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Expedient Metal-Free Preparation of Aryl Aziridines via Thermal Cycloaddition Reactions

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Electronic Supporting Information

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NMR Spectra of New Compounds

1. General Considerations

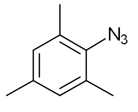
All reactions were carried out in air using technical solvents without any particular precautions to exclude moisture or oxygen. All chemicals were obtained from commercial sources and used without further purification. Column chromatography and TLC were performed on silica gel (Kieselgel 60), using UV light and a phosphomolybdic acid dip to visualize the products. Basified silica was prepared by submerging silica gel into petroleum ether containing 2% v/v NEt_3 overnight. Melting points were determined on an Electrothermal Gallenhamp apparatus and are uncorrected. Infrared spectra were recorded using a Perkin Elmer 100 series FT-IR spectrometer, equipped with a beam-condensing accessory (samples were sandwiched between diamond compressor cells). NMR spectra were measured on Bruker AVANCE 400 spectrometers (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz) at 20 °C. The chemical shifts (δ) are given in ppm relatively to a tetramethylsilane (0.00 ppm), 1-fluorobenzene (–113.15 ppm), or solvents residual peaks. The multiplicity is given as br, s, d, t, q, sept, and m for broad, singlet, doublet, triplet, quartet, septet, and multiplet. Assignments of some ^{1}H and ^{13}C NMR signals rely on COSY, HSQC, HMBC and/or DEPT-135 experiments. High resolution mass spectra (HRMS) were recorded on a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using EI, CI or ESI techniques at the Mass Spectrometry Service of Imperial College London.

2. Synthesis of Azides

All aryl azides used in this work are thermally stable at the reported reaction temperatures and they can be stores for extended periods of time (i.e. months or even years) at room temperature with no particular precautions.

General procedure for the preparation of aryl azides: Following a modified literature procedure,[1] the chosen aniline was added to HCl (1 mL per 1 mmol of aniline; 12 M) in water (1 mL per 1 mmol of aniline) at 0 °C. A solution of $NaNO_2$ (1.2 equiv.) in water (1 mL per 1 mmol of aniline) was added portion-wise and the solution was stirred at 0 °C for 2 h. A solution of NaN_3 (1.5 equiv.) in water (0.5 mL per 1 mmol of aniline) was added dropwise at 0 °C (CAUTION: vigorous release of N_2) and the reaction was stirred for 2 h and allowed to warm to room temperature. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed with water, sodium bicarbonate, brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the corresponding pure aryl azide.

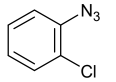
Mesityl azide (1a)



Following the general procedure from mesidine (10.0 g, 74.0 mmol), the title compound was obtained as an orange oil (9.3 g, 78%). Spectroscopic data for this compound is in accordance with the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 2.36 (s, 6H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 135.3, 134.4, 131.9, 129.5, 20.7, 18.1.

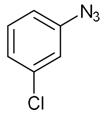
1-Azido-2-chlorobenzene (1b)



Following the general procedure from 2-chloroaniline (4.12 mL, 39.2 mmol), the title compound was obtained as an orange oil (4.99 g, 83%). Spectroscopic data for this compound is in accordance with the literature.[3]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40–7.34 (m, 1H), 7.32–7.25 (m, 1H), 7.20–7.14 (m, 1H), 7.11–7.04 (m, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 137.2, 130.7, 127.9, 125.6, 125.0, 119.7.

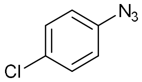
1-Azido-3-chlorobenzene (1c)



Following the general procedure from 3-chloroaniline (3.45 mL, 32.6 mmol), the title compound was obtained as a dark orange oil (3.55 g, 71%). Spectroscopic data for this compound is in accordance with the literature.[4]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28–7.22 (m, 1H), 7.12–7.07 (m, 1H), 7.01–6.98 (m, 1H), 6.92–6.88 (m, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 141.4, 135.4, 130.6, 125.1, 119.3, 117.2.

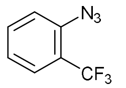
1-Azido-4-chlorobenzene (1d)



Following the general procedure from 4-chloroaniline (10.0 g, 78.4 mmol), the title compound was obtained as a dark orange oil (8.0 g, 66%). Spectroscopic data for this compound is in accordance with the literature.[5]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 138.7, 130.2, 129.8, 120.3.

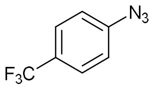
1-Azido-2-trifluoromethylbenzene (1e)



Following the general procedure from 2-trifluoromethylaniline (5.00 mL, 39.8 mmol), the title compound was obtained as a pale orange solid (6.95 g, 93%). Spectroscopic data for this compound is in accordance with the literature.[6]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66–7.52 (m, 2H), 7.31–7.19 (m, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 138.5, 133.1, 127.4 (q, *J* = 5 Hz), 124.5, 123.0 (q, *J* = 272 Hz), 121.1 (q, *J* = 32 Hz), 119.5; ^{19}F NMR (377 MHz, CDCl$_3$) δ –61.9 (s).

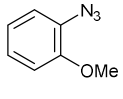
1-Azido-4-trifluoromethylbenzene (1f)



Following the general procedure from 4-trifluoromethylaniline (15.00 mL, 119.5 mmol), the title compound was obtained as an orange oil (21.23 g, 95%). Spectroscopic data for this compound is in accordance with the literature.[7]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 143.7, 127.1 (q, *J* = 33 Hz), 127.0 (q, *J* = 3 Hz), 124.0 (q, *J* = 272 Hz), 119.2; ^{19}F NMR (377 MHz, CDCl$_3$) δ -62.2 (s).

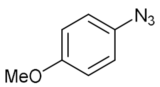
2-Azidoanisole (1g)



Following the general procedure from 2-methoxyaniline (10.00 mL, 88.7 mmol), the title compound was obtained as a yellow oil (10.56 g, 80%). Spectroscopic data for this compound is in accordance with the literature.[5]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.96–6.88 (m, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 151.8, 128.3, 125.7, 121.2, 120.2, 112.1, 55.8.

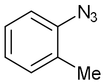
1-Azido-4-methoxybenzene (1h)



Following the general procedure from 4-methoxyaniline (9.65 g, 78.4 mmol), the title compound was obtained as a brown solid (10.90 g, 93%). Spectroscopic data for the title compound are in accordance with the literature.[8]

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 157.0, 132.3, 120.0, 115.1, 55.5.

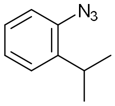
1-Azido-2-methylbenzene (1i)



Following the general procedure from 2-methylaniline (6.43 g, 60 mmol), the title compound was obtained as a brown solid (2.70 g, 34%) after purification by column chromatography (petroleum ether). Spectroscopic data for the title compound are in accordance with the literature.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26–7.19 (m, 1H), 7.19–7.08 (m, 2H), 7.07–7.00 (m, 1H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 130.7, 129.1, 126.8, 124.4, 117.7, 17.2.

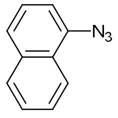
1-Azido-2-isopropylbenzene (1j)



Following the general procedure from 2-isopropylaniline (8.49 mL, 60.0 mmol), the title compound was obtained as an orange oil (7.36 g, 80%). Spectroscopic data for the title compound are in accordance with the literature.[10]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28–7.20 (m, 2H), 7.15–7.08 (m, 2H), 3.21 (sept, *J* = 7.0 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 140.0, 137.1, 126.9, 126.6, 124.9, 118.0, 27.9, 22.8.

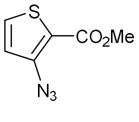
1-Azidonaphthalene (1k)



I-BuONO (1.8 mL, 15 mmol) was added dropwise to a solution of 1-naphthylamine (1.43 g, 10 mmol) in acetonitrile (20 mL) at 0 °C, followed by TMSN$_3$ (1.6 mL, 12 mmol) also dropwise. The reaction mixture was stirred at room temperature overnight, then concentrated under reduced pressure. The resulting residue was purified by column chromatography to obtain the title compound as a light brown solid (1.21 g, 71%) . Spectroscopic data for the title compound are in accordance with the literature.[11]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13–8.05 (m, 1H), 7.85–7.77 (m, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.53–7.37 (m, 3H), 7.29–7.18 (m, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 136.6, 134.4, 127.7, 127.0, 126.4, 126.3, 125.5, 124.7, 122.7, 113.9.

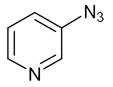
Methyl 3-azidothiophene-2-carboxylate (1l)



Following the general procedure from methyl 3-aminothiophene-2-carboxylate (7.5 g, 47.7 mmol), the title compound was obtained as a yellow solid (8.0 g, 91%). Spectroscopic data for this compound is in accordance with the literature.[12]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, *J* = 5.5 Hz, 1H), 6.93 (d, *J* = 5.5 Hz, 1H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 161.3, 142.2, 131.2, 122.1, 117.1, 52.1.

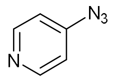
3-Azidopyridine (1m)



Following the general procedure for preparing aryl azides from 3-aminopyridine (5.00 g, 53.1 mmol), the title compound was obtained as an orange oil (3.75 g, 59%). Spectroscopic data for this compound is in accordance with the literature.[13]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41–8.36 (m, 2H), 7.38–7.34 (m, 1H), 7.32–7.28 (m, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 146.0, 141.3, 137.1, 125.9, 124.1.

4-Azidopyridine (1n)



Following a reported procedure,[14] a solution of 4-chloropyridine hydrochloride (7.15 g, 47.7 mmol) in water (20 mL) was neutralised with aqueous solution of NaOH (1 M) to pH 7 before adding MeOH (40 mL). Then, a solution of NaN$_3$ (6.20 g, 95.3 mmol) in water (20 mL) was added and the mixture was refluxed overnight, cooled to room temperature, concentrated under reduced pressure and treated with saturated aqueous solution of K$_2$CO$_3$. The aqueous layer was extracted twice with Et$_2$O and the combined organic layers were washed with water and brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure to yield the title compound as a red oil (4.65 g, 75%). Spectroscopic data for this compound is in accordance with the literature.[15]

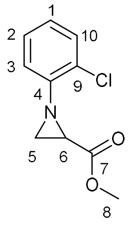
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.55–8.51 (m, 2H), 6.97–6.93 (m, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 151.1, 148.7, 114.1.

3. Synthesis of Aryl Aziridines

General procedure: Azide (1.0 equiv.) and alkene (2.0 equiv.) were stirred in technical toluene (0.5 M) at the given temperature on a heating block for 16–24 h. The reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was then purified by column chromatography (the reaction crude was dry-loaded onto the stationary phase), unless stated otherwise.

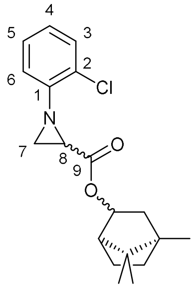
Methyl 1-(2-chlorophenyl)aziridine-2-carboxylate (4ba)

Following the general procedure at 80 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and methyl acrylate (1.17 mL, 13.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 0→20% gradient) as a yellow oil (1.15 g, 83%).



R$_f$ = 0.24 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (dd, *J* = 8.0; 1.0 Hz, 1H, H^{10}), 7.18 (td, *J* = 8.0; 1.0 Hz, 1H, H^2), 6.98 (td, *J* = 8.0; 1.0 Hz, 1H, H^1), 6.94 (dd, *J* = 8.0; 1.0 Hz, 1H, H^3), 3.82 (s, 3H, H^8), 2.84 (dd, *J* = 6.5; 3.0 Hz, 1H, H^6), 2.78 (dd, *J* = 3.0; 1.0 Hz, 1H, H^5), 2.44 (dd, *J* = 6.5; 1.0 Hz, 1H, H^5); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 170.1 (C^7), 147.9 (C^4), 129.9 (C^{10}), 127.3 (C^2), 127.1 (C^9), 124.1 (C^1), 121.1 (C^3), 52.6 (C^8), 38.5 (C^6), 34.4 (C^5); IR: ν_{max} (cm^{-1}) 2953, 1743 (s, C=O), 1590, 1476, 1440, 1398, 1294, 1264, 1203, 1179, 1152, 1081, 1052, 1036, 919, 841, 825, 791, 753, 727; HRMS (ES+) calculated for C$_{10}$H$_{11}$NO$_2$^{35}Cl: 212.0478, found: 212.0487 ([M + H]$^+$).

4,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 1-(2-chlorophenyl)aziridine-2-carboxylate(4bb)

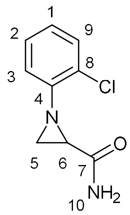


Following the general procedure at 80 °C for 16 h from **1b** (0.31 g, 2.0 mmol) and isobornyl acrylate (0.85 mL, 4.0 mmol), the title compound was isolated as a yellow oil (0.60 g, 90%) by column chromatography (petroleum ether/EtOAc, 90:10) as a 55:45 mixture of diastereoisomers.

R_f = 0.60 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 8.0; 1.5 Hz, 1H, H^5), 7.16 (td, J = 8.0; 1.5 Hz, 1H, H^1), 6.96 (td, J = 7.5; 1.5 Hz, 1H, H^6), 6.92 (d, J = 8.0 Hz, 1H, H^2), 4.84 (dd, J = 7.5; 3.5 Hz, 1H, H^{IBA}), 4.75 (dd, J = 7.5; 3.5 Hz, 1H, H^{IBA}), 2.78 (dd, J = 8.0; 3.5 Hz, 2H, H^8), 2.73 (dd, J = 3.5; 1.5 Hz, 2H, H^7), 2.43–2.40 (m, 2H, H^7), 1.88–167 (m, 8H, H^{IBA}), 1.61–1.53 (m, 2H, H^{IBA}), 1.22–1.06 (m, 4H, H^{IBA}), 1.03 (s, 3H, H^{IBA}), 1.00 (s, 3H, H^{IBA}), 0.92 (s, 3H, H^{IBA}), 0.88 (s, 3H, H^{IBA}), 0.85 (s, 6H, H^{IBA}); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.1 (C^9), 148.2 (C^3), 129.8 (C^5), 127.3 (C^1), 123.9 (C^6), 120.9 (C^2), 82.2 (CH^{IBA}), 81.9 (CH^{IBA}), 48.9 (C^{IBA}), 48.7 (C^{IBA}) , 47.0 (C^{IBA}), 46.9 (C^{IBA}), 45.0 (CH^{IBA}), 44.9 (CH^{IBA}), 38.9 (CH^{IBA}), 38.7 (C^8), 38.6 (CH^{IBA}), 38.5 (CH^{IBA}), 34.0 (C^7), 33.7 (CH^{IBA}), 33.6 (CH^{IBA}), 27.0 (CH^{IBA}), 20.08 (CH^{IBA}), 20.06 (CH^{IBA}), 19.89 (CH^{IBA}), 19.86 (CH^{IBA}), 11.5 (CH^{IBA}), 11.4 (CH^{IBA}); IR: ν_{max} (cm^{-1}) 3063, 2950, 2873, 1729 (s, C=O), 1635, 1587, 1051, 1285, 1195, 1178, 1051, 1017, 749, 725; HRMS (ESI) m/z: Calcd for $C_{19}H_{25}NO_2{}^{35}Cl$ $[M+H]^+$ 334.1574; Found 334.1581.

1-(2-Chlorophenyl)aziridine-2-carboxamide (4bc)

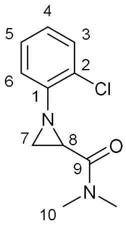
Following the general procedure at 80 °C for 16 h from **1b** (1.00 g, 6.5 mmol) and acrylamide (0.93 g, 13.0 mmol), the title compound was isolated as a yellow solid (0.71 g, 55%) after washing the reaction crude with water and triturating the precipitate with Et_2O/EtOAc (9:1).



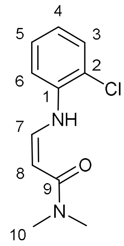
Mp 159.0–160.2 °C; R_f = 0.11 (petroleum ether/EtOAc = 50:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J = 8.0; 1.5 Hz, 1H, H^9), 7.20 (td, J = 8.0; 1.5 Hz, 1H, H^2), 7.02 (td, J = 8.0; 1.5 Hz, 1H, H^1), 6.93 (dd, J = 8.0; 1.5 Hz, 1H, H^3), 6.55 (br s, 1H, H^{10}), 5.70 (br s, 1H, H^{10}), 2.73 (ddd, J = 7.0; 3.0; 1.0 Hz, 1H, H^6), 2.61 (dd, J = 3.0; 0.5 Hz, 1H, H^5), 2.46 (dd, J = 7.0; 0.5 Hz, 1H, H^5); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 172.2 (C^7), 147.6 (C^4), 130.1 (C^9), 127.5 (C^2), 127.4 (C^8), 124.5 (C^1), 121.0 (C^3), 40.1 (C^6), 35.3 (C^5); IR: ν_{max} (cm^{-1}) 3324 (br m, N–H), 3180 (br m, N–H), 1669 (s, C=O), 1590, 1475, 1460, 1440, 1331, 1284, 1184, 1115, 1052, 1037, 937, 831, 748, 727, 718, 695; HRMS (ES+) calculated for $C_9H_{10}N_2O^{35}Cl$: 197.0482, found: 197.0481 ($[M + H]^+$).

1-(2-Chlorophenyl)-*N*,*N*-dimethylaziridine-2-carboxamide (4bd)

Following the general procedure at 80 °C for 16 h from **1b** (0.31 g, 2.0 mmol) and *N*,*N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30 gradient) as a pale yellow oil (0.60 g, 90%). From this reaction, (*Z*)-3-[(2-chlorophenyl)amino]-*N*,*N*-dimethylacrylamide **7bd** was also isolated as a yellow oil (0.03 g, 7%).



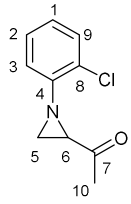
4bd: R_f= 0.54 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (br d, *J* = 8.0 Hz, 1H, H^3), 7.17 (br t, *J* = 8.0 Hz, 1H, H^5), 6.95 (br t, *J* = 8.0 Hz, 2H, H^4 and H^6), 3.24 (s, 3H, H^{10}), 3.07–2.99 (m containing a singlet at 3.04, 4H, H^8 and $H^{10'}$), 2.79 (dd, *J* = 3.5; 1.5 Hz, 1H, H^7), 3.39 (dd, *J* = 6.0; 1.5 Hz, 1H, H^7); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 167.8 (C^9), 148.9 (C^1), 129.8 (C^3), 127.3 (C^5), 127.0 (C^2), 123.7 (C^4), 121.2 (C^6), 37.1 (C^8), 36.9 (C^{10}), 36.2 ($C^{10'}$), 34.2 (C^7); IR: ν_{max} (cm^{-1}) 3058, 2984, 2931, 1643 (s, C=O), 1586, 1472, 1352, 1190, 1142, 1049, 751, 722, 664; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}N_2O^{35}Cl$ $[M+H]^+$ 225.0795; Found 225.0794.



7bd: R_f= 0.33 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.35 (d, *J* = 11.0 Hz, 1H, NH), 7.34 (dd, *J* = 8.0; 1.0 Hz, 1H, H^3), 7.20 (dd, *J* = 11.0; 8.5 Hz, 1H, H^7), 7.16 (d, *J* = 3.0 Hz, 1H, H^6), 7.05 (dd, *J* = 8.0; 1.0 Hz, 1H, H^5), 6.86 (td, *J* = 8.0; 1.0 Hz, H^4), 5.15 (d, *J* = 8.5 Hz, 1H, H^8), 3.04 (s, 6H, H^{10}); IR: ν_{max} (cm^{-1}) 3336 (br s, NH), 2922, 1625 (s, C=O), 1587, 1483, 1367, 1282, 1140, 1051, 741; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}N_2O^{35}Cl$ $[M+H]^+$ 225.0795; Found 225.0801.

1-[1-(2-Chlorophenyl)aziridin-2-yl]ethan-1-one (4be)

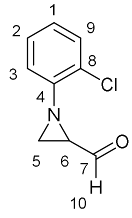
Following the general procedure at 80 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and methyl vinyl ketone (1.06 mL, 13.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→20% gradient) as a yellow oil (1.09 g, 86%).



R_f = 0.30 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.0; 1.5 Hz, 1H, H^9), 7.18 (td, *J* = 8.0; 1.5 Hz, 1H, H^2), 6.99 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.91 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 2.76 (dd, *J* = 6.5; 3.0 Hz, 1H, H^6), 2.69 (dd, *J* = 3.0; 1.0 Hz, 1H, H^5), 2.47 (dd, *J* = 6.5; 1.0 Hz, 1H, H^5), 2.23 (s, 3H, H^{10}); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 205.9 (C^7), 148.0 (C^4), 129.9 (C^9), 127.5 (C^2), 127.2 (C^8), 124.2 (C^1), 120.8 (C^3), 45.6 (C^6), 34.2 (C^5), 25.1 (C^{10}); IR: ν_{max} (cm^{-1}) 3067, 2995, 2921, 1704 (s, C=O), 1645, 1588, 1569, 1475 (s), 1444, 1421, 1356 (m), 1294 (m), 1247 (s), 1197, 1170, 1131, 1106, 1077, 1050 (m), 1035, 936, 920 (m), 881, 749 (s), 720, 678 (m); HRMS (ES+) calculated for $C_{10}H_{11}NO^{35}Cl$: 196.0529, found: 196.0524 ($[M + H]^+$).

1-(2-Chlorophenyl)aziridine-2-carbaldehyde (4bf)

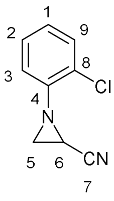
Following the general procedure at 80 °C for 16 h from **1b** (1.50 g, 9.8 mmol) and acrolein (1.30 mL, 19.6 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→20% gradient) as a yellow oil (0.91 g, 51%).



R_f = 0.31 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (d, *J* = 6.0 Hz, 1H, H^{10}), 7.34 (dd, *J* = 8.0; 1.5 Hz, 1H, H^9), 7.19 (td, *J* = 8.0; 1.5 Hz, 1H, H^2), 7.01 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.94 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 2.80 (d, *J* = 3.0 Hz, 1H, H^5), 2.78 (ddd, *J* = 6.5; 6.0; 3.0 Hz, 1H, H^6), 2.57 (d, *J* = 6.5 Hz, 1H, H^5); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 198.4 (C^7), 147.3 (C^4), 130.0 (C^9), 127.5 (C^2), 127.2 (C^8), 124.4 (C^1), 121.0 (C^3), 45.0 (C^6), 32.3 (C^5); IR: ν_{max} (cm^{-1}) 3065, 2991, 1719 (s, C=O), 1588, 1475, 1443, 1287, 1158, 1051, 1034, 931, 867, 752, 721, 671; HRMS (ES+) calculated for $C_9H_9NO^{35}Cl$: 182.0373, found: 182.0380 ($[M + H]^+$).

1-(2-Chlorophenyl)aziridine-2-carbonitrile (4bg)

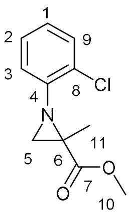
Following the general procedure at 80 °C for 16 h from **1b** (1.00 g, 6.5 mmol) and acrylonitrile (0.86 mL, 13.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→20% gradient) as a yellow solid (1.16 g, 99%).



Mp 64.4–65.9 °C; R$_f$ = 0.29 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39 (dd, *J* = 8.0; 1.5 Hz, 1H, H^9), 7.22 (td, *J* = 8.0; 1.5 Hz, 1H, H^2), 7.06 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.93 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 2.84 (d, *J* = 3.0 Hz, 1H, H^5), 2.83–2.77 (m, 1H, H^6), 2.57 (d, *J* = 6.0 Hz, 1H, H^5); ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.4 (C^4), 130.3 (C^9), 127.6 (C^2), 127.4 (C^8), 125.1 (C^1), 120.9 (C^3), 117.3 (C^7), 34.3 (C^6), 25.4 (C^5); IR: ν$_{max}$ (cm^{-1}) 3092, 3059, 2246 (m, C≡N), 1589, 1476, 1445, 1368, 1293, 1253, 1183, 1095, 1050, 1039, 1011, 944, 753, 741, 715, 681; HRMS (EI+) calculated for $C_9H_7N_2{}^{35}Cl$: 178.0298, found: 178.0304 ([M]$^+$).

Methyl 1-(2-chlorophenyl)-2-methylaziridine-2-carboxylate (4bi)

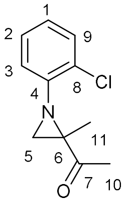
Following the general procedure at 90 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and methyl methacrylate (1.40 mL, 13.1 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→10% gradient) as an orange oil (0.88 g, 60%).



R$_f$ = 0.45 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (dd, *J* = 8.0; 1.5 Hz, 1H, H^9), 7.18 (td, *J* = 8.0; 1.5 Hz, 1H, H^2), 6.95 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.87 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 3.70 (s, 3H, H^{10}), 2.83 (s, 1H, H^5), 2.33 (s, 1H, H^5), 1.46 (s, 3H, H^{11}); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 171.1 (C^7), 145.4 (C^4), 129.6 (C^9), 127.4 (C^8), 127.3 (C^2), 123.6 (C^1), 120.9 (C^3), 52.6 (C^{10}), 42.4 (C^6), 39.2 (C^5), 16.3 (C^{11}); IR: ν$_{max}$ (cm^{-1}) 3067, 2987, 2951, 1728 (s, C=O), 1589, 1474, 1443, 1321, 1301, 1267, 1238, 1195, 1156, 1114, 1057, 1036, 752, 724, 664; HRMS (ES+) calculated for $C_{11}H_{13}NO_2{}^{35}Cl$: 226.0635, found: 226.0633 ([M + H]$^+$).

1-[1-(2-Chlorophenyl)-2-methylaziridin-2-yl]ethan-1-one (4bj)

Following the general procedure at 90 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and 3-methyl-3-buten-2-one (1.29 mL, 13.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→10% gradient) as a yellow oil (0.99 g, 72%).

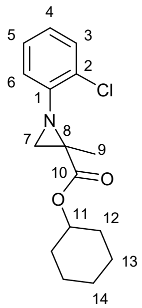


R$_f$ = 0.42 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (dd, *J* = 8.0; 1.5 Hz, 1H, H^9), 7.20 (td, *J* = 8.0; 1.5 Hz, 1H, H^2), 6.99 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.85 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 2.74 (s, 1H, H^5), 2.30 (s, 1H, H^5), 2.24 (s, 3H, H^{10}), 1.20 (s, 3H, H^{11}); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 207.7 (C^7), 145.0 (C^4), 129.9 (C^9), 128.1 (C^8), 127.5 (C^2), 123.9 (C^1), 120.8 (C^3), 48.7 (C^6), 38.0 (C^5), 24.1 (C^{10}), 13.4 (C^{11}); IR: ν$_{max}$ (cm^{-1}) 3067, 2981, 1702 (s, C=O), 1588, 1473, 1442, 1360, 1347, 1230, 1135, 1059, 872, 756, 725, 683; HRMS (ES+) calculated for $C_{11}H_{13}NO^{35}Cl$: 210.0686, found: 210.0690 ([M + H]$^+$).

Cyclohexyl 1-(2-chlorophenyl)-2-methylaziridine-2-carboxylate (4bk)

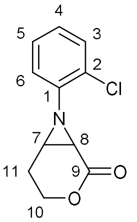
Following the general procedure at 110 °C for 24 h from **1b** (0.31 g, 2.0 mmol) and cyclohexyl methacrylate (0.70 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 95:5) as a pale yellow oil (0.41 g, 70%).

R_f = 0.60 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (dd, *J* = 8.0; 1.0 Hz, 2H, H^3), 7.17 (td, *J* = 8.0; 1.5 Hz, 2H, H^5), 6.93 (td, *J* = 7.5; 1.5 Hz, 2H, H^4), 6.88 (dd, *J* = 8.0; 1.0 Hz, 2H, H^6), 4.73–4.68 (m, 1H, H^{Cy}), 2.80 (s, 1H, H^7), 2.35 (s, 1H, H^7), 1.73–1.18 (m, 13H, H^{Cy}), 1.55 (s, 3H, H^9); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 169.7 (C^{10}), 146.0 (C^1), 129.4 (C^3), 127.22 (C^2), 127.18 (C^5), 123.2 (C^4), 121.0 (C^6), 73.5 (CH^{Cy}), 42.7 (C^8), 39.2 (C^7), 31.0 (CH$_2$^{Cy}), 25.2 (CH$_2$^{Cy}), 23.4 (C^9), 17.3 (CH$_2$^{Cy}). IR: ν$_{max}$ (cm^{-1}) 3064, 2981, 2933, 2857, 1718 (s, C=O), 1587, 1473, 1442, 1294, 1167, 1150, 1058, 1035, 1012, 747; HRMS (ESI) m/z: Calcd for $C_{16}H_{21}NO_2{}^{35}Cl$ [M+H]$^+$ 294.1261; Found 294.1264.

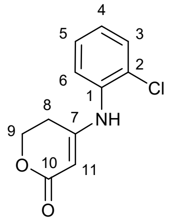


7-(2-Chlorophenyl)-3-oxa-7-azabicyclo[4.1.0]heptan-2-one (4bl)

Following the general procedure at 90 °C for 24 h from **1b** (0.31 g, 2.0 mmol) and 5,6-dihydro-2*H*-pyran-2-one (0.34 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→20% gradient) as a yellow oil (0.18 g, 40%). From this reaction, 4-[(2-chlorophenyl)amino]-5,6-dihydro-2*H*-pyran-2-one **7bl** was also isolated from the column and was further purified by trituration twice with diethyl ether to be isolated as a pale brown solid (0.03 g, 6%).



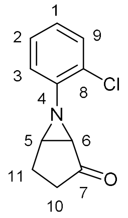
4bl: R_f= 0.15 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.35 (dd, *J* = 8.0; 1.5 Hz, 1H, H^3), 7.20 (td, *J* = 8.0; 1.5 Hz, 1H, H^5), 7.02 (dd, *J* = 8.0; 1.5 Hz, 1H, H^6), 7.01 (td, *J* = 8.0; 1.5 Hz, 1H, H^4), 4.69 (ddd, *J* = 13.0; 11.0; 3.5 Hz, 1H, H^{10}), 4.27 (dd, *J* = 11.0; 5.5 Hz, 1H, H^{10}), 3.08 (d, *J* = 6.0 Hz, 1H, H^8), 3.03 (ddd, *J* = 6.0; 1.5; 1.0 Hz, 1H, H^7), 2.51 (ddd, *J* = 14.5; 3.5; 1.0 Hz, 1H, H^{11}), 2.19 (dddd, *J* = 14.5; 13.0; 5.5; 1.5 Hz, 1H, H^{11}); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 167.5 (C^9), 146.9 (C^1), 130.1 (C^3), 127.6 (C^5), 126.8 (C^2), 124.4 (C^4), 121.2 (C^6), 64.7 (C^{10}), 40.6 (C^8), 40.0 (C^7), 23.1 (C^{11}); IR: ν$_{max}$ (cm^{-1}) 3072, 2971, 2921, 1733 (s, C=O), 1651, 1588, 1475, 1445, 1389, 1339, 1274, 1250, 1223, 1188, 1160, 1133, 1109, 1070, 1036, 949, 913, 913, 896, 850, 825, 753, 723, 664; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NO_2{}^{35}Cl$ [M+H]$^+$ 224.0478; Found 224.0482.



7bl: Mp 183.2–187.3 °C; R_f = 0.64 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.44 (td, *J* = 8.0; 1.0 Hz, 2H, H^3 and H^5), 7.30 (dd, *J* = 7.5; 1.0 Hz, 1H, H^6), 7.14 (td, *J* = 7.5; 1.0 Hz, 1H, H^4), 6.23 (br s, 1H, NH), 5.27 (s, 1H, H^{11}), 4.41 (t, *J* = 6.0 Hz, 2H, H^9), 2.66 (t, *J* = 6.0 Hz, H^8); ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 167.6 (C^{10}), 155.6 (C^7), 134.7 (C^1), 130.1 (C^3), 127.6 (C^2), 127.4 (C^6), 126.4 (C^4), 124.9 (C^5), 87.9 (C^{11}), 64.1 (C^9), 28.2 (C^8); IR: ν$_{max}$ (cm^{-1}) 3228 (br s, NH), 3035, 2898, 1648 (s, C=O), 1601, 1576, 1531, 1477, 1464, 1302, 1216, 1086, 1056, 797, 732; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NO_2{}^{35}Cl$ [M+H]$^+$ 224.0478; Found 224.0482.

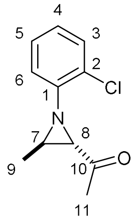
6-(2-Chlorophenyl)-6-azabicyclo[3.1.0]hexan-2-one (4bm)

Following the general procedure at 90 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and 2-cyclopenten-1-one (1.09 mL, 13.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc 0→5% gradient) as a yellow oil (0.52 g, 39%).



R$_f$ = 0.38 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (dd, *J* = 8.0; 1.5 Hz, 1H, H^{9}), 7.16 (td, *J* = 8.0; 1.5 Hz, 1H, H^{2}), 6.97 (td, *J* = 8.0; 1.5 Hz, 1H, H^{1}), 6.94 (dd, *J* = 8.0; 1.5 Hz, 1H, H^{3}), 3.37–3.34 (m, 1H, H^{5}), 3.00 (d, *J* = 4.0 Hz, 1H, H^{6}), 2.55–2.44 (m, 1H, H^{10}), 2.28–2.08 (m, 3H, H^{10} and H^{11}); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 210.3 (C^{7}), 146.4 (C^{4}), 130.2 (C^{9}), 127.5 (C^{2}), 126.8 (C^{8}), 123.9 (C^{1}), 121.0 (C^{3}), 47.4 (C^{6}), 46.4 (C^{5}), 32.7 (C^{10}), 23.3 (C^{11}); IR: ν_{max} (cm^{-1}) 3059, 2939, 1740 (s, C=O), 1588, 1473, 1444, 1236, 1156, 1058, 1033, 885, 756, 679; HRMS (ES+) calculated for $C_{11}H_{11}NO^{35}Cl$: 208.0529, found: 208.0533 ([M + H]$^{+}$).

trans-1-[1-(2-Chlorophenyl)-3-methylaziridin-2-yl]ethan-1-one (4bn)

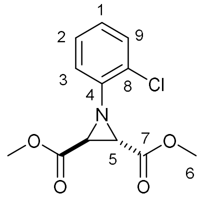


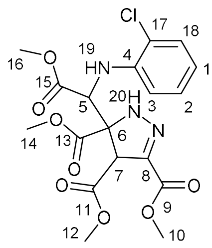
Following the general procedure at 90 °C for 24 h from **1b** (0.31 g, 2.0 mmol) and 3-penten-2-one (0.56 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 95:5) as a pale yellow oil (0.16 g, 36%). R$_f$ = 0.43 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (400 MHz, acetone-d$_6$): δ 7.34 (d, *J* = 8.0 Hz, 1H, H^{3}), 7.23 (t, *J* = 8.5 Hz, 1H, H^{5}), 7.03 (d, *J* = 8.0 Hz, 1H, H^{6}), 7.00 (t, *J* = 8.5 Hz, H^{4}), 3.04 (d, *J* = 2.5 Hz, 1H, H^{8}), 2.92 (qd, *J* = 5.5; 2.5 Hz, 1H, H^{7}), 2.20 (s, 3H, H^{11}), 1.29 (d, *J* = 5.5 Hz, 3H, H^{9}); ^{13}C{^{1}H} NMR (101 MHz, acetone-d$_6$): δ 203.7 (C^{10}), 146.2 (C^{1}), 130.3 (C^{3}), 128.3 (C^{5}), 126.8 (C^{2}), 123.9 (C^{4}), 122.6 (C^{6}), 50.7 (C^{11}), 43.0 (C^{8}), 27.4 (C^{7}), 15.7 (C^{9}); IR: ν_{max} (cm^{-1}) 3061, 2998, 2969, 2926, 1700 (s, C=O), 1586, 1474, 1441, 1354, 1243, 1174, 1058, 1033, 751; HRMS (ESI) m/z: Calcd for $C_{11}H_{13}NO^{35}Cl$ [M+H]$^{+}$ 210.0686; Found 210.0691.

Dimethyl *trans*-1-(2-chlorophenyl)aziridine-2,3-dicarboxylate (*trans*-4bo)

Following the general procedure at 100 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and dimethyl fumarate (1.88 g, 13.0 mmol), the title compound was isolated as a yellow solid (1.20 g, 68%) after column chromatography (petroleum ether/EtOAc 0→10% gradient) and trituration with pentane at -18 °C. From this reaction, trimethyl 5-{1-[(2-chlorophenyl)amino]-2-methoxy-2-oxoethyl}-Δ^{2}-pyrazoline-3,4,5-tricarboxylate **6bo** was also isolated as a white solid (0.15 g, 5%) after column chromatography (petroleum ether/EtOAc 0→75% gradient) and trituration with Et$_2$O.

4bo: Single crystals for X-ray diffraction were grown from Et$_2$O; Mp 89.7–91.4 °C; R$_f$ = 0.26 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (dd, *J* = 8.0; 1.5 Hz, 1H, H^{9}), 7.20 (td, *J* = 8.0; 1.5 Hz, 1H, H^{2}), 6.99 (td, *J* = 8.0; 1.5 Hz, 1H, H^{1}), 6.95 (dd, *J* = 8.0; 1.5 Hz, 1H, H^{3}), 3.76 (s, 6H, H^{6}), 3.55 (s, 2H, H^{5}); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 167.4 (C^{7}), 143.2 (C^{4}), 129.7 (C^{9}), 127.3 (C^{2}), 125.7 (C^{8}), 124.2 (C^{1}), 121.0 (C^{3}), 52.9 (C^{6}), 42.6 (C^{5}); IR: ν_{max} (cm^{-1}) 3078, 3011, 1750 (s, C=O), 1735 (s, C=O), 1477, 1435, 1342, 1303, 1279, 1204, 1172, 1134, 1016, 905, 800, 780, 753, 715, 678; HRMS (ES+) calculated for $C_{12}H_{13}NO_4{}^{35}Cl$: 270.0533, found: 270.0536 ([M + H]$^{+}$).

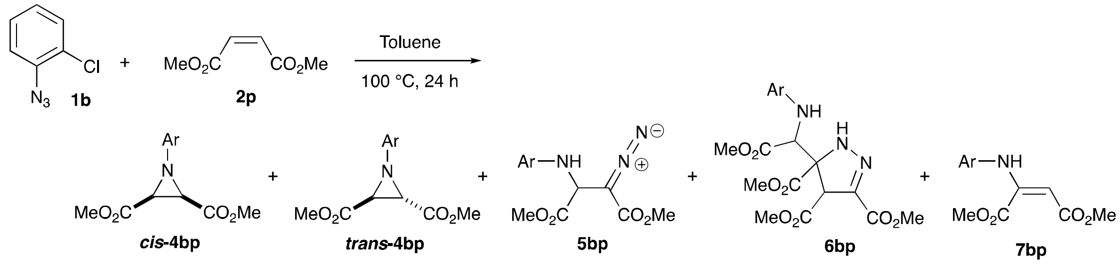




6bo: Mp 171.7–173.9 °C; $R_f = 0.38$ (petroleum ether/EtOAc = 50:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 8.0; 1.0 Hz, 1H, H^{18}), 7.17 (br s, 1H, H^{20}), 7.15 (td, J = 8.0; 1.0 Hz, 1H, H^2), 6.74 (td, J = 8.0; 1.0 Hz, 1H, H^1), 6.72 (dd, J = 8.0; 1.0 Hz, 1H, H^3), 5.74 (d, J = 11.0 Hz, 1H, H^{19}), 4.44 (d, J = 11.0 Hz, 1H, H^5), 4.38 (s, 1H, H^7), 3.82 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.73 (s, 6H, H^{10} and OCH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 171.2 (C=O), 170.2 (C=O), 168.3 (C=O), 161.3 (C=O), 142.2 (C^8), 139.7 (C^4), 129.7 (C^{18}), 127.8 (C^2), 120.3 (C^{17}), 119.2 (C^1), 111.4 (C^3), 78.4 (C^6), 62.2 (C^5), 57.5 (C^7), 53.7 (OCH_3), 53.2 (OCH_3), 53.0 (OCH_3), 52.6 (OCH_3); IR: ν_{max} (cm^{-1}) 3398 (w, N–H), 3354 (m, N–H), 1742 (s, C=O), 1714 (s, C=O), 1598, 1514 , 1442, 1306, 1246, 1202, 1172, 1135, 1107, 1082, 1069, 1032, 941, 746, 702, 686; HRMS (ES+) calculated for $C_{18}H_{21}N_3O_8{}^{35}Cl$: 442.1017, found: 442.1015 ([M + H]$^+$).

Dimethyl *trans*-1-(2-chlorophenyl)aziridine-2,3-dicarboxylate (*trans*-4bp)

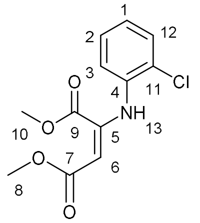
The reaction of **1b** and dimethyl maleate led to the formation of at least five different products, including both ***cis***- and ***trans*-4bp** and diazo compound **5bp** that could be isolated by column chromatography and fully characterised (Scheme S1). Unfortunately, ***cis*-4bp** could not be isolated pure, but the observed differences between both isomers (singlet at 3.21 ppm for the heterocyclic protons in ***cis*-4bp** compared to 3.55 ppm for ***trans*-4bp**) were analogous to documented pairs of *cis*- and *trans*-disubstituted aziridines.[16]



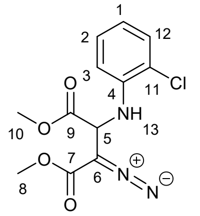
^{1}H NMR yield:	17%	17%	12%	<5%	15%
Isolated yield:	-	13%	6%	3%	14%

Scheme S1. Reaction of **1b** and dimethyl maleate

Following the general procedure at 100 °C for 24 h from **1b** (1.00 g, 6.5 mmol) and dimethyl maleate (1.63 mL, 13.0 mmol), the title compound was isolated as a yellow solid (0.23 g, 13%) after column chromatography (petroleum ether/EtOAc 0→20% gradient) and trituration with pentane at -18 °C. From this reaction, dimethyl 2-[(2-chlorophenyl)amino]fumarate **7bp** (yellow solid, 0.25 g, 14%), dimethyl 2-[(2-chlorophenyl)amino]-3-diazosuccinate **5bp** (yellow oil, 0.11 g, 6%) and trimethyl 5-{1-[(2-chlorophenyl)amino]-2-methoxy-2-oxoethyl}-Δ^2-pyrazoline-3,4,5-tricarboxylate **6bp** (white solid, 0.10 g, 3%) were also isolated after column chromatography (petroleum ether/EtOAc 0→75% gradient). Purification of compound **6bp** required trituration with Et_2O after column chromatography. Spectroscopic data for compounds ***trans*-4bp** and **6bp** is in accordance with previously reported values in this manuscript (see compounds ***trans*-4bo** and **6bo** above).

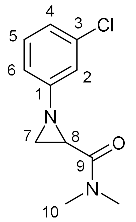


7bp: Mp 63.1–65.0 °C; R_f = 0.50 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (br s, 1H, H^{13}), 7.39 (dd, *J* = 8.0; 1.5 Hz, 1H, H^{12}), 7.15 (td, *J* = 8.0; 1.0 Hz, 1H, H^2), 7.01 (td, *J* = 8.0; 1.5 Hz, 1H, H^1), 6.78 (dd, *J* = 8.0; 1.0 Hz, 1H, H^3), 5.55 (s, 1H, H^6), 3.77 (s, 3H, H^{10}), 3.72 (s, 3H, H^8); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 169.6 (C^9), 164.4 (C^7), 146.5 (C^4), 137.4 (C^5), 129.9 (C^{12}), 127.1 (C^2), 125.6 (C^{11}), 124.6 (C^1), 120.8 (C^3), 95.9 (C^6), 52.9 (C^{10}), 51.4 (C^8); IR: ν_{max} (cm^{-1}) 3269 (br w, N–H), 3021, 2999, 1736 (s, C=O), 1669, 1610, 1590, 1501, 1458, 1436, 1271, 1239, 1215, 118, 1157, 1146, 1124, 1052, 1033, 990, 821, 778, 761, 755, 740, 722, 671; HRMS (ES+) calculated for $C_{12}H_{13}NO_4{}^{35}Cl$: 270.0533, found: 270.0528 ($[M + H]^+$).



5bp: R_f = 0.40 (petroleum ether/EtOAc = 80:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 8.0; 1.0 Hz, 1H, H^{12}), 7.16 (td, *J* = 8.0; 1.0 Hz, 1H, H^2), 6.75 (td, *J* = 8.0; 1.0 Hz, 1H, H^1), 6.66 (dd, *J* = 8.0; 1.0 Hz, 1H, H^3), 5.36 (d, *J* = 6.5 Hz, 1H, H^{13}), 5.06 (d, *J* = 6.5 Hz, 1H, H^5), 3.87 (s, 3H, H^{10}), 3.84 (s, 3H, H^8); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 170.0 (C^9), 165.7 (C^7), 140.8 (C^4), 129.5 (C^{12}), 128.0 (C^2), 120.3 (C^{11}), 119.3 (C^1), 112.4 (C^3), 58.6 (C^6), 53.4 (C^{10}), 52.3 (C^8), 51.8 (C^5); IR: ν_{max} (cm^{-1}) 3398 (br w, N–H), 2955, 2094 (s, diazo), 1742 (s, C=O), 1690 (s, C=O), 1596, 1504, 1435, 1352, 1324, 1283 , 1240, 1209, 1164, 1147, 1092, 1036, 743; HRMS (ES+) calculated for $C_{12}H_{13}N_3O_4{}^{35}Cl$: 298.0595, found: 298.0591 ($[M + H]^+$).

