# Supporting information

# for

## 3-Halo-5,6-dihydro-4*H*-1,2-oxazine *N*-oxides as synthetic equivalents of unsaturated nitrile oxides in the [3+2]-cycloaddition with arynes. Synthesis of substituted 3-vinyl-1,2-benzisoxazoles

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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), ethyl acetate, and *tert*-butyl methyl ether (MTBE) were distilled. $CH_3CN$, $CH_2Cl_2$, $CHCl_3$ and toluene were distilled from $CaH_2$ prior to use. Triethylamine was distilled from $CaH_2$. Brine refers to saturated aqueous solution of NaCl. TLC was performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV and/or anisaldehyde/$H_2SO_4$/EtOH stain and/or $I_2$/silica. 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), 282 MHz ($^{19}$F NMR). Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad), app (apparent). Assignment was made using 2D NMR spectra for selected products. For other products signals were assigned by analogy. High resolution mass spectra were acquired on Bruker micrOTOF spectrometer using electrospray ionization (ESI). Melting points were determined in capillary tubes on melting point determination apparatus or on a Koffler melting point apparatus and are uncorrected.

### X-ray crystallography

X-ray diffraction data for **3ac** were collected at 100 K with a Bruker Quest D8 CMOS diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction data for **4da** 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 and the intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[s1a] Structures were solved using Intrinsic Phasing with the ShelXT[s1b] structure solution program in Olex2[s1c] and then refined with the XL[s1d,s1e] refinement package using Least-Squares minimization against $F^2_{hkl}$ in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Tables S1 and S2.

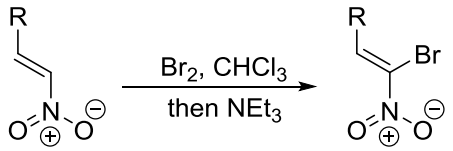
**Table S1.** Crystal data and structure refinement parameters for **3ac.**

| | |
|---|---|
| Empirical formula | $C_{15}H_{10}ClNO$ |
| Formula weight | 255.69 |
| T, K | 100 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Z | 4 |
| a, Å | 7.37990(10) |
| b, Å | 13.7636(3) |
| c, Å | 11.7474(2) |
| α, ° | 90 |
| β, ° | 91.6480(10) |
| γ, ° | 90 |
| V, $Å^3$ | 1192.74(4) |
| $D_{calc}$ (g $cm^{-3}$) | 1.424 |
| Linear absorption, $\mu$ ($cm^{-1}$) | 3.05 |
| F(000) | 528 |
| $2\theta_{max}$, ° | 58 |
| Reflections measured | 15544 |
| Independent reflections | 3168 |
| Observed reflections [$I > 2\sigma(I)$] | 2982 |
| Parameters | 163 |
| R1 | 0.0314 |
| wR2 | 0.0815 |
| GOF | 1.038 |
| $\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e $Å^{-3}$) | 0.337/-0.279 |

**Table S2.** Crystal data and structure refinement parameters for **4da.**

| | |
|---|---|
| Empirical formula | $C_{19}H_{18}BrNO_3$ |
| Formula weight | 388.25 |
| T, K | 100.00(10) |
| Wavelength, Å | 1.54184 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| a, Å | 8.15719(7) |
| b, Å | 16.71710(15) |
| c, Å | 12.13404(8) |
| α, ° | 90 |
| β, ° | 92.3390(7) |
| γ, ° | 90 |
| V, $Å^3$ | 1653.27(2) |
| Z | 4 |
| $D_{calc}$ (g $cm^{-3}$) | 1.560 |
| Absorption coefficient ($mm^{-1}$) | 3.534 |
| F(000) | 792 |
| Crystal size | 0.537 x 0.35 x 0.205 $mm^3$ |
| Theta range for data collection | 4.505 to 80.103°. |
| Index ranges | -10<=h<=10, -21<=k<=21, -15<=l<=14 |
| Reflections collected | 19247 |
| Independent reflections | 3602 [R(int) = 0.0440] |
| Observed reflections | 3575 |
| Completeness to theta = 67.684° | 100.0 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.664 and 0.351 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3602 / 0 / 221 |
| Goodness-of-fit on $F^2$ | 1.097 |
| Final R indices [I>2sigma(I)] | R1 = 0.0337, wR2 = 0.0908 |
| R indices (all data) | R1 = 0.0340, wR2 = 0.0910 |
| Extinction coefficient | 0.0061(3) |
| Largest diff. peak and hole | 0.714 and -0.914 e.$Å^{-3}$ |

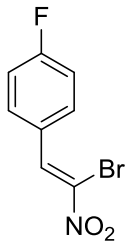
**Preparation of bromonitroalkenes (GP-1):**




Bromonitroalkenes were prepared using a reported procedure.[s2] as follows:

The solution of $Br_2$ (1.01 equiv.) in $CHCl_3$ (1.1 mL / 1 mmol of $Br_2$) was added to the corresponding nitroalkene. The mixture was refluxed for 3-6 h, cooled to 0 °C, and $Et_3N$ (1.3 equiv.) was added. The reaction mixture was maintained for 60 min and poured into a mixture of EtOAc (20 mL) and $H_2O$ (15 mL). The organic layer was washed with $H_2O$ (15 mL), brine (15 mL), dried ($Na_2SO_4$) and concentrated under reduced pressure to give title compound.

**(*Z*)-1-(2-Bromo-2-nitrovinyl)-4-fluorobenzene**

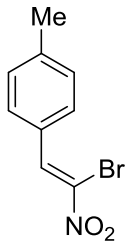



Starting nitroalkene was prepared according to the literature procedure.[s3]

Prepared from (*E*)-1-fluoro-4-(2-nitrovinyl)benzene (165 mg, 0.99 mmol) according to GP-1. The mixture was refluxed for 4 h. Yield: 223 mg (92%) of title compound as yellow solid, that was used without additional purification.

NMR matched previously reported data.[s4]

**(*Z*)-1-(2-Bromo-2-nitrovinyl)-4-methylbenzene**



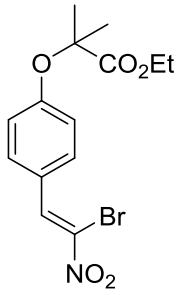

Starting nitroalkene was prepared according to the literature procedure.[s3]

Prepared from (*E*)-1-methyl-4-(2-nitrovinyl)benzene (148 mg, 0.91 mmol). according to GP-1. The mixture was refluxed for 4 h. Column chromatograpy (PE/EtOAc, 50:1) afforded 150 mg (68%) of title compound as yellow solid.

$R_f$ = 0.75 (PE/EtOAc, 10:1, UV, anisaldehyde).

NMR matched previously reported data.[s4]

**(*Z*)-Ethyl 2-(4-(2-bromo-2-nitrovinyl)phenoxy)-2-methylpropanoate**




Starting nitroalkene was prepared according to the literature procedure.[s3]

Prepared from ethyl (*E*)-2-methyl-2-(4-(2-nitrovinyl)phenoxy)propanoate (250 mg, 0.90 mmol) according to GP-1. The mixture was refluxed for 3 h. The crude product was subjected to column chromatography on silica gel (PE/ EtOAc, 20:1) to give 266 mg (83%) of title compound as yellow oil.

$R_f$ = 0.49 (PE/EtOAc, 5:1, UV, anisaldehyde).

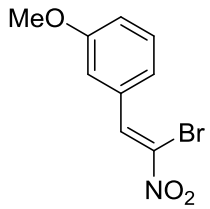
*Z*-configuration was assigned by similarity with other halonitroalkenes.[s3,s4]

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.69 (s, 6H, $Me_2C$), 4.26 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 6.91 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.88 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 8.63 (s, 1H, =CH).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 14.1 ($CH_2\underline{C}H_3$), 25.4 ($\underline{Me}_2C$), 61.8 ($O\underline{C}H_2CH_3$), 79.5 ($Me_2\underline{C}$–O), 118.0 ($CH_{Ar}$), 123.0 (C), 125.8 (C), 133.0 ($CH_{Ar}$), 136.1 (=CH), 159.1 ($\underline{C}_{Ar}$–O), 173.5 ($CO_2$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{14}H_{17}{}^{79}BrNO_5$ 358.0285; found: 358.0282.

**(*Z*)-1-(2-Bromo-2-nitrovinyl)-3-methoxybenzene**

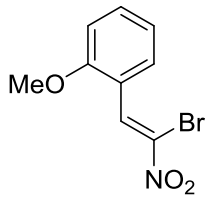



Mixture of $BrCH_2NO_2$ (50 μL, 100 mg, 0.71 mmol, 1.0 equiv.), 3-methoxybenzaldehyde (124 μL, 139 mg, 1.02 mmol, 1.43 equiv), and $NH_4OAc$ (19 mg, 0.25 mmol, 0.35 equiv.) in AcOH (5 mL) was refluxed for 2 h. After cooling to r.t., it was poured into a mixture of EtOAc (20 mL) and $H_2O$ (15 mL). The organic layer was washed with $H_2O$ (15 mL), $NaHCO_3$ (15mL), brine (15 mL), dried ($Na_2SO_4$) and concentrated under reduced pressure. Crude product was subjected to column chromatography on silica gel (PE/ EtOAc, 50:1) to give 50 mg (27%) of title compound as yellow solid.

$R_f$ = 0.75 (PE/EtOAc, 10:1, UV, anisaldehyde).

NMR matched previously reported data.[s5]

**(*Z*)-1-(2-Bromo-2-nitrovinyl)-2-methoxybenzene**

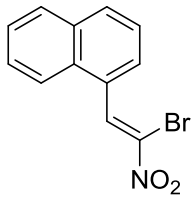



Starting nitroalkene was prepared according to the literature procedure.[s6]

Prepared from (*E*)-1-methoxy-2-(2-nitrovinyl)benzene (200 mg, 1.12 mmol) according to GP-1. The mixture was refluxed for 4 h. Yield: 288 mg (99%) of title compound as yellow solid, that was used without additional purification.

NMR matched previously reported data.[s4]

**(*Z*)-1-(2-Bromo-2-nitrovinyl)naphthalene**

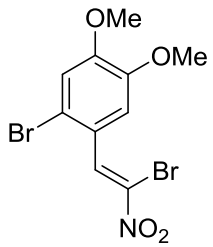



Starting nitroalkene was prepared according to the literature procedure.[s6]

Prepared from (*E*)-1-(2-nitrovinyl)naphthalene (200 mg, 1.00 mmol). according to GP-1. The mixture was refluxed for 6 h. Yield: 279 mg (99%) of title compound as yellow solid, that was used without additional purification.

NMR matched previously reported data.[s5]

**(*Z*)-1-Bromo-2-(2-bromo-2-nitrovinyl)-4,5-dimethoxybenzene**

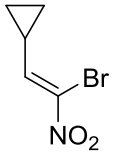



Starting nitroalkene was prepared according to the literature procedure.[s3]

Prepared from (*E*)-1-bromo-4,5-dimethoxy-2-(2-nitrovinyl)benzene (165 mg, 0.57 mmol) according to GP-1. The mixture was refluxed for 4 h. Yield: 206 mg (98%) of title compound as yellow solid, that was used without additional purification.

NMR matched previously reported data.[s7]

**(*Z*)-(2-Bromo-2-nitrovinyl)cyclopropane**




Bromonitromethane (300 mg, 150 μL, 2.14 mmol, 1.5 equiv.) was dissolved in THF/$^{t}$BuOH mixture (0.72 mL/0.72 mL). The solution was cooled to 0 °C (ice bath) and then $^{t}$BuOK (16 mg, 0.14 mmol, 0.1 equiv) and cyclopropanecarbaldehyde (100 mg, 1.3 mmol, 1 equiv.) were consequtively added. The reaction was allowed to warm to r.t., stirred overnight (14 h) and poured into a mixture of EtOAc (15 mL) and $H_2O$ (15 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous $Na_2SO_4$, and carefully concentrated under reduced pressure (37 °C, 150 mbar) to give 200 mg (67%) of crude 2-bromo-1-cyclopropyl-2-nitroethan-1-ol that was used without further purification.

To the cold solution (0 ℃) of 2-bromo-1-cyclopropyl-2-nitroethan-1-ol (200 mg, 0.95 mmol) in $CH_2Cl_2$ (3.8 mL) was added MsCl (100 μL, 164 mg, 1.43 mmol, 1.5 equiv.). After 20 min of stirring, freshly distilled $Et_3N$ (330 μL, 241 mg, 2.38 mmol, 2.5 equiv.) was added dropwise over 10 min. The reaction mixture was stirred for 60 min, kept in a fridge (0 ℃) overnight (14 h) and poured into a mixture of $Et_2O$ (50 mL) and $NaHSO_4$ aq. solution (0.5 M, 50 mL). The organic phase was separated, and the aqueous phase was extracted with $Et_2O$ (50 mL). The combined organic layers were washed with brine (50 mL), dried ($Na_2SO_4$), and carefully concentrated under reduced pressure (37 °C, 150 mbar). The resulting crude product was subjected to column chromatography on silica gel (eluent: PE/EtOAc, 5:1, then 2:1) to give 138 mg (75%) of target nitroalkene as yellow oil.

$R_f$ = 0.75 (PE/EtOAc, 10:1, UV, anisaldehyde).

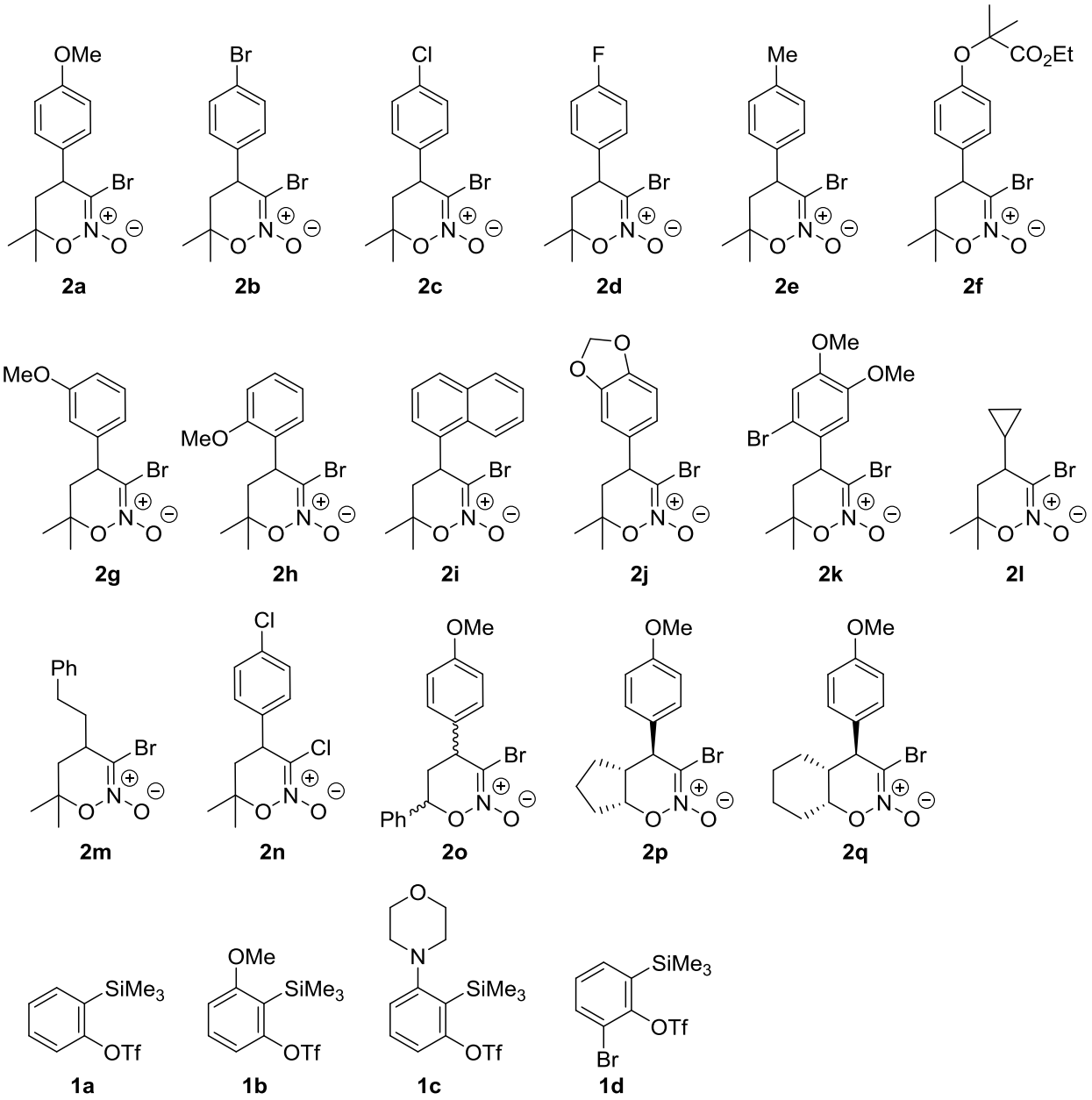
*Z*-configuration was assigned by similarity with other halonitroalkenes.[s3,s4]

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 0.92-0.98 (m, 2H), 1.24-1.30 (m, 2H), 1.85 (dtt, *J* = 10.6, 7.9, 4.5 Hz, 1H, CH), 7.15 (d, *J* = 10.6 Hz, 1H, =CH).

$^{13}$C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 10.2 ($CH_2$), 14.7 (CH), 128.1 (Br–C–$NO_2$), 147.2 (=CH).

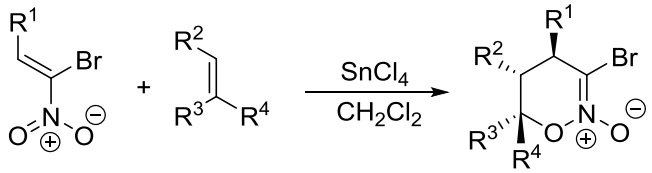
HRMS (ESI-TOF): *m/z* $[M + Na]^+$calcd. for $C_5H_6{}^{79}BrNO_2Na$ 213.9474; found: 213.9478.

**List of starting compounds 1-2.**




Arynes precursors **1** were commercially available and were used as received.

**Preparation of starting 5,6-dihydro-4*H*-1,2-oxazine *N*-oxides 2 (GP-2):**

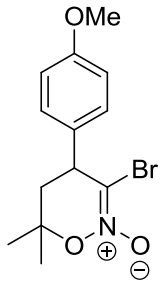



Nitronates **2** were prepared using a reported procedure[s2] as follows:

$SnCl_4$ (1.1-1.2 equiv) was added to the stirred solution of the corresponding bromonitroalkene (1 equiv.) in $CH_2Cl_2$ (0.066 – 0.1 M) at -78 °C (unless otherwise stated) under

argon atmosphere. The reaction mixture was stirred for 10 min and then the corresponding alkene (2-30 equiv.) was added. The reaction mixture was stirred for 15 min – 72 h and then poured into a mixture of EtOAc (150 mL) and $NaHCO_3$ (sat. aq. soln, 100 mL). The organic layer was washed with saturated aqueous solution of $NaHCO_3$ (sat. aq. soln, 50 mL), $H_2O$ (100 mL), brine (50 mL), dried over $Na_2SO_4$, and evaporated under vacuum. Title compounds were isolated by column chromatography or recrystallistion from PE/EtOAc mixture.

**3-Bromo-4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2a**

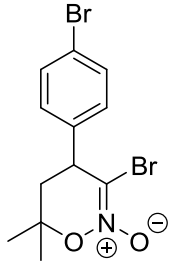



Starting bromonitroalkene was prepared according to the literature procedure.[s2]

Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene (2.50 g, 9.7 mmol) and 2-methylpropene (2.7 g, 49 mmol, 5 equiv.) in $CH_2Cl_2$ (97 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -50 °C for 30 min. Recrystallization (hexane–EtOAc, 3:1) afforded 2.69 g (88%) of title compound as pale white crystals.

NMR matched previously reported data.[s2]

**3-Bromo-4-(4-bromophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2b**




Starting bromonitroalkene was prepared according to the literature procedure.[s8]

Prepared according to GP-2 from (*Z*)-1-bromo-4-(2-bromo-2-nitrovinyl)benzene (376 mg, 1.22 mmol) and 2-methylpropene (1.37 g, 25 mmol, 20 equiv.) in toluene (12.3 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -50 °C for 30 min and then kept at the fridge (-30˚C) for 60 h. Column chromatography (eluent: PE/EtOAc, 5:1, then 1:1) afforded 250 mg (56%) of target compound as white solid.

$R_f$ = 0.24 (PE/EtOAc, 3:1, UV, anisaldehyde).

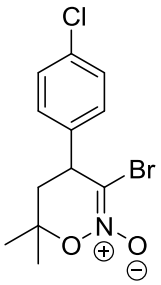
mp = 127-128 °C (PE/EtOAc, 3:1).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me(6)), 1.54 (s, 3H, Me(6)), 2.15 (dd, *J* = 13.9, 11.0 Hz, 1H, $CH_{2a}$(5)), 2.27 (dd, *J* = 13.9, 8.0 Hz, 1H, $CH_{2b}$(5)), 4.03 (dd, *J* = 11.0, 8.0 Hz, 1H, CH(4)), 7.10 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$), 7.52 (d, *J* = 8.4 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.2 (Me(6)), 27.3 (Me(6)), 43.3 ($CH_2$(5)), 47.0 (CH(4)), 83.3 (C(6)), 109.6 (C(3)=N), 122.0 ($C_{Ar}$), 129.6 ($CH_{Ar}$), 132.4 ($CH_{Ar}$), 139.0 ($C_{Ar}$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{12}H_{14}{}^{79}Br^{81}Br\,NO_2$ 363.9366; found: 363.9365.

**3-Bromo-4-(4-chlorophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2c**




Starting bromonitroalkene was prepared according to the literature procedure.[s8]

Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-chlorobenzene (228 mg, 0.87 mmol) and 2-methylpropene (244 mg, 4.3 mmol, 5 equiv.) in $CH_2Cl_2$ (13.2 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 60 min and then kept at the fridge (-30 °C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 3:1, then 1:1) afforded 100 mg (56%) of target compound as white solid and 112 mg (49%) of starting bromonitroalkene.

$R_f$ = 0.30 (PE/EtOAc, 2:1, UV, anisaldehyde).

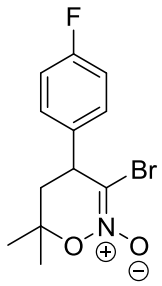
mp = 129-131 °C (dec.).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me(6)), 1.54 (s, 3H, Me(6)), 2.15 (dd, *J* = 13.8, 11.1 Hz, 1H, $CH_{2a}$(5)), 2.27 (dd, *J* = 13.9, 8.0 Hz, 1H, $CH_{2b}$(5)), 4.04 (dd, *J* = 10.9, 8.0 Hz, 1H, CH(4)), 7.16 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.36 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.2 (Me(6)), 27.3 (Me(6)), 43.3 ($CH_2$(5)), 46.9 (CH(4)), 83.3 (C(6)), 109.7 (C(3)=N), 129.2 ($CH_{Ar}$), 129.4 ($CH_{Ar}$), 133.9 ($C_{Ar}$), 138.5 ($C_{Ar}$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{12}H_{14}{}^{79}BrClNO_2$ 317.9891; found: 317.9896.

**3-Bromo-4-(4-fluorophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2d**




Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-fluorobenzene (220 mg, 0.89 mmol) and 2-methylpropene (250 mg, 4.5 mmol, 5 equiv.) in $CH_2Cl_2$ (13.6 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 30 min and then kept at the fridge (-30˚C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 10:1, then 2:1) afforded 161 mg (60%) of target compound as pale yellow solid.

$R_f$ = 0.33 (PE/EtOAc, 3:1, UV, anisaldehyde).

mp = 122-124 °C (dec.) (PE/EtOAc, 5:1).

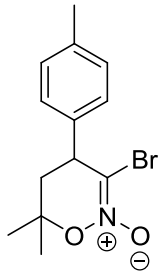
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me), 1.55 (s, 3H, Me), 2.17 (dd, *J* = 13.8, 11.1 Hz, 1H, $CH_{2a}$(5)), 2.27 (dd, *J* = 13.9, 8.0 Hz, 1H, $CH_{2b}$(5)), 4.04 (dd, *J* = 10.9, 8.0 Hz, 1H, CH(4)), 7.07 (t, *J* = 8.6 Hz, 2H, $CH_{Ar}$), 7.20 (dd, *J* = 8.7, 5.2 Hz, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.2 (Me), 27.3 (Me), 43.5 ($CH_2$(5)), 46.8 (CH(4)), 83.3 (C(6)), 110.2 (C(3)=N), 116.2 (d, $^2J_{CF}$ = 21.8 Hz, $CH_{Ar}$), 129.5 (d, $^3J_{CF}$ = 8.2 Hz, $CH_{Ar}$), 135.8 (d, $^4J_{CF}$ = 3.3 Hz, $C_{Ar}$), 162.3 (d, $^1J_{CF}$ = 247.4 Hz, C–F).

$^{19}$F NMR (282 MHz, $CDCl_3$): δ -113.8 (tt, *J* = 8.4, 5.2 Hz).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{12}H_{14}F^{79}BrNO_2$ 302.0186; found: 302.0184.

**3-Bromo-6,6-dimethyl-4-*p*-tolyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2e**




Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methylbenzene (140 mg, 0.58 mmol) and 2-methylpropene (325 mg, 5.8 mmol, 10 equiv.) in $CH_2Cl_2$ (5.8 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 30 min, then additional portion of 2-methylpropene (325 mg, 5.8 mmol, 10 equiv.) was added and the reaction mixture was stirred for 2 h. Column chromatography (eluent: PE/EtOAc, 3:1 then 2:1) afforded 123 mg (72%) of target compound as pale yellow solid.

$R_f$ = 0.43 (PE/EtOAc, 3:1, UV, anisaldehyde).

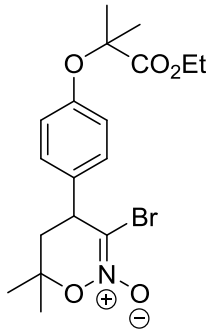
mp = 124-125 °C (PE/EtOAc, 3:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me), 1.55 (s, 3H, Me), 2.12- 2.32 (m, 2H, $CH_2$(5)), 2.37 (s, 3H, Ar–C$\underline{H}_3$), 4.01 (dd, *J* = 10.8, 8.2 Hz, 1H, CH(4)), 7.11 (d, *J* = 8.0 Hz, 2H, $CH_{Ar}$), 7.20 (d, *J* = 8.0 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 21.2 (Me), 22.2 (Me), 27.3 (Ar–$\underline{C}H_3$), 43.5 ($CH_2$(5)), 47.1 (CH(4)), 83.3 (C(6)), 110.8 (C(3)=N), 127.7 ($CH_{Ar}$), 129.9 ($CH_{Ar}$), 137.0 ($C_{Ar}$), 137.9 ($C_{Ar}$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{17}{}^{79}BrNO_2$ 298.0437; found: 298.0427.

**3-Bromo-4-(4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2f**




Prepared according to GP-2 from ethyl (*Z*)-2-(4-(2-bromo-2-nitrovinyl)phenoxy)-2-methylpropanoate (260 mg, 0.73 mmol) and 2-methylpropene (814 mg, 14 mmol, 20 equiv.) in $CHCl_3$ (11 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 3 h and then kept at the fridge (-30 °C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 10:1 then 3:1 then 1:1) afforded 157 mg (52%) of target compound as colorless oil.

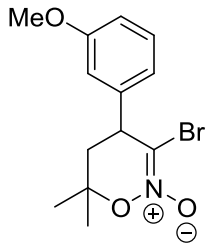
$R_f$ = 0.30 (PE/EtOAc, 3:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.42 (s, 3H, Me(6)), 1.51 (s, 3H, Me(6)), 1.59 (s, 6H, $Me_2C$), 2.11-2.27 (m, 2H, $CH_2$(5)), 3.96 (dd, *J* = 10.8, 8.1 Hz, 1H, CH(4)), 4.22 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 6.81 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.06 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 14.1 ($CH_2\underline{C}H_3$), 22.2 (Me(6)), 25.37 and 25.41 ($\underline{Me}_2C$), 27.3 (Me(6)), 43.4 ($CH_2$(5)), 46.7 (CH(4)), 61.5 ($O\underline{C}H_2CH_3$), 79.2 ($Me_2\underline{C}$–O), 83.3 (C(6)), 111.9 (C(3)=N), 119.4 ($CH_{Ar}$), 128.7 ($CH_{Ar}$), 133.2 ($C_{Ar}$), 155.2 ($\underline{C}_{Ar}$–O), 174.0 ($CO_2$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{18}H_{25}{}^{79}BrNO_5$ 414.0911; found: 414.0903.

**3-Bromo-4-(3-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2g**




Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-3-methoxybenzene (50 mg, 0.19 mmol) and 2-methylpropene (300 mg, 5.4 mmol, 28 equiv.) in $CH_2Cl_2$ (2.95 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 60 min and then kept at the fridge (-30 °C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 5:1, then 1:1) afforded 40 mg (66%) of target compound as pale yellow solid.

$R_f$ = 0.51 (PE/EtOAc, 3:1, UV, anisaldehyde).

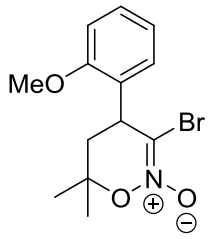
mp = 126-128 °C (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, 3H, Me), 1.55 (s, 3H, Me), 2.16-2.31 (m, 2H, $CH_2$(5)), 3.83 (s, 3H, OMe), 4.02 (dd, *J* = 10.6, 8.3 Hz, 1H, CH(4)), 6.74 (br s, 1H, $CH_{Ar}$), 6.81 (br d, *J* = 7.6 Hz, 1H, $CH_{Ar}$), 6.88 (dd, *J* = 8.2, 2.0 Hz, 1H, $CH_{Ar}$), 7.31 (app t, *J* = 7.0 Hz, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.2 (Me), 27.3 (Me), 43.3 ($CH_2$(5)), 47.5 (CH(4)), 55.4 (OMe), 83.3 (C(6)), 110.3 (C(3)=N), 113.3 ($CH_{Ar}$), 113.6 ($CH_{Ar}$), 120.1 ($CH_{Ar}$), 130.2 ($CH_{Ar}$), 141.5 ($C_{Ar}$), 160.1 ($\underline{C}_{Ar}$–OMe).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{17}{}^{79}BrNO_3$ 314.0386; found: 314.0392.

**3-Bromo-4-(2-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2h**




Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-2-methoxybenzene (200 mg, 0.78 mmol) and 2-methylpropene (217 mg, 3.9 mmol, 5 equiv.) in $CH_2Cl_2$ (11.7 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 60 min and then kept at the fridge (-30 °C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 3:1) afforded 203 mg (60%) of target compound as white solid.

$R_f$ = 0.51 (PE/EtOAc, 3:1, UV, anisaldehyde).

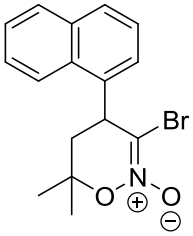
mp = 129-130 °C (dec.) (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.43 (s, 3H, Me), 1.55 (s, 3H, Me), 2.19 (d, *J* = 9.4 Hz, 2H, $CH_2$(5)), 3.86 (s, 3H, OMe), 4.36 (t, *J* = 9.4 Hz, 1H, CH(4)), 6.93 (app d, *J* = 8.3 Hz, 1H, $CH_{Ar}$), 6.97 (app td, *J* = 7.5, 1.0 Hz, 1H, $CH_{Ar}$), 7.13 (dd, *J* = 7.5, 1.7 Hz, 1H, $CH_{Ar}$), 7.31 (app td, *J* = 8.3, 1.7 Hz, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 22.2 (Me), 27.4 (Me), 40.7 ($CH_2$(5)), 42.3 (CH(4)), 55.7 (OMe), 83.2 (C(6)), 111.2 ($CH_{Ar}$ and C(3)=N), 121.1 ($CH_{Ar}$), 127.9 ($C_{Ar}$), 129.2 ($CH_{Ar}$), 129.3 ($CH_{Ar}$), 156.7 ($C_{Ar}$–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{17}{}^{79}BrNO_3$ 314.0386; found: 314.0388.

**3-Bromo-6,6-dimethyl-4-(naphthalen-1-yl)-5,6-dihydro-4H-1,2-oxazine 2-oxide 2i**




Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)naphthalene (190 mg, 0.68 mmol) and 2-methylpropene (192 mg, 3.4 mmol, 5 equiv.) in $CH_2Cl_2$ (10.3 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 60 min, then additional portion of 2-methylpropene (192 mg, 3.4 mmol, 5 equiv.) was added. The resulting mixture was stirred for additional 90 min. Column chromatography (eluent: PE/EtOAc, 3:1, then 2:1) afforded 55 mg (24%) of target compound as pale yellow solid and 110 mg (58%) of starting nitroalkene.

$R_f$ = 0.38 (PE/EtOAc, 3:1, UV, anisaldehyde).

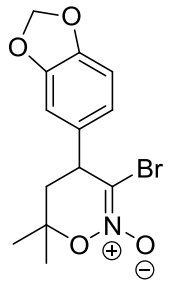
mp = 153-154 °C (dec.) (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.47 (s, 3H, Me(6)), 1.66 (s, 3H, Me(6)), 2.40 (d, *J* = 9.4 Hz, 2H, $CH_2$(5)), 4.78 (t, *J* = 9.4 Hz, 1H, CH(4)), 7.39 (app d, *J* = 7.1 Hz, 1H, $CH_{Ar}$), 7.46-7.61 (m, 3H, $CH_{Ar}$), 7.86 (d, *J* = 8.1 Hz, 1H, $CH_{Ar}$), 7.91-7.95 (m, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 22.5 (Me(6)), 27.5 (Me(6)), 42.0 ($CH_2$(5)), 45.0 (br, CH(4)), 83.7 (C(6)), 111.1 (C(3)=N), 122.1 ($CH_{Ar}$), 125.7 ($CH_{Ar}$), 126.1 ($CH_{Ar}$), 126.8 (br, $CH_{Ar}$), 127.0 ($CH_{Ar}$), 128.9 ($CH_{Ar}$), 129.5 ($CH_{Ar}$), 130.5 ($C_{Ar}$), 134.3 ($C_{Ar}$), 135.5 ($C_{Ar}$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{17}{}^{79}BrNO_2$ 334.0437; found: 334.0425.

**4-(Benzo[d][1,3]dioxol-5-yl)-3-bromo-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2j**



Starting bromonitroalkene was prepared according to the literature procedure.[s8]

Prepared according to GP-2 from (*Z*)-5-(2-bromo-2-nitrovinyl)benzo[d][1,3]dioxole (515 mg, 1.9 mmol) and 2-methylpropene (1.59 g, 28 mmol, 15 equiv.) in $CH_2Cl_2$ (19 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -50 °C for 90 min. Column chromatography (eluent: PE/EtOAc, 3:1, then 2:1) afforded 395 mg (64%) of target compound as pale yellow solid.

$R_f$ = 0.41 (PE/EtOAc, 2:1, UV, anisaldehyde).

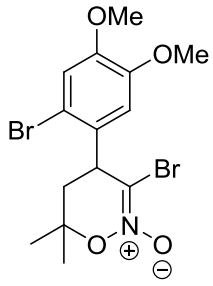
mp = 135-136 °C (dec.) (PE/EtOAc, 2:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 3H, Me(6)), 1.52 (s, 3H, Me(6)), 2.12-2.28 (m, 2H, $CH_2$(5)), 3.95 (dd, *J* = 10.8, 8.1 Hz, 1H, CH(4)), 5.98 (s, 2H, O–$CH_2$–O), 6.66-6.69 (m, 2H, 2×$CH_{Ar}$), 6.79 (d, *J* = 8.4 Hz, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.2 (Me(6)), 27.3 (Me(6)), 43.4 ($CH_2$(5)), 47.2 (CH(4)), 83.3 (C(6)), 101.4 (O–$CH_2$–O), 108.0 ($CH_{Ar}$), 108.6 ($CH_{Ar}$), 110.7 (C(3)=N), 121.4 ($CH_{Ar}$), 133.6 ($C_{Ar}$), 147.4 ($\underline{C}_{Ar}$–O), 148.3 ($\underline{C}_{Ar}$–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{15}{}^{79}BrNO_4$ 328.0179; found: 328.0178.

**3-Bromo-4-(2-bromo-4,5-dimethoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2k**



Prepared according to GP-2 from (*Z*)-1-bromo-2-(2-bromo-2-nitrovinyl)-4,5-dimethoxybenzene (185 mg, 0.50 mmol) and 2-methylpropene (283 mg, 5.0 mmol, 10 equiv.) in $CH_2Cl_2$ (5.0 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 30 min. Column chromatography (eluent: PE/EtOAc, 5:1 then 1:1) afforded 100 mg (47%) of target compound as pale yellow solid.

$R_f$ = 0.38 (PE/EtOAc, 3:1, UV, anisaldehyde).

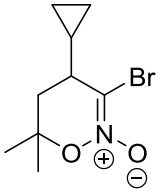
mp = 152-153 °C (dec.) (PE/EtOAc, 5:1).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me), 1.55 (s, 3H, Me), 2.06 (dd, *J* = 13.9, 10.9 Hz, 1H, $CH_{2a}$(5)), 2.30 (dd, *J* = 13.9, 7.9 Hz, 1H, $CH_{2b}$(5)), 3.86 (s, 3H, OMe), 3.87 (s, 3H, OMe), 4.50 (dd, *J* = 10.9, 7.9 Hz, 1H, CH(4)), 6.61 (s, 1H, $CH_{Ar}$), 7.00 (s, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.1 (Me), 27.3 (Me), 41.1 ($CH_2$(5)), 46.7(CH(4)), 56.2 (OMe), 56.4 (OMe), 83.5 (C(6)), 109.8 (C(3)=N), 111.3 ($CH_{Ar}$), 113.4 ($C_{Ar}$–Br), 115.6 ($CH_{Ar}$), 130.5 ($C_{Ar}$), 149.3 ($\underline{C}_{Ar}$–OMe), 149.4 ($\underline{C}_{Ar}$–OMe).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{14}H_{18}{}^{79}Br_2NO_4$ 423.9577; found: 423.9565.

**3-Bromo-4-cyclopropyl-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2l**




Prepared according to GP-2 from (Z)-(2-bromo-2-nitrovinyl)cyclopropane (136 mg, 0.71 mmol) and 2-methylpropene (200 mg, 3.5 mmol, 5 equiv.) in $CH_2Cl_2$ (11 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 3 h. Column chromatography (eluent: PE/EtOAc, 5:1, then 2:1) afforded 108 mg (52%) of target compound as white solid.

$R_f$ = 0.40 (PE/EtOAc, 3:1, UV, anisaldehyde).

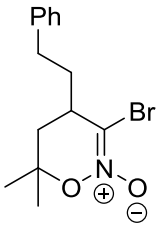
mp = 81-82 °C

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 0.10-0.19 (m, 1H), 0.46-0.64 (m, 2H), 0.73-0.90 (m, 2H), 1.36 (s, 3H, Me), 1.42 (s, 3H, Me), 1.94-2.07 (m, 3H, CH(4) and $CH_2$(5)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 2.8 ($CH_2$), 6.8 ($CH_2$), 16.1 (CH), 22.9 (Me), 27.3 (Me), 40.1 ($CH_2$(5)), 44.5 (CH(4)), 82.9 (C(6)), 112.1 (C(3)=N).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_9H_{15}{}^{79}BrNO_2$ 248.0281; found: 248.0279.

**3-Bromo-6,6-dimethyl-4-phenethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2m**




Starting bromonitroalkene was prepared according to the literature procedure.[s8]

Prepared according to GP-2 from (*Z*)-(4-bromo-4-nitrobut-3-en-1-yl)benzene (170 mg, 0.66 mmol) and 2-methylpropene (372 mg, 6.6 mmol, 10 equiv.) in $CH_2Cl_2$ (10.1 ml) using 1.2

equiv of $SnCl_4$. The reaction was stirred at -30 °C for 60 min and then kept at the fridge (-30 °C) for 72 h. Column chromatography (eluent: PE/EtOAc, 5:1, then 2:1) afforded 108 mg (52%) of target compound as colorless solid.

$R_f$ = 0.24 (PE/EtOAc, 3:1, UV, anisaldehyde).

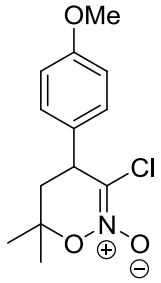
mp = 90-92 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 3H, Me), 1.45 (s, 3H, Me), 1.78-1.91 (m, 1H, $PhCH_2C\underline{H}_{2a}$), 1.95 (dd, *J* = 13.5, 10.0 Hz, 1H, $CH_{2a}$(5)), 2.08 (dd, *J* = 13.5, 7.9 Hz, 1H, $CH_{2b}$(5)), 2.23 (dddd, *J* = 13.8, 10.3, 6.7, 3.4 Hz, 1H, $PhCH_2C\underline{H}_{2b}$), 2.60 (ddd, *J* = 13.7, 10.1, 6.7 Hz, 1H, $PhC\underline{H}_{2a}$), 2.74 (ddd, *J* = 13.7, 10.5, 5.0 Hz, 1H, $PhC\underline{H}_{2b}$), 2.82-2.93 (m, 1H, CH(4)), 7.18-7.27 (m, 3H, $CH_{Ph}$),7.29-7.35 (m, 2H, $CH_{Ph}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.5 (Me), 27.4 (Me), 32.0 ($CH_2$), 35.6 ($CH_2$), 39.0 ($CH_2$), 39.2 (CH(4)), 82.8 (C(6)), 112.4 (C(3)=N), 126.4 ($CH_{Ph}$), 128.3 ($CH_{Ph}$), 128.7 ($CH_{Ph}$), 140.4 ($C_{Ph}$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{14}H_{19}{}^{79}BrNO_2$ 312.0594; found: 312.0590.

**3-Chloro-4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2n**




Starting chloronitroalkene was prepared according to the literature procedure. [s3]

Prepared according to GP-2 from (*Z*)-1-(2-chloro-2-nitrovinyl)-4-methoxybenzene (200 mg, 0.94 mmol) and 2-methylpropene (263 mg, 4.7 mmol, 5 equiv.) in $CH_2Cl_2$ (14.2 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -78 °C for 60 min and then kept at the fridge (-30 °C) overnight (14 h). Column chromatography (eluent: PE/EtOAc, 3:1, then 1:1) afforded 200 mg (79%) of target compound as white solid.

$R_f$ = 0.29 (PE/EtOAc, 2:1, UV, anisaldehyde).

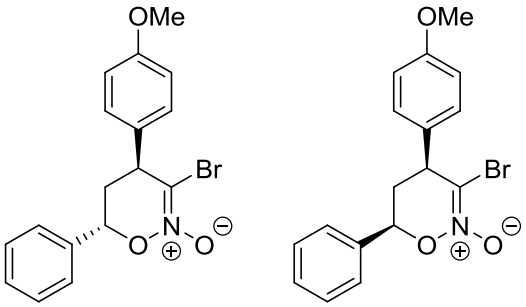
mp = 148-150 °C (dec.)

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H, Me), 1.53 (s, 3H, Me), 2.16 (dd, *J* = 13.9, 11.1 Hz, 1H, $CH_{2a}$(5)), 2.27 (dd, *J* = 13.9, 8.0 Hz, 1H, $CH_{2b}$(5)), 3.81 (s, 3H, OMe), 3.94 (dd, *J* = 11.1, 8.0 Hz, 1H, CH(4)), 6.90 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.14 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$) δ 22.1 (Me), 27.3 (Me), 43.3 ($CH_2$(5)), 44.9 (CH(4)), 55.3 (OMe), 83.2 (C(6)), 114.6 ($CH_{Ar}$), 119.8 (C(3)=N), 128.9 ($CH_{Ar}$), 130.8 ($C_{Ar}$), 159.3 ($\underline{C}_{Ar}$–OMe).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{17}ClNO_3$ 270.0891; found: 270.0901.

**3-Bromo-4-(4-methoxyphenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2o**




(4*S**,6*S**)-isomer (4*S**,6*R**)-isomer

Starting bromonitroalkene was prepared according to the literature procedure.[s2]

Prepared according to GP-2 from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene (500 mg, 1.94 mmol) and styrene (404 mg, 444 μl, 3.87 mmol, 2 equiv.) in toluene (12.3 ml) using 1.1 equiv of $SnCl_4$. The reaction was stirred at -50 °C for 30 min and then kept at the fridge (-30 °C) for 60 h. Recrystallisation from PE/EtOAc 3:1 afforded 386 mg (55%) of title compouns as pale yellow solid (dr (4*S**,6*S**) : (4*S**,6*R**) = 1.1:1). Column chromatography of mother liqoir (eluent: PE/EtOAc, 5:1, then 3:1) afforded additional 120 mg (17%) of (4*S**,6*S**)-diastereomer as colorless oil. Total isolated: yield – 72%, dr – 1.7 : 1.

$R_f$ = 0.42 (PE/EtOAc, 3:1, UV, anisaldehyde).

mp (for diastereomeric mixture) = 119-121 °C (dec.) (PE/EtOAc, 3:1).

Relative configuration was assigned by analogy with literature data for corresponding 3-methyl-1,2-oxazine-N-oxide.[s9]

(4*S**,6*S**)-isomer:

$^1$H NMR (300 MHz, $CDCl_3$): δ 2.32 (app dt, *J* = 13.9, 2.6 Hz, 1H, $CH_{2a}$(5)), 2.81 (ddd, *J* = 13.9, 10.3, 6.7 Hz, 1H, $CH_{2b}$(5)), 3.85 (s, 3H, OMe), 4.21 (dd, *J* = 6.7, 3.0 Hz, 1H, CH(4)), 5.59 (dd, *J* = 10.3, 2.1 Hz, 1H, CH(6)–O), 6.97 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.22 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.33-7.41 (m, 5H, $CH_{Ph}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 36.6 ($CH_2$(5)), 46.8 (CH(4)), 55.4 (OMe), 80.4 (CH(6)–O), 108.4 (C(3)=N), 114.7, 126.7, 128.87, 128.91, and 129.3 (all $CH_{Ar}$ and $CH_{Ph}$), 132.6 and 135.8 ($C_{Ar}$ and $C_{Ph}$), 159.3 ($C_{Ar}$–O).

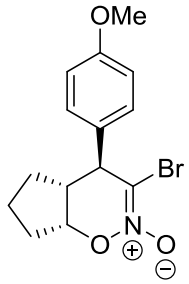
(4*S**,6*R**)-isomer:

$^1$H NMR (300 MHz, $CDCl_3$): δ 2.53 (ddd, *J* = 14.1, 11.5, 10.5 Hz, 1H, $CH_{2a}$(5)), 2.66 (ddd, *J* = 14.1, 8.1, 2.0 Hz, 1H, $CH_{2b}$(5)), 3.83 (s, 3H, OMe), 4.25 (dd, *J* = 10.5, 8.1 Hz, 1H, CH(4)), 5.58 (app d, *J* = 11.0, 1H, CH(6)–O), 6.93 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.19 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.33-7.41 (m, 5H, $CH_{Ph}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 39.6 ($CH_2$(5)), 48.8 (CH(4)), 55.4 (OMe), 83.6 (CH(6)–O), 111.8 (C(3)=N), 114.6, 127.0, 128.8, 128.9, and 129.6 (all $CH_{Ar}$ and $CH_{Ph}$), 132.1 and 135.5 ($C_{Ar}$ and $C_{Ph}$), 159.4 ($C_{Ar}$–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{17}H_{17}{}^{79}BrNO_3$ 362.0386; found: 362.0377.

**(4*S**,4a*R**,7a*R**)-3-Bromo-4-(4-methoxyphenyl)-4,4a,5,6,7,7a-hexahydrocyclopenta[e][1,2]oxazine 2-oxide 2p**




Starting bromonitroalkene was prepared according to the literature procedure.[s2]

Prepared according to GP-2 from (Z)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene (516 mg, 2.0 mmol) and cyclopentene (0.68 g, 0.88 mL, 10.0 mmol, 5 equiv.) in $CH_2Cl_2$ (20 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -30 °C for 60 min and then kept in the fridge (-30 °C) overnight (14 h). Recrystallization (hexane–EtOAc, 3:1) afforded 604 mg (93%) of title compound as pale yellow crystals.

$R_f$ = 0.24 (PE/EtOAc, 3:1, UV, anisaldehyde).

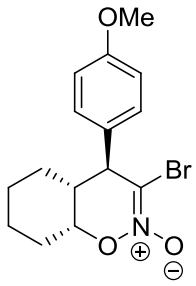
mp = 113-114 °C (dec.) (PE/EtOAc, 3:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.58-1.75 (m, 2H, $CH_2$), 1.86-2.07 (m, 4H, $CH_2$), 2.57-2.65 (m, 1H, CH), 3.83 (s, 3H, OMe), 3.90 (d, *J* = 5.3 Hz, 1H, C<u>H</u>–Ar), 5.05 (app td, *J* = 5.2, 2.4 Hz, 1H, CH–O), 6.92 (d *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.16 (d, *J* = 8.7 Hz, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 22.6 ($CH_2$), 30.5 ($CH_2$), 31.9 ($CH_2$), 48.9 (CH), 51.2 (CH), 55.3 (OMe), 86.4 (CH–O), 112.2 (C(3)=N), 114.4 ($CH_{Ar}$), 129.4 ($CH_{Ar}$), 131.8 ($C_{Ar}$), 159.3 ($C_{Ar}$–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{14}H_{17}{}^{79}BrNO_3$ 326.0386; found: 326.0384.

**(4*S**,4a*R**,8a*R**)-3-bromo-4-(4-methoxyphenyl)-4a,5,6,7,8,8a-hexahydro-4H-benzo[e][1,2]oxazine 2-oxide 2q**




Starting bromonitroalkene was prepared according to the literature procedure.[s2]

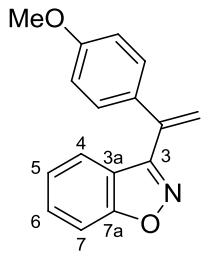
Prepared according to GP-2 from (Z)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene (516 mg, 2.0 mmol) and cyclohexene (0.41 mL, 328 mg, 4.0 mmol, 2 equiv.) in $CH_2Cl_2$ (20 ml) using 1.2 equiv of $SnCl_4$. The reaction was stirred at -30 °C for 60 min and then kept at the fridge (-30 °C) for 7 days. Column chromatography (eluent: PE/EtOAc, 5:1, then 2:1) afforded 303 mg (45%) of target compound as pale yellow solid.

NMR matched previously reported data. [s2]

**General procedure for reaction of aryne precursors 1 and *N*-oxides 2. Synthesis of vinyl benzisoxazoles 3 and benzofurooxazines 4 (GP-3):**

CsF (145 mg, 0.95 mmol, 3.0 equiv) was placed in a Schlenk tube and dried at ~250 °C (heat gun) in a vacuum (1-2 mmHg) for ~1 min. After cooling to r.t., nitronate **2** (0.32 mmol, 1.0 equiv) and anhydrous acetonitrile (2.56 mL) were added under an argon atmosphere (if nitronate was an oil, it was added to dry CsF as 0.125 M solution in MeCN). After dissolution of nitronate **2**, aryne precursor **1** (0.48 mmol, 1.5 equiv) was added and the reaction mixture was stirred for 12-16 h (TLC control). Then, EtOAc (~2 mL) and water (~4 mL) were added upon vigorous stirring. After ~1 min, the mixture was transferred into a separating funnel containing EtOAc (15 mL) and water (15 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (30 mL), dried with anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The resulting crude product was subjected to column chromatography on silica gel (PE/ EtOAc gradient).

**3-(1-(4-Methoxyphenyl)vinyl)benzo[d]isoxazole 3aa**




1. Prepared from 3-bromonitronate **2a** (200 mg, 0.64 mmol) and silane **1a** (232 μL, 285 mg, 0.96 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 150 mg (94%) of title compound as colorless oil.
2. Scale up reaction was performed for 3-bromonitronate **2a** (1.26 g, 4.0 mmol) and silane **1a** (1.46 mL, 1.79 g, 6.0 mmol) according to the general procedure. Column chromatography (eluent: PE, then PE/EtOAc, 20:1, then 15:1) afforded 776 mg (77%) of title compound as white solid and 182 mg of the mixture of title compound and 3-(6-methoxy-9,10-dihydrophenanthren-9-yl)benzo[d]isoxazole **12** (molar ratio 5:1). Recrystallization of this mixture from PE/MTBE 1:1 afforded 110 mg of pure title compound as white crystalls. Total yield 886 mg (88%).
3. Prepared from 3-chloronitronate **2n** (20 mg, 0.07 mmol) and silane **1a** (27 μL, 33 mg, 0.11 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 10:1) afforded 14 mg (75%) of title compound as colorless oil.
4. Prepared from 3-bromonitronate **2o** (100 mg, 0.28 mmol) (dr (4*S**,6*S**) : (4*S**,6*R**) = 1.1:1) and silane **1a** (101 μL, 124 mg, 0.41 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 10:1, then 1:1) afforded 44 mg (64%) of title compound as colorless oil and 23 mg (23%) of starting nitronate.

$R_f$ = 0.66 (PE/EtOAc, 5:1, UV, anisaldehyde).

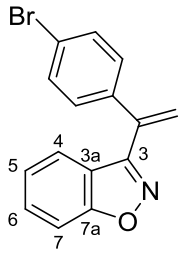
mp = 53-54 °C (PE/MTBE, 1:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H, OMe), 5.88 (d, *J* = 0.8 Hz, 1H, $=CH_{2a}$), 5.91 (d, *J* = 0.8 Hz, 1H, $=CH_{2b}$), 6.93 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 7.24 (ddd, *J* = 7.9, 6.9, 0.9 Hz, 1H, CH(5)), 7.35 (app d, *J* = 7.9 Hz, 1H, CH(4)), 7.41 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 7.56 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H, CH(6)), 7.64 (app d, *J* = 8.4 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 55.3 (OMe), 110.0 (CH(7)), 113.9 ($CH_{Ar}$), 118.5 ($=CH_2$), 121.2 (C(3a)), 122.7 (CH(4)), 123.5 (CH(5)), 128.9 ($CH_{Ar}$), 129.7 (CH(6)), 130.6 ($C_{Ar}$), 137.1 ($\underline{C}=CH_2$), 158.2 (C(3)=N), 160.0 ($\underline{C}_{Ar}$–OMe), 163.4 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{14}NO_2$ 252.1019; found: 252.1025.

**3-(1-(4-Bromophenyl)vinyl)benzo[d]isoxazole 3ab**




Prepared from 3-bromonitronate **2b** (100 mg, 0.28 mmol) and silane **1a** (100 μL, 123 mg, 0.41 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 78 mg (94%) of title compound as pale yellow solid.

$R_f$ = 0.58 (PE/EtOAc, 20:1, UV, anisaldehyde).

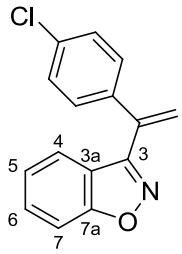
mp = 68-69 °C (PE/EtOAc, 3:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 5.97 (s, 1H, $=CH_{2a}$(8)), 6.05 (s, 1H, $=CH_{2b}$(8)), 7.27 (app t, *J* = 7.4 Hz, 1H, CH(5)), 7.35-7.38 (m, 3H, CH(4) and $CH_{Ar}$), 7.53 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.55-7.60 (m, CH(6)), 7.65 (app d, *J* = 8.4 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 110.1 (CH(7)), 120.75 ($=CH_2$), 120.83 (C(3a)), 122.4 (CH(4)), 122.9 (C–Br), 123.8 (CH(5)), 129.3 ($CH_{Ar}$), 129.9 (CH(6)), 131.7 ($CH_{Ar}$), 136.9 and 137.1 ($C_{Ar}$ and $\underline{C}=CH_2$), 157.4 (C(3)=N), 163.5 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{11}{}^{79}BrNO$ 300.0019; found: 300.0015.

**3-(1-(4-Chlorophenyl)vinyl)benzo[d]isoxazole 3ac**




Prepared from 3-bromonitronate **3c** (73 mg, 0.23 mmol) and silane **1a** (84 μL, 103 mg, 0.34 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 15:1, then 10:1) afforded 56 mg (96%) of title compound as white solid.

$R_f$ = 0.65 (PE/EtOAc, 5:1, UV, anisaldehyde).

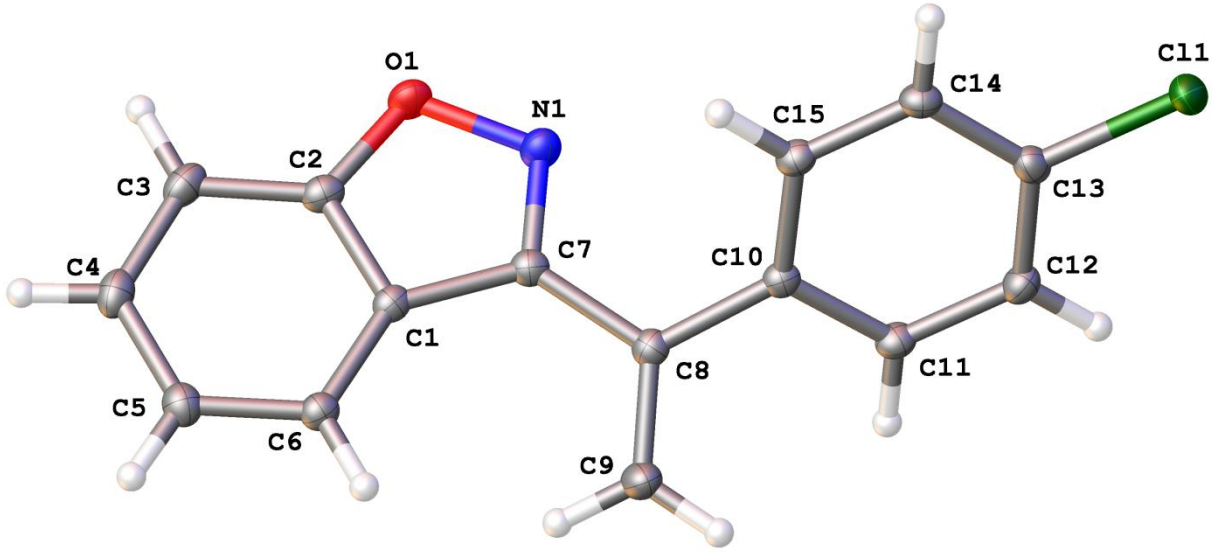
mp = 82-84°C (dec.) (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 5.96 (s, 1H, $=CH_{2a}$), 6.05 (s, 1H, $=CH_{2b}$), 7.25-7.30 (m, 1H, CH(5)), 7.37 (d, *J* = 8.7 Hz, 2H), 7.39-7.45 (m, 3H, $CH_{Ar}$ and CH(4)), 7.55-7.60 (m, 1H, CH(6)), 7.65 (app d, *J* = 8.5 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 110.1 (CH(7)), 120.7 (=$CH_2$), 120.9 (C(3a)), 122.4 (CH(4)), 123.7 (CH(5)), 128.8 ($CH_{Ar}$), 129.0 ($CH_{Ar}$), 129.9 (CH(6)), 134.7, 136.6, and 136.9 ($C_{Ar}$, C–Cl and C=$CH_2$), 157.5 (C(3)=N), 163.5 ($C_{Ar}$(7a)–O).

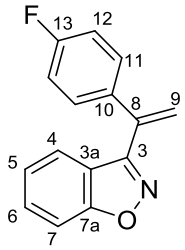
HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{11}ClNO$ 256.0524; found: 256.0526.

The crystallographic information for compound **3ac** was deposited in the Cambridge Crystallographic Data Centre (CCDC 2337550).




General view of benzisoxazole **3ac** in representation of atoms *via* thermal ellipsoids at 50% probability level.

**3-(1-(4-Fluorophenyl)vinyl)benzo[d]isoxazole 3ad**




Prepared from 3-bromonitronate **2d** (100 mg, 0.33 mmol) and silane **1a** (121 μL, 148 mg, 0.50 mmol) according to the GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 10:1) afforded 99 mg (78%) of title compound as white solid.

$R_f$ = 0.63 (PE/EtOAc, 10:1, UV, anisaldehyde).

mp = 81-82 °C (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 5.93 (s, 1H, =$CH_{2a}$), 6.02 (s, 1H, =$CH_{2b}$), 7.10 (t, *J* = 8.7 Hz, 2H, $CH_{Ar}$), 7.27 (app td, *J* = 6.8, 0.9 Hz, 1H, CH(5)), 7.37 (app d, *J* = 8.0 Hz, 1H, CH(4)), 7.47 (dd, *J*

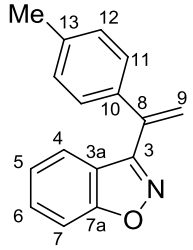
= 8.8, 5.3 Hz, 2H, $CH_{Ar}$), 7.57 (app td, *J* = 6.8, 1.2 Hz, 1H, CH(6)), 7.65 (app d, *J* = 8.5 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 110.1 (CH(7)), 115.5 (d, $^2J_{CF}$ = 21.7 Hz, $CH_{Ar}$), 120.2 (=$CH_2$), 120.9 (C(3a)), 122.4 (CH(4)), 123.7 (CH(5)), 129.5 (d, $^3J_{CF}$ = 8.2 Hz, $CH_{Ar}$), 129.9 (CH(6)), 134.3 (d, $^4J_{CF}$ = 3.4 Hz, $C_{Ar}$), 136.9 (<u>C</u>=$CH_2$), 157.7 (C(3)=N), 163.0 (d, $^1J_{CF}$ = 248.3 Hz, C–F), 163.5 ($C_{Ar}$(7a)–O).

$^{19}$F NMR (282 MHz, $CDCl_3$): δ -113.1 (tt, *J* = 8.5, 5.3 Hz).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{11}FNO$ 240.0819; found: 240.0822.

**3-(1-(*p*-Tolyl)vinyl)benzo[d]isoxazole 3ae**




Prepared from 3-bromonitronate **2e** (100 mg, 0.34 mmol) and silane **1a** (122 μL, 150 mg, 0.50 mmol) according to the GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 71 mg (90%) of title compound as colorless oil.

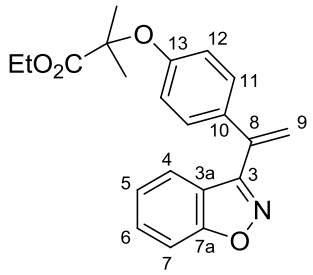
$R_f$ = 0.75 (PE/EtOAc, 20:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.42 (s, 3H, Me), 5.93 (d, *J* = 0.8 Hz, 1H, =$CH_{2a}$), 5.98 (d, *J* = 0.8 Hz, 1H, =$CH_{2b}$), 7.20-7.24 (m, 2H, CH(11 or 12)), 7.25-7.28 (m, 1H, CH(5)), 7.34 (app d, *J* = 8.0 Hz, 1H, CH(4)), 7.38 (d, *J* = 8.2 Hz, 2H, CH(12 or 11)), 7.56 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H, CH(6)), 7.64 (app d, *J* = 8.5 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 21.3 (Me), 110.0 (CH(7)), 119.4 (=$CH_2$(9)), 121.2 (C(3a)), 122.7 (CH(4)), 123.5 (CH(5)), 127.5 and 129.3 ($CH_{Ar}$(11) and $CH_{Ar}$(12)), 129.7 (CH(6)), 135.3, 137.6 and 138.6 ($C_{Ar}$(10), $C_{Ar}$(13), and <u>C</u>(8)=$CH_2$), 158.1 (C(3)=N), 163.5 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{14}NO$ 236.1070; found: 236.1078.

**Ethyl 2-(4-(1-(benzo[d]isoxazol-3-yl)vinyl)phenoxy)-2-methylpropanoate 3af**



Prepared from 3-bromonitronate **2f** (100 mg, 0.24 mmol) and silane **1a** (88 μL, 108 mg, 0.36 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 10:1) afforded 81 mg (96%) of title compound as colorless oil.

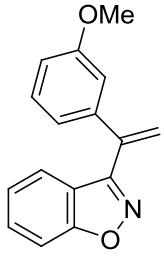
$R_f$ = 0.66 (PE/EtOAc, 5:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.85 (s, 6H, $Me_2C$), 4.26 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 5.88 (s, 1H, $=CH_{2a}$(8)), 5.91 (s, 1H, $=CH_{2b}$(8)), 6.85 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(12)), 7.22 (app t, *J* = 7.4 Hz, 1H, CH(5)), 7.32 (app d, *J* = 8.0 Hz, 1H, CH(4)), 7.36 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(11)), 7.54 (app td, *J* = 6.9, 1.1 Hz, 1H, CH(6)), 7.62 (app d, *J* = 8.4 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 14.1 ($CH_2\underline{C}H_3$), 25.4 ($\underline{Me}_2C$), 61.5 ($O\underline{C}H_2CH_3$), 79.2 ($Me_2\underline{C}$–O), 110.0 (CH(7)), 118.7 ($CH_{Ar}$(12)), 118.9 ($=CH_2$(9)), 121.2 (C(3a)), 122.6 (CH(4)), 123.5 (CH(5)), 128.5 ($CH_{Ar}$(11)), 129.7 (CH(6)), 131.7 ($C_{Ar}$(10)), 137.0 ($\underline{C}$(8)=$CH_2$), 156.0 ($C_{Ar}$(13)–O), 158.1 (C(3)=N), 163.4 ($C_{Ar}$(7a)–O), 174.1 ($CO_2$).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{21}H_{22}NO_4$ 352.1543; found: 352.1539.

**3-(1-(3-Methoxyphenyl)vinyl)benzo[d]isoxazole 3ag**



Prepared from 3-bromonitronate **2g** (35 mg, 0.11 mmol) and silane **1a** (41 μL, 50 mg, 0.17 mmol) according to the GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 10:1) afforded 27 mg (96%) of title compound as colorless oil, that solidified upon storage in a fridge.

$R_f$ = 0.66 (PE/EtOAc, 10:1, UV, anisaldehyde).

mp = 70-72 °C (PE/EtOAc, 3:1).

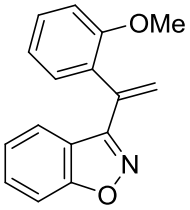
$^1$H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H, OMe), 5.96 (d, *J* = 0.7 Hz, 1H, $=CH_{2a}$), 6.02 (d, *J* = 0.7 Hz, 1H, $=CH_{2b}$), 6.96 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 7.02-7.07 (m, 2H), 7.24 (app td, *J* = 7.4,

0.9 Hz, 1H), 7.32 (app t, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.59 (app d, *J* = 8.5 Hz, 1H).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 55.3 (OMe), 110.0 (CH), 113.3 (CH), 114.2 (CH), 120.2 (CH), 120.4 (=$CH_2$), 121.1 (C), 122.6 (CH), 123.6 (CH), 129.6 (CH), 129.8 (CH), 137.7 and 139.5 ($C_{Ar}$ and $\underline{C}$=$CH_2$), 157.9 (C(3)=N), 159.7 ($\underline{C}_{Ar}$–OMe), 163.5 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{14}NO_2$ 252.1019; found: 252.1018.

**3-(1-(2-Methoxyphenyl)vinyl)benzo[d]isoxazole 3ah**




Prepared from 3-bromonitronate **2h** (70 mg, 0.22 mmol) and silane **1a** (81 μL, 100 mg, 0.33 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 10:1) afforded 52 mg (93%) of title compound as white solid.

$R_f$ = 0.78 (PE/EtOAc, 3:1, UV, anisaldehyde).

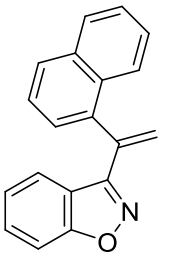
mp = 67-69 °C (PE/EtOAc, 3:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 3.56 (s, 3H, OMe), 5.82 (d, *J* = 1.2 Hz, 1H, =$CH_{2a}$), 6.23 (d, *J* = 1.2 Hz, 1H, =$CH_{2b}$), 6.93 (d, *J* = 8.0 Hz, 1H), 7.07 (app t, *J* = 7.5 Hz, 1H), 7.16-7.25 (m, 2H), 7.39-7.46 (m, 2H), 7.51 (app td, *J* = 6.5, 1.6 Hz, 1H), 7.59 (app d, *J* = 8.4 Hz, 1H).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 55.5 (OMe), 109.8 (CH), 111.3 (CH), 120.9 (CH), 121.0 (C), 121.7 (=$CH_2$), 122.1 (CH), 123.3 (CH), 128.3 (C), 129.3 (CH), 130.1 (CH), 130.6 (CH), 135.9 ($\underline{C}$=$CH_2$), 157.2 (C(3)=N), 158.1 ($\underline{C}_{Ar}$–OMe), 163.3 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{14}NO_2$ 252.1019; found: 252.1024.

**3-(1-(Naphthalen-1-yl)vinyl)benzo[d]isoxazole 3ai**




Prepared from 3-bromonitronate **2i** (50 mg, 0.15 mmol) and silane **1a** (55 μL, 67 mg, 0.22 mmol) according to the GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 35 mg (86%) of title compound as colorless oil.

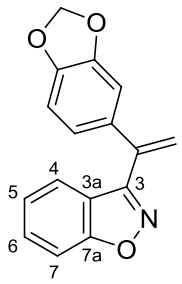
$R_f$ = 0.60 (PE/EtOAc, 10:1, UV, anisaldehyde).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 5.90 (d, *J* = 1.3 Hz, 1H, $=CH_{2a}$), 6.57 (d, *J* = 1.3 Hz, 1H, $=CH_{2b}$), 7.06-7.15 (m, 2H), 7.39 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.46-7.51 (m, 2H), 7.55-7.63 (m, 3H), 7.88-7.97 (m, 3H).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 110.0 (CH(7)), 120.4 (C(3a)), 122.2 (CH), 123.3 ($=CH_2$), 123.7 (CH), 125.4 (CH), 125.5 (CH), 126.1 (CH), 126.5 (CH), 127.3 (CH), 128.5 (CH), 129.0 (CH), 129.6 (CH), 131.6 (C), 133.7 (C), 137.0 (C), 137.5 (C), 158.0 (C(3)=N), 163.7 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{19}H_{14}NO$ 272.1070; found: 272.1075.

**3-(1-(Benzo[d][1,3]dioxol-5-yl)vinyl)benzo[d]isoxazole 3aj**




Prepared from 3-bromonitronate **2j** (100 mg, 0.31 mmol) and silane **1a** (111 μL, 136 mg, 0.46 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1) afforded 62 mg (77%) of title compound as white solid.

$R_f$ = 0.70 (PE/EtOAc, 5:1, UV, anisaldehyde).

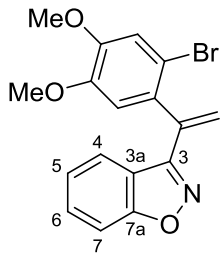
mp = 82-84 °C (PE/EtOAc, 3:1).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 5.86 (s, 1H, $=CH_{2a}$(8)), 5.91 (s, 1H, $=CH_{2b}$(8)), 6.01 (s, 2H, O–$CH_2$–O), 6.82 (d, *J* = 8.0 Hz, 1H, $CH_{Ar}$), 6.93-6.98 (m, 2H, 2×$CH_{Ar}$), 7.26 (app t, *J* = 7.4 Hz, 1H, CH(5)), 7.39 (app d, *J* = 7.9 Hz, 1H, CH(4)), 7.56 (app t, *J* = 7.6 Hz, 1H, CH(6)), 7.63 (app d, *J* = 8.4 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 101.3 (O–$CH_2$–O), 108.0 ($CH_{Ar}$), 108.3 ($CH_{Ar}$), 110.0 (CH(7)), 119.1 ($=CH_2$), 121.1 (C(3a)), 121.7 ($CH_{Ar}$), 122.6 (CH(4)), 123.6 (CH(5)), 129.8 (CH(6)), 132.3 ($C_{Ar}$), 137.3 ($\underline{C}=CH_2$), 147.9 ($C_{Ar}$–O), 148.1 ($C_{Ar}$–O), 158.1 (C(3)=N), 163.5 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{12}NO_3$ 266.0812; found: 266.0813.

**3-(1-(2-Bromo-4,5-dimethoxyphenyl)vinyl)benzo[d]isoxazole 3ak**




Prepared from 3-bromonitronate **2k** (87 mg, 0.21 mmol) and silane **1a** (75 μL, 92 mg, 0.31 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 10:1) afforded 51 mg (69%) of title compound as white solid.

$R_f$ = 0.26 (PE/EtOAc, 7:1, UV, anisaldehyde).

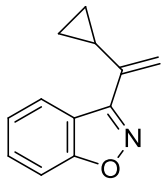
mp = 117-119 °C (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, OMe), 3.92 (s, 3H, OMe), 5.78 (s, 1H, $=CH_{2a}$), 6.36 (s, 1H, $=CH_{2b}$), 6.96 (s, 1H, $CH_{Ar}$), 7.10 (s, 1H, $CH_{Ar}$), 7.27 (app t, *J* = 7.2 Hz, 1H, CH(5)), 7.40 (d, *J* = 8.0 Hz, 1H, CH(4)), 7.55 (app t, *J* = 7.5 Hz, 1H, CH(6)), 7.61 (d, *J* = 8.4 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 56.2 (OMe), 56.3 (OMe), 110.1 (CH(7)), 113.3 ($C_{Ar}$–Br), 113.9 ($CH_{Ar}$), 115.8 ($CH_{Ar}$), 120.6 (C(3a)), 122.2 (CH(4)), 123.1 ($=CH_2$), 123.8 (CH(5)), 129.6 (CH(6)), 132.1 ($C_{Ar}$), 138.1 ($\underline{C}=CH_2$), 148.5 ($\underline{C}_{Ar}$–OMe), 149.6 ($\underline{C}_{Ar}$–OMe), 157.0 (C(3)=N), 163.6 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{17}H_{15}{}^{79}BrNO_3$ 360.0230; found: 360.0241.

**3-(1-Cyclopropylvinyl)benzo[d]isoxazole 3al**




Prepared from 3-bromonitronate **2l** (75 mg, 0.30 mmol) and silane **1a** (110 μL, 135 mg, 0.45 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 49 mg (88%) of title compound as colorless oil.

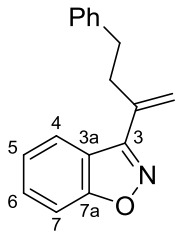
$R_f$ = 0.83 (PE/EtOAc, 20:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.73-0.78 (m, 2H), 0.90-0.97 (m, 2H), 2.00-2.09 (m, 1H, CH), 5.42 (s, 1H, $=CH_{2a}$), 5.78 (s, 1H, $=CH_{2b}$), 7.34 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H, $CH_{Ar}$), 7.52-7.63 (m, 2H, $CH_{Ar}$), 7.86 (d, *J* = 8.0 Hz, 1H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 7.2 ($CH_2$), 14.8 (CH), 110.0 ($CH_{Ar}$), 115.4 ($=CH_2$), 120.6 (C), 122.5 (CH), 123.7 (CH), 129.5 (CH), 140.2 ($\underline{C}=CH_2$), 157.9 (C(3)=N), 163.4 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{12}H_{12}NO$ 186.0913; found: 186.0921.

**3-(4-Phenylbut-1-en-2-yl)benzo[d]isoxazole 3am**




Prepared from 3-bromonitronate **2m** (100 mg, 0.32 mmol) and silane **1a** (117 μL, 143 mg, 0.48 mmol) according to the GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 20:1) followed by crystallization (PE/EtOAc, 5:1) afforded 73 mg (91%) of title compound as white crystals.

$R_f$ = 0.30 (PE/EtOAc, 10:1, UV, anisaldehyde).

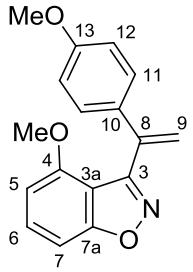
mp = 60-62 °C (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, $CDCl_3$): δ 2.96-3.10 (m, 4H, $CH_2CH_2$), 5.58 (br s, 1H, $=CH_{2a}$), 5.95 (s, 1H, $=CH_{2b}$), 7.20-7.41 (m, 7H, $CH_{Ph}$ and CH(5)), 7.59 (app td, *J* = 6.8, 1.1 Hz, 1H, CH(4)), 7.64 (app t, *J* = 8.3 Hz, 1H, CH(6)), 7.87 (d, *J* = 8.0 Hz, 1H, CH(7)).

$^{13}$C NMR (75 MHz, DEPT, $CDCl_3$): δ 34.6 ($CH_2$), 36.8 ($CH_2$), 110.1 (CH(7)), 119.5 ($=CH_2$), 120.5 (C(3a)), 122.5 (CH(4)), 123.8 (CH(5)), 126.0 ($CH_{Ph}$), 128.4 ($CH_{Ph}$), 128.6 ($CH_{Ph}$), 129.6 (CH(6)), 138.3 and 141.5 (=C and $C_{Ph}$), 157.1 (C(3)=N), 163.6 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{17}H_{16}NO$ 250.1226; found: 250.1221.

**4-Methoxy-3-(1-(4-methoxyphenyl)vinyl)benzo[d]isoxazole 3ba**




Prepared from 3-bromonitronate **2a** (100 mg, 0.32 mmol) and silane **1b** (157 mg, 0.48 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 10:1) afforded 64 mg (71%) of title compound as white solid.

$R_f$ = 0.55 (PE/EtOAc, 3:1, UV, anisaldehyde).

mp = 109-110 °C (PE/EtOAc, 5:1).

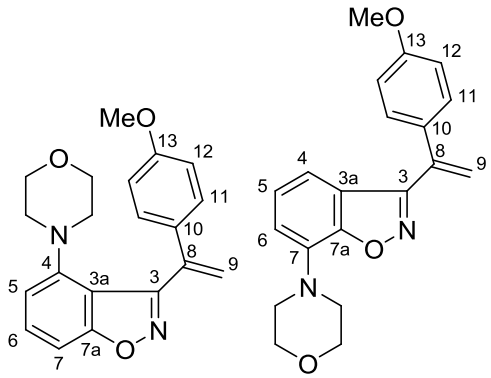
$^1$H NMR (300 MHz, $CDCl_3$): δ 3.59 (s, 3H, OMe(4)), 3.83 (s, 3H, OMe(13)), 5.71 (d, *J* = 0.8 Hz, 1H, $=CH_{2a}$), 5.87 (d, *J* = 0.8 Hz, 1H, $=CH_{2b}$), 6.56 (d, *J* = 7.9 Hz, 1H, CH(5)), 6.87 (d, *J* = 8.8

Hz, 2H, $CH_{Ar}$(12)), 7.19 (d, *J* = 8.4 Hz, 1H, CH(7)), 7.32 (d, *J* = 8.8 Hz, 2H, $CH_{Ar(}$11)), 7.47 (app t, *J* = 8.2 Hz, 1H, CH(6)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 55.3 (OMe), 55.5 (OMe), 102.4 (CH(7)), 103.7 (CH(5)), 111.8 (C(3a)), 113.6 ($CH_{Ar}$(12)), 117.9 (=$CH_2$(9)), 128.0 ($CH_{Ar}$(11)), 131.5 (CH(6)), 131.7 ($C_{Ar}$(10)), 137.4 (C(8)=$CH_2$), 154.7 ($C_{Ar}$(4)–OMe), 158.0 (C(3)=N), 159.5 ($C_{Ar}$(13)–OMe), 165.2 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{17}H_{16}NO_3$ 282.1125; found: 282.1127.

**4-Methoxy-3-(1-(4-methoxyphenyl)vinyl)benzo[d]isoxazole 3ca** and **3-(1-(4-methoxyphenyl)vinyl)-7-morpholinobenzo[d]isoxazole 3'ca**




Prepared from 3-bromonitronate **2a** (100 mg, 0.32 mmol) and silane **1c** (183 mg, 0.48 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 15:1) afforded 9 mg (8%) of mixture of **3'ca** and **3ca** (**3'ca** : **3ca** = 1.8:1), 40 mg (37%) of mixture of **3ca**:**3'ca** (16:1 ratio) as colorless oils, and 21 mg (17%) of **4ca** as pale yellow crystals. Total yield of **3ca** and **3'ca** 45%, total ratio **3ca** : **3'ca** = 5:1.

$R_f$ (**3'ca**) = 0.50 (PE/EtOAc, 2:1, UV, anisaldehyde).

$R_f$ (**3ca**) = 0.45 (PE/EtOAc, 2:1, UV, anisaldehyde).

mp (**3ca**) = 117-119 °C (PE/EtOAc, 3:1).

**3ca**:

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 2.91-2.94 (m, 4H, $CH_2$–N), 3.47-3.50 (m, 4H, $CH_2$–O), 3.82 (s, 3H, OMe), 5.69 (s, 1H, =$CH_{2a}$), 6.06 (s, 1H, =$CH_{2b}$), 6.76 (d, *J* = 7.7 Hz, 1H, CH(5)), 6.86 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$(12)), 7.31 (d, *J* = 8.3 Hz, 1H, CH(7)), 7.36 (d, *J* = 8.9 Hz, 2H, $CH_{Ar(}$11)), 7.49 (app t, *J* = 8.0 Hz, 1H, CH(6)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 52.6 ($CH_2$–N), 55.4 (OMe), 66.3 ($CH_2$–O), 104.5 (CH(7)), 111.5 (CH(5)), 113.7 ($CH_{Ar}$(12)), 114.9 (C(3a)), 116.6 (=$CH_2$(9)), 127.7 ($CH_{Ar}$(11)), 129.8 ($C_{Ar}$(10)), 130.9 (CH(6)), 137.2 (C(8)=$CH_2$), 148.7 ($C_{Ar}$(4)–N), 157.7 (C(3)=N), 159.9 ($C_{Ar}$(13)–OMe), 165.4 ($C_{Ar}$(7a)–O).

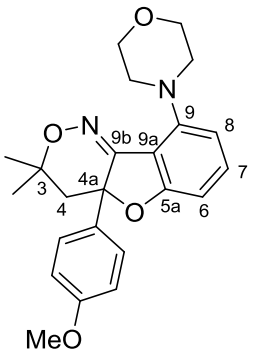
**3'ca**:

$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 3.42-3.45 (m, 4H, $CH_2$–N), 3.85 (s, 3H, OMe), 3.97-4.00 (m, 4H, $CH_2$–O), 5.86 (s, 1H, =$CH_{2a}$), 5.87 (s, 1H, =$CH_{2b}$), 6.85-6.94 (m, 4H, CH(4), CH(6), and $CH_{Ar}$(12)), 7.14 (app t, *J* = 7.8 Hz, 1H, CH(5)), 7.40 (d, *J* = 9.0 Hz, 2H, $CH_{Ar(}$11)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 49.7 ($CH_2$–N), 55.3 (OMe), 66.9 ($CH_2$–O), 113.9 ($CH_{Ar}$(12)), 114.2 and 114.3 (CH(4) and CH(6)), 118.4 (=$CH_2$(9)), 122.6 (C(3a)), 124.7 (CH(5)), 128.8 ($CH_{Ar}$(11)), 130.6 ($C_{Ar}$(10)), 136.5 ($\underline{C}_{Ar}$(7)–N), 137.0 ($\underline{C}$(8)=$CH_2$), 155.9 ($C_{Ar}$(7a)–O), 158.6 (C(3)=N), 159.9 ($\underline{C}_{Ar}$(13)–OMe).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{20}H_{21}N_2O_3$ 337.1547; found: 337.1548.

**4a-(4-Methoxyphenyl)-3,3-dimethyl-9-morpholino-4,4a-dihydro-3H-benzofuro[3,2-c][1,2]oxazine 4ca**




Obtained as a side product during the synthesis of **3ca**.

$R_f$ = 0.36 (PE/EtOAc, 2:1, UV, anisaldehyde).

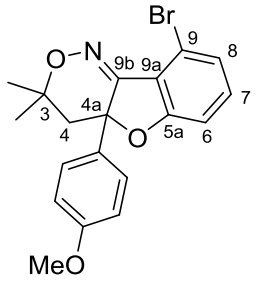
mp = 153-155 °C (PE/EtOAc, 3:1).

$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.05 (s, 3H, $Me_a$(3)), 1.31 (s, 3H, $Me_b$(3)), 2.22 (d, *J* = 12.7 Hz, 1H, $CH_{2a}$(4)), 3.09 (d, *J* = 12.7 Hz, 1H, $CH_{2b}$(4)), 3.11-3.17 (m, 2H, $CH_2$–N), 3.47-3.54 (m, 2H, $CH_2$–N), 3.80 (s, 3H, OMe), 3.88-4.04 (m, 4H, $CH_2$–O), 6.50 (d, *J* = 8.2 Hz, 1H) and 6.51 (d, *J* = 8.1 Hz, 1H) (CH(6) and CH(8)), 6.88 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 7.32 (app t, *J* = 8.1 Hz, 1H, CH(7)), 7.35 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 28.4 ($Me_a$(3)), 30.3 ($Me_b$(3)), 48.4 ($CH_2$(4)), 50.2 ($CH_2$–N), 55.3 (OMe), 67.0 ($CH_2$–O), 73.7 (C(3)–O), 85.2 (C(4a)–O), 104.1 (CH(6 or 8), 108.5 (C(9a)), 108.7 (CH(8 or 6), 113.9 ($CH_{Ar}$), 127.7 ($CH_{Ar}$), 129.3 ($C_{Ar}$), 134.8 (CH(7)), 150.2 ($\underline{C}_{Ar}$(9)–N), 159.6 ($\underline{C}_{Ar}$–OMe), 164.2 ($C_{Ar}$(5a)–O), 170.6 (C(9b)=N).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{23}H_{27}N_2O_4$ 395.1965; found: 395.1951.

**9-Bromo-4a-(4-methoxyphenyl)-3,3-dimethyl-4,4a-dihydro-3H-benzofuro[3,2-c][1,2]oxazine 4da**




Prepared from 3-bromonitronate **2a** (55 mg, 0.18 mmol) and silane **1d** (69 μL, 100 mg, 0.27 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 15:1, then 10:1) afforded 42 (61%) of title compound as pale yellow solid and 18 mg (33%) of starting nitronate.

$R_f$ = 0.57 (PE/EtOAc, 3:1, UV, anisaldehyde).

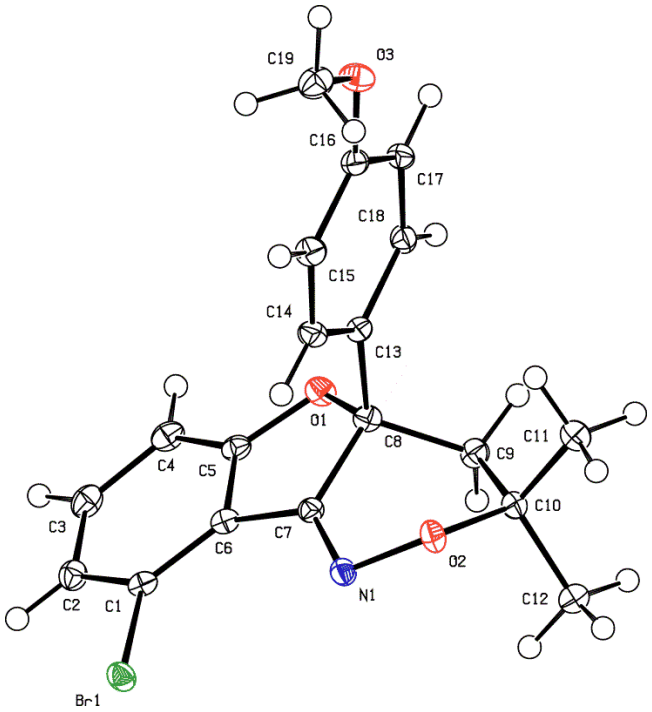
mp = 121-123 °C (dec.) (PE/EtOAc, 5:1).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.04 (s, 3H, $Me_a$(3)), 1.34 (s, 3H, $Me_b$(3)), 2.24 (d, *J* = 12.6 Hz, 1H, $CH_{2a}$(4)), 3.13 (d, *J* = 12.6 Hz, 1H, $CH_{2b}$(4)), 3.79 (s, 3H, OMe), 6.83-6.88 (m, overlapped, 1H, CH(6)), 6.88 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 7.20-7.26 (m, 2H, CH(7) and CH(8)), 7.37 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 28.3 ($Me_a$(3)), 30.5 ($Me_b$(3)), 48.4 ($CH_2$(4)), 55.3 (OMe), 74.5 (C(3)–O), 86.6 (C(4a)–O), 110.7 (CH(6)), 114.0 ($CH_{Ar}$), 118.0 and 119.0 (C(9a) and C(9)–Br), 126.2 (CH(8)), 127.9 ($CH_{Ar}$), 128.2 ($C_{Ar}$), 134.2 (CH(7)), 159.9 ($\underline{C}_{Ar}$–OMe), 163.4 ($C_{Ar}$(5a)–O), 170.1 (C(9b)=N).

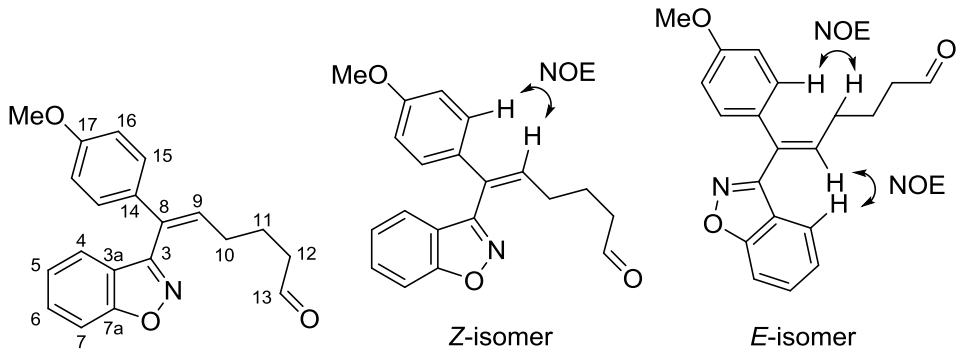
HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{19}H_{19}{}^{79}BrNO_3$ 388.0543; found: 388.0542.

The crystallographic information for compound **4da** was deposited in the Cambridge Crystallographic Data Centre (CCDC 2346577).




General view of benzisoxazole **4da** in representation of atoms *via* thermal ellipsoids at 50% probability level.

**6-(Benzo[d]isoxazol-3-yl)-6-(4-methoxyphenyl)hex-5-enal 3ap**




Prepared from 3-bromonitronate **2p** (150 mg, 0.46 mmol) and silane **1a** (167 μL, 206 mg, 0.69 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 15:1, then 10:1) afforded 51 mg (34%) of **3ap** (*Z*-only) and 38 mg (26%) of **3ap** (*E*/*Z* = 1.7:1) as colorless oil. Total yield – 60%. Total *Z*/*E* = 2.7:1.

*Z*/*E* ratio in reaction mixture = 2.7:1.

$R_f$ ((*Z*)-**3ap**) = 0.35 (PE/EtOAc, 3:1, UV, anisaldehyde).

$R_f$ ((*E*)-**3ap**) = 0.30 (PE/EtOAc, 3:1, UV, anisaldehyde).

*Z*-isomer

$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.86 (app quint, *J* = 7.4 Hz, 2H, $CH_2$(11)), 2.33 (app q, *J* = 7.6 Hz, 2H, $CH_2$(10)), 2.49 (td, *J* = 7.3, 1.4 Hz, 2H, $CH_2$(12)), 3.81 (s, 3H, OMe), 6.37 (t, *J* = 7.6 Hz, 1H, =CH(9)), 6.85 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(16)), 7.13-7.21 (m, 2H, CH(4) and CH(5)), 7.25 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(15)), 7.53 (ddd, *J* = 8.4, 6.4, 1.7 Hz, 1H, CH(6)), 7.62 (app d, *J* = 8.5 Hz, 1H, CH(7)), 9.76 (t, *J* = 1.4 Hz, 1H, CHO(13)).

Characteristic NOESY interaction: =CH(9) / $CH_{Ar}$(15).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 22.0 ($CH_2$(11)), 29.4 ($CH_2$(10)), 43.2 ($CH_2$(12)), 55.3 (OMe), 109.9 (CH(7)), 113.9 ($CH_{Ar}$(16)), 122.0 (C(3a)), 122.4 (CH(4)), 123.5 (CH(5)), 128.1 ($CH_{Ar}$(15)), 129.2 (C(8)=CH), 129.8 (CH(6)), 131.5 ($C_{Ar}$(14)), 134.1 (=CH(9)), 156.5 (C(3)=N), 159.5 ($C_{Ar}$(17)–OMe), 163.2 ($C_{Ar}$(7a)–O), 202.2 (CH(14)=O).

*E*-isomer

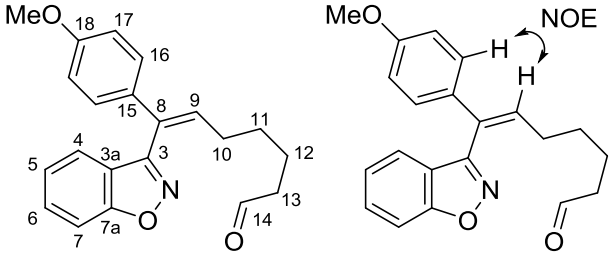
$^{1}$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.88 (app quint, *J* = 7.4 Hz, 2H, $CH_2$(11)), 2.40 (app q, *J* = 7.5 Hz, 2H, $CH_2$(10)), 2.46-2.55 (m, 2H, $CH_2$(12)), 3.87 (s, 3H, OMe), 6.62 (t, *J* = 7.5 Hz, 1H, =CH(9)), 6.96 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(16)), 7.05 (app d, *J* = 7.9 Hz, 1H, CH(4)), 7.15-7.19 (m, 1H, CH(5)), 7.24 (d, *J* = 8.8 Hz, 2H, $CH_{Ar}$(15)), 7.48 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H, CH(6)), 7.56 (app d, *J* = 8.4 Hz, 1H, CH(7)), 9.77 (t, *J* = 1.5 Hz, 1H, CHO(13)).

Characteristic NOESY interaction: =$CH_2$(10) / $CH_{Ar}$(15); CH(9) / CH(4).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 21.9 ($CH_2$(11)), 28.6 ($CH_2$(10)), 43.3 ($CH_2$(12)), 55.3 (OMe), 109.9 (CH(7)), 114.0 ($CH_{Ar}$(16)), 120.9 (C(3a)), 122.7 (CH(4)), 123.3 (CH(5)), 129.0 ($C_{Ar}$(14)), 129.5 (CH(6)), 130.76 ($CH_{Ar}$(15)), 130.82 (C(8)=CH). 135.0 (=CH(9)), 158.8 (C(3)=N), 159.3 ($C_{Ar}$(17)–OMe), 163.5 ($C_{Ar}$(7a)–O), 202.0 (CH(14)=O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{20}H_{20}NO_3$ 322.1438; found: 322.1431.

**(*Z*)-7-(Benzo[d]isoxazol-3-yl)-7-(4-methoxyphenyl)hept-6-enal 3aq**




Prepared from 3-bromonitronate **2q** (150 mg, 0.44 mmol) and silane **1a** (161 μL, 197 mg, 0.66 mmol) according to the GP-3. Column chromatography (eluent: PE/EtOAc, 20:1, then 15:1, then 10:1) afforded 13 mg (9%) of **4aq**, 59 mg (40%) of **3aq** (Z-only), and 44 mg (30%) of **3aq** (*E*/*Z*=1.6:1) as colorless oils.

$R_f$ (*Z*-isomer) = 0.40 (PE/EtOAc, 3:1, UV, anisaldehyde).

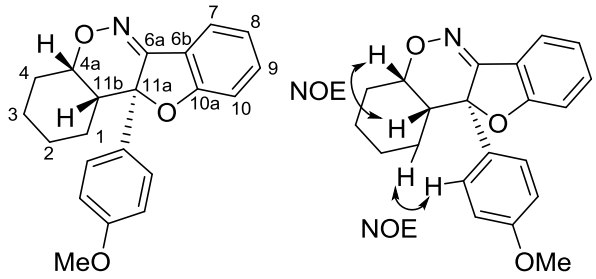
$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.50-1.65 (m, 2H, $CH_2$(11)), 1.58-1.74 (m, 2H, $CH_2$(12)), 2.31 (app q, *J* = 7.4 Hz, 2H, $CH_2$(10)), 2.41 (td, *J* = 7.1, 1.6 Hz, 2H, $CH_2$(13)), 3.81 (s, 3H, OMe), 6.39 (t, *J* = 7.6 Hz, 1H, =CH(9)), 6.85 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$(17)), 7.14-7.22 (m, 2H, CH(4) and CH(5)), 7.26 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$(16)), 7.53 (ddd, *J* = 8.4, 6.2, 2.0 Hz, 1H, CH(6)), 7.63 (app d, *J* = 8.5 Hz, 1H, CH(7)), 9.73 (t, *J* = 1.7 Hz, 1H, CHO(14)).

Characteristic NOESY interaction: =CH(9) / $CH_{Ar}$(16).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 21.6 ($CH_2$(12)), 29.2 ($CH_2$(11)), 29.7 ($CH_2$(10)), 43.6 ($CH_2$(13)), 55.3 (OMe), 109.9 (CH(7)), 113.9 ($CH_{Ar}$(17)), 122.1 (C(3a)), 122.5 and 123.5 (CH(4) and CH(5)), 128.1 ($CH_{Ar}$(16)), 128.6 (C(8)=CH). 129.7 (CH(6)), 131.7 ($C_{Ar}$(15)), 134.8 (=CH(9)), 156.6 (C(3)=N), 159.4 ($C_{Ar}$(18)–OMe), 163.2 ($C_{Ar}$(7a)–O), 202.5 (C(14)=O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{21}H_{22}NO_3$ 336.1594; found: 336.1588.

**(4a*S**,11a*R**,11b*R**)-11a-(4-Methoxyphenyl)-2,3,4,4a,11a,11b-hexahydro-1H-benzo[e]benzofuro[3,2-c][1,2]oxazine 4aq**




Obtained as a side product during the synthesis of **3aq**.

$R_f$ = 0.50 (PE/EtOAc, 3:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.28-1.47 (m, 2H, $CH_2$(2)), 1.37-1.54 (m, 2H, $CH_2$(3)), 1.42-1.54 (m, 2H, $CH_2$(1)), 1.72-1.78 (m, 2H, $CH_2$(4)), 2.69 (dt, *J* = 9.0, 6.6 Hz, 1H, CH(11b)), 3.78 (s, 3H, OMe), 3.91 (app q, *J* = 6.6 Hz, 1H, CH(4a)), 6.84 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 6.96-7.05 (m, 2H, CH(8) and CH(10)), 7.37 (app td, *J* = 8.1, 1.3 Hz, 1H, CH(9)), 7.44 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$), 7.67 (d, *J* = 7.6 Hz, 1H, CH(7)).

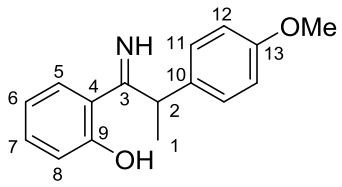
Characteristic NOESY interactions: CH(4a) / CH(11b); $CH_{Ar}$ / $CH_2$(1).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 20.3 ($CH_2$(3)), 22.3 ($CH_2$(2)), 24.3 ($CH_2$(1)), 27.6 ($CH_2$(4)), 44.8 (CH(11b)), 55.2 (OMe), 74.9 (CH(4a)–O), 87.5 (C(11a)–O), 111.9 (CH(10)), 113.3 ($CH_{Ar}$), 119.6 (C(6b)), 122.0 (CH(8)), 123.0 (CH(7)), 128.3 ($C_{Ar}$), 128.5 ($CH_{Ar}$), 133.3 (CH(9)), 159.4 ($C_{Ar}$–OMe), 162.0 ($C_{Ar}$(10a)–O), 170.4 (C(6a)=N).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{21}H_{22}NO_3$ 336.1594; found: 336.1595.

**Post transformations of benzisoxazole 3aa.**

**2-(1-Imino-2-(4-methoxyphenyl)propyl)phenol 7**




To a solution of benzisoxazole **3aa** (50 mg, 0.20 mmol) in MeOH (2 ml) in a 10 mL Schlenk tube 10% palladium on carbon (10 mg) was added. The tube was equipped with balloon with $H_2$, carefully evacuated by a water jet pump and back-filled with $H_2$ (repeated 3 times). The mixture was hydrogenated under $H_2$ atmosphere (balloon) for 1 h at r.t. upon vigorous stirring. Then reaction mixture was filtered through celite. Celite was then washed with EtOAc. Filtrate was concentrated under reduced pressure, and the crude product was subjected to column chromatography on silica gel (PE/ EtOAc, 5:1, then 4:1) to give 23 mg (45%) of title product as yellow oil.

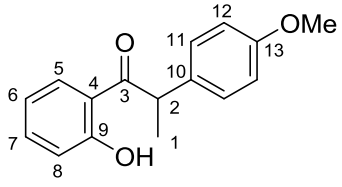
$R_f$ = 0.38 (PE/EtOAc, 2:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.59 (d, *J* = 7.2 Hz, 3H, CH–Me(1)), 3.82 (s, 3H, OMe), 4.56 (q, *J* = 7.2 Hz, 1H, CH(2)–Me), 6.78 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H, CH(6)), 6.92 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$(12)), 7.01 (dd, *J* = 8.5, 1.1 Hz, 1H, CH(8)), 7.18 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$(11)), 7.33 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H, CH(7)), 7.64 (dd, *J* = 8.1, 1.5 Hz, 1H, CH(5)), 9.28 (br s, 1H, OH).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 19.5 (CH–Me(1)), 43.2 (CH(2)–Me), 55.3 (OMe), 114.6 ($CH_{Ar}$(12)), 117.4 (CH(6)), 117.5 (C(4)), 118.9 (CH(8)), 128.6 (CH(5)), 128.9 ($CH_{Ar}$(11)), 132.4 ($C_{Ar}$(10)), 133.1 (CH(7)), 158.9 ($C_{Ar}$(13)–OMe), 164.3 (C(9)–OH), 183.5 (C(3)=N).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{18}NO_2$ 256.1332; found: 256.1337.

**1-(2-Hydroxyphenyl)-2-(4-methoxyphenyl)propan-1-one 8**




To a solution of benzisoxazole **3aa** (50 mg, 0.20 mmol) in MeOH (8 ml) in a 25 mL Schlenk tube 5% palladium on carbon (5 mg) was added. The tube was equipped with balloon with $H_2$, carefully evacuated by a water jet pump and back-filled with $H_2$ (repeated 3 times). The

mixture was hydrogenated under $H_2$ atmosphere (balloon) for 5 h at r.t. upon vigorous stirring. Then reaction mixture was filtered through celite. Celite was then washed with MeOH (8 mL). To the filtrate $H_2O$ (3.2 mL) was added and the resulting solution was kept at r.t. overnight (14 h). Then mixture was concentrated under reduced pressure to remove MeOH. The residue was transferred to separatory funnel, diluted with EtOAc (25 mL) and washed with brine (20 mL). Organic layer was dried ($Na_2SO_4$), and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel (PE/ EtOAc, 5:1) to give 43 mg (84%) of title product as colorless oil.

