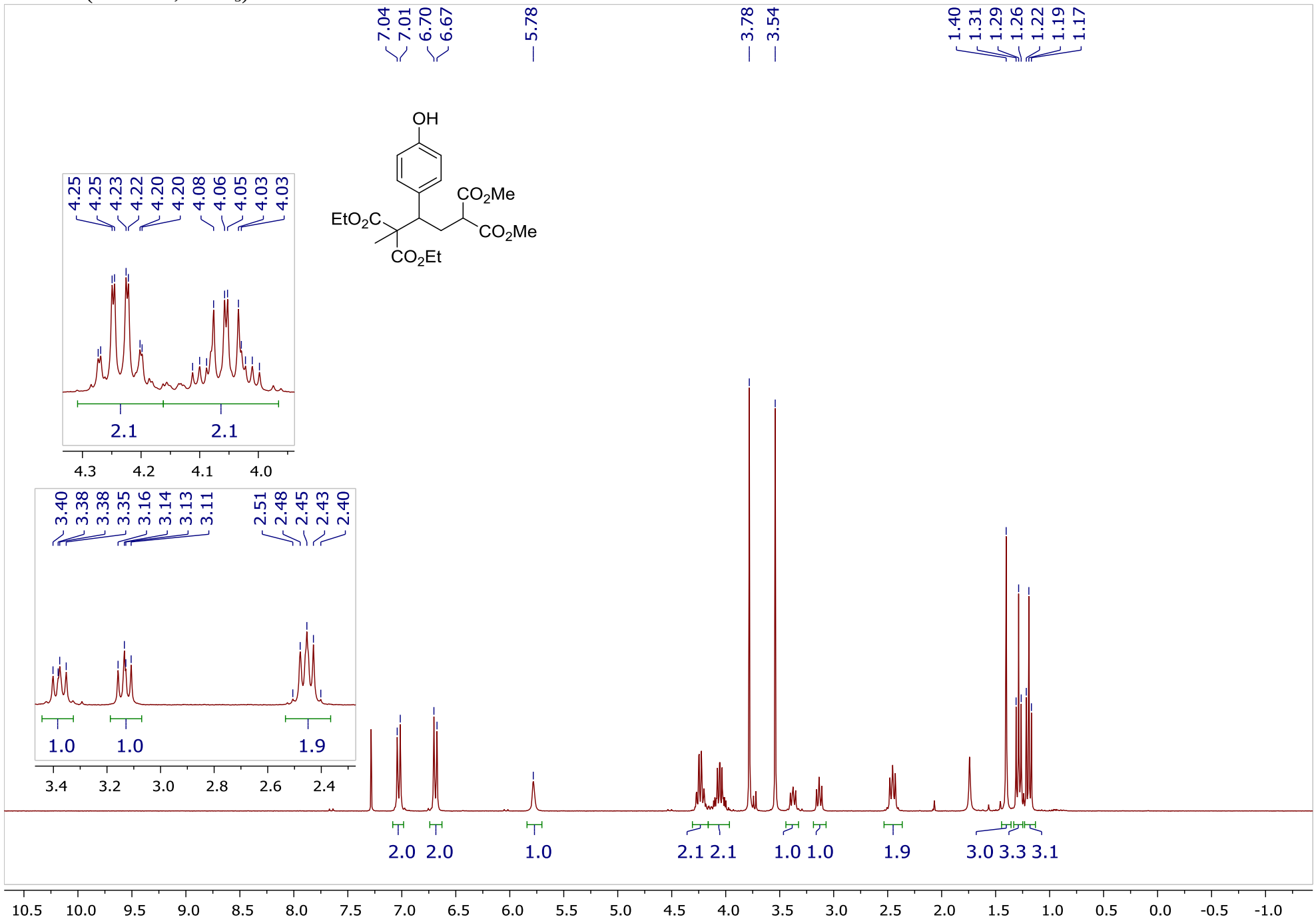

OH
CO2Me
MeO2C
CO2Me
MeO2C
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HSQC

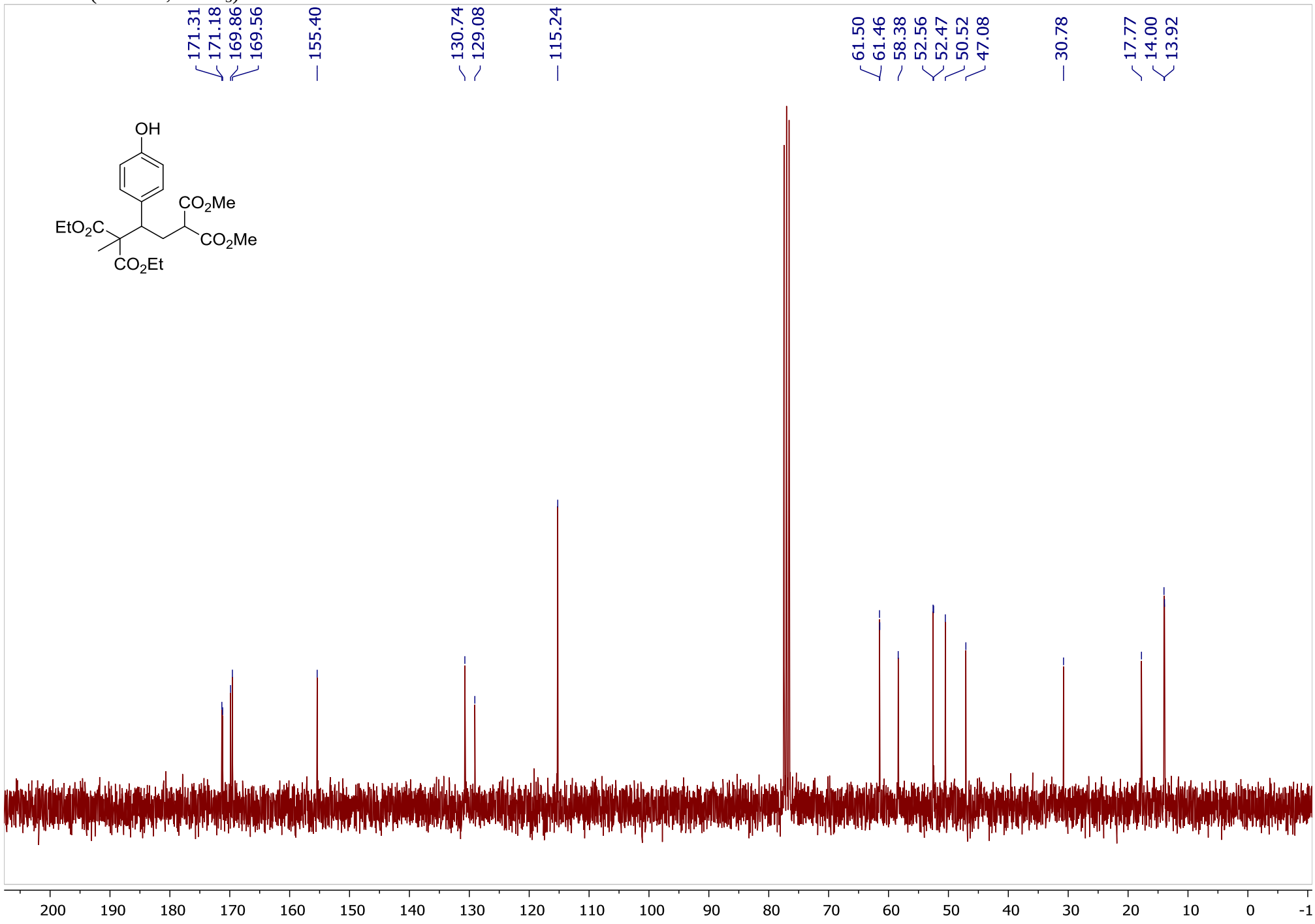

OH
CO2Me
MeO2C
CO2Me
MeO2C
20
30
40
50
60
70
80
90
100
110
120
130
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**4,4-Diethyl 1,1-dimethyl 3-(4-hydroxyphenyl)pentane-1,1,4,4-tetracarboxylate (7b)**

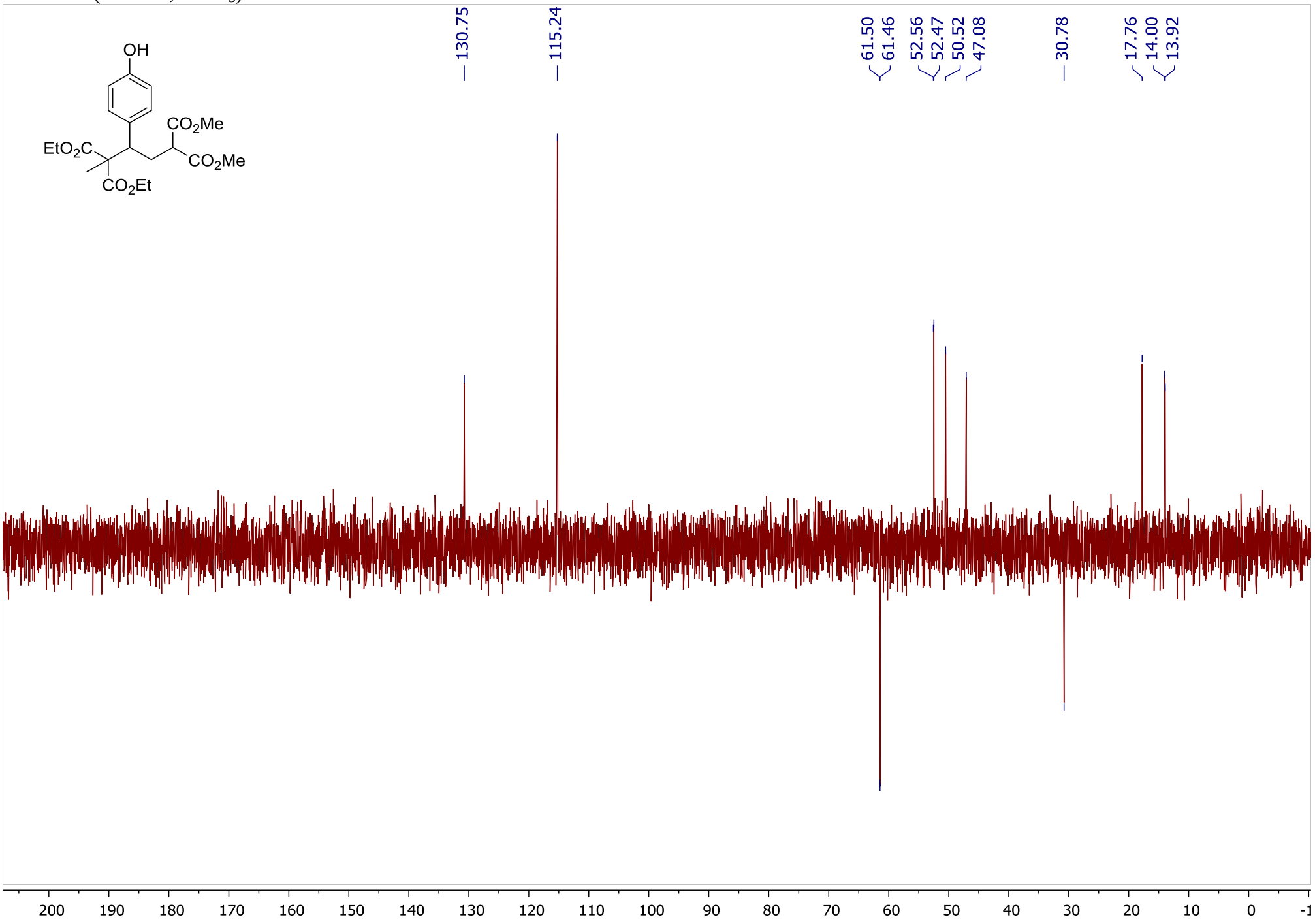
$^1$H NMR (300 MHz, $CDCl_3$)



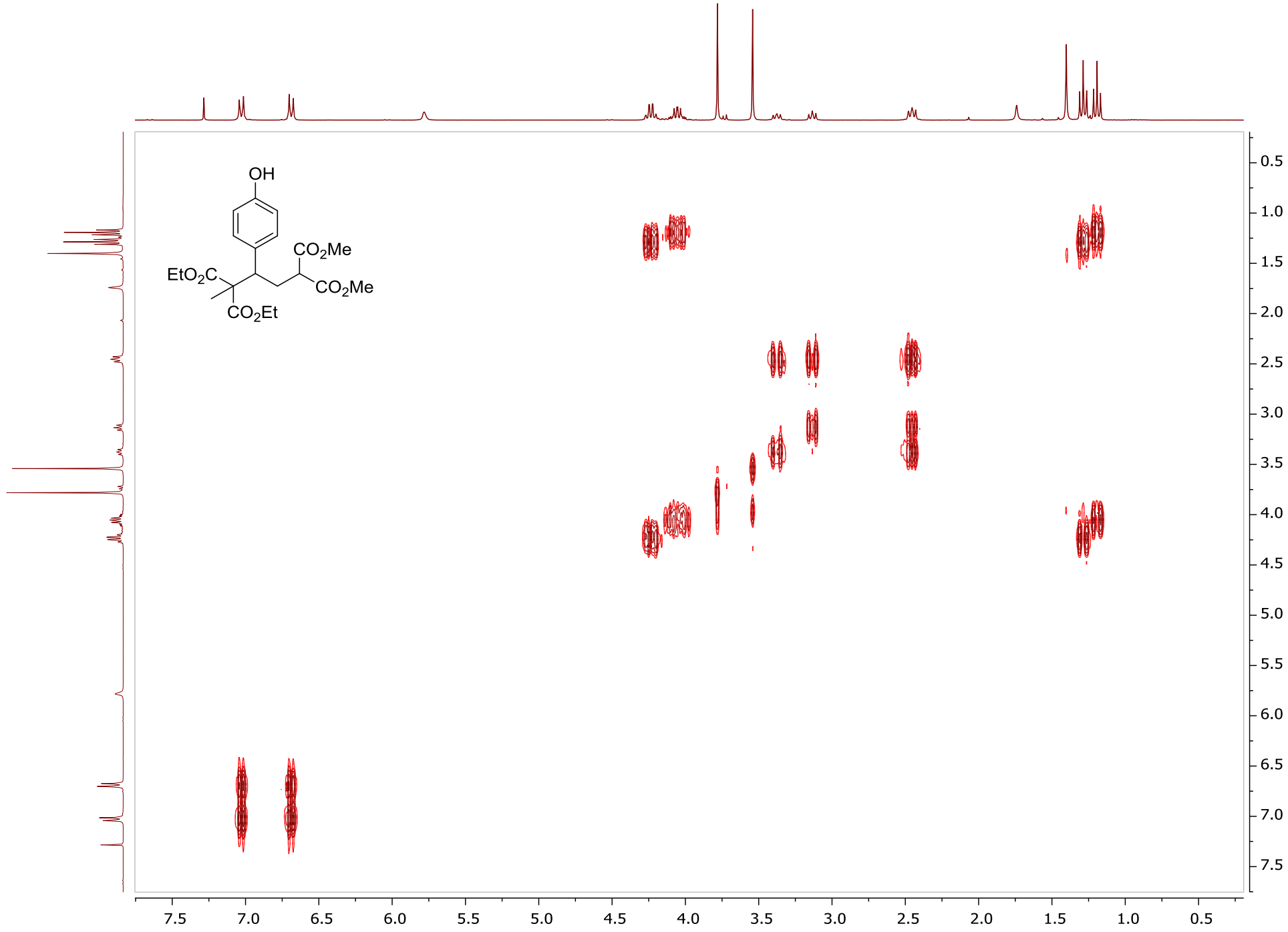
$^{13}$C NMR (75 MHz, $CDCl_3$)



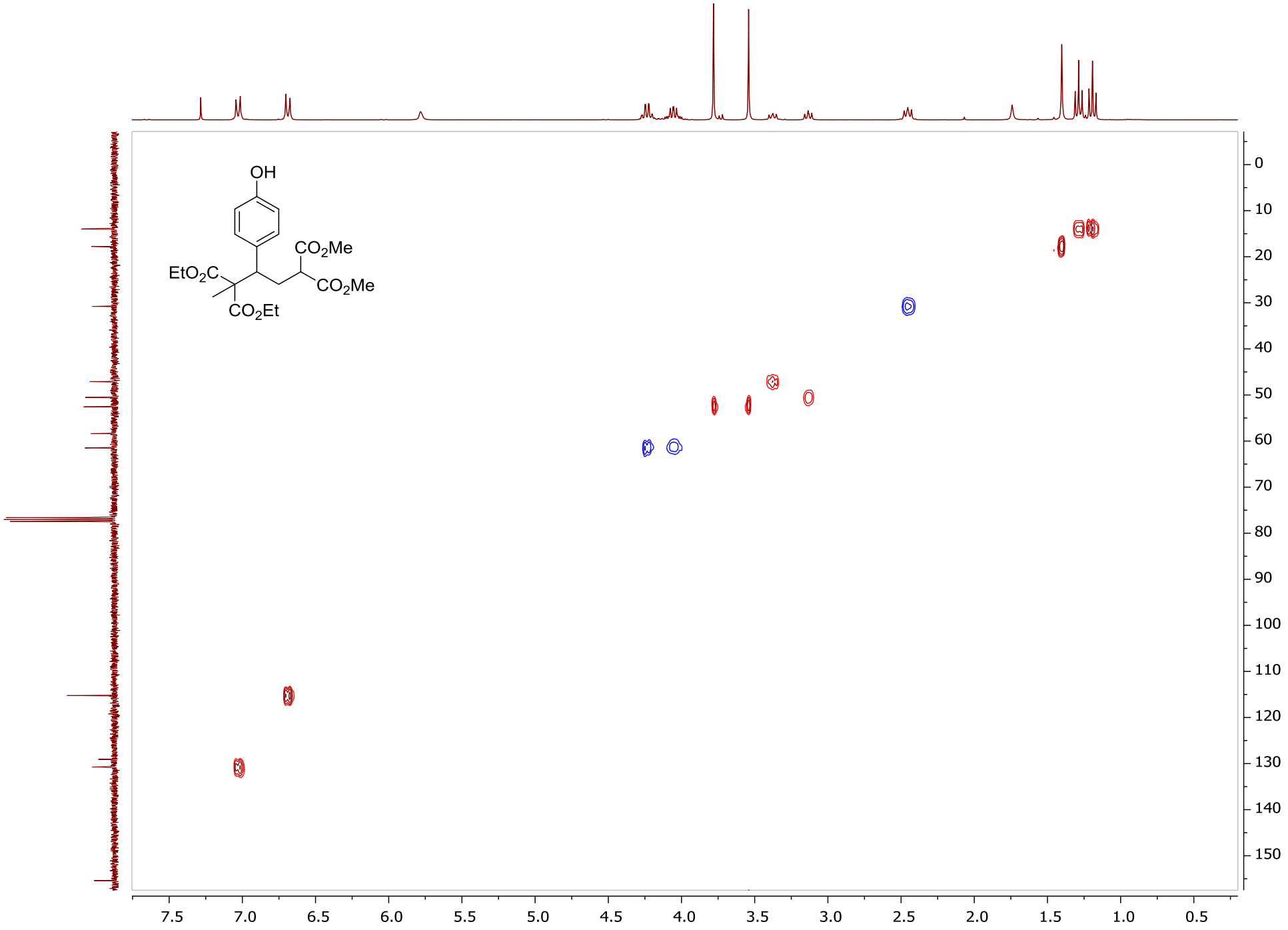
$^{13}$C DEPT (75 MHz, $CDCl_3$)



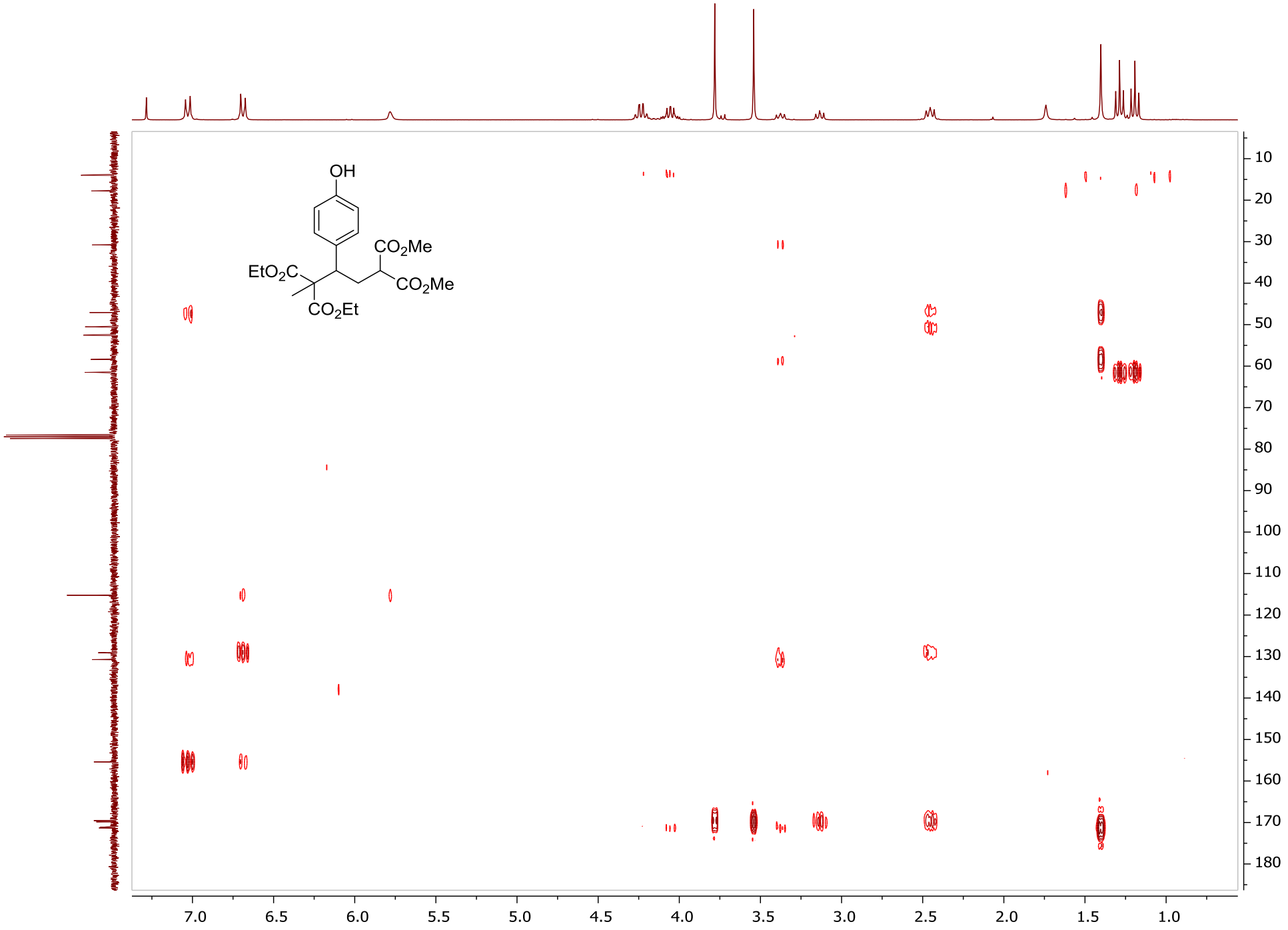
$^{1}H$-$^{1}H$ COSY


OH
CO2Me
EtO2C
CO2Me
CO2Et
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC

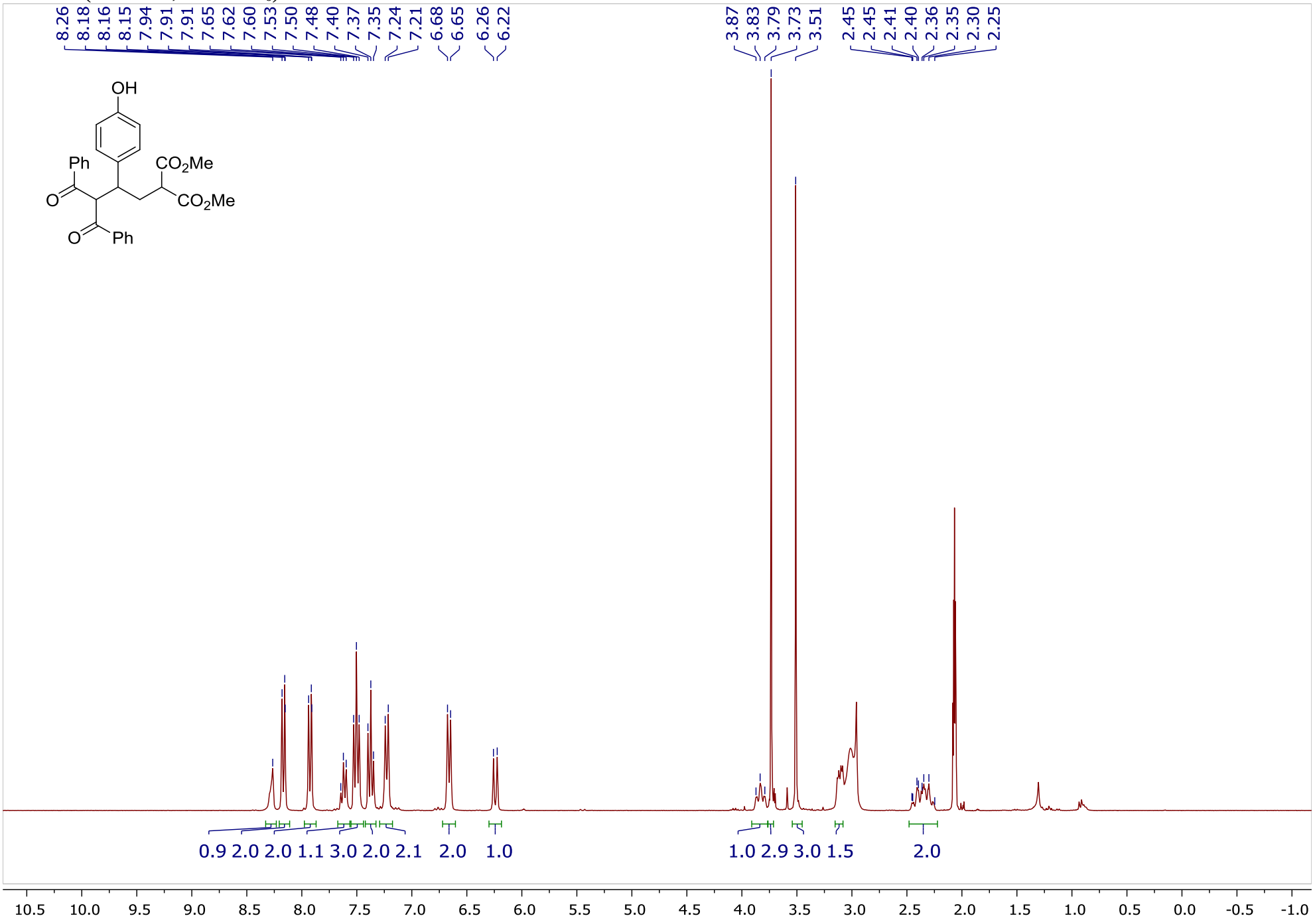

OH
CO2Me
EtO2C
CO2Me
CO2Et
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HMBC

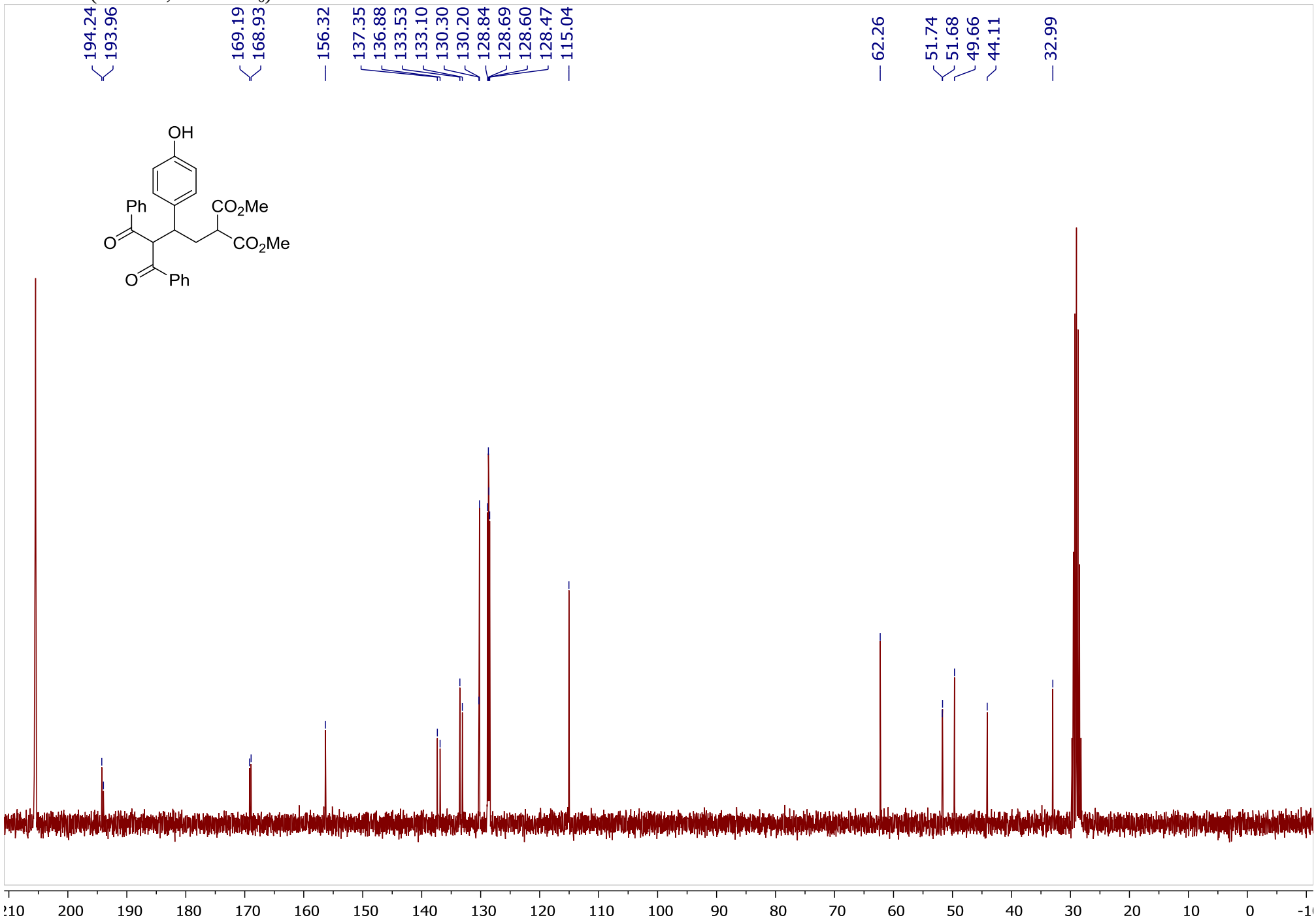

OH
CO2Me
EtO2C
CO2Me
CO2Et
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**Dimethyl 2-(3-benzoyl-2-(4-hydroxyphenyl)-4-oxo-4-phenylbutyl)malonate (7c)**

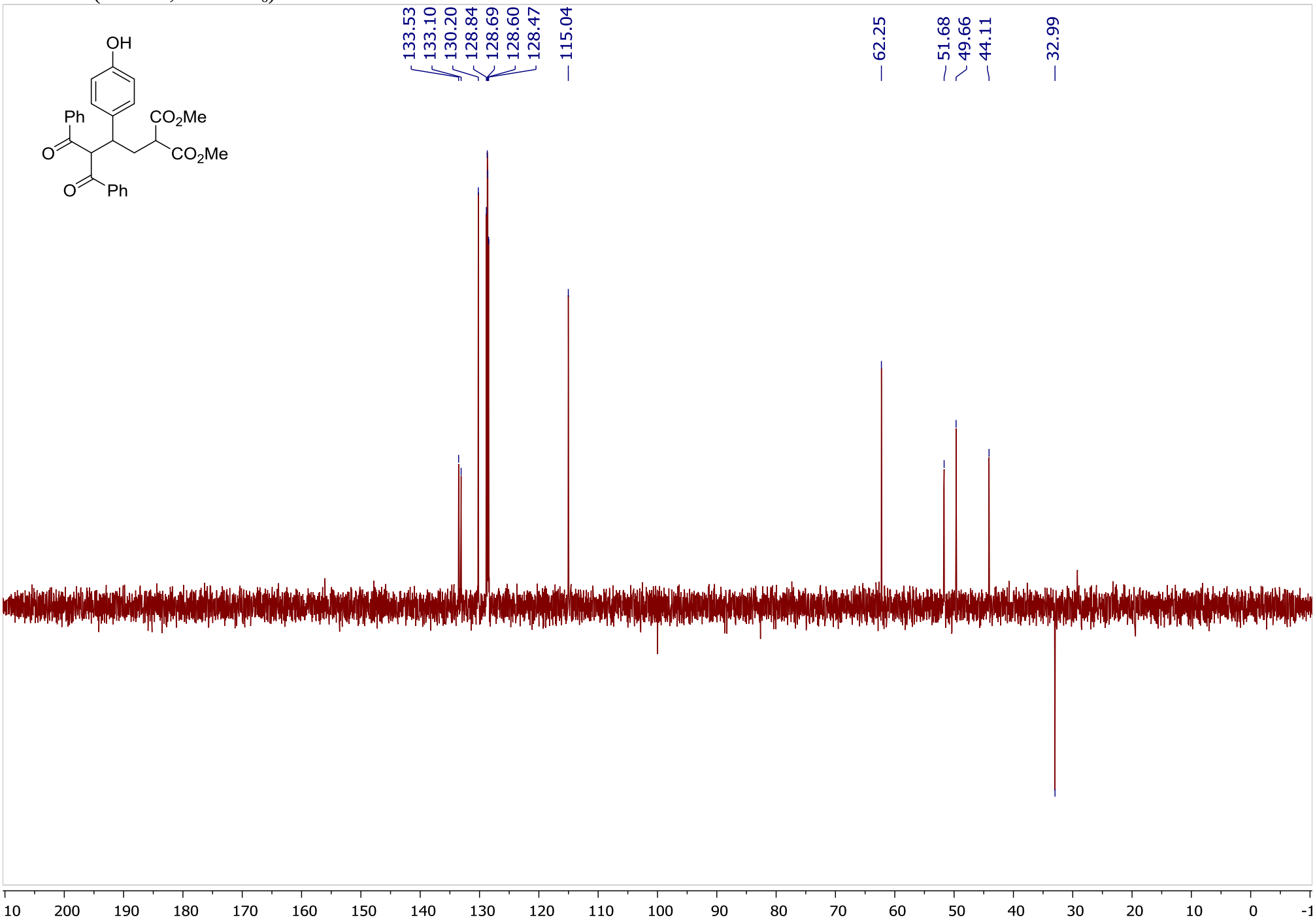
$^1$H NMR (300 MHz, acetone-$d_6$)



