Reversible aryl migrations in metallated ureas: controlled inversion of configuration at a quaternary carbon atom

Daniel J. Tetlow, Mark A. Vincent, Ian H. Hillier and Jonathan Clayden

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

E-mail: clayden@man.ac.uk

SUPPORTING INFORMATION

Contents

General information and procedures

NMR spectra were recorded on a Bruker Ultrashield 300, 400 or 500 MHz spectrometer. The chemical shifts (*δ*) are reported in ppm downfield of trimethylsilane and coupling constants (*J*) reported in Hertz and rounded to 0.5 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), mulitiplet (m), broad (br), or a combination of these. Solvents were used as internal standard when assigning NMR spectra (δH: $CDCl_3$ 7.27 ppm; δC: $CDCl_3$ 77.0 ppm).

Low and high resolution mass spectra were recorded by staff at the University of Manchester. EI and CI spectra were recorded on a Micromass Trio 2000; ES and APCI spectra were recorded on a Waters Platform II; high resolution mass spectra (HRMS, EI and ES) were recorded on a Thermo Finnigan MAT95XP mass spectrometer. Infrared spectra were recorded on a Perkin Elmer *Spectrum RX I* FTIR spectrometer as a film on a sodium chloride plate. Absorptions reported are sharp and strong, only absorption maxima of interest are reported. Melting points (mpt) were determined on a Gallenkamp apparatus and are uncorrected. Optical rotations $[\alpha]^T_D$ were measured with a Perkin-Elmer 241 Polarimeter using a cell with a pathlength of 0.25 dm. Concentrations (*c.*) are given in grams per 100 ml.

Thin layer chromatography (TLC) was performed using commercially available pre-coated plates (Macherey-Nagel alugram Sil G/$_{UV254}$ or Machery-Nagel polygram. Alox N/$_{UV254}$) and visualised with UV light at 254 nm and phosphomolybdic acid dip (5 % in ethanol). Flash chromatography was carried out using Fluorochem Davisil 40-63u 60 Å (unless otherwise stated), under a positive pressure by means of compressed air, followed by removal of the solvent under reduced pressure after purification.

Enantiomeric ratios were determined by HPLC on a Hewlett-Packard system with UV detection at 254 and 214 nm. A Chirapak AD-H column and hexane/2-propanol (IPA) 90/10 as eluent were used for all separations, unless otherwise stated.

All reactions were conducted under an atmosphere of dry nitrogen in flame-dried glassware. Tetrahydrofuran (THF) was distilled under nitrogen from sodium using benzophenone as indicator. Diisopropylamine (DIPA) and Dichloromethane were obtained by distillation from calcium hydride under nitrogen. Toluene and Et_2O were collected under inert conditions from a Innovative Technologies PureSolve PS-MP-5 solvent purification system. All other solvents and commercially obtained reagents were used as received or purified using standard procedures.

Lithium amides were freshly prepared before use from either the free amine or hydrochloride salt. The amine was cooled in THF (0.6 M) to 0°C and ^{n}Butyl Lithium (2.5M in hexanes, 1 equiv for free amines, 2 equiv for amine salts) was added dropwise. The solution stirred for 20 minutes before immediate use.[1]

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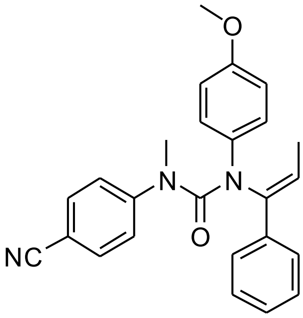
[1] Clayden, J.P.; Menet, C.J.; Mansfield, D.J. *Chem. Commun.* ***2002***, 38.

Experimental procedures and characterisation data

Compounds **2a**, **2b**, **2c**, **2d**, **2e**, **2g** and **2h** were prepared by previously reported precedures.[2]

1-(4-Cyanophenyl)-3-(4-methoxyphenyl)-1-methyl-3-((Z)-1-phenylpropenyl)urea *1a*



To (*R*)-1-[1-(4-Cyano-phenyl)-1-phenyl-allyl]-1-(4-methoxy-phenyl)-3-methyl-urea[2] **2a** (0.100 g, 0.25 mmol) in DMF (5 mL) was added NaH (0.002 g 0.050 mmol). The reaction was stirred at room temperature for 10 minutes. MeOH was added dropwise and the reaction mixture partitioned between Et_2O (20 mL) and H_2O (20 mL). The organic phase was separated, washed with water (2 × 20 mL) and brine (20 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. The title compound was used without further purification (0.100 g, 0.25 mmol, 100 %). ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.27; **IR** ν_{max} (film)/cm^{-1} 2225 (CN), 1672 (C=O) and 1510 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.52 (2H, d, *J* = 9.0 Hz), 7.34-7.28 (3H, m), 7.19-7.14 (4H, m), 7.00 (2H, d, *J* = 9.0 Hz), 6.86 (2H, d, *J* = 9.0 Hz), 5.36 (1H, q, *J* = 7.0 Hz), 3.80 (3H, s), 2.90 (3H, s) and 1.22 (3H, d, *J* = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.3, 156.7, 148.4, 144.8, 141.1, 139.5, 136.6, 132.6, 128.5, 128.0, 126.6, 125.0, 123.4, 121.7, 118.9 , 114.3, 107.5, 55.5, 37.6 and 14.5; **MS** m/z (ES$^+$) 398 (30%, M+H$^+$), 420 (100%, M+Na$^+$); **HRMS** calcd for $C_{25}H_{24}N_3O_2$ (M+H$^+$) 398.1863, found 398.1873; **Elem. anal.** Calcd : C 75.54, H 5.83, N 10.57 Found : C 75.21, H 5.90, N 10.35. **Matches previously reported data**[3]

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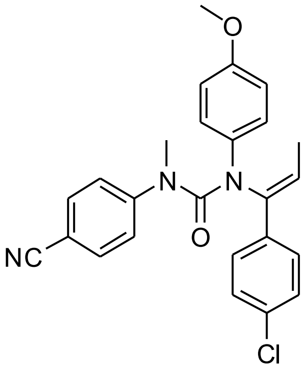
[2] Clayden, J.; Tetlow, D. J.; Hennecke, U.; Raftery, J.; Waring, M. J.; Clarke, D. S. *Org. Lett.* **2010**, *12*, 5442.

[3] Clayden, J.; Lefranc, J.; Tetlow, D. J.; Donnard, M.; Minassi, A.; Galvez, E. *Org. Lett.* **2011**, *13*, 296.

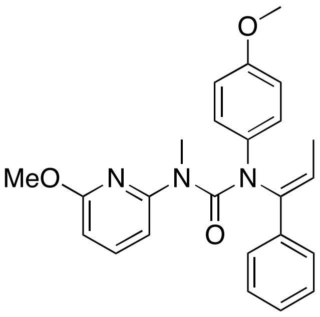
1-[(Z)-1-(4-Chlorophenyl)propenyl]-3-(4-cyanophenyl)-1-(4-methoxyphenyl)-3-methylurea *1b*



To (±) 1-[1-(4-Chloro-phenyl)-1-(4-cyano-phenyl)-allyl]-1-(4-methoxy-phenyl)-3-methyl-urea[2] **2b** (0.043 g, 0.99 mmol) in EtOH (4.0 mL) was added Na_2CO_3 (0.10 g). The reaction was stirred at reflux for 16 hours. The reaction was cooled to room temperature and Et_2O (20 mL) was added. The reaction mixture was filtered and the solvent removed under reduced pressure. The title compound was used without further purification (complete conversion by ^{1}H-NMR and crude weight). ***R***$_F$(2:1 Petroleum Ether-EtOAc) 0.32; **IR** ν_{max} (film)/cm^{-1} 2225 (CN), 1671 (C=O) and 1510 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.54 (2H, d, *J* = 9.0 Hz), 7.29 (2H, d, *J* = 8.5 Hz), 7.13-7.10 (4H, m), 7.03 (2H, d, *J* = 9.0 Hz), 6.84 (2H, d, *J* = 9.0 Hz), 5.35 (1H, q, *J* = 7.5 Hz), 3.79 (3H, s), 2.95 (3H, s) and 1.24 (3H, d, *J* = 7.5 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.3, 156.8, 148.4, 140.2, 138.0, 136.2, 133.7, 132.7, 128.7, 126.5, 124.8, 123.6, 122.3, 118.7, 114.4, 107.6, 55.5, 37.9 and 14.5; **MS** m/z (ES$^+$) 432 (100%, M+H$^+$), 454 (100%, M+Na$^+$); **HRMS** calcd for $C_{25}H_{23}{}^{35}ClN_3O_2$ (M+H$^+$) 432.1473, found 432.1470.

Matches previously reported data[2]

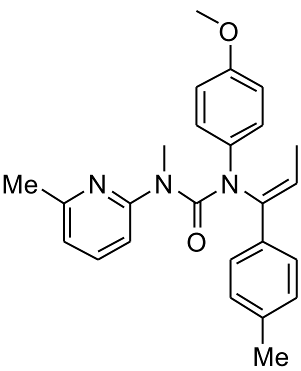
1-(4-Methoxyphenyl)-3-(6-methoxypyridin-2-yl)-3-methyl-1-((Z)-1-phenylpropenyl)urea *1c*



To (±)-1-(4-Methoxyphenyl)-1-(1-(6-methoxypyridin-2-yl)-1-phenylallyl)-3-methylurea[2] **2c** (0.020 g, 0.049 mmol) in EtOH (2 mL) was added Na_2CO_3 (0.10 mmol). The reaction was stirred at reflux for 16 hours. The reaction was cooled to room temperature and Et_2O (20 mL) was added. The reaction mixture was filtered and the solvent removed under reduced pressure. The title compound was used without further purification (complete conversion by ^{1}H-NMR and crude weight). ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.38; **IR** ν_{max} (film)/cm^{-1} 1675 (C=O) and 1505 (C=C); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.40 (1H, t, *J* = 8.0 Hz), 7.28-7.20 (5H, m), 7.17 (2H, d, *J* = 9.0 Hz), 6.80 (2H, d, *J* = 9.0 Hz), 6.55 (1H, dd, *J* = 8.0 and 0.5 Hz), 6.34 (1H, dd, *J* = 8.0 and 0.5 Hz), 5.47 (1H, q, *J* = 7.0 Hz), 3.84 (3H, s), 3.77 (3H, s), 2.95 (3H, s) and 1.33 (3H, d, *J* = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 162.8, 160.0, 156.4, 154.2, 141.3, 139.7, 139.4, 136.7, 128.3, 127.6, 125.5, 124.9, 121.4, 114.2, 108.9, 104.9, 55.5, 53.2, 35.7 and 14.2; **MS** m/z (ES$^+$) 404 (100%, M+H$^+$); **HRMS** calcd for $C_{24}H_{26}N_3O_3$ (M+H$^+$) 404.1969, found 404.1963.

Matches previously reported data[2]

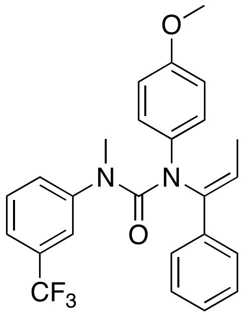
1-(4-Methoxyphenyl)-3-methyl-3-(6-methylpyridin-2-yl)-1-((Z)-1-*p*-tolylpropenyl)urea *1d*



To (±)1-(4-Methoxy-phenyl)-3-methyl-1-[1-(6-methyl-pyridin-2-yl)-1-*p*-tolyl-allyl]-urea[2] **2d** (0.023 g, 0.57 mmol) in EtOH (2 mL) was added Na_2CO_3 (0.050 g). The reaction was stirred at reflux for 16 hours. The reaction was cooled to room temperature and Et_2O (10 mL) was added. The reaction mixture was filtered and the solvent removed under reduced pressure. The title compound was purified by flash column chromatography to give the title compound as a pale orange gum (0.010 g, 0.25 mmol, 44 %). ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.23; **IR** ν_{max} (film)/cm^{-1} 1672 (C=O) and 1509 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.38 (1H, t, *J* = 8.0 Hz), 7.22 (2H, d, *J* = 8.0 Hz), 7.14 (2H, d, *J* = 9.0 Hz), 7.06 (2H, d, *J* = 9.0 Hz), 6.78-6.72 (4H, m), 5.48 (1H, q, *J* = 7.0 Hz), 3.75 (3H, s), 3.06 (3H, s), 2.42 (3H, s), 2.31 (3H, s) and 1.40 (3H, d, *J* = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 167.0, 160.1, 157.1, 156.6, 156.1, 141.6, 137.5, 137.0, 136.9, 129.2, 125.8, 125.6, 120.9, 118.4, 114.3, 114.2, 55.6, 36.3, 24.3, 21.3 and 14.4; **MS** m/z (ES$^+$) 402 (100%, M+H$^+$), 424 (40%, M+Na$^+$); **HRMS** calcd for $C_{25}H_{28}N_3O_2$ (M+H$^+$) 402.2176, found 402.2178.

Matches previously reported data[2]

(Z)-1-(4-methoxyphenyl)-3-methyl-1-(1-phenylprop-1-enyl)-3-(3-(trifluoromethyl) phenyl)urea *1f*

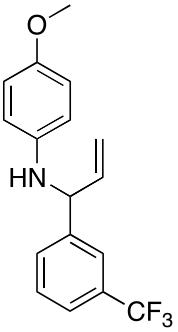


To 1-(4-methoxyphenyl)-3-methyl-1-(1-phenyl-1-(3-(trifluoromethyl) phenyl)allyl)urea **2f** (0.046 g, 0.104 mmol) in DMF (2 mL) was added NaH (0.010 g 0.21 mmol). The reaction was stirred at room temperature for 16 hours. MeOH was added dropwise and the reaction mixture partitioned between Et_2O (20 mL) and H_2O (20 mL). The organic phase was separated, washed with water (20 mL) mL) and brine (20 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash column chromatography gave the title compound as a gum (0.021 g, 0.047 mmol, 45 %). ***R*$_F$** (2:1 Petroleum Ether-EtOAc) 0.36; **IR** ν_{max} (film)/cm^{-1} 1670 (C=O) and 1509; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.37-7.27 (5H, m), 7.22-7.12 (6H, m), 6.84 (2H, d, *J* = 9.0 Hz), 5.33 (1H, q, *J* = 7.0 Hz), 3.80 (3H, s), 2.99 (3H, s) and 1.18 (3H, d, *J* = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 160.0, 156.7, 145.3, 141.5, 139.7, 137.3, 131.5 (q, J_{CF} = 30.0 Hz) 129.4, 128.6, 128.4, 128.0, 125.6, 125.3, 121.7 (q, J_{CF} = 4.5 Hz), 121.6 (q, J_{CF} = 4.5 Hz), 121.3, 114.4, 55.7, 38.9 and 14.6; CF_3 not visible in ^{13}C spectra. **MS** m/z (ES^+) 441 (100 %, $M+H^+$); **HRMS** calcd for $C_{25}H_{24}N_2O_2F_3$ ($M+H^+$) 441.1789, found 441.1784.

Matches previously reported data[3]

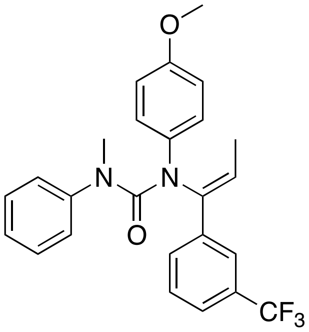
Direct comparison of crude ^{1}H-NMR to both (*Z*)-1-(4-methoxyphenyl)-3-methyl-3-phenyl-1-(1-(3-(trifluoromethyl)phenyl)prop-1-enyl)urea ***1f*** and (Z)-1-(4-methoxyphenyl)-3-methyl-1-(1-phenylprop-1-enyl)-3-(3-(trifluoromethyl) phenyl)urea ***1f’*** is shown in supplementary information.

N-(4-methoxyphenyl)-1-(3-trifluoromethylphenyl)allylamine A



To 3-(trifluoromethyl)-benzaldehyde (1.71 mL, 12.8 mmol) in CH_2Cl_2 (25 mL) was added *p*-anisidine (1.58 g, 12.8 mmol) and molecular sieves (2.0 g, 4Å powdered), the reaction was stirred at room temperature for 16 h. The crude reaction mixture was filtered through Celite and the solvent removed under reduced pressure. To the crude imine (12.8 mmol) in THF (25 mL) at -78 °C was added freshly prepared vinyl lithium (25.6 mmol) slowly over 15 minutes. The reaction was stirred for 1 hour at -78 ºC. The reaction mixture was quenched with saturated aqueous NH4Cl, warmed to room temperature and extracted twice with Et_2O. The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash column chromatography gave the title compound as an orange oil (3.76 g, 12.2 mmol, 95 %); ***R***$\boldsymbol{R_F}$(2:1 Petroleum Ether-EtOAc) 0.55; **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.66 (1H, s), 7.58 (1H, d, *J* = 7.5 Hz), 7.54 (1H, d, *J* = 8.0 Hz), 7.46 (1H, t, *J* = 8.0 and 7.5 Hz), 6.74 (2H, d, *J* = 8.5 Hz), 6.54 (2H, d, *J* = 8.5 Hz), 6.02 (1H, ddd, *J* = 16.5, 10.5 and 6.5 Hz), 5.28-5.24 (2H, m), 4.93-4.91 (1H, m), 3.81 (1H, brd, *J* = 3.0 Hz) and 3.73 (3H, s); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 152.5, 143.2, 140.9, 138.7, 130.9 (q, J_{CF} = 32.0 Hz), 130.5, 129.1, 124.2 (q, *J* = 4.5 Hz), 123.9 (q, J_{CF} = 4.5 Hz), 116.9, 115.0, 114.8, 61.5 and 55.7. CF_3 not visible in ^{13}C spectra.

(*Z*)-1-(4-methoxyphenyl)-3-methyl-3-phenyl-1-(1-(3-(trifluoromethyl)phenyl)prop-1-enyl)urea[4] *1f'*



Phenyl isocyanate (0.58 mL, 5.30 mmol) was added to (4-methoxy-phenyl)-(1-(3-(trifluoromethyl)phenyl)-allyl)-amine **A** (1.63 g, 5.30 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred for 16 hours and the solvent removed under reduced pressure. The crude urea was dissolved in DMF (10 mL) and cooled to 0 °C. NaH (0.53 g, 13.25 mmol) and MeI (0.98 mL, 15.9 mmol) were added and the reaction mixture slowly warmed to room temperature. The reaction was stirred for 16 hours and quenched with MeOH. Et_2O (50 mL) was added, the mixture extracted with water (3 × 50 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash column chromatography gave the title compound as a gum, which solidified upon standing (2.08 g, 4.72 mmol, 89 %). ***R*$_F$**(1:1 Pentane-EtOAc) 0.67; **MP** 113-115 °C; **IR** ν_{max} (film)/cm^{-1} 1665 (C=O) and 1508 (C=C); **^{1}H-NMR** ($CDCl_3$, 300 MHz,) δ 7.51 (1H, d, J = 7.0 Hz), 7.46-7.39 (2H, m), 7.36 (1H, s), 7.24 (2H, dd, J = 8.0 and 7.5 Hz), 7.14-7.07 (3H, m), 6.94-6.91 (2H, m), 6.83 (2H, d, J = 9.0 Hz), 5.43 (1H, q, J = 7.0 Hz), 3.79 (3H, s), 3.02 (3H, s) and 1.27 (3H, d, J = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 159.8, 156.4, 144.4, 140.3, 140.1, 130.4 (q, J_{CF} = 32.0 Hz), 128.8, 128.6, 128.4, 125.6, 125.1, 124.9, 124.1 (q, J_{CF} = 272.5 Hz), 123.9 (q, J_{CF} = 4.0 Hz), 122.9, 122.7 (q, J_{CF} = 4.0 Hz), 114.2, 55.4, 39.1 and 14.3; **MS** m/z (ES$^+$) 441 (100% M+H$^+$); **HRMS** calcd for $C_{25}H_{24}N_2OF_3$ (M+H$^+$) 441.1785, found 441.1786.

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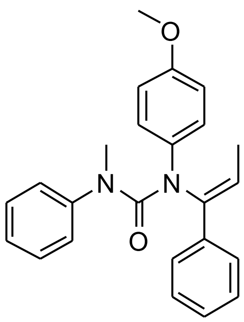
[4] Prepared so that direct comparison with **1f** would confirm which aryl ring had undergone migration.