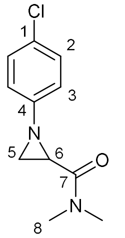
1-(3-Chlorophenyl)-*N*,*N*-dimethylaziridine-2-carboxamide (4cd)



Following the general procedure at 80 °C for 16 h from **1c** (0.31 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30) as a yellow oil (0.40 g, 89%).

R_f = 0.33 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 8.0 Hz, 1H, H^5), 6.99-6.95 (m, 2H, H^2 and H^4), 6.89 (d, *J* = 8.0 Hz, H^6), 3.24 (s, 1H, H^{10}), 3.03 (s, 1H, $H^{10'}$), 2.98 (dd, *J* = 6.5; 3.5 Hz, 1H, H^8), 2.65 (dd, *J* = 3.5; 1.0 Hz, 1H, H^7), 2.31 (dd, *J* = 6.5; 1.0 Hz, 1H, H^7); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.7 (C^9), 154.5 (C^1), 134.4 (C^3), 130.1 (C^5), 123.1 (C^4), 120.9 (C^2), 119.0 (C^6), 37.0 (C^8), 37.0 (C^{10}), 36.1 ($C^{10'}$), 33.46 (C^7); IR: ν_{max} (cm^{-1}) 3056, 2985, 2931, 1641 (s, C=O), 1589, 1472, 1419, 1354, 1259, 1138, 1069, 995, 775, 685; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}N_2O^{35}Cl$ $[M+H]^+$ 225.0795; Found 225.0793.

1-(4-Chlorophenyl)-*N*,*N*-dimethylaziridine-2-carboxamide (4dd)



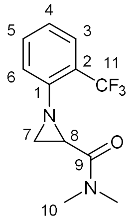
Following the general procedure at 80 °C for 16 h from **1d** (0.31 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30) as a yellow solid (0.42 g, 95%).

Mp = 120.3-121.9 °C; R_f = 0.23 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 6.93 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 3.25 (s, 3H, H^8), 3.03 (s, 3H, $H^{8'}$), 2.95 (dd, *J* = 6.5; 3.5 Hz, 1H, H^6), 2.66 (dd, *J* = 3.5; 1.5 Hz, 1H, H^5), 2.28 (dd, *J* = 6.5; 1.5 Hz, 1H, H^5); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.8 (C^7), 151.8 (C^4), 129.1 (C^2), 128.1

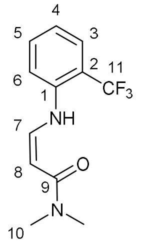
(C^1), 122.0 (C^3), 37.2 (C^6), 37.0 (C^8), 36.2 ($C^{8'}$), 33.6 (C^5); IR: ν_{max} (cm^{-1}) 3067, 3049, 3031, 2932, 1638 (s, C=O), 1586, 1486, 1429, 1472, 1354, 1166, 1137, 1107, 1081, 1000, 840, 821, 722, 591; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}N_2O^{35}Cl$ $[M+H]^+$ 225.0795; Found 225.0792.

_N,N_-Dimethyl-1-[2-(trifluoromethyl)phenyl]aziridine-2-carboxamide (4ed)

Following the general procedure at 80 °C for 16 h from **1e** (0.37 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30) as a yellow solid (0.34 g, 66%). From this reaction, (*Z*)-*N,N*-dimethyl-3-[(2-(trifluoromethyl)phenyl]-amino)acrylamide **7ed** was also isolated as a white solid (0.05 g, 10%).

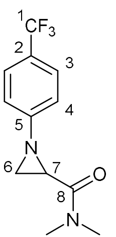


4ed: R_f = 0.23 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H, H^3), 7.42 (t, *J* = 8.0 Hz, 1H, H^5), 7.09 (t, *J* = 8.0 Hz, 1H, H^4), 7.01 (d, *J* = 8.0 Hz, 1H, H^6), 3.20 (br s, 4H, H^8 and H^{10}), 3.03 (s, 3H, $H^{10'}$), 2.76-2.72 (m, 1H, H^7), 2.45 (br d, *J* = 6.5 Hz, 1H, H^7); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 167.5 (C^9), 149.8 (C^1), 132.6 (C^5), 127.0 (q, *J* = 5 Hz, C^3), 124.1 (q, *J* = 274 Hz, C^{11}), 122.6 (C^4), 122.3 (q, *J* = 31 Hz, C^2), 121.3 (C^6), 37.1 (C^8), 36.8 (C^{10}), 36.2 ($C^{10'}$), 33.6 (C^7); ^{19}F NMR (377 MHz, $CDCl_3$): δ -60.5; IR: ν_{max} (cm^{-1}) 2991, 2935, 1645 (s, C=O), 1603, 1578, 1488, 1451, 1313, 1107, 1053, 1034, 1007, 959, 902, 756, 645; HRMS (ESI) m/z: Calcd for $C_{12}H_{14}N_2OF_3$ $[M+H]^+$ 259.1058; Found 259.1062.



7ed: Mp = 78.1-79.3 °C; R_f = 0.33 (petroleum ether/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.51 (d, *J* = 10.5 Hz, 1H, NH), 7.55 (d, *J* = 7.5 Hz, 1H, H^3), 7.45 (t, *J* = 7.5 Hz, 1H, H^5), 7.16 (d, *J* = 8.5 Hz, 1H, H^7), 7.13 (d, *J* = 7.5 Hz, 1H, H^6), 7.00 (t, *J* = 7.5 Hz, 1H, H^4), 5.18 (d, *J* = 8.5 Hz, 1H, H^8), 3.03 (s, 1H, 6H, H^{10}); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.0 (C^9), 140.0 (C^5), 139.7 (C^1), 133.1 (C^7), 127.0 (q, *J* = 5 Hz, C^3), 121.9 (q, *J* = 196 Hz, C^{11}), 120.9 (C^4), 117.3 (q, *J* = 30 Hz, C^2), 115.0 (C^6), 89.6 (C^8), 37.5 (C^{10}), 35.3 (C^{10}); ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.1; IR: ν_{max} (cm^{-1}) 3200 (br s, NH), 2929, 1632 (s, C=O), 1575, 1476, 1457, 1371, 1263, 1106, 1089, 1032, 761, 701, 684, 643; HRMS (ESI) m/z: Calcd for $C_{12}H_{14}N_2OF_3$ $[M+H]^+$ 259.1058; Found 259.1062.

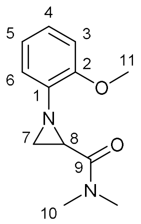
_N,N_-Dimethyl-1-[4-(trifluoromethyl)phenyl]aziridine-2-carboxamide (4fd)



Following the general procedure at 80 °C for 16 h from **1f** (0.37 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.42 mL, 4.0 mmol), the title compound was isolated as a yellow solid (0.36 g, 70%) after column chromatography (petroleum ether/EtOAc, 80:20→70:30) and trituration (petroleum ether/Et_2O, 80:20) at -18°C.

Mp = 104.8-106.3 °C; R_f = 0.36 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.5 Hz, 2H, H^{Ar}), 7.07 (d, *J* = 8.5 Hz, 2H, H^{Ar}), 3.26 (s, 3H, H^9), 3.05 (s, 3H, $H^{9'}$), 3.02 (dd, *J* = 7.0; 3.0 Hz, 1H, H^7), 2.72 (dd, *J* = 3.0; 1.5 Hz, 1H, H^6), 2.35 (dd, *J* = 7.0; 1.5 Hz, 1H, H^6); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 167.5 (C^8), 156.2 (C^5), 126.3 (q, *J* = 4 Hz, C^3), 124.9 (q, *J* = 32 Hz, C^2), 124.3 (q, *J* = 272 Hz, C^1), 120.7 (C^4), 36.94 (C^7), 36.91 (C^9), 36.1 ($C^{9'}$), 33.3 (C^6); ^{19}F NMR (377 MHz, $CDCl_3$): δ -61.9; IR: ν_{max} (cm^{-1}) 2933, 1646 (s, C=O), 1610, 1515, 1506, 1319, 1367, 1286, 1159, 1106, 1092, 1064, 1021, 840, 730, 592, 521, 506, 404; HRMS (ESI) m/z: Calcd for $C_{12}H_{14}N_2OF_3$ $[M+H]^+$ 259.1058; Found 259.1063.

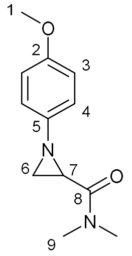
1-(2-Methoxyphenyl)-*N,N*-dimethylaziridine-2-carboxamide (4gd)



Following the general procedure at 80 °C for 16 h from **1g** (0.30 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30) as a yellow oil (0.40 g, 90%).

R_f = 0.23 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (td, *J* = 7.5; 1.5 Hz, 1H, H^{Ar}), 6.91-6.82 (m, 3H, H^{Ar}), 3.84 (s, 3H, H^{11}), 3.25 (s, 3H, H^{10}), 3.03 (s, 3H, $H^{10'}$), 2.91 (dd, *J* = 5.0; 3.0 Hz, 1H, H^8), 2.72 (dd, *J* = 3.0; 1.0 Hz, 1H, H^7), 2.24 (dd, *J* = 5.0; 1.0 Hz, 1H, H^7); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.5 (C^9), 152.1 (C^2), 141.7 (C^1), 123.3 (C^4), 120.7 (C^5), 120.3 (C^6), 111.1 (C^3), 55.5 (C^{11}), 36.9 (C^{10}), 36.3 ($C^{10'}$), 36.1 (C^8), 33.8 (C^7); IR: ν_{max} (cm^{-1}) 2983, 2933, 2832, 1635 (s, C=O), 1589, 1494, 1453, 1436, 1353, 1231, 1177, 1114, 1045, 1021, 744, 614, 478; HRMS (ESI) m/z: Calcd for $C_{12}H_{17}N_2O_2$ $[M+H]^+$ 221.1290; Found 221.1296.

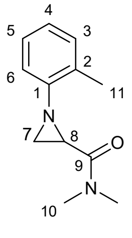
1-(4-Methoxyphenyl)-*N,N*-dimethylaziridine-2-carboxamide (4hd)



Following the general procedure at 80 °C for 16 h from **1h** (1.49 g, 10.0 mmol) and *N,N*-dimethylacrylamide (2.06 mL, 20.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 70:30) as a brown oil (1.94 g, 88%).

R_f = 0.33 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 6.79 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 3.76 (s, 3H, H^1), 3.25 (s, 3H, H^9), 3.03 (s, 3H, $H^{9'}$), 2.89 (dd, *J* = 6.0; 3.0 Hz, 1H, H^7), 2.62 (br s, 1H, H^6), 2.24 (dd, *J* = 6.0; 1.5 Hz, 1H, H^6); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.3 (C^8), 155.5 (C^2), 146.5 (C^5), 121.4 (C^4), 114.2 (C^3), 55.4 (C^1), 37.3 (C^7), 36.9 (C^9), 36.0 ($C^{9'}$), 33.5 (C^6); IR: ν_{max} (cm^{-1}) 2987, 2936, 2832, 1641 (s, C=O), 1502, 1364, 1237, 1187, 1028, 830, 664; HRMS (ESI) m/z: Calcd for $C_{12}H_{17}N_2O_2$ $[M+H]^+$ 221.1290; Found 221.1297.

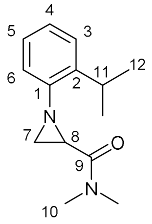
N,N-Dimethyl-1-(*o*-tolyl)aziridine-2-carboxamide (4id)



Following the general procedure at 80 °C for 16 h from **1i** (0.27 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 70:30) as a brown oil (0.30 g, 74%).

R_f = 0.33 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (td, *J* = 8.0; 1.0 Hz, 2H, H^3 and H^5), 6.95 (td, *J* = 7.5; 1.0 Hz, 1H, H^4), 6.83 (d, *J* = 8.0 Hz, 1H, H^6), 3.22 (s, 3H, H^{10}), 3.05 (s, 3H, $H^{10'}$), 2.88 (dd, *J* = 6.5; 3.0 Hz, 1H, H^8), 2.67 (dd, *J* = 3.0; 2.0 Hz, 1H, H^7), 2.32 (s, 3H, H^{11}), 2.28 (dd, *J* = 6.5; 2.0 Hz, 1H, H^7); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.4 (C^9), 150.7 (C^1), 130.7 (C^2), 130.6 (C^3), 126.4 (C^5), 123.0 (C^4), 118.8 (C^6), 36.9 (C^8), 36.9 (C^{10}), 36.1 ($C^{10'}$), 33.8 (C^7), 17.9 (C^{11}); IR: ν_{max} (cm^{-1}) 3021, 2981, 2944, 1643 (s, C=O), 1487, 1355, 1296, 1144, 1107, 908, 767, 723; HRMS (ESI) m/z: Calcd for $C_{12}H_{17}N_2O$ $[M+H]^+$ 205.1391; Found 205.1392.

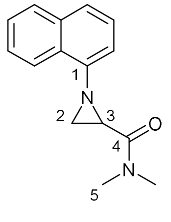
1-(2-Isopropylphenyl)-*N,N*-dimethylaziridine-2-carboxamide (4jd)



Following the general procedure at 80 °C for 16 h from **1j** (0.35 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 100:0→75:25) as a yellow oil (0.33 g, 71%).

R_f= 0.43 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 7.5; 1.5 Hz, 1H, H^{Ar}), 7.11-7.01 (m, 2H, H^{Ar}), 6.83 (dd, *J* = 7.5; 1.5 Hz, 1H, H^{Ar}), 3.47 (sept, *J* = 7.0 Hz, 1H, H^{11}), 3.21 (s, 3H, H^{10}), 3.05 (s, 3H, $H^{10'}$), 2.91 (dd, *J* = 6.5; 3.0 Hz, 1H, H^8), 2.66 (dd, *J* = 3.0; 2.0 Hz, 1H, H^7), 2.29 (dd, *J* = 6.5; 2.0 Hz, 1H, H^7), 1.25 (t, *J* = 6.5 Hz, 6H, H^{12}); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.5 (C^9), 149.3 (C^1), 141.7 (C^2), 126.1 (C^3), 126.1 (C^5) 123.5 (C^4), 119.1 (C^6), 37.3 (C^8), 37.0 (C^{10}), 36.2 ($C^{10'}$), 33.9 (C^7), 26.8 (C^{11}), 23.6 (C^{12}); IR: ν_{max} (cm^{-1}) 3058, 2959, 2929, 2866, 1645 (s, C=O), 1483, 1447, 1353, 1185, 1136, 747; HRMS (ESI) m/z: Calcd for $C_{14}H_{21}N_2O$ $[M+H]^+$ 233.1654; Found 233.1657.

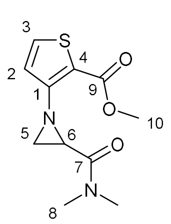
N,N-Dimethyl-1-(naphthalen-1-yl)aziridine-2-carboxamide (4kd)



Following the general procedure at 80 °C for 16 h from **1k** (0.34 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 70:30) as a brown solid (0.45 g, 94%).

Mp = 139.1-143.3 °C; R_f= 0.36 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33-8.31 (m, 1H, H^{Np}), 7.86-7.83 (m, 1H, H^{Np}), 7.57-7.49 (m, 3H, H^{Np}), 7.36 (t, *J* = 7.5 Hz, 1H, H^{Np}), 6.96 (dd, *J* = 7.5; 0.5 Hz, 1H, H^{Np}), 3.2 (s, 3H, H^5), 3.12 (s, 3H, $H^{5'}$), 2.97 (dd, *J* = 6.5; 3.5 Hz, 1H, H^3), 2.85 (dd, *J* = 3.5; 1.5 Hz, 1H, H^2), 2.51 (dd, *J* = 6.5; 1.5 Hz, 1H, H^2); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.3 (C^4), 148.6 (C^1), 134.1 (C^{Np}), 128.2 (CH^{Np}), 128.2 (C^{Np}), 126.2 (CH^{Np}), 125.8 (CH^{Np}), 125.5 (CH^{Np}), 123.6 (CH^{Np}), 122.9 (CH^{Np}), 114.0 (CH^{Np}), 37.83 (C^3), 36.97 (C^5), 36.16 ($C^{5'}$), 33.59 (C^2); IR: ν_{max} (cm^{-1}) 3043, 2984, 2937, 1635 (s, C=O), 1573, 1396, 1358, 1293, 802, 775; HRMS (ESI) m/z: Calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$ 241.1341; Found 241.1343.

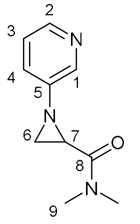
Methyl 3-[2-(dimethylcarbamoyl)aziridin-1-yl]thiophene-2-carboxylate (4ld)



Following the general procedure at 80 °C for 16 h from **1l** (0.37 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→70:30) as a brown oil (0.50 g, 98%).

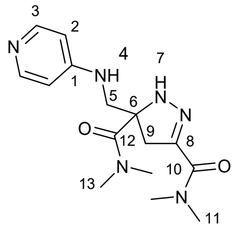
R_f= 0.36 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 5.5 Hz, 1H, H^3), 6.77 (d, *J* = 5.5 Hz, 1H, H^2), 3.81 (s, 3H, H^{10}), 3.23 (s, 3H, H^8), 3.21 (dd, *J* = 6.0; 3.5 Hz, 1H, H^6), 3.05 (s, 3H, $H^{8'}$), 2.77 (dd, *J* = 3.5; 1.5 Hz, 1H, H^5), 2.42 (dd, *J* = 6.0, 1.5 Hz, 1H, H^5); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 167.8 (C^9), 162.1 (C^9), 157.4 (C^1), 130.6 (C^3), 124.0 (C^2), 115.3 (C^4), 51.6 (C^{10}), 38.2 (C^6), 37.1 (C^8), 36.2 ($C^{8'}$), 35.4 (C^5); IR: ν_{max} (cm^{-1}) 3070, 2985, 2946, 1699 (s, C=O), 1645 (s, C=O), 1527, 1438, 1395, 1234, 1148, 1073, 741, 662; HRMS (ESI) m/z: Calcd for $C_{11}H_{15}N_2O_3S$ $[M+H]^+$ 255.0803; Found 255.0799.

N,*N*-Dimethyl-1-(pyridin-3-yl)aziridine-2-carboxamide (4md)



Following the general procedure at 80 °C for 16 h from **1m** (0.24 g, 2.0 mmol) and *N*,*N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated by column chromatograpy (EtOAc/MeOH, 95:5→90:10) as a brown oil (0.32 g, 83%). R$_f$ = 0.21 (EtOAc/MeOH, 90:10). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.33 (br s, 1H, H^1), 8.23 (d, *J* = 4.0 Hz, 1H, H^2), 7.31 (d, *J* = Hz, 1H, H^4), 7.21–7.15 (m, 1H, H^3), 3.26 (s, 3H, H^9), 3.11–3.04 (m, 1H, H^7), 3.02 (s, 3H, H^9), 2.69 (br s, 1H, H^6), 2.34 (d, *J* = 5.9 Hz, 1H, H^6); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 167.1 (C^8), 148.8 (C^5), 143.8 (C^2), 142.7 (C^1), 127.5 (C^4), 123.2 (C^3), 36.6 (C^9), 36.3 (C^9), 35.7 (C^7), 32.7 (C^6); IR: ν$_{max}$ (cm^{-1}) 3027, 2937, 1640 (s, C=O), 1580, 1476, 1297, 1185, 902, 813, 808; HRMS (ESI) m/z: Calcd for $C_{10}H_{14}N_3O$ [M+H]$^+$ 192.1137; Found 192.1130.

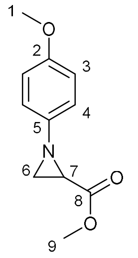
N^3,*N*^{3},*N*^{5},*N*^{5}-Tetramethyl-5-[(pyridin-4-ylamino)methyl]-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxamide (6nd)



Following the general procedure at 80 °C for 16 h from **1n** (0.24 g, 2.0 mmol) and *N,N*-dimethylacrylamide (0.41 mL, 4.0 mmol), the title compound was isolated as a white solid (0.30 g, 48%) by trituration (petroleum ether/Et$_2$O, 80:20→50:50) at room temperature.

Mp = 177–182 °C; R$_f$ = 0.70 (MeOH); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19 (dd, *J* = 4.5; 1.5 Hz, 2H, H^2), 6.94 (br s, 1H, H^7), 6.44 (dd, *J* = 4.5; 1.5 Hz, 2H H^3), 4.87 (dd, *J* = 7.5; 4.5 Hz, 1H, H^4), 3.48–3.39 (m, 2H, H^5), 3.36 (s, 3H. H^{13}), 3.34 (d, *J* = 18.0 Hz, 1H, H^9), 3.16 (d, *J* = 18.0 Hz, 1H, H^9), 3.07 (s, 6H, H^{11}), 3.00 (s, 3H, H$^{13'}$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 170.9 (C^{12}), 162.2 (C^{10}), 153.5 (C^1), 150.2 (C^2), 147.0 (C^6), 107.7 (C^3), 69.3 (C^8), 47.9 (C^5), 41.8 (C^9), 38.7 (C^{13}), 38.1 (C^{11}), 37.3 (C$^{11'}$), 36.5 (C$^{13'}$); IR: ν$_{max}$ (cm^{-1}) 3332 (s, NH), 3035, 2929, 2825, 1612 (s, C=O), 1512, 1505, 1416, 1398, 1261, 1083, 1049, 985, 820, 620, 533, 490; HRMS (ESI) m/z: Calcd for $C_{15}H_{23}N_6O_2$ [M+H]$^+$ 319.1882; Found 319.1872.

Methyl 1-(4-methoxyphenyl)aziridine-2-carboxylate (4ha)



Following the general procedure at 80 °C for 16 h from **1h** (0.75 g, 5.0 mmol) and methyl acrylate (0.90 mL, 10.0 mmol), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 90:10→80:20) as a yellow solid (0.72 g, 90%).

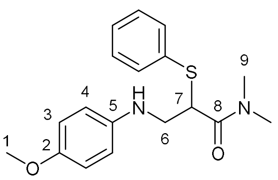
Mp = 54.9–56.5 °C; R$_f$ = 0.63 (EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 (d, *J* = 9.0 Hz, 2H, H^{Ar}) 6.79 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 3.81 (s, 3H, H^1), 3.76 (s, 3H, H^9), 2.74 (dd, *J* = 5.5; 3.0 Hz, 1H, H^7), 2.63 (dd, *J* = 3.0; 1.5 Hz, 1H, H^6), 2.27 (dd, *J* = 5.5; 1.5 Hz, 1H, H^6); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 170.7 (C^8), 155.8 (C^2), 145.7 (C^5), 121.4 (C^4), 114.3 (C^3), 55.5 (C^1), 52.5 (C^9), 37.8 (C^7), 34.1 (C^6); IR: ν$_{max}$ (cm^{-1}) 3034, 2993, 2951, 2832, 1742 (s, C=O), 1504 (s, C=O), 1436, 1457, 1277, 1237, 1200, 1109, 1073, 1029, 909, 829, 769, 547, 520; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}NO_3$ [M+H]$^+$ 208.0974; Found 208.0973.

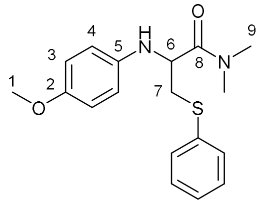
4. Reactivity of Aryl Aziridines

General procedure for the reactions with nucleophiles: Aziridine **4hd** and the chosen nucleophile were stirred neat at room temperature for 18 h, unless stated otherwise. The obtained mixture was then purified by column chromatography (the reaction crude was dry-loaded onto stationary phase).

3-[(4-Methoxyphenyl)amino]-*N*,*N*-dimethyl-2-(phenylthio)propenamide (8A) &
2-[(4-methoxyphenyl)amino]-*N*,*N*-dimethyl-3-(phenylthio)propanamide (9A)

Following the general procedure from **4hd** (0.44 g, 2.0 mmol) and thiophenol (14.40 mL, 14.0 mmol), the title compounds were isolated by column chromatography (petroleum ether/EtOAc, 70:30→0:100) as a white solid (0.65 g, 99%) as a 80:20 mixture of regioisomers.





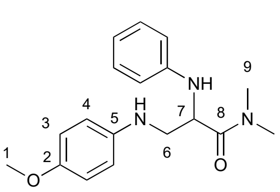
R$_f$ = 0.33 (petroleum ether/EtOAc, 1:1); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 171.6 (**9A**-C^8), 169.4 (**8A**-C^8), 152.9 (**9A**-C^2), 152.2 (**8A**-C^2), 141.2 (**8A**-C^5), 140.1 (**9A**-C^5), 135.4, 133.9, 131.9, 129.7, 129.0, 128.9, 128.5, 126.5, 115.8, 114.8, 114.3, 55.7 (**8A**-C^1), 55.6 (**9A**-C^1), 54.2 (**9A**-C^6), 46.4 (**8A**-C^7), 45.8 (**8A**-C^6), 37.4 (**8A**-C^9), 37.2 (**9A**-C^9), 36.0 (**8A**-C$^{9'}$), 35.8 (**9A**-C$^{9'}$). IR: ν$_{max}$ (cm^{-1}) 3332 (br s, NH), 2981, 2929, 2847, 2821, 1621 (s, C=O), 1505, 1345, 1230, 1177, 1080, 1036, 820, 741, 618; HRMS (ESI) m/z: Calcd for $C_{18}H_{23}N_2O_2S$ $[M + H]^+$ 331.1480; Found 331.1472.

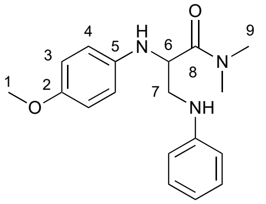
8A: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.48–7.46 (m, 2H, H^{Ar}), 7.35–7.29 (m, 3H, H^{Ar}), 6.75–6.70 (m, 2H, H^{Ar}), 6.47 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 4.05 (dd, *J* = 9.0; 5.0 Hz, 1H, H^6), 3.94 (br s, 1H, NH), 3.73 (s, 3H, H^1), 3.67 (dd, *J* = 14.0, 9.0 Hz, 1H, H^7), 3.43 (dd, *J* = 14.0; 5.0 Hz, 1H, H^6), 2.95 (s, 3H, H^9), 2.93 (s, 3H, H$^{9'}$).

9A: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41–7.37 (m, 3H, H$^{Ar'}$), 7.25–7.21 (m, 2H, H^{Ar}), 6.75–6.70 (m, 2H, H^{Ar}), 6.54 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 4.45–4.37 (br m, 1H, H^6), 4.22–4.16 (br, 1H, NH), 3.74 (s, 3H, H^1), 3.25 (d, *J* = 8.0 Hz, 2H, H^7), 2.96 (s, 3H, H^9), 2.88 (s, 3H, H$^{9'}$).

3-[(4-Methoxyphenyl)amino]-*N*,*N*-dimethyl-2-(phenylamino)propenamide (8B) &
2-[(4-methoxyphenyl)amino]-*N*,*N*-dimethyl-3-(phenylamino)propanamide (9B)

Following the general procedure neat at room temperature for 48 h from **4hd** (0.22 g, 1.0 mmol), in basified silica (500 mg, 2% w/w aniline) the title compounds were isolated by column chromatography (petroleum ether/EtOAc, 80:20→50:50) as a light brown oil (0.23 g, 75%).

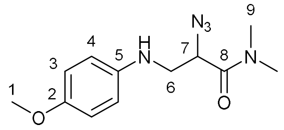


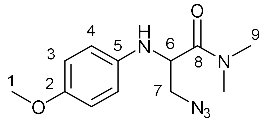


R$_f$ = 0.23 (petroleum ether/EtOAc, 1:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18–7.14 (m, H^{Ar}), 6.79–6.73 (m, H^{Ar}), 6.65–6.59 (m, H^{Ar}), 4.57 (br t, *J* = 5.3 Hz, 1H, **8B**-H^7), 4.47 (t, *J* = 6.0 Hz, 1H, **9B**-H^6), 3.73 (s, 3H, **8B**-H^1), 3.72 (s, 3H, **9B**-H^1), 3.51–3.47 (m, 1H, **9B**-H^7), 3.46 (dd, *J* = 12.5; 5.3 Hz, 1H, **8B**-H^6), 3.28–3.22 (m, **8B**-H$^{6'}$ + **9B**-H$^{7'}$), 3.03 (s, 3H, **8B**-H^9), 3.01 (s, 3H, **9B**-H^9), 2.94 (s, 3H, **8B**-H$^{9'}$), 2.93 (s, 3H, **9B**-H$^{9'}$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 171.9 (C^8), 171.7 (**9B**-C^8), 153.0 (**9B**-C^2), 152.3 (**8B**-C^2), 147.1 (**8B**-C^5), 147.7 (**9B**-C^5), 141.7, 141.0, 129.3, 129.2, 118.5, 117.8, 116.1, 114.8, 114.6, 114.0, 113.1, 55.6 (**8B**-C^1), 55.5 (**9B**-C^1), 54.7 (**9B**-C^6), 53.2 (**8B**-C^7), 46.9 (**8B**-C^6), 45.8 (**9B**-C^7), 36.9 (C^9), 35.7 (C$^{9'}$); IR: ν_{max} (cm^{-1}) 3343 (br s, NH), 2996, 2929, 2829, 1632 (s, C=O), 1599, 1505, 1397, 1312, 1230, 1114, 1032, 820, 745, 693, 506; HRMS (ESI) m/z: Calcd for $C_{18}H_{24}N_3O_2$ [M + H]$^+$ 314.1869; Found 314.1859.

2-Azido-3-[(4-methoxyphenyl)amino]-*N*,*N*-dimethylpropanamide (8C) & 3-azido-2-[(4-ethoxyphenyl)amino]-*N*,*N*-dimethylpropanamide (9C)

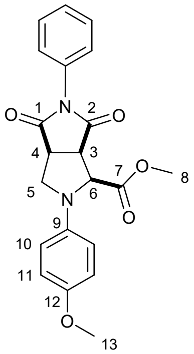
Following the general procedure at reflux for 18 h from **4hd** (0.44 g, 2.0 mmol) and trimethylsilyl azide (0.53 g, 4.0 mmol, 2.0 equiv.) in MeCN (4.0 mL), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 70:30) as a 82:18 mixture of regioisomers as a light brown oil (0.20 g, 37%).



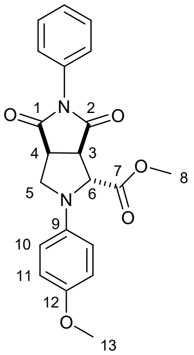


R$_f$ = 0.13 (EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.78 (d, *J* = 9.0 Hz, H^{Ar}), 6.66 (d, *J* = 9.0 Hz, 2H, **9C**-H^{Ar}), 6.61 (d, *J* = 9.0 Hz, 2H, **8C**-H^{Ar}), δ 4.40 (t, *J* = 6.5 Hz, 1H, **9C**-H^6), 4.13 (t, *J* = 6.5 Hz, 1H, **8C**-H^7), 3.74 (s, H^1), 3.70–3.61 (m, **8C**-H^6 + **9C**-H^7), 3.55–3.47 (m, **8C**-H^6 + **9C**-H^7), 3.09 (s, 3H, **9C**-H^9), 2.99 (s, 9H, **8C**-H^9 + **9C**-H$^{9'}$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 170.6 (**9C**-C^8), 168.2 (**8C**-C^8), 153.0 (**9C**-C^2), 152.5 (C^2), 140.9 (**8C**-C^5), 140.0 (**9C**-C^5), 114.9 (C^3), 114.3 (C^4), 56.7 (**8C**-C^7), 55.65 (**8C**-C^1), 55.60 (**9C**-C^1), 54.8 (**9C**-C^7), 52.5 (**9C**-C^6), 45.6 (**8C**-C^6), 37.0 (C^9), 35.9 (**9C**-C$^{9'}$), 35.8 (**8C**-C$^{9'}$); IR: ν_{max} (cm^{-1}) 3473 (br w, NH), 2986, 2929, 2832, 2094 (s, N=N=N), 1640 (s, C=O), 1502, 1359, 1423, 1274, 1237, 1185, 1136, 1110, 1028, 831, 745, 656, 536; HRMS (ESI) m/z: Calcd for $C_{12}H_{17}N_2O_2$ [M–N$_3$]$^+$ 221.1290; Found 221.1289.

Methyl-2-(4-methoxyphenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (10)



2,3-***syn***-3,4-***syn*-11**



2,3-***anti***-3,4-***syn*-11**

1-Azido-4-methoxybenzene **1h** (0.30 g, 2.0 mmol, 1.0 equiv.) and methyl acrylate (0.36 g, 4.0 mmol, 2.0 equiv.) were stirred in technical toluene (4.0 mL) at 80 °C in microwave vial for 16 h. The solution was then heated to 145 °C before adding *N*-phenylmaleimide (1.16 g, 6.6 mmol, 3.3 equiv.) and stirred for 24 h. The crude mixture was then cooled to room temperature and concentrated under reduced pressure. The title compound was isolated as a brown oil (0.54 g, 71%) by column chromatography (petroleum ether/EtOAc, 80:20→60:40; the reaction crude was dry loaded onto the stationary phase) as a 53:47 mixture of diastereoisomers.

R$_f$ = 0.46 (petroleum ether/EtOAc, 1:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49–7.20 (m, H^{Ar}), 7.40–7.32 (m, H^{Ar}), 7.29–7.22 (m, H^{Ar}), 6.82 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 6.68 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 4.94 (s, 1H, ***as***-H^6), 4.54 (d, *J* = 9.5 Hz, 1H, ***ss***-H^6), 4.04 (d, *J* = 8.5 Hz, 1H, ***as***-H^3), 3.96 (d, *J* = 9.5 Hz, 1H, ***ss***-H^3), 3.87–3.83 (m, H^4), 3.71 (s, H^{13}), 3.66 (s, H^8), 3.62–3.54 (m, H^5); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 177.3 (CO), 176.6 (CO), 175.8 (CO), 174.8 (CO), 171.3 (CO), 171.0 (CO), 153.6 (C^{Ar}), 153.2 (C^{Ar}), 140.0 (C^{Ar}), 139.5 (C^{Ar}), 131.7 (C^{Ar}), 131.6 (C^{Ar}), 129.19 (CH^{Ar}), 129.15 (CH^{Ar}), 128.8 (CH^{Ar}), 126.5 (CH^{Ar}), 126.3 (CH^{Ar}), 116.4 (CH^{Ar}), 115.7 (CH^{Ar}), 114.82 (CH^{Ar}), 114.78 (CH^{Ar}), 64.2, (C^{6}), 63.5 (C$^{6'}$), 55.54 (C^{13}), 55.52 (C$^{13'}$), 52.5, 52.2, 50.9, 49.0, 47.7, 44.2, 43.6. IR: ν_{max} (cm^{-1}) 2996, 2948, 2832, 1707 (s, C=O), 1509, 1382, 1241, 1155, 1032, 905, 820, 752, 726, 689, 648; HRMS (ESI) m/z: Calcd for $C_{21}H_{21}N_2O_5$ [M + H]$^+$ 381.1450; Found 381.1443.

3-(4-Methoxyphenyl)-*N*,*N*-dimethyl-2-oxazolidone-5-carboxamide (11)

Azide **1h** (0.30 g, 2 mmol) and *N*,*N*-dimethylacrylamide (0.41 mL, 4 mmol) were stirred in technical toluene (4 mL) at 80 °C for 18 h. The reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was introduced in a round bottomed flask fitted with a condenser together with methyl chloroformate (0.23 mL, 3 mmol) and technical acetonitrile (7 mL). The solution was refluxed for 18 h, cooled down to room temperature and concentrated under reduced pressure. The title compound was isolated by column chromatography (petroleum ether/EtOAc, 80:20→50:50) as a white solid (0.47 g, 88%).

Mp = 104.0–105.0 °C; R_f = 0.26 (EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 6.91 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 5.21 (dd, *J* = 9.0; 6.5 Hz, 1H, H^{7}), 4.70 (dd, *J* = 9.0; 6.5 Hz, 1H, H^{8}), 4.00 (t, *J* = 9.0 Hz, 1H, H^{8}), 3.80 (s, 3H, H^{1}), 3.20 (s, 3H, H^{10}), 3.03 (s, 3H, H^{10}); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 165.7 (C^{9}), 156.5 (C^{2}), 153.6 (C^{6}), 130.8 (C^{5}), 120.6 (C^{3}), 114.2 (C^{4}), 69.0 (C^{7}), 55.4 (C^{1}), 46.9 (C^{8}), 37.1 (C^{10}), 36.2 (C^{10}); IR: ν_{max} (cm^{-1}) 3067, 2952, 2832, 1748 (s, C=O), 1647 (s, C=O), 1513, 1401, 1315, 1155, 1121, 1028, 965, 834, 745, 682, 525; HRMS (ESI) m/z Calcd for $C_{13}H_{17}N_2O_4$: [M + H]$^+$ 265.1188; Found 265.1200.

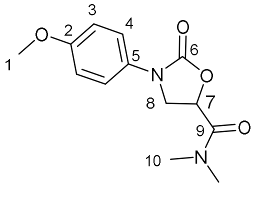
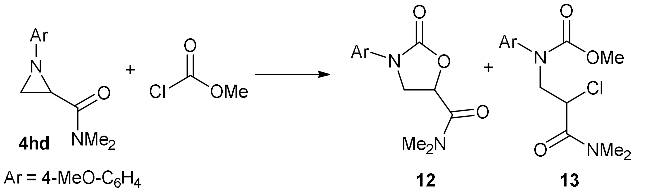


Table S1. Synthesis of 2-oxazolidine **12** from **4hd**.

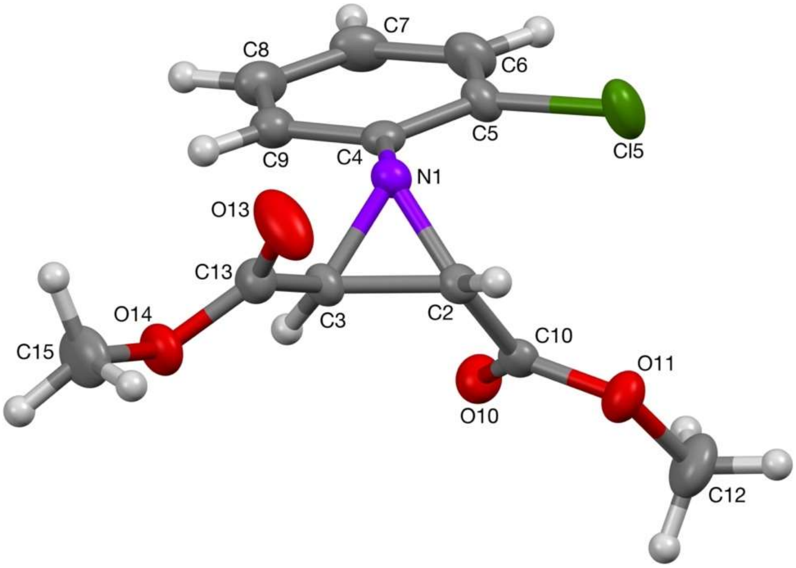


Entry	Conditions	**12** (%)^a	**13** (%)^a
1	Toluene, 80 °C, 18 h	<5	92
2	Toluene, 110 °C, 18 h	15	86
3	MeCN, reflux, 18 h	>95	-

^{a} ^{1}H NMR yields were calculated using 1,3,5-trimethoxybenzene as internal standard and are the average of at least two independent experiments.

5. Crystallographic Data

***trans*-4bo**: $C_{12}H_{12}ClNO_4$, *M* = 269.68, monoclinic, *Cc* (no. 9), *a* = 9.0510(5), *b* = 13.7353(8), *c* = 10.1333(5) Å, β = 98.133(5)°, *V* = 1247.08(11) Å^3, *Z* = 4, D_c = 1.436 g cm^{-3}, μ(Mo-Kα) = 0.312 mm^{-1}, *T* = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 1620 independent measured reflections ($R_{\mathrm{int}} = 0.0179$), F^2 refinement,[17,18] $R_1(\mathrm{obs}) = 0.0295$, $wR_2(\mathrm{all}) = 0.0725$, 1548 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to $\theta_{\mathrm{full}}(25.2°) = 99.3\%$], 165 parameters. The absolute structure of ***trans*-4bo** was determined by use of the Flack parameter [$x = -0.05(6)$]. CCDC 2129406.