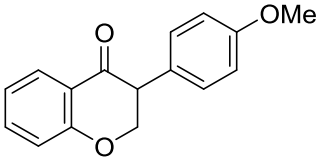
$R_f$ = 0.70 (PE/EtOAc, 3:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 1.55 (d, *J* = 6.9 Hz, 3H, CH–Me(1)), 3.79 (s, 3H, OMe), 4.73 (q, *J* = 6.9 Hz, 1H, CH(2)–Me), 6.81-6.86 (m, 1H, CH(6)), 6.89 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$(12)), 6.98 (dd, *J* = 8.4, 0.9 Hz, 1H, CH(8)), 7.25 (d, *J* = 8.7 Hz, 2H, $CH_{Ar}$(11)), 7.42 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H, CH(7)), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H, CH(5)), 12.50 (br s, 1H, OH).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 19.3 (CH–Me(1)), 46.4 (CH(2)–Me), 55.3 (OMe), 114.5 ($CH_{Ar}$(12)), 118.6 (C(4)), 118.7 and 118.9 (CH(6) and CH(8)), 128.7 ($CH_{Ar}$(11)), 130.5 (CH(5)), 133.2 ($C_{Ar}$(10)), 136.2 (CH(7)), 158.7 ($C_{Ar}$(13)–OMe), 163.2 (C(9)–OH), 206.8 (C(3)=N).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{17}O_3$ 257.1172; found: 257.1175.

**3-(4-Methoxyphenyl)chroman-4-one 9**



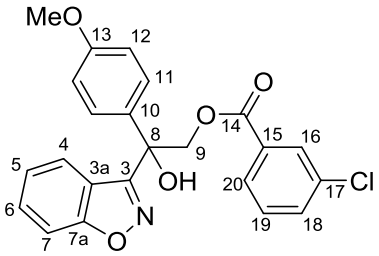

Mixture of benzisoxazole **3aa** (50 mg, 0.20 mmol, 1.0 equiv), $Mo(CO)_6$ (121 mg, 0.46 mmol, 2.3 equiv.) and $Me_3N^+O^-$ (64 mg, 0.86 mmol, 4.3 equiv.) in MeCN/$H_2O$ (5/1 v/v, total 3.32 ml) was stirred at 60 °C (oil bath) for 60 min. Reaction was quenched with saturated aqueous $NH_4Cl$ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried with $Na_2SO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (PE/ EtOAc, 3:1) to give 31 mg (61%) of title product as pale yellow soild.

$R_f$ = 0.48 (PE/EtOAc, 3:1, UV, anisaldehyde).

mp = 95-96 °C (PE/EtOAc, 3:1) (lit.[s10] 93-95 °C).

$^1$H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H, OMe), 3.97 (dd, *J* = 7.7, 6.6 Hz, 1H, CH(3)), 4.61-4.68 (m, 2H, $CH_2$(2)–O), 6.92 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.02-7.09 (m, 2H, 2×$CH_{Ar}$), 7.23 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}$), 7.53 (t, *J* = 7.7 Hz, 1H, $CH_{Ar}$), 7.99 (d, *J* = 7.7 Hz, 1H, $CH_{Ar}$).
NMR matched previously reported data. [s10]

**2-(Benzo[d]isoxazol-3-yl)-2-hydroxy-2-(4-methoxyphenyl)ethyl 3-chlorobenzoate 10**




To a solution of benzisoxazole **3aa** (25.0 mg, 0.10 mmol) in $CH_2Cl_2$ (1 ml) *m*CPBA (34 mg, 0.20 mmol, 2 equiv.) and $NaHCO_3$ (17 mg, 0.20 mmol, 2 equiv.) were consequtively added at 0 °C (ice-water bath). The cooling bath was removed and the reaction was stirred at r.t. overnight (14 h). Then reaction was quenched by the sat. aq. $Na_2S_2O_3$ (2 mL) and transferred into $CH_2Cl_2$ / $H_2O$ (10 mL / 5 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2×10 mL). The organic layers were combined, washed with water (7 mL), brine (7 mL), dried ($Na_2SO_4$) and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel (PE/ EtOAc, 15:1, then 10:1) to give 23.8 mg (56%) of title product as pale yellow oil.

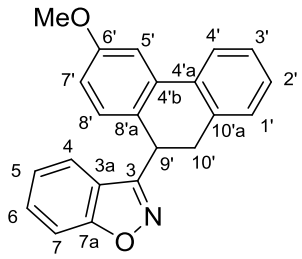
$R_f$ = 0.25 (PE/EtOAc, 5:1, UV, iodine).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 3.80 (s, 3H, OMe), 3.92 (s, 1H, OH), 4.95 (d, *J* = 11.7 Hz, 1H, $CH_{2a}$(9)–O), 5.29 (d, *J* = 11.7 Hz, 1H, $CH_{2b}$(9)–O), 6.91 (d, *J* = 8.9 Hz, 2H, $CH_{Ar}$(12)), 7.18-7.23 (m, 1H, CH(5)), 7.32 (app t, *J* = 7.8 Hz, 1H, CH(19)), 7.48-7.59 (m, 5H, CH(6), CH(7), $CH_{Ar}$(11), and CH(18)), 7.67 (app d, *J* = 8.0 Hz, 1H, CH(4)), 7.81 (app d, *J* = 7.8 Hz, 1H, CH(20)), 7.90 (t, *J* = 1.7 Hz, 1H, CH(16)).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 55.3 (OMe), 70.7 ($CH_2$(9)–O), 75.6 (C(8)–OH), 109.7 (CH(7)), 114.0 ($CH_{Ar}$(12)), 120.2 (C(3a)), 123.59 and 123.64 (CH(4) and (CH(5)), 127.0 ($CH_{Ar}$(11)), 127.9 (CH(20)), 129.7, 129.8, and 129.9 (CH(6), CH(16), and CH(19)), 131.2 and 131.6 (C(10) and C(15)), 133.3 (CH(18)), 134.5 (C(17)–Cl), 159.5 and 159.9 ($\underline{C}_{Ar}$(13)–OMe and C(3)=N), 163.5 ($C_{Ar}$(7a)–O), 165.7 (C(14)=O).

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. for $C_{23}H_{19}ClNO_5$+$Na^+$]: 446.0766; found: 446.0767.

**3-(6-Methoxy-9,10-dihydrophenanthren-9-yl)benzo[d]isoxazole 12**




CsF (67 mg, 0.44 mmol, 2.2 equiv.) was placed in a Schlenk tube and dried at ~250 °C (heat gun) in a vacuum (1-2 mmHg) for ~1 min. After cooling to r.t., benzisoxazole **3aa** (50 mg, 0.20 mmol, 1.0 equiv.) and anhydrous acetonitrile (1.6 mL) were added under an argon atmosphere. Then, aryne precursor **1a** (53 μL, 65 mg, 0.22 mmol, 1.1 equiv.) was added and the reaction mixture was stirred overnight (14 h). Then, EtOAc (~2 mL) and water (~4 mL) were added upon vigorous stirring. After ~1 min, the mixture was transferred into a separating funnel containing EtOAc (15 mL) and water (15 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (30 mL), dried with anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (PE/ EtOAc, 30:1) to give 50 mg (77%) of title product as colorless oil.

$R_f$ = 0.36 (PE/EtOAc, 5:1, UV, anisaldehyde).

$^1$H NMR (300 MHz, COSY, $CDCl_3$): δ 3.29 (dd, *J* = 15.1, 5.5 Hz, 1H, $CH_{2a}$(10')), 3.53 (dd, *J* = 15.1, 10.2 Hz, 1H, $CH_{2b}$(10')), 3.90 (s, 3H, OMe), 4.78 (dd, *J* = 10.1, 5.5 Hz, 1H, CH(9')), 6.78 (dd, *J* = 8.4, 2.6 Hz, 1H, CH(7')), 6.98 (d, *J* = 8.4 Hz, 1H, CH(8')), 7.16 (app t, *J* = 7.4 Hz, 1H, CH(5)), 7.22-7.27 (m, 1H, CH(4)), 7.24-7.32 (m, 2H, CH(1') and CH(2')), 7.37-7.43 (m, 1H, CH(3')), 7.47 (d, *J* = 2.6 Hz, 1H, CH(5')), 7.51 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H, CH(6)), 7.59 (app d, *J* = 8.5 Hz, 1H, CH(7)), 7.85 (d, *J* = 7.7 Hz, 1H, CH(4')).

$^{13}$C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 34.8 ($CH_2$(10')), 36.5 (CH(9')), 55.4 (OMe), 110.0 (CH(5')), 110.1 (CH(7)), 113.0 (CH(7')), 120.7 (C(3a)), 122.6 (CH(4)), 123.2 (CH(5)), 123.9 (CH(4')), 127.6 (CH(3')), 127.7 (C(8'a)), 128.1 (CH(2')), 128.6 (CH(1')), 129.0 (CH(8')), 129.6 (CH(6)), 133.9 (C(4'a)), 135.1 (C(10'a)), 135.7 (C(4'b)), 159.5 ($\underline{C}_{Ar}$(6')–OMe), 160.1 (C(3)=N), 163.6 ($C_{Ar}$(7a)–O).

HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{22}H_{18}NO_2$ 328.1332; found: 328.1333.

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s8. A. A. Fadeeva, S. L Ioffe and A. A. Tabolin, *Tetrahedron Lett*., 2021, **73**, 153106.

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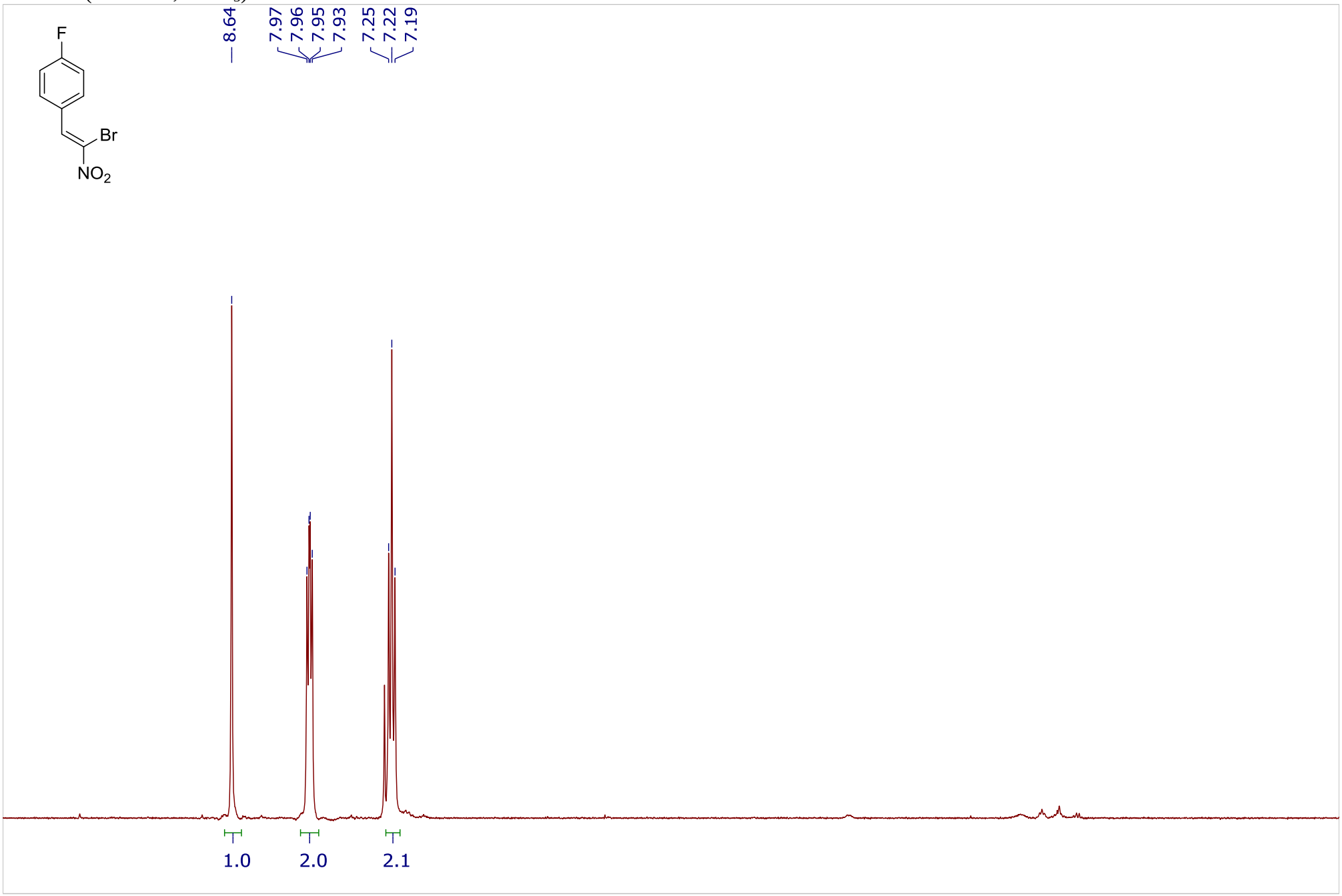
# Copies of NMR spectra

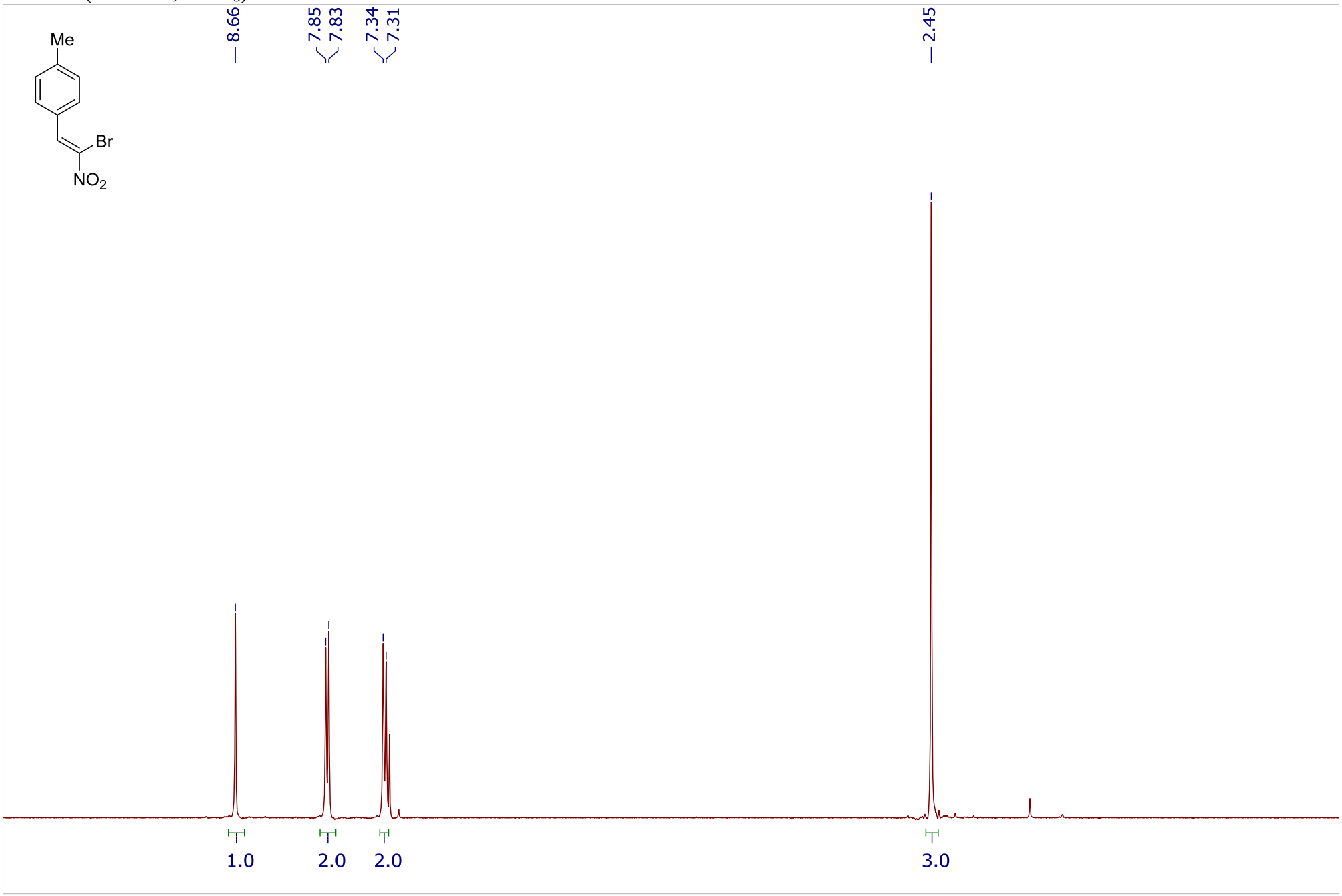
**(*Z*)-1-(2-Bromo-2-nitrovinyl)-4-fluorobenzene**

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



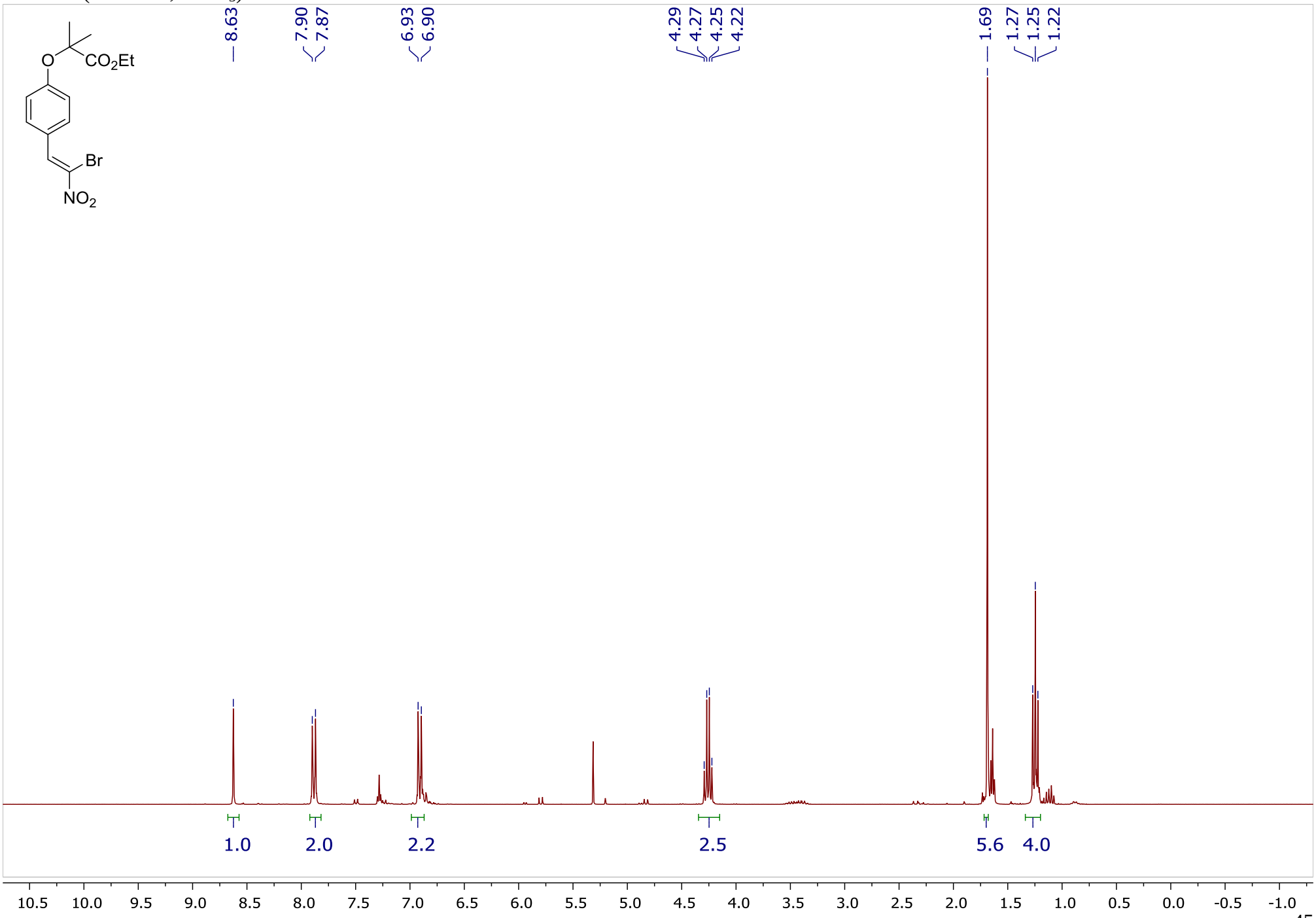
**(Z)-1-(2-Bromo-2-nitrovinyl)-4-methylbenzene**

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

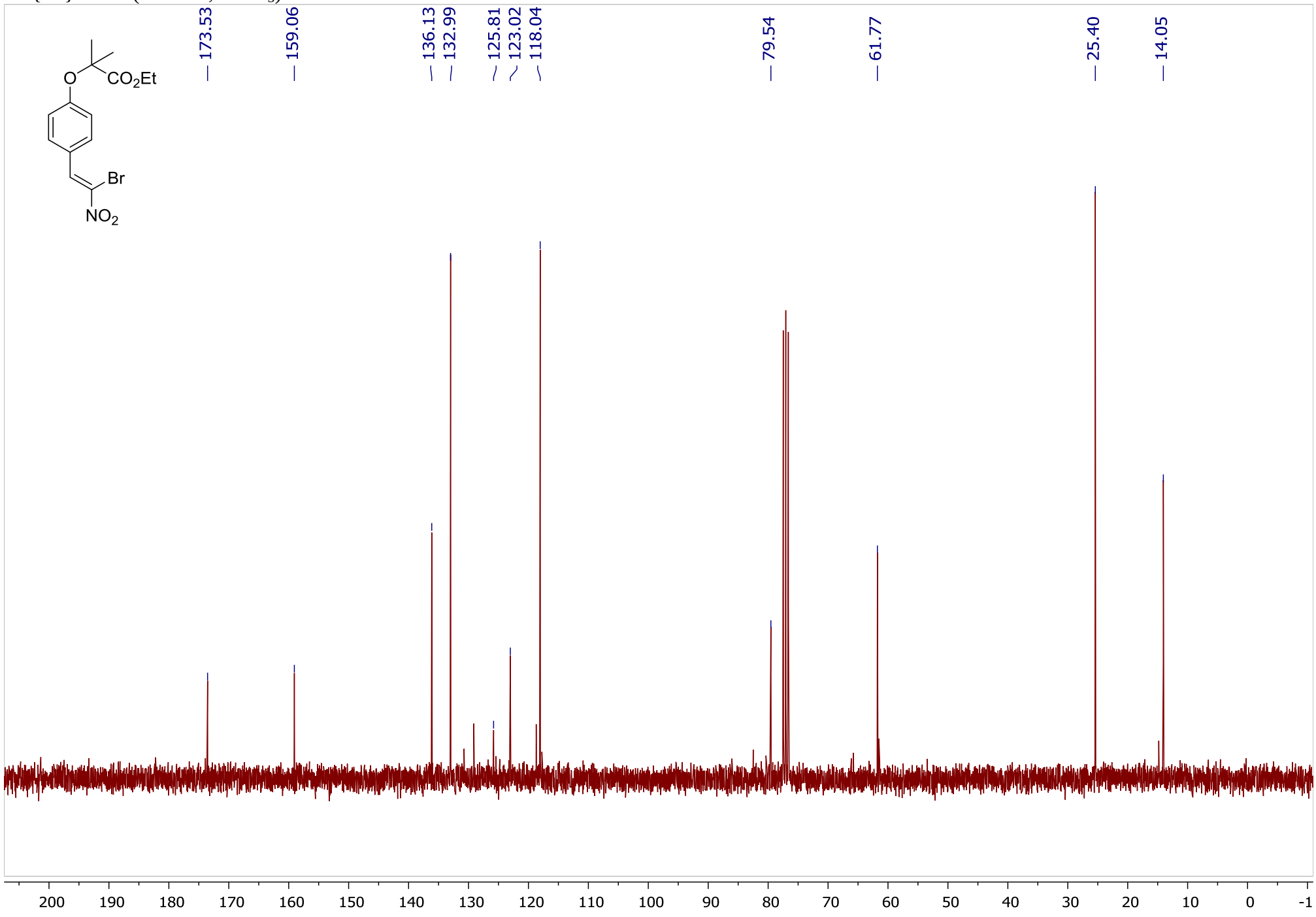


**(*Z*)-Ethyl 2-(4-(2-bromo-2-nitrovinyl)phenoxy)-2-methylpropanoate**

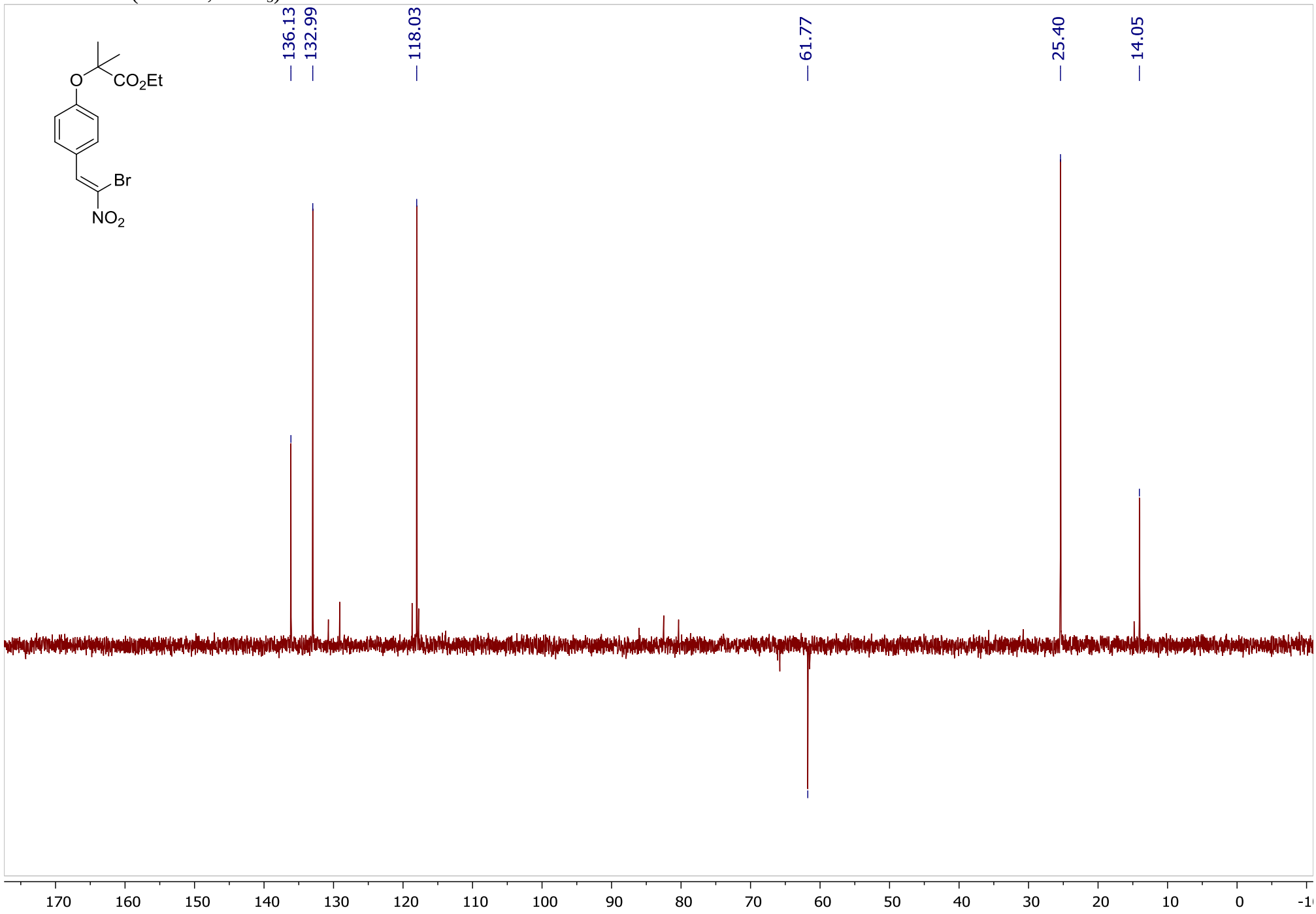
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



**(*Z*)-1-(2-Bromo-2-nitrovinyl)-3-methoxybenzene**

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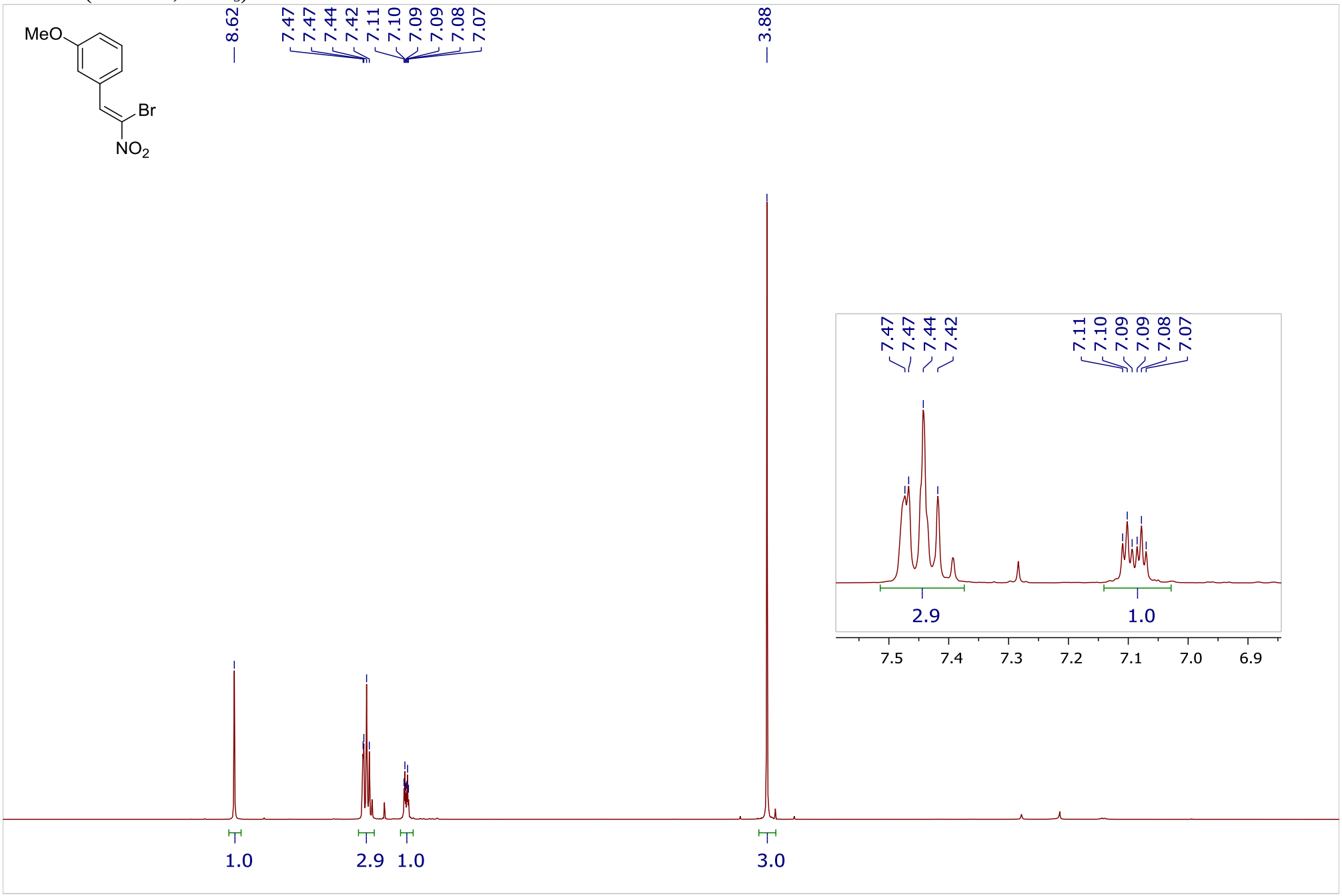

**(*Z*)-1-(2-Bromo-2-nitrovinyl)-2-methoxybenzene**

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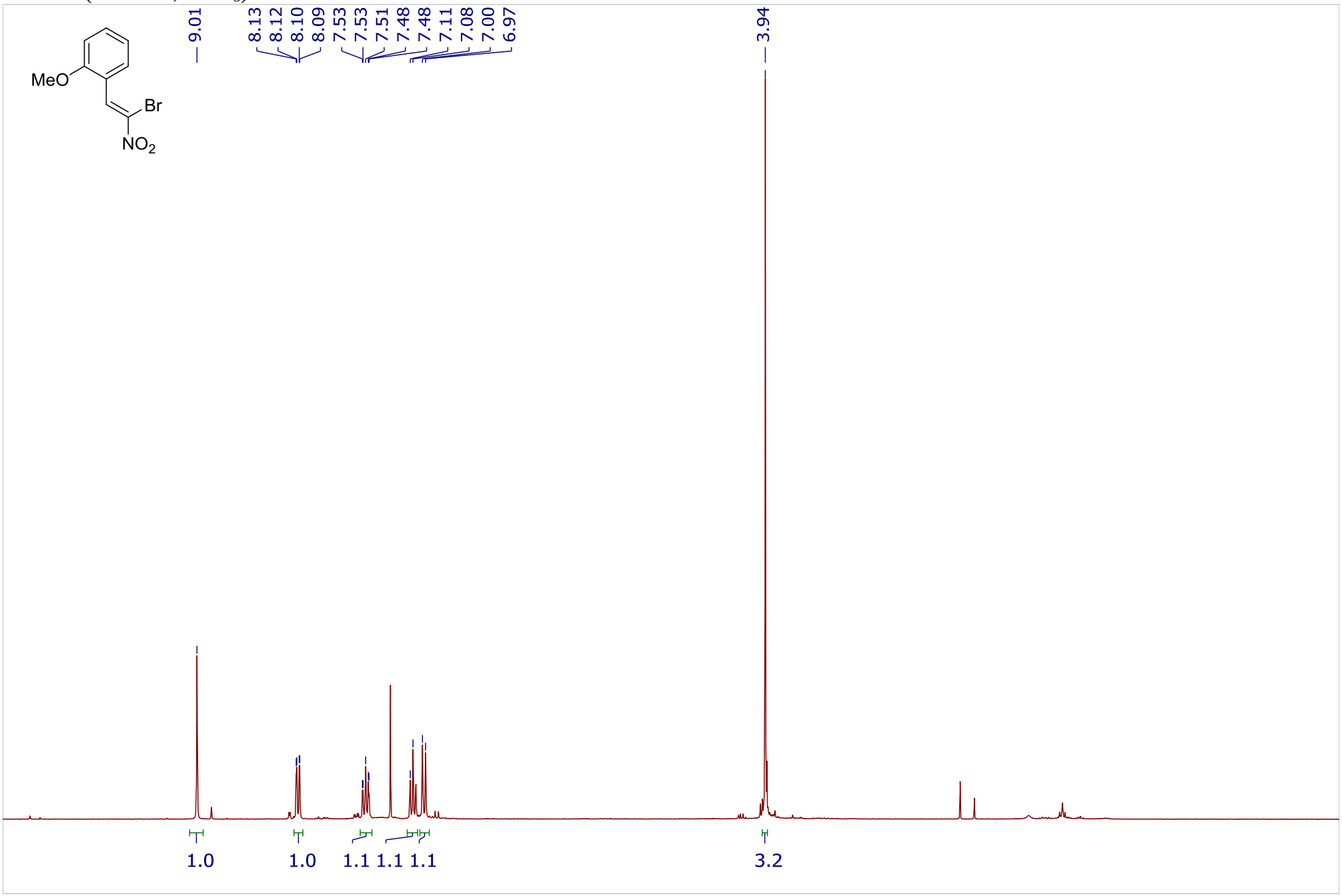
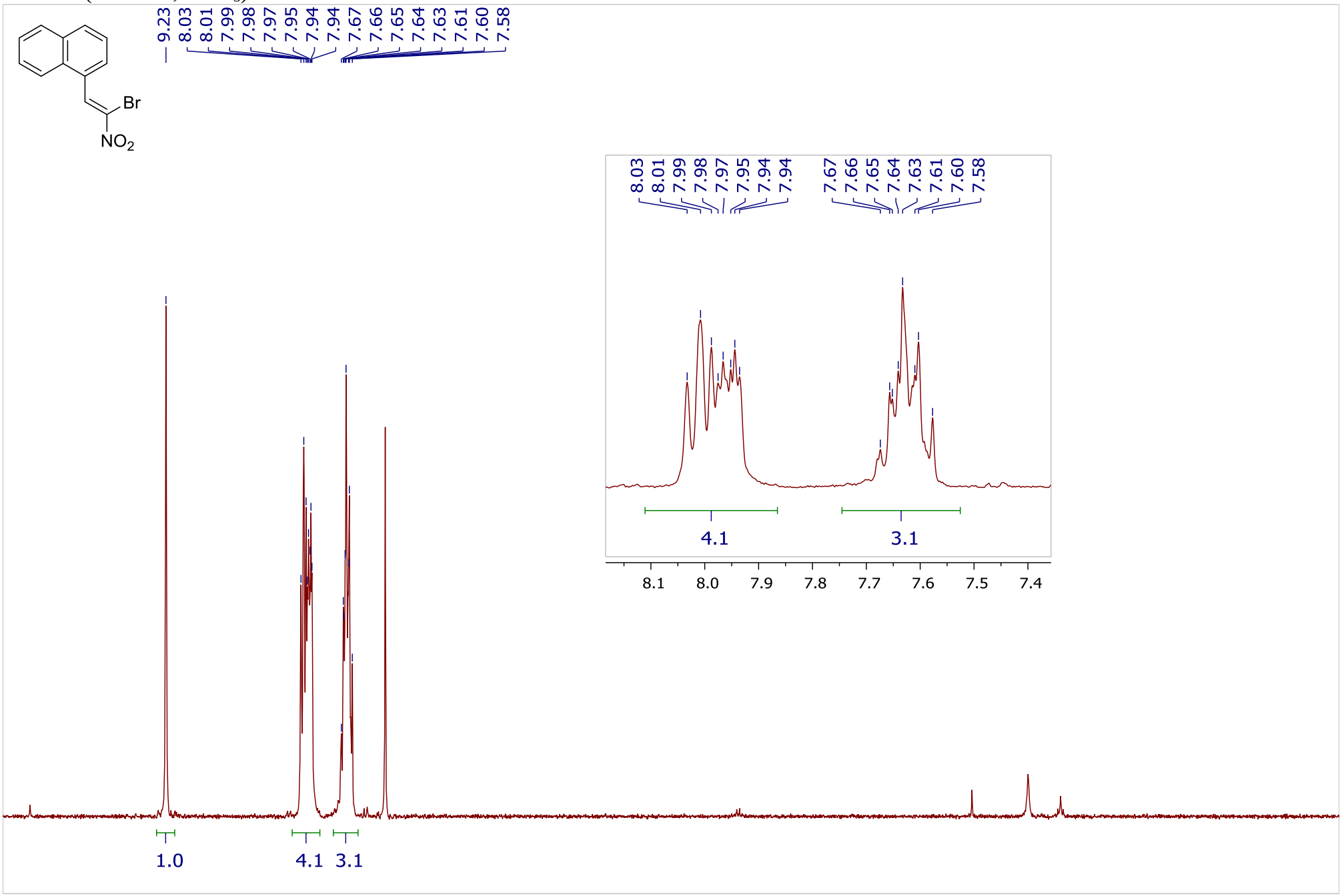


**(*Z*)-1-(2-Bromo-2-nitrovinyl)naphthalene**

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



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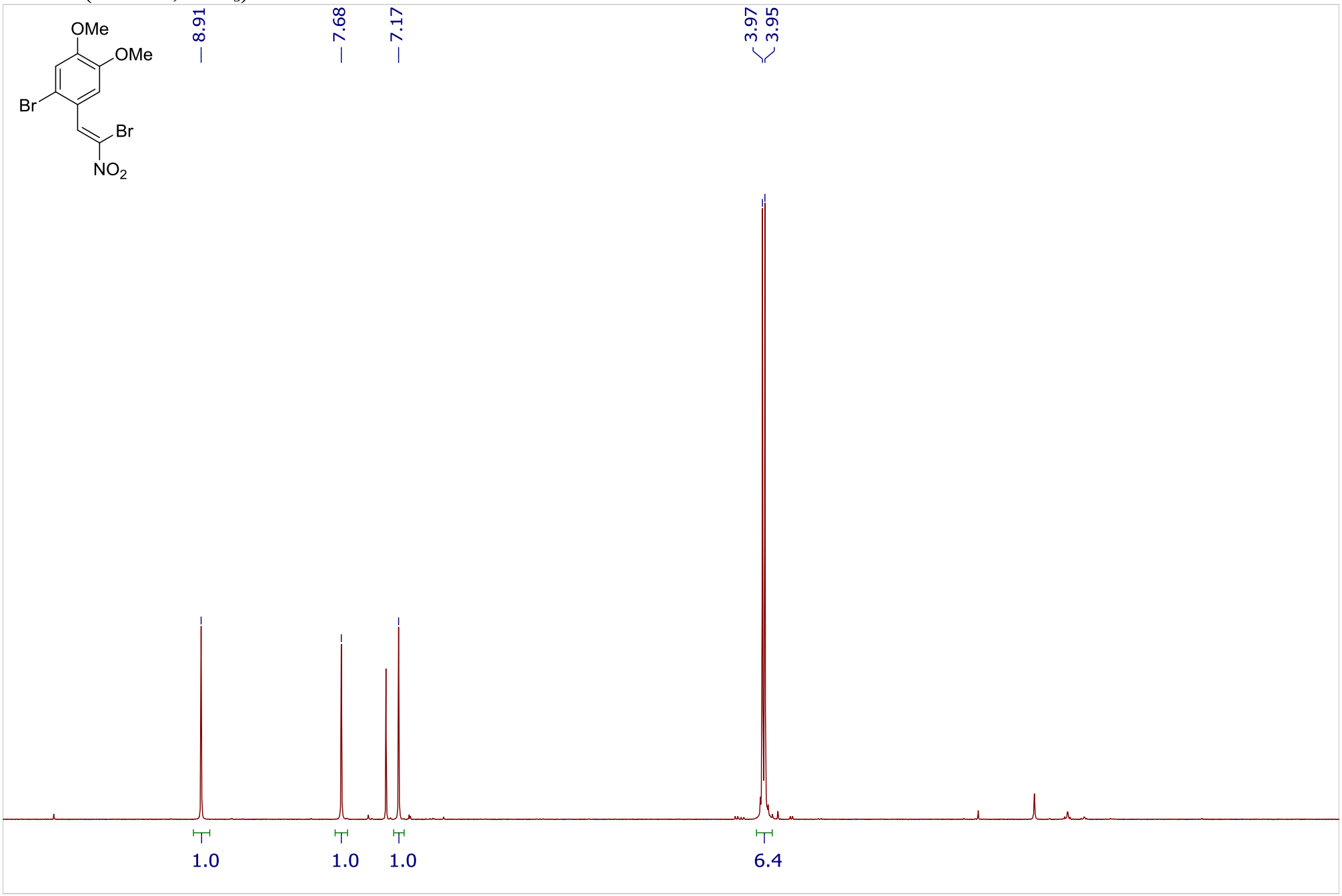
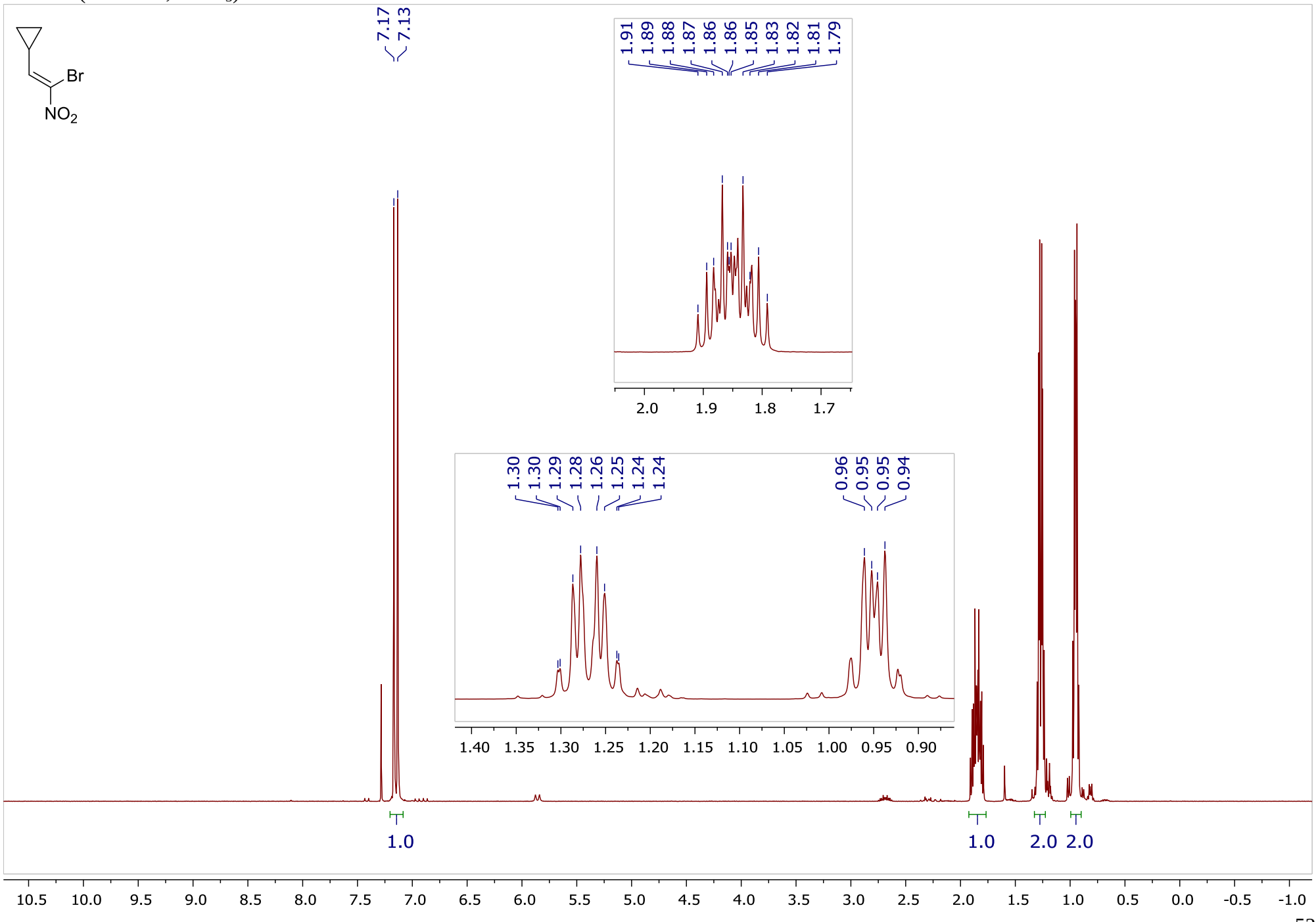
$^1$H NMR (300 MHz, $CDCl_3$)

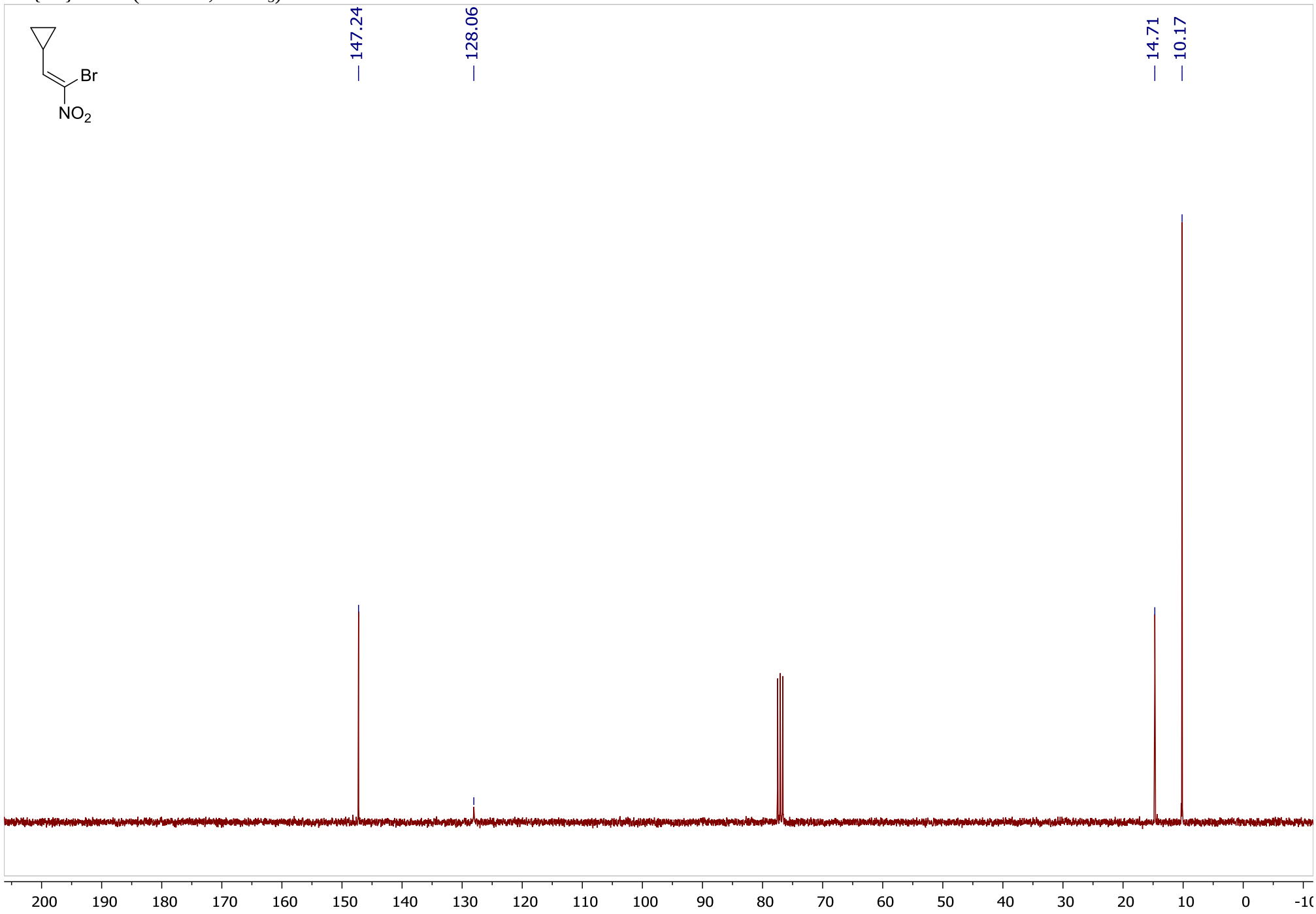


**(Z)-(2-Bromo-2-nitrovinyl)cyclopropane**

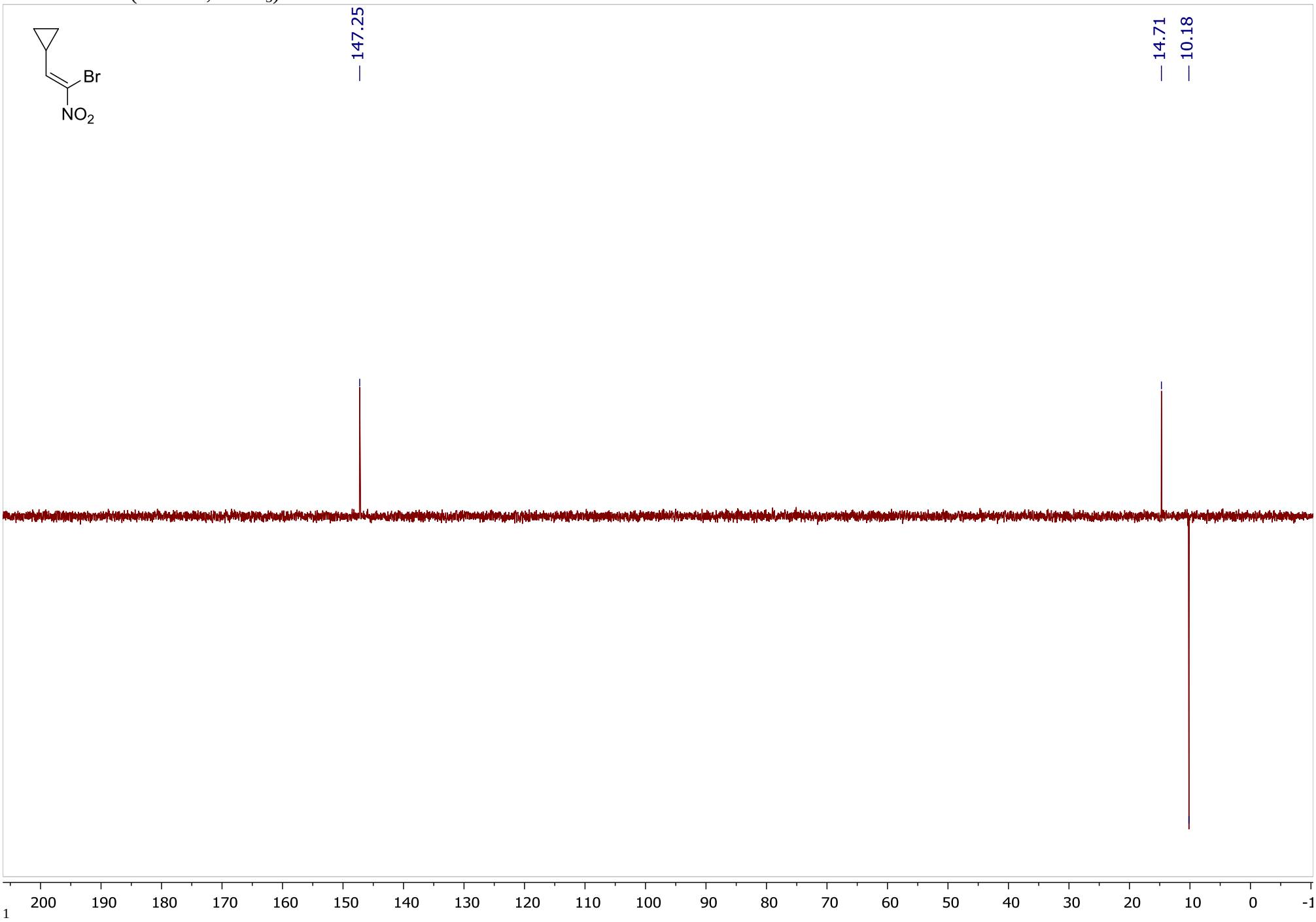
$^1$H NMR (300 MHz, $CDCl_3$)



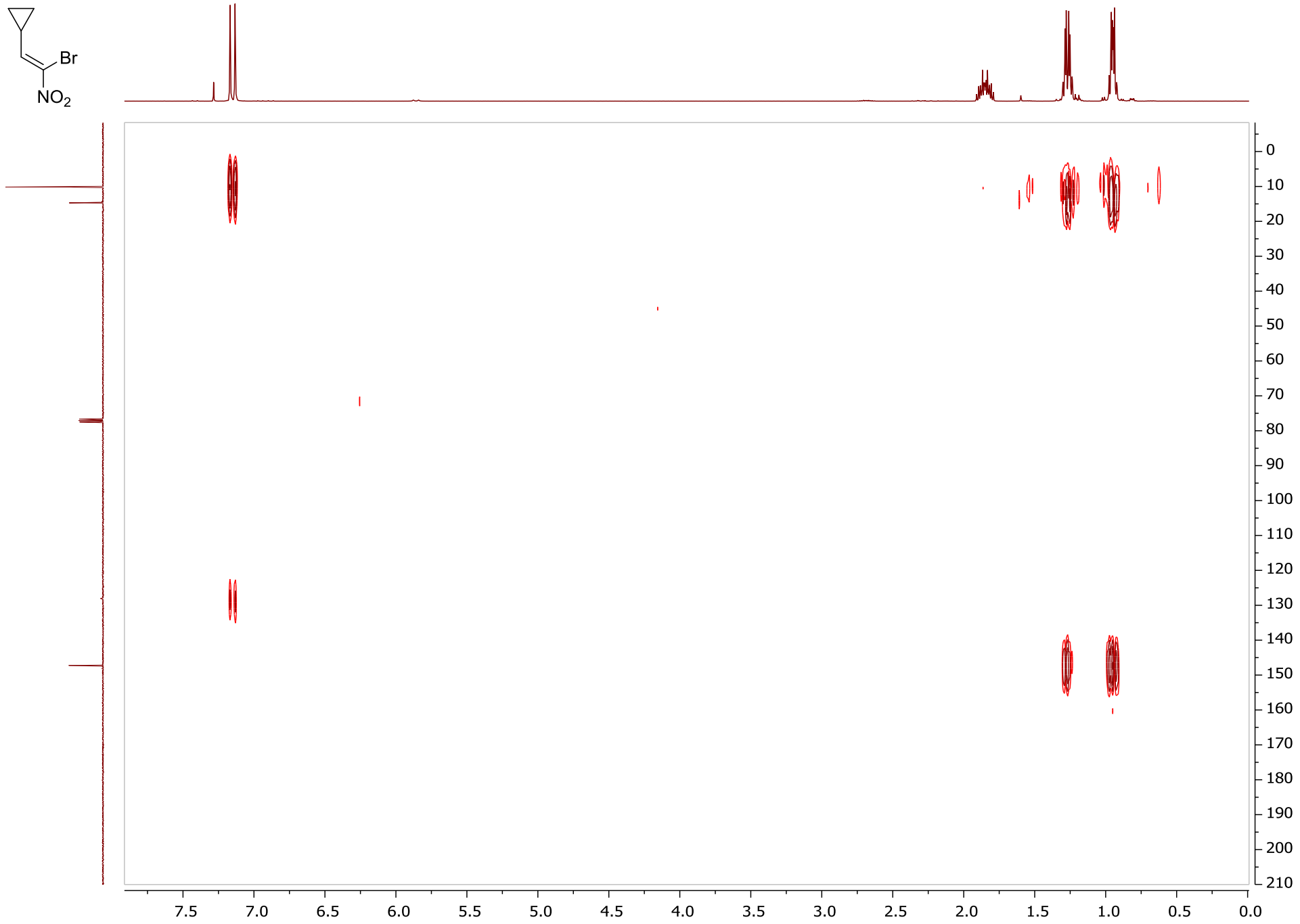
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



$^{1}H$-$^{13}C$ HMBC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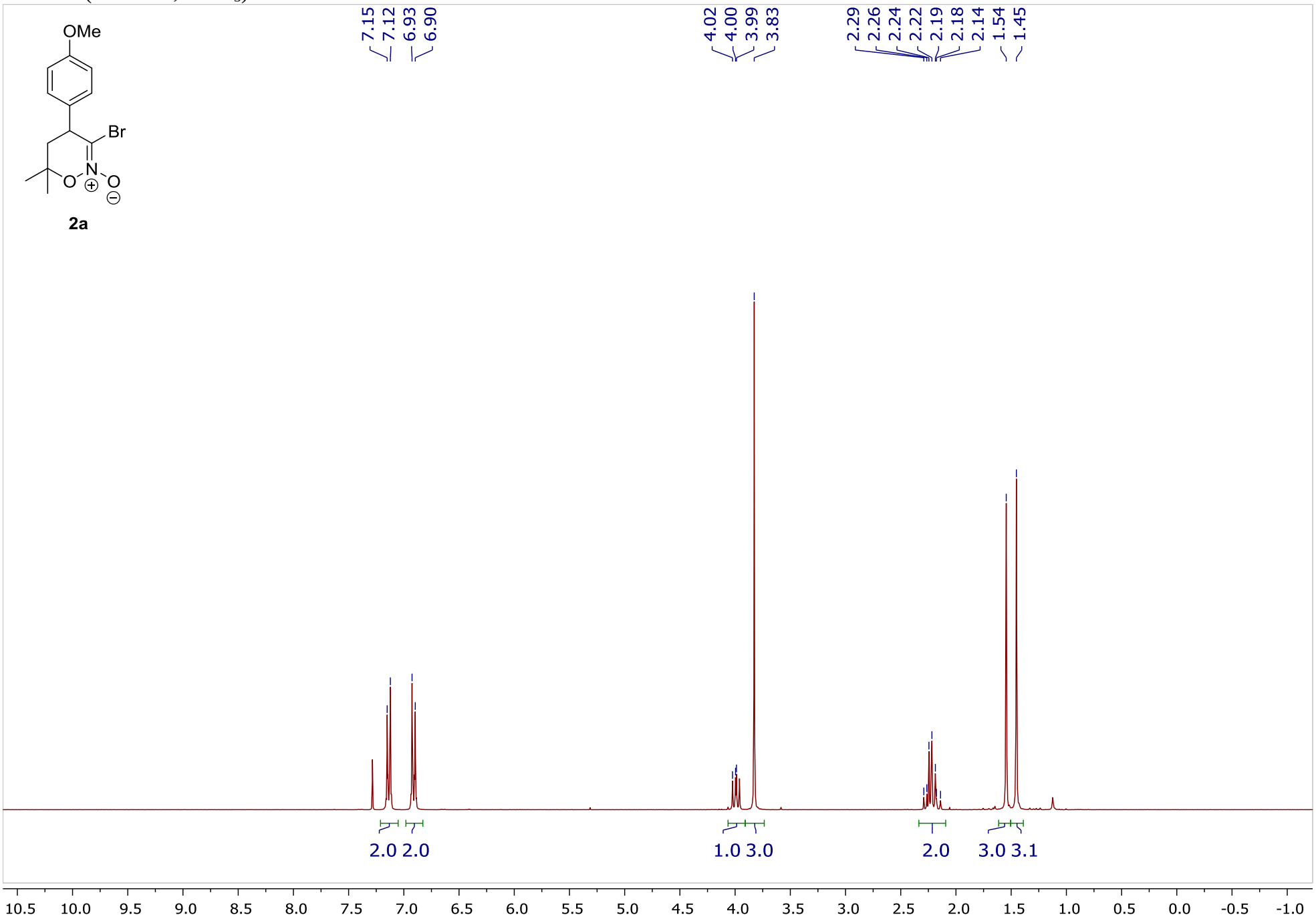
1.5
1.0
0.5
0.0

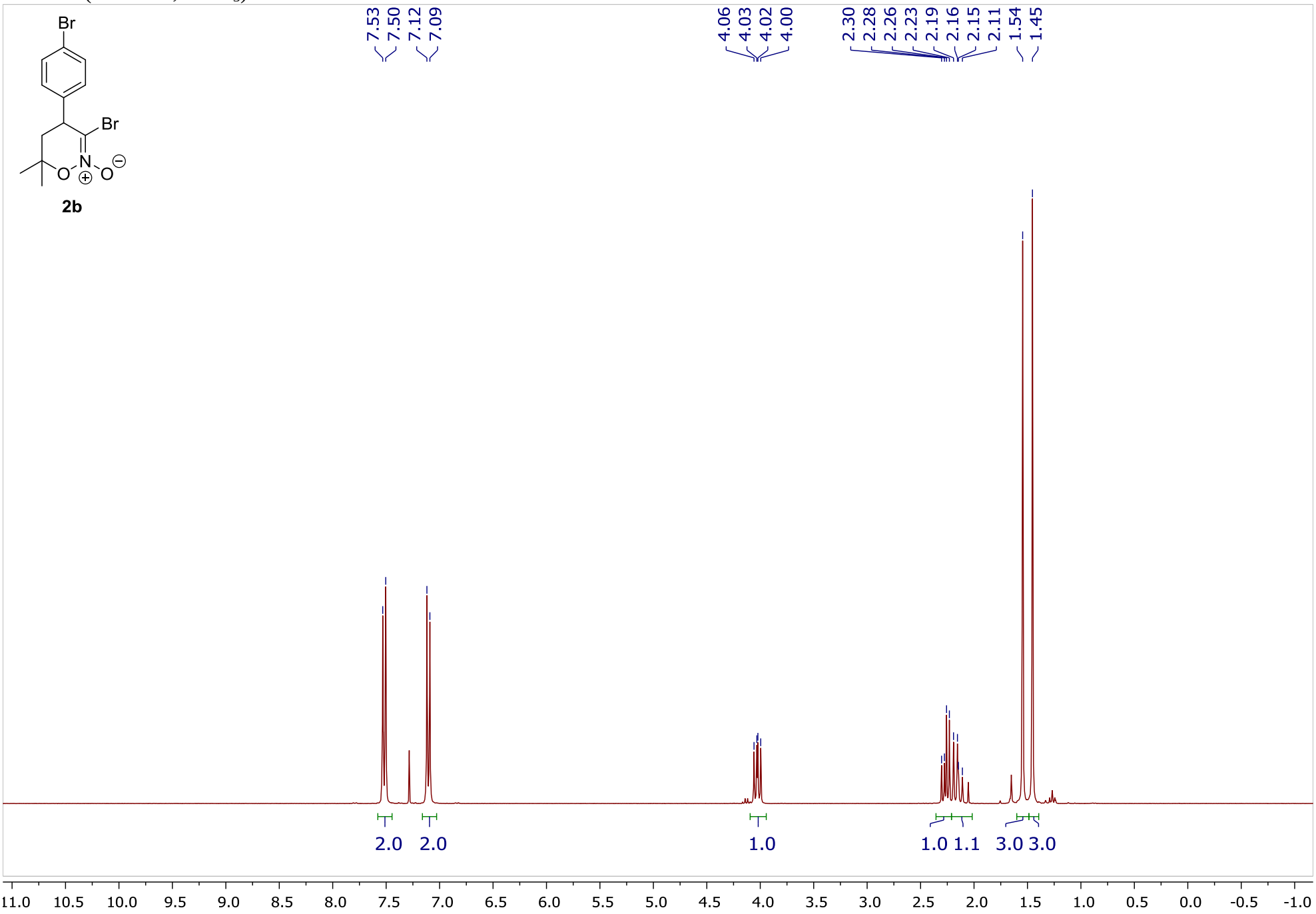
**3-Bromo-4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2a**

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

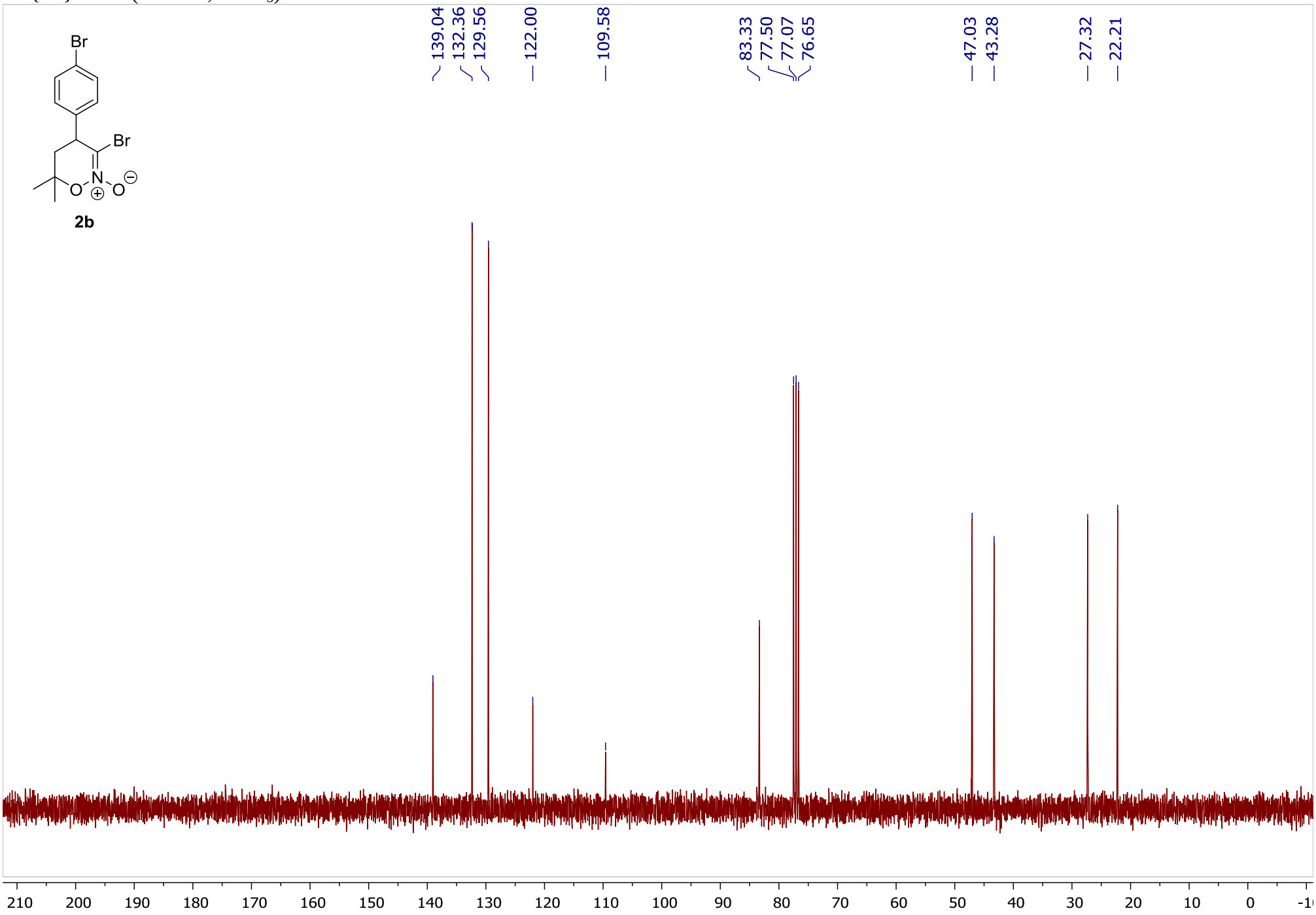


**3-Bromo-4-(4-bromophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2b**

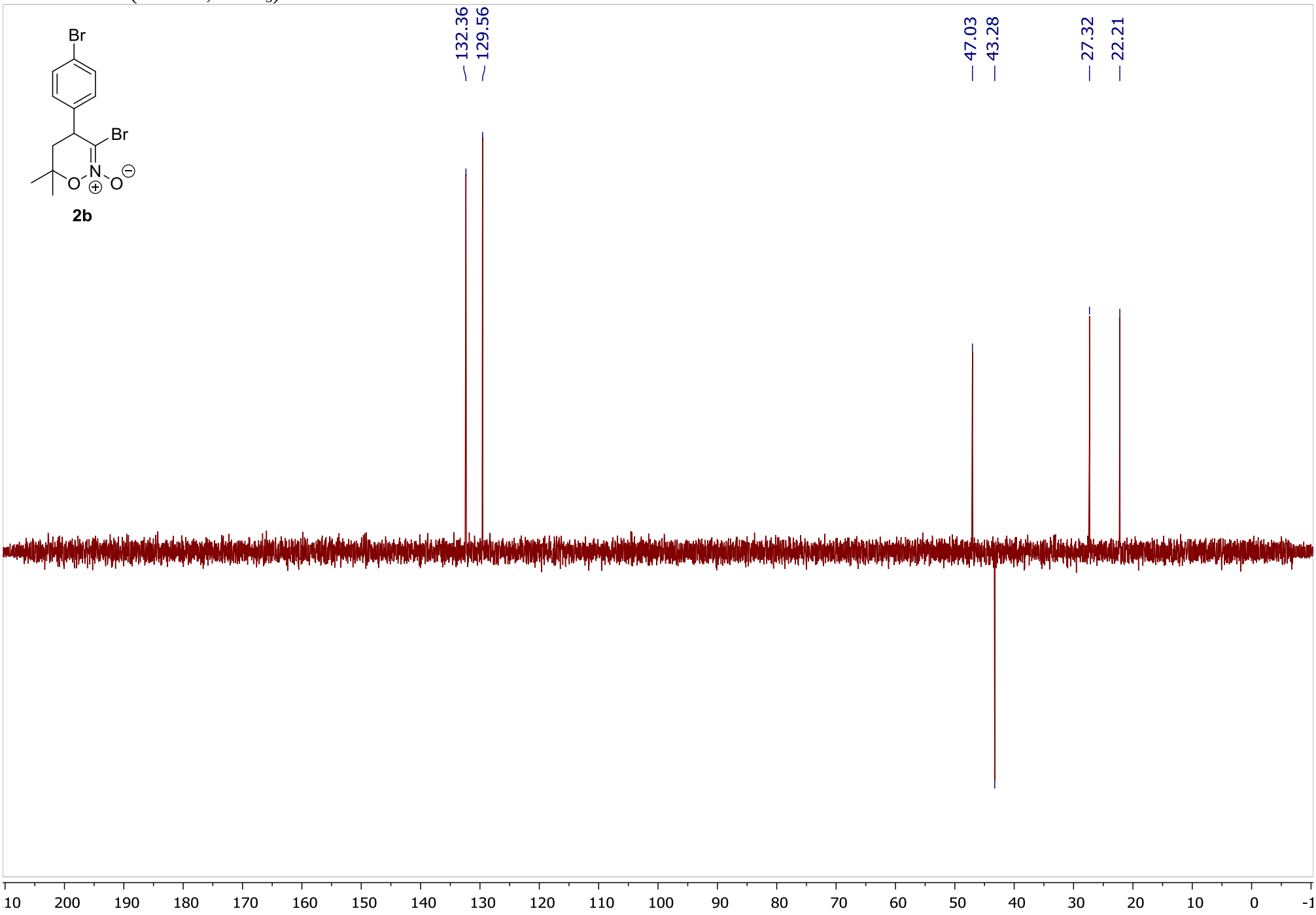
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

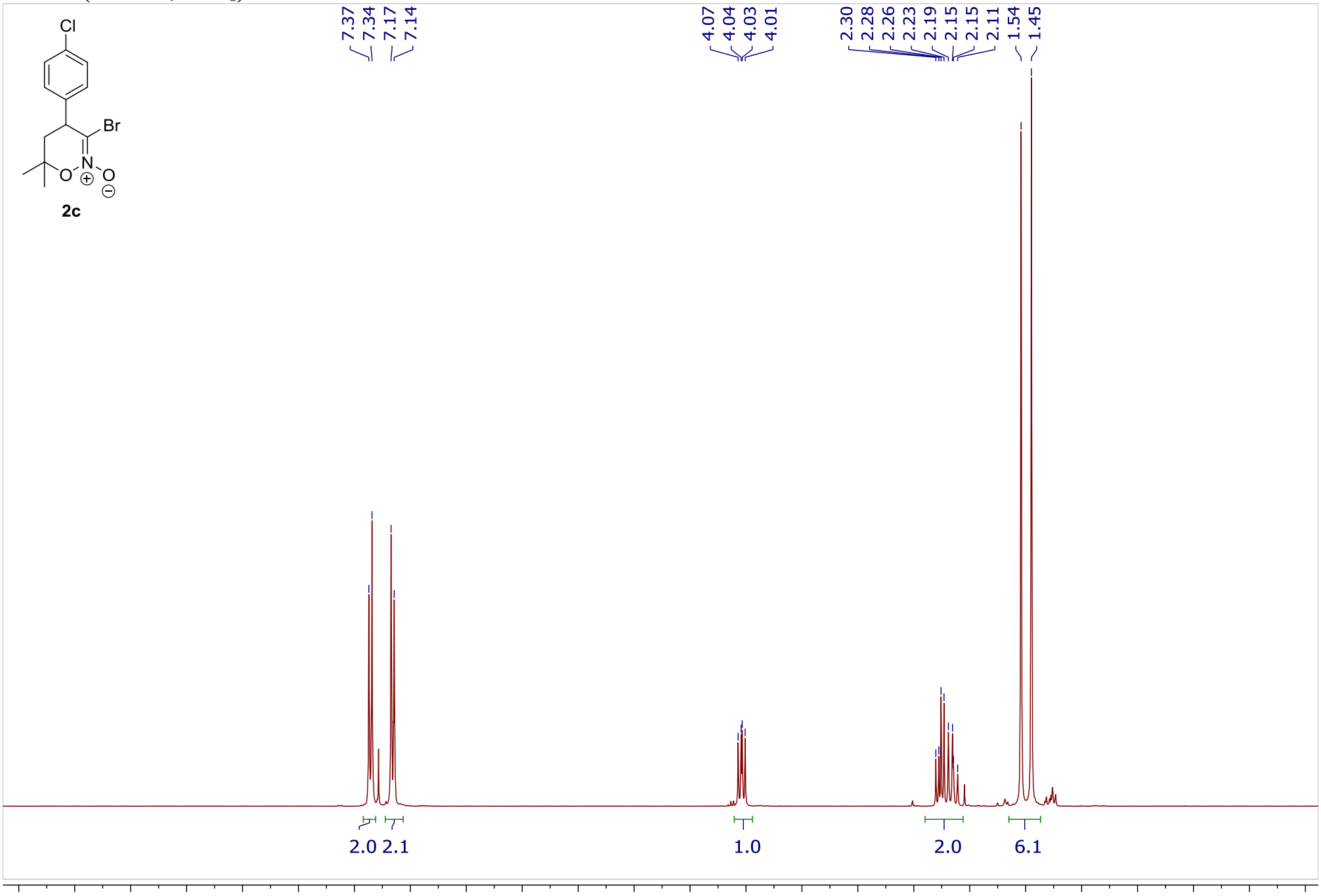


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

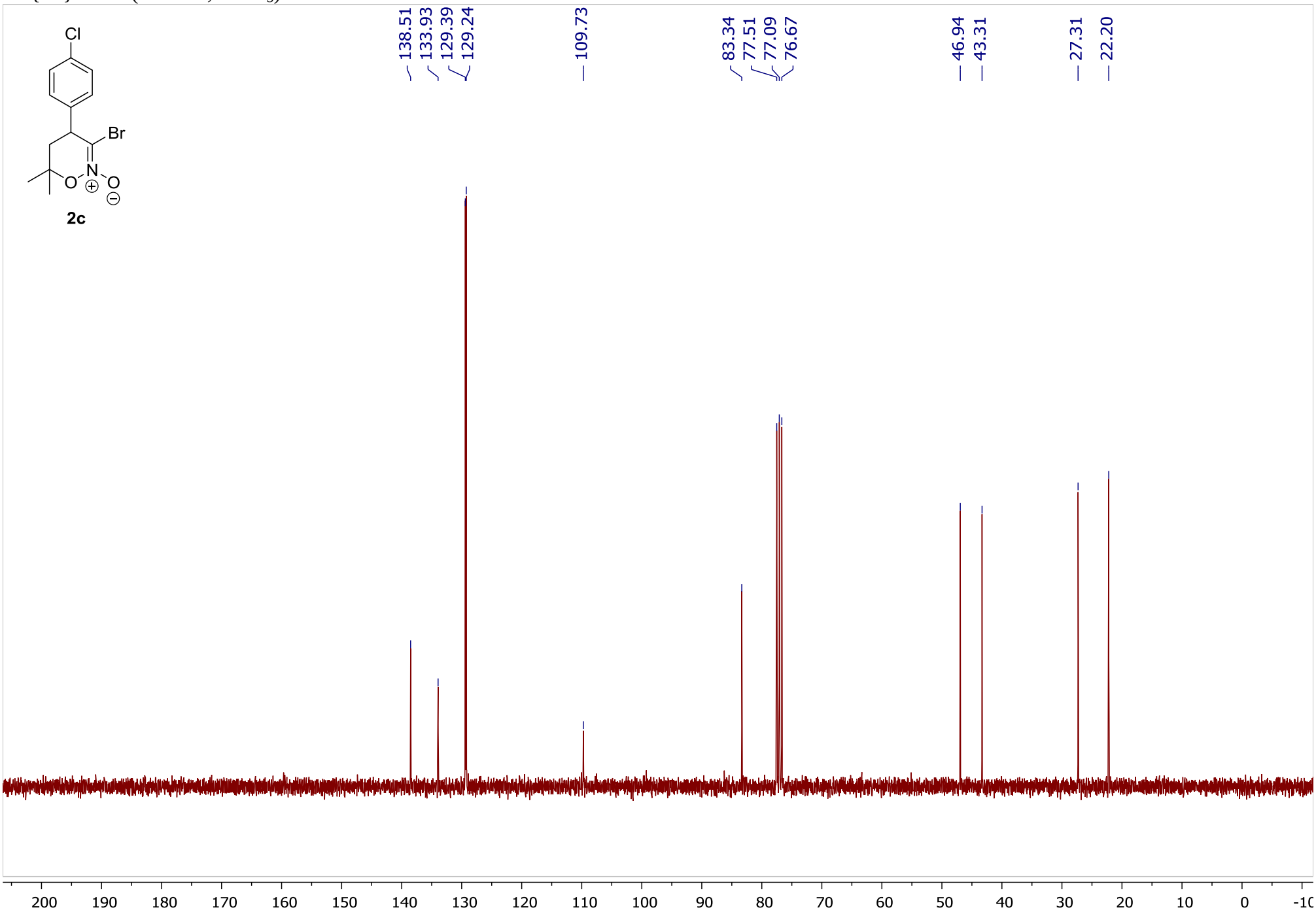


**3-Bromo-4-(4-chlorophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2c**

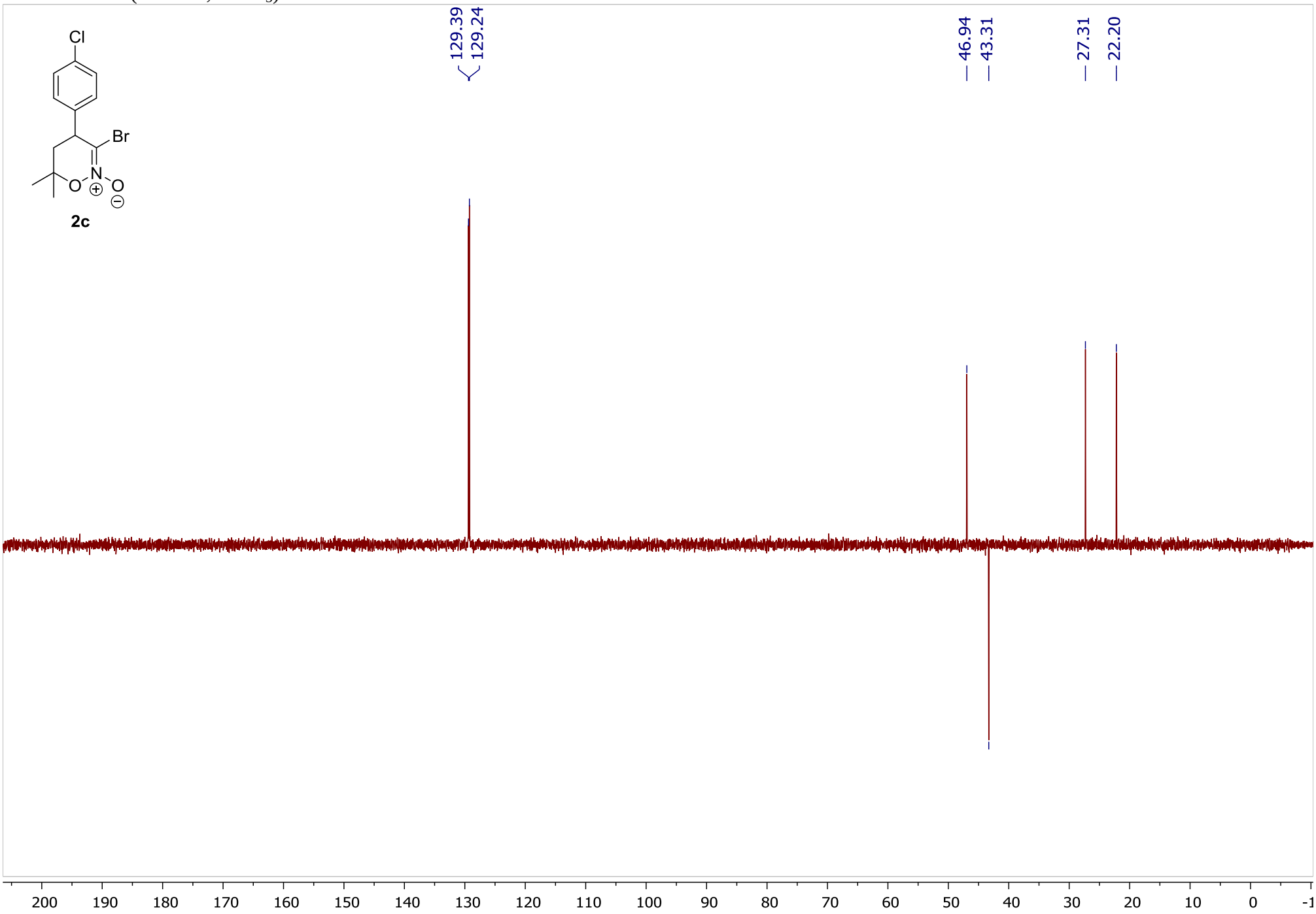
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

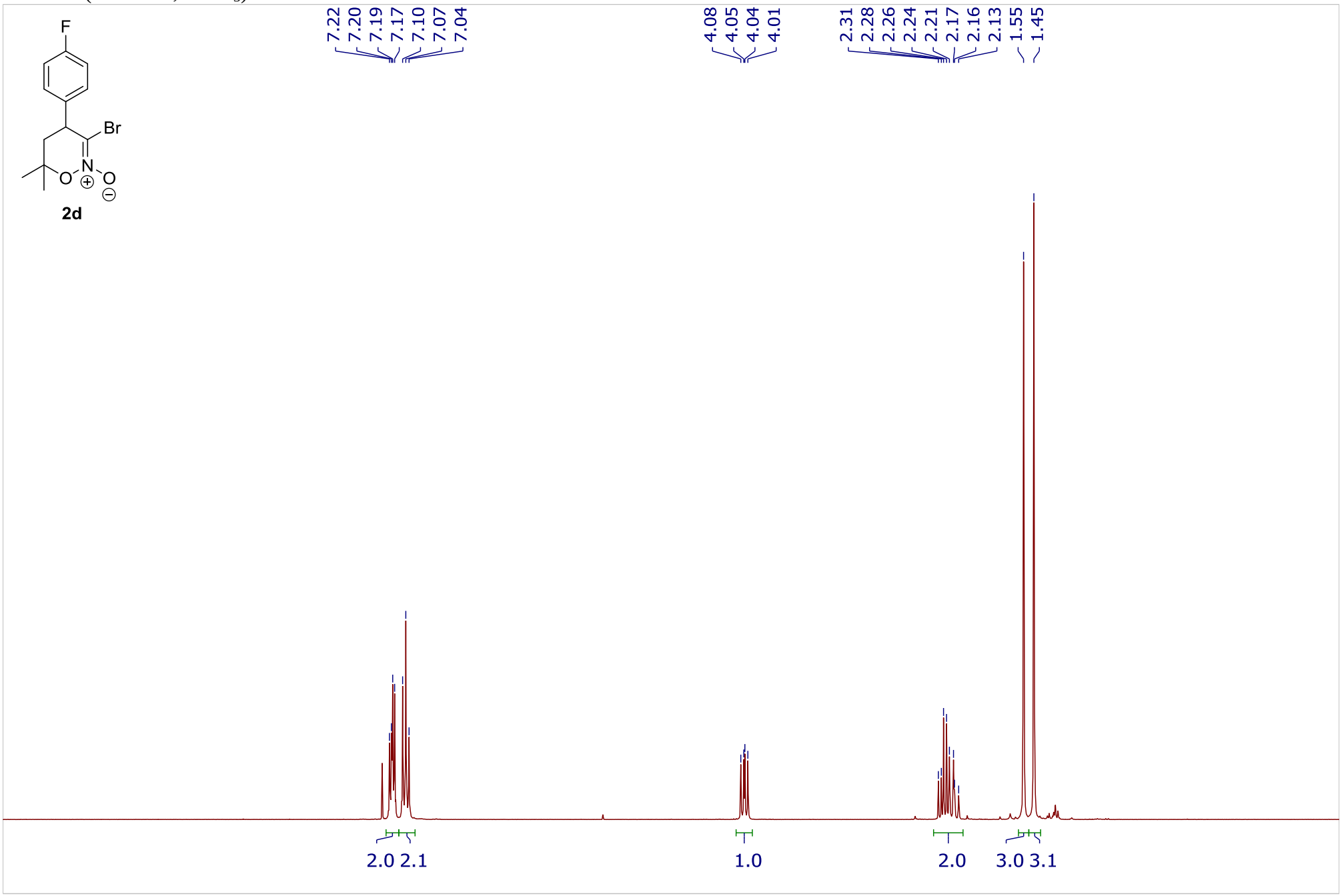


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

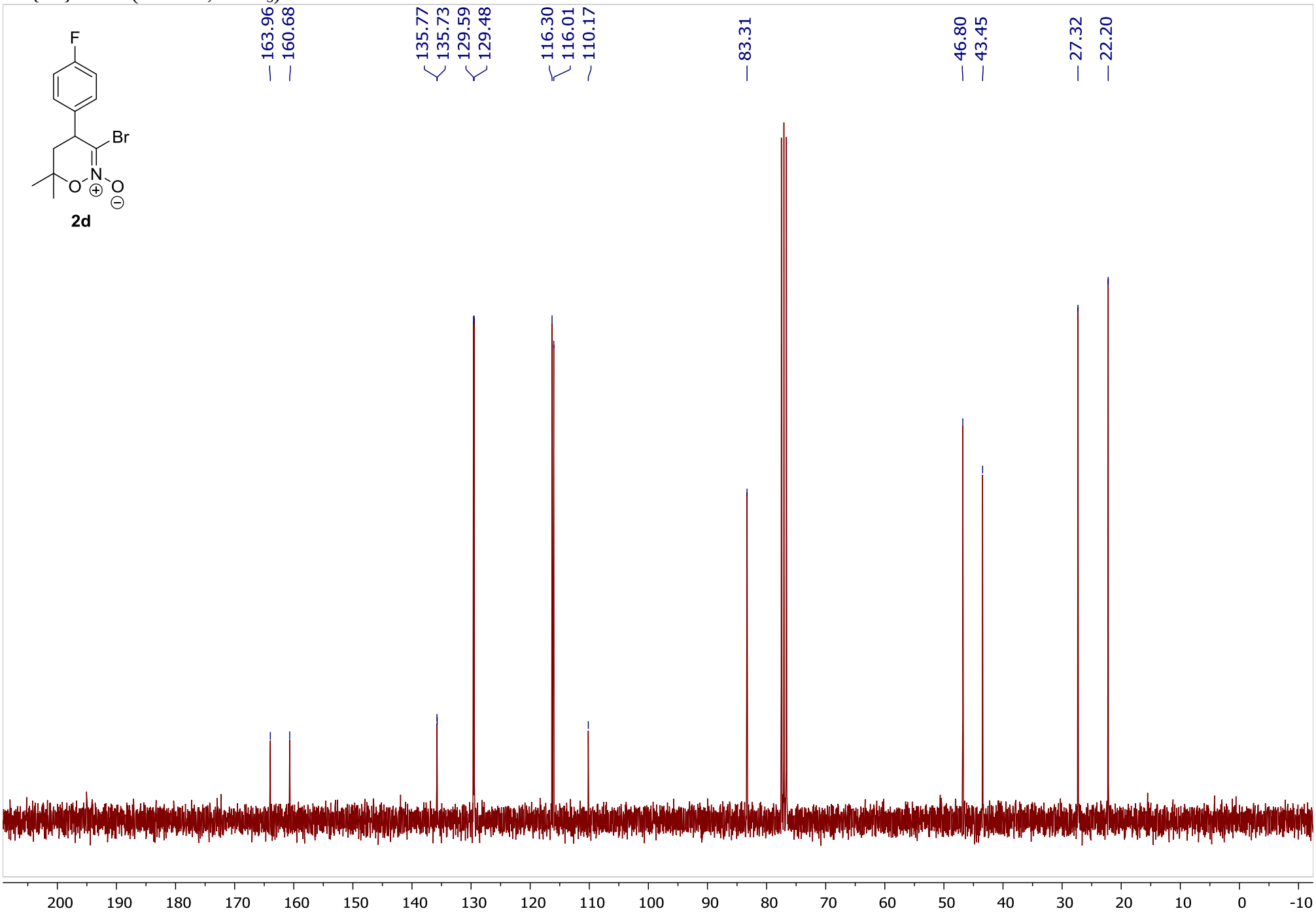


**3-Bromo-4-(4-fluorophenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2d**

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



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



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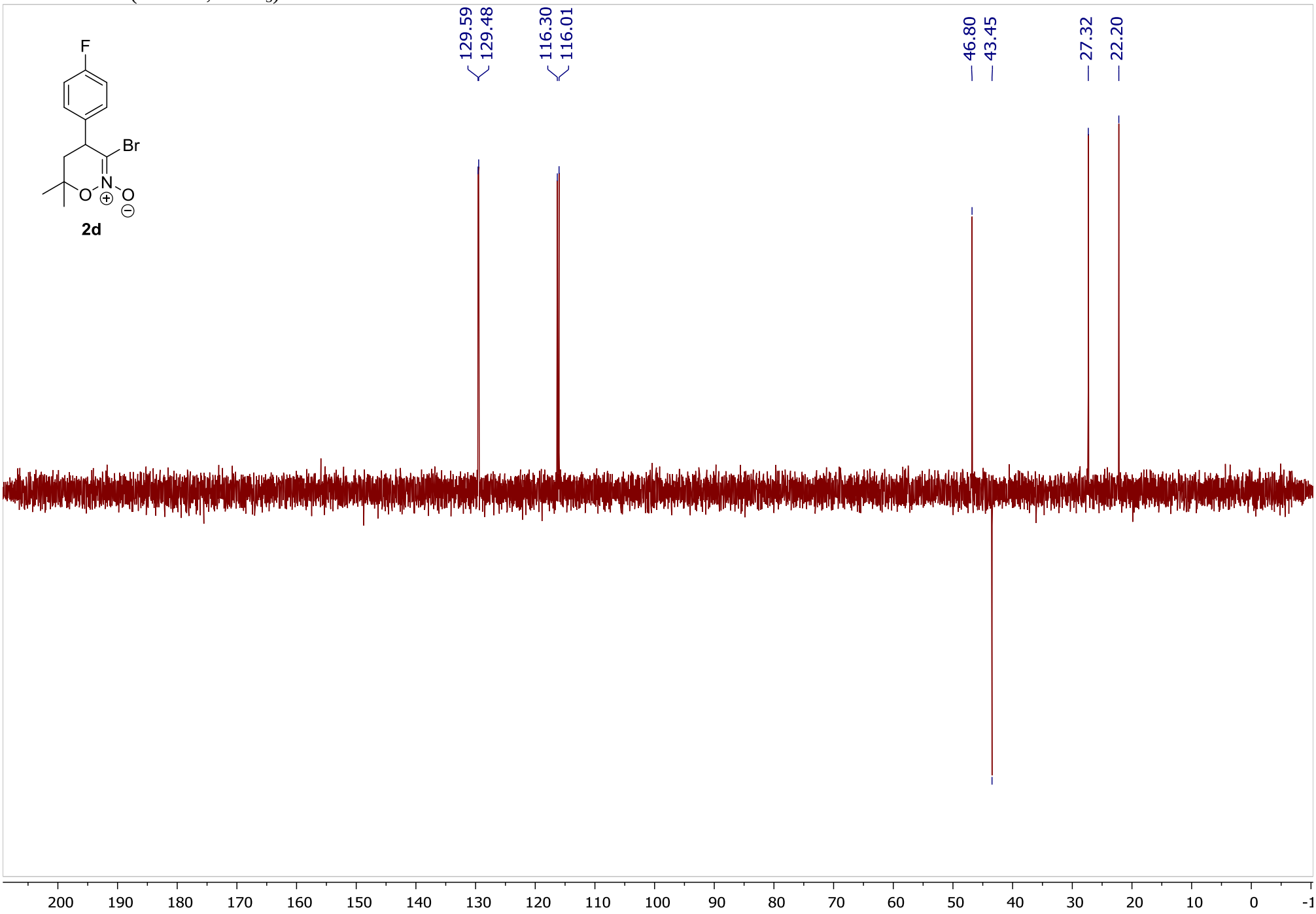
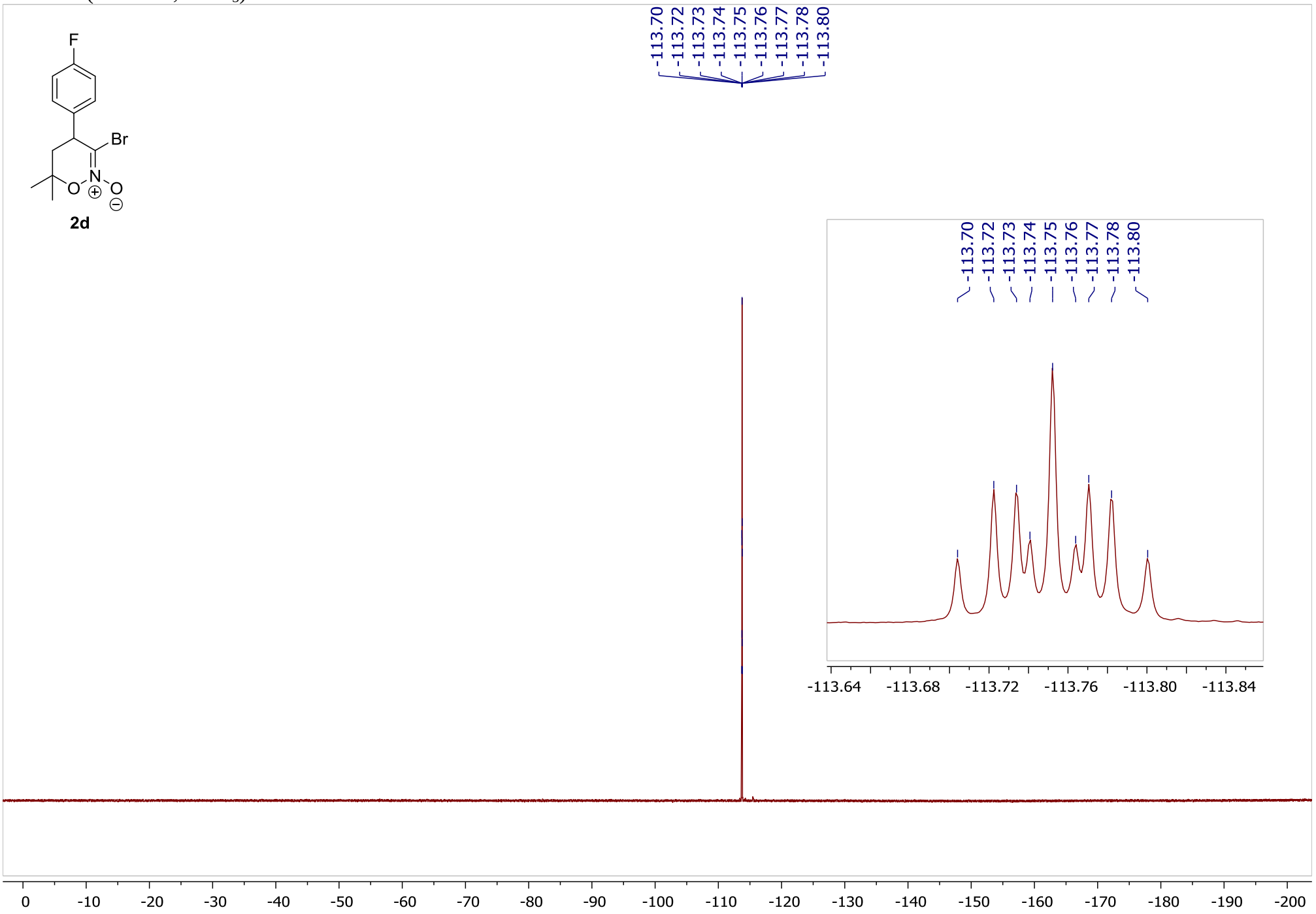
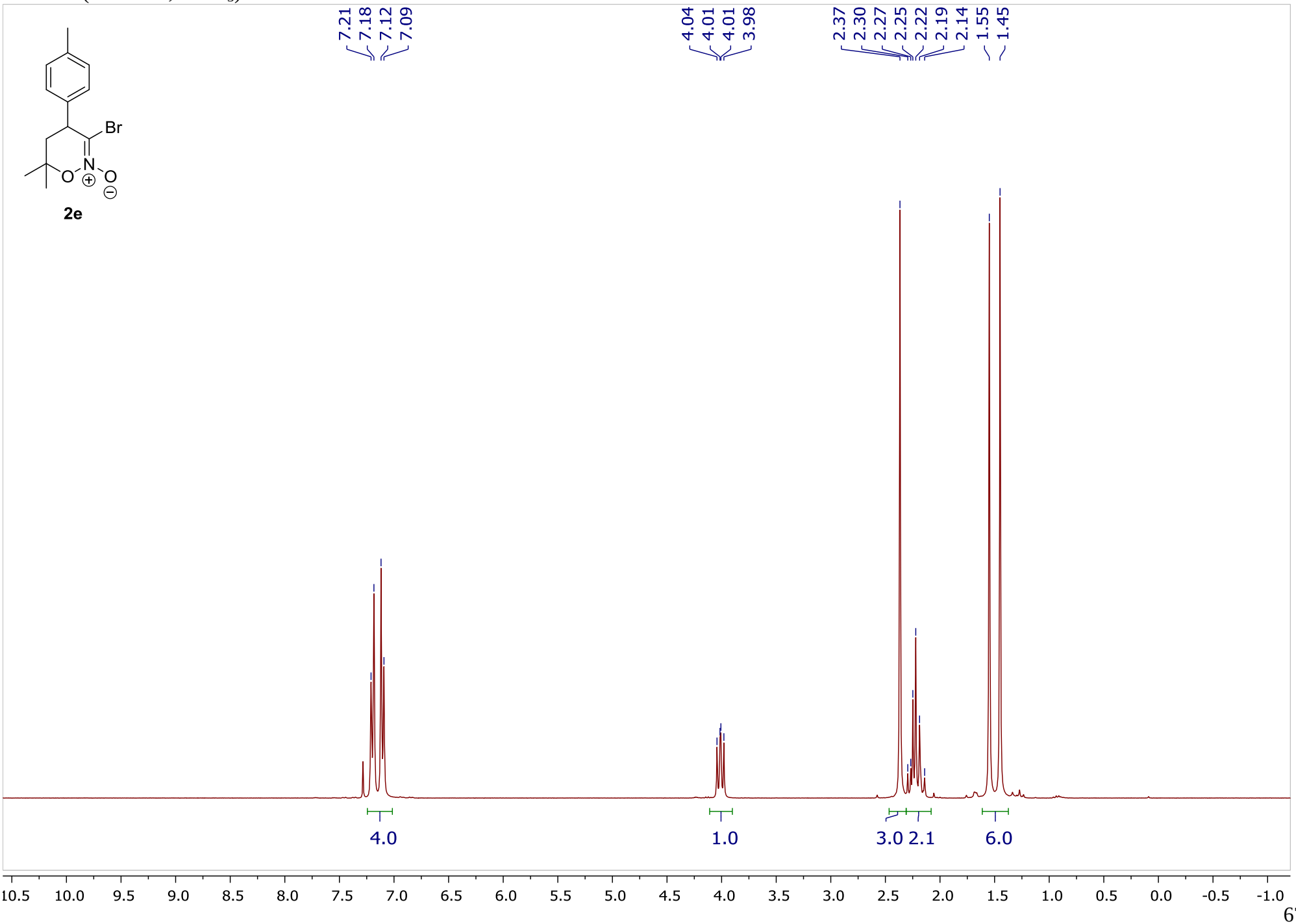


