Supporting information

Tandem double acylation/[3,3]-rearrangement of aliphatic nitro compounds: route to α-oxygenated oxime derivatives

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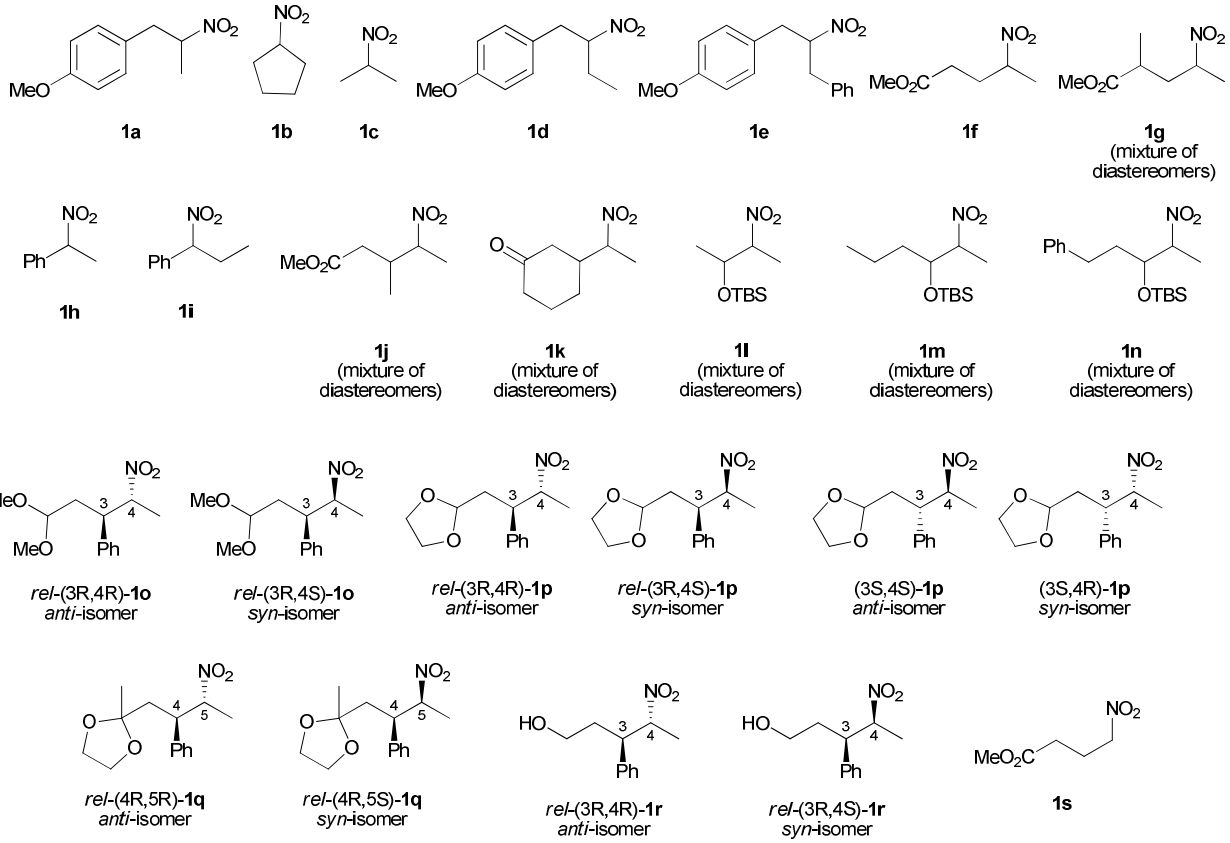
General experimental

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled. MeCN and CH_2Cl_2 were distilled from CaH_2 prior to use. Triethylamine and pivaloyl chloride were distilled from CaH_2. Brine refers to saturated aqueous solution of NaCl. TLC were performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV and/or anisaldehyde/H_2SO_4/EtOH stain and/or ninhydrine/AcOH/EtOH and/or Hanessian stain ($Ce(SO_4)_2$/$(NH_4)_6Mo_7O_{24}$/H_2SO_4/H_2O). Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded 300K on Bruker AM300 and Fourier 300HD spectrometers at the following spectrometer frequencies: 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR). Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), sex (sextet), m (multiplet), br (broad), app (apparent). High resolution mass spectra were acquired on Bruker micrOTOF spectrometer using electrospray ionization (ESI). Melting points were determined on a Koffler melting point apparatus and are uncorrected. Optical rotations were measured on JASCO P-2000 polarimeter. Concentrations *c* in optical rotation angles are given in g/100 mL. Chiral HPLC analysis was performed on a Shimadzu LC-20 Prominence with a UV-VIS photodiode array detector. Enantiomeric excess was determined by integration of the respective peak areas.

List of starting nitro compounds **1**:

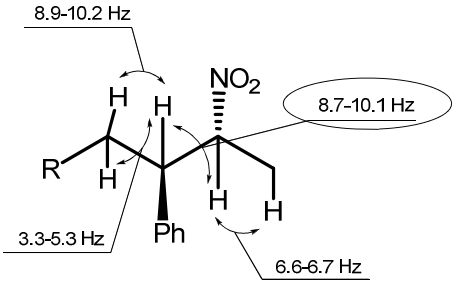


Determination of configuration of obtained compounds

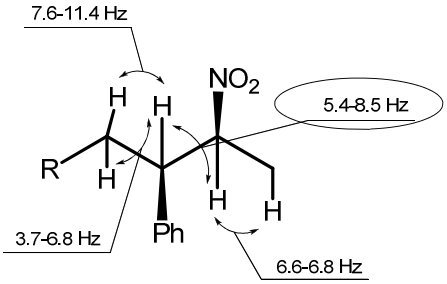
Determination of *syn*- or *anti*- relative configuration in nitro compounds **1o,1p,1q,1r** was made using coupling constants between C<u>H</u>–Ph and C<u>H</u>–NO_2 protons:

J (anti-isomer) > *J* (*syn*-isomer). For *syn*-isomer this often results in the fact that multiplet of C<u>H</u>–NO_2 is an apparent quintet due to close values of coupling constants in doublet of quadruplets.

Overall coupling constants lie within the following ranges:



anti-isomer



syn-isomer

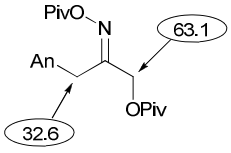
Configurations of similar isomers were determined by X-ray in Ref.[s1] (NB: Here "*syn*-" and "*anti*-" descriptors are used relatively to R–CH_2–CH–CH–CH_3 carbon chain written in a "zig-zag" manner. In Ref.[s1c] relative configuration was determined relatively to R–CH_2–CH–CH–NO_2 chain. Thus "*anti*-" in Ref.[s1c] corresponds to "*syn*-" in the present paper).

Absolute configuration of CH*–Ph stereocenter in *anti*-**1p**, *syn*-**1p** and **2p** was assigned on the basis of the literature data, that TMS-diphenylprolinol catalyst (*S*)-**8** provides (*S*)-configuration of

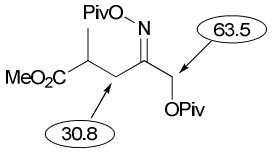
CH*–Ph during Michael addition of nitroalkane (e.g., nitromethane) to cinnamaldehydes, while (*R*)-**8** provides (*R*)-configuration of CH*–Ph.[s2]

E,*Z*-configuration of oxime group in target oxime esters **2** was determined on the basis of ^{13}C NMR data. *Anti*-arrangement towards oxime OR-group results in higher chemical shift of α-carbon as compared with *syn*-arrangement (see Figure below).[s3]

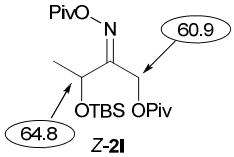
Chemical shifts (δ, ppm) of α-carbons in *E*,*Z*-isomers for selected products **2**:



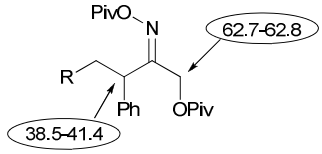
E-**2a**



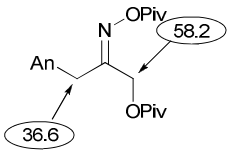
E-**2g**



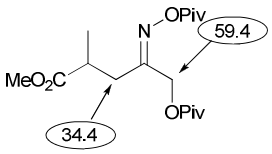
Z-**2l**



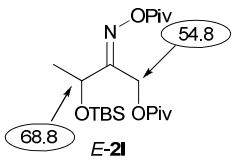
E-**2o,p,q,r**



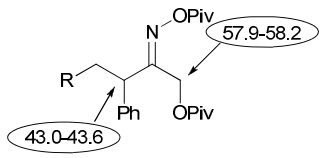
Z-**2a**



Z-**2g**

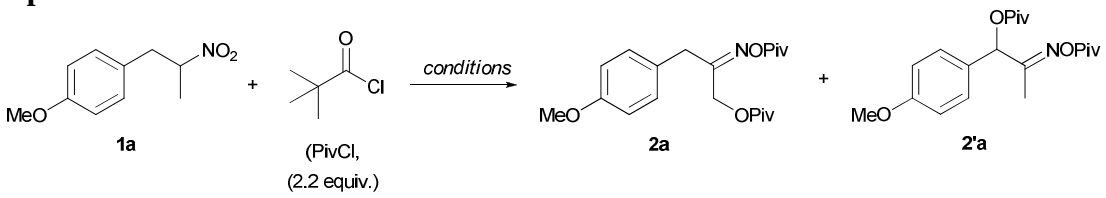


E-**2l**



Z-**2p,q**

Optimization table



№	Base (equiv.)	Solvent (conc. of 1a)	T, °C	time, h	Recovery 1a, %[a]	Total yield 2a+2a', %[a]	Ratio 2a:2a'[a]
1	NEt_3 (2.5)	CH_2Cl_2 (0.2M)	0	24	30	12	6:1
2	NEt_3 (2.5)	CH_2Cl_2 (0.5M)	0	24	38	46	4:1
3	NEt_3 (2.5)	THF (0.5M)	0	24	87	0	n.a.
4	NEt_3 (2.5)	DMF (0.5M)	0	48	29	27	4:1
5[b]	NEt_3 (2.5)	CH_3CN (0.5M)	0	24	17	81	15:1
6	NEt_3 (2.5)	CH_3CN (0.5M)	0	48	0	91	15:1
7	NEt_3 (2.5)	CH_3CN (0.5M)	-20	72	25	57	only **2a**
8	DIPEA (2.5)	CH_3CN (0.5M)	0	48	87	2	n.a.
9	DIPEA (2.5)	CH_3CN (0.5M)	25	96	73	23	1:2
10	NEt_3 (1) + DIPEA (1.5)	CH_3CN (0.5M)	0	24	40	50	10:1
11	Py (2.5)	CH_3CN (0.5M)	0	24	100	0	-
12	**NEt_3 (2.5) + DMAP (0.1)**	**CH_3CN (0.5M)**	**0**	**24**	**0**	**93**	**10:1**
13	NEt_3 (2.5) + DMAP (0.1)	CH_3CN (0.5M)	-20	48	89	0	-
14	NEt_3 (2.5) + DMAP (0.1)	CH_3CN (0.5M)	-20	96	20	65	20:1
15[c]	NEt_3 (1.2) + DMAP (0.1)	CH_3CN (0.5M)	0	24	37	22	10:1

[a] Determined by ^1H NMR with an internal standard (1,4-dinitrobenzene).

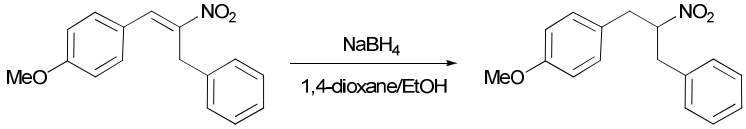
[b] We should note that different batches of NEt_3 from different suppliers gave fluctuating results in terms of time necessary for full conversion of nitro compound **1a**. In most cases 100% consumption of **1a** was observed within 1 day in the presence of DMAP (0.1 equiv.) (Entry 12) or within 2 days without a promotor (Entry 6). However in some cases full conversion was irreproducibly achieved within 1 day without a promotor. We can attribute it to some trace impurities (e.g. lower amines) presented in NEt_3 that act as basic/nucleophilic promotors - the role usually played by DMAP.

[c] 1.0 equiv. of PivCl.

Synthesis of starting nitro compounds 1

Starting compounds were prepared according to literature procedures: **1a**,[s4] **1b**,[s5] **1d**,[s6] **1f**,[s7] **1g**,[s8] **1h**,[s9] **1i**,[s10] **1k**,[s11] **1s**.[s12]

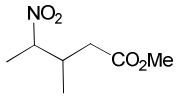
1-Methoxy-4-(2-nitro-3-phenylpropyl)benzene 1e



1e

Nitro compound **1e** was prepared similar to reported procedure.[s13]
Solution of 1-methoxy-4-(2-nitro-3-phenylprop-1-enyl)benzene[s14] (0.80 g, 3 mmol) in 1,4-dioxane (5 mL) was added dropwise to a stirring suspension of $NaBH_4$ (0.25 g, 6.6 mmol) in 1,4-dioxane (5 mL) / EtOH (1.25 mL) at 0 °C during 5 min. The reaction mixture was stirred stirred at r.t. for 1 h, cooled to 0°C and glacial AcOH (0.25 mL) was added slowly (gas evolution). After that the reaction mixture was transferred into EtOAc (75 mL)/ H_2O (50 mL). The organic layer was washed with saturated aqueous solution of $NaHCO_3$ (15 mL), brine (75 mL), dried (Na_2SO_4) and evaporated. The residue was subjected to column chromatography (eluent: PE/EtOAc, 7:1) to give target nitro compound **1e** (0.51 g, 62 %) as a white solid.
R_f = 0.44 (PE/EtOAc, 5:1, UV, anisaldehyde).
mp = 88-90 °C (PE/EtOAc, 10:1).
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.06 (dd, *J* = 14.1, 5.5 Hz, 1H, CH_{2a}), 3.10 (dd, *J* = 14.1, 5.5 Hz, 1H, CH_{2b}), 3.27 (dd, *J* = 14.1, 8.9 Hz, 1H, CH_{2c}), 3.32 (dd, *J* = 14.1, 8.9 Hz, 1H, CH_{2d}), 3.81 (s, 3H, OMe), 4.87-4.96 (tt, *J* = 8.9, 5.5 Hz, 1H, CH–NO_2), 6.86 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.10 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.18 (d, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.26-7.37 (m, 3H, CH_{Ar}).
^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 39.0 (CH_2), 39.5 (CH_2), 55.2 (OMe), 91.3 (CH–NO_2), 114.3 (CH_{Ar}), 127.3 (C_{Ar}), 127.5 (CH_{Ar}), 128.8 (CH_{Ar}), 128.9 (CH_{Ar}), 129.9 (CH_{Ar}), 135.5 (C_{Ph}), 159.0 ($\underline{C}_{Ar}$–OMe)..
HRMS (ESI): m/z calcd. for [$C_{16}H_{17}NO_3$ + Na^+]: 294.1101, found: 294.1098.

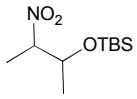
Methyl 3-methyl-4-nitropentanoate 1j



1j

To a solution of methyl crotonate (2.1 ml, 2.0 g, 20 mmol) and nitroethane (1.9 ml, 2.0 g, 26.6 mmol) in CH_3CN (10 ml) DBU (0.30 ml, 0.30 g, 2.0 mmol) was added with stirring. The reaction mixture was left at r.t. overnight, diluted with water (25 ml) and transferred into EtOAc (150 mL)/H_2O(75 mL). The organic layer was washed with saturated aqueous solution of NH_4Cl (50 mL), brine (100 mL), dried (Na_2SO_4) and evaporated. Vacuum distillation of the residue afforded 2.35 g (67%) of the title product **1j** as light yellow oil. bp 73-75 °C / 1.53 Torr. dr ≈ 1:1 (^{1}H NMR). ^{1}H NMR matches previously reported data.[s15]
^{1}H NMR (300 MHz, COSY, $CDCl_3$, for dr ≈ 1:1): δ 1.02 (d, *J* = 6.7 Hz) and 1.03 (d, *J* = 6.9 Hz) (total 3H, $C\underline{H}_3$–$CHCH_2$), 1.50 (d, *J* = 6.7 Hz) and 1.52 (d, *J* = 6.6 Hz) (total 3H, $C\underline{H}_3$–$CHNO_2$), 2.19-2.67 (m, 3H, CH–CH_2), 3.69 (s) and 3.70 (s) (total 3H, OMe), 4.54-4.67 (m, 1H, CH–NO_2).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$, for dr ≈ 1:1): δ 15.3, 15.47, 15.50 and 16.2 (2 × CH–$\underline{C}H_3$), 34.2 and 34.4 ($\underline{C}$HMe), 37.0 and 37.3 (CH_2), 51.8 (OMe), 86.4 (CH–NO_2), 171.8 and 172.0 ($\underline{C}O_2$Me).

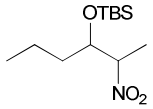
***tert*-Butyldimethyl(3-nitrobutan-2-yloxy)silane 1l**



1l

Nitro compound **1l** was prepared similar to reported procedure.[s16]
A mixture of the 3-nitro-2-butanol[s17] (347 mg, 2.9 mmol), TBSCl (525 mg, 3.5 mmol), imidazole (496 mg, 7.3 mmol) and DMF (0.73 mL) was stirred at r.t. overnight. The reaction mixture was diluted with water (20 mL) and extracted with PE (40 mL). The organic layer was washed with $NaHSO_4$ (0.5M in H_2O, 20 mL), brine (30 ml), dried (Na_2SO_4) and evaporated to give silylated nitroalcohol **1l** (555 mg, 82 %) as a slightly yellow oil. dr ≈ 1:1 (^{1}H NMR). NMR matches previously reported data.[s18]
^{1}H NMR (300 MHz, $CDCl_3$, for dr ≈ 1:1): δ 0.03, 0.04, 0.07 and 0.08 (all s, total 6H, MeSi), 0.86 and 0.88 (both s, total 9H, *t*-BuSi), 1.20 (d, *J* = 6.2 Hz) and 1.22 (d, *J* = 6.2 Hz) (total 3H, Me), 1.47 (d, *J* = 6.8 Hz) and 1.51 (d, *J* = 6.5 Hz) (total 3H, Me), 4.20 (app quint, *J* = 6.2 Hz) and 4.35-4.51 (m) (total 2H, CH–NO_2 and CH–O).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$, for dr ≈ 1:1): δ -5.5, -5.4, -4.6 and -4.5 (MeSi), 12.1 and 15.5 (Me), 17.8 and 17.9 ($Me_3\underline{C}Si$), 19.6 and 20.6 (Me), 25.5 and 25.6 ($\underline{Me}_3CSi$), 69.7 and 70.4 (CH–O), 87.6 and 89.3 (CH–NO_2).

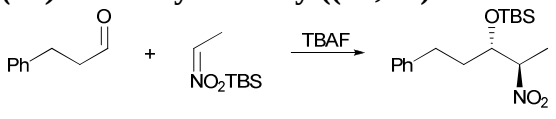
***tert*-Butyldimethyl((2-nitrohexan-3-yl)oxy)silane 1m**



1m

Nitro compound **1m** was prepared similar to reported procedure.[s16]
A mixture of the 2-nitro-3-hexanol[s19] (431 mg, 2.9 mmol), TBSCl (531 mg, 3.5 mmol), imidazole (500 mg, 7.4 mmol) and DMF (0.73 ml) was stirred at r.t. overnight. The reaction mixture was diluted with water (20 mL) and extracted with PE (40 mL). The organic layer was washed with $NaHSO_4$ (0.5M in H_2O, 20 mL), brine (30 ml), dried (Na_2SO_4) and evaporated. Crude product was subjected to column chromatography (eluent: PE/EtOAc, 20:1) afforded to give silylated nitroalcohol **1m** (360 mg, 47 %) as a slightly yellow oil. R_f = 0.70 (PE/EtOAc, 9:1, anisaldehyde). dr ≈ 1:1 (^{1}H NMR).
^{1}H NMR (300 MHz, $CDCl_3$, for dr ≈ 1:1): δ 0.00, 0.03, 0.06 and 0.07 (all s, total 6H, MeSi), 0.86 and 0.87 (both s, total 9H, *t*-BuSi), 0.88-0.98 (m) and 1.20-1.55 (m) (total 10H, 2 × CH_2 and 2 × CH_3), 4.14 (dt, *J* = 7.8, 4.2 Hz) and 4.31-4.36 (m) (total 1H, CH–O), 4.46 (qd, *J* = 6.7, 3.3 Hz) and 4.58 (app quint, *J* = 6.9 Hz) (total 1 H, CH–NO_2).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$, for dr ≈ 1:1): δ -5.4, -5.2, -4.6 and -4.5 (MeSi), 11.3, 14.0, 14.2 and 15.1 (2 × Me), 16.6 and 18.5 (CH_2), 17.92 and 17.94 ($Me_3\underline{C}Si$), 25.6 and 25.7 ($\underline{Me}_3CSi$), 34.8 and 36.8 (CH_2), 73.5 and 73.6 (CH–O), 85.6 and 87.1 (CH–NO_2).
HRMS (ESI): m/z calcd. for [$C_{12}H_{27}NO_3Si + Na^+$]: 284.1652, found: 284.1642.

***(rel)-tert*-Butyldimethyl((3*S*,4*R*)-4-nitro-1-phenylpentan-3-yloxy)silane 1n**



1n

Nitro compound **1n** was prepared similar to reported procedure.[s16,s20]
A solution of TBAF·3H_2O (340 mg, 0.11 mmol) in CH_2Cl_2 (3.6 ml) was stirred with MS 4 Å (120 mg, pre-dried by heating for 10 min under vacuum) for 20 min at r.t.. The solution was cooled to -78 °C, after that 3-phenylpropionic aldehyde (290 mg, 2.2 mmol) and TBS-ether of *aci*-nitroethane[s21] (450 mg, 2.4 mmol) was added. The resulting solution was stirred at -78°C for 1 h, allowed to warm and then stirred at r.t. overnight. It was then transferred into 150 ml of

EtOAc, and washed with 3 × 30 ml of water, $NaHSO_4$ (0.5M in H_2O, 50 ml), Brine (50 ml), dried with Na_2SO_4 and evaporated. Column chromatography (eluent: PE/EtOAc, 7:1) afforded 487 mg (70%) of target nitro compound **1n** as colorless oil. R_f = 0.62 (PE/EtOAc, 3:1, anisaldehyde). dr = 5.5:1 (^{1}H NMR). Relative configuration of stereocenters in major diastereomer was assumed *anti*- analogous to literature data.[s16]

Major isomer:

^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.03 and 0.10 (both s, total 6H, MeSi), 0.92 (s, 9H, *t*-BuSi), 1.54 (d, *J* = 6.7 Hz, 3H, CH_3), 1.83-1.90 (m, 2H, C<u>H</u>$_2$–CH), 2.59-2.81 (m, 2H, C<u>H</u>$_2$–Ph), 4.40 (td, *J* = 6.1, 3.7 Hz, 1H, CH–O), 4.56 (qd, *J* = 6.7, 3.7 Hz, CH–NO_2), 7.20-7.36 (m, 5H, Ph).

^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ -5.1 and -4.4 (MeSi), 11.8 (Me), 18.0 (Me_3<u>C</u>Si), 25.7 (<u>Me</u>$_3$CSi), 31.6 (C<u>H</u>$_2$–Ph), 36.5 (C<u>H</u>$_2$–CH), 73.4 (CH–O), 85.6 (CH–NO_2), 126.2 (CH_{Ph}), 128.2 (CH_{Ph}), 128.6 (CH_{Ph}), 141.0 (C_{Ph}).

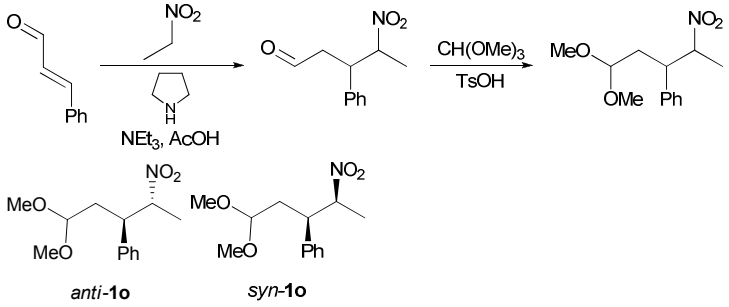
Minor isomer:

^{1}H NMR (300 MHz, COSY, $CDCl_3$, characteristic signals): δ 4.25 (dt, *J* = 7.7, 4.6 Hz, 1H, CH–O), 4.56 (app quint, *J* = 7.1 Hz, CH–NO_2).

^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$, characteristic signals): δ 15.2 (Me), 73.9 (CH–O), 86.9 (CH–NO_2).

HRMS (ESI): m/z calcd. for [$C_{17}H_{29}NO_3Si$ + Na^+]: 346.1809, found: 346.1817.

(*rel*)-((3*R*,4*R*)-1,1-dimethoxy-4-nitropentan-3-yl)benzene *anti*-1o and **(*rel*)-((3*R*,4*S*)-1,1-dimethoxy-4-nitropentan-3-yl)benzene *syn*-1o**



Used procedure is based on the literature precedent.[s2b]

To the solution of cinnamaldehyde (0.63 mL, 0.66 g, 5 mmol) in CH_2Cl_2 (9 mL) / MeOH (1 mL) nitroethane (0.72 mL, 0.75 g, 10 mmol), pyrrolidine (8 µL, 7 mg, 0.1 mmol), NEt_3 (70 µL, 51 mg, 0.5 mmol) and AcOH (29 µL, 30 mg, 0.5 mmol) were subsequently added with stirring. The reaction mixture was maintained for 2 d and transferred into EtOAc (150 mL)/H_2O (100 mL). The organic layer was washed with $NaHSO_4$ (0.5 M in H_2O, 100 mL), brine (100 mL), dried (Na_2SO_4) and evaporated to give crude 4-nitro-3-phenyl-pentanal (1.08 g, ca. 100%), which was used in the next step without subsequent purification.

Solution of crude 4-nitro-3-phenyl-pentanal (1.08 g, 5 mmol) in MeOH (2 mL) was cooled to 0 °C. Then trimethyl orthoformate (0.82 mL, 0.80 g, 7.5 mmol) and TsOH·H_2O (19 mg, 0.1 mmol) were subssequently added with stirring. The reaction mixture was left at r.t. for 3 d. NEt_3 (20 µL, 14 mg, 0.14 mmol) was added, the mixture was stirred for 5 min and diluted with EtOAc. (3 mL). After that it was evaporated and preadsorbed on Celite®. Column chromatography (eluent: PE/EtOAc, 10:1, then 5:1) afforded 509 mg (40%) of *anti*-**1o** and 505 mg (40%) of *syn*-**1o** as colorless oils.

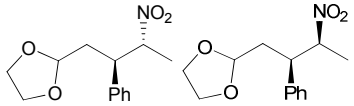
anti-**1o**: R_f = 0.47 (PE/EtOAc, 5:1, UV, anisaldehyde).

syn-**1o**: R_f = 0.27 (PE/EtOAc, 5:1, UV, anisaldehyde).

anti-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.31 (d, *J* = 6.6 Hz, 3H, Me), 1.88-2.03 (m, 2H, CH_2), 3.18 (s, 3H, OMe), 3.22 (s, 3H, OMe), 3.29 (app td, *J* = 10.1, 5.1 Hz, CHPh), 3.98 (dd, *J* = 7.6, 4.3 Hz, C<u>H</u>$(OMe)_2$), 4.75 (dq, *J* = 10.1, 6.6 Hz, CH–NO_2), 7.18-7.21 (m, 2H, CH_{Ph}), 7.30-7.39 (m, 3H, CH_{Ph}).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 18.0 (Me), 35.3 (CH_2), 46.4 (<u>C</u>HPh), 51.9 (OMe), 52.8 (OMe), 87.8 (CH–NO_2), 101.6 (<u>C</u>H$(OMe)_2$), 127.8 (CH_{Ph}), 128.3 (CH_{Ph}), 129.1 (CH_{Ph}), 138.1 (C_{Ph}).
syn-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (d, *J* = 6.7 Hz, 3H, Me), 1.92 (ddd, *J* = 13.7, 11.4, 3.3 Hz, 1H, CH_{2a}), 2.09 (ddd, *J* = 13.7, 8.4, 4.0 Hz, 1H, CH_{2b}), 3.23 (s, 3H, OMe), 3.27 (s, 3H, OMe), 3.33 (ddd, *J* = 11.4, 8.5, 4.0 Hz, CHPh), 3.99 (dd, *J* = 8.4, 3.3 Hz, C<u>H</u>$(OMe)_2$), 4.80 (dq, *J* = 8.5, 6.7 Hz, CH–NO_2), 7.19-7.22 (m, 2H, CH_{Ph}), 7.25-7.36 (m, 3H, C<u>H</u>$_2$–Ph).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 17.2 (Me), 34.1 (CH_2), 46.2 (<u>C</u>HPh), 53.19 (OMe), 53.21 (OMe), 87.8 (CH–NO_2), 102.4 (<u>C</u>H$(OMe)_2$), 127.7 (CH_{Ph}), 128.1 (CH_{Ph}), 128.8 (CH_{Ph}), 138.5 (C_{Ph}).
HRMS (ESI): m/z calcd. for [$C_{13}H_{19}NO_4$ + Na^+]: 276.1206, found: 276.1202.

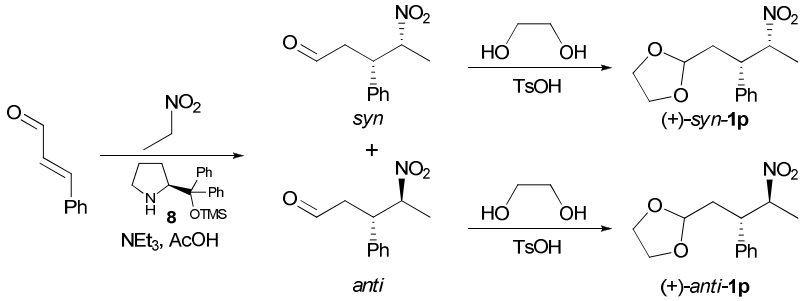
(*rel*)-2-((2*R*,3*R*)-3-nitro-2-phenylbutyl)-1,3-dioxolane *anti*-1p and **(*rel*)-2-((2*R*,3*S*)-3-nitro-2-phenylbutyl)-1,3-dioxolane *syn*-1p**



anti-**1p** *syn*-**1p**

Crude 4-nitro-3-phenyl-pentanal was obtained as described for **1o**.
Solution of crude 4-nitro-3-phenyl-pentanal (7 mmol), ethylene glycol (0.47 ml, 0.52 g, 8.4 mmol) and TsOH·H_2O (133 mg, 0.7 mmol) in toluene (14 mL) was maintained for 75 min at 80 °C (oil bath). NEt_3 (0.2 mL, 0.14 g, 1.4 mmol) was added, the mixture was stirred for 5 min and diluted with CH_2Cl_2 (5 mL). After that it was evaporated and preadsorbed on Celite®. Column chromatography (eluent: PE/EtOAc, 10:1, then 7:1) afforded 774 mg (44%) of *anti*-**1p** as slightly yellow oil and 542 mg (31%) of *syn*-**1p** as white solid.
anti-**1p**: R_f = 0.56 (PE/EtOAc, 3:1, anisaldehyde).
syn-**1p**: R_f = 0.33 (PE/EtOAc, 3:1, anisaldehyde).
syn-**1p**: mp = 61-63 °C (PE/EtOAc, 20:1).
anti-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (d, *J* = 6.6 Hz, 3H, Me), 1.84 (ddd, *J* = 13.7, 7.5, 4.1 Hz, 1H, CH_{2a}), 2.18 (ddd, *J* = 13.7, 10.9, 2.7 Hz, 1H, CH_{2b}), 3.42 (app td, *J* = 10.2, 4.1 Hz, CHPh), 3.69-3.81 (m, 2H) and 3.83-3.94 (m, 2H) (OCH_2CH_2O), 4.55 (dd, *J* = 7.5, 2.7 Hz, C<u>H</u>$(OMe)_2$), 4.78 (dq, *J* = 9.5, 6.6 Hz, CH–NO_2), 7.18-7.21 (m, 2H, CH_{Ph}), 7.27-7.39 (m, 3H, C<u>H</u>$_2$–Ph).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 17.4 (Me), 36.9 (CH_2), 46.2 (<u>C</u>HPh), 64.7 and 64.8 (OCH_2CH_2O), 87.7 (CH–NO_2), 102.1 (<u>C</u>H$(OCH_2)_2$), 127.8 (CH_{Ph}), 128.3 (CH_{Ph}), 129.0 (CH_{Ph}), 137.9 (C_{Ph}).
syn-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (d, *J* = 6.6 Hz, 3H, Me), 2.00 (ddd, *J* = 13.7, 7.2, 4.1 Hz, 1H, CH_{2a}), 2.16 (ddd, *J* = 13.7, 11.0, 3.0 Hz, 1H, CH_{2b}), 3.45 (ddd, *J* = 10.9, 8.4, 4.1 Hz, CHPh), 3.75-3.82 (m, 2H) and 3.88-3.96 (m, 2H) (OCH_2CH_2O), 4.56 (dd, *J* = 7.2, 3.0 Hz, C<u>H</u>$(OMe)_2$), 4.84 (dq, *J* = 8.3, 6.7 Hz, CH–NO_2), 7.21-7.24 (m, 2H, CH_{Ph}), 7.27-7.36 (m, 2H, CH_{Ph}), 7.31-7.41 (m, 3H, C<u>H</u>$_2$–Ph).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 17.2 (Me), 35.4 (CH_2), 46.1 (<u>C</u>HPh), 64.8 and 64.9 (OCH_2CH_2O), 87.7 (CH–NO_2), 102.2 (<u>C</u>H$(OCH_2)_2$), 127.7 (CH_{Ph}), 128.1 (CH_{Ph}), 128.7 (CH_{Ph}), 138.3 (C_{Ph}).
HRMS (ESI): m/z calcd. for [$C_{13}H_{17}NO_4$ + Na^+]: 274.1050, found: 274.1056.

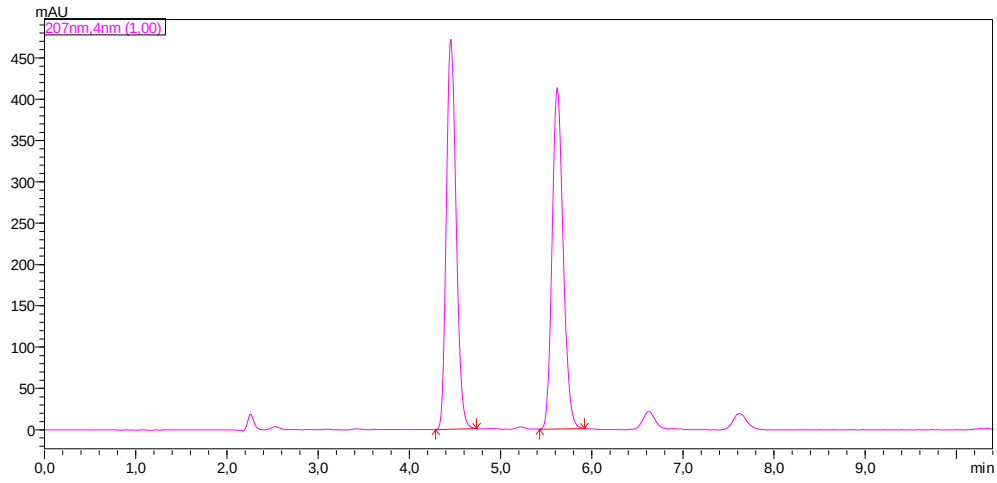
2-((2*S*,3*S*)-3-Nitro-2-phenylbutyl)-1,3-dioxolane (+)-*anti*-1p and **2-((2*S*,3*R*)-3-Nitro-2-phenylbutyl)-1,3-dioxolane** (+)-***syn*-1p**



Enantioenriched 4-nitro-3-phenyl-pentanal was prepared similar to reported procedure.[s2b]
To the solution of cinnamaldehyde (0.63 mL, 0.66 g, 5 mmol) in CH_2Cl_2 (9 mL) / MeOH (1 mL) nitroethane (1.1 mL, 1.1 g, 15 mmol), α,α-diphenylprolinol *O*-trimethylsilyl ether (*S*)-**8** (31.9 mg, 0.1 mmol), NEt_3 (70 µL, 51 mg, 0.5 mmol) and AcOH (29 µL, 30 mg, 0.5 mmol) were subsequently added with stirring at r.t.. The reaction mixture was maintained for 1 d and transferred into EtOAc (150 mL)/H_2O (100 mL). The organic layer was washed with $NaHSO_4$ (0.5 M in H_2O, 100 mL), brine (100 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 10:1, then 7:1, then 3:1) afforded 456 mg (44%) of *anti*-4-nitro-3-phenyl-pentanal as slightly yellow oil and 472 mg (46%) of *syn*-4-nitro-3-phenyl-pentanal as white solid. mp (*syn*-isomer) = 35-37 °C (PE/EtOAc, 20:1).
Thus obtained enentioenriched *syn*- and *anti*- isomers of 4-nitro-3-phenyl-pentanal were subjected to dioxolane protection as described above for the synthesis of racemic **1p**:
From *anti*-isomer (361 mg, 1.74 mmol) 390 mg (89%, ee = 95%) of (+)-*anti*-**1p** were obtained. Light yellow oil. $[a]^{25}_D$ = +32.4 (*c* = 1.0, MeOH, 95% ee).
From *syn*-isomer (313 mg, 1.51 mmol) 339 mg (89%, ee = 96%) of (+)-*syn*-**1p** were obtained. White solid. mp = 58-60 °C (PE/EtOAc, 20:1). $[a]^{25}_D$ = +1.7 (*c* = 1.0, MeOH, 96% ee).

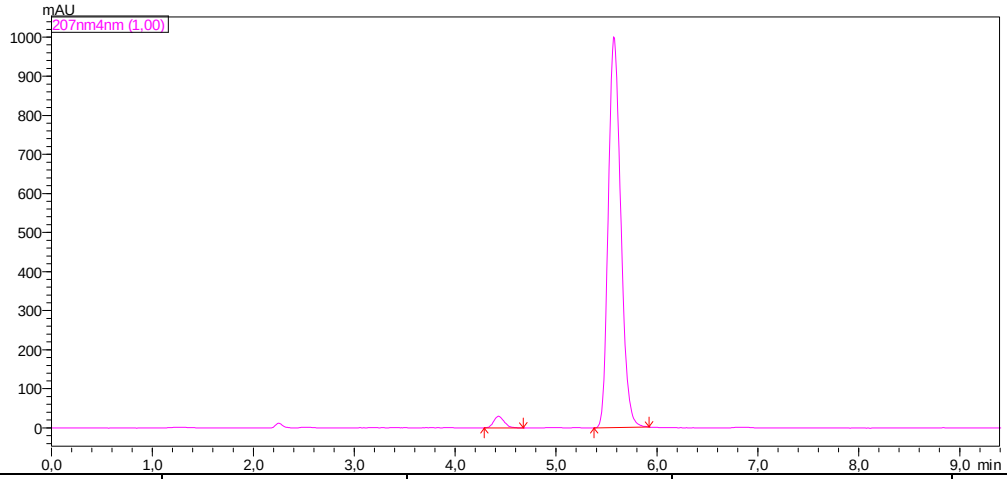
HPLC separation conditions:
column: Chiralcel OD-3, 150 x 4.6 mm, temp. 40 °C,
eluent: Hexane-*i*-PrOH, 90:10, 1 mL/min, detection at 207 nm.
anti-**1p**: t_R = 4.5 min (minor), 5.6 min (major).
syn-**1p**: t_R = 5.0 min (minor), 7.1 min (major).

anti-**1p**, racemic



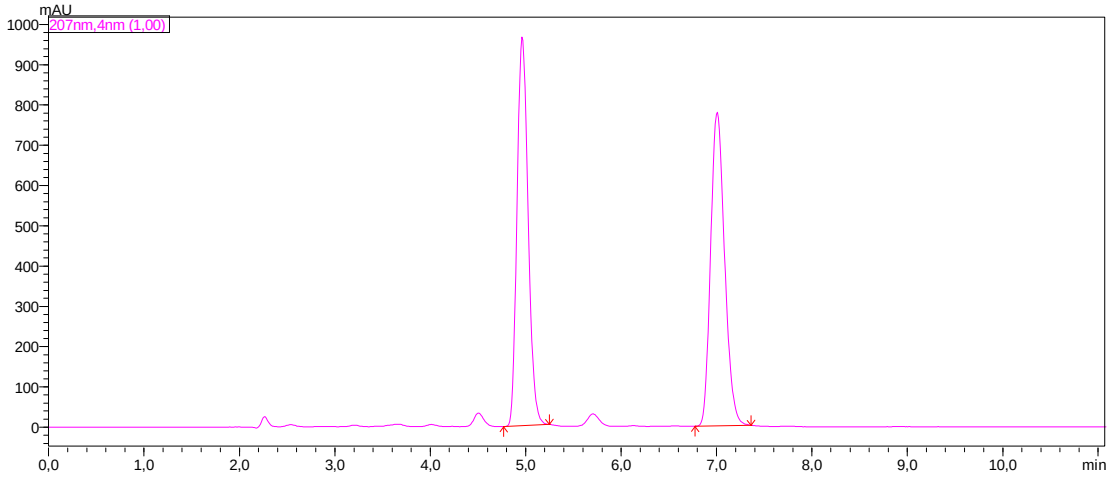
Peak#	Ret. Time	Area	Height	Area%
1	4,456	3491550	471637	49,957
2	5,621	3497626	413004	50,043
Total		6989176	884642	100,000

anti-**1p**, enantioenriched



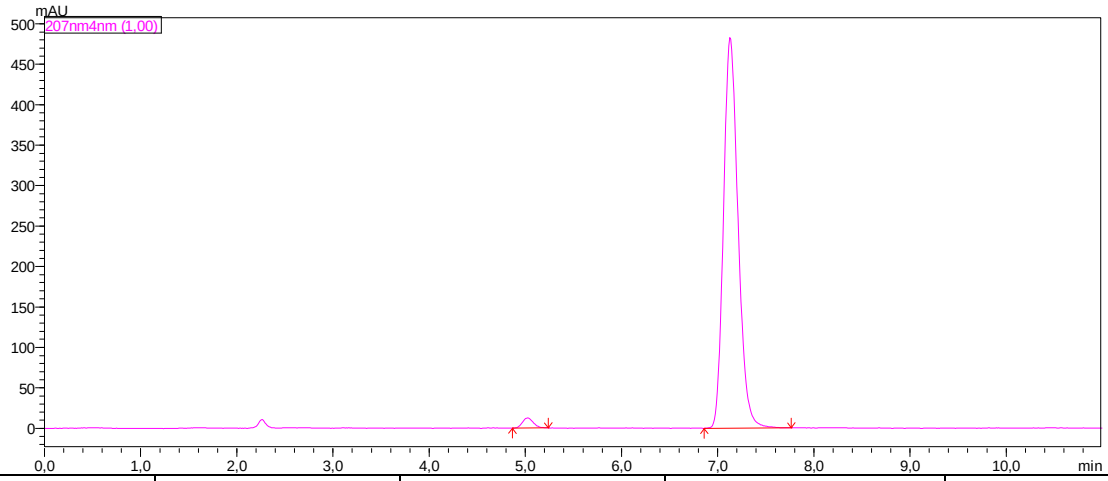
Peak#	Ret. Time	Area	Height	Area%
1	4,429	215216	29803	2,446
2	5,573	8584576	1000167	97,554
Total		8799792	1029970	100,000

syn-**1p**, racemic



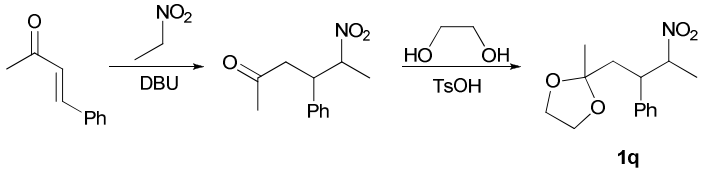
Peak#	Ret. Time	Area	Height	Area%
1	4,963	7800727	965227	49,504
2	7,005	7957112	779056	50,496
Total		15757839	1744283	100,000

syn-**1p**, enantioenriched

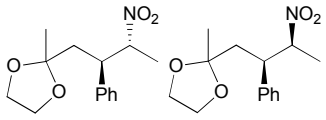


Peak#	Ret. Time	Area	Height	Area%
1	5,022	100036	12687	1,927
2	7,129	5091848	482738	98,073
Total		5191883	495425	100,000

(*rel*)-2-Methyl-2-((2R,3R)-3-nitro-2-phenylbutyl)-1,3-dioxolane *anti*-1q and **(*rel*)-2-Methyl-2-((2R,3S)-3-nitro-2-phenylbutyl)-1,3-dioxolane *syn*-1q**



1q



anti-**1q** *syn*-**1q**

Solution of benzylideneacetone (736 mg, 5 mmol), nitroethane (0.48 mL, 0.50 g, 6.7 mmol) and DBU (75 µL, 76 mg, 0.5 mmol) in MeCN (2.5 mL) was maintained at r.t. for 1 d. Then it was transferred into EtOAc (50 mL)/H_2O (40 mL). The organic layer was washed with NH_4Cl (sat. aq. solution, 40 mL), brine (40 mL), dried (Na_2SO_4) and evaporated to give 1.1 g (ca. 100%) of crude 5-nitro-4-phenyl-2-hexanone as yellow oil, which was used in the next step without additional purification.

Crude 5-nitro-4-phenyl-2-hexanone (546 mg, 2.5 mmol), ethylene glycol (0.24 ml, 0.26 g, 4.3 mmol) and $TsOH \cdot H_2O$ (48 mg, 0.25 mmol) in toluene (7.5 mL) was refluxed for 4 h with Hickman still head acting as water separator. NEt_3 (37 µL, 27 mg, 0.25 mmol) was added, the mixture was stirred for 5 min and transferred into EtOAc (100 mL)/H_2O (75 mL). The organic layer was washed with $NaHSO_4$ (0.5 M in H_2O, 75 mL), brine (75 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 10:1, then 7:1) afforded 270 mg (41%) of *anti*-**1q** and 264 mg (40%) of *syn*-**1q** as slightly yellow oils.

anti-**1q**: R_f = 0.56 (PE/EtOAc, 3:1, anisaldehyde).

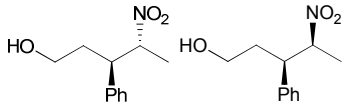
syn-**1q**: R_f = 0.38 (PE/EtOAc, 3:1, anisaldehyde).

anti-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.15 (s, 3H, Me), 1.28 (d, *J* = 6.6 Hz, 3H, Me), 2.00 (dd, *J* = 14.5, 4.0 Hz, 1H, CH_{2a}), 2.23 (dd, *J* = 14.5, 8.9 Hz, 1H, CH_{2b}), 3.50 (td, *J* = 8.9, 4.0 Hz, CHPh), 3.70-3.90 (m, 4H, OCH_2CH_2O), 4.79 (dq, *J* = 8.7, 6.7 Hz, CH–NO_2), 7.16-7.19 (m, 2H, CH_{Ph}), 7.25-7.37 (m, 3H, CH_{Ph}).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 16.9 (Me), 24.6 (Me), 40.9 (CH_2), 45.9 (CHPh), 64.37 and 64.43 (OCH_2CH_2O), 87.8 (CH–NO_2), 109.0 ($C(OCH_2)_2$), 127.4 (CH_{Ph}), 128.5 (CH_{Ph}), 128.7 (CH_{Ph}), 139.4 (C_{Ph}).

syn-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.17 (s, 3H, Me), 1.56 (d, *J* = 6.7 Hz, 3H, Me), 2.16 (dd, *J* = 14.5, 3.7 Hz, 1H, CH_{2a}), 2.25 (dd, *J* = 14.5, 8.7 Hz, 1H, CH_{2b}), 3.45 (ddd, *J* = 8.7, 7.7, 3.7 Hz, CHPh), 3.70-3.92 (m, 4H, OCH_2CH_2O), 4.78 (app quint, *J* = 6.7 Hz, CH–NO_2), 7.20-7.23 (m, 2H, CH_{Ph}), 7.25-7.34 (m, 3H, CH_{Ph}).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 16.6 (Me), 24.6 (Me), 39.2 (CH_2), 45.8 (CHPh), 64.4 and 64.5 (OCH_2CH_2O), 88.0 (CH–NO_2), 109.2 ($C(OCH_2)_2$), 127.4 (CH_{Ph}), 128.3 (CH_{Ph}), 128.5 (CH_{Ph}), 140.0 (C_{Ph}).
HRMS (ESI): m/z calcd. for [$C_{14}H_{19}NO_4$ + H^+]: 266.1387, found: 266.1390.

(*rel*)-(3R,4R)-4-nitro-3-phenylpentan-1-ol *anti*-1r and **(*rel*)-(3R,4S)-4-nitro-3-phenylpentan-1-ol *syn*-1r**

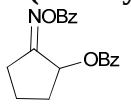


anti-**1r** *syn*-**1r**

To the solution of cinnamaldehyde (0.63 mL, 0.66 g, 5 mmol) in CH_2Cl_2 (9 mL) / MeOH (1 mL) nitroethane (0.72 mL, 0.75 g, 10 mmol), pyrrolidine (8 µL, 7 mg, 0.1 mmol), NEt_3 (70 µL, 51 mg, 0.5 mmol) and AcOH (29 µL, 30 mg, 0.5 mmol) were subsequently added with stirring. The reaction mixture was maintained for 2 d. Then $NaBH_4$ (480 mg, 12.6 mmol) was added portionwise during 30 min. After that the mixture was transferred into EtOAc (125 mL)/H_2O (75 mL). The organic layer was washed with $NaHSO_4$ (0.5 M in H_2O, 75 mL), brine (75 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 3:1, then 1:1) afforded 415 mg (40%) of *anti*-**1r** and 354 mg (34%) of *syn*-**1r** as slightly yellow oil. *Syn*-**1r** solidified upon storage in a fridge.
anti-**1r**: R_f = 0.60 (PE/EtOAc, 3:1, UV, anisaldehyde).
syn-**1r**: R_f = 0.33 (PE/EtOAc, 3:1, UV, anisaldehyde).
syn-**1r**: mp = 34-36 °C (PE/EtOAc, 20:1).
NMR matches previously reported data.[s22]

Data for products 2

2-(Benzoyloxyimino)cyclopentyl benzoate 2bb



2bb

Oxime ester **2bb** was obtained from nitro compound **1b** (56 mg, 0.48 mmol) and benzoyl chloride (0.12 mL, 0.15 g, 1.1 mmol) according to GP (0 °C, 1 d). Column chromatography (eluent: PE/EtOAc, 10:1, then 5:1) afforded 107 mg (69 %) of target oxime ester **2bb** as yellow oil that solidifies in a fridge. R_f = 0.20 (PE/EtOAc, 5:1, UV, anisaldehyde). mp = 117-119 °C (PE/EtOAc, 3:1).

(E)-**2bb**:*(Z)*-**2bb** = 3:1.

^{1}H NMR (300 MHz, COSY, $CDCl_3$):

(E)-**2a**: δ 1.84-2.41 (m, 4H, 2 × CH_2), 2.71-3.08 (m, 2H, CH_2), 5.96 (t, *J* = 5.2 Hz, 1H, CH–O), 7.37-7.63 (m, 6H, CH_{Ph}), 8.06-8.10 (m, 4H, CH_{Ph}).

(Z)-**2a** (characteristic signals): δ 6.26 (t, *J* = 6.0 Hz, 1H, CH–O), 7.24 (t, *J* = 7.7 Hz, 2H, CH_{Ph}), 7.87 (d, *J* = 7.5 Hz, 2H, CH_{Ph}), 8.00 (d, *J* = 7.5 Hz, 2H, CH_{Ph}).

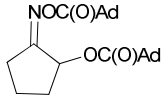
^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$):

(E)-**2a**: δ 20.8 (CH_2), 28.1 (CH_2), 32.4 (CH_2), 74.5 (CH–O), 128.4 (CH_{Ph}), 128.6 (CH_{Ph}), 128.8 (C_{Ph}), 129.7 (CH_{Ph}), 129.8 (C_{Ph}), 129.9 (CH_{Ph}), 133.2 (CH_{Ph}), 133.5 (CH_{Ph}), 163.6 (C=O), 165.5 (C=O), 171.7 (C=N).

(Z)-**2a** (characteristic signals): δ 22.0 (CH_2), 30.6 (CH_2), 32.7 (CH_2), 70.5 (CH–O), 128.3 (CH_{Ph}), 128.4 (CH_{Ph}), 129.4 (C_{Ph}), 129.6 (CH_{Ph}), 129.7 (CH_{Ph}), 133.4 (CH_{Ph}), 163.7 (C=O), 165.4 (C=O), 170.9 (C=N).

HRMS (ESI): m/z calcd. for [$C_{19}H_{17}NO_4$+Na^+]: 346.1050, found: 346.1051.

2-(1-Adamantanecarbonyloxyimino)cyclopentyl adamantane-1-carboxylate 2bc



2bc

Preparation of adamantanecarbonyl chloride AdC(O)Cl: To a stirring solution of adamantane-carboxylic acid (587 mg, 3.3 mmol) in CH_2Cl_2 (2.2 mL) oxalyl chloride (0.85 mL, 1.2 g, 9.8 mmol) was added dropwise during 15 min followed by DMF (2 drops, ca. 0.05 mL) at r.t. under Ar atmosphere. The mixture was stirred for 1.5 h and evaporated to dryness to give solid AdC(O)Cl (693 mg, quant.) which was used in the next step.

Oxime ester **2bc** was obtained from nitro compound **1b** (58 mg, 0.51 mmol) and AdC(O)Cl (223 mg, 1.12 mmol) according to GP (0 °C, 1 d) with the following change: AdC(O)Cl was added in the CH_3CN/CH_2Cl_2 (0.4/0.1 ml) to the solution of nitrocyclopenthane, NEt_3 and DMAP in CH_3CN (0.51 ml). Column chromatography (eluent: PE/EtOAc, 7:1) afforded 197 mg (88 %) of target oxime ester **2bc** as white solid. R_f = 0.33 (PE/EtOAc, 5:1, anisaldehyde). mp = 155-157 °C (PE/EtOAc, 10:1).

(E)-**2bc**:*(Z)*-**2bc** = 3:1.

^{1}H NMR (300 MHz, COSY, $CDCl_3$):

(E)-**2a**: δ 1.71-2.05 (m, 34H, all CH_{Ad}, all CH_{2Ad}, 2 × CH_2), 2.54-2.81 (m, 2H, CH_2), 5.60 (t, *J* = 5.0 Hz, 1H, CH–O).

(Z)-**2a** (characteristic signals): δ 5.84 (dd, *J* = 6.1, 2.6 Hz, 1H, CH–O).

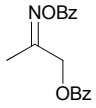
^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$):

(E)-**2a**: δ 20.6 (CH_2), 27.7 (CH_2), 27.9 (all CH_{Ad}), 32.2 (CH_2), 36.4, 38.6 and 38.9 (all CH_{2Ad}), 40.8 (C_{Ad}), 73.4 (CH–O), 171.2 (C=N), 174.0 (C=O), 176.4 (C=O).

(Z)-**2a** (characteristic signals): δ 22.0 (CH_2), 30.3 (CH_2), 33.0 (CH_2), 68.9 (CH–O).

HRMS (ESI): m/z calcd. for [$C_{27}H_{37}NO_4$+Na^+]: 462.2615, found: 462.2606.

2-(Benzoyloxyimino)propyl benzoate 2cb



2cb

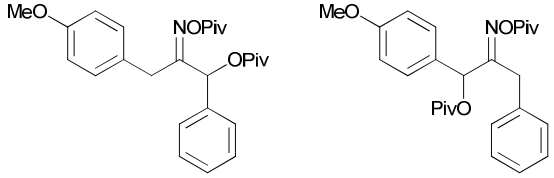
Oxime ester **2cb** was obtained from nitro compound **1c** (90 µL, 89 mg, 1.0 mmol) and benzoyl chloride (0.23 mL, 0.28 g, 2.2 mmol) according to GP (0 °C, 1 d). Column chromatography (eluent: PE/EtOAc, 7:1) afforded 175 mg (59 %) of target oxime ester **2cb** as colorless oil, that solidifies in a fridge. R_f = 0.24 (PE/EtOAc, 5:1, UV, anisaldehyde). mp = 76-78 °C (PE/EtOAc, 50:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 5.12 (s, 2H, CH_2–O), 7.44-7.51 (m, 4H, CH_{Ph}), 7.57-7.64 (m, 2H, CH_{Ph}), 8.07-8.11 (m, 4H, CH_{Ph}).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 13.8 (CH_3), 65.0 (CH_2–O), 128.5 (CH_{Ph}), 128.6 (CH_{Ph}), 128.7 (C_{Ph}), 129.2 (C_{Ph}), 129.7 (CH_{Ph}), 129.8 (CH_{Ph}), 133.5 (CH_{Ph}), 133.6 (CH_{Ph}), 162.5 (C=N), 163.5 (C=O), 165.9 (C=O).

HRMS (ESI): m/z calcd. for [$C_{17}H_{15}NO_4$+Na^+]: 320.0893, found: 320.0895.

3-(4-Methoxyphenyl)-1-phenyl-2-(pivaloyloxyimino)propyl pivalate 2e and **1-(4-Methoxyphenyl)-3-phenyl-2-(pivaloyloxyimino)propyl pivalate 2'e**



2e **2'e**

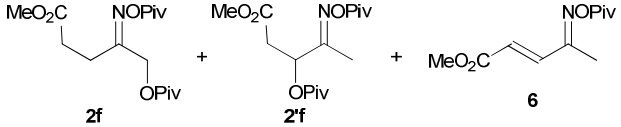
Oxime esters **2e** and **2'e** were obtained from nitro compound **1e** (157 mg, 0.58 mmol) and pivaloyl chloride (0.16 mL, 0.15 g, 1.3 mmol) according to GP (r.t., 2 d). Column chromatography (eluent: PE/EtOAc, 15:1, then 9:1) afforded 194 mg of target oxime esters **2e** and **2'e** (**2e** : **2'e** = 1:1, ^{1}H NMR, total yield 76 %) as a white solid. R_f = 0.30 (PE/EtOAc, 9:1, UV, anisaldehyde). mp (**2e**+**2'e**) = 83-89 °C (PE/EtOAc, 10:1).

^{1}H NMR (300 MHz, $CDCl_3$, for **2e**+**2'e** mixture): δ 1.13 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu), 1.16 (s, 18H, 2 × *t*-Bu), 3.67 (s, 2H, CH_2, **2e**), 3.73 (s, 2H, CH_2, **2'e**), 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 6.51 (s, 1H, CH–O, **2'e**), 6.55 (s, 1H, CH–O, **2e**), 6.78 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 6.90 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 6.95 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.05 (d, *J* = 7.1 Hz, CH_{Ar}), 7.16-7.42 (m, 10H, CH_{Ar}).

^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, for **2e**+**2'e** mixture): δ 27.0 and 27.1 (all $\underline{Me}_3$C–C), 32.0 (CH_2, **2e**), 32.9 (CH_2, **2'e**), 38.57 ($Me_3\underline{C}$), 38.60 ($Me_3\underline{C}$), 38.86 ($Me_3\underline{C}$), 38.89 ($Me_3\underline{C}$), 55.3 (OMe), 75.1 (CH–O, **2'e**), 75.3 (CH–O, **2e**), 114.0 (CH_{Ar}), 114.2 (CH_{Ar}), 126.5 (C_{Ar}), 126.6 (CH_{Ar}), 126.7 (CH_{Ar}), 127.7 (C_{Ar}), 128.1 (CH_{Ar}), 128.2 (CH_{Ar}), 128.6 (CH_{Ar}), 128.7 (CH_{Ar}), 129.2 (CH_{Ar}), 134.7 (C_{Ph}, **2'e**), 135.8 (C_{Ph}, **2e**), 158.4 ($\underline{C}_{Ar}$–OMe), 159.9 ($\underline{C}_{Ar}$–OMe), 164.3 (C=N), 164.5 (C=N), 174.6 (C=O), 176.6 (C=O), 176.7 (C=O).

HRMS (ESI): m/z calcd. for [$C_{26}H_{33}NO_5$+Na^+]: 462.2251, found: 462.2259.

Methyl 5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2f, Methyl 3-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2'f and **(2*E*)-Methyl 4-(pivaloyloxyimino)pent-2-enoate 6**

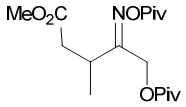


2f **2'f** **6**

Oxime esters **2f** and **2'f** was obtained from nitro compound **1f** (146 mg, 0.9 mmol) and pivaloyl chloride (0.25 mL, 0.24 g, 2.0 mmol) according to GP (0 °C, 1 d). Column chromatography (eluent: PE/EtOAc, 4:1, then 3:1) afforded 206 mg of mixture **2f**+**2'f**+**6**

(**2f**:**2'f**:**6** = 8:2:1 (^{1}H NMR), yields: **2f**: 53 %, **2'f**: 7 %, **6**: 13 %) as colorless oil. R_f = 0.22 (PE/EtOAc, 5:1, anisaldehyde). NMR for (*E*)-**2f**, **2'f** and **6** matches previously reported data.[s23]
(E)-**2f**:*(Z)*-**2f** = 2:1.
(*Z*)-**2f**: ^{1}H NMR (300 MHz, $CDCl_3$, characteristic signals): δ 4.98 (s, 2H, CH_2–O).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$, characteristic signals): δ 26.9 (CH_2–C=O), 29.9 (CH_2–C=N), 59.5 (CH_2–O).

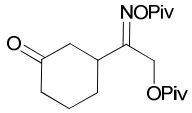
Methyl 3-methyl-5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2j



2j

Oxime ester **2j** was obtained from nitro compound **1j** (80 mg, 0.46 mmol) and pivaloyl chloride (0.13 mL, 0.12 g, 1.0 mmol) according to GP (r.t., 1 d). Column chromatography (eluent: PE/EtOAc, 5:1) afforded 100 mg (63 %) of target oxime ester **2j** as colorless oil. R_f = 0.33 (PE/EtOAc, 5:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H, *t*-Bu), 1.26 (d, overlapped, 3H, Me), 1.32 (s, 9H, *t*-Bu), 2.53 (dd, *J* = 16.2, 8.1 Hz, 1H, CH_{2a}), 2.75 (dd, *J* = 16.2, 6.8 Hz, 1H, CH_{2b}), 3.53 (app sex, *J* = 7.2 Hz, 1H, CH), 3.71 (s, 3H, CO_2Me), 4.77 (d, *J* = 13.0 Hz, 1H, CH_{2a}–O), 4.84 (d, *J* = 13.0 Hz, 1H, CH_{2a}–O).
^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 16.5 (Me), 27.16 ($\underline{Me}_3C$), 27.20 ($\underline{Me}_3C$), 30.7 (CH), 37.6 (CH_2), 38.7 ($Me_3\underline{C}$), 38.9 ($Me_3\underline{C}$), 51.9 ($CO_2\underline{Me}$), 63.6 (CH_2–O), 165.6 (C=N), 171.6 ($\underline{C}O_2Me$), 174.7 (C=O), 177.5 (C=O).
HRMS (ESI): m/z calcd. for [$C_{17}H_{29}NO_6$+Na^+]: 366.1887, found: 366.1894.

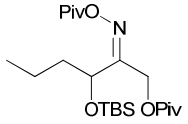
2-(3-Oxocyclohexyl)-2-(pivaloyloxyimino)ethyl pivalate 2k



2k

Oxime ester **2k** was obtained from nitro compound **1k** (118 mg, 0.69 mmol) and pivaloyl chloride (0.19 mL, 0.18 g, 1.52 mmol) according to GP (r.t., 2 d). Column chromatography (eluent: PE/EtOAc, 9:1, then 5:1) afforded 194 mg (83 %) of target oxime ester **2k** as slightly yellow oil. R_f = 0.53 (PE/EtOAc, 3:1, anisaldehyde).
(E)-**2k**:*(Z)*-**2k** = 1:6.
^{1}H NMR (300 MHz, $CDCl_3$):
(Z)-**2k**: δ 1.24 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.61-1.90 (m, 2H) and 2.09-2.21 (m, 2H) (2 × CH_2), 2.28-2.45 (m, 2H, CH_2), 2.52-2.71 (m, 2H, CH_2), 2.90 (app tt, *J* = 11.4, 3.8 Hz, 1H, CH), 4.98 (s, 2 H, CH_2–O).
(E)-**2k** (characteristic signals): δ 4.75-4.86 (m, 2H, CH_2–O).
^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$):
(Z)-**2k**: δ 25.0 (CH_2), 27.1 ($\underline{Me}_3C$), 27.2 ($\underline{Me}_3C$), 28.9 (CH_2), 38.8 ($Me_3\underline{C}$), 38.9 ($Me_3\underline{C}$), 40.5 (CH), 41.0 (CH_2), 44.2 (CH_2), 58.6 (CH_2–O), 165.7 (C=N), 174.2 (OC=O), 177.5 (OC=O), 209.2 (C=O).
(E)-**2k** (characteristic signals): δ 38.6 (CH), 41.2 (CH_2), 43.1 (CH_2), 62.9 (CH_2–O).
HRMS (ESI): m/z calcd. for [$C_{18}H_{29}NO_5$+Na^+]: 362.1938, found: 362.1935.

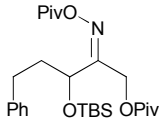
3-(*tert*-Butyldimethylsilyloxy)-2-(pivaloyloxyimino)hexyl pivalate 2m



(*Z*)-**2m**

Oxime ester **2m** was obtained from nitro compound **1m** (107 mg, 0.41 mmol) and pivaloyl chloride (0.11 mL, 0.11 g, 0.9 mmol) according to GP (r.t., 2 d). Column chromatography (eluent: PE/EtOAc, 30:1) afforded 110 mg (63 %) of target oxime ester **2m** as colorless oil. R_f = 0.67 (PE/EtOAc, 9:1, anisaldehyde).
only *(Z)*-**2m**. Configuration of C=N bond was assigned based on spectra similarity with *(Z)*-**2l**.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 3 H, MeSi), 0.08 (s, 3 H, MeSi), 0.90 (s, 9H, *t*-BuSi), 0.95 (t, *J* = 7.2 Hz, 3H, Me), 1.24 (s, 9H, *t*-Bu-C), 1.28 (s, 9H, *t*-Bu-C), 1.30-1.41 (m, 1H, CH_{2a}), 1.44-1.65 (m, 2H, $CH_{2b,c}$), 1.71-1.83 (m, 1H, CH_{2d}), 4.70 (d, *J* = 13.7 Hz, 1H, C$\underline{H}_{2a}$–OPiv), 5.03 (dd, *J* = 8.1, 4.5 Hz, 1H, C$\underline{H}$–OTBS), 5.04 (d, *J* = 13.7 Hz, 1H, C$\underline{H}_{2b}$–OPiv).
^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ -5.12 (MeSi), -5.09 (MeSi), 14.0 (Me), 18.0 (C-Si), 18.6 (CH_2), 25.7 (*t*-BuSi), 27.15 ($\underline{Me}_3$C–C), 27.19 ($\underline{Me}_3$C–C), 37.5 (CH_2), 38.6 ($Me_3\underline{C}$), 38.7 ($Me_3\underline{C}$), 60.8 (CH_2–O), 67.9 (CH–O), 166.3 (C=N), 174.0 (C=O), 177.6 (C=O).
HRMS (ESI): m/z calcd. for [$C_{22}H_{43}NO_5Si+Na^+$]: 452.2803, found: 452.2804.

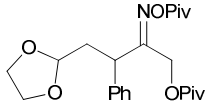
3-(*tert*-Butyldimethylsilyloxy)-5-phenyl-2-(pivaloyloxyimino)pentyl pivalate 2n



(*Z*)-**2n**

Oxime ester **2n** was obtained from nitro compound **1n** (169 mg, 0.52 mmol) and pivaloyl chloride (0.14 mL, 0.14 g, 1.1 mmol) according to GP (r.t., 2 d). Column chromatography (eluent: PE/EtOAc, 20:1) afforded 191 mg (75 %) of target oxime ester **2n** as colorless oil, that solidifies n a fridge. R_f = 0.62 (PE/EtOAc, 5:1, anisaldehyde). mp = 73-75 °C (PE/EtOAc, 20:1).
only *(Z)*-**2n**. Configuration of C=N bond was assigned based on spectra similarity with *(Z)*-**2l**.
^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.10 (s, 3 H, MeSi), 0.14 (s, 3 H, MeSi), 0.96 (s, 9H, *t*-BuSi), 1.26 (s, 9H, *t*-Bu-C), 1.28 (s, 9H, *t*-Bu-C), 1.92-2.04 (m, 1H, C$\underline{H}_{2a}$CH–O), 2.06-2.19 (m, 1H, C$\underline{H}_{2b}$CH–O), 2.63 (ddd, *J* = 13.4, 11.4, 5.7 Hz, 1H, C$\underline{H}_{2a}$–Ph), 2.85 (ddd, *J* = 13.4, 11.8, 5.0 Hz, 1H, C$\underline{H}_{2b}$–Ph), 4.75 (d, *J* = 14.0 Hz, 1H, C$\underline{H}_{2a}$–OPiv), 5.08-5.13 (m, 1H, C$\underline{H}$–OTBS), 5.11 (d, *J* = 14.0 Hz, 1H, C$\underline{H}_{2b}$–OPiv).
^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ -5.02 (MeSi), -4.97 (MeSi), 18.1 (C-Si), 18.6 (CH_2), 25.7 (*t*-BuSi), 27.19 ($\underline{Me}_3$C–C), 27.20 ($\underline{Me}_3$C–C), 31.8 ($\underline{C}H_2$–Ph), 37.5 ($\underline{C}H_2$CH–O), 38.7 ($Me_3\underline{C}$), 38.9 ($Me_3\underline{C}$), 60.8 (CH_2–O), 67.9 (CH–O), 126.1 (CH_{Ph}), 128.2 (CH_{Ph}), 128.5 (CH_{Ph}), 141.1 (C_{Ph}), 166.0 (C=N), 174.0 (C=O), 177.6 (C=O).
HRMS (ESI): m/z calcd. for [$C_{27}H_{45}NO_5Si+H^+$]: 514.2959, found: 514.2969.

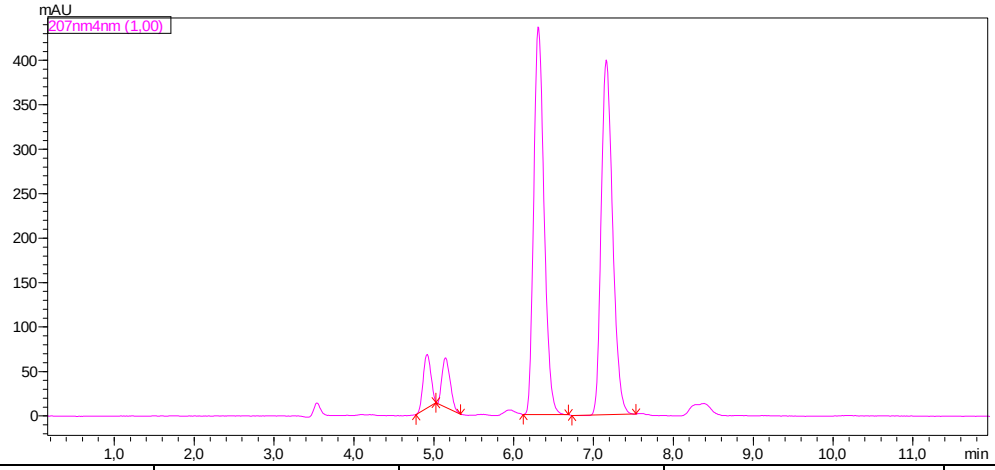
4-(1,3-Dioxolan-2-yl)-3-phenyl-2-(pivaloyloxyimino)butyl pivalate 2p



2p

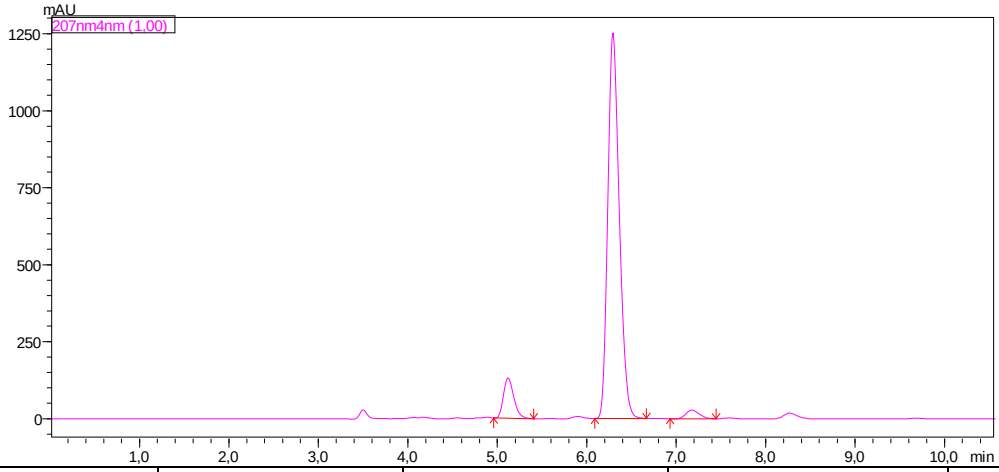
HPLC separation conditions:
column: Chiralpak AD-3, 250 x 4.6 mm, temp. 25 °C,
eluent: Hexane-*i*-PrOH, 90:10, 1 mL/min, detection at 207 nm.
t_R = 4.9 min (*Z*-isomer, minor), 5.2 min (*Z*-isomer, major), 6.3 min (*E*-isomer, major), 7.1 (*E*-isomer, minor).

2p, racemic, *E*+*Z*-mixture



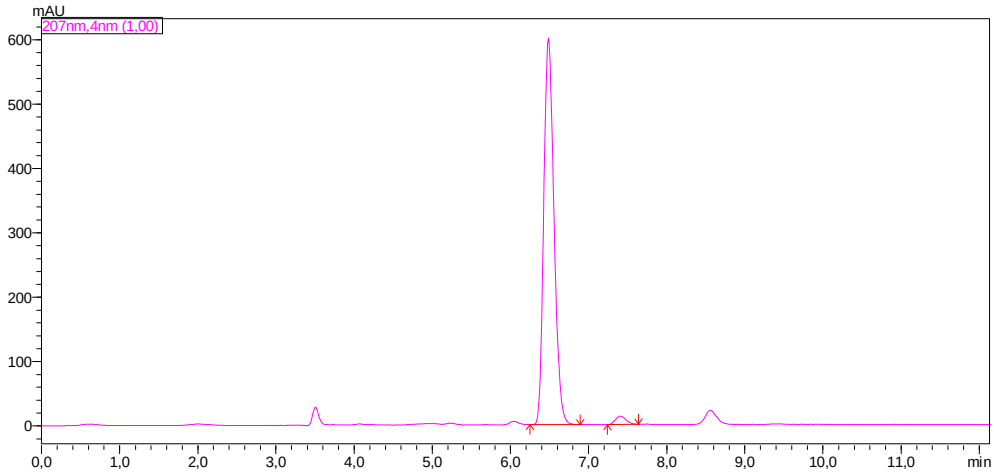
Peak#	Ret. Time	Area	Height	Area%
1	4,916	408857	60119	4,685
2	5,147	393479	55597	4,509
3	6,309	3952598	435982	45,292
4	7,160	3972017	399225	45,514
Total		8726951	950923	100,000

2p, enantioenriched, obtained from *anti*-**1p**, *E*+*Z*-mixture



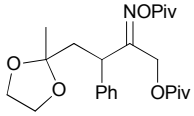
Peak#	Ret. Time	Area	Height	Area%
1	5,120	1047171	130713	8,402
2	6,292	11132354	1252509	89,326
3	7,174	283135	27735	2,272
Total		12462660	1410958	100,000

2p, enantioenriched, obtained from *syn*-**1p**, *E*-isomer



Peak#	Ret. Time	Area	Height	Area%
1	6,485	5459815	600224	97,806
2	7,405	122485	12842	2,194
Total		5582299	613065	100,000

4-(2-Methyl-1,3-dioxolan-2-yl)-3-phenyl-2-(pivaloyloxyimino)butyl pivalate 2q



2q

Oxime ester **2q** was obtained from nitro compound *anti*-**1q** (109 mg, 0.41 mmol) and pivaloyl chloride (0.11 mL, 0.11 g, 0.9 mmol) according to GP (r.t., 2 d). Column chromatography (eluent: PE/EtOAc, 6:1) afforded 140 mg (76 %) of target oxime ester **2q** as colorless oil, that solidifies in a fridge. R_f = 0.36 (PE/EtOAc, 5:1, anisaldehyde). mp = 65-67 °C (PE).

Similar procedure for *syn*-**1q** (112 mg, 0.42 mmol) gave 152 mg (84 %) of target oxime ester **2q**. Maintaining NMR sample in $CDCl_3$ at r.t. for 3d resulted in a change of ratio *(E)*-**2q**:*(Z)*-**2q** = from 4:1 to 2:1.

^{1}H NMR (300 MHz, $CDCl_3$):

(E)-**2q**: δ 1.06 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu), 1.34 (s, 1 H, CH_3), 2.40 (dd, *J* = 14.8, 4.5 Hz, 1H, CH_{2a}), 2.56 (dd, *J* = 14.8, 9.8 Hz, 2H, CH_{2b}), 3.79-3.97 (m, 4H, OCH_2CH_2O), 4.78 (d, *J* = 13.1 Hz, 1H, $C\underline{H}_{2a}OPiv$), 4.84 (dd, *J* = 9.8, 4.5 Hz, 1H, CHPh), 4.97 (d, *J* = 13.1 Hz, 1H, $C\underline{H}_{2b}OPiv$), 7.17-7.39 (m, 5H, Ph).

(Z)-**2q**: δ 1.12 (s, 9H, *t*-Bu), 1.30 (s, 9H, *t*-Bu), 1.32 (s, 1 H, CH_3), 2.23 (dd, *J* = 14.6, 5.0, 1H, CH_{2a}), 2.79 (dd, *J* = 14.6, 9.0, 2H, CH_{2b}), 3.79-3.97 (m, 4H, OCH_2CH_2O), 4.20 (dd, *J* = 9.0, 5.0 Hz, 1H, CHPh), 4.57 (d, *J* = 14.4 Hz, 1H, $C\underline{H}_{2a}OPiv$), 4.96 (d, *J* = 14.4 Hz, 1H, $C\underline{H}_{2b}OPiv$), 7.17-7.39 (m, 5H, Ph).

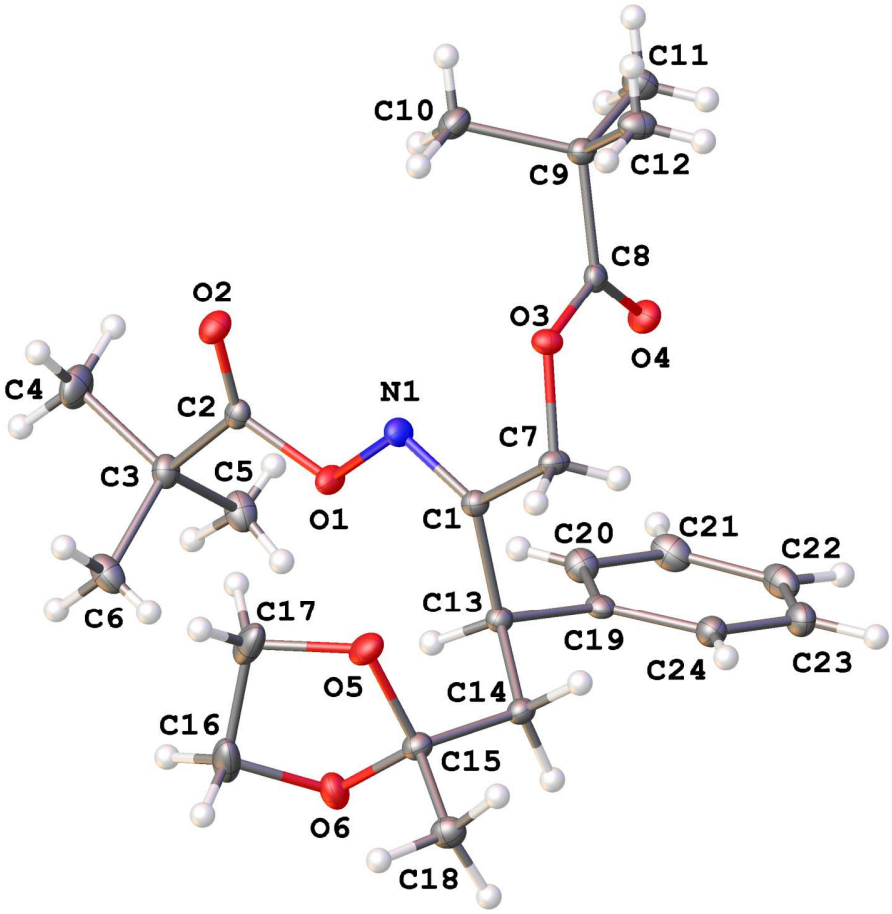
^{13}C NMR (75 MHz, DEPT, $CDCl_3$):

(E)-**2q**: δ 24.4 (Me), 27.0 ($\underline{Me}_3C$), 27.2 ($\underline{Me}_3C$), 38.5 ($\underline{C}HPh$), 38.6 ($Me_3\underline{C}$), 38.7 ($Me_3\underline{C}$), 39.8 (CH_2), 62.7 ($\underline{C}H_2$–OPiv), 64.4 and 64.6 (OCH_2CH_2O), 108.8 ($\underline{C}(OCH_2)_2$), 127.0 (CH_{Ph}), 127.6 (CH_{Ph}), 128.6 (CH_{Ph}), 138.8 (C_{Ph}), 165.4 (C=N), 174.7 (C=O), 177.6 (C=O).