6. References

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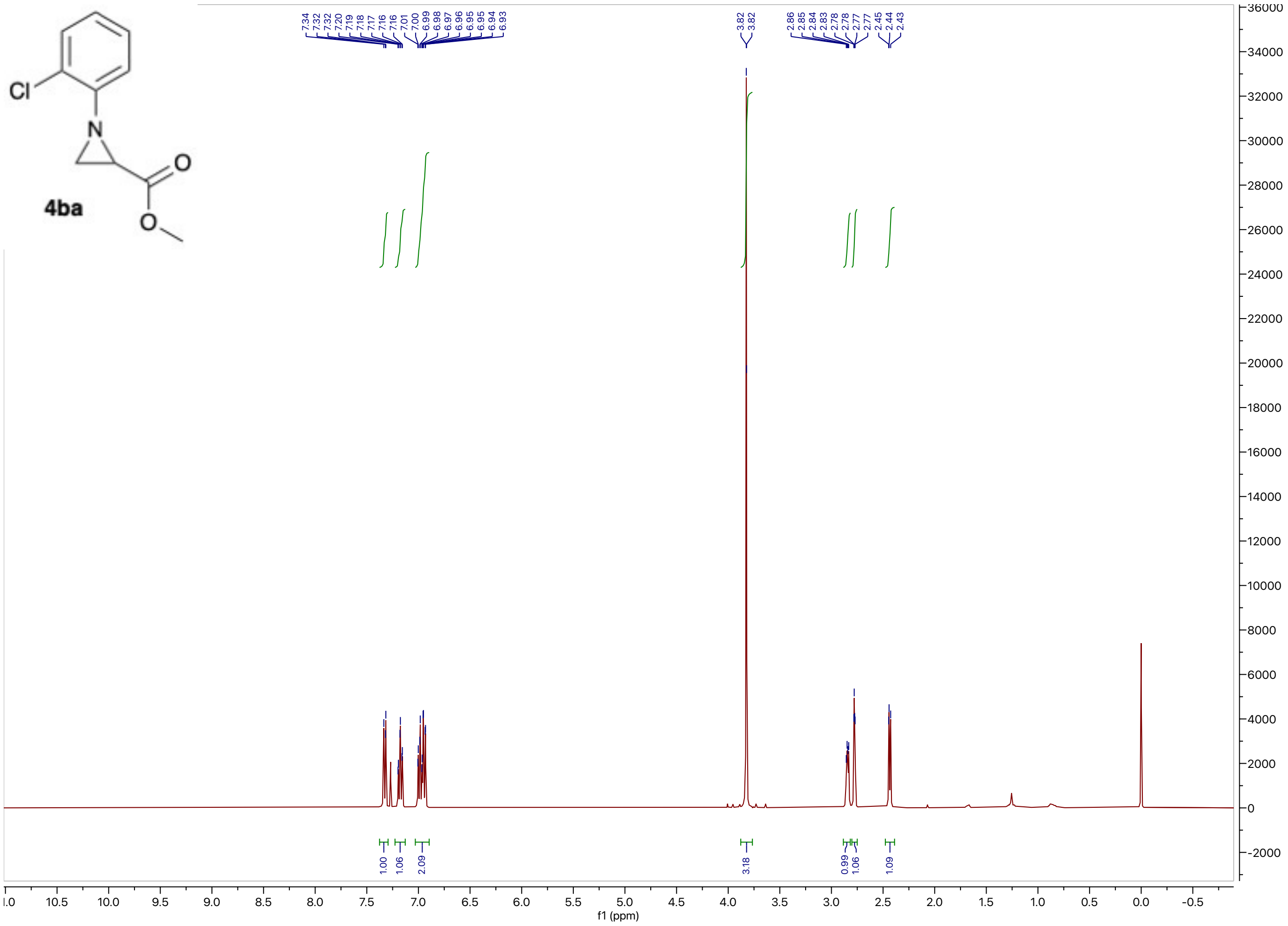
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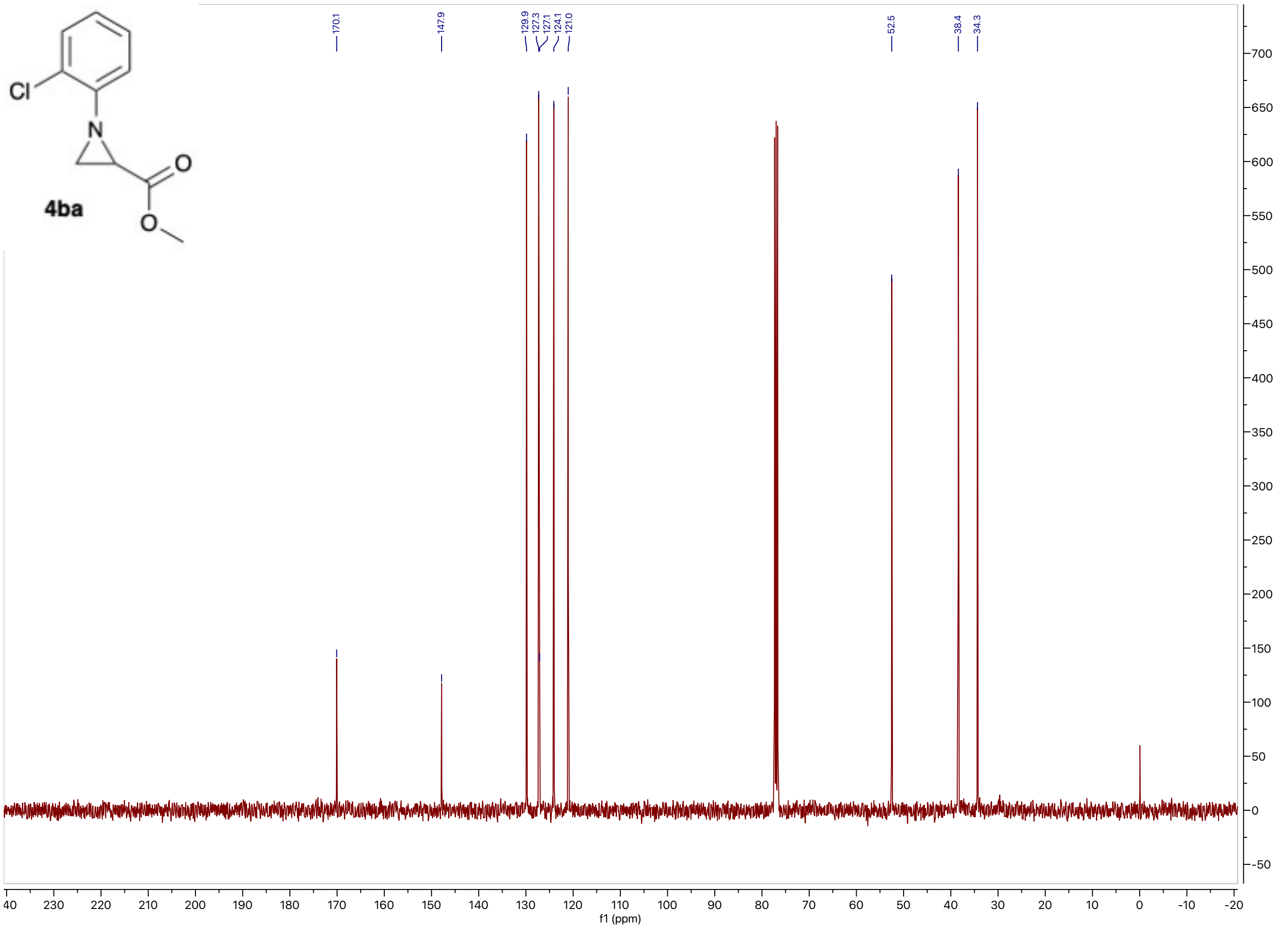
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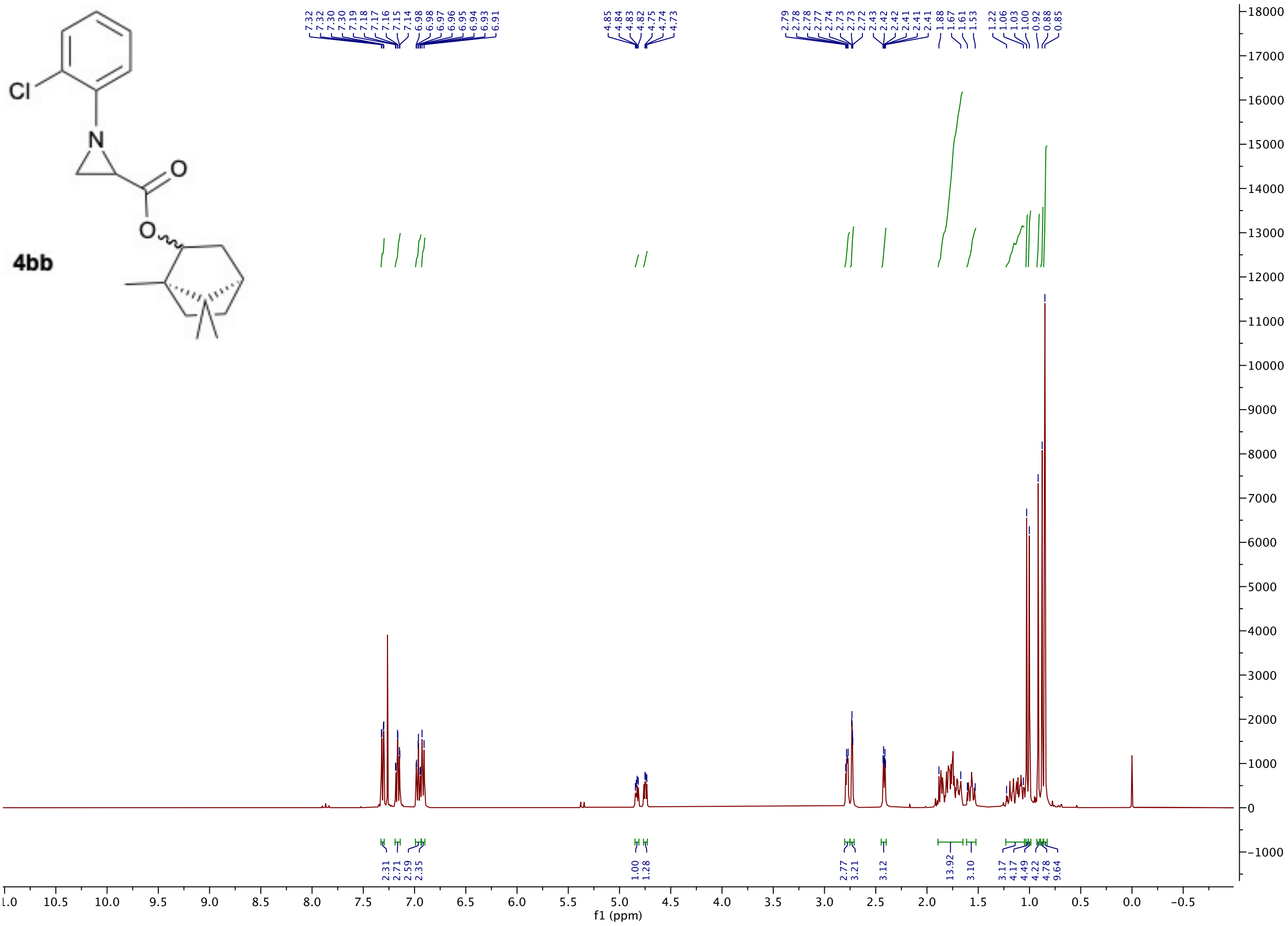
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4.85 4.84 4.83 4.82 4.75 4.74 4.73
2.79 2.78 2.77 2.74 2.73 2.73 2.72 2.43 2.42 2.42 2.41 2.41 2.41 1.88 1.67 1.61 1.53 1.22 1.06 1.03 1.00 0.92 0.88 0.85
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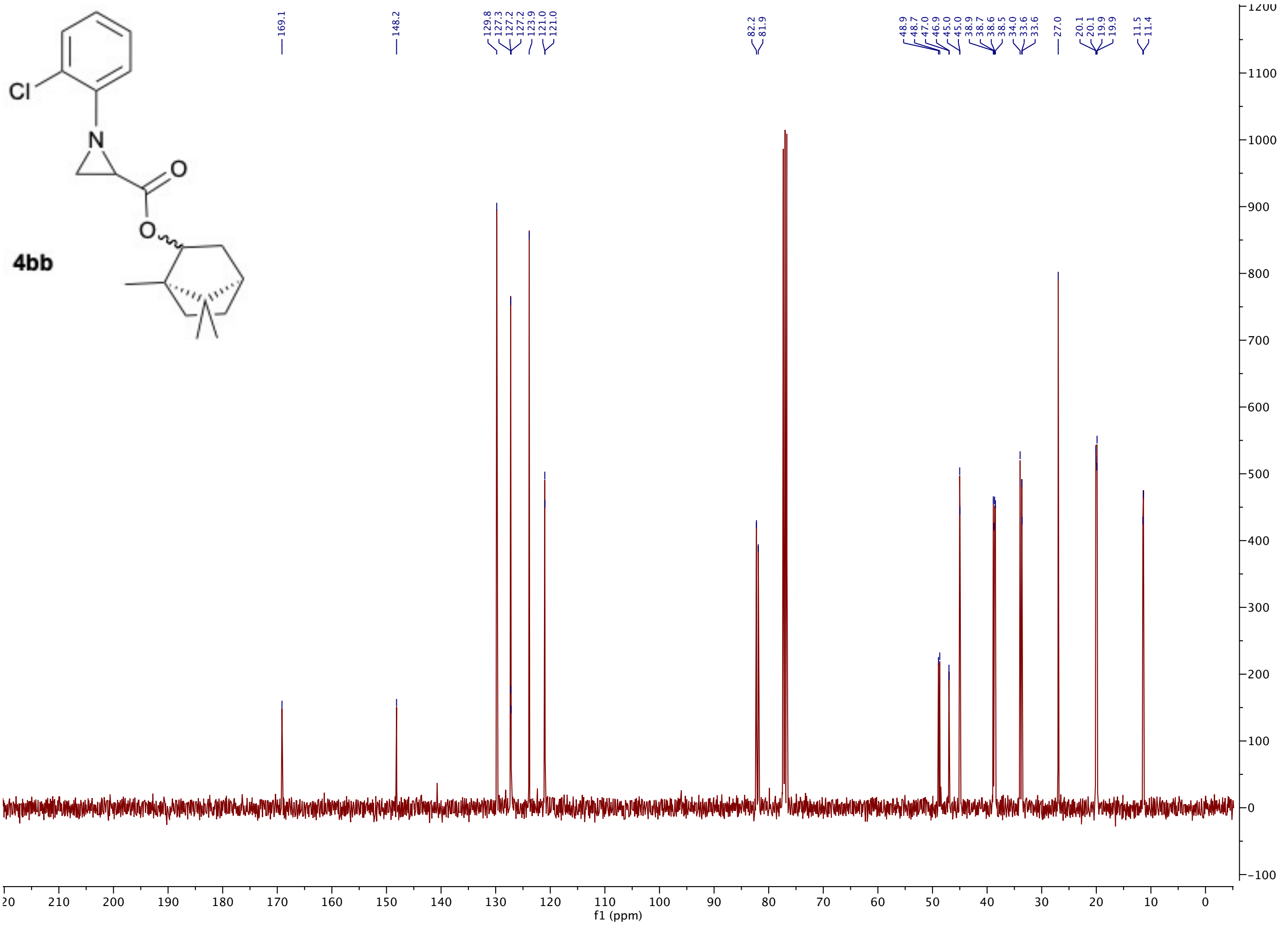
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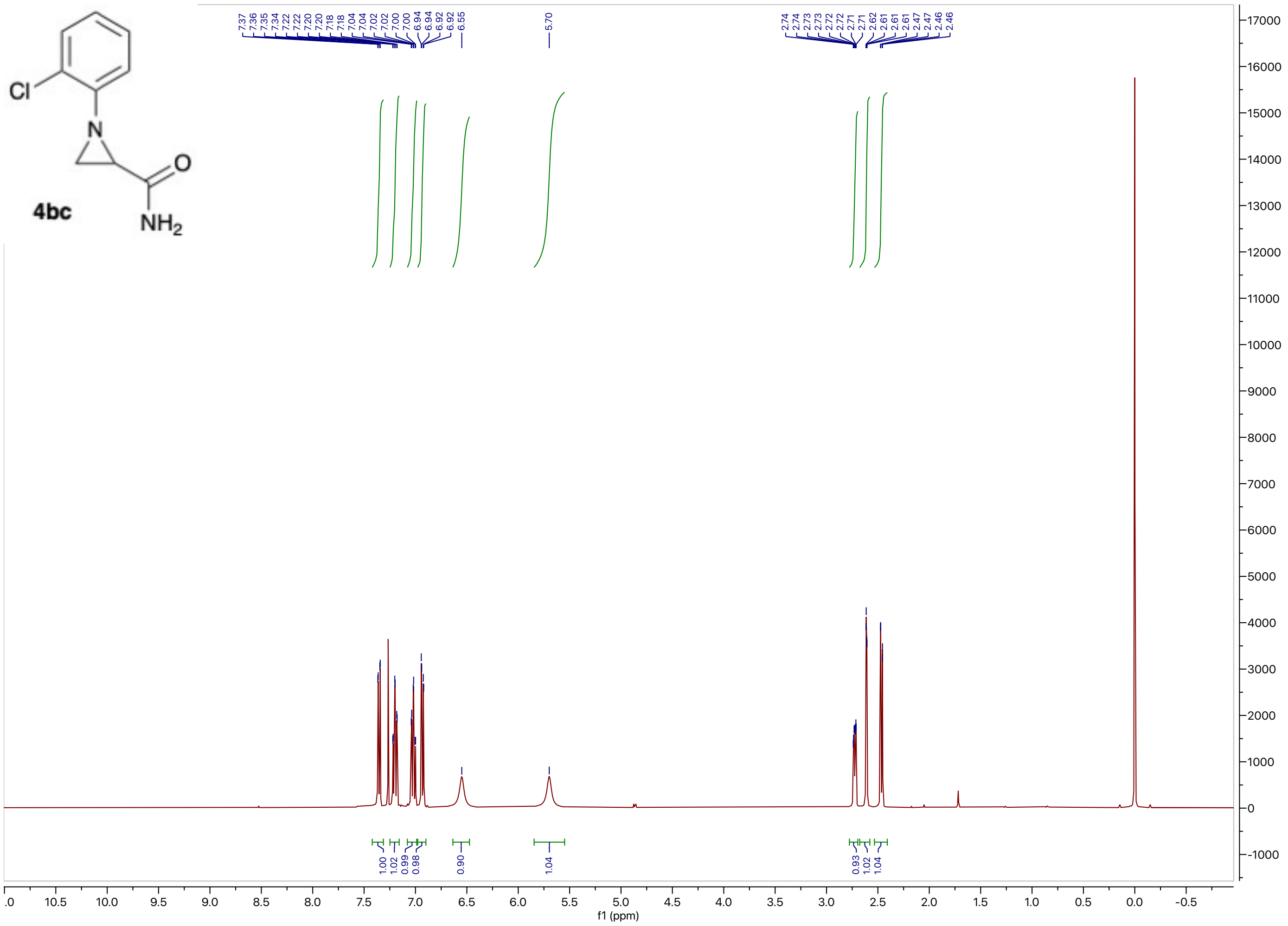
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12000
11000
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6000
5000
4000
3000
2000
1000
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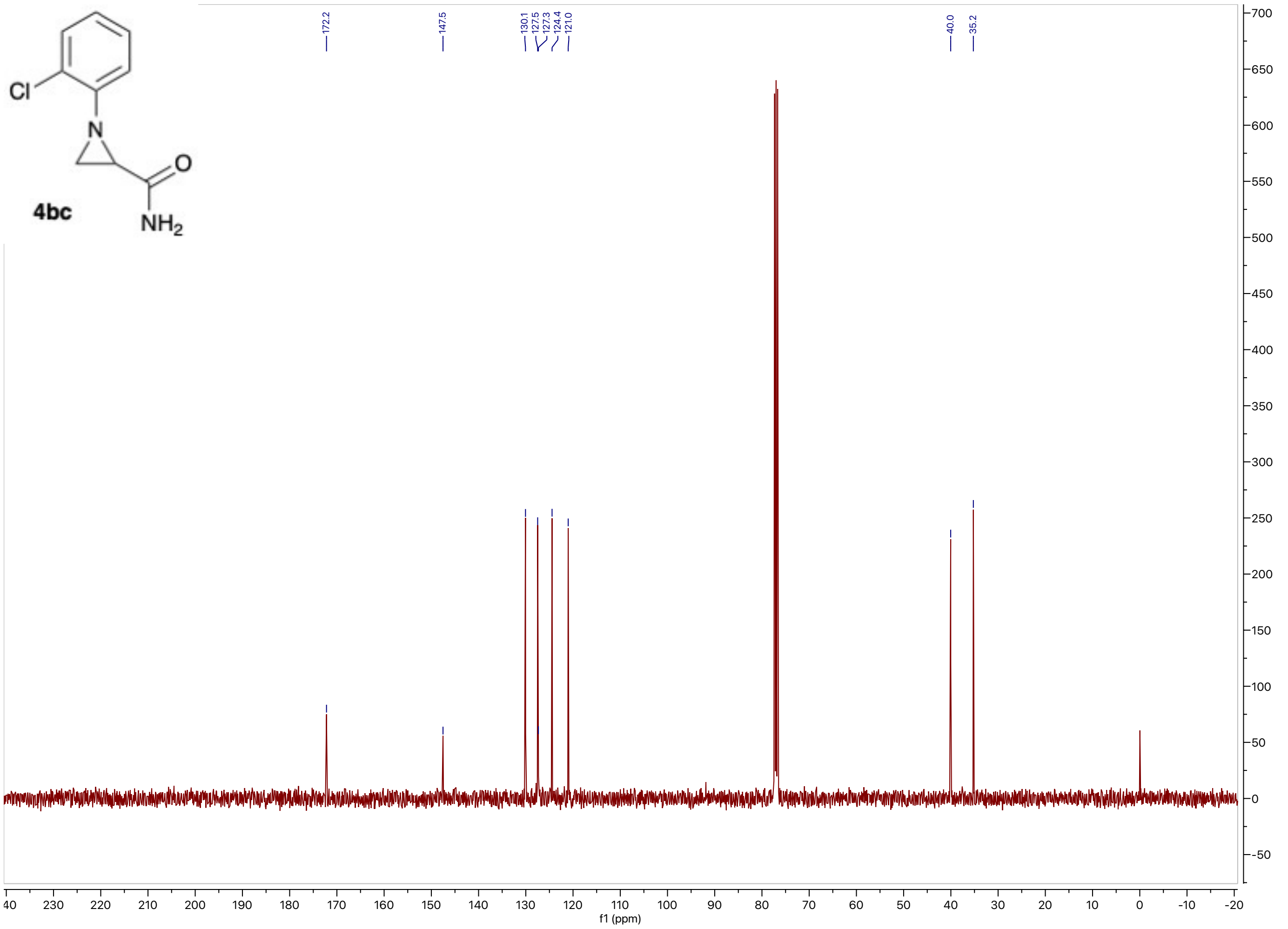
f1 (ppm)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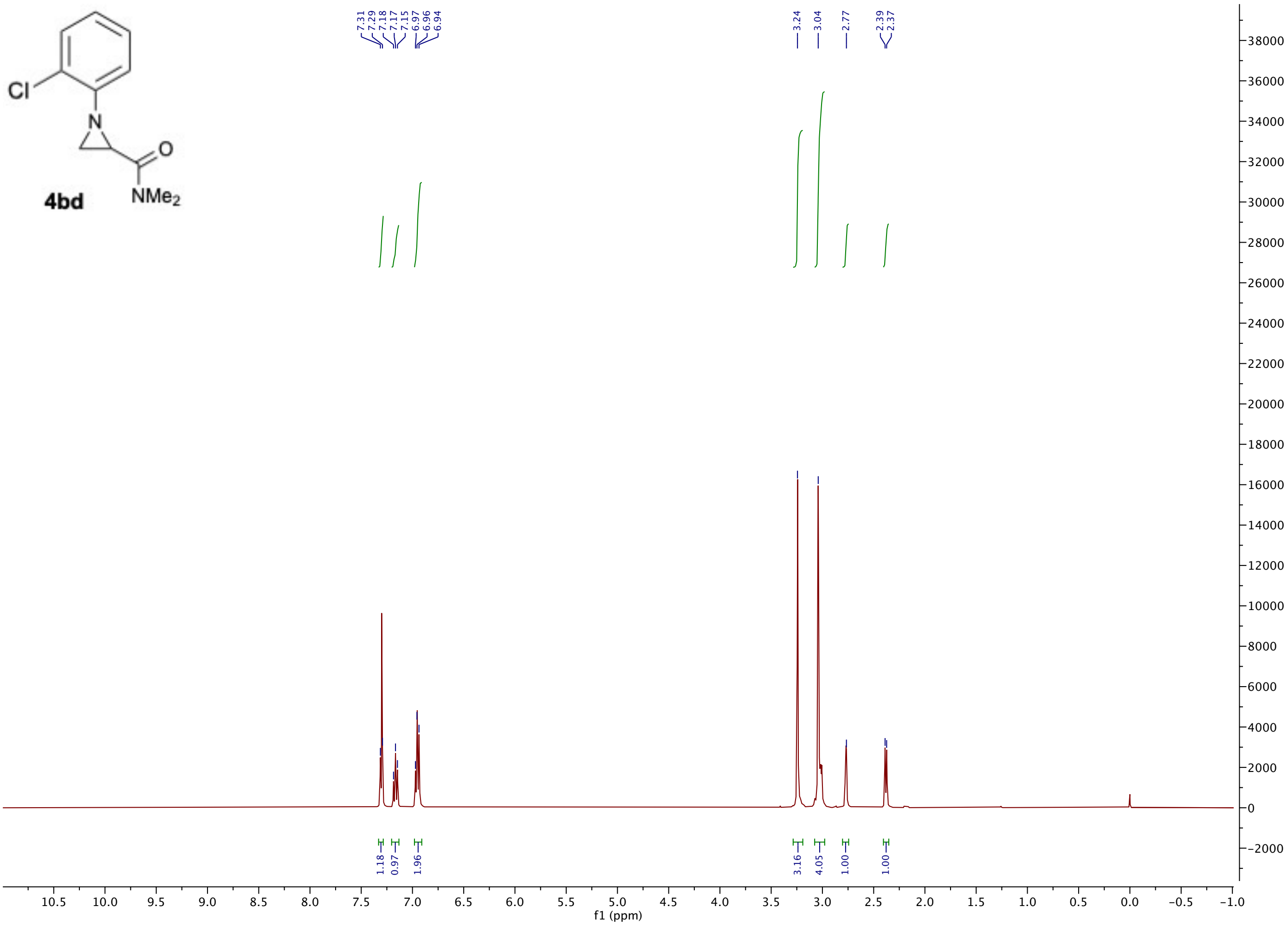
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12000
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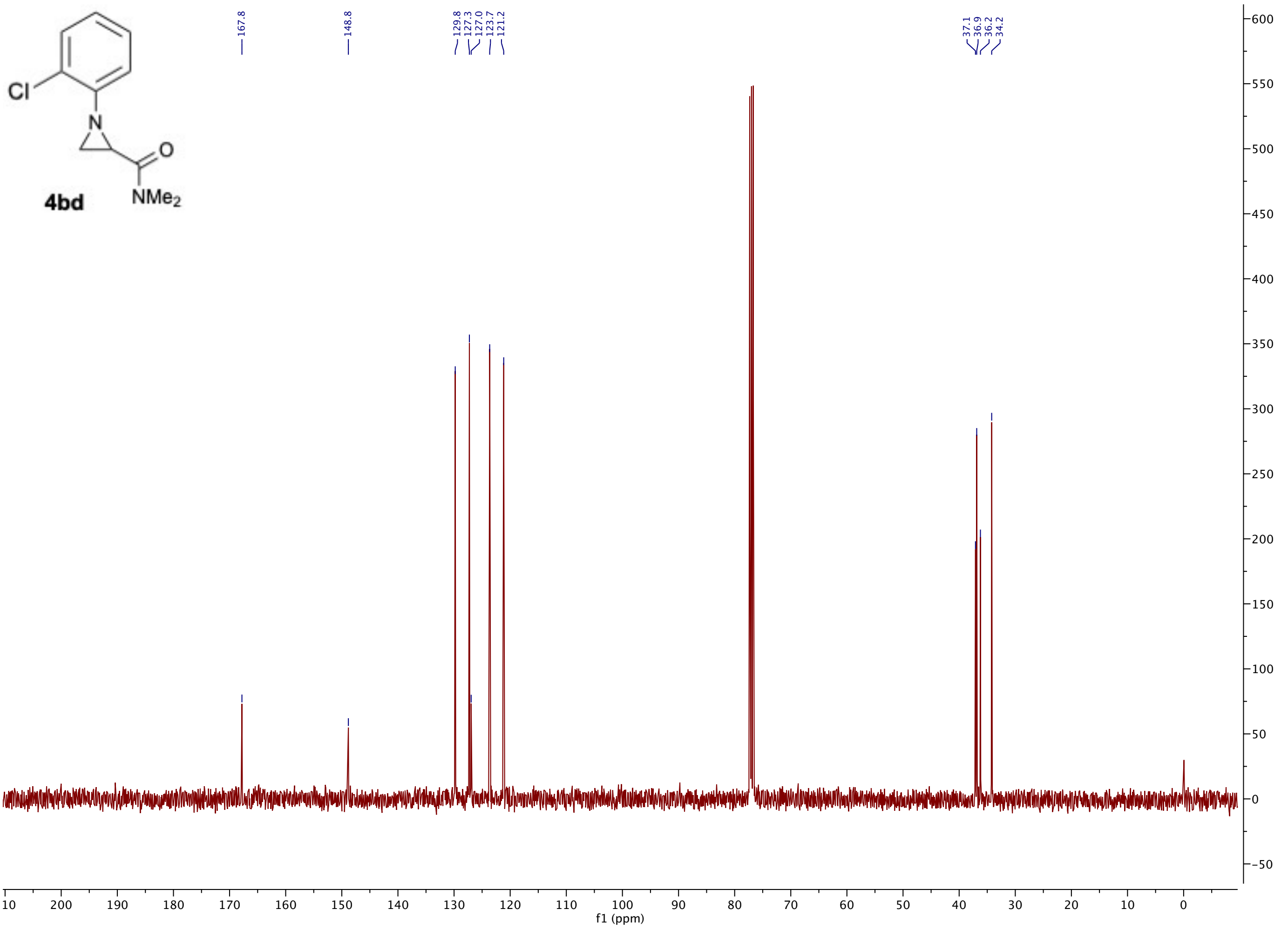
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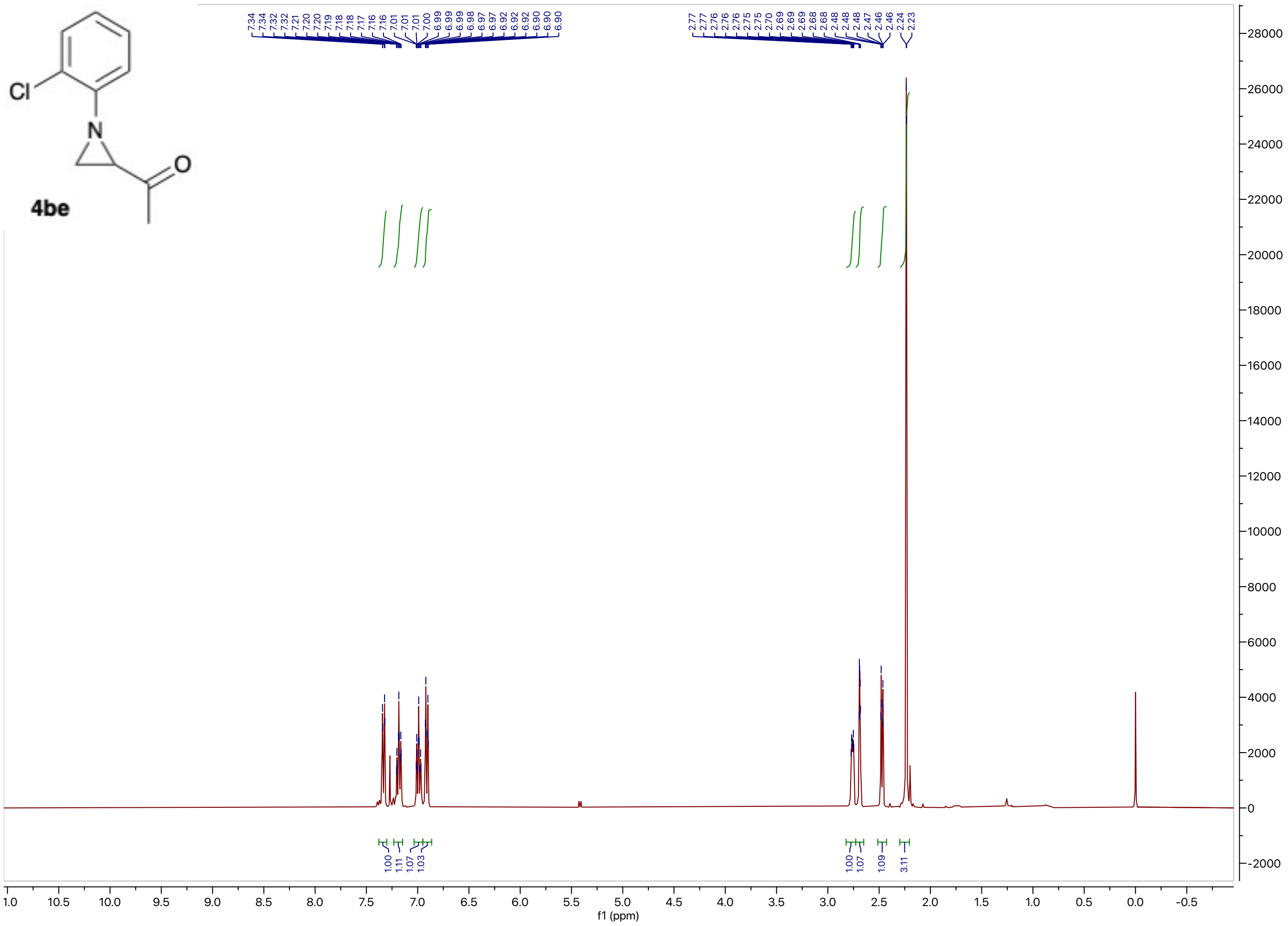
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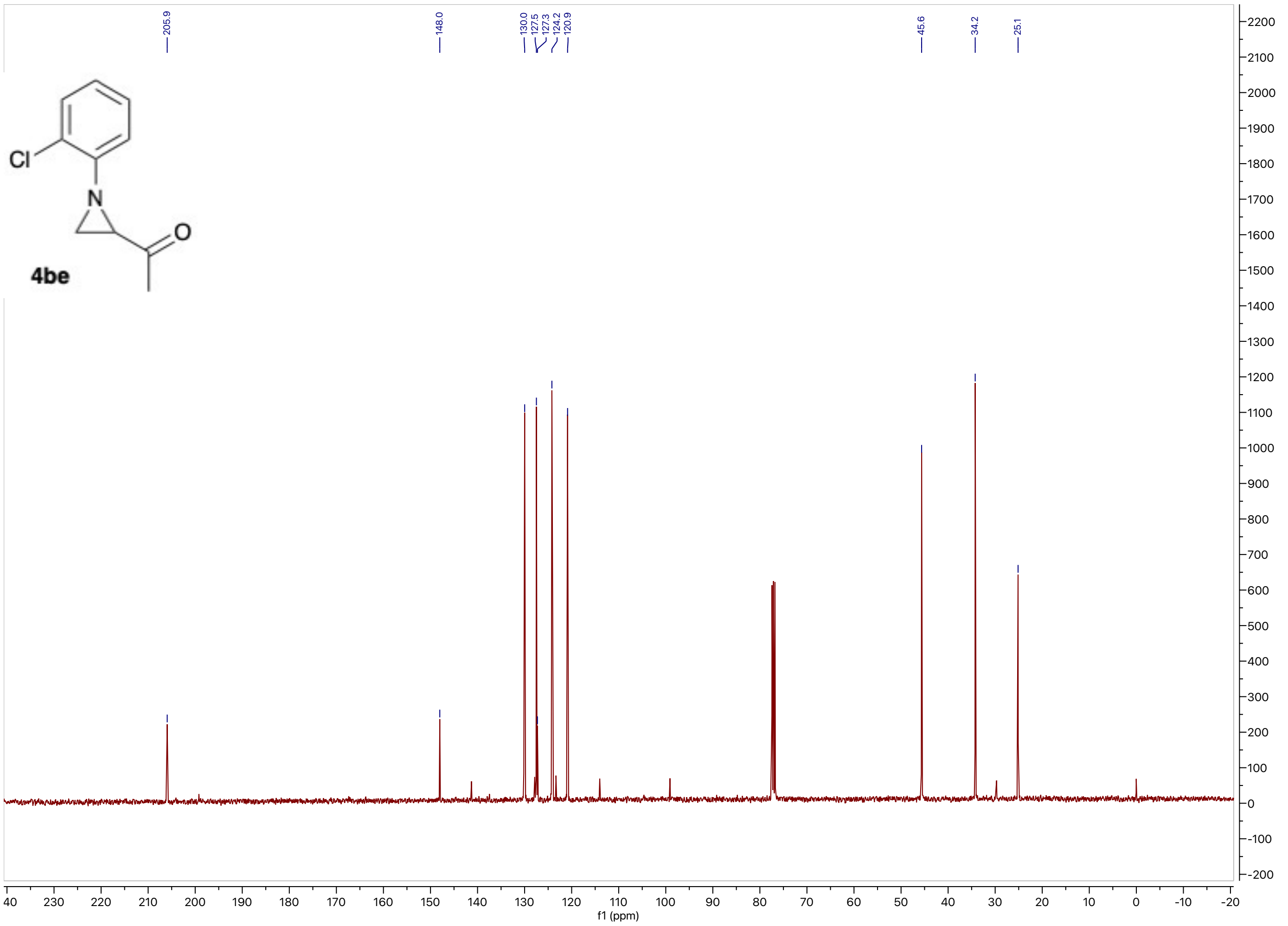
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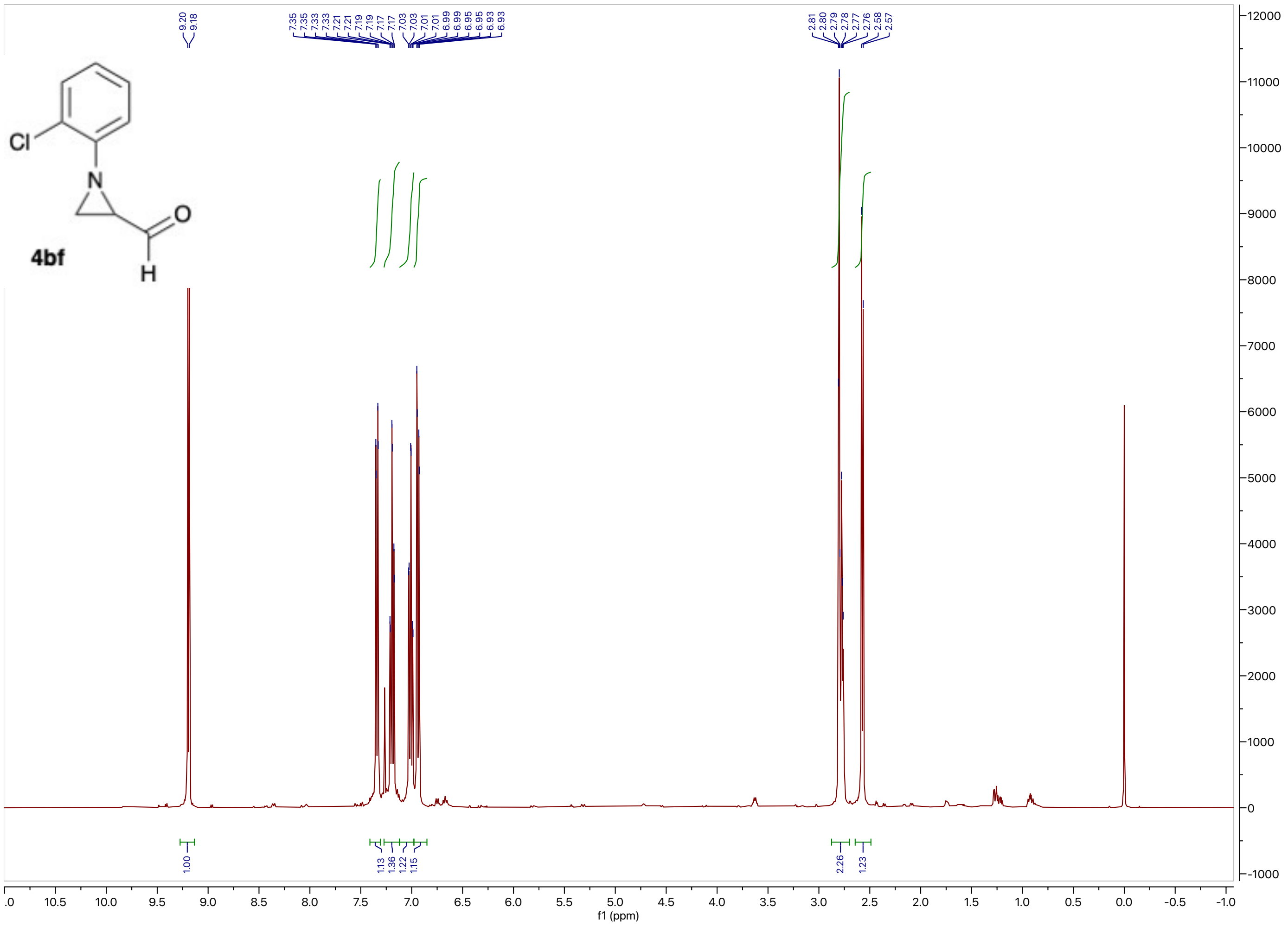
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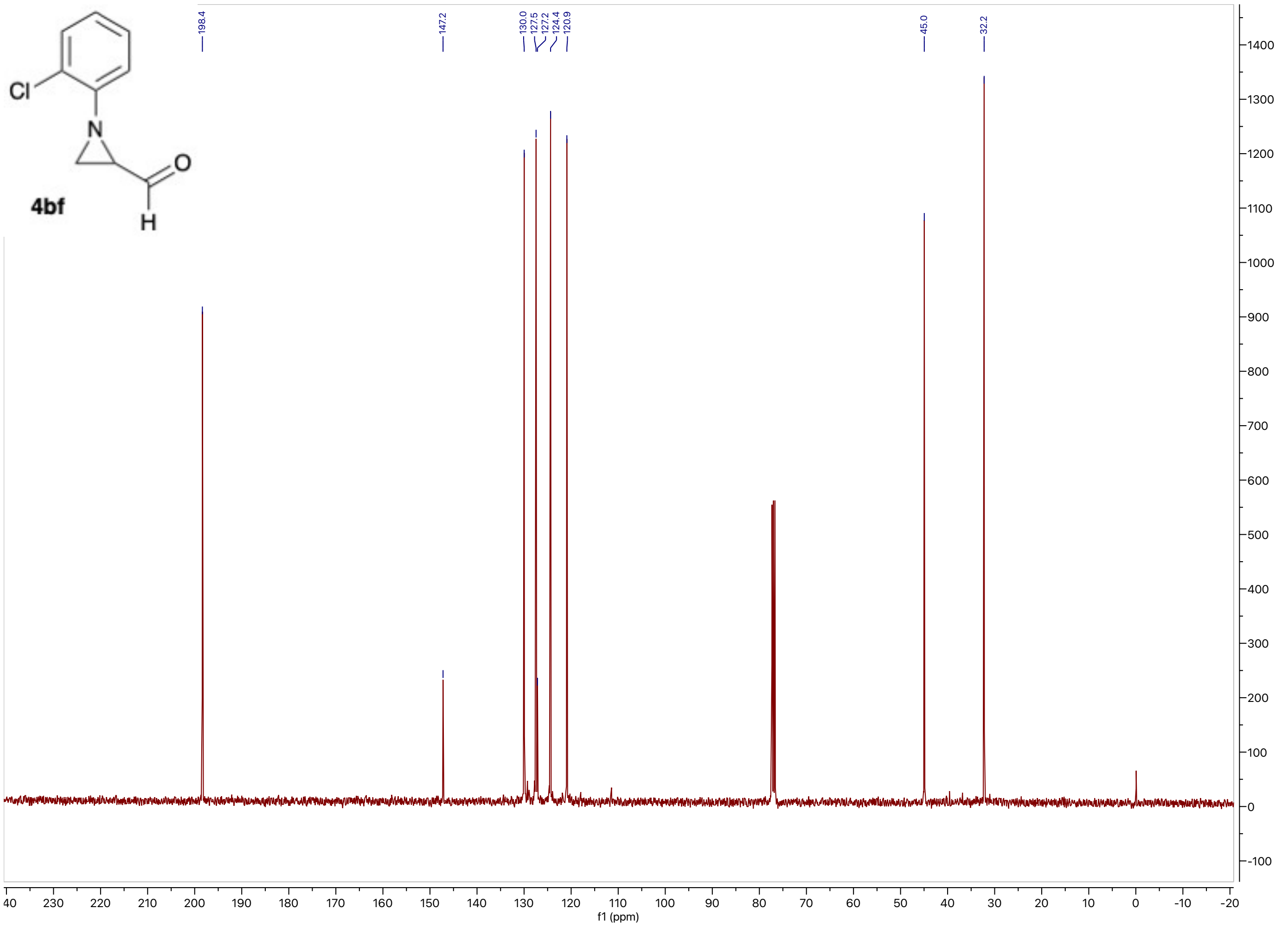
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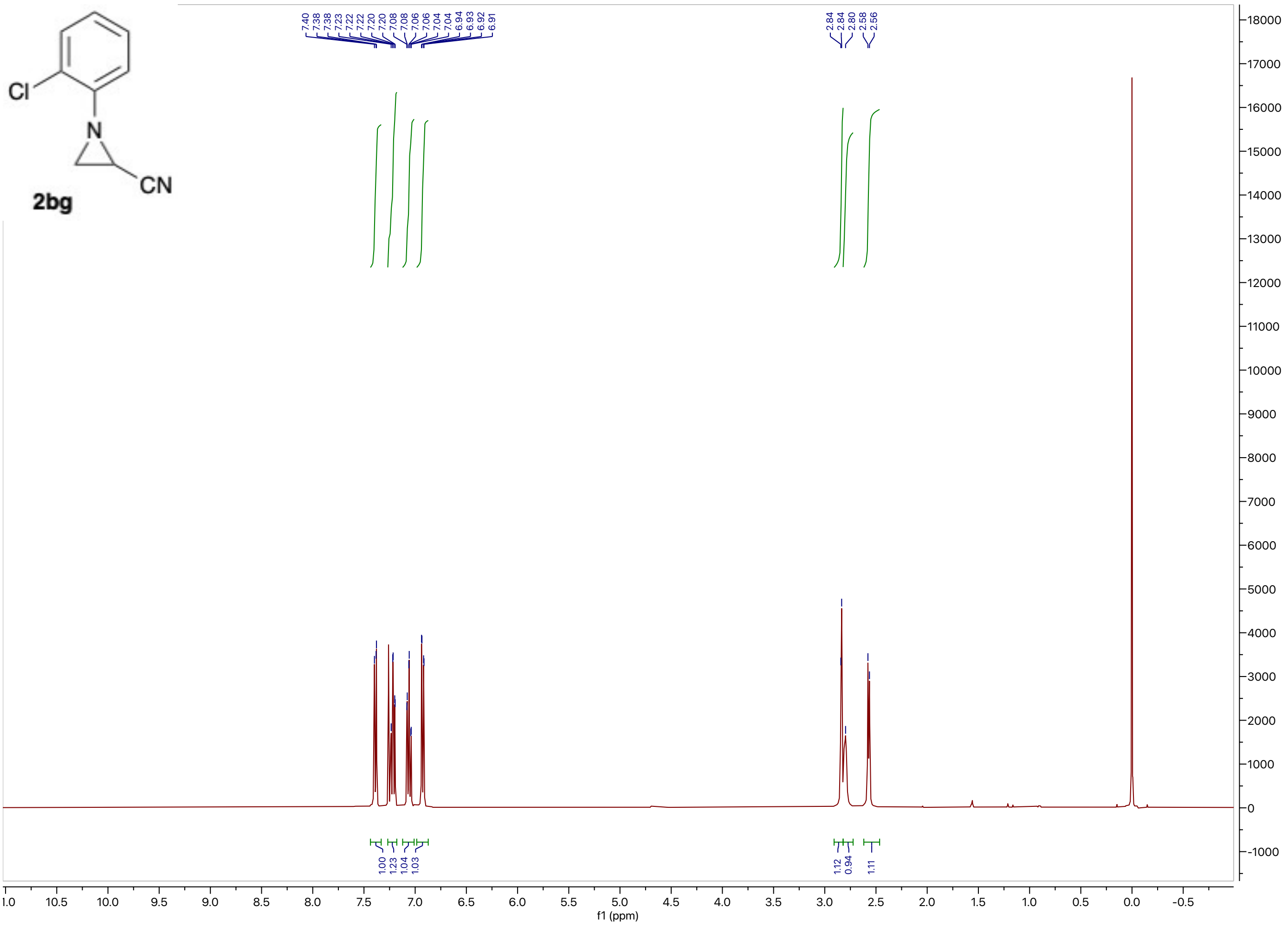
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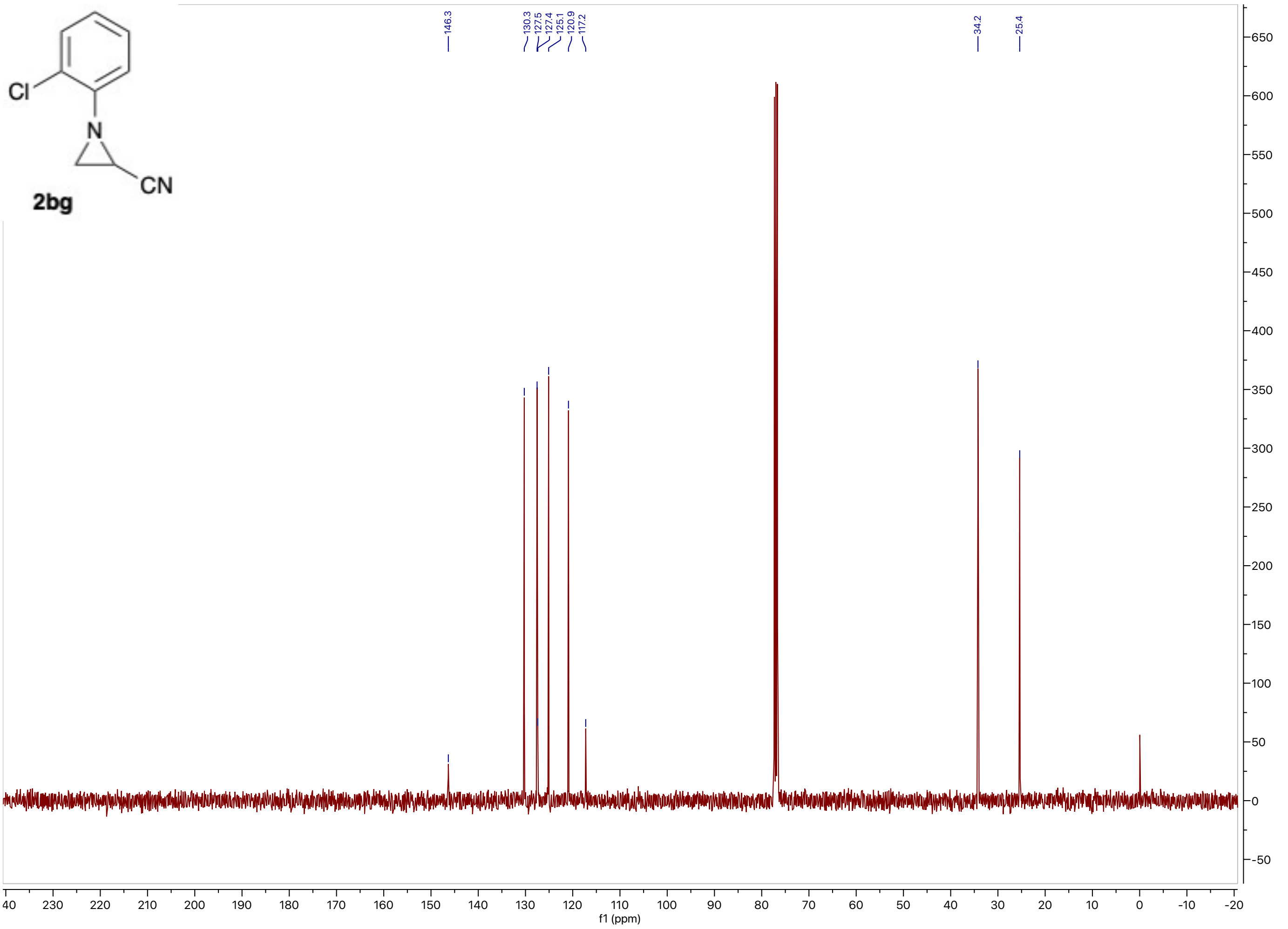
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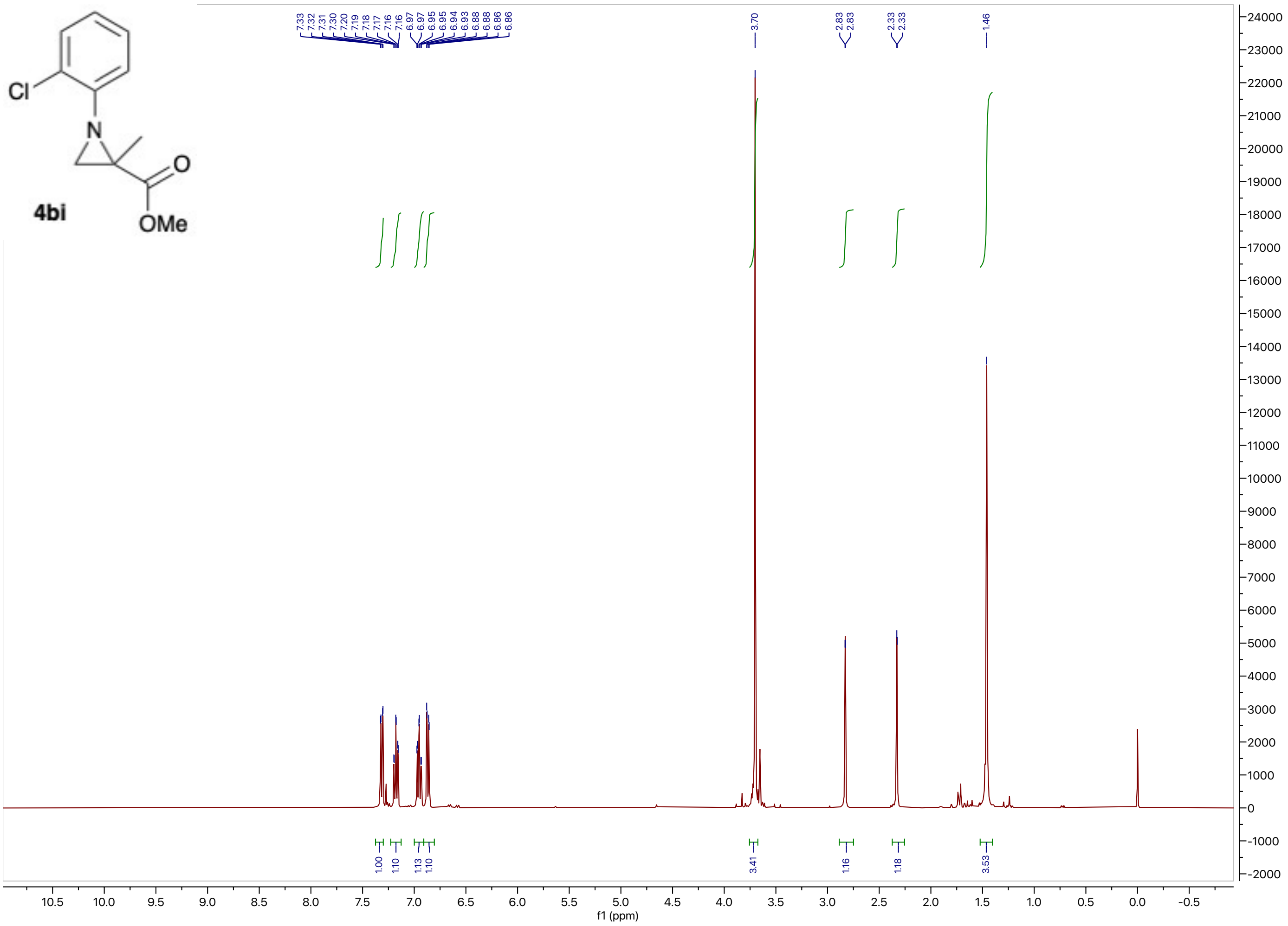
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21000
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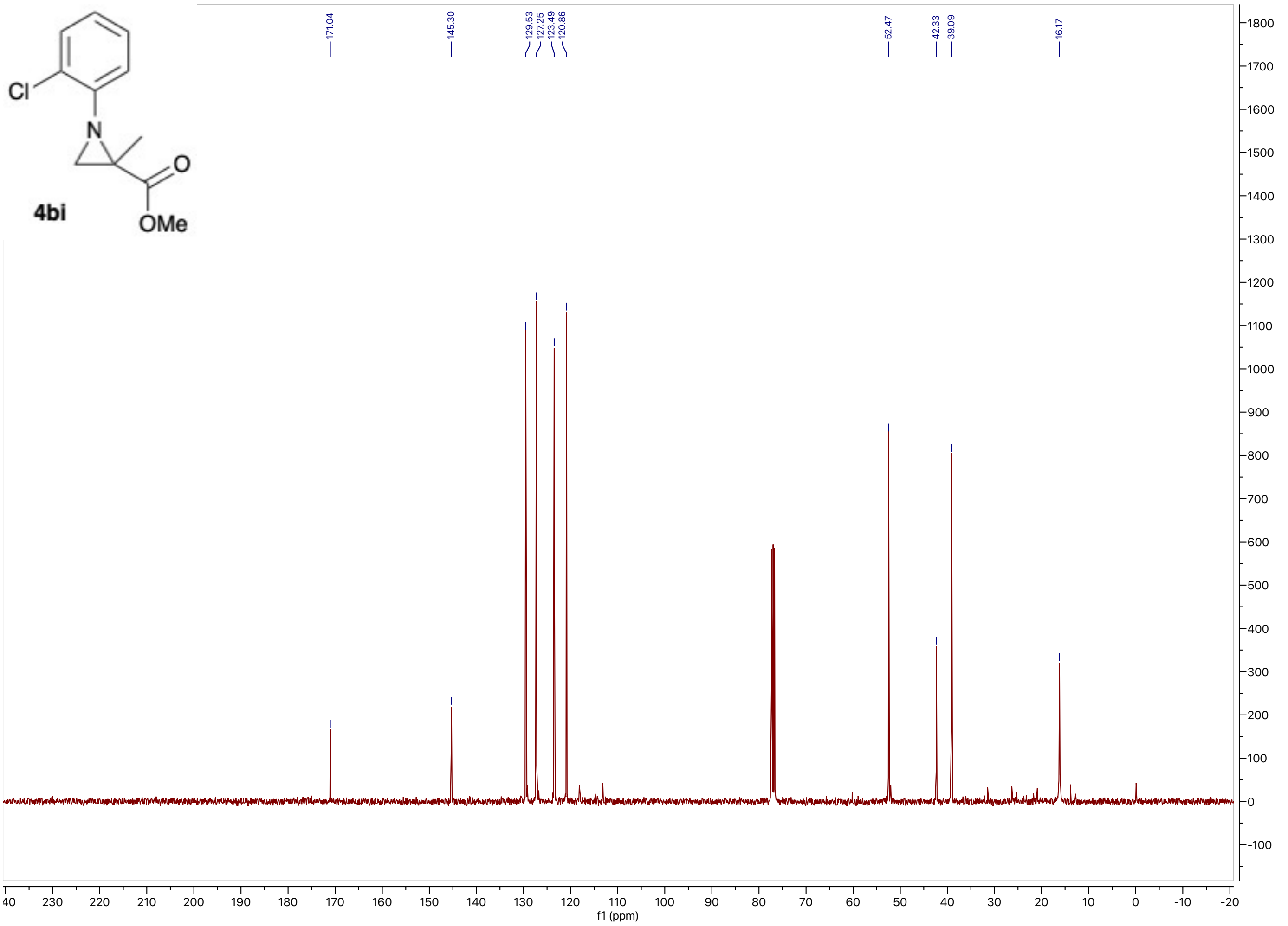
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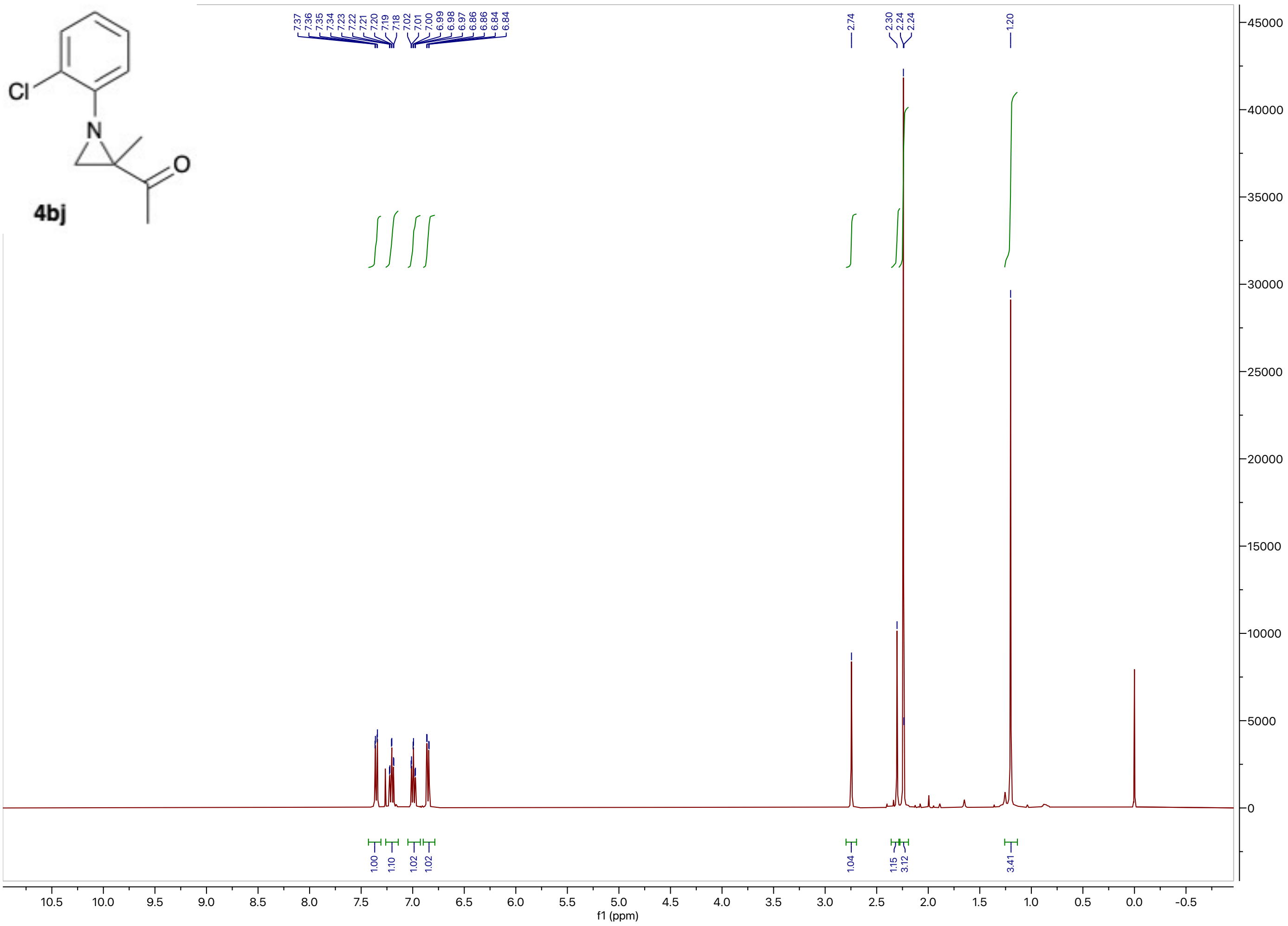
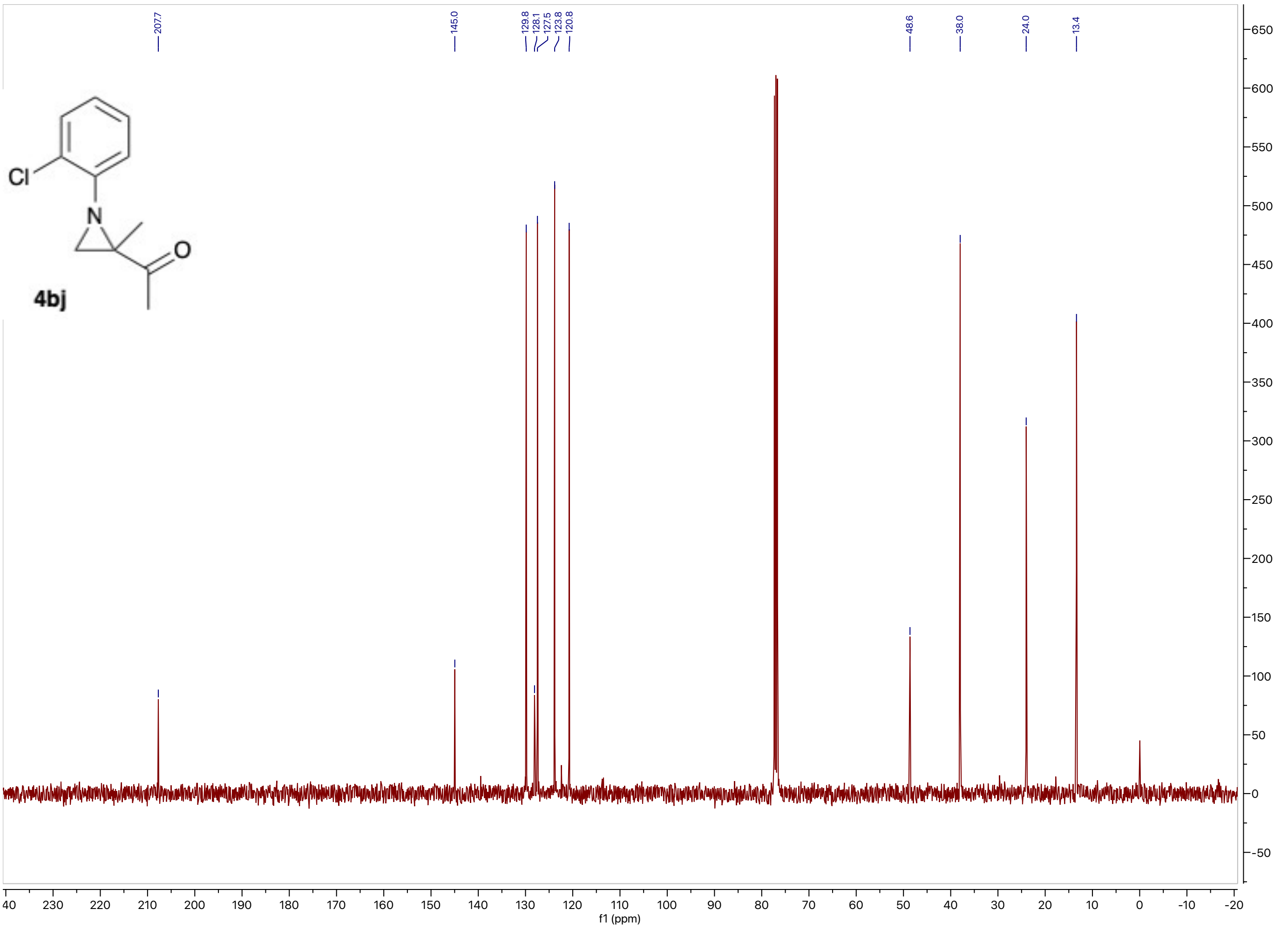
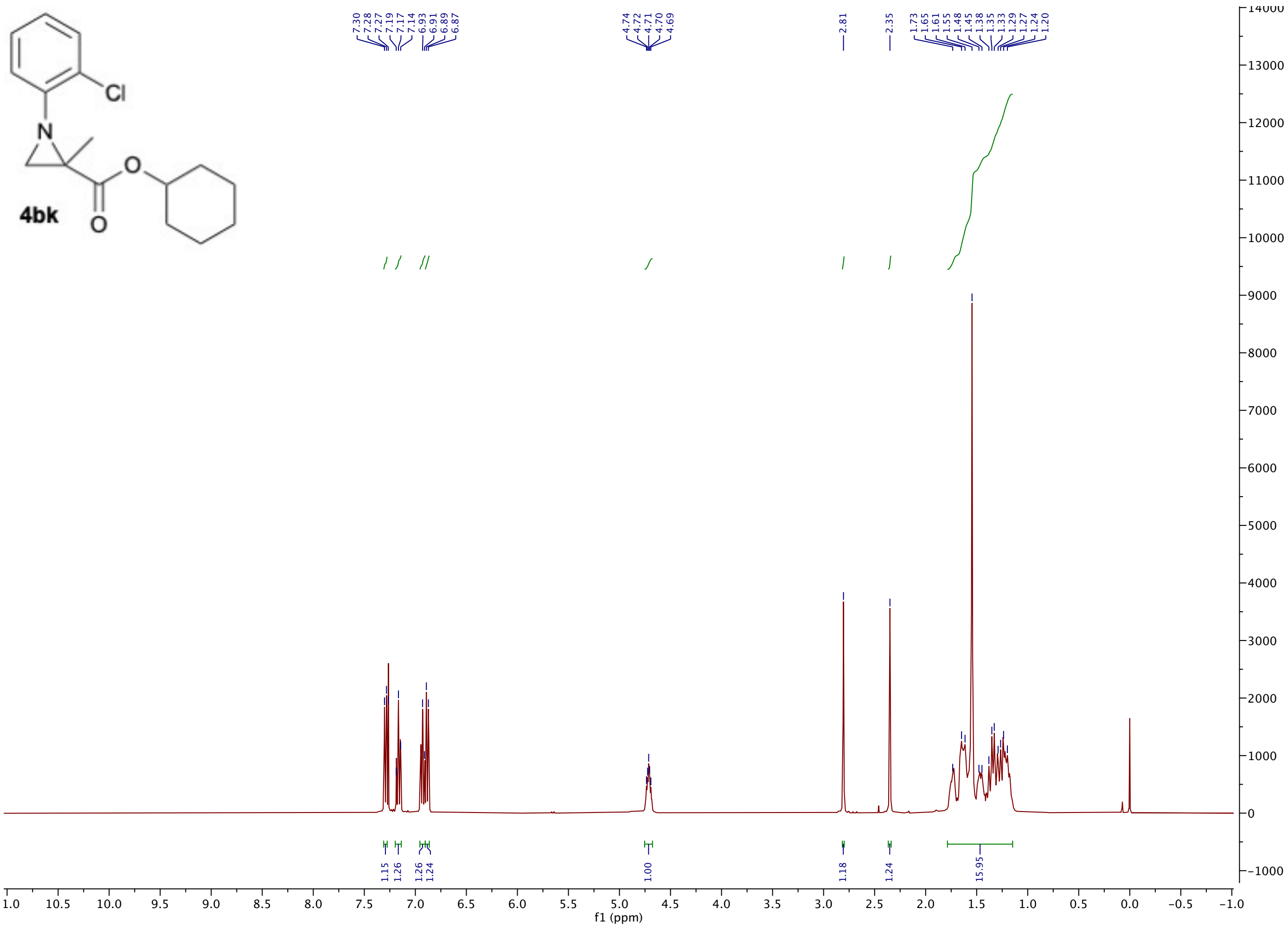
42.33
39.09
16.17
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