$^{19}$F NMR (282 MHz, $CDCl_3$)

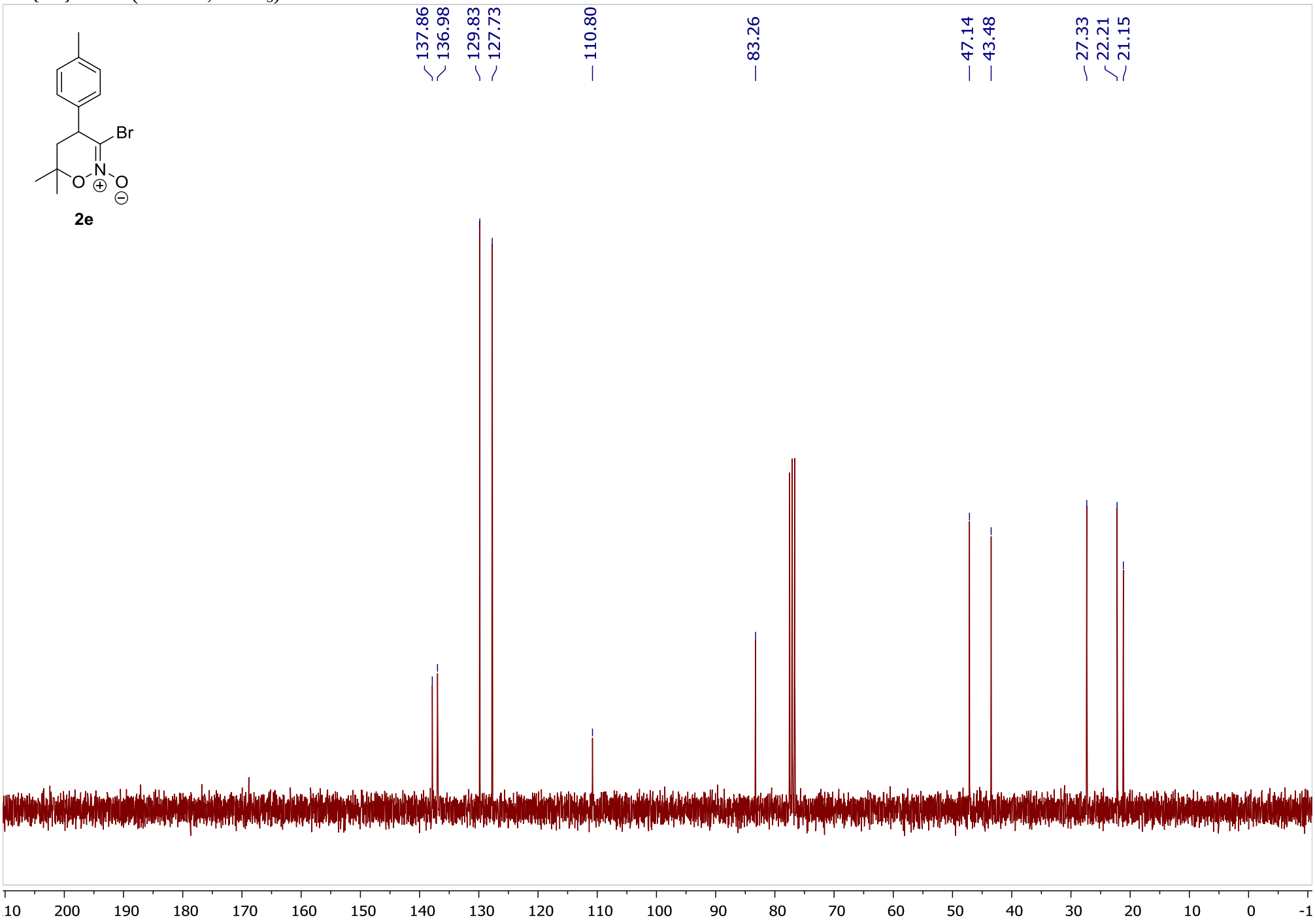


**3-Bromo-6,6-dimethyl-4-*p*-tolyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2e**

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



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



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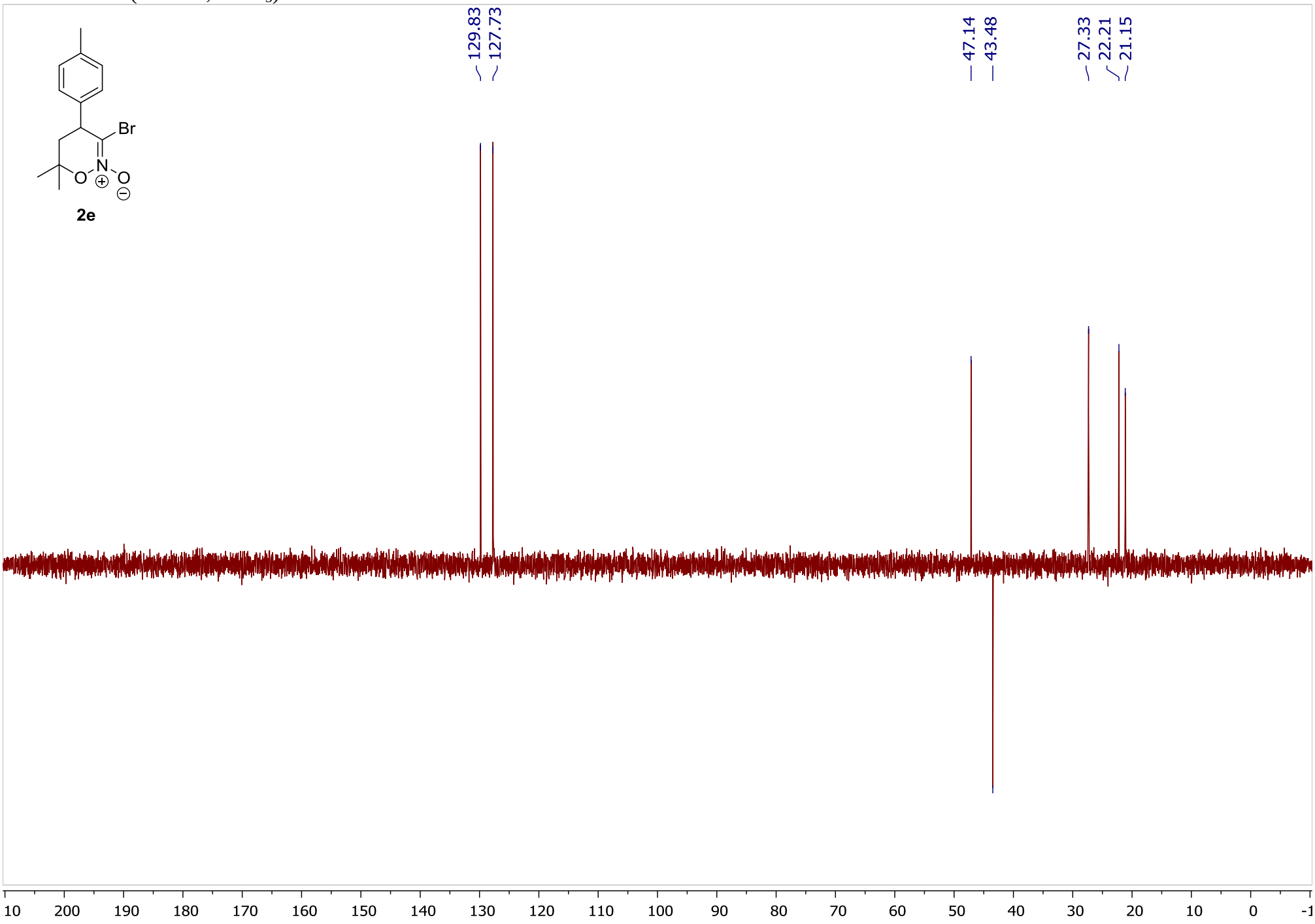
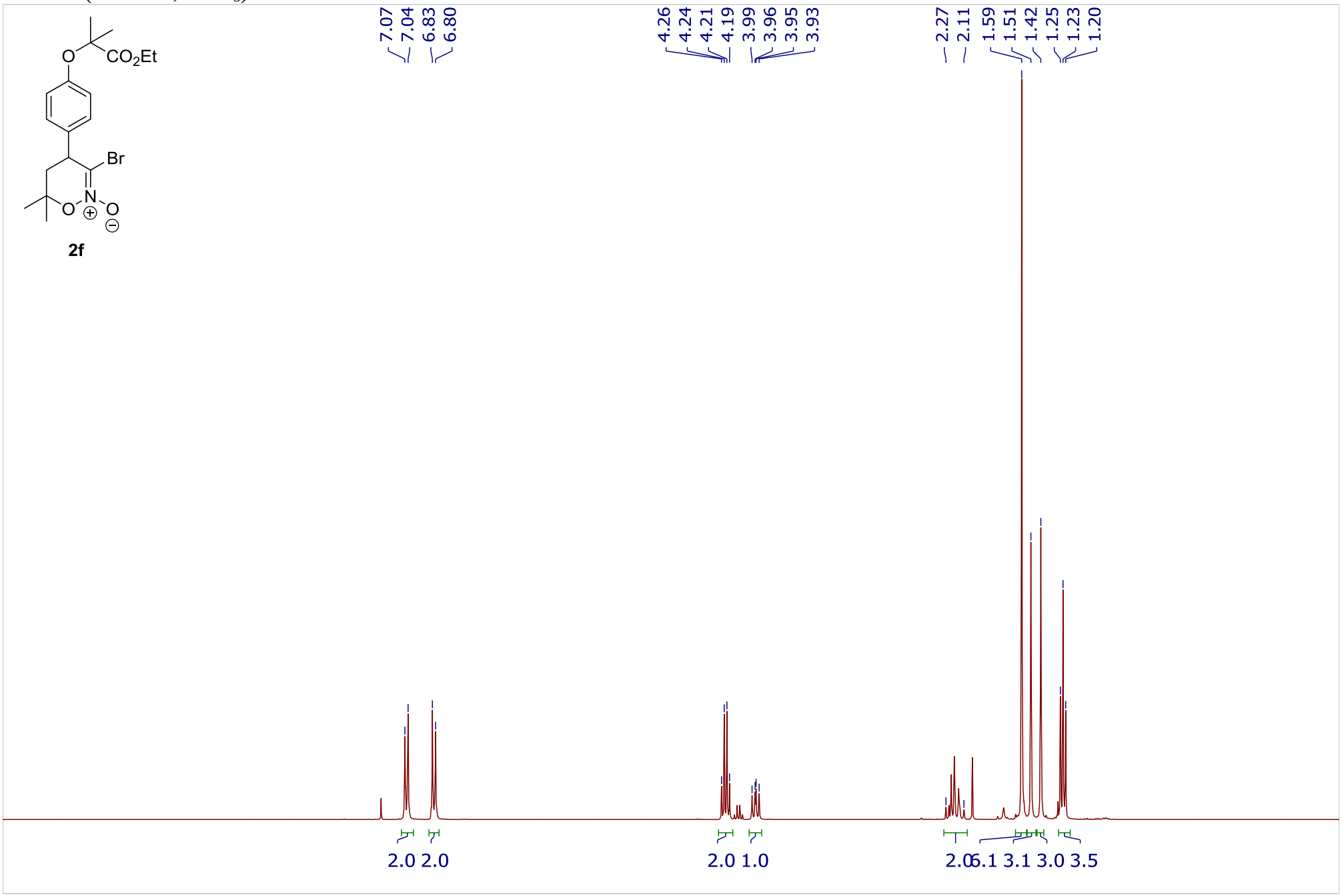


**3-Bromo-4-(4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2f**

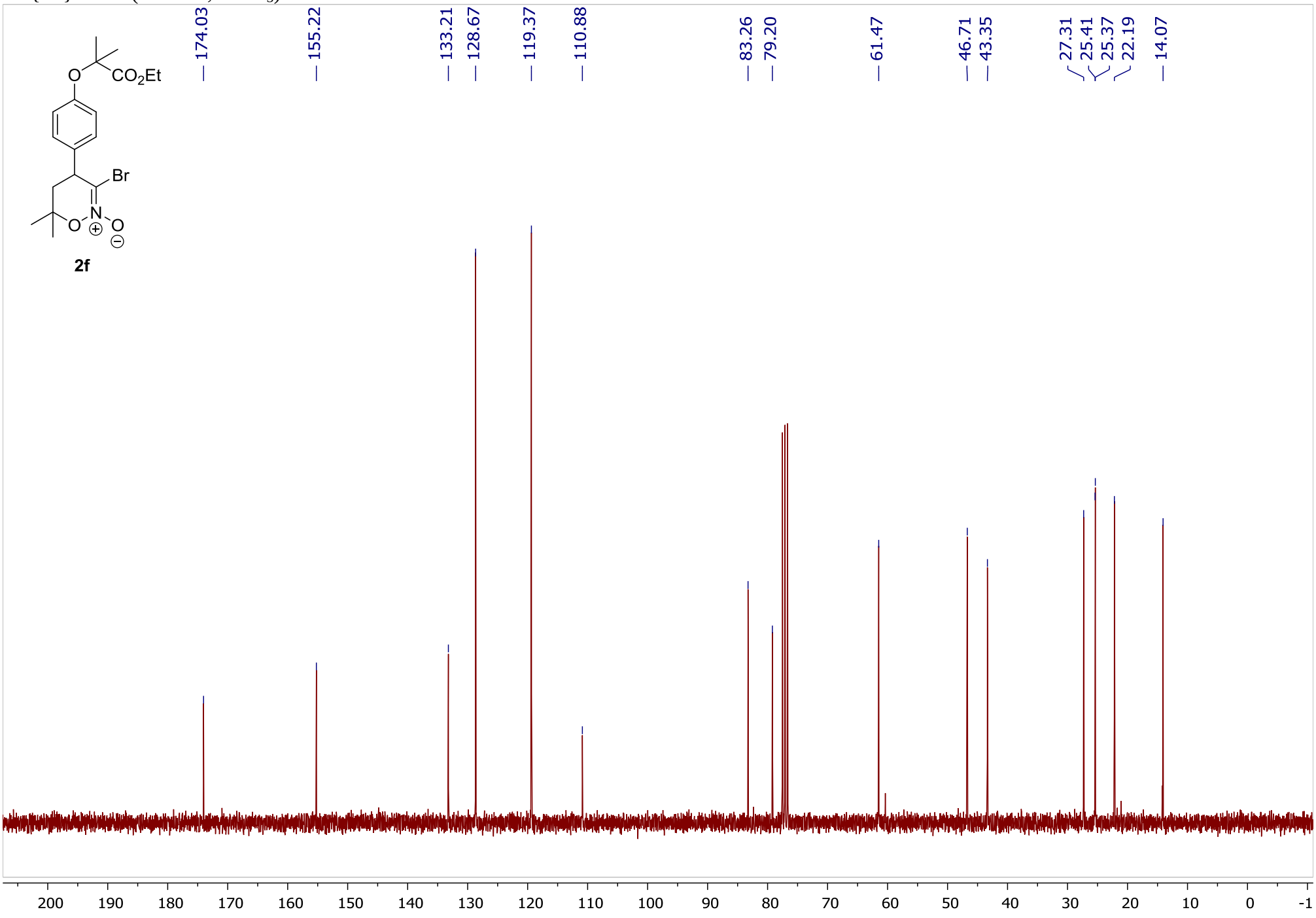
$^1$H NMR (300 MHz, $CDCl_3$)



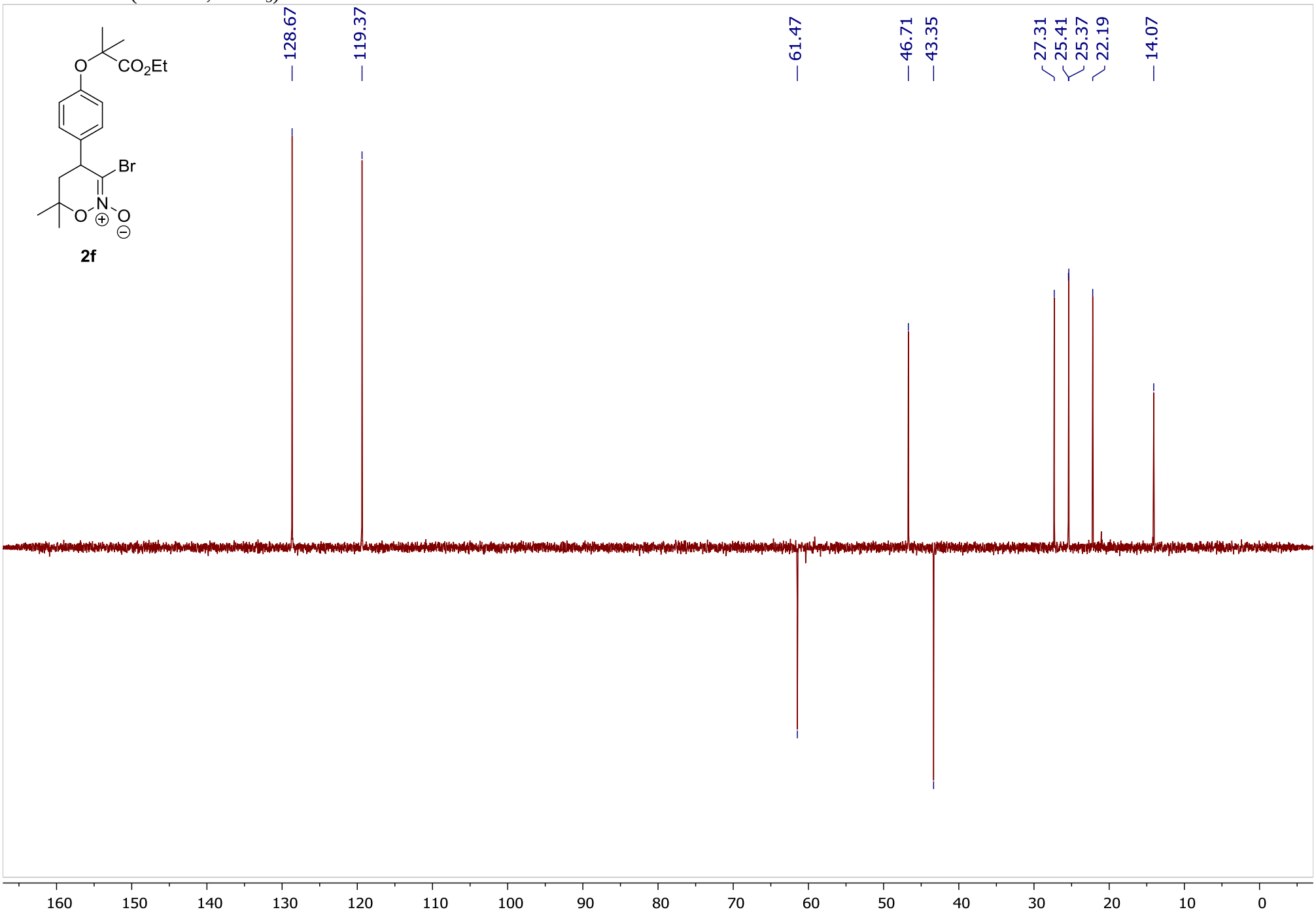



**2f**

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



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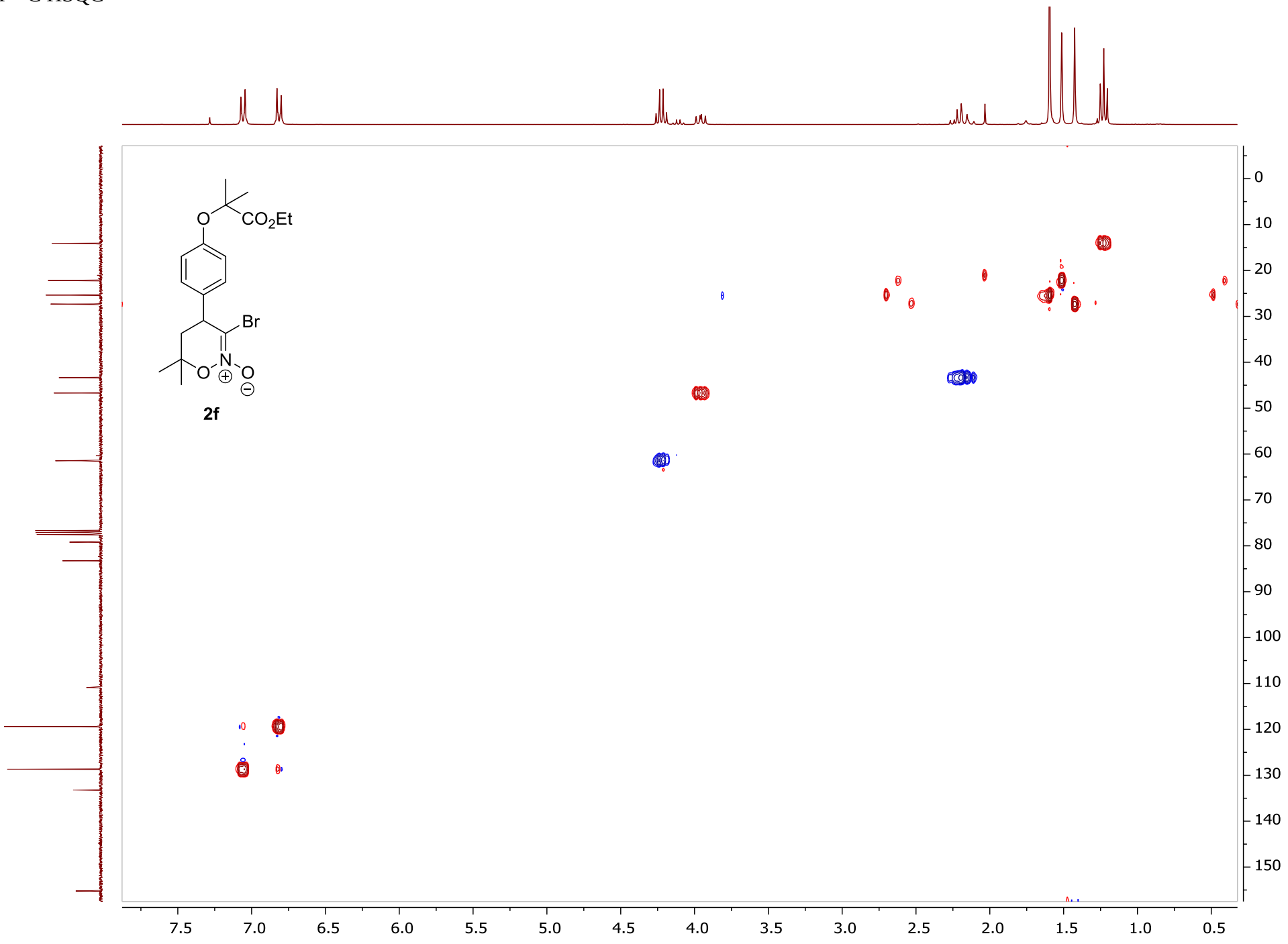
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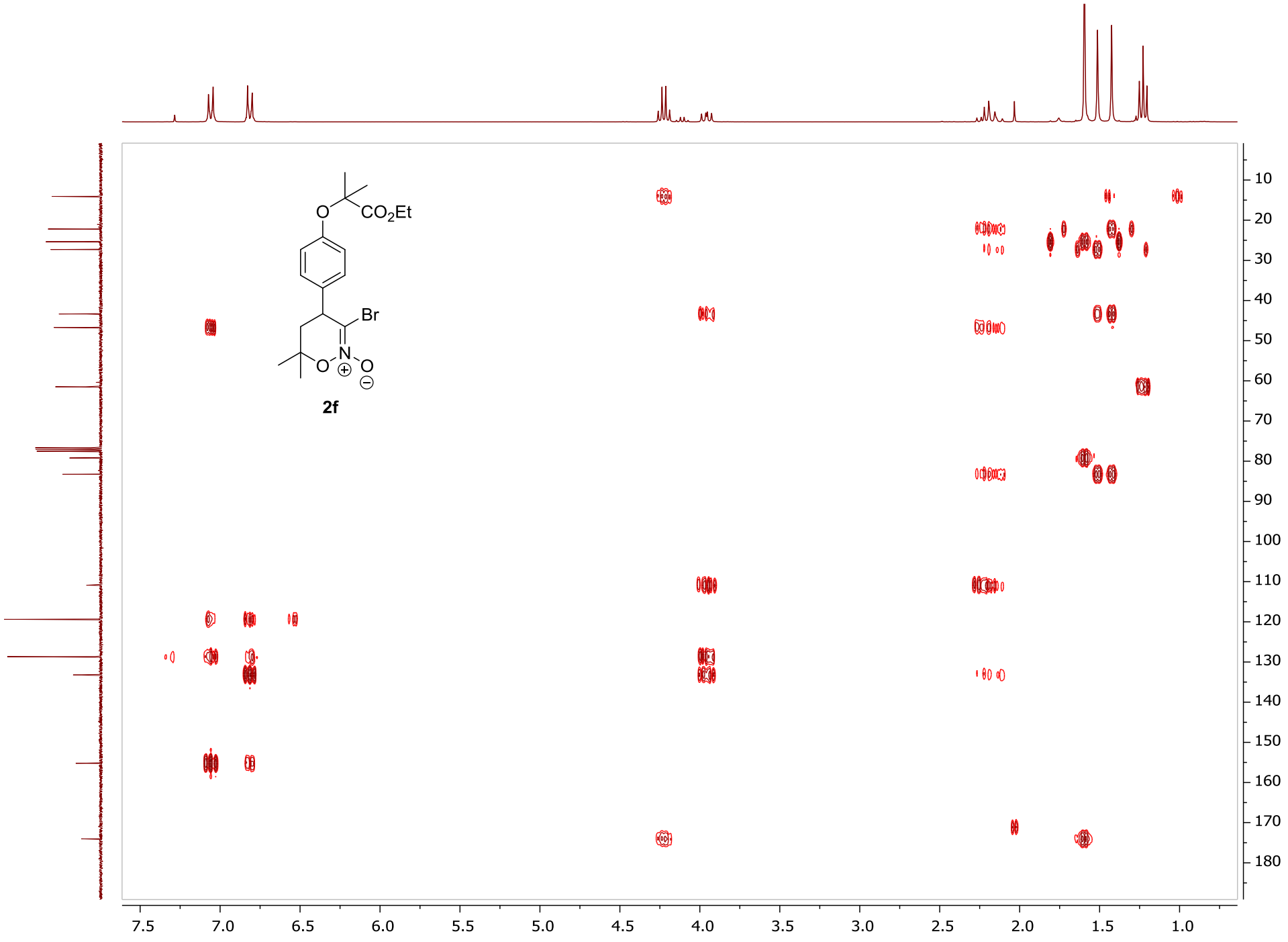
$^{1}$H-$^{13}$C HMBC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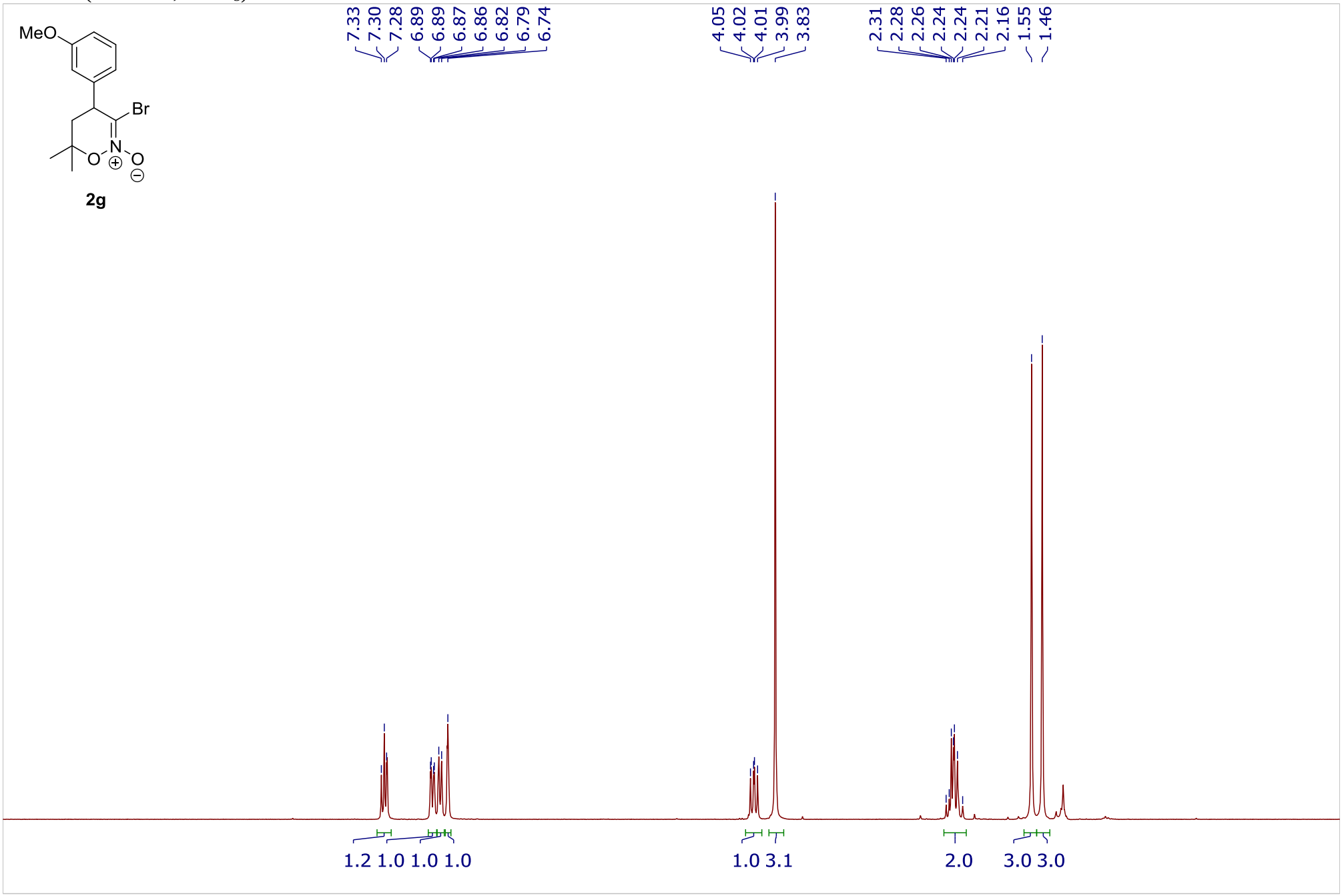
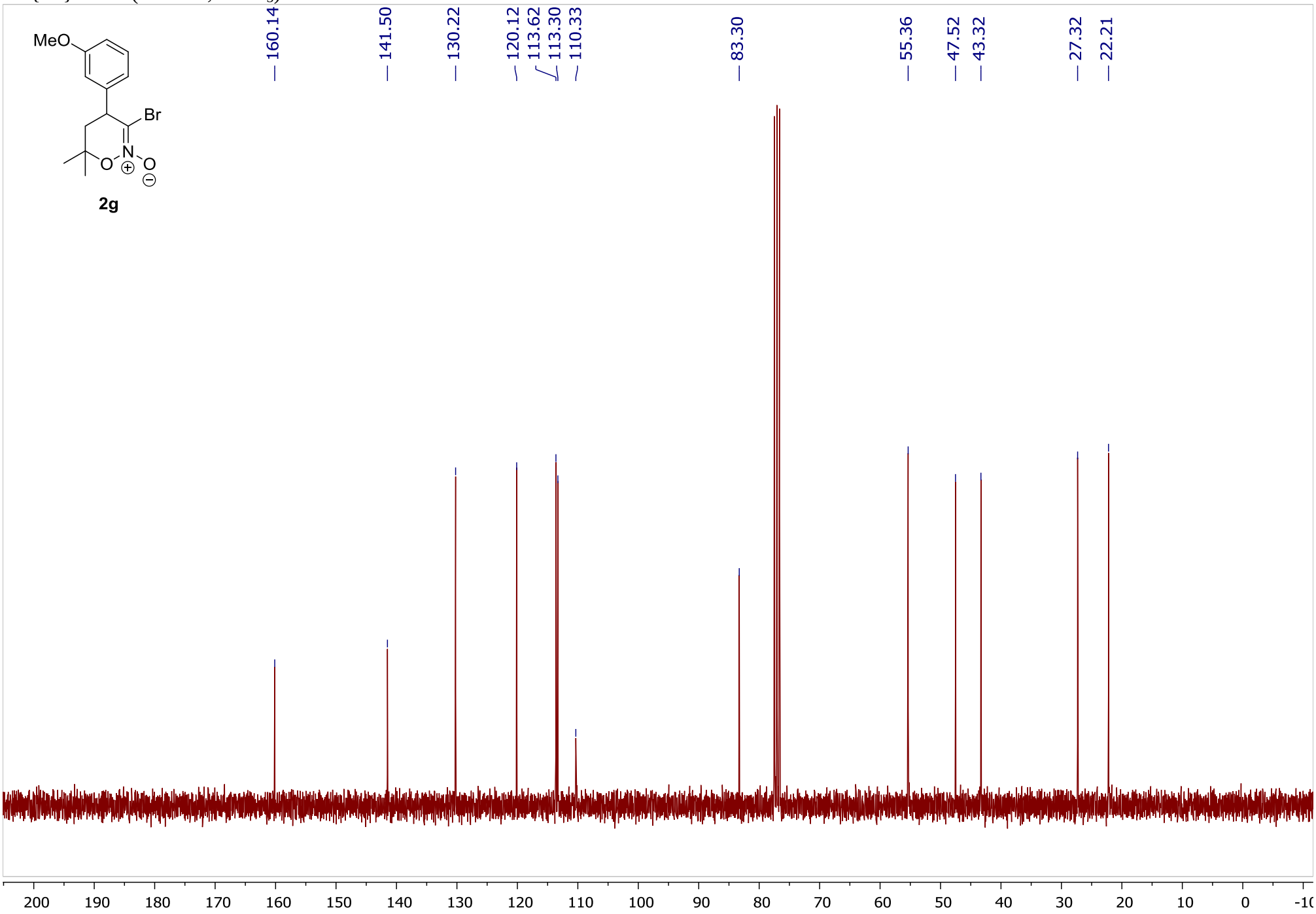
**3-Bromo-4-(3-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2g**

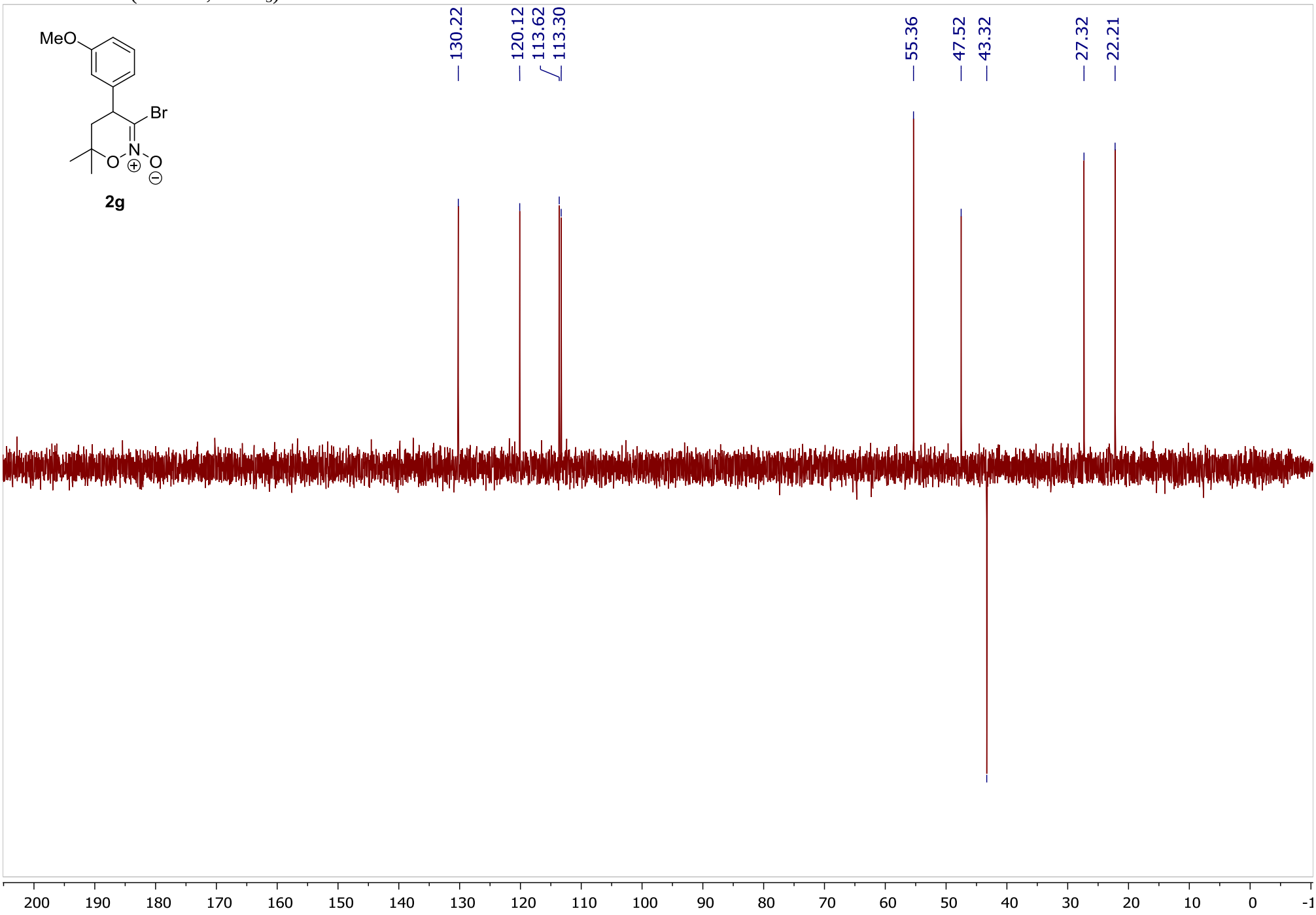
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

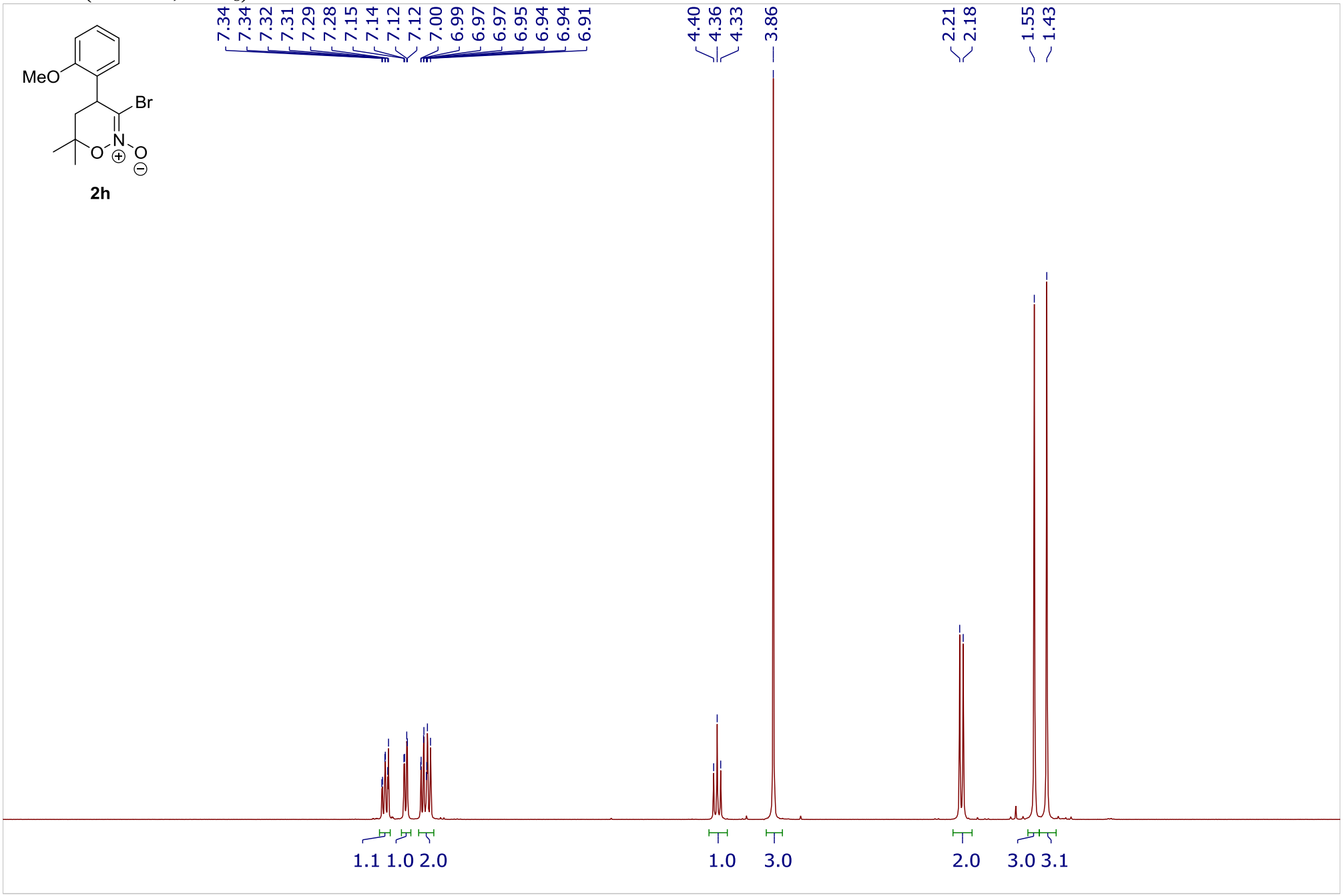


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

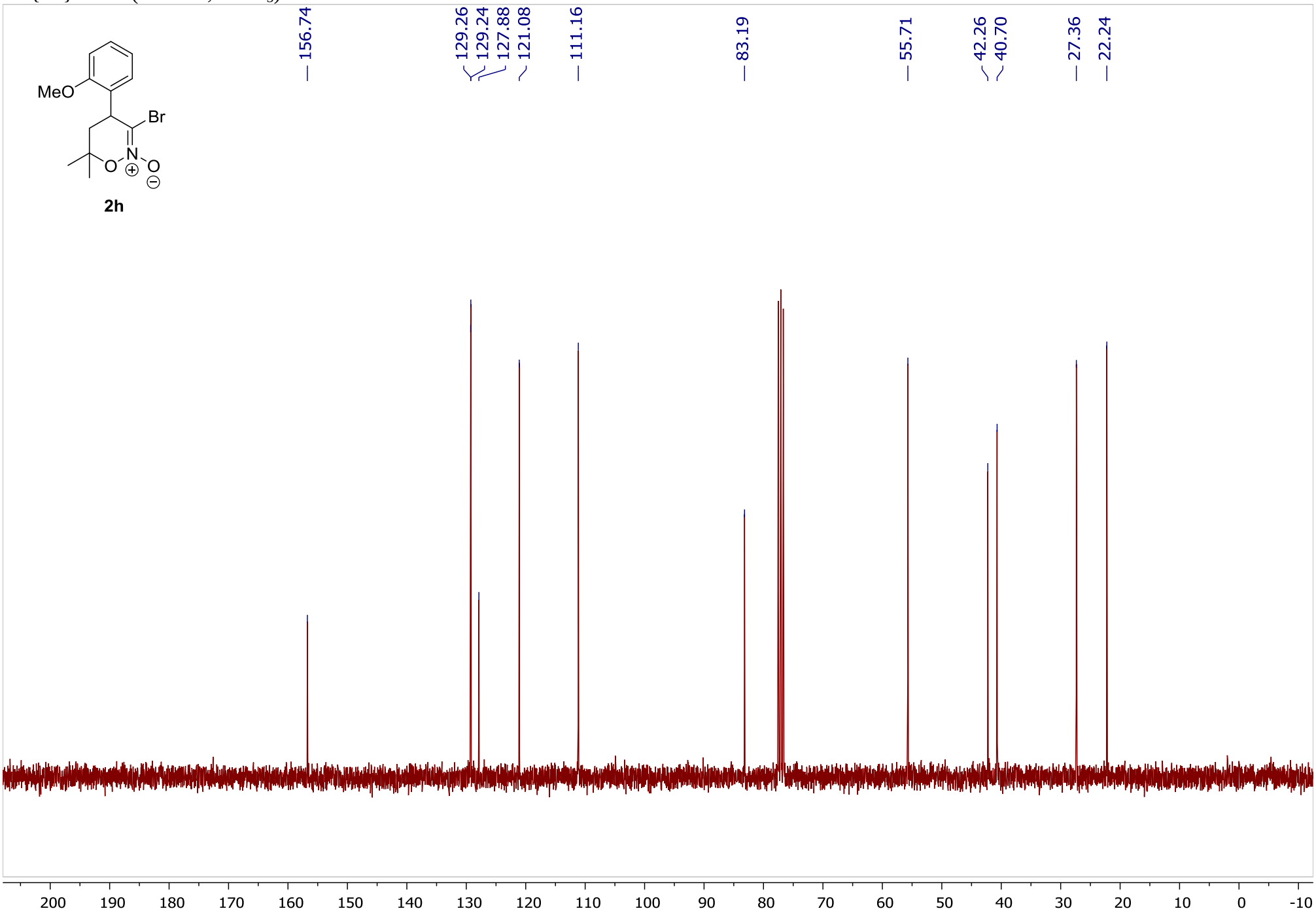


**3-Bromo-4-(2-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2h**

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



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



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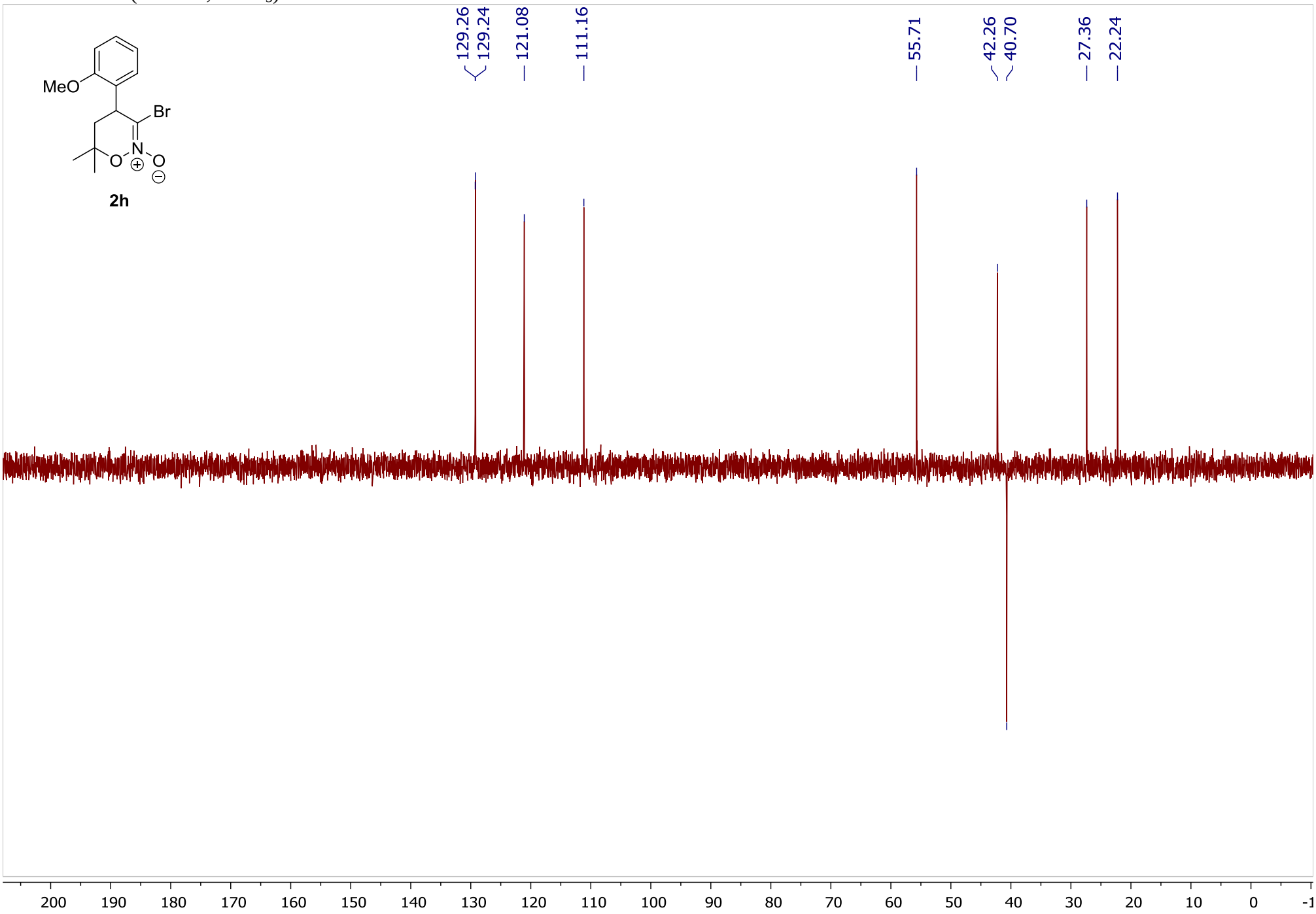
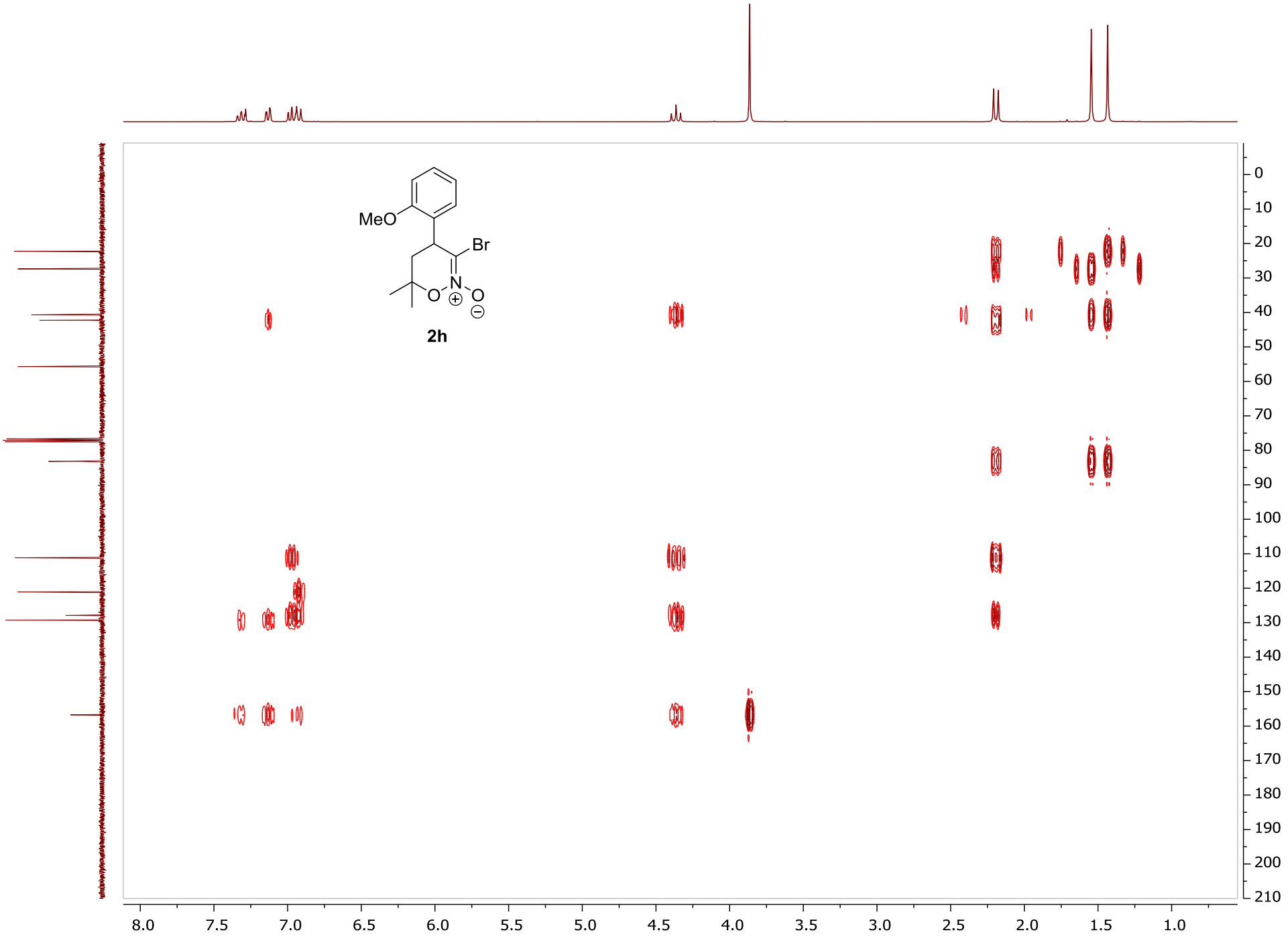


$^{1}$H-$^{13}$C HMBC


MeO
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O
O
2h
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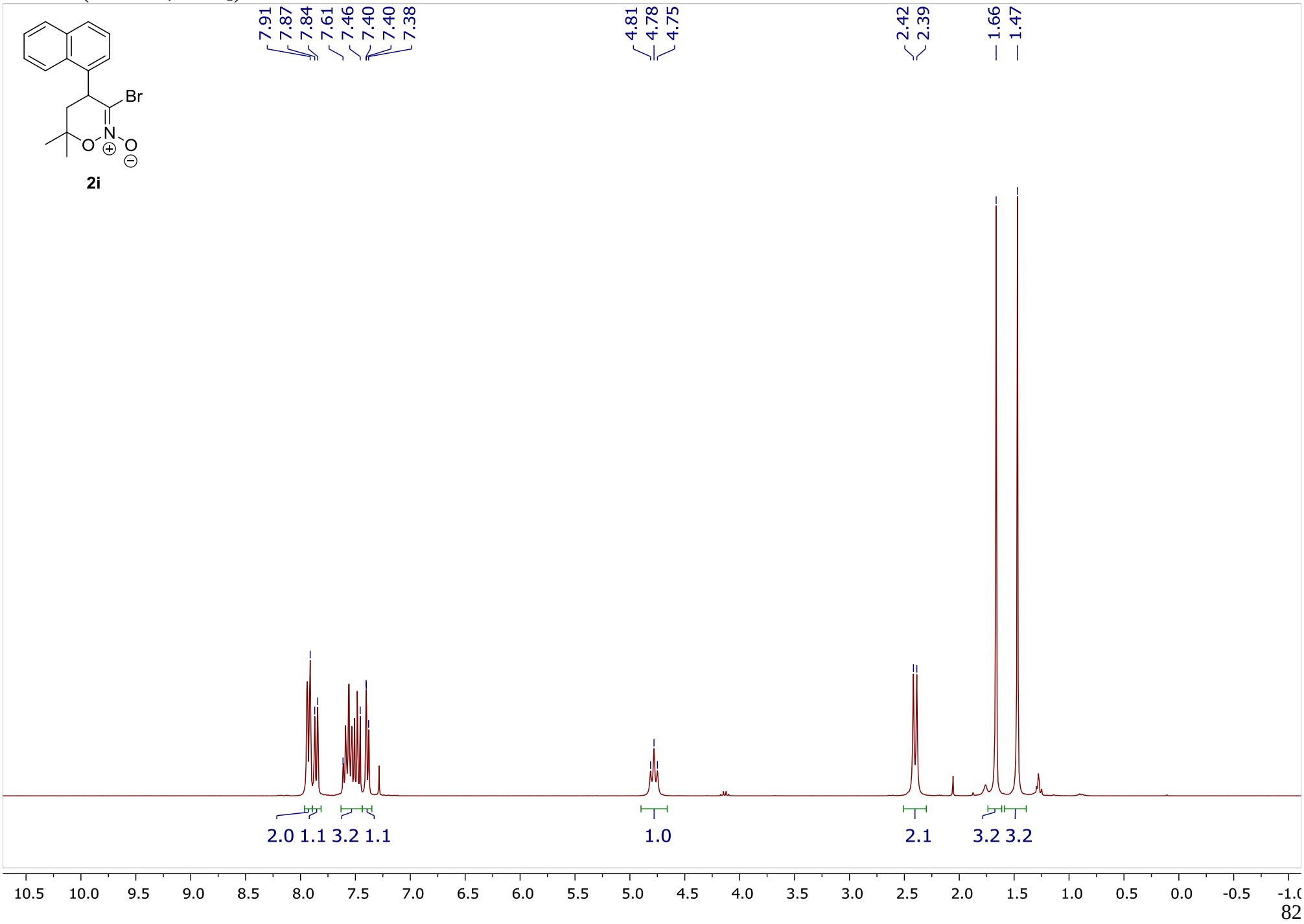
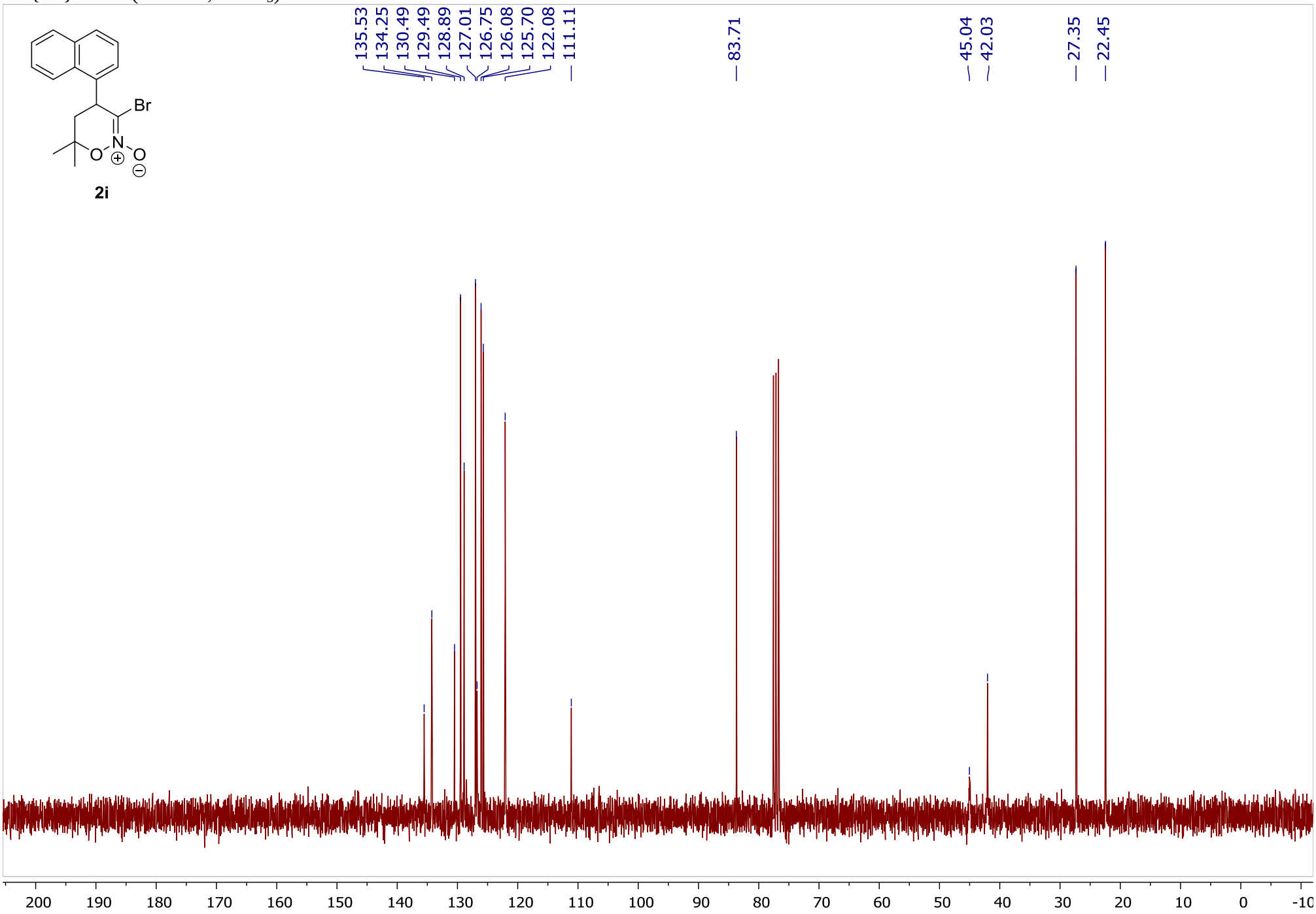
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

**3-Bromo-6,6-dimethyl-4-(naphthalen-1-yl)-5,6-dihydro-4H-1,2-oxazine 2-oxide 2i**

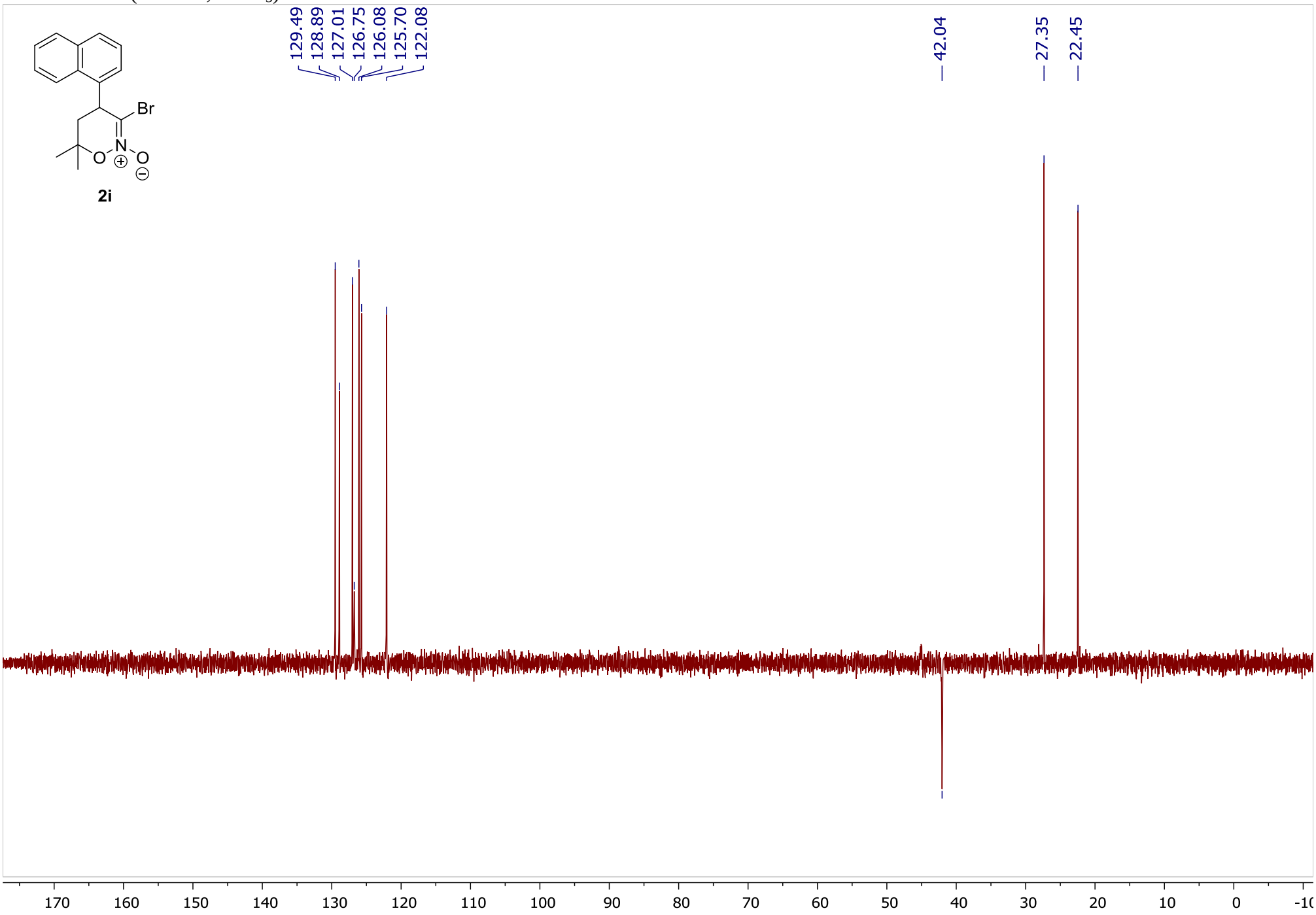
$^1$H NMR (300 MHz, $CDCl_3$)



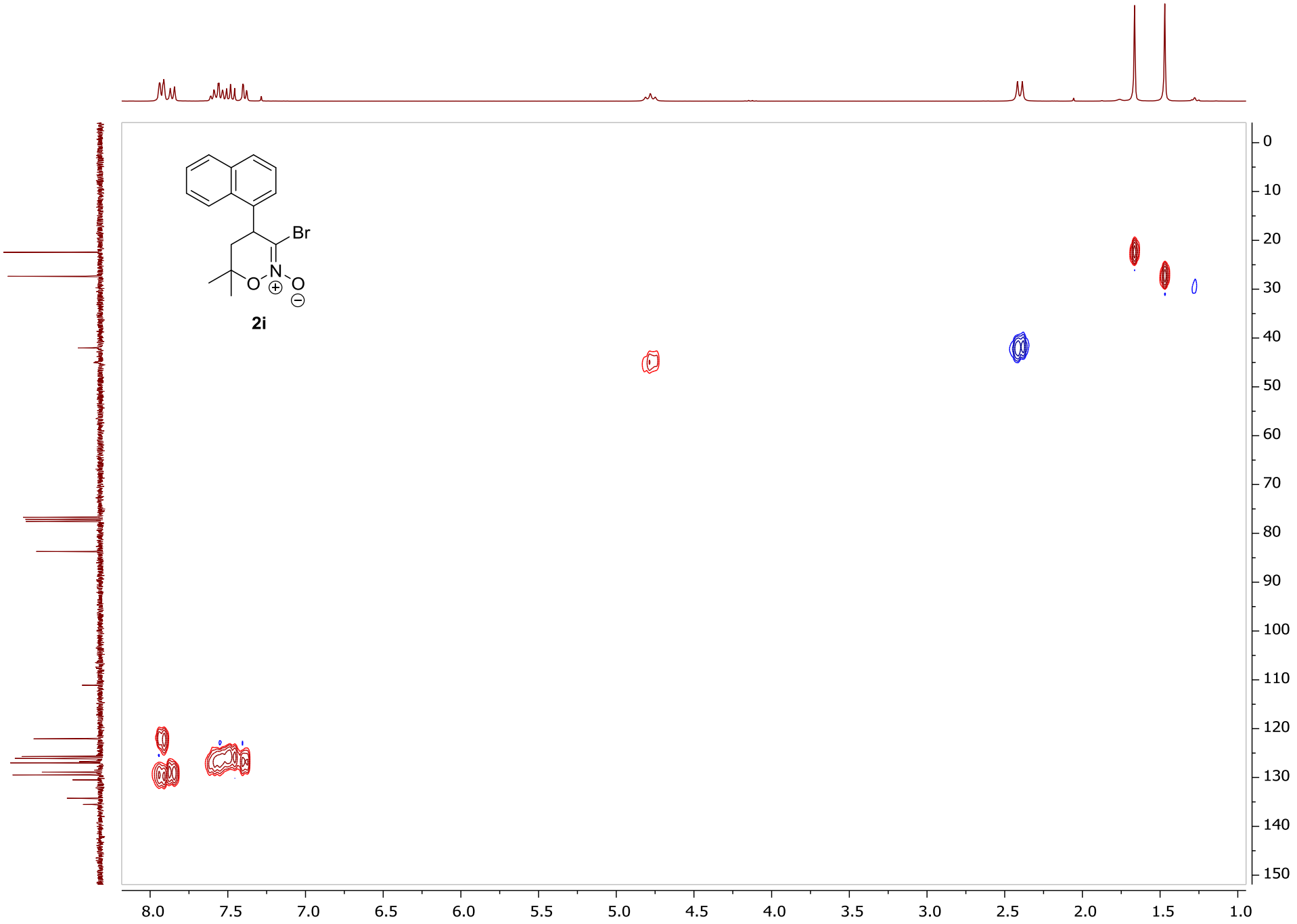
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



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


Br
N
O
O
2i
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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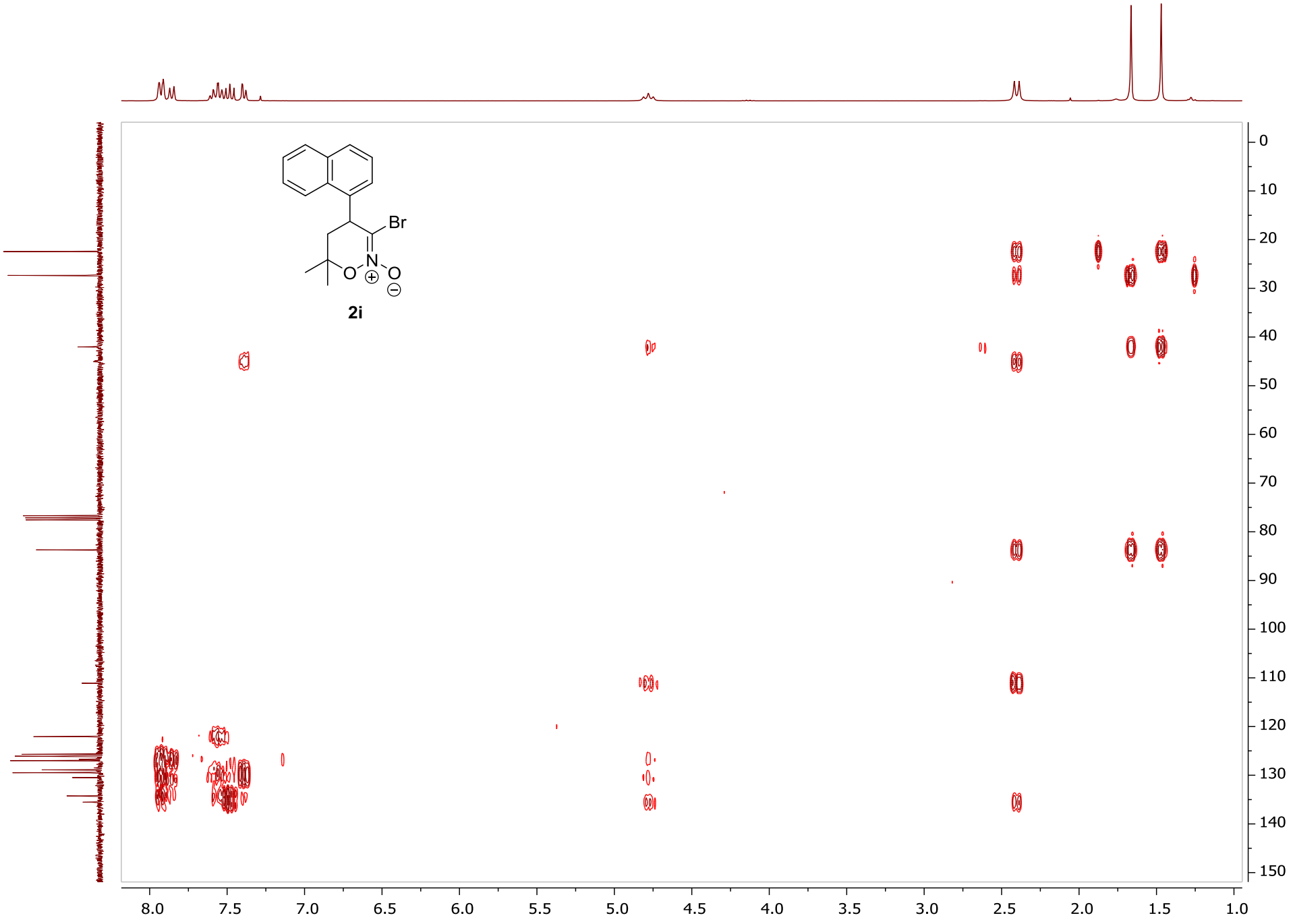
3.5
3.0
2.5
2.0
1.5
1.0

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


Br
N
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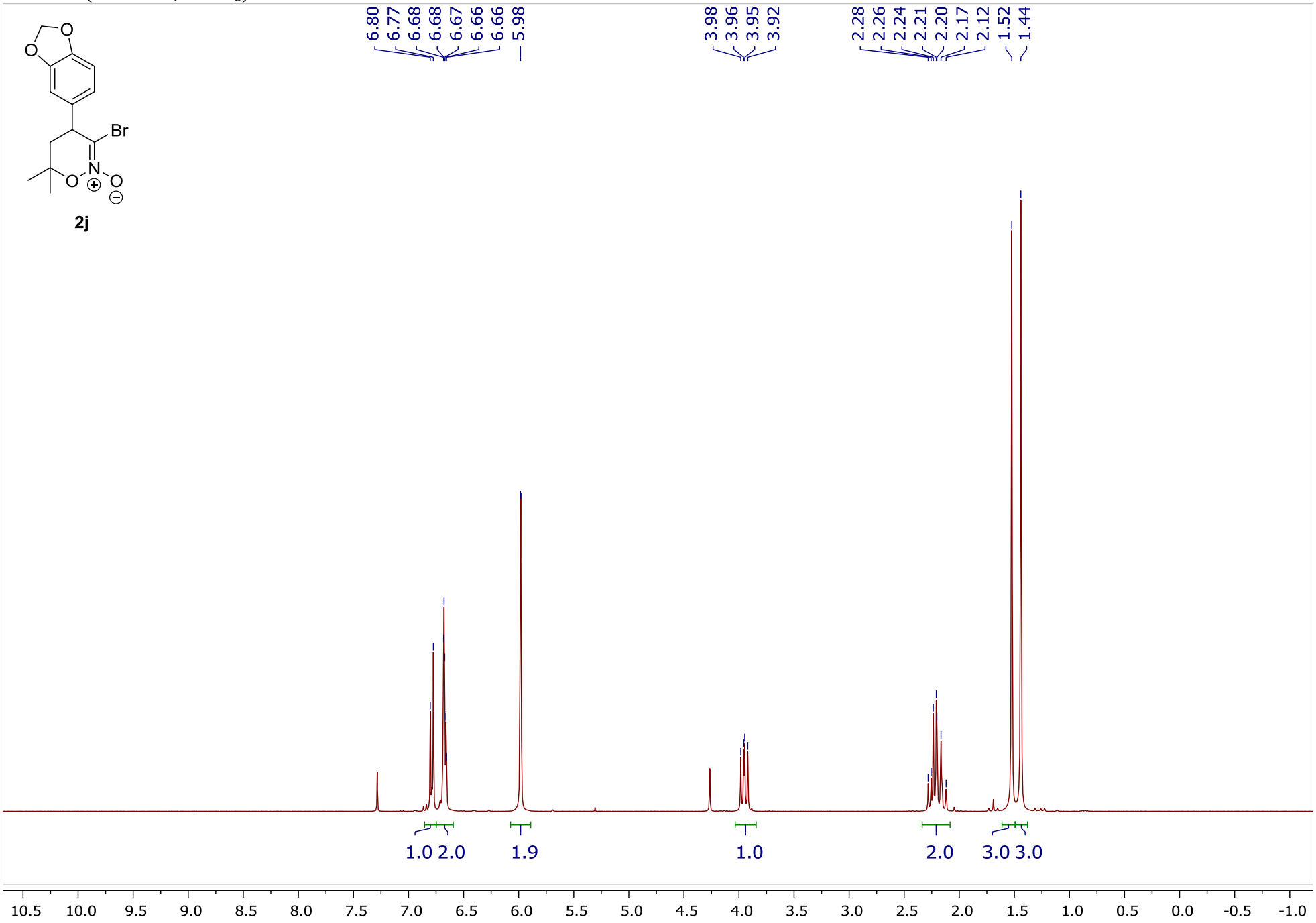
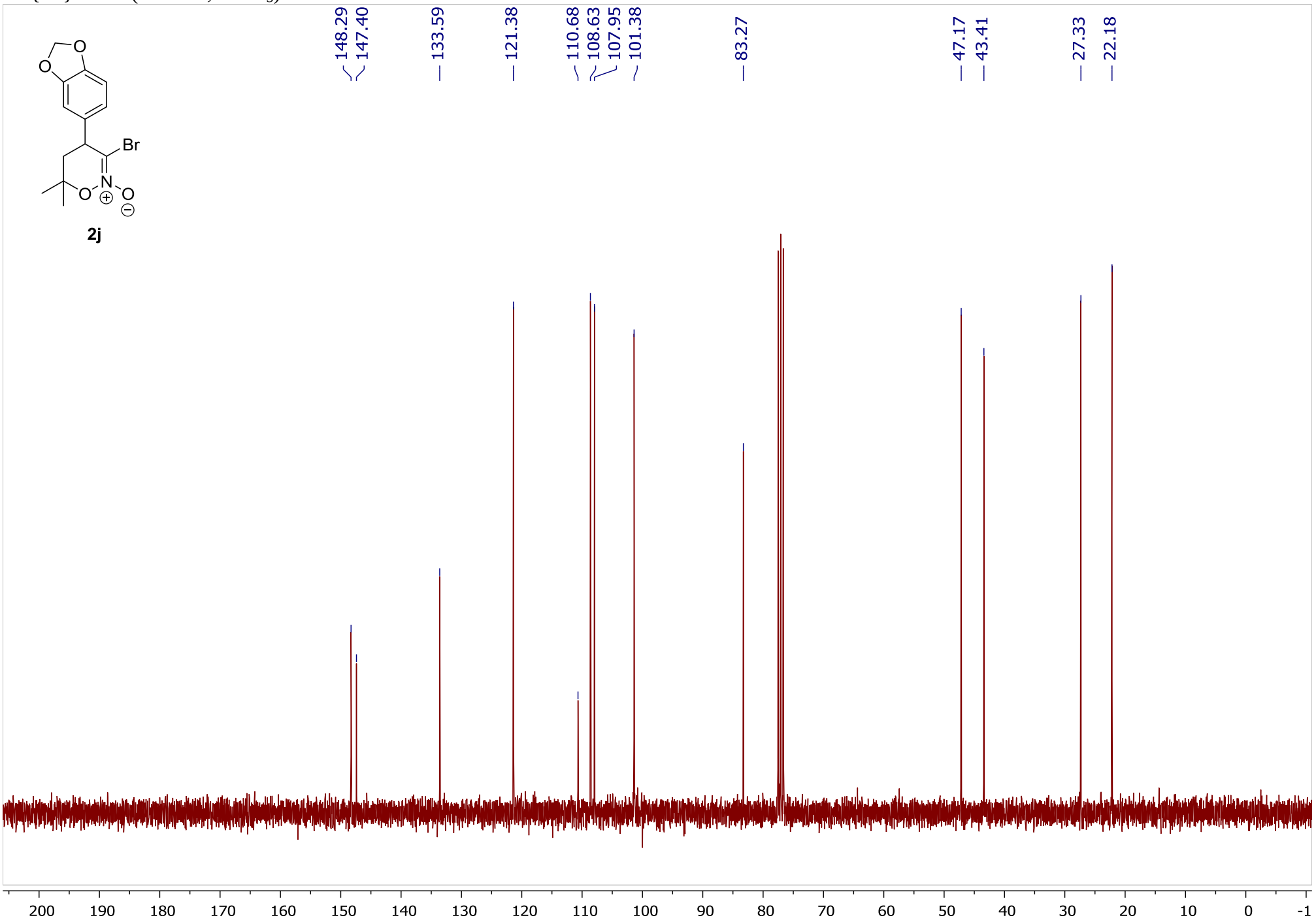
O
2i
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**4-(Benzo[d][1,3]dioxol-5-yl)-3-bromo-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2j**

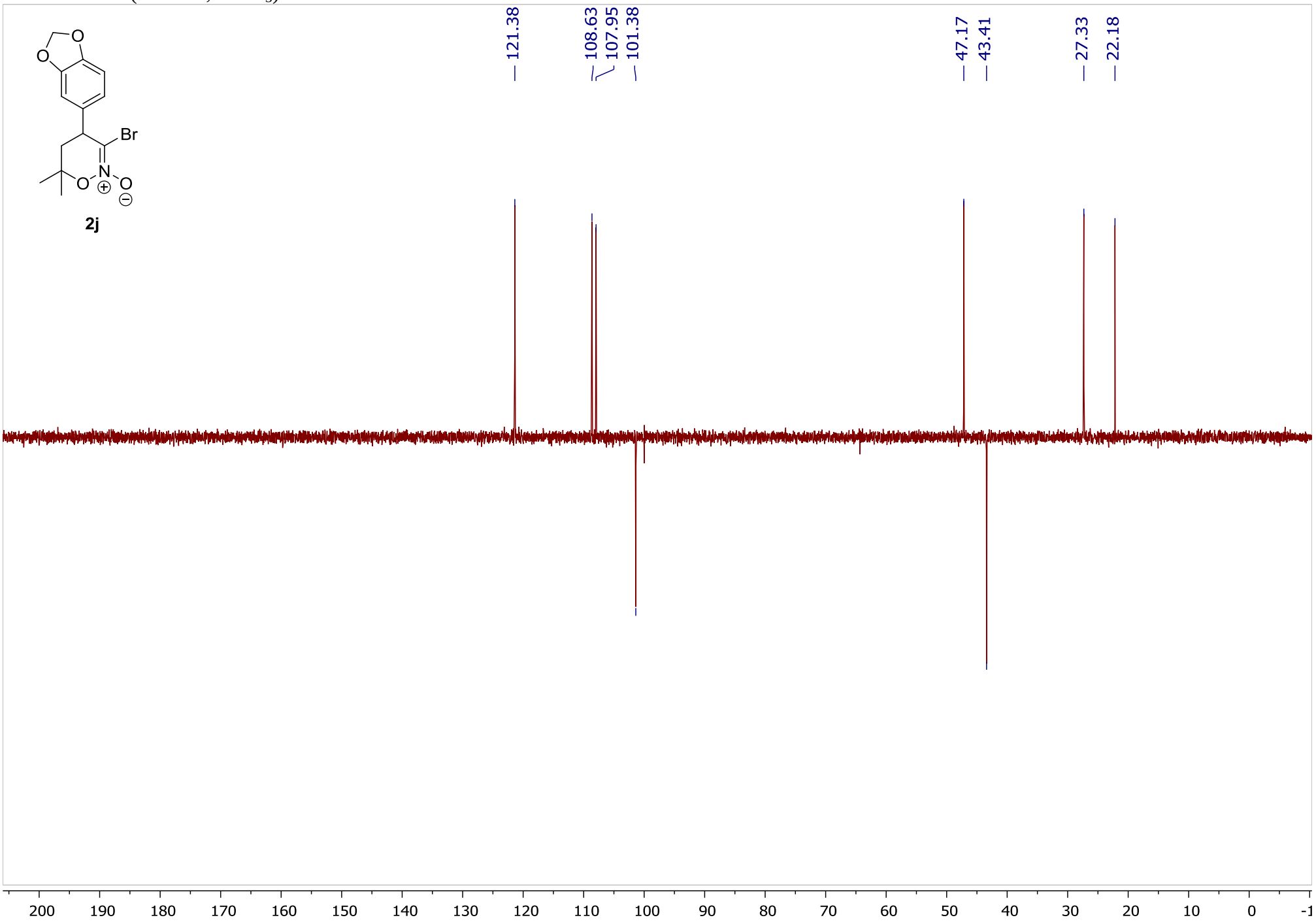
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

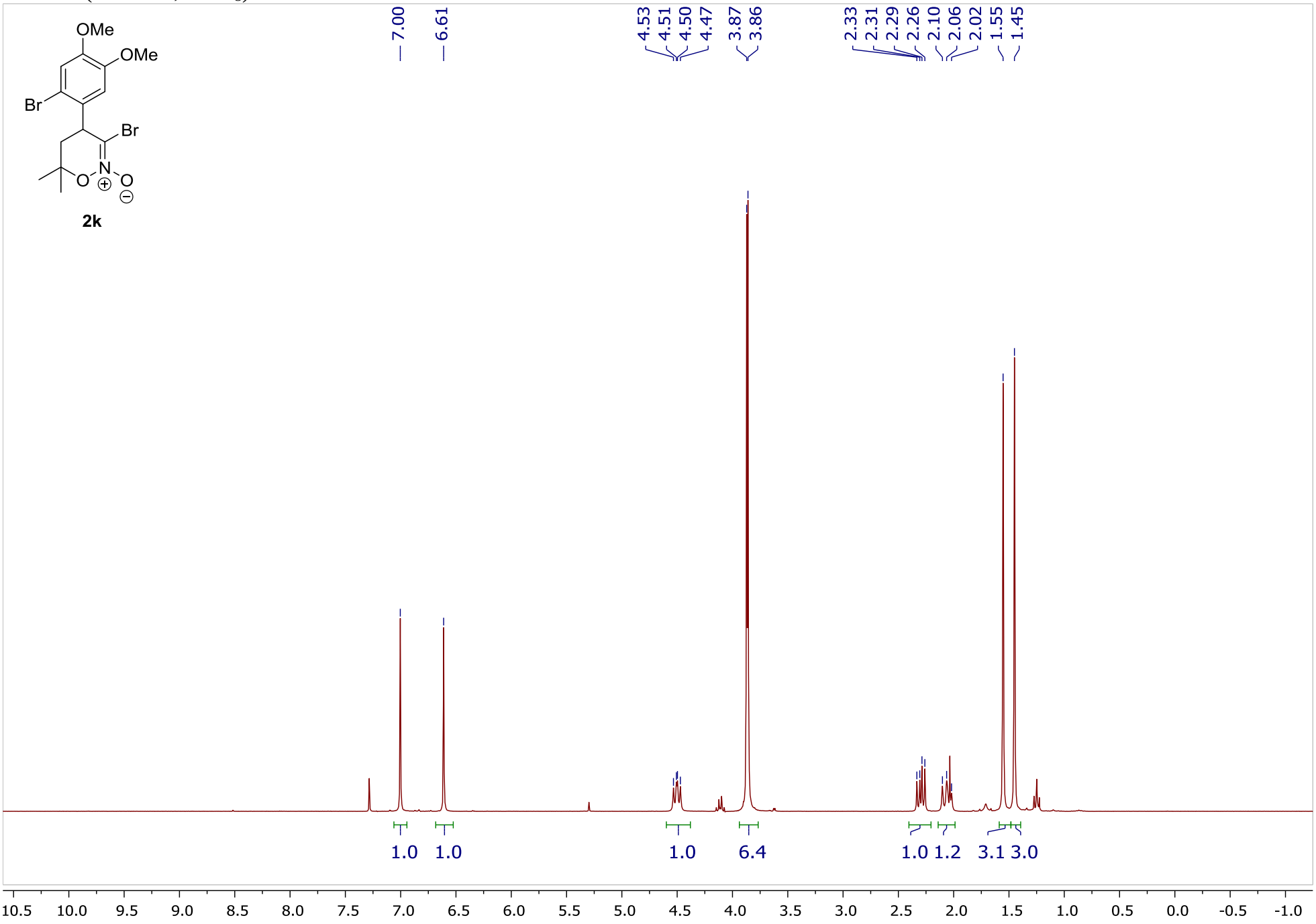


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

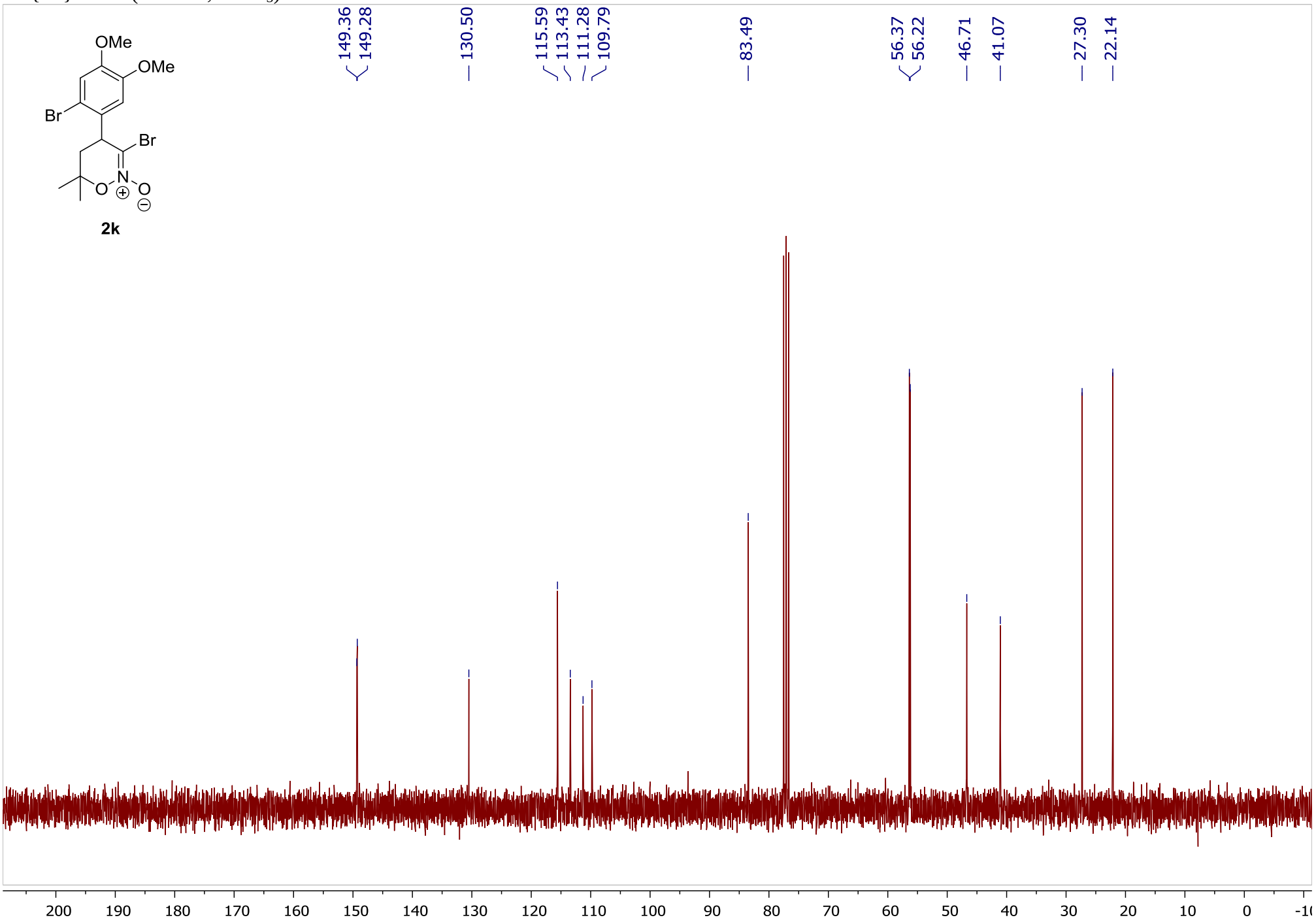


**3-Bromo-4-(2-bromo-4,5-dimethoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2k**

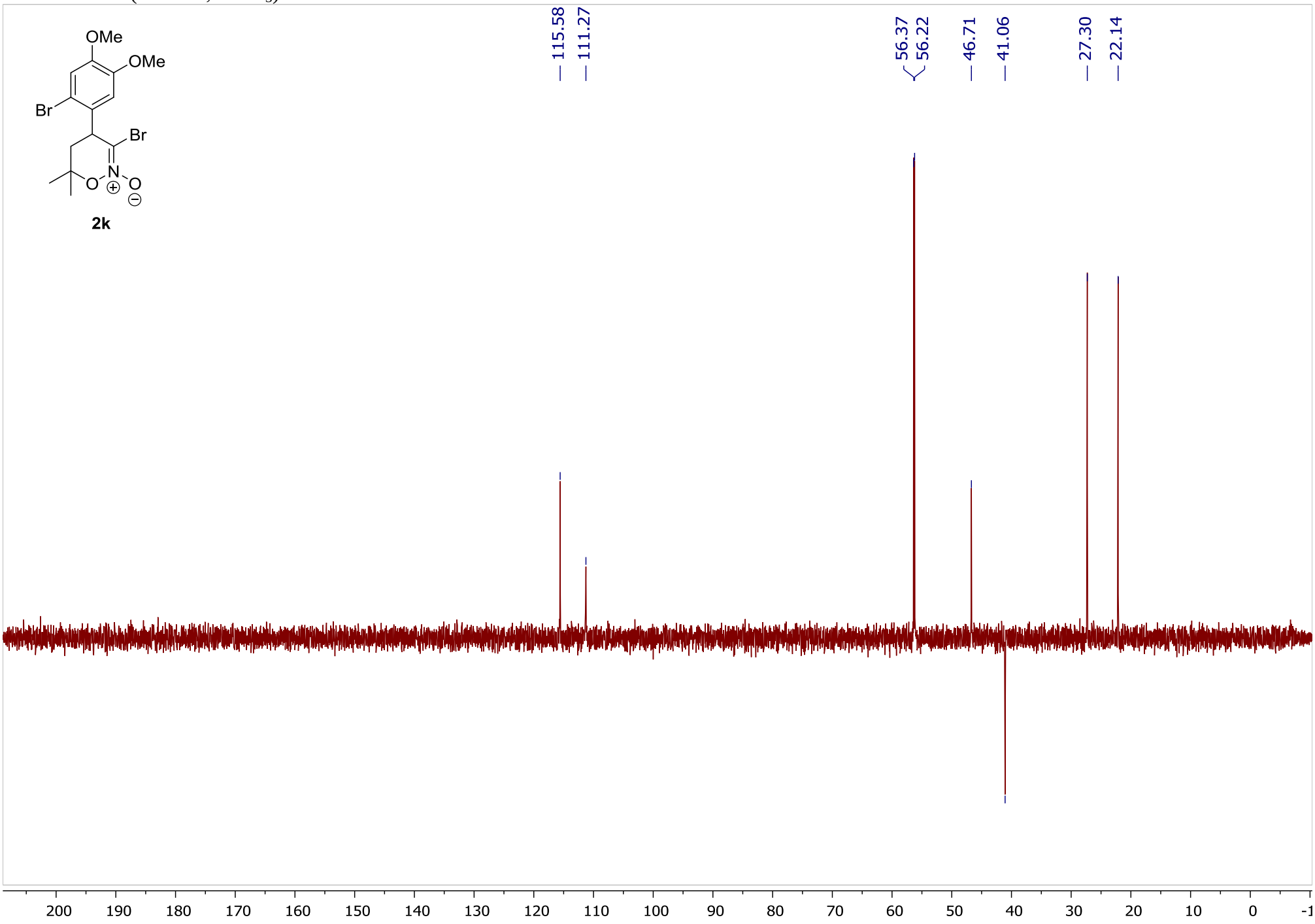
$^1$H NMR (300 MHz, $CDCl_3$)



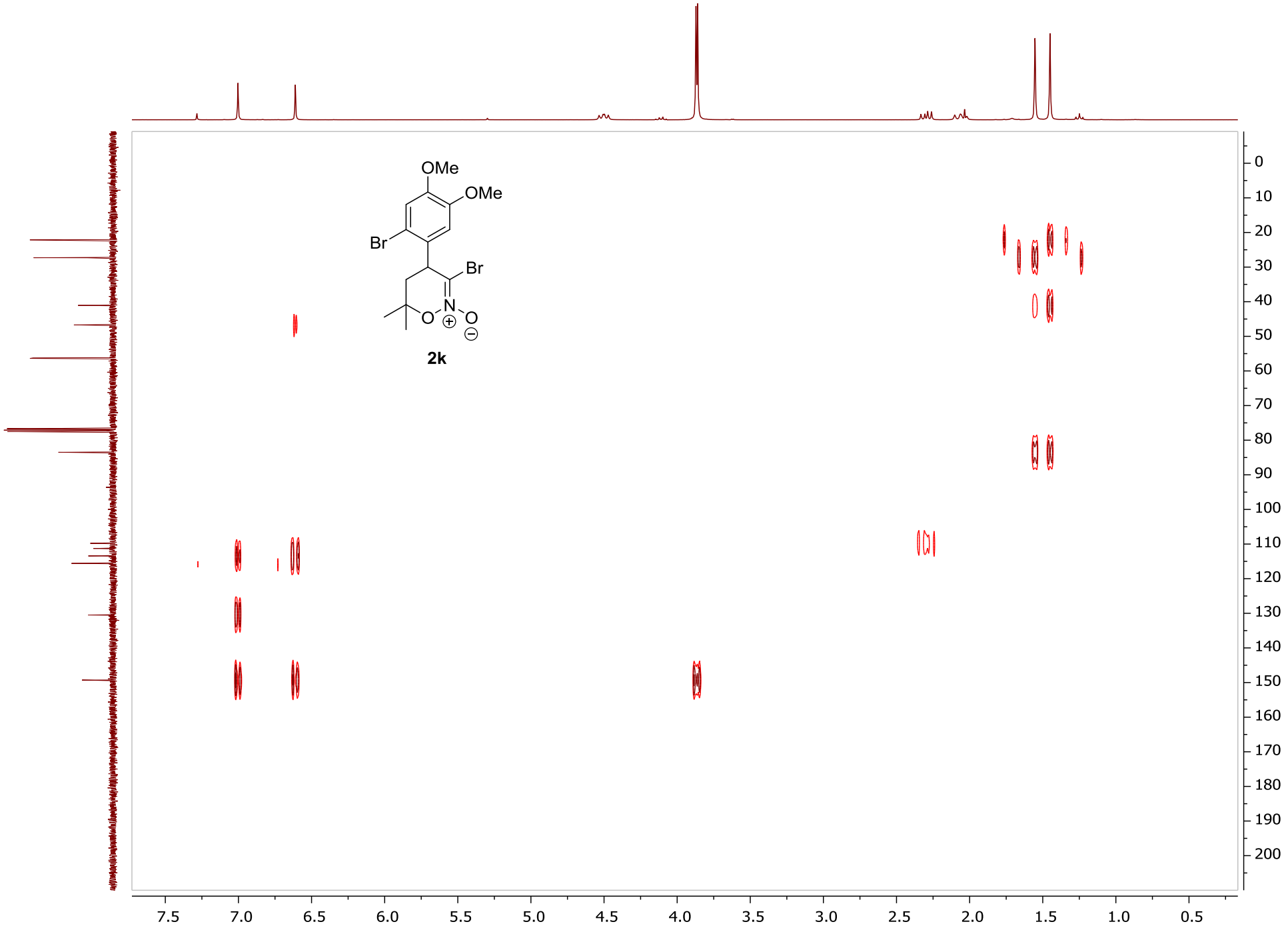
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