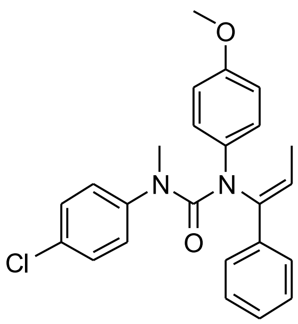
1-(4-Methoxy-phenyl)-3-methyl-3-phenyl-1-((Z)-1-phenyl-propenyl)-urea *1g*



To 1-(1,1-diphenyl-allyl)-1-(4-methoxy-phenyl)-3-methyl-urea[2] **2g** (0.067 g, 0.181 mmol) in DMF (2 mL) was added NaH (0.018 g, 0.45 mmol). The reaction was stirred at room temperature for 16 h. MeOH was added dropwise and the reaction mixture partitioned between Et_2O (15 mL) and H_2O (15 mL). The organic phase was separated, washed with water (15 mL) and brine (15 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash column chromatography yielded the title compound as a colourless oil (0.013 g, 0.038 mmol, 20 %). ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.26; **IR** ν_{max} (film)/cm^{-1}1667 (C=O) and 1513 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.25-7.14 (7H, m), 7.07-7.00 (3H, m), 6.86 (2H, d, J = 7.5 Hz), 6.74 (2H, d, *J* = 9.0 Hz), 5.20 (1H, q, *J* = 7.0 Hz), 3.71 (3H, s), 2.89 (3H, s) and 1.04 (3H, d, *J* = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz) 160.3, 156.1, 144.7, 141.1, 139.7, 137.5, 128.7, 127.5, 125.4, 125.3, 124.9, 124.8, 121.3, 114.1, 55.5, 38.9 and 14.4; **MS** m/z (ES$^-$) 371 (M-H$^+$); **HRMS** calcd for $C_{24}H_{25}N_2O_2$ (M+H$^+$) 373.1911, found 373.1915.

Matches previously reported data[2]

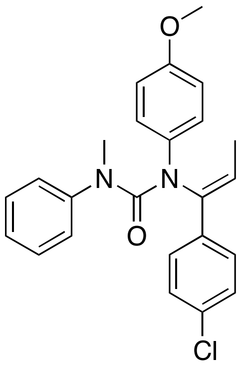
1-(4-Chloro-phenyl)-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-phenyl-propenyl)-urea *1h*



To 1-(1-(4-Chlorophenyl)-1-phenylallyl)-1-(4-methoxyphenyl)-3-methylurea[2] **2h** (0.100 g, 0.25 mmol) in DMF (3 mL) was added NaH (0.019 g, 0.49 mmol). The reaction was stirred at room temperature for 2 hours. MeOH was added dropwise and the reaction mixture partitioned between Et_2O and H_2O. The organic phase was separated, washed with water (15 mL) and brine (15 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography to give the title compound as a pale yellow film (0.072 g, 0.18 mmol, 72 %). ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.35; **IR** ν_{max} (film)/cm^{-1} 1667 (C=O) and 1511 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.25-7.18 (3H, m), 7.15-7.11 (4H, m), 7.04 (2H, d, J = 9.0 Hz), 6.78 (2H, d, J = 9.0 Hz), 6.75 (2H, d, J = 9.0 Hz), 5.28 (1H, q, J = 7.0 Hz), 3.71 (3H, s), 2.86 (3H, s) and 1.10 (3H, d, J = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 160.0, 156.3, 143.2, 141.1, 139.5, 137.2, 130.6, 128.7, 128.4, 127.7, 126.1, 125.3, 124.8, 121.5, 114.1, 55.5, 38.8 and 14.4; **MS** m/z (ES$^+$) 407 (95%, M+H$^+$) 429 (100%, M+Na$^+$); **HRMS** calcd for $C_{24}H_{23}{}^{35}ClN_2O_2Na$ (M+Na$^+$) 429.1340, found 429.1330.

Matches previously reported data[2]

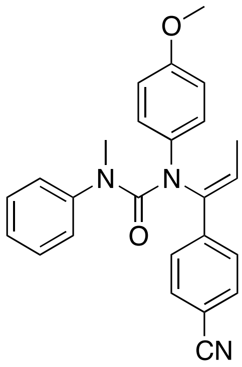
1-Phenyl-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-(4-chloro-phenyl)-propenyl)-urea *1i*



To (4-methoxy-phenyl)-(1-p-chloro-phenyl-allyl)-amine (1.05 g, 3.844 mmol) in CH_2Cl_2 (10 mL) at room temperature was added phenyl isocyanate (0.40 mL, 3.844 mmol). The reaction mixture was stirred for 16 hours and the solvent removed under reduced pressure. The crude urea was dissolved in THF (10 mL) and cooled to 0 °C. NaH (0.385 g, 9.61 mmol) and MeI (0.718 mL, 11.53 mmol) were added and the reaction mixture slowly warmed to room temperature. The reaction was stirred for 16 hours, quenched (MeOH). Et_2O (50 mL) was added, the mixture extracted with water (3 × 50 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude urea was purified by flash column chromatography to give the title compound as a yellow foam (0.861 g, mmol, 55 %). ***R*$_F$**(1:1 Petroleum Ether-Et_2O) 0.30; **IR** ν_{max} (film)/cm^{-1}1667 (C=O) and 1509 (C=C); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.22 (5H, m), 7.07-7.00 (4H, m), 6.87 (2H, d, J = 8.5 Hz), 6.74 (2H, d, J = 9.0 Hz), 5.26 (1H, q, J = 7.0 Hz), 3.75 (3H, s), 2.98 (3H, s) and 1.13 (3H, d, J = 7.0 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 160.3, 156.5, 144.8, 140.5, 138.4, 137.3, 133.4, 129.0, 128.6, 127.0, 125.7, 125.3, 125.0, 122.2, 114.4, 55.7, 39.4 and 14.5; **MS** m/z (ES$^+$) 429 (100 %, M+Na$^+$); **HRMS** calcd for $C_{24}H_{23}{}^{35}ClN_2O_2Na$ (M+Na$^+$) 429.1340, found 429.1346.

Matches previously reported data[3]

(Z)-1-(1-(4-cyanophenyl)prop-1-enyl)-1-(4-methoxyphenyl)-3-methyl-3-phenylurea[5] *1a'*



To 4-cyanobenzaldehyde (0.816 mL, 6.23 mmol) in CH_2Cl_2 (12 mL) was added *p*-anisidine (0.766 g, 6.23 mmol) and Mol sieves (1.0 g, 4Å powdered). The reaction was stirred at room temperature for 16 h. The crude reaction mixture was filtered through Celite and the solvent removed under reduced pressure. To the crude imine (assumed 6.23 mmol) in THF (25 mL) at -78 °C was added freshly prepared vinyl lithium (12.46 mmol) slowly over 15 minutes. The reaction was stirred for 1 hour at -78 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl, warmed to room temperature and extracted twice with Et_2O. The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude amine was used without further purification. To the amine (assumed 6.23 mmol) in CH_2Cl_2 (20 mL) at room temperature was added phenyl isocyanate (0.68 mL, 6.23 mmol). The reaction mixture was stirred for 16 hours and the solvent removed under reduced pressure. The crude urea was dissolved in DMF (20 mL) and cooled to 0 °C. NaH (0.623 g, 15.58 mmol) and MeI (1.16 mL, 18.69 mmol) were added and the reaction mixture slowly warmed to room temperature. The reaction was stirred for 16 hours and quenched with MeOH. Et_2O (50 mL) was added, the mixture extracted with water (3 × 50 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude urea was purified by flash column chromatography to give the title compound as a crystalline solid (0.501 g, 1.26 mmol, 20 %). ***R***$_F$(2:1 Petroleum Ether-EtOAc) 0.32; **MP** 167-170 °C; (Et_2O); **IR** ν_{max} (film)/cm^{-1} 2225 (CN), 1664 (C=O) and 1508 (C=C); ^{1}**H-NMR** ($CDCl_3$, 300 MHz) δ 7.56 (2H, d, *J* = 8.5 Hz), 7.29-7.20 (4H, m), 7.13-7.04 (3H, m), 6.93 (2H, d, *J* = 8.5 Hz), 6.81 (2H, d, *J* = 9.0 Hz), 5.49 (1H, q, *J* = 7.0 Hz), 3.77 (3H, s), 3.00 (3H, s) and 1.25 (3H, d, *J* = 7.0 Hz); ^{13}**C-NMR** ($CDCl_3$, 75 MHz) δ 159.9, 156.5, 144.5, 144.0, 139.9, 136.6, 132.1, 129.0, 125.9, 125.8, 125.2, 124.7 119.9, 114.3, 110.9, 55.5, 39.3 and 14.5; **MS** m/z (ES$^+$) 398 (100 %, M+H$^+$); **HRMS** calcd for $C_{25}H_{24}N_3O_2$ (M+H$^+$) 398.1863, found 398.1869;

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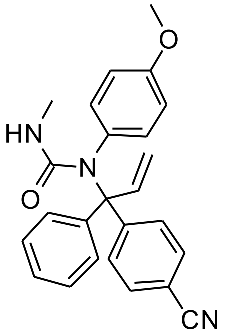
[5] Prepared so that direct comparison with **1a** would confirm which aryl ring had undergone migration.

(±) 1-[1-(4-Cyanophenyl)-1-phenylallyl]-1-(4-methoxyphenyl)-3-methylurea[2] 2a



To 1-(4-cyanophenyl)-3-(4-methoxyphenyl)-1-methyl-3-((Z)-1-phenylpropenyl)urea ***1a*** (0.118 g, 0.29 mmol) in THF (4 mL) at -78°C was added lithium diisopropyl amide (0.59 mmol).[6] After 10 minutes DMPU (0.40 mL) was added and stirred for a further 3 hours. MeOH was added and the mixture allowed to warm to room temperature. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 × 30 mL). The organic phases were combined and washed with brine (20 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The product was washed with cold petroleum ether to give the title compound as a solid to be used without any further purification (0.087 g, 0.22 mmol, 75 %). **MP** 154-156 °C**;** ***R*$_F$**(2:1 Petroleum Ether-EtOAc) 0.12; **IR** ν_{max} (film)/cm^{-1} 3426 (NH), 2226 (CN), 1667 (C=O) and 1509 (C=C); **^{1}H-NMR** ($CDCl_3$, 300MHz) δ 7.60 (2H, d, *J* = 8.5 Hz), 7.50 (2H, d, *J* = 9.0 Hz), 7.39-7.25 (5H, s), 7.13 (2H, d, *J* = 9.0 Hz), 6.86 (2H, d, *J* = 9.0 Hz), 5.95 (1H, dd, *J* = 17.0 and 10.5 Hz), 5.19 (1H, d, *J* = 10.5 Hz), 4.66 (1H, d, *J* = 17.0 Hz), 4.13 (1H, q, *J* = 4.5 Hz), 3.80 (3H, s) and 2.62 (3H, d, *J* = 4.5 Hz); **^{13}C-NMR** ($CDCl_3$, 400 MHz) δ 159.3, 157.4, 149.3, 142.1, 141.0, 132.7, 132.5, 131.3, 129.6, 129.4, 127.8, 119.2, 117.1, 114.8, 110.1, 74.0, 55.5 and 27.5; **MS** m/z (ES$^+$) 398 (80%, M+H$^+$), 420 (100%, M+Na$^+$); **HRMS** calcd for $C_{25}H_{24}N_3O_2$ (M+H$^+$) 398.1863, found 398.1871.

***(S)*-1-[1-(4-Cyanophenyl)-1-phenylallyl]-1-(4-methoxyphenyl)-3-methylurea 2a**

To 1-(4-cyano-phenyl)-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-phenyl-propenyl)-urea ***1a*** (0.101g, 0.25 mmol) in THF (3 mL) at -78 °C was added lithium *S*-(–)-*N*-isopropyl-1-phenylethyl amide (0.50 mmol, formed from HCl salt).[7] The reaction mixture was stirred at -78 °C for 20 minutes. MeOH was added and the mixture allowed to warm to room temperature. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 × 50 mL). The organic phases were combined and washed with $CuSO_4$ solution (30 mL) and brine. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash column chromatography yielded the title compound as a solid (0.082 g, 0.21 mmol, 82 %). **$[\alpha]_D^{25}$** = –32.4 (c. 1.24 in $CDCl_3$); **HPLC**: 95:5 er: Chiralpak AD-H, 90:10 Hexane:IPA 1mL/min. t_r 12.6 major, 14.3 minor. Absolute configuration assigned by analogy with the results reported in ref. 2.

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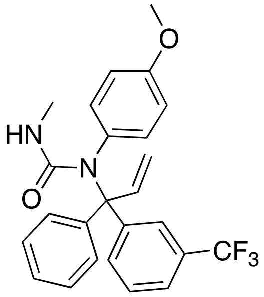
[6] Prepared as follows: To a cooled solution of amine (1 equiv) in THF (0.6M) at 0°C was added nBuLi (1 equiv, 2.5M in hexanes). The reaction mixture was stirred at 0°C for 20 minutes before immediate use.

[7] Prepared as follows: To a cooled solution of amine (1 equiv) in THF (0.5M) at 0°C was added nBuLi (1 equiv for free amines or 2 equiv for hydrochloride salts, 2.5M in hexanes). The reaction mixture was stirred at 0°C for 20 minutes before immediate use.

(*R)*-1-[1-(4-Cyanophenyl)-1-phenyl-allyl]-1-(4-methoxyphenyl)-3-methylurea 2a

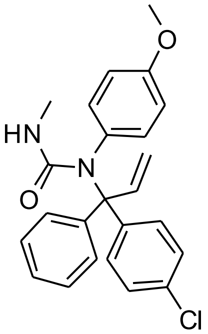
1-(4-cyano-phenyl)-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-phenyl-propenyl)-urea ***1a*** (0.050 g, 0.125 mmol) was taken up in THF (3 mL) and cooled to -78°C. Lithium (*R)*-(–)-*N*-isopropyl-1-phenylethyl (0.25 mmol, prepared from HCl salt)[7] was added and the reaction stirred for a 15 minutes at -78°C. MeOH (1 mL) was added dropwise and the resulting solution was allowed to warm to room temperature. Saturated aqueous NH_4Cl was added and the mixture extracted twice (Et_2O) and washed with H_2O, dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting solid was then washed with cold petroleum ether to give the title compound which was used without any further purification as a brown solid (0.045 g, 0.113 mmol, 91 %). $[\alpha]_D^{25}$ = +25.7 (c. 1.55 in $CDCl_3$); **HPLC:** 6:94 er: Chiralpak AD-H, 90:10 Hexane:IPA 1mL/min. t_r 12.5 minor, 14.4 major**.** Absolute configuration assigned by analogy with the results reported in ref. 2.

1-(4-methoxyphenyl)-3-methyl-1-(1-phenyl-1-(3-(trifluoromethyl)phenyl)allyl)urea 2f



To (Z)-1-(4-methoxyphenyl)-3-methyl-1-(1-phenylprop-1-enyl)-3-(3-(trifluoromethyl)phenyl)urea[3] ***1f*** (0.350 g, 0.795 mmol) in THF (5 mL) was added lithium *N*-isopropyl-1-phenylethyl amide (From HCl salt, 1.59 mmol). The reaction mixture was stirred at -78 °C for 20 minutes. MeOH was added and the mixture allowed to warm to room temperature. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 × 50 mL). The organic phases were combined and washed with $CuSO_4$ solution (30 mL) and brine. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography yielded the title compound as a film (0.308 g, 0.70 mmol, 88 %). ***R***$_F$(2:1 Petroleum Ether-EtOAc) 0.17; **IR** ν_{max} (film)/cm^{-1}3459 (NH), 1667 (C=O) and 1509 (C=C); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.50 (2H, d, *J* = 8.0 Hz), 7.40 (1H, d, *J* = 7.5 Hz), 7.32 (1H, dd, *J* = 8.0 and 7.5 Hz), 7.29-7.27 (2H, m), 7.28 (2H, dd, *J* = 8.0 and 7.5 Hz), 7.18-7.15 (1H, m), 7.03 (2H, d, *J* = 9.0 Hz), 6.75 (2H, d, *J* = 9.0 Hz), 6.00 (1H, dd, *J* = 16.5 and 11.0 Hz), 5.11 (1H, d, *J* = 11.0 Hz), 4.64 (1H, d, *J* = 16.5 Hz), 4.02 (1H, q, *J* = 4.5 Hz), 3.72 (3H, s) and 2.52 (3H, d, *J* = 4.5 Hz); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 159.4, 157.6, 144.4, 142.6, 141.9, 133.2, 132.8, 132.7, 129.7 (q, J_{CF} = 31.5 Hz), 129.5, 128.0, 127.8, 127.2, 126.1 (q, J_{CF} = 4.0 Hz), 124.5 (q, J_{CF} = 271.0 Hz), 123.6 (q, J_{CF} = 3.5 Hz), 116.9, 114.9, 74.3, 55.6 and 27.7; **MS** m/z (ES$^+$) 441 (100%, M+H$^+$); **HRMS** calcd for $C_{25}H_{24}N_2O_2F_3$ (M+H$^+$) 441.1785, found 441.1785;

(±)1-(1-(4-Chlorophenyl)-1-phenylallyl)-1-(4-methoxyphenyl)-3-methylurea 2h

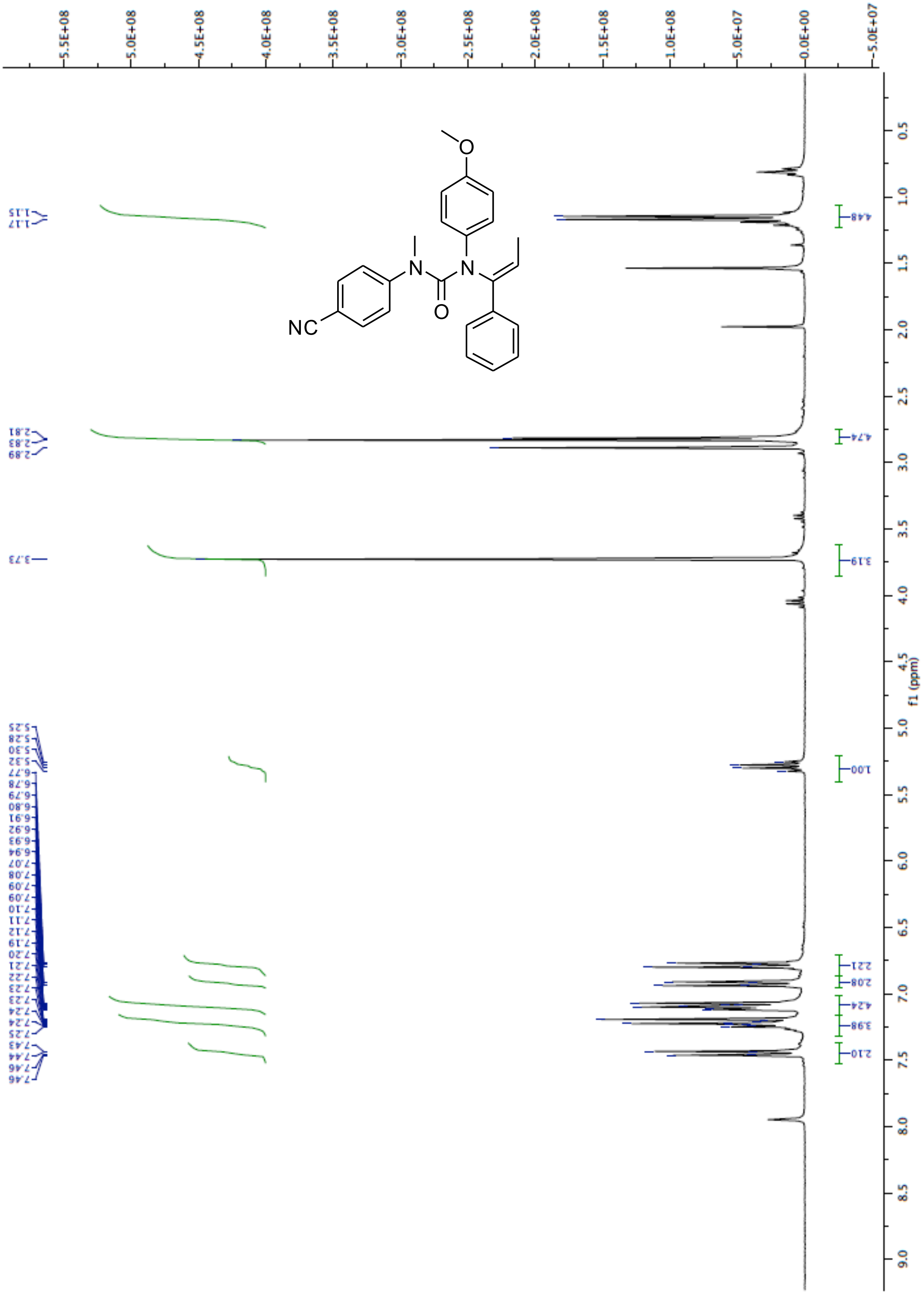


To 1-(4-Chloro-phenyl)-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-phenyl-propenyl)-urea[2] ***1h*** (0.10 g, 0.24 mmol) in THF (2.5 mL) at -78 °C was added freshly prepared lithium diisopropyl amide (0.675 mmol).[6] After 10 minutes DMPU (0.25 mL) was added and stirred for a further 3 hours at -78 °C. MeOH was added and the mixture allowed to warm to room temperature. Saturated aqueous NH_4Cl (20 mL) was added and the mixture was extracted with Et_2O (2 × 30 mL). The organic phases were combined and washed with brine (20 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash column chromatography yielded the title compound as a yellow solid (0.086 g, 0.295 mmol, 86 %). ***R***$_F$(1:1 Petroleum Ether-Et_2O) 0.11; **IR** ν_{max} (film)/cm^{-1}3460 (NH), 1647 (C=O) and 1507 (C=C); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.26-7.16 (9H, m), 7.04 (2H, d, *J* = 9.0 Hz), 6.75 (2H, d, *J* = 9.0 Hz), 5.94 (1h, dd, *J* = 17.0 and 10.5 Hz), 5.08 (1H, d, *J* = 10.5 Hz), 4.64 (1H, d, *J* = 17.0 Hz), 4.01 (1H, q, *J* = 4.5 Hz), 3.72 (3H, s) and 2.53 (3H, d, *J* = 4.5 Hz); **^{13}C-NMR** ($CDCl_3$, 400 MHz) δ 159.3, 157.7, 142.8, 142.3, 141.9, 133.5, 132.7, 132.5, 130.8, 129.5, 127.7, 127.7, 127.0, 116.6, 114.9, 74.1, 55.7 and 27.7; **MS** m/z (ES$^+$) 429 (100%, Na+H$^+$); **HRMS** calcd for $C_{24}H_{23}ClN_2O_2Na$ (M+Na$^+$) 429.1341, found 429.1332.

