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Supporting Information

Application of Chiral Bis(phosphine) Monoxide Ligand to Catalytic Enantioselective Addition of Dialkylzinc Reagents to β-Nitroalkenes

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Experimental procedures. Characterization data. ^{1}H and ^{13}C NMR spectra.

General: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH_2Cl_2, benzene, DMF, CH_3CN, toluene, hexane, methanol) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et_3N, $ClCH_2CH_2Cl$, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME, 1,4-dioxane). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F254). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.[2] Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^{1}H, ^{13}C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a Bruker AV 300, AMX 300, AV 400, ARX 400, or DMX 600 spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sx = sextet, sep = septet, o = octet, n = nonet, m = multiplet and br = broad), coupling constant in Hz, integration, and assignment. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central

[1] Shriver, D.F.; Drezdzon, M. A. the manipulation of air-sensitive compounds; 2nd ed.;Wiley: New York, 1986.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

peak of deuterochloroform (77.00 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments. Optical rotations were determined with a Perkin-Elmer 341 polarimeter at 589 or 546 nm. Data are reported as follows: ([α]λ temp, concentration (c in g/100 mL), and solvent. High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l'Université de Montréal. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal. Analytical gas chromatography was carried out on a Hewlett Packard 5880A gas chromatograph equipped with a splitless mode capillary injector and a flame ionization detector or with an Agilent 6890 Series GC system equipped with an Agilent 5973 EI mass detector. Unless otherwise noted, the injector and detector temperatures were set to 250 °C and hydrogen was used as the carrier gas (63 psi). Data are reported as follows: (column type, column length, initial-final temperature, rate: retention time (t_r)).

Reagents: Unless otherwise stated, commercial reagents were used without purification. The nitroalkenes **4b**, **4c**, **4d**, **4e**, **4i**, **4j** were synthesized using the appropriate general procedure (aromatic or aliphatic substrates). Commercial nitroalkenes were purified by crystallization in a mixture of Et_2O and Hexane (The traces of impurities in commercial reagents slightly affect the reproducibility of the reactions). The **2a** ligand (BozPHOS or Me-DuPHOS monoxide)[3] and the (**2a**)$_2$CuOTf complex[4] were synthesized according to previously reported procedures.

General procedure for the synthesis of aromatic nitroalkenes 4b, 4c, 4d and 4e.
(Modified literature procedure[5])

To a stirred solution of NH_4OAc (8.73 g, 113.3 mmol) in AcOH (67.0 mL) in a flame-dried, round-bottomed 200 mL flask equipped with a condenser and a football-shaped magnetic stirring bar (under Ar atmosphere) was added CH_3NO_2 (17.6 mL, 326.5 mmol) followed by the aldehyde (47.4 mmol) at room temperature. The clear slightly yellow solution was then heated to 100 °C using an oil bath for 5 h 30 min. The resulting dark-orange solution was allowed to cool to room temperature and poured in H_2O (200 mL). The pH was then regulated to 7 using $NaOH_{(aq)}$ 2M, and the resulting aqueous phase was extracted with 4 x 100 mL EtOAc. The combined organic layers were dried on $MgSO_4$, filtered and concentrated under vacuum to give the crude nitroalkene as a brown solid. In order to get the pure (*E*)-nitroalkene, this solid was further crystallized using 10% EtOAc in hexane as solvent, and filtered at boiling point temperature to remove brown oily impurities, affording the desired compound as pale yellow needles.

[3] Boezio, A. A.; Pytkowicz, J.; Côté, A.; Charette, A. B. *J. Am. Chem. Soc.* **2003**, *125*, 14260–14261.
[4] Côté, A.; Charette, A. B. *J. Org. Chem.* **2005**, *70*, 10864-10867.
[5] Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, *5*, 2559–2561.

General procedure for the synthesis of aliphatic nitroalkenes 4i and 4j

(Modified literature procedure[6])

In a flame-dried, round-bottomed 100 mL flask equipped with an egg-shaped magnetic stirring bar (under Ar atmosphere) were added at 0 °C the aldehyde (39.0 mmol), THF (10.0 mL), *t*-BuOH (10.0 mL) and CH_3NO_2 (3.2 mL, 58.5 mmol). Vigourous stirring was maintained to obtain a colorless clear solution. Then *t*-BuOK (0.438 g, 3.9 mmol) was added in one portion, and the solution was allowed to stir at this temperature for 15 minutes before the ice bath was removed. The solution allowed to stir at room temperature for 16 additional hours. The resulting light green-yellow solution was poured in H_2O (130 mL) and extracted with 4 x 80 mL *t*-BuOMe. The combined organic layers were washed with H_2O (130 mL), sat. $NaCl_{(aq)}$ (100 mL), dried on $MgSO_4$, filtered on celite and concentrated under vacuum to give the crude β-nitroalcohol as a light yellow oil. In a flame-dried, round-bottomed 100 mL flask equipped with an egg-shaped magnetic stirring bar (under Ar atmosphere), a solution of the crude β-nitroalcohol (39.0 mmol) in dry CH_2Cl_2 (50.0 mL) was prepared. When temperature reached -10 °C, TFAA (5.50 mL, 39.0 mmol) was added dropwise. The resulting clear light yellow solution was allowed to stir for exactly 2 minutes before Et_3N (10.9 mL, 78.0 mmol) was added over 15 minutes at -10 °C. The solution was stirred for an additional 35 minutes at this temperature before being diluted in CH_2Cl_2 (200 mL) and washed with 2 x 100 mL sat. $NH_4Cl_{(aq)}$. The aqueous layer was separated and extracted with 2 x 50 mL CH_2Cl_2. All organic layers were combined, washed with 100 mL sat. $NaCl_{(aq)}$, dried on $MgSO_4$, filtered and concentrated under vacuum, giving the crude nitroalkene as a dark-yellow oil. Flash column chromatography using 5% EtOAc in Hexane as eluent (R_f = 0.40) gave the desired compound as a light yellow oil.

General procedure for the synthesis of racemic nitroalkanes

(CAUTION: Et_2Zn IS EXTREMELY PYROPHORIC, GAS-TIGHT SYRINGES ONLY)

In a flame-dried, round-bottomed 5 mL flask equipped with an egg-shaped magnetic stirring bar (under Ar atmosphere) was added the β-nitroalkene (0.515 mmol) and anhydrous CuCN (23.1 mg, 0.258 mmol). Dry Et_2O (3.5 mL) was then added, and the resulting heterogeneous milky solution was allowed to stir for 10 minutes at room temperature. Neat Et_2Zn (106 μL, 1.031 mmol) was then added dropwise, and the solution was allowed to stir for 2 hours at room temperature. Excess Et_2Zn was quenched by slow addition of 1.0 mL MeOH (caution: exothermic ethane formation). The resulting solution was poured in 20 mL sat. $NH_4Cl_{(aq)}$ and extracted with 3 x 15 mL CH_2Cl_2. The combined organic layers were dried on Na_2SO_4, filtered and concentrated under vacuum to give the crude racemic nitroalkane as a brown oily residue. Flash column chromatography using 20% Et_2O in Hexane as eluent gave the pure racemic nitroalkane as a colorless oil.

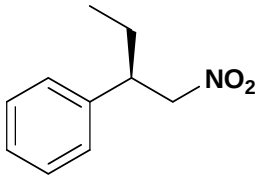
[6] Denmark, S. E.; Marcin, L. R. *J. Org. Chem.* **1993**, *58*, 3850–3856.

General procedure for the enantioselective catalytic addition of Et_2Zn to nitroalkenes

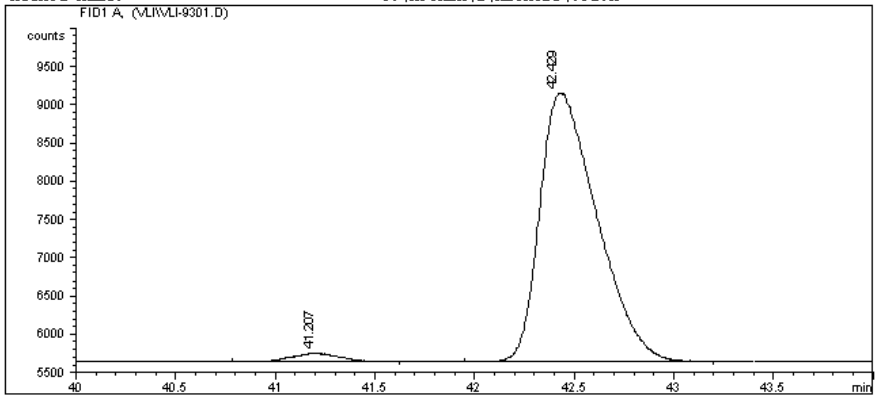
(CAUTION: Et_2Zn IS EXTREMELY PYROPHORIC, GAS-TIGHT SYRINGES ONLY)
In a glove-box under Ar atmosphere, a flame-dried, pear-shaped 10 mL flask equipped with an egg-shaped magnetic stirring bar was charged with the β-nitroalkene (1.00 mmol), (**2a**)$_2$CuOTf (10.7 mg, 0.0125 mmol) and **2a** (8.1 mg, 0.025 mmol) *(Note: The results in Table 3 were obtained by replacing this 0.025 mmol of **2a** with 0.200 mmol of the additive)*. The flask was closed with a rubber septum, taken out of the glove-box and dry Et_2O (5.0 mL, 0.2 M concentration of substrate) was added to afford a heterogeneous pale yellow solution which was then stirred for another 30 minutes at room temperature before being allowed to cool to -70 °C for 45 minutes using a cryostat ethanol bath. Neat Et_2Zn (205 □L, 2.00 mmol) was added dropwise (within 10 seconds) at -70 °C, and the resulting dark-yellow heterogeneous solution was allowed to stir for 16 hours at this temperature (at medium stirring). Excess Et_2Zn was quenched by slow addition of 2.0 mL MeOH at -70 °C (caution: exothermic ethane formation) to the clear light yellow solution. It was then stirred for 5 minutes at this temperature and slowly warmed to room temperature. The resulting mixture was poured in 30 mL sat. $NH_4Cl_{(aq)}$ and extracted with 3 x 30 mL CH_2Cl_2. The combined organic layers were dried on Na_2SO_4, filtered and concentrated under vacuum to give the crude nitroalkane as a light-brown oil. Flash column chromatography using 20% Et_2O in Hexane as eluent afforded the pure compound as a colorless oil.

General procedure for the enantioselective catalytic addition of Me_2Zn to nitroalkenes

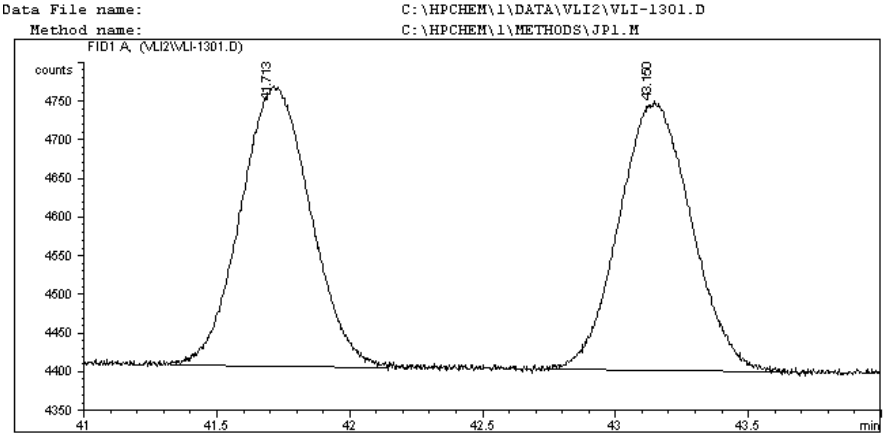
(CAUTION: Me_2Zn IS EXTREMELY PYROPHORIC, GAS-TIGHT SYRINGES ONLY)
In a glove-box under Ar atmosphere, a flame-dried, round-bottomed 5 mL flask equipped with an egg-shaped magnetic stirring bar was charged with β-nitroalkene (0.50 mmol), (**2a**)$_2$CuOTf (5.4 mg, 0.00625 mmol) and **2a** (4.0 mg, 0.0125 mmol). The flask was closed with a rubber septum, taken out of the glove-box and dry CH_2Cl_2 (2.5 mL, 0.2 M concentration of substrate) was added to afford a clear yellow solution, which was stirred for another 30 minutes at room temperature before being allowed to cool to -40 °C for 45 minutes using a cryostat ethanol bath. Neat Me_2Zn (172 μL, 2.50 mmol) was then added dropwise (within 10 seconds) at -40 °C, and the resulting heterogeneous dark-yellow solution was allowed to stir for 48 hours at this temperature (at medium stirring). Excess Me_2Zn was quenched by slow addition of 3.0 mL MeOH at -40 °C (caution: exothermic methane formation) to the clear light-yellow solution. It was then stirred for 5 minutes at this temperature and slowly warmed to room temperature. The resulting mixture was poured in 20 mL sat. $NH_4Cl_{(aq)}$ and extracted with 3 x 20 mL CH_2Cl_2. The combined organic layers were dried on Na_2SO_4, filtered and concentrated under vacuum to give the crude nitroalkane as a light-brown oil. Flash column chromatography using 20% Et_2O in Hexane as eluent afforded the pure compound as a colorless oil.



[(1*R*)-1-(nitromethyl)propyl]benzene (5a). (colorless oil) *The specific procedure for the addition of Et_2Zn described in the experimental section was followed.* *Isolated yield 92%, 95% ee.* GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 115 °C isotherm): (*S*)-**5a** t_r = 41.21 min, (*R*)-**5a** t_r = 42.43 min). R_f 0.40 (20% Et_2O in Hexane); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.22 (m, 3H, Ar**H**), 7.21-7.15 (m, 2H, Ar**H**), 4.62-4.48 (m, 2H, C**H**$_2$NO$_2$), 3.41-3.30 (m, 1H, ArC**H**CH_2NO_2), 1.80-1.62 (m, 2H, C**H**$_2$CH$_3$), 0.83 (t, *J* = 7.6 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.2, 129.8, 128.5, 128.4, 81.6, 46.9, 27.0, 12.4. All spectral data are consistent with the literature values.[7,8]

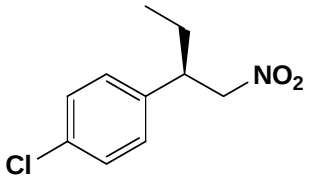


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
41.21	1904.1	109.4	2.6	0.290	1.031
42.43	7009->	3511.3	97.4	0.333	0.530

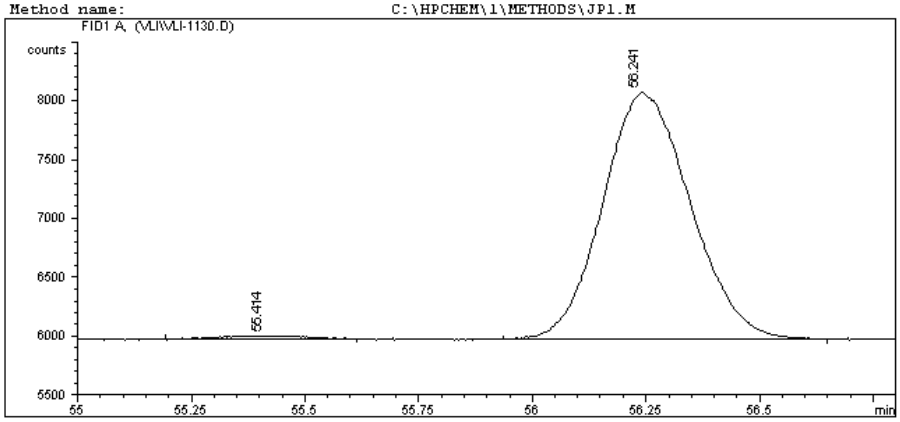


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
41.71	6601.3	363.1	50.0	0.303	0.884
43.15	6613.6	349.5	50.0	0.315	0.974

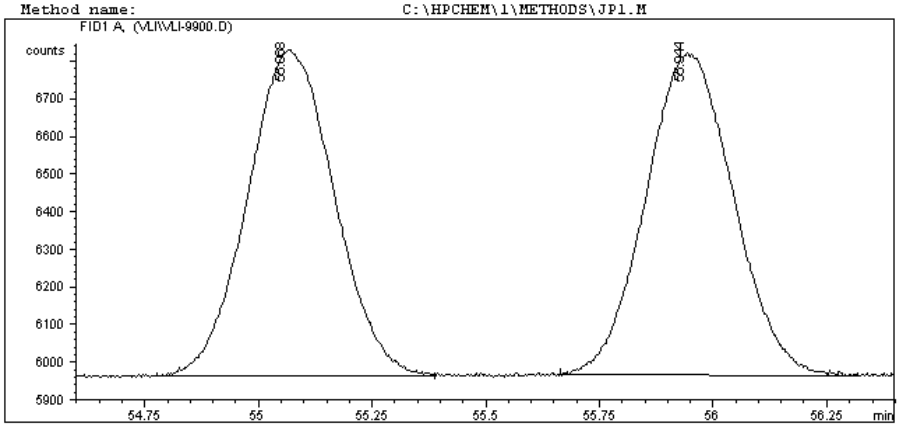
[7] Mampreian, D. M.; Hoveyda, A. H. *Org. Lett.* **2004**, *6*, 2829−2832.
[8] Choi, H.; Hua, Z.; Ojima, I. *Org. Lett.* **2004**, *6*, 2689−2691.