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


OMe
OMe
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Br
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O
O
2k
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10
20
30
40
50
60
70
80
90
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130
140
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160
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180
190
200
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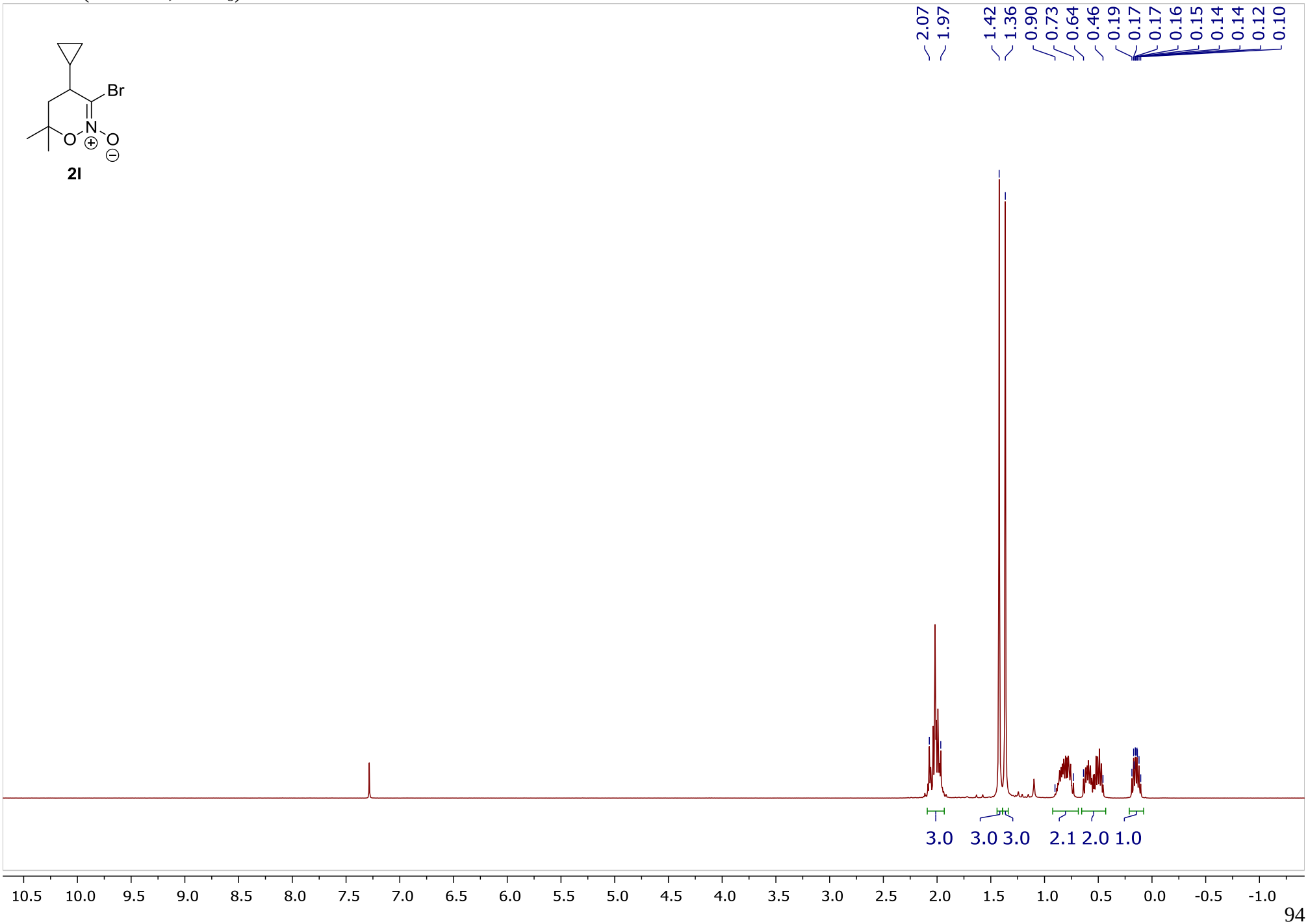
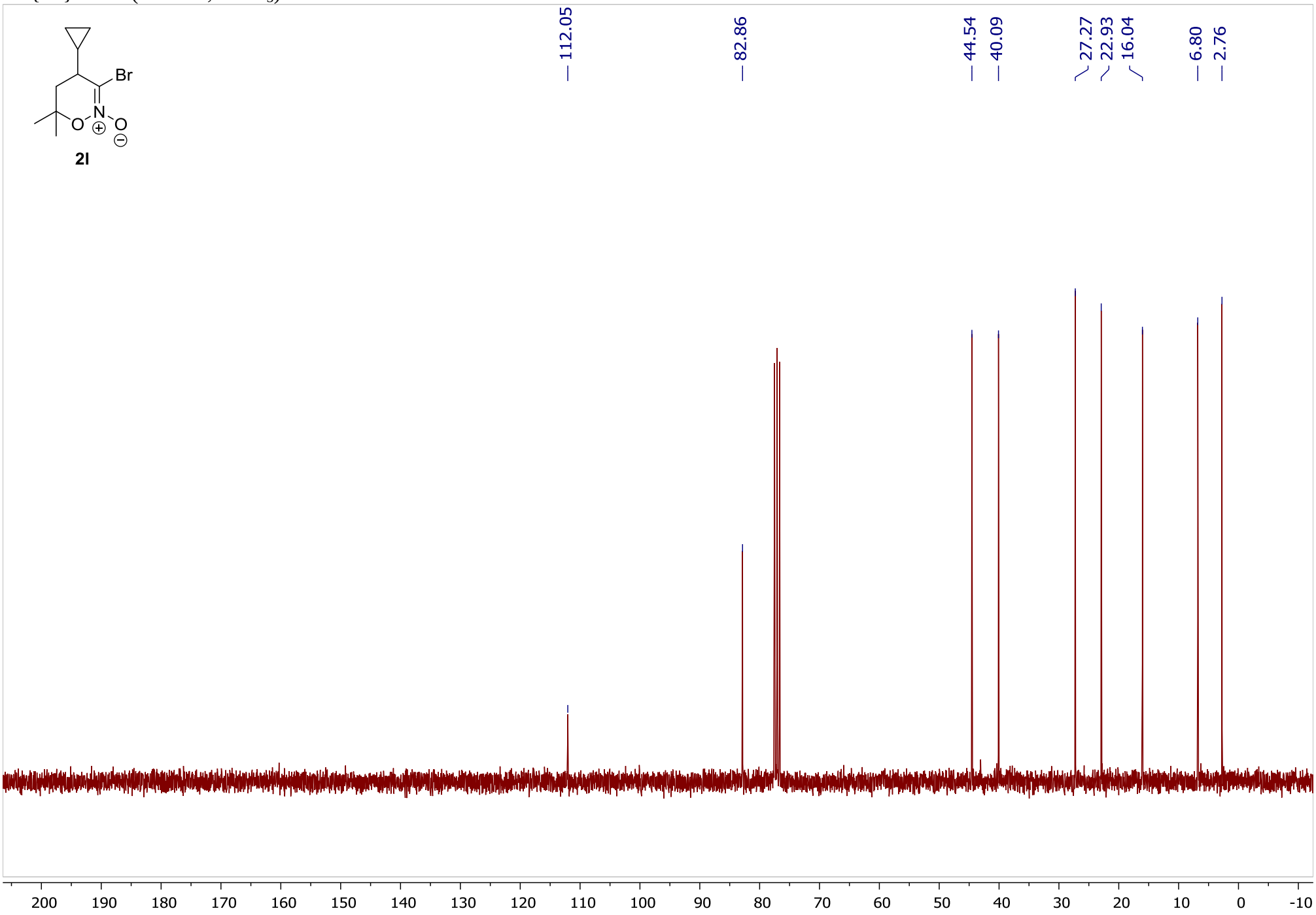
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**3-Bromo-4-cyclopropyl-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2l**

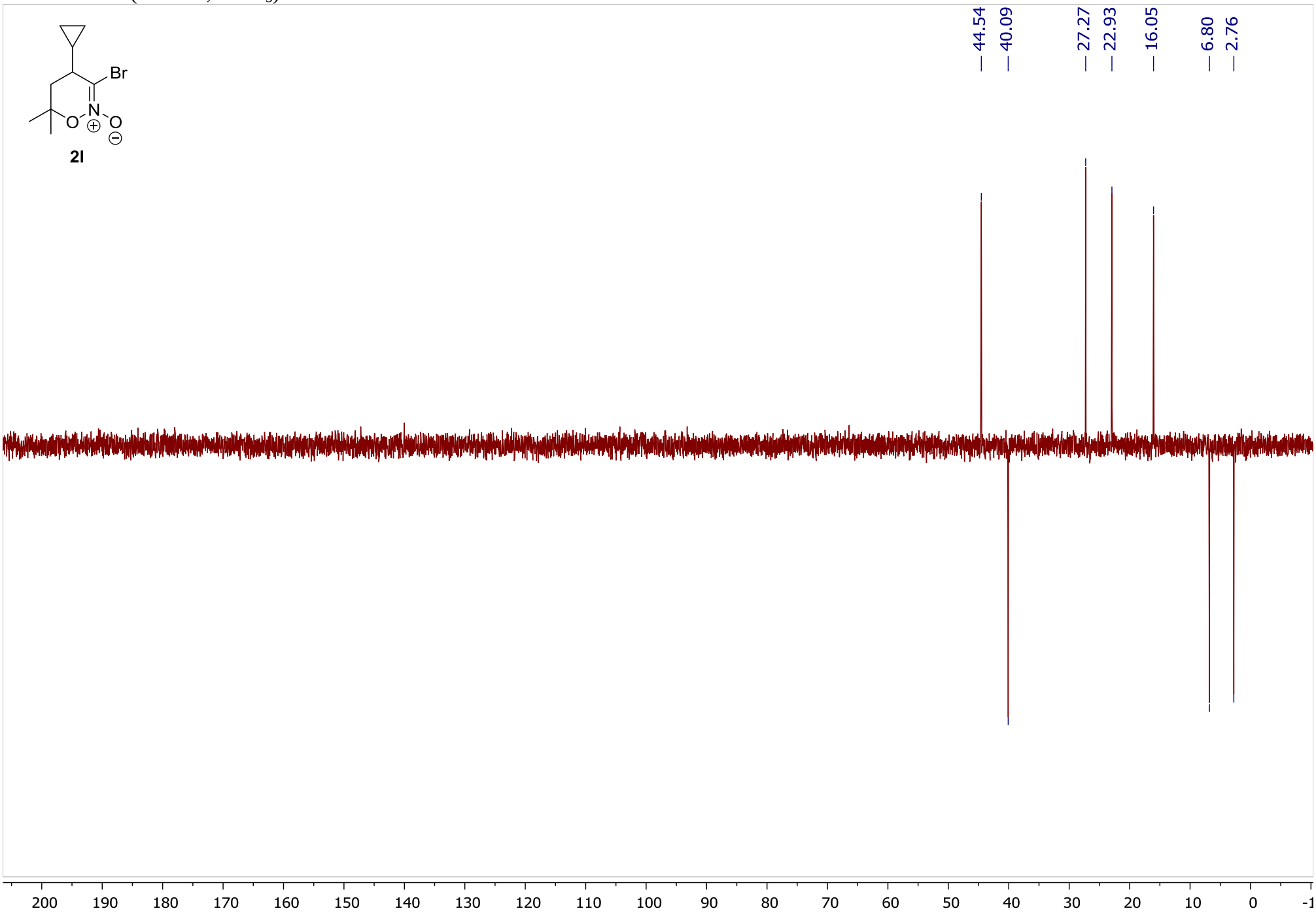
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

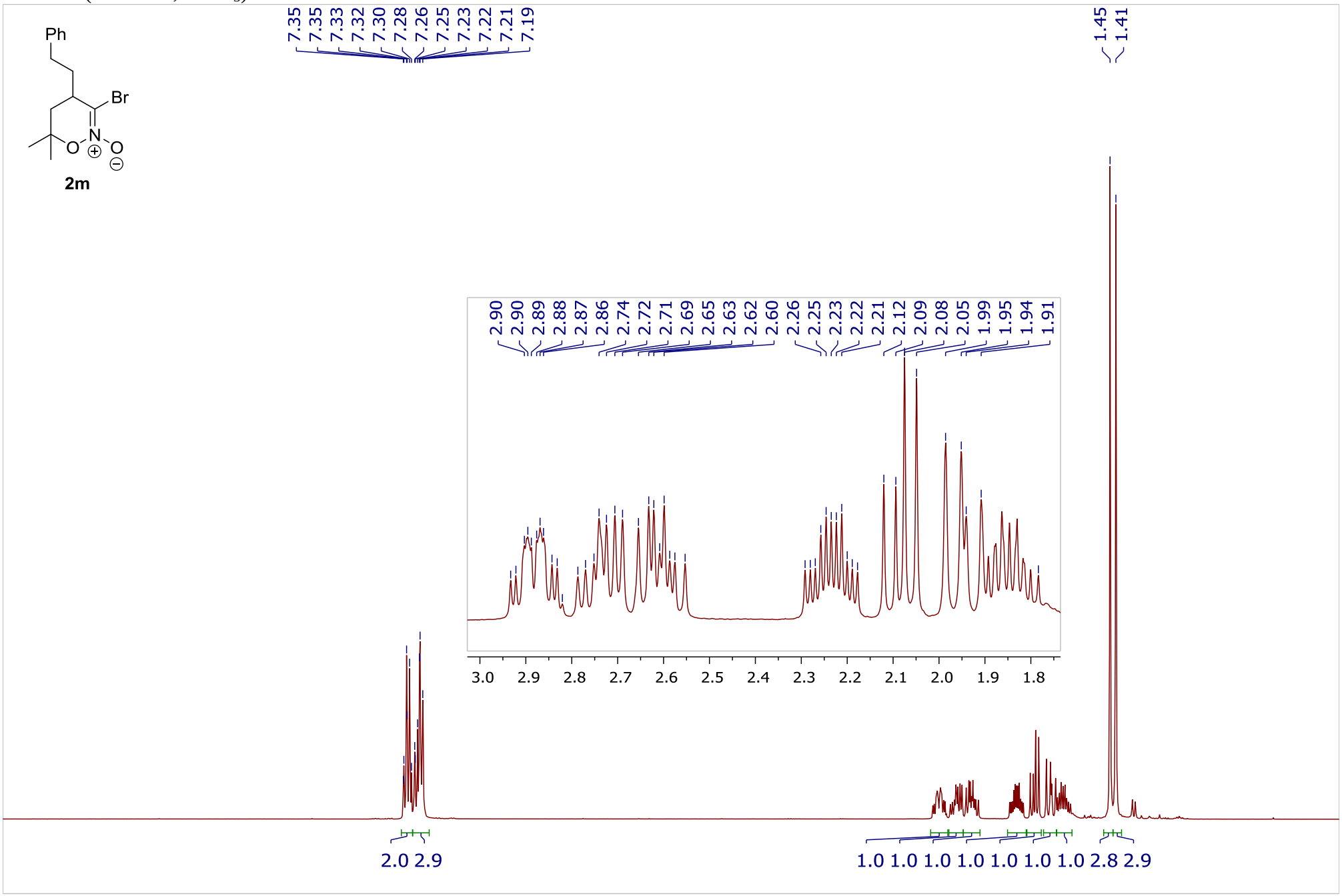


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

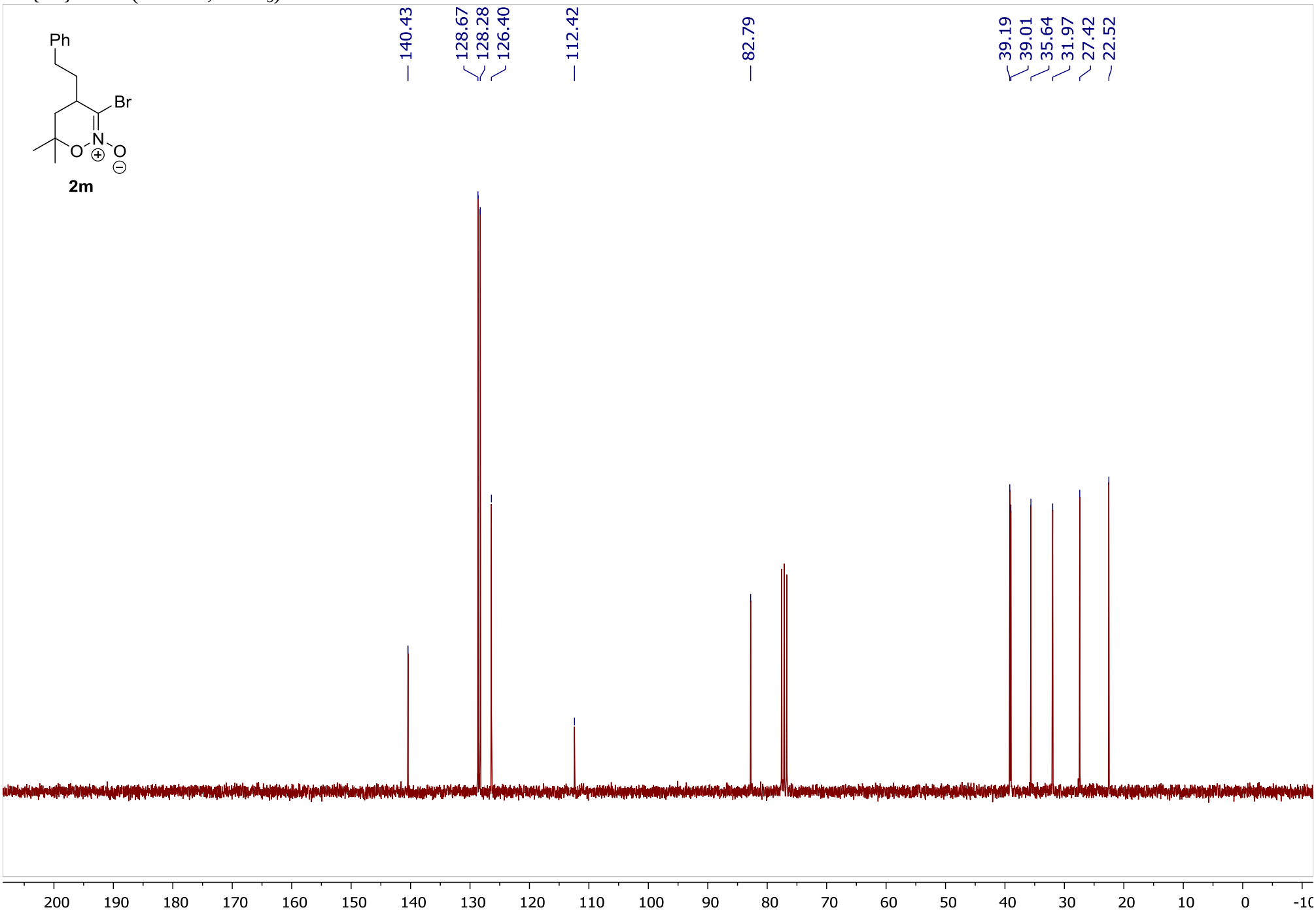


**3-Bromo-6,6-dimethyl-4-phenethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2m**

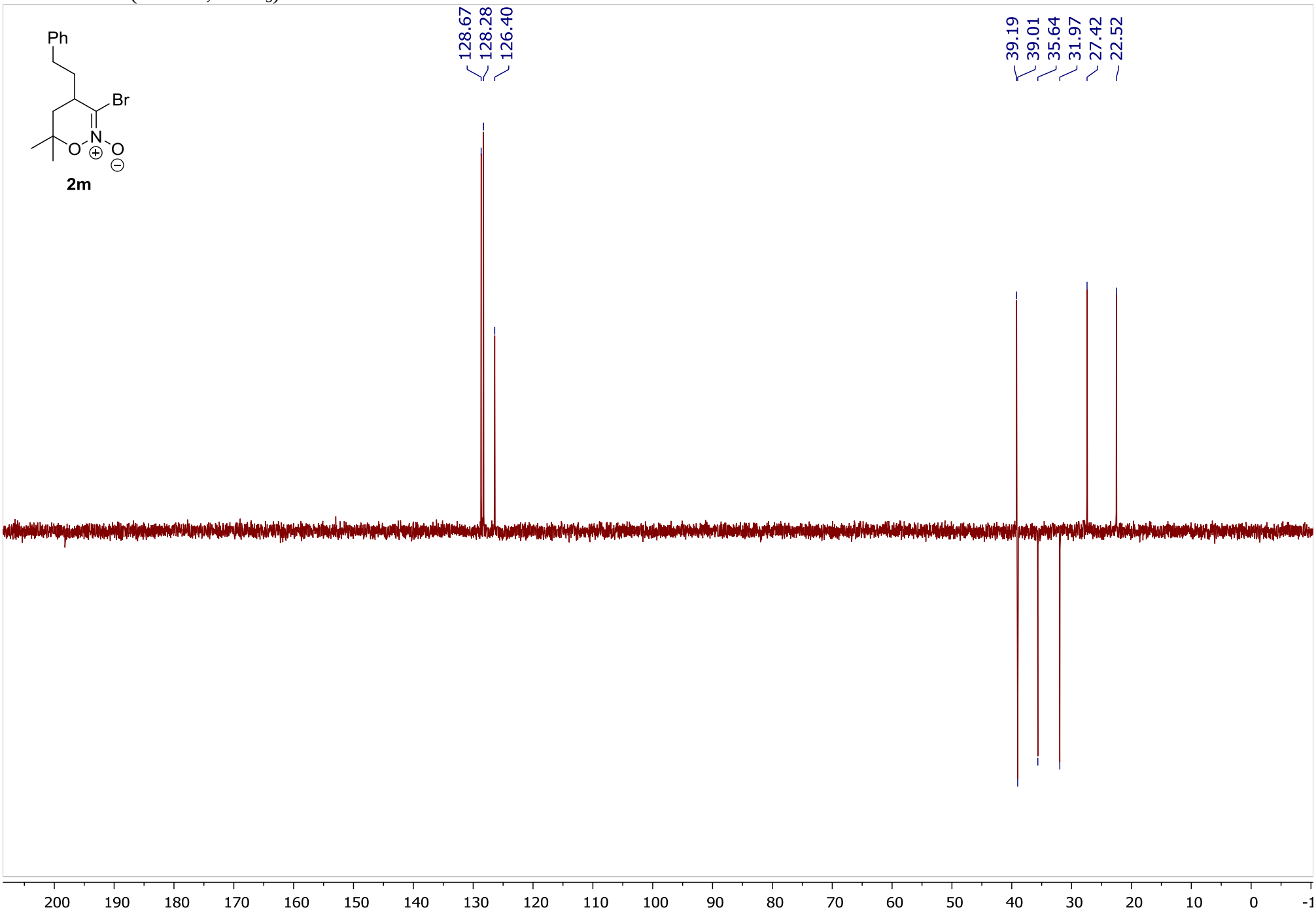
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

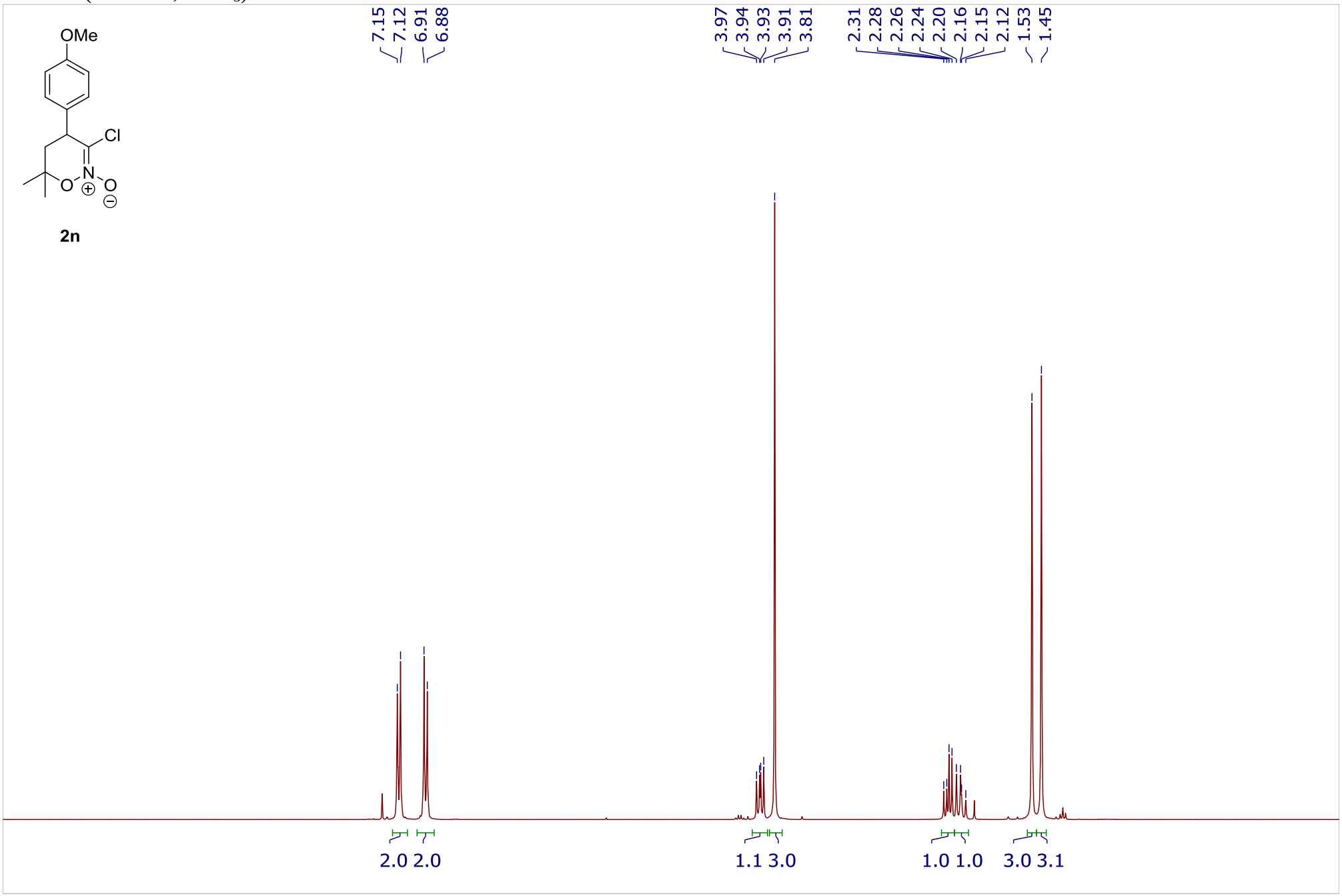


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

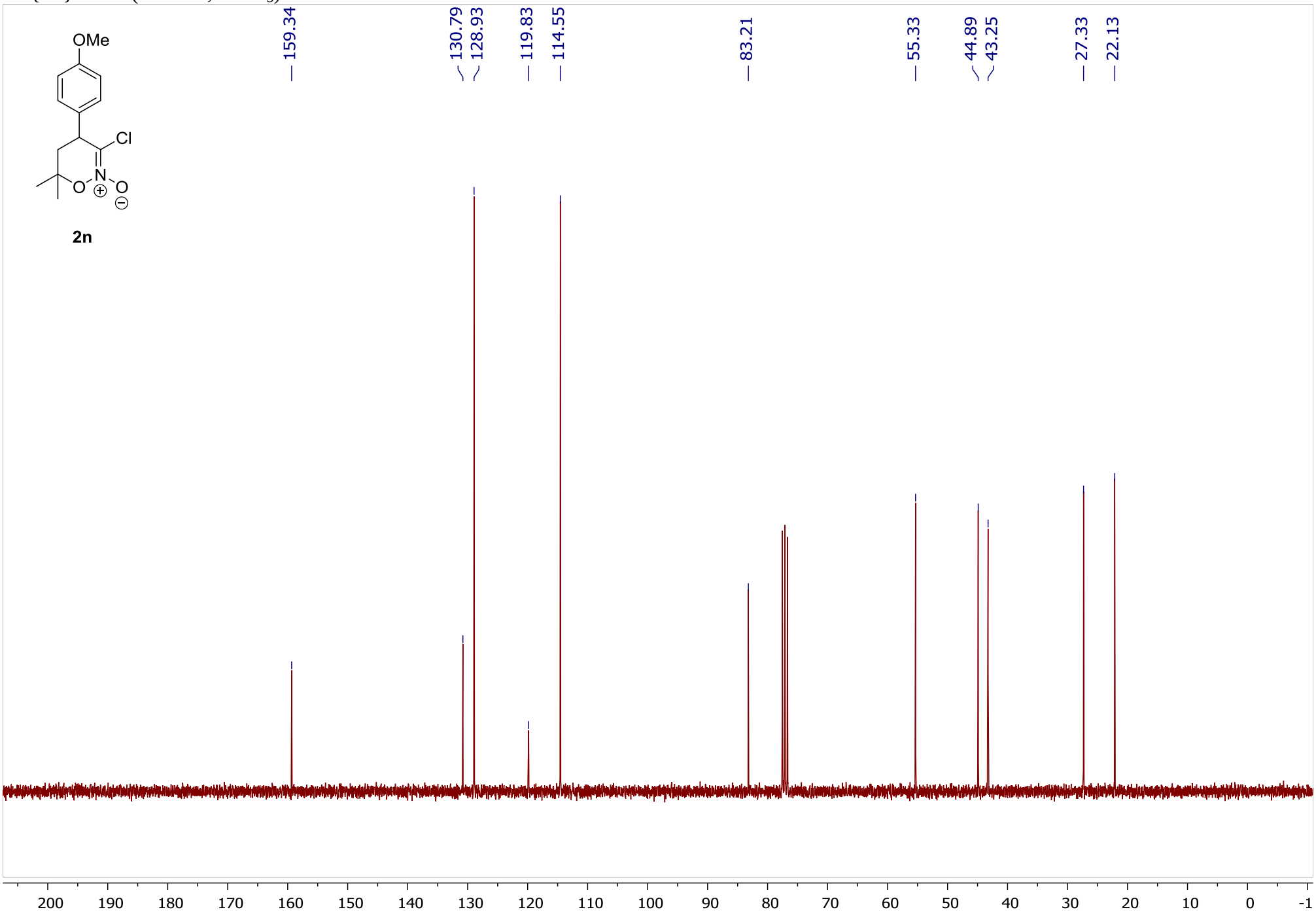


**3-Chloro-4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2n**

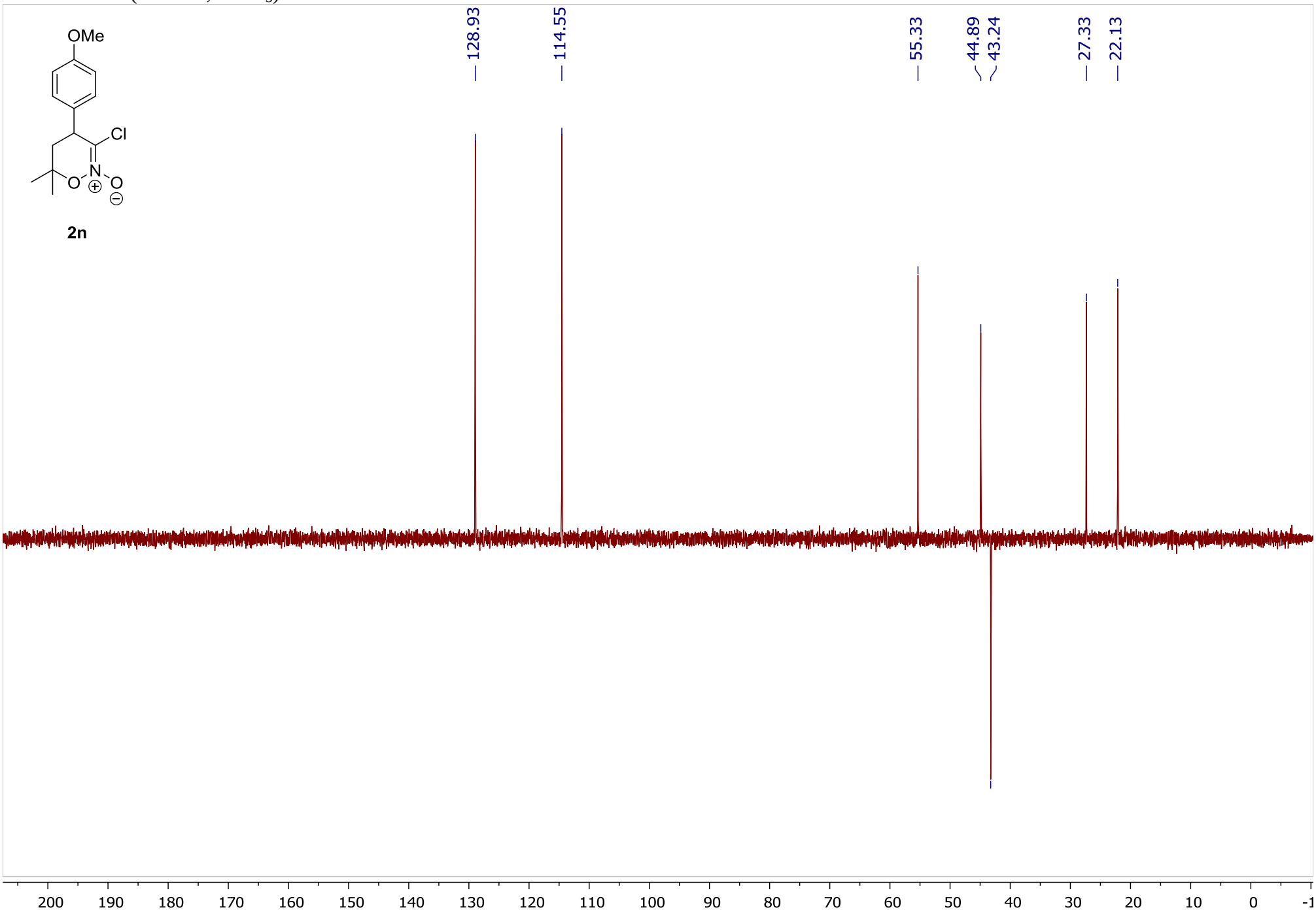
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

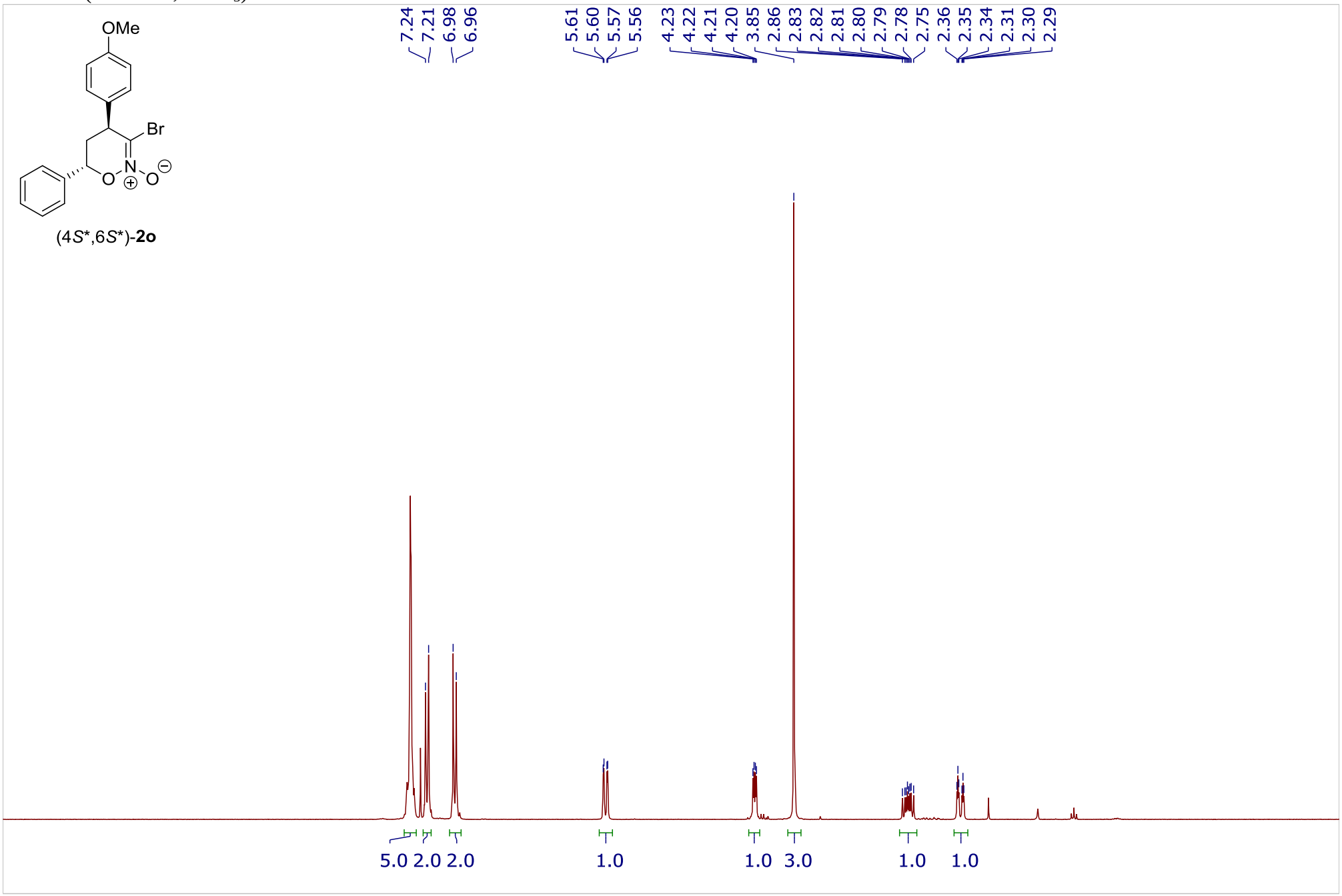


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

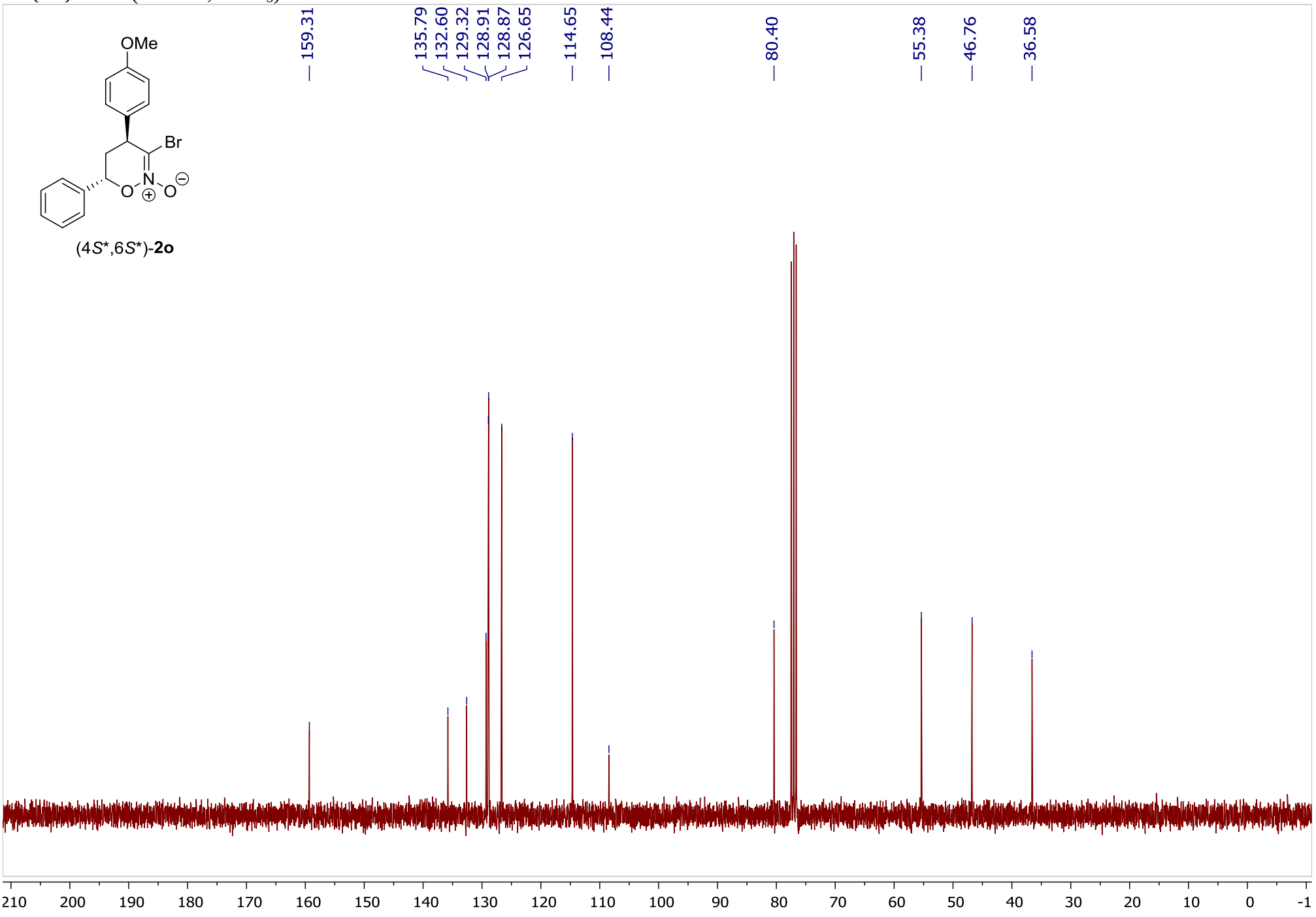


**3-Bromo-4-(4-methoxyphenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2o,** (4*S**,6*S**)-isomer

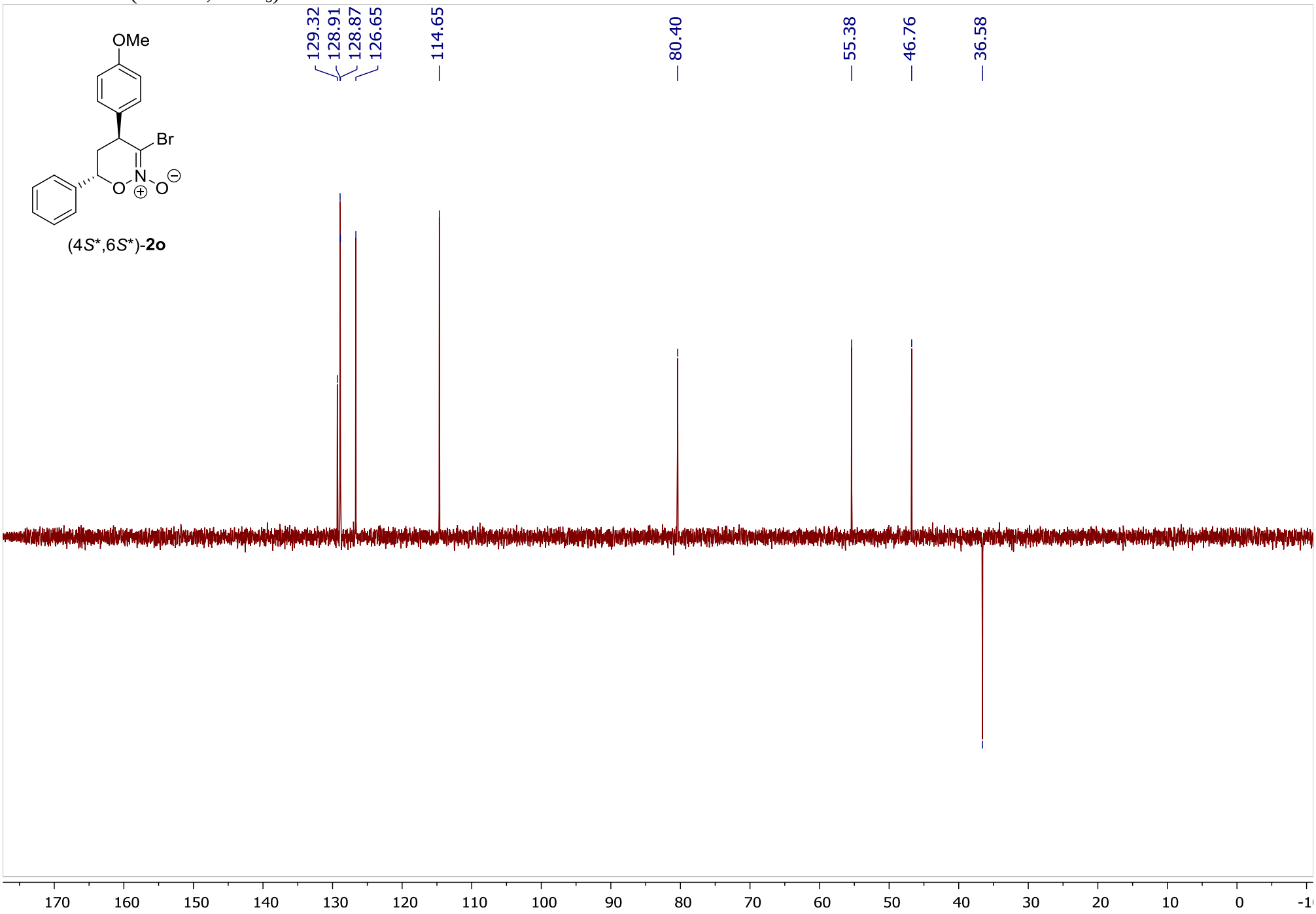
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

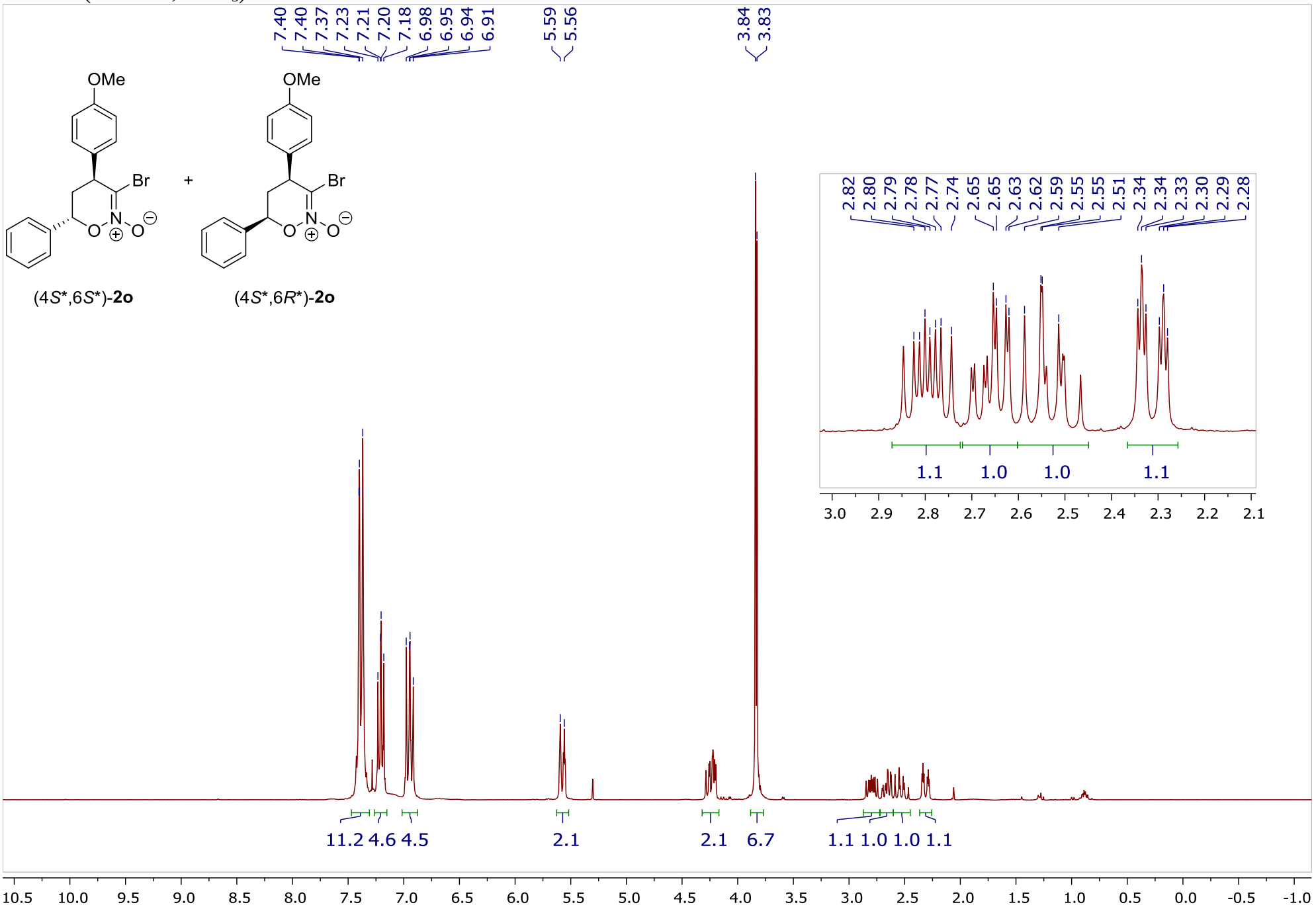


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

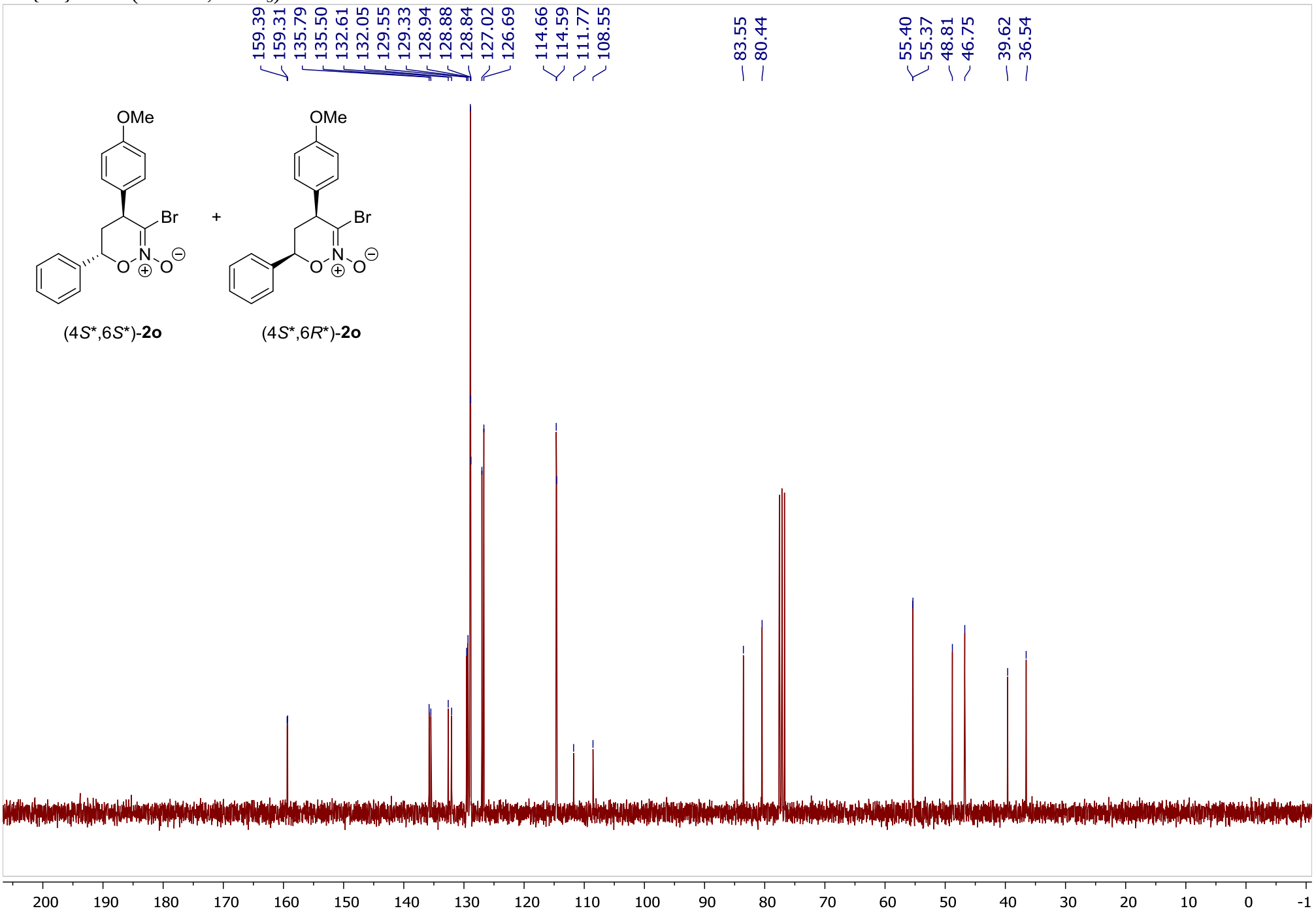


**3-Bromo-4-(4-methoxyphenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine 2-oxide 2o,** (4*S**,6*S**)-isomer : (4*S**,6*R**)-isomer = 1.1 : 1.

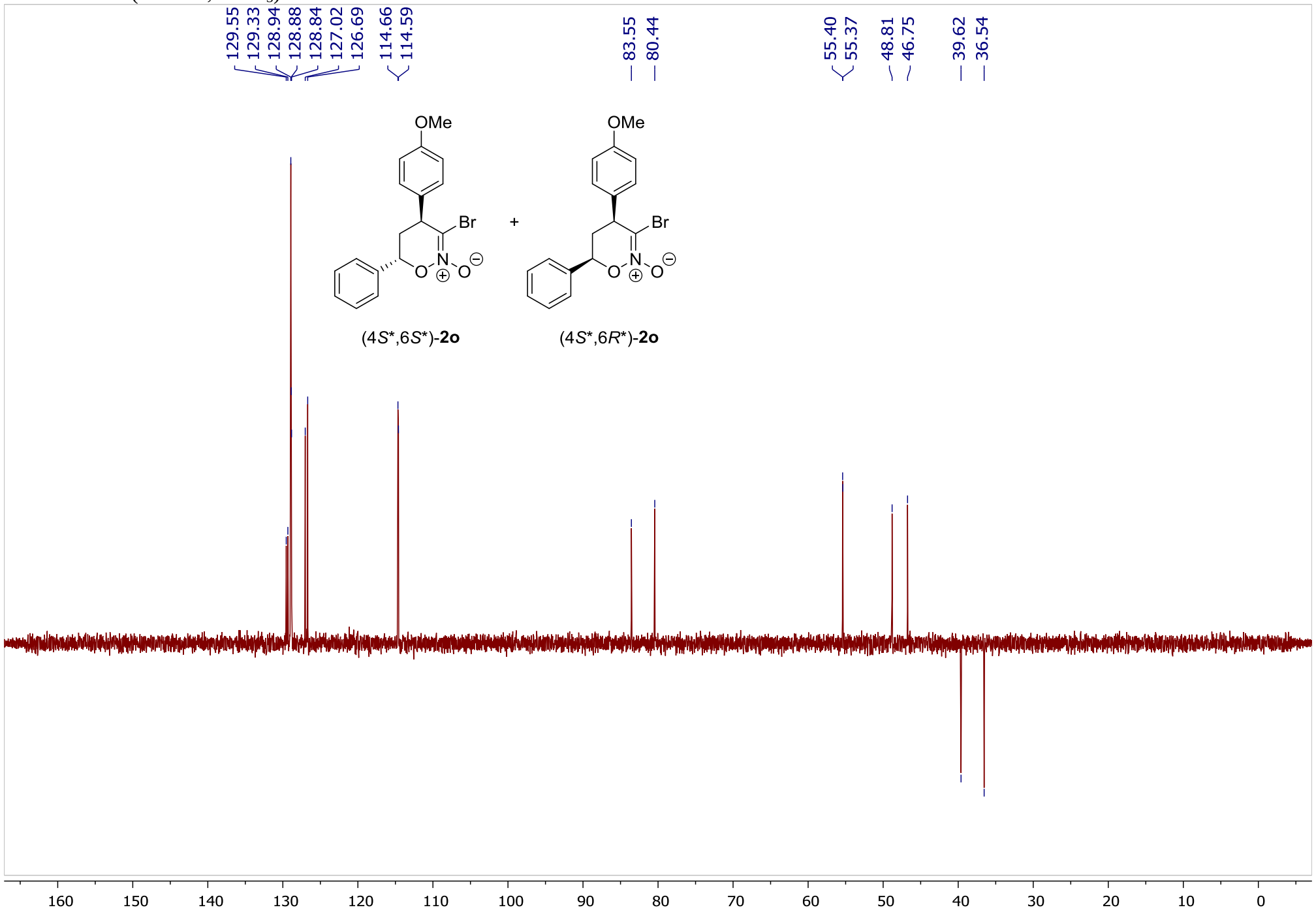
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

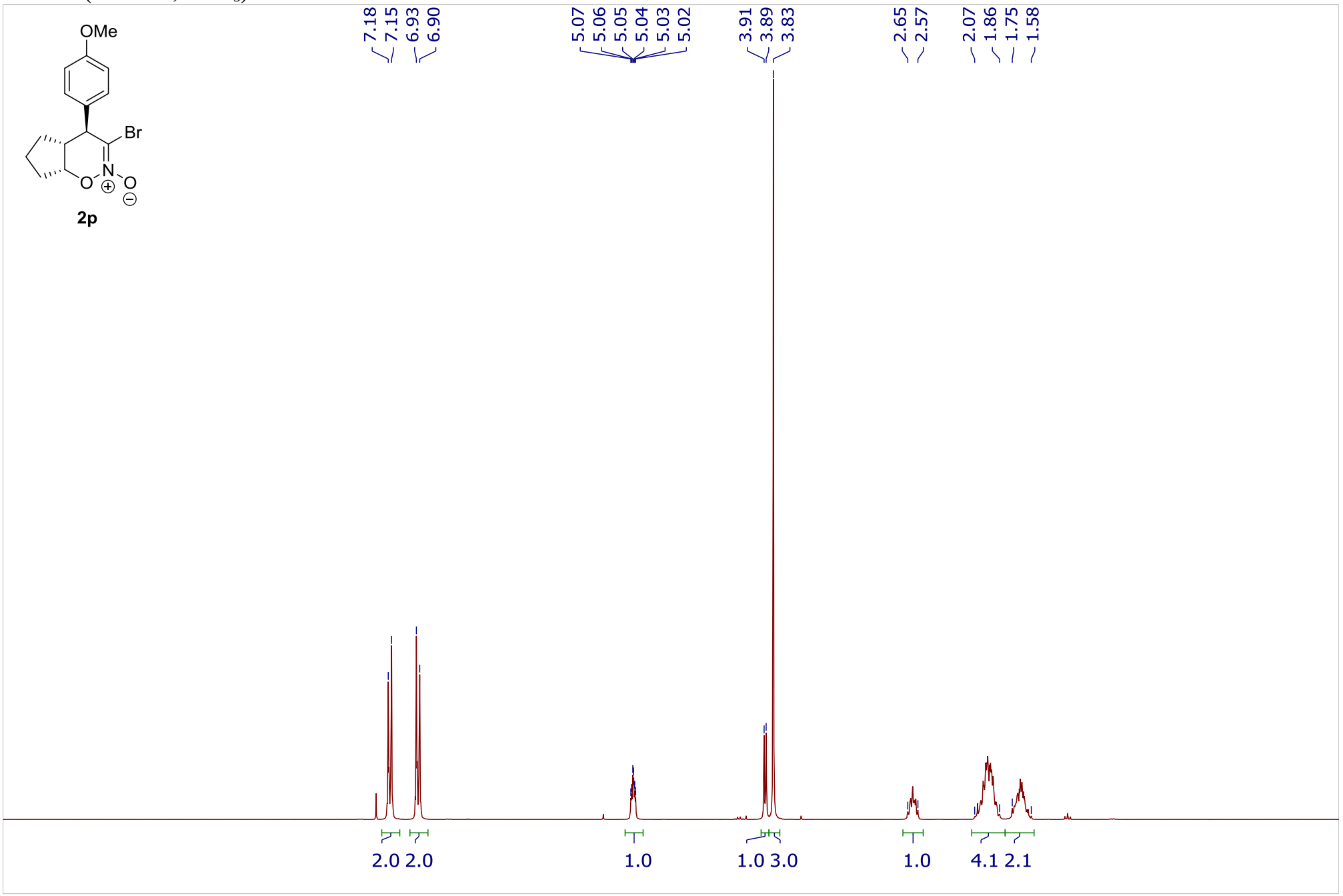


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

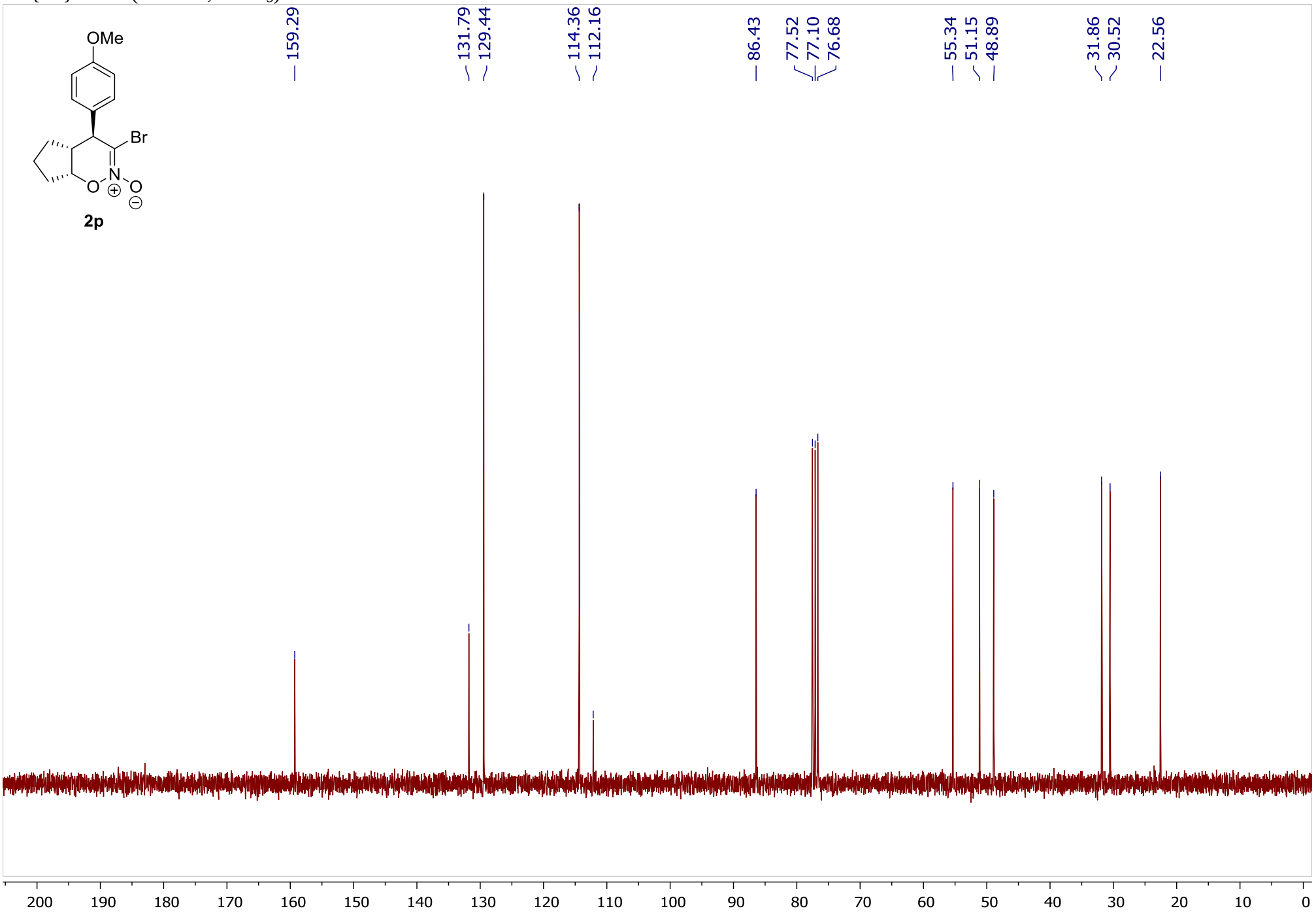


**(4*S**,4a*R**,7a*R**)-3-Bromo-4-(4-methoxyphenyl)-4,4a,5,6,7,7a-hexahydrocyclopenta[e][1,2]oxazine 2-oxide 2p**

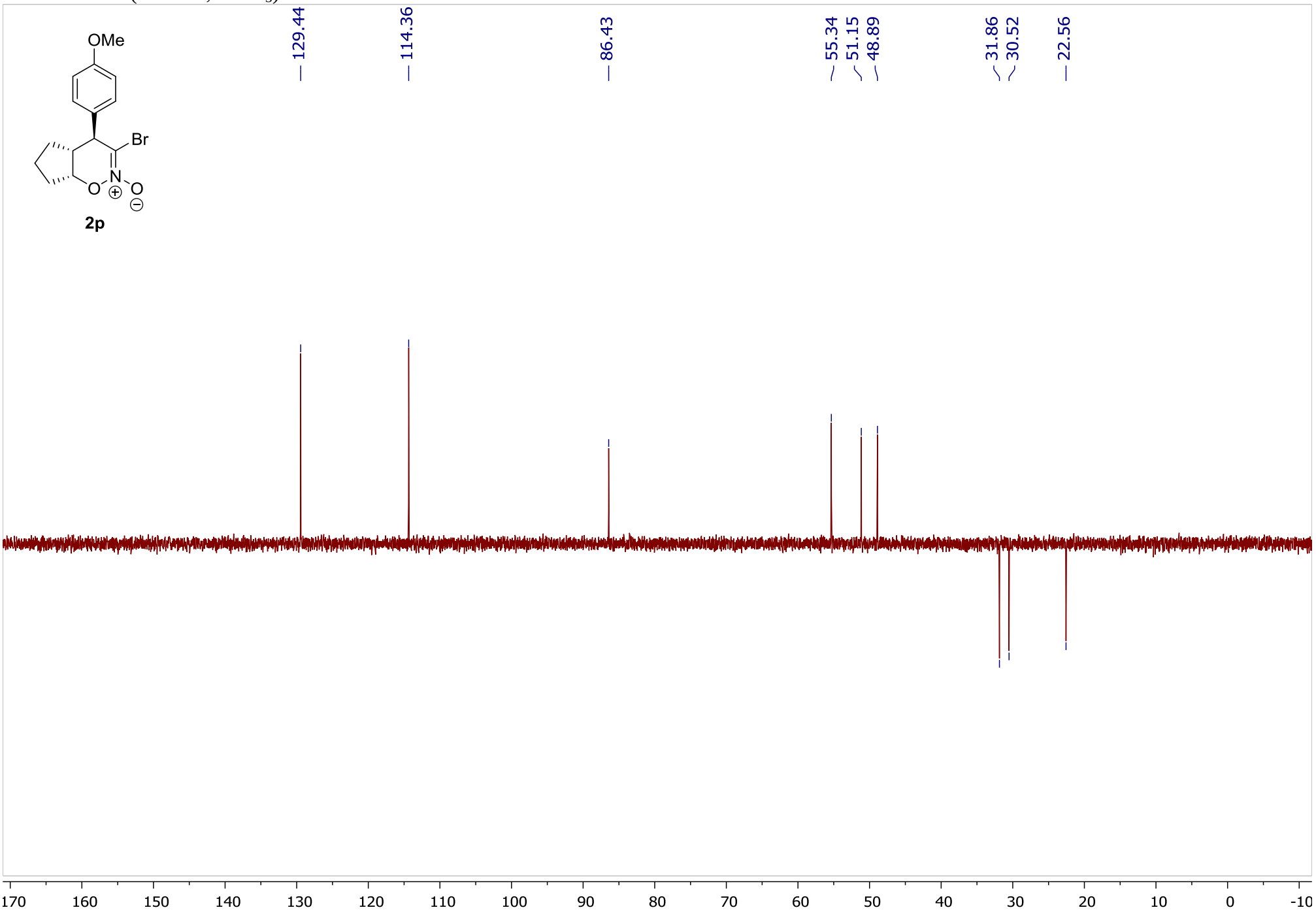
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

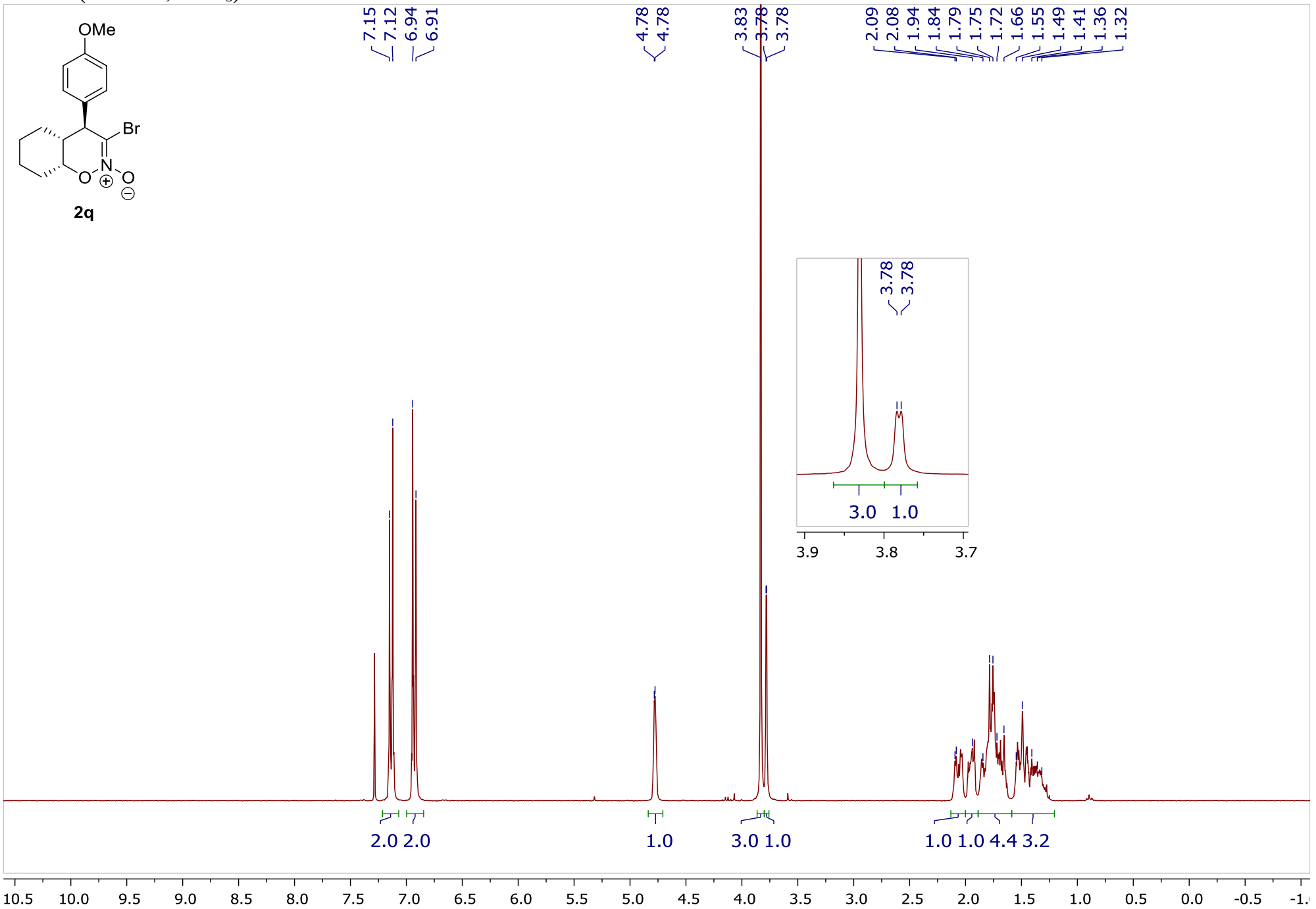


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



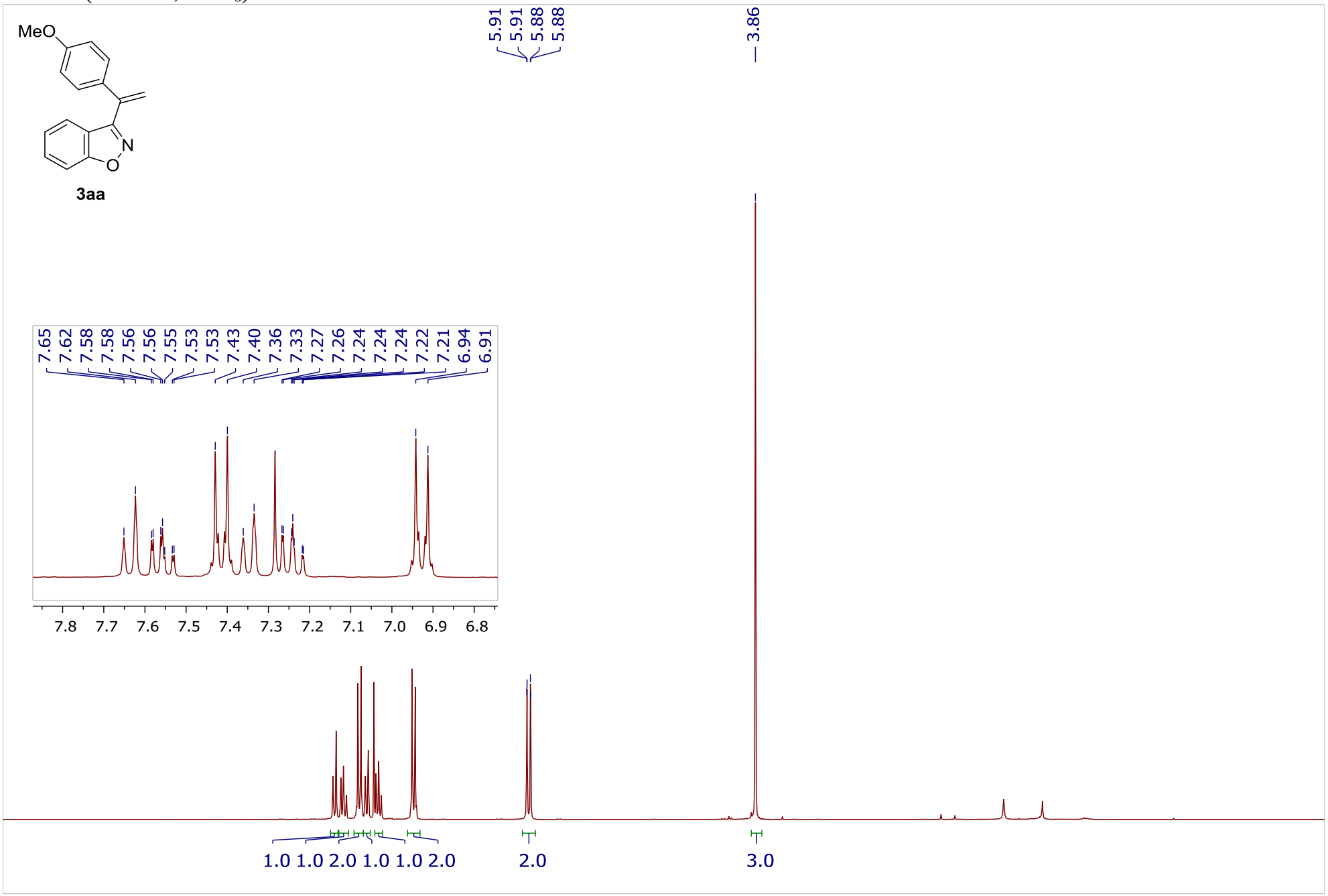
**(4*S**,4a*R**,8a*R**)-3-bromo-4-(4-methoxyphenyl)-4a,5,6,7,8,8a-hexahydro-4H-benzo[e][1,2]oxazine 2-oxide 2q**

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

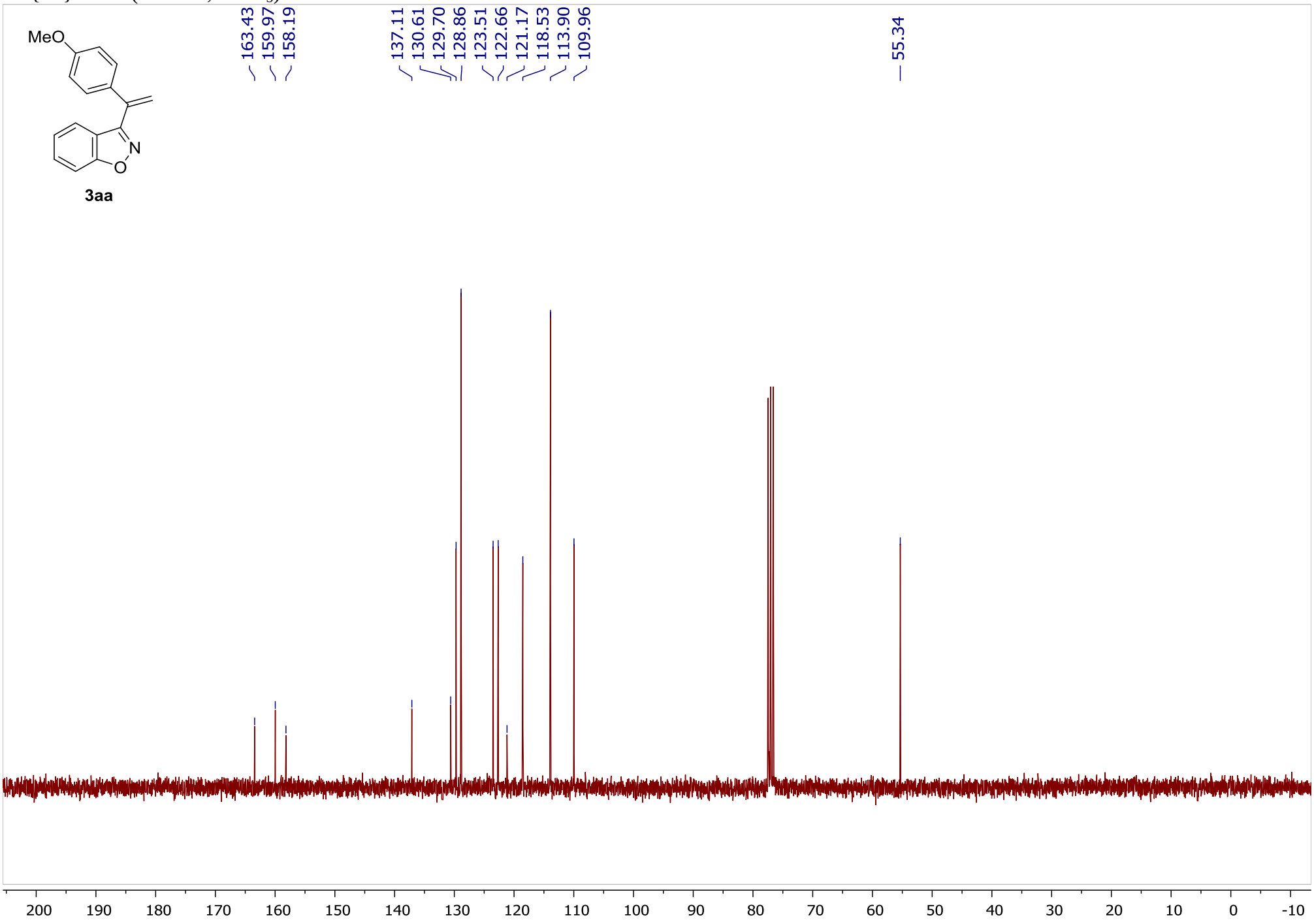


**3-(1-(4-Methoxyphenyl)vinyl)benzo[d]isoxazole 3aa**

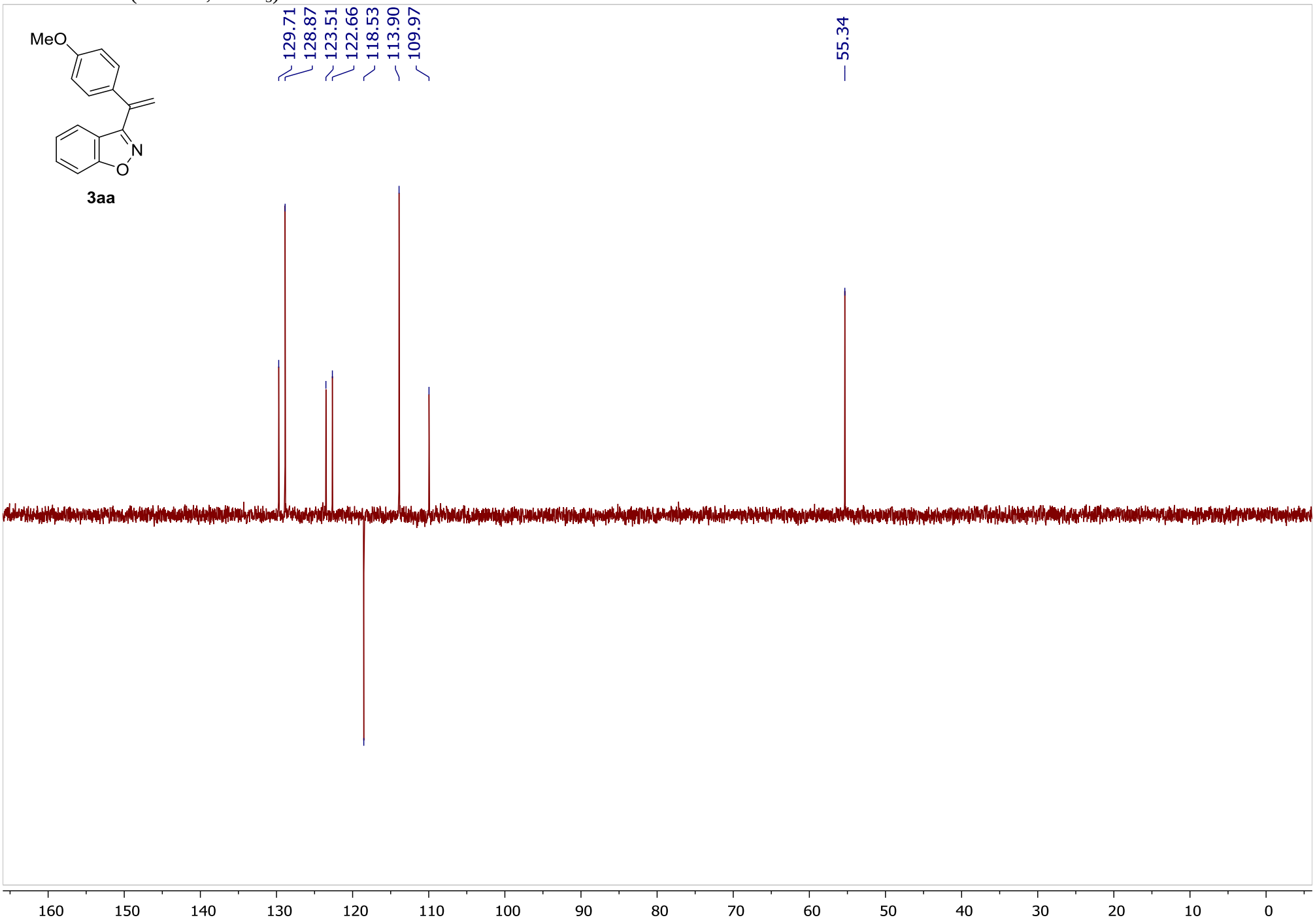
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

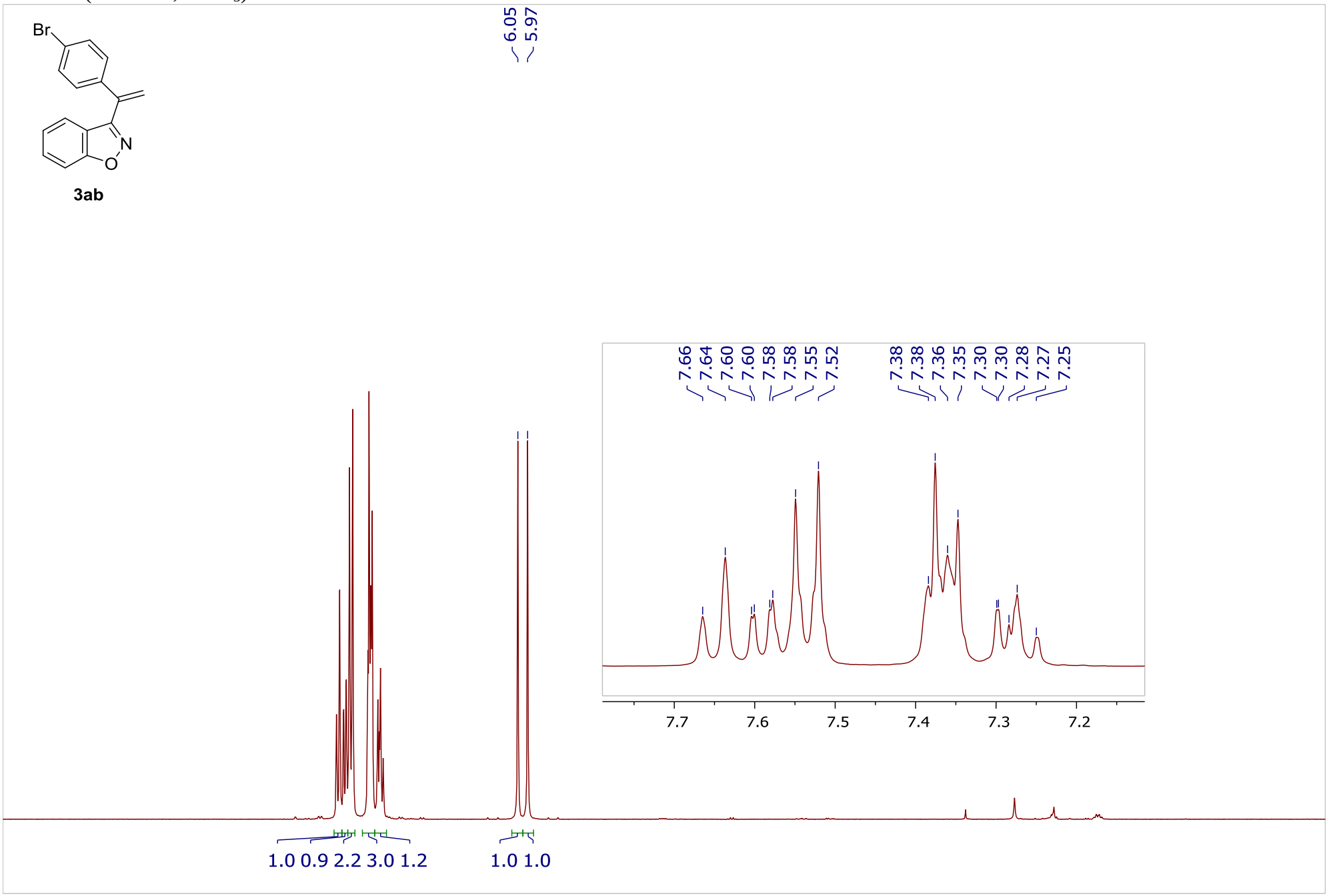


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

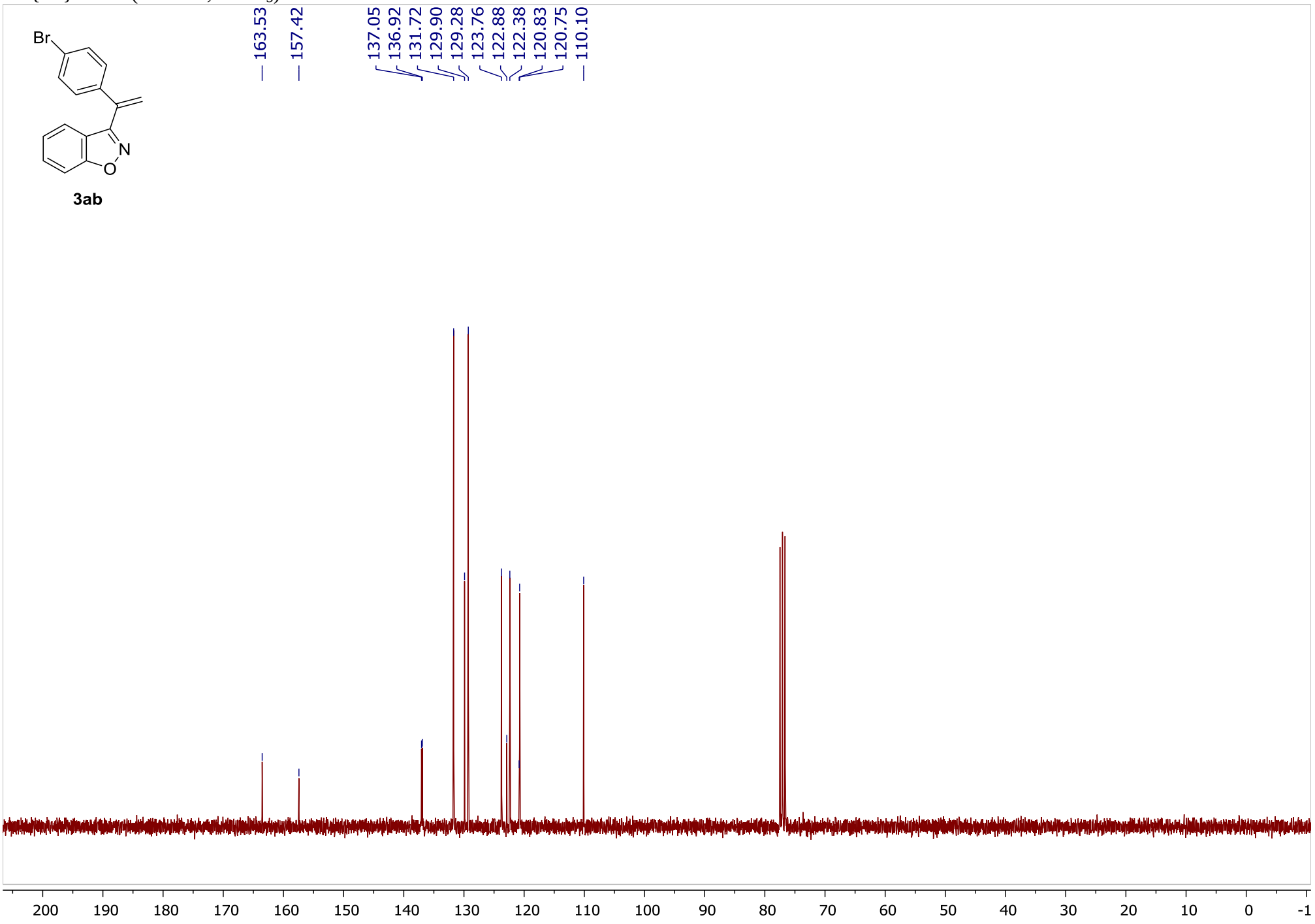


**3-(1-(4-Bromophenyl)vinyl)benzo[d]isoxazole 3ab**

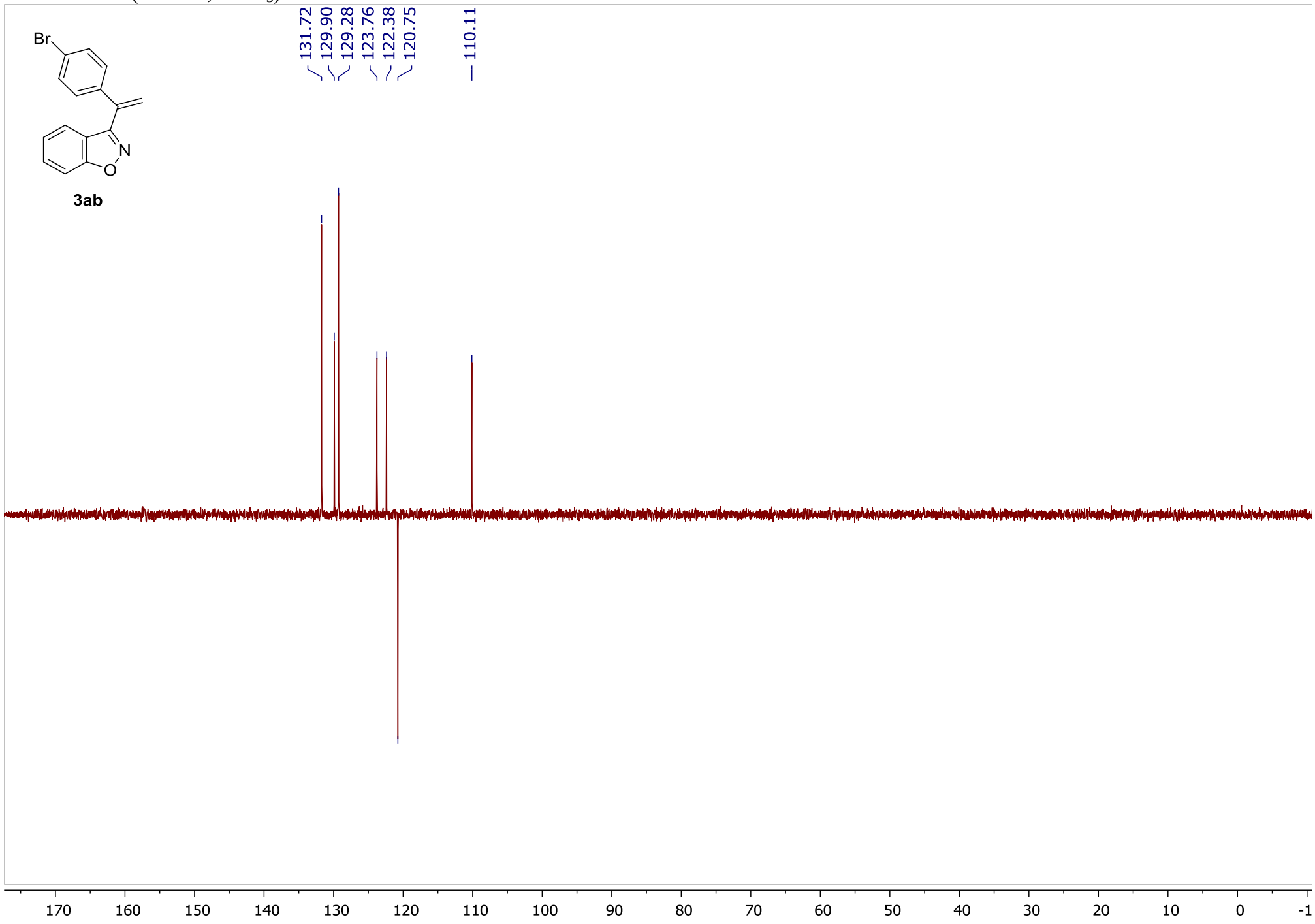
$^1$H NMR (300 MHz, $CDCl_3$)



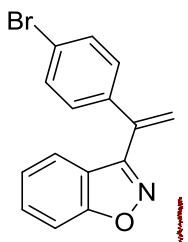
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

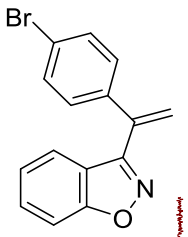


$^{1}H$-$^{13}C$ HSQC




**3ab**

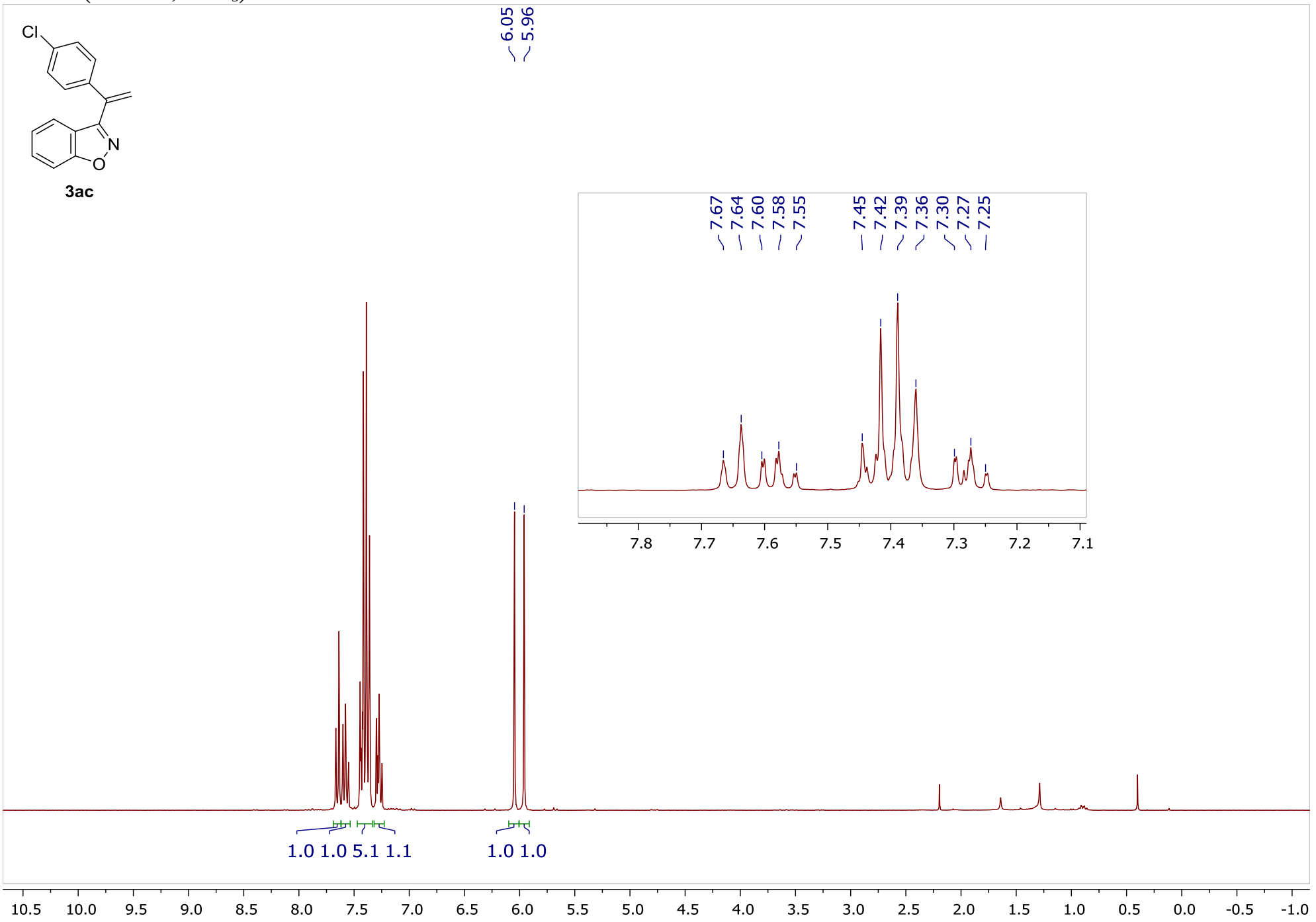
$^{1}H$-$^{13}C$ HMBC



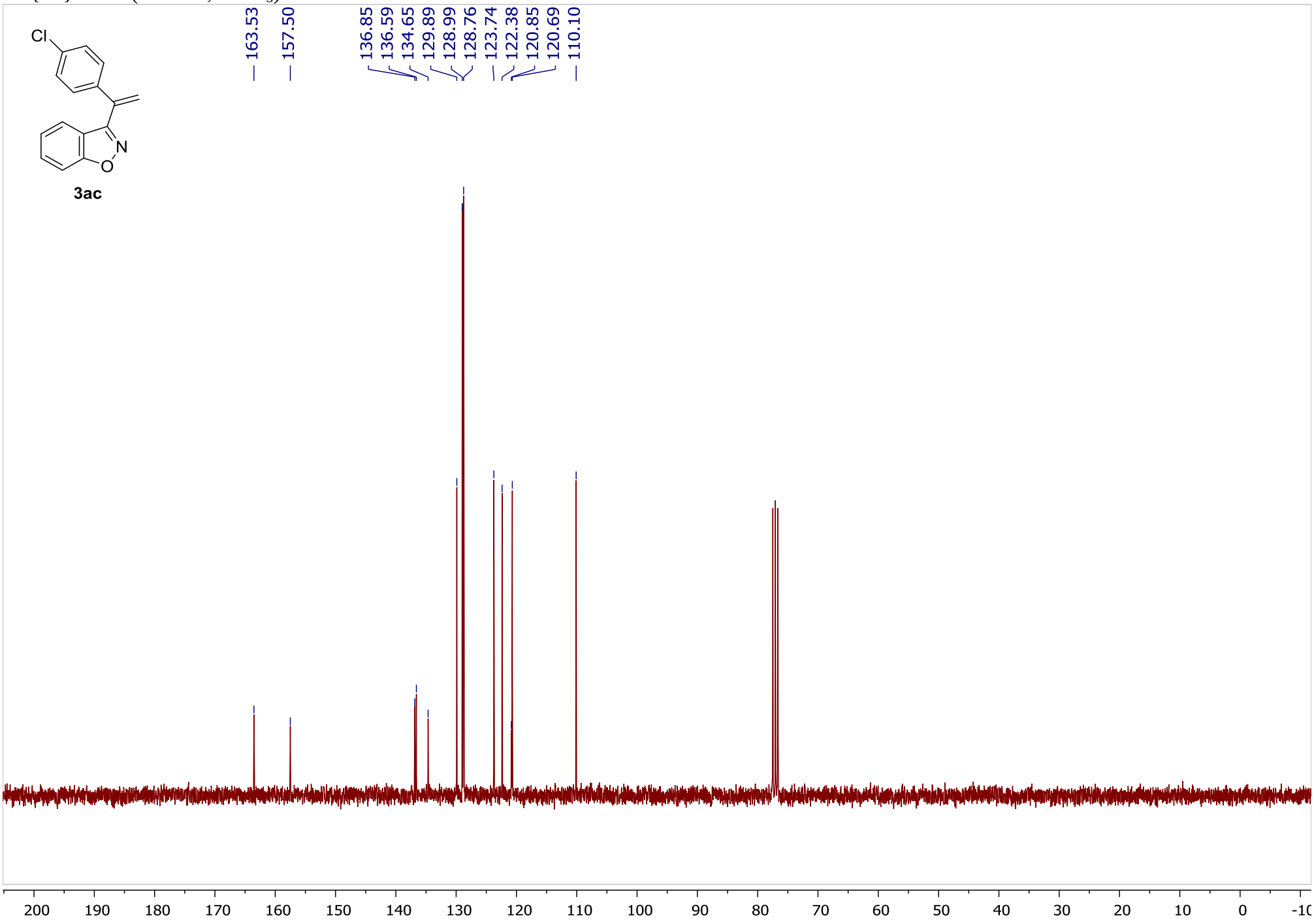

**3ab**

**3-(1-(4-Chlorophenyl)vinyl)benzo[d]isoxazole 3ac**

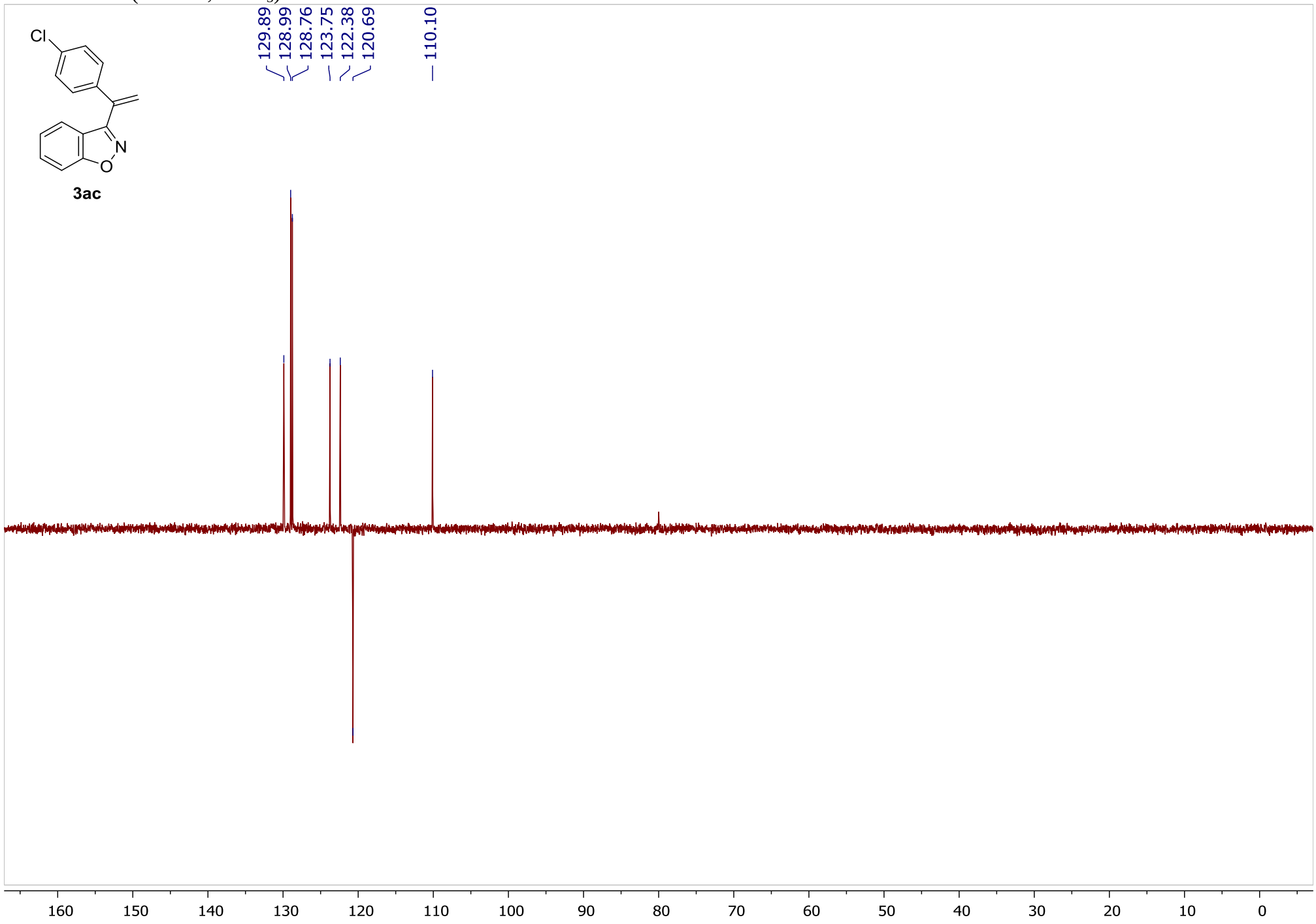
$^1$H NMR (300 MHz, $CDCl_3$)



