Electronic Supplementary Material (ESI) for ChemComm.

Visible-Light-Induced Radical Cascade Cyclization of Oxime Esters and Aryl Isonitriles: Synthesis of Cyclopenta[*b*]quinoxalines

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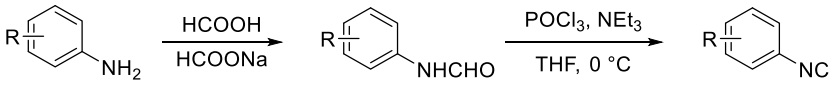
1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. Anhydrous DMF, DMSO, DCE, and CH_3CN were freshly distilled from calcium hydride. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on 400 MHz and 500 MHz spectrometers. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.00 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh).

2. Preparation of Substrates

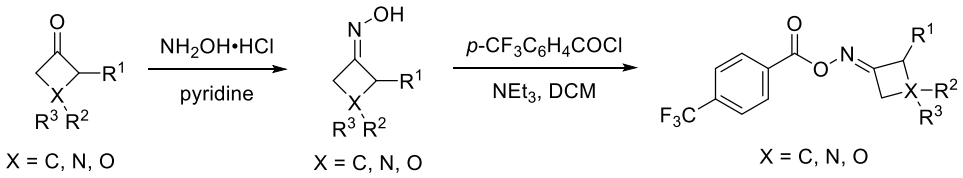
2.1 Preparation of aryl isonitriles[1]



A mixture of aryl amine (1.0 equiv), formic acid (4.0 equiv) and sodium formate (0.2 equiv) in a round-bottom flask was stirred with a magnet at room temperature for 4 hours. Then EtOAc was added to the mixture, and the organic solvent was washed with water and saturated solution of $NaHCO_3$. After drying with Na_2SO_4 the solvent was removed under reduced pressure. The resulting residue was taken on to the next step without further purification.

To a solution of formamide (1.0 equiv) and NEt_3 (3.0 equiv) in anhydrous THF was added dropwise $POCl_3$ (1.2 equiv) in THF at 0 °C under nitrogen atmosphere over 30min. After keeping 0 °C for 1 hour the reaction mixture was poured into a saturated solution of K_2CO_3. Then the mixture was extracted by 2-methoxy-2-methylpropane and the organic phase was dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by reduced pressure distillation (or silica-gel column chromatography) to give pure aryl isonitriles.

2.2 Preparation of cyclobutanone oxime esters[2]

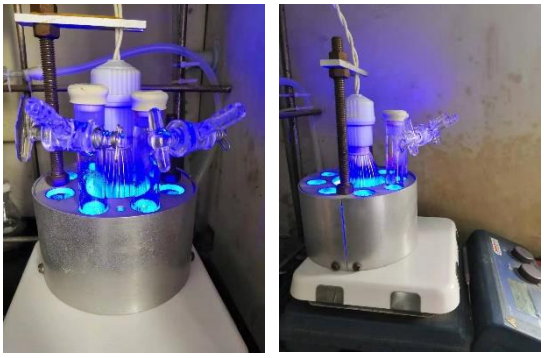


To a stirred solution of cyclobutanones (1.0 equiv) in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at room temperature. After stirring for 2 hours, pyridine was removed under reduced pressure and the residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuum to give the crude material without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) was added *p*-CF_3-benzoyl chloride (1.5 equiv) at 0 °C. The progress of the reaction was monitored by TLC. When the reaction finished, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography to give cyclobutanone oxime esters.

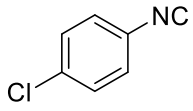
2.3 A general procedure for the visible-light-induced radical cascade cyclization of oxime esters and aryl isonitriles

An oven dried Schlenk tube equipped with a stirrer bar which was evacuated and backfilled with nitrogen was added aryl isonitriles (0.2 mmol), oxime esters (0.4 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol %), DMA (6 mL). The reaction mixture was degassed by the freeze-pump-thaw method and then irradiated with a 7 W blue LED (distance app. 5 cm) for 24 h. The pure products were obtained by silica gel column chromatography.



3. Spectral Data for Substrates and Products

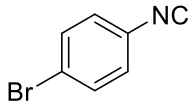
1-Chloro-4-isocyanobenzene[1]



1a

White solid, 5.0 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 135.5, 129.8, 127.7, 125.1 (t, *J* = 14.4 Hz).

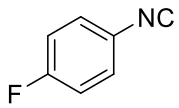
1-Bromo-4-isocyanobenzene[1]



1b

White solid, 4.1 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.30 – 7.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 132.8, 127.9, 125.6 (t, *J* = 13.3 Hz), 123.5.

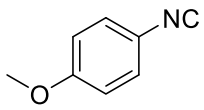
1-Fluoro-4-isocyanobenzene[1]



1c

Yellow green liquid, 2.7 g (12 mm Hg, 59 °C), 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.12 – 7.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 163.5, 161.0, 128.3 (d, *J* = 8.8 Hz), 122.8 (td, *J* = 14.0, 3.0 Hz), 116.7, 116.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.8.

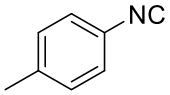
1-Isocyano-4-methoxybenzene[1]



1d

Green liquid, 15.6 g, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.89 – 6.84 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 159.9, 127.7, 119.4 (t, *J* = 14.0 Hz), 114.6, 55.6.

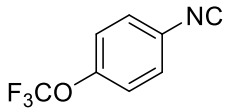
1-Isocyano-4-methylbenzene[1]



1e

Yellow liquid, 2.5 g (9.5 mm Hg, 69 °C). 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 139.5, 129.8, 125.9, 123.8 (t, *J* = 13.5 Hz), 21.1.

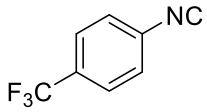
1-Isocyano-4-(trifluoromethoxy)benzene[3]



1f

Green liquid, 1.2 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 149.0, 127.9, 124.9 (t, *J* = 12.7 Hz), 121.7, 120.1 (q, *J* = 256.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.1.

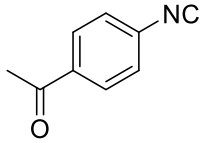
1-Isocyano-4-(trifluoromethyl)benzene[4]



1g

Blue liquid, 1.1 g, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 131.4 (q, *J* = 33.6 Hz), 129.4 (t, *J* = 13.8 Hz), 126.9, 126.8 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 273.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0.

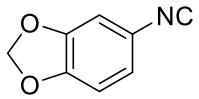
1-(4-Isocyanophenyl)ethan-1-one[1]



1h

Green solid, 1.8 g (2.5 mm Hg, 91 °C), 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.98 (m, 1H), 7.97 – 7.95 (m, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 167.2, 137.2, 129.7, 129.4, 126.5, 26.6.

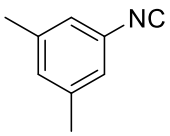
5-Isocyanobenzo[*d*][1,3]dioxole[1]



1i

White solid, 1.7 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.82 (d, *J* = 1.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 148.5, 148.1, 120.9, 120.3 (t, *J* = 13.3 Hz), 108.5, 107.3, 102.3.

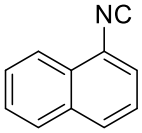
1-Isocyano-3,5-dimethylbenzene[1]



1j

Colorless liquid, 4.0 g (4 mm Hg, 67 °C), 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.96 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 139.2, 130.9, 126.1 (t, *J* = 13.0 Hz), 123.7, 20.8.

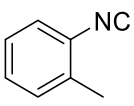
1-Isocyanonaphthalene[1]



1k

Glaucous liquid, 3.0 g, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.68 – 7.53 (m, 3H), 7.44 – 7.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 133.1, 129.5, 128.0, 127.6, 127.5, 127.1, 124.6, 124.1, 123.1 (t, *J* = 13.0 Hz), 122.4.

1-Isocyano-2-methylbenzene[1]

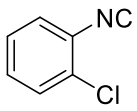


1l

Colorless liquid, 2.7 g (5.5 mm Hg, 51.5 °C), 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35

(d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 6.4 Hz, 2H), 7.25 – 7.19 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 134.6, 130.3, 129.1, 126.5, 126.4, 126.3, 18.3.

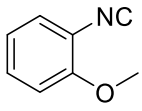
1-chloro-2-isocyanobenzene[4]



1m

Green solid, 6.0 g, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.36 – 7.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 130.6, 130.3, 130.1, 127.9, 127.6, 125.3 (t, *J* = 15.9 Hz).

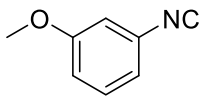
1-Isocyano-2-methoxybenzene[1]



1n

Yellow liquid, 1.0 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 6.97−6.90 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 155.1, 130.8, 127.8, 120.7, 116.2 (t, *J* = 13.3 Hz), 112.0, 56.2.

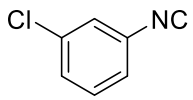
1-Isocyano-3-methoxybenzene[5]



1o

Yellow liquid, 1.2 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.88 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 159.8, 130.0, 127.1 (t, *J* = 12.9 Hz), 118.4, 115.4, 111.6, 55.3.

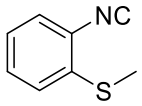
1-Chloro-3-isocyanobenzene[5]



1p

Green liquid, 0.8 g, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 135.2, 130.6, 129.9, 127.5 (t, *J* = 13.6 Hz), 126.7, 124.7.

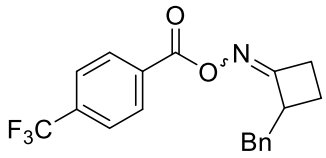
(2-Isocyanophenyl)(methyl)sulfane[6]



1q

Orange liquid, 6.0 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 136.2, 129.4, 126.6, 125.1, 124.8, 124.0, 14.5.

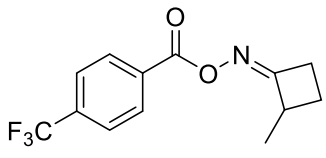
2-Benzylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[2]



2a

White solid, 1.2 g, 72% yield. M.P.: 50.4-51.2 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 3.70 (dtq, *J* = 7.0, 5.0, 4.0, 2.5 Hz, 1H), 3.26 (dd, *J* = 14.0, 5.0 Hz, 1H), 3.09 – 2.90 (m, 3H), 2.16 (dtd, *J* = 11.0, 9.5, 6.0 Hz, 1H), 1.88 (ddt, *J* = 11.5, 9.5, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 162.8, 138.4, 134.5 (q, *J* = 32.7 Hz), 132.4, 129.9, 128.8, 128.5, 126.5, 125.5 (q, *J* = 3.8 Hz, CF_3), 123.5 (q, *J* = 273.3 Hz), 46.4, 37.8, 29.0, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1.

2-Methylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[2]

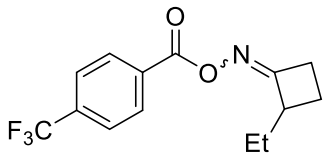


2b

White solid, 1.0 g, 77% yield. M.P.: 55.3-56.0 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 6.5 Hz, 2H), 3.55 – 3.42 (m, 1H), 3.12 (dddq, *J* = 18.0, 10.0, 5.0, 2.5 Hz, 1H), 3.06 – 2.94 (m, 1H), 2.28 (tt, *J* = 11.0, 5.5 Hz, 1H), 1.69 (tdd, *J* = 11.0, 6.5, 2.5 Hz, 1H), 1.36 (tt, *J* = 7.0, 3.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 162.9, 134.6 (q, *J* =

32.7 Hz), 132.6, 130.0, 125.5 (q, *J* = 3.8 Hz, CF_3), 123.6 (q, *J* = 272.8 Hz), 40.6, 29.2, 22.8, 17.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

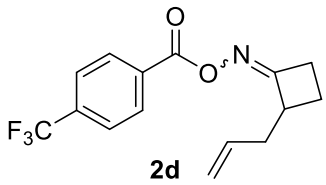
2-Ethylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[7]



2c

White solid, 1.2 g, 84% yield. M.P.: 42.2-43.8 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 3.43 (ddddd, *J* = 14.0, 10.5, 5.5, 3.0, 1.5 Hz, 1H), 3.09 – 2.95 (m, 2H), 2.19 (dtd, *J* = 11.5, 9.5, 6.5 Hz, 1H), 1.95 (dddd, *J* = 15.0, 12.5, 7.5, 5.0 Hz, 1H), 1.76 (dddd, *J* = 14.0, 9.0, 6.5, 2.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 163.1, 134.8 (q, *J* = 32.7 Hz), 132.6, 130.0, 125.7 (q, *J* = 3.8 Hz, CF_3), 123.7 (q, *J* = 272.8 Hz), 47.8, 29.0, 24.6, 19.4, 11.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

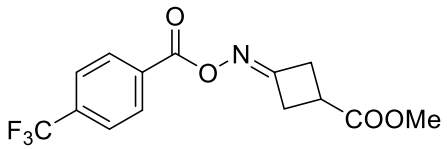
2-Allylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[2]



2d

Colorless liquid, 1.1 g, 74% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 5.76 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.12 – 5.05 (m, 2H), 3.55 (dddd, *J* = 12.0, 10.0, 5.5, 2.5 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.61 (dddt, *J* = 14.5, 6.5, 5.0, 1.5 Hz, 1H), 2.48 (dddt, *J* = 14.5, 8.5, 7.0, 1.5 Hz, 1H), 2.16 (dtd, *J* = 11.5, 9.5, 7.0 Hz, 1H), 1.84 – 1.78 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 162.9, 134.7 (q, *J* = 32.8 Hz), 134.1, 132.4, 130.0, 125.7 (q, *J* = 3.8 Hz, CF_3), 121.8 (q, *J* = 272.8 Hz), 117.7, 45.3, 35.4, 28.9, 19.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

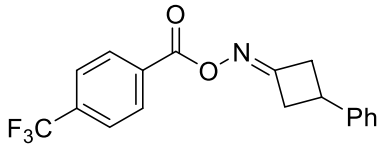
Methyl 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1-carboxylate[8]



2e

White solid, 1.3 g, 82% yield. M.P.: 80.2-80.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 7.0 Hz, 2H), 3.76 – 3.71 (m, 3H), 3.39 (td, *J* = 9.0, 8.0, 4.5 Hz, 4H), 3.28 (q, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.6, 165.2, 162.6, 134.8 (q, *J* = 32.8 Hz), 132.1, 130.1, 125.6 (q, *J* = 3.8 Hz, CF_3), 123.6 (q, *J* = 272.8 Hz), 52.5, 35.8, 35.7, 30.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.3.

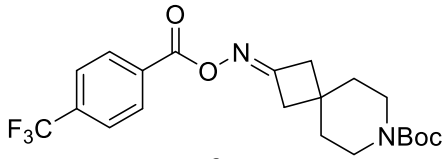
3-Phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[9]



2f

White solid, 0.6 g, 80% yield. M.P.: 112.4-113.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 3.73 (p, *J* = 8.0 Hz, 1H), 3.68 – 3.56 (m, 2H), 3.32 – 3.21 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 162.9, 142.9, 134.9 (q, *J* = 32.7 Hz), 132.4, 130.1, 128.9, 127.1, 126.4, 125.7 (q, *J* = 3.7 Hz, CF_3), 123.6 (q, *J* = 272.8 Hz), 39.7, 39.6, 32.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

Tert-butyl 2-(((4-(trifluoromethyl)benzoyl)oxy)imino)-7-azaspiro[3.5]nonane-7-carboxylate[2]

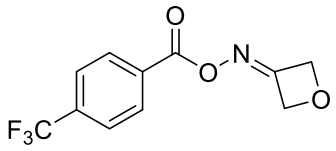


2g

White solid, 1.4 g, 66% yield. M.P.: 137.7-138.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 5.5 Hz, 4H), 2.87 (d, *J* = 4.0 Hz, 4H), 1.66 (q, *J* = 5.0 Hz, 4H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.0, 162.8, 154.9, 134.8 (q,

J = 32.7 Hz), 132.3, 130.1, 125.6 (q, *J* = 3.7 Hz, CF_3), 123.6 (q, *J* = 272.7 Hz), 79.9, 41.97, 41.95, 41.0, 36.4, 33.5, 28.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

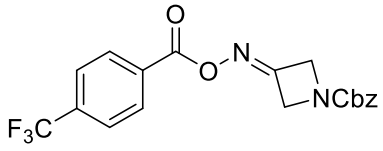
Oxetan-3-one *O*-(4-(trifluoromethyl)benzoyl) oxime[2]



2h

White solid, 1.2 g, 92% yield. M.P.: 109.4-110.1 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 5.45 (dd, *J* = 4.0, 2.0 Hz, 2H), 5.44 – 5.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.8, 162.1, 135.1 (q, *J* = 32.8 Hz), 131.4, 130.1, 125.7 (q, *J* = 3.8 Hz, CF_3), 123.5 (q, *J* = 272.8 Hz), 72.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.3.

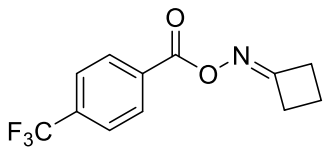
Benzyl 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)azetidine-1-carboxylate[2]



2i

White solid, 1.2 g, 61% yield. M.P.: 153.6-154.0 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 5H), 5.16 (s, 2H), 4.93 – 4.89 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.1, 158.9, 156.3, 135.9, 135.3 (q, *J* = 32.8 Hz), 131.4, 130.2, 128.8, 128.6, 128.4, 125.8 (q, *J* = 3.7 Hz, CF_3), 123.5 (q, *J* = 272.9 Hz), 67.9, 58.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.3.

Cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime[2]

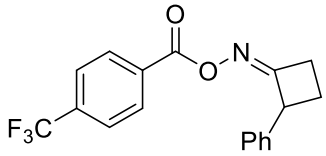


2j

White solid, 1.1 g, 61% yield. M.P.: 91.2-92.0 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 4H), 2.12 (p, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.1, 162.9, 134.7 (q, *J* = 32.7 Hz), 132.5, 130.1, 125.6 (q, *J* =

3.7 Hz, CF_3), 123.6 (q, *J* = 272.8 Hz), 31.97, 31.96, 14.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.3.

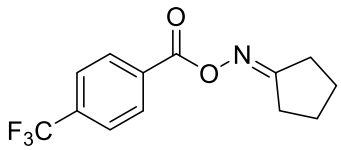
2-Phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime[10]



2k

White solid, 0.4 g, 40% yield. M.P.: 117.5-118.4 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 4.69 (ddd, *J* = 10.0, 7.0, 3.0 Hz, 1H), 3.28 – 3.12 (m, 2H), 2.64 (dtd, *J* = 11.0, 10.0, 6.0 Hz, 1H), 2.30 (ddt, *J* = 11.0, 10.0, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.7, 162.8, 138.6, 134.8 (q, *J* = 32.8 Hz), 132.5, 130.1, 128.8, 127.3, 127.2, 125.6 (q, *J* = 3.7 Hz, CF_3), 123.6 (q, *J* = 272.8 Hz), 49.7, 29.6, 23.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2.

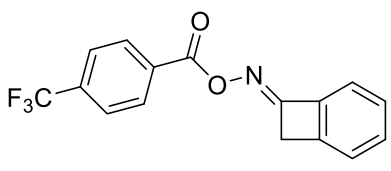
Cyclopentanone *O*-(4-(trifluoromethyl)benzoyl) oxime



2l

White solid, 1.1 g, 81% yield. M.P.: 100.9-101.7 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 2.75 – 2.67 (m, 2H), 2.67 – 2.54 (m, 2H), 1.86 (p, *J* = 6.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.0, 163.0, 134.7 (q, *J* = 32.8 Hz), 132.7, 130.1, 125.6 (q, *J* = 3.7 Hz, CF_3), 123.7 (q, *J* = 272.6 Hz), 31.7, 29.6, 25.3, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. HRMS-ESI (m/z): Calculated for $C_{13}H_{12}F_3NNaO_2$ $(M + Na)^+$: 294.0718, Found: 294.0726.

Bicyclo[4.2.0]octa-1(6),2,4-trien-7-one *O*-(4-(trifluoromethyl)benzoyl) oxime[2]

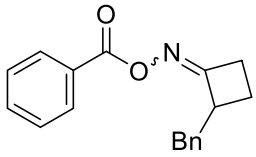


2m

White solid, 0.6 g, 67% yield. M.P.: 100.9-101.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J*

= 8.0 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.42 – 7.34 (m, 2H), 4.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 161.6, 144.7, 139.2, 135.0 (q, *J* = 32.9 Hz), 133.7, 132.3, 130.2, 129.2, 125.8 (q, *J* = 3.7 Hz, CF_3), 123.7 (q, *J* = 273.8 Hz), 123.6, 121.9, 40.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

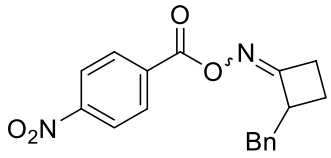
2-Benzylcyclobutan-1-one *O*-benzoyl oxime[2]



2n

Yellow liquid, 1.4 g, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 3H), 3.78 (tt, *J* = 10.0, 4.0 Hz, 1H), 3.31 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.02 (dd, *J* = 14.0, 9.5 Hz, 1H), 2.99 – 2.92 (m, 2H), 2.13 (dtd, *J* = 11.5, 9.0, 7.0 Hz, 1H), 1.86 – 1.78 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 163.8, 138.1, 133.0, 129.3, 128.7, 128.6, 128.4, 128.3, 126.4, 46.7, 37.0, 28.6, 19.3.

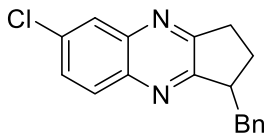
2-Benzylcyclobutan-1-one *O*-(4-nitrobenzoyl) oxime



2o

White solid, 3.2 g, 73% yield. M.P.: 103.5-104.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 3.85 – 3.72 (m, 1H), 3.23 (dd, *J* = 14.0, 7.0 Hz, 1H), 3.09 – 2.93 (m, 3H), 2.19 (dtd, *J* = 11.5, 9.0, 7.5 Hz, 1H), 1.90 – 1.78 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 162.3, 150.7, 138.4, 134.4, 130.7, 128.8, 128.7, 126.8, 123.6, 47.3, 37.8, 29.2, 19.9. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}N_2NaO_4$ $(M + H)^+$: 347.1008, Found: 347.0997.

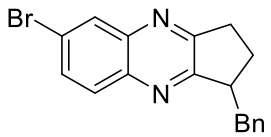
1-Benzyl-6-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3aa

White solid, 54.5 mg, 92% yield. M.P.: 83.4-84.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.62 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 3.62 – 3.54 (m, 2H), 3.07 – 3.02 (m, 2H), 2.82 – 2.74 (m, 1H), 2.32 (dtd, *J* = 13.0, 8.0, 5.5 Hz, 1H), 1.96 (dq, *J* = 13.0, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.4,161.8, 142.3, 140.3, 139.5, 134.6, 130.2, 129.7, 129.2, 128.6, 127.9, 126.5, 45.4, 39.2, 30.9, 27.7. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}ClN_2$ $(M + H)^+$: 295.1002, Found: 295.1004.

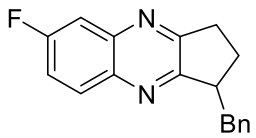
1-Benzyl-6-bromo-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ba

White solid, 56.3 mg, 83% yield. M.P.: 86.8-87.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 3H), 3.57 (ddt, *J* = 12.5, 8.5, 4.5 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.84 – 2.76 (m, 1H), 2.32 (dt, *J* = 14.0, 6.5 Hz, 1H), 1.96 (dt, *J* = 17.0, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.6, 161.9, 142.6, 140.6, 139.5, 132.3, 131.3, 130.4, 129.2, 128.6, 126.5, 122.7, 45.5, 39.2, 31.0, 27.7. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}BrN_2$ $(M + H)^+$: 341.0476, Found: 341.0484.

1-Benzyl-6-fluoro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline

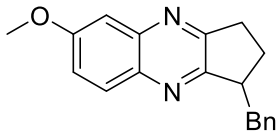


3ca

White solid, 44.3 mg, 80% yield. M.P.: 132.0-132.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.67 (dd, *J* = 9.5, 3.0 Hz, 1H), 7.48 (td, *J* = 8.5, 3.0 Hz, 1H), 7.32 (dd,

J = 8.0, 7.0 Hz, 2H), 7.28 – 7.23 (m, 3H), 3.65 – 3.57 (m, 2H), 3.10 – 3.02 (m, 2H), 2.80 (dd, *J* = 14.5, 11.0 Hz, 1H), 2.34 (dtd, *J* = 13.5, 7.5, 5.5 Hz, 1H), 2.02 – 1.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.3, 161.8, 161.6 (d, *J* = 21.8 Hz), 161.3, 142.7 (d, *J* = 12.7 Hz), 139.6, 138.9, 130.8 (d, *J* = 9.9 Hz), 129.2, 128.6, 126.5, 118.7 (d, *J* = 25.4 Hz), 112.7 (d, *J* = 21.8 Hz), 45.3, 39.3, 31.0, 27.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.3. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}FN_2$ $(M + H)^+$: 279.1298, Found: 279.1303.

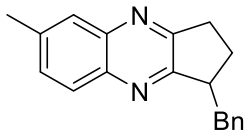
1-Benzyl-6-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3da

White solid, 50.0 mg, 86% yield. M.P.: 96.2-97.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 10.0, 1.0 Hz, 1H), 7.35 (ddt, *J* = 5.5, 2.5, 1.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 3H), 3.95 (s, 3H), 3.62 – 3.54 (m, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.77 (dd, *J* = 14.5, 11.0 Hz, 1H), 2.30 (dq, *J* = 13.5, 7.0 Hz, 1H), 1.96 (dq, *J* = 16.5, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.7, 160.2, 159.5, 143.5, 139.9, 137.7, 129.9, 129.3, 128.6, 126.4, 121.4, 107.1, 55.8, 45.2, 39.6, 31.0, 27.8. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2O$ $(M + H)^+$: 291.1497, Found: 291.1496.

1-Benzyl-6-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline

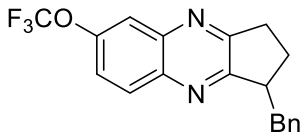


3ea

White solid, 41.5 mg, 76% yield. M.P.: 84.5-84.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.52 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.27 – 7.20 (m, 3H), 3.58 (ddt, *J* = 13.0, 8.0, 4.5 Hz, 2H), 3.07 – 3.00 (m, 2H), 2.78 (dd, *J* = 14.5, 11.0 Hz, 1H), 2.58 (s, 3H), 2.30 (dtd, *J* = 13.5, 8.0, 5.5 Hz, 1H), 1.98 – 1.93 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2, 160.6, 142.0, 140.2, 139.8, 139.4, 131.0, 129.2, 128.6, 128.5, 128.0, 126.4, 45.4, 39.4, 30.9, 27.8, 21.8. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2$ $(M + H)^+$:

275.1548, Found: 275.1551.

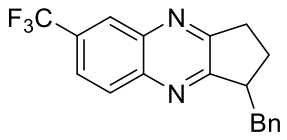
1-Benzyl-6-(trifluoromethoxy)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3fa

White solid, 45.3 mg, 66% yield. M.P.: 88.1-88.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 1H), 7.87 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 3.66 – 3.55 (m, 2H), 3.11 – 3.05 (m, 2H), 2.84 – 2.77 (m, 1H), 2.35 (dtd, *J* = 13.5, 7.5, 5.5 Hz, 1H), 1.99 (dq, *J* = 13.0, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9, 162.2, 149.0 (d, *J* = 2.0 Hz), 142.2, 140.2, 139.5, 130.7, 129.2, 128.7, 126.6, 122.6, 120.7 (q, *J* = 258.5 Hz), 119.2, 45.5, 39.3, 31.0, 27.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.8. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}F_3N_2O$ $(M + H)^+$: 345.1215, Found: 345.1219.

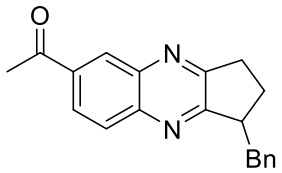
1-Benzyl-6-(trifluoromethyl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ga

Yellow liquid, 24.0 mg, 37% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 3.68 – 3.58 (m, 2H), 3.13 – 3.07 (m, 2H), 2.87 – 2.80 (m, 1H), 2.37 (dtd, *J* = 13.5, 7.5, 5.5 Hz, 1H), 2.01 (dq, *J* = 13.0, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.6, 162.6, 143.1, 141.1, 139.4, 130.3, 129.3, 128.7, 126.9 (q, *J* = 4.3 Hz), 126.6, 125.0, 124.7 (q, *J* = 3.1 Hz), 122.9, 45.6, 39.2, 31.0, 27.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}F_3N_2$ $(M + H)^+$: 329.1266, Found: 329.1262.

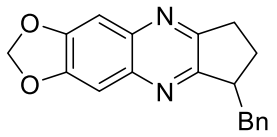
1-(1-Benzyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxalin-6-yl)ethan-1-one



3ha

Yellow solid, 15.2 mg, 25% yield. M.P.: 110.9-111.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.0 Hz, 1H), 8.27 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.25 (d, *J* = 11.5 Hz, 3H), 3.66 – 3.59 (m, 2H), 3.12 – 3.07 (m, 2H), 2.85 – 2.79 (m, 1H), 2.75 (s, 3H), 2.36 (td, *J* = 13.5, 7.5 Hz, 1H), 2.05 – 1.97 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.5, 164.6, 162.2, 144.3, 141.4, 139.5, 137.0, 130.7, 129.6, 129.2, 128.7, 127.2, 126.6, 45.7, 39.2, 31.0, 27.7, 26.9. HRMS-ESI (m/z): Calculated for $C_{20}H_{19}N_2O$ $(M + H)^+$: 303.1497, Found: 303.1494.

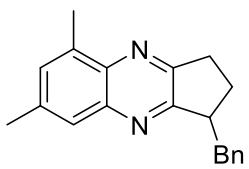
6-Benzyl-7,8-dihydro-6*H*-cyclopenta[*b*][1,3]dioxolo[4,5-*g*]quinoxaline



3ia

White solid, 43.3 mg, 71% yield. M.P.: 142.0-143.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.31 – 7.26 (m, 3H), 7.25 – 7.18 (m, 3H), 6.13 (s, 2H), 3.54 (tq, *J* = 9.2, 4.4 Hz, 2H), 3.04 – 2.95 (m, 2H), 2.73 (dd, *J* = 14.6, 11.0 Hz, 1H), 2.27 (dtd, *J* = 13.8, 7.6, 6.0 Hz, 1H), 1.92 (dtd, *J* = 13.2, 8.4, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 157.8, 150.0, 149.9, 140.1, 140.0, 139.9, 129.2, 128.5, 126.3, 105.0, 104.8, 102.3, 45.2, 39.6, 30.6, 27.8. HRMS-ESI (m/z): Calculated for $C_{19}H_{17}N_2O_2$ $(M + H)^+$: 305.1290, Found: 305.1288.

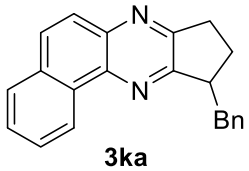
1-Benzyl-5,7-dimethyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ja

Yellow liquid, 46.1 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.37 (s, 1H), 7.32 – 7.21 (m, 5H), 3.63 – 3.54 (m, 2H), 3.14 – 3.00 (m, 2H), 2.80 – 2.73 (m, 4H), 2.53 (s, 3H), 2.30 (dtd, *J* = 13.2, 8.0, 5.2 Hz, 1H), 1.95 (dq, *J* = 12.8, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.4, 158.6, 142.0, 140.0, 139.6, 138.7, 136.4, 131.5, 129.3, 128.6, 126.4, 126.1, 45.4, 39.5, 31.0, 27.8, 21.8, 17.6. HRMS-ESI (m/z): Calculated for $C_{20}H_{21}N_2$ $(M + H)^+$: 289.1705, Found: 289.1704.

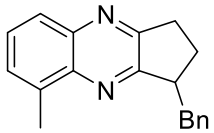
10-benzyl-9,10-dihydro-8*H*-benzo[*f*]cyclopenta[*b*]quinoxaline



3ka

Orange solid, 34.2 mg, 55% yield. M.P.: 120.2-121.3 °C. 1H NMR (500 MHz, $CDCl_3$) δ 9.32 (dd, J = 8.5, 4.5 Hz, 1H), 7.96 (ddt, J = 21.5, 9.0, 4.5 Hz, 3H), 7.79 – 7.70 (m, 2H), 7.36 – 7.30 (m, 4H), 7.26 (tt, J = 6.5, 3.0 Hz, 1H), 3.71 (ddt, J = 18.0, 15.5, 4.5 Hz, 2H), 3.13 (dt, J = 8.5, 5.5 Hz, 2H), 2.93 (ddd, J = 14.0, 9.0, 5.0 Hz, 1H), 2.41 (tq, J = 12.0, 5.5, 4.0 Hz, 1H), 2.02 (dqt, J = 13.0, 8.5, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.3, 159.9, 141.1, 140.1, 140.0, 133.1, 131.4, 130.4, 129.4, 128.5, 128.3, 127.9, 127.3, 126.9, 126.4, 124.4, 45.5, 39.7, 31.0, 28.2. HRMS-ESI (m/z): Calculated for $C_{22}H_{19}N_2$ $(M + H)^+$: 311.1548, Found: 311.1554.

1-Benzyl-8-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline

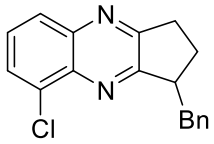


3la

White solid, 34.0 mg, 62% yield. M.P.: 78.3-79.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.23 (ddd, *J* = 7.0, 5.0, 3.0 Hz, 1H), 3.60 (td, *J* = 13.5, 5.0 Hz, 2H), 3.10 – 3.04 (m, 2H), 2.89 – 2.84 (m, 1H), 2.82 (s, 3H), 2.36 (dtd, *J* = 13.0, 7.5, 5.5 Hz, 1H), 1.99 – 1.93 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.8, 160.0, 141.9, 141.0, 140.0, 137.4, 129.3, 129.0, 128.6, 128.5, 126.7, 126.3, 45.4, 39.4, 30.9, 28.1, 17.4. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2$ $(M + H)^+$:

275.1548, Found: 275.1544.

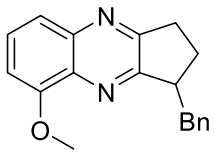
1-Benzyl-8-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ma

White solid, 27.0 mg, 46% yield. M.P.: 66.8-67.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.79 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.22 (ddd, *J* = 8.5, 5.5, 2.0 Hz, 1H), 3.74 – 3.61 (m, 2H), 3.08 (dd, *J* = 8.5, 6.5 Hz, 2H), 2.86 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.36 (ddt, *J* = 13.0, 8.0, 6.5 Hz, 1H), 2.04 – 1.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.0, 161.7, 143.0, 139.5, 138.8, 133.1, 129.4, 129.0, 128.6, 128.5, 128.0, 126.4, 45.5, 39.2, 30.9, 27.7. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}ClN_2$ $(M + H)^+$: 295.1002, Found: 295.1002.

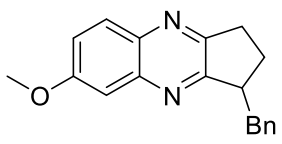
1-Benzyl-8-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3na

White solid, 36.1 mg, 62% yield. M.P.: 121.9-122.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 7.08 (dd, *J* = 5.5, 3.5 Hz, 1H), 4.12 (s, 3H), 3.73 – 3.66 (m, 2H), 3.09 – 3.03 (m, 2H), 2.79 – 2.72 (m, 1H), 2.33 – 2.25 (m, 1H), 2.02 – 1.94 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2, 161.1, 155.3, 142.9, 139.8, 133.8, 129.2, 129.0, 128.6, 126.4, 120.8, 107.7, 55.5, 45.4, 39.7, 30.8, 27.4. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2O$ $(M + H)^+$: 291.1497, Found: 291.1491.

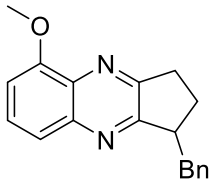
1-Benzyl-7-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3oa

White solid, 21.5 mg, 37% yield. M.P.: 61.1-62.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 3.0 Hz, 1H), 7.34 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 3H), 3.97 (s, 3H), 3.64 – 3.54 (m, 2H), 3.08 – 3.01 (m, 2H), 2.81 – 2.74 (m, 1H), 2.30 (dtd, *J* = 13.0, 8.0, 5.5 Hz, 1H), 1.96 (dq, *J* = 13.0, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.1, 160.1, 158.1, 143.4, 139.9, 137.9, 129.7, 129.3, 128.6, 126.4, 121.6, 107.2, 55.9, 45.6, 39.5, 30.7, 27.8. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2O$ $(M + H)^+$: 291.1497, Found: 291.1506.

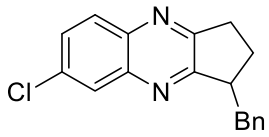
1-Benzyl-5-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3oa'

White solid, 19.0 mg, 33% yield. M.P.: 105.7-106.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 7.06 (dd, *J* = 7.5, 1.0 Hz, 1H), 4.09 (s, 3H), 3.63 – 3.56 (m, 2H), 3.17 – 3.04 (m, 2H), 2.83 – 2.74 (m, 1H), 2.30 (tt, *J* = 8.0, 5.0 Hz, 1H), 2.00 – 1.91 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.5, 159.5, 155.2, 142.8, 139.7, 133.9, 129.2, 128.8, 128.6, 126.4, 121.0, 107.6, 56.3, 45.4, 39.4, 31.1, 27.7. HRMS-ESI (m/z): Calculated for $C_{19}H_{19}N_2O$ $(M + H)^+$: 291.1497, Found: 291.1498.

1-Benzyl-7-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline

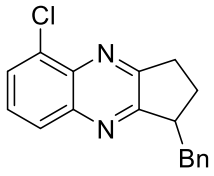


3pa

Yellow liquid, 3.0 mg, 5% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 3.65 – 3.56 (m, 2H), 3.09 – 3.03 (m, 2H), 2.84 – 2.77 (m, 1H), 2.34 (dtd, *J* = 13.6, 7.6, 6.0 Hz, 1H), 1.98 (dq, *J* = 13.2, 8.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.3, 161.2, 142.3, 140.5,

139.6, 134.6, 130.1, 129.9, 129.3, 128.6, 128.2, 126.5, 45.5, 39.3, 31.0, 27.8. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}ClN_2$ $(M + H)^+$: 295.1002, Found: 295.0997.

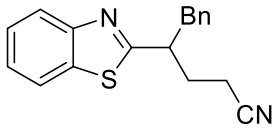
1-Benzyl-5-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3pa'

White solid, 30.2 mg, 51% yield. M.P.: 96.5-97.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.21 (m, 5H), 3.68 – 3.55 (m, 2H), 3.25 – 3.08 (m, 2H), 2.86 – 2.76 (m, 1H), 2.35 (dtd, *J* = 13.2, 8.0, 5.2 Hz, 1H), 1.99 (dq, *J* = 13.2, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 161.8, 143.0, 139.5, 138.9, 132.7, 129.3, 129.2, 128.7, 128.6, 128.3, 126.5, 45.4, 39.3, 31.3, 27.8. HRMS-ESI (m/z): Calculated for $C_{18}H_{16}ClN_2$ $(M + H)^+$: 295.1002, Found: 295.0994.

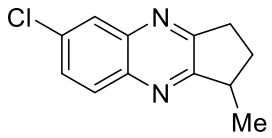
4-(Benzo[*d*]thiazol-2-yl)-5-phenylpentanenitrile



3qa

Colorless liquid, 31.5 mg, 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.49 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 3.62 – 3.54 (m, 1H), 3.27 (dd, *J* = 13.5, 7.0 Hz, 1H), 3.05 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.43 – 2.27 (m, 3H), 2.20 – 2.13 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.5, 153.2, 138.1, 134.7, 129.1, 128.8, 126.9, 126.3, 125.3, 123.0, 121.8, 119.2, 45.5, 42.3, 30.2, 15.4. HRMS-ESI (m/z): Calculated for $C_{18}H_{17}N_2S$ $(M + H)^+$: 293.1112, Found: 293.1111.

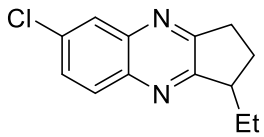
6-Chloro-1-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ab

White solid, 25.3 mg, 58% yield. M.P.: 78.6-79.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.35 (ddt, *J* = 15.5, 8.5, 7.0 Hz, 1H), 3.22 – 3.08 (m, 2H), 2.55 (dtd, *J* = 12.5, 8.0, 4.0 Hz, 1H), 1.85 (dq, *J* = 13.0, 9.0 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.1, 161.7, 142.1, 140.5, 134.5, 130.2, 129.7, 127.9, 38.6, 31.2, 30.8, 18.2. HRMS-ESI (m/z): Calculated for $C_{12}H_{12}ClN_2$ $(M + H)^+$: 219.0689, Found: 219.0691.

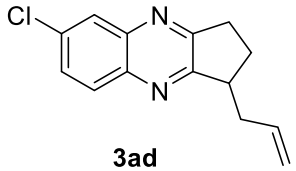
6-Chloro-1-ethyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3ac

White solid, 31.5 mg, 68% yield. M.P.: 76.3-77.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.5 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.59 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.22 – 3.06 (m, 3H), 2.53 – 2.46 (m, 1H), 2.15 (dqd, *J* = 15.0, 7.5, 5.0 Hz, 1H), 1.91 (dq, *J* = 13.0, 8.5 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.4, 162.0, 142.2, 140.4, 134.4, 130.2, 129.6, 127.9, 45.3, 31.2, 27.7, 26.5, 11.8. HRMS-ESI (m/z): Calculated for $C_{13}H_{14}ClN_2$ $(M + H)^+$: 233.0846, Found: 233.0842.

1-Allyl-6-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline

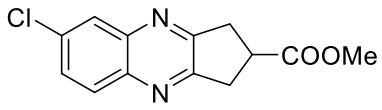


3ad

White solid, 41.3 mg, 84% yield. M.P.: 53.4-54.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.95 – 5.86 (m, 1H),

5.15 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.09 (ddt, *J* = 10.0, 2.0, 1.0 Hz, 1H), 3.42 – 3.34 (m, 1H), 3.23 – 3.07 (m, 2H), 2.89 (dddt, *J* = 14.0, 6.0, 4.5, 1.5 Hz, 1H), 2.48 (dtd, *J* = 13.5, 8.5, 5.0 Hz, 1H), 2.37 (dddt, *J* = 14.0, 9.0, 7.5, 1.0 Hz, 1H), 2.02 – 1.94 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.7, 161.9, 142.3, 140.5, 135.7, 134.6, 130.2, 129.7, 127.9, 117.2, 43.3, 37.7, 31.1, 27.5. HRMS-ESI (m/z): Calculated for $C_{14}H_{14}ClN_2$ $(M + H)^+$: 245.0846, Found: 245.0843.

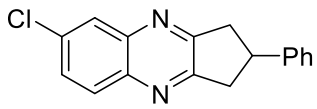
Methyl 6-chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline-2-carboxylate



3ae

White solid, 21.3 mg, 40% yield. M.P.: 108.7-108.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.5 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.63 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.78 (s, 3H), 3.56 – 3.52 (m, 1H), 3.51 – 3.45 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5, 159.3, 158.5, 142.3, 140.5, 135.0, 130.2, 130.1, 128.0, 52.6, 39.5, 35.8, 35.7. HRMS-ESI (m/z): Calculated for $C_{13}H_{12}ClN_2O_2$ $(M + H)^+$: 263.0587, Found: 263.0591.

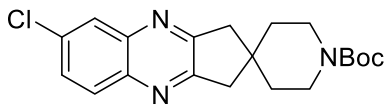
6-Chloro-2-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3af

White solid, 24.8 mg, 44% yield. M.P.: 146.5-147.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.31 – 7.28 (m, 1H), 3.89 (p, *J* = 8.5 Hz, 1H), 3.64 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.61 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.36 (ddd, *J* = 17.5, 9.5, 5.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.9, 160.1, 143.4, 142.4, 140.6, 134.8, 130.2, 130.0, 129.0, 128.1, 127.2, 127.0, 41.4, 40.6, 40.5. HRMS-ESI (m/z): Calculated for $C_{17}H_{14}ClN_2$ $(M + H)^+$: 281.0846, Found: 281.0841.

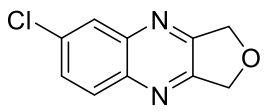
Tert-butyl 6-chloro-1,3-dihydrospiro[cyclopenta[*b*]quinoxaline-2,4'-piperidine]-1'-carboxylate



3ag

White solid, 55.2 mg, 74% yield. M.P.: 173.9-174.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.53 – 3.48 (m, 4H), 3.09 (d, *J* = 3.5 Hz, 4H), 1.66 (t, *J* = 5.5 Hz, 4H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.3, 159.5, 154.9, 142.4, 140.5, 134.8, 130.0, 129.9, 128.0, 79.9, 44.3, 44.2, 39.2, 36.8, 28.6. HRMS-ESI (m/z): Calculated for $C_{20}H_{25}ClN_3O_2$ $(M + H)^+$: 374.1635, Found: 374.1640.

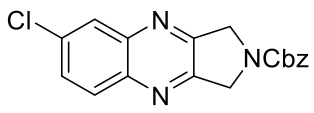
6-Chloro-1,3-dihydrofuro[3,4-*b*]quinoxaline



3ah

White solid, 33.0 mg, 80% yield. M.P.: 176.7-177.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.5 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.70 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.23 (d, *J* = 3.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.8, 156.1, 142.4, 140.5, 135.7, 130.9, 130.4, 128.3, 71.2, 71.1. HRMS-ESI (m/z): Calculated for $C_{10}H_8ClN_2O$ $(M + H)^+$: 207.0325, Found: 207.0328.

Benzyl 6-chloro-1,3-dihydro-2*H*-pyrrolo[3,4-*b*]quinoxaline-2-carboxylate

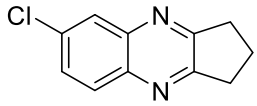


3ai

White solid, 31.2 mg, 46% yield. M.P.: 172.5-172.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.5, 2.5 Hz, 1H), 8.00 (t, *J* = 9.0 Hz, 1H), 7.70 (dt, *J* = 9.0, 2.0 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 5.28 (s, 2H), 4.94 (dd, *J* = 6.0, 4.0 Hz, 4H). ^{13}C

NMR (126 MHz, $CDCl_3$): δ 155.0, 154.4, 154.1, 153.6, 153.3, 142.6, 140.8, 136.4, 135.92, 135.89, 131.1, 131.0, 130.45, 130.40, 128.7, 128.4, 128.3, 128.28, 182.24, 67.7, 51.24, 51.19, 51.03, 50.98. (The mixture of two possible isomers attribute to the rotation barriers of the carbamate.) HRMS-ESI (m/z): Calculated for $C_{18}H_{15}ClN_3O_2$ $(M + H)^+$: 340.0853, Found: 340.0849.

6-Chloro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoxaline



3aj

White solid, 13.2 mg, 32% yield. M.P.: 118.3-119.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.20 (td, *J* = 7.5, 4.0 Hz, 4H), 2.32 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.9, 161.1, 142.1, 140.2, 134.5, 130.0, 129.8, 128.0, 32.6, 32.5, 21.4. HRMS-ESI (m/z): Calculated for $C_{11}H_{10}ClN_2$ $(M + H)^+$: 205.0533, Found: 205.0528.

4. Reference

(1) Yuan, Y.; Dong, W.; Gao, X.; Gao, H.; Xie, X.; Zhang, Z. *J. Org. Chem.* **2018**, *83*, 2840-2846.

(2) Yu, X.-Y.; Chen, J.-R.; Wang, P.-Z.; Yang, M.-N.; Liang, D.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2018**, *57*, 738-743.

(3) Chen, Y.; Feng, G. *Org. Biomol. Chem.* **2015**, *13*, 4260-4265.

(4) Wang, S.; Yang, L.-J.; Zeng, J.-L.; Zheng, Y.; Ma, J.-A. *Org. Chem. Front.* **2015**, *2*, 1468-1474.

(5) Sun, X.; Li, J.; Ni, Y.; Ren, D.; Hu, Z.; Yu, S. *Asian J. Org. Chem.* **2014**, *3*, 1317-1325.

(6) Yuan, Y.; Dong, W.; Gao, X.; Xie, X.; Zhang, Z. *Org. Lett.* **2019**, *21*, 469-472.

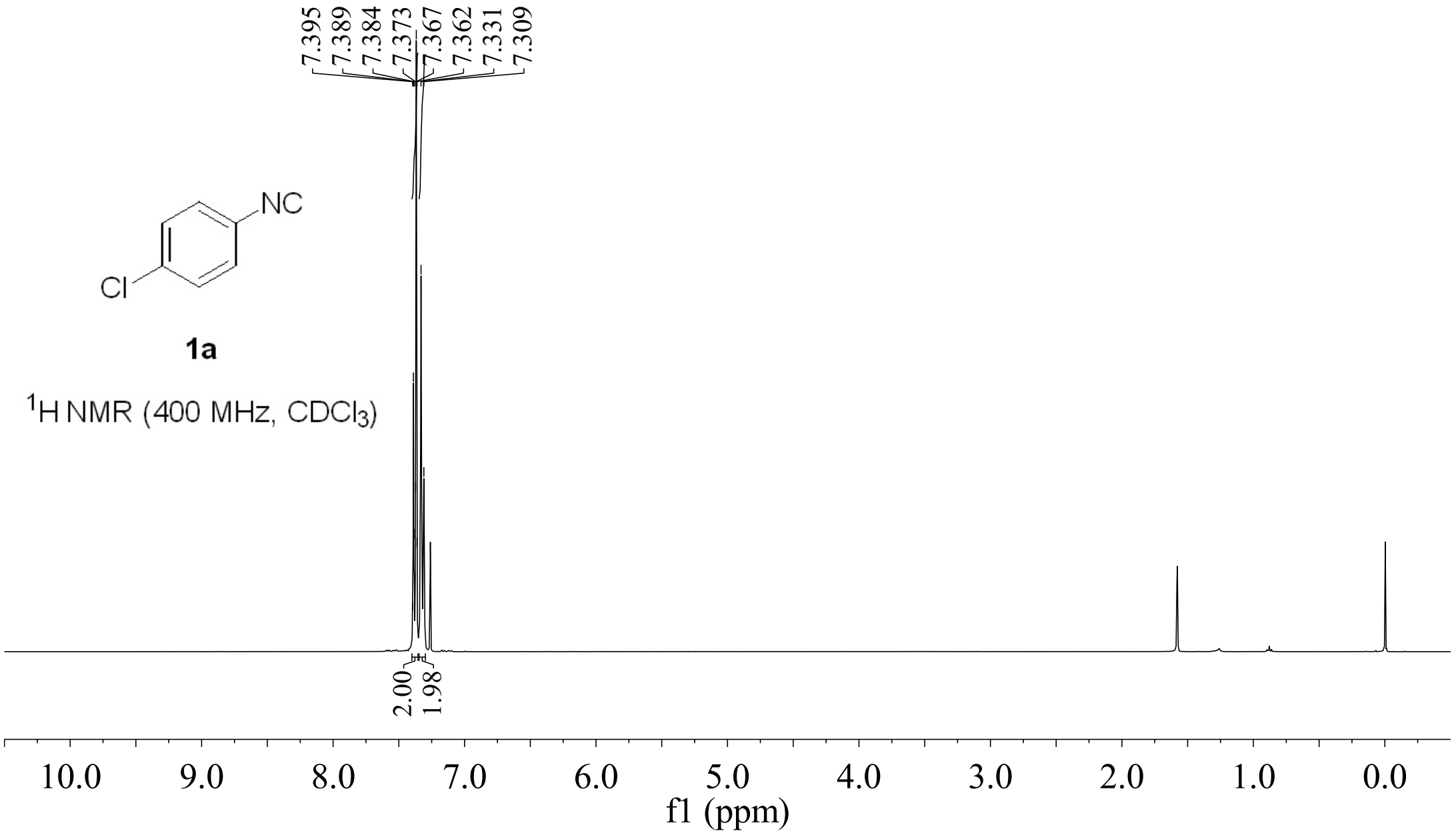
(7) Yin, Z.; Rabeah, J.; Brückner, A.; Wu, X.-F. *ACS Catal.* **2018**, *8*, 10926-10930.

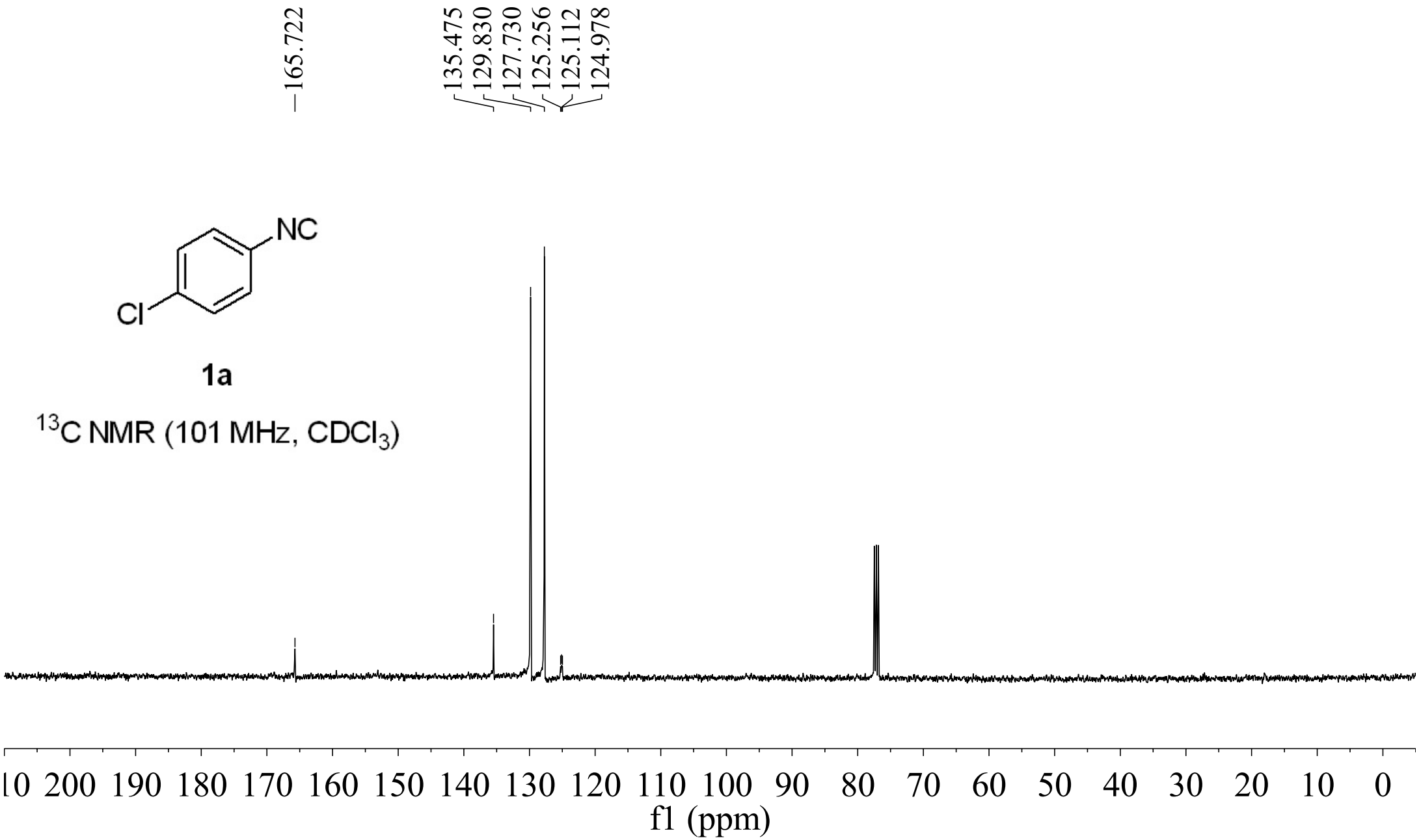
(8) He, B.-Q.; Yu, X.-Y.; Wang, P.-Z.; Chen, J.-R.; Xiao, W.-J. *Chem. Commun.* **2018**, *54*, 12262-12265.

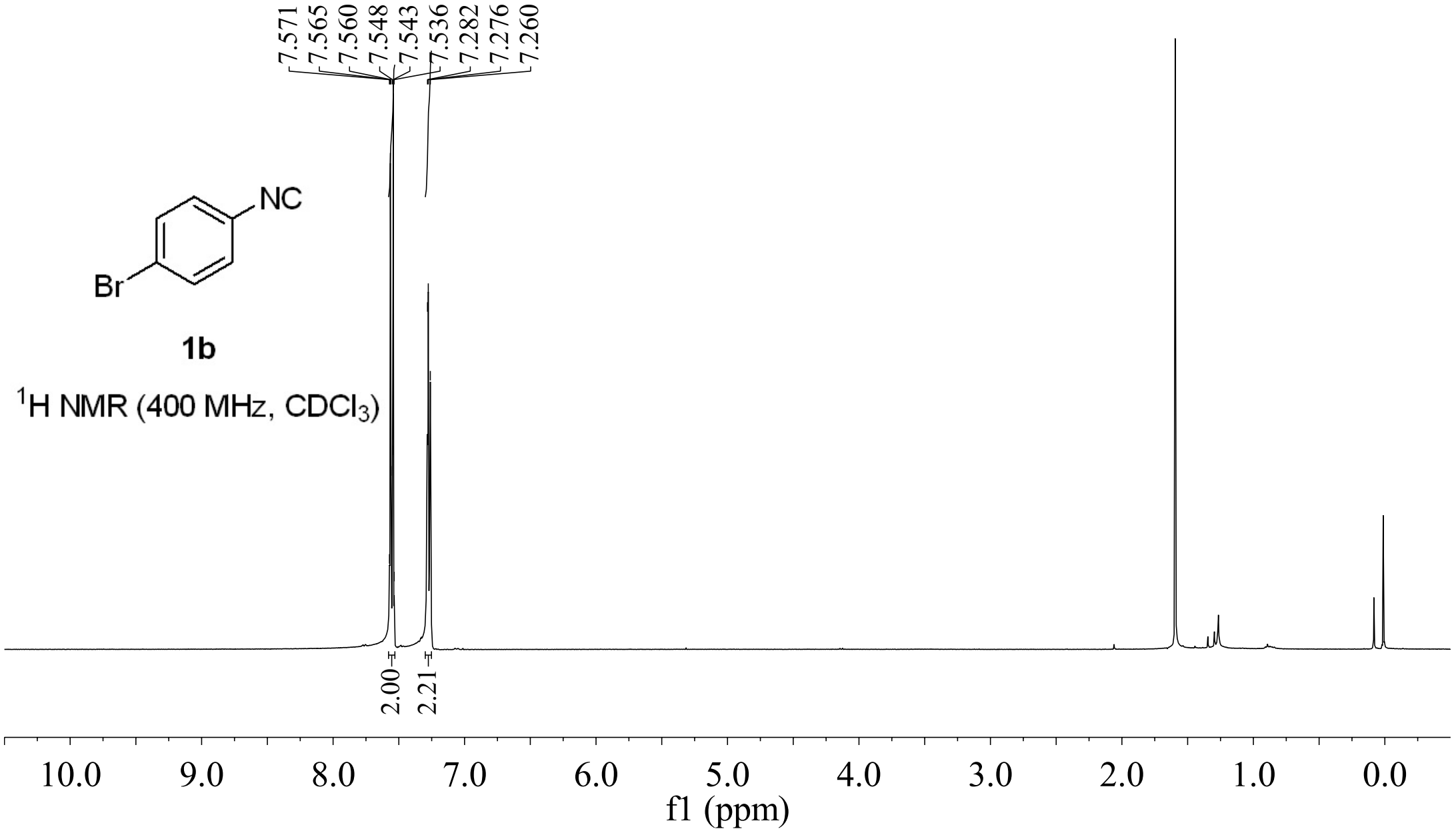
(9) Yu, X.-Y.; Zhao, Q.-Q.; Chen, J.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2018**, *57*, 15505-15509.

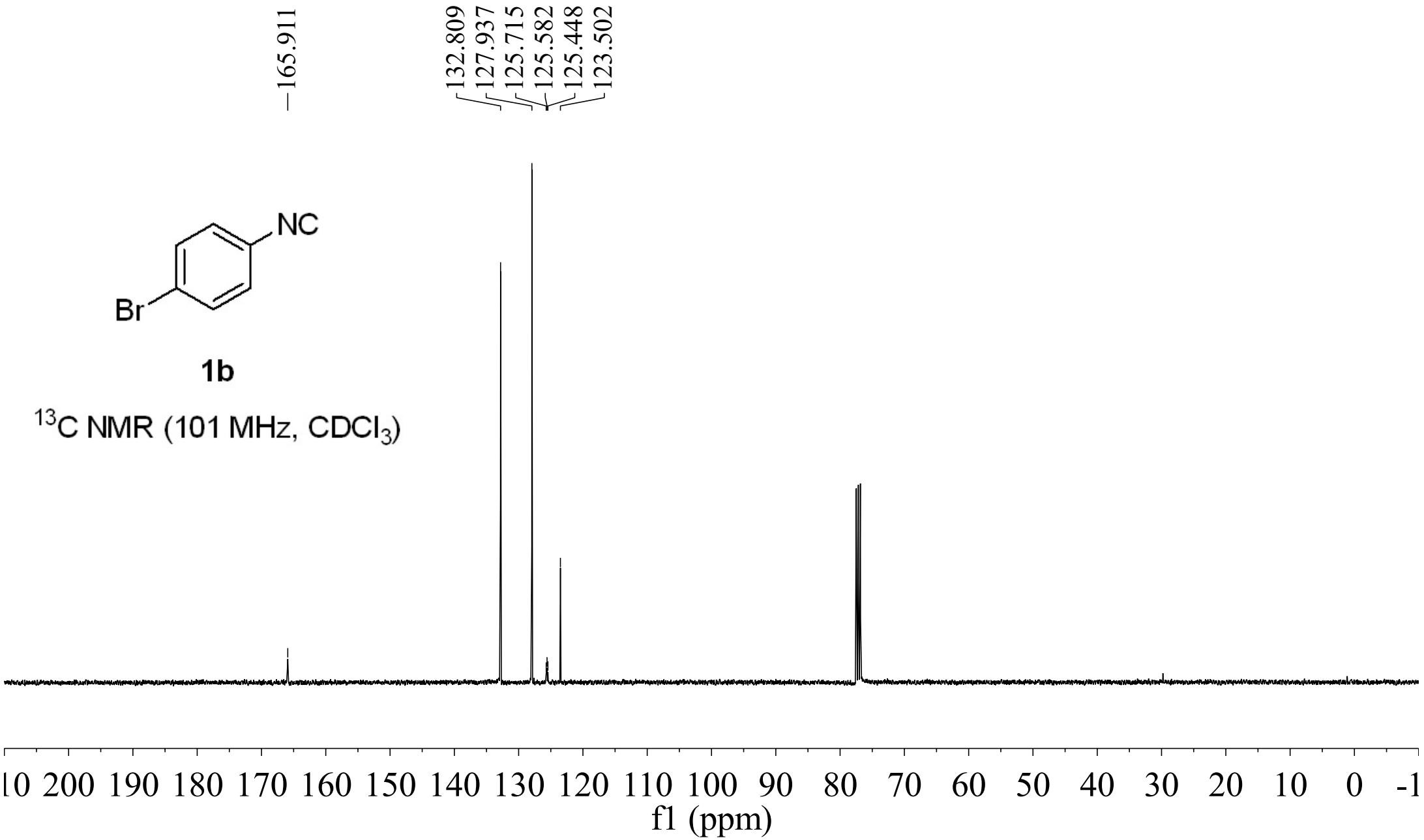
(10) Ai, W.; Liu, Y.; Wang, Q.; Lu, Z.; Liu, Q. *Org. Lett.* **2018**, *20*, 409-412.

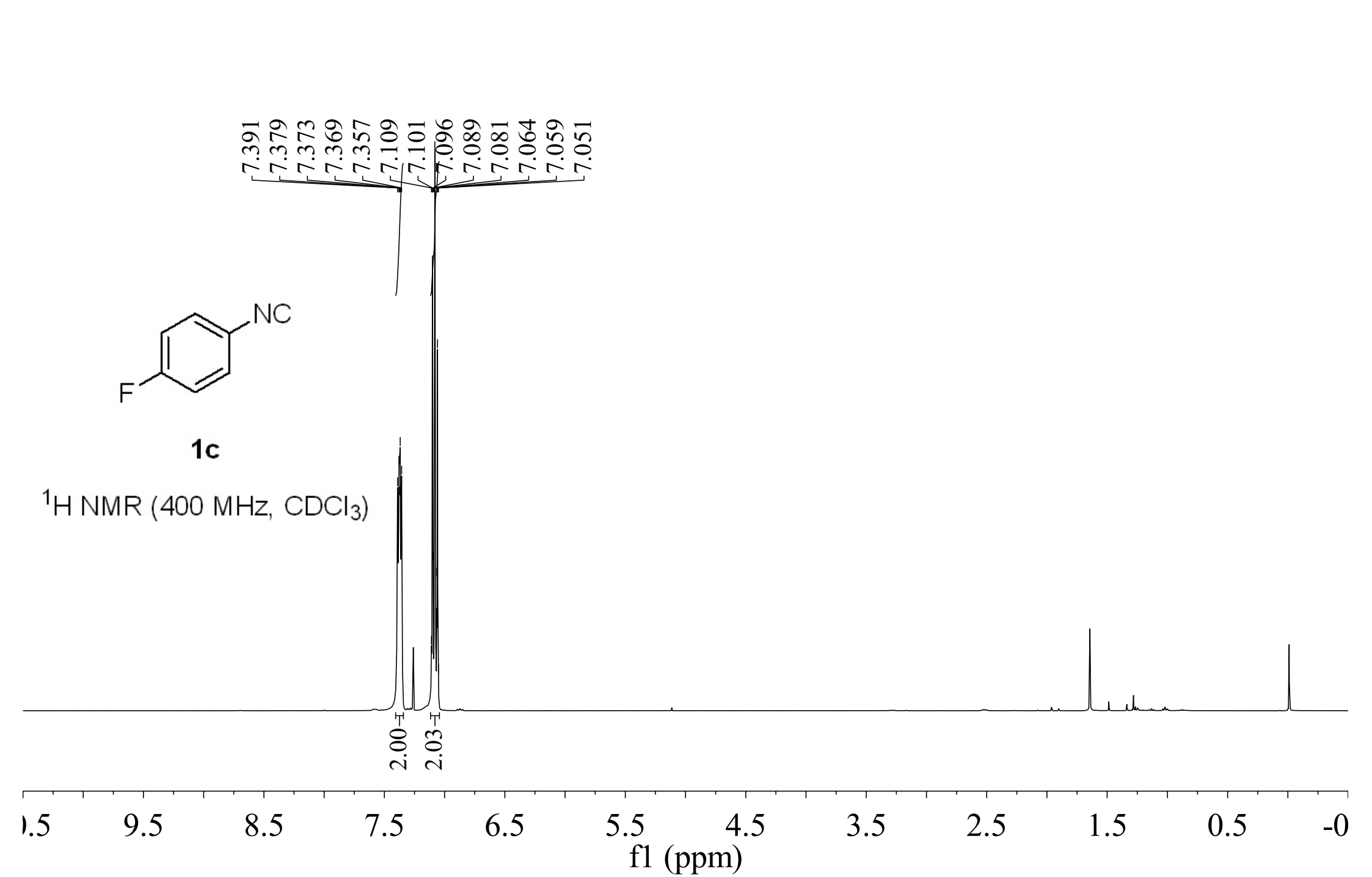
5. NMR Spectra of Substrates and Products

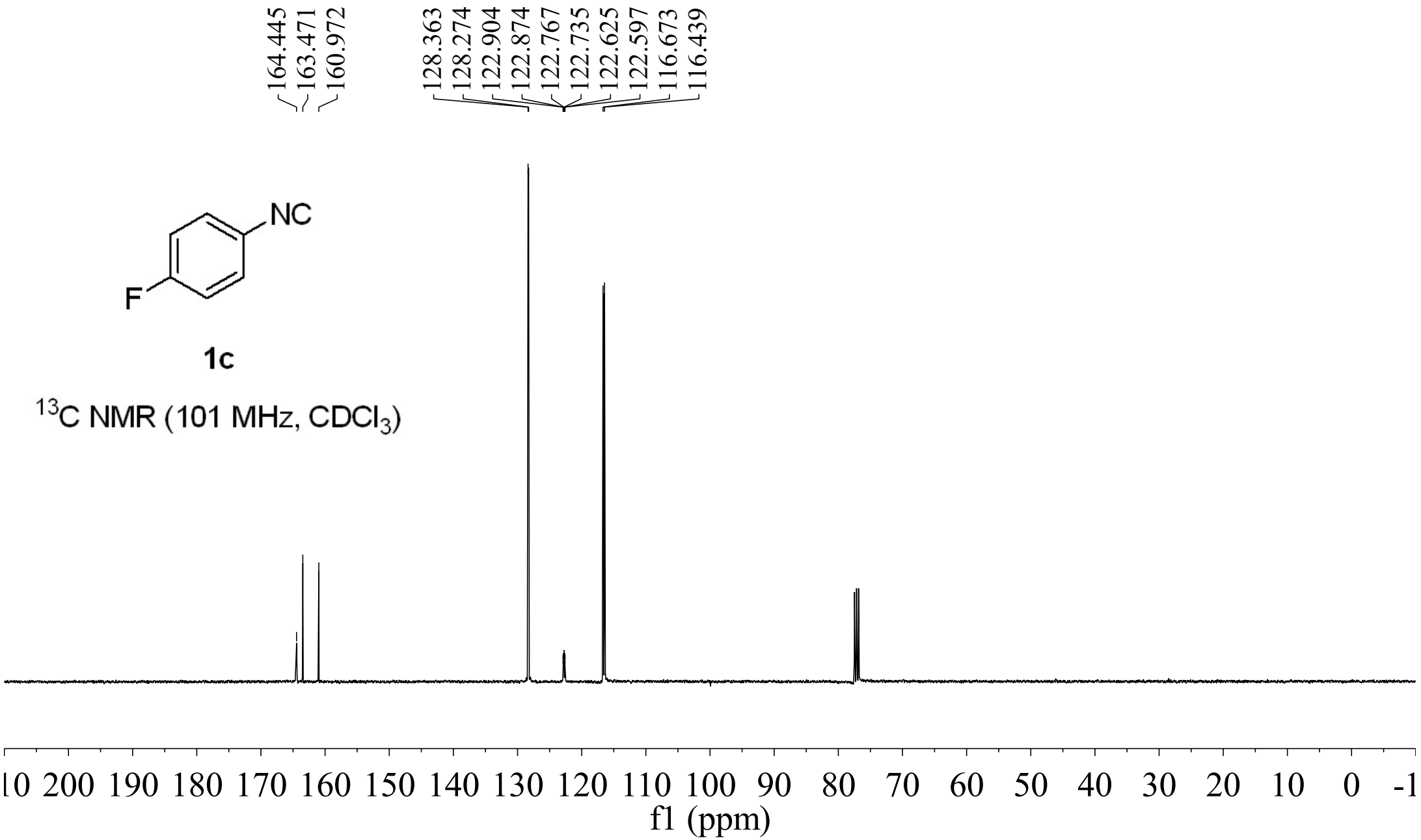



165.722
135.475
129.830
127.730
125.256
125.112
124.978
NC
Cl
1a
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.571
7.565
7.560
7.548
7.543
7.536
7.282
7.276
7.260
NC
Br
1b
1H NMR (400 MHz, CDCl3)
2.00
2.21
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

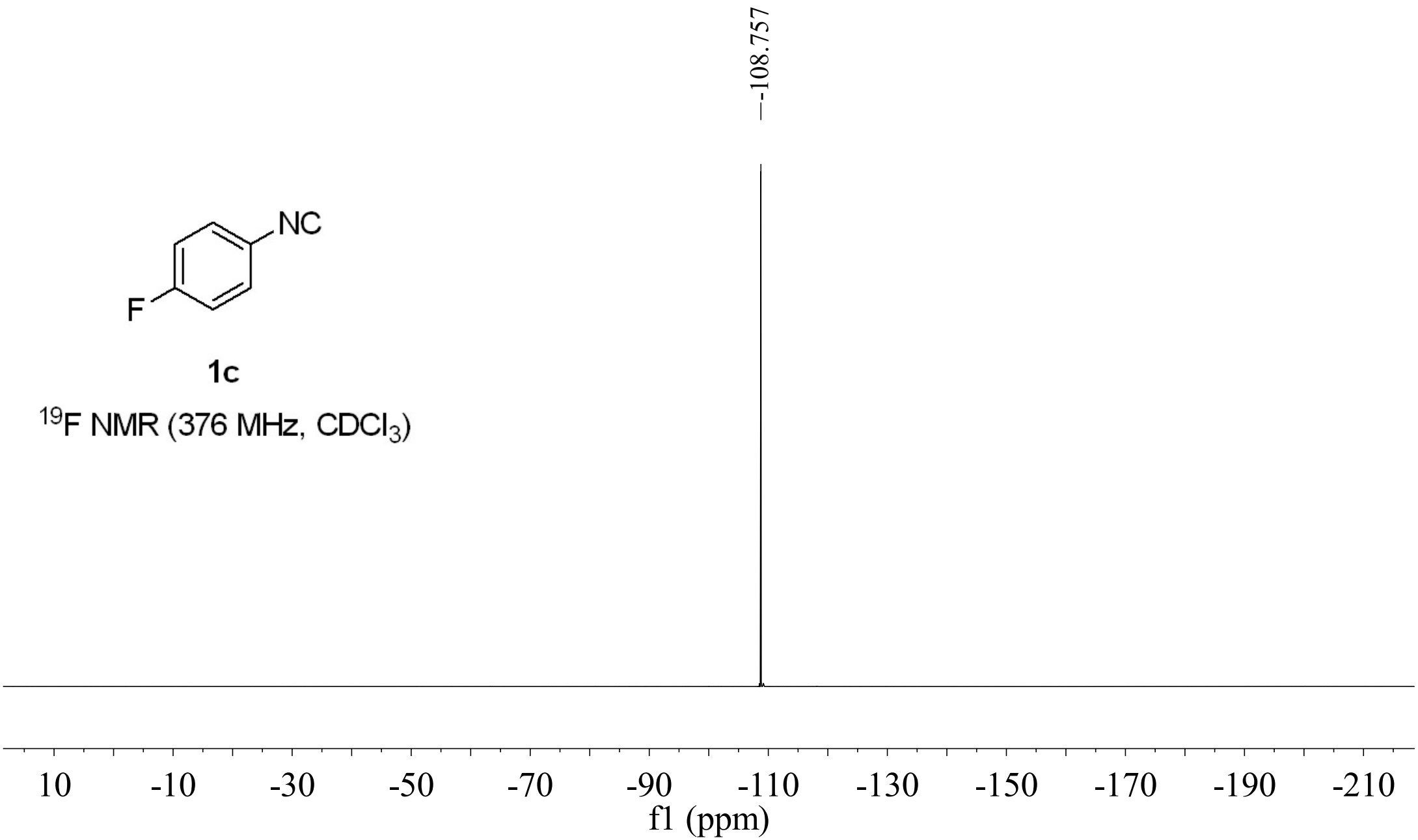

165.911
132.809
127.937
125.715
125.582
125.448
123.502
NC
Br
1b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