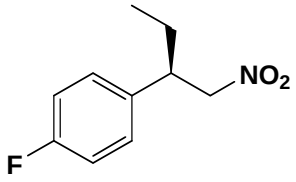
1-chloro-4-[(1*R*)-1-(nitromethyl)propyl]benzene (5b).
(colorless oil)
The specific procedure for the addition of Et_2Zn described in the experimental section was followed. *Isolated yield 93%, 98% ee.*
GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-160 °C, 0.5 °C/min): (*S*)-**5b** t_r = 55.41 min, (*R*)-**5b** t_r = 56.24 min. R_f 0.37 (20% Et_2O in Hexane); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.31 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.13 (d, *J* = 8.4 Hz, 2H, Ar**H**), 4.63-4.45 (m, 2H, C**H**$_2$NO$_2$), 3.41-3.29 (m, 1H, ArC**H**CH_2NO_2), 1.81-1.58 (m, 2H, C**H**$_2$CH$_3$), 0.83 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.8, 133.1, 128.9, 128.8, 80.3, 45.2, 25.0, 11.3. All spectral data are consistent with the literature values.[7]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
55.41	334.3	30.1	1.2	0.185	1.067
56.24	2802->	2097.4	98.8	0.223	0.798



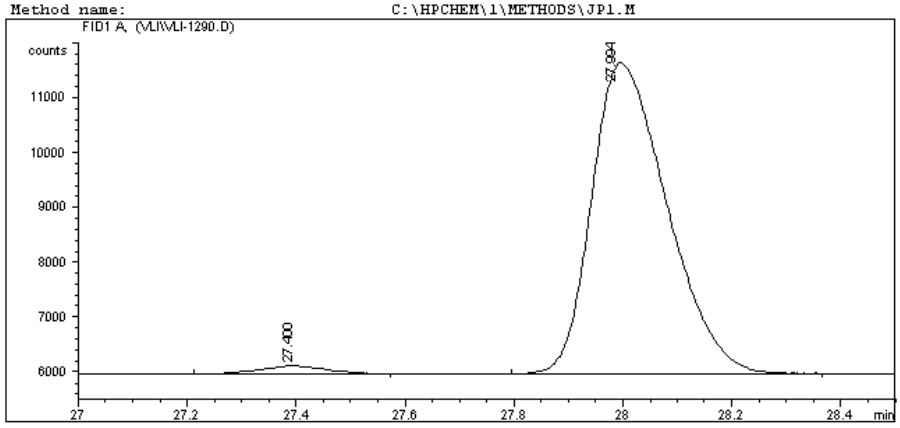
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
55.07	1145->	865.6	50.0	0.221	0.911
55.94	1145->	857.8	50.0	0.222	0.903



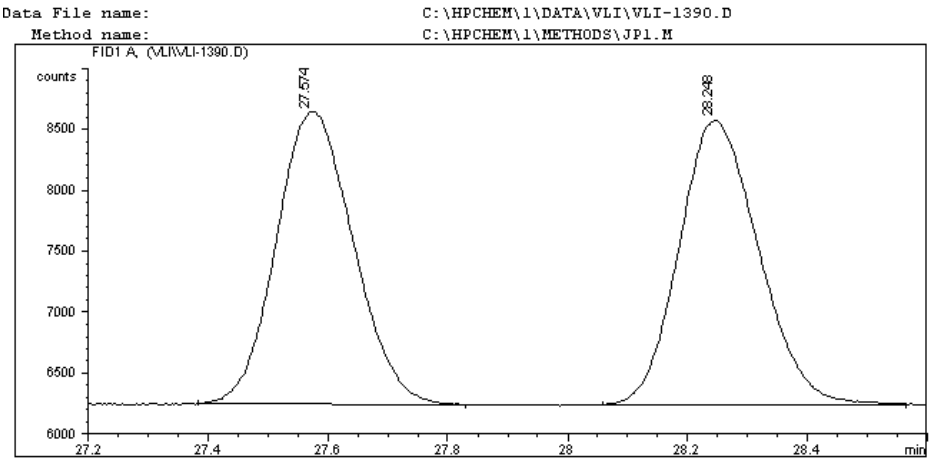
1-fluoro-4-[(1*R*)-1-(nitromethyl)propyl]benzene (5c).

(colorless oil)

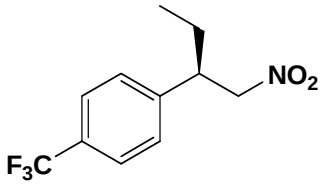
A modified procedure for the addition of Et_2Zn, different from the one described in the experimental section, was followed, in which the reaction was run at -60 ºC. Isolated yield 99%, 96% ee. GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-170 °C, 0.5 °C/min): (*S*)-**5c** t_r = 27.40 min, (*R*)-**5c** t_r = 27.99 min. R_f 0.36 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.21-7.13 (m, 2H, Ar**H**), 7.07-6.98 (m, 2H, Ar**H**), 4.63-4.47 (m, 2H, C**H**$_2$NO$_2$), 3.42-3.29 (m, 1H, ArC**H**CH$_2$NO$_2$), 1.82-1.57 (m, 2H, C**H**$_2$CH$_3$), 0.83 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.0 (d, 246.0 Hz), 135.0 (d, *J* = 3.2 Hz), 129.0 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.3 Hz), 80.6, 45.2, 26.1, 11.4. All spectral data are consistent with the literature values.[8]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
27.40	1177.3	137.1	2.1	0.143	1.129
27.99	5433->	5659.9	97.9	0.160	0.593

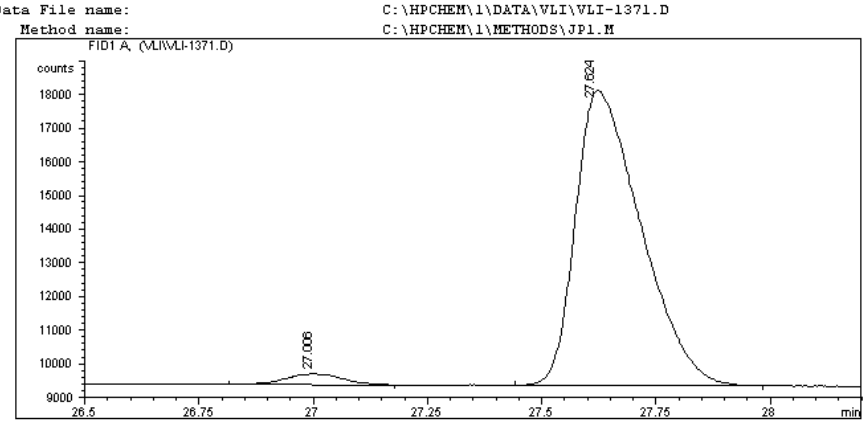


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
27.57	2149->	2402.5	50.0	0.149	0.864
28.25	2148->	2325.8	50.0	0.154	0.858

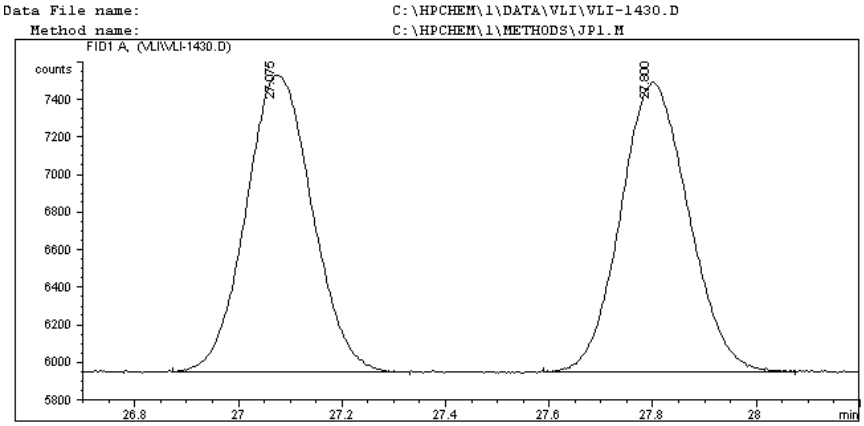


1-[(1*R*)-1-(nitromethyl)propyl]-4-(trifluoromethyl)benzene (5d). (colorless oil)

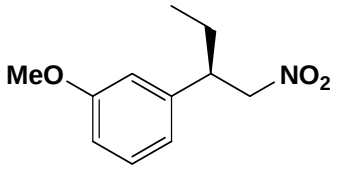
A modified procedure for the addition of Et_2Zn, different from the one described in the experimental section, was followed, in which the reaction was run at -60 ºC. Isolated yield 92%, 94% ee. GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-170 °C, 0.5 °C/min): (*S*)-**5d** t_r = 27.04 min, (*R*)-**5d** t_r = 27.72 min. R_f 0.33 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.33 (d, *J* = 8.1 Hz, 2H, Ar**H**), 4.68-4.51 (m, 2H, C**H**$_2$NO$_2$), 3.52-3.39 (m, 1H, ArC**H**CH$_2$NO$_2$), 1.80-1.62 (m, 2H, C**H**$_2$CH$_3$), 0.84 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.6, 129.7 (q, *J* = 32.3 Hz), 128.0, 125.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 271.6 Hz), 80.0, 45.7, 26.0, 11.3. All spectral data are consistent with the literature values.[8]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
27.01	2834.3	330.4	3.1	0.143	1.110
27.62	8715->	8755.9	96.9	0.166	0.517

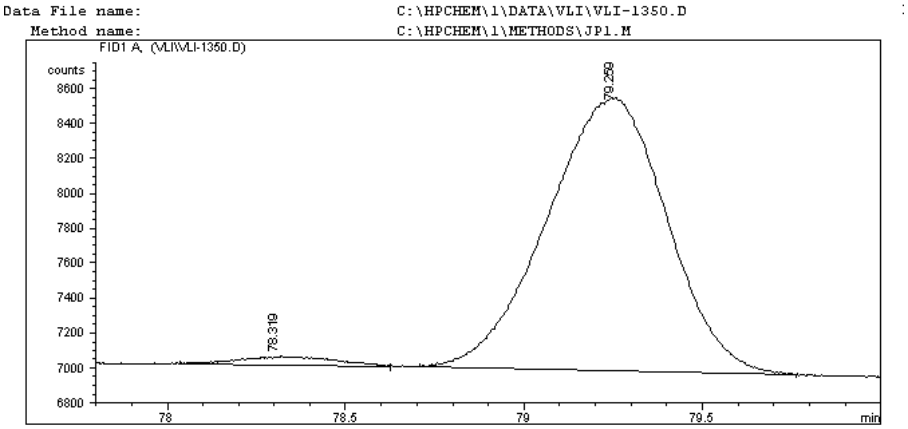


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
27.08	1399->	1577.7	49.9	0.148	0.903
27.80	1403->	1539.6	50.1	0.152	0.886

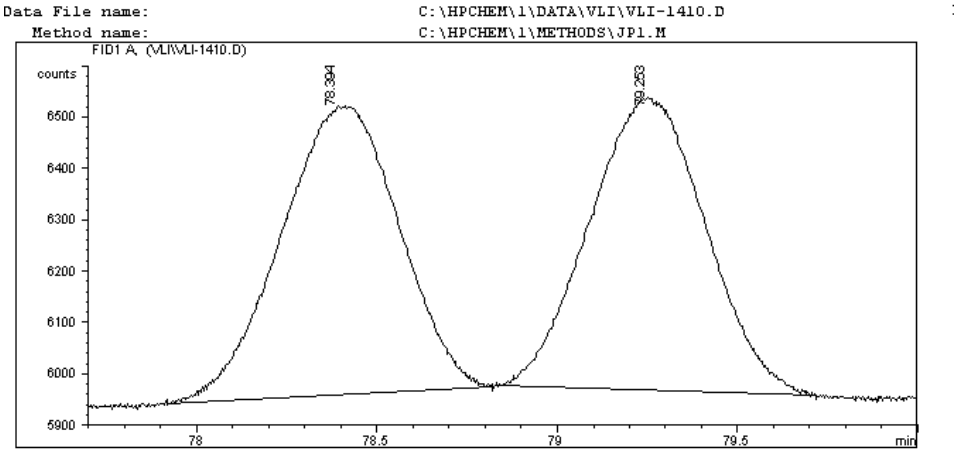


1-methoxy-3-[(1*R*)-1-(nitromethyl)propyl]benzene (**5e**).
(colorless oil)

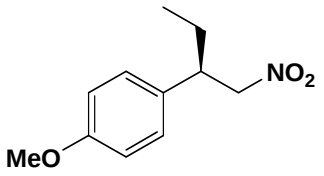
A modified procedure for the addition of Et_2Zn, different from the one described in the experimental section, was followed, in which the reaction being run at -60 ºC and at a 0,1M concentration of substrate. Isolated yield 98%, 95% ee. GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-160 °C, 0.2 °C/min): (*S*)-**5e** t_r = 78.32 min, (*R*)-**5e** t_r = 79.26 min. R_f 0.31 (20% Et_2O in Hexane); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.26 (t, *J* = 8.1 Hz, 1H, Ar**H**), 6.85-6.72 (m, 3H, Ar**H**), 4.62-4.49 (m, 2H, C**H**$_2$NO$_2$), 3.40-3.28 (m, 1H, ArC**H**CH$_2$NO$_2$), 1.80-1.62 (m, 2H, C**H**$_2$CH$_3$), 0.85 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.7, 140.8, 129.7, 119.6, 113.5, 112.2, 80.4, 54.9, 45.8, 25.9, 11.3. All spectral data are consistent with the literature values.[8]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
78.32	932.4	49.9	2.5	0.311	0.775
79.26	3644->	1563.0	97.5	0.389	1.311

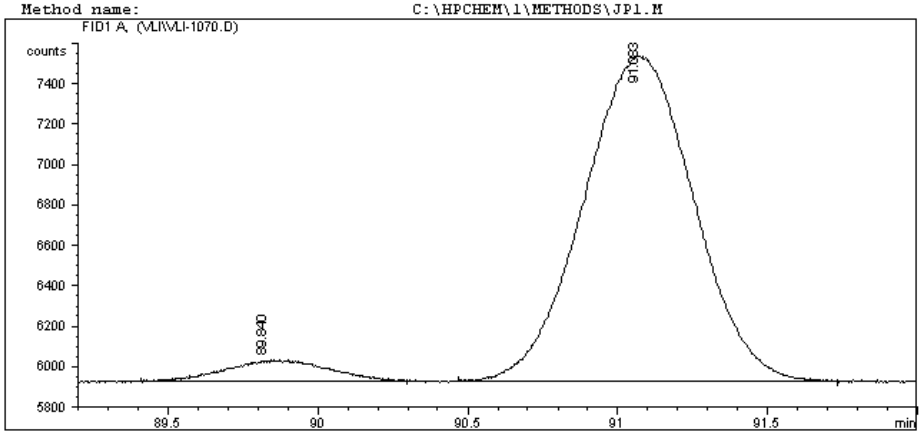


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
78.39	1280->	563.7	50.1	0.379	0.961
79.25	1278->	571.9	49.9	0.372	1.001