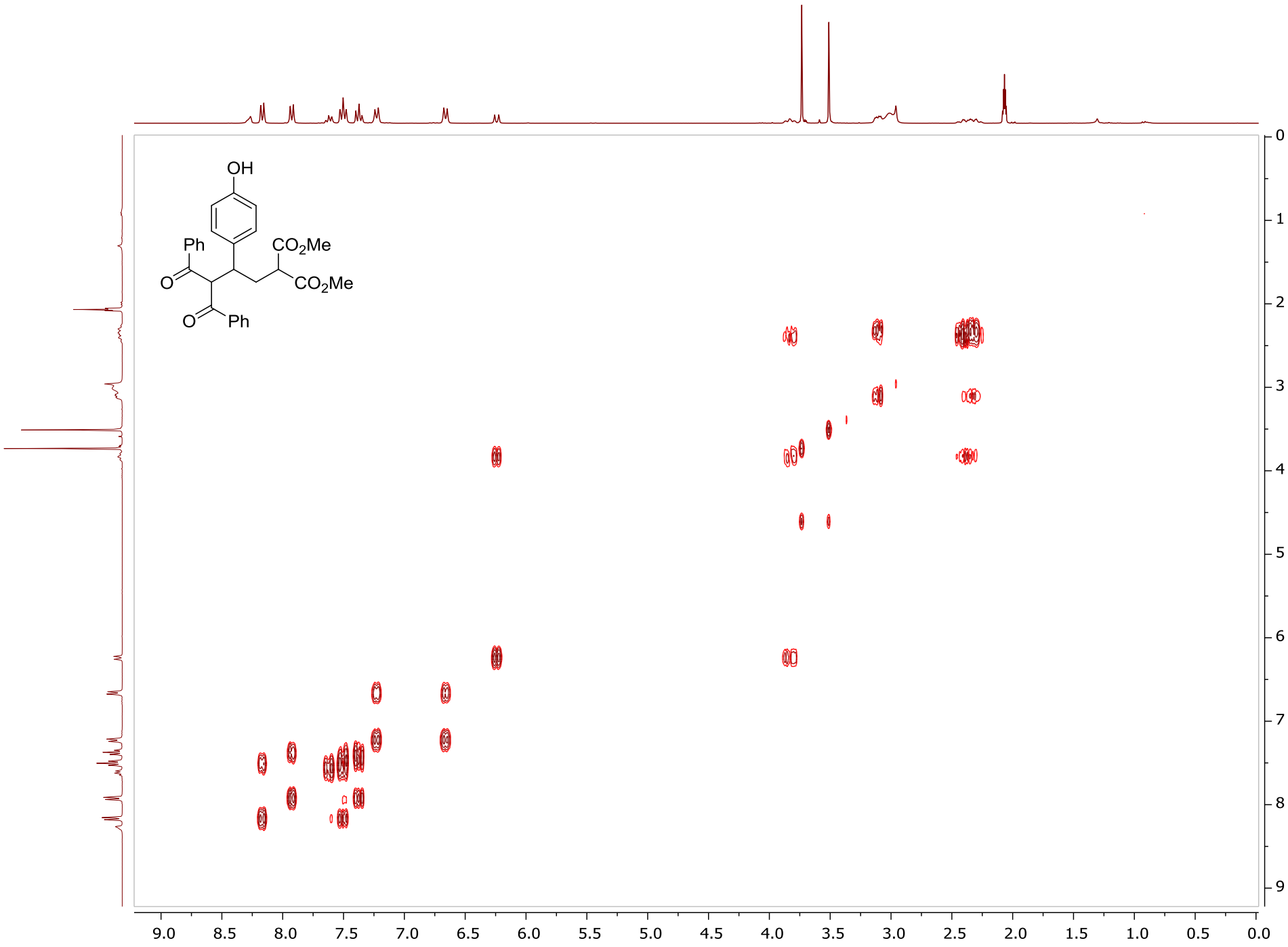
$^{13}$C NMR (75 MHz, acetone-$d_6$)



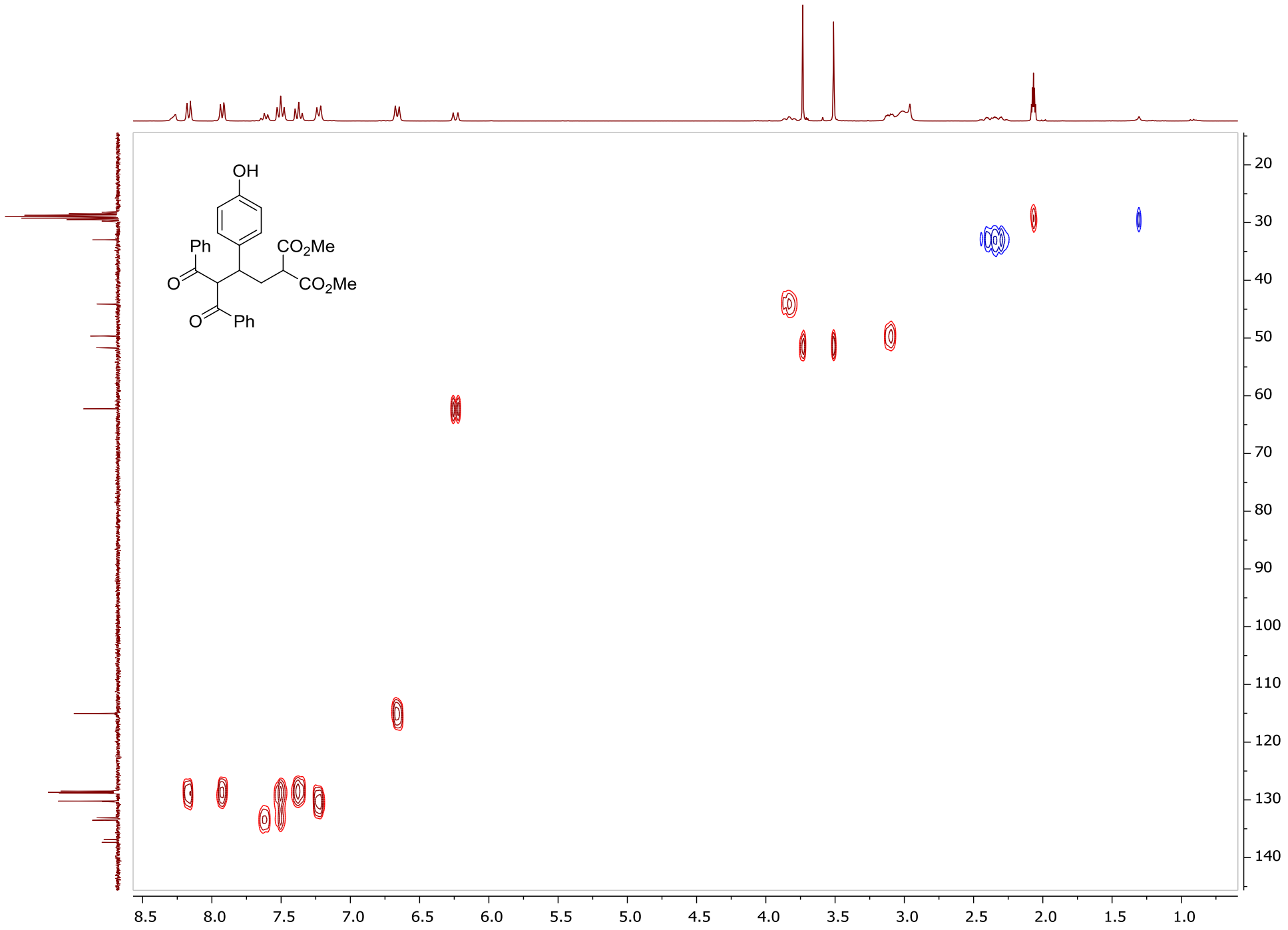
$^{13}$C DEPT (75 MHz, acetone-$d_6$)



$^{1}$H-$^{1}$H COSY

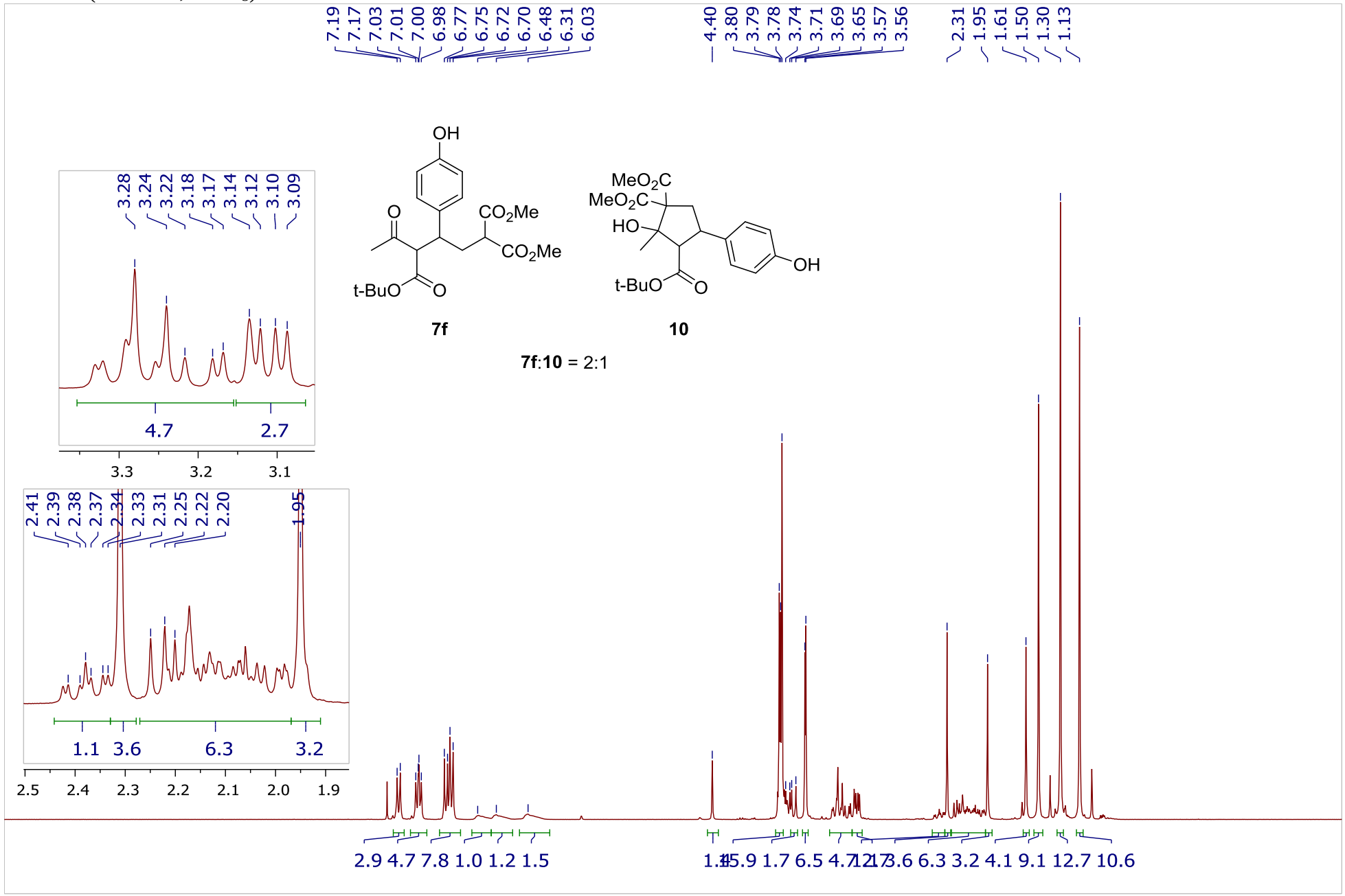

OH
Ph
CO2Me
O
CO2Me
O
Ph
0
1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

$^{1}$H-$^{13}$C HSQC

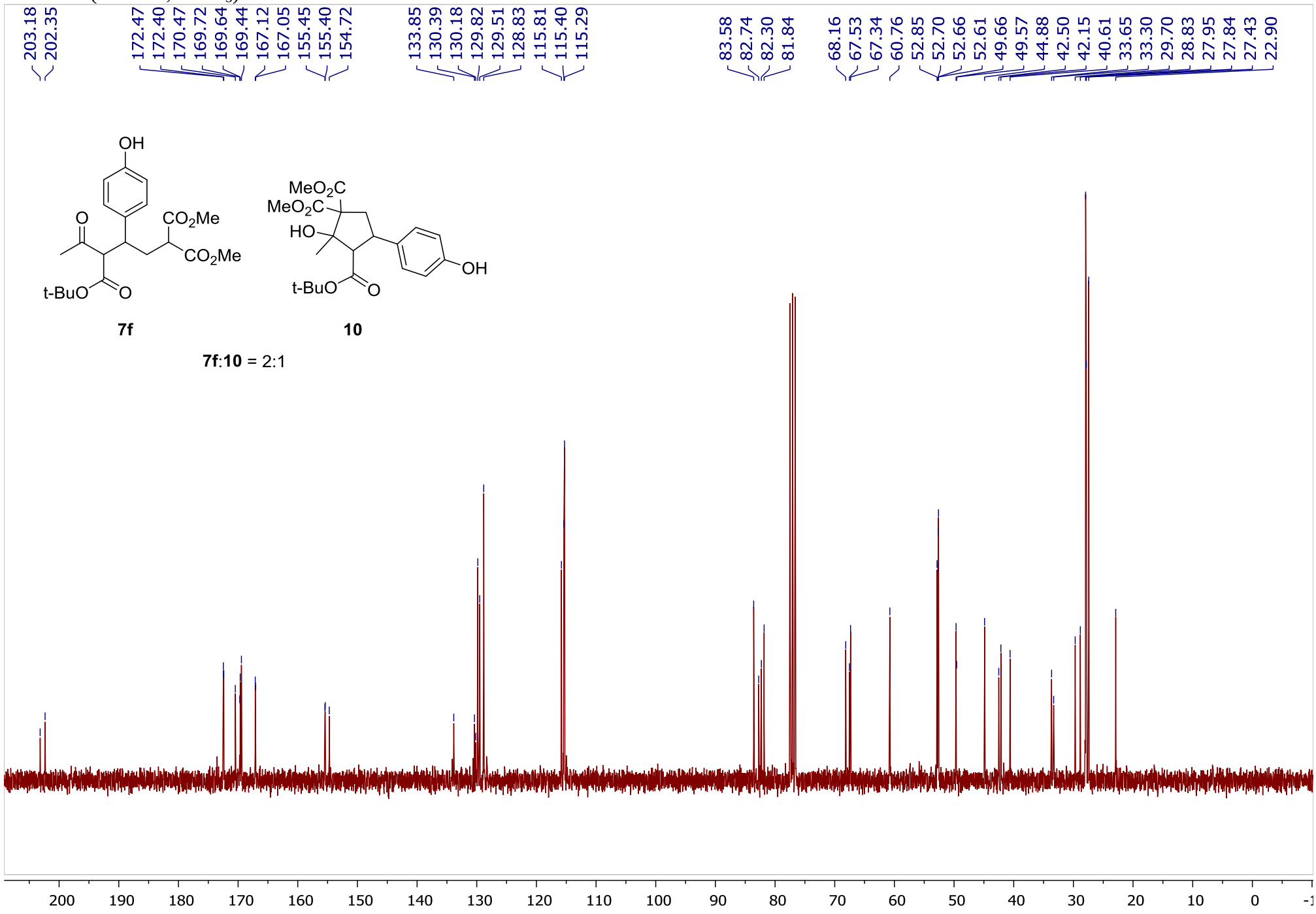

OH
Ph
CO2Me
O
CO2Me
O
Ph
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**4-tert-Butyl 1,1-dimethyl 3-(4-hydroxyphenyl)-5-oxohexane-1,1,4-tricarboxylate (7f) and 3-tert-butyl 1,1-dimethyl 2-hydroxy-4-(4-hydroxyphenyl)-2-methylcyclopentane-1,1,3-tricarboxylate (10)**, **7f** : **10** = 2 : 1

$^1$H NMR (300 MHz, $CDCl_3$)



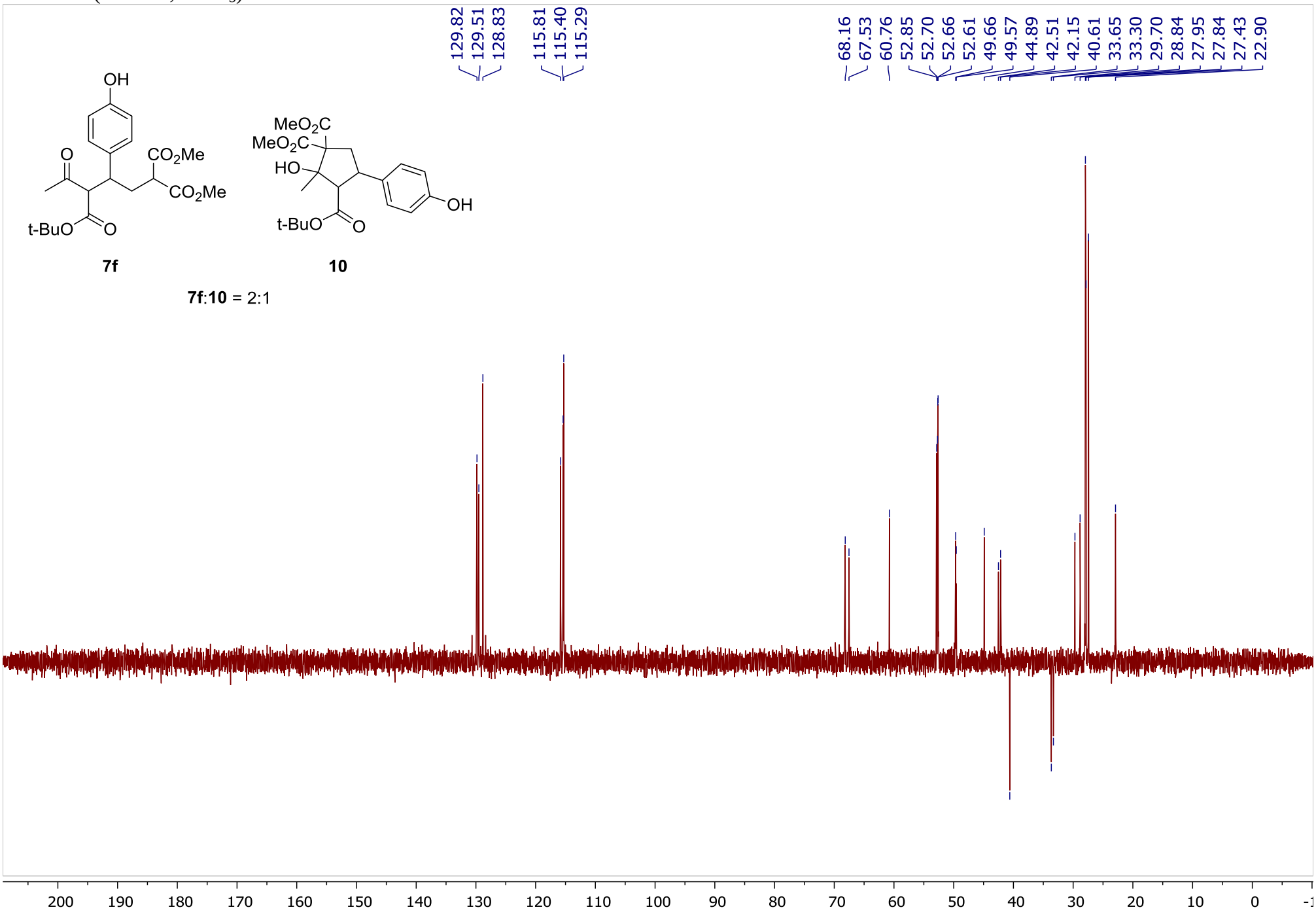
$^{13}$C NMR (75 MHz, $CDCl_3$)



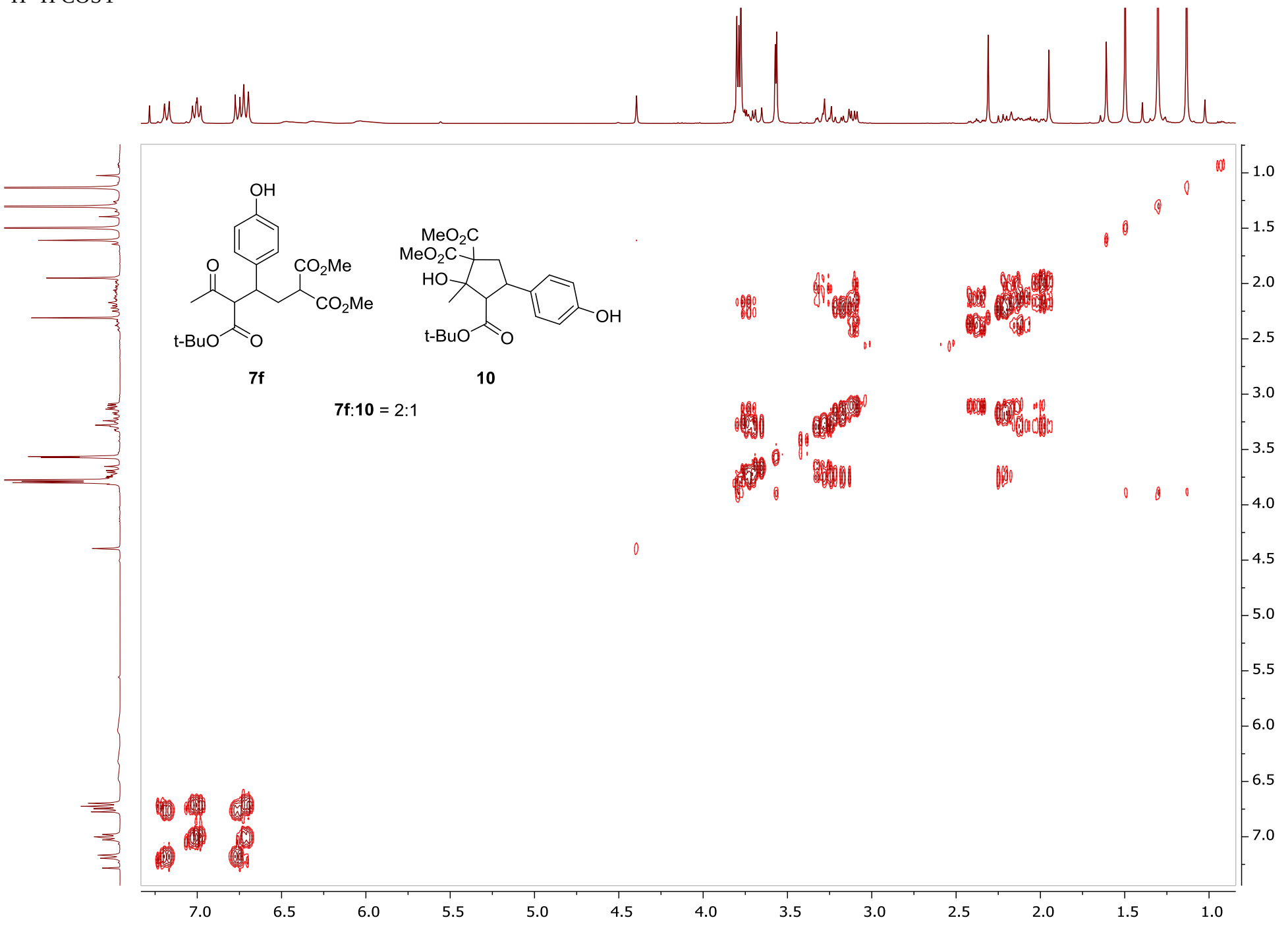

**7f** **10**

**7f**:**10** = 2:1

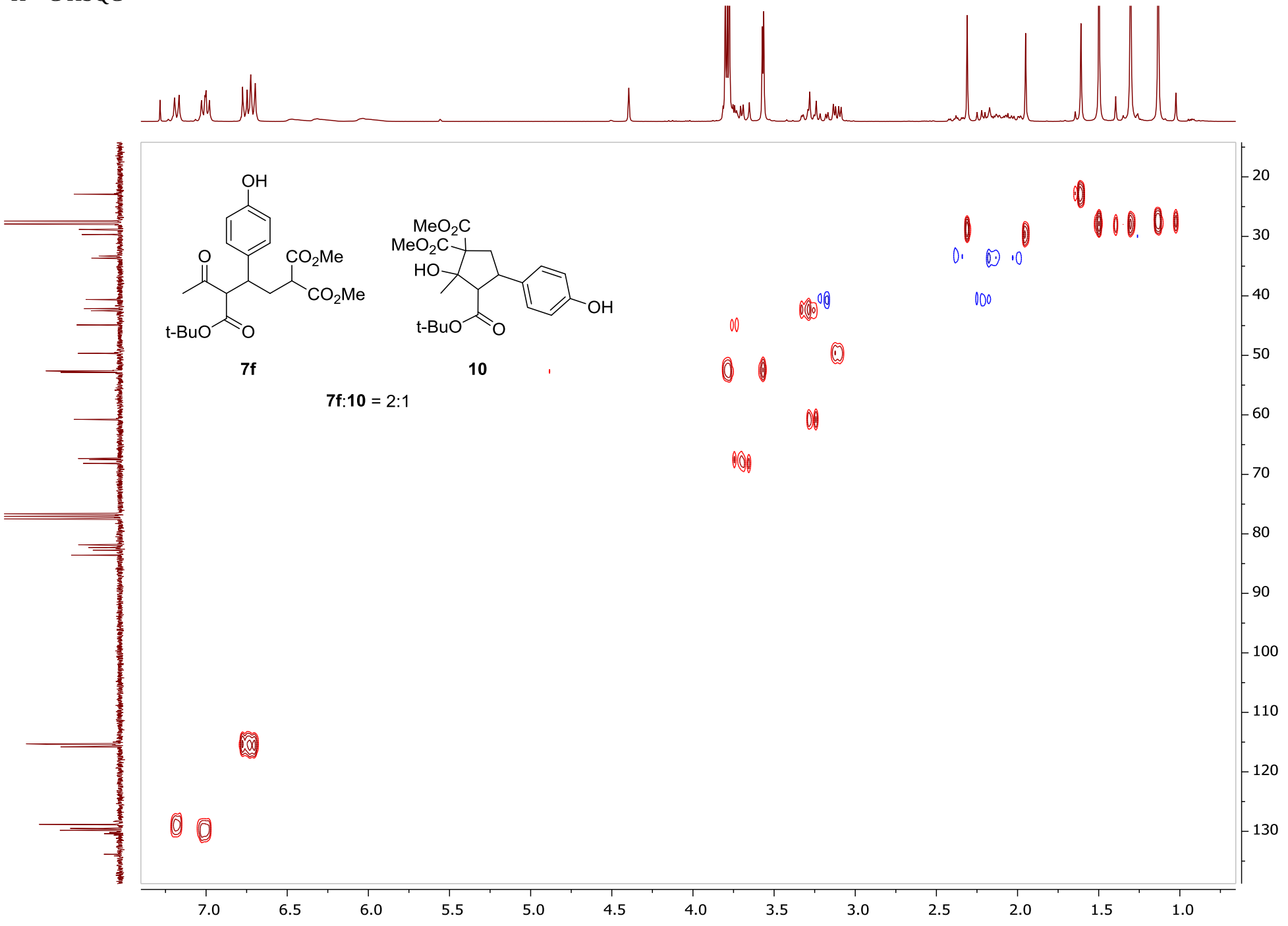
$^{13}$C DEPT (75 MHz, $CDCl_3$)



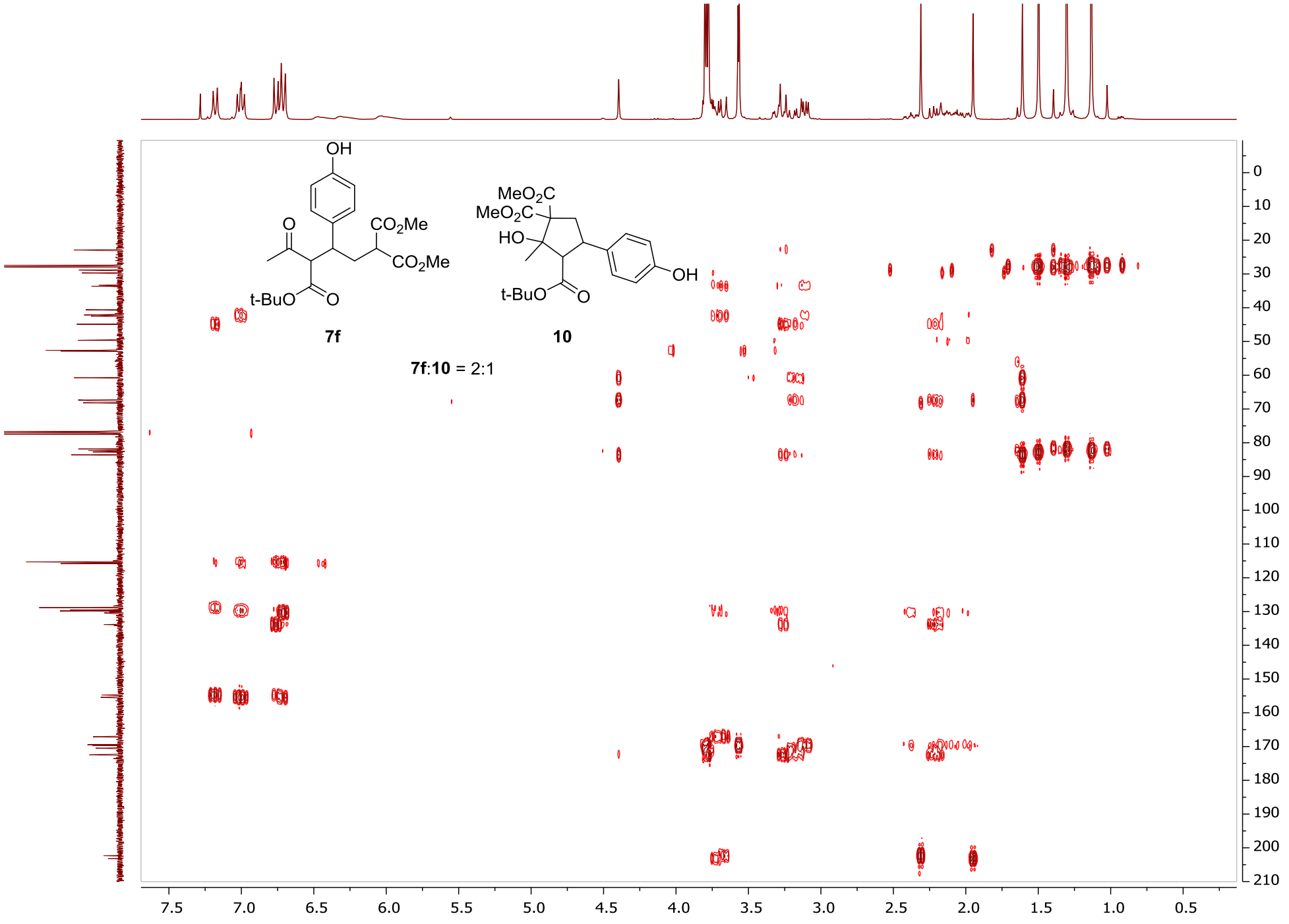
$^{1}$H-$^{1}$H COSY


OH
O
CO2Me
CO2Me
t-BuO
O
7f
MeO2C
MeO2C
HO
OH
t-BuO
O
10
7f:10 = 2:1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}$H-$^{13}$C HSQC

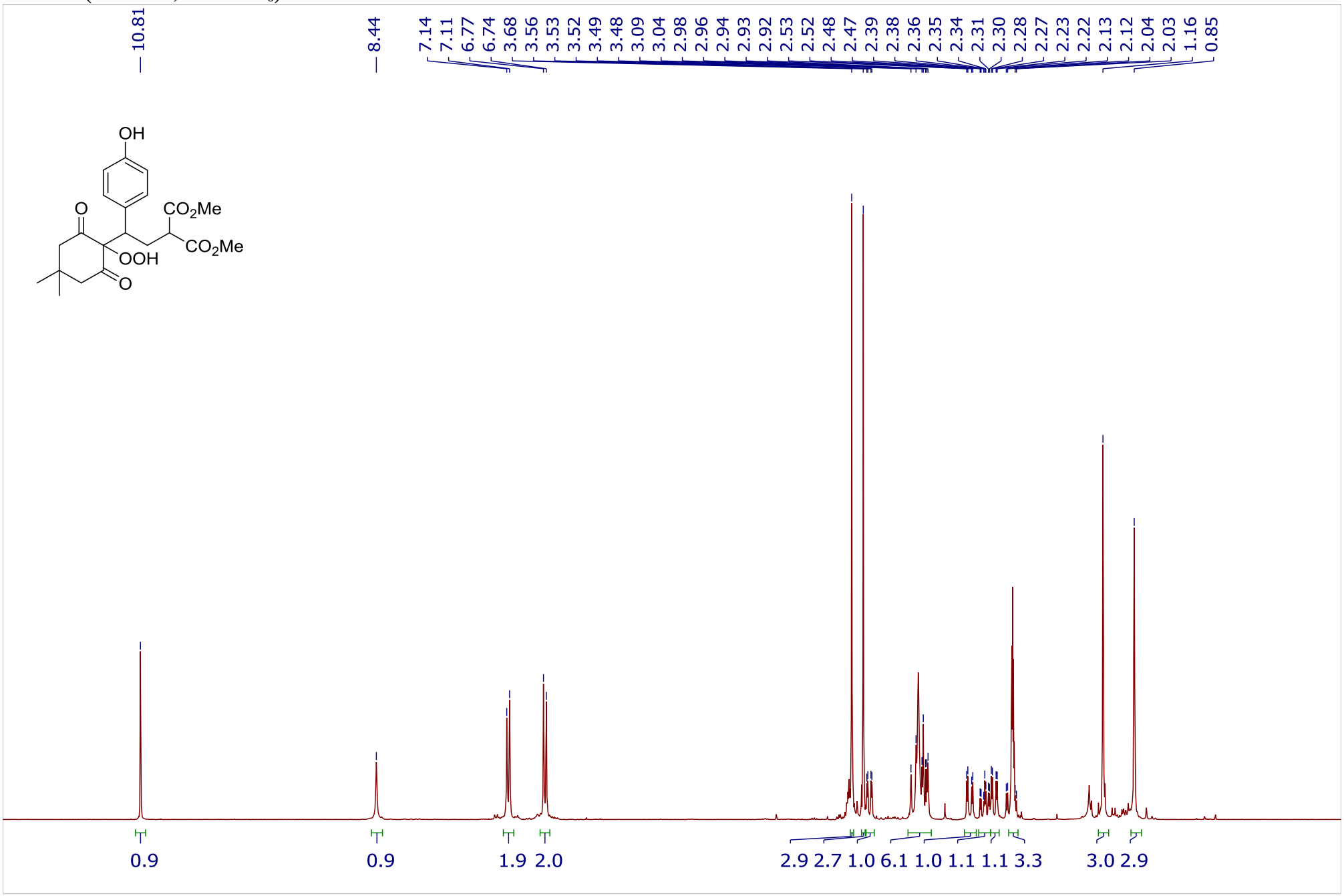

OH
O
CO2Me
CO2Me
t-BuO
O
7f
MeO2C
MeO2C
HO
OH
t-BuO
O
10
7f:10 = 2:1
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}$H-$^{13}$C HMBC

