Supporting Information for

Highly Diastereoselective Functionalization of Piperidines by Photoredox Catalyzed α-Amino C–H Arylation and Epimerization

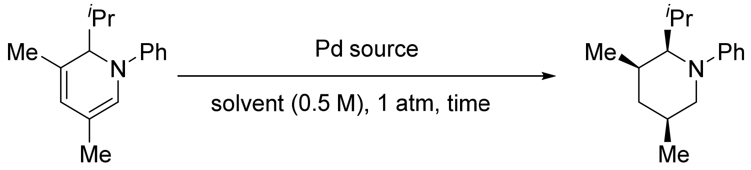
Morgan M. Walker, Brian Koronkiewicz, Shuming Chen, K. N. Houk,* James M. Mayer,* and Jonathan A. Ellman*

Table of Contents

Supplemental Optimization Tables

I. Piperidine formation

Supplemental Optimization Table S1



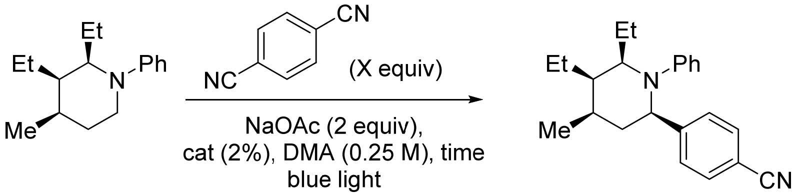
(±)-4f **(±)-1f**

Entry[a]	Pd Source (20 wt %)	Solvent	Time (h)	% Yield 1f[b]
1	Pd/C	EtOH	4	69
2	Pd/C	EtOH	14	72
3	Pd/C	EtOH + 2.0 equiv AcOH	4	47
4	Pd(OH)$_2$/C	EtOH	4	42
5	Pd(OH)$_2$/C	EtOH	14	68
6	PtO$_2$	EtOH	4	47
7	Pd/C	THF	4	72 (74%)[c]

[a] Conditions: 0.2 mmol of **4f**, Pd Source (20 wt %), solvent (0.5 M), stir at 1000 rpm. [b] Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard. [c] Isolated yield from silica gel chromatography.

II. Reaction conditions

Supplemental Optimization Table S2

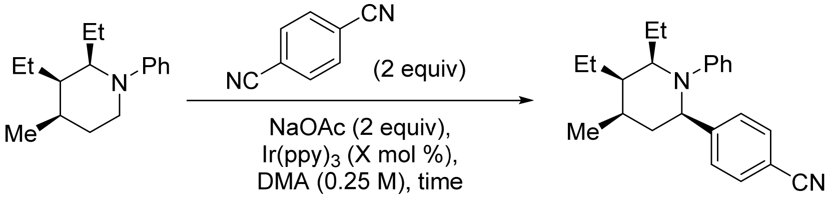


(±)-1a **(±)-2a**

Entry[a]	Catalyst (2 mol %)	Cyanoarene Equiv	Time (h)	% Yield 2a[b]
1	Ir(ppy)$_3$	1.0	16	61
2	Ir(ppy)$_3$	2.0	16	79
3	Ir(ppy)$_3$	2.0	72	78
4	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	2.0	16	73
5	No cat[c]	2.0	16	10
6	Ir(ppy)$_3$ (no light)	2.0	16	<5
7	Ir(ppy)$_3$ (set up in air)	1.0	16	<5 (decomp)

[a] Conditions: 0.06 mmol of **1a**, handmade blue light setup. [b] Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard. [c] Glassware cleaned with aqua regia prior to use.

Supplemental Optimization Table S3



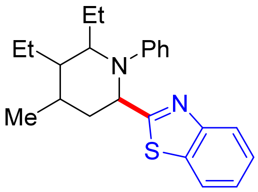
(±)-1a **(±)-2a**

Entry[a]	Scale (mmol)	Ir(ppy)$_3$ (X mol %)	Time (h)	% Yield 2a[b]
1	0.06	2	16	79
2	0.2	1	16	78
3	0.2	1	2	83 (86)[c]

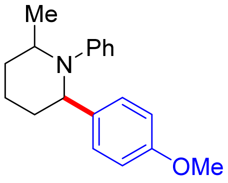
[a]Conditions: **1a** is the limiting reagent. Photoreactor 50% LED. [b]Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard. [c]Isolated yield from silica gel chromatography.

Table S4. Unsuccessful reactants

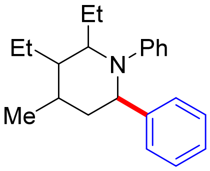
Examining other arene coupling partners:



<10%
(from 2-chlorobenzothiazole)

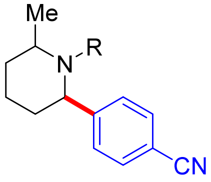


<5%

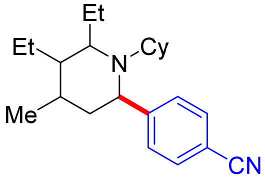


<5%

Examining additional N-substituents



R = Piv, <5%
= Ts, <5%
= Boc, <5%



<10%

General Methods

For air-sensitive reactions, glassware was dried at 150 °C for at least 12 h and allowed to cool under an inert atmosphere. Air-senstive experiments were set up inside a Vacuum Atmospheres glovebox under nitrogen atmosphere with oxygen and moisture levels not exceeding 10 ppm. All photoredox catalyzed reactions were set up on the bench top and subsequently were submitted to 3 freeze/pump/thaw cycles in the dark. Solvents for air-sensitive reactions were dried by passing through activated alumina, degassed and stored over 3 Å molecular sieves in a glove box. Dimethylacetamide was distilled prior to use over BaO under reduced pressure and stored in a Schlenk flask on the benchtop. Solvents of ACS reagent grade were used for work-up and purification. Alkynes and liquid amines were distilled under a nitrogen atmosphere or *in vacuo*, and stored in a glovebox prior to use.

$Ir(ppy)_3$ was purchased from Strem and stored in a dessicator. Stock solutions of the $Ir(ppy)_3$ catalyst were prepared by dissolving $Ir(ppy)_3$ (2.5 mg, 3.8 μmol) in 150 μL of DMA and were used immediately. $[Ir(dtbbpy)(ppy)_2]PF_6$ was purchased from Strem and stored in a dessicator. Stock solutions of the $[Ir(dtbbpy)(ppy)_2]PF_6$ catalyst were prepared by dissolving $[Ir(dtbbpy)(ppy)_2]PF_6$ (5.0 mg, 5.5 μmol) in 220 μL of DMA and were used immediately. Sodium acetate (NaOAc) was crushed with a mortar and pestle, then dried at 130 °C overnight and stored in a dessicator. 1,4-Dicyanobenzene and 4-cyanopyridine were crushed with a mortar and pestle prior to use. $[RhCl(coe)_2]_2$ was purchased from Strem and stored inside an N_2-filled glovebox at -25 °C. The ligand, p-Me_2N-C_6H_4-PEt_2, was purchased from Sigma-Aldrich and stored inside an N_2-filled inert atmosphere glovebox at -25 °C. Stock solutions of the rhodium catalyst were prepared by dissolving $[RhCl(coe)_2]_2$ (200 mg, 279 μmol) and p-Me_2N-C_6H_4-PEt_2 (117 mg, 558 μmol) in anhydrous toluene until a total volume of 6.0 mL was reached. Stock solutions could be used immediately after mixing, and showed no difference in catalytic activity after being stored for months in a -25 °C freezer inside an N_2-filled glovebox.

Flash-column chromatography was performed with Sorbent Technologies 40-63 Å silica (230-400 mesh). Preparative thin-layer chromatography was carried out with plates from Analtech (1 mm SiO_2, 20 x 20 cm). Reverse phase chromatography was performed with a Teledyne Isco automated chromatography system using C18 gold columns. The products were visualized on TLC by UV or through staining with $KMnO_4$. NMR characterization was performed on either a 400, 500, or 600 MHz instrument. NMR data are reported in the following format: chemical shift in ppm, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc.), coupling constant J in Hz, and integration. All spectra were referenced against residual solvent peaks (^1H: 7.26 ppm for $CDCl_3$; ^{13}C: 77.0 ppm for $CDCl_3$, 206.3 for $(CD_3)_2CO$). IR spectra were obtained using FT-IR instruments. Melting points are reported uncorrected. High resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time-of-flight (TOF) mass spectrometer.

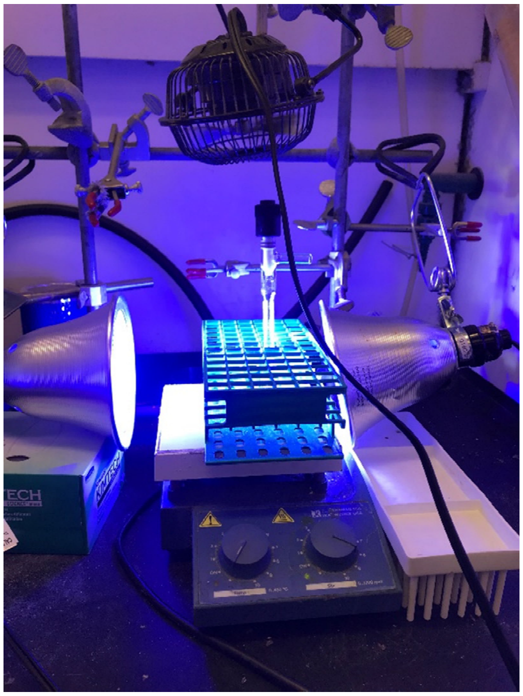
Spectroelectrochemistry experiments were done in a 3-electrode setup in a (10 X 2) mm cuvette, using conductive contacts and fiber optic cables to take measurements in an N_2-glovebox. Electrochemistry data was collected with a CH Instruments potentiostat (model 600D) using a Pt-mesh working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl pseudoreference electrode in 0.1M $[n\text{-}Bu_4N][PF_6]$ DMA. Absorbance measurements were recorded on a Cary 60 UV-Vis (Agilent), through the short pathlength of the cuvette after holding the electrode a potential which oxidizes $Ir(ppy)_3$. The Pt-mesh working electrode was carefully kept in the short pathlength portion of the cuvette while the auxiliary and reference electrodes were submerged in the electrolyte solution near the top of the cuvette.

Time-correlated single photon counting (TCSPC) measurements were taken on a HORIBA Jobin Yvon TD-Fluor Fluorolog-3 fluorimeter using a HORIBA 390 nm NanoLED excitation pulse and measuring emission at 530 nm. Measurements were taken with 60μM $Ir(ppy)_3$ in DMA unless otherwise noted. Solutions were prepared in an N_2 glovebox in 10 x 2 mm cuvettes having an air-tight Kontes adapter, with excitation in the 10 mm path and fluorescence measured from the 2mm path. Data analysis and fitting was done with Igor Pro 8 software package.

Transient absorption spectroscopy was performed a previously reported setup.[1] Excitation was provided by a Spectra-Physics Nd/YAG laser (Quanta-Ray) and basiScan OPO at 430nm. Absorbance changes were monitored at a 90˚ angle to the excitation beam using an Edinburgh Instruments Xe900 xenon lamp and an LP920-K UV-Vis detector. The excitation power measured and optimized before measurements. Typical powers were between 6-8 mJ/pulse.

Light Set ups

I. Handmade light setup



Schlenk flasks were used for all optimization reactions and placed in a test tube rack on a stir plate. A fan was placed overhead to keep the area cool from the lights. The lights were bought from Amazon – ABI LED Aquarium Light Bulb, 23 W Blue and White PAR 38. Two lights were used and placed on either side of the Schlenk flask – one 5 cm from the Schlenk flask, the other 13 cm from the Schlenk flask. The stir rate was >1000 rpm.

II. Photoreactor

The Penn Optical Coatings Photoreactor (http://www.pennoc.com/photo-reactor/) was used for the scope and epimerization studies. The 450 nm light source was used. The touch screen on the photoreactor was used to set the light source to 50% LED for all reactions, set the stir rate to 1000 rpm, and set the fan to 6800 rpm. Schlenk flasks were used for all reactions that measured 12 cm tall with the Teflon cap on.

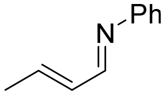
Preparation of Intermediates

I. Imines

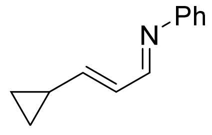
Imines: (1*E*,2*E*)-*N*,3-diphenylprop-2-en-1-imine, (1*E*,2*E*)-2-methyl-*N*-phenylbut-2-en-1-imine were prepared according to previous literature procedures.[2]

General Procedure A for the preparation of imines:

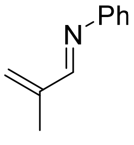
The following protocol is adapted from a literature procedure.[3] A round-bottom flask equipped with a stir bar was charged with enal (1.0 equiv), dry tetrahydrofuran (THF) (0.7 M), titanium(IV) ethoxide (2.0 equiv), and aniline (1.0 equiv). The flask was put under an N_2 atmosphere and stirred for 1 h at rt. The reaction mixture was diluted with diethyl ether (Et_2O), and saturated sodium bicarbonate was added to the mixture. A white precipitate formed and the mixture was filtered over celite and washed with Et_2O. The filtrates were poured into a separatory funnel, and the layers were separated. The organic layer was washed with brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. The residue was filtered through basic Al_2O_3 (eluent: pentane), and the filtrate was concentrated *in vacuo* to give imine **3** which was stored at -25 °C under an N_2 atmosphere in a glovebox.



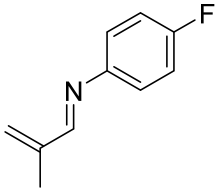
3a: General Procedure A was followed using (*E*)-but-2-enal (1.2 mL, 15 mmol, 1.0 equiv), dry THF (21 mL, 0.7 M), titanium(IV) ethoxide (7.3 mL, 30 mmol, 2.0 equiv) and aniline (1.4 mL, 15 mmol, 1.0 equiv). Filtration through Al_2O_3 (eluent: pentane) provided imine **3a** as a pale yellow oil (436 mg, 20%). Spectroscopic data are in agreement with reported values.[4]



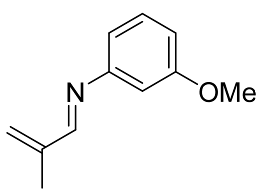
3b: General Procedure A was followed using (*E*)-3-cyclopropylprop-2-enal (2.24 g, 23.3 mmol, 1.0 equiv), dry THF (33 mL, 0.7 M), titanium(IV) ethoxide (11.5 mL, 46.6 mmol, 2.0 equiv) and aniline (2.21 mL, 23.3 mmol, 1.0 equiv). Filtration through Al_2O_3 (eluent: pentane) provided imine **3b** as a pale yellow oil (691 mg, 17%). Material must be used immediately – decomposition occurs. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 9.1 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.20 – 7.16 (m, 1H), 7.11 – 7.09 (m, 2H), 6.51 (dd, *J* = 15.4, 9.1 Hz, 1H), 5.92 (dd, *J* = 15.4, 9.5 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.00 – 0.95 (m, 2H), 0.66 – 0.62 (m, 2H).



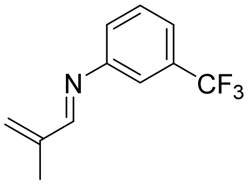
3e: General Procedure A was followed using 2-methylprop-2-enal (1.6 mL, 20 mmol, 1.0 equiv), dry THF (29 mL, 0.7 M), titanium(IV) ethoxide (8.4 mL, 40 mmol, 2.0 equiv) and aniline (1.9 mL, 20 mmol, 1.0 equiv). Filtration through Al_2O_3 (eluent: pentane) provided imine **3e** as a pale yellow oil (1.53 g, 54%). Spectroscopic data are in agreement with reported values.[5]



3i: General Procedure A was followed using 2-methylprop-2-enal (828 µL, 10.0 mmol, 1.00 equiv), dry THF (14 mL, 0.7 M), titanium(IV) ethoxide (4.9 mL, 20 mmol, 2.0 equiv) and 4-fluoroaniline (947 µL, 10 mmol, 1.0 equiv). Filtration through Al_2O_3 (eluent: pentane) provided imine **3i** as a pale yellow oil (599 mg, 37%). IR (neat): 2964, 1607, 1499, 1226, 1198, 913, 828, 776 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.11 – 7.01 (m, 4H), 5.77 (s, 1H), 5.59 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 161.1 (d, *J* = 244.2 Hz), 148.1, 144.1, 126.7, 122.2 (d, *J* = 8.3 Hz), 115.7 (d, *J* = 22.5 Hz), 16.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.7 – -117.8 (m).



3j: A modification to General Procedure A was followed using 2-methylprop-2-enal (828 µL, 10.0 mmol, 1.00 equiv), dry THF (14 mL, 0.7 M), titanium(IV) ethoxide (4.9 mL, 20 mmol, 2.0 equiv) and 3-methoxyaniline (1.1 mL, 10 mmol, 1.0 equiv). Following work-up, the crude was not filtered and directly gave approximately 80-90% pure imine **3j** (1.04 g, 60%) as a yellow oil. IR (neat): 2957, 2835, 1591, 1480, 1261, 1160, 1143, 1038, 753, 687 cm^{-1}. ^1H NMR (600 MHz, Chloroform-d) δ 8.09 (s, 1H), 7.27 – 7.24 (m, 1H), 6.77 – 6.75 (m, 1H), 6.70 – 6.67 (m, 2H), 5.77 (s, 1H), 5.59 (s, 1H), 3.82 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.6, 160.2, 153.6, 144.1, 129.8, 126.8, 112.8, 111.6, 106.5, 55.3, 16.8.

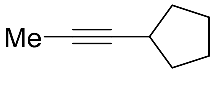


3k: General Procedure A was followed using 2-methylprop-2-enal (828 µL, 10.0 mmol, 1.00 equiv), dry THF (14 mL, 0.7 M), titanium(IV) ethoxide (4.9 mL, 20 mmol, 2.0 equiv) and 3-(trifluoromethyl)aniline (1.3 mL, 10 mmol, 1.0 equiv). Filtration through Al_2O_3 (eluent: pentane) provided imine **3k** as a pale yellow oil (710 mg, 33%). IR (neat): 2958, 1612, 1439, 1323, 1162, 1119, 1065, 900, 795, 697 cm^{-1}. ^1H NMR (600 MHz, Chloroform-d) δ 8.08 (s, 1H), 7.47 – 7.44 (m, 2H), 7.35 – 7.34 (m, 1H), 7.27 – 7.25 (m, 1H), 5.83 (s, 1H), 5.64 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) 164.8, 152.6, 143.9, 131.5 (q, *J* = 32.3 Hz), 129.5, 127.8, 124.02, 123.99 (q, *J* = 272.5 Hz), 122.2 (q, *J* = 3.7 Hz), 117.7 (q, *J* = 3.8 Hz), 16.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.7.

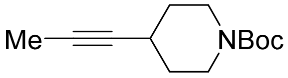
II. Alkynes

General Procedure B for the preparation of alkynes:

The following protocol is adapted from a literature procedure.[6] A flame dried 250-mL round-bottom flask equipped with a stir bar was placed under N_2 and charged with the terminal alkyne (1.0 equiv) and dry THF (0.3 M total concentration). The mixture was cooled to -78 °C and *n*-BuLi (2.1 M in hexanes, 1.0 equiv) was added dropwise. The reaction mixture was slowly warmed to rt, then MeI (1.5 equiv) was added dropwise. The reaction mixture was stirred overnight at rt. The reaction was quenched with water (100 mL), and the resulting solution was diluted with diethyl ether (Et_2O) (100 mL), and the layers were separated. The organic layer was additionally washed with water (50 mL) followed by brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified via silica gel chromatography to provide the product **alkyne**.

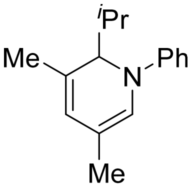


alkyne a: General procedure B was followed using ethynylcyclopentane (3.0 g, 32 mmol, 1.0 equiv) dissolved in 92 mL of THF, *n*-BuLi (2.1 M in hexanes, 15 mL, 32 mmol, 1.0 equiv) and MeI (3.0 mL, 48 mmol, 1.5 equiv). Purification by silica gel chromatography (eluent: pentane) provided the product **alkyne a** (1.61 g, 47%) as a clear oil. IR (neat): 2957, 2870, 1451, 1345 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.56 – 2.51 (m, 1H), 1.91 – 1.85 (m, 2H), 1.79 (d, *J* = 2.4 Hz, 3H), 1.73 – 1.68 (m, 2H), 1.57 – 1.50 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 83.6, 74.9, 34.0, 30.3, 24.9, 3.6. HRMS-EI (m/z): [M] calcd for [C_8H_{12}], 108.0939; found, 108.0943.



alkyne b: General procedure B was followed using *tert*-butyl 4-ethynylpiperidine-1-carboxylate (1.0 g, 4.8 mmol, 1.0 equiv) dissolved in 14 mL of THF, *n*-BuLi (2.1 M in hexanes, 2.3 mL, 4.8 mmol, 1.0 equiv) and MeI (450 µL, 7.2 mmol, 1.5 equiv). Purification by silica gel chromatography (eluent 1:10:89 NEt_3/EtOAc/hexanes) provided the product **alkyne b** (663 mg, 62%) as a clear oil. Spectroscopic data are in agreement with reported values.[6]

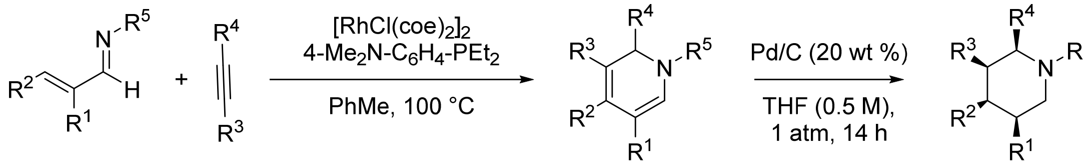
III. Dihydropyridines



(±)-4f: The following protocol is based on a literature procedure.[3] In an N_2-filled glove box, a 20-mL vial was charged with imine **3e** (576 mg, 3.97 mmol, 1.00 equiv). Rh stock solution (see General Methods) (2.1 mL, 0.20 mmol, 5 mol %) was added to the vial, and the contents were transferred to a Schlenk flask. The vial was rinsed with toluene (0.5 mL x 2), and the washings were likewise transferred to the Schlenk flask. 4-Methylpent-2-yne (550 µL, 4.8 mmol, 1.2 equiv) was added to the Schlenk flask and toluene (5 mL) was added. The contents were thoroughly mixed and *ca*. 0.6 mL was removed by pipet and transferred to a J. Young NMR tube equipped with a C_6D_6 capillary (for locking and shimming). The Schlenk flask and the J. Young tube were capped and then taken to a fume hood where they were heated to 100 °C for 24 h, at which point analysis by ^{1}H NMR of the J. Young tube indicated complete conversion to the 1,2-dihydropyridine. The crude reaction mixture was then concentrated *in vacuo* and filtered through buffered silica gel (pre-treated with 10:90 NEt_3/pentane overnight; eluent: 1:99 NEt_3/pentane) to give the indicated DHP **4f** (869 mg, 96%) as a pale yellow oil which was stored at -25 °C under an N_2 atmosphere in a glovebox. IR (neat): 2955, 2927, 1584, 1498, 1380, 1297, 1228, 1033, 967, 847, 746, 691 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 2H), 6.95 – 6.94 (m, 2H), 6.87 – 6.84 (m, 1H), 6.07 (s, 1H), 5.72 (s, 1H), 3.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.87 (s, 3H), 1.84 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.9, 129.0, 126.2, 122.3, 121.2, 119.3, 115.4, 114.9, 65.3, 31.6, 23.4, 20.9, 19.0, 17.6. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{16}H_{21}N+H$]$^+$, 228.1747; found, 228.1752.

IV. Piperidines

General procedure C for the formation of piperidines on small scale:

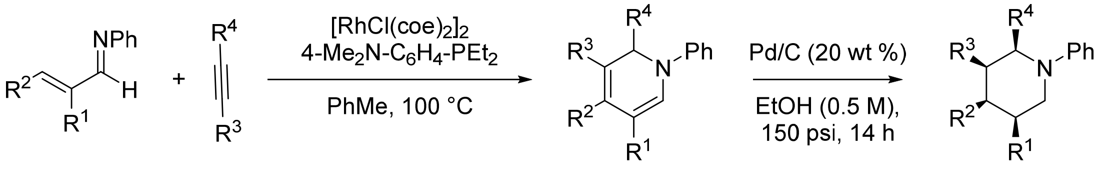


crude
(±)-4

(±)-1

In an N_2-filled glove box, a 4-mL vial was charged with the indicated imine (1.0 equiv). Rh stock solution (see General Methods) was added to the vial, and the contents were transferred to a J. Young NMR tube equipped with a C_6D_6 capillary (for locking and shimming). The vial was rinsed with toluene (0.1 mL x 2), and the washings were likewise transferred to the J. Young tube. Alkyne (1.5 equiv) was added to the J. Young tube, and toluene was added until the total volume reached *ca.* 0.6 mL. The J. Young tube was quickly capped, and the contents were thoroughly mixed. The J. Young tube was then taken to a fume hood where it was heated to 100 °C for 24 h, at which point analysis by ^{1}H NMR often indicated complete conversion to the 1,2-dihydropyridine. If incomplete conversion was observed, the J. Young tube was taken back into the glove box where an additional amount of Rh stock solution was added directly. The J. Young tube was then taken to a fume hood where it was heated to 100 °C for 24 h. The addition of Rh stock solution was continued every 24 h until complete conversion to the 1,2-dihydropyridine was observed by ^{1}H NMR. The crude reaction mixture was then concentrated *in vacuo* and filtered through buffered silica gel (pre-treated with 10:90 NEt_3/pentane overnight; eluent: 1:99 NEt_3/pentane) to give the indicated DHP **4**. The entire crude DHP **4** was then taken onto the hydrogenation reaction by transferring the crude product with THF (0.5 M, sparged for 15 minutes prior to use) to a 4-mL vial equipped with a magnetic stir bar. Pd/C (20 wt %, based on theoretical yield of DHP **4**) was then added to the solution and the vial was purged with N_2 for 5 min. The vial was then purged with an H_2 balloon three times, and then electrical tape and Parafilm were used to seal the vial. The reaction mixture was then stirred at 1000 rpm for 14 h under an H_2 atmosphere (1 atm). The H_2 balloon was removed and the heterogeneous mixture was filtered over Celite (eluent: diethyl ether) and concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography to give the indicated product. Yield indicates overall yield from the starting imine **3**.

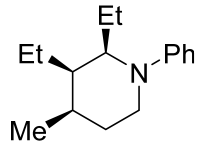
General procedure D for the formation of piperidines on larger scale:



crude
(±)-4

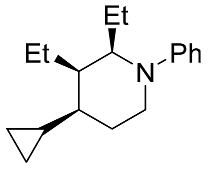
(±)-1

In an N_2-filled glove box, a 20-mL vial was charged with the indicated imine (1.0 equiv). Rh stock solution (see General Methods) was added to the vial, and the contents were transferred to a Schlenk flask. The vial was rinsed with toluene (0.5 mL x 2), and the washings were likewise transferred to the Schlenk flask. Alkyne (1.2 equiv) was added to the Schlenk flask, and toluene was added until the total concentration reached *ca.* 0.5 M. The contents were thoroughly mixed and *ca.* 0.6 mL was removed by pipet and transferred to a J. Young NMR tube equipped with a C_6D_6 capillary (for locking and shimming). The Schlenk flask and the J. Young tube were capped and then taken to a fume hood where they were heated to 100 °C for 24 h, at which point analysis by ^{1}H NMR of the J. Young tube indicated complete conversion to the 1,2-dihydropyridine. The crude reaction mixture was then concentrated *in vacuo* and filtered through buffered silica gel (pre-treated with 10:90 NEt_3/pentane overnight; eluent: 1:99 NEt_3/pentane) to give the indicated DHP **4**. The entire crude DHP **4** was then taken onto the hydrogenation reaction by transferring the crude product with EtOH (sparged for 15 min prior to use) to a 20-mL vial equipped with a magnetic stir bar. Pd/C (20 wt %, based on mass of crude mixture) was then added to the solution, and the vial was placed in a Parr reactor. The Parr reactor was purged with H_2, then pressurized to ~150 psi. After stirring for 14 h at 1000 rpm, the Parr reactor was opened and the heterogeneous mixture was filtered over Celite (eluent: diethyl ether) and concentrated *in vacuo*. The crude product was then purified by C18 reverse phase chromatography to give the indicated product. Yield indicates overall yield from the starting imine **3**.

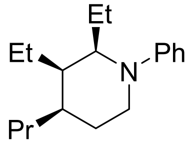


(±)-1a: General procedure D was followed using the imine **3a** (436 mg, 3.00 mmol, 1.00 equiv) and hexyne (409 µL, 3.6 mmol, 1.20 equiv). Rh stock solution (798 µL, 75.0 µmol, 2.5 mol %) was added and the reaction was carried out for 24 h. Following concentration, 415 mg of a crude mixture was obtained and dissolved in EtOH (3.7 mL). Pd/C (83 mg, 20 wt % of crude mass) was then added to the crude mixture and hydrogenation was conducted per general procedure D. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **1a** (177 mg, 25%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2960, 2873, 1596, 1500, 1397, 1220, 1150, 942, 746, 690 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.18 (m, 2H), 6.91 – 6.89 (m, 2H), 6.72 – 6.68 (m, 1H), 3.56 – 3.52 (m, 1H), 3.33 (dt, *J* = 13.9, 4.1 Hz, 1H), 3.25 – 3.18 (m, 1H), 1.98 – 1.82 (m, 2H), 1.75 – 1.69 (m, 1H), 1.67 – 1.48 (m, 2H), 1.44 – 1.32 (m, 3H), 1.02 (d, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.4, 129.0, 117.3, 116.0, 63.0, 42.9, 39.0, 30.6, 30.0, 22.9, 21.5, 15.5, 13.1, 12.3. HRMS-ESI (m/z): [M+H]$^{+}$ calcd for $[C_{16}H_{25}N+H]^{+}$, 232.2060; found, 232.2065.

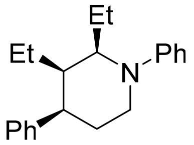
(±)-1b + (±)-1c: A modification to General procedure D was followed using the imine **3b** (2.93 g, 17.1 mmol, 1.00 equiv) and 3-hexyne (2.3 mL, 20.5 mmol, 1.20 equiv). Rh stock solution (9.1 mL, 0.86 mmol, 5 mol %) was added. After 24 h, ^{1}H NMR analysis indicated complete conversion to a mixture of the cyclopropyl and propyl 1,2-dihydropyridine products. Following concentration, 297 mg of a crude mixture was obtained and dissolved in EtOH (2.3 mL). Pd/C (234 mg, 20 wt % of crude mass) was then added to the crude mixture and hydrogenation was conducted per general procedure D. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided each of the products separately [the isolated yield of each compound was not optimized; mixed fractions were discarded].



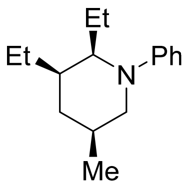
Isolated product **(±)-1b** (76.0 mg, 2% of pure isolated compound, >95:5 *dr*) as a pale yellow oil. IR (neat): 2959, 2872, 1596, 1499, 1377, 1254, 1155, 951, 746, 691 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.20 (m, 2H), 6.94 – 6.92 (m, 2H), 6.76 – 6.73 (m, 1H), 3.53 – 3.49 (m, 1H), 3.32 (dt, *J* = 13.6, 4.2 Hz, 1H), 3.29 – 3.24 (m, 1H), 1.81 – 1.76 (m, 2H), 1.69 – 1.64 (m, 2H), 1.63 – 1.58 (m, 1H), 1.56 – 1.51 (m, 2H), 0.95 – 0.88 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.59 – 0.55 (m, 1H), 0.44 – 0.39 (m, 1H), 0.26 – 0.22 (m, 1H), -0.05 – -0.09 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 129.0, 117.9, 116.9, 63.4, 43.7, 42.7, 41.5, 29.5, 22.8, 21.6, 13.1, 13.0, 12.4, 6.1, 3.1. HRMS-ESI (m/z): [M+H]$^{+}$ calcd for $[C_{18}H_{27}N+H]^{+}$, 258.2216; found, 258.2222.



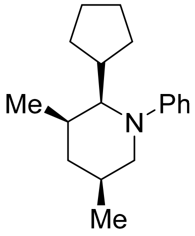
Isolated product **(±)-1c** (93.6 mg, 2% of pure isolated compound, >95:5 *dr*) as a pale yellow oil. IR (neat): 2957, 2871, 1596, 1500, 1377, 1248, 1127, 952, 746, 691 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.20 (m, 2H), 6.93 – 6.92 (m, 2H), 6.76 – 6.74 (m, 1H), 3.46 – 3.43 (m, 1H), 3.27 (dt, *J* = 13.6, 4.1 Hz, 1H), 3.18 – 3.14 (m, 1H), 1.77 – 1.65 (m, 3H), 1.57 – 1.29 (m, 8H), 1.24 – 1.16 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.6, 129.0, 117.9, 116.9, 63.5, 43.2, 40.8, 36.4, 31.3, 27.4, 22.3, 21.6, 14.5, 12.8. HRMS-ESI (m/z): [M+H]$^{+}$ calcd for $[C_{18}H_{29}N+H]^{+}$, 260.2373; found, 260.2378.



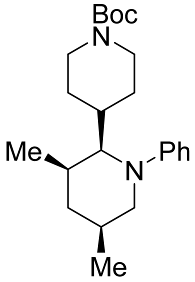
(±)-1d: General procedure C was followed using (1*E*,2*E*)-*N*,3-diphenylprop-2-en-1-imine (104 mg, 0.500 mmol, 1.00 equiv) and 3-hexyne (86 µL, 0.75 mmol, 1.5 equiv). Rh stock solution (266 µL, 25.0 µmol, 5 mol %) was added at t = 0, 24, and 48 h. After 72 h, ^{1}H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (29.0 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by silica gel chromatography (eluent 1:99 NEt_3:hexanes) provided the product **1d** (121 mg, 82%, >95:5 *dr*) as a pale yellow solid (mp: 43-45 °C). IR (neat): 2963, 2873, 1596, 1491, 1379, 1248, 1127, 974, 750, 696 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 6H), 7.24 – 7.21 (m, 1H), 7.16 – 7.14 (m, 2H), 7.12 – 7.10 (m, 1H), 3.26 – 3.23 (m, 1H), 3.01 – 2.96 (m, 2H), 2.87 – 2.84 (m, 1H), 2.24 – 2.17 (m, 1H), 1.98 – 1.97 (m, 1H), 1.79 – 1.77 (m, 1H), 1.64 – 1.57 (m, 1H), 1.31 – 1.22 (m, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.50 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 144.7, 128.6, 128.0, 127.5, 125.8, 125.5, 124.0, 68.7, 55.9, 46.2, 44.4, 25.8, 23.7, 17.3, 15.8, 11.2. HRMS-ESI (m/z): [M+H]$^{+}$ calcd for $[C_{21}H_{27}N+H]^{+}$, 294.2216; found, 294.2222.