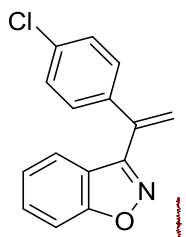
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



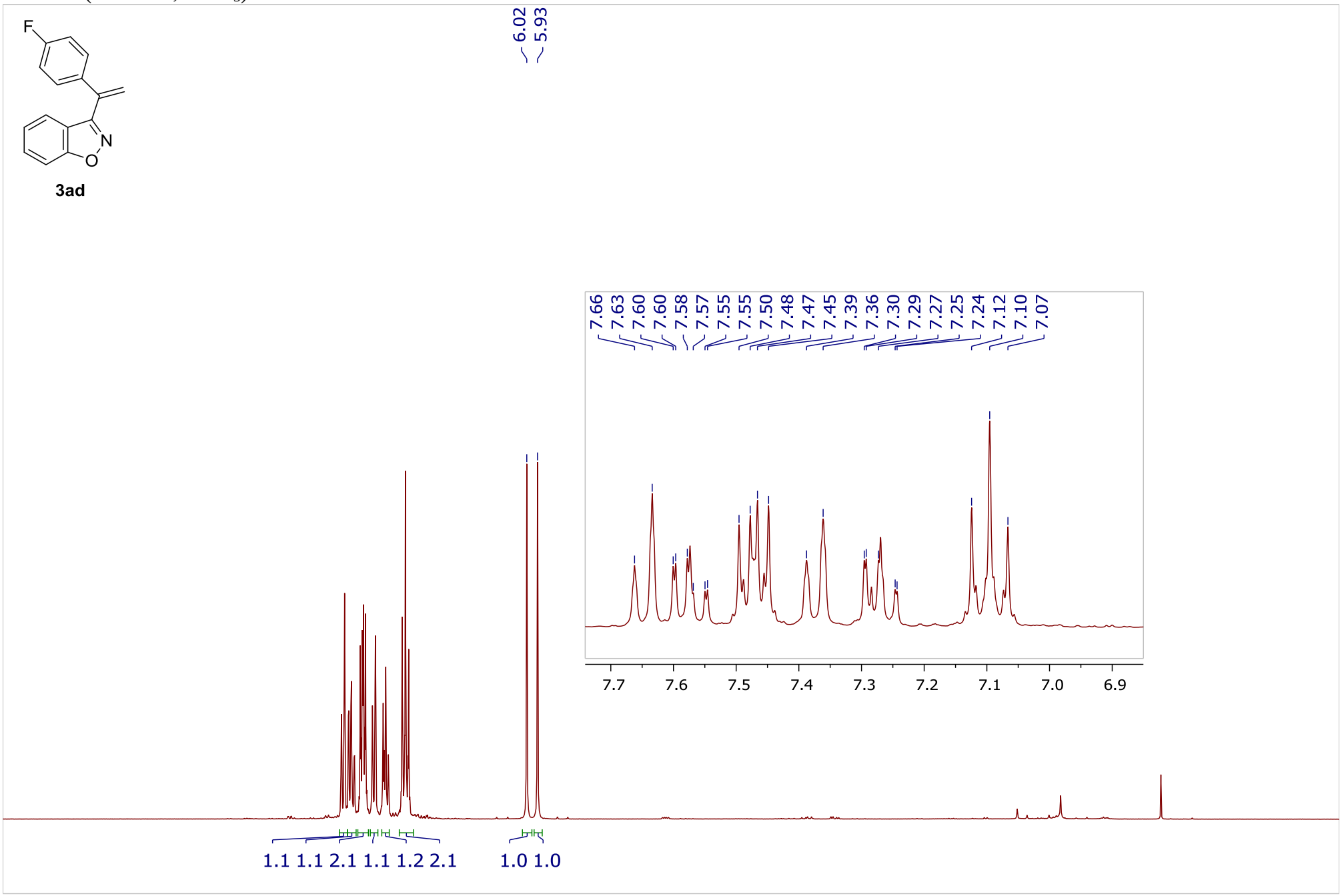
$^{1}$H-$^{13}$C HSQC



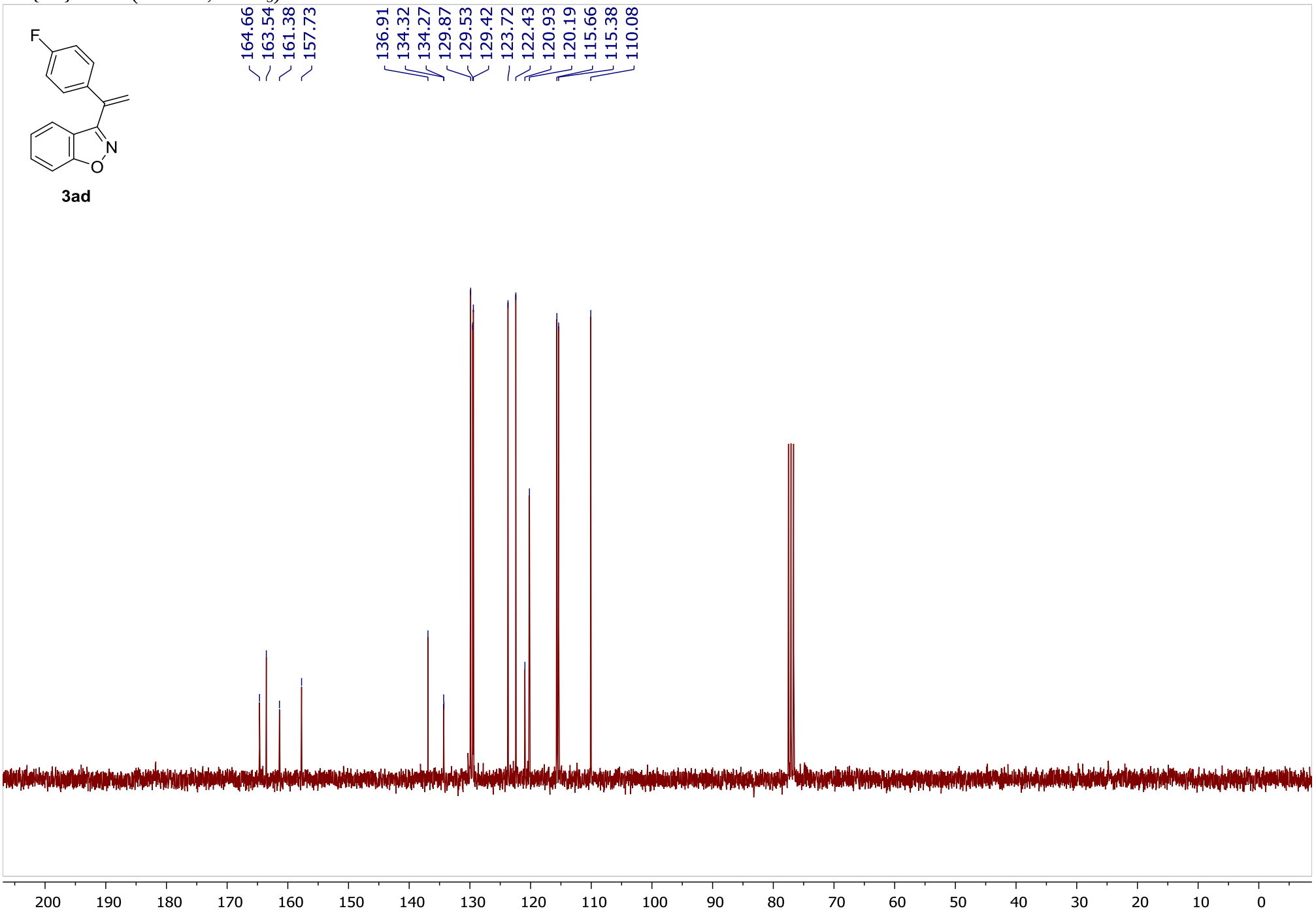

3ac

**3-(1-(4-Fluorophenyl)vinyl)benzo[d]isoxazole 3ad**

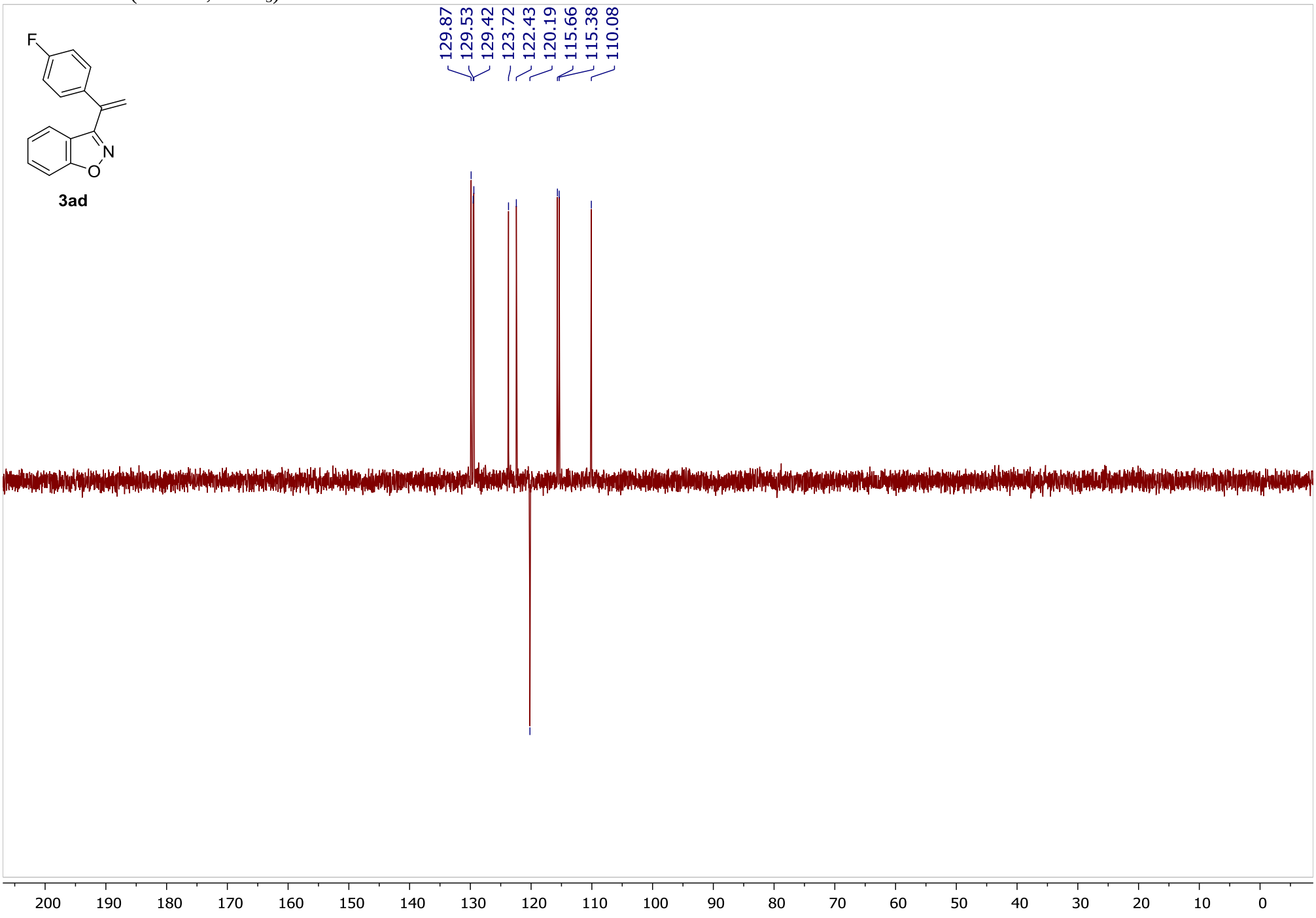
$^1$H NMR (300 MHz, $CDCl_3$)



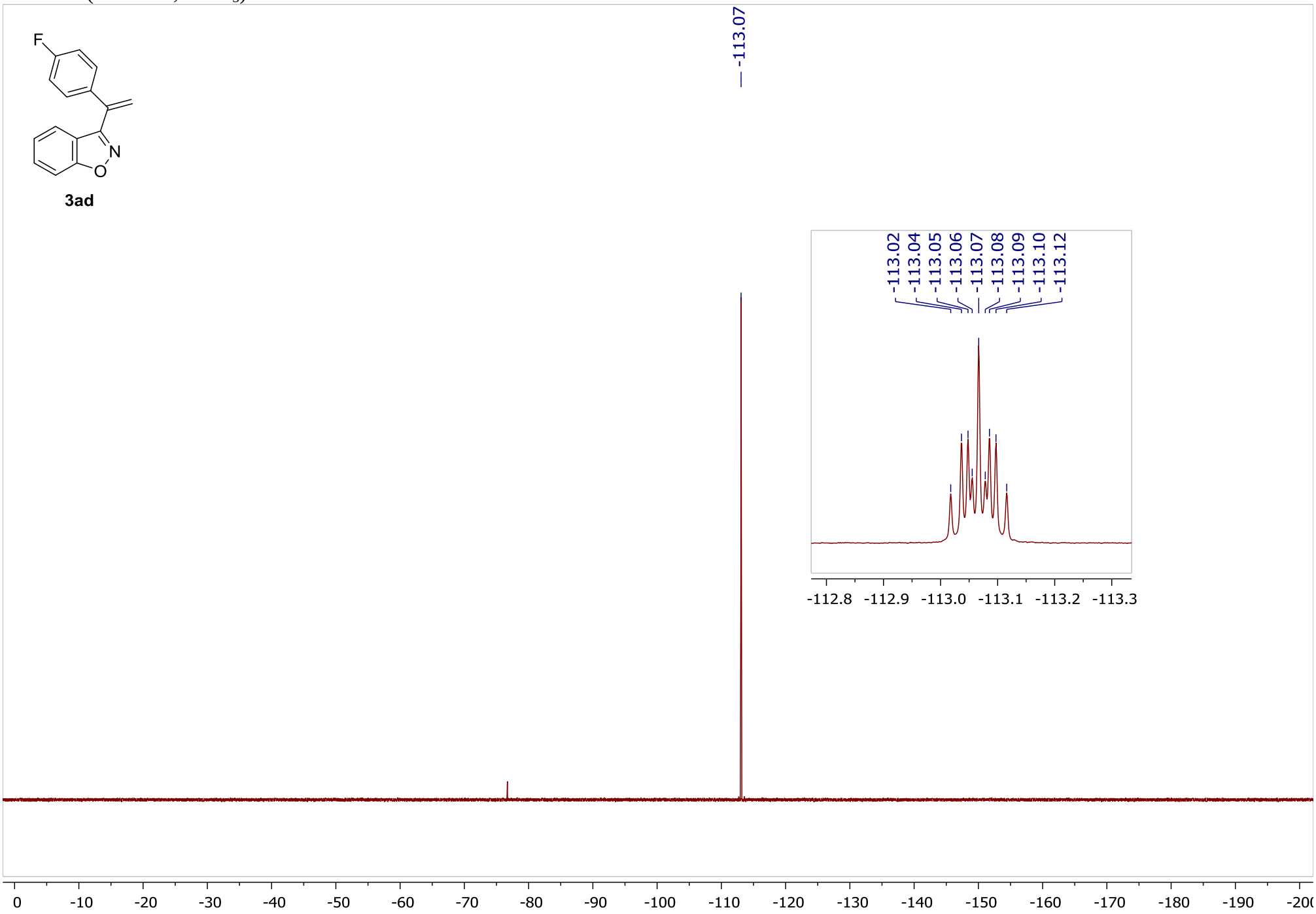
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

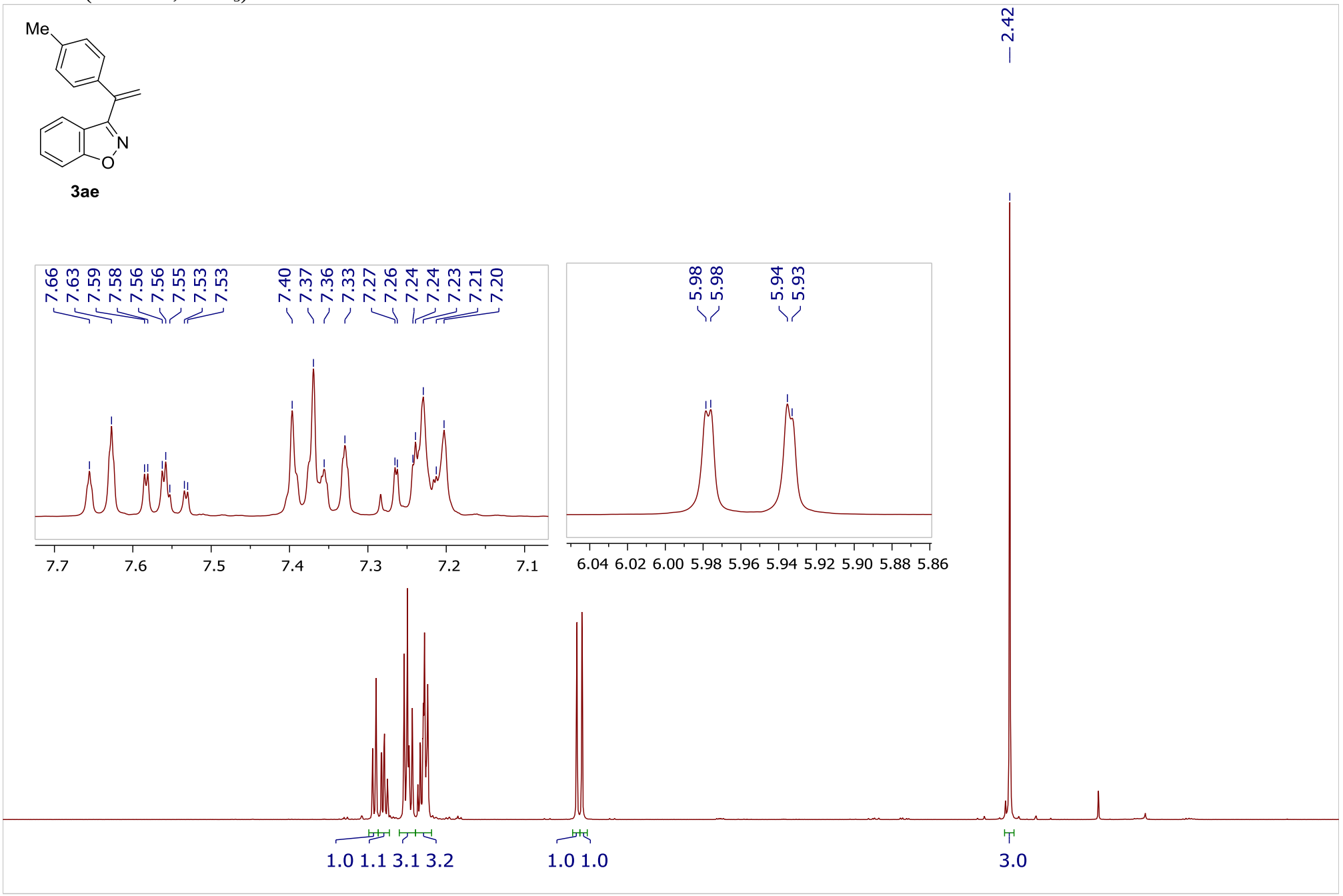


$^{19}$F NMR (282 MHz, $CDCl_3$)

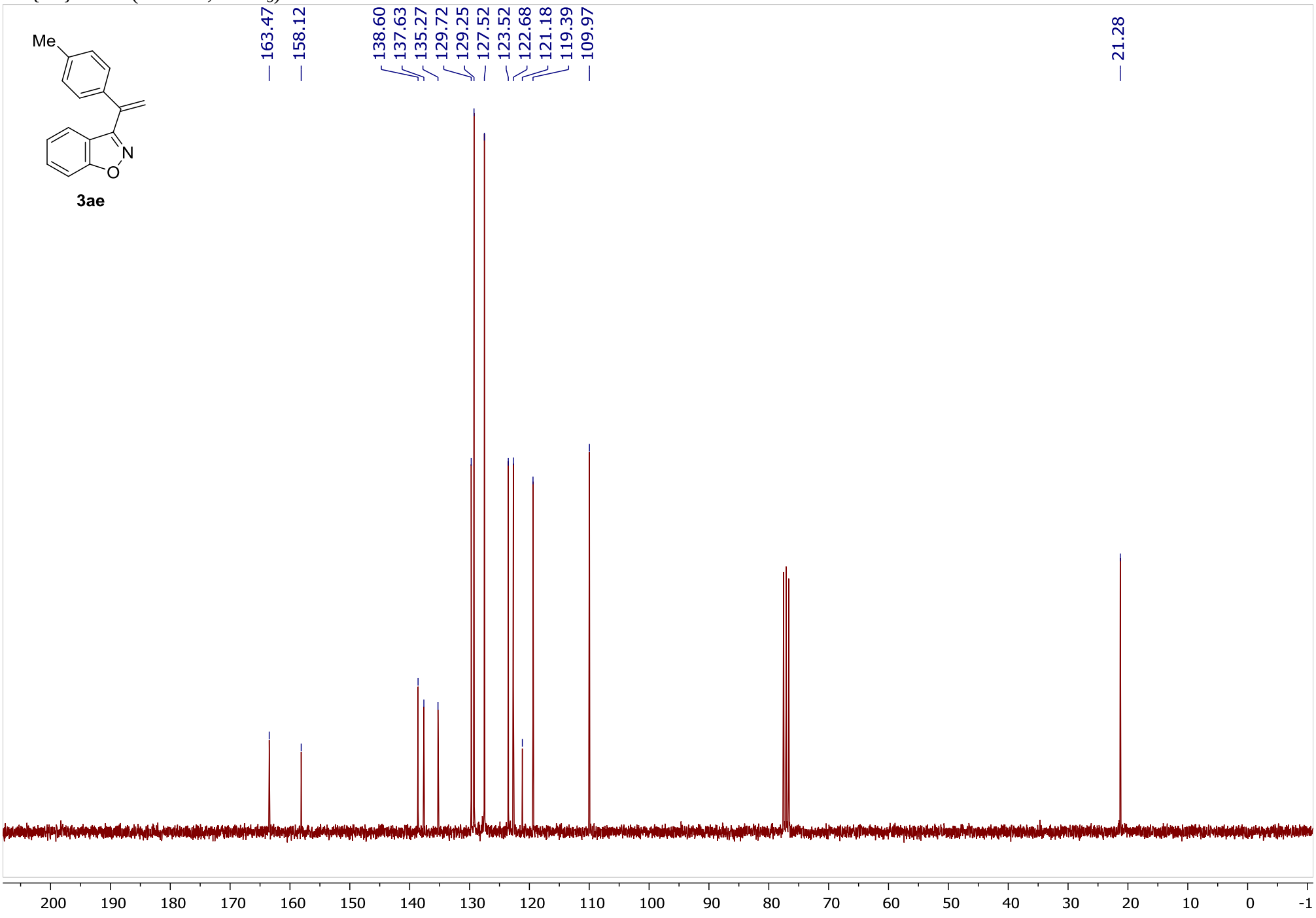


**3-(1-(*p*-Tolyl)vinyl)benzo[d]isoxazole 3ae**

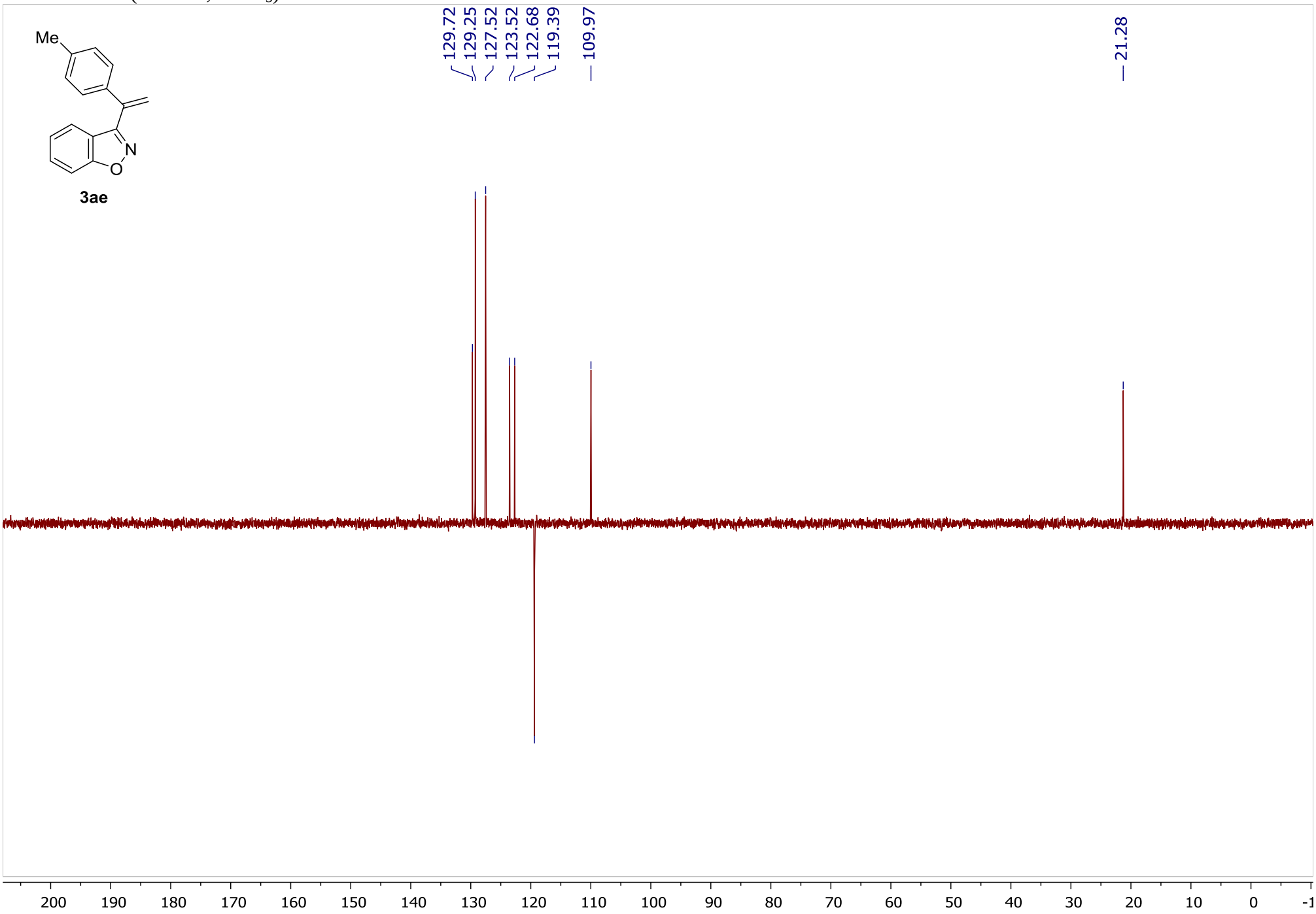
$^1$H NMR (300 MHz, $CDCl_3$)



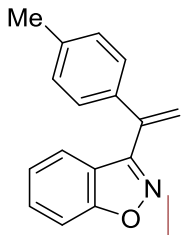
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



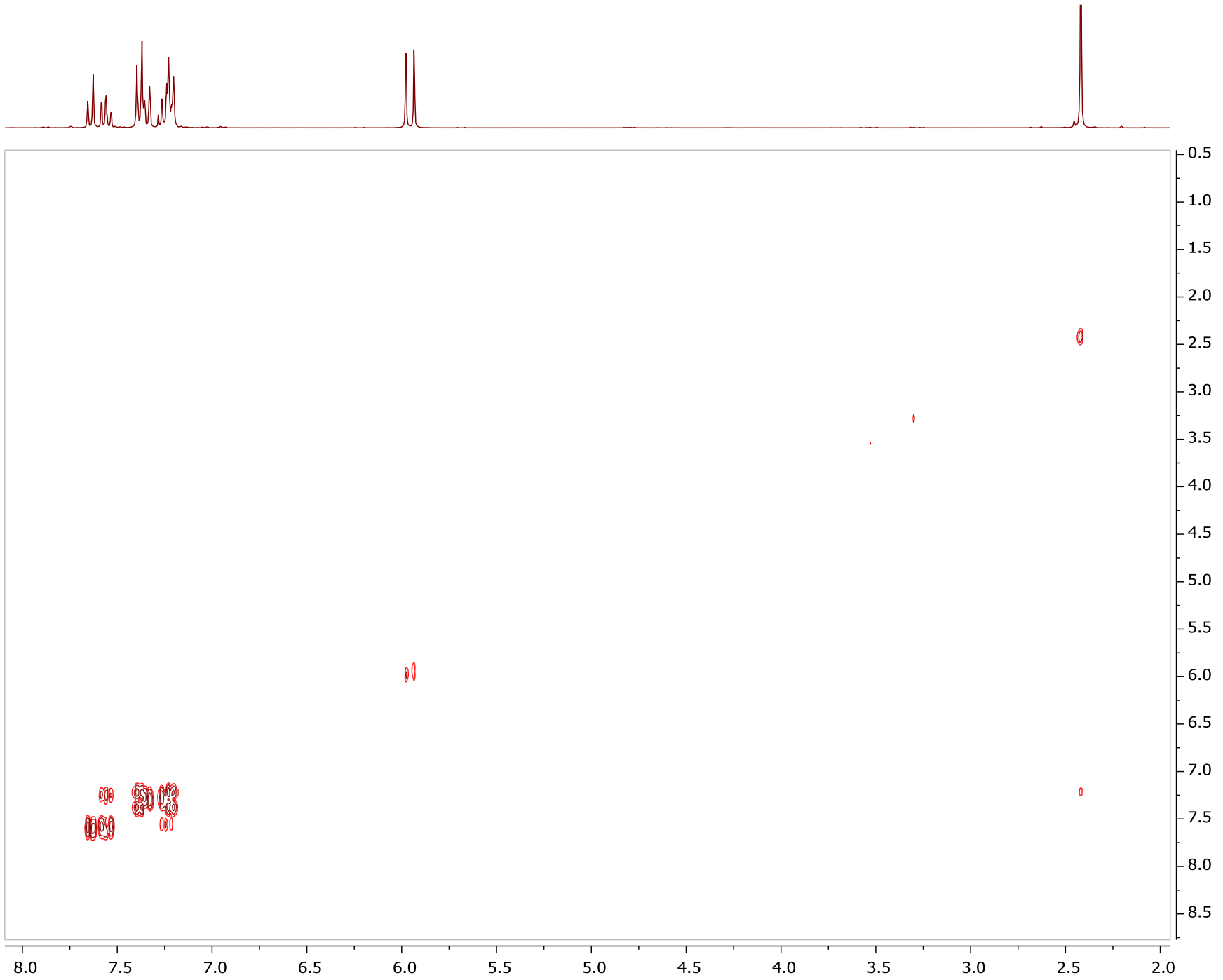
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



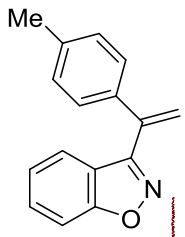
$^{1}$H-$^{1}$H COSY




**3ae**



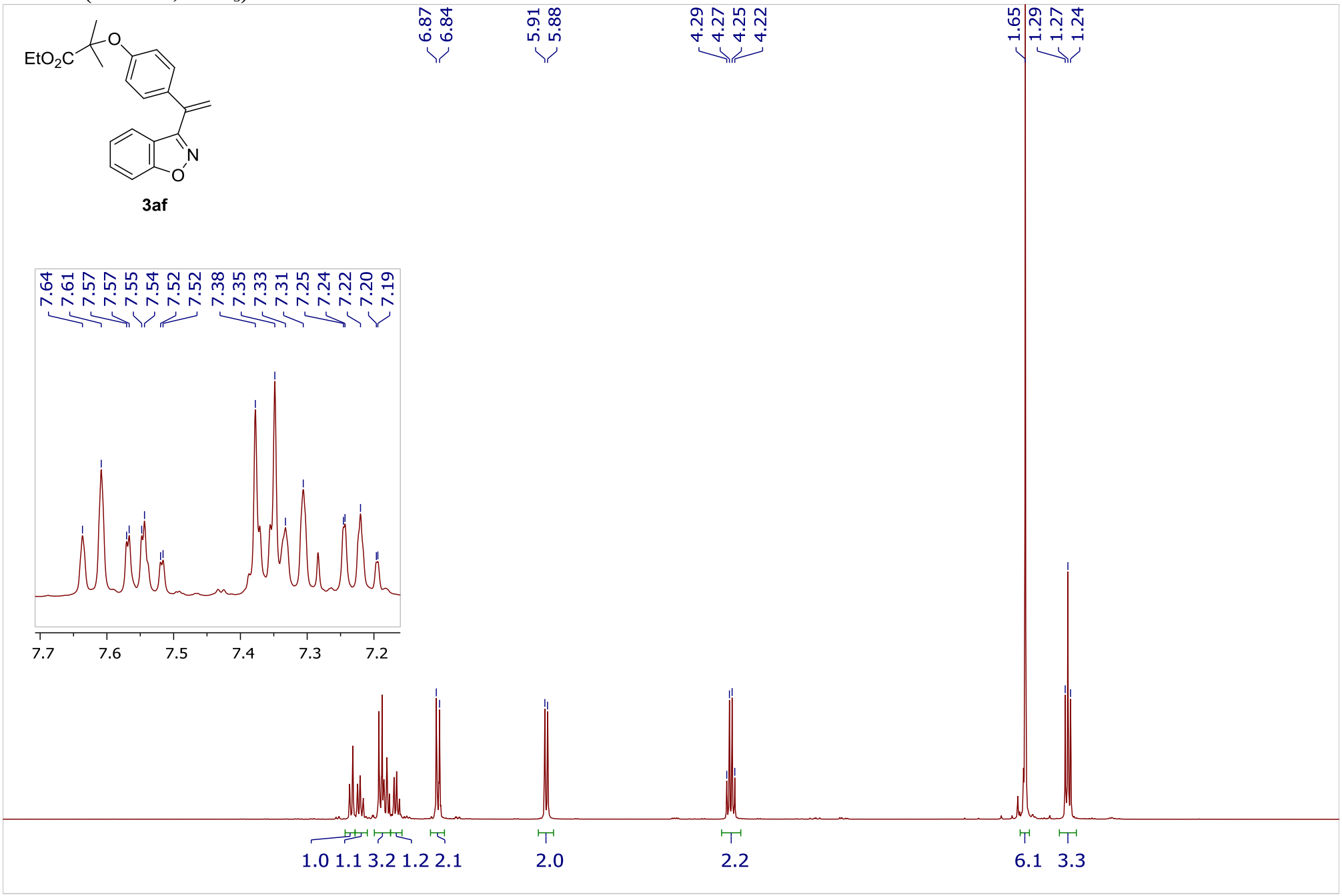
$^{1}$H-$^{13}$C HSQC



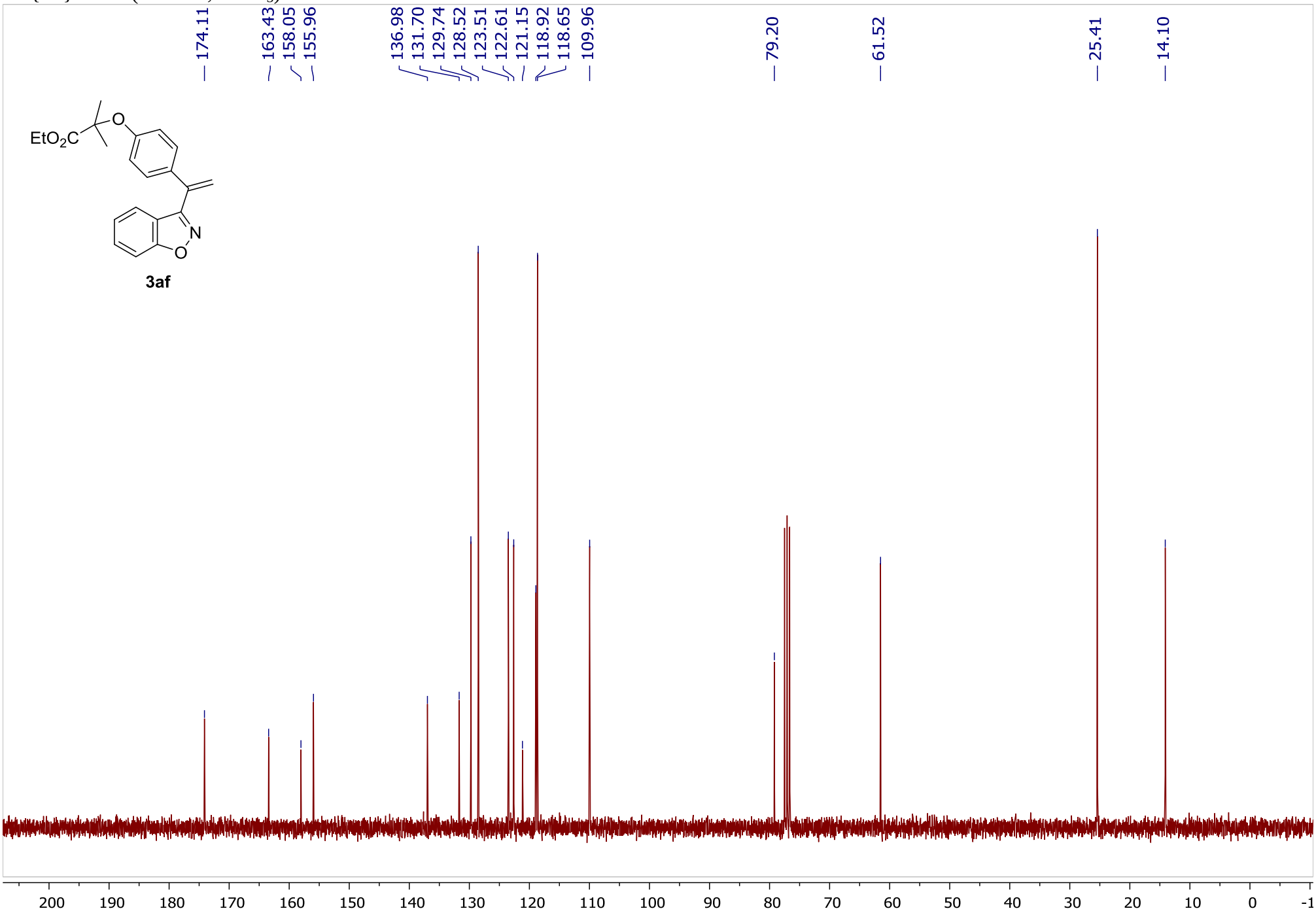

**3ae**

**Ethyl 2-(4-(1-(benzo[d]isoxazol-3-yl)vinyl)phenoxy)-2-methylpropanoate 3af**

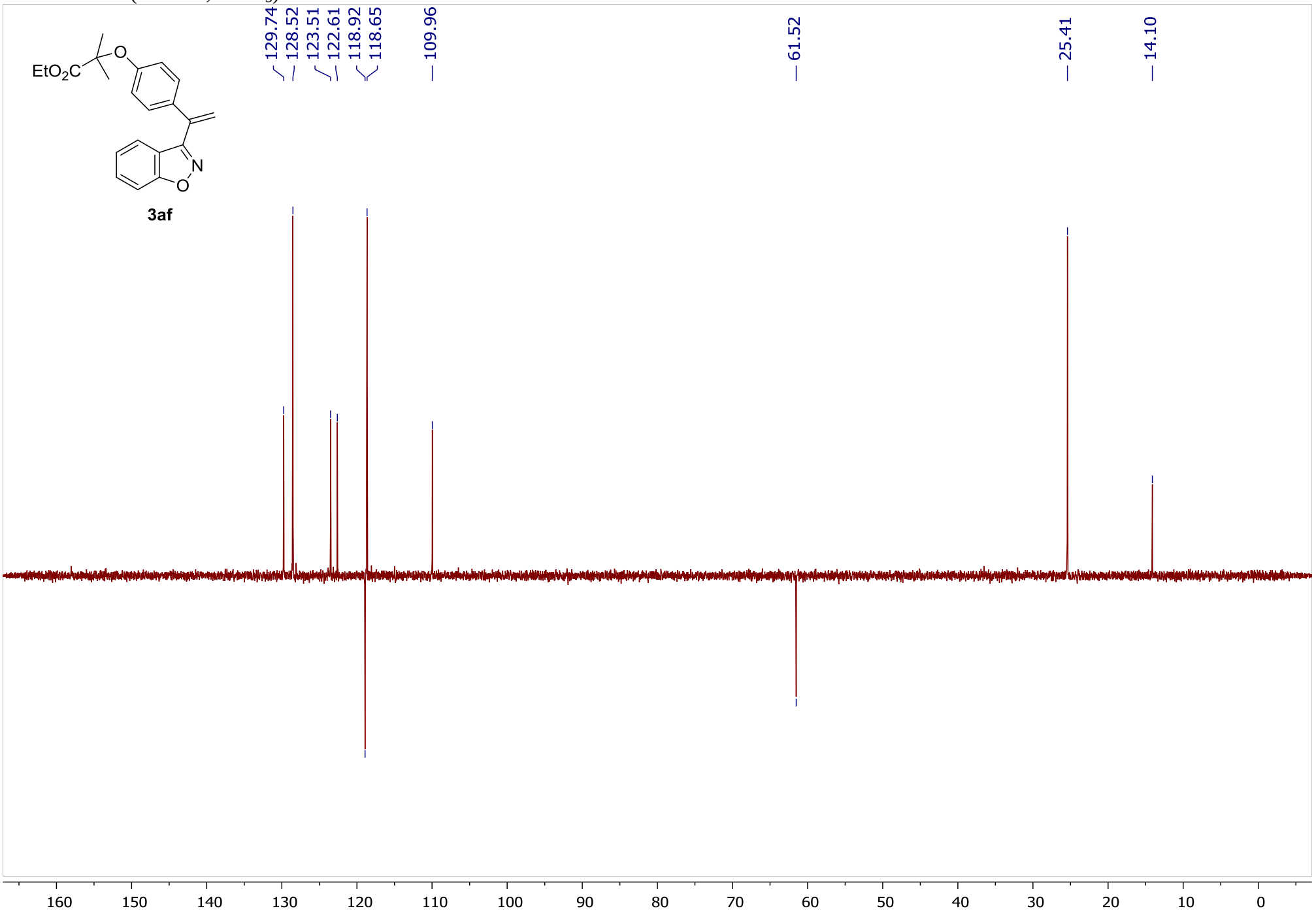
$^1$H NMR (300 MHz, $CDCl_3$)



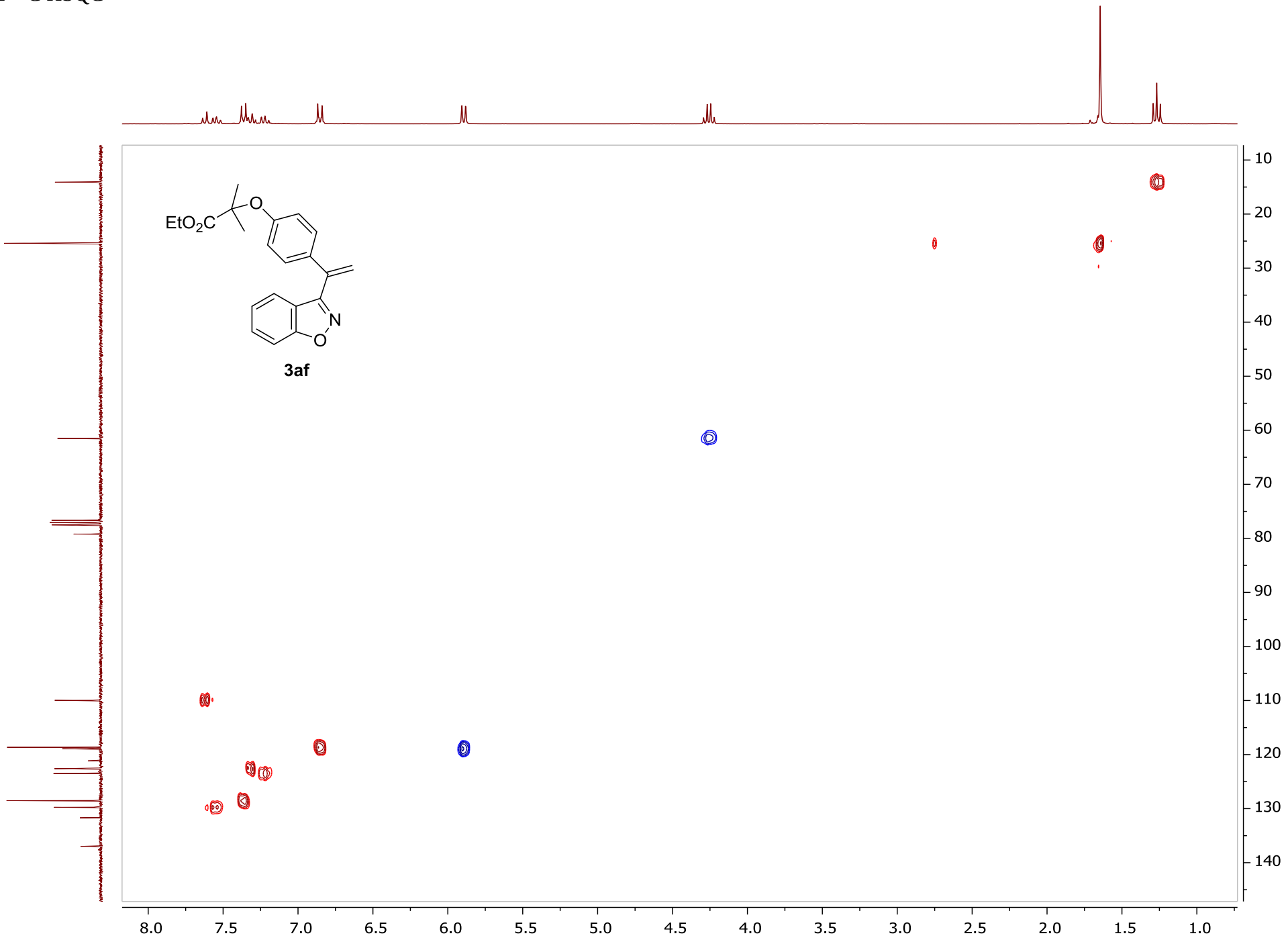
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



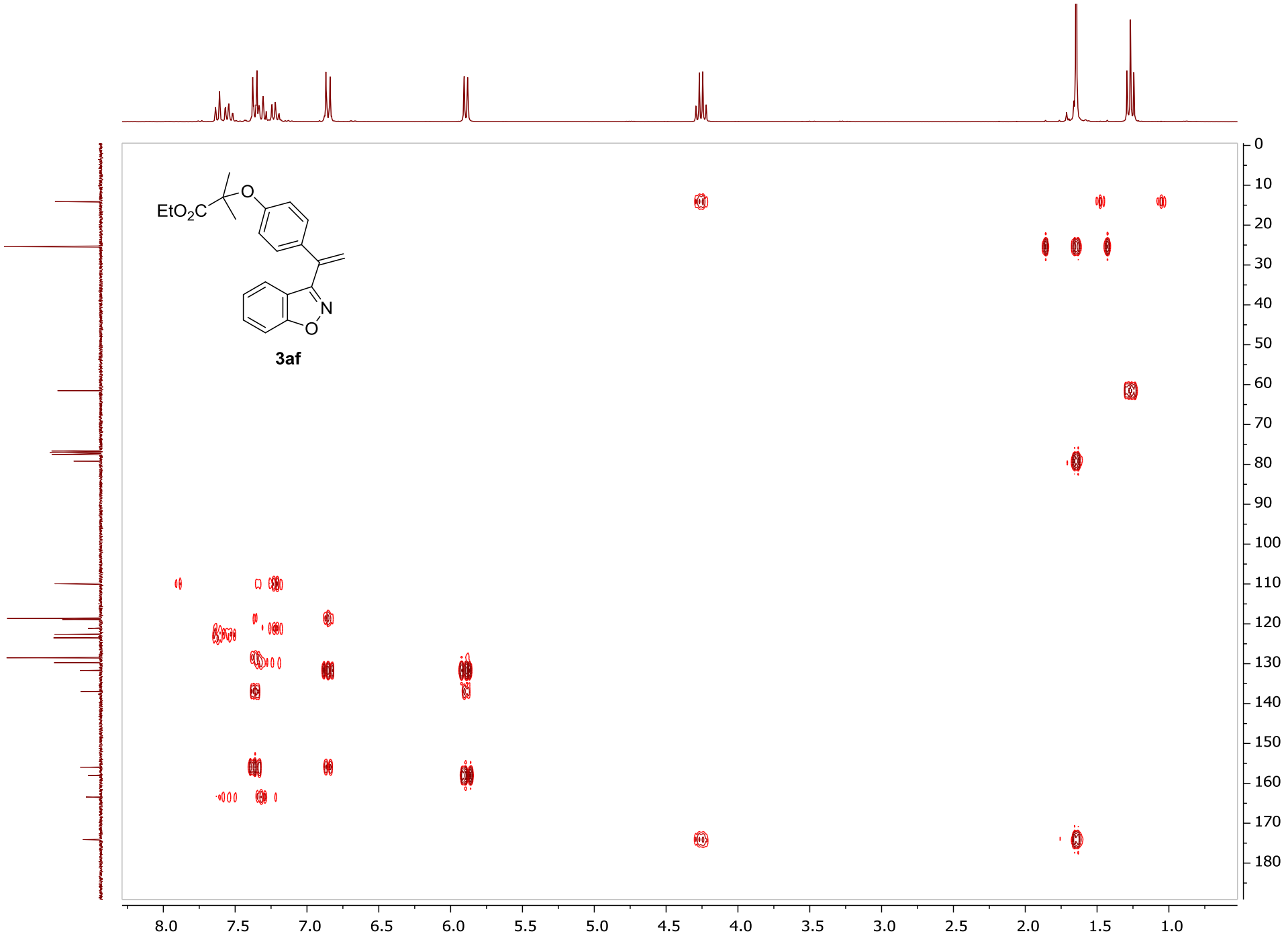
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



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


EtO2C
O
N
O
3af
10
20
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
1.5
1.0

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


EtO2C
O
N
O
3af
0
10
20
30
40
50
60
70
80
90
100
110
120
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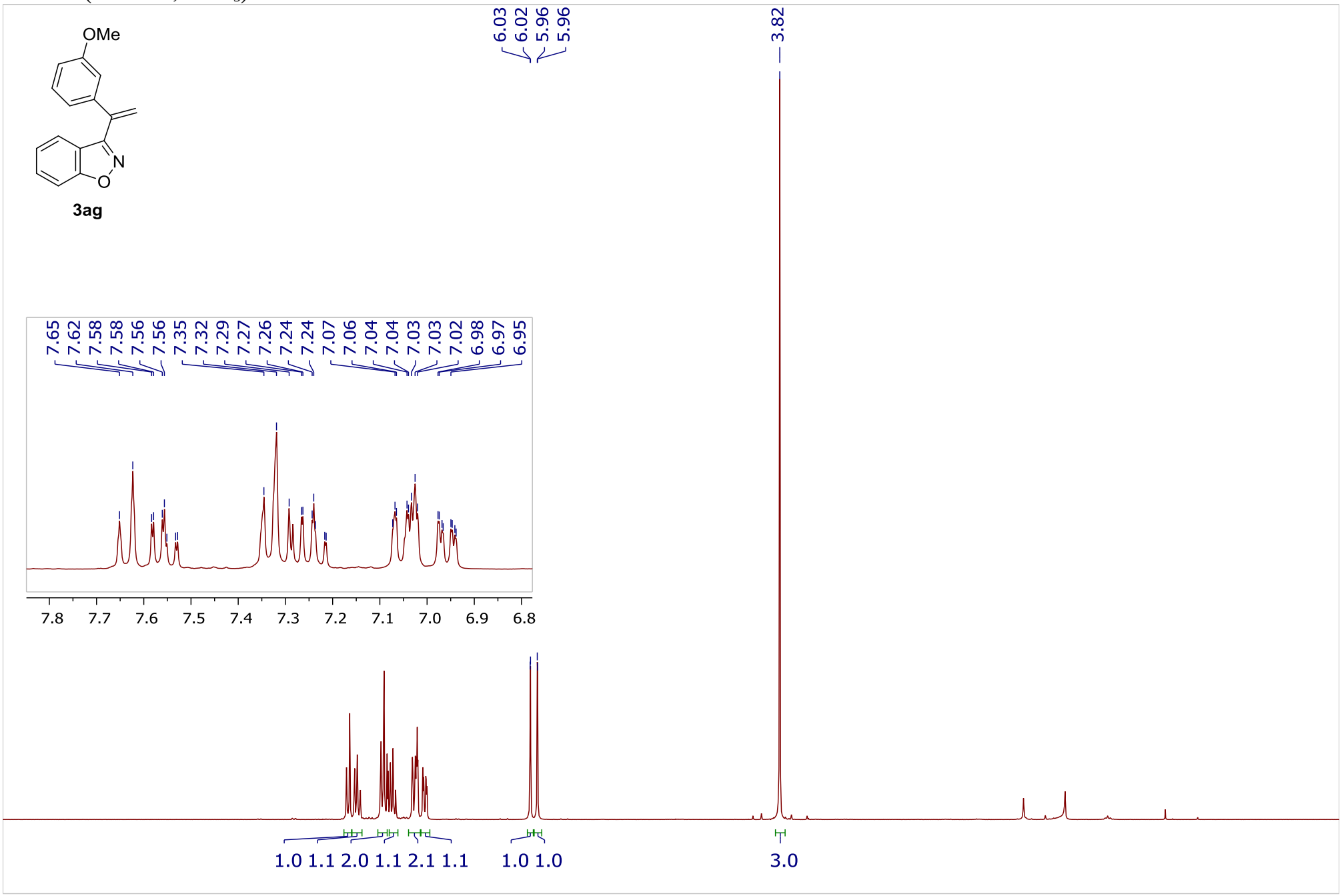
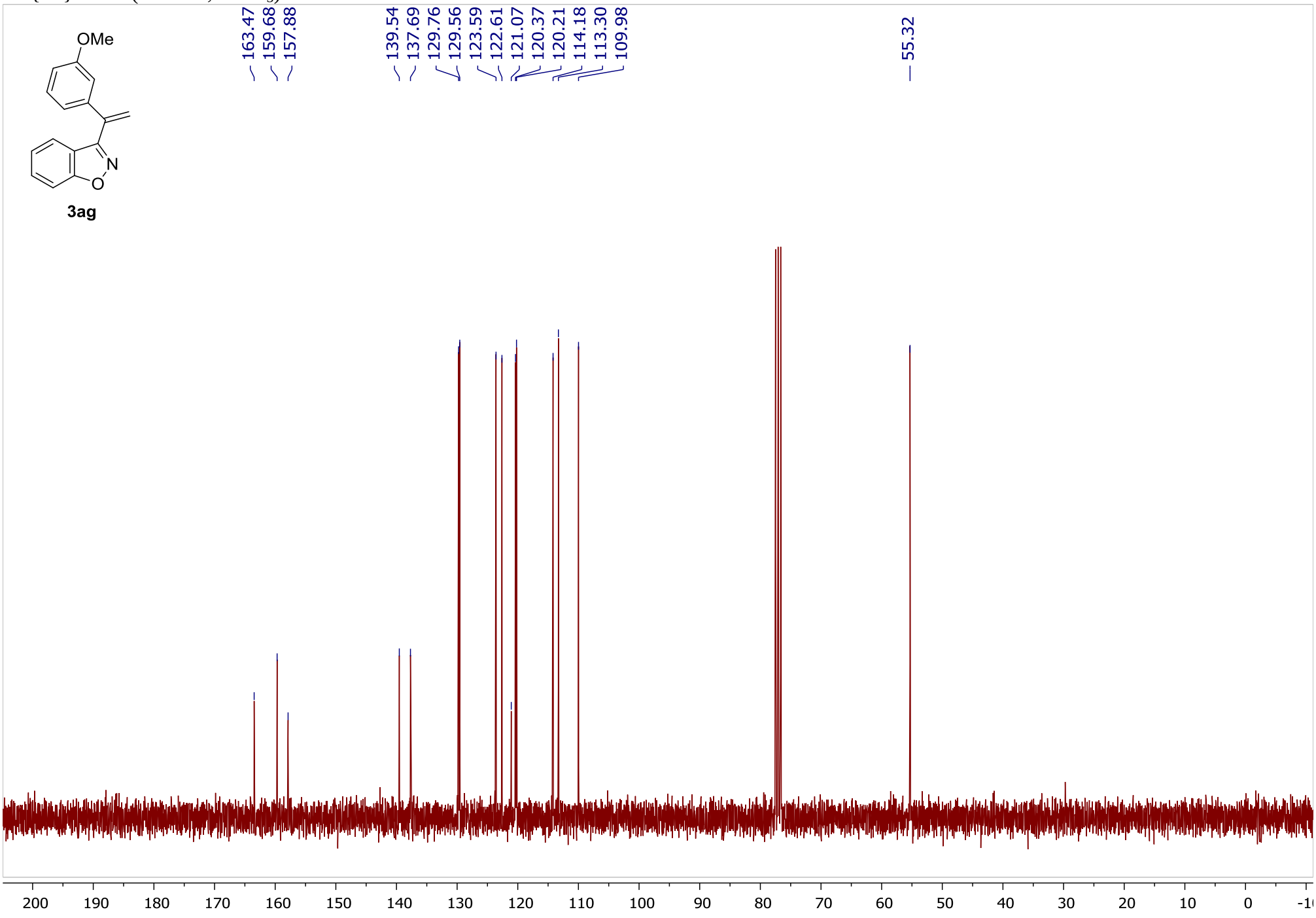
140
150
160
170
180
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

**3-(1-(3-Methoxyphenyl)vinyl)benzo[d]isoxazole 3ag**

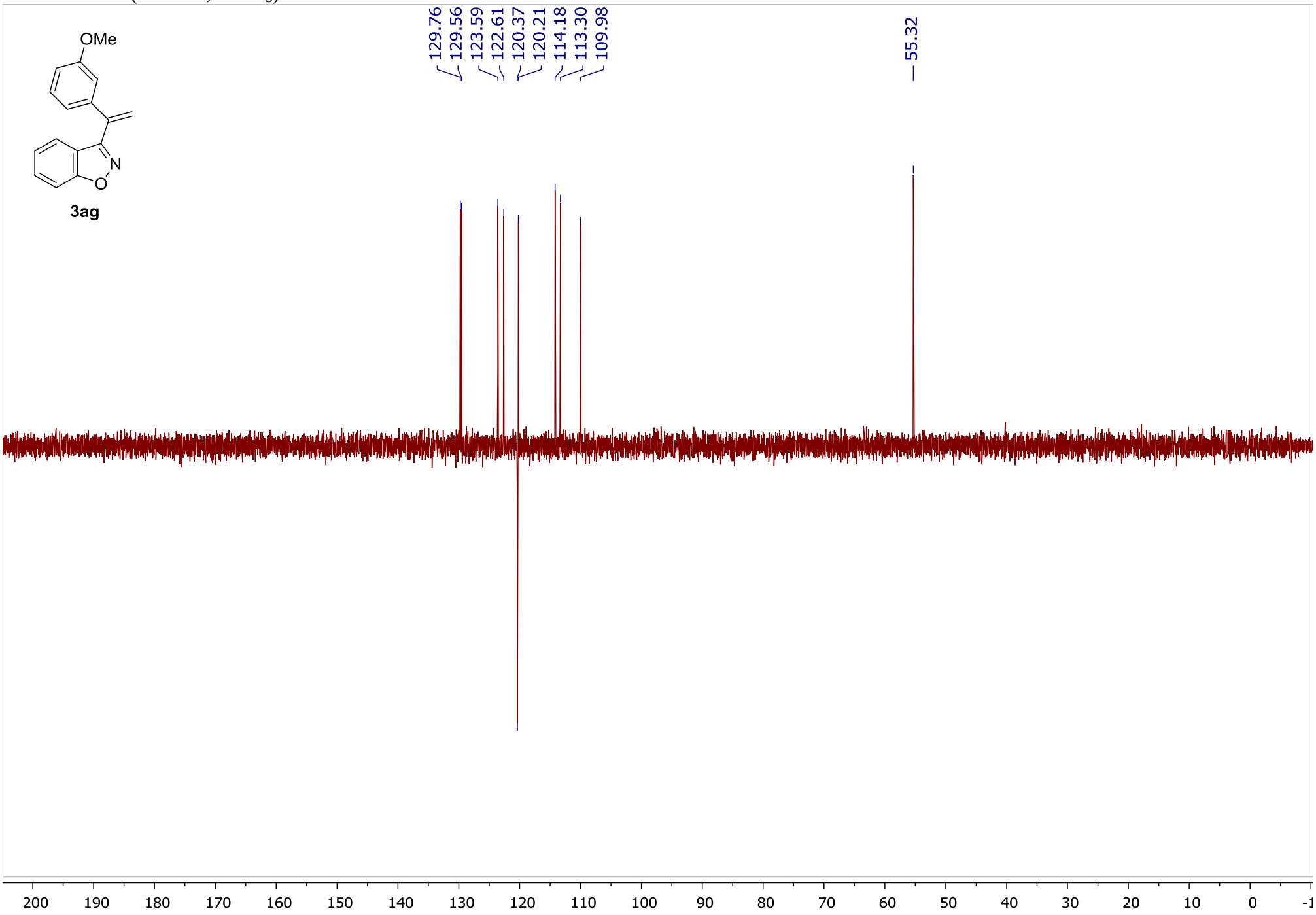
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

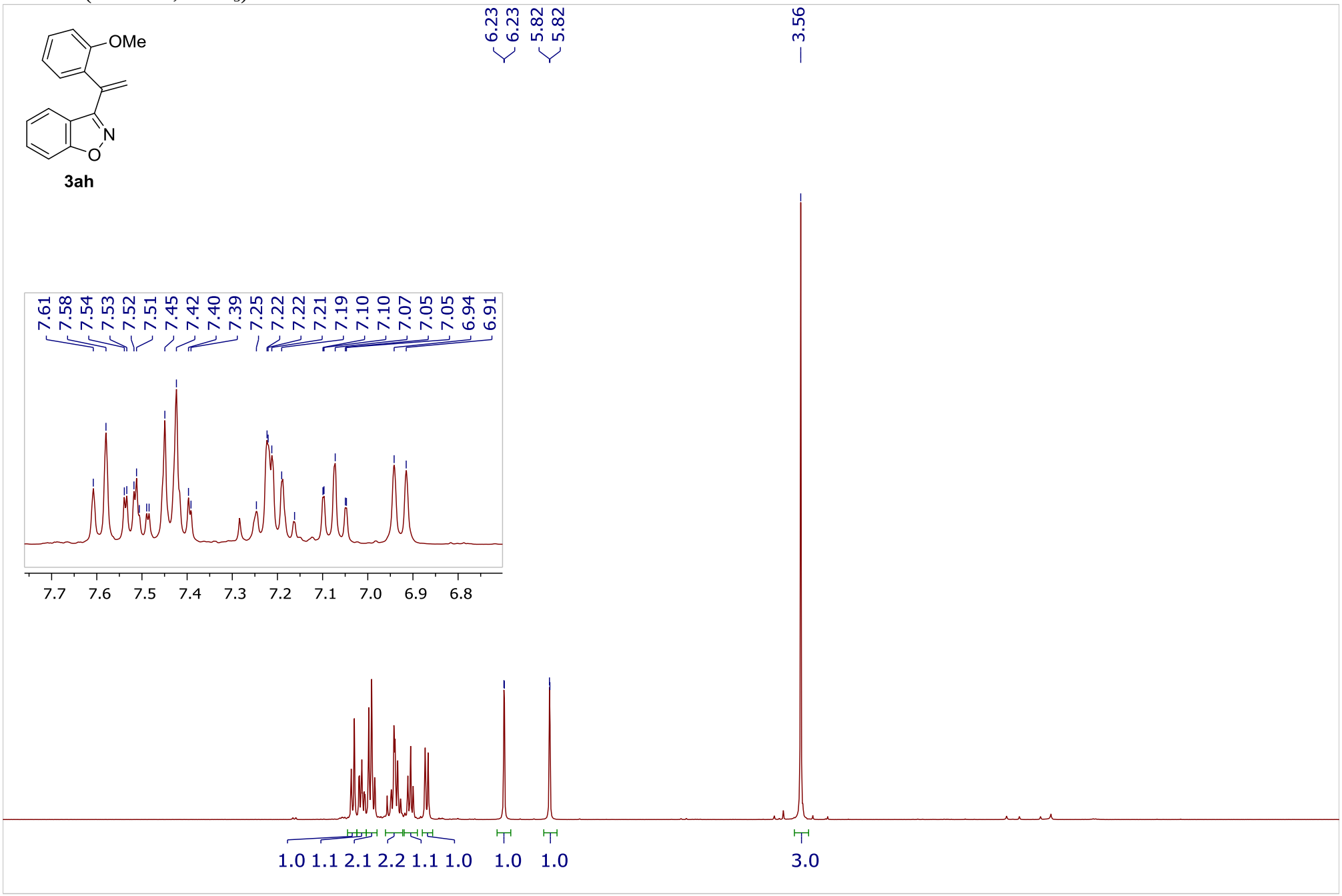


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

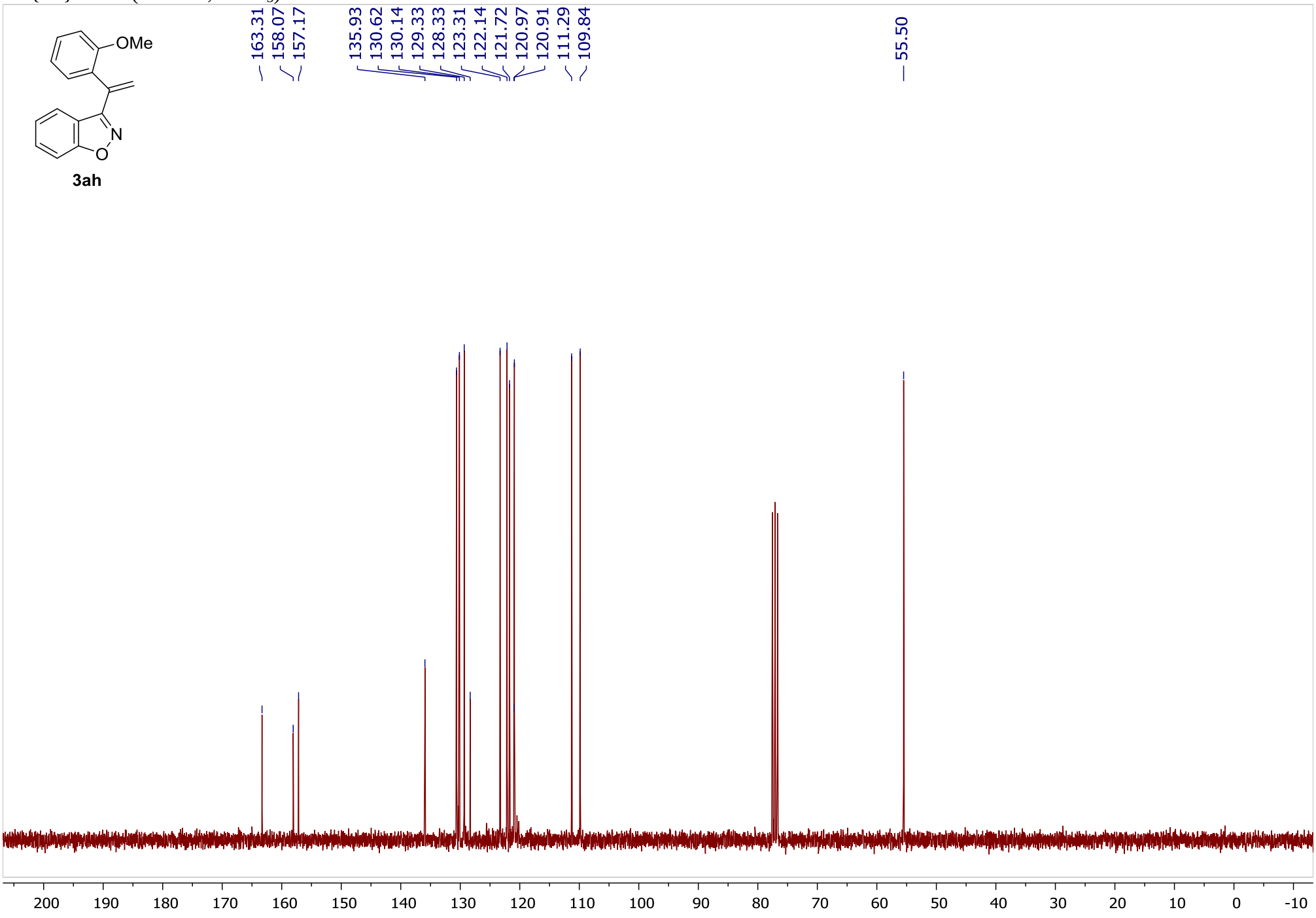


**3-(1-(2-Methoxyphenyl)vinyl)benzo[d]isoxazole 3ah**

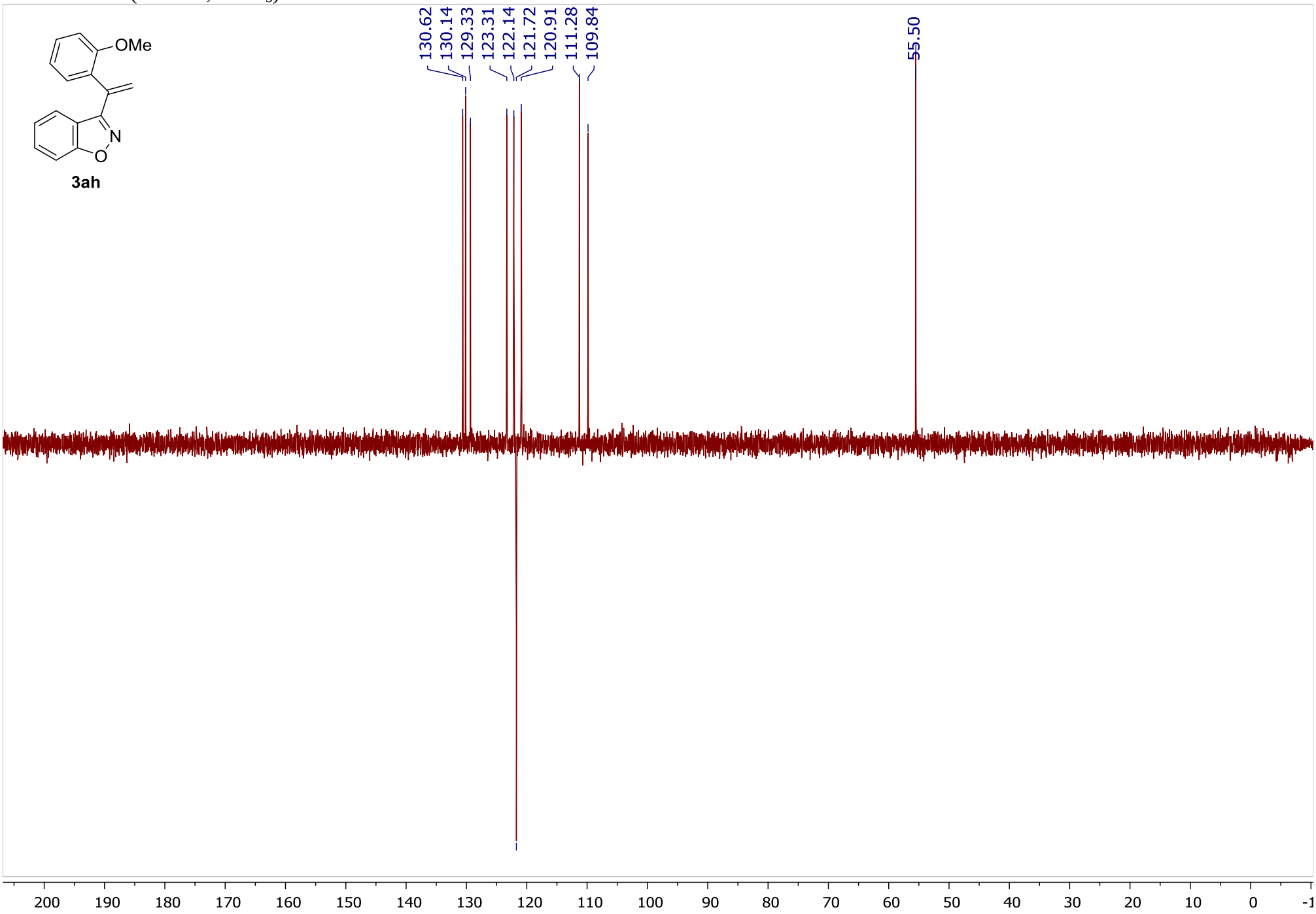
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

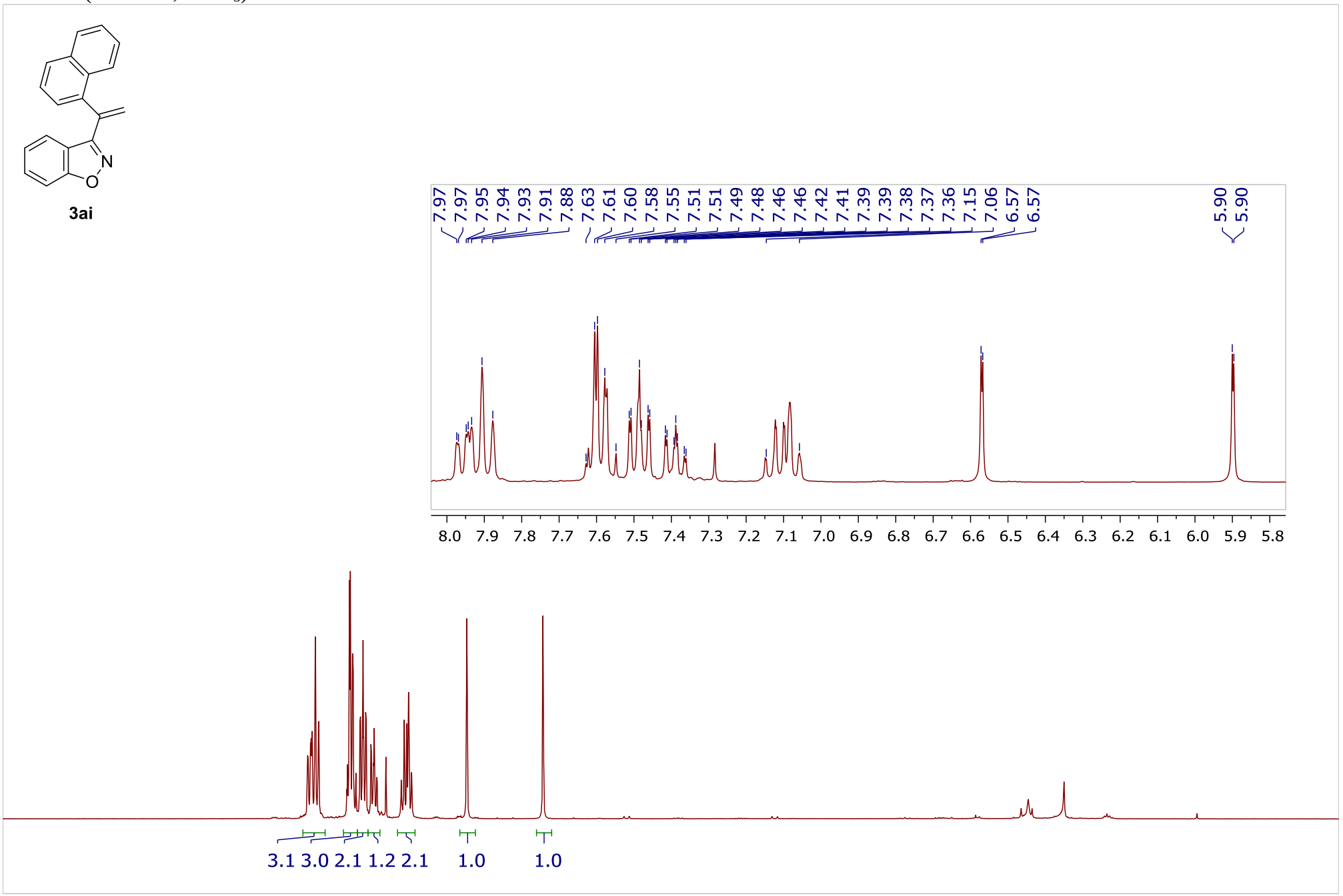


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

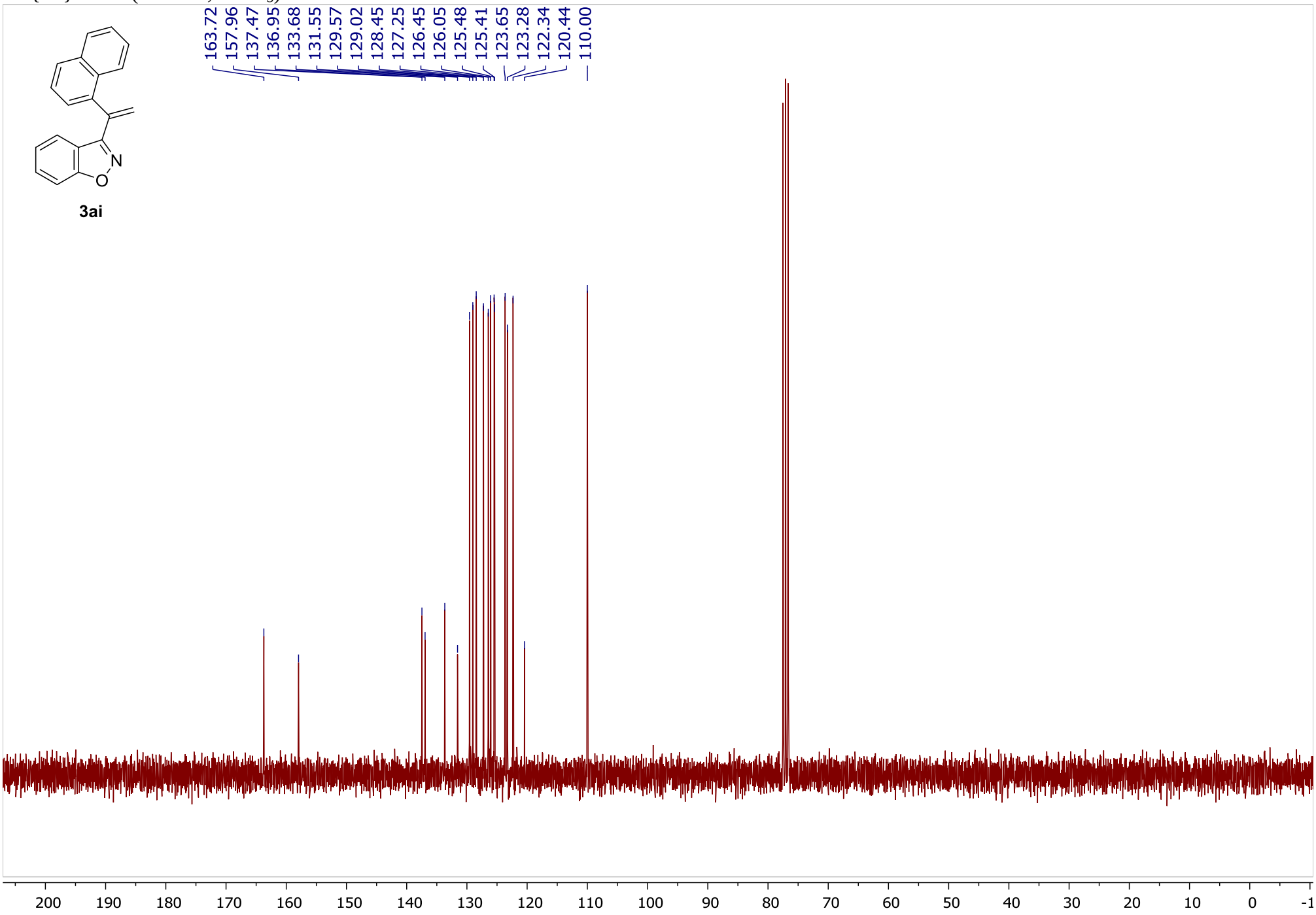


**3-(1-(Naphthalen-1-yl)vinyl)benzo[d]isoxazole 3ai**

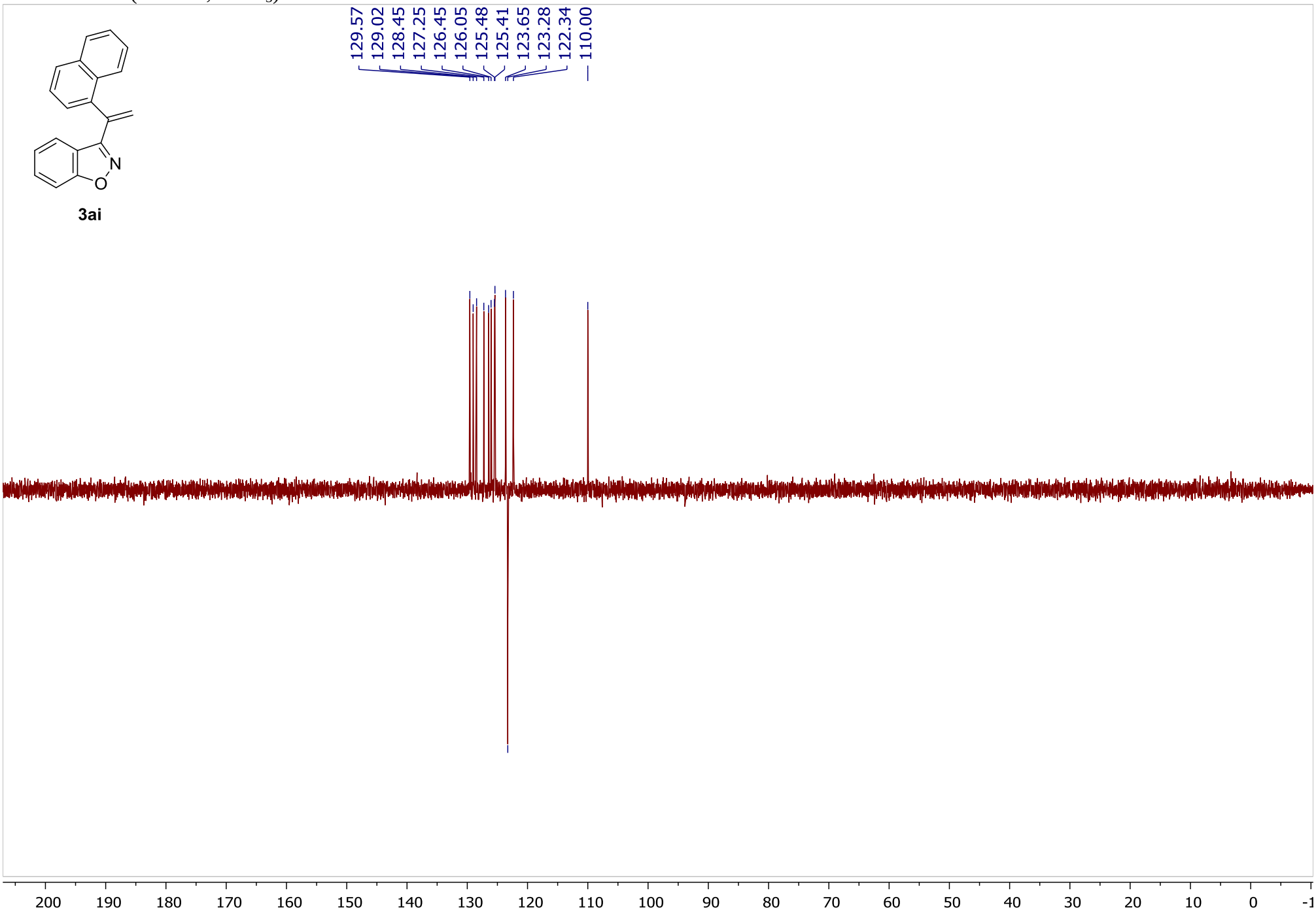
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

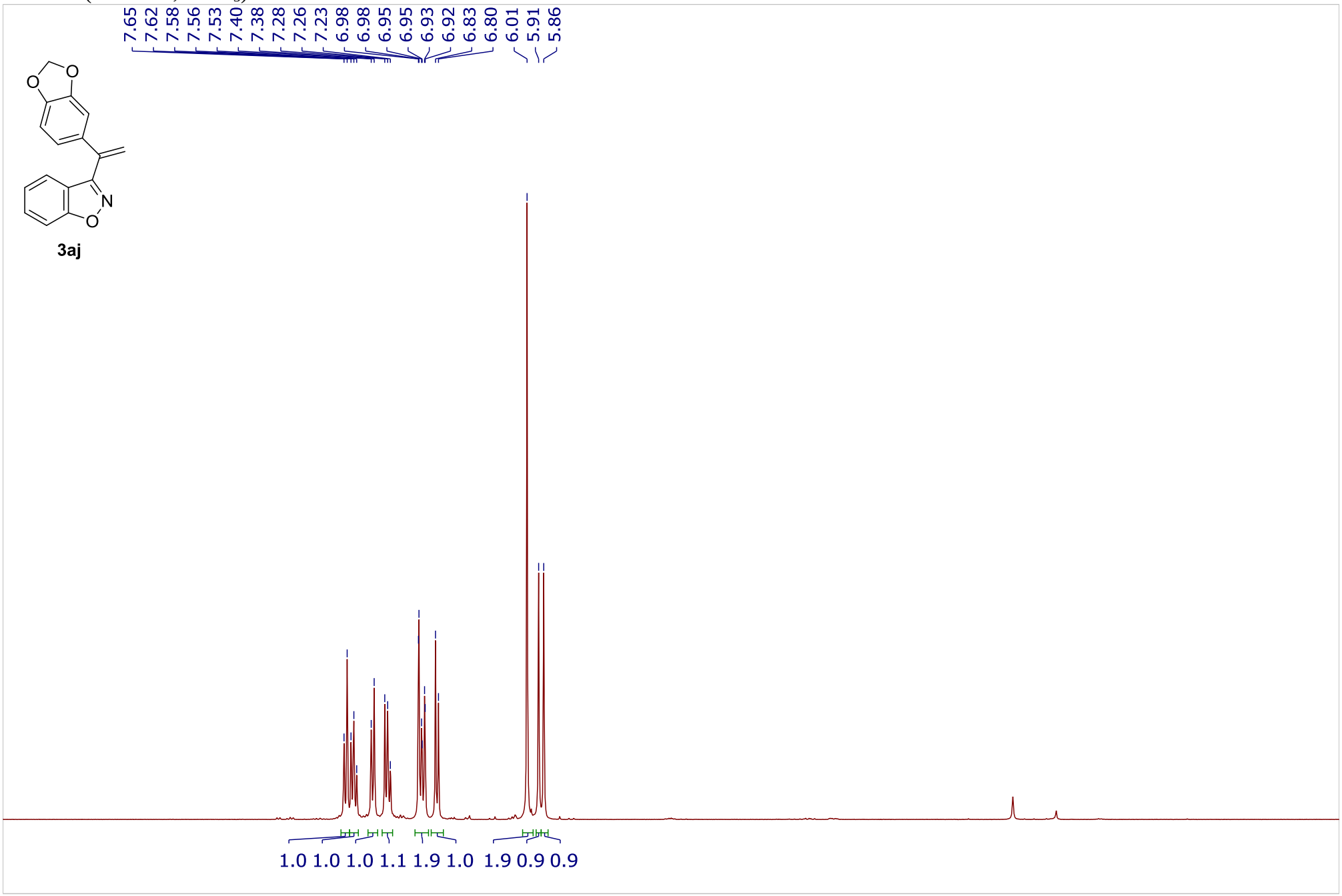


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

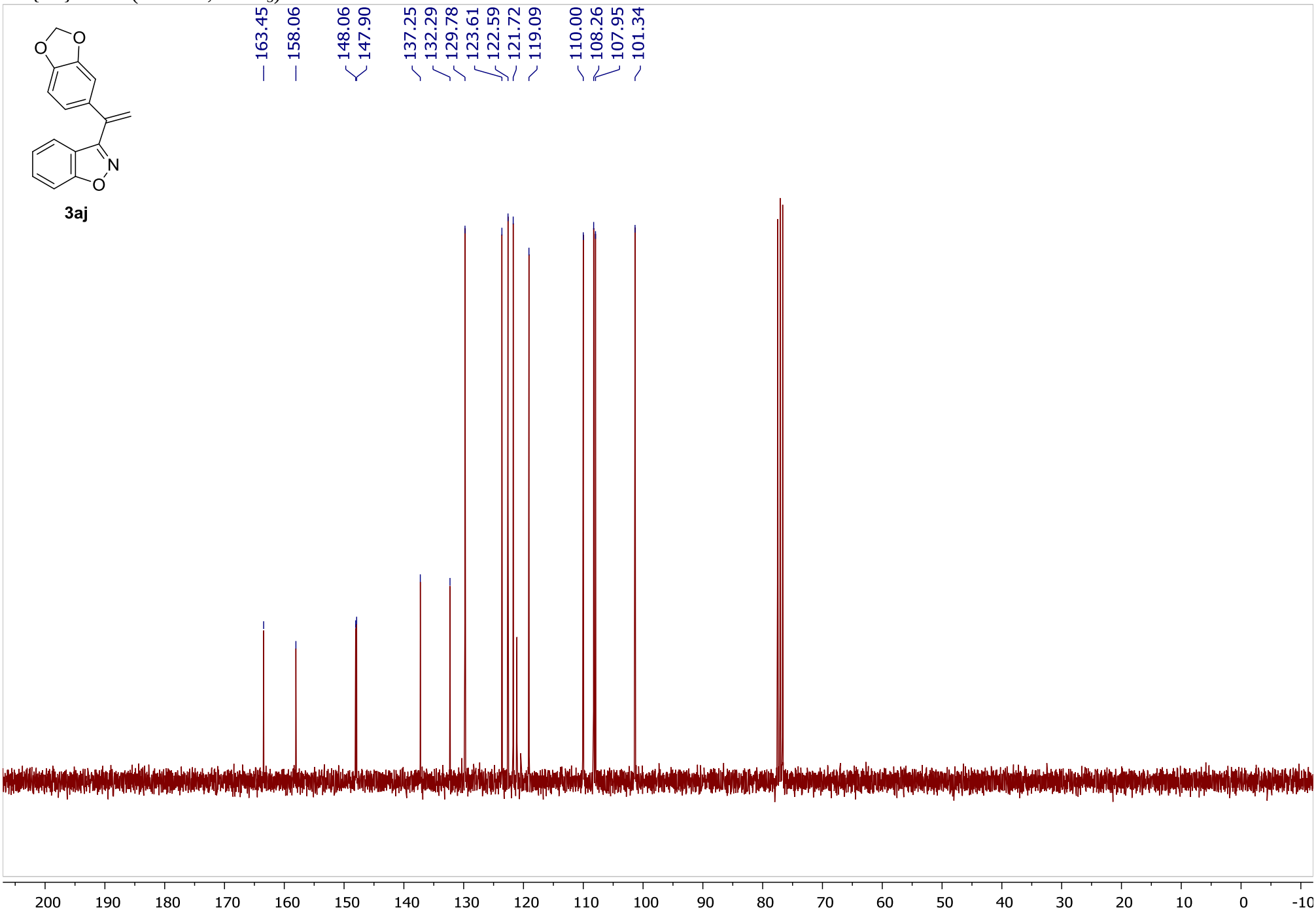


**3-(1-(Benzo[d][1,3]dioxol-5-yl)vinyl)benzo[d]isoxazole 3aj**

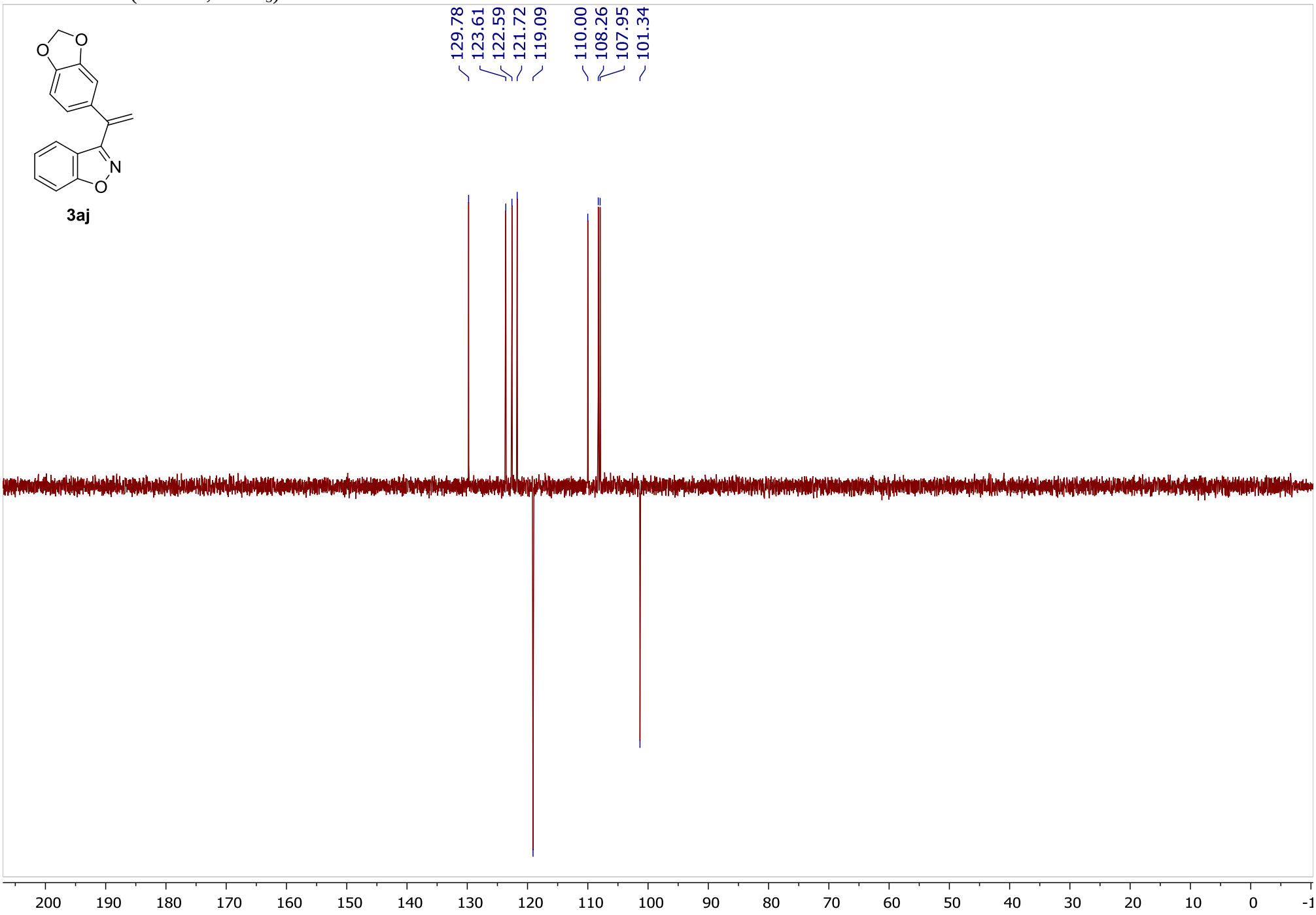
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

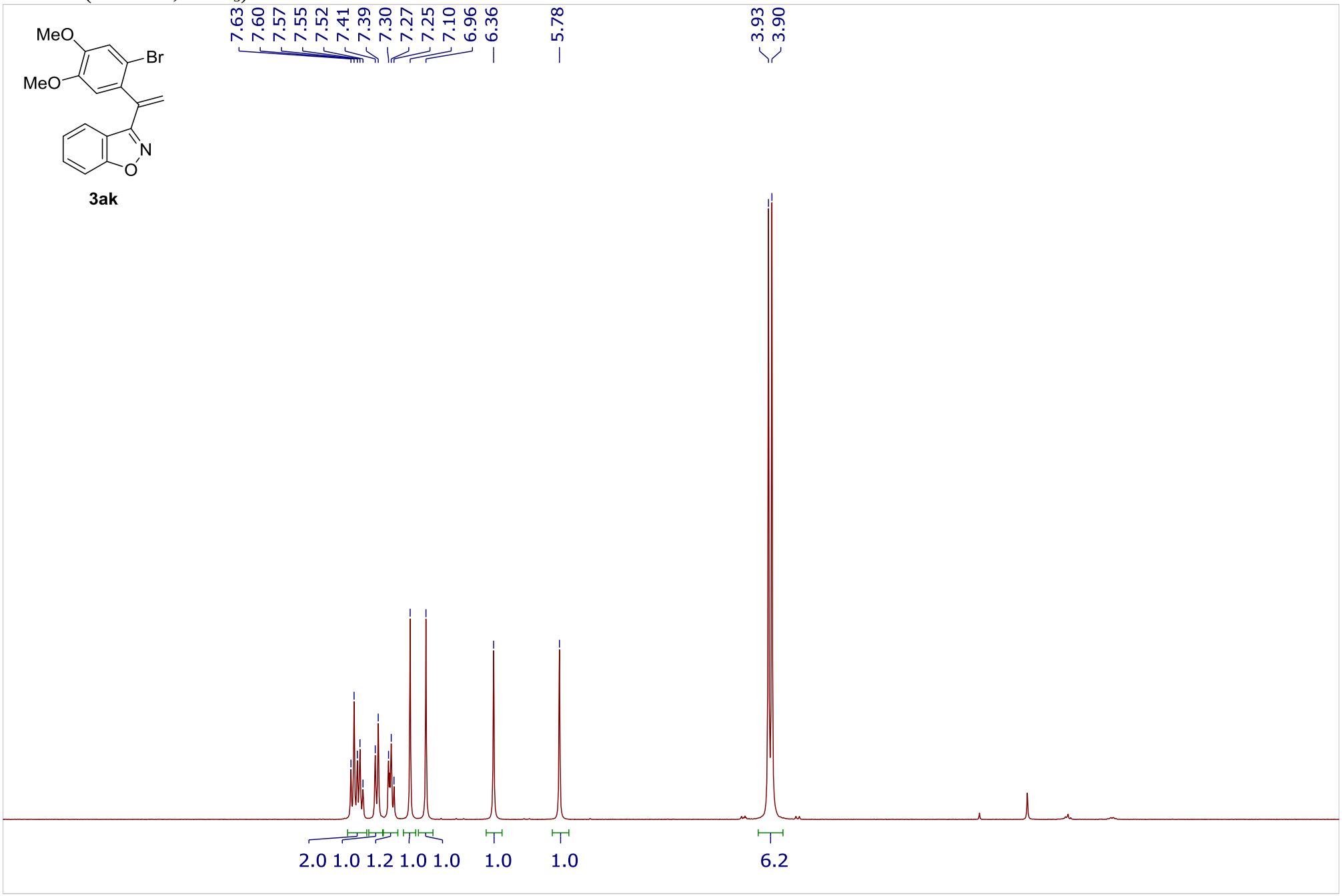


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

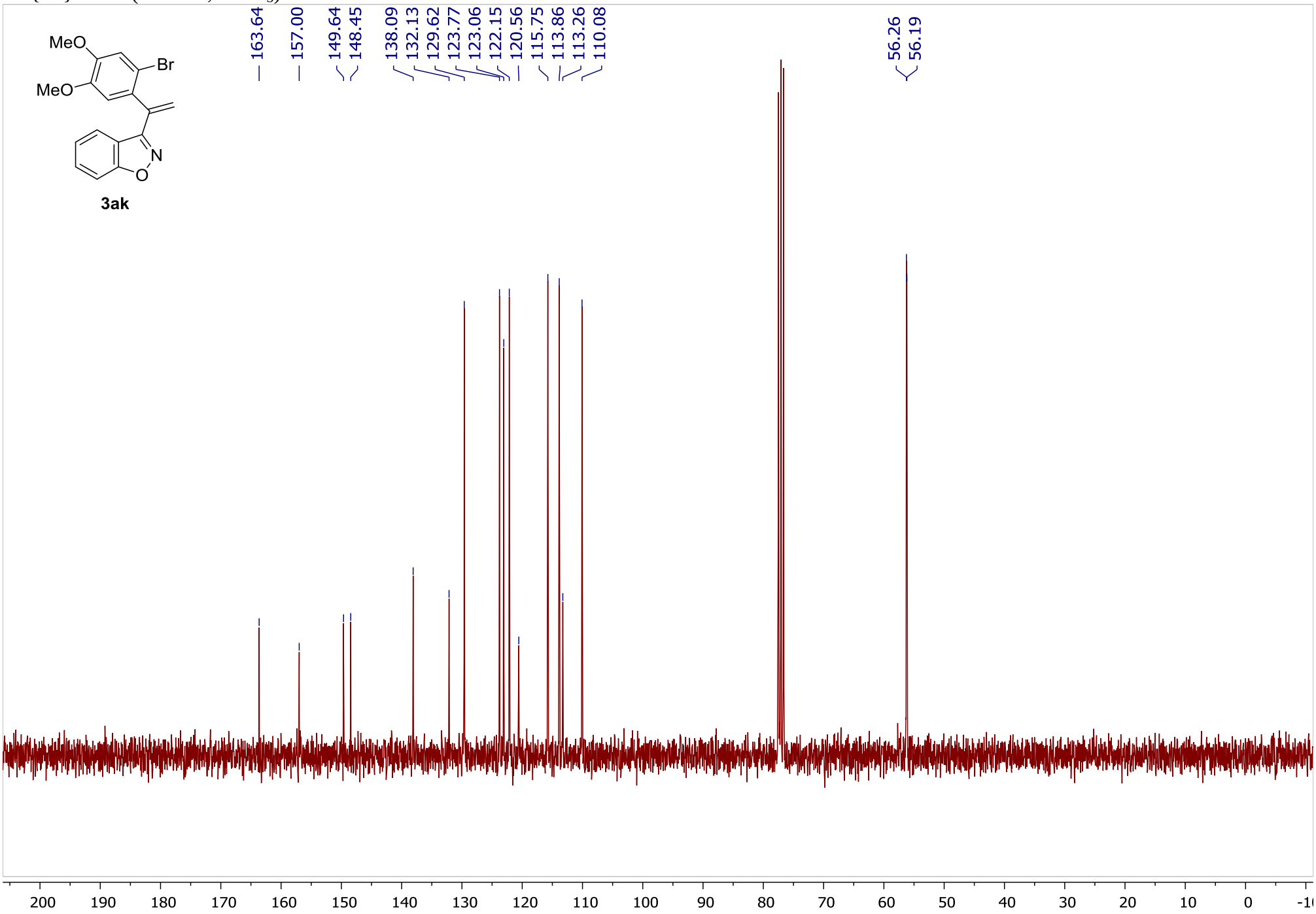


**3-(1-(2-Bromo-4,5-dimethoxyphenyl)vinyl)benzo[d]isoxazole 3ak**

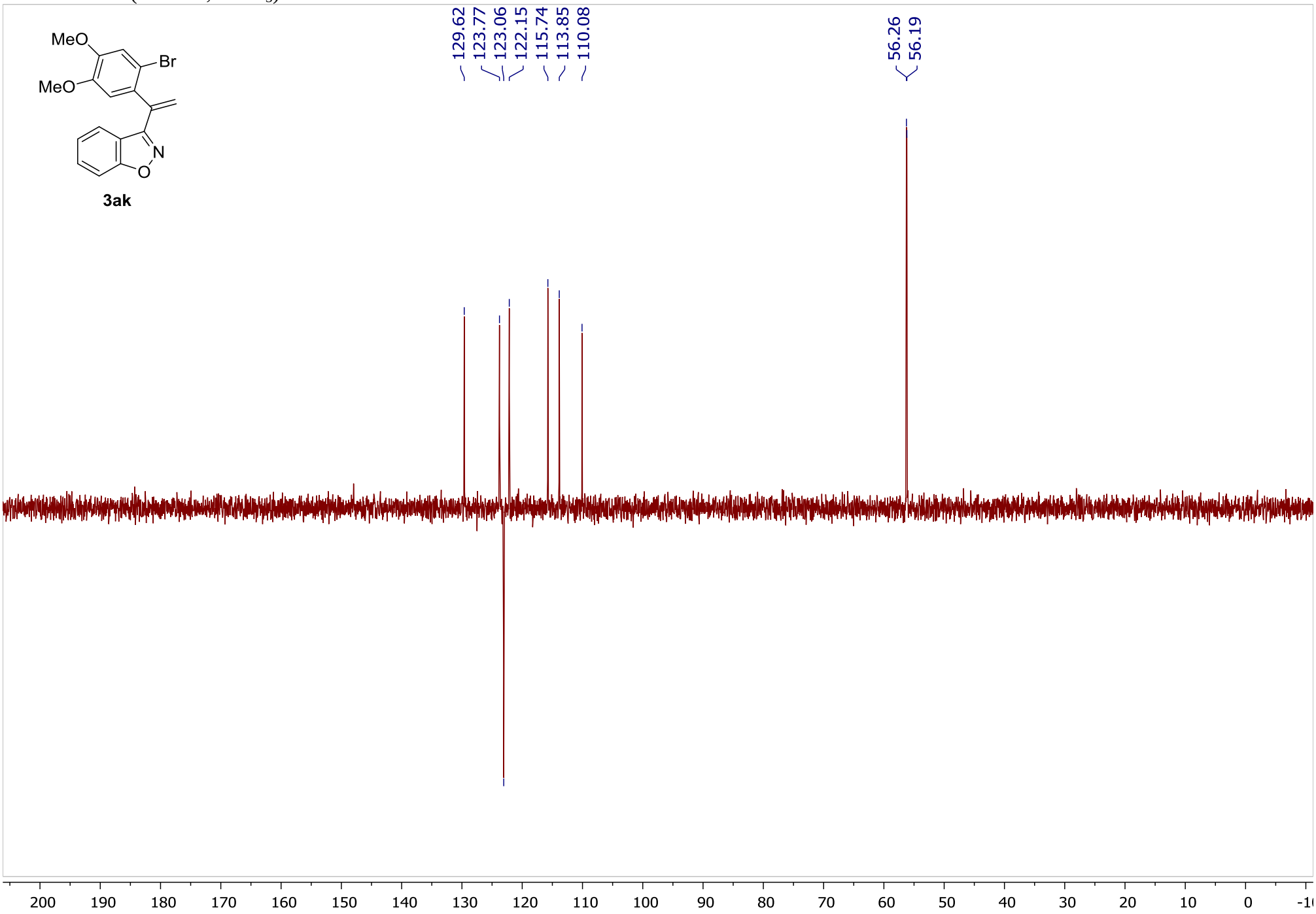
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