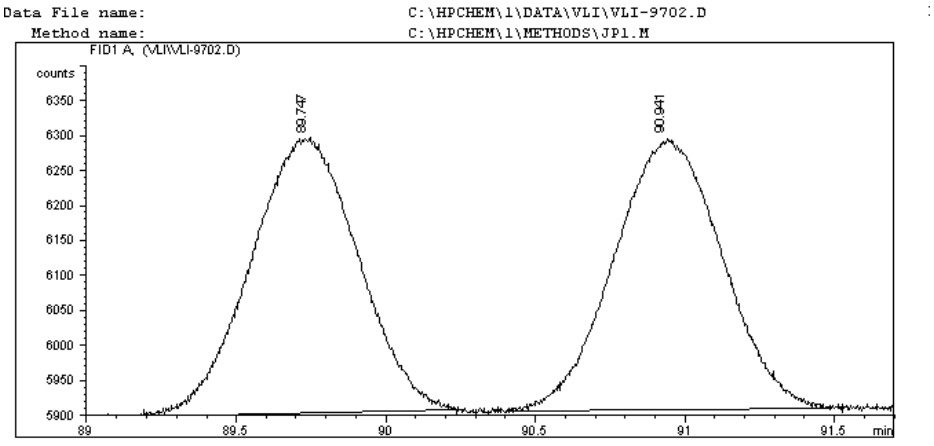


1-methoxy-4-[(1*R*)-1-(nitromethyl)propyl]benzene (**5f**).
(pale yellow oil)

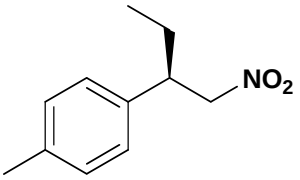
A modified procedure for the addition of Et_2Zn, different from the one described in the experimental section, was followed, in which the reaction was run at -60 ºC. Isolated yield 95%, 89% ee. GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-160 °C, 0.2 °C/min): (*S*)-**5f** t_r = 89.84 min, (*R*)-**5f** t_r = 91.08 min. R_f 0.26 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16-7.08 (m, 2H, Ar**H**), 6.91-6.84 (m, 2H, Ar**H**), 4.60-4.46 (m, 2H, C**H**$_2$NO$_2$), 3.37-3.26 (m, 1H, ArC**H**CH$_2$NO$_2$), 1.80-1.58 (m, 2H, C**H**$_2$CH$_3$), 0.84 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.7, 131.0, 128.4, 114.0, 80.8, 55.0, 45.1, 26.0, 11.3. All spectral data are consistent with the literature values.[7, 8]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
89.84	2493.1	103.2	5.7	0.403	0.780
91.08	4109->	1609.0	94.3	0.426	1.105

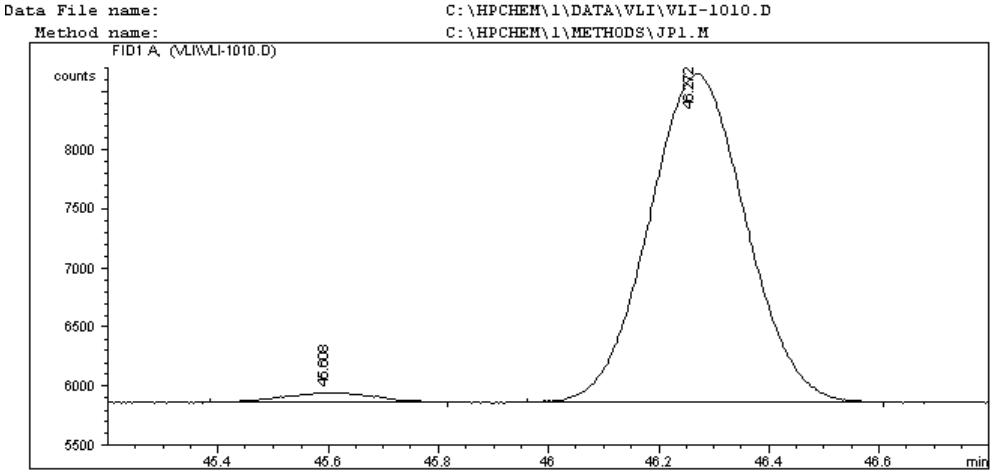


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
89.75	9786.0	393.8	50.1	0.414	1.170
90.94	9753.7	388.6	49.9	0.418	0.964

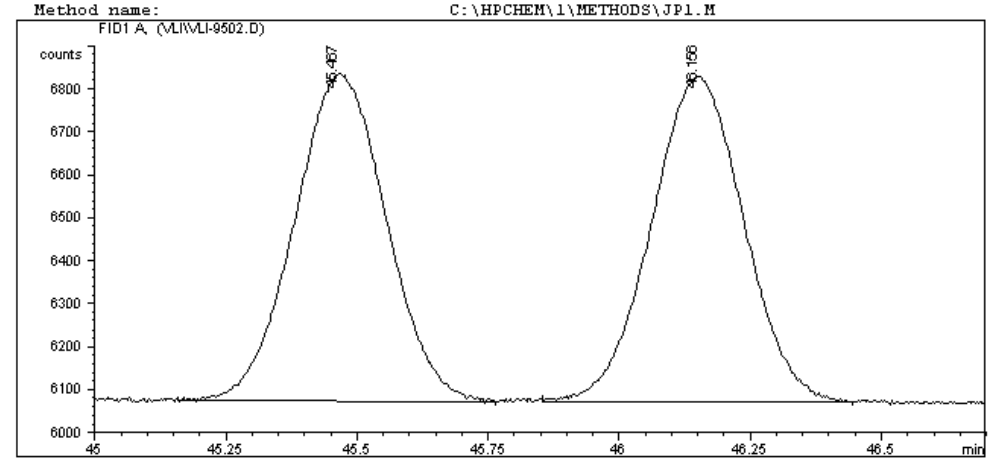


1-methyl-4-[(1*R*)-1-(nitromethyl)propyl]benzene (**5g**).
(colorless oil)

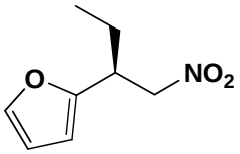
The specific procedure for the addition of Et_2Zn described in the experimental section was followed. *Isolated yield 89%, 95% ee.*
GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 110-140 °C, 0.5 °C/min): (*S*)-**5g** t_r = 45.61 min, (*R*)-**5g** t_r = 46.27 min. R_f 0.42 (20% Et_2O in Hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.17 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.10 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.62-4.51 (m, 2H, C**H**$_2$NO$_2$), 3.38-3.27 (m, 1H, ArC**H**CH$_2$NO$_2$), 2.35 (s, 3 H, ArC**H**$_3$), 1.81-1.65 (m, 2H, C**H**$_2$CH$_3$), 0.86 (dd, *J* = 7.6, 7.6 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3, 136.3, 129.7, 127.5, 81.0, 45.8, 26.2, 21.1, 11.7. All spectral data are consistent with the literature values. [8]



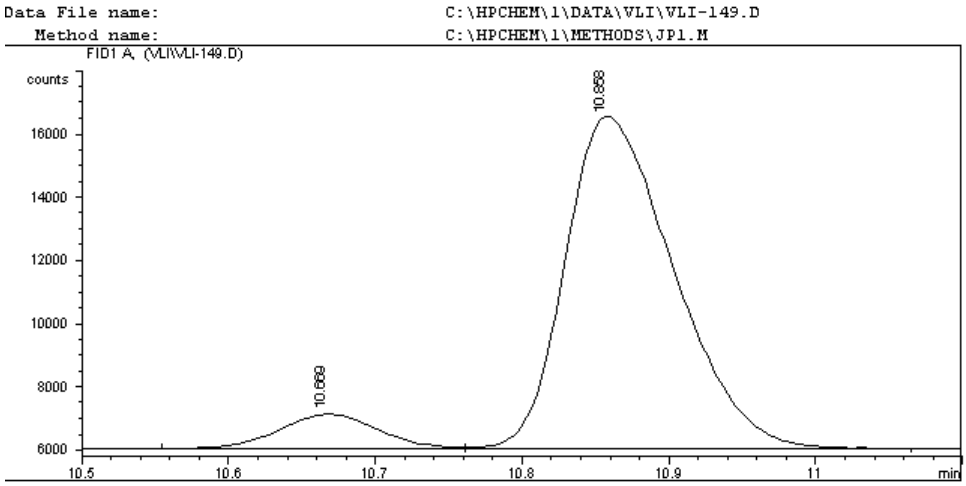
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
45.61	938.3	82.4	2.7	0.190	1.125
46.27	3402->	2790.8	97.3	0.203	1.007



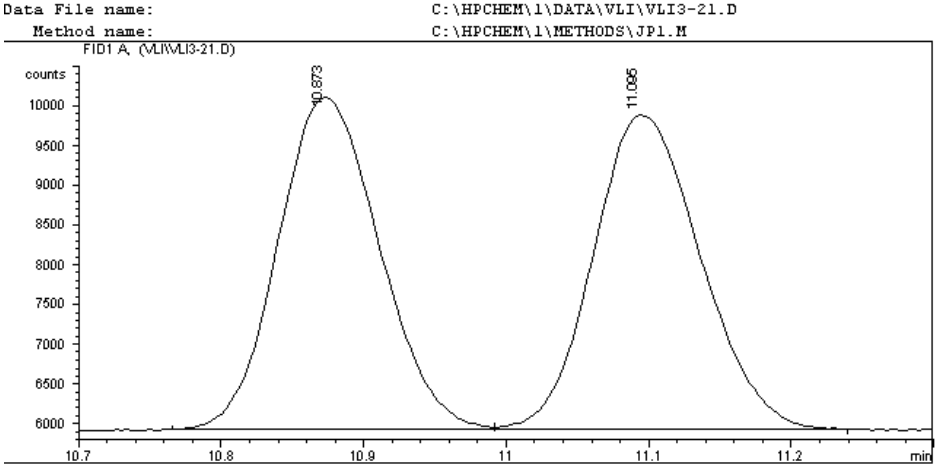
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
45.47	9265.9	760.7	50.1	0.203	0.966
46.16	9237.7	758.9	49.9	0.203	1.097



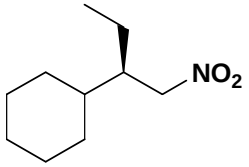
2-[(1*S*)-1-(nitromethyl)propyl]furan (**5h**)**.** (pale yellow oil)
The specific procedure for the addition of Et_2Zn described in the experimental section was followed. *Isolated yield 90%, 83% ee.* GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120 °C isotherm): (*S*)-**5h** t_r = 10.67 min, (*R*)-**5h** t_r = 10.86 min. R_f 0.54 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.32 (m, 1H, Ar**H**), 6.34-6.27 (m, 1H, Ar**H**), 6.17-6.11 (m, 1H, Ar**H**), 4.67-4.49 (m, 2H, C**H**$_2$NO$_2$), 3.58-3.47 (m, 1H, ArC**H**CH$_2$NO$_2$), 1.83-1.64 (m, 2H, C**H**$_2$CH$_3$), 0.90 (dd, *J* = 7.5, 7.5 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.3, 142.1, 110.2, 107.2, 78.2, 39.4, 24.1, 11.2. All spectral data are consistent with the literature values.[7, 8]



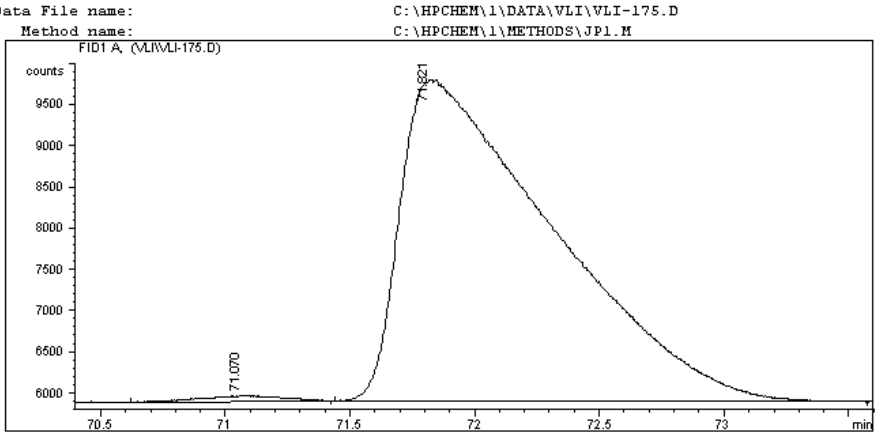
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
10.67	4920.2	1072.5	8.4	0.076	1.012
10.86	5344->	1050->	91.6	0.085	0.639



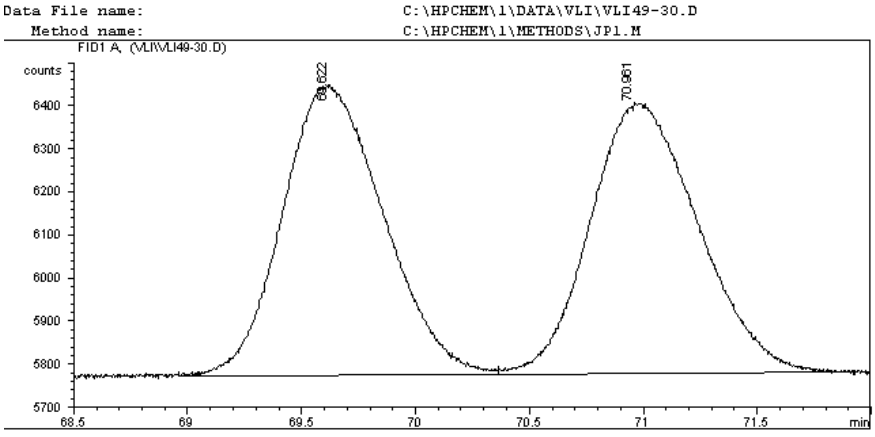
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
10.87	2064->	4183.2	50.0	0.082	0.863
11.09	2066->	3954.3	50.0	0.087	0.794



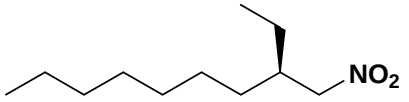
[(1*R*)-1-(nitromethyl)propyl]cyclohexane (**5i**)**.** (colorless oil) *A modified procedure for the addition of Et_2Zn, different from the one described in the experimental section, was followed, in which the substrate was added continuously over a period of 12 hours to the CuOTf/**2a**/Et_2Zn/Et_2O solution at -70 ºC and the resulting solution was stirred for 4 additional hours. Isolated yield 70%, 98% ee.* GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 100 °C isotherm): (*S*)-**5i** t_r = 71.07 min, (*R*)-**5i** t_r = 71.82 min. R_f 0.59 (20% Et_2O in Hexane); ^1H NMR ($CDCl_3$, 300 MHz): δ 4.44-4.35 (m, 1H, C**H**HNO2), 4.31-4.22 (m, 1H, CH**H**NO2), 2.09-1.97 (m, 1H, (C_6H_{11})C**H**CH_2NO_2), 1.83-0.95 (m, 13H, C_6H_{11} and C$\mathbf{H}_2$CH3), 0.92 (dd, *J* = 7.5, 7.5 Hz, 3H, CH2C**H**3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 77.6, 44.2, 38.3, 29.6, 29.2, 26.4, 26.4, 26.4, 21.3, 11.3. All spectral data are consistent with the literature values.[7]



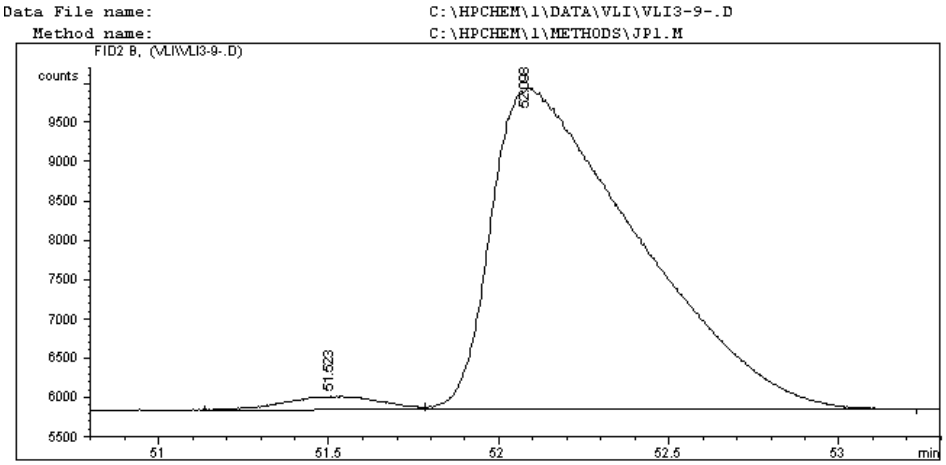
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
71.07	1453.9	65.8	0.9	0.368	1.037
71.82	1660->	3900.6	99.1	0.710	0.243