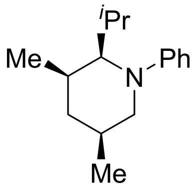
(±)-1e: General procedure D was followed using the imine **3e** (436 mg, 3.00 mmol, 1.00 equiv) and 3-hexyne (409 µL, 3.6 mmol, 1.20 equiv). Rh stock solution (1.6 mL, 150 µmol, 5 mol %) was added and the reaction was carried out for 24 h. Following concentration, 583 mg of a crude mixture was obtained and dissolved in EtOH (5.1 mL). Pd/C (117 mg, 20 wt % of crude mass) was then added to the crude mixture and hydrogenation was conducted per general procedure D. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **1e** (345 mg, 50%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2957, 2870, 1596, 1497, 1395, 1243, 1144, 992, 748, 689 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.20 – 7.18 (m, 2H), 6.86 – 6.85 (m, 2H), 6.66 – 6.64 (m, 1H), 3.78 – 3.74 (m, 1H), 3.44 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.61 (dd, *J* = 13.8, 11.6 Hz, 1H), 1.76 – 1.61 (m, 4H), 1.43 – 1.36 (m, 1H), 1.29 – 1.23 (m, 1H), 1.21 – 1.13 (m, 1H), 1.00 (apparent q, *J* = 12.4 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.4, 129.1, 116.4, 114.7, 59.9, 48.2, 40.4, 35.0, 29.7, 26.2, 19.3, 17.0, 11.7, 11.6. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{216}H_{25}N+H]^+$, 232.2060; found, 232.2065.



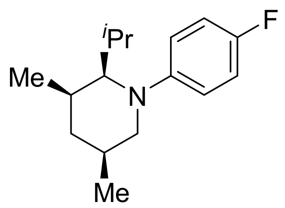
(±)-1f: General procedure C was followed using the imine **3e** (72.6 mg, 0.500 mmol, 1.00 equiv) and prop-1-ynylcyclopentane (81.1 mg, 0.750, 1.50 equiv). Rh stock solution (266 µL, 25.0 µmol, 5 mol %) was added at t = 0. After 24 h, ^1H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (25.4 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by silica gel chromatography (eluent 1:99 NEt_3:hexanes) provided the product **1f** (94.7 mg, 74%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2950, 2867, 1594, 1498, 1391, 1244, 1136, 991, 745, 689 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.19 – 7.16 (m, 2H), 6.80 – 6.78 (m, 2H), 6.62 – 6.59 (m, 1H), 3.57 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.50 – 3.47 (m, 1H), 2.60 (dd, *J* = 14.0, 11.7 Hz, 1H), 2.36 – 2.28 (m, 1H), 1.96 – 1.87 (m, 2H), 1.79 – 1.73 (m, 1H), 1.72 – 1.60 (m, 3H), 1.55 – 1.51 (m, 2H), 1.40 – 1.15 (m, 4H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.8, 129.2, 115.7, 113.8, 65.0, 49.0, 38.0, 37.8, 34.0, 33.0, 31.3, 29.5, 26.2, 24.5, 20.2, 19.2. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{18}H_{27}N+H]^+$, 258.2216; found, 258.2222.



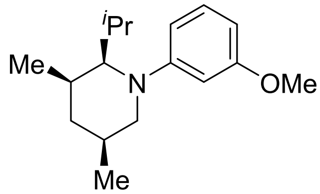
(±)-1g: A modification to general procedure C was followed using the imine **3e** (72.6 mg, 0.500 mmol, 1.00 equiv) and *tert*-butyl 4-prop-1-ynylpiperidine-1-carboxylate (112 mg, 0.500 mmol, 1.00 equiv). Rh stock solution (266 µL, 25.0 µmol, 5 mol %) was added at t = 0 h. After 24 h, ^1H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (36.8 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by silica gel chromatography (eluent 1:10:89 NEt_3/EtOAc/hexanes) provided the product **1g** (149 mg, 80%, >95:5 *dr*) as a pale yellow solid (mp: 94-96 °C). IR (neat): 2949, 2867, 1695, 1595, 1503, 1365, 1253, 1166, 993, 741, 687 cm^{-1}. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.17 (m, 2H), 6.78 – 6.77 (m, 2H), 6.65 – 6.62 (m, 1H), 4.15 – 4.07 (m, 2H), 3.57 – 3.51 (m, 2H), 2.72 – 2.68 (m, 2H), 2.50 (apparent t, *J* = 12.8 Hz, 1H), 1.99 – 1.93 (m, 3H), 1.80 – 1.73 (m, 1H), 1.66 – 1.59 (m, 2H), 1.44 (s, 9H), 1.39 – 1.32 (m, 1H), 1.24 – 1.16 (m, 2H), 1.00 (d, *J* = 7.3 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.7, 150.8, 129.2, 116.2, 114.0, 79.2, 63.2, 49.8, 43.7 (2 broad peaks), 38.0, 34.7, 33.0, 29.73, 29.69, 28.4, 20.9, 19.1. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{23}H_{36}N_2O_2+H]^+$, 373.2850; found, 373.2855.



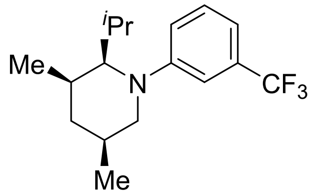
(±)-1h: General procedure C was followed using the imine **3e** (72.6 mg, 0.500 mmol, 1.00 equiv) and 4-methylpent-2-yne (87 µL, 0.75 mmol, 1.5 equiv). Rh stock solution (266 µL, 25.0 µmol, 5 mol %) was added at t = 0 h. After 24 h, ^1H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (22.8 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by silica gel chromatography (eluent 1:99 NEt_3:hexanes) provided the product **1h** (78.1 mg, 68%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2953, 2870, 1594, 1498, 1381, 1247, 1143, 993, 744, 689 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.19 – 7.17 (m, 2H), 6.80 – 6.79 (m, 2H), 6.62 – 6.60 (m, 1H), 3.52 – 3.49 (m, 1H), 3.45 (dd, *J* = 9.0, 4.6 Hz, 1H), 2.56 (dd, *J* = 14.0, 11.7 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.99 – 1.93 (m, 1H), 1.79 – 1.73 (m, 1H), 1.57 – 1.54 (m, 1H), 1.19 (apparent q, *J* = 12.5 Hz, 1H), 1.09 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 7.3 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.0, 129.1, 115.7, 113.8, 65.0, 49.4, 38.0, 34.7, 29.7, 26.1, 23.5, 21.5, 21.0, 19.2. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{16}H_{25}N+H]^+$, 232.2060; found, 232.2065.



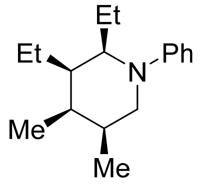
(±)-1i: General procedure C was followed using the imine **3i** (163 mg, 1.00 mmol, 1.00 equiv) and 4-methylpent-2-yne (173 µL, 1.5 mmol, 1.5 equiv). Rh stock solution (532 µL, 50.0 µmol, 5 mol %) was added at t = 0 h. After 24 h, ^{1}H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (49.0 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by preparatory TLC (eluent 1:99 NEt_3:hexanes) provided the product **1i** (156 mg, 62%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2954, 2871, 1505, 1458, 1226, 1142, 947, 808, 744 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.90 – 6.88 (m, 2H), 6.73 – 6.71 (m, 2H), 3.41 – 3.40 (m, 1H), 3.36 (dd, *J* = 8.8, 4.6 Hz, 1H), 2.59 (dd, *J* = 13.9, 11.7 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.99 – 1.95 (m, 1H), 1.80 – 1.74 (m, 1H), 1.58 – 1.55 (m, 1H), 1.19 (apparent q, *J* = 12.5 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 7.3 Hz, 3H), 0.90 (apparent t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.6 (d, *J* = 234.8 Hz), 147.9, 115.3 (d, *J* = 21.9 Hz), 115.0 (d, *J* = 7.2 Hz), 65.9, 50.0, 37.9, 34.5, 29.6, 26.3, 23.6, 21.6, 20.9, 19.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -129.8 – -129.9 (m). HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{16}H_{24}FN+H]^+$, 250.1966; found, 250.1962.



(±)-1j: General procedure C was followed using the imine **3j** (175 mg, 1.00 mmol, 1.00 equiv) and 4-methylpent-2-yne (173 µL, 1.5 mmol, 1.5 equiv). Rh stock solution (532 µL, 50.0 µmol, 5 mol %) was added at t = 0, 24 h. After 48 h, ^{1}H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (51.4 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by preparatory TLC (eluent 1:5:94 NEt_3/EtOAc/hexanes) provided the product **1j** (138 mg, 53%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2953, 2871, 1607, 1494, 1455, 1215, 1136, 1055, 829, 747, 685 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.11 – 7.08 (m, 1H), 6.44 – 6.42 (m, 1H), 6.34 – 6.33 (m, 1H), 6.20 – 6.19 (m, 1H), 3.78 (s, 3H), 3.50 – 3.47 (m, 1H), 3.43 (dd, *J* = 9.0, 4.6 Hz, 1H), 2.54 (dd, *J* = 14.0, 11.7 Hz, 1H), 2.19 – 2.13 (m, 1H), 1.98 – 1.92 (m, 1H), 1.78 – 1.71 (m, 1H), 1.56 – 1.54 (m, 1H), 1.18 (apparent q, *J* = 12.5 Hz, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 7.3 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.8, 152.3, 129.8, 107.1, 100.5, 100.0, 65.0, 55.1, 49.5, 38.0, 34.8, 29.8, 26.0, 23.5, 21.4, 21.0, 19.1. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{17}H_{27}NO+H]^+$, 262.2165; found, 262.2171.

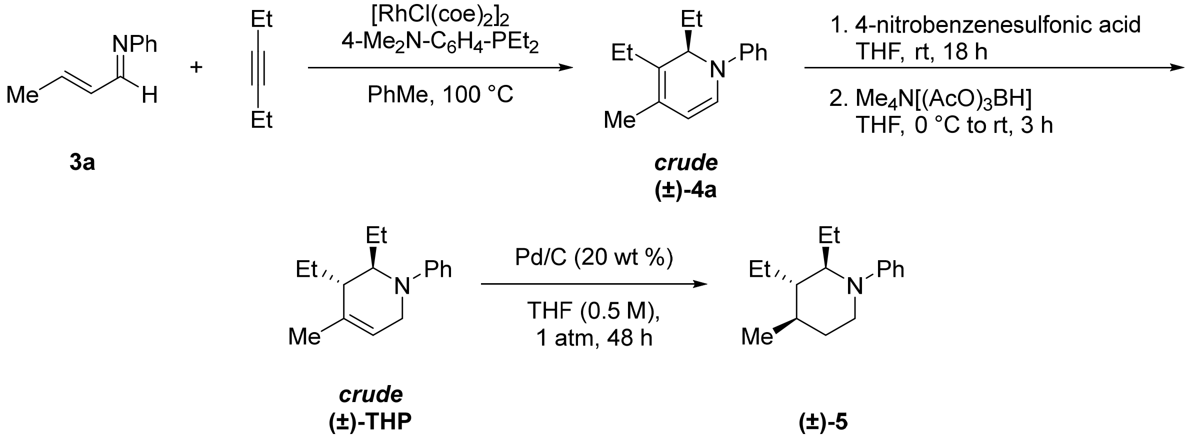


(±)-1k: General procedure C was followed using the imine **3k** (213 mg, 1.00 mmol, 1.00 equiv) and 4-methylpent-2-yne (173 µL, 1.5 mmol, 1.5 equiv). Rh stock solution (532 µL, 50.0 µmol, 5 mol %) was added at t = 0. After 24 h, ^{1}H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (59.0 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by preparatory TLC (eluent 1:99 NEt_3/hexanes) provided the product **1k** (214 mg, 72%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2957, 2873, 1606, 1496, 1452, 1318, 1160, 1117, 1075, 996, 776, 694 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 1H), 6.95 – 6.91 (m, 2H), 6.84 – 6.82 (m, 1H), 3.52 – 3.50 (m, 1H), 3.47 (dd, *J* = 9.0, 4.7 Hz, 1H), 2.61 – 2.57 (m, 1H), 2.21 – 2.16 (m, 1H), 1.97 – 1.93 (m, 1H), 1.76 – 1.70 (m, 1H), 1.59 – 1.57 (m, 1H), 1.20 (apparent q, *J* = 12.5 Hz, 1H), 1.10 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 7.3 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.0, 131.4 (q, *J* = 31.2 Hz), 129.5, 124.6 (q, *J* = 272.4 Hz), 116.6, 112.1 (q, *J* = 4.0 Hz), 109.9 (q, *J* = 4.0 Hz), 64.9, 49.5, 37.8, 35.0, 29.9, 26.2, 23.5, 21.4, 20.8, 19.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.8. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{17}H_{24}F_3N+H]^+$, 300.1934; found, 300.1932.



(±)-1l: General procedure C was followed using (1*E*,2*E*)-2-methyl-N-phenylbut-2-en-1-imine (79.6 mg, 0.500 mmol, 1.00 equiv) and 3-hexyne (86 µL, 0.75 mmol, 1.5 equiv). Rh stock solution (266 µL, 25.0 µmol, 5 mol %) was added at t = 0, 24, and 48 h. After 72 h, ^{1}H NMR analysis indicated complete conversion to the 1,2-dihydropyridine. Pd/C (24.2 mg, 20 wt % of theoretical yield) was then added to the crude mixture and hydrogenation was conducted per general procedure C. Purification by silica gel chromatography (eluent 1:99 NEt_3:hexanes) provided the product **1l** (71.9 mg, 59%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2959, 2872, 1597, 1497, 1387, 1221, 1144, 929, 746, 690 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.18 (m, 2H), 6.87 – 6.85 (m, 2H), 6.67 – 6.65 (m, 1H), 3.66 – 3.64 (m, 1H), 3.20 (d, *J* = 14.3 Hz, 1H), 2.93 (apparent t, *J* = 13.0 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.88 – 1.83 (m, 1H), 1.75 – 1.71 (m, 1H), 1.64 – 1.51 (m, 2H), 1.40 – 1.35 (m, 2H), 0.91 – 0.88 (m, 9H), 0.84 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.4, 129.1, 116.4, 114.8, 62.1, 44.4, 43.2, 34.8, 32.7, 23.7, 21.3, 16.5, 13.5, 11.7, 8.8. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{17}H_{27}N+H]^+$, 246.2216; found, 246.2222.

Preparation of piperidine 5:



3a

crude
(±)-4a

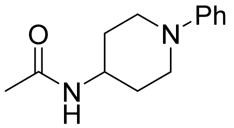
crude
(±)-THP

(±)-5

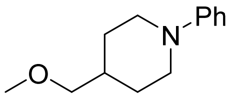
The following protocol is a modification of a previous literature procedure.[7] In an N_2-filled glove box, a 4-mL vial was charged with imine **3a** (1.69 g, 11.6 mmol, 1.00 equiv). Rh stock solution (see General Methods) (6.2 mL, 0.58 mmol, 5 mol %) was added to the vial, and the contents were transferred to a Schlenk flask. The vial was rinsed with toluene (0.5 mL x 2), and the washings were likewise transferred to the Schlenk flask. 3-hexyne (1.59 mL, 14.0 mmol, 1.2 equiv) was added to the Schlenk flask, followed by toluene (20 mL). The contents were thoroughly mixed and *ca.* 0.6 mL was removed by pipet and transferred to a J. Young NMR tube equipped with a C_6D_6 capillary (for locking and shimming). The Schlenk flask and the J. Young tube were capped and then taken to a fume hood where they were heated to 100 °C for 24 h, at which point analysis by ^{1}H NMR of the J. Young tube indicated complete conversion to the 1,2-dihydropyridine. In a fume hood, the crude DHP **4a** solution was then added to a 250-mL round-bottom flask containing 4-nitrobenzenesulfonic acid hydrate (1.3 g, 58 mmol, 5.0 equiv), THF (60 mL), and a magnetic stir bar. The flask was placed under N_2, and the mixtxure was stirred at rt for 18 h. A separate 500-mL round-bottom flask containing a magnetic stir was charged with Me$_4$N[(AcO)$_3$BH] (1.4 g, 52 mmol, 4.5 equiv) and THF was added (130 mL). The suspension was cooled to 0 °C and the resulting iminium solution was transferred via cannula. The mixture was stirred at 0 °C for 2 h and then allowed to warm to room temperature over 1 h. 1 M NaOH was then added until the pH reached *ca.* 11. The reaction mixture was added to a separatory funnel and the layers were separated. The aqueous layer was further extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was plugged through silica (eluent: 1:10:89 NEt$_3$:EtOAc:hexanes) and concentrated *in vacuo* to give the crude THP product. The entire crude THP was then taken onto the hydrogenation reaction by transferring the crude product with THF (23 mL, sparged for 15 min prior to use) to a 50-mL round-bottom flask containing a magnetic stir bar. Pd/C (532 mg, 20 wt %, based on theoretical yield of THP) was then added to the solution, and the flask was capped with a rubber septum and purged with N_2 for 5 min. The flask was then purged with an H_2 balloon three times, and then electrical tape and Parafilm were used to seal the flask. The reaction mixture was then stirred at 1000 rpm for 48 h under an H_2 atmosphere (1 atm). The H_2 balloon was removed and the heterogeneous mixture was filtered over Celite (eluent: diethyl ether) and concentrated *in vacuo*. The crude product was then purified by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) followed by preparatory TLC (1:5:94 NEt$_3$:EtOAc:hexanes) to give piperidine **5** (369 mg, 14%) as a pale yellow oil. Yield indicates overall yield from the starting imine **3a** and is not optimized with only pure fractions collected. IR (neat): 2958, 2872, 1596, 1501, 1379, 1217, 1035, 744, 688 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.23 – 7.21 (m, 2H), 6.83 – 6.81 (m, 2H), 6.73 – 6.70 (m, 1H), 3.45 – 3.42 (m, 1H), 3.22 – 3.19 (m, 2H), 1.89 – 1.84 (m, 1H), 1.68 – 1.61 (m, 1H), 1.57 – 1.49 (m, 2H), 1.47 – 1.41 (m, 3H), 1.24 – 1.20 (m, 1H), 1.04 (d, J = 6.7 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.3, 129.0, 116.9, 114.4, 59.2, 46.2, 44.0, 31.3, 30.2, 26.7, 26.4, 21.3, 11.3, 11.2. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{16}H_{25}N$+H]$^+$, 232.2060; found, 232.2065.

Piperidines prepared by alternative methods:

2-methyl-1-phenylpiperidine **1j** was prepared according to a previous literature procedure.[8]



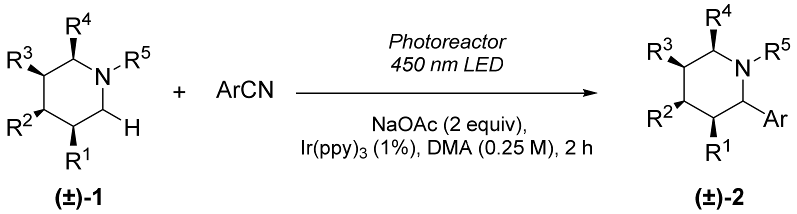
(±)-6a: An oven-dried 25-mL round-bottom flask was charged with a magnetic stir bar and 1-phenylpiperidin-4-amine (150 mg, 0.851 mmol, 1.00 equiv) and placed under N_2. Dry CH_2Cl_2 (4.3 mL, 0.2 M), acetic anhydride (97 μL, 1.0 mmol, 1.2 equiv) and triethylamine (356 μL, 2.55 mmol, 3.00 equiv) were added, and the reaction mixture was stirred at rt. After stirring for 18 h, the reaction mixture was concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography (eluent 1:20:79 NEt_3/EtOAc/hexanes) to provide product **6a** (117 mg, 63%) as a white solid (mp: 137-139 °C). IR (neat): 2934, 1635, 1598, 1494, 1312, 1219, 1131, 918, 756, 689 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 6.92 – 6.91 (m, 2H), 6.84 – 6.82 (m, 1H), 5.56 (s, 1H), 3.95 – 3.89 (m, 1H), 3.62 – 3.60 (m, 2H), 2.84 (t, *J* = 12.0 Hz, 2H), 2.03 – 2.00 (m, 2H), 1.96 (s, 3H), 1.54 (qd, *J* = 11.8, 3.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.4, 151.1, 129.1, 119.7, 116.6, 48.7, 46.6, 31.9, 23.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{13}H_{18}N_2O+H]^+$, 219.1492; found, 219.1491.



(±)-6b: The following protocol is based on a literature procedure.[7] An oven-dried Schlenk flask was charged with a magnetic stir bar, RuPhos Pd G3 (37.2 mg, 0.04 mmol, 0.01 equiv), RuPhos (20.7 mg, 0.04 mmol, 0.01 equiv), 4-(methoxymethyl)piperidine-HCl salt (880 mg, 5.33 mmol, 1.20 equiv), and NaO*t*-Bu (1.03 g, 10.7 mmol, 2.40 equiv). Under a counterflow of N_2, dry THF (9 mL, 0.5 M) and chlorobenzene (510 μL, 4.44 mmol, 1.00 equiv) were added. The Schlenk flask was placed in a preheated oil bath at 85 °C, and the reaction mixture was stirred vigorously for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc, and added to a separatory funnel containing 20 mL of water. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography (eluent 1:5:94 NEt_3/EtOAc/hexanes) to provide the product **6b** (645 mg, 71%) as a pale yellow oil. IR (neat): 2918, 2806, 1599, 1495, 1385, 1244, 1103, 909, 754, 690 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 2H), 6.95 – 6.94 (m, 2H), 6.84 – 6.81 (m, 1H), 3.70 – 3.68 (m, 2H), 3.36 (s, 3H), 3.27 (d, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 12.3 Hz, 2H), 1.85 – 1.83 (m, 2H), 1.78 – 1.71 (m, 1H), 1.40 (qd, *J* = 12.2, 4.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.8, 129.0, 119.3, 116.5, 77.8, 58.9, 49.6, 36.1, 29.1. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{13}H_{19}NO+H]^+$, 206.1539; found, 206.1543.

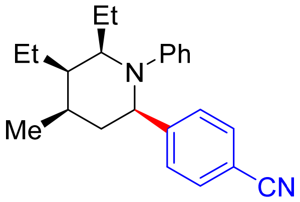
Preparation of Products

General procedure E for the amine α-arylation:

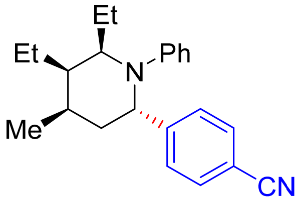


The following protocol is adapted from a literature procedure.[10] A flame-dried Schlenk flask equipped with a magnetic stir bar was charged with the indicated cyanoarene (0.400 mmol, 2.00 equiv) and NaOAc (32.8 mg, 0.400 mmol, 2.00 equiv), and the side arm of the Schlenk flask was connected to a double manifold Schlenk line and placed under N_2. Dry DMA (0.25 M total) was then used to transfer the *N*-phenyl piperidine **1** (0.200 mmol, 1.00 equiv) to the Schlenk flask (240 μL x 3). $Ir(ppy)_3$ (80 μL, 0.0020 mmol, 0.010 equiv) was then added as a stock solution in DMA (0.025 M). The Schlenk flask was then degassed using three freeze/pump/thaw cycles under nitrogen in the dark. The Schlenk flask was placed in the Penn Photoreactor, and the mixture was stirred at 1000 rpm while being irradiated at 450 nm (50% LED). After 2 h, the reaction mixture was diluted with EtOAc and added to a separatory funnel containing 10 mL of a saturated aqueous solution of Na_2CO_3. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was then purified by silica gel column chromatography, preparative thin layer chromatography (TLC), or C18 reverse phase chromatography to give the indicated product **2**.

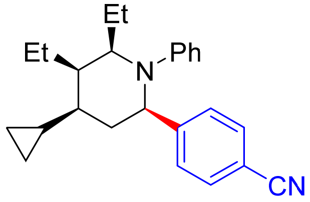
Safety warning: NaCN is a byproduct of the reaction and is highly toxic and when treated with acid can form the toxic gas HCN. Aqueous cyanide-containing waste should be kept basic and disposed of separately in accord with institutional guidelines.



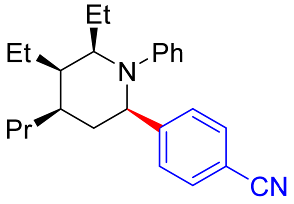
(±)-2a-syn: General procedure E was followed using the piperidine **1a** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by silica gel chromatography (eluent 1:3:96 NEt$_3$/EtOAc/hexanes) provided the product **2a-syn** *(major diastereomer)* (57.1 mg, 86%, >95:5 *dr*) as a pale yellow waxy solid. IR (neat): 2957, 2879, 2225, 1596, 1491, 1245, 1116, 1020, 828, 774, 696 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.26 (m, 2H), 7.08 – 7.05 (m, 2H), 6.95 – 6.94 (m, 2H), 6.92 – 6.89 (m, 1H), 4.04 (dd, *J* = 10.3, 4.6 Hz, 1H), 2.80 – 2.78 (m, 1H), 1.98 – 1.93 (m, 1H), 1.80 – 1.73 (m, 1H), 1.66 – 1.63 (m, 1H), 1.60 – 1.53 (m, 2H), 1.48 – 1.41 (m, 1H), 1.35 – 1.27 (m, 1H), 1.07 – 0.99 (m, 1H), 1.04 (t, *J* = 7.7 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.9, 150.0, 131.7, 128.5, 128.3, 127.2, 124.5, 119.1, 109.8, 69.9, 68.1, 42.6, 40.1, 35.6, 24.4, 19.3, 16.8, 16.4, 11.4. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{23}$H$_{28}$N$_2$+H]$^+$, 333.2325; found, 333.2331.



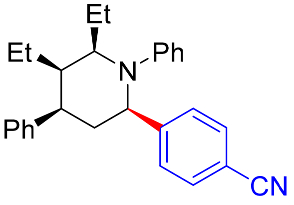
(±)-2a-anti: A modification to general procedure E was followed using the piperidine **1a** (116 mg, 0.500 mmol, 1.00 equiv), 1,4-dicyanobenzene (128 mg, 1.00 mmol, 2.00 equiv) and a 16 min reaction time. ^{1}H crude NMR analysis provided a 50:50 mixture of diastereomers. Purification of the mixture by preparative TLC (1:3:96 NEt$_3$/EtOAc/hexanes) provided the "minor" diastereomer **2a-anti** (66.0 mg, 40%, >95:5 *dr*) as a pale yellow solid (mp: 90-92 °C). IR (neat) 2951, 2870, 2226, 1595, 1496, 1261, 1097, 1020, 828, 760, 697 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.06 (m, 2H), 6.73 – 6.66 (m, 1H), 6.69 – 6.64 (m, 2H), 4.61 (dd, *J* = 8.5, 3.2 Hz, 1H), 3.68 – 3.66 (m, 1H), 2.09 – 2.02 (m, 2H), 1.93 – 1.88 (m, 2H), 1.67 – 1.59 (m, 2H), 1.52 – 1.42 (m, 2H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.68 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.6, 149.4, 132.1, 128.5, 127.8, 120.0, 119.4, 119.1, 109.8, 64.7, 54.6, 44.0, 41.5, 27.9, 23.3, 22.7, 16.1, 15.0, 12.4. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{23}$H$_{28}$N$_2$+H]$^+$, 333.2325; found, 333.2331.



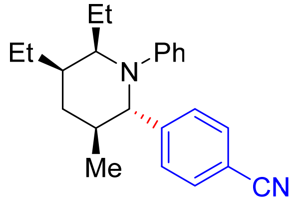
(±)-2b: General procedure E was followed using the piperidine **1b** (51.5 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2b** as a mixture of diastereomers (87:13 *dr*). Purification by preparative TLC (1:3:96 NEt$_3$/EtOAc/hexanes) provided the major diastereomer **2b** (42.9 mg, 60%, >95:5 *dr*) as a pale yellow solid (mp: 99-101 °C). IR (neat): 2963, 2887, 2225, 1596, 1490, 1216, 1109, 1016, 834, 777, 704 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.26 (m, 2H), 7.07 – 7.04 (m, 2H), 6.94 – 6.90 (m, 3H), 3.95 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.67 – 2.65 (m, 1H), 1.85 – 1.80 (m, 2H), 1.75 – 1.72 (m, 2H), 1.63 – 1.55 (m, 1H), 1.34 – 1.26 (m, 1H), 1.11 (t, *J* = 7.5 Hz, 3H), 1.02 – 0.96 (m, 1H), 0.90 – 0.85 (m, 1H), 0.77 – 0.72 (m, 1H), 0.73 (t, *J* = 7.5 Hz, 3H), 0.47 – 0.46 (m, 2H), 0.23 – 0.20 (m, 1H), 0.09 – 0.07 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.8, 150.1, 131.7, 128.6, 128.3, 127.6, 124.8, 119.1, 109.8, 69.8, 68.5, 47.3, 41.6, 38.2, 24.4, 17.4, 16.2, 14.6, 11.3, 4.5, 3.6. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{25}$H$_{30}$N$_2$+H]$^+$, 359.2482; found, 359.2487.



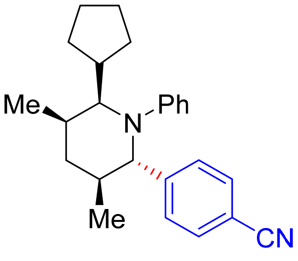
(±)-2c: General procedure E was followed using the piperidine **1c** (51.9 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt$_3$/EtOAc/hexanes) provided the product **2c** (66.4 mg, 92%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2958, 2873, 2226, 1597, 1492, 1224, 1117, 1025, 831, 777, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.25 (m, 2H), 7.08 – 7.05 (m, 2H), 6.96 – 6.91 (m, 3H), 4.00 (dd, *J* = 11.3, 3.5 Hz, 1H), 2.74 – 2.72 (m, 1H), 1.84 – 1.79 (m, 1H), 1.78 – 1.72 (m, 2H), 1.63 – 1.60 (m, 1H), 1.52 – 1.48 (m, 1H), 1.46 – 1.34 (m, 4H), 1.32 – 1.23 (m, 2H), 1.05 – 0.96 (m, 1H), 1.04 (t, *J* = 7.7 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.73 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.9, 150.1, 131.7, 128.6, 128.3, 127.8, 124.9, 119.1, 109.8, 70.2, 68.7, 41.3, 40.9, 38.3, 35.8, 24.3, 20.4, 16.9, 16.4, 14.4, 11.3. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{25}$H$_{32}$N$_2$+H]$^+$, 361.2638; found, 361.2644.



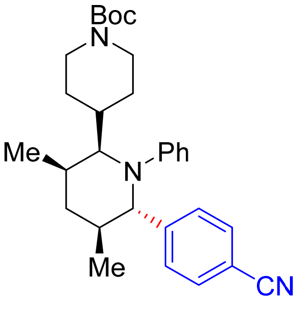
(±)-2d: A modification to General procedure E was followed using the piperidine **1d** (58.7 mg, 0.200 mmol, 1.00 equiv), 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv), and a 16 h reaction time. Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2d** (56.8 mg, 72%, >95:5 *dr*) as a pale yellow solid (mp: 90-93 °C). IR (neat): 2954, 2874, 2223, 1595, 1496, 1222, 1122, 1018, 840, 757, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.31 (m, 4H), 7.26 – 7.25 (m, 2H), 7.22 – 7.20 (m, 1H), 7.10 – 7.08 (m, 2H), 7.02 – 7.01 (m, 2H), 6.97 – 6.94 (m, 1H), 4.15 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.20 – 3.16 (m, 1H), 2.98 – 2.96 (m, 1H), 2.20 – 2.14 (m, 1H), 2.07 – 2.06 (m, 1H), 1.91 – 1.89 (m, 1H), 1.83 – 1.76 (m, 1H), 1.36 – 1.25 (m, 2H), 1.08 – 1.01 (m, 1H), 0.75 (t, *J* = 7.4 Hz, 3H), 0.53 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.4, 149.8, 143.8, 131.8, 128.7, 128.4, 128.3, 128.2, 127.2, 126.1, 125.4, 119.0, 110.1, 70.4, 68.8, 46.0, 43.9, 35.6, 24.4, 16.7, 15.8, 11.2. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{28}H_{30}N_2+H]^+$, 395.2482; found, 395.2487.



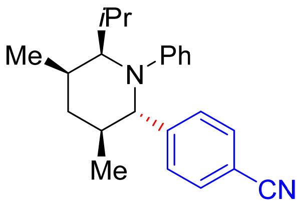
(±)-2e: General procedure E was followed using the piperidine **1e** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by silica gel chromatography (eluent 1:3:86 NEt_3/EtOAc/hexanes) provided the product **2e** (58.9 mg, 89%, >95:5 *dr*) as a pale yellow solid (mp: 72-74 °C). IR (neat): 2953, 2873, 2231, 1597, 1491, 1233, 1122, 1021, 825, 762, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.01 – 6.99 (m, 2H), 6.82 – 6.80 (m, 2H), 6.75 – 6.73 (m, 1H), 3.87 (d, *J* = 9.7 Hz, 1H), 3.54 (apparent q, *J* = 4.4 Hz, 1H), 2.16 – 2.10 (m, 1H), 1.68 (dt, *J* = 13.3, 3.7 Hz, 1H), 1.63 – 1.55 (m, 2H), 1.43 – 1.35 (m, 2H), 1.31 – 1.24 (m, 1H), 1.15 (apparent q, *J* = 12.5 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.73 (d, *J* = 6.6 Hz, 3H), 0.49 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.9, 149.8, 131.5, 129.4, 127.9, 125.3, 121.6, 119.0, 109.9, 68.4, 64.8, 43.5, 40.4, 34.1, 26.1, 19.1, 16.7, 15.0, 12.0. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{23}H_{28}N_2+H]^+$, 333.2325; found, 333.2331.



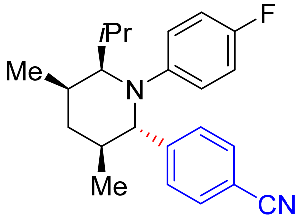
(±)-2f: General procedure E was followed using the piperidine **1f** (51.5 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2f** (61.0 mg, 85%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2954, 2870, 2226, 1596, 1493, 1244, 1107, 1018, 819, 762, 699 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.89 (m, 2H), 6.67 – 6.61 (m, 3H), 4.12 (d, *J* = 9.8 Hz, 1H), 3.71 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.47 – 2.30 (m, 2H), 1.85 – 1.78 (m, 2H), 1.72 – 1.67 (m, 2H), 1.50 – 1.40 (m, 4H), 1.37 – 1.29 (m, 1H), 1.18 – 1.05 (m, 2H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.2, 149.9, 131.5, 129.4, 127.5, 124.3, 119.7, 119.0, 109.8, 69.9, 65.4, 40.4, 39.5, 37.1, 36.1, 32.9, 32.2, 24.8, 24.5, 20.1, 19.4. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{25}H_{30}N_2+H]^+$, 359.2482; found, 359.2487.