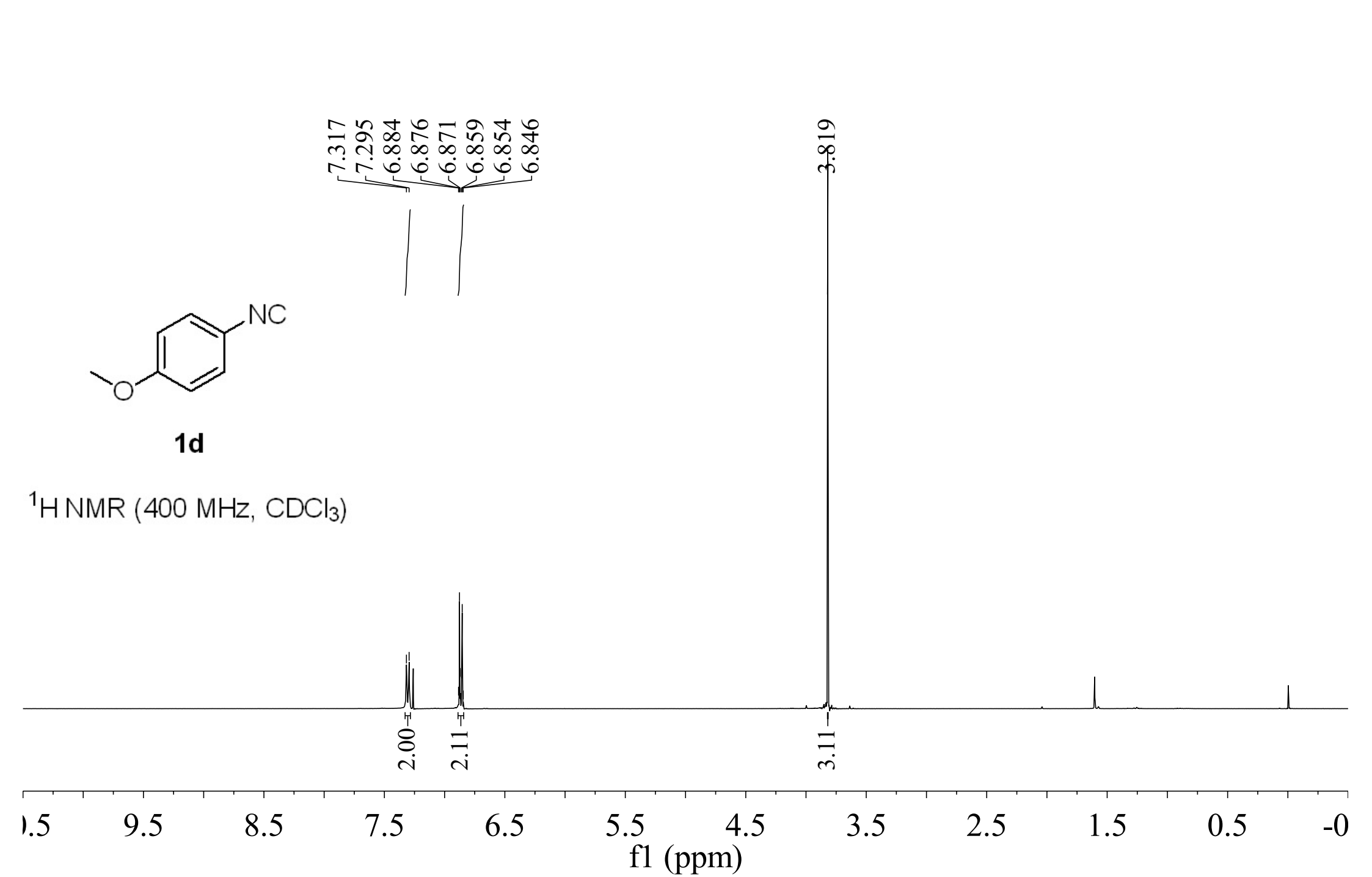

7.391
7.379
7.373
7.369
7.357
7.109
7.101
7.096
7.089
7.081
7.064
7.059
7.051
NC
F
1c
1H NMR (400 MHz, CDCl3)
2.00
2.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

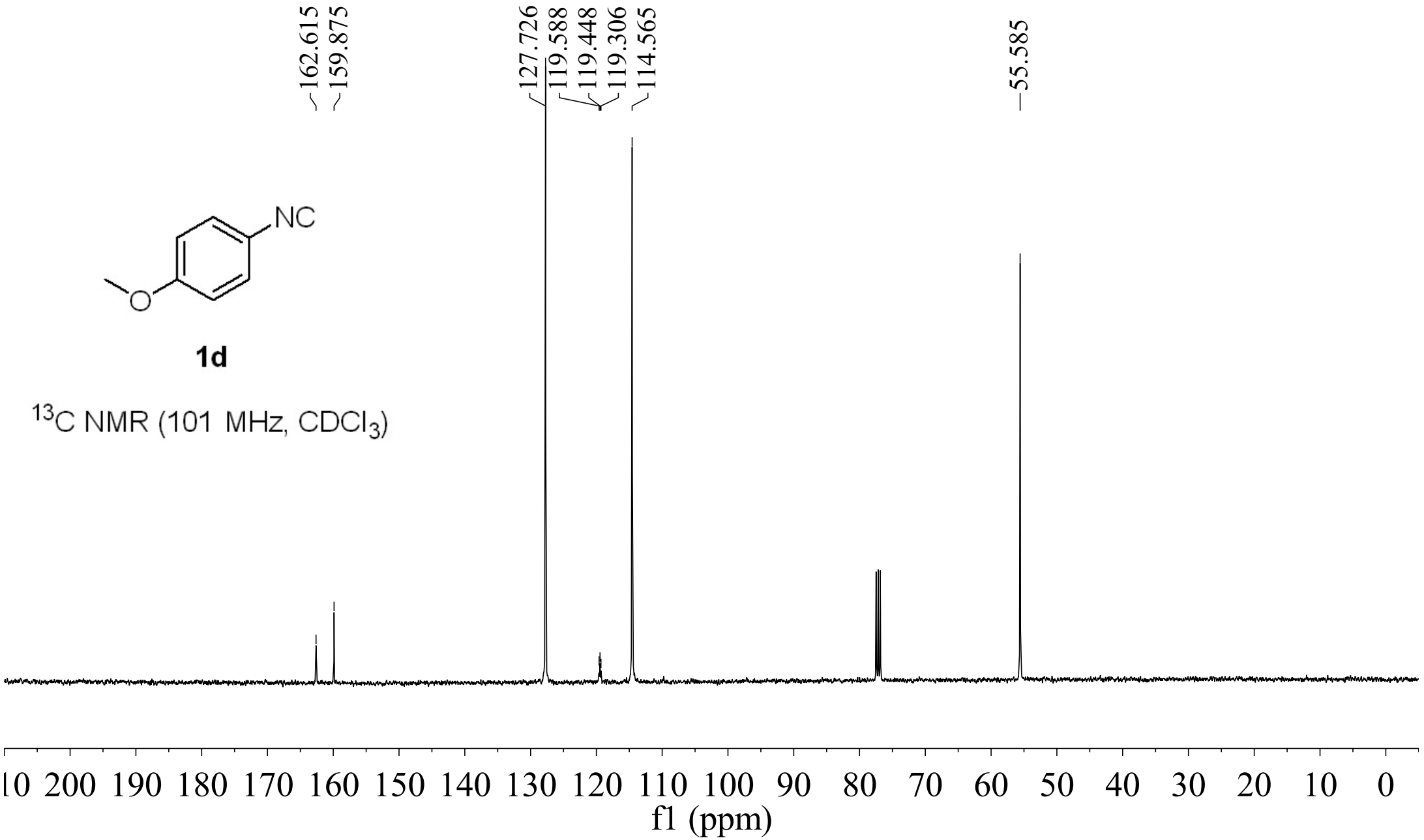

164.445
163.471
160.972
128.363
128.274
122.904
122.874
122.767
122.735
122.625
122.597
116.673
116.439
NC
F
1c
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

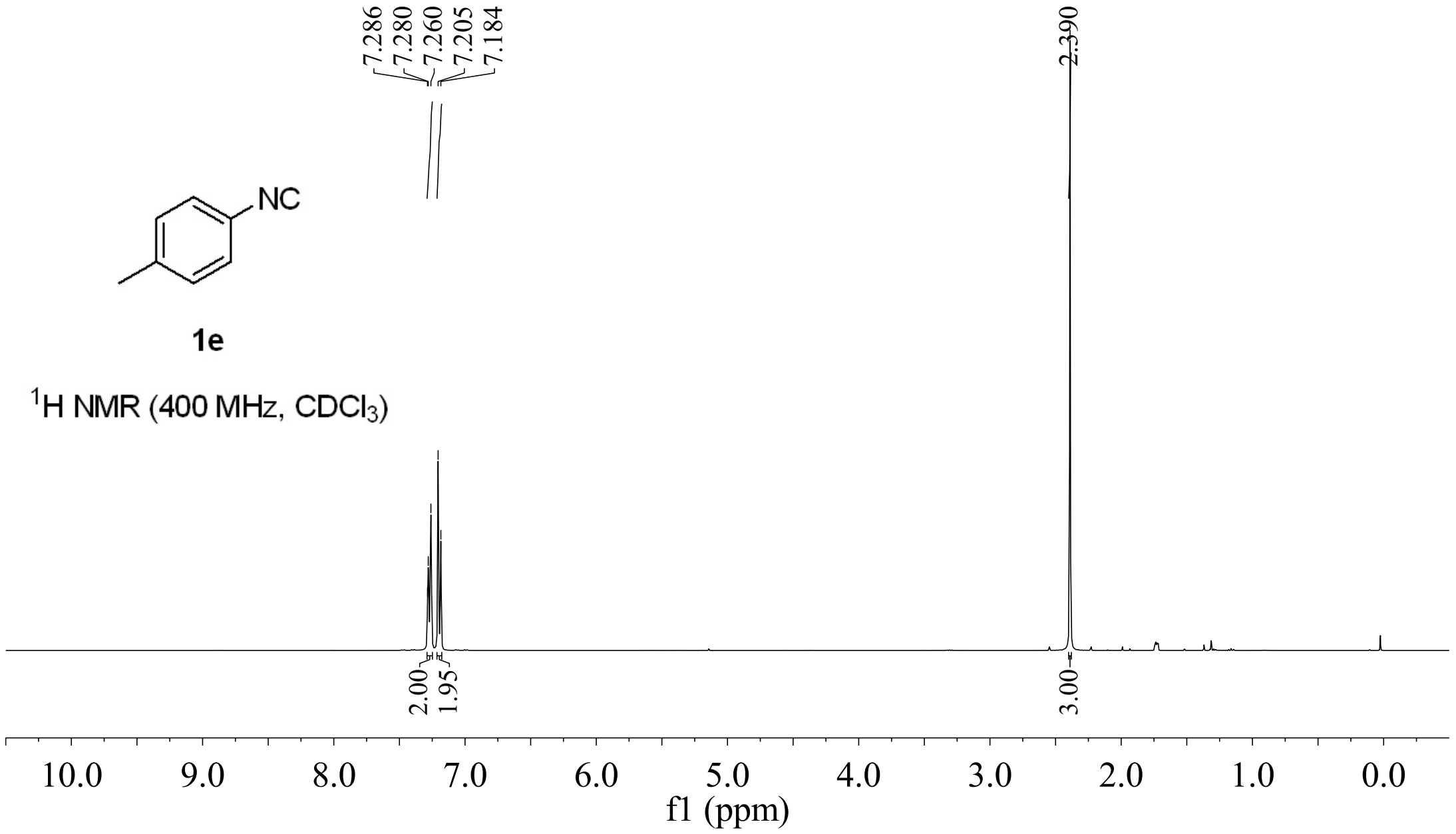
1c

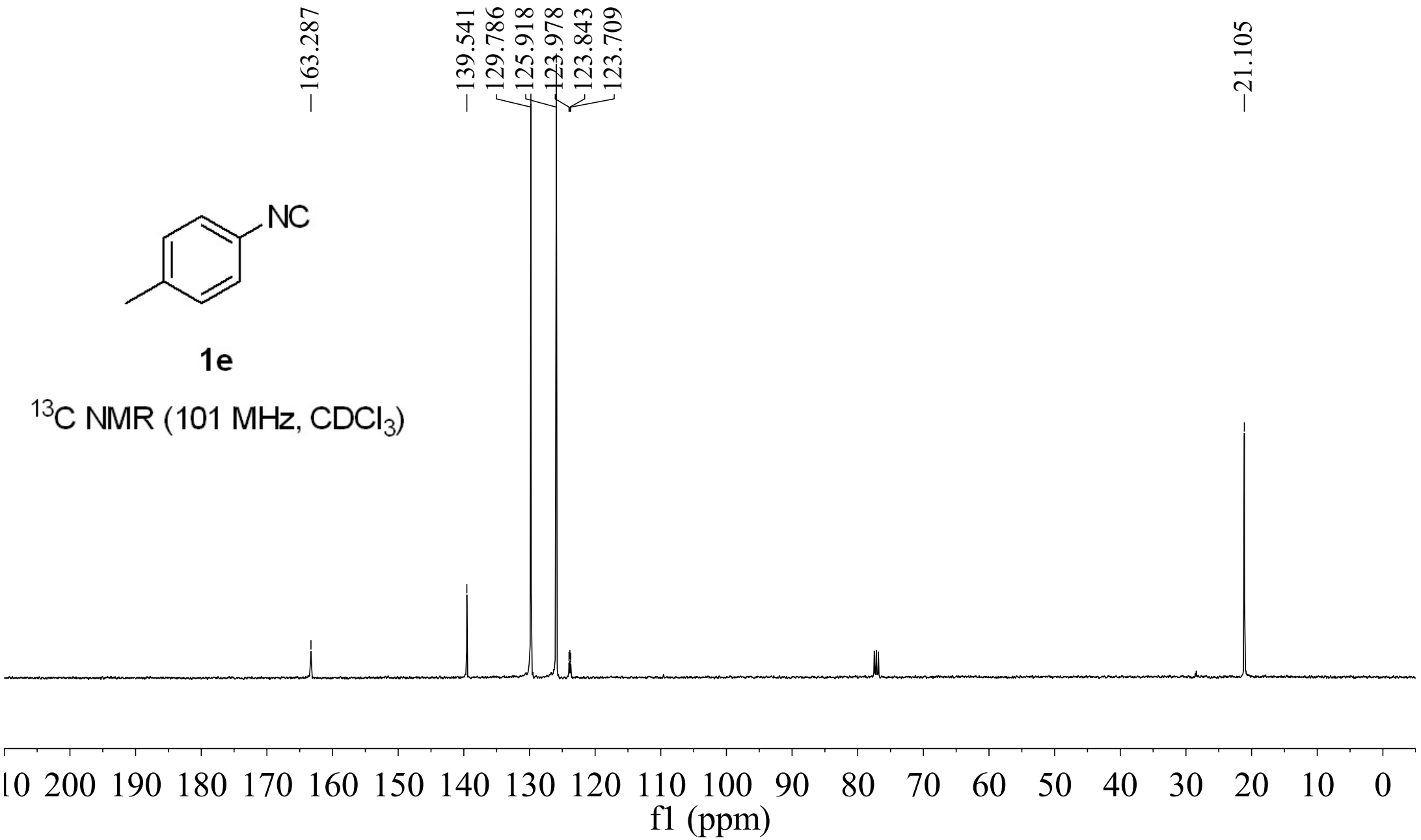
^{19}F NMR (376 MHz, $CDCl_3$)

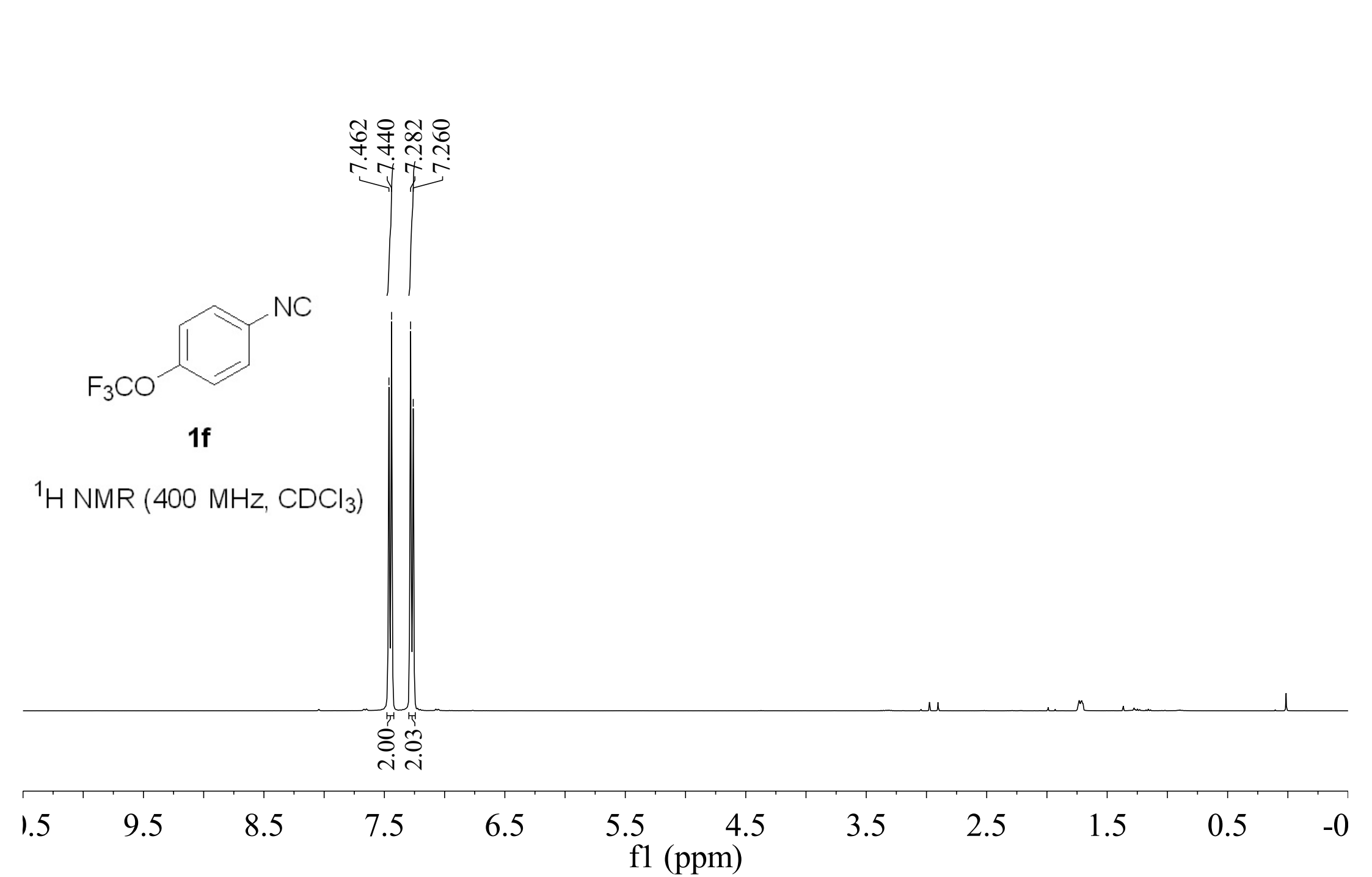


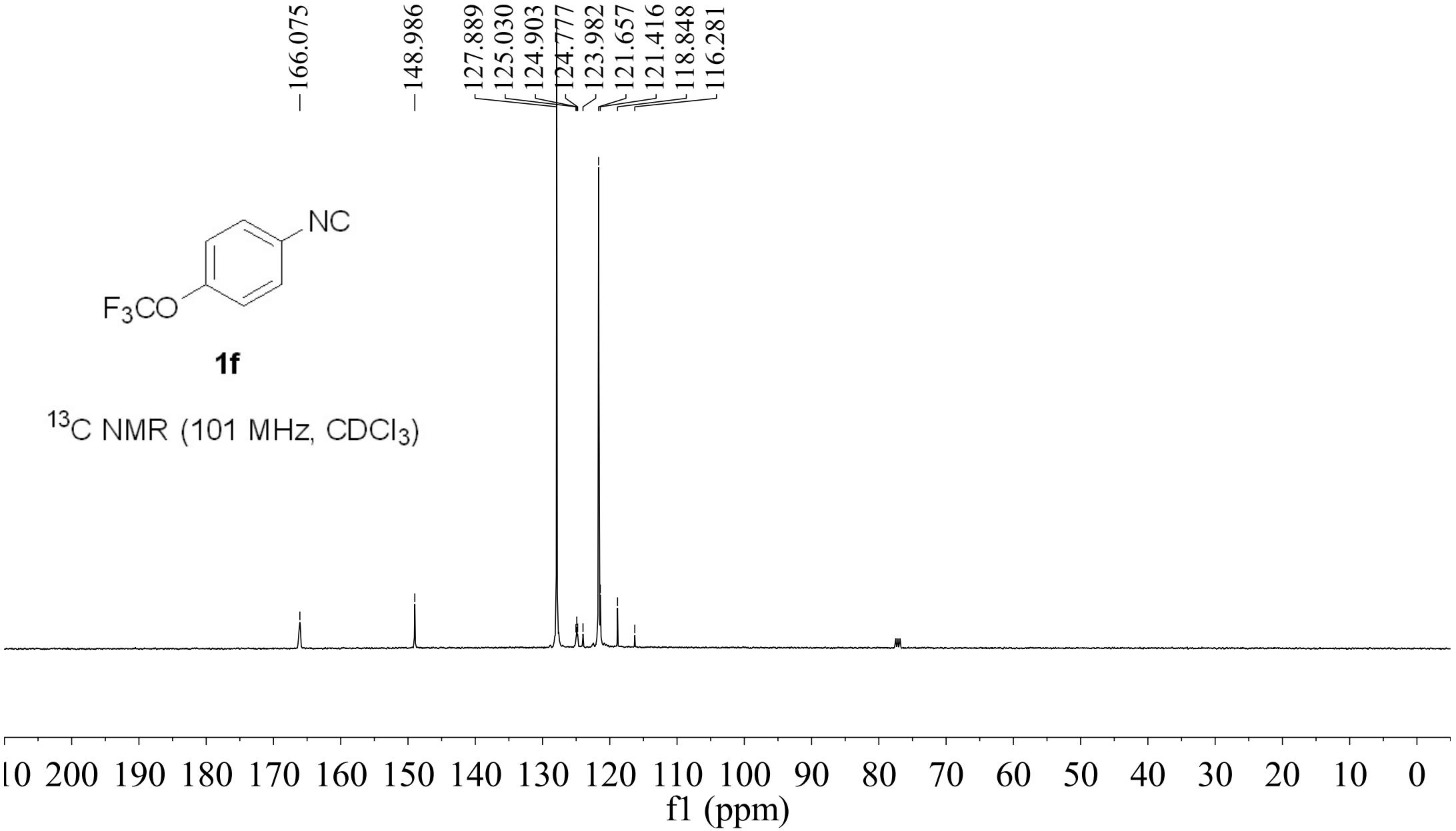

7.317
7.295
6.884
6.876
6.871
6.859
6.854
6.846
3.819
NC
O
1d
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.11
3.11
f1 (ppm)


162.615
159.875
127.726
119.588
119.448
119.306
114.565
55.585
NC
O
1d
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.286
7.280
7.260
7.205
7.184
2.390
NC
1e
1H NMR (400 MHz, CDCl3)
2.00
1.95
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

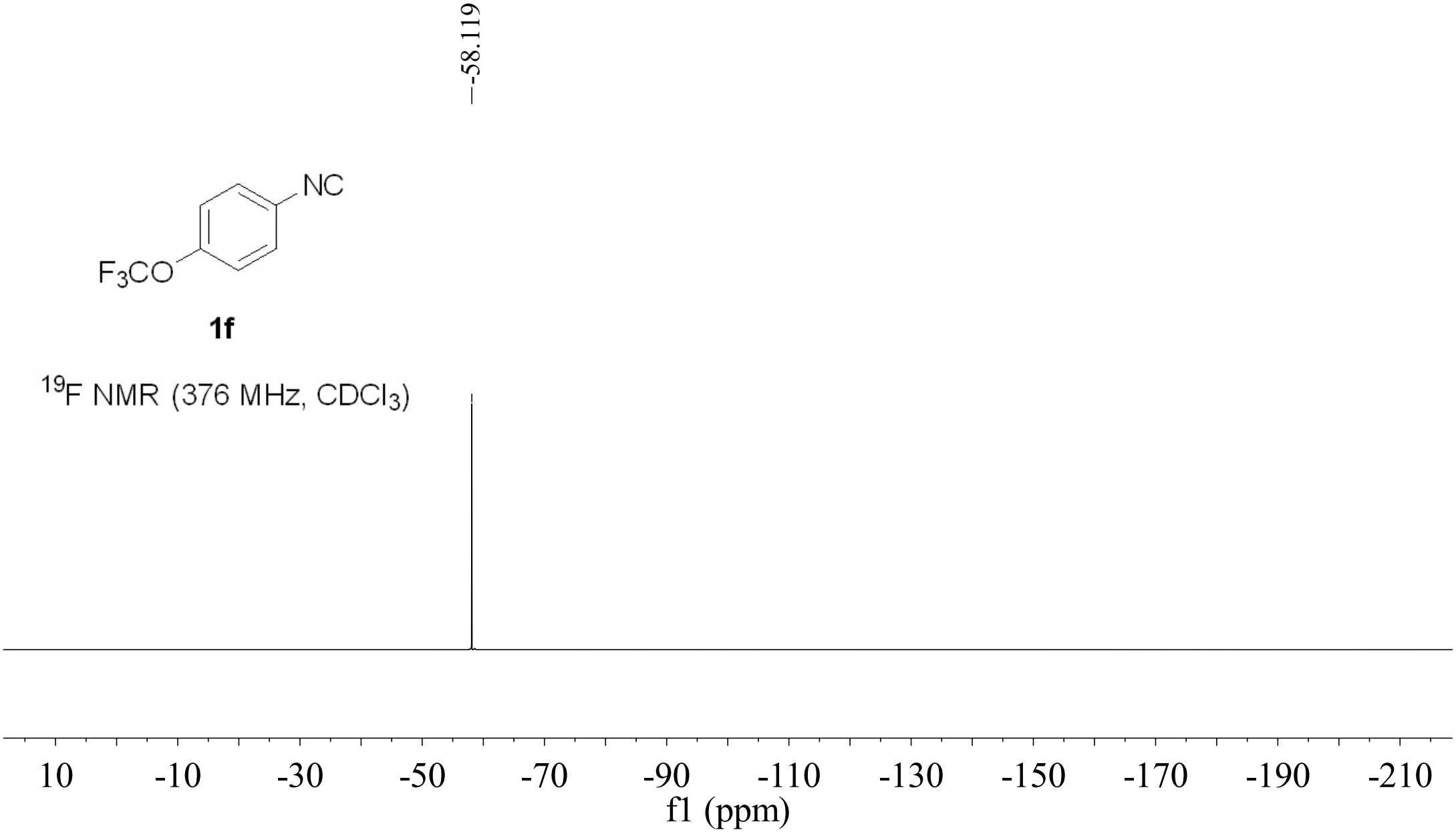

163.287
139.541
129.786
125.918
123.978
123.843
123.709
21.105
NC
1e
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

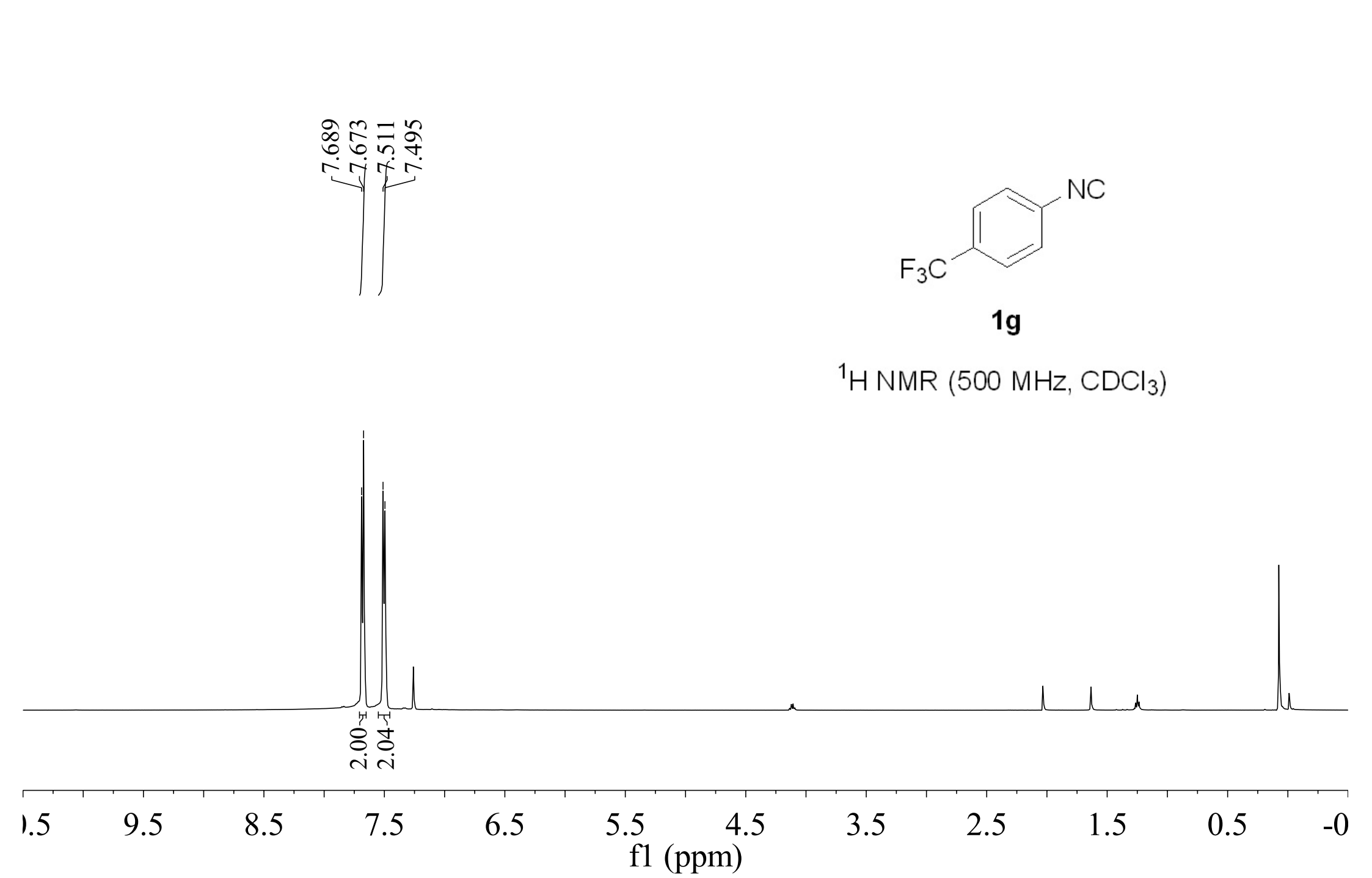

7.462
7.440
7.282
7.260
NC
F3CO
1f
1H NMR (400 MHz, CDCl3)
2.00
2.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

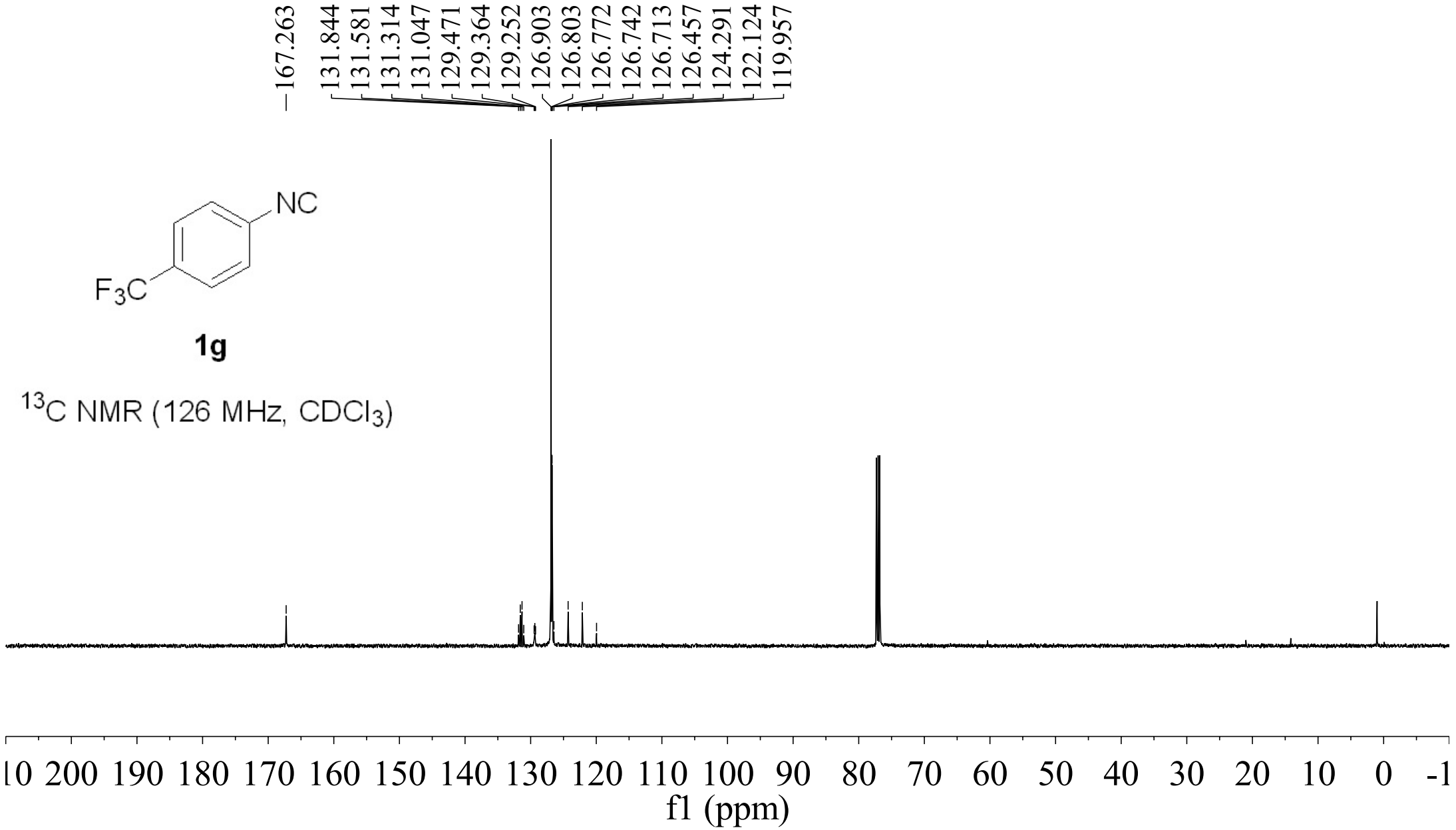

166.075
148.986
127.889
125.030
124.903
124.777
123.982
121.657
121.416
118.848
116.281
NC
F3CO
1f
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1f

^{19}F NMR (376 MHz, $CDCl_3$)

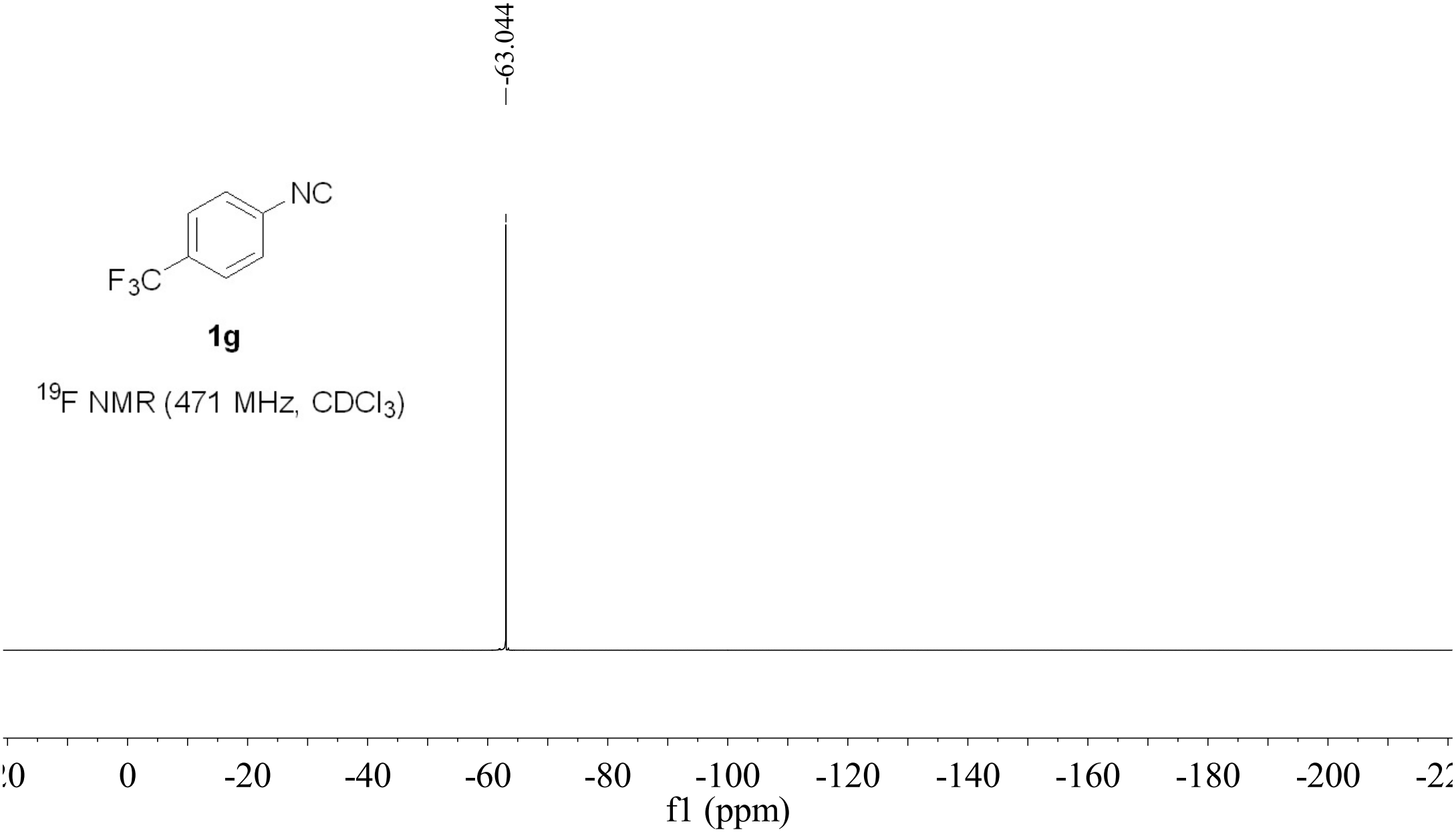


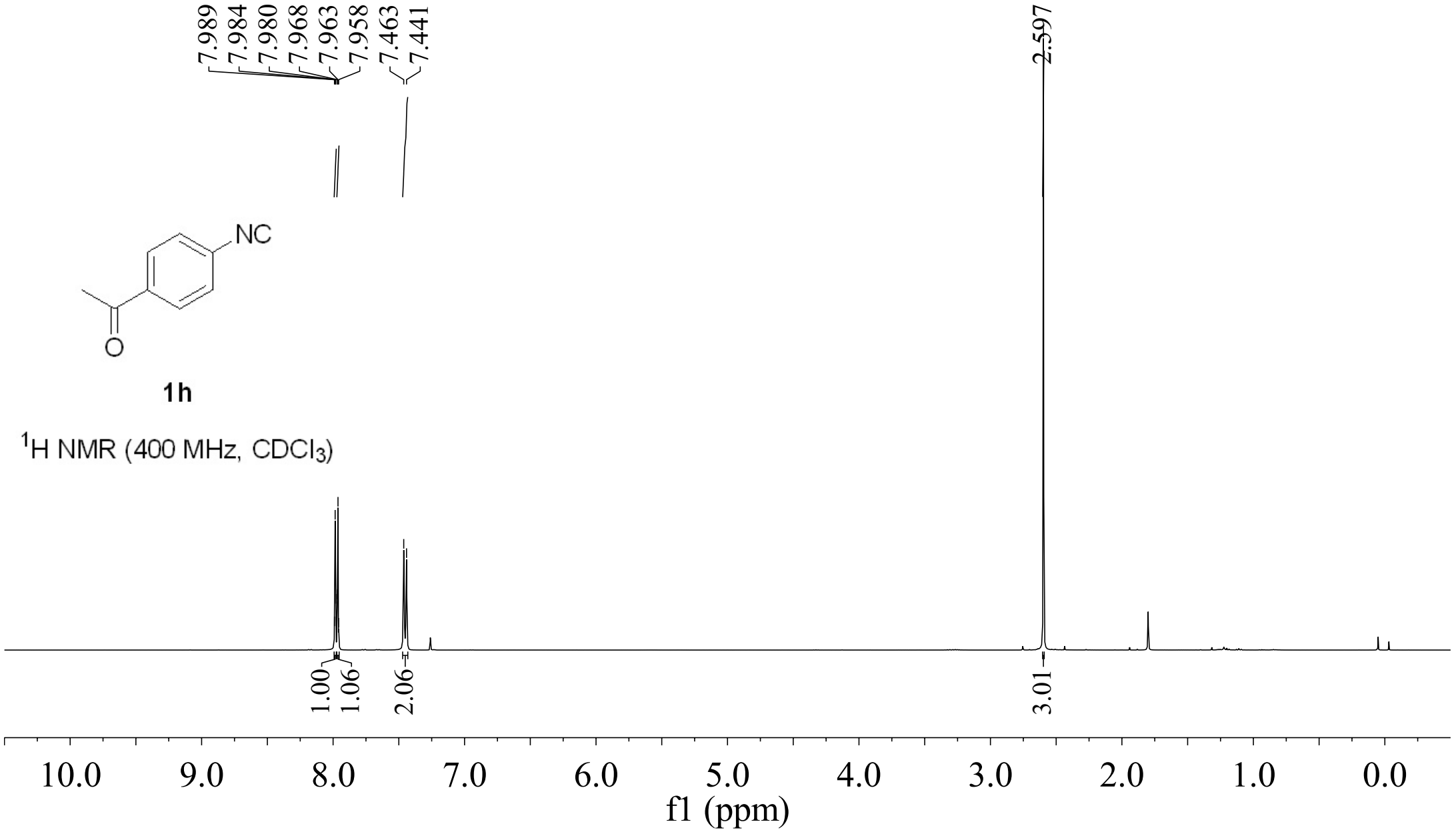

7.689
7.673
7.511
7.495
NC
F3C
1g
1H NMR (500 MHz, CDCl3)
2.00
2.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


167.263
131.844
131.581
131.314
131.047
129.471
129.364
129.252
126.903
126.803
126.772
126.742
126.713
126.457
124.291
122.124
119.957
NC
F3C
1g
13C NMR (126 MHz, CDCl3)
f1 (ppm)

1g

^{19}F NMR (471 MHz, $CDCl_3$)




7.989
7.984
7.980
7.968
7.963
7.958
7.463
7.441
2.597
NC
O
1h
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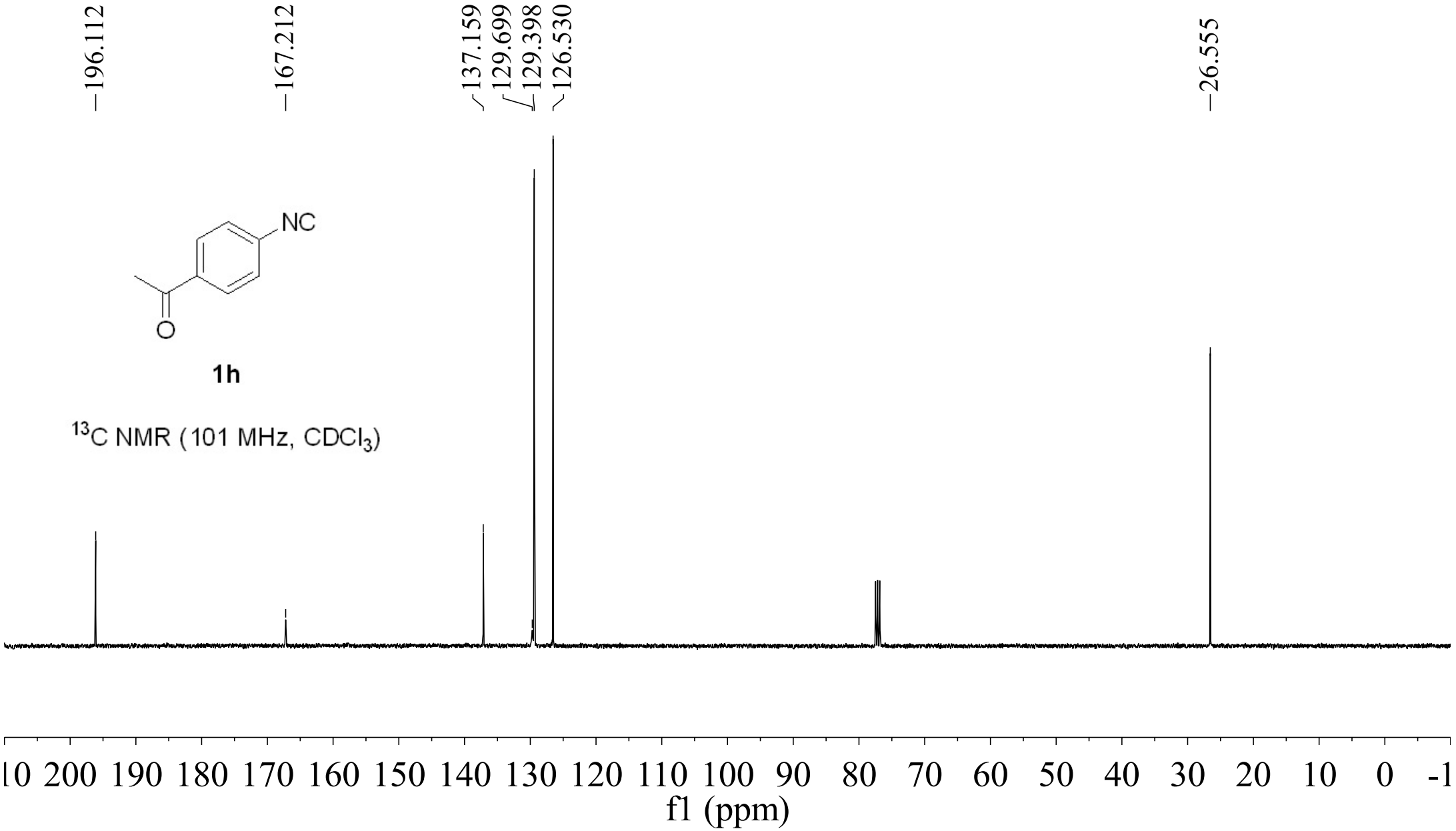
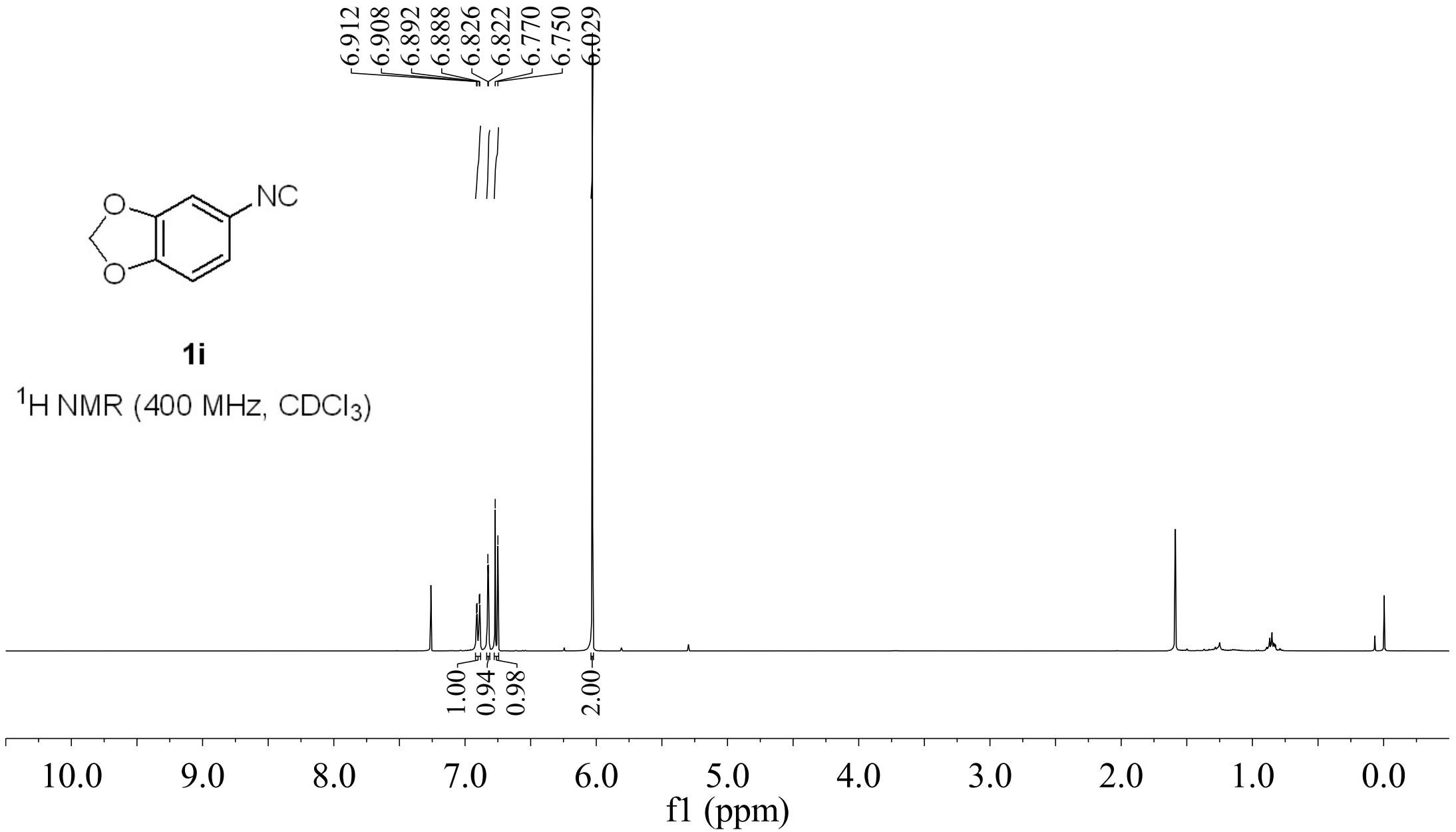
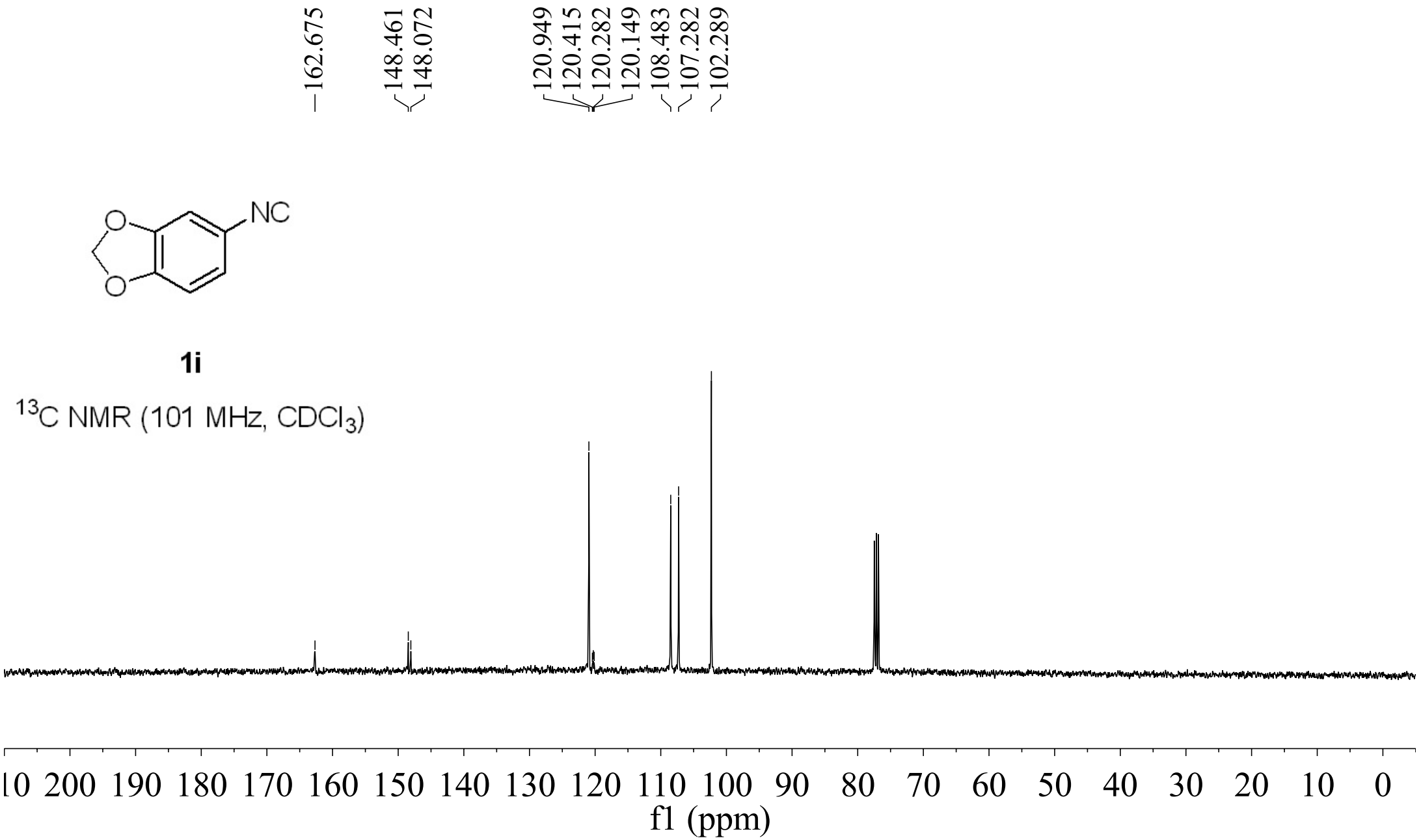
1.00
1.06
2.06
3.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

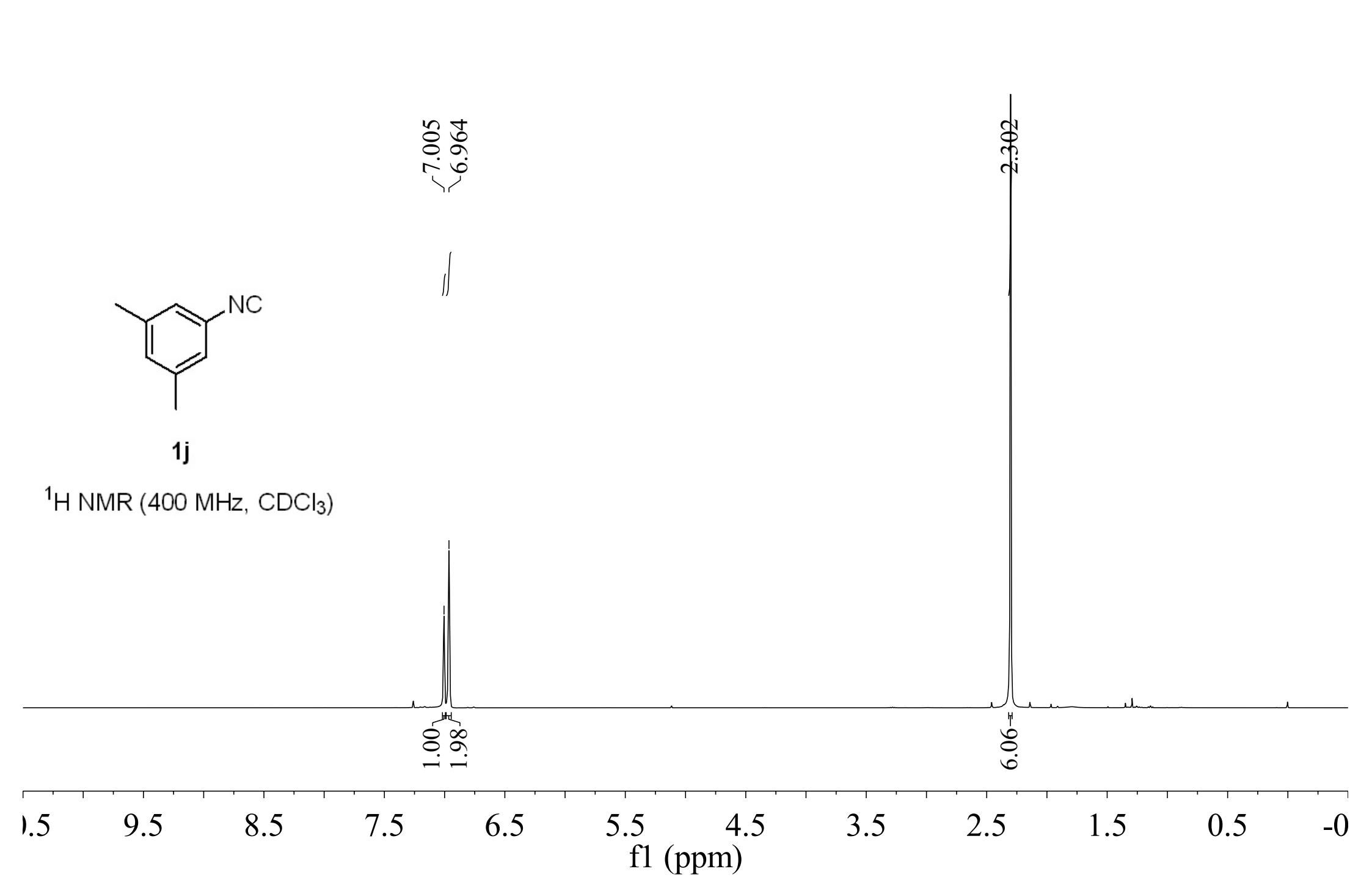

196.112
167.212
137.159
129.699
129.398
126.530
26.555
NC
O
1h
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

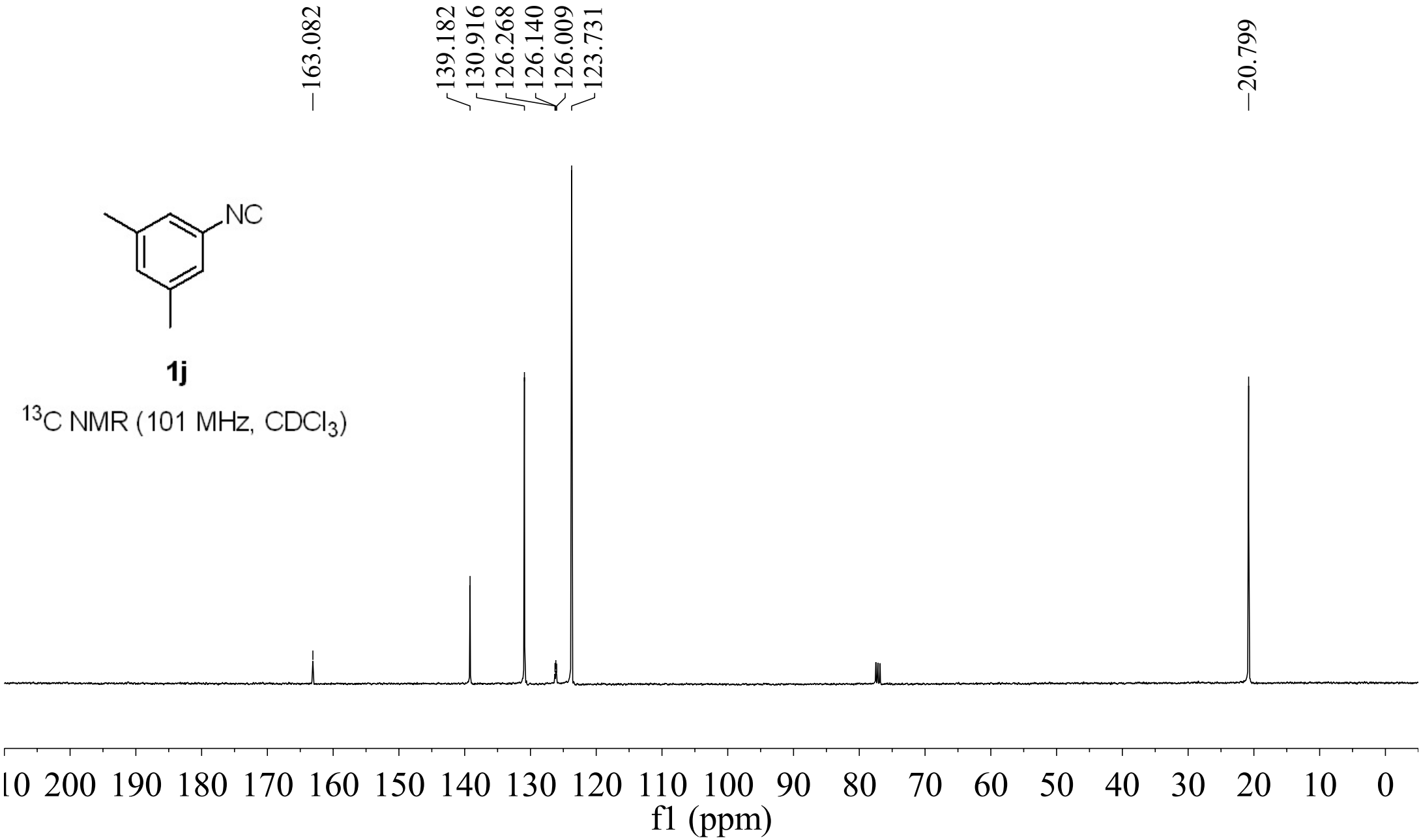


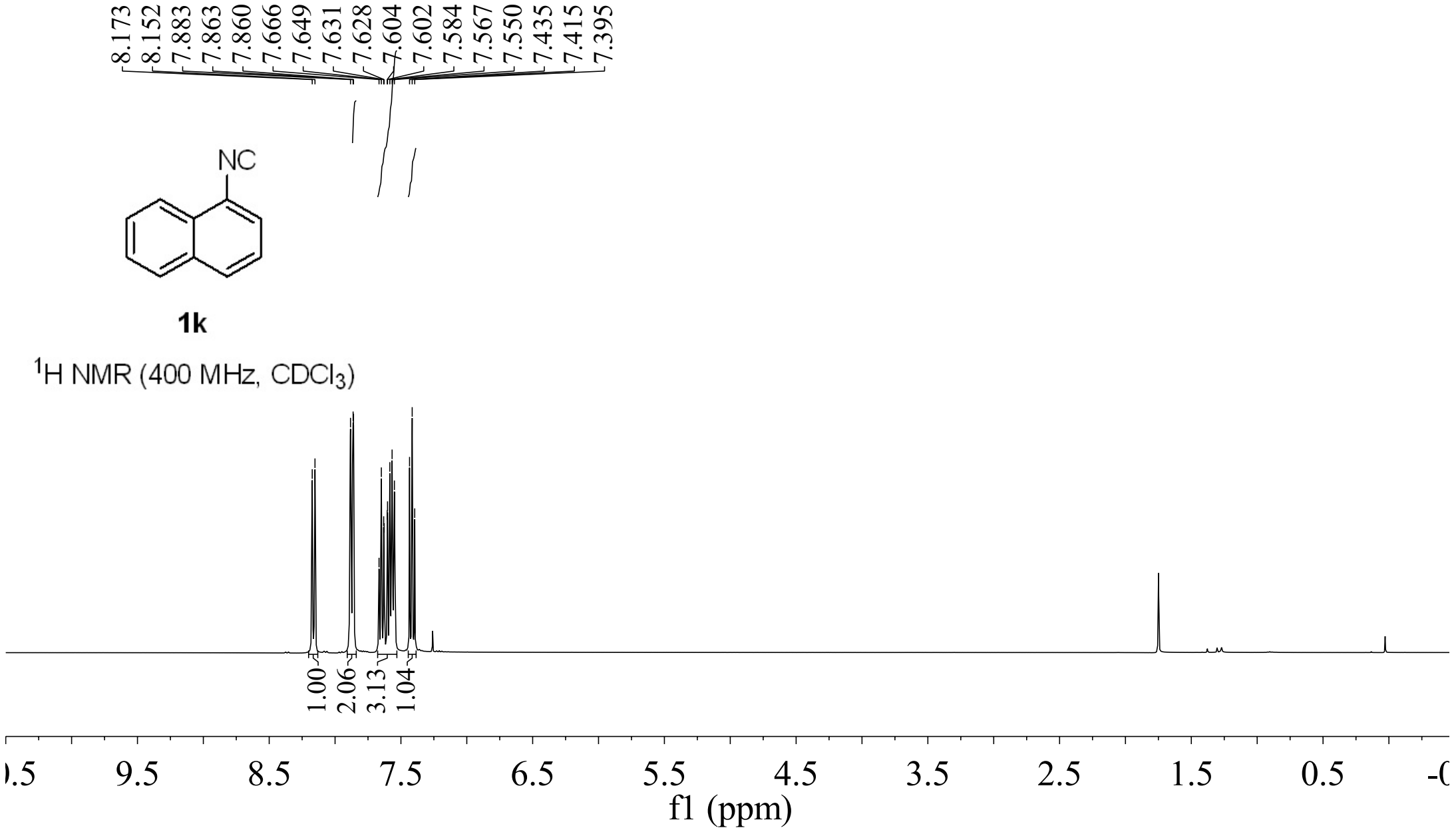
1i

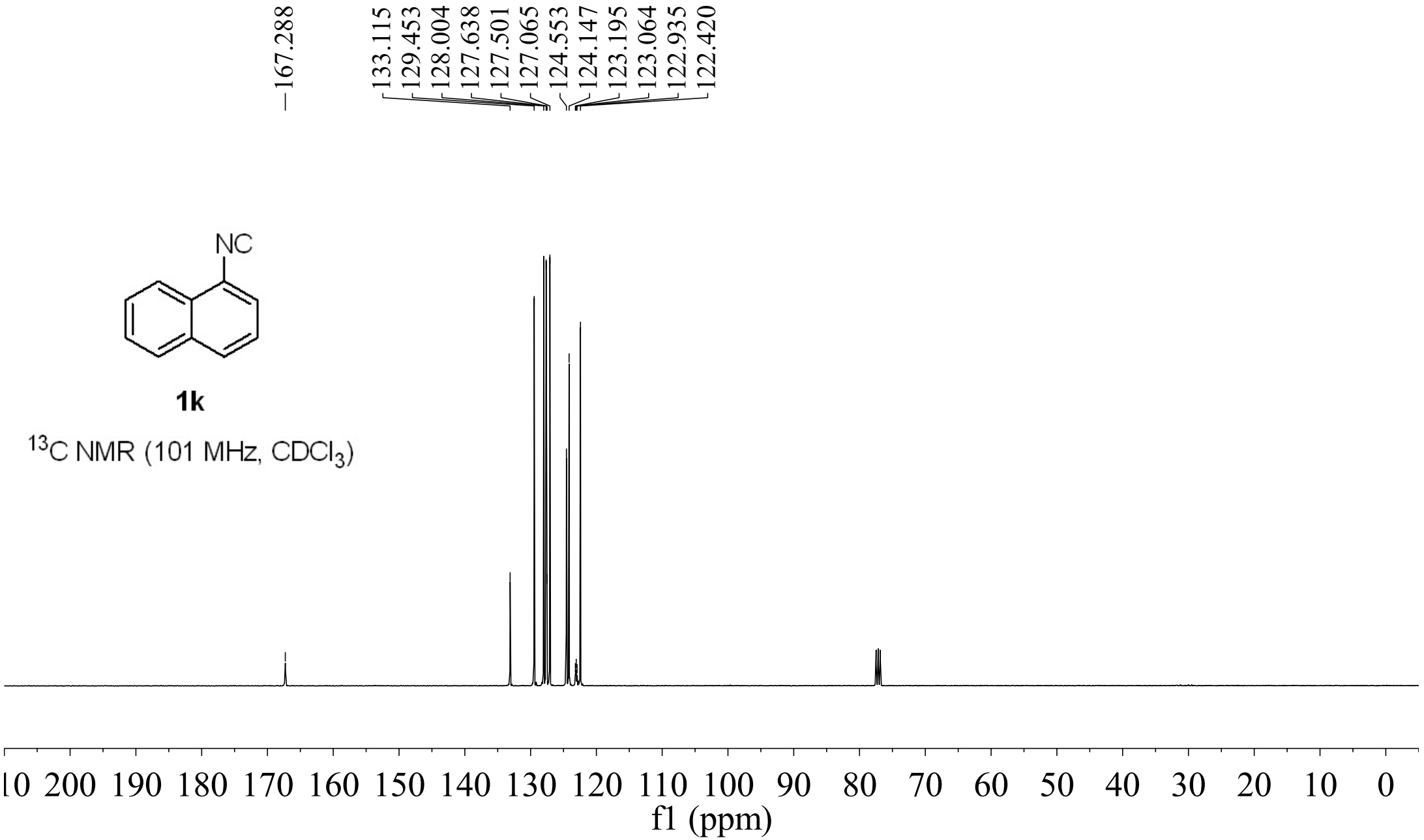
^{1}H NMR (400 MHz, $CDCl_3$)

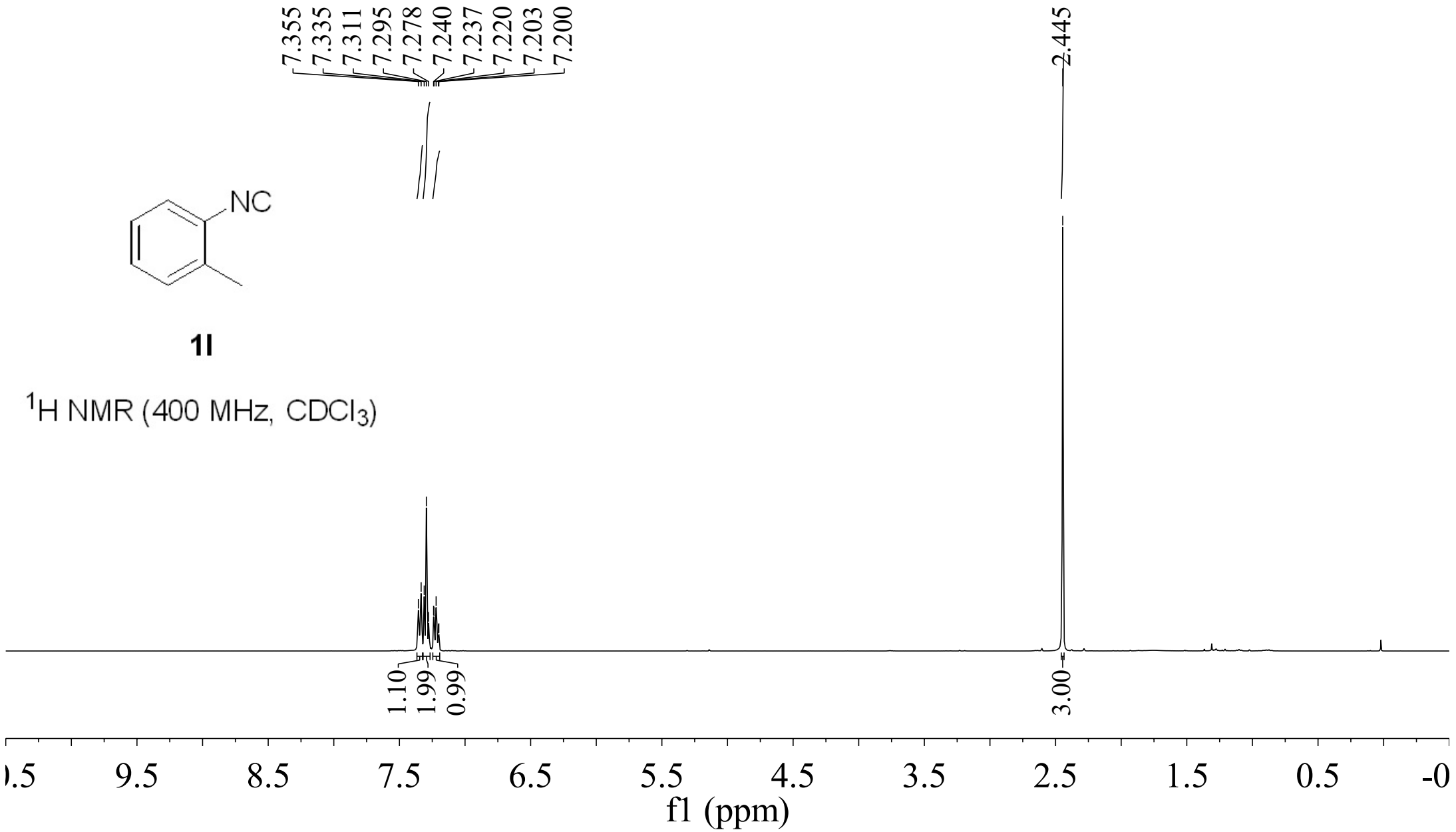

162.675
148.461
148.072
120.949
120.415
120.282
120.149
108.483
107.282
102.289
NC
O
O
1i
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

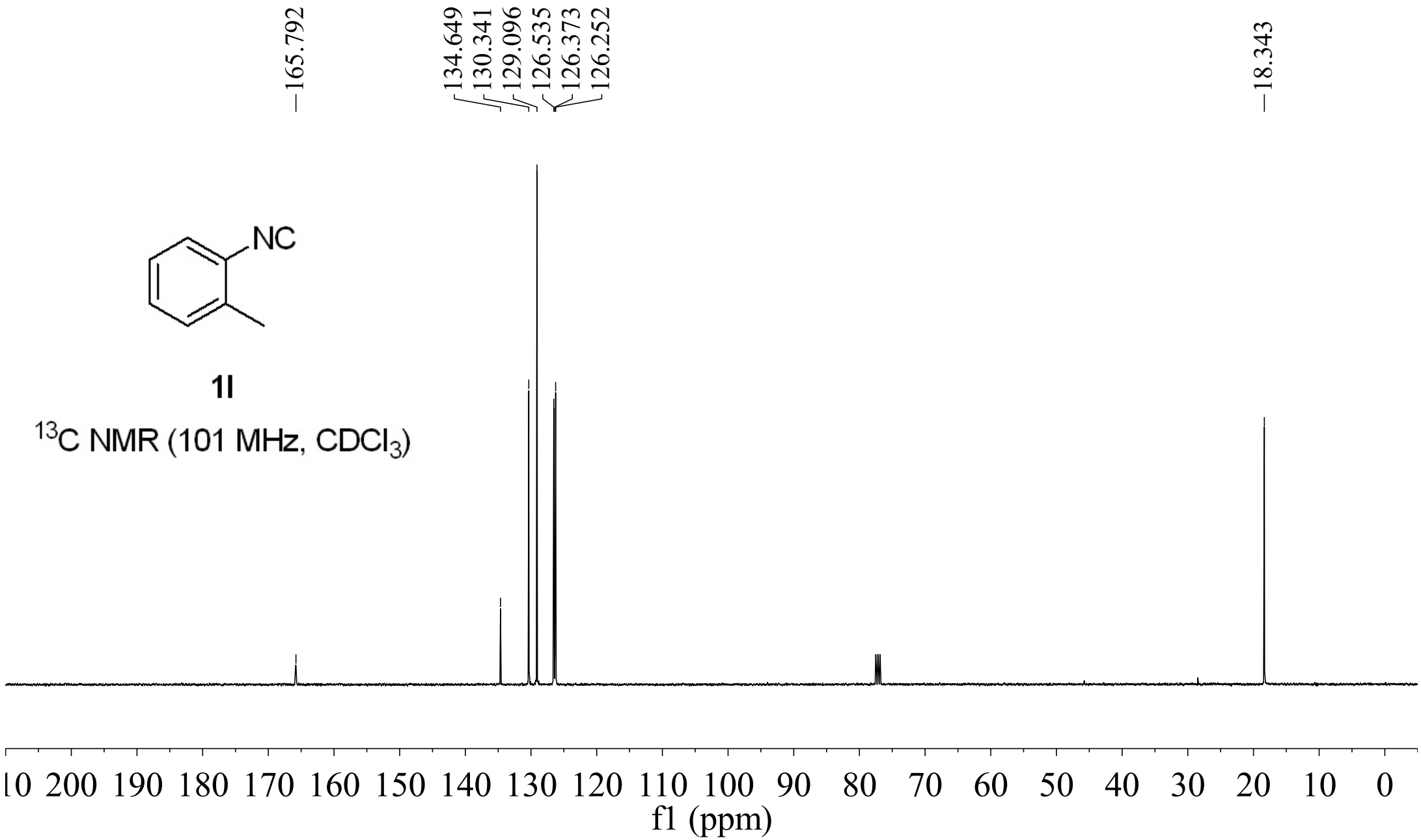

NC
1j
1H NMR (400 MHz, CDCl3)
7.005
6.964
2.302
1.00
1.98
6.06
f1 (ppm)