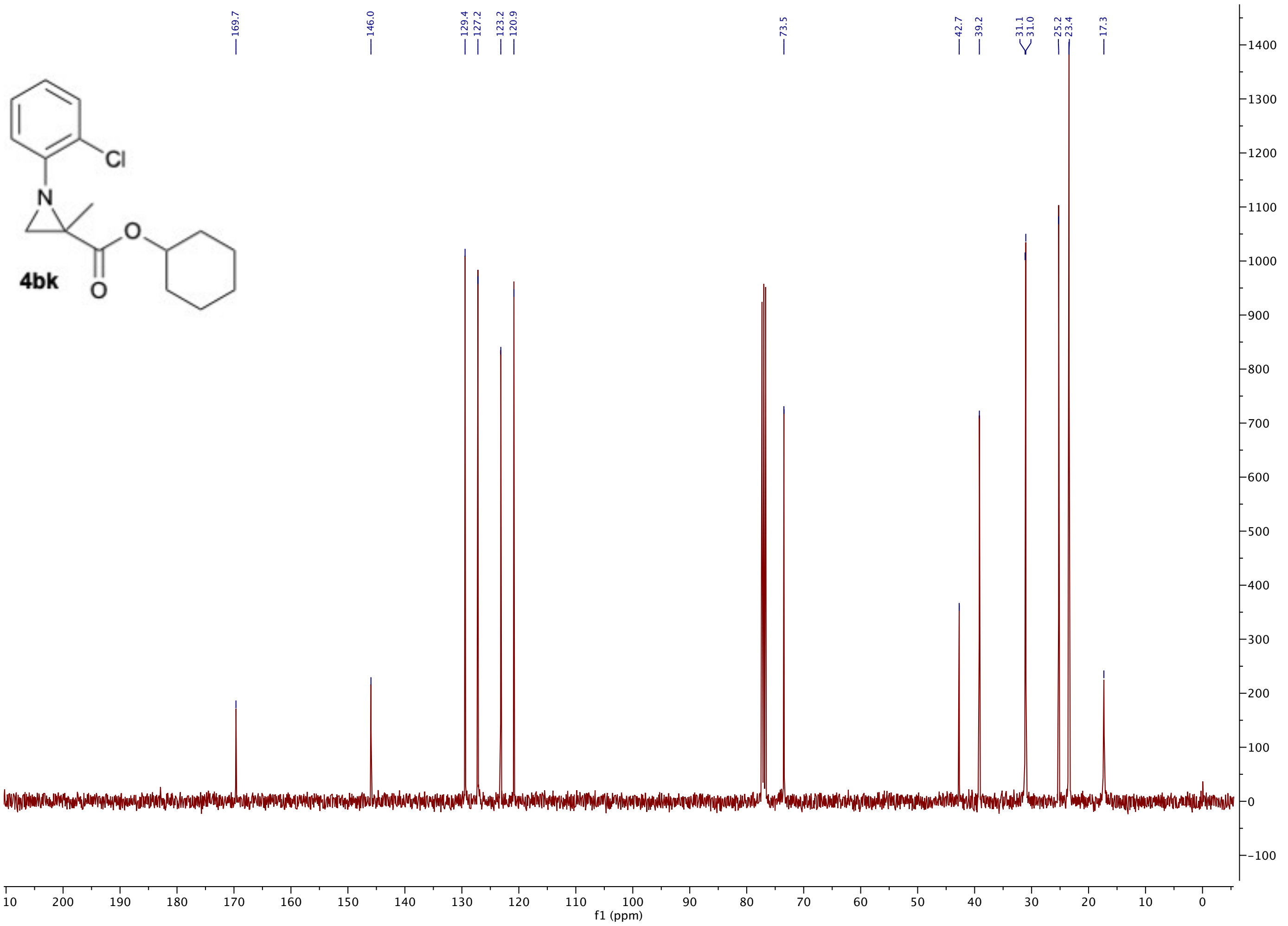


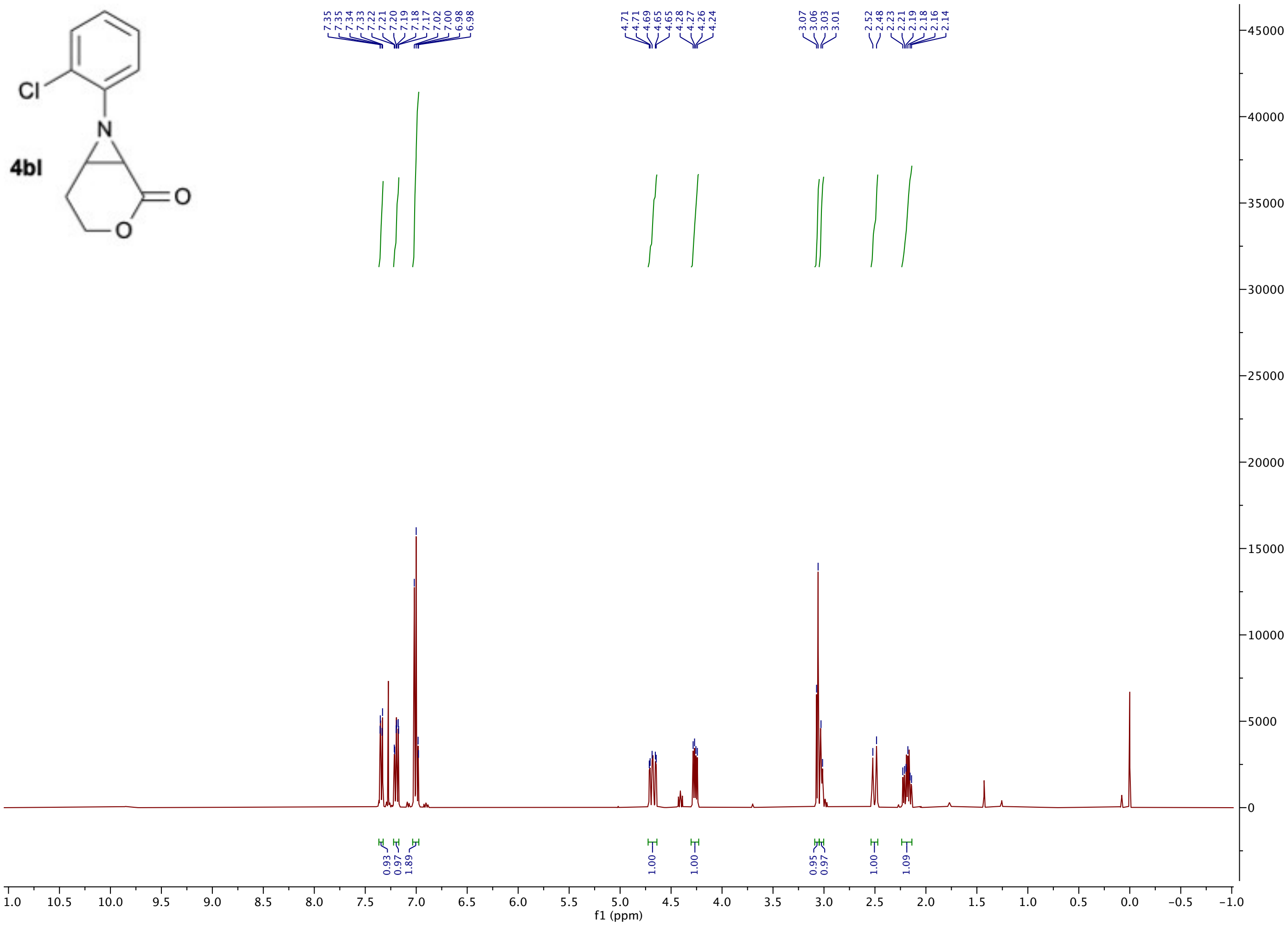
Cl
N
O
4bj
7.37
7.36
7.35
7.34
7.23
7.22
7.21
7.20
7.19
7.18
7.02
7.01
7.00
6.99
6.98
6.97
6.86
6.86
6.84
6.84
2.74
2.30
2.24
2.24
1.20
1.00
1.10
1.02
1.02
1.04
1.15
3.12
3.41
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

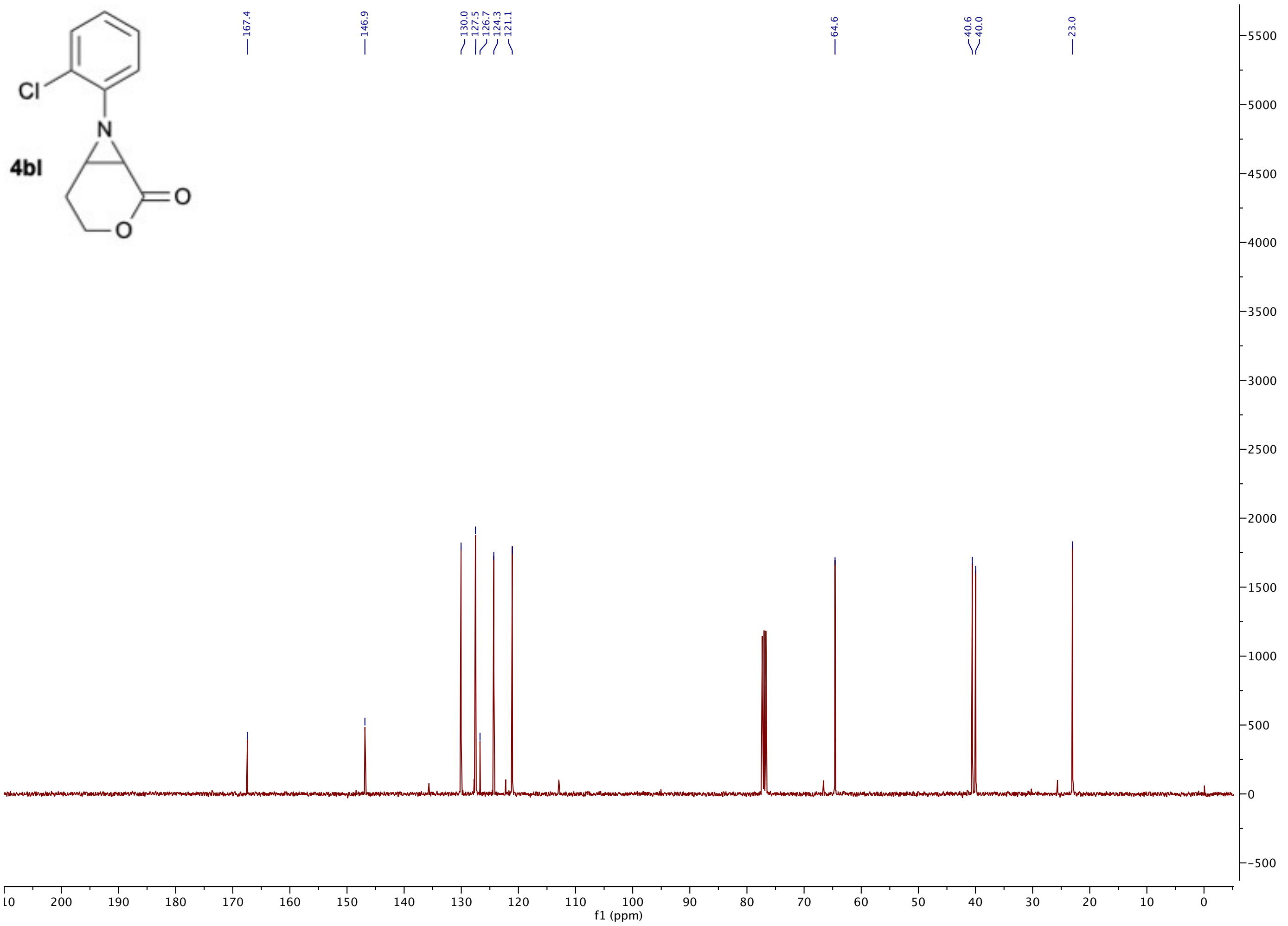


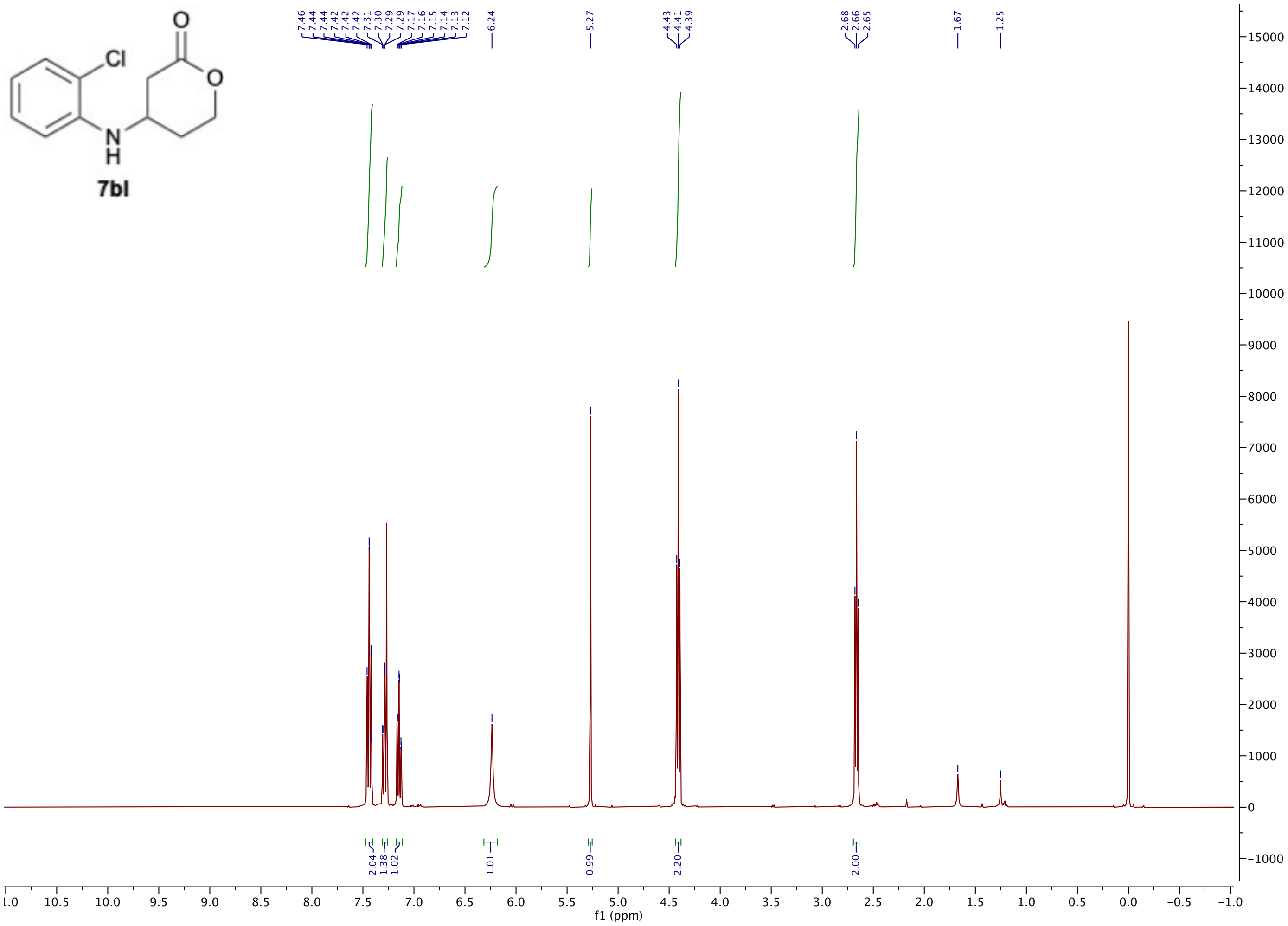
Cl
N
O
4bj
207.7
145.0
129.8
128.1
127.5
123.8
120.8
48.6
38.0
24.0
13.4
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

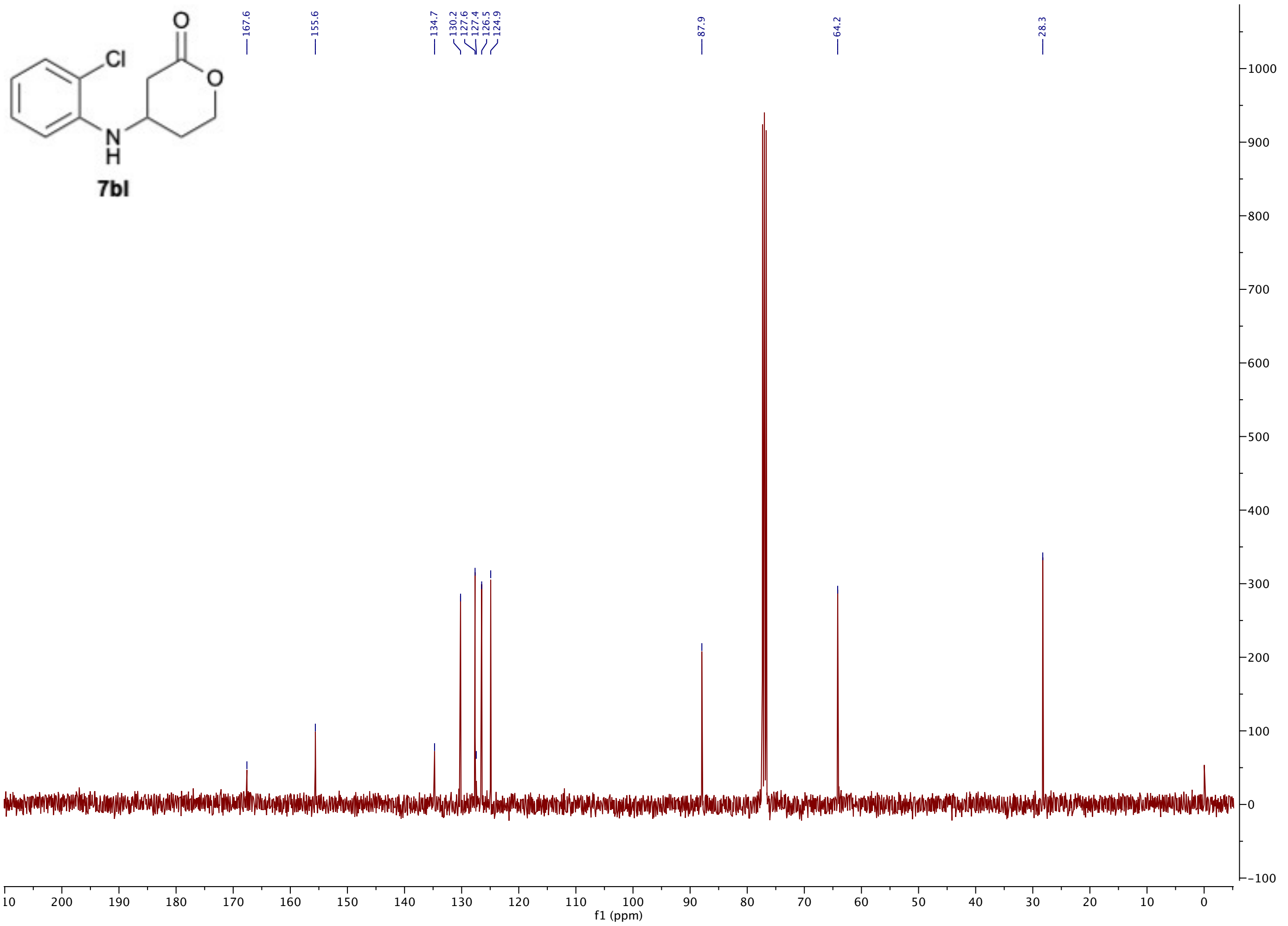

Cl
N
O
O
4bk
7.30
7.28
7.27
7.19
7.17
7.14
6.93
6.91
6.89
6.87
4.74
4.72
4.71
4.70
4.69
2.81
2.35
1.73
1.65
1.61
1.55
1.48
1.45
1.38
1.35
1.33
1.29
1.27
1.24
1.20
1.15
1.26
1.26
1.24
1.00
1.18
1.24
15.95
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000

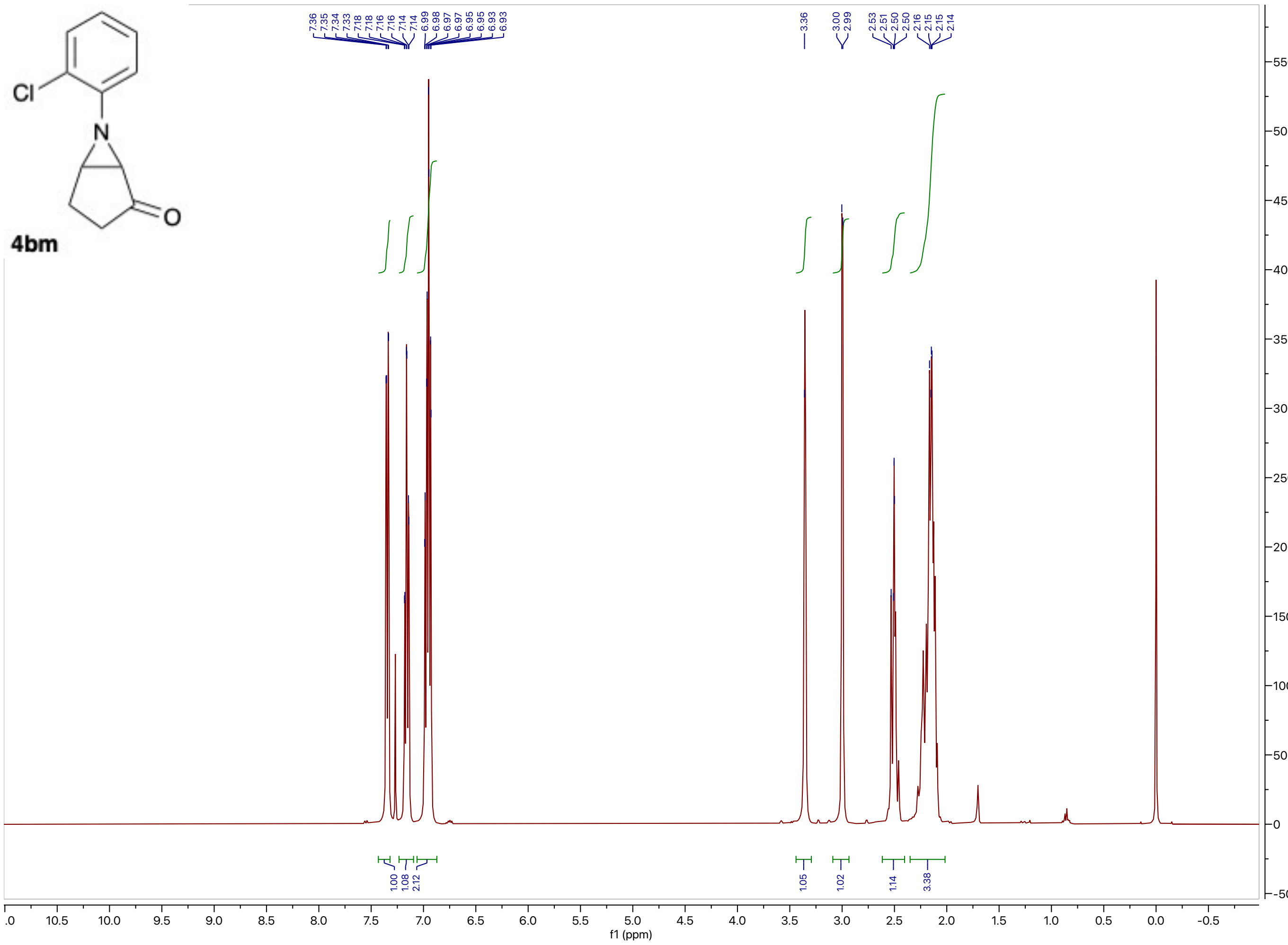

Cl
N
O
O
4bk
169.7
146.0
129.4
127.2
123.2
120.9
73.5
42.7
39.2
31.1
31.0
25.2
23.4
17.3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100