(Z)-**2q**: δ 24.6 (Me), 27.0 ($\underline{Me}_3C$), 27.2 ($\underline{Me}_3C$), 38.7 ($Me_3\underline{C}$), 38.8 ($Me_3\underline{C}$), 40.7 (CH_2), 43.0 ($\underline{C}HPh$), 57.9 ($\underline{C}H_2$–OPiv), 64.3 and 64.6 (OCH_2CH_2O), 109.1 ($\underline{C}(OCH_2)_2$), 127.1 (CH_{Ph}), 128.2 (CH_{Ph}), 128.6 (CH_{Ph}), 139.5 (C_{Ph}), 166.1 (C=N), 174.7 (C=O), 177.6 (C=O).

HRMS (ESI): m/z calcd. for $[C_{24}H_{35}NO_6+Na^+]$: 456.2357, found: 456.2352.

The crystallographic information for compound **2q** was deposited in the Cambridge Crystallographic Data Centre (CCDC 1906181).



General view of the compound (*E*)-**2q** in representation of atoms *via* thermal ellipsoids at 50% probability level. Only one of the two symmetry-independent molecules is shown.

References

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Copies of NMR spectra

1-Methoxy-4-(2-nitro-3-phenylpropyl)benzene 1e

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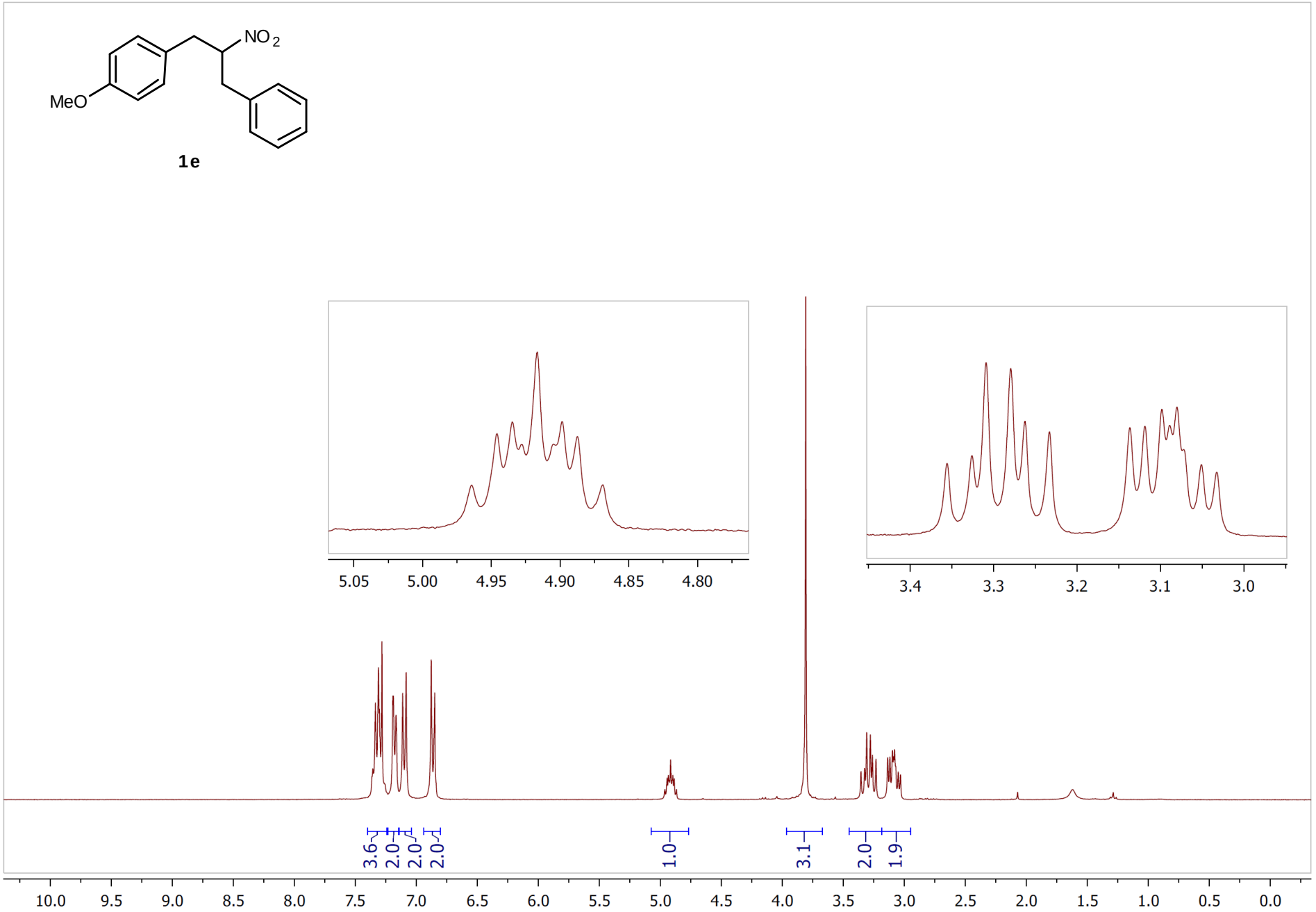
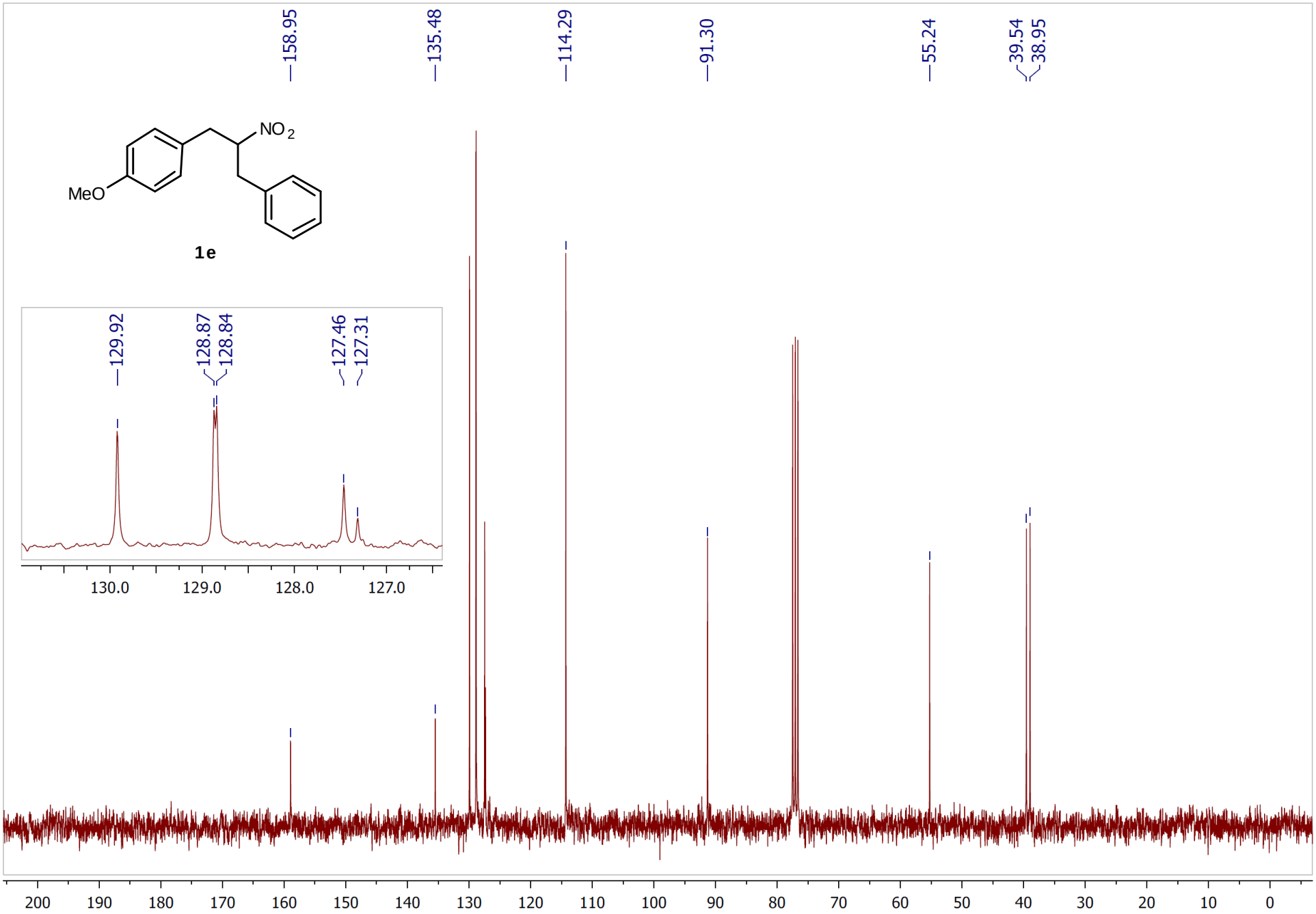


^{13}C NMR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127.31
130.0
129.0
128.0
127.0
200
190
180
170
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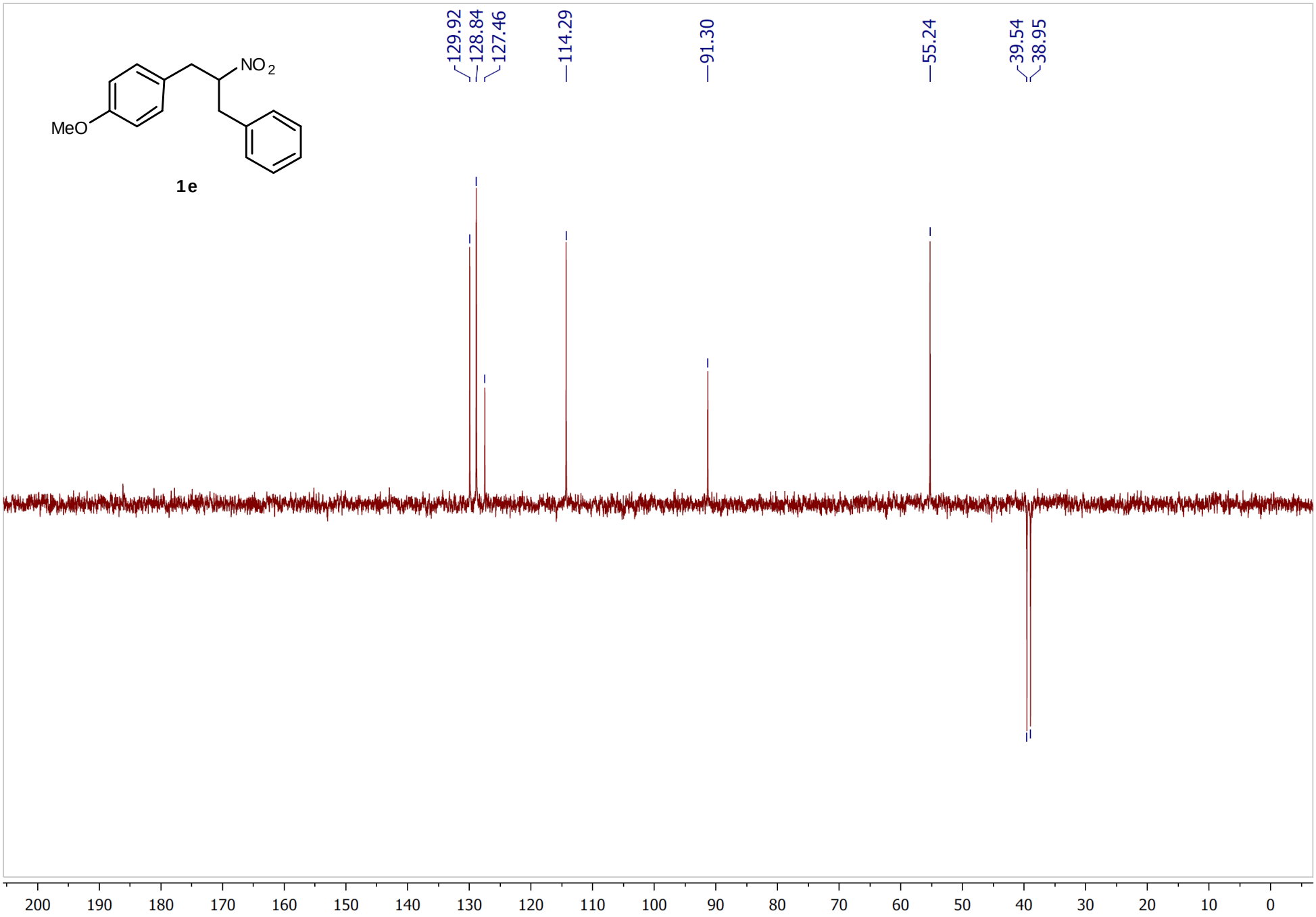
^{13}C NMR DEPT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1e
200
190
180
170
160
150
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70
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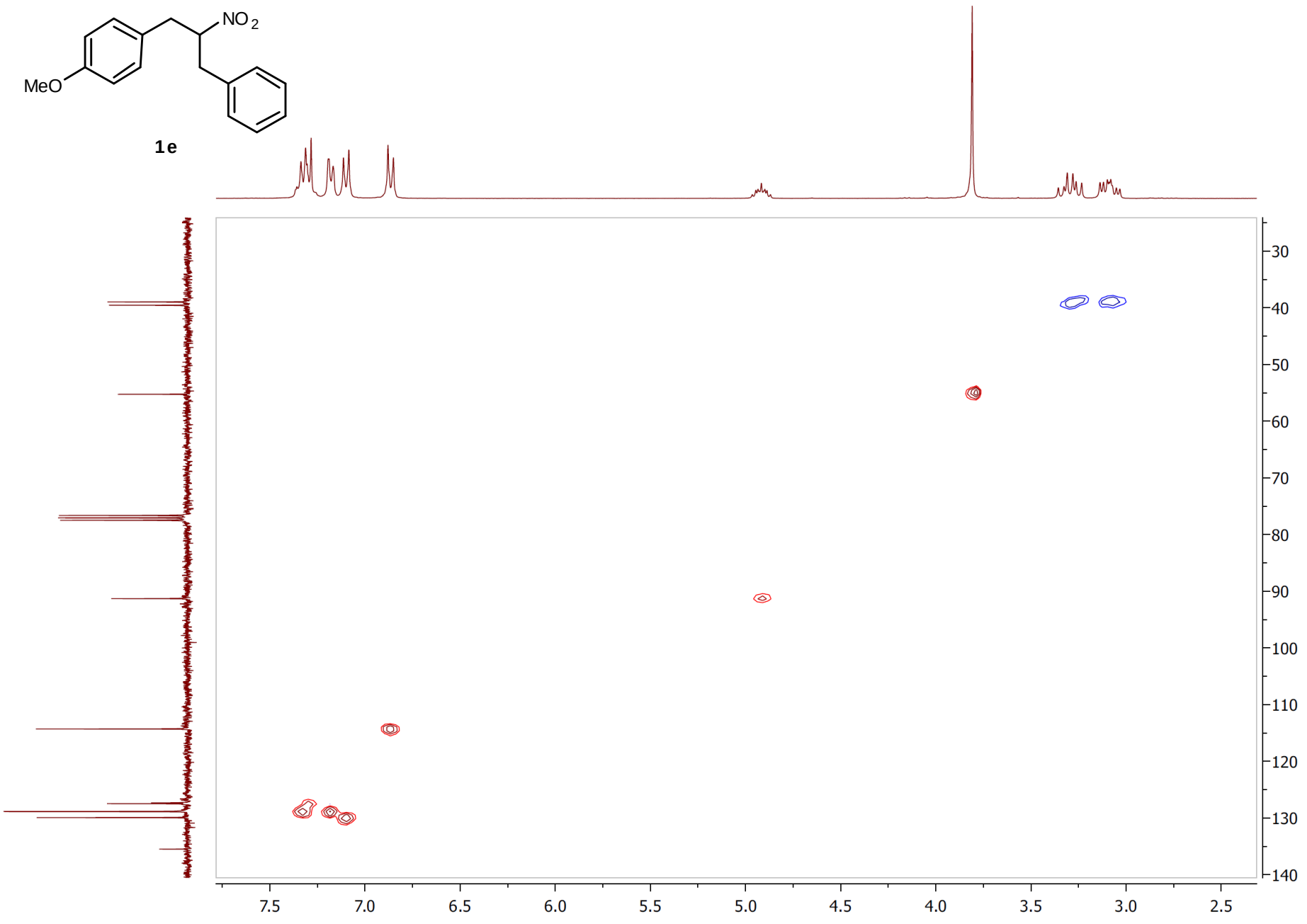
0

^{1}H-^{13}C HSQC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140
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6.5
6.0
5.5
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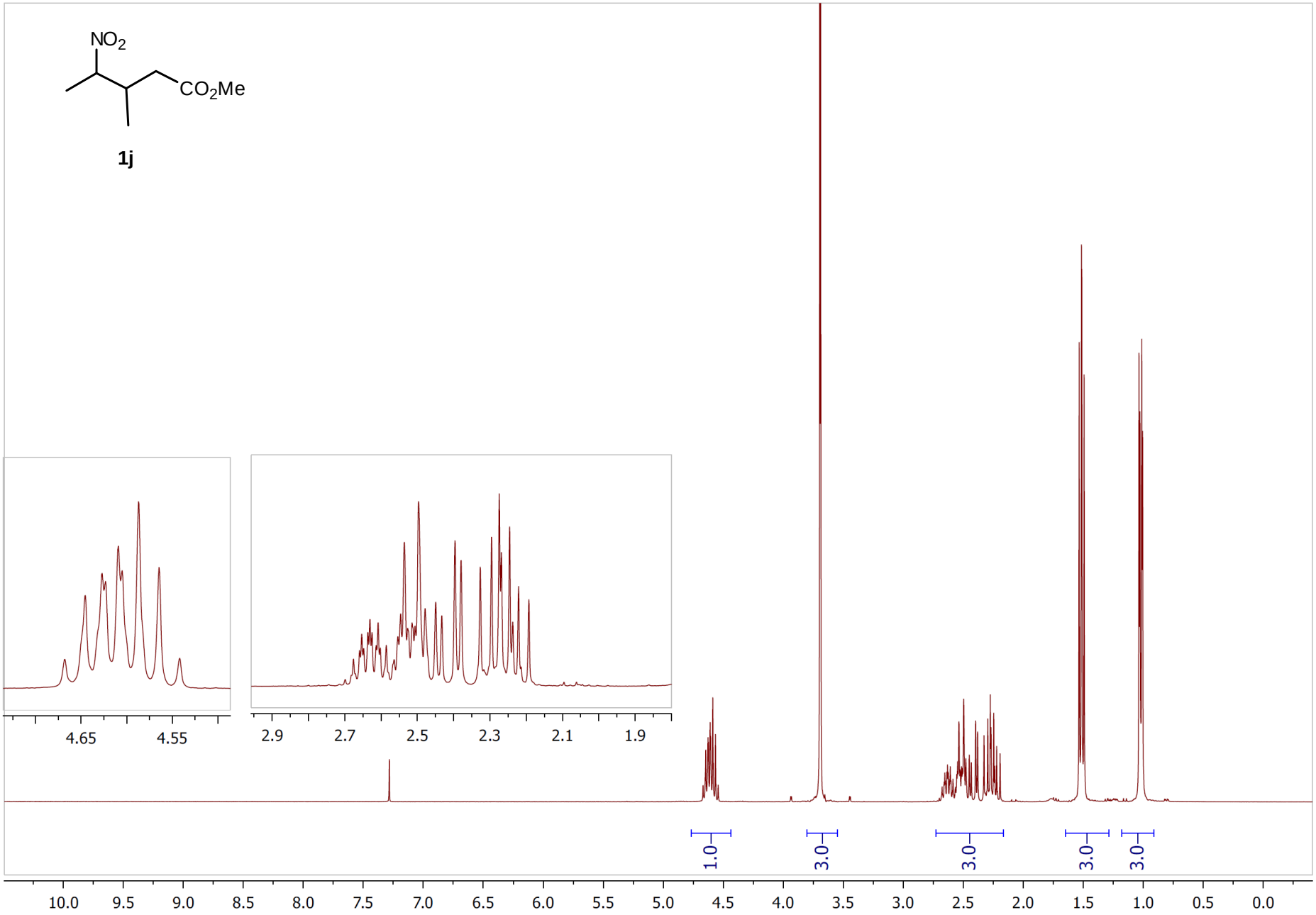
4.5
4.0
3.5
3.0
2.5

Methyl 3-methyl-4-nitropentanoate 1j

^{1}H NMR



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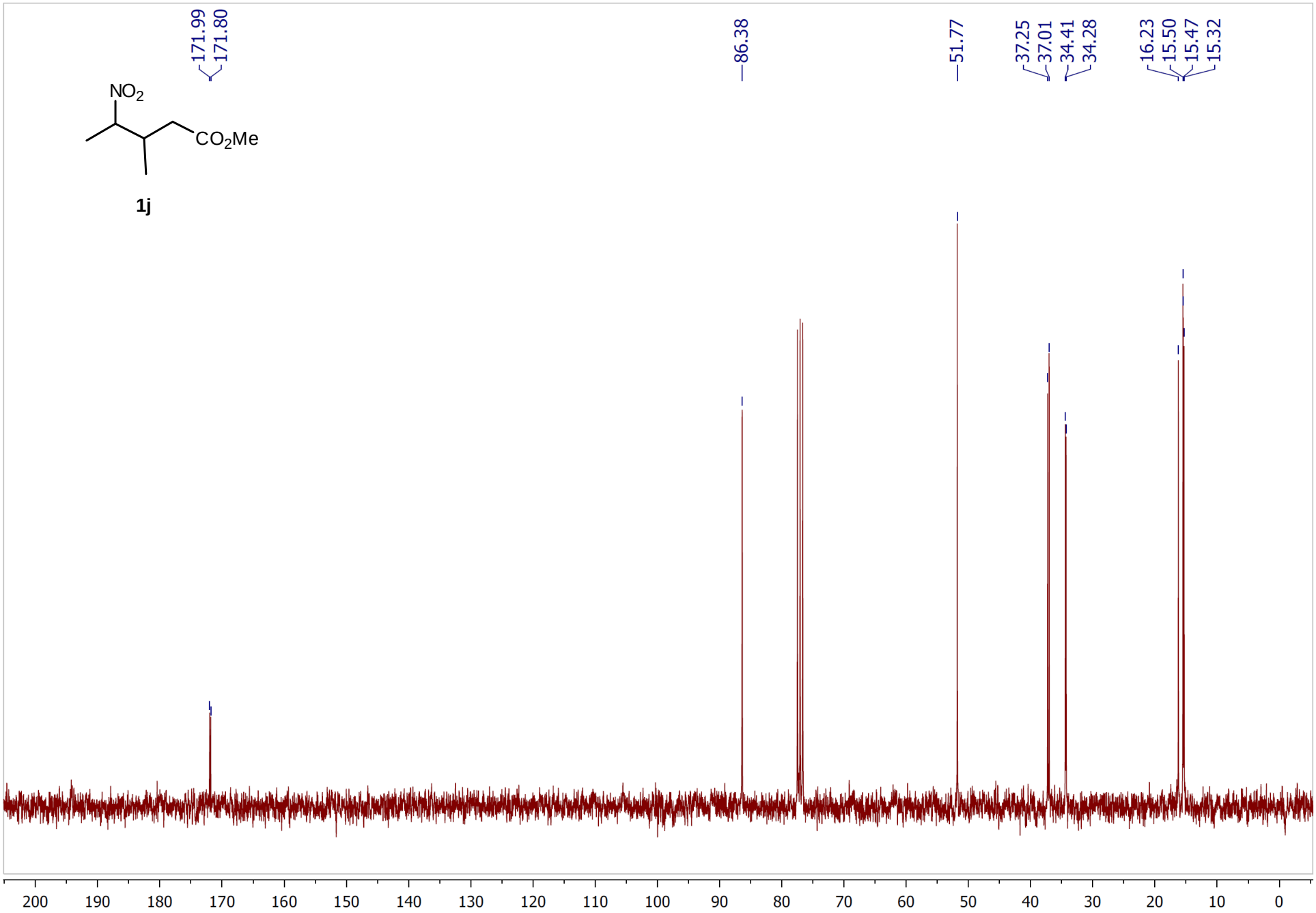
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34.28
16.23
15.50
15.47
15.32
NO2
CO2Me
1j
200
190
180
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20
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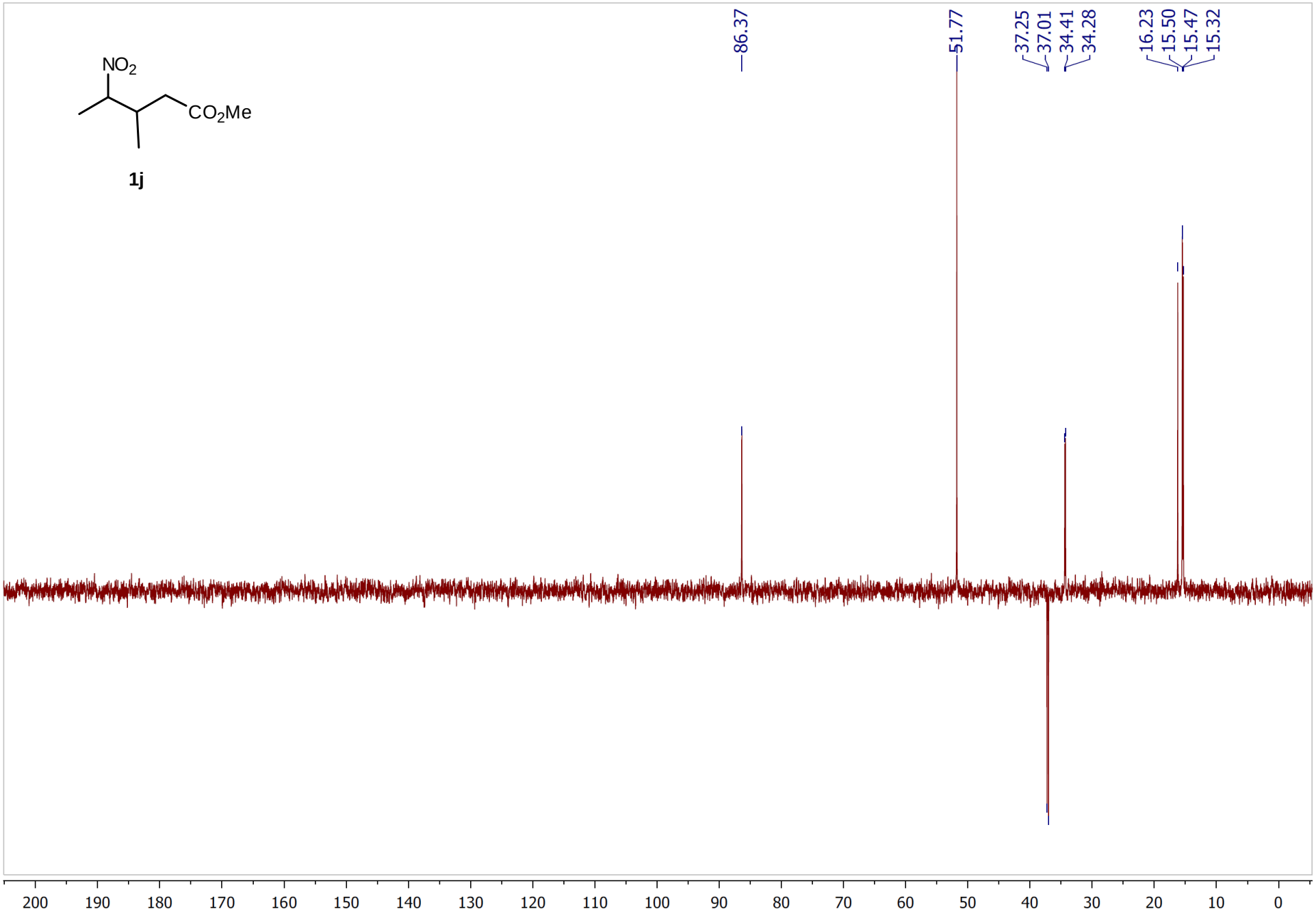
0

^{13}C NMR DEPT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15.32
200
190
180
170
160
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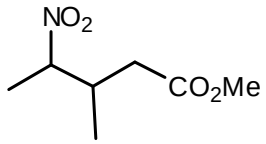
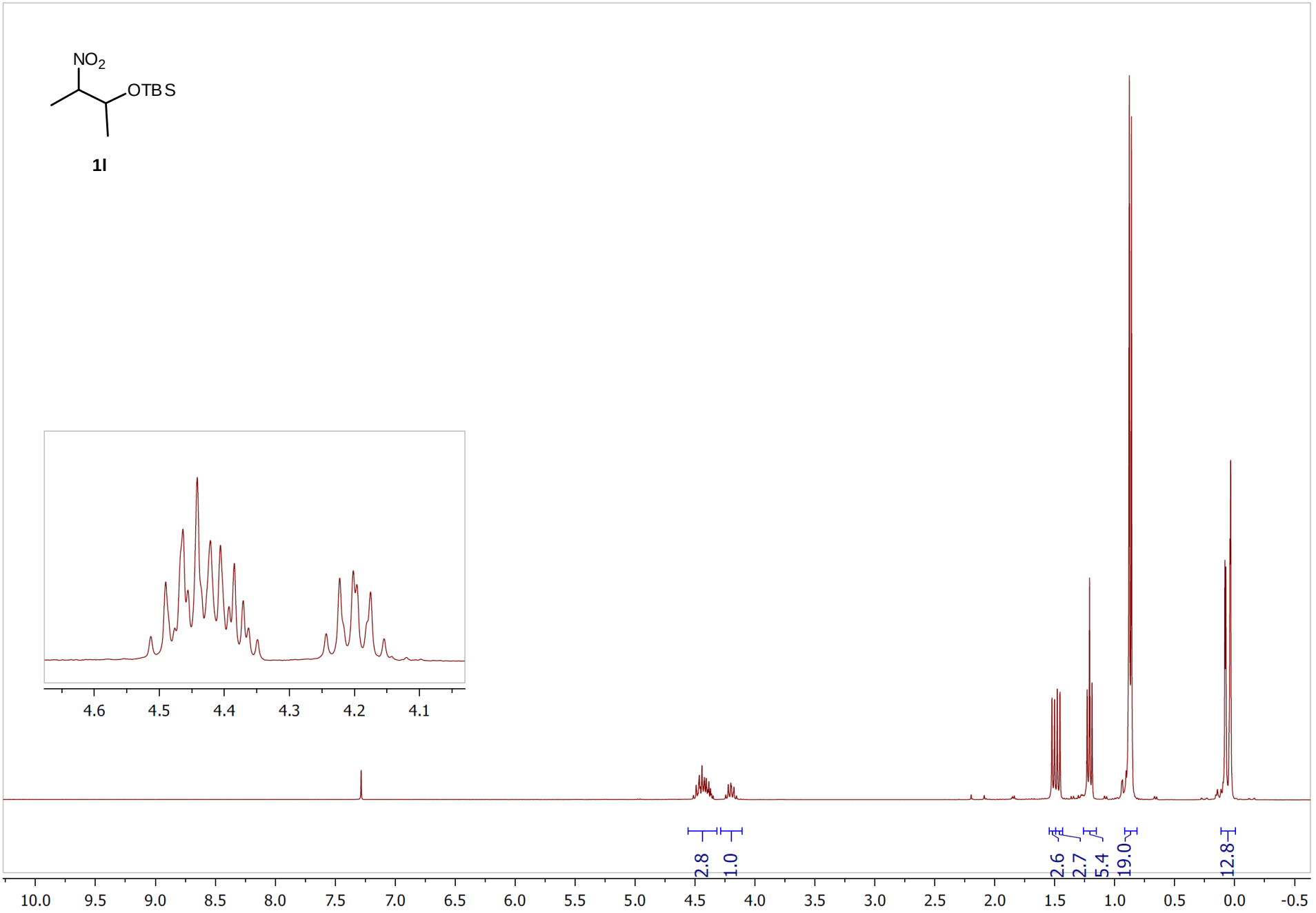
^{1}H-^{1}H COSY



1j

***tert*-Butyldimethyl(3-nitrobutan-2-yloxy)silane 1l**

^{1}H NMR



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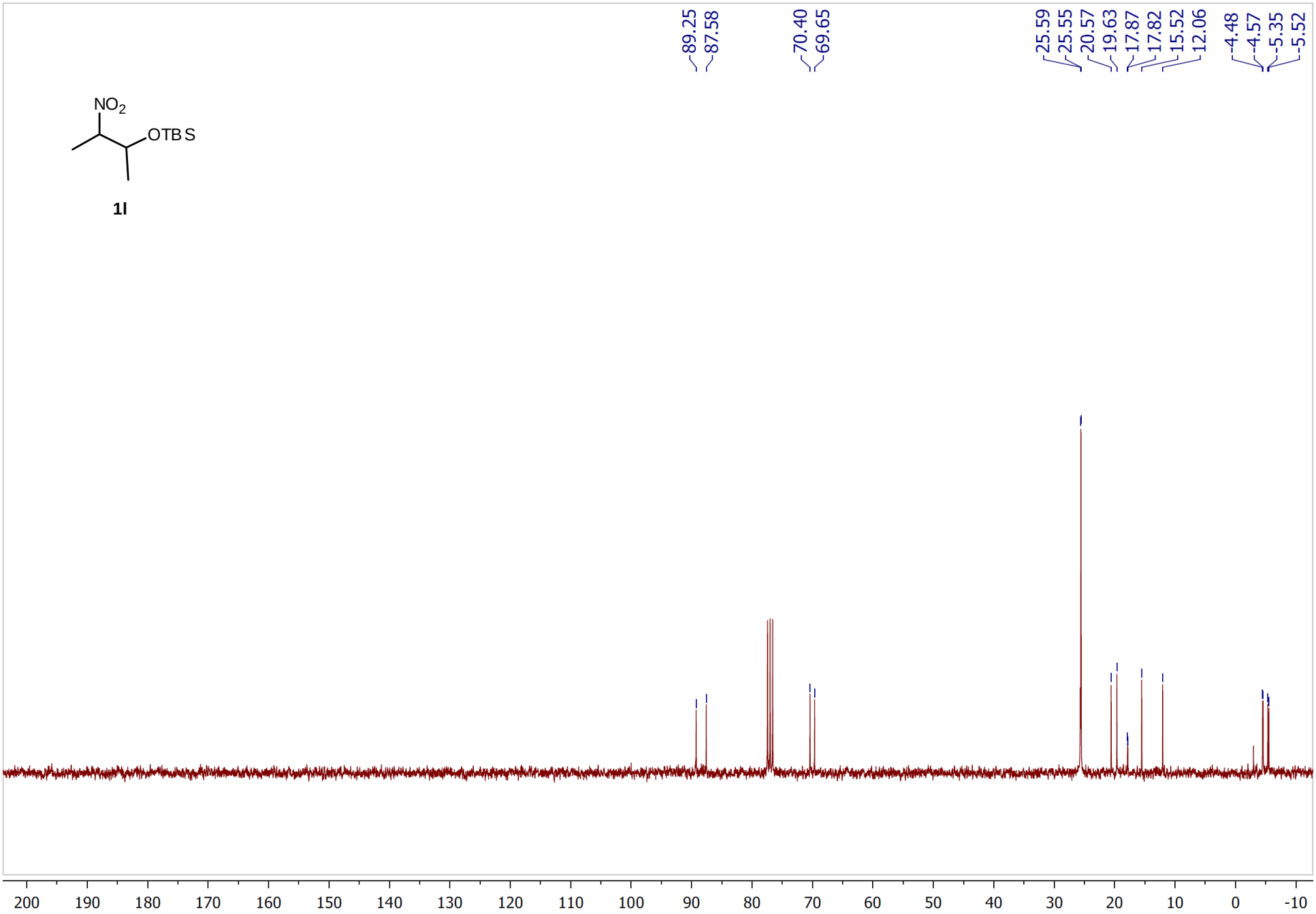
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25.55
20.57
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17.82
15.52
12.06
-4.48
-4.57
-5.35
-5.52
NO2
OTBS
1l
200
190
180
170
160
150
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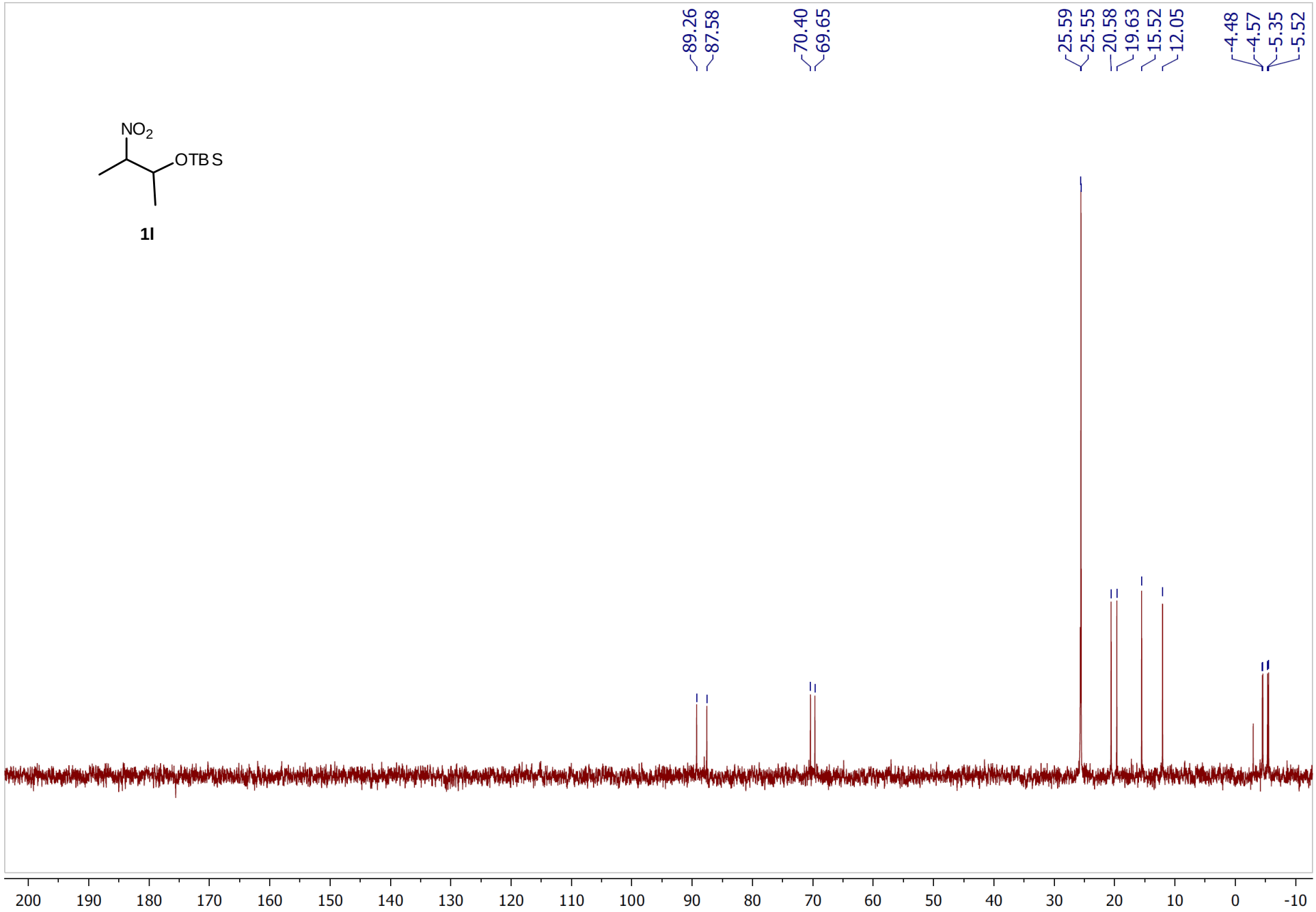
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT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-5.52
NO2
OTBS
1l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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20
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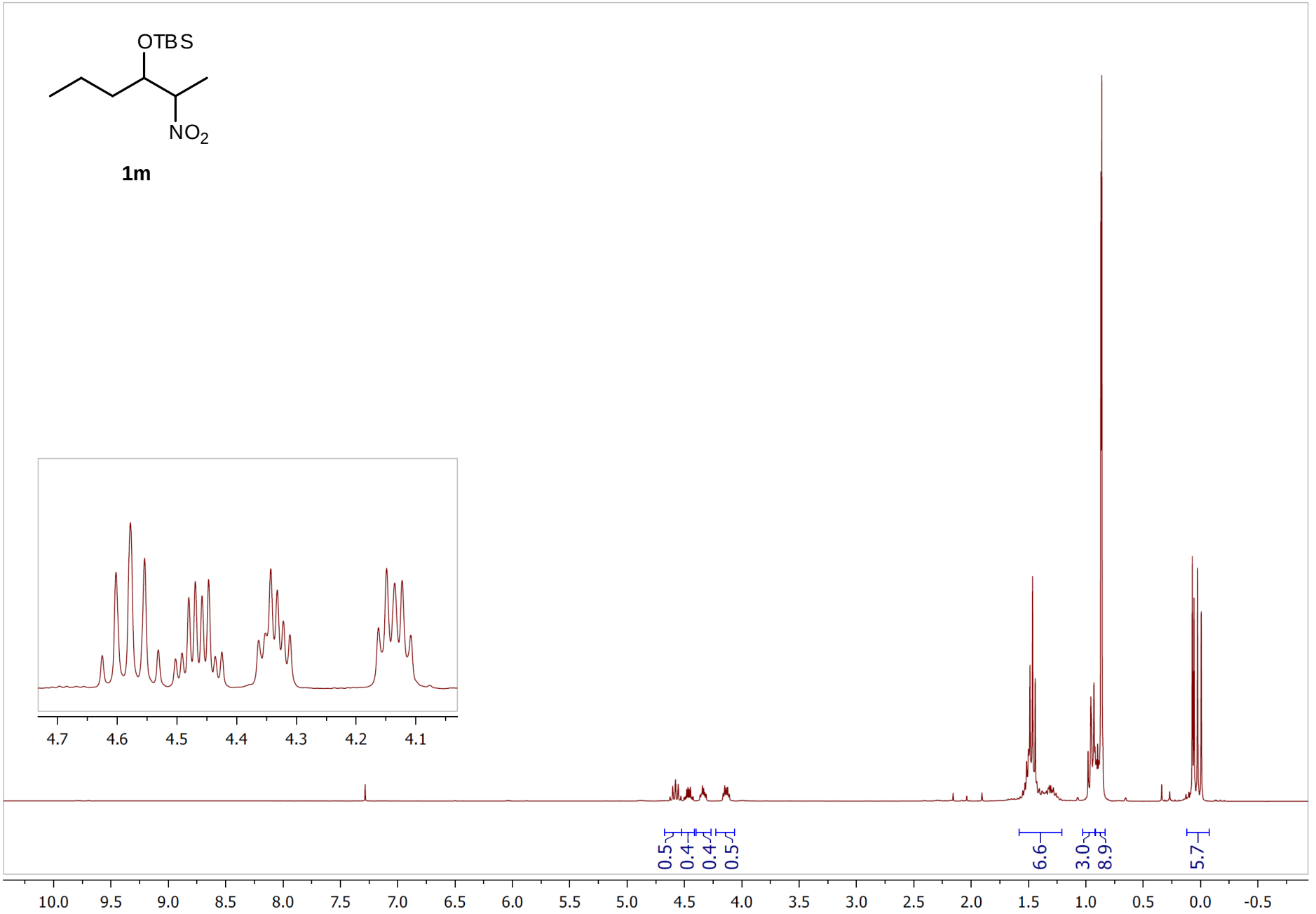
0
-10

***tert*-Butyldimethyl((2-nitrohexan-3-yl)oxy)silane 1m**

^{1}H NMR



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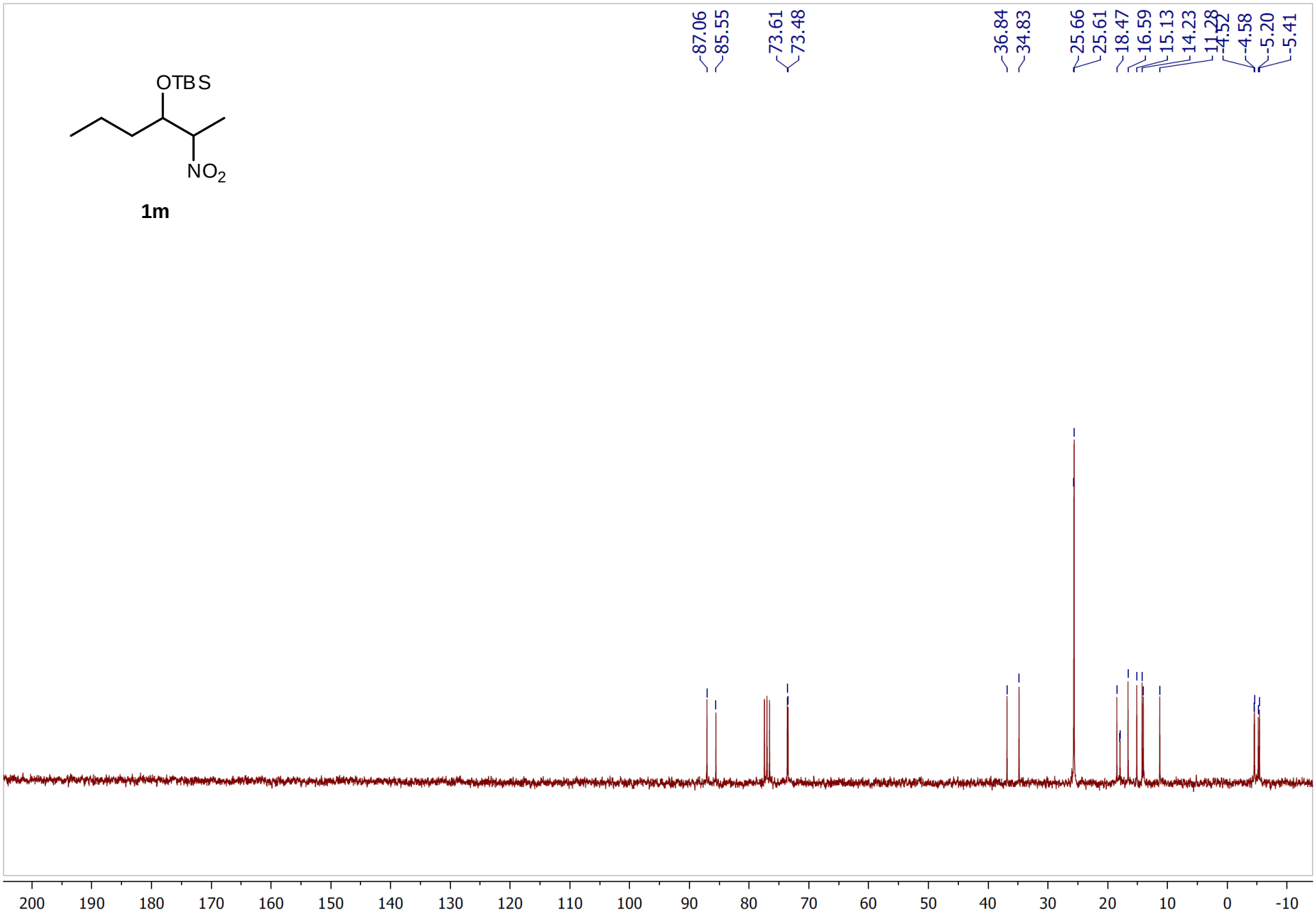
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15.13
14.23
11.28
-4.52
-4.58
-5.20
-5.41
200
190
180
170
160
150
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130
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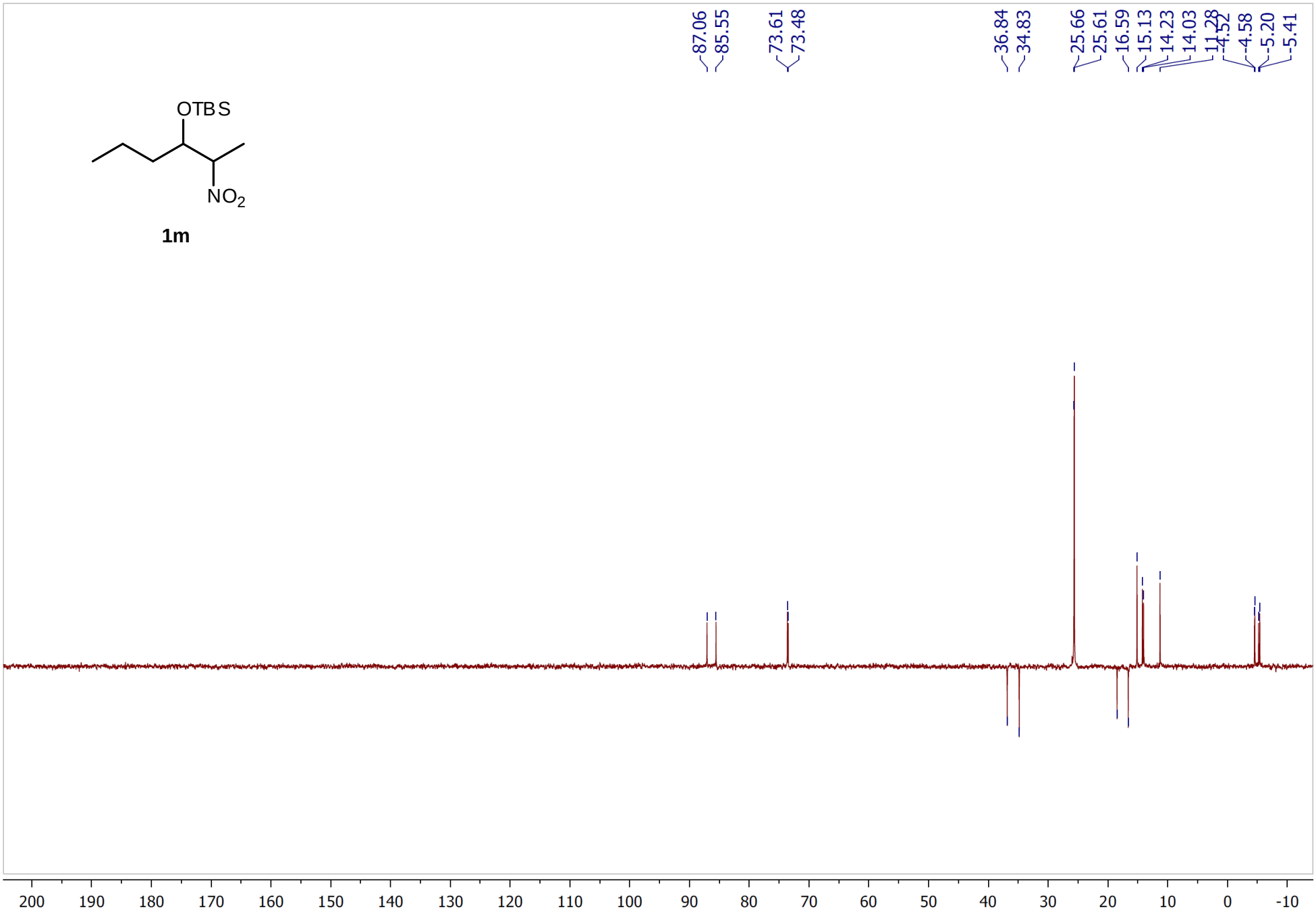
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT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36.84
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25.61
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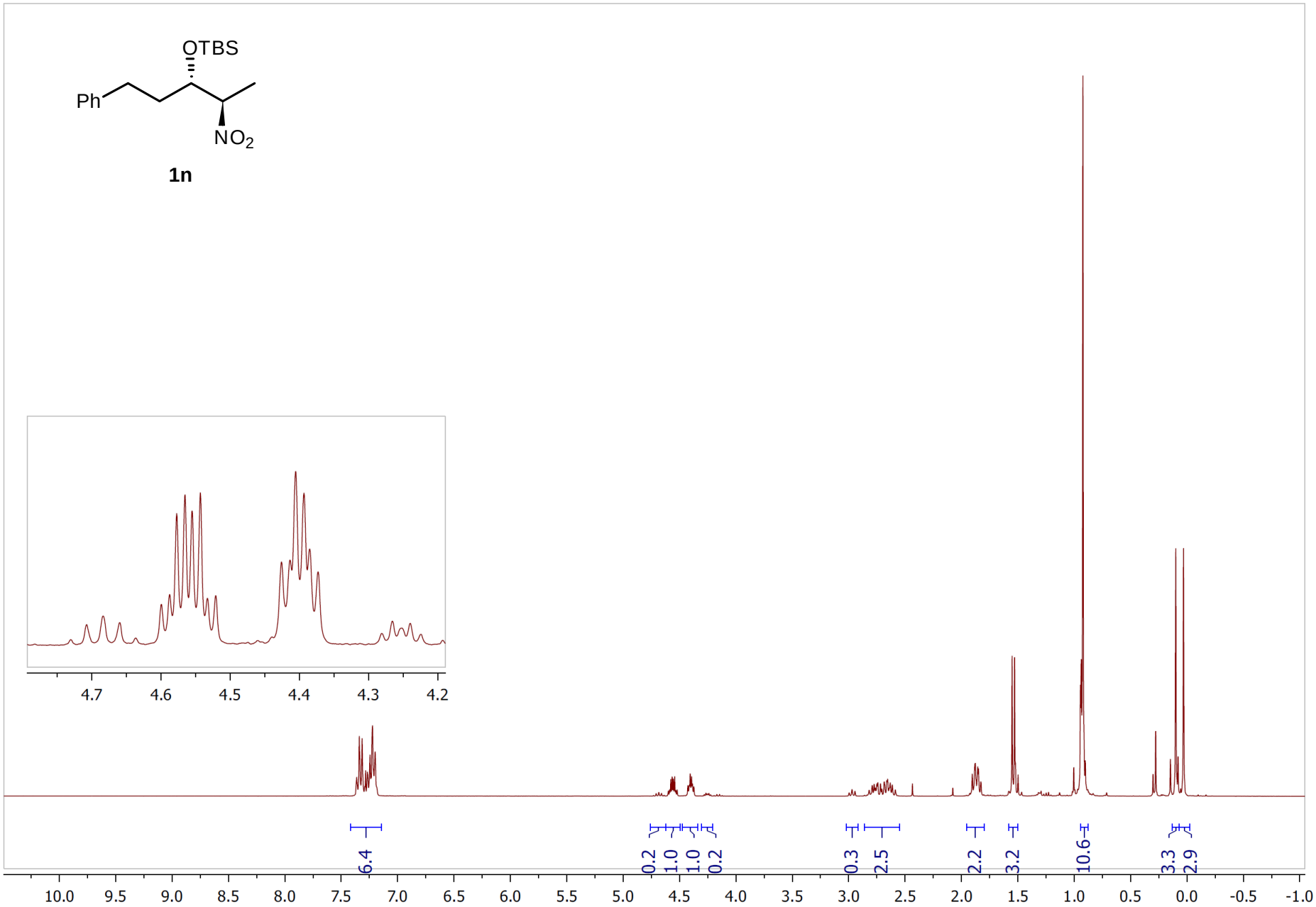
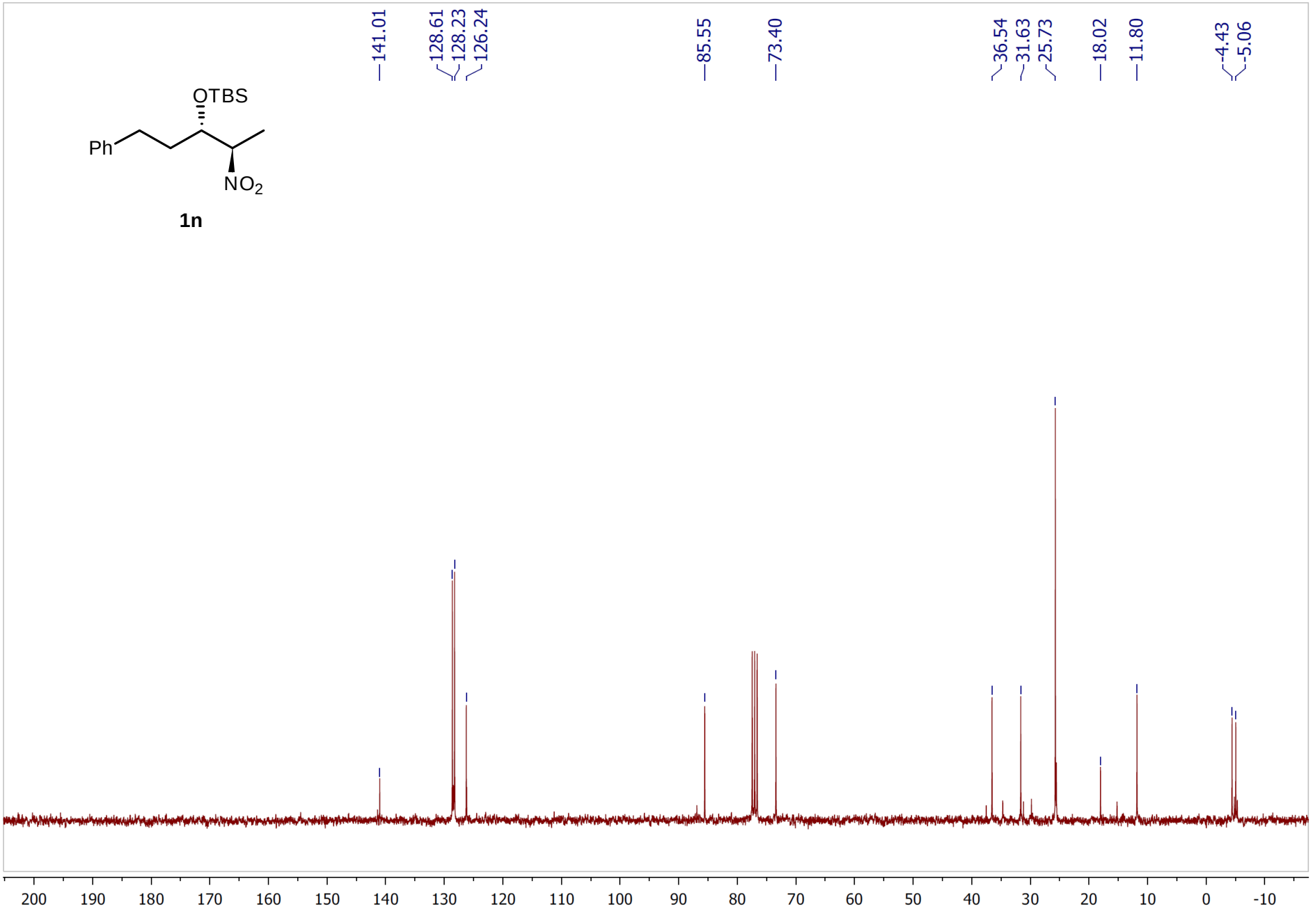
15.13
14.23
14.03
11.28
-4.52
-4.58
-5.20
-5.41
OTBS
NO2
1m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

***(rel)-tert*-Butyldimethyl((3*S*,4*R*)-4-nitro-1-phenylpentan-3-yloxy)silane 1n**

^{1}H NMR



^{13}C NMR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OTBS
Ph
NO2
1n
200
190
180
170
160
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70
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30
20
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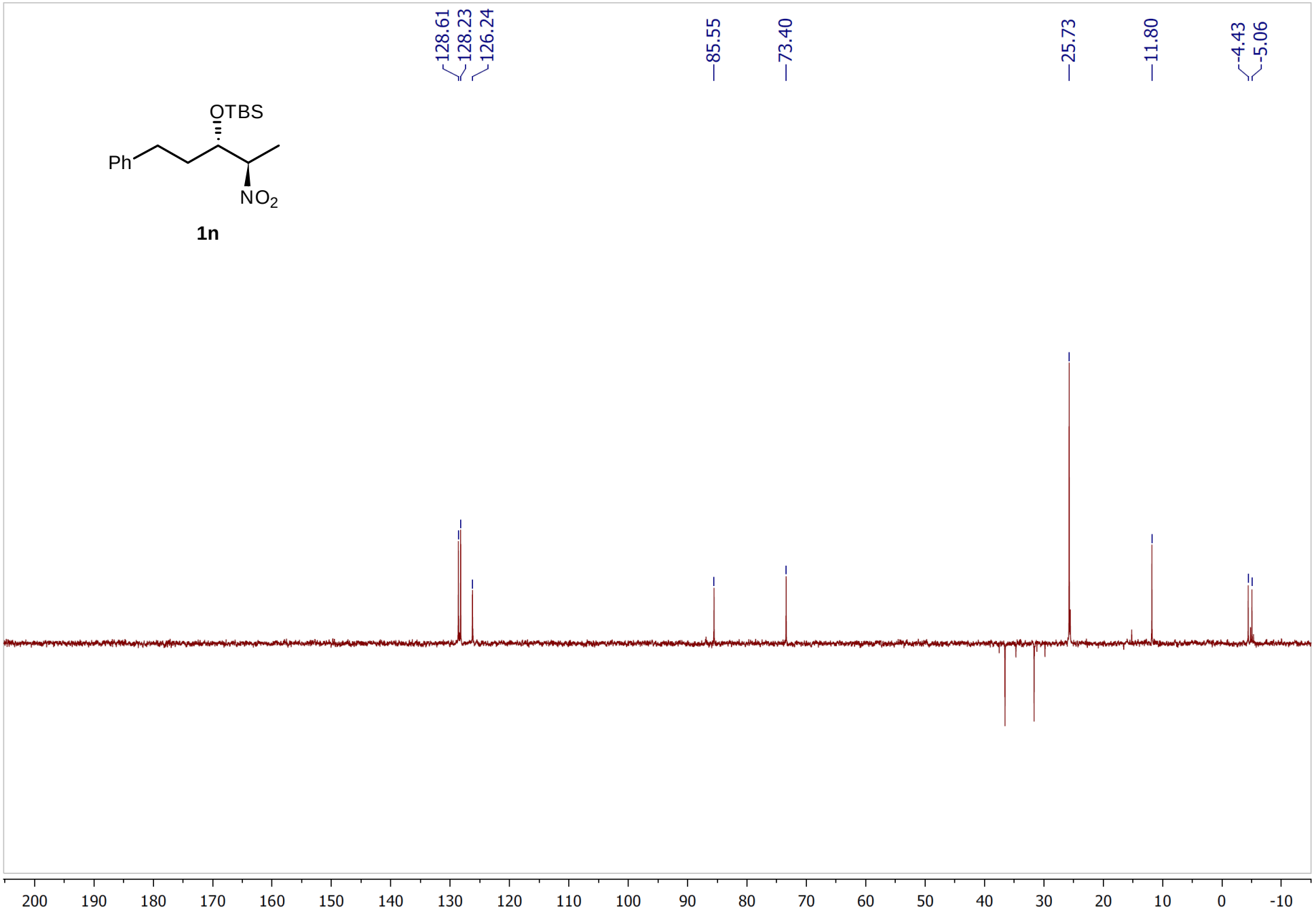
0
-10

^{13}C NMR DEPT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1n
200
190
180
170
160
150
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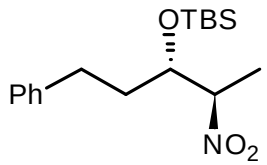
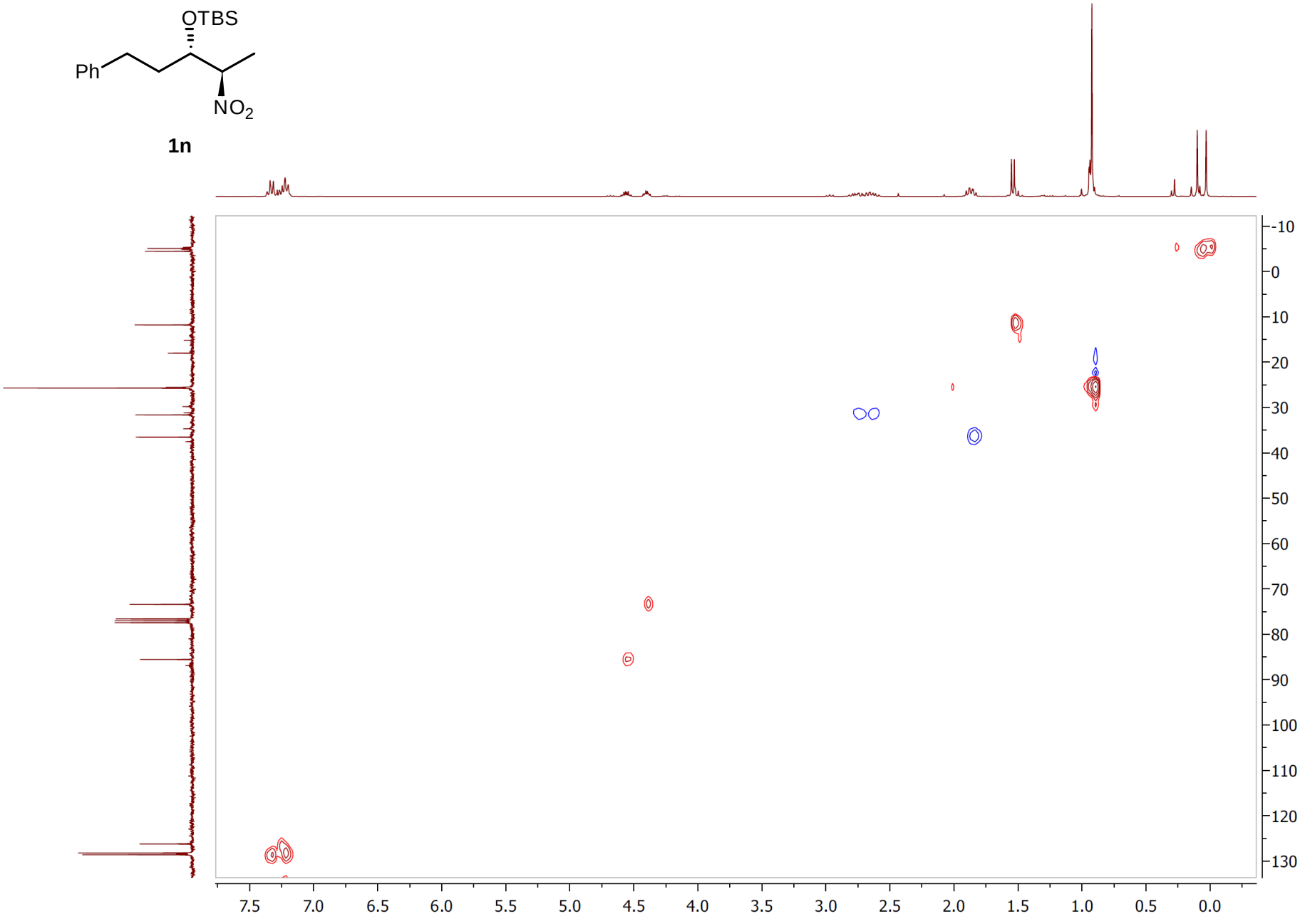
^{1}H-^{1}H COSY



1n

^{1}H-^{13}C HSQC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6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
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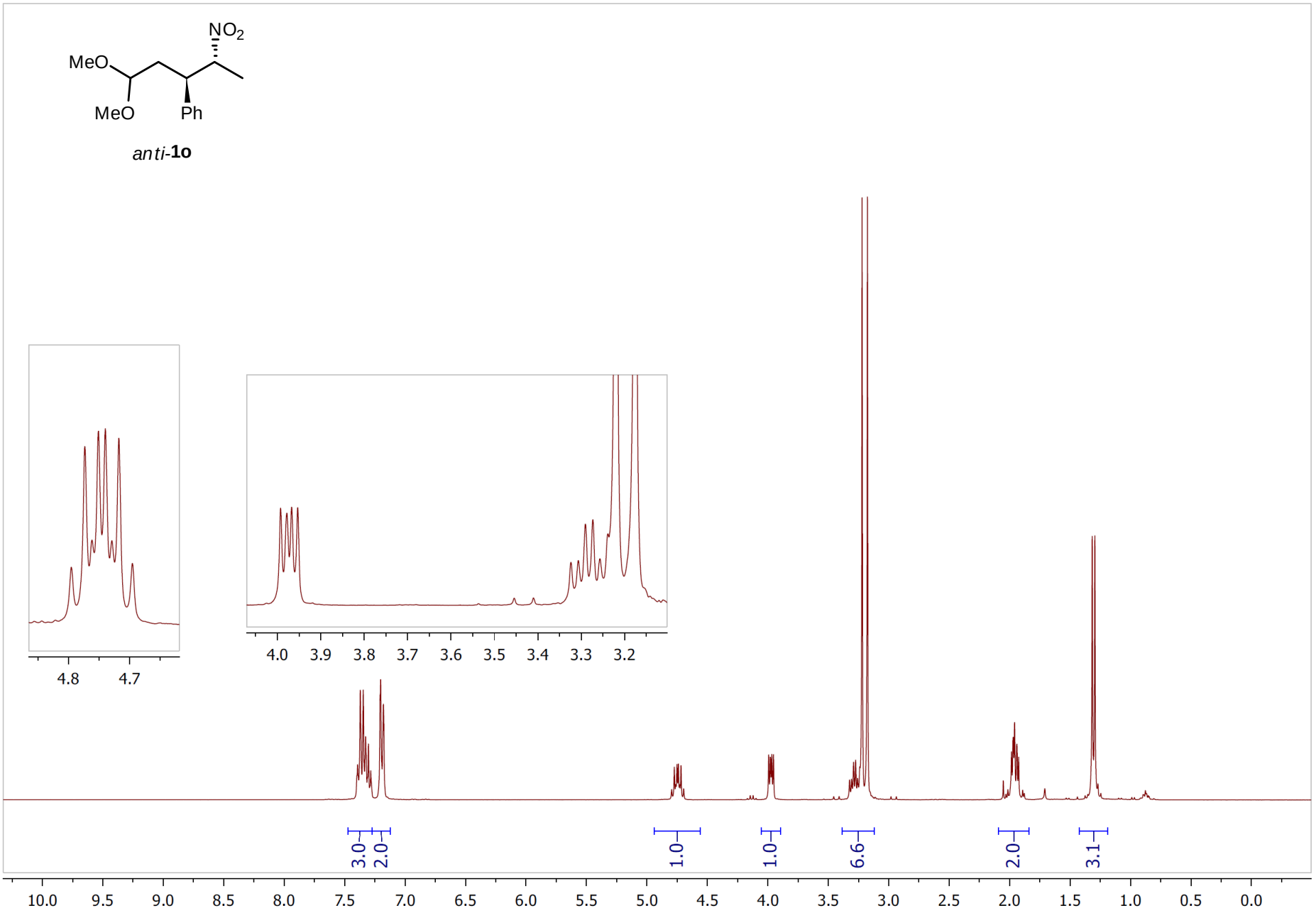
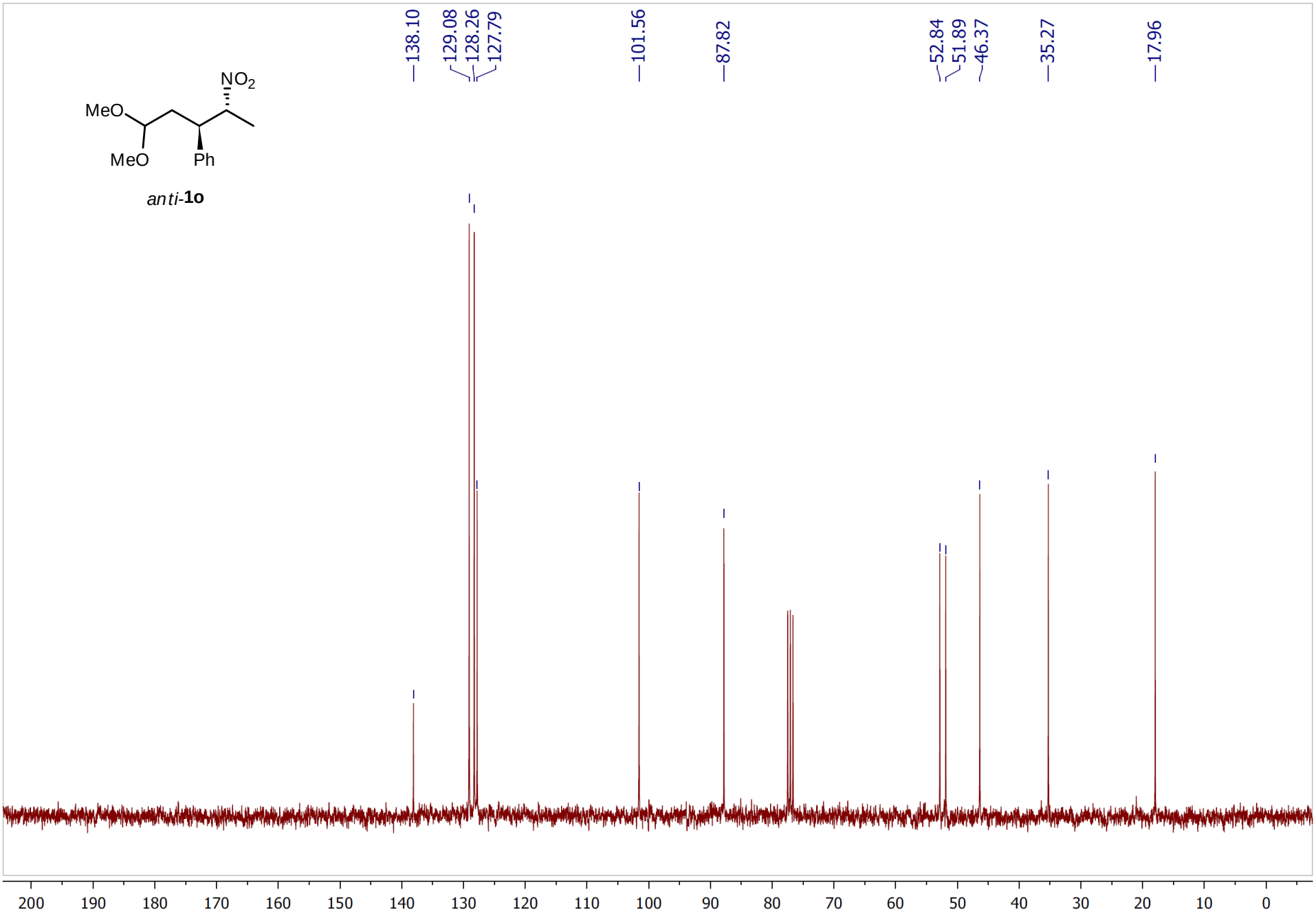
(*rel*)-((3*R*,4*R*)-1,1-dimethoxy-4-nitropentan-3-yl)benzene *anti*-1o

^{1}H NMR



^{13}C NMR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MeO
Ph
anti-1o
200
190
180
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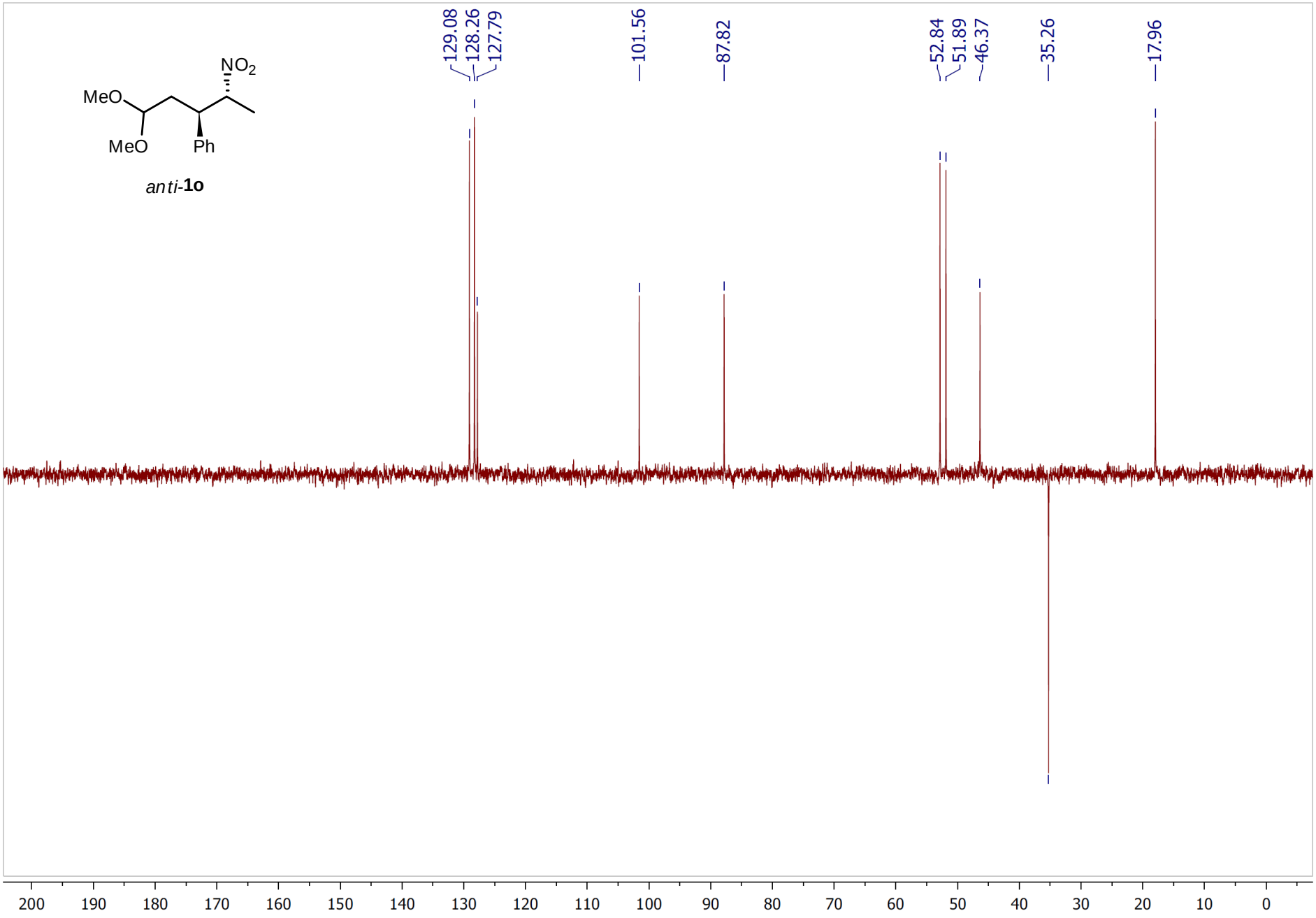
^{13}C NMR DEPT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200
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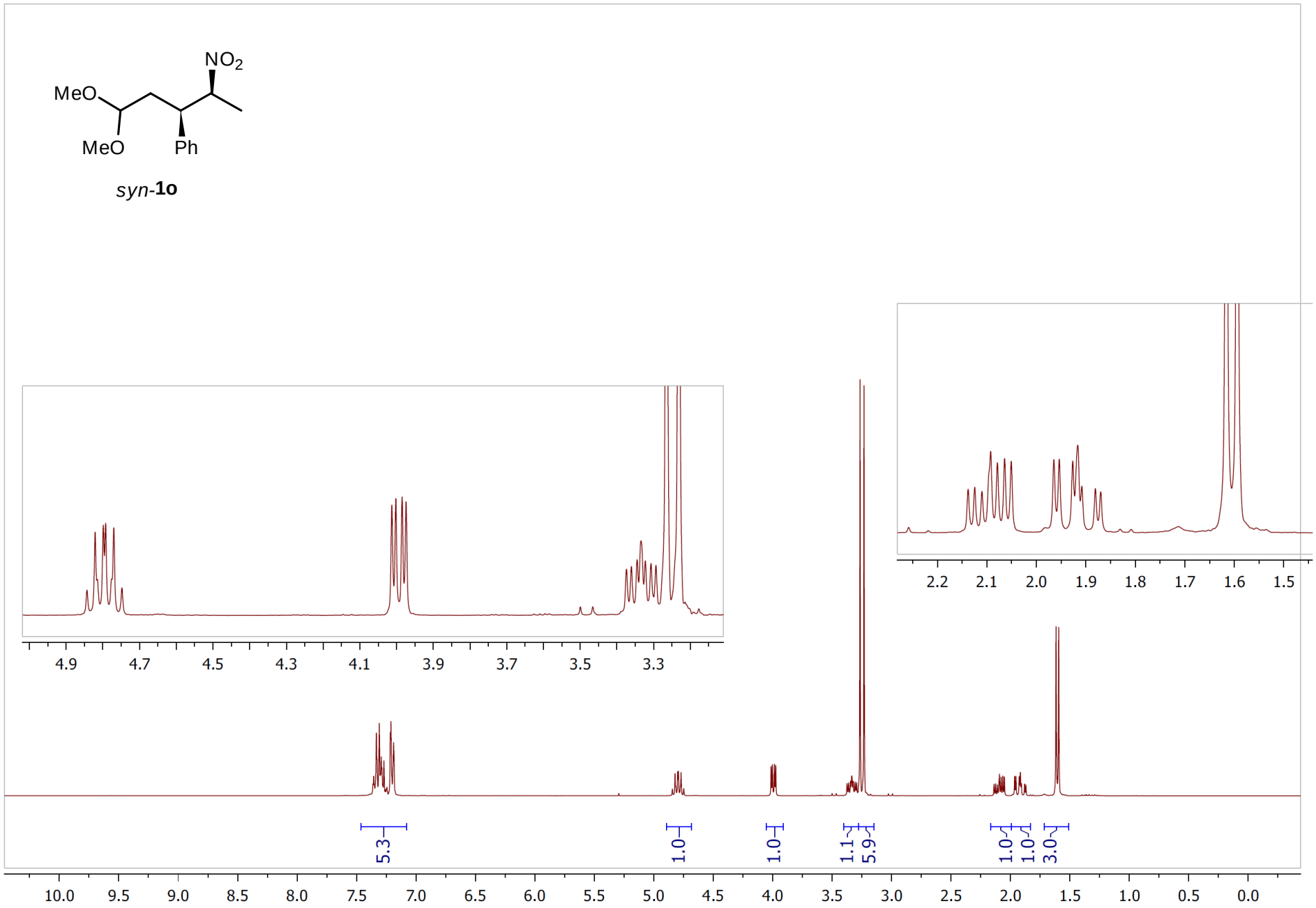
(*rel*)-((3*R*,4*S*)-1,1-dimethoxy-4-nitropentan-3-yl)benzene *syn*-1o