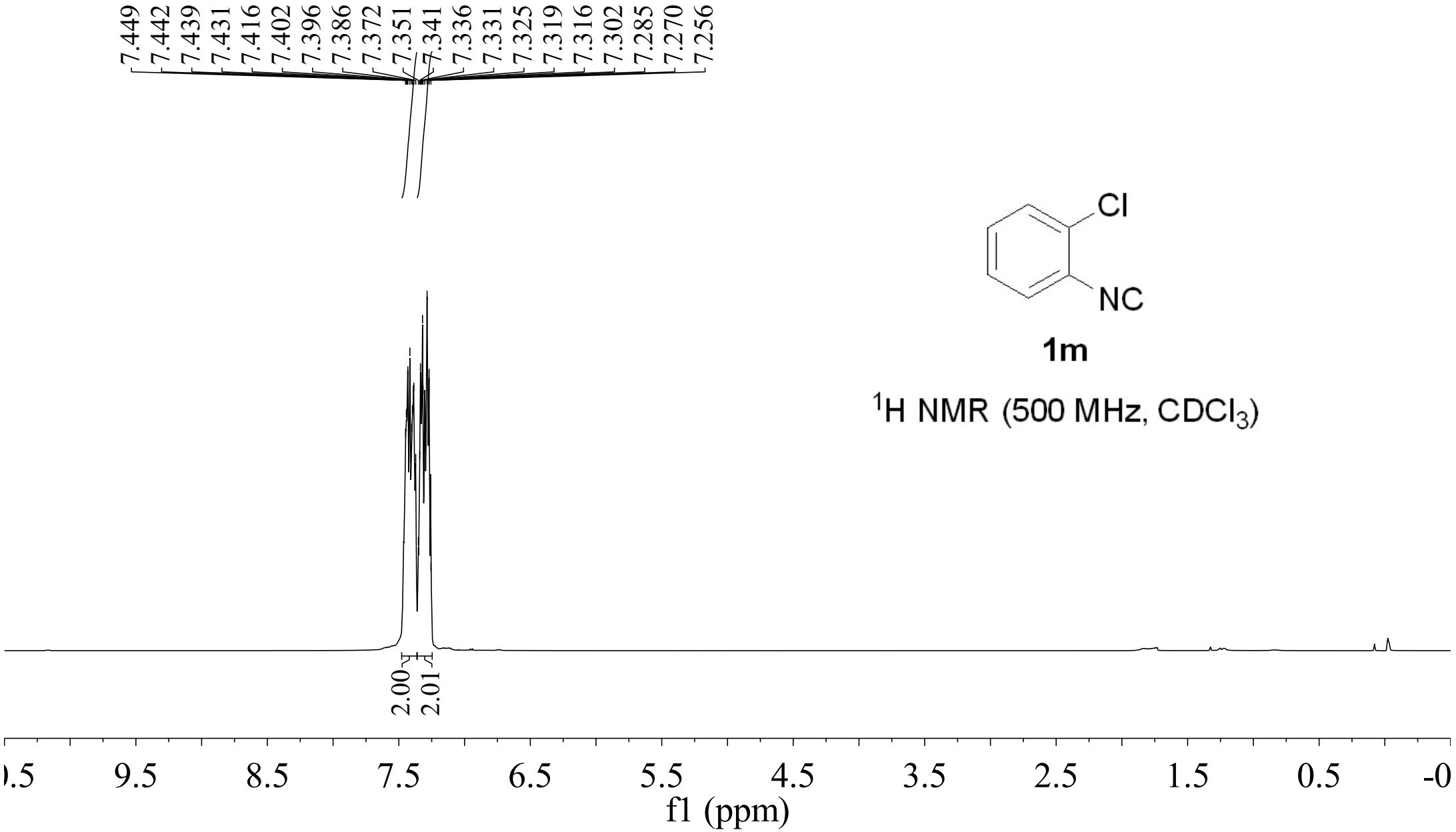

163.082
139.182
130.916
126.268
126.140
126.009
123.731
20.799
NC
1j
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

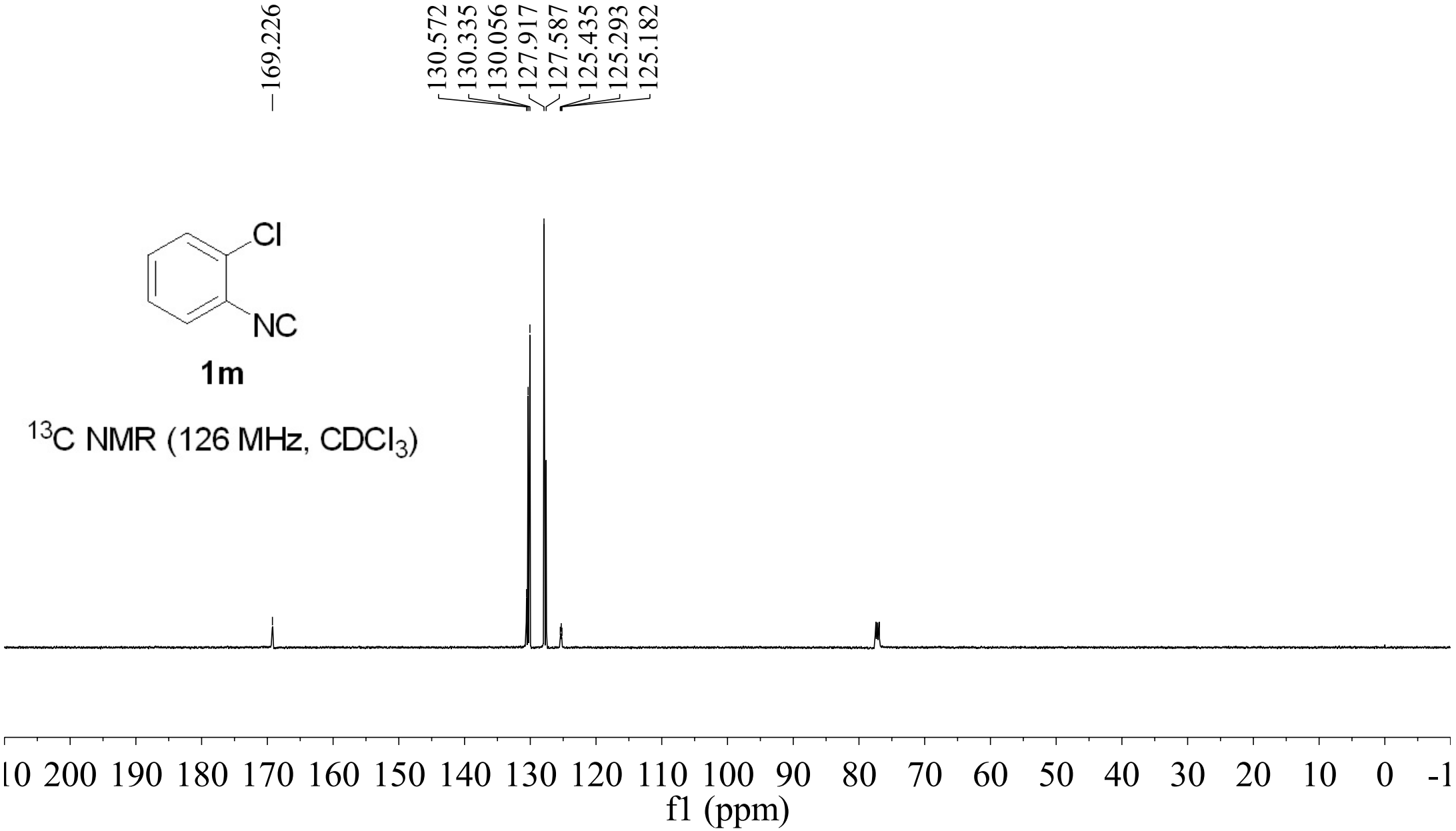

8.173
8.152
7.883
7.863
7.860
7.666
7.649
7.631
7.628
7.604
7.602
7.584
7.567
7.550
7.435
7.415
7.395
NC
1k
1H NMR (400 MHz, CDCl3)
1.00
2.06
3.13
1.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

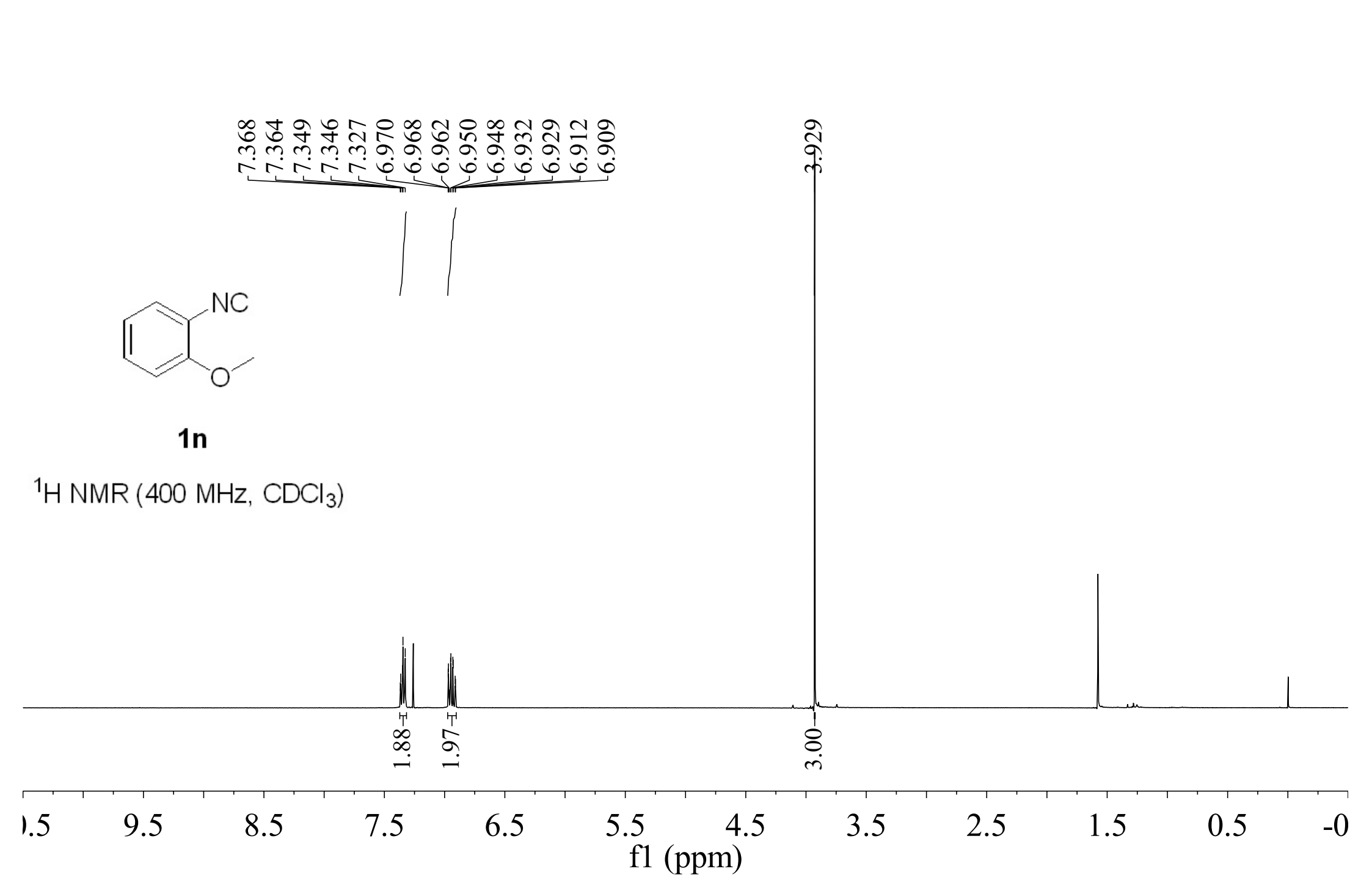

167.288
133.115
129.453
128.004
127.638
127.501
127.065
124.553
124.147
123.195
123.064
122.935
122.420
NC
1k
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

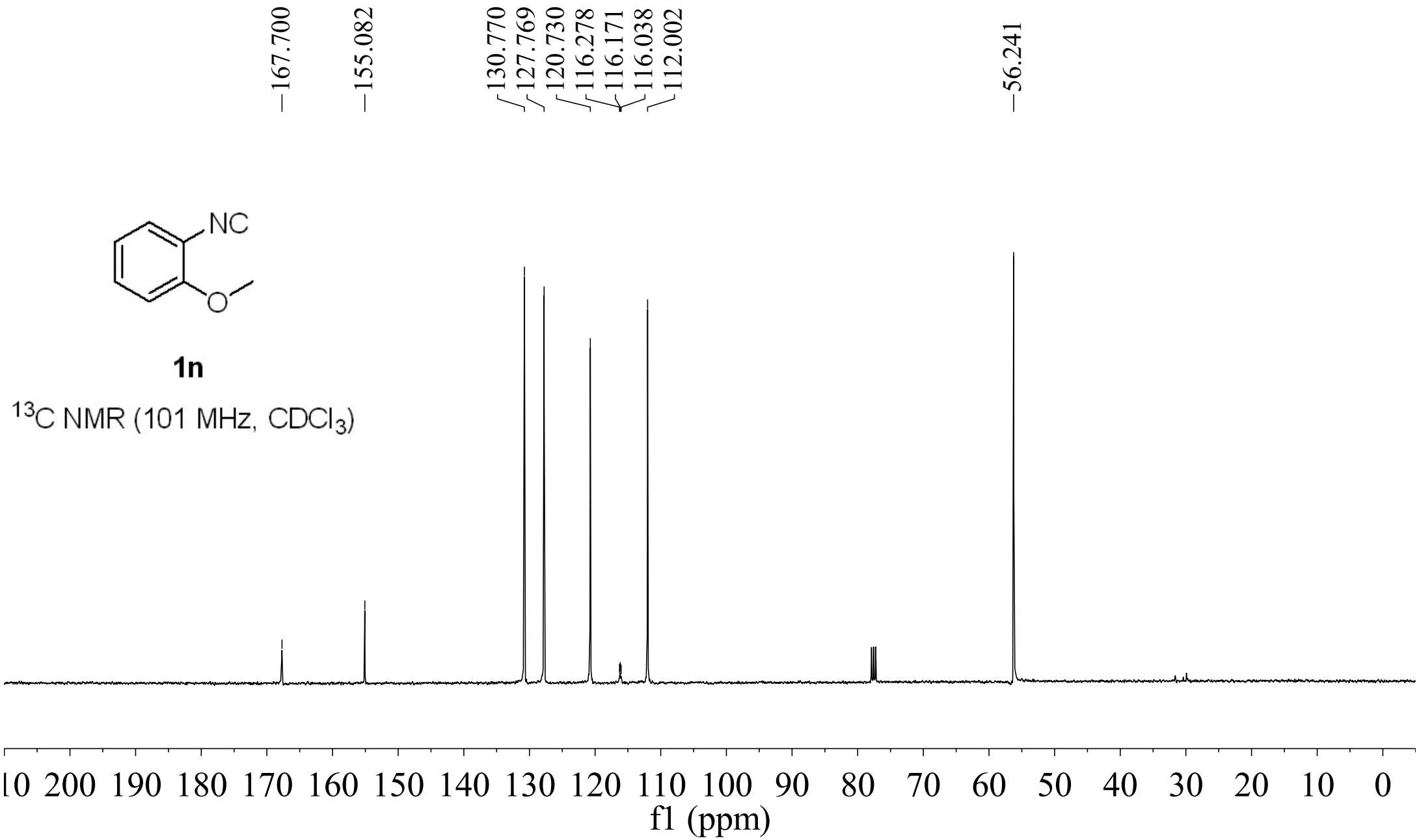

7.355
7.335
7.311
7.295
7.278
7.240
7.237
7.220
7.203
7.200
2.445
NC
1l
^{1}H NMR (400 MHz, CDCl$_3$)
1.10
1.99
0.99
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

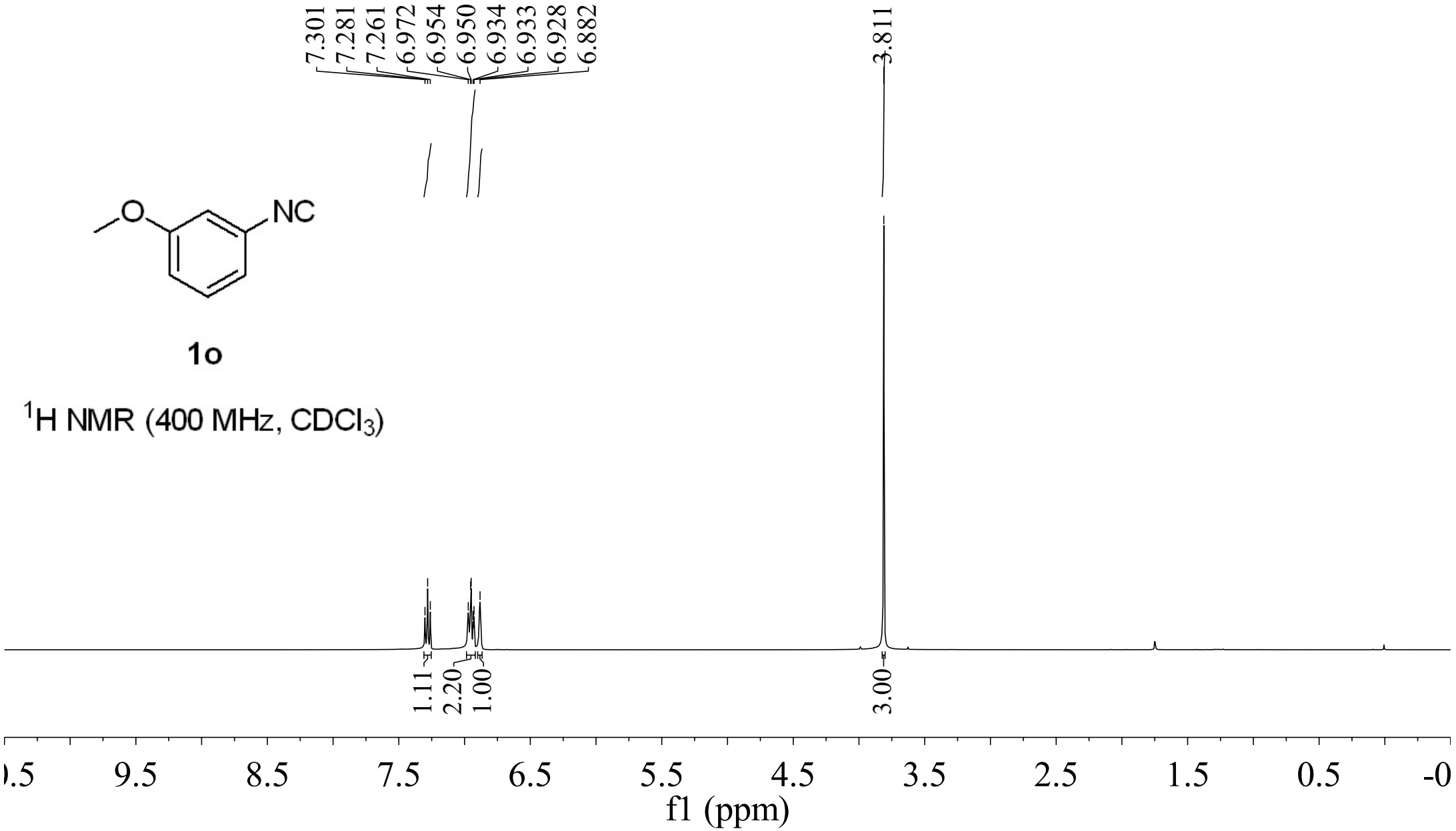

165.792
134.649
130.341
129.096
126.535
126.373
126.252
18.343
NC
1l
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

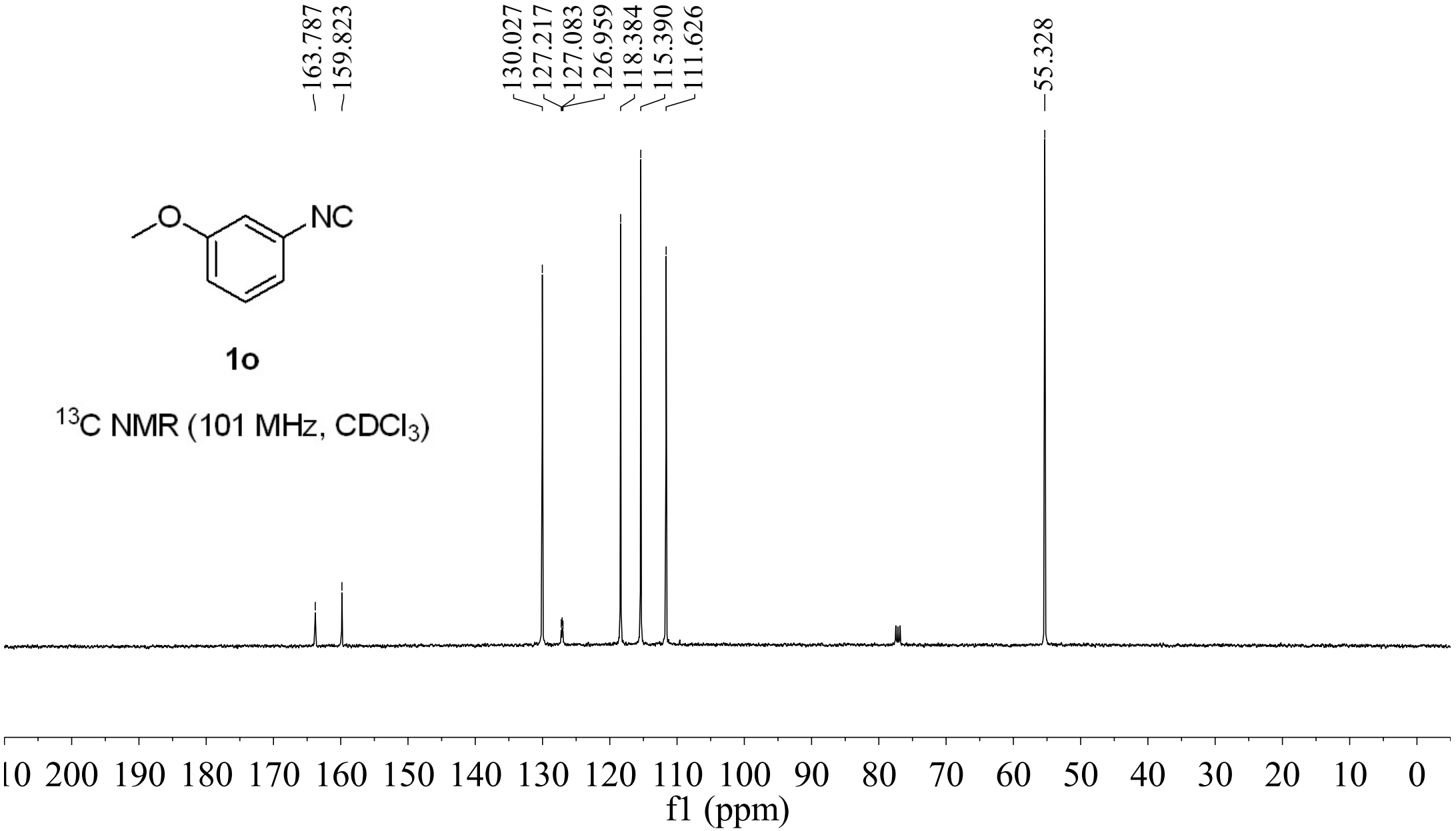

7.449
7.442
7.439
7.431
7.416
7.402
7.396
7.386
7.372
7.351
7.341
7.336
7.331
7.325
7.319
7.316
7.302
7.285
7.270
7.256
Cl
NC
1m
^{1}H NMR (500 MHz, $CDCl_3$)
2.00
2.01
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

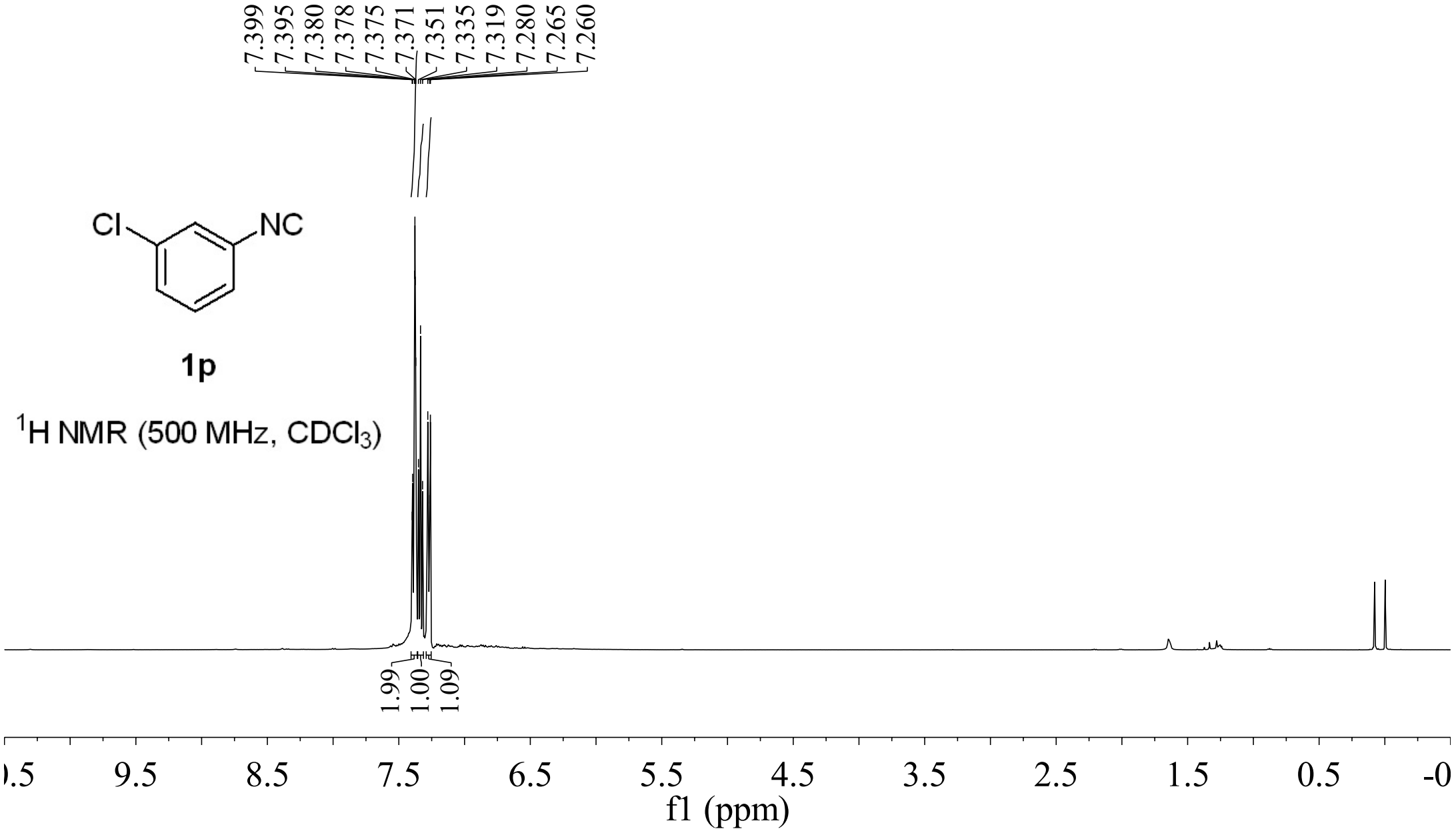

169.226
130.572
130.335
130.056
127.917
127.587
125.435
125.293
125.182
Cl
NC
1m
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

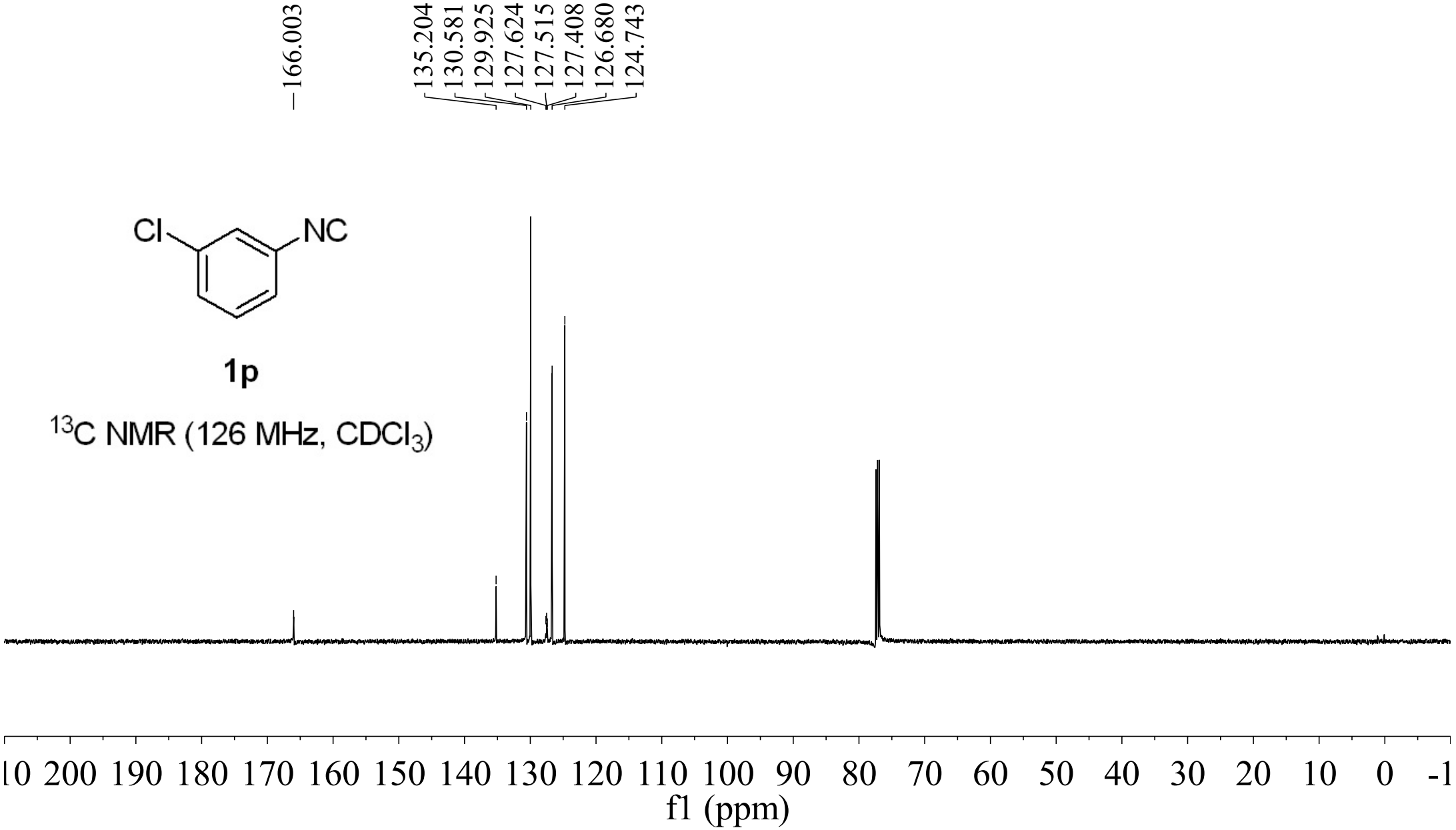

7.368
7.364
7.349
7.346
7.327
6.970
6.968
6.962
6.950
6.948
6.932
6.929
6.912
6.909
3.929
NC
O
1n
1H NMR (400 MHz, CDCl3)
1.88
1.97
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

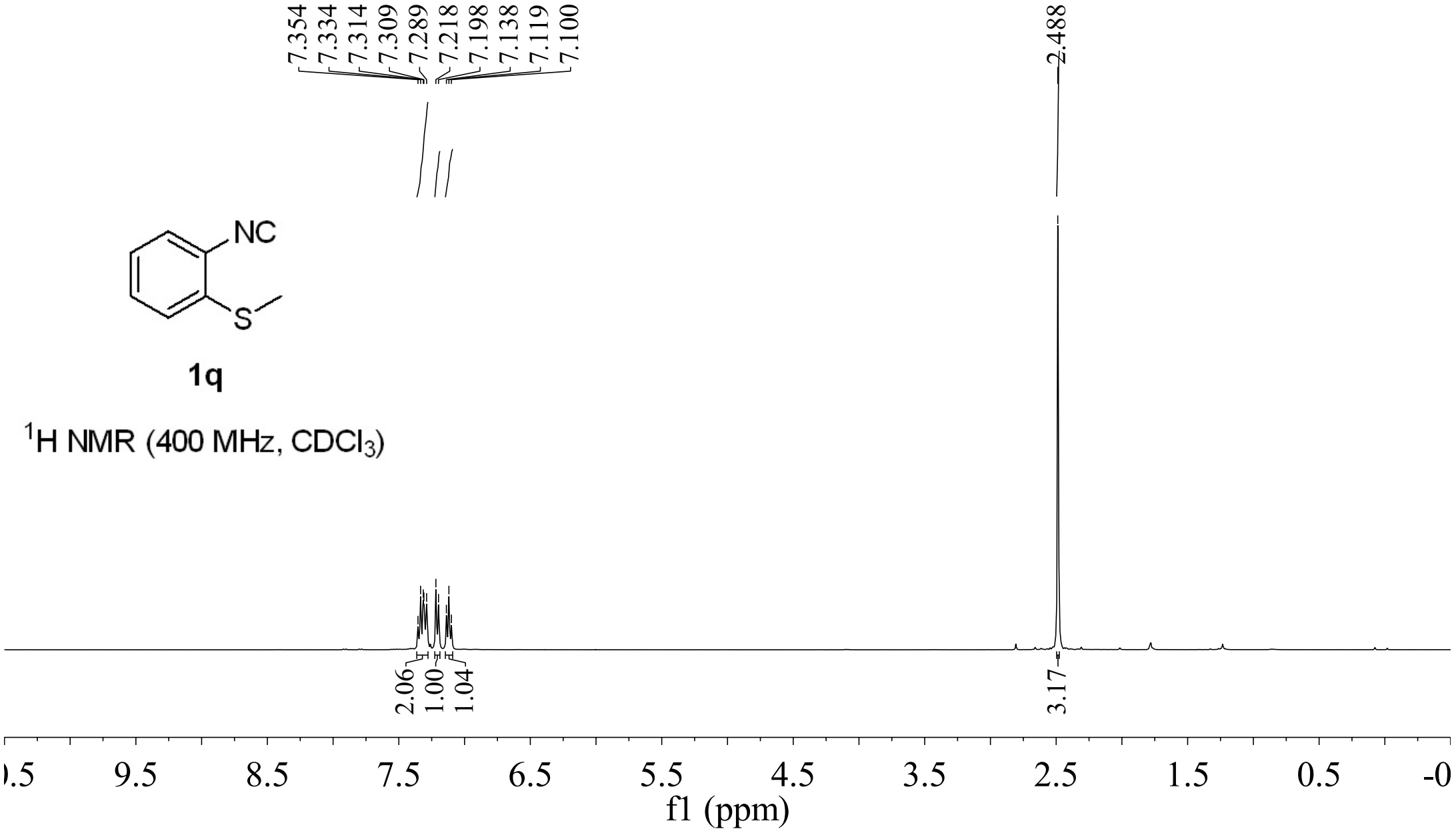

167.700
155.082
130.770
127.769
120.730
116.278
116.171
116.038
112.002
56.241
NC
O
1n
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

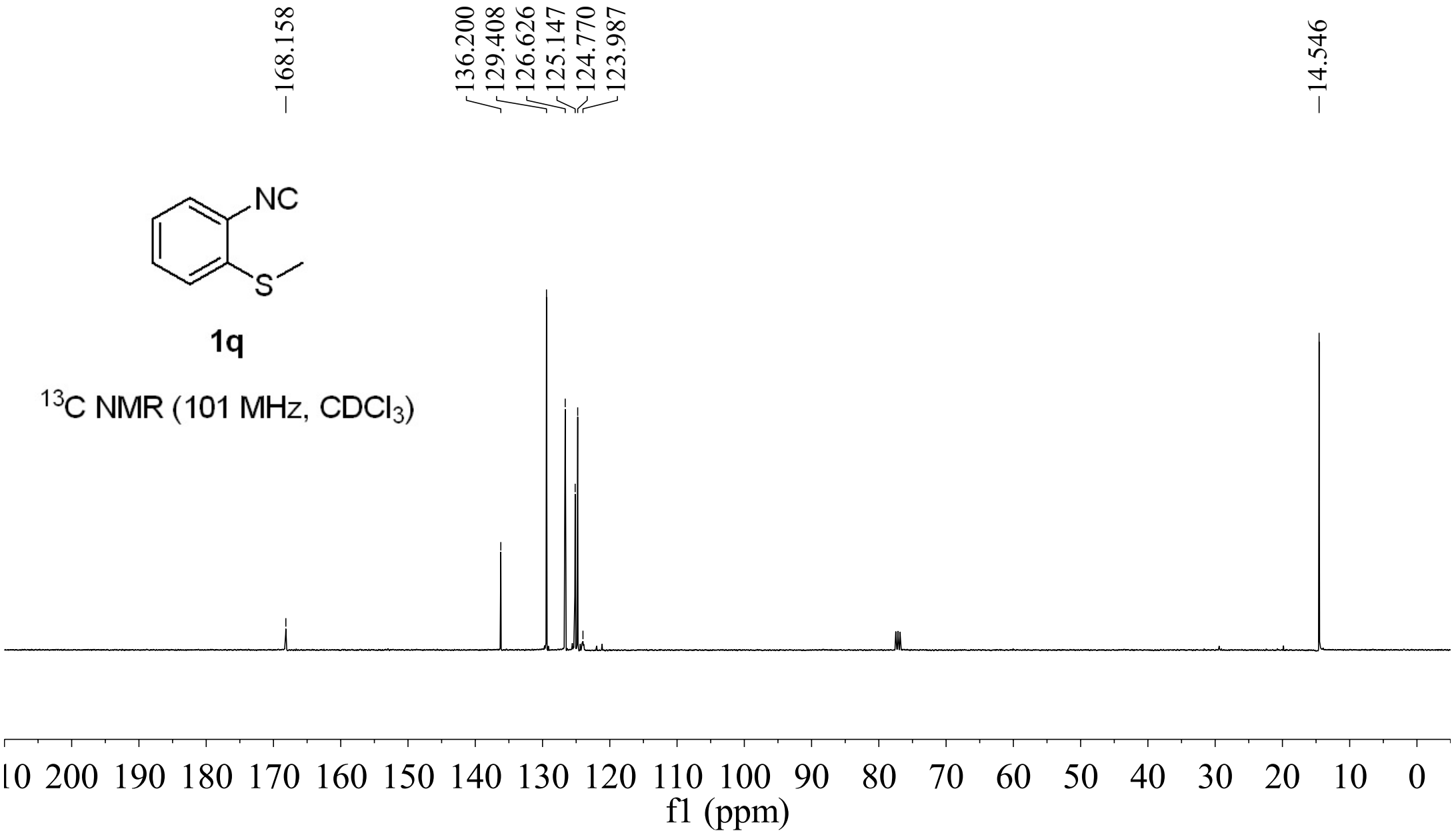

7.301
7.281
7.261
6.972
6.954
6.950
6.934
6.933
6.928
6.882
3.811
O
NC
1o
1H NMR (400 MHz, CDCl3)
1.11
2.20
1.00
3.00
f1 (ppm)

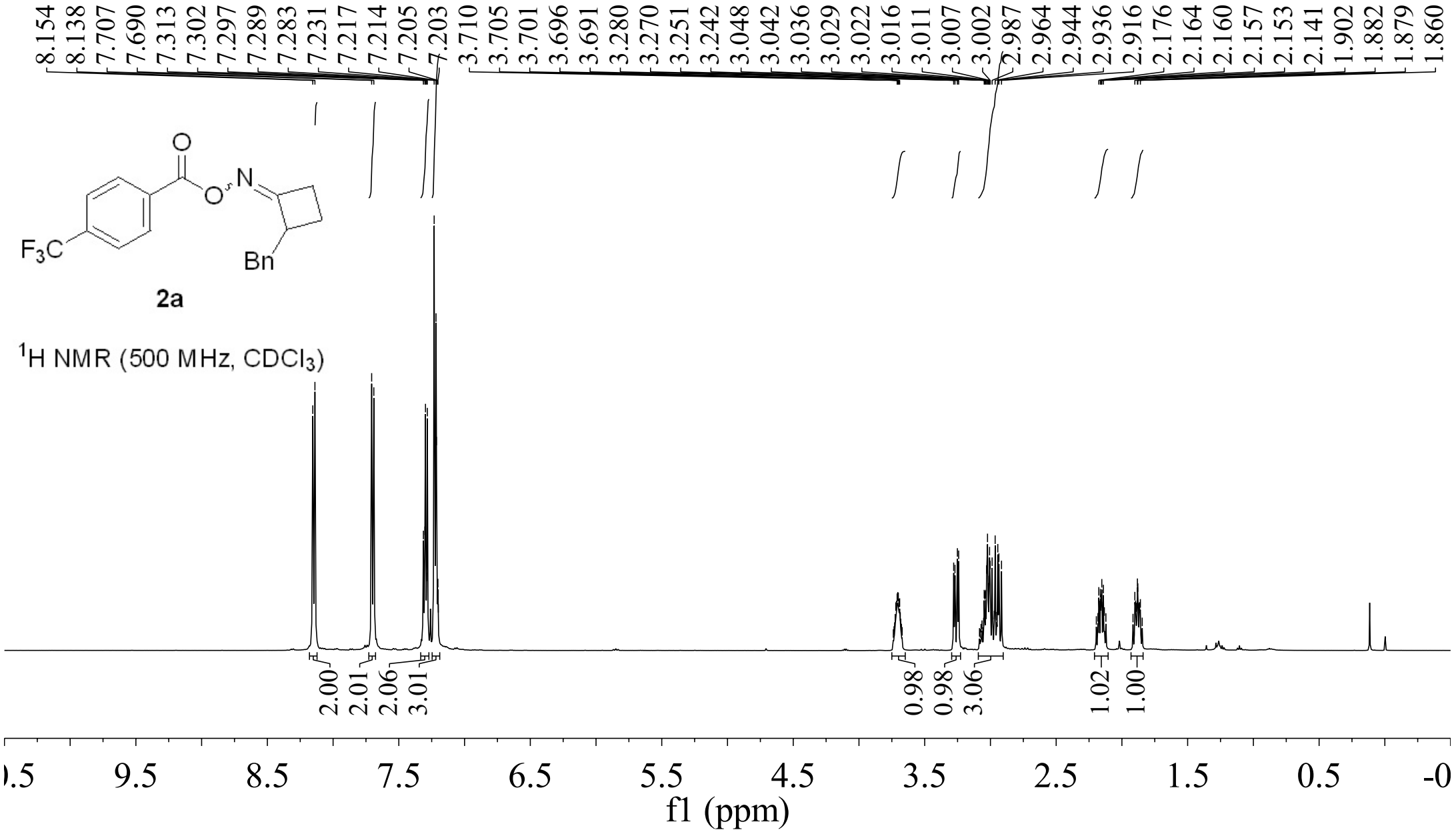

163.787
159.823
130.027
127.217
127.083
126.959
118.384
115.390
111.626
55.328
O
NC
1o
^{13}C NMR (101 MHz, $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

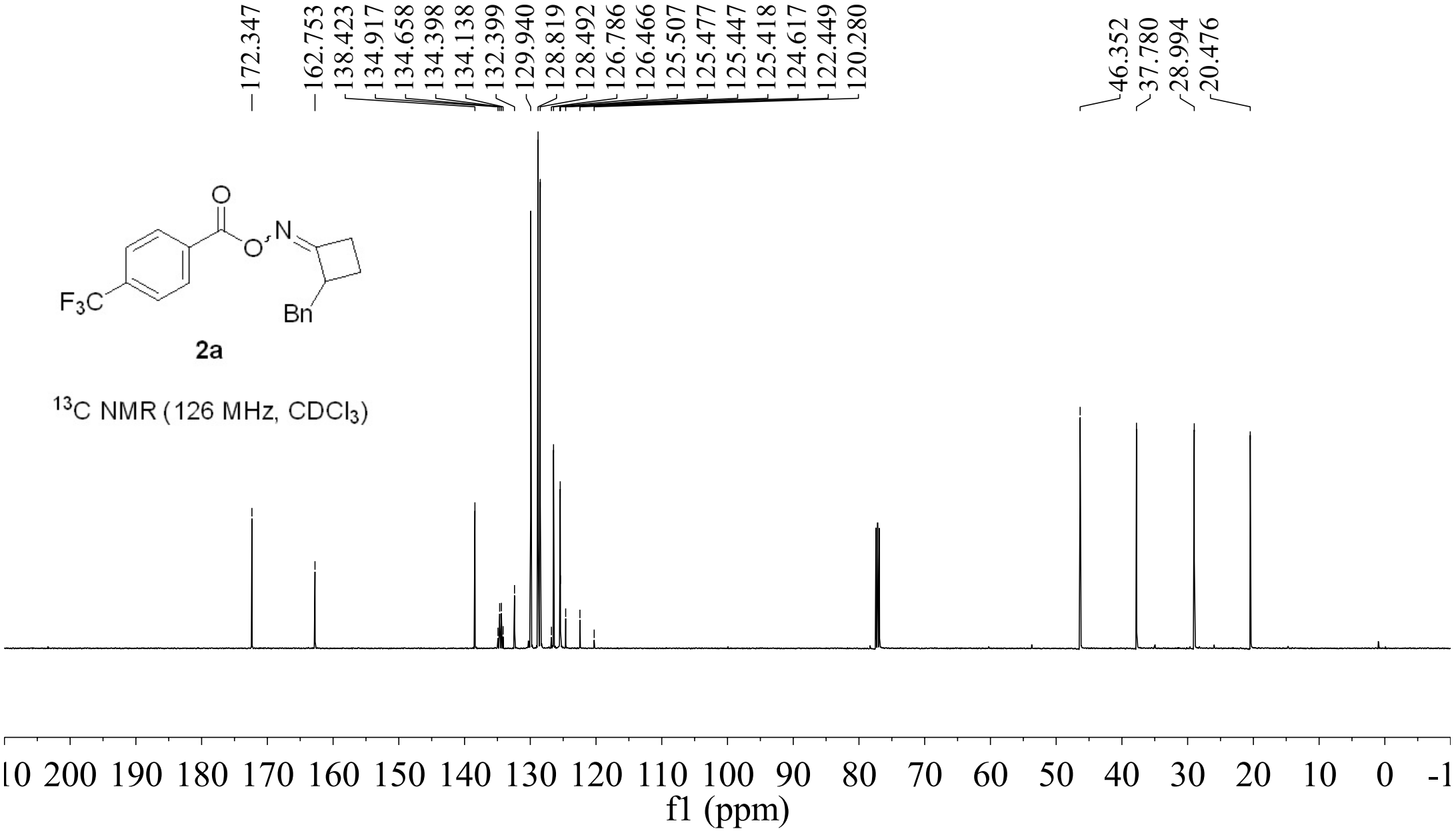

7.399
7.395
7.380
7.378
7.375
7.371
7.351
7.335
7.319
7.280
7.265
7.260
Cl
NC
1p
^{1}H NMR (500 MHz, CDCl$_3$)
1.99
1.00
1.09
f1 (ppm)


166.003
135.204
130.581
129.925
127.624
127.515
127.408
126.680
124.743
Cl
NC
1p
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.354
7.334
7.314
7.309
7.289
7.218
7.198
7.138
7.119
7.100
2.488
NC
S
1q
1H NMR (400 MHz, CDCl3)
2.06
1.00
1.04
3.17
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

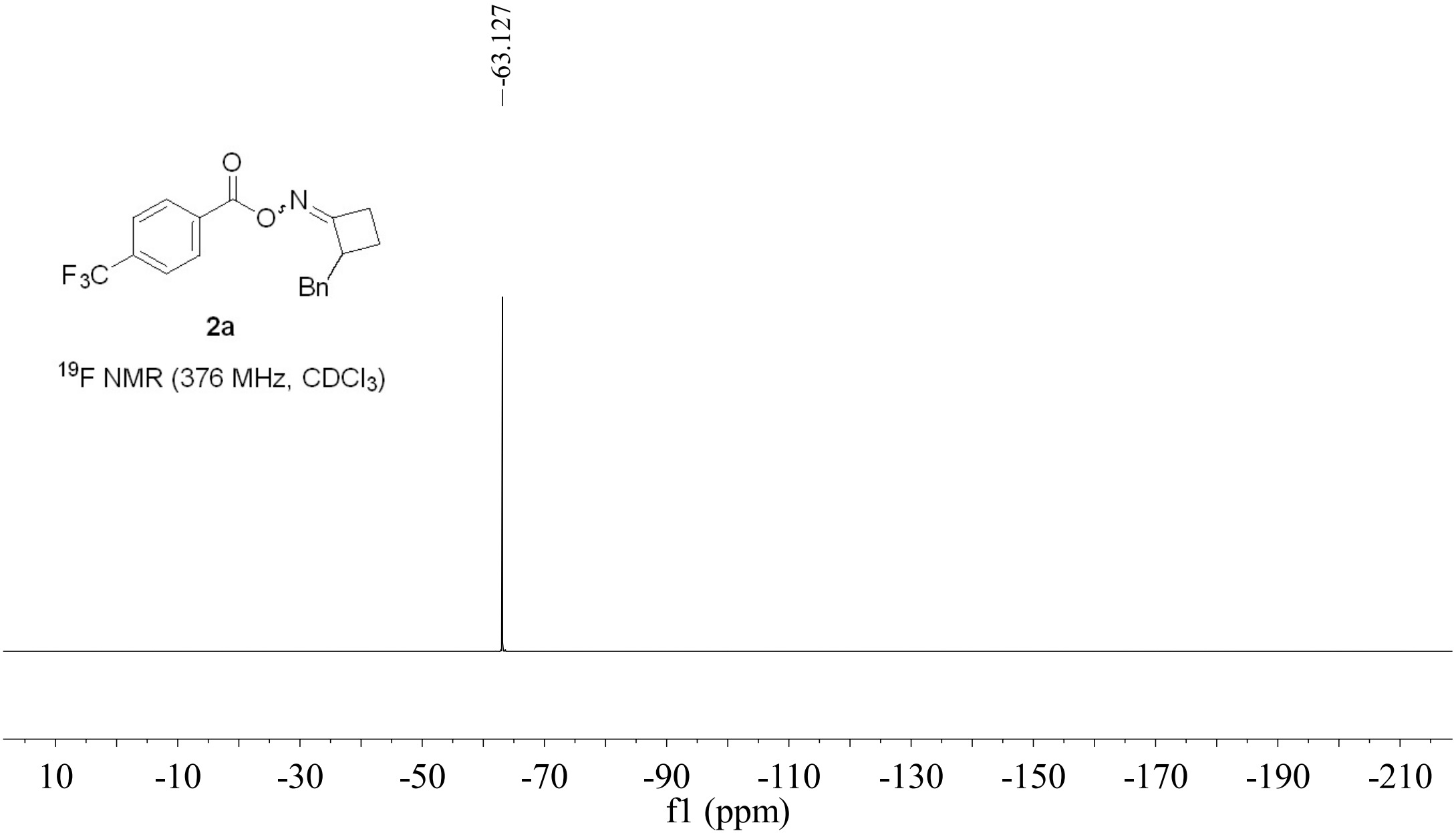

168.158
136.200
129.408
126.626
125.147
124.770
123.987
14.546
NC
S
1q
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

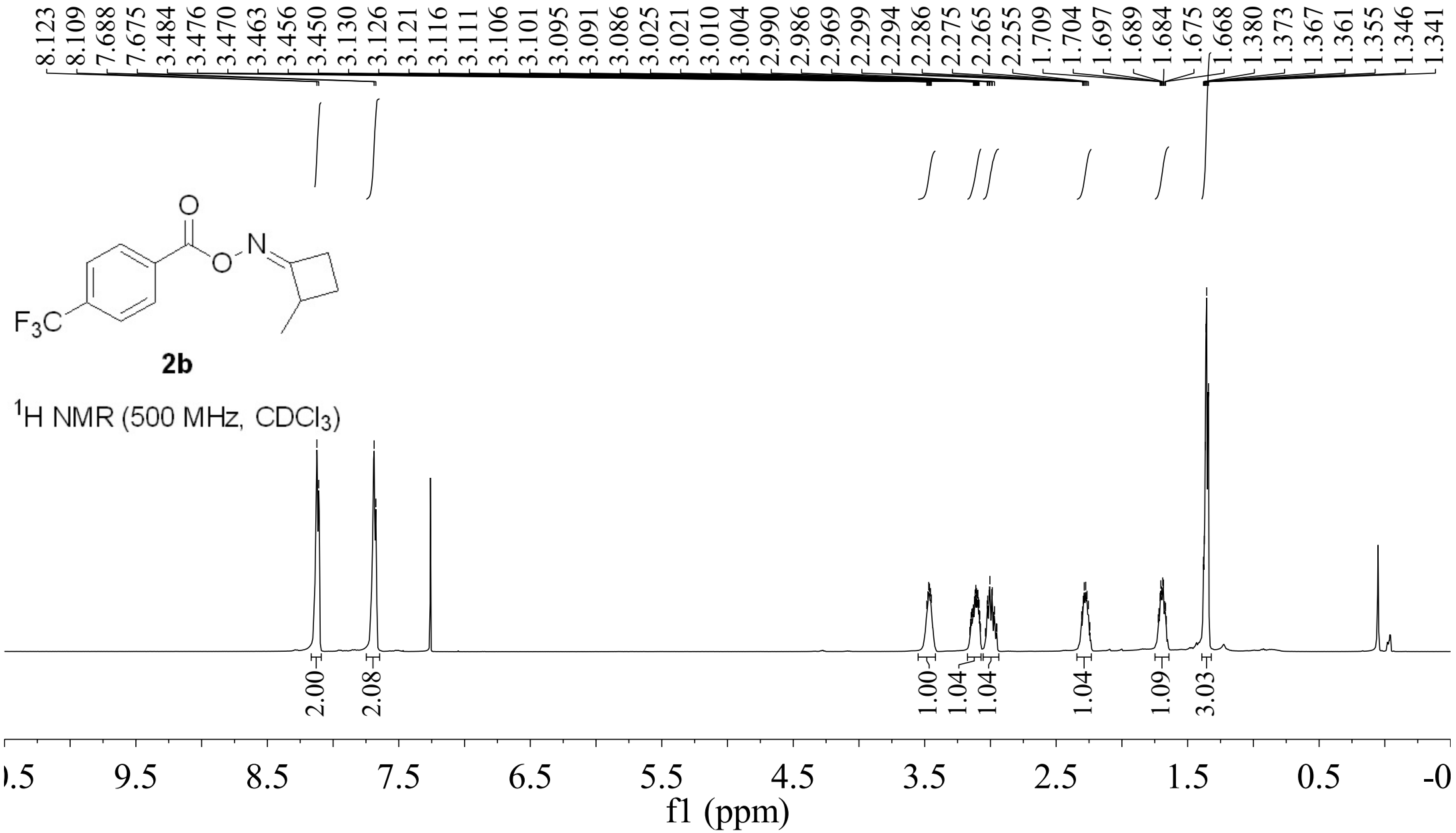

8.154
8.138
7.707
7.690
7.313
7.302
7.297
7.289
7.283
7.231
7.217
7.214
7.205
7.203
3.710
3.705
3.701
3.696
3.691
3.280
3.270
3.251
3.242
3.048
3.042
3.036
3.029
3.022
3.016
3.011
3.007
3.002
2.987
2.964
2.944
2.936
2.916
2.176
2.164
2.160
2.157
2.153
2.141
1.902
1.882
1.879
1.860
O
O
N
F3C
Bn
2a
1H NMR (500 MHz, CDCl3)
2.00
2.01
2.06
3.01
0.98
0.98
3.06
1.02
1.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

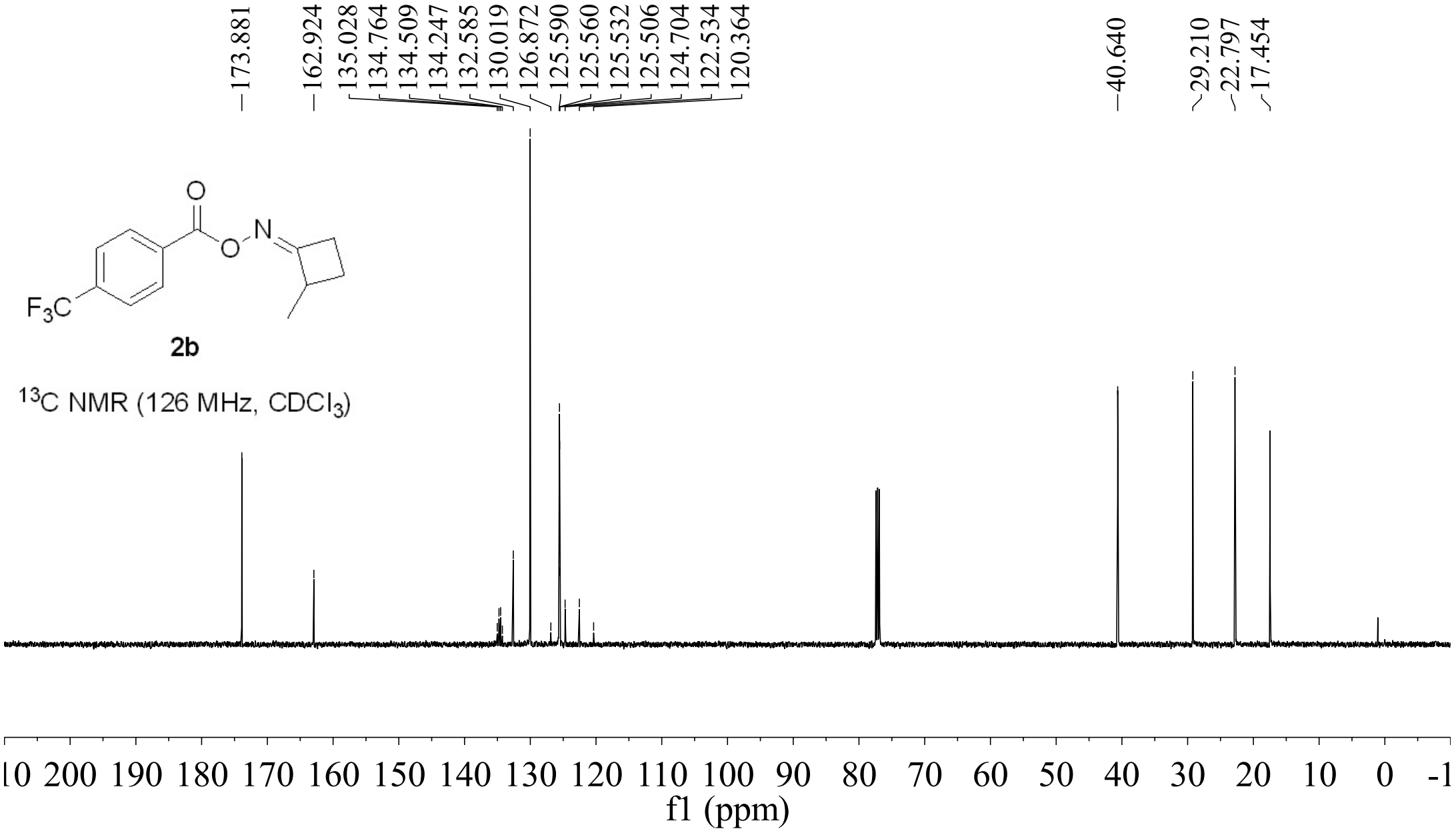

172.347
162.753
138.423
134.917
134.658
134.398
134.138
132.399
129.940
128.819
128.492
126.786
126.466
125.507
125.477
125.447
125.418
124.617
122.449
120.280
46.352
37.780
28.994
20.476
O
O
N
F3C
Bn
2a
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2a

^{19}F NMR (376 MHz, $CDCl_3$)

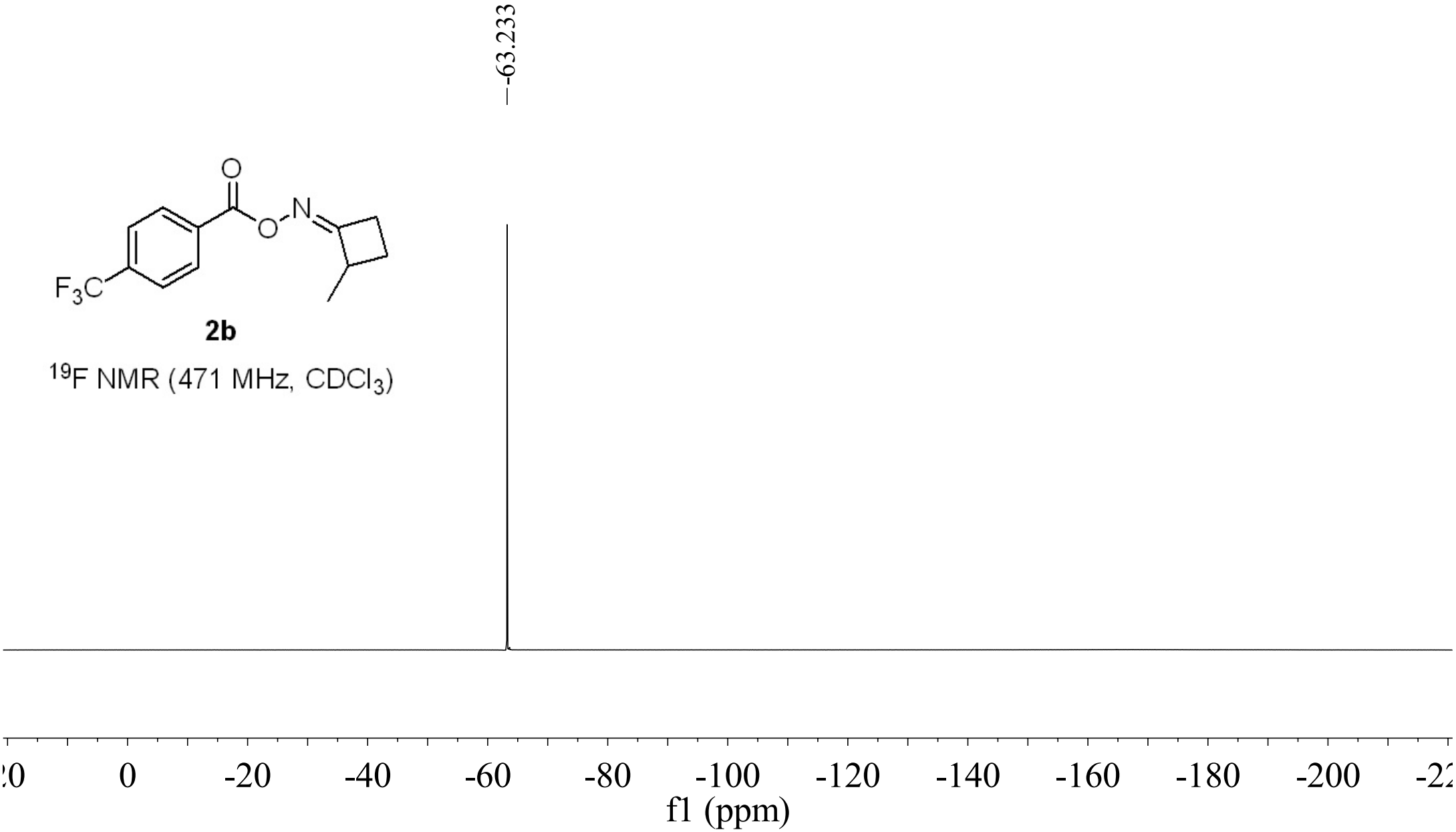


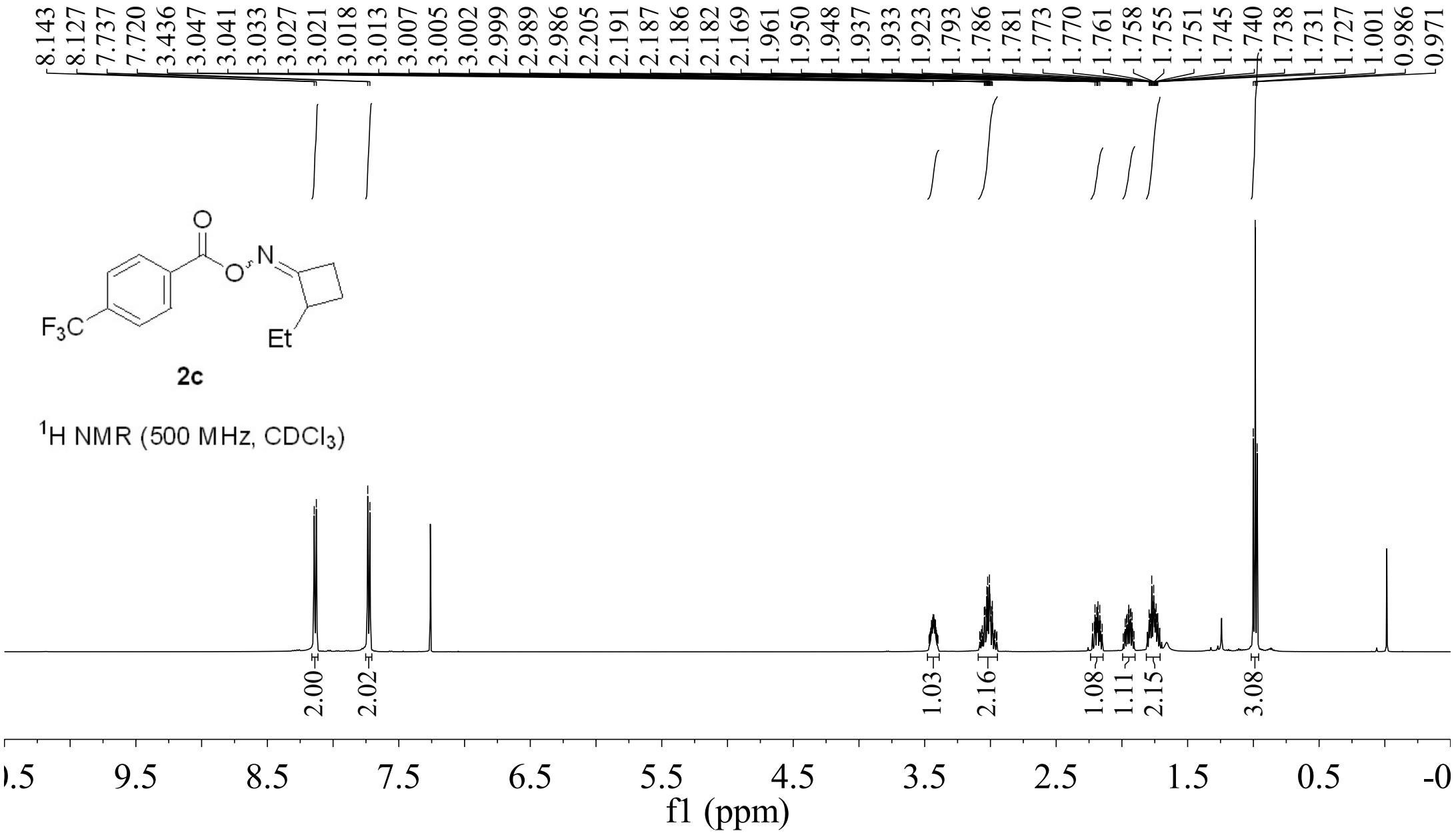

8.123
8.109
7.688
7.675
3.484
3.476
3.470
3.463
3.456
3.450
3.130
3.126
3.121
3.116
3.111
3.106
3.101
3.095
3.091
3.086
3.025
3.021
3.010
3.004
2.990
2.986
2.969
2.299
2.294
2.286
2.275
2.265
2.255
1.709
1.704
1.697
1.689
1.684
1.675
1.668
1.380
1.373
1.367
1.361
1.355
1.346
1.341
O
O
N
F3C
2b
1H NMR (500 MHz, CDCl3)
2.00
2.08
1.00
1.04
1.04
1.04
1.09
3.03
f1 (ppm)

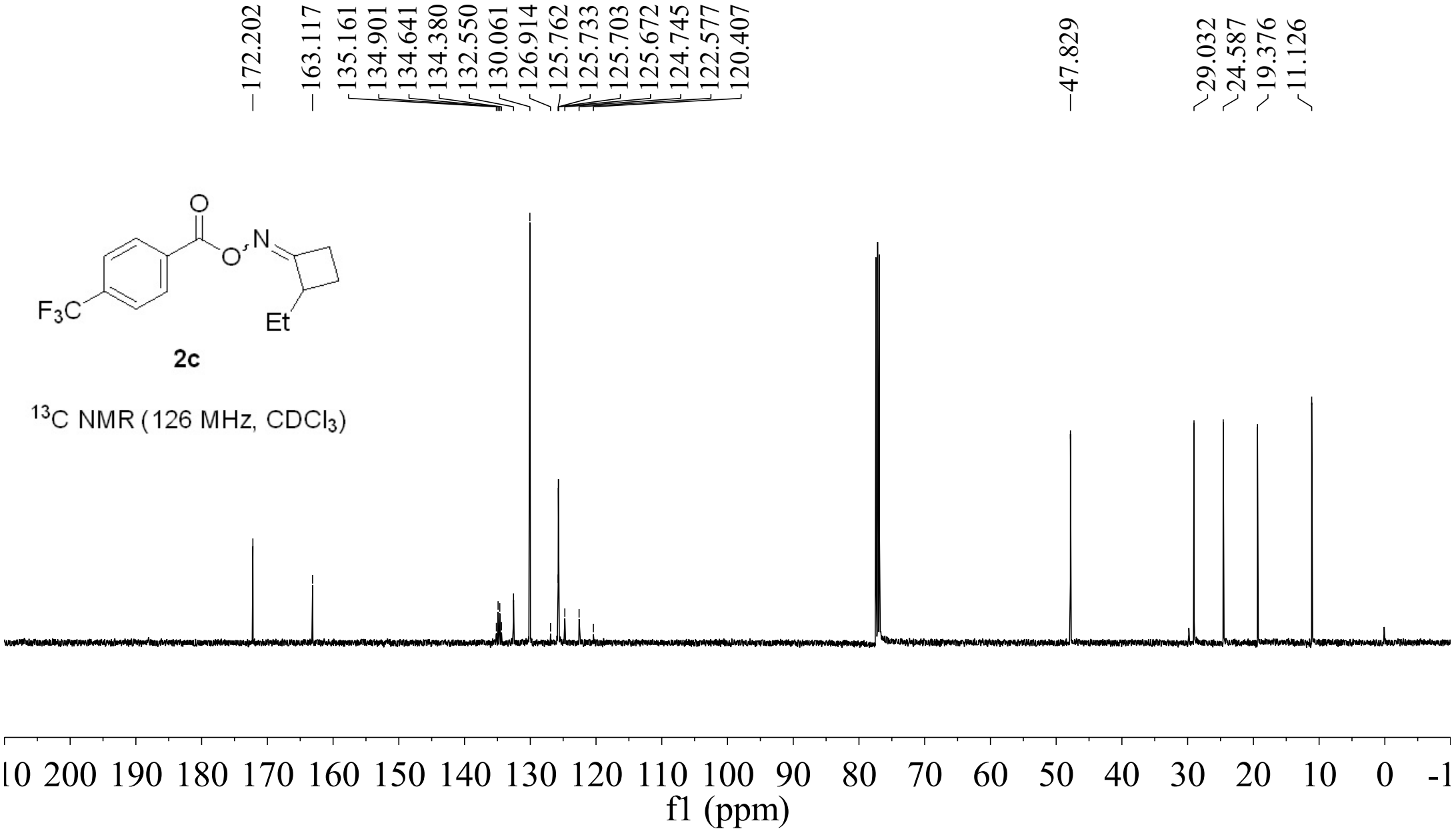

173.881
162.924
135.028
134.764
134.509
134.247
132.585
130.019
126.872
125.590
125.560
125.532
125.506
124.704
122.534
120.364
40.640
29.210
22.797
17.454
O
O
N
F3C
2b
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2b

^{19}F NMR (471 MHz, $CDCl_3$)