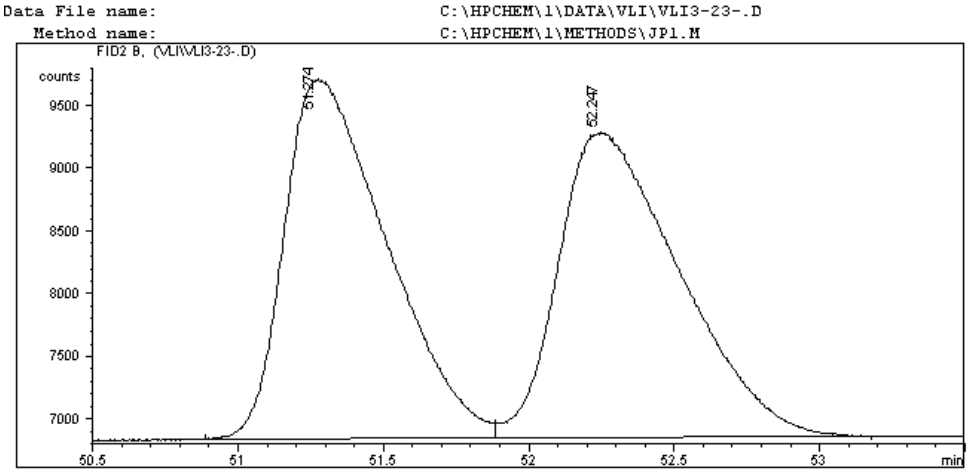
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
69.62	2067->	675.1	50.0	0.510	
70.96	2066->	631.3	50.0	0.545	0.701



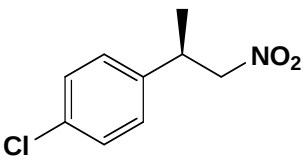
(3*R*)-3-(nitromethyl)decane (**5j**)**.** (colorless oil) *The specific procedure for the addition of Et_2Zn described in the experimental section was followed. Isolated yield 91%, 95% ee.* GC analysis of the product on chiral stationary phase (β-dex, 30 m, 100 °C isotherm): (*S*)-**5j** t_r = 51.52 min, (*R*)-**5j** t_r = 52.10 min**.** R_f 0.64 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.30 (d, *J* = 6.9 Hz, 2H, C**H**$_2$NO$_2$), 2.20-2.05 (m, 1H, (*n*-C_7H_{15})C**H**CH_2NO_2), 1.49-1.15 (m, 14H, aliphatic C**H**$_2$), 0.92 (t, *J* = 7.5 Hz, 3H, C**H**$_3$), 0.87 (t, *J* = 6.0 Hz, 3H, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 79.2, 38.7, 31.7, 30.7, 29.5, 29.1, 26.1, 23.8, 22.6, 13.0, 10.3. All spectral data are consistent with the literature values.[7]



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
51.52	3318.4	171.2	2.6	0.323	
52.10	1221->	4091.1	97.4	0.498	0.374

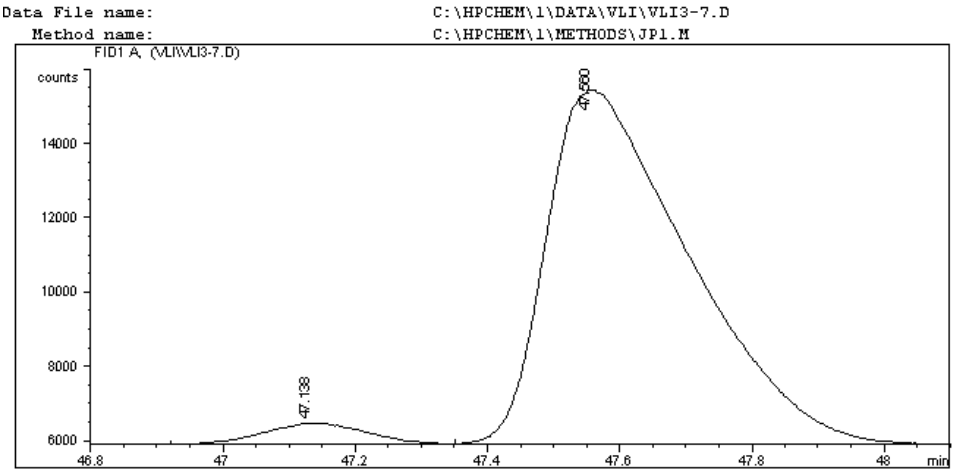


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
51.27	7015->	2874.6	49.9	0.407	
52.25	7034->	2433.0	50.1	0.482	0.533

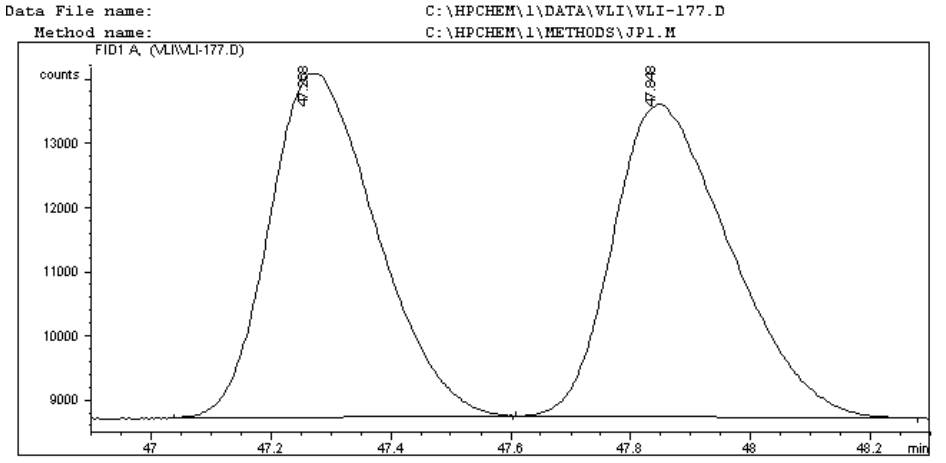


1-Chloro-4-[(1*R*)-1-methyl-2-nitroethyl]benzene (**6b**).
(colorless oil)

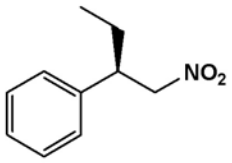
The specific procedure for the addition of Me_2Zn described in the experimental section was followed. *Isolated yield 95%, 92% ee.* GC analysis of the product on chiral stationary phase (γ-dex, 30 m, 120-160 °C, 0.5 °C/min): (*S*)-**6b** t_r = 47.14 min, (*R*)-**6b** t_r = 47.56 min. R_f 0.35 (20% Et_2O in Hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.28 (m, 2H, Ar**H**), 7.22-7.13 (m, 2H, Ar**H**), 4.57-4.44 (m, 2H, C**H**$_2$NO$_2$), 3.70-3.56 (m, 1H, ArC**H**CH_2NO_2), 1.37 (d, *J* = 6.9 Hz, 3H, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.3, 133.3, 129.1, 128.2, 81.5, 38.0, 18.6. All spectral data are consistent with the literature values.[7]



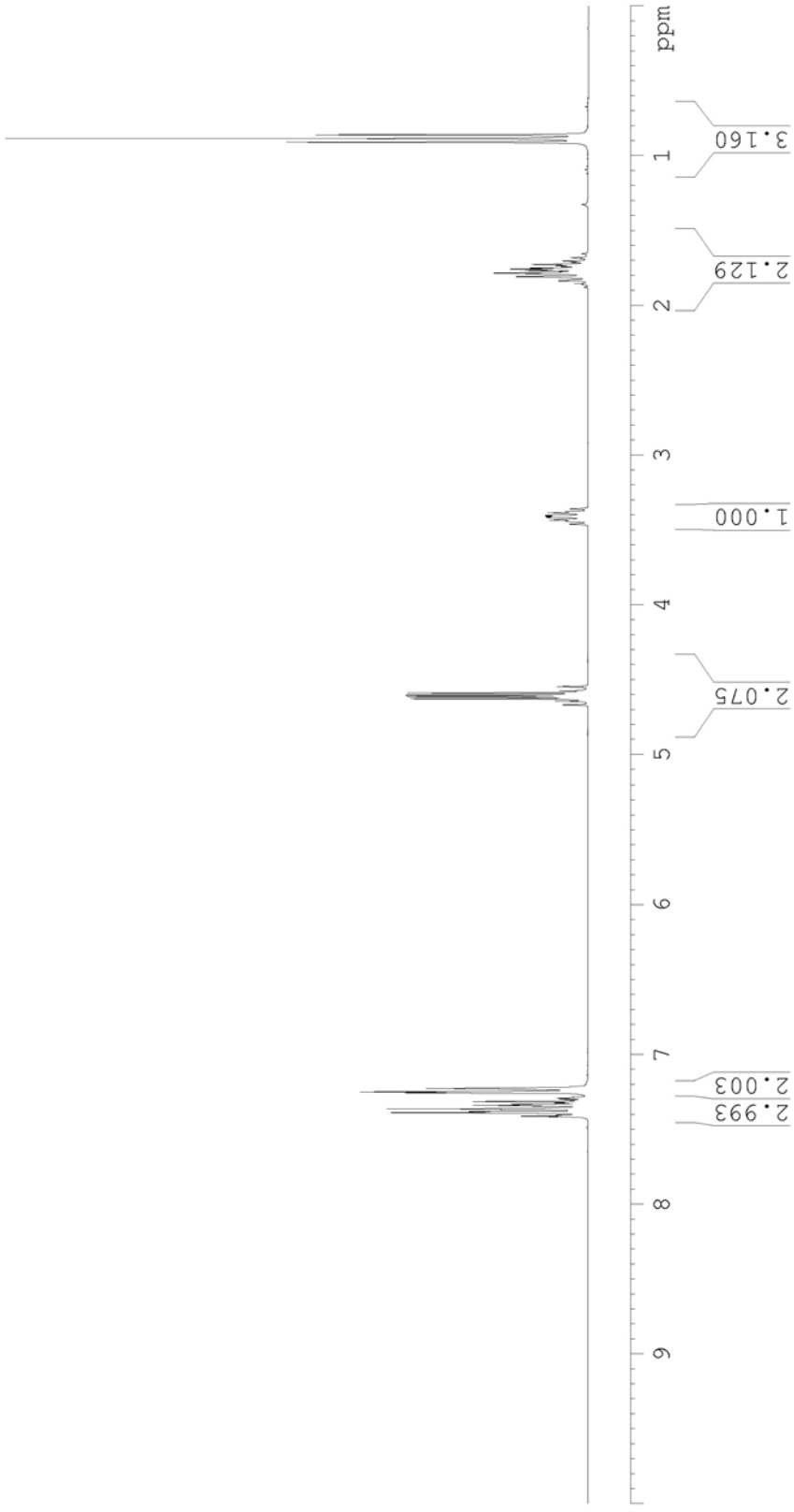
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
47.14	5861.8	546.6	4.0	0.179	0.965
47.56	1420->	9526.2	96.0	0.249	0.478

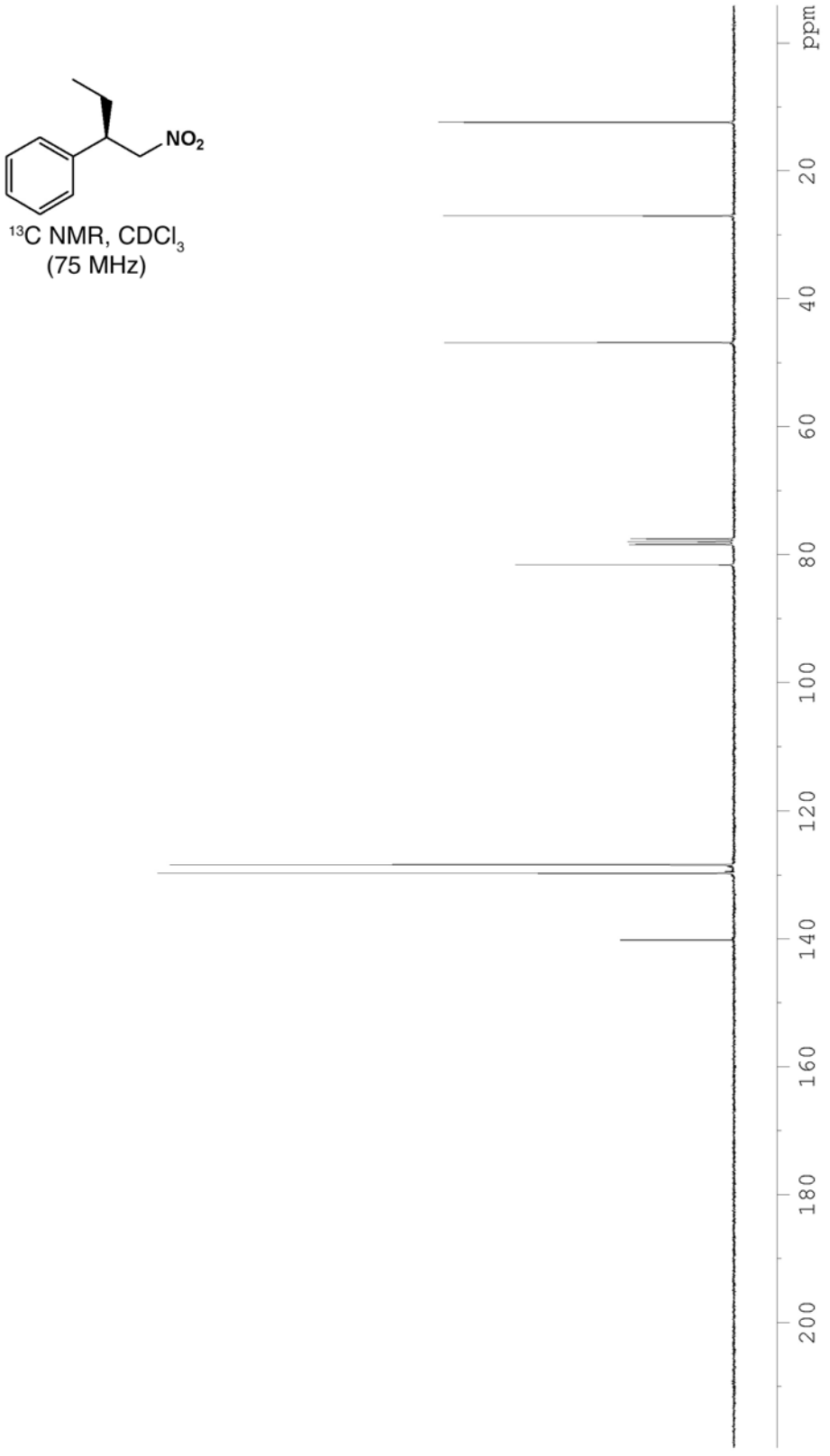


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
47.27	6631->	5351.2	50.1	0.207	0.657
47.85	6610->	4883.8	49.9	0.226	0.647