^{1}H NMR



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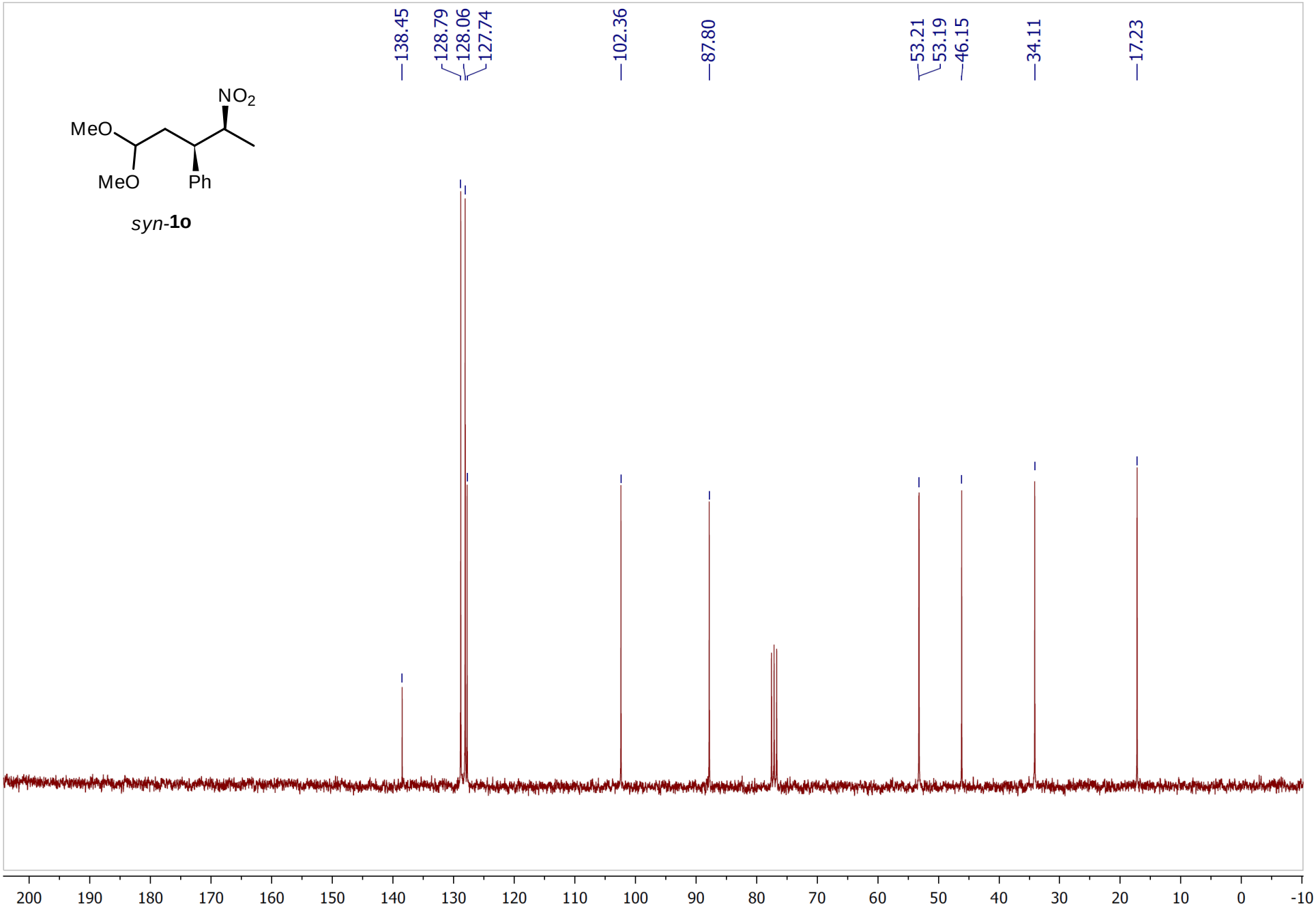
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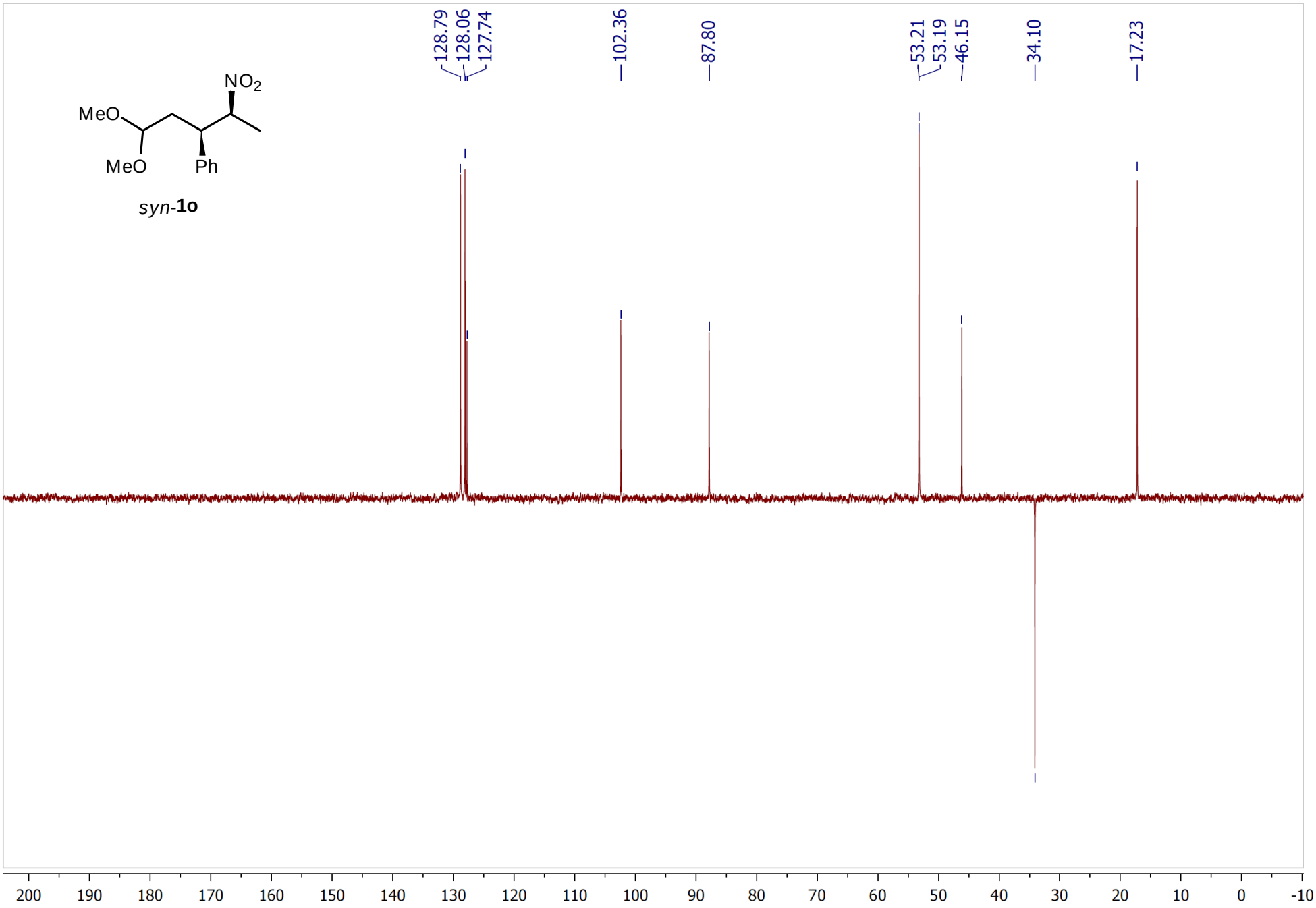
-10

^{13}C NMR DEPT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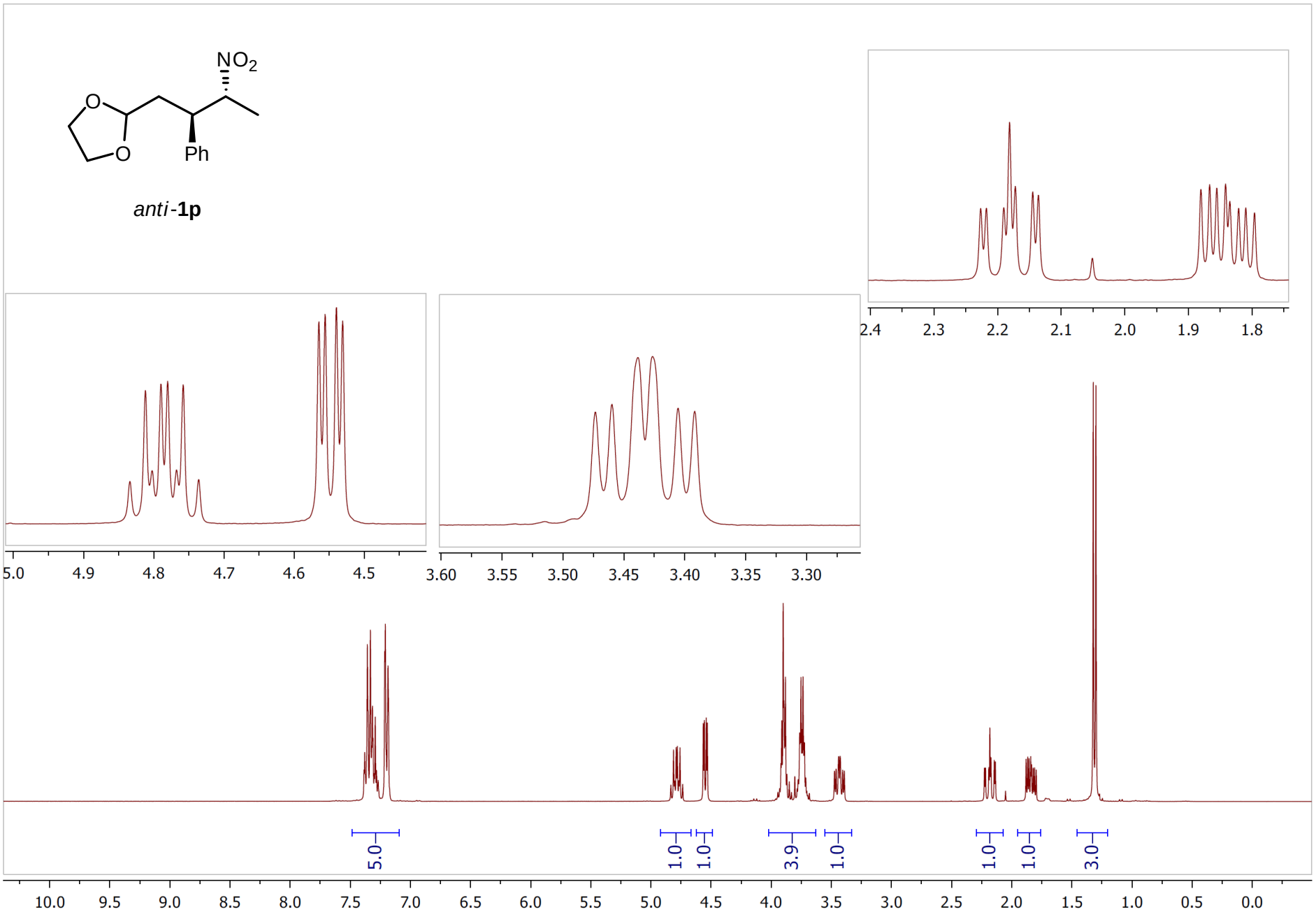
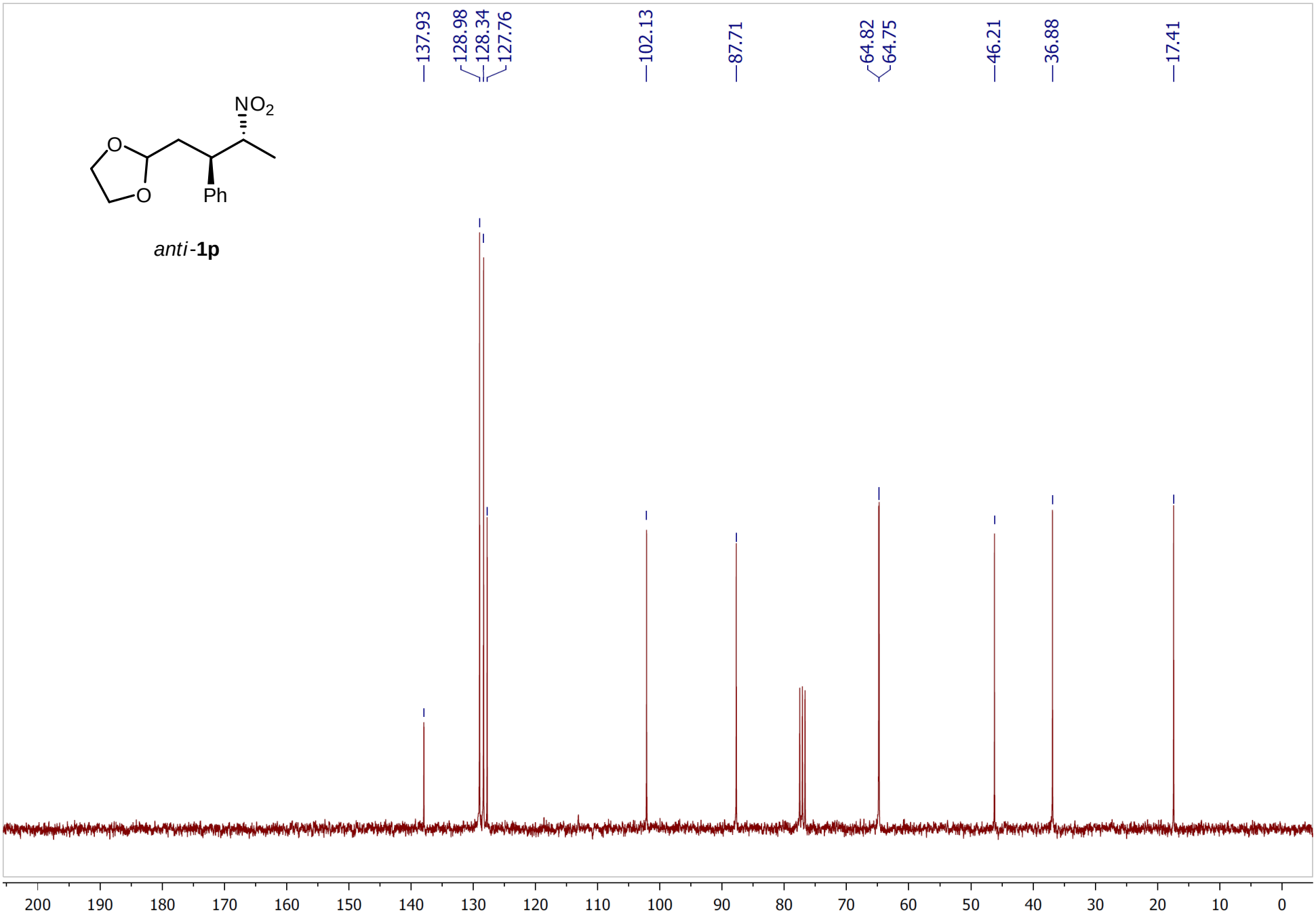
(*rel*)-2-((2*R*,3*R*)-3-nitro-2-phenylbutyl)-1,3-dioxolane *anti*-1p

^{1}H NMR



^{13}C NMR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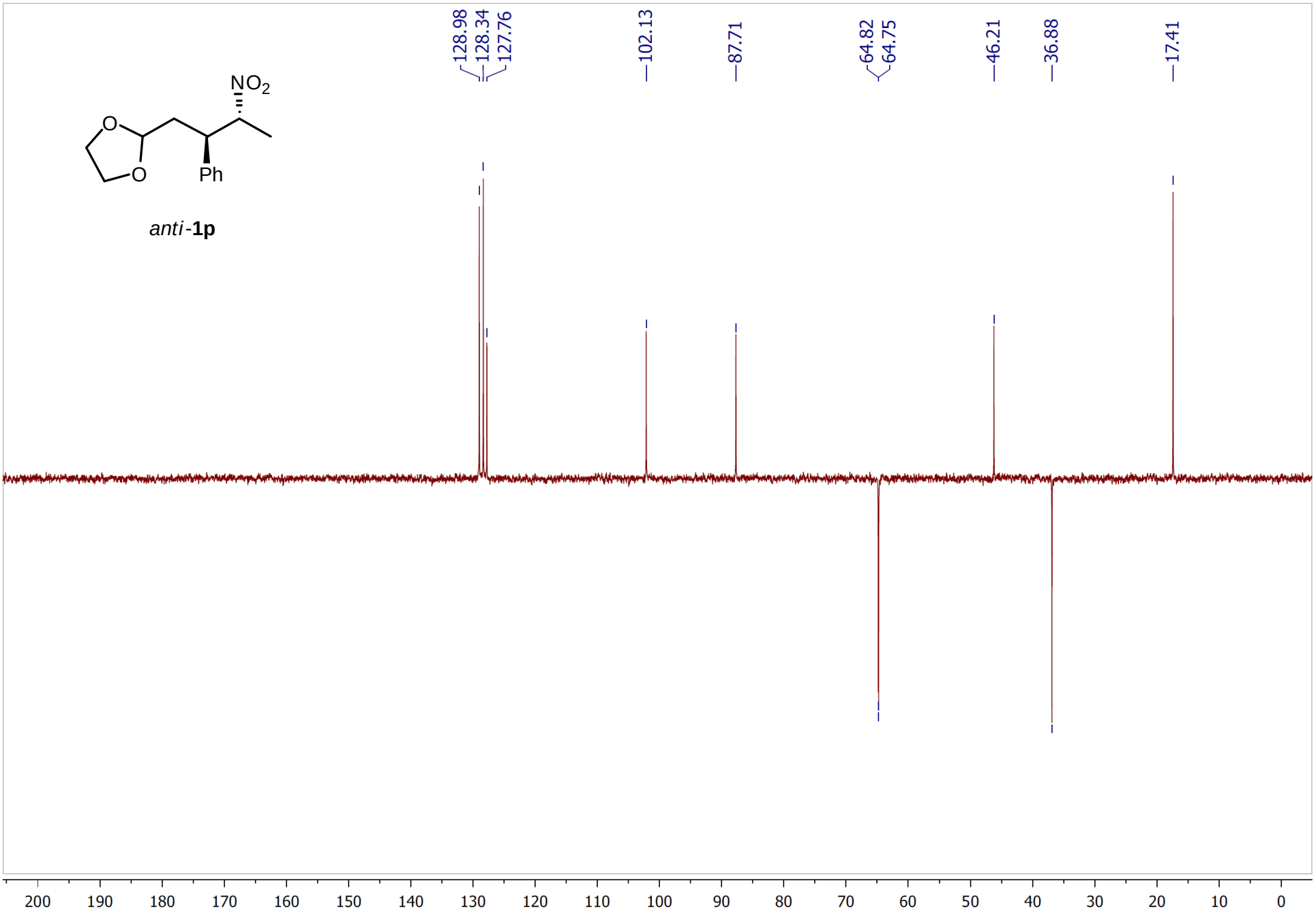
^{13}C NMR DEPT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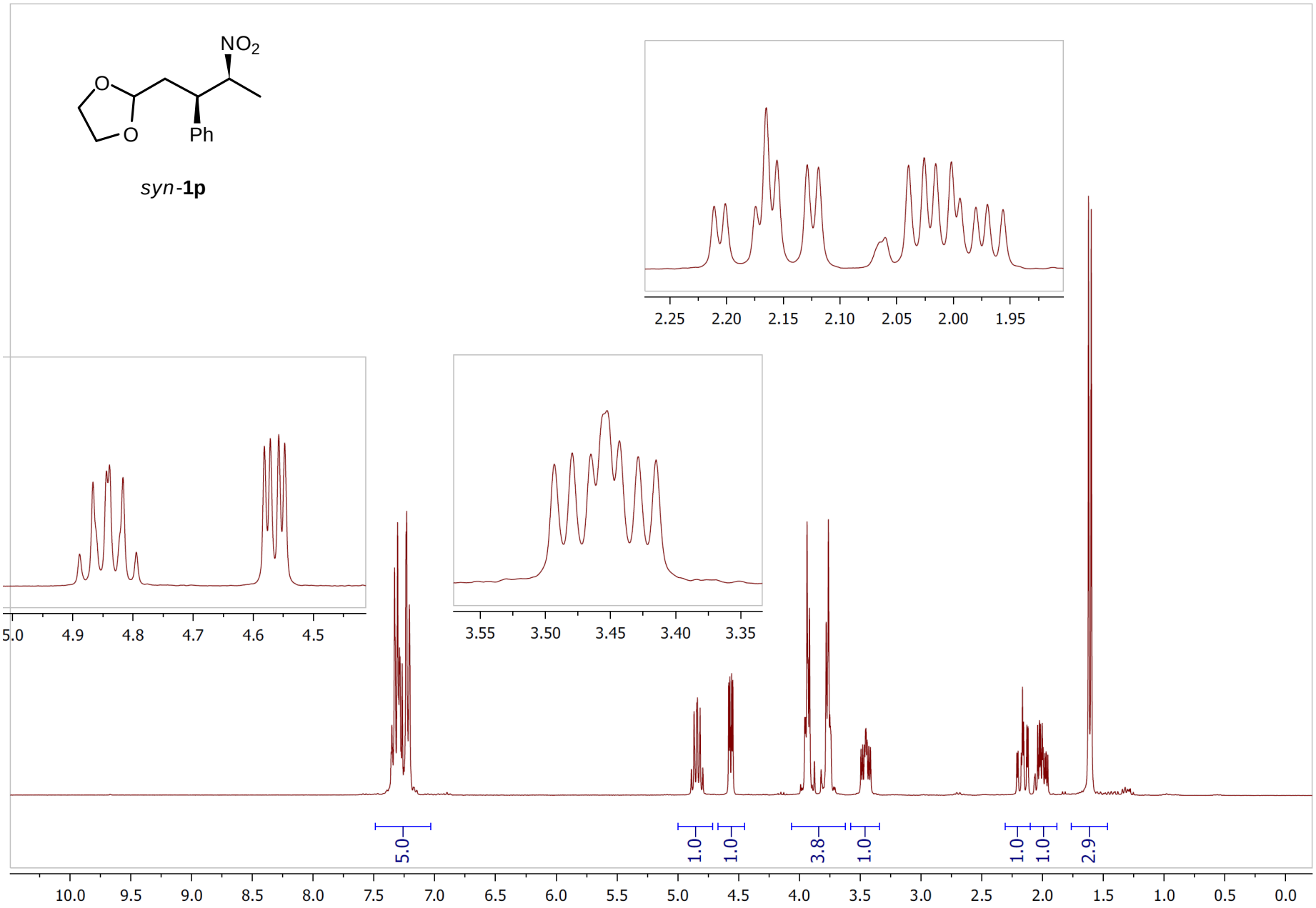
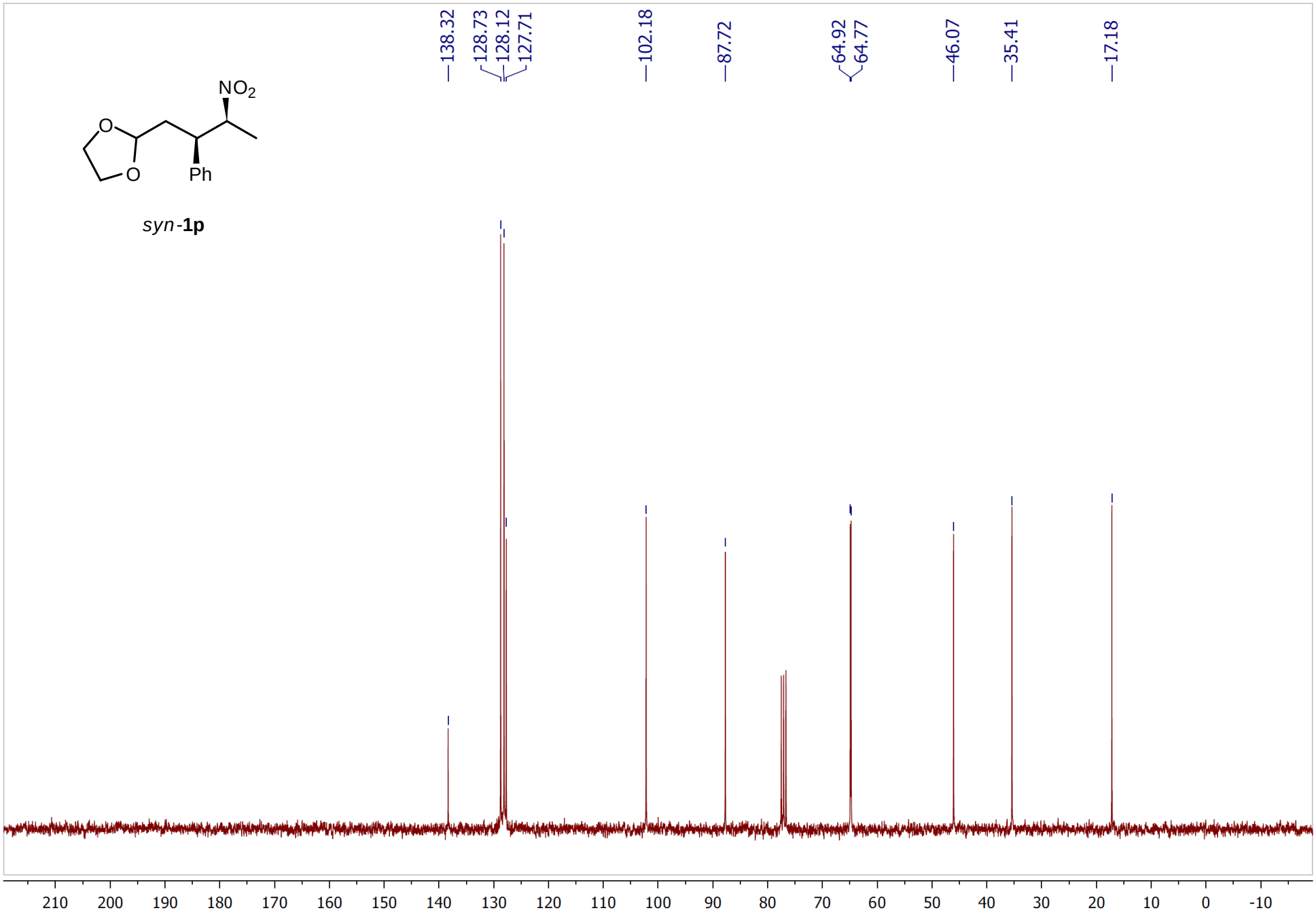
10
0

(*rel*)-2-((2*R*,3*S*)-3-nitro-2-phenylbutyl)-1,3-dioxolane *syn*-1p

^{1}H NMR

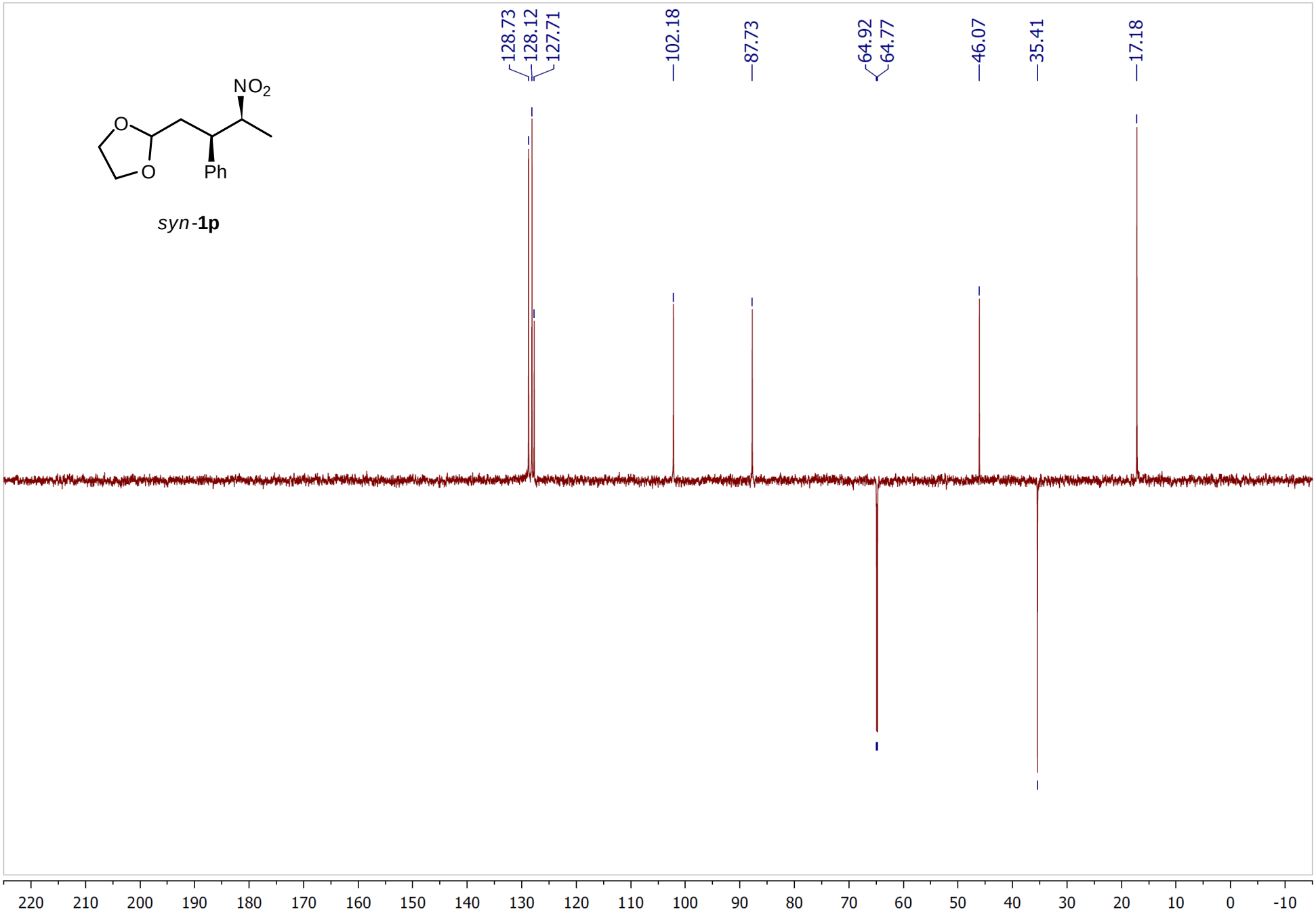


^{13}C NMR



syn-**1p**

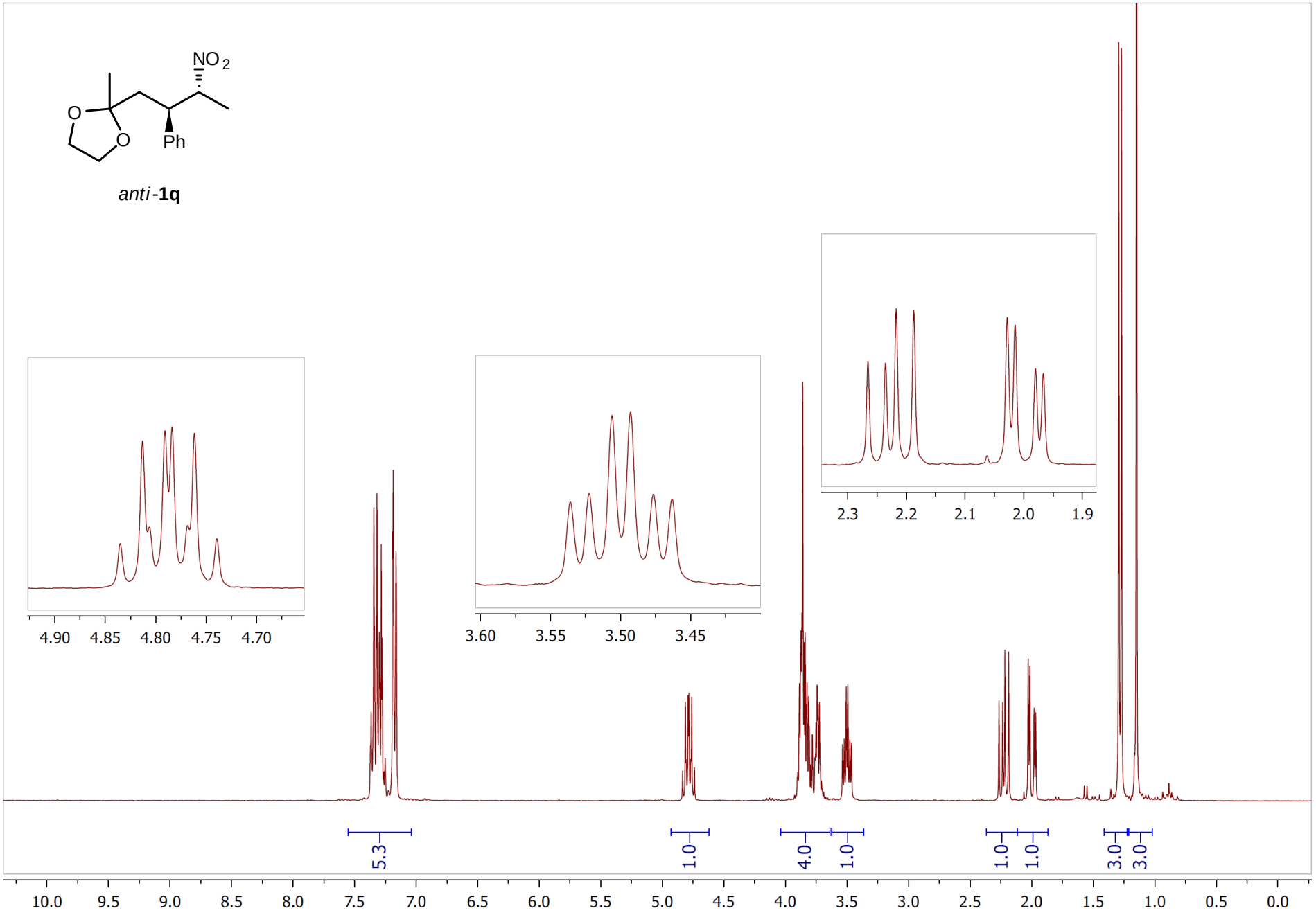
^{13}C NMR DEPT



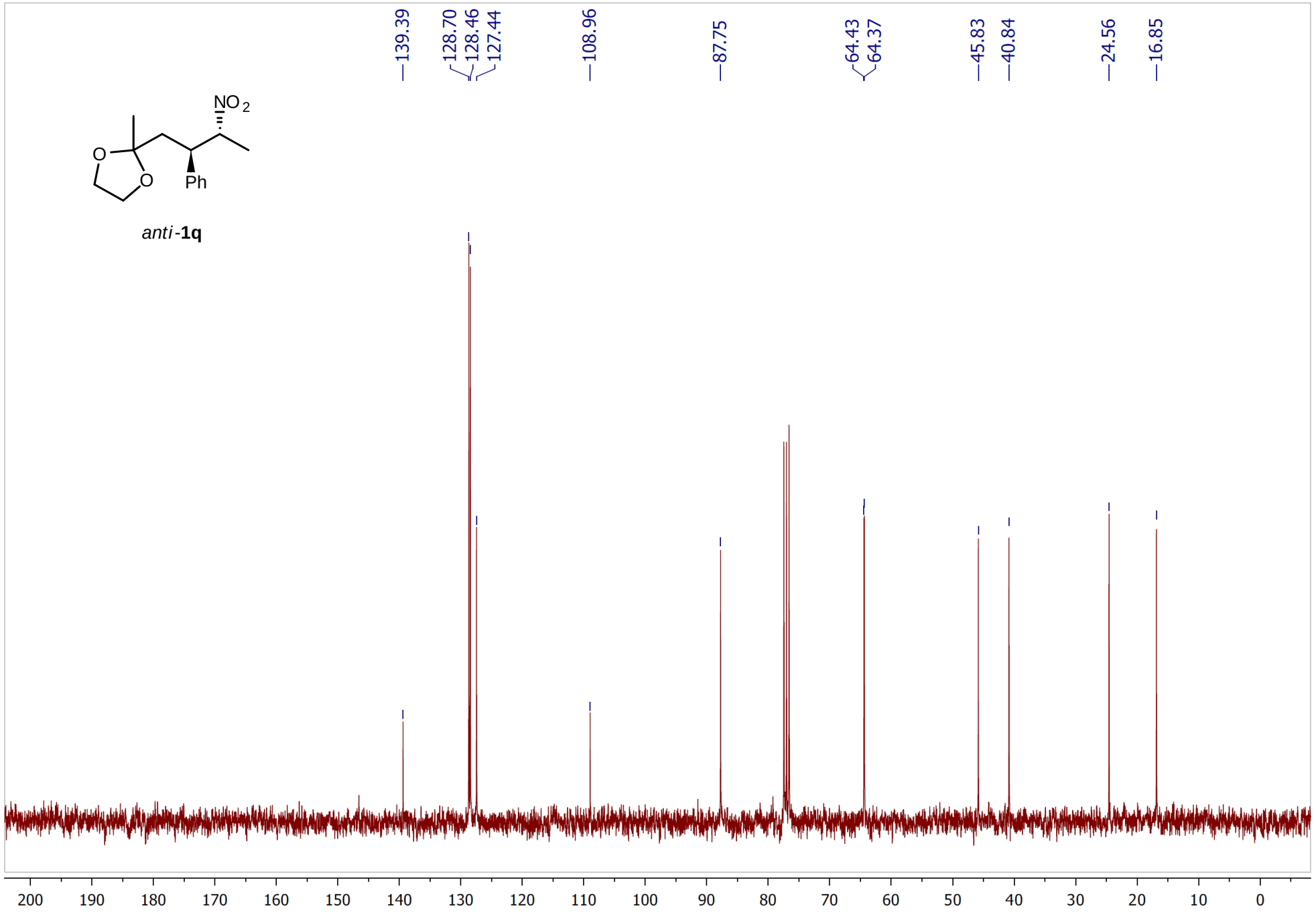
syn-**1p**

(*rel*)-2-Methyl-2-((2R,3R)-3-nitro-2-phenylbutyl)-1,3-dioxolane *anti*-1q

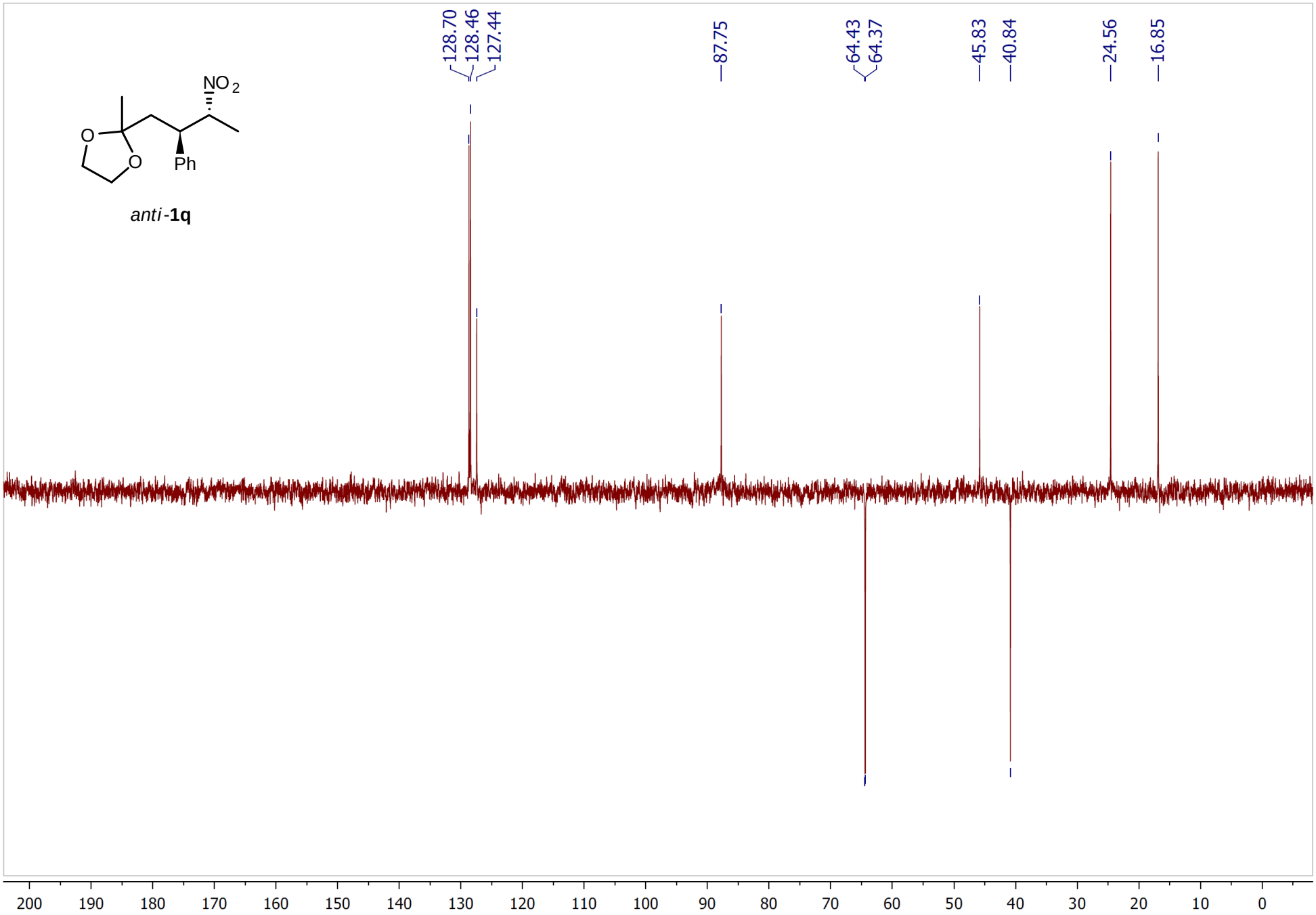
^{1}H NMR



^{13}C NMR

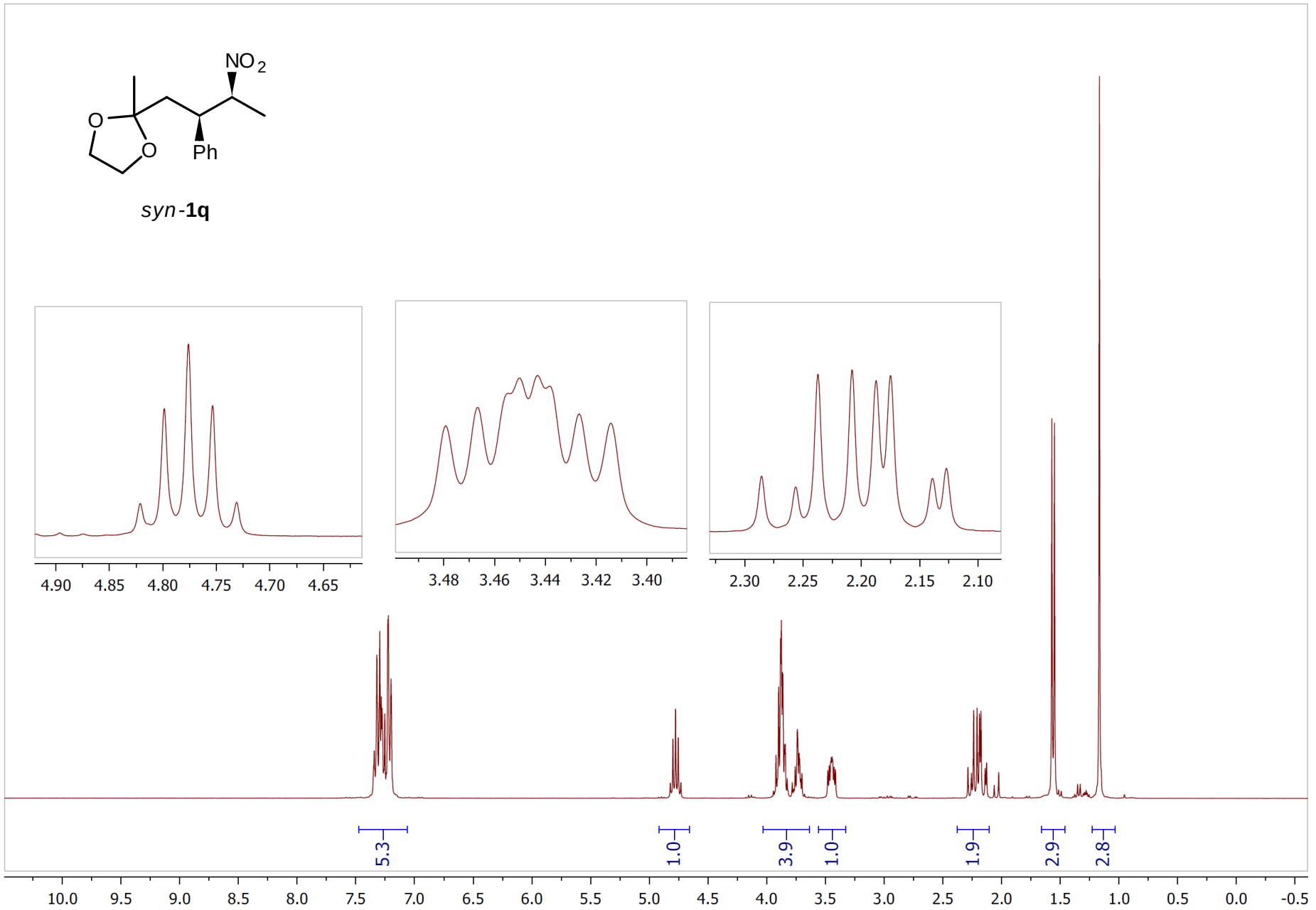

139.39
128.70
128.46
127.44
108.96
87.75
64.43
64.37
45.83
40.84
24.56
16.85
NO2
O
O
Ph
anti-1q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

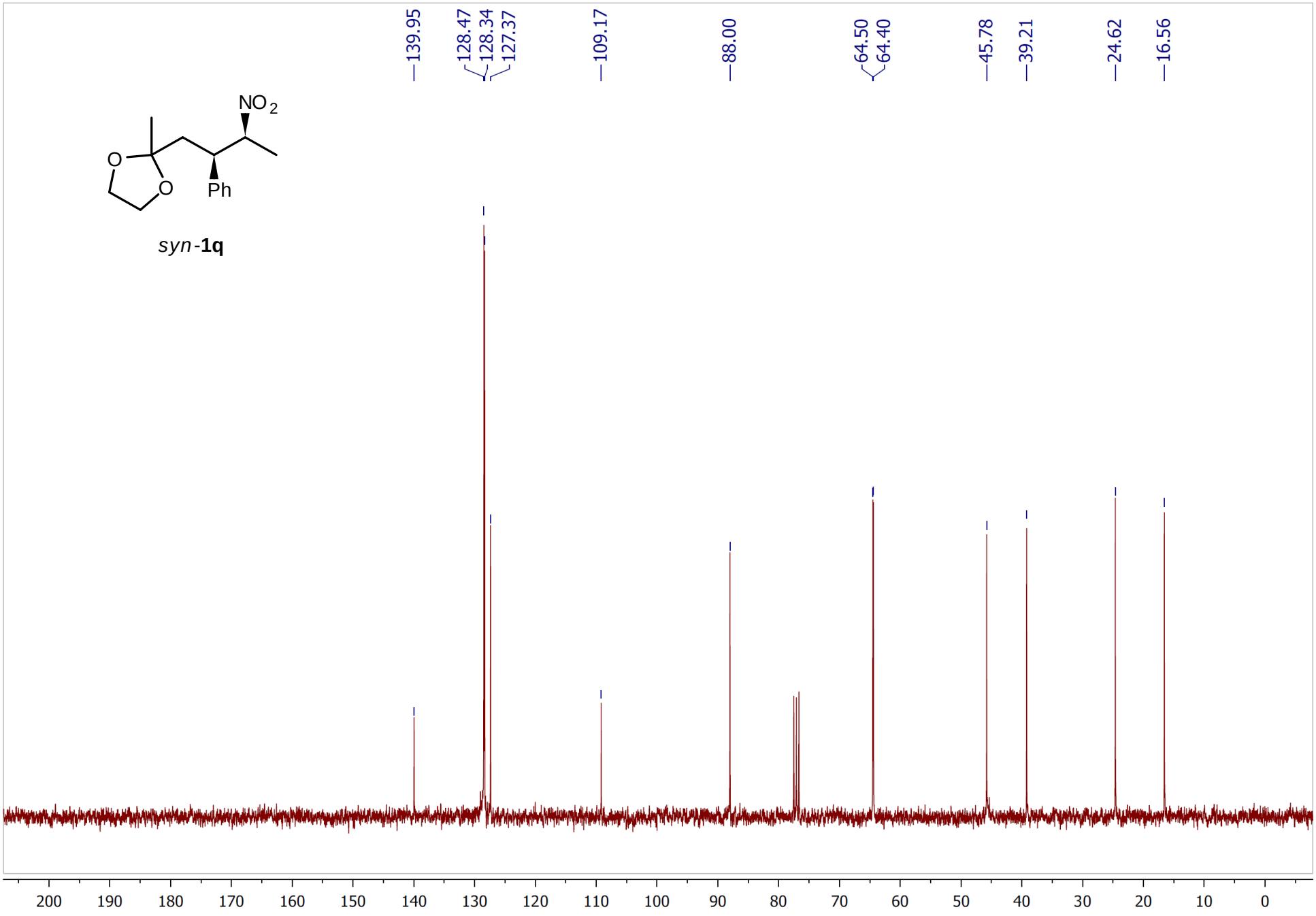

128.70
128.46
127.44
87.75
64.43
64.37
45.83
40.84
24.56
16.85
NO2
O
O
Ph
anti-1q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

(*rel*)-2-Methyl-2-((2R,3S)-3-nitro-2-phenylbutyl)-1,3-dioxolane *syn*-1q

^{1}H NMR

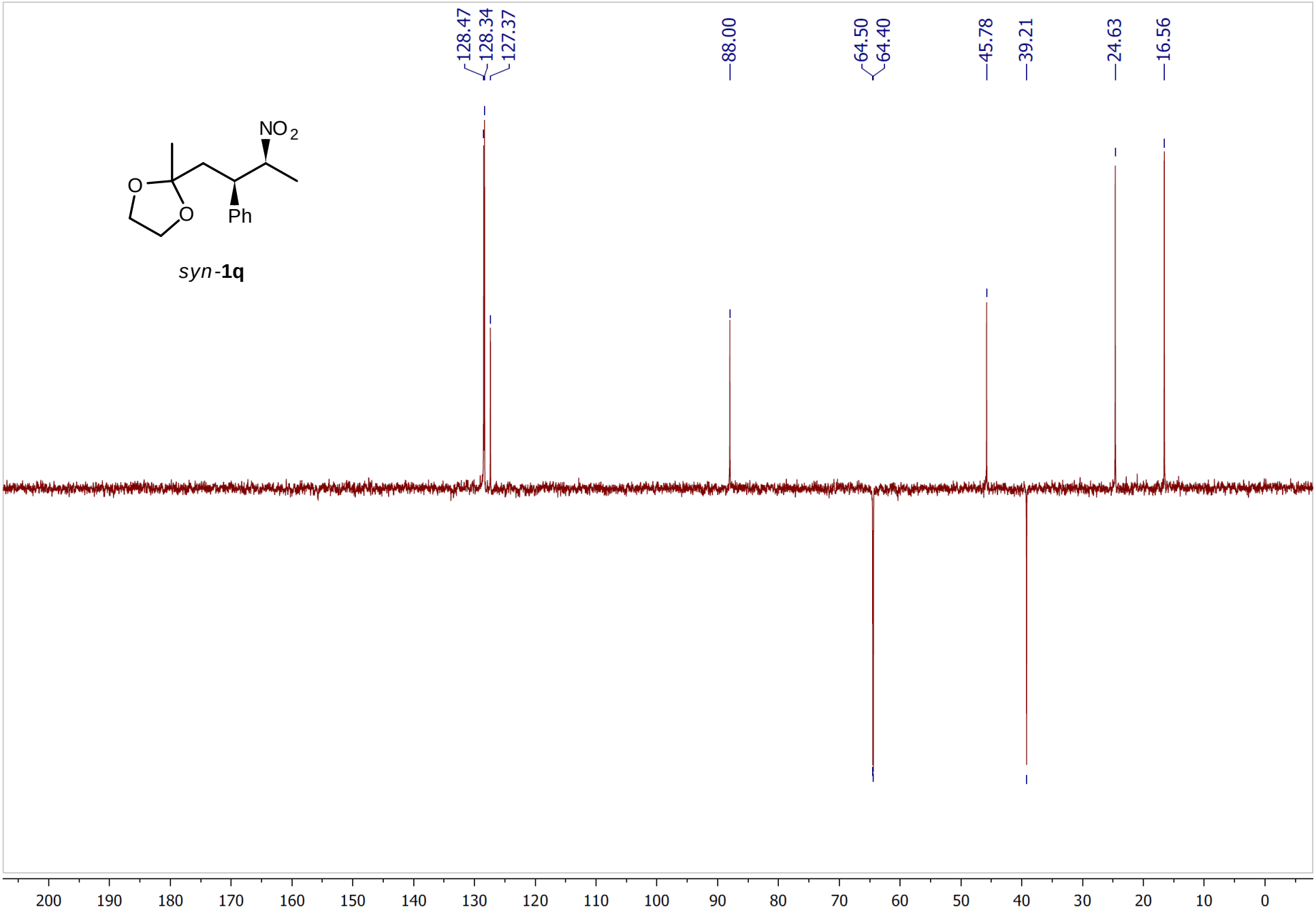


^{13}C NMR



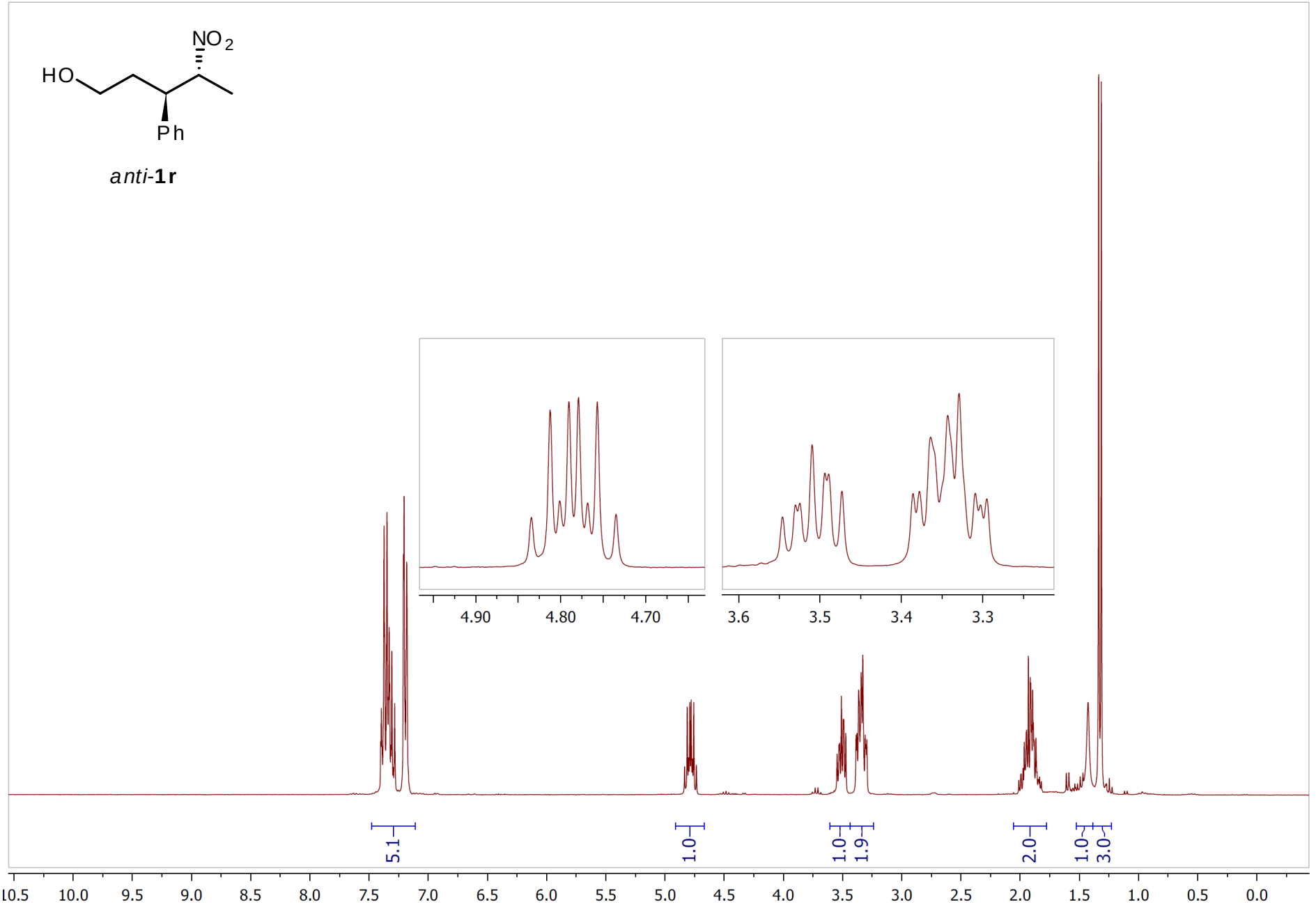
syn-**1q**

^{13}C NMR DEPT


128.47
128.34
127.37
88.00
64.50
64.40
45.78
39.21
24.63
16.56
NO2
O
O
Ph
syn-1q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

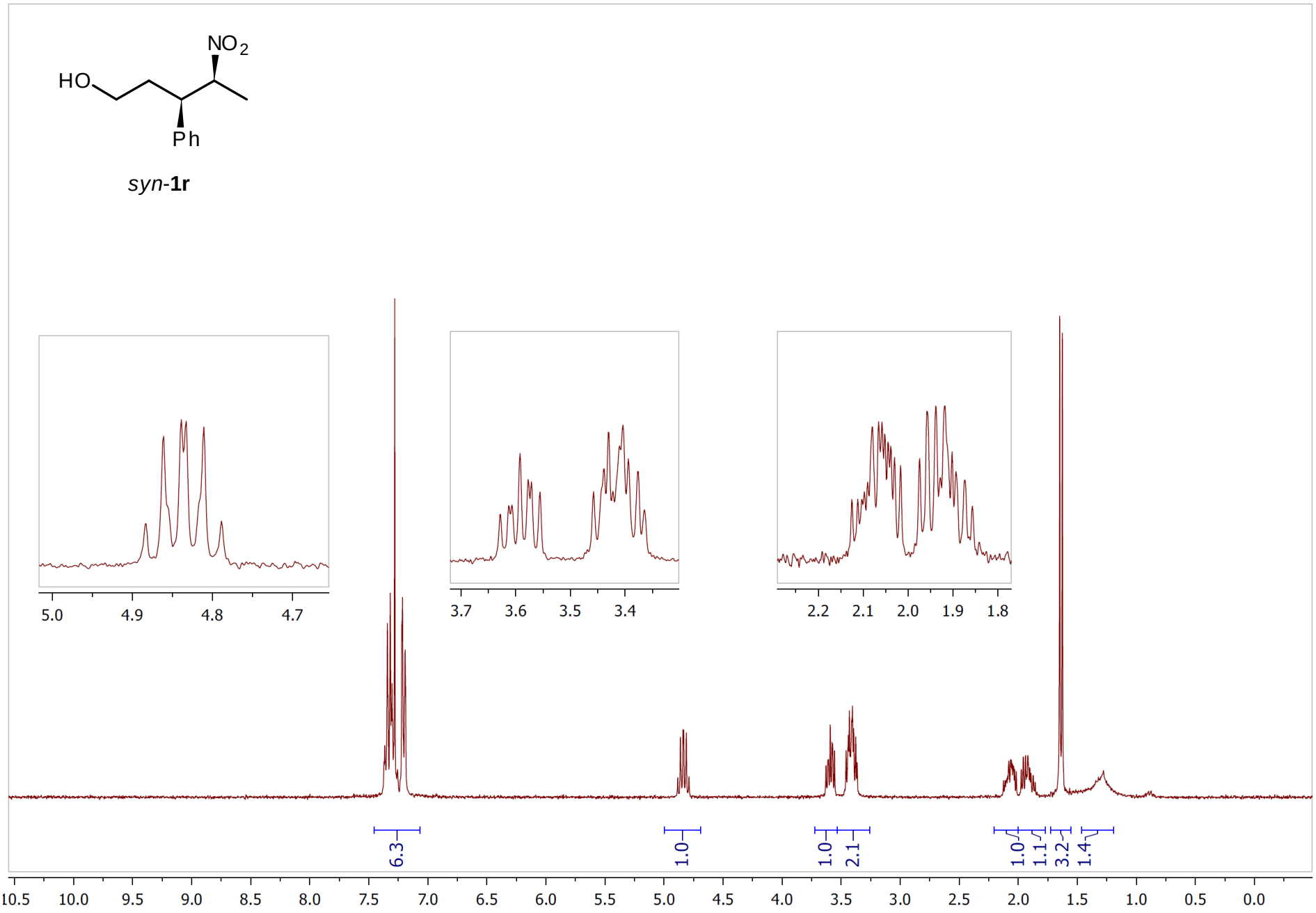
(*rel*)-(3R,4R)-4-nitro-3-phenylpentan-1-ol *anti*-1r

^{1}H NMR

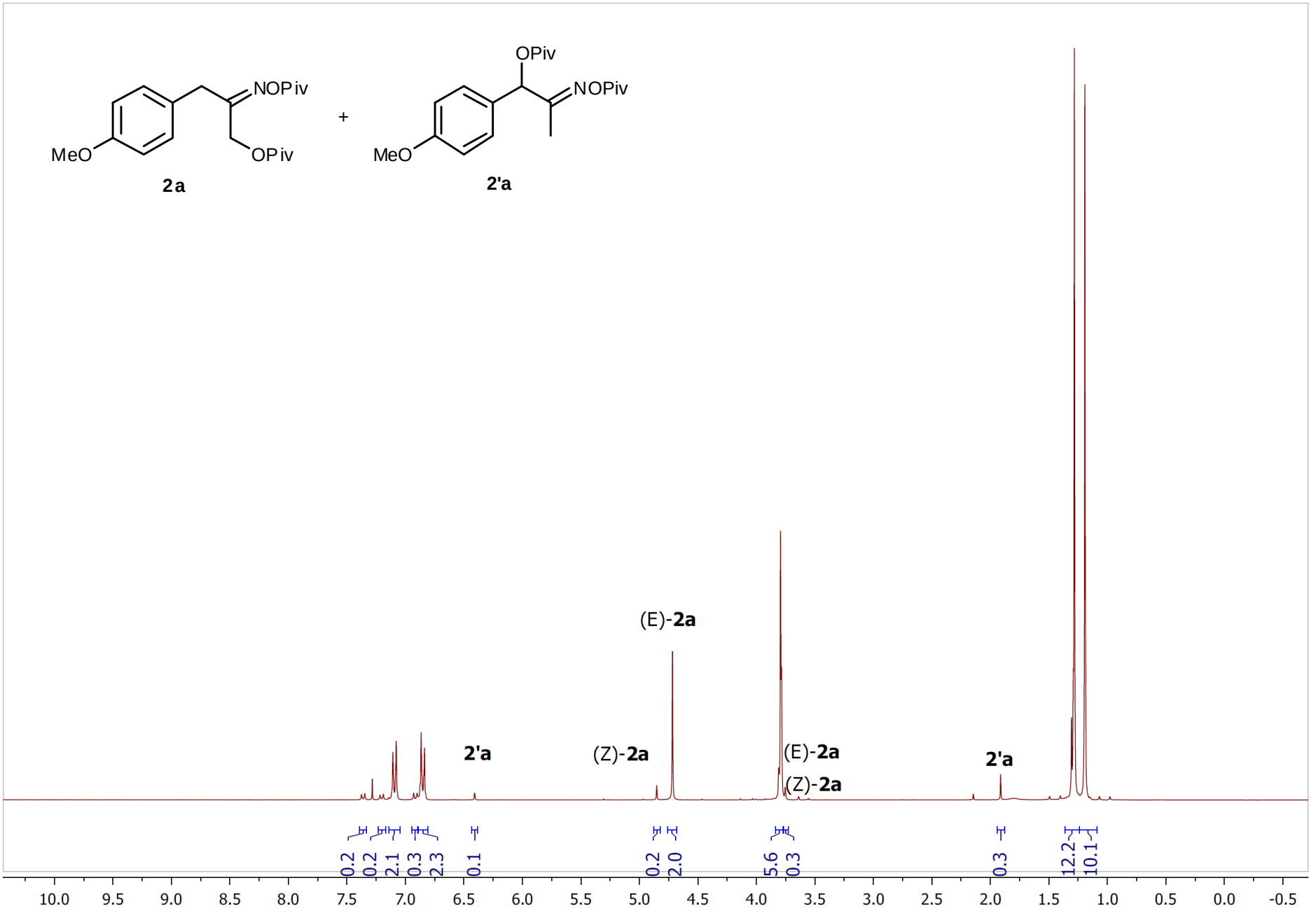


(*rel*)-(3R,4S)-4-nitro-3-phenylpentan-1-ol *syn*-1r

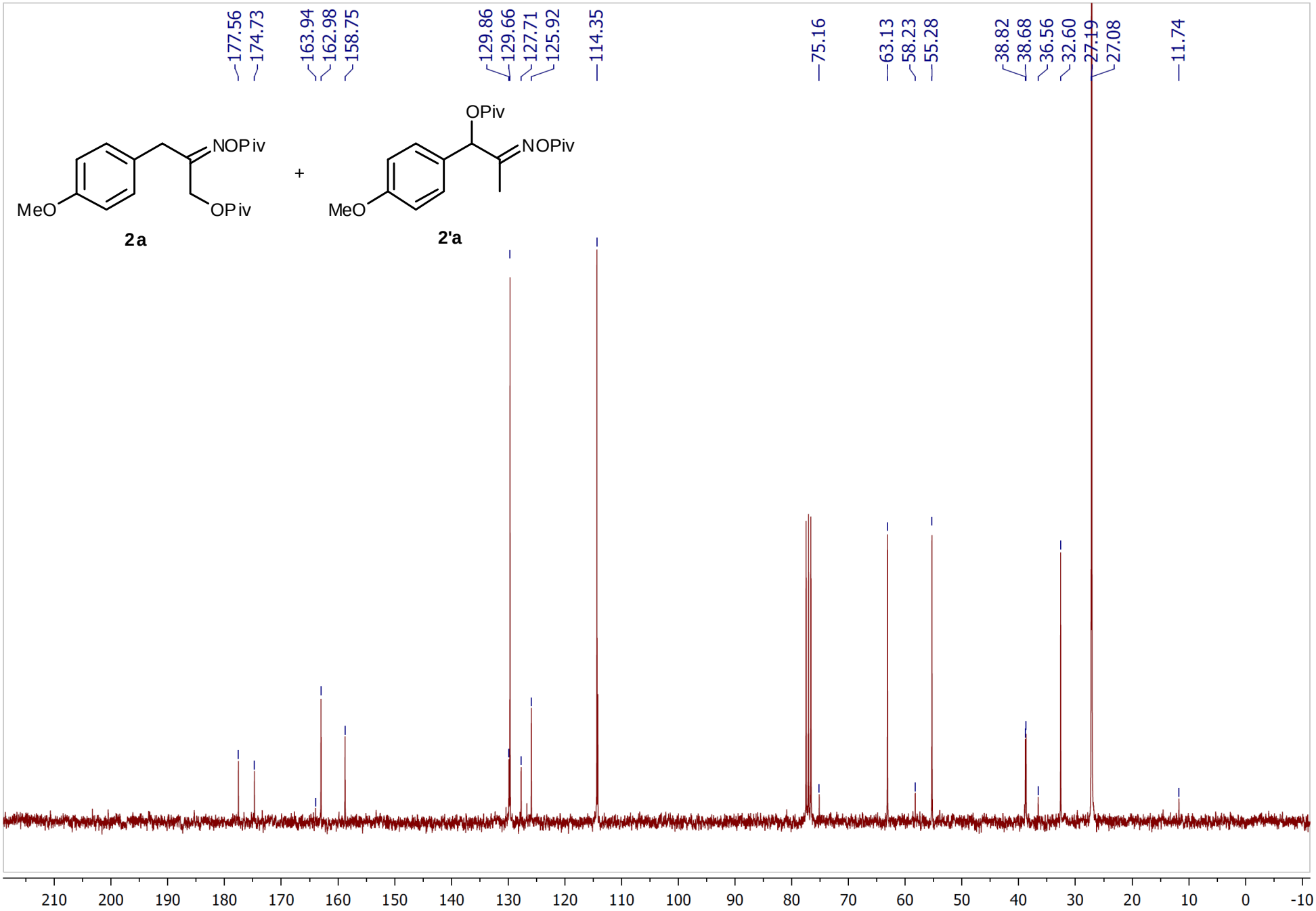
^{1}H NMR



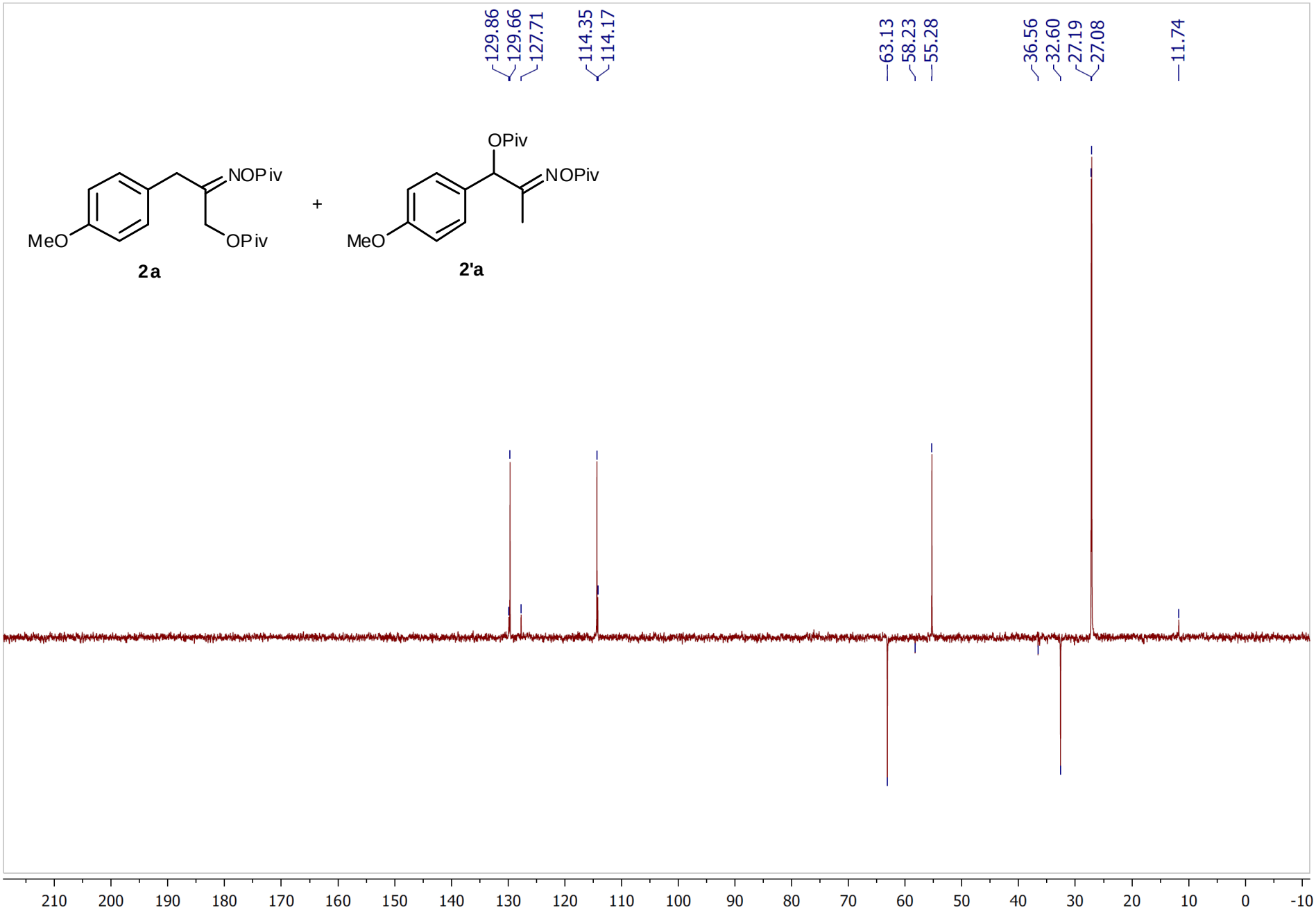
3-(4-Methoxyphenyl)-2-(pivaloyloxyimino)propyl pivalate 2a and **1-(4-Methoxyphenyl)-2-(pivaloyloxyimino)propyl pivalate 2'a**
^{1}H NMR



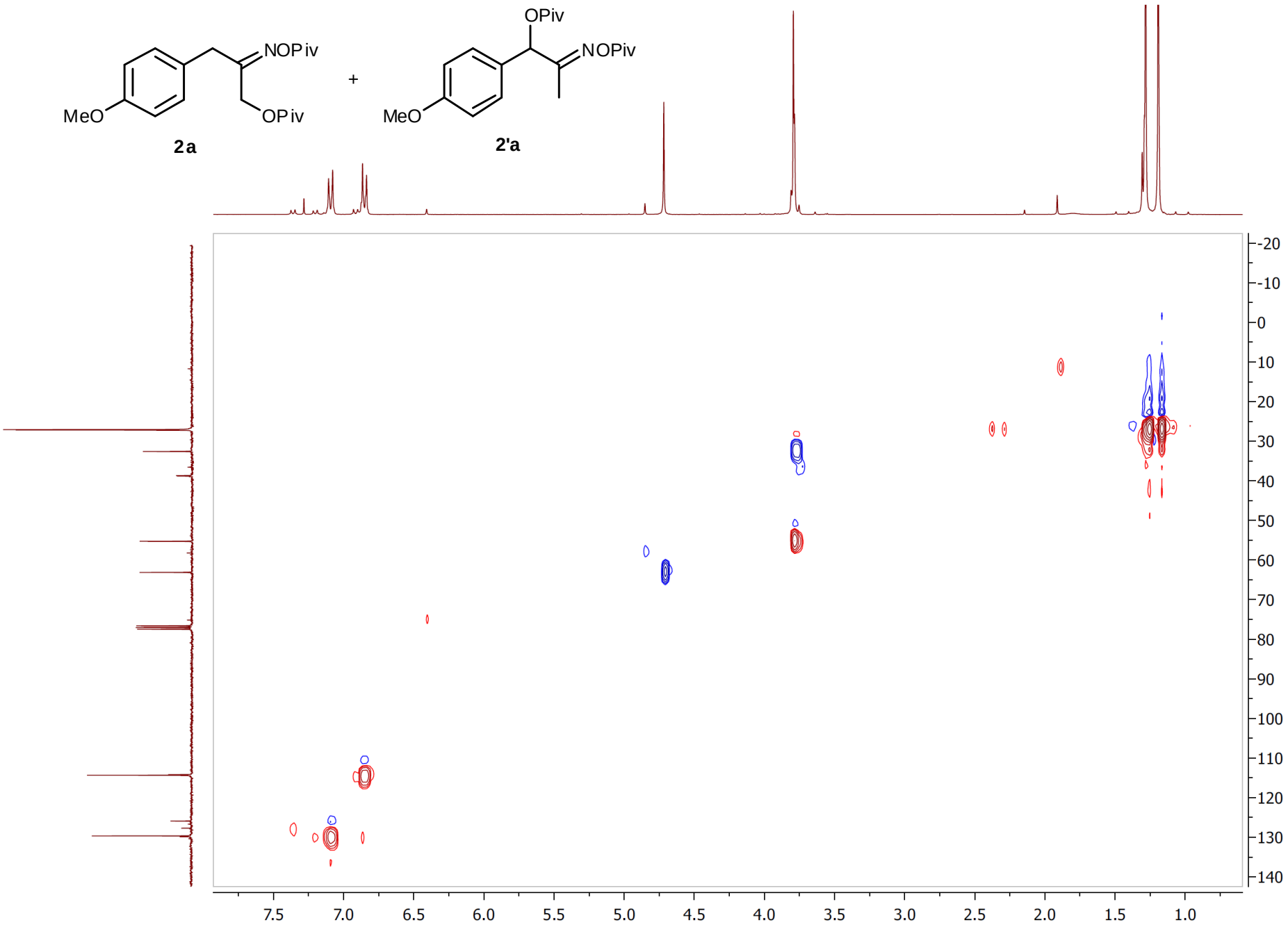
^{13}C NMR


177.56
174.73
163.94
162.98
158.75
129.86
129.66
127.71
125.92
114.35
75.16
63.13
58.23
55.28
38.82
38.68
36.56
32.60
27.19
27.08
11.74
NOPiv
OPiv
MeO
2a
+
OPiv
NOPiv
MeO
2'a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