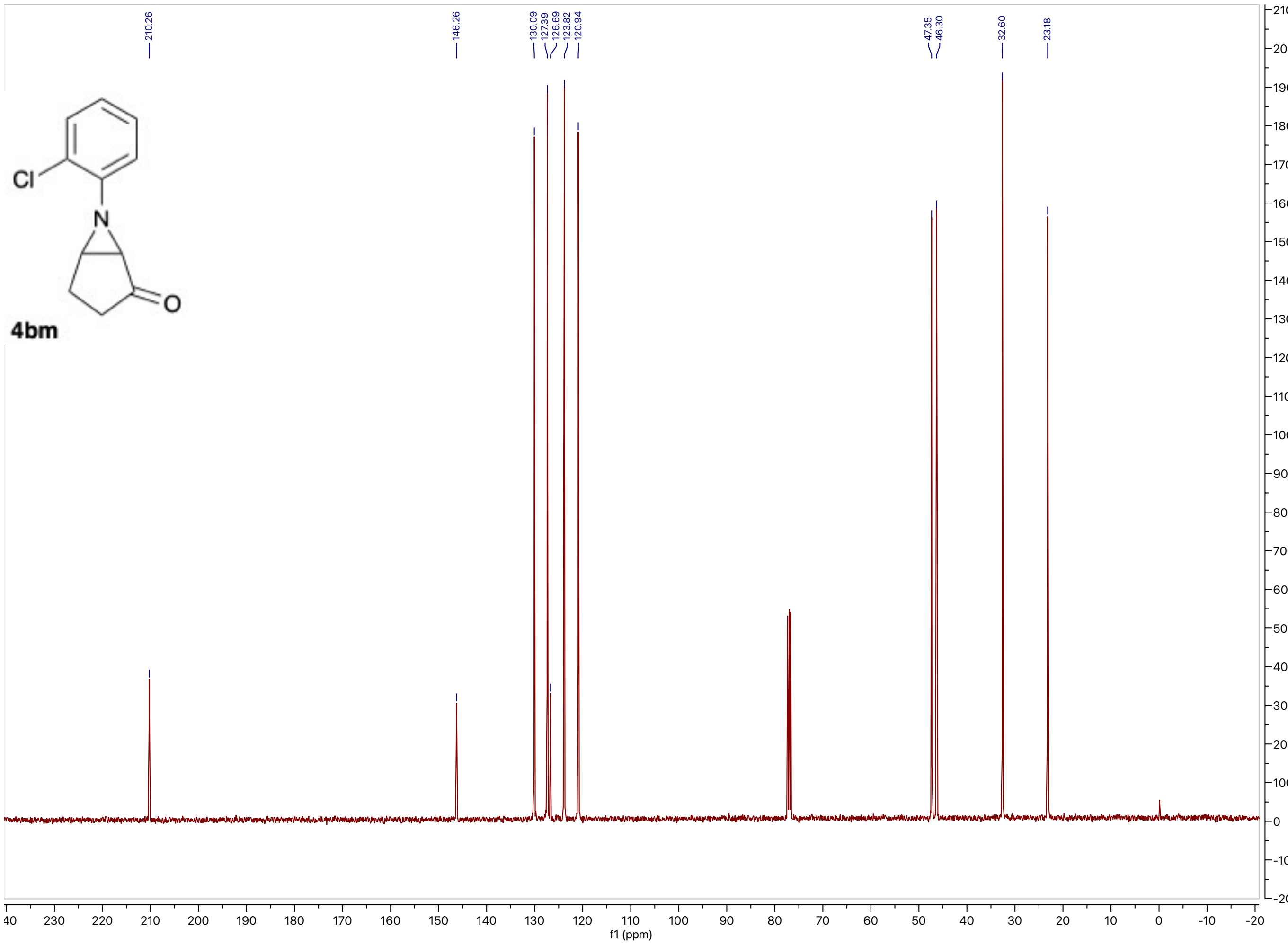

4bl
Cl
N
O
O
7.35
7.35
7.34
7.33
7.22
7.21
7.20
7.19
7.18
7.17
7.02
7.00
6.98
6.98
4.71
4.71
4.69
4.65
4.65
4.28
4.27
4.26
4.24
3.07
3.06
3.03
3.01
2.52
2.48
2.23
2.21
2.19
2.18
2.16
2.14
0.93
0.97
1.89
1.00
1.00
0.95
0.97
1.00
1.09
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

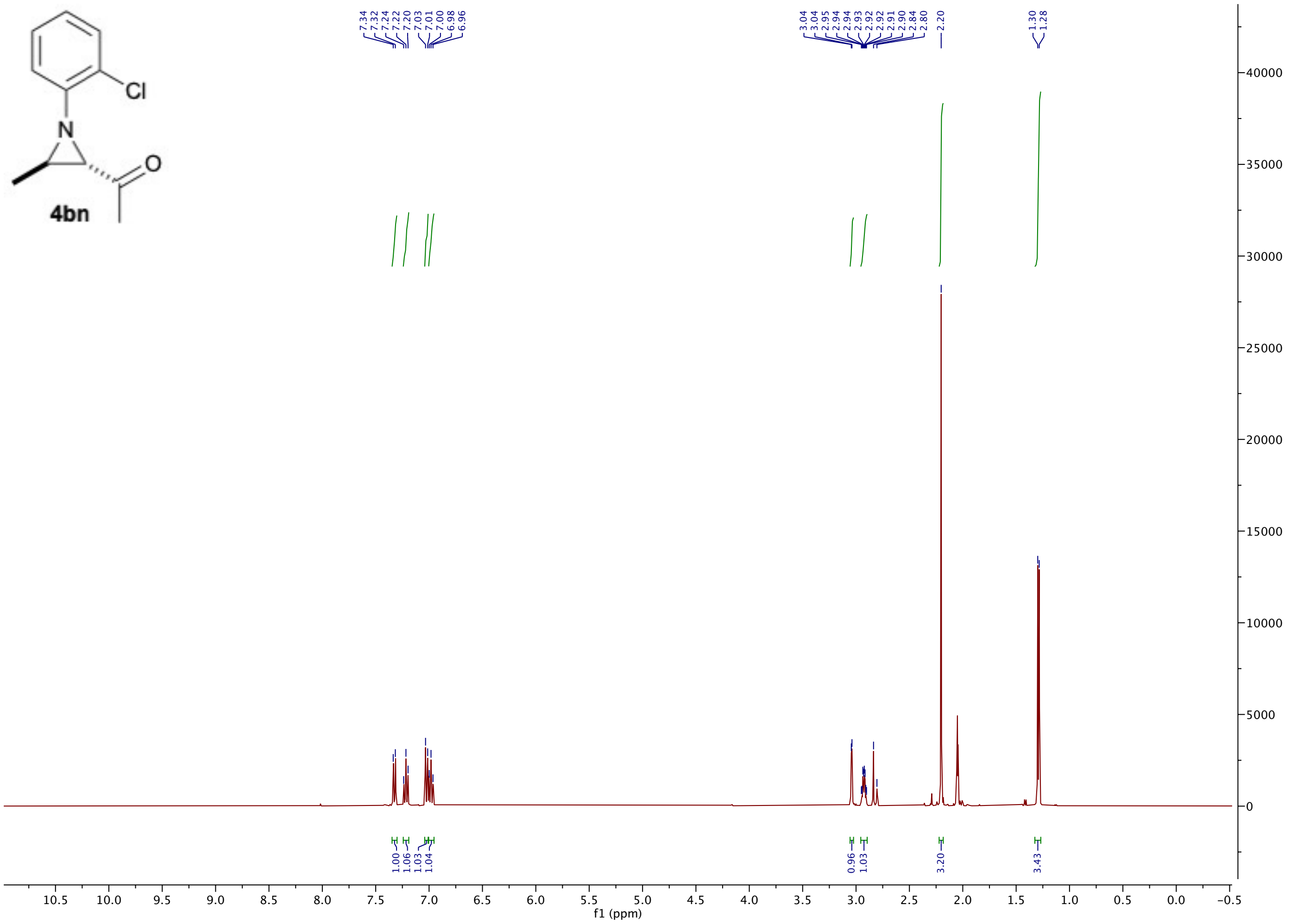

4bl
Cl
N
O
O
167.4
146.9
130.0
127.5
126.7
124.3
121.1
64.6
40.6
40.0
23.0
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

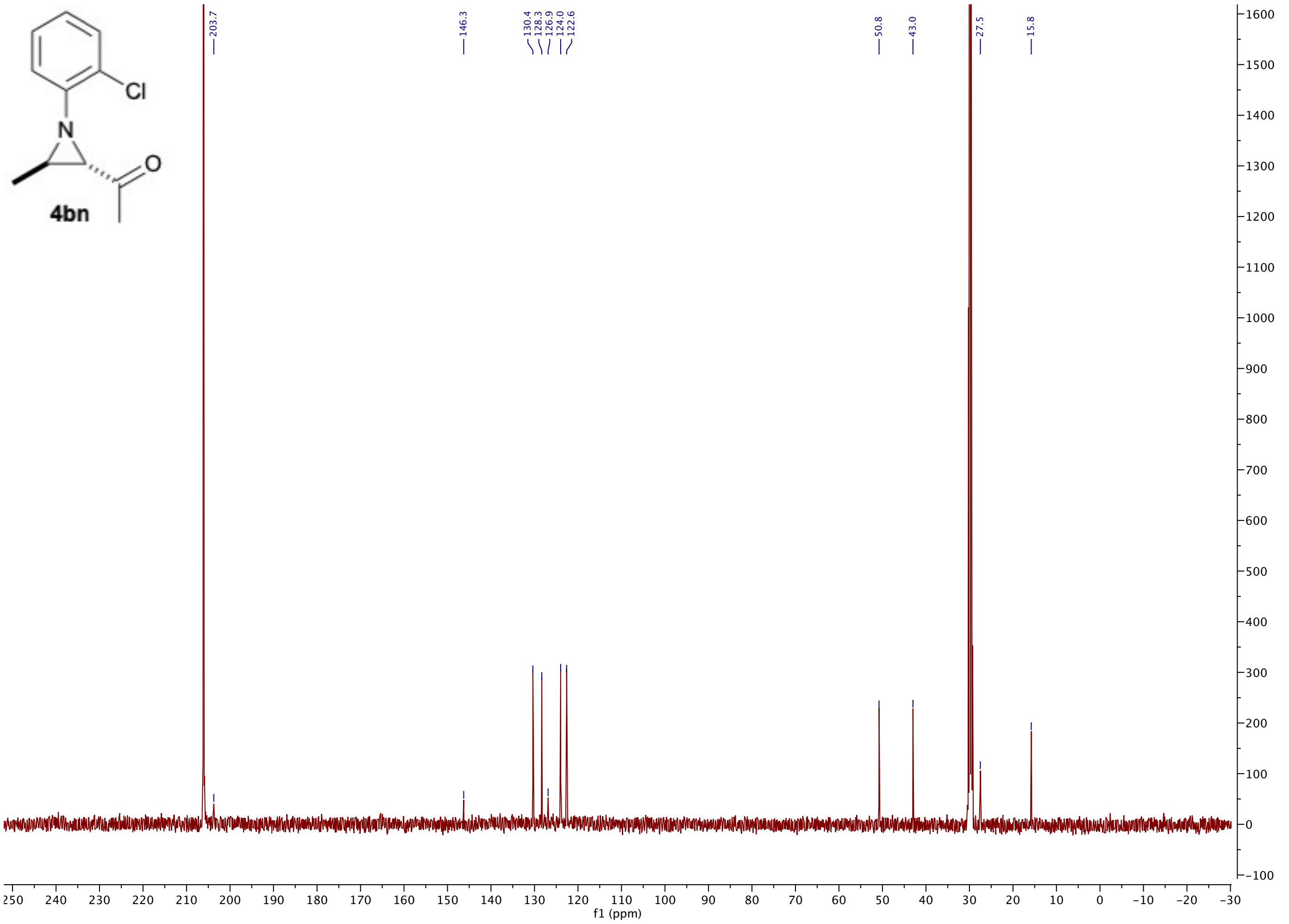

7bl
Cl
O
O
N
H
7.46
7.44
7.44
7.42
7.42
7.42
7.31
7.30
7.29
7.29
7.17
7.16
7.15
7.14
7.13
7.12
6.24
5.27
4.43
4.41
4.39
2.68
2.66
2.65
1.67
1.25
2.04
1.38
1.02
1.01
0.99
2.20
2.00
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000

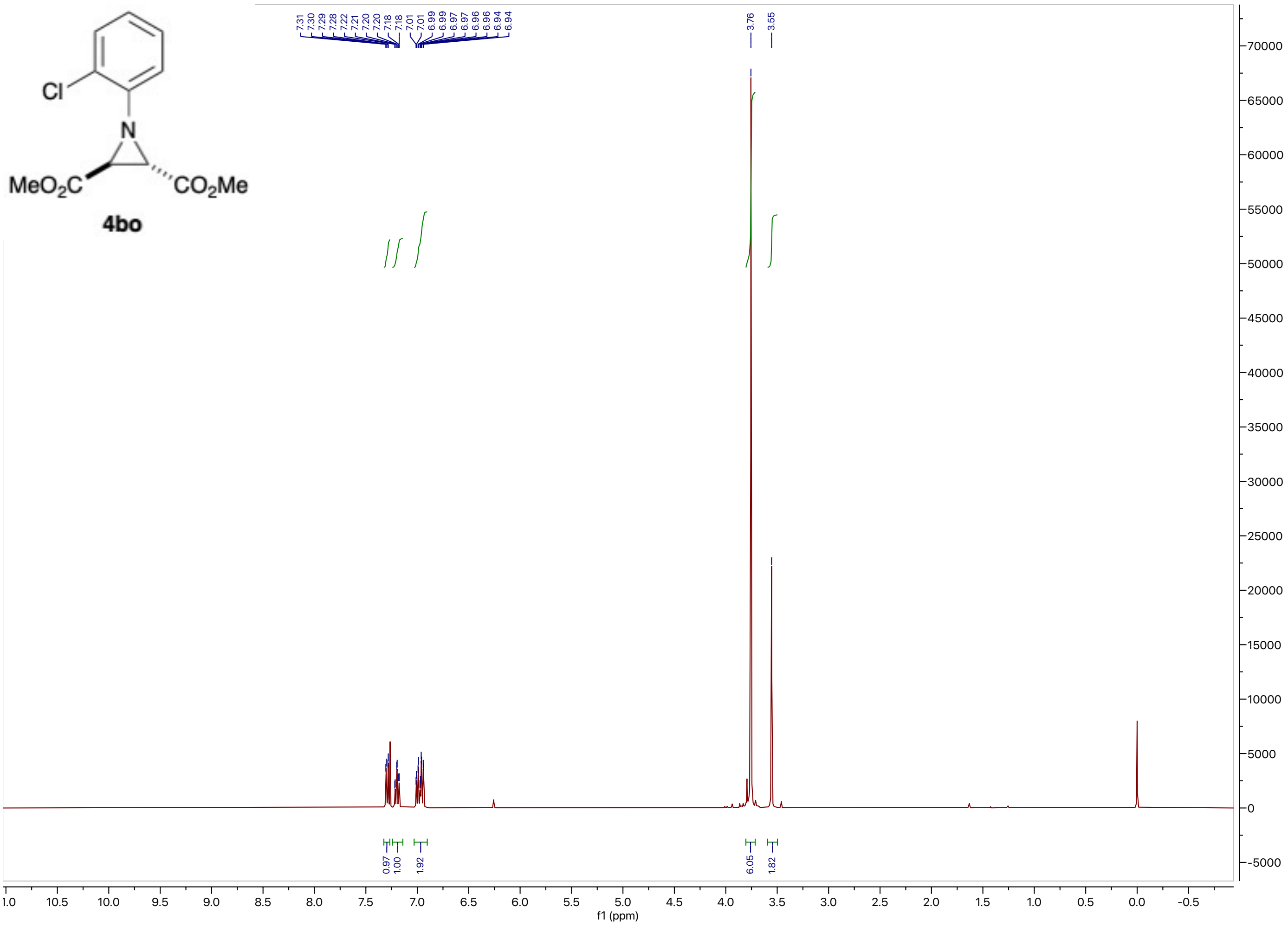

7bl
Cl
O
O
N
H
167.6
155.6
134.7
130.2
127.6
127.4
126.5
124.9
87.9
64.2
28.3
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1000
900
800
700
600
500
400
300
200
100
0
−100


4bm
Cl
N
O
7.36
7.35
7.34
7.33
7.18
7.18
7.16
7.16
7.14
7.14
6.99
6.98
6.97
6.97
6.95
6.95
6.93
6.93
3.36
3.00
2.99
2.53
2.51
2.50
2.50
2.16
2.15
2.15
2.14
1.00
1.08
2.12
1.05
1.02
1.14
3.38
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


4bm
Cl
N
O
210.26
146.26
130.09
127.39
126.69
123.82
120.94
47.35
46.30
32.60
23.18
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

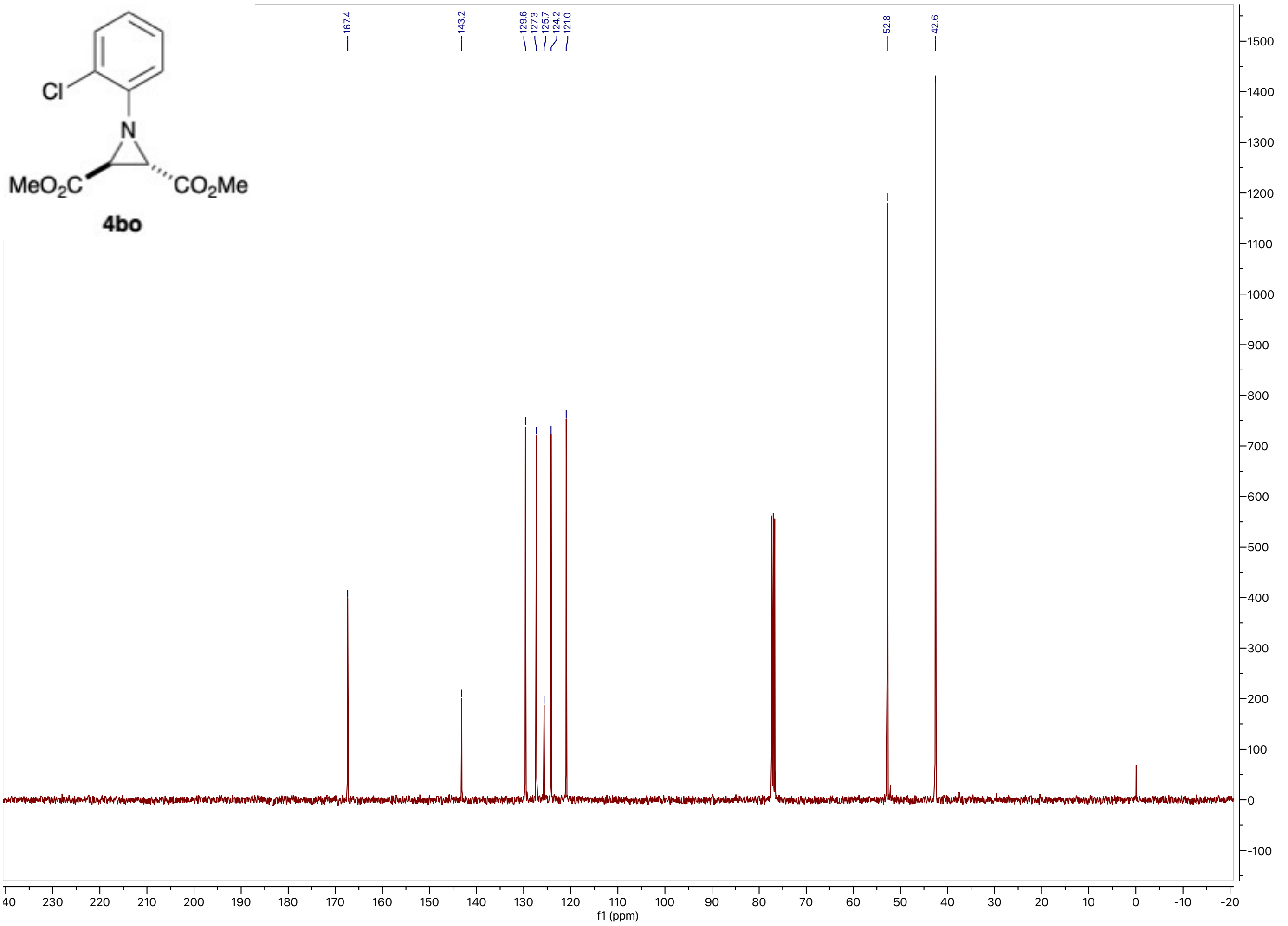

4bn
Cl
N
O
7.34
7.32
7.24
7.22
7.20
7.03
7.01
7.00
6.98
6.96
3.04
3.04
2.95
2.94
2.94
2.93
2.92
2.92
2.91
2.90
2.84
2.80
2.20
1.30
1.28
1.00
1.06
1.03
1.04
0.96
1.03
3.20
3.43
40000
35000
30000
25000
20000
15000
10000
5000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


4bn
Cl
N
O
203.7
146.3
130.4
128.3
126.9
124.0
122.6
50.8
43.0
27.5
15.8
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)



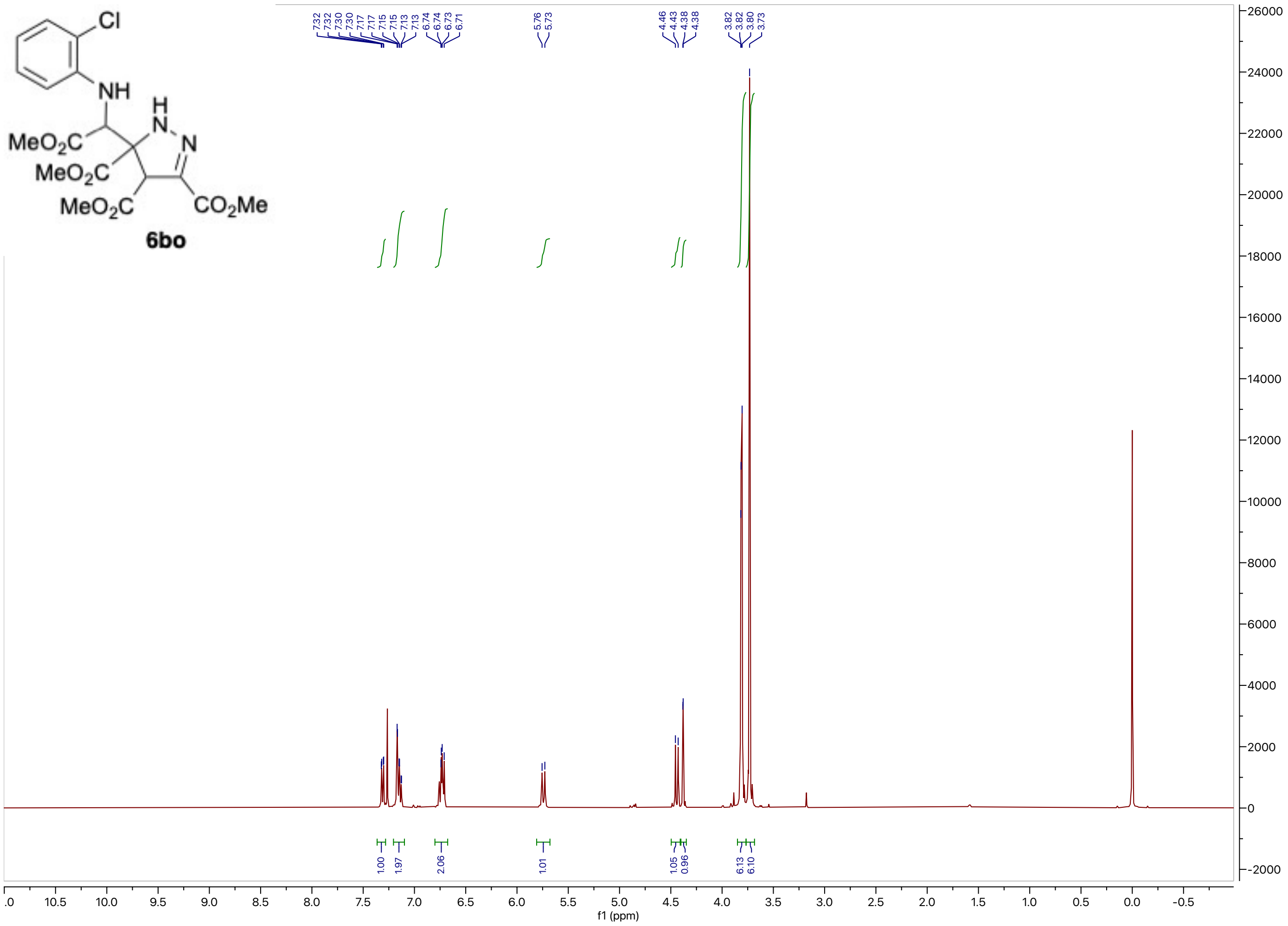
Cl
N
MeO2C
CO2Me
7.31
7.30
7.29
7.28
7.22
7.21
7.20
7.18
7.18
7.01
7.01
6.99
6.99
6.97
6.97
6.96
6.96
6.94
6.94
3.76
3.55
0.97
1.00
1.92
6.05
1.82
f1 (ppm)

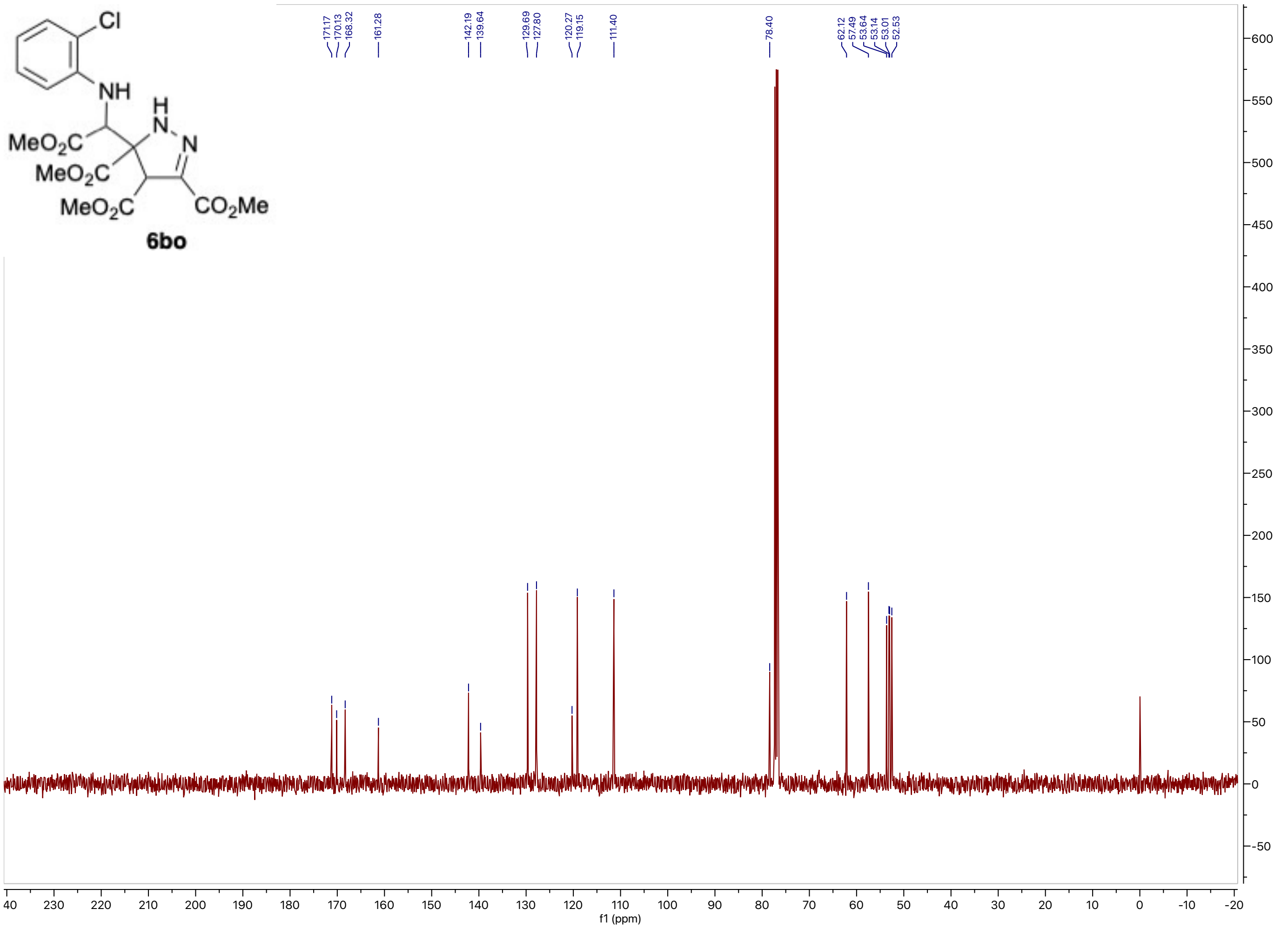
4bo

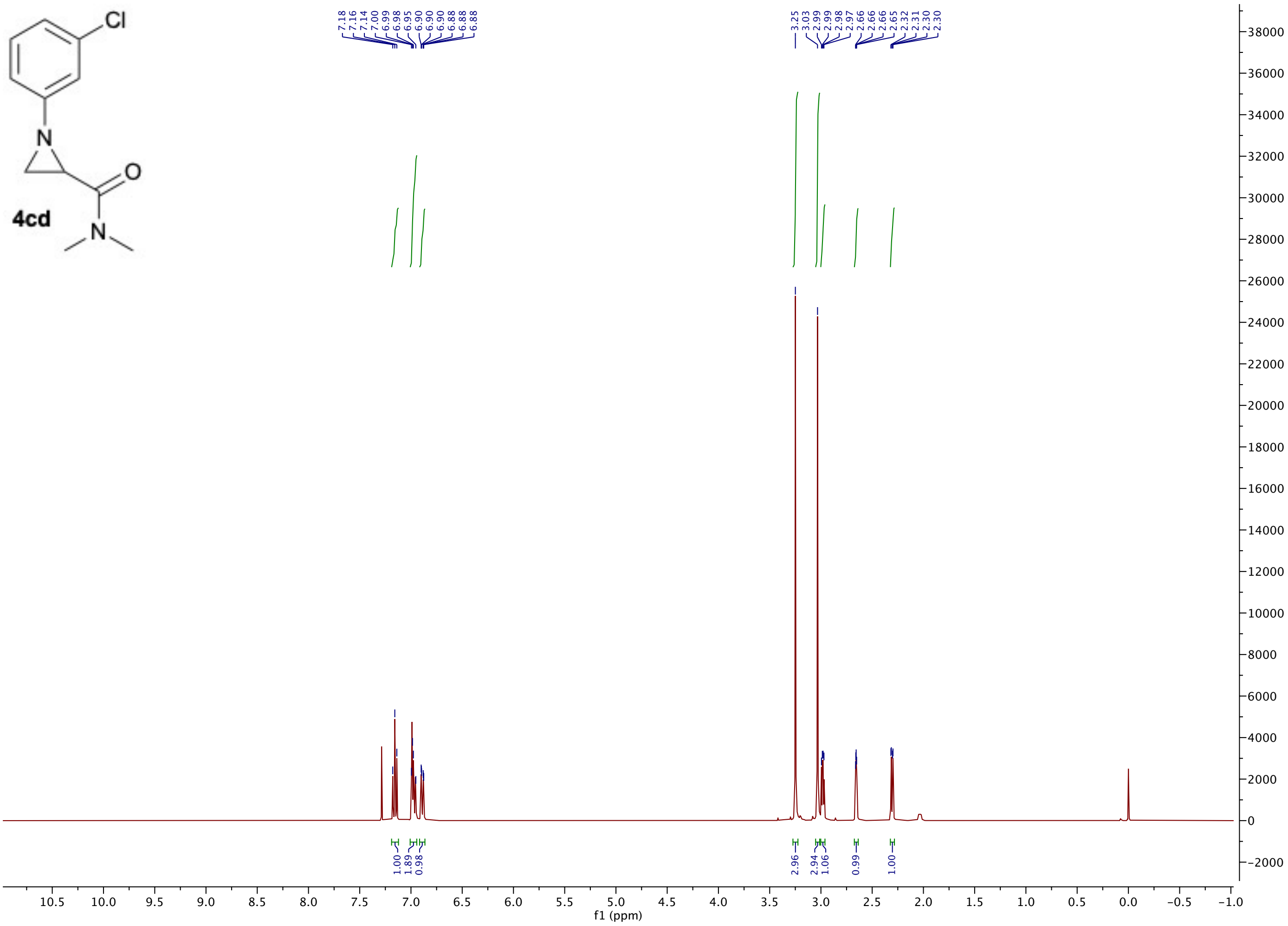


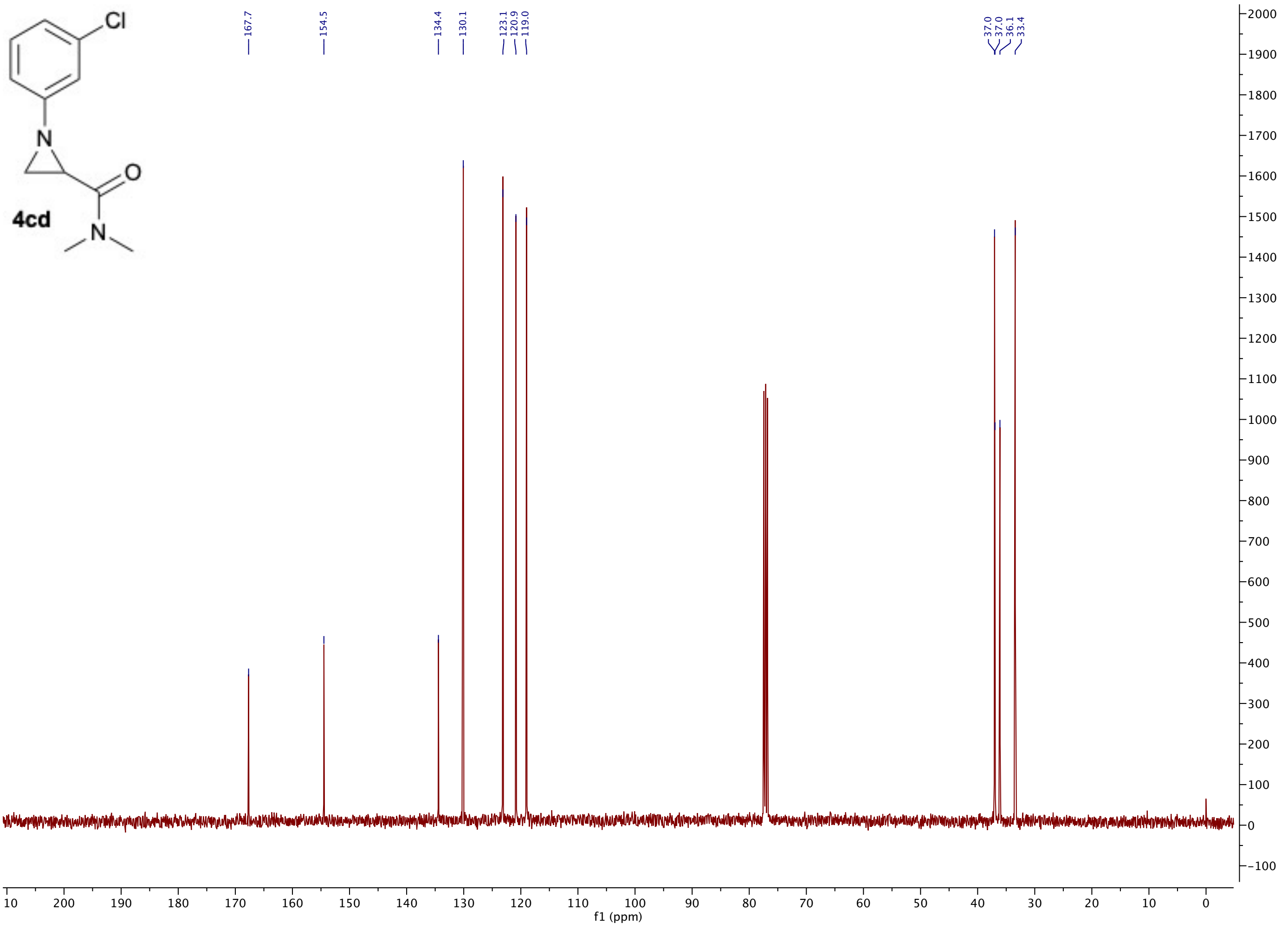
Cl
N
MeO2C
CO2Me
167.4
143.2
129.6
127.3
125.7
124.2
121.0
52.8
42.6
f1 (ppm)

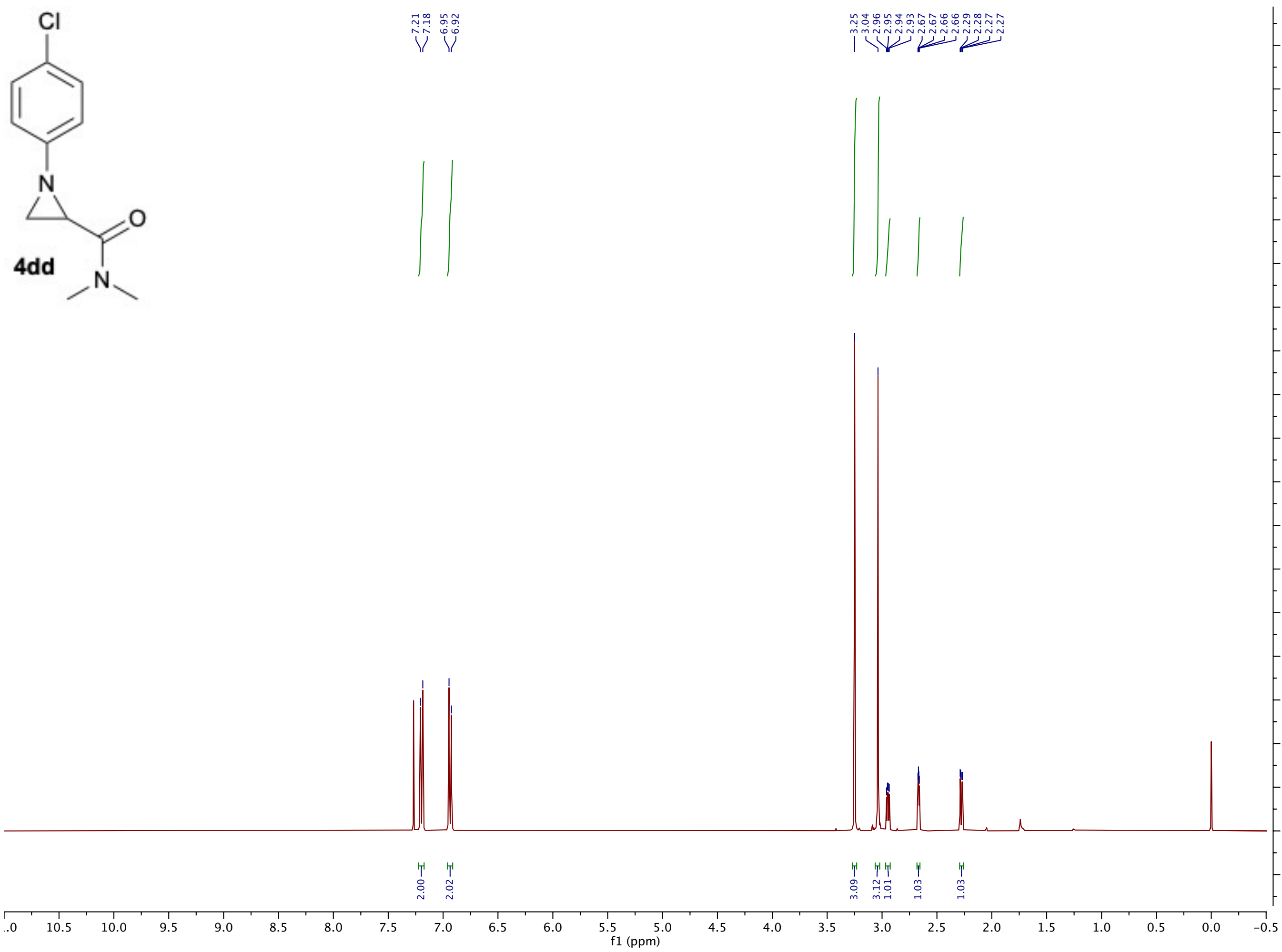
4bo

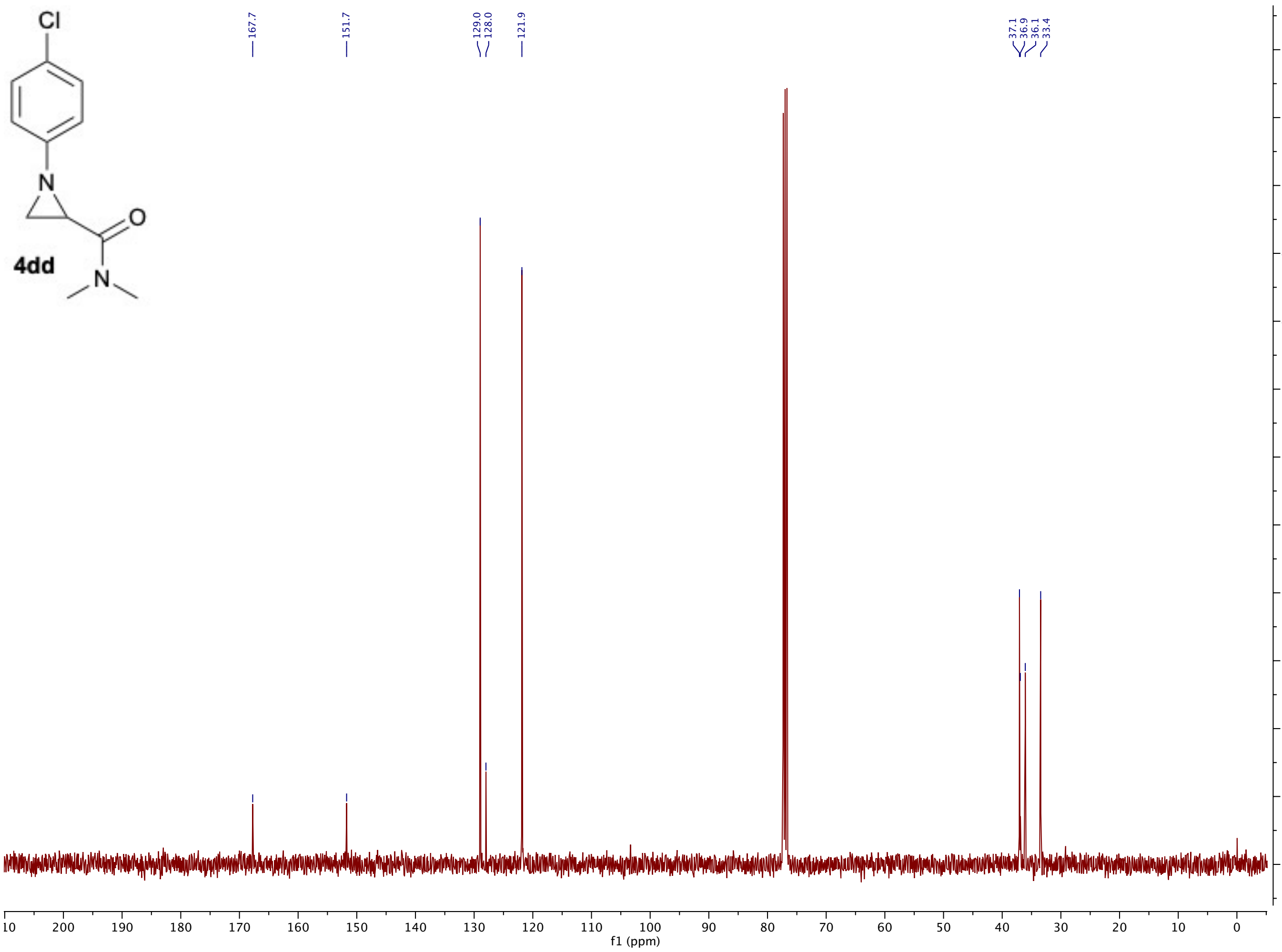

6bo
Cl
NH
H
N
N
MeO2C
MeO2C
MeO2C
CO2Me
7.32
7.32
7.30
7.30
7.17
7.17
7.15
7.15
7.13
7.13
6.74
6.74
6.73
6.71
5.76
5.73
4.46
4.43
4.38
4.38
3.82
3.82
3.80
3.73
1.00
1.97
2.06
1.01
1.05
0.96
6.13
6.10
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