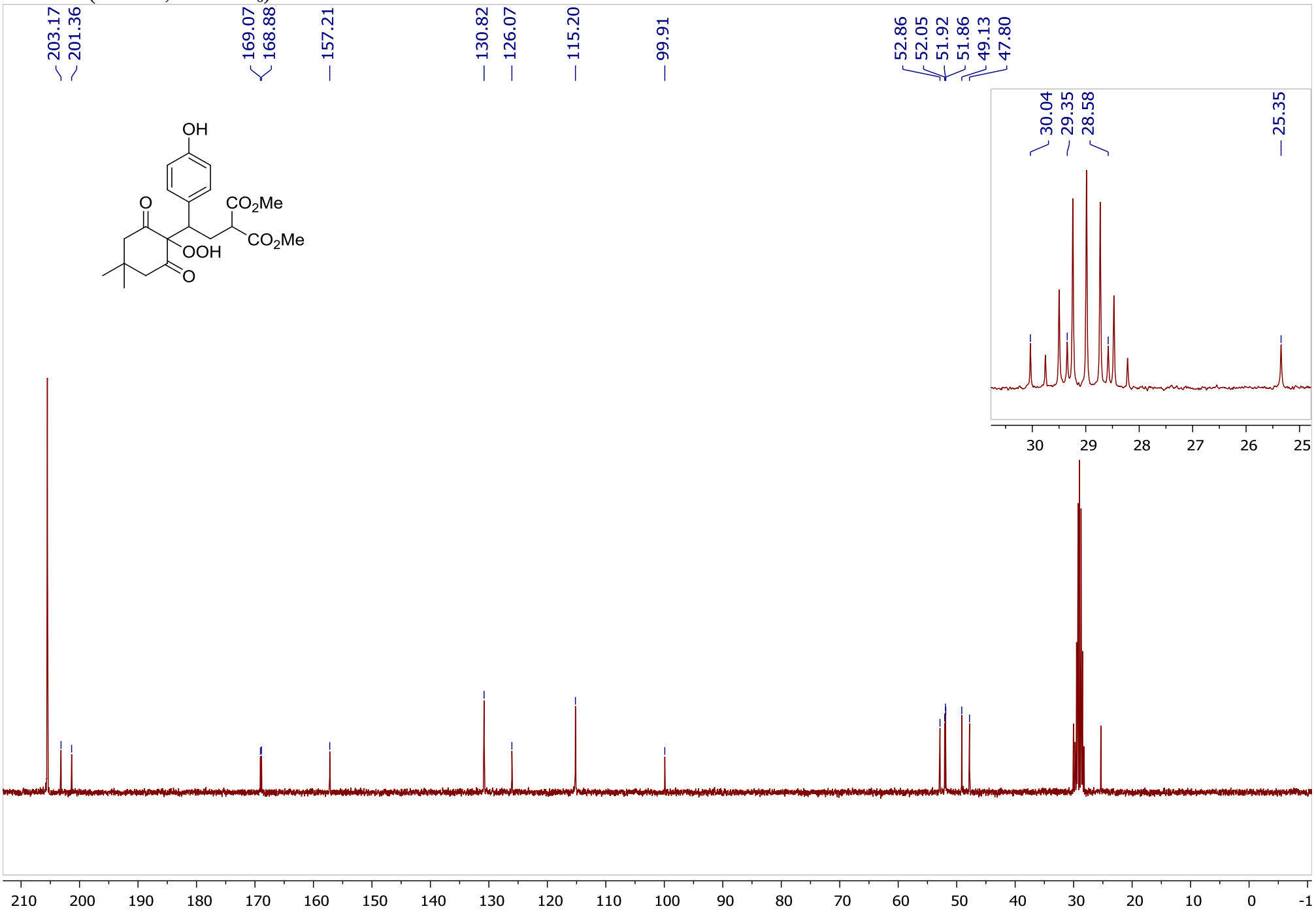

OH
O
CO2Me
CO2Me
t-BuO
O
7f
MeO2C
MeO2C
HO
OH
t-BuO
O
10
7f:10 = 2:1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Dimethyl 2-(2-(1-hydroperoxy-4,4-dimethyl-2,6-dioxocyclohexyl)-2-(4-hydroxyphenyl)ethyl)malonate (8)**

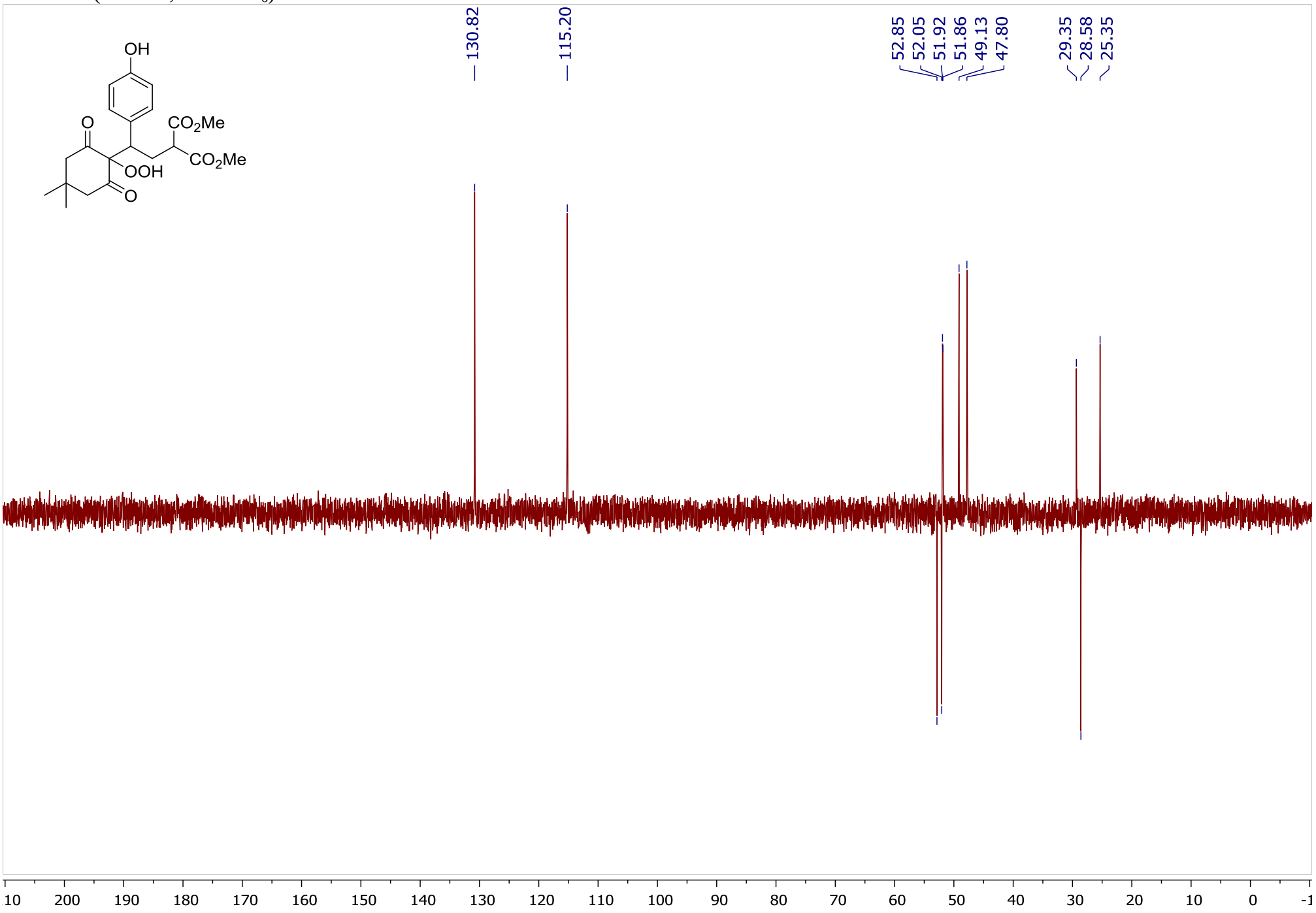
$^1$H NMR (300 MHz, acetone-$d_6$)



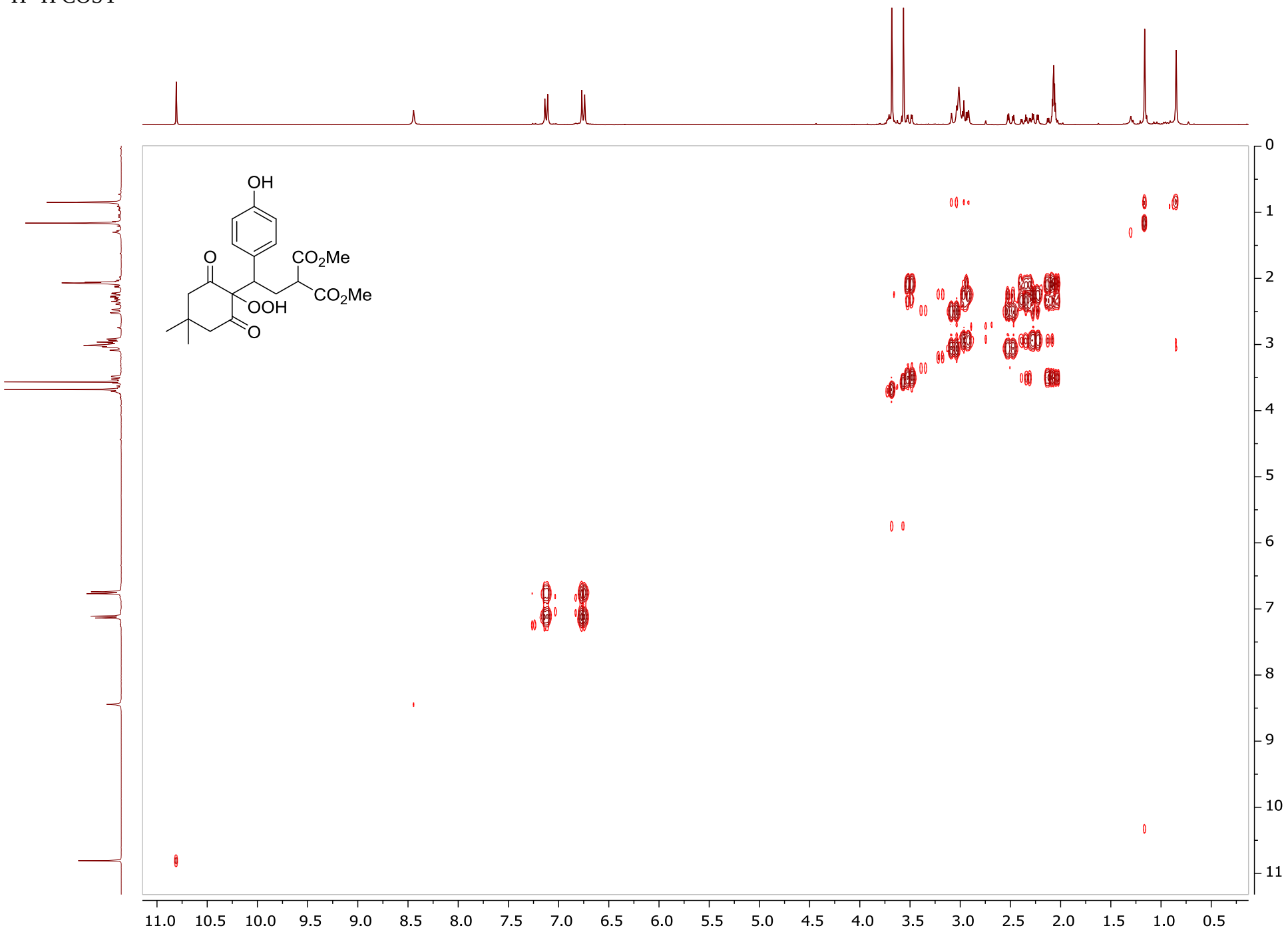
$^{13}$C NMR (75 MHz, acetone-$d_6$)



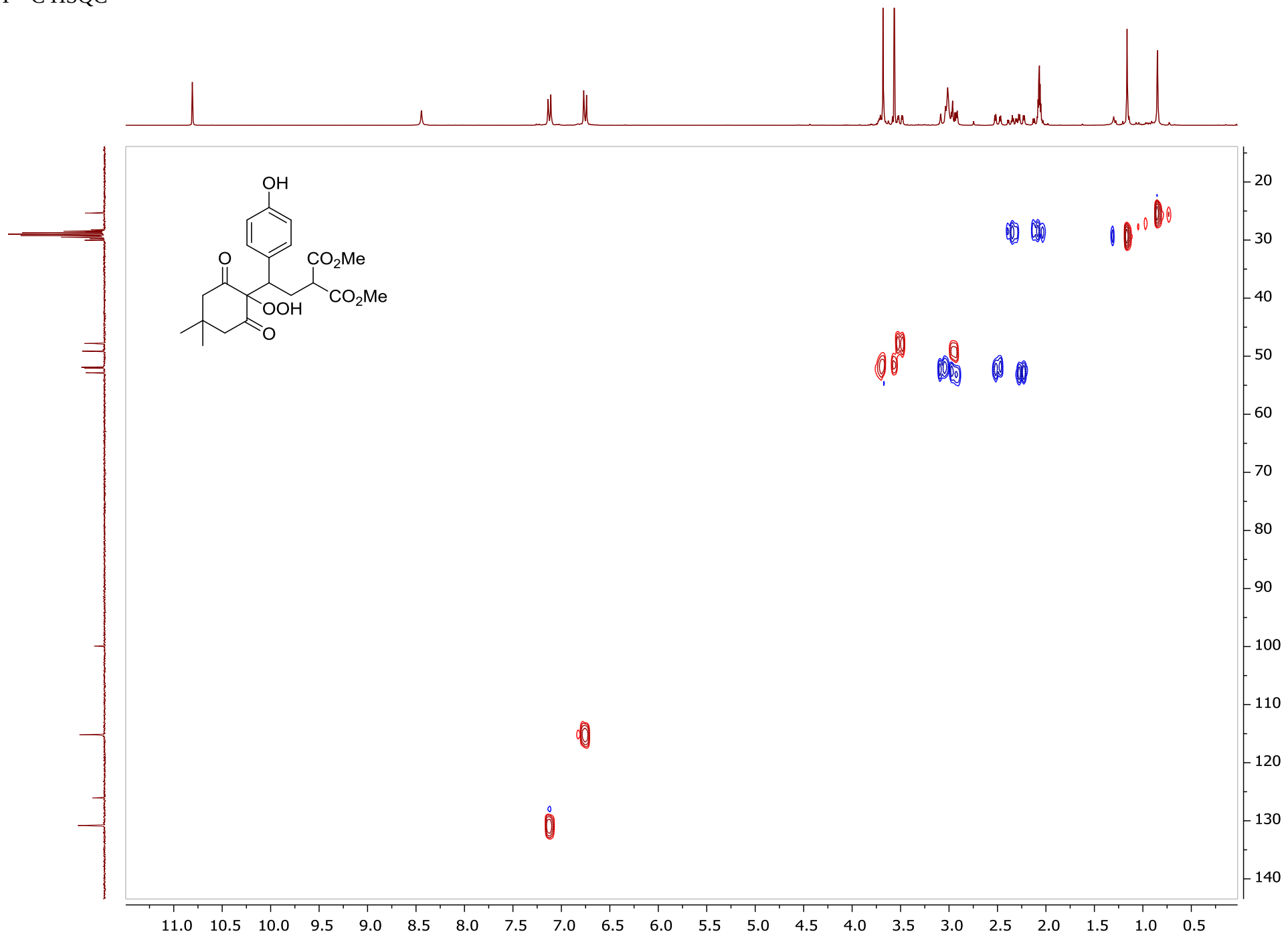
$^{13}$C DEPT (75 MHz, acetone-$d_6$)



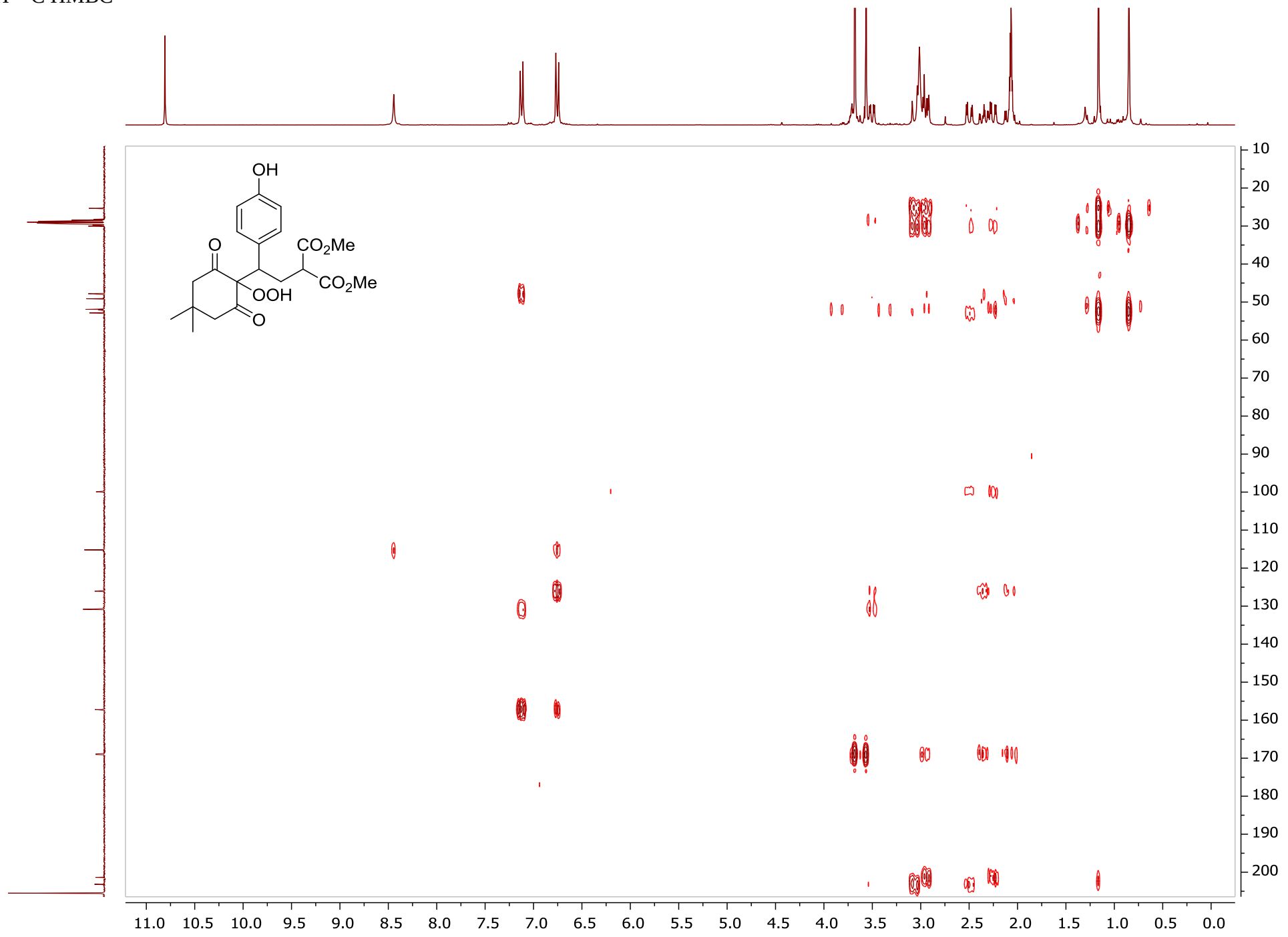
$^{1}$H-$^{1}$H COSY


OH
O
CO2Me
CO2Me
OOH
O
0
1
2
3
4
5
6
7
8
9
10
11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC

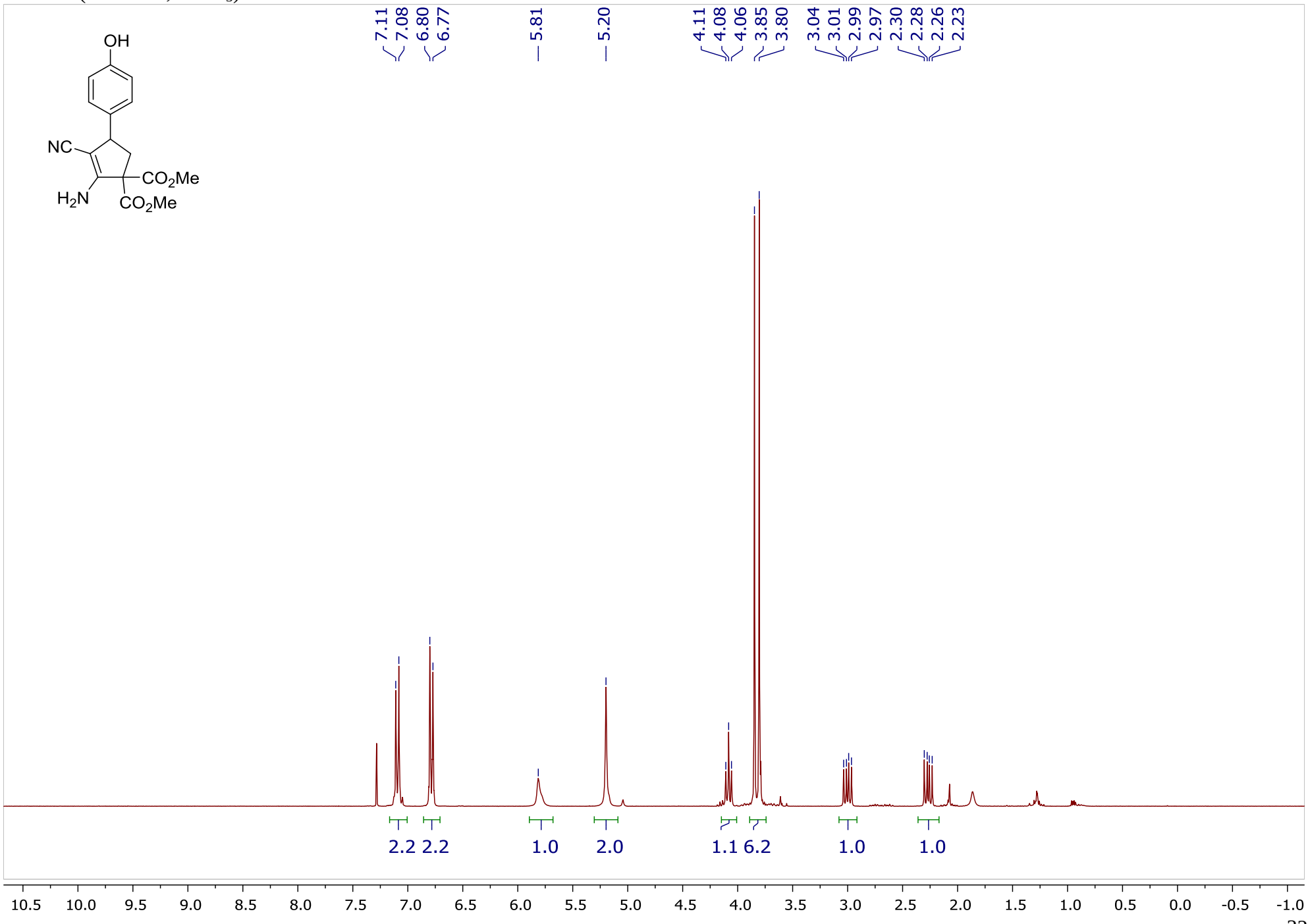

OH
O
CO2Me
CO2Me
OOH
O
20
30
40
50
60
70
80
90
100
110
120
130
140
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HMBC

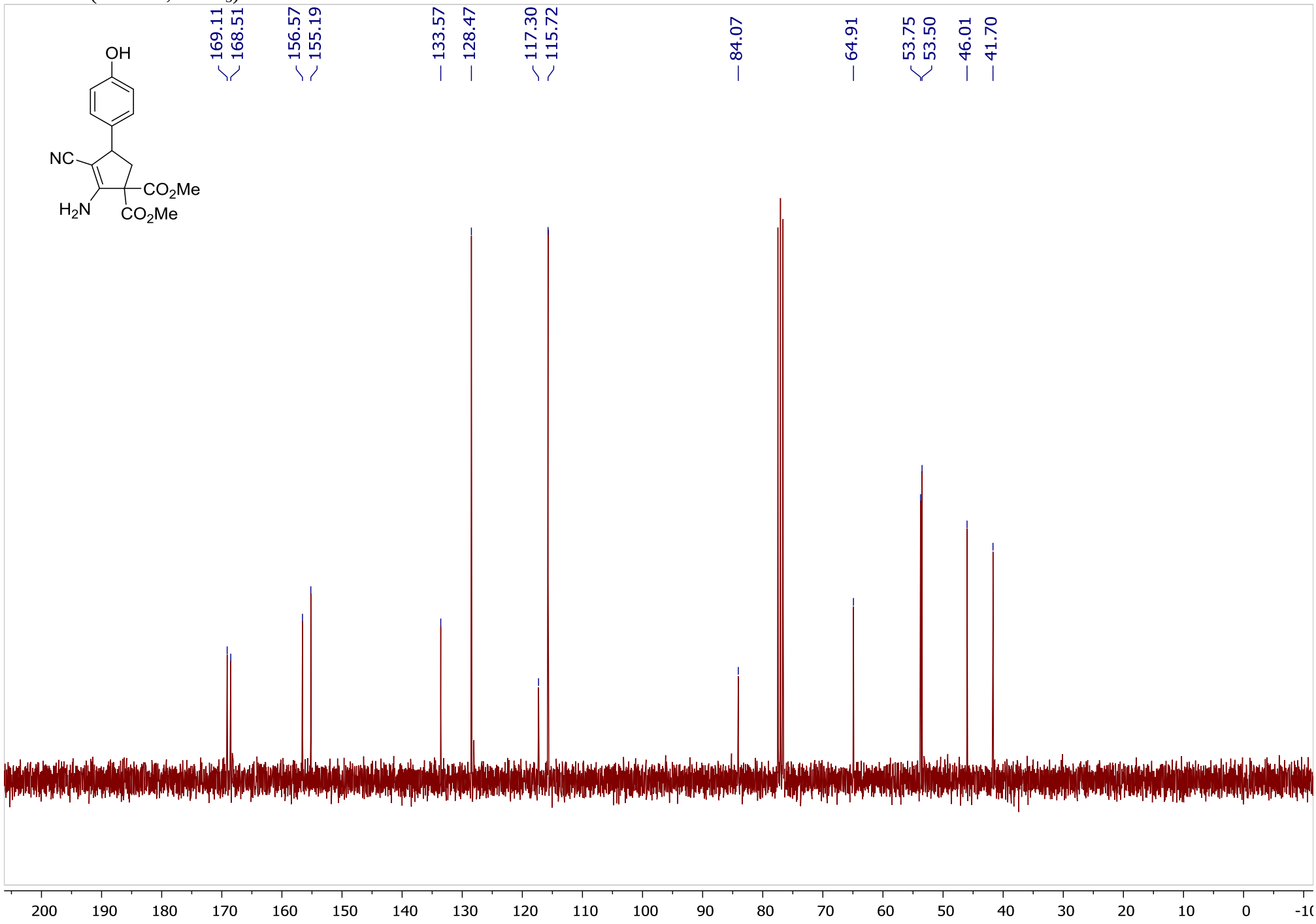

OH
O
CO2Me
CO2Me
OOH
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**Dimethyl 2-amino-3-cyano-4-(4-hydroxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (9)**

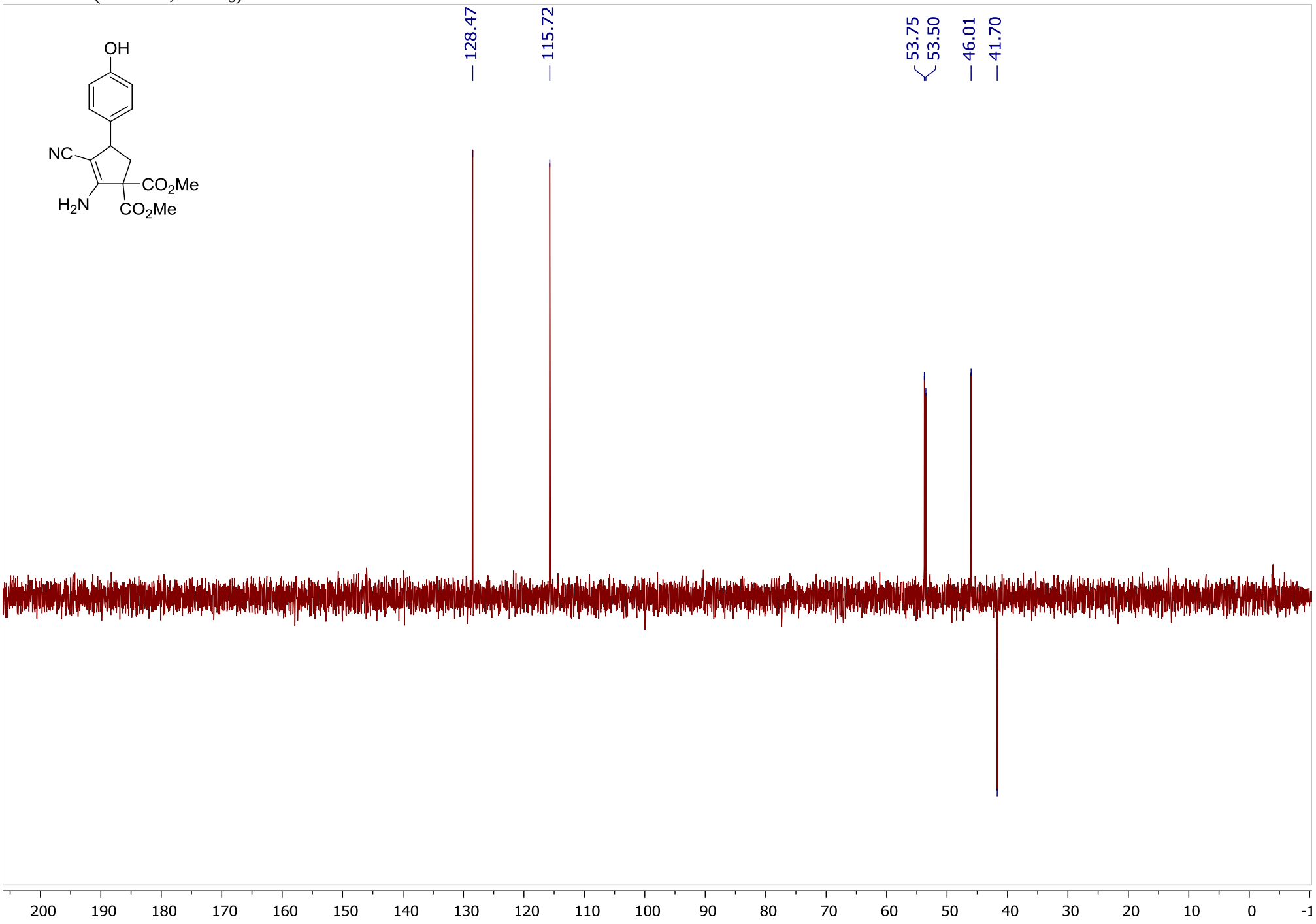
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)

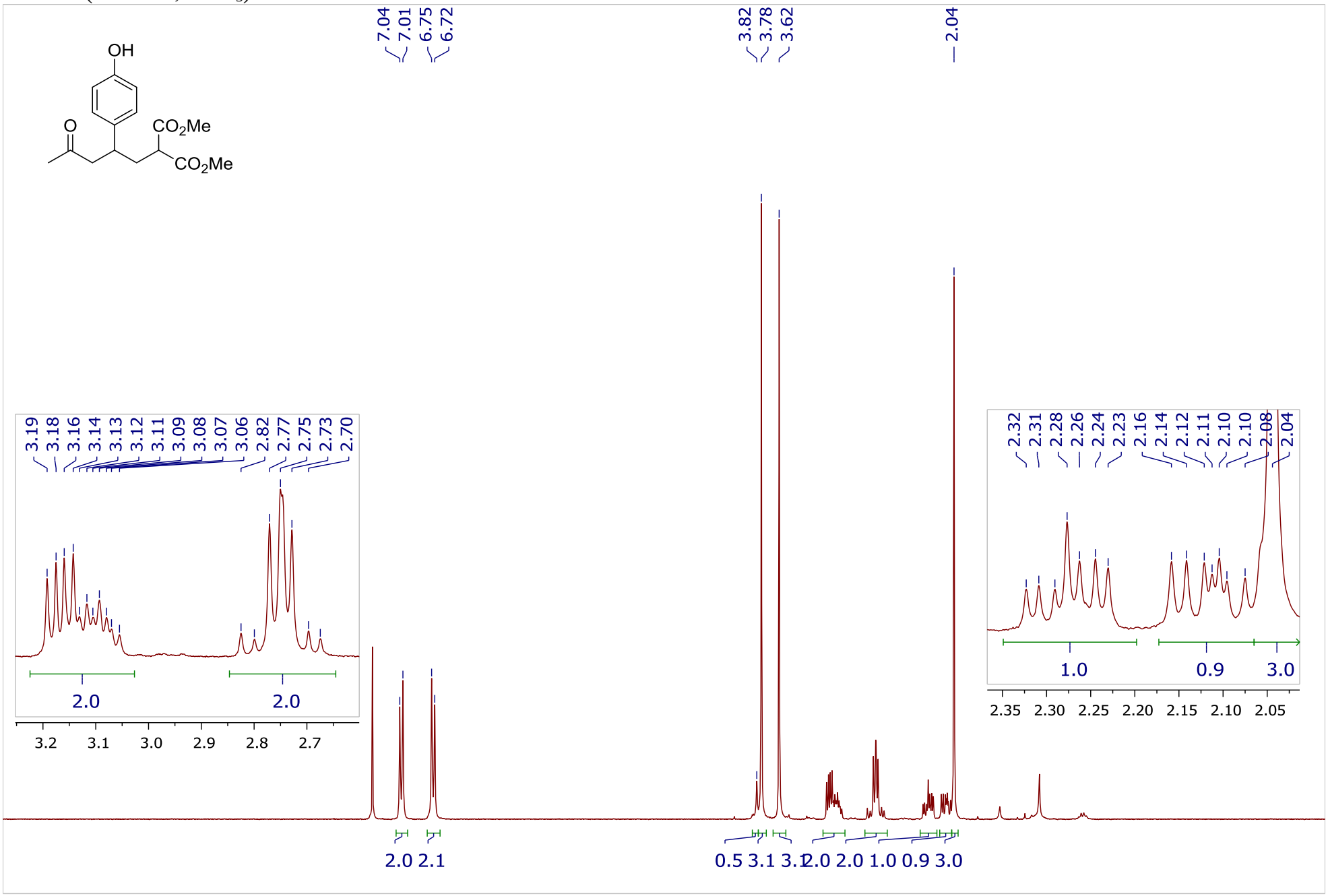


$^{13}$C DEPT (75 MHz, $CDCl_3$)