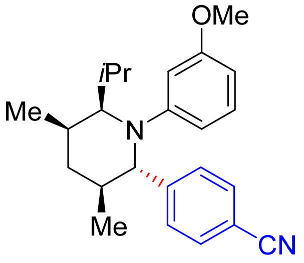
(±)-2g: General procedure E was followed using the piperidine **1g** (74.5 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:20:79 NEt_3/EtOAc/hexanes) followed by purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **2g** (66.0 mg, 70%, >95:5 *dr*) as a pale yellow waxy solid. IR (neat): 2957, 2873, 2226, 1686, 1595, 1494, 1236, 1165, 910, 730, 700 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.97 – 6.93 (m, 2H), 6.74 – 6.72 (m, 2H), 6.67 – 6.63 (m, 1H), 4.20 (d, *J* = 9.5 Hz, 1H), 3.99 (br s, 2H), 3.71 – 3.69 (m, 1H), 2.57 – 2.41 (m, 3H), 2.00 – 1.95 (m, 1H), 1.69 – 1.66 (m, 3H), 1.55 – 1.34 (m, 4H), 1.39 (s, 9H), 1.11 (d, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, acetone-*d*$_6$) δ 155.0, 151.9, 132.4, 130.6, 128.8, 125.0, 121.0, 119.5, 110.8, 79.2, 68.7, 67.1, 45.9, 45.0, 41.1, 39.9, 37.5, 37.2, 35.1, 32.5, 28.7, 20.1, 19.6. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{30}H_{39}N_3O_2+H]^+$, 474.3115; found, 474.3120.



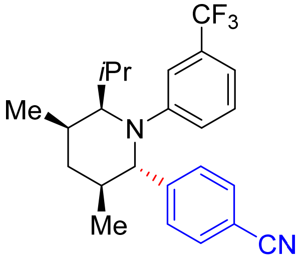
(±)-2h: General procedure E was followed using the piperidine **1h** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2h** (48.1 mg, 72%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2957, 2874, 2226, 1594, 1495, 1244, 1107, 1017, 821, 760, 699 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.95 (m, 2H), 6.76 – 6.75 (m, 2H), 6.66 – 6.63 (m, 1H), 4.27 (d, *J* = 9.7 Hz, 1H), 3.71 (apparent t, *J* = 5.0 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.27 – 2.20 (m, 1H), 1.77 – 1.69 (m, 1H), 1.67 – 1.63 (m, 1H), 1.45 (apparent q, *J* = 12.6 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.1, 150.8, 131.6, 129.1, 127.8, 123.4, 119.8, 119.0, 109.9, 68.3, 66.8, 39.7, 36.9, 36.0, 29.5, 24.5, 22.6, 19.7, 19.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{23}H_{28}N_2+H]^+$, 333.2325; found, 333.2331.



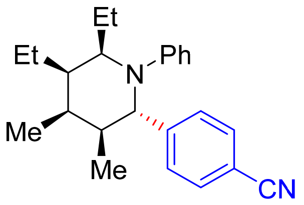
(±)-2i: General procedure E was followed using the piperidine **1i** (49.9 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2i** (65.3 mg, 93%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2958, 2874, 2227, 1607, 1504, 1216, 1107, 1017, 822, 732 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.42 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 6.72 – 6.69 (m, 2H), 6.68 – 6.64 (m, 2H), 4.23 (d, J = 9.7 Hz, 1H), 3.62 (t, J = 4.6 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.21 – 2.17 (m, 1H), 1.75 – 1.70 (m, 1H), 1.63 (dt, J = 13.4, 4.1 Hz, 1H), 1.47 (apparent q, J = 12.7 Hz, 1H), 1.10 (d, J = 7.2 Hz, 3H), 0.98 (d, J = 7.1 Hz, 3H), 0.88 (d, J = 7.0 Hz, 3H), 0.80 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.8 (d, *J* = 240.0 Hz), 150.3, 147.2 (d, *J* = 2.4 Hz), 131.6, 129.2, 125.4, 118.9, 114.4 (d, *J* = 22.0 Hz), 110.0, 69.1, 66.5, 39.9, 36.7, 36.2, 29.5, 24.7, 22.8, 19.6, 19.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -123.2 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{23}H_{27}FN_2+H]^+$, 351.2231; found, 351.2237.



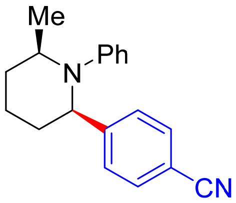
(±)-2j: General procedure E was followed using the piperidine **1j** (52.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:10:89 NEt_3/EtOAc/hexanes) provided the product **2j** (48.2 mg, 67%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2956, 2874, 2226, 1596, 1487, 1213, 1158, 1046, 822, 730, 702 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.86 (m, 1H), 6.39 – 6.38 (m, 1H), 6.30 – 6.29 (m, 1H), 6.23 – 6.21 (m, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.69 – 3.67 (m, 1H), 3.63 (s, 3H), 2.39 – 2.34 (m, 1H), 2.28 – 2.22 (m, 1H), 1.76 – 1.70 (m, 1H), 1.64 (dt, *J* = 13.5, 4.2 Hz, 1H), 1.42 (apparent q, *J* = 12.5 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 152.5, 150.9, 131.7, 128.9, 128.4, 119.1, 115.9, 109.9, 109.5, 104.6, 68.0, 67.1, 55.0, 39.5, 36.9, 35.7, 29.5, 24.4, 22.5, 19.62, 19.57. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{24}H_{30}N_2O+H]^+$, 363.2431; found, 363.2430.



(±)-2k: A modification to General procedure E was followed using the piperidine **1k** (59.9 mg, 0.200 mmol, 1.00 equiv), 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv), $Ir(ppy)_3$ (160 µL, 0.004 mmol, 0.020 equiv) as a stock solution in DMA (0.025 M), and a reaction time of 72 h. Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2k** (44.3 mg, 55%, >95:5 *dr*) as a pale yellow waxy solid. IR (neat): 2961, 2875, 2227, 1608, 1324, 1161, 1120, 1019, 822, 733, 103 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.07 – 7.04 (m, 1H), 6.97 – 6.96 (m, 1H), 6.91 – 6.86 (m, 2H), 4.25 (d, J = 9.7 Hz, 1H), 3.77 – 3.75 (m, 1H), 2.44 – 2.37 (m, 1H), 2.27 – 2.21 (m, 1H), 1.82 – 1.73 (m, 1H), 1.67 (dt, J = 13.5, 4.1 Hz, 1H), 1.44 (apparent q, J = 12.6 Hz, 1H), 1.13 (d, J = 7.2 Hz, 3H), 0.94 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 149.9, 131.8, 130.2 (q, *J* = 31.8 Hz), 129.0, 128.3, 125.8, 124.1 (q, *J* = 272.3 Hz), 119.4, 118.8, 116.0, 110.3, 68.3, 66.9, 39.7, 36.6, 35.9, 29.6, 24.7, 22.4, 19.6, 19.5. ^{19}F NMR (470 MHz, Chloroform-d) δ -62.9. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{24}H_{27}F_3N_2+H]^+$, 401.2199; found, 401.2193.



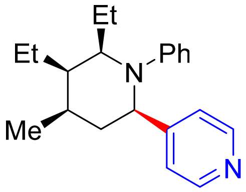
(±)-2l: General procedure E was followed using the piperidine **1l** (49.1 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2l** as a mixture of diastereomers (84:16 *dr*). Purification by preparative TLC (1:5:94 NEt$_3$/EtOAc/hexanes) provided the product **2l** (59.4 mg, 86%, 85:15 *dr*) as a pale yellow solid (mp: 98-100 °C). IR (neat): 2959, 2873, 2221, 1596, 1493, 1228, 1132, 1012, 824, 755, 702 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.1 Hz, 1.7H), 7.36 (d, *J* = 8.2 Hz, 1.7H), 7.30 (d, *J* = 8.0 Hz, 0.3H), 7.17 (d, *J* = 8.0 Hz, 0.3H), 7.09 – 7.06 (m, 0.3H), 7.01 – 6.98 (m, 2H), 6.94 – 6.92 (m, 0.15H), 6.85 – 6.83 (m, 1.7H), 6.75 – 6.73 (m, 0.85H), 4.36 (d, *J* = 3.6 Hz, 0.15H), 4.08 (d, *J* = 9.9 Hz, 0.85H), 3.52 (q, *J* = 4.5 Hz, 0.85H), 2.61 – 2.58 (m, 0.15H), 2.28 – 2.24 (m, 0.85H), 2.17 – 2.12 (m, 0.15H), 1.92 – 1.81 (m, 1.7H), 1.77 – 1.67 (m, 0.3H), 1.54 – 1.44 (m, 3.55), 1.34 – 1.26 (m, 0.3H), 1.12 (d, *J* = 7.0 Hz, 0.45H), 1.01 (t, *J* = 7.3 Hz, 2.55H), 1.02 – 0.97 (m, 0.45H), 0.95 – 0.85 (m, 0.15H), 0.91 (d, *J* = 7.4 Hz, 2.55H), 0.68 – 0.64 (m, 0.9H), 0.59 (d, *J* = 6.9 Hz, 2.55H), 0.26 (t, *J* = 7.5 Hz, 2.55H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.8, 150.1, 149.9, 148.4, 131.5, 130.8, 130.0, 129.4, 128.2, 128.0, 125.8, 125.6, 124.9, 121.9, 119.12, 119.08, 109.8, 109.1, 73.8, 73.1, 68.4, 59.9, 47.0, 44.3, 43.5, 41.4, 40.1, 35.6, 24.2, 23.6, 20.6, 18.9, 17.8, 17.3, 17.0, 16.1, 12.0, 11.6, 10.9, 9.6. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{24}$H$_{30}$N$_2$+H]$^+$, 347.2482; found, 347.2487.



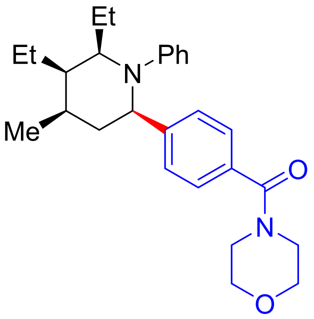
(±)-2m: General procedure E was followed using the piperidine **1m** (35.1 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2m** as a mixture of diastereomers (64:36 *dr*). Purification by preparative TLC (1:5:94 NEt$_3$/EtOAc/hexanes) provided the product **2m** (46.9 mg, 85%, 63:37 *dr*) as a pale yellow oil. Purification by C18 reverse phase chromatography (0-60% CH$_3$CN:H$_2$O containing 0.1 % TFA) provided fractions of each of the diastereomers separately for characterization (major: 10.6 mg, 19%; minor: 5.0 mg, 9%).

(±)-2m-syn *(major diastereomer)*: pale yellow solid (mp: 118-120 °C). IR (neat): 2932, 2224, 1596, 1487, 1228, 1095, 1048, 836, 772, 705 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.09 – 7.06 (m, 2H), 7.00 – 6.99 (m, 2H), 6.95 – 6.92 (m, 1H), 3.98 (dd, *J* = 10.7, 2.8 Hz, 1H), 2.94 – 2.88 (m, 1H), 1.91 – 1.87 (m, 1H), 1.84 – 1.81 (m, 2H), 1.74 – 1.59 (m, 2H), 1.56 – 1.48 (m, 1H), 0.81 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.4, 150.3, 131.7, 128.8, 128.3, 127.7, 125.2, 119.1, 110.0, 68.5, 58.8, 36.4, 35.0, 24.7, 22.1. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{19}$H$_{20}$N$_2$+H]$^+$, 277.1699; found, 277.1705.

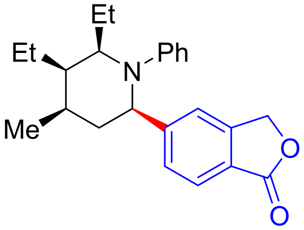
(±)-2m-anti *(minor diastereomer)*: pale yellow solid (mp: 113-115 °C). IR (neat): 2933, 2224, 1597, 1491, 1254, 1137, 1012, 836, 769, 701 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.07 – 7.04 (m, 2H), 6.79 – 6.77 (m, 3H), 4.41 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.02 – 3.97 (m, 1H), 2.13 – 2.07 (m, 1H), 1.94 – 1.91 (m, 1H), 1.83 – 1.73 (m, 2H), 1.67 – 1.64 (m, 1H), 1.55 – 1.46 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.7, 150.5, 132.1, 128.2, 127.7, 124.0, 121.4, 119.1, 109.8, 57.1, 56.1, 37.5, 31.5, 18.6, 11.9. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{19}$H$_{20}$N$_2$+H]$^+$, 277.1699; found, 277.1705.



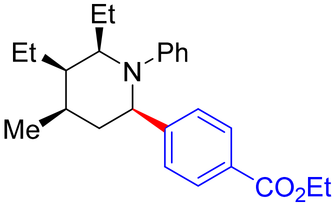
(±)-2n: A modification to general procedure E was followed using the piperidine **1n** (46.3 mg, 0.200 mmol, 1.00 equiv), isonicotinonitrile (41.6 mg, 0.400 mmol, 2.00 equiv). In place of Ir(ppy)$_3$, [Ir(dtbbpy)(ppy)$_2$]PF$_6$ (80 µL, 0.0020 mmol, 0.010 equiv) was added as a stock solution in DMA (0.025 M). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt$_3$/EtOAc/hexanes) provided the product **2n** (30.7 mg, 50%, >95:5 *dr*) as a pale yellow solid (mp: 77-80 °C). IR (neat): 2961, 2874, 1599, 1490, 1227, 1107, 1020, 816, 778, 702 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 – 8.30 (m, 2H), 7.09 – 7.05 (m, 4H), 6.96 – 6.95 (m, 2H), 6.91 – 6.88 (m, 1H), 3.99 (dd, *J* = 10.9, 4.1 Hz, 1H), 2.80 – 2.77 (m, 1H), 1.98 – 1.91 (m, 1H), 1.78 – 1.71 (m, 1H), 1.65 – 1.62 (m, 1H), 1.61 – 1.52 (m, 2H), 1.47 – 1.40 (m, 1H), 1.36 – 1.27 (m, 1H), 1.08 – 1.01 (m, 1H), 1.02 (t, *J* = 7.7 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.3, 150.0, 149.3, 128.3, 126.9, 124.4, 123.0, 69.8, 67.3, 42.5, 39.9, 35.4, 24.5, 19.3, 16.9, 16.3, 11.4. HRMS-ESI (m/z): [M+H]$^+$ calcd for [C$_{21}$H$_{28}$N$_2$+H]$^+$, 309.2325; found, 309.2331.



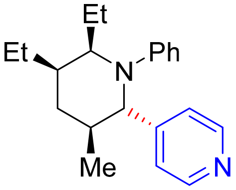
(±)-2o: General procedure E was followed using the piperidine **1o** (46.3 mg, 0.200 mmol, 1.00 equiv) and 4-(morpholine-4-carbonyl)benzonitrile (86.5 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by silica gel chromatography (eluent 1:20:79 NEt_3/EtOAc/hexanes) provided the product **2o** (56.2 mg, 67%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2959, 2873, 1631, 1425, 1276, 1114, 836, 728, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.04 – 7.01 (m, 2H), 6.94 – 6.93 (m, 2H), 6.86 – 6.84 (m, 1H), 4.01 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.67 – 3.29 (br m, 8H), 2.83 – 2.80 (m, 1H), 1.99 – 1.92 (m, 1H), 1.78 – 1.71 (m, 1H), 1.65 – 1.62 (m, 1H), 1.62 – 1.59 (m, 2H), 1.49 – 1.42 (m, 1H), 1.38 – 1.26 (m, 1H), 1.08 – 1.01 (m, 1H), 1.02 (t, J = 7.7 Hz, 3H), 1.02 (d, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 150.5, 147.6, 132.8, 128.1, 127.9, 126.9, 126.8, 124.0, 69.8, 67.8, 66.9, 48.2, 42.6, 40.3, 35.3, 24.6, 19.3, 17.1, 16.3, 11.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{27}H_{36}N_2O_2+H]^+$, 421.2850; found, 421.2855.



(±)-2p: General procedure E was followed using the piperidine **1p** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (63.7 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2v** as a mixture of diastereomers (88:12 *dr*). Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) followed by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **2p** (35.1 mg, 48%, 88:12 *dr*) as a pale yellow solid (mp: 113-115 °C). IR (neat): 2957, 2975, 1746, 1618, 1491, 1333, 1248, 1045, 995, 776, 696 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 0.12H), 7.63 (d, *J* = 7.9 Hz, 0.88H), 7.47 (d, *J* = 8.1 Hz, 0.12H), 7.38 – 7.36 (m, 1H), 7.26 (s, 0.88H), 7.08 – 7.04 (m, 2H), 6.97 – 6.96 (m, 1.76H), 6.90 – 6.88 (m, 0.88H), 6.72 – 6.69 (m, 0.36H), 5.21 (d, 15.1 Hz, 0.12H), 5.17 (d, 15.1 Hz, 0.12H), 5.13 (s, 1.76H), 4.68 (dd, *J* = 8.4, 3.3 Hz, 0.12H), 4.13 (dd, *J* = 10.6, 4.4 Hz, 0.88H), 3.70 – 3.68 (m, 0.12H), 2.82 – 2.79 (m, 0.88H), 2.12 – 2.06 (m, 0.12H), 2.01 – 1.91 (m, 1H), 1.81 – 1.74 (m, 0.88H), 1.65 – 1.58 (m, 3H), 1.51 – 1.42 (m, 1H), 1.36 – 1.29 (m, 1H), 1.07 – 1.00 (m, 1.36H), 1.04 (t, *J* = 7.7 Hz, 2.64H), 1.03 (d, *J* = 6.9 Hz, 2.64H), 0.97 (t, *J* = 7.4 Hz, 0.36H), 0.76 (t, *J* = 7.4 Hz, 2.64H), 0.68 (t, *J* = 7.6 Hz, 0.36H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.04, 170.97, 152.7, 152.5, 150.1, 149.4, 146.8, 146.4, 128.9, 128.5, 128.3, 128.2, 127.1, 125.5, 125.1, 124.5, 123.9, 123.8, 121.1, 120.5, 120.0, 119.4, 70.0, 69.5, 69.4, 68.2, 54.9, 44.1, 42.6, 41.9, 40.4, 35.6, 29.7, 27.9, 24.5, 23.3, 22.7, 19.3, 16.9, 16.4, 16.1, 15.0, 12.4, 11.4. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{24}H_{29}NO_2+H]^+$, 364.2271; found, 364.2278.

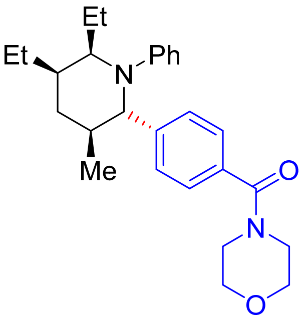


(±)-2q: General procedure E was followed using the piperidine **1q** (46.3 mg, 0.200 mmol, 1.00 equiv) and ethyl 4-cyanobenzoate (70.1 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **2q** (33.9 mg, 45%, >95:5 *dr*) as a pale yellow solid (mp: 74-77 °C). IR (neat): 2966, 2873, 1718, 1461, 1272, 1108, 1020, 770, 701 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.05 – 7.03 (m, 2H), 6.96 – 6.95 (m, 2H), 6.88 – 6.85 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.05 (dd, *J* = 8.5, 6.4 Hz, 1H), 2.81 – 2.79 (m, 1H), 1.99 – 1.92 (m, 1H), 1.80 – 1.73 (m, 1H), 1.65 – 1.63 (m, 1H), 1.61 – 1.58 (m, 2H), 1.50 – 1.43 (m, 1H), 1.36 – 1.29 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.06 – 1.01 (m, 1H), 1.04 (t, *J* = 7.6 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.6, 150.7, 150.4, 129.2, 128.3, 128.1, 127.7, 127.1, 124.2, 69.9, 68.0, 60.6, 42.6, 40.3, 35.5, 24.6, 19.3, 17.0, 16.4, 14.3, 11.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{25}H_{33}NO_2+H]^+$, 380.2584; found, 380.2589.

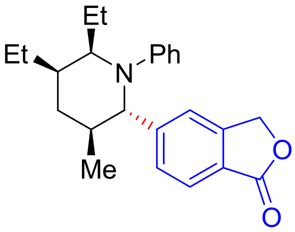


(±)-2r: A modification to general procedure E was followed using the piperidine **1r** (46.3 mg, 0.200 mmol, 1.00 equiv), isonicotinonitrile (41.6 mg, 0.400 mmol, 2.00 equiv). In place of $Ir(ppy)_3$, $[Ir(dtbbpy)(ppy)_2]PF_6$ (80 µL, 0.0020 mmol, 0.010 equiv) was added as a stock solution in DMA (0.025 M). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by preparative TLC (1:5:94 NEt_3/EtOAc/hexanes) provided the product **2r** (25.6 mg, 42%, >95:5 *dr*) as a pale yellow waxy solid. IR (neat): 2959, 2873, 1597, 1493, 1235, 1128, 990, 811, 753, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 5.9 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 7.01 – 6.98 (m, 2H), 6.83 – 6.82 (m, 2H), 6.74 – 6.72 (m, 1H), 3.81 (d, *J* = 9.7 Hz, 1H), 3.53 (q, *J* = 4.4 Hz, 1H), 2.15 – 2.10 (m, 1H), 1.68 (dt, *J* = 13.2, 3.7 Hz, 1H), 1.63 – 1.54 (m, 2H), 1.42 – 1.34 (m, 2H), 1.31 – 1.23 (m, 1H), 1.14 (apparent q, *J* = 12.6 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.49 (t, *J* = 7.6

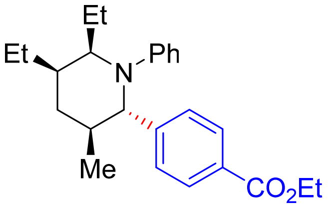
Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.4, 150.9, 149.0, 128.0, 125.2, 124.1, 121.6, 68.3, 64.3, 43.5, 40.1, 34.0, 26.1, 19.1, 16.7, 15.0, 12.0. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{21}H_{28}N_2$+H]$^+$, 309.2325; found, 309.2331.



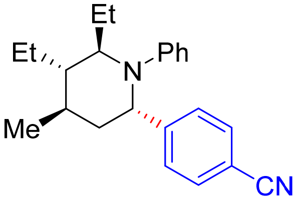
(±)-2s: General procedure E was followed using the piperidine **1s** (46.3 mg, 0.200 mmol, 1.00 equiv) and 4-(morpholine-4-carbonyl)benzonitrile (86.5 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by silica gel chromatography (eluent 1:20:79 NEt$_3$/EtOAc/hexanes) provided the product **2s** (48.8 mg, 58%, >95:5 *dr*) as a pale yellow oil. IR (neat): 2959, 2872, 1630, 1426, 1277, 1114, 1012, 911, 728, 699 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.96 – 6.93 (m, 2H), 6.82 – 6.81 (m, 2H), 6.68 – 6.66 (m, 1H), 3.82 (d, *J* = 9.5 Hz, 1H), 3.66 – 3.28 (br m, 8H), 3.54 (apparent q, *J* = 4.5 Hz, 1H), 2.15 – 2.10 (m, 1H), 1.68 – 1.56 (m, 3H), 1.42 – 1.34 (m, 2H), 1.30 – 1.22 (m, 1H), 1.13 (apparent q, *J* = 12.4 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.73 (d, *J* = 6.4 Hz, 3H), 0.48 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 151.3, 146.2, 132.7, 128.8, 127.7, 126.6, 125.4, 121.1, 68.4, 66.8, 64.6, 48.1, 43.5, 42.5, 40.3, 34.2, 26.1, 19.3, 16.7, 15.0, 12.0. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{27}H_{36}N_2O_2$+H]$^+$, 421.2850; found, 421.2855.



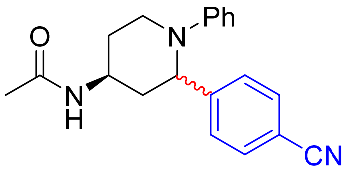
(±)-2t: General procedure E was followed using the piperidine **1t** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (63.7 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by silica gel chromatography (eluent 1:5:94 NEt$_3$/EtOAc/hexanes) provided the product **2t** (52.7 mg, 73%, >95:5 *dr*) as a pale yellow solid (mp: 99-101 °C). IR (neat): 2954, 2873, 1756, 1596, 1492, 1239, 1046, 1001, 757, 697 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.39 (s, 1H), 7.00 – 6.97 (m, 2H), 6.84 – 6.83 (m, 2H), 6.73 – 6.71 (m, 1H), 5.17 (d, *J* = 15.1 Hz, 1H), 5.11 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.55 (apparent q, *J* = 4.4 Hz, 1H), 2.17 – 2.11 (m, 1H), 1.71 – 1.56 (m, 3H), 1.44 – 1.36 (m, 2H), 1.32 – 1.24 (m, 1H), 1.16 (apparent q, *J* = 12.5 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.74 (d, *J* = 6.4 Hz, 3H), 0.49 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 151.6, 151.0, 146.3, 130.1, 128.0, 125.3, 124.7, 123.9, 121.7, 121.6, 69.4, 68.5, 65.0, 43.6, 40.7, 34.1, 26.1, 19.2, 16.7, 15.0, 12.0. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{24}H_{29}NO_2$+H]$^+$, 364.2271; found, 364.2277.



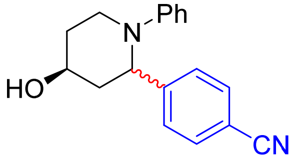
(±)-2u: General procedure E was followed using the piperidine **1u** (46.3 mg, 0.200 mmol, 1.00 equiv) and ethyl 4-cyanobenzoate (70.1 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined the ratio of diastereomers to be >95:5. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided the product **2u** (43.9 mg, 58%, >95:5 *dr*) as a pale yellow solid (mp: 78-80 °C). IR (neat): 2959, 2878, 1707, 1609, 1494, 1369, 1266, 1109, 1022, 770, 703 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 6.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.99 – 6.97 (m, 2H), 6.85 – 6.84 (m, 2H), 6.72 – 6.69 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 9.5 Hz, 1H), 3.56 (apparent q, *J* = 4.5 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.69 – 1.58 (m, 3H), 1.44 – 1.35 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.24 (m, 1H), 1.15 (apparent q, *J* = 12.5 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.73 (d, *J* = 6.2 Hz, 3H), 0.50 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.6, 151.3, 149.4, 128.9, 128.7, 128.3, 127.8, 125.4, 121.3, 68.5, 64.8, 60.6, 43.6, 40.4, 34.2, 26.2, 19.2, 16.7, 15.0, 14.3, 12.1. HRMS-ESI (m/z): [M+H]$^+$ calcd for [$C_{25}H_{33}NO_2$+H]$^+$, 380.2584; found, 380.2589.



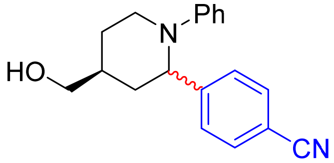
(±)-2v: General procedure E was followed using the piperidine **5** (46.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (51.3 mg, 0.400 mmol, 2.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2v** as a mixture of diastereomers (84:16 *dr*). Purification by silica gel chromatography (eluent 1:3:96 NEt$_3$/EtOAc/hexanes) provided the product **2v** (52.8 mg, 79%, 84:16 *dr*) as a pale yellow oil. IR (neat): 2958, 2873, 2227, 1596, 1497, 1461, 1251, 1018, 909, 843, 731, 691 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 1.68H), 7.46 (d, *J* = 7.9 Hz, 0.32H), 7.40 (d, *J* = 7.9 Hz, 1.68H), 7.33 (d, *J* = 7.9 Hz, 0.32H), 7.11 – 7.06 (m, 2H), 6.78 – 6.74 (m, 0.48H), 6.70 – 6.65 (m, 2.52H), 4.75 – 4.74 (m, 0.84H), 4.40 – 4.37 (m, 0.16H), 3.70 – 3.67 (m, 0.84H), 3.40 – 3.36 (m, 0.16H), 2.30 – 2.24 (m, 0.84H), 1.92 – 1.89 (m, 0.16H), 1.81 – 1.73 (m, 1H), 1.69 – 1.66 (m, 0.84H), 1.60 – 1.51 (m, 2.84H), 1.46 – 1.43 (m, 0.64H), 1.35 – 1.31 (m, 0.84H), 1.28 – 1.24 (m, 0.84H), 1.08 – 1.05 (m, 3H), 1.01 (t, *J* = 7.3 Hz, 0.48H), 0.96 (d, *J* = 6.6 Hz, 2.52H), 0.91 – 0.88 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) 151.3, 151.2, 150.1, 148.9, 132.2, 132.0, 128.7, 127.7, 127.5, 120.2, 119.5, 119.0, 118.2, 117.5, 110.0, 63.7, 61.8, 61.2, 57.1, 46.6, 45.5, 41.8, 38.0, 32.5, 28.0, 27.9, 27.7, 27.6, 25.4, 21.9, 21.5, 12.0, 11.9, 10.3, 9.7. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{23}H_{28}N_2+H]^+$, 333.2325; found, 333.2331.



(±)-2w: A modification to General procedure E was followed using N-(1-phenylpiperidin-4-yl)acetamide **6a** (43.7 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (25.6 mg, 0.200 mmol, 1.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2w** as a mixture of diastereomers (56:44 *dr*). Purification by preparatory TLC (eluent 1:99 NEt_3:EtOAc) provided the product **2w** (60.3 mg, 94%, 57:43 *dr*) as a pale yellow waxy solid. IR (neat): 2941, 2227, 1650, 1587, 1493, 11369, 1109, 909, 835, 727, 698 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2 Hz, 0.86H), 7.50 (d, *J* = 8.1 Hz, 0.86H), 7.44 (d, *J* = 8.2 Hz, 1.14H), 7.36 (d, *J* = 8.1 Hz, 1.14H), 7.24 – 7.21 (m, 0.86H), 7.12 – 7.09 (m, 1.14H), 6.91 – 6.87 (m, 2.57H), 6.82 – 6.79 (m, 0.43H), 5.40 (d, *J* = 7.5 Hz, 0.43H), 5.35 (d, *J* = 8.1 Hz, 0.57H), 5.07 – 5.06 (m, 0.43H), 4.21 (dd, *J* = 10.9, 3.0 Hz, 0.57H), 4.10 – 3.98 (m, 1H), 3.68 (dt, *J* = 14.0, 4.4 Hz, 0.43H), 3.53 (dt, *J* = 12.7, 3.7 Hz, 0.57H), 3.22 – 3.17 (m, 0.43H), 2.96 – 2.91 (m, 0.57H), 2.53 – 2.50 (m, 0.43H), 2.25 – 2.23 (m, 0.57H), 2.10 – 2.08 (m, 0.57H), 1.98 – 1.96 (m, 0.43H), 1.98 (s, 1.29H), 1.96 (s, 1.71H), 1.90 – 1.85 (m, 0.43H), 1.74 (dq, *J* = 12.0, 4.1 Hz, 0.57H), 1.65 – 1.58 (m, 0.43H), 1.46 (apparent q, *J* = 11.5 Hz, 0.57H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 169.4, 151.3, 149.7, 149.2, 146.8, 132.5, 132.2, 129.5, 128.8, 127.92, 127.87, 123.8, 123.5, 119.1, 118.8, 115.6, 110.7, 110.4, 62.7, 57.5, 56.1, 46.9, 43.5, 43.4, 42.8, 34.9, 32.9, 30.8, 23.48, 23.46. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{20}H_{21}N_3O+H]^+$, 320.1757; found, 320.1758.



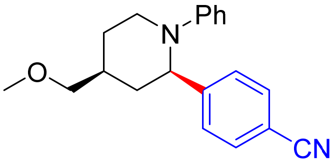
(±)-2x: A modification to General procedure E was followed using 1-phenylpiperidin-4-ol (35.4 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (25.6 mg, 0.200 mmol, 1.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2x** as a mixture of diastereomers (1:1 *dr*). Purification by C18 reverse phase chromatography (0-100% $CH_3CN:H_2O$ containing 0.1 % TFA) provided the product **2x** (26.1 mg, 47%, 48:52 *dr*) as a pale yellow waxy solid. IR (neat): 2926, 2227, 1596, 1493, 1258, 1064, 980, 824, 751, 697 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.2 Hz, 1.04H), 7.46 (d, *J* = 8.1 Hz, 0.96H), 7.41 (d, *J* = 8.1 Hz, 1.04H), 7.37 (d, *J* = 8.1 Hz, 0.96H), 7.19 – 7.15 (m, 1.04H), 7.12 – 7.09 (m, 0.96H), 6.91 – 6.87 (m, 2.48H), 6.85 – 6.82 (m, 0.52H), 4.89 – 4.87 (m, 0.52H), 4.18 (dd, *J* = 10.7, 3.2 Hz, 0.48H), 4.01 – 3.99 (m, 0.52H), 3.92 – 3.86 (m, 0.48H), 3.58 – 3.53 (m, 1H), 3.25 – 3.20 (m, 0.52H), 2.91 (t, *J* = 11.0 Hz, 0.48H), 2.21 – 2.16 (m, 1H), 2.12 – 2.06 (m, 1H), 2.02 – 1.97 (m, 0.52H), 1.86 (qd, *J* = 12.0, 4.2 Hz, 0.48H), 1.80 – 1.74 (m, 0.52H), 1.67 (apparent q, *J* = 10.8 Hz, 0.48H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.2, 150.7, 149.4, 148.8, 132.3, 132.2, 129.1, 128.7, 127.84, 127.82, 123.4, 123.1, 120.7, 119.1, 118.8, 110.30, 110.29 68.6, 64.6, 62.0, 57.7, 54.8, 46.6, 45.0, 40.3, 35.4, 33.7. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{18}H_{18}N_2O+H]^+$, 279.1492; found, 279.1495.



(±)-2y: A modification to General procedure E was followed using (1-phenylpiperidin-4-yl)methanol (38.3 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (25.6 mg, 0.200 mmol, 1.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2y** as a mixture of diastereomers (68:32 *dr*). Purification by C18 reverse phase chromatography (0-100% $CH_3CN:H_2O$ containing 0.1 % TFA) provided the product **2y** (31.9 mg, 55%, 68:32 *dr*) as a pale yellow waxy solid. Purification by preparatory TLC (eluent 90:10 DCM:EtOAc) provided fractions of each of the diastereomers separately for characterization (major: 15.8 mg, 27%; minor: 4.4 mg, 8%).