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

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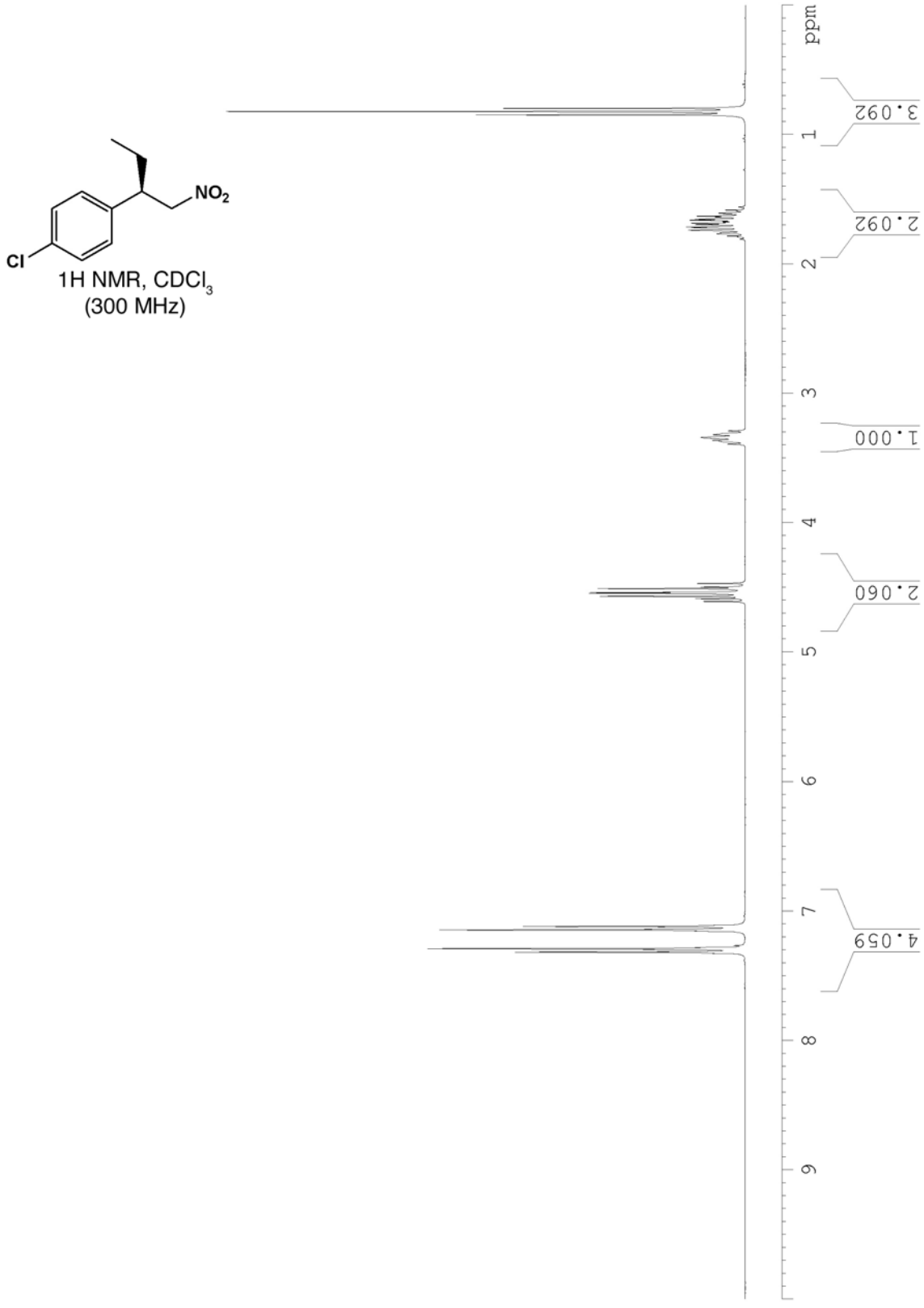
13C NMR, CDCl3
(75 MHz)
ppm
20
40
60
80
100
120
140
160
180
200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Cl
1H NMR, CDCl3
(300 MHz)
ppm
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4
5
6
7
8
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2.092
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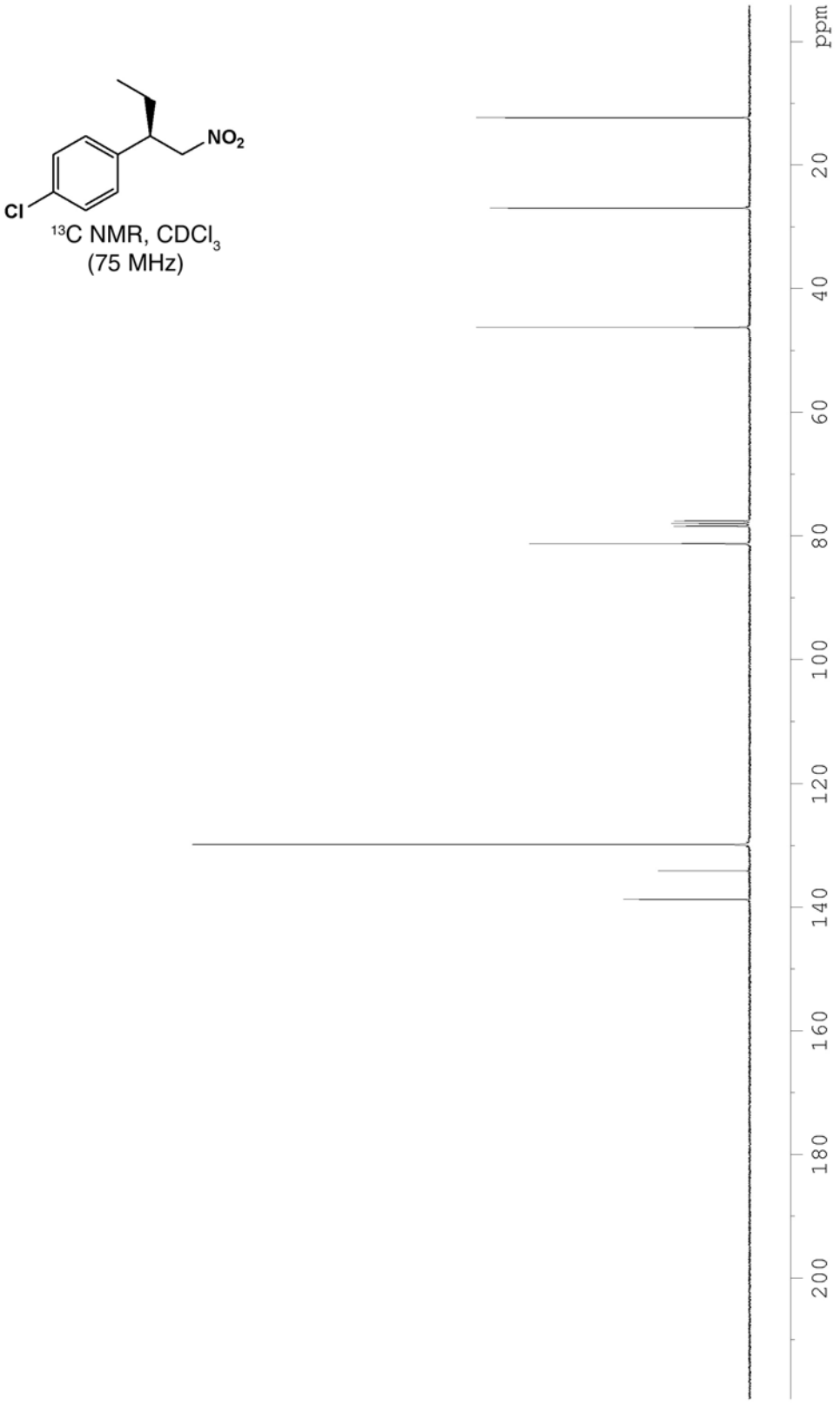
2.060
4.059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Cl
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(75 MHz)
ppm
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80
100
120
140
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180
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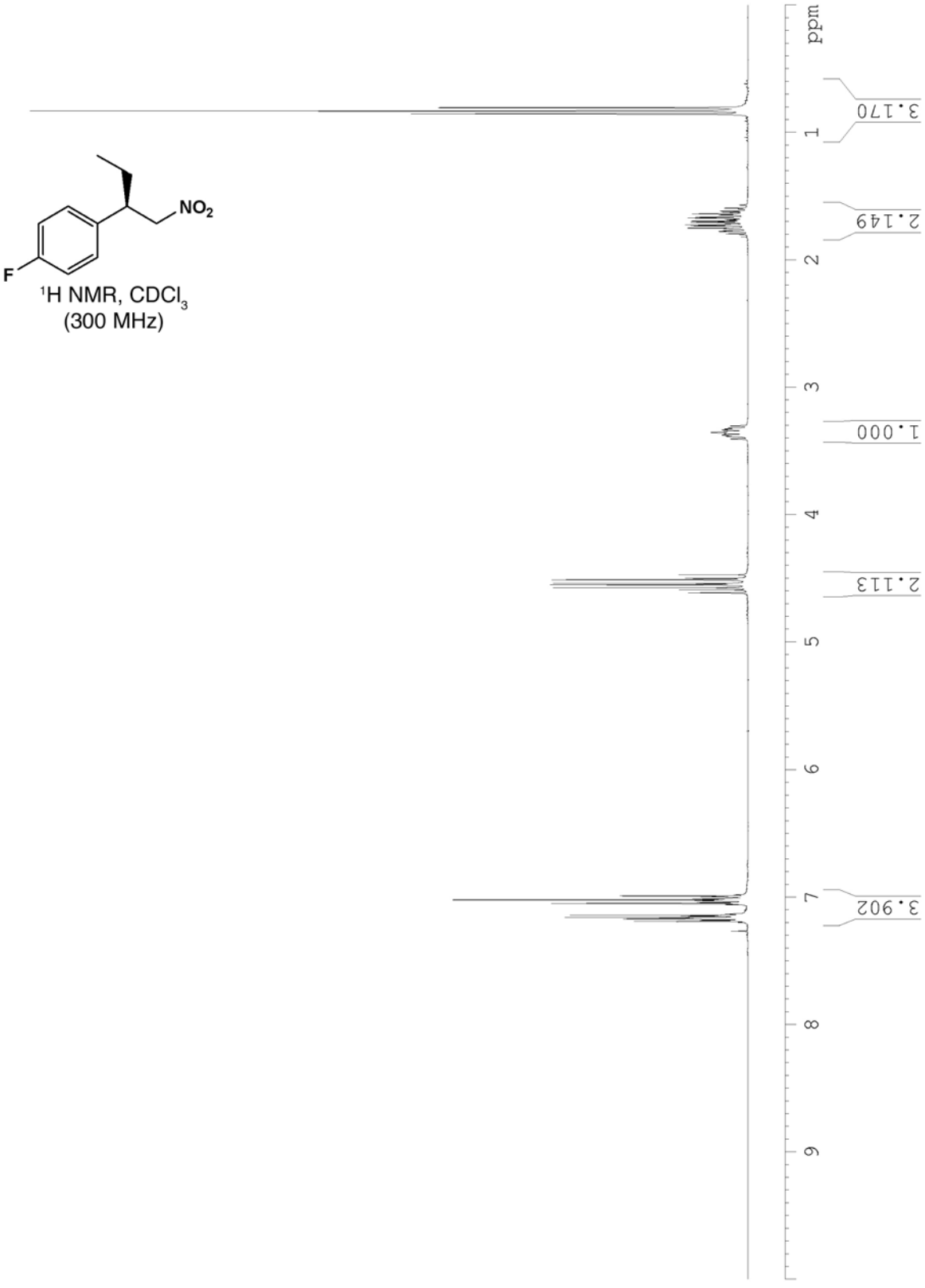
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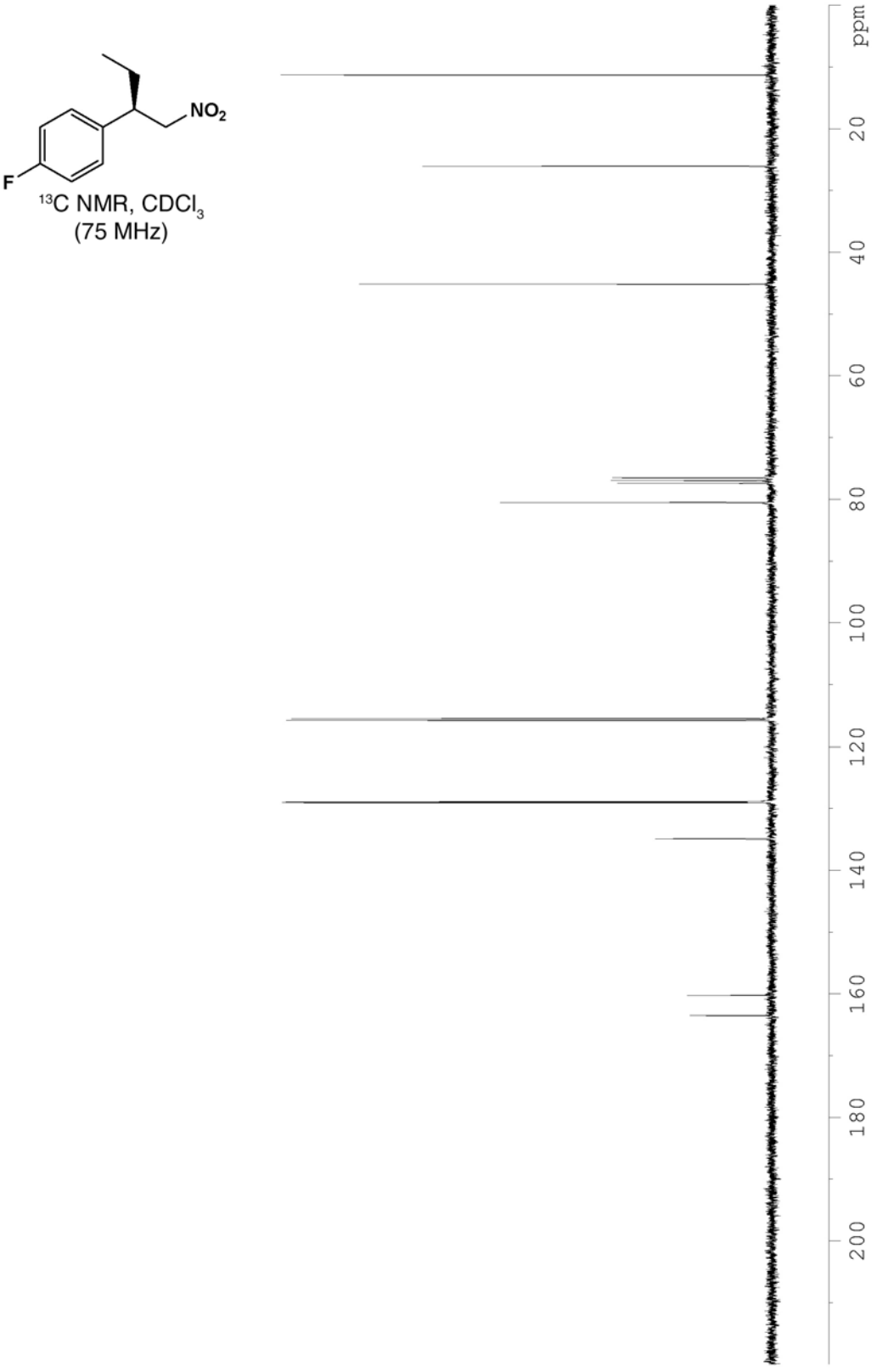
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F