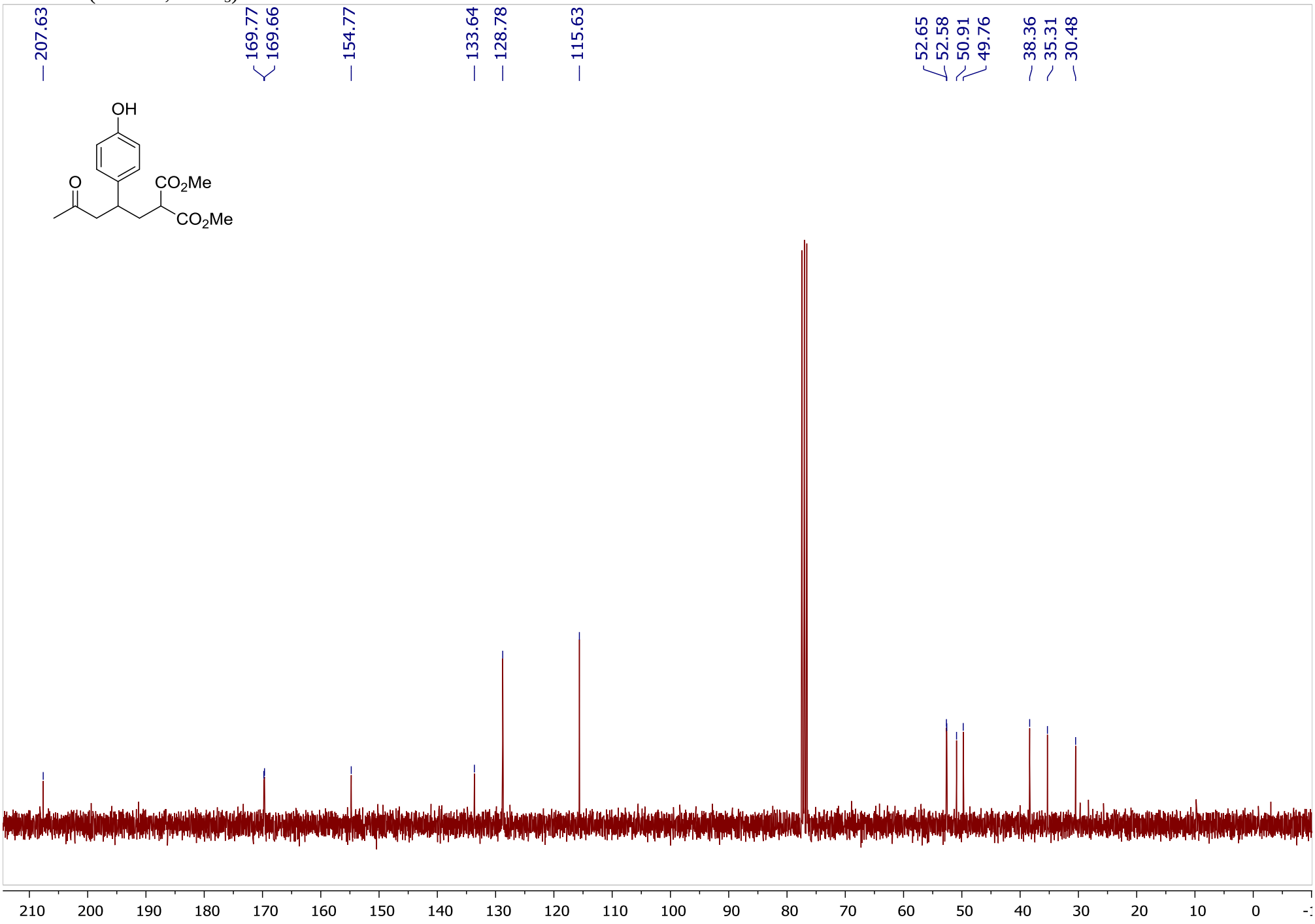


**Dimethyl 2-(2-(4-hydroxyphenyl)-4-oxopentyl)malonate (11)**

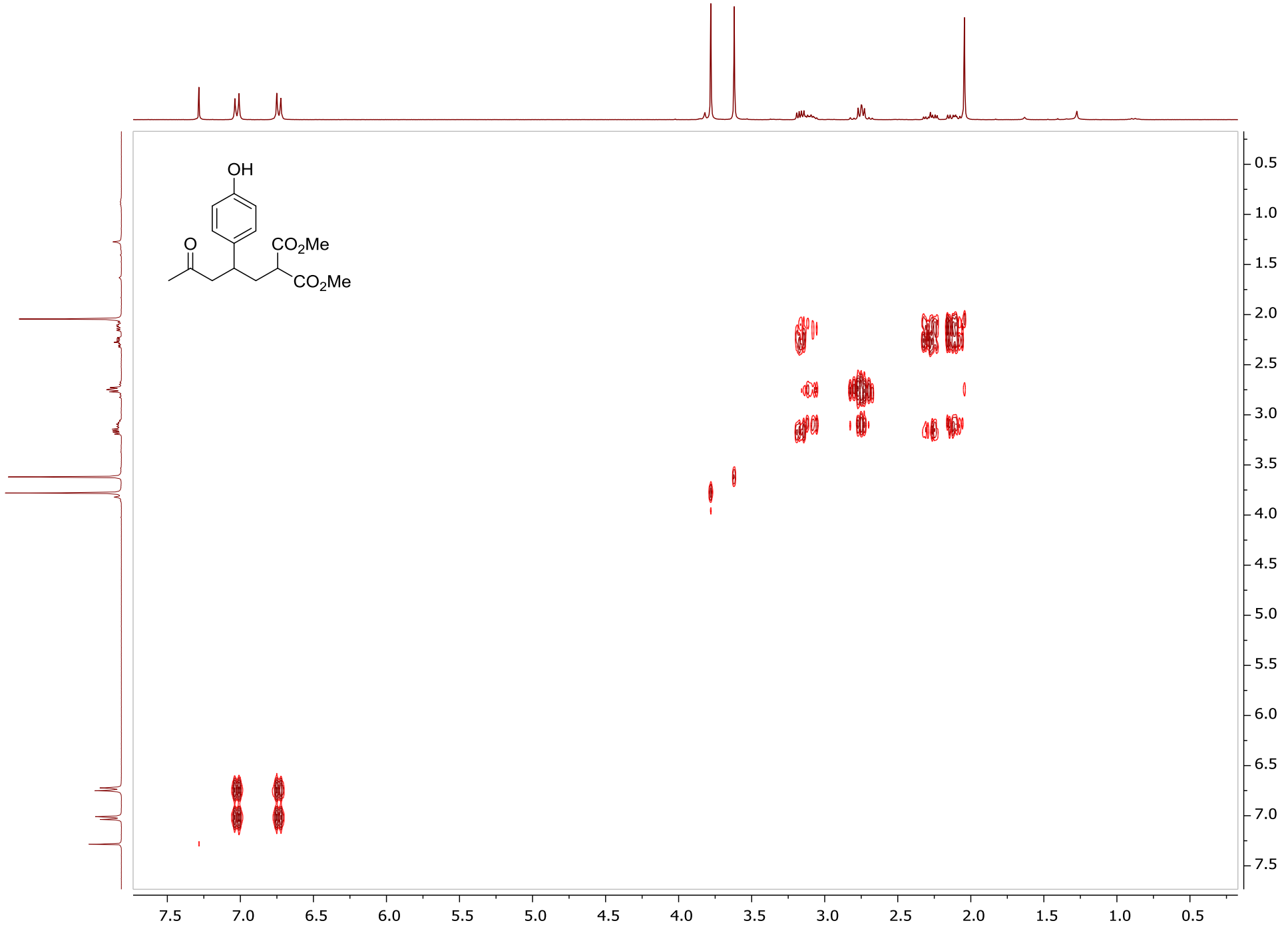
$^1$H NMR (300 MHz, $CDCl_3$)



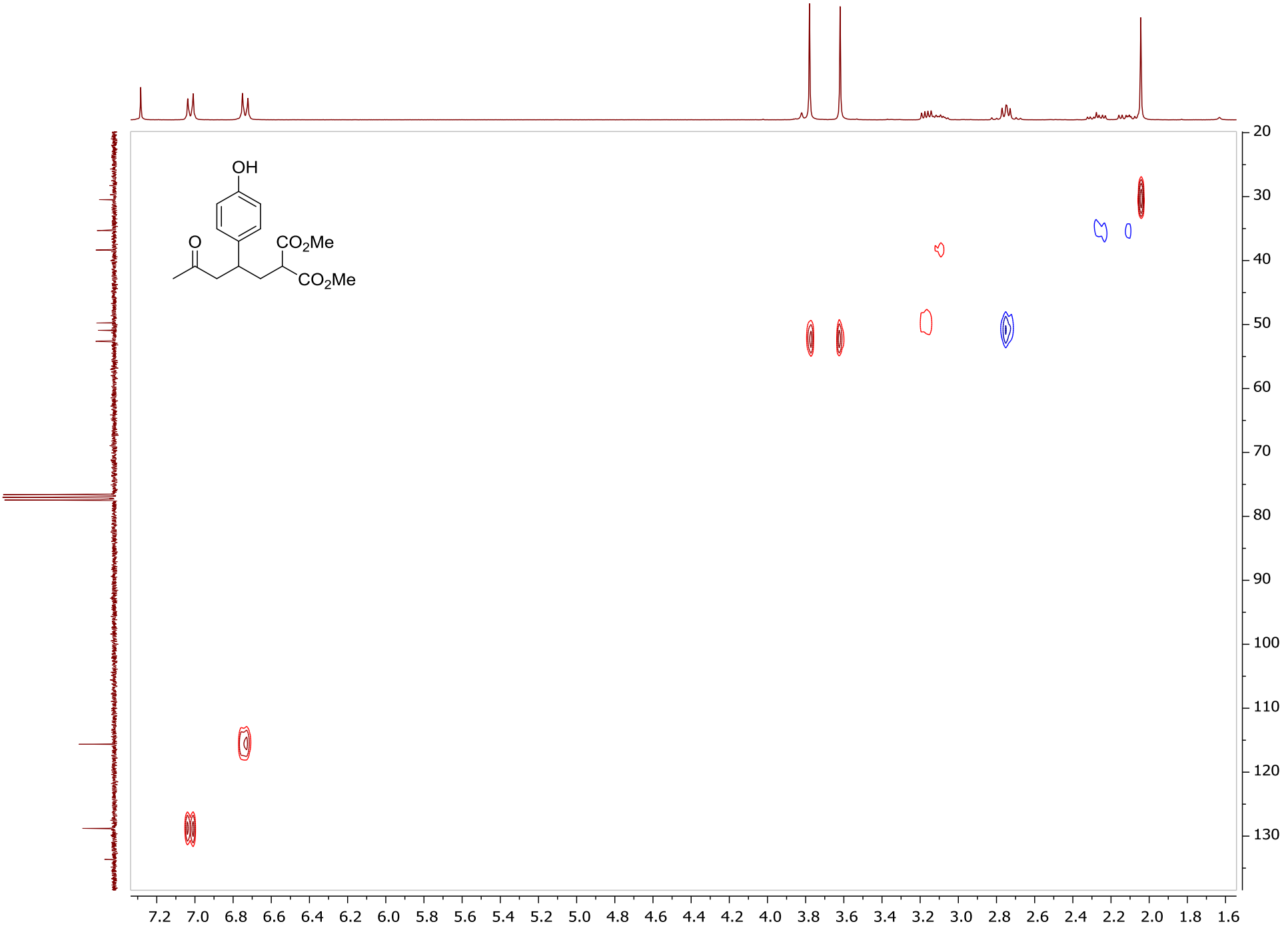
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY

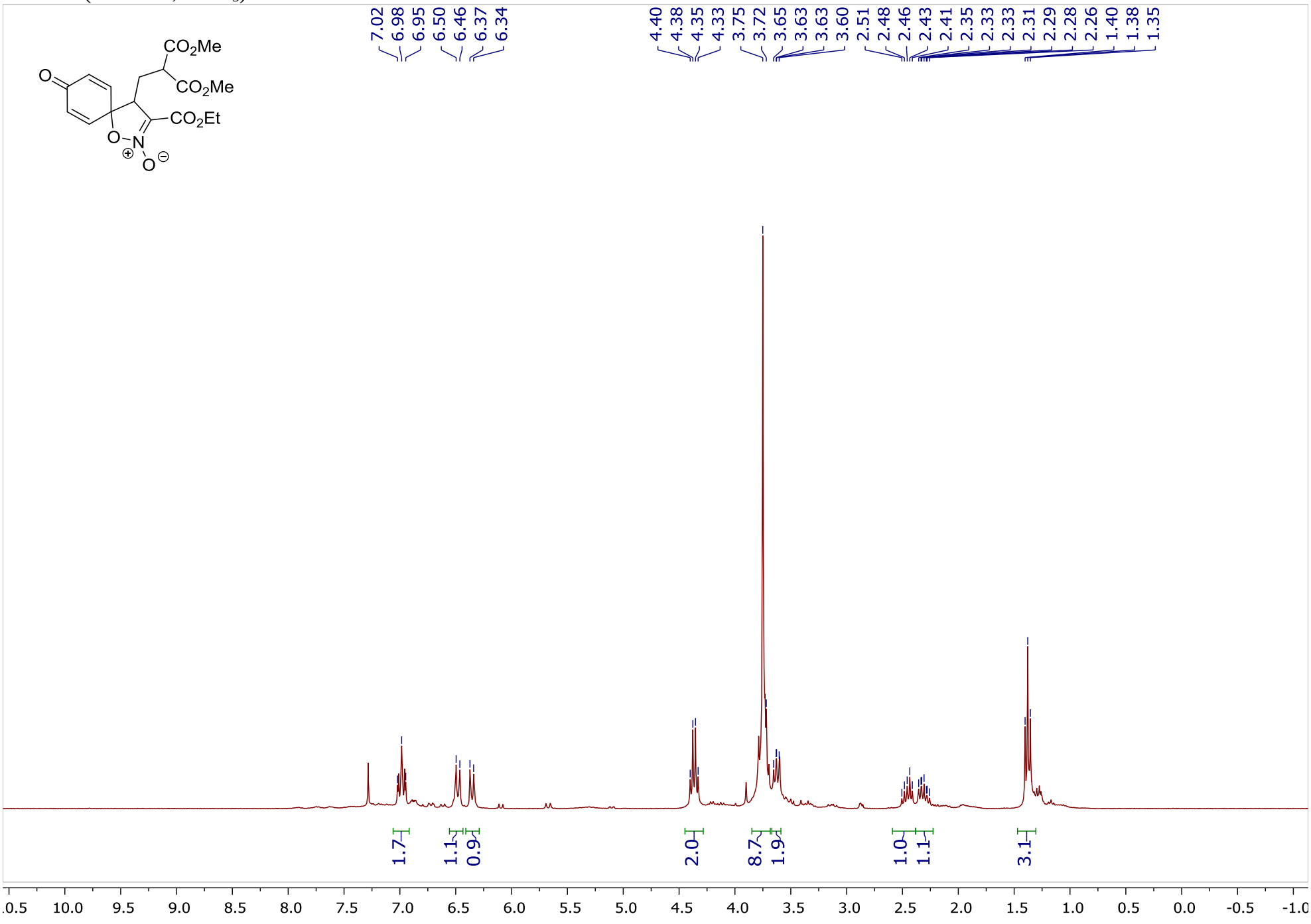

OH
O
CO2Me
CO2Me
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC

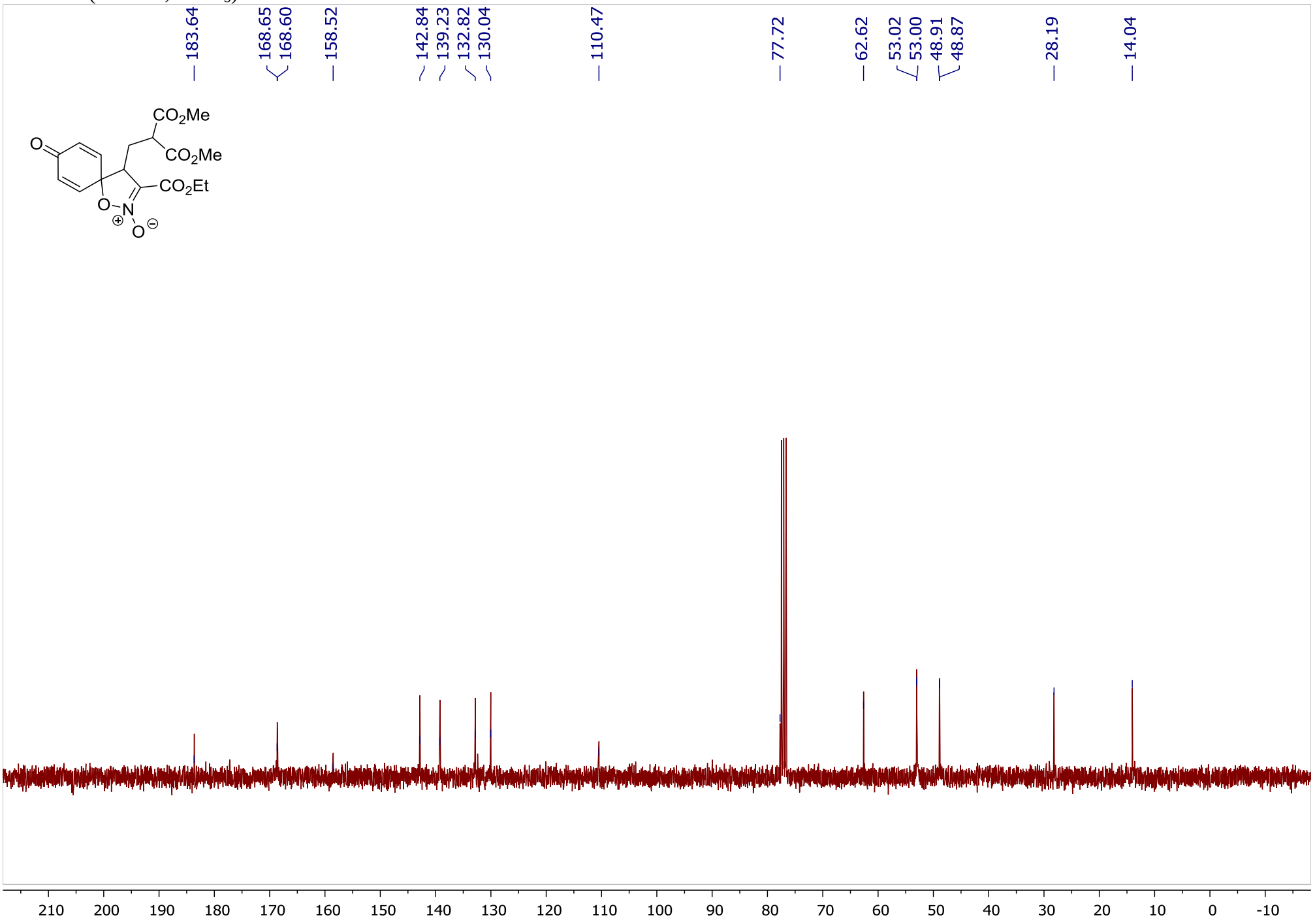

OH
O
CO2Me
CO2Me
20
30
40
50
60
70
80
90
100
110
120
130
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

**3-(Ethoxycarbonyl)-4-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl)-8-oxo-1-oxa-2-azaspiro[4.5]deca-2,6,9-triene 2-oxide (13)**

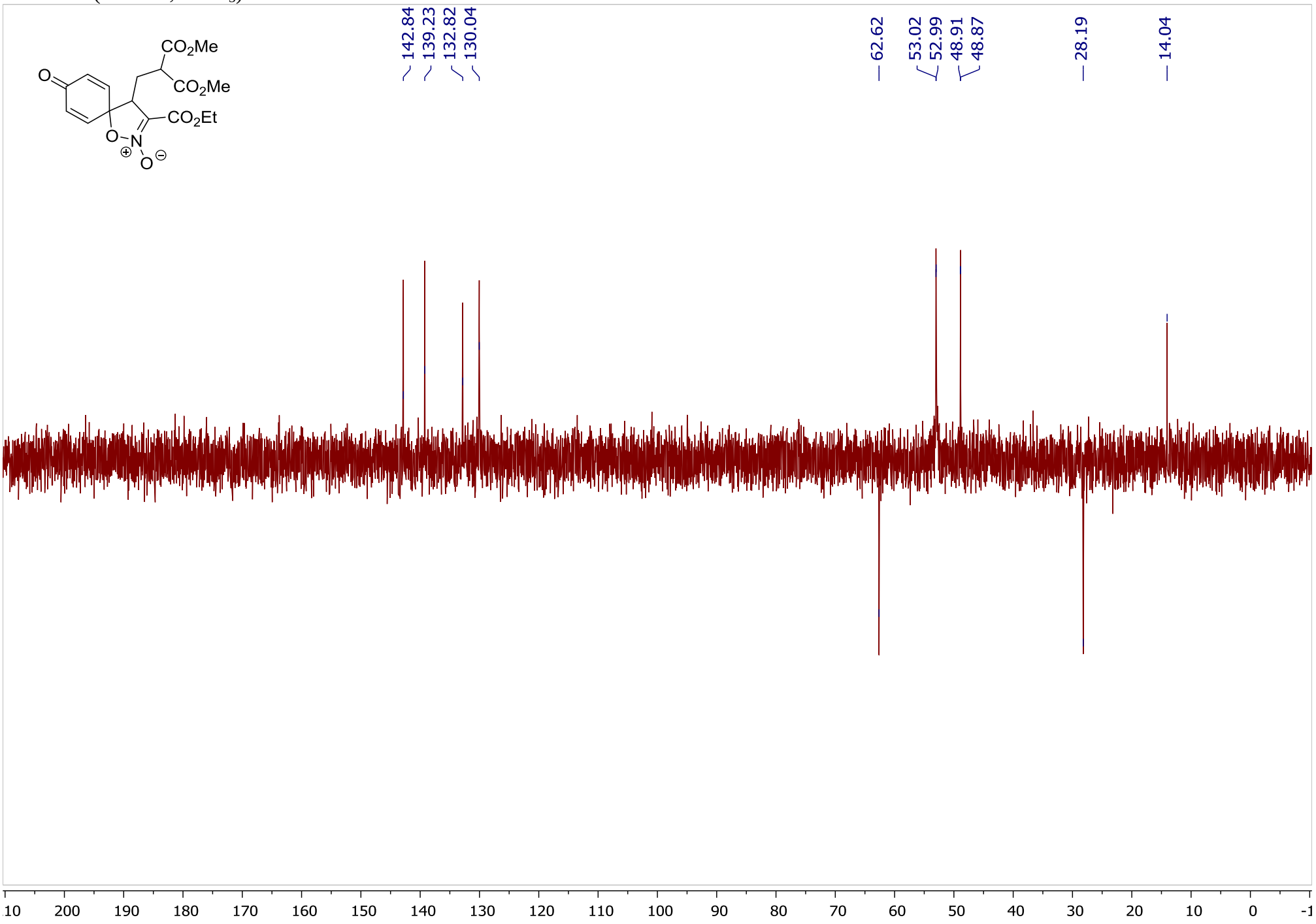
$^1$H NMR (300 MHz, $CDCl_3$)



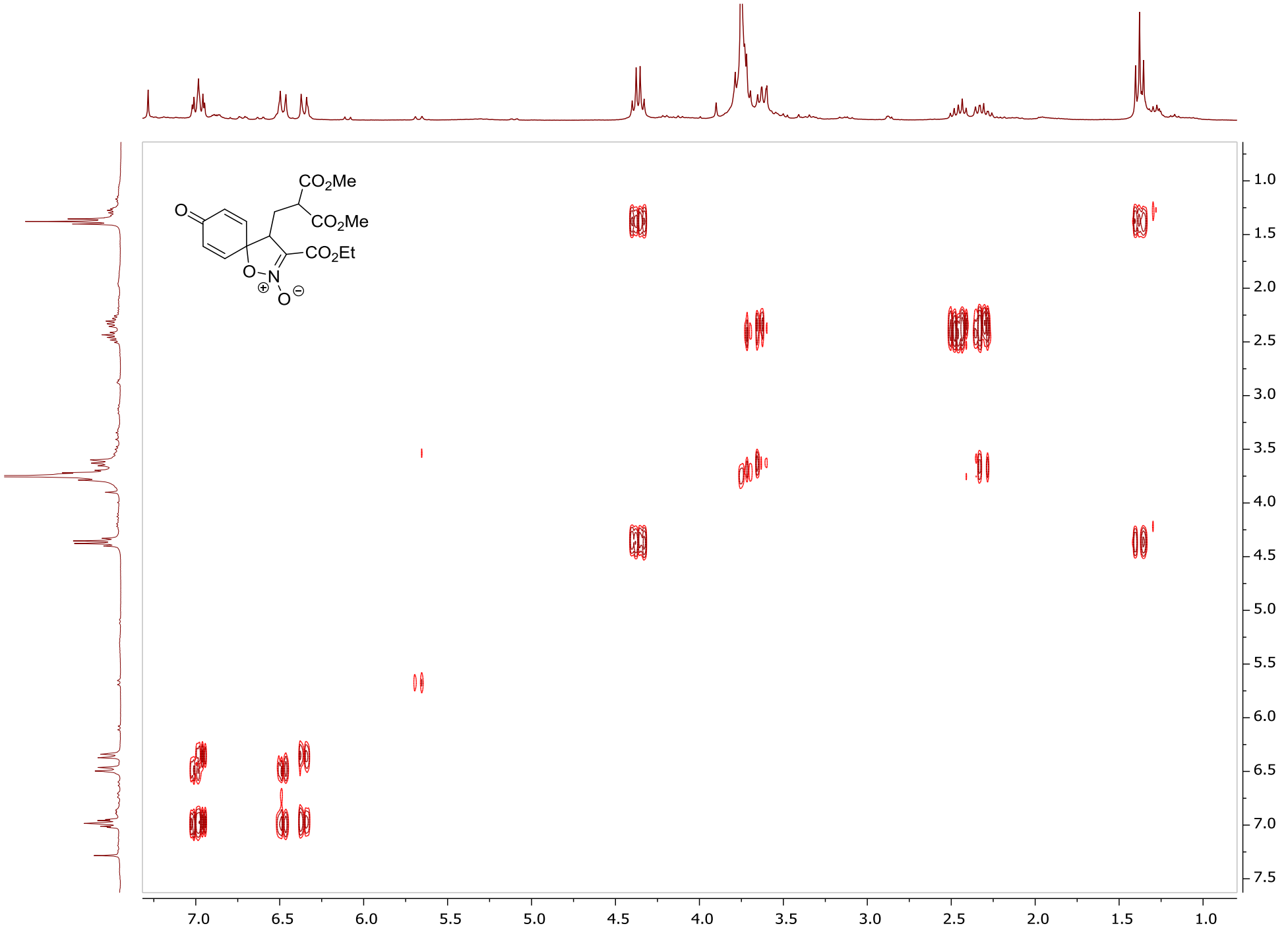
$^{13}$C NMR (75 MHz, $CDCl_3$)



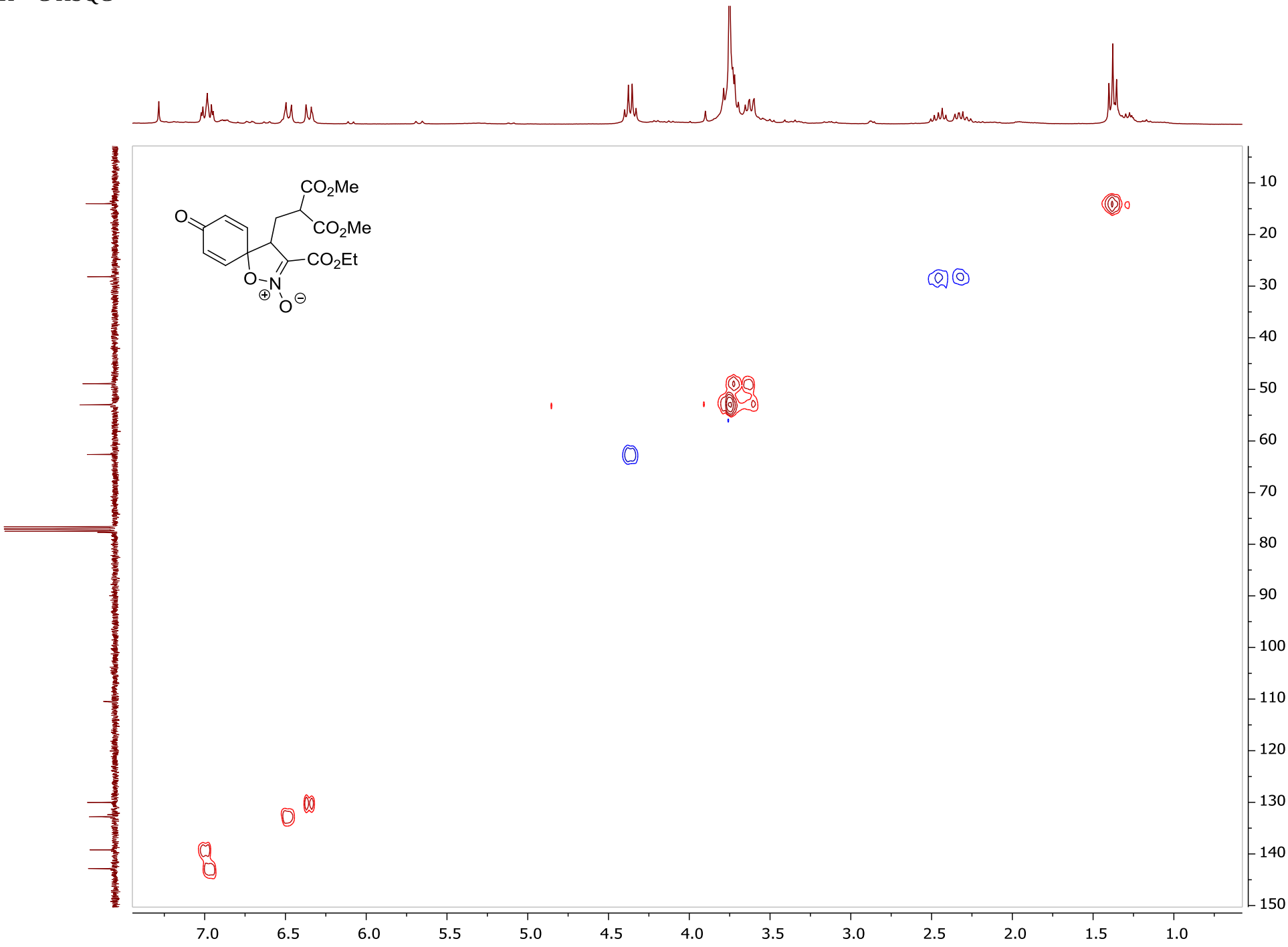
$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY

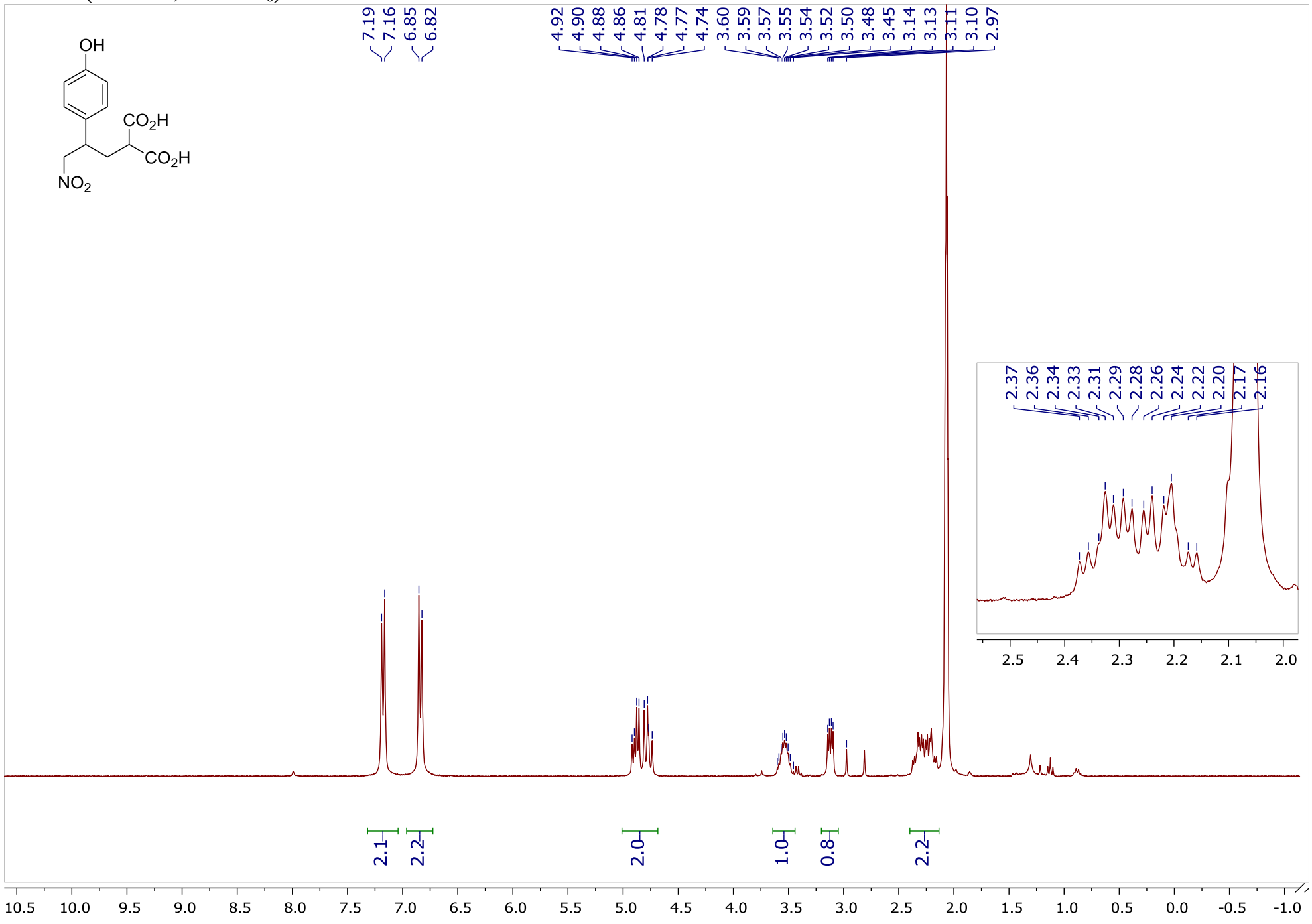

CO2Me
CO2Me
CO2Et
O
O
N
O
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HSQC

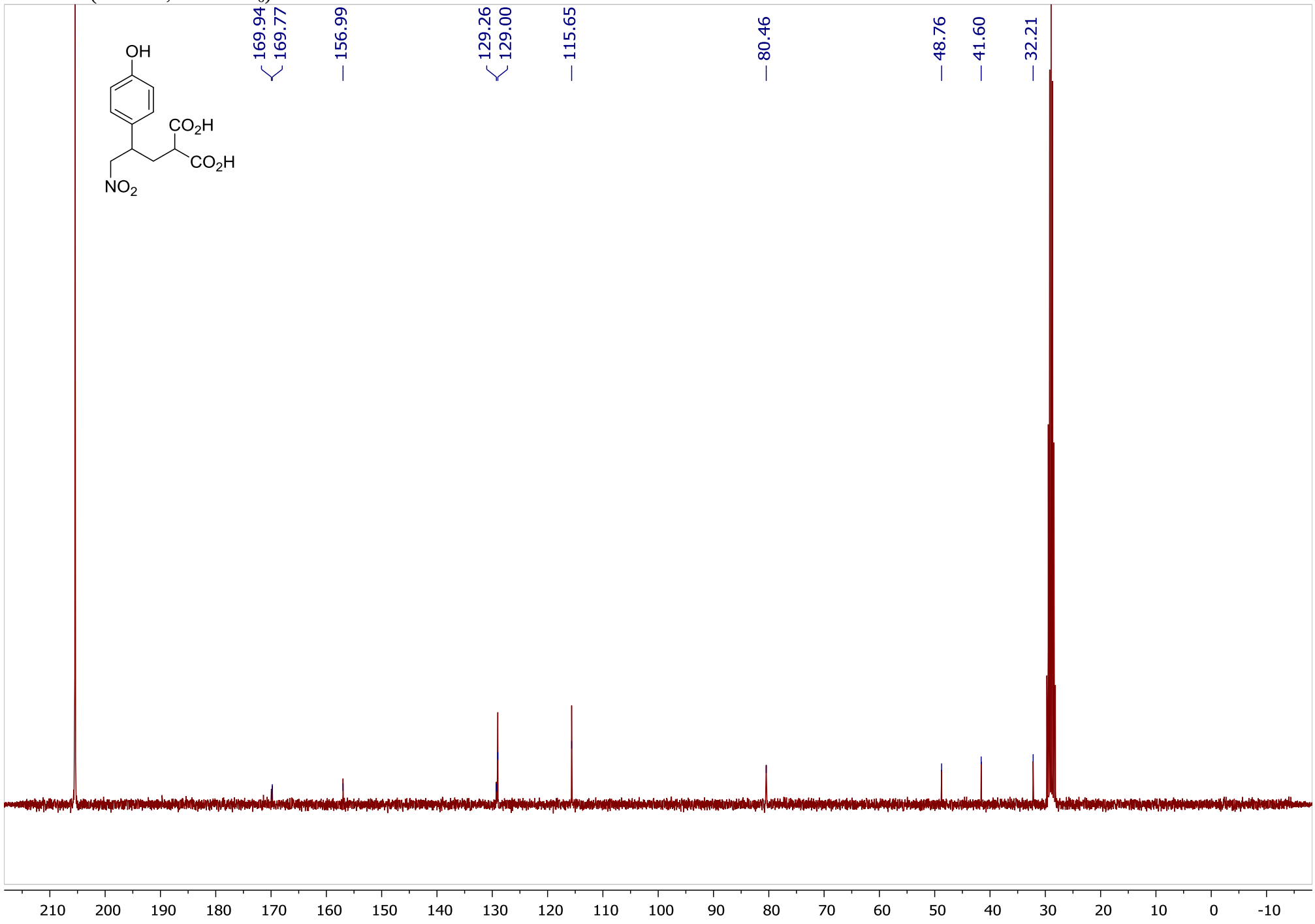

CO2Me
CO2Me
CO2Et
O
O
N
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**2-(2-(4-Hydroxyphenyl)-3-nitropropyl)malonic acid (14)**