(±)-2y-syn *(major diastereomer)*: IR (neat): 2916, 2226, 1597, 1492, 1222, 1027, 913, 833, 769, 698 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.09 (m, 2H), 6.91 – 6.90 (m, 2H), 6.89 – 6.86 (m, 1H), 4.10 (dd, *J* = 11.0, 3.1 Hz, 1H), 3.60 – 3.57 (m, 2H), 3.54 – 3.51 (m, 1H), 2.86 (td, *J* = 12.1, 2.8 Hz, 1H), 2.04 – 2.01 (m, 1H), 1.91 – 1.88 (m, 1H), 1.86 – 1.79 (m, 1H), 1.58 (qd, *J* = 12.1, 4.2 Hz, 1H), 1.33 (apparent q, *J* = 12.0 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.9, 150.5, 132.2, 128.7, 127.8, 123.6, 123.0, 118.9, 110.2, 67.5, 63.4, 56.8, 39.8, 38.8, 29.2. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{19}H_{20}N_2O+H]^+$, 293.1648; found, 293.1654.

(±)-2y-anti *(minor diastereomer*): IR (neat): 2923, 2227, 1596, 1500, 1251, 1031, 988, 835, 750, 690 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.20 (m, 2H), 6.84 – 6.82 (m, 2H), 6.76 – 6.74 (m, 1H), 5.16 – 5.15 (m, 1H), 3.79 (dt, *J* = 13.3, 4.3 Hz, 1H), 3.56 – 3.50 (m, 2H), 3.25 – 3.21 (m, 1H), 2.34 – 2.31 (m, 1H), 1.86 – 1.80 (m, 2H), 1.73 – 1.66 (m, 1H), 1.50 – 1.43 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.8, 148.0, 132.3, 129.4, 128.0, 118.9, 118.0, 114.3, 110.3, 67.4, 57.1, 43.0, 33.3, 32.4, 27.4. HRMS-ESI (m/z): $[M+H]^+$ calcd for $[C_{19}H_{20}N_2O+H]^+$, 293.1648; found, 293.1654.



(±)-2z: A modification to General procedure E was followed using 4-(methoxymethyl)-1-phenylpiperidine **6b** (41.1 mg, 0.200 mmol, 1.00 equiv) and 1,4-dicyanobenzene (25.6 mg, 0.200 mmol, 1.00 equiv). Crude ^{1}H NMR analysis of the reaction mixture determined that the reaction gave the desired product **2z** as a mixture of diastereomers (59:41 *dr*). Purification by preparative TLC (eluent 1:20:79 NEt_3/EtOAc/hexanes) provided the product **2z** (41.7 mg, 68%, 62:38 *dr*) as a pale yellow waxy solid. Purification by C18 reverse phase chromatography (0-100% CH_3CN:H_2O containing 0.1 % TFA) provided fractions of each of the diastereomers separately for characterization (major: 21.3 mg, 35%; minor: 15.1 mg, 25%).

(±)-2z-syn *(major diastereomer)*: IR (neat): 2922, 2226, 1597, 1492, 1218, 1096, 947, 832, 769, 698 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.44 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.11 – 7.09 (m, 2H), 6.91 – 6.89 (m, 2H), 6.88 – 6.85 (m, 1H), 4.09 (dd, J = 11.1, 3.2 Hz, 1H), 3.57 (dt, *J* = 12.1, 3.5 Hz, 1H), 3.33 (s, 3H), 3.33 – 3.30 (m, 1H), 3.23 – 3.21 (m, 1H), 2.85 (td, J = 12.1, 2.6 Hz, 1H), 2.04 – 2.01 (m, 1H), 1.94 – 1.84 (m, 2H), 1.57 (qd, J = 12.0, 4.1 Hz, 1H), 1.33 (apparent q, J = 11.7 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) 152.0, 150.5, 132.1, 128.6, 127.8, 123.5, 122.9, 119.0, 110.1, 77.5, 63.4, 59.0, 56.8, 40.3, 36.6, 29.5. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{20}H_{22}N_2O+H]^+$, 307.1805; found, 307.1810.

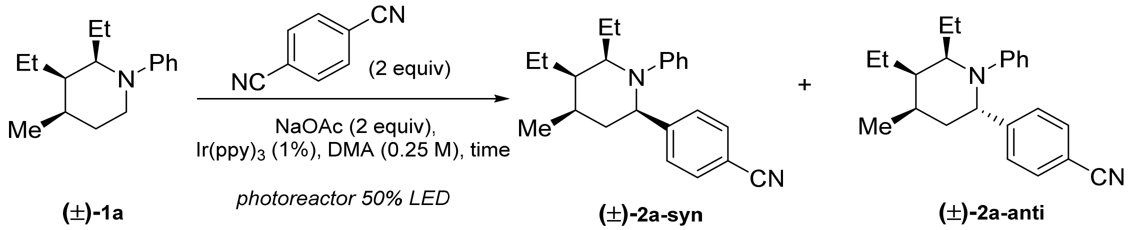
(±)-2z-anti *(minor diastereomer)*: IR (neat): 2923, 2852, 2226, 1596, 1501, 1251, 1095, 979, 837, 750, 691 cm^{-1}. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.20 (m, 2H), 6.83 – 6.81 (m, 2H), 6.76 – 6.73 (m, 1H), 5.13 – 5.12 (m, 1H), 3.76 (dt, *J* = 13.4, 4.2 Hz, 1H), 3.31 (s, 3H), 3.27 – 3.19 (m, 3H), 2.32 – 2.29 (m, 1H), 1.84 – 1.77 (m, 3H), 1.49 – 1.42 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.8, 148.1, 132.3, 129.4, 128.0, 118.9, 117.9, 114.2, 110.3, 77.3, 58.9, 57.1, 43.0, 32.7, 30.9, 27.7. HRMS-ESI (m/z): [M+H]$^+$ calcd for $[C_{20}H_{22}N_2O+H]^+$, 307.1805; found, 308.1810.

Stereochemical Assignments

1. The relative stereochemistry of **(±)-2a** was determined by X-ray crystallography (see section S66) and all other 2,3,4,6-substituted analogues were assigned by analogy.
2. The relative stereochemistry of **(±)-2e** was determined by X-ray crystallography (see section S66) and all other 2,3,5,6-substituted analogues were assigned by analogy.
3. The relative stereochemistry of the major diastereomer of **(±)-2z** was determined by X-ray crystallography (see section S66) and all other 4,6-substituted analogues were assigned by analogy.
4. The relative stereochemistries of **(±)-2l** and **(±)-2m** were each determined by 1D selective NOE experiments (see section S136).
5. The relative stereochemistry of **(±)-5** and **(±)-2v** were each determined by X-ray crystallography (see section S66).

Epimerization Studies

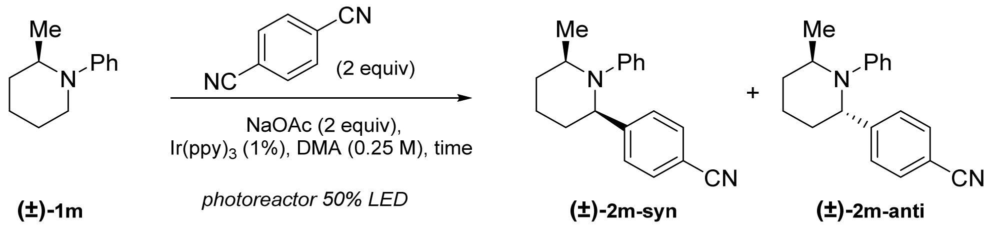
Supplemental Table S5



Entry[a]	Time (min)	% Yield 2a-syn[b]	% Yield 2a-anti[b]	% Yield 1a[b]
1	2	12	13	66
2	4	19	20	51
3	8	31	34	23
4	16	38	37	<5
5	24	60	28	<5
6	32	63	21	<5
7	48	73	14	<5
8	120	83	<5	<5
9	120 (16 min with light then dark for 104 min)	46	36	<5

[a]Conditions: 0.1 mmol of **1a**, photoreactor 50% LED, 450 nm. [b]Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard.

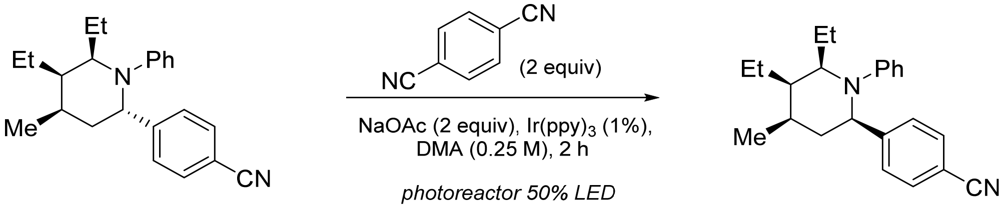
Supplemental Table S6



Entry[a]	Time (min)	% Yield 2m-syn[b]	% Yield 2m-anti[b]	% Yield 1m[b,c]
1	1	9	7	44
2	2	17	14	10
3	3	22	18	13
4	5	31	26	20
5	10	45	36	<5
6	20	47	36	<5
7	120	50	28	<5

[a]Conditions: 0.1 mmol of **1m**, photoreactor 50% LED, 450 nm. [b]Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard. [c]**1m** is volatile, mass balance isn't accurate.

Supplemental Table S7



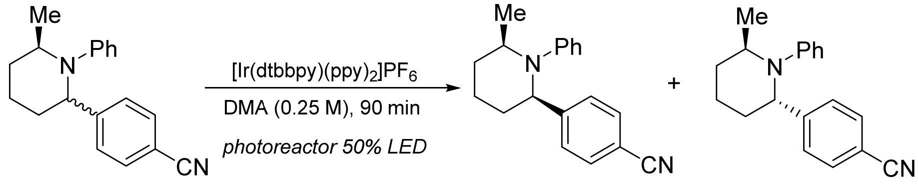
(±)-2a-anti
minor diastereomer
>95:5 dr

(±)-2a-syn
major diastereomer

Entry[a]	**Conditions**	**% Yield 2a-anti**[b]	**% Yield 2a-syn**[b]
1	As above	<5	85
2	No 1,4-dicyanobenzene	67	21
3	No NaOAc	<5	74
4	No 1,4-dicyanobenzene, no NaOAc	62	15
5	No NaOAc, no Ir(ppy)$_3$	60	28
6	No NaOAc, no 1,4-dicyanobenzene, 16 h [Ir(dtbbpy)(ppy)$_2$]PF$_6$ instead of Ir(ppy)$_3$	<5	72

[a]Conditions: 0.05 mmol of **2a-anti**, photoreactor 50% LED, 450 nm. [b]Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard.

Supplemental Table S8



(±)-2m

(±)-2m-syn

(±)-2m-anti

Entry[a]	**Starting isomer**	**% Yield 2m-syn**[b]	**% Yield 2m-anti**[b]
1	**2m-syn** (>95:5 *dr*)	27	62
2	**2m-anti** (>95:5 *dr*)	22	74

[a]Conditions: 0.1 mmol of **2m**, photoreactor 50% LED, 450 nm. [b]Yields determined by crude ^{1}H NMR analysis with 2,6-dimethoxytoluene as an external standard.

Mechanistic Experiments on the formation of DCB•- and Ir(ppy)$_3^{+}$

I. Excited State Quenching Measurements with TCSPC

TCSPC was used to measure excited state ET rate constants between Ir(ppy)$_3$ and various reagents. Each TCSPC trace was modeled to a single-exponential decay appropriate for the unimolecular or pseudo-first order kinetics. Raw TSCPC data for *Ir(ppy)$_3$ quenching with DCB is given in Figure S1A. The plot of k_{obs} versus [DCB] is shown in Figure S1B giving k_{quench} as the slope. The excited state lifetime of the Ir(ppy)$_3$ was measured as τ = 1.525 μs in DMA.

Ir(ppy)$_3$* quenching with dicyanobenzene

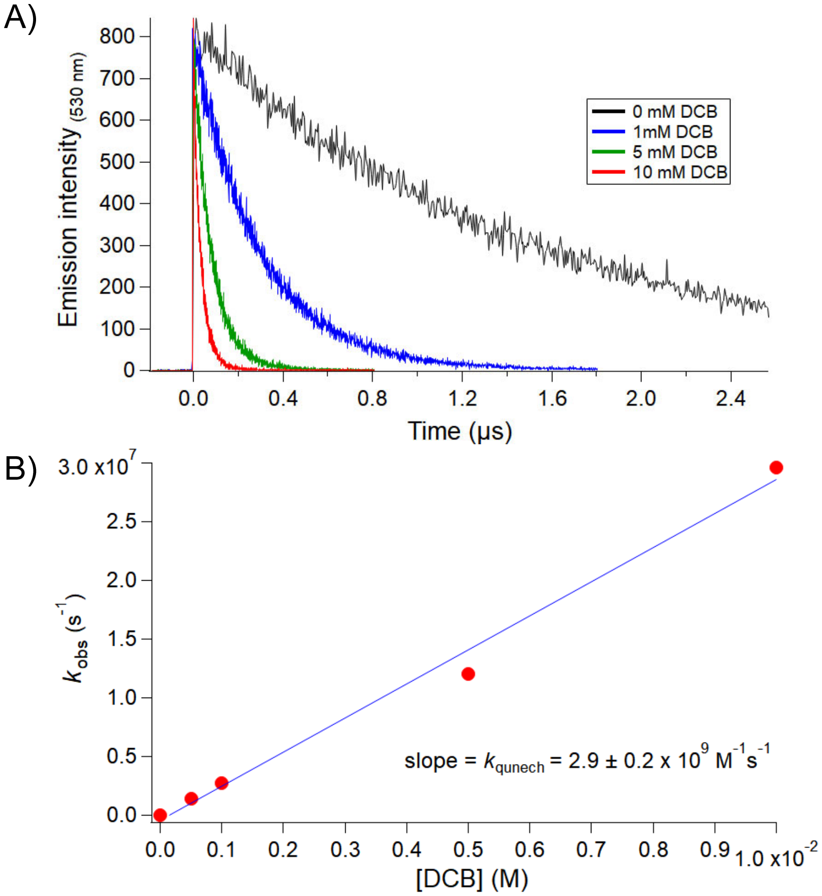


Figure S1: A) TCSPC data of Ir(ppy)$_3$ in the presence of increasing amounts of DCB. Time zero indicates when the 390 nm excitation pulse occurred. Excited state decay was modeled to a single exponential, yielding a pseudo first-order k_{obs}. B) Plot of k_{obs} obtained from single exponential fits to data in A vs [DCB]. Slope of the line gives the second order rate constant for excited state ET from *Ir(ppy)$_3$ to DCB, k_{quench}.

*Ir(ppy)$_3$ quenching with piperidine 1m

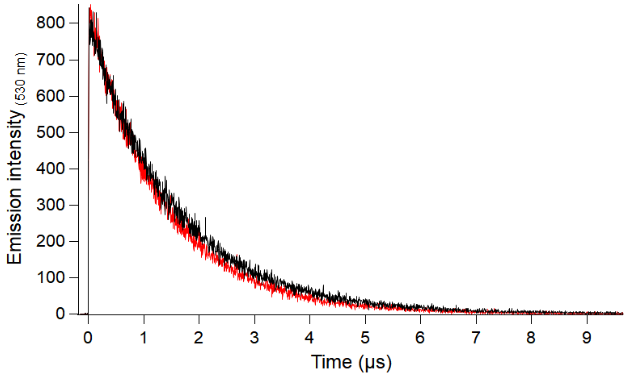


Figure S2: TCSPC data for Ir(ppy)$_3$* without and with piperidine **1m**. Ir(ppy)$_3$ only (black) and 0.25 M piperidine **1m** added to Ir(ppy)$_3$ (red) are shown. Less than 10% excited state lifetime quenching is observed at the high [**1m**].

II. Spectroelectrochemistry measurements of Ir(ppy)$_3$ oxidation to Ir(ppy)$_3^+$

Spectroelectrochemistry was used to obtain an authentic spectrum of Ir(ppy)$_3^+$ (Figure S3). Figure S3 shows our electrochemical and spectroelectrochemical investigations of Ir(ppy)$_3^+$.

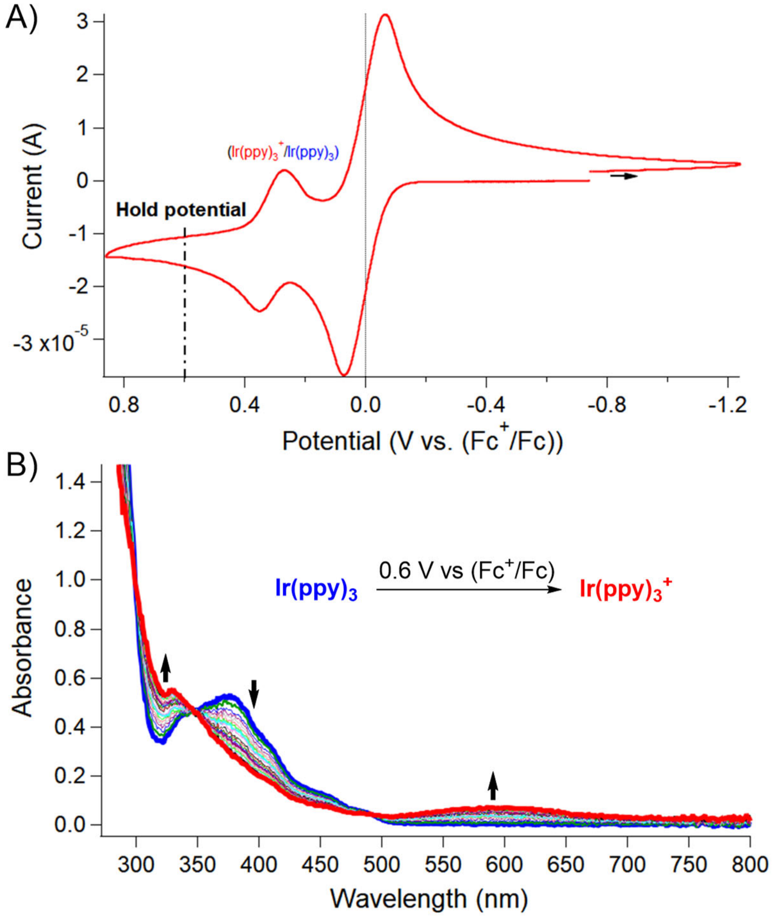


Figure S3: A) Cyclic voltammogram of ~10^{-5} M Ir(ppy)$_3$ in 100 mM tetrabutylammonium hexafluorophoshate (TBAPF$_6$) solution of DMA with added ferrocene (Fc) as an internal standard. The (Ir(ppy)$_3^+$/Ir(ppy)$_3$) couple was observed at 0.31 V vs (Fc$^+$/Fc). We chose 0.6 V as the hold potential for our bulk spectroelectrochemistry measurement. Initial sweep direction is indicated with an arrow. Measurement used a glassy carbon working electrode, platinum wire auxiliary electrode, and a Ag$^+$/Ag pseudo-reference in 100 mM TBAPF$_6$ DMA solution. B) Spectroelectrochemistry data collected for 0.4 mM Ir(ppy)$_3$ in a 0.2 cm pathlength spectroelectrochemistry cell in 100 mM TBAPF$_6$ DMA solution. Scan rate for UV-Vis collection was 60 nm/sec with 12 seconds in between spectra collection.

Bolded blue spectrum was obtained before any charge was passed, corresponding to Ir(ppy)$_3$. Changes in absorption over time are indicated with arrows. A platinum mesh was used at the working electrode. Absorption spectra were collected every 10 seconds until no changes were observed and no more charge was passed, indicating full conversion to Ir(ppy)$_3^+$. This species is indicated by the bolded red spectrum.

III. Transient absorption measurements

Transient absorption measurements were used to monitor the formation and decay of DCB$^{\bullet -}$ and Ir(ppy)$_3^+$. The Ir(ppy)$_3$/Ir(ppy)$_3^+$ isosbestic point observed at 346 nm was used to observe absorbance changes associated with only the DCB$^{\bullet -}$. Data at 390 nm, corresponding to the Ir(ppy)$_3$ absorbance, was used to monitor the formation and decay of Ir(ppy)$_3^+$.

Recombination of DCB$^{\bullet -}$ and Ir(ppy)$_3^+$

We performed flash-quench TA measurements in the absence of piperidine substrate to confirm the formation of Ir(ppy)$_3^+$ and DCB$^{\bullet -}$ implicated by excited state quenching and also to monitor charge recombination between Ir(ppy)$_3^+$ and DCB$^{\bullet -}$ (Figure S4). As seen in Figure S4A, immediately after 430 nm excitation, large absorption changes were seen at 346 nm and 380 nm, with another broad band at 600 nm. The intense positive ΔmOD feature at 346 nm was consistent with the formation of DCB$^{\bullet -}$ based on the reported intense absorption band at 346 nm. The negative ΔmOD feature at 380 nm and the broad feature at 600 nm were consistent with the formation of Ir(ppy)$_3^+$ based on the spectroelectrochemistry data in Figure S3B. Because Ir(ppy)$_3^+$ is more absorbing between 350-400 nm, the oxidation of Ir(ppy)$_3$ to Ir(ppy)$_3^+$ was seen as a large negative ΔmOD in Figure S4A. We also see the growth of the broad 600 nm band observed for Ir(ppy)$_3^+$, where Ir(ppy)$_3$ shows no absorbance. These data further support the formation of Ir(ppy)$_3^+$ and DCB$^{\bullet -}$ implicated by the excited state electron transfer from *Ir(ppy)$_3$ to DCB shown in Figure S1. Charge recombination of DCB$^{\bullet -}$ with Ir(ppy)$_3^+$ was measured in the absence of a piperidine substrate by monitoring the decay of DCB$^{\bullet -}$ absorbance at 346 nm (Figure S4B). The kinetics were modelled to bimolecular kinetics of equal concentration reactants (eq S1).

$$[DCB^{\bullet -}]_t = \frac{[DCB^{\bullet -}]_i}{(1+k_{rec}t[DCB^{\bullet -}]_i)} \qquad \text{(eq S1)}$$

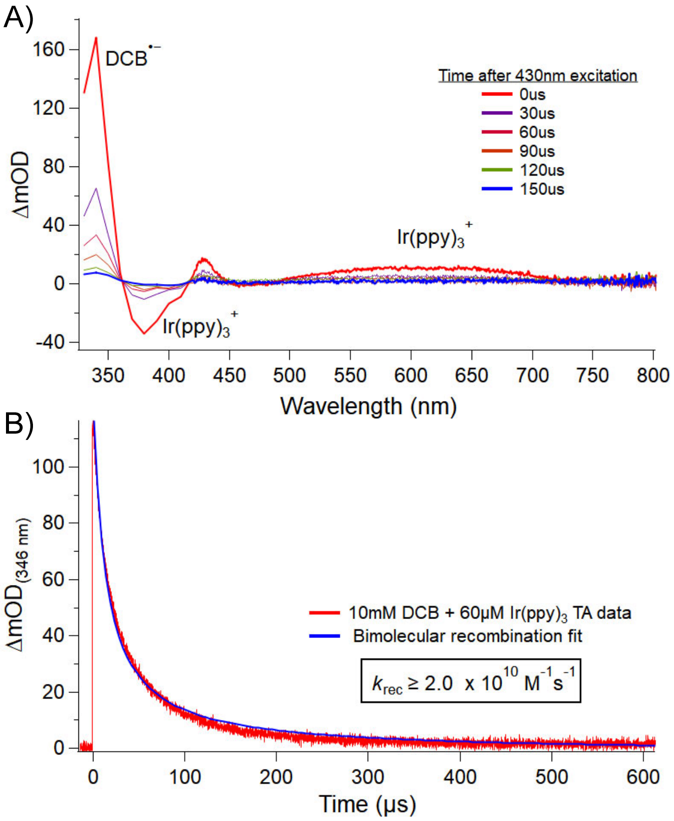


Figure S4: A) TA difference spectra collected with 10 mM DCB and 40 μM Ir(ppy)$_3$ different times after the 430 nm laser flash. Immediately after the laser flash we see the growth of signals consistent with Ir(ppy)$_3^+$ and DCB$^{\bullet -}$ B) Single wavelength TA data collected at 346 nm with 10 mM of DCB and 40 μM Ir(ppy)$_3$ in DMA. At this concentration of DCB, the excited state lifetime is < 10 ns, which leads to rapid formation of DCB$^{\bullet -}$ after the laser flash. The decay of this species was modeled as an equal-concentration bimolecular recombination shown in eq S1, and the rate constant was estimated using the reported ε_{346nm} = 34,000 M^{-1} cm^{-1} for $DCB^{\bullet-}$ in water. This fit is shown in blue. The recombination of $DCB^{\bullet-}$ and $Ir(ppy)_3^+$ formed from excited state electron transfer proceeds at or near diffusion limit.

Oxidation of reactant piperidine 1m by $Ir(ppy)_3^+$

As described above, excited state ET between DCB and $Ir(ppy)_3$ generates $Ir(ppy)_3^+$. $Ir(ppy)_3^+$ is thermodynamically capable of oxidizing the reactant piperidine present in a large excess under the reaction conditions. To estimate the rate constant for reactant piperidine oxidation by photogenerated $Ir(ppy)_3^+$ (k_{ox}, eq S3), we monitored the return in absorbance at 390 nm as a function of increasing concentration of piperidine **1m**. As seen in Figure S5, $Ir(ppy)_3^+$ has a lower ε_{390} than $Ir(ppy)_3$, so forming $Ir(ppy)_3^+$ results in a large negative ΔOD_{390} (Figure S7). The return of this absorbance corresponds to the reduction of $Ir(ppy)_3^+$ by **1m** (eq S3) or by recombination with $DCB^{\bullet-}$ to reform $Ir(ppy)_3$ (eq S2). The absorbance return at 390 nm was modeled to a combination of bimolecular recombination between the $Ir(ppy)_3^+$ and $DCB^{\bullet-}$ and pseudo-first-order ET between piperidine **1m** (eq S5).

$$\mathrm{Ir(ppy)_3}^+ + DCB^{\bullet-} \xrightarrow{k_{rec}} \mathrm{Ir(ppy)_3} + DCB \qquad \text{(eq S2)}$$

$$\mathrm{Ir(ppy)_3}^+ + \mathrm{pip} \xrightarrow{k_{ox}} \mathrm{Ir(ppy)_3} + pip^{\bullet+} \qquad \text{(eq S3)}$$

$$pip^{\bullet+} + DCB^{\bullet-} \xrightarrow{k_{rec,\ pip}} \mathrm{pip} + \mathrm{DCB} \qquad \text{(eq S4)}$$

$$[Ir(ppy)_3{}^+]_t = \left(\frac{[Ir(ppy)_3{}^+]_i \exp(-k_{obs}t)}{1 + k_{rec}t[DCB^{\bullet-}]_i}\right) \qquad \text{(eq S5)}$$

where k_{obs} is the observed rate constant for **1m** oxidation by $Ir(ppy)_3^+$ under pseudo-first order conditions ([**1m**]>>>[$Ir(ppy)_3^+$]) and k_{rec} was fixed to the value obtained for the 390 nm and 346 nm data in the absence of **1m** (see Figure S4B).

Eq S5 was applied to only the initial *increased absorbance* after the laser flash for the TA data in Figure S5, as this should pertain to the reduction of $Ir(ppy)_3^+$ to $Ir(ppy)_3$ (an absorbance growth). The residual positive ΔmOD was due to residual $DCB^{\bullet-}$ absorbance at 390 nm, which did not recombine with $Ir(ppy)_3^+$ due to the competitive reaction with abundant **1m**. The decay of this positive ΔmOD feature occurs on a similar timescale as the recombination in the absence of **1m**, suggesting that $\mathbf{1m}^{\bullet+}$ reacts with $DCB^{\bullet-}$ ($k_{rec,\ pip}$ eq S4) with a similar rate constant to k_{rec}. The similarity of the rate constants for $\mathbf{1m}^{\bullet+}$ reacting with $DCB^{\bullet-}$ and for $Ir(ppy)_3^+$ recombination with $DCB^{\bullet-}$ is an inherent assumption in eq S5. where it is assumed throughout that $[Ir(ppy)_3^+]_t = [DCB^{\bullet-}]_t$.

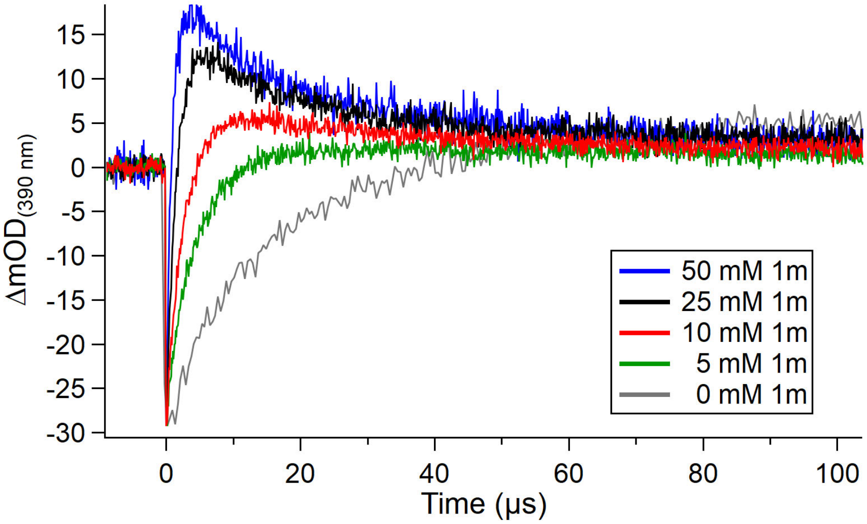


Figure S5: Transient absorption data collected at 390 nm with 10 mM of DCB, 40 of μM $Ir(ppy)_3$, and increasing concentrations of **1m**. The laser flash leads to rapid oxidation of the $Ir(ppy)_3$, yielding a large negative absorbance change because the $Ir(ppy)_3^+$ species has a smaller ε_{390} than $Ir(ppy)_3$. **1m** oxidation by $Ir(ppy)_3^+$ is observed as a return in the absorbance at 390 nm as $Ir(ppy)_3^+$ is reduced to $Ir(ppy)_3$. The fit of this absorbance return to eq S2 is shown as a solid line on the data traces. k_{obs} at each concentration of **1m** was obtained from the fits. We observe that the return in $Ir(ppy)_3$ absorbance is faster with larger concentrations of **1m**, and that a new positive absorbance can be observed at sufficiently high concentrations of **1m**. This is consistent with an intermolecular ET reaction between **1m** and the $Ir(ppy)_3^+$ generated in the laser flash (eq S3). The residual absorbance is due to leftover $DCB^{\bullet-}$ which was not able to recombine with $Ir(ppy)_3^+$ before it could be reduced by **1m**. The decay of what we assign as residual $DCB^{\bullet-}$ absorbance matches well with the bimolecular recombination kinetics in Figure S7, suggesting perhaps that the reaction of **1m**$^+$ and $DCB^{\bullet-}$ occurs with a similar rate constant (eq S4).

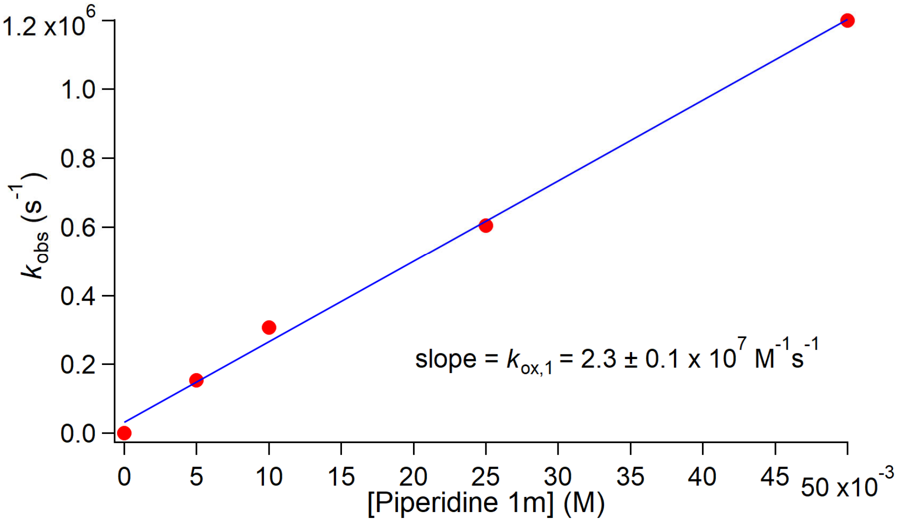


Figure S6: Observed rate constants for $Ir(ppy)_3^+$ reduction by **1m** at 390 nm obtained from the fits shown in Figure S5. The slope of the concentration dependence corresponds to the second order rate constant for **1m** oxidation with $Ir(ppy)_3^+$.

Oxidation of arylated piperidines 2a-syn and 2a-anti with $Ir(ppy)_3^+$

As described in the main text, the C-H arylated products were found to undergo a selective epimerization which yielded the observed distribution of diastereomers. One possibility we explored was that epimerization occurs more rapidly with one diastereomer than the other, leading to enrichment in the slower reacting diastereomer. To determine if the initial oxidation of the arylated piperidines kinetically controlled the observed *dr*, we measured the rate constants for oxidation of piperidine **2a-syn** ($k_{ox,syn}$) and **2a-anti** ($k_{ox,syn}$) in the same way as described above for **1m** oxidation. If the observed diastereoselectivity, 95:5 ≥ (**2a-syn**:**2a-anti**), was a result of the different rate constants for initial oxidation of the **2a** diastereomers, then $k_{ox,anti}$ would need to be 19 times larger than $k_{ox,syn}$.

The rate constants for oxidizing the **2a** diastereomers are smaller than those reported above for piperidine **1m**, which is consistent with the addition of an electron withdrawing cyanobenzene group. As can been seen in Figure S9, the change in the 390 nm TA data with added piperidine **2a** (Figure S7) was much smaller than the changes seen in Figure S7. With the rate constants being much smaller, the accuracy of the fit in eq S5 suffered, as much of the absorbance growth after the laser flash at 390 nm was dominated by $Ir(ppy)_3^+$ recombination with $DCB^{\bullet-}$ (eq S2).

Furthermore, the residual positive ΔmOD at 390 nm, attributed to leftover $DCB^{\bullet-}$ absorbance, does *not* decay appreciably with the **2a** diastereomers. We hypothesize that, unlike with **1m⁺** (see discussion above and Figures S5 and S6), $k_{rec,pip}$ was not similar to the k_{rec} in the case of piperidine **2a** radical cation (eq S4). This causes deviation from the model in eq S5, as this model assumes that $k_{rec} \approx k_{rec,pip}$. We therefore attributed the non-zero y-intercepts in the k_{obs} versus [**2a**] plot in Figure S8 to deviations from the mass-balanced bimolecular recombination behavior assumed in eq S5 and insufficient accountancy for recombination in the kinetic fit. Still, Figure S8 shows that both diastereomers react with $Ir(ppy)_3^+$ with nearly indistinguishable rate constants. These results rule out that diastereoselectivity is controlled by initial oxidation of the arylated piperidines as the ratio of the rate constants ($k_{ox,anti}/k_{ox,syn}$) would need to be greater than 20. Therefore, the below data does not a support that the observed *dr* was kinetically controlled by initial arylated piperidine oxidation.