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(75 MHz)
ppm
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40
60
80
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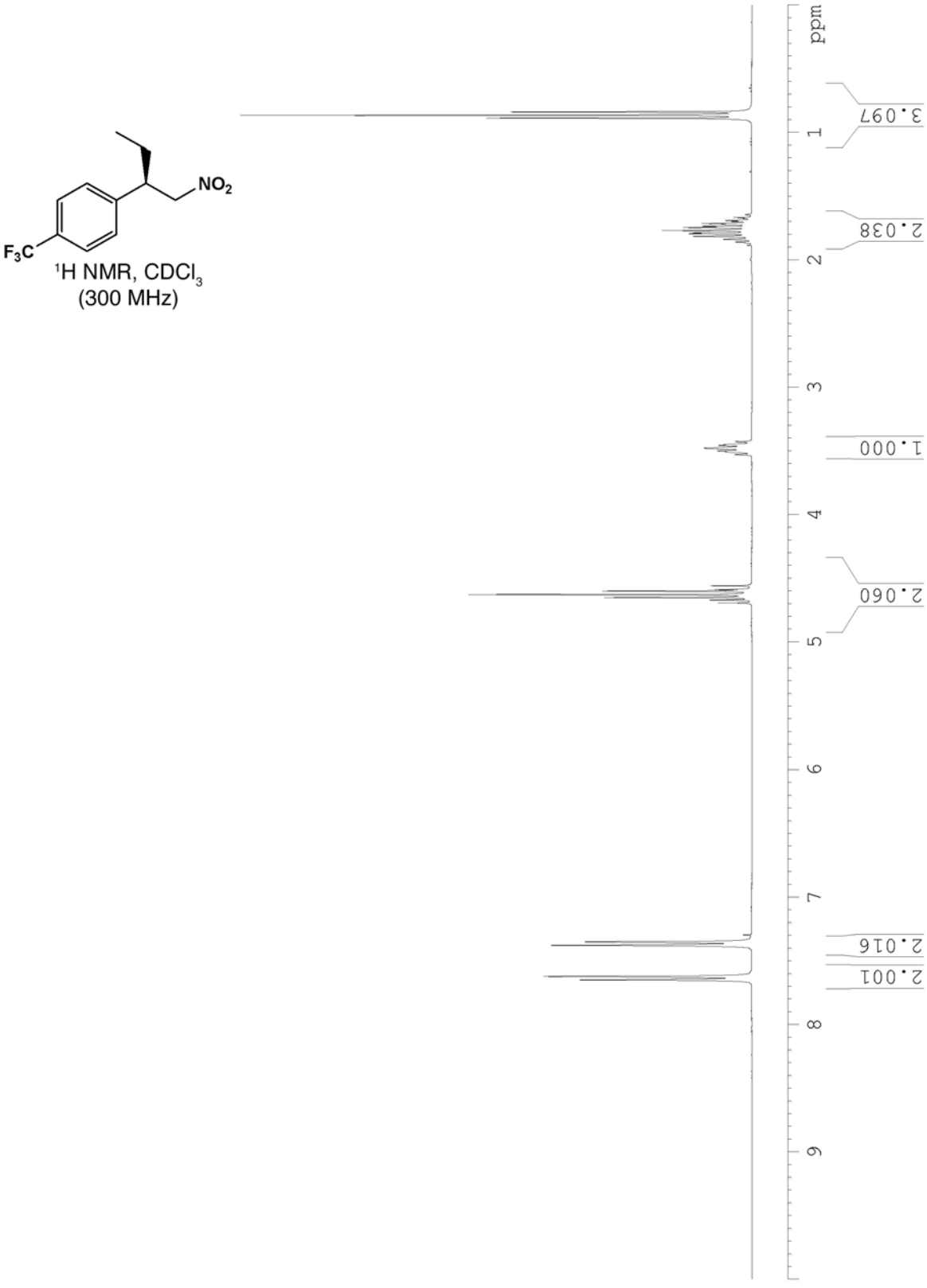
120
140
160
180
200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(300 MHz)
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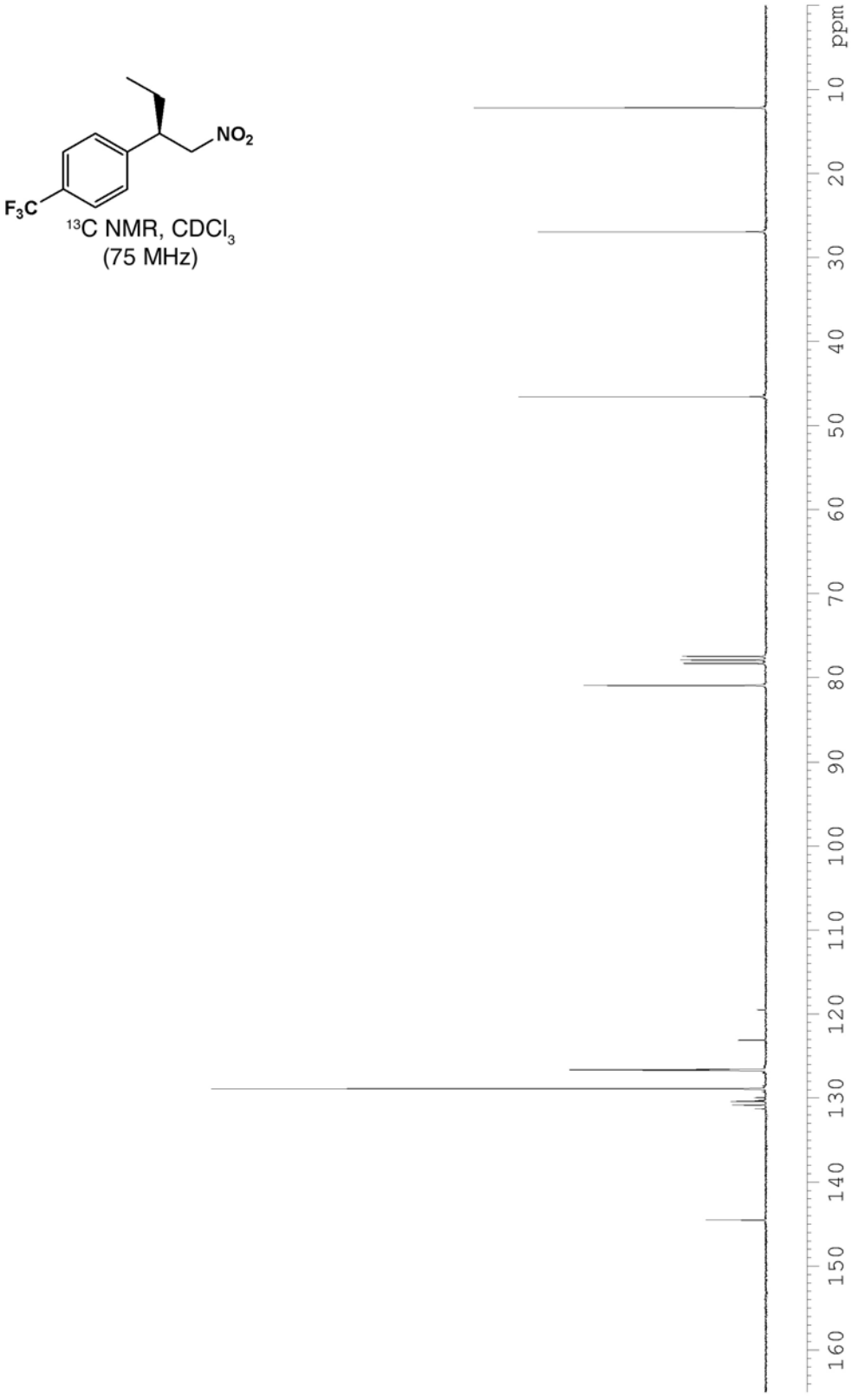
2.001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F3C
13C NMR, CDCl3
(75 MHz)
ppm
10
20
30
40
50
60
70
80
90
100
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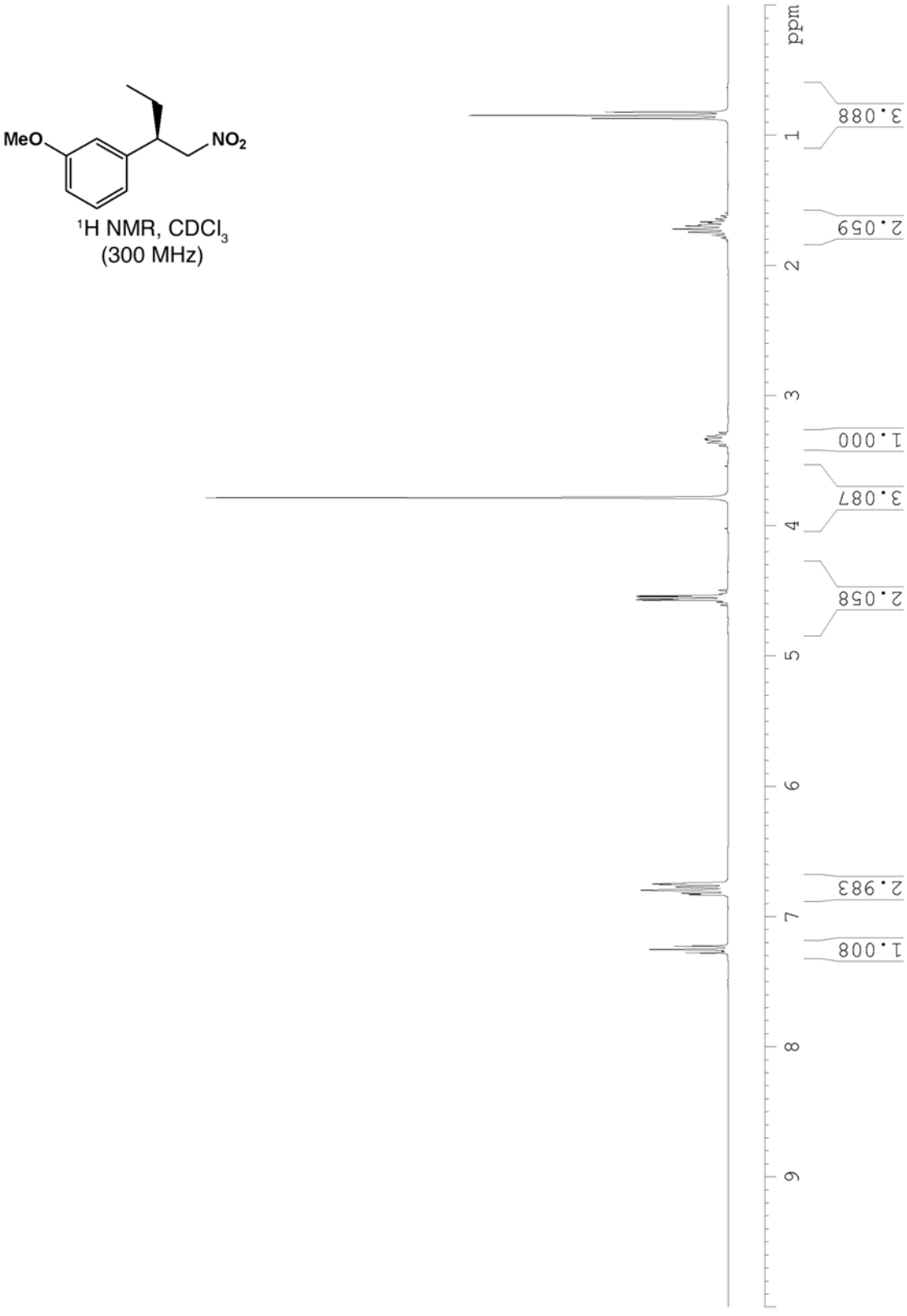
120
130
140
150
160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NO2
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(300 MHz)
ppm
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1.000
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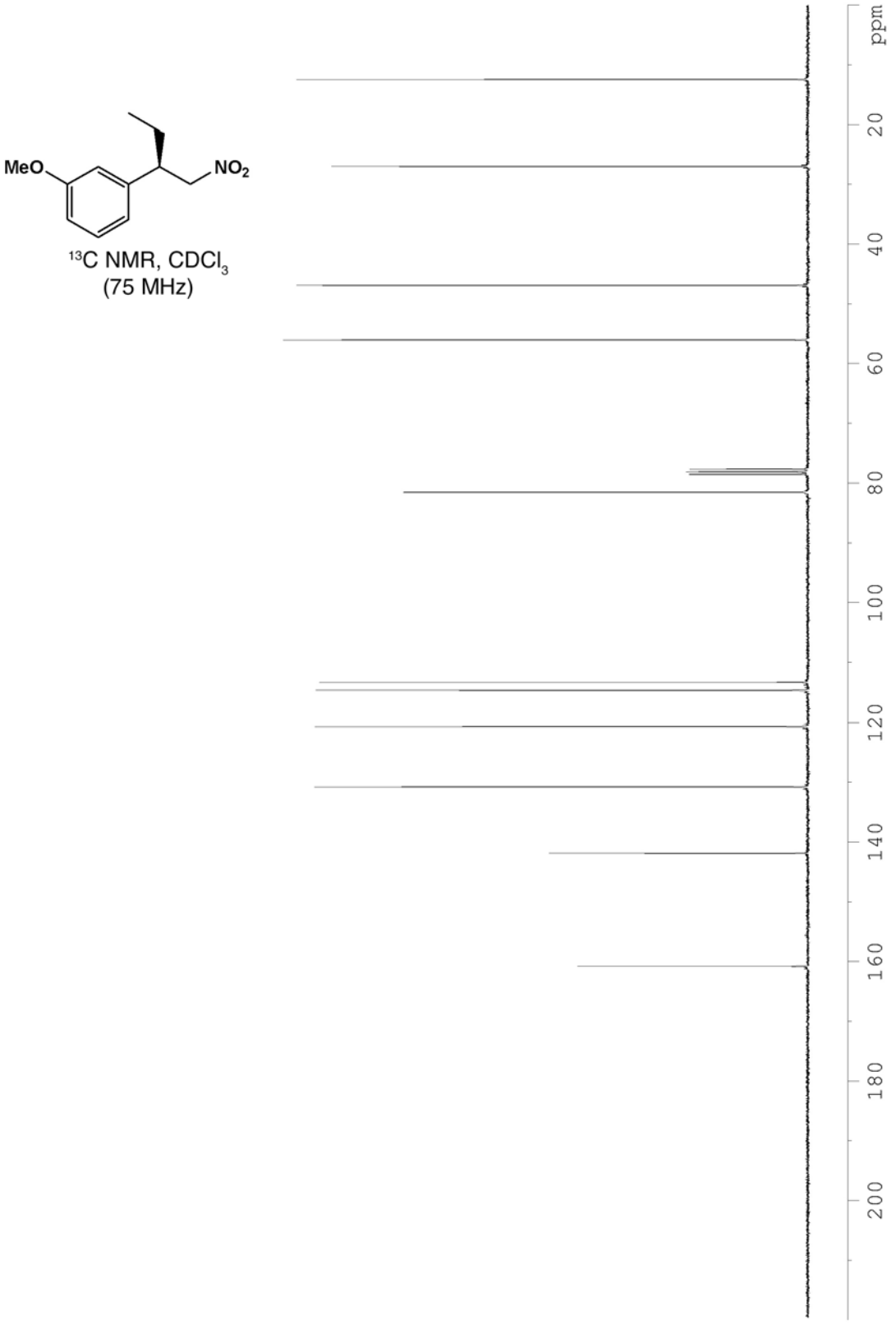
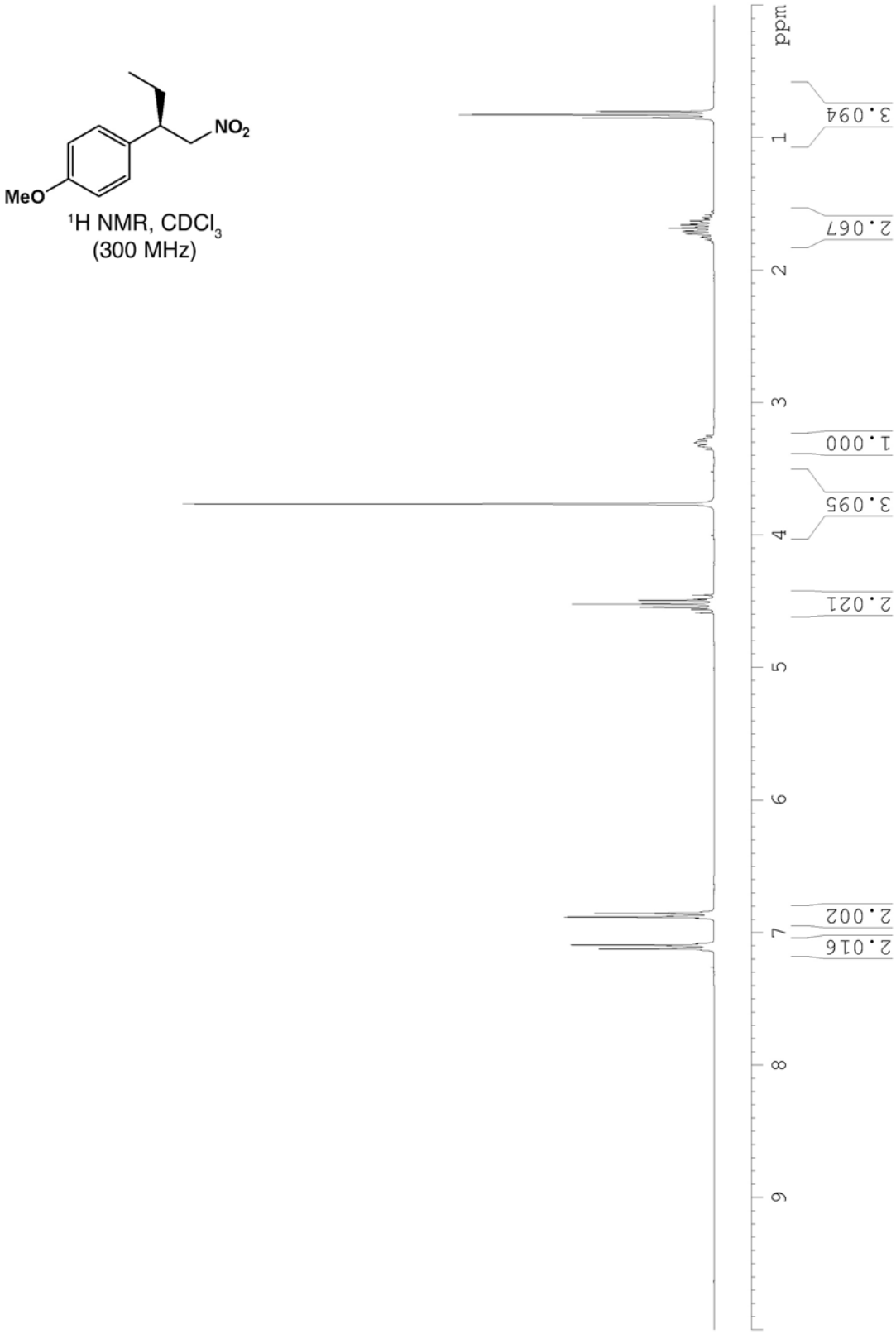
2.058
2.983
1.008