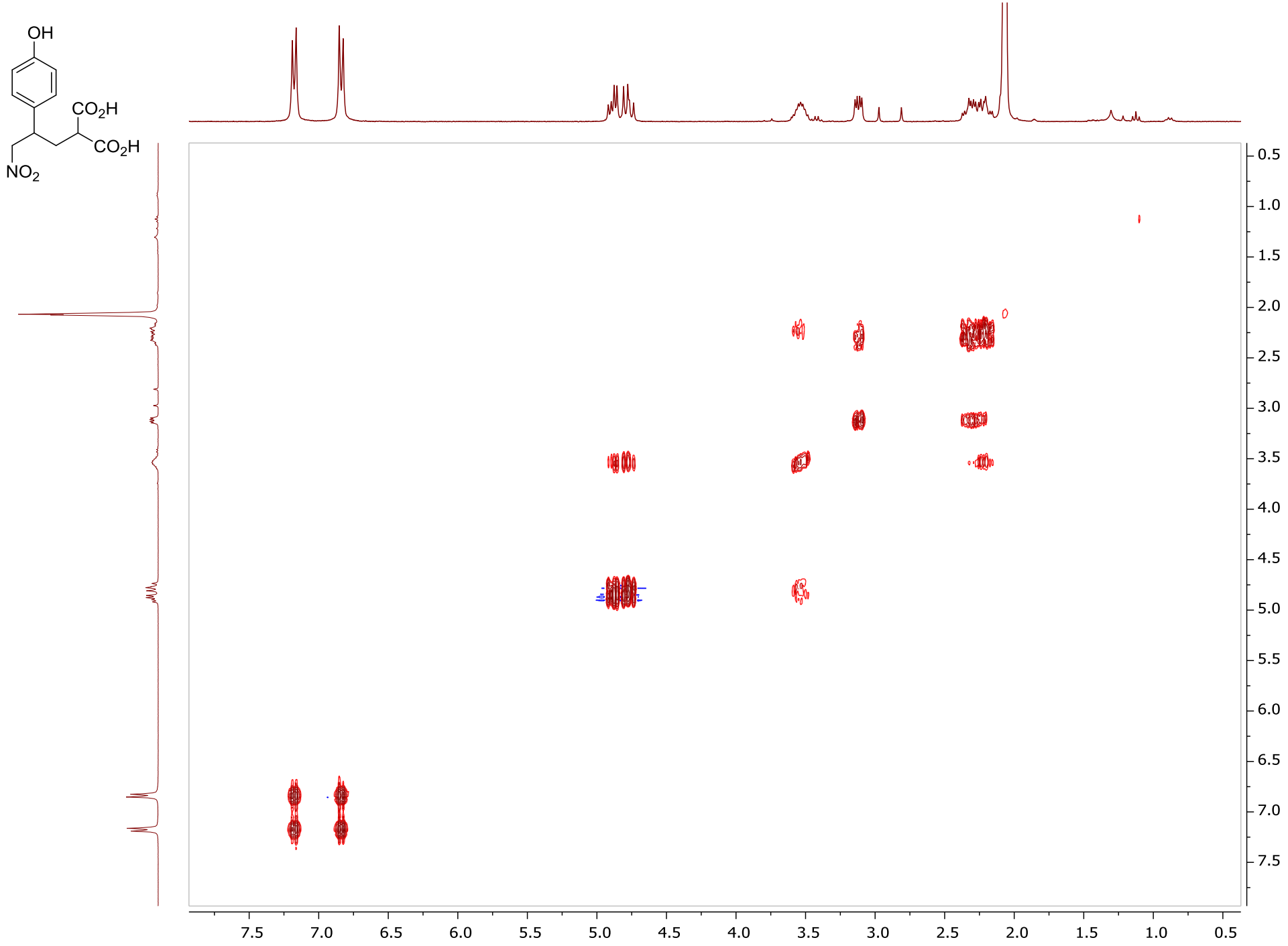
$^1$H NMR (300 MHz, acetone-$d_6$)



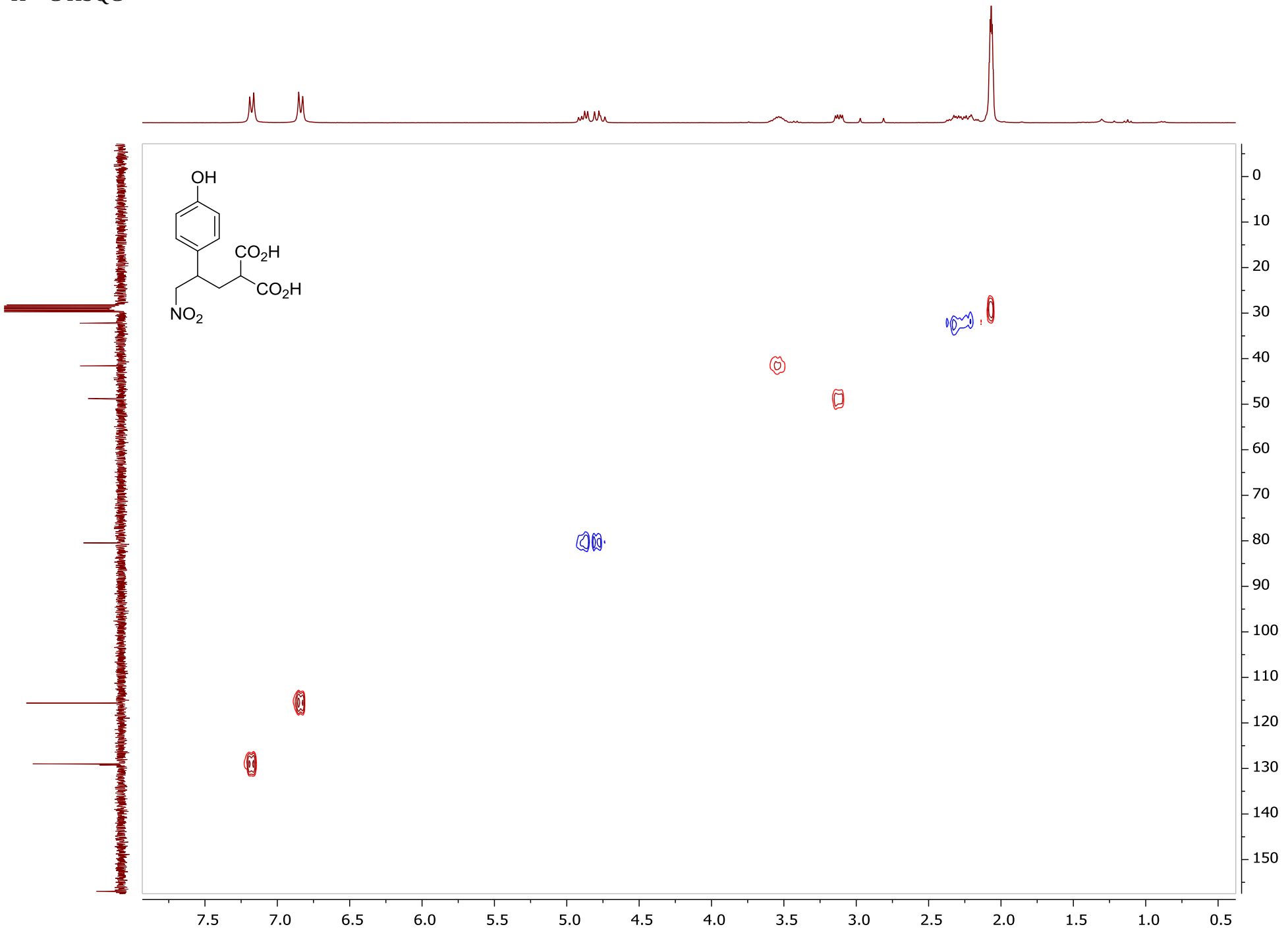
$^{13}$C NMR (75 MHz, acetone-$d_6$)



$^{1}H$-$^{1}H$ COSY

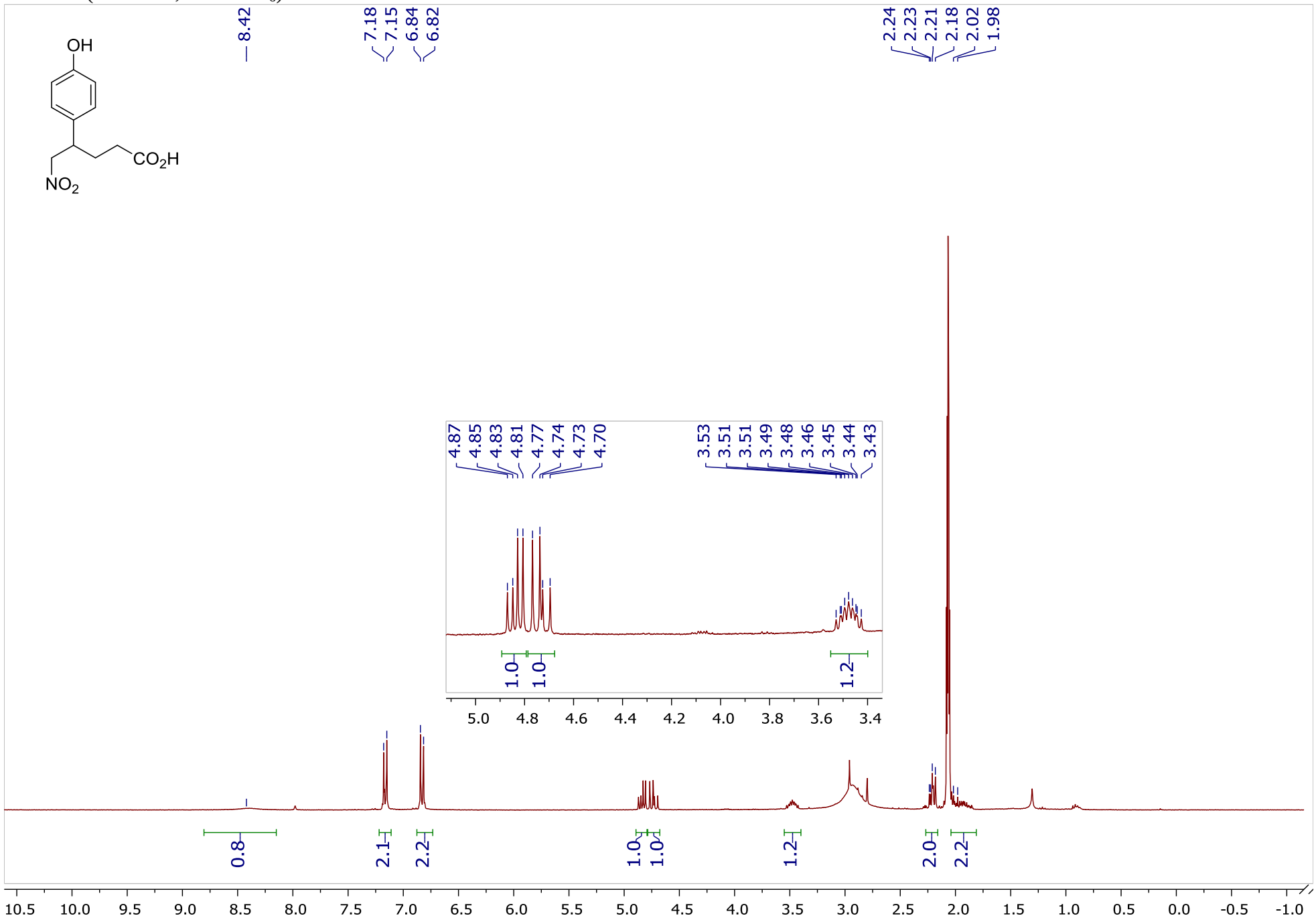

OH
CO2H
CO2H
NO2
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HSQC

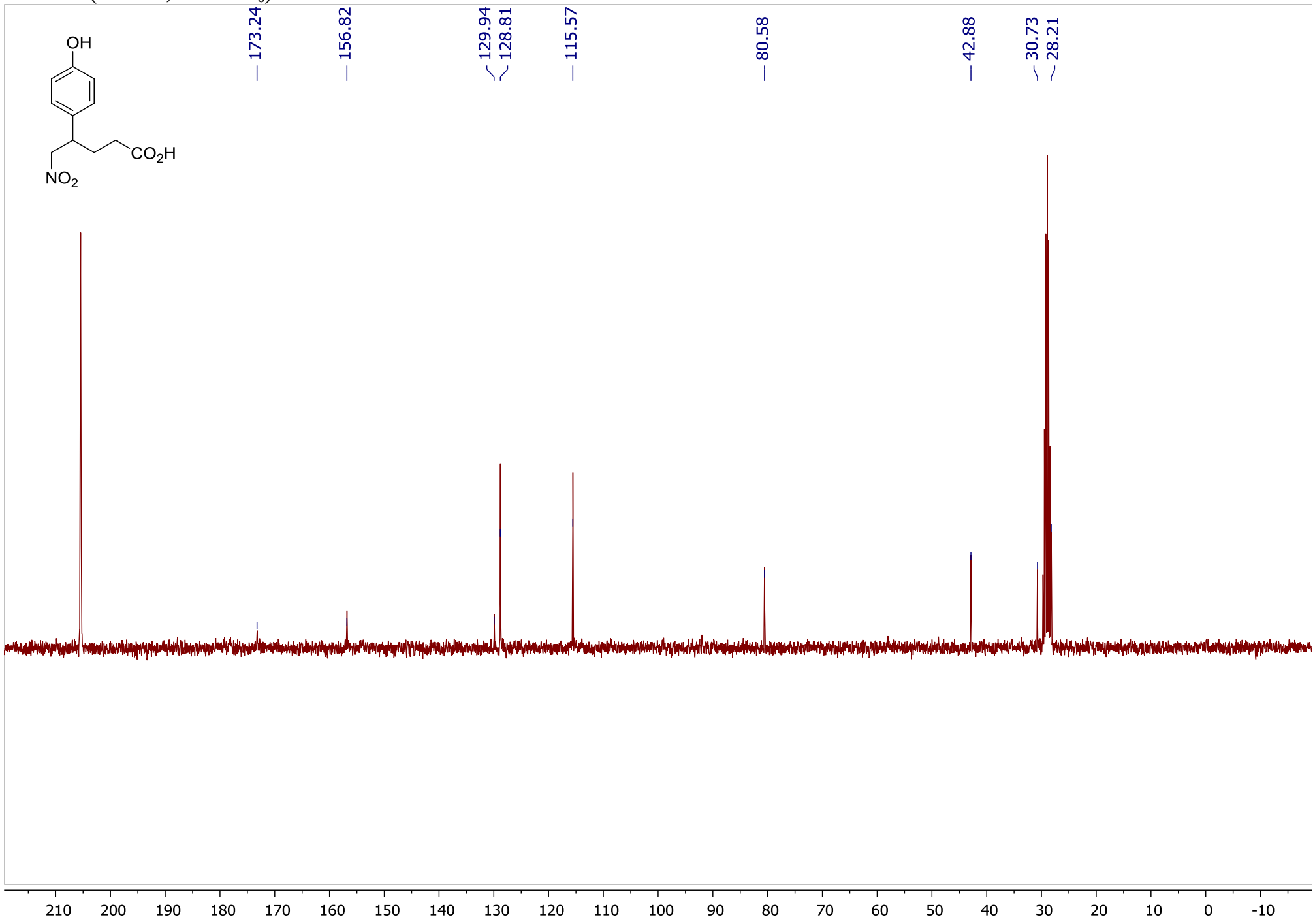

OH
CO2H
CO2H
NO2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**4-(4-Hydroxyphenyl)-5-nitropentanoic acid (15)**

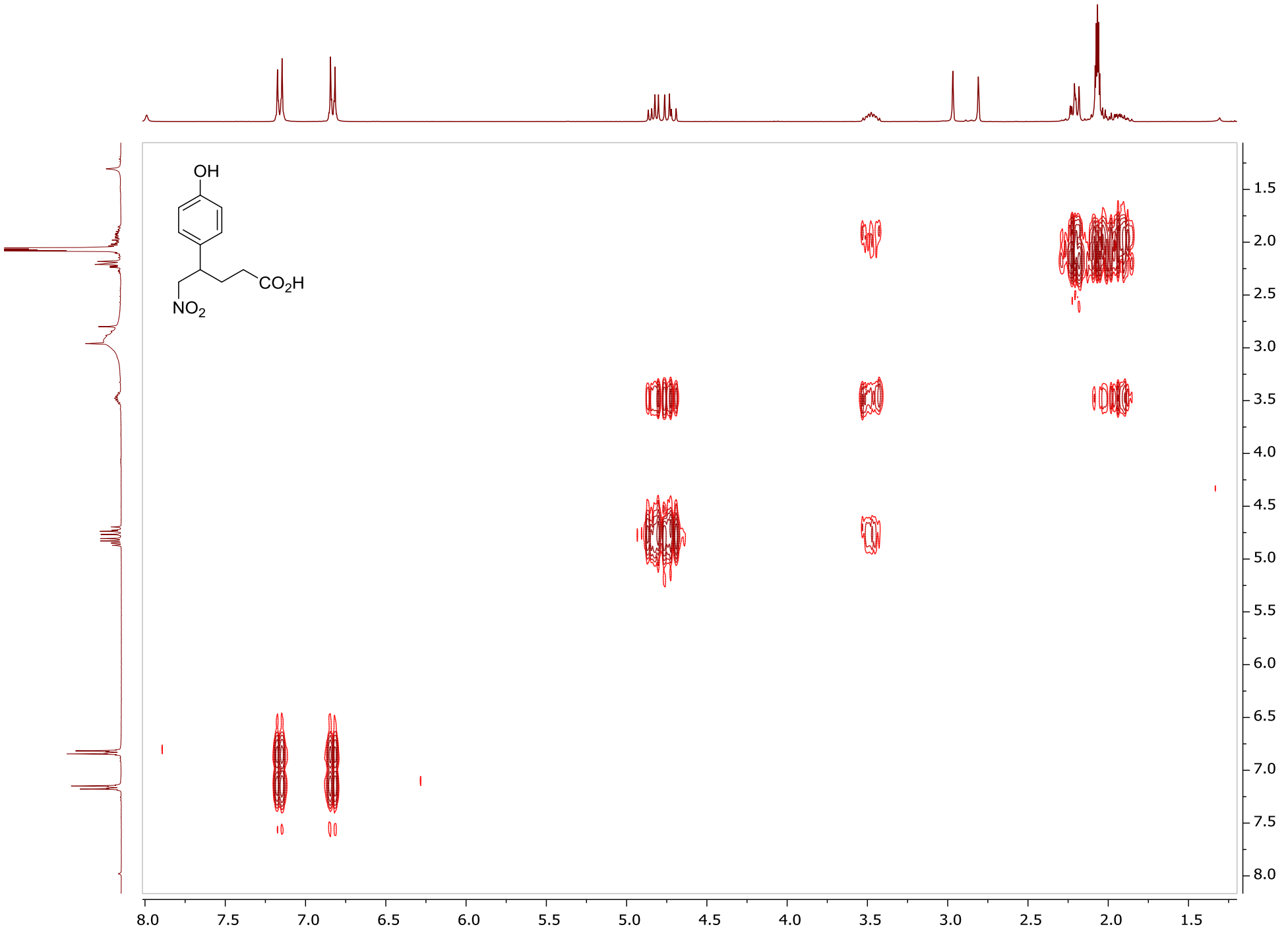
$^1$H NMR (300 MHz, acetone-$d_6$)



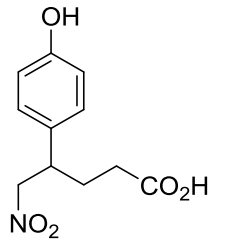
$^{13}$C NMR (75 MHz, acetone-$d_6$)

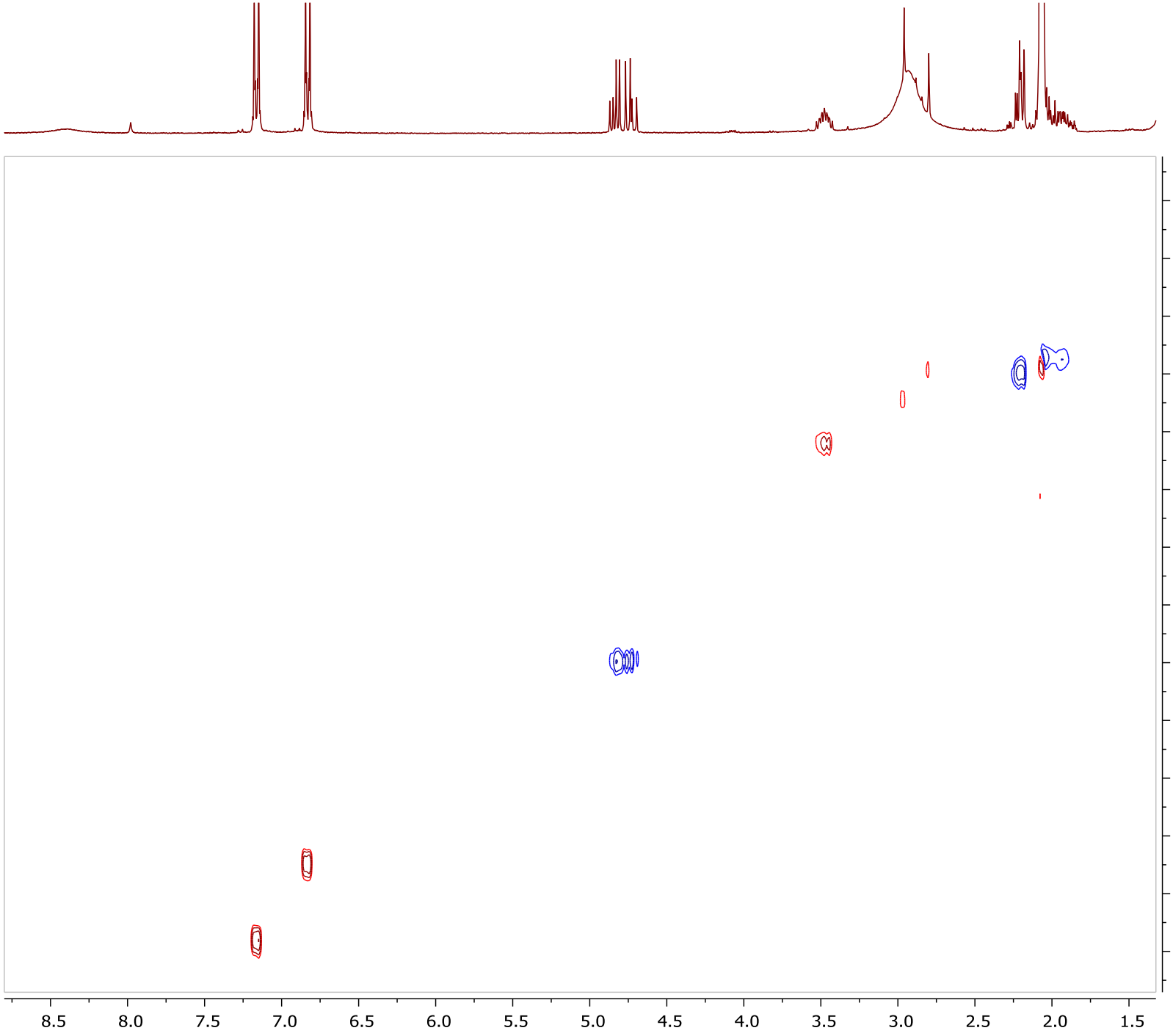


$^{1}H$-$^{1}H$ COSY



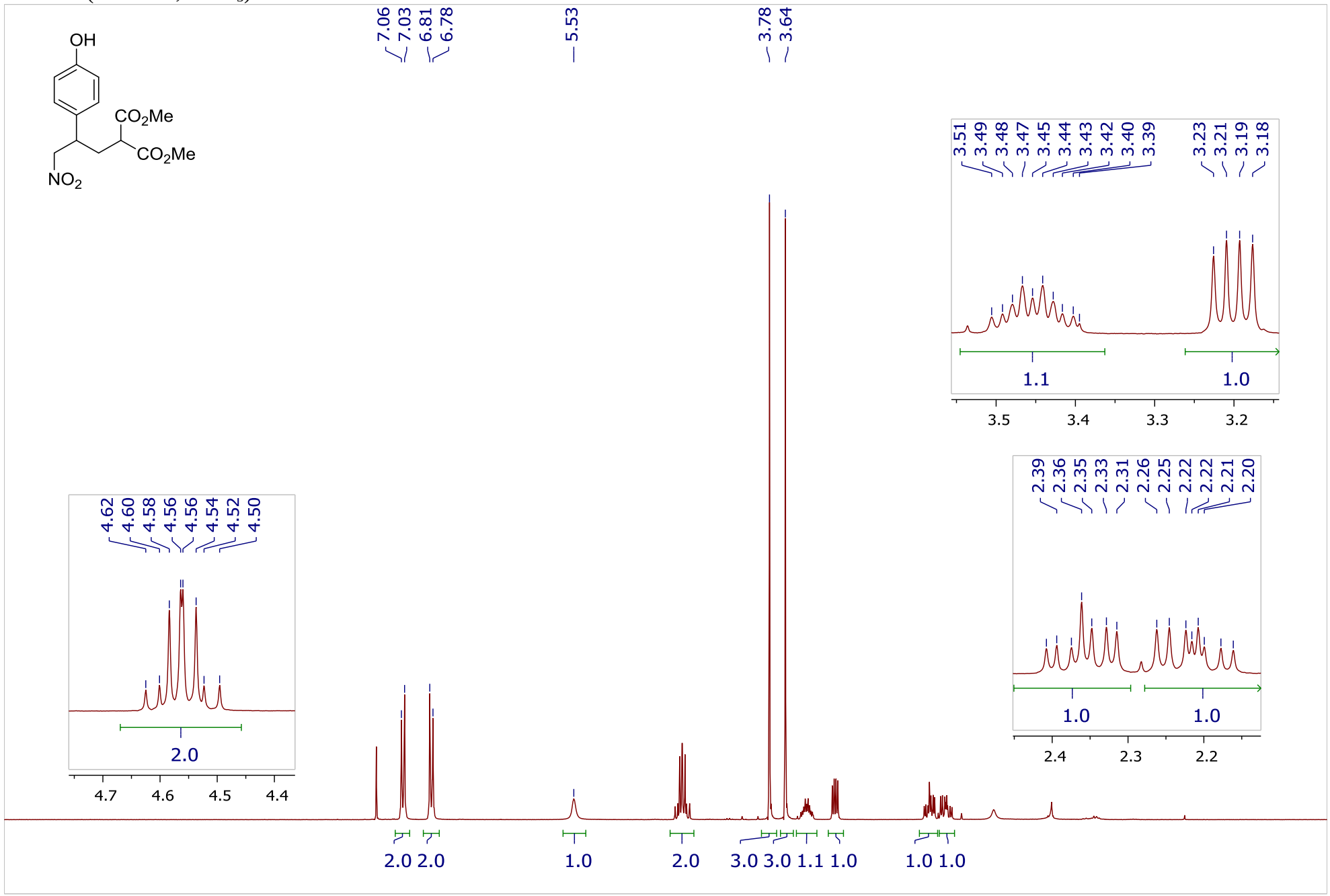
$^{1}H$-$^{13}C$ HSQC


OH
CO2H
NO2

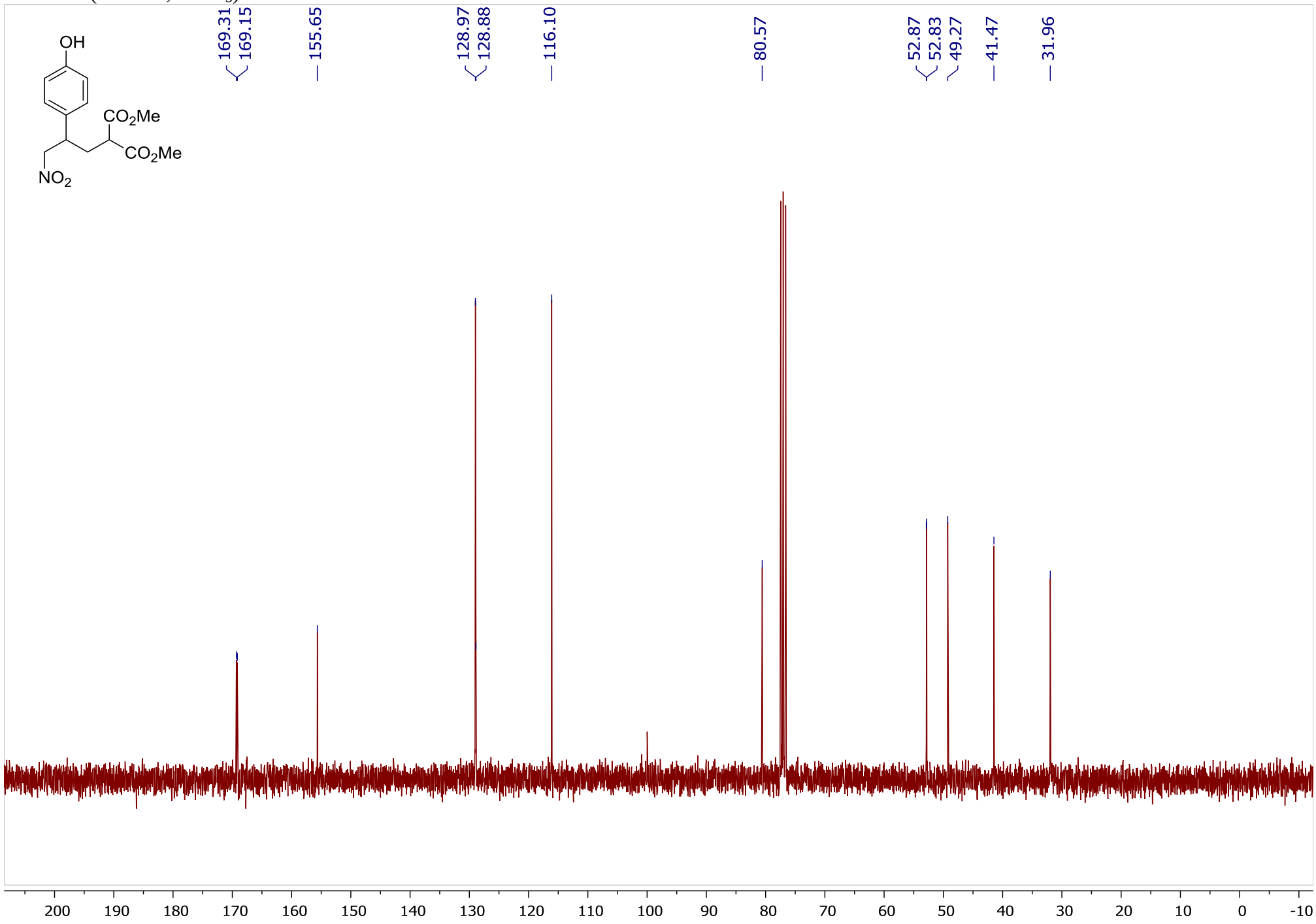

0
10
20
30
40
50
60
70
80
90
100
110
120
130
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-nitropropyl)malonate (16)**

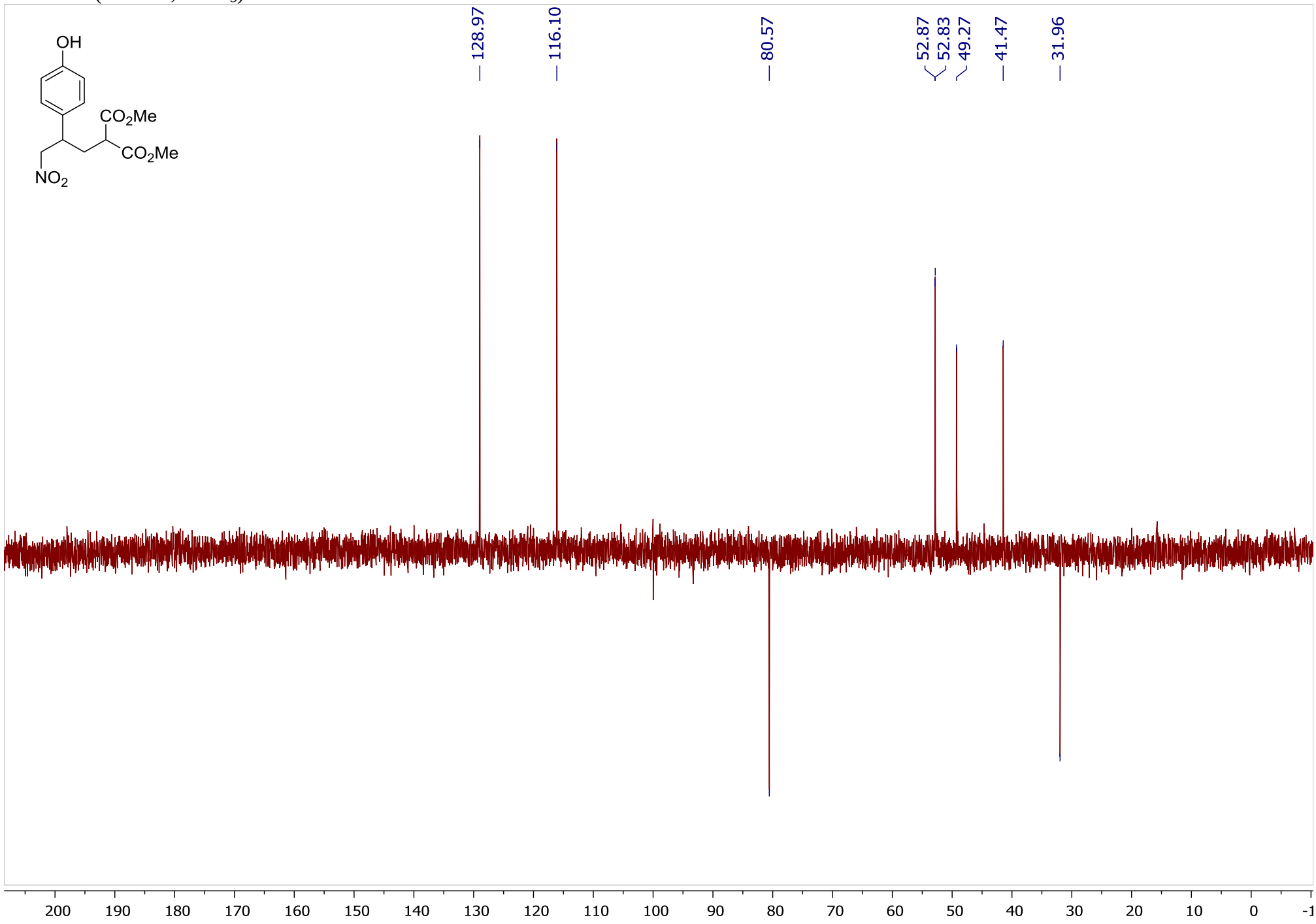
$^1$H NMR (300 MHz, $CDCl_3$)