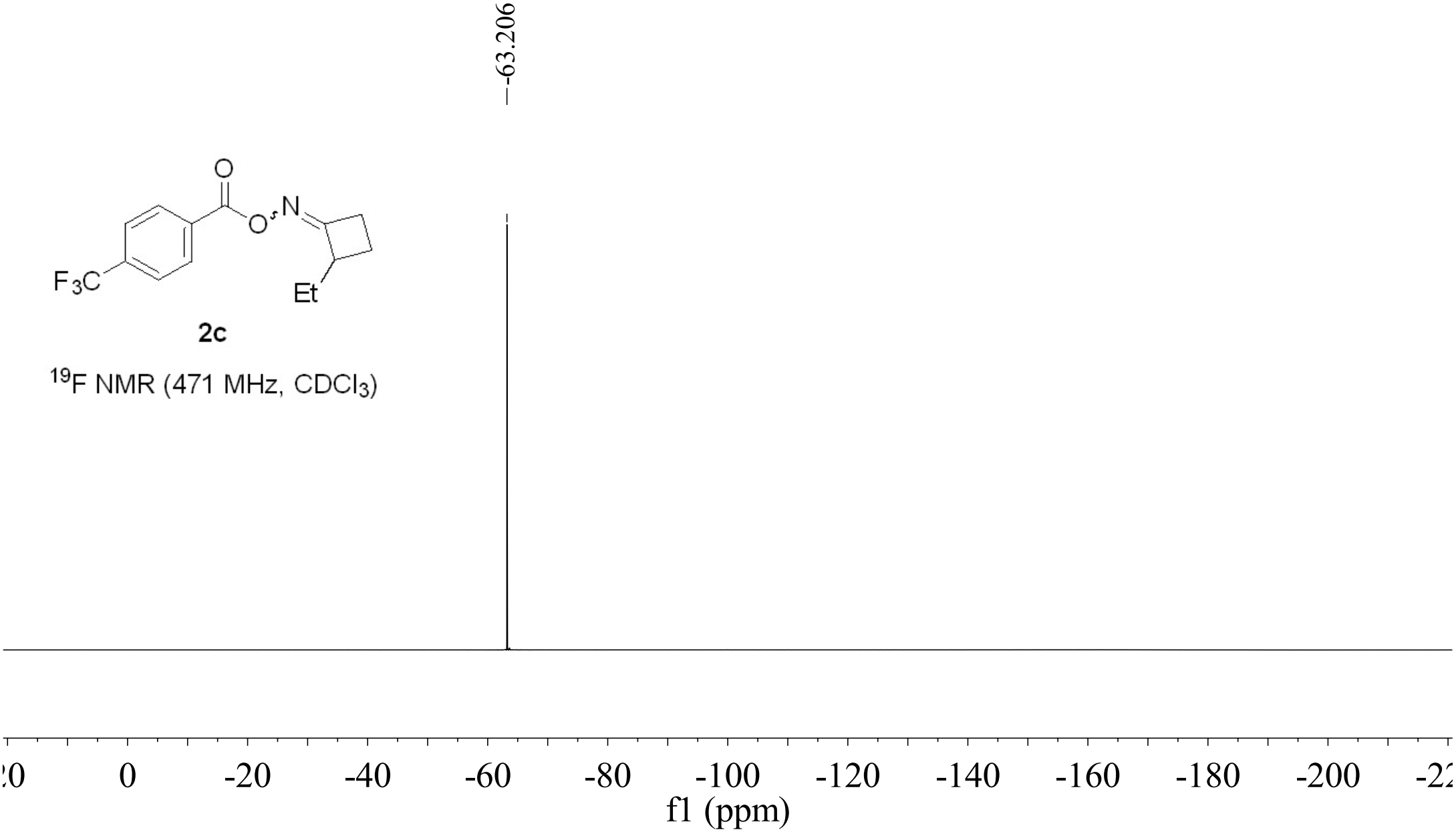


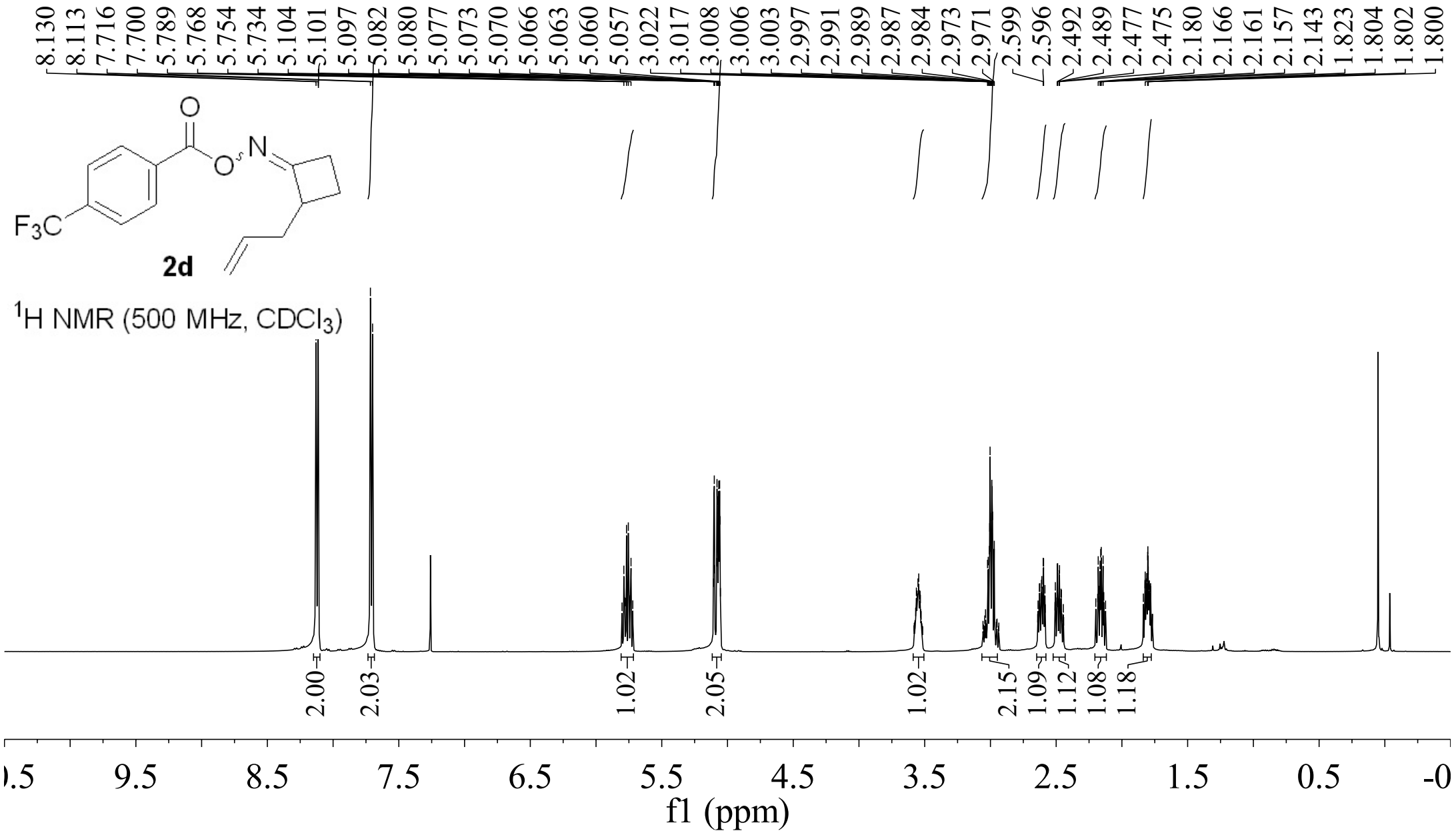

8.143
8.127
7.737
7.720
3.436
3.047
3.041
3.033
3.027
3.021
3.018
3.013
3.007
3.005
3.002
2.999
2.989
2.986
2.205
2.191
2.187
2.186
2.182
2.169
1.961
1.950
1.948
1.937
1.933
1.923
1.793
1.786
1.781
1.773
1.770
1.761
1.758
1.755
1.751
1.745
1.740
1.738
1.731
1.727
1.001
0.986
0.971
O
O
N
F3C
Et
2c
1H NMR (500 MHz, CDCl3)
2.00
2.02
1.03
2.16
1.08
1.11
2.15
3.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

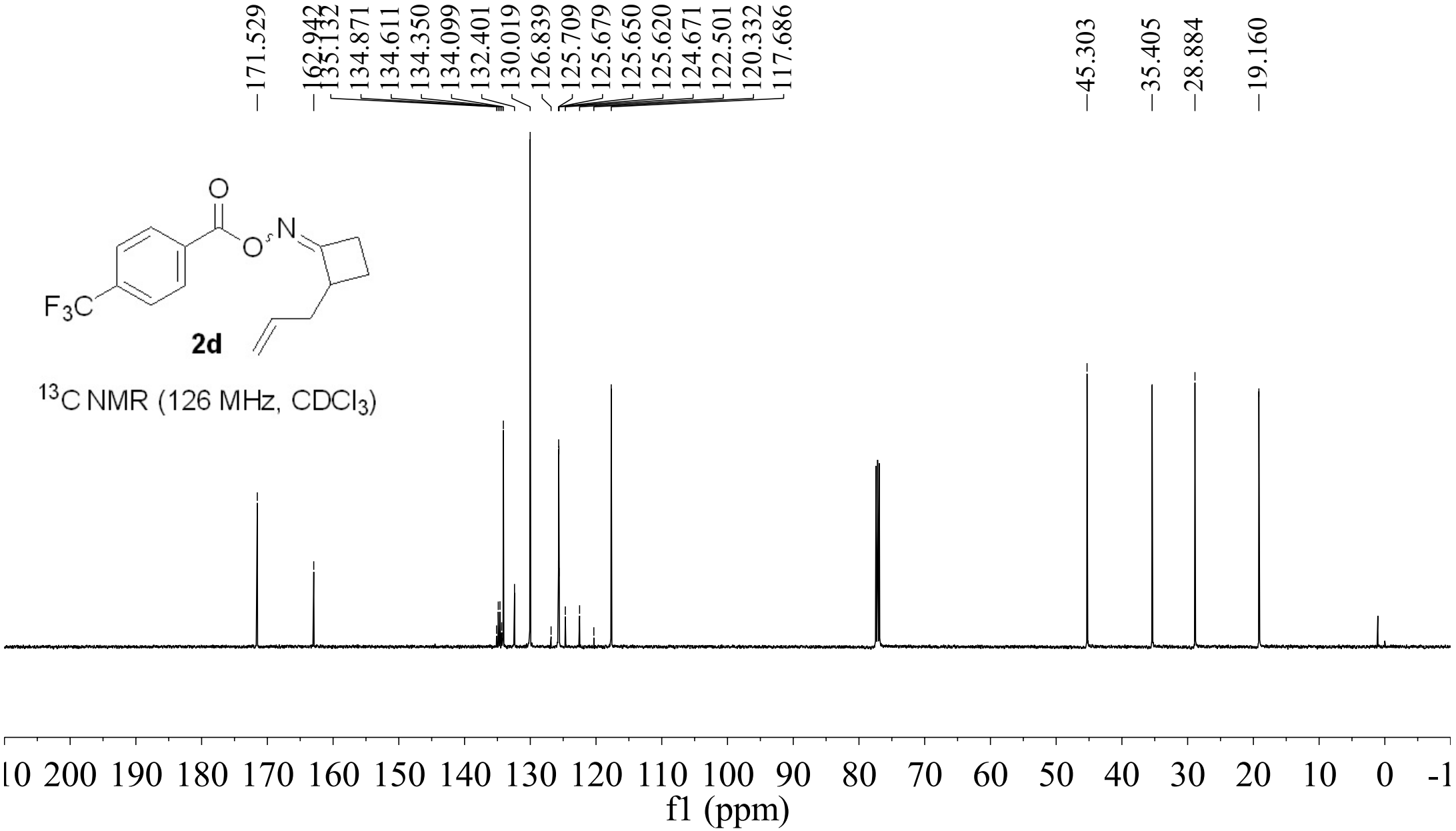

172.202
163.117
135.161
134.901
134.641
134.380
132.550
130.061
126.914
125.762
125.733
125.703
125.672
124.745
122.577
120.407
47.829
29.032
24.587
19.376
11.126
O
O
N
F3C
Et
2c
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2c

^{19}F NMR (471 MHz, $CDCl_3$)

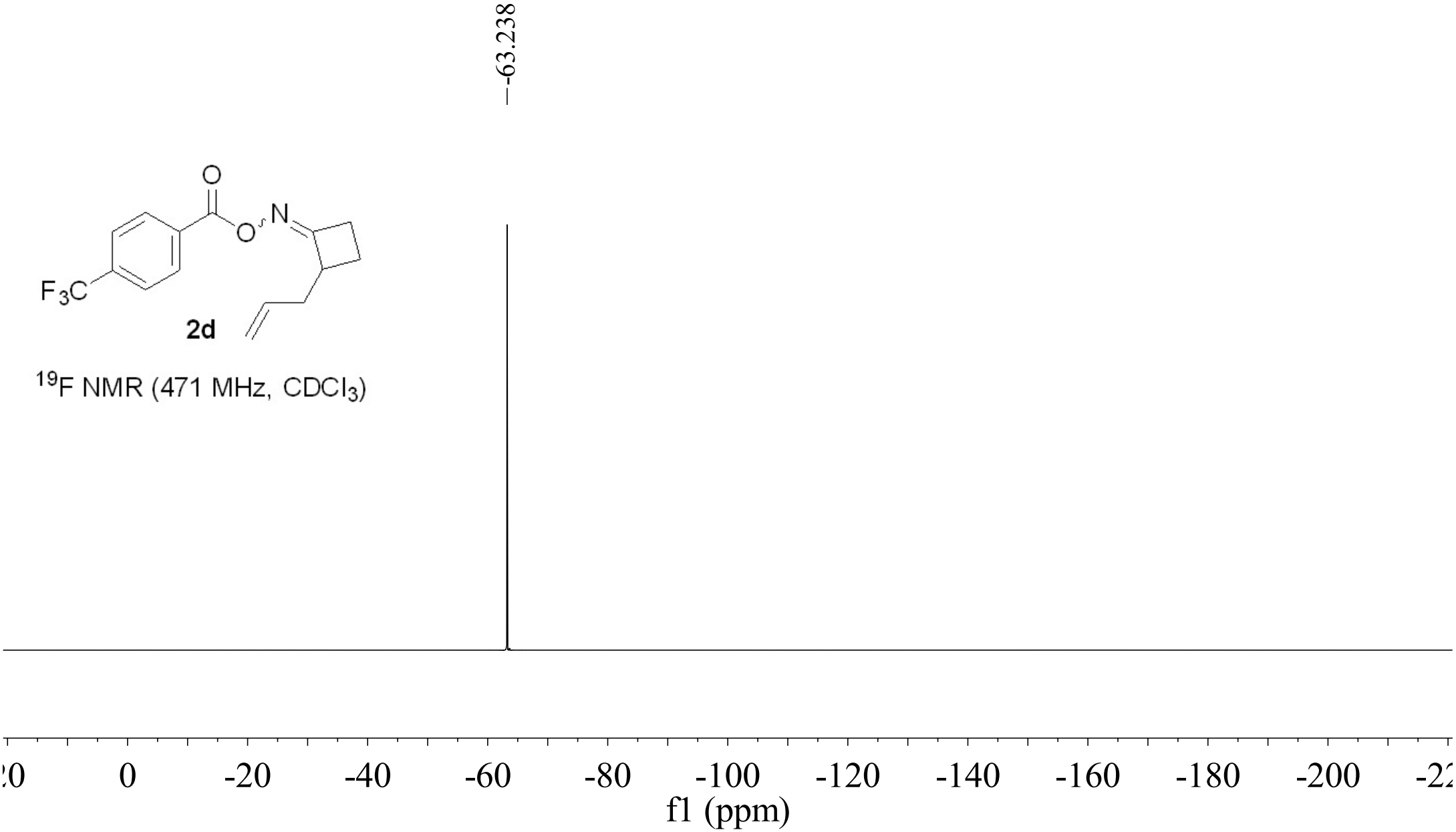


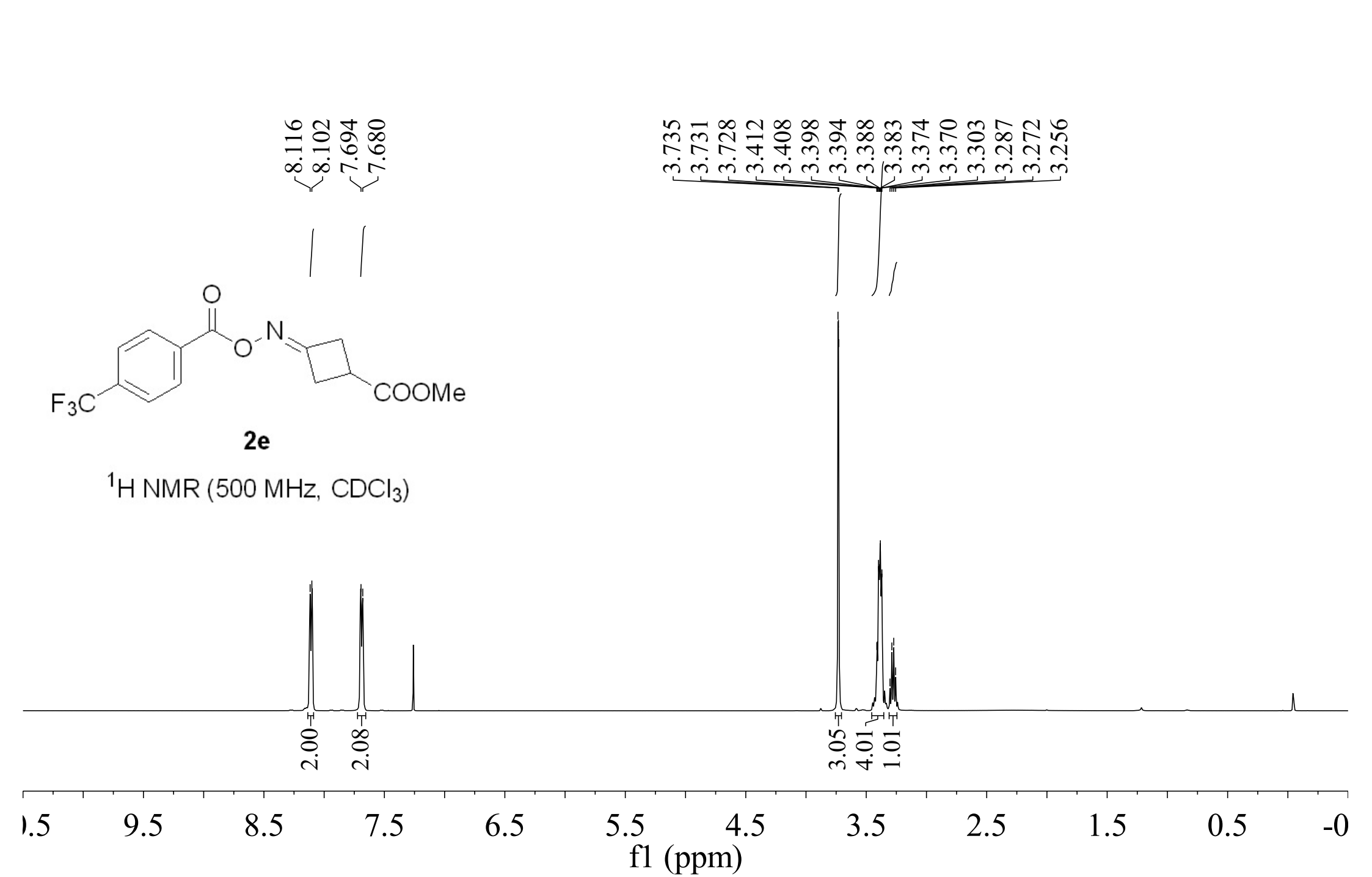

8.130
8.113
7.716
7.700
5.789
5.768
5.754
5.734
5.104
5.101
5.097
5.082
5.080
5.077
5.073
5.070
5.066
5.063
5.060
5.057
3.022
3.017
3.008
3.006
3.003
2.997
2.991
2.989
2.987
2.984
2.973
2.971
2.599
2.596
2.492
2.489
2.477
2.475
2.180
2.166
2.161
2.157
2.143
1.823
1.804
1.802
1.800
O
O
N
F3C
2d
1H NMR (500 MHz, CDCl3)
2.00
2.03
1.02
2.05
1.02
2.15
1.09
1.12
1.08
1.18
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

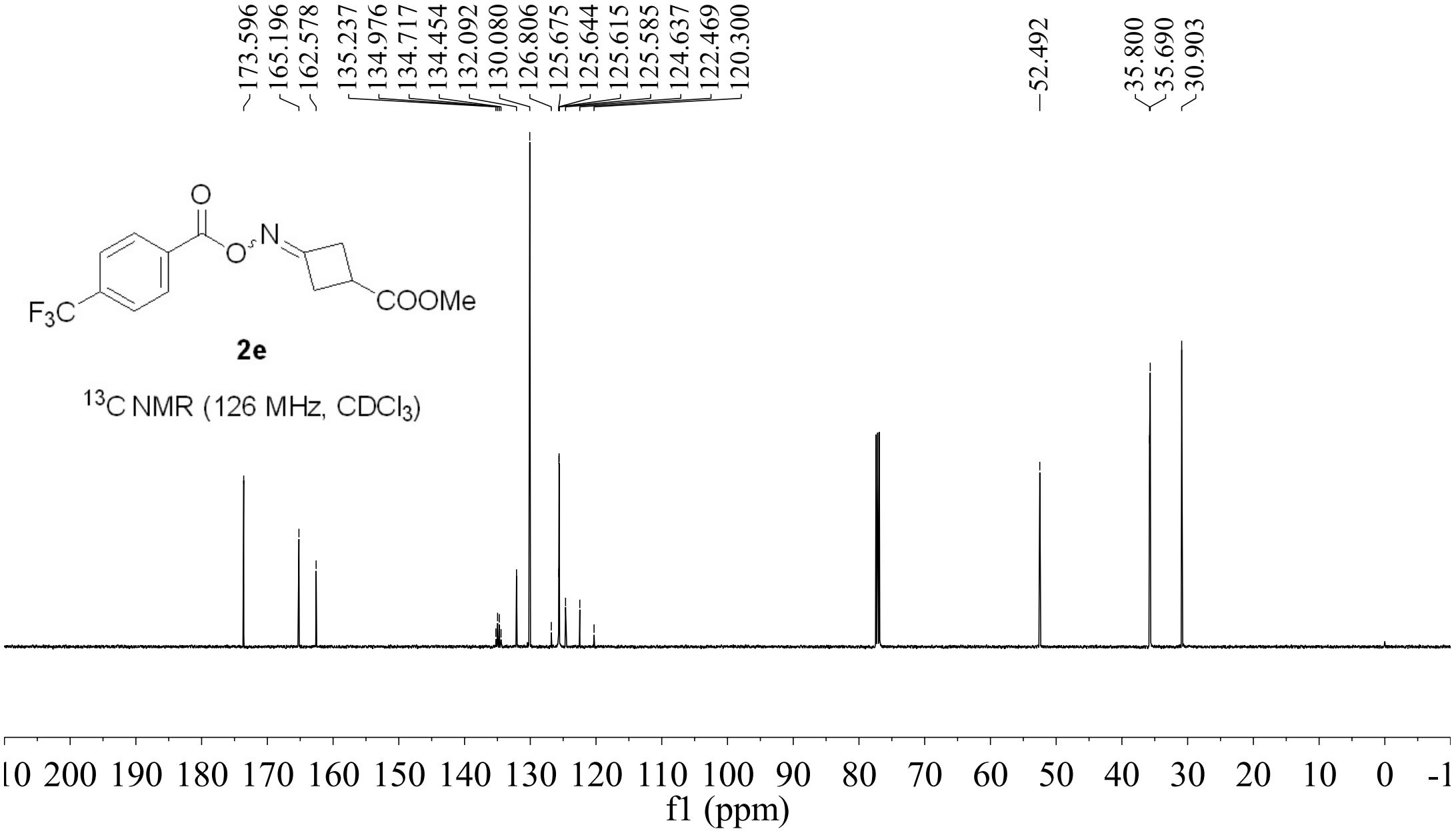

171.529
162.942
135.132
134.871
134.611
134.350
134.099
132.401
130.019
126.839
125.709
125.679
125.650
125.620
124.671
122.501
120.332
117.686
45.303
35.405
28.884
19.160
O
O
N
F3C
2d
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

2d

^{19}F NMR (471 MHz, $CDCl_3$)

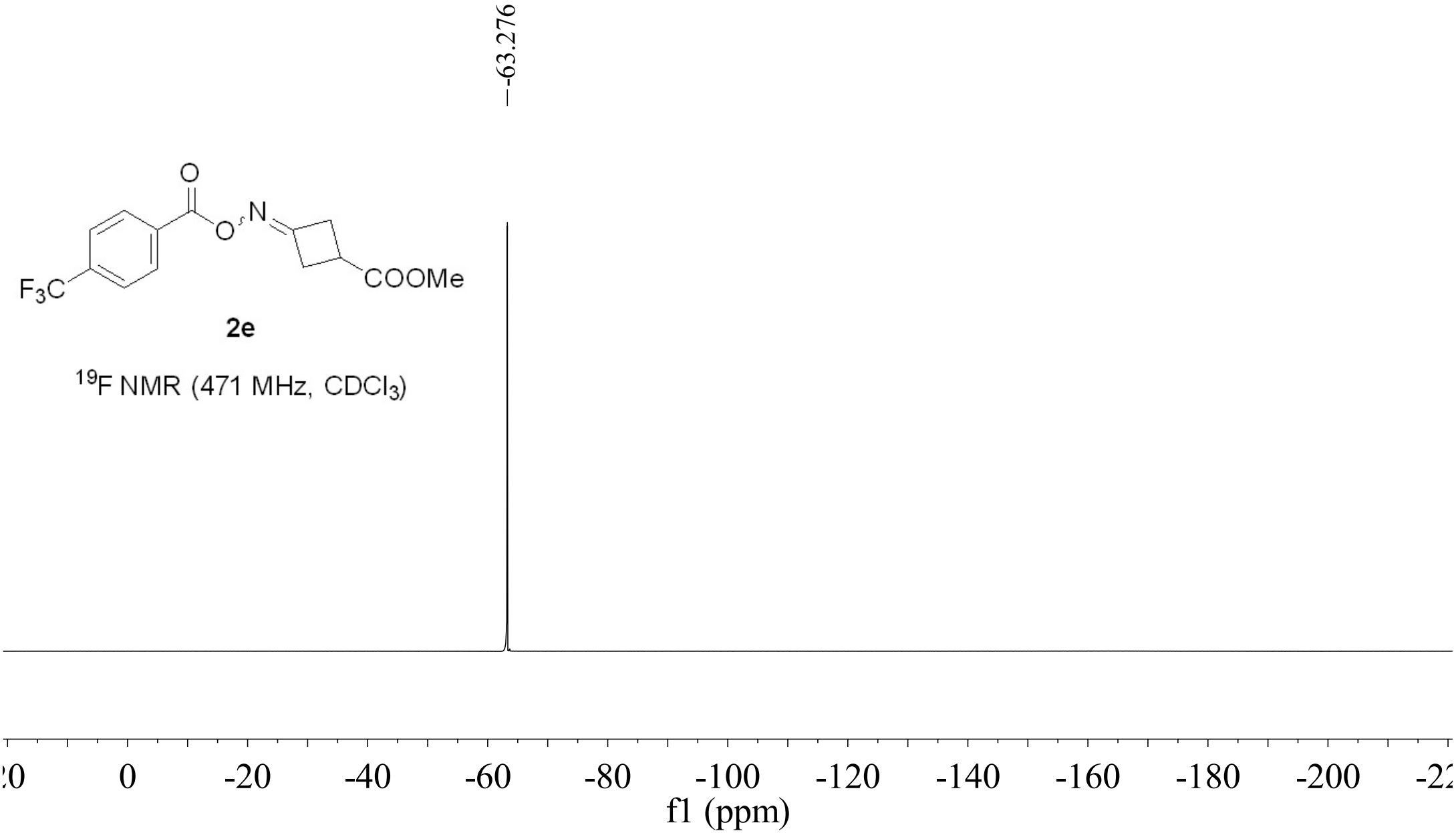


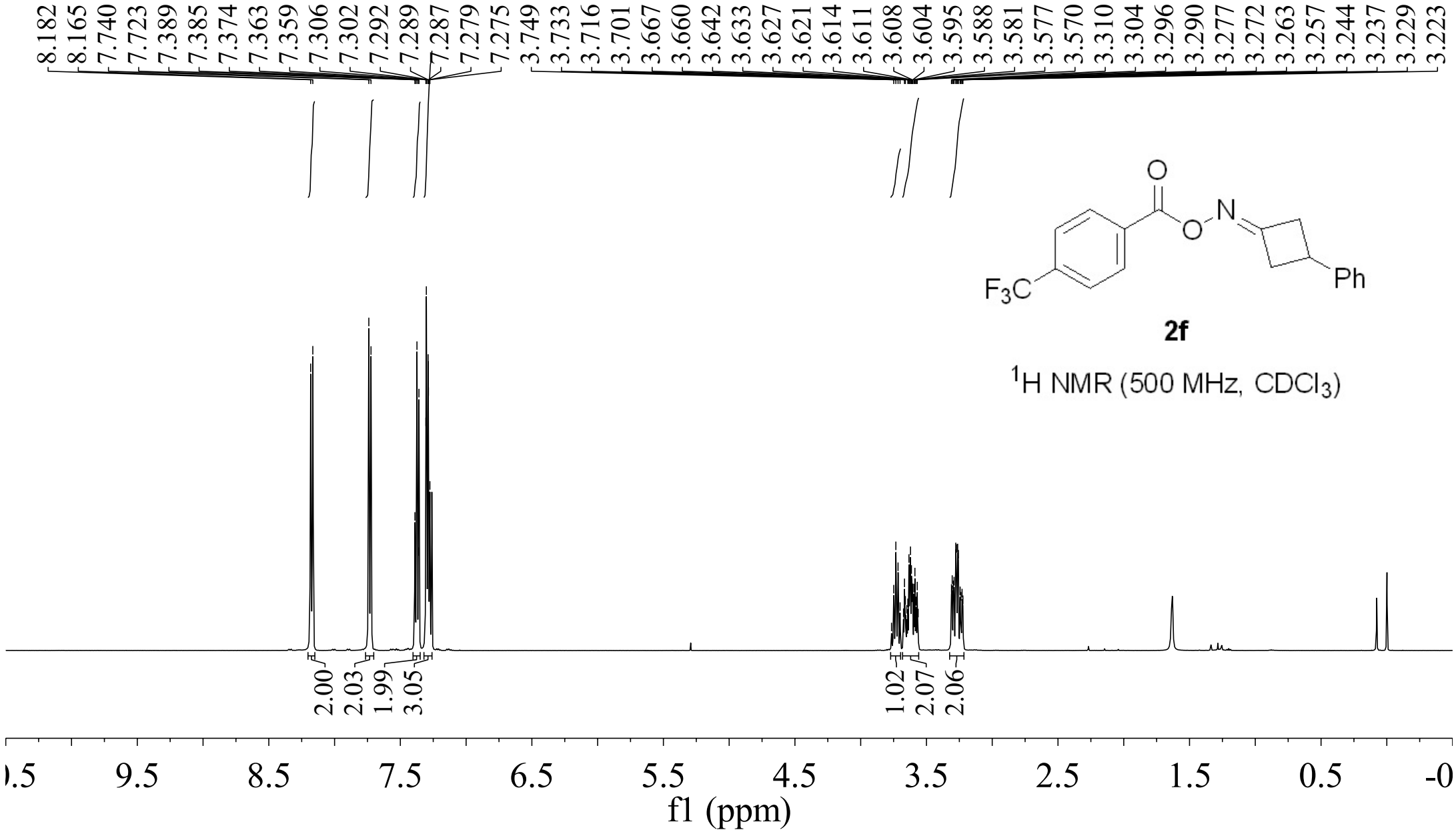

8.116
8.102
7.694
7.680
3.735
3.731
3.728
3.412
3.408
3.398
3.394
3.388
3.383
3.374
3.370
3.303
3.287
3.272
3.256
O
O
N
F3C
COOMe
2e
1H NMR (500 MHz, CDCl3)
2.00
2.08
3.05
4.01
1.01
f1 (ppm)

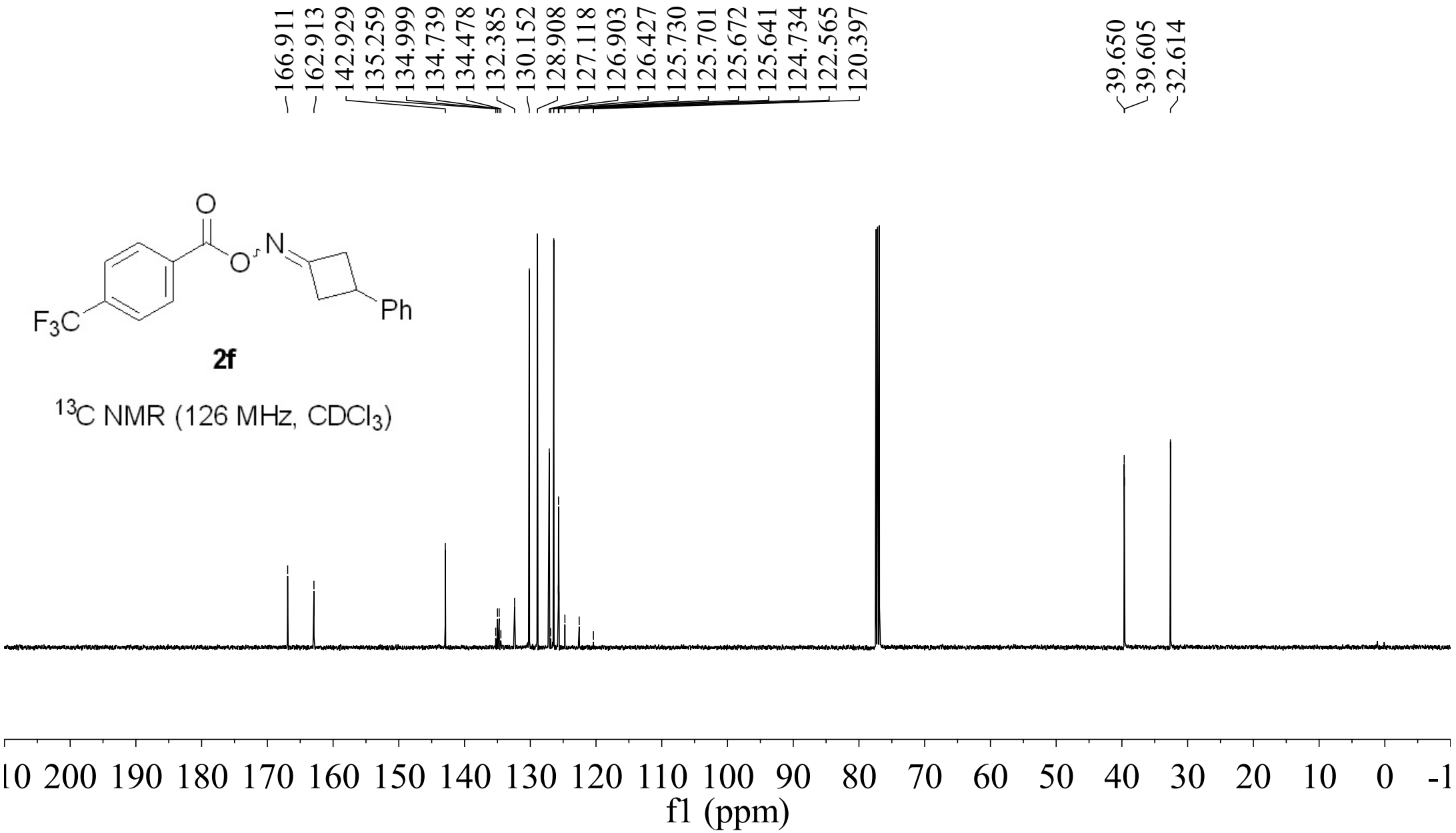

173.596
165.196
162.578
135.237
134.976
134.717
134.454
132.092
130.080
126.806
125.675
125.644
125.615
125.585
124.637
122.469
120.300
52.492
35.800
35.690
30.903
O
O
N
F3C
COOMe
2e
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

2e

^{19}F NMR (471 MHz, $CDCl_3$)

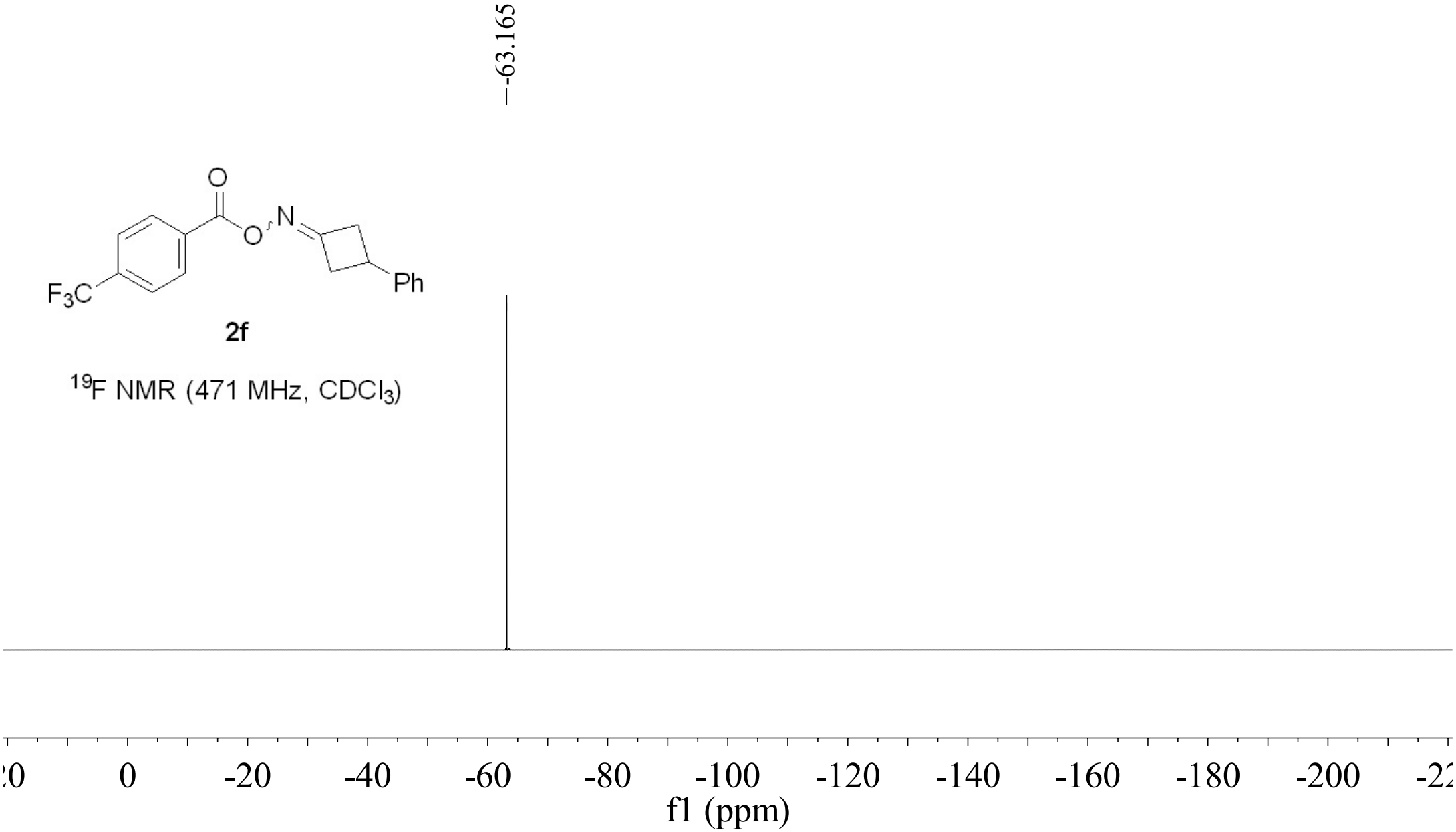


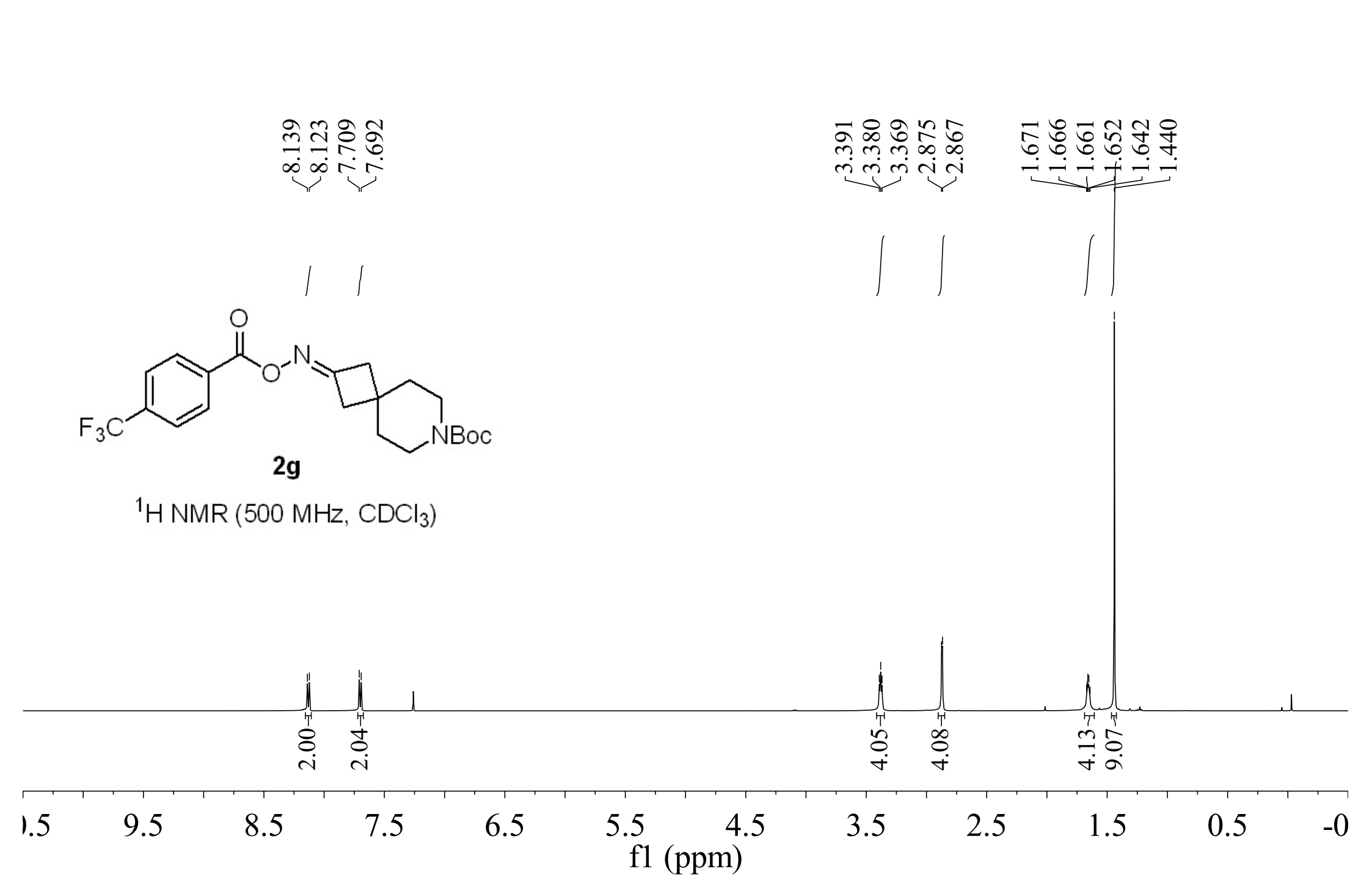

8.182
8.165
7.740
7.723
7.389
7.385
7.374
7.363
7.359
7.306
7.302
7.292
7.289
7.287
7.279
7.275
3.749
3.733
3.716
3.701
3.667
3.660
3.642
3.633
3.627
3.621
3.614
3.611
3.608
3.604
3.595
3.588
3.581
3.577
3.570
3.310
3.304
3.296
3.290
3.277
3.272
3.263
3.257
3.244
3.237
3.229
3.223
O
O
N
F3C
Ph
2f
1H NMR (500 MHz, CDCl3)
2.00
2.03
1.99
3.05
1.02
2.07
2.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

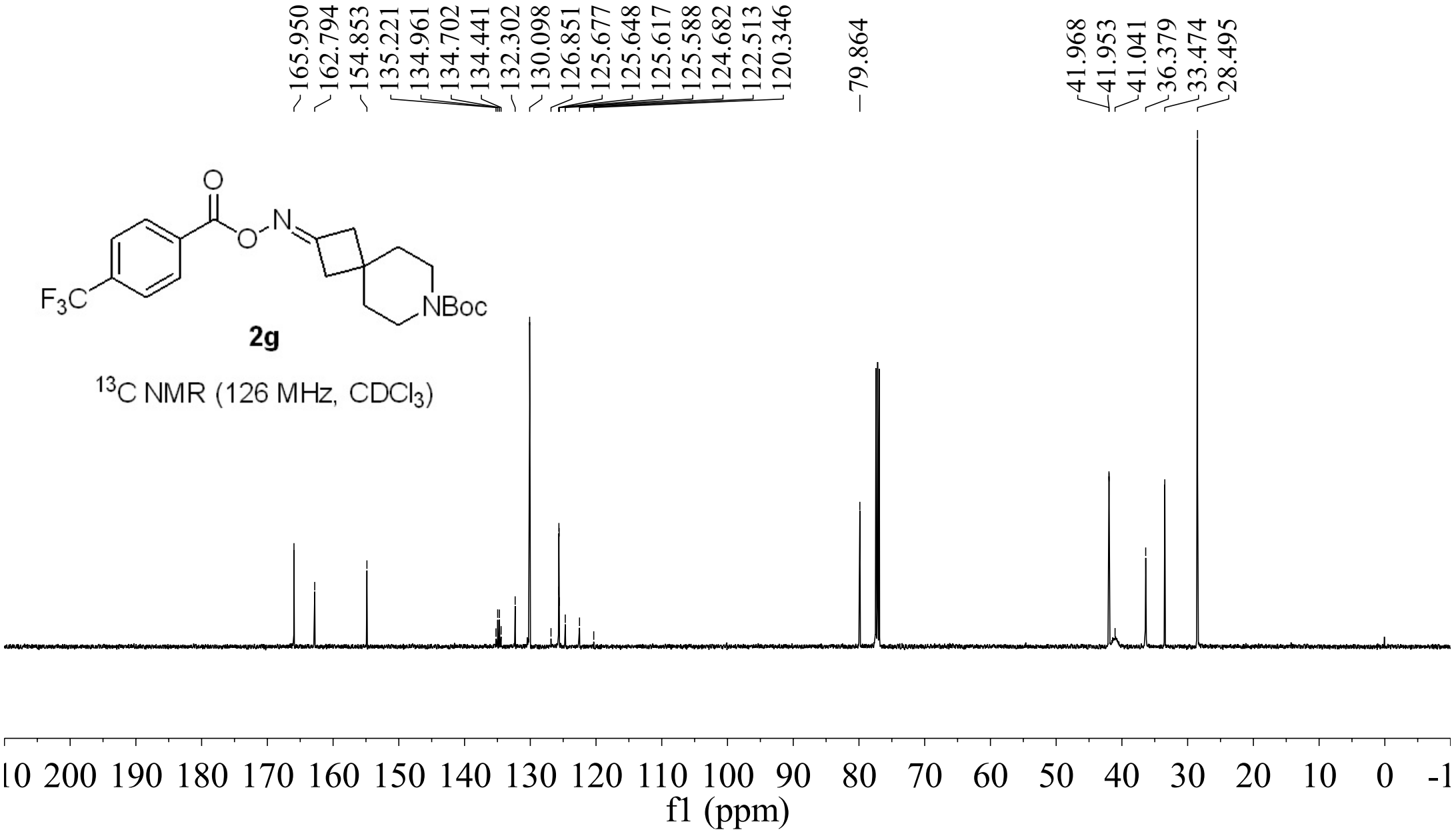

166.911
162.913
142.929
135.259
134.999
134.739
134.478
132.385
130.152
128.908
127.118
126.903
126.427
125.730
125.701
125.672
125.641
124.734
122.565
120.397
39.650
39.605
32.614
O
O
N
Ph
F3C
2f
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2f

^{19}F NMR (471 MHz, $CDCl_3$)

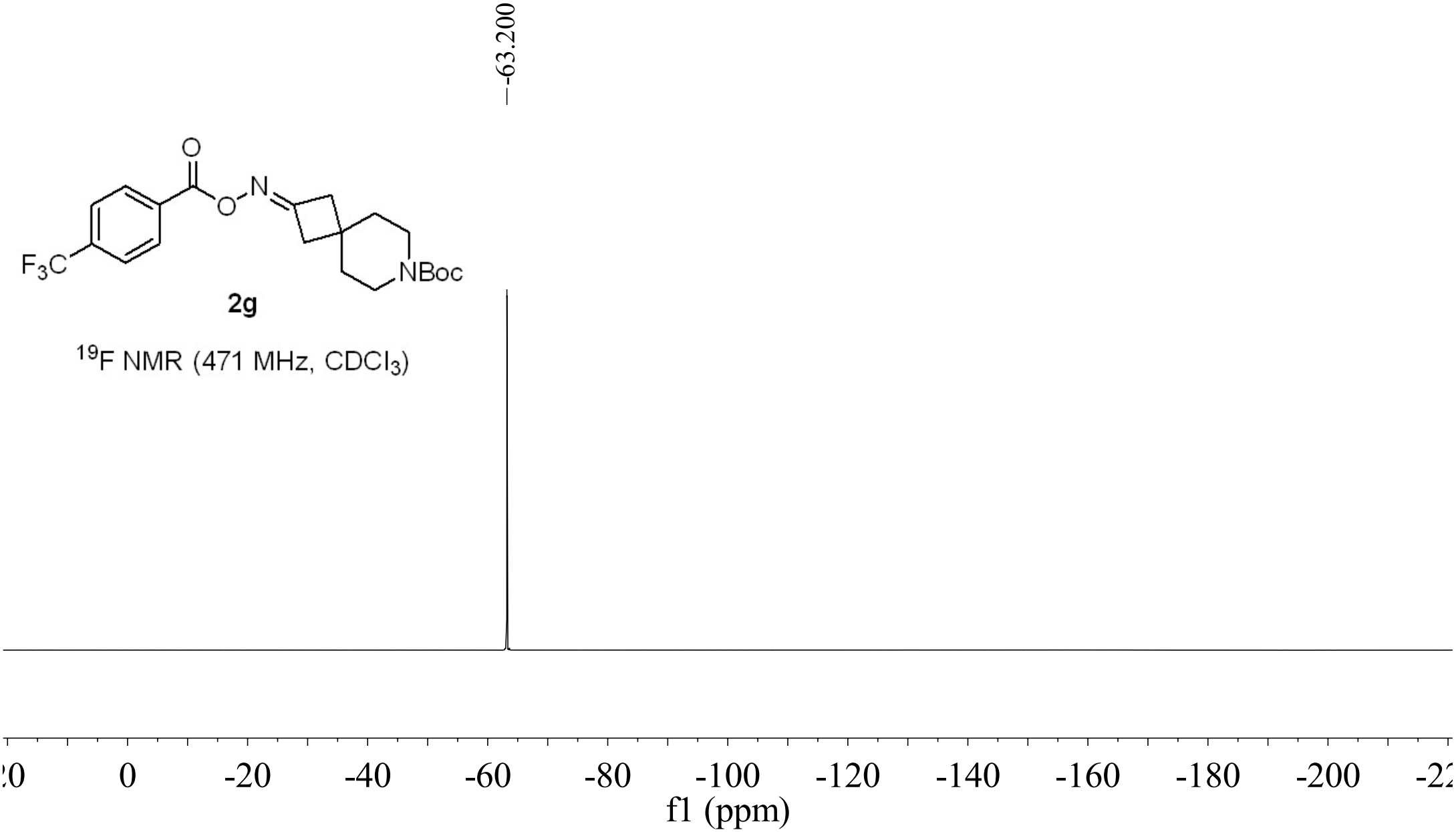


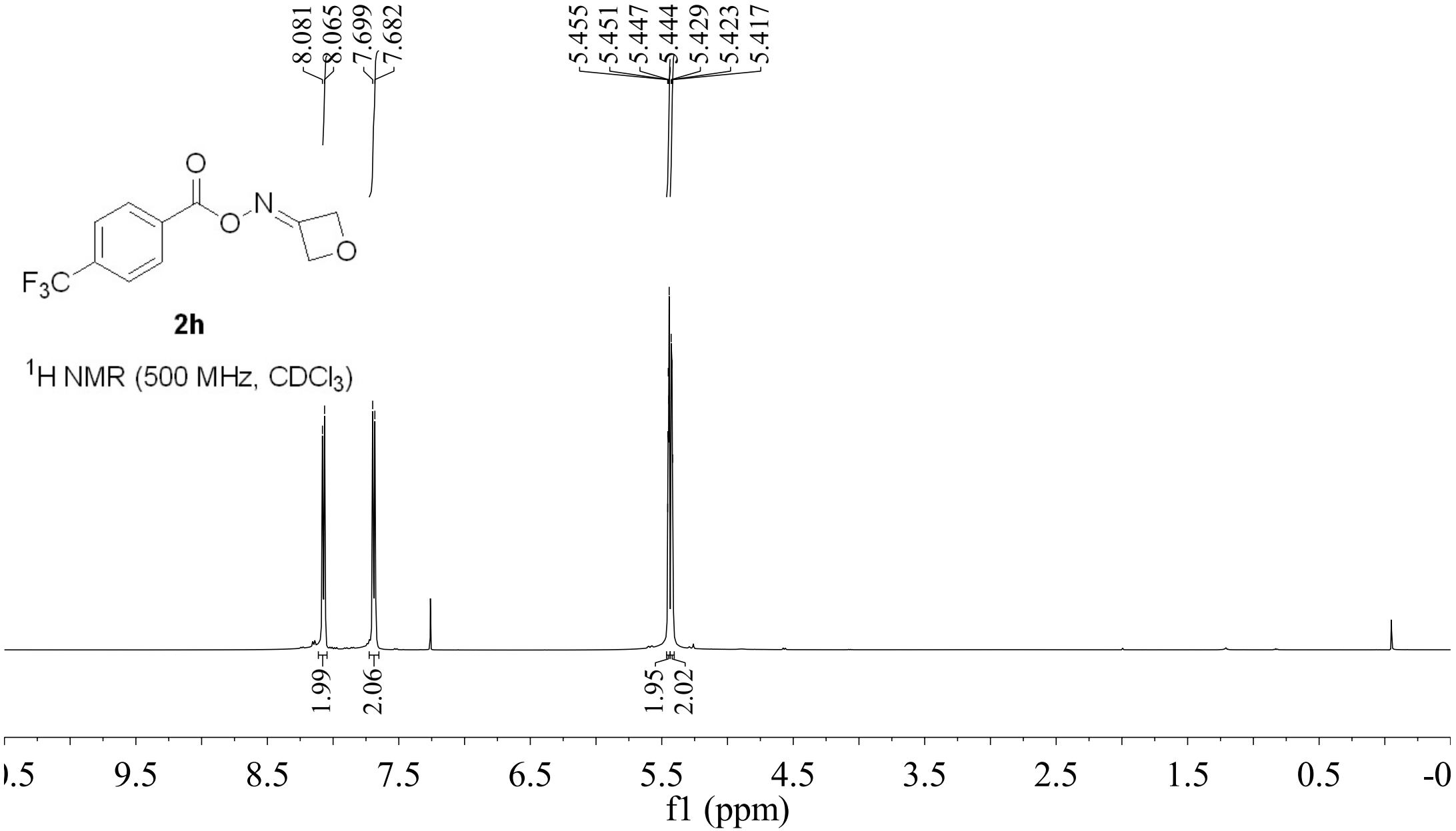

8.139
8.123
7.709
7.692
3.391
3.380
3.369
2.875
2.867
1.671
1.666
1.661
1.652
1.642
1.440
O
O
N
F3C
NBoc
2g
1H NMR (500 MHz, CDCl3)
2.00
2.04
4.05
4.08
4.13
9.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

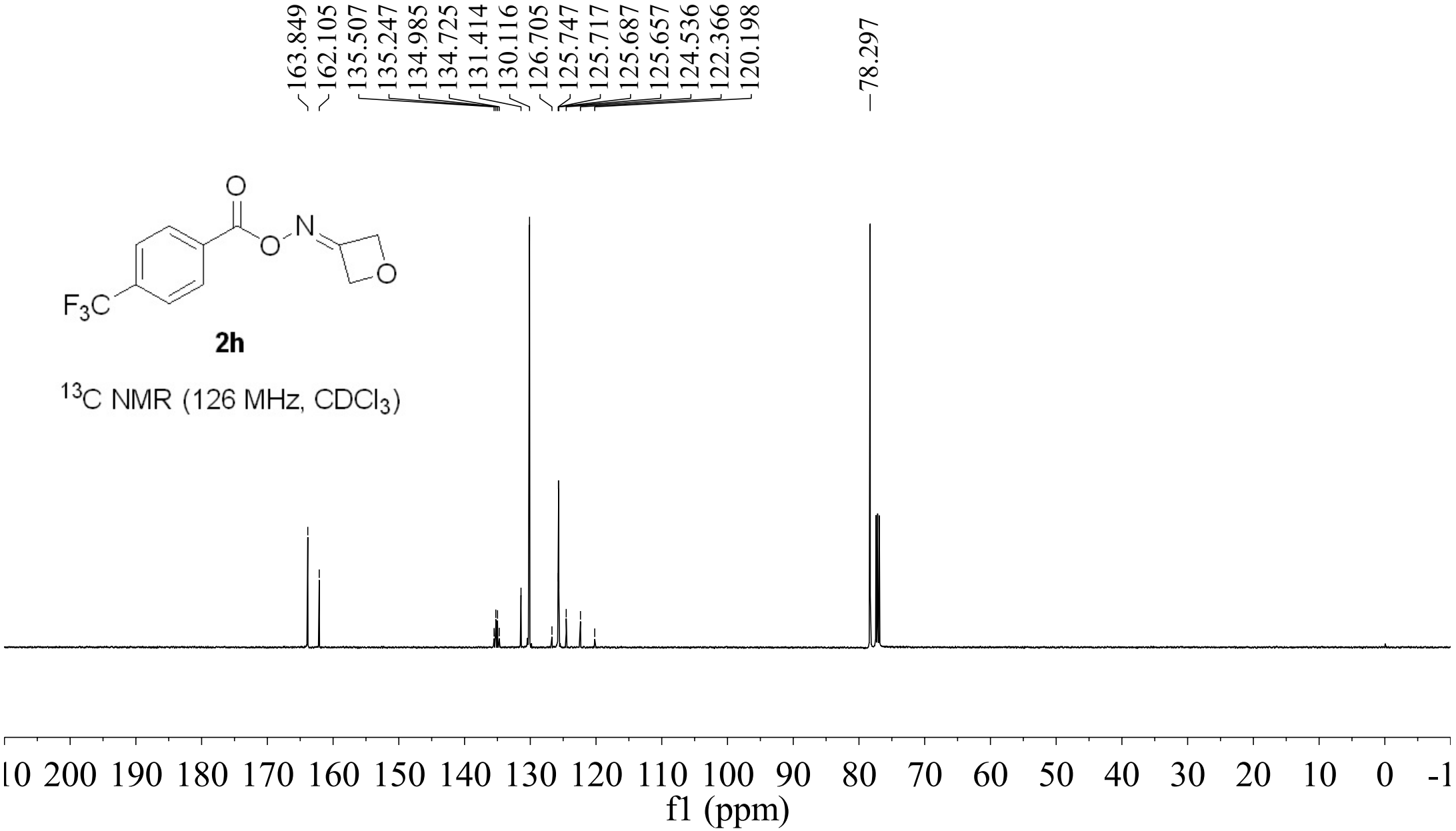

165.950
162.794
154.853
135.221
134.961
134.702
134.441
132.302
130.098
126.851
125.677
125.648
125.617
125.588
124.682
122.513
120.346
79.864
41.968
41.953
41.041
36.379
33.474
28.495
O
O
N
F3C
NBoc
2g
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

2g

^{19}F NMR (471 MHz, $CDCl_3$)

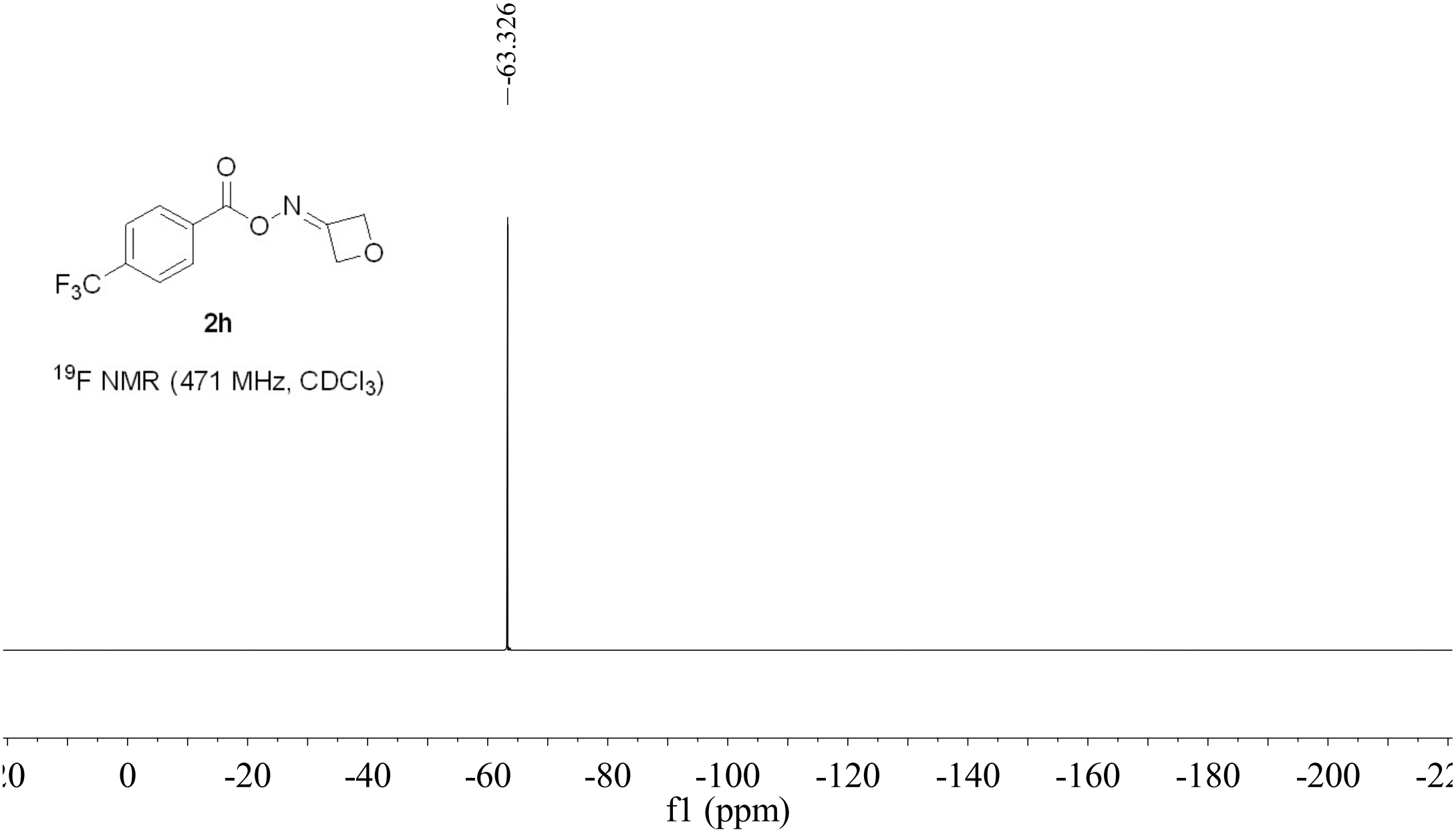


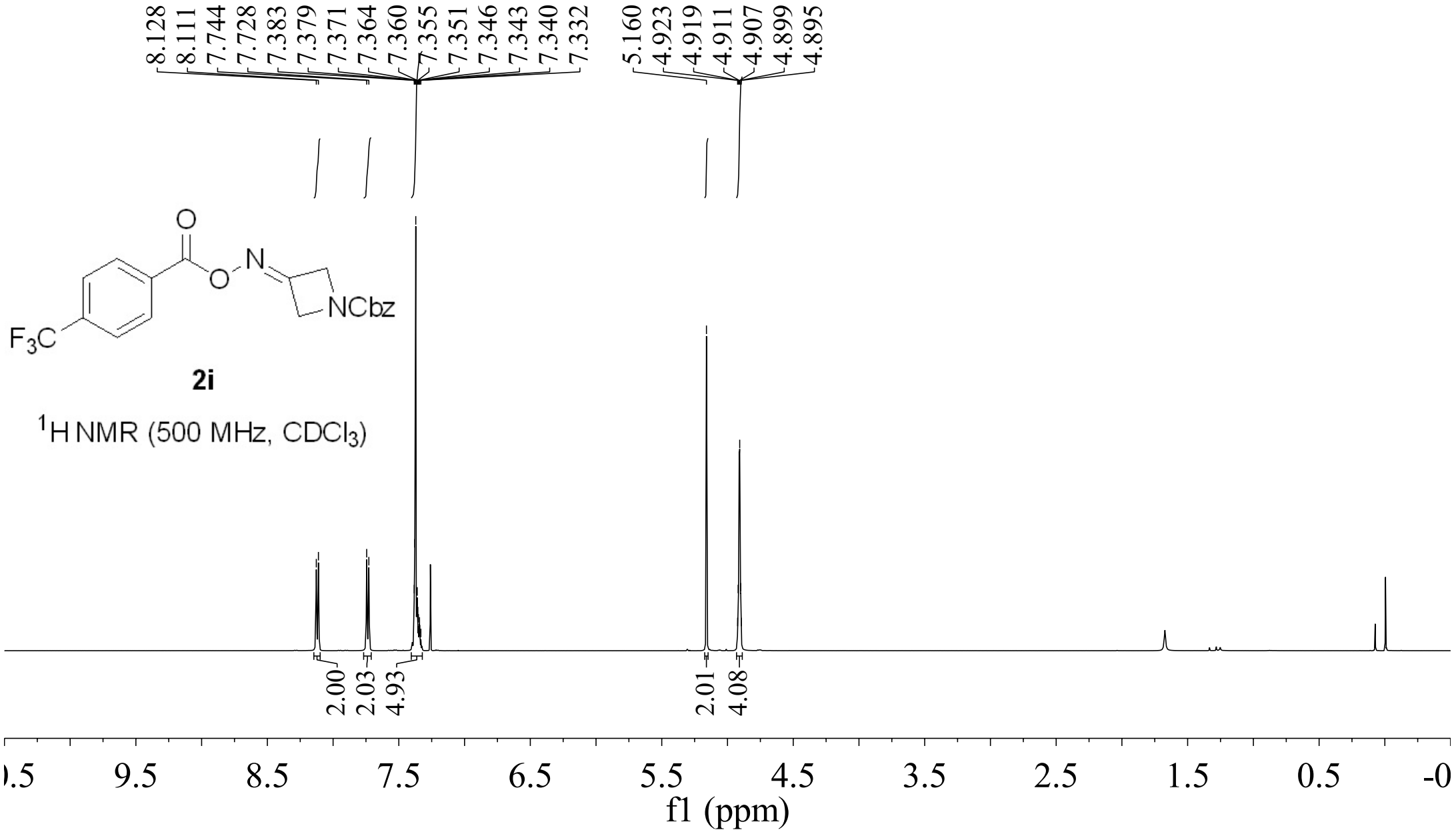

8.081
8.065
7.699
7.682
5.455
5.451
5.447
5.444
5.429
5.423
5.417
O
O
N
O
O
F3C
2h
1H NMR (500 MHz, CDCl3)
1.99
2.06
1.95
2.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

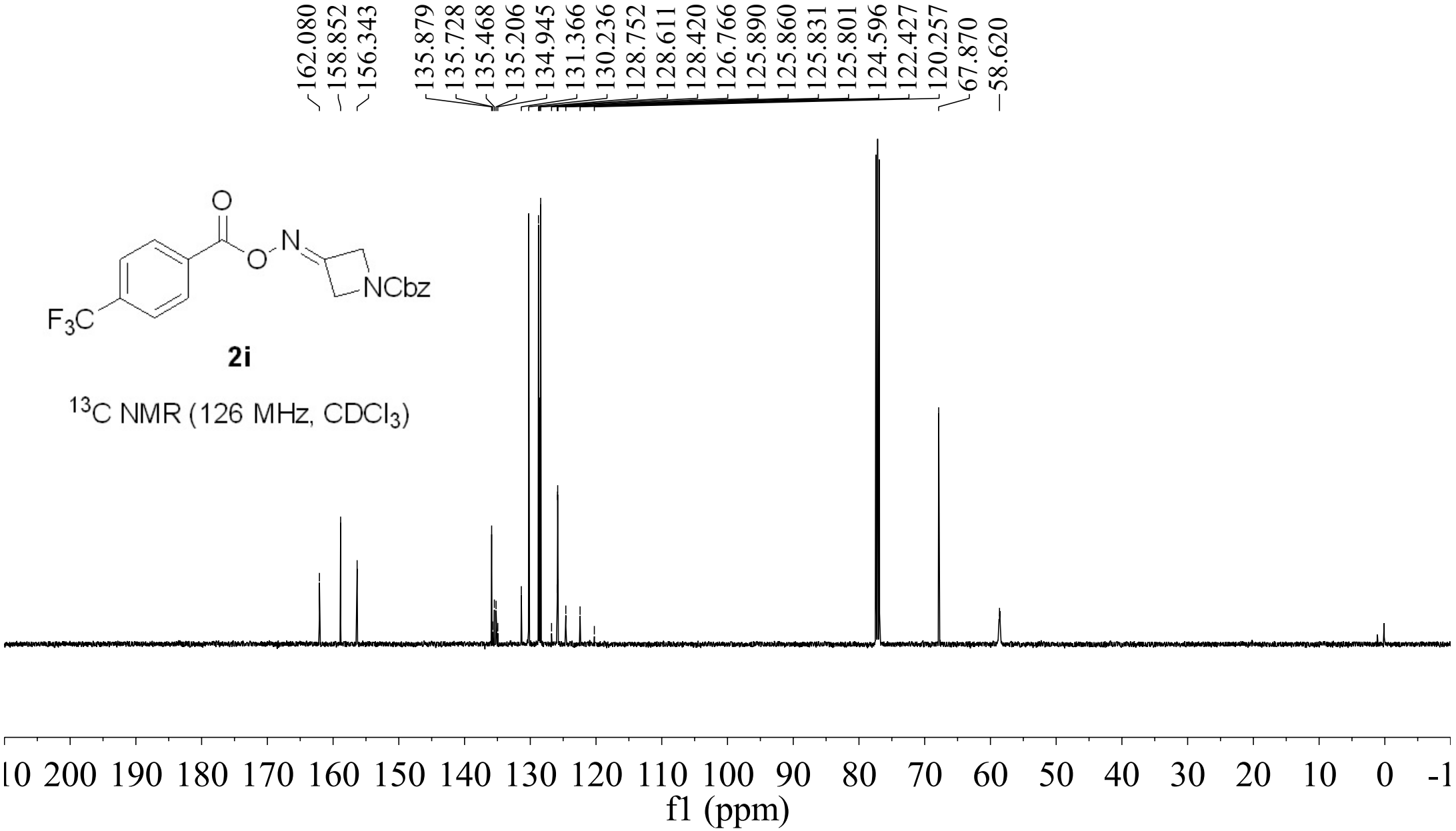

163.849
162.105
135.507
135.247
134.985
134.725
131.414
130.116
126.705
125.747
125.717
125.687
125.657
124.536
122.366
120.198
78.297
O
O
N
O
F3C
2h
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

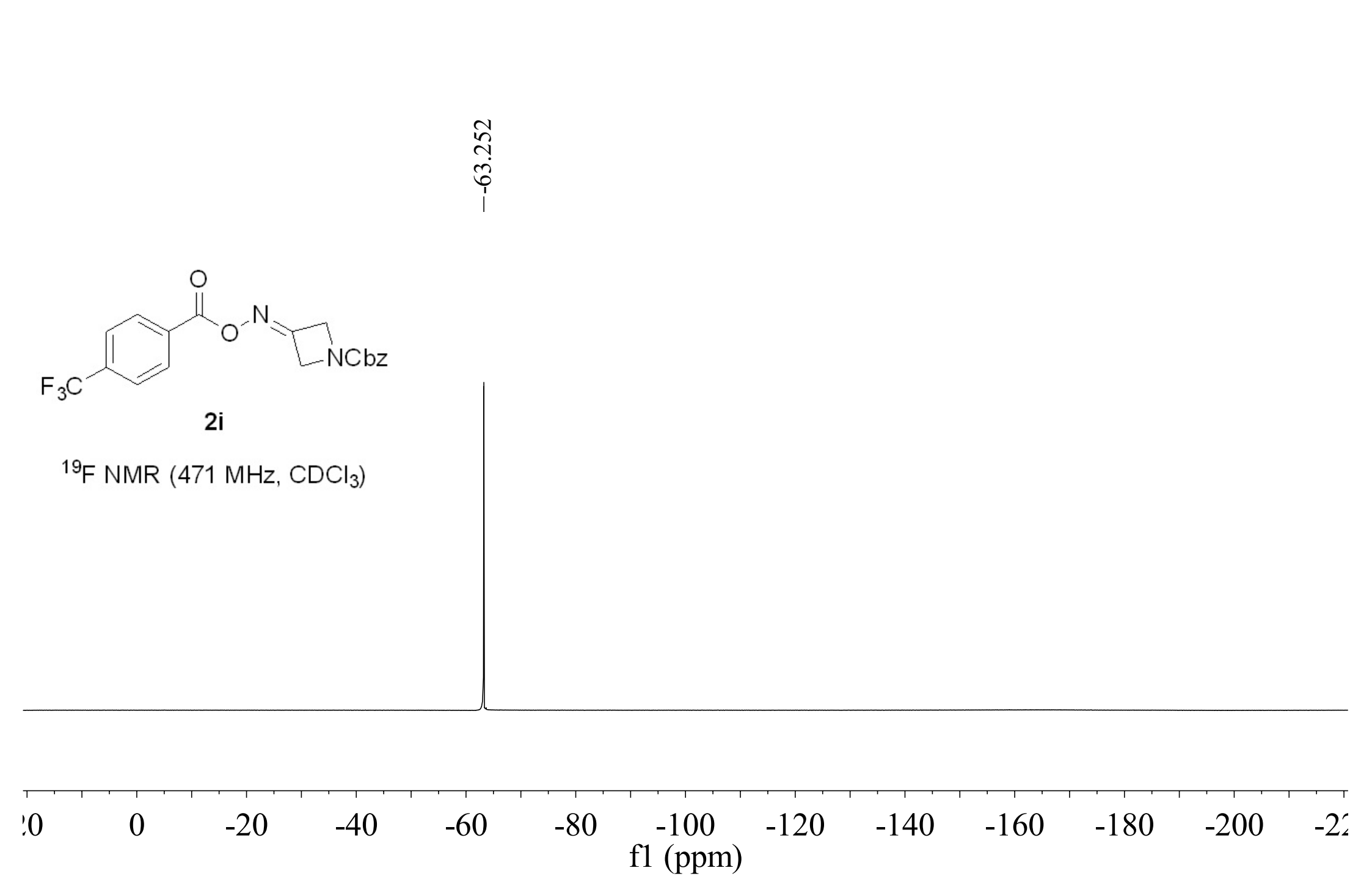
2h

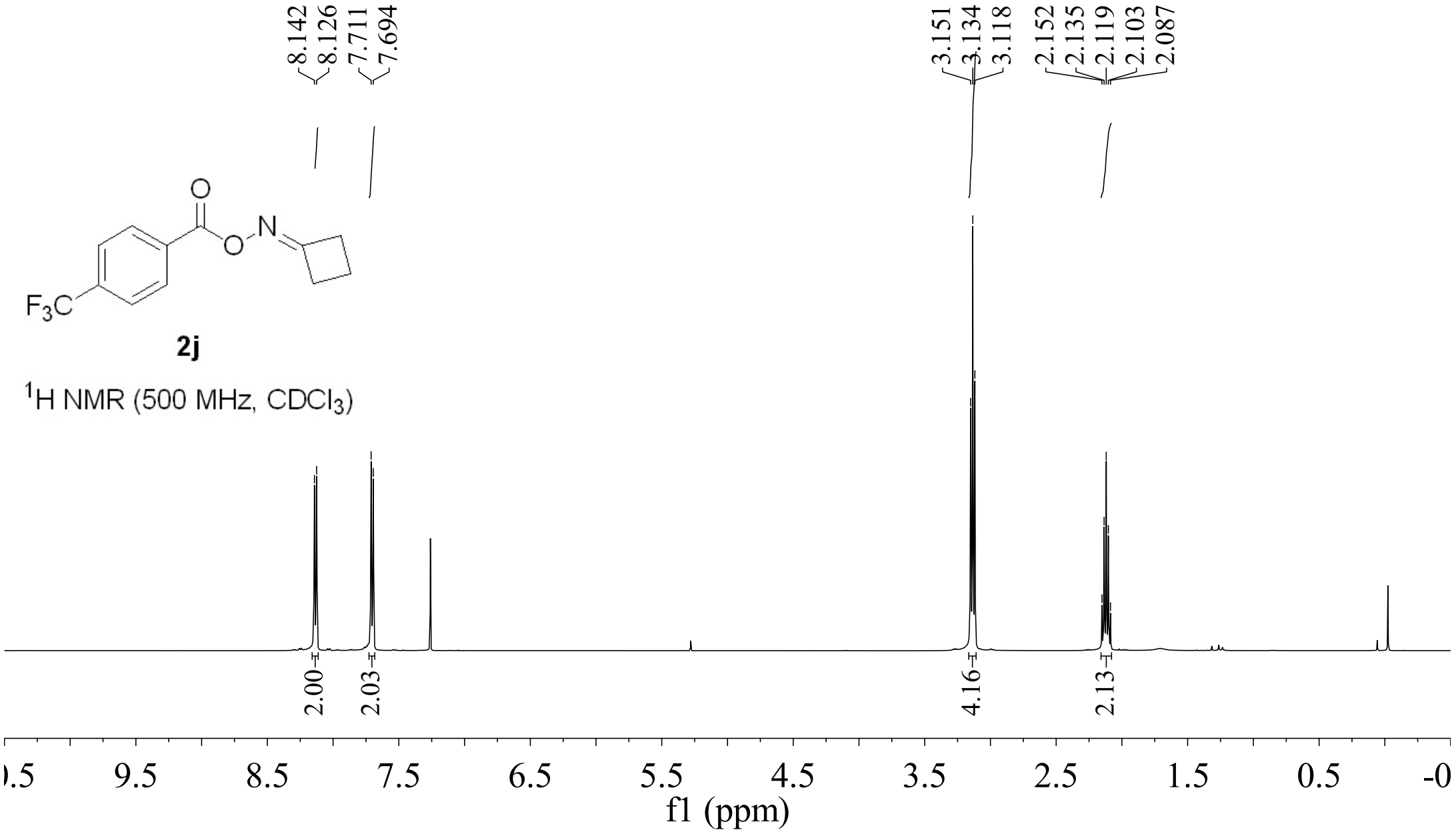
^{19}F NMR (471 MHz, $CDCl_3$)