MeO
NO2
13C NMR, CDCl3
(75 MHz)
ppm
20
40
60
80
100
120
140
160
180
200


NO2
MeO
1H NMR, CDCl3
(300 MHz)
ppm
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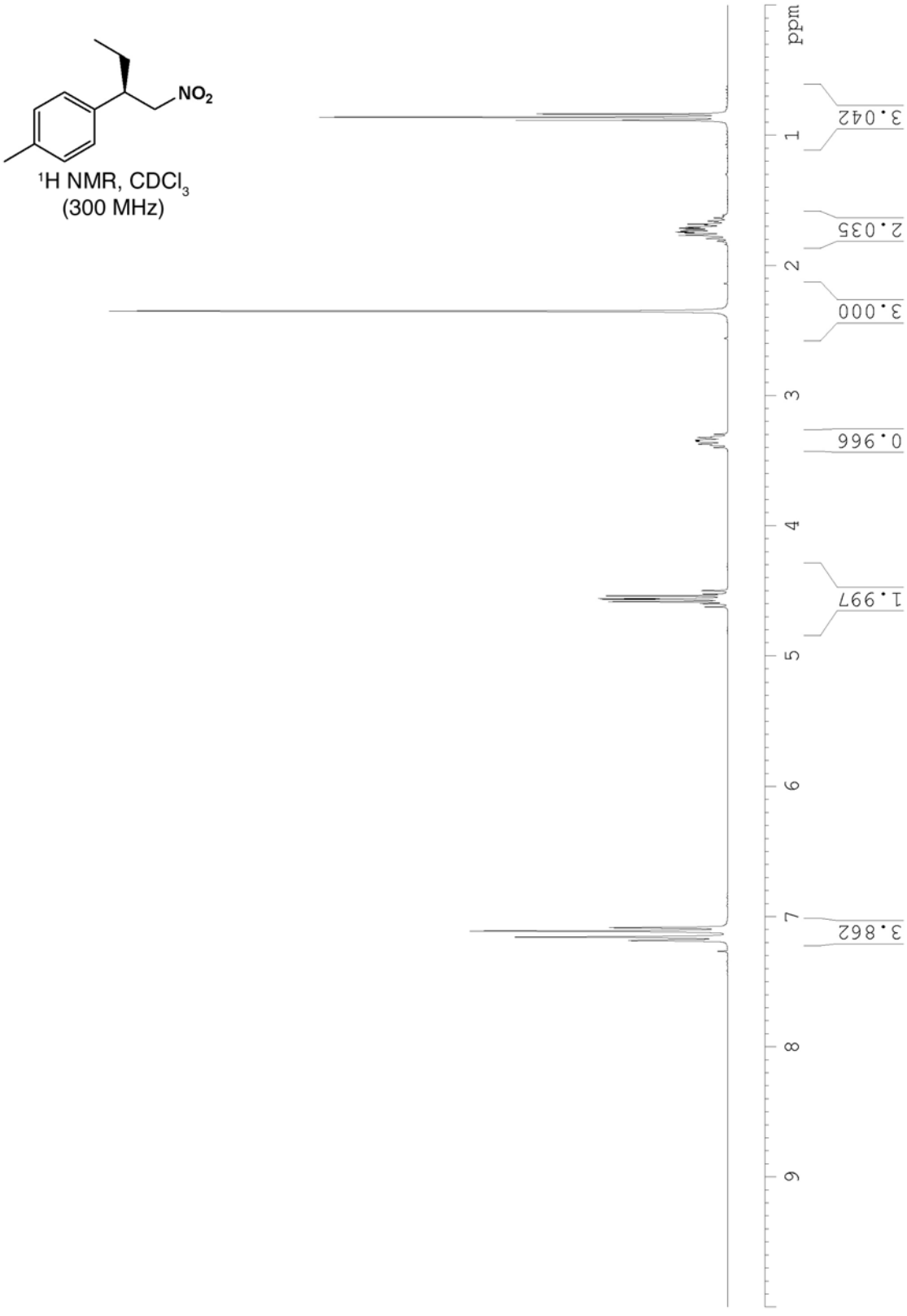
1.000
3.095
2.021
2.002
2.016


NO2
MeO
13C NMR, CDCl3
(75 MHz)
ppm
20
40
60
80
100
120
140
160
180
200


NO2
1H NMR, CDCl3
(300 MHz)
ppm
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2
3
4
5
6
7
8
9
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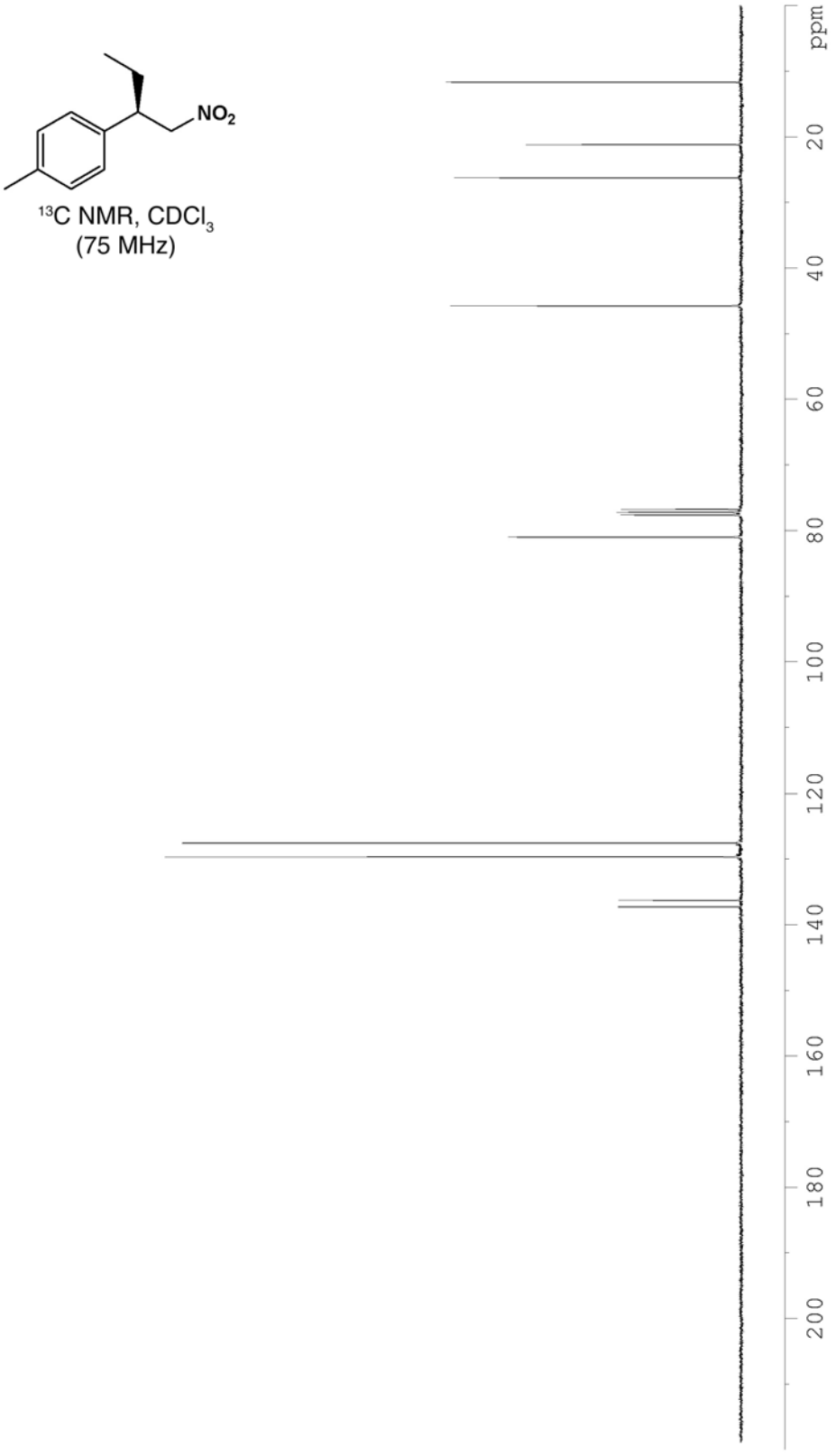
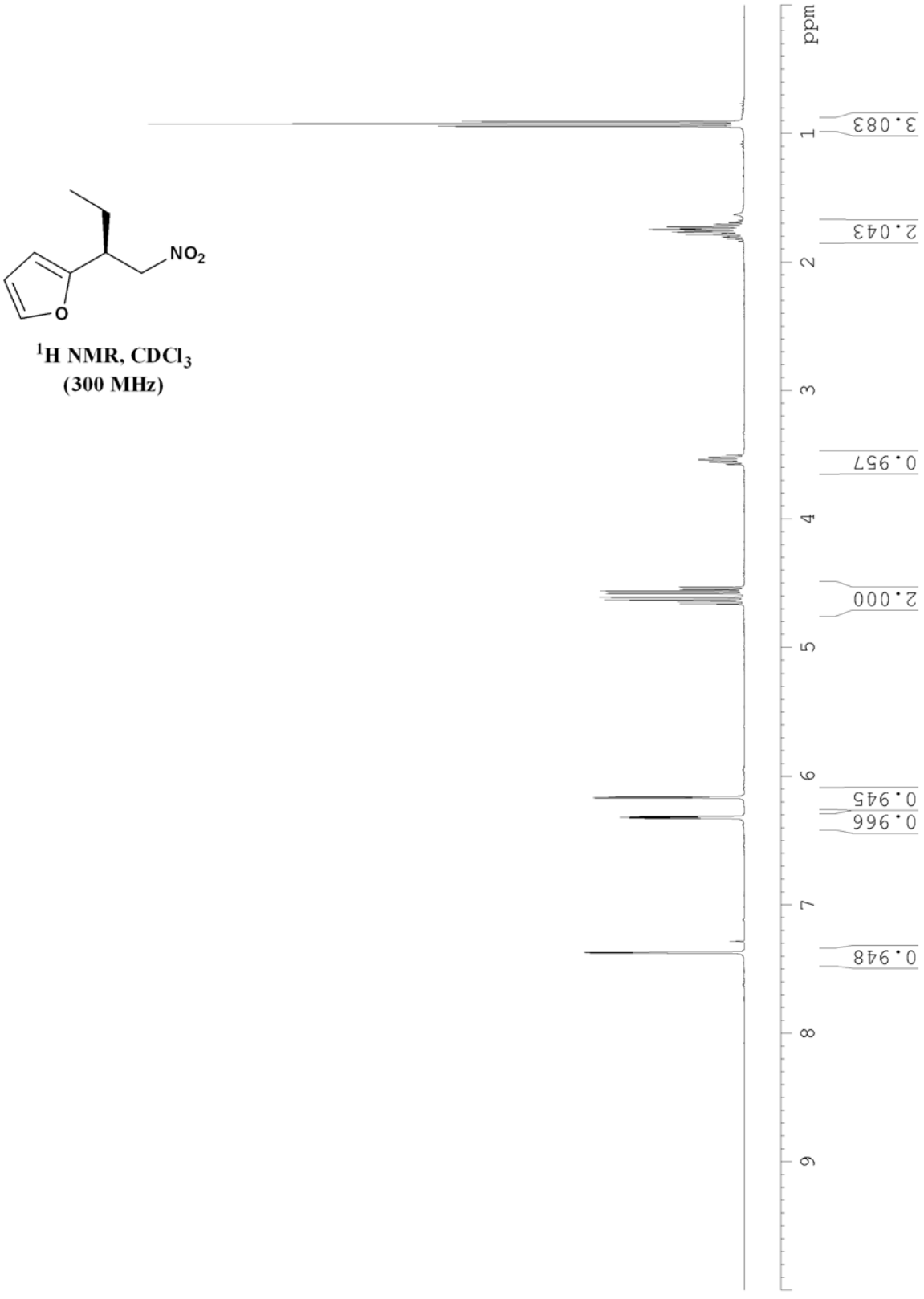
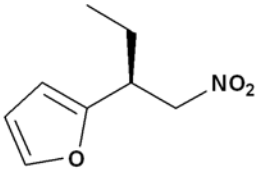
3.000
0.966
1.997
3.862

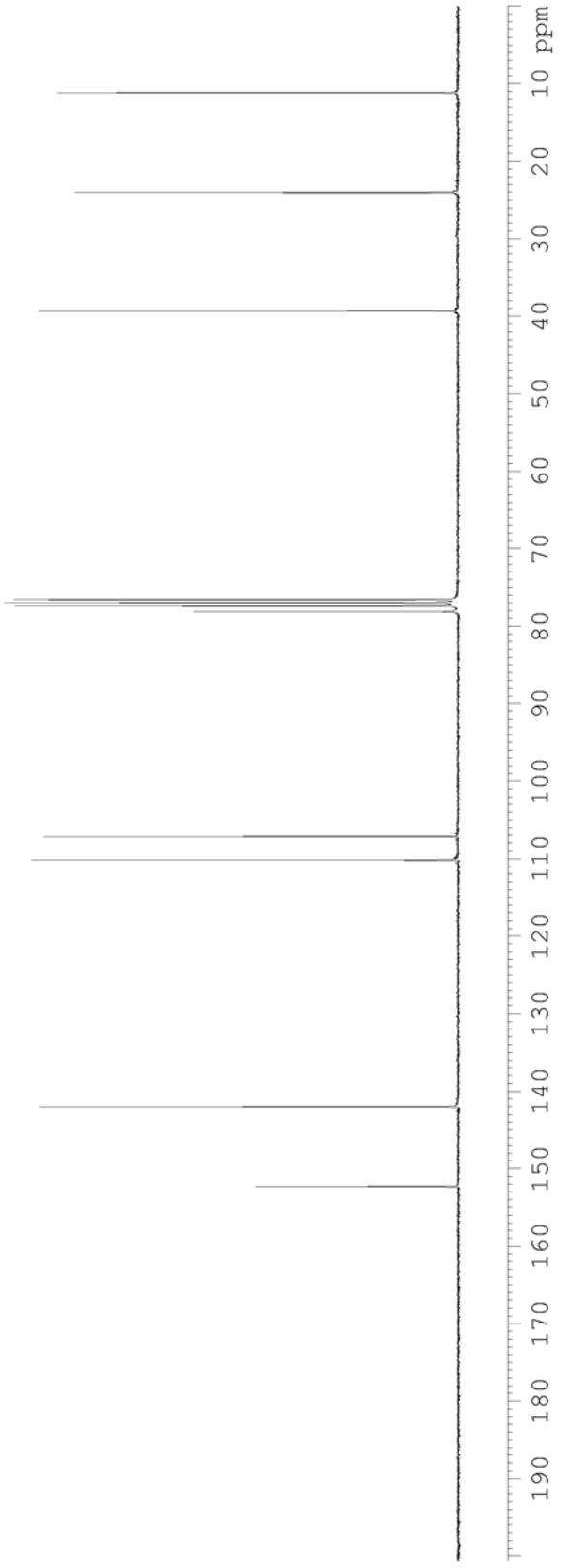

NO2
13C NMR, CDCl3
(75 MHz)
ppm
20
40
60
80
100
120
140
160
180
200



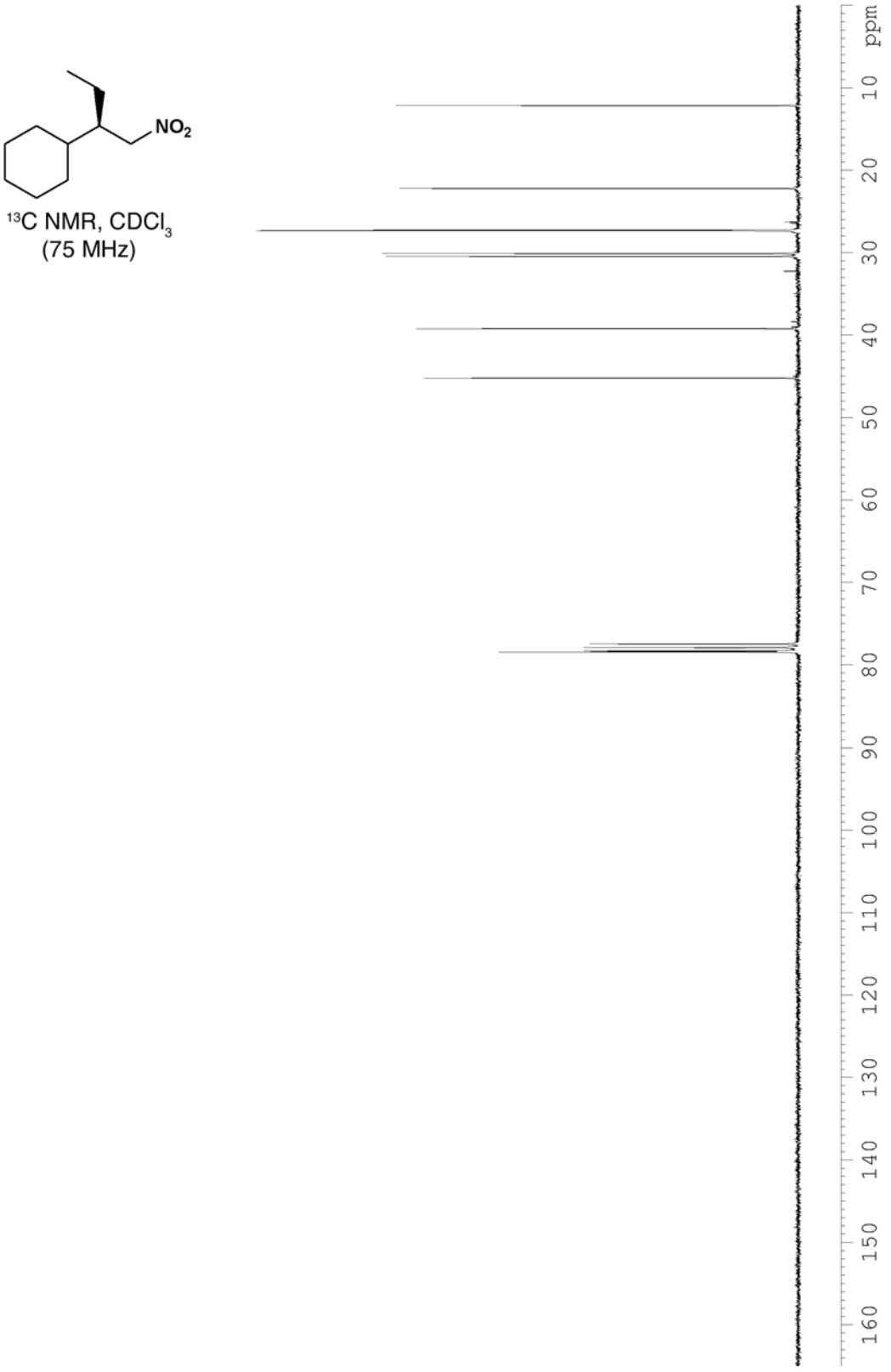
^{1}H NMR, $CDCl_3$
(300 MHz)