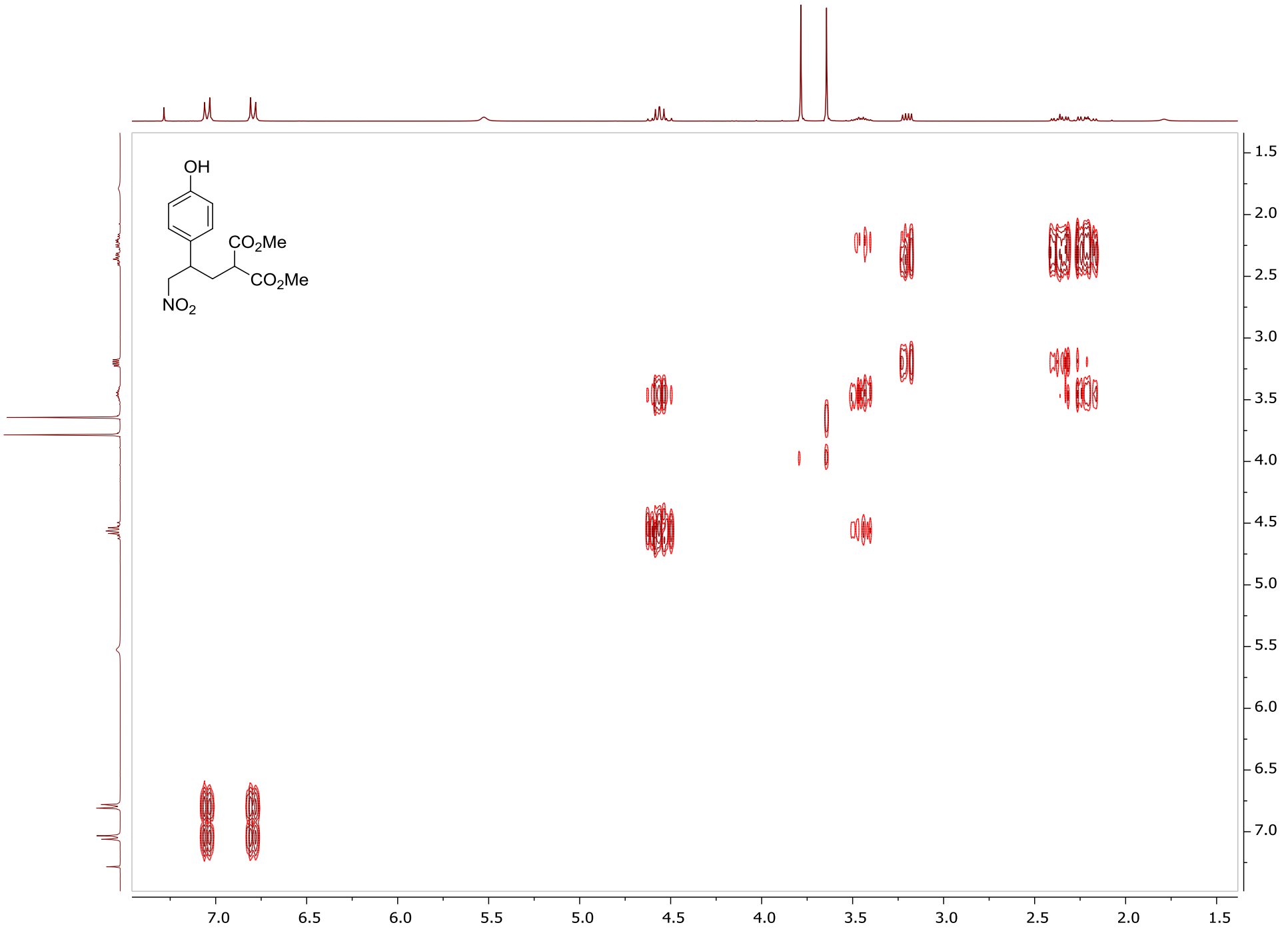
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
CO2Me
NO2
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
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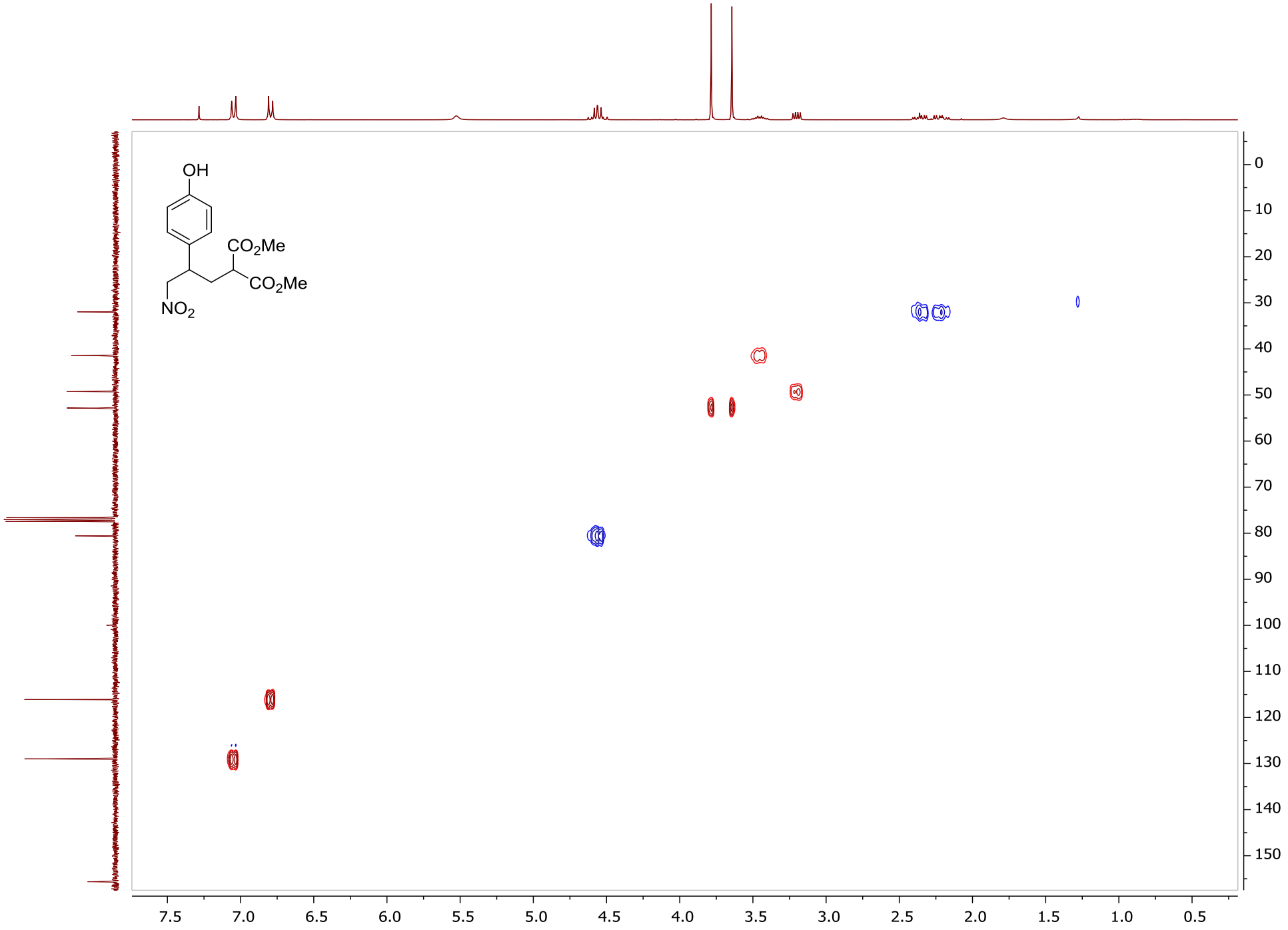
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}H$-$^{13}C$ HSQC


OH
CO2Me
CO2Me
NO2
0
10
20
30
40
50
60
70
80
90
100
110
120
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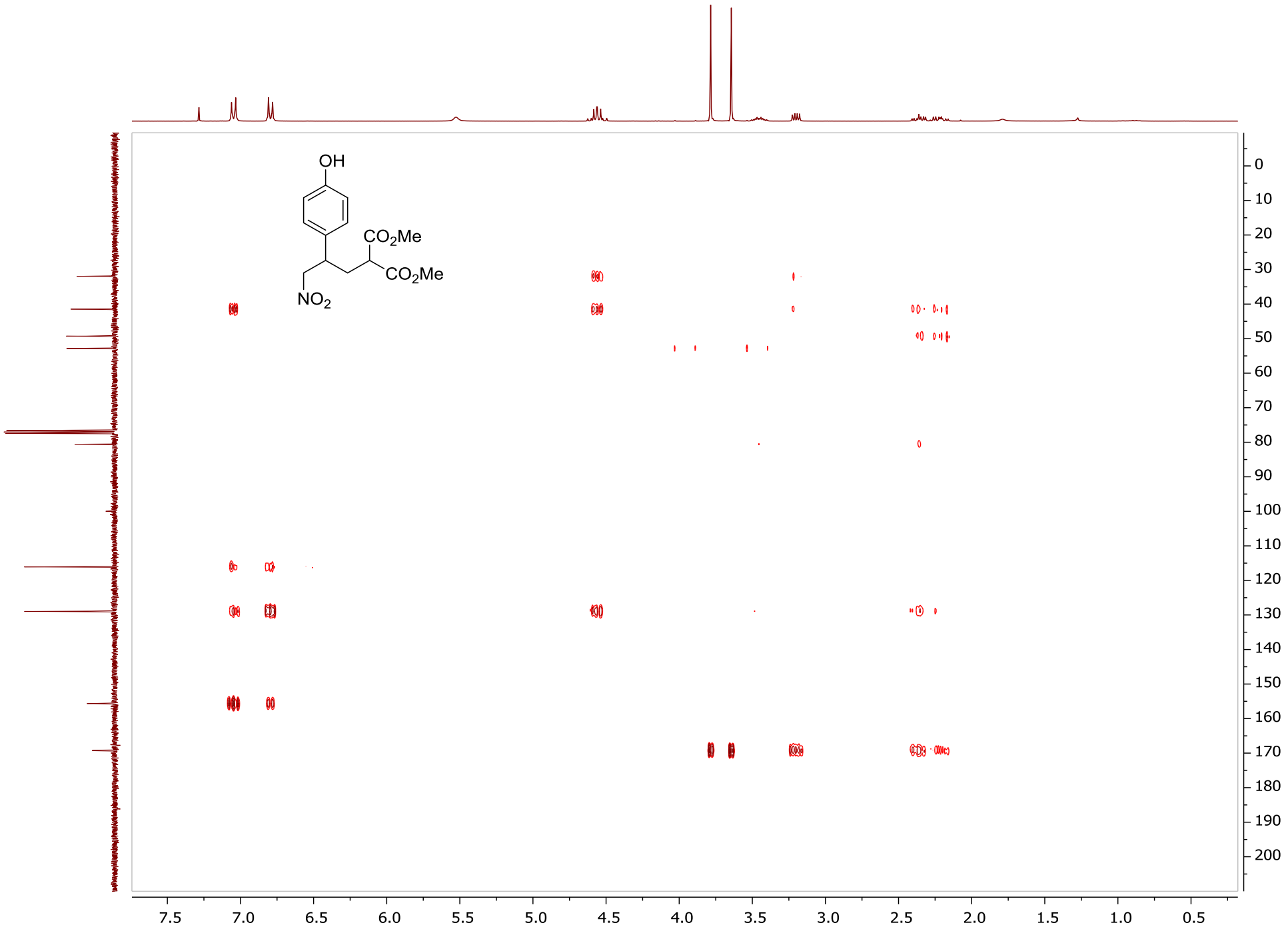
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}H$-$^{13}C$ HMBC


OH
CO2Me
CO2Me
NO2
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40
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60
70
80
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110
120
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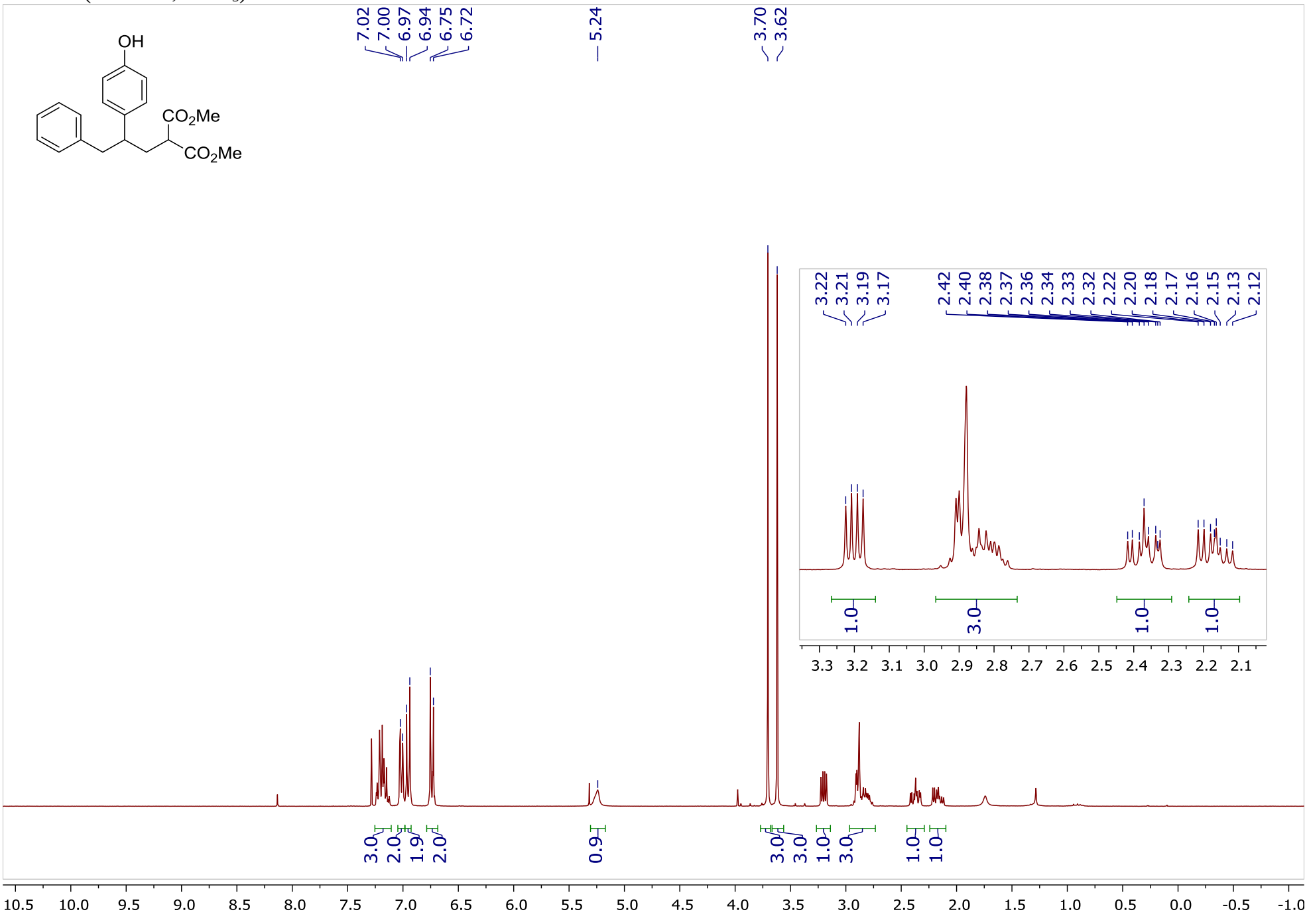
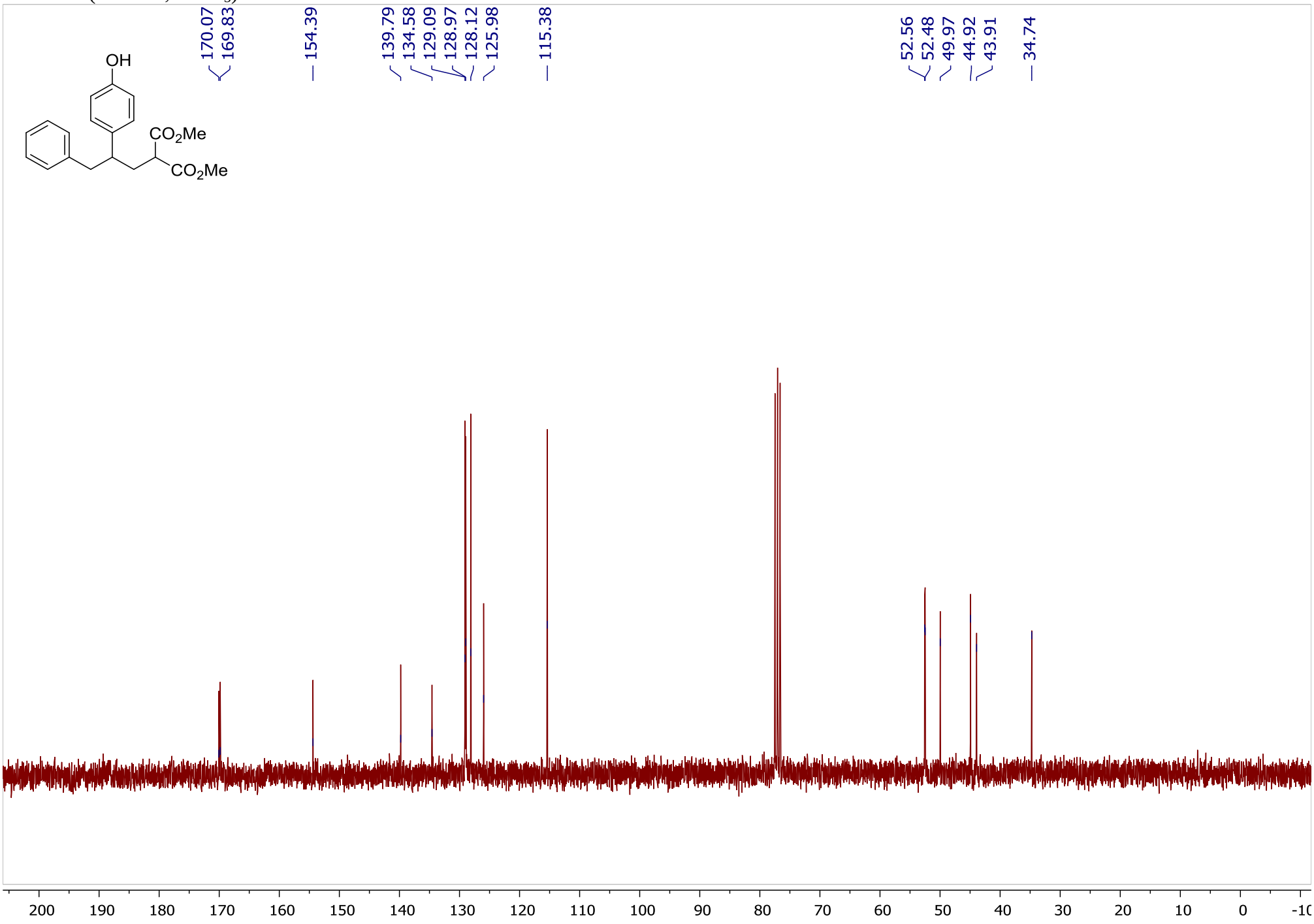
180
190
200
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**Dimethyl 2-(2-(4-hydroxyphenyl)-3-phenylpropyl)malonate (17)**

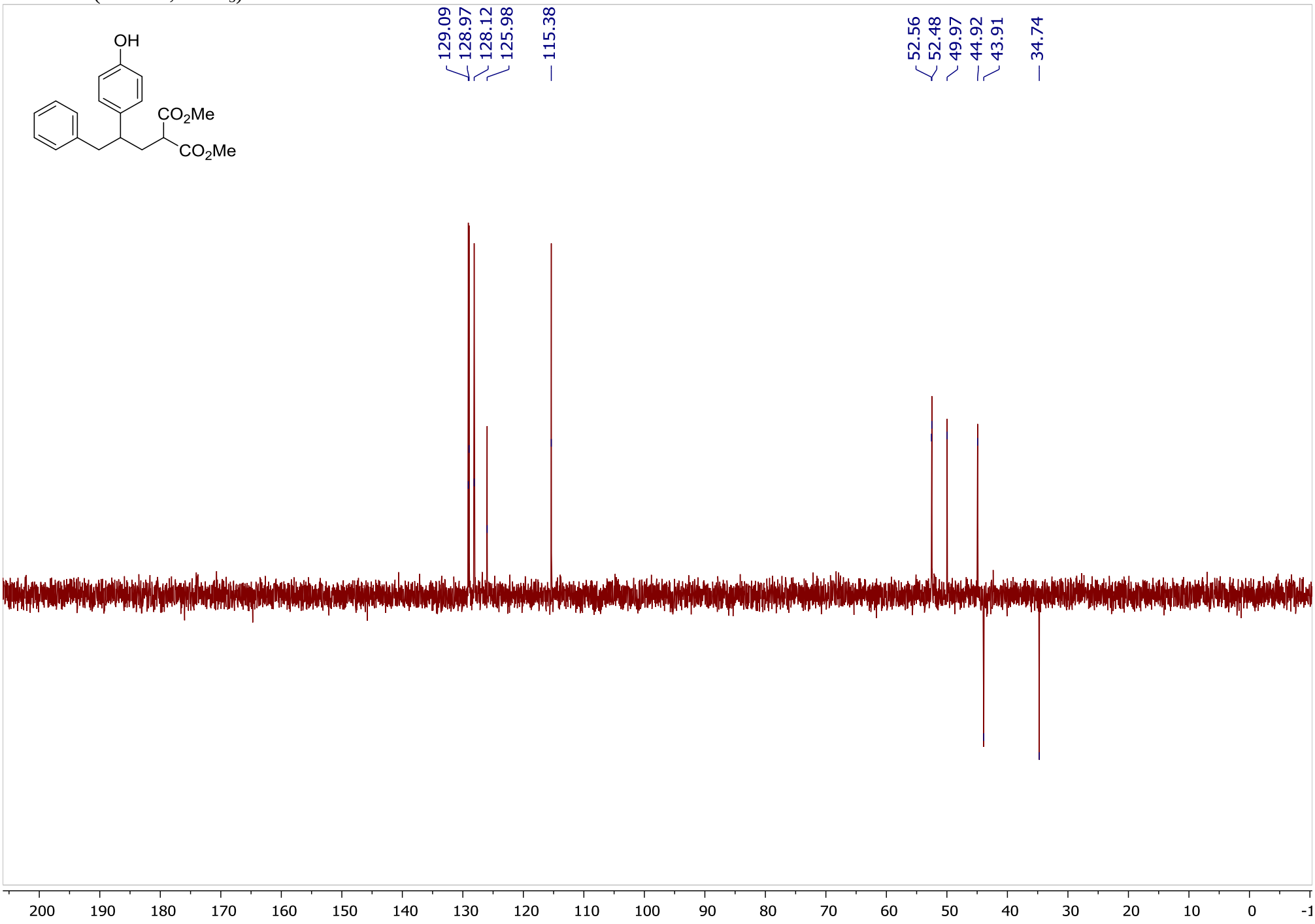
$^1$H NMR (300 MHz, $CDCl_3$)



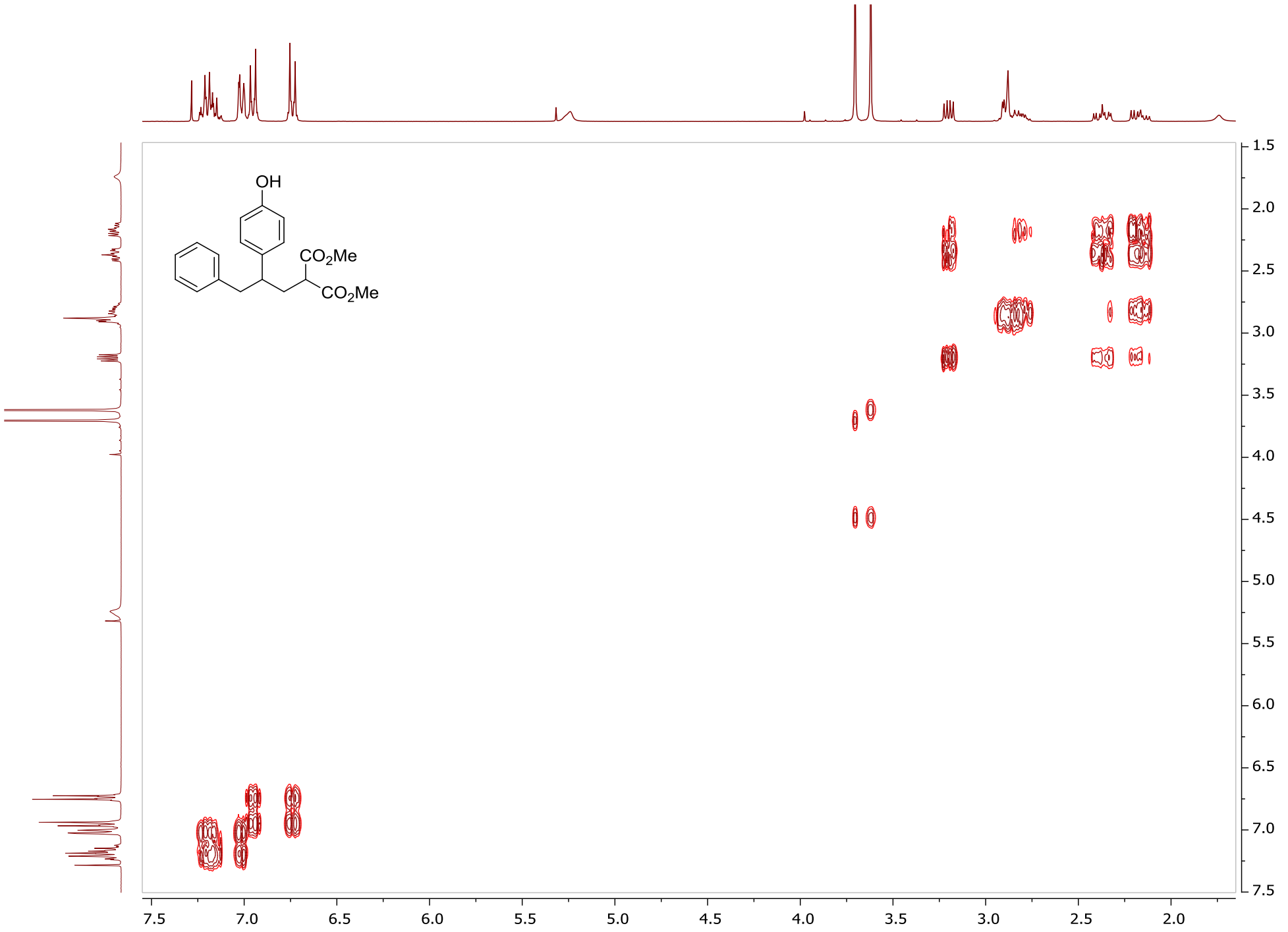
$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY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CO2Me
CO2Me
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
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6.5
7.0
7.5
7.5
7.0
6.5
6.0
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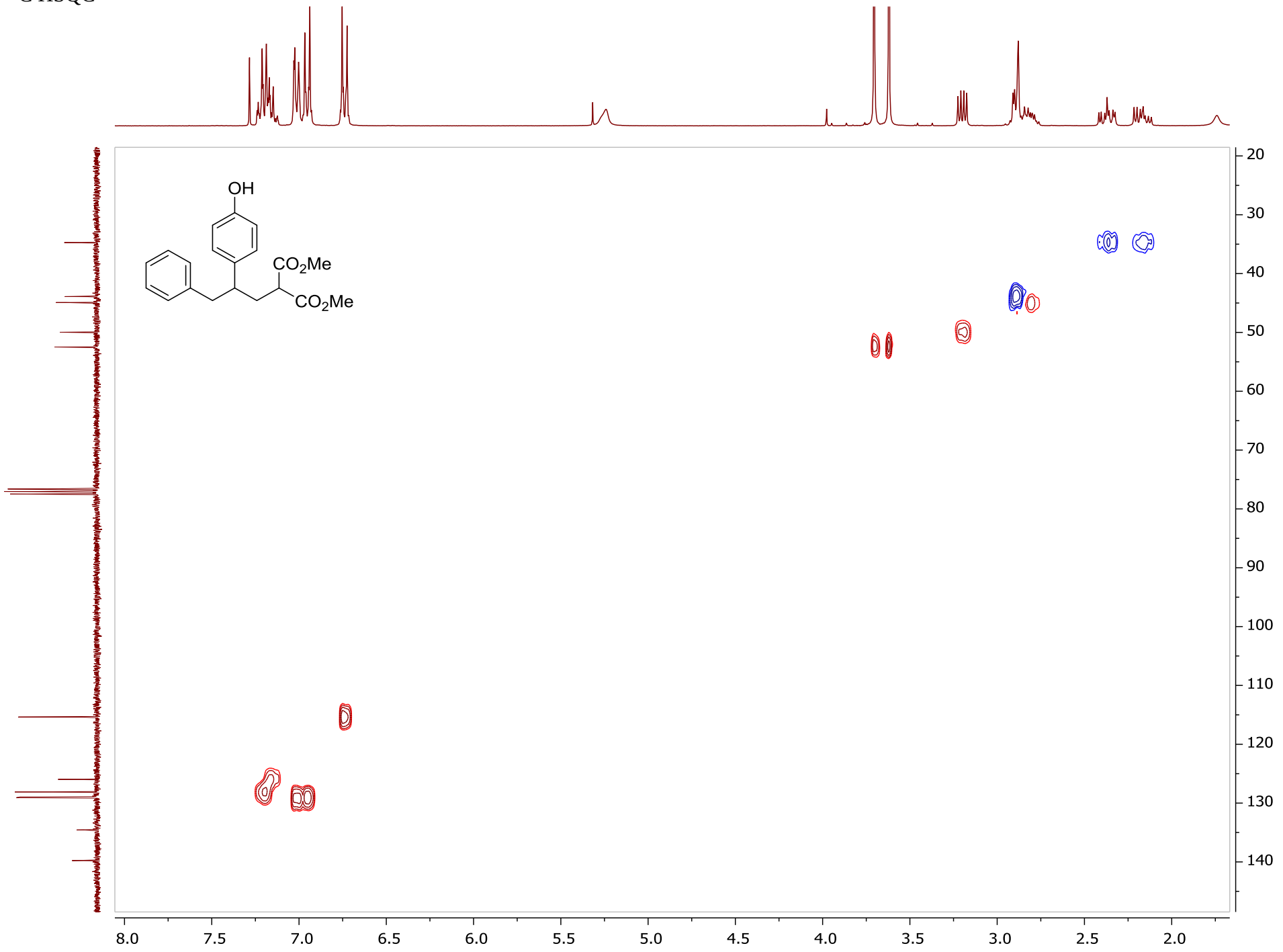
4.5
4.0
3.5
3.0
2.5
2.0

$^{1}H$-$^{13}C$ HSQC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CO2Me
CO2Me
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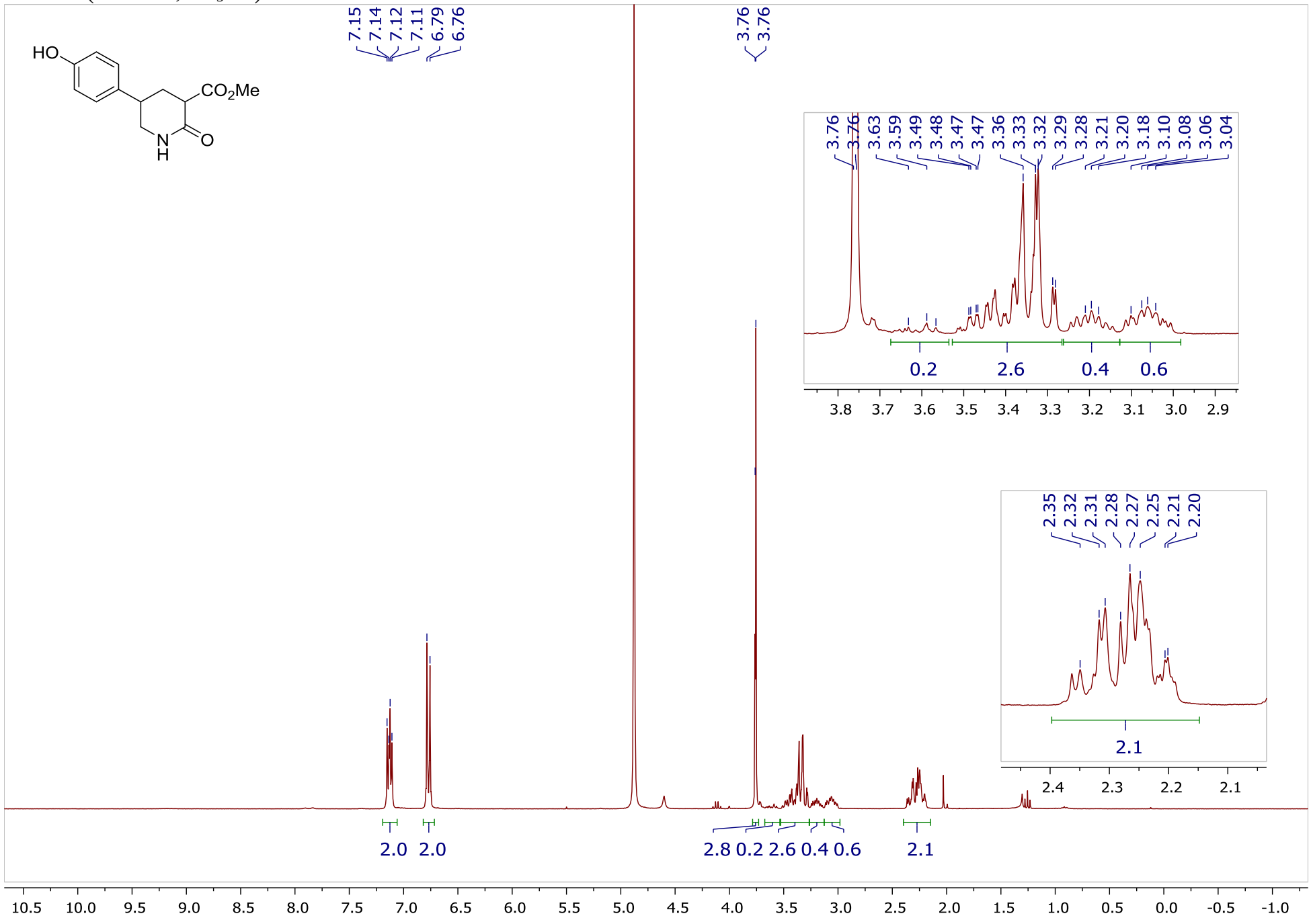
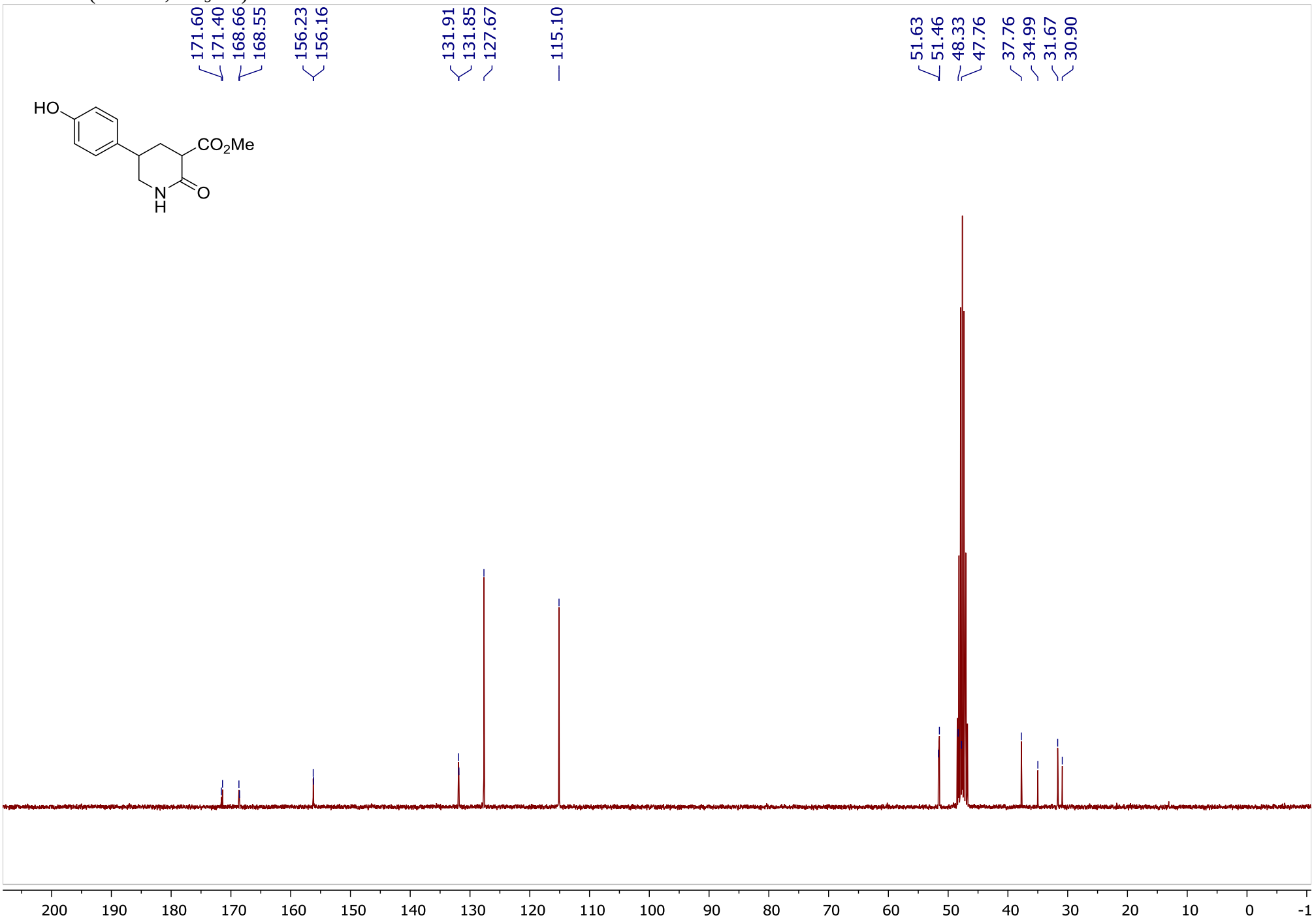
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