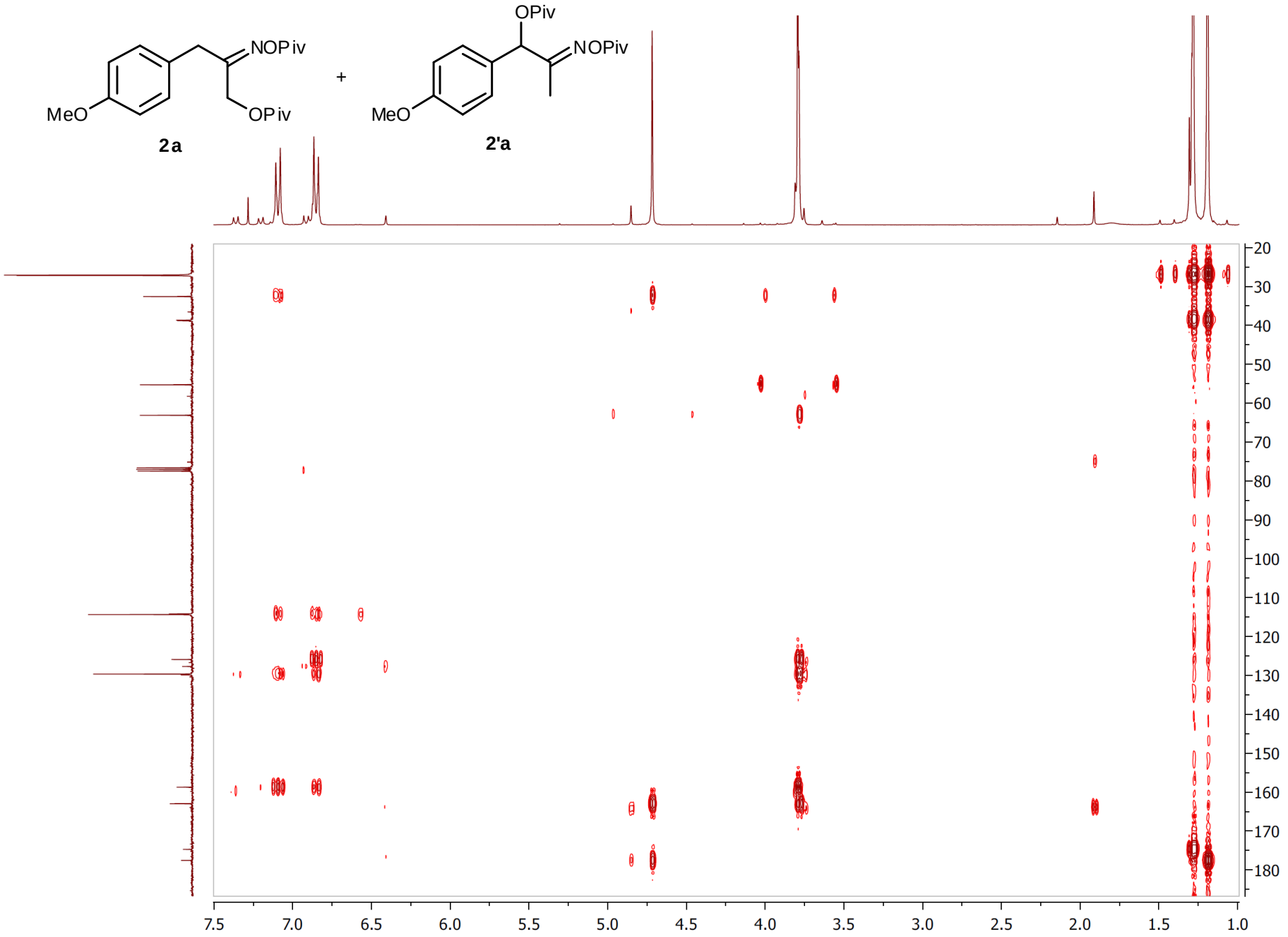
^{13}C NMR DEPT


129.86
129.66
127.71
114.35
114.17
63.13
58.23
55.28
36.56
32.60
27.19
27.08
11.74
NOPiv
OPiv
MeO
2a
+
OPiv
NOPiv
MeO
2'a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

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

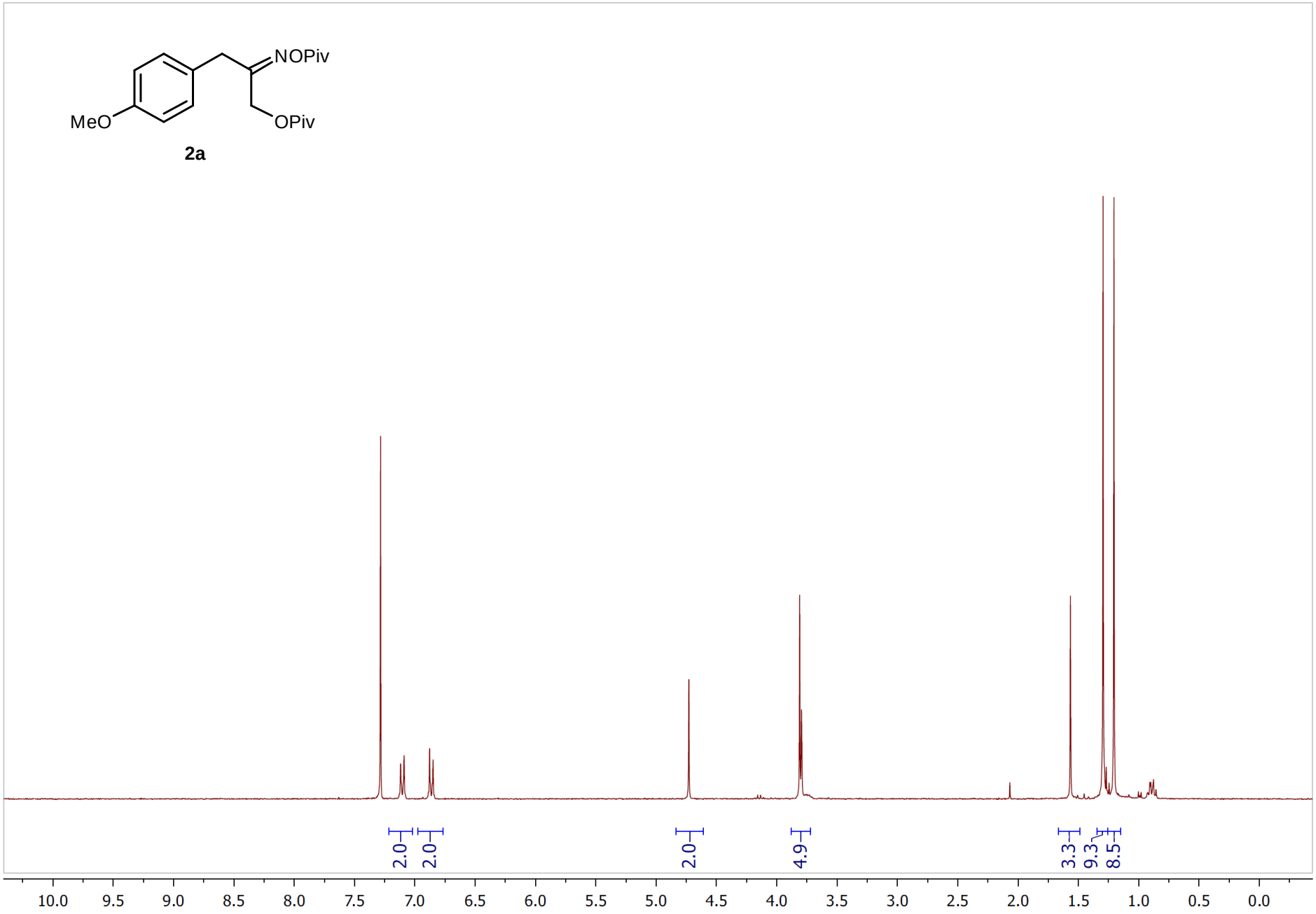

NOPiv
OPiv
MeO
2a
+
OPiv
NOPiv
MeO
2'a
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

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


NOPiv
OPiv
MeO
2a
+
OPiv
NOPiv
MeO
2'a
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

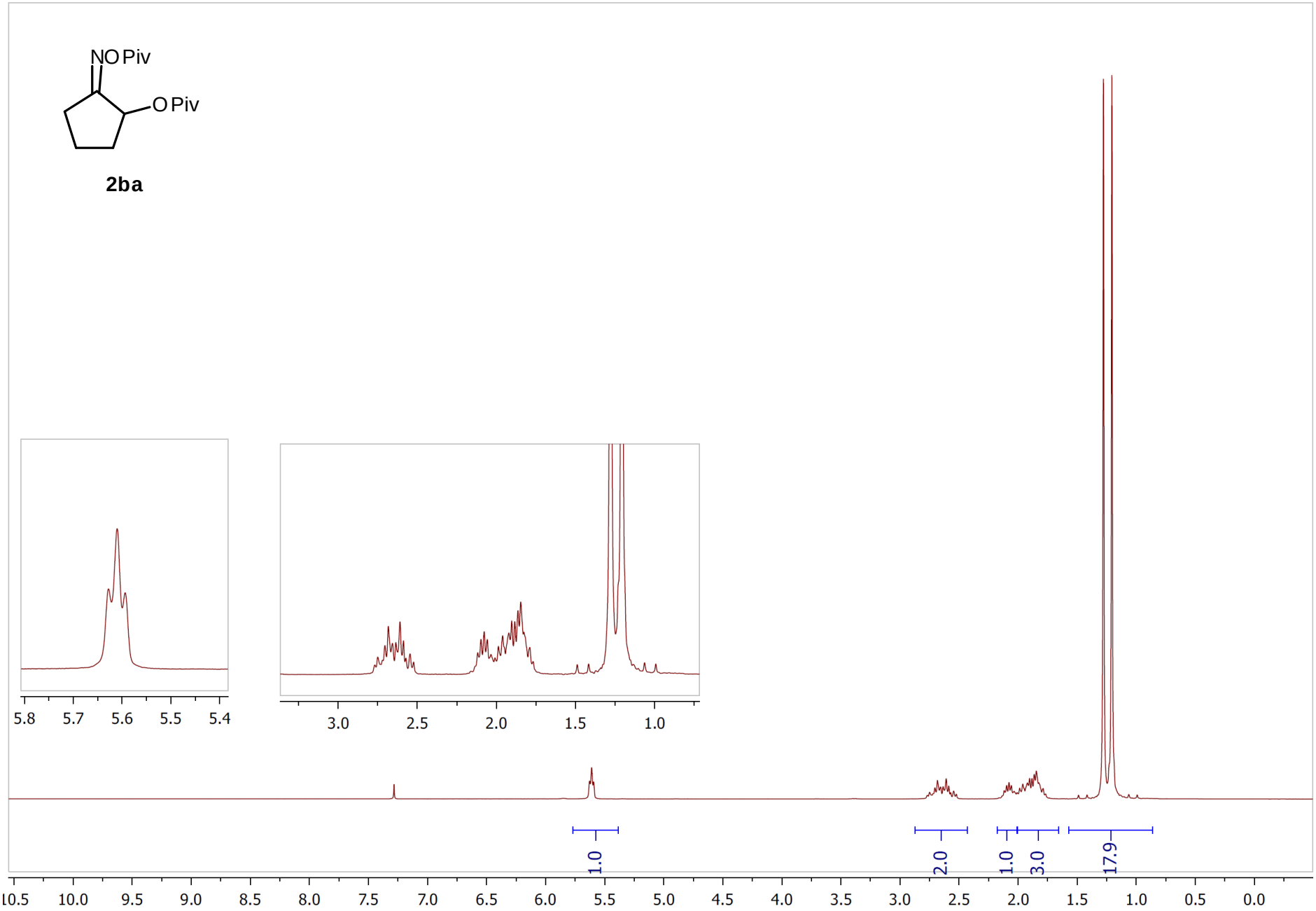
3-(4-Methoxyphenyl)-2-(pivaloyloxyimino)propyl pivalate 2a pure, after crystallization

^{1}H NMR

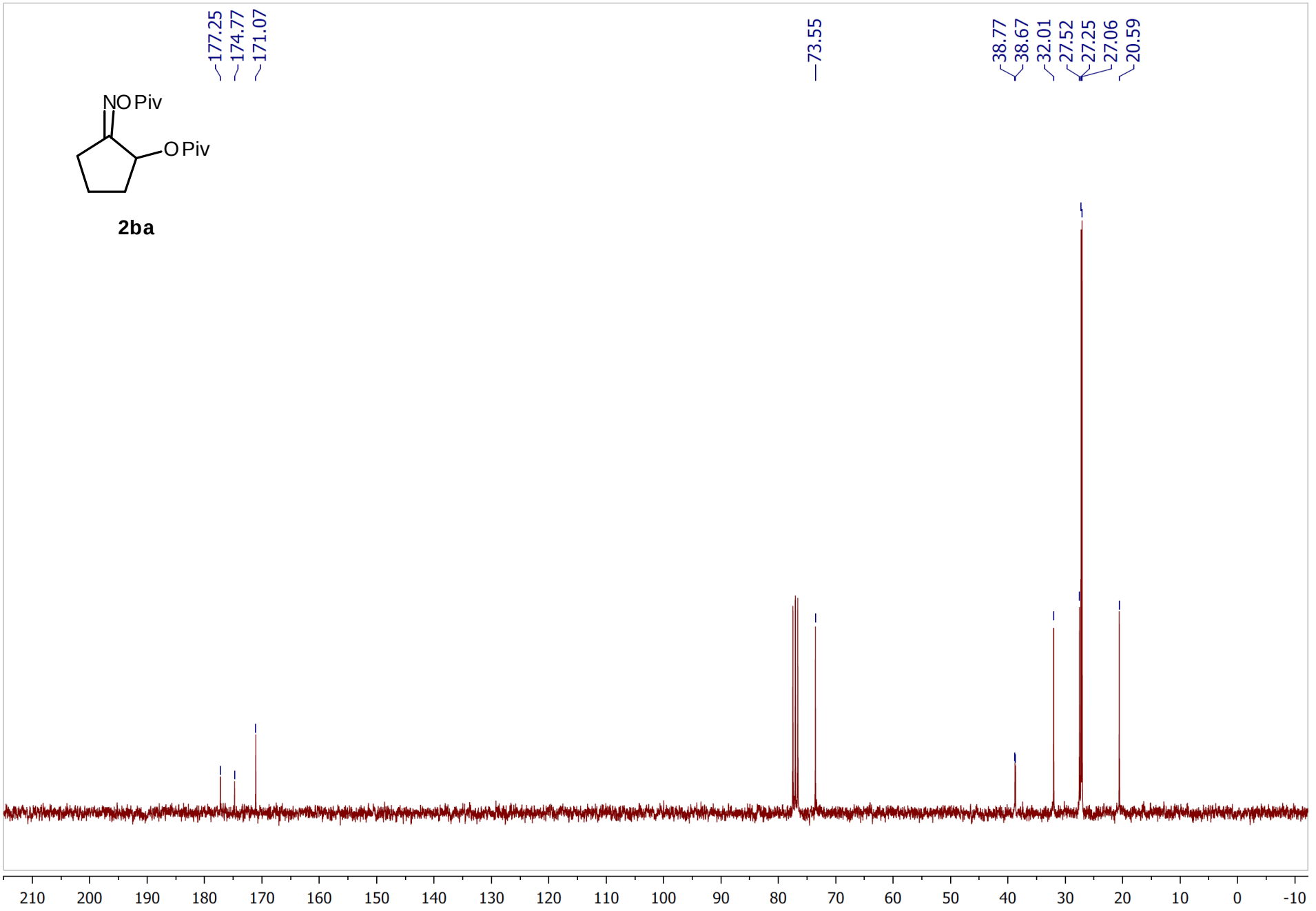


2-(Pivaloyloxyimino)cyclopentyl pivalate 2ba

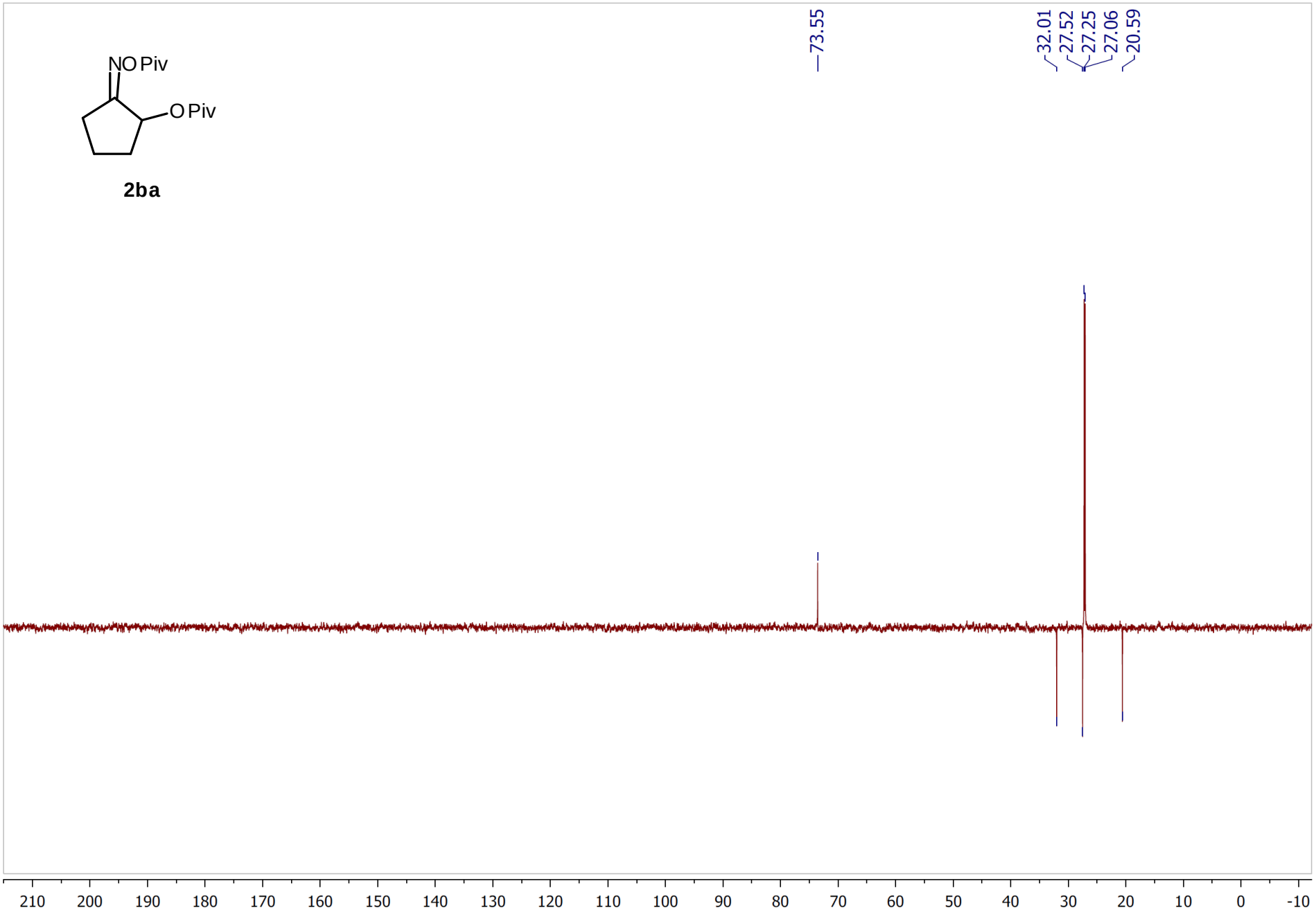
^{1}H NMR



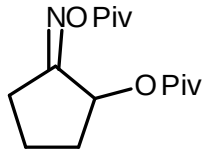
^{13}C NMR


177.25
174.77
171.07
73.55
38.77
38.67
32.01
27.52
27.25
27.06
20.59
NO Piv
O Piv
2ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT


NO Piv
O Piv
2ba
73.55
32.01
27.52
27.25
27.06
20.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

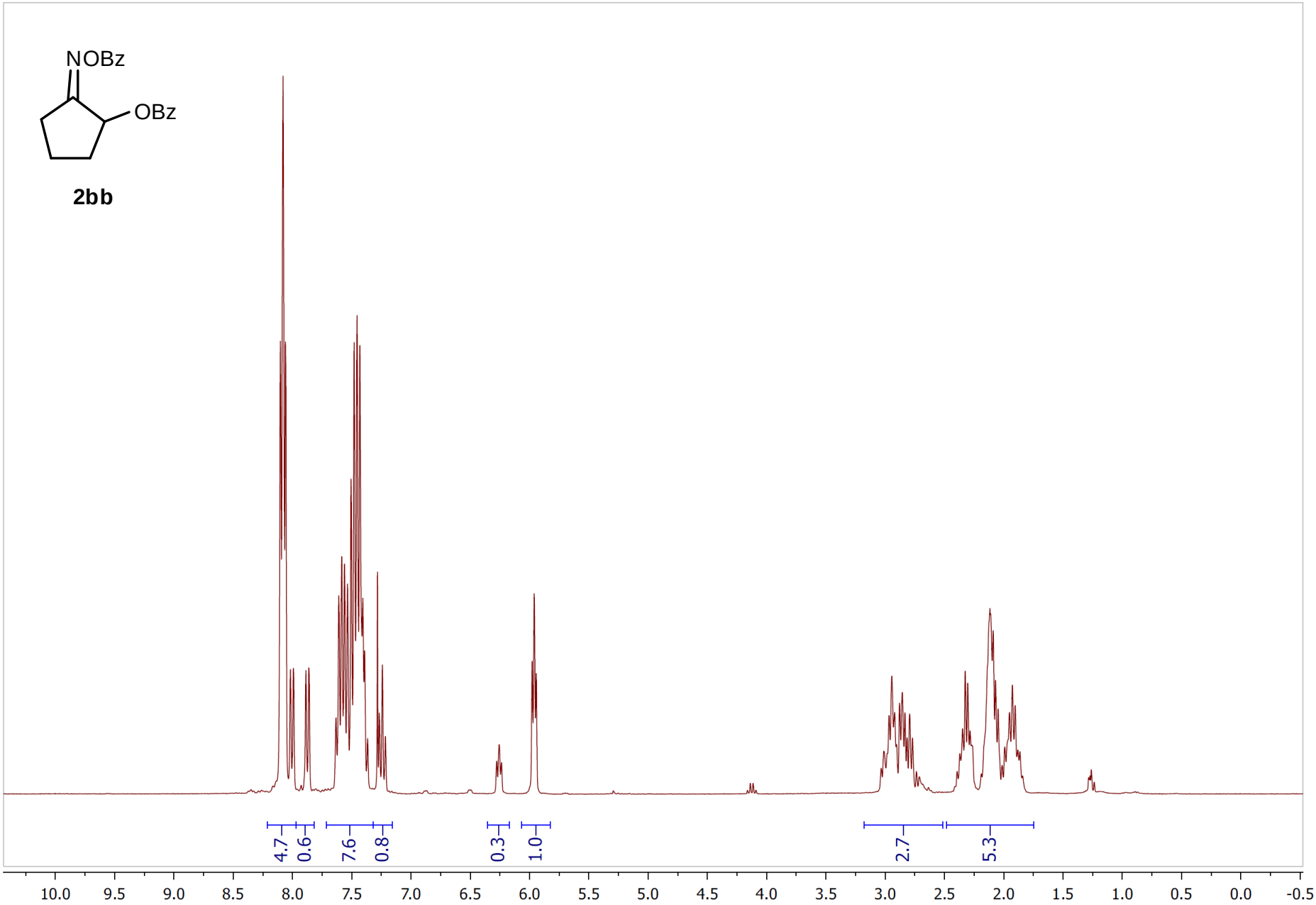
^{1}H-^{13}C HSQC



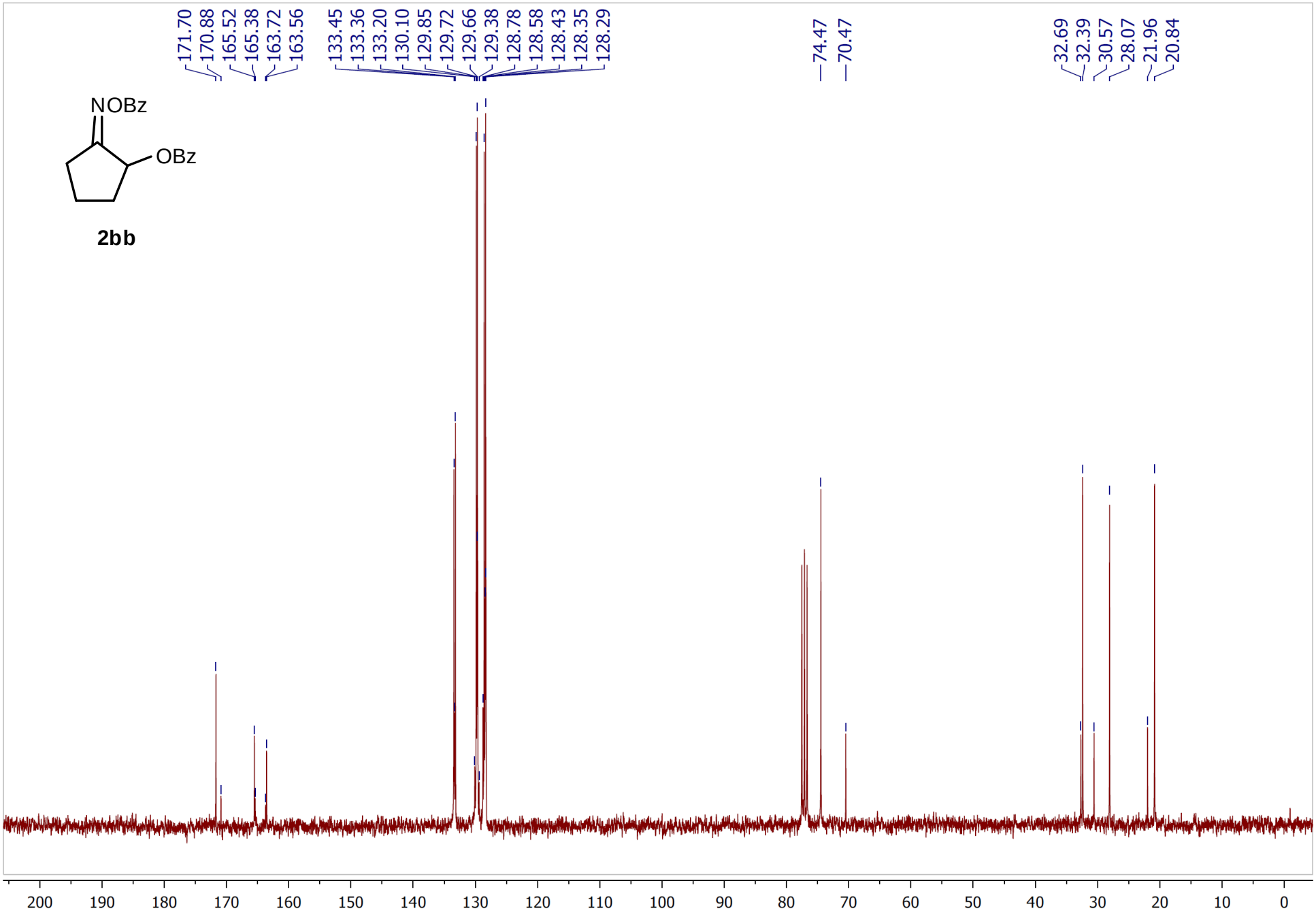
2ba

2-(Benzoyloxyimino)cyclopentyl benzoate 2bb

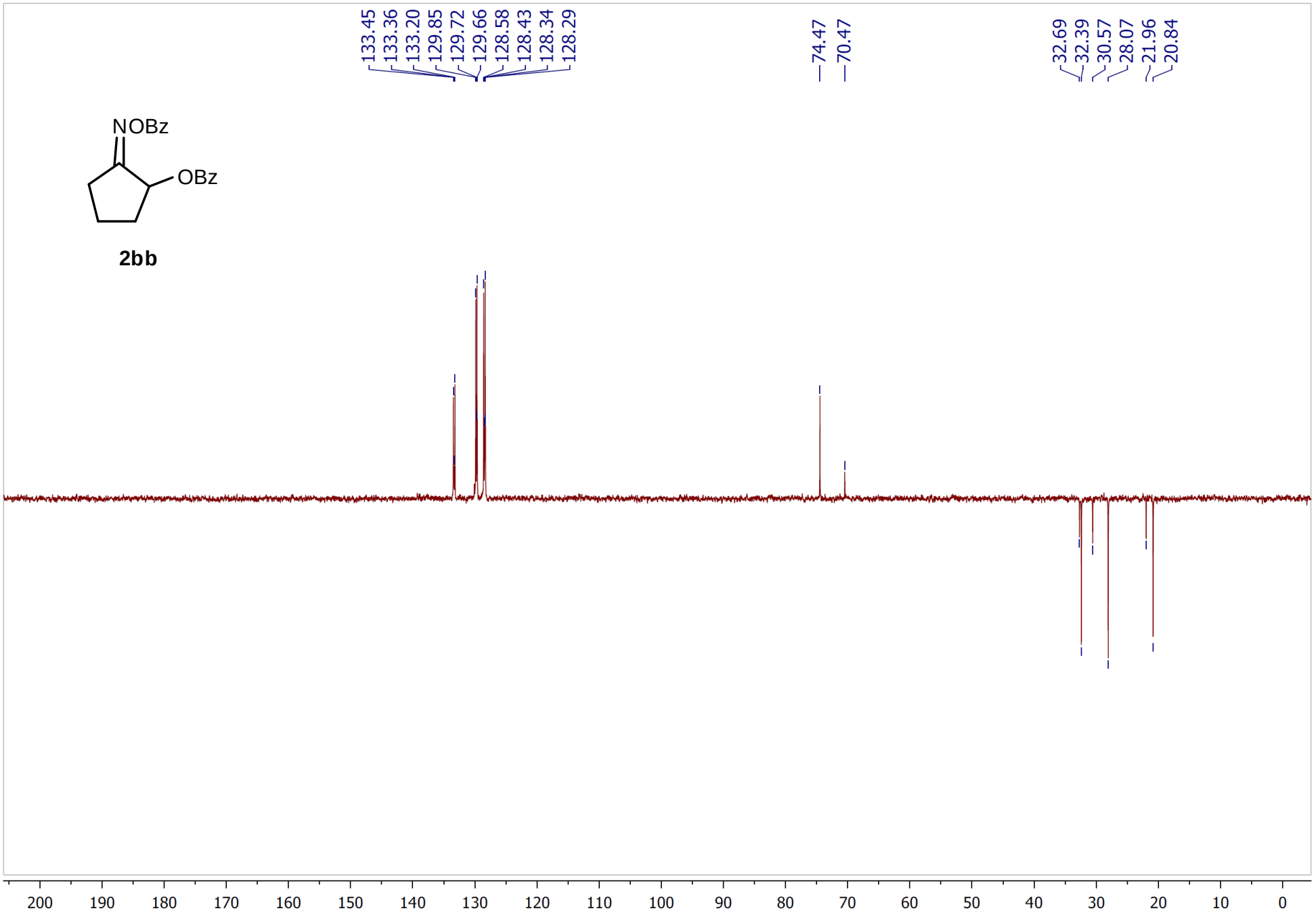
^{1}H NMR



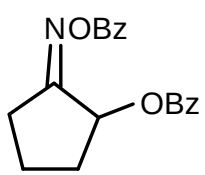
^{13}C NMR


171.70
170.88
165.52
165.38
163.72
163.56
133.45
133.36
133.20
130.10
129.85
129.72
129.66
129.38
128.78
128.58
128.43
128.35
128.29
74.47
70.47
32.69
32.39
30.57
28.07
21.96
20.84
NOBz
OBz
2bb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

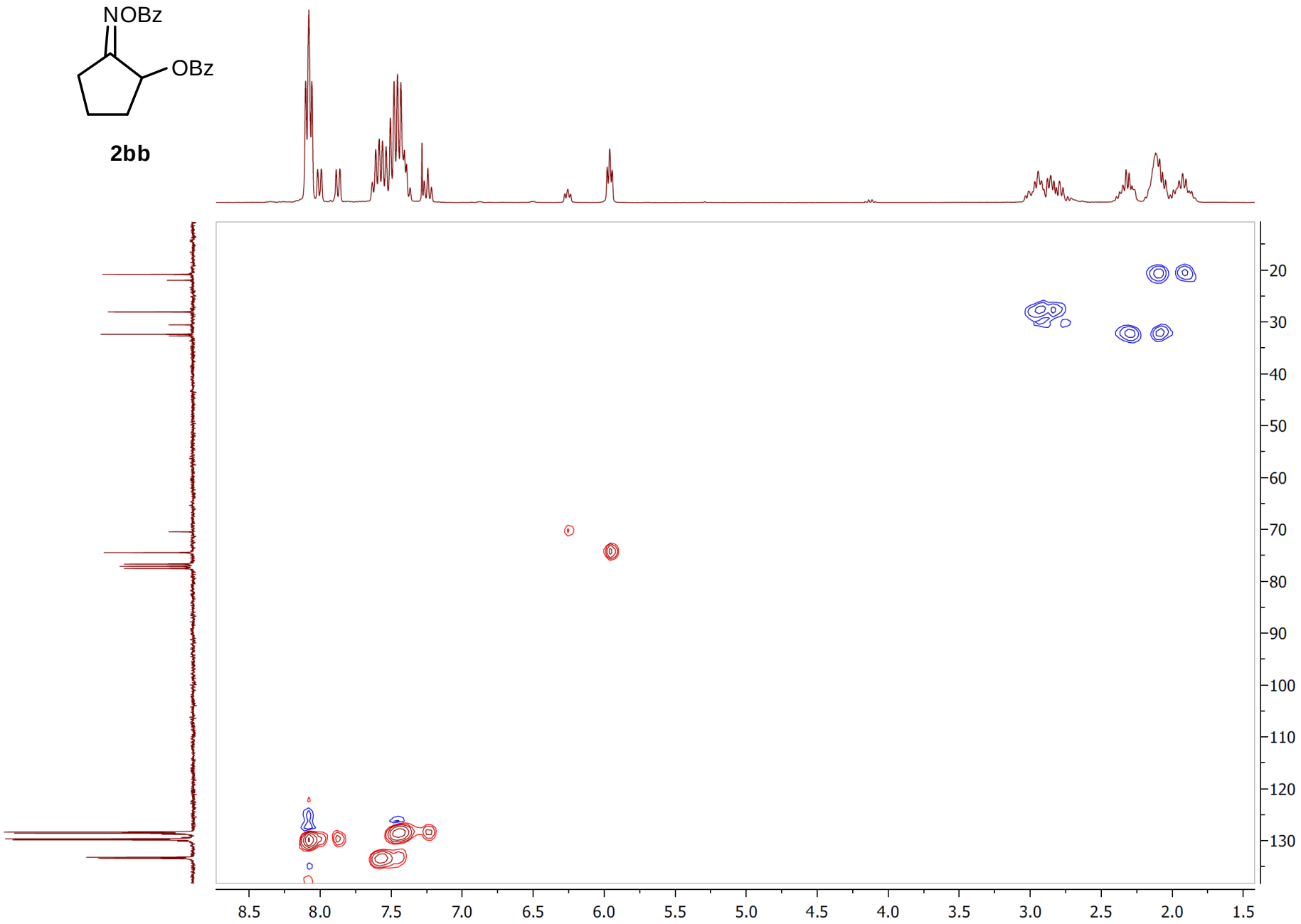

133.45
133.36
133.20
129.85
129.72
129.66
128.58
128.43
128.34
128.29
74.47
70.47
32.69
32.39
30.57
28.07
21.96
20.84
NOBz
OBz
2bb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

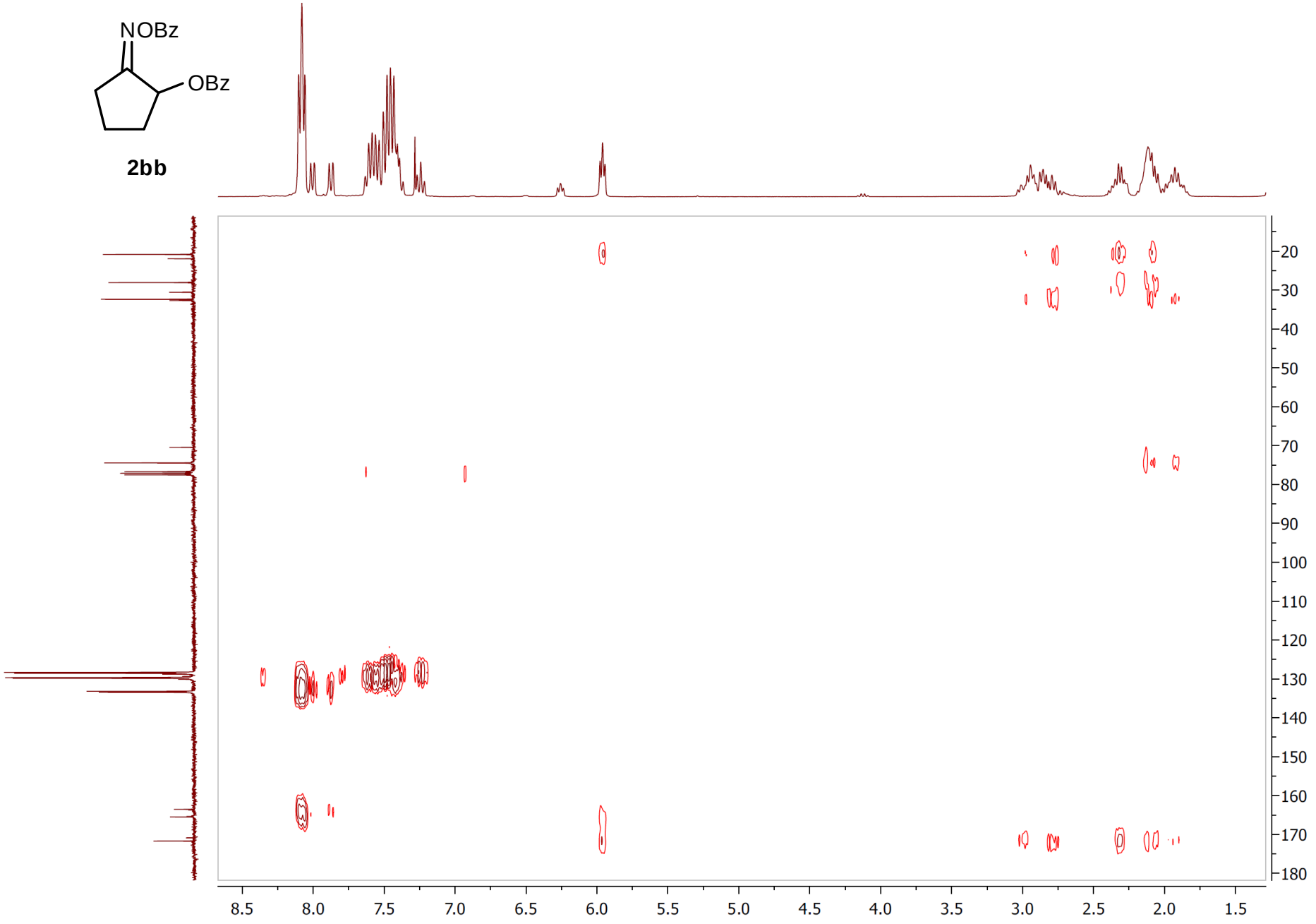


2bb

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

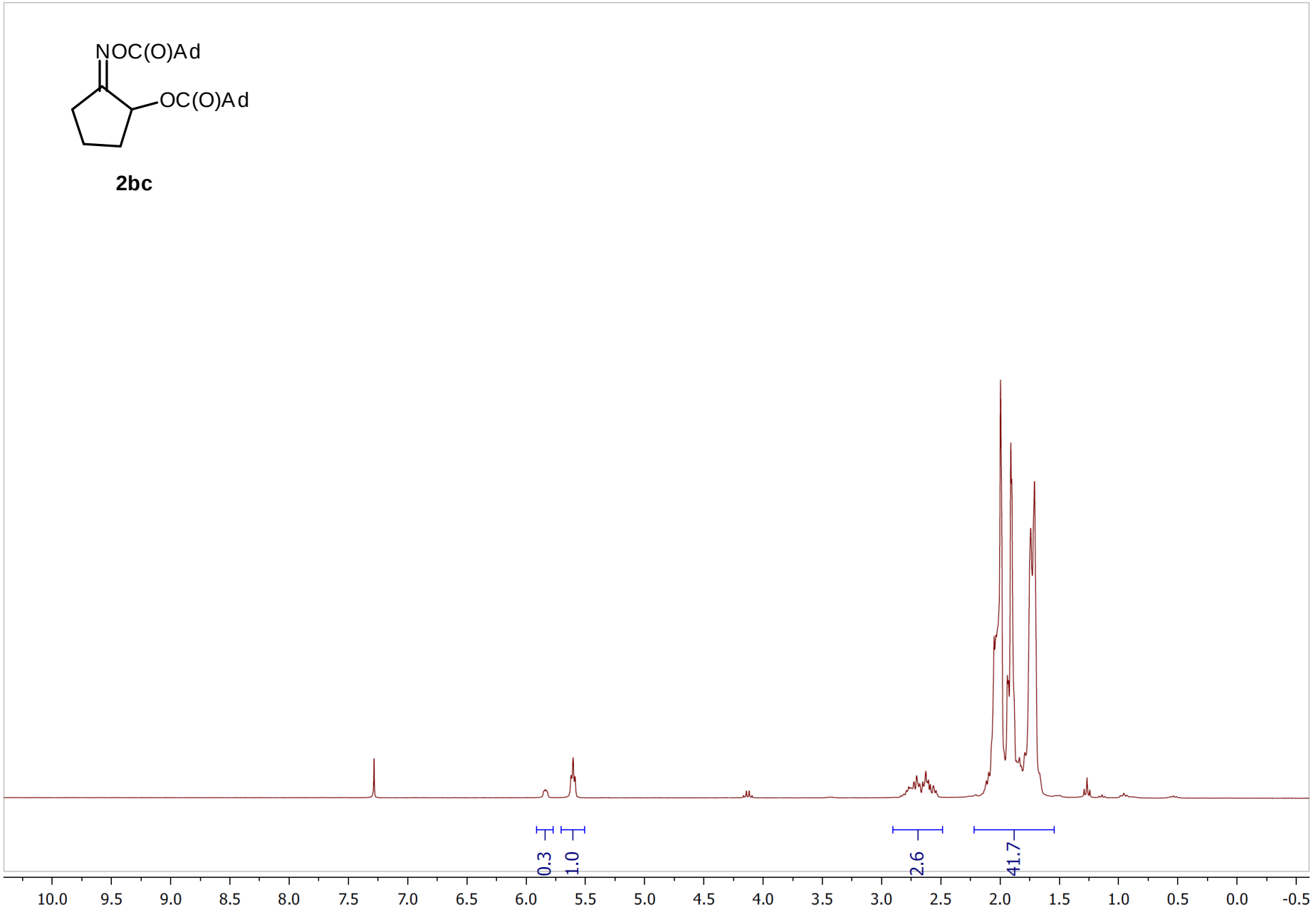

NOBz
OBz
2bb
20
30
40
50
60
70
80
90
100
110
120
130
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

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

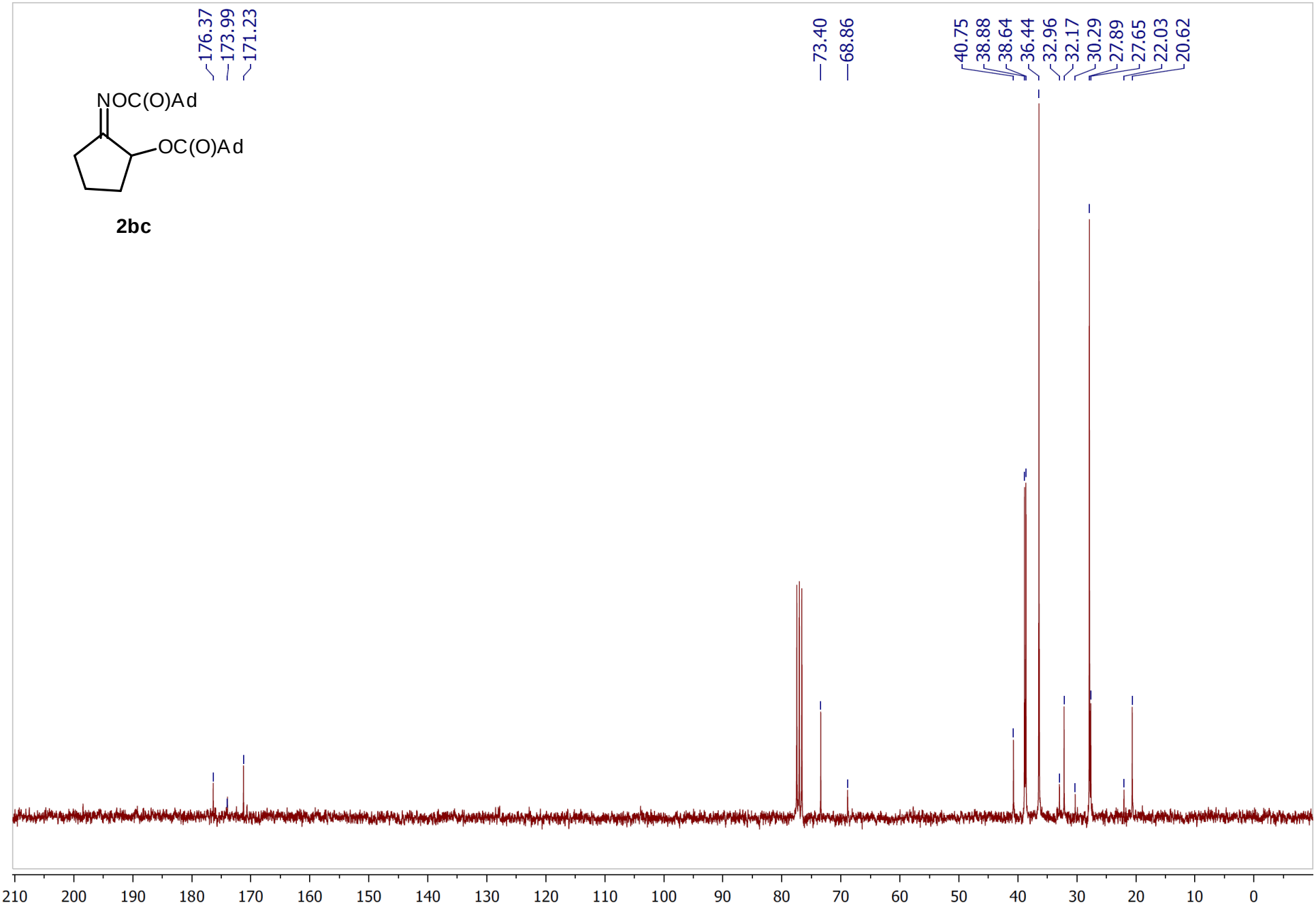

NOBz
OBz
2bb
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

2-(1-Adamantanecarbonyloxyimino)cyclopentyl adamantane-1-carboxylate 2bc

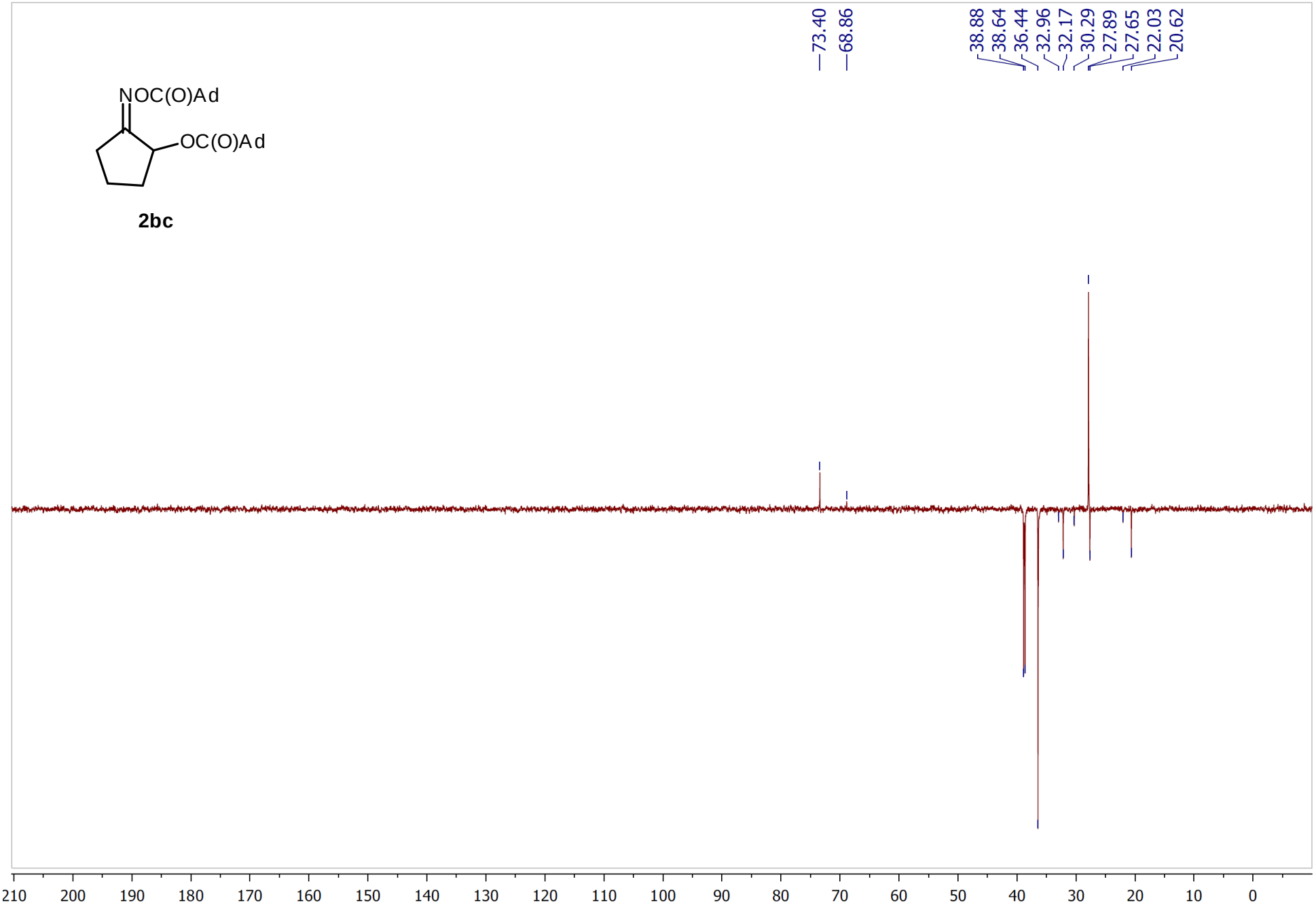
^{1}H NMR



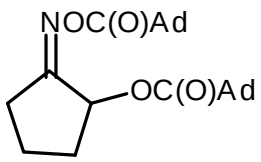
^{13}C NMR


176.37
173.99
171.23
73.40
68.86
40.75
38.88
38.64
36.44
32.96
32.17
30.29
27.89
27.65
22.03
20.62
NOC(O)Ad
OC(O)Ad
2bc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT


73.40
68.86
38.88
38.64
36.44
32.96
32.17
30.29
27.89
27.65
22.03
20.62
NOC(O)Ad
OC(O)Ad
2bc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

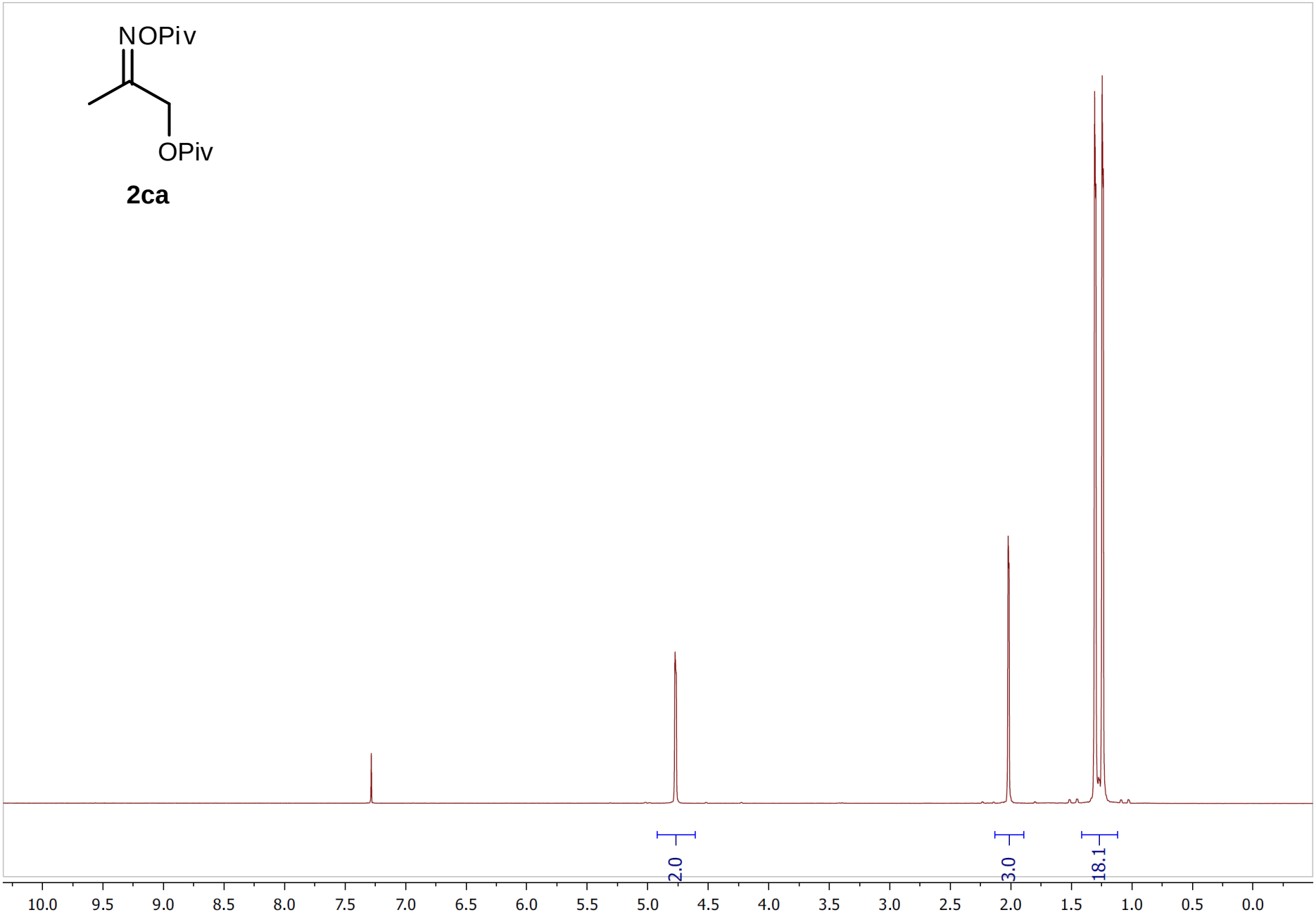
^{1}H-^{13}C HSQC



2bc

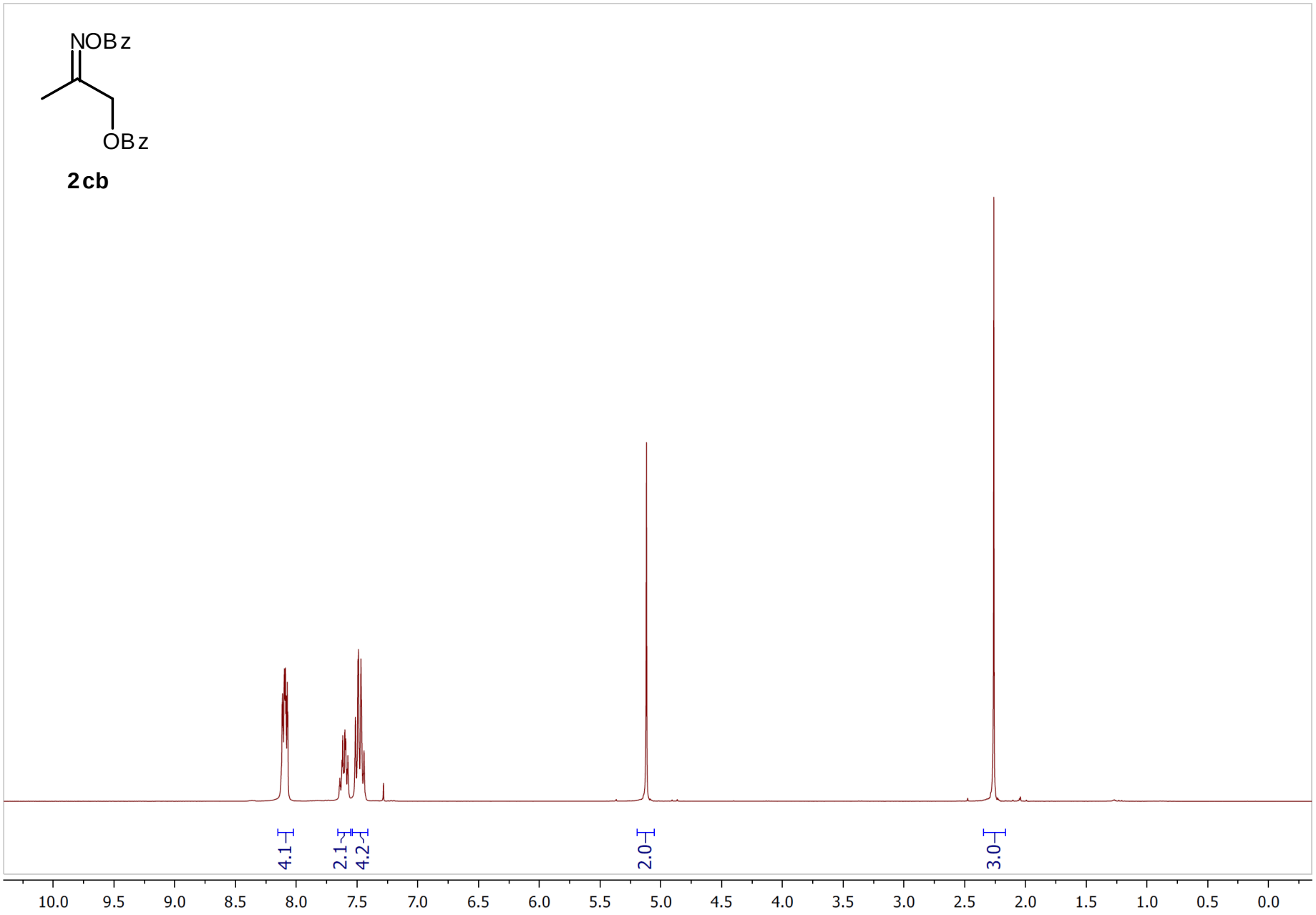
2-(Pivaloyloxyimino)propyl pivalate 2ca

^{1}H NMR

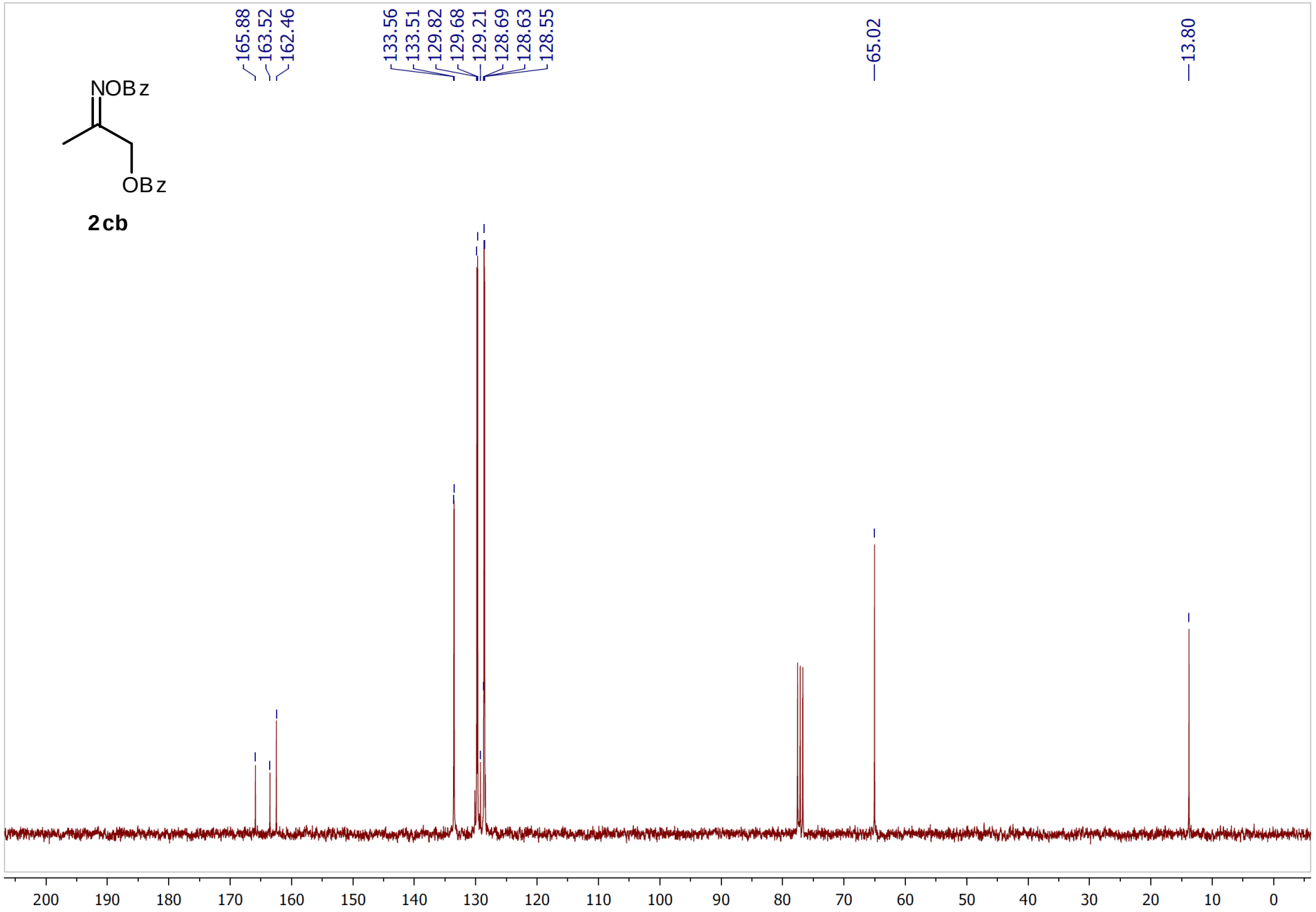


2-(Benzoyloxyimino)propyl benzoate 2cb

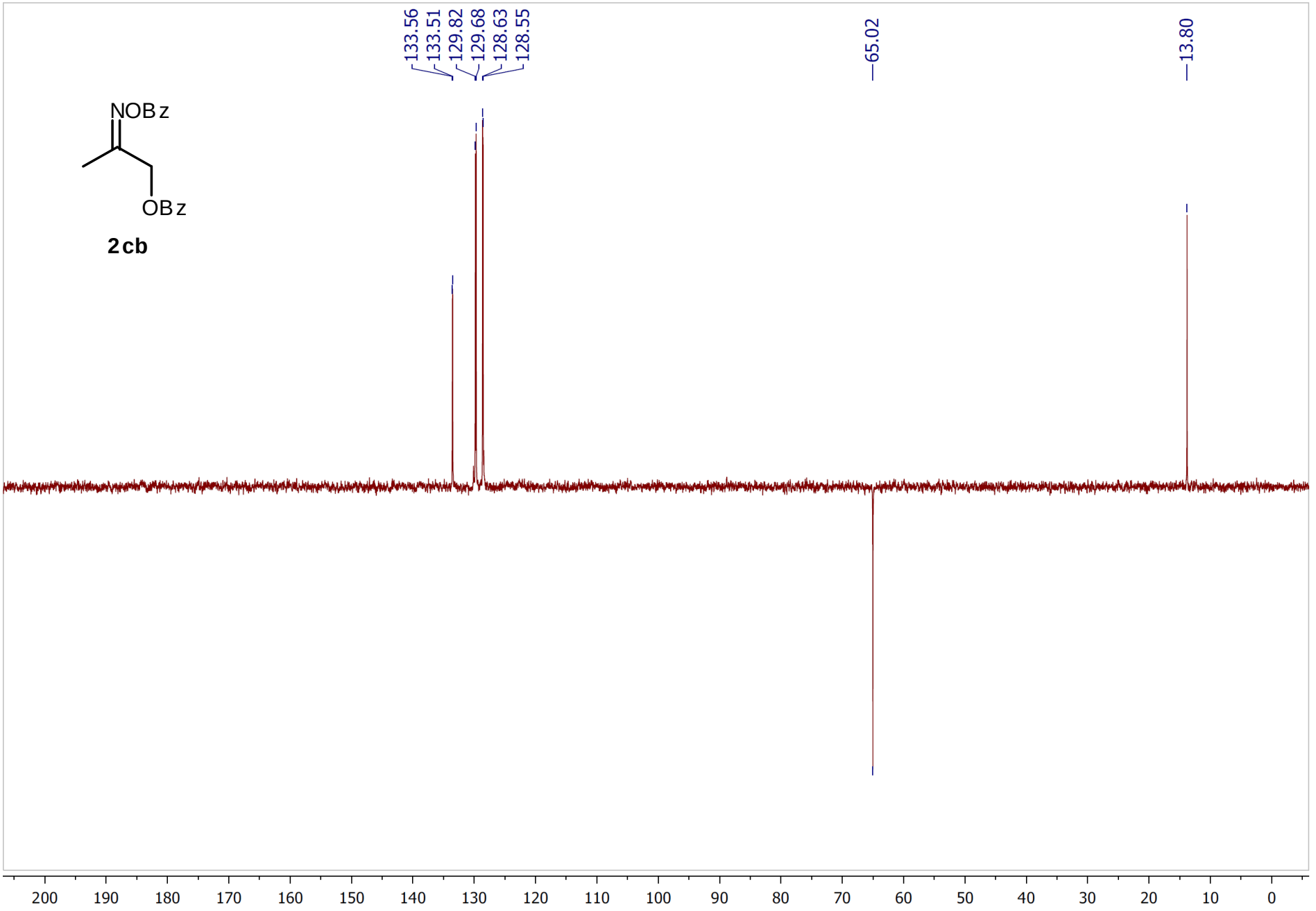
^{1}H NMR



^{13}C NMR

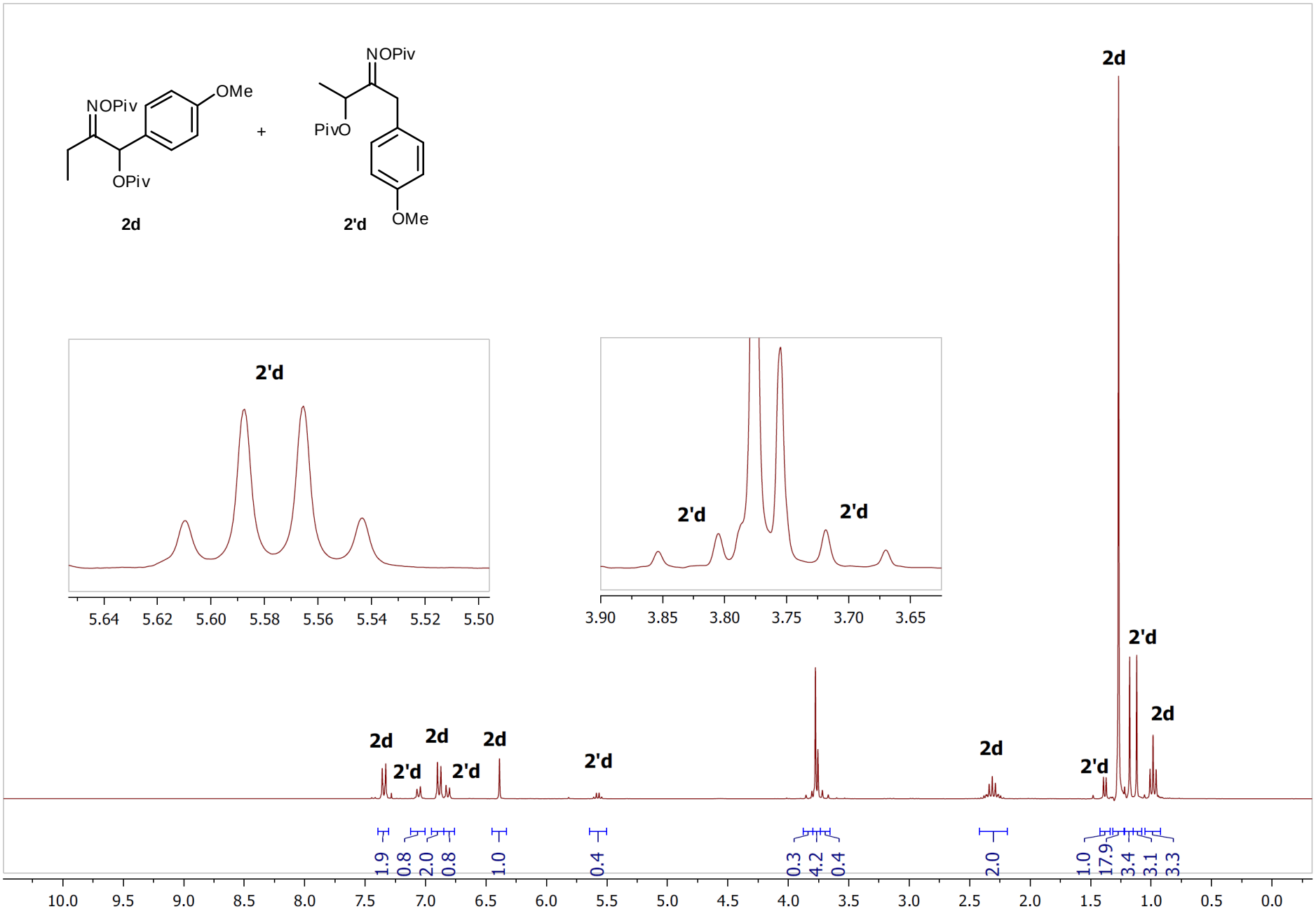

165.88
163.52
162.46
133.56
133.51
129.82
129.68
129.21
128.69
128.63
128.55
65.02
13.80
NOBz
OBz
2cb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

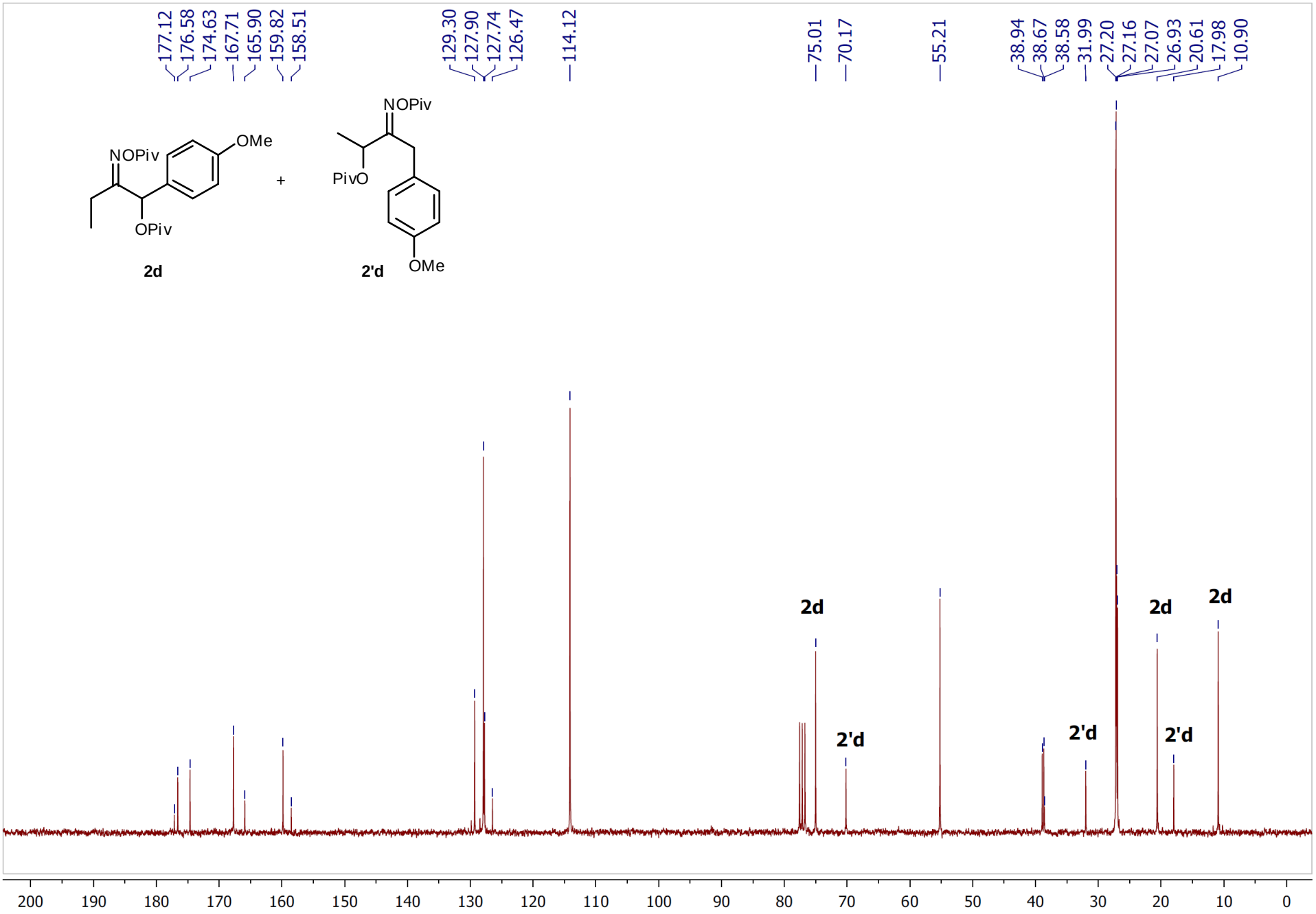

133.56
133.51
129.82
129.68
128.63
128.55
65.02
13.80
NOBz
OBz
2cb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1-(4-Methoxyphenyl)-2-(pivaloyloxyimino)butyl pivalate 2d and **4-(4-Methoxyphenyl)-3-(pivaloyloxyimino)butan-2-yl pivalate 2'd**