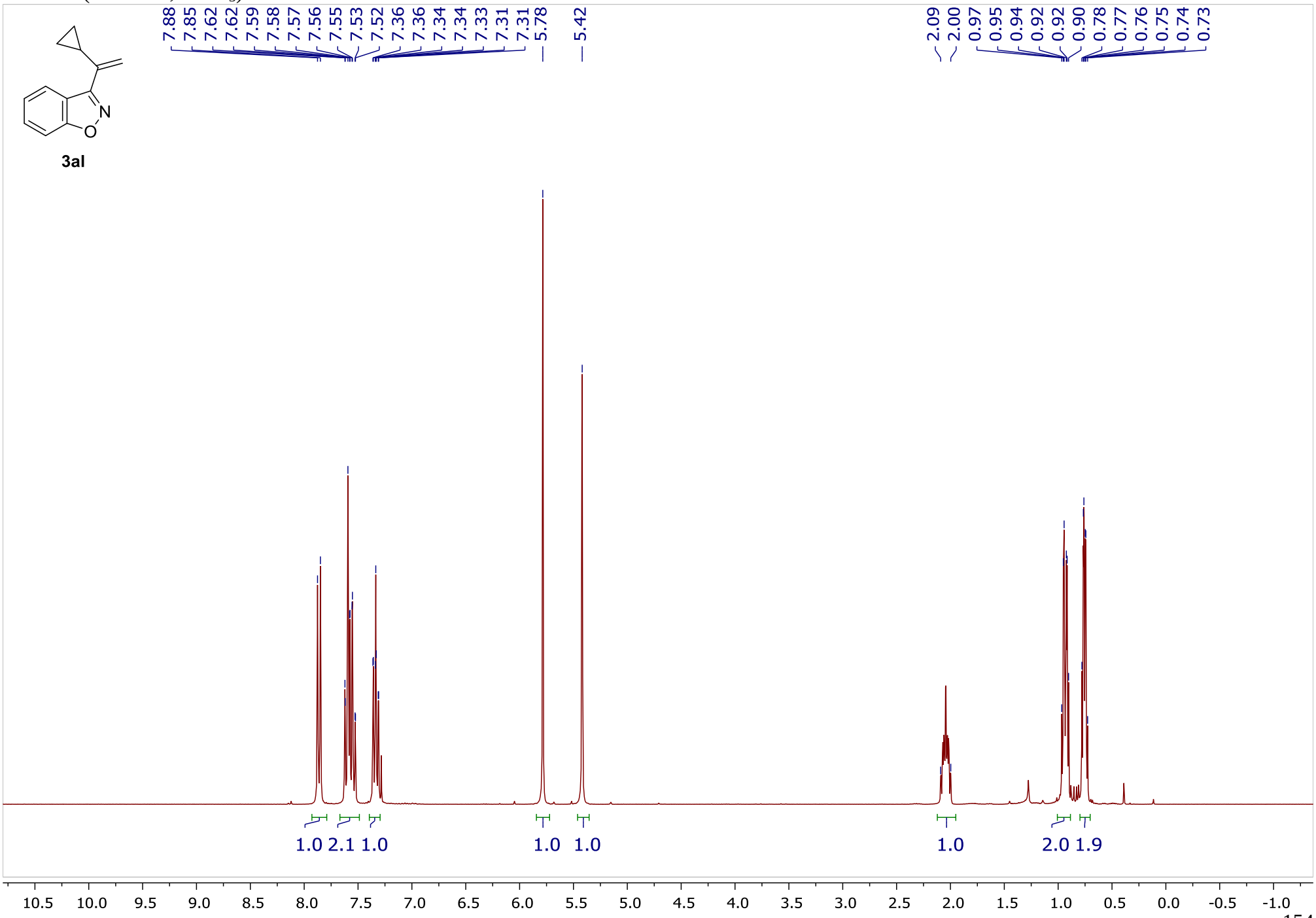


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

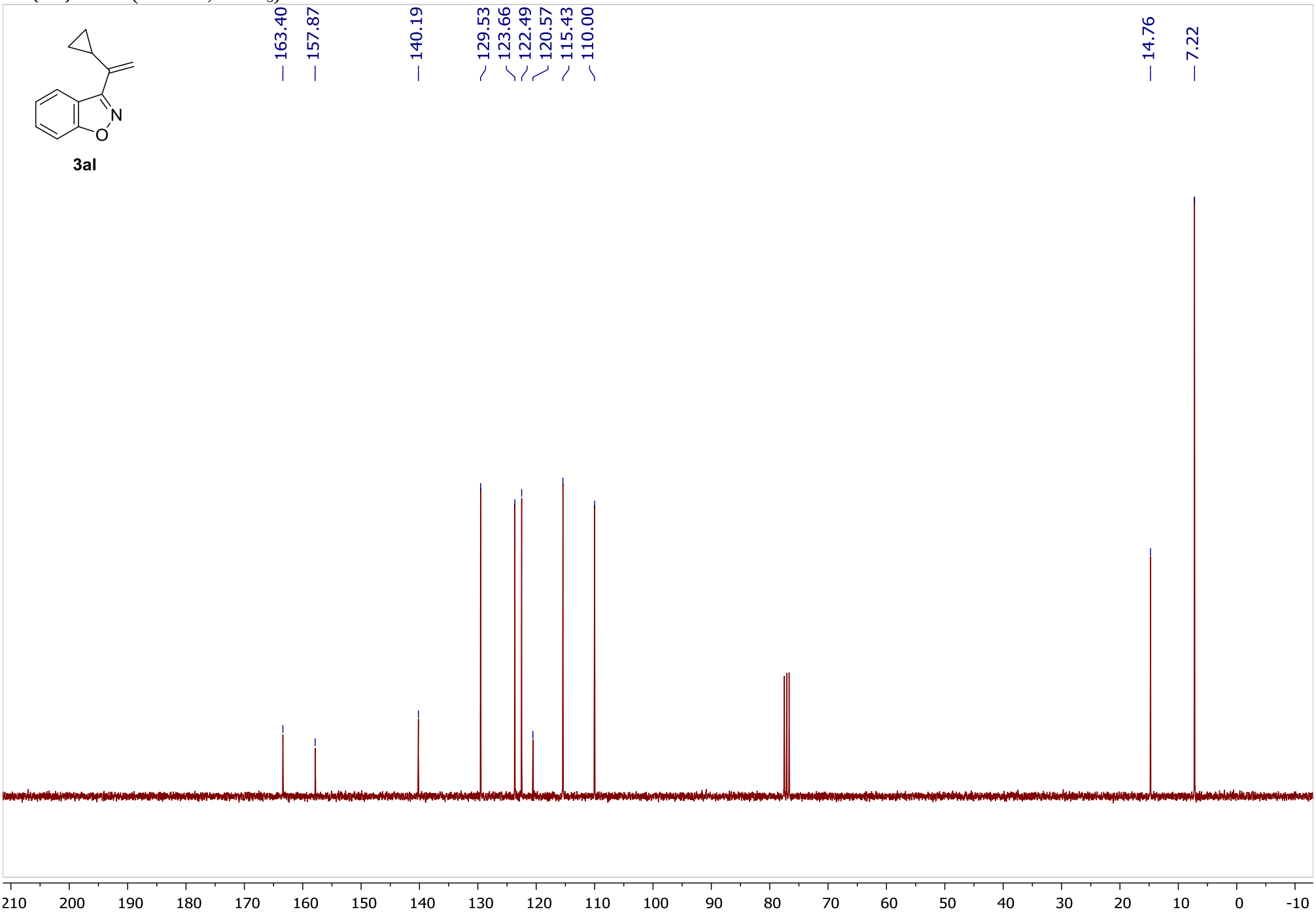


**3-(1-Cyclopropylvinyl)benzo[d]isoxazole 3al**

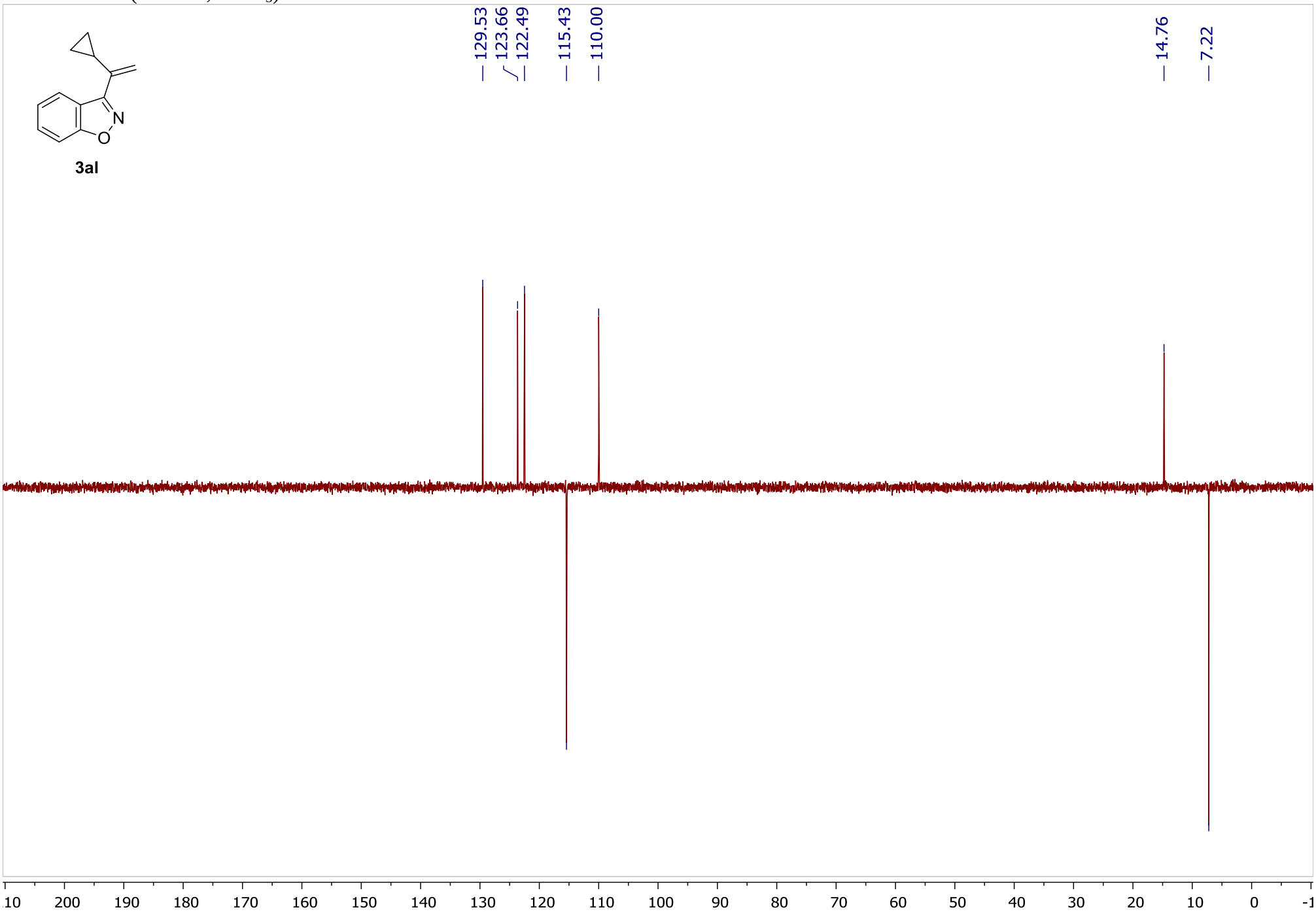
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

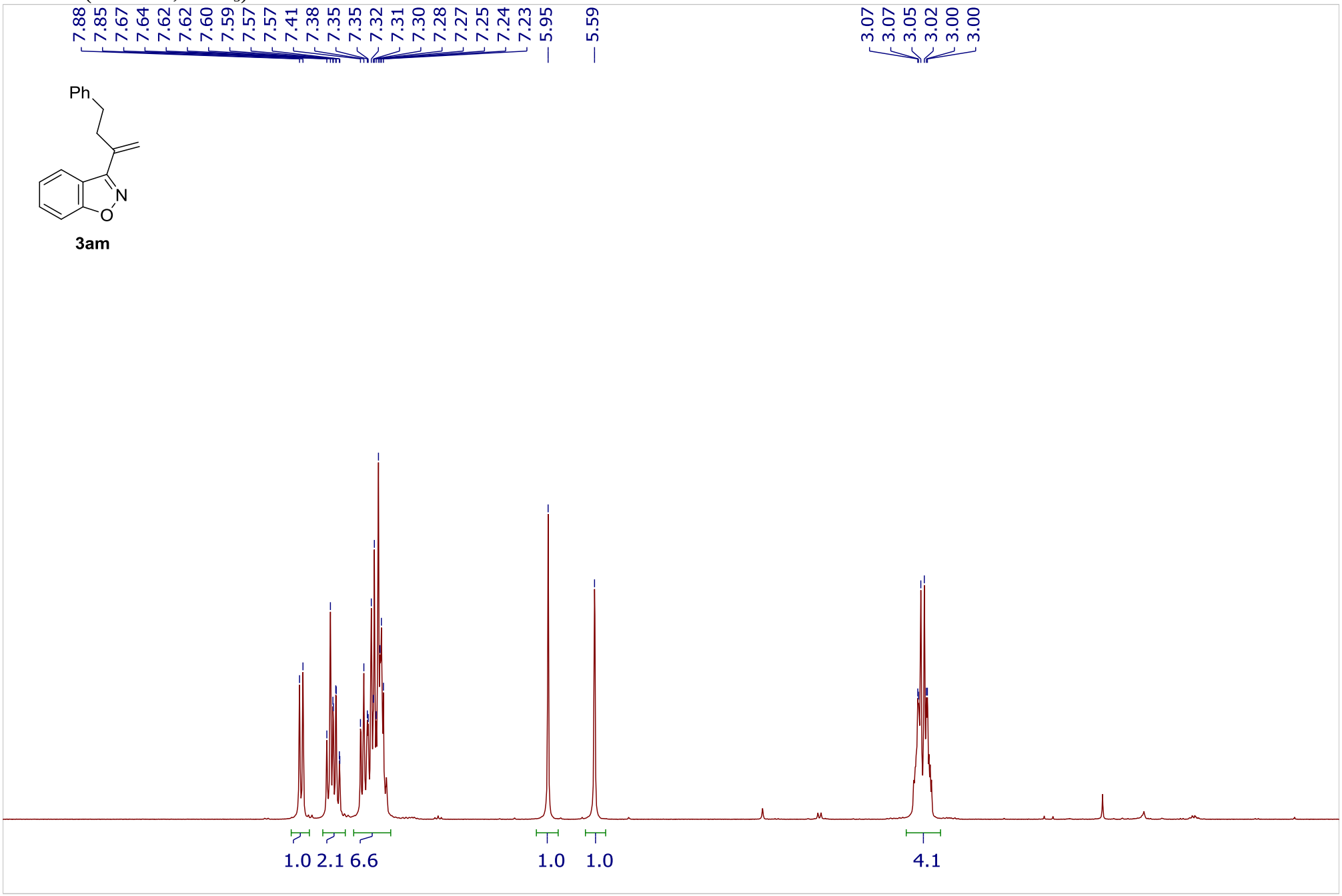


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

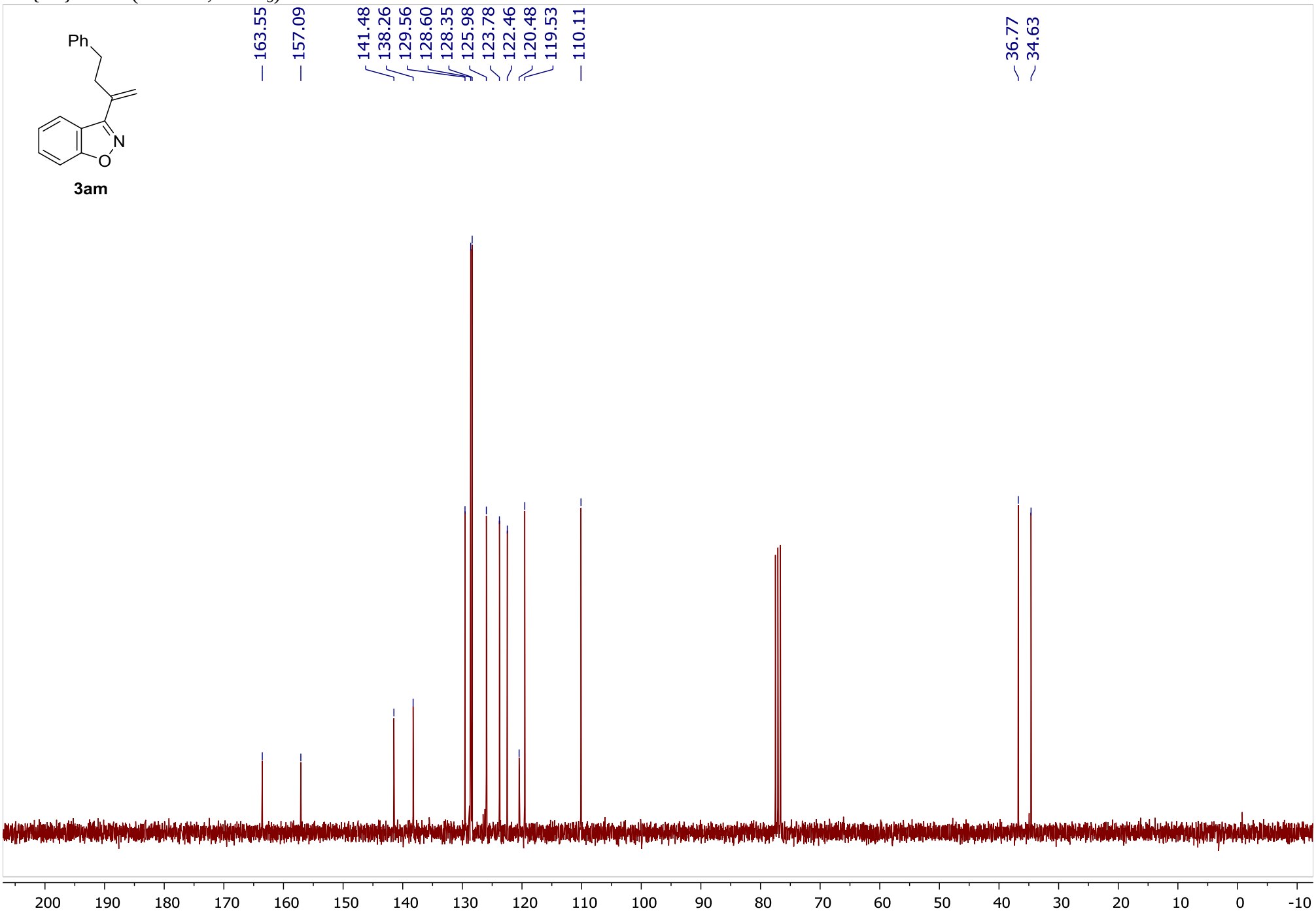


**3-(4-Phenylbut-1-en-2-yl)benzo[d]isoxazole 3am**

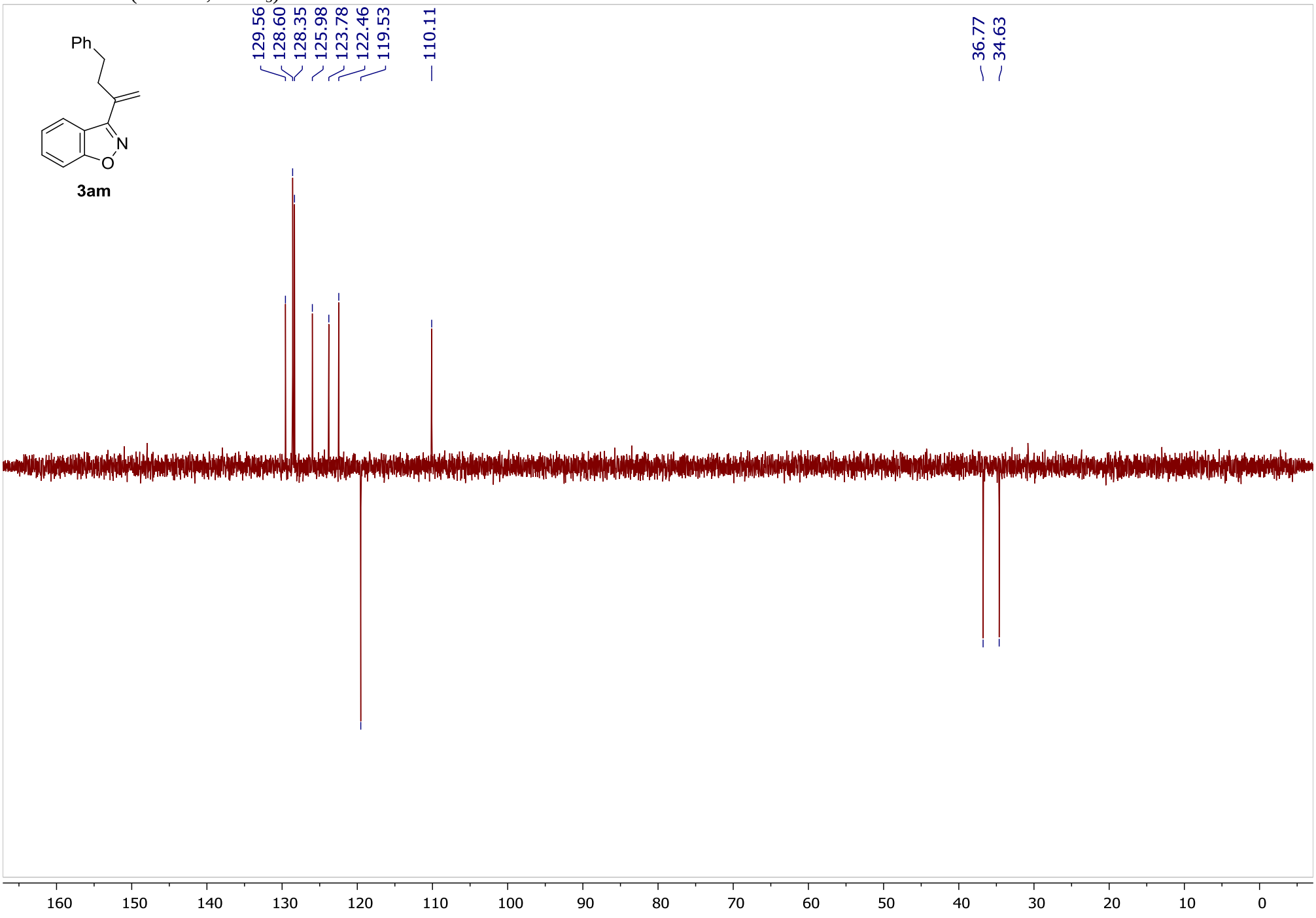
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

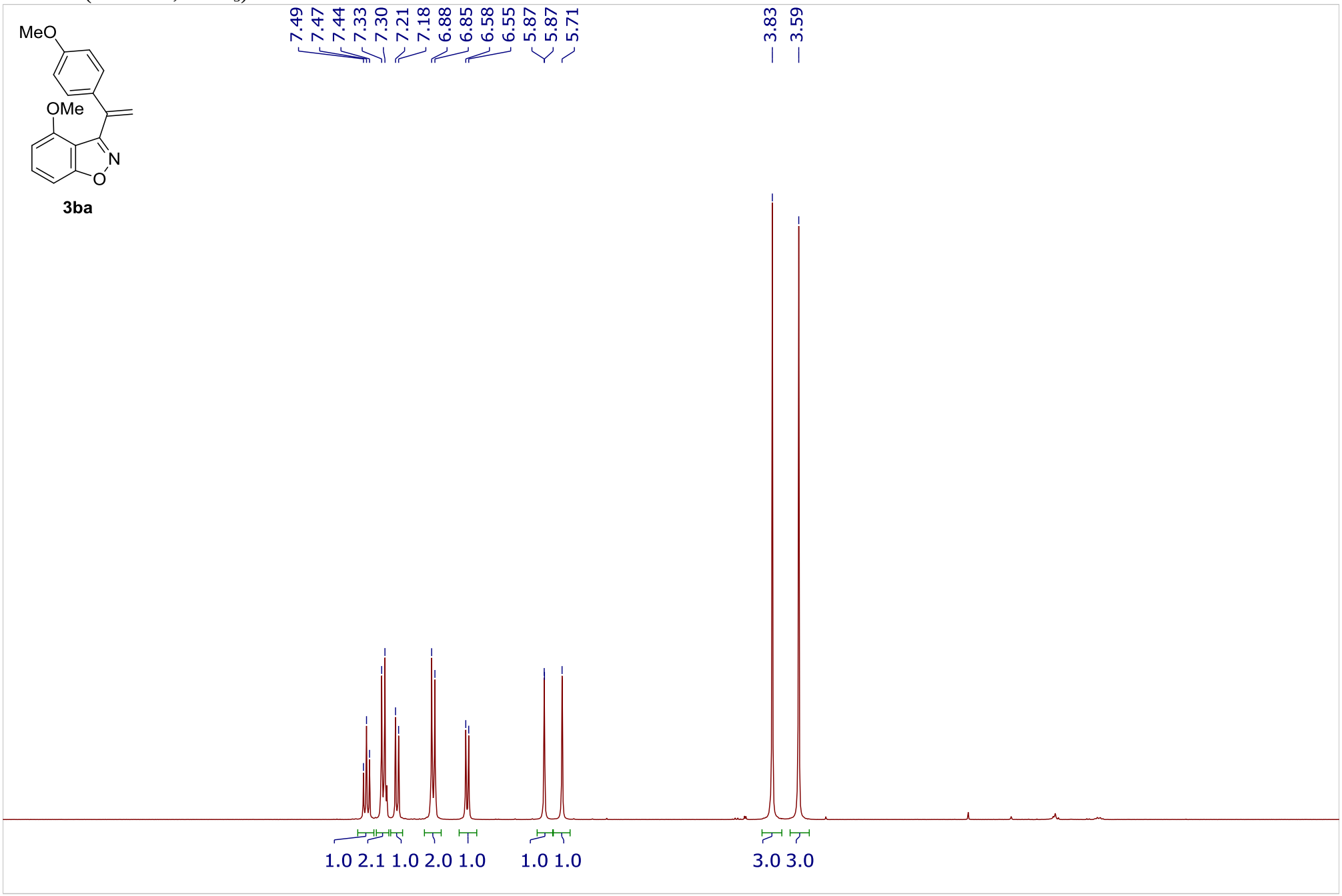


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

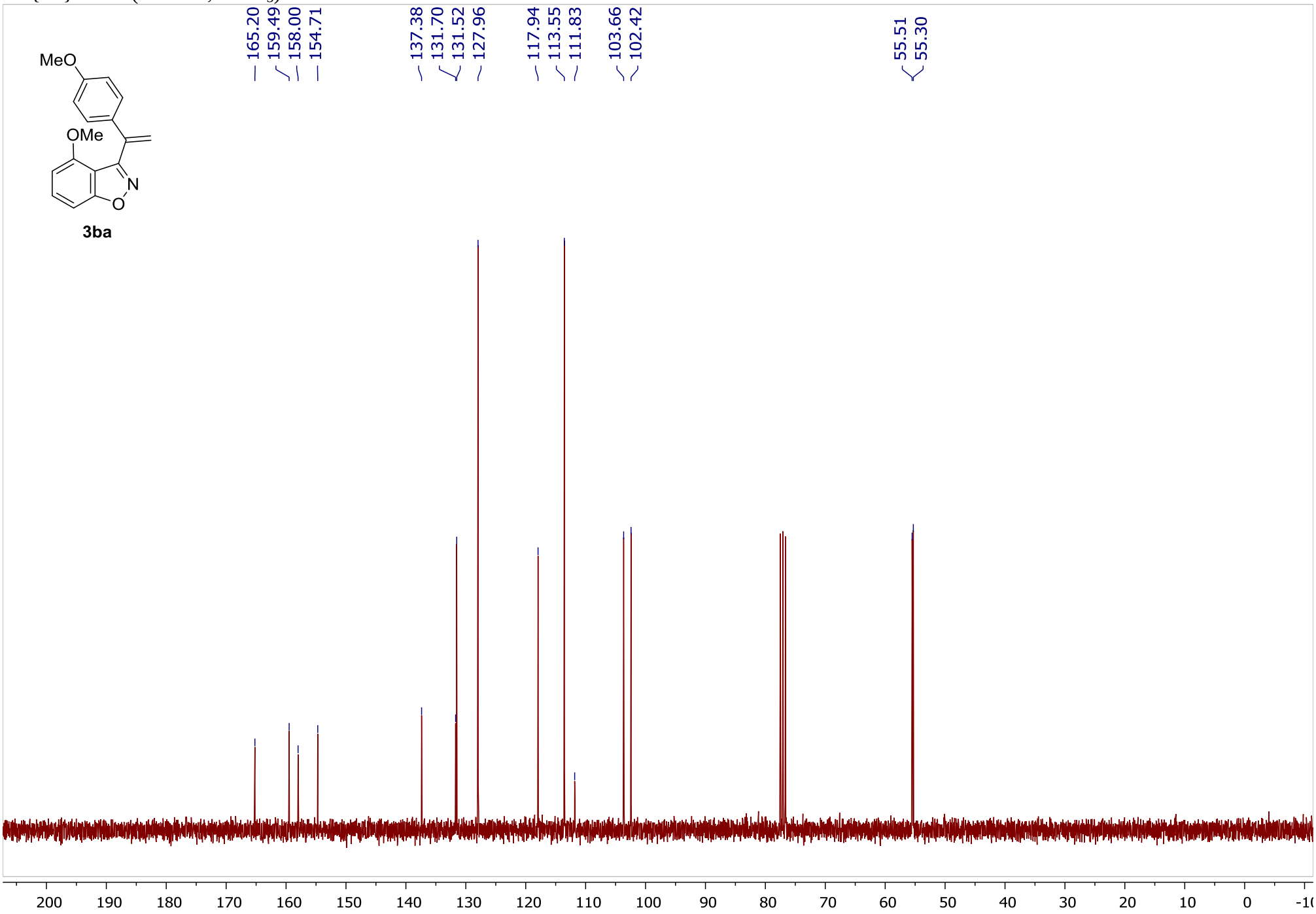


**4-Methoxy-3-(1-(4-methoxyphenyl)vinyl)benzo[d]isoxazole 3ba**

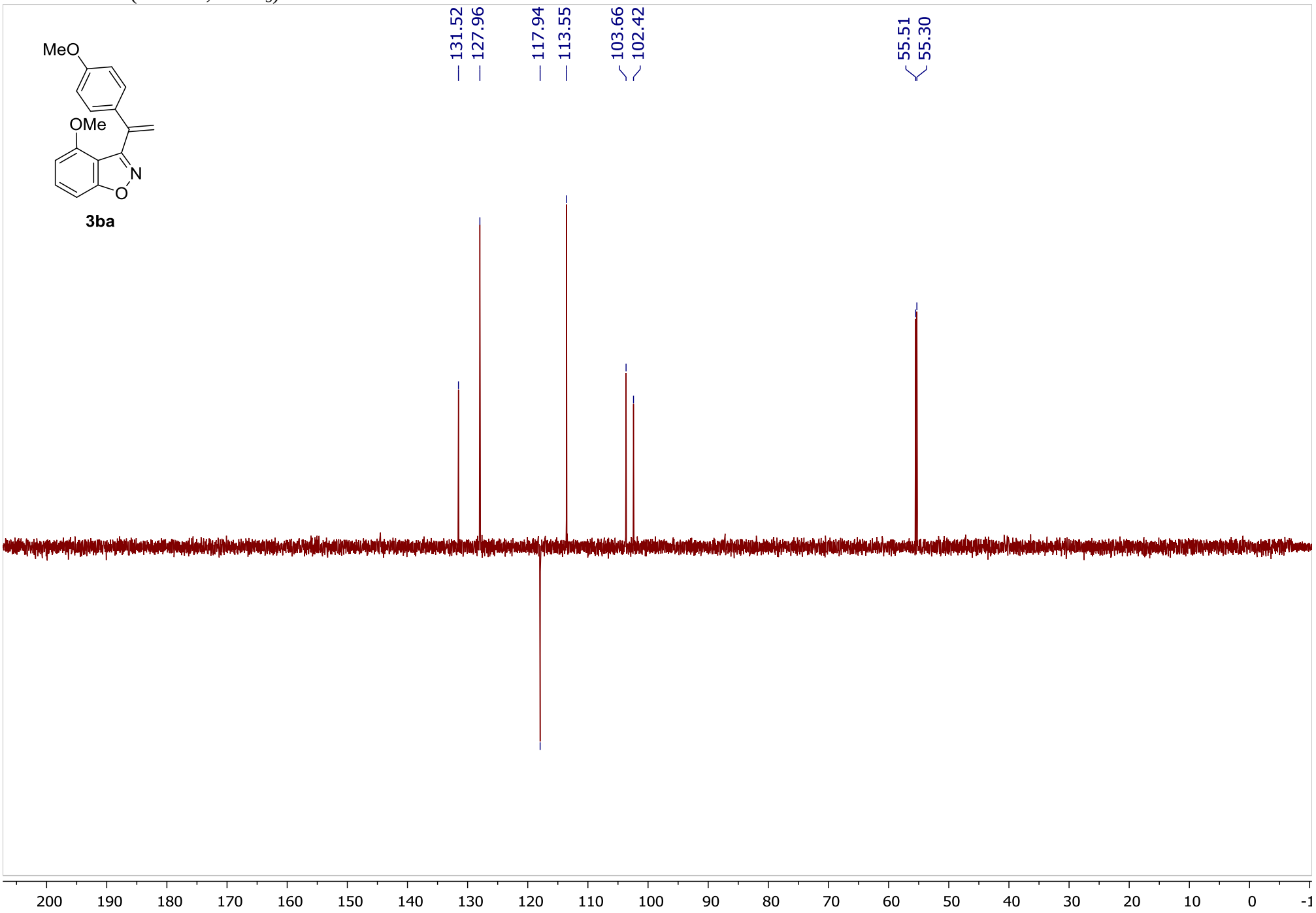
$^1$H NMR (300 MHz, $CDCl_3$)



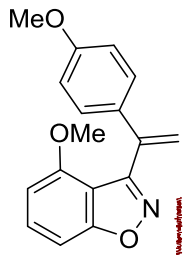
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

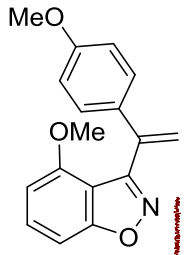


$^{1}$H-$^{13}$C HSQC

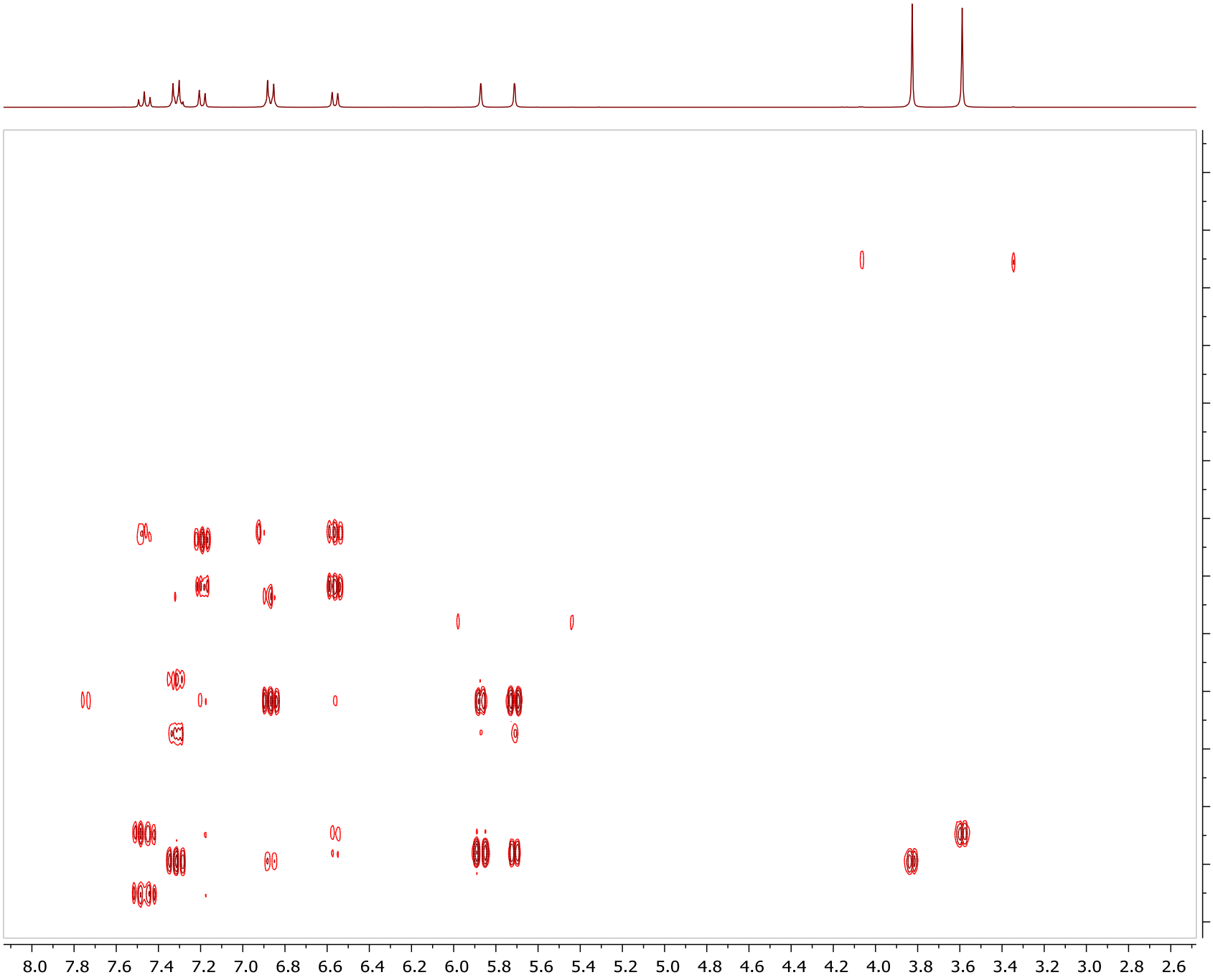



**3ba**

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

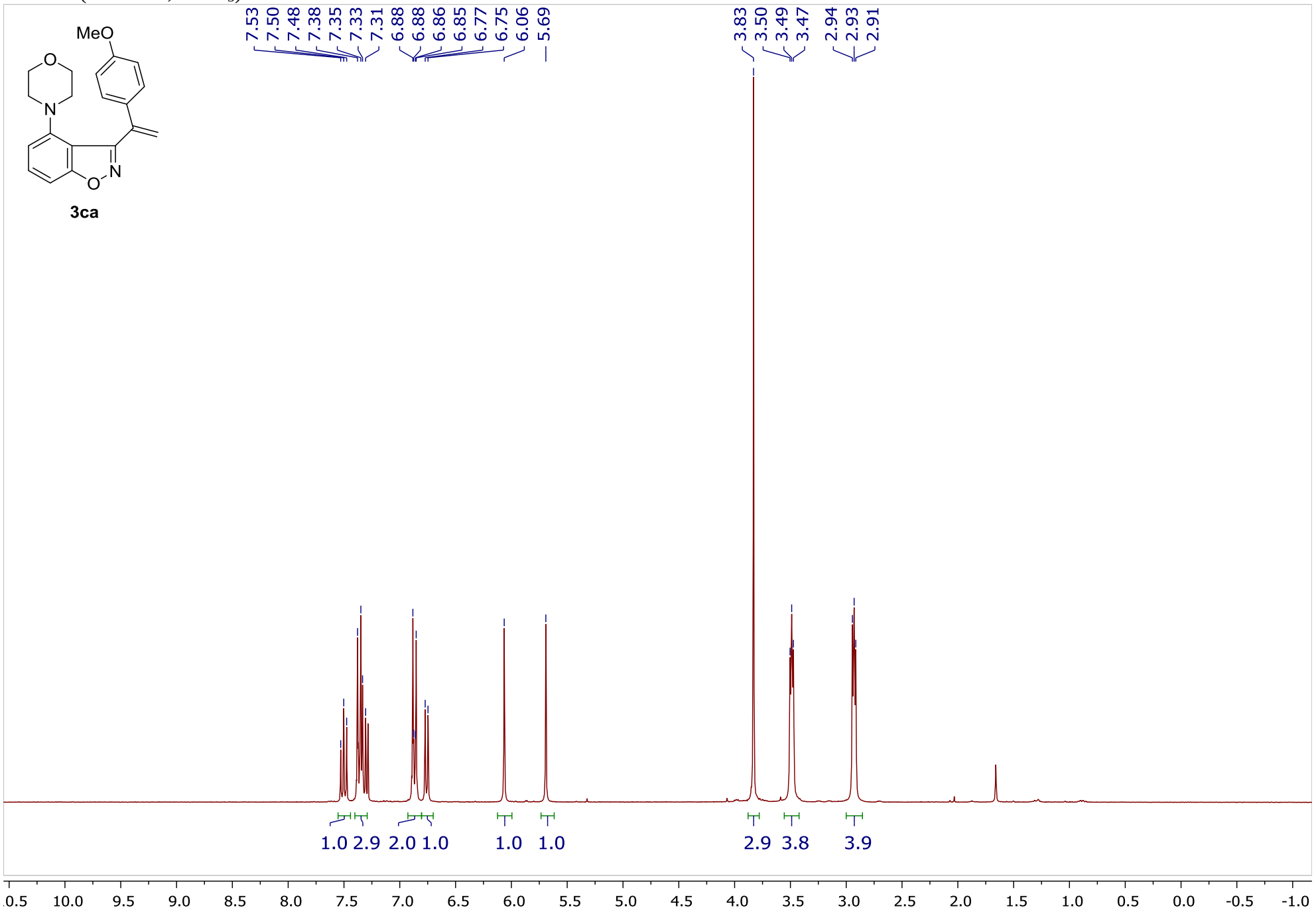



**3ba**

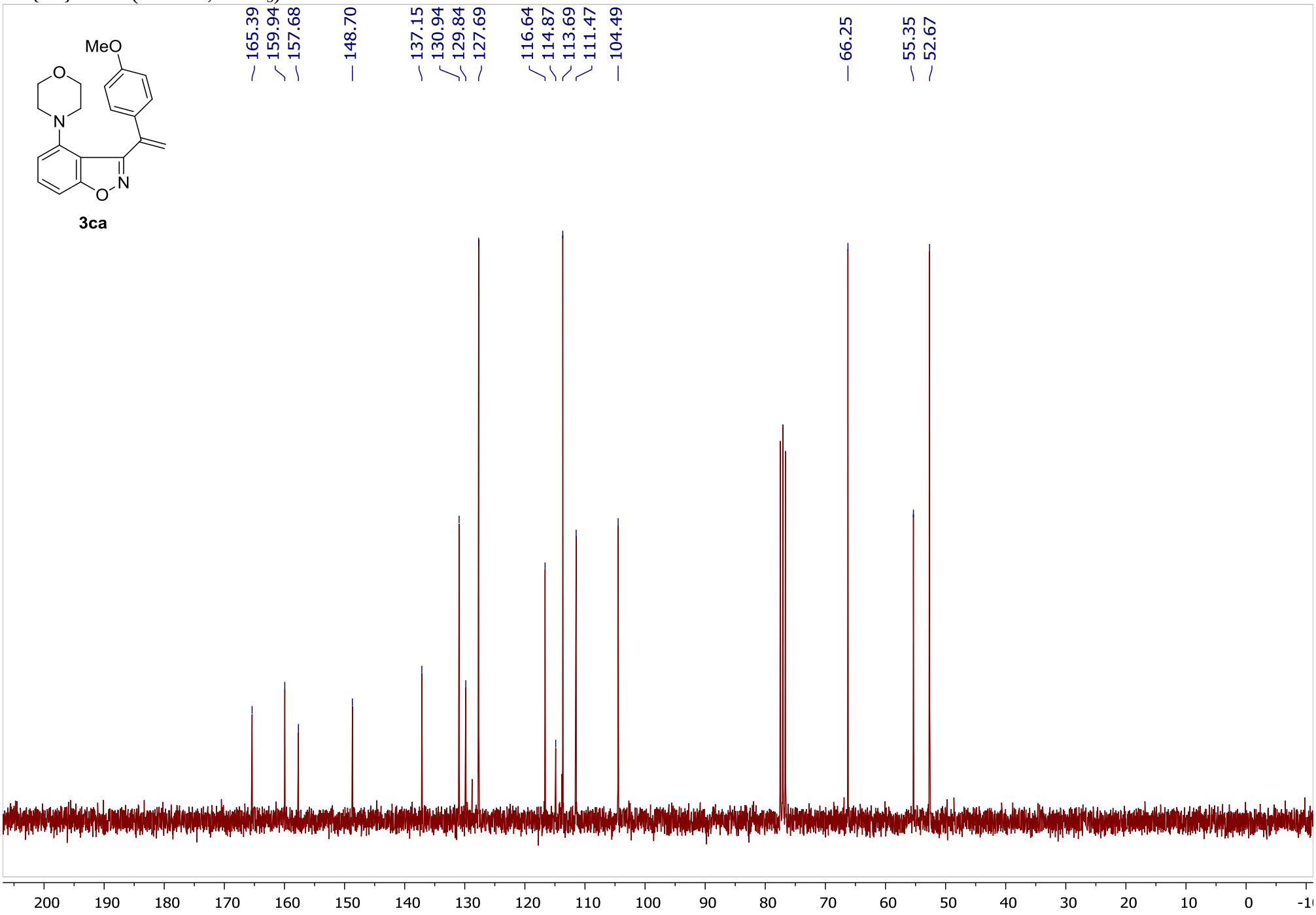


**4-Methoxy-3-(1-(4-methoxyphenyl)vinyl)benzo[d]isoxazole 3ca**

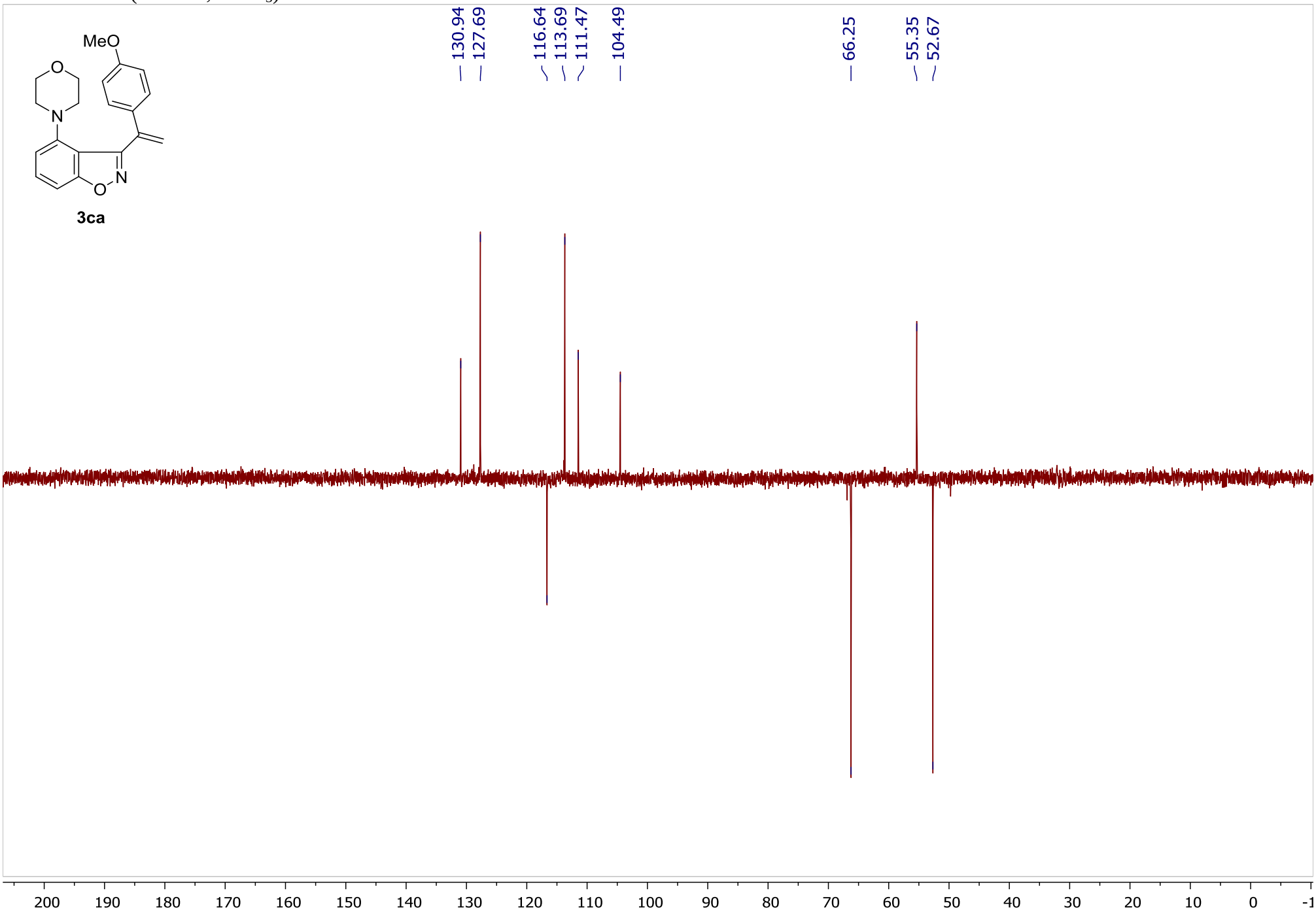
$^1$H NMR (300 MHz, $CDCl_3$)



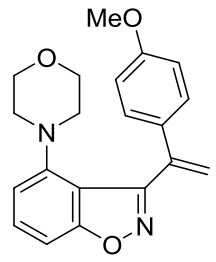
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

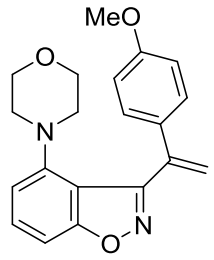


$^{1}$H-$^{1}$H COSY

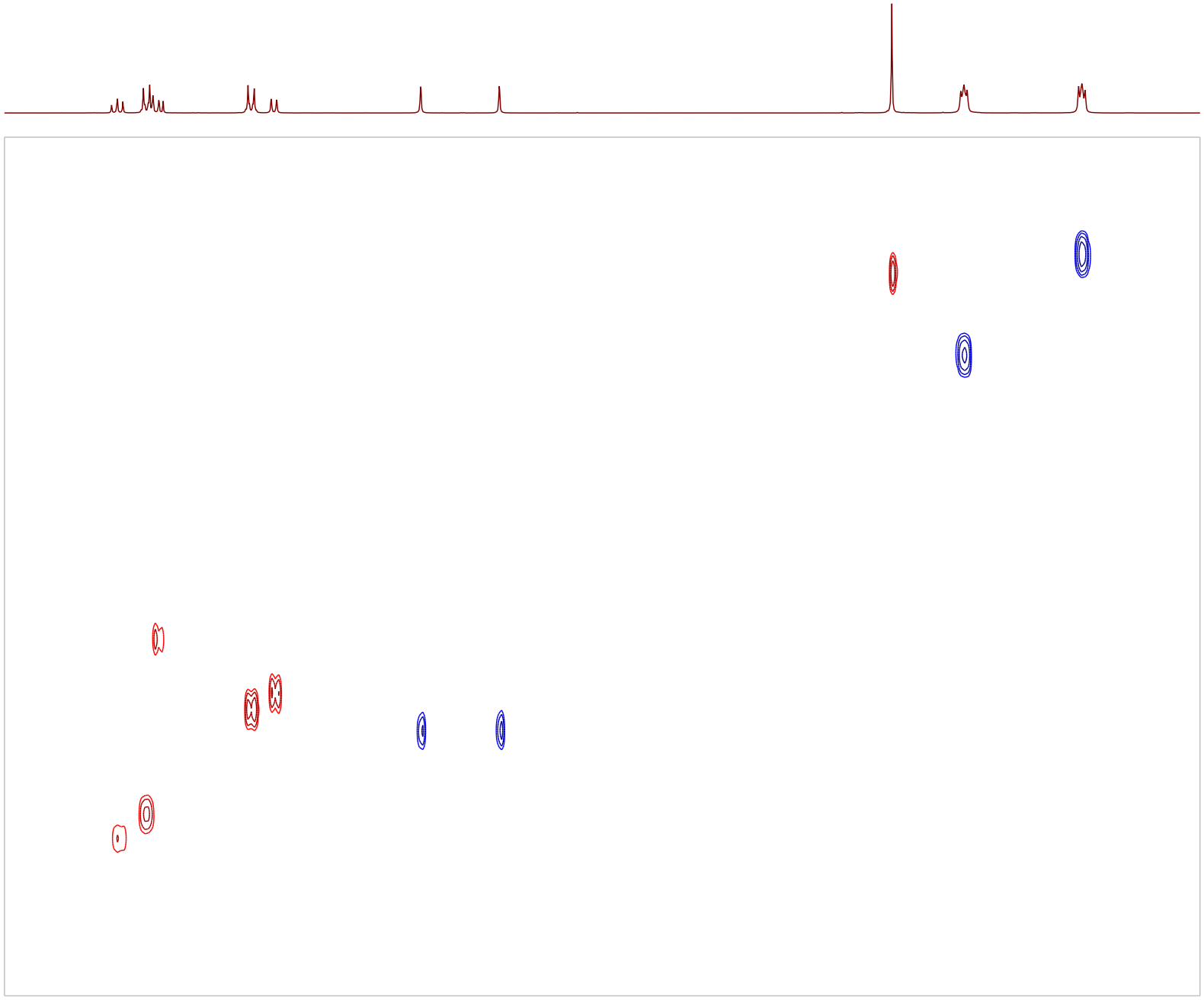



**3ca**

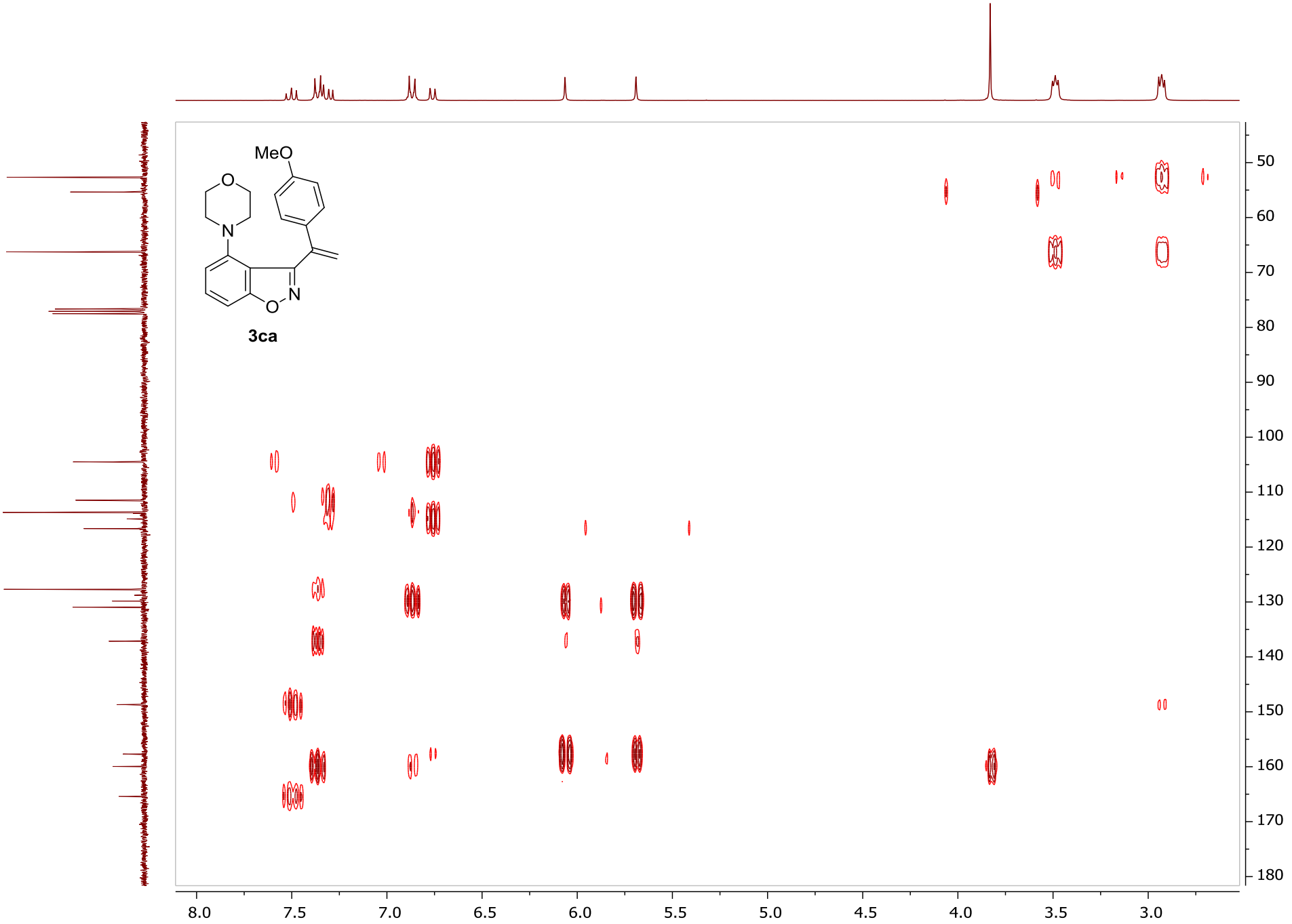
$^{1}$H-$^{13}$C HSQC




**3ca**



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


MeO
O
N
O
N
3ca
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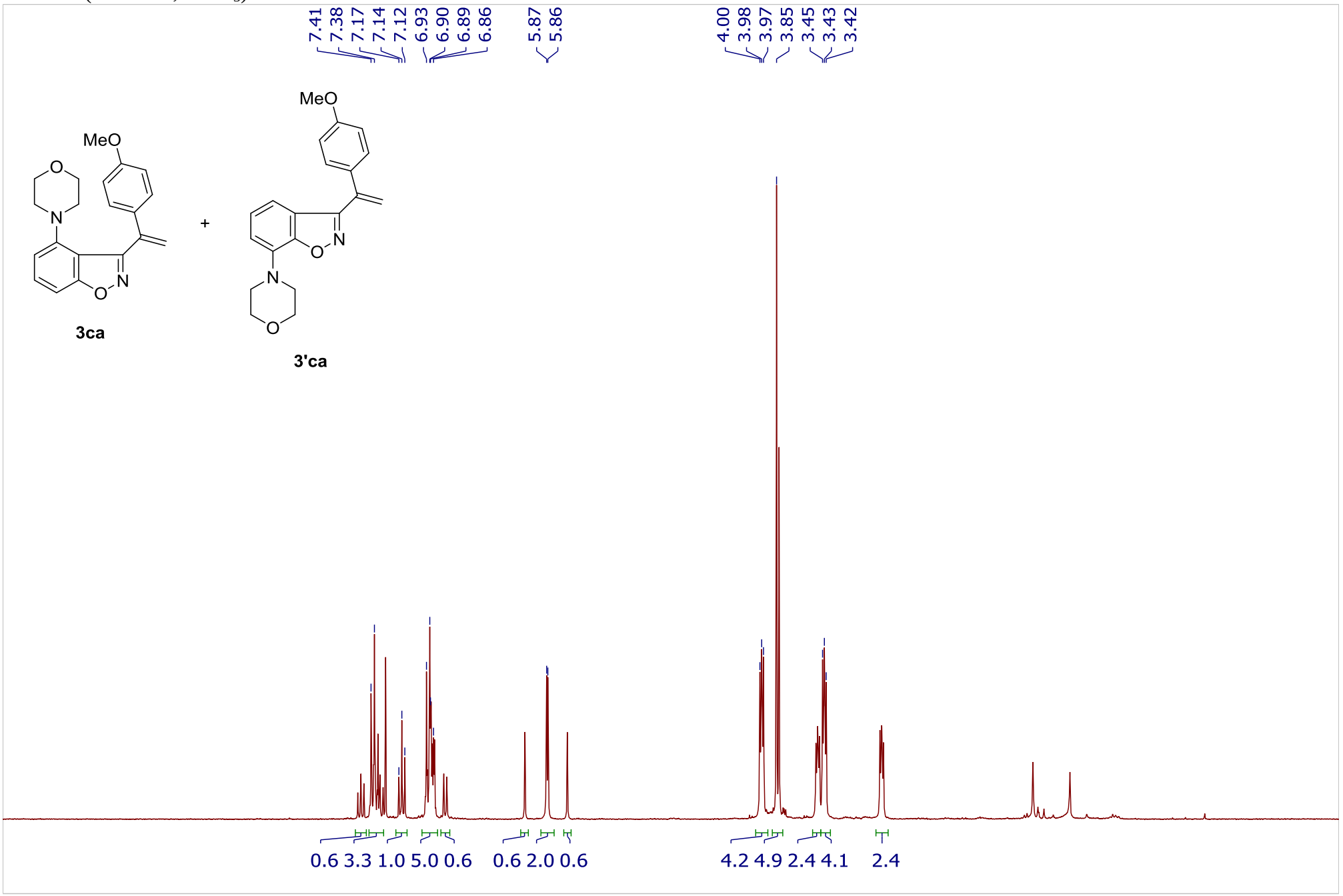
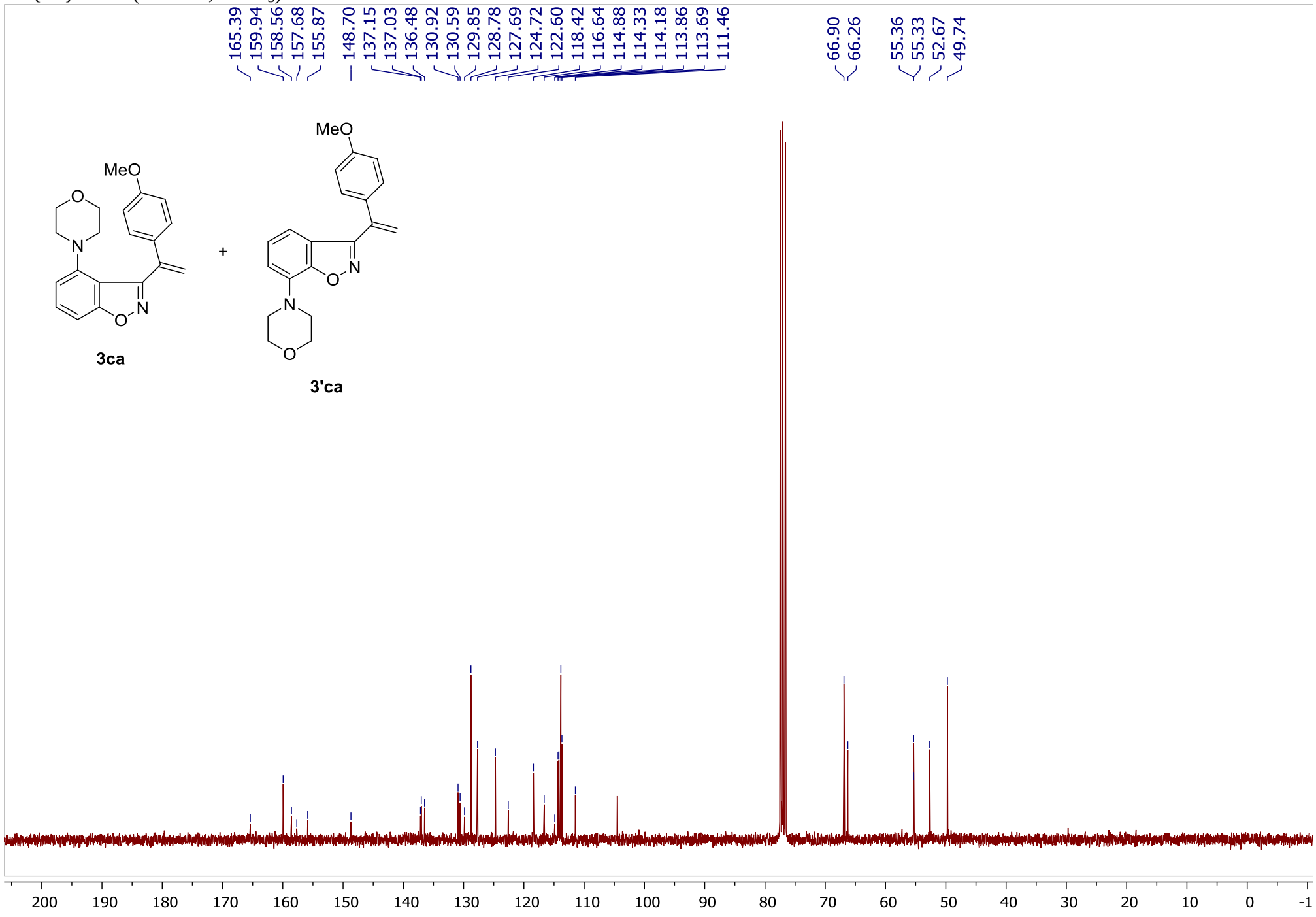
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
50
60
70
80
90
100
110
120
130
140
150
160
170
180

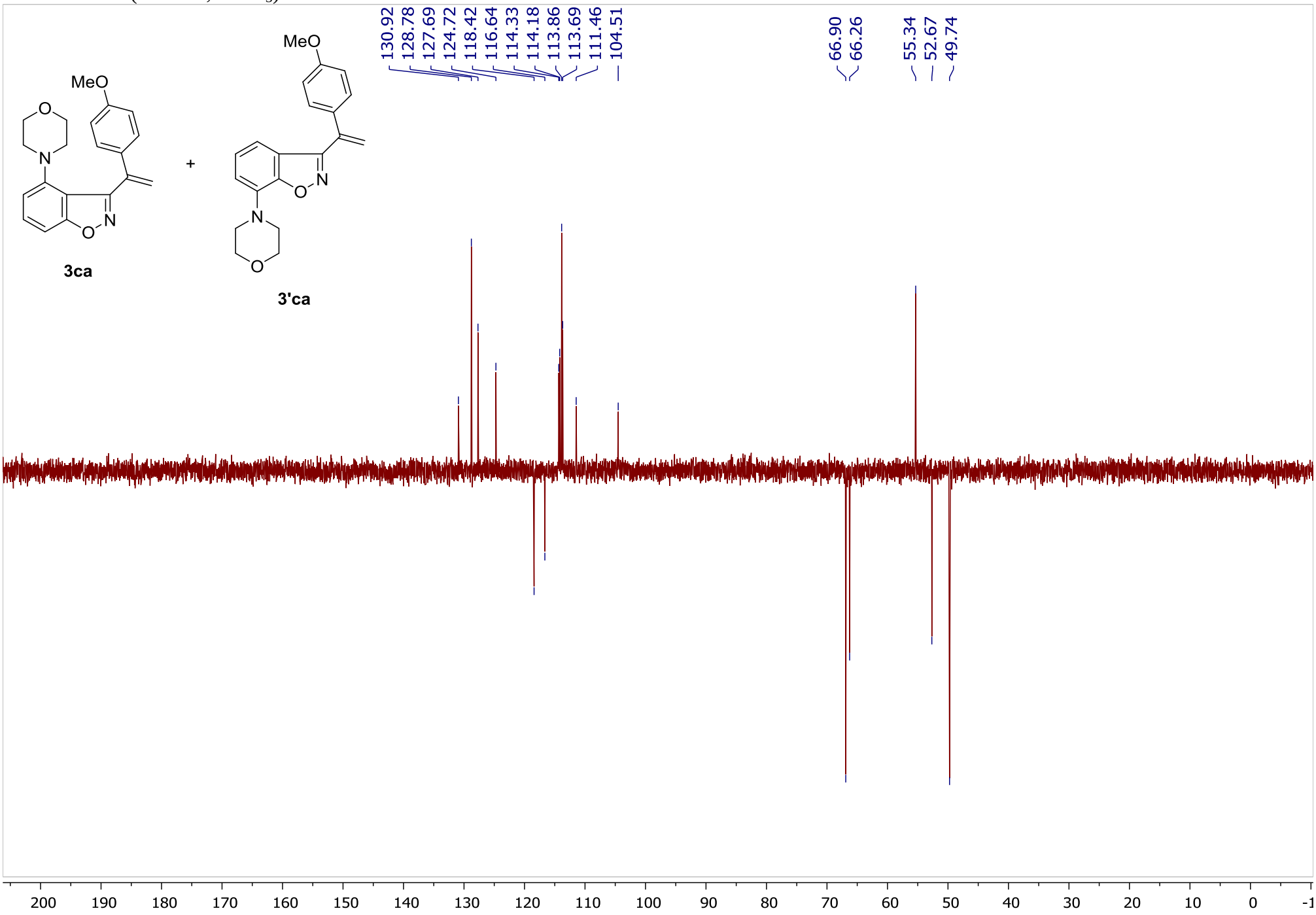
**4-Methoxy-3-(1-(4-methoxyphenyl)vinyl)benzo[d]isoxazole 3ca** and **3-(1-(4-methoxyphenyl)vinyl)-7-morpholinobenzo[d]isoxazole 3'ca**
$^1$H NMR (300 MHz, $CDCl_3$) **3ca** : **3'ca** = 1:1.8.



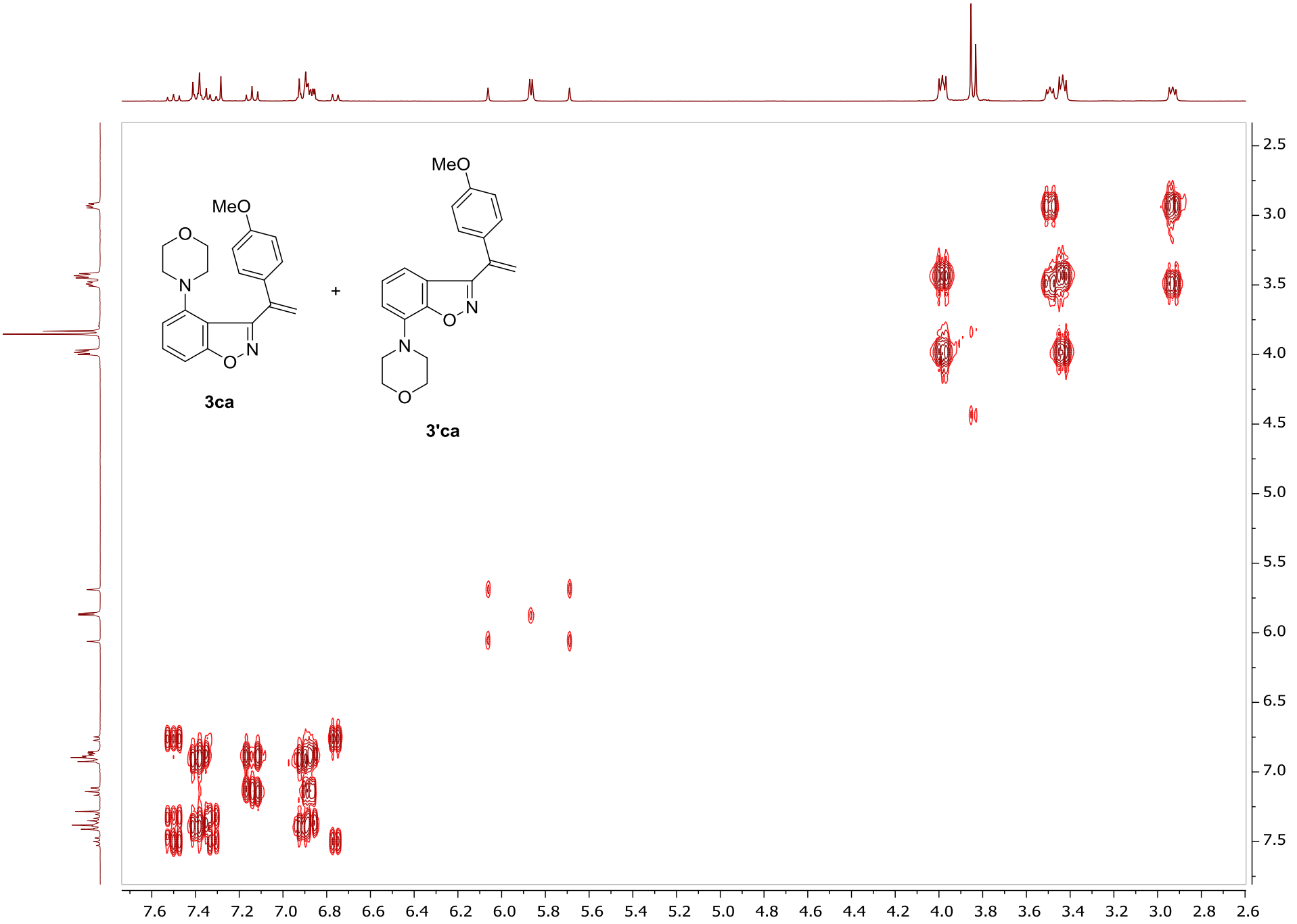
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



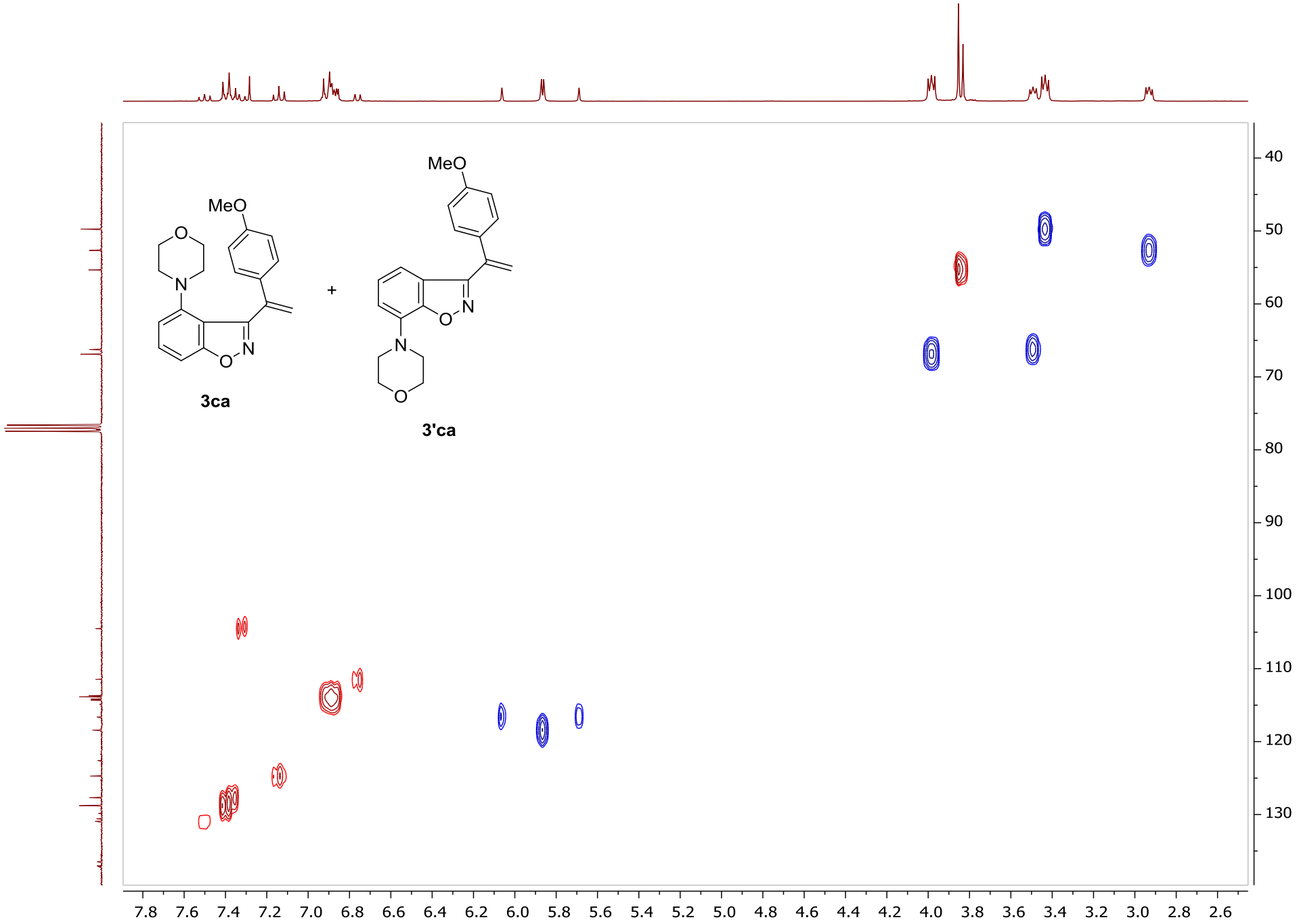
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



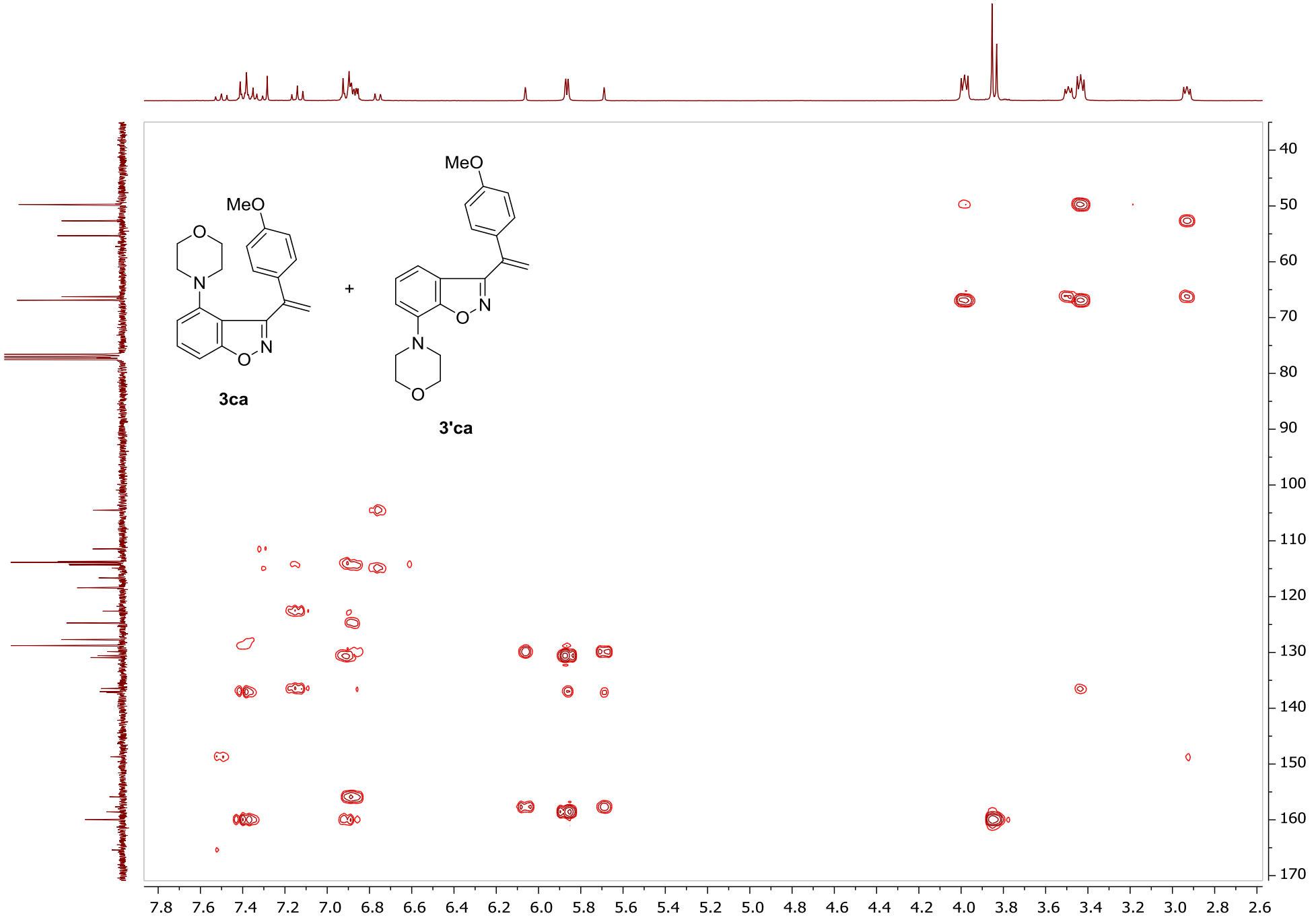
$^{1}$H-$^{1}$H COSY


MeO
O
N
O
N
3ca
+
MeO
N
O
N
O
3'ca
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.6
7.4
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

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

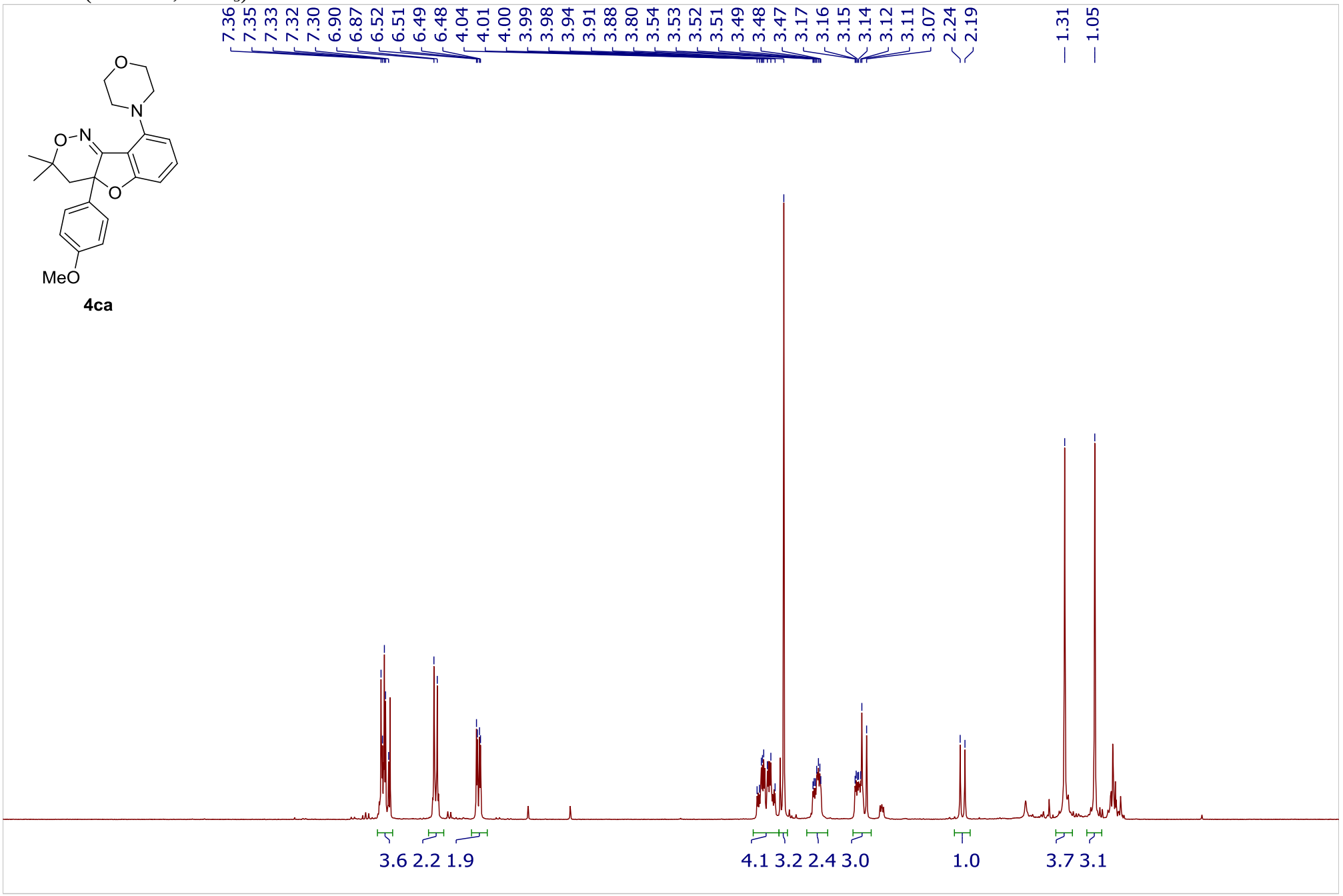

MeO
O
N
O
N
3ca
+
MeO
N
O
N
O
3'ca
40
50
60
70
80
90
100
110
120
130
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6

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

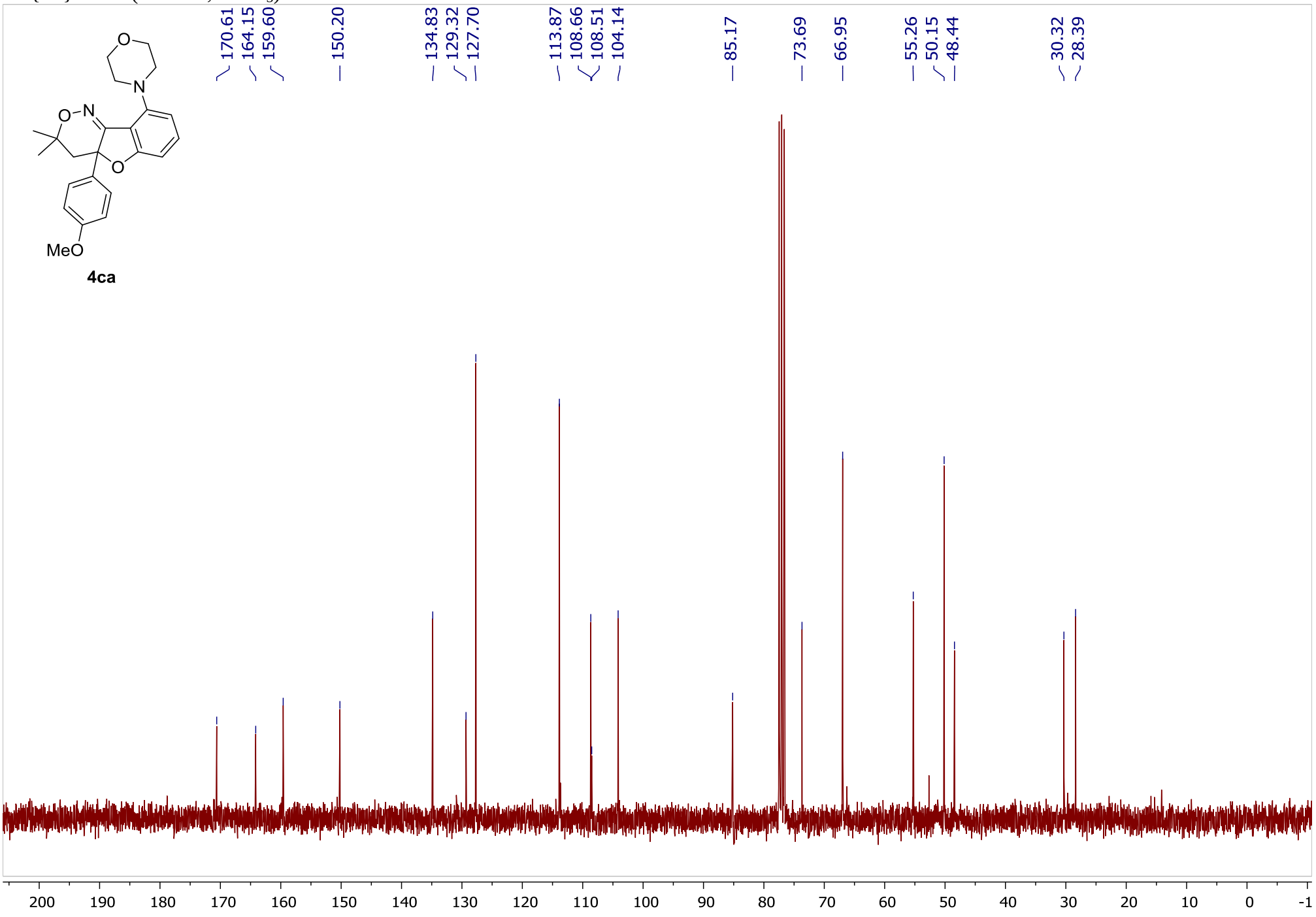

MeO
O
N
O
N
3ca
+
MeO
O
N
N
O
3'ca
40
50
60
70
80
90
100
110
120
130
140
150
160
170
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6

**4a-(4-Methoxyphenyl)-3,3-dimethyl-9-morpholino-4,4a-dihydro-3H-benzofuro[3,2-c][1,2]oxazine 4ca**

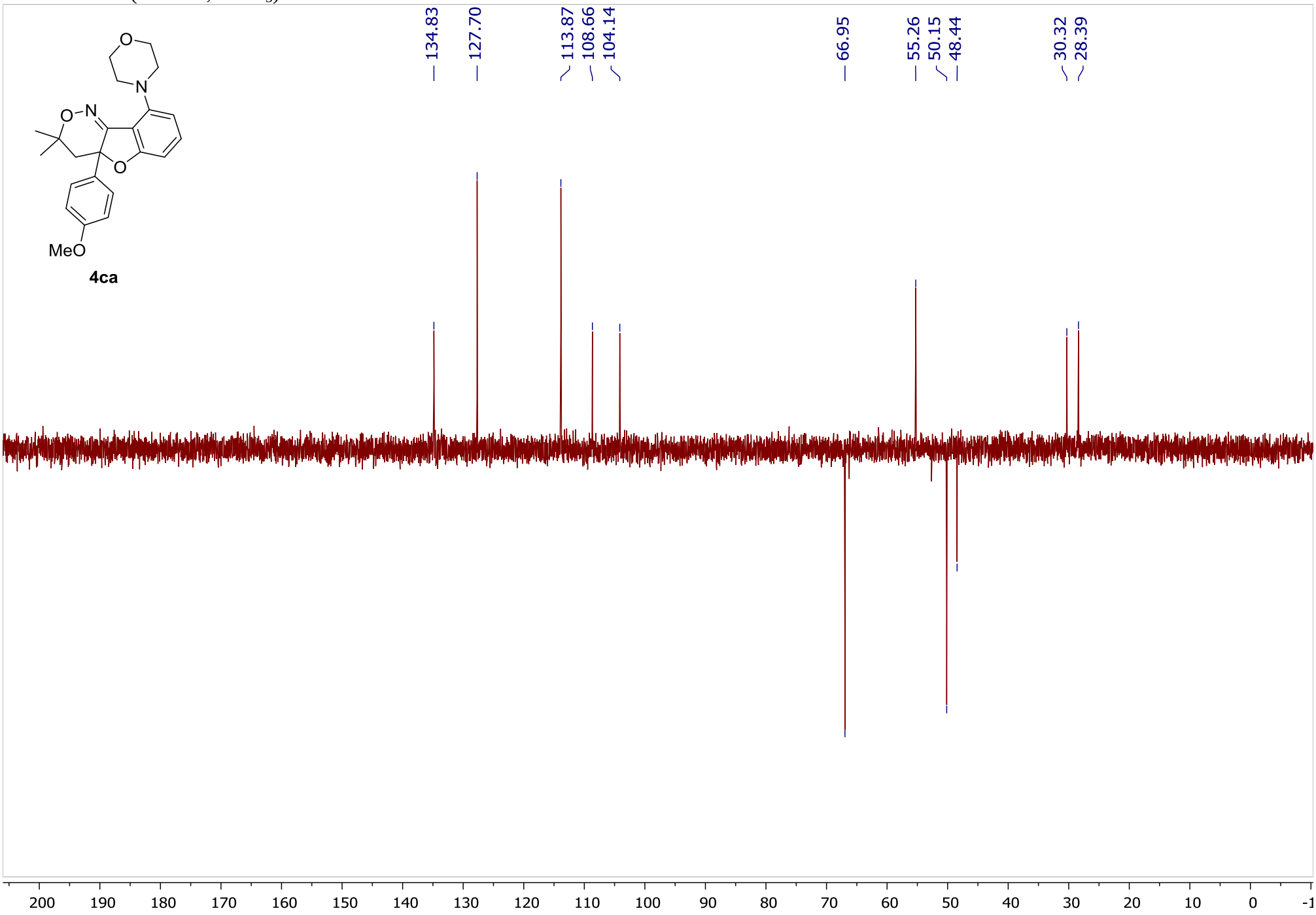
$^1$H NMR (300 MHz, $CDCl_3$)



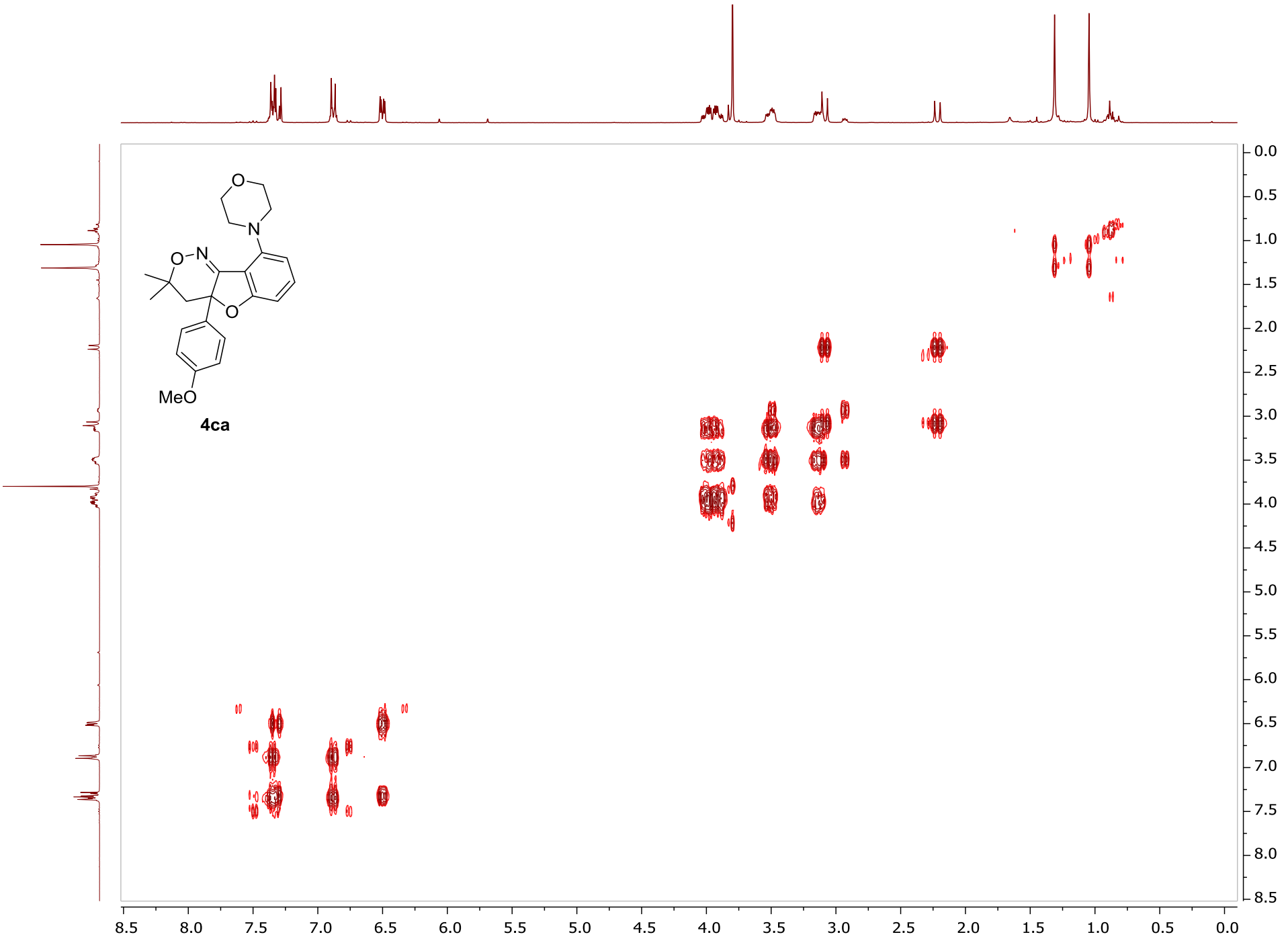
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



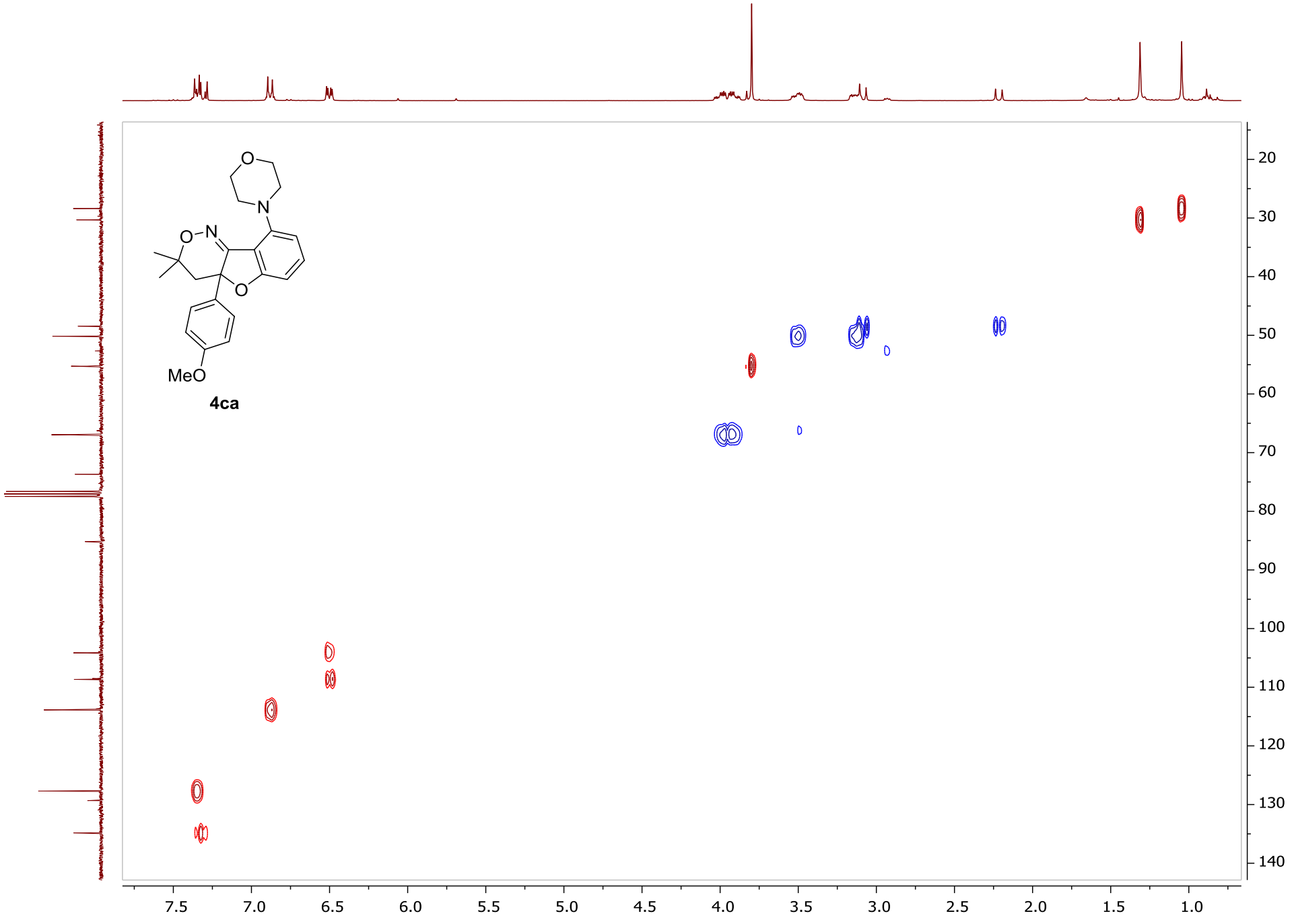
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