**Methyl 5-(4-hydroxyphenyl)-2-oxopiperidine-3-carboxylate (18)**, dr = 1.4:1

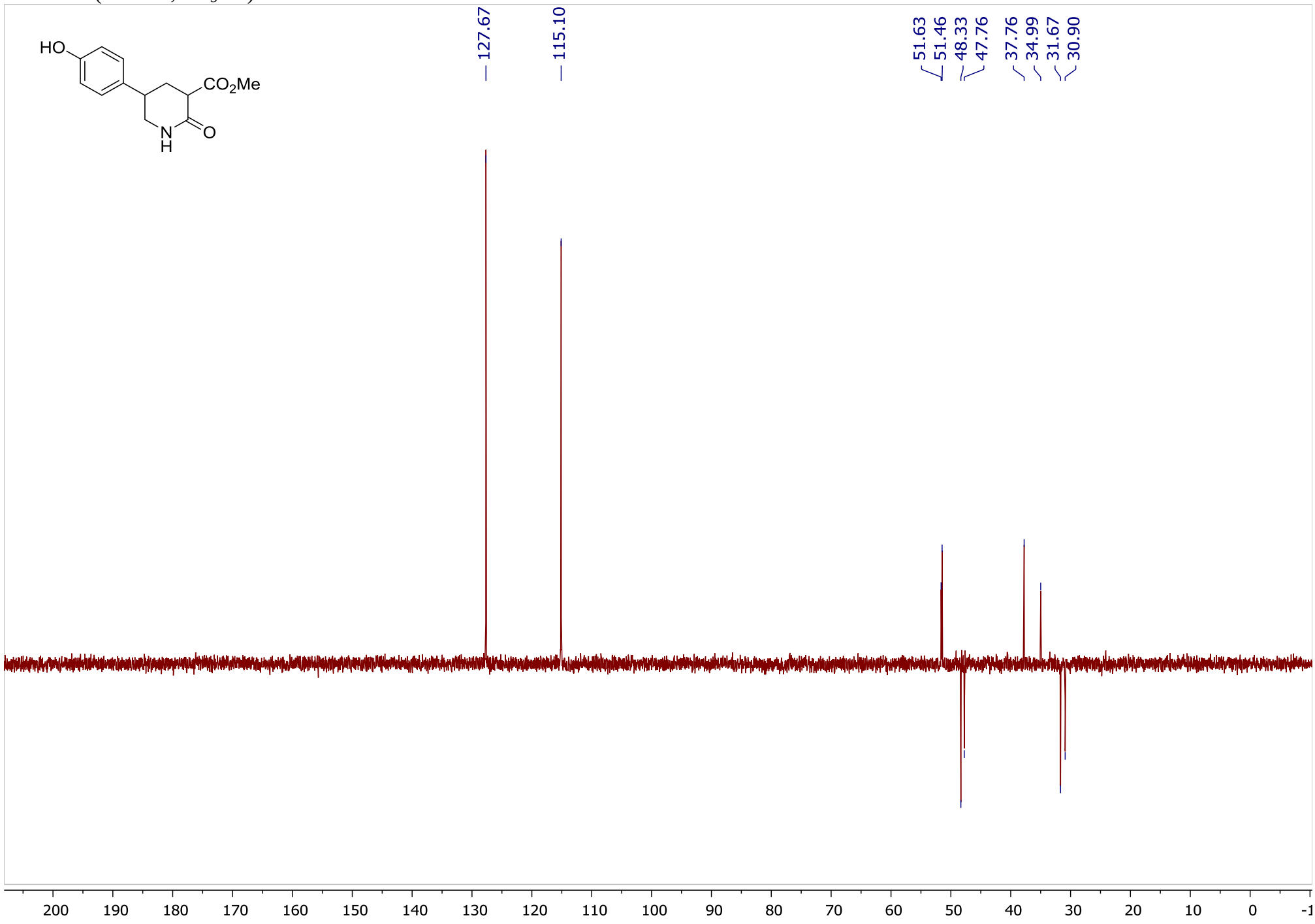
$^1$H NMR (300 MHz, $CD_3OD$)



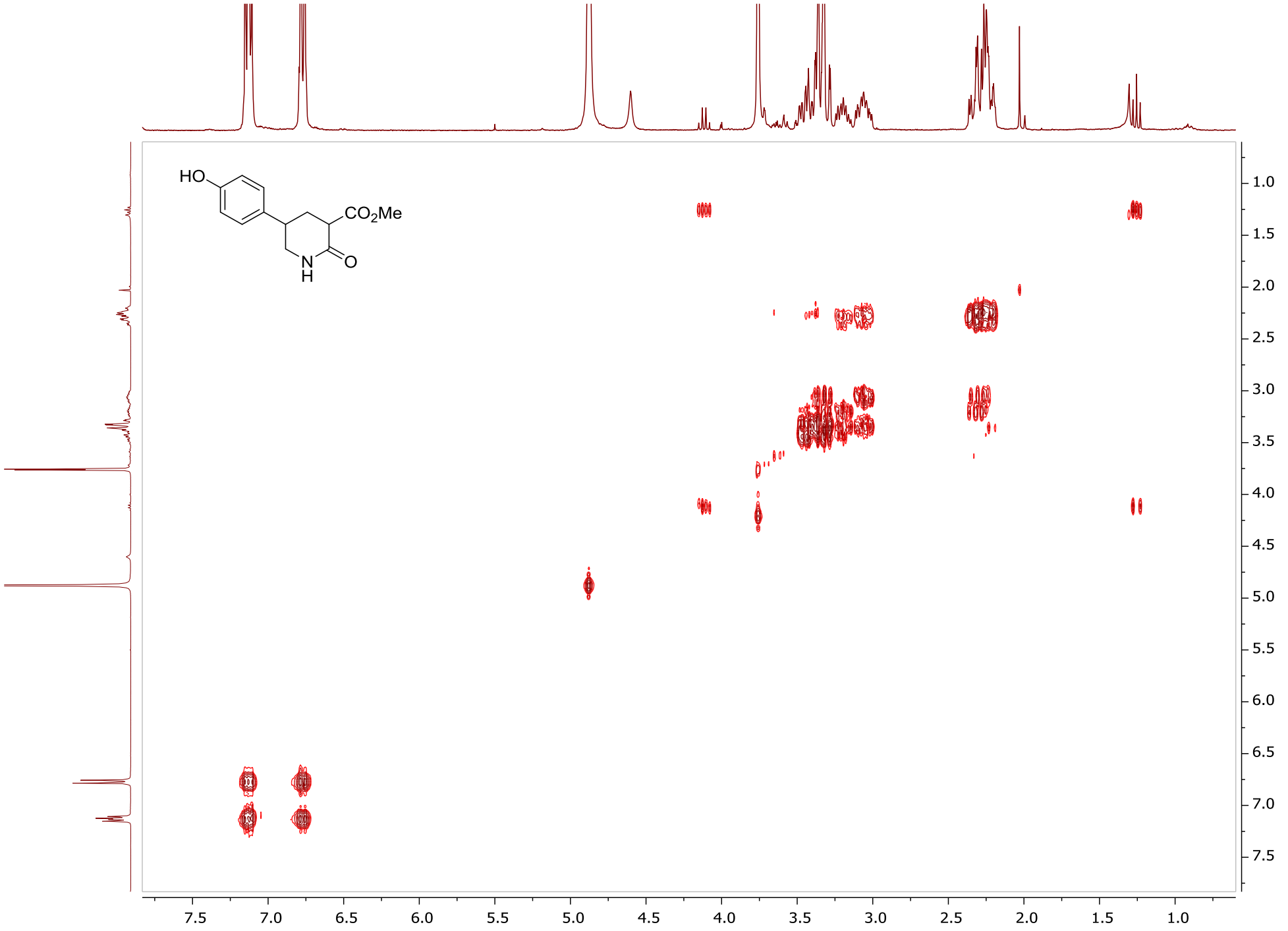
$^{13}$C NMR (75 MHz, $CD_3OD$)



$^{13}$C DEPT (75 MHz, $CD_3OD$)



$^{1}$H-$^{1}$H COSY


HO
CO2Me
N
H
O
1.0
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2.0
2.5
3.0
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5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
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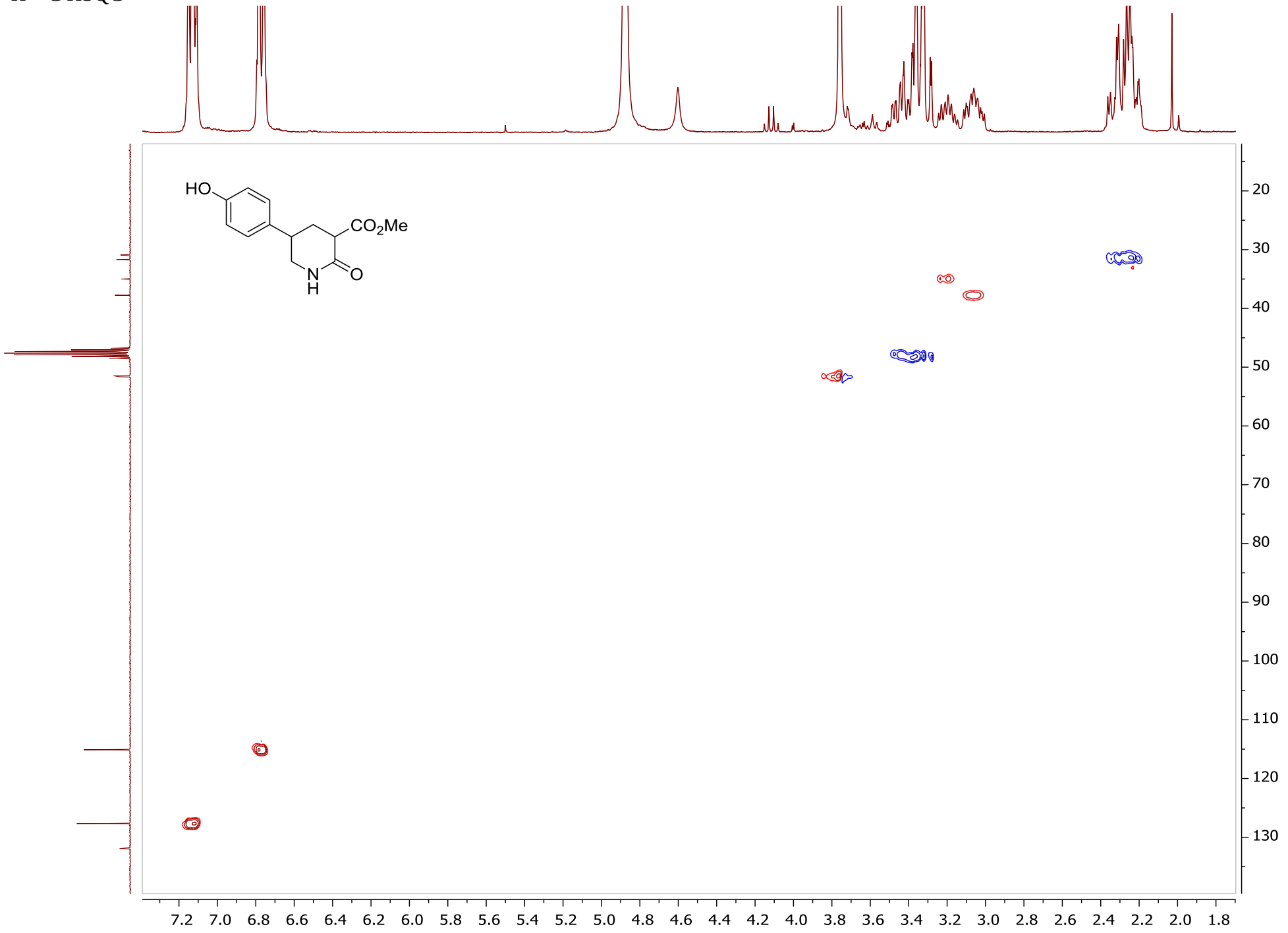
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HSQC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110
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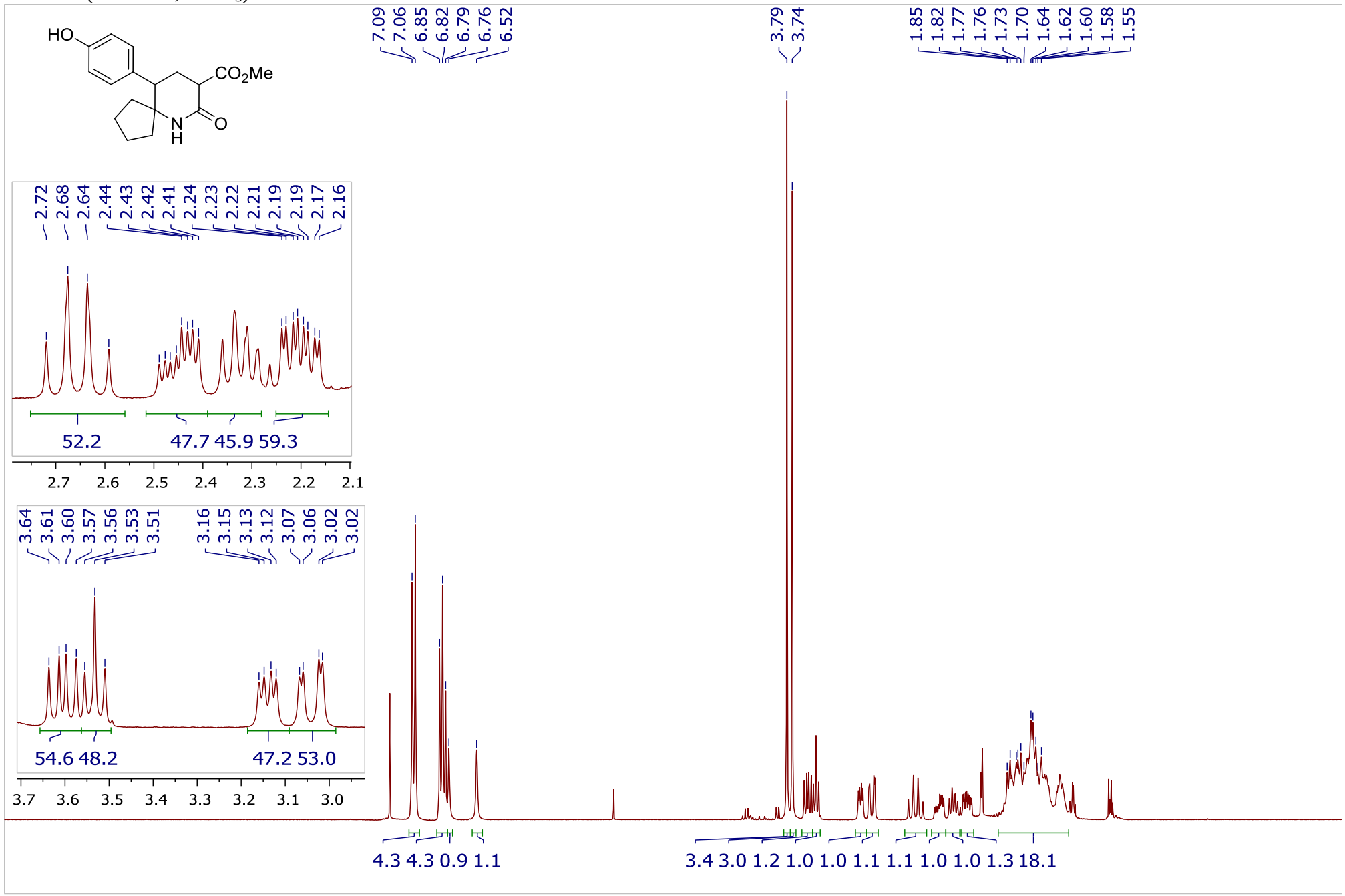
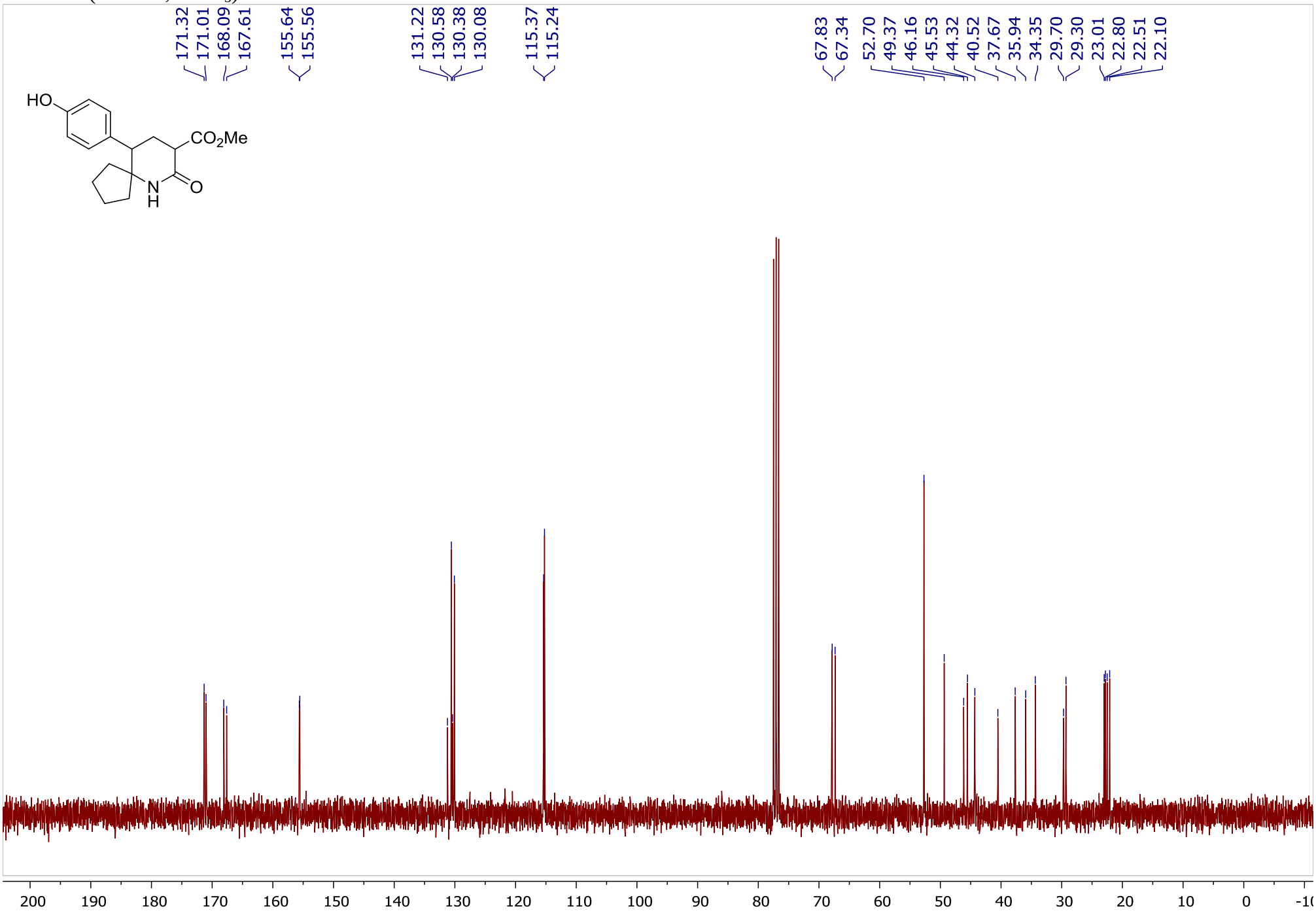
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8

**Methyl 10-(4-hydroxyphenyl)-7-oxo-6-azaspiro[4.5]decane-8-carboxylate (19)**, dr = 1.1 : 1

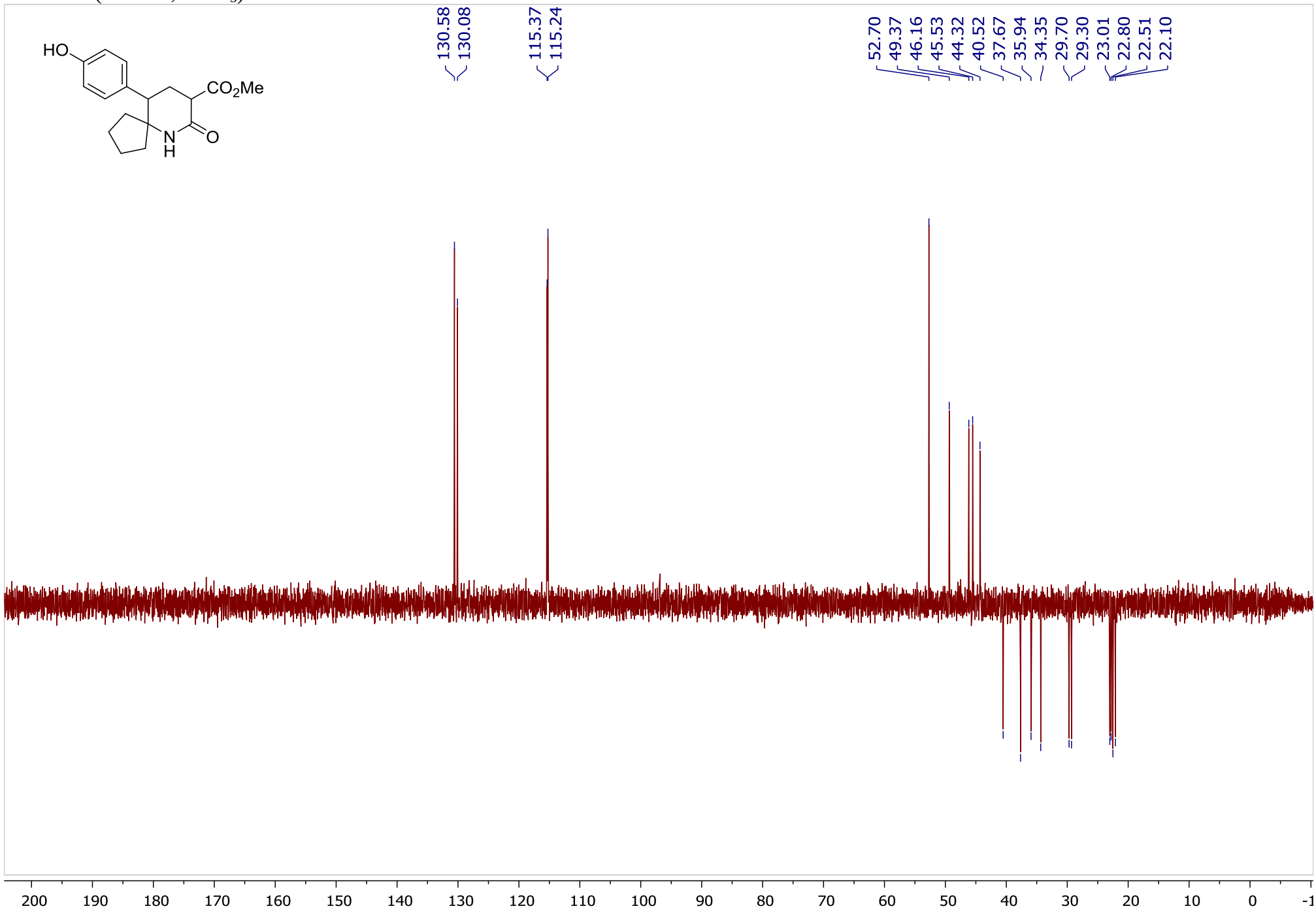
$^1$H NMR (300 MHz, $CDCl_3$)



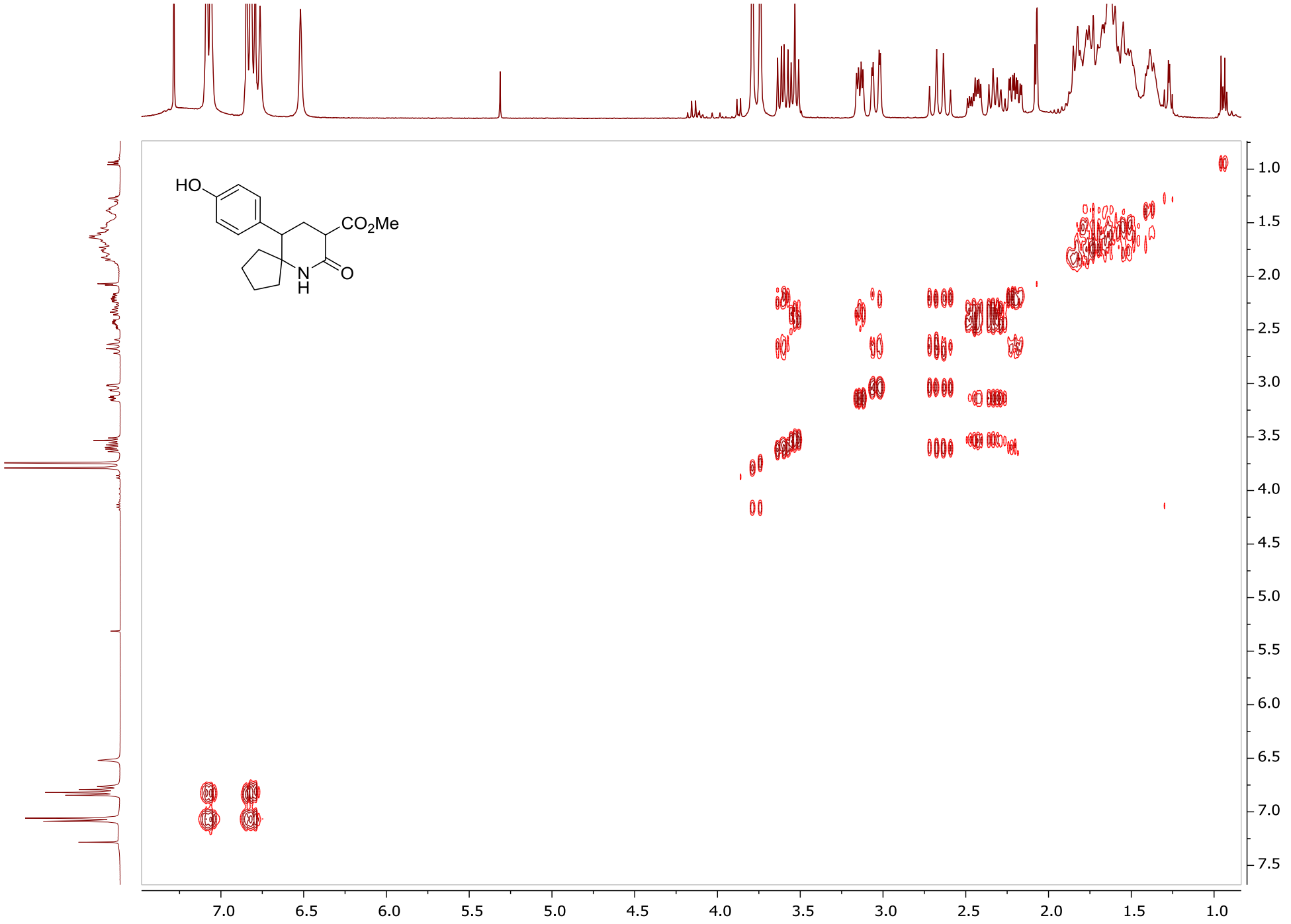
$^{13}$C NMR (75 MHz, $CDCl_3$)



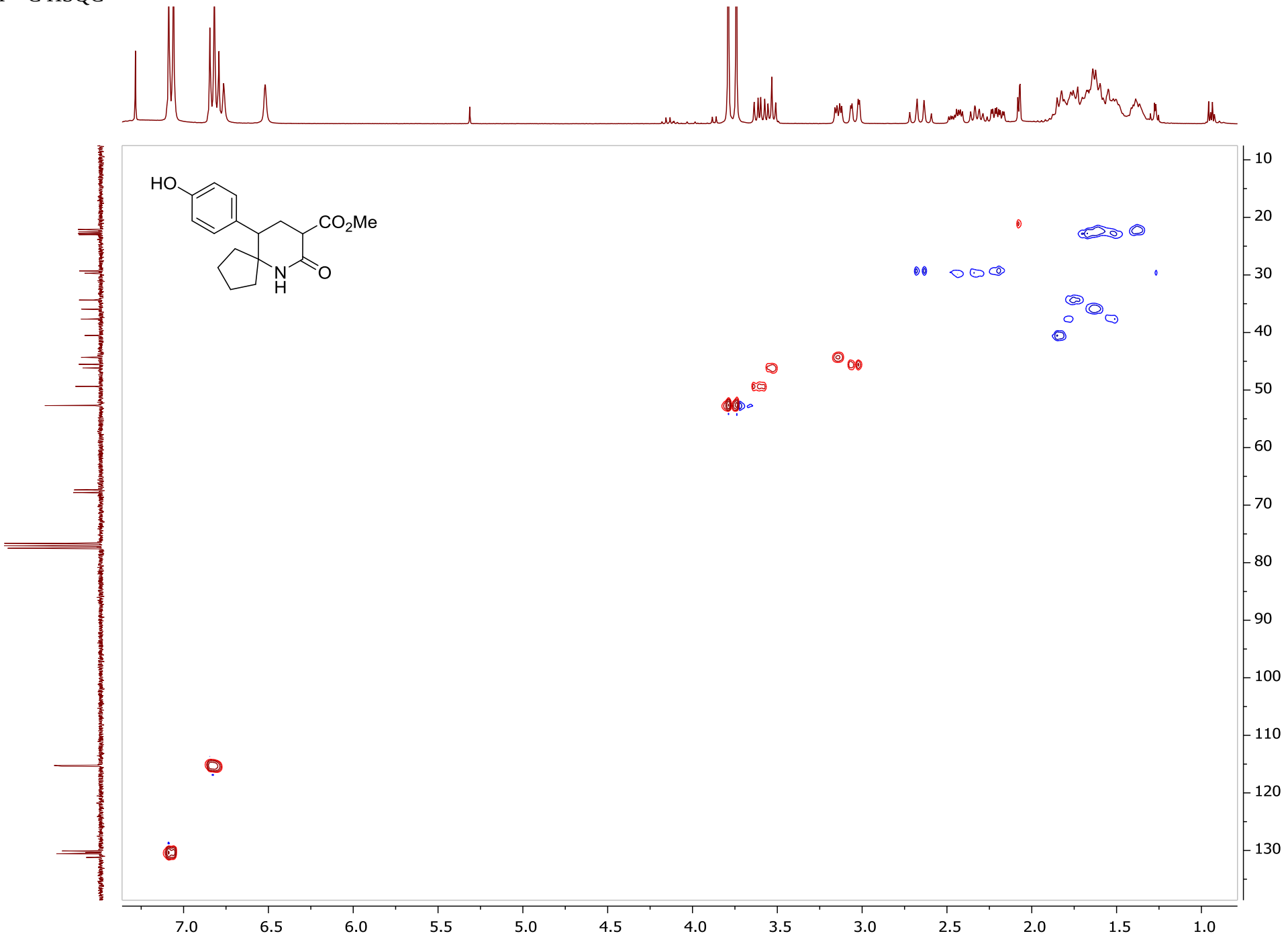
$^{13}$C DEPT (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY



$^{1}H$-$^{13}C$ HSQC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CO2Me
N
H
O
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120
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7.0
6.5
6.0
5.5
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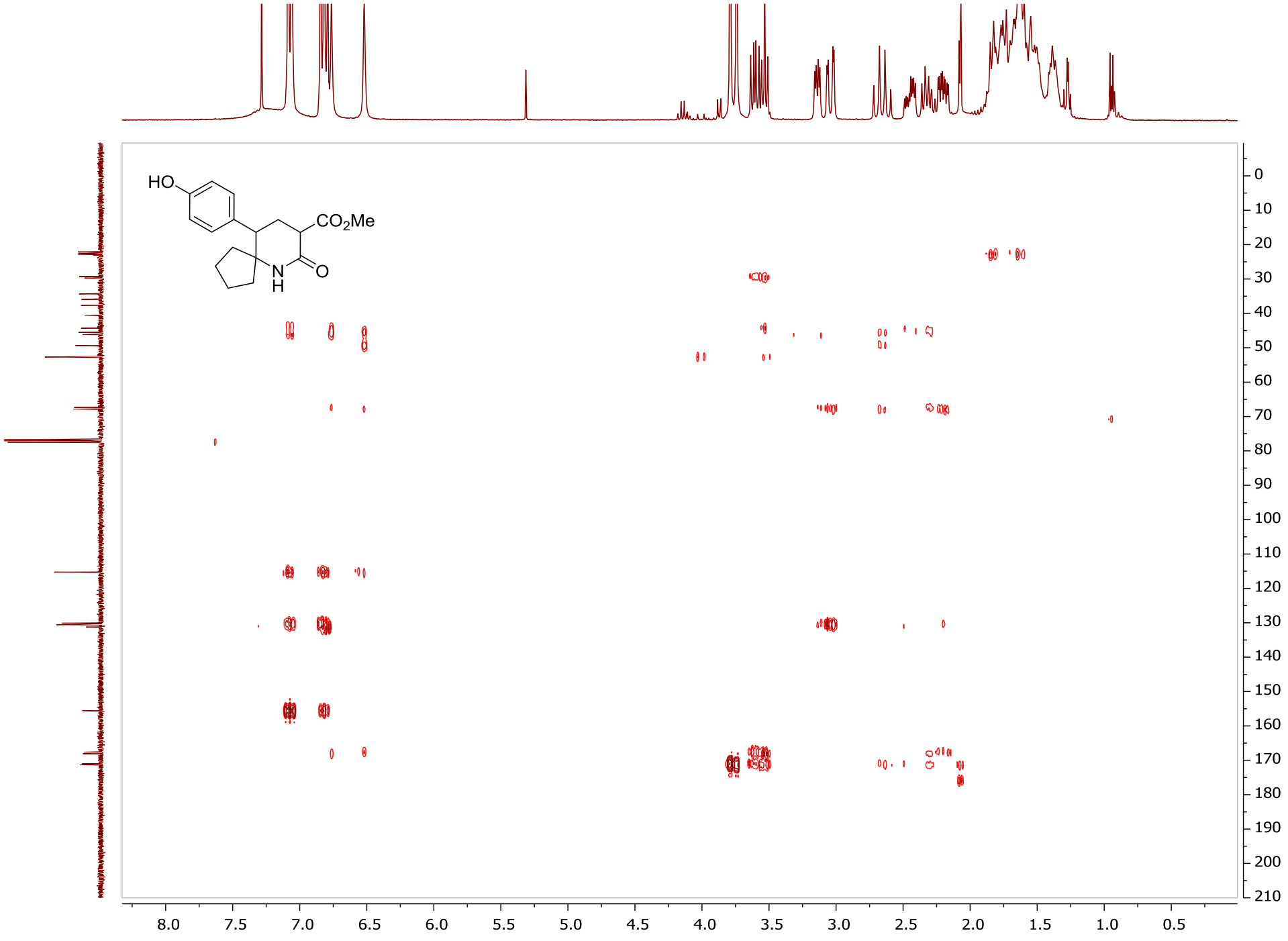
4.0
3.5
3.0
2.5
2.0
1.5
1.0