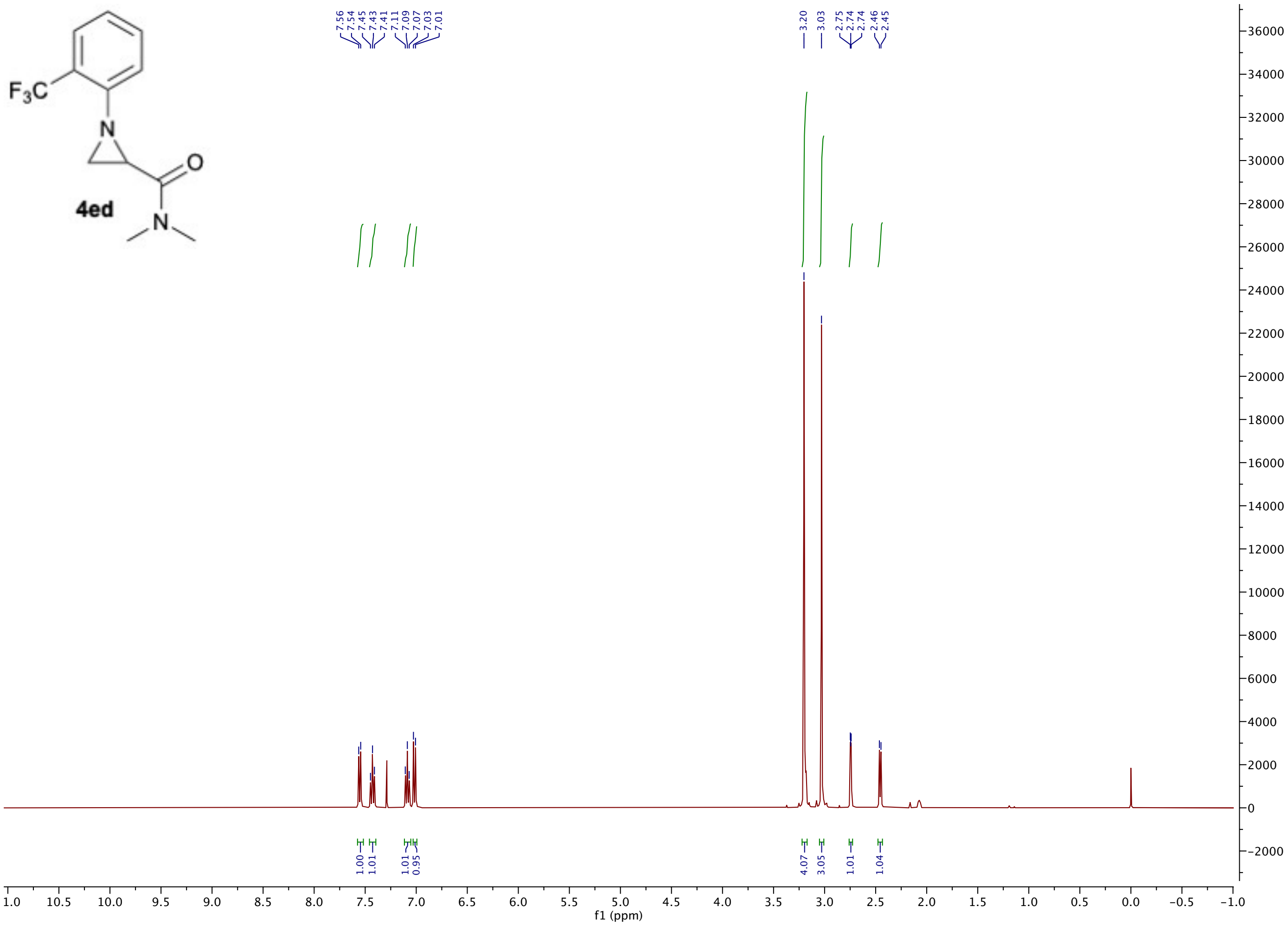

6bo
Cl
NH
H
N
N
MeO2C
MeO2C
MeO2C
CO2Me
171.17
170.13
168.32
161.28
142.19
139.64
129.69
127.80
120.27
119.15
111.40
78.40
62.12
57.49
53.64
53.14
53.01
52.53
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

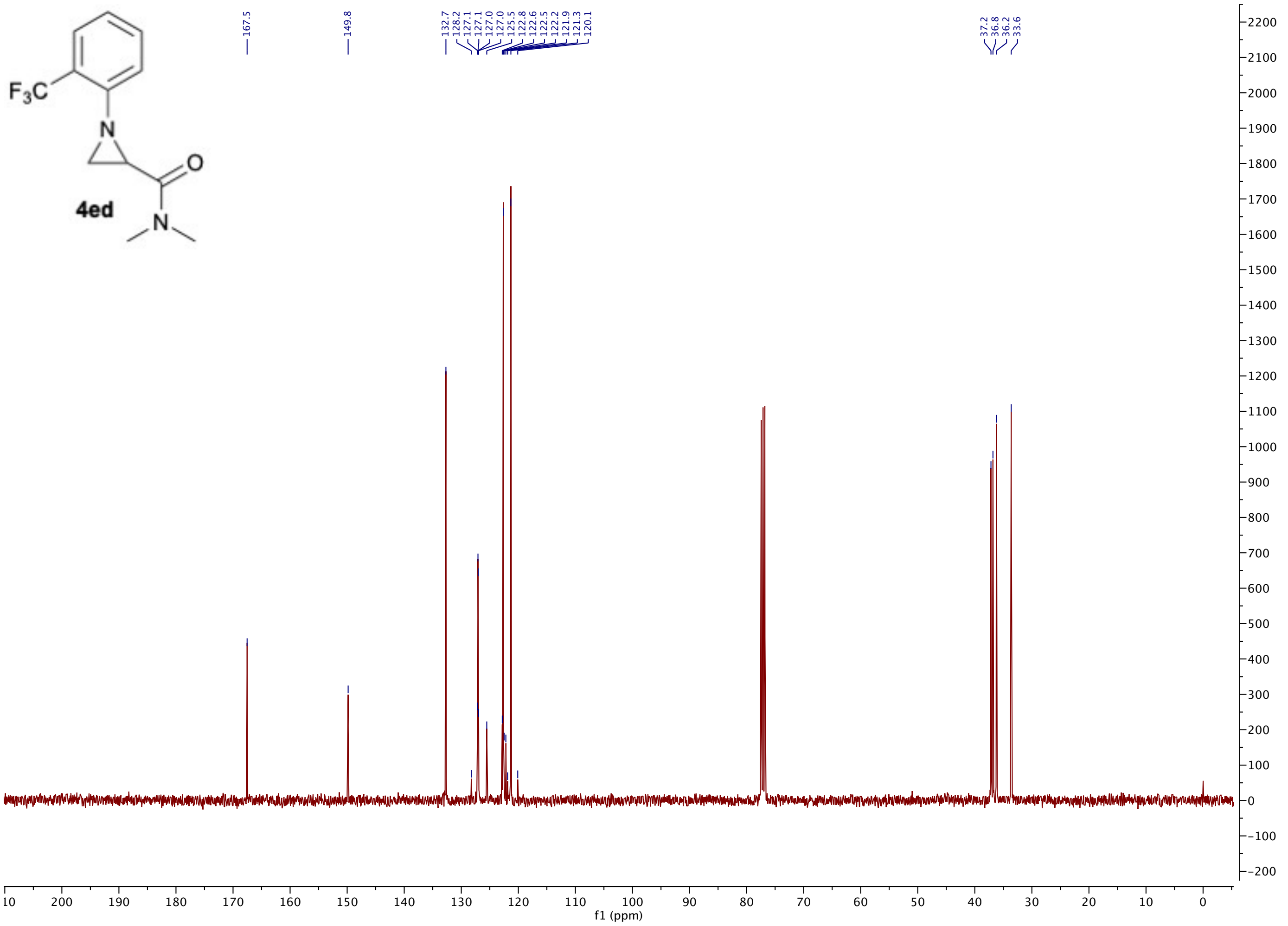

Cl
N
O
N
4cd
7.18
7.16
7.14
7.00
6.99
6.98
6.95
6.90
6.90
6.90
6.88
6.88
6.88
3.25
3.03
2.99
2.99
2.98
2.97
2.66
2.66
2.66
2.65
2.32
2.31
2.30
2.30
1.00
1.89
0.98
2.96
2.94
1.06
0.99
1.00
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

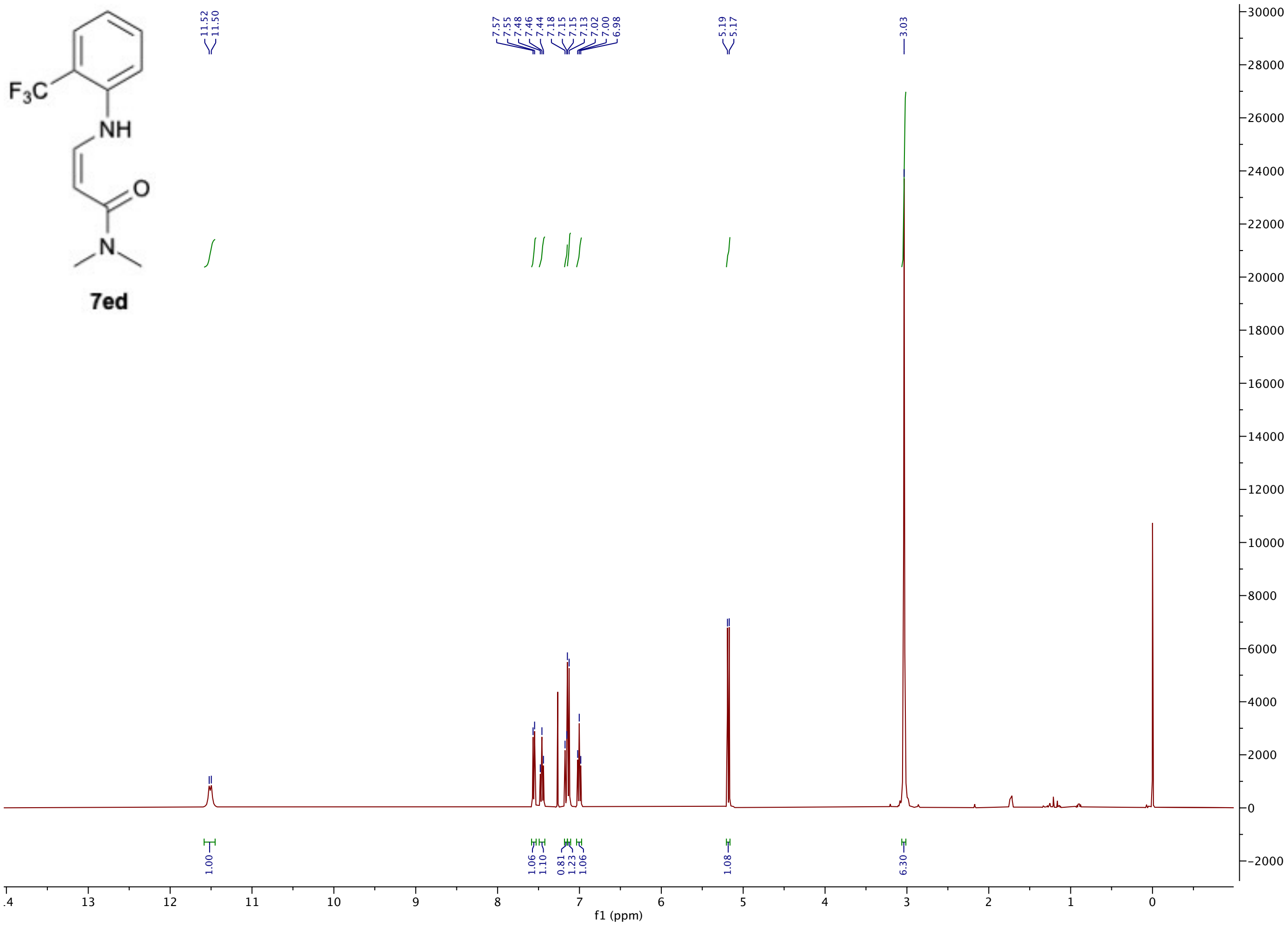

Cl
N
O
N
4cd
167.7
154.5
134.4
130.1
123.1
120.9
119.0
37.0
37.0
36.1
33.4
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
N
O
4dd
N
7.21
7.18
6.95
6.92
3.25
3.04
2.96
2.95
2.94
2.93
2.67
2.67
2.66
2.66
2.29
2.28
2.27
2.27
2.00
2.02
3.09
3.12
1.01
1.03
1.03
f1 (ppm)

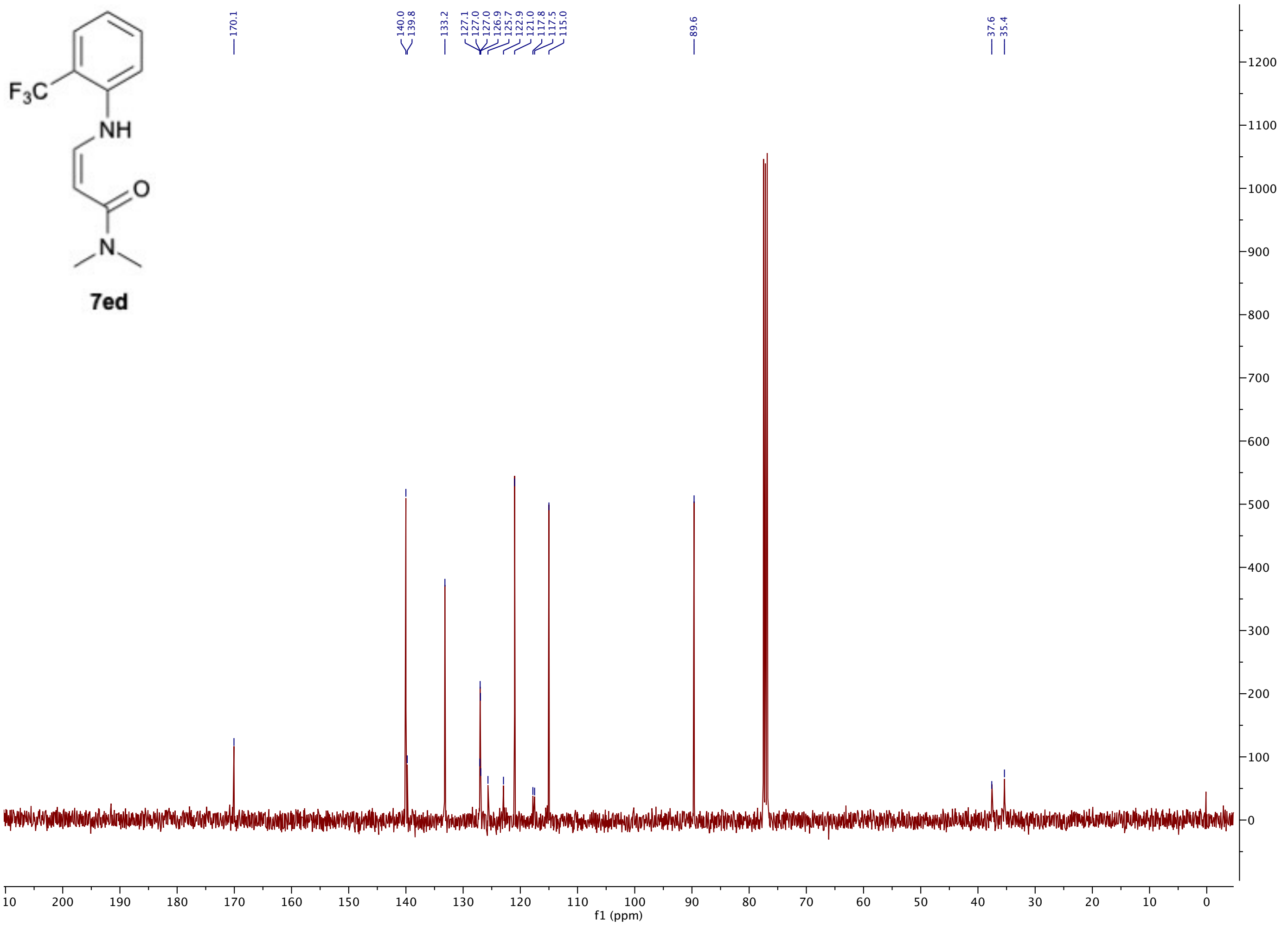

Cl
N
O
4dd
N
167.7
151.7
129.0
128.0
121.9
37.1
36.9
36.1
33.4
f1 (ppm)


F3C
N
O
4ed
N
7.56
7.54
7.45
7.43
7.41
7.11
7.09
7.07
7.03
7.01
3.20
3.03
2.75
2.74
2.74
2.46
2.45
1.00
1.01
1.01
0.95
4.07
3.05
1.01
1.04
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

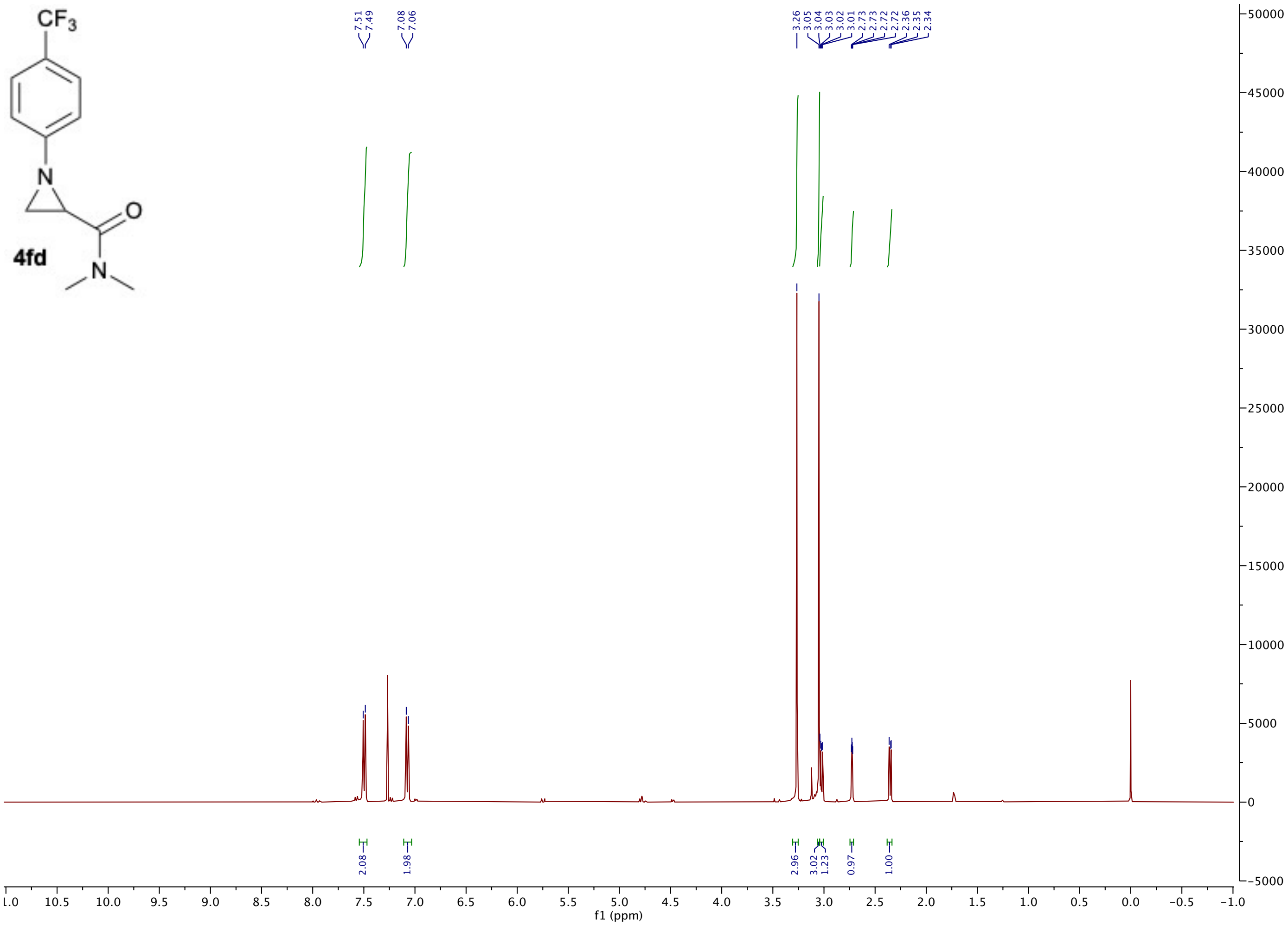

F3C
N
O
4ed
N
167.5
149.8
132.7
128.2
127.1
127.0
125.5
122.8
122.6
122.5
122.2
121.9
121.3
120.1
37.2
36.8
36.2
33.6
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

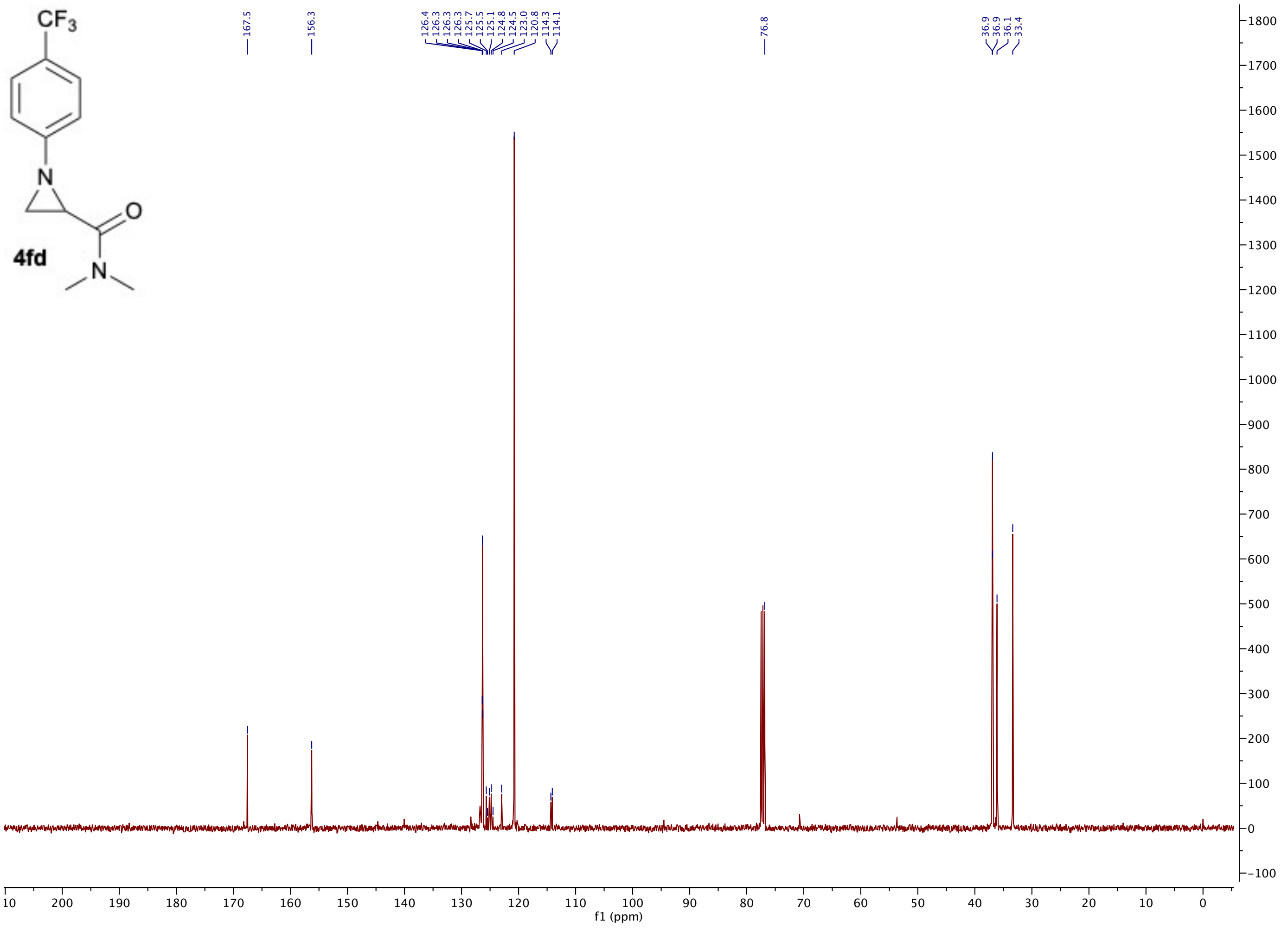

7ed

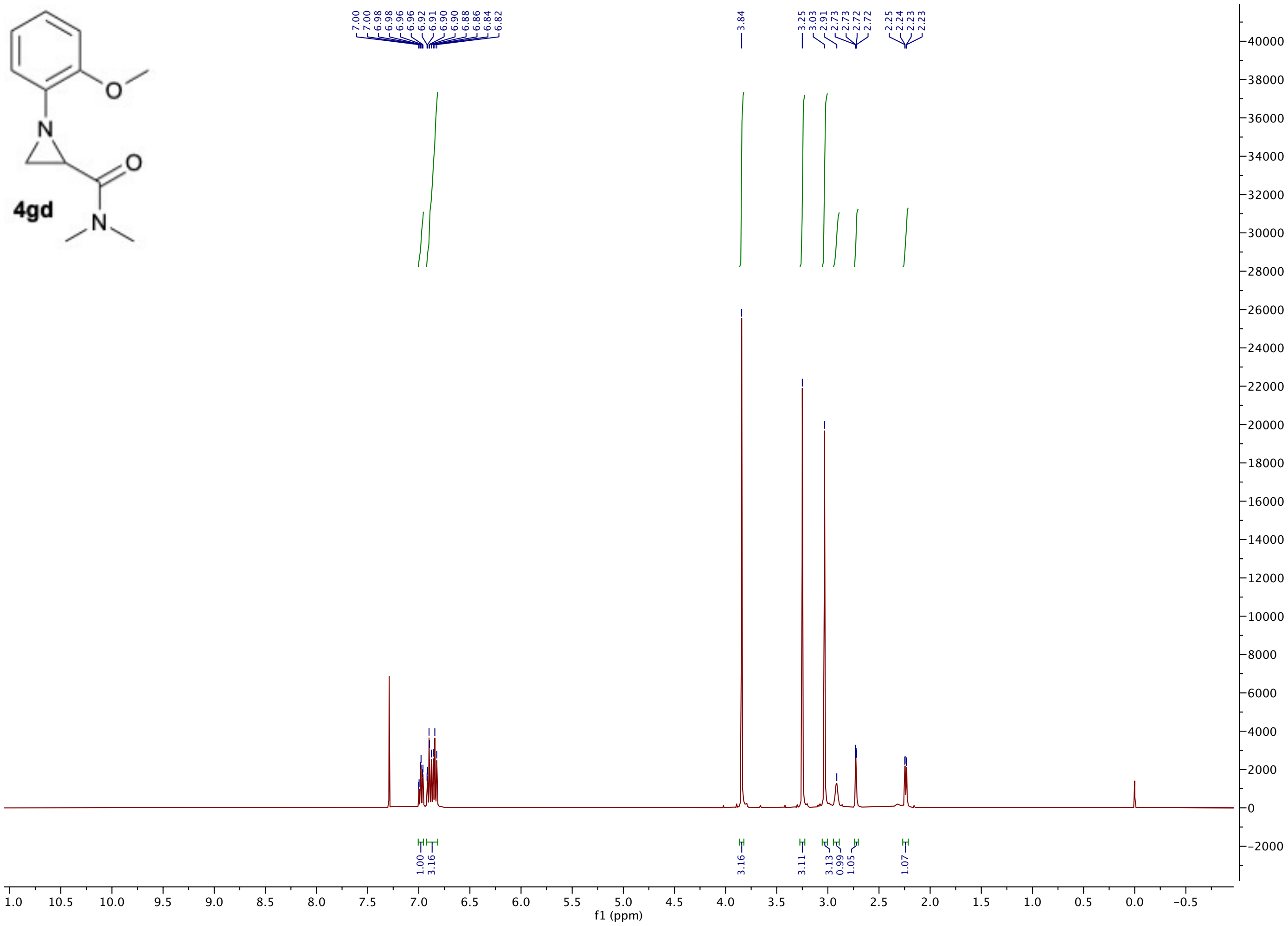
11.52
11.50
7.57
7.55
7.48
7.46
7.44
7.18
7.15
7.15
7.13
7.02
7.00
6.98
5.19
5.17
3.03
1.00
1.06
1.10
0.81
1.23
1.06
1.08
6.30
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


7ed

170.1
140.0
139.8
133.2
127.1
127.0
127.0
126.9
125.7
122.9
121.0
117.8
117.5
115.0
89.6
37.6
35.4
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

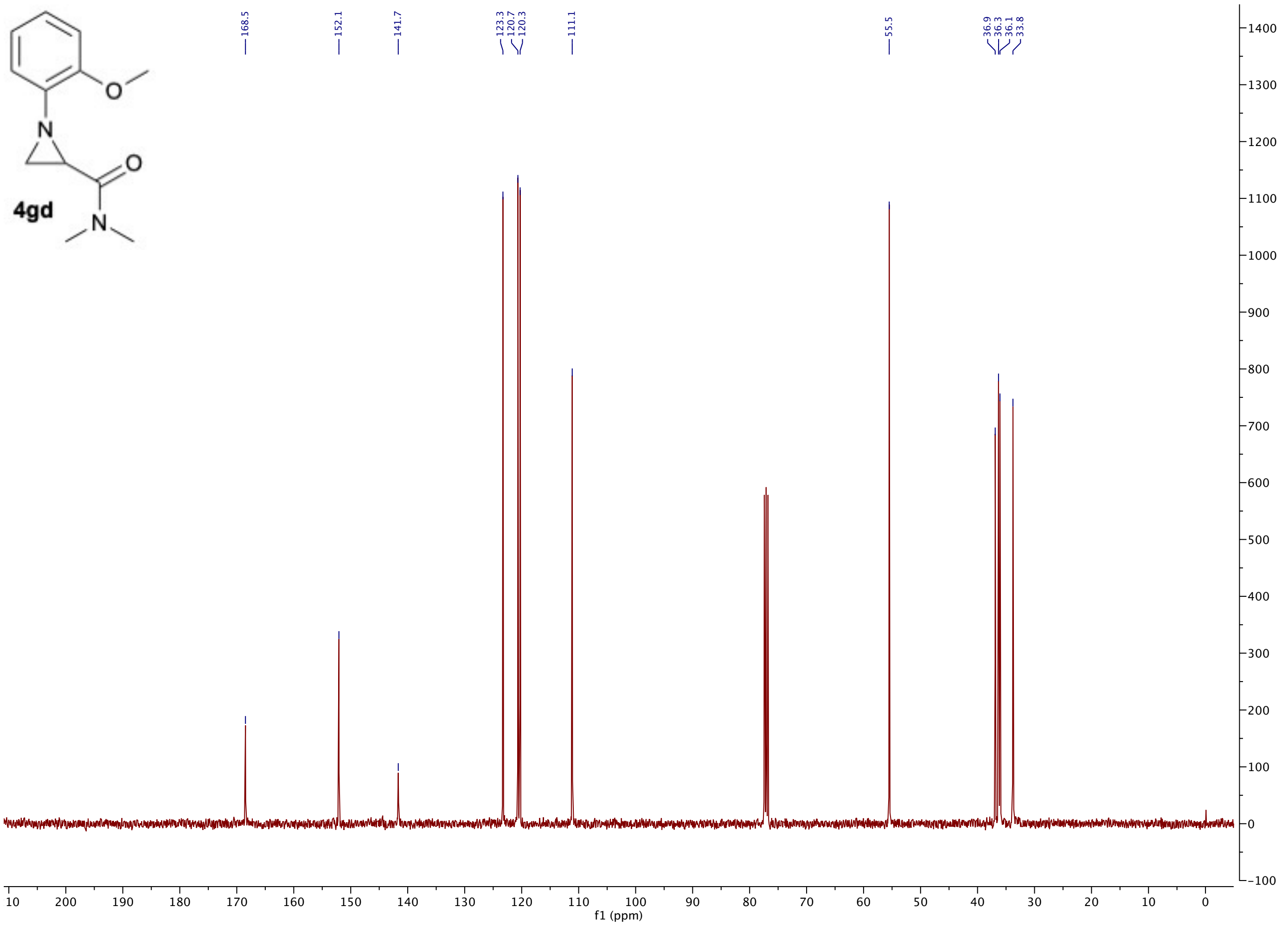

CF3
N
O
N
4fd
7.51
7.49
7.08
7.06
3.26
3.05
3.04
3.03
3.02
3.01
2.73
2.73
2.72
2.72
2.36
2.35
2.34
2.08
1.98
2.96
3.02
1.23
0.97
1.00
f1 (ppm)


CF3
N
O
N
4fd
167.5
156.3
126.4
126.3
126.3
126.3
125.7
125.5
125.1
124.8
124.5
123.0
120.8
114.3
114.1
76.8
36.9
36.9
36.1
33.4
f1 (ppm)



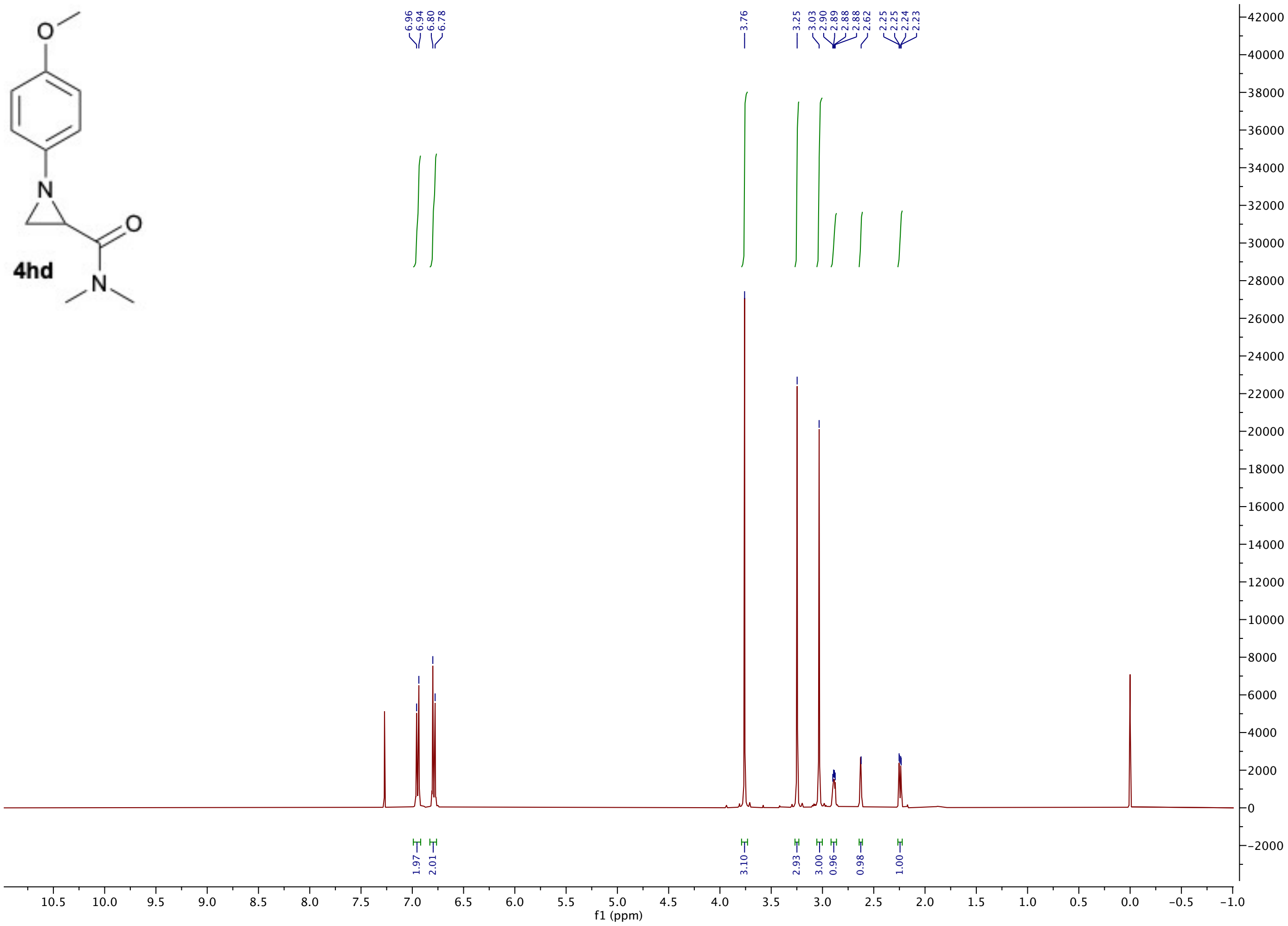
4gd

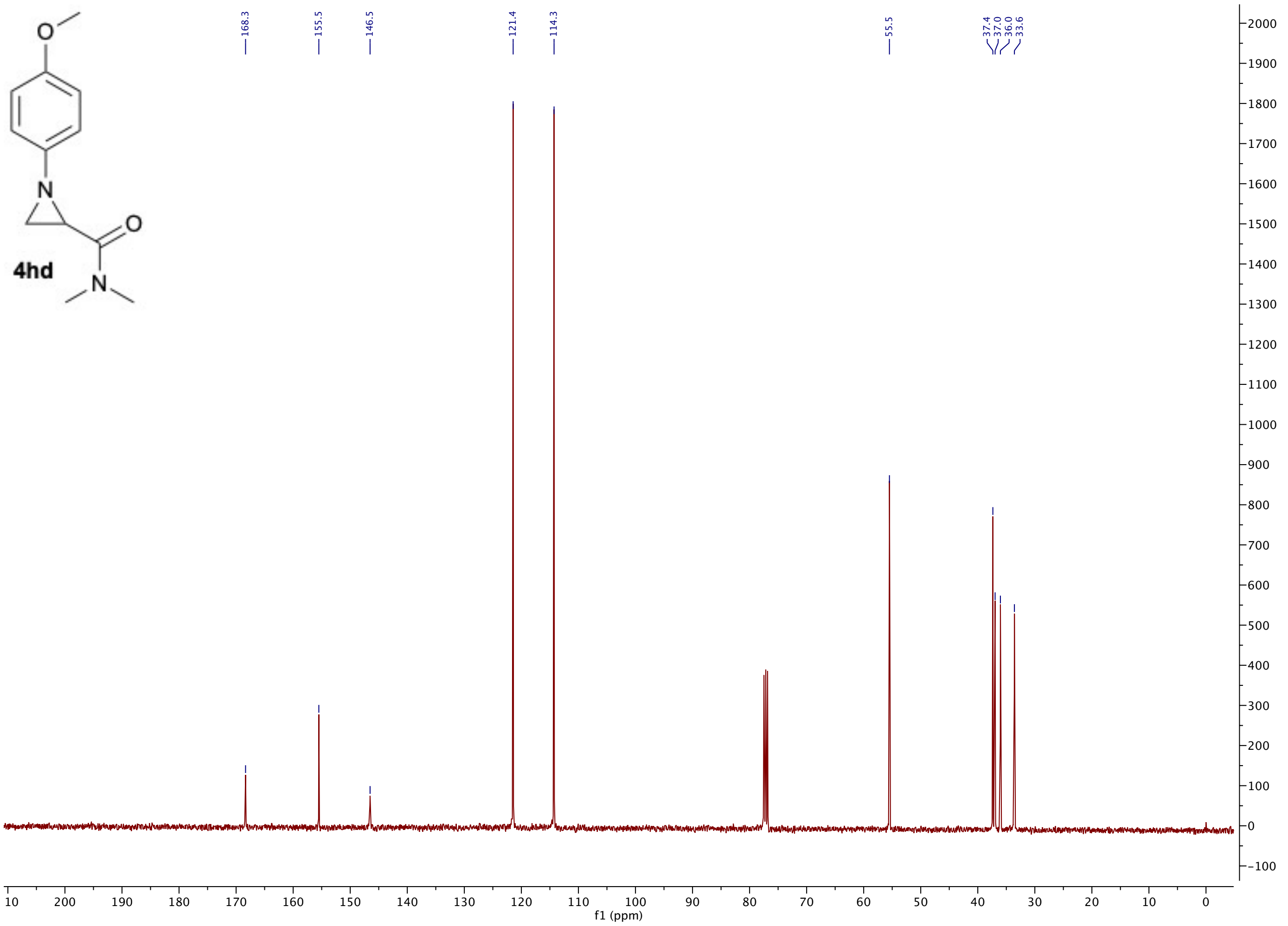
7.00
7.00
6.98
6.98
6.96
6.96
6.92
6.91
6.90
6.90
6.88
6.86
6.84
6.82
3.84
3.25
3.03
2.91
2.73
2.73
2.72
2.72
2.25
2.24
2.24
2.23
1.00
3.16
3.16
3.11
3.13
0.99
1.05
1.07
O
N
O
N
f1 (ppm)
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

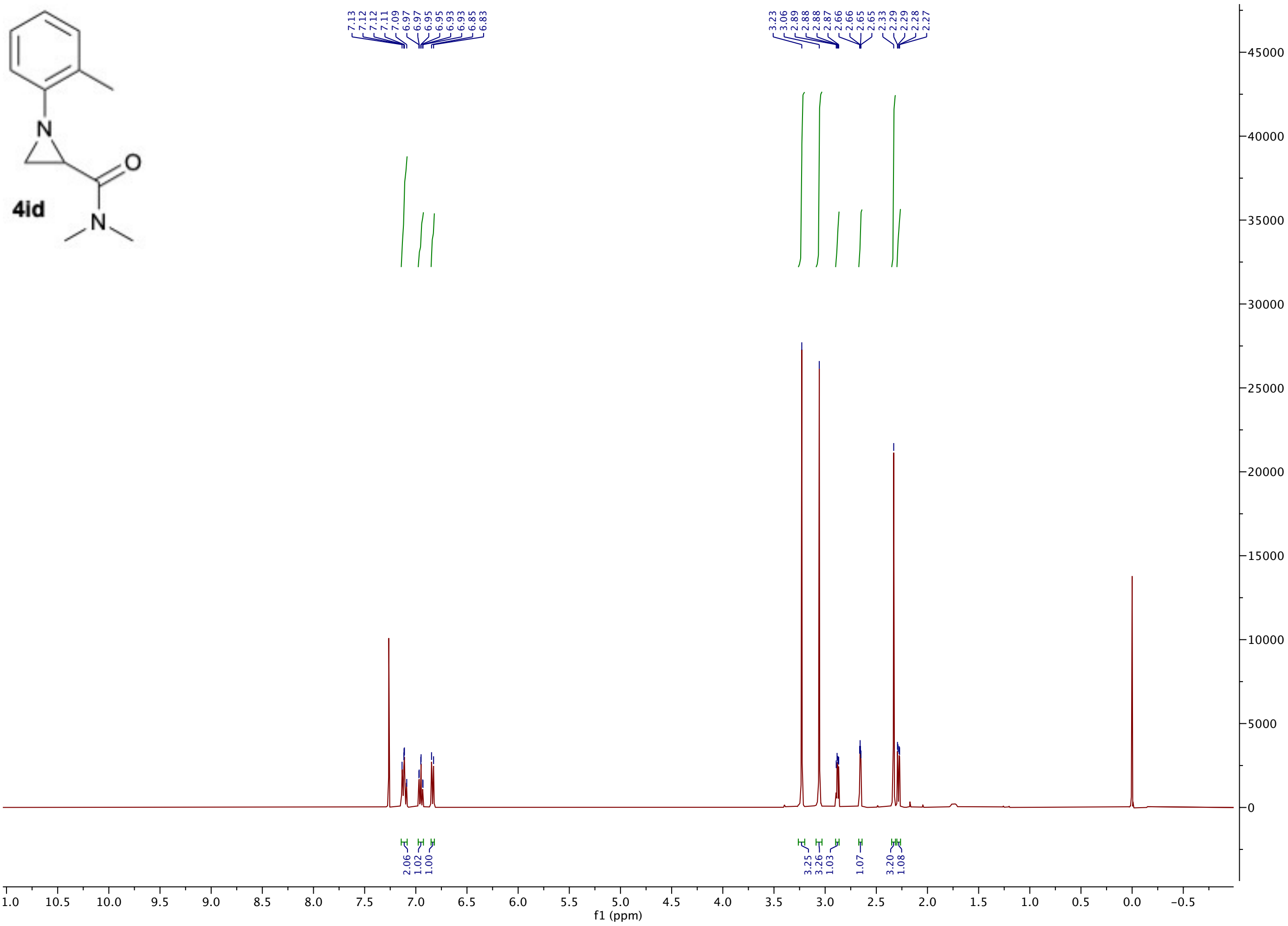


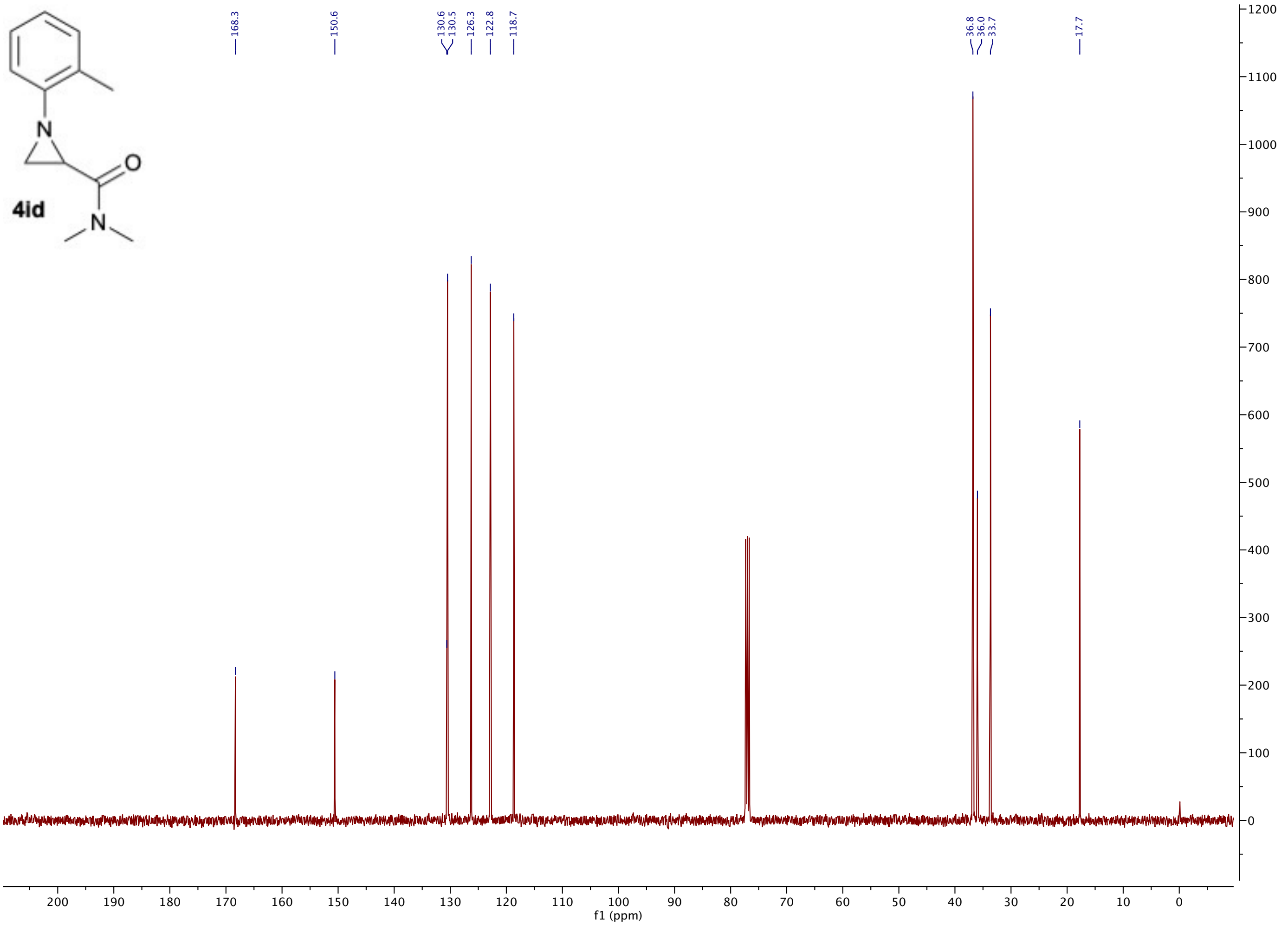
4gd

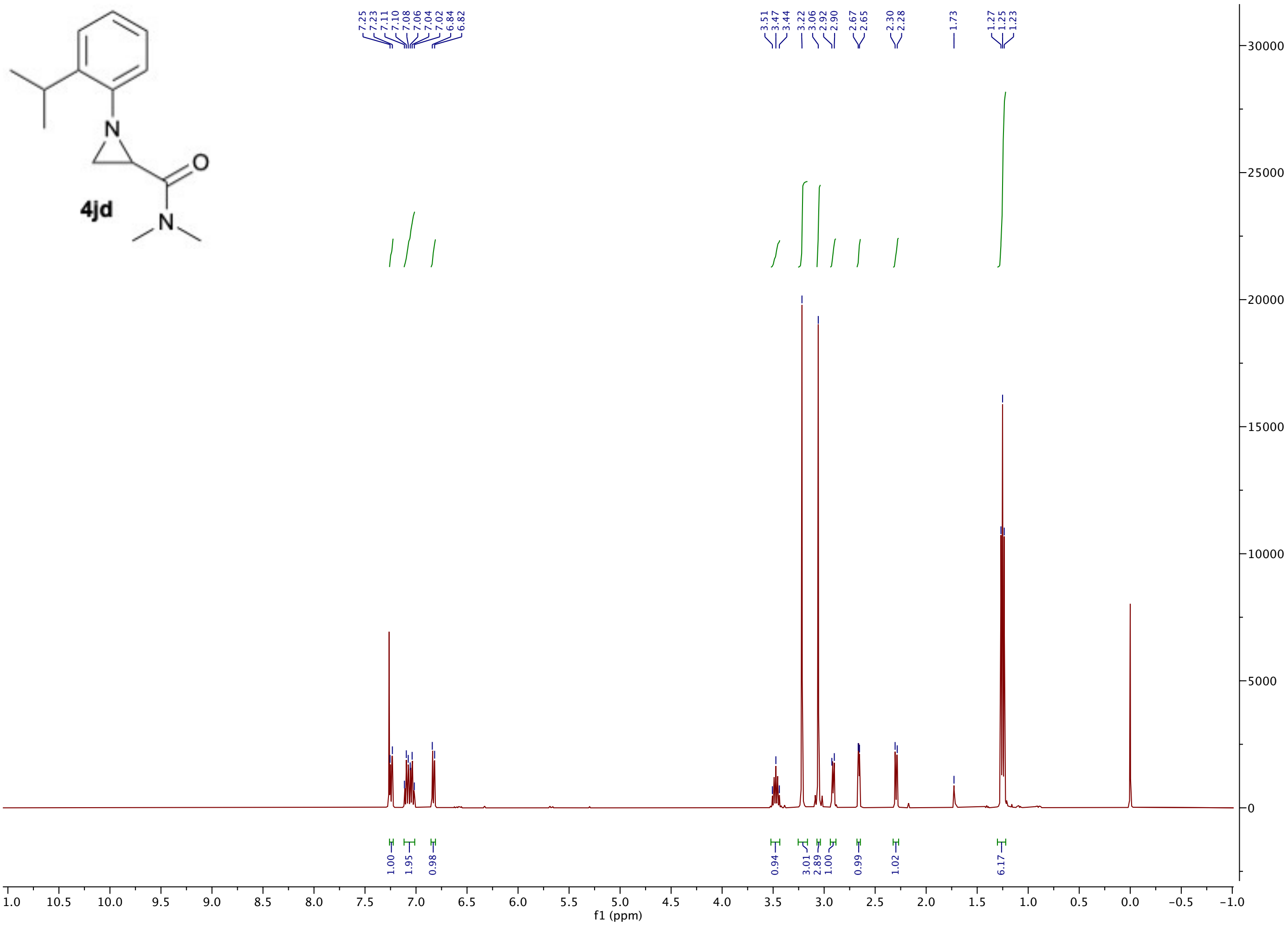
168.5
152.1
141.7
123.3
120.7
120.3
111.1
55.5
36.9
36.3
36.1
33.8
O
N
O
N
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