^{1}H NMR



^{13}C NMR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176.58
174.63
167.71
165.90
159.82
158.51
129.30
127.90
127.74
126.47
114.12
75.01
70.17
55.21
38.94
38.67
38.58
31.99
27.20
27.16
27.07
26.93
20.61
17.98
10.90
NOPiv
OMe
OPiv
2d
+
NOPiv
PivO
OMe
2'd
2d
2'd
2'd
2d
2'd
2d
200
190
180
170
160
150
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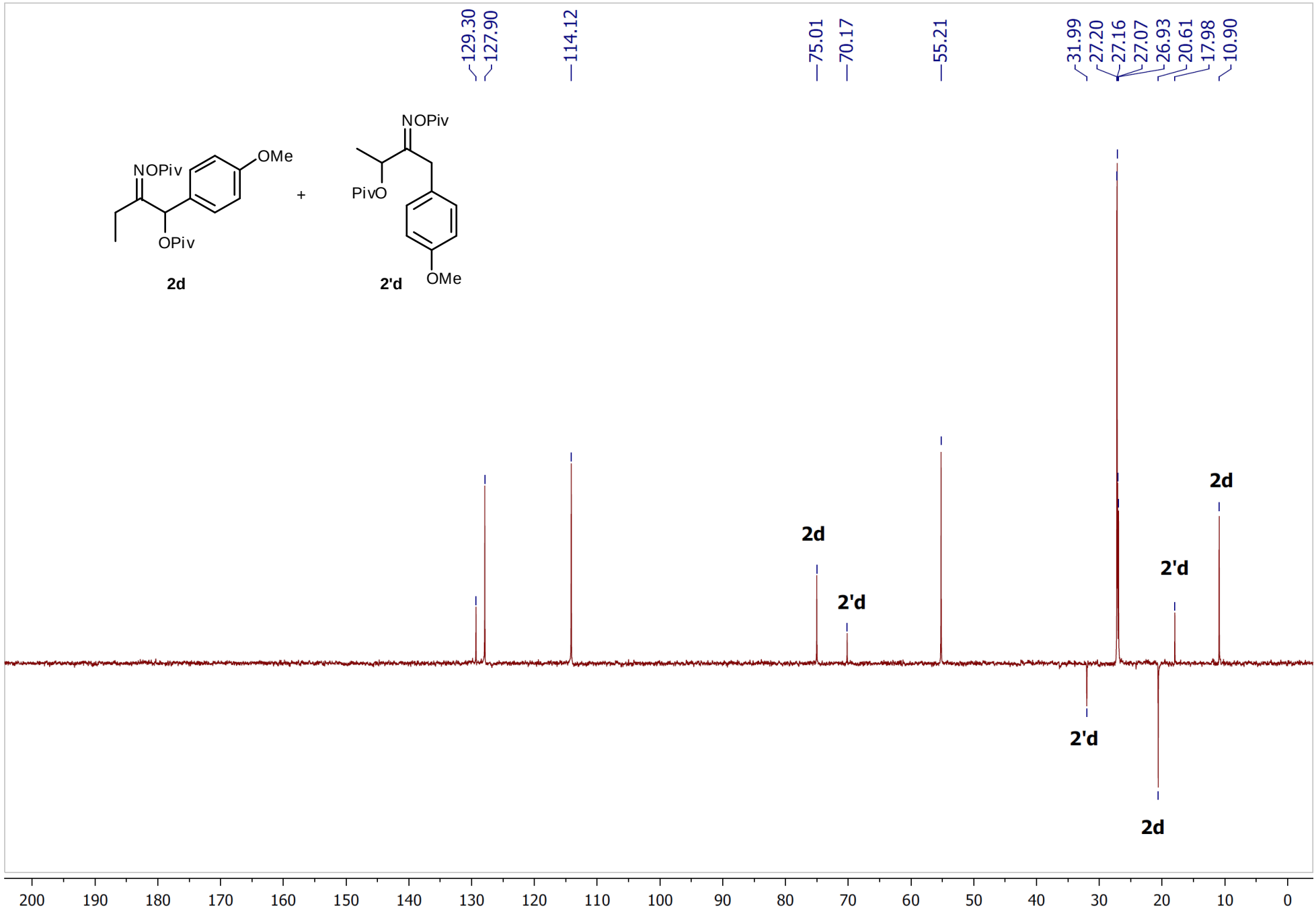
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT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127.90
114.12
75.01
70.17
55.21
31.99
27.20
27.16
27.07
26.93
20.61
17.98
10.90
NOPiv
OMe
OPiv
2d
+
NOPiv
PivO
OMe
2'd
2d
2'd
2'd
2d
2'd
2d
200
190
180
170
160
150
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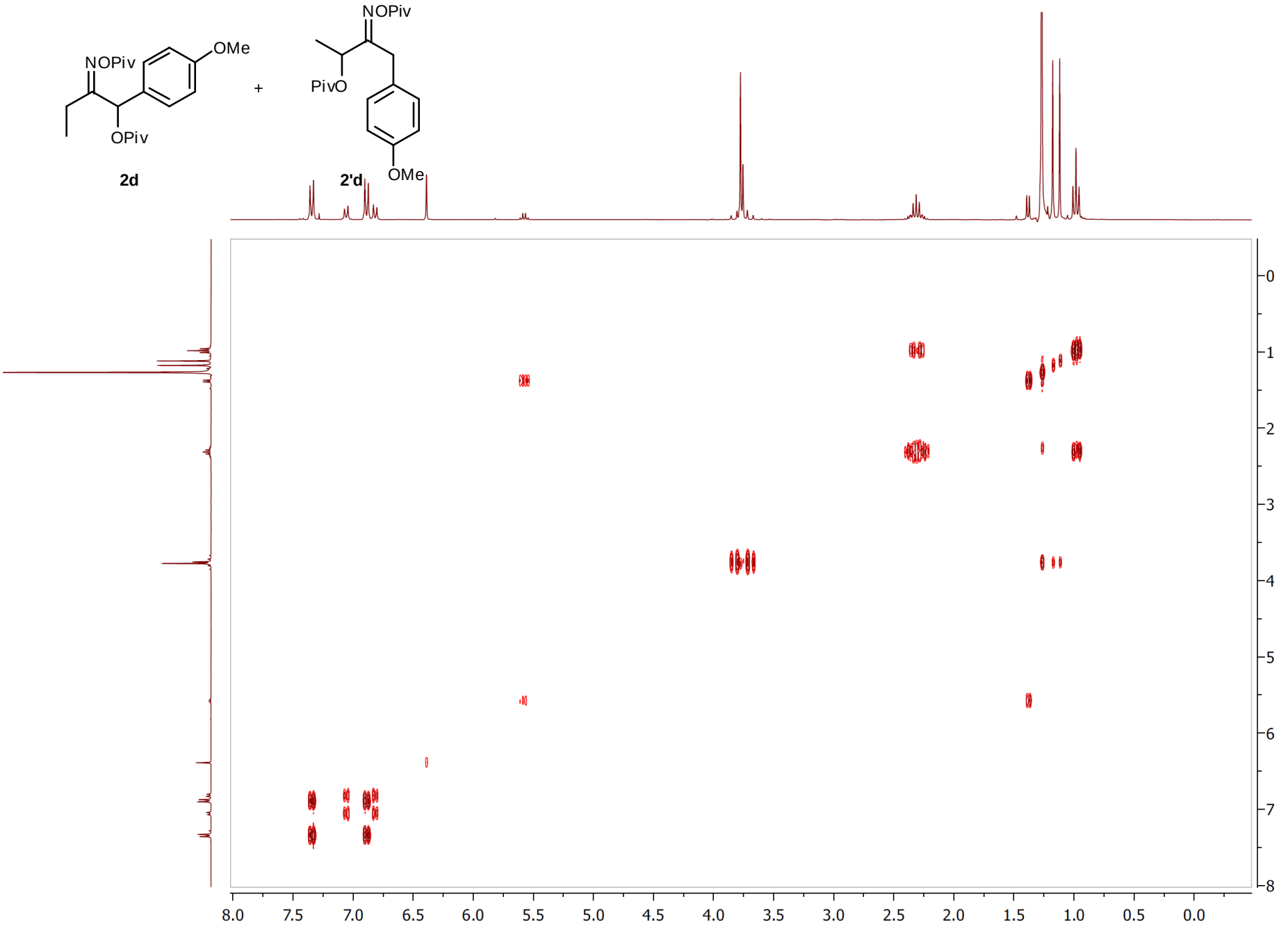
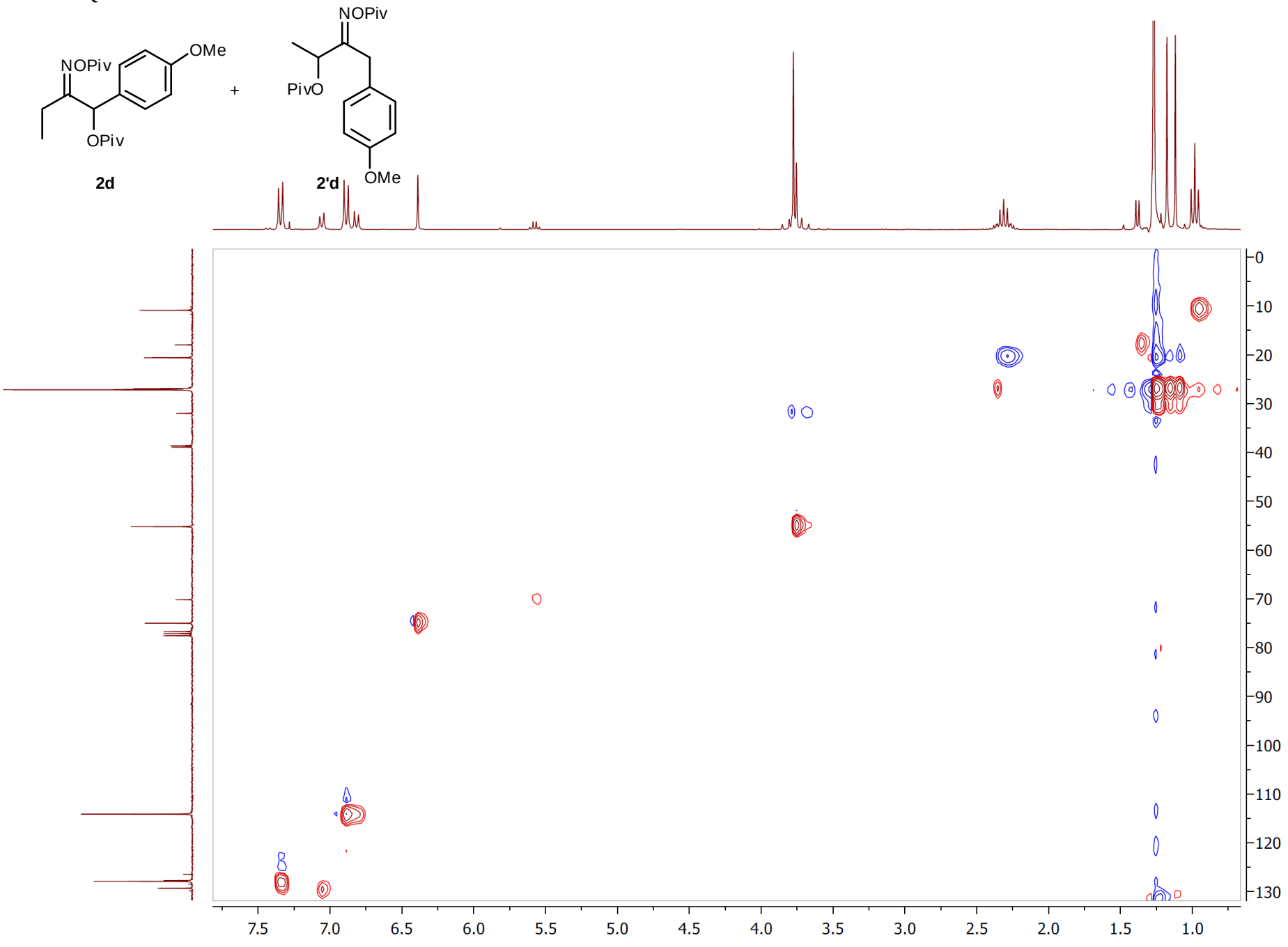
30
20
10
0

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


NOPiv
OMe
OPiv
2d
+
NOPiv
PivO
OMe
2'd
0
1
2
3
4
5
6
7
8
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


NOPiv
OMe
OPiv
2d
+
NOPiv
PivO
OMe
2'd
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
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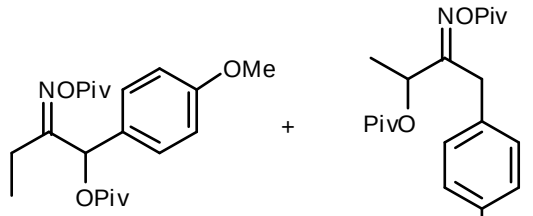
4.0
3.5
3.0
2.5
2.0
1.5
1.0

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

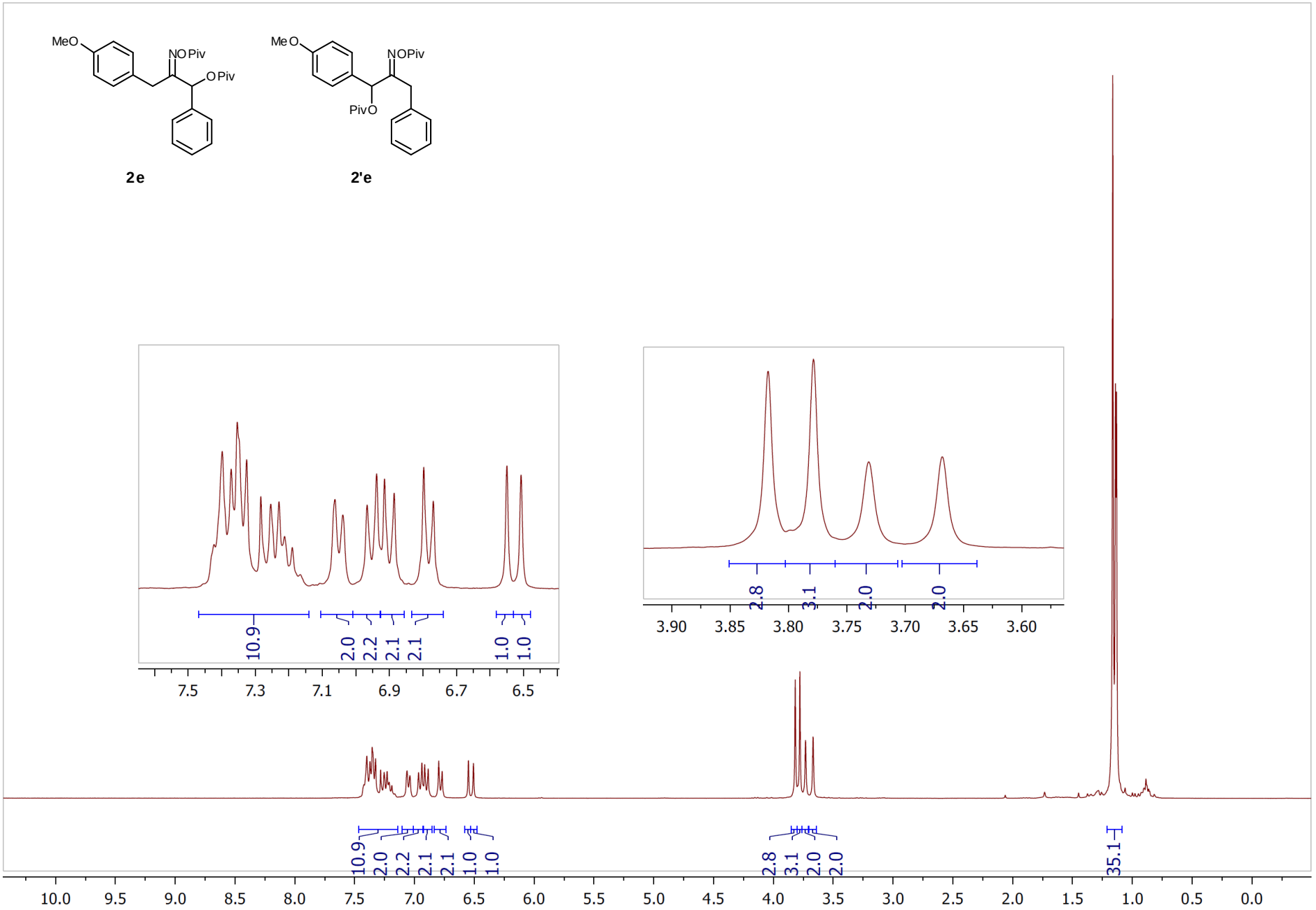


2d

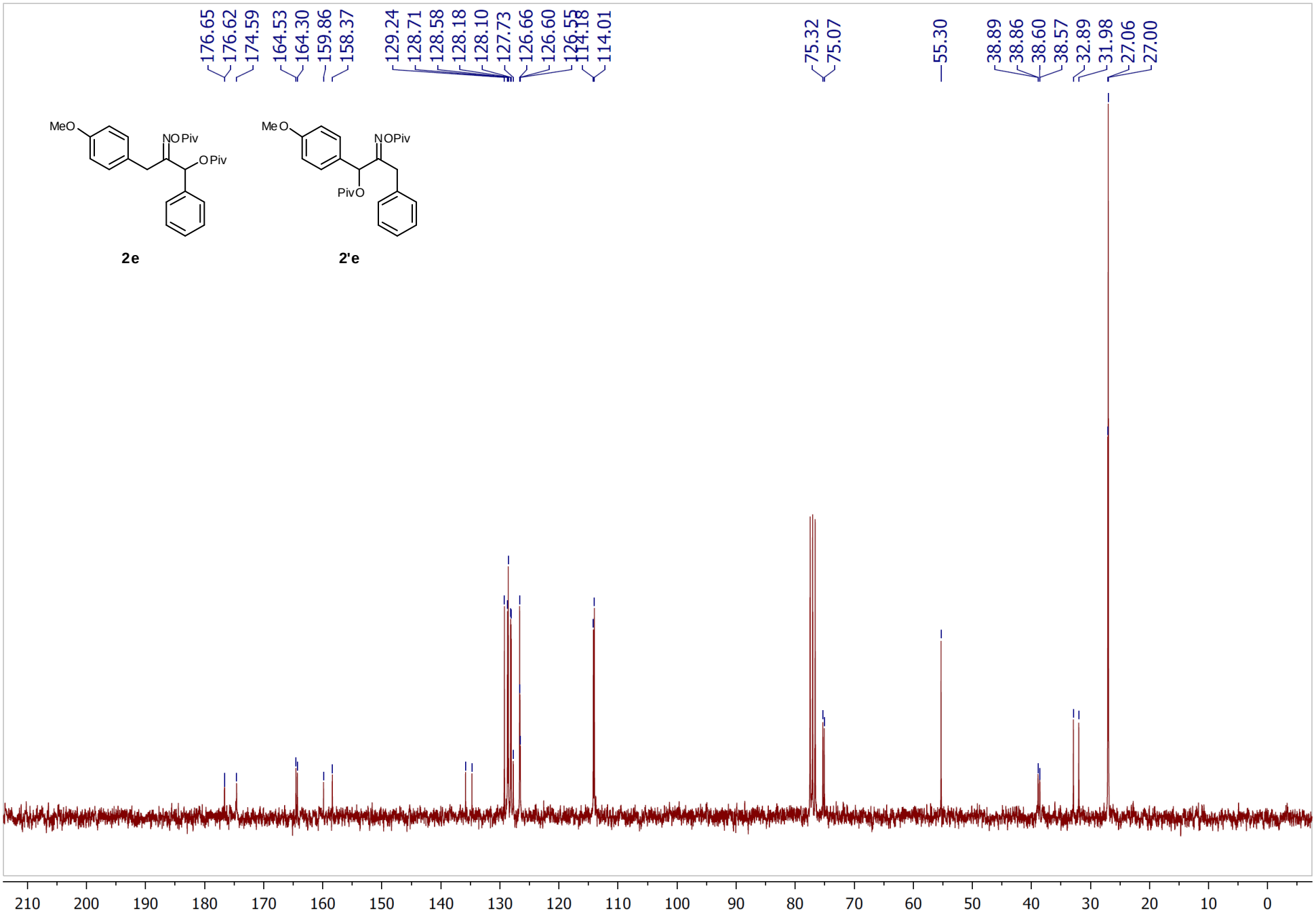
+

2'd

3-(4-Methoxyphenyl)-1-phenyl-2-(pivaloyloxyimino)propyl pivalate 2e and **1-(4-Methoxyphenyl)-3-phenyl-2-(pivaloyloxyimino)propyl pivalate 2'e**
^{1}H NMR



^{13}C NMR


176.65
176.62
174.59
164.53
164.30
159.86
158.37
129.24
128.71
128.58
128.18
128.10
127.73
126.66
126.60
126.55
114.18
114.01
75.32
75.07
55.30
38.89
38.86
38.60
38.57
32.89
31.98
27.06
27.00
MeO
NOPiv
OPiv
2e
MeO
NOPiv
PivO
2'e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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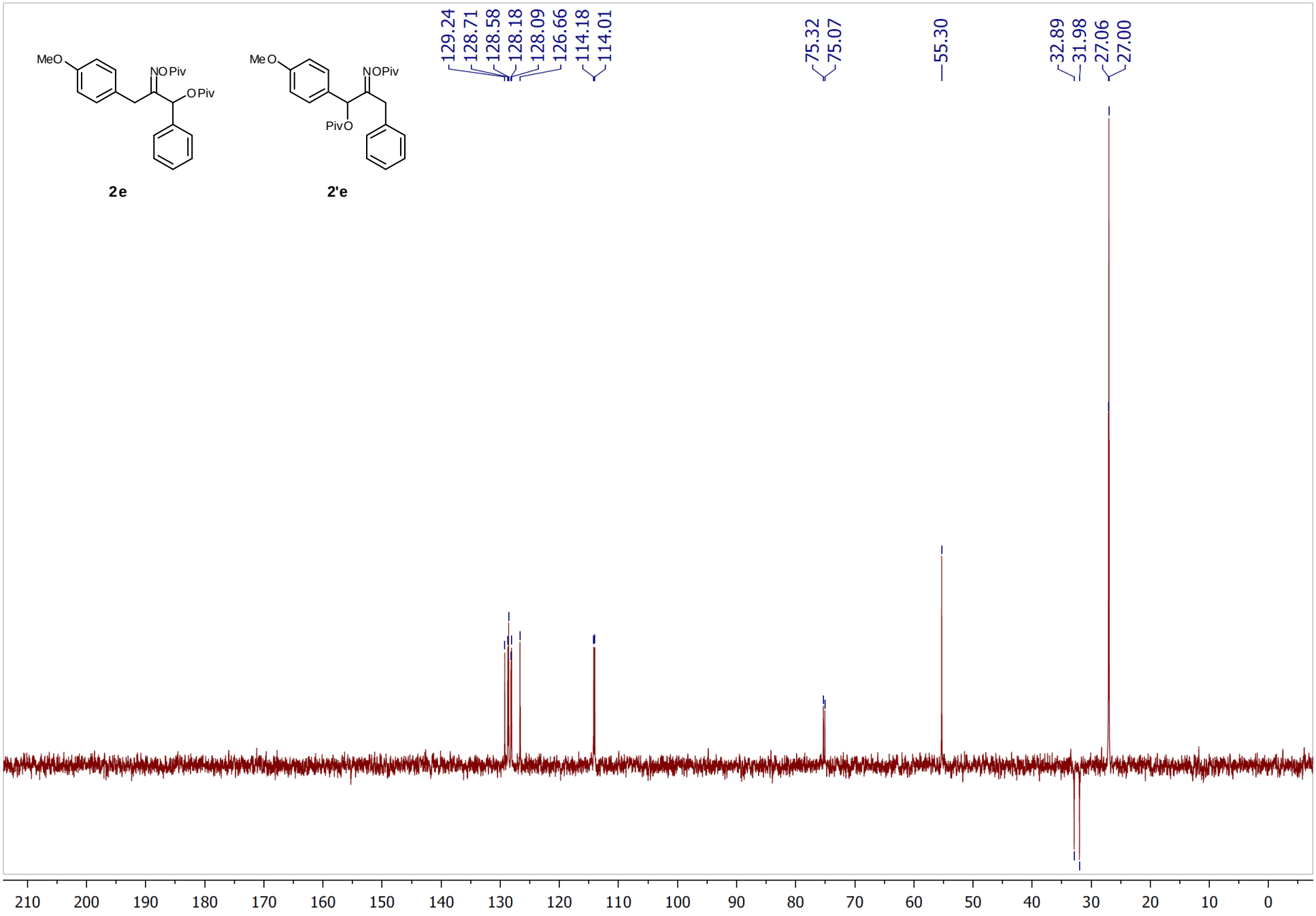
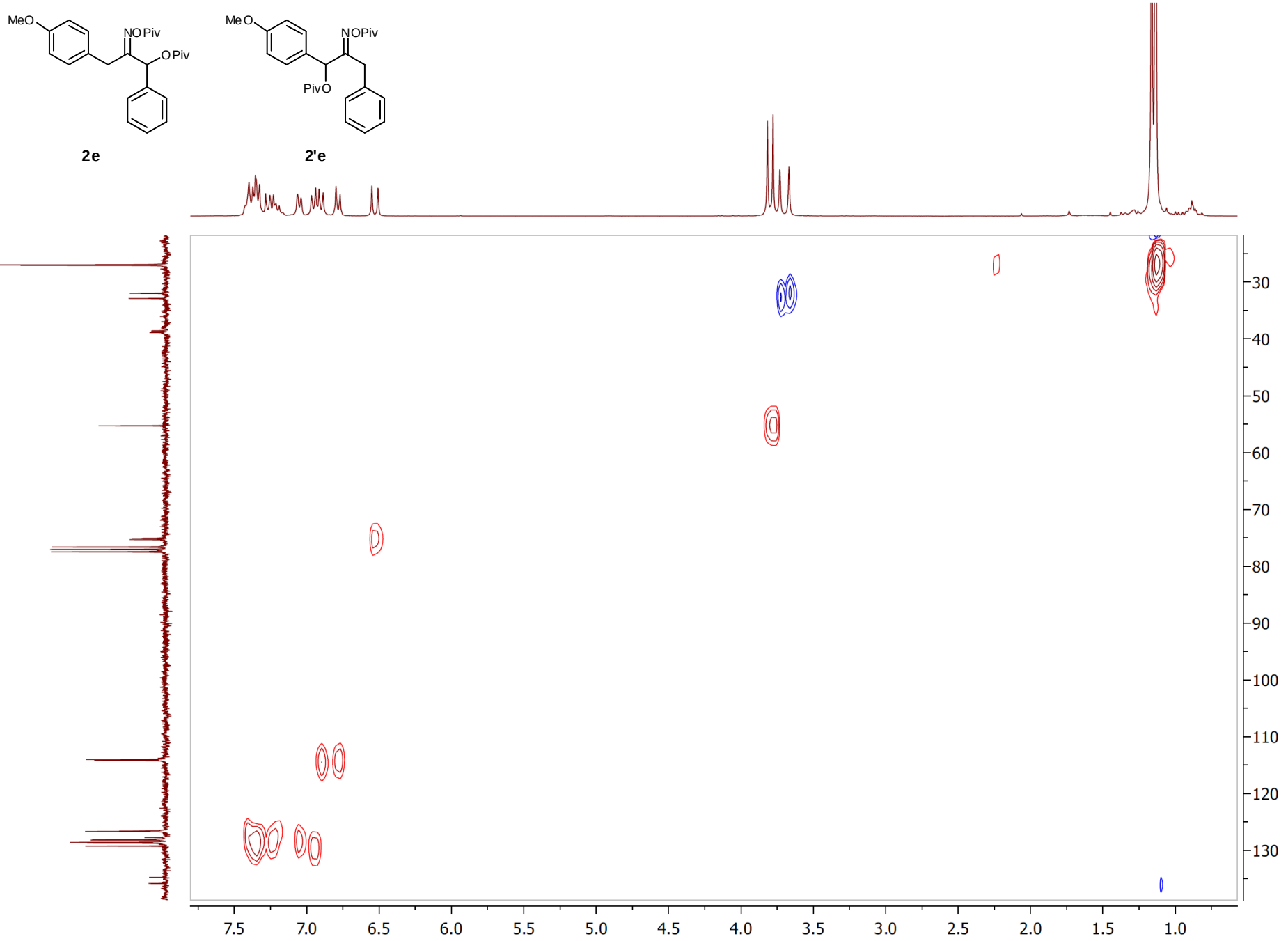
60
50
40
30
20
10
0

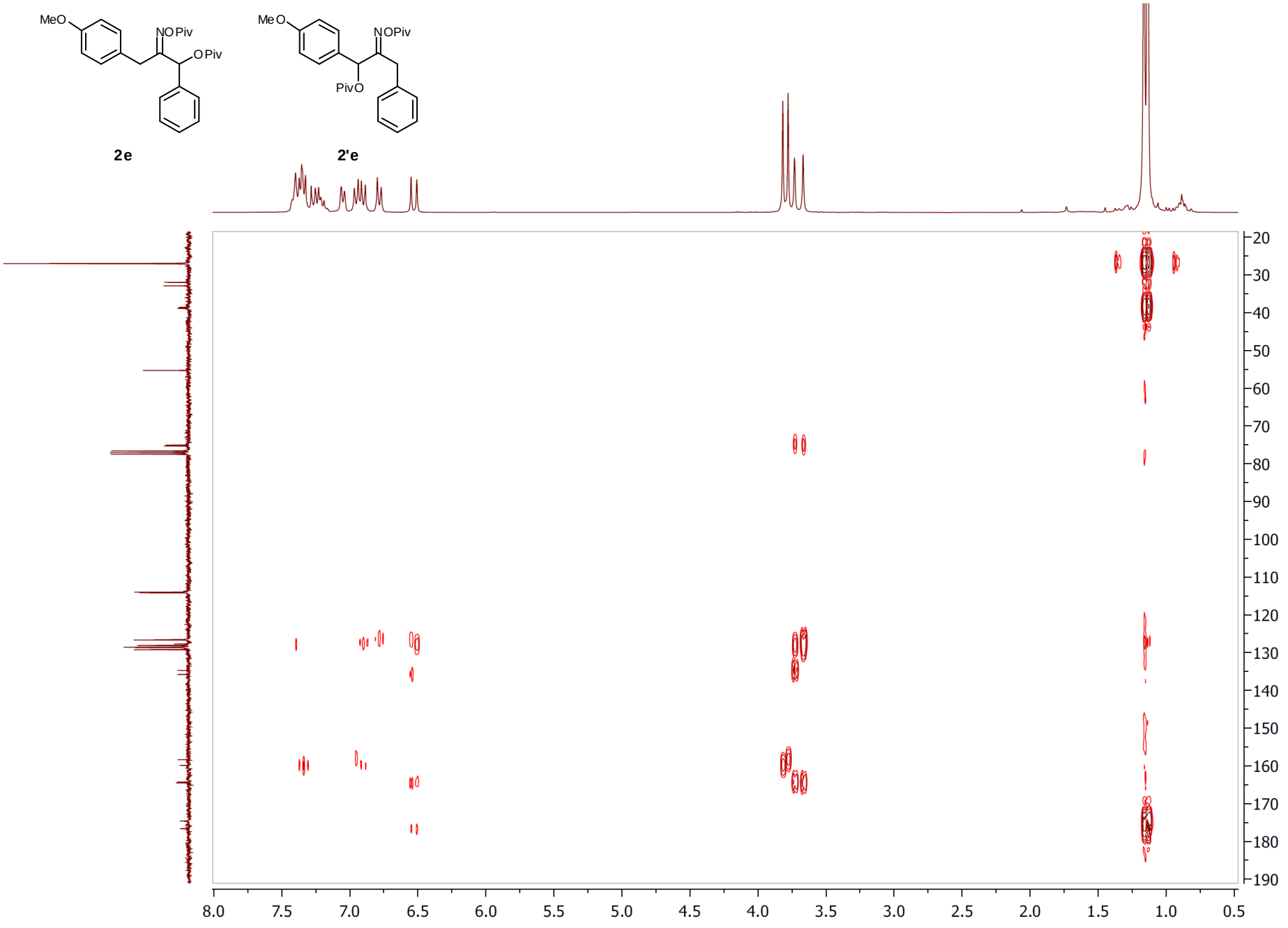
^{13}C NMR DEPT


MeO
NOPiv
OPiv
2e
MeO
NOPiv
PivO
2'e
129.24
128.71
128.58
128.18
128.09
126.66
114.18
114.01
75.32
75.07
55.30
32.89
31.98
27.06
27.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

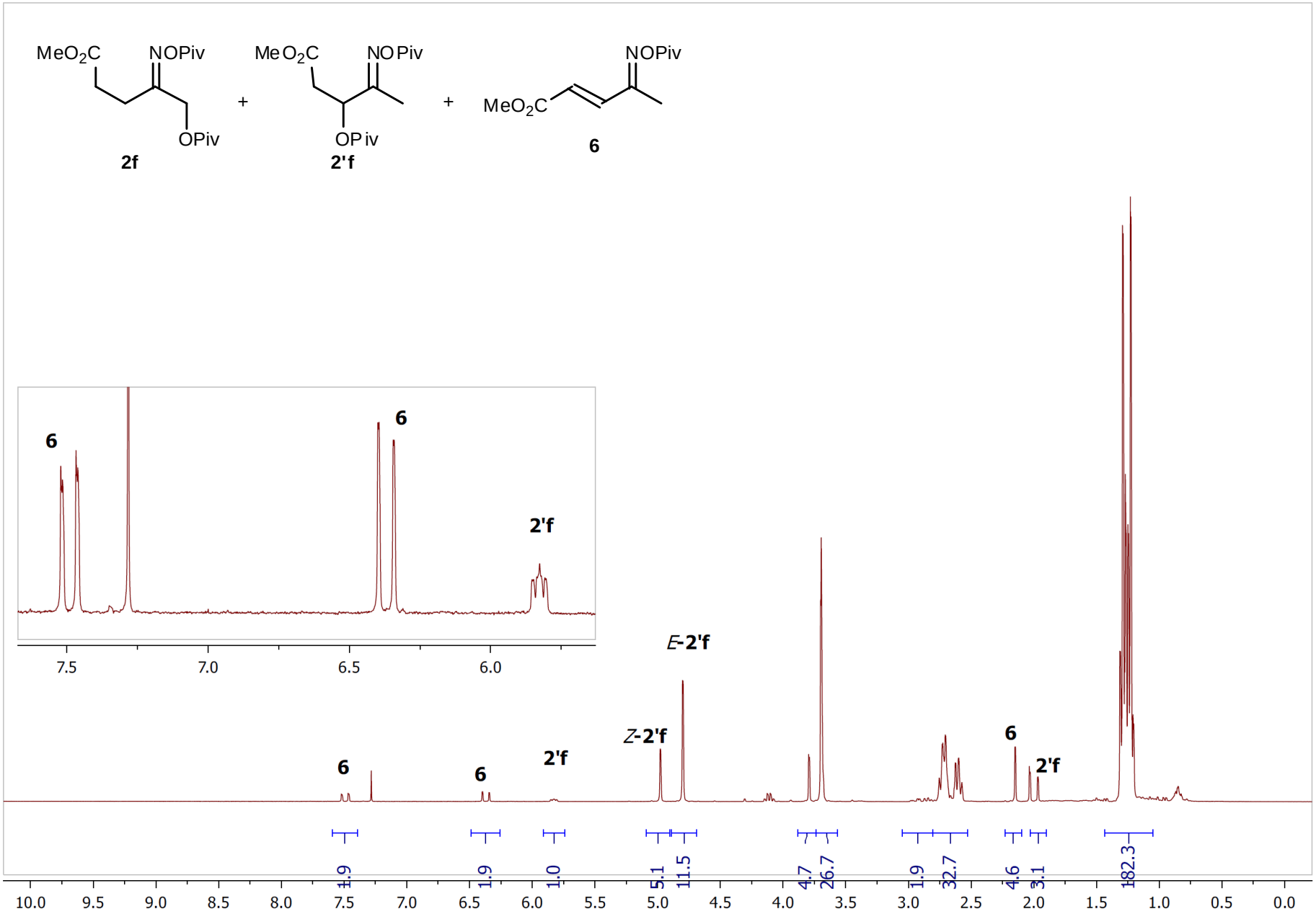

MeO
NOPiv
OPiv
2e
MeO
NOPiv
PivO
2'e
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

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

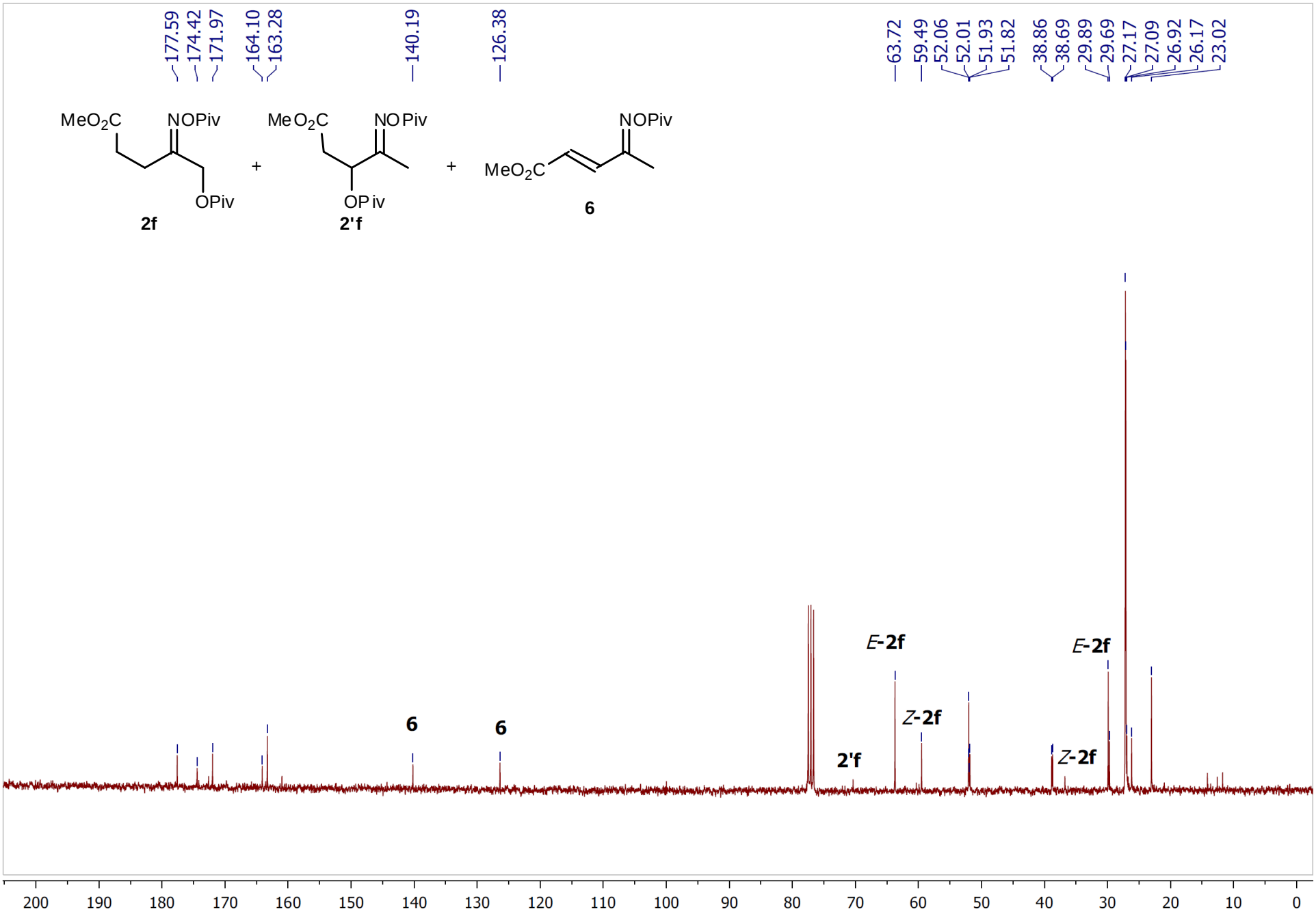

MeO
NOPiv
OPiv
2e
MeO
NOPiv
PivO
2'e
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Methyl 5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2f, Methyl 3-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2'f and **(2*E*)-Methyl 4-(pivaloyloxyimino)pent-2-enoate 6**

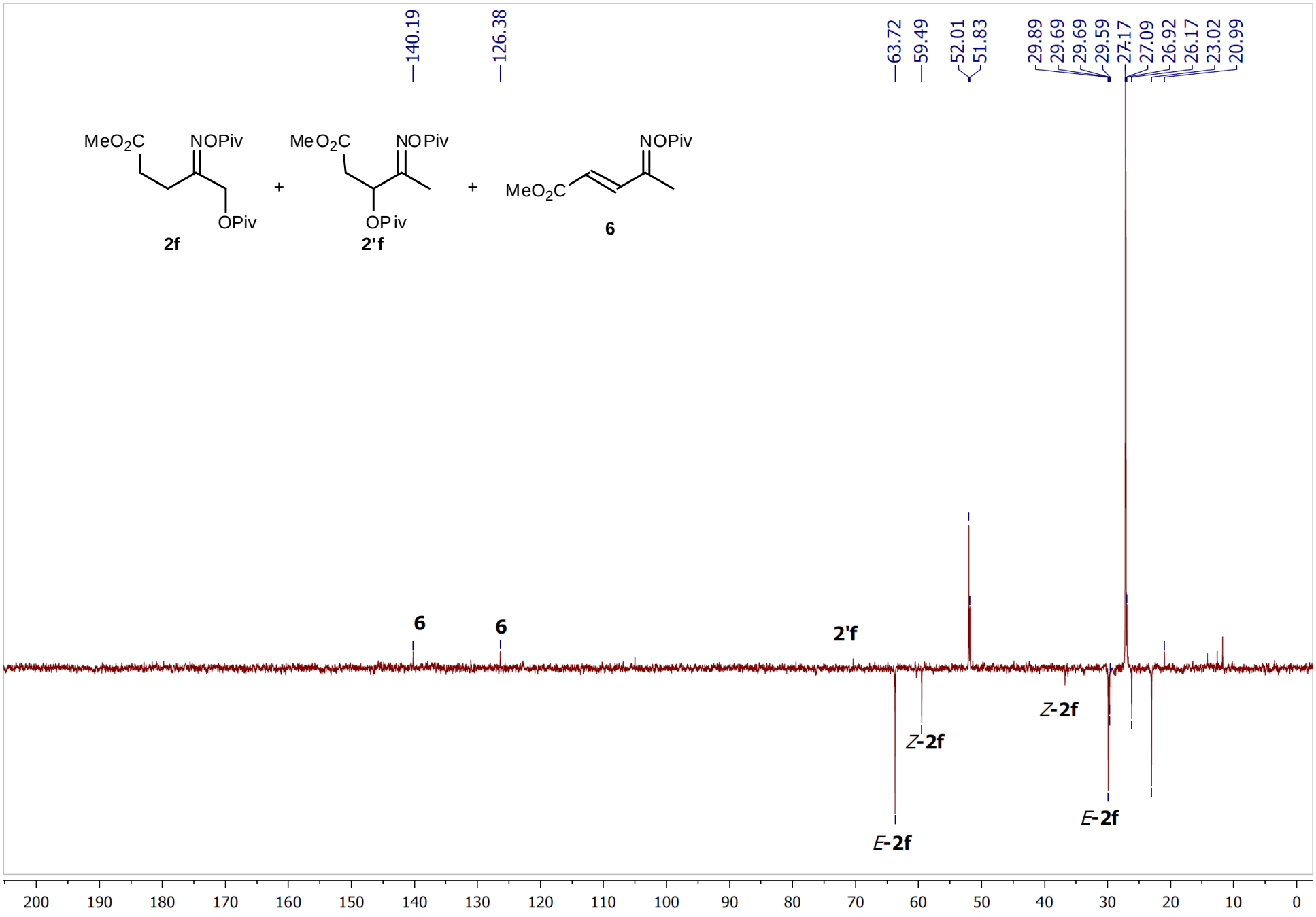
^{1}H NMR



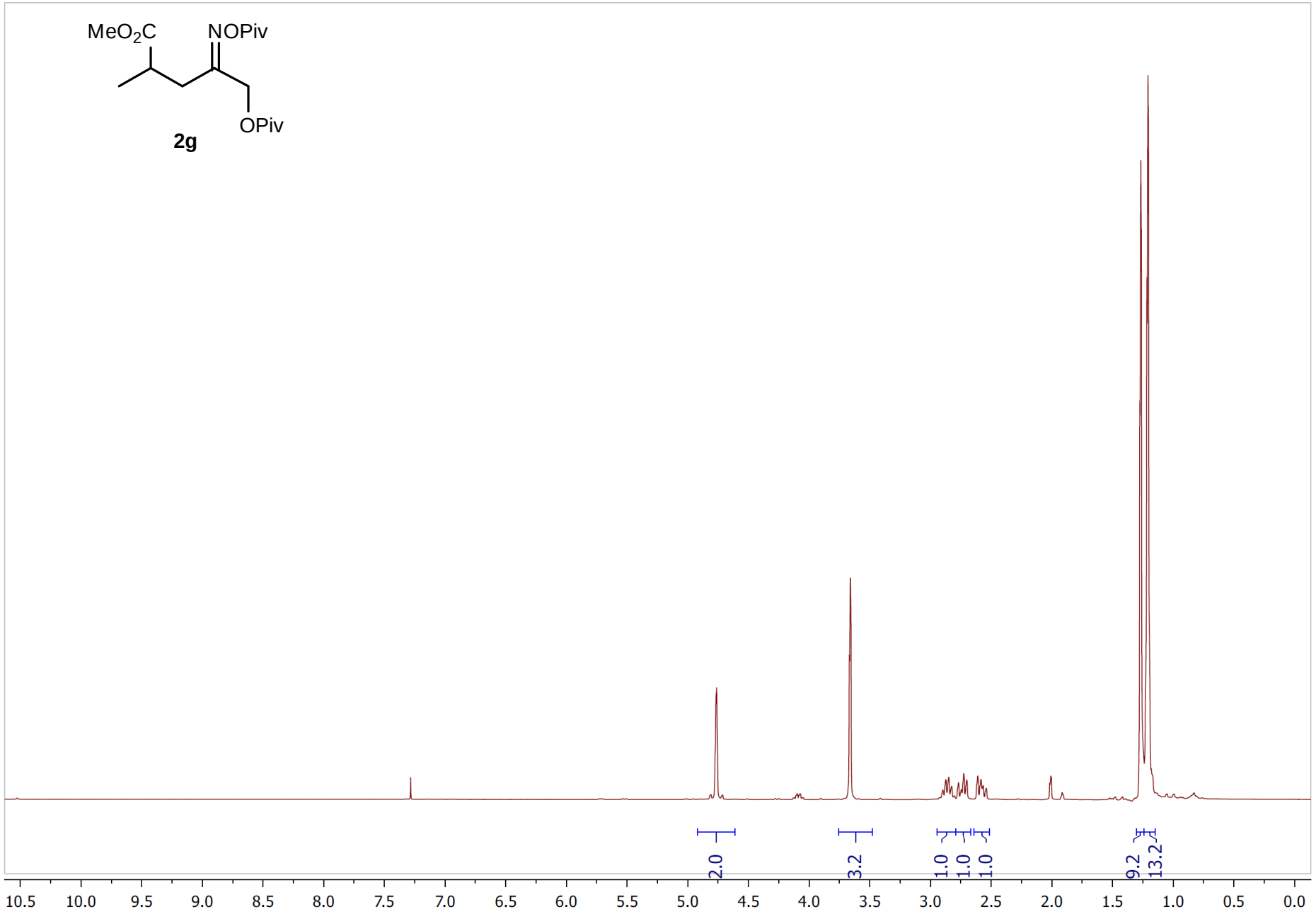
^{13}C NMR


177.59
174.42
171.97
164.10
163.28
140.19
126.38
63.72
59.49
52.06
52.01
51.93
51.82
38.86
38.69
29.89
29.69
27.17
27.09
26.92
26.17
23.02
MeO2C
NOPiv
OPiv
2f
+
MeO2C
NOPiv
OPiv
2'f
+
MeO2C
NOPiv
6
E-2f
Z-2f
2'f
6
6
E-2f
Z-2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

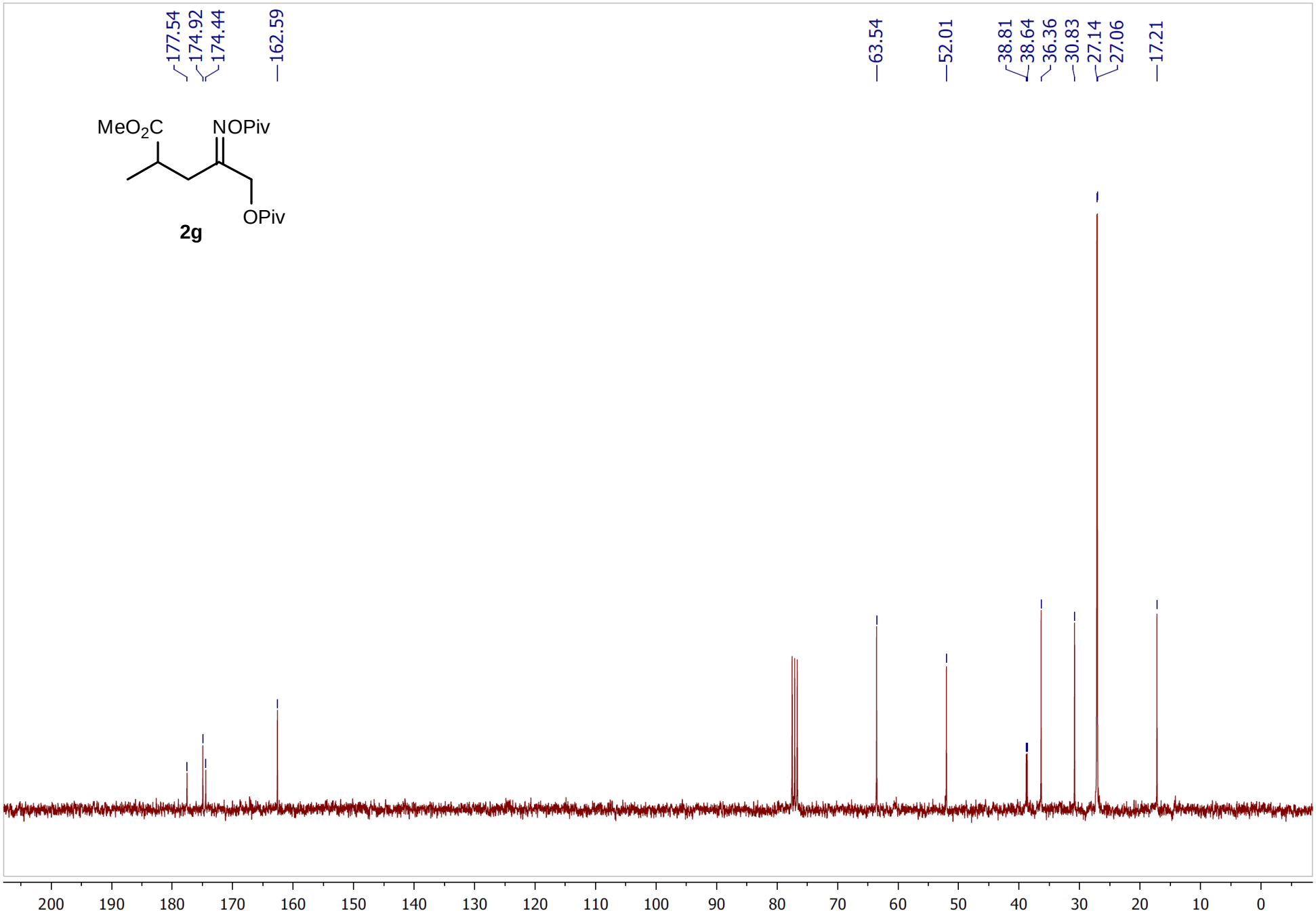
^{13}C NMR DEPT


140.19
126.38
63.72
59.49
52.01
51.83
29.89
29.69
29.69
29.59
27.17
27.09
26.92
26.17
23.02
20.99
MeO2C
NOPiv
OPiv
2f
+
MeO2C
NOPiv
OPiv
2'f
+
MeO2C
NOPiv
6
6
6
2'f
E-2f
Z-2f
Z-2f
E-2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

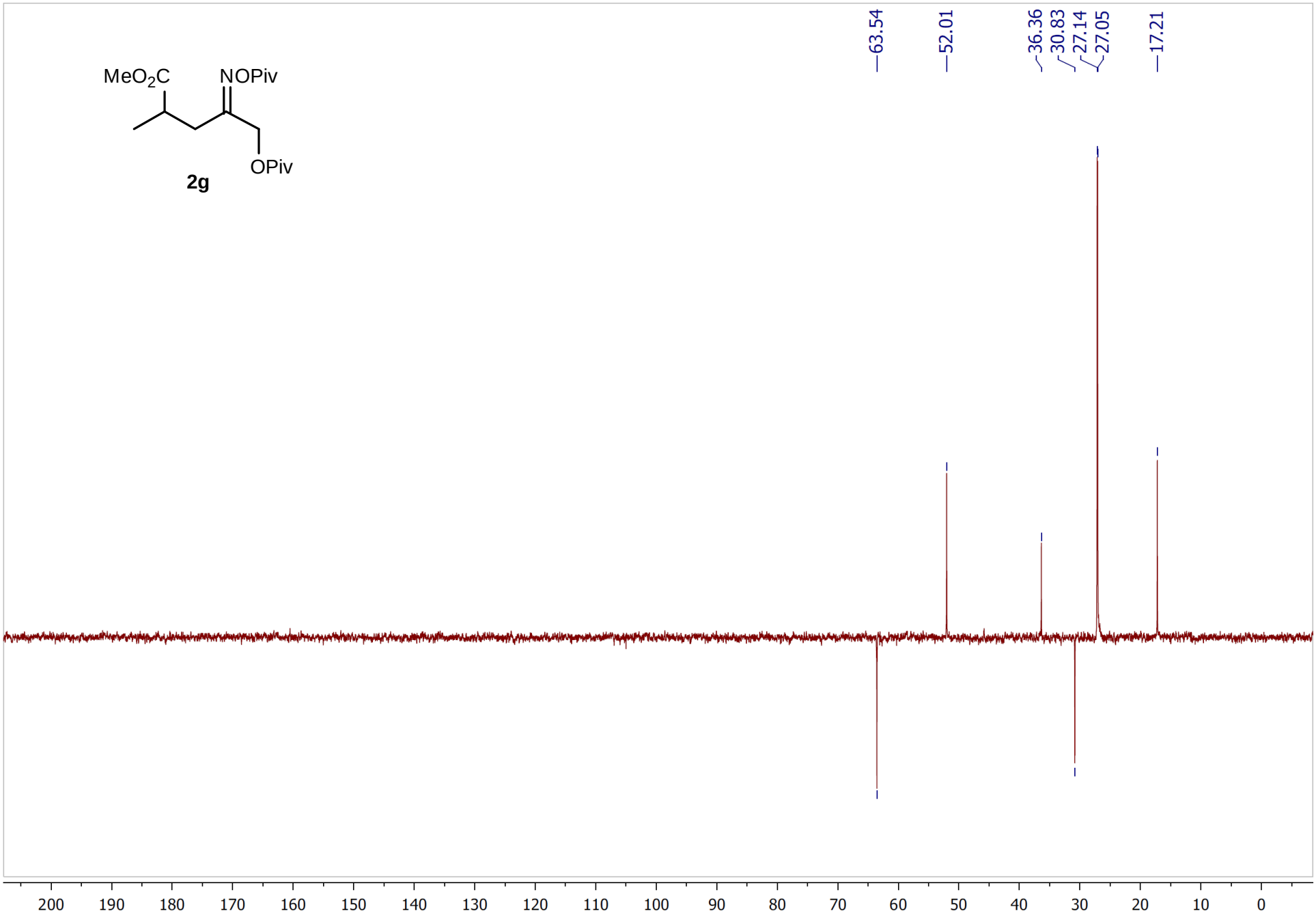
Methyl 2-methyl-5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2g, pure *E*-isomer
^{1}H NMR



^{13}C NMR

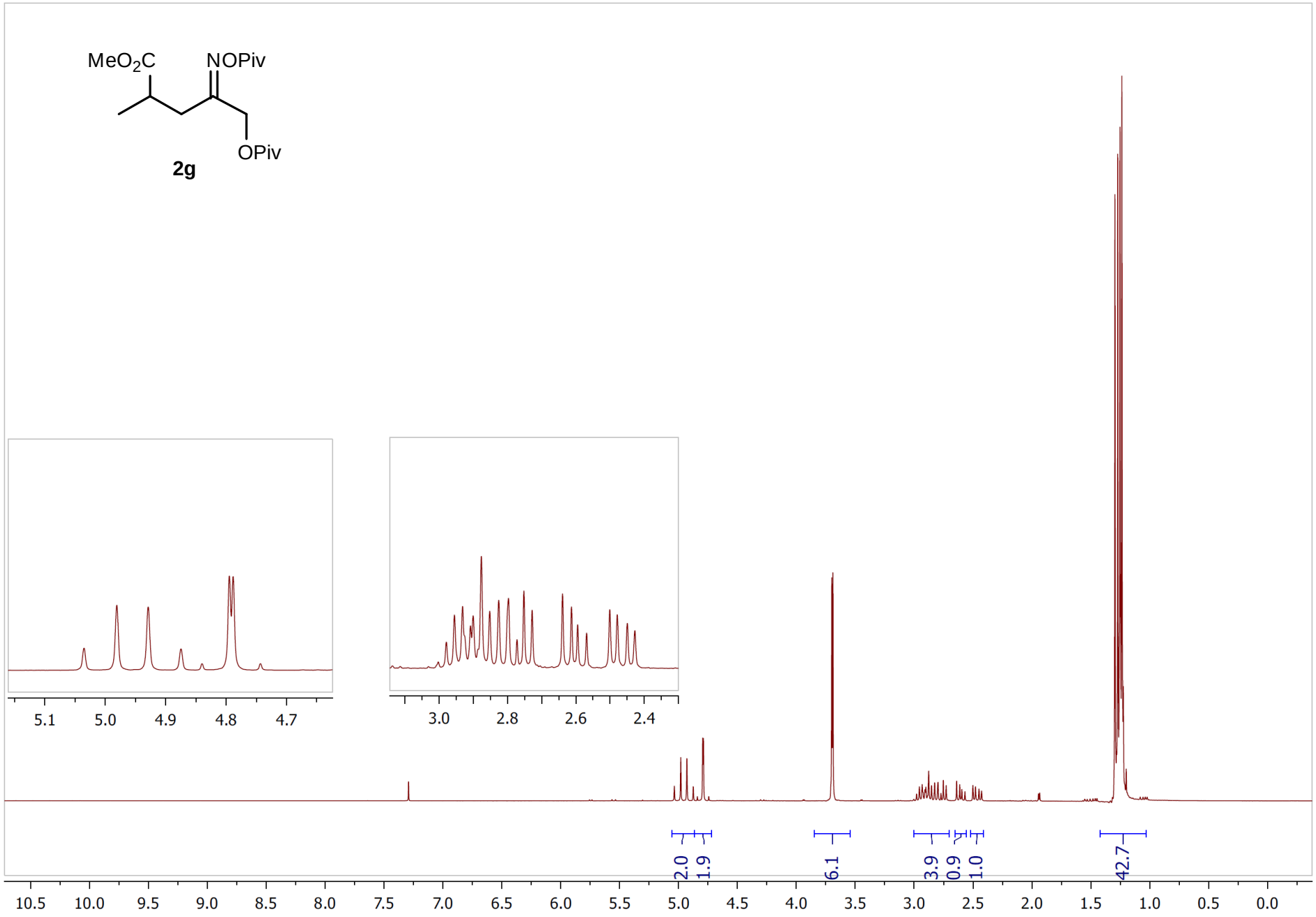

177.54
174.92
174.44
162.59
63.54
52.01
38.81
38.64
36.36
30.83
27.14
27.06
17.21
MeO2C
NOPiv
OPiv
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

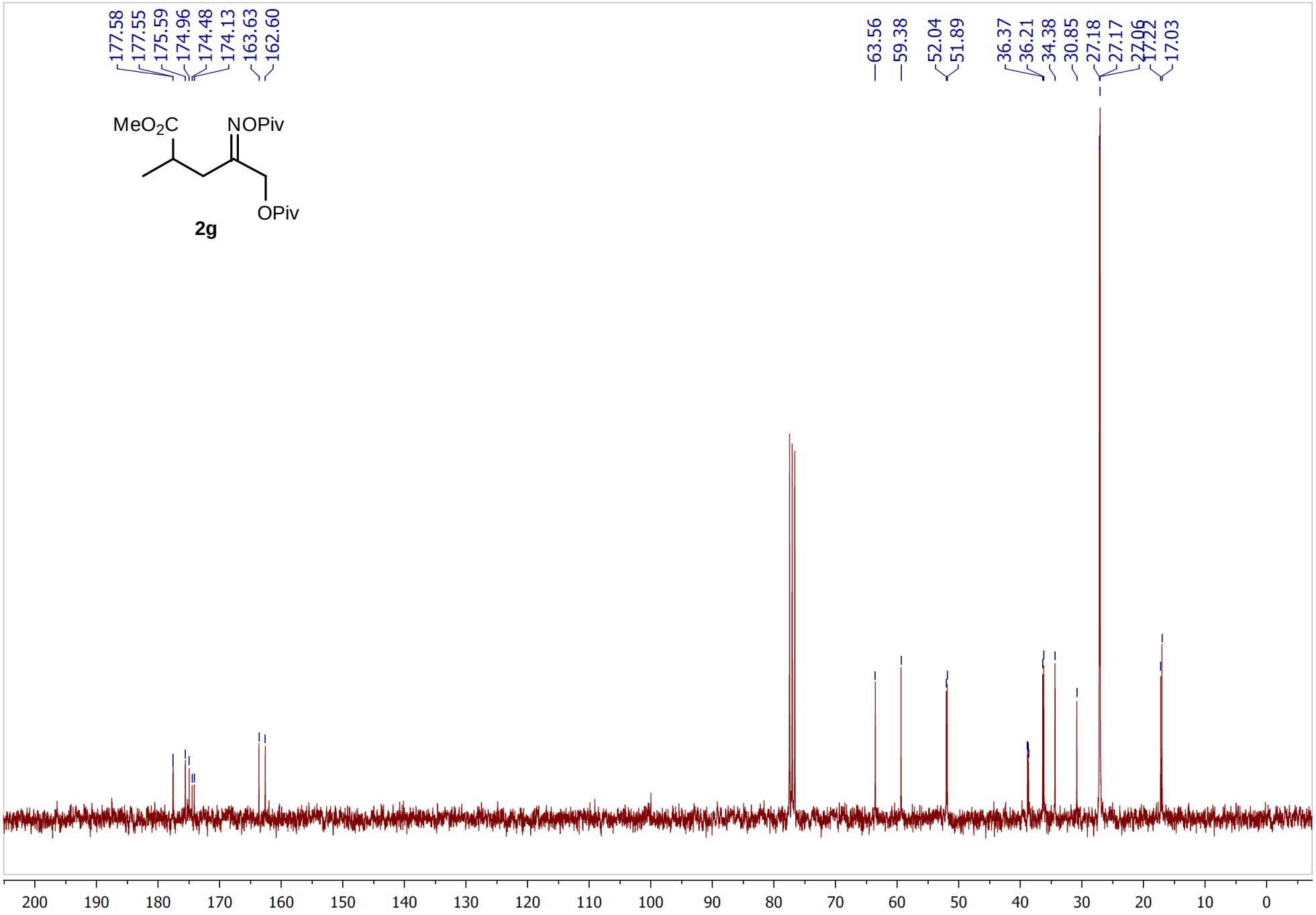

MeO2C
NOPiv
OPiv
2g
63.54
52.01
36.36
30.83
27.14
27.05
17.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Methyl 2-methyl-5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2g, *E*,*Z*-isomeric mixture

^{1}H NMR



^{13}C NMR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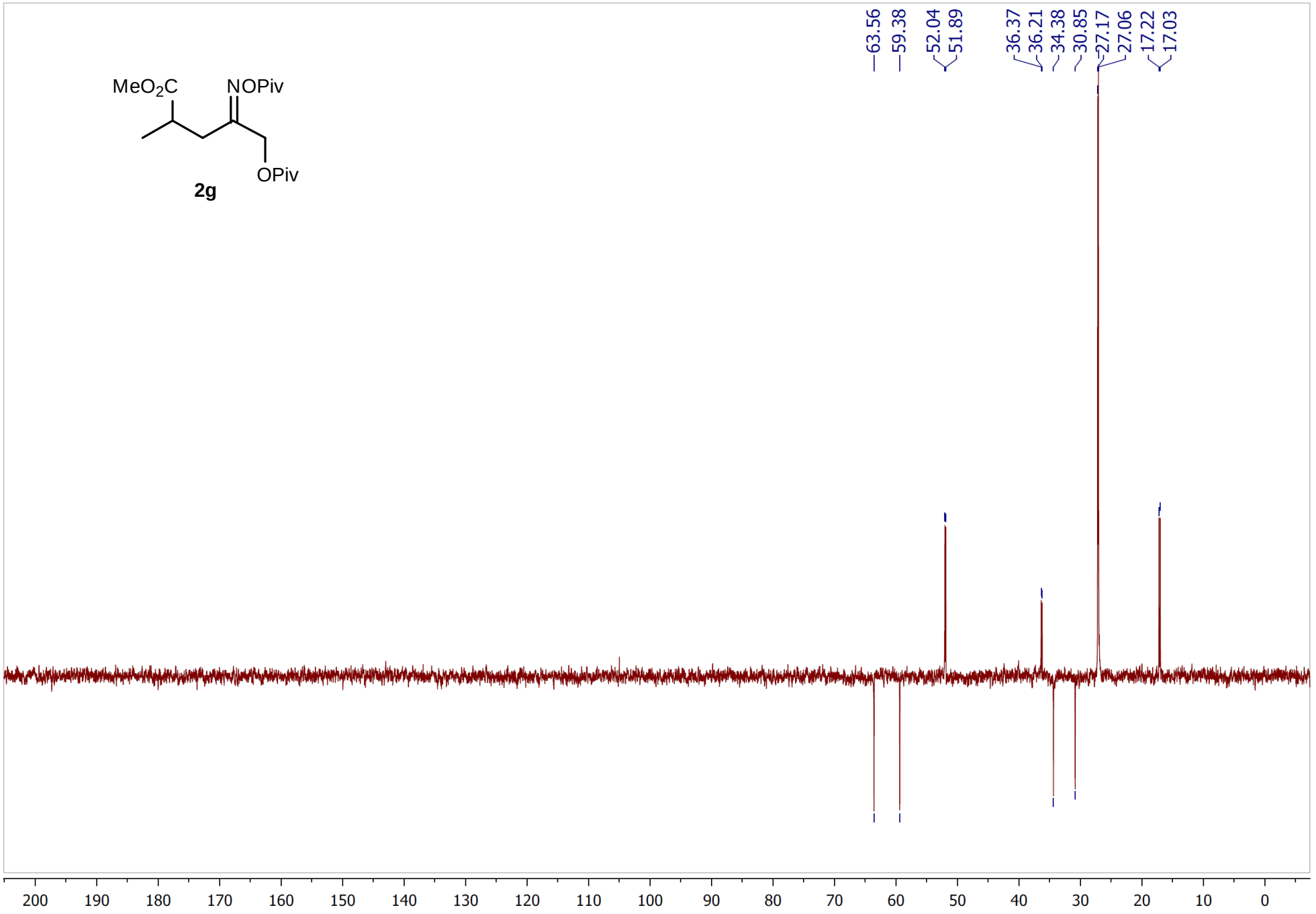
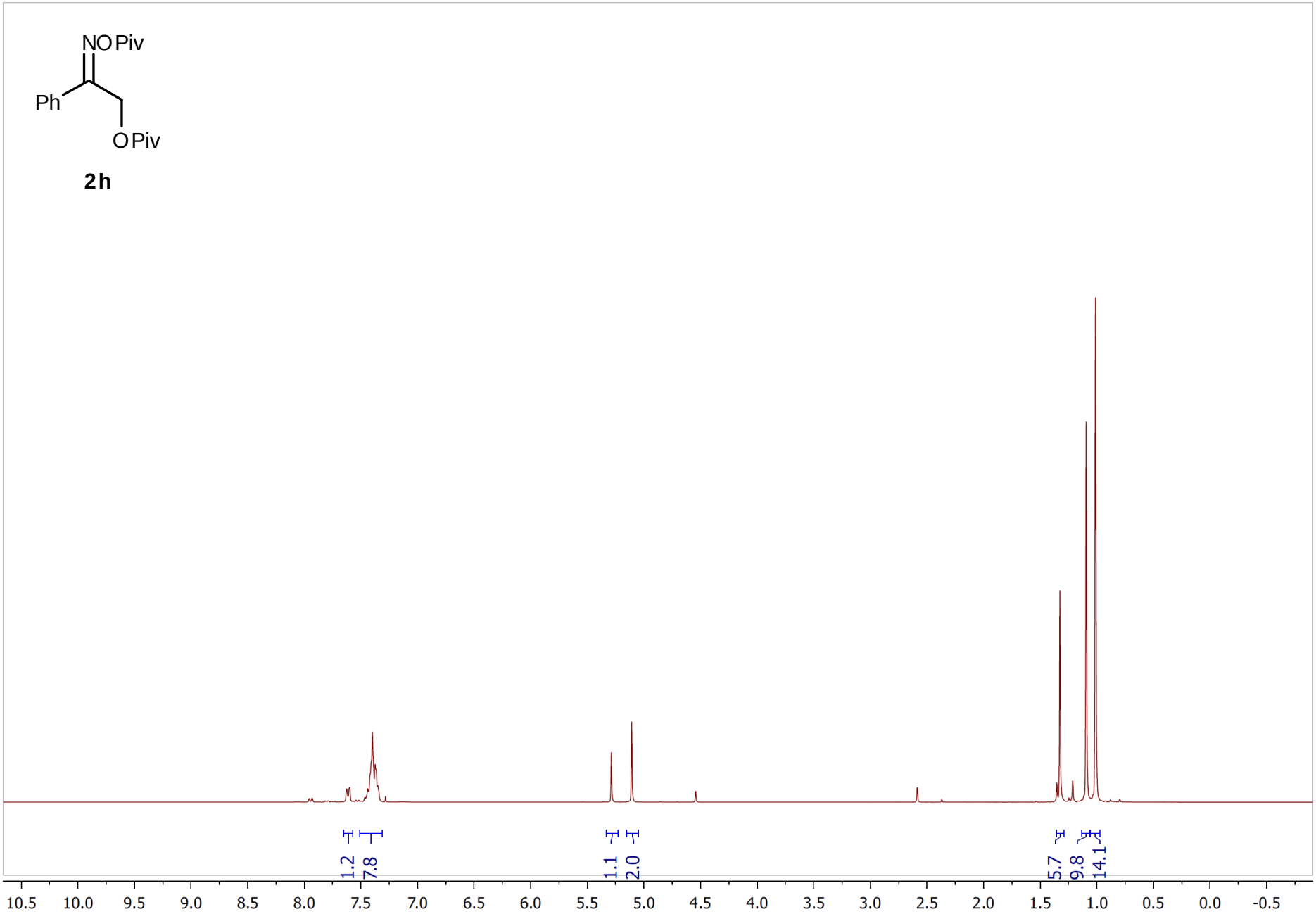
175.59
174.96
174.48
174.13
163.63
162.60
63.56
59.38
52.04
51.89
36.37
36.21
34.38
30.85
27.18
27.17
27.06
17.22
17.03
MeO2C
NOPiv
OPiv
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

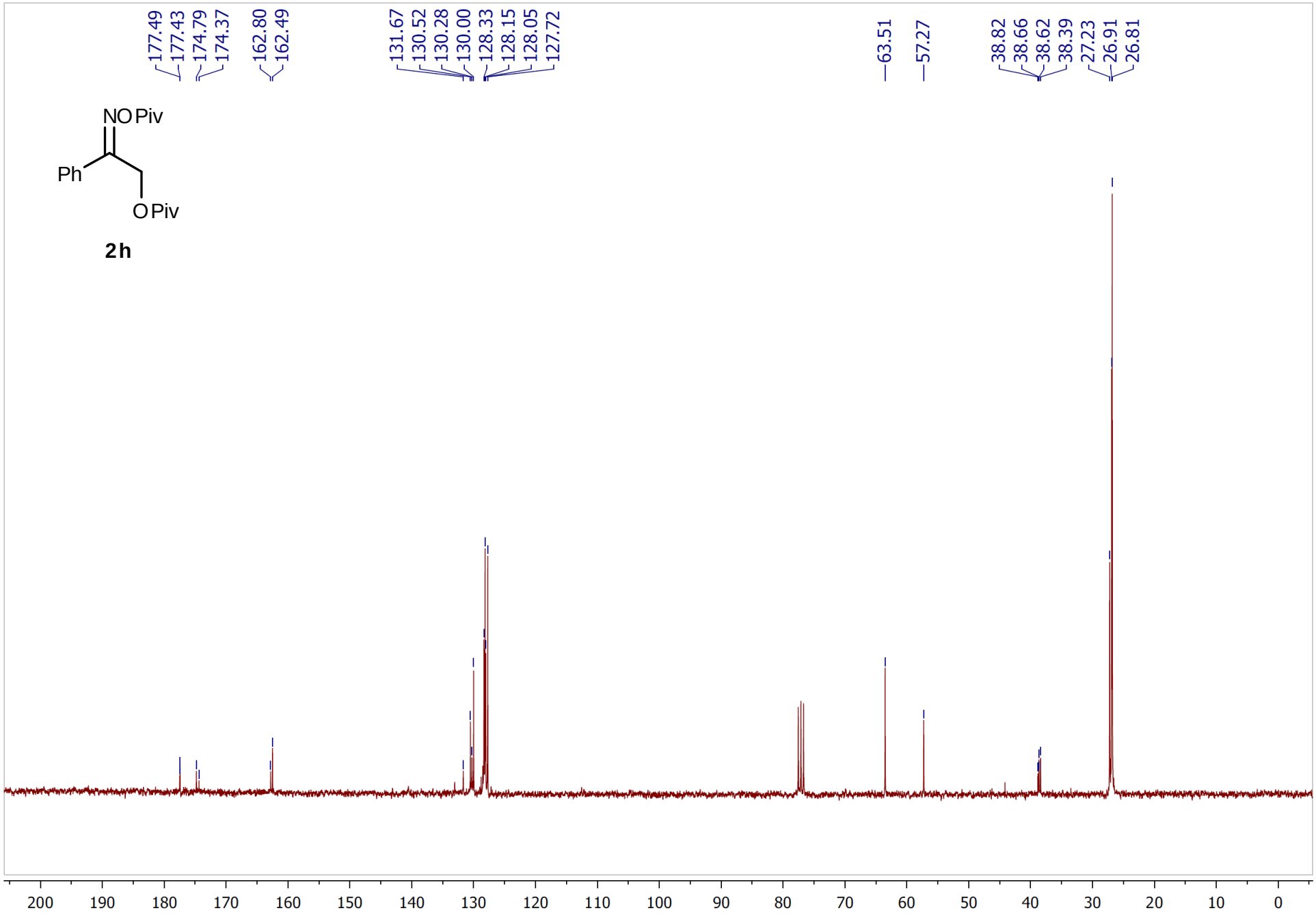

63.56
59.38
52.04
51.89
36.37
36.21
34.38
30.85
27.17
27.06
17.22
17.03
MeO2C
NOPiv
OPiv
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2-Phenyl-2-(pivaloyloxyimino)ethyl pivalate 2h

^{1}H NMR



^{13}C NMR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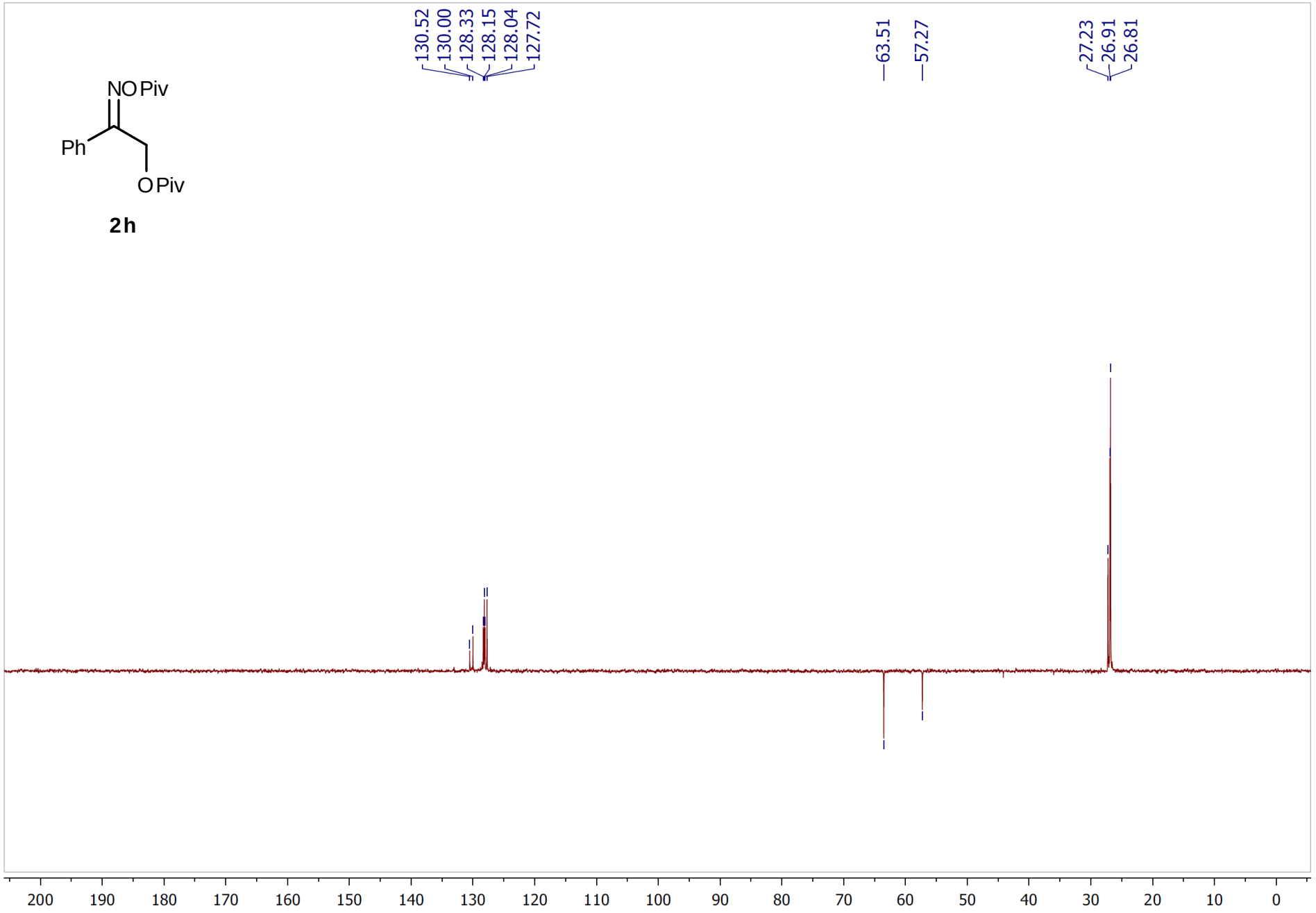
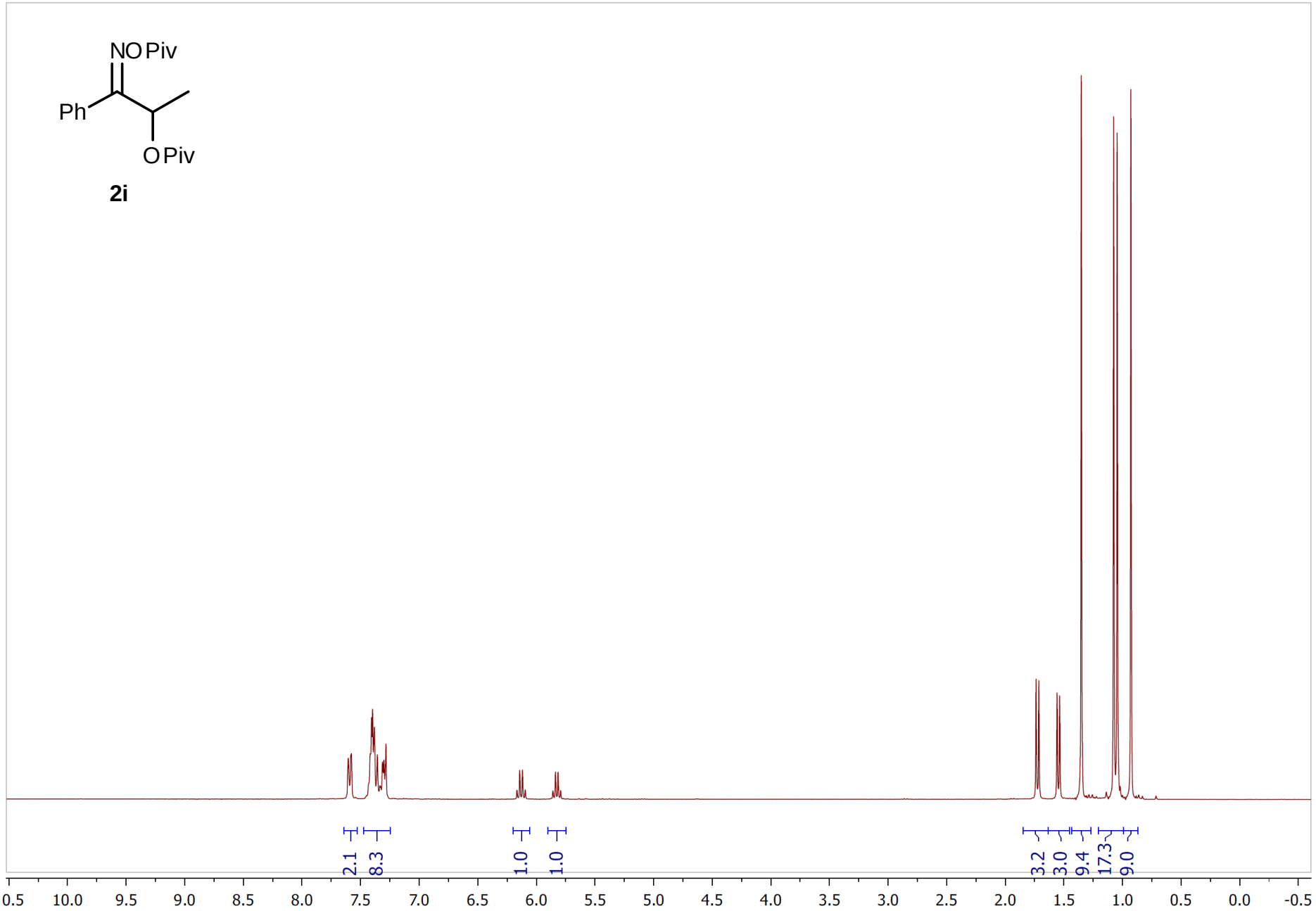
130.00
128.33
128.15
128.05
127.72
63.51
57.27
38.82
38.66
38.62
38.39
27.23
26.91
26.81
NO Piv
Ph
O Piv
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

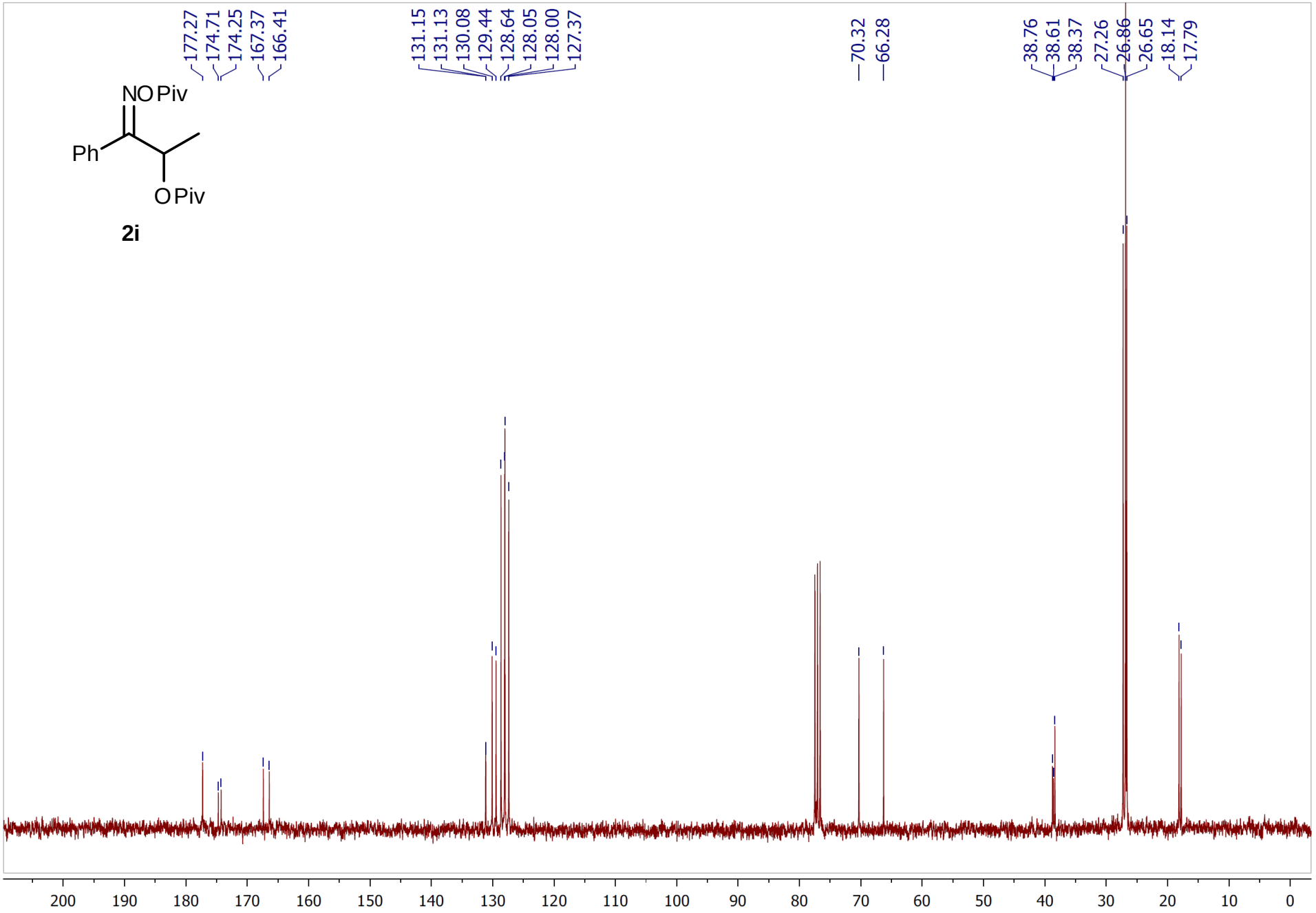

130.52
130.00
128.33
128.15
128.04
127.72
63.51
57.27
27.23
26.91
26.81
NO Piv
Ph
O Piv
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1-Phenyl-1-(pivaloyloxyimino)propan-2-yl pivalate 2i