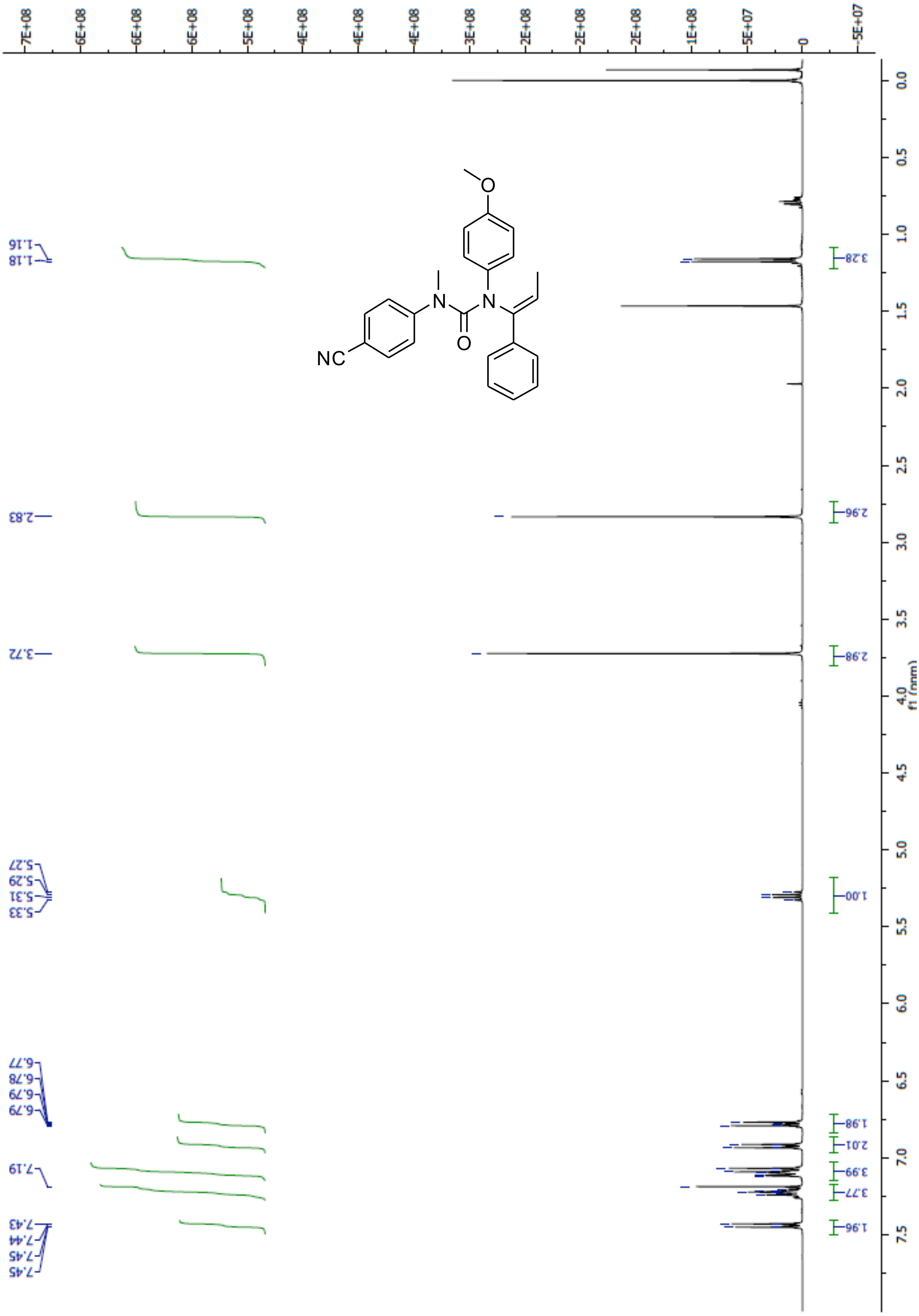
Alternatively, to 1-Phenyl-3-(4-methoxy-phenyl)-1-methyl-3-((Z)-1-(4-chloro-phenyl)-propenyl)-urea[2] ***1i*** (0.137 g, 0.337 mmol) in THF (4 mL) was added lithium diisopropyl amide (0.675 mmol)[7] at -78 °C. After 10 minutes DMPU (0.4 mL) was added, the reaction mixture was warmed to -60 °C and stirred for a further 3 hours. MeOH was added and the mixture allowed to warm to room temperature. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 × 30 mL). The organic phases were combined and washed with brine (20 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash column chromatography yielded the title compound as a yellow solid (0.120 g, 0.295 mmol, 87 %).

NMR Spectra and HPLC Data

Crude 1a



1a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O
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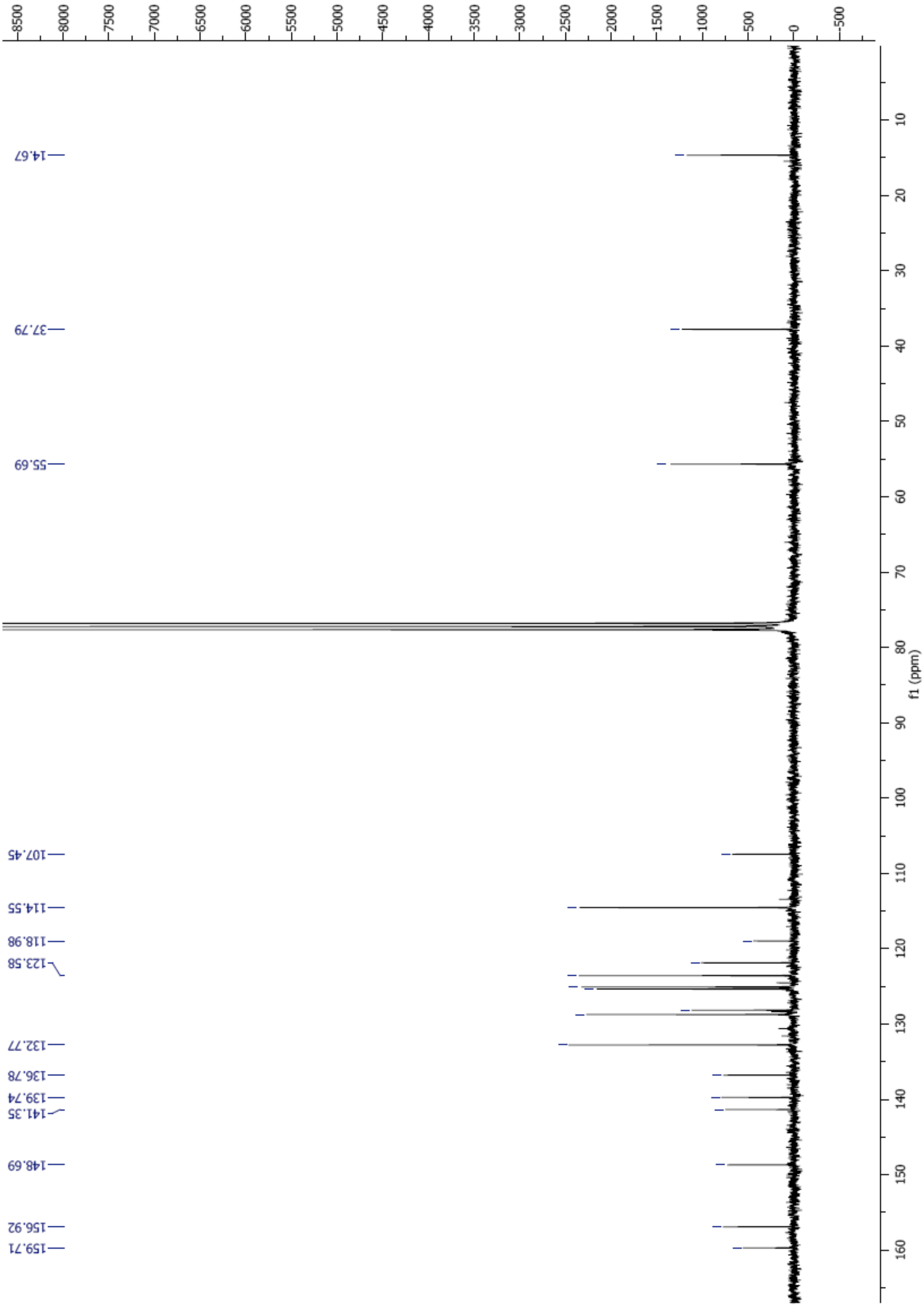
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6000
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4000
3500
3000
2500
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1500
1000
500
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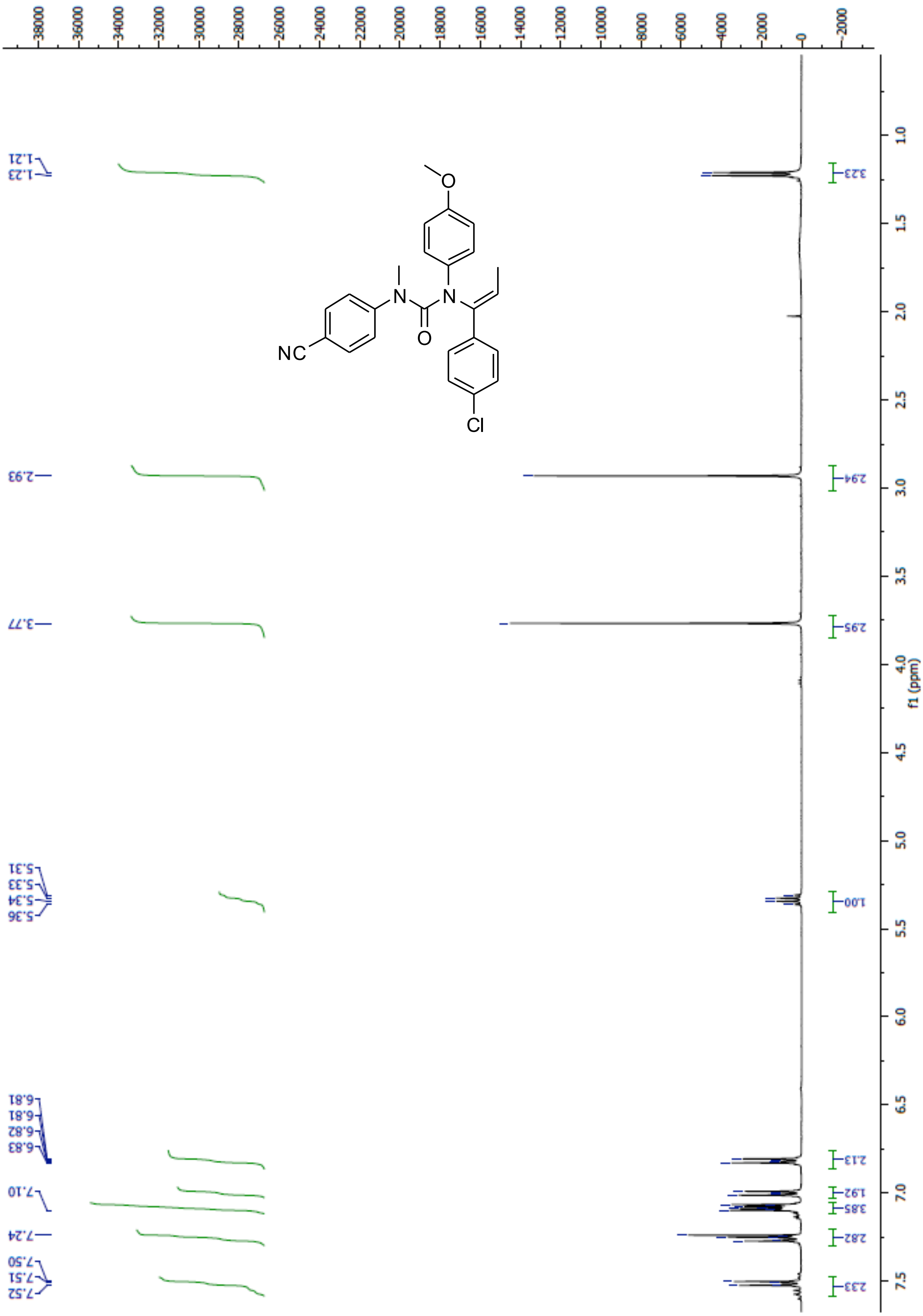
f1 (ppm)

1b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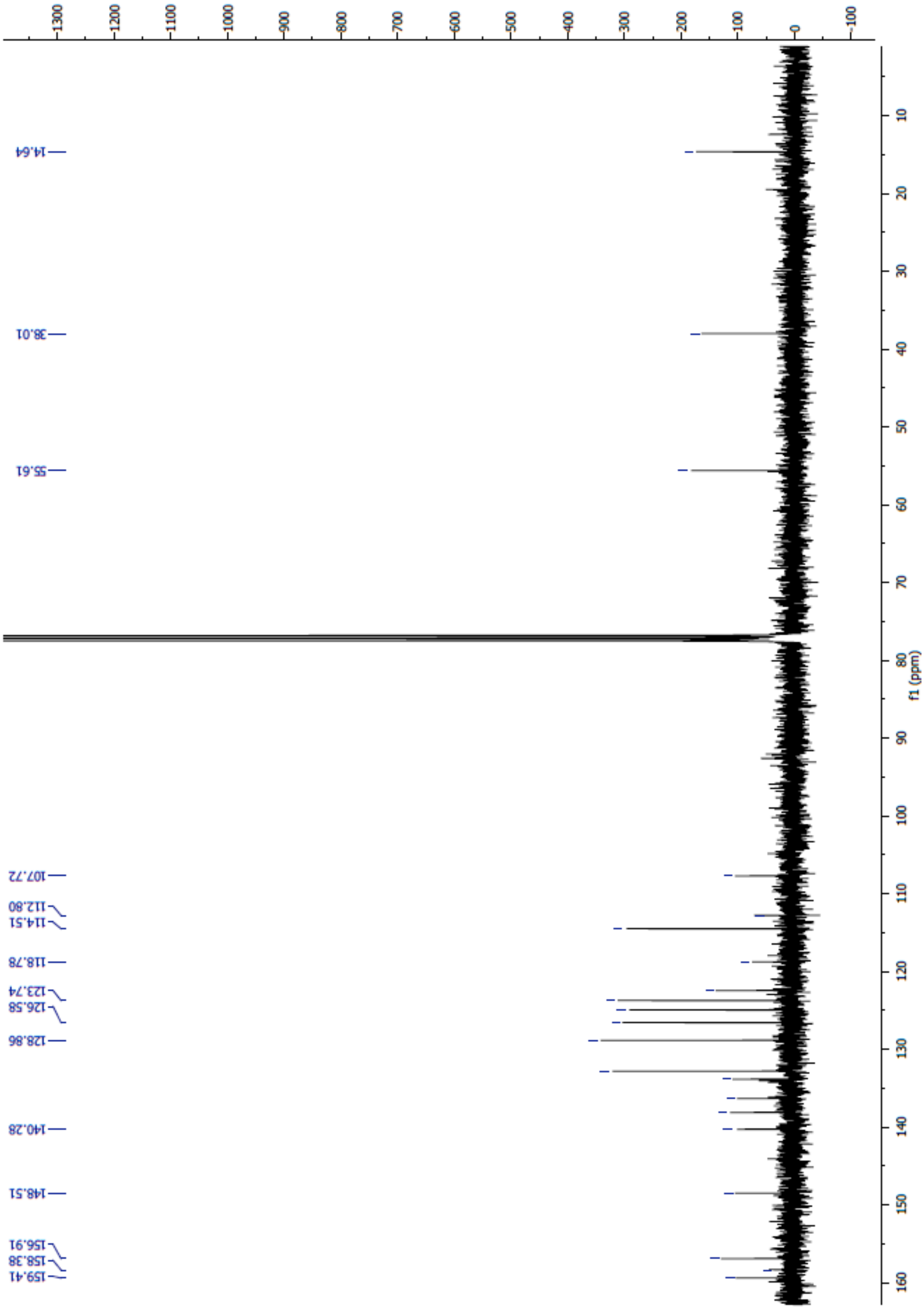
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158.38
159.41
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
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60
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80
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130
140
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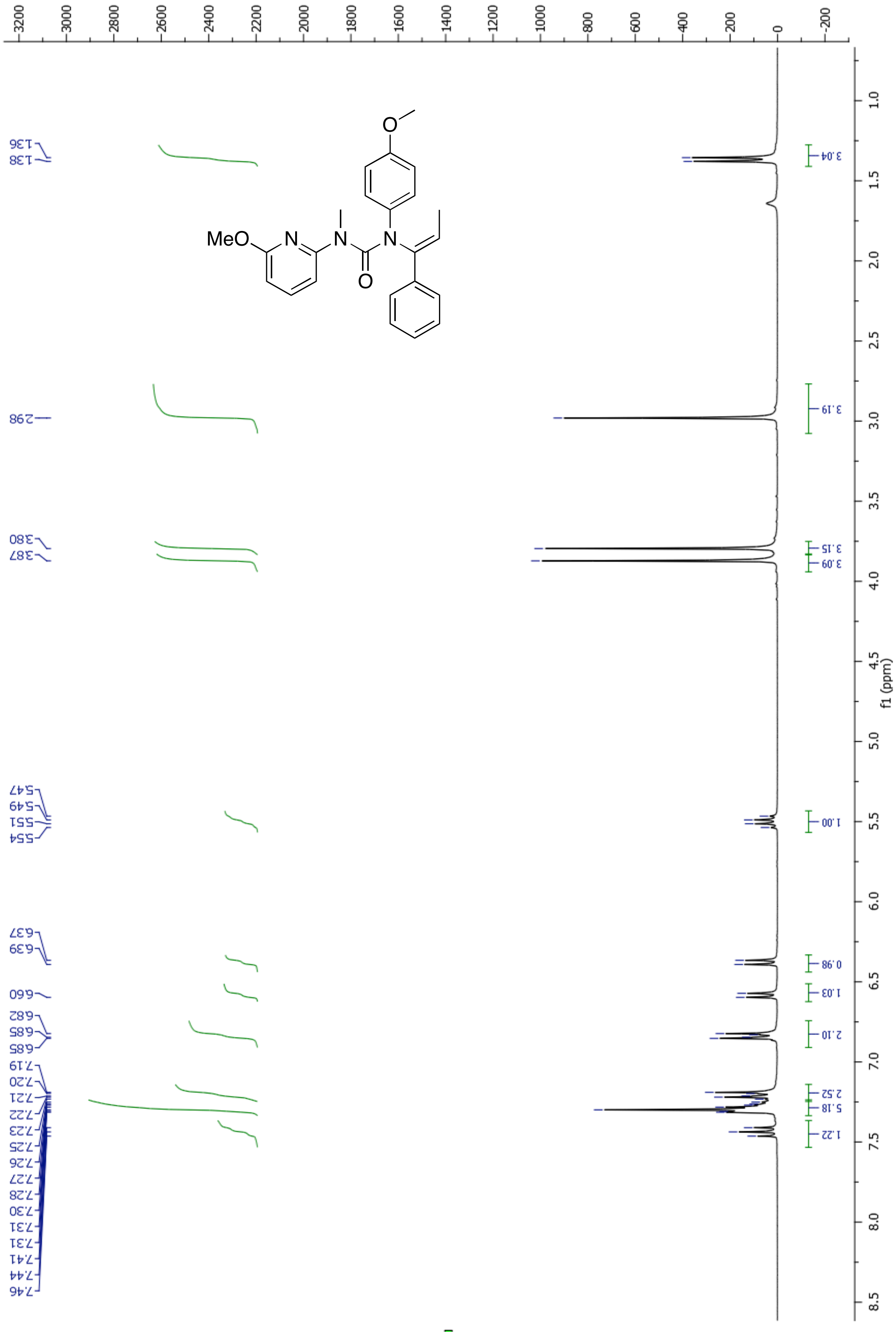
f1 (ppm)