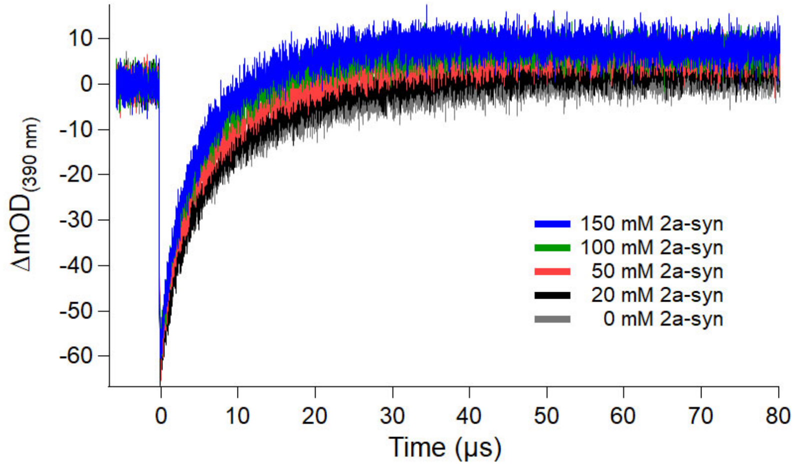


Figure S7: 390 nm transient absorption data for **2a-syn** oxidation by photogenerated $Ir(ppy)_3^+$ as a function of increasing piperidine concentration. The return in absorbance was faster with added **2a-syn**, indicating faster $Ir(ppy)_3^+$ decay in the presence of added piperidine and indicating **2a-syn** oxidation by $Ir(ppy)_3^+$. The TA data was fit to equation S5 as described for **1m** oxidation.

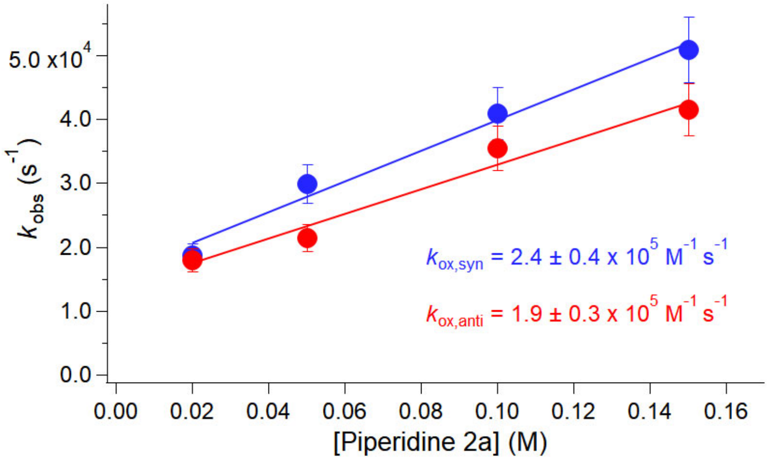


Figure S8: Plot of k_{obs} vs. **2a-syn** or **2a-anti** concentration when the data in Figure S9 was fit to eq S5. The slope of the dependence is the rate constant $k_{ox,\ syn}$ for **2a-syn** (blue) and $k_{ox,\ anti}$ for **2a-anti** (red).

Quantum Yield Measurements

Quantum yield measurements were performed using the $Ru(bpy)_3^{2+}$ endoperoxide actinometer standardized by Scaiano *et al*[11] in the same photoreactor and Kontes capped reaction vessels used for the arylation reaction. Samples were found to absorb 3.4 x 10^{-7} (mol hv)/sec in the photoreactor based on the consumption of diphenylanthracene absorption at 372 nm. Quantum yields for the piperidine α-arylation varied between 0.6-0.4 from 2-8 minutes for piperidine **1a** based on product conversions given in Table S4 for piperidine **1a**.

DFT Calculations

I. Computational Methods

DFT calculations were performed using Gaussian 09.[12] Geometry optimizations and frequency calculations were performed at the ωB97X-D/6-31G(d) level of theory[13] using the conductor-like polarizable continuum model (CPCM)[14] using *N*,*N*-dimethylacetamide (ε = 37.8) to incorporate solvation effects. A pruned (99,590) grid (requested by the keyword "int=ultrafine") was used in geometry optimizations to minimize orientational variations in calculated free energy corrections.[15] Thermal contributions to free energies were calculated from vibrational frequencies using the quasi-rigid rotor-harmonic oscillator (RRHO) approach of Grimme.[16] Optimized geometries were confirmed by frequency computations as minima or first-order saddle-point structures. Single-point energy calculations were computed at the ωB97X-D/6-311+G(d,p), CPCM (*N*,*N*-dimethylacetamide) level of theory. Conformational searches were carried out in Spartan '16 using the MMFFs force field. Computed structures were visualized using CYLview.[17]

II. Calculated Energies

Structure	**E** [ωB97X-D/6-311+G(d,p), CPCM (DMA) // ωB97X-D/6-31G(d), CPCM (DMA)]	**ΔG** [ωB97X-D/6-31G(d), CPCM (DMA)]	**G** (**E** + **ΔG**)
2a-syn	-1002.756731	0.417116	-1002.339615
2a-anti	-1002.756005	0.418444	-1002.337561
2e-syn	-1002.754029	0.418651	-1002.335378
2e-anti	-1002.760037	0.417743	-1002.342294
2m-syn	-845.507318	0.307919	-845.199399
2m-anti	-845.507066	0.308659	-845.198407

Table S9. Computed energies in Hartrees. ΔG values provided are corrected values after applying the quasi-rigid rotor-harmonic oscillator (RRHO) approach of Grimme.[14]

III. Cartesian Coordinates of Calculated Structure

2a-syn

C	-0.07339900	-0.67570200	-0.88493200
C	-0.77593000	-2.03104400	-0.73551900
C	-2.27305900	-1.93925200	-1.02206600
C	-2.90810200	-0.83303000	-0.15597500
C	-2.17343500	0.49164200	-0.44673100
H	-0.30064000	-2.74360600	-1.42021700
H	-0.10791800	-0.40773200	-1.95704400
H	-2.38772500	-1.61992900	-2.06899200
H	-3.93624000	-0.70396900	-0.51892200
H	-2.24864100	0.66175900	-1.54063300
N	-0.74726000	0.35173500	-0.07494200
C	-0.02553200	1.59817900	-0.07594000
C	0.32648000	2.16493500	1.14799000
C	0.33049100	2.25420600	-1.25758500
C	1.02095700	3.37076900	1.19652400
H	0.04602800	1.64471300	2.05878300
C	1.02940100	3.45729900	-1.21085700
H	0.05719000	1.82739200	-2.21869400
C	1.37652700	4.01959200	0.01620400
H	1.28884800	3.80083600	2.15716700
H	1.30142000	3.95817600	-2.13542100
H	1.92222100	4.95769600	0.05136300
C	1.37947200	-0.81937900	-0.48169000
C	2.38304500	-0.86337200	-1.44893300
C	1.72620700	-0.95832000	0.86617600
C	3.71269400	-1.04411000	-1.08893200
H	2.12449200	-0.74948500	-2.49777100
C	3.04728500	-1.13445000	1.24453600
H	0.94689700	-0.91196300	1.62026000
C	4.04621400	-1.17848400	0.26234700
H	4.48854300	-1.07491600	-1.84638900
H	3.31156400	-1.23682100	2.29165800
C	5.41771200	-1.35841800	0.64558700
N	6.52604200	-1.50394200	0.95584800
C	-2.81467800	1.71493200	0.22419800
H	-2.30498300	2.61297100	-0.13781100
C	-4.30902200	1.85765700	-0.06216300
H	-4.67025700	2.82945700	0.28848600
H	-4.51391700	1.79253600	-1.13738000
H	-4.90134700	1.08596100	0.43849600
C	-2.97023800	-1.17945200	1.34888400
H	-2.69146900	-0.30500300	1.94548700
H	-2.22045900	-1.94030100	1.59391300
H	-2.64142300	1.68648800	1.30629800
C	-4.34521800	-1.67019200	1.80554600
H	-4.33996100	-1.92060300	2.87195500
H	-5.10991700	-0.90091400	1.64770000
H	-4.65776300	-2.56251600	1.25312100
C	-2.95008700	-3.30127900	-0.87928700
H	-4.02304100	-3.23251500	-1.09090000
H	-2.51233200	-4.02312800	-1.57778300
H	-2.82974000	-3.70583700	0.13232600
H	-0.60761800	-2.40966100	0.28030900

2a-anti

C	-0.08513200	-0.80251500	0.47090800
C	-0.69875300	-2.14688900	0.04143400
C	-2.22766800	-2.17754600	0.12323500
C	-2.76876100	-0.97777200	-0.67785500
C	-2.15256800	0.36572700	-0.24229100

H	-0.38983600	-2.33799900	-0.99386700
H	-0.26524500	-0.67255400	1.55231000
H	-2.54961700	-3.08609200	-0.40146200
H	-2.40208100	-1.12778100	-1.70482700
H	-2.43960600	1.08273700	-1.02059900
N	-0.67283100	0.28073300	-0.31799500
C	-0.05078000	1.55860400	-0.20591100
C	0.62827100	1.98875000	0.93820400
C	-0.14106700	2.42915000	-1.29888800
C	1.19666000	3.26030900	0.98614100
H	0.71354500	1.33721800	1.80161300
C	0.41131500	3.70248500	-1.24240900
H	-0.64885700	2.09017700	-2.19759300
C	1.08656900	4.12586100	-0.09752300
H	1.72129100	3.57525200	1.88364000
H	0.32813400	4.36198900	-2.10144700
H	1.52740900	5.11709500	-0.05537900
C	1.41419200	-0.89152100	0.25874300
C	2.25428200	-1.21197300	1.32579000
C	1.96548600	-0.72749500	-1.01566600
C	3.62150500	-1.36302500	1.13674700
H	1.83543700	-1.33984600	2.32011500
C	3.32854400	-0.87017000	-1.22204400
H	1.31433800	-0.47330100	-1.84561000
C	4.16167700	-1.18878400	-0.14165400
H	4.26862700	-1.60807000	1.97203500
H	3.75196800	-0.73625800	-2.21176500
C	5.57476700	-1.33411000	-0.34673000
N	6.71689400	-1.45158400	-0.51285300
C	-2.66111100	0.94000200	1.10930200
H	-1.89209200	0.80571400	1.87955500
C	-3.03774700	2.42046800	1.02610700
H	-3.39394600	2.78975600	1.99377100
H	-2.18390000	3.03401900	0.72181300
H	-3.83870500	2.57312500	0.29304600
C	-4.29861100	-0.90186400	-0.77231500
H	-4.55980900	-0.01572000	-1.36613500
H	-4.74609000	-0.74503100	0.21577200
H	-3.53241900	0.38036700	1.46022700
C	-4.93278800	-2.13768100	-1.41094600
H	-6.00622200	-1.98737700	-1.56448500
H	-4.47962500	-2.35446500	-2.38544300
H	-4.81139700	-3.02531800	-0.78082700
C	-2.72396800	-2.30274100	1.56793600
H	-3.81781000	-2.30202900	1.61965300
H	-2.37320900	-3.24780400	1.99709400
H	-2.36049600	-1.49589200	2.21101000
H	-0.26411000	-2.93956900	0.66182500

2e-syn

C	-0.00043200	-0.11495100	1.17893800
C	-0.42025800	1.06581000	2.07778100
C	-0.66212500	2.34782300	1.27601600
C	-1.64791800	2.09562400	0.13136700
C	-1.16041600	0.94739300	-0.78487500
H	-1.41006800	0.76584000	2.45192200
H	-0.13828500	-1.01486100	1.78323500
H	-1.07197400	3.11377200	1.94687000
H	0.27456300	2.76057600	0.88022100
H	-2.58156700	1.72886200	0.58652900
H	-2.00098900	0.68325000	-1.43213500
N	-0.89154400	-0.25947800	0.02221300
C	-1.87147800	-1.26807300	0.03637100

C	-2.36466000	-1.76932900	-1.18224600
C	-2.38145900	-1.82502200	1.22107800
C	-3.32854200	-2.76894100	-1.21171600
H	-1.96494400	-1.38545500	-2.11518400
C	-3.33117200	-2.84289600	1.18287400
H	-2.05829300	-1.45475200	2.18840300
C	-3.81880800	-3.32086800	-0.02918900
H	-3.68311700	-3.13380900	-2.17169200
H	-3.70408600	-3.24970100	2.11876300
H	-4.56431100	-4.10941900	-0.05369900
C	1.45997300	-0.22100400	0.72205500
C	1.87395800	-1.48229000	0.27324900
C	2.38946400	0.82010100	0.70419600
C	3.16026100	-1.70488800	-0.18808300
H	1.16271900	-2.30370200	0.27669400
C	3.68593200	0.61966800	0.24382000
H	2.11494800	1.81398300	1.03387500
C	4.07504900	-0.64429400	-0.20508100
H	3.46005200	-2.68871100	-0.53252900
H	4.39194400	1.44298100	0.23056900
C	5.41196600	-0.85683200	-0.68191600
N	6.49211700	-1.02924000	-1.06816100
C	-0.00068600	1.33435000	-1.71565900
H	0.85952500	1.68841700	-1.14060500
C	0.42942500	0.20457900	-2.64639700
H	1.27940600	0.51131300	-3.26458400
H	0.72172000	-0.68337600	-2.07839400
H	-0.38735100	-0.07857500	-3.32125300
C	-1.98704800	3.39321400	-0.61223800
H	-1.07154800	3.84184000	-1.01891100
H	-2.36879800	4.10833700	0.12782600
C	0.46384000	1.25914900	3.31076600
H	-0.02061300	1.94992200	4.00899300
H	0.61864300	0.30796100	3.83308700
H	1.44802600	1.67061300	3.07158400
H	-0.32902300	2.18617600	-2.32187100
C	-3.02394700	3.22896100	-1.72367500
H	-3.93008900	2.74314800	-1.34292500
H	-3.31154300	4.20169000	-2.13526600
H	-2.64446500	2.62100900	-2.55250500

2e-anti

C	-0.06287900	-0.92161400	0.52179700
C	-0.49782400	-2.35394500	0.12438700
C	-2.01696600	-2.50044400	0.18799800
C	-2.70764600	-1.43212500	-0.65379000
C	-2.30142400	-0.03962200	-0.14698900
H	-0.19369800	-2.50055900	-0.92149400
H	-0.21926900	-0.83206400	1.61239800
H	-2.29746700	-3.50093800	-0.16485900
H	-2.35352700	-2.43048000	1.23324500
H	-2.30819700	-1.50287200	-1.67643800
H	-2.68776600	0.69197500	-0.86409800
N	-0.82545500	0.08161800	-0.22827500
C	-0.38469500	1.43163200	-0.09734700
C	0.23672800	1.93273700	1.05091700
C	-0.60457800	2.30027100	-1.17296900
C	0.62259600	3.26989800	1.11939900
H	0.41394200	1.28589400	1.90359300
C	-0.23479600	3.63727300	-1.09603100
H	-1.06676300	1.90929900	-2.07520000
C	0.38436000	4.13059300	0.05231300
H	1.10442500	3.63939400	2.02012100
H	-0.41656700	4.29363900	-1.94217000

H	0.68312000	5.17272200	0.11027800
C	1.42106500	-0.76026300	0.24440500
C	2.35317100	-0.82325100	1.28068300
C	1.87482800	-0.59811300	-1.06789800
C	3.71434100	-0.72815000	1.02336100
H	2.01089200	-0.94560900	2.30445500
C	3.22924000	-0.49758500	-1.34378500
H	1.15060100	-0.53519300	-1.87364400
C	4.15449700	-0.56310100	-0.29387300
H	4.43212800	-0.77594300	1.83513900
H	3.57497300	-0.36787400	-2.36375600
C	5.55887600	-0.45746300	-0.57097100
N	6.69381400	-0.37214900	-0.79547600
C	-2.87188500	0.32267600	1.24915700
H	-2.10868800	0.14924500	2.01684700
C	-3.37040700	1.76613200	1.34948100
H	-3.77917900	1.96960500	2.34501500
H	-2.56617300	2.48344500	1.16081200
H	-4.16489300	1.95528800	0.61798700
C	-4.22108000	-1.66448200	-0.73920000
H	-4.64969500	-1.75417200	0.26715500
H	-4.37321900	-2.64188600	-1.21462500
C	0.19157800	-3.40938100	0.98891000
H	-0.15882400	-4.40887400	0.71119300
H	1.27941800	-3.39041900	0.87414700
H	-0.04006300	-3.25588900	2.05015700
H	-3.69924700	-0.34911200	1.50188000
C	-4.98332100	-0.59965700	-1.52723600
H	-6.02713900	-0.89567900	-1.67263600
H	-4.98473000	0.36540200	-1.00918900
H	-4.53558000	-0.44670600	-2.51636500

2m-syn

C	0.68281400	-1.19532900	0.54810900
C	0.99901500	-2.65410900	0.18962900
C	2.48105500	-2.95452100	0.37865700
C	3.30754200	-1.95775600	-0.42598400
C	2.96460800	-0.51166500	-0.06335700
H	0.37884300	-3.30841200	0.81206800
H	0.88607600	-1.07328300	1.62778900
H	2.73971800	-2.87273300	1.44320500
H	4.37836300	-2.11682400	-0.25627500
H	3.23306700	-0.35739700	0.99995700
N	1.51524100	-0.27522800	-0.24704800
C	1.15436500	1.10308900	-0.02582200
C	1.17417200	1.68179600	1.24611100
C	0.77647000	1.88035300	-1.11971300
C	0.81433200	3.01582400	1.41793300
H	1.47173700	1.08967900	2.10732200
C	0.42060800	3.21583900	-0.95018600
H	0.76573600	1.42109900	-2.10331300
C	0.43601900	3.78678500	0.32043800
H	0.83087900	3.45432000	2.41146000
H	0.12706700	3.80925200	-1.81112400
H	0.15462800	4.82681500	0.45546000
C	-0.78936100	-0.92380800	0.31506000
C	-1.66671800	-0.80242500	1.39234800
C	-1.29405300	-0.83655500	-0.98640100
C	-3.02560200	-0.59940700	1.18632900
H	-1.28355800	-0.86129800	2.40698100
C	-2.64551600	-0.63026000	-1.21151300
H	-0.61087300	-0.91692600	-1.82576000
C	-3.51652500	-0.51172900	-0.11999800

H	-3.70164600	-0.50322800	2.02911200
H	-3.03112800	-0.55907400	-2.22293400
C	-4.91773400	-0.29555100	-0.34434700
N	-6.05010900	-0.12108800	-0.52623600
C	3.78763800	0.45371600	-0.91206300
H	3.50105300	0.37020000	-1.96644900
H	4.84982700	0.20543700	-0.82072700
H	0.71561000	-2.82931000	-0.85596400
H	3.65511400	1.49325900	-0.60190100
H	3.12006000	-2.10134700	-1.49876600
H	2.70471200	-3.98174400	0.07146400

2m-anti

C	-0.64398200	-1.18923700	0.41585200
C	-0.88165200	-2.62170900	-0.09973100
C	-2.35648200	-3.00856400	-0.08253100
C	-3.15725500	-1.97243600	-0.86706300
C	-2.92903700	-0.55791100	-0.32949500
H	-0.50271300	-2.68181300	-1.12810000
H	-0.87247600	-1.18244400	1.49591000
H	-2.48614500	-4.00358500	-0.52133700
H	-2.84543400	-2.00016000	-1.91856200
H	-3.38590100	0.14196700	-1.03634800
N	-1.48016800	-0.24324500	-0.32756500
C	-1.22238100	1.14163900	-0.11389400
C	-0.68267000	1.65347400	1.07122300
C	-1.52846100	2.03462400	-1.14855400
C	-0.44586900	3.01989600	1.20887300
H	-0.44465700	0.98975500	1.89569700
C	-1.30945700	3.39892100	-1.00140100
H	-1.92640800	1.64153300	-2.08000900
C	-0.76086900	3.90038700	0.17868000
H	-0.02031500	3.39504400	2.13523400
H	-1.55184600	4.07157200	-1.81908500
H	-0.57760800	4.96462200	0.29032400
C	0.82993900	-0.87283100	0.24484800
C	1.71001700	-1.03279000	1.31572200
C	1.33638600	-0.48996600	-1.00084000
C	3.07198900	-0.81289400	1.15828700
H	1.32579600	-1.32740300	2.28838400
C	2.69230900	-0.26243700	-1.17529800
H	0.65184900	-0.35911600	-1.83252200
C	3.56526800	-0.42395700	-0.09142400
H	3.74945200	-0.93499900	1.99653400
H	3.07940300	0.03963400	-2.14261600
C	4.97034200	-0.18693000	-0.26363700
N	6.10597100	0.00451000	-0.40338500
C	-3.59572700	-0.33261200	1.03525500
H	-3.19466000	-0.99467900	1.80927300
H	-4.67214500	-0.51874500	0.96070900
H	-0.28478100	-3.30967900	0.50881300
H	-3.45118600	0.69953300	1.36940000
H	-4.22893300	-2.19758800	-0.83629000
H	-2.71636200	-3.07029600	0.95200700

X-Ray Crystallographic Data

Product 2a

Crystal Growth
2a (10 mg) and picrylsulfonic acid dihydrate (0.9 equiv) were dissolved in a mixture of ethyl acetate (0.5 mL) and methanol (dropwise addition until complete dissolution occurred). The solution was transferred to an NMR tube and layered with hexanes (1.0 mL). Single crystals suitable for X-ray diffraction grew at room temperature over 3-5 days.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007c-19018. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). This data was refined as a 2-component twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.3543(10). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (201 e/Å^3), it is likely that ~4 ethyl acetate molecules are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information. The full numbering scheme of compound 007c-19018 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1968320 (007c-19018) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

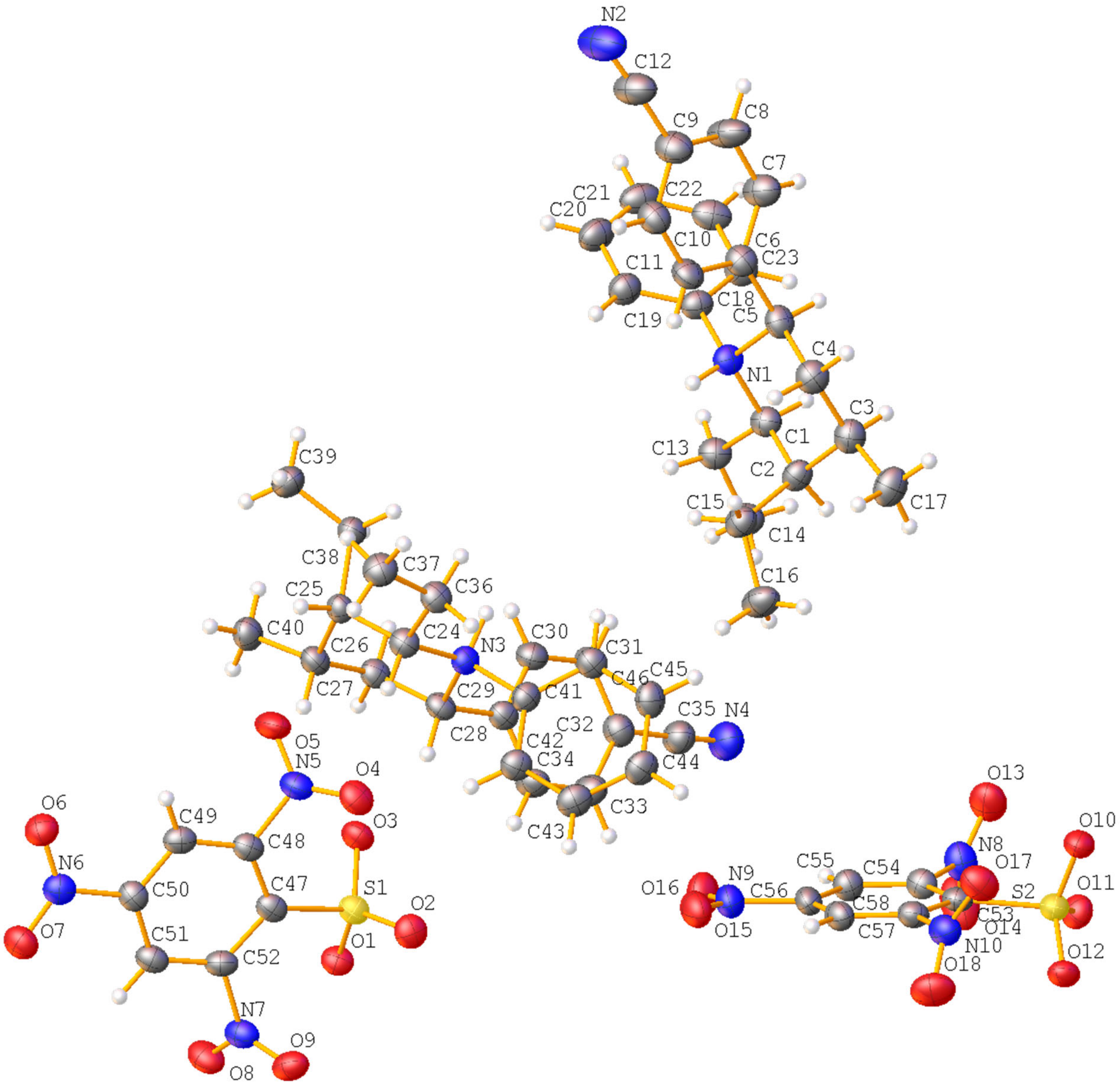


Figure S9. The complete numbering scheme of 007b-19018 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S10. Crystal data and structure refinement for 007b-19018.

Identification code	007b-19018	
Empirical formula	C29 H31 N5 O9 S	
Formula weight	625.65	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2796(3) Å	α= 90°.

	b = 32.4638(7) Å	β= 98.611(3)°.
	c = 24.8002(7) Å	γ = 90°.
Volume	6590.8(3) Å^3	
Z	8	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	1.359 mm^{-1}	
F(000)	2624	
Crystal size	0.200 x 0.200 x 0.100 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.258 to 67.132°.	
Index ranges	-9<=h<=9, -38<=k<=38, -29<=l<=29	
Reflections collected	22919	
Independent reflections	22919 [R(int) = 0.1726]	
Observed reflections (I > 2sigma(I))	16141	
Completeness to theta = 67.132°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92914	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	22919 / 0 / 808	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.1666	
R indices (all data)	R1 = 0.1007, wR2 = 0.1839	
Largest diff. peak and hole	0.398 and -0.537 e.Å^{-3}	

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 007b-19018. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7926(1)	9716(1)	5977(1)	31(1)
O(1)	6879(3)	9997(1)	6216(1)	32(1)
O(2)	9619(3)	9735(1)	6208(1)	38(1)
O(3)	7253(3)	9304(1)	5896(1)	36(1)

O(4)	9806(4)	9169(1)	5238(1)	41(1)
O(5)	7757(4)	8941(1)	4672(1)	48(1)
O(6)	6372(4)	10005(1)	3267(1)	40(1)
O(7)	6054(4)	10636(1)	3531(1)	41(1)
O(8)	5927(4)	10791(1)	5579(1)	44(1)
O(9)	8533(4)	10700(1)	5825(1)	42(1)
N(5)	8535(5)	9218(1)	4929(2)	36(1)
N(6)	6406(4)	10273(1)	3618(1)	34(1)
N(7)	7225(5)	10616(1)	5551(2)	36(1)
C(47)	7780(5)	9899(1)	5275(2)	30(1)
C(48)	7906(5)	9640(1)	4836(2)	31(1)
C(49)	7475(5)	9755(1)	4297(2)	32(1)
C(50)	6902(5)	10145(1)	4192(2)	31(1)
C(51)	6759(5)	10426(1)	4599(2)	33(1)
C(52)	7240(5)	10296(1)	5128(2)	32(1)
S(2)	11301(1)	8116(1)	11462(1)	33(1)
O(10)	12086(3)	7746(1)	11309(1)	36(1)
O(11)	10291(4)	8061(1)	11883(1)	40(1)
O(12)	12388(3)	8469(1)	11551(1)	36(1)
O(13)	7619(4)	7633(1)	11267(2)	55(1)
O(14)	6670(5)	8208(1)	11550(2)	69(1)
O(15)	7155(4)	8880(1)	9149(1)	49(1)
O(16)	5103(4)	8733(1)	9575(2)	56(1)
O(17)	12975(4)	8210(1)	10381(2)	49(1)
O(18)	12661(4)	8871(1)	10396(2)	56(1)
N(8)	7448(5)	8005(1)	11263(2)	45(1)
N(9)	6552(5)	8742(1)	9541(2)	42(1)
N(10)	12152(5)	8518(1)	10403(2)	40(1)
C(53)	9879(5)	8272(1)	10869(2)	32(1)
C(54)	8193(5)	8234(1)	10843(2)	33(1)
C(55)	7083(5)	8389(1)	10423(2)	36(1)
C(56)	7708(5)	8581(1)	10001(2)	34(1)
C(57)	9349(5)	8626(1)	9991(2)	36(1)
C(58)	10393(5)	8468(1)	10426(2)	34(1)
N(1)	7525(4)	5935(1)	7493(1)	32(1)

N(2)	8638(7)	4605(2)	5083(2)	71(1)
C(1)	7524(5)	6169(1)	8035(2)	34(1)
C(2)	9097(5)	6415(1)	8177(2)	33(1)
C(3)	10545(5)	6120(2)	8214(2)	39(1)
C(4)	10568(5)	5899(2)	7677(2)	40(1)
C(5)	9028(5)	5651(1)	7513(2)	35(1)
C(6)	8974(5)	5420(1)	6979(2)	36(1)
C(7)	8741(6)	4999(2)	6970(2)	47(1)
C(8)	8725(7)	4778(2)	6489(2)	56(1)
C(9)	8921(6)	4988(2)	6010(2)	47(1)
C(10)	9199(5)	5408(1)	6020(2)	40(1)
C(11)	9215(5)	5624(1)	6503(2)	38(1)
C(12)	8794(7)	4770(2)	5497(2)	56(1)
C(13)	5973(5)	6420(1)	8008(2)	38(1)
C(14)	5939(6)	6689(2)	8512(2)	42(1)
C(15)	9230(6)	6795(1)	7811(2)	38(1)
C(16)	9894(6)	7182(2)	8125(2)	48(1)
C(17)	12181(5)	6328(2)	8412(2)	47(1)
C(18)	6009(5)	5684(1)	7337(2)	34(1)
C(19)	5103(5)	5752(2)	6831(2)	39(1)
C(20)	3745(6)	5503(2)	6671(2)	46(1)
C(21)	3334(6)	5200(2)	7016(2)	45(1)
C(22)	4260(5)	5138(1)	7519(2)	40(1)
C(23)	5615(5)	5385(1)	7687(2)	38(1)
N(3)	7573(4)	8136(1)	6185(1)	28(1)
N(4)	6028(5)	7901(1)	9071(2)	54(1)
C(24)	7659(5)	8193(1)	5571(2)	32(1)
C(25)	5954(5)	8125(1)	5232(2)	30(1)
C(26)	4736(5)	8427(1)	5437(2)	33(1)
C(27)	4621(5)	8348(1)	6032(2)	32(1)
C(28)	6261(5)	8405(1)	6390(2)	31(1)
C(29)	6217(5)	8301(1)	6983(2)	31(1)
C(30)	5746(5)	7910(1)	7128(2)	35(1)
C(31)	5731(5)	7805(1)	7666(2)	36(1)
C(32)	6145(5)	8102(1)	8063(2)	38(1)

C(33)	6589(6)	8499(2)	7923(2)	46(1)
C(34)	6639(5)	8595(1)	7386(2)	39(1)
C(35)	6092(6)	7995(2)	8629(2)	43(1)
C(36)	9007(5)	7910(1)	5422(2)	36(1)
C(37)	9107(6)	7902(2)	4815(2)	41(1)
C(38)	5376(5)	7676(1)	5192(2)	33(1)
C(39)	4581(6)	7551(2)	4621(2)	46(1)
C(40)	3034(5)	8406(2)	5095(2)	39(1)
C(41)	9170(5)	8224(1)	6522(2)	31(1)
C(42)	9802(5)	8618(1)	6538(2)	34(1)
C(43)	11232(5)	8700(2)	6883(2)	39(1)
C(44)	12031(5)	8388(2)	7201(2)	39(1)
C(45)	11414(5)	7995(2)	7169(2)	40(1)
C(46)	9957(5)	7906(1)	6828(2)	34(1)

Table S12. Bond lengths [Å] and angles [°] for 007b-19018.