^{1}H NMR



^{13}C NMR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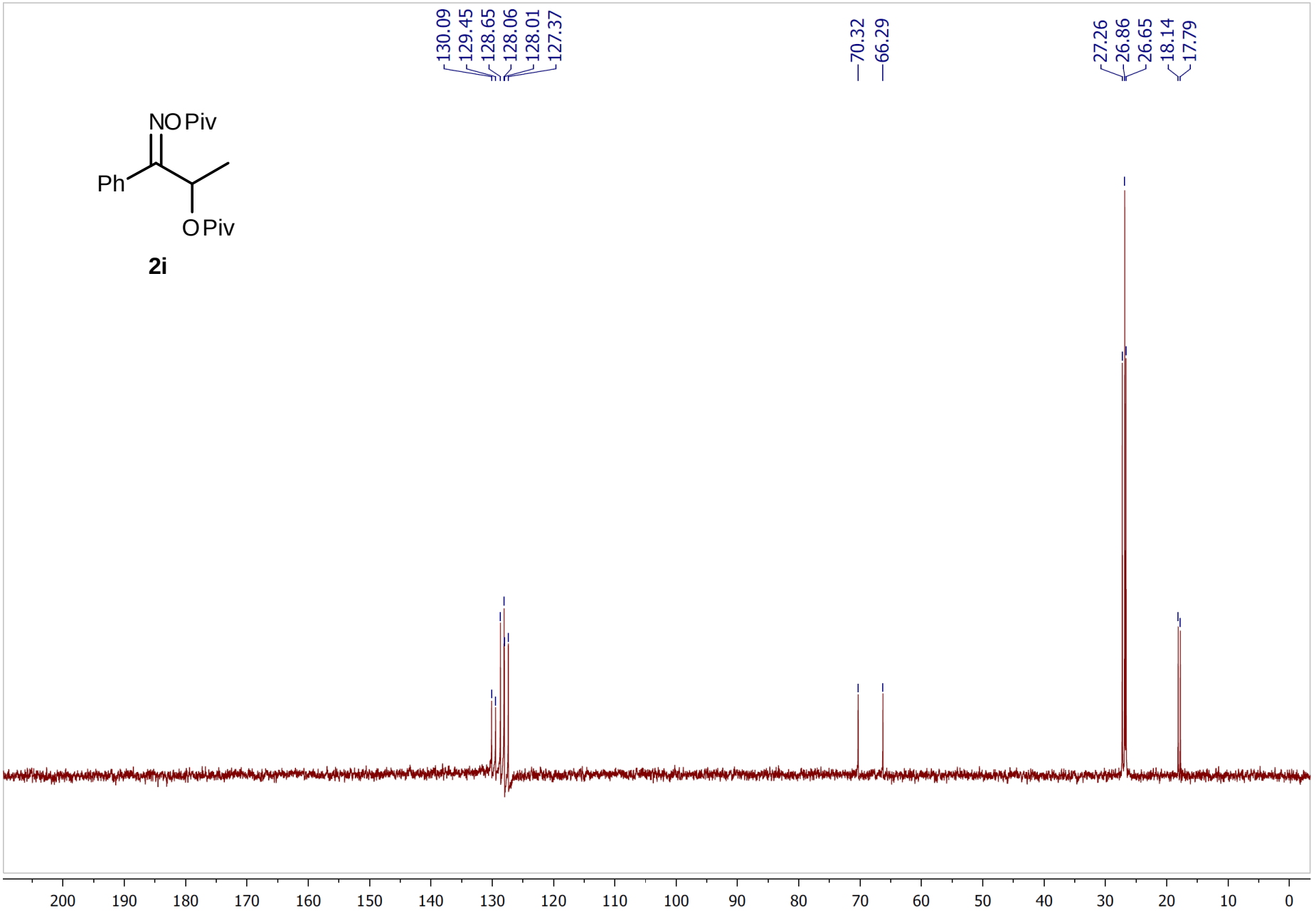
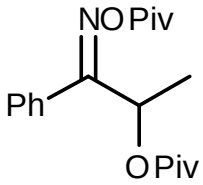
167.37
166.41
131.15
131.13
130.08
129.44
128.64
128.05
128.00
127.37
70.32
66.28
38.76
38.61
38.37
27.26
26.86
26.65
18.14
17.79
NO Piv
Ph
O Piv
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT


130.09
129.45
128.65
128.06
128.01
127.37
70.32
66.29
27.26
26.86
26.65
18.14
17.79
NO Piv
Ph
O Piv
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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


NOPiv
Ph
OPiv

2i

1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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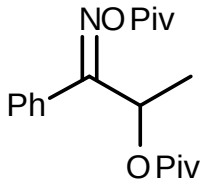
3.5
3.0
2.5
2.0
1.5
1.0
0.5

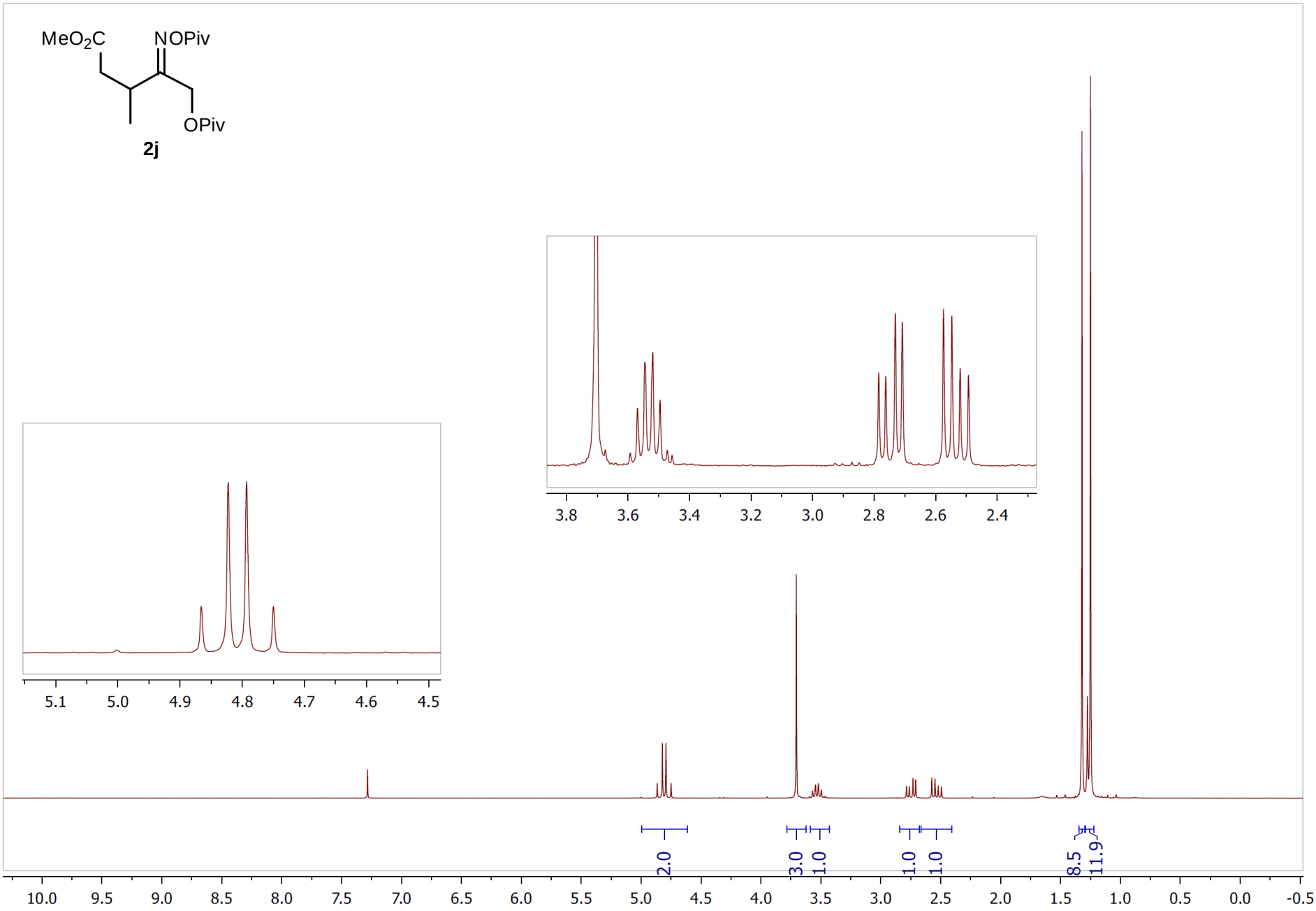
^{1}H-^{13}C HSQC



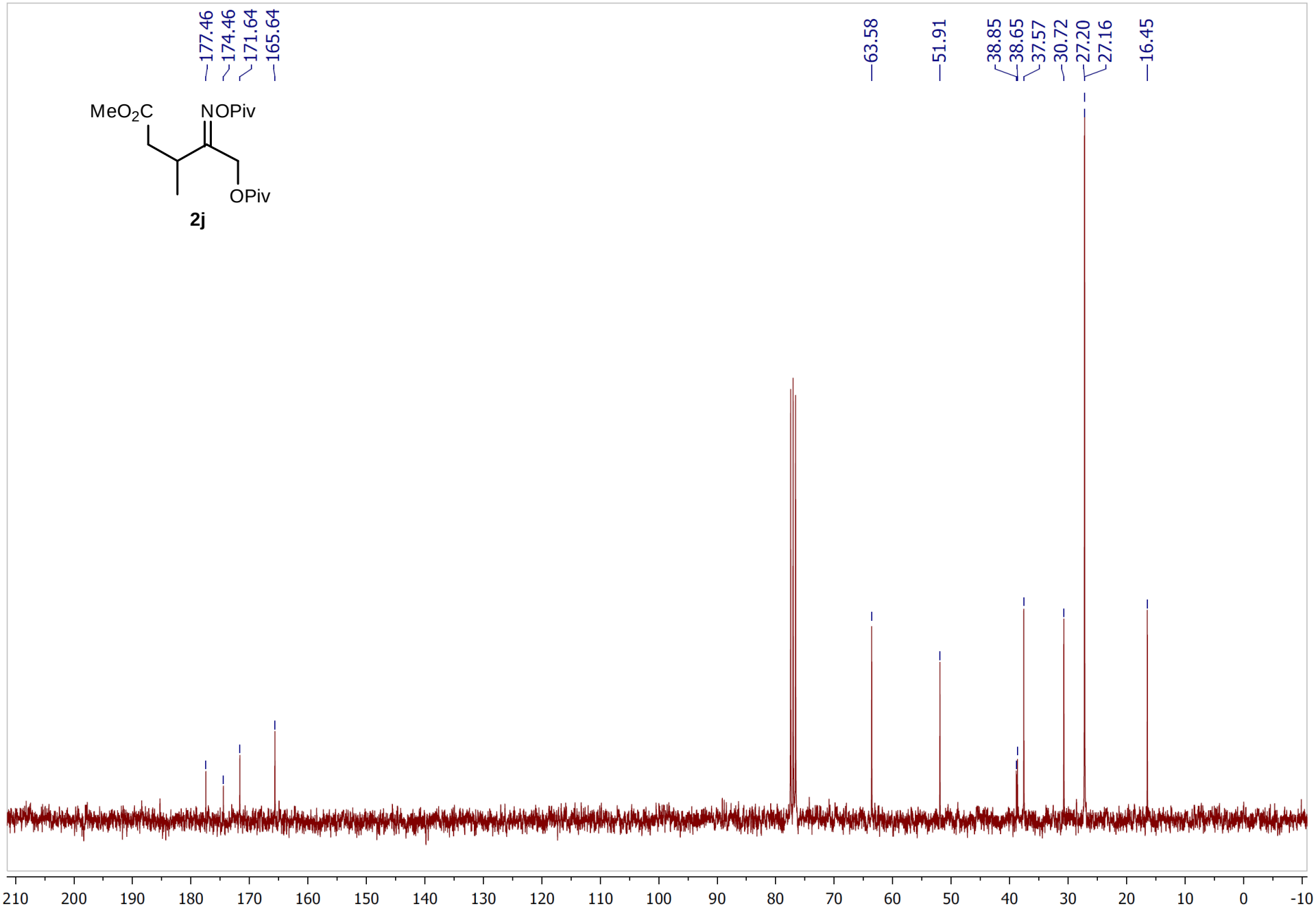
2i

Methyl 3-methyl-5-(pivaloyloxy)-4-(pivaloyloxyimino)pentanoate 2j

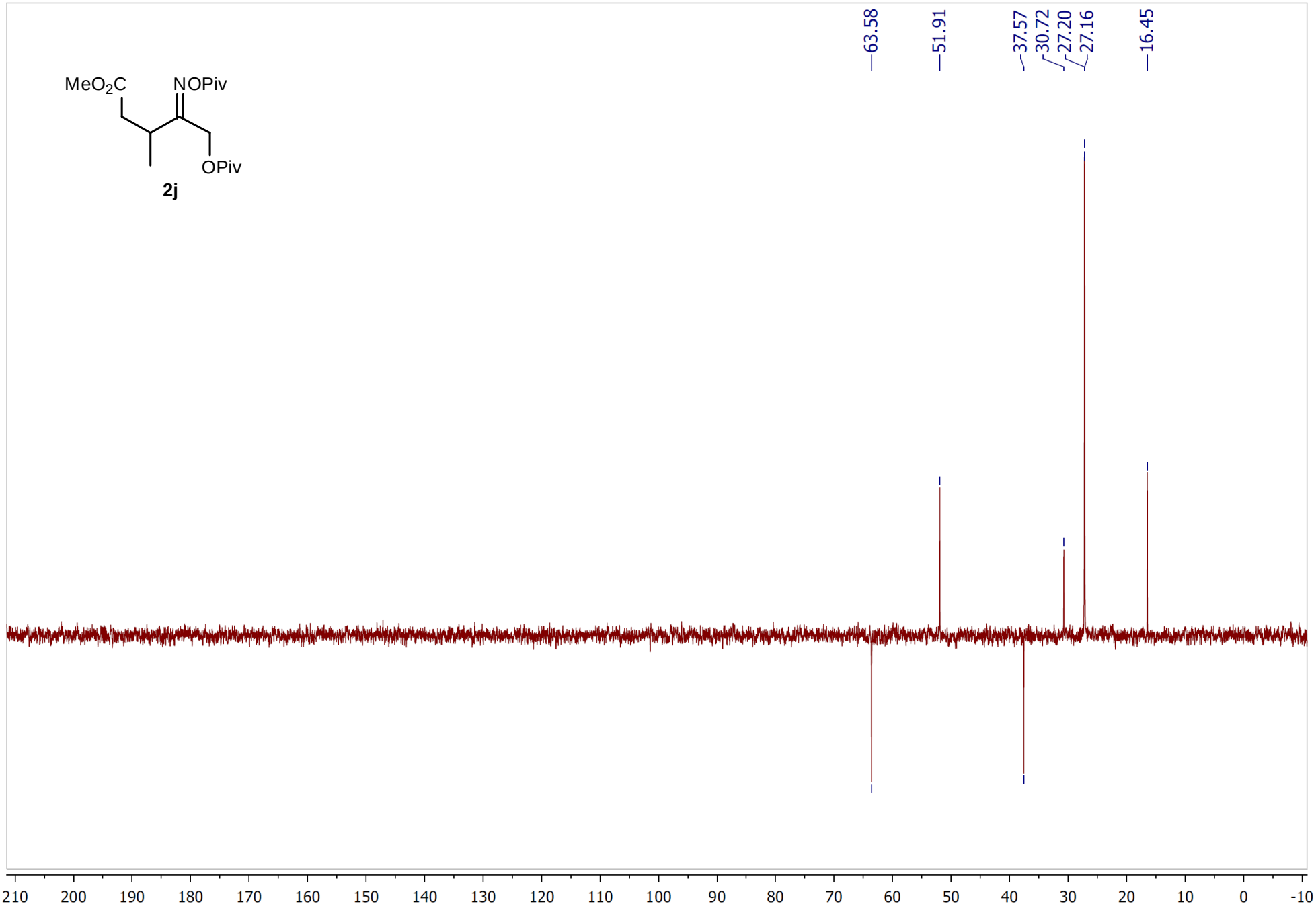
^{1}H NMR



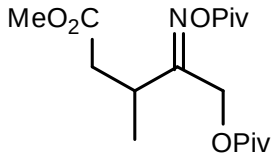
^{13}C NMR


177.46
174.46
171.64
165.64
63.58
51.91
38.85
38.65
37.57
30.72
27.20
27.16
16.45
MeO2C
NOPiv
OPiv
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT


63.58
51.91
37.57
30.72
27.20
27.16
16.45
MeO2C
NOPiv
OPiv
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

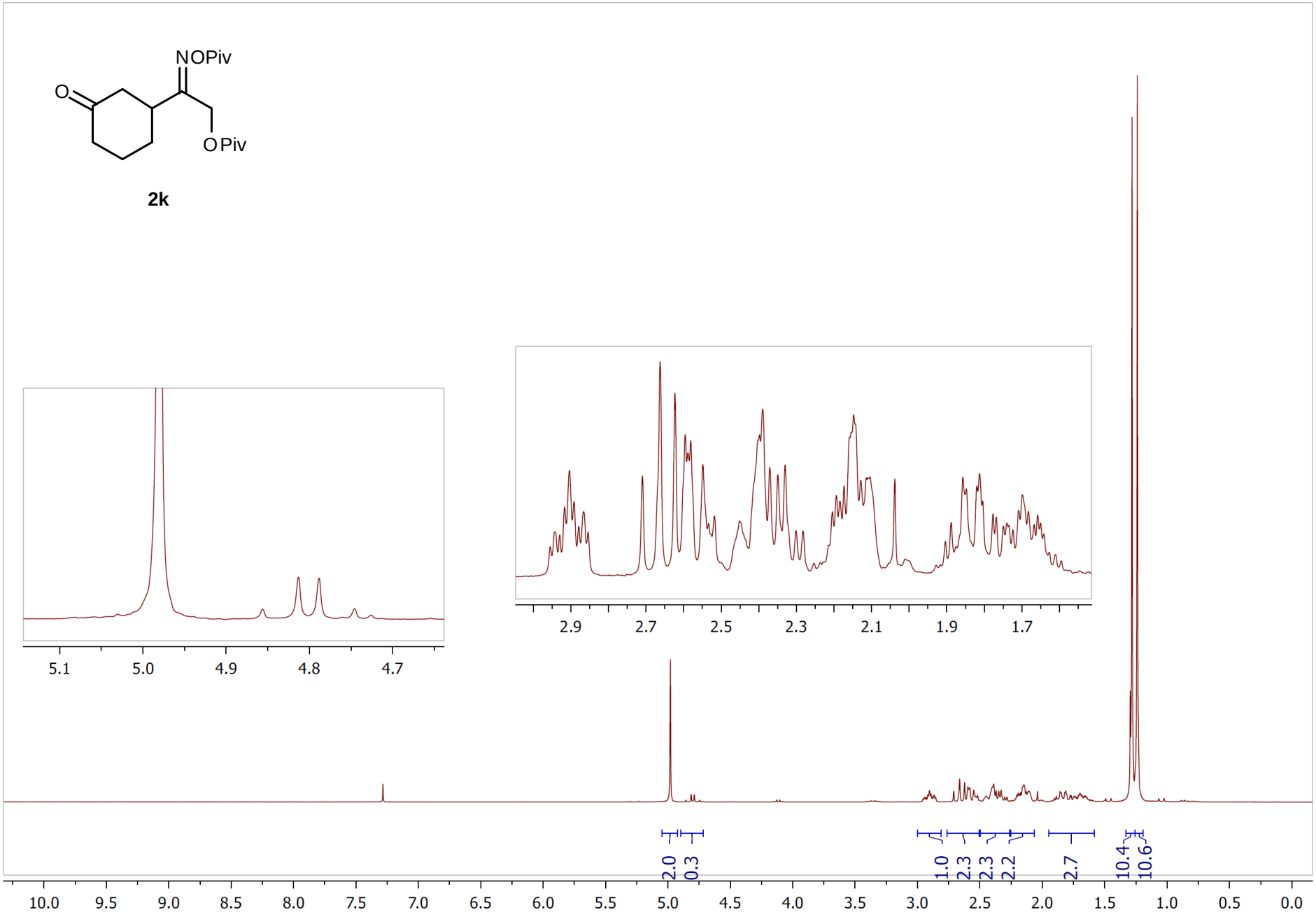
^{1}H-^{13}C HMBC



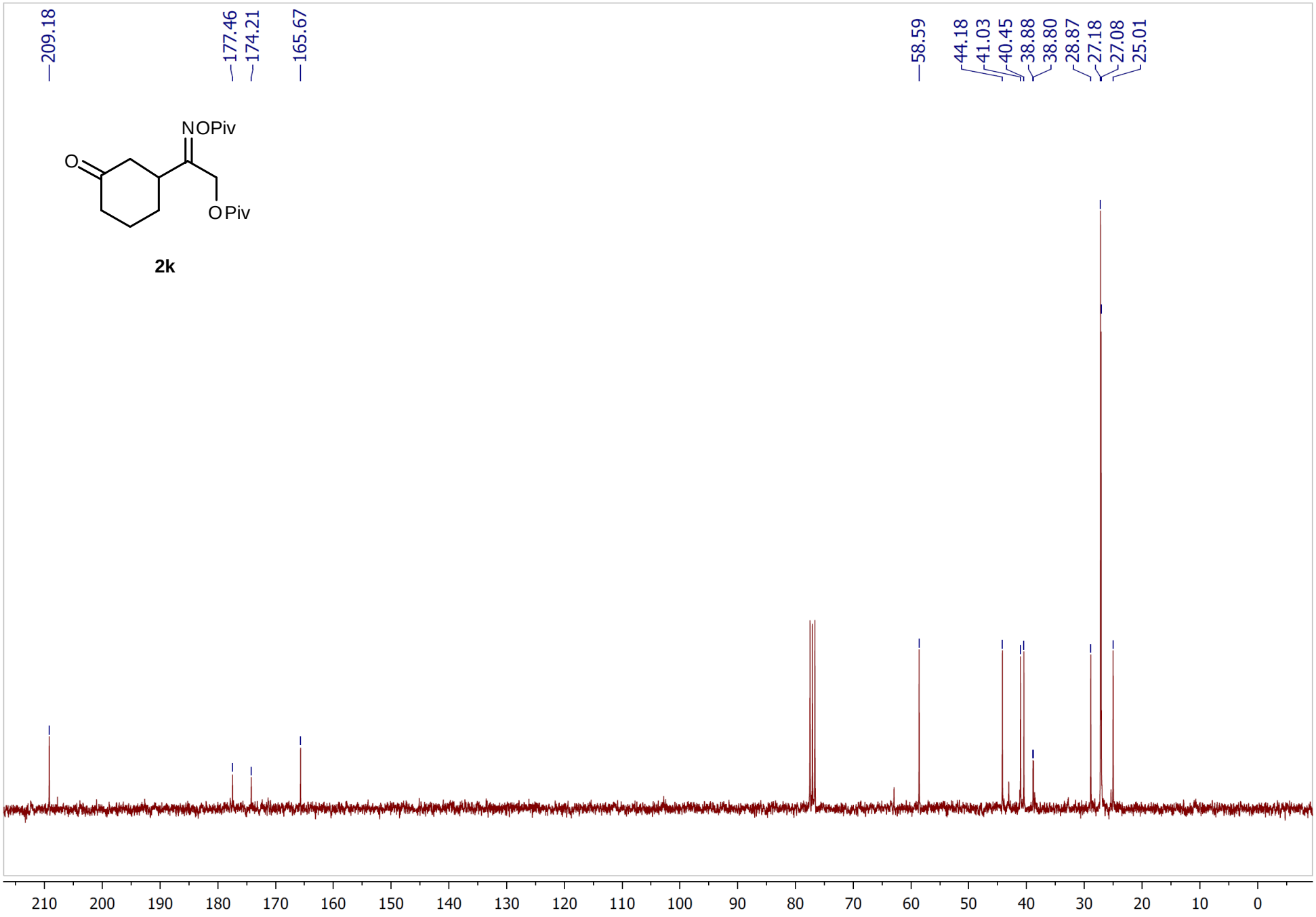
2j

2-(3-Oxocyclohexyl)-2-(pivaloyloxyimino)ethyl pivalate 2k

^{1}H NMR



^{13}C NMR


209.18
177.46
174.21
165.67
58.59
44.18
41.03
40.45
38.88
38.80
28.87
27.18
27.08
25.01
NOPiv
O
OPiv
2k
210
200
190
180
170
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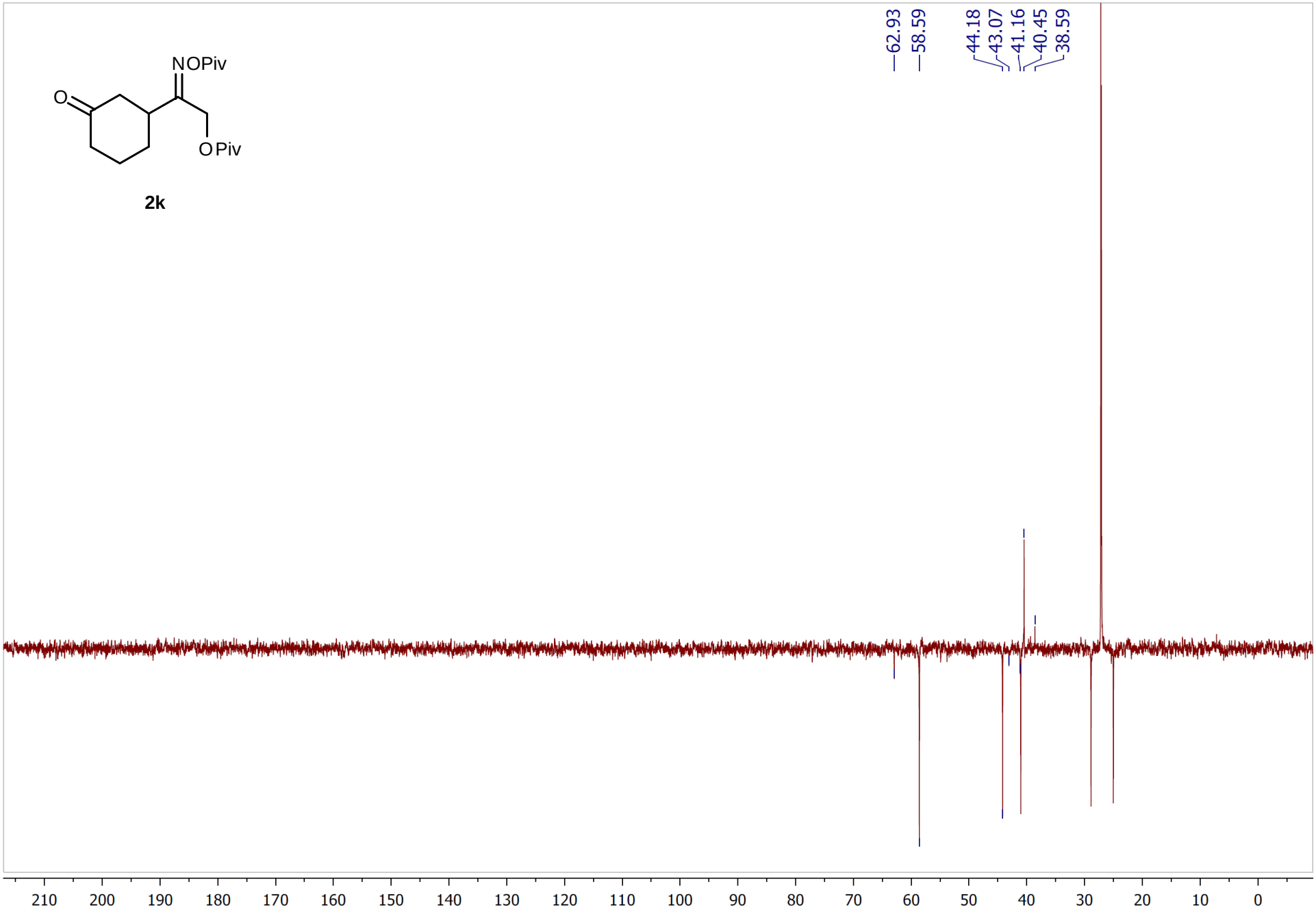
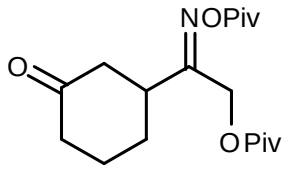
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT


NOPiv
O
OPiv
2k
62.93
58.59
44.18
43.07
41.16
40.45
38.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

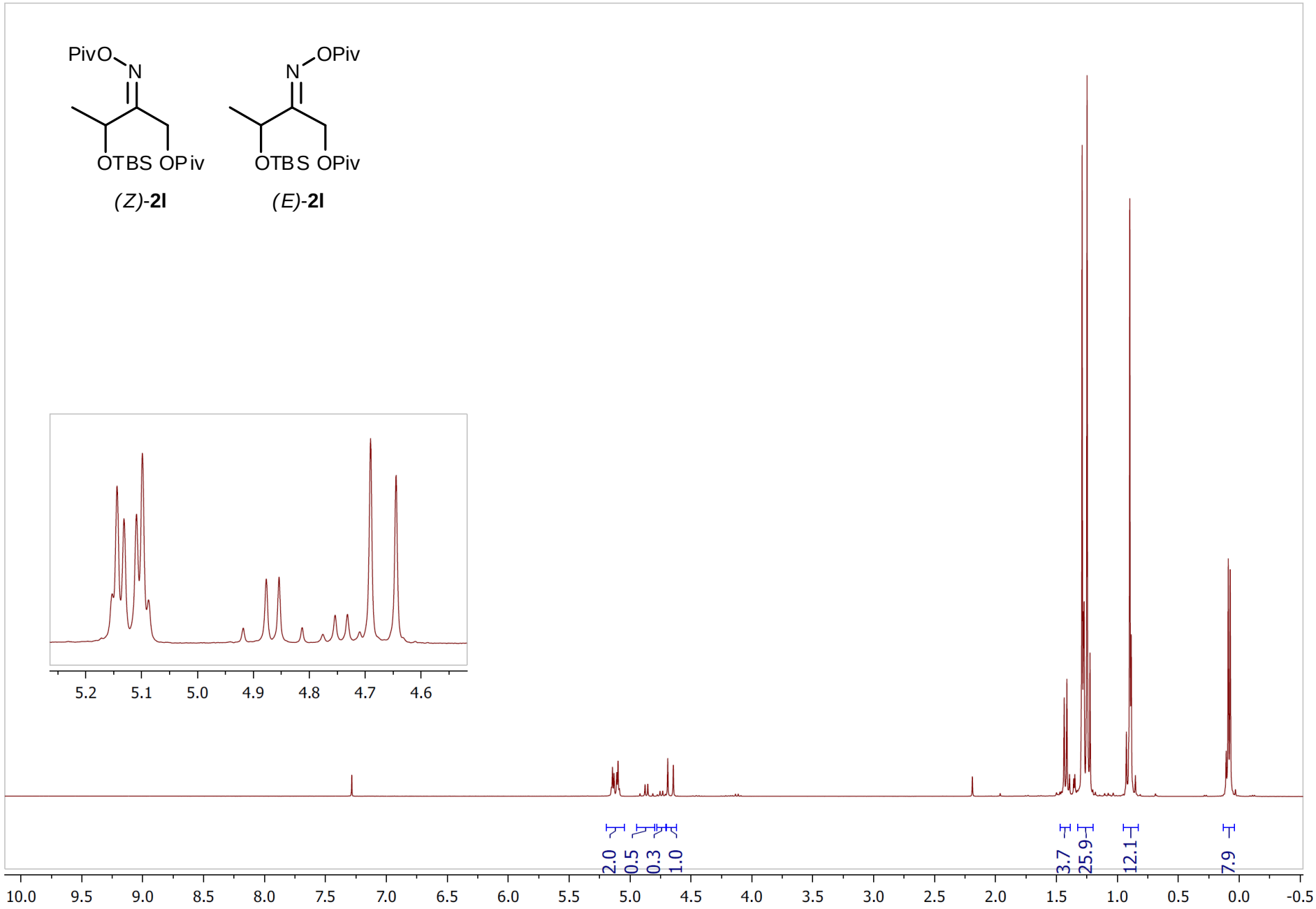
^{1}H-^{13}C HSQC



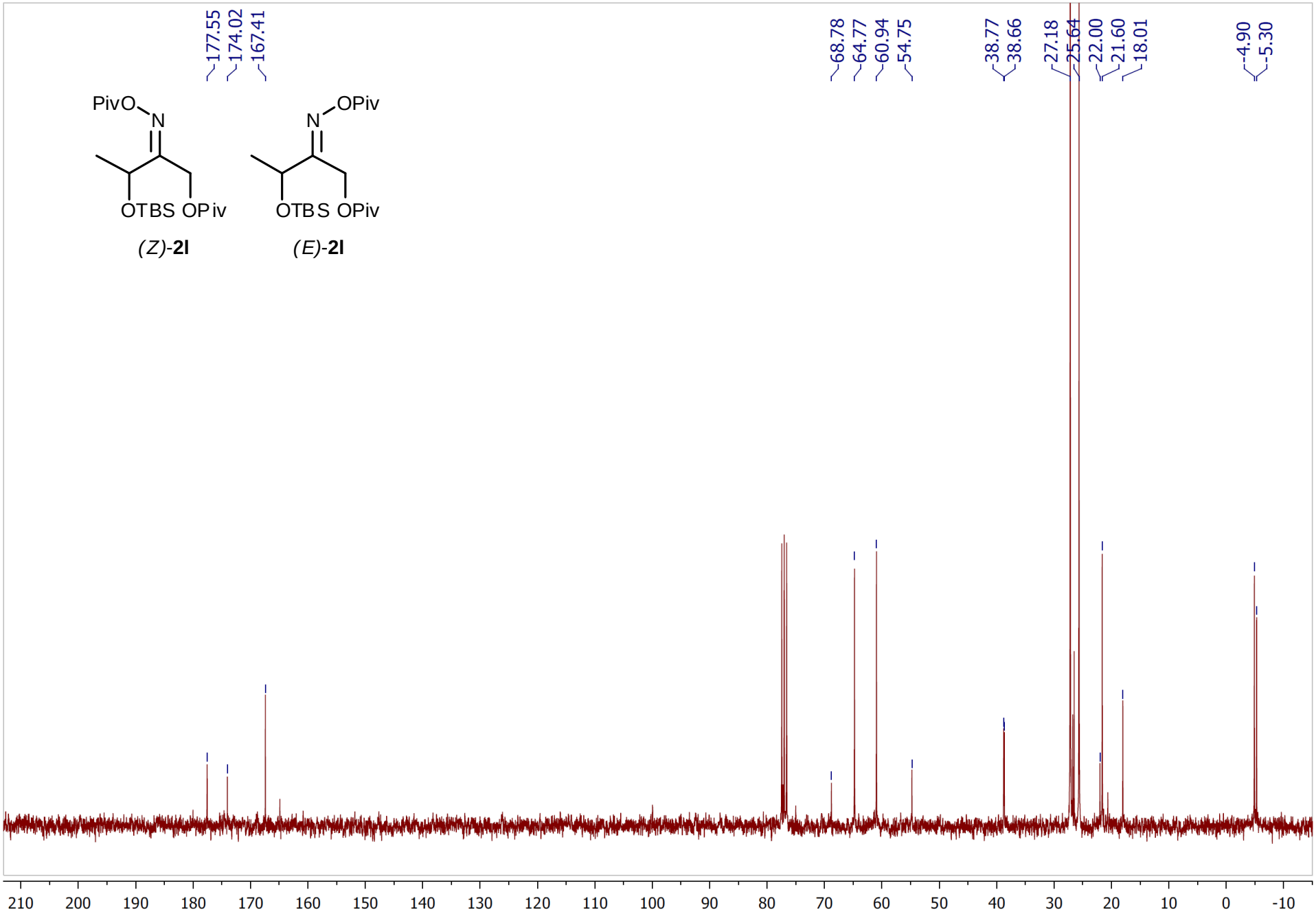
2k

3-(*tert*-Butyldimethylsilyloxy)-2-(pivaloyloxyimino)butyl pivalate 2l

^{1}H NMR



^{13}C NMR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174.02
167.41
68.78
64.77
60.94
54.75
38.77
38.66
27.18
25.64
22.00
21.60
18.01
-4.90
-5.30
PivO
N
OTBS
OPiv
N
OPiv
OTBS
OPiv
(Z)-2l
(E)-2l
210
200
190
180
170
160
150
140
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100
90
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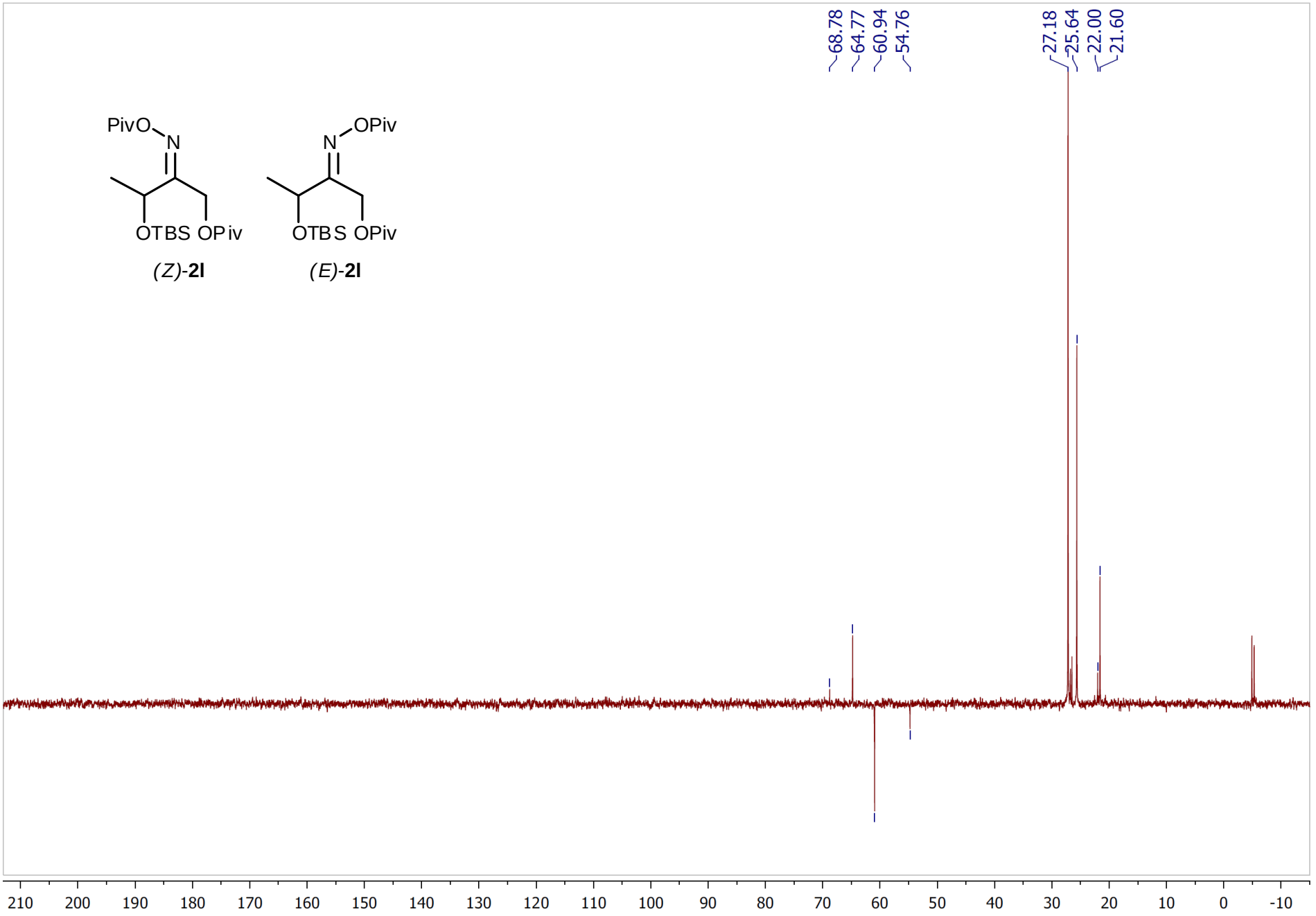
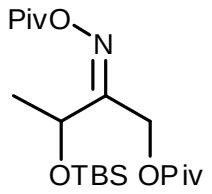
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT

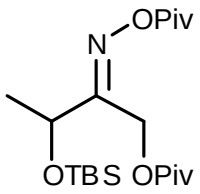


(Z)-**2l** *(E)*-**2l**

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

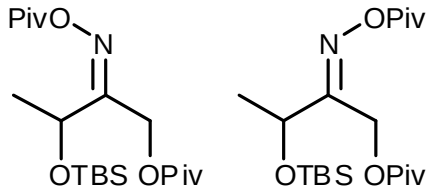


(Z)-**2l**



(E)-**2l**

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

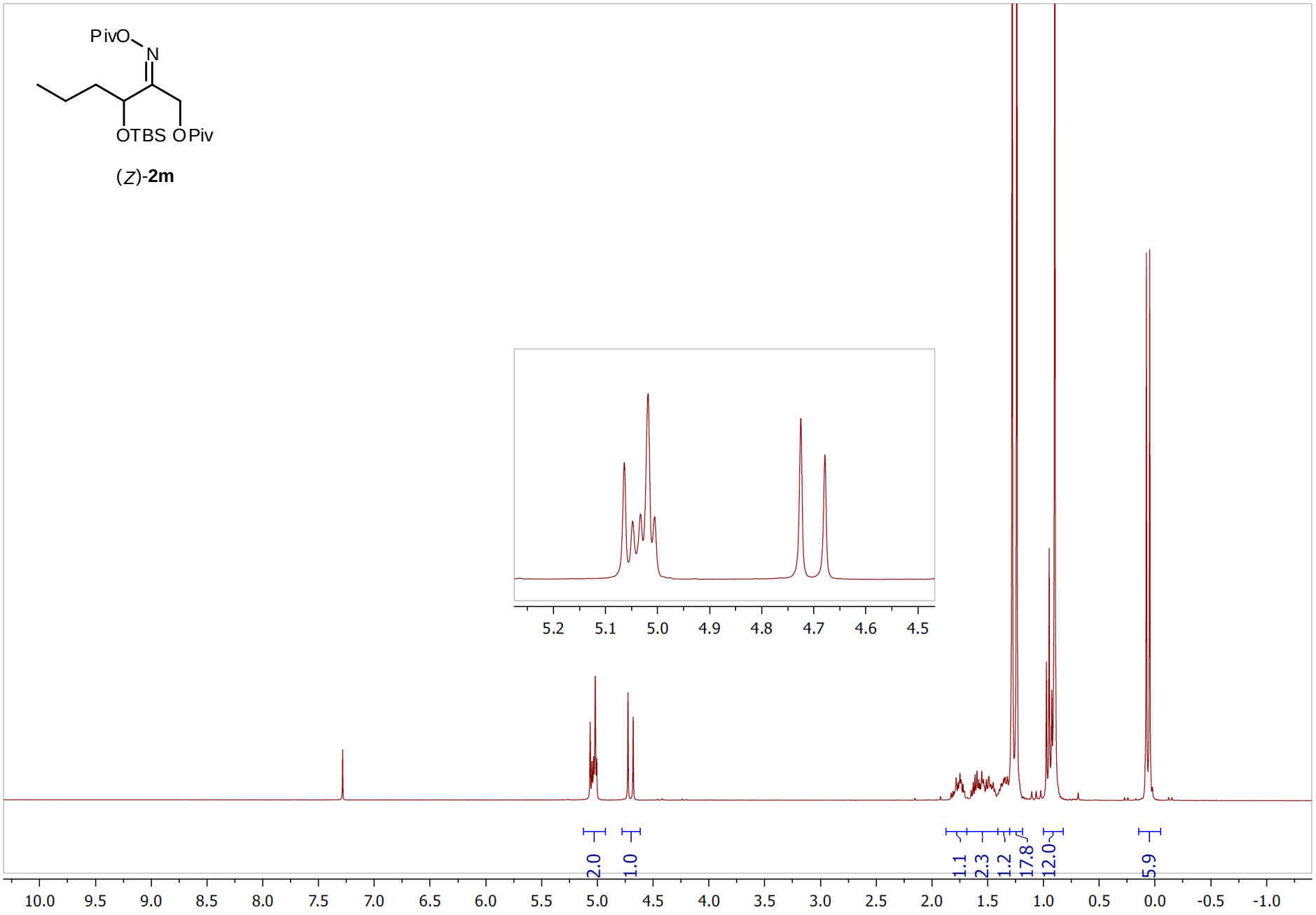


(Z)-**2l**

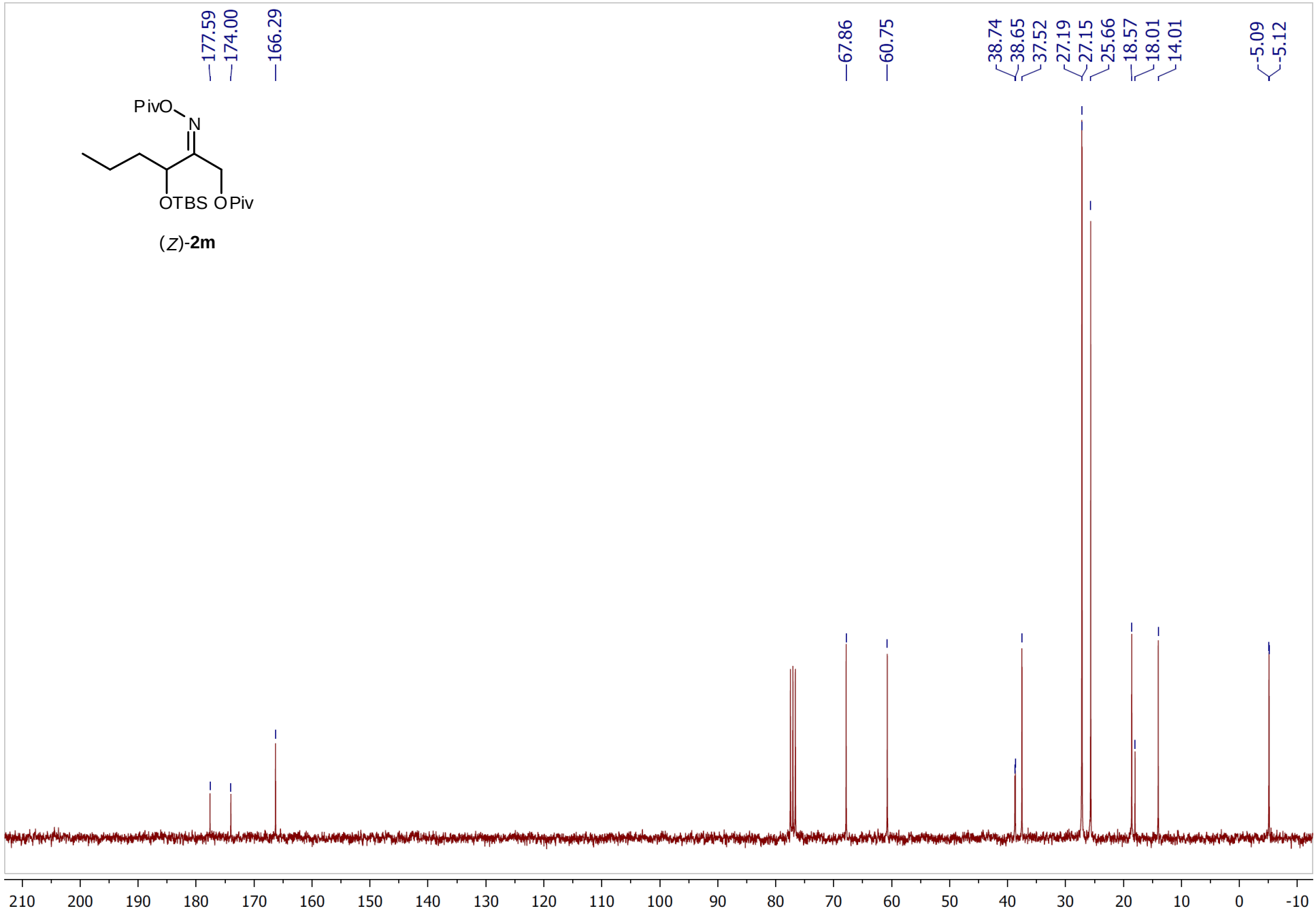
(E)-**2l**

3-(*tert*-Butyldimethylsilyloxy)-2-(pivaloyloxyimino)hexyl pivalate 2m

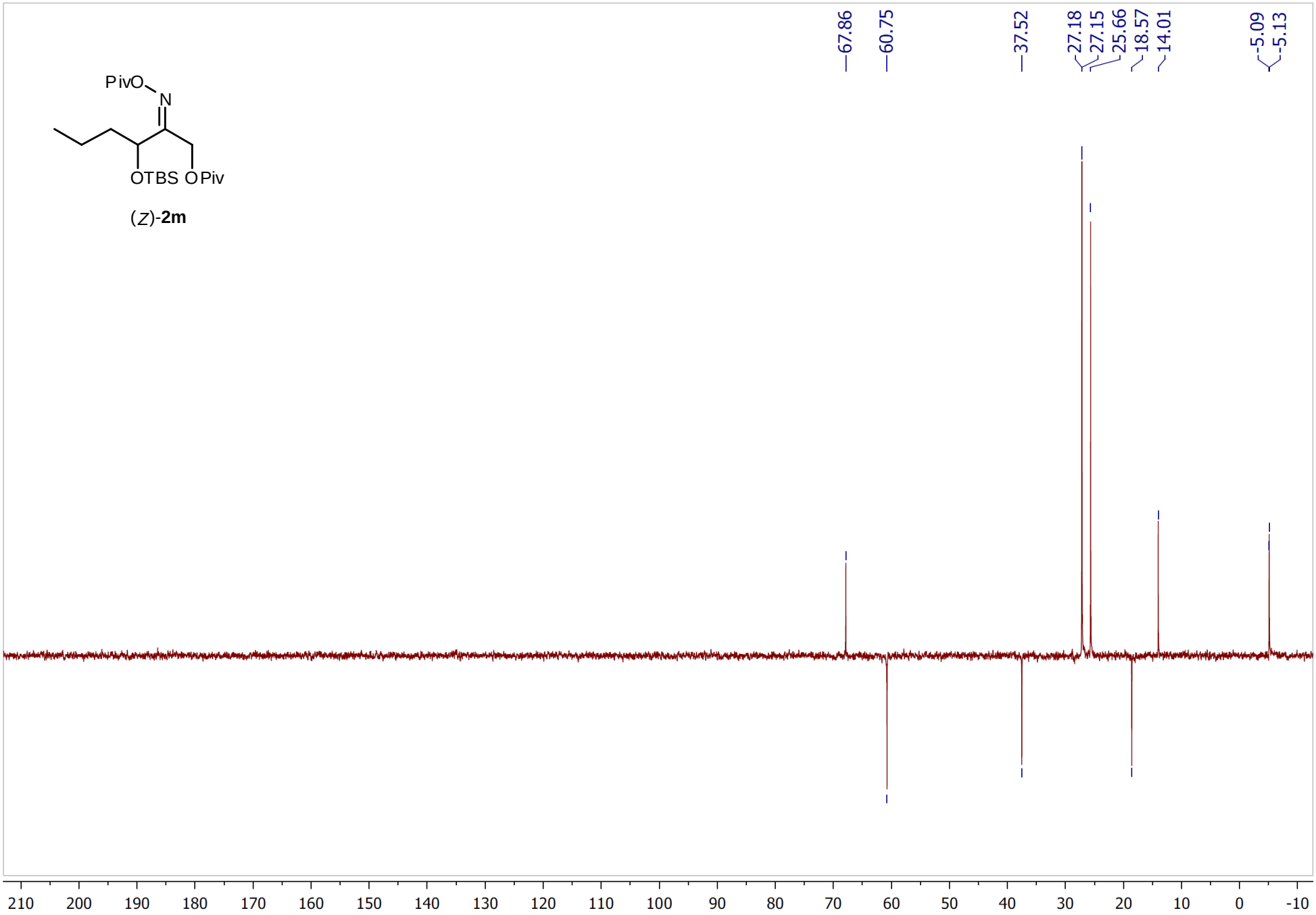
^{1}H NMR



^{13}C NMR

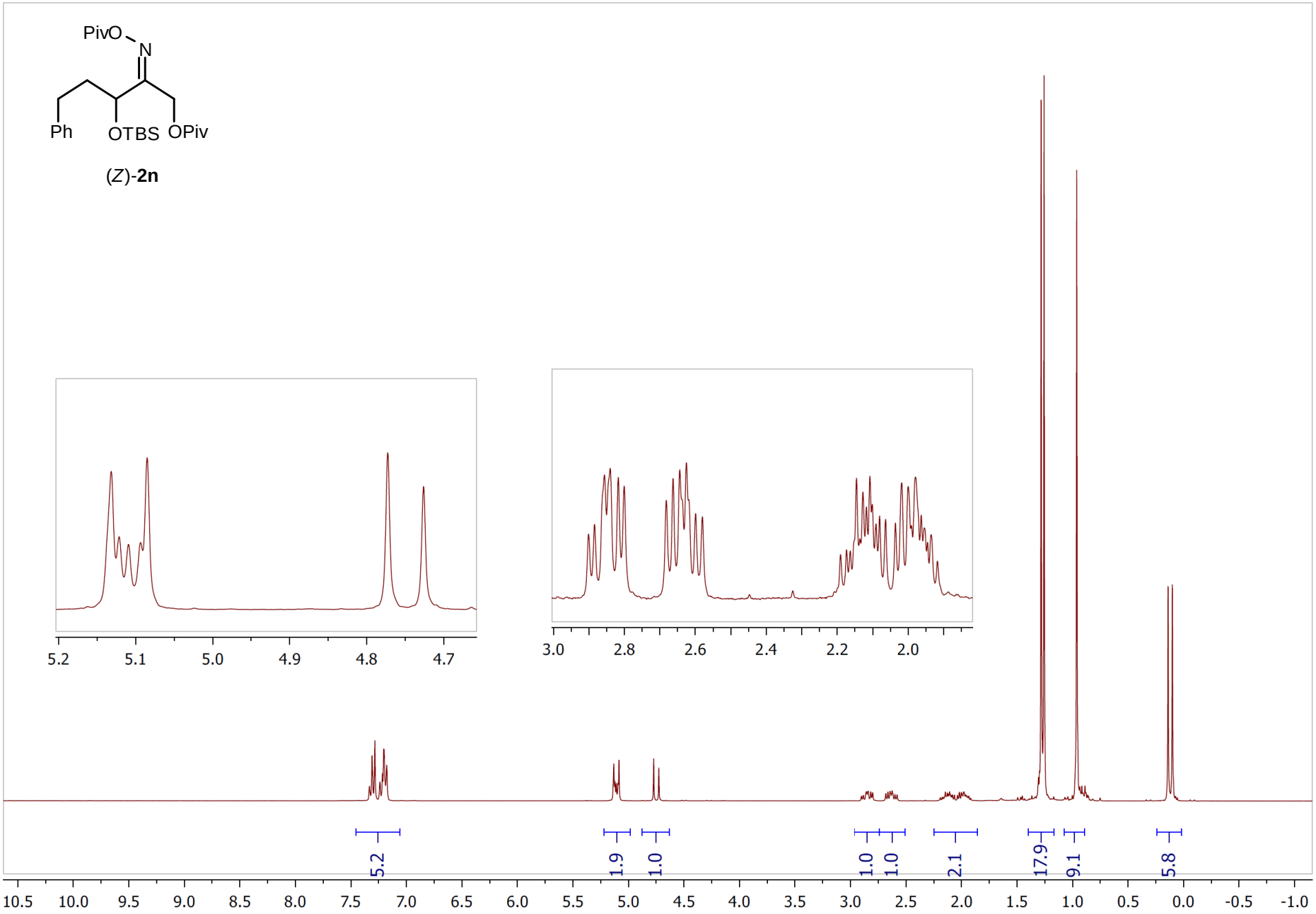

177.59
174.00
166.29
67.86
60.75
38.74
38.65
37.52
27.19
27.15
25.66
18.57
18.01
14.01
-5.09
-5.12
PivO
N
OTBS
OPiv
(Z)-2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT

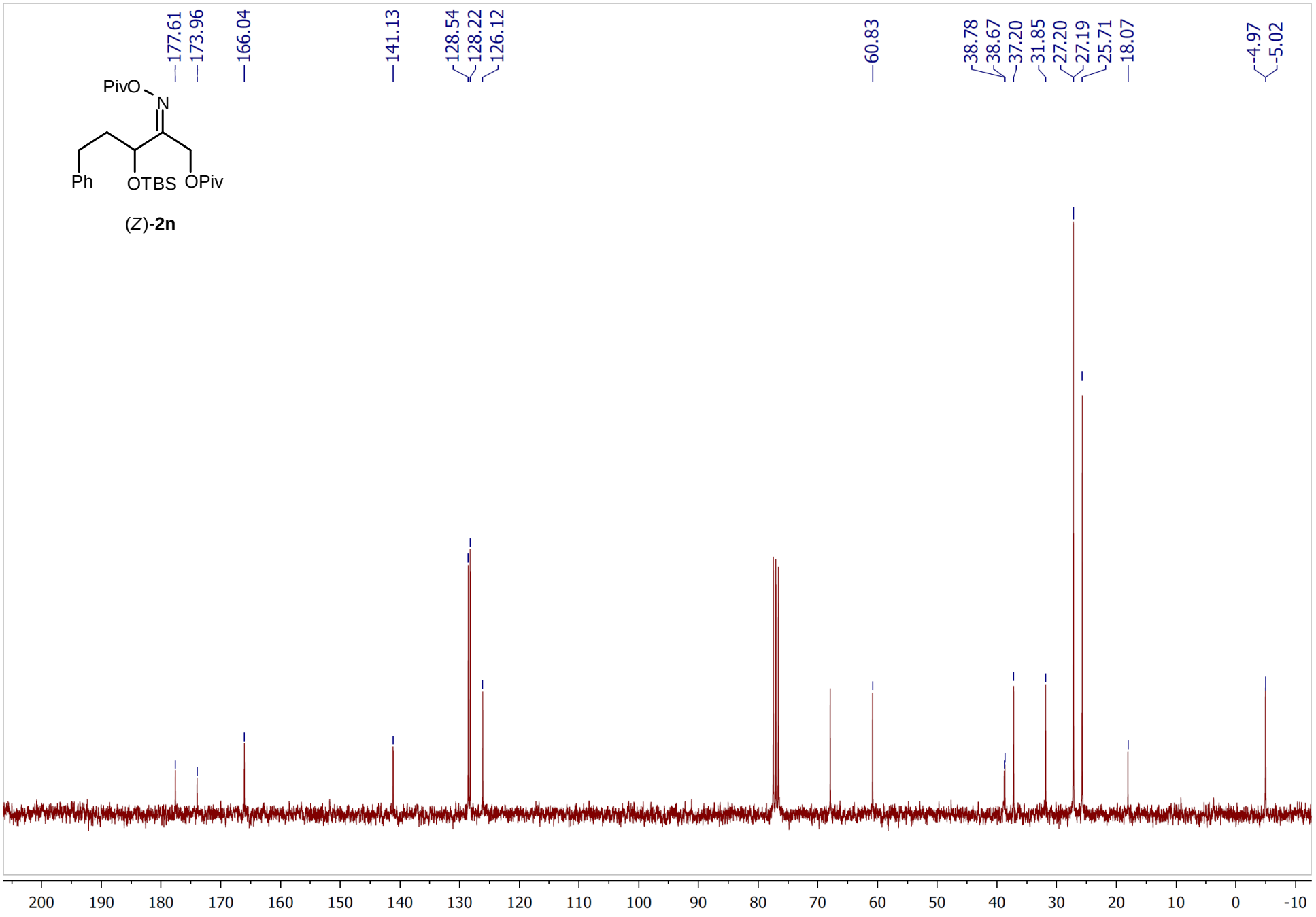

67.86
60.75
37.52
27.18
27.15
25.66
18.57
14.01
-5.09
-5.13
PivO
N
OTBS OPiv
(Z)-2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

3-(*tert*-Butyldimethylsilyloxy)-5-phenyl-2-(pivaloyloxyimino)pentyl pivalate 2n

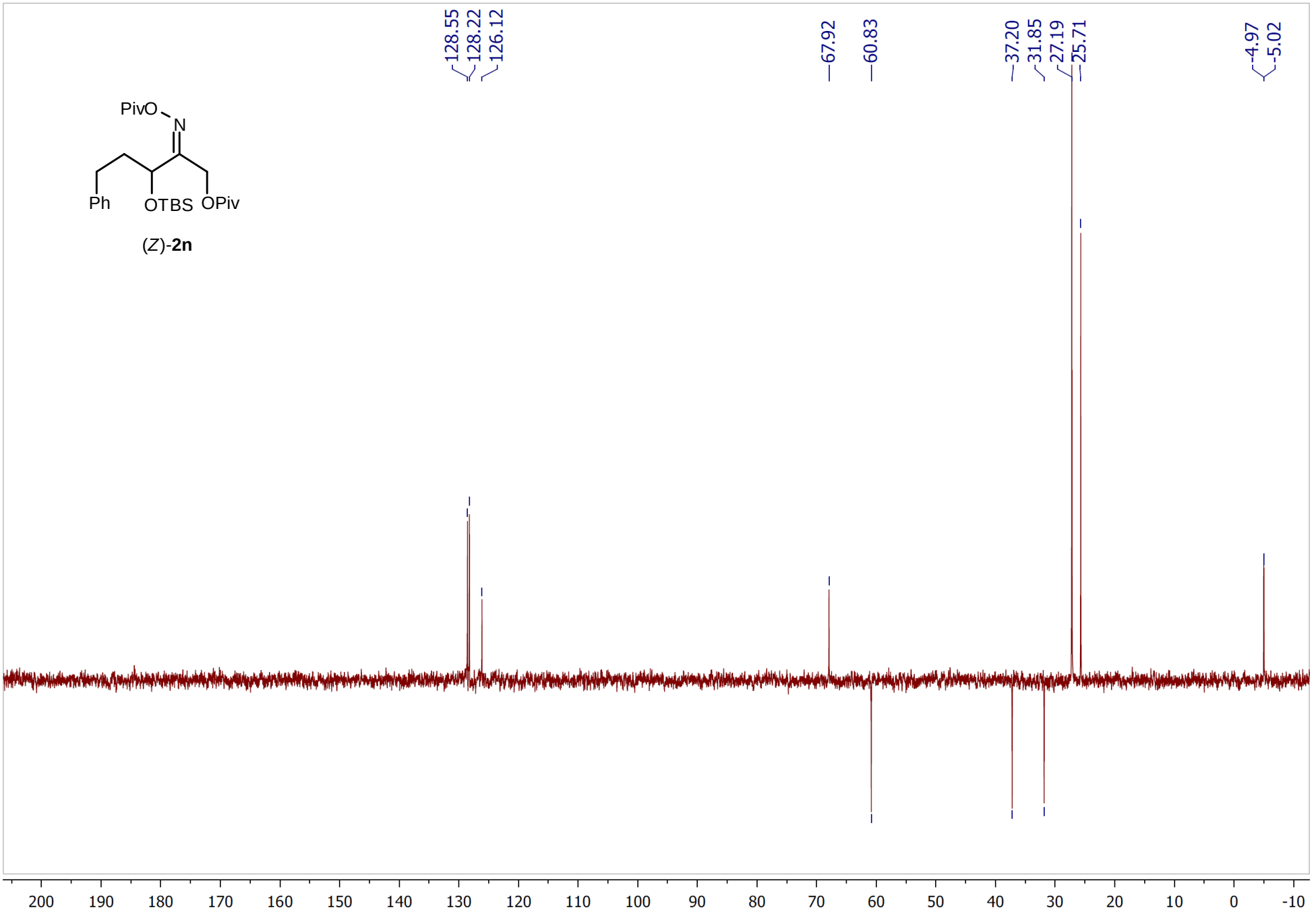
^{1}H NMR



^{13}C NMR


177.61
173.96
166.04
141.13
128.54
128.22
126.12
60.83
38.78
38.67
37.20
31.85
27.20
27.19
25.71
18.07
-4.97
-5.02
PivO
N
Ph
OTBS
OPiv
(Z)-2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT


128.55
128.22
126.12
67.92
60.83
37.20
31.85
27.19
25.71
-4.97
-5.02
PivO
N
Ph
OTBS
OPiv
(Z)-2n
200
190
180
170
160
150
140
130
120
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100
90
80
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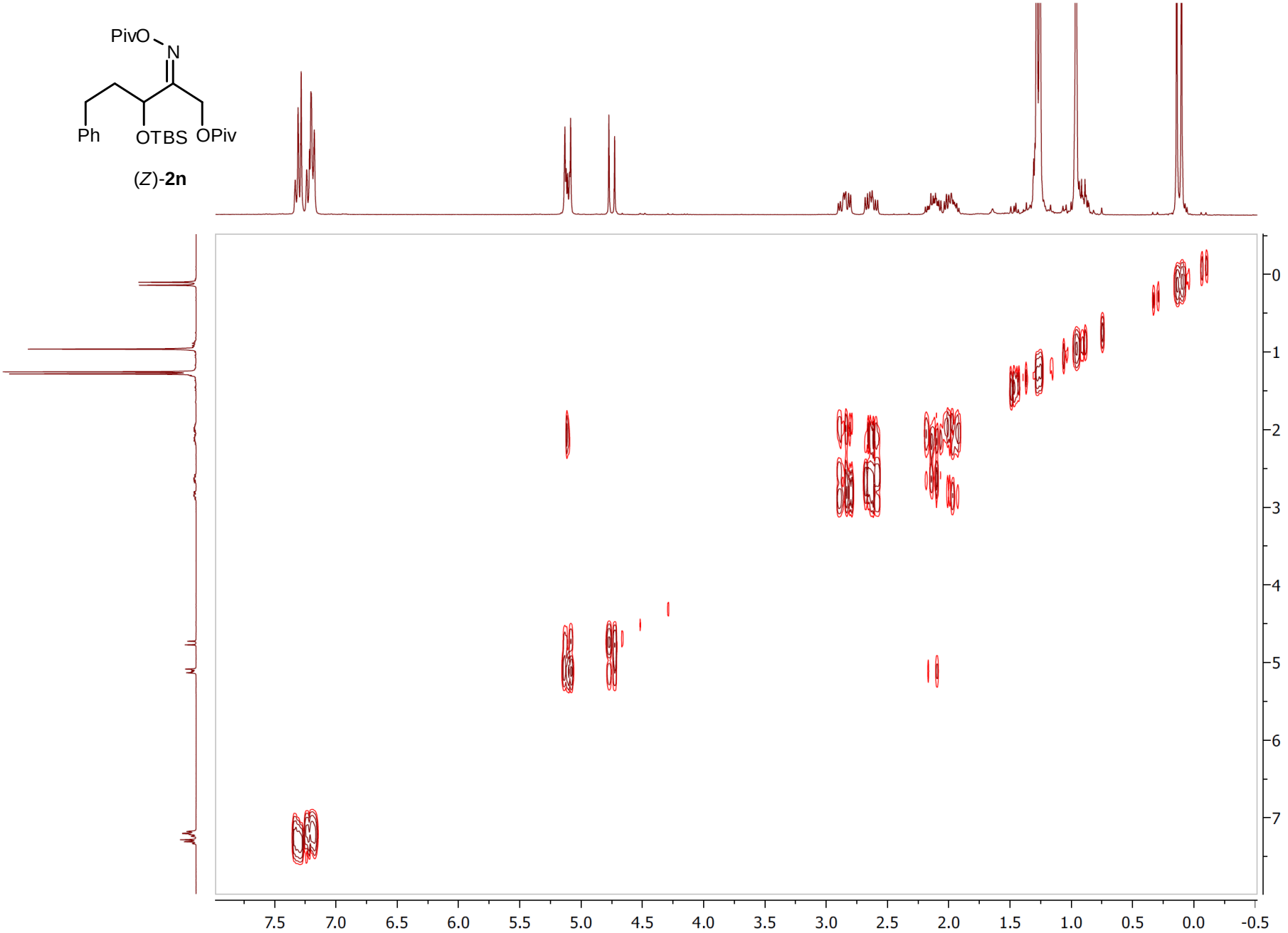
60
50
40
30
20
10
0
-10

^{1}H-^{1}H COSY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N
Ph
OTBS
OPiv
(Z)-2n
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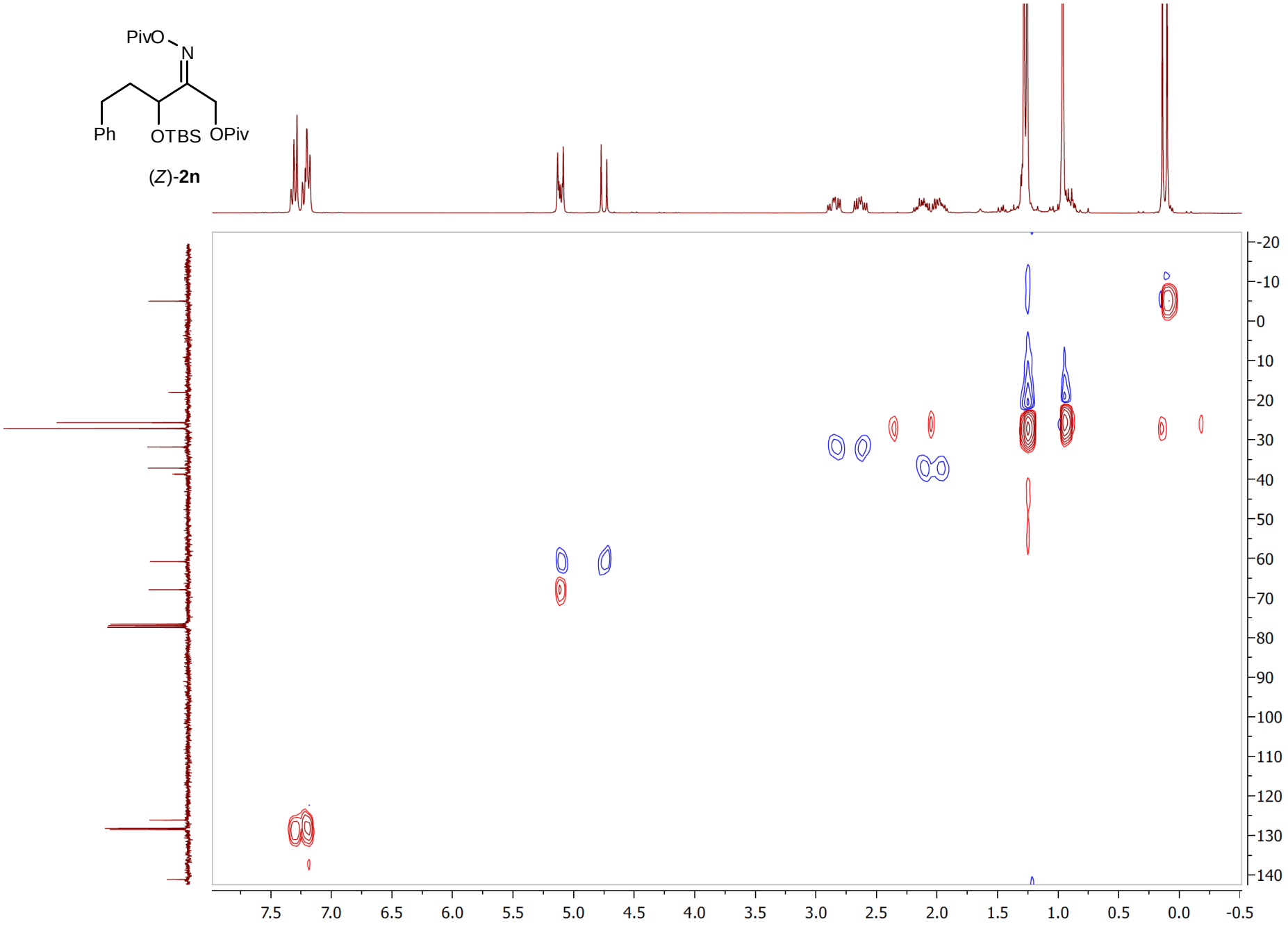
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7

^{1}H-^{13}C HSQC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N
Ph
OTBS
OPiv
(Z)-2n
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-10
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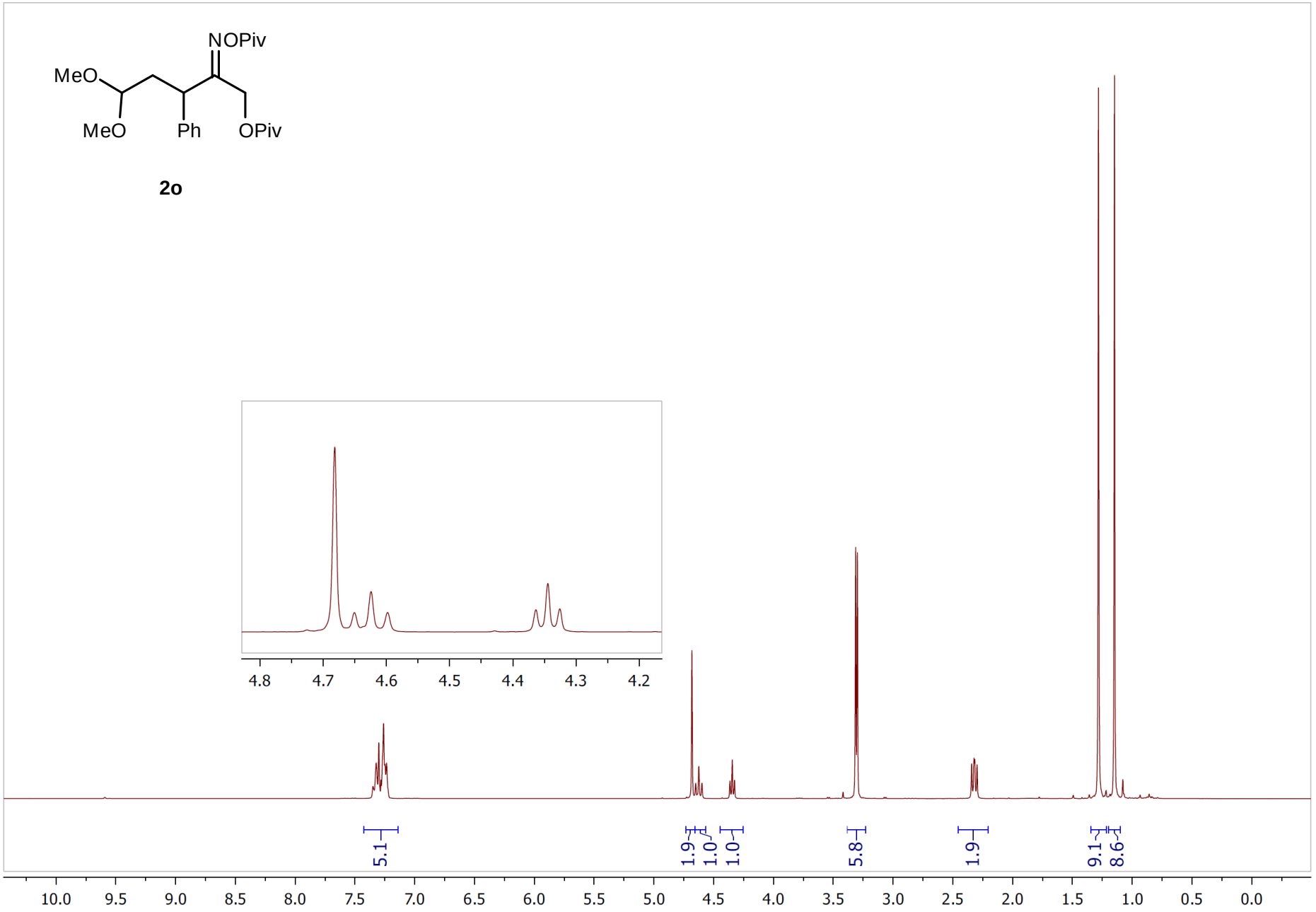
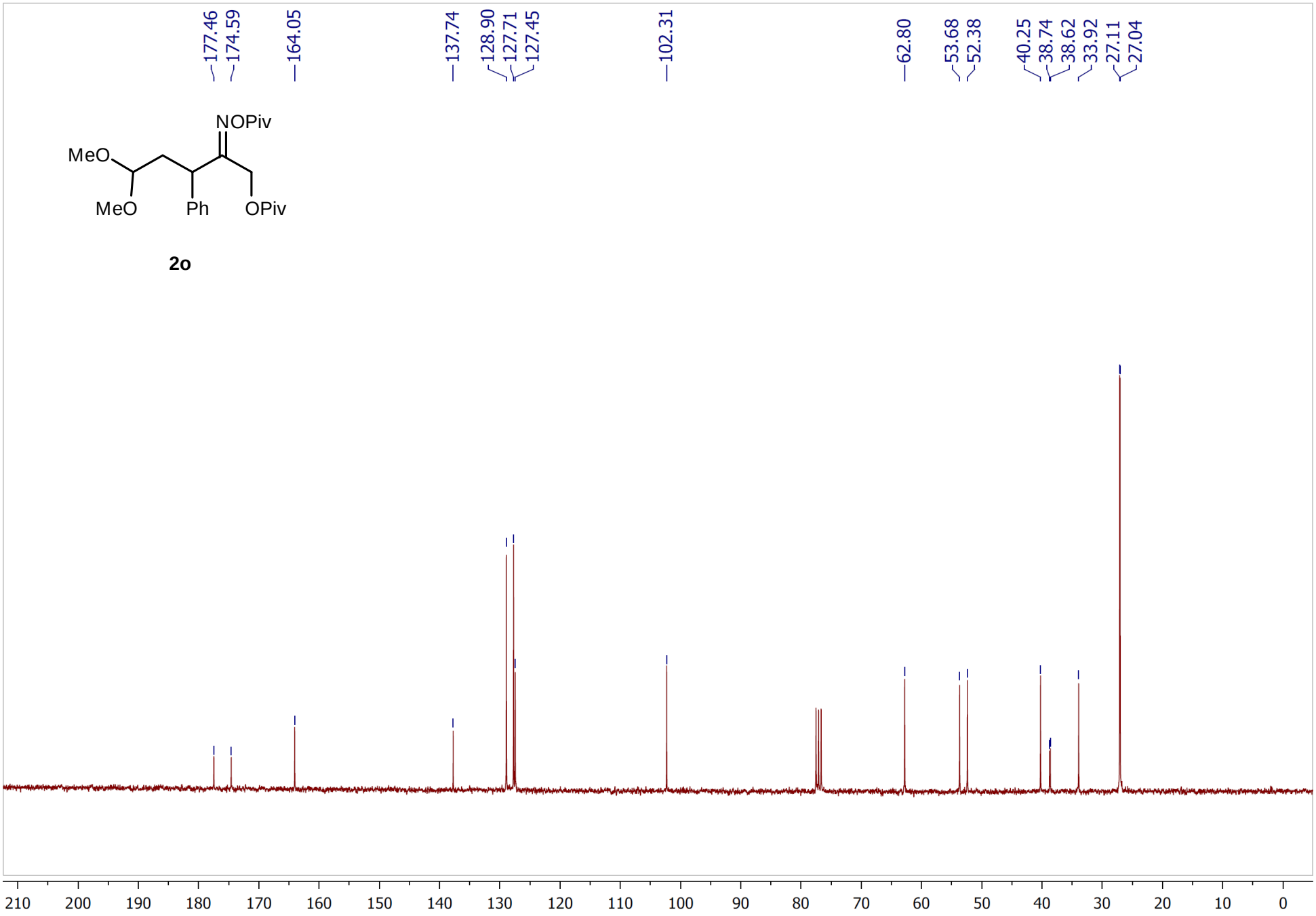
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