1c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200
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3.09
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2.52
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2.0
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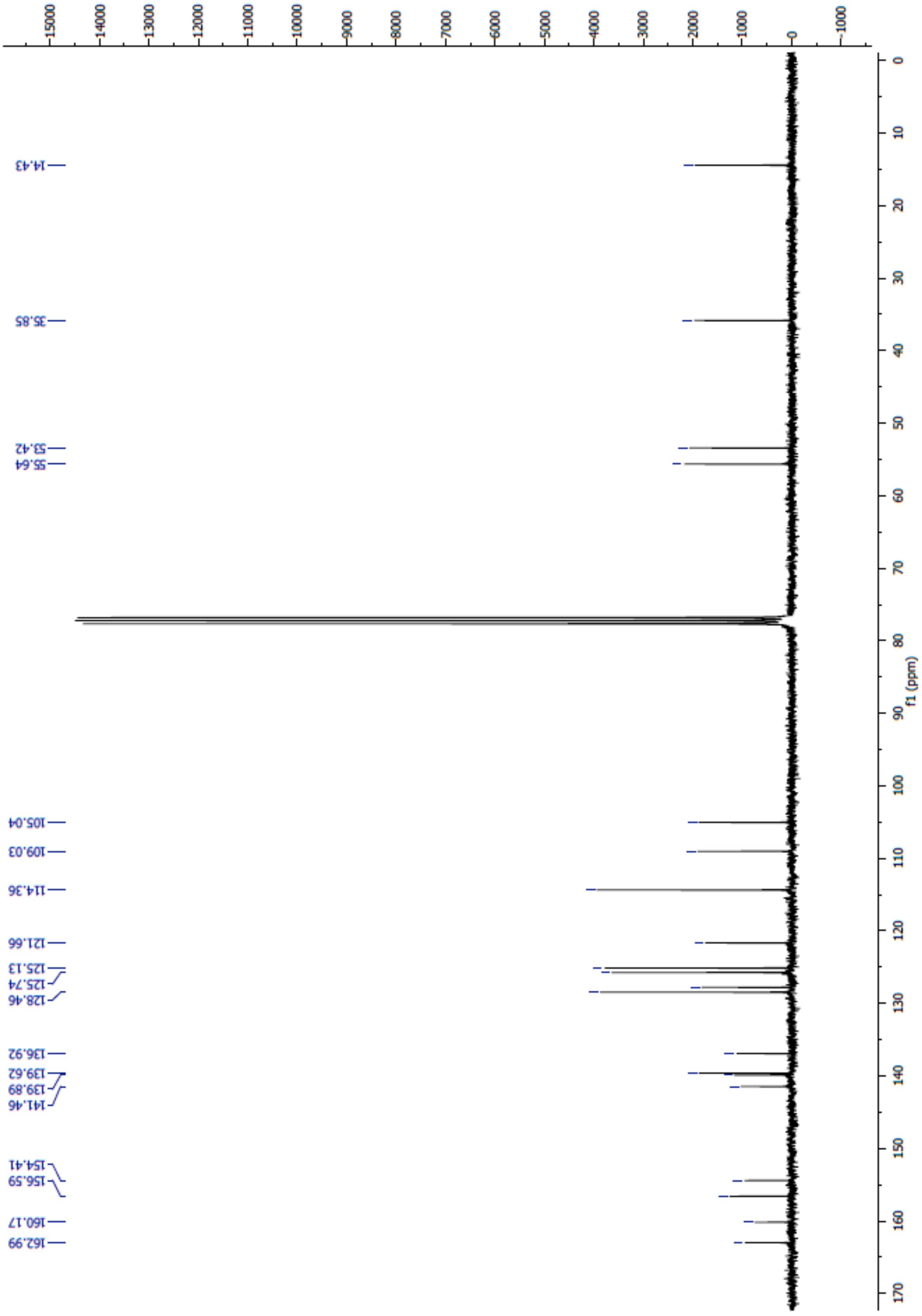
f1 (ppm)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141.46
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160.17
162.99
f1 (ppm)
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20
30
40
50
60
70
80
90
100
110
120
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140
150
160
170
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4000
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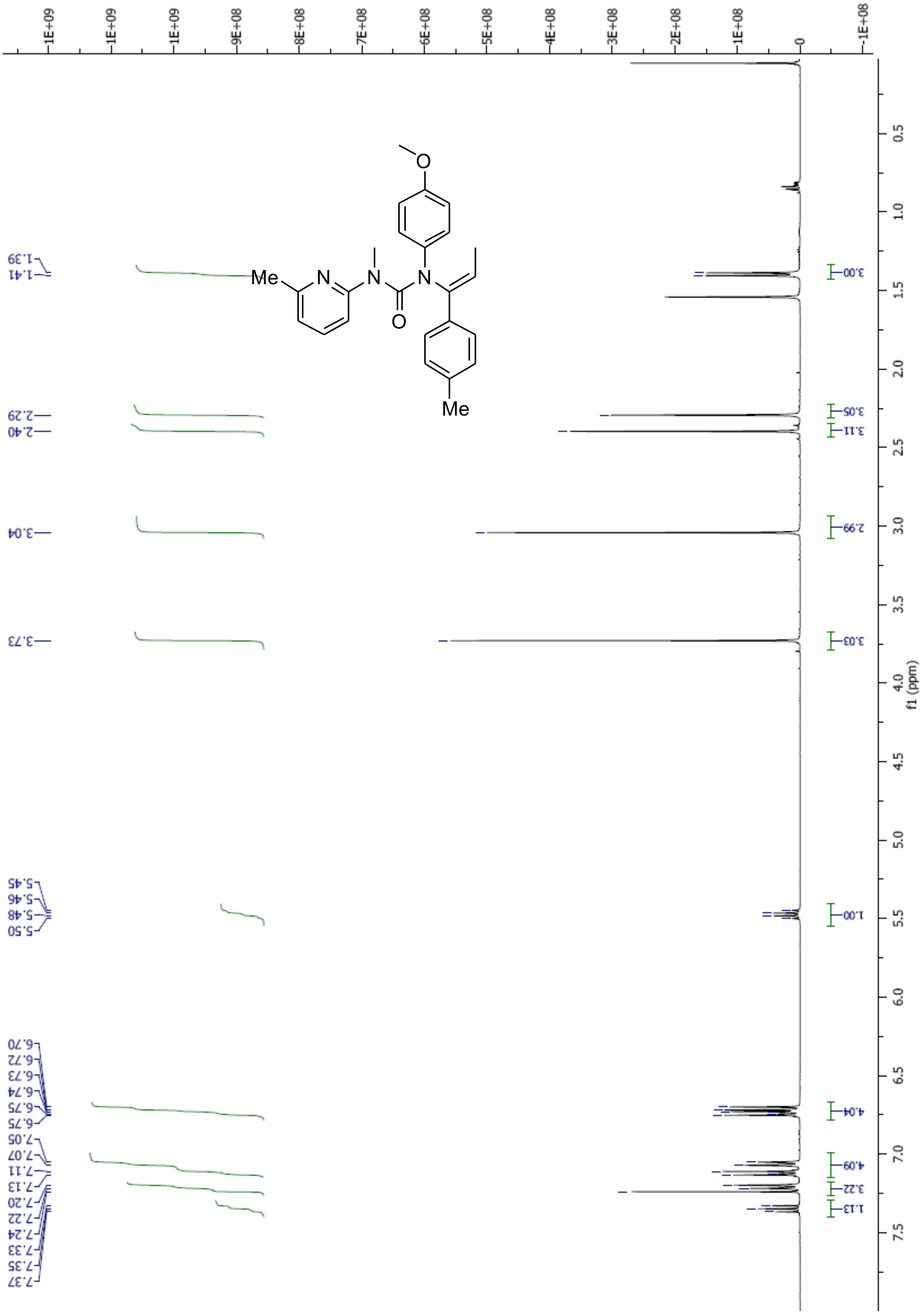
1d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1.39
1.13
3.22
4.09
4.04
1.00
3.03
2.99
3.11
3.05
3.00
f1 (ppm)
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
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6.5
7.0
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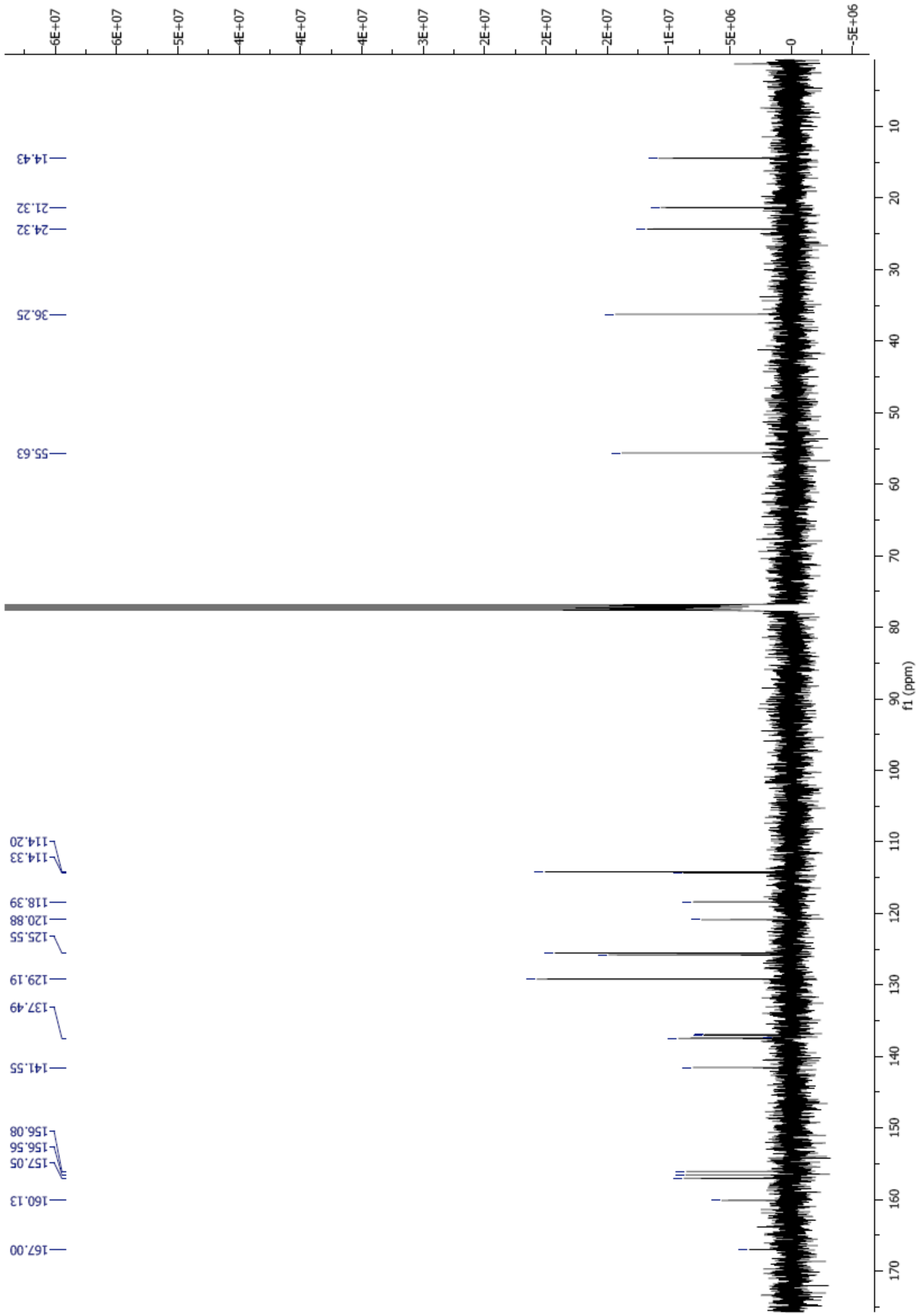
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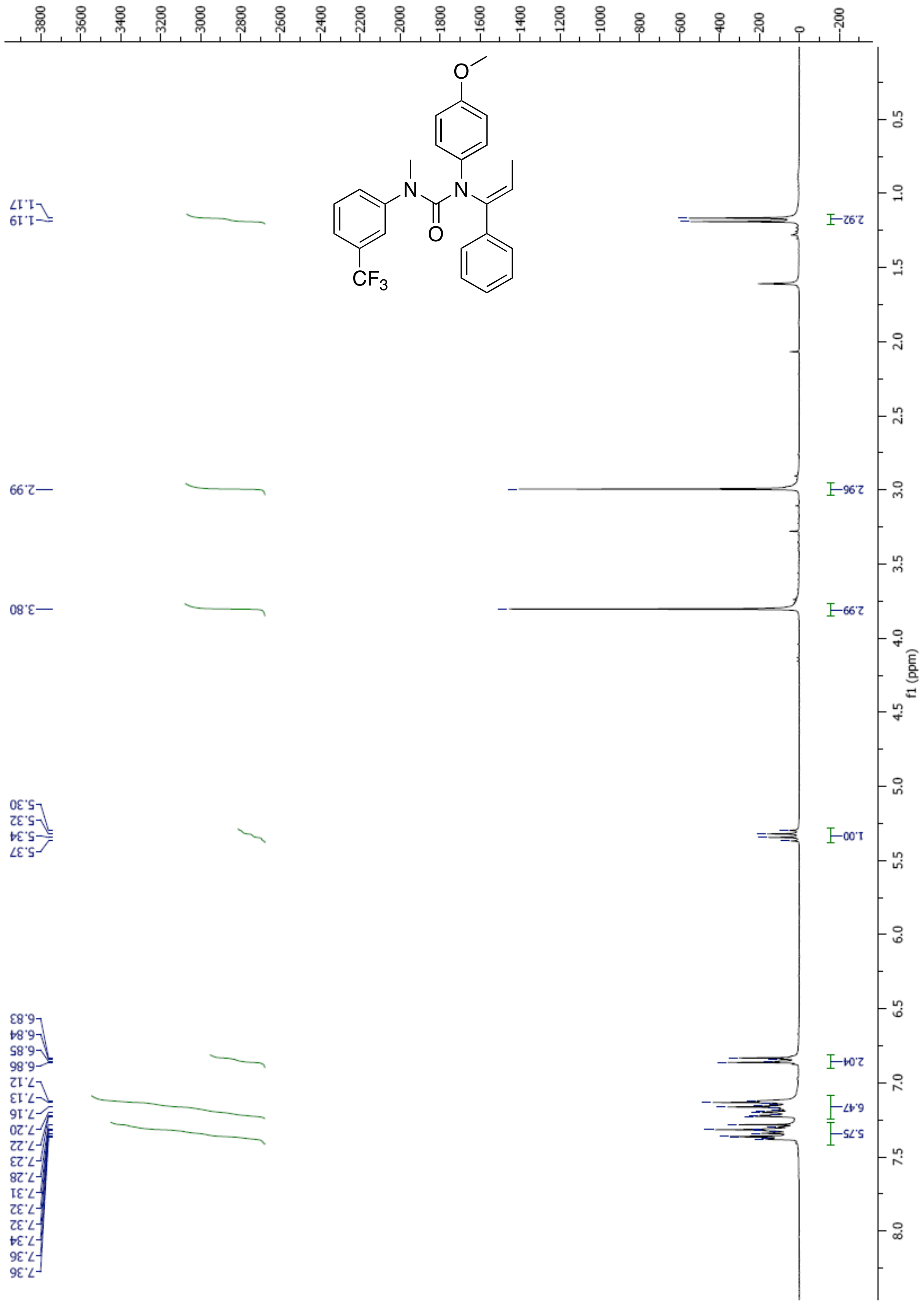
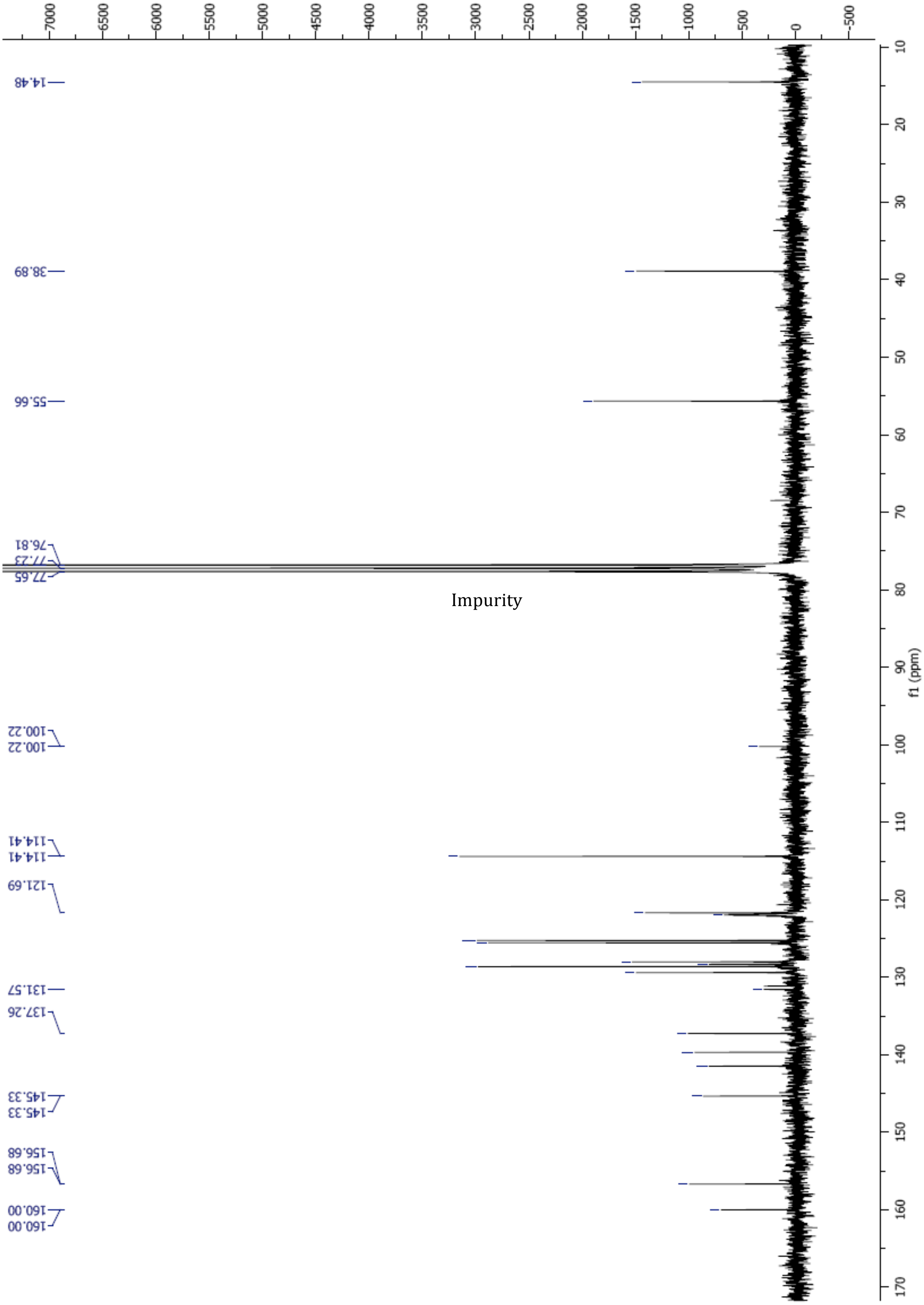
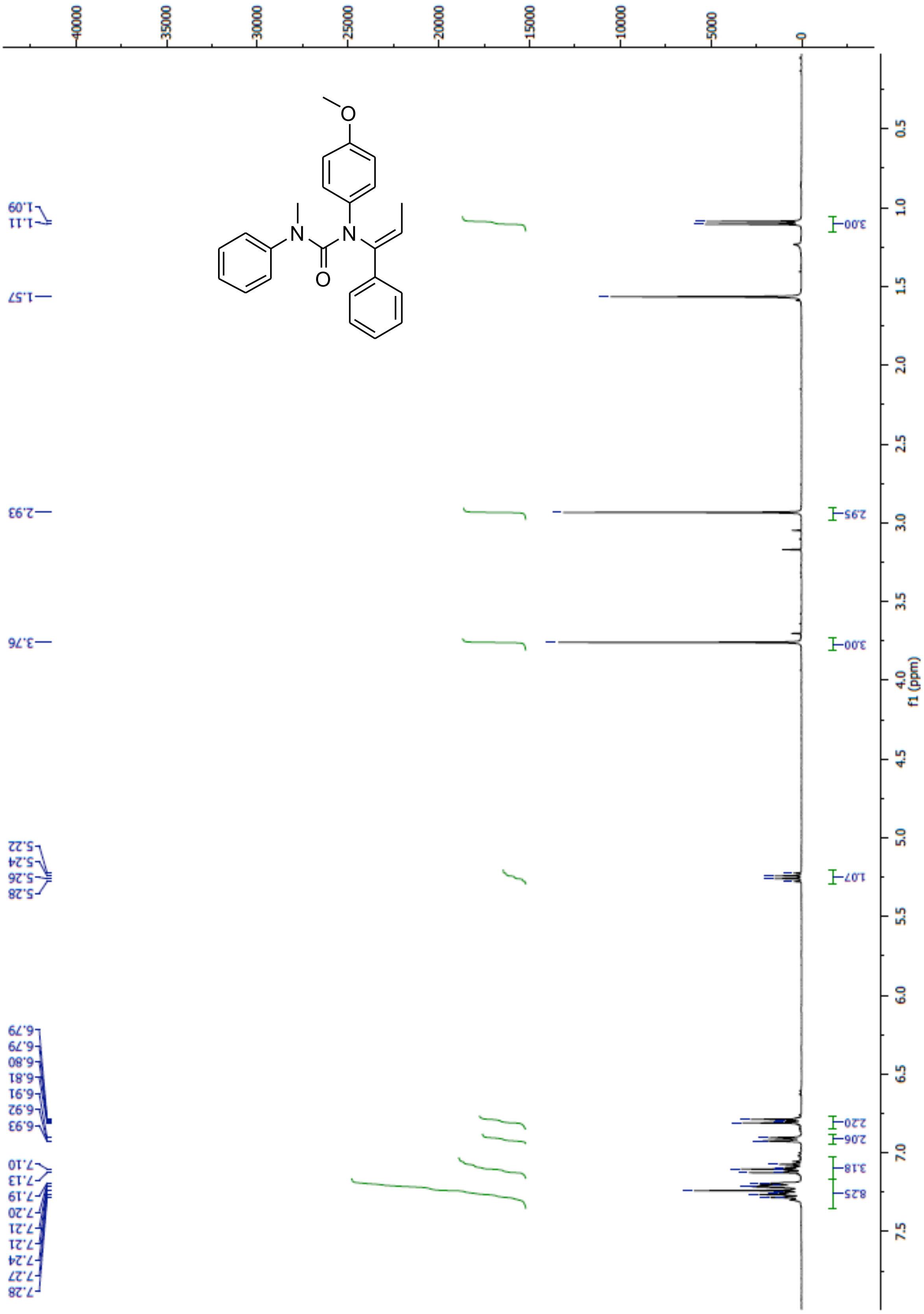
156.08
156.56
157.05
160.13
167.00
6E+07
6E+07
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
-5E+06
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