S(1)-O(2)	1.434(3)
S(1)-O(1)	1.446(3)
S(1)-O(3)	1.450(3)
S(1)-C(47)	1.827(4)
O(4)-N(5)	1.215(5)
O(5)-N(5)	1.228(5)
O(6)-N(6)	1.230(5)
O(7)-N(6)	1.223(5)
O(8)-N(7)	1.226(5)
O(9)-N(7)	1.221(5)
N(5)-C(48)	1.471(5)
N(6)-C(50)	1.481(5)
N(7)-C(52)	1.478(5)
C(47)-C(52)	1.393(6)
C(47)-C(48)	1.394(6)
C(48)-C(49)	1.382(6)

C(49)-C(50)	1.364(6)
C(49)-H(49)	0.9500
C(50)-C(51)	1.379(6)
C(51)-C(52)	1.380(6)
C(51)-H(51)	0.9500
S(2)-O(11)	1.443(3)
S(2)-O(10)	1.445(3)
S(2)-O(12)	1.452(3)
S(2)-C(53)	1.814(4)
O(13)-N(8)	1.218(6)
O(14)-N(8)	1.222(6)
O(15)-N(9)	1.241(5)
O(16)-N(9)	1.215(5)
O(17)-N(10)	1.214(5)
O(18)-N(10)	1.224(5)
N(8)-C(54)	1.485(6)
N(9)-C(56)	1.470(6)
N(10)-C(58)	1.475(6)
C(53)-C(58)	1.390(6)
C(53)-C(54)	1.393(6)
C(54)-C(55)	1.377(6)
C(55)-C(56)	1.384(6)
C(55)-H(55)	0.9500
C(56)-C(57)	1.370(6)
C(57)-C(58)	1.377(6)
C(57)-H(57)	0.9500
N(1)-C(18)	1.497(5)
N(1)-C(1)	1.543(5)
N(1)-C(5)	1.544(5)
N(1)-H(1)	0.93(6)
N(2)-C(12)	1.148(7)
C(1)-C(13)	1.515(6)
C(1)-C(2)	1.524(6)
C(1)-H(1A)	1.0000
C(2)-C(3)	1.527(6)

C(2)-C(15)	1.547(6)
C(2)-H(2)	1.0000
C(3)-C(4)	1.515(6)
C(3)-C(17)	1.527(7)
C(3)-H(3)	1.0000
C(4)-C(5)	1.511(6)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.516(6)
C(5)-H(5)	1.0000
C(6)-C(7)	1.380(7)
C(6)-C(11)	1.393(6)
C(7)-C(8)	1.392(7)
C(7)-H(7)	0.9500
C(8)-C(9)	1.399(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.385(7)
C(9)-C(12)	1.446(7)
C(10)-C(11)	1.385(6)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(13)-C(14)	1.529(6)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.536(6)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800

C(17)-H(17C)	0.9800
C(18)-C(23)	1.374(6)
C(18)-C(19)	1.381(6)
C(19)-C(20)	1.393(6)
C(19)-H(19)	0.9500
C(20)-C(21)	1.380(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.377(7)
C(21)-H(21)	0.9500
C(22)-C(23)	1.392(6)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
N(3)-C(41)	1.483(5)
N(3)-C(28)	1.538(5)
N(3)-C(24)	1.546(5)
N(3)-H(3A)	1.01(5)
N(4)-C(35)	1.147(6)
C(24)-C(36)	1.532(6)
C(24)-C(25)	1.547(6)
C(24)-H(24)	1.0000
C(25)-C(38)	1.532(6)
C(25)-C(26)	1.545(6)
C(25)-H(25)	1.0000
C(26)-C(27)	1.516(6)
C(26)-C(40)	1.533(6)
C(26)-H(26)	1.0000
C(27)-C(28)	1.518(6)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.515(6)
C(28)-H(28)	1.0000
C(29)-C(34)	1.389(6)
C(29)-C(30)	1.392(6)
C(30)-C(31)	1.379(6)
C(30)-H(30)	0.9500

C(31)-C(32)	1.384(6)
C(31)-H(31)	0.9500
C(32)-C(33)	1.397(7)
C(32)-C(35)	1.453(6)
C(33)-C(34)	1.375(6)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(36)-C(37)	1.520(6)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-C(39)	1.524(6)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.382(6)
C(41)-C(46)	1.384(6)
C(42)-C(43)	1.379(6)
C(42)-H(42)	0.9500
C(43)-C(44)	1.388(7)
C(43)-H(43)	0.9500
C(44)-C(45)	1.372(7)
C(44)-H(44)	0.9500
C(45)-C(46)	1.396(6)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
O(2)-S(1)-O(1)	114.75(18)

O(2)-S(1)-O(3)	115.37(18)
O(1)-S(1)-O(3)	113.39(17)
O(2)-S(1)-C(47)	106.75(18)
O(1)-S(1)-C(47)	103.11(17)
O(3)-S(1)-C(47)	101.43(18)
O(4)-N(5)-O(5)	124.8(4)
O(4)-N(5)-C(48)	118.3(3)
O(5)-N(5)-C(48)	116.9(4)
O(7)-N(6)-O(6)	125.2(4)
O(7)-N(6)-C(50)	117.7(3)
O(6)-N(6)-C(50)	117.1(4)
O(9)-N(7)-O(8)	125.3(4)
O(9)-N(7)-C(52)	116.8(4)
O(8)-N(7)-C(52)	117.8(4)
C(52)-C(47)-C(48)	114.4(4)
C(52)-C(47)-S(1)	121.6(3)
C(48)-C(47)-S(1)	123.1(3)
C(49)-C(48)-C(47)	123.6(4)
C(49)-C(48)-N(5)	116.0(4)
C(47)-C(48)-N(5)	120.4(4)
C(50)-C(49)-C(48)	117.9(4)
C(50)-C(49)-H(49)	121.0
C(48)-C(49)-H(49)	121.0
C(49)-C(50)-C(51)	122.7(4)
C(49)-C(50)-N(6)	118.9(4)
C(51)-C(50)-N(6)	118.4(4)
C(50)-C(51)-C(52)	116.7(4)
C(50)-C(51)-H(51)	121.6
C(52)-C(51)-H(51)	121.6
C(51)-C(52)-C(47)	124.6(4)
C(51)-C(52)-N(7)	115.3(4)
C(47)-C(52)-N(7)	120.1(4)
O(11)-S(2)-O(10)	114.72(19)
O(11)-S(2)-O(12)	113.61(18)
O(10)-S(2)-O(12)	113.82(18)

O(11)-S(2)-C(53)	104.19(19)
O(10)-S(2)-C(53)	106.36(18)
O(12)-S(2)-C(53)	102.53(18)
O(13)-N(8)-O(14)	126.8(4)
O(13)-N(8)-C(54)	116.3(4)
O(14)-N(8)-C(54)	116.8(4)
O(16)-N(9)-O(15)	125.3(4)
O(16)-N(9)-C(56)	118.3(4)
O(15)-N(9)-C(56)	116.4(4)
O(17)-N(10)-O(18)	125.0(4)
O(17)-N(10)-C(58)	118.4(4)
O(18)-N(10)-C(58)	116.5(4)
C(58)-C(53)-C(54)	115.3(4)
C(58)-C(53)-S(2)	122.0(3)
C(54)-C(53)-S(2)	122.5(3)
C(55)-C(54)-C(53)	123.5(4)
C(55)-C(54)-N(8)	114.4(4)
C(53)-C(54)-N(8)	122.1(4)
C(54)-C(55)-C(56)	117.0(4)
C(54)-C(55)-H(55)	121.5
C(56)-C(55)-H(55)	121.5
C(57)-C(56)-C(55)	123.0(4)
C(57)-C(56)-N(9)	118.7(4)
C(55)-C(56)-N(9)	118.2(4)
C(56)-C(57)-C(58)	117.0(4)
C(56)-C(57)-H(57)	121.5
C(58)-C(57)-H(57)	121.5
C(57)-C(58)-C(53)	124.0(4)
C(57)-C(58)-N(10)	115.9(4)
C(53)-C(58)-N(10)	120.2(4)
C(18)-N(1)-C(1)	112.5(3)
C(18)-N(1)-C(5)	108.9(3)
C(1)-N(1)-C(5)	111.8(3)
C(18)-N(1)-H(1)	112(3)
C(1)-N(1)-H(1)	104(3)

C(5)-N(1)-H(1)	107(3)
C(13)-C(1)-C(2)	114.7(4)
C(13)-C(1)-N(1)	109.7(3)
C(2)-C(1)-N(1)	110.3(3)
C(13)-C(1)-H(1A)	107.3
C(2)-C(1)-H(1A)	107.3
N(1)-C(1)-H(1A)	107.3
C(1)-C(2)-C(3)	108.7(4)
C(1)-C(2)-C(15)	114.6(3)
C(3)-C(2)-C(15)	114.3(4)
C(1)-C(2)-H(2)	106.2
C(3)-C(2)-H(2)	106.2
C(15)-C(2)-H(2)	106.2
C(4)-C(3)-C(2)	110.9(4)
C(4)-C(3)-C(17)	111.3(4)
C(2)-C(3)-C(17)	113.1(4)
C(4)-C(3)-H(3)	107.0
C(2)-C(3)-H(3)	107.0
C(17)-C(3)-H(3)	107.0
C(5)-C(4)-C(3)	111.5(4)
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4B)	109.3
C(3)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(6)	114.3(4)
C(4)-C(5)-N(1)	109.5(4)
C(6)-C(5)-N(1)	110.4(3)
C(4)-C(5)-H(5)	107.5
C(6)-C(5)-H(5)	107.5
N(1)-C(5)-H(5)	107.5
C(7)-C(6)-C(11)	119.6(4)
C(7)-C(6)-C(5)	119.2(4)
C(11)-C(6)-C(5)	121.1(4)
C(6)-C(7)-C(8)	120.6(5)

C(6)-C(7)-H(7)	119.7
C(8)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	119.2(5)
C(7)-C(8)-H(8)	120.4
C(9)-C(8)-H(8)	120.4
C(10)-C(9)-C(8)	120.4(4)
C(10)-C(9)-C(12)	119.1(4)
C(8)-C(9)-C(12)	120.5(5)
C(11)-C(10)-C(9)	119.6(4)
C(11)-C(10)-H(10)	120.2
C(9)-C(10)-H(10)	120.2
C(10)-C(11)-C(6)	120.6(4)
C(10)-C(11)-H(11)	119.7
C(6)-C(11)-H(11)	119.7
N(2)-C(12)-C(9)	177.5(7)
C(1)-C(13)-C(14)	113.0(4)
C(1)-C(13)-H(13A)	109.0
C(14)-C(13)-H(13A)	109.0
C(1)-C(13)-H(13B)	109.0
C(14)-C(13)-H(13B)	109.0
H(13A)-C(13)-H(13B)	107.8
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(2)	114.0(4)
C(16)-C(15)-H(15A)	108.8
C(2)-C(15)-H(15A)	108.8
C(16)-C(15)-H(15B)	108.8
C(2)-C(15)-H(15B)	108.8
H(15A)-C(15)-H(15B)	107.7
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(3)-C(17)-H(17A)	109.5
C(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(23)-C(18)-C(19)	122.6(4)
C(23)-C(18)-N(1)	119.4(4)
C(19)-C(18)-N(1)	117.9(4)
C(18)-C(19)-C(20)	118.1(4)
C(18)-C(19)-H(19)	121.0
C(20)-C(19)-H(19)	121.0
C(21)-C(20)-C(19)	120.1(5)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	120.6(4)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-C(23)	120.1(4)
C(21)-C(22)-H(22)	120.0
C(23)-C(22)-H(22)	120.0
C(18)-C(23)-C(22)	118.4(4)
C(18)-C(23)-H(23)	120.8
C(22)-C(23)-H(23)	120.8
C(41)-N(3)-C(28)	108.6(3)
C(41)-N(3)-C(24)	111.4(3)
C(28)-N(3)-C(24)	113.5(3)
C(41)-N(3)-H(3A)	105(2)
C(28)-N(3)-H(3A)	110(2)
C(24)-N(3)-H(3A)	108(2)
C(36)-C(24)-N(3)	108.0(3)

C(36)-C(24)-C(25)	115.0(4)
N(3)-C(24)-C(25)	110.2(3)
C(36)-C(24)-H(24)	107.8
N(3)-C(24)-H(24)	107.8
C(25)-C(24)-H(24)	107.8
C(38)-C(25)-C(26)	114.3(3)
C(38)-C(25)-C(24)	114.9(3)
C(26)-C(25)-C(24)	108.6(3)
C(38)-C(25)-H(25)	106.1
C(26)-C(25)-H(25)	106.1
C(24)-C(25)-H(25)	106.1
C(27)-C(26)-C(40)	110.1(3)
C(27)-C(26)-C(25)	110.7(3)
C(40)-C(26)-C(25)	112.5(4)
C(27)-C(26)-H(26)	107.8
C(40)-C(26)-H(26)	107.8
C(25)-C(26)-H(26)	107.8
C(26)-C(27)-C(28)	111.6(3)
C(26)-C(27)-H(27A)	109.3
C(28)-C(27)-H(27A)	109.3
C(26)-C(27)-H(27B)	109.3
C(28)-C(27)-H(27B)	109.3
H(27A)-C(27)-H(27B)	108.0
C(29)-C(28)-C(27)	113.0(3)
C(29)-C(28)-N(3)	108.5(3)
C(27)-C(28)-N(3)	110.6(3)
C(29)-C(28)-H(28)	108.2
C(27)-C(28)-H(28)	108.2
N(3)-C(28)-H(28)	108.2
C(34)-C(29)-C(30)	119.5(4)
C(34)-C(29)-C(28)	120.4(4)
C(30)-C(29)-C(28)	120.0(4)
C(31)-C(30)-C(29)	121.2(4)
C(31)-C(30)-H(30)	119.4
C(29)-C(30)-H(30)	119.4

C(30)-C(31)-C(32)	118.7(4)
C(30)-C(31)-H(31)	120.7
C(32)-C(31)-H(31)	120.7
C(31)-C(32)-C(33)	120.8(4)
C(31)-C(32)-C(35)	118.8(4)
C(33)-C(32)-C(35)	120.5(4)
C(34)-C(33)-C(32)	119.9(4)
C(34)-C(33)-H(33)	120.1
C(32)-C(33)-H(33)	120.1
C(33)-C(34)-C(29)	120.0(4)
C(33)-C(34)-H(34)	120.0
C(29)-C(34)-H(34)	120.0
N(4)-C(35)-C(32)	178.0(5)
C(37)-C(36)-C(24)	113.4(4)
C(37)-C(36)-H(36A)	108.9
C(24)-C(36)-H(36A)	108.9
C(37)-C(36)-H(36B)	108.9
C(24)-C(36)-H(36B)	108.9
H(36A)-C(36)-H(36B)	107.7
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(39)-C(38)-C(25)	113.6(4)
C(39)-C(38)-H(38A)	108.8
C(25)-C(38)-H(38A)	108.8
C(39)-C(38)-H(38B)	108.8
C(25)-C(38)-H(38B)	108.8
H(38A)-C(38)-H(38B)	107.7
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5

H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(26)-C(40)-H(40A)	109.5
C(26)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(26)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(42)-C(41)-C(46)	122.0(4)
C(42)-C(41)-N(3)	119.7(4)
C(46)-C(41)-N(3)	118.3(4)
C(43)-C(42)-C(41)	118.8(4)
C(43)-C(42)-H(42)	120.6
C(41)-C(42)-H(42)	120.6
C(42)-C(43)-C(44)	120.2(4)
C(42)-C(43)-H(43)	119.9
C(44)-C(43)-H(43)	119.9
C(45)-C(44)-C(43)	120.3(4)
C(45)-C(44)-H(44)	119.9
C(43)-C(44)-H(44)	119.9
C(44)-C(45)-C(46)	120.5(4)
C(44)-C(45)-H(45)	119.8
C(46)-C(45)-H(45)	119.8
C(41)-C(46)-C(45)	118.1(4)
C(41)-C(46)-H(46)	120.9
C(45)-C(46)-H(46)	120.9

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2$ x 10^3) for 007b-19018. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	30(1)	30(1)	35(1)	2(1)	10(1)	-1(1)
O(1)	31(2)	32(2)	36(2)	-1(1)	13(1)	1(1)

O(2)	29(2)	44(2)	44(2)	2(1)	9(1)	-1(1)
O(3)	39(2)	28(2)	41(2)	5(1)	9(1)	-2(1)
O(4)	34(2)	41(2)	49(2)	3(1)	12(1)	7(1)
O(5)	70(2)	27(2)	45(2)	-2(1)	5(2)	-2(2)
O(6)	42(2)	42(2)	36(2)	-2(1)	10(1)	-2(1)
O(7)	46(2)	36(2)	43(2)	7(1)	12(1)	-2(1)
O(8)	54(2)	36(2)	45(2)	1(1)	19(2)	9(2)
O(9)	51(2)	37(2)	38(2)	-5(1)	10(1)	-11(1)
N(5)	42(2)	28(2)	41(2)	0(2)	12(2)	2(2)
N(6)	31(2)	36(2)	38(2)	1(2)	11(1)	-4(2)
N(7)	46(2)	30(2)	35(2)	1(2)	15(2)	-2(2)
C(47)	24(2)	28(2)	39(2)	3(2)	10(2)	-3(2)
C(48)	26(2)	28(2)	39(2)	0(2)	9(2)	0(2)
C(49)	28(2)	31(2)	38(2)	-4(2)	11(2)	-4(2)
C(50)	29(2)	33(2)	34(2)	3(2)	10(2)	-1(2)
C(51)	32(2)	28(2)	40(2)	1(2)	12(2)	-1(2)
C(52)	34(2)	28(2)	37(2)	-5(2)	11(2)	-4(2)
S(2)	36(1)	28(1)	33(1)	-1(1)	3(1)	0(1)
O(10)	40(2)	29(2)	39(2)	-3(1)	3(1)	4(1)
O(11)	44(2)	45(2)	31(2)	2(1)	7(1)	-2(1)
O(12)	37(2)	27(2)	44(2)	-2(1)	2(1)	-5(1)
O(13)	55(2)	49(2)	61(2)	15(2)	5(2)	-14(2)
O(14)	58(2)	94(3)	61(2)	21(2)	30(2)	29(2)
O(15)	62(2)	46(2)	38(2)	7(2)	5(2)	6(2)
O(16)	40(2)	69(3)	57(2)	8(2)	-2(2)	9(2)
O(17)	40(2)	42(2)	65(2)	5(2)	12(2)	-2(2)
O(18)	56(2)	47(2)	66(2)	-6(2)	18(2)	-18(2)
N(8)	38(2)	53(3)	46(2)	10(2)	9(2)	2(2)
N(9)	45(3)	39(2)	39(2)	4(2)	0(2)	6(2)
N(10)	48(2)	35(2)	36(2)	3(2)	7(2)	-3(2)
C(53)	37(2)	23(2)	36(2)	-3(2)	5(2)	0(2)
C(54)	34(2)	34(2)	32(2)	2(2)	10(2)	-1(2)
C(55)	32(2)	37(2)	38(2)	2(2)	6(2)	-1(2)
C(56)	38(3)	29(2)	33(2)	1(2)	0(2)	6(2)
C(57)	45(3)	31(2)	31(2)	3(2)	6(2)	0(2)

C(58)	35(2)	27(2)	39(2)	-2(2)	6(2)	-1(2)
N(1)	26(2)	35(2)	35(2)	-1(2)	7(1)	1(1)
N(2)	117(4)	49(3)	54(3)	-3(2)	31(3)	-10(3)
C(1)	37(2)	35(2)	32(2)	0(2)	10(2)	-1(2)
C(2)	29(2)	39(3)	32(2)	0(2)	5(2)	-6(2)
C(3)	35(3)	45(3)	38(2)	3(2)	8(2)	-2(2)
C(4)	36(3)	43(3)	42(2)	1(2)	10(2)	-1(2)
C(5)	30(2)	40(3)	36(2)	4(2)	7(2)	6(2)
C(6)	34(2)	38(2)	37(2)	0(2)	10(2)	3(2)
C(7)	62(3)	43(3)	40(2)	-1(2)	16(2)	-8(2)
C(8)	85(4)	38(3)	49(3)	-8(2)	19(3)	-17(3)
C(9)	56(3)	41(3)	46(3)	-4(2)	17(2)	2(2)
C(10)	42(3)	39(3)	40(2)	2(2)	11(2)	4(2)
C(11)	41(3)	33(2)	42(2)	0(2)	8(2)	9(2)
C(12)	80(4)	42(3)	49(3)	-6(2)	21(3)	-10(3)
C(13)	35(3)	38(3)	41(2)	-1(2)	10(2)	-1(2)
C(14)	42(3)	41(3)	46(3)	-5(2)	12(2)	-1(2)
C(15)	40(3)	40(3)	33(2)	-1(2)	6(2)	-6(2)
C(16)	60(3)	42(3)	43(3)	-3(2)	9(2)	-18(2)
C(17)	34(3)	64(3)	43(3)	0(2)	6(2)	-5(2)
C(18)	28(2)	35(2)	39(2)	-4(2)	7(2)	-2(2)
C(19)	34(3)	42(3)	42(2)	-3(2)	4(2)	-3(2)
C(20)	35(3)	49(3)	52(3)	-10(2)	1(2)	-3(2)
C(21)	34(3)	45(3)	59(3)	-15(2)	11(2)	-5(2)
C(22)	35(3)	36(2)	55(3)	-5(2)	20(2)	-2(2)
C(23)	33(2)	41(3)	43(2)	1(2)	10(2)	-1(2)
N(3)	24(2)	31(2)	31(2)	0(1)	5(1)	1(1)
N(4)	68(3)	54(3)	41(2)	7(2)	8(2)	-4(2)
C(24)	31(2)	34(2)	33(2)	1(2)	9(2)	0(2)
C(25)	30(2)	29(2)	31(2)	4(2)	4(2)	-1(2)
C(26)	30(2)	29(2)	38(2)	3(2)	5(2)	1(2)
C(27)	27(2)	32(2)	37(2)	1(2)	6(2)	2(2)
C(28)	29(2)	27(2)	37(2)	1(2)	9(2)	4(2)
C(29)	26(2)	31(2)	37(2)	1(2)	6(2)	-2(2)
C(30)	37(3)	30(2)	39(2)	-2(2)	8(2)	1(2)

C(31)	36(2)	32(2)	40(2)	5(2)	9(2)	1(2)
C(32)	38(3)	39(3)	39(2)	4(2)	8(2)	1(2)
C(33)	59(3)	42(3)	37(2)	-2(2)	7(2)	-10(2)
C(34)	47(3)	32(2)	39(2)	0(2)	9(2)	-10(2)
C(35)	49(3)	43(3)	37(3)	1(2)	6(2)	-3(2)
C(36)	30(2)	38(2)	40(2)	1(2)	9(2)	4(2)
C(37)	40(3)	45(3)	41(2)	-3(2)	11(2)	1(2)
C(38)	34(2)	30(2)	35(2)	1(2)	3(2)	-1(2)
C(39)	55(3)	41(3)	39(2)	-3(2)	-2(2)	-6(2)
C(40)	33(2)	41(3)	43(2)	4(2)	1(2)	1(2)
C(41)	25(2)	36(2)	33(2)	-2(2)	4(2)	-1(2)
C(42)	28(2)	36(2)	40(2)	0(2)	8(2)	-4(2)
C(43)	31(2)	44(3)	44(2)	-3(2)	10(2)	-7(2)
C(44)	28(2)	47(3)	42(2)	-1(2)	5(2)	-6(2)
C(45)	30(2)	49(3)	41(2)	6(2)	4(2)	3(2)
C(46)	28(2)	35(2)	38(2)	2(2)	7(2)	-2(2)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 007b-19018.

	x	y	z	U(eq)
H(49)	7576	9568	4009	38
H(51)	6349	10696	4519	39
H(55)	5940	8365	10423	43
H(57)	9748	8759	9696	43
H(1A)	7507	5958	8328	41
H(2)	9092	6524	8554	40
H(3)	10381	5905	8490	47
H(4A)	10681	6104	7389	48
H(4B)	11526	5713	7710	48
H(5)	8965	5442	7805	42
H(7)	8591	4860	7296	57
H(8)	8582	4487	6486	67

H(10)	9378	5548	5698	48
H(11)	9392	5913	6509	46
H(13A)	5024	6231	7968	45
H(13B)	5862	6599	7681	45
H(14A)	6067	6515	8839	64
H(14B)	4893	6836	8479	64
H(14C)	6834	6889	8541	64
H(15A)	9955	6726	7540	45
H(15B)	8135	6858	7607	45
H(16A)	9208	7248	8403	73
H(16B)	9879	7414	7871	73
H(16C)	11017	7132	8301	73
H(17A)	12094	6491	8739	71
H(17B)	12472	6508	8125	71
H(17C)	13028	6117	8500	71
H(19)	5397	5963	6598	47
H(20)	3101	5543	6325	55
H(21)	2404	5032	6905	54
H(22)	3974	4926	7751	49
H(23)	6252	5348	8035	46
H(24)	7992	8484	5514	39
H(25)	6049	8213	4851	36
H(26)	5164	8712	5405	39
H(27A)	4226	8064	6075	38
H(27B)	3817	8541	6152	38
H(28)	6592	8700	6368	37
H(30)	5428	7711	6851	42
H(31)	5443	7535	7762	43
H(33)	6856	8701	8199	55
H(34)	6961	8863	7291	47
H(36A)	10070	8003	5622	43
H(36B)	8809	7627	5544	43
H(37A)	8093	7788	4617	62
H(37B)	10032	7731	4750	62
H(37C)	9259	8183	4687	62

H(38A)	6324	7494	5307	40
H(38B)	4582	7633	5448	40
H(39A)	5387	7570	4370	69
H(39B)	3664	7736	4498	69
H(39C)	4181	7268	4628	69
H(40A)	3120	8460	4712	59
H(40B)	2324	8613	5226	59
H(40C)	2568	8131	5129	59
H(42)	9261	8829	6314	41
H(43)	11671	8971	6904	47
H(44)	13009	8447	7441	47
H(45)	11983	7782	7381	48
H(46)	9519	7635	6807	40
H(3A)	7350(50)	7836(15)	6252(18)	32(11)
H(1)	7630(60)	6143(18)	7240(20)	52(15)

Table S15. Torsion angles [°] for 007b-19018.

O(2)-S(1)-C(47)-C(52)	-102.0(3)
O(1)-S(1)-C(47)-C(52)	19.3(4)
O(3)-S(1)-C(47)-C(52)	136.9(3)
O(2)-S(1)-C(47)-C(48)	89.9(4)
O(1)-S(1)-C(47)-C(48)	-148.8(3)
O(3)-S(1)-C(47)-C(48)	-31.3(4)
C(52)-C(47)-C(48)-C(49)	-2.5(6)
S(1)-C(47)-C(48)-C(49)	166.4(3)
C(52)-C(47)-C(48)-N(5)	177.1(4)
S(1)-C(47)-C(48)-N(5)	-14.0(5)
O(4)-N(5)-C(48)-C(49)	130.1(4)
O(5)-N(5)-C(48)-C(49)	-47.3(5)
O(4)-N(5)-C(48)-C(47)	-49.5(5)
O(5)-N(5)-C(48)-C(47)	133.1(4)
C(47)-C(48)-C(49)-C(50)	0.2(6)

N(5)-C(48)-C(49)-C(50)	-179.4(4)
C(48)-C(49)-C(50)-C(51)	0.8(6)
C(48)-C(49)-C(50)-N(6)	-179.0(3)
O(7)-N(6)-C(50)-C(49)	-172.7(4)
O(6)-N(6)-C(50)-C(49)	7.7(5)
O(7)-N(6)-C(50)-C(51)	7.4(5)
O(6)-N(6)-C(50)-C(51)	-172.1(4)
C(49)-C(50)-C(51)-C(52)	0.5(6)
N(6)-C(50)-C(51)-C(52)	-179.7(3)
C(50)-C(51)-C(52)-C(47)	-3.1(6)
C(50)-C(51)-C(52)-N(7)	174.2(4)
C(48)-C(47)-C(52)-C(51)	4.0(6)
S(1)-C(47)-C(52)-C(51)	-165.1(3)
C(48)-C(47)-C(52)-N(7)	-173.2(4)
S(1)-C(47)-C(52)-N(7)	17.7(5)
O(9)-N(7)-C(52)-C(51)	-117.6(4)
O(8)-N(7)-C(52)-C(51)	58.5(5)
O(9)-N(7)-C(52)-C(47)	59.8(5)
O(8)-N(7)-C(52)-C(47)	-124.1(4)
O(11)-S(2)-C(53)-C(58)	160.9(3)
O(10)-S(2)-C(53)-C(58)	-77.5(4)
O(12)-S(2)-C(53)-C(58)	42.3(4)
O(11)-S(2)-C(53)-C(54)	-13.6(4)
O(10)-S(2)-C(53)-C(54)	108.0(4)
O(12)-S(2)-C(53)-C(54)	-132.2(3)
C(58)-C(53)-C(54)-C(55)	-2.0(6)
S(2)-C(53)-C(54)-C(55)	172.8(4)
C(58)-C(53)-C(54)-N(8)	175.5(4)
S(2)-C(53)-C(54)-N(8)	-9.7(6)
O(13)-N(8)-C(54)-C(55)	107.9(5)
O(14)-N(8)-C(54)-C(55)	-69.0(6)
O(13)-N(8)-C(54)-C(53)	-69.8(6)
O(14)-N(8)-C(54)-C(53)	113.3(5)
C(53)-C(54)-C(55)-C(56)	1.9(7)
N(8)-C(54)-C(55)-C(56)	-175.8(4)

C(54)-C(55)-C(56)-C(57)	-0.9(7)
C(54)-C(55)-C(56)-N(9)	178.7(4)
O(16)-N(9)-C(56)-C(57)	-173.8(4)
O(15)-N(9)-C(56)-C(57)	5.7(6)
O(16)-N(9)-C(56)-C(55)	6.5(6)
O(15)-N(9)-C(56)-C(55)	-173.9(4)
C(55)-C(56)-C(57)-C(58)	0.1(6)
N(9)-C(56)-C(57)-C(58)	-179.5(4)
C(56)-C(57)-C(58)-C(53)	-0.3(6)
C(56)-C(57)-C(58)-N(10)	179.6(4)
C(54)-C(53)-C(58)-C(57)	1.1(6)
S(2)-C(53)-C(58)-C(57)	-173.7(3)
C(54)-C(53)-C(58)-N(10)	-178.7(4)
S(2)-C(53)-C(58)-N(10)	6.5(6)
O(17)-N(10)-C(58)-C(57)	-116.6(5)
O(18)-N(10)-C(58)-C(57)	62.2(5)
O(17)-N(10)-C(58)-C(53)	63.3(5)
O(18)-N(10)-C(58)-C(53)	-118.0(5)
C(18)-N(1)-C(1)-C(13)	-53.3(5)
C(5)-N(1)-C(1)-C(13)	-176.2(4)
C(18)-N(1)-C(1)-C(2)	179.5(3)
C(5)-N(1)-C(1)-C(2)	56.6(4)
C(13)-C(1)-C(2)-C(3)	177.5(4)
N(1)-C(1)-C(2)-C(3)	-58.1(4)
C(13)-C(1)-C(2)-C(15)	-53.2(5)
N(1)-C(1)-C(2)-C(15)	71.3(5)
C(1)-C(2)-C(3)-C(4)	60.0(5)
C(15)-C(2)-C(3)-C(4)	-69.5(5)
C(1)-C(2)-C(3)-C(17)	-174.1(4)
C(15)-C(2)-C(3)-C(17)	56.4(5)
C(2)-C(3)-C(4)-C(5)	-59.9(5)
C(17)-C(3)-C(4)-C(5)	173.2(4)
C(3)-C(4)-C(5)-C(6)	-179.8(4)
C(3)-C(4)-C(5)-N(1)	55.8(5)
C(18)-N(1)-C(5)-C(4)	-179.3(3)

C(1)-N(1)-C(5)-C(4)	-54.4(4)
C(18)-N(1)-C(5)-C(6)	54.0(4)
C(1)-N(1)-C(5)-C(6)	178.9(3)
C(4)-C(5)-C(6)-C(7)	123.7(5)
N(1)-C(5)-C(6)-C(7)	-112.4(5)
C(4)-C(5)-C(6)-C(11)	-53.9(6)
N(1)-C(5)-C(6)-C(11)	70.0(5)
C(11)-C(6)-C(7)-C(8)	-0.8(7)
C(5)-C(6)-C(7)-C(8)	-178.4(5)
C(6)-C(7)-C(8)-C(9)	-1.0(8)
C(7)-C(8)-C(9)-C(10)	2.8(8)
C(7)-C(8)-C(9)-C(12)	-175.6(5)
C(8)-C(9)-C(10)-C(11)	-2.7(7)
C(12)-C(9)-C(10)-C(11)	175.7(5)
C(9)-C(10)-C(11)-C(6)	0.8(7)
C(7)-C(6)-C(11)-C(10)	0.9(7)
C(5)-C(6)-C(11)-C(10)	178.5(4)
C(2)-C(1)-C(13)-C(14)	-50.5(5)
N(1)-C(1)-C(13)-C(14)	-175.2(4)
C(1)-C(2)-C(15)-C(16)	136.8(4)
C(3)-C(2)-C(15)-C(16)	-96.7(5)
C(1)-N(1)-C(18)-C(23)	-58.5(5)
C(5)-N(1)-C(18)-C(23)	66.0(5)
C(1)-N(1)-C(18)-C(19)	124.6(4)
C(5)-N(1)-C(18)-C(19)	-110.9(4)
C(23)-C(18)-C(19)-C(20)	-0.5(7)
N(1)-C(18)-C(19)-C(20)	176.3(4)
C(18)-C(19)-C(20)-C(21)	0.1(7)
C(19)-C(20)-C(21)-C(22)	-0.3(7)
C(20)-C(21)-C(22)-C(23)	0.7(7)
C(19)-C(18)-C(23)-C(22)	0.9(7)
N(1)-C(18)-C(23)-C(22)	-175.8(4)
C(21)-C(22)-C(23)-C(18)	-1.0(7)
C(41)-N(3)-C(24)-C(36)	57.0(4)
C(28)-N(3)-C(24)-C(36)	179.9(3)

C(41)-N(3)-C(24)-C(25)	-176.6(3)
C(28)-N(3)-C(24)-C(25)	-53.7(4)
C(36)-C(24)-C(25)-C(38)	49.7(5)
N(3)-C(24)-C(25)-C(38)	-72.6(4)
C(36)-C(24)-C(25)-C(26)	179.1(3)
N(3)-C(24)-C(25)-C(26)	56.8(4)
C(38)-C(25)-C(26)-C(27)	69.0(4)
C(24)-C(25)-C(26)-C(27)	-60.8(4)
C(38)-C(25)-C(26)-C(40)	-54.7(5)
C(24)-C(25)-C(26)-C(40)	175.5(3)
C(40)-C(26)-C(27)-C(28)	-174.8(4)
C(25)-C(26)-C(27)-C(28)	60.2(5)
C(26)-C(27)-C(28)-C(29)	-176.2(3)
C(26)-C(27)-C(28)-N(3)	-54.3(5)
C(41)-N(3)-C(28)-C(29)	-59.4(4)
C(24)-N(3)-C(28)-C(29)	176.2(3)
C(41)-N(3)-C(28)-C(27)	176.1(3)
C(24)-N(3)-C(28)-C(27)	51.7(4)
C(27)-C(28)-C(29)-C(34)	-121.3(4)
N(3)-C(28)-C(29)-C(34)	115.6(4)
C(27)-C(28)-C(29)-C(30)	58.5(5)
N(3)-C(28)-C(29)-C(30)	-64.6(5)
C(34)-C(29)-C(30)-C(31)	-1.7(6)
C(28)-C(29)-C(30)-C(31)	178.5(4)
C(29)-C(30)-C(31)-C(32)	2.1(6)
C(30)-C(31)-C(32)-C(33)	-0.8(7)
C(30)-C(31)-C(32)-C(35)	178.6(4)
C(31)-C(32)-C(33)-C(34)	-0.9(7)
C(35)-C(32)-C(33)-C(34)	179.8(5)
C(32)-C(33)-C(34)-C(29)	1.3(7)
C(30)-C(29)-C(34)-C(33)	0.0(7)
C(28)-C(29)-C(34)-C(33)	179.8(4)
N(3)-C(24)-C(36)-C(37)	174.1(4)
C(25)-C(24)-C(36)-C(37)	50.6(5)
C(26)-C(25)-C(38)-C(39)	96.6(4)

C(24)-C(25)-C(38)-C(39)	-136.8(4)
C(28)-N(3)-C(41)-C(42)	-60.2(5)
C(24)-N(3)-C(41)-C(42)	65.4(5)
C(28)-N(3)-C(41)-C(46)	117.7(4)
C(24)-N(3)-C(41)-C(46)	-116.7(4)
C(46)-C(41)-C(42)-C(43)	-2.3(6)
N(3)-C(41)-C(42)-C(43)	175.5(4)
C(41)-C(42)-C(43)-C(44)	1.2(6)
C(42)-C(43)-C(44)-C(45)	0.7(7)
C(43)-C(44)-C(45)-C(46)	-1.5(7)
C(42)-C(41)-C(46)-C(45)	1.4(6)
N(3)-C(41)-C(46)-C(45)	-176.4(4)
C(44)-C(45)-C(46)-C(41)	0.5(6)

Symmetry transformations used to generate equivalent atoms:

Table S16. Hydrogen bonds for 007b-19018 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3A)...O(10)#1	1.01(5)	1.91(5)	2.913(5)	173(4)
N(1)-H(1)...O(12)#1	0.93(6)	2.11(6)	3.023(5)	166(5)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,z-1/2

Product 2e

Crystal Growth

2e (10 mg) and picrylsulfonic acid dihydrate (0.9 equiv) were dissolved in a mixture of toluene (0.5 mL) and methanol (dropwise addition until complete dissolution occurred). Added a few drops of hexanes until the cloud point was reached. Single crystals suitable for X-ray diffraction grew at room temperature over 3-5 days.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007c-19019. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception I H1, which was found in the difference map and freely refined. The full numbering scheme of compound 007c-19019 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1968319 (007c-19019) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif.