5,5-Dimethoxy-3-phenyl-2-(pivaloyloxyimino)pentyl pivalate 2o

^{1}H NMR



^{13}C NMR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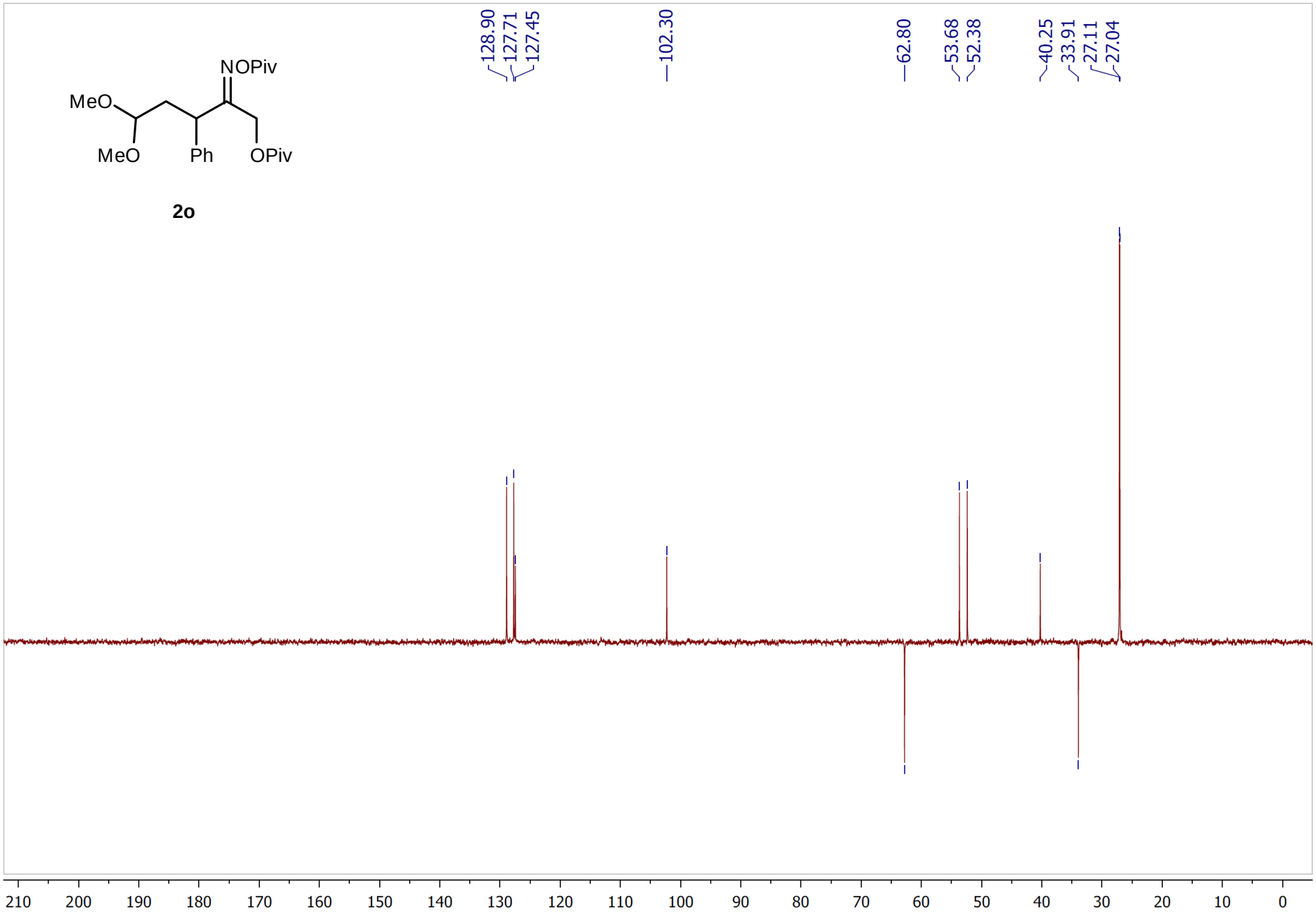
174.59
164.05
137.74
128.90
127.71
127.45
102.31
62.80
53.68
52.38
40.25
38.74
38.62
33.92
27.11
27.04
NOPiv
MeO
MeO
Ph
OPiv
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT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MeO
MeO
Ph
OPiv
2o
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127.45
102.30
62.80
53.68
52.38
40.25
33.91
27.11
27.04
210
200
190
180
170
160
150
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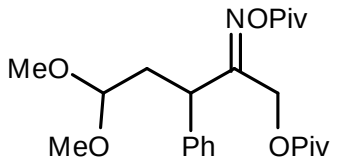
110
100
90
80
70
60
50
40
30
20
10
0

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


NOPiv
MeO
MeO
Ph
OPiv

2o

0
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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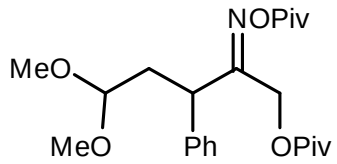
3.0
2.5
2.0
1.5
1.0
0.5
0.0

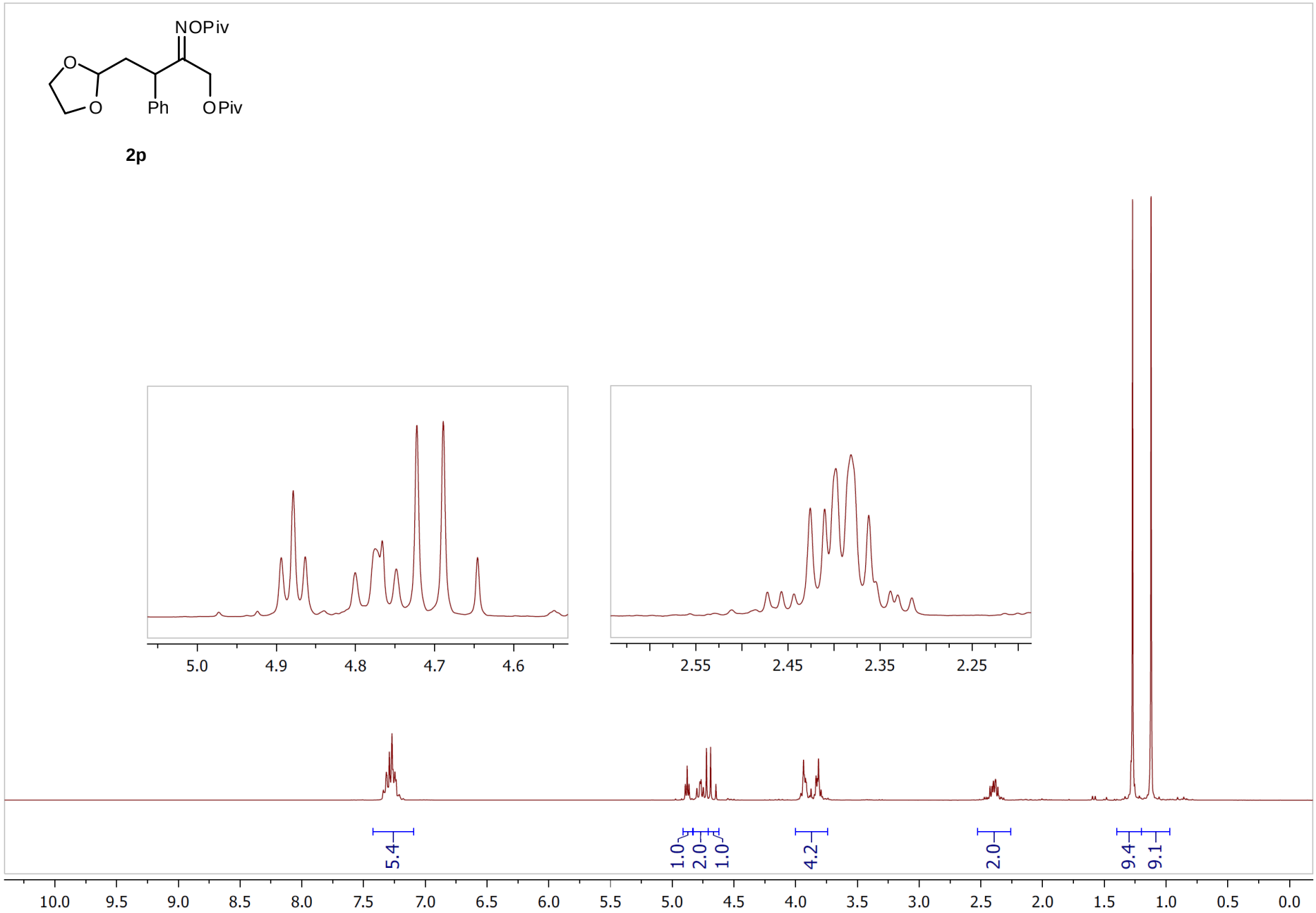
^{1}H-^{13}C HSQC



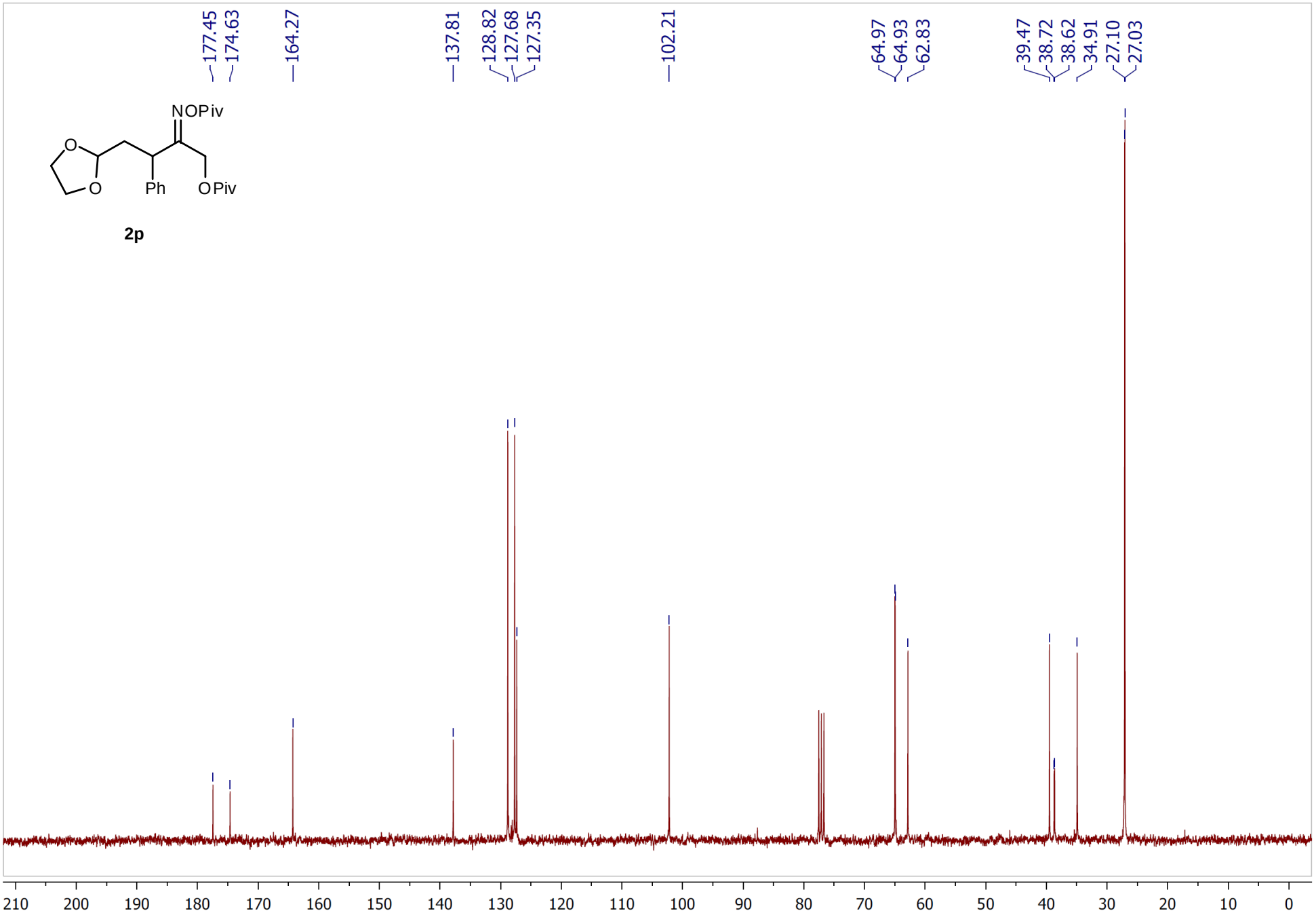
2o

4-(1,3-Dioxolan-2-yl)-3-phenyl-2-(pivaloyloxyimino)butyl pivalate 2p, predominantly *E*-isomer

^{1}H NMR



^{13}C NMR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174.63
164.27
137.81
128.82
127.68
127.35
102.21
64.97
64.93
62.83
39.47
38.72
38.62
34.91
27.10
27.03
NOPiv
O
O
Ph
OPiv
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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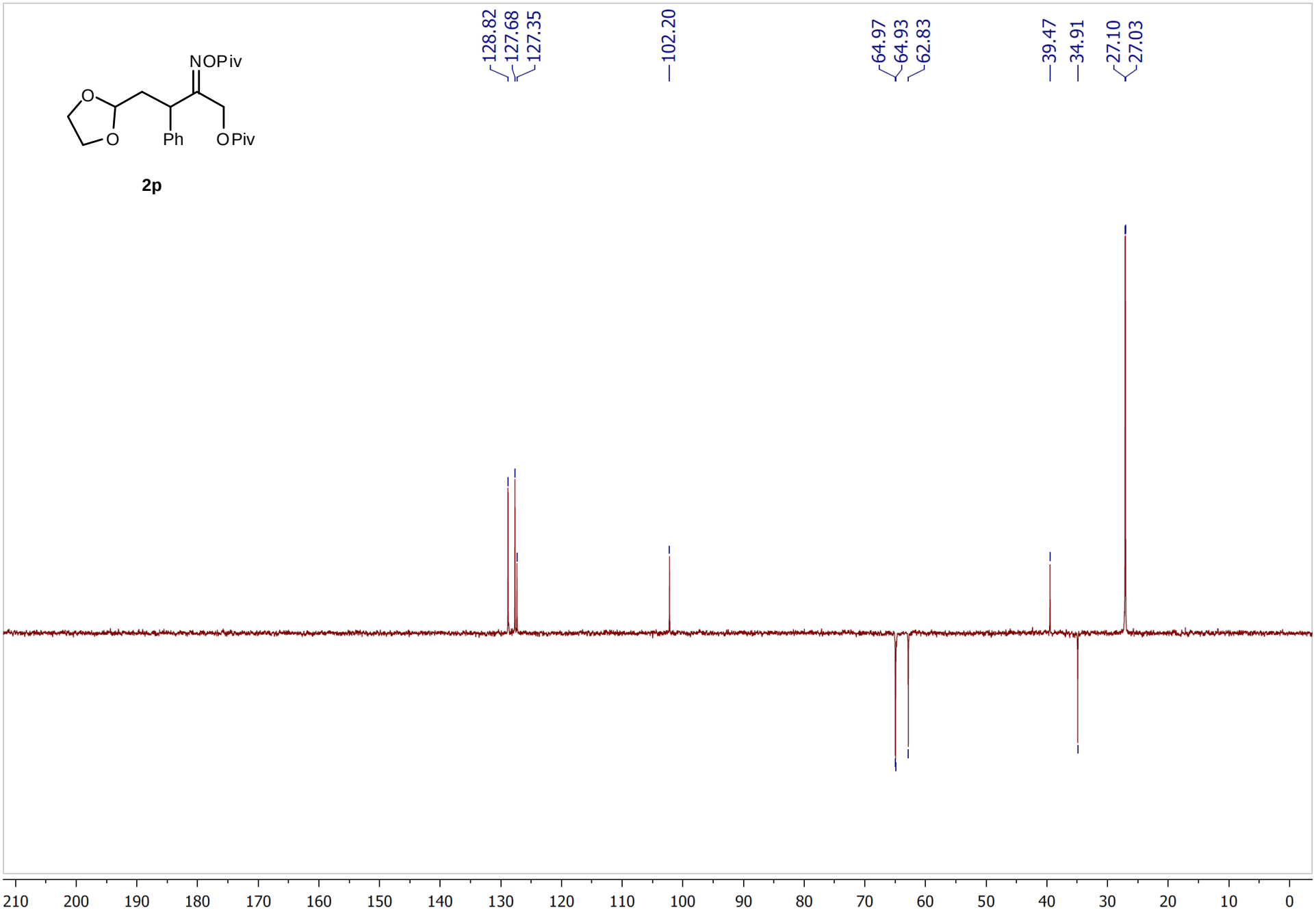
60
50
40
30
20
10
0

^{13}C NMR DEPT


NOPiv
O
O
Ph
OPiv
2p
128.82
127.68
127.35
102.20
64.97
64.93
62.83
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34.91
27.10
27.03
210
200
190
180
170
160
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100
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70
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50
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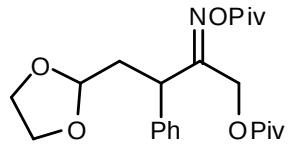
30
20
10
0

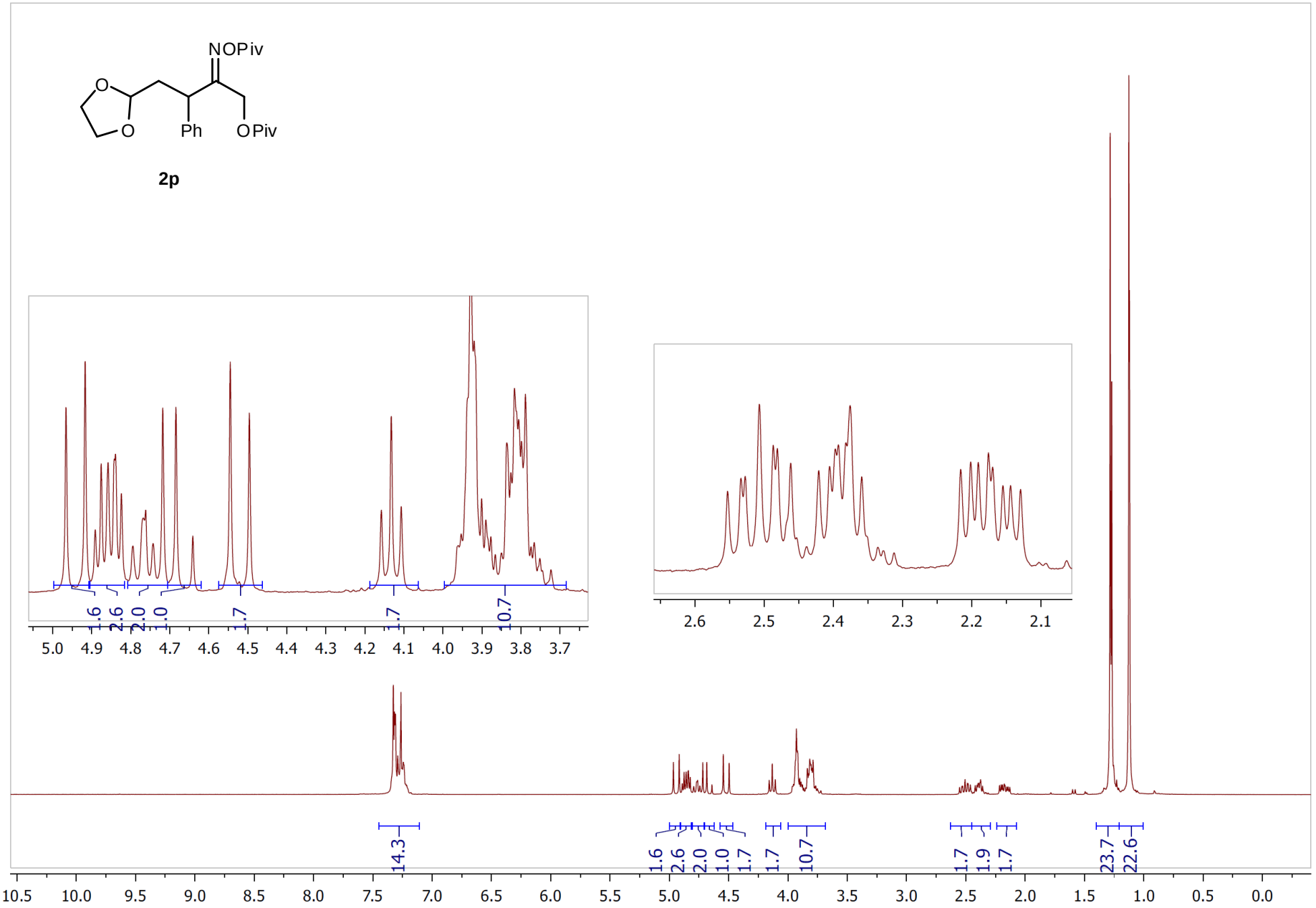
^{1}H-^{13}C HSQC



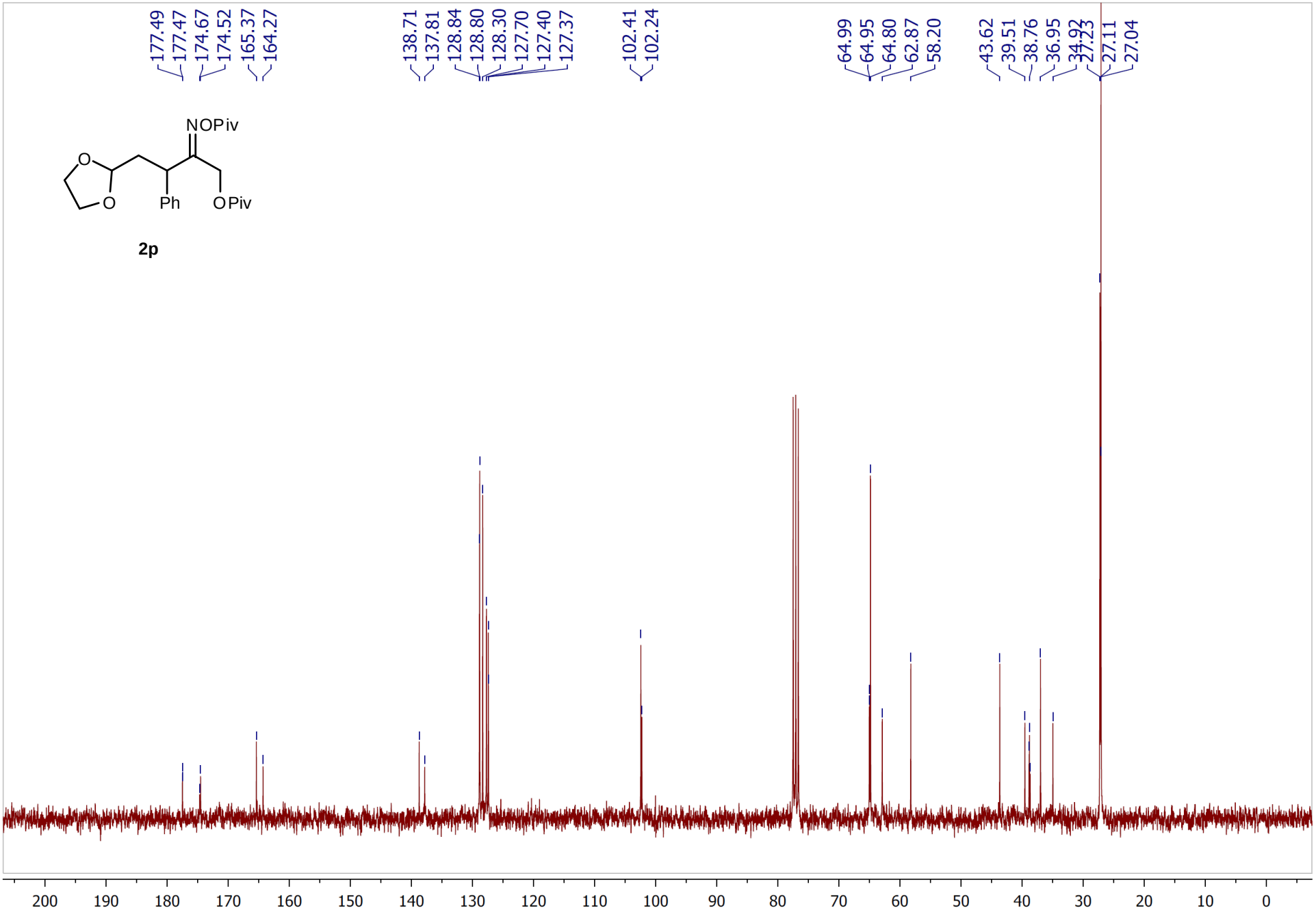
2p

4-(1,3-Dioxolan-2-yl)-3-phenyl-2-(pivaloyloxyimino)butyl pivalate 2p, *E*,*Z*-mixture

^{1}H NMR



^{13}C NMR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164.27
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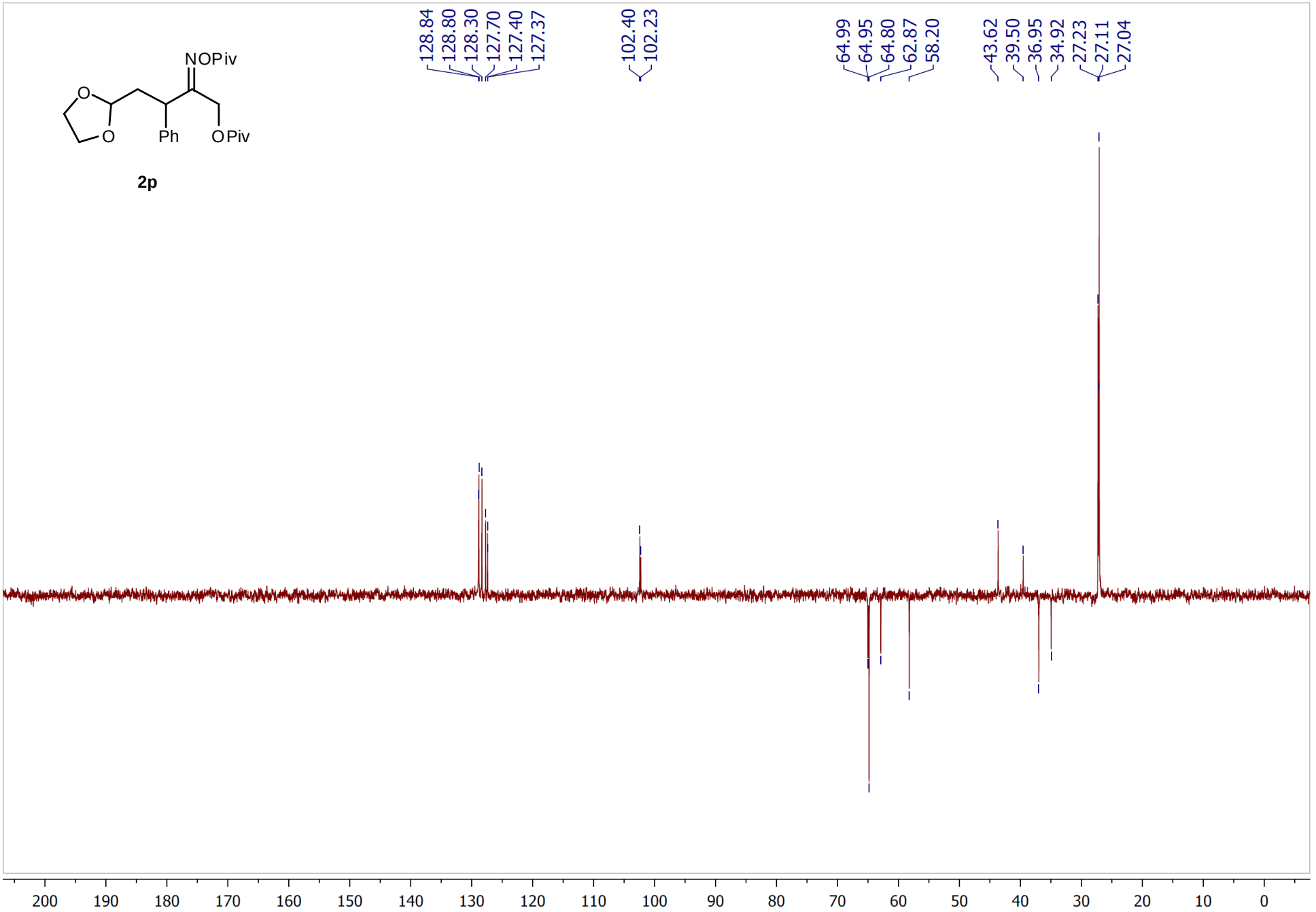
137.81
128.84
128.80
128.30
127.70
127.40
127.37
102.41
102.24
64.99
64.95
64.80
62.87
58.20
43.62
39.51
38.76
36.95
34.92
27.23
27.11
27.04
NOPiv
O
O
Ph
OPiv
2p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT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102.23
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62.87
58.20
43.62
39.50
36.95
34.92
27.23
27.11
27.04
NOPiv
O
O
Ph
OPiv
2p
200
190
180
170
160
150
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110
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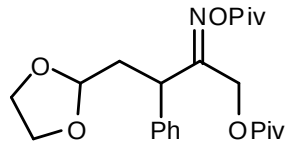
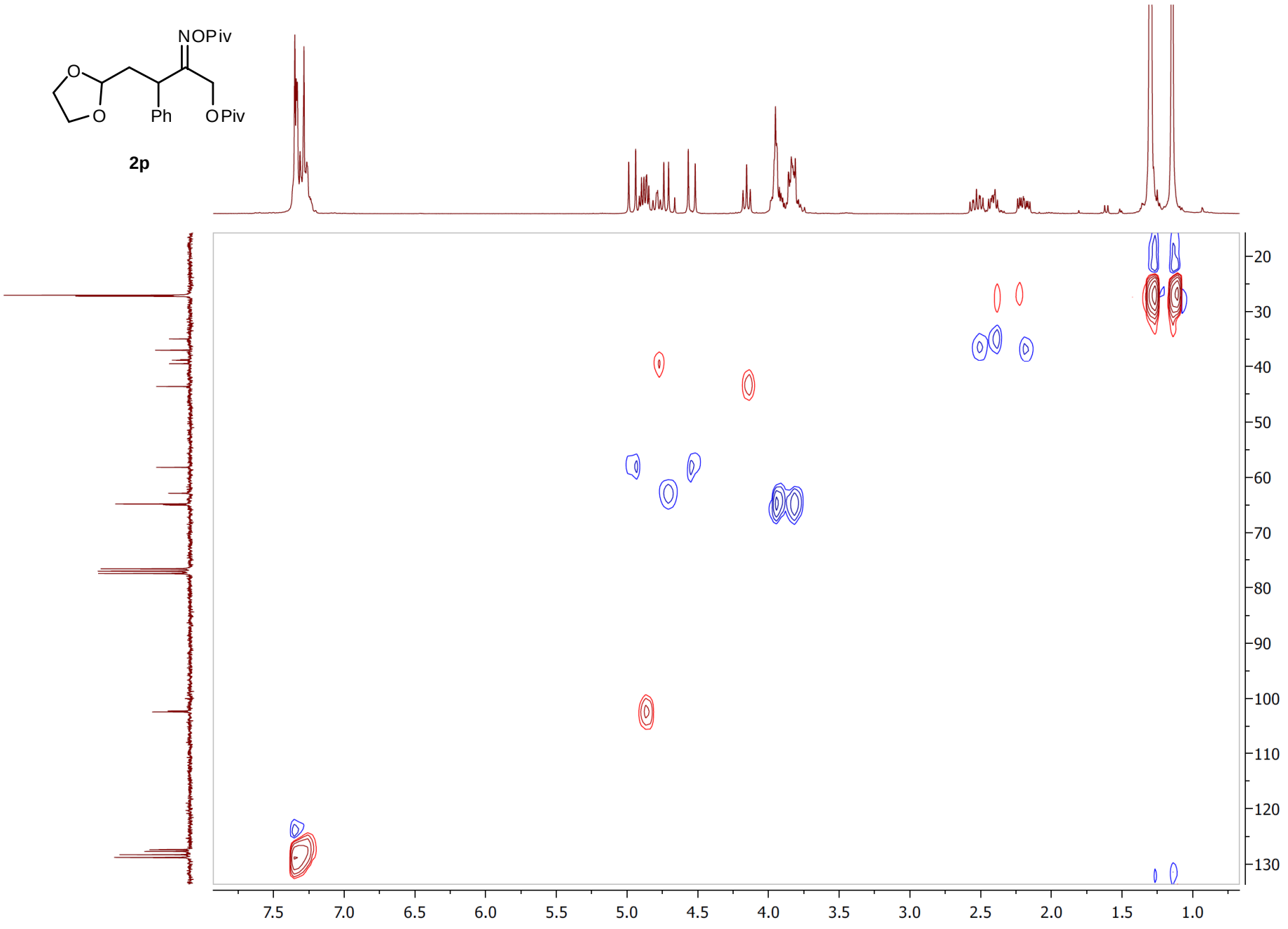
^{1}H-^{1}H COSY



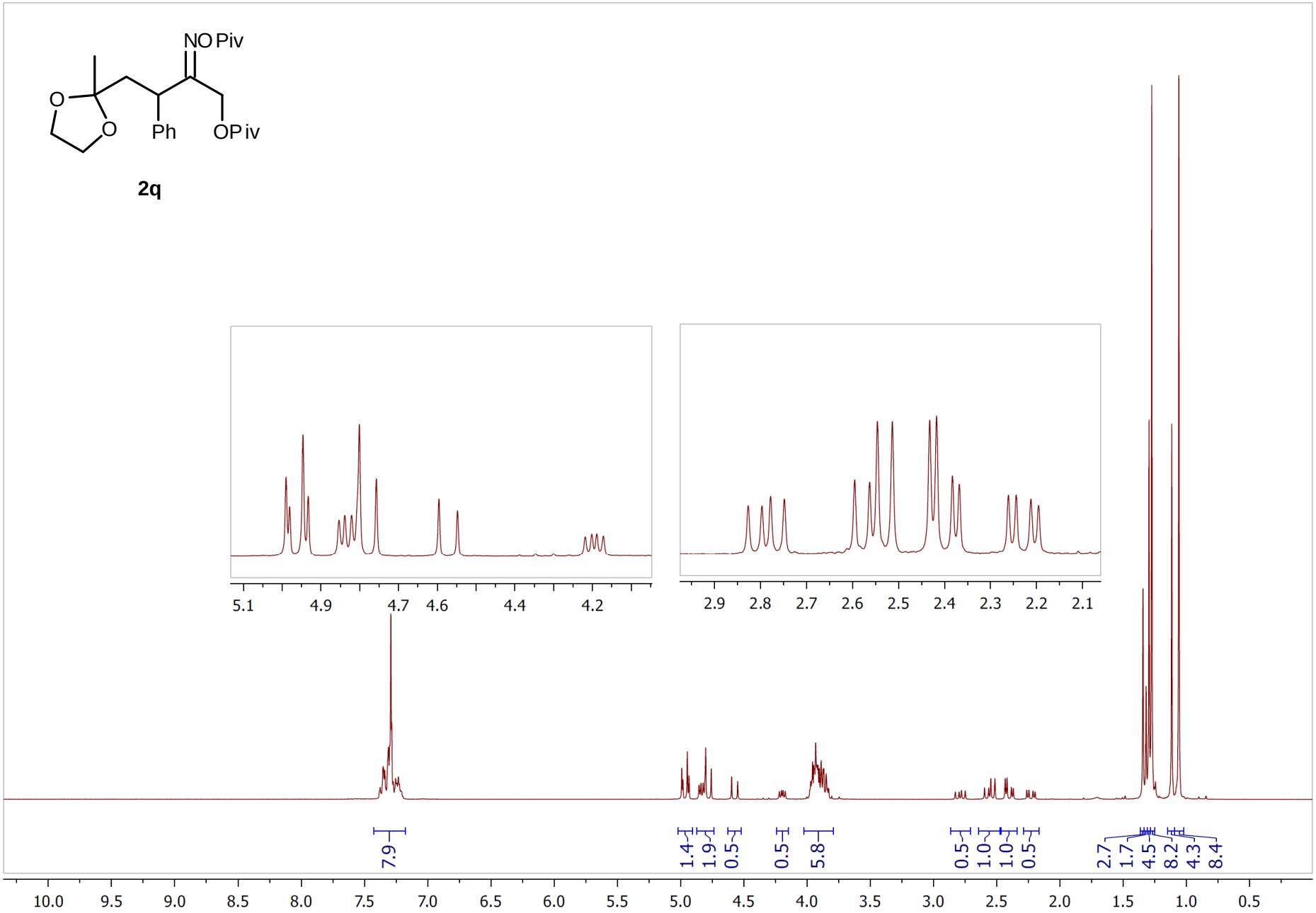
2p

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

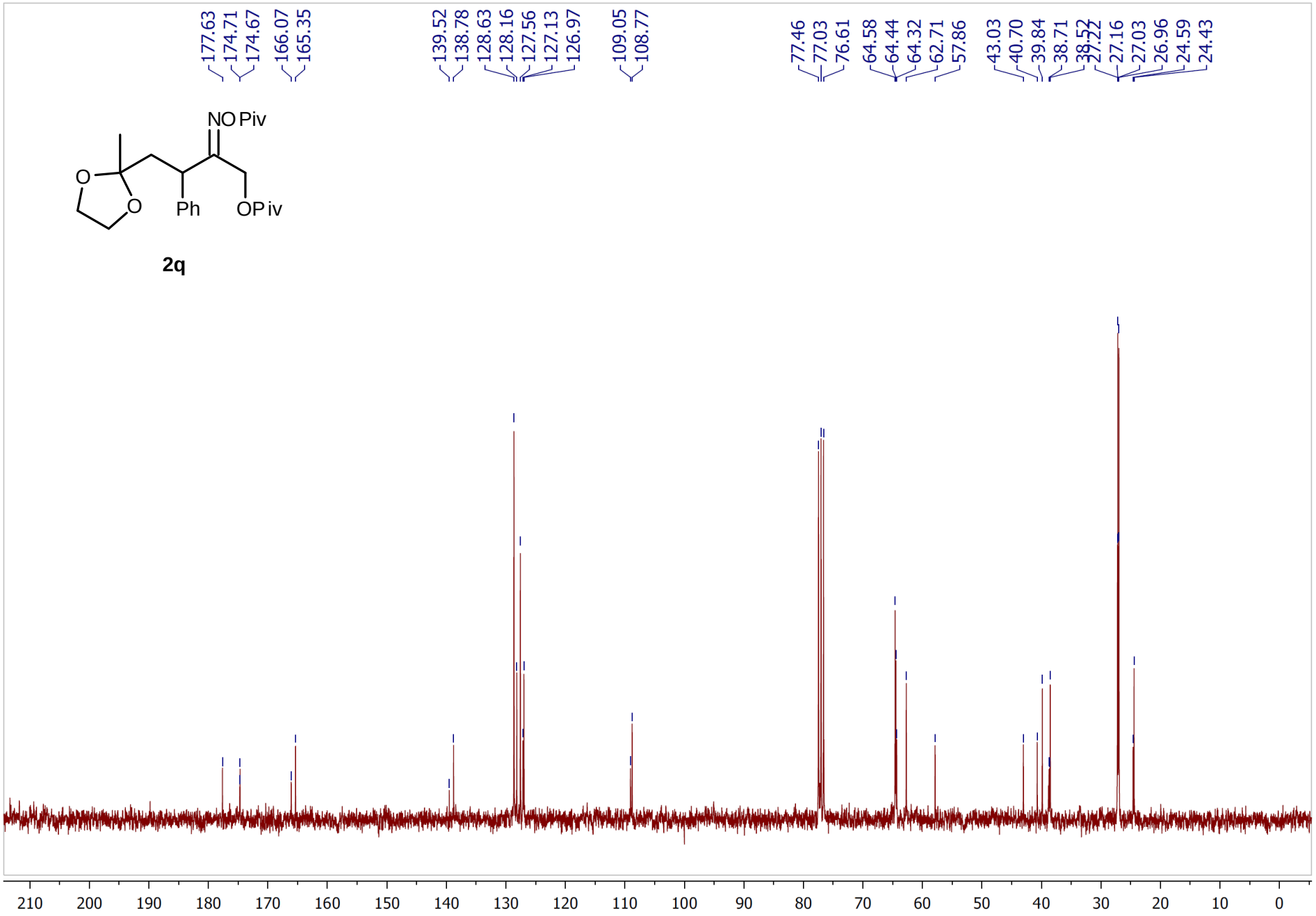

NOPiv
O
O
Ph
OPiv
2p
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

4-(2-Methyl-1,3-dioxolan-2-yl)-3-phenyl-2-(pivaloyloxyimino)butyl pivalate 2q

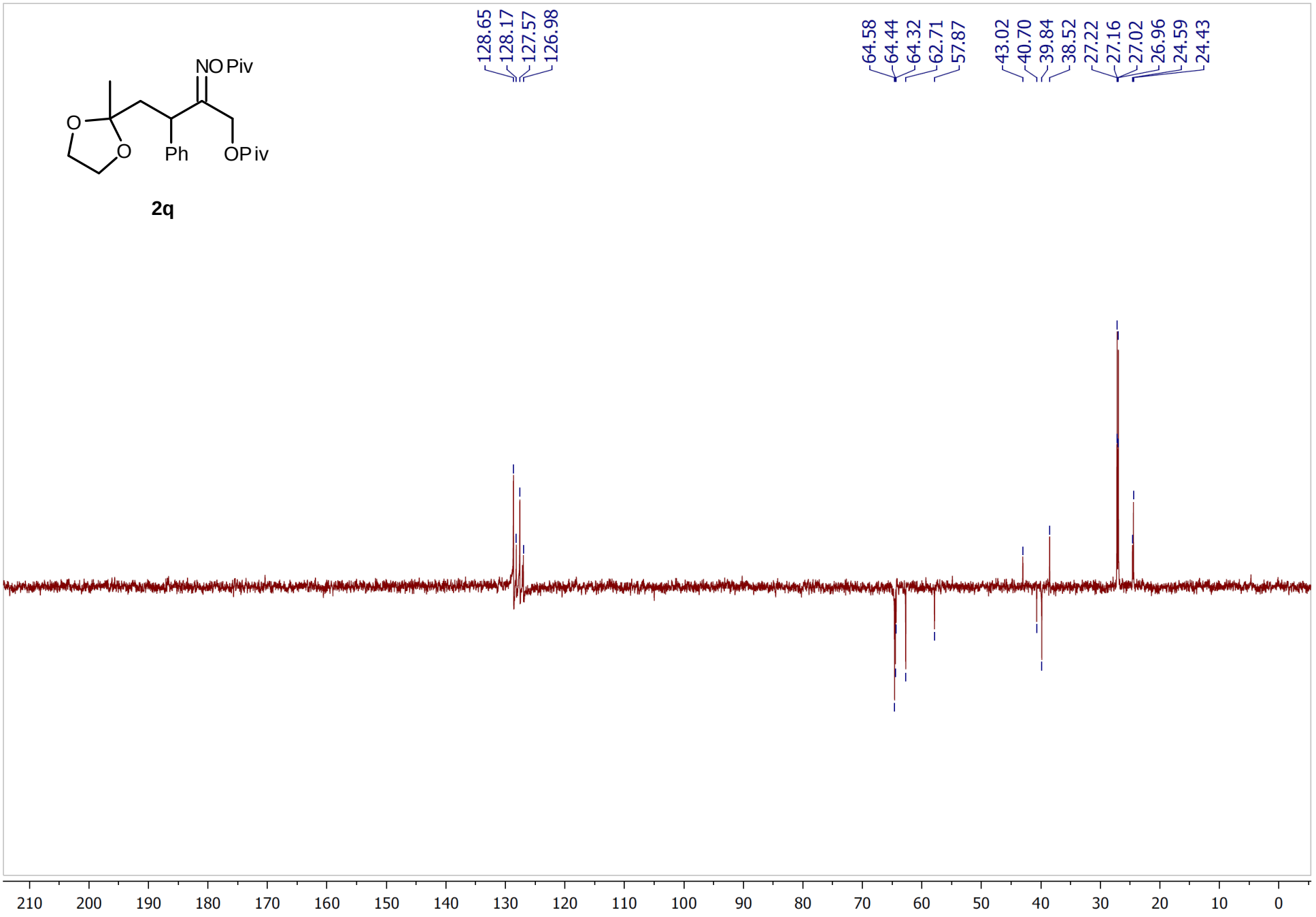
^{1}H NMR



^{13}C NMR

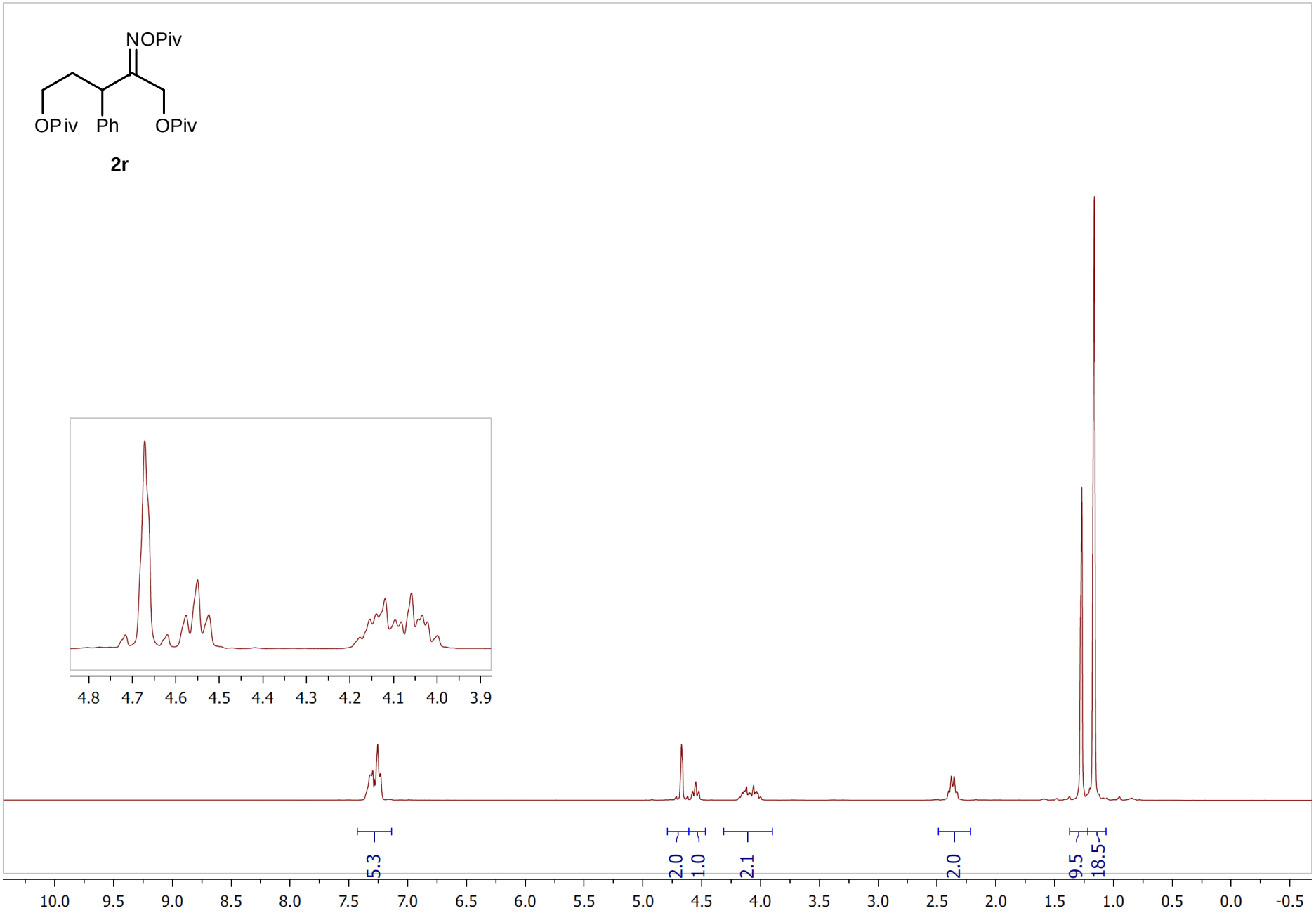

177.63
174.71
174.67
166.07
165.35
139.52
138.78
128.63
128.16
127.56
127.13
126.97
109.05
108.77
77.46
77.03
76.61
64.58
64.44
64.32
62.71
57.86
43.03
40.70
39.84
38.71
38.52
27.22
27.16
27.03
26.96
24.59
24.43
NO Piv
O
O
Ph
OP iv
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

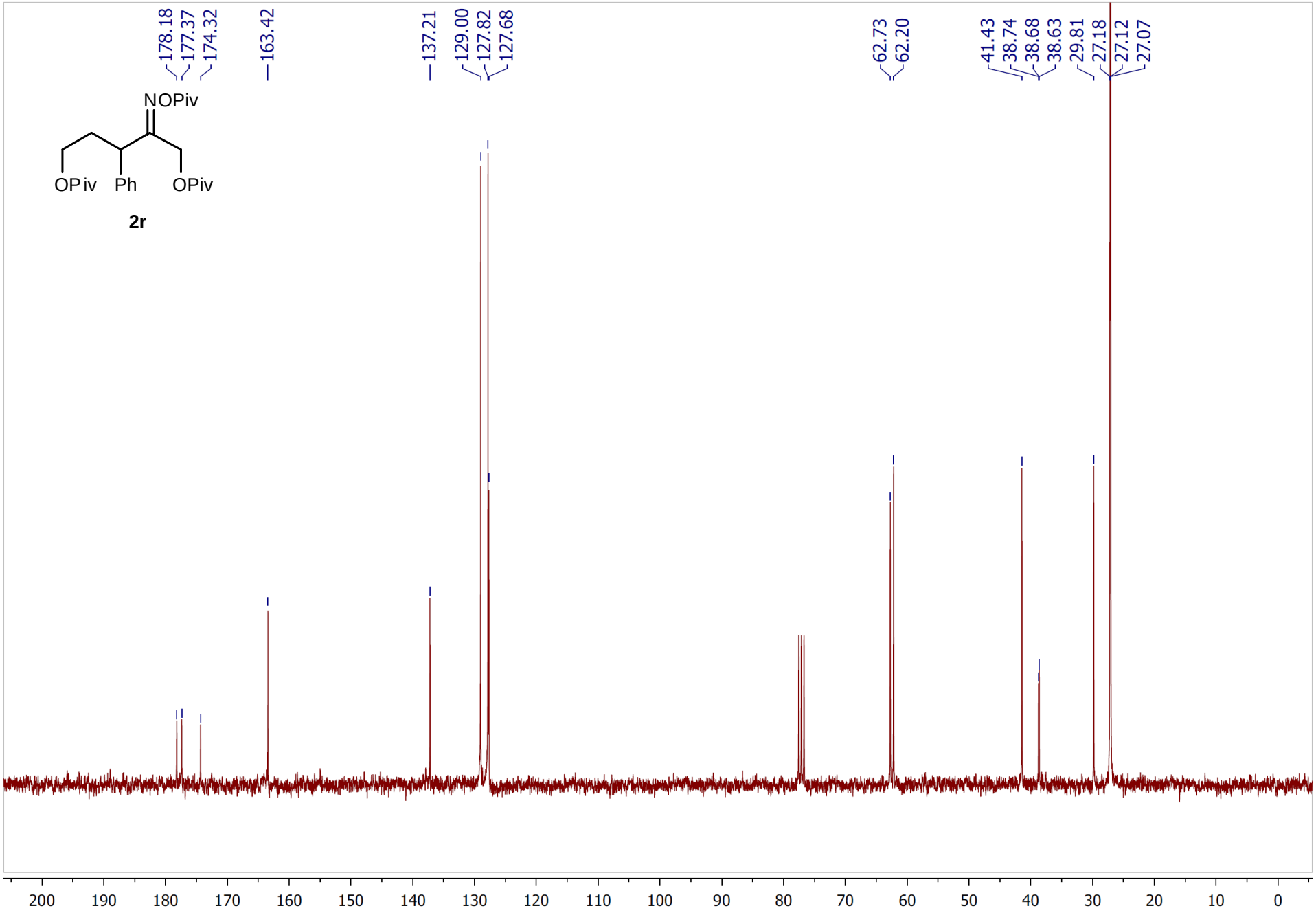

128.65
128.17
127.57
126.98
64.58
64.44
64.32
62.71
57.87
43.02
40.70
39.84
38.52
27.22
27.16
27.02
26.96
24.59
24.43
NO Piv
O
O
Ph
OP iv
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3-Phenyl-2-(pivaloyloxyimino)pentane-1,5-diyl bis(2,2-dimethylpropanoate) 2r

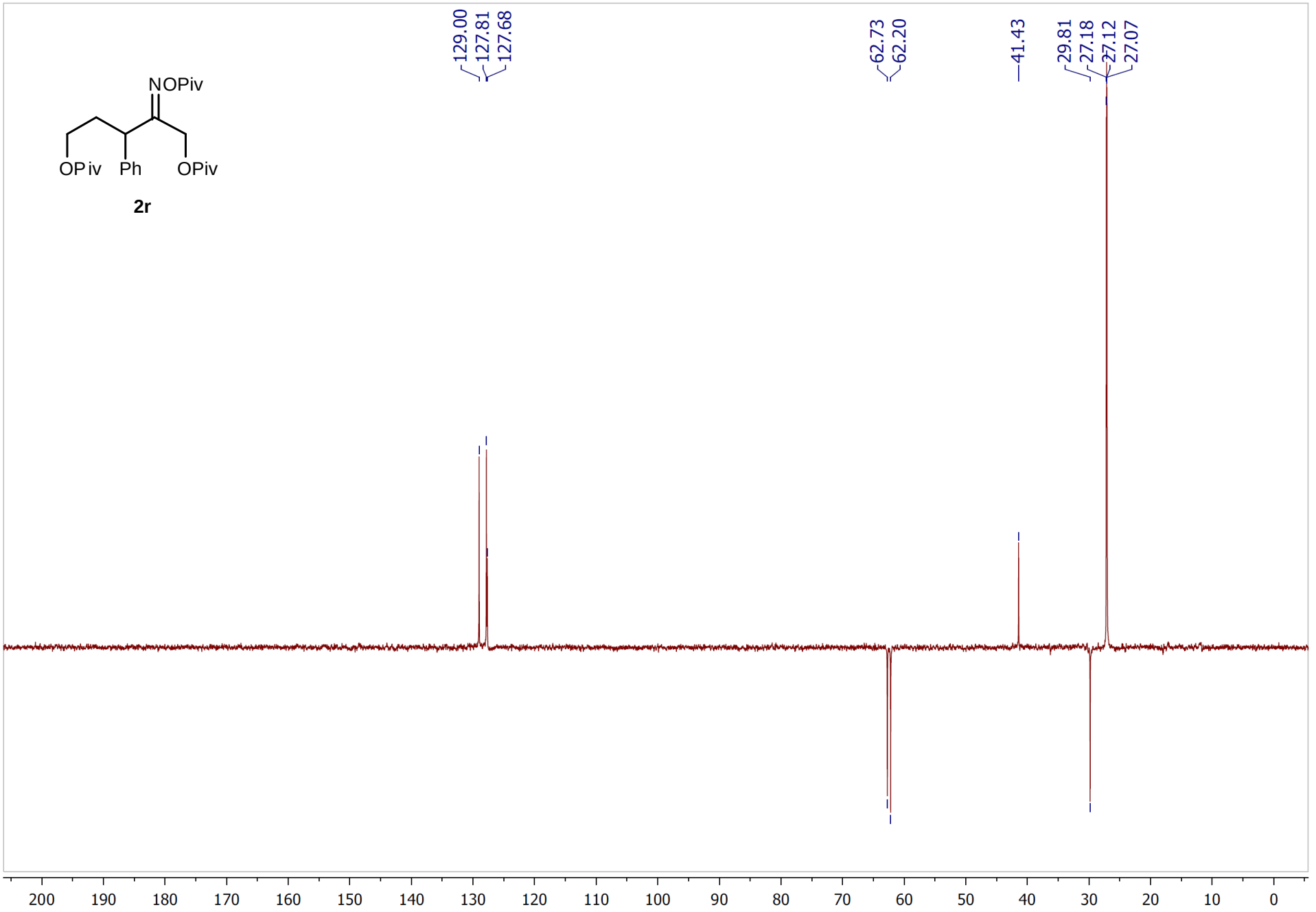
^{1}H NMR



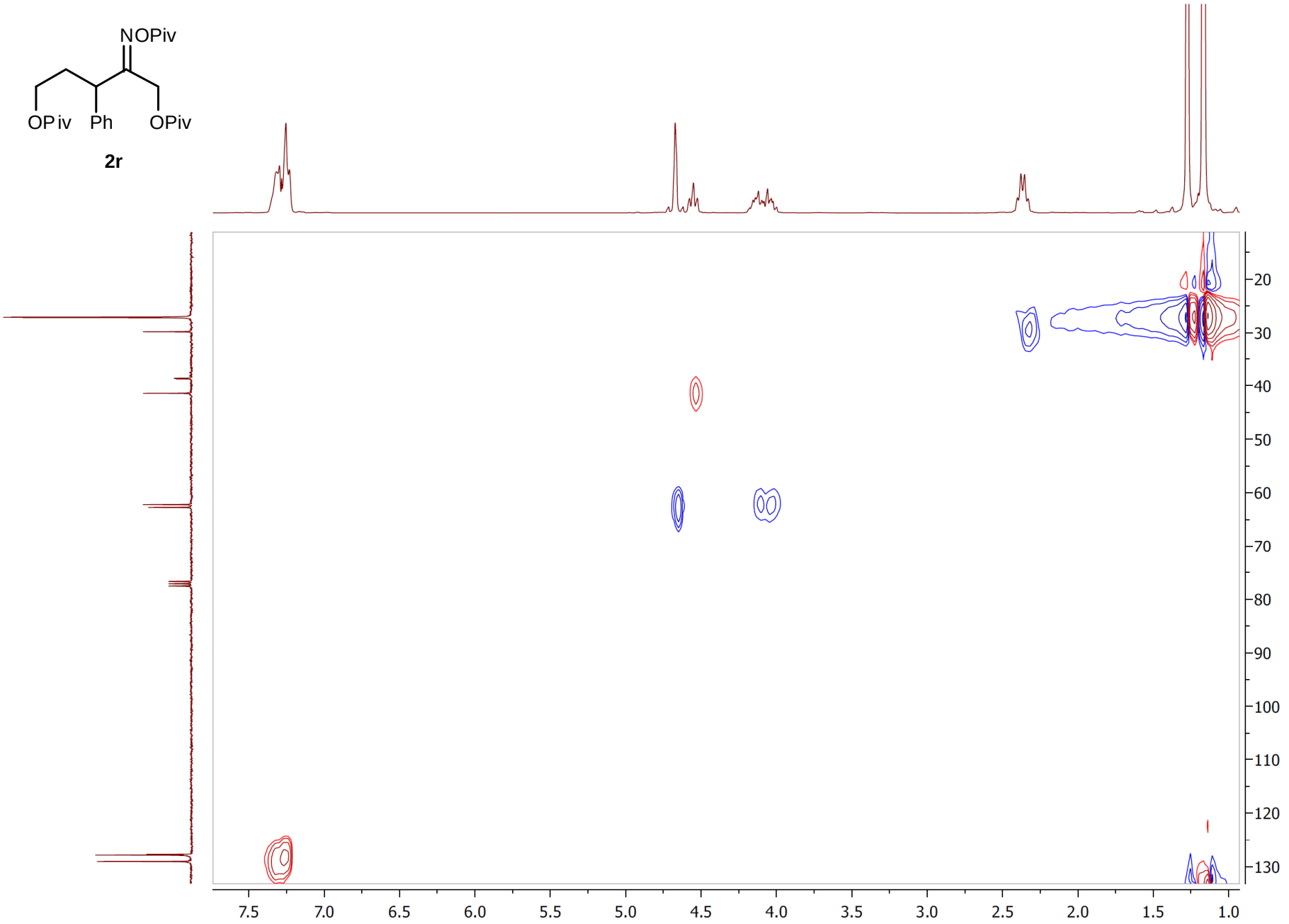
^{13}C NMR


178.18
177.37
174.32
163.42
137.21
129.00
127.82
127.68
62.73
62.20
41.43
38.74
38.68
38.63
29.81
27.18
27.12
27.07
NOPiv
OPiv
Ph
OPiv
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

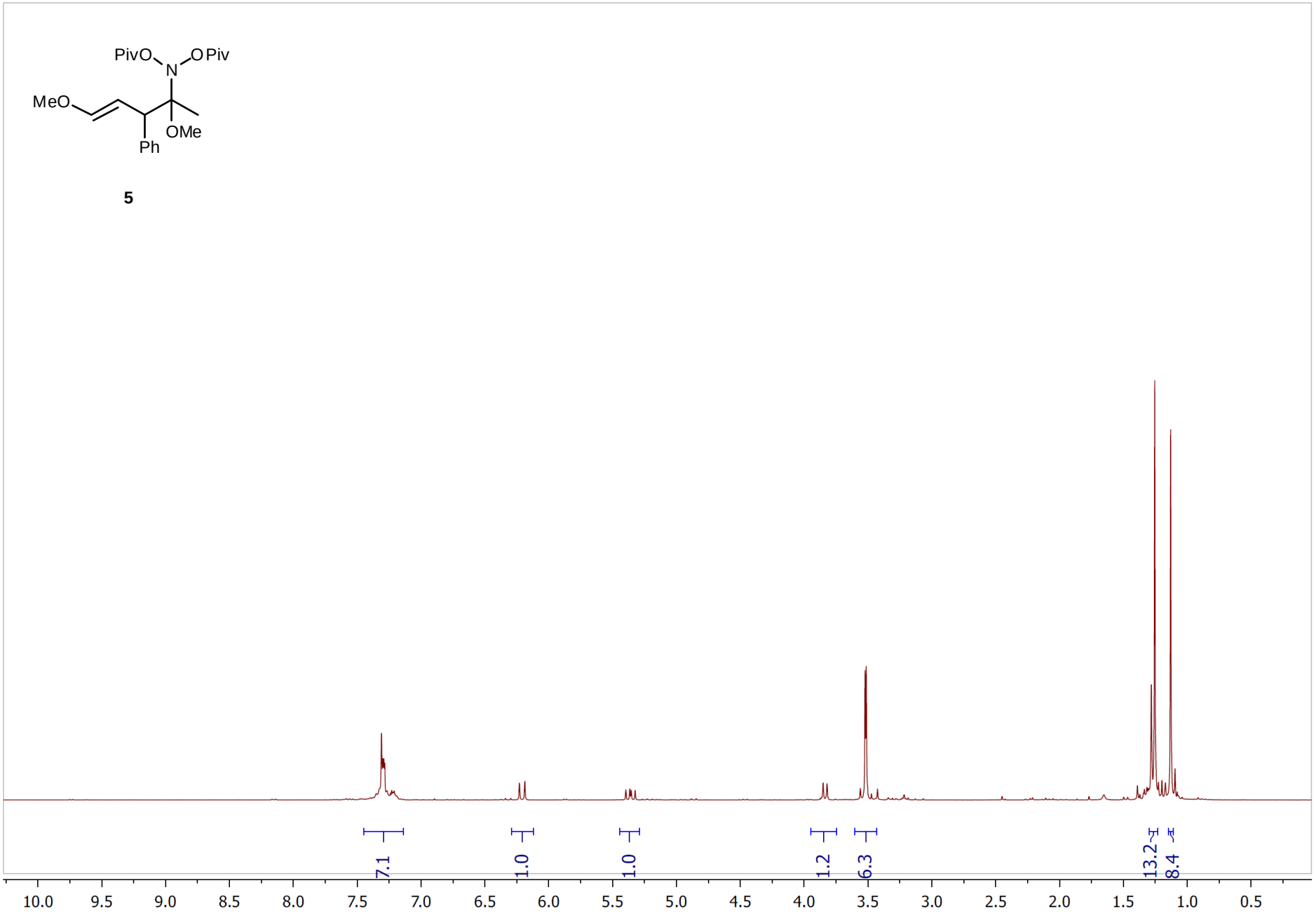

129.00
127.81
127.68
62.73
62.20
41.43
29.81
27.18
27.12
27.07
NOPiv
OPiv
Ph
OPiv
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

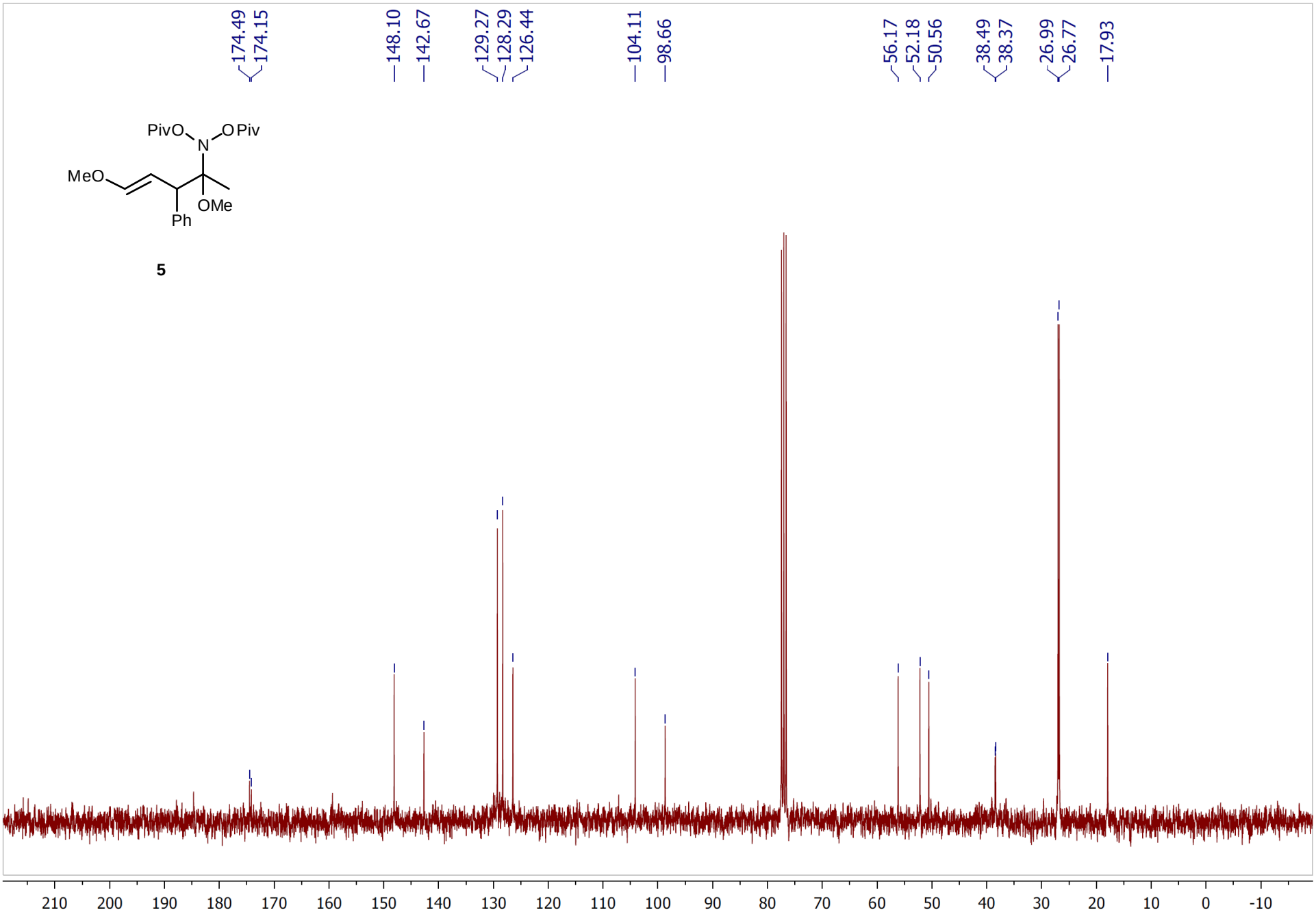

NOPiv
OPiv
Ph
OPiv
2r
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

_O_-Pivaloyl-_N_-(pivaloyloxy)-_N_-((3_E_)-1,4-dimethoxy-1-methylbut-3-en-1-yl)hydroxylamine 5

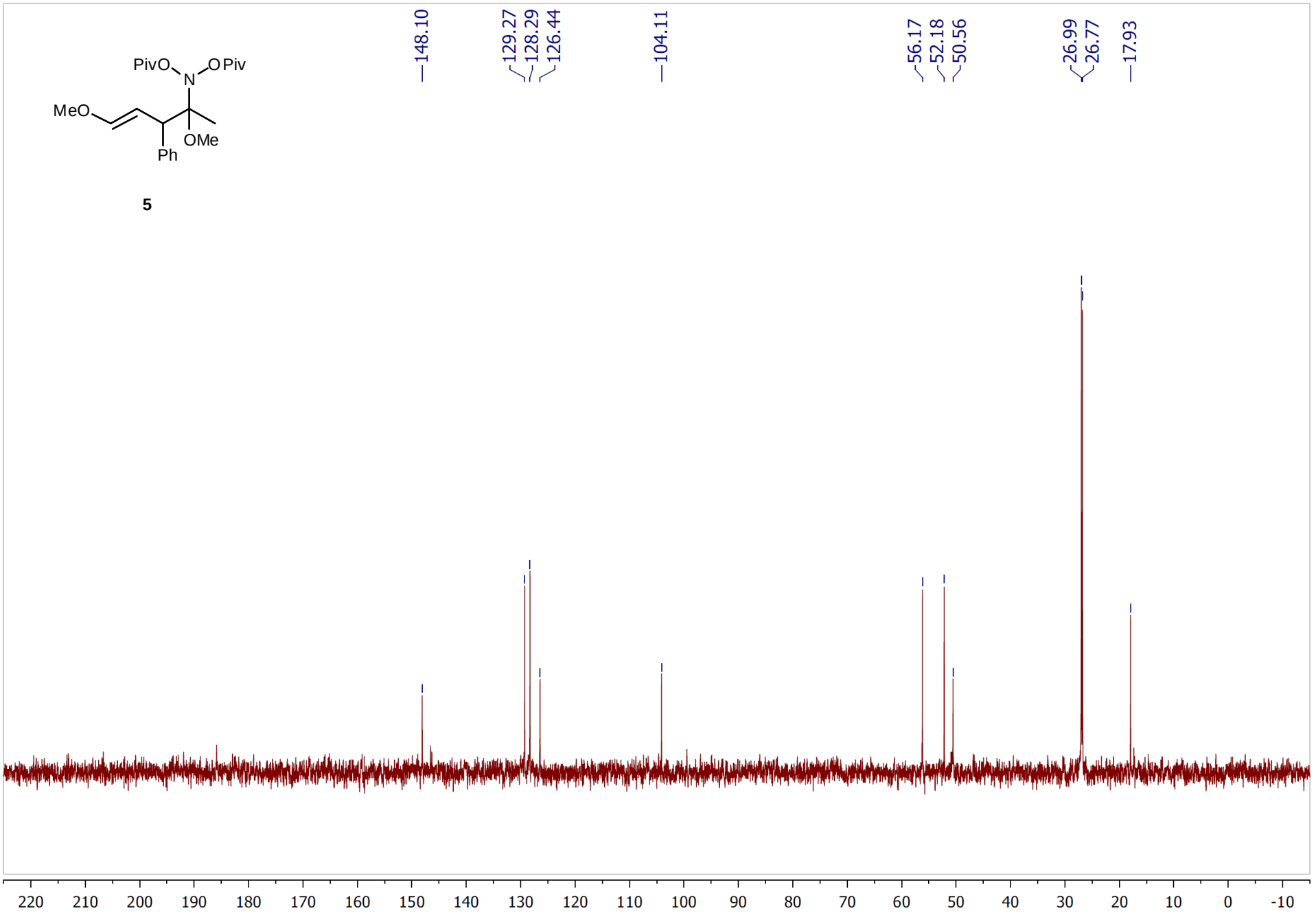
^{1}H NMR



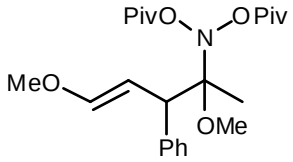
^{13}C NMR


174.49
174.15
148.10
142.67
129.27
128.29
126.44
104.11
98.66
56.17
52.18
50.56
38.49
38.37
26.99
26.77
17.93
PivO
N
OPiv
MeO
OMe
Ph
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{13}C NMR DEPT


148.10
129.27
128.29
126.44
104.11
56.17
52.18
50.56
26.99
26.77
17.93
PivO
N
OPiv
MeO
OMe
Ph
5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

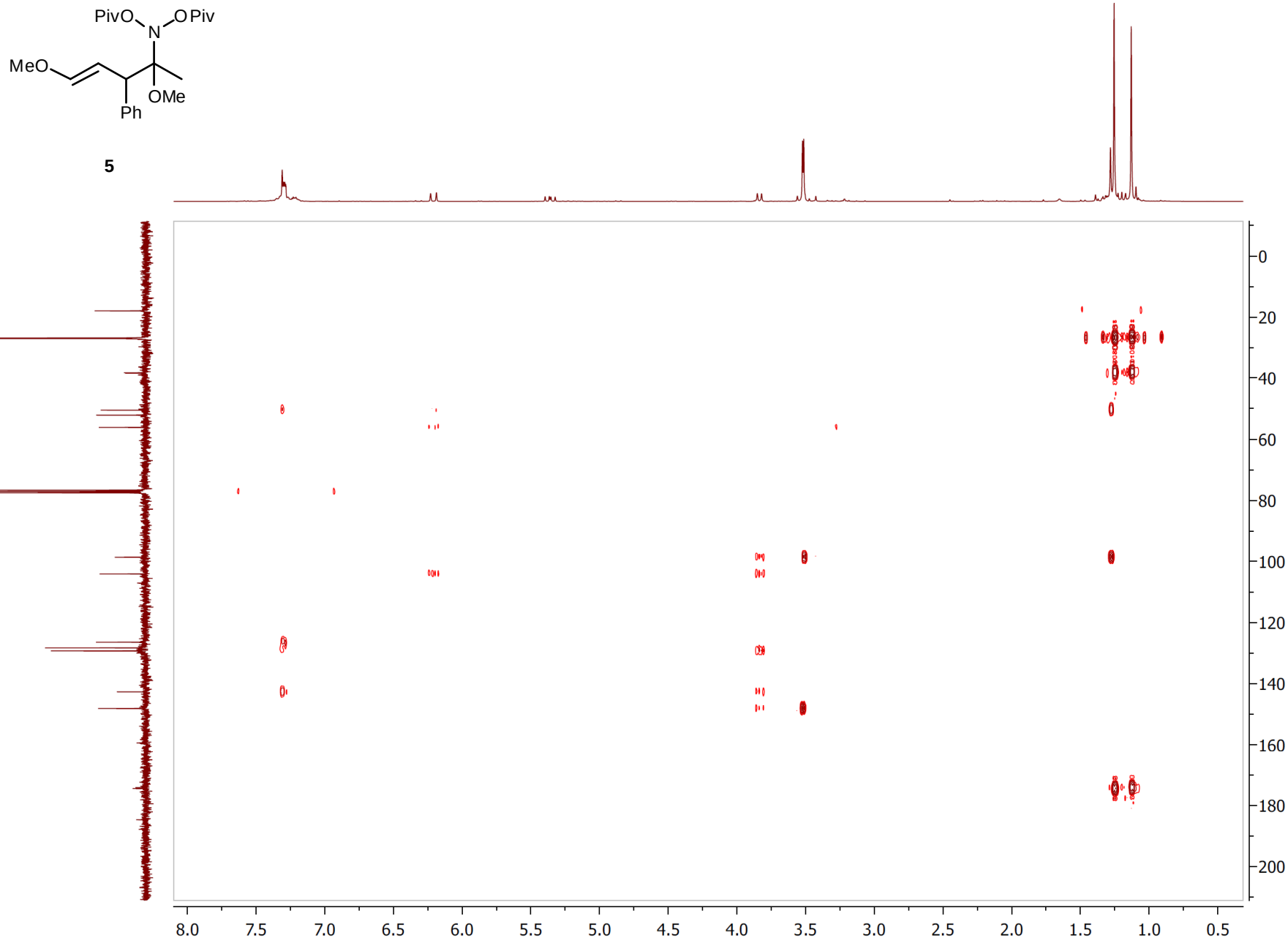
^{1}H-^{13}C HSQC


PivO
N
OPiv
MeO
OMe
Ph

5

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

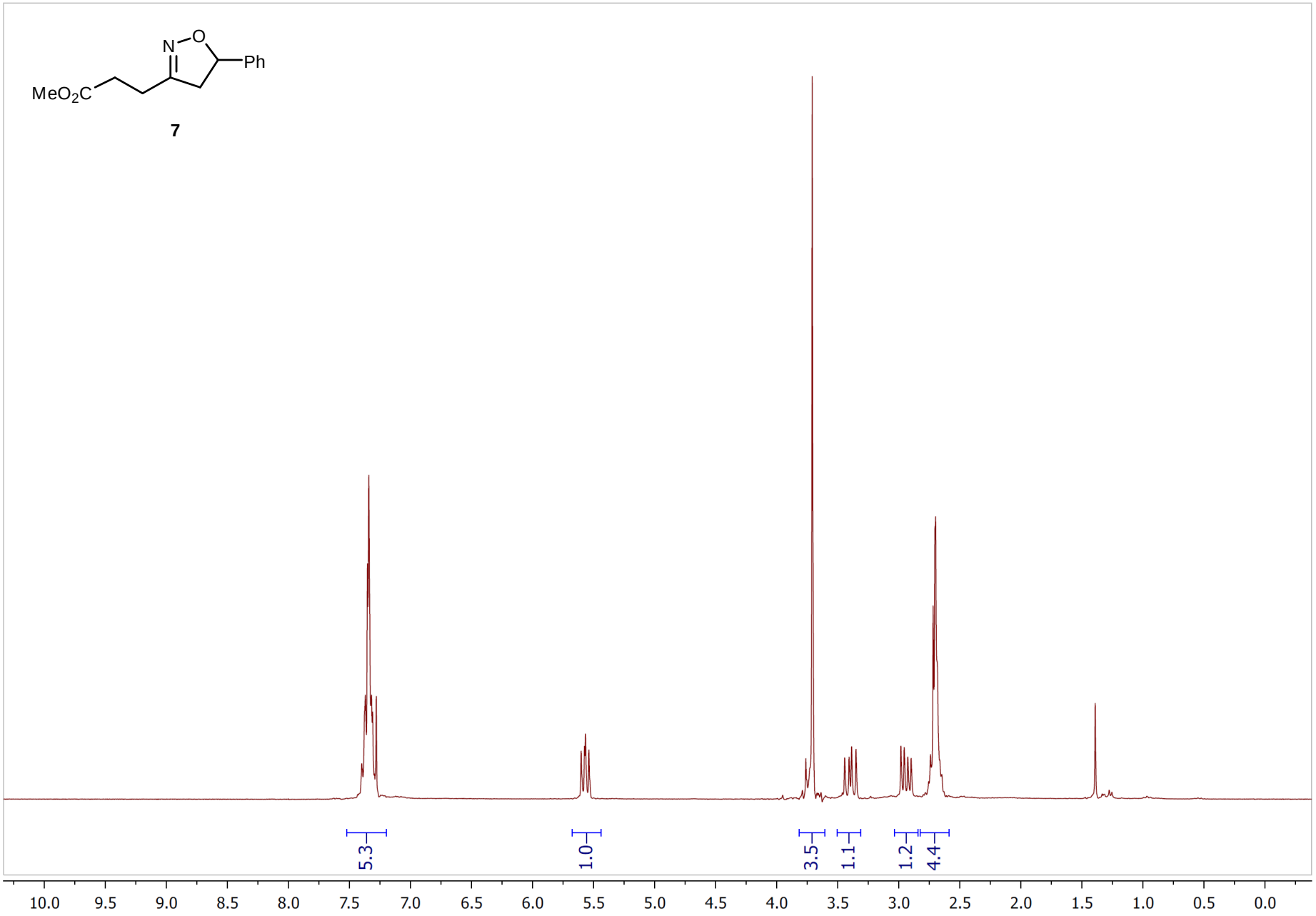
^{1}H-^{13}C HMBC


PivO
N
OPiv
MeO
OMe
Ph
0
20
40
60
80
100
120
140
160
180
200
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