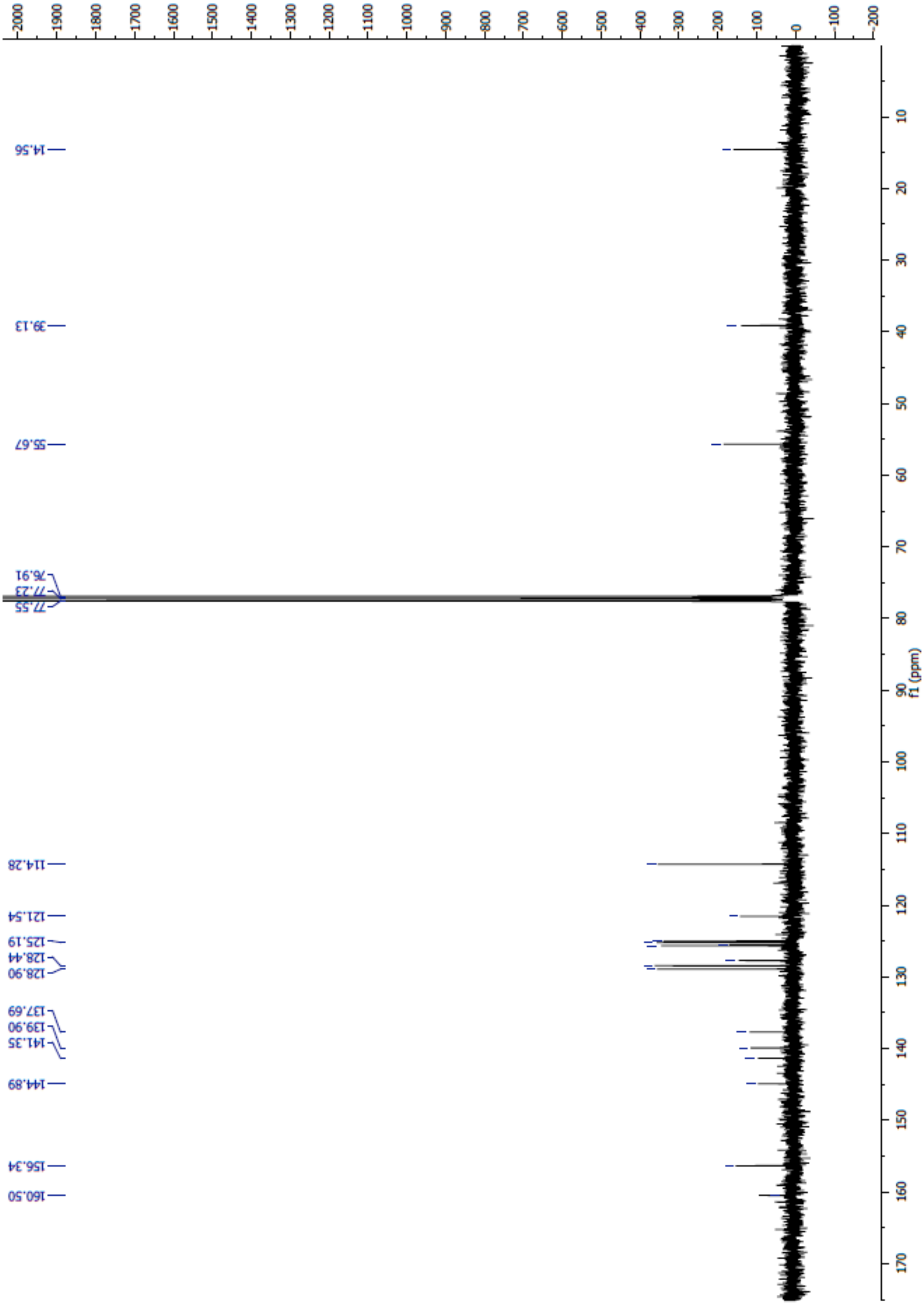
1f


O
N
N
O
CF3
1.17
1.19
2.99
3.80
5.30
5.32
5.34
5.37
6.83
6.84
6.85
6.86
7.12
7.13
7.16
7.20
7.22
7.23
7.28
7.31
7.32
7.32
7.34
7.36
7.36
2.92
2.96
2.99
1.00
2.04
6.47
5.75
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

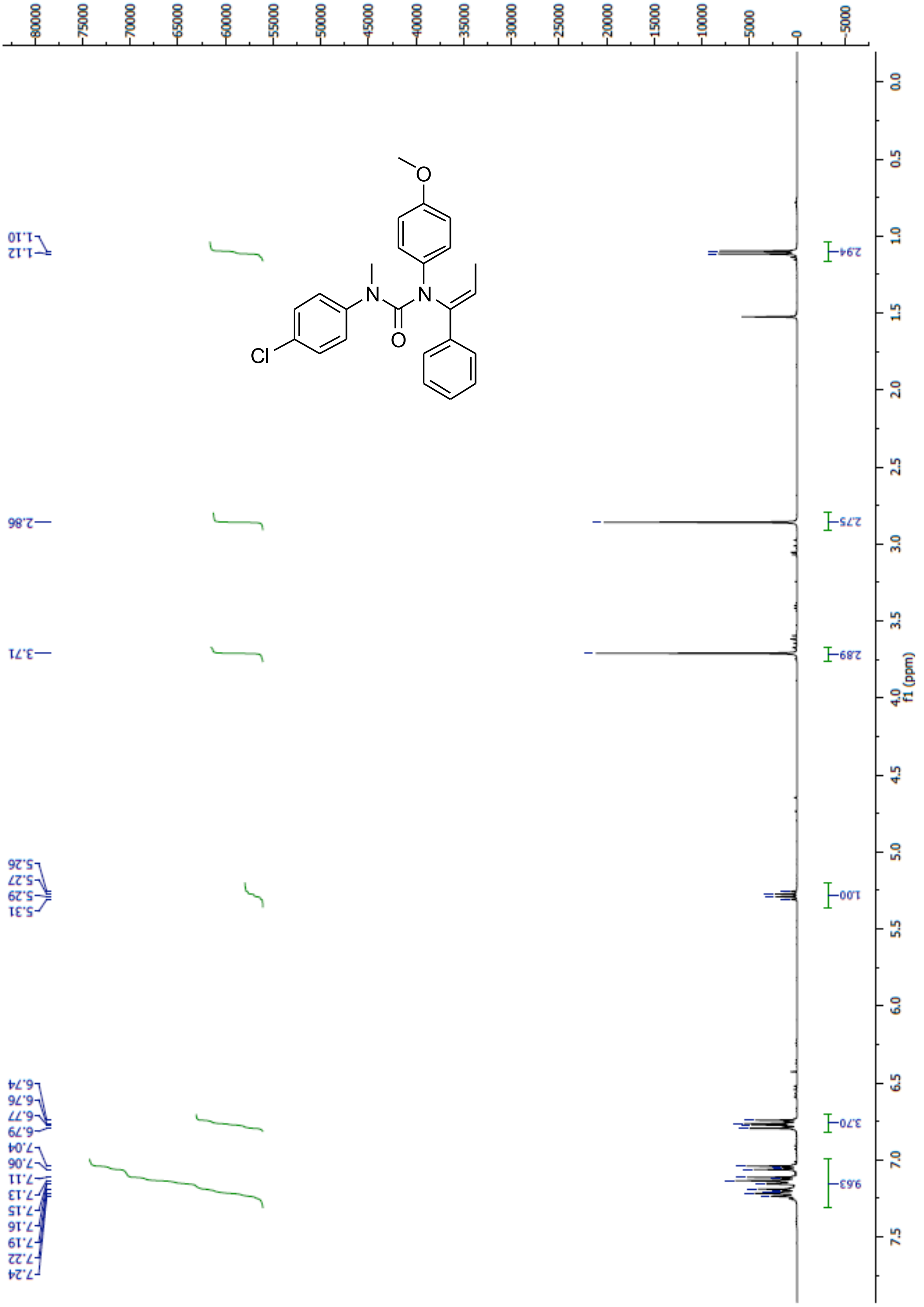

14.48
38.89
55.66
76.81
77.23
77.65
Impurity
100.22
100.22
114.41
114.41
121.69
131.57
137.26
145.33
145.33
156.68
156.68
160.00
160.00
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

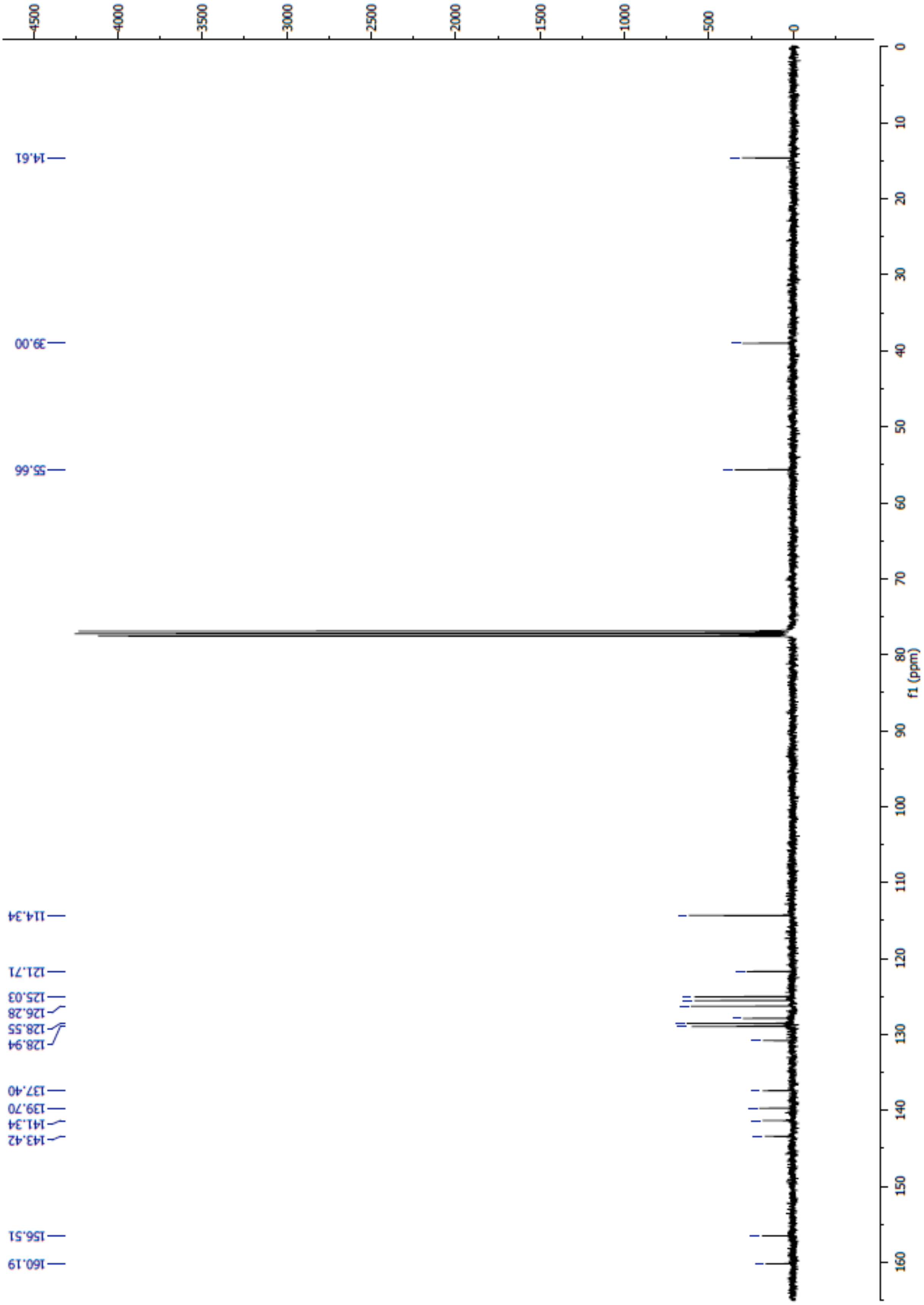
1g


1.09
1.11
1.57
2.93
3.76
5.22
5.24
5.26
5.28
6.79
6.79
6.80
6.81
6.91
6.92
6.93
7.10
7.13
7.19
7.20
7.21
7.21
7.24
7.27
7.28
40000
35000
30000
25000
20000
15000
10000
5000
0
3.00
2.95
3.00
1.07
2.20
2.06
3.18
8.25
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
O
N
N
O

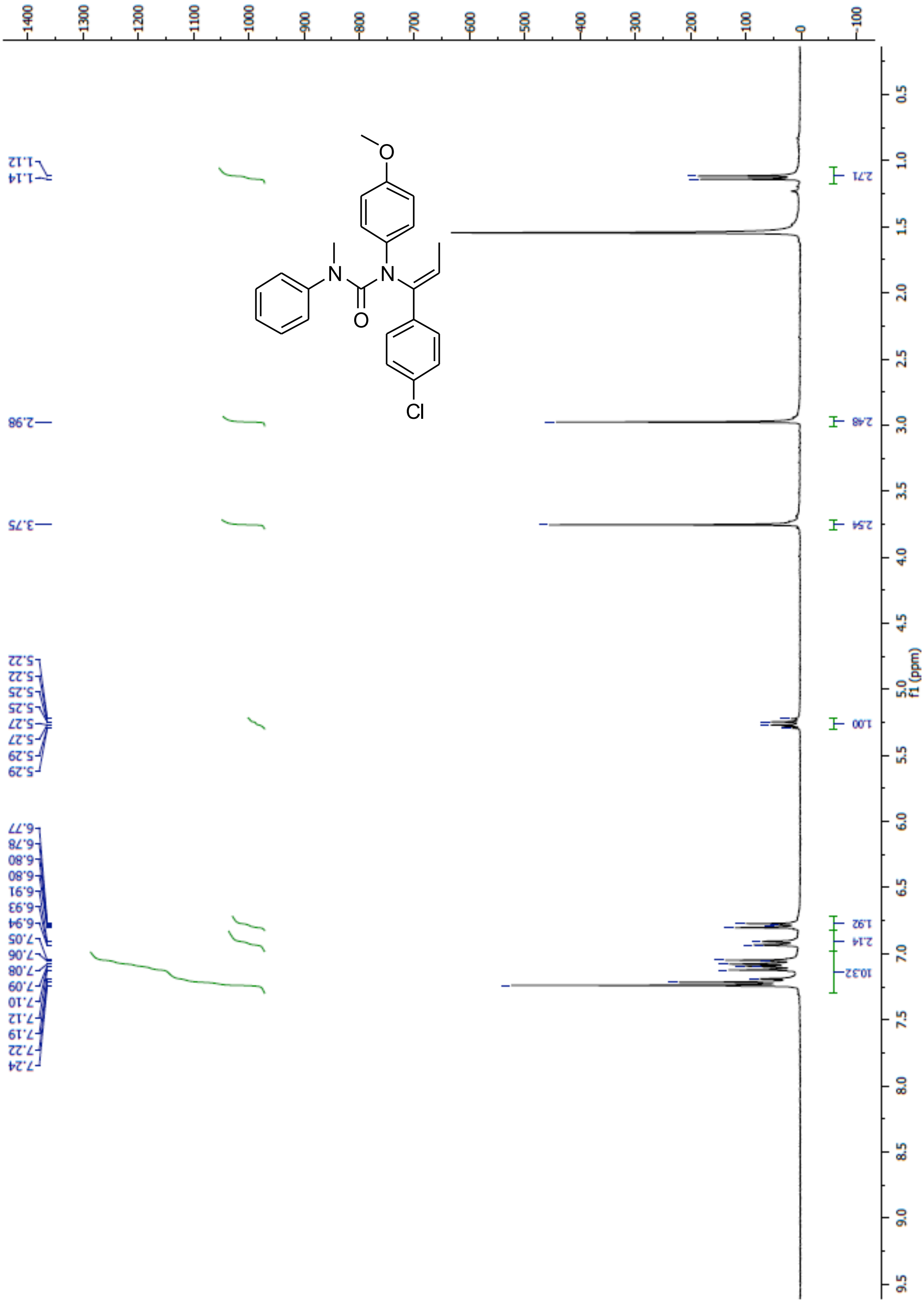

160.50
156.34
144.89
141.35
139.90
137.69
128.90
128.44
125.19
121.54
114.28
77.55
77.23
76.91
55.67
39.13
14.56
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