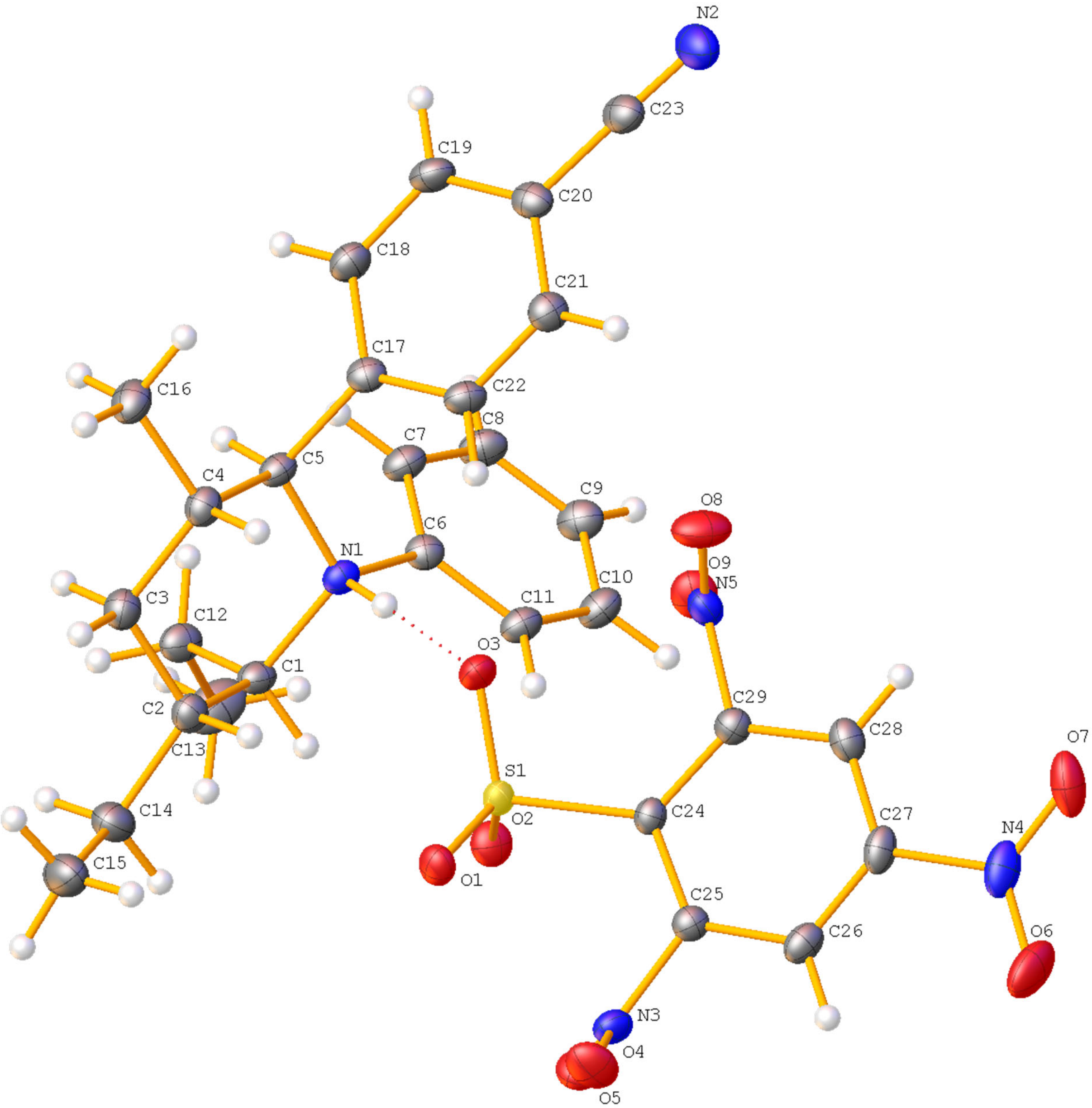


Figure S10. The complete numbering scheme of 007c-19019 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S17. Crystal data and structure refinement for 007c-19019.

Identification code	007c-19019	
Empirical formula	C29 H31 N5 O9 S	
Formula weight	625.65	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7906(4) Å	α= 90°.
	b = 17.2290(7) Å	β= 102.724(4)°.
	c = 18.2219(8) Å	γ = 90°.
Volume	2998.2(2) $Å^3$	
Z	4	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.170 mm^{-1}	
F(000)	1312	
Crystal size	0.100 x 0.100 x 0.100 mm^3	
Crystal color and habit	Yellow Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.887 to 27.484°.	
Index ranges	-12<=h<=12, -22<=k<=22, -23<=l<=23	
Reflections collected	69321	
Independent reflections	6873 [R(int) = 0.0416]	
Observed reflections (I > 2sigma(I))	5922	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.75438	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	6873 / 0 / 404	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0873	
R indices (all data)	R1 = 0.0423, wR2 = 0.0906	
Largest diff. peak and hole	0.399 and -0.342 e.$Å^{-3}$	

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007c-19019. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2328(1)	1317(1)	10110(1)	17(1)
O(1)	2812(1)	1500(1)	10894(1)	23(1)
O(2)	893(1)	1530(1)	9790(1)	25(1)
O(3)	3283(1)	1545(1)	9640(1)	24(1)
O(4)	2162(1)	171(1)	11930(1)	33(1)
O(5)	323(1)	580(1)	11121(1)	28(1)
O(6)	1972(1)	-2522(1)	10699(1)	42(1)
O(7)	2917(1)	-2554(1)	9723(1)	36(1)
O(8)	4537(1)	124(1)	8939(1)	36(1)
O(9)	2383(1)	428(1)	8428(1)	30(1)
N(3)	1443(1)	242(1)	11289(1)	22(1)
N(4)	2448(1)	-2210(1)	10203(1)	28(1)
N(5)	3289(1)	162(1)	8934(1)	22(1)
C(24)	2349(1)	264(1)	10107(1)	16(1)
C(25)	1956(1)	-155(1)	10683(1)	18(1)
C(26)	1988(1)	-954(1)	10734(1)	21(1)
C(27)	2451(1)	-1356(1)	10182(1)	22(1)
C(28)	2903(1)	-990(1)	9607(1)	22(1)
C(29)	2831(1)	-186(1)	9582(1)	19(1)
N(1)	2202(1)	2848(1)	8562(1)	17(1)
N(2)	6600(1)	779(1)	6314(1)	32(1)
C(1)	1321(1)	3362(1)	8982(1)	20(1)
C(2)	2257(1)	3564(1)	9749(1)	21(1)
C(3)	3565(1)	3992(1)	9650(1)	23(1)
C(4)	4419(1)	3511(1)	9203(1)	21(1)
C(5)	3524(1)	3253(1)	8440(1)	18(1)
C(6)	1296(1)	2508(1)	7873(1)	18(1)
C(7)	1174(1)	2849(1)	7174(1)	22(1)
C(8)	261(1)	2523(1)	6560(1)	25(1)
C(9)	-506(1)	1862(1)	6645(1)	25(1)
C(10)	-354(1)	1523(1)	7351(1)	24(1)

C(11)	544(1)	1850(1)	7969(1)	21(1)
C(12)	671(1)	4057(1)	8494(1)	24(1)
C(13)	-901(2)	3976(1)	8202(1)	41(1)
C(14)	1426(2)	4000(1)	10246(1)	28(1)
C(15)	2228(2)	4059(1)	11063(1)	34(1)
C(16)	5677(1)	3981(1)	9077(1)	26(1)
C(17)	4292(1)	2721(1)	8004(1)	19(1)
C(18)	4670(1)	2995(1)	7356(1)	23(1)
C(19)	5314(2)	2512(1)	6928(1)	25(1)
C(20)	5593(1)	1743(1)	7148(1)	22(1)
C(21)	5255(1)	1466(1)	7805(1)	22(1)
C(22)	4619(1)	1955(1)	8231(1)	21(1)
C(23)	6164(1)	1210(1)	6682(1)	24(1)

Table S19. Bond lengths [Å] and angles [°] for 007c-19019.

S(1)-O(1)	1.4378(9)
S(1)-O(2)	1.4454(10)
S(1)-O(3)	1.4539(10)
S(1)-C(24)	1.8135(12)
O(4)-N(3)	1.2291(15)
O(5)-N(3)	1.2197(15)
O(6)-N(4)	1.2274(17)
O(7)-N(4)	1.2261(17)
O(8)-N(5)	1.2219(16)
O(9)-N(5)	1.2193(15)
N(3)-C(25)	1.4784(17)
N(4)-C(27)	1.4735(16)
N(5)-C(29)	1.4773(17)
C(24)-C(29)	1.3925(18)
C(24)-C(25)	1.3960(17)
C(25)-C(26)	1.3805(18)
C(26)-C(27)	1.377(2)

C(26)-H(26)	0.9500
C(27)-C(28)	1.376(2)
C(28)-C(29)	1.3872(18)
C(28)-H(28)	0.9500
N(1)-C(6)	1.4883(16)
N(1)-C(5)	1.5296(16)
N(1)-C(1)	1.5505(16)
N(1)-H(1)	0.892(16)
N(2)-C(23)	1.1453(19)
C(1)-C(2)	1.5334(18)
C(1)-C(12)	1.5428(18)
C(1)-H(1A)	1.0000
C(2)-C(3)	1.5225(18)
C(2)-C(14)	1.5397(19)
C(2)-H(2)	1.0000
C(3)-C(4)	1.5326(18)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(16)	1.5324(18)
C(4)-C(5)	1.5377(18)
C(4)-H(4)	1.0000
C(5)-C(17)	1.5172(18)
C(5)-H(5)	1.0000
C(6)-C(11)	1.3840(18)
C(6)-C(7)	1.3842(18)
C(7)-C(8)	1.3881(19)
C(7)-H(7)	0.9500
C(8)-C(9)	1.390(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3898(19)
C(9)-H(9)	0.9500
C(10)-C(11)	1.3872(19)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-C(13)	1.520(2)

C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.526(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.3942(18)
C(17)-C(22)	1.3984(18)
C(18)-C(19)	1.384(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.393(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.3936(19)
C(20)-C(23)	1.4443(19)
C(21)-C(22)	1.3836(19)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
O(1)-S(1)-O(2)	115.05(6)
O(1)-S(1)-O(3)	114.36(6)
O(2)-S(1)-O(3)	112.79(6)
O(1)-S(1)-C(24)	102.80(6)
O(2)-S(1)-C(24)	105.26(6)
O(3)-S(1)-C(24)	105.03(6)
O(5)-N(3)-O(4)	125.56(12)
O(5)-N(3)-C(25)	117.87(11)
O(4)-N(3)-C(25)	116.48(11)
O(7)-N(4)-O(6)	125.20(12)

O(7)-N(4)-C(27)	117.45(12)
O(6)-N(4)-C(27)	117.35(13)
O(9)-N(5)-O(8)	125.77(12)
O(9)-N(5)-C(29)	117.28(11)
O(8)-N(5)-C(29)	116.86(11)
C(29)-C(24)-C(25)	114.83(11)
C(29)-C(24)-S(1)	124.39(10)
C(25)-C(24)-S(1)	120.64(10)
C(26)-C(25)-C(24)	124.11(12)
C(26)-C(25)-N(3)	114.68(11)
C(24)-C(25)-N(3)	121.20(11)
C(27)-C(26)-C(25)	117.25(12)
C(27)-C(26)-H(26)	121.4
C(25)-C(26)-H(26)	121.4
C(28)-C(27)-C(26)	122.60(12)
C(28)-C(27)-N(4)	118.76(12)
C(26)-C(27)-N(4)	118.64(12)
C(27)-C(28)-C(29)	117.42(12)
C(27)-C(28)-H(28)	121.3
C(29)-C(28)-H(28)	121.3
C(28)-C(29)-C(24)	123.73(12)
C(28)-C(29)-N(5)	114.18(11)
C(24)-C(29)-N(5)	122.09(11)
C(6)-N(1)-C(5)	115.04(10)
C(6)-N(1)-C(1)	110.37(9)
C(5)-N(1)-C(1)	113.05(10)
C(6)-N(1)-H(1)	105.6(10)
C(5)-N(1)-H(1)	105.9(10)
C(1)-N(1)-H(1)	106.1(10)
C(2)-C(1)-C(12)	115.89(11)
C(2)-C(1)-N(1)	107.06(10)
C(12)-C(1)-N(1)	111.30(10)
C(2)-C(1)-H(1A)	107.4
C(12)-C(1)-H(1A)	107.4
N(1)-C(1)-H(1A)	107.4

C(3)-C(2)-C(1)	110.58(11)
C(3)-C(2)-C(14)	113.59(11)
C(1)-C(2)-C(14)	111.05(11)
C(3)-C(2)-H(2)	107.1
C(1)-C(2)-H(2)	107.1
C(14)-C(2)-H(2)	107.1
C(2)-C(3)-C(4)	111.85(11)
C(2)-C(3)-H(3A)	109.2
C(4)-C(3)-H(3A)	109.2
C(2)-C(3)-H(3B)	109.2
C(4)-C(3)-H(3B)	109.2
H(3A)-C(3)-H(3B)	107.9
C(16)-C(4)-C(3)	110.15(11)
C(16)-C(4)-C(5)	109.51(11)
C(3)-C(4)-C(5)	111.57(10)
C(16)-C(4)-H(4)	108.5
C(3)-C(4)-H(4)	108.5
C(5)-C(4)-H(4)	108.5
C(17)-C(5)-N(1)	109.46(10)
C(17)-C(5)-C(4)	113.50(10)
N(1)-C(5)-C(4)	109.42(10)
C(17)-C(5)-H(5)	108.1
N(1)-C(5)-H(5)	108.1
C(4)-C(5)-H(5)	108.1
C(11)-C(6)-C(7)	121.62(12)
C(11)-C(6)-N(1)	116.76(11)
C(7)-C(6)-N(1)	121.59(11)
C(6)-C(7)-C(8)	118.67(12)
C(6)-C(7)-H(7)	120.7
C(8)-C(7)-H(7)	120.7
C(7)-C(8)-C(9)	120.59(13)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7
C(10)-C(9)-C(8)	119.81(13)
C(10)-C(9)-H(9)	120.1

C(8)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	120.06(13)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(6)-C(11)-C(10)	119.25(12)
C(6)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(13)-C(12)-C(1)	112.77(12)
C(13)-C(12)-H(12A)	109.0
C(1)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12B)	109.0
C(1)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(2)	112.39(12)
C(15)-C(14)-H(14A)	109.1
C(2)-C(14)-H(14A)	109.1
C(15)-C(14)-H(14B)	109.1
C(2)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.9
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(4)-C(16)-H(16A)	109.5
C(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(4)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	118.93(12)
C(18)-C(17)-C(5)	119.54(11)
C(22)-C(17)-C(5)	121.52(11)
C(19)-C(18)-C(17)	120.82(12)
C(19)-C(18)-H(18)	119.6
C(17)-C(18)-H(18)	119.6
C(18)-C(19)-C(20)	119.60(12)
C(18)-C(19)-H(19)	120.2
C(20)-C(19)-H(19)	120.2
C(19)-C(20)-C(21)	120.27(12)
C(19)-C(20)-C(23)	120.77(13)
C(21)-C(20)-C(23)	118.88(12)
C(22)-C(21)-C(20)	119.66(12)
C(22)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(17)	120.66(12)
C(21)-C(22)-H(22)	119.7
C(17)-C(22)-H(22)	119.7
N(2)-C(23)-C(20)	178.88(15)

Symmetry transformations used to generate equivalent atoms:

Table S20. Anisotropic displacement parameters ($Å^2$x 10^3) for 007c-19019. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	22(1)	13(1)	16(1)	1(1)	5(1)	0(1)
O(1)	31(1)	21(1)	17(1)	-2(1)	5(1)	-2(1)
O(2)	26(1)	22(1)	26(1)	4(1)	3(1)	5(1)
O(3)	32(1)	19(1)	24(1)	2(1)	13(1)	-3(1)
O(4)	46(1)	35(1)	18(1)	7(1)	8(1)	10(1)
O(5)	22(1)	29(1)	36(1)	1(1)	12(1)	3(1)

O(6)	39(1)	20(1)	67(1)	15(1)	15(1)	2(1)
O(7)	48(1)	19(1)	34(1)	-6(1)	-7(1)	7(1)
O(8)	29(1)	44(1)	39(1)	12(1)	19(1)	8(1)
O(9)	37(1)	29(1)	20(1)	5(1)	2(1)	3(1)
N(3)	26(1)	19(1)	22(1)	5(1)	10(1)	0(1)
N(4)	25(1)	16(1)	40(1)	3(1)	-4(1)	2(1)
N(5)	29(1)	18(1)	19(1)	-1(1)	8(1)	2(1)
C(24)	16(1)	14(1)	18(1)	1(1)	2(1)	0(1)
C(25)	17(1)	18(1)	18(1)	2(1)	3(1)	1(1)
C(26)	18(1)	19(1)	25(1)	6(1)	2(1)	0(1)
C(27)	20(1)	14(1)	28(1)	2(1)	-2(1)	1(1)
C(28)	22(1)	20(1)	23(1)	-3(1)	1(1)	3(1)
C(29)	19(1)	19(1)	18(1)	1(1)	3(1)	0(1)
N(1)	16(1)	17(1)	18(1)	4(1)	3(1)	1(1)
N(2)	32(1)	34(1)	33(1)	-10(1)	10(1)	-7(1)
C(1)	19(1)	20(1)	22(1)	3(1)	8(1)	1(1)
C(2)	24(1)	18(1)	21(1)	2(1)	5(1)	1(1)
C(3)	23(1)	20(1)	24(1)	-1(1)	5(1)	-1(1)
C(4)	19(1)	18(1)	23(1)	2(1)	3(1)	0(1)
C(5)	15(1)	19(1)	22(1)	4(1)	5(1)	-1(1)
C(6)	15(1)	21(1)	19(1)	1(1)	3(1)	1(1)
C(7)	18(1)	24(1)	24(1)	5(1)	5(1)	-1(1)
C(8)	22(1)	32(1)	20(1)	7(1)	4(1)	0(1)
C(9)	21(1)	32(1)	22(1)	1(1)	2(1)	-2(1)
C(10)	21(1)	25(1)	27(1)	5(1)	4(1)	-4(1)
C(11)	18(1)	22(1)	22(1)	5(1)	5(1)	0(1)
C(12)	23(1)	22(1)	27(1)	6(1)	7(1)	5(1)
C(13)	22(1)	42(1)	58(1)	21(1)	5(1)	8(1)
C(14)	32(1)	27(1)	29(1)	-1(1)	13(1)	2(1)
C(15)	40(1)	35(1)	31(1)	-8(1)	14(1)	-9(1)
C(16)	20(1)	23(1)	35(1)	-1(1)	5(1)	-2(1)
C(17)	14(1)	22(1)	19(1)	2(1)	3(1)	0(1)
C(18)	23(1)	22(1)	23(1)	5(1)	5(1)	-1(1)
C(19)	26(1)	30(1)	21(1)	3(1)	9(1)	-5(1)
C(20)	16(1)	27(1)	21(1)	-3(1)	4(1)	-2(1)

C(21)	20(1)	22(1)	23(1)	2(1)	4(1)	2(1)
C(22)	19(1)	24(1)	20(1)	5(1)	6(1)	1(1)
C(23)	22(1)	28(1)	23(1)	-3(1)	6(1)	-6(1)

Table S21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for 007c-19019.

	x	y	z	U(eq)
H(26)	1702	-1217	11133	25
H(28)	3252	-1277	9243	26
H(1A)	532	3036	9076	24
H(2)	2573	3062	10007	25
H(3A)	4155	4115	10151	27
H(3B)	3288	4488	9384	27
H(4)	4775	3038	9502	25
H(5)	3232	3728	8129	22
H(7)	1704	3298	7115	26
H(8)	159	2752	6077	30
H(9)	-1132	1644	6223	30
H(10)	-865	1067	7409	29
H(11)	642	1624	8454	25
H(12A)	863	4538	8797	28
H(12B)	1125	4108	8062	28
H(13A)	-1256	4426	7889	62
H(13B)	-1361	3948	8628	62
H(13C)	-1099	3501	7901	62
H(14A)	1206	4529	10041	34
H(14B)	529	3727	10227	34
H(15A)	3077	4369	11089	52
H(15B)	2488	3538	11260	52
H(15C)	1636	4308	11363	52
H(16A)	5344	4444	8779	39
H(16B)	6235	3662	8808	39

H(16C)	6256	4138	9565	39
H(18)	4484	3519	7207	28
H(19)	5565	2703	6487	30
H(21)	5462	945	7959	26
H(22)	4401	1769	8682	25
H(1)	2497(16)	2447(9)	8865(9)	19(4)

Table S22. Torsion angles [°] for 007c-19019.

O(1)-S(1)-C(24)-C(29)	-137.50(11)
O(2)-S(1)-C(24)-C(29)	101.70(11)
O(3)-S(1)-C(24)-C(29)	-17.57(12)
O(1)-S(1)-C(24)-C(25)	38.01(11)
O(2)-S(1)-C(24)-C(25)	-82.79(11)
O(3)-S(1)-C(24)-C(25)	157.94(10)
C(29)-C(24)-C(25)-C(26)	-1.85(18)
S(1)-C(24)-C(25)-C(26)	-177.77(10)
C(29)-C(24)-C(25)-N(3)	179.09(11)
S(1)-C(24)-C(25)-N(3)	3.18(16)
O(5)-N(3)-C(25)-C(26)	-112.20(13)
O(4)-N(3)-C(25)-C(26)	64.56(15)
O(5)-N(3)-C(25)-C(24)	66.94(16)
O(4)-N(3)-C(25)-C(24)	-116.30(13)
C(24)-C(25)-C(26)-C(27)	0.61(19)
N(3)-C(25)-C(26)-C(27)	179.72(11)
C(25)-C(26)-C(27)-C(28)	1.63(19)
C(25)-C(26)-C(27)-N(4)	-177.72(11)
O(7)-N(4)-C(27)-C(28)	3.43(18)
O(6)-N(4)-C(27)-C(28)	-176.36(12)
O(7)-N(4)-C(27)-C(26)	-177.19(12)
O(6)-N(4)-C(27)-C(26)	3.02(18)
C(26)-C(27)-C(28)-C(29)	-2.4(2)
N(4)-C(27)-C(28)-C(29)	176.97(11)

C(27)-C(28)-C(29)-C(24)	1.0(2)
C(27)-C(28)-C(29)-N(5)	-177.99(11)
C(25)-C(24)-C(29)-C(28)	1.02(18)
S(1)-C(24)-C(29)-C(28)	176.76(10)
C(25)-C(24)-C(29)-N(5)	179.91(11)
S(1)-C(24)-C(29)-N(5)	-4.34(18)
O(9)-N(5)-C(29)-C(28)	106.92(13)
O(8)-N(5)-C(29)-C(28)	-69.66(15)
O(9)-N(5)-C(29)-C(24)	-72.07(16)
O(8)-N(5)-C(29)-C(24)	111.34(14)
C(6)-N(1)-C(1)-C(2)	169.65(10)
C(5)-N(1)-C(1)-C(2)	-59.91(12)
C(6)-N(1)-C(1)-C(12)	-62.78(13)
C(5)-N(1)-C(1)-C(12)	67.67(13)
C(12)-C(1)-C(2)-C(3)	-65.63(14)
N(1)-C(1)-C(2)-C(3)	59.21(13)
C(12)-C(1)-C(2)-C(14)	61.42(15)
N(1)-C(1)-C(2)-C(14)	-173.75(10)
C(1)-C(2)-C(3)-C(4)	-58.76(14)
C(14)-C(2)-C(3)-C(4)	175.61(11)
C(2)-C(3)-C(4)-C(16)	176.73(11)
C(2)-C(3)-C(4)-C(5)	54.90(14)
C(6)-N(1)-C(5)-C(17)	-50.05(13)
C(1)-N(1)-C(5)-C(17)	-178.10(10)
C(6)-N(1)-C(5)-C(4)	-175.01(10)
C(1)-N(1)-C(5)-C(4)	56.94(13)
C(16)-C(4)-C(5)-C(17)	62.46(14)
C(3)-C(4)-C(5)-C(17)	-175.33(10)
C(16)-C(4)-C(5)-N(1)	-174.95(10)
C(3)-C(4)-C(5)-N(1)	-52.75(13)
C(5)-N(1)-C(6)-C(11)	148.91(11)
C(1)-N(1)-C(6)-C(11)	-81.71(13)
C(5)-N(1)-C(6)-C(7)	-33.30(16)
C(1)-N(1)-C(6)-C(7)	96.08(13)
C(11)-C(6)-C(7)-C(8)	0.7(2)

N(1)-C(6)-C(7)-C(8)	-177.01(12)
C(6)-C(7)-C(8)-C(9)	-0.6(2)
C(7)-C(8)-C(9)-C(10)	-0.3(2)
C(8)-C(9)-C(10)-C(11)	1.0(2)
C(7)-C(6)-C(11)-C(10)	0.0(2)
N(1)-C(6)-C(11)-C(10)	177.83(11)
C(9)-C(10)-C(11)-C(6)	-0.9(2)
C(2)-C(1)-C(12)-C(13)	-129.48(14)
N(1)-C(1)-C(12)-C(13)	107.90(14)
C(3)-C(2)-C(14)-C(15)	-66.71(15)
C(1)-C(2)-C(14)-C(15)	167.91(12)
N(1)-C(5)-C(17)-C(18)	127.92(12)
C(4)-C(5)-C(17)-C(18)	-109.52(13)
N(1)-C(5)-C(17)-C(22)	-51.30(15)
C(4)-C(5)-C(17)-C(22)	71.26(15)
C(22)-C(17)-C(18)-C(19)	2.24(19)
C(5)-C(17)-C(18)-C(19)	-177.00(12)
C(17)-C(18)-C(19)-C(20)	-0.2(2)
C(18)-C(19)-C(20)-C(21)	-1.5(2)
C(18)-C(19)-C(20)-C(23)	175.17(12)
C(19)-C(20)-C(21)-C(22)	1.2(2)
C(23)-C(20)-C(21)-C(22)	-175.58(12)
C(20)-C(21)-C(22)-C(17)	0.9(2)
C(18)-C(17)-C(22)-C(21)	-2.59(19)
C(5)-C(17)-C(22)-C(21)	176.64(12)

Symmetry transformations used to generate equivalent atoms:

Table S23. Hydrogen bonds for 007c-19019 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)	0.892(16)	2.126(16)	3.0173(14)	176.1(14)

Symmetry transformations used to generate equivalent atoms:

Intermediate 5

Crystal Growth

5 (10 mg) and picrylsulfonic acid dihydrate (0.9 equiv) were dissolved in a mixture of toluene (0.25 mL) and DCM (0.25 mL) in a 1-dram vial. Methanol was added dropwise addition until complete dissolution occurred. A few drops of hexanes were added until the cloud point was reached. Single crystals suitable for X-ray diffraction grew at room temperature over 3-5 days.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007a-20018. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). This data was refined as a 2-component twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.2331(16). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H1, which was found in the difference map and freely refined. The toluene crystallized near the inversion center. The best model was obtained by suppressing the special position constraints and placing a whole model toluene (see Guzei, I. A. (2014). J. Appl. Crystallogr. 47, 806-809). The model was then allowed to freely refine at half occupancy. The full numbering scheme of compound 007a-20018 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1989517 (007a-20018) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

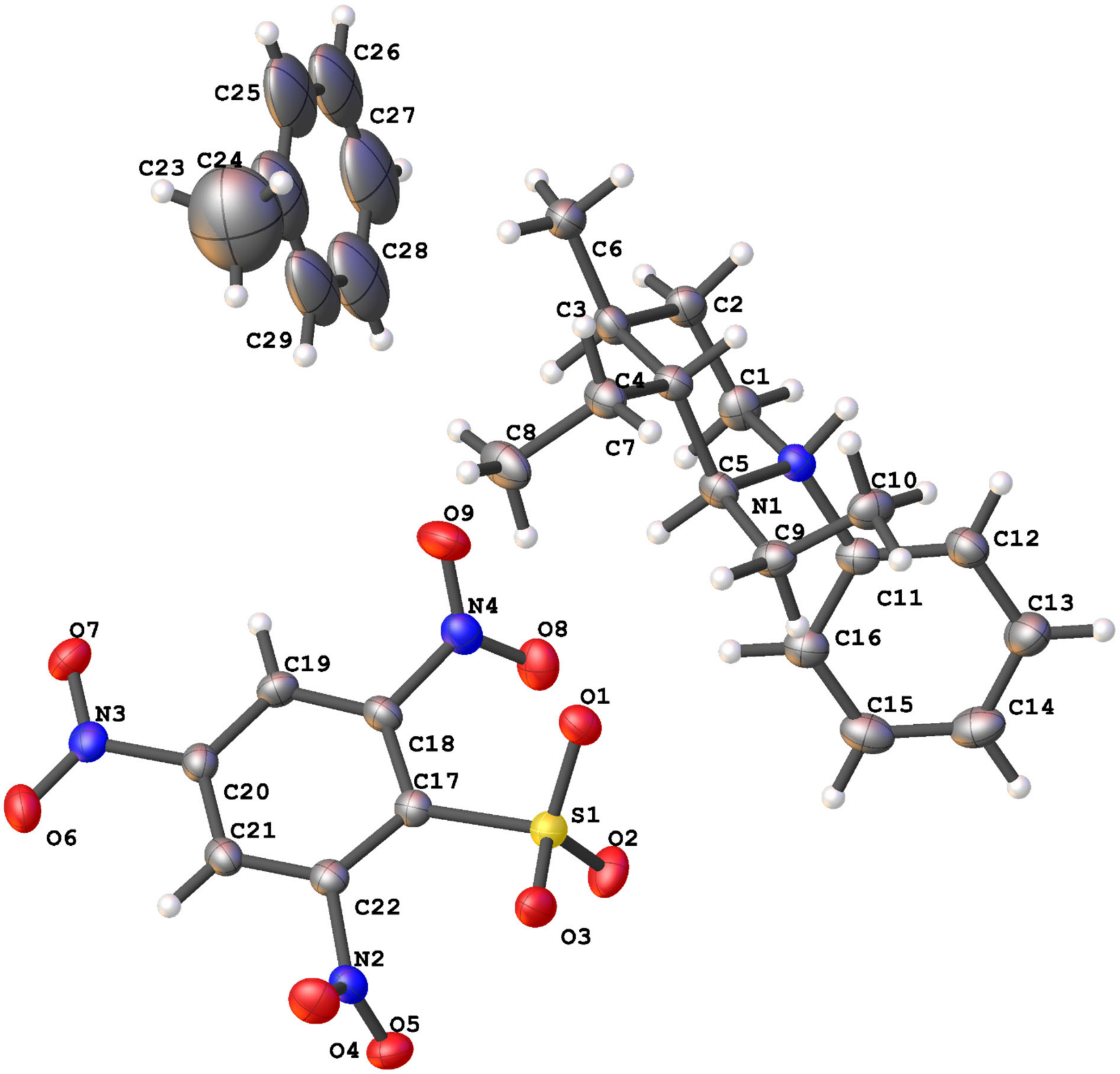


Figure S12. The complete numbering scheme of 007a-20018 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S24. Crystal data and structure refinement for 007a-20018.

Identification code	007a-20018
Empirical formula	C25.50 H32 N4 O9 S
Formula weight	570.61
Temperature	93(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$

Unit cell dimensions	a = 8.09190(10) Å	□= 90°.
	b = 21.6444(3) Å	□= 90.1140(10)°.
	c = 15.4490(2) Å	□ = 90°.
Volume	2705.80(6) Å3	
Z	4	
Density (calculated)	1.401 Mg/m3	
Absorption coefficient	1.583 mm-1	
F(000)	1204	
Crystal size	0.220 x 0.180 x 0.160 mm3	
Crystal color and habit	? ?	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	3.515 to 66.639°.	
Index ranges	-9<=h<=9, -25<=k<=25, 0<=l<=18	
Reflections collected	4779	
Independent reflections	4779 [R(int) = 0.1818]	
Observed reflections (I > 2sigma(I))	4483	
Completeness to theta = 66.639°	100.0 %	
Absorption correction	None	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4779 / 87 / 384	
Goodness-of-fit on F2	1.112	
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1486	
R indices (all data)	R1 = 0.0612, wR2 = 0.1509	
Largest diff. peak and hole	0.500 and -0.469 e.Å-3	

Table S25. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for 007a-20018. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	2250(1)	8728(1)	10189(1)	24(1)
O(1)	2968(3)	8464(1)	9427(2)	29(1)
O(2)	561(3)	8558(1)	10345(2)	35(1)
O(3)	3277(4)	8680(1)	10960(2)	32(1)

O(4)	4356(3)	9888(1)	11782(2)	37(1)
O(5)	1719(3)	9730(1)	11884(2)	34(1)
O(6)	3264(3)	11804(1)	9907(2)	34(1)
O(7)	2508(3)	11621(1)	8587(2)	33(1)
O(8)	212(3)	9047(1)	8542(2)	36(1)
O(9)	2153(4)	9406(2)	7727(2)	48(1)
N(2)	2968(4)	9843(1)	11479(2)	27(1)
N(3)	2833(4)	11461(1)	9327(2)	27(1)
N(4)	1414(4)	9373(2)	8408(2)	30(1)
C(17)	2251(4)	9552(2)	9950(2)	22(1)
C(18)	1975(4)	9780(2)	9116(2)	24(1)
C(19)	2173(4)	10395(2)	8889(2)	25(1)
C(20)	2676(4)	10800(2)	9529(2)	25(1)
C(21)	2982(4)	10611(2)	10361(2)	26(1)
C(22)	2758(4)	9994(2)	10554(2)	24(1)
N(1)	1891(4)	7304(1)	7204(2)	24(1)
C(1)	1032(5)	7755(2)	6611(2)	30(1)
C(2)	2172(5)	7959(2)	5892(2)	30(1)
C(3)	3815(5)	8215(2)	6226(2)	26(1)
C(4)	4630(4)	7742(2)	6844(2)	24(1)
C(5)	3464(4)	7591(2)	7601(2)	24(1)
C(6)	4920(5)	8379(2)	5470(2)	33(1)
C(7)	6334(5)	7955(2)	7162(2)	29(1)
C(8)	6324(5)	8554(2)	7676(3)	41(1)
C(9)	4164(5)	7164(2)	8293(2)	28(1)
C(10)	4681(5)	6524(2)	7991(2)	32(1)
C(11)	731(4)	7059(2)	7856(2)	25(1)
C(12)	262(5)	6451(2)	7774(2)	31(1)
C(13)	-786(5)	6197(2)	8384(3)	39(1)
C(14)	-1359(5)	6557(2)	9057(3)	38(1)
C(15)	-892(5)	7171(2)	9119(3)	35(1)
C(16)	168(5)	7428(2)	8517(2)	30(1)
C(23)	7570(30)	10071(14)	5665(17)	163(9)
C(24)	5835(13)	10014(6)	5266(9)	102(4)
C(25)	5465(15)	9999(5)	4388(8)	96(4)

C(26)	3842(18)	9914(4)	4116(6)	95(4)
C(27)	2590(13)	9844(4)	4723(9)	106(4)
C(28)	2961(14)	9859(4)	5601(8)	102(4)
C(29)	4583(17)	9944(5)	5873(6)	88(4)

Table S26. Bond lengths [Å] and angles [°] for 007a-20018.