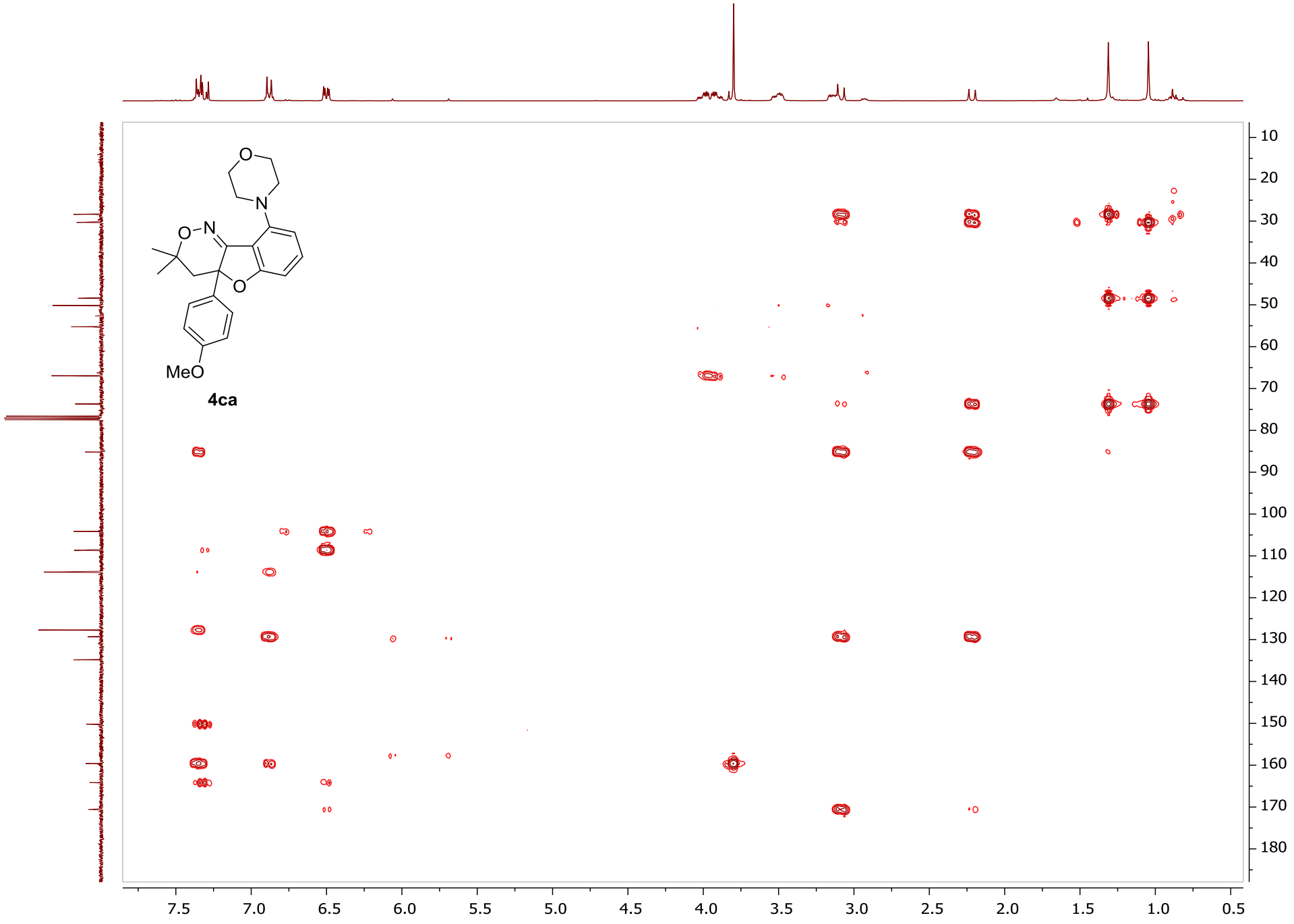
$^{1}$H-$^{1}$H COSY


O
N
O
N
O
MeO
4ca
0.0
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
8.0
8.5
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

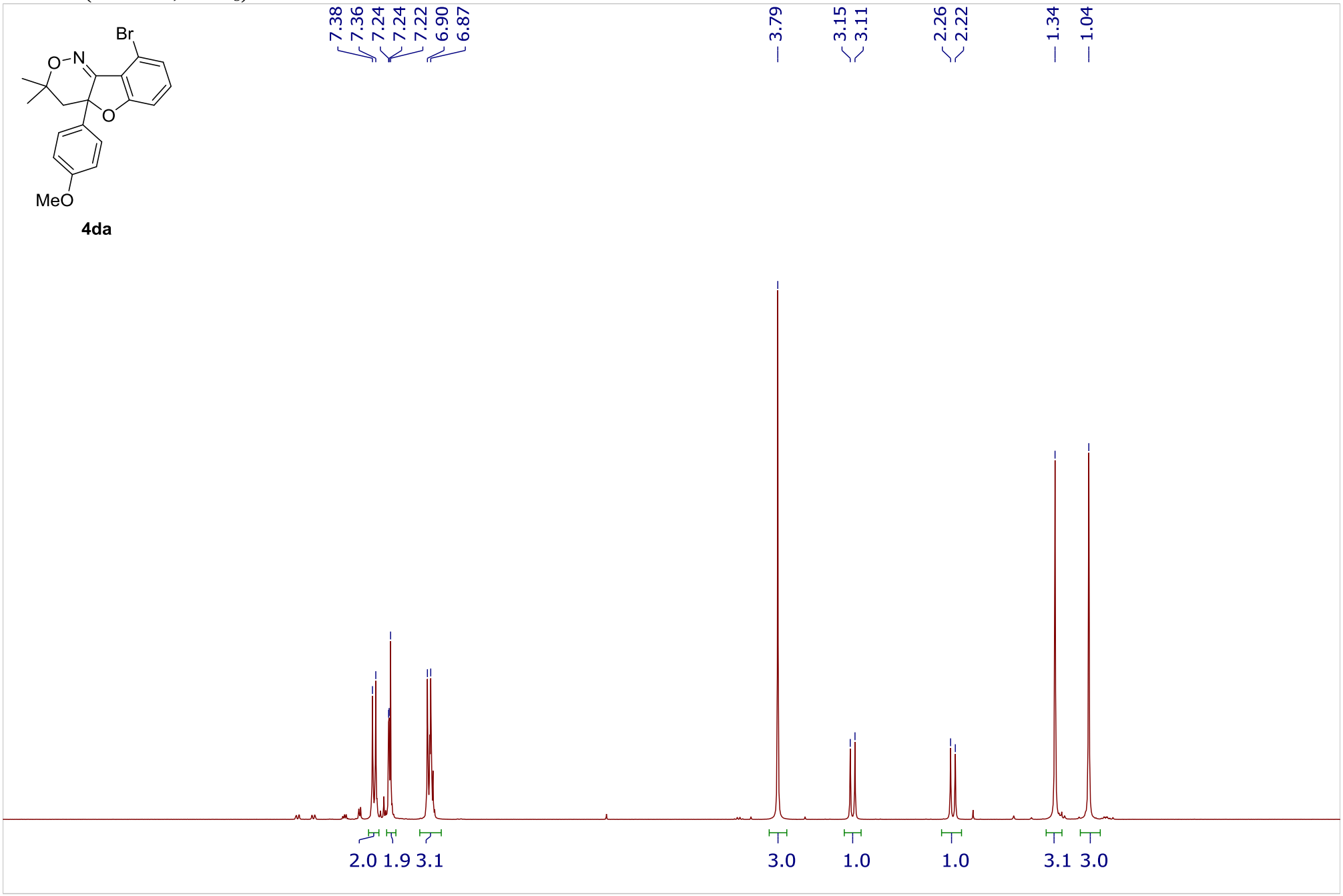

O
N
O
N
O
MeO
4ca
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

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

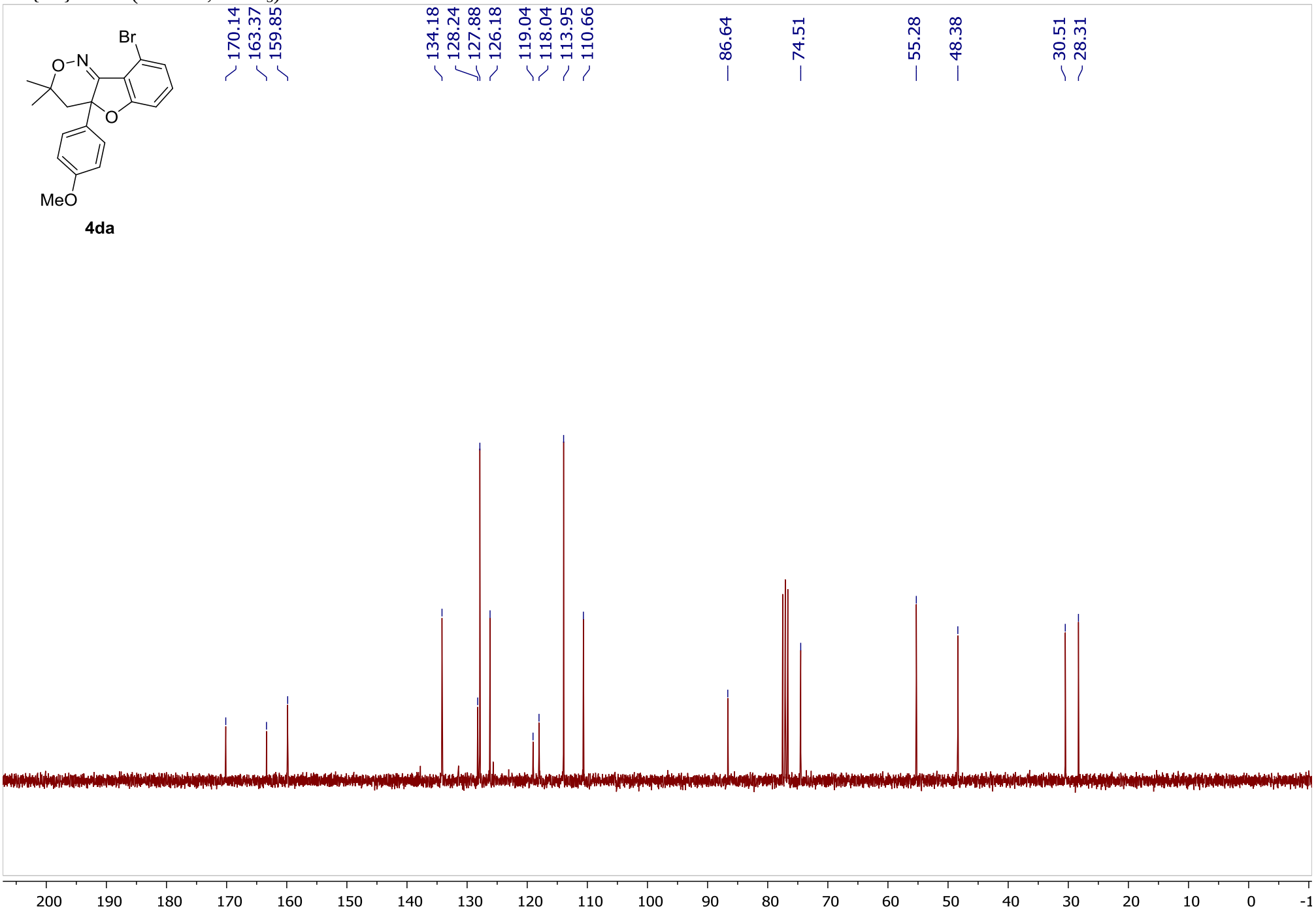

O
N
O
N
O
MeO
4ca
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**9-Bromo-4a-(4-methoxyphenyl)-3,3-dimethyl-4,4a-dihydro-3H-benzofuro[3,2-c][1,2]oxazine 4da**

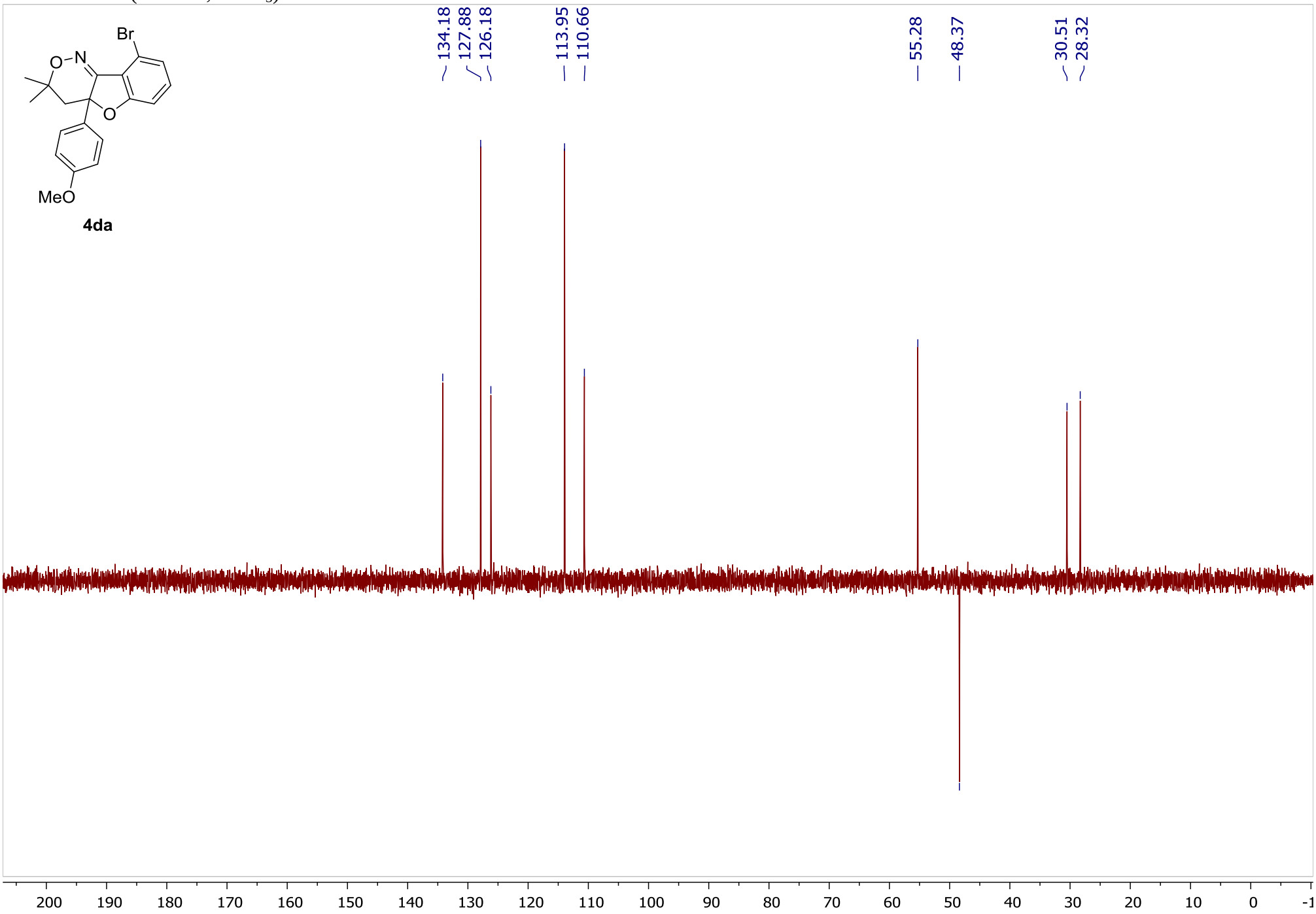
$^1$H NMR (300 MHz, $CDCl_3$)



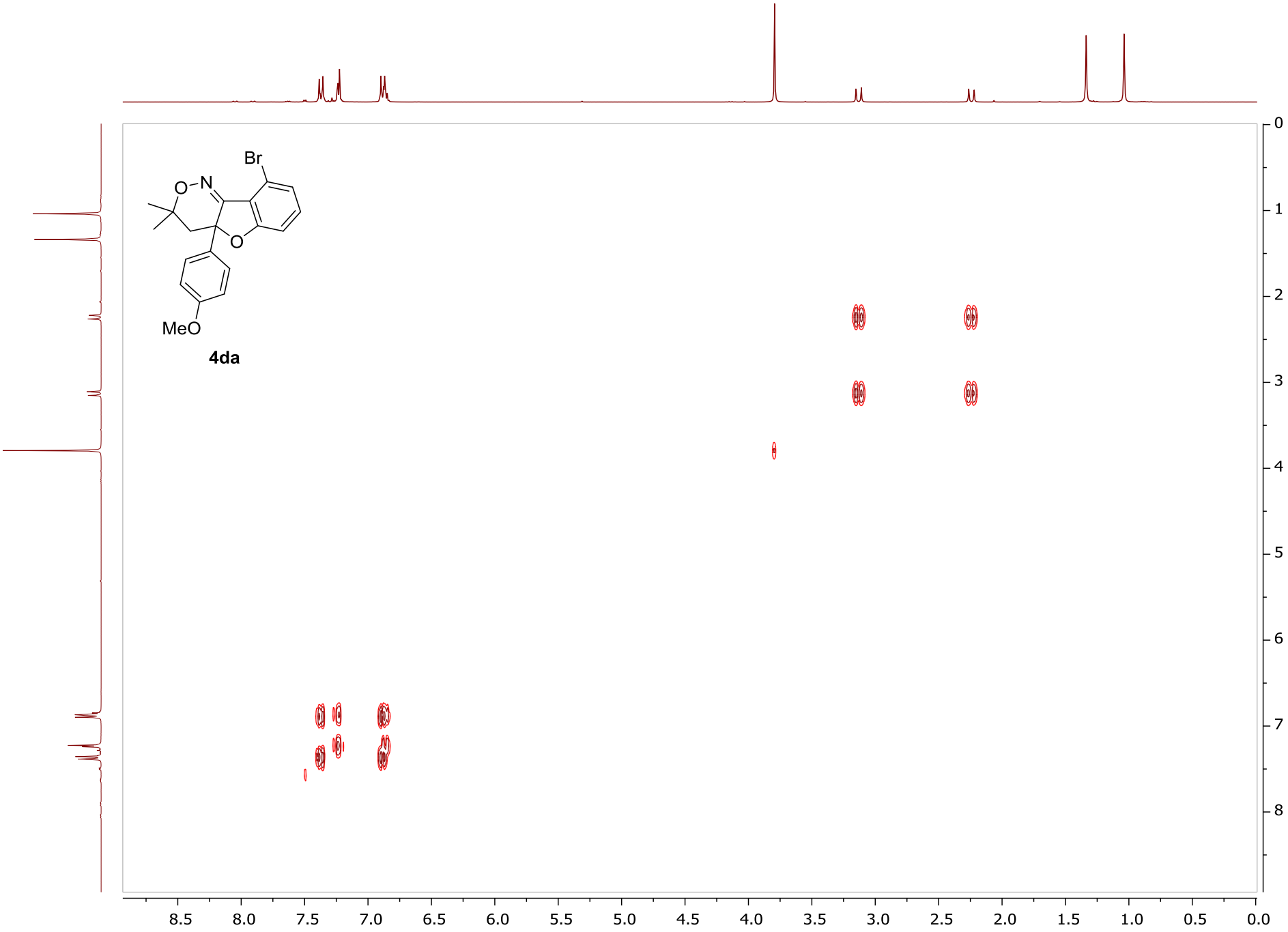
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



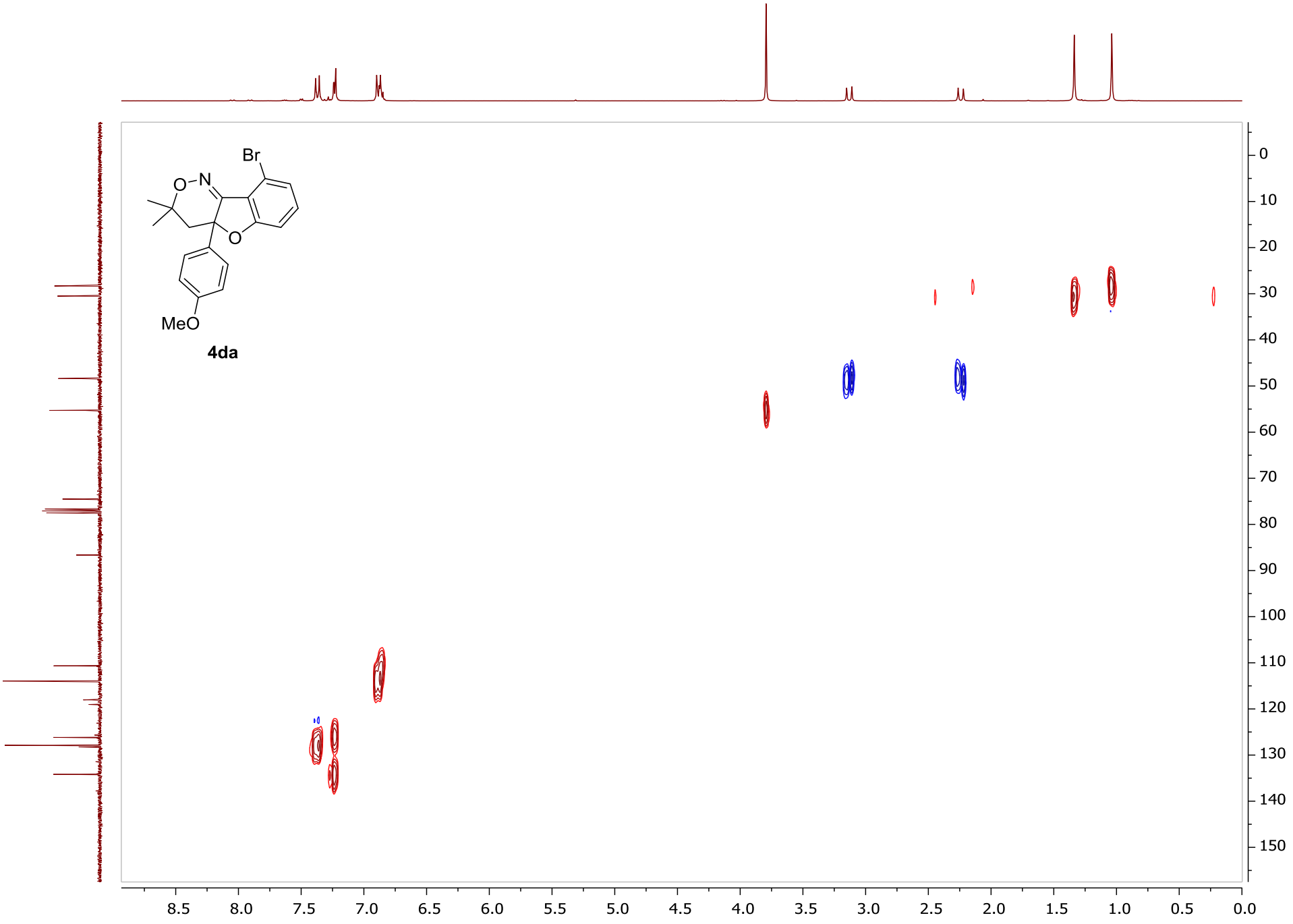
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



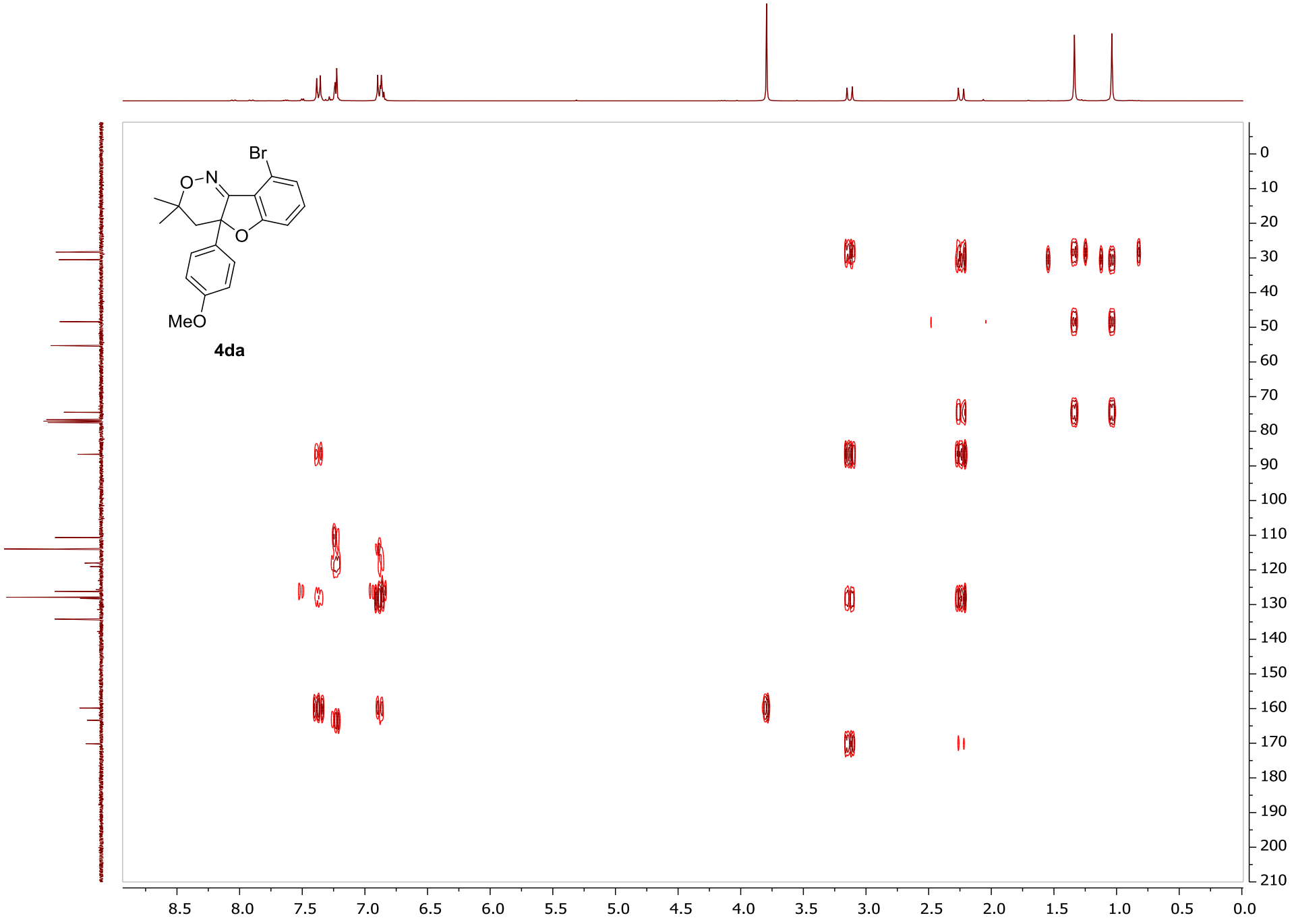
$^{1}$H-$^{1}$H COSY


Br
O
N
O
MeO
4da
0
1
2
3
4
5
6
7
8
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

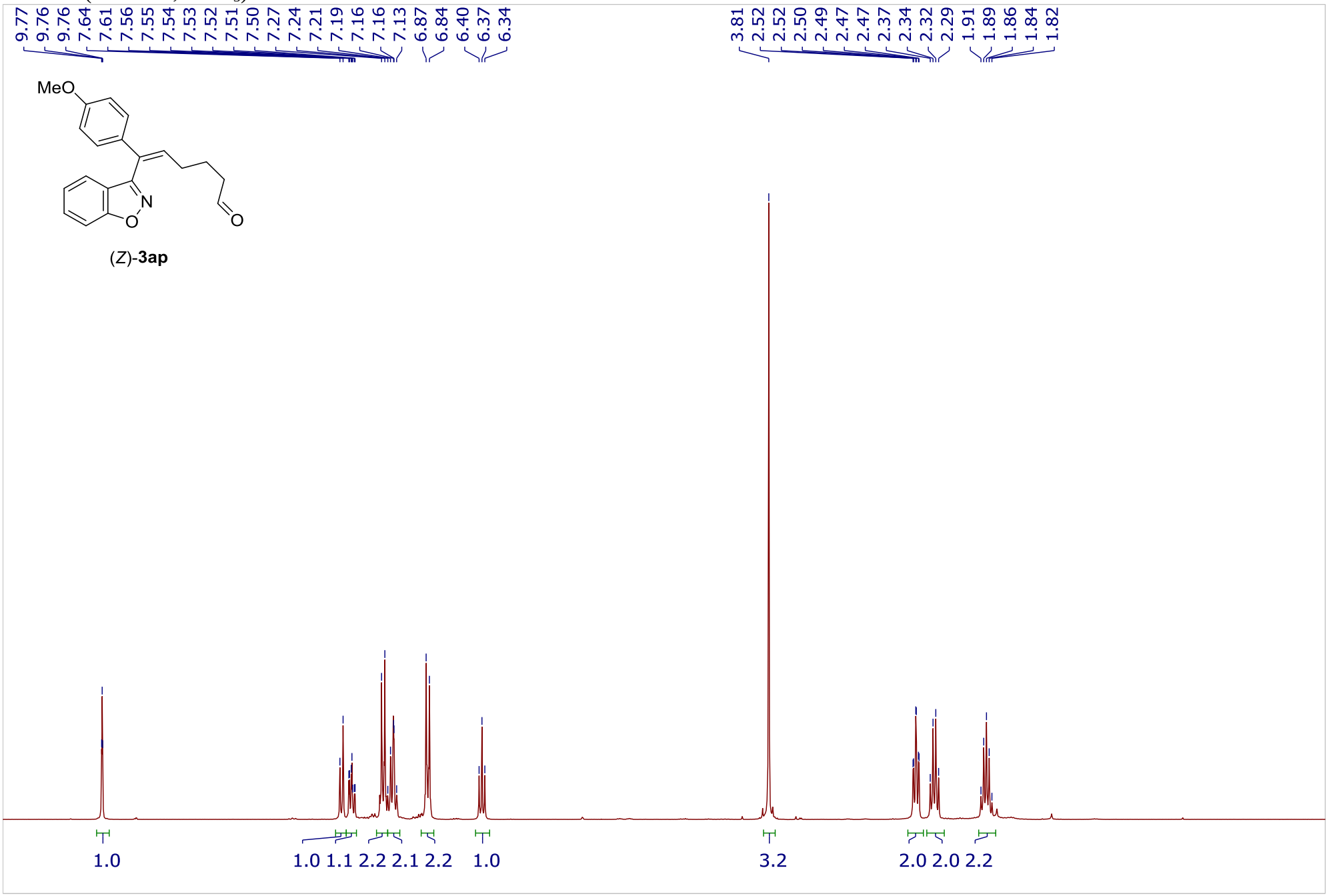

Br
O
N
O
MeO
4da
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

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

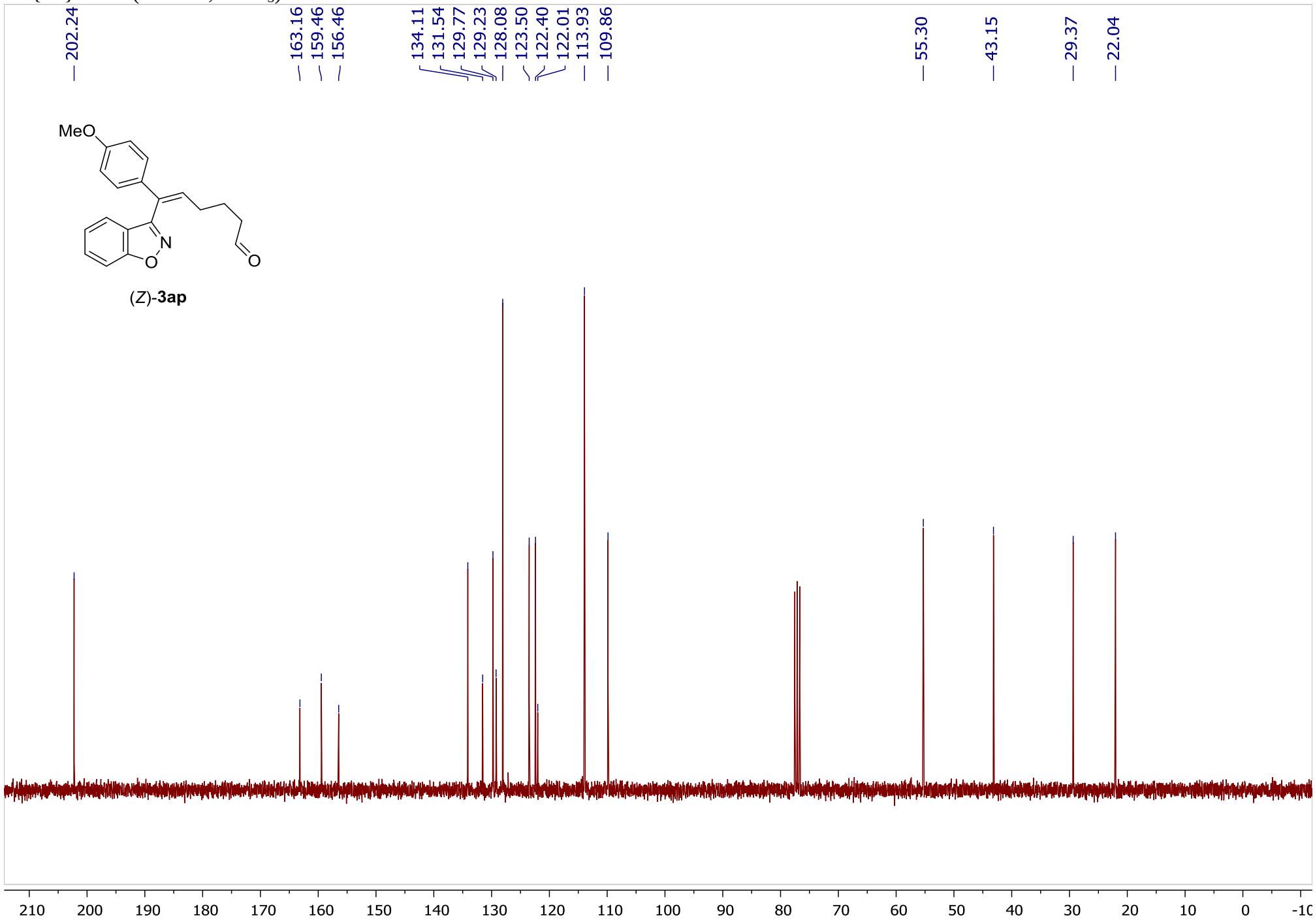

Br
O
N
O
MeO
4da
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**6-(Benzo[d]isoxazol-3-yl)-6-(4-methoxyphenyl)hex-5-enal 3ap, *Z*-isomer**

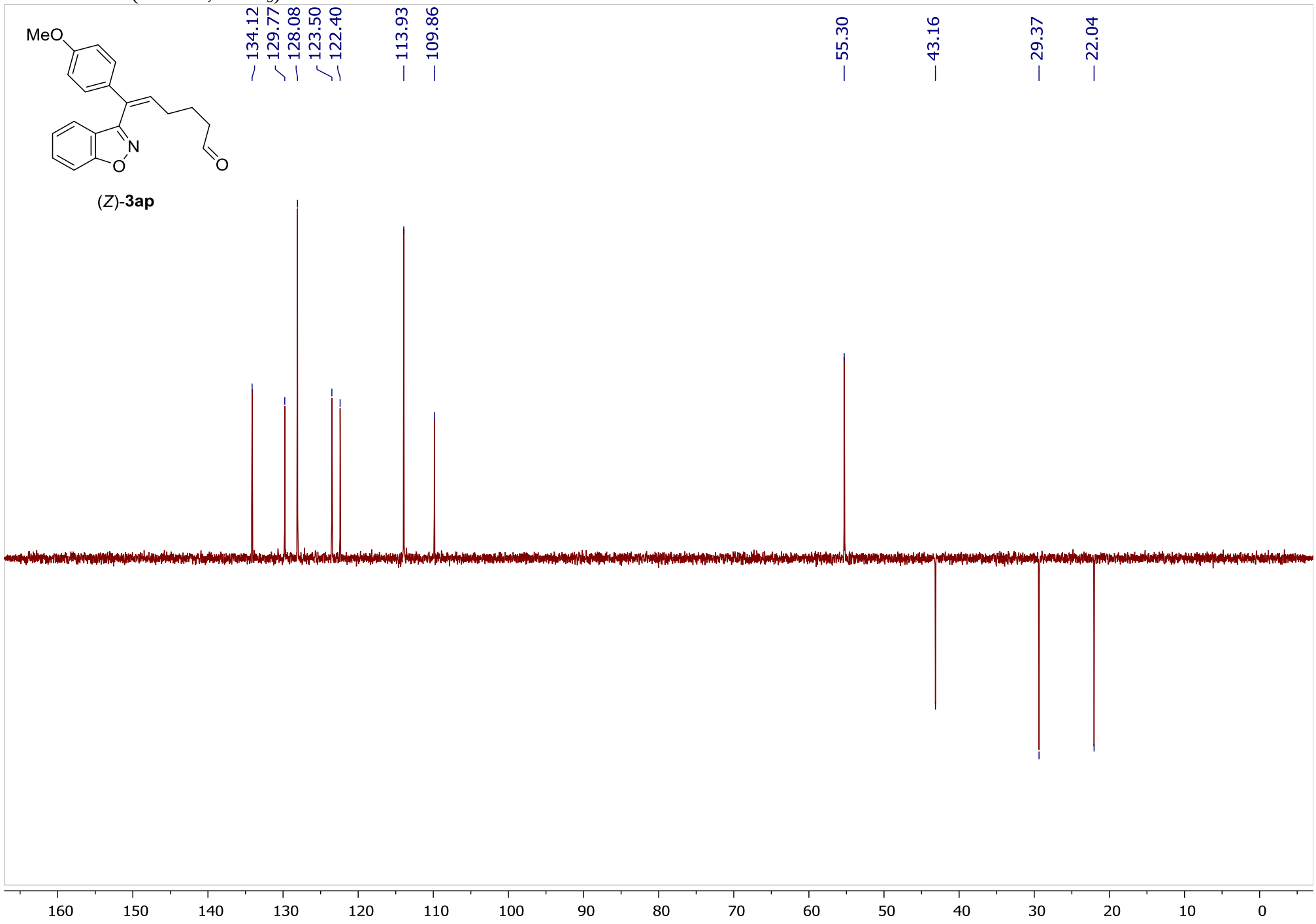
$^1$H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

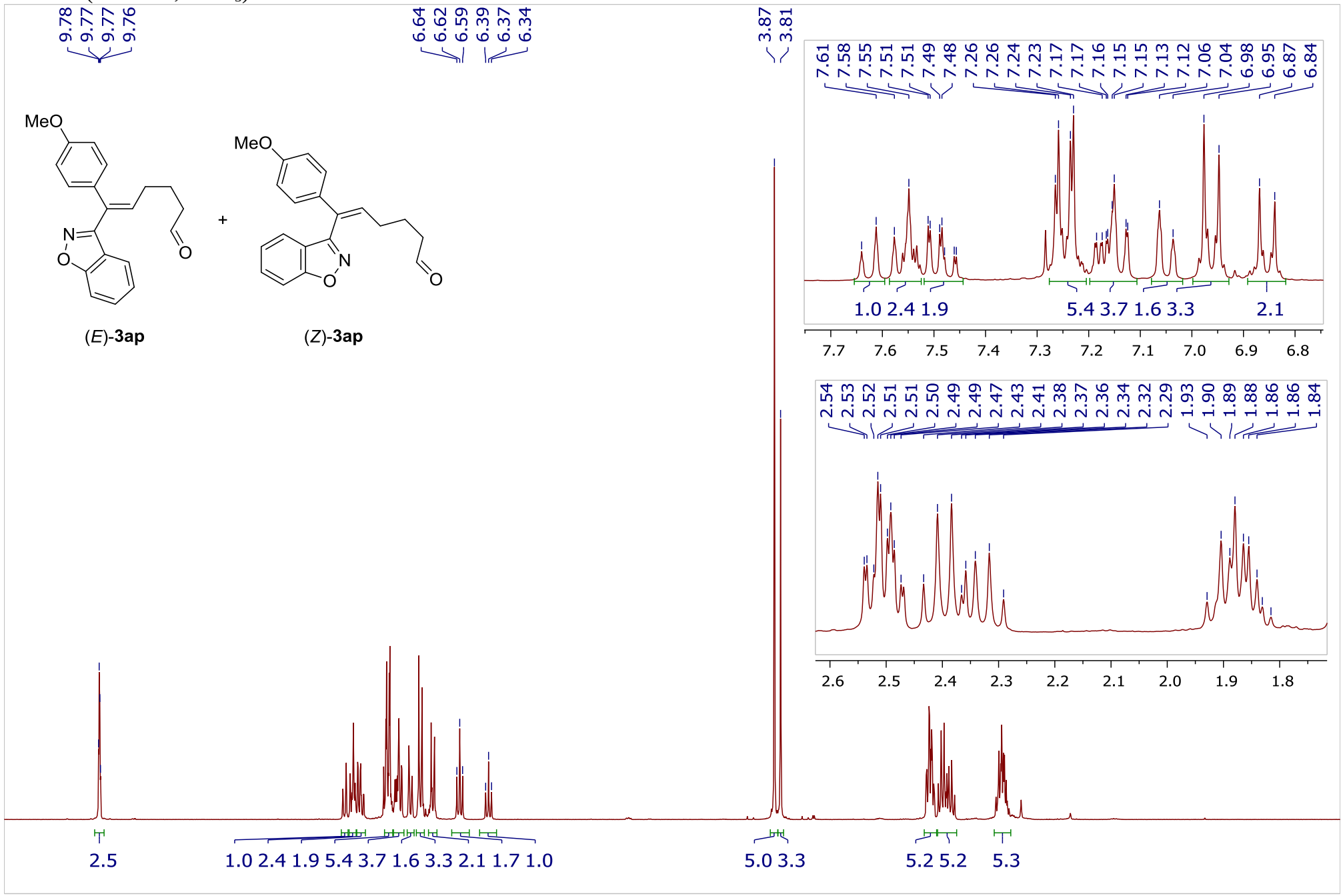


$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

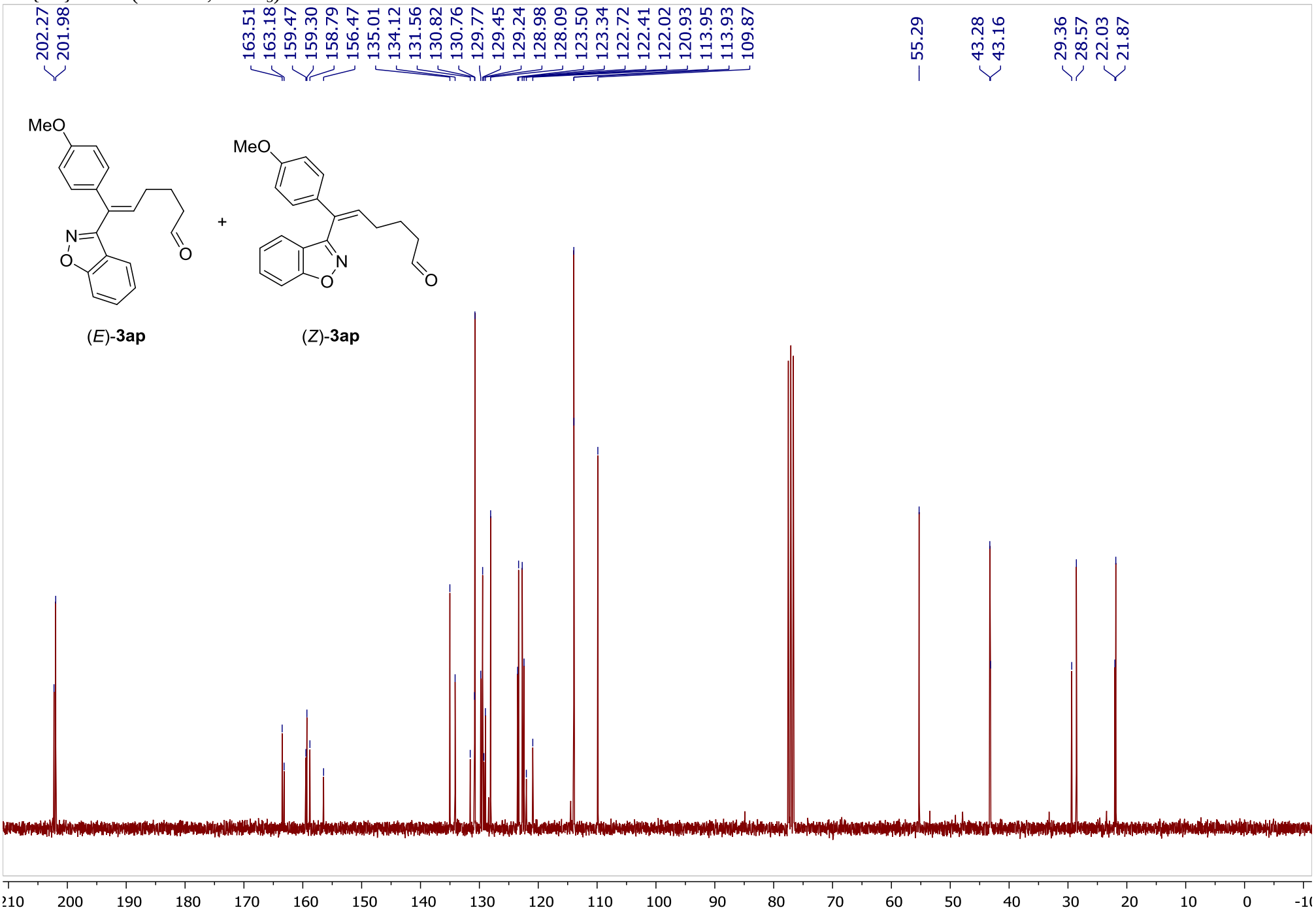


**6-(benzo[d]isoxazol-3-yl)-6-(4-methoxyphenyl)hex-5-enal 3ap,** *Z*:*E*=1:1.7

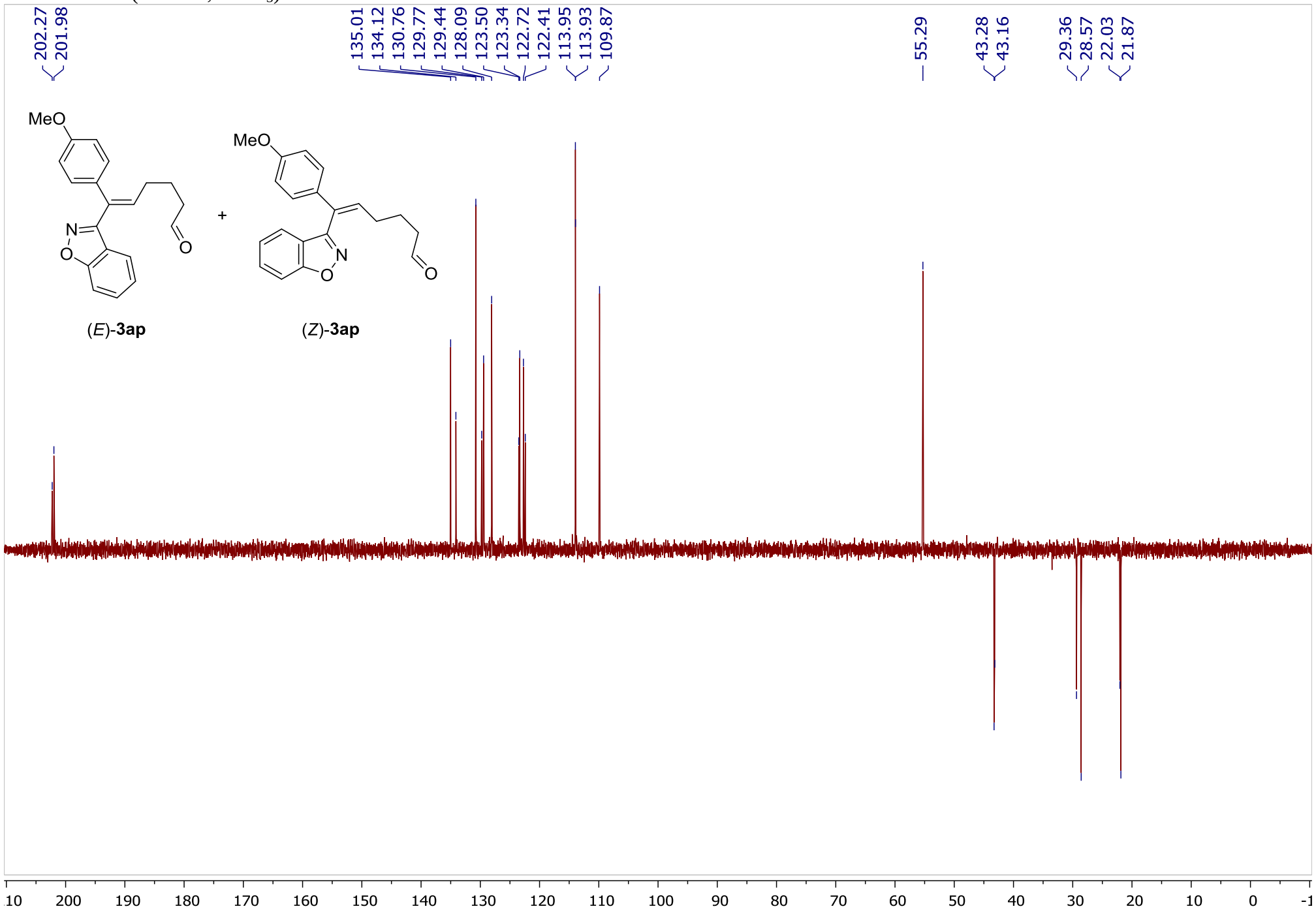
$^1$H NMR (300 MHz, $CDCl_3$)



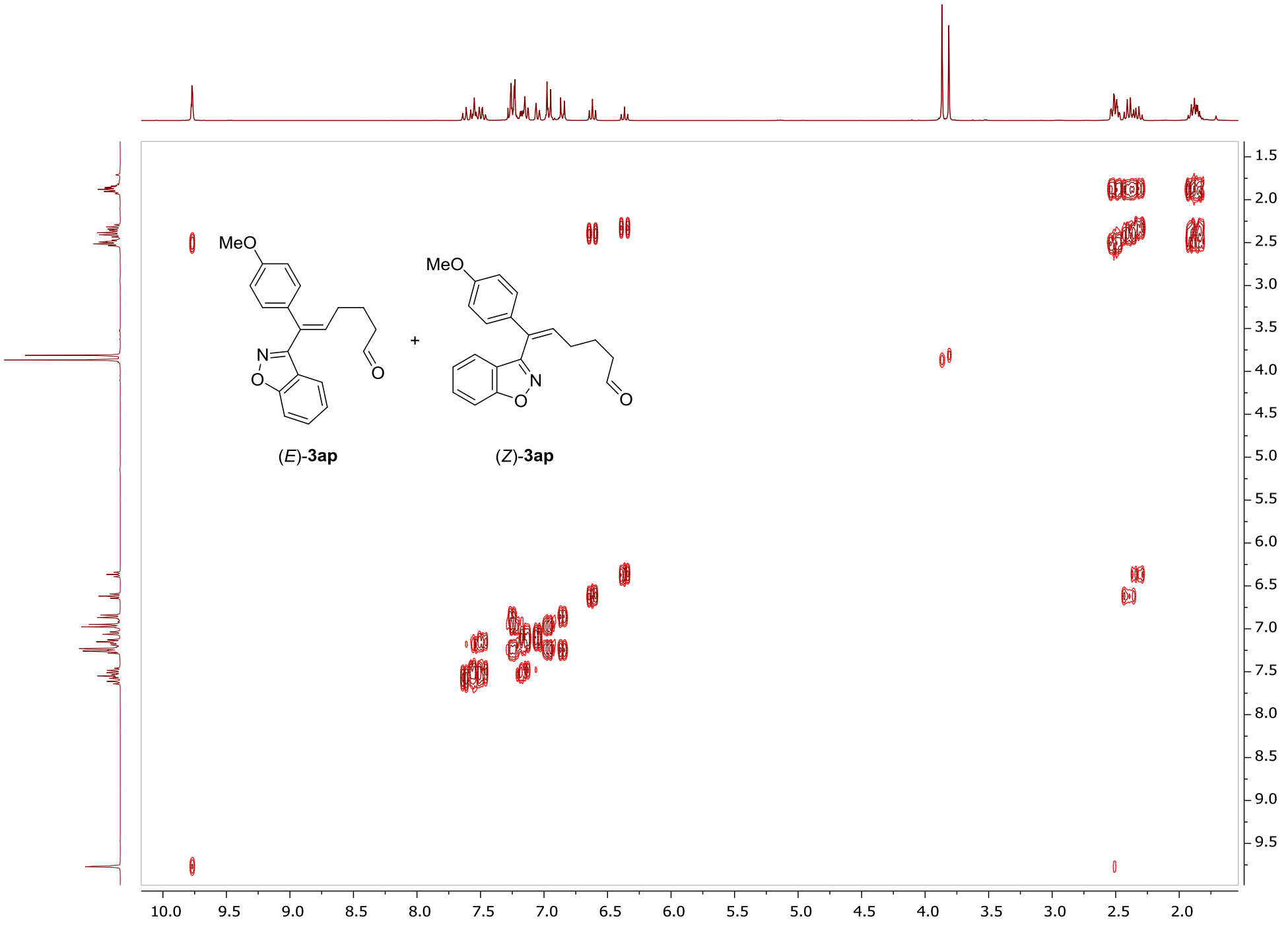
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



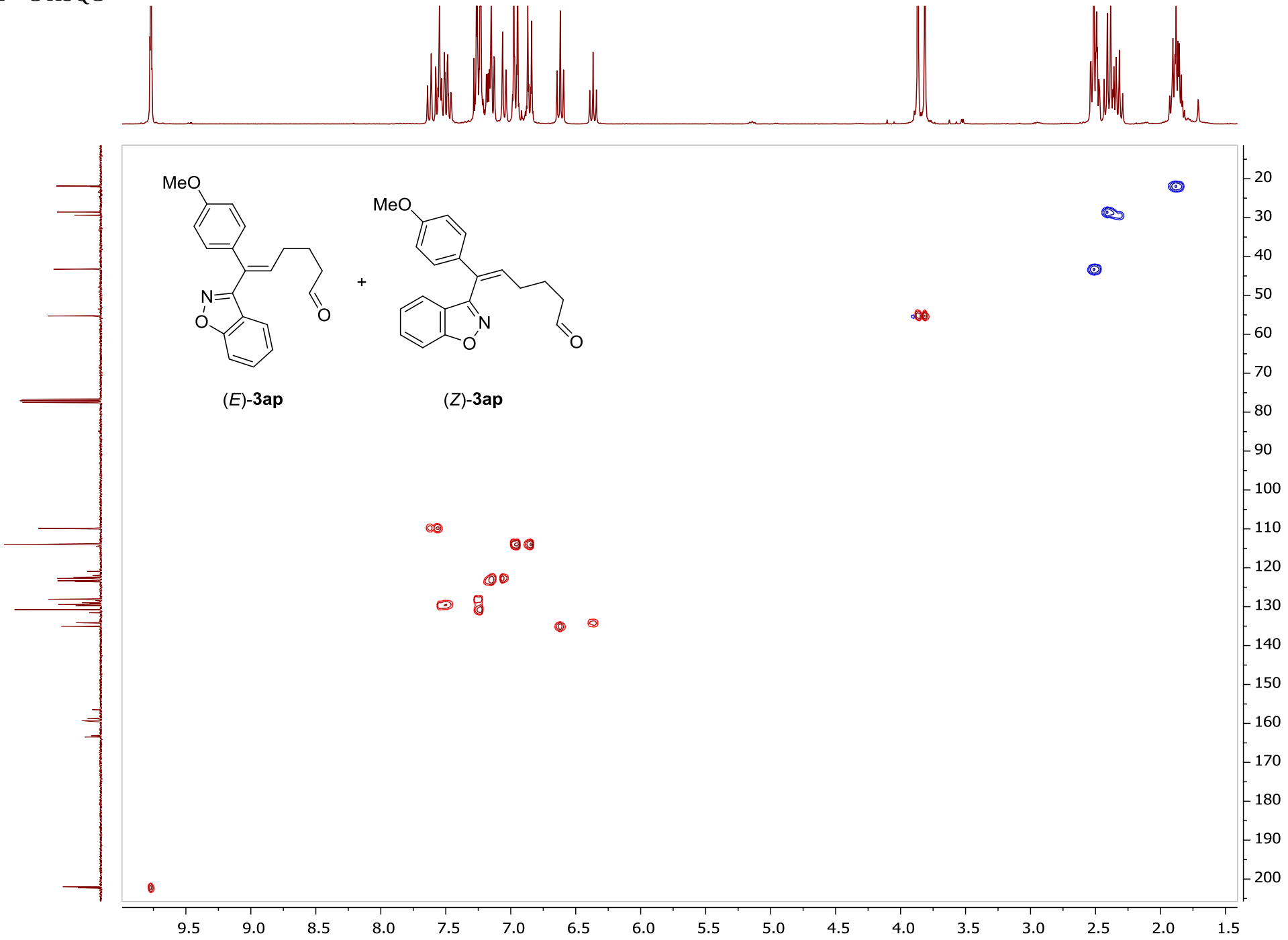
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



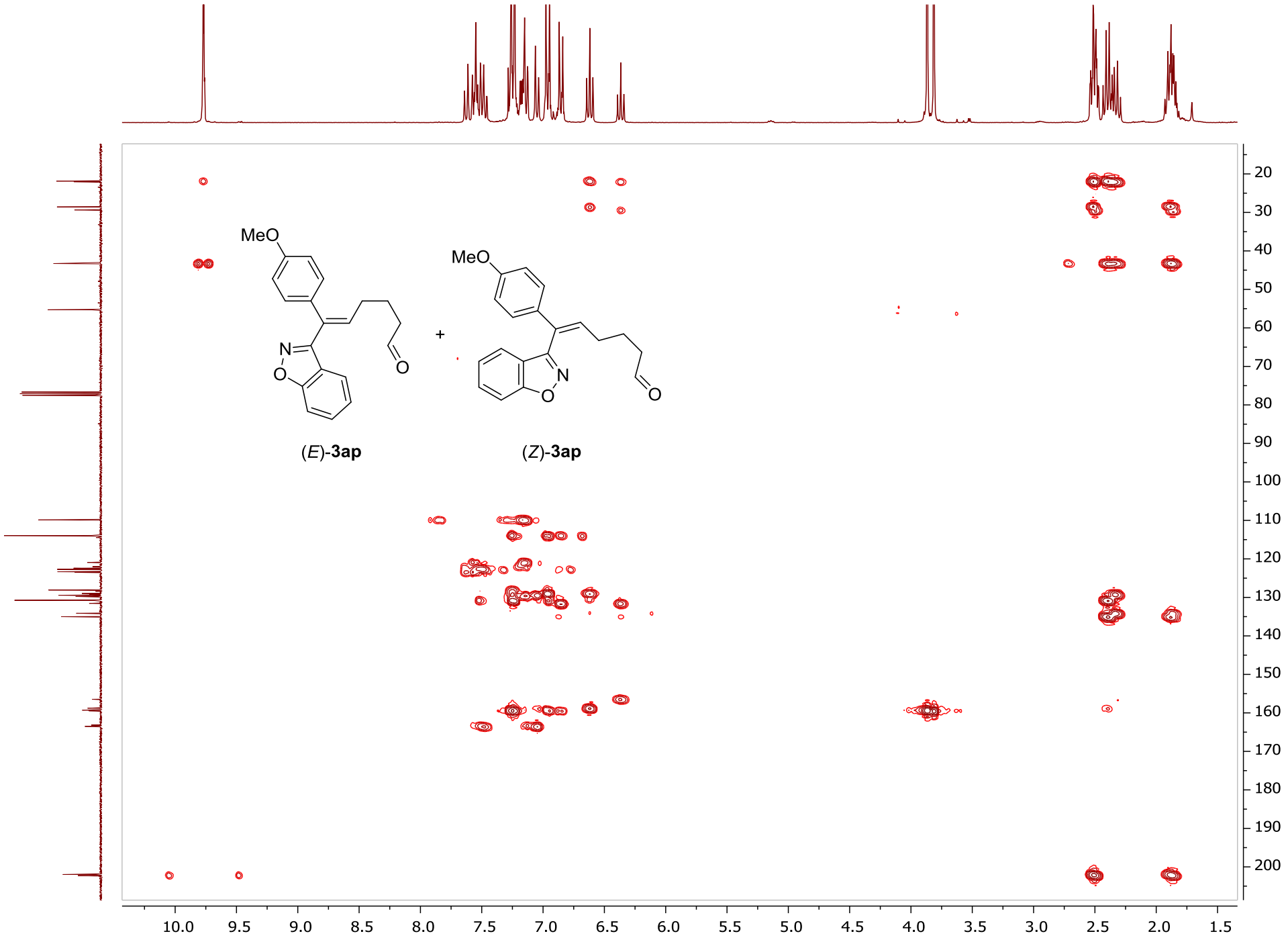
$^{1}$H-$^{1}$H COSY


MeO
N
O
O
(E)-3ap
+
MeO
N
O
O
(Z)-3ap
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
9.0
9.5
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

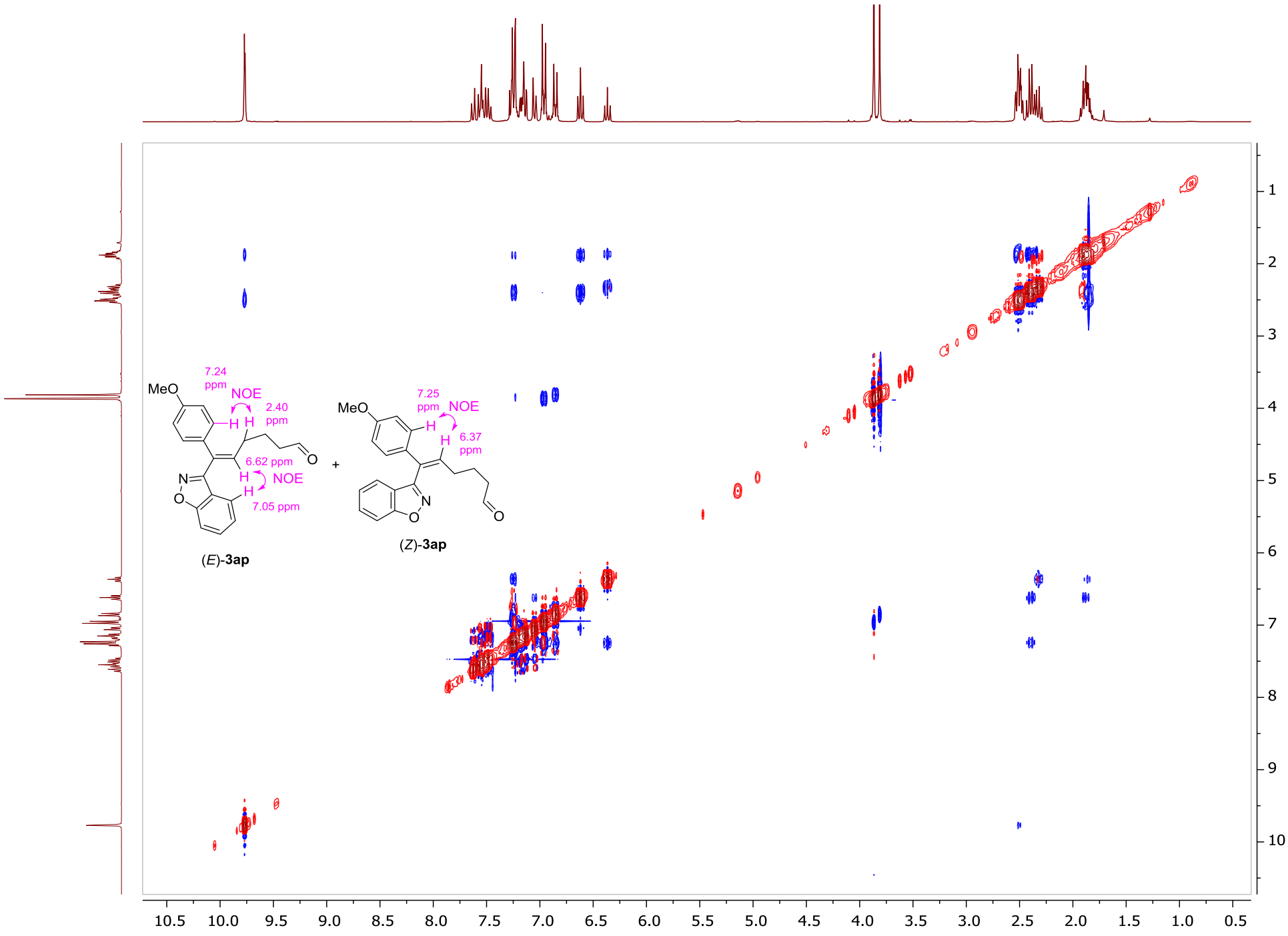
$^{1}$H-$^{13}$C HSQC


MeO
N
O
O
(E)-3ap
+
MeO
N
O
O
(Z)-3ap
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
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

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

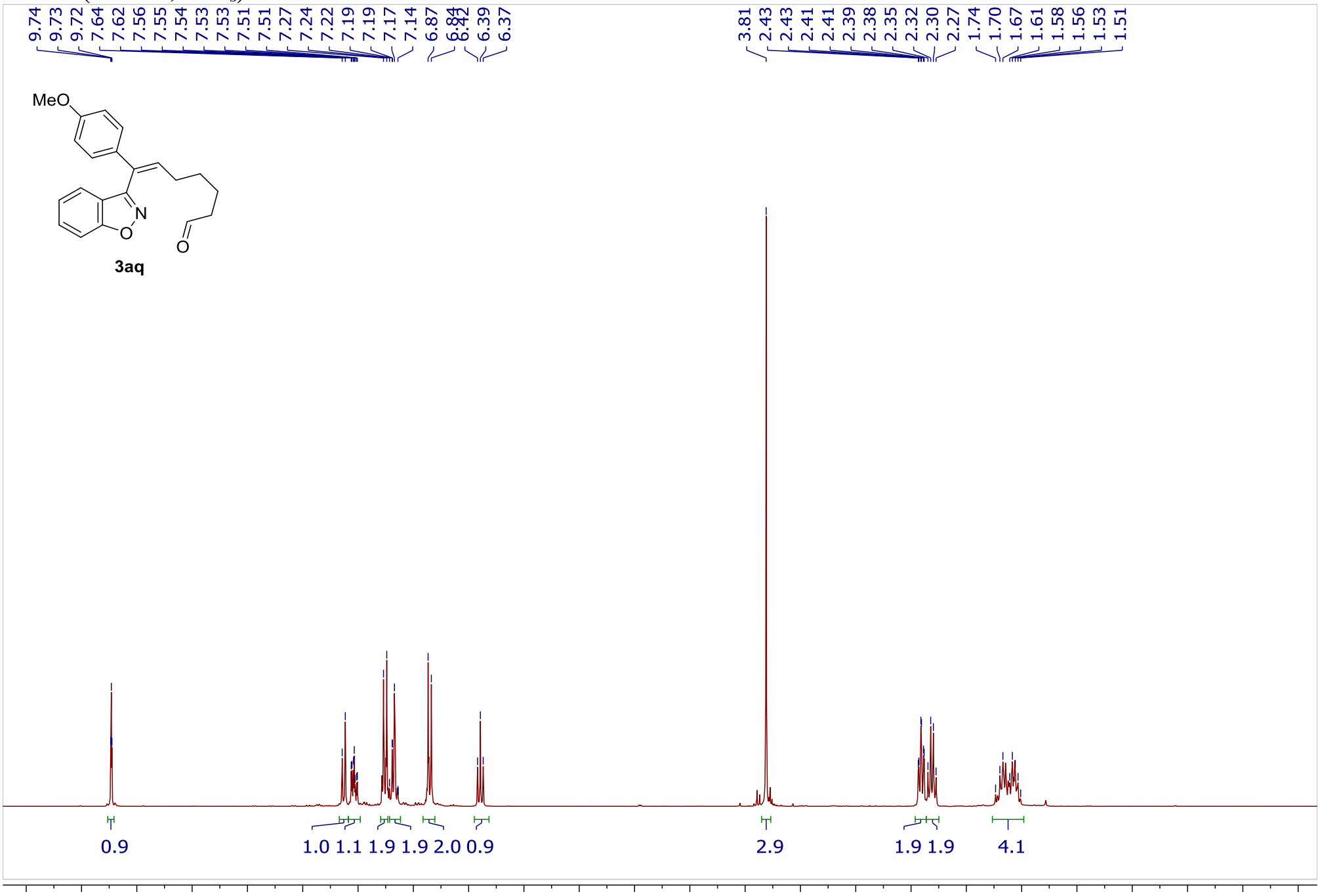

MeO
N
O
O
(E)-3ap
+
MeO
N
O
O
(Z)-3ap
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

$^{1}$H-$^{1}$H NOESY

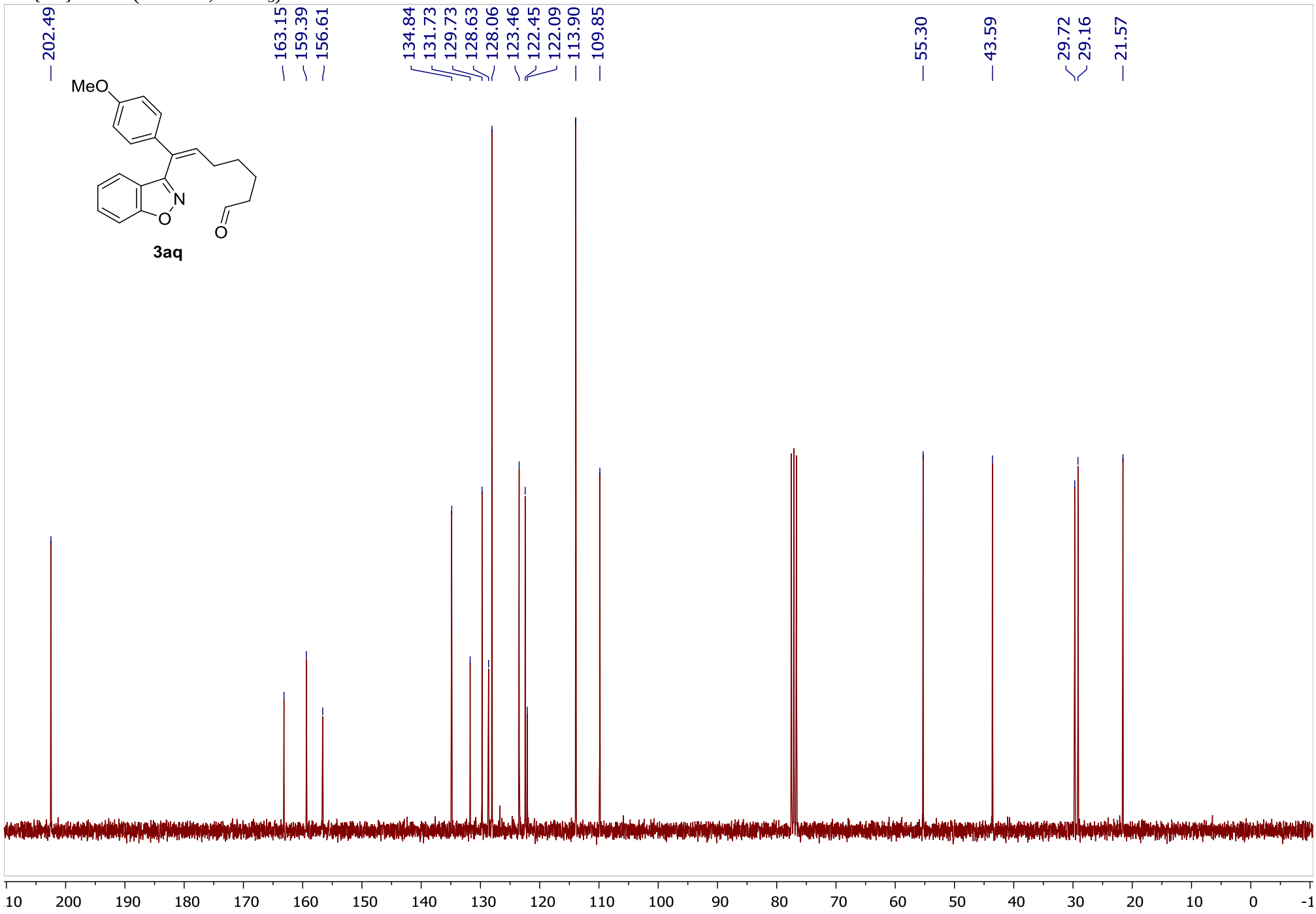

7.24 ppm
NOE
2.40 ppm
MeO
6.62 ppm
NOE
7.05 ppm
(E)-3ap
+
7.25 ppm
NOE
6.37 ppm
MeO
(Z)-3ap
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1 2 3 4 5 6 7 8 9 10

**(Z)-7-(Benzo[d]isoxazol-3-yl)-7-(4-methoxyphenyl)hept-6-enal 3aq**

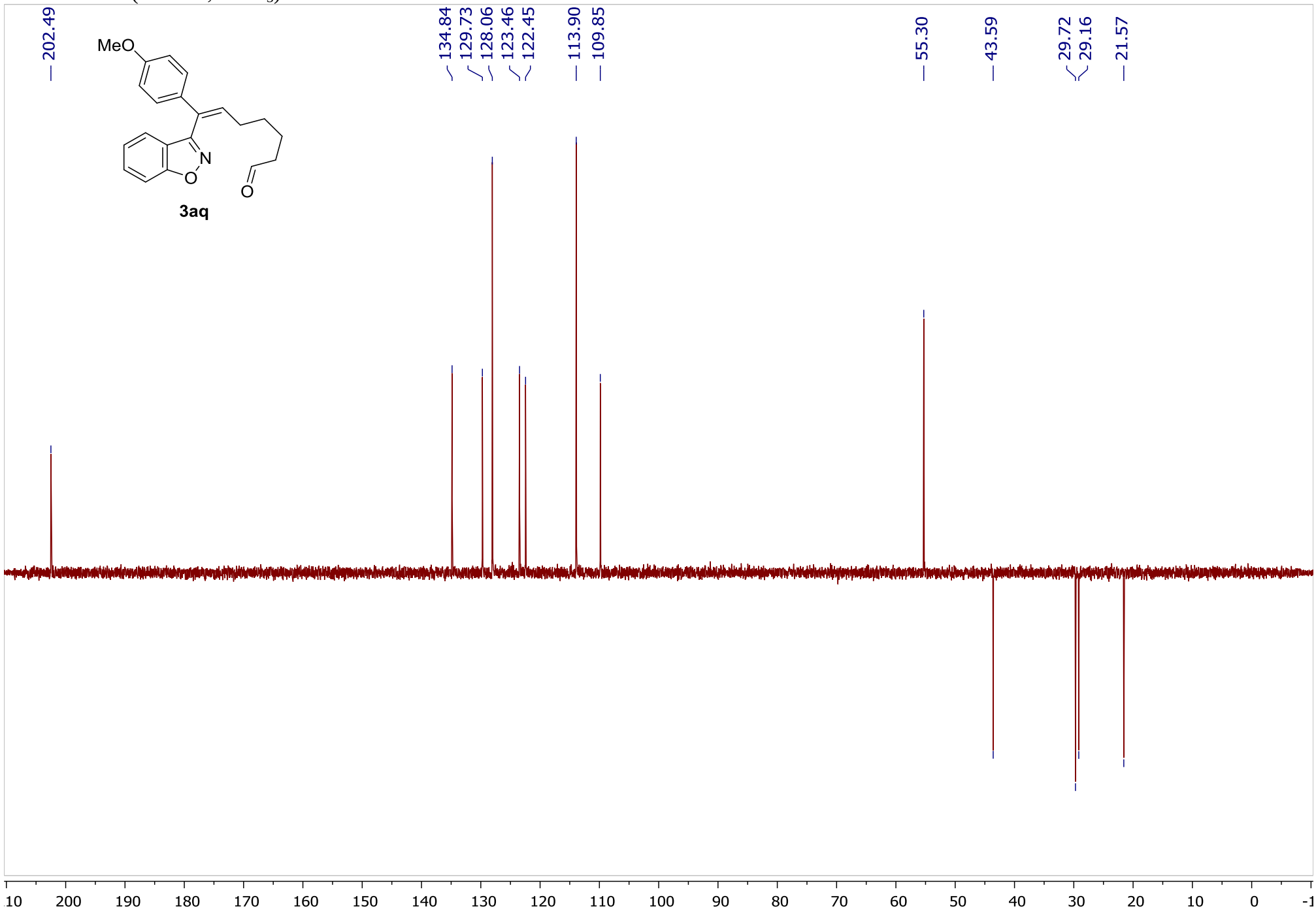
$^1$H NMR (300 MHz, $CDCl_3$)



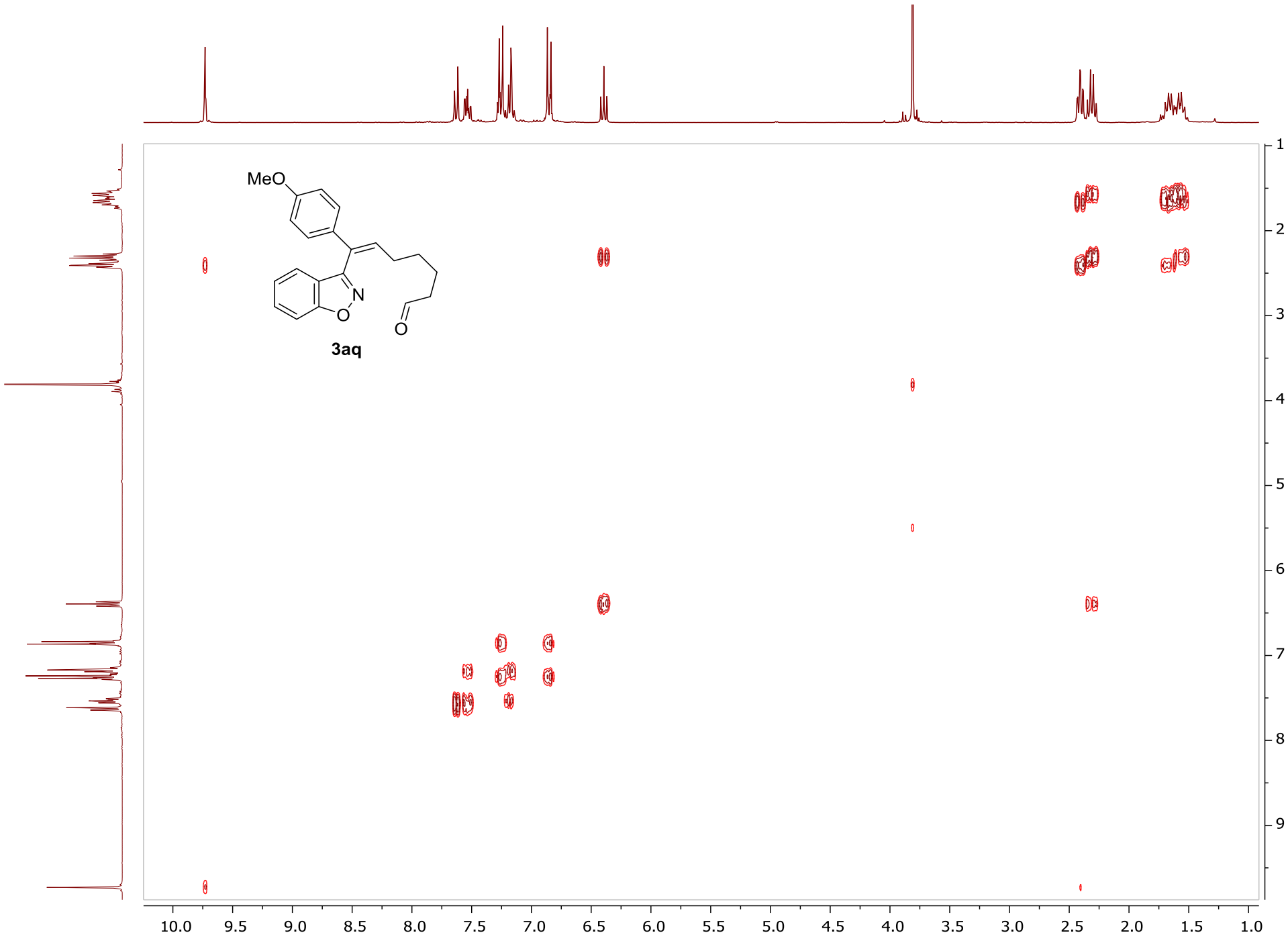
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



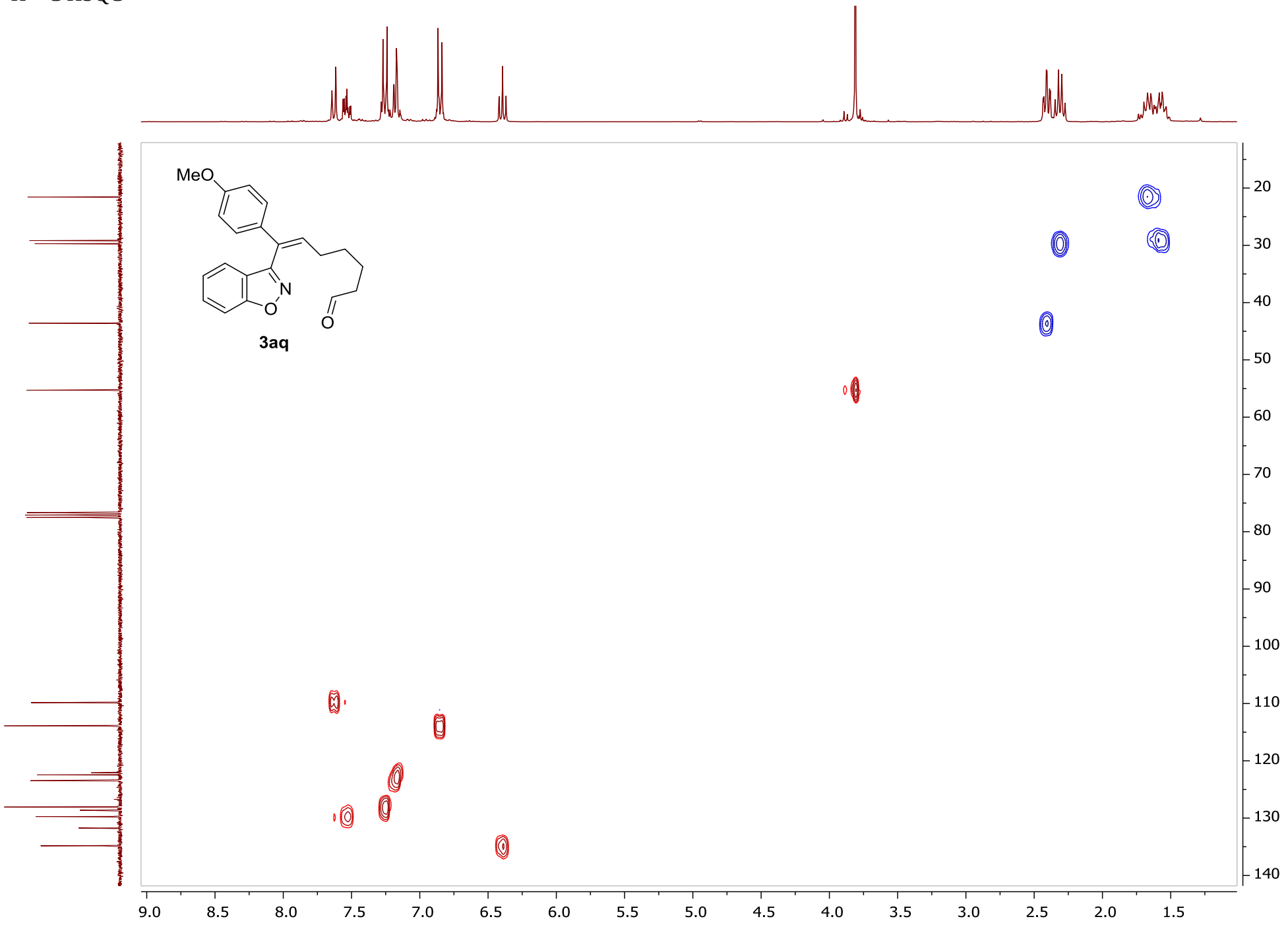
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



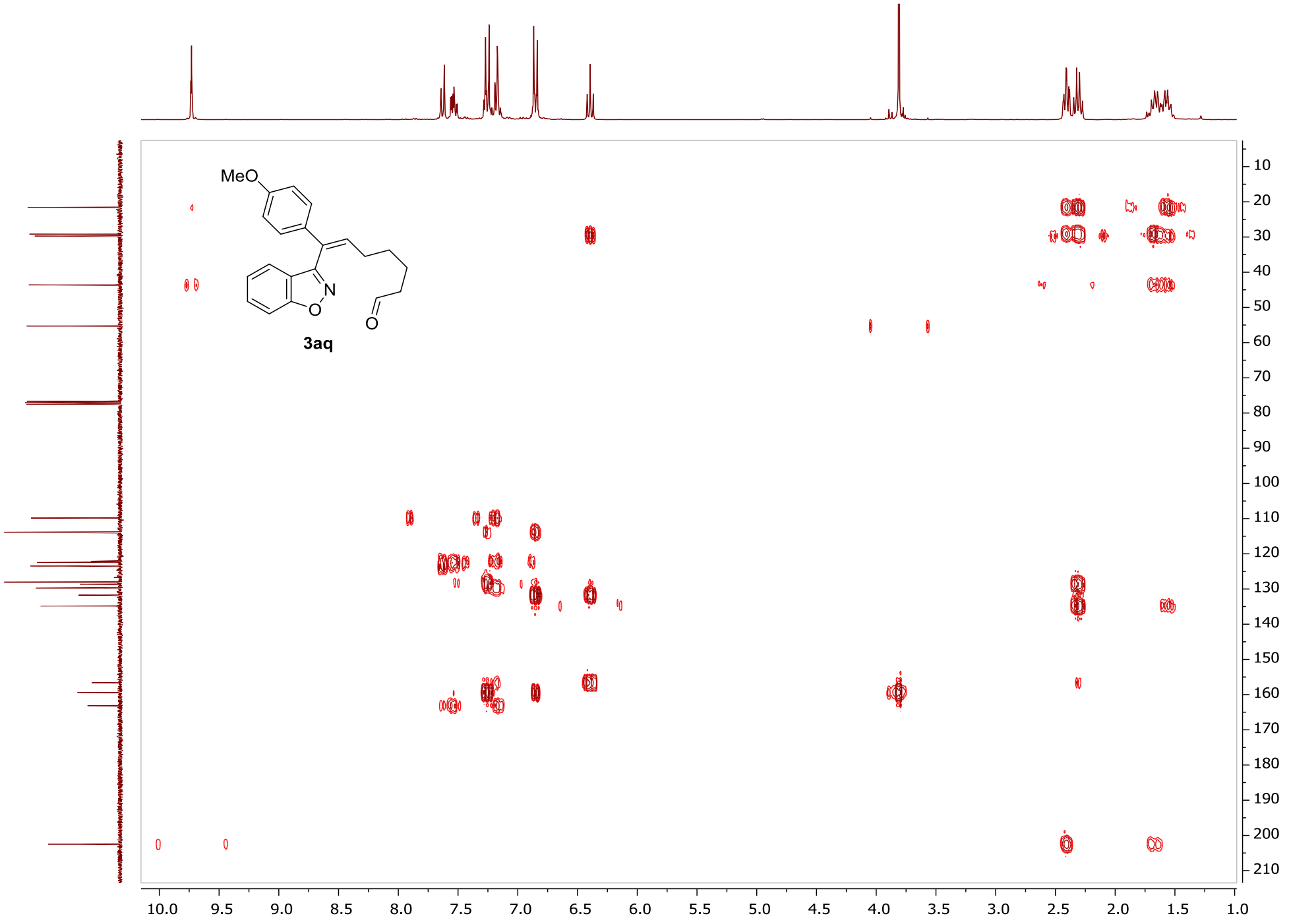
$^{1}$H-$^{1}$H COSY


MeO
N
O
O
3aq
1
2
3
4
5
6
7
8
9
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

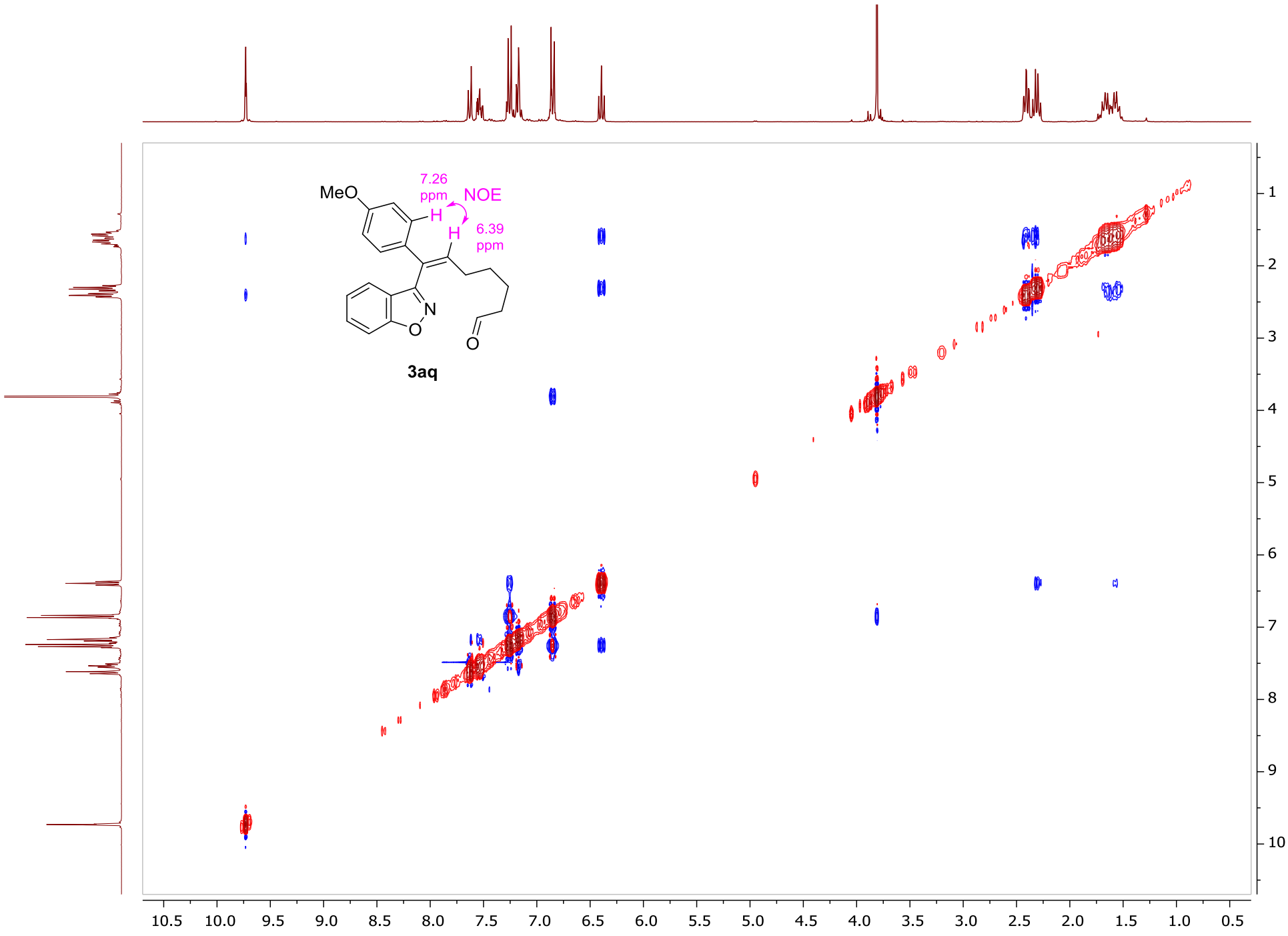
$^{1}$H-$^{13}$C HSQC


MeO
N
O
O
3aq
20
30
40
50
60
70
80
90
100
110
120
130
140
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

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

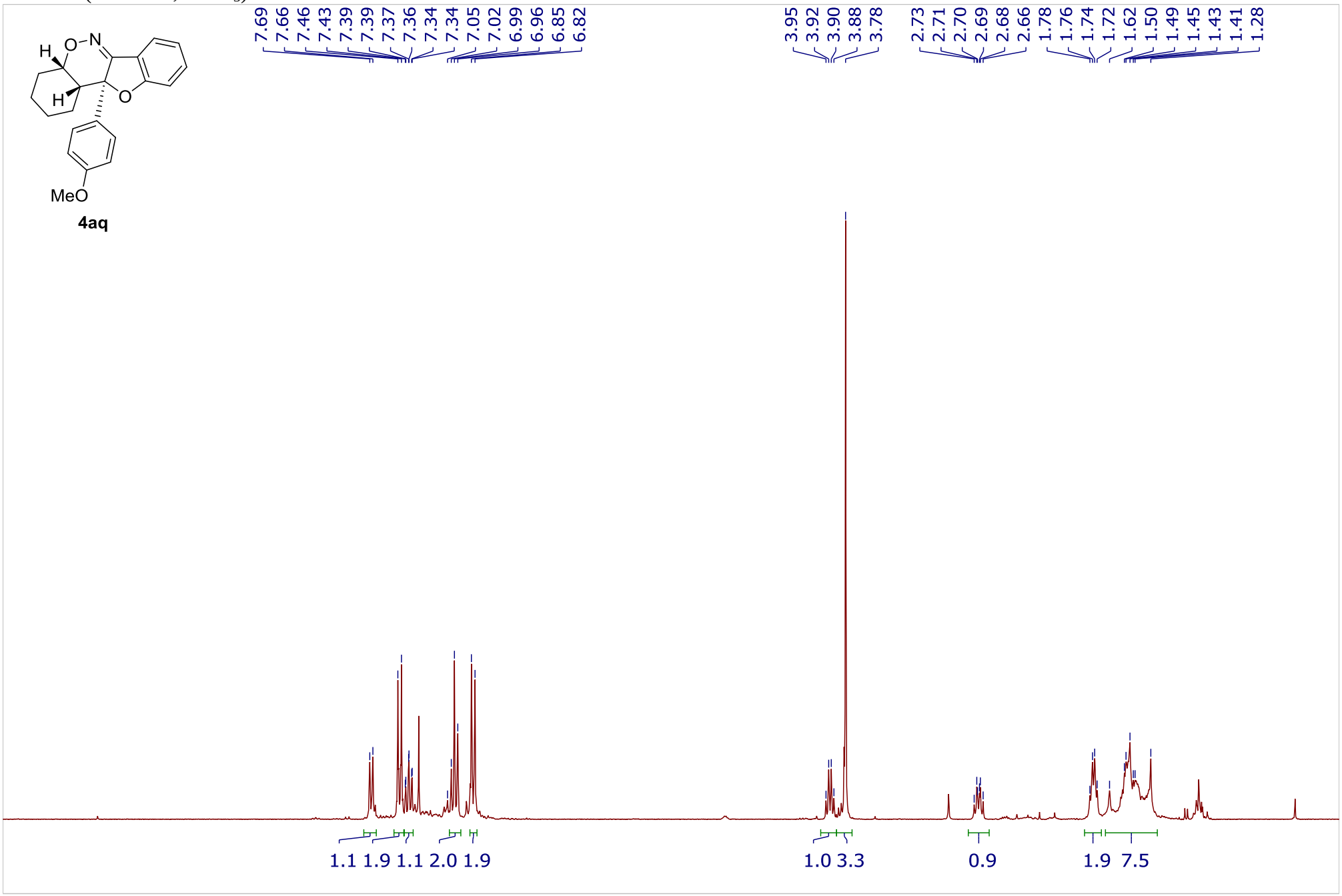

MeO
N
O
O
3aq
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

$^{1}$H-$^{1}$H NOESY

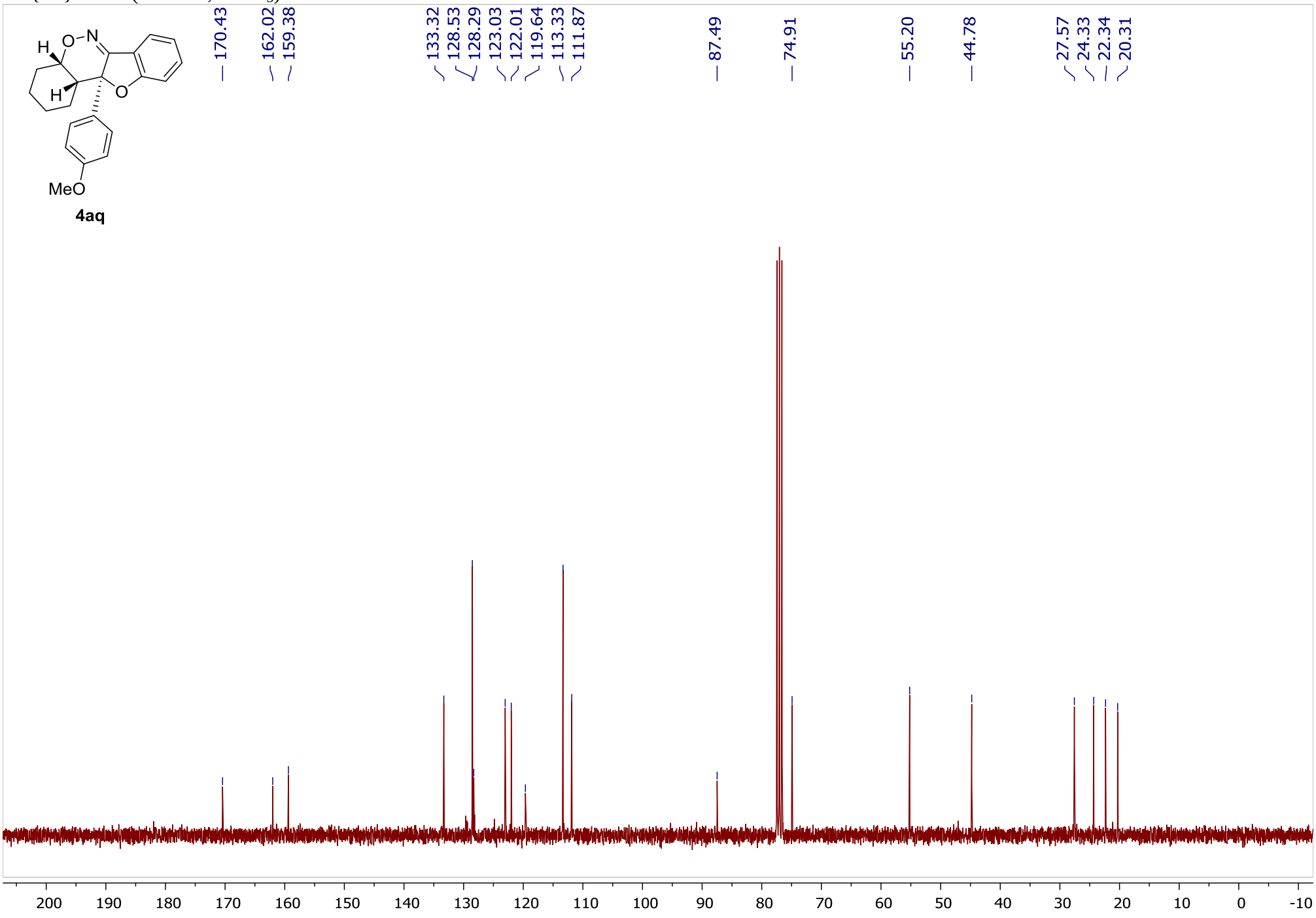

MeO
7.26 ppm
NOE
H
H
6.39 ppm
N
O
O
3aq
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1
2
3
4
5
6
7
8
9
10

**(4a*S**,11a*R**,11b*R**)-11a-(4-Methoxyphenyl)-2,3,4,4a,11a,11b-hexahydro-1H-benzo[e]benzofuro[3,2-c][1,2]oxazine 4aq**