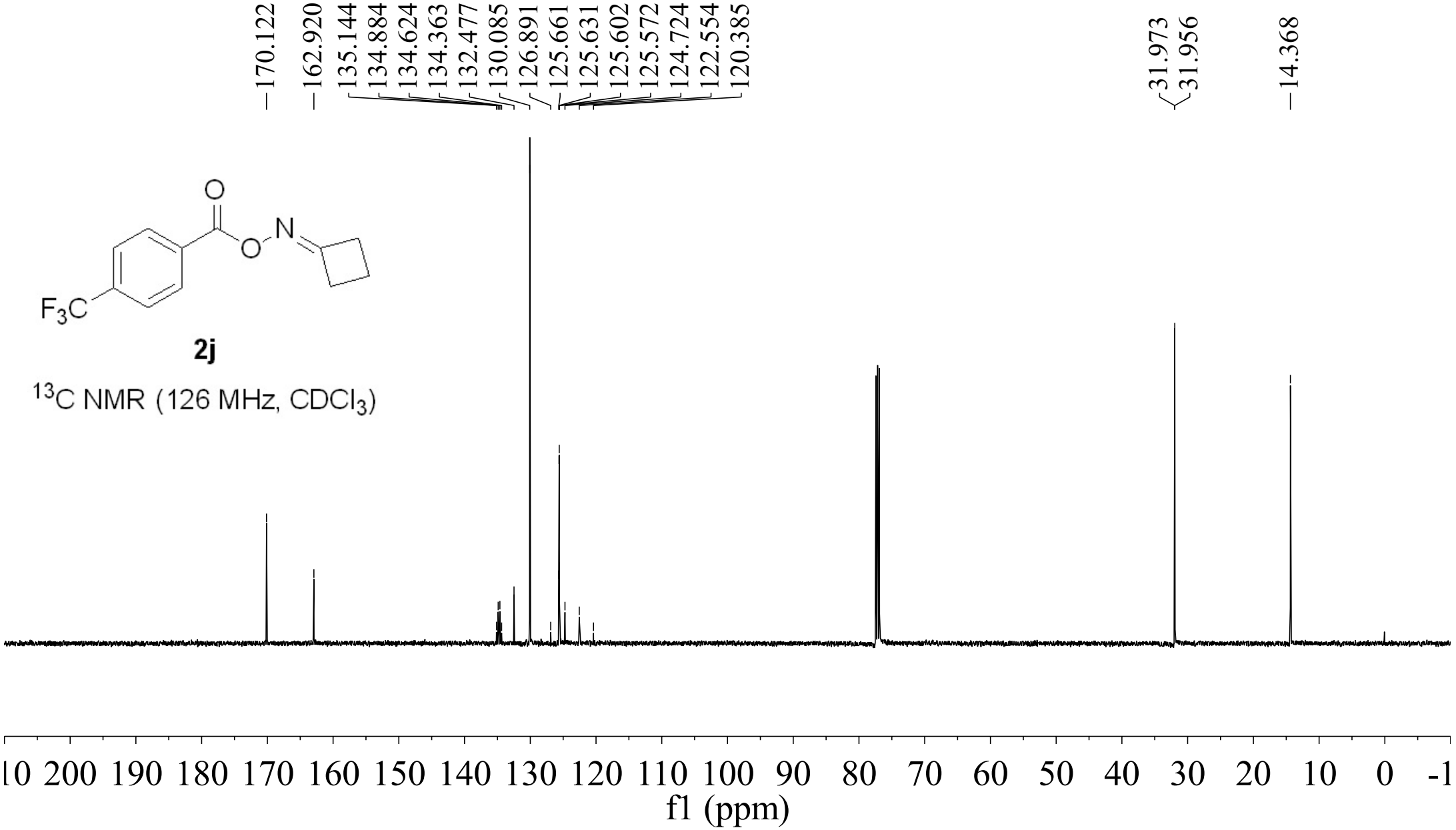



8.128
8.111
7.744
7.728
7.383
7.379
7.371
7.364
7.360
7.355
7.351
7.346
7.343
7.340
7.332
5.160
4.923
4.919
4.911
4.907
4.899
4.895
O
O
N
NCbz
F3C
2i
1H NMR (500 MHz, CDCl3)
2.00
2.03
4.93
2.01
4.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


162.080
158.852
156.343
135.879
135.728
135.468
135.206
134.945
131.366
130.236
128.752
128.611
128.420
126.766
125.890
125.860
125.831
125.801
124.596
122.427
120.257
67.870
58.620
O
O
N
NCbz
F3C
2i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

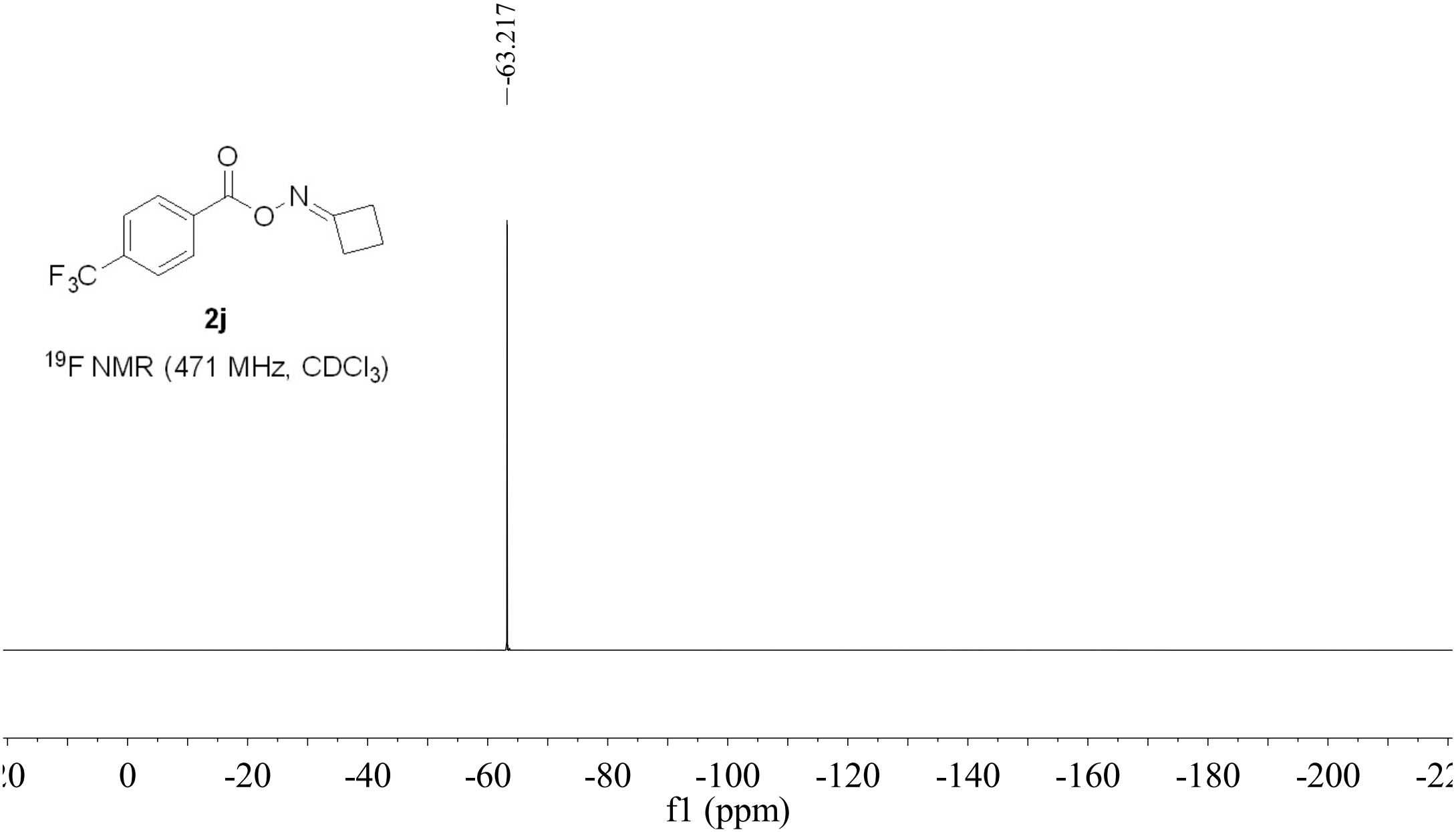

-63.252
O
O
N
NCbz
F3C
2i
19F NMR (471 MHz, CDCl3)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

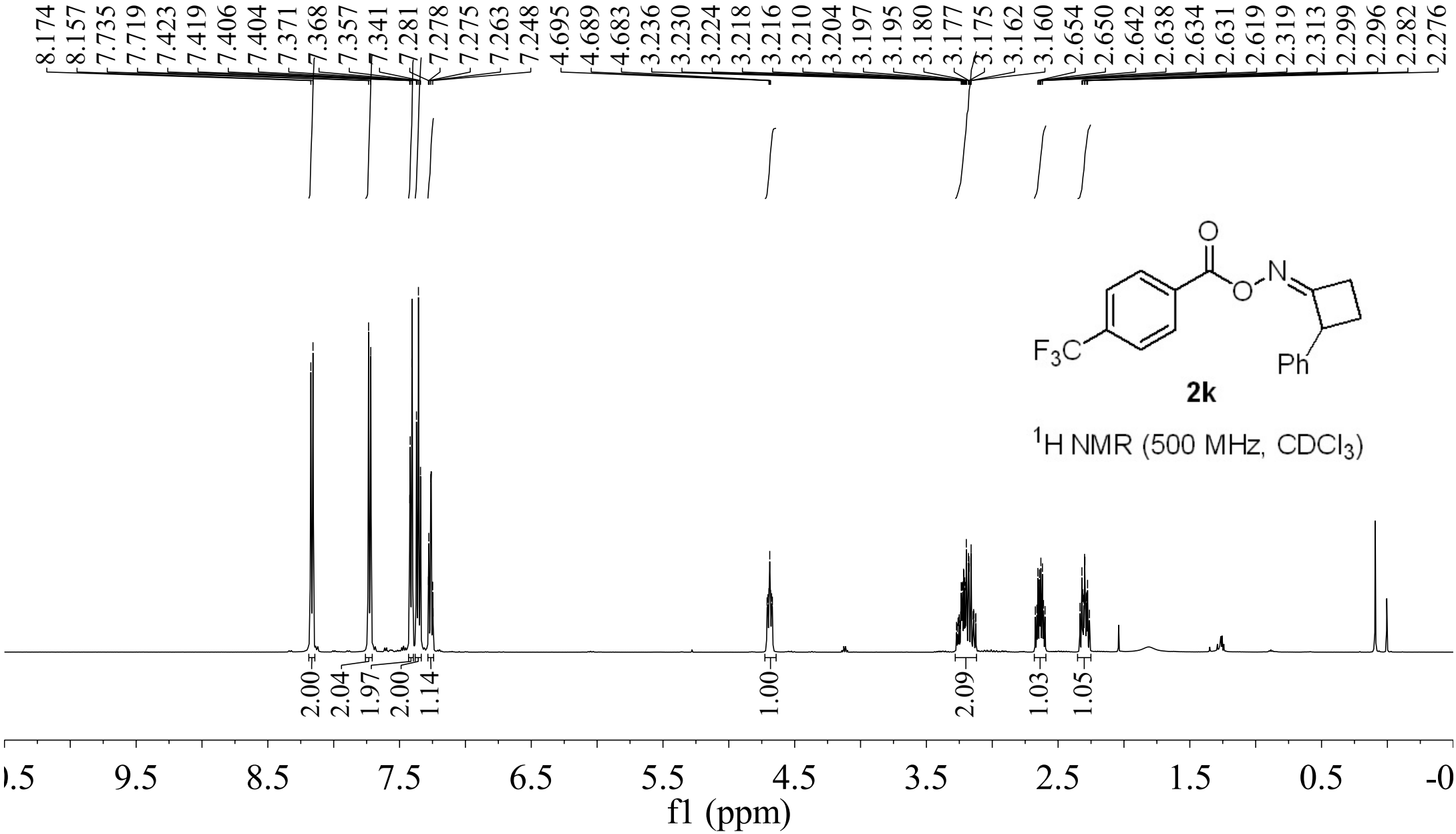

8.142
8.126
7.711
7.694
3.151
3.134
3.118
2.152
2.135
2.119
2.103
2.087
O
O
N
F3C
2j
1H NMR (500 MHz, CDCl3)
2.00
2.03
4.16
2.13
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

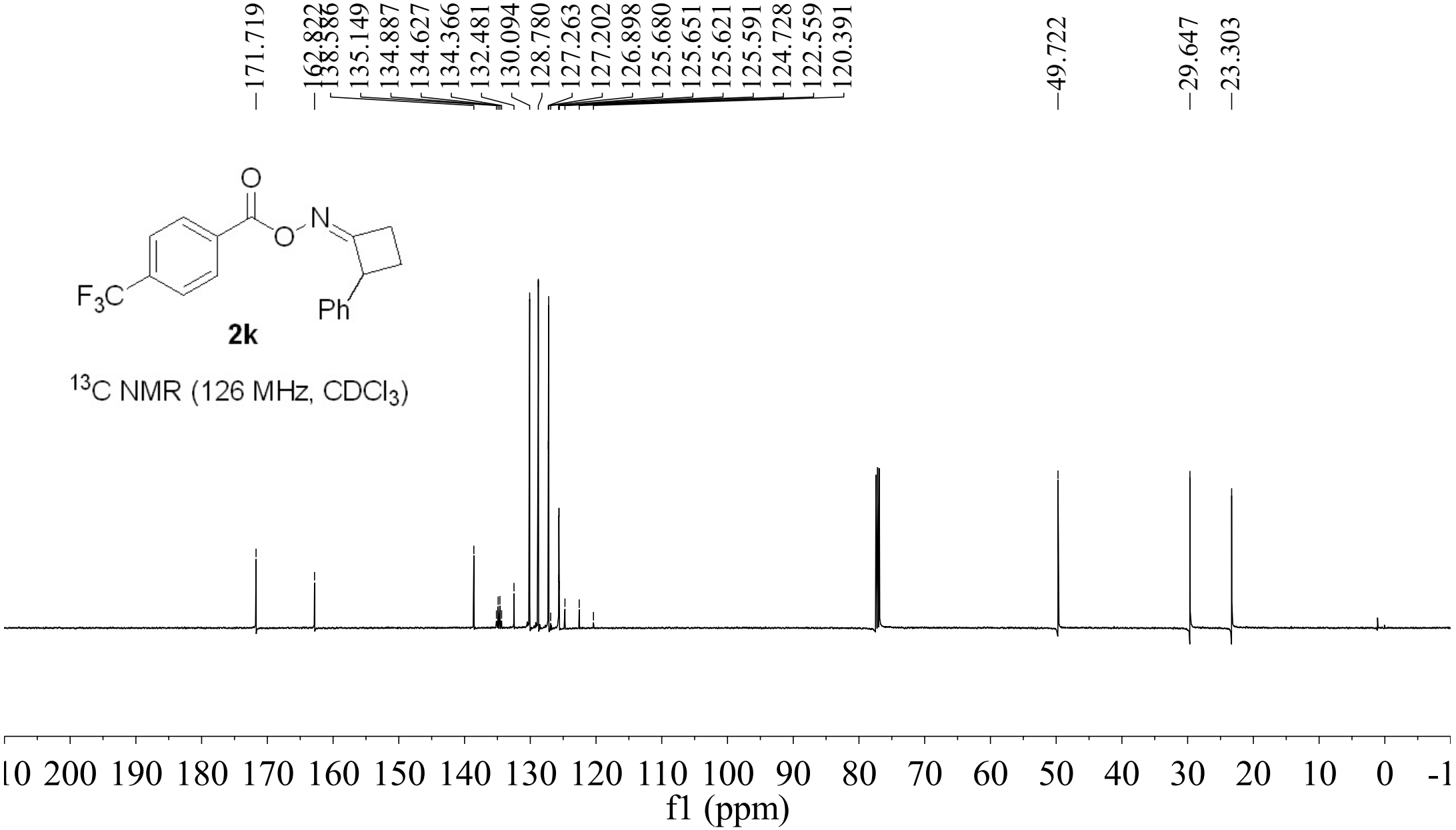

170.122
162.920
135.144
134.884
134.624
134.363
132.477
130.085
126.891
125.661
125.631
125.602
125.572
124.724
122.554
120.385
31.973
31.956
14.368
O
O
N
F3C
2j
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2j

^{19}F NMR (471 MHz, $CDCl_3$)

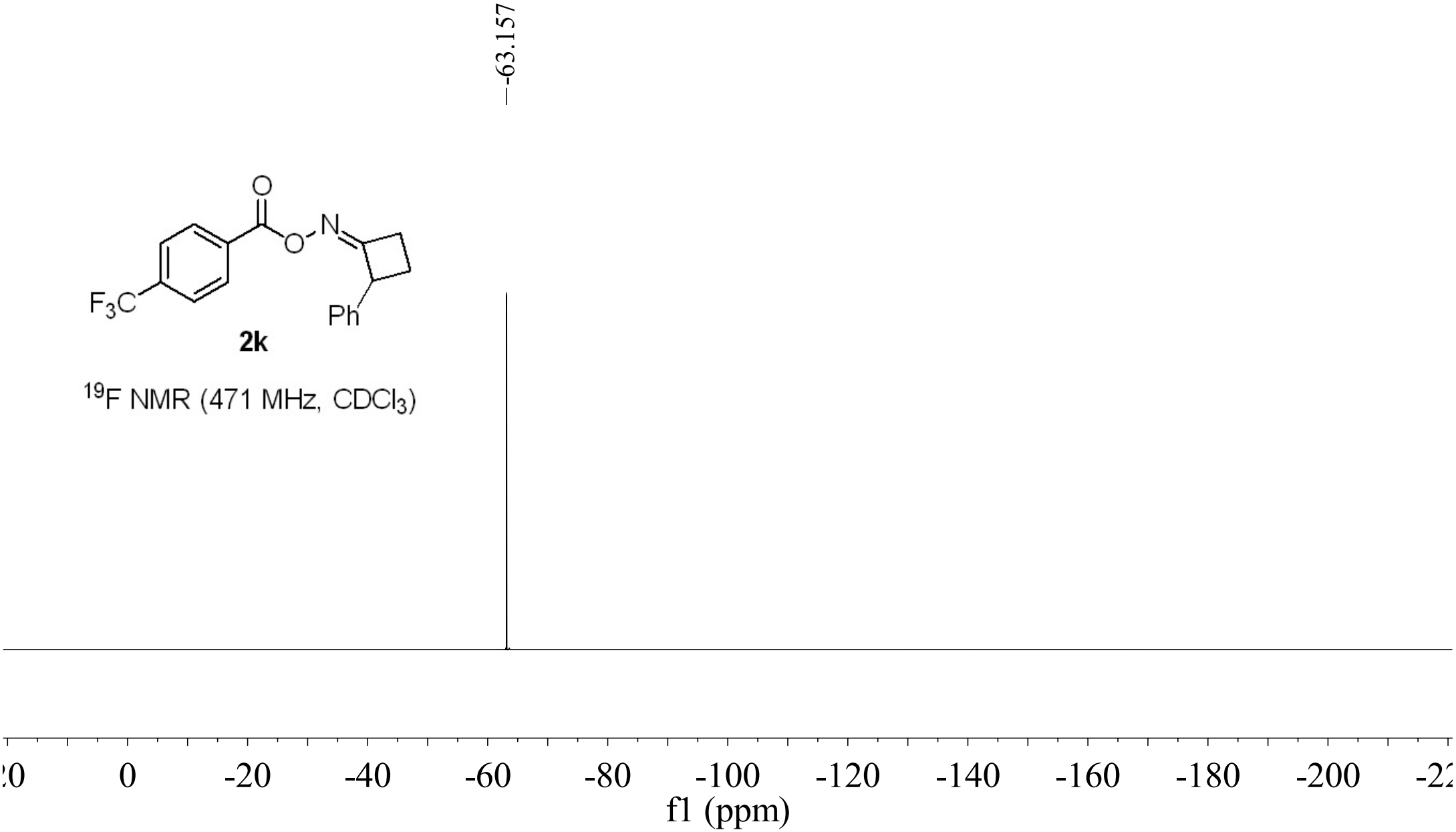


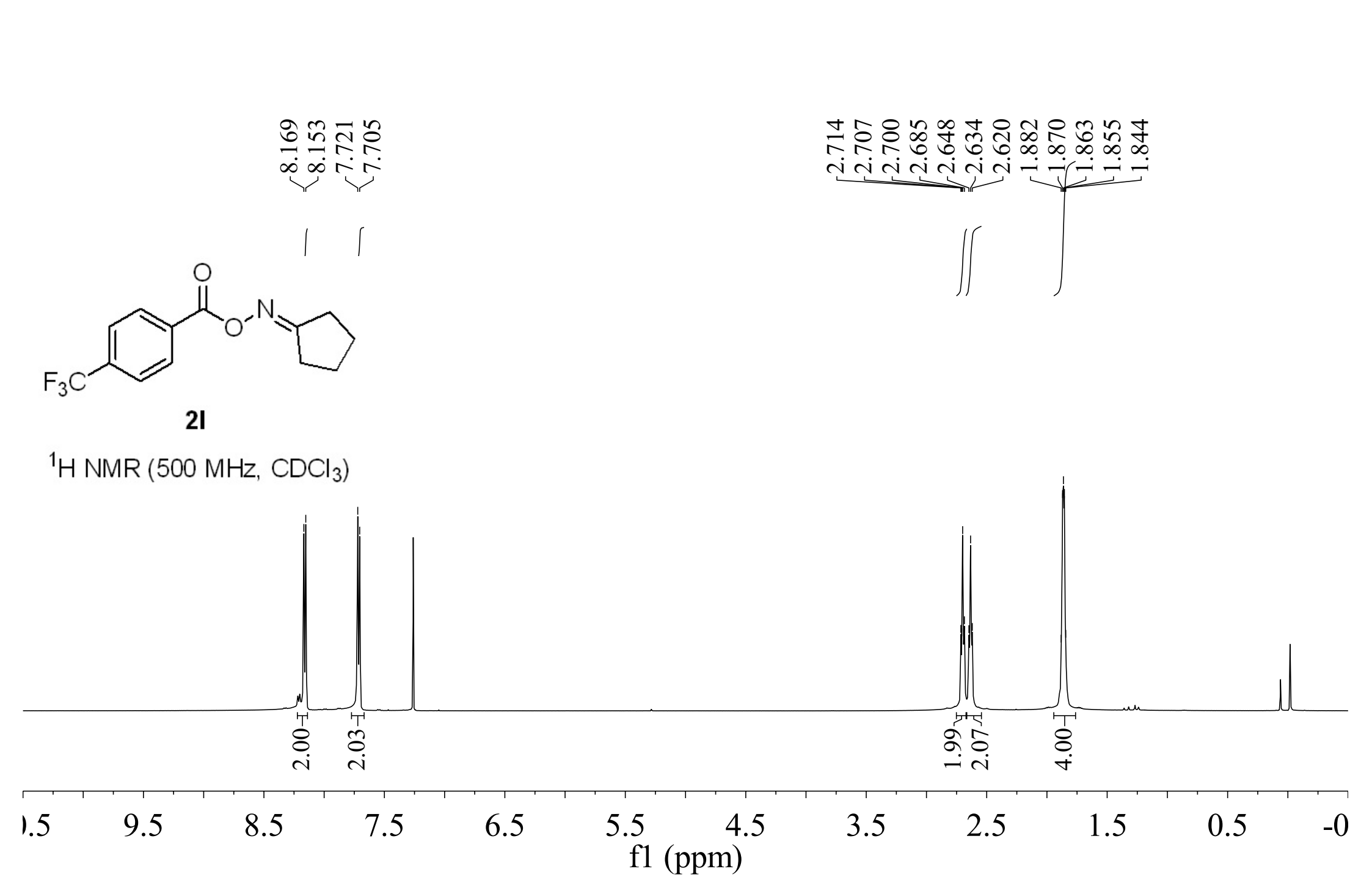

8.174
8.157
7.735
7.719
7.423
7.419
7.406
7.404
7.371
7.368
7.357
7.341
7.281
7.278
7.275
7.263
7.248
4.695
4.689
4.683
3.236
3.230
3.224
3.218
3.216
3.210
3.204
3.197
3.195
3.180
3.177
3.175
3.162
3.160
2.654
2.650
2.642
2.638
2.634
2.631
2.619
2.319
2.313
2.299
2.296
2.282
2.276
O
N
O
F3C
Ph
2k
1H NMR (500 MHz, CDCl3)
2.00
2.04
1.97
2.00
1.14
1.00
2.09
1.03
1.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

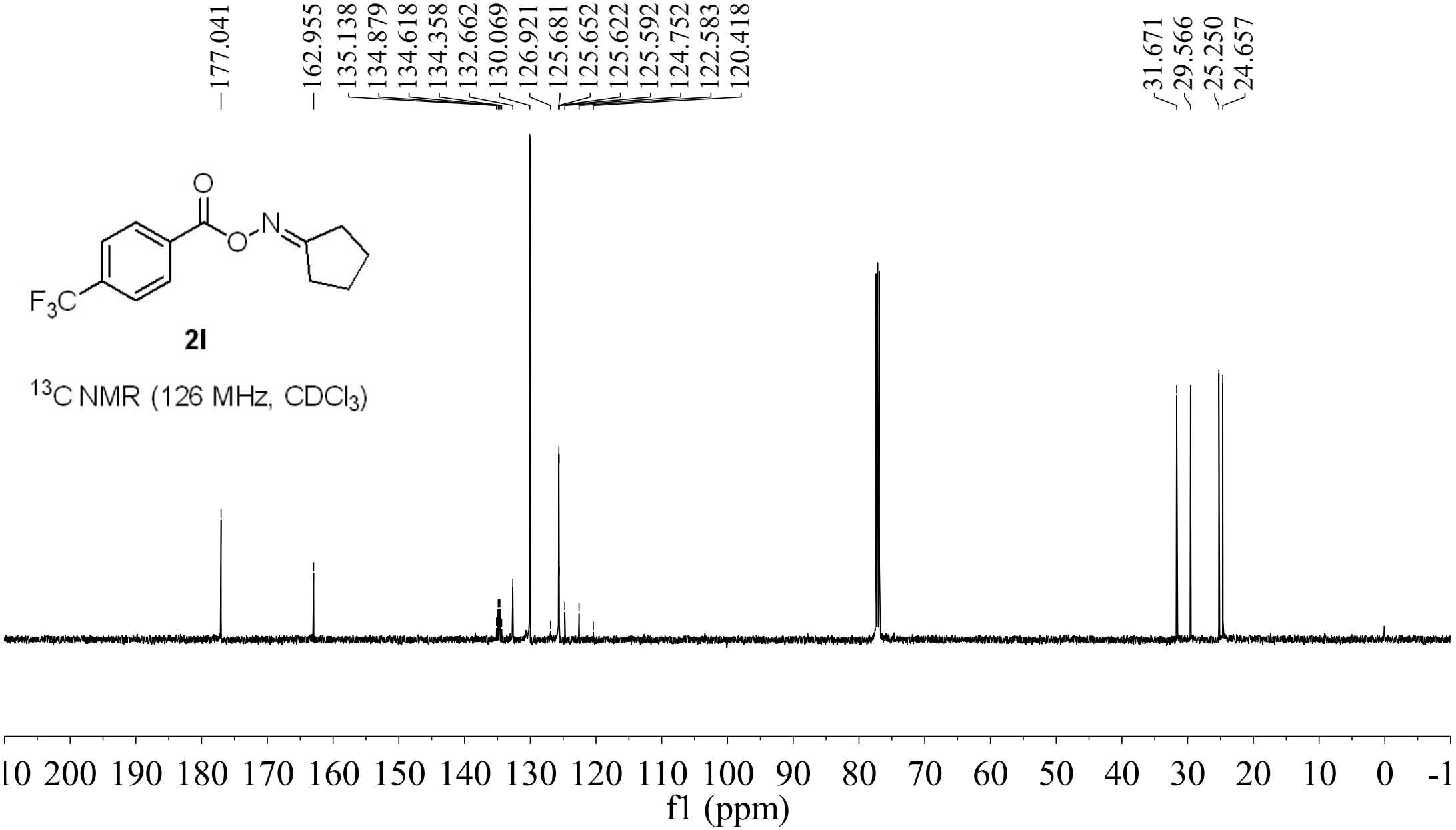

171.719
162.822
138.586
135.149
134.887
134.627
134.366
132.481
130.094
128.780
127.263
127.202
126.898
125.680
125.651
125.621
125.591
124.728
122.559
120.391
49.722
29.647
23.303
O
N
O
F3C
Ph
2k
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

2k

^{19}F NMR (471 MHz, $CDCl_3$)

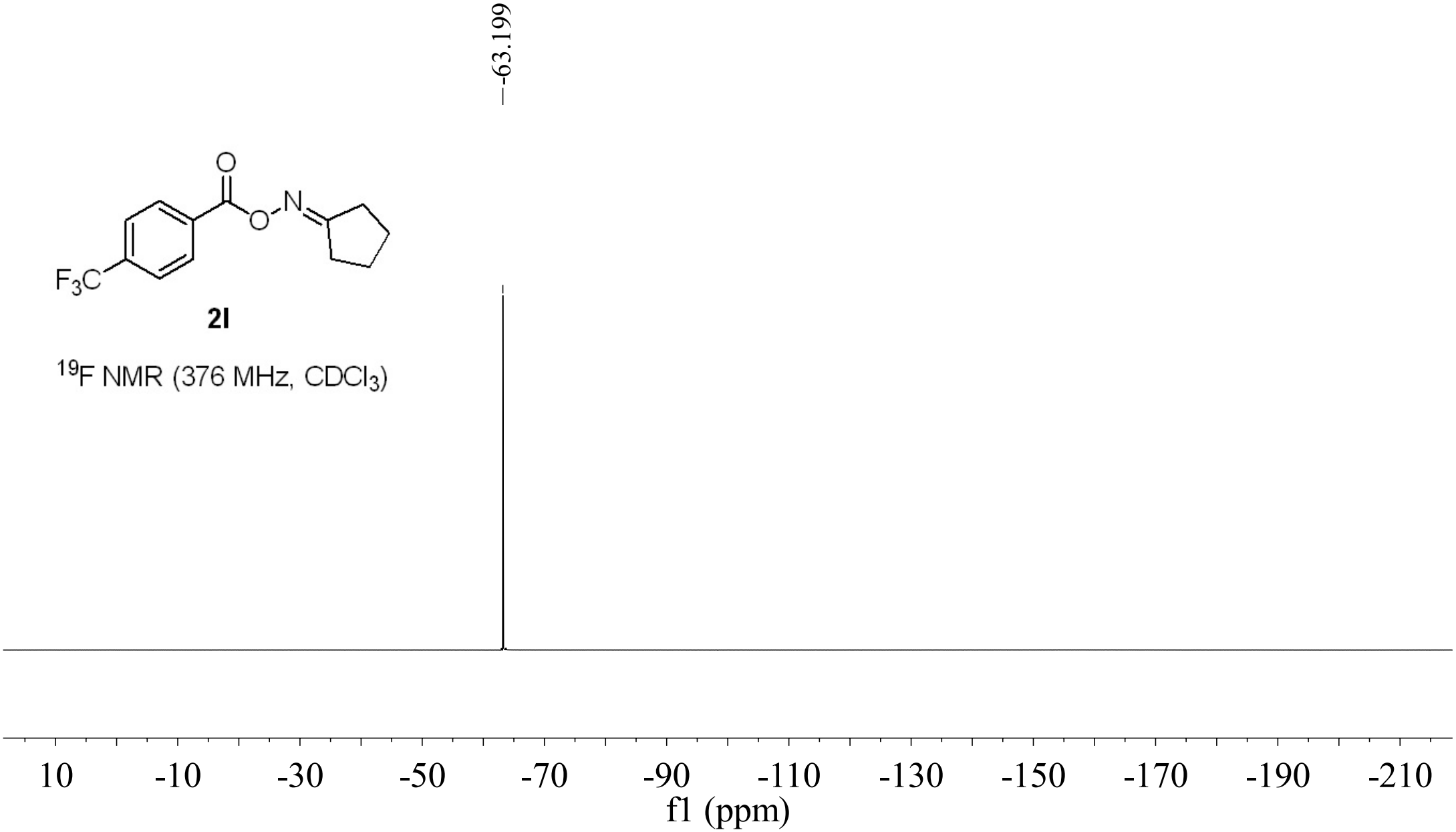


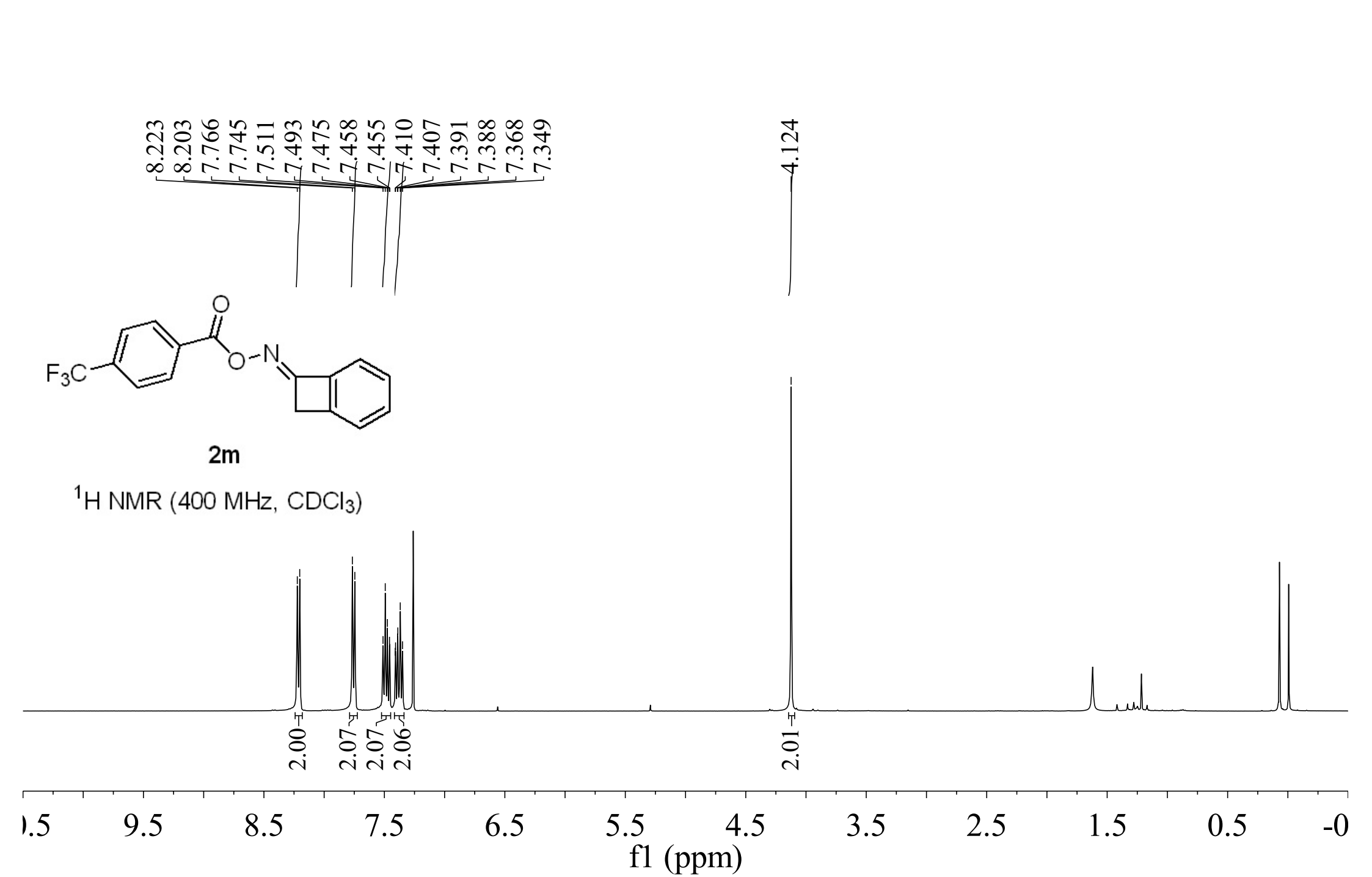

8.169
8.153
7.721
7.705
2.714
2.707
2.700
2.685
2.648
2.634
2.620
1.882
1.870
1.863
1.855
1.844
O
O
N
F3C
2I
1H NMR (500 MHz, CDCl3)
2.00
2.03
1.99
2.07
4.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

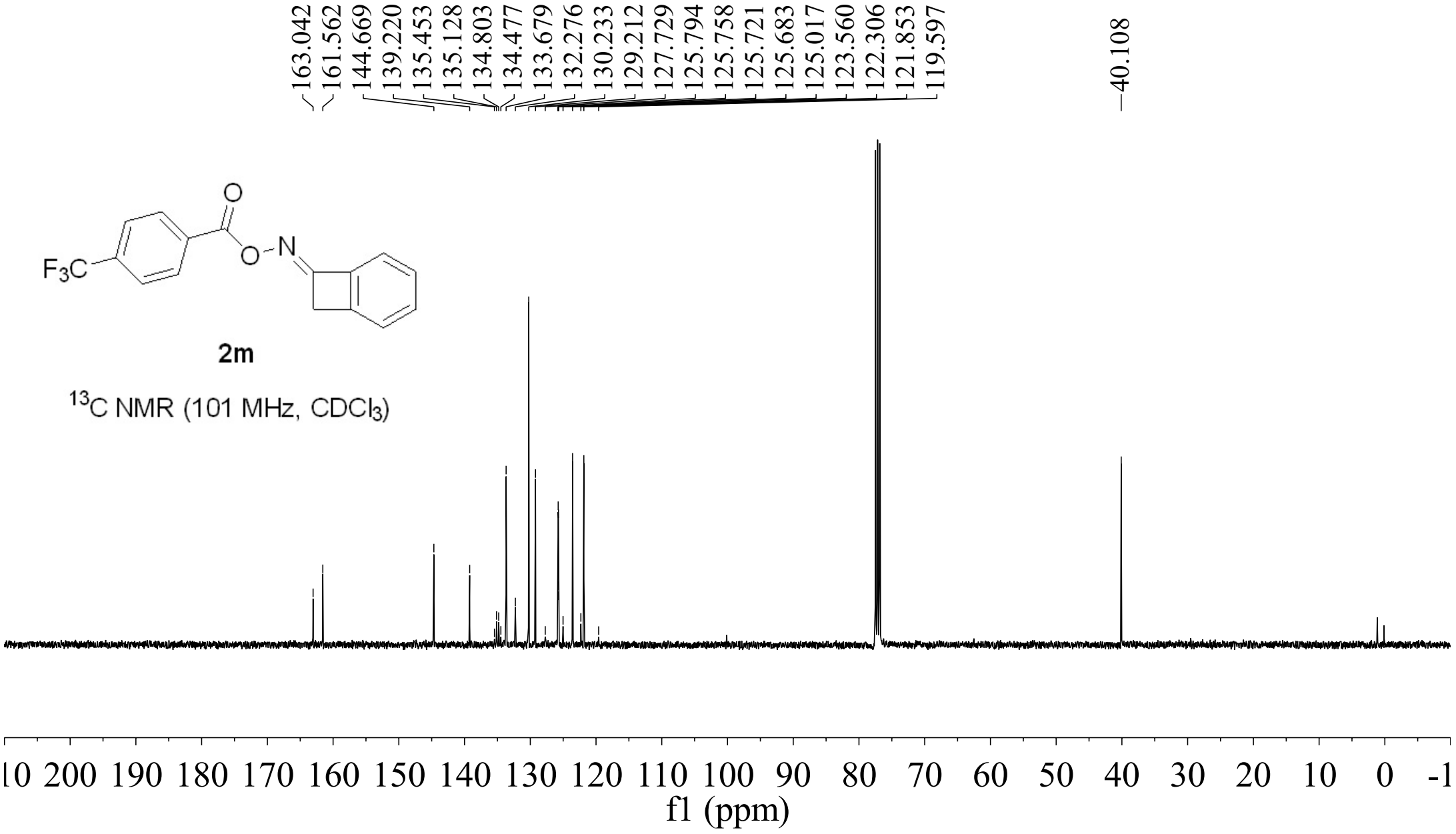

177.041
162.955
135.138
134.879
134.618
134.358
132.662
130.069
126.921
125.681
125.652
125.622
125.592
124.752
122.583
120.418
31.671
29.566
25.250
24.657
O
O
N
F3C
2l
13C NMR (126 MHz, CDCl3)
f1 (ppm)

2l

^{19}F NMR (376 MHz, $CDCl_3$)

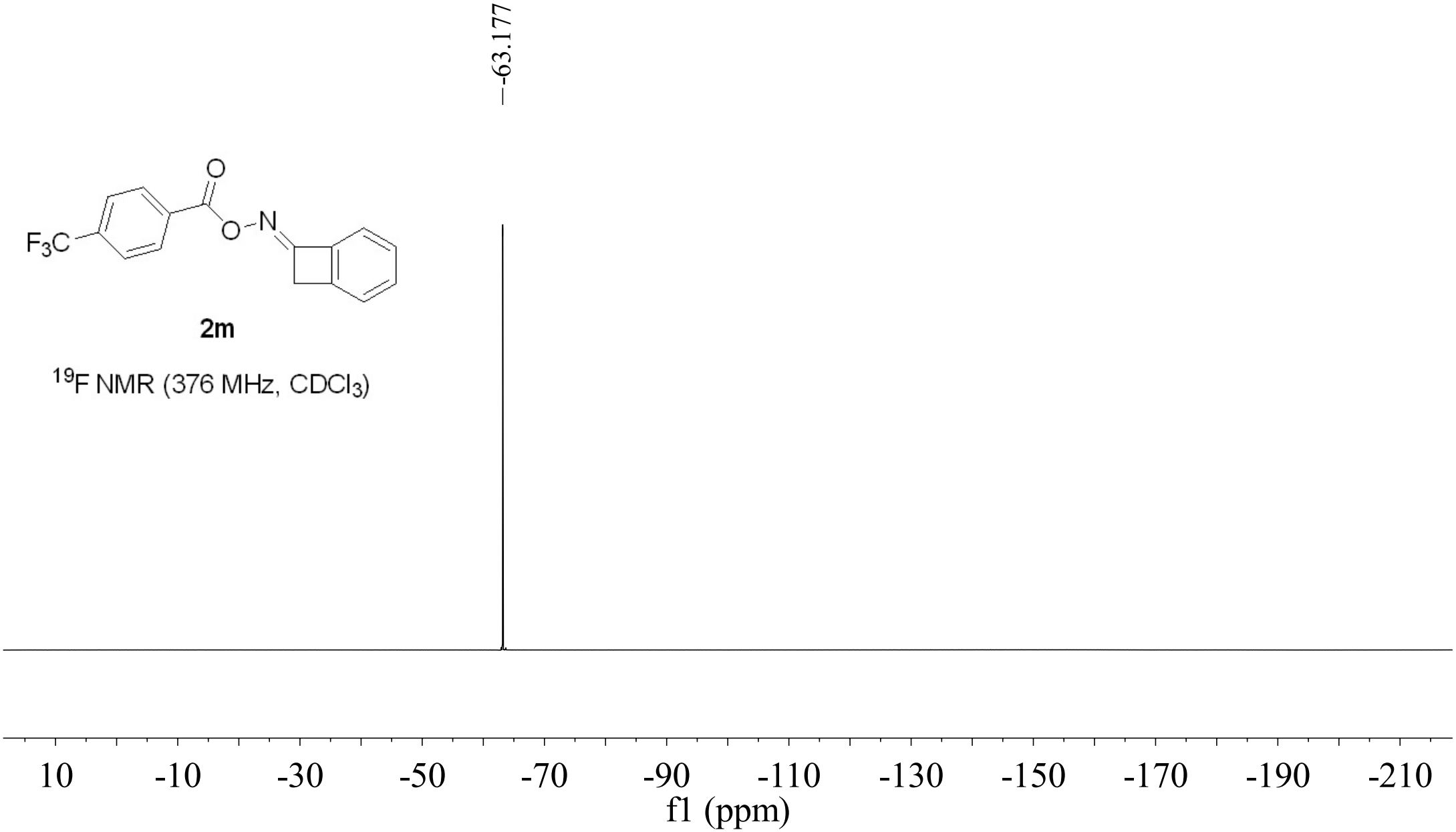


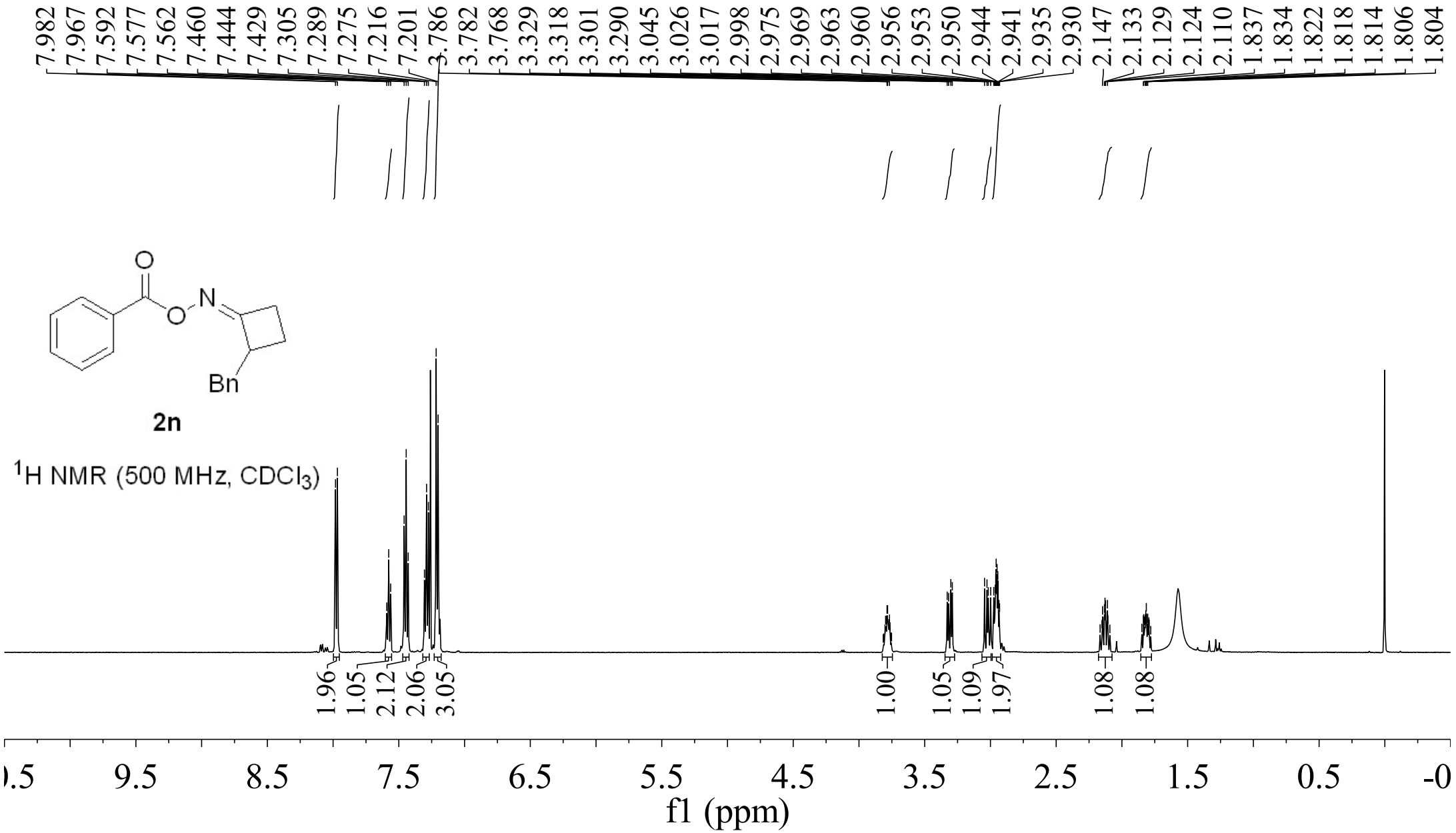

8.223
8.203
7.766
7.745
7.511
7.493
7.475
7.458
7.455
7.410
7.407
7.391
7.388
7.368
7.349
4.124
O
O
N
F3C
2m
1H NMR (400 MHz, CDCl3)
2.00
2.07
2.07
2.06
2.01
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

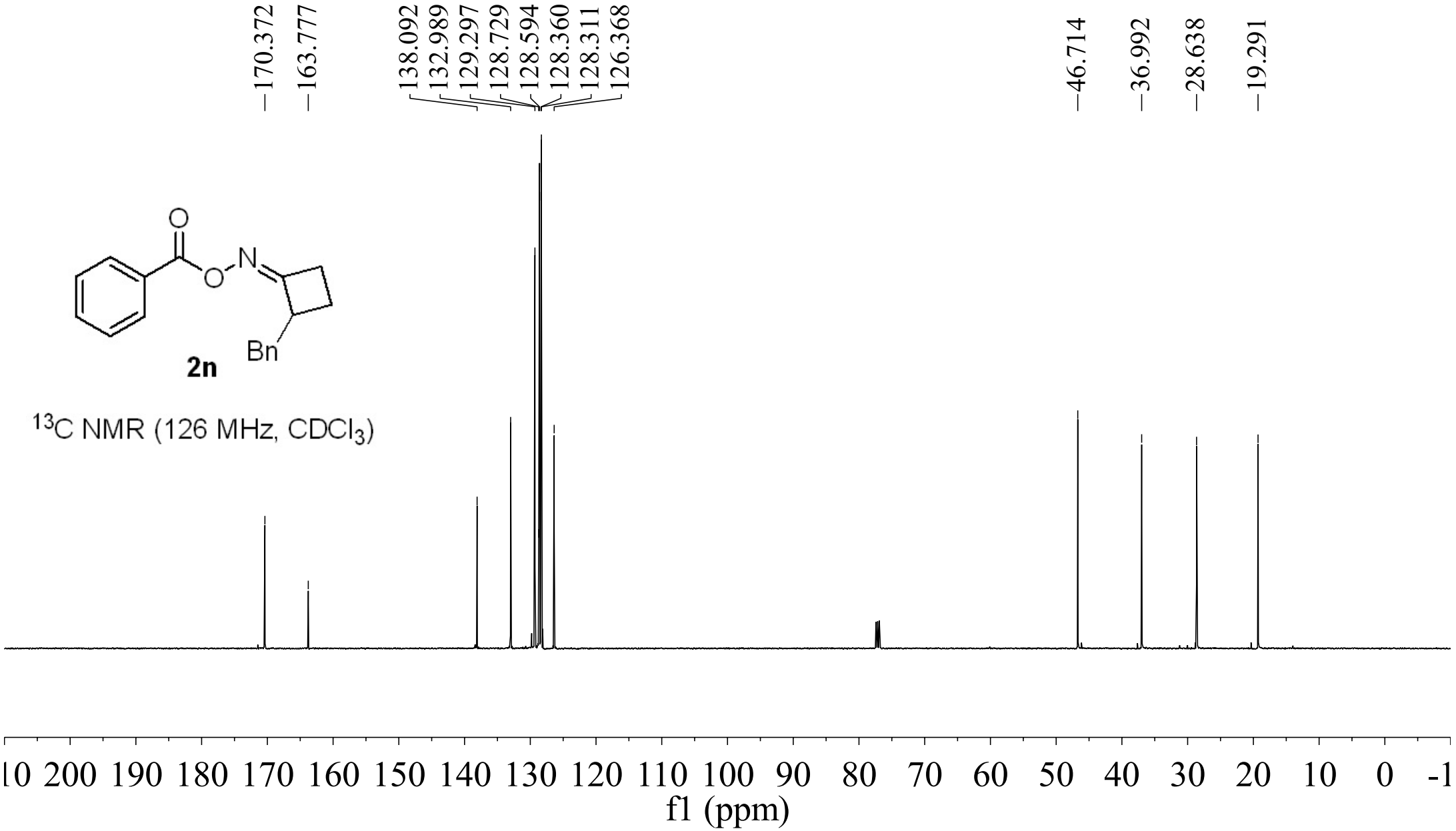

163.042
161.562
144.669
139.220
135.453
135.128
134.803
134.477
133.679
132.276
130.233
129.212
127.729
125.794
125.758
125.721
125.683
125.017
123.560
122.306
121.853
119.597
40.108
O
O
N
F3C
2m
13C NMR (101 MHz, CDCl3)
f1 (ppm)

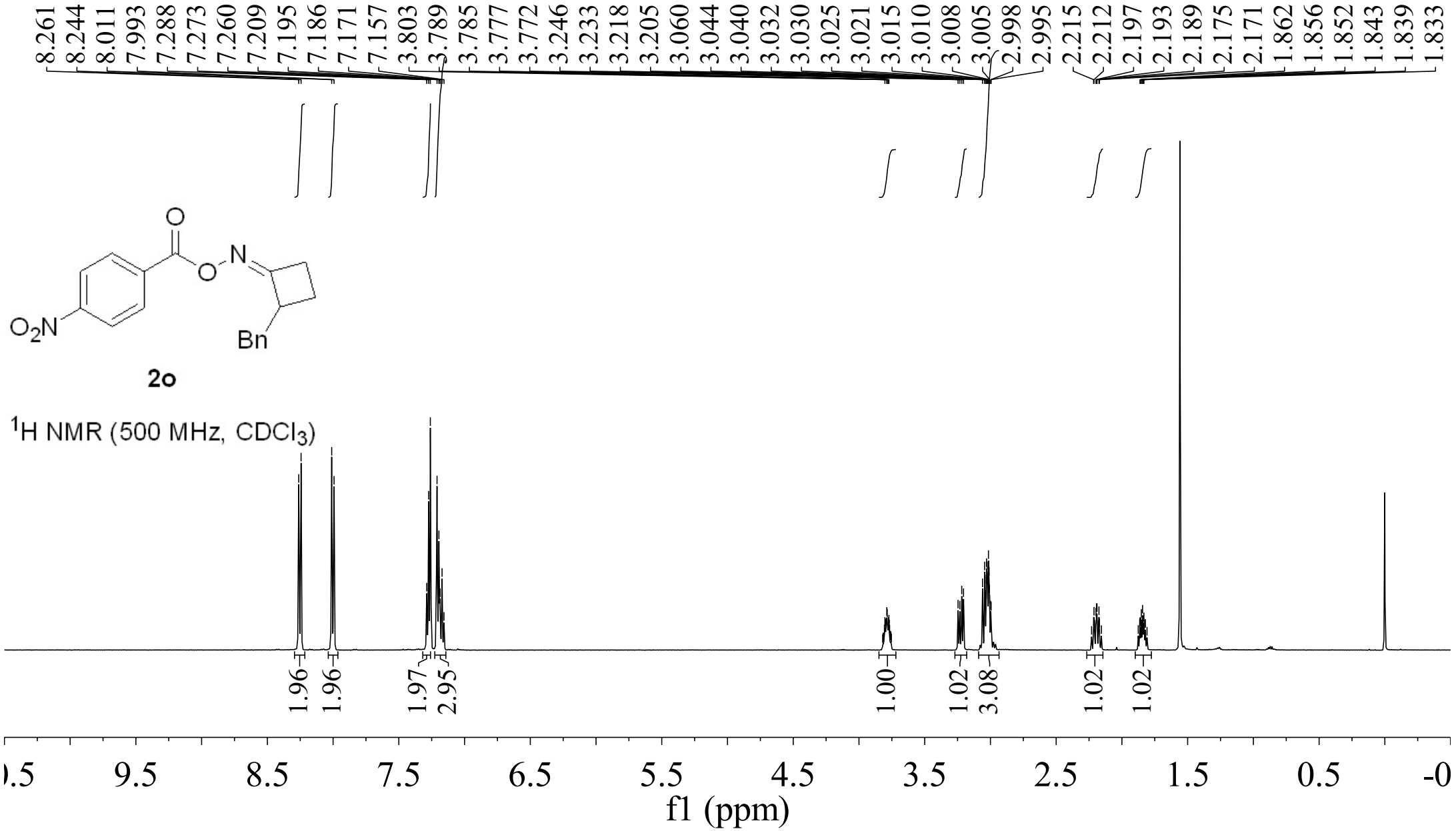
2m

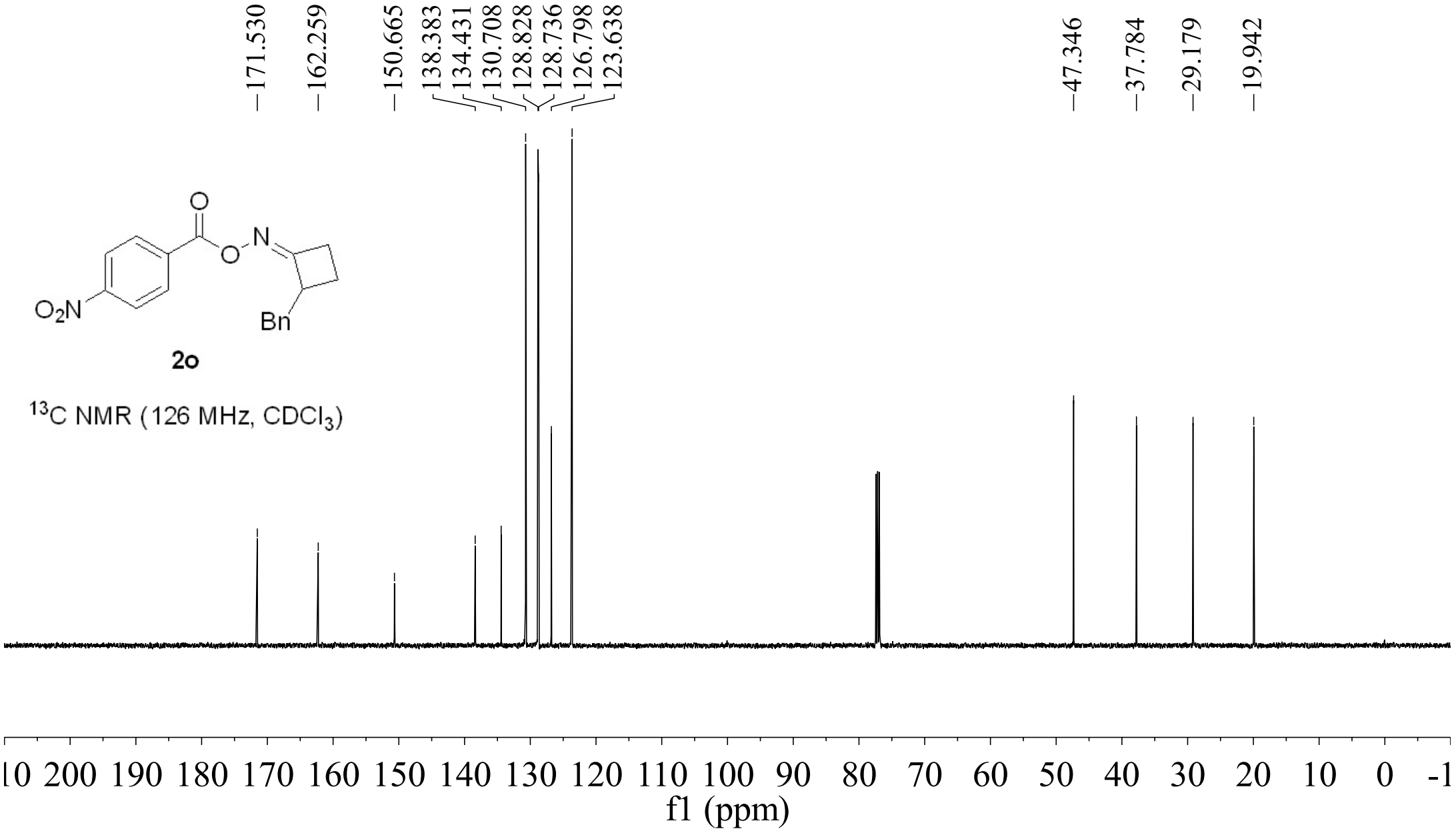
^{19}F NMR (376 MHz, $CDCl_3$)

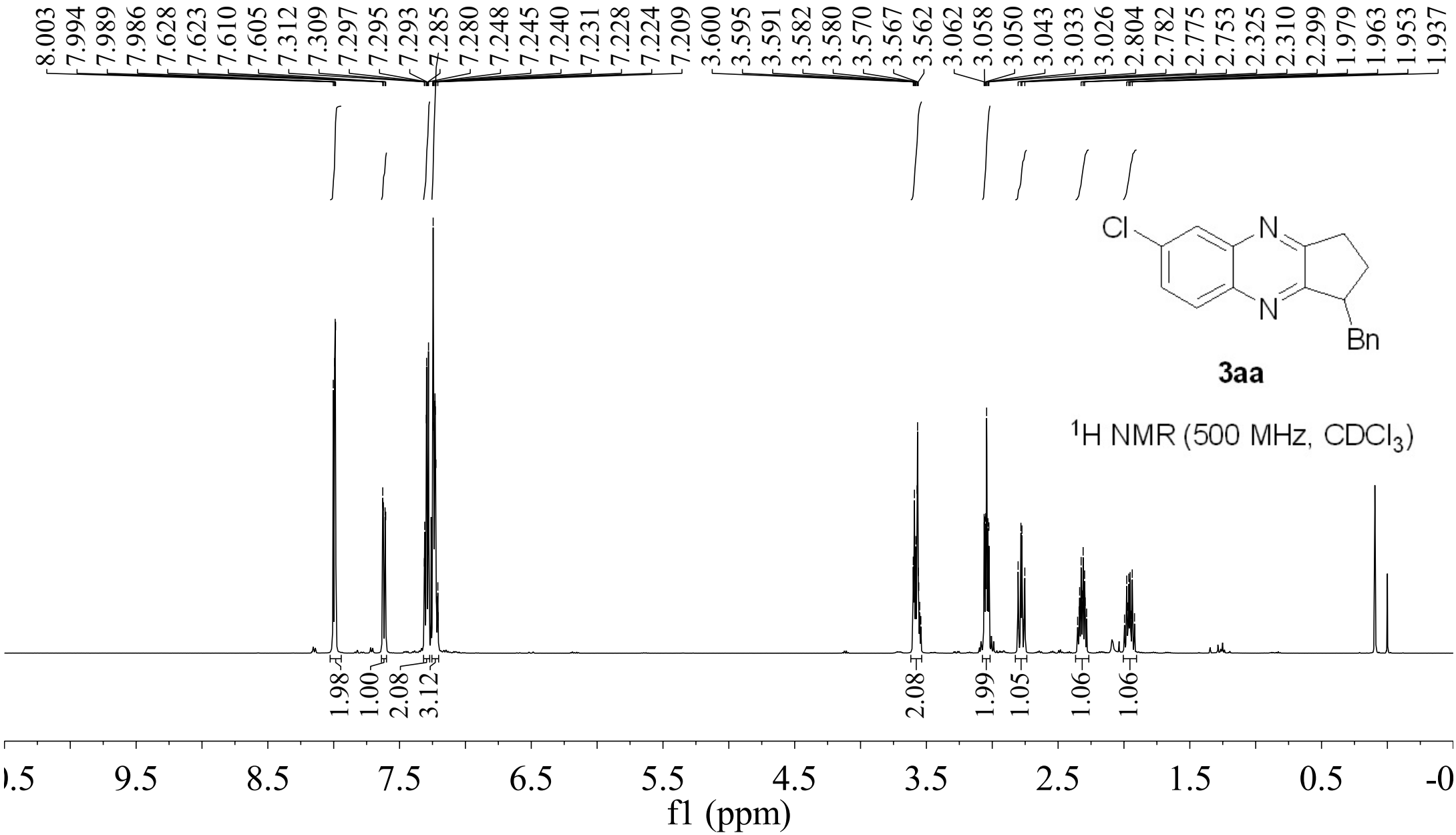


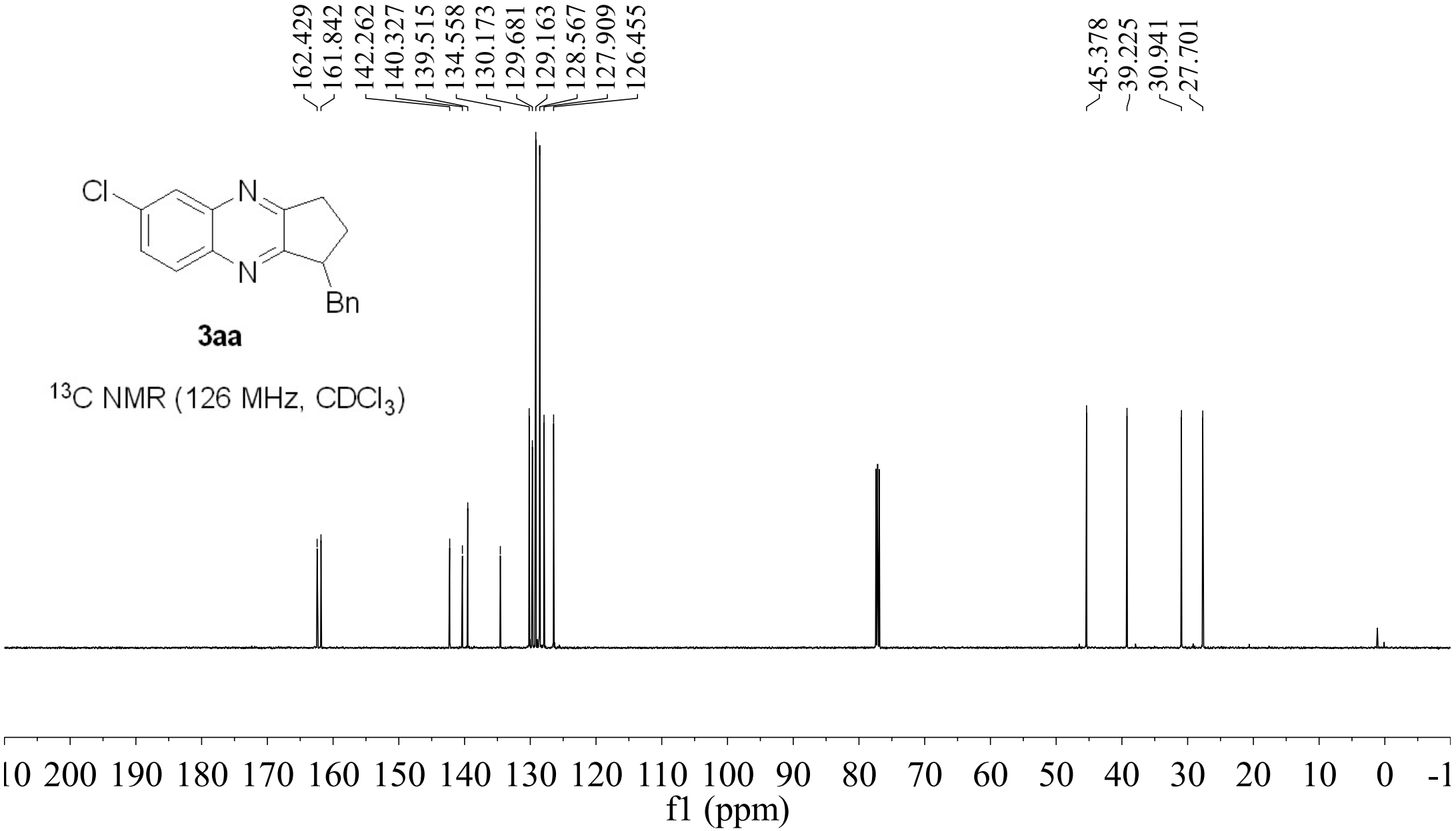

7.982
7.967
7.592
7.577
7.562
7.460
7.444
7.429
7.305
7.289
7.275
7.216
7.201
3.786
3.782
3.768
3.329
3.318
3.301
3.290
3.045
3.026
3.017
2.998
2.975
2.969
2.963
2.960
2.956
2.953
2.950
2.944
2.941
2.935
2.930
2.147
2.133
2.129
2.124
2.110
1.837
1.834
1.822
1.818
1.814
1.806
1.804
O
N
O
Bn
2n
1H NMR (500 MHz, CDCl3)
1.96
1.05
2.12
2.06
3.05
1.00
1.05
1.09
1.97
1.08
1.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

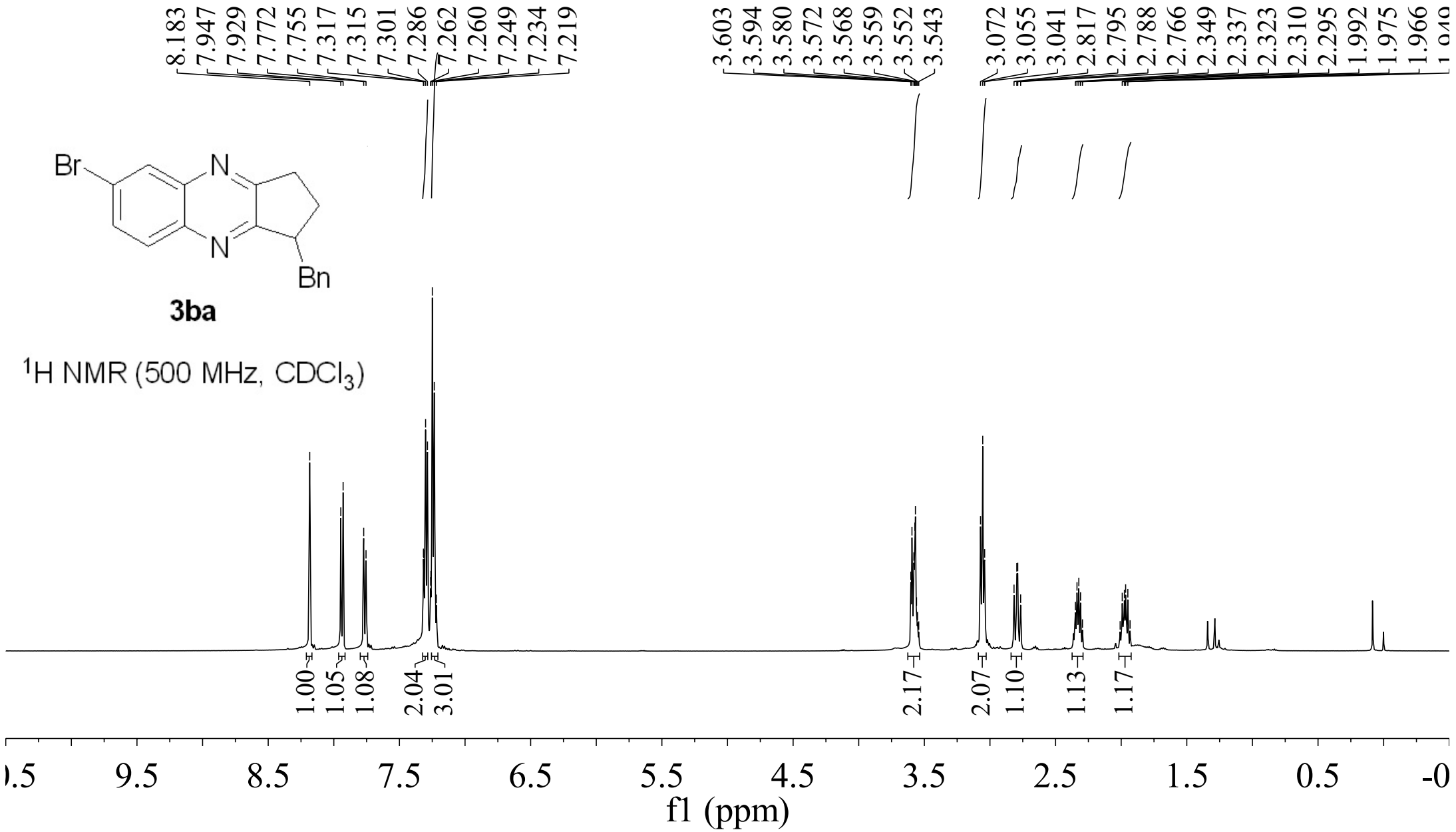

170.372
163.777
138.092
132.989
129.297
128.729
128.594
128.360
128.311
126.368
46.714
36.992
28.638
19.291
O
O
N
Bn
2n
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

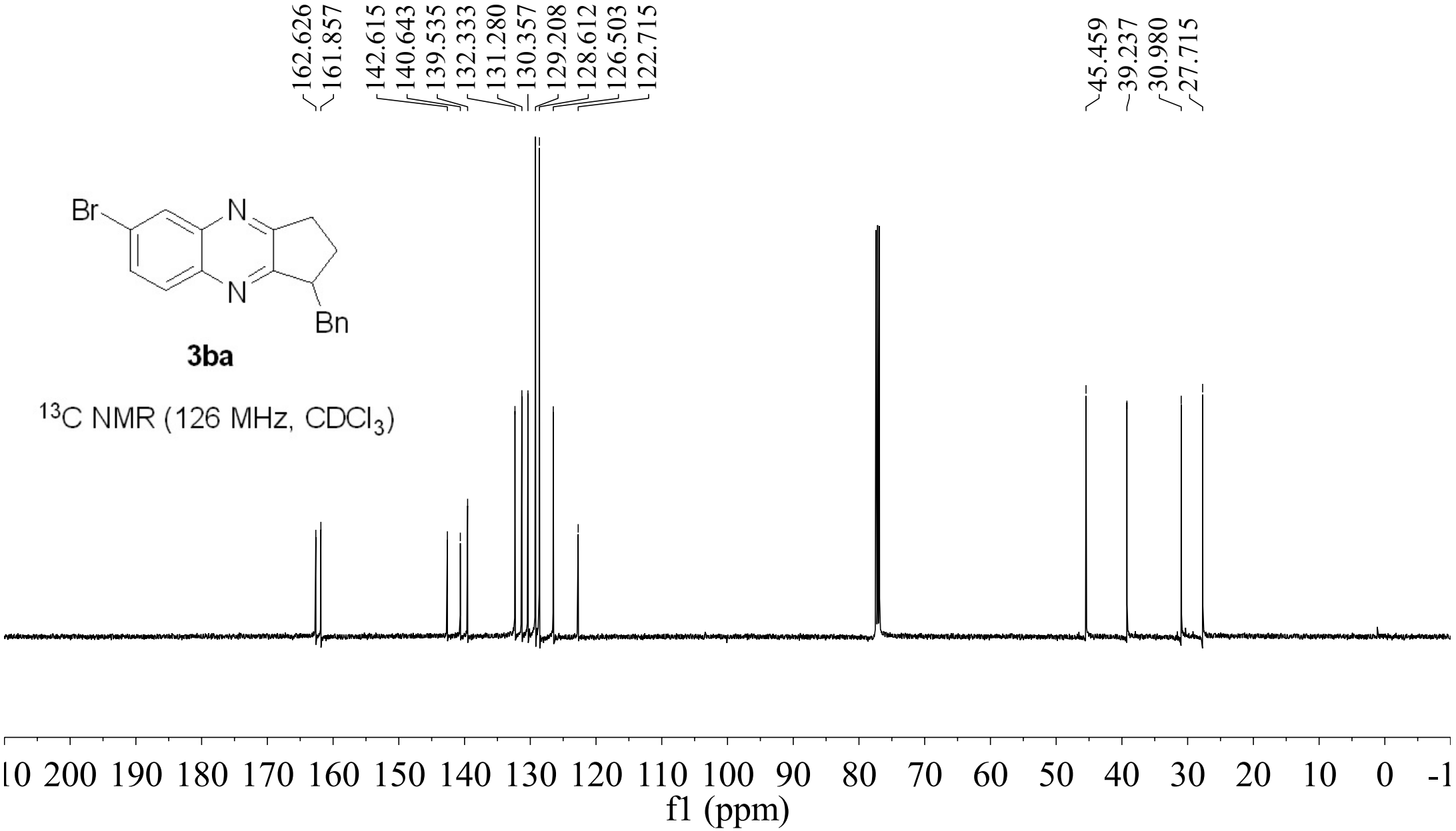

8.261
8.244
8.011
7.993
7.288
7.273
7.260
7.209
7.195
7.186
7.171
7.157
3.803
3.789
3.785
3.777
3.772
3.246
3.233
3.218
3.205
3.060
3.044
3.040
3.032
3.030
3.025
3.021
3.015
3.010
3.008
3.005
2.998
2.995
2.215
2.212
2.197
2.193
2.189
2.175
2.171
1.862
1.856
1.852
1.843
1.839
1.833
O
O
N
O2N
Bn
2o
1H NMR (500 MHz, CDCl3)
1.96
1.96
1.97
2.95
1.00
1.02
3.08
1.02
1.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