$^{1}H$-$^{13}C$ HMBC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CO2Me
N
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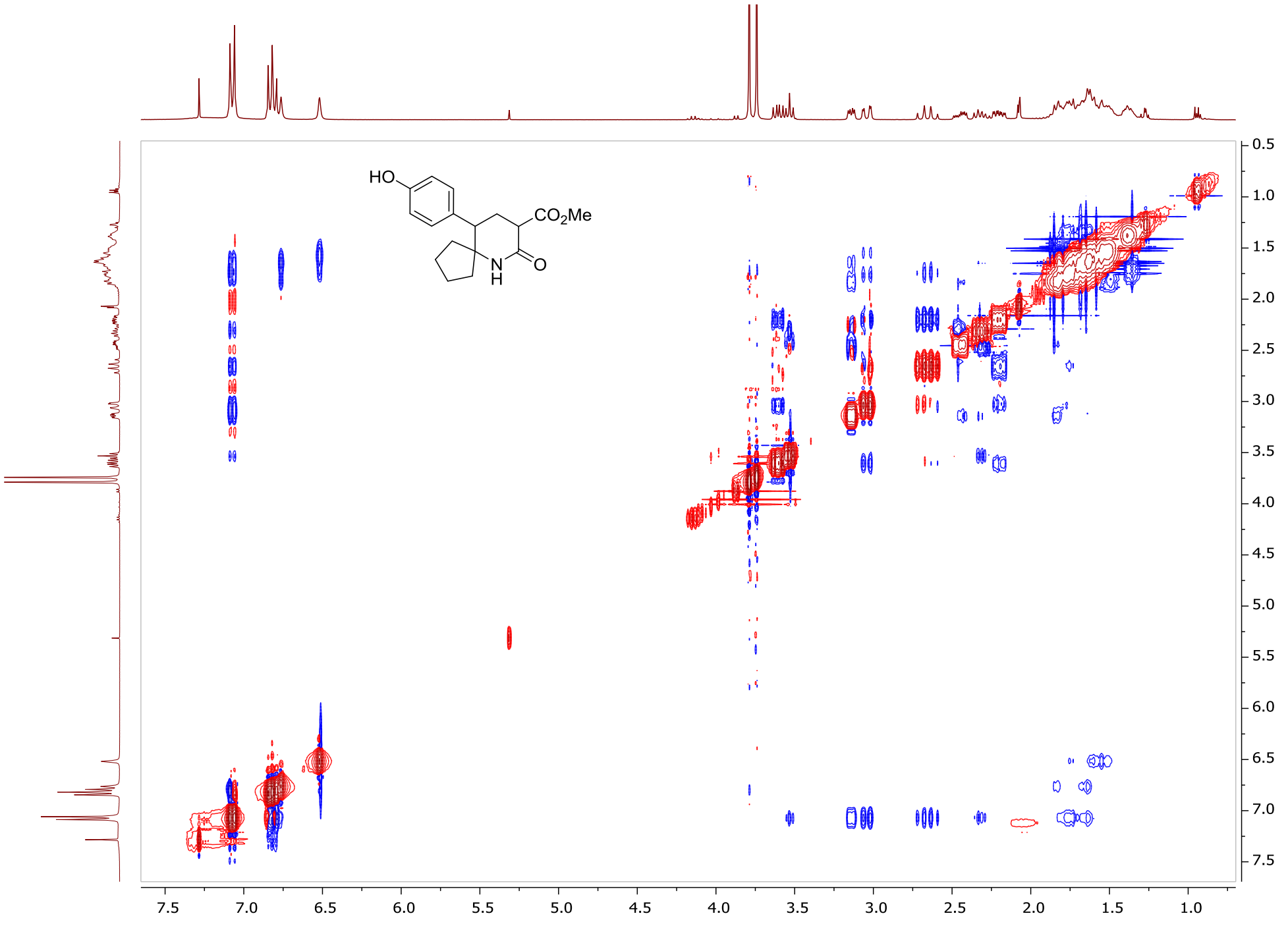
100
110
120
130
140
150
160
170
180
190
200
210
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}$H-$^{1}$H NOESY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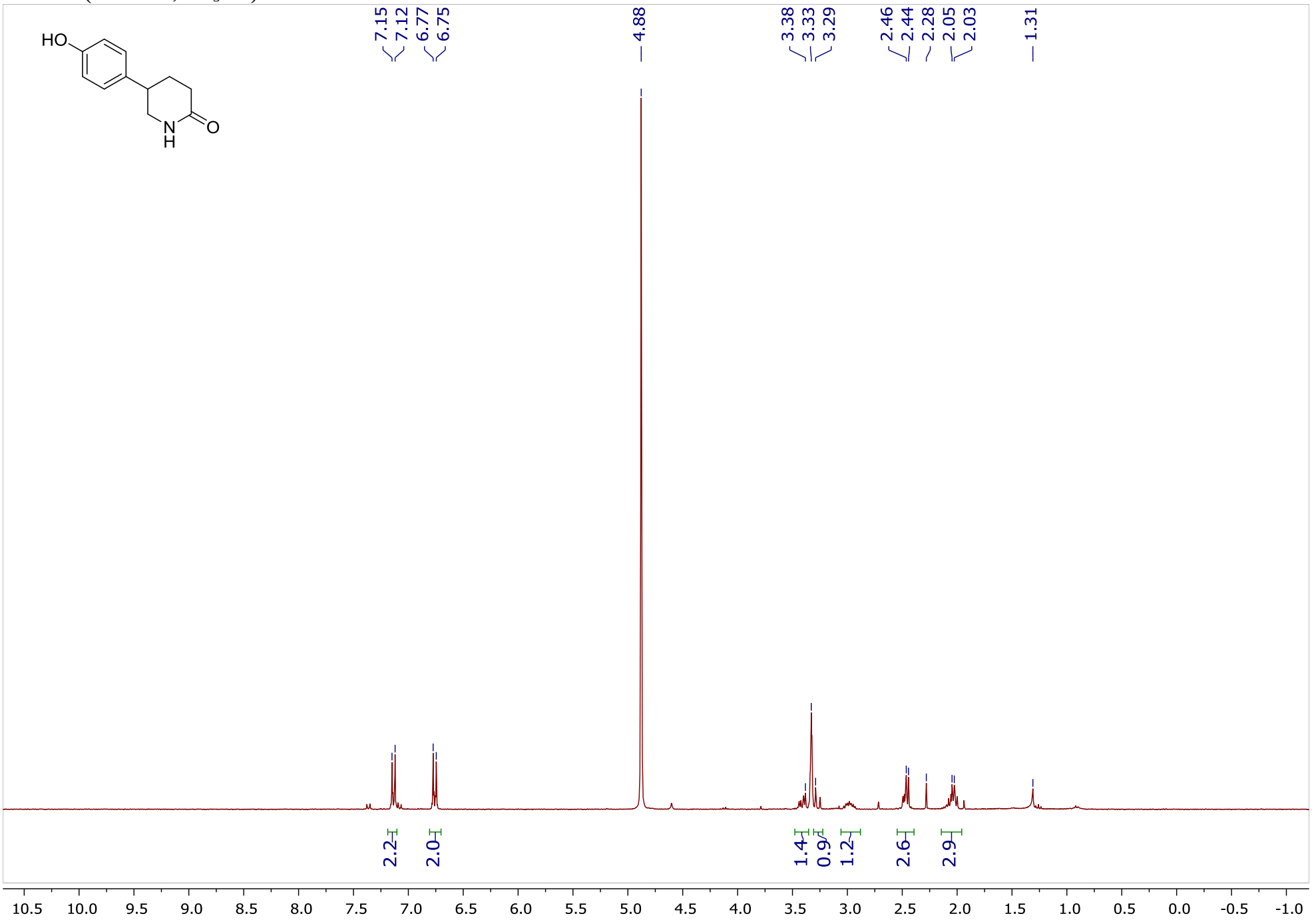
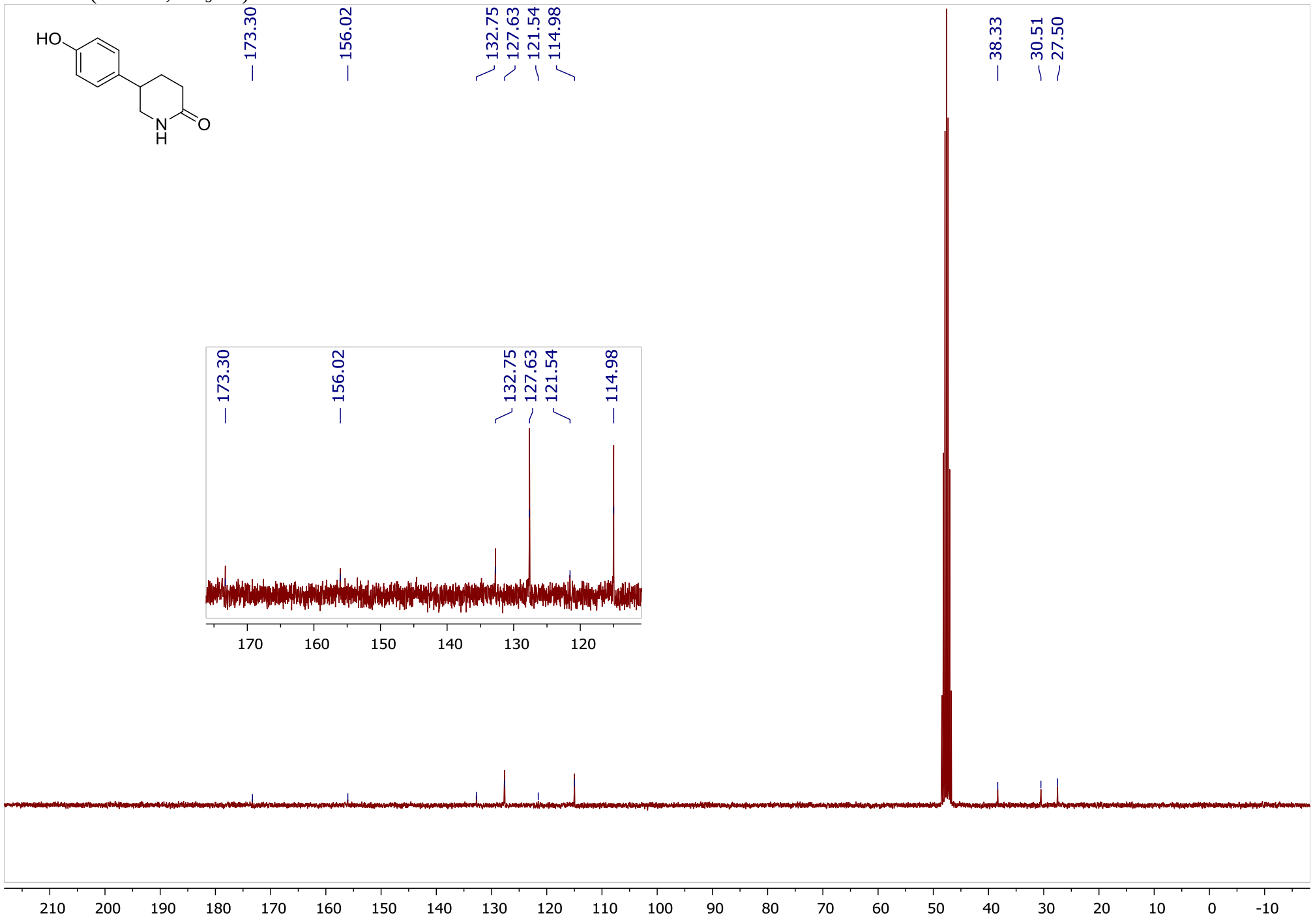
CO2Me
N
H
O
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**5-(4-Hydroxyphenyl)piperidin-2-one (20)**

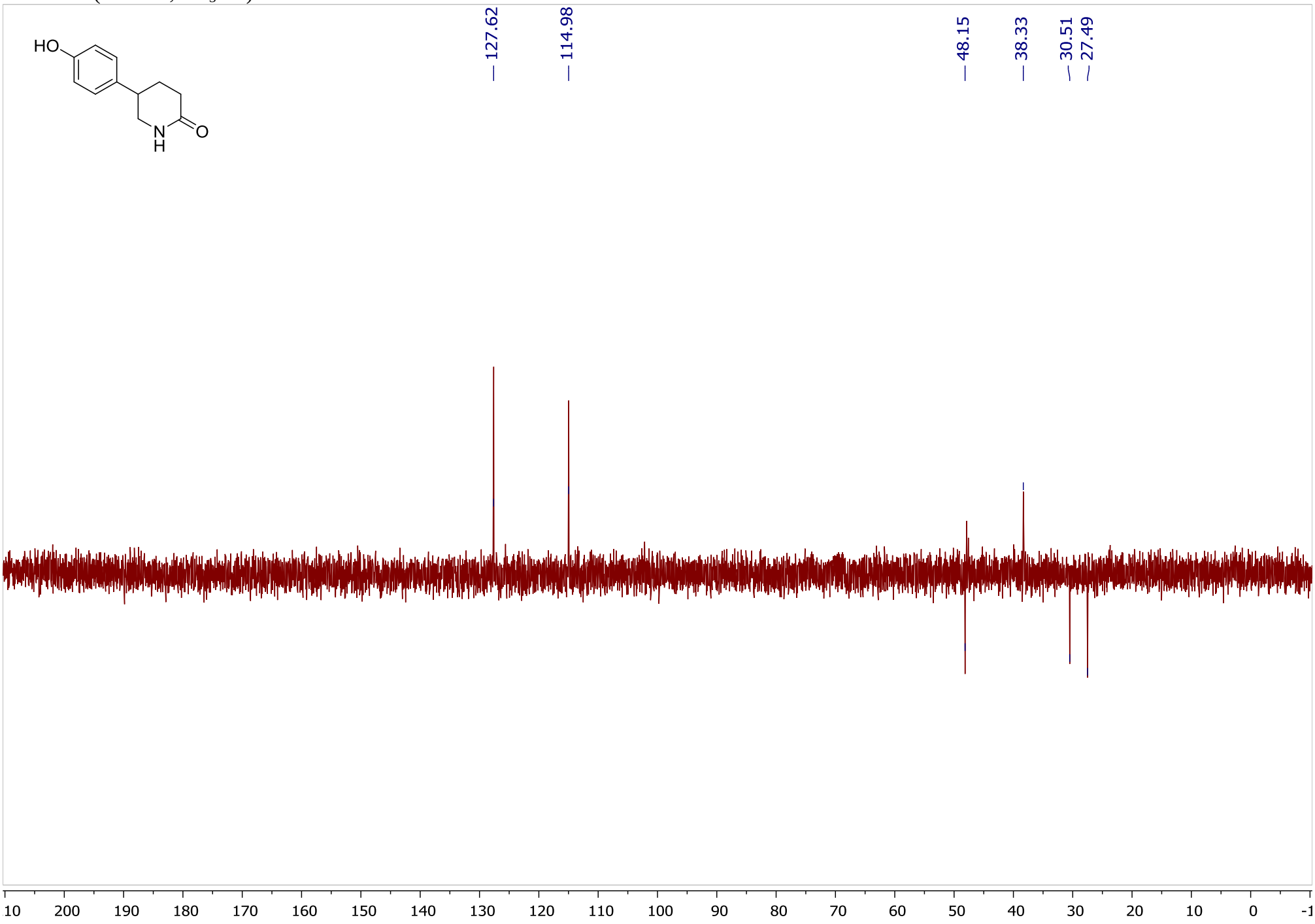
$^1$H NMR (300 MHz, $CD_3OD$)



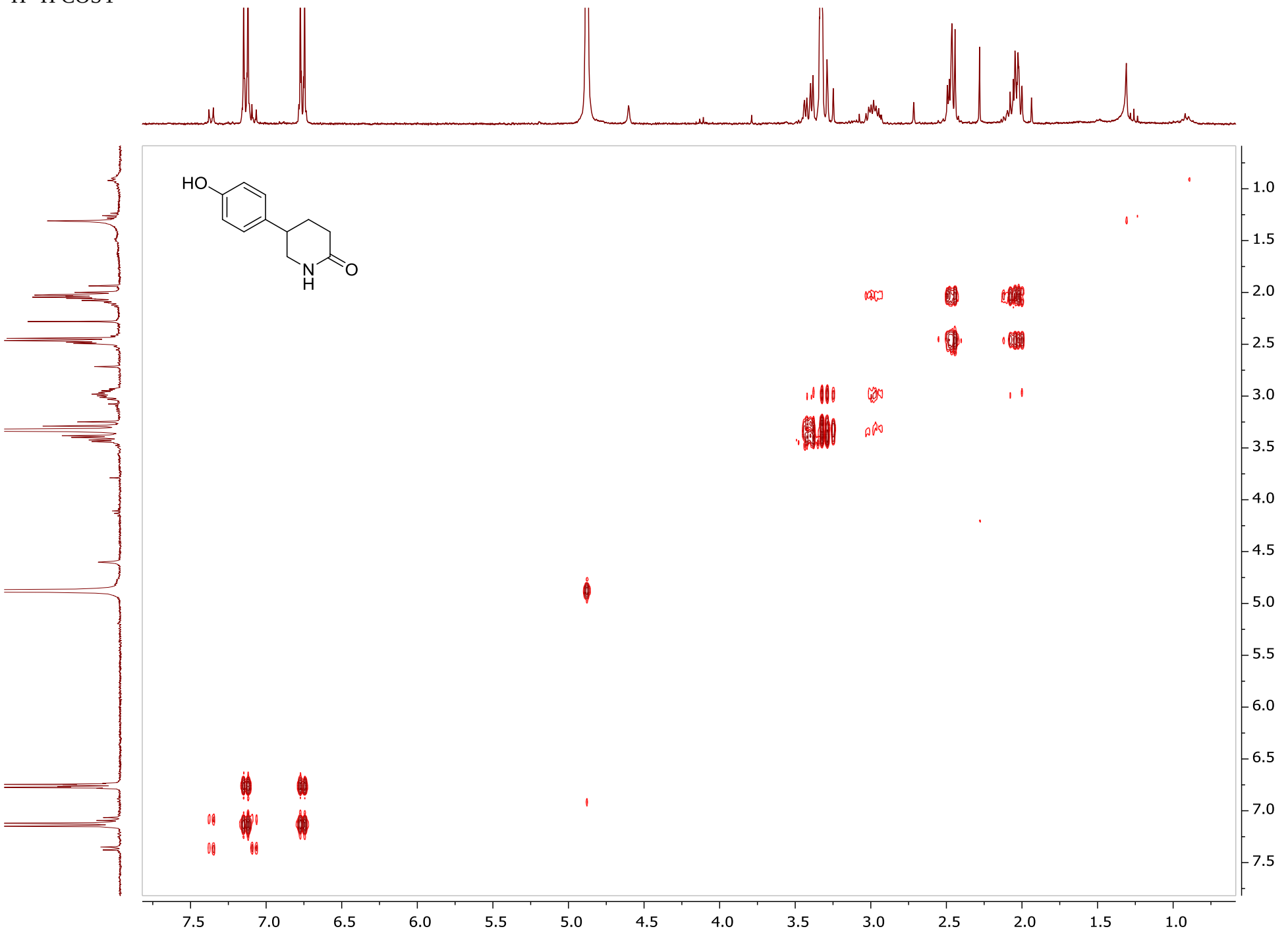
$^{13}$C NMR (75 MHz, $CD_3OD$)



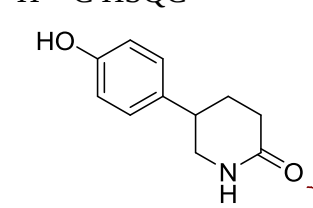
$^{13}$C DEPT (75 MHz, $CD_3OD$)



$^{1}$H-$^{1}$H COSY



$^{1}$H-$^{13}$C HSQC


HO
N
H
O


0
10
20
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40
50
60
70
80
90
100
110
120
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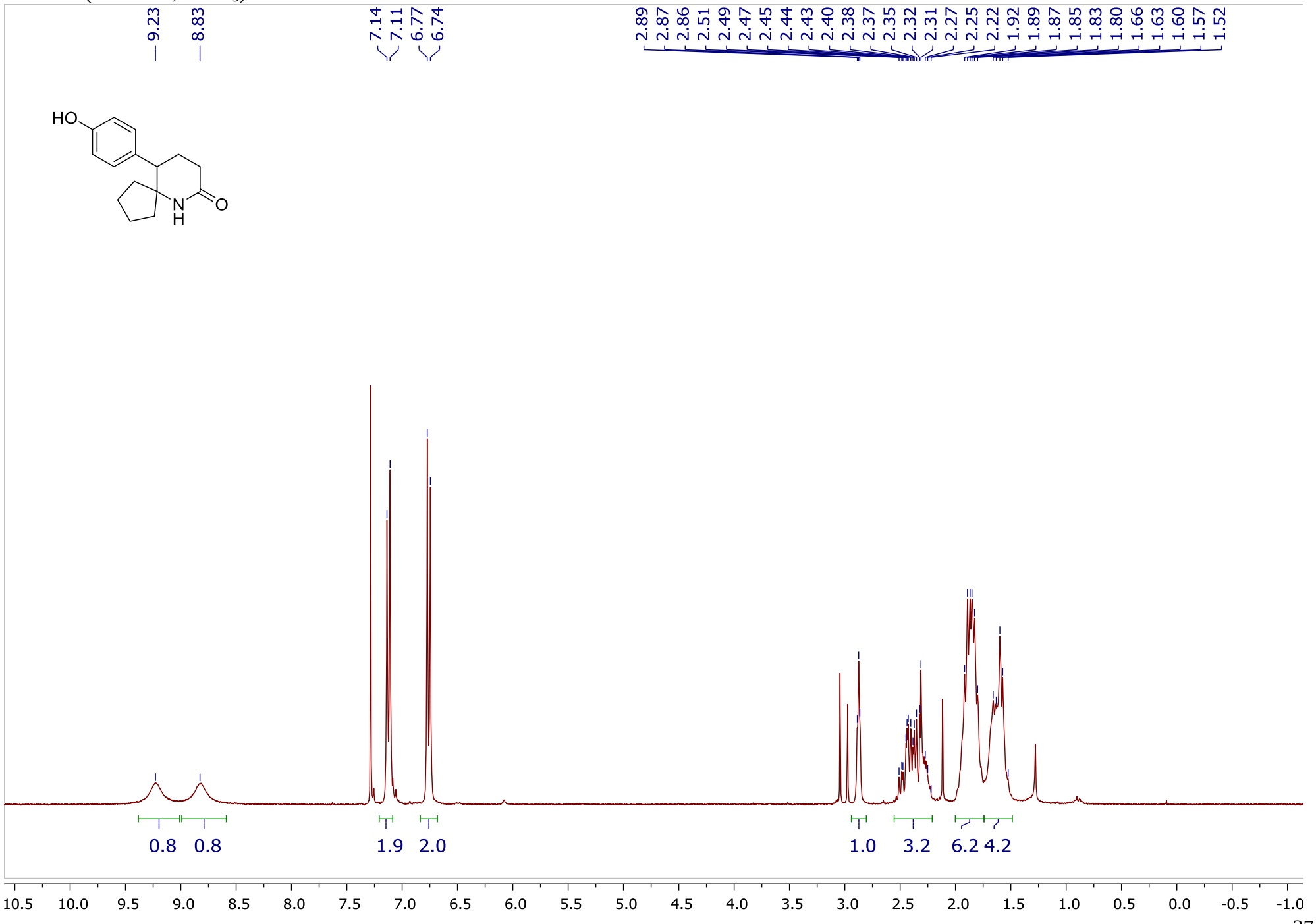
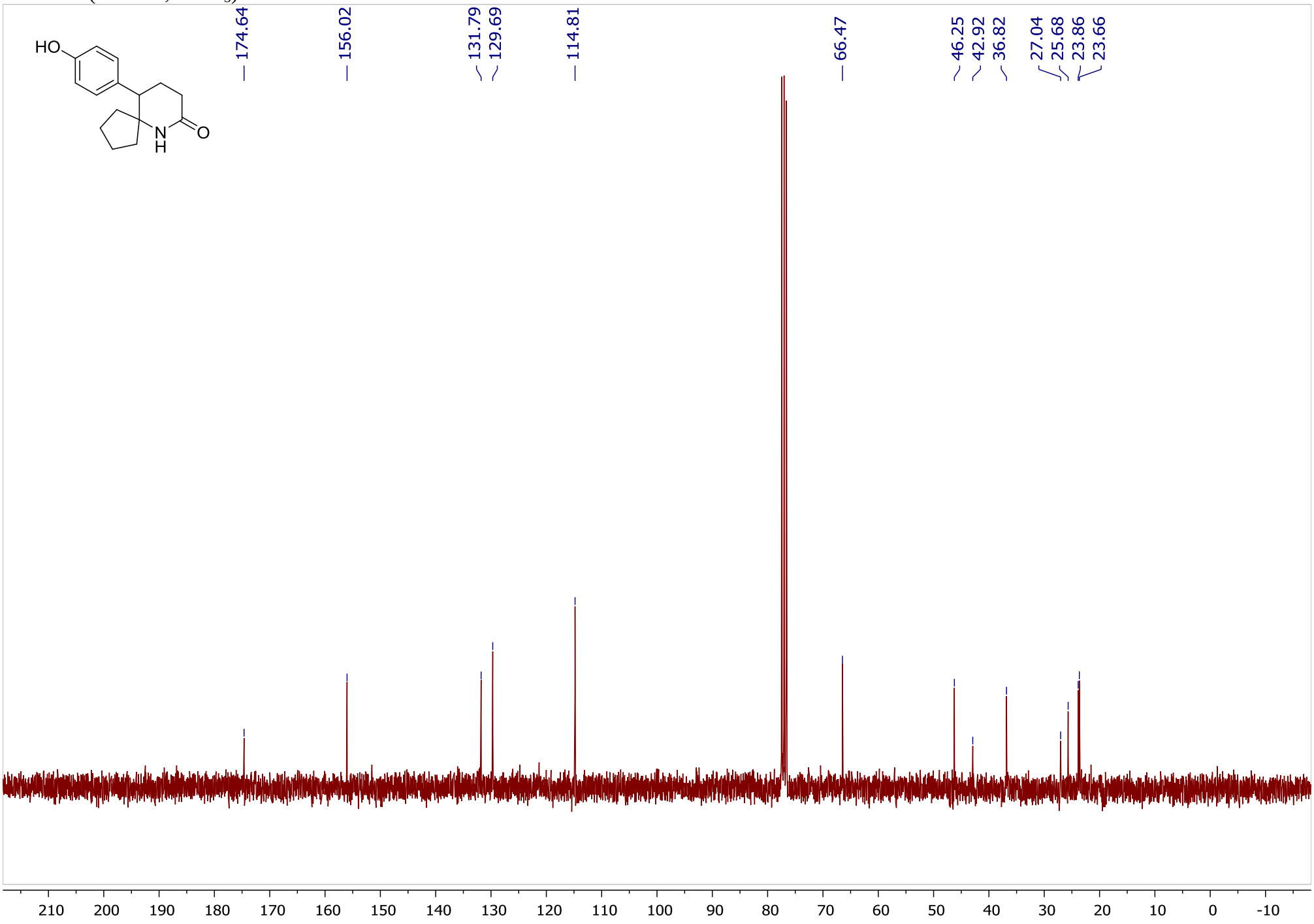
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**10-(4-Hydroxyphenyl)-6-azaspiro[4.5]decan-7-one (21)**

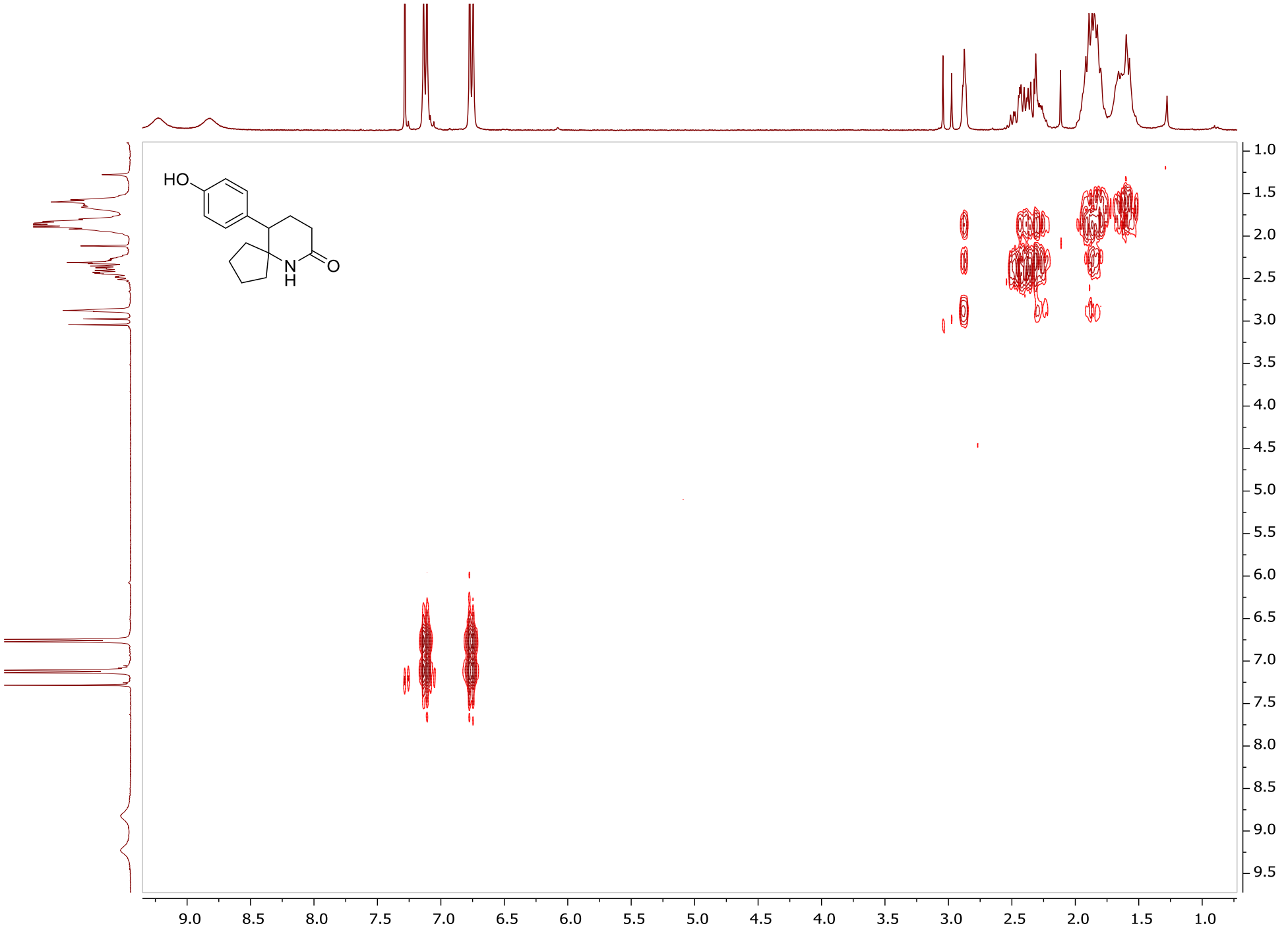
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}$C NMR (75 MHz, $CDCl_3$)



$^{1}$H-$^{1}$H COSY


HO
N
H
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
4.0
4.5
5.0
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7.0
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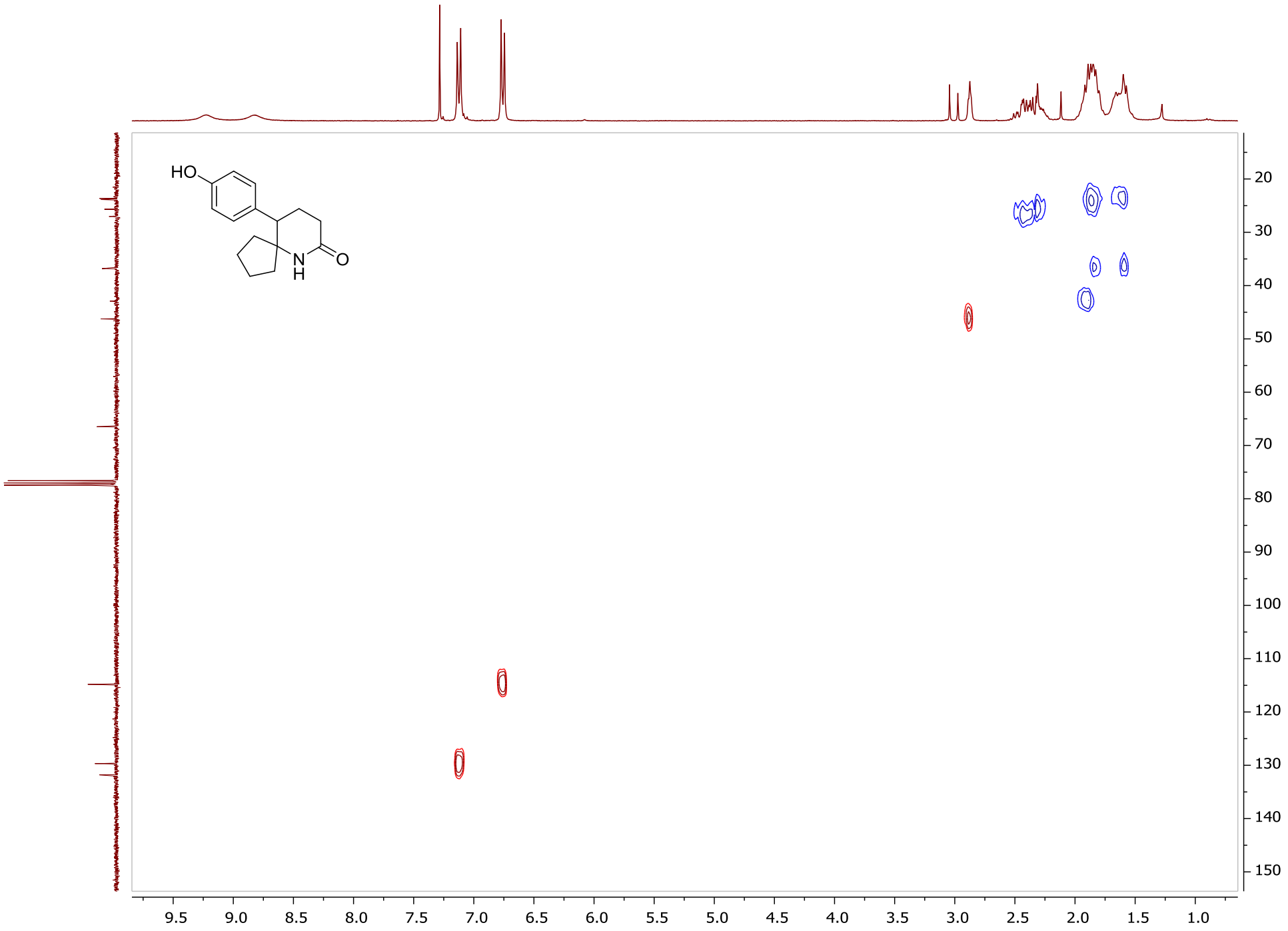
9.0
9.5

$^{1}H$-$^{13}C$ HSQC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N
H
O
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0