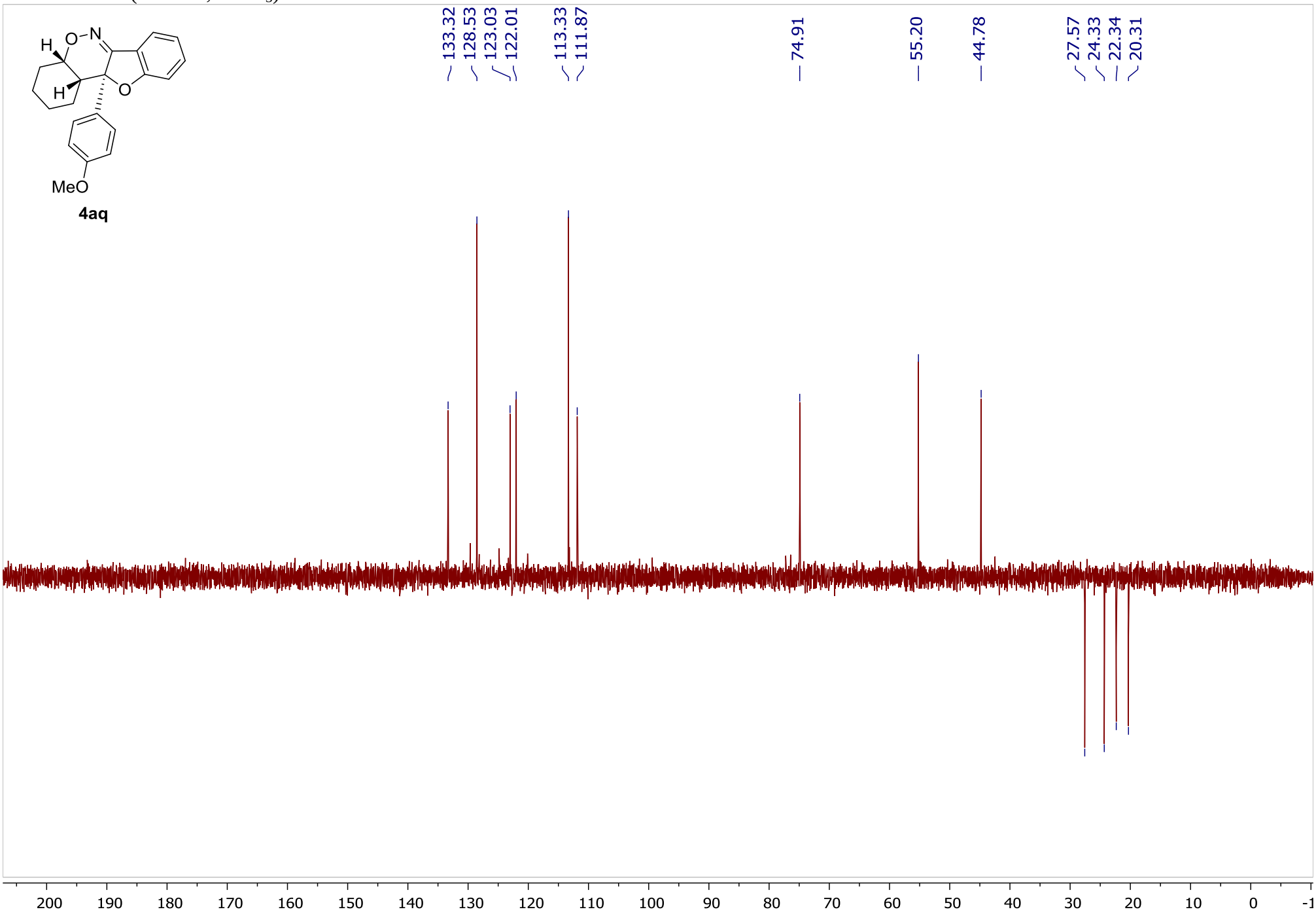
$^1$H NMR (300 MHz, $CDCl_3$)



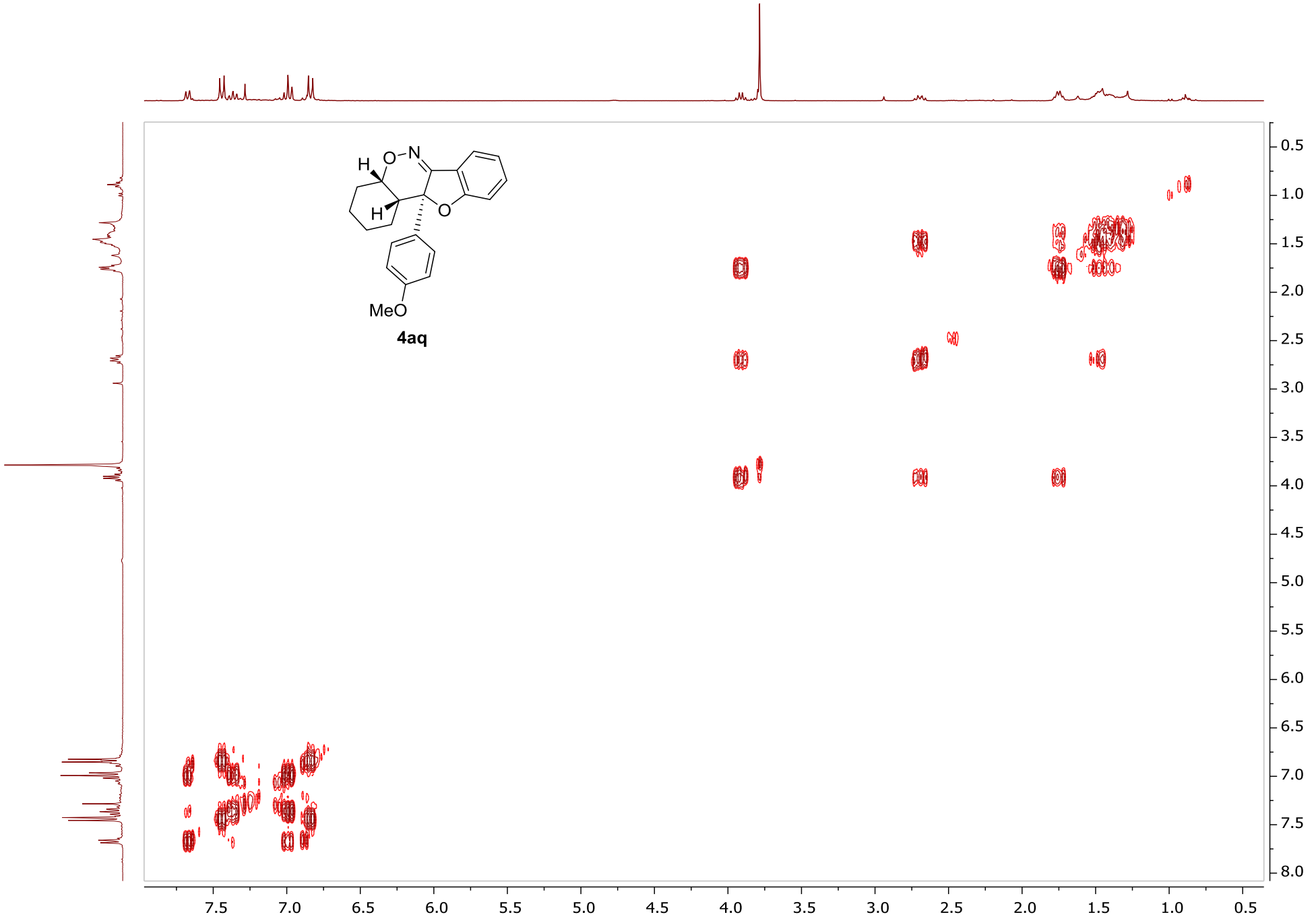
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



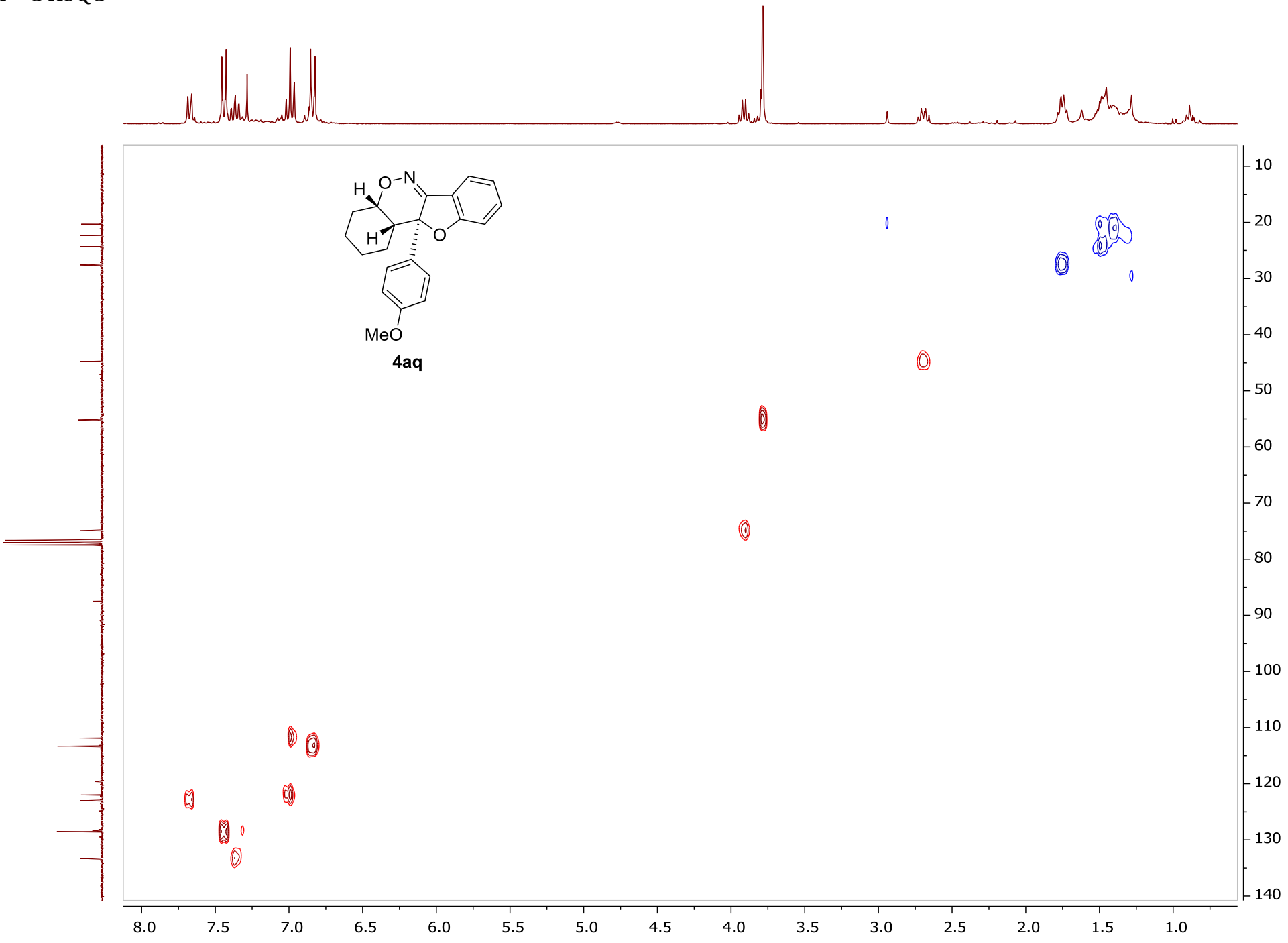
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



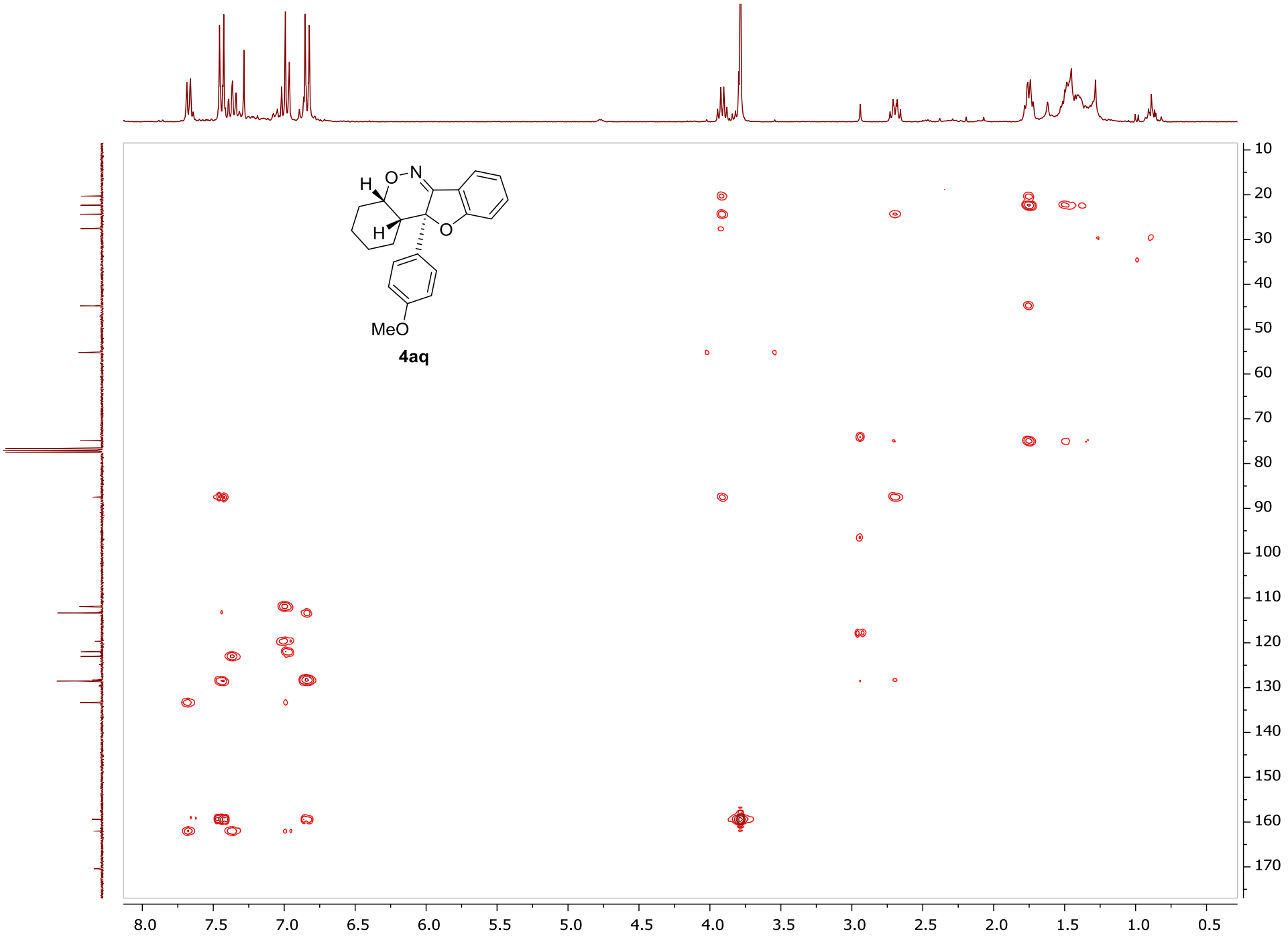
$^{1}$H-$^{1}$H COSY


H
O–N
H
O
MeO
4aq
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
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

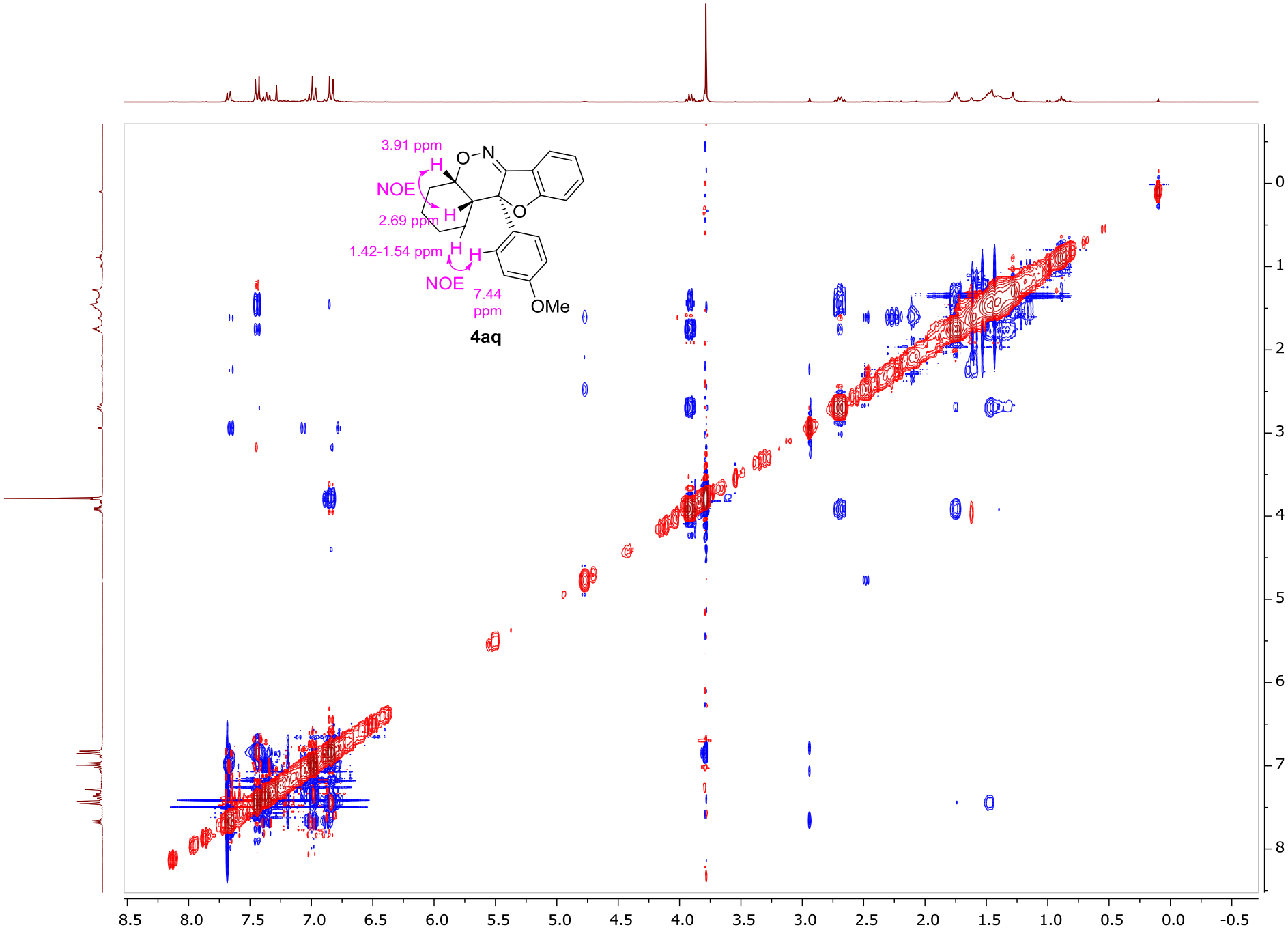
$^{1}$H-$^{13}$C HSQC


H
O
N
H
O
MeO
4aq
10
20
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
1.5
1.0

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

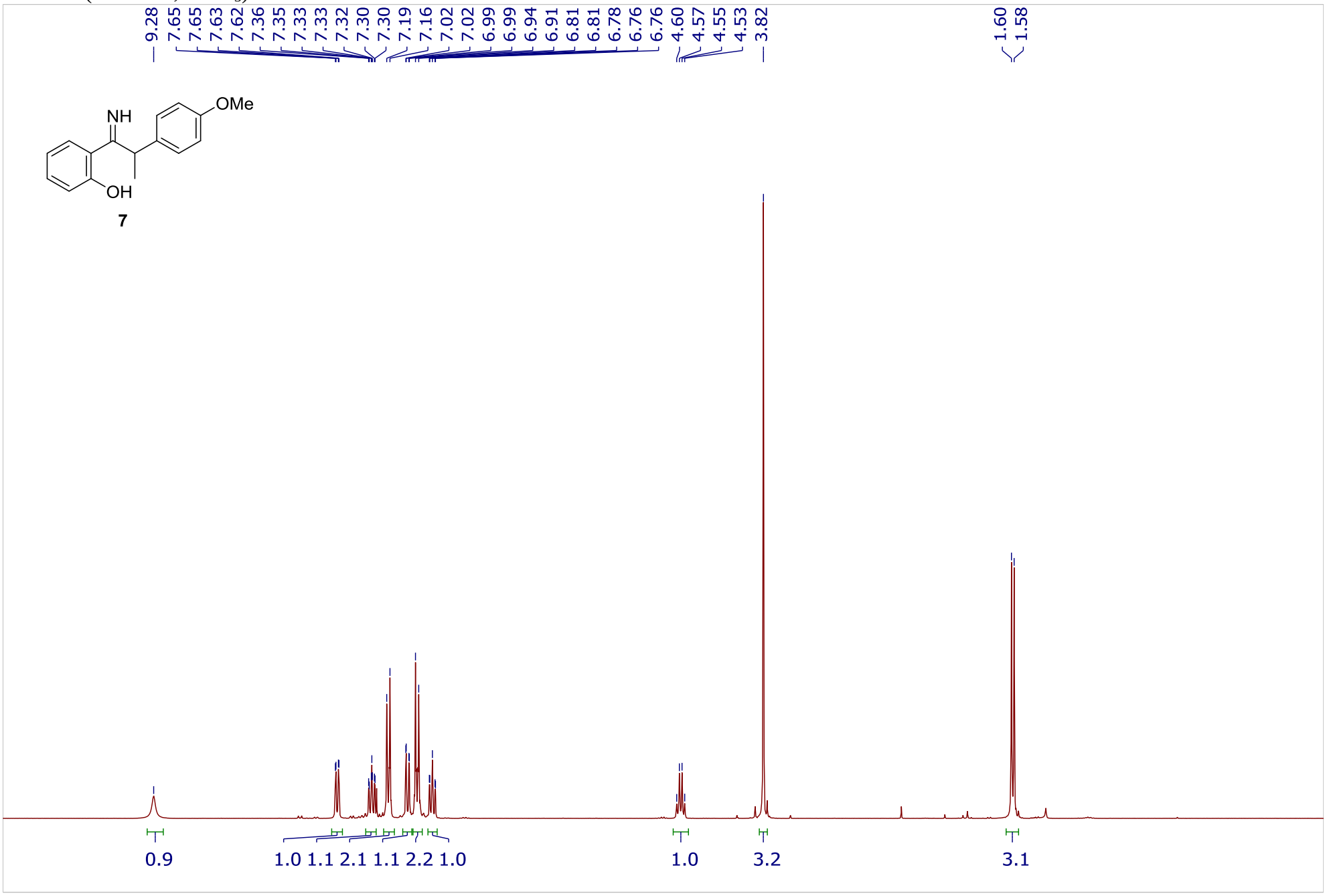

H
O
N
H
O
MeO
4aq
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

$^{1}$H-$^{1}$H NOESY

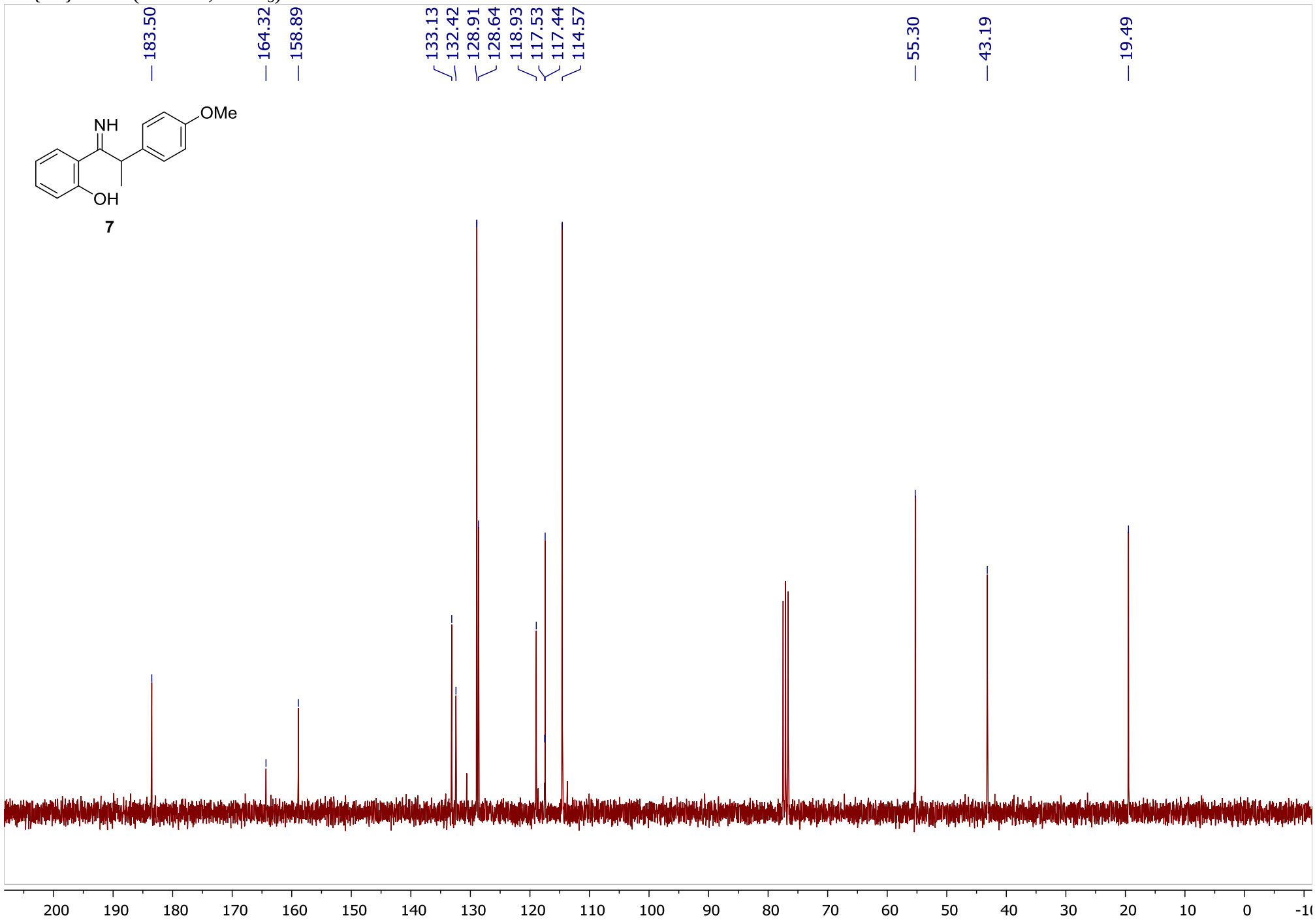

3.91 ppm
H
O
N
NOE
H
2.69 ppm
O
1.42-1.54 ppm
H
H
NOE
7.44
ppm
OMe
4aq
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7
8

**2-(1-Imino-2-(4-methoxyphenyl)propyl)phenol 7**

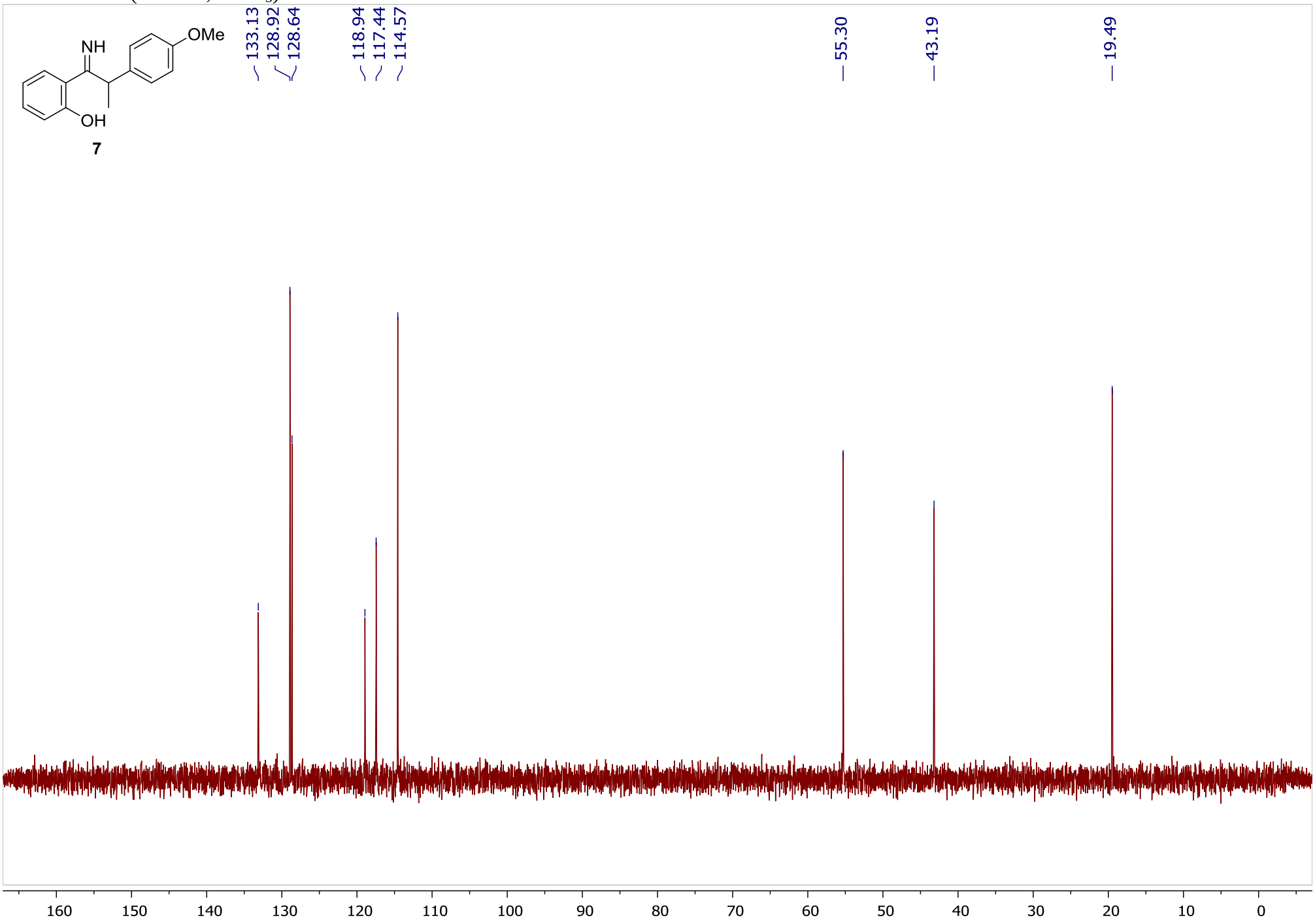
$^1$H NMR (300 MHz, $CDCl_3$)



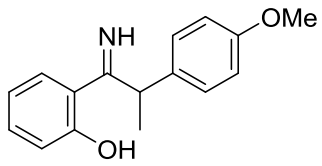
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)

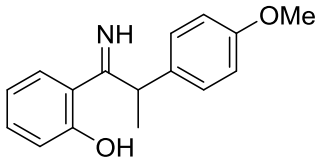


$^{1}H$-$^{1}H$ COSY

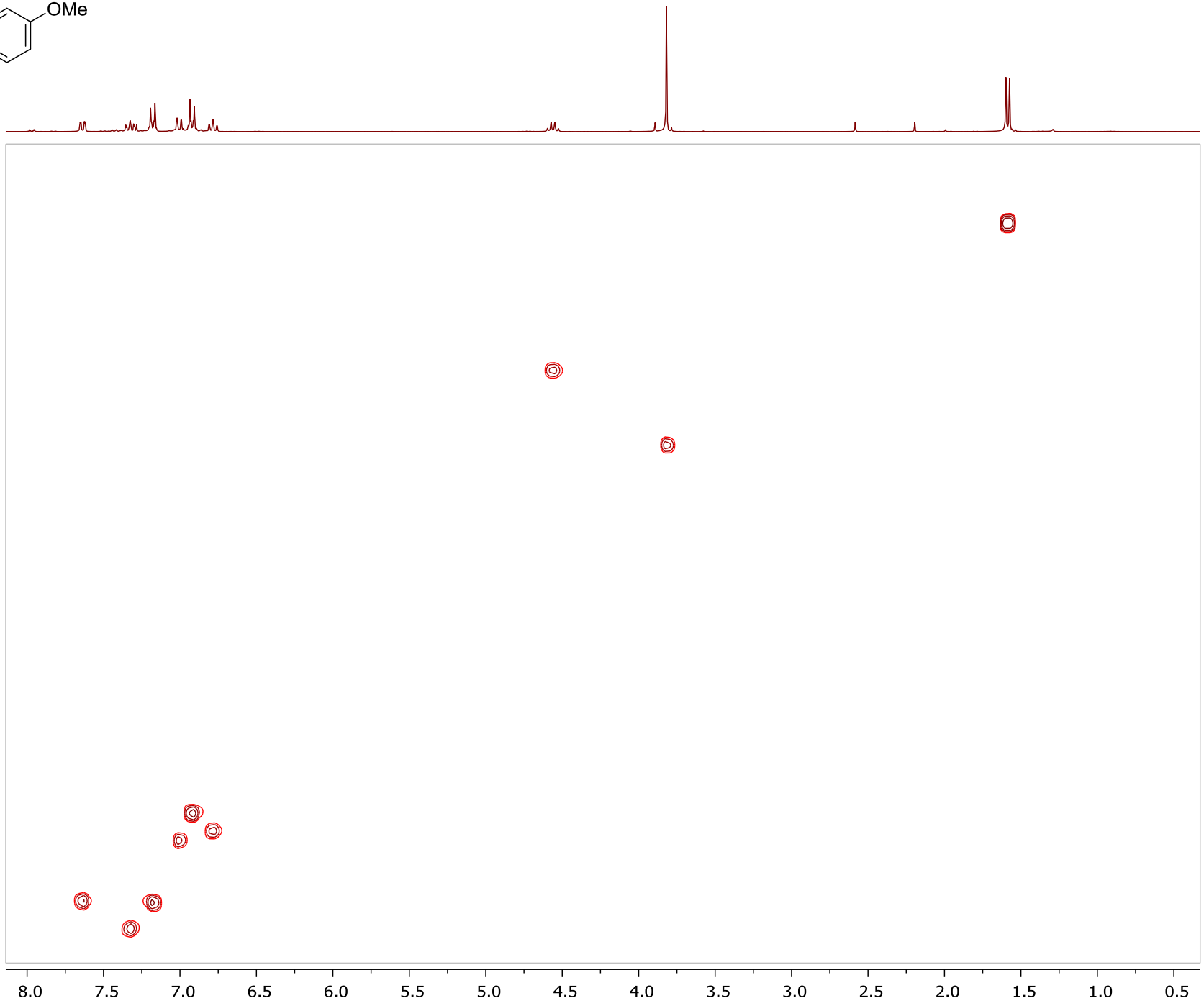



**7**

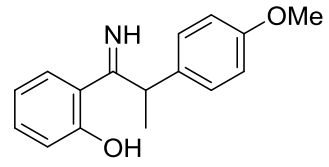
$^{1}H$-$^{13}C$ HSQC


NH
OMe
OH

**7**


10
20
30
40
50
60
70
80
90
100
110
120
130
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

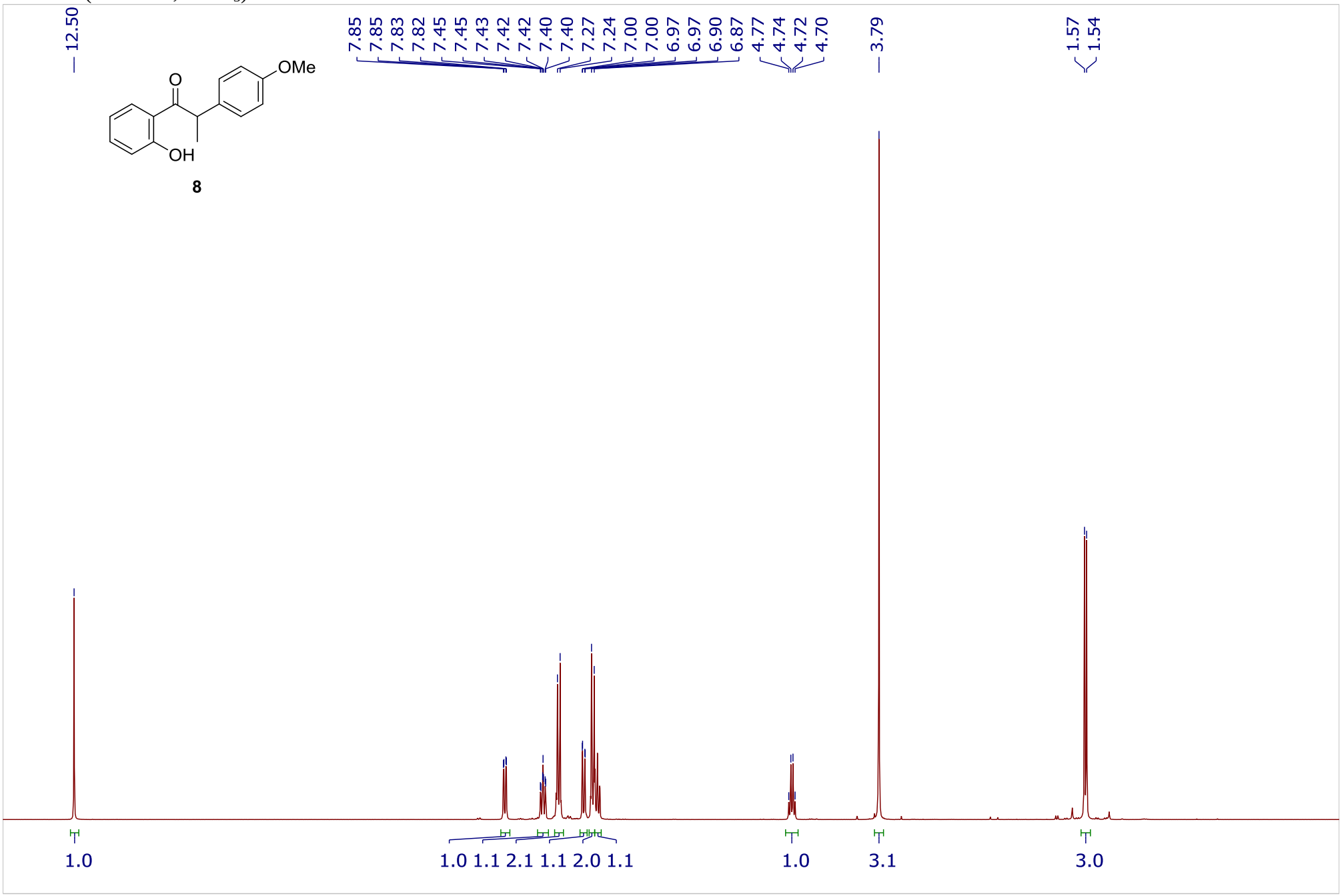

NH
OMe
OH

**7**

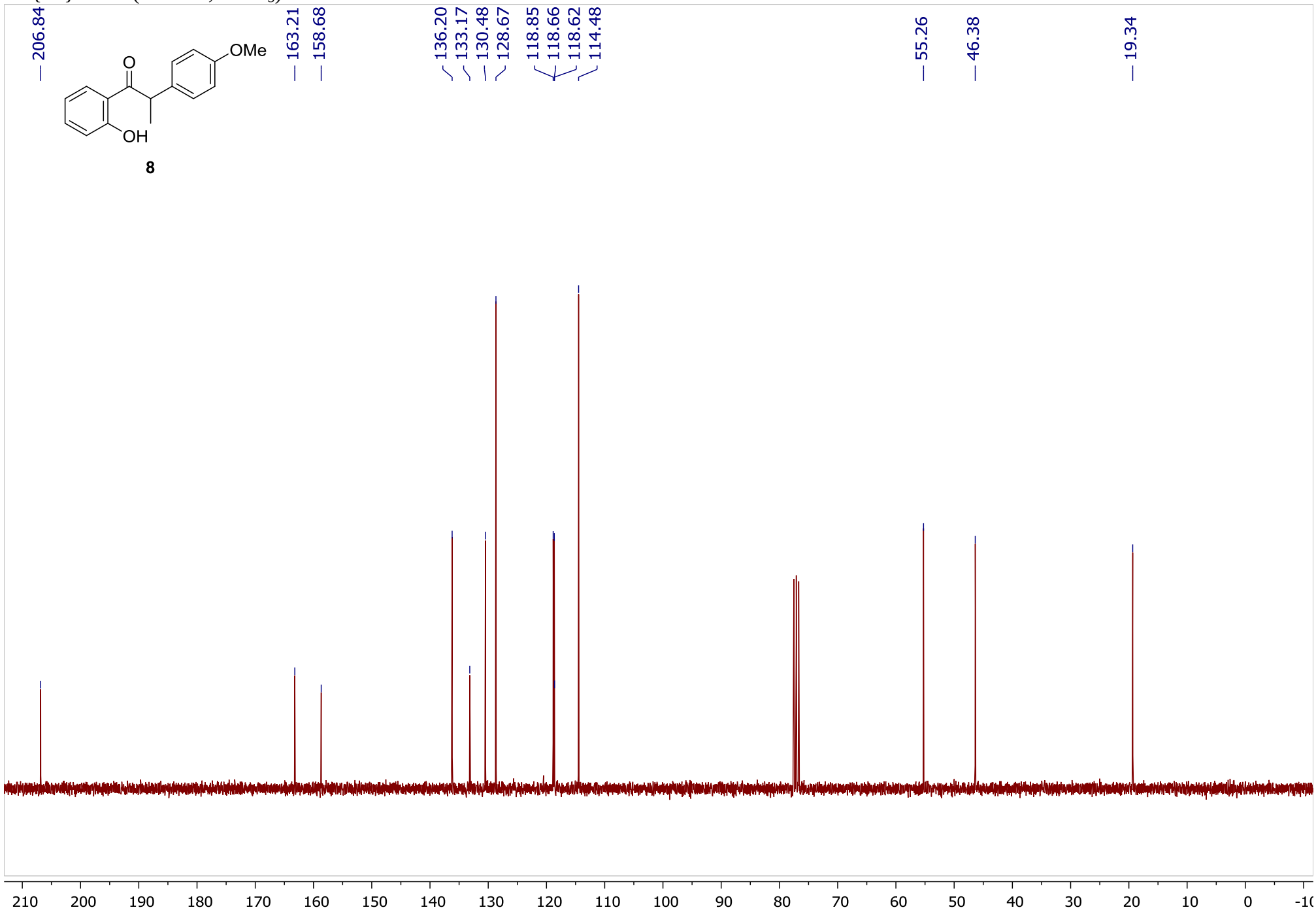

10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

**1-(2-Hydroxyphenyl)-2-(4-methoxyphenyl)propan-1-one 8**

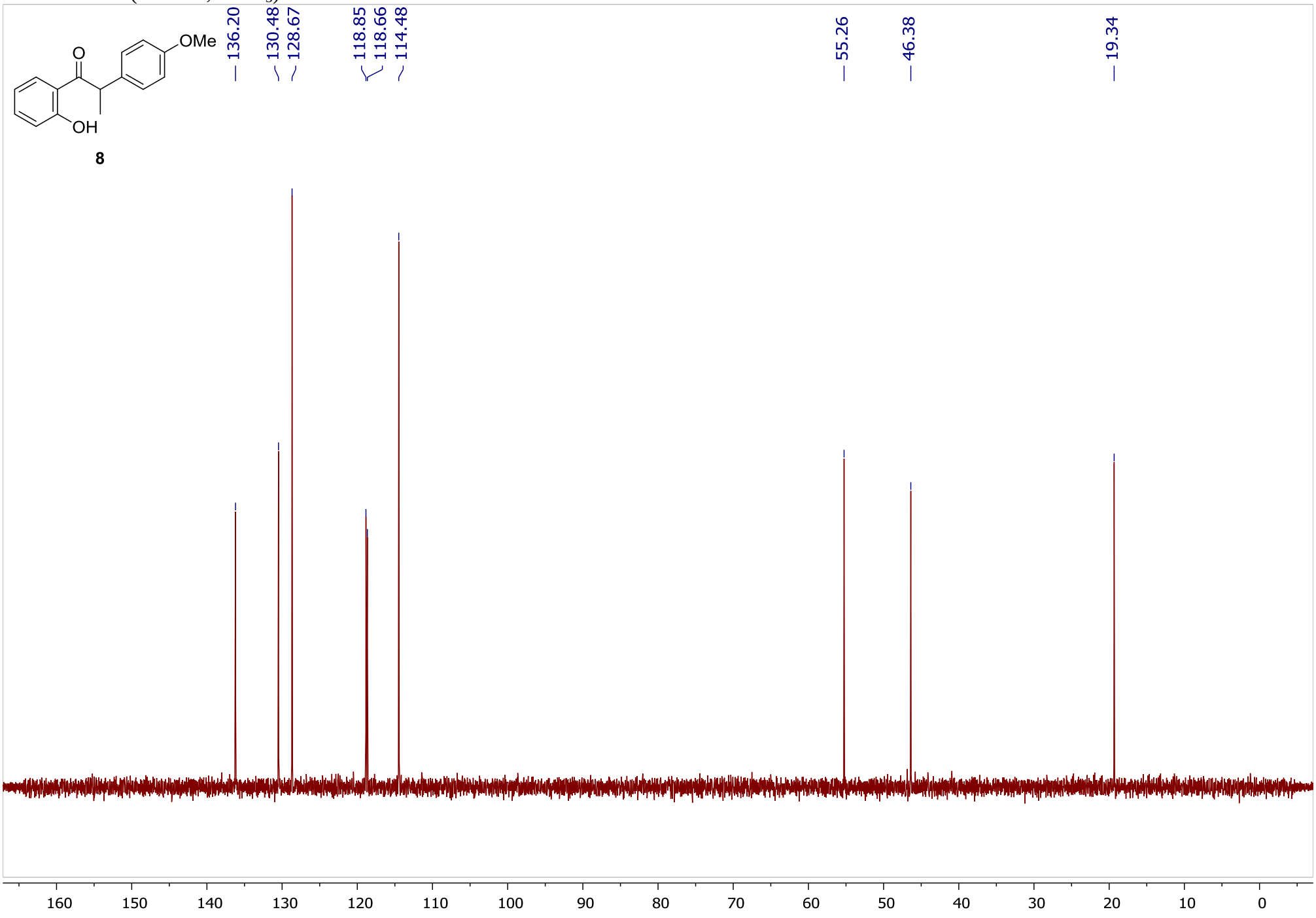
$^1$H NMR (300 MHz, $CDCl_3$)



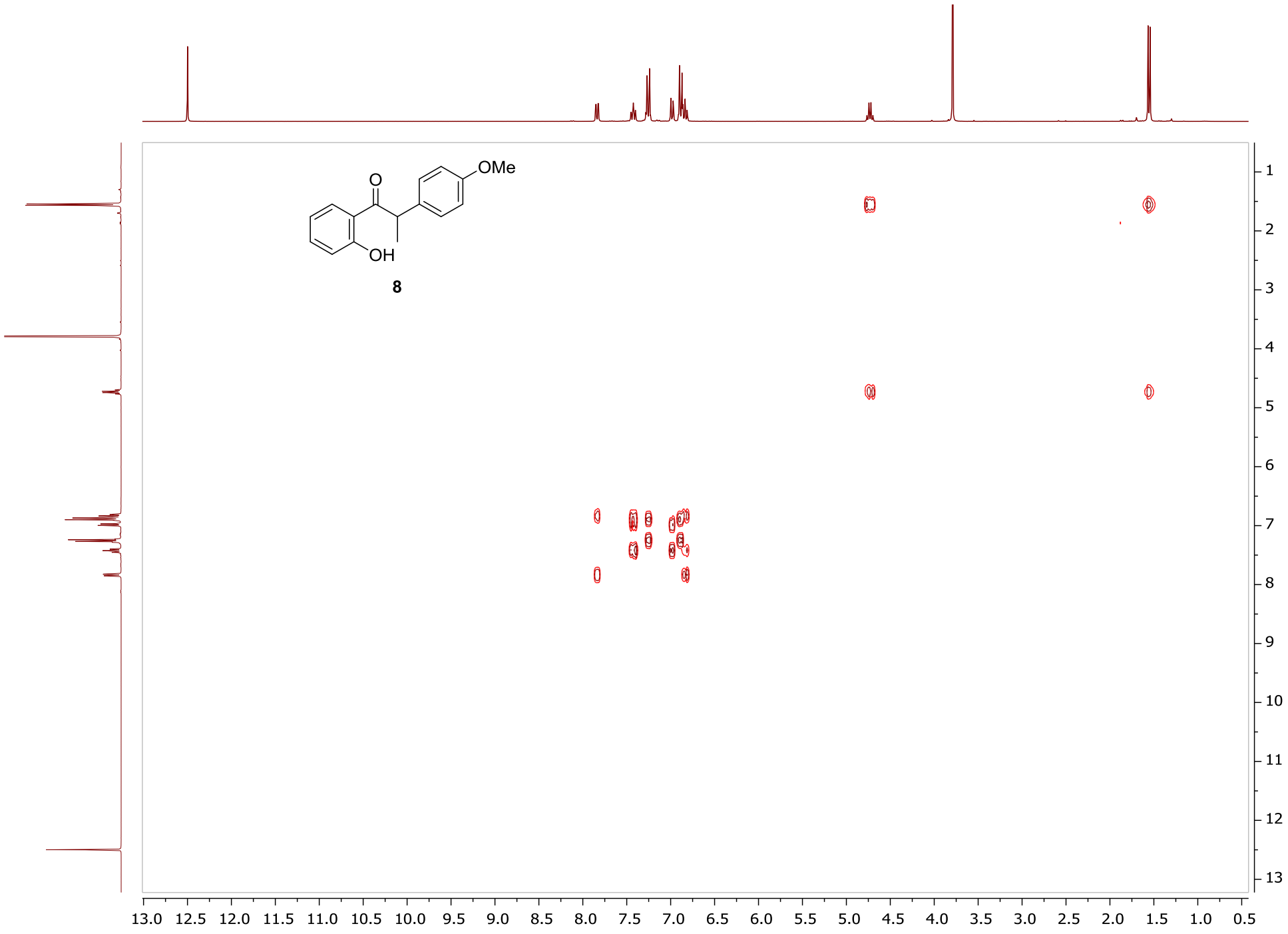
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



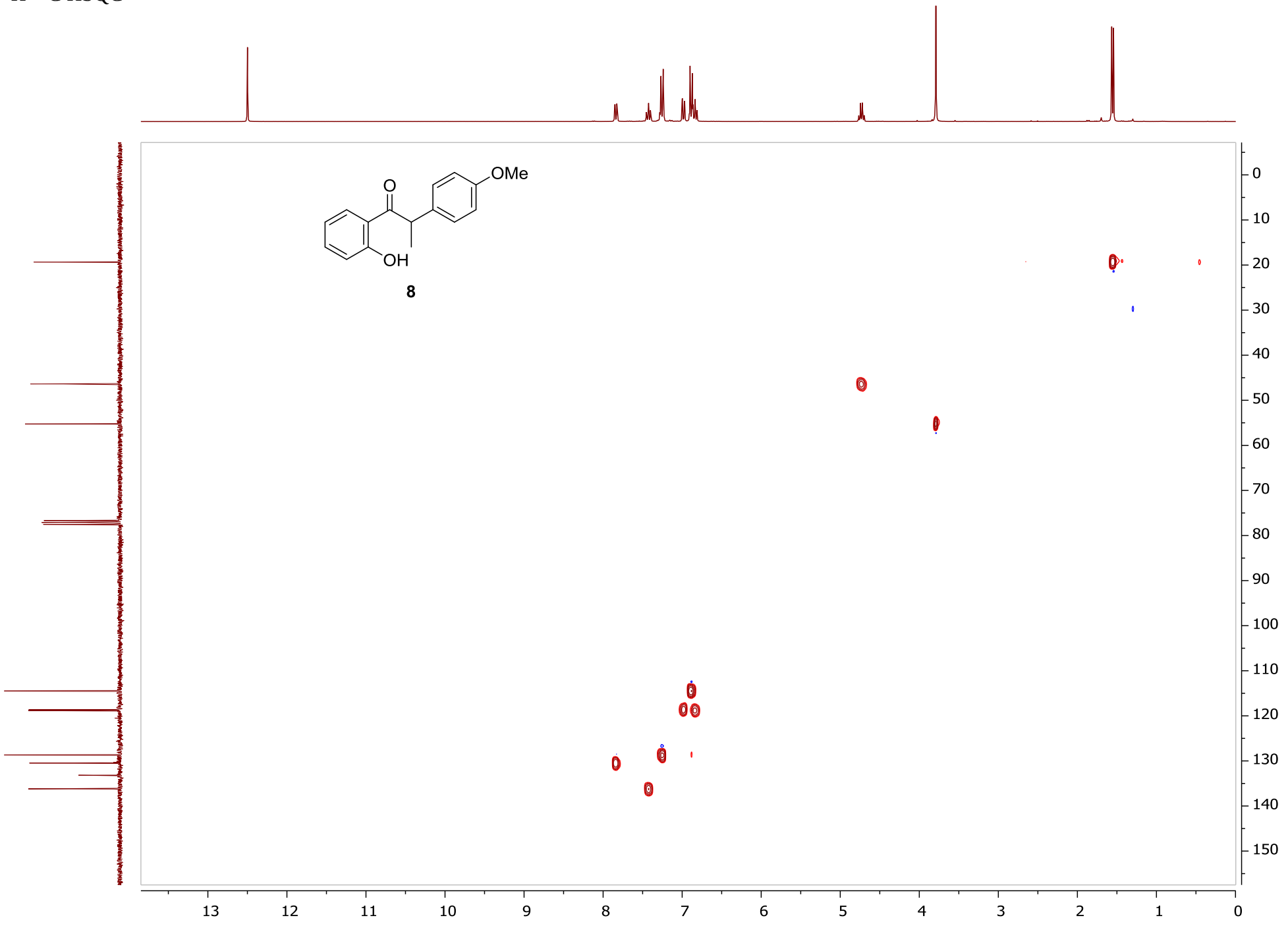
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



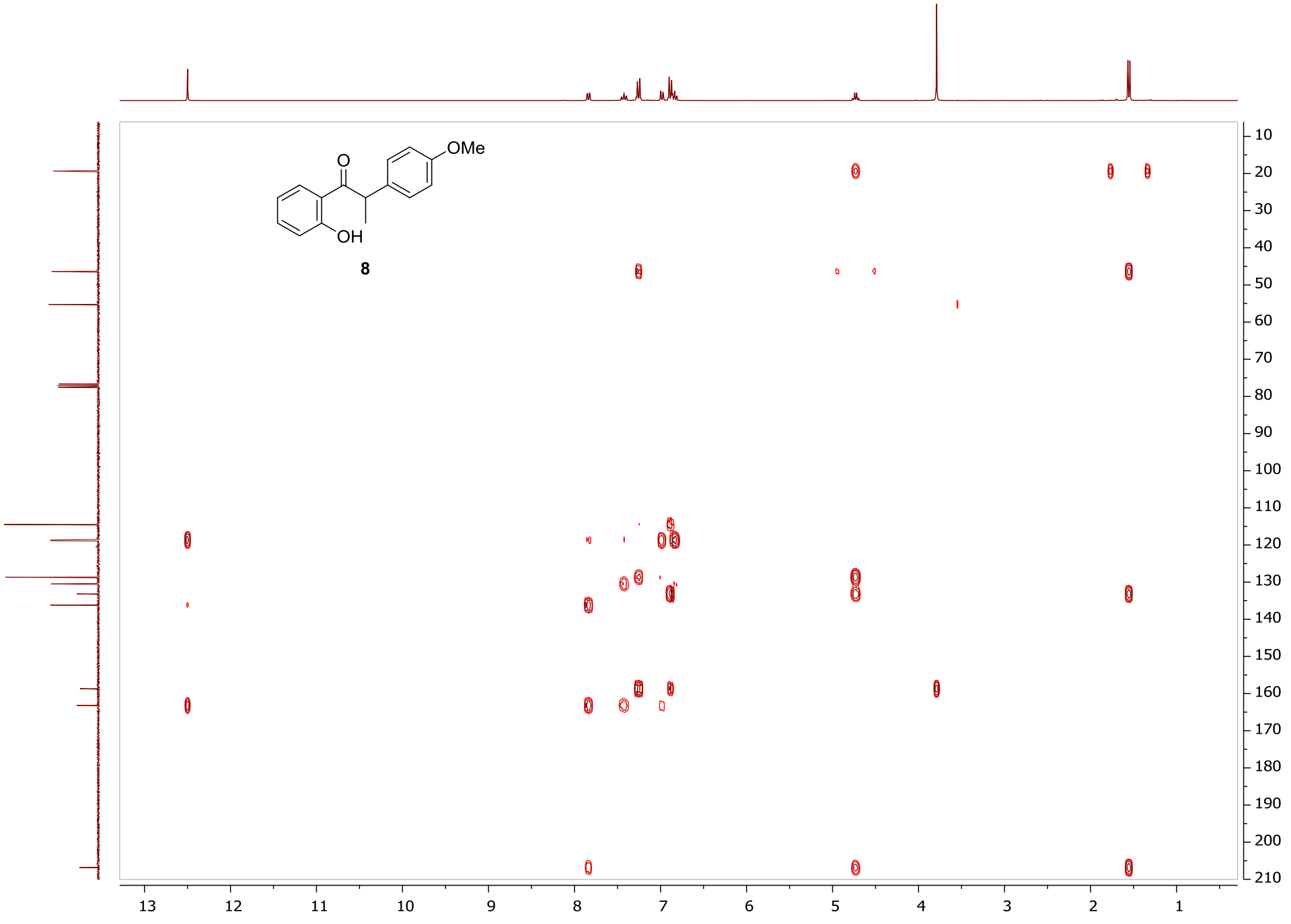
$^{1}$H-$^{1}$H COSY


O
OMe
OH
8
1
2
3
4
5
6
7
8
9
10
11
12
13
13.0 12.5 12.0 11.5 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

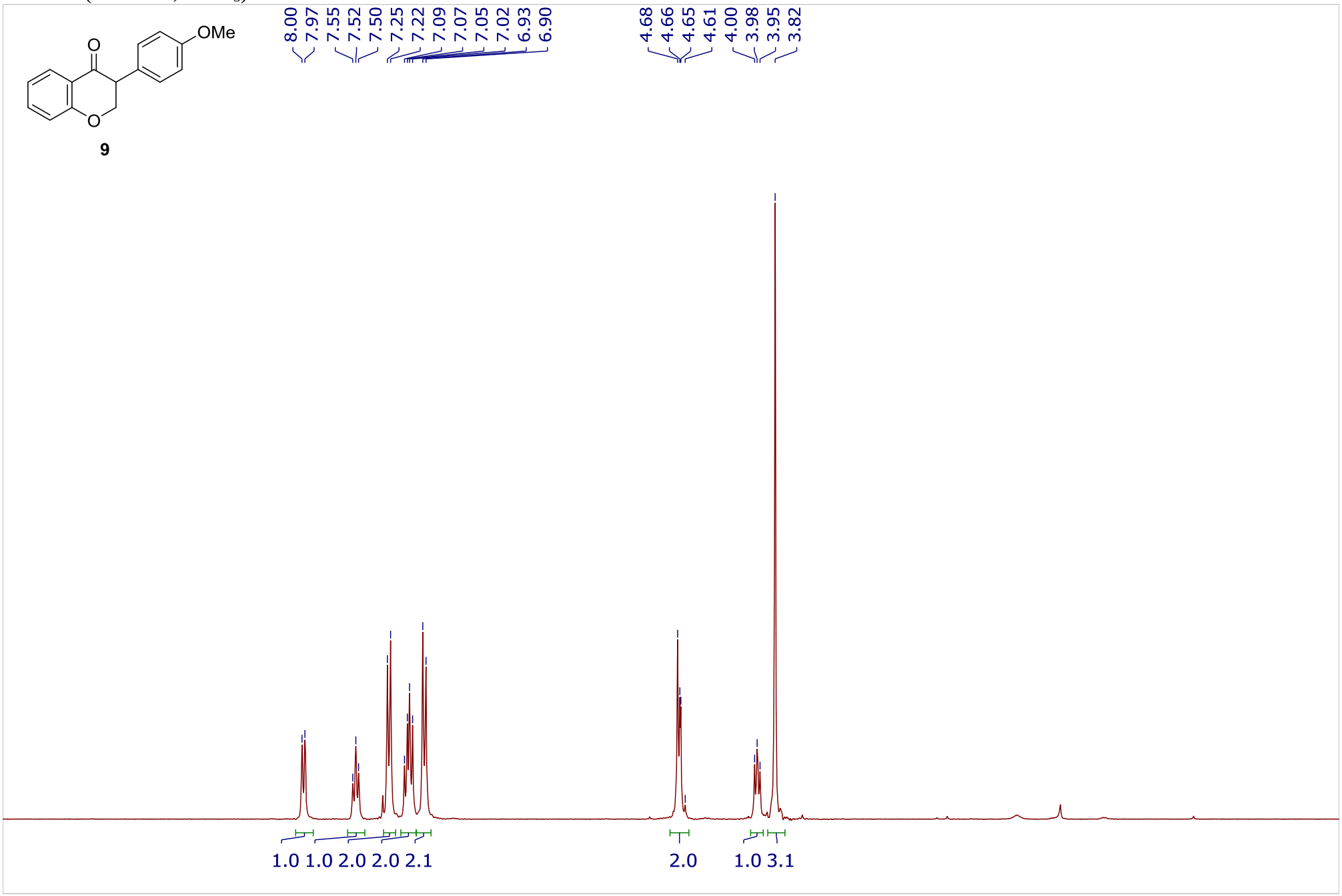

O
OMe
OH
8
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
13
12
11
10
9
8
7
6
5
4
3
2
1
0

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


O
OMe
OH
8
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
13
12
11
10
9
8
7
6
5
4
3
2
1

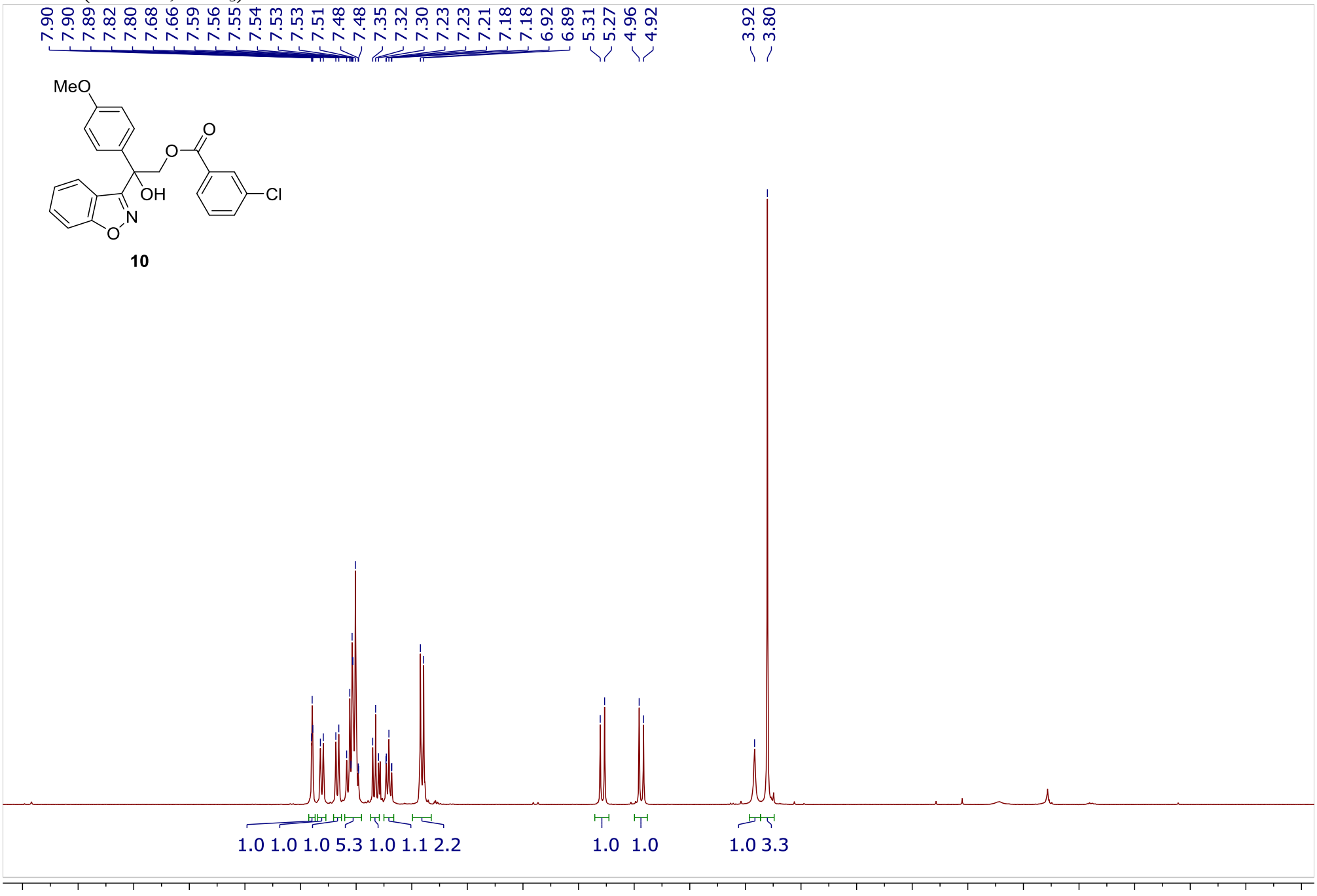
**3-(4-Methoxyphenyl)chroman-4-one 9**

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

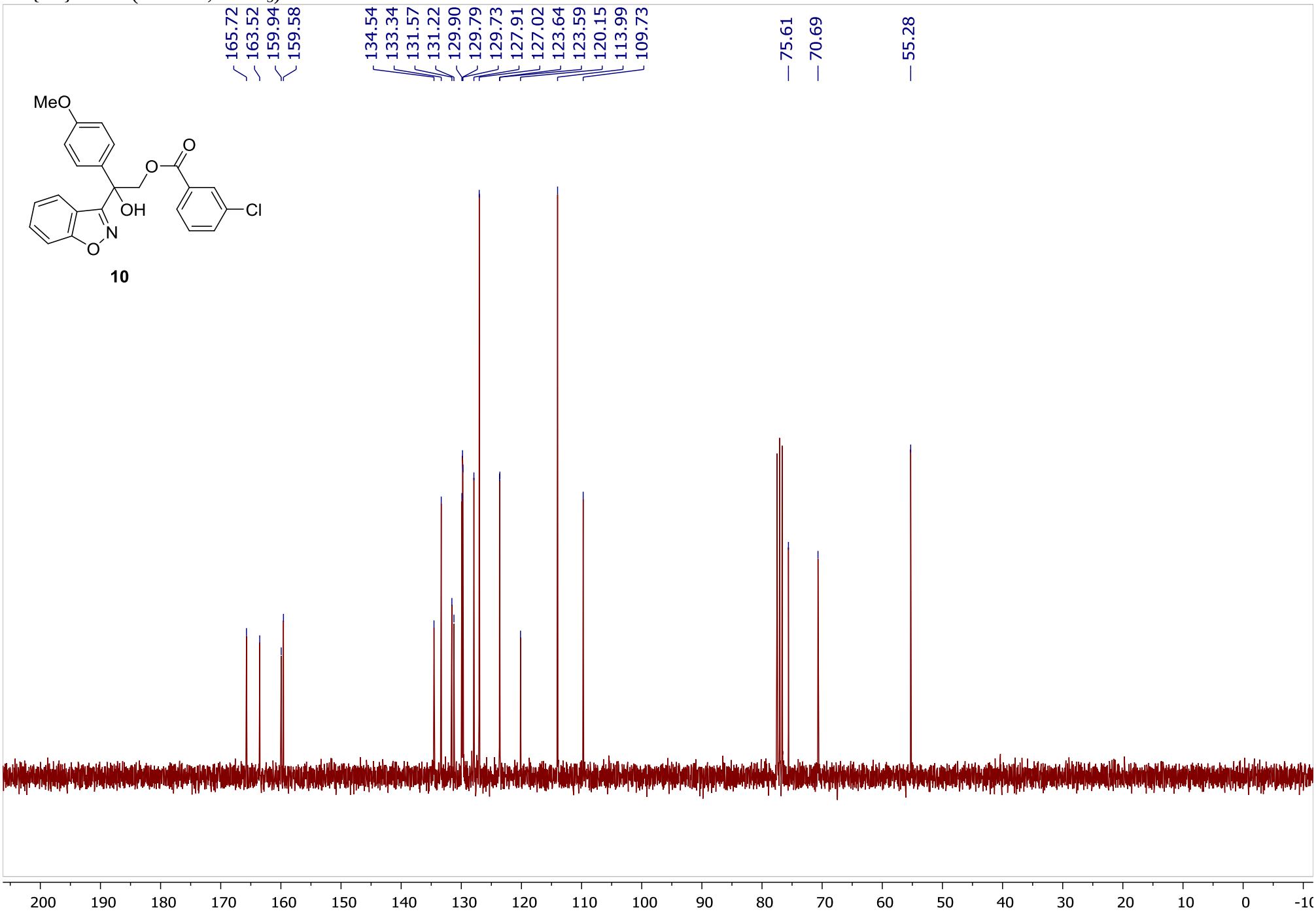


**2-(Benzo[d]isoxazol-3-yl)-2-hydroxy-2-(4-methoxyphenyl)ethyl 3-chlorobenzoate 10**

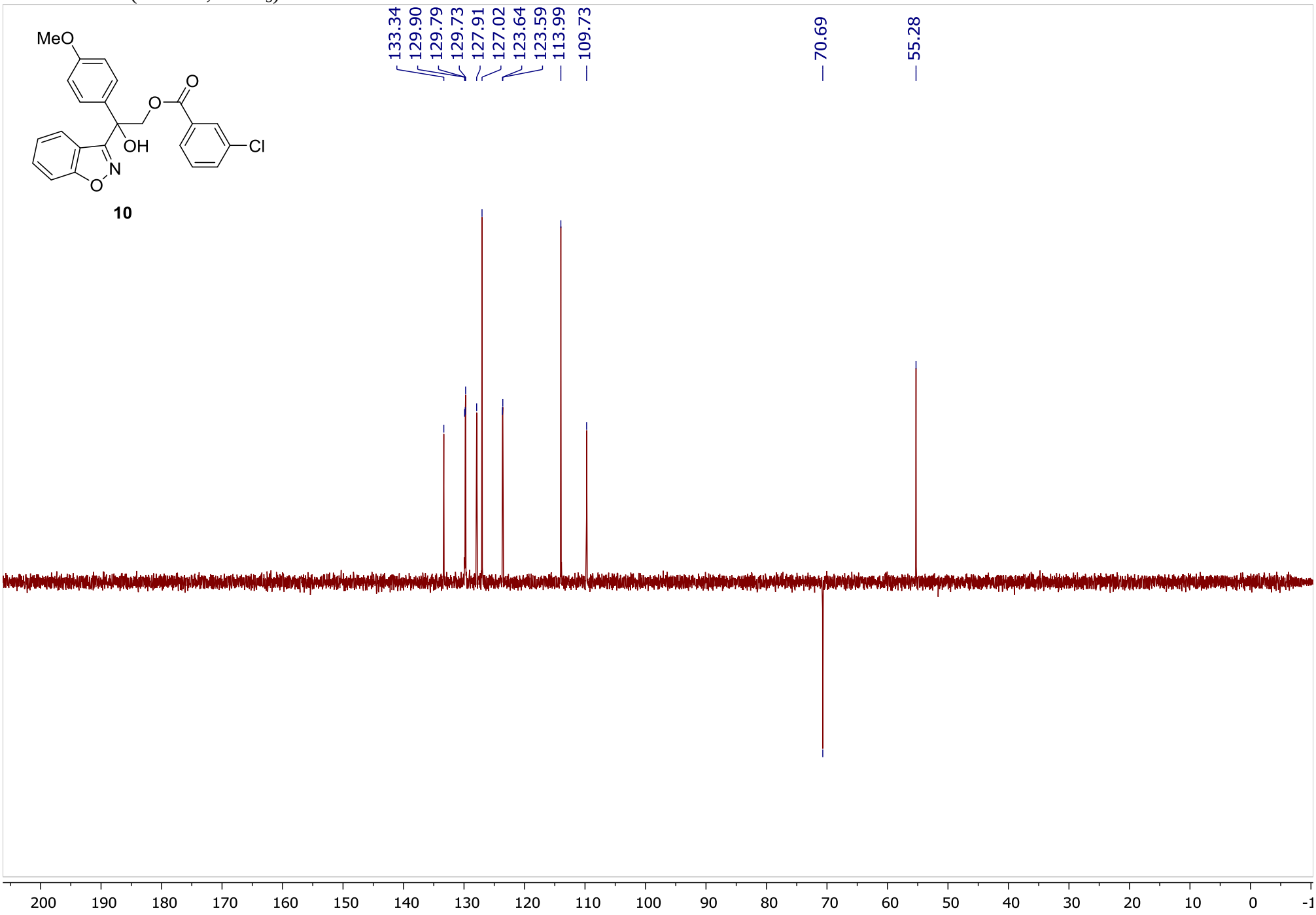
$^1$H NMR (300 MHz, $CDCl_3$)



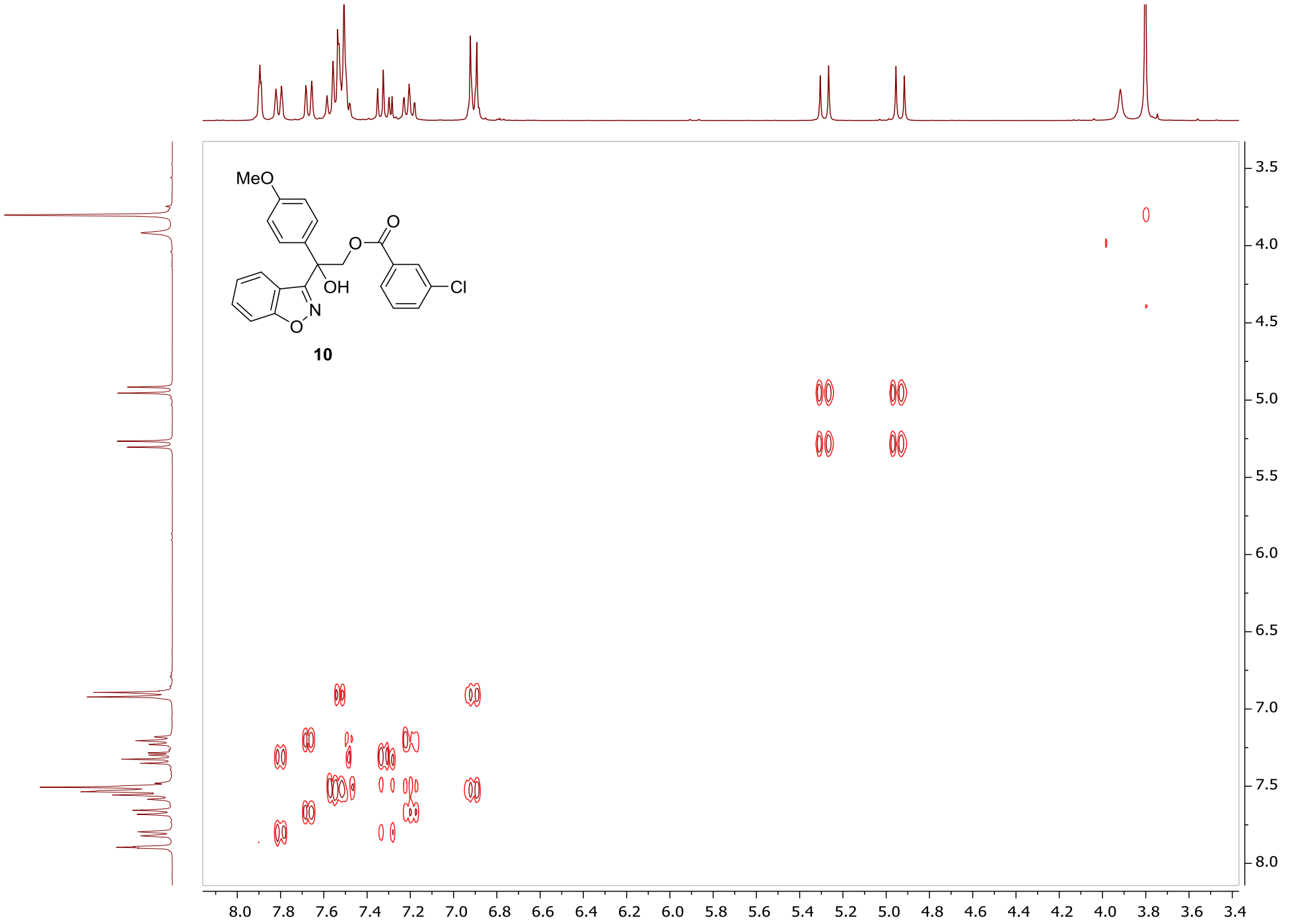
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



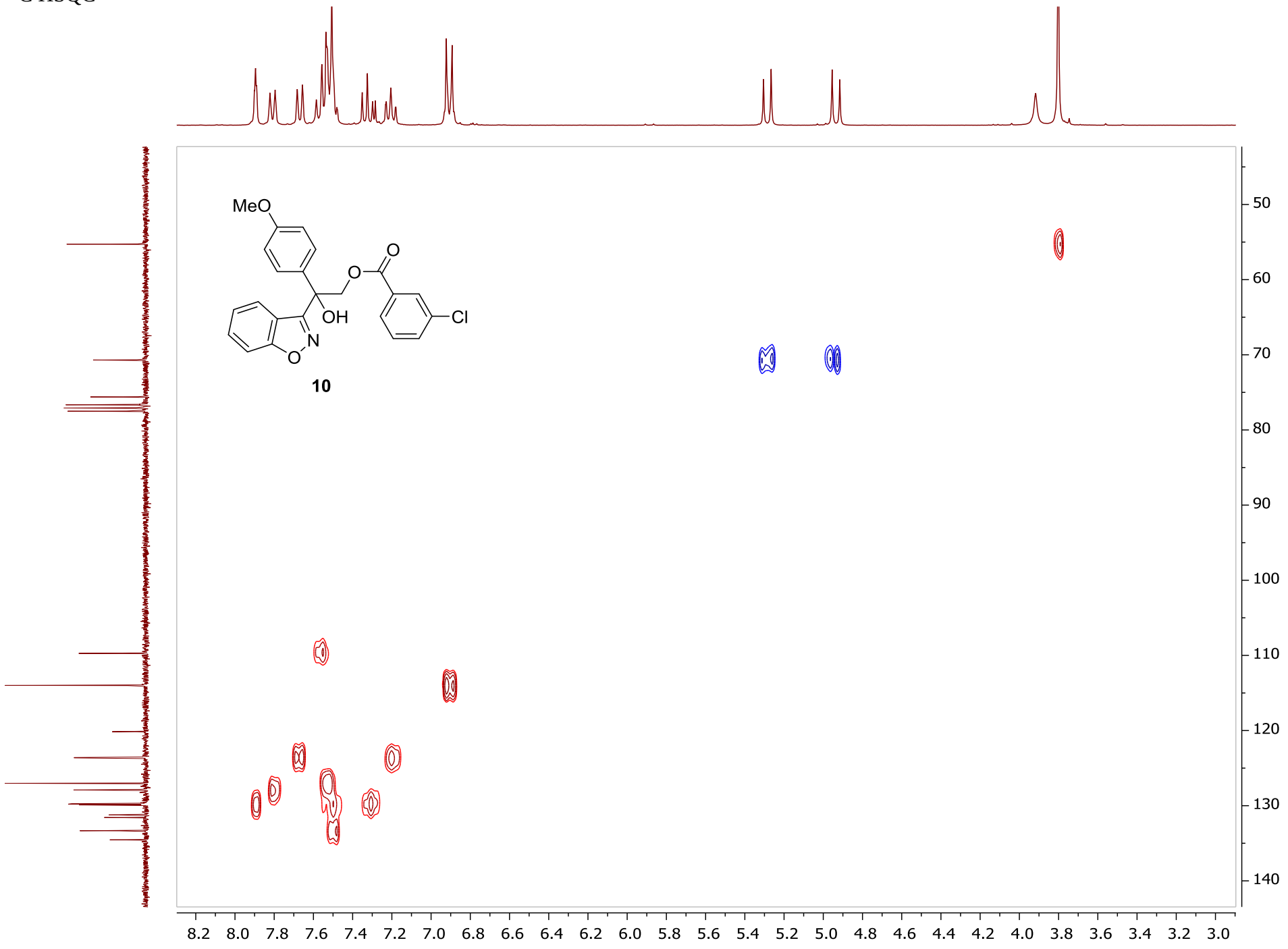
$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



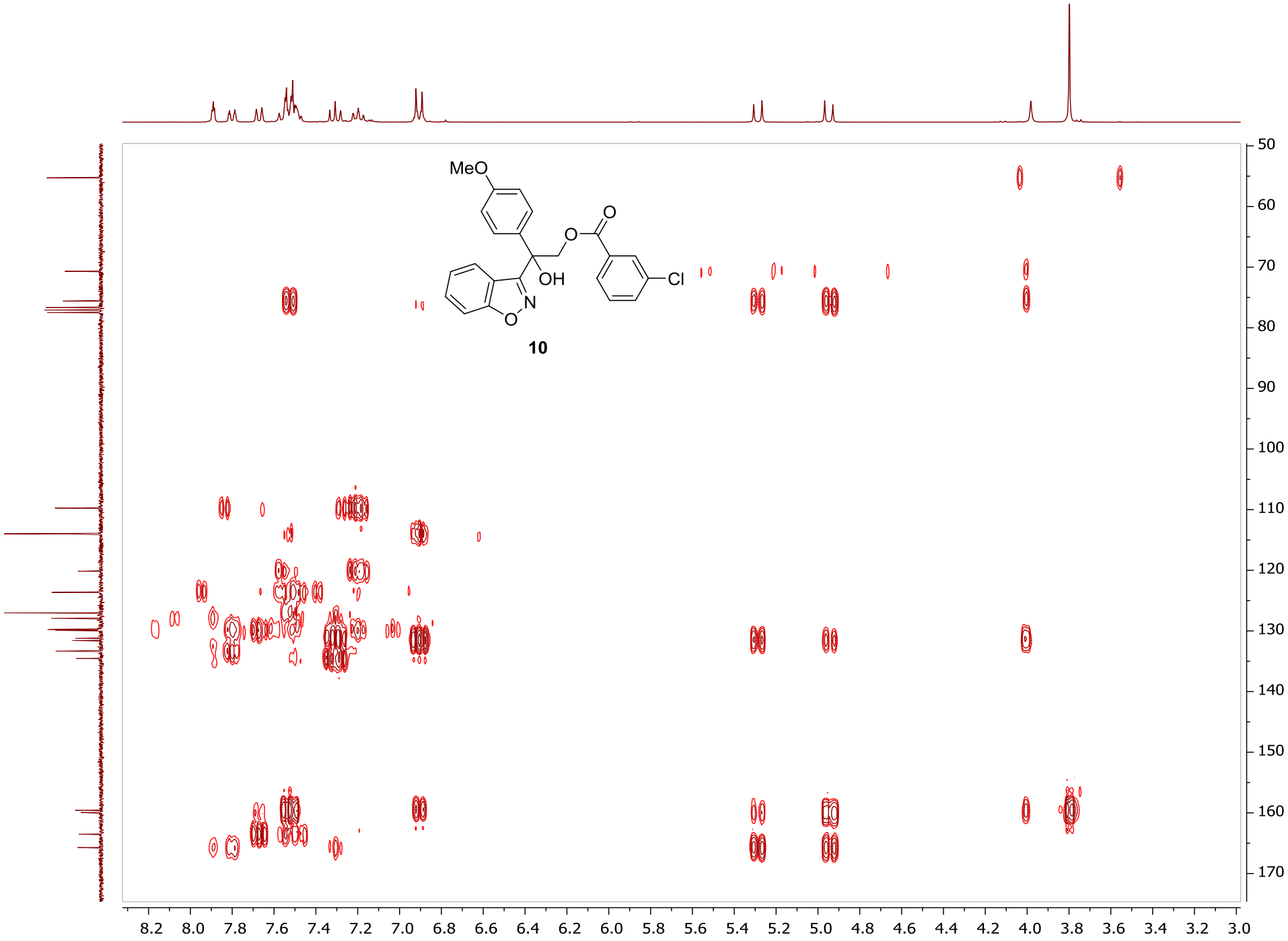
$^{1}$H-$^{1}$H COSY


MeO
O
O
OH
N
O
Cl
10
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.8 7.6 7.4 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

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

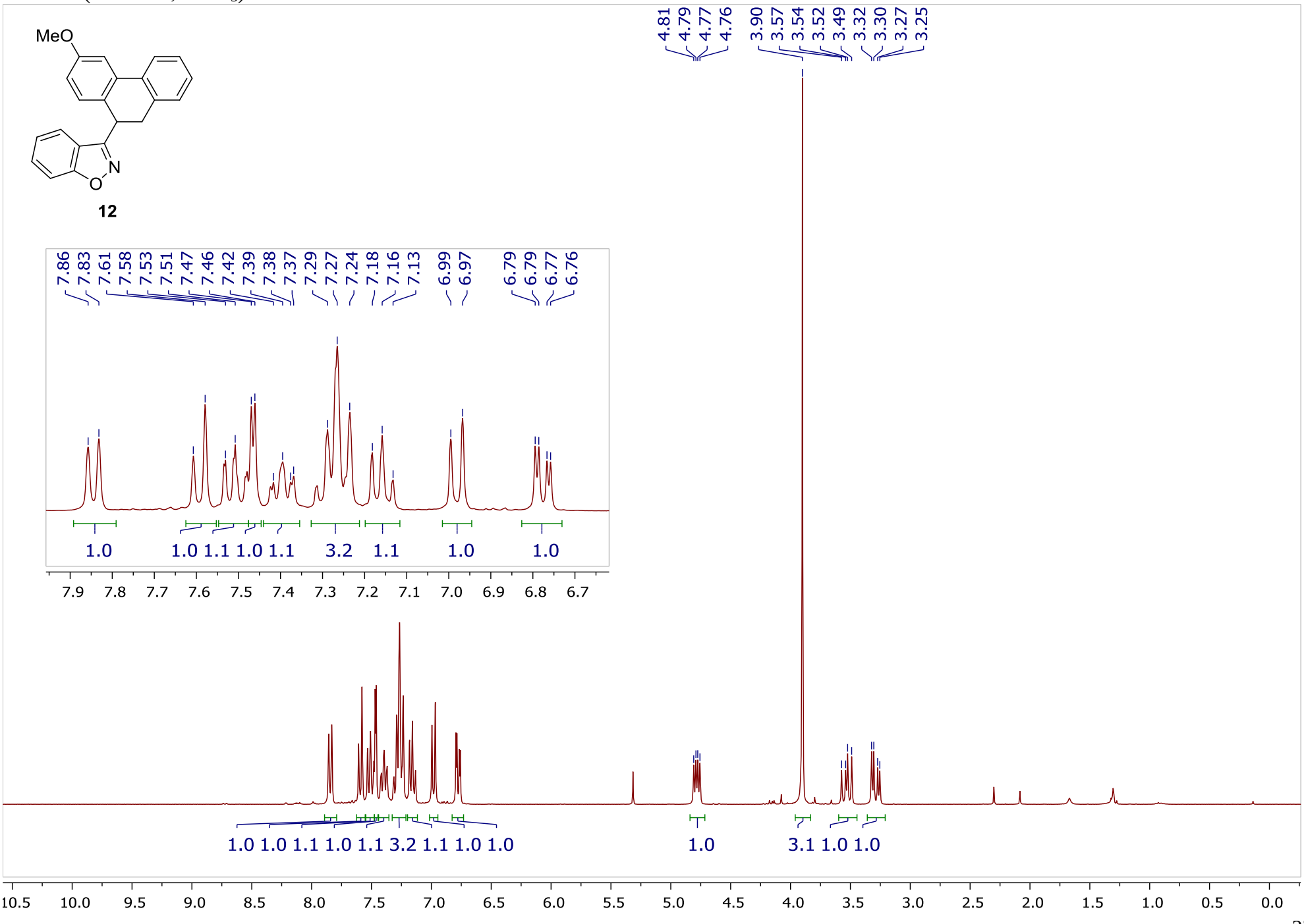

MeO
O
O
OH
N
O
Cl
10
50
60
70
80
90
100
110
120
130
140
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0

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

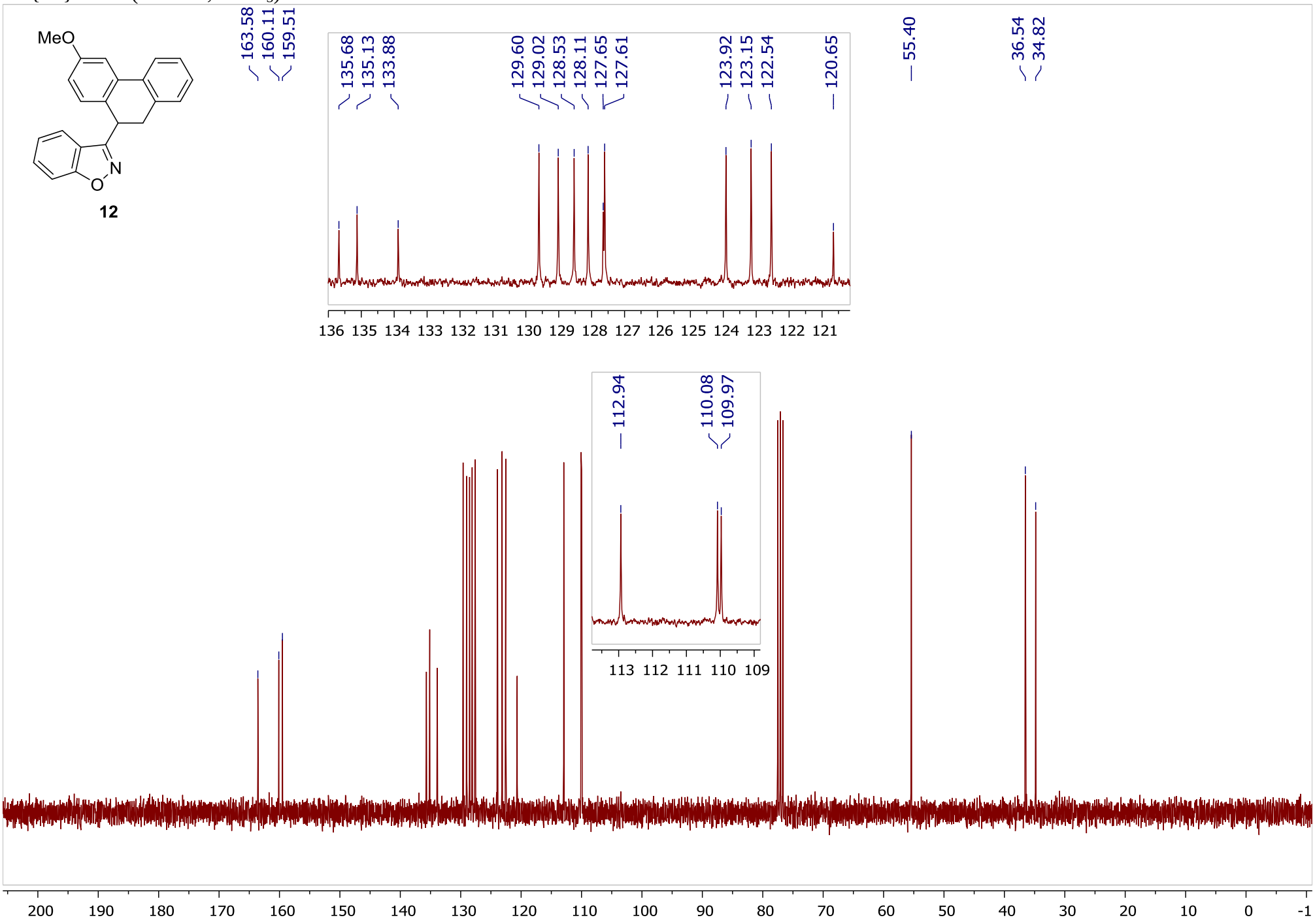

MeO
O
O
OH
N
O
Cl
10
50
60
70
80
90
100
110
120
130
140
150
160
170
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0

**3-(6-Methoxy-9,10-dihydrophenanthren-9-yl)benzo[d]isoxazole 12**

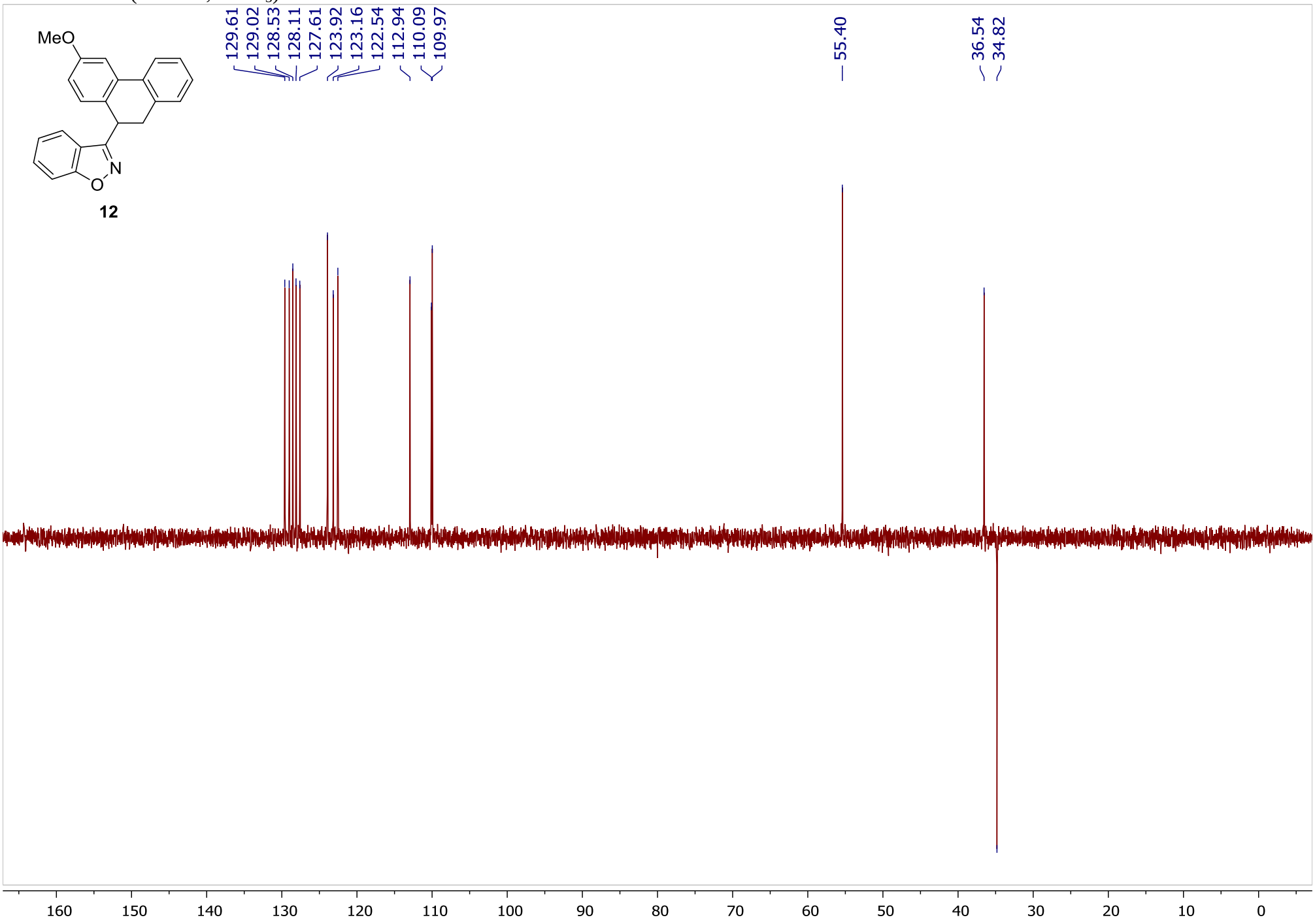
$^1$H NMR (300 MHz, $CDCl_3$)



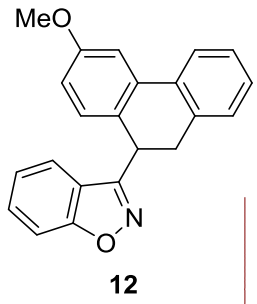
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



$^{13}$C DEPT 135 (75 MHz, $CDCl_3$)



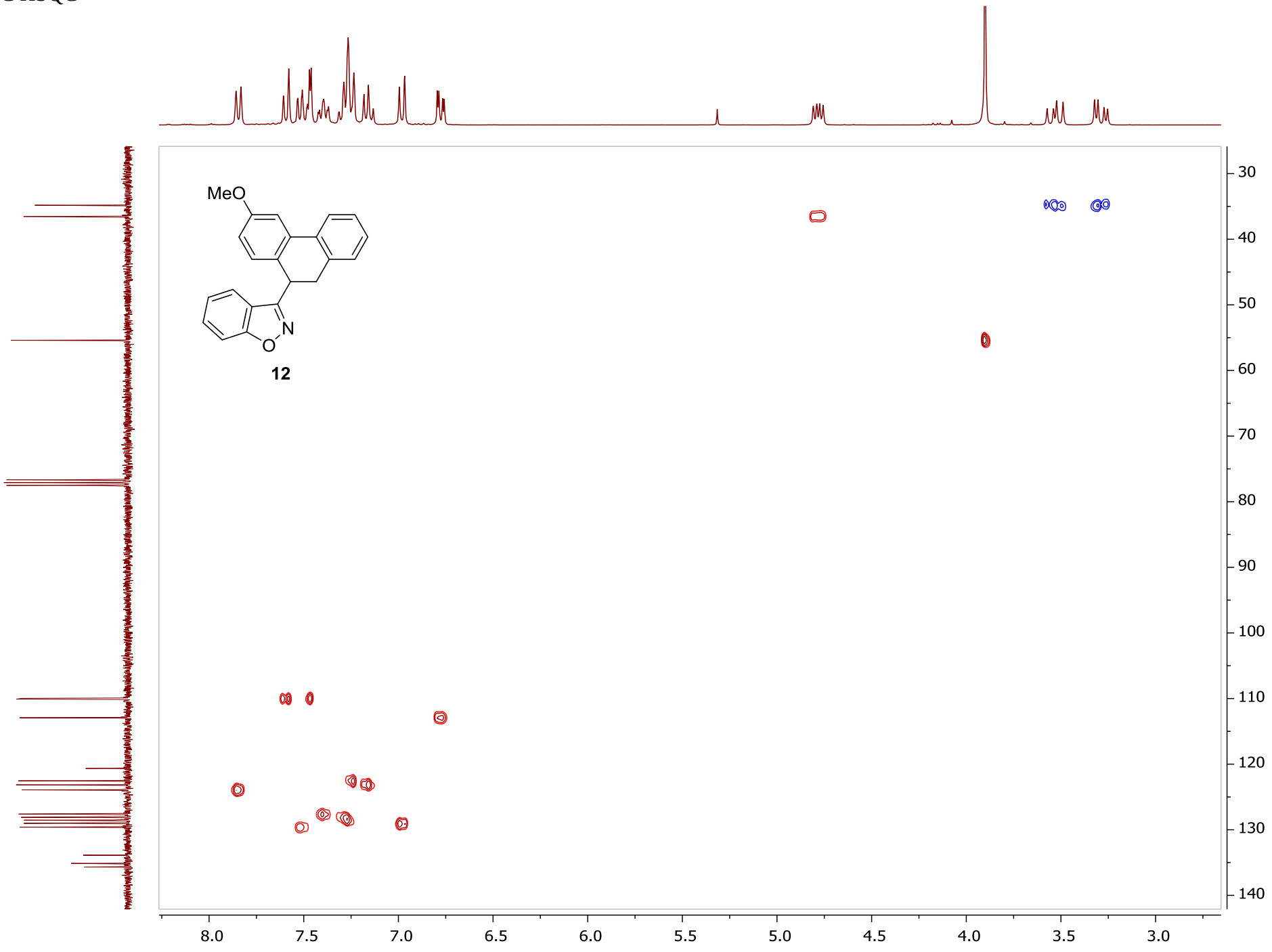
$^{1}H$-$^{1}H$ COSY


MeO
O
N

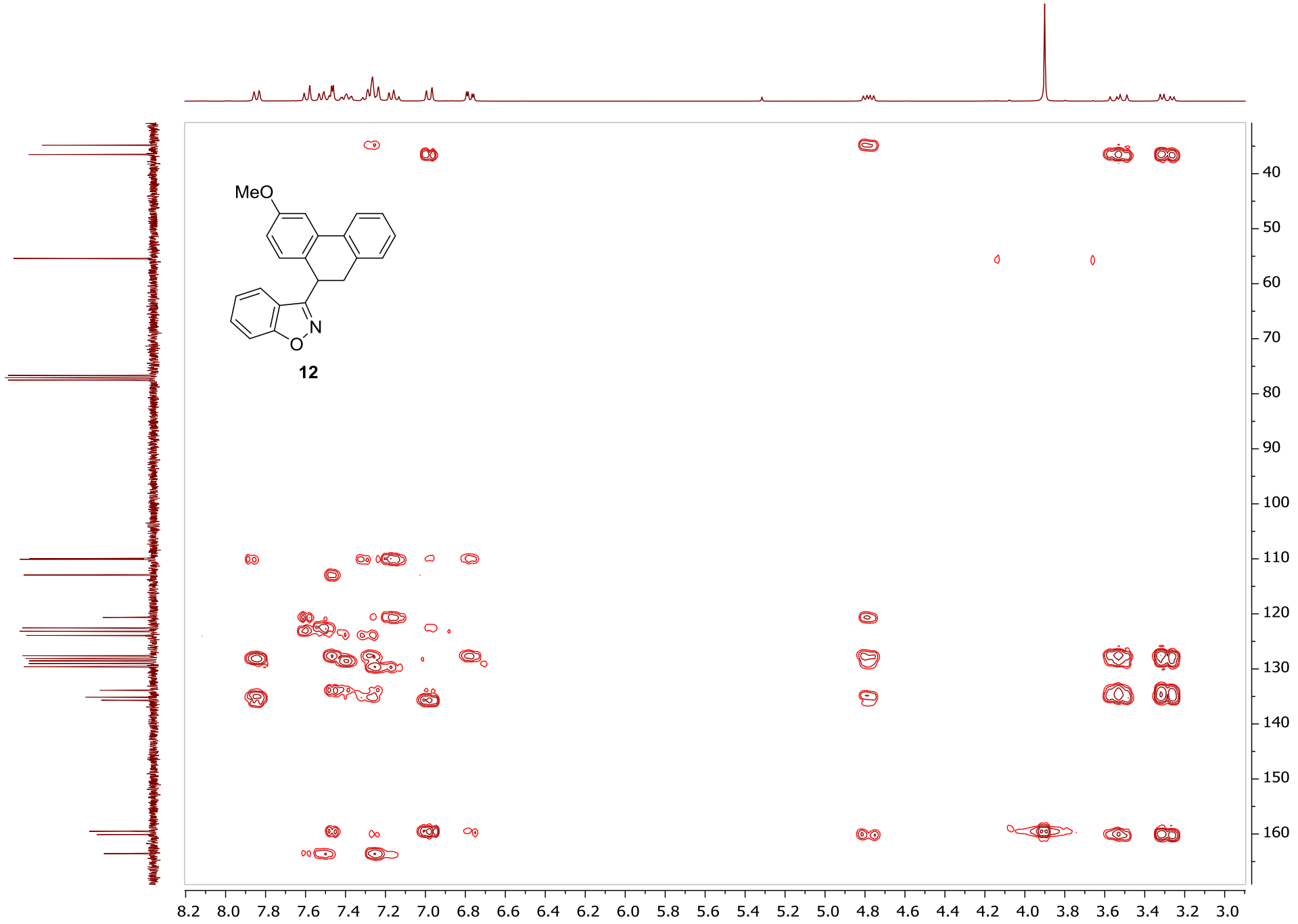
**12**


8.0 7.8 7.6 7.4 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
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

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


MeO
N
O
12
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

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


MeO
N
O
12
40
50
60
70
80
90
100
110
120
130
140
150
160
8.2
8.0
7.8
7.6
7.4
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