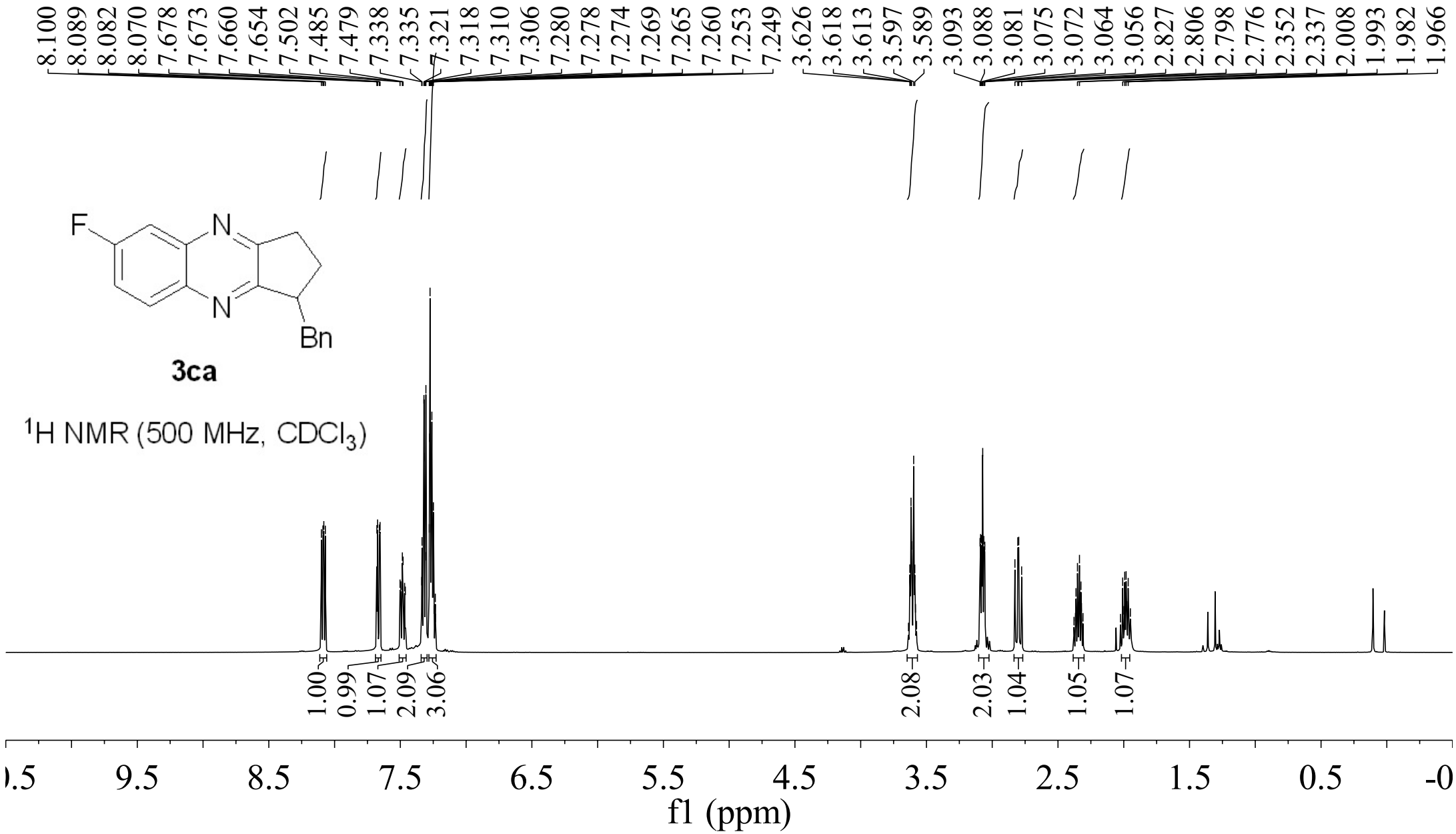

171.530
162.259
150.665
138.383
134.431
130.708
128.828
128.736
126.798
123.638
47.346
37.784
29.179
19.942
O
N
O
O2N
Bn
2o
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

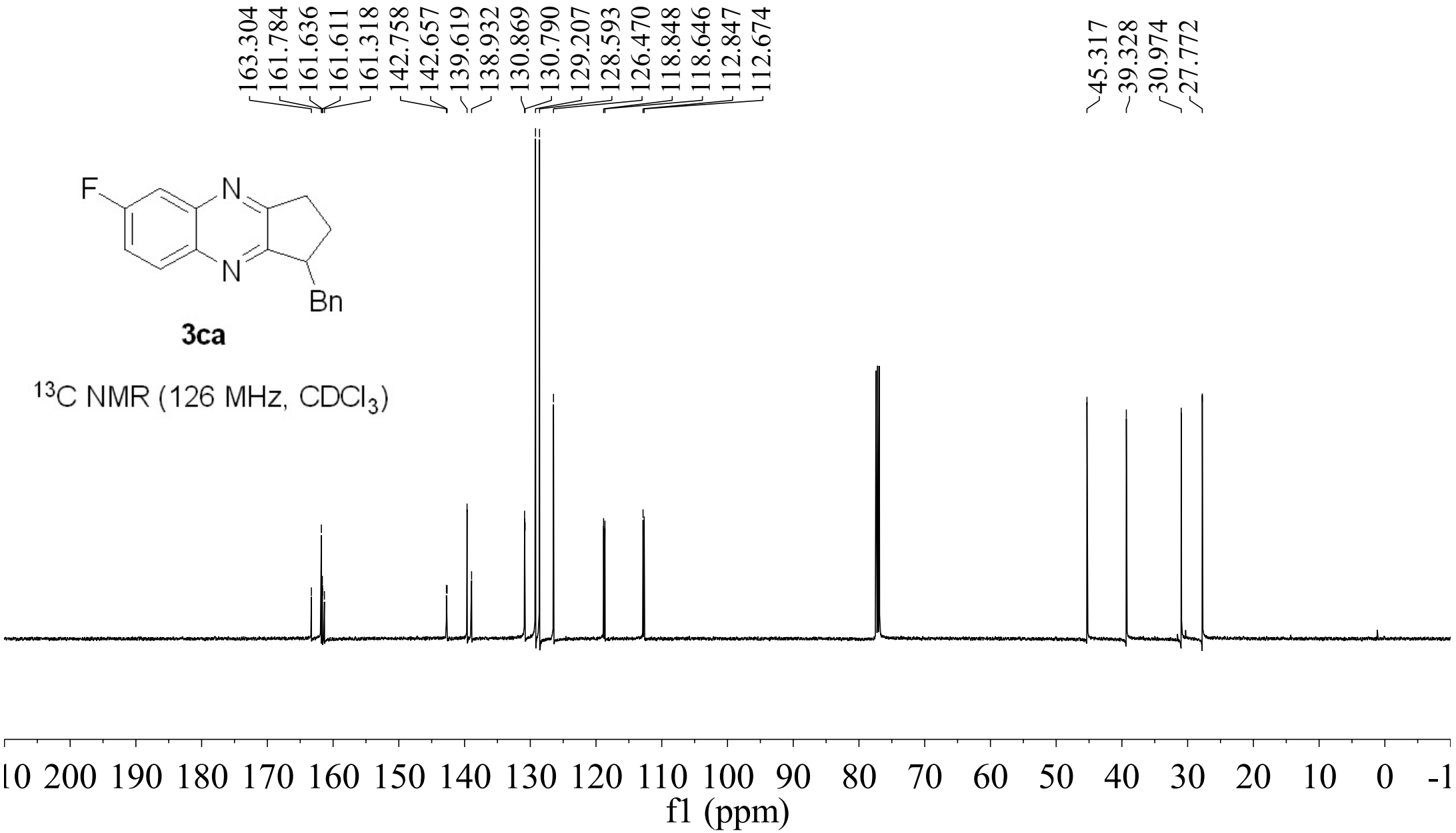

8.003
7.994
7.989
7.986
7.628
7.623
7.610
7.605
7.312
7.309
7.297
7.295
7.293
7.285
7.280
7.248
7.245
7.240
7.231
7.228
7.224
7.209
3.600
3.595
3.591
3.582
3.580
3.570
3.567
3.562
3.062
3.058
3.050
3.043
3.033
3.026
2.804
2.782
2.775
2.753
2.325
2.310
2.299
1.979
1.963
1.953
1.937
Cl
N
N
Bn
3aa
1H NMR (500 MHz, CDCl3)
1.98
1.00
2.08
3.12
2.08
1.99
1.05
1.06
1.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


162.429
161.842
142.262
140.327
139.515
134.558
130.173
129.681
129.163
128.567
127.909
126.455
45.378
39.225
30.941
27.701
Cl
N
N
Bn
3aa
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)


8.183
7.947
7.929
7.772
7.755
7.317
7.315
7.301
7.286
7.262
7.260
7.249
7.234
7.219
3.603
3.594
3.580
3.572
3.568
3.559
3.552
3.543
3.072
3.055
3.041
2.817
2.795
2.788
2.766
2.349
2.337
2.323
2.310
2.295
1.992
1.975
1.966
Br
N
N
Bn
3ba
1H NMR (500 MHz, CDCl3)
1.00
1.05
1.08
2.04
3.01
2.17
2.07
1.10
1.13
1.17
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

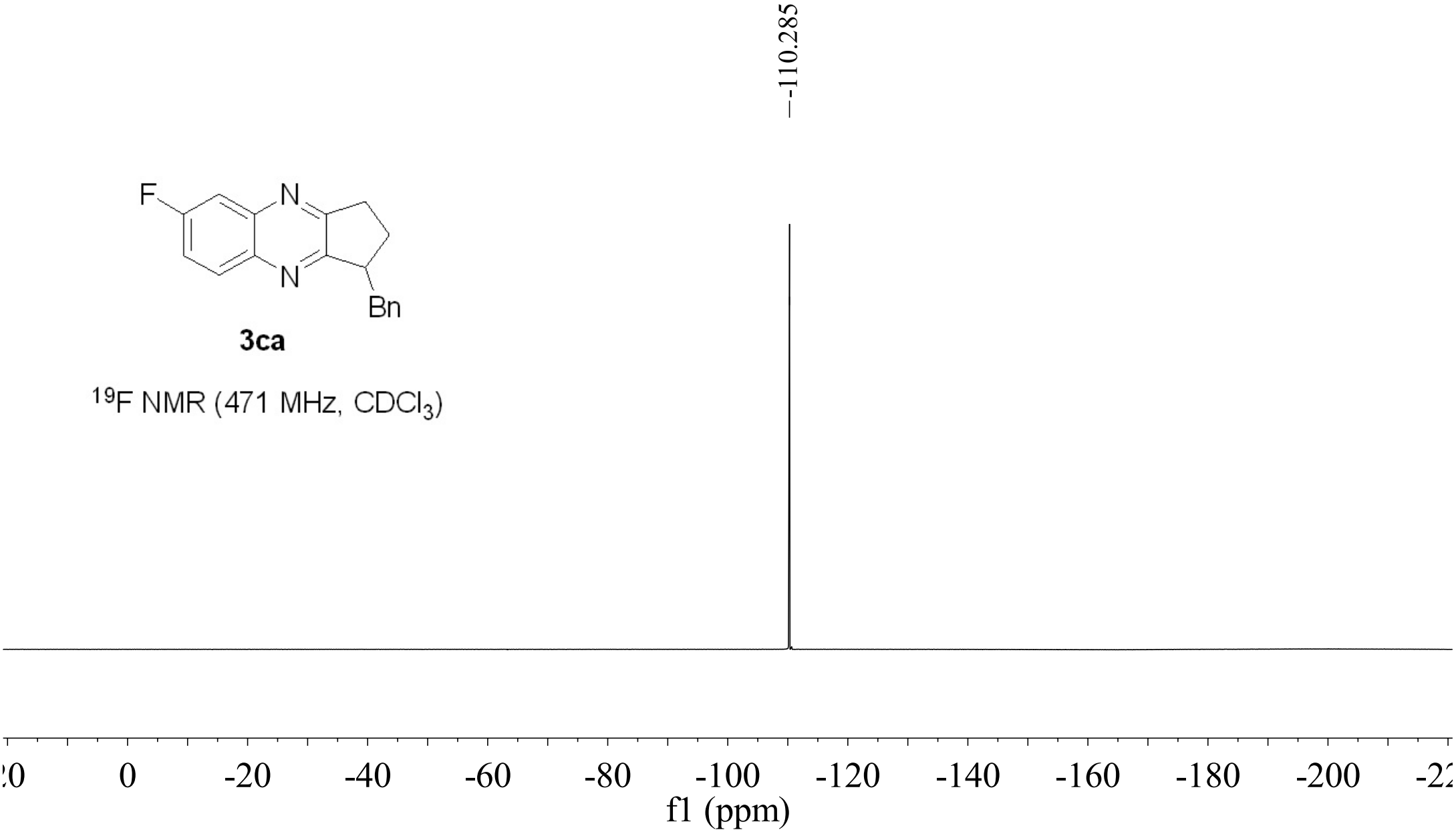

162.626
161.857
142.615
140.643
139.535
132.333
131.280
130.357
129.208
128.612
126.503
122.715
45.459
39.237
30.980
27.715
Br
N
N
Bn
3ba
13C NMR (126 MHz, CDCl3)
f1 (ppm)

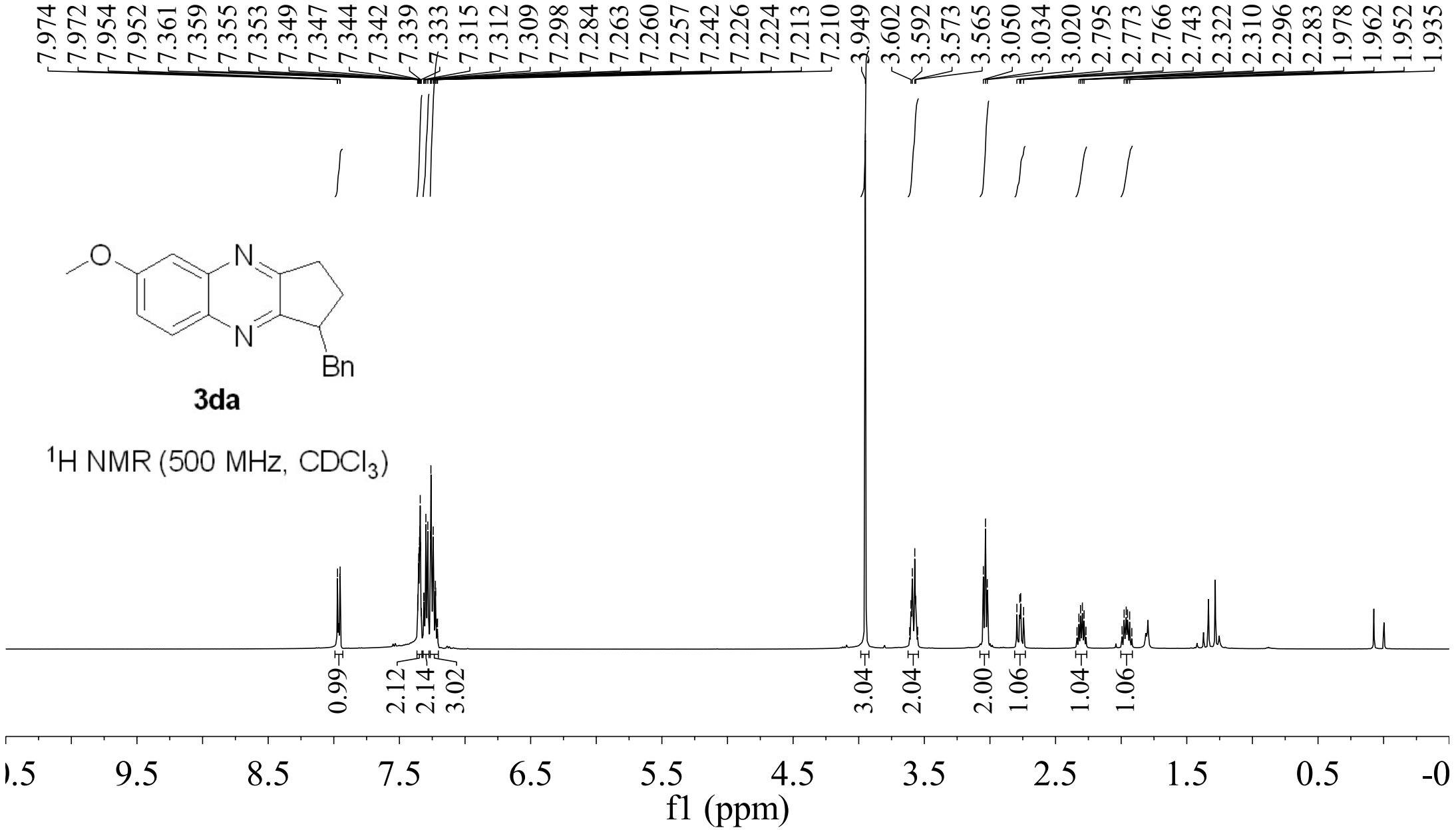

8.100
8.089
8.082
8.070
7.678
7.673
7.660
7.654
7.502
7.485
7.479
7.338
7.335
7.321
7.318
7.310
7.306
7.280
7.278
7.274
7.269
7.265
7.260
7.253
7.249
3.626
3.618
3.613
3.597
3.589
3.093
3.088
3.081
3.075
3.072
3.064
3.056
2.827
2.806
2.798
2.776
2.352
2.337
2.008
1.993
1.982
1.966
F
N
N
Bn
3ca
1H NMR (500 MHz, CDCl3)
1.00
0.99
1.07
2.09
3.06
2.08
2.03
1.04
1.05
1.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

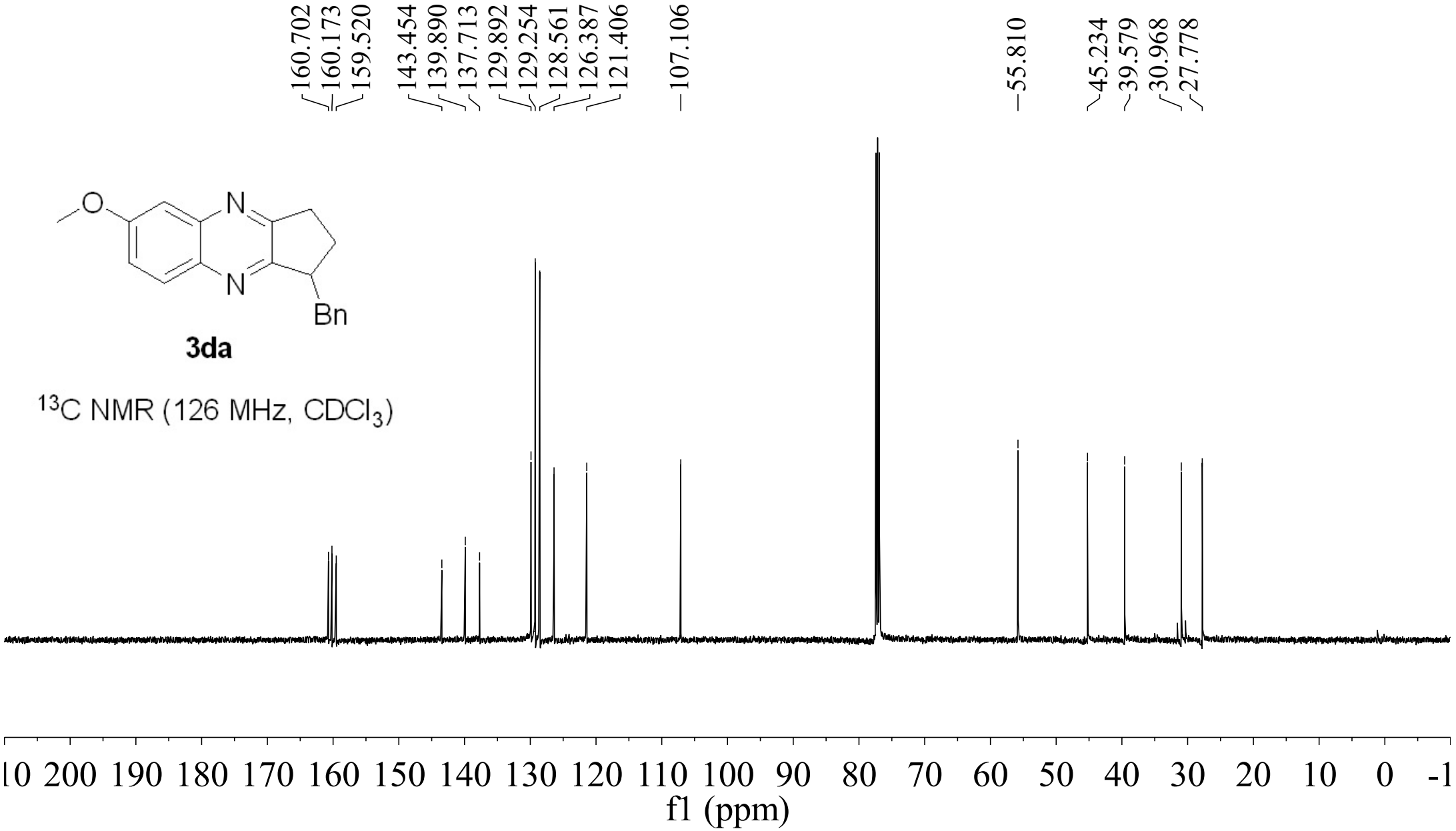

163.304
161.784
161.636
161.611
161.318
142.758
142.657
139.619
138.932
130.869
130.790
129.207
128.593
126.470
118.848
118.646
112.847
112.674
45.317
39.328
30.974
27.772
F
N
N
Bn
3ca
13C NMR (126 MHz, CDCl3)
f1 (ppm)

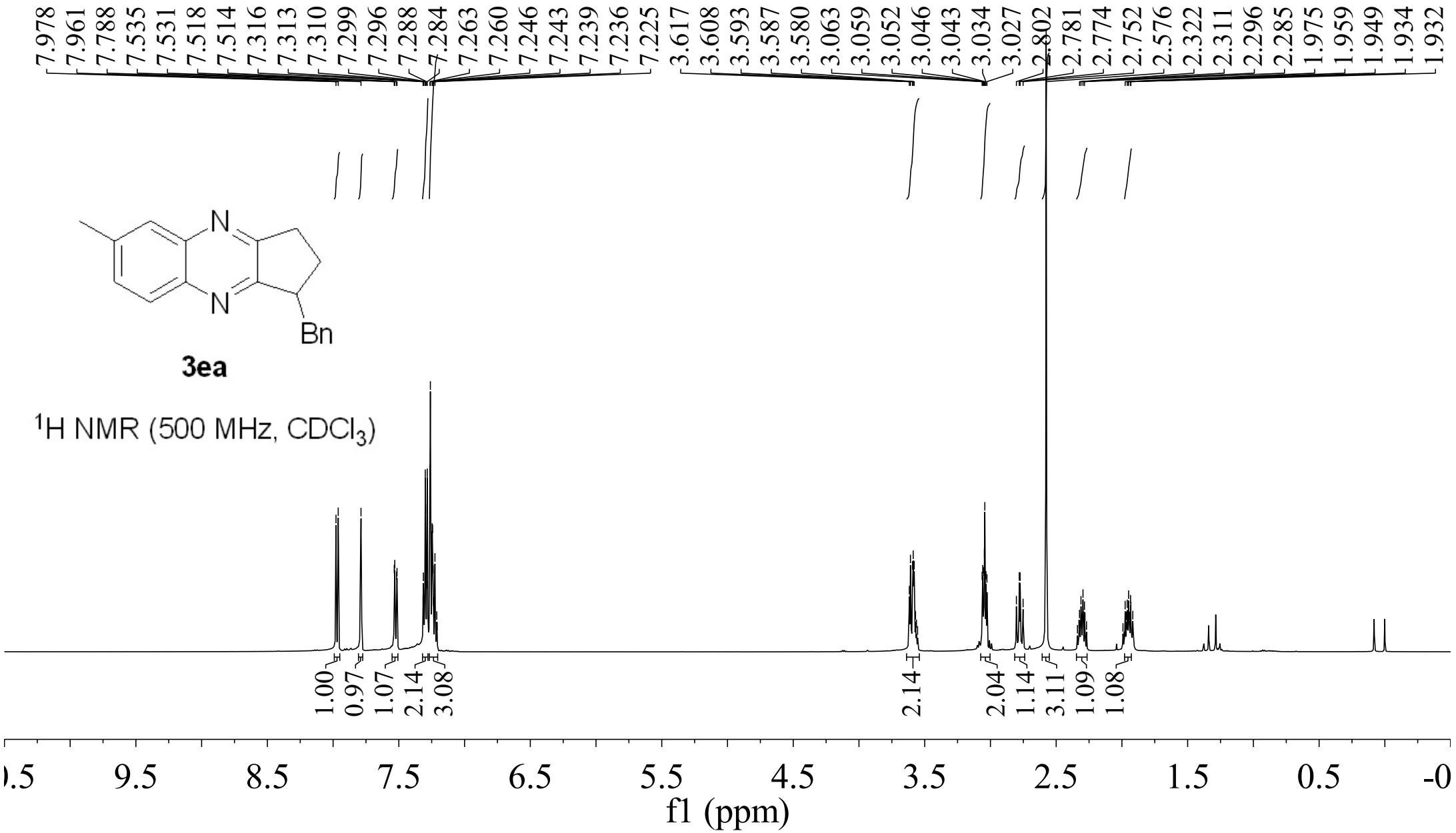
3ca

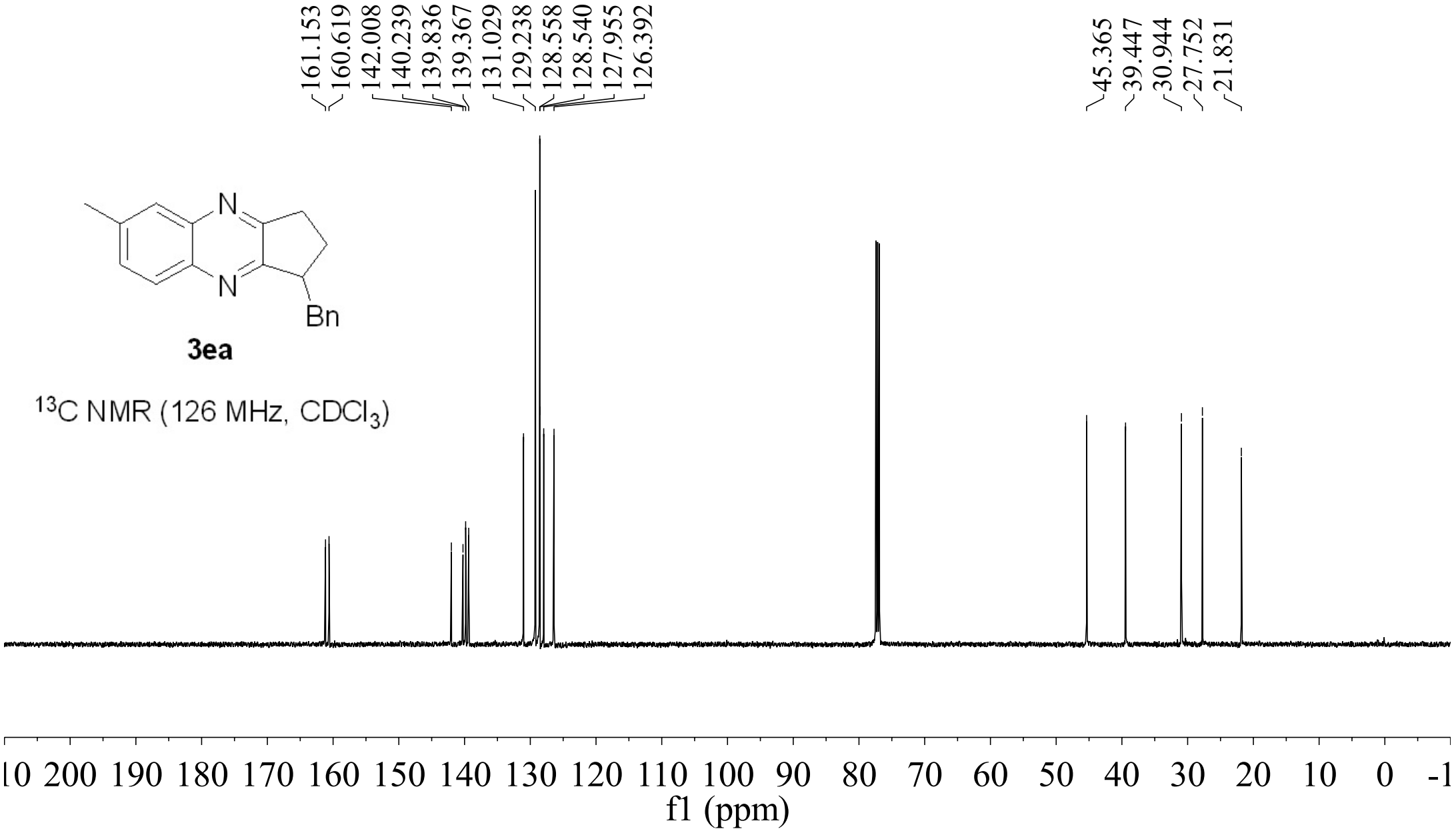
^{19}F NMR (471 MHz, $CDCl_3$)

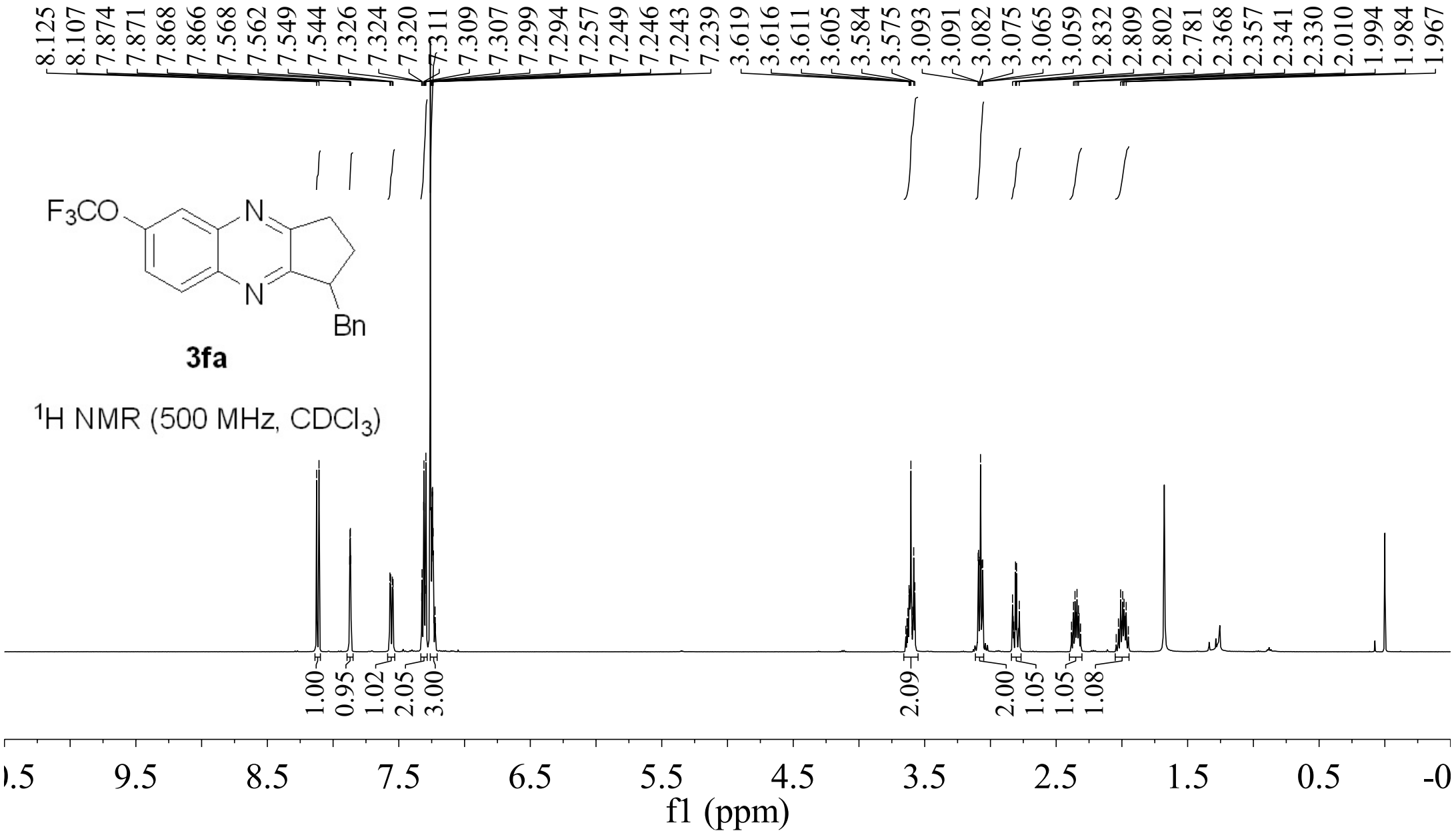


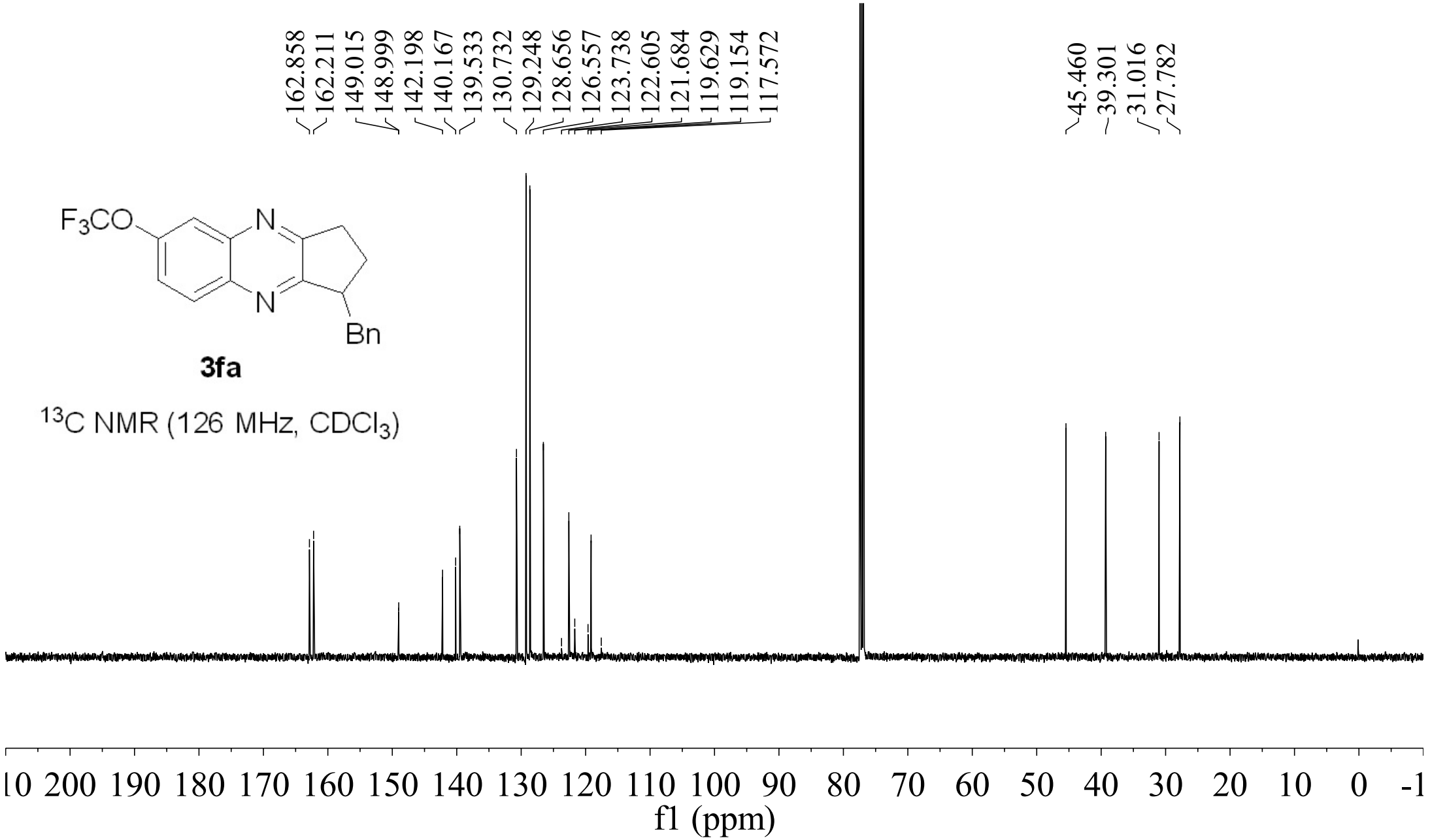

7.974
7.972
7.954
7.952
7.361
7.359
7.355
7.353
7.349
7.347
7.344
7.342
7.339
7.333
7.315
7.312
7.309
7.298
7.284
7.263
7.260
7.257
7.242
7.226
7.224
7.213
7.210
3.949
3.602
3.592
3.573
3.565
3.050
3.034
3.020
2.795
2.773
2.766
2.743
2.322
2.310
2.296
2.283
1.978
1.962
1.952
1.935
O
N
N
Bn
3da
1H NMR (500 MHz, CDCl3)
0.99
2.12
2.14
3.02
3.04
2.04
2.00
1.06
1.04
1.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


160.702
160.173
159.520
143.454
139.890
137.713
129.892
129.254
128.561
126.387
121.406
107.106
55.810
45.234
39.579
30.968
27.778
O
N
N
Bn
3da
^{13}C NMR (126 MHz, $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.978
7.961
7.788
7.535
7.531
7.518
7.514
7.316
7.313
7.310
7.299
7.296
7.288
7.284
7.263
7.260
7.246
7.243
7.239
7.236
7.225
3.617
3.608
3.593
3.587
3.580
3.063
3.059
3.052
3.046
3.043
3.034
3.027
2.802
2.781
2.774
2.752
2.576
2.322
2.311
2.296
2.285
1.975
1.959
1.949
1.934
1.932
N
N
Bn
3ea
1H NMR (500 MHz, CDCl3)
1.00
0.97
1.07
2.14
3.08
2.14
2.04
1.14
3.11
1.09
1.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

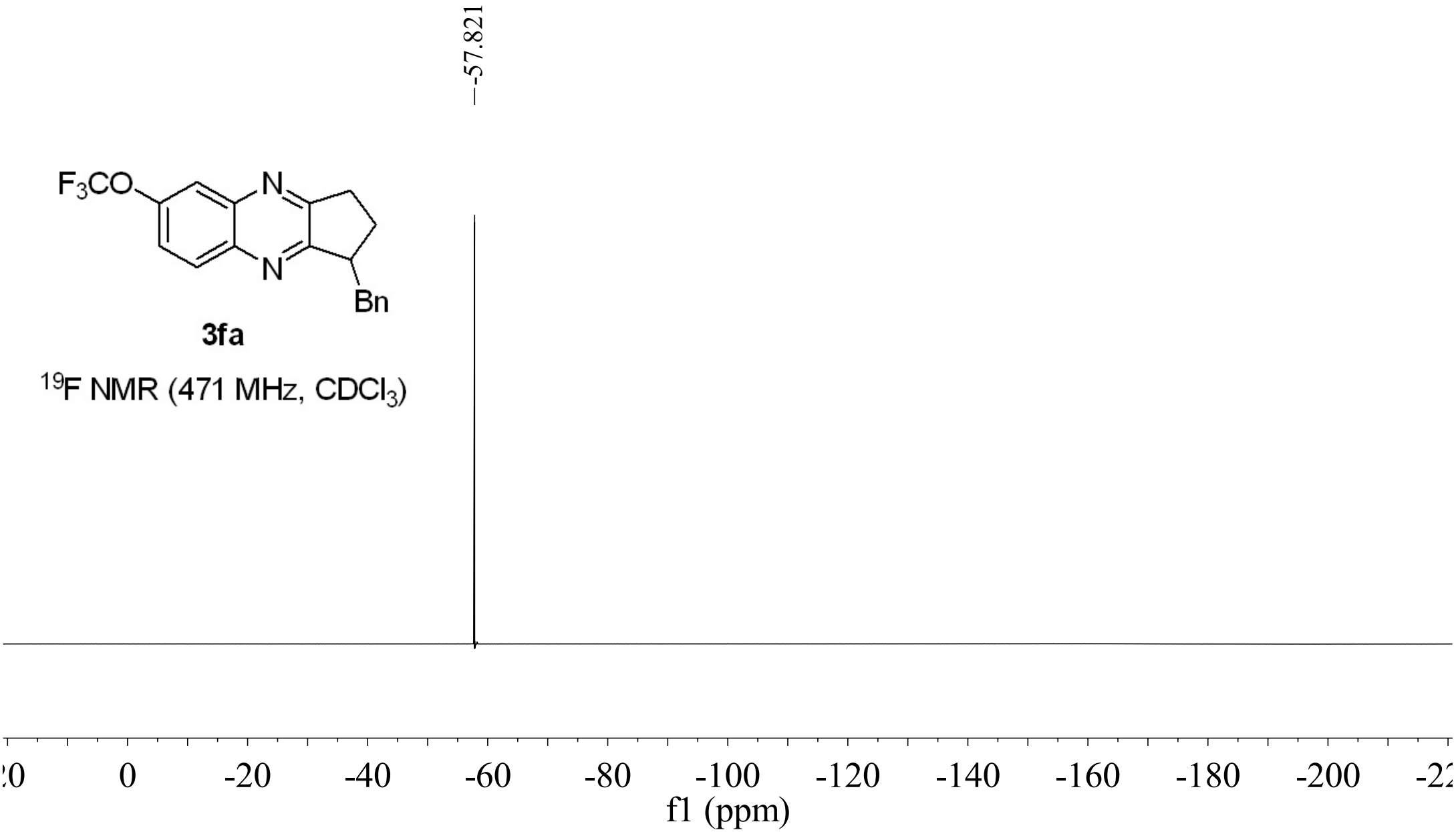

161.153
160.619
142.008
140.239
139.836
139.367
131.029
129.238
128.558
128.540
127.955
126.392
45.365
39.447
30.944
27.752
21.831
N
N
Bn
3ea
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

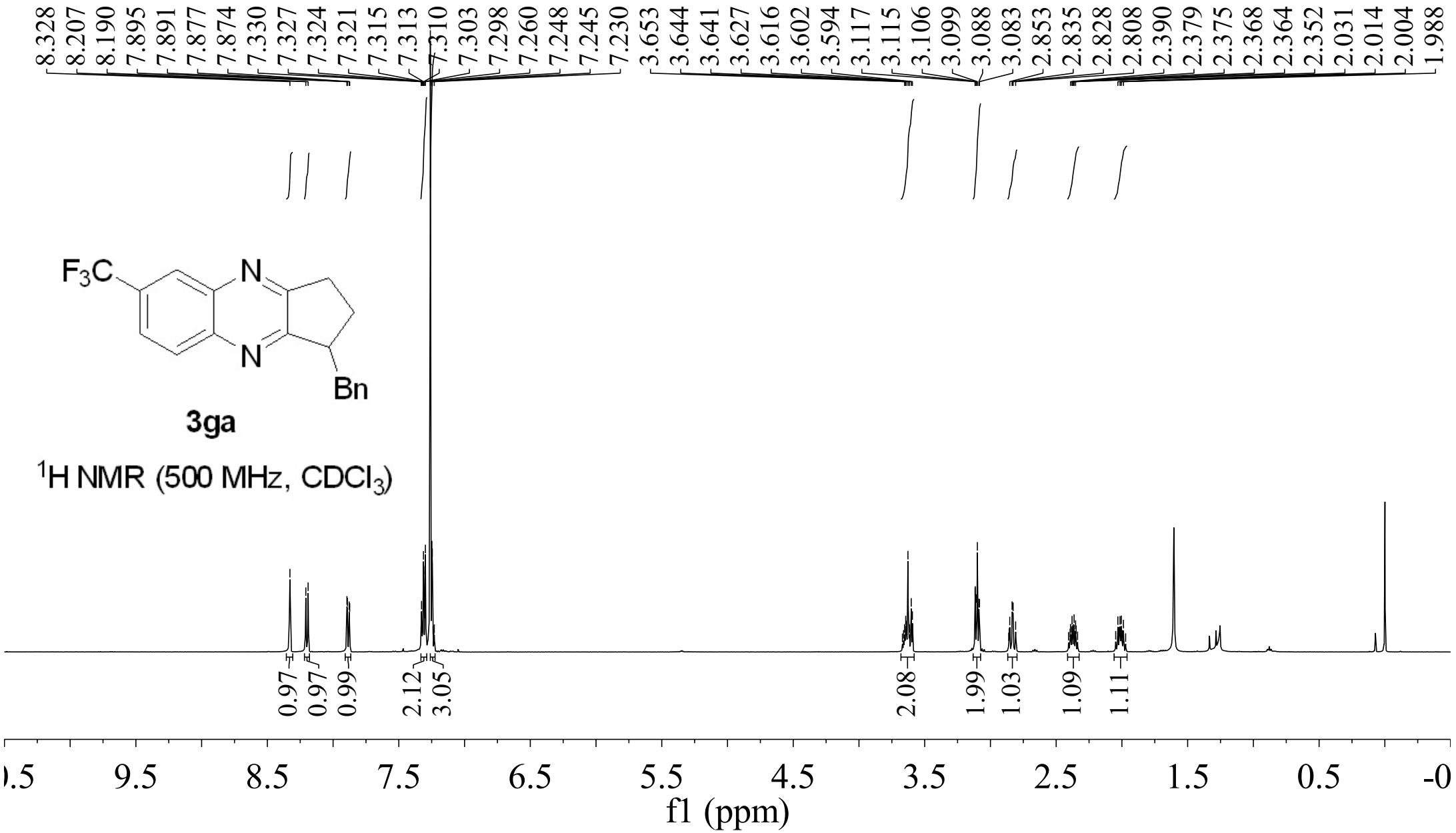

8.125
8.107
7.874
7.871
7.868
7.866
7.568
7.562
7.549
7.544
7.326
7.324
7.320
7.311
7.309
7.307
7.299
7.294
7.257
7.249
7.246
7.243
7.239
3.619
3.616
3.611
3.605
3.584
3.575
3.093
3.091
3.082
3.075
3.065
3.059
2.832
2.809
2.802
2.781
2.368
2.357
2.341
2.330
2.010
1.994
1.984
1.967
F3CO
N
N
Bn
3fa
1H NMR (500 MHz, CDCl3)
1.00
0.95
1.02
2.05
3.00
2.09
2.00
1.05
1.05
1.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

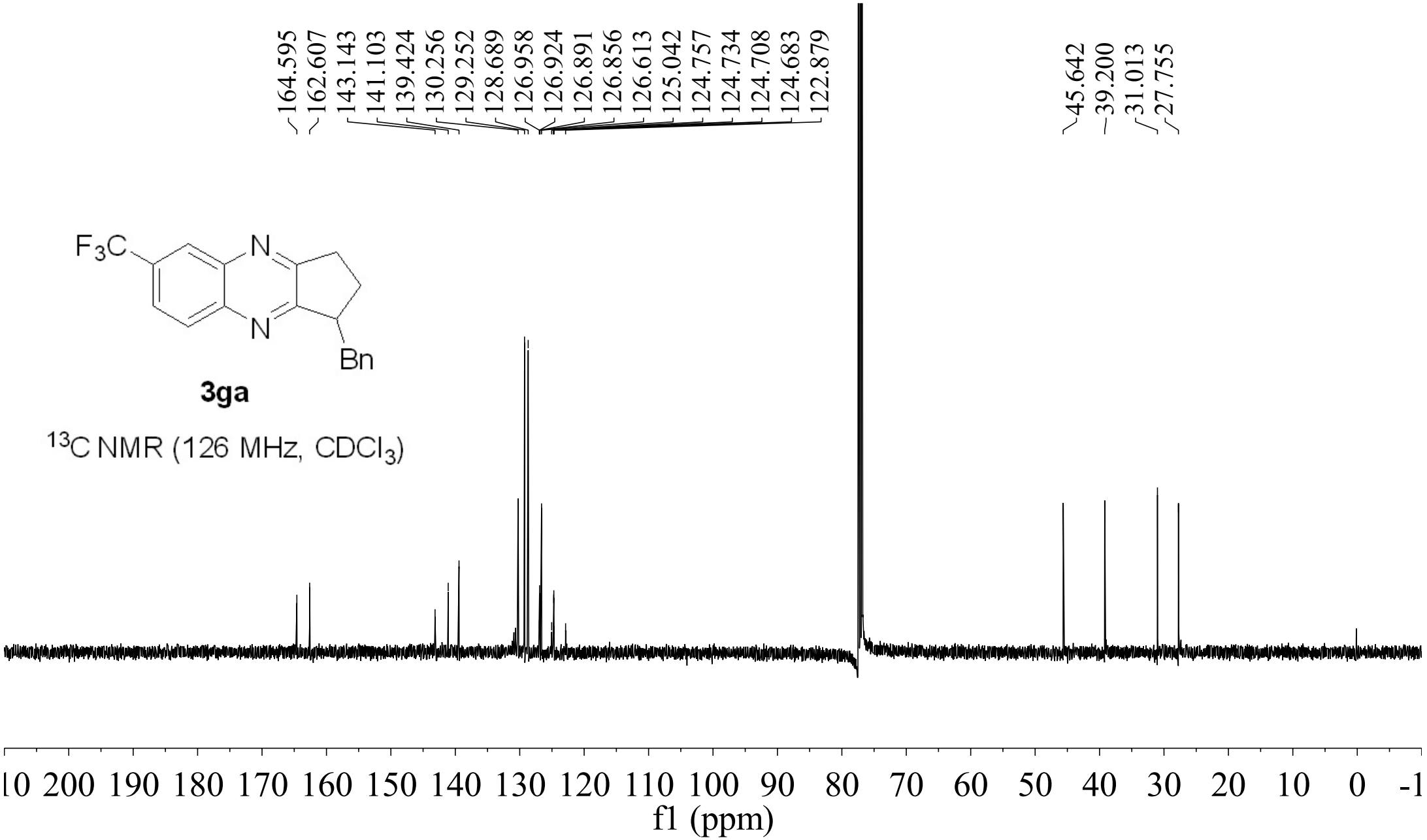

162.858
162.211
149.015
148.999
142.198
140.167
139.533
130.732
129.248
128.656
126.557
123.738
122.605
121.684
119.629
119.154
117.572
45.460
39.301
31.016
27.782
F3CO
N
N
Bn
3fa
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

3fa

^{19}F NMR (471 MHz, $CDCl_3$)

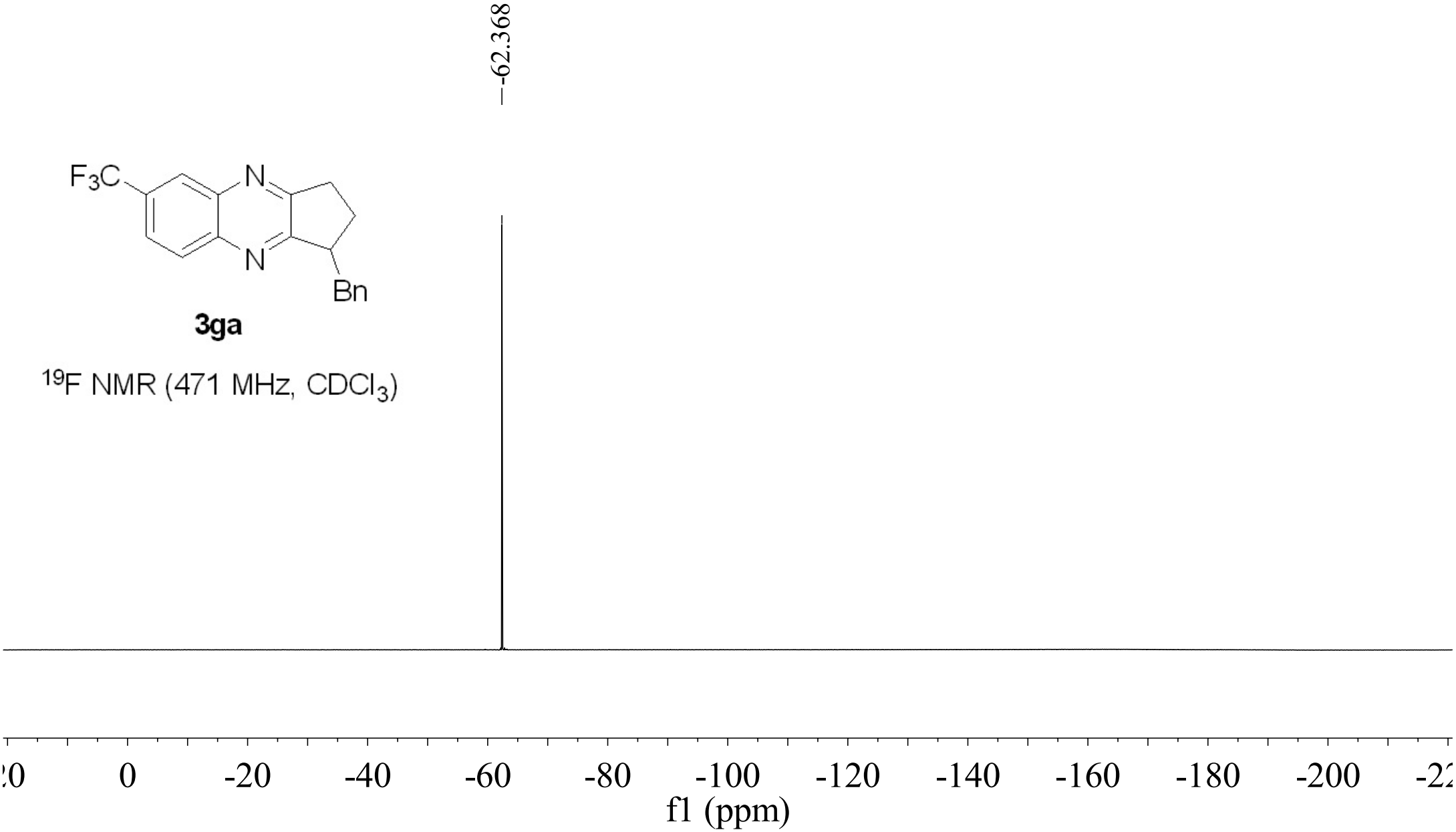


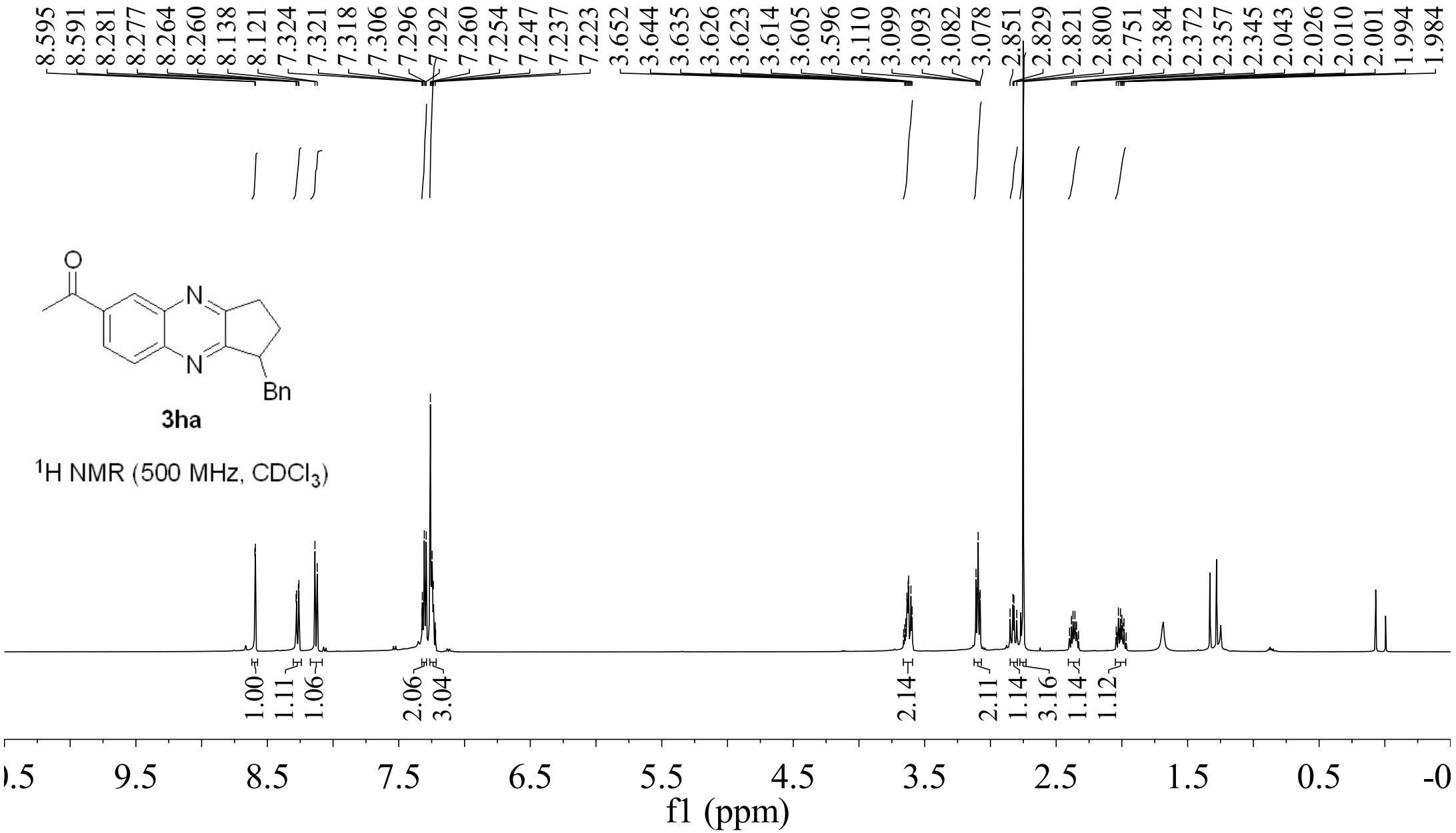

8.328
8.207
8.190
7.895
7.891
7.877
7.874
7.330
7.327
7.324
7.321
7.315
7.313
7.310
7.303
7.298
7.260
7.248
7.245
7.230
3.653
3.644
3.641
3.627
3.616
3.602
3.594
3.117
3.115
3.106
3.099
3.088
3.083
2.853
2.835
2.828
2.808
2.390
2.379
2.375
2.368
2.364
2.352
2.031
2.014
2.004
1.988
F3C
N
N
Bn
3ga
1H NMR (500 MHz, CDCl3)
0.97
0.97
0.99
2.12
3.05
2.08
1.99
1.03
1.09
1.11
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

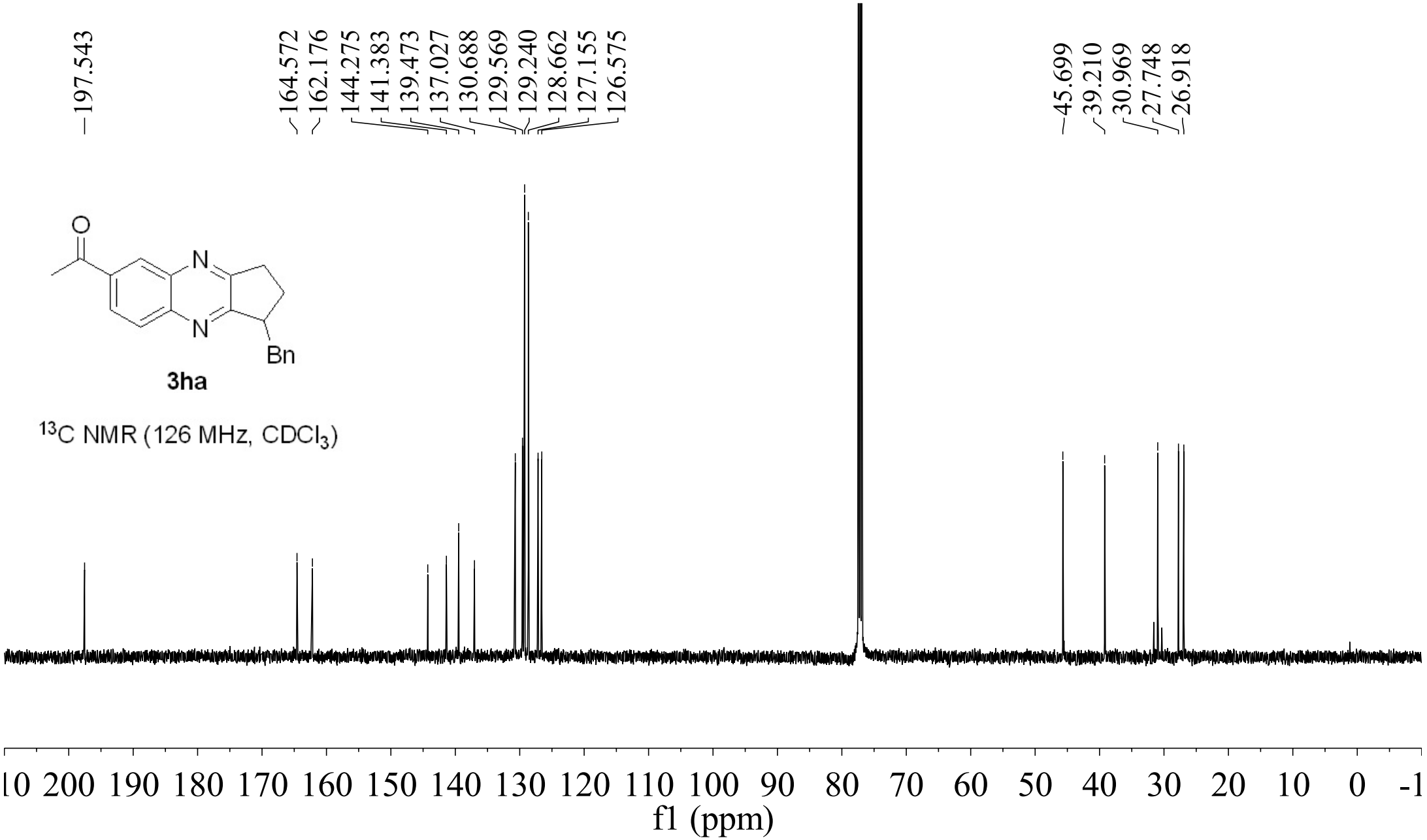

164.595
162.607
143.143
141.103
139.424
130.256
129.252
128.689
126.958
126.924
126.891
126.856
126.613
125.042
124.757
124.734
124.708
124.683
122.879
45.642
39.200
31.013
27.755
F3C
N
N
Bn
3ga
13C NMR (126 MHz, CDCl3)
f1 (ppm)

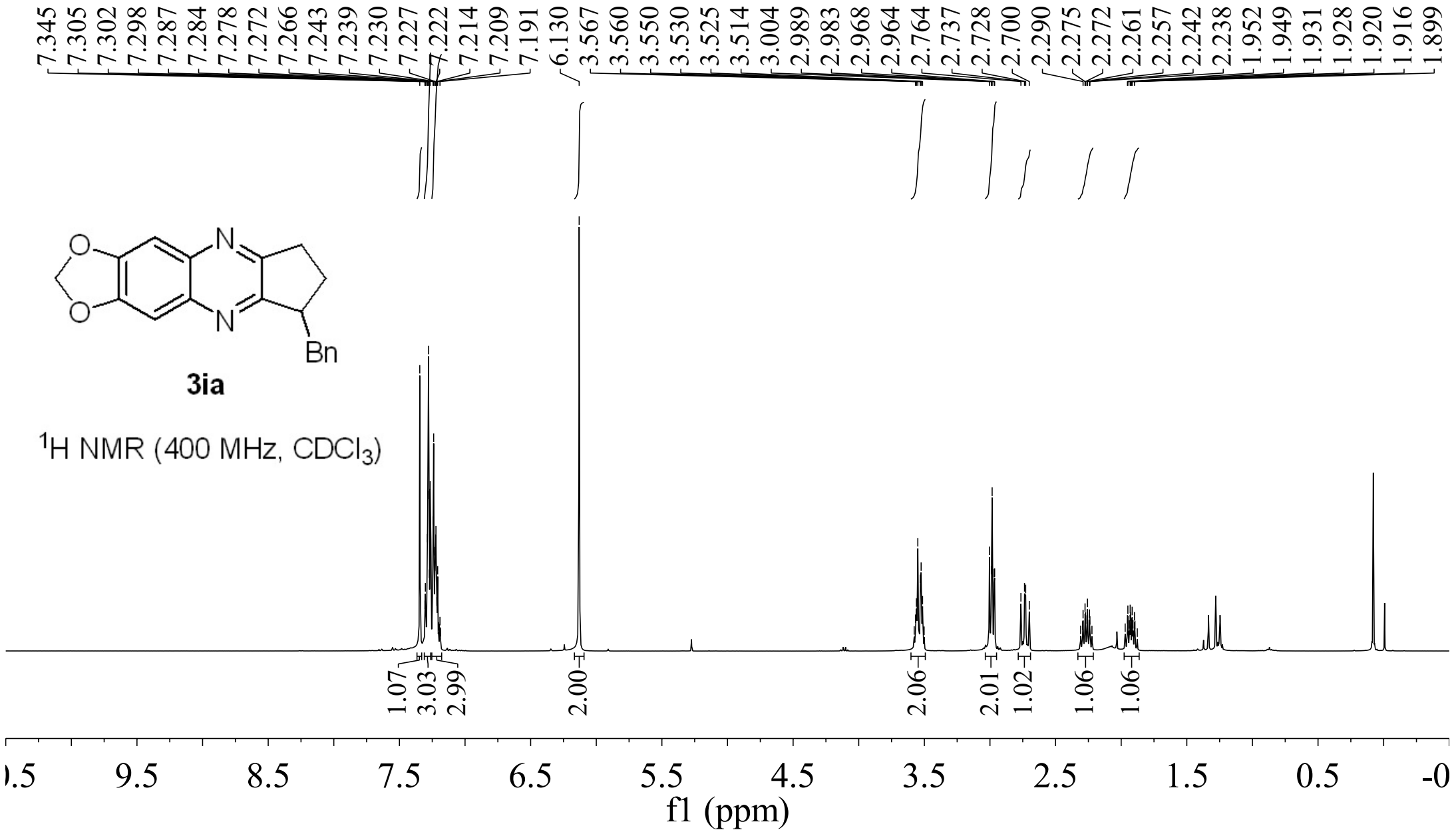
3ga

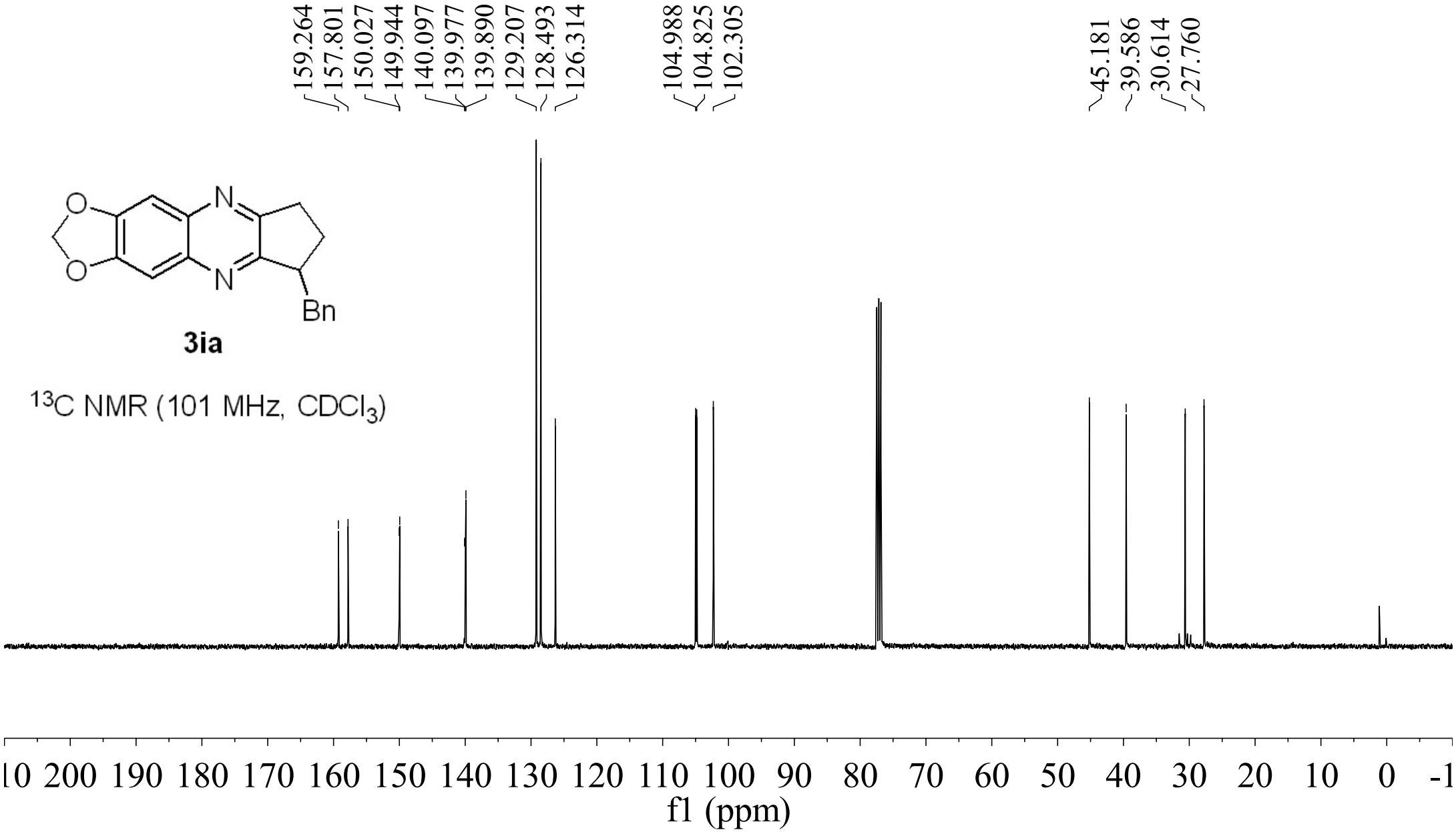
^{19}F NMR (471 MHz, $CDCl_3$)

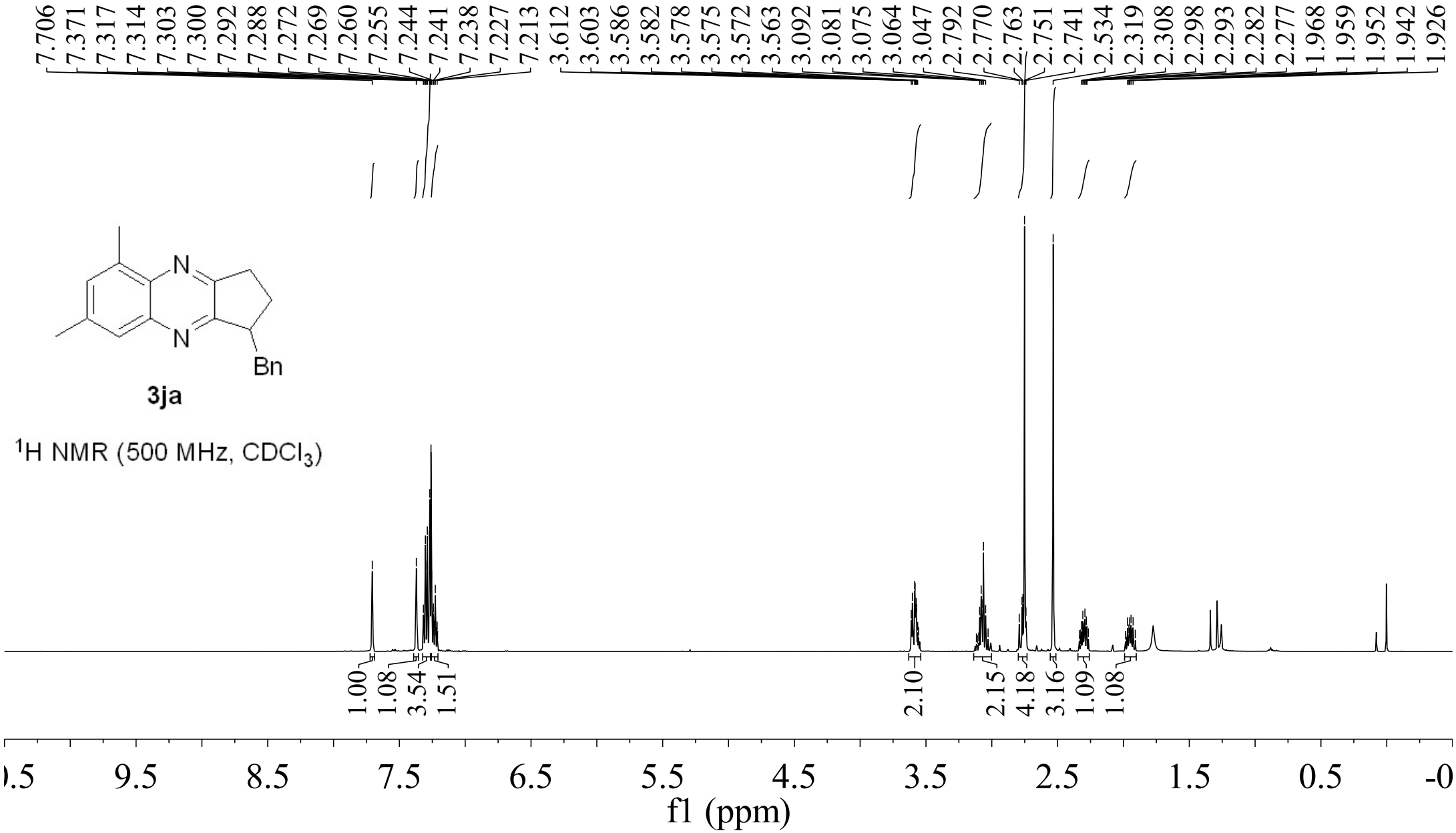


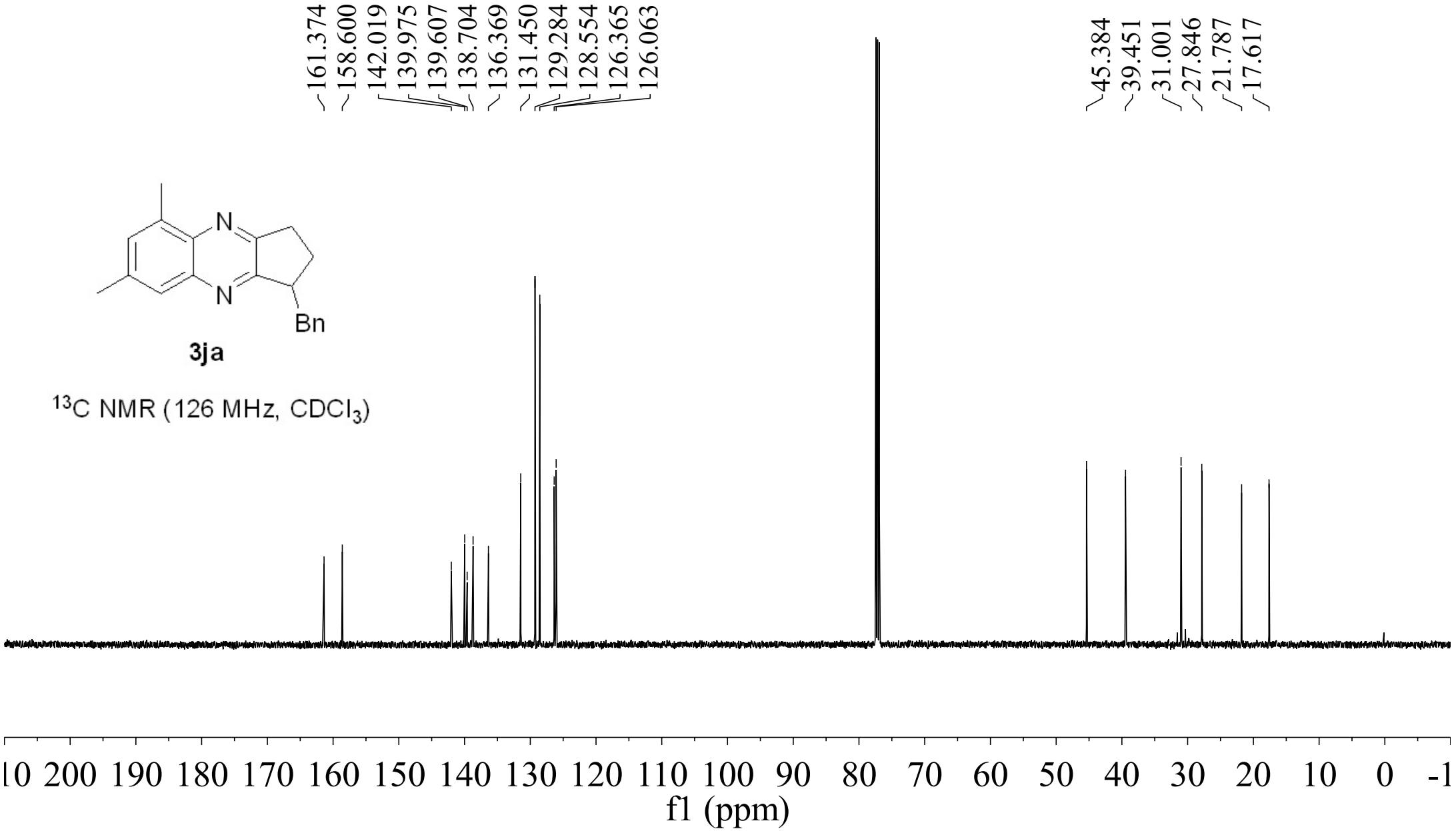

8.595
8.591
8.281
8.277
8.264
8.260
8.138
8.121
7.324
7.321
7.318
7.306
7.296
7.292
7.260
7.254
7.247
7.237
7.223
3.652
3.644
3.635
3.626
3.623
3.614
3.605
3.596
3.110
3.099
3.093
3.082
3.078
2.851
2.829
2.821
2.800
2.751
2.384
2.372
2.357
2.345
2.043
2.026
2.010
2.001
1.994
1.984
O
N
N
Bn
3ha
1H NMR (500 MHz, CDCl3)
1.00
1.11
1.06
2.06
3.04
2.14
2.11
1.14
3.16
1.14
1.12
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