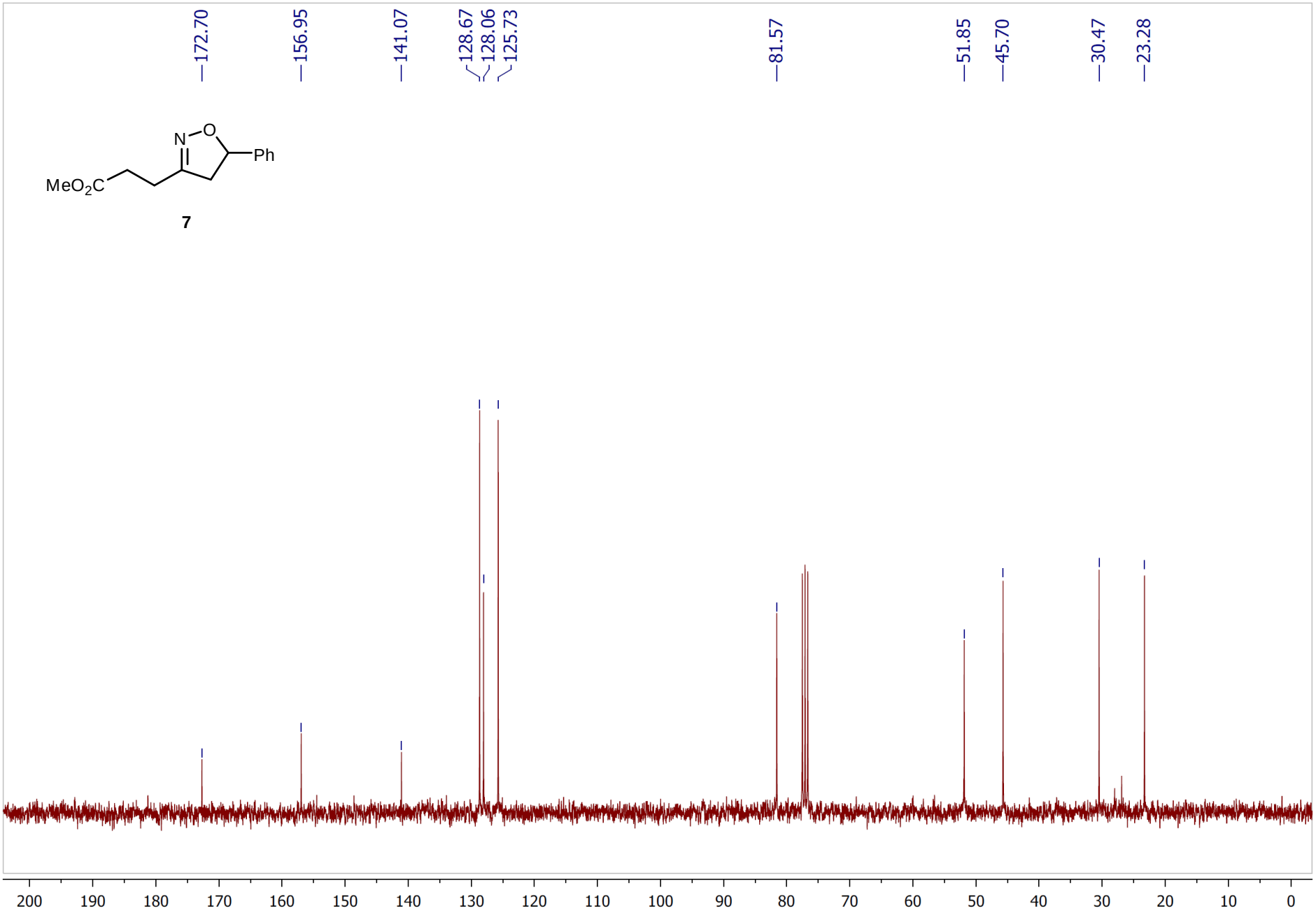
5

Methyl 3-(5-phenyl-4,5-dihydroisoxazol-3-yl)propanoate 7

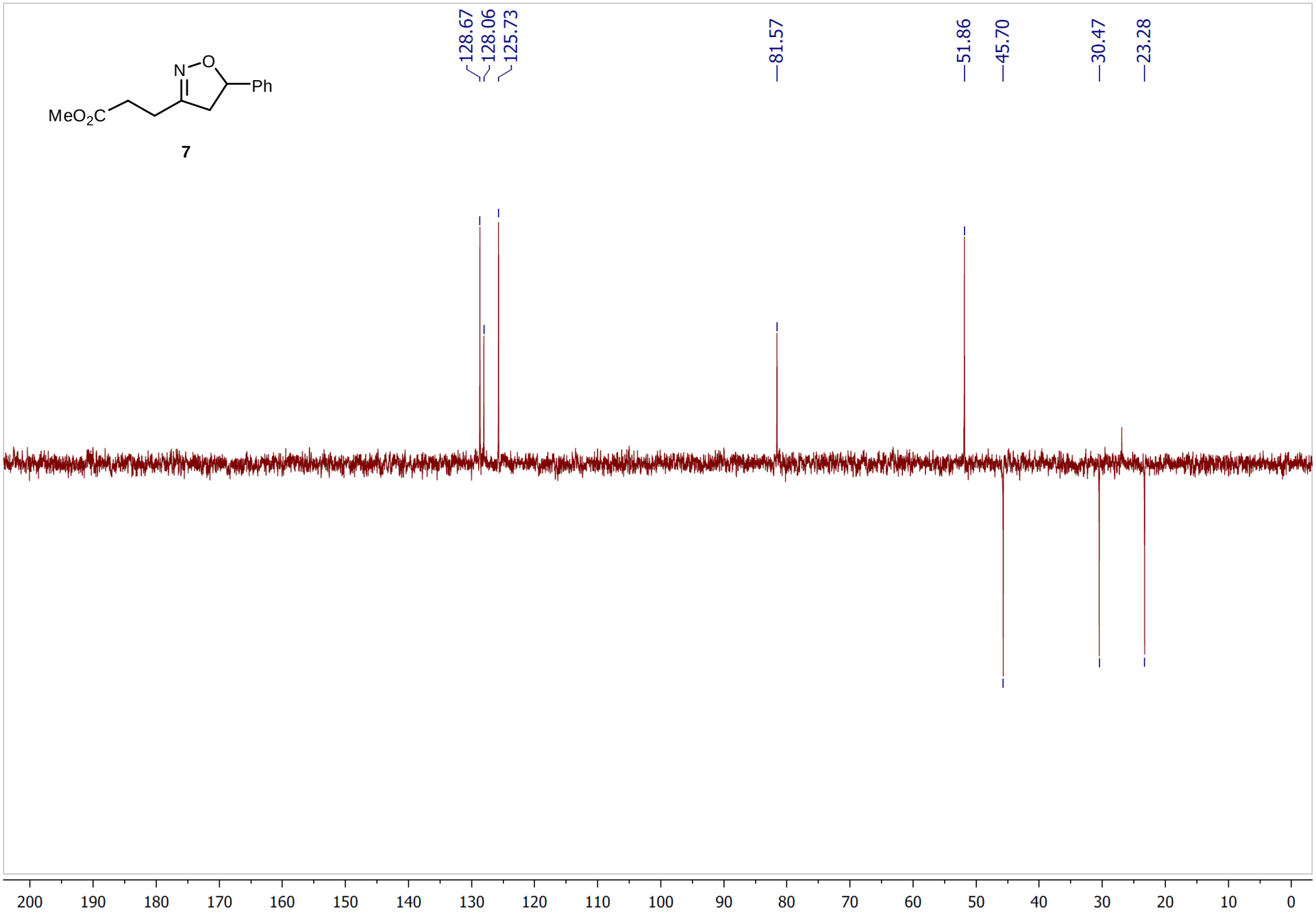
^{1}H NMR



^{13}C NMR

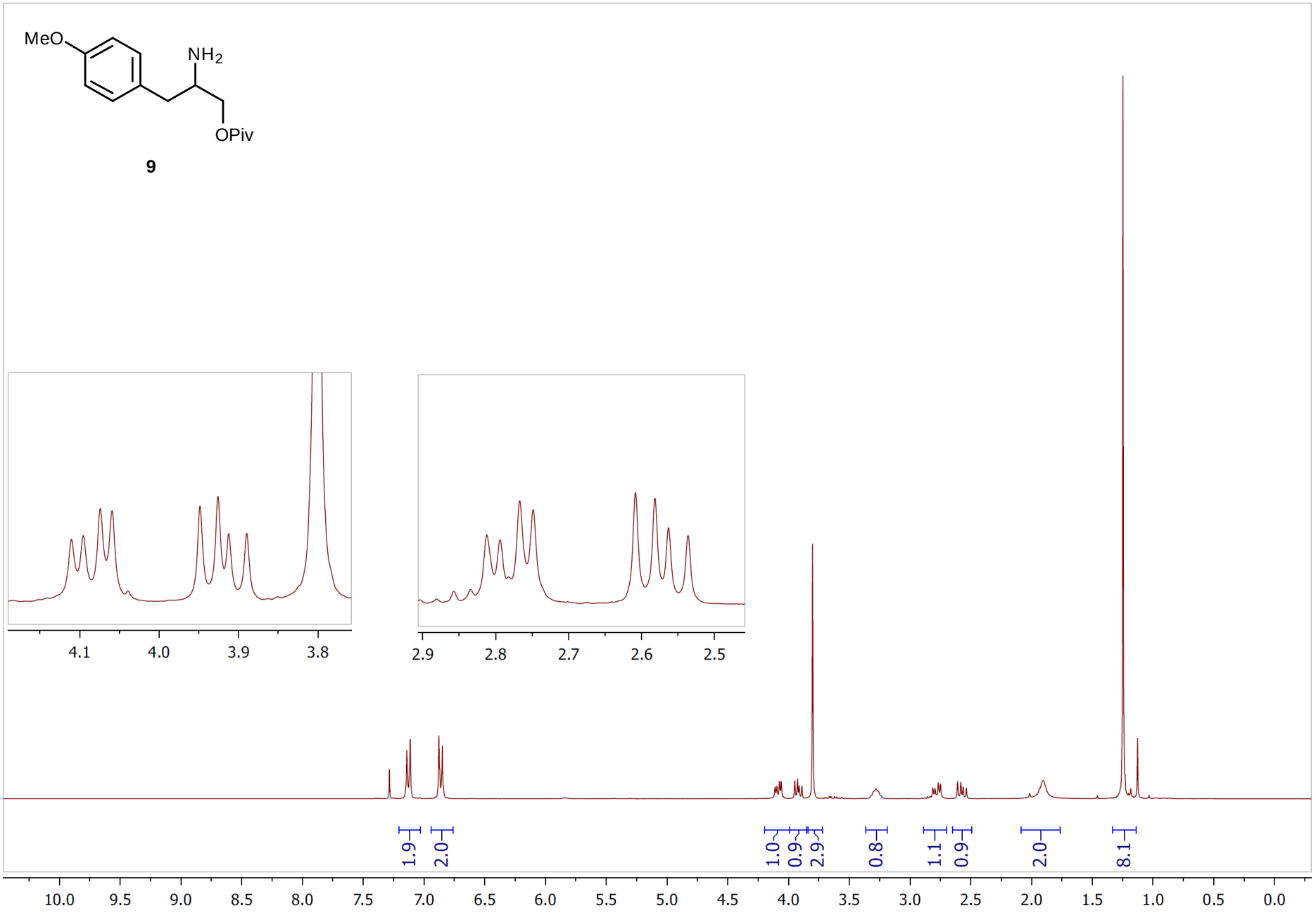

172.70
156.95
141.07
128.67
128.06
125.73
81.57
51.85
45.70
30.47
23.28
N
O
Ph
MeO2C
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

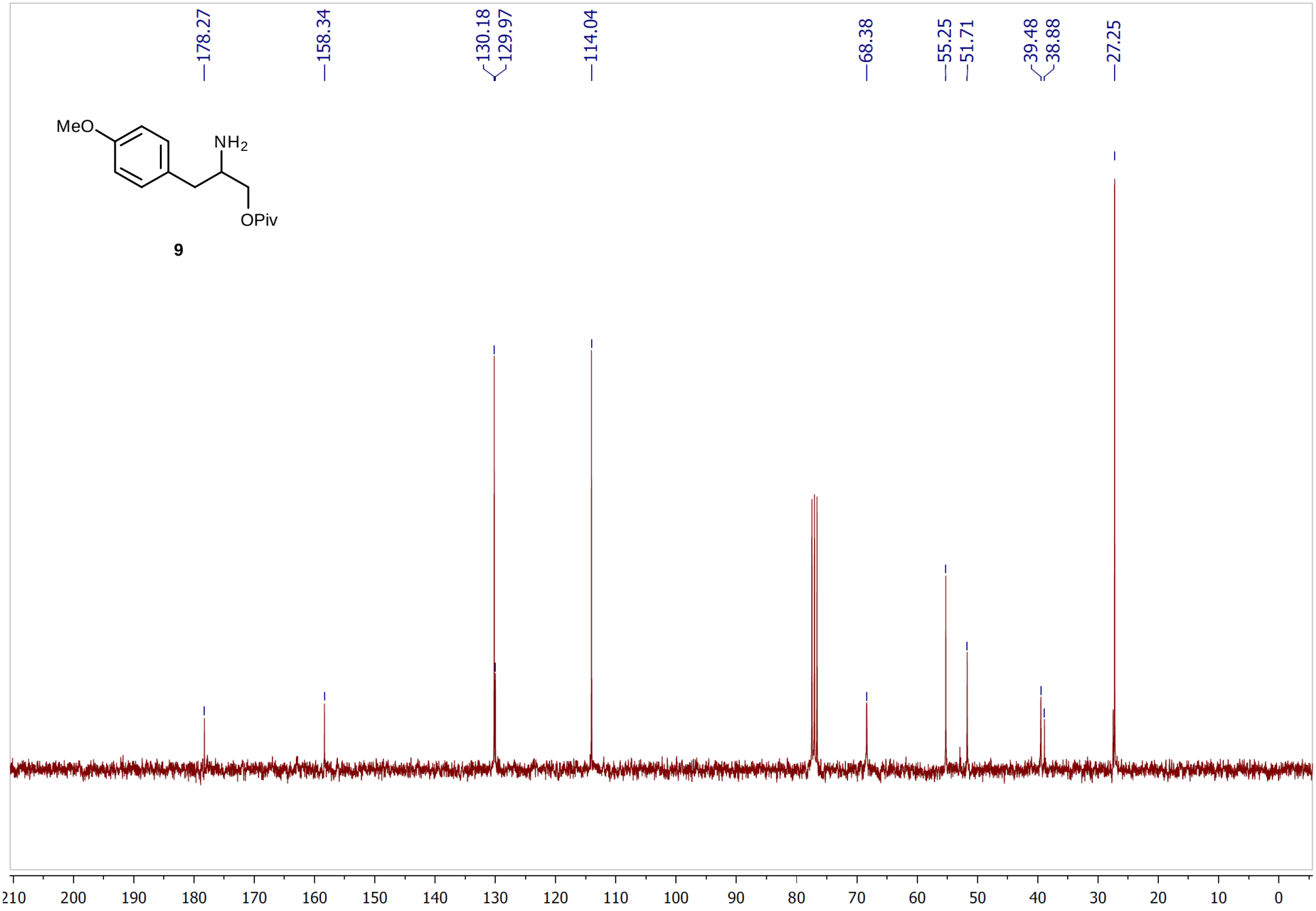

128.67
128.06
125.73
81.57
51.86
45.70
30.47
23.28
N
O
Ph
MeO2C
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2-Amino-3-(4-methoxyphenyl)propyl pivalate 9

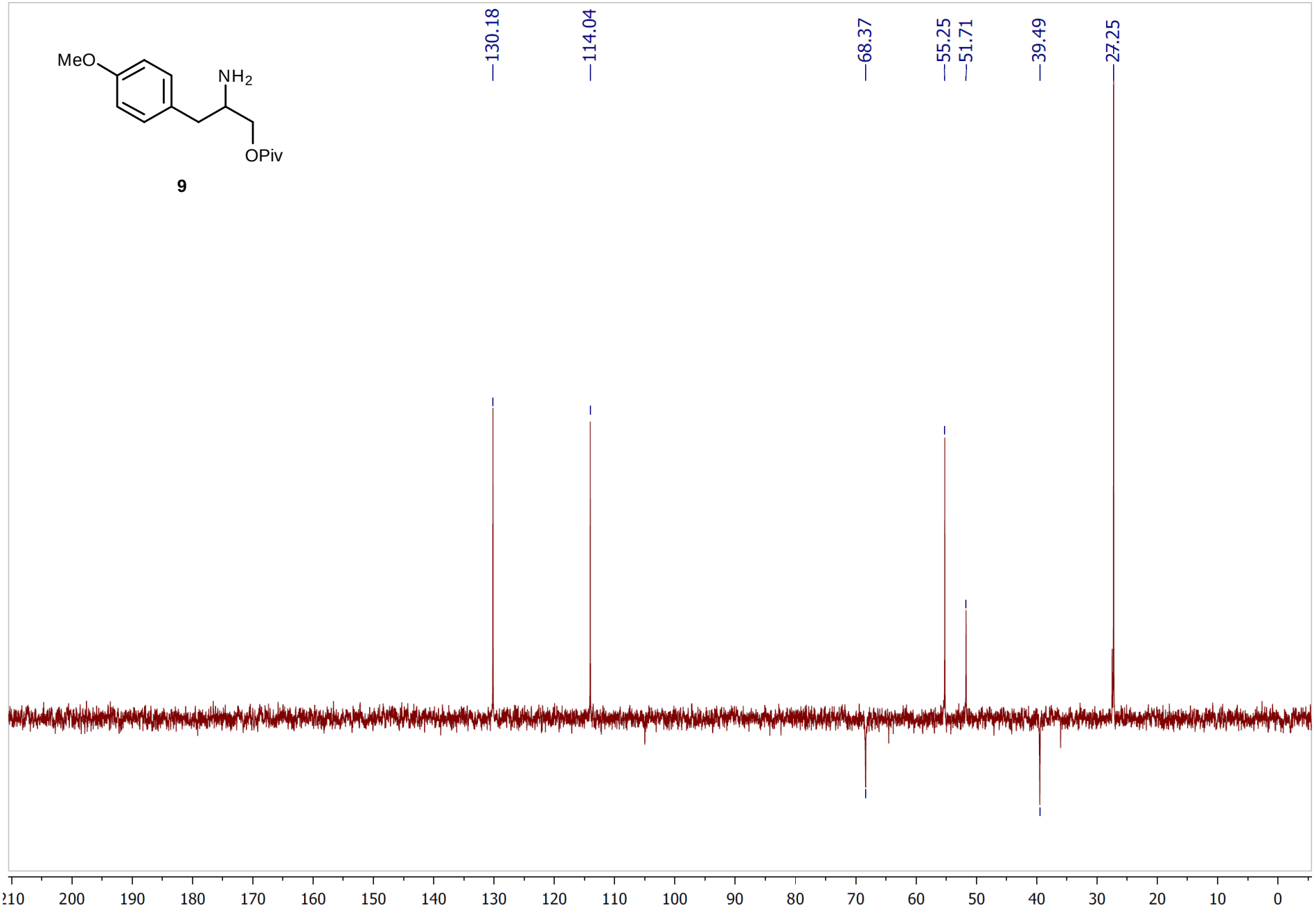
^{1}H NMR



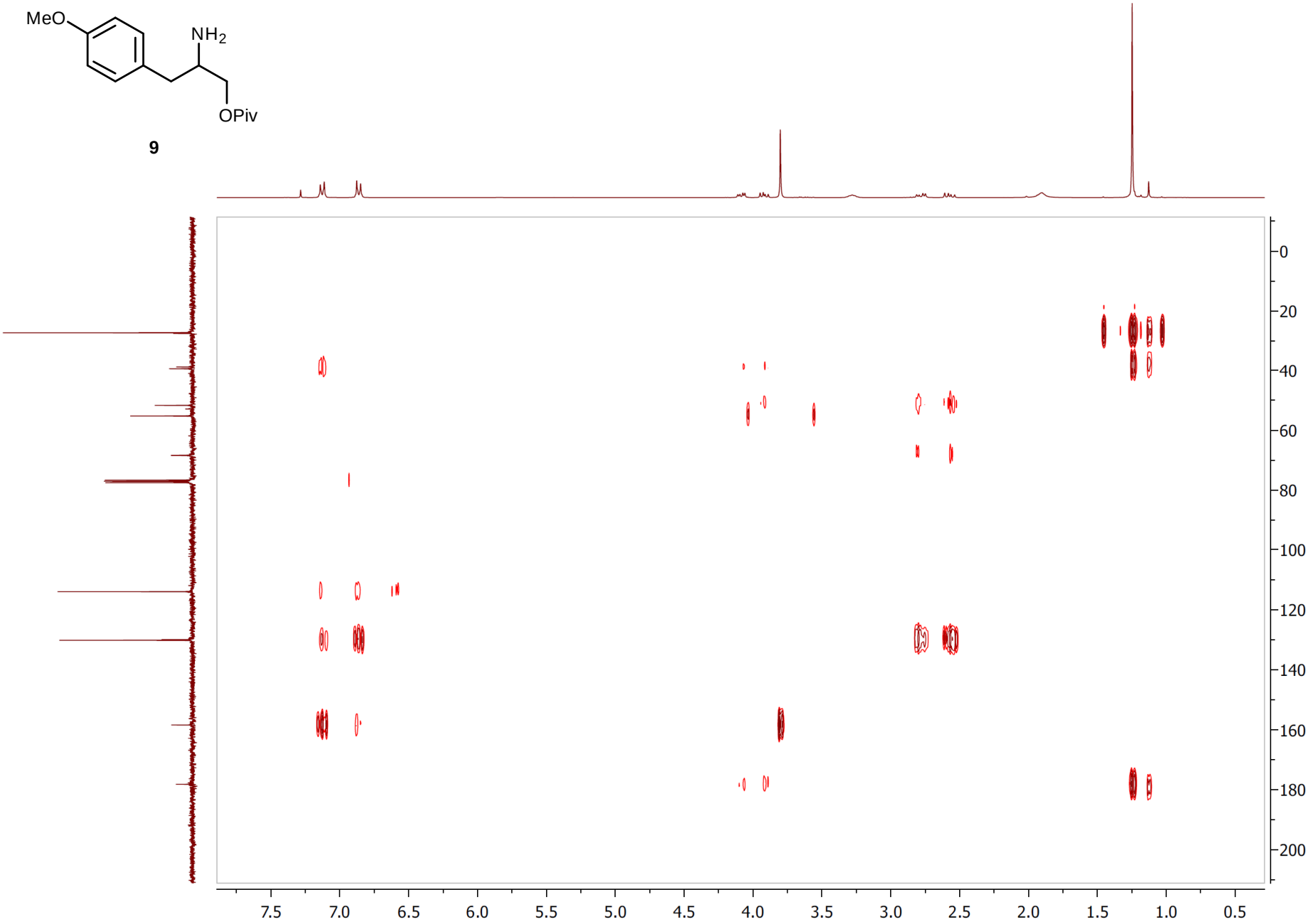
^{13}C NMR


178.27
158.34
130.18
129.97
114.04
68.38
55.25
51.71
39.48
38.88
27.25
MeO
NH2
OPiv
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

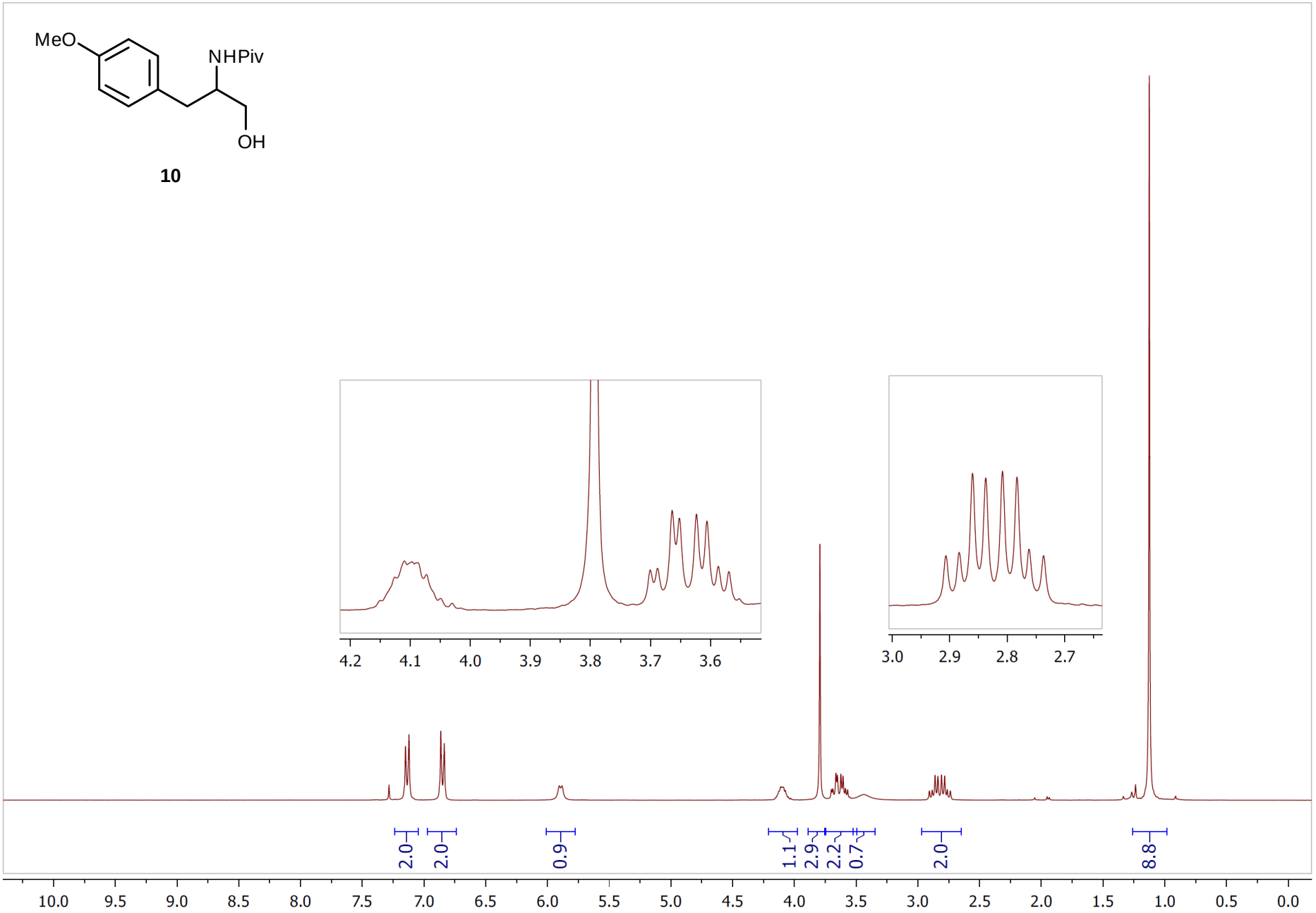

MeO
NH2
OPiv
9
130.18
114.04
68.37
55.25
51.71
39.49
27.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

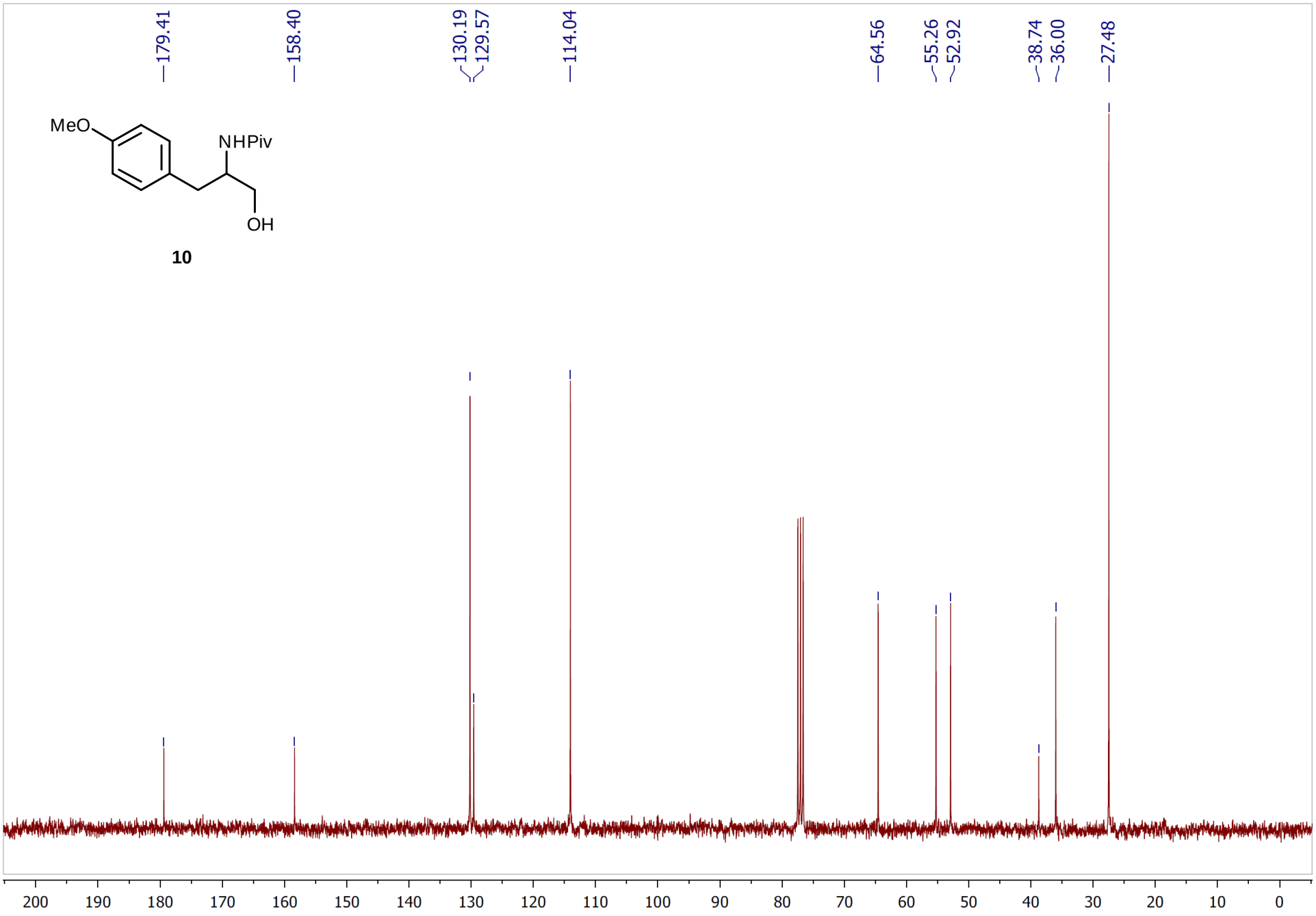

MeO
NH2
OPiv
9
0
20
40
60
80
100
120
140
160
180
200
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

_N_-(1-Hydroxy-3-(4-methoxyphenyl)propan-2-yl)pivalamide 10

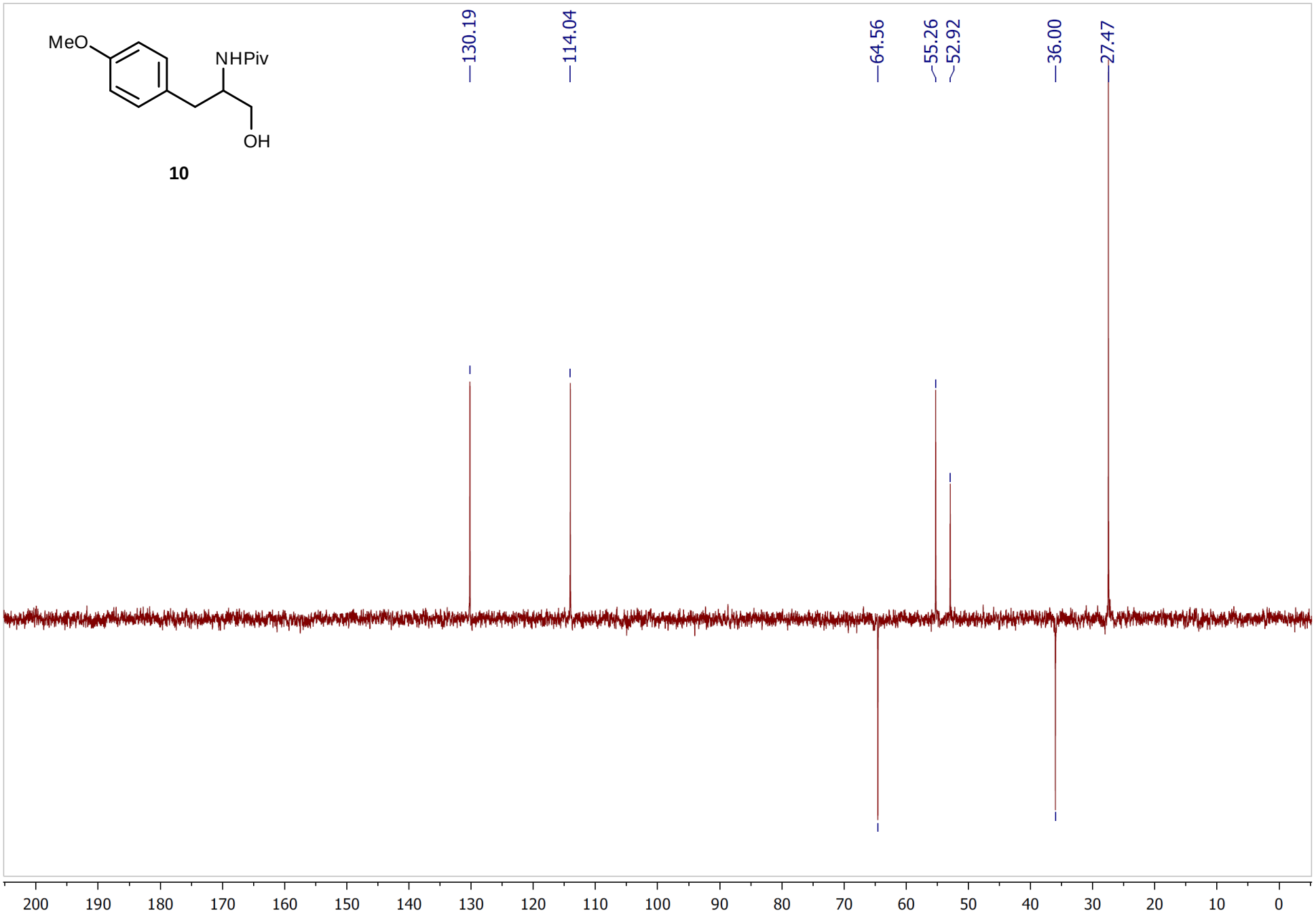
^{1}H NMR



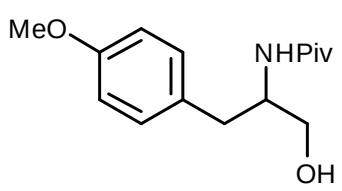
^{13}C NMR


179.41
158.40
130.19
129.57
114.04
64.56
55.26
52.92
38.74
36.00
27.48
MeO
NHPiv
OH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT


MeO
NHPiv
OH
10
130.19
114.04
64.56
55.26
52.92
36.00
27.47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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


MeO
NHPiv
OH

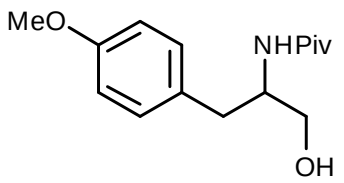
10

1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

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


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

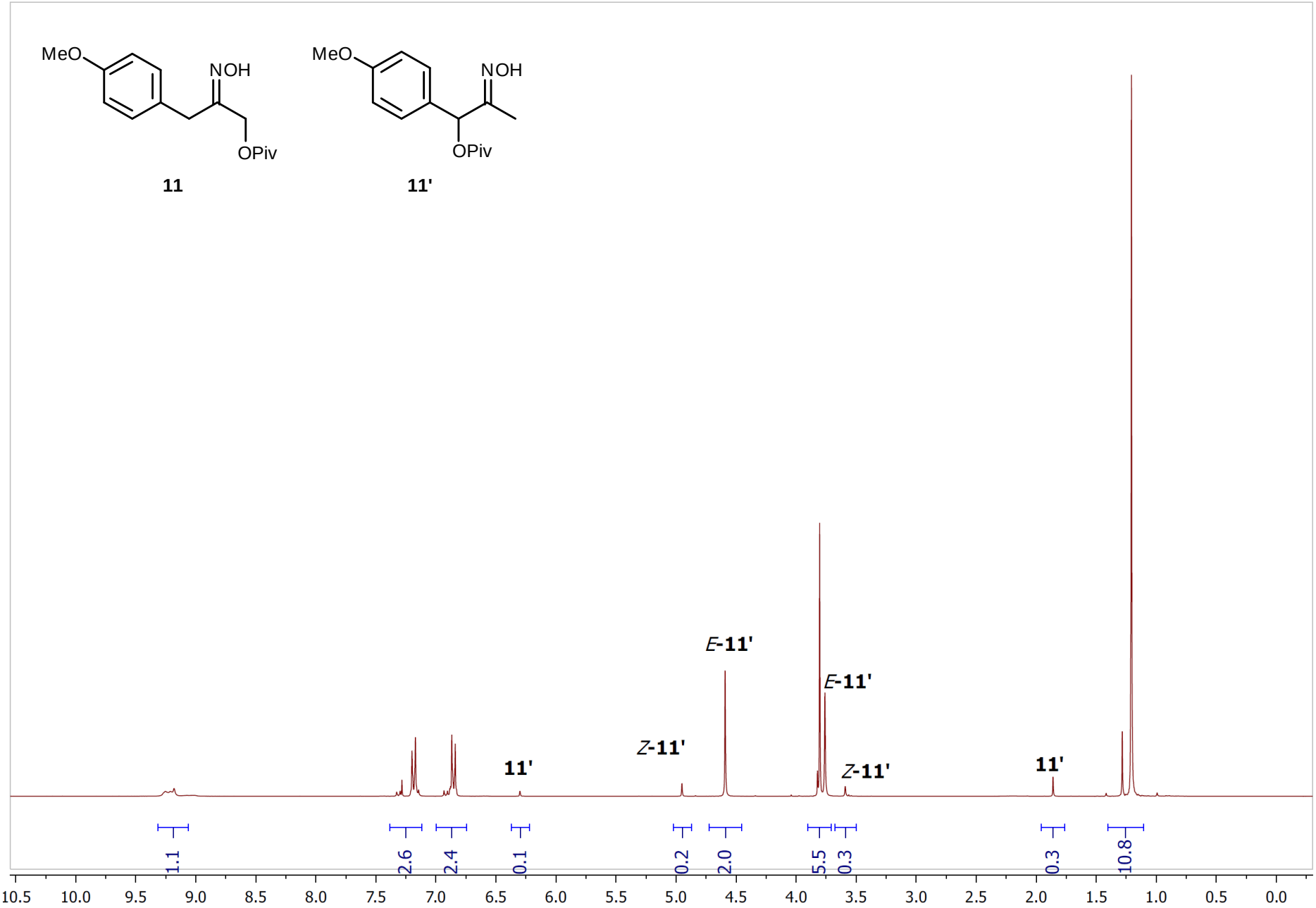
^{1}H-^{13}C HMBC



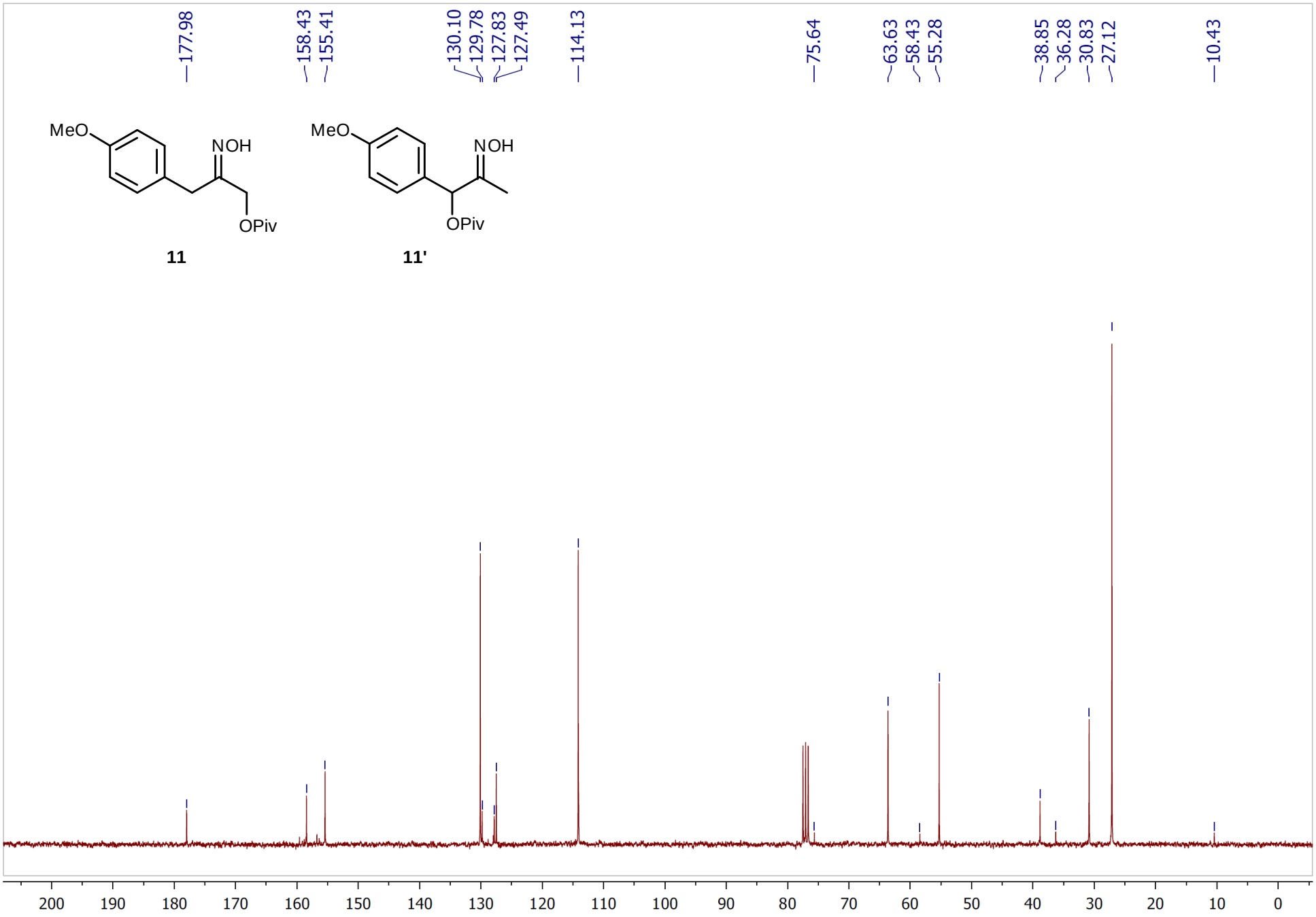
10

2-(Hydroxyimino)-3-(4-methoxyphenyl)propyl pivalate 11 and **2-(Hydroxyimino)-1-(4-methoxyphenyl)propyl pivalate 11'**

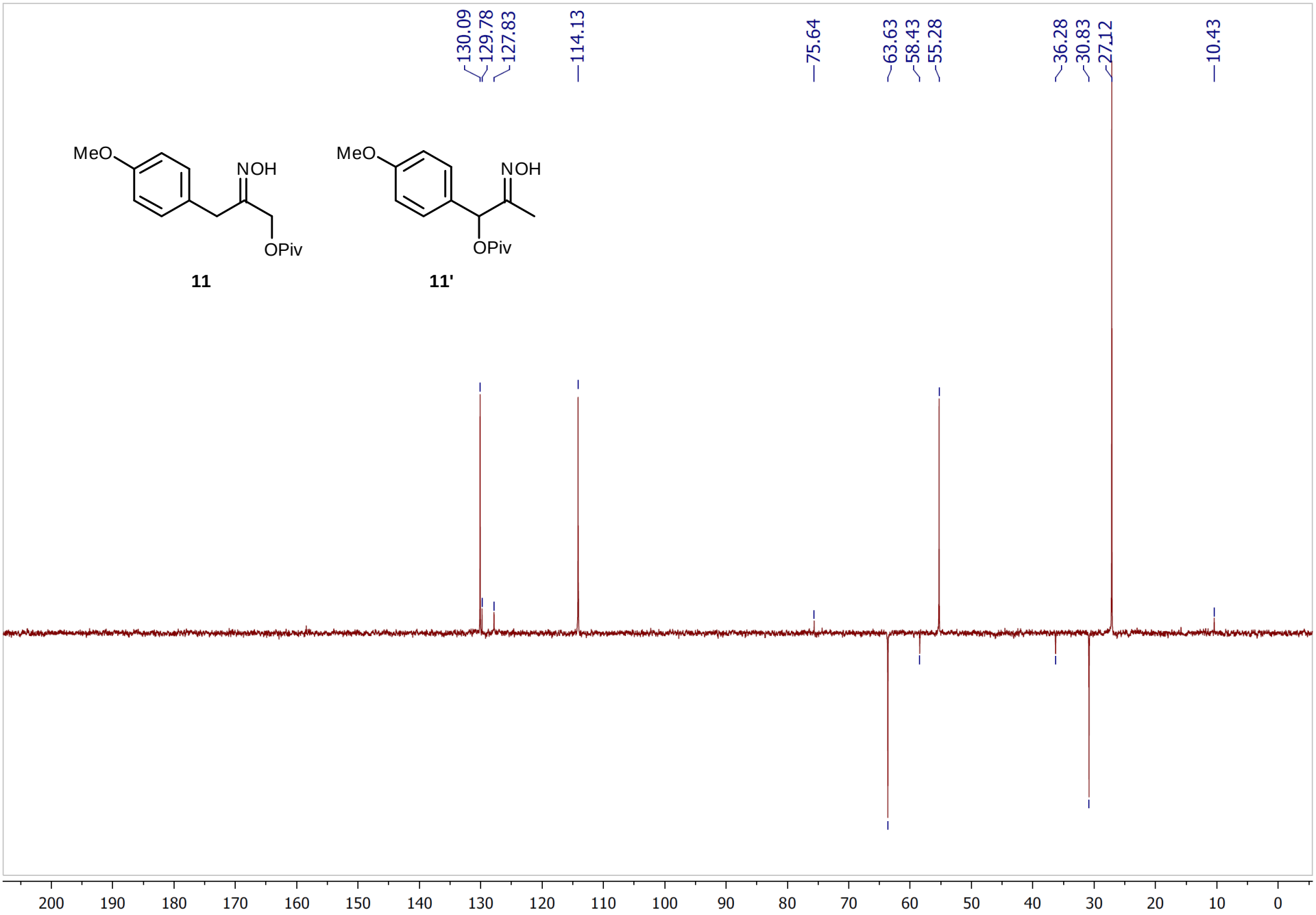
^{1}H NMR



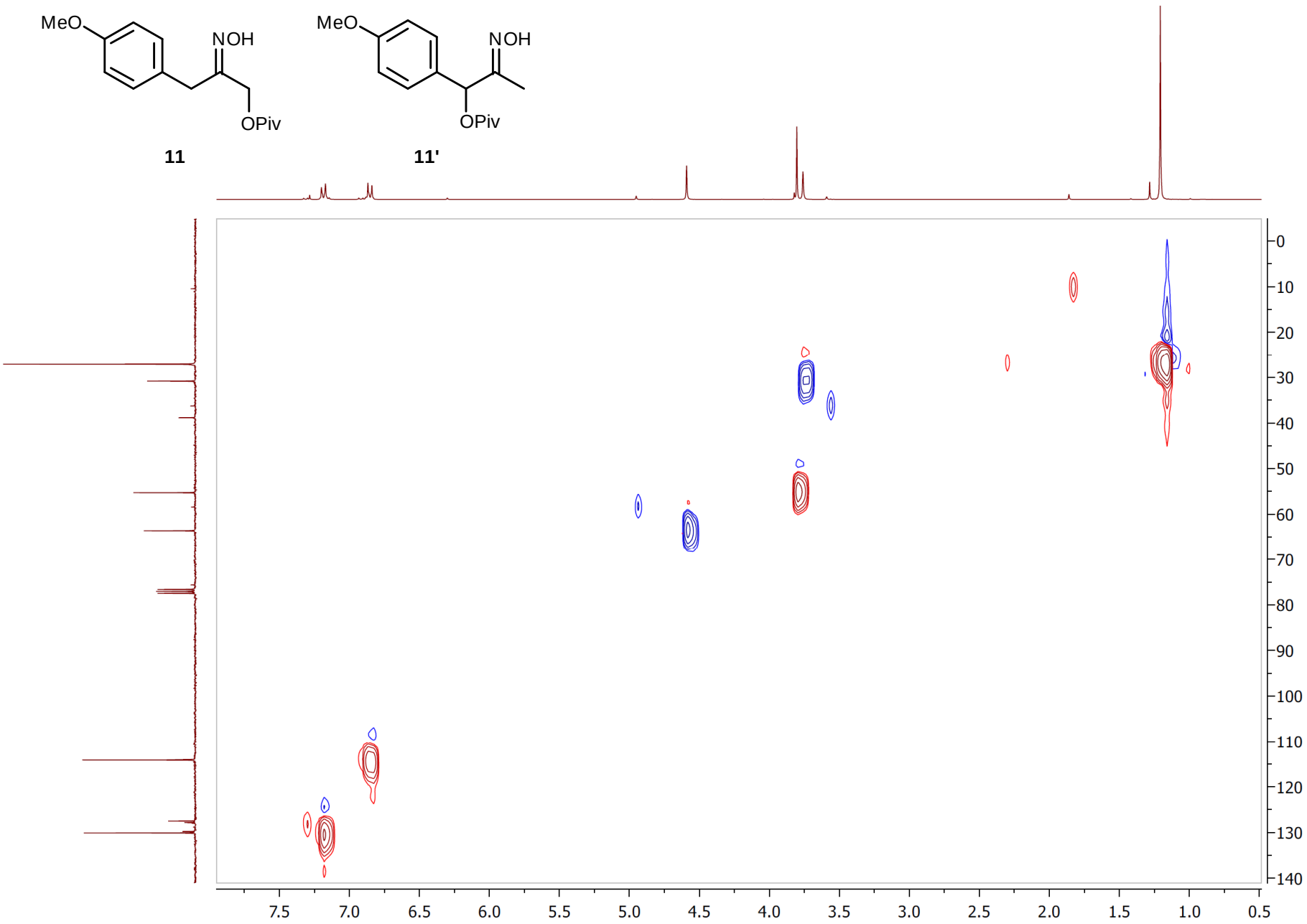
^{13}C NMR


177.98
158.43
155.41
130.10
129.78
127.83
127.49
114.13
75.64
63.63
58.43
55.28
38.85
36.28
30.83
27.12
10.43
MeO
NOH
OPiv
11
MeO
NOH
OPiv
11'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

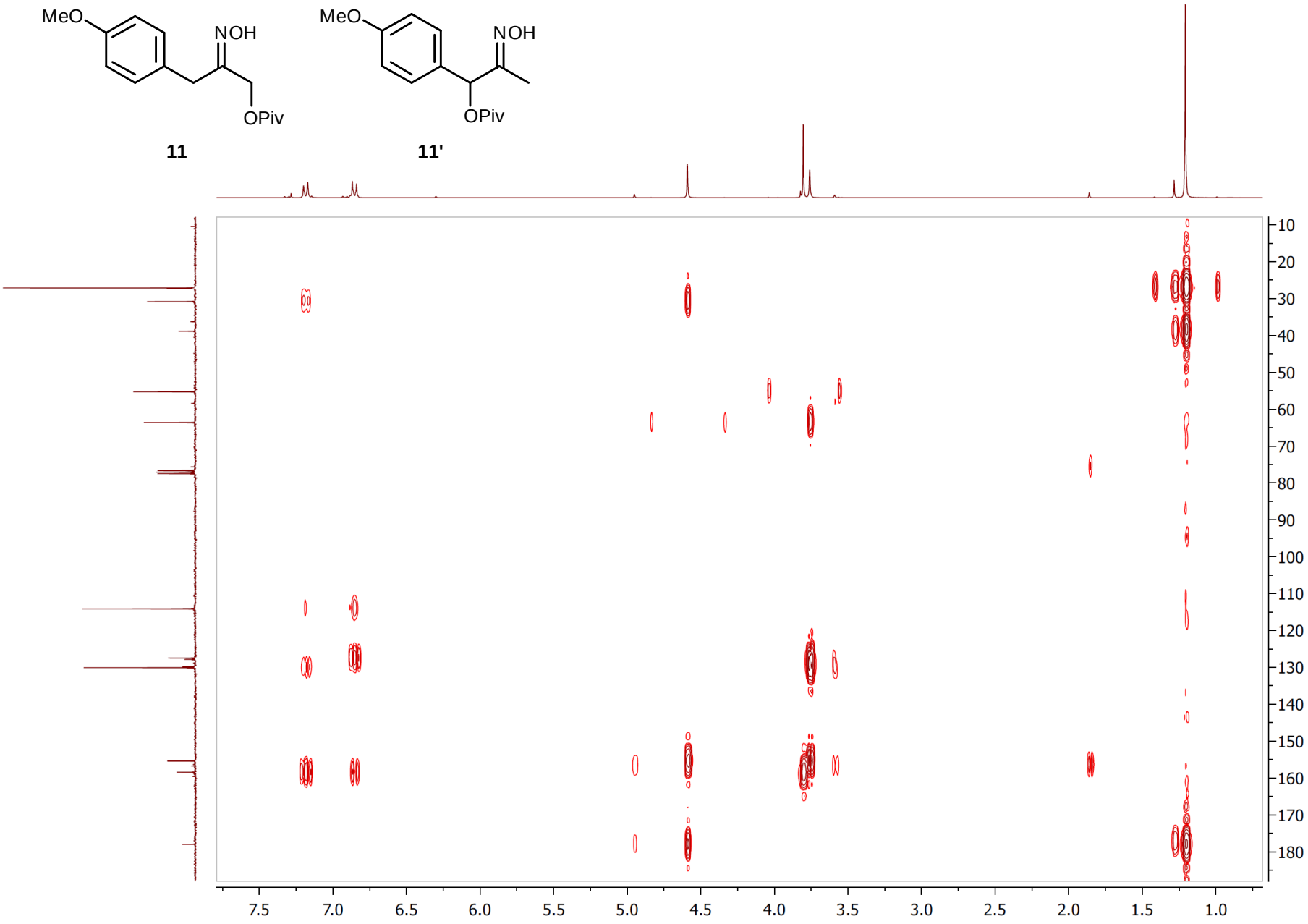
^{13}C NMR DEPT


130.09
129.78
127.83
114.13
75.64
63.63
58.43
55.28
36.28
30.83
27.12
10.43
MeO
NOH
OPiv
11
MeO
NOH
OPiv
11'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

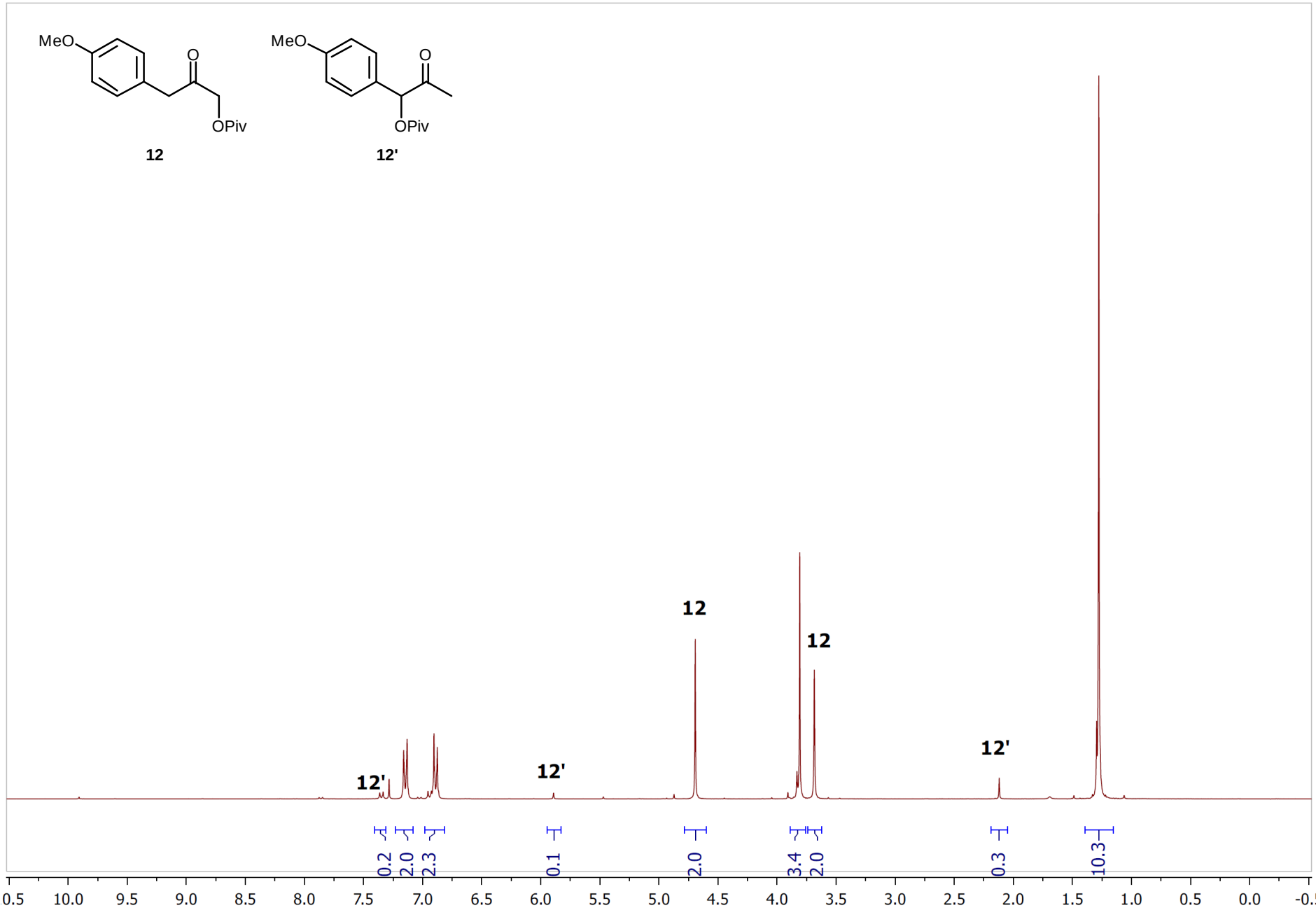

MeO
NOH
OPiv
11
MeO
NOH
OPiv
11'
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

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

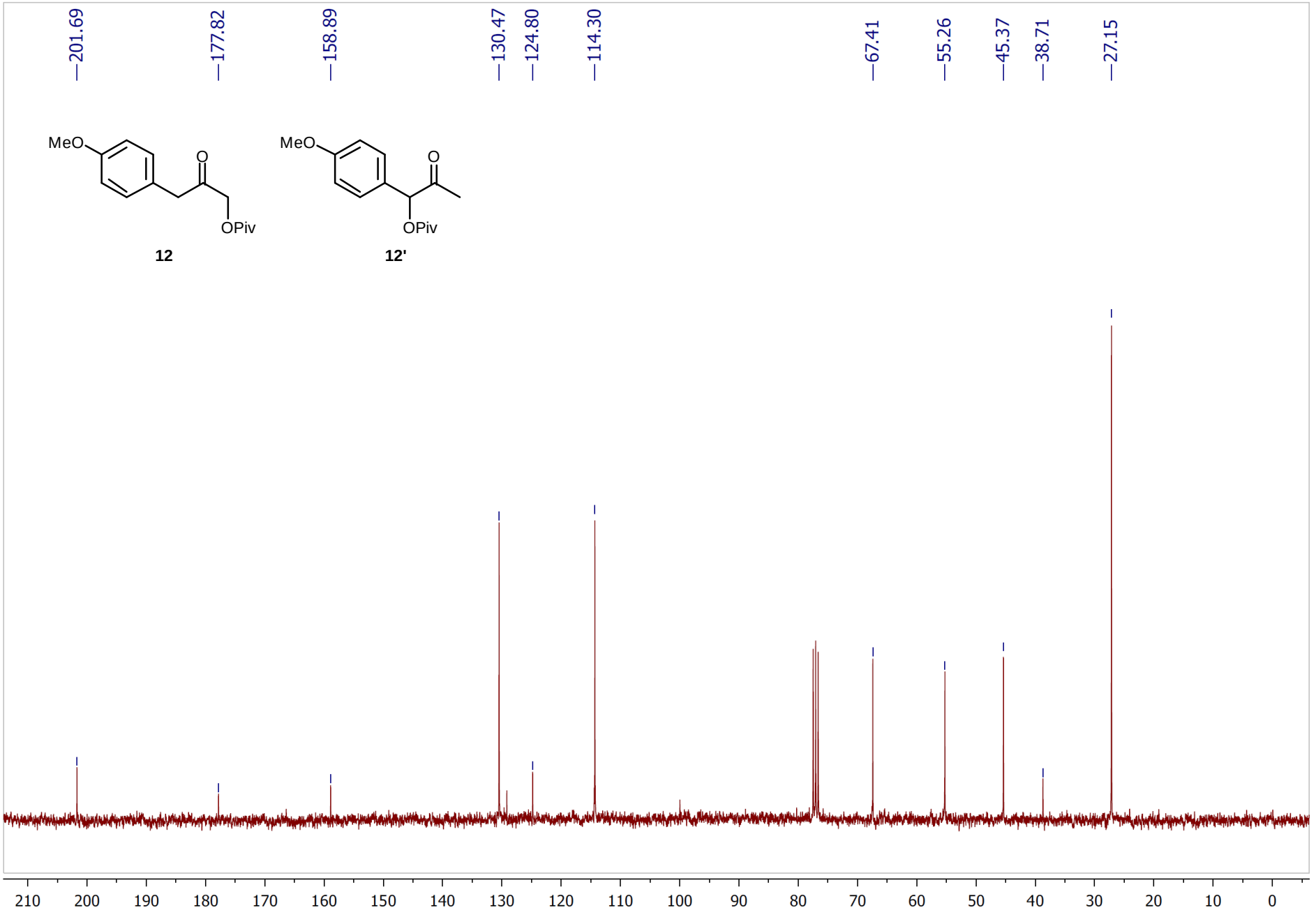

MeO
NOH
OPiv
11
MeO
NOH
OPiv
11'
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

3-(4-Methoxyphenyl)-2-oxopropyl pivalate 12 and **3-(4-methoxyphenyl)-2-oxopropyl pivalate 12'**

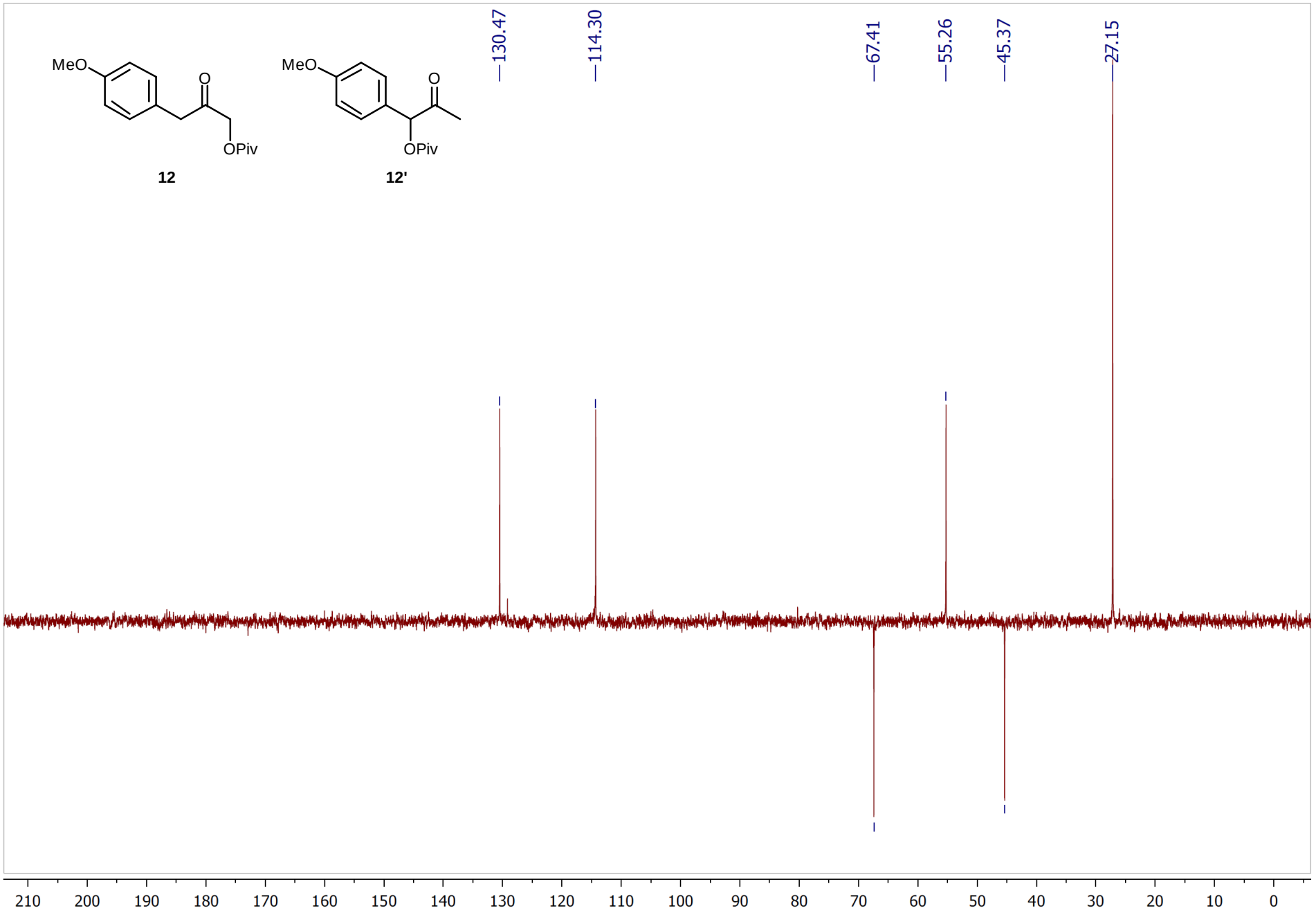
^{1}H NMR



^{13}C NMR

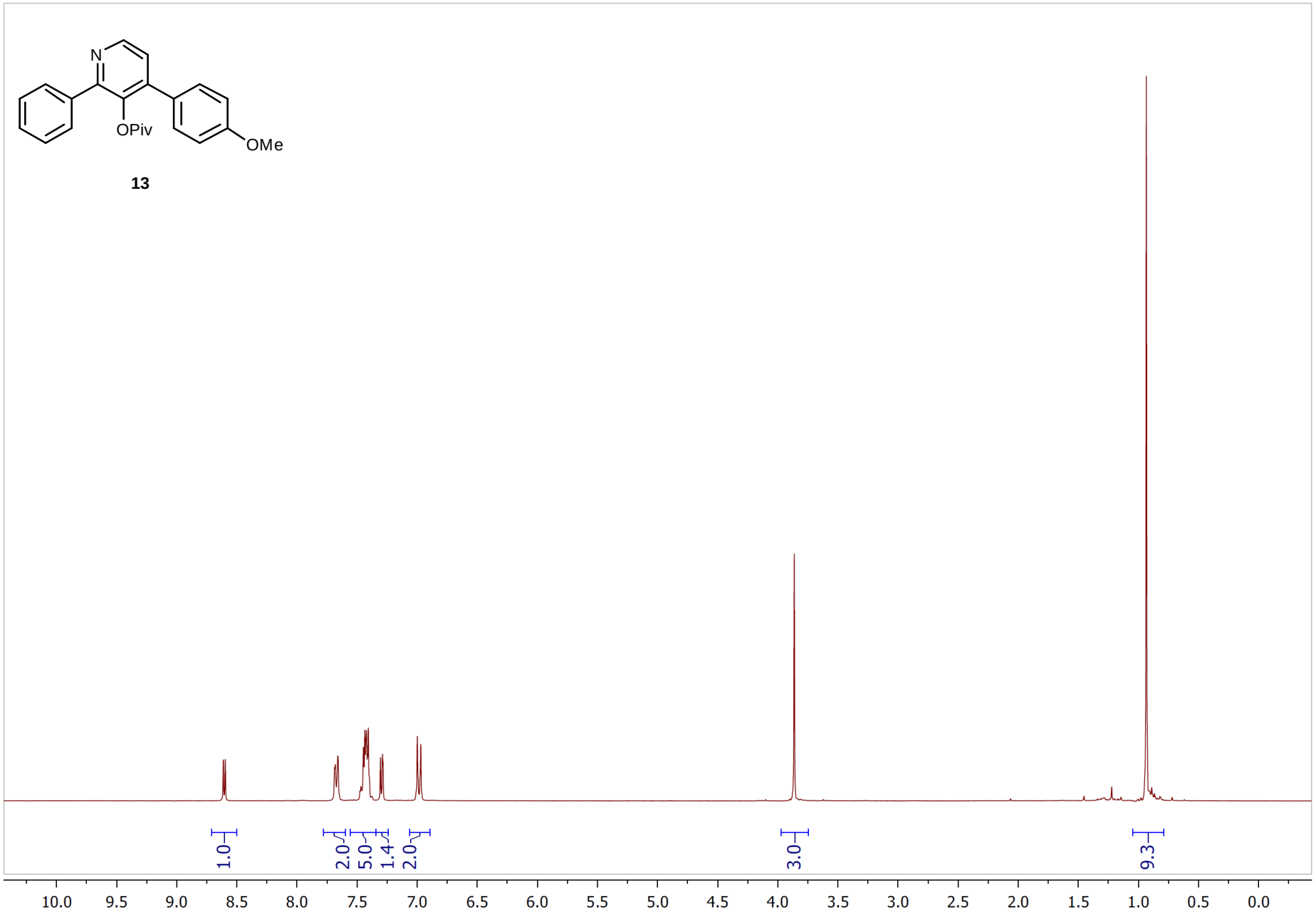

201.69
177.82
158.89
130.47
124.80
114.30
67.41
55.26
45.37
38.71
27.15
MeO
O
OPiv
12
MeO
O
OPiv
12'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT

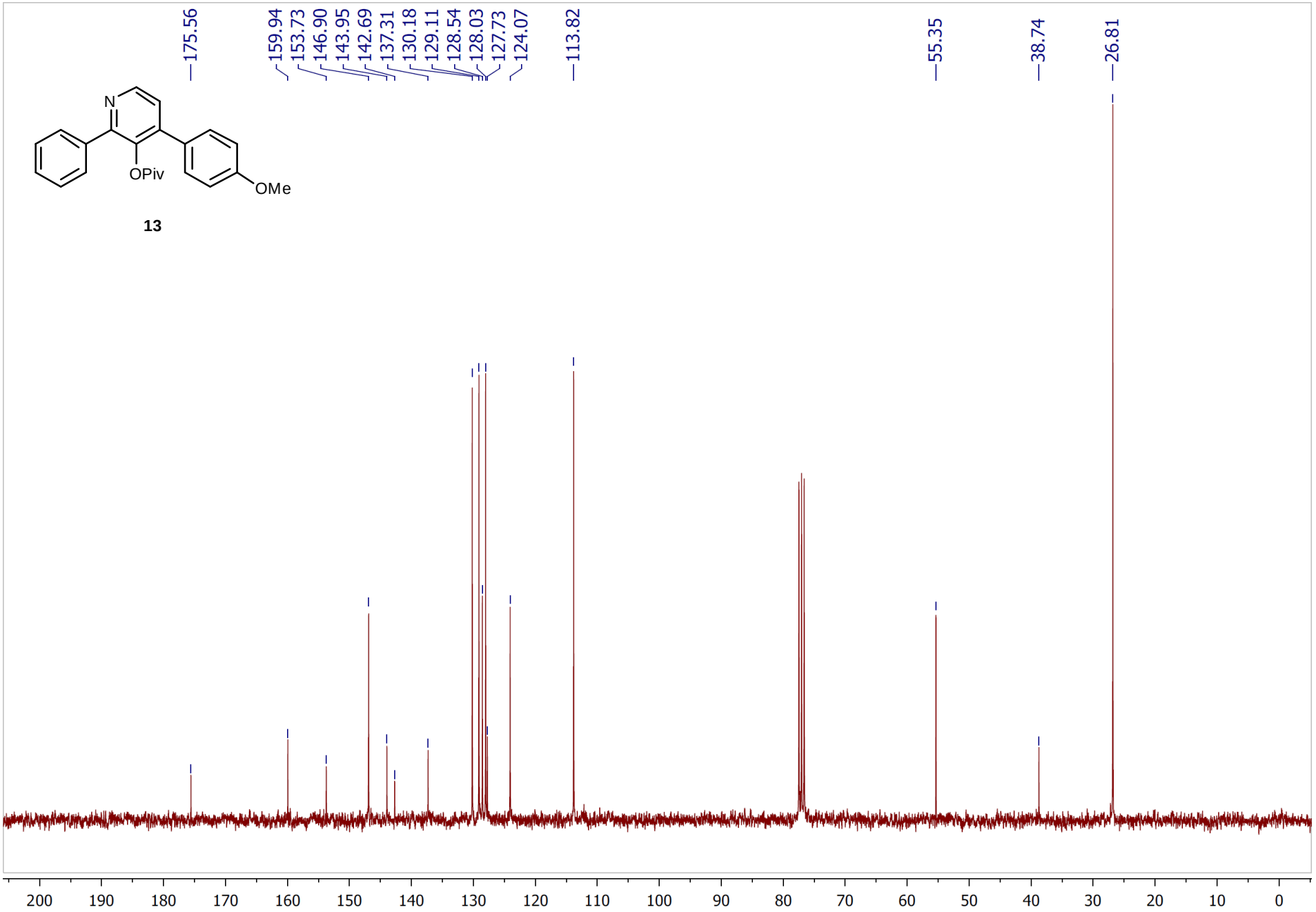

MeO
O
OPiv
12
MeO
O
OPiv
12'
130.47
114.30
67.41
55.26
45.37
27.15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4-(4-Methoxyphenyl)-2-phenylpyridin-3-yl pivalate 13

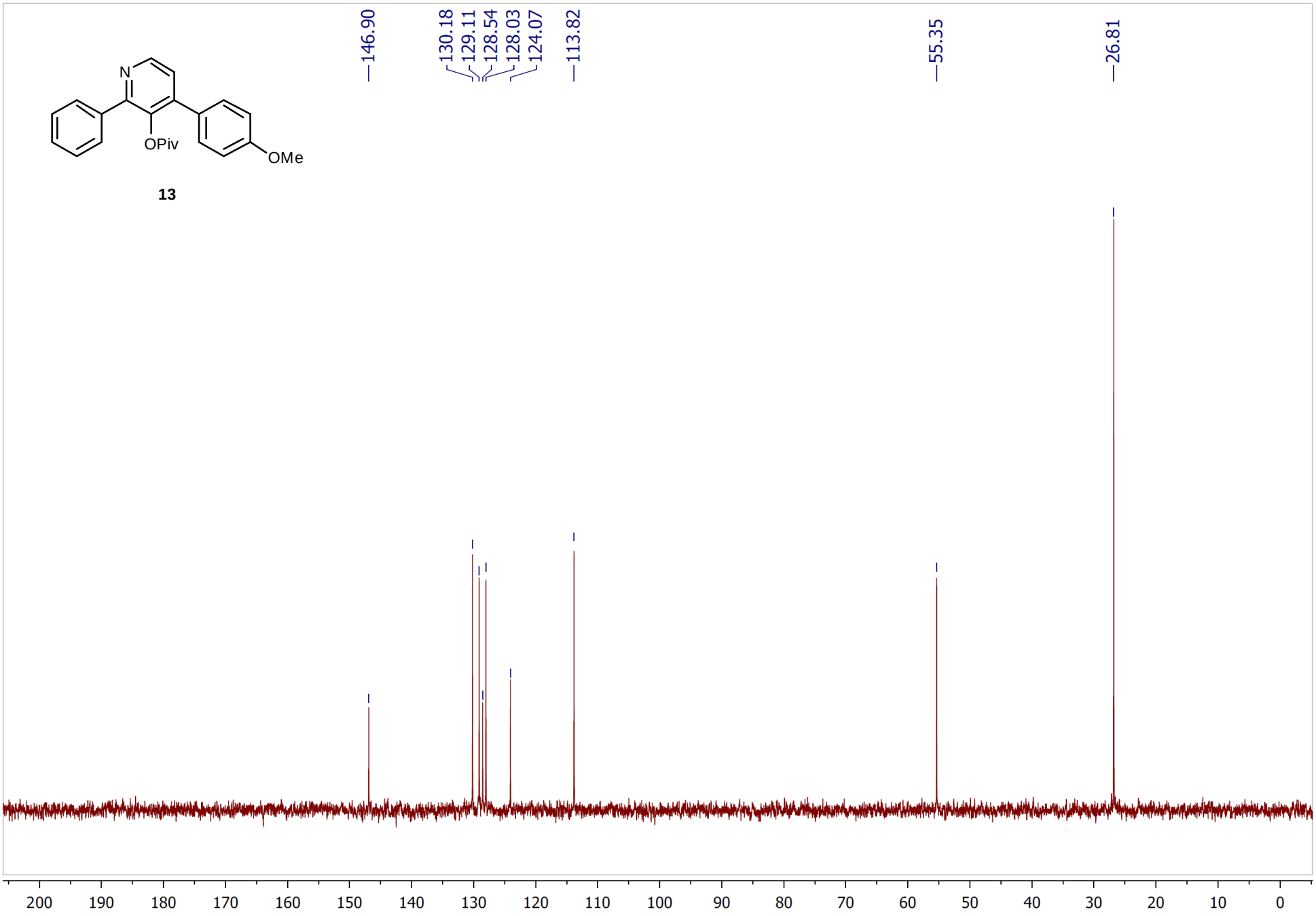
^{1}H NMR



^{13}C NMR


175.56
159.94
153.73
146.90
143.95
142.69
137.31
130.18
129.11
128.54
128.03
127.73
124.07
113.82
55.35
38.74
26.81
N
OPiv
OMe
13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{13}C NMR DEPT


146.90
130.18
129.11
128.54
128.03
124.07
113.82
55.35
26.81
N
OPiv
OMe
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200
190
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160
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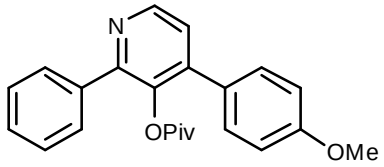
20
10
0

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


N
OPiv
OMe

13

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1
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3
4
5
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7
8
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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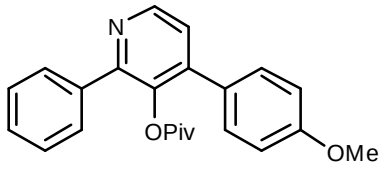
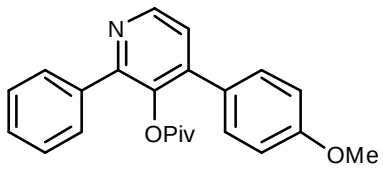
2.5
2.0
1.5
1.0
0.5
0.0

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



13

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



13