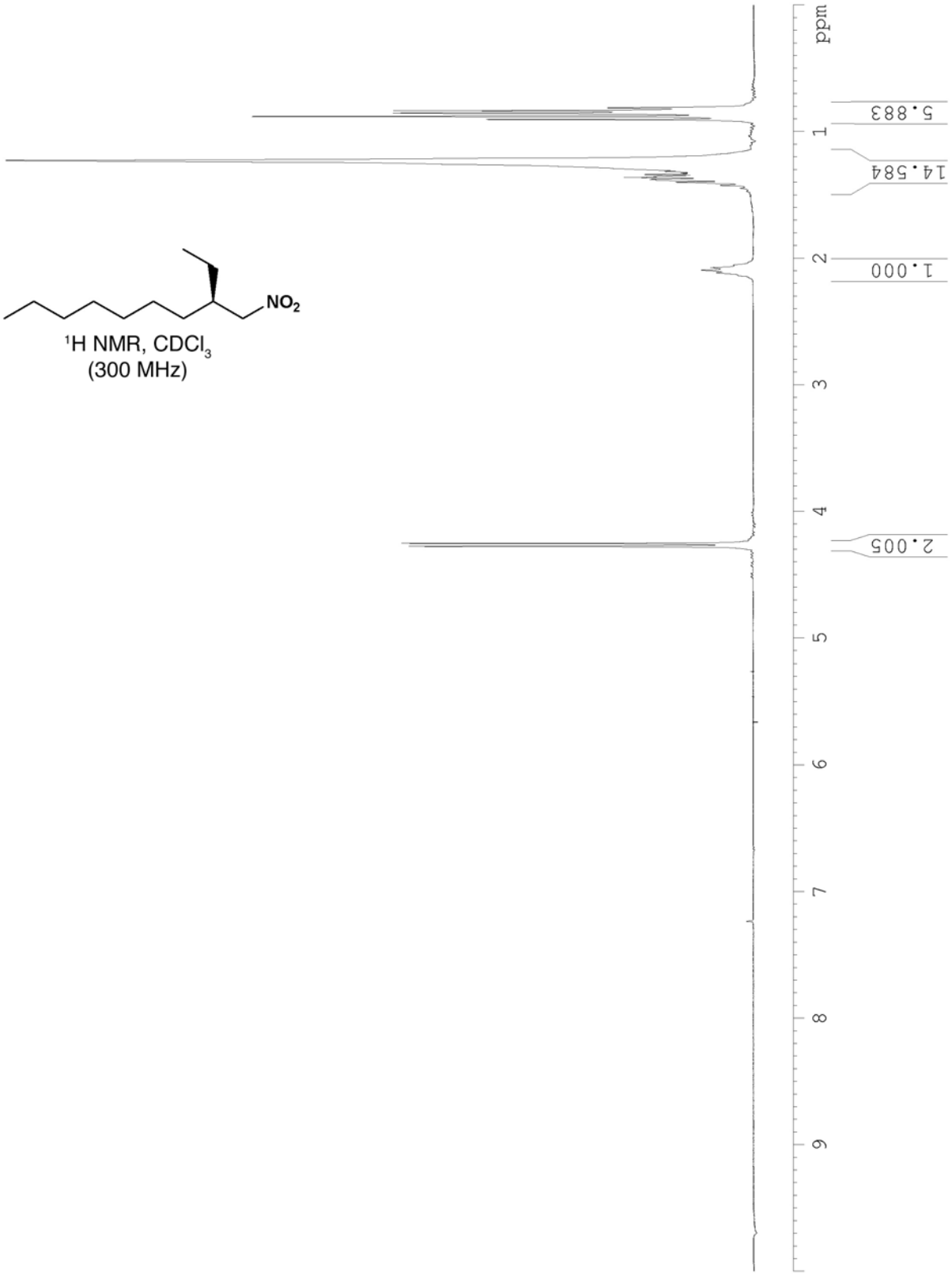


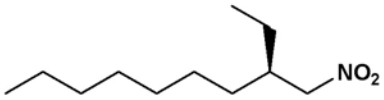
^{13}C NMR, $CDCl_3$
(75 MHz)



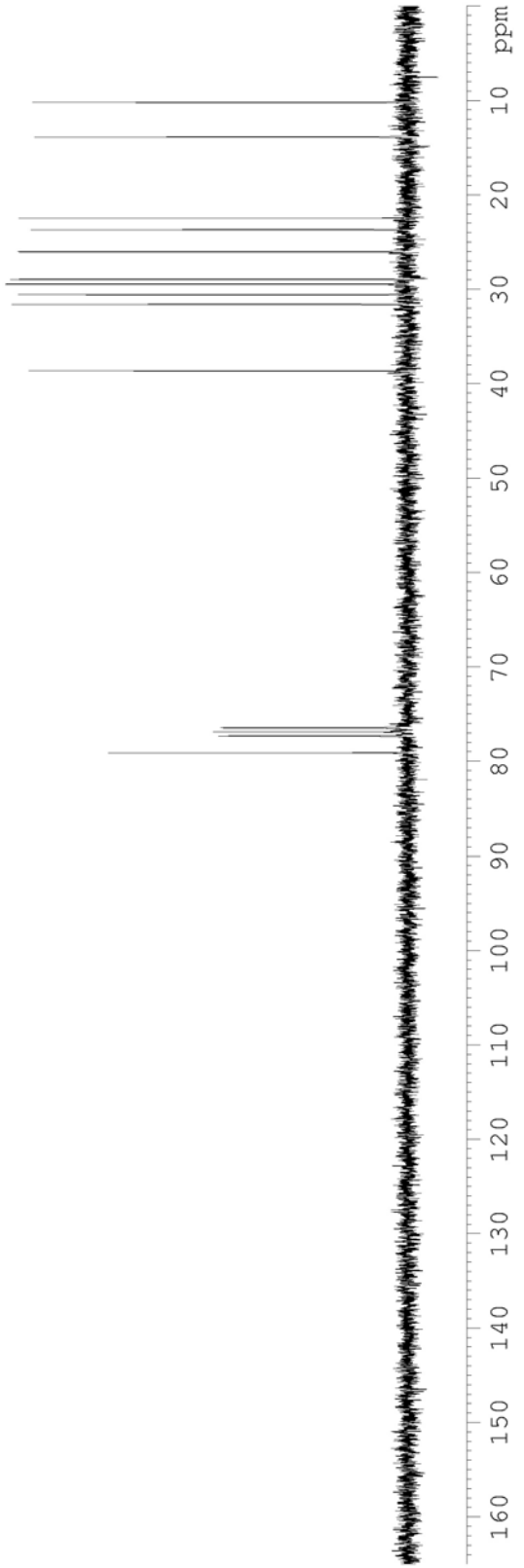

NO2
1H NMR, CDCl3
(300 MHz)
ppm
1
2
3
4
5
6
7
8
9
17.022
1.000
2.044

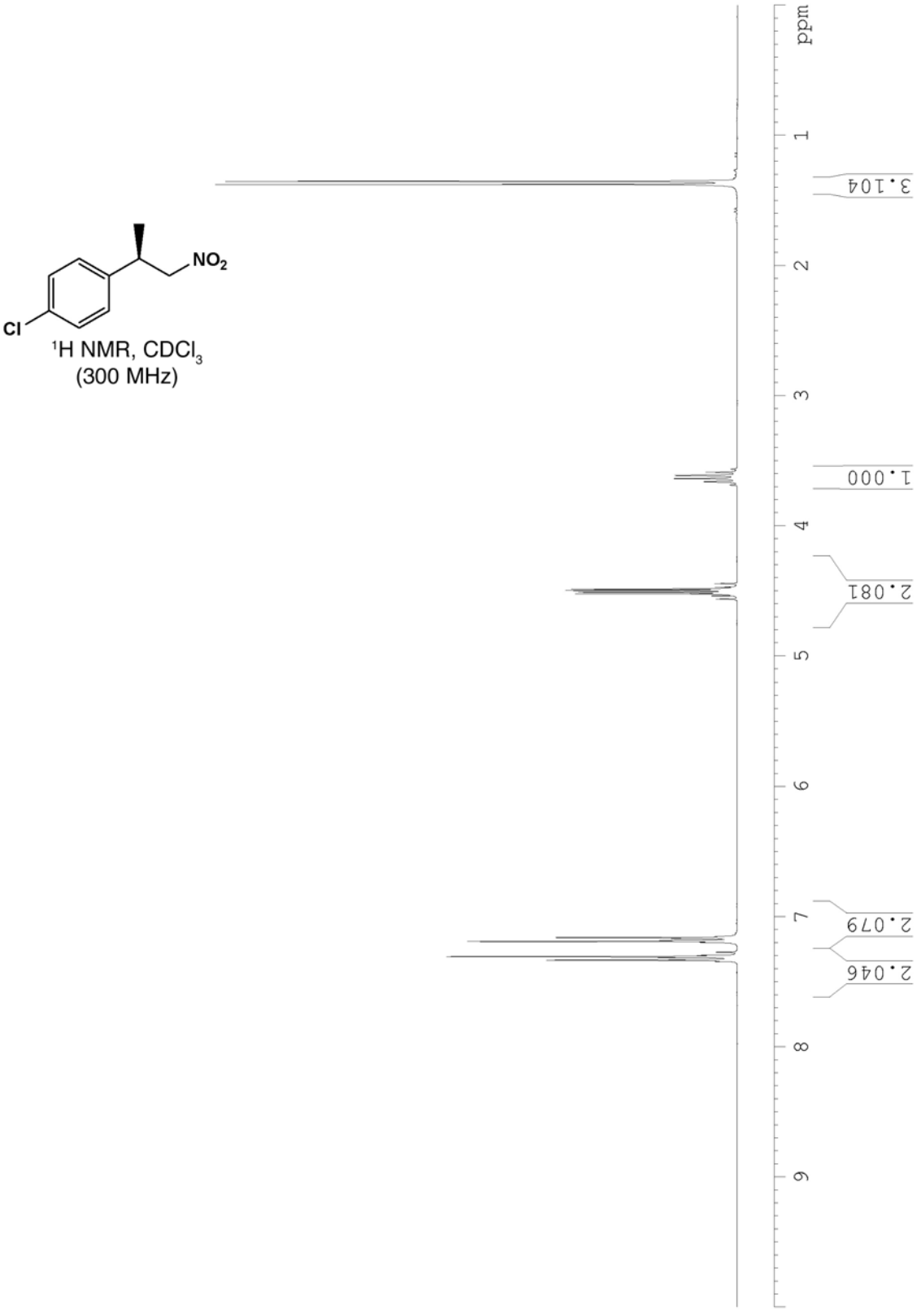

NO2
13C NMR, CDCl3
(75 MHz)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

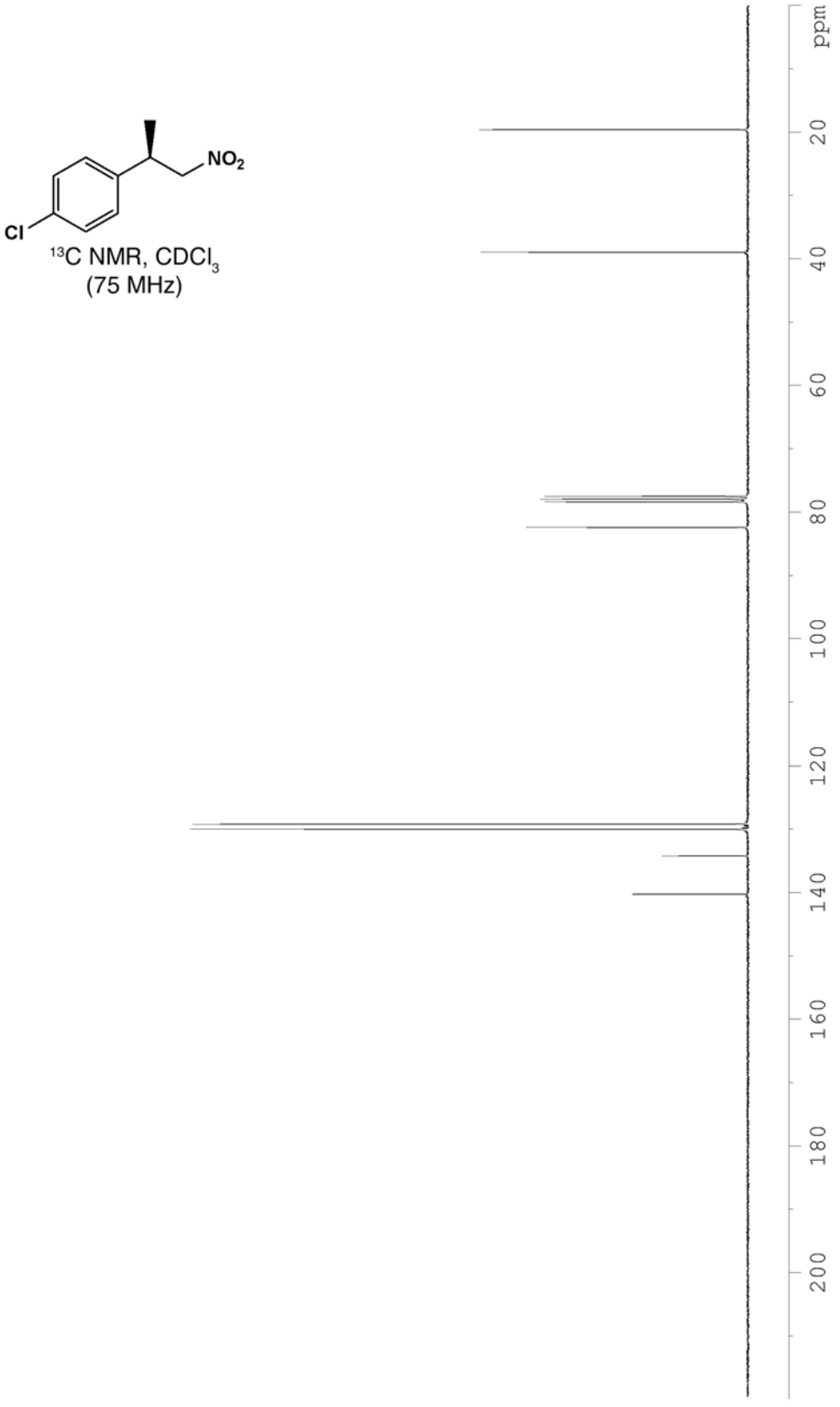

NO2
1H NMR, CDCl3
(300 MHz)
ppm
5.883
14.584
1.000
2.005



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




NO2
Cl
1H NMR, CDCl3
(300 MHz)
ppm
1
2
3
4
5
6
7
8
9
3.104
1.000
2.081
2.079
2.046


NO2
Cl
13C NMR, CDCl3
(75 MHz)
ppm
20
40
60
80
100
120
140
160
180
200