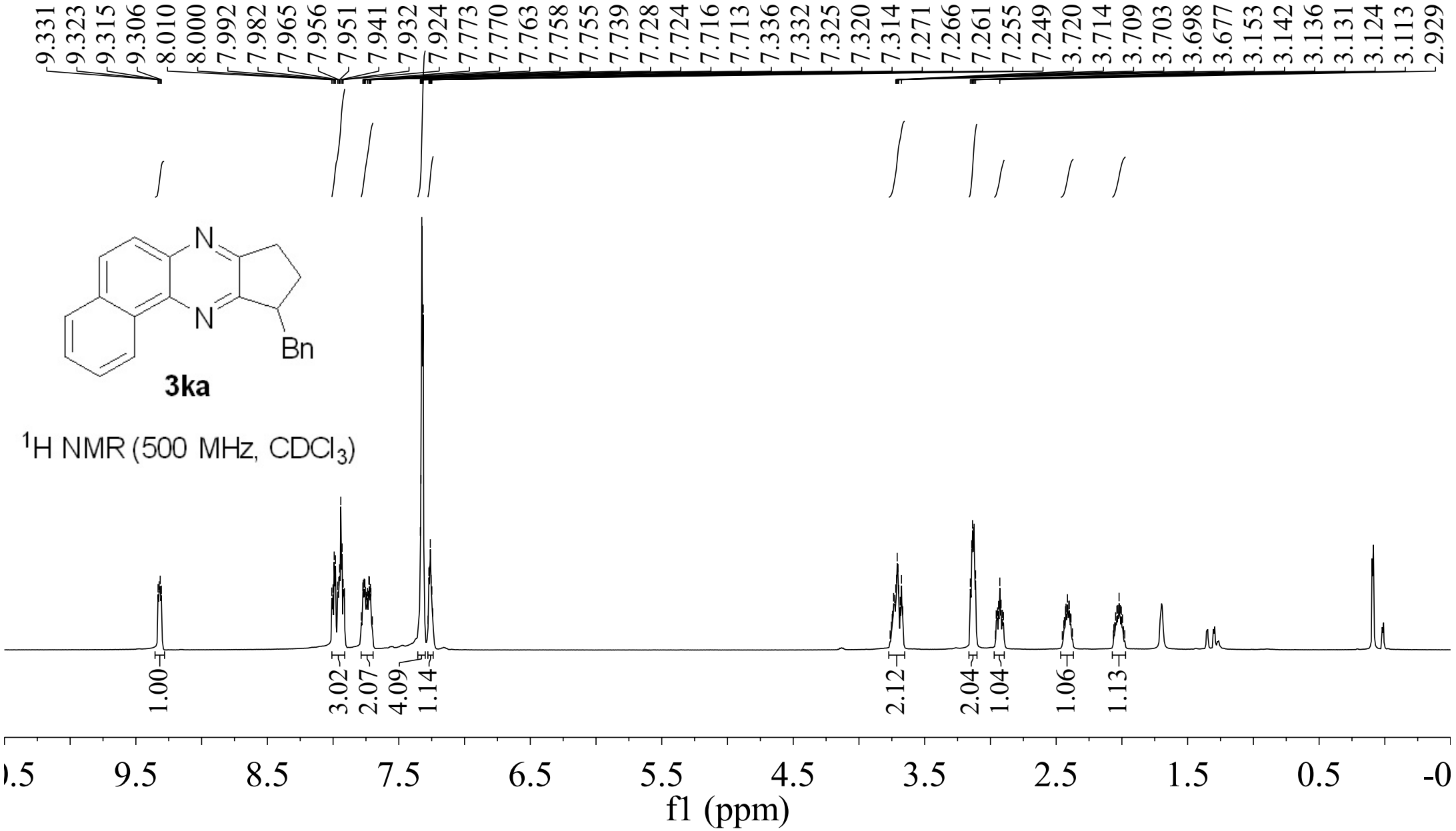

197.543
164.572
162.176
144.275
141.383
139.473
137.027
130.688
129.569
129.240
128.662
127.155
126.575
45.699
39.210
30.969
27.748
26.918
O
N
N
Bn
3ha
13C NMR (126 MHz, CDCl3)
f1 (ppm)

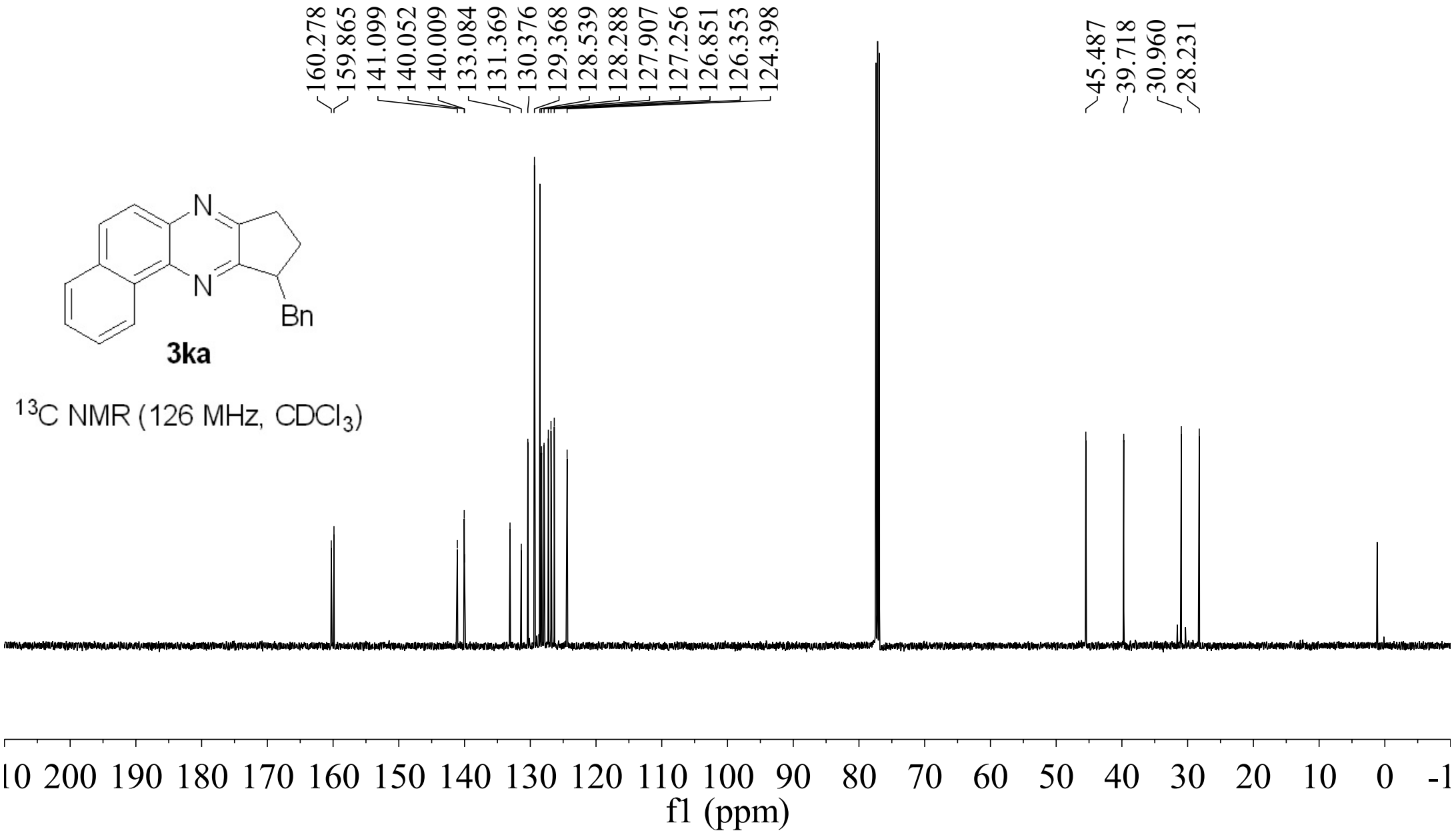

7.345
7.305
7.302
7.298
7.287
7.284
7.278
7.272
7.266
7.243
7.239
7.230
7.227
7.222
7.214
7.209
7.191
6.130
3.567
3.560
3.550
3.530
3.525
3.514
3.004
2.989
2.983
2.968
2.964
2.764
2.737
2.728
2.700
2.290
2.275
2.272
2.261
2.257
2.242
2.238
1.952
1.949
1.931
1.928
1.920
1.916
1.899
O
O
N
N
Bn
3ia
1H NMR (400 MHz, CDCl3)
1.07
3.03
2.99
2.00
2.06
2.01
1.02
1.06
1.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

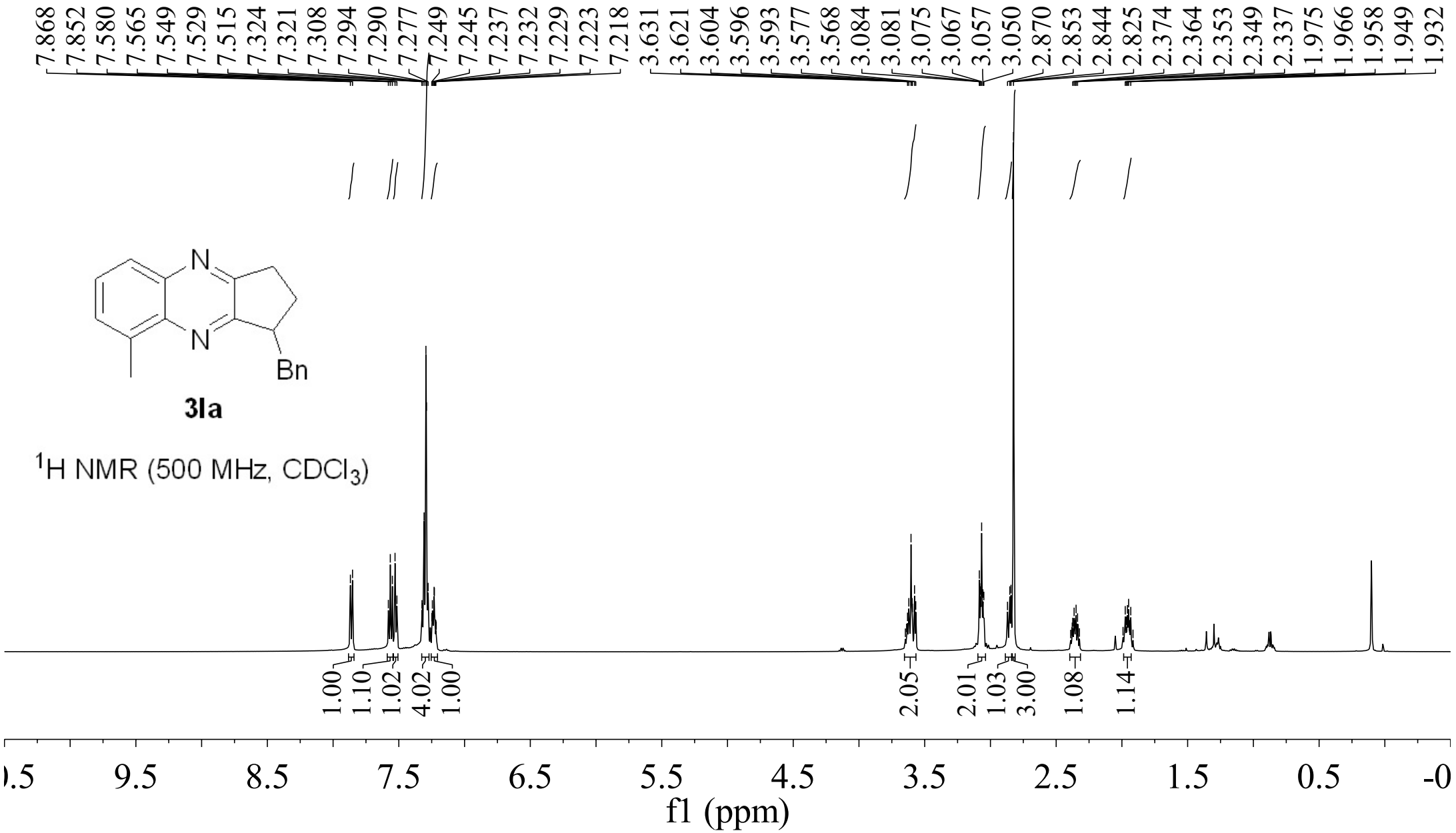

159.264
157.801
150.027
149.944
140.097
139.977
139.890
129.207
128.493
126.314
104.988
104.825
102.305
45.181
39.586
30.614
27.760
O
O
N
N
Bn
3ia
13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

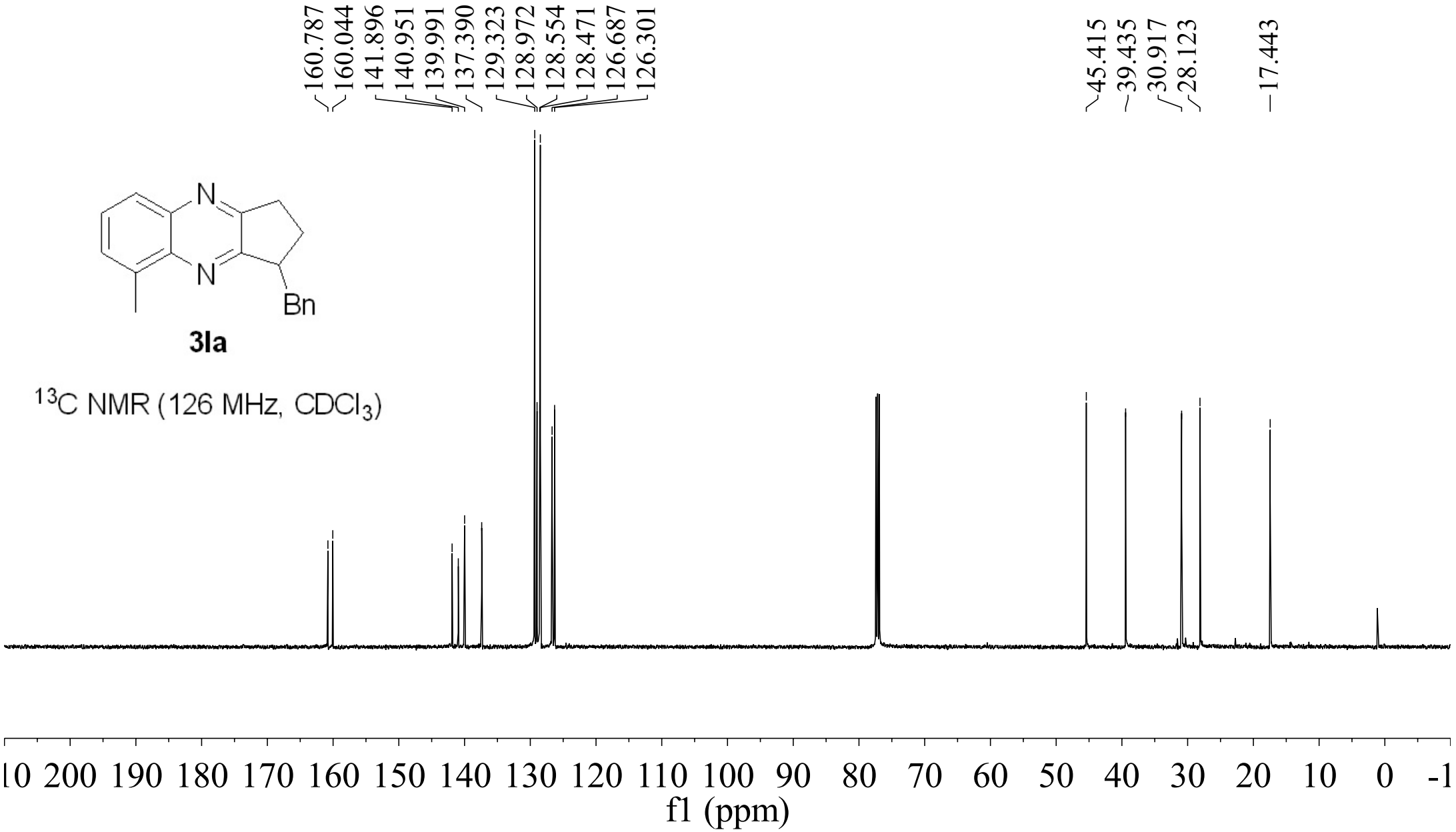

7.706
7.371
7.317
7.314
7.303
7.300
7.292
7.288
7.272
7.269
7.260
7.255
7.244
7.241
7.238
7.227
7.213
3.612
3.603
3.586
3.582
3.578
3.575
3.572
3.563
3.092
3.081
3.075
3.064
3.047
2.792
2.770
2.763
2.751
2.741
2.534
2.319
2.308
2.298
2.293
2.282
2.277
1.968
1.959
1.952
1.942
1.926
N
N
Bn
3ja
1H NMR (500 MHz, CDCl3)
1.00
1.08
3.54
1.51
2.10
2.15
4.18
3.16
1.09
1.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

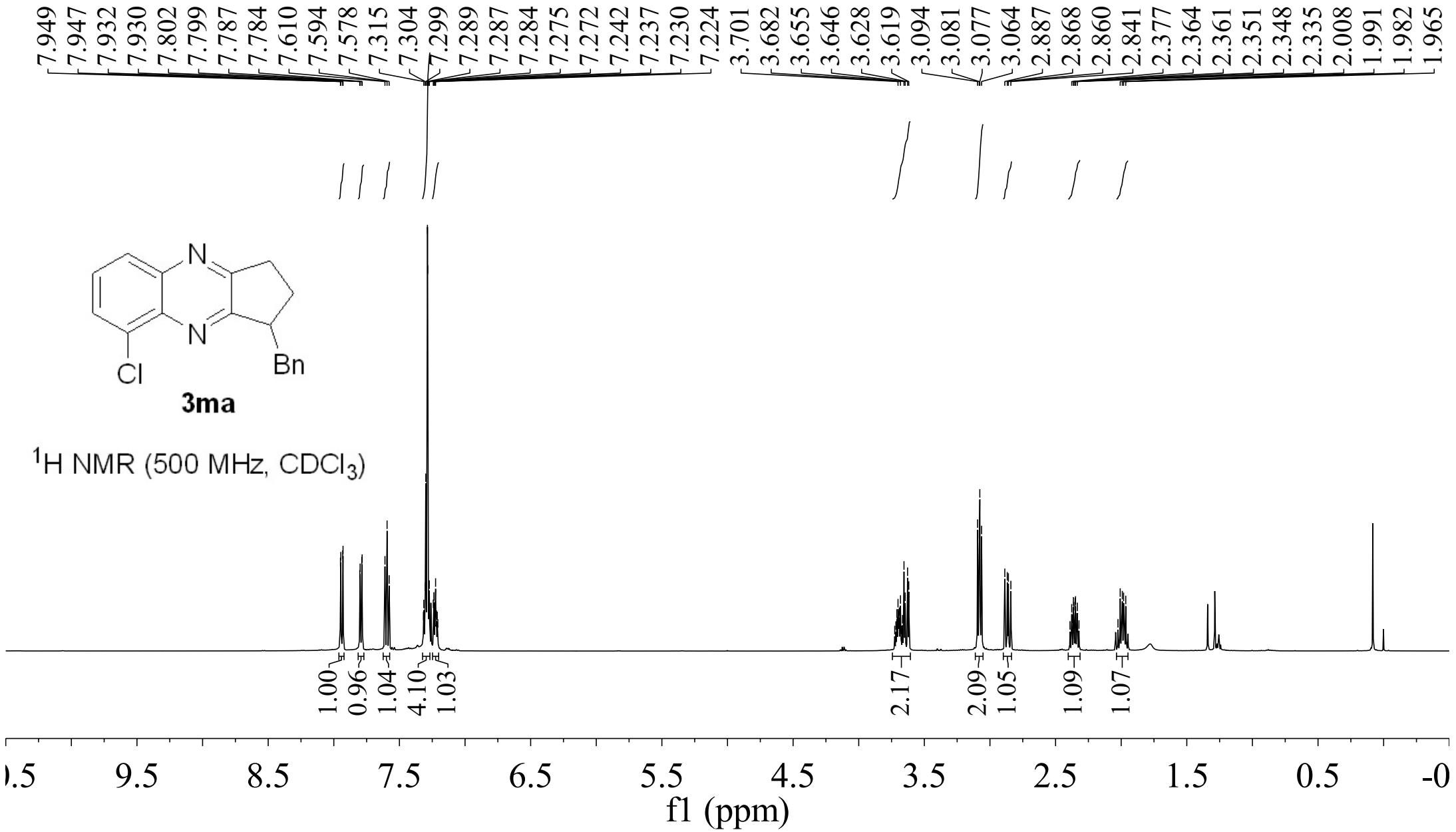

161.374
158.600
142.019
139.975
139.607
138.704
136.369
131.450
129.284
128.554
126.365
126.063
45.384
39.451
31.001
27.846
21.787
17.617
N
N
Bn
3ja
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

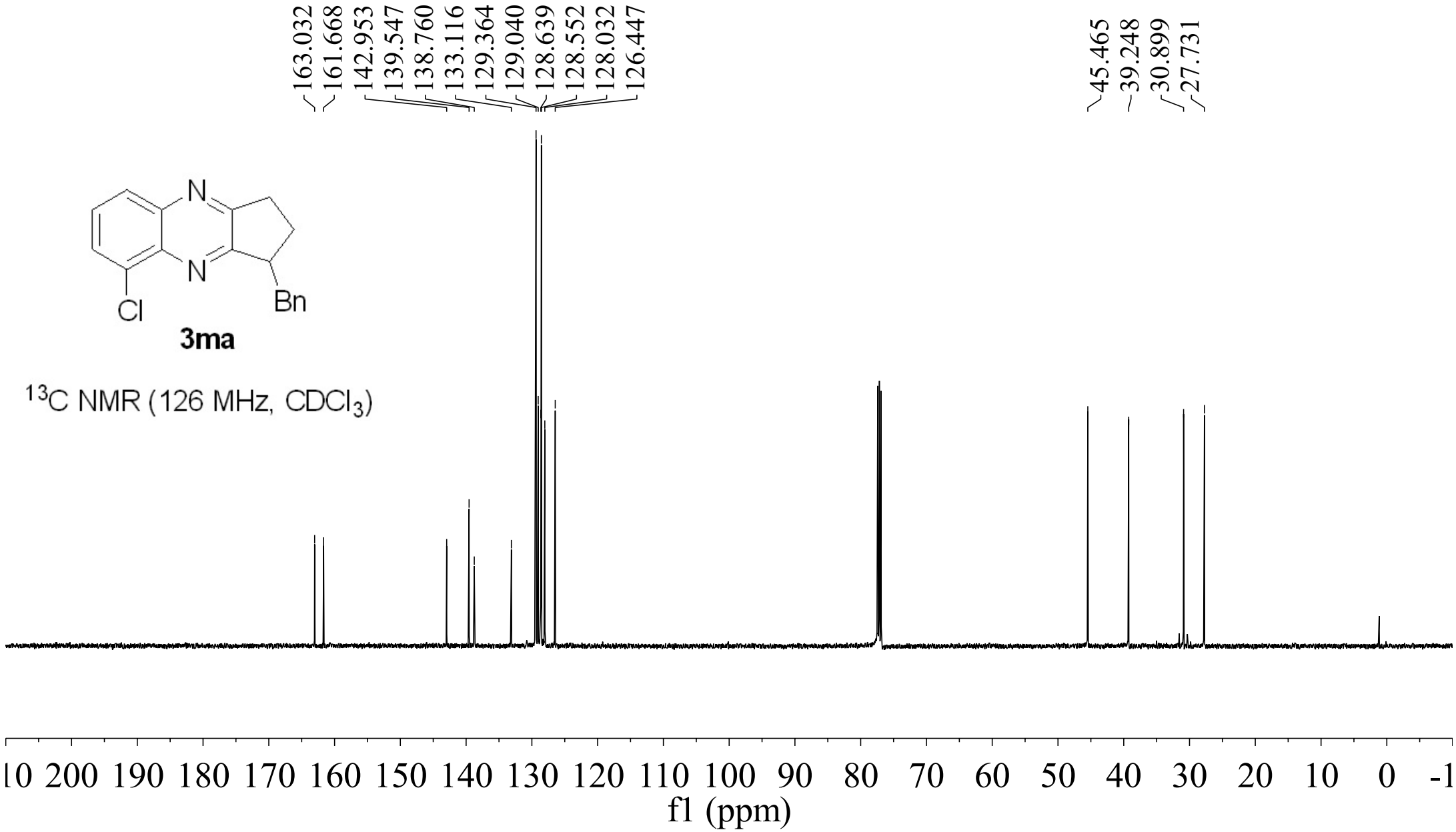

9.331
9.323
9.315
9.306
8.010
8.000
7.992
7.982
7.965
7.956
7.951
7.941
7.932
7.924
7.773
7.770
7.763
7.758
7.755
7.739
7.728
7.724
7.716
7.713
7.336
7.332
7.325
7.320
7.314
7.271
7.266
7.261
7.255
7.249
3.720
3.714
3.709
3.703
3.698
3.677
3.153
3.142
3.136
3.131
3.124
3.113
2.929
N
N
Bn
3ka
1H NMR (500 MHz, CDCl3)
1.00
3.02
2.07
4.09
1.14
2.12
2.04
1.04
1.06
1.13
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

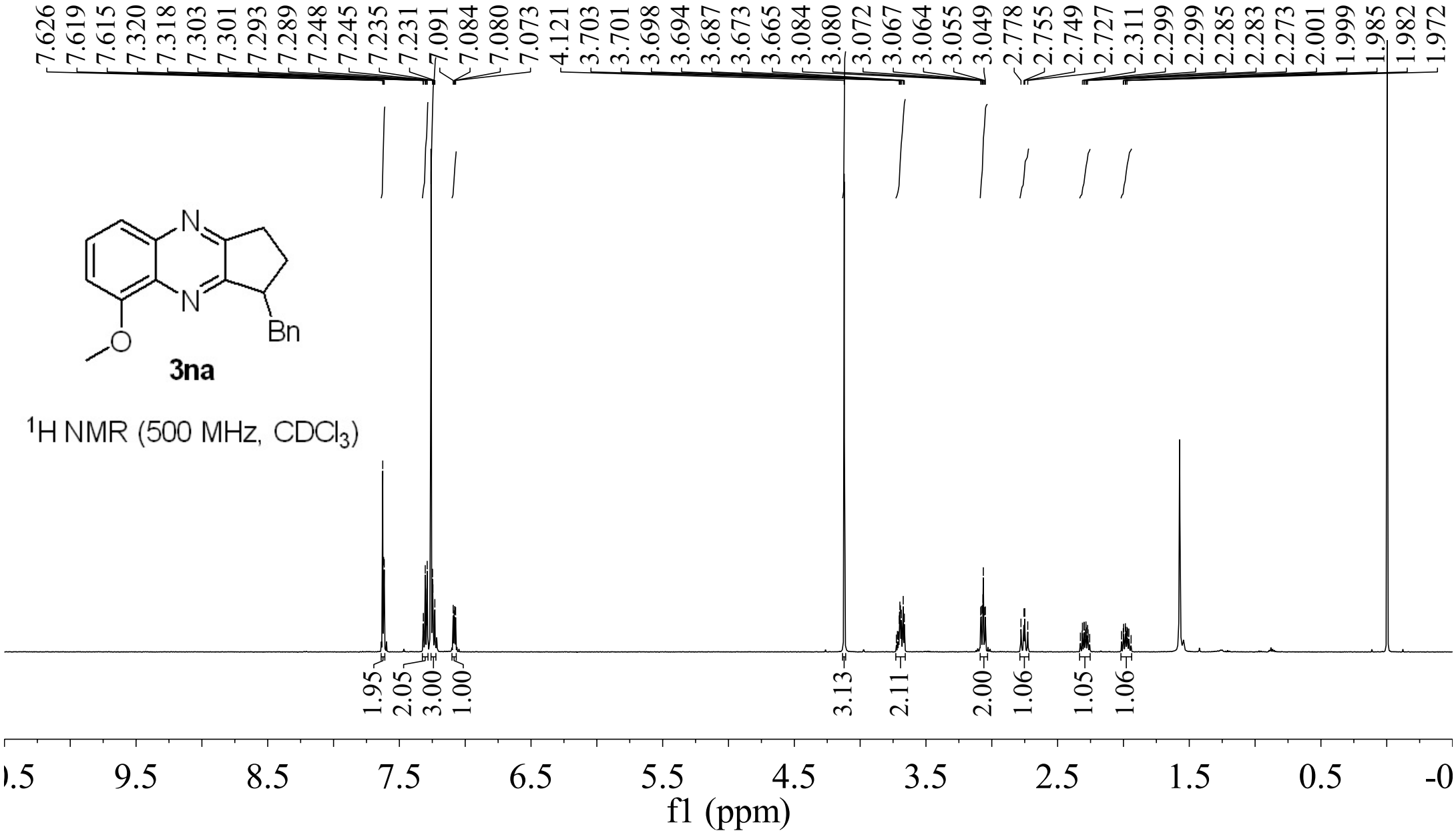

160.278
159.865
141.099
140.052
140.009
133.084
131.369
130.376
129.368
128.539
128.288
127.907
127.256
126.851
126.353
124.398
45.487
39.718
30.960
28.231
N
N
Bn
3ka
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

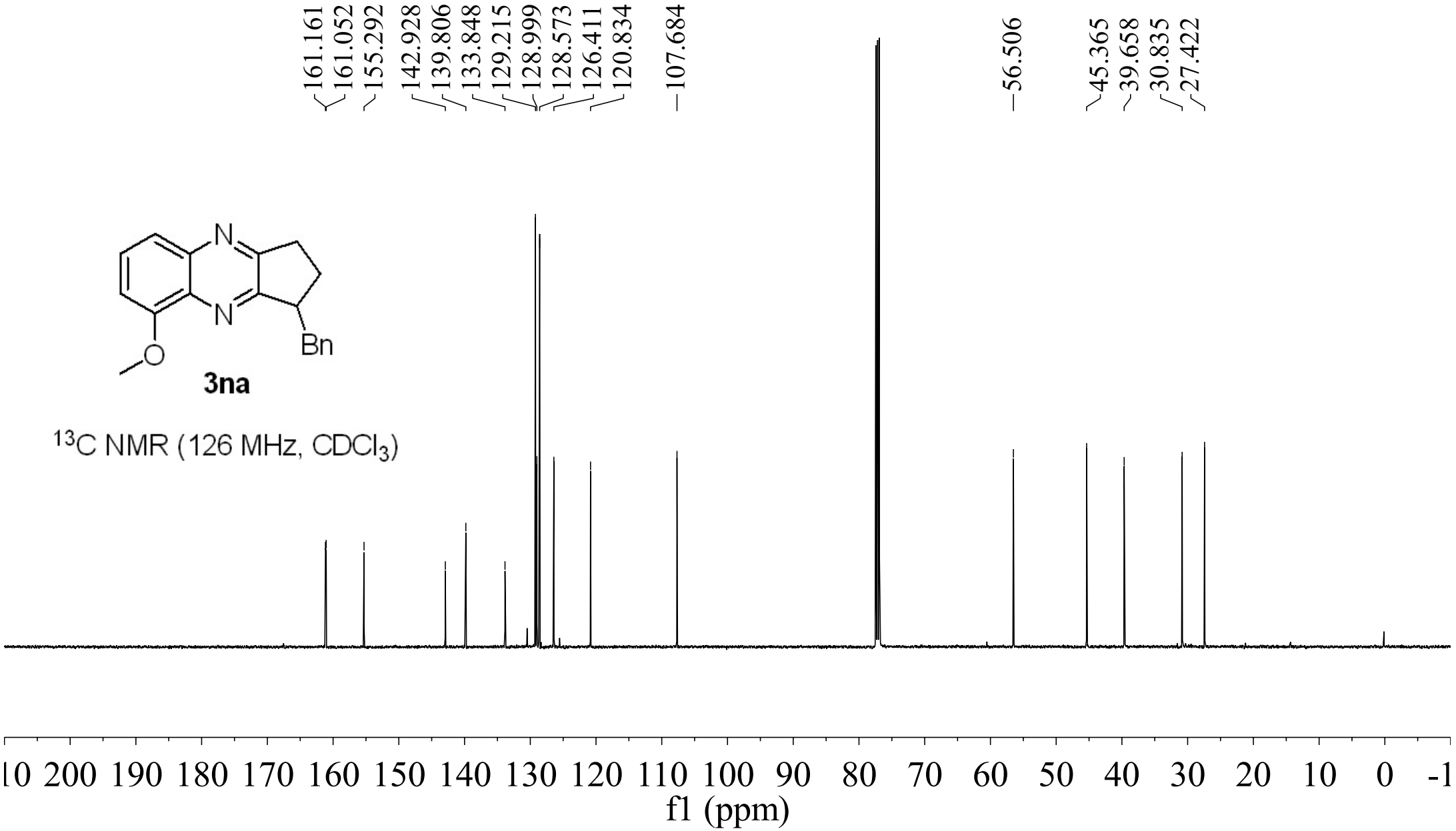

7.868
7.852
7.580
7.565
7.549
7.529
7.515
7.324
7.321
7.308
7.294
7.290
7.277
7.249
7.245
7.237
7.232
7.229
7.223
7.218
3.631
3.621
3.604
3.596
3.593
3.577
3.568
3.084
3.081
3.075
3.067
3.057
3.050
2.870
2.853
2.844
2.825
2.374
2.364
2.353
2.349
2.337
1.975
1.966
1.958
1.949
1.932
N
N
Bn
3la
1H NMR (500 MHz, CDCl3)
1.00
1.10
1.02
4.02
1.00
2.05
2.01
1.03
3.00
1.08
1.14
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

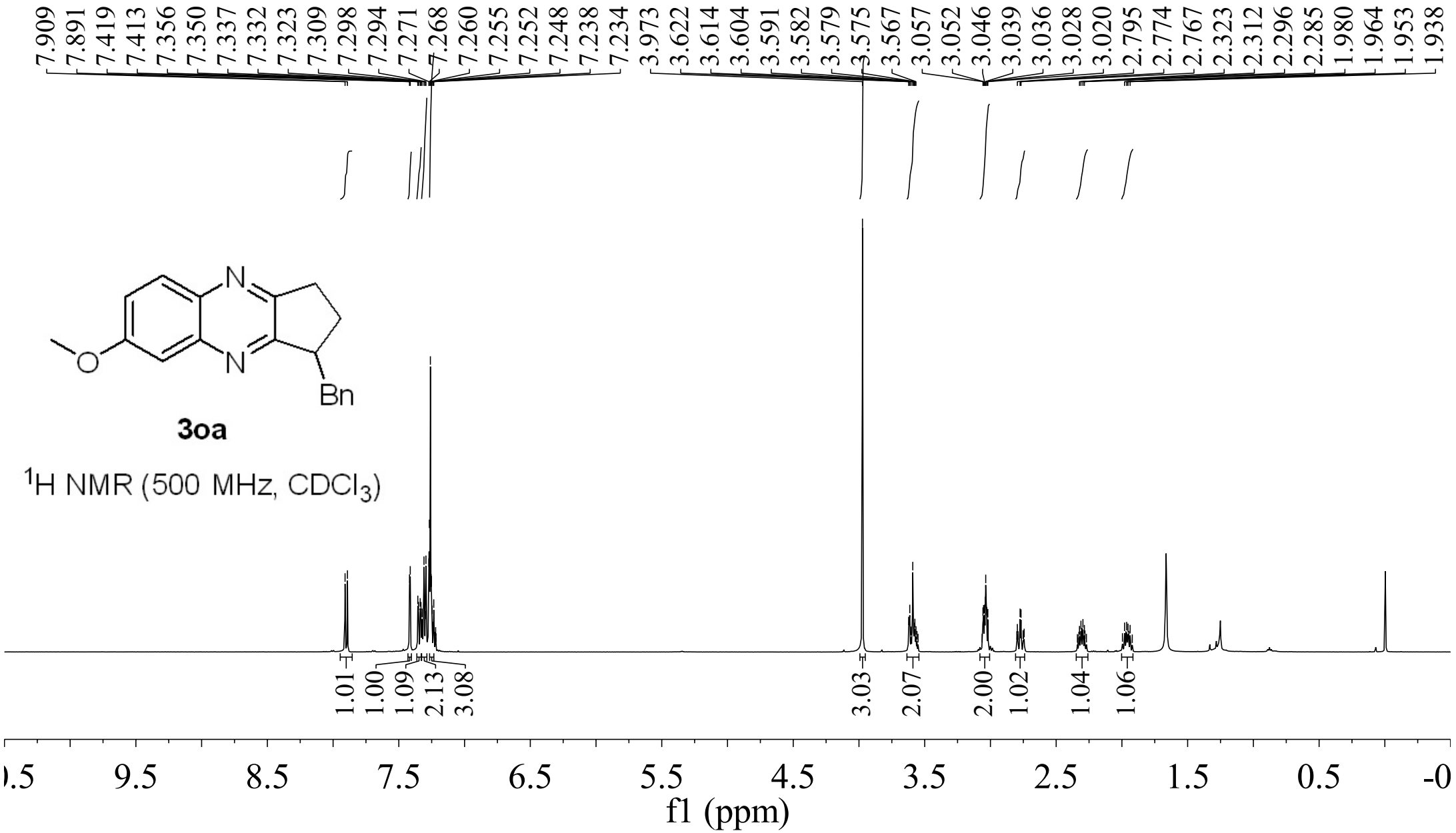

160.787
160.044
141.896
140.951
139.991
137.390
129.323
128.972
128.554
128.471
126.687
126.301
45.415
39.435
30.917
28.123
17.443
N
N
Bn
3la
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

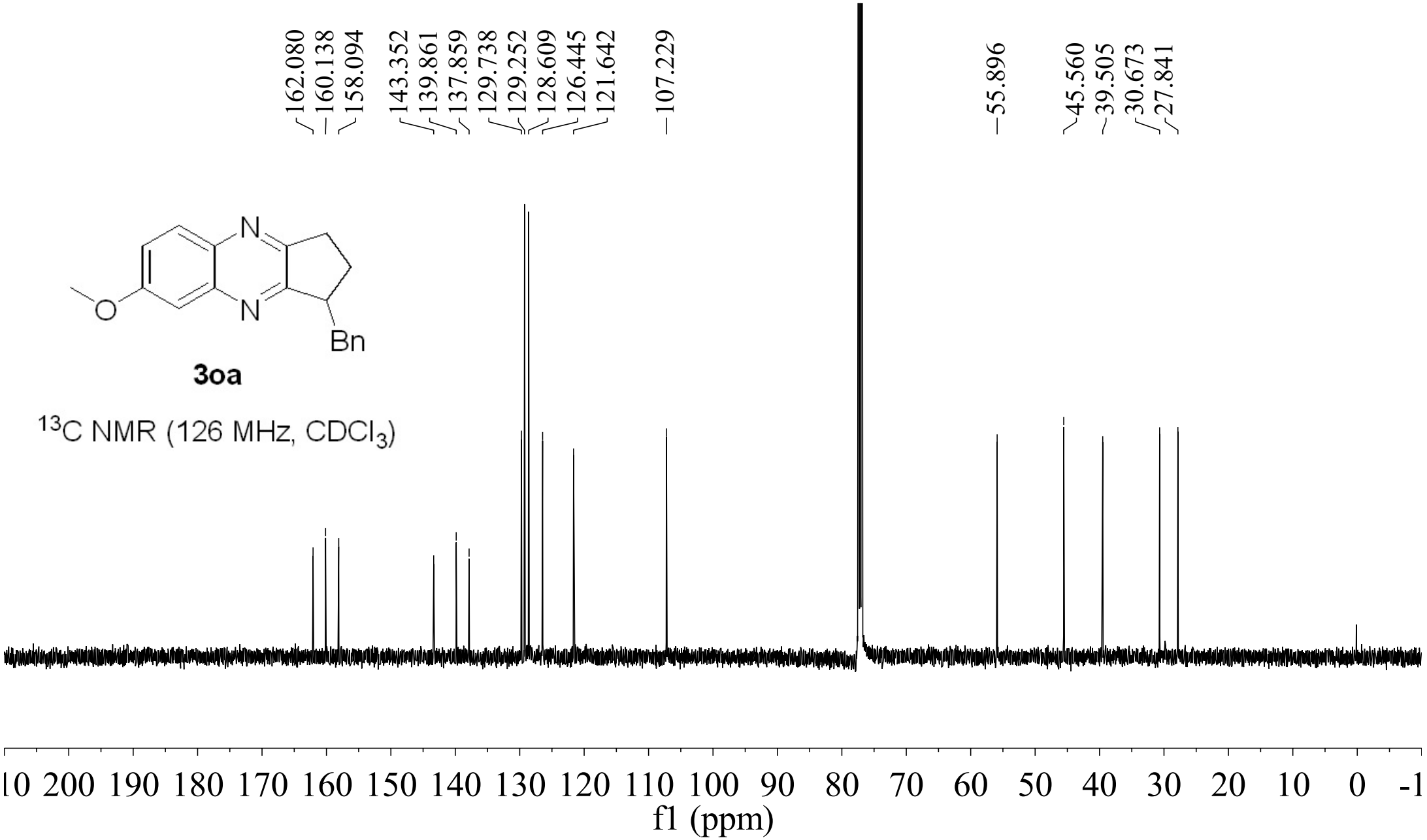

7.949
7.947
7.932
7.930
7.802
7.799
7.787
7.784
7.610
7.594
7.578
7.315
7.304
7.299
7.289
7.287
7.284
7.275
7.272
7.242
7.237
7.230
7.224
3.701
3.682
3.655
3.646
3.628
3.619
3.094
3.081
3.077
3.064
2.887
2.868
2.860
2.841
2.377
2.364
2.361
2.351
2.348
2.335
2.008
1.991
1.982
1.965
N
N
Cl
Bn
3ma
1H NMR (500 MHz, CDCl3)
1.00
0.96
1.04
4.10
1.03
2.17
2.09
1.05
1.09
1.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

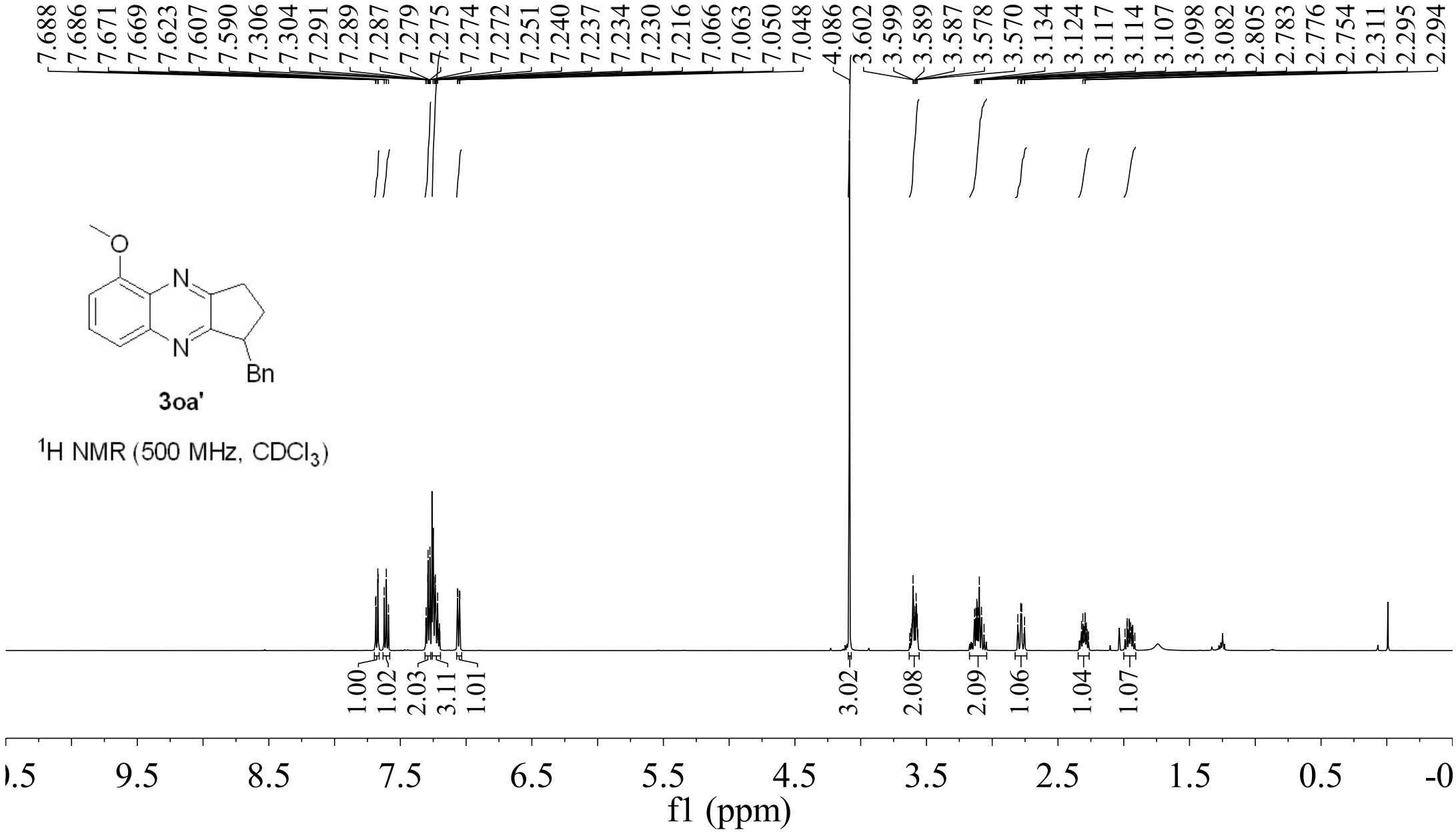

163.032
161.668
142.953
139.547
138.760
133.116
129.364
129.040
128.639
128.552
128.032
126.447
45.465
39.248
30.899
27.731
N
N
Cl
Bn
3ma
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

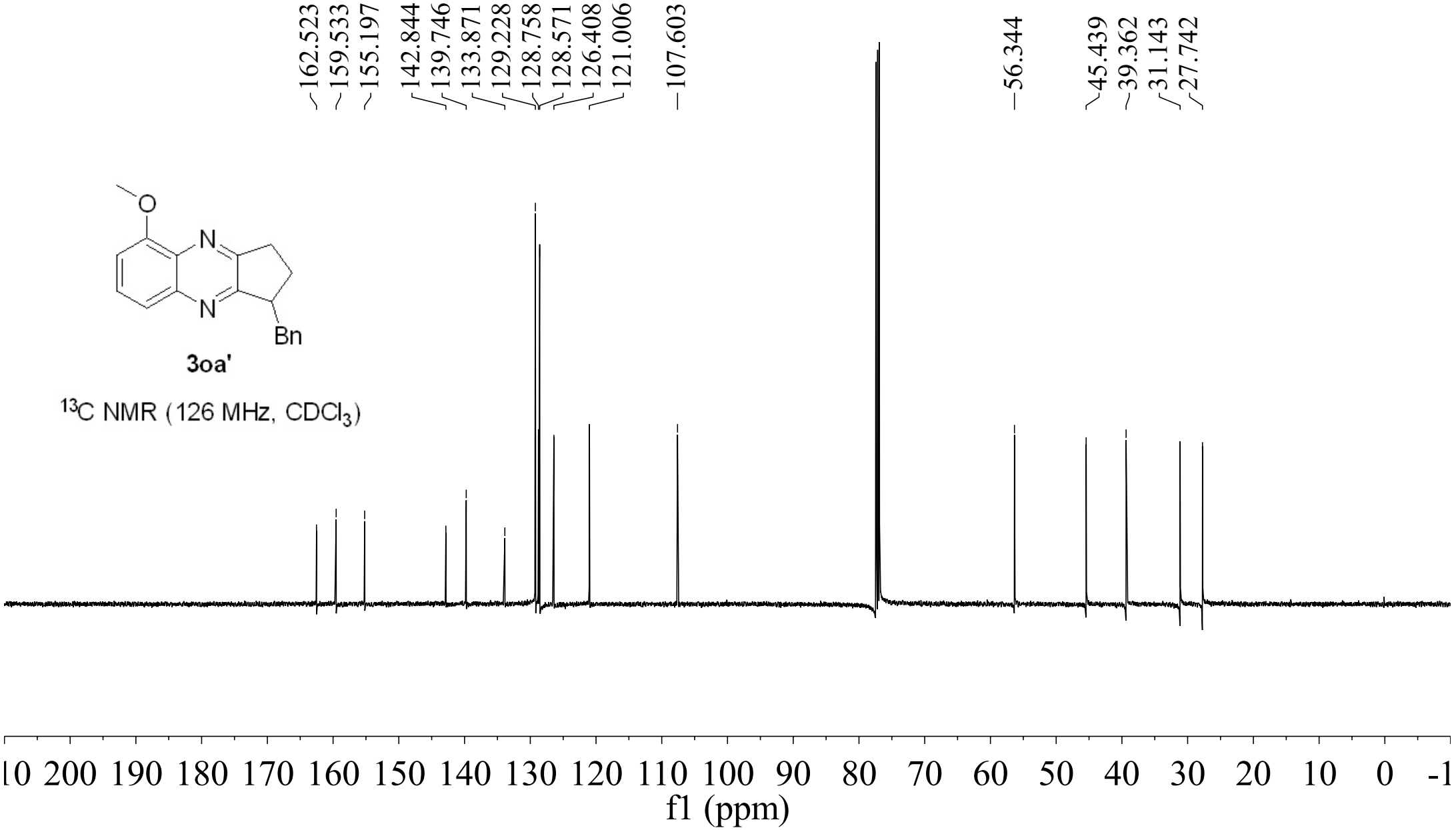

7.626
7.619
7.615
7.320
7.318
7.303
7.301
7.293
7.289
7.248
7.245
7.235
7.231
7.091
7.084
7.080
7.073
4.121
3.703
3.701
3.698
3.694
3.687
3.673
3.665
3.084
3.080
3.072
3.067
3.064
3.055
3.049
2.778
2.755
2.749
2.727
2.311
2.299
2.299
2.285
2.283
2.273
2.001
1.999
1.985
1.982
1.972
N
N
O
Bn
3na
1H NMR (500 MHz, CDCl3)
1.95
2.05
3.00
1.00
3.13
2.11
2.00
1.06
1.05
1.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

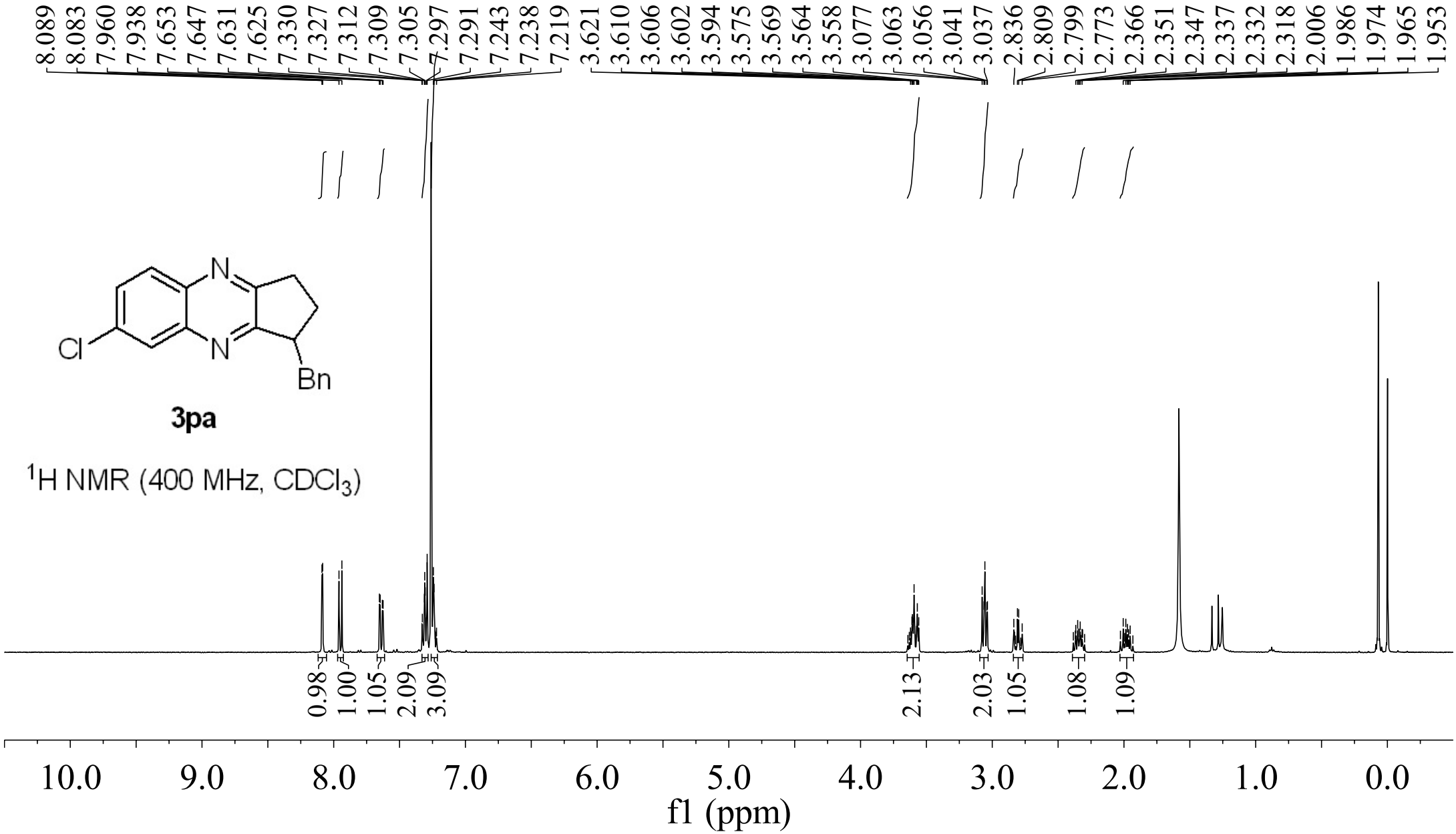

161.161
161.052
155.292
142.928
139.806
133.848
129.215
128.999
128.573
126.411
120.834
107.684
56.506
45.365
39.658
30.835
27.422
N
N
O
Bn
3na
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

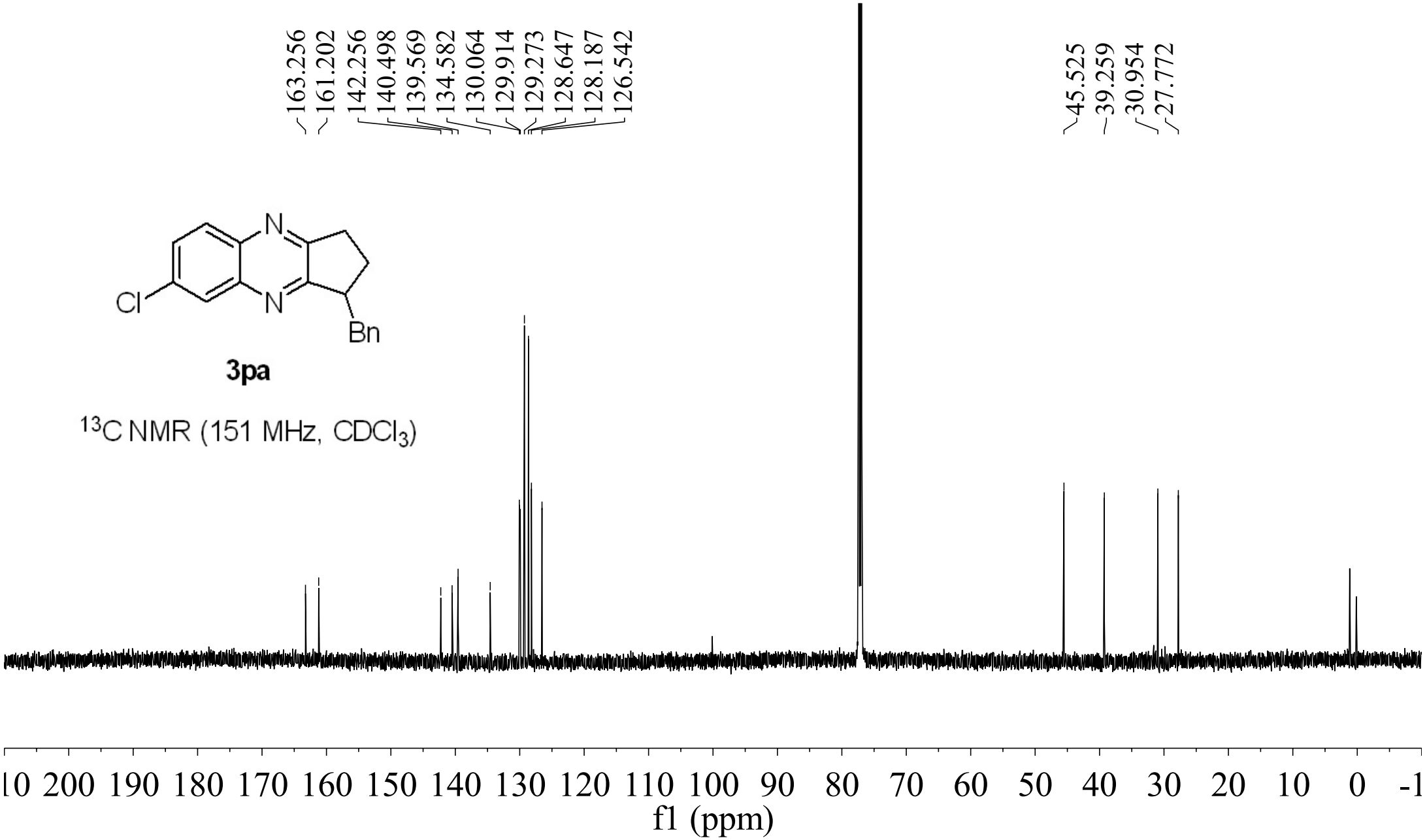

7.909
7.891
7.419
7.413
7.356
7.350
7.337
7.332
7.323
7.309
7.298
7.294
7.271
7.268
7.260
7.255
7.252
7.248
7.238
7.234
3.973
3.622
3.614
3.604
3.591
3.582
3.579
3.575
3.567
3.057
3.052
3.046
3.039
3.036
3.028
3.020
2.795
2.774
2.767
2.323
2.312
2.296
2.285
1.980
1.964
1.953
1.938
N
N
O
Bn
3oa
1H NMR (500 MHz, CDCl3)
1.01
1.00
1.09
2.13
3.08
3.03
2.07
2.00
1.02
1.04
1.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

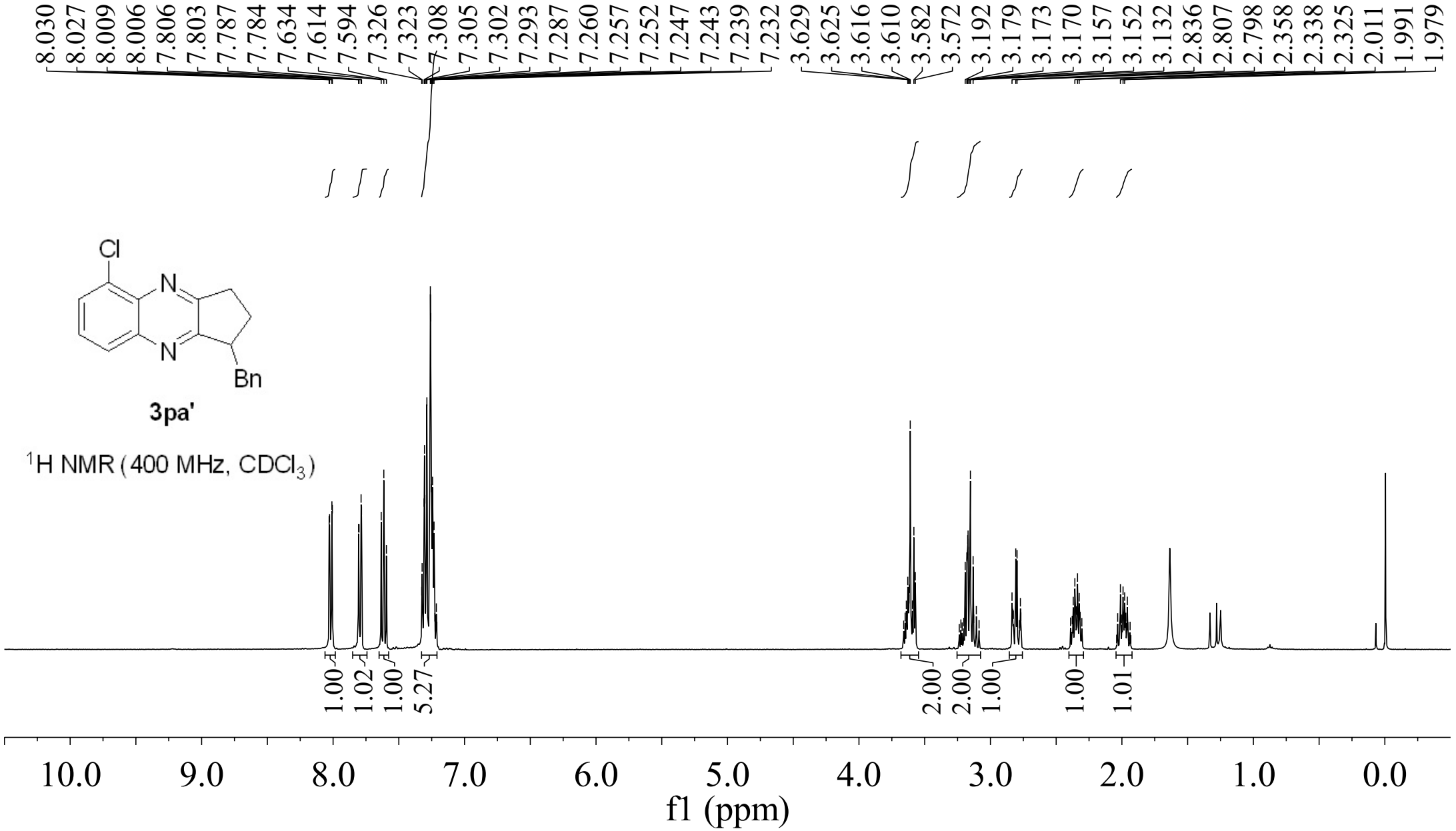

162.080
160.138
158.094
143.352
139.861
137.859
129.738
129.252
128.609
126.445
121.642
107.229
55.896
45.560
39.505
30.673
27.841
N
N
O
Bn
3oa
13C NMR (126 MHz, CDCl3)
f1 (ppm)

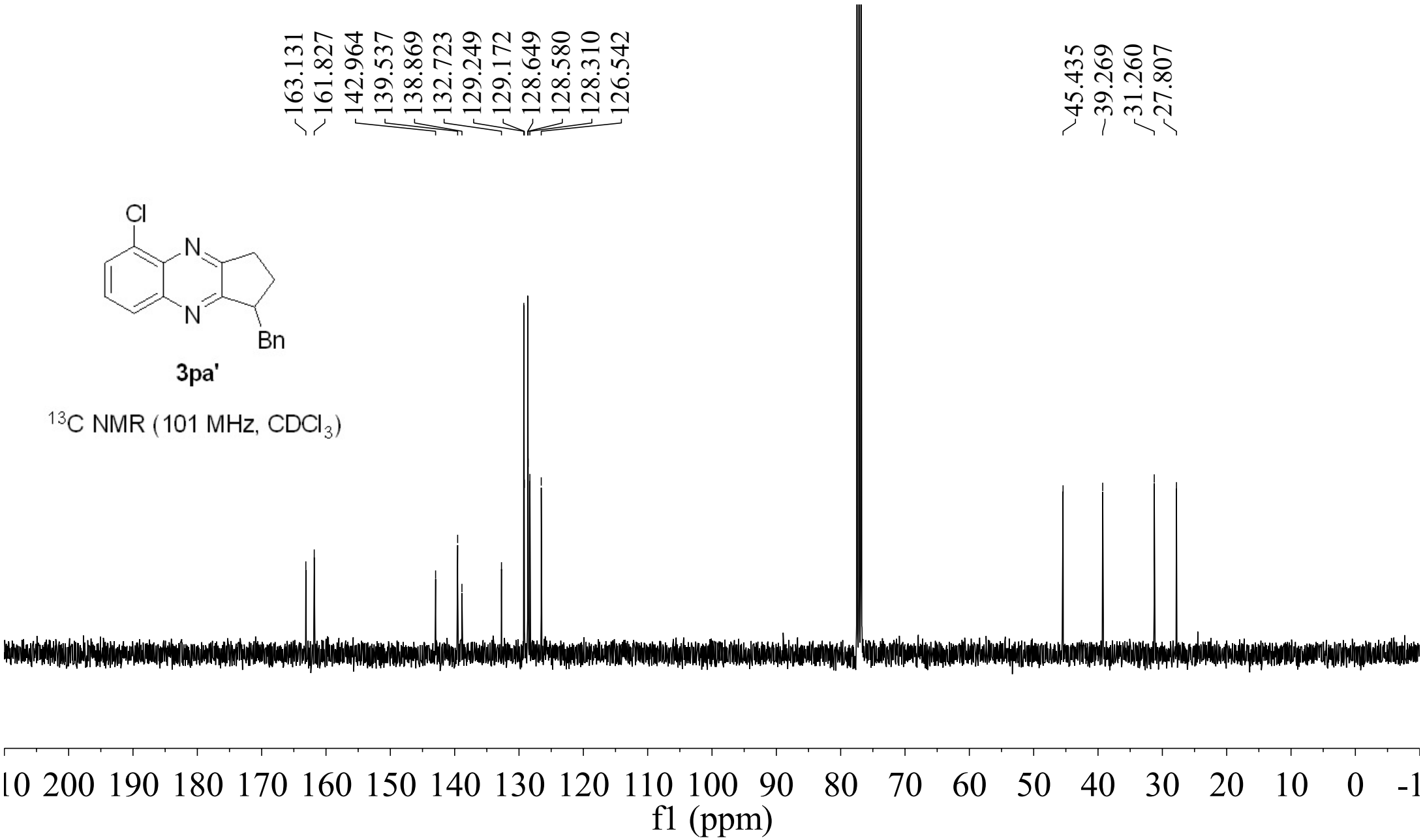

7.688
7.686
7.671
7.669
7.623
7.607
7.590
7.306
7.304
7.291
7.289
7.287
7.279
7.275
7.274
7.272
7.251
7.240
7.237
7.234
7.230
7.216
7.066
7.063
7.050
7.048
4.086
3.602
3.599
3.589
3.587
3.578
3.570
3.134
3.124
3.117
3.114
3.107
3.098
3.082
2.805
2.783
2.776
2.754
2.311
2.295
2.294
O
N
N
Bn
3oa'
1H NMR (500 MHz, CDCl3)
1.00
1.02
2.03
3.11
1.01
3.02
2.08
2.09
1.06
1.04
1.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

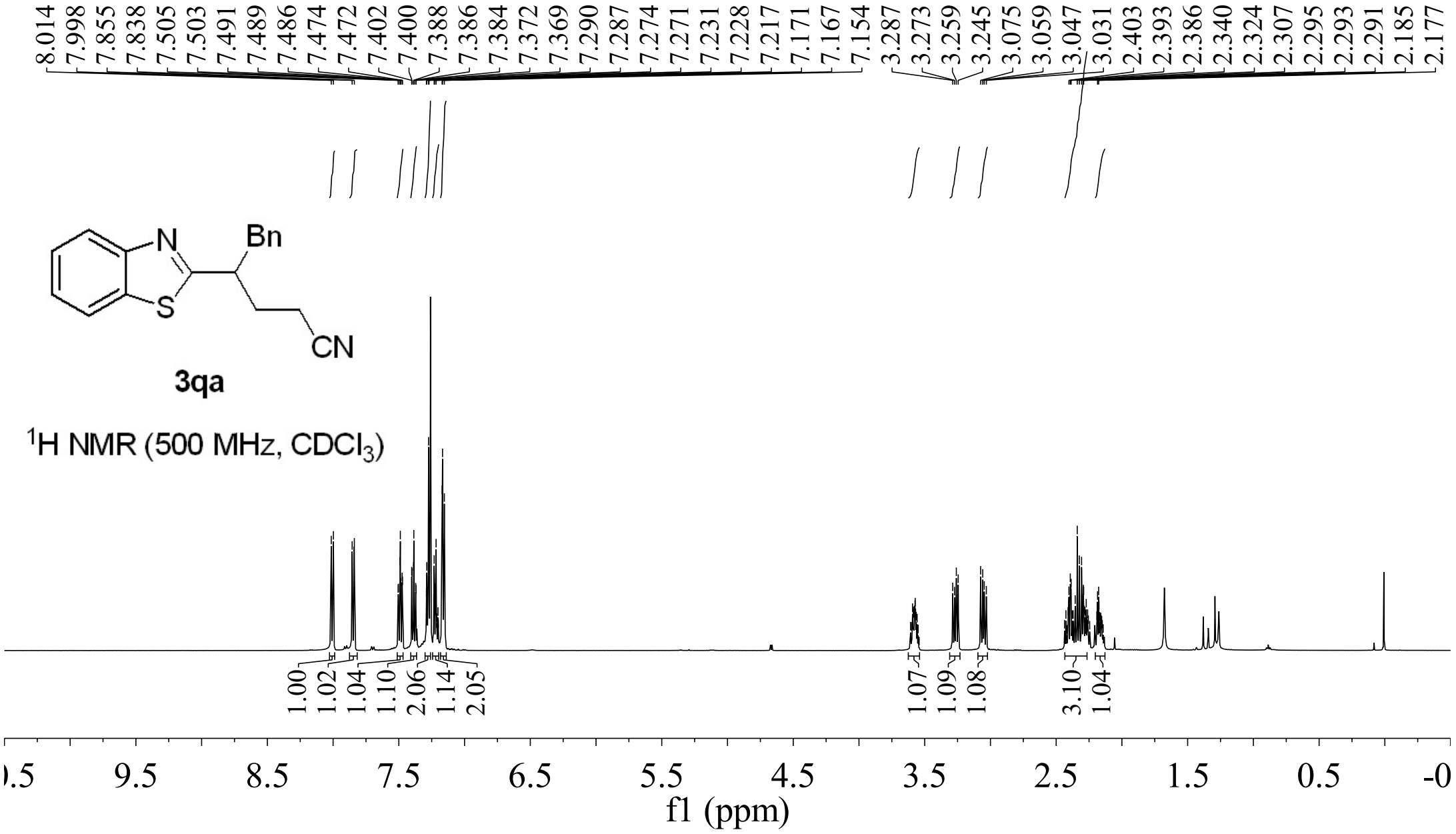

162.523
159.533
155.197
142.844
139.746
133.871
129.228
128.758
128.571
126.408
121.006
107.603
56.344
45.439
39.362
31.143
27.742
O
N
N
Bn
3oa'
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

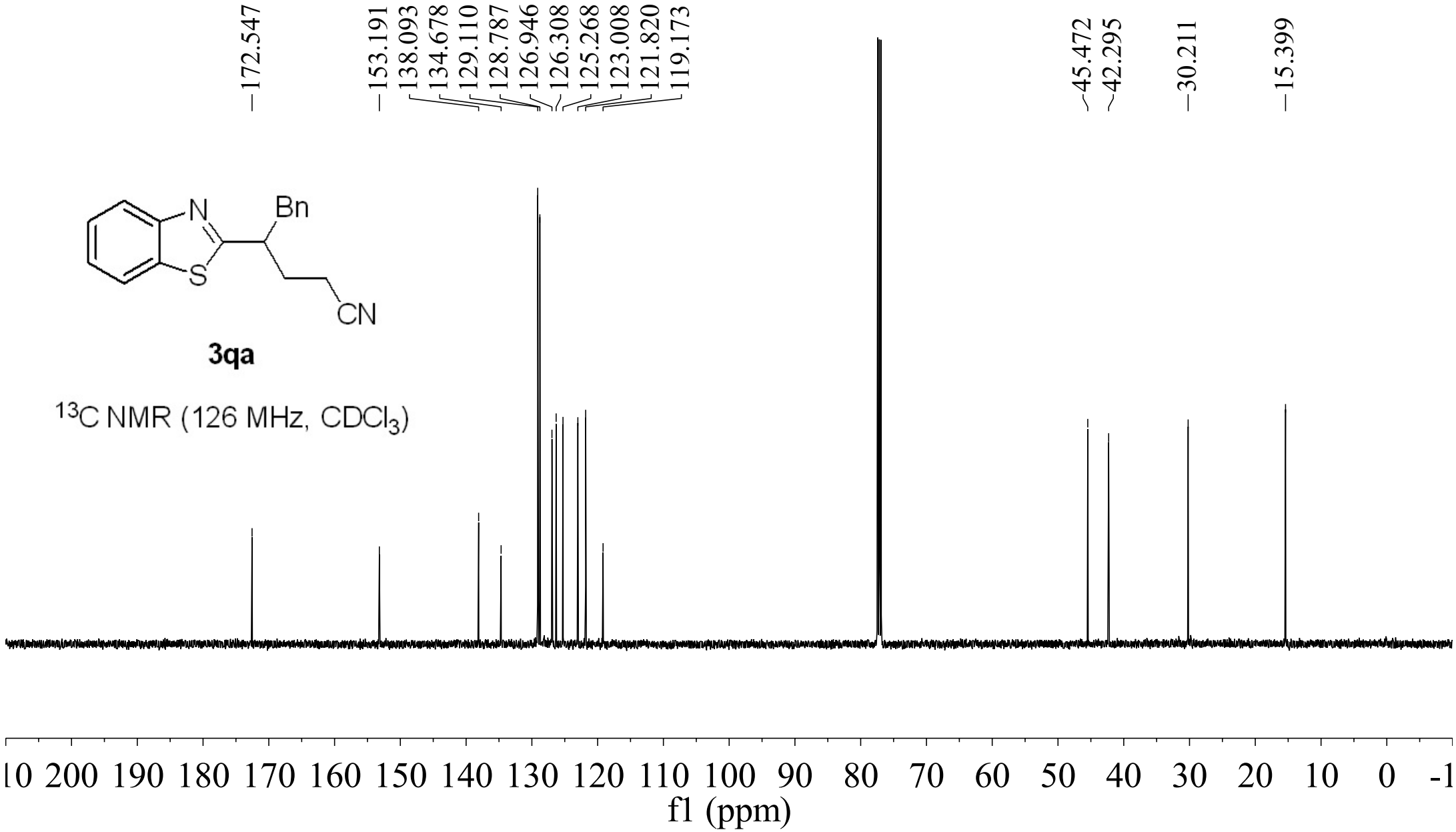

8.089
8.083
7.960
7.938
7.653
7.647
7.631
7.625
7.330
7.327
7.312
7.309
7.305
7.297
7.291
7.243
7.238
7.219
3.621
3.610
3.606
3.602
3.594
3.575
3.569
3.564
3.558
3.077
3.063
3.056
3.041
3.037
2.836
2.809
2.799
2.773
2.366
2.351
2.347
2.337
2.332
2.318
2.006
1.986
1.974
1.965
1.953
N
N
Cl
Bn
3pa
1H NMR (400 MHz, CDCl3)
0.98
1.00
1.05
2.09
3.09
2.13
2.03
1.05
1.08
1.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