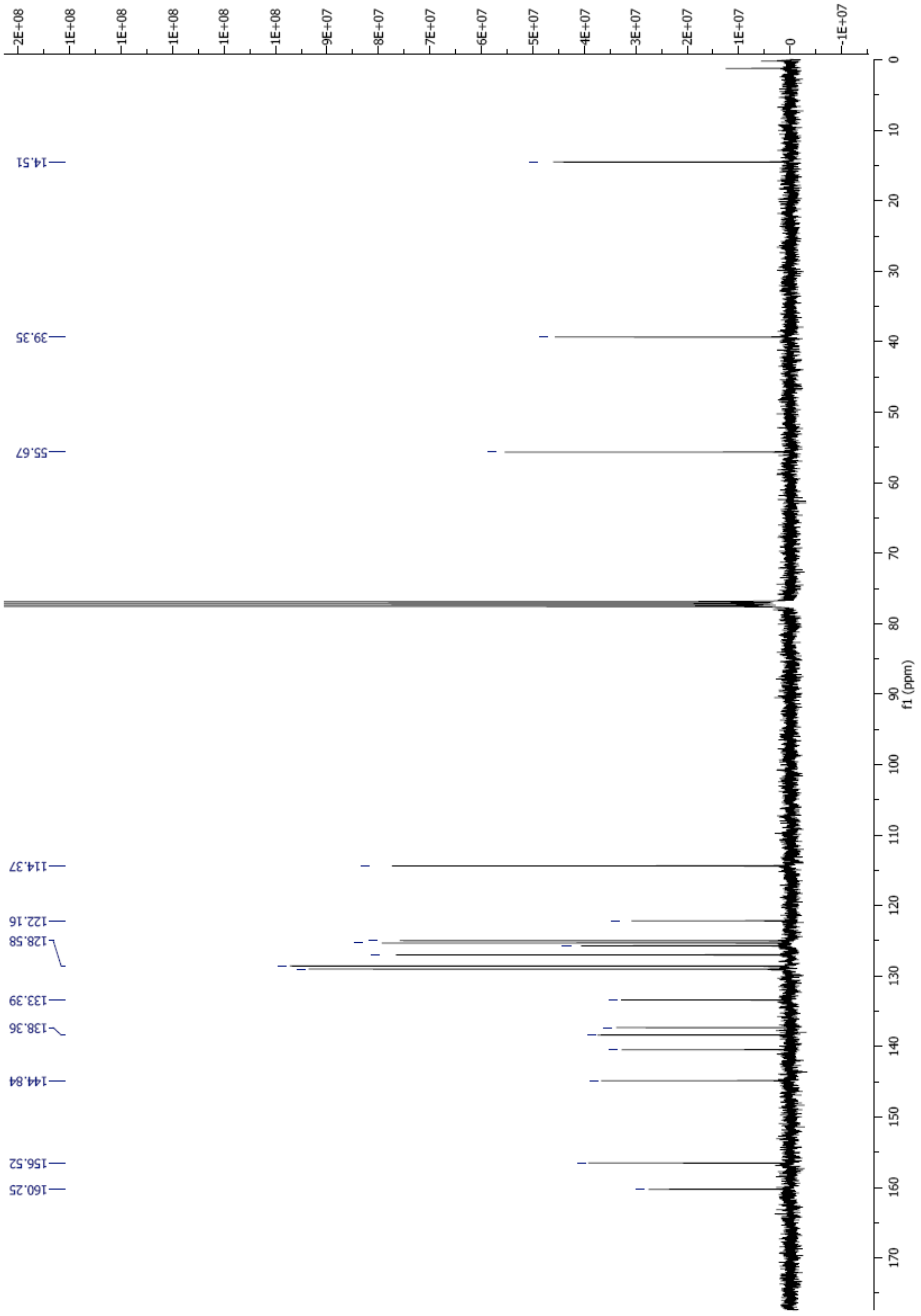
1h


O
N
N
O
Cl
1.10
1.12
2.86
3.71
5.26
5.27
5.29
5.31
6.74
6.76
6.77
6.79
7.04
7.06
7.11
7.13
7.15
7.16
7.19
7.22
7.24
2.94
2.75
2.89
1.00
3.70
9.63
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

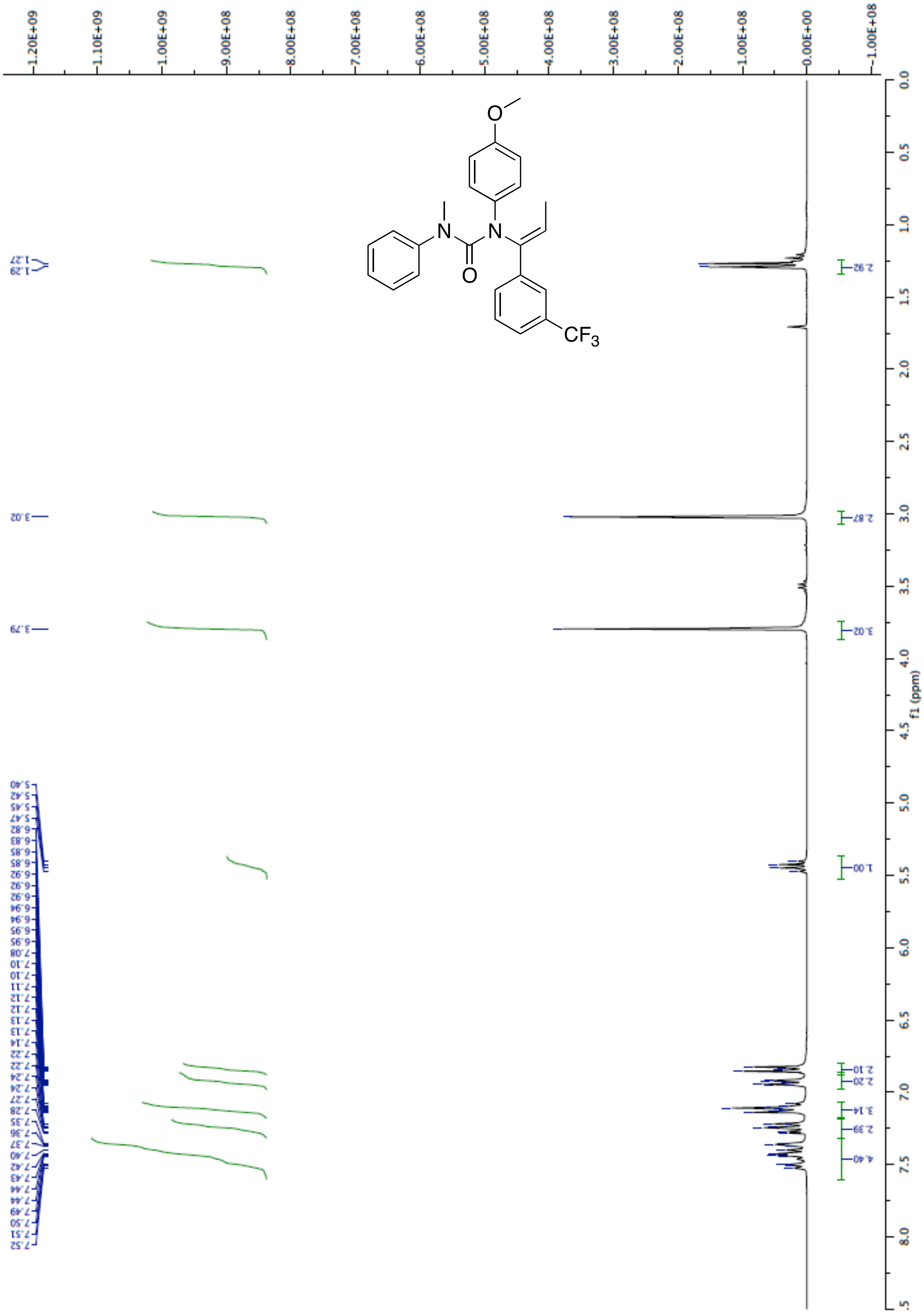

14.61
39.00
55.66
114.34
121.71
125.03
126.28
128.55
128.94
137.40
139.70
141.34
143.42
156.51
160.19
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

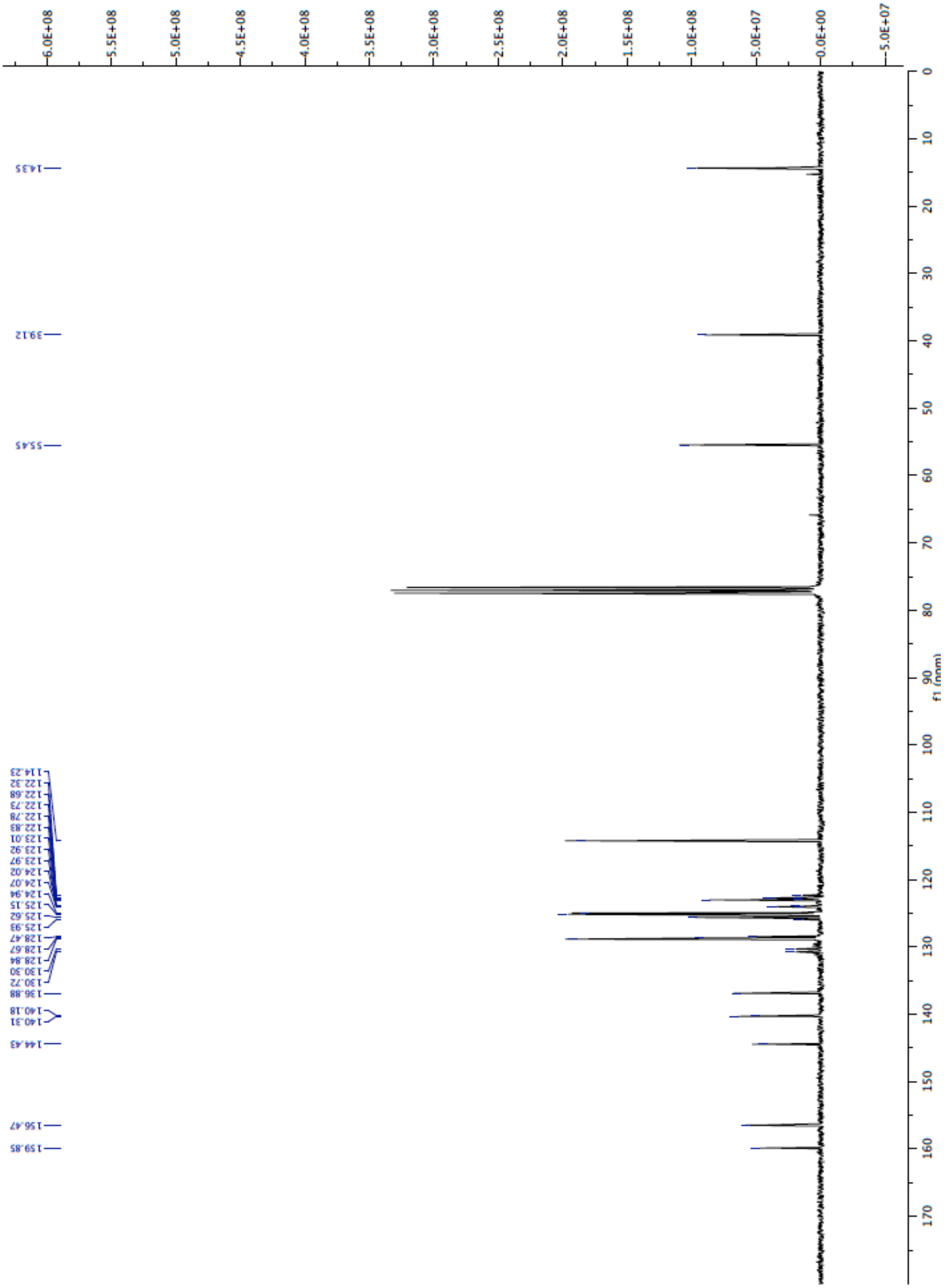
1i


1.12
1.14
2.98
3.75
5.22
5.22
5.25
5.25
5.27
5.27
5.29
5.29
6.77
6.78
6.80
6.80
6.91
6.93
6.94
7.05
7.06
7.08
7.09
7.10
7.12
7.19
7.22
7.24
2.71
2.48
2.54
1.00
1.92
2.14
10.32
f1 (ppm)
O
N
N
O
Cl

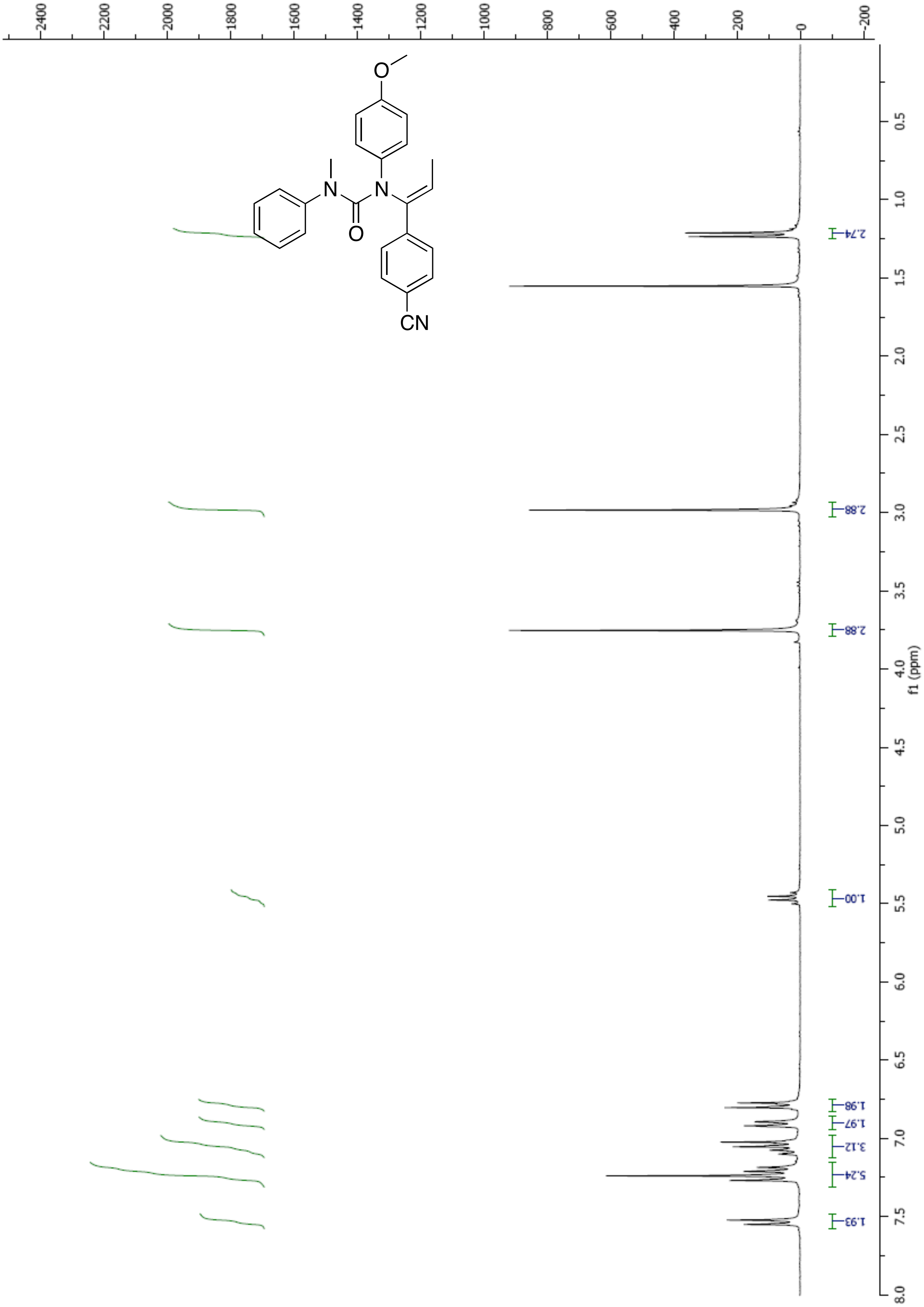

14.51
39.35
55.67
114.37
122.16
128.58
133.39
138.36
144.84
156.52
160.25
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07

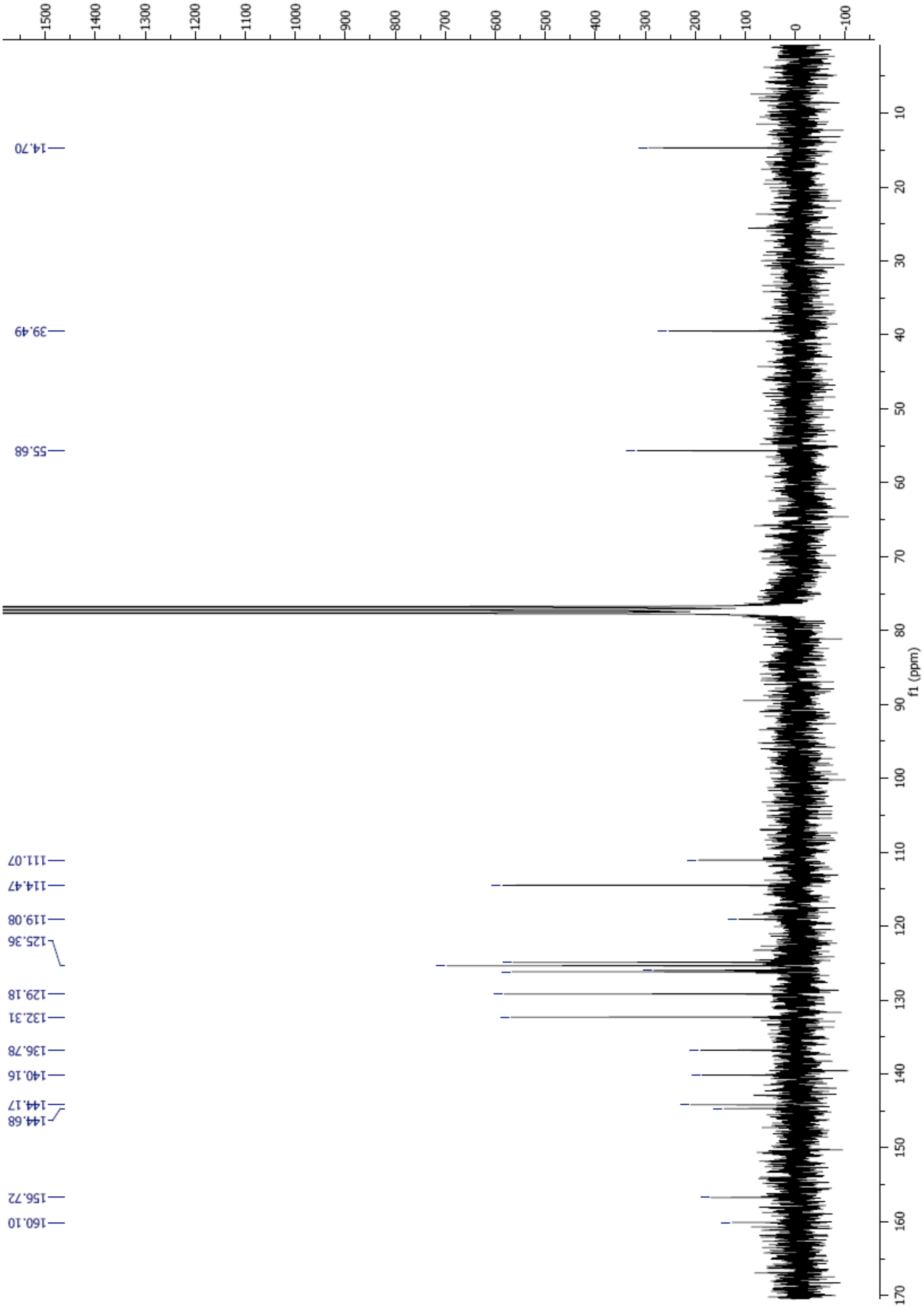
1f'


1.27
1.29
3.02
3.79
5.40
5.42
5.45
5.47
6.82
6.83
6.83
6.85
6.92
6.92
6.92
6.94
6.94
6.95
6.95
7.08
7.10
7.10
7.11
7.12
7.12
7.13
7.13
7.14
7.22
7.22
7.24
7.24
7.27
7.28
7.35
7.36
7.37
7.40
7.42
7.43
7.44
7.44
7.49
7.50
7.51
7.52
2.92
2.87
3.02
1.00
2.10
2.20
3.14
2.39
4.40
f1 (ppm)
O
N
N
O
CF3