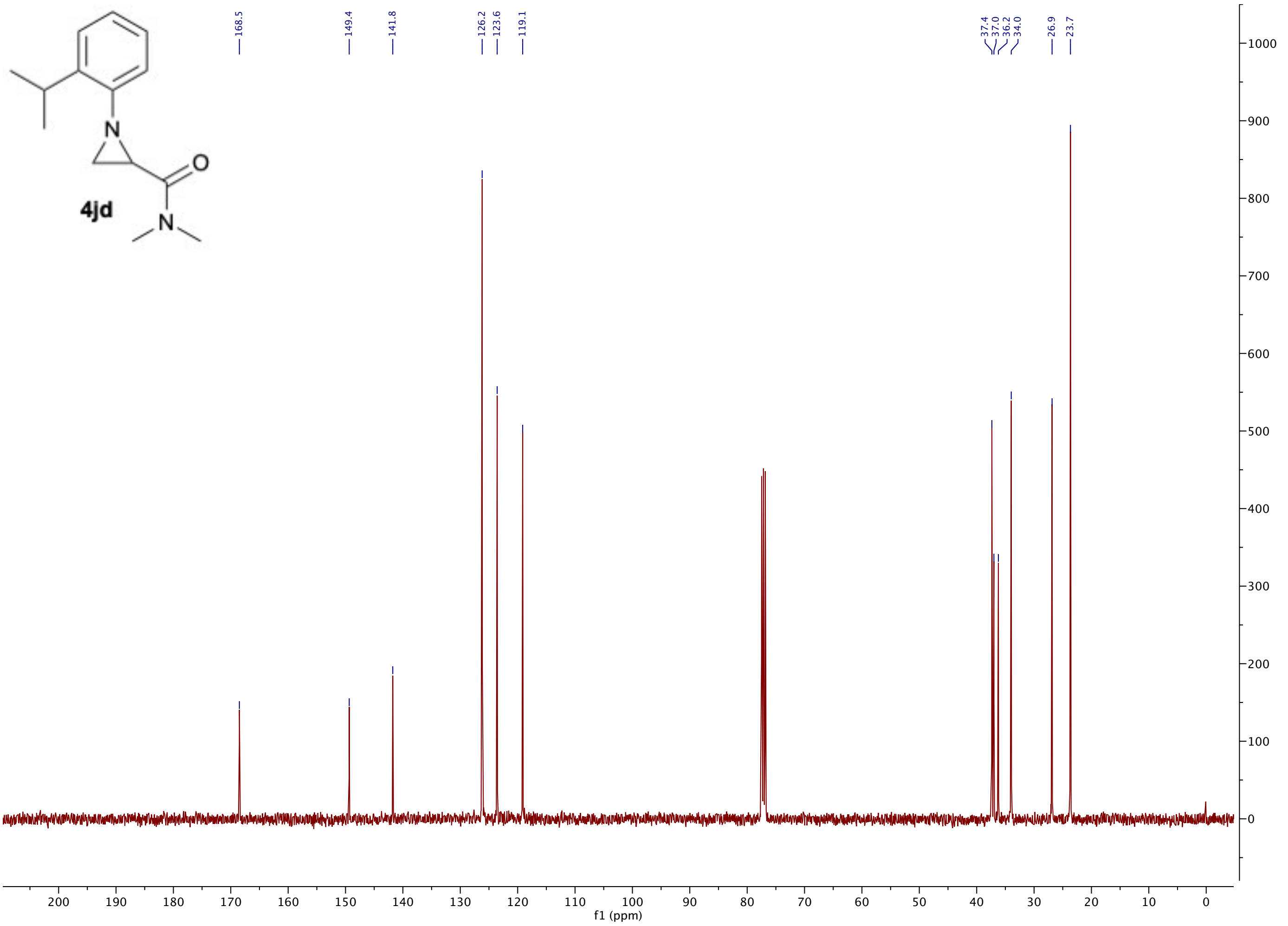

4hd
6.96
6.94
6.80
6.78
3.76
3.25
3.03
2.90
2.89
2.88
2.88
2.62
2.25
2.25
2.24
2.23
1.97
2.01
3.10
2.93
3.00
0.96
0.98
1.00
f1 (ppm)

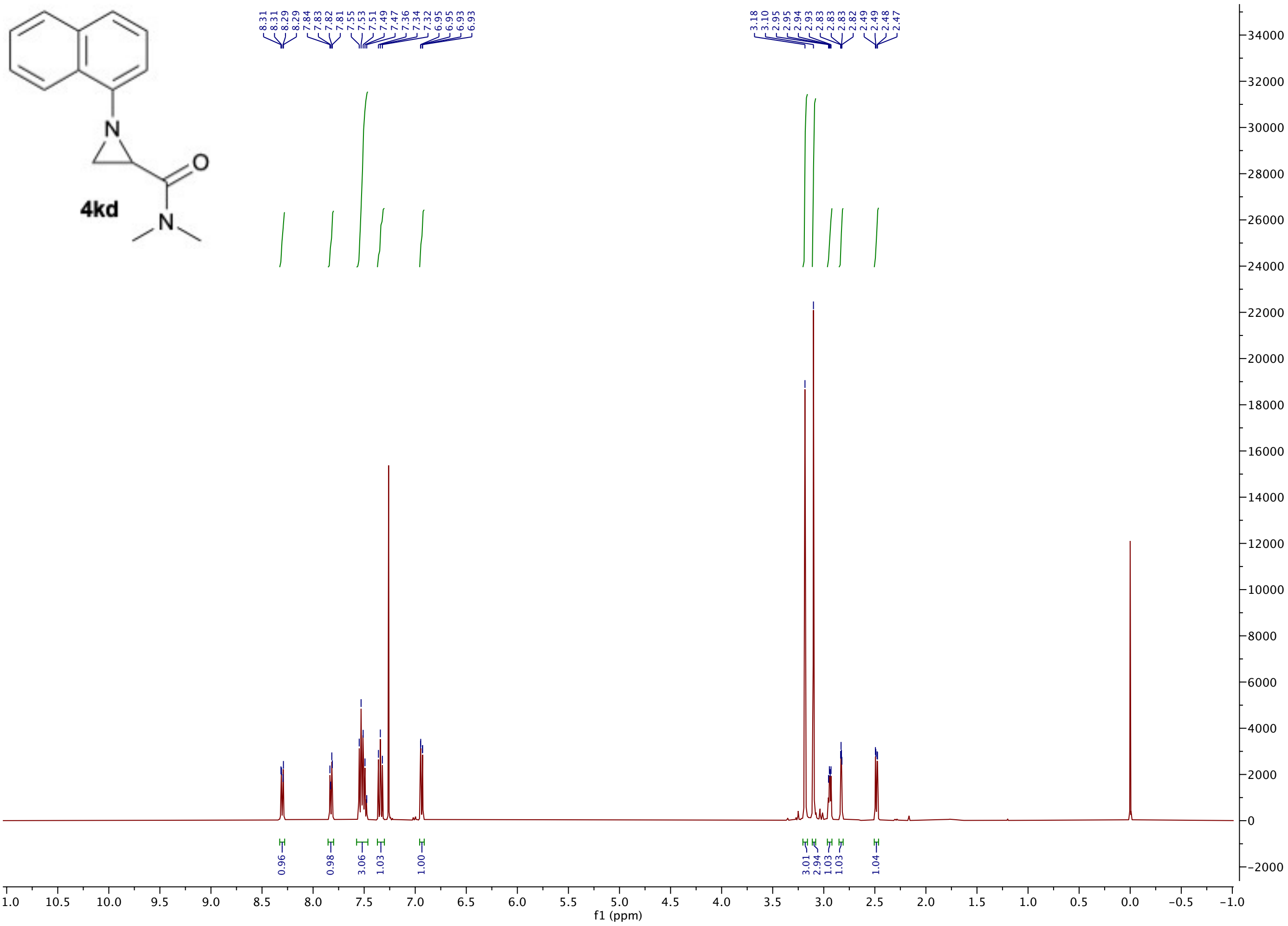

4hd
168.3
155.5
146.5
121.4
114.3
55.5
37.4
37.0
36.0
33.6
f1 (ppm)

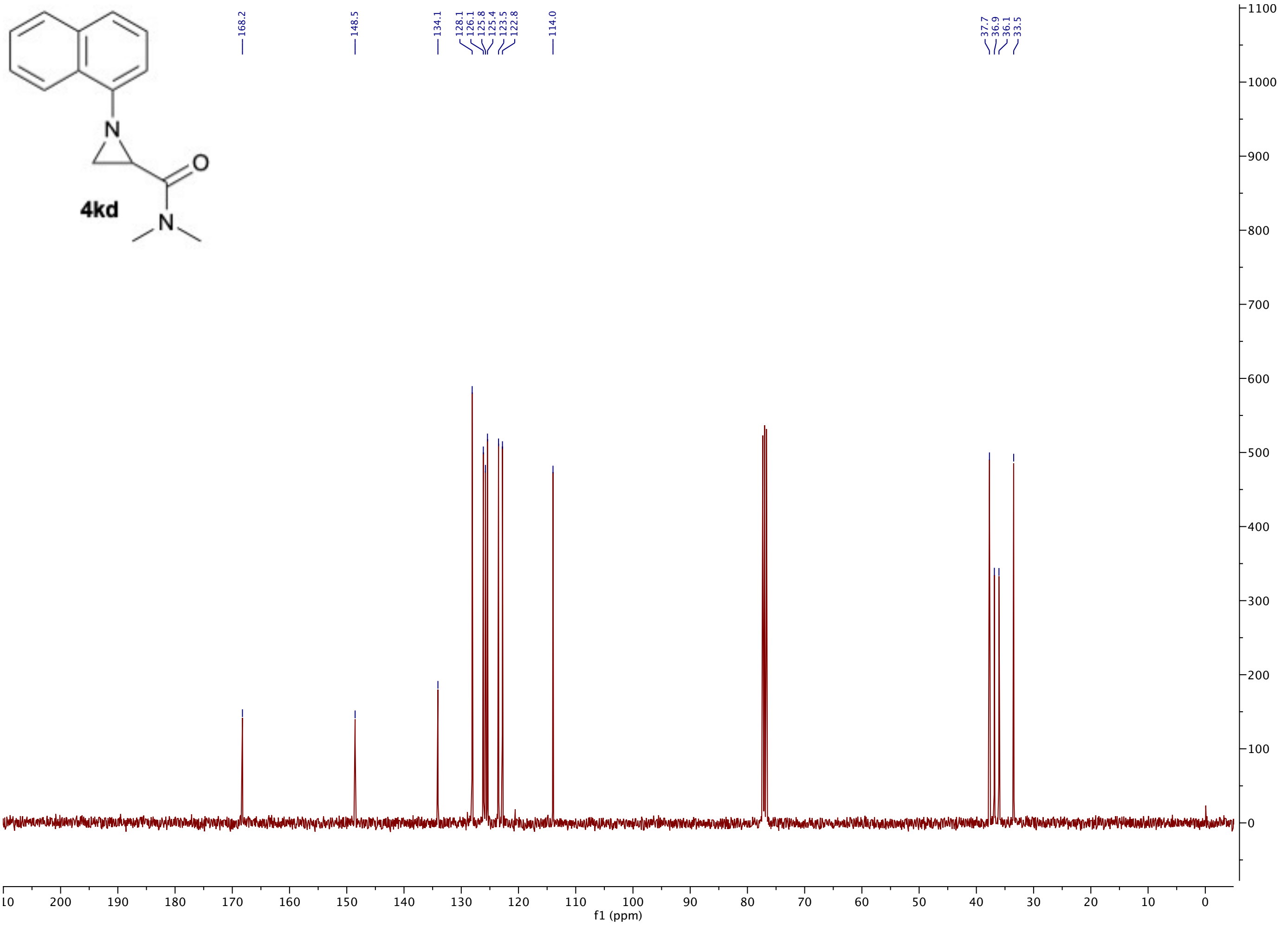

4id
N
O
N
7.13
7.12
7.12
7.11
7.09
6.97
6.97
6.95
6.95
6.93
6.93
6.85
6.83
3.23
3.06
2.89
2.88
2.88
2.87
2.66
2.66
2.65
2.65
2.33
2.29
2.29
2.28
2.27
2.06
1.02
1.00
3.25
3.26
1.03
1.07
3.20
1.08
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

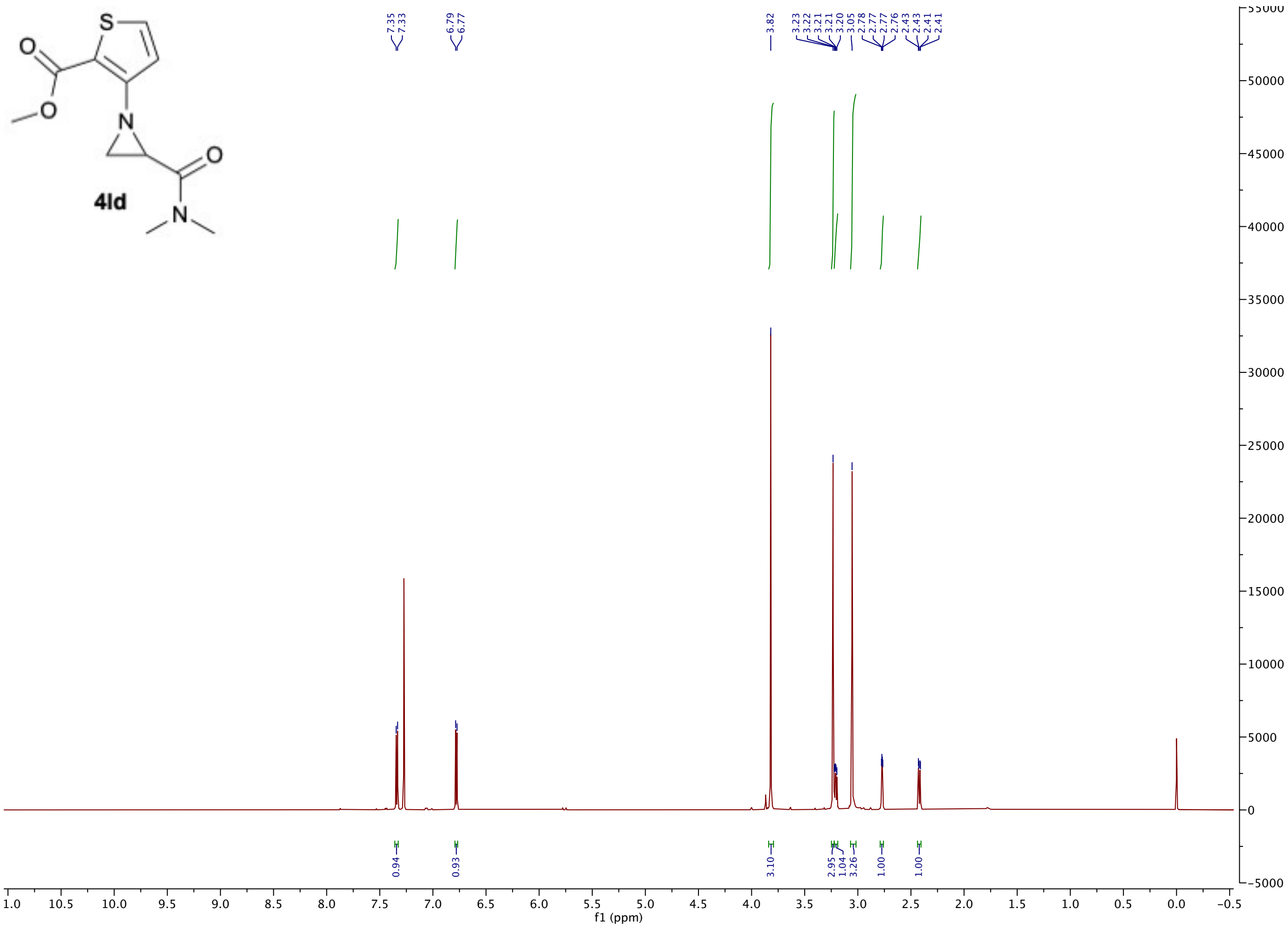

4id
N
O
N
168.3
150.6
130.6
130.5
126.3
122.8
118.7
36.8
36.0
33.7
17.7
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

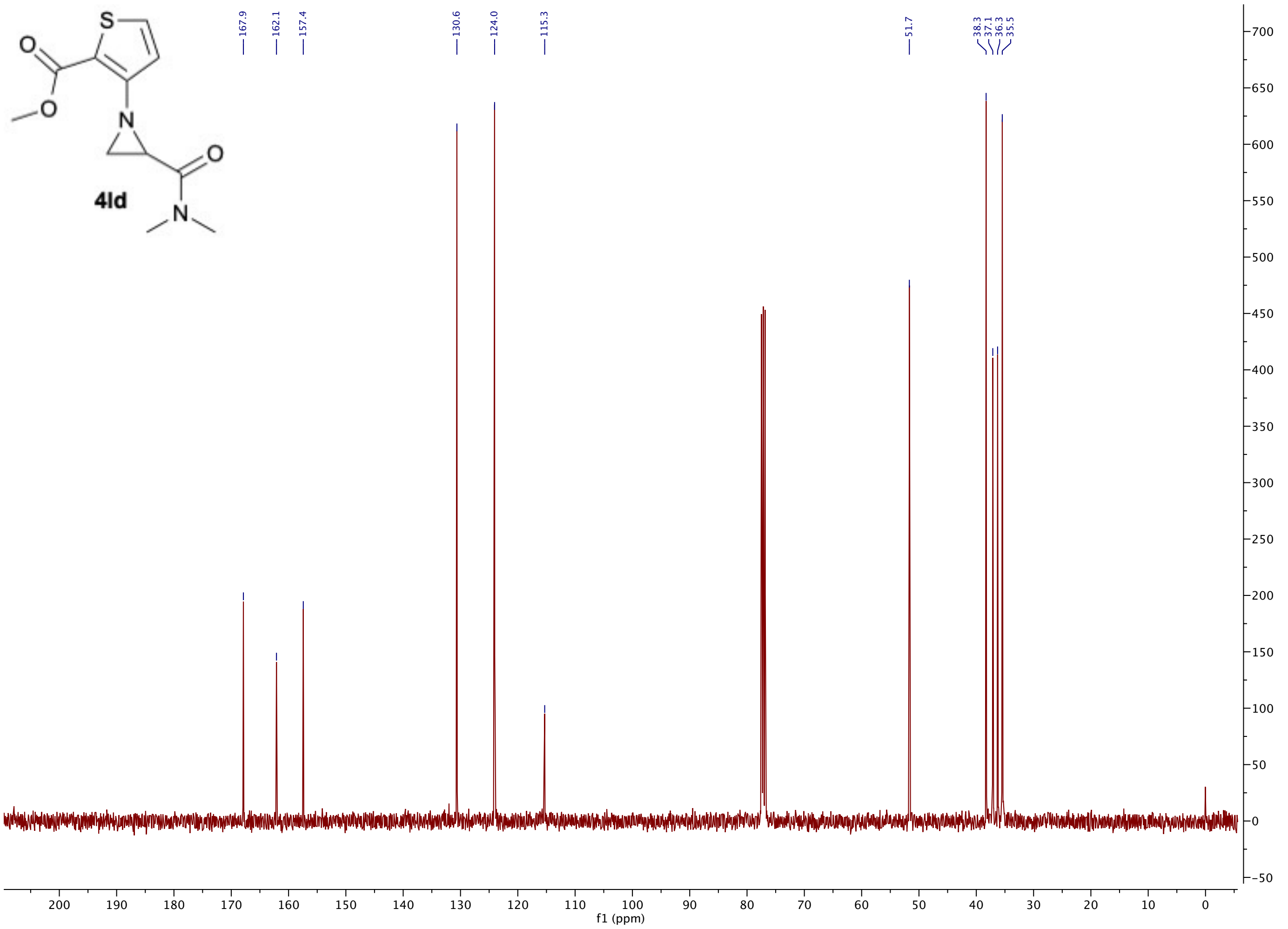

4jd
7.25
7.23
7.11
7.10
7.08
7.06
7.04
7.02
6.84
6.82
3.51
3.47
3.44
3.22
3.06
2.92
2.90
2.67
2.65
2.30
2.28
1.73
1.27
1.25
1.23
1.00
1.95
0.98
0.94
3.01
2.89
1.00
0.99
1.02
6.17
30000
25000
20000
15000
10000
5000
0
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

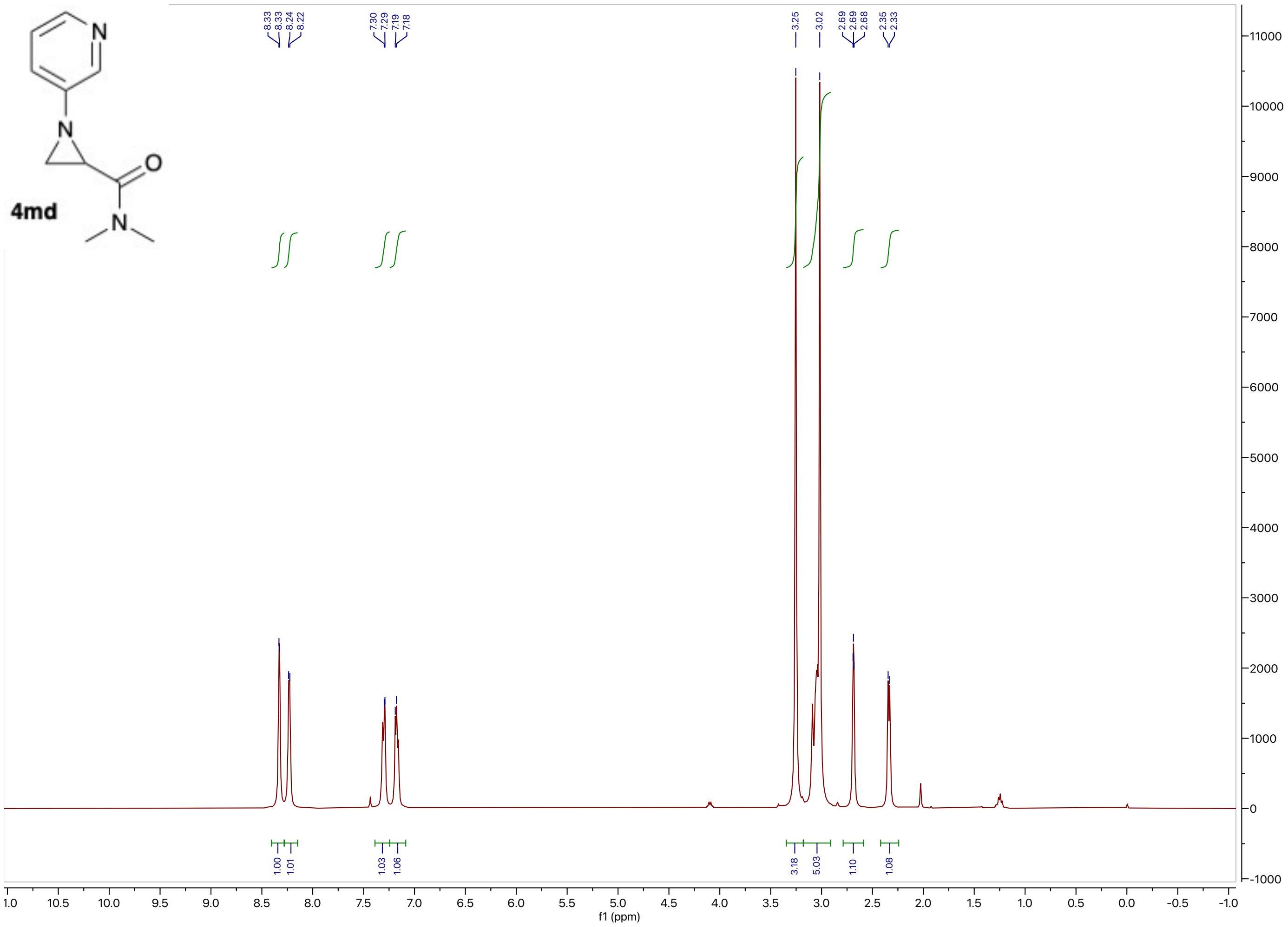

4jd
168.5
149.4
141.8
126.2
123.6
119.1
37.4
37.0
36.2
34.0
26.9
23.7
1000
900
800
700
600
500
400
300
200
100
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

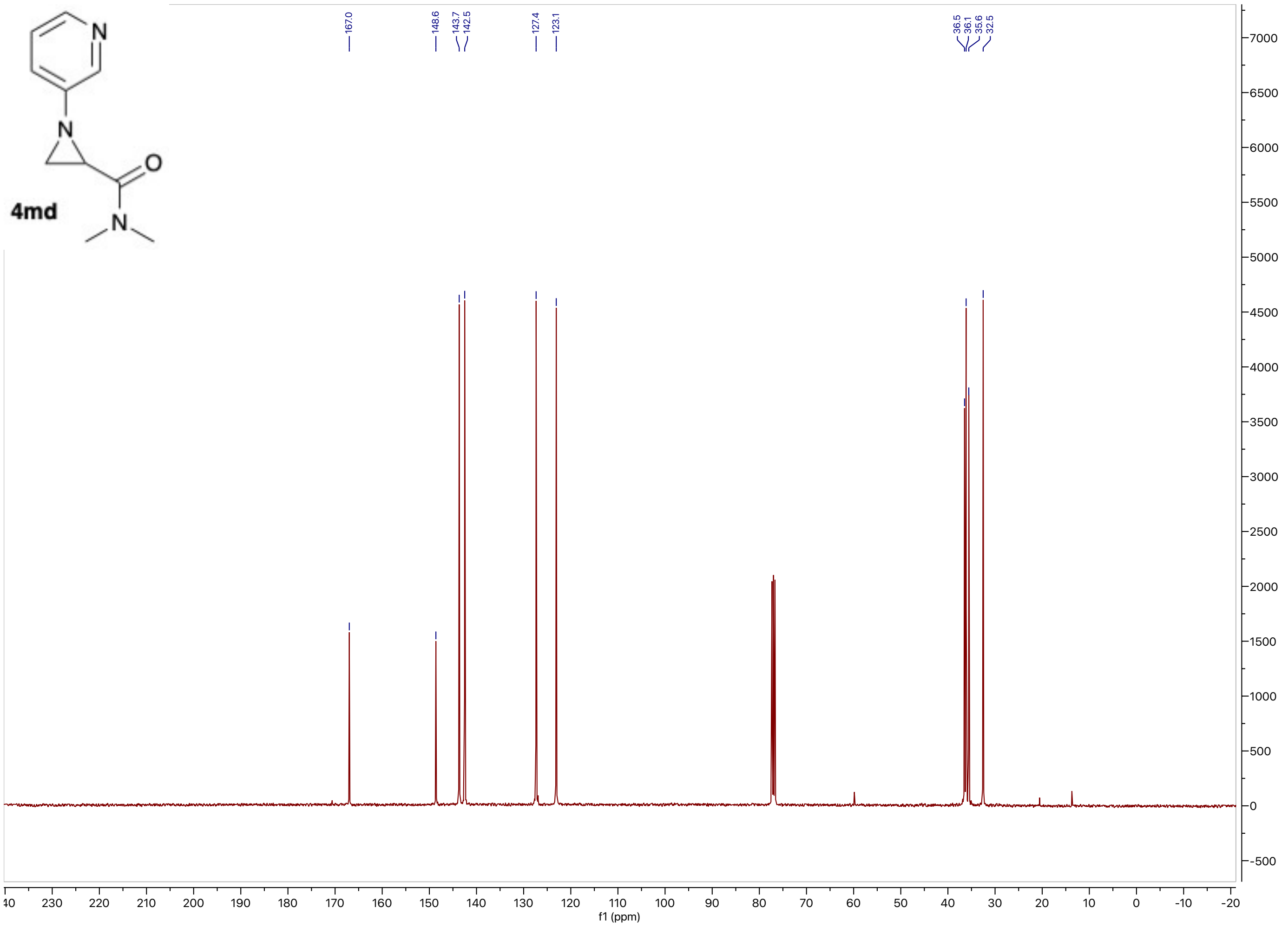

4kd
8.31
8.31
8.29
8.29
7.84
7.83
7.82
7.81
7.55
7.53
7.51
7.49
7.47
7.36
7.34
7.32
6.95
6.95
6.93
6.93
3.18
3.10
2.95
2.95
2.94
2.93
2.83
2.83
2.82
2.82
2.49
2.48
2.47
0.96
0.98
3.06
1.03
1.00
3.01
2.94
1.03
1.03
1.04
f1 (ppm)

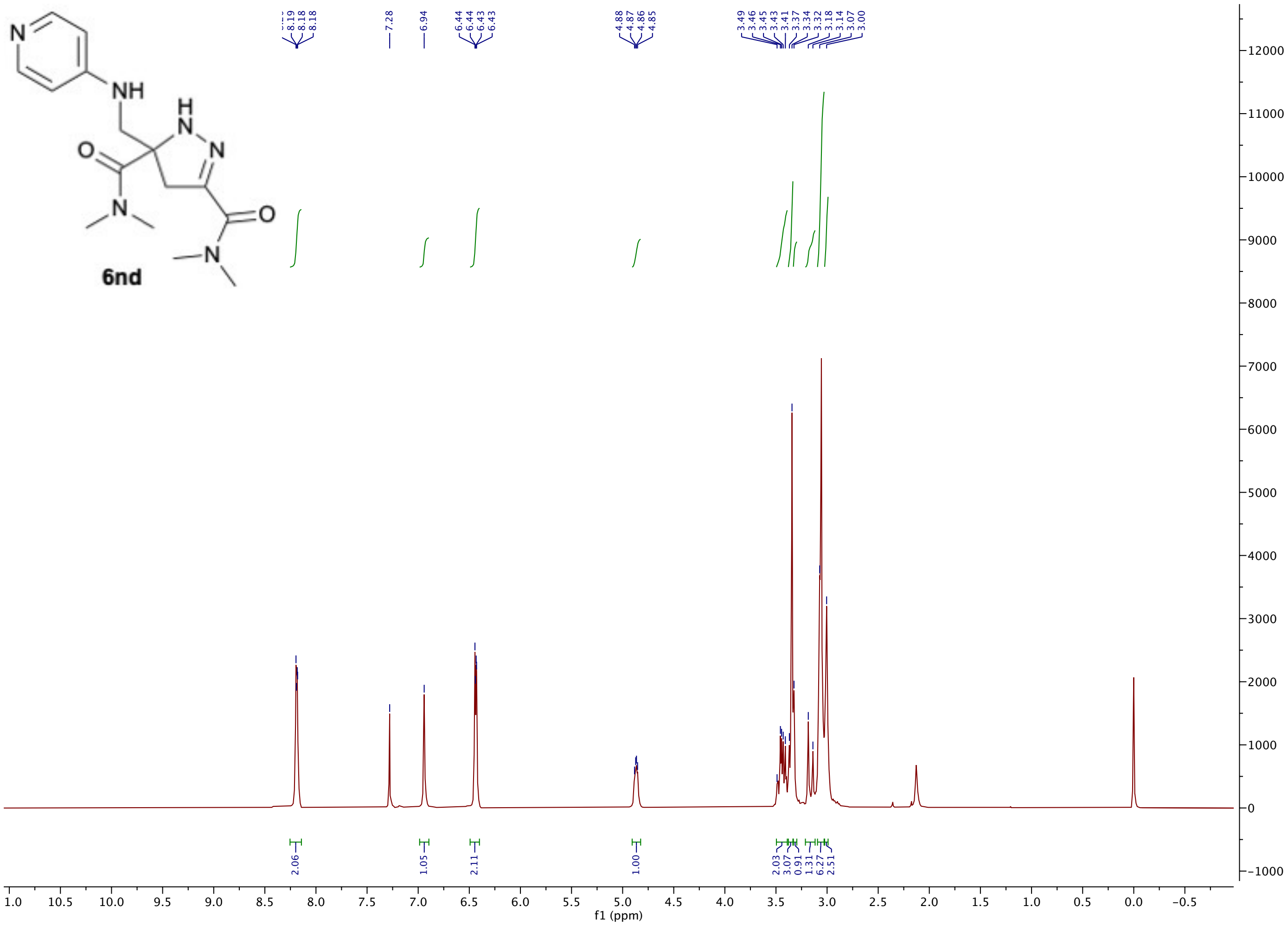

4kd
168.2
148.5
134.1
128.1
126.1
125.8
125.4
123.5
122.8
114.0
37.7
36.9
36.1
33.5
f1 (ppm)

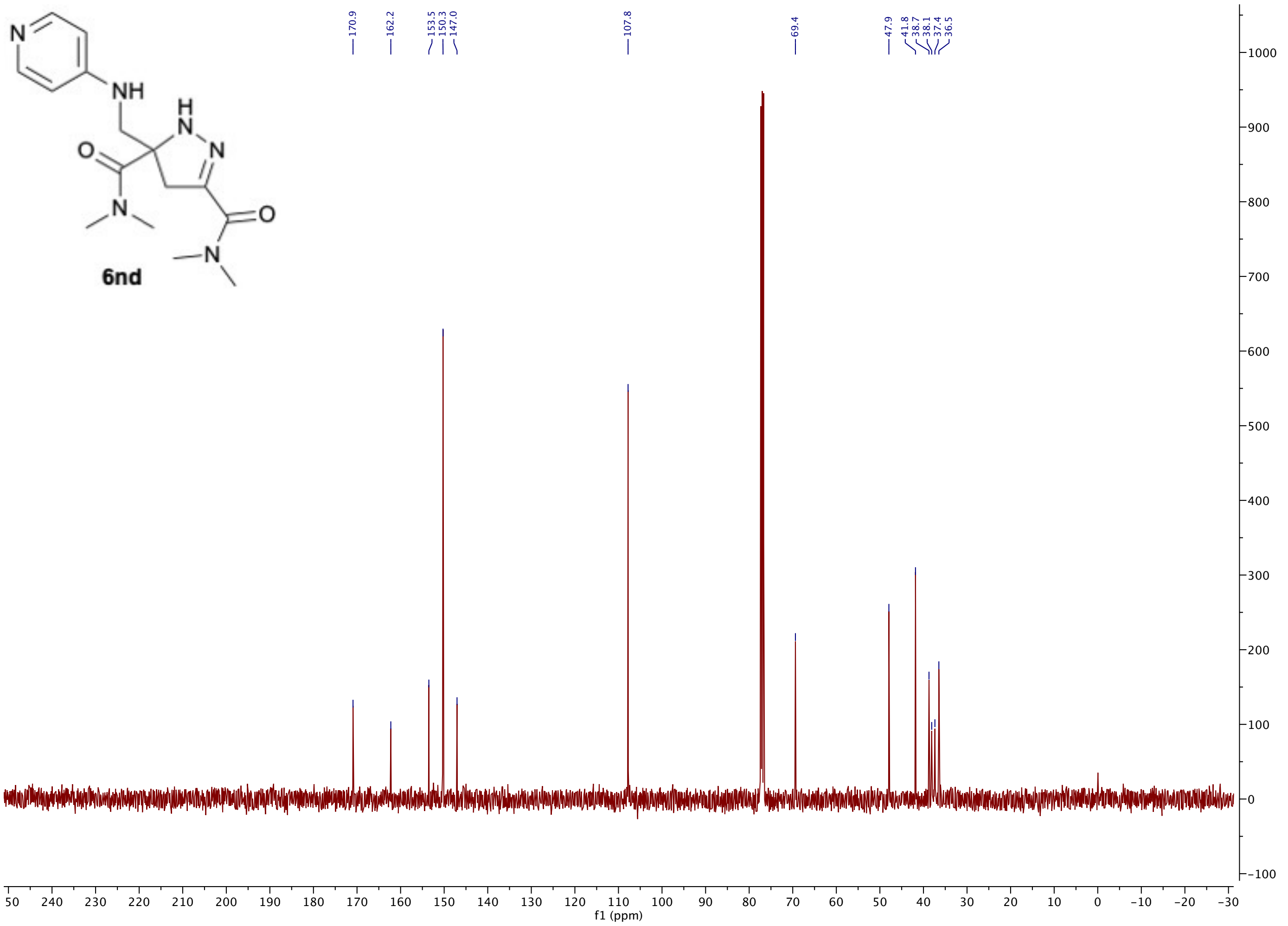

S
O
O
N
O
N
4ld
7.35
7.33
6.79
6.77
3.82
3.23
3.22
3.21
3.21
3.20
3.05
2.78
2.77
2.77
2.76
2.43
2.43
2.41
2.41
0.94
0.93
3.10
2.95
1.04
3.26
1.00
1.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

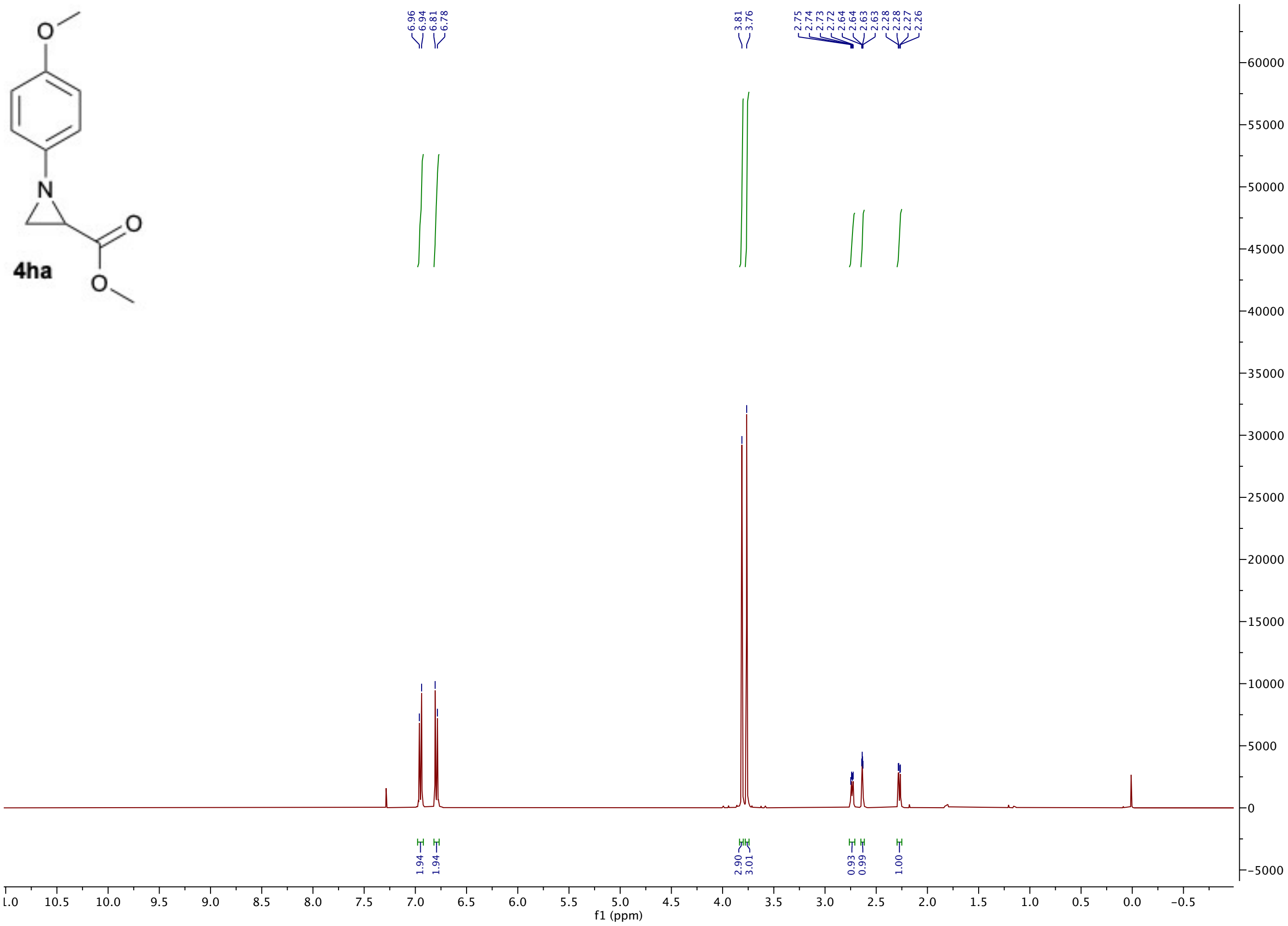

S
O
O
N
O
N
4ld
167.9
162.1
157.4
130.6
124.0
115.3
51.7
38.3
37.1
36.3
35.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