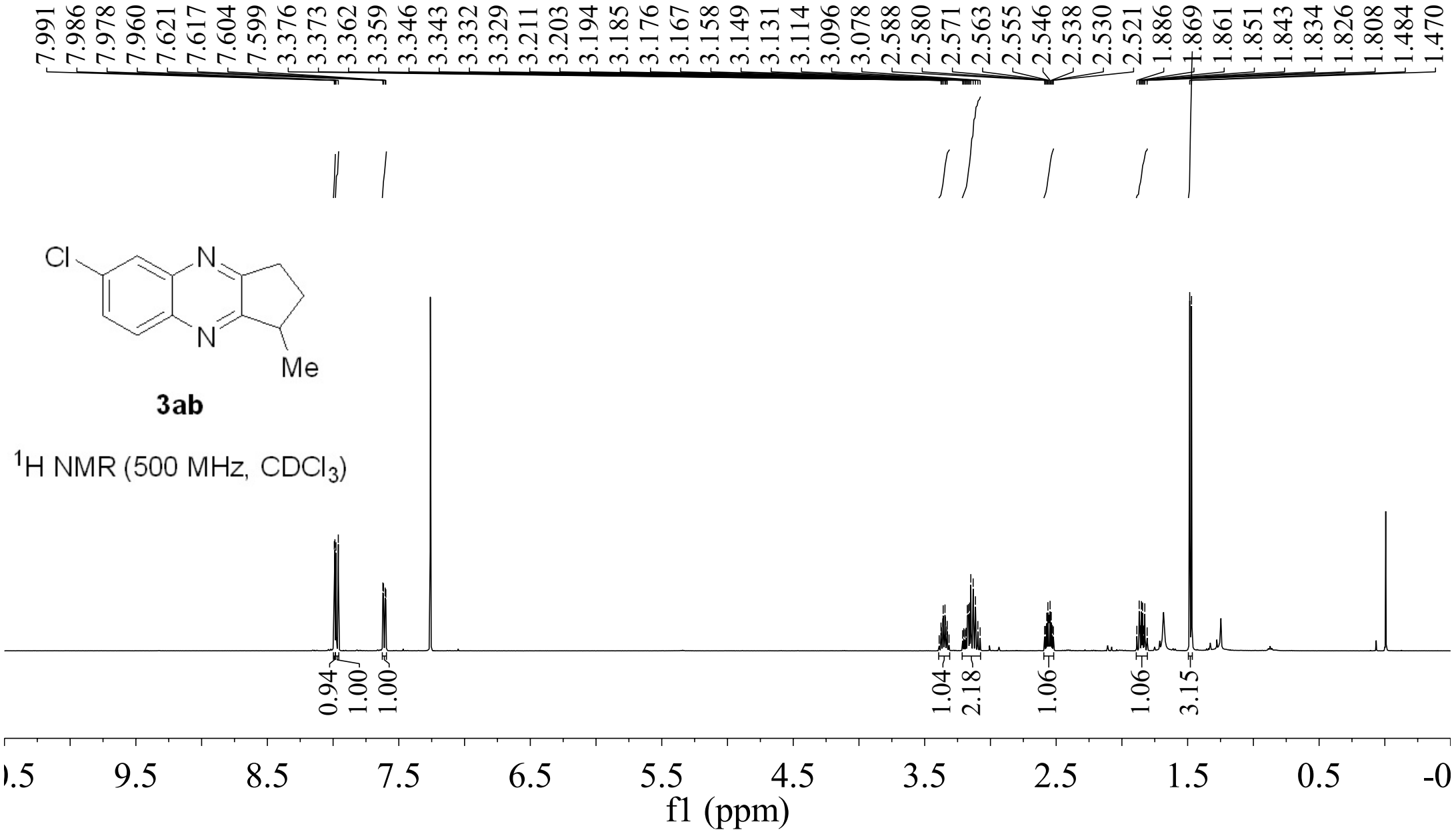

163.256
161.202
142.256
140.498
139.569
134.582
130.064
129.914
129.273
128.647
128.187
126.542
45.525
39.259
30.954
27.772
N
N
Cl
Bn
3pa
13C NMR (151 MHz, CDCl3)
f1 (ppm)

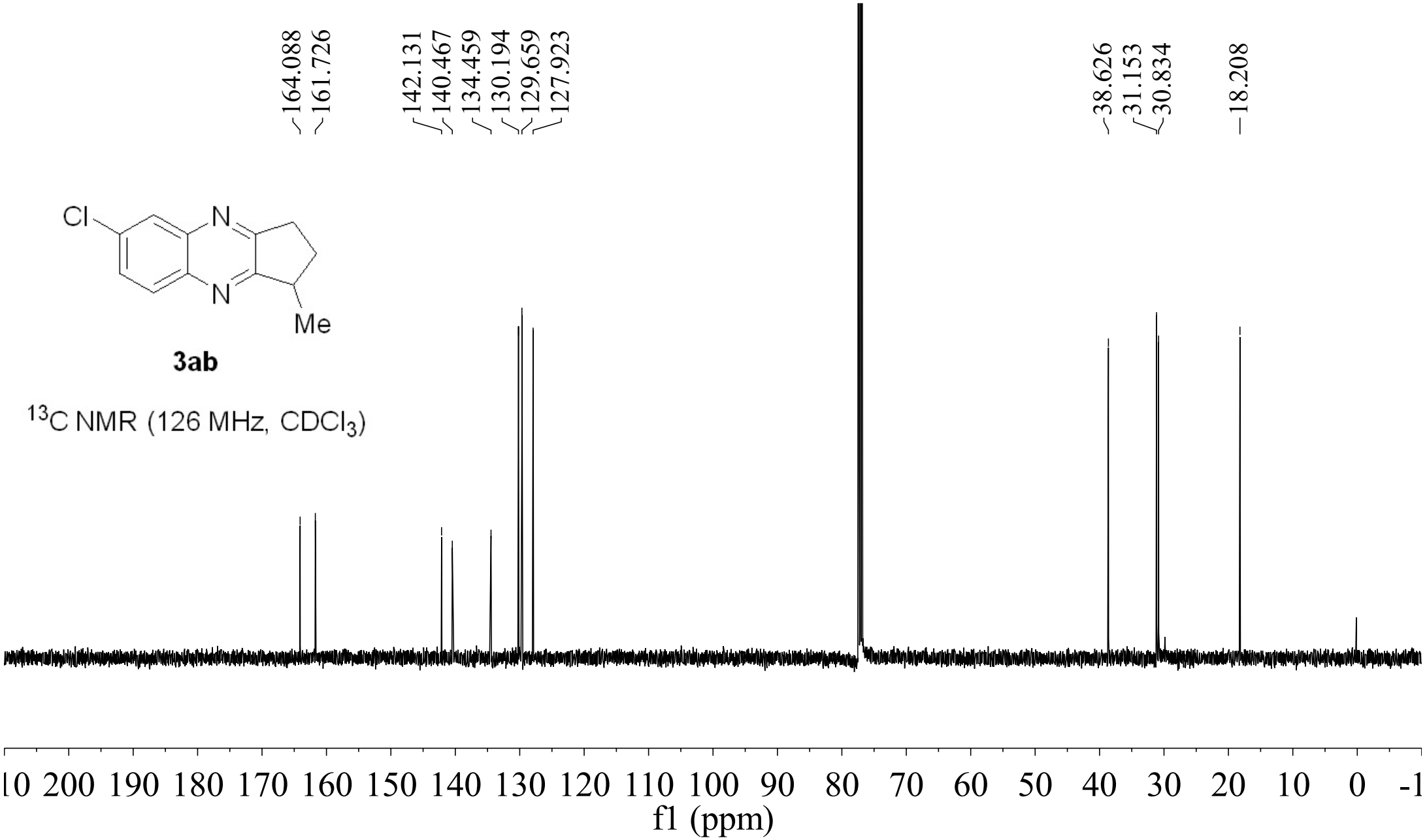

8.030
8.027
8.009
8.006
7.806
7.803
7.787
7.784
7.634
7.614
7.594
7.326
7.323
7.308
7.305
7.302
7.293
7.287
7.260
7.257
7.252
7.247
7.243
7.239
7.232
3.629
3.625
3.616
3.610
3.582
3.572
3.192
3.179
3.173
3.170
3.157
3.152
3.132
2.836
2.807
2.798
2.358
2.338
2.325
2.011
1.991
1.979
Cl
N
N
Bn
3pa'
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.00
5.27
2.00
2.00
1.00
1.00
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

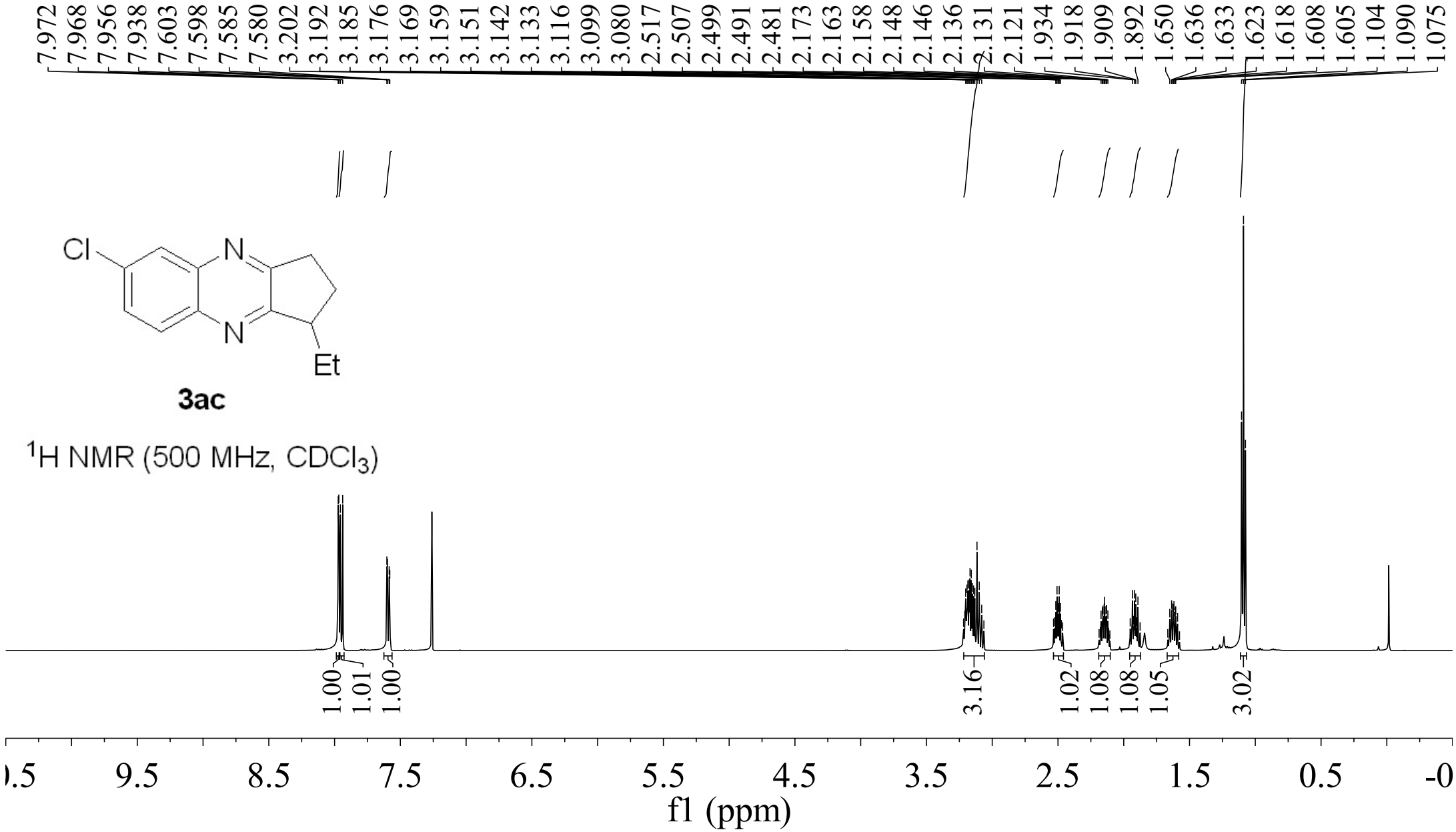

163.131
161.827
142.964
139.537
138.869
132.723
129.249
129.172
128.649
128.580
128.310
126.542
45.435
39.269
31.260
27.807
Cl
N
N
Bn
3pa'
13C NMR (101 MHz, CDCl3)
f1 (ppm)

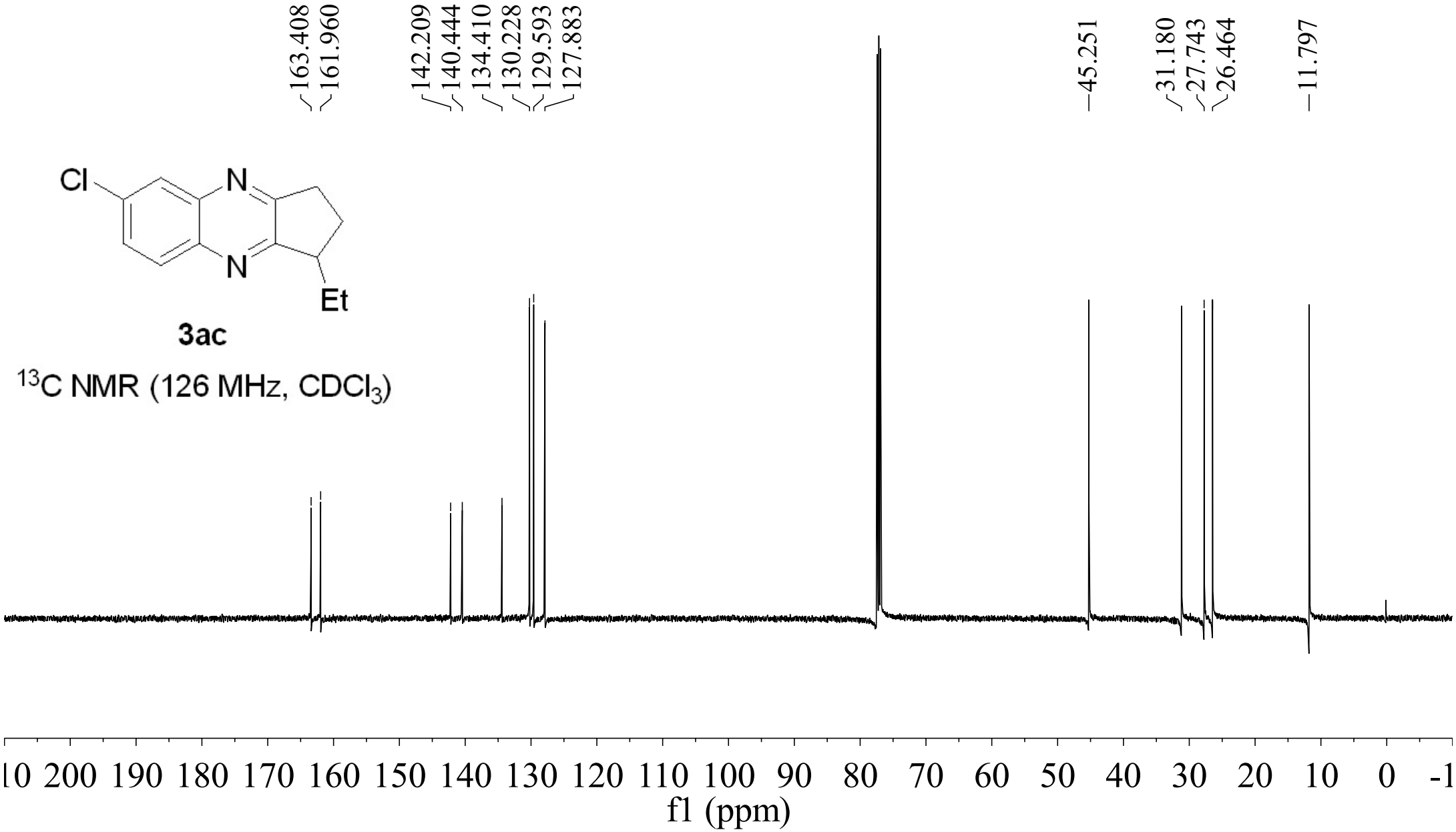

8.014
7.998
7.855
7.838
7.505
7.503
7.491
7.489
7.486
7.474
7.472
7.402
7.400
7.388
7.386
7.384
7.372
7.369
7.290
7.287
7.274
7.271
7.231
7.228
7.217
7.171
7.167
7.154
3.287
3.273
3.259
3.245
3.075
3.059
3.047
3.031
2.403
2.393
2.386
2.340
2.324
2.307
2.295
2.293
2.291
2.185
2.177
N
Bn
S
CN
3qa
1H NMR (500 MHz, CDCl3)
1.00
1.02
1.04
1.10
2.06
1.14
2.05
1.07
1.09
1.08
3.10
1.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

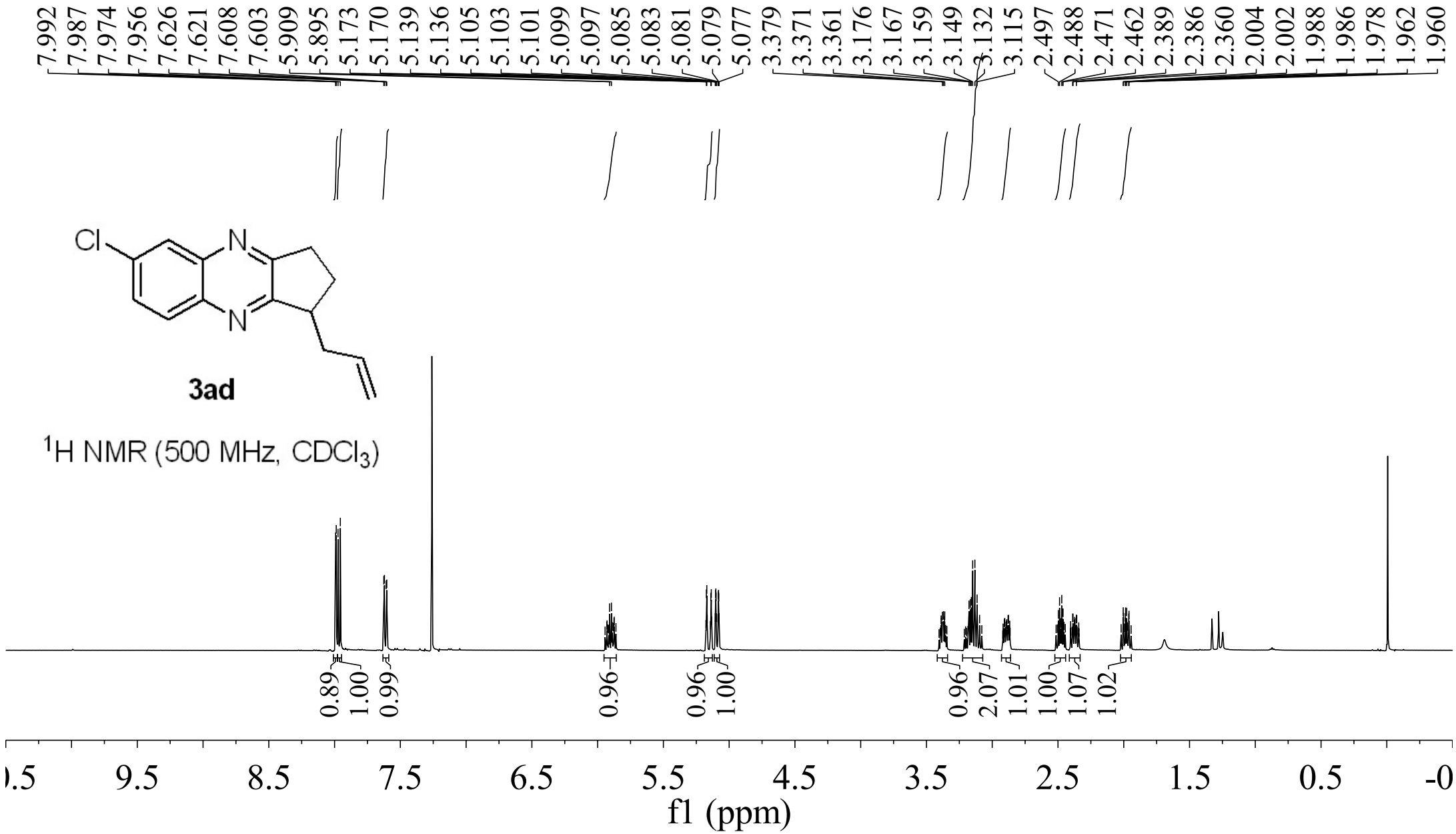

172.547
153.191
138.093
134.678
129.110
128.787
126.946
126.308
125.268
123.008
121.820
119.173
45.472
42.295
30.211
15.399
N
Bn
S
CN
3qa
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

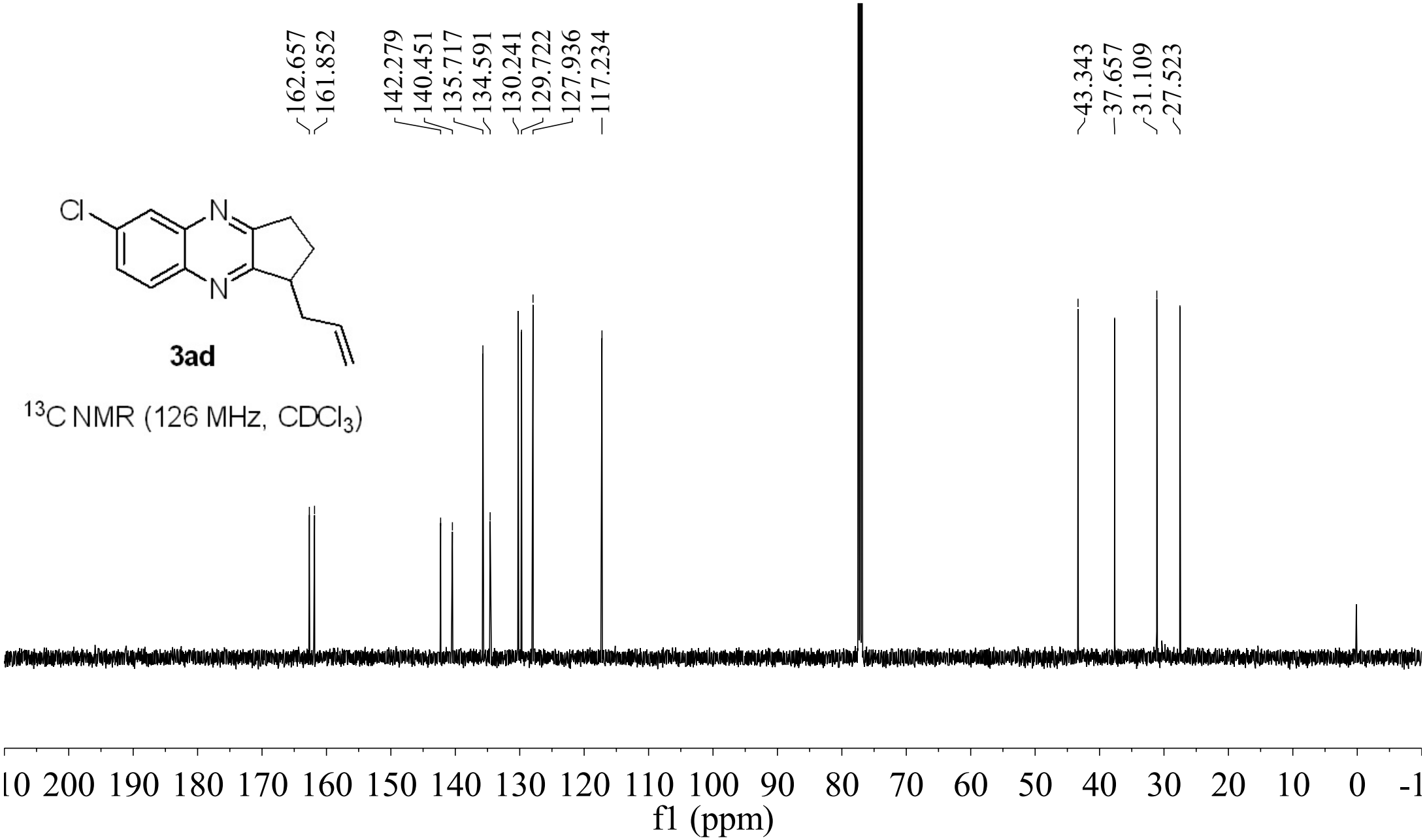

7.991
7.986
7.978
7.960
7.621
7.617
7.604
7.599
7.376
7.373
7.362
7.359
7.346
7.343
7.332
7.329
7.211
7.203
7.194
7.185
7.176
7.167
7.158
7.149
7.131
7.114
7.096
7.078
2.588
2.580
2.571
2.563
2.555
2.546
2.538
2.530
2.521
1.886
1.869
1.861
1.851
1.843
1.834
1.826
1.808
1.484
1.470
Cl
N
N
Me
3ab
1H NMR (500 MHz, CDCl3)
0.94
1.00
1.00
1.04
2.18
1.06
1.06
3.15
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

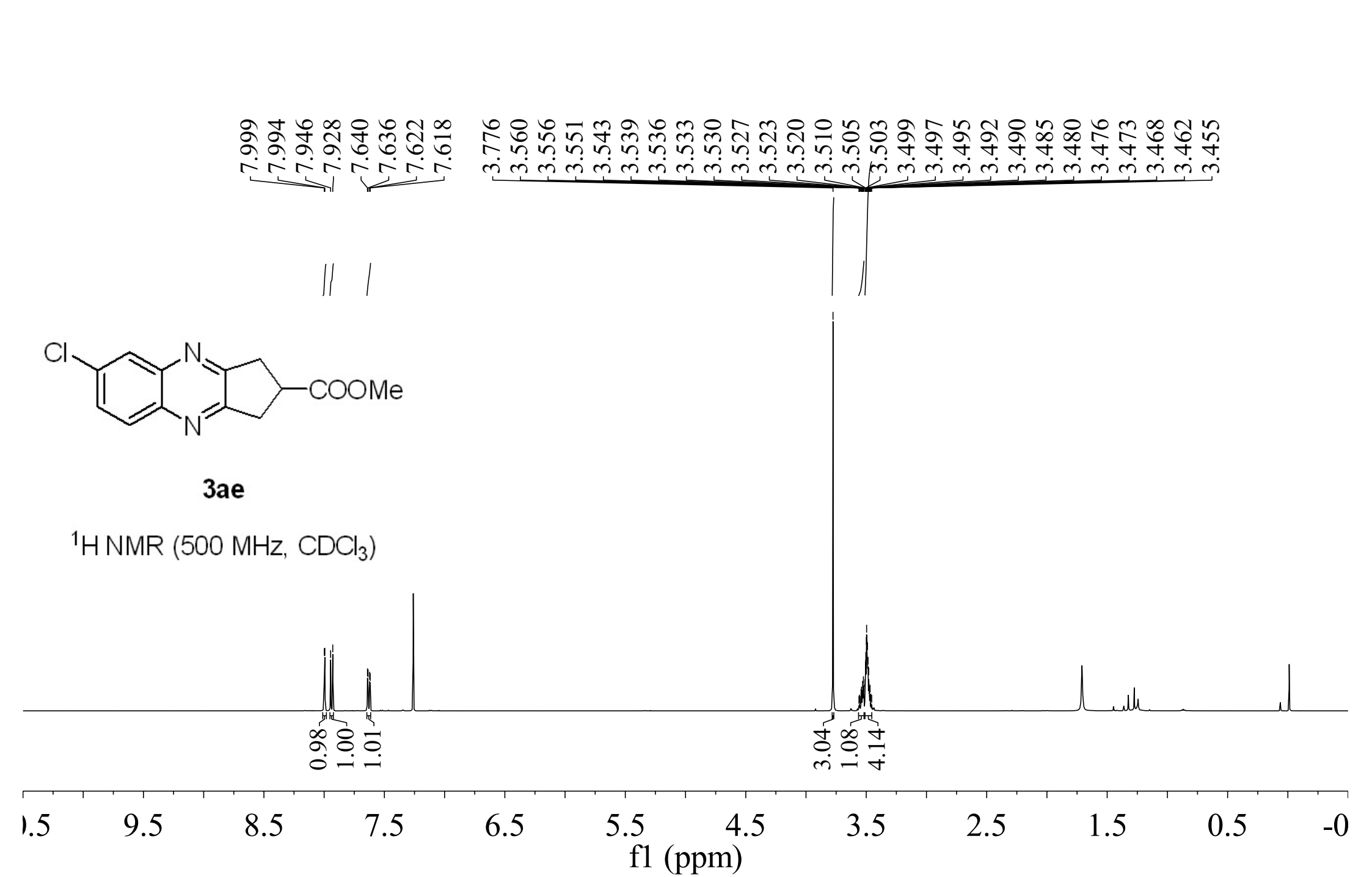

164.088
161.726
142.131
140.467
134.459
130.194
129.659
127.923
38.626
31.153
30.834
18.208
Cl
N
N
Me
3ab
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

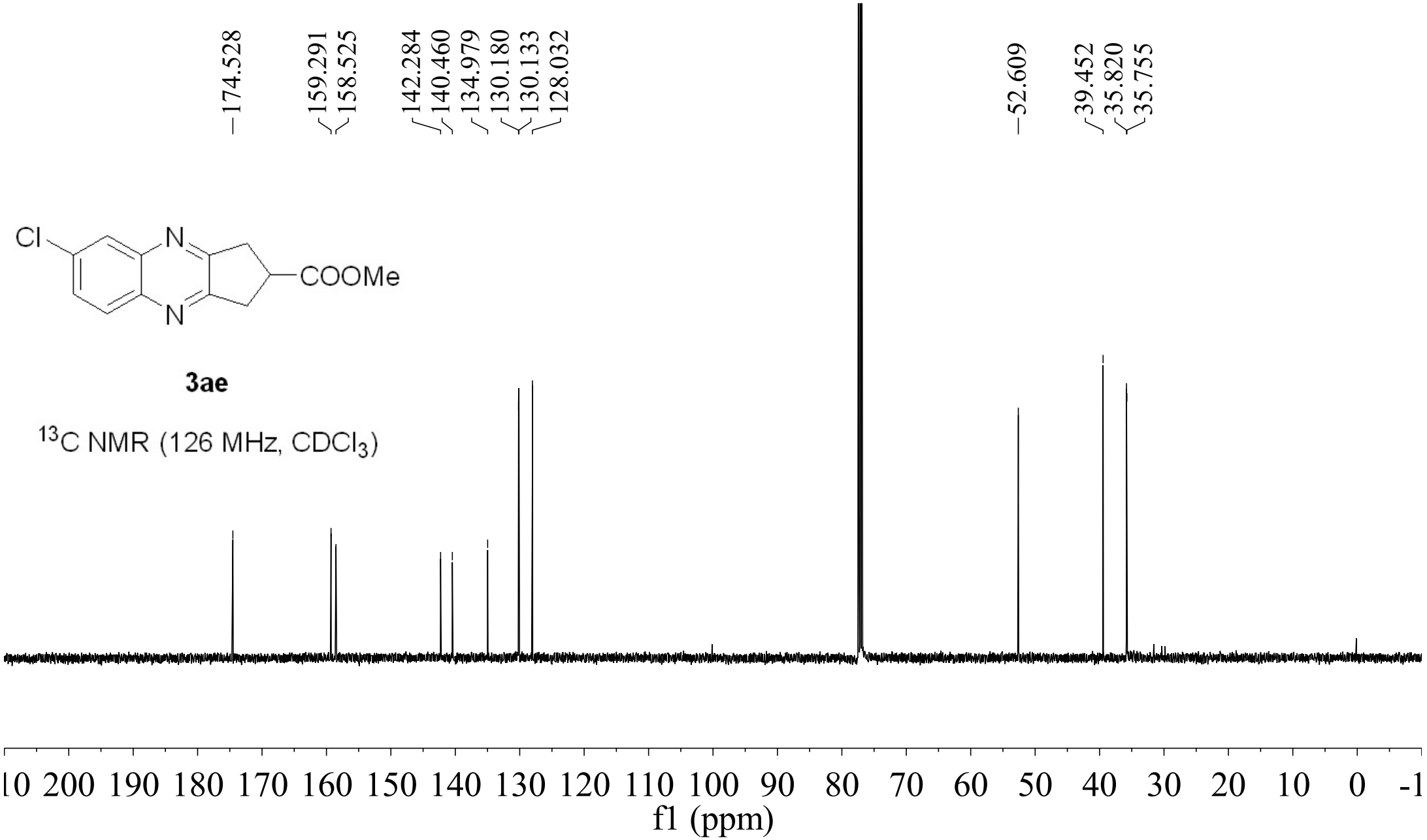

7.972
7.968
7.956
7.938
7.603
7.598
7.585
7.580
3.202
3.192
3.185
3.176
3.169
3.159
3.151
3.142
3.133
3.116
3.099
3.080
2.517
2.507
2.499
2.491
2.481
2.173
2.163
2.158
2.148
2.146
2.136
2.131
2.121
1.934
1.918
1.909
1.892
1.650
1.636
1.633
1.623
1.618
1.608
1.605
1.104
1.090
1.075
Cl
N
N
Et
3ac
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.00
3.16
1.02
1.08
1.08
1.05
3.02
f1 (ppm)

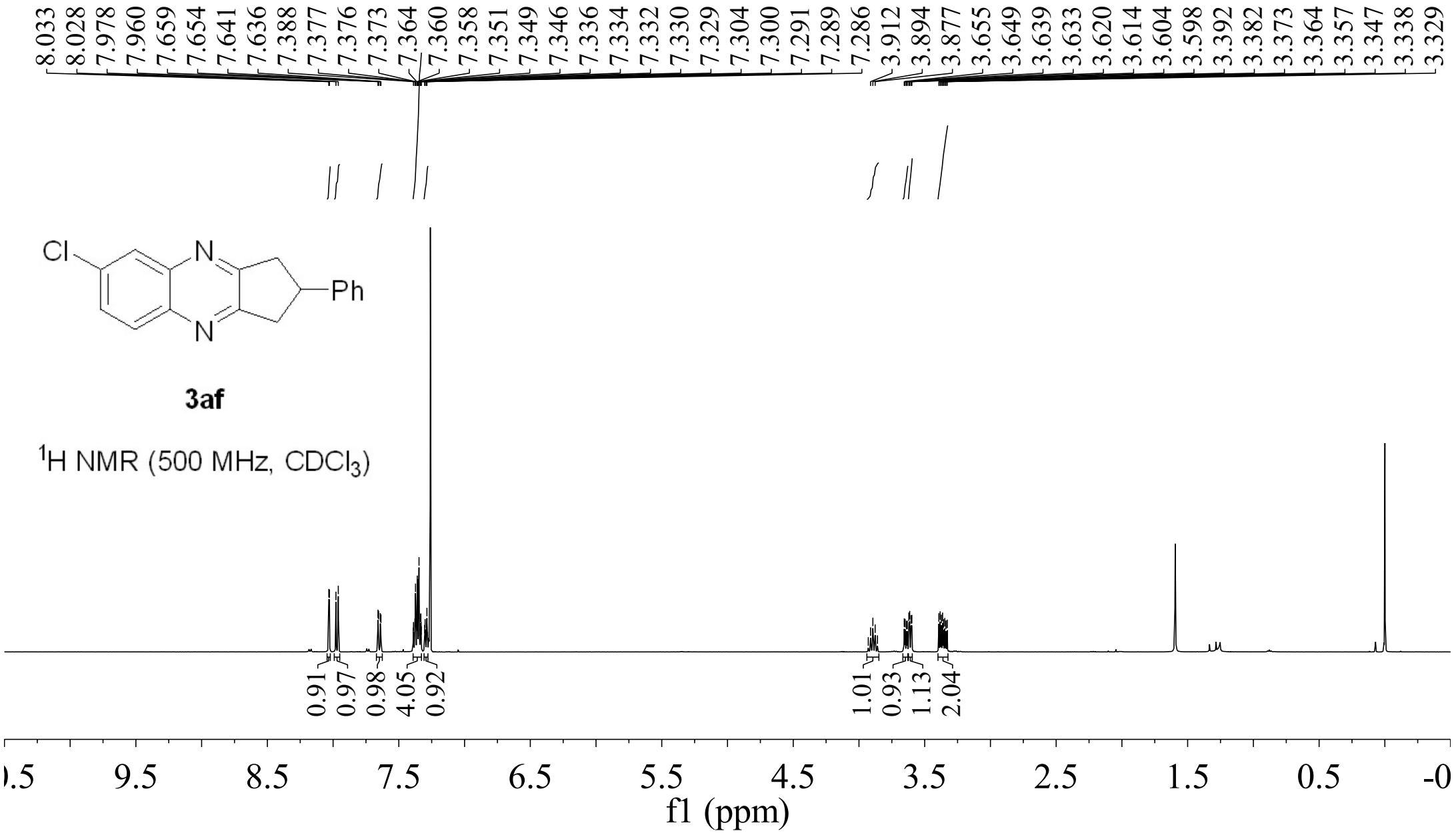

163.408
161.960
142.209
140.444
134.410
130.228
129.593
127.883
45.251
31.180
27.743
26.464
11.797
Cl
N
N
Et
3ac
13C NMR (126 MHz, CDCl3)
f1 (ppm)

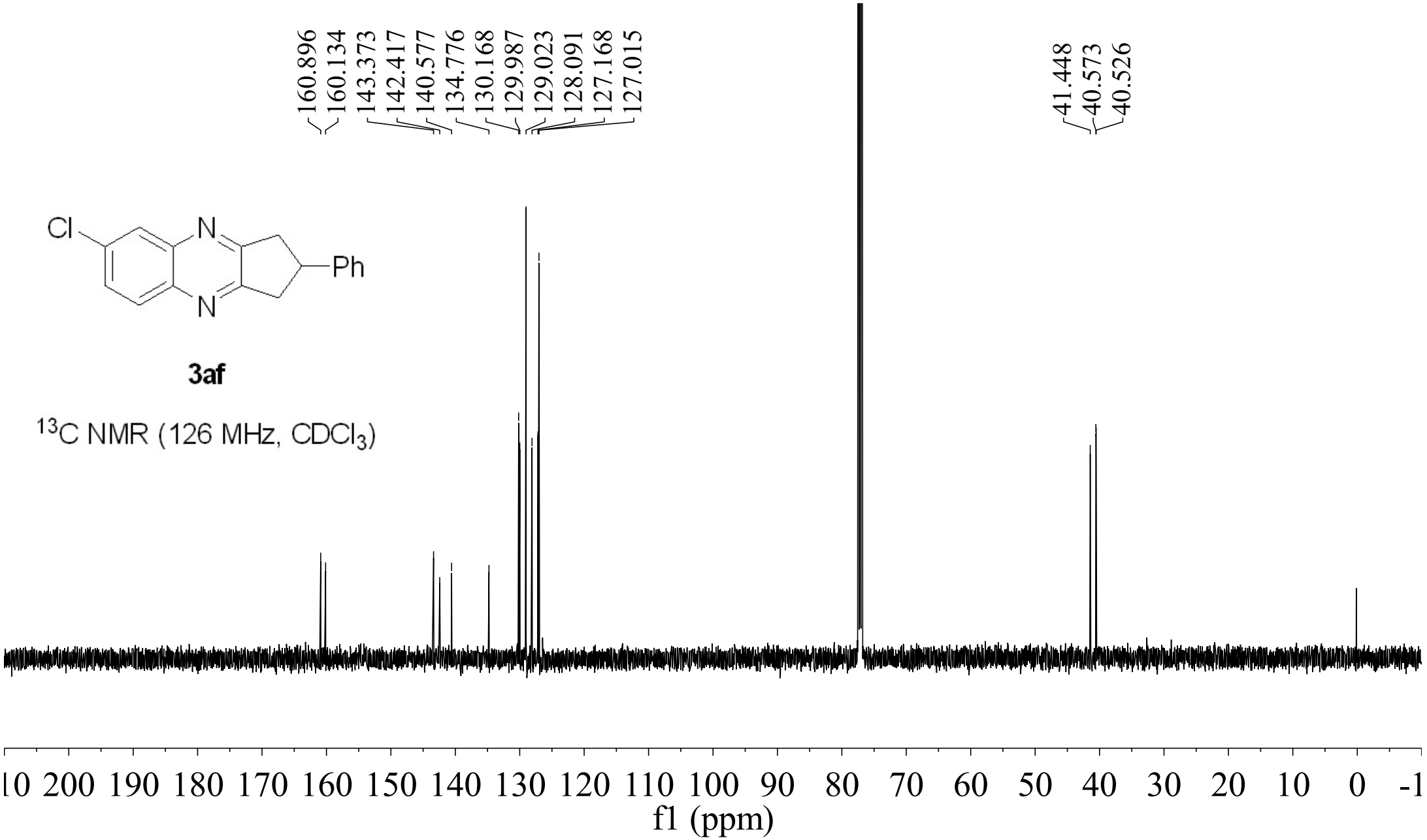

7.992
7.987
7.974
7.956
7.626
7.621
7.608
7.603
5.909
5.895
5.173
5.170
5.139
5.136
5.105
5.103
5.101
5.099
5.097
5.085
5.083
5.081
5.079
5.077
3.379
3.371
3.361
3.176
3.167
3.159
3.149
3.132
3.115
2.497
2.488
2.471
2.462
2.389
2.386
2.360
2.004
2.002
1.988
1.986
1.978
1.962
1.960
Cl
N
N
3ad
1H NMR (500 MHz, CDCl3)
0.89
1.00
0.99
0.96
0.96
1.00
0.96
2.07
1.01
1.00
1.07
1.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

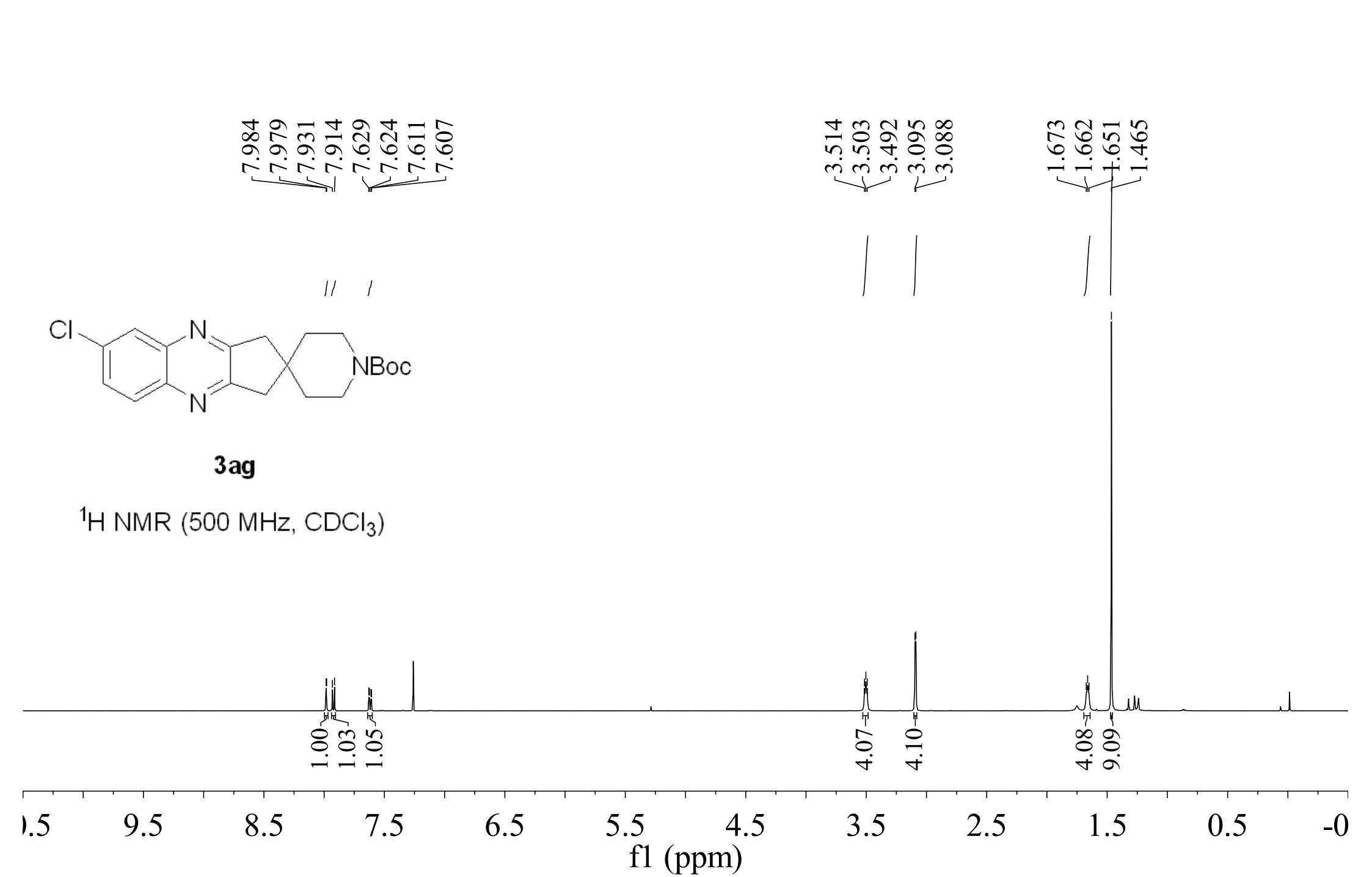

162.657
161.852
142.279
140.451
135.717
134.591
130.241
129.722
127.936
117.234
43.343
37.657
31.109
27.523
Cl
N
N
3ad
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

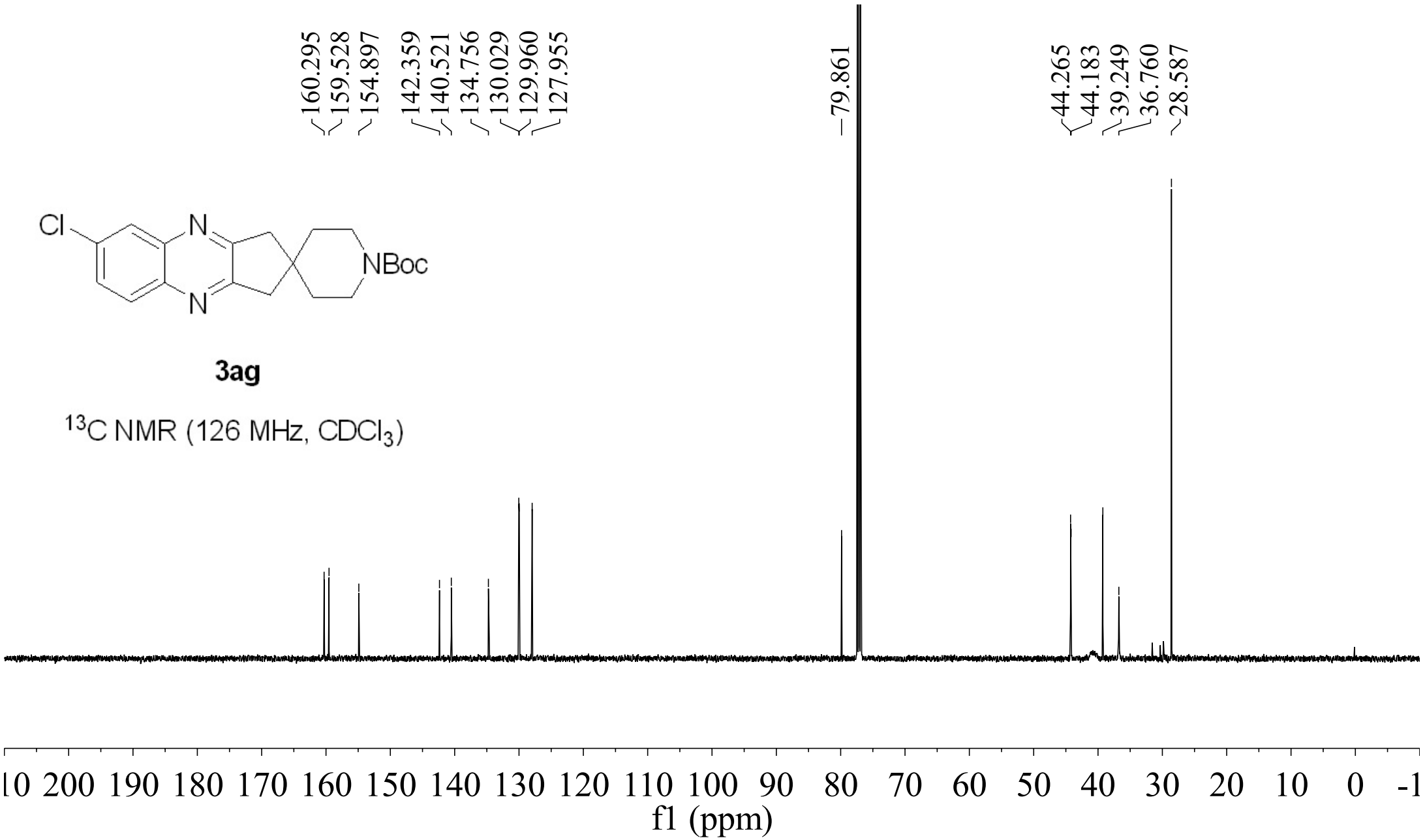

7.999
7.994
7.946
7.928
7.640
7.636
7.622
7.618
3.776
3.560
3.556
3.551
3.543
3.539
3.536
3.533
3.530
3.527
3.523
3.520
3.510
3.505
3.503
3.499
3.497
3.495
3.492
3.490
3.485
3.480
3.476
3.473
3.468
3.462
3.455
Cl
N
N
COOMe
3ae
1H NMR (500 MHz, CDCl3)
0.98
1.00
1.01
3.04
1.08
4.14
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

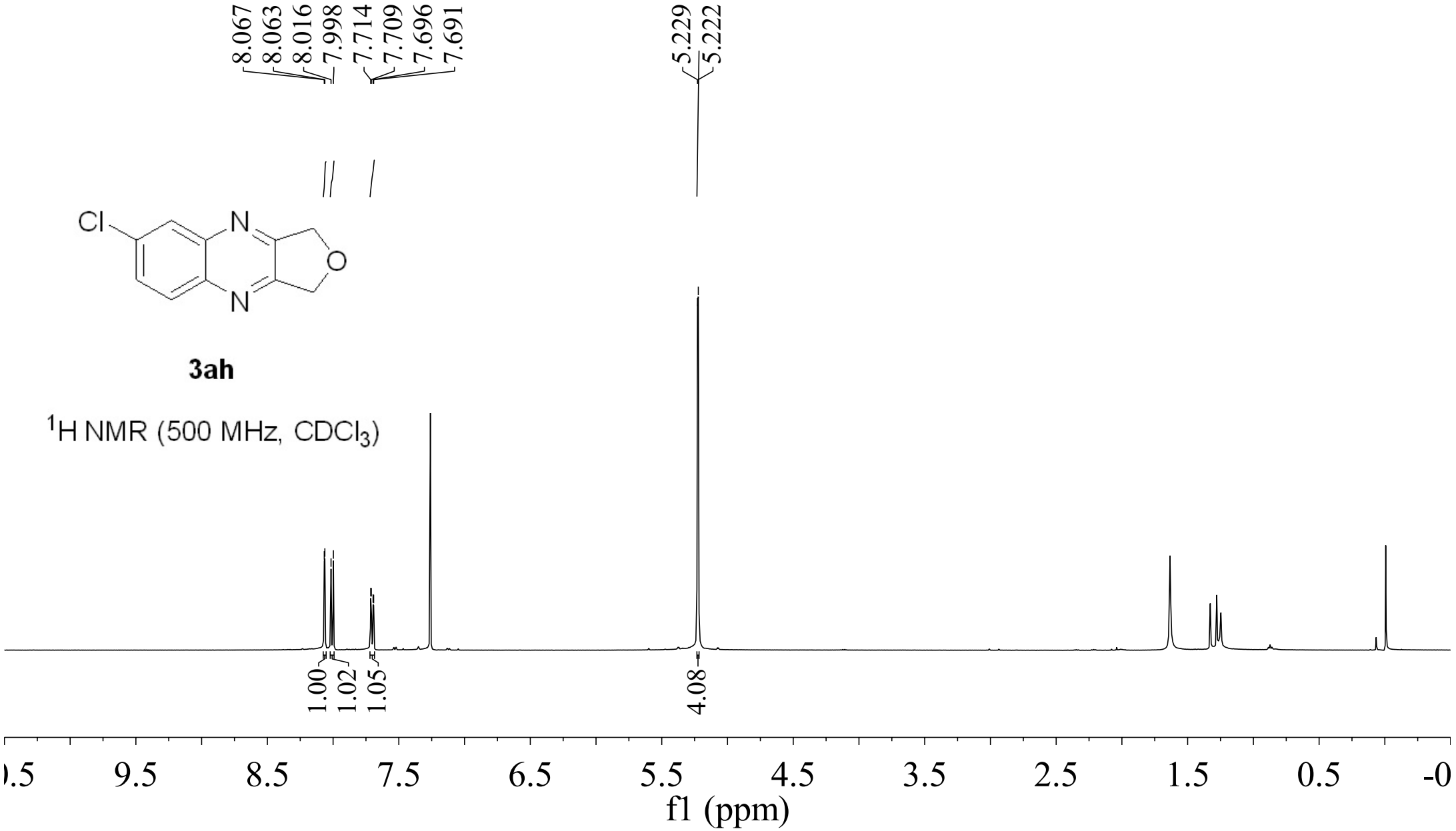

174.528
159.291
158.525
142.284
140.460
134.979
130.180
130.133
128.032
52.609
39.452
35.820
35.755
Cl
N
N
COOMe
3ae
13C NMR (126 MHz, CDCl3)
f1 (ppm)

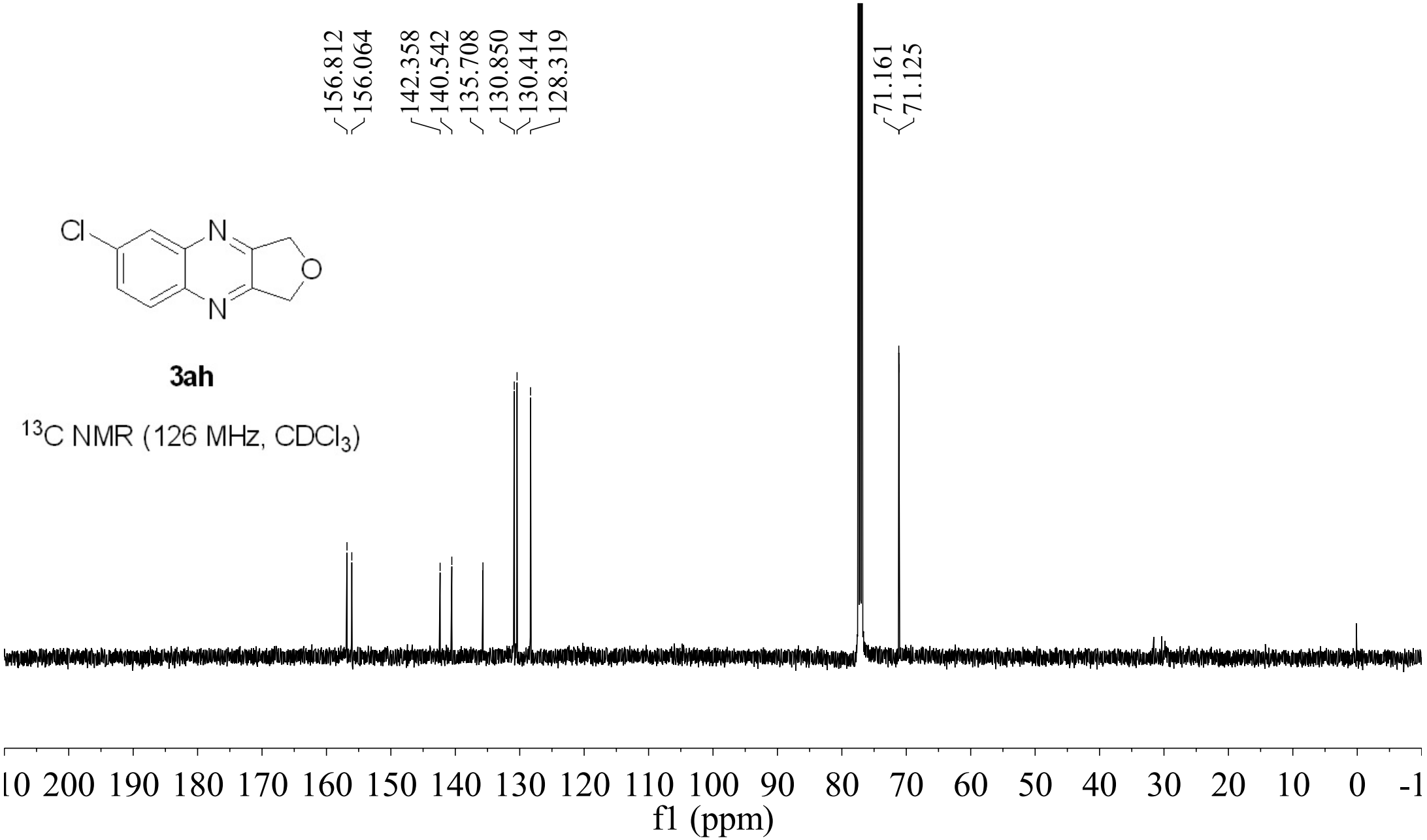

8.033
8.028
7.978
7.960
7.659
7.654
7.641
7.636
7.388
7.377
7.376
7.373
7.364
7.360
7.358
7.351
7.349
7.346
7.336
7.334
7.332
7.330
7.329
7.304
7.300
7.291
7.289
7.286
3.912
3.894
3.877
3.655
3.649
3.639
3.633
3.620
3.614
3.604
3.598
3.392
3.382
3.373
3.364
3.357
3.347
3.338
3.329
Cl
N
N
Ph
3af
1H NMR (500 MHz, CDCl3)
0.91
0.97
0.98
4.05
0.92
1.01
0.93
1.13
2.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

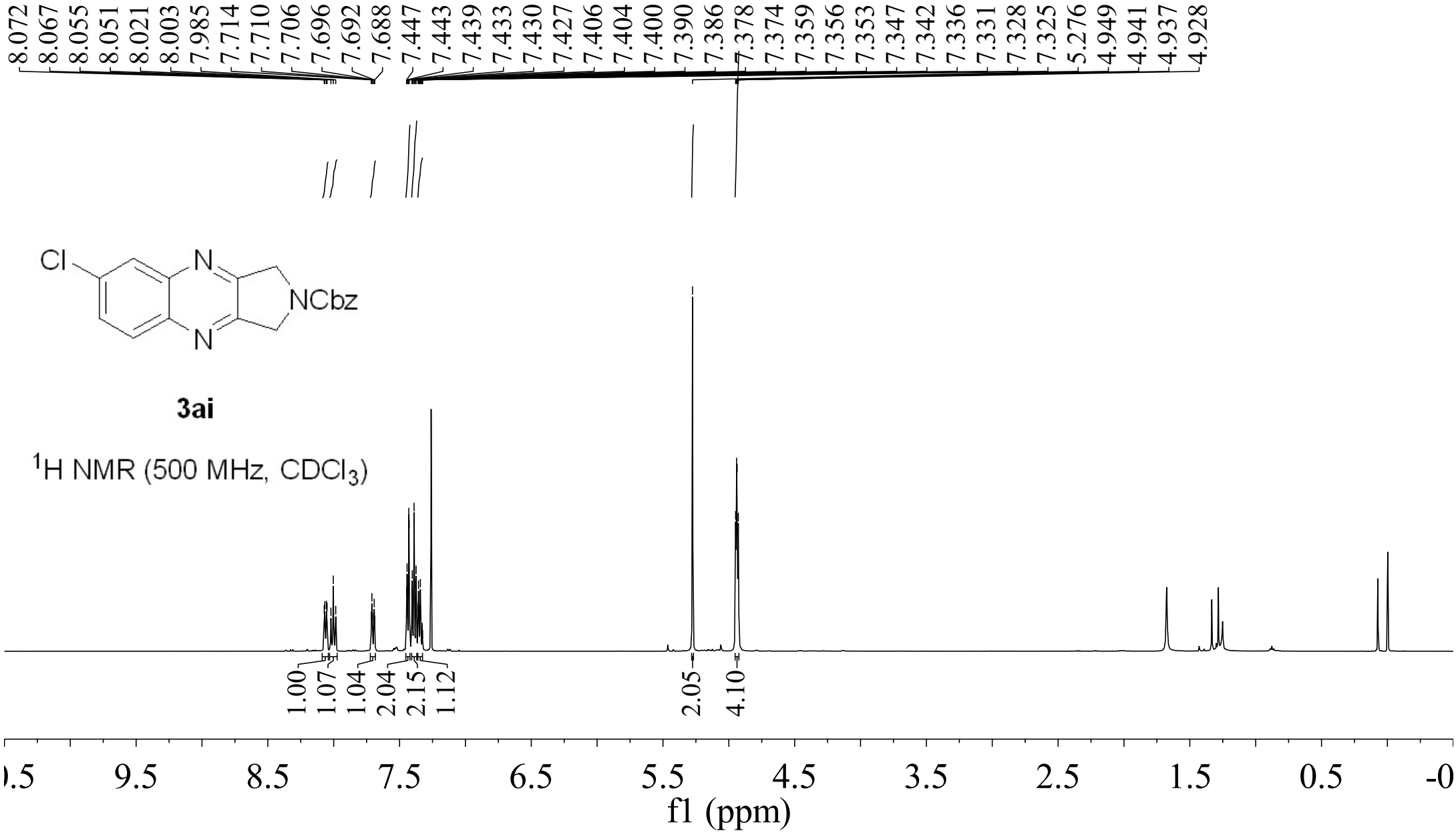

160.896
160.134
143.373
142.417
140.577
134.776
130.168
129.987
129.023
128.091
127.168
127.015
41.448
40.573
40.526
Cl
N
N
Ph
3af
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

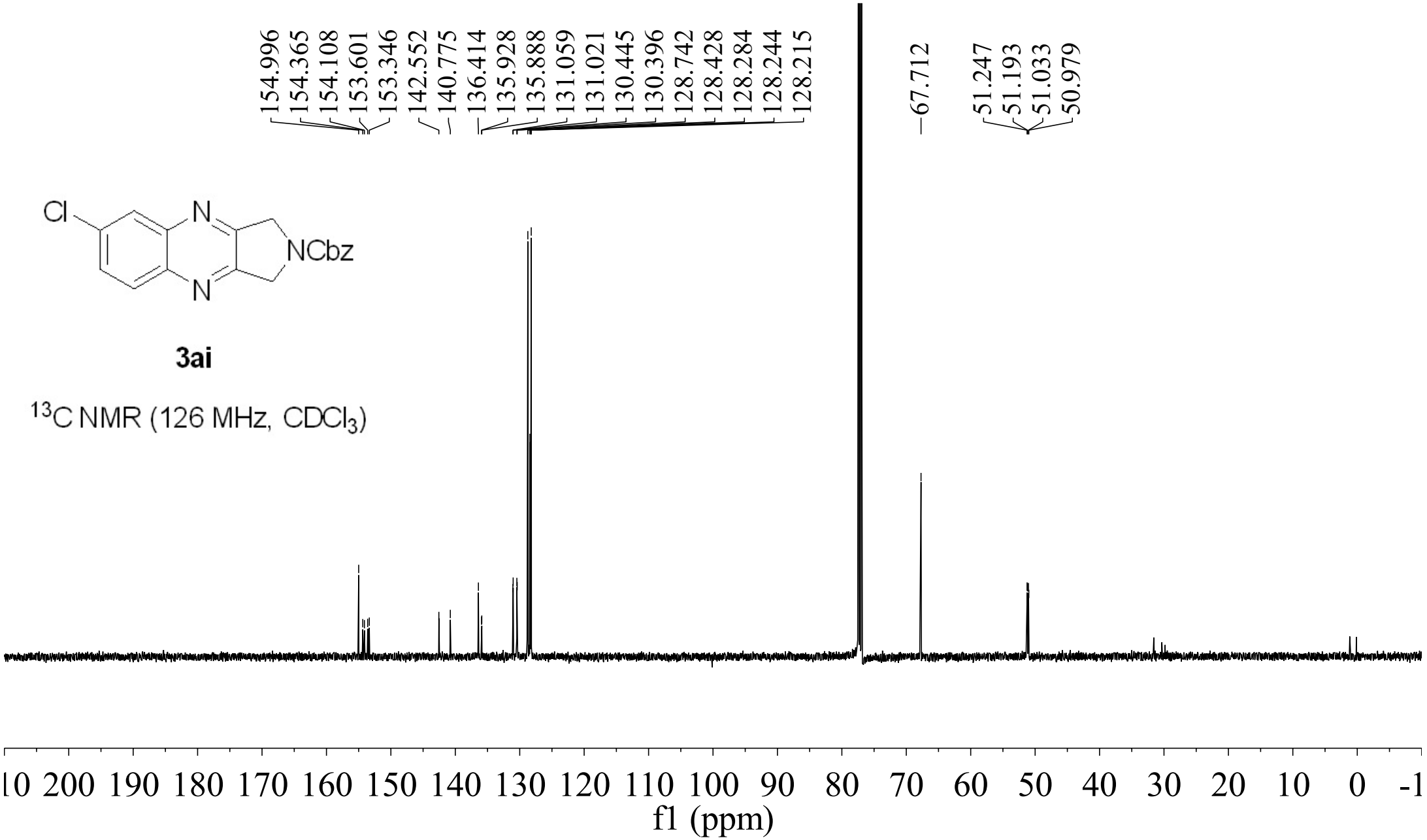

7.984
7.979
7.931
7.914
7.629
7.624
7.611
7.607
3.514
3.503
3.492
3.095
3.088
1.673
1.662
1.651
1.465
Cl
N
N
NBoc
3ag
1H NMR (500 MHz, CDCl3)
1.00
1.03
1.05
4.07
4.10
4.08
9.09
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

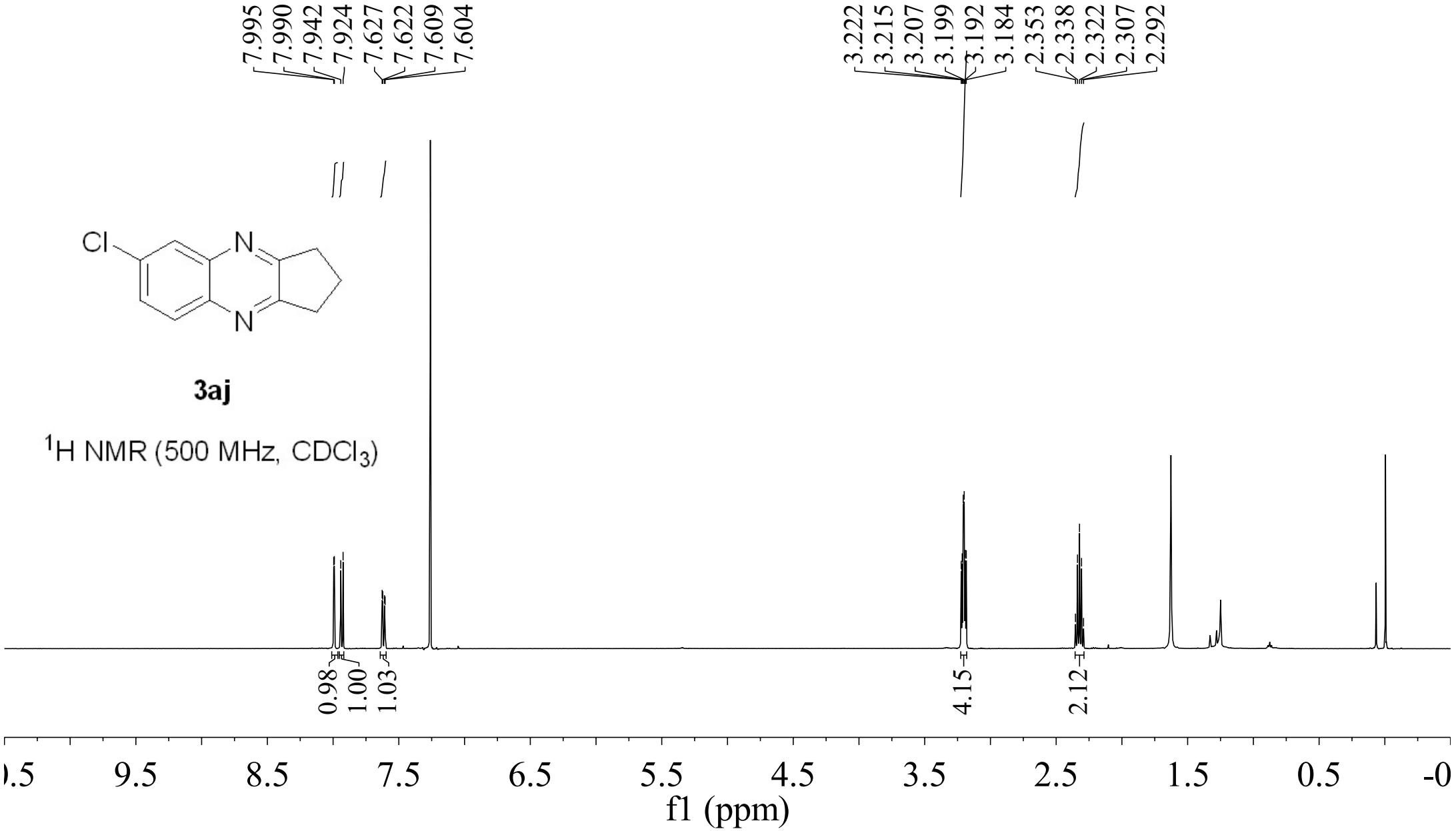

160.295
159.528
154.897
142.359
140.521
134.756
130.029
129.960
127.955
79.861
44.265
44.183
39.249
36.760
28.587
Cl
N
N
NBoc
3ag
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

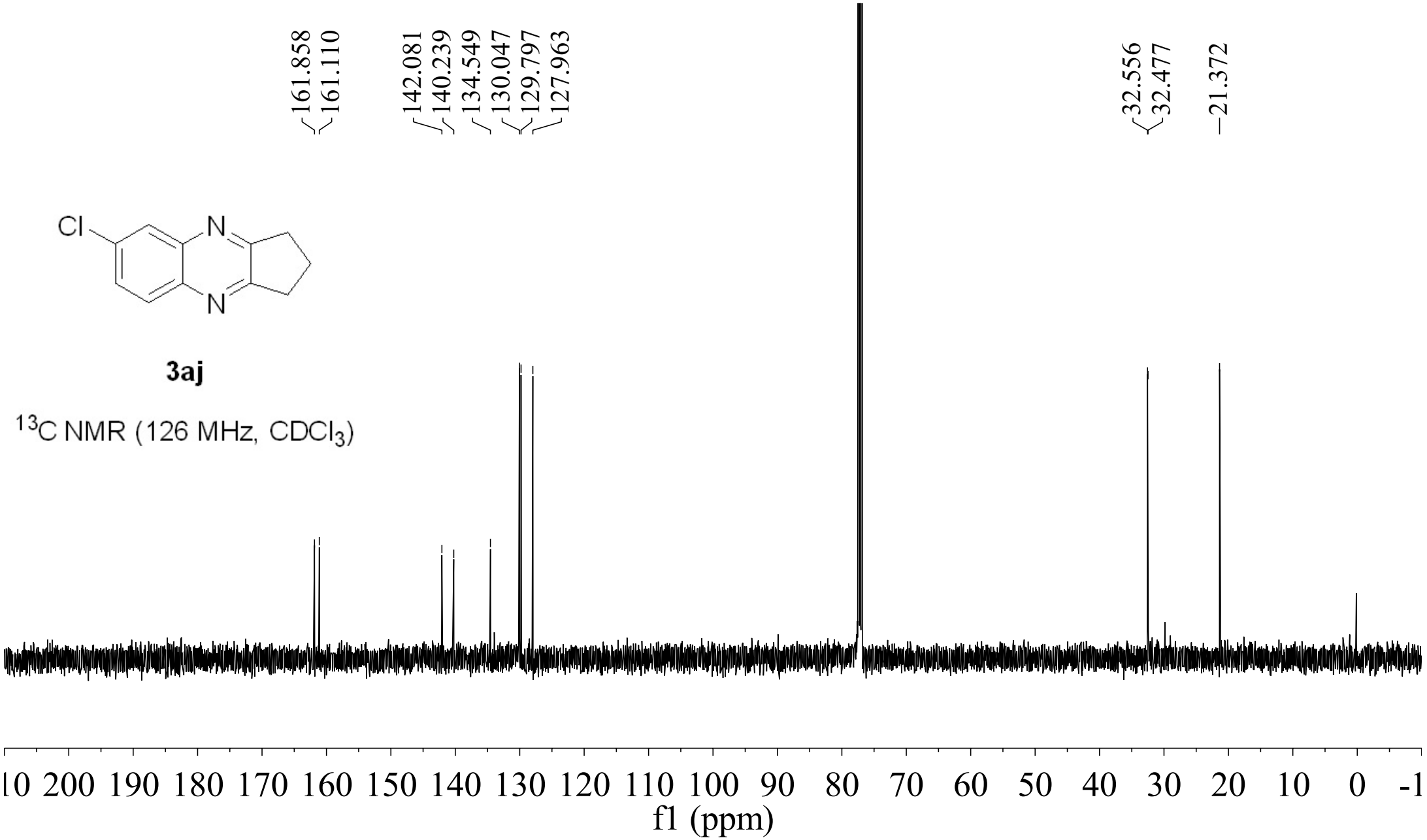

8.067
8.063
8.016
7.998
7.714
7.709
7.696
7.691
5.229
5.222
Cl
N
O
N
3ah
1H NMR (500 MHz, CDCl3)
1.00
1.02
1.05
4.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


156.812
156.064
142.358
140.542
135.708
130.850
130.414
128.319
71.161
71.125
Cl
N
O
N
3ah
^{13}C NMR (126 MHz, $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


8.072
8.067
8.055
8.051
8.021
8.003
7.985
7.714
7.710
7.706
7.696
7.692
7.688
7.447
7.443
7.439
7.433
7.430
7.427
7.406
7.404
7.400
7.390
7.386
7.378
7.374
7.359
7.356
7.353
7.347
7.342
7.336
7.331
7.328
7.325
5.276
4.949
4.941
4.937
4.928
Cl
N
NCbz
N
3ai
1H NMR (500 MHz, CDCl3)
1.00
1.07
1.04
2.04
2.15
1.12
2.05
4.10
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


154.996
154.365
154.108
153.601
153.346
142.552
140.775
136.414
135.928
135.888
131.059
131.021
130.445
130.396
128.742
128.428
128.284
128.244
128.215
67.712
51.247
51.193
51.033
50.979
Cl
N
N
NCbz
3ai
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.995
7.990
7.942
7.924
7.627
7.622
7.609
7.604
3.222
3.215
3.207
3.199
3.192
3.184
2.353
2.338
2.322
2.307
2.292
Cl
N
N
3aj
1H NMR (500 MHz, CDCl3)
0.98
1.00
1.03
4.15
2.12
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


161.858
161.110
142.081
140.239
134.549
130.047
129.797
127.963
32.556
32.477
21.372
Cl
N
N
3aj
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)