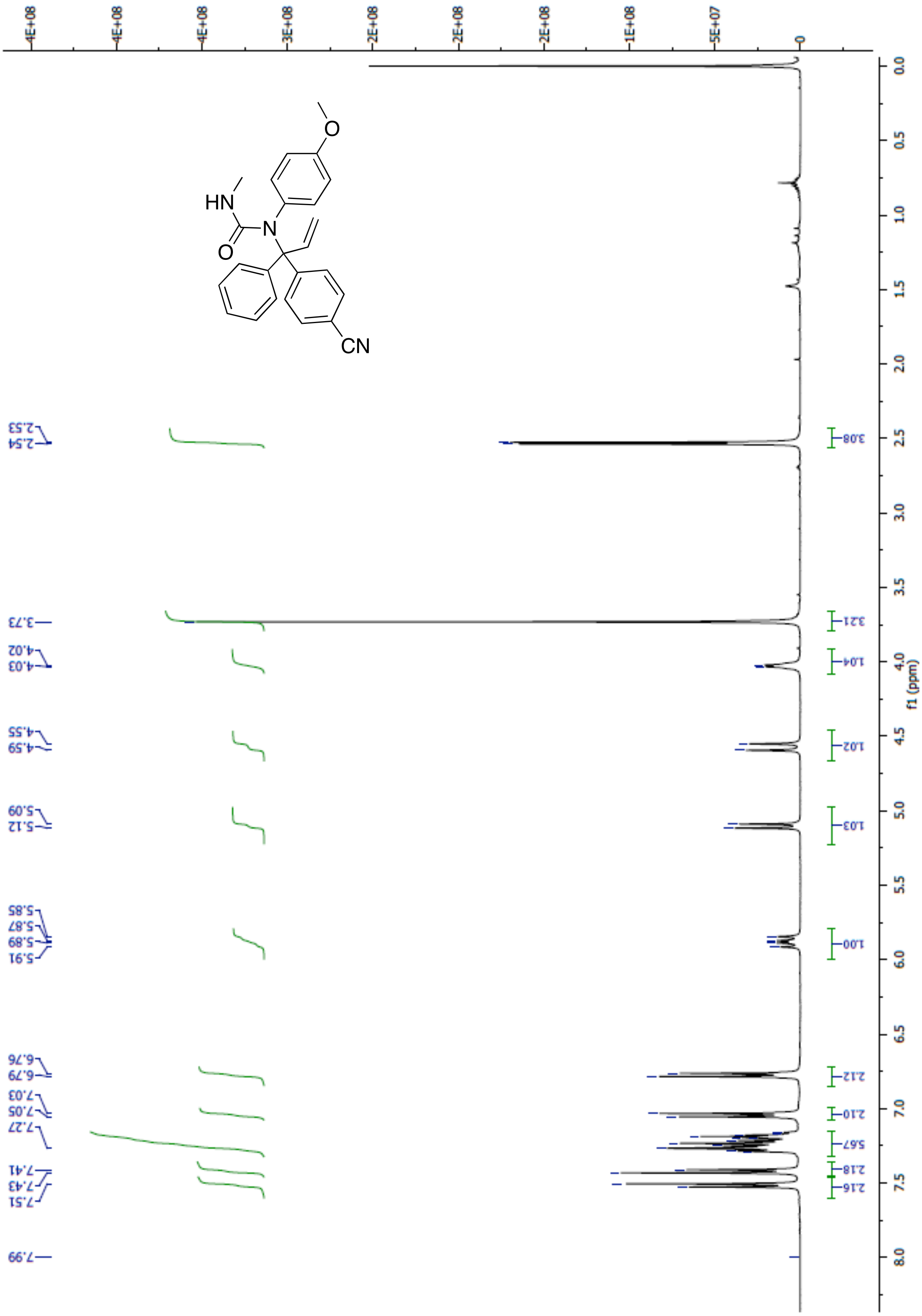

14.35
39.12
55.45
114.23
122.32
122.68
122.73
122.78
122.83
123.01
123.92
123.97
124.02
124.07
124.94
125.15
125.62
125.93
128.47
128.67
128.84
130.30
130.72
136.88
140.18
140.31
144.43
156.47
159.85
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

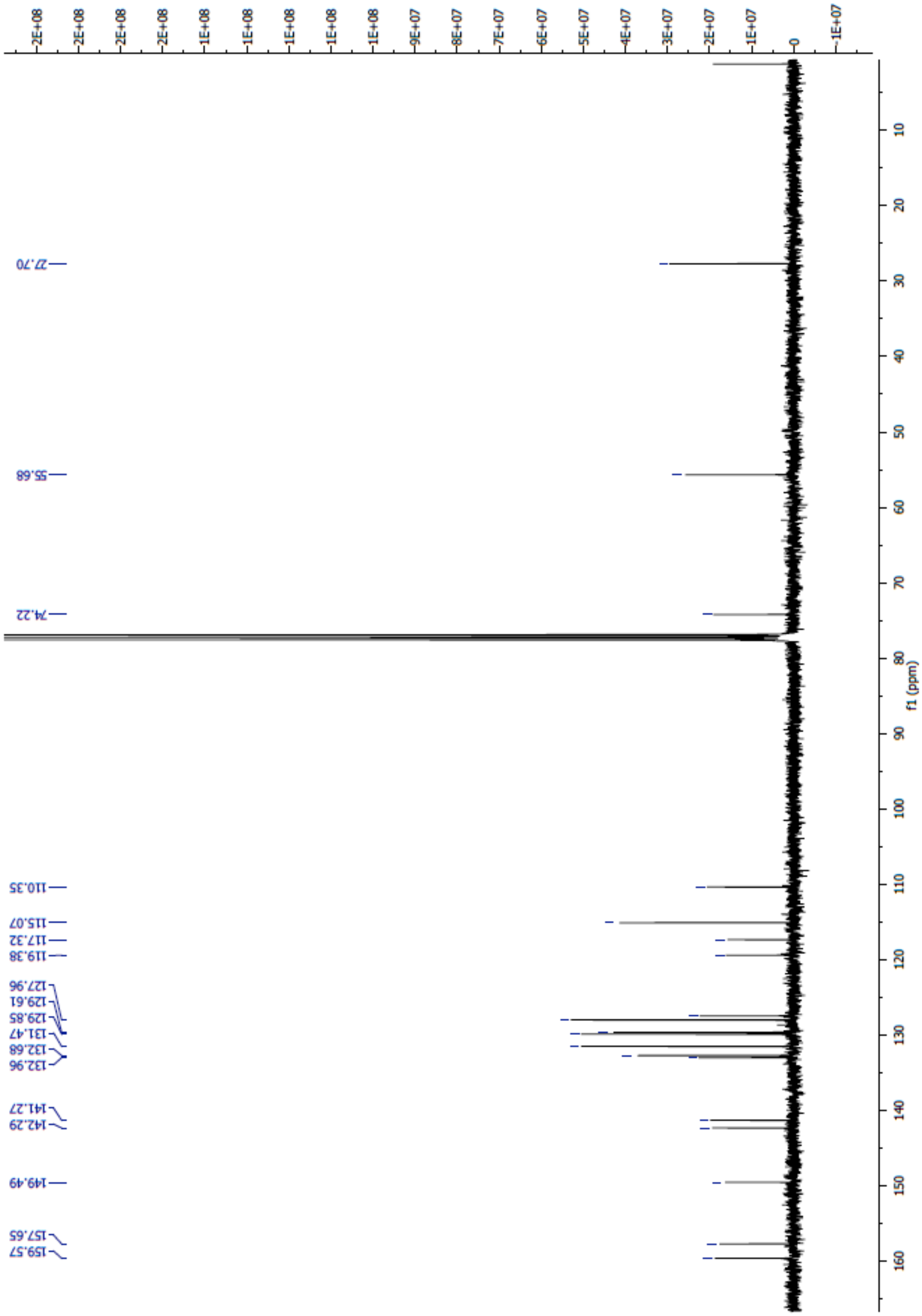
1a’


O
N
N
O
CN
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
2.74
2.88
2.88
1.00
1.98
1.97
3.12
5.24
1.93

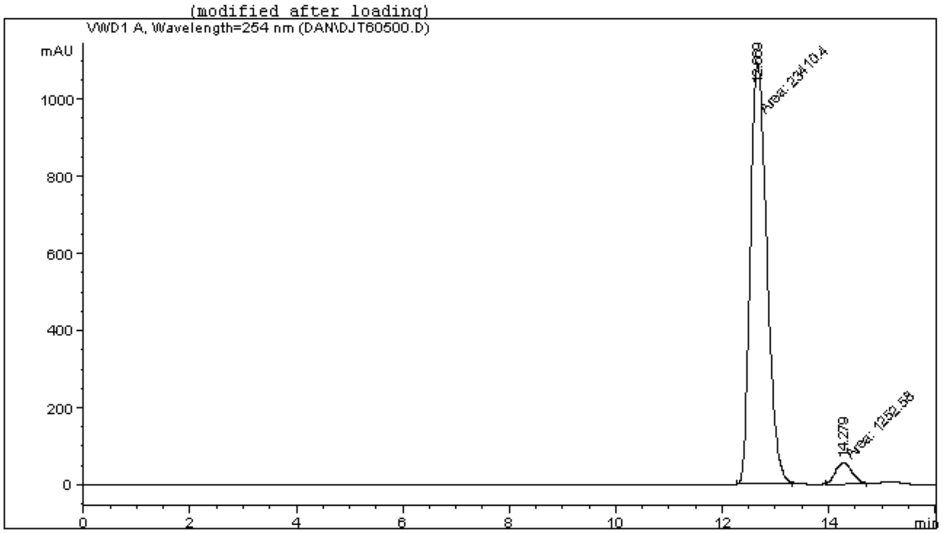

14.70
39.49
55.68
111.07
114.47
119.08
125.36
129.18
132.31
136.78
140.16
144.17
144.68
156.72
160.10
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

2a


HN
N
O
O
CN
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
2.53
2.54
3.73
4.02
4.03
4.55
4.59
5.09
5.12
5.85
5.87
5.89
5.91
6.76
6.79
7.03
7.05
7.27
7.41
7.43
7.51
7.99
3.08
3.21
1.04
1.02
1.03
1.00
2.12
2.10
5.67
2.18
2.16
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

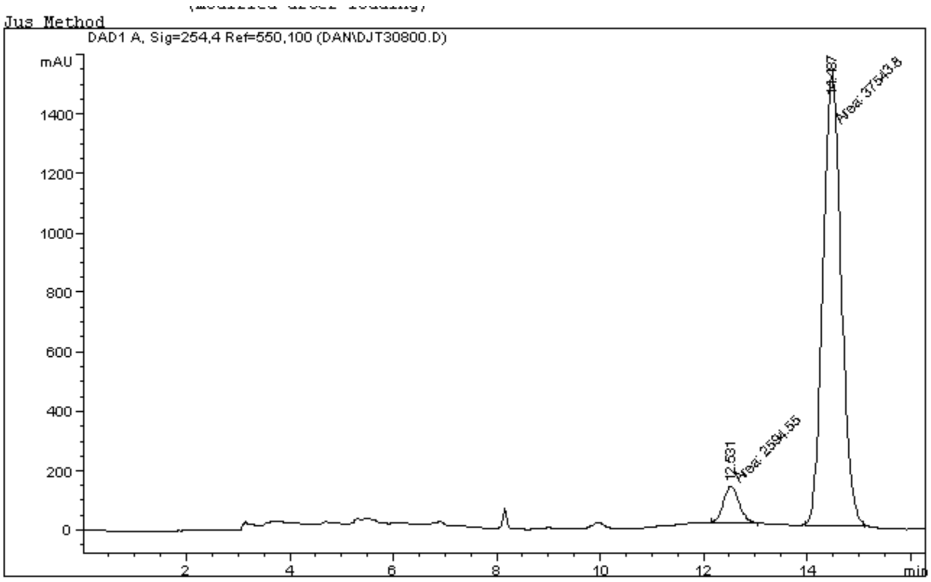

27.70
55.68
74.22
110.35
115.07
117.32
119.38
127.96
129.61
129.85
131.47
132.68
132.96
141.27
142.29
149.49
157.65
159.57
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07

(*S*)-1-[1-(4-Cyano-phenyl)-1-phenyl-allyl]-1-(4-methoxy-phenyl)-3-methyl-urea 2a



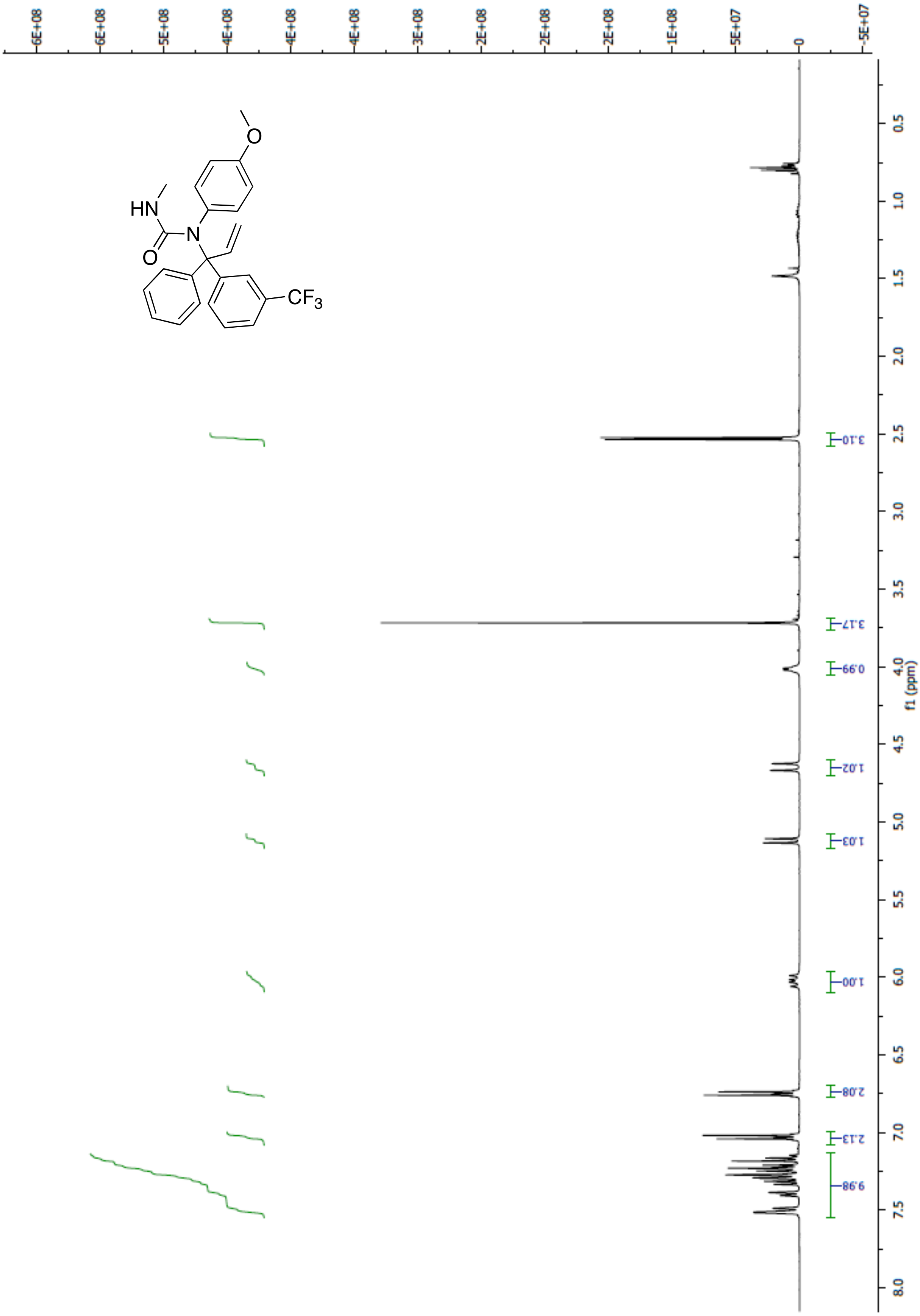
```
Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.669 MM    0.3576 2.34104e4 1091.05530  94.9212
   2  14.279 MM    0.3661 1252.57886   57.02322   5.0788

Totals :                  2.46629e4 1148.07851
```

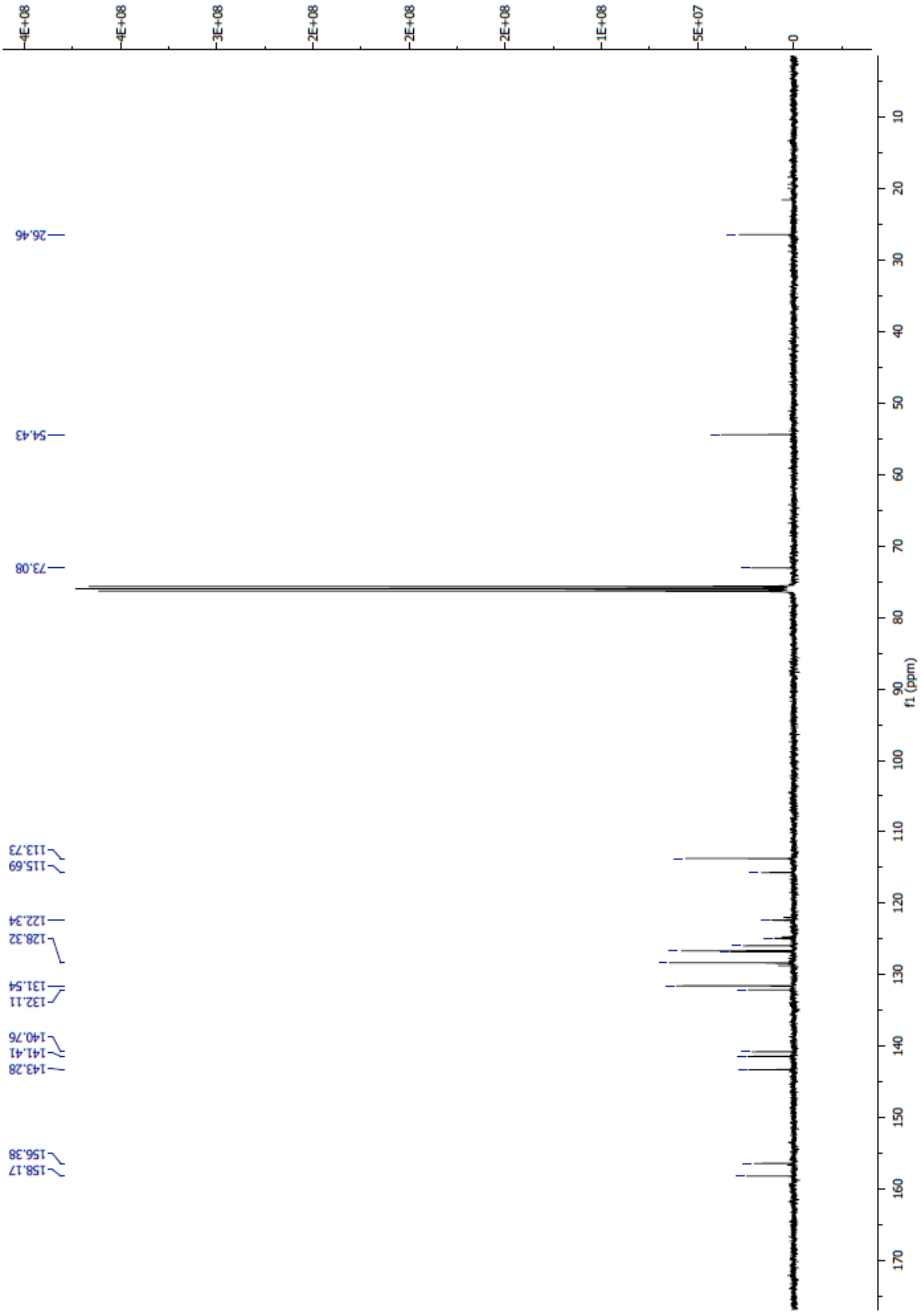
(*R*)-1-[1-(4-Cyano-phenyl)-1-phenyl-allyl]-1-(4-methoxy-phenyl)-3-methyl-urea 2a