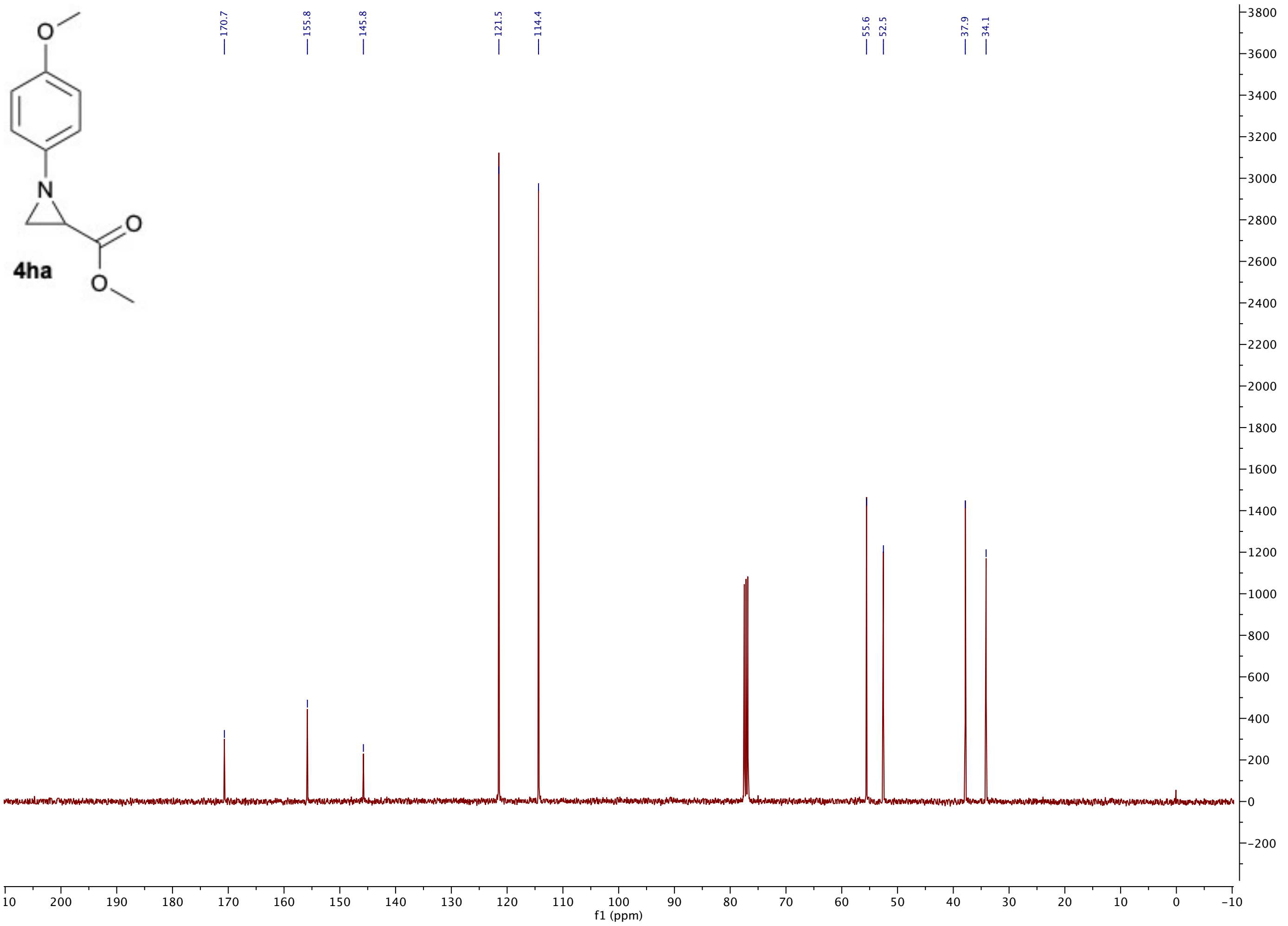

4md
N
N
O
N
8.33
8.33
8.24
8.22
7.30
7.29
7.19
7.18
3.25
3.02
2.69
2.69
2.68
2.35
2.33
1.00
1.01
1.03
1.06
3.18
5.03
1.10
1.08
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

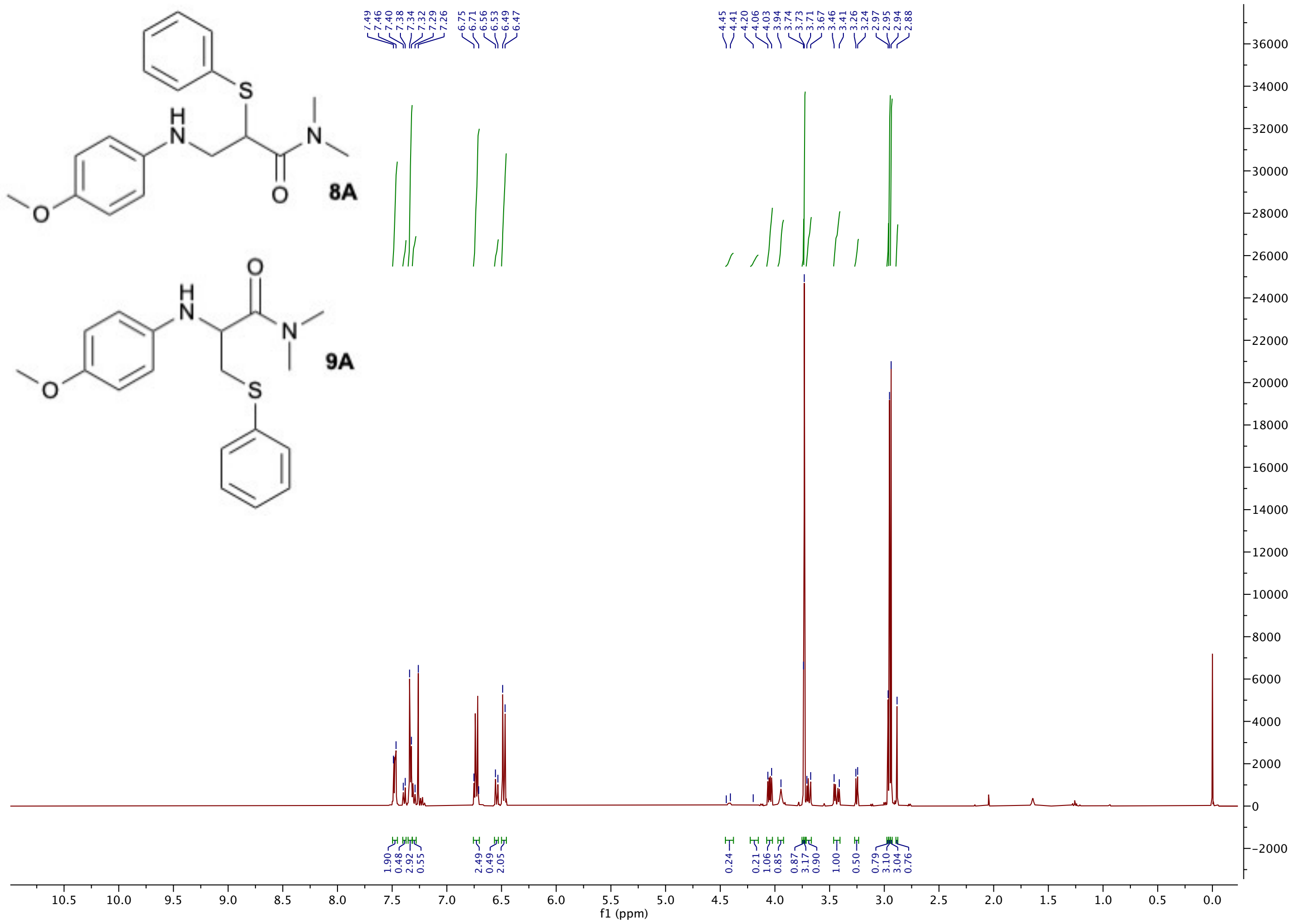

4md
N
N
O
N
167.0
148.6
143.7
142.5
127.4
123.1
36.5
36.1
35.6
32.5
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

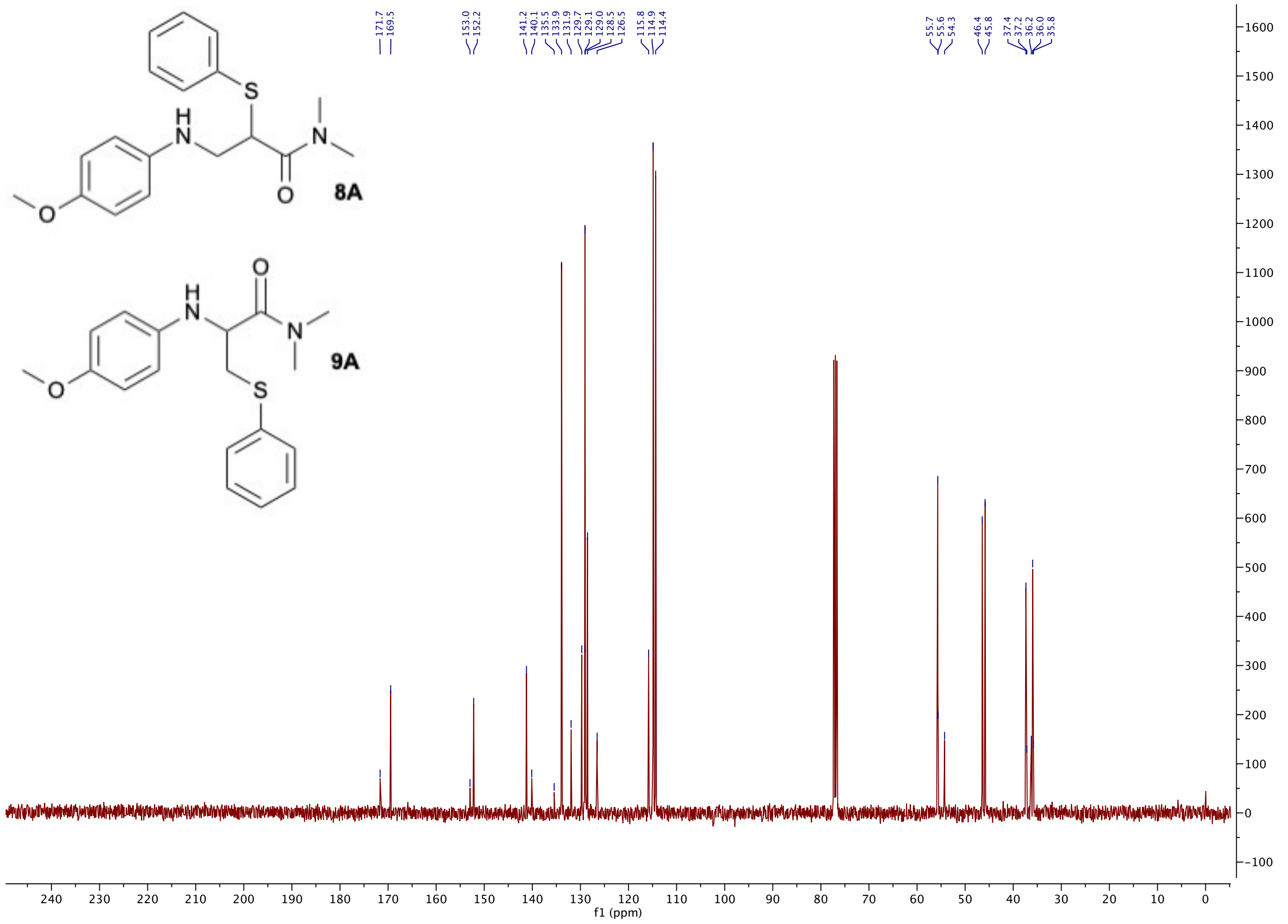

N
NH
H
N
N
O
N
O
N
6nd
8.19
8.18
8.18
7.28
6.94
6.44
6.44
6.43
6.43
4.88
4.87
4.86
4.85
3.49
3.46
3.45
3.43
3.41
3.37
3.34
3.32
3.18
3.14
3.07
3.00
2.06
1.05
2.11
1.00
2.03
3.07
0.91
1.31
6.27
2.51
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

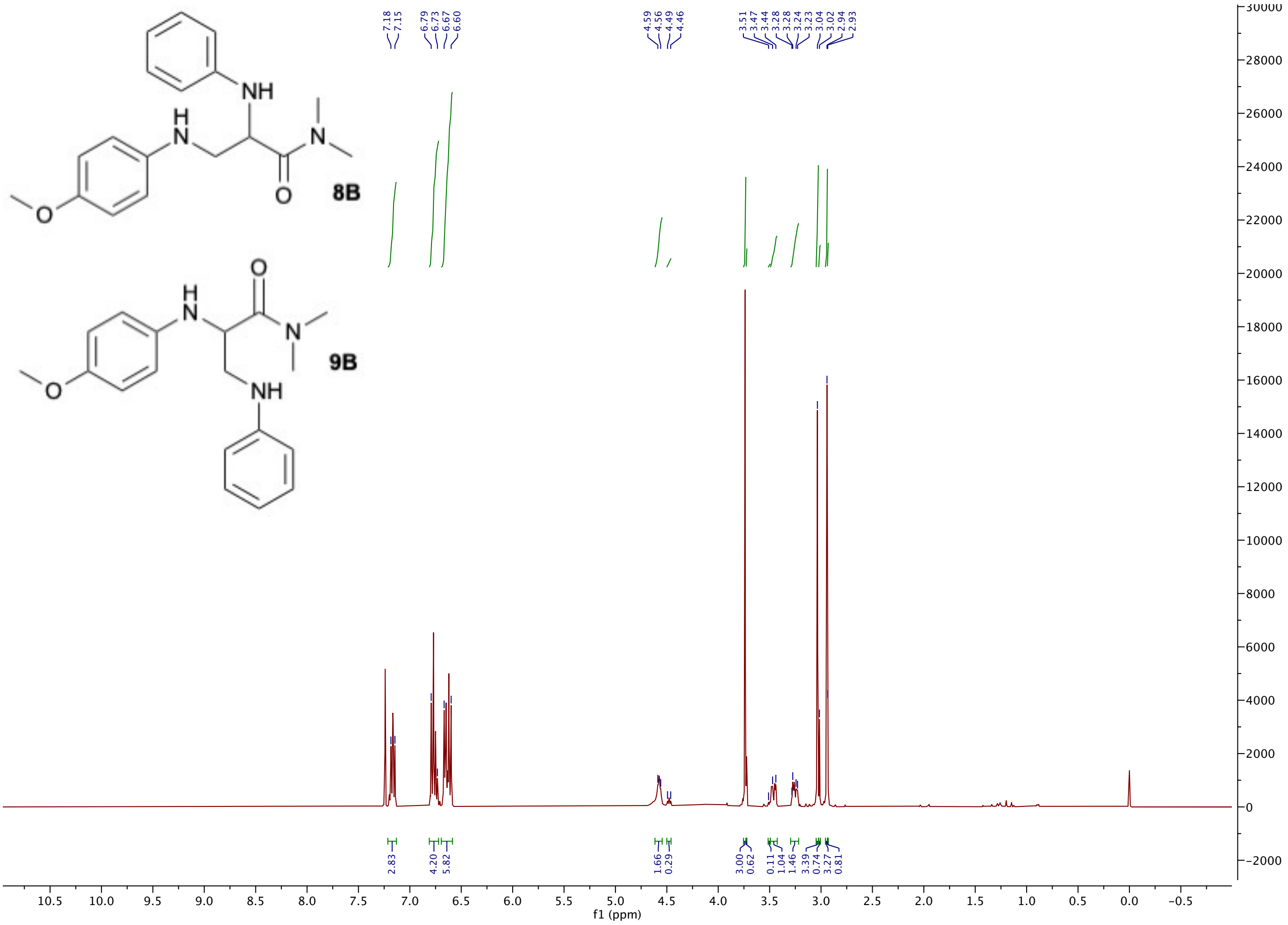

N
NH
H
N
N
O
N
O
N
6nd
170.9
162.2
153.5
150.3
147.0
107.8
69.4
47.9
41.8
38.7
38.1
37.4
36.5
1000
900
800
700
600
500
400
300
200
100
0
−100
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)

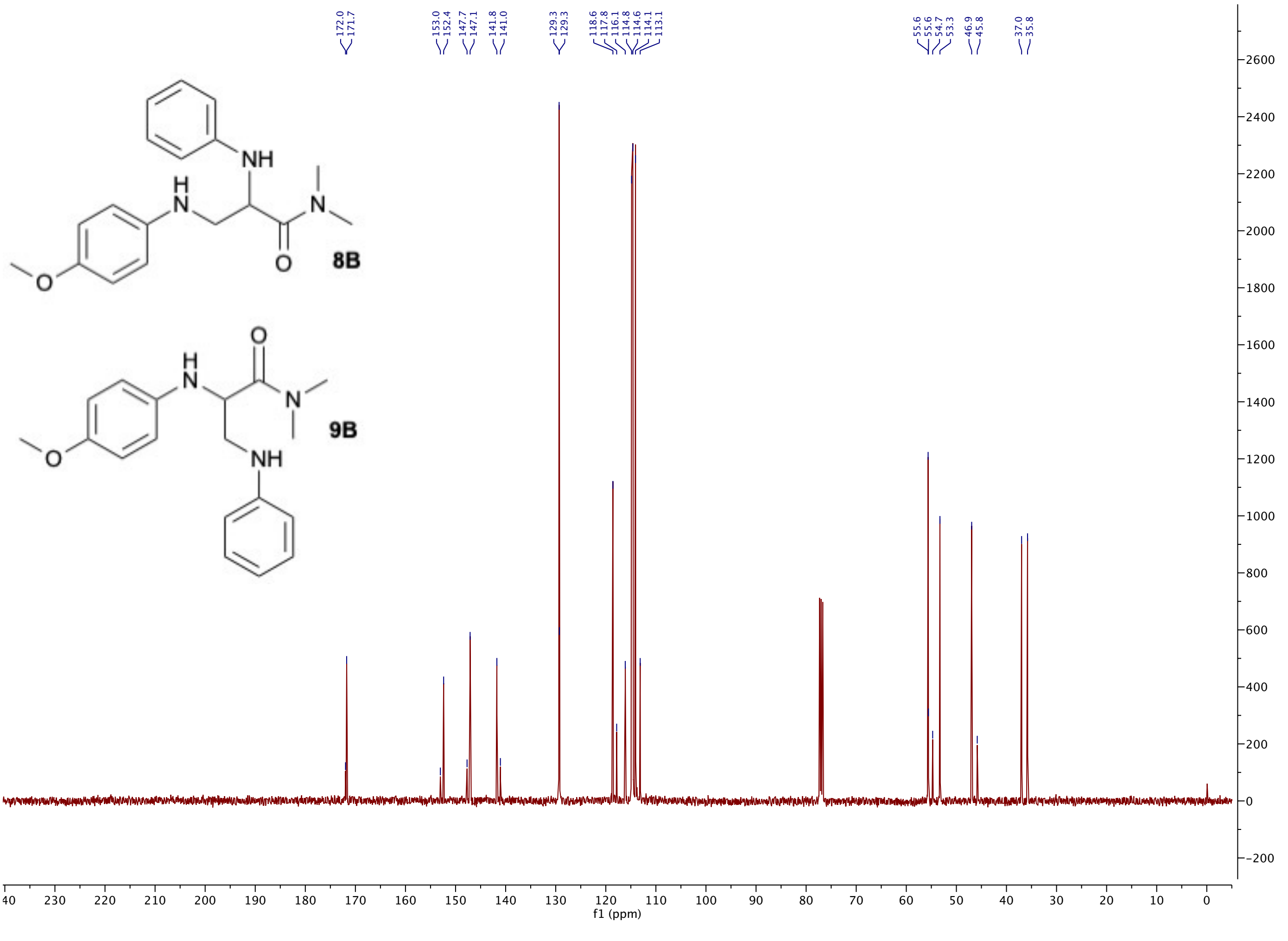

O
N
O
O
4ha
6.96
6.94
6.81
6.78
3.81
3.76
2.75
2.74
2.73
2.72
2.64
2.64
2.63
2.63
2.28
2.28
2.27
2.26
1.94
1.94
2.90
3.01
0.93
0.99
1.00
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

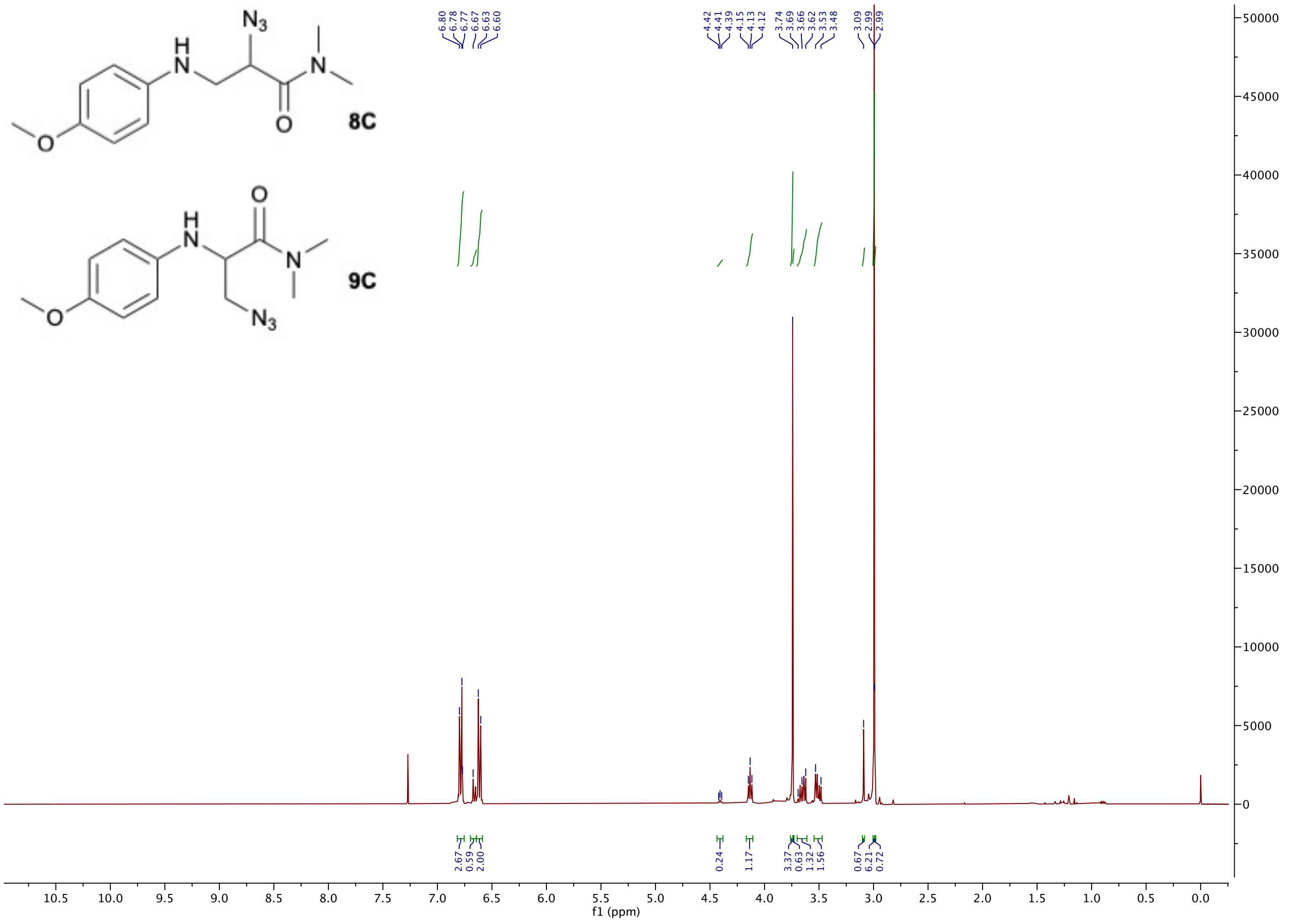

O
N
O
O
4ha
170.7
155.8
145.8
121.5
114.4
55.6
52.5
37.9
34.1
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

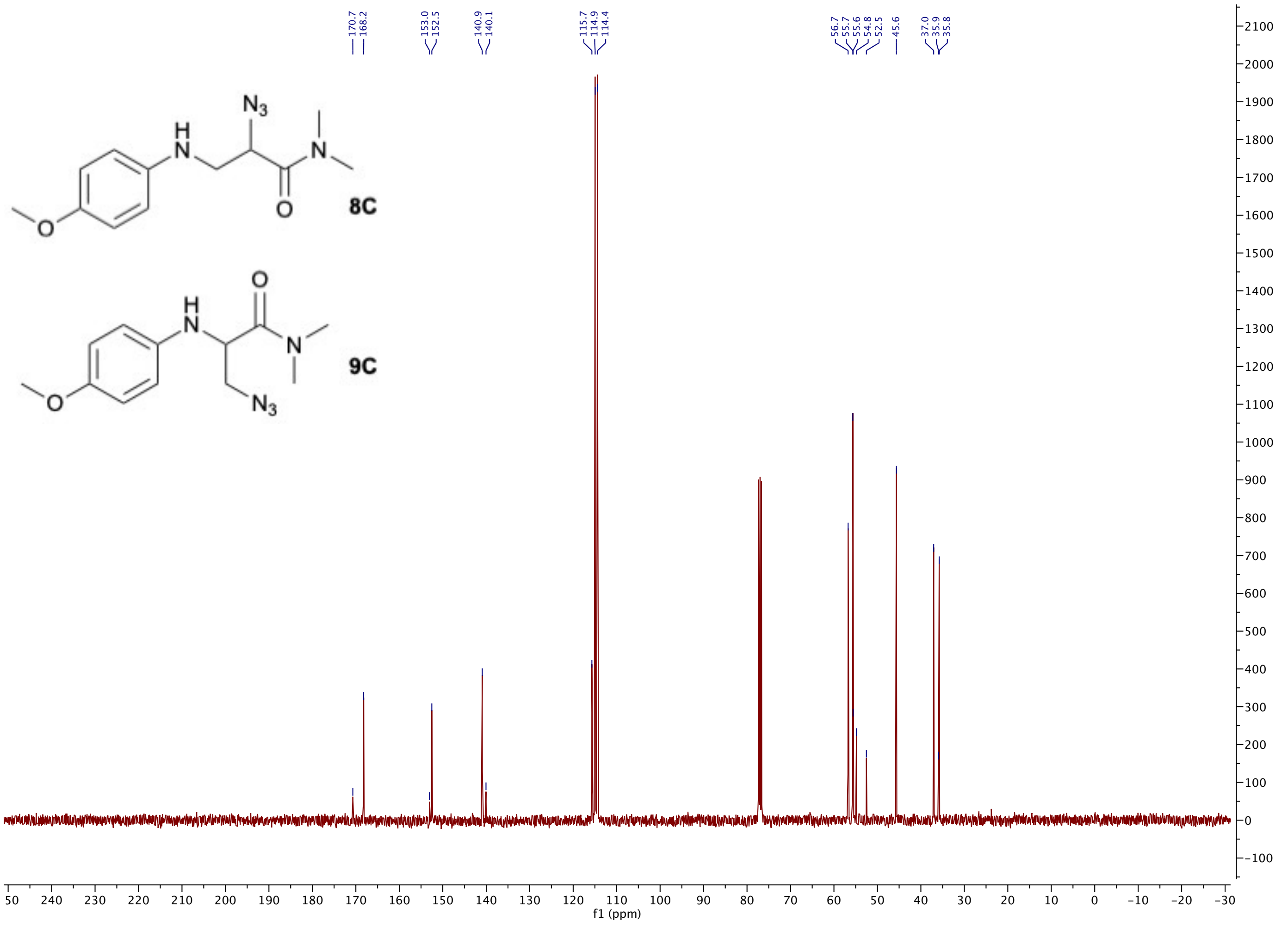

8A
9A
7.49
7.46
7.40
7.38
7.34
7.32
7.29
7.26
6.75
6.71
6.56
6.53
6.49
6.47
4.45
4.41
4.20
4.06
4.03
3.94
3.74
3.73
3.71
3.67
3.46
3.41
3.26
3.24
2.97
2.95
2.94
2.88
1.90
0.48
2.92
0.55
2.49
0.49
2.05
0.24
0.21
1.06
0.85
0.87
3.17
0.90
1.00
0.50
0.79
3.10
3.04
0.76
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

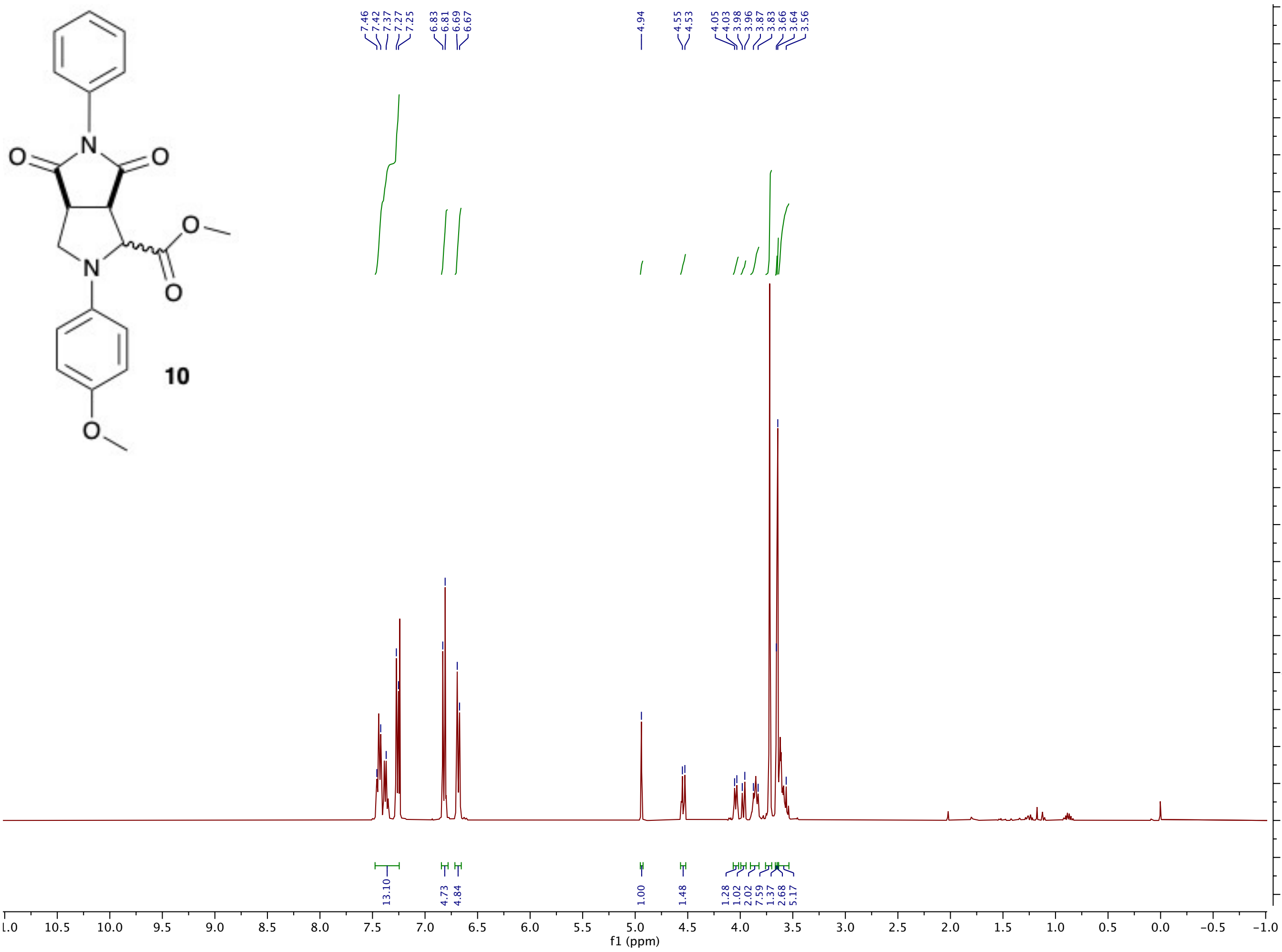

8A
9A
171.7
169.5
153.0
152.2
141.2
140.1
135.5
133.9
131.9
129.7
129.1
129.0
128.5
126.5
115.8
114.9
114.4
55.7
55.6
54.3
46.4
45.8
37.4
37.2
36.2
36.0
35.8
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

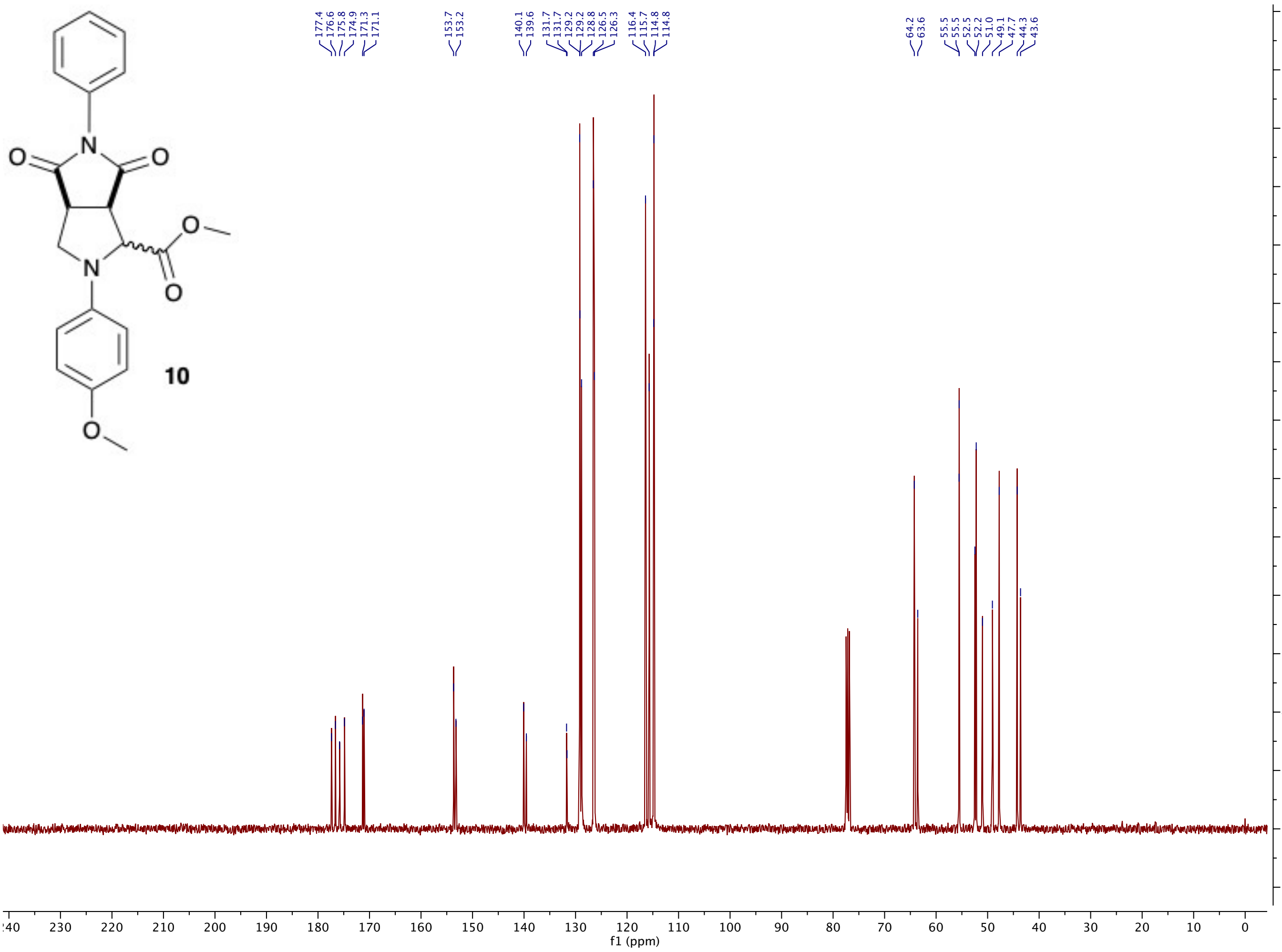

8B
9B
7.18
7.15
6.79
6.73
6.67
6.60
4.59
4.56
4.49
4.46
3.51
3.47
3.44
3.28
3.24
3.23
3.04
3.02
2.94
2.93
2.83
4.20
5.82
1.66
0.29
3.00
0.62
0.11
1.04
1.46
3.39
0.74
3.27
0.81
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

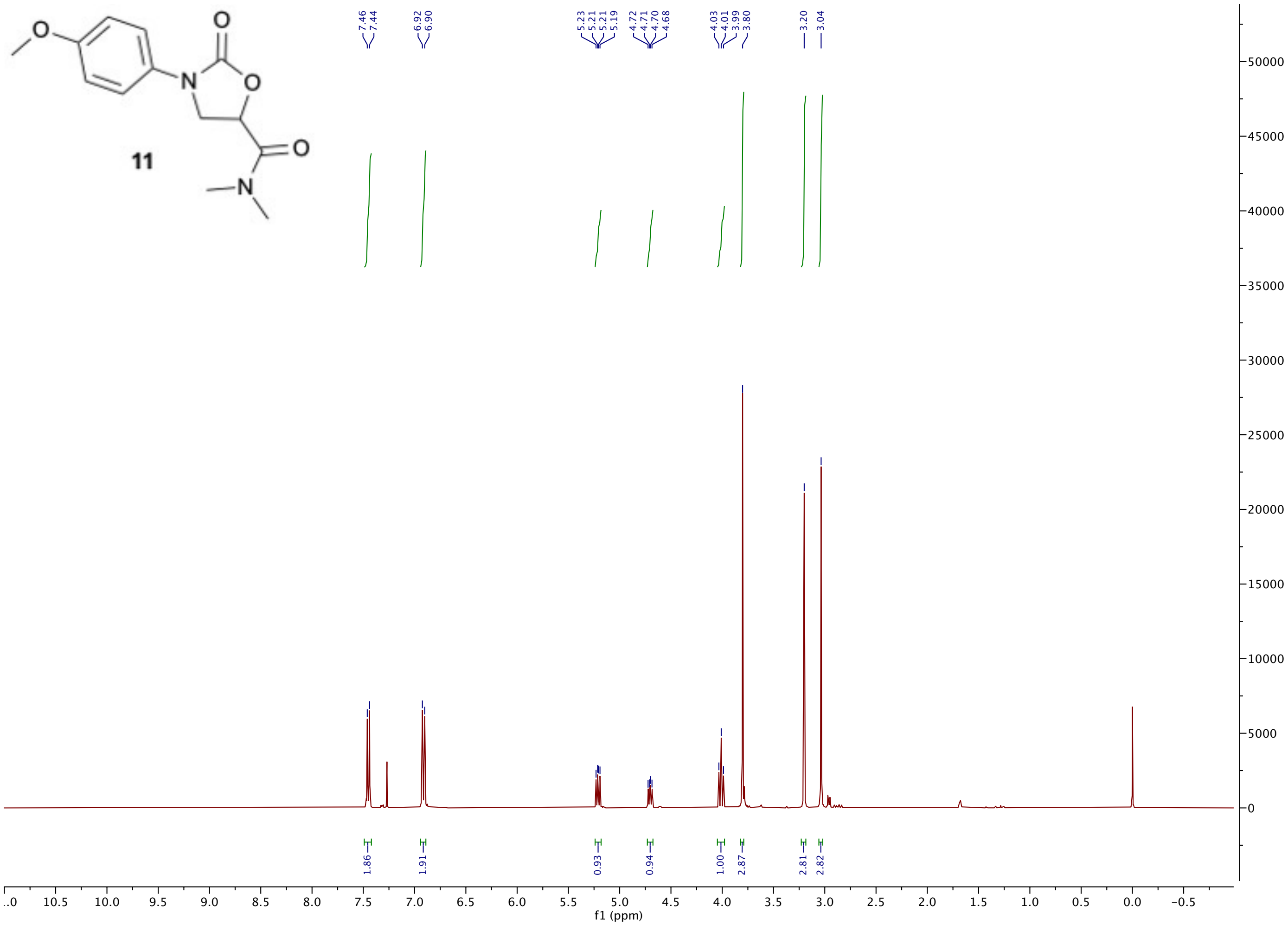

8B
9B
172.0
171.7
153.0
152.4
147.7
147.1
141.8
141.0
129.3
129.3
118.6
117.8
116.1
114.8
114.6
114.1
113.1
55.6
55.6
54.7
53.3
46.9
45.8
37.0
35.8
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

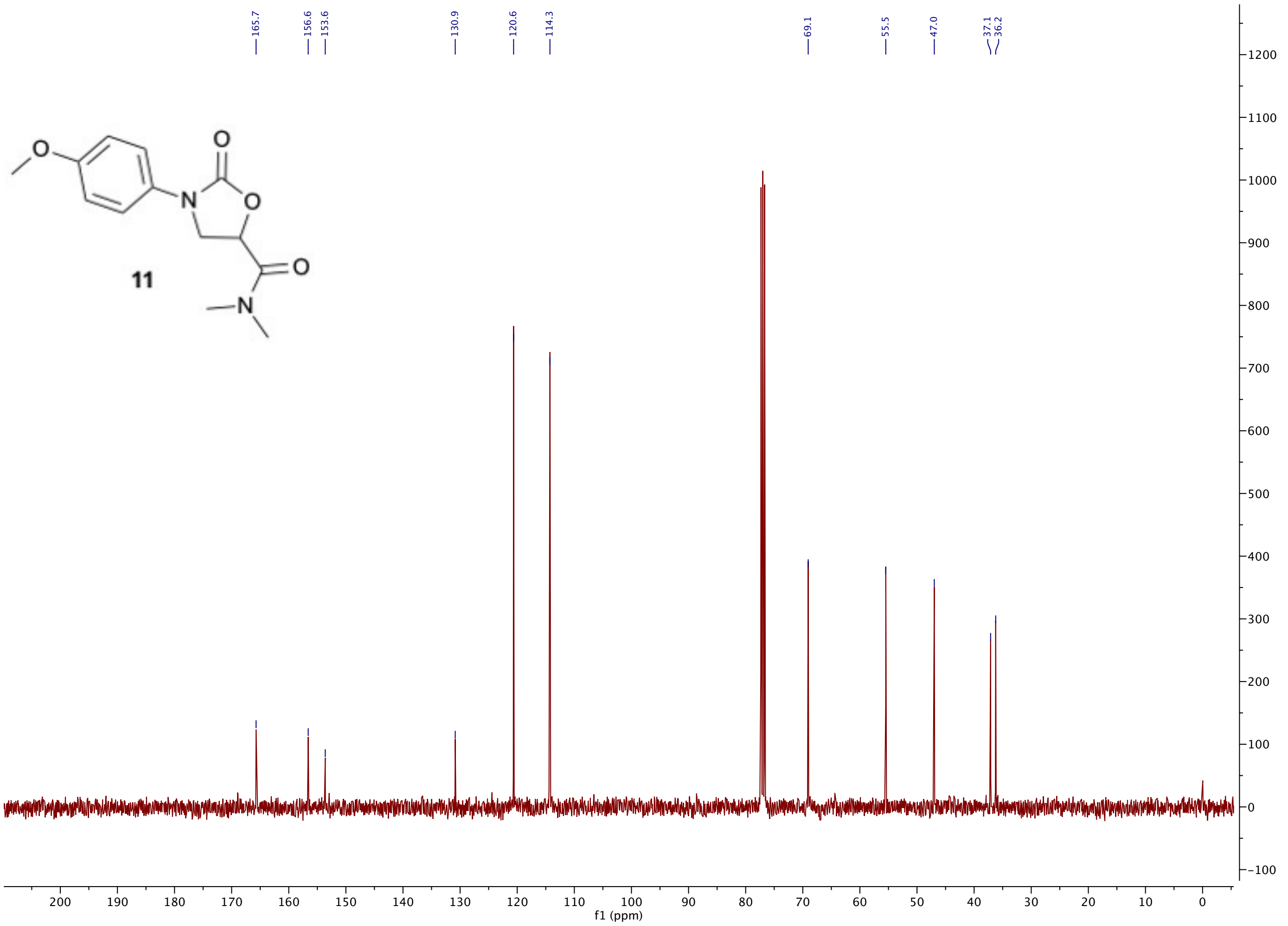

N3
H
N
N
O
O
8C
O
H
N
N
O
N3
9C
6.80
6.78
6.77
6.67
6.63
6.60
4.42
4.41
4.39
4.15
4.13
4.12
3.74
3.69
3.66
3.62
3.53
3.48
3.09
2.99
2.99
2.67
0.59
2.00
0.24
1.17
3.37
0.63
1.32
1.56
0.67
6.21
0.72
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0


N3
H
N
N
O
O
8C
O
H
N
N
O
N3
9C
170.7
168.2
153.0
152.5
140.9
140.1
115.7
114.9
114.4
56.7
55.7
55.6
54.8
52.5
45.6
37.0
35.9
35.8
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


10
7.46
7.42
7.37
7.27
7.25
6.83
6.81
6.69
6.67
4.94
4.55
4.53
4.05
4.03
3.98
3.96
3.87
3.83
3.66
3.64
3.56
13.10
4.73
4.84
1.00
1.48
1.28
1.02
2.02
7.59
1.37
2.68
5.17
f1 (ppm)


10
177.4
176.6
175.8
174.9
171.3
171.1
153.7
153.2
140.1
139.6
131.7
129.2
128.8
126.5
126.3
116.4
115.7
114.8
114.8
64.2
63.6
55.5
55.5
52.5
52.2
51.0
49.1
47.7
44.3
43.6
f1 (ppm)


11
7.46
7.44
6.92
6.90
5.23
5.21
5.21
5.19
4.72
4.71
4.70
4.68
4.03
4.01
3.99
3.80
3.20
3.04
1.86
1.91
0.93
0.94
1.00
2.87
2.81
2.82
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)


11
165.7
156.6
153.6
130.9
120.6
114.3
69.1
55.5
47.0
37.1
36.2
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
f1 (ppm)