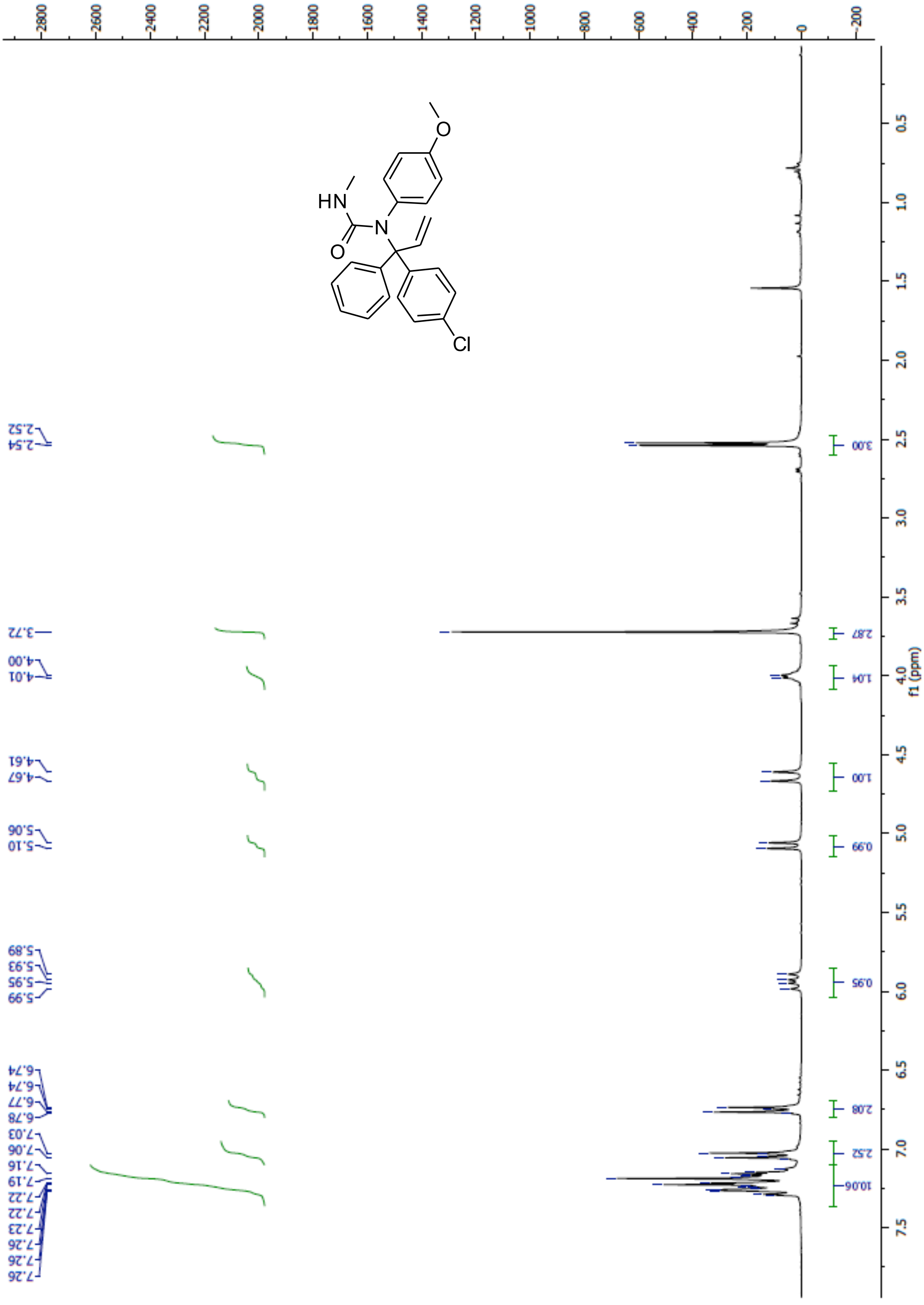
```
Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.531 MM    0.3517 2594.54883  122.95458   6.4640
   2  14.487 MM    0.4137 3.75438e4 1512.53735  93.5360
```

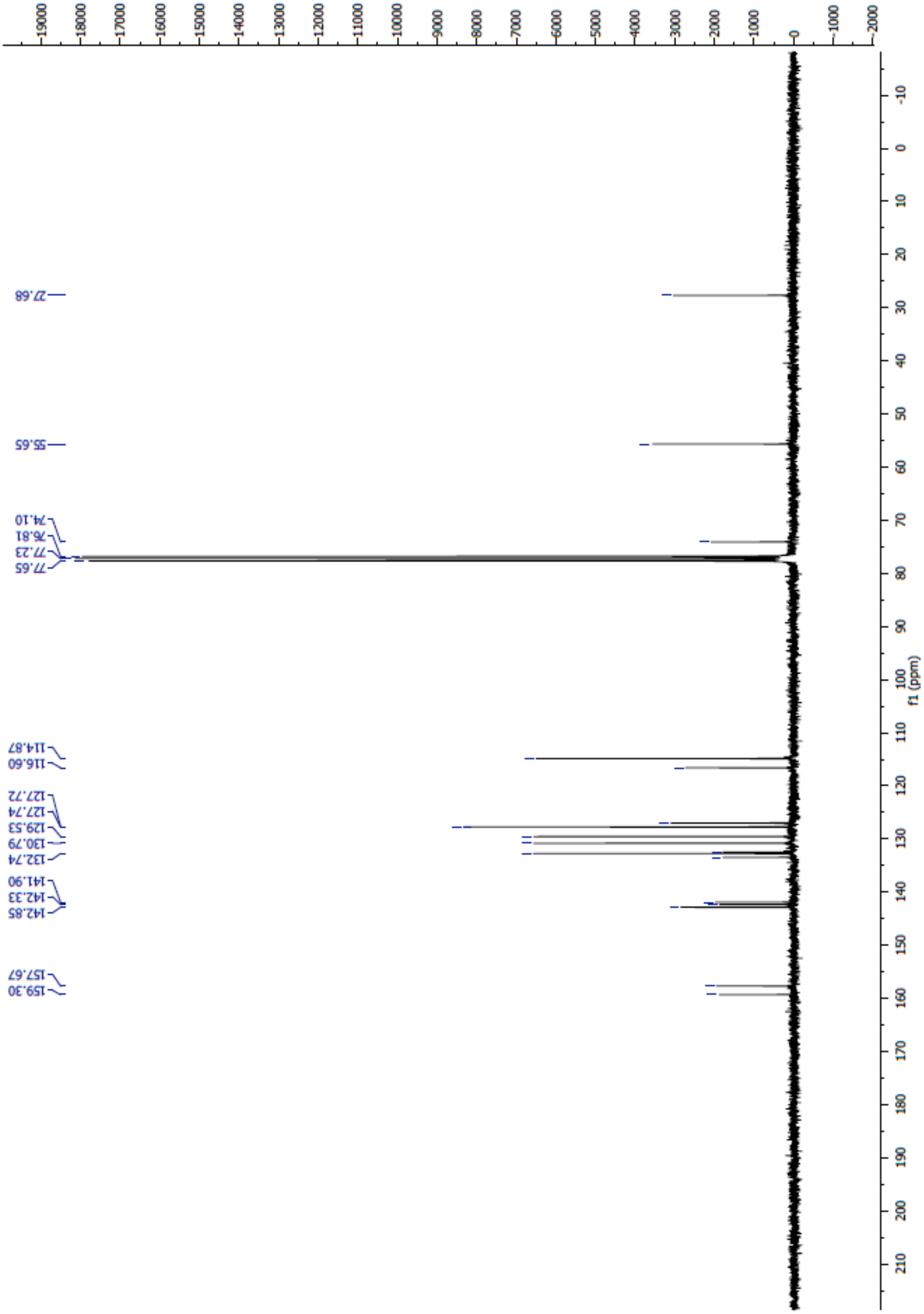
2f

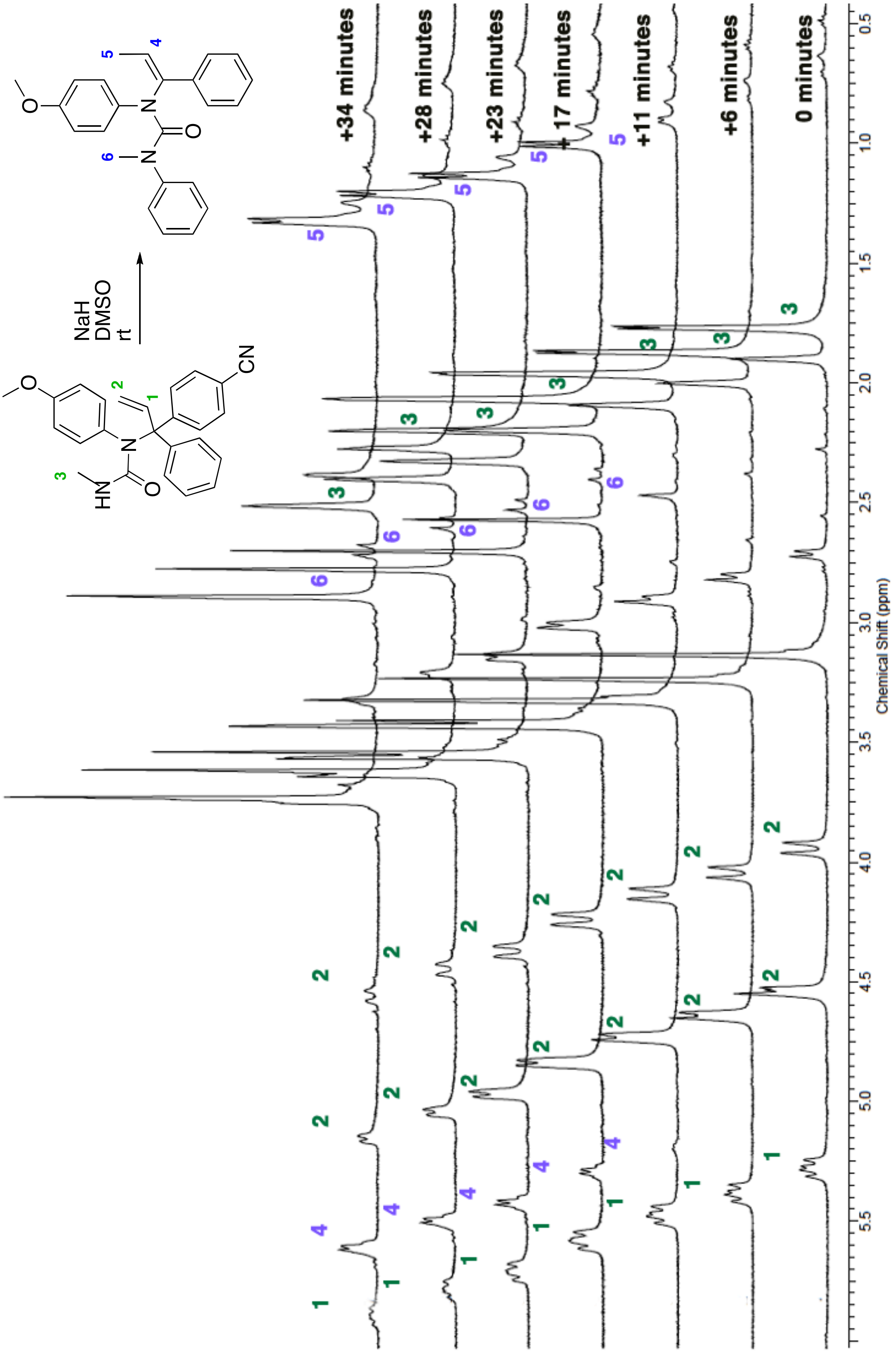

HN
N
O
O
CF3
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
3.10
3.17
0.99
1.02
1.03
1.00
2.08
2.13
9.98
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)


26.46
54.43
73.08
113.73
115.69
122.34
128.32
131.54
132.11
140.76
141.41
143.28
156.38
158.17
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

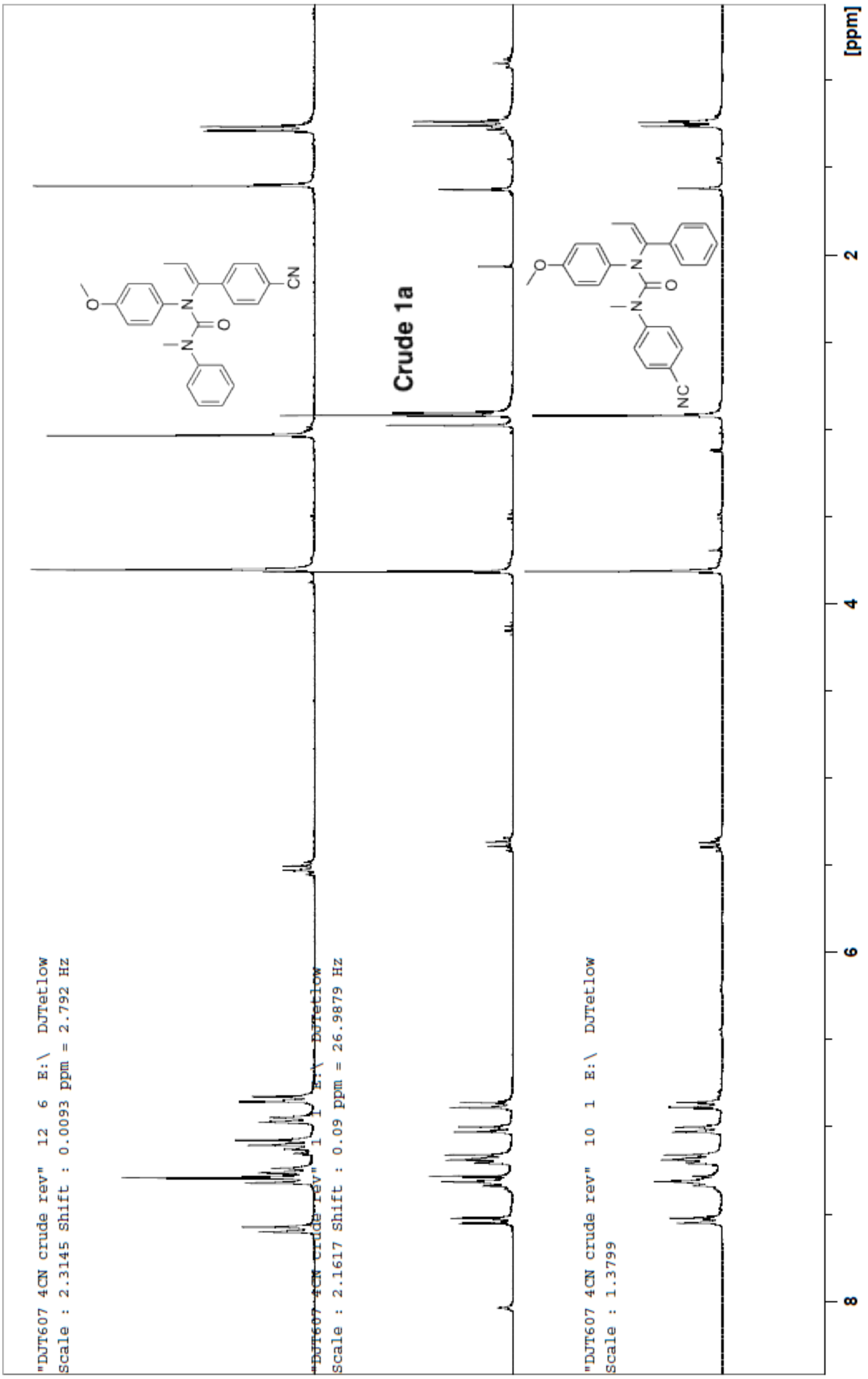
2h


2.52
2.54
3.72
4.00
4.01
4.61
4.67
5.06
5.10
5.89
5.93
5.95
5.99
6.74
6.74
6.77
6.78
7.03
7.06
7.16
7.19
7.22
7.22
7.23
7.26
7.26
7.26
3.00
2.87
1.04
1.00
0.99
0.95
2.08
2.52
10.06
f1 (ppm)
O
HN
N
O
Cl

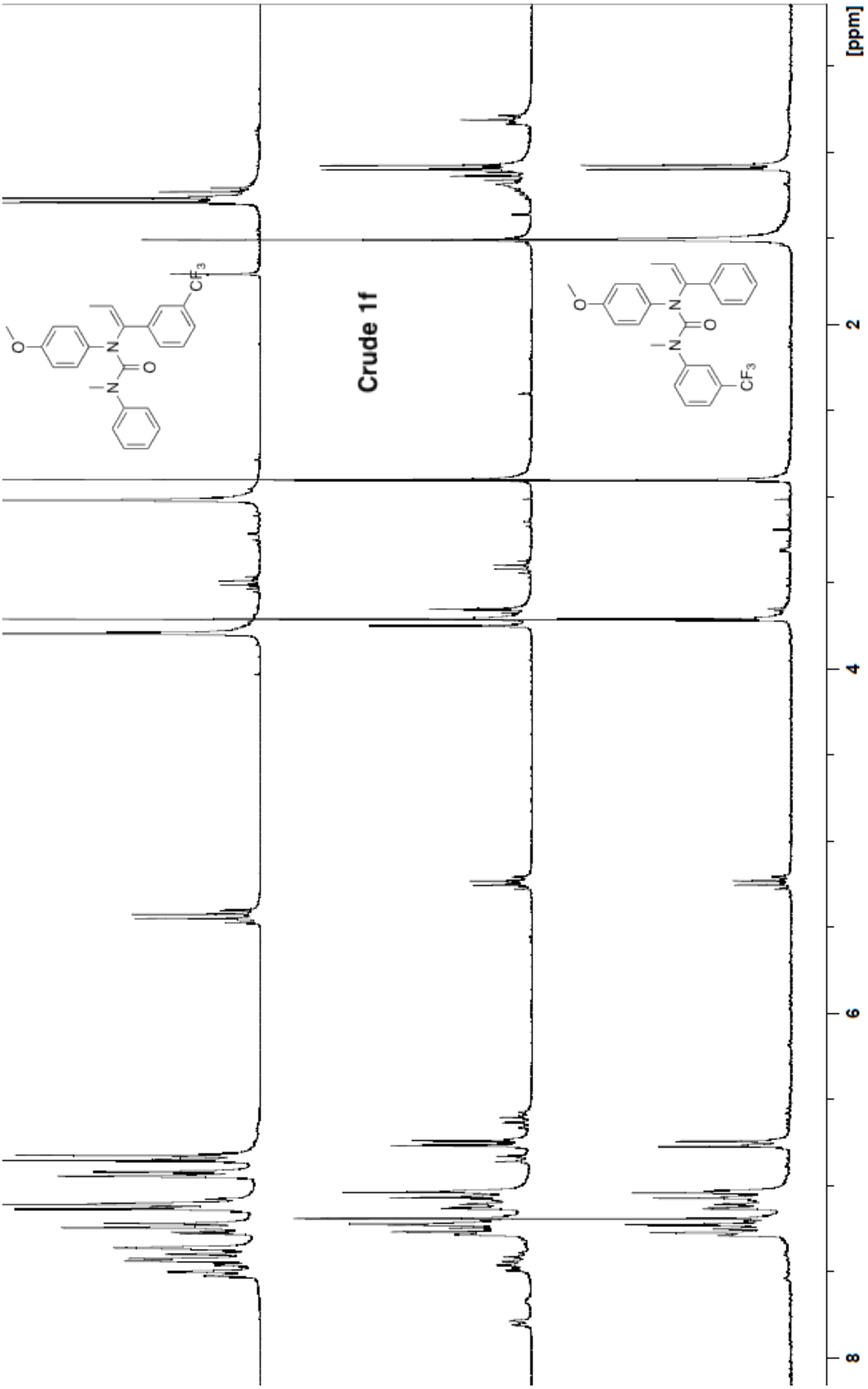

27.68
55.65
74.10
76.81
77.23
77.65
114.87
116.60
127.72
127.74
129.53
130.79
132.74
141.90
142.33
142.85
157.67
159.30
f1 (ppm)


NaH
DMSO
rt
CN
HN
N
O
3
2
1
4
5
6
+34 minutes
+28 minutes
+23 minutes
+17 minutes
+11 minutes
+6 minutes
0 minutes
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
Chemical Shift (ppm)

Comparison of crude 1a from rearrangement with authentic 1a' and 1a[2]



Comparison of crude 1f from rearrangement with authentic 1f' and 1f[3]



Comparison of crude 1h from rearrangement with authentic 1h and 1i[2]