S(1)-O(1)	1.433(3)
S(1)-O(2)	1.436(3)
S(1)-O(3)	1.454(3)
S(1)-C(17)	1.821(3)
O(4)-N(2)	1.220(4)
O(5)-N(2)	1.215(4)
O(6)-N(3)	1.215(4)
O(7)-N(3)	1.222(4)
O(8)-N(4)	1.219(4)
O(9)-N(4)	1.214(4)
N(2)-C(22)	1.475(4)
N(3)-C(20)	1.470(5)
N(4)-C(18)	1.474(5)
C(17)-C(18)	1.397(5)
C(17)-C(22)	1.398(5)
C(18)-C(19)	1.388(5)
C(19)-C(20)	1.381(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.370(5)
C(21)-C(22)	1.380(5)
C(21)-H(21)	0.9500
N(1)-C(11)	1.477(5)
N(1)-C(1)	1.509(4)
N(1)-C(5)	1.542(4)
N(1)-H(1)	0.96(5)
C(1)-C(2)	1.510(5)

C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.529(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(6)	1.515(5)
C(3)-C(4)	1.547(5)
C(3)-H(3)	1.0000
C(4)-C(7)	1.534(5)
C(4)-C(5)	1.538(5)
C(4)-H(4)	1.0000
C(5)-C(9)	1.522(5)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(8)	1.521(6)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.520(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(16)	1.375(5)
C(11)-C(12)	1.375(6)
C(12)-C(13)	1.382(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.381(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(6)

C(14)-H(14)	0.9500
C(15)-C(16)	1.383(6)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(23)-C(24)	1.54(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.3900
C(24)-C(29)	1.3900
C(25)-C(26)	1.3900
C(25)-H(25)	0.9500
C(26)-C(27)	1.3900
C(26)-H(26)	0.9500
C(27)-C(28)	1.3900
C(27)-H(27)	0.9500
C(28)-C(29)	1.3900
C(28)-H(28)	0.9500
C(29)-H(29)	0.9500
O(1)-S(1)-O(2)	115.02(17)
O(1)-S(1)-O(3)	114.36(15)
O(2)-S(1)-O(3)	112.80(17)
O(1)-S(1)-C(17)	102.85(15)
O(2)-S(1)-C(17)	106.58(16)
O(3)-S(1)-C(17)	103.66(15)
O(5)-N(2)-O(4)	125.8(3)
O(5)-N(2)-C(22)	116.7(3)
O(4)-N(2)-C(22)	117.3(3)
O(6)-N(3)-O(7)	125.2(3)
O(6)-N(3)-C(20)	117.6(3)
O(7)-N(3)-C(20)	117.2(3)
O(9)-N(4)-O(8)	125.1(3)
O(9)-N(4)-C(18)	117.2(3)
O(8)-N(4)-C(18)	117.7(3)

C(18)-C(17)-C(22)	114.8(3)
C(18)-C(17)-S(1)	122.2(3)
C(22)-C(17)-S(1)	122.4(3)
C(19)-C(18)-C(17)	123.6(3)
C(19)-C(18)-N(4)	114.9(3)
C(17)-C(18)-N(4)	121.5(3)
C(20)-C(19)-C(18)	117.5(3)
C(20)-C(19)-H(19)	121.2
C(18)-C(19)-H(19)	121.2
C(21)-C(20)-C(19)	122.3(3)
C(21)-C(20)-N(3)	118.3(3)
C(19)-C(20)-N(3)	119.3(3)
C(20)-C(21)-C(22)	117.8(3)
C(20)-C(21)-H(21)	121.1
C(22)-C(21)-H(21)	121.1
C(21)-C(22)-C(17)	123.8(3)
C(21)-C(22)-N(2)	114.1(3)
C(17)-C(22)-N(2)	121.9(3)
C(11)-N(1)-C(1)	110.7(3)
C(11)-N(1)-C(5)	113.5(3)
C(1)-N(1)-C(5)	111.0(3)
C(11)-N(1)-H(1)	108(3)
C(1)-N(1)-H(1)	102(3)
C(5)-N(1)-H(1)	111(3)
N(1)-C(1)-C(2)	110.8(3)
N(1)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	108.1
C(1)-C(2)-C(3)	112.9(3)
C(1)-C(2)-H(2A)	109.0
C(3)-C(2)-H(2A)	109.0
C(1)-C(2)-H(2B)	109.0
C(3)-C(2)-H(2B)	109.0

H(2A)-C(2)-H(2B)	107.8
C(6)-C(3)-C(2)	109.8(3)
C(6)-C(3)-C(4)	112.3(3)
C(2)-C(3)-C(4)	109.7(3)
C(6)-C(3)-H(3)	108.3
C(2)-C(3)-H(3)	108.3
C(4)-C(3)-H(3)	108.3
C(7)-C(4)-C(5)	111.9(3)
C(7)-C(4)-C(3)	112.3(3)
C(5)-C(4)-C(3)	110.3(3)
C(7)-C(4)-H(4)	107.3
C(5)-C(4)-H(4)	107.3
C(3)-C(4)-H(4)	107.3
C(9)-C(5)-C(4)	115.7(3)
C(9)-C(5)-N(1)	109.9(3)
C(4)-C(5)-N(1)	106.9(3)
C(9)-C(5)-H(5)	108.0
C(4)-C(5)-H(5)	108.0
N(1)-C(5)-H(5)	108.0
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(4)	114.7(3)
C(8)-C(7)-H(7A)	108.6
C(4)-C(7)-H(7A)	108.6
C(8)-C(7)-H(7B)	108.6
C(4)-C(7)-H(7B)	108.6
H(7A)-C(7)-H(7B)	107.6
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5

H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(5)	116.1(3)
C(10)-C(9)-H(9A)	108.3
C(5)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9B)	108.3
C(5)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(16)-C(11)-C(12)	122.2(4)
C(16)-C(11)-N(1)	120.7(3)
C(12)-C(11)-N(1)	117.1(3)
C(11)-C(12)-C(13)	119.1(4)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-H(12)	120.5
C(14)-C(13)-C(12)	119.8(4)
C(14)-C(13)-H(13)	120.1
C(12)-C(13)-H(13)	120.1
C(13)-C(14)-C(15)	120.1(4)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0
C(16)-C(15)-C(14)	120.5(4)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(11)-C(16)-C(15)	118.3(4)
C(11)-C(16)-H(16)	120.9
C(15)-C(16)-H(16)	120.9
C(24)-C(23)-H(23A)	109.5
C(24)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5

C(24)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(29)	120.0
C(25)-C(24)-C(23)	126.0(13)
C(29)-C(24)-C(23)	113.9(13)
C(24)-C(25)-C(26)	120.0
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(27)	120.0
C(25)-C(26)-H(26)	120.0
C(27)-C(26)-H(26)	120.0
C(28)-C(27)-C(26)	120.0
C(28)-C(27)-H(27)	120.0
C(26)-C(27)-H(27)	120.0
C(29)-C(28)-C(27)	120.0
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(28)-C(29)-C(24)	120.0
C(28)-C(29)-H(29)	120.0
C(24)-C(29)-H(29)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S27. Anisotropic displacement parameters (Å2x 103) for 007a-20018. The anisotropic displacement factor exponent takes the form: -2π2[h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	25(1)	23(1)	23(1)	0(1)	1(1)	1(1)
O(1)	32(1)	28(1)	26(1)	-3(1)	-2(1)	4(1)
O(2)	26(1)	31(1)	49(2)	3(1)	9(1)	

						-4(1)
O(3)	44(2)	26(1)	27(1)	3(1)	1(1)	4(1)
O(4)	36(2)	44(2)	30(1)	0(1)	-11(1)	1(1)
O(5)	38(2)	36(2)	26(1)	1(1)	8(1)	0(1)
O(6)	36(2)	25(1)	41(2)	-4(1)	2(1)	-4(1)
O(7)	37(2)	32(1)	30(1)	8(1)	2(1)	-2(1)
O(8)	33(2)	33(2)	41(2)	-1(1)	-10(1)	-4(1)
O(9)	62(2)	55(2)	28(2)	-12(1)	5(2)	-12(2)
N(2)	33(2)	24(2)	25(2)	-3(1)	-1(1)	1(1)
N(3)	23(2)	28(2)	30(2)	0(1)	4(1)	-1(1)
N(4)	33(2)	29(2)	27(2)	-2(1)	-6(1)	1(1)
C(17)	17(2)	25(2)	24(2)	0(1)	0(1)	0(1)
C(18)	23(2)	28(2)	22(2)	-5(1)	-2(1)	-1(2)
C(19)	24(2)	30(2)	21(2)	4(1)	-1(1)	1(2)
C(20)	24(2)	23(2)	27(2)	-1(1)	3(1)	-1(1)
C(21)	22(2)	27(2)	27(2)	-5(1)	3(2)	-2(2)
C(22)	19(2)	27(2)	25(2)	-2(1)	2(1)	1(2)
N(1)	25(2)	24(2)	23(1)	-2(1)	-2(1)	1(1)

C(1)	28(2)	29(2)	31(2)	2(2)	-8(2)	3(2)
C(2)	35(2)	28(2)	26(2)	1(2)	-6(2)	2(2)
C(3)	31(2)	23(2)	26(2)	-4(2)	-3(2)	-1(2)
C(4)	25(2)	26(2)	22(2)	-2(1)	-1(1)	0(2)
C(5)	21(2)	29(2)	22(2)	-5(2)	-4(1)	-2(2)
C(6)	42(2)	29(2)	28(2)	-1(2)	3(2)	-2(2)
C(7)	24(2)	34(2)	30(2)	-6(2)	1(2)	-4(2)
C(8)	31(2)	51(3)	42(2)	-17(2)	-2(2)	-10(2)
C(9)	24(2)	36(2)	23(2)	0(2)	0(1)	-2(2)
C(10)	33(2)	35(2)	27(2)	6(2)	-1(2)	6(2)
C(11)	19(2)	34(2)	23(2)	-1(2)	-1(1)	1(2)
C(12)	30(2)	35(2)	28(2)	-5(2)	-1(2)	-3(2)
C(13)	38(2)	43(2)	35(2)	0(2)	5(2)	-9(2)
C(14)	27(2)	56(3)	31(2)	3(2)	4(2)	-3(2)
C(15)	28(2)	48(3)	29(2)	-7(2)	-1(2)	8(2)
C(16)	27(2)	36(2)	28(2)	-2(2)	-1(2)	1(2)
C(23)	163(11)	150(20)	174(16)	-1(15)	-47(11)	2(11)
C(24)	143(9)	42(7)	121(8)	-11(6)	-33(7)	

						17(7)
C(25)	155(10)	27(7)	107(8)	-4(6)	-23(7)	20(7)
C(26)	157(10)	28(6)	100(8)	-8(6)	-32(7)	20(7)
C(27)	148(10)	34(6)	136(8)	-10(6)	-37(8)	30(7)
C(28)	145(9)	39(6)	123(8)	-16(6)	-29(7)	31(7)
C(29)	147(9)	31(7)	86(8)	-8(5)	-35(7)	21(6)

Table S28. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for 007a-20018.

	x	y	z	U(eq)
H(19)	1971	10534	8315	30
H(21)	3336	10896	10791	31
H(1)	2170(50)	6980(20)	6810(30)	35(11)
H(1A)	672	8120	6947	35
H(1B)	38	7558	6358	35
H(2A)	1612	8281	5544	36
H(2B)	2395	7603	5508	36
H(3)	3584	8601	6560	32
H(4)	4796	7351	6509	29
H(5)	3147	7989	7885	29
H(6A)	5294	7999	5185	50
H(6B)	5879	8611	5679	50
H(6C)	4300	8632	5055	50
H(7A)	6816	7625	7528	35

H(7B)	7064	8008	6654	35
H(8A)	5904	8889	7311	62
H(8B)	7451	8651	7866	62
H(8C)	5610	8507	8183	62
H(9A)	5137	7368	8557	33
H(9B)	3324	7116	8753	33
H(10A)	5531	6563	7543	48
H(10B)	3720	6307	7752	48
H(10C)	5126	6291	8482	48
H(12)	653	6209	7304	37
H(13)	-1110	5777	8339	47
H(14)	-2075	6384	9478	46
H(15)	-1302	7418	9579	42
H(16)	499	7848	8560	36
H(23A)	7490	10071	6298	244
H(23B)	8254	9721	5479	244
H(23C)	8086	10458	5473	244
H(25)	6321	10047	3973	116
H(26)	3589	9903	3515	114
H(27)	1481	9786	4537	128
H(28)	2105	9812	6016	123
H(29)	4836	9955	6474	106

Table S29. Torsion angles [°] for 007a-20018.

O(1)-S(1)-C(17)-C(18)	35.4(3)
O(2)-S(1)-C(17)-C(18)	-85.9(3)
O(3)-S(1)-C(17)-C(18)	154.8(3)
O(1)-S(1)-C(17)-C(22)	-135.1(3)
O(2)-S(1)-C(17)-C(22)	103.6(3)
O(3)-S(1)-C(17)-C(22)	-15.7(3)
C(22)-C(17)-C(18)-C(19)	-0.3(5)
S(1)-C(17)-C(18)-C(19)	-171.5(3)

C(22)-C(17)-C(18)-N(4)	-179.2(3)
S(1)-C(17)-C(18)-N(4)	9.6(5)
O(9)-N(4)-C(18)-C(19)	49.4(5)
O(8)-N(4)-C(18)-C(19)	-128.1(4)
O(9)-N(4)-C(18)-C(17)	-131.6(4)
O(8)-N(4)-C(18)-C(17)	50.8(5)
C(17)-C(18)-C(19)-C(20)	0.2(6)
N(4)-C(18)-C(19)-C(20)	179.1(3)
C(18)-C(19)-C(20)-C(21)	0.3(5)
C(18)-C(19)-C(20)-N(3)	-177.4(3)
O(6)-N(3)-C(20)-C(21)	1.6(5)
O(7)-N(3)-C(20)-C(21)	-177.9(3)
O(6)-N(3)-C(20)-C(19)	179.4(3)
O(7)-N(3)-C(20)-C(19)	-0.2(5)
C(19)-C(20)-C(21)-C(22)	-0.6(5)
N(3)-C(20)-C(21)-C(22)	177.1(3)
C(20)-C(21)-C(22)-C(17)	0.4(5)
C(20)-C(21)-C(22)-N(2)	-174.7(3)
C(18)-C(17)-C(22)-C(21)	0.0(5)
S(1)-C(17)-C(22)-C(21)	171.2(3)
C(18)-C(17)-C(22)-N(2)	174.8(3)
S(1)-C(17)-C(22)-N(2)	-14.1(5)
O(5)-N(2)-C(22)-C(21)	106.6(4)
O(4)-N(2)-C(22)-C(21)	-68.2(4)
O(5)-N(2)-C(22)-C(17)	-68.7(4)
O(4)-N(2)-C(22)-C(17)	116.6(4)
C(11)-N(1)-C(1)-C(2)	-174.5(3)
C(5)-N(1)-C(1)-C(2)	58.4(4)
N(1)-C(1)-C(2)-C(3)	-53.9(4)
C(1)-C(2)-C(3)-C(6)	177.2(3)
C(1)-C(2)-C(3)-C(4)	53.3(4)
C(6)-C(3)-C(4)-C(7)	54.3(4)
C(2)-C(3)-C(4)-C(7)	176.7(3)
C(6)-C(3)-C(4)-C(5)	179.9(3)
C(2)-C(3)-C(4)-C(5)	-57.7(4)

C(7)-C(4)-C(5)-C(9)	-50.0(4)
C(3)-C(4)-C(5)-C(9)	-175.9(3)
C(7)-C(4)-C(5)-N(1)	-172.7(3)
C(3)-C(4)-C(5)-N(1)	61.4(4)
C(11)-N(1)-C(5)-C(9)	46.2(4)
C(1)-N(1)-C(5)-C(9)	171.8(3)
C(11)-N(1)-C(5)-C(4)	172.5(3)
C(1)-N(1)-C(5)-C(4)	-61.9(4)
C(5)-C(4)-C(7)-C(8)	-63.5(4)
C(3)-C(4)-C(7)-C(8)	61.3(4)
C(4)-C(5)-C(9)-C(10)	-60.3(4)
N(1)-C(5)-C(9)-C(10)	60.8(4)
C(1)-N(1)-C(11)-C(16)	-71.3(4)
C(5)-N(1)-C(11)-C(16)	54.4(4)
C(1)-N(1)-C(11)-C(12)	109.3(4)
C(5)-N(1)-C(11)-C(12)	-125.0(3)
C(16)-C(11)-C(12)-C(13)	-1.2(6)
N(1)-C(11)-C(12)-C(13)	178.2(3)
C(11)-C(12)-C(13)-C(14)	0.7(6)
C(12)-C(13)-C(14)-C(15)	0.3(6)
C(13)-C(14)-C(15)-C(16)	-0.9(6)
C(12)-C(11)-C(16)-C(15)	0.6(6)
N(1)-C(11)-C(16)-C(15)	-178.8(3)
C(14)-C(15)-C(16)-C(11)	0.5(6)
C(29)-C(24)-C(25)-C(26)	0.0
C(23)-C(24)-C(25)-C(26)	176.7(18)
C(24)-C(25)-C(26)-C(27)	0.0
C(25)-C(26)-C(27)-C(28)	0.0
C(26)-C(27)-C(28)-C(29)	0.0
C(27)-C(28)-C(29)-C(24)	0.0
C(25)-C(24)-C(29)-C(28)	0.0
C(23)-C(24)-C(29)-C(28)	-177.1(16)

Symmetry transformations used to generate equivalent atoms:

Table S30. Hydrogen bonds for 007a-20018 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)#1	0.96(5)	2.13(5)	3.082(4)	169(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z-1/2

Pr**oduct 2v**

Crystal Growth

2v (10 mg) and picrylsulfonic acid dihydrate (0.9 equiv) were dissolved in a mixture of toluene (0.25 mL) and DCM (0.25 mL) in a 1-dram vial. Methanol was added dropwise addition until complete dissolution occurred. A few drops of hexanes were added until the cloud point was reached. Single crystals suitable for X-ray diffraction grew at room temperature over 3-5 days.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007b-20020. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The isoproplyl and phenyl group are disordered over two positions. The phenyl site occupancies were freely refined to 0.88/0.12. The chemically equivalent C-C distances were restrained to be similar. Due to the small electron density, the thermal parameters of the minor component were constrained to be identical to the major. The site occupacies of the isopropyl were refined to 0.82/12, and a similar approach was used for refining the atomic and thermal parameters. The full numbering scheme of compound 007b-20020 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1989519 (007b-20020) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

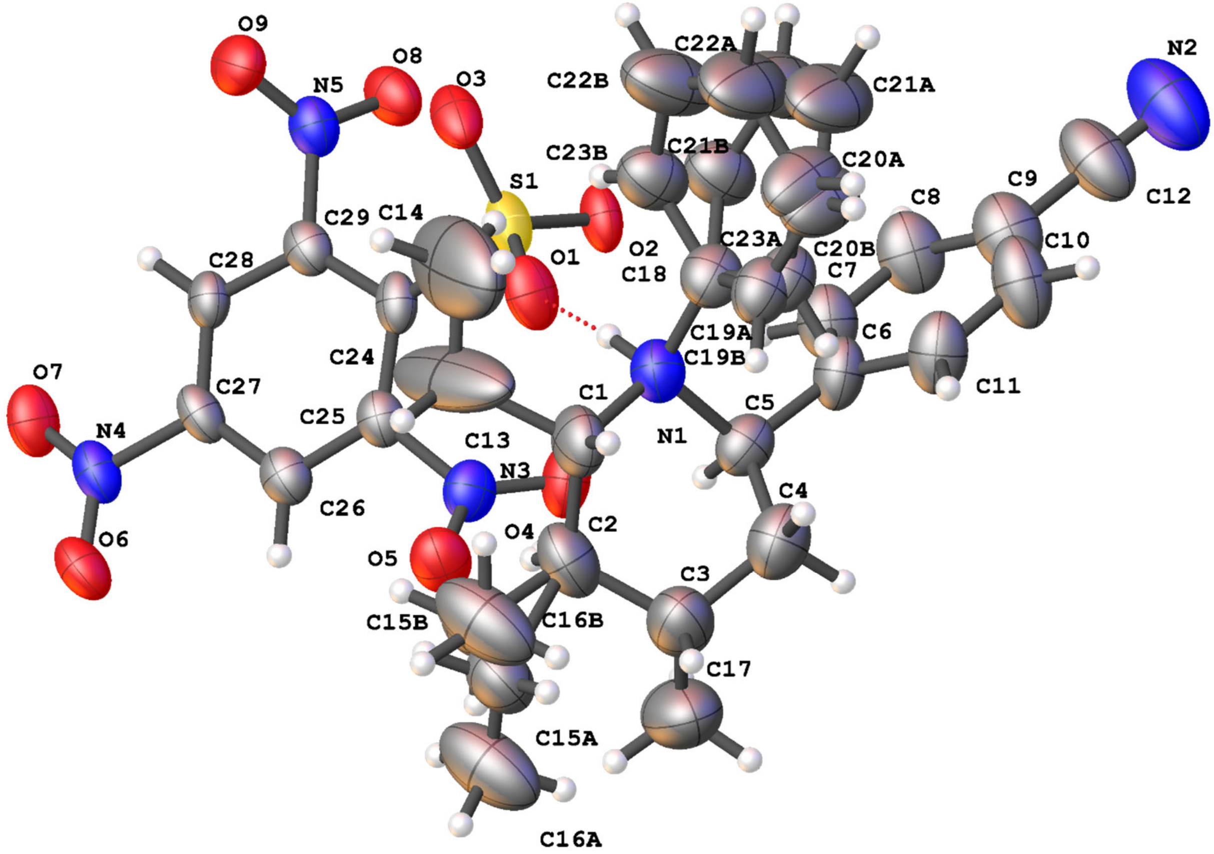


Figure S13. The complete numbering scheme of 007b-20020 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S31. Crystal data and structure refinement for 007b-20020.

Identification code	007b-20020	
Empirical formula	C29 H31 N5 O9 S	
Formula weight	625.65	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.1117(3) Å	□= 90°.
	b = 19.7564(8) Å	□= 92.656(4)°.
	c = 18.3015(9) Å	□ = 90°.
Volume	2929.8(2) Å3	
Z	4	
Density (calculated)	1.418 Mg/m3	
Absorption coefficient	1.529 mm-1	

F(000)	1312
Crystal size	0.040 x 0.040 x 0.020 mm3
Crystal color and habit	Colorless Plate
Diffractometer	Rigaku Saturn 944+ CCD
Theta range for data collection	3.294 to 66.601°.
Index ranges	-9<=h<=9, -23<=k<=23, 0<=l<=21
Reflections collected	5182
Independent reflections	5182 [R(int) = 0.2324]
Observed reflections (I > 2sigma(I))	3141
Completeness to theta = 66.601°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.41680
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	5182 / 66 / 413
Goodness-of-fit on F2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0910, wR2 = 0.2056
R indices (all data)	R1 = 0.1490, wR2 = 0.2395
Largest diff. peak and hole	0.581 and -0.348 e.Å-3

Table S32. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for 007b-20020. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	7434(2)	3652(1)	5180(1)	46(1)
O(1)	7866(5)	3453(2)	5928(2)	57(1)
O(2)	5875(4)	3390(2)	4896(2)	46(1)
O(3)	8781(4)	3584(2)	4690(2)	55(1)
O(4)	4952(5)	4105(2)	6366(2)	58(1)
O(5)	6636(6)	4633(2)	7127(2)	60(1)
O(6)	7469(5)	6923(2)	6192(2)	54(1)
O(7)	7770(5)	7057(2)	5027(2)	54(1)
O(8)	6988(5)	4451(2)	3641(2)	53(1)
O(9)	9471(5)	4883(2)	3766(2)	55(1)

N(3)	6079(6)	4507(2)	6512(3)	48(1)
N(4)	7567(5)	6712(2)	5564(3)	45(1)
N(5)	8105(6)	4752(2)	3993(3)	46(1)
C(24)	7191(6)	4565(2)	5264(3)	38(1)
C(25)	6741(6)	4893(3)	5898(3)	39(1)
C(26)	6843(6)	5581(3)	6016(3)	43(1)
C(27)	7420(6)	5970(2)	5458(3)	40(1)
C(28)	7854(6)	5704(2)	4803(3)	38(1)
C(29)	7704(6)	5005(3)	4724(3)	39(1)
N(1)	8360(6)	2522(2)	7152(3)	54(1)
N(2)	2811(9)	102(4)	4985(5)	110(3)
C(1)	9365(8)	2887(4)	7757(4)	67(2)
C(2)	8277(10)	3337(3)	8201(4)	74(2)
C(3)	6893(10)	2959(4)	8554(4)	79(2)
C(4)	6396(9)	2325(4)	8134(4)	73(2)
C(5)	6509(7)	2443(3)	7335(3)	52(2)
C(6)	5674(7)	1929(3)	6836(4)	58(2)
C(7)	4983(8)	2134(3)	6159(4)	63(2)
C(8)	4262(9)	1670(3)	5681(4)	71(2)
C(9)	4224(9)	986(4)	5870(4)	76(2)
C(10)	4897(9)	768(4)	6539(4)	80(2)
C(11)	5595(8)	1241(3)	7016(4)	68(2)
C(12)	3424(10)	493(4)	5365(5)	85(2)
C(13)	10765(11)	3349(8)	7360(8)	190(8)
C(14)	11742(15)	2974(7)	6913(9)	193(7)
C(15A)	9100(70)	3720(30)	9130(30)	79(3)
C(15B)	9304(14)	3790(5)	8715(7)	79(3)
C(16A)	8130(70)	4110(30)	9380(30)	120(5)
C(16B)	10517(15)	3416(6)	9185(7)	120(5)
C(17)	5376(12)	3410(5)	8677(5)	113(3)
C(19B)	9671(10)	1404(4)	7420(5)	59(2)
C(20A)	10197(16)	789(5)	7157(7)	92(3)
C(21A)	10139(17)	647(5)	6408(6)	119(5)
C(22A)	9526(17)	1123(5)	5906(6)	115(4)
C(23A)	9005(12)	1749(4)	6152(4)	70(3)

C(23B)	9910(50)	1997(17)	6274(14)	70(3)
C(18)	9083(8)	1882(3)	6911(3)	58(2)
C(19A)	9380(60)	1291(14)	7310(20)	59(2)
C(20B)	10500(80)	820(20)	7070(30)	92(3)
C(21B)	11320(70)	930(30)	6430(30)	119(5)
C(22B)	11030(60)	1520(30)	6040(20)	115(4)

Table S33. Bond lengths [Å] and angles [°] for 007b-20020.

S(1)-O(2)	1.441(4)
S(1)-O(3)	1.451(4)
S(1)-O(1)	1.452(4)
S(1)-C(24)	1.823(5)
O(4)-N(3)	1.231(6)
O(5)-N(3)	1.220(6)
O(6)-N(4)	1.230(6)
O(7)-N(4)	1.213(6)
O(8)-N(5)	1.240(5)
O(9)-N(5)	1.230(6)
N(3)-C(25)	1.478(7)
N(4)-C(27)	1.483(6)
N(5)-C(29)	1.478(7)
C(24)-C(25)	1.393(7)
C(24)-C(29)	1.393(7)
C(25)-C(26)	1.379(7)
C(26)-C(27)	1.377(8)
C(26)-H(26)	0.9500
C(27)-C(28)	1.369(7)
C(28)-C(29)	1.394(7)
C(28)-H(28)	0.9500
N(1)-C(18)	1.471(7)
N(1)-C(1)	1.526(8)
N(1)-C(5)	1.561(7)

N(1)-H(1)	1.0000
N(2)-C(12)	1.138(9)
C(1)-C(2)	1.515(10)
C(1)-C(13)	1.650(15)
C(1)-H(1A)	1.0000
C(2)-C(3)	1.517(10)
C(2)-C(15B)	1.518(12)
C(2)-C(15A)	1.95(5)
C(2)-H(2B)	1.0000
C(2)-H(2A)	1.0000
C(3)-C(4)	1.514(10)
C(3)-C(17)	1.544(12)
C(3)-H(3)	1.0000
C(4)-C(5)	1.488(9)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.505(9)
C(5)-H(5)	1.0000
C(6)-C(7)	1.396(8)
C(6)-C(11)	1.400(9)
C(7)-C(8)	1.378(9)
C(7)-H(7)	0.9500
C(8)-C(9)	1.394(9)
C(8)-H(8)	0.9500
C(9)-C(10)	1.387(10)
C(9)-C(12)	1.473(11)
C(10)-C(11)	1.382(9)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(13)-C(14)	1.381(15)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(15A)-C(16A)	1.21(7)
C(15A)-H(15A)	0.9900
C(15A)-H(15B)	0.9900
C(15B)-C(16B)	1.475(16)
C(15B)-H(15C)	0.9900
C(15B)-H(15D)	0.9900
C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800
C(16A)-H(16C)	0.9800
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(19B)-C(20A)	1.381(9)
C(19B)-C(18)	1.395(8)
C(19B)-H(19B)	0.9500
C(20A)-C(21A)	1.398(11)
C(20A)-H(20A)	0.9500
C(21A)-C(22A)	1.391(10)
C(21A)-H(21A)	0.9500
C(22A)-C(23A)	1.388(9)
C(22A)-H(22A)	0.9500
C(23A)-C(18)	1.412(8)
C(23A)-H(23A)	0.9500
C(23B)-C(18)	1.3900
C(23B)-C(22B)	1.3900
C(23B)-H(23B)	0.9500
C(18)-C(19A)	1.3900
C(19A)-C(20B)	1.3900
C(19A)-H(19A)	0.9500
C(20B)-C(21B)	1.3900
C(20B)-H(20B)	0.9500
C(21B)-C(22B)	1.3900

C(21B)-H(21B)	0.9500
C(22B)-H(22B)	0.9500
O(2)-S(1)-O(3)	114.7(2)
O(2)-S(1)-O(1)	114.3(2)
O(3)-S(1)-O(1)	113.7(3)
O(2)-S(1)-C(24)	106.8(2)
O(3)-S(1)-C(24)	103.3(2)
O(1)-S(1)-C(24)	102.2(2)
O(5)-N(3)-O(4)	124.9(5)
O(5)-N(3)-C(25)	117.6(5)
O(4)-N(3)-C(25)	117.4(5)
O(7)-N(4)-O(6)	125.7(5)
O(7)-N(4)-C(27)	117.6(5)
O(6)-N(4)-C(27)	116.7(5)
O(9)-N(5)-O(8)	125.0(5)
O(9)-N(5)-C(29)	118.4(4)
O(8)-N(5)-C(29)	116.5(5)
C(25)-C(24)-C(29)	113.6(5)
C(25)-C(24)-S(1)	124.3(4)
C(29)-C(24)-S(1)	121.4(4)
C(26)-C(25)-C(24)	124.9(5)
C(26)-C(25)-N(3)	114.3(5)
C(24)-C(25)-N(3)	120.8(4)
C(27)-C(26)-C(25)	117.0(5)
C(27)-C(26)-H(26)	121.5
C(25)-C(26)-H(26)	121.5
C(28)-C(27)-C(26)	123.1(5)
C(28)-C(27)-N(4)	118.1(5)
C(26)-C(27)-N(4)	118.9(5)
C(27)-C(28)-C(29)	116.5(5)
C(27)-C(28)-H(28)	121.7
C(29)-C(28)-H(28)	121.7
C(24)-C(29)-C(28)	124.9(5)
C(24)-C(29)-N(5)	121.0(5)

C(28)-C(29)-N(5)	114.1(5)
C(18)-N(1)-C(1)	114.7(5)
C(18)-N(1)-C(5)	112.3(5)
C(1)-N(1)-C(5)	112.3(5)
C(18)-N(1)-H(1)	105.6
C(1)-N(1)-H(1)	105.6
C(5)-N(1)-H(1)	105.6
C(2)-C(1)-N(1)	111.2(5)
C(2)-C(1)-C(13)	110.0(7)
N(1)-C(1)-C(13)	107.3(6)
C(2)-C(1)-H(1A)	109.4
N(1)-C(1)-H(1A)	109.4
C(13)-C(1)-H(1A)	109.4
C(1)-C(2)-C(3)	113.6(6)
C(1)-C(2)-C(15B)	111.2(7)
C(3)-C(2)-C(15B)	115.0(8)
C(1)-C(2)-C(15A)	120.9(19)
C(3)-C(2)-C(15A)	92.8(18)
C(1)-C(2)-H(2B)	105.3
C(3)-C(2)-H(2B)	105.3
C(15B)-C(2)-H(2B)	105.3
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
C(15A)-C(2)-H(2A)	109.4
C(4)-C(3)-C(2)	112.1(6)
C(4)-C(3)-C(17)	110.9(7)
C(2)-C(3)-C(17)	112.8(7)
C(4)-C(3)-H(3)	106.9
C(2)-C(3)-H(3)	106.9
C(17)-C(3)-H(3)	106.9
C(5)-C(4)-C(3)	110.0(6)
C(5)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4A)	109.7
C(5)-C(4)-H(4B)	109.7
C(3)-C(4)-H(4B)	109.7

H(4A)-C(4)-H(4B)	108.2
C(4)-C(5)-C(6)	116.4(5)
C(4)-C(5)-N(1)	109.3(5)
C(6)-C(5)-N(1)	110.4(5)
C(4)-C(5)-H(5)	106.8
C(6)-C(5)-H(5)	106.8
N(1)-C(5)-H(5)	106.8
C(7)-C(6)-C(11)	117.9(6)
C(7)-C(6)-C(5)	119.6(5)
C(11)-C(6)-C(5)	122.4(6)
C(8)-C(7)-C(6)	120.8(6)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(7)-C(8)-C(9)	120.0(7)
C(7)-C(8)-H(8)	120.0
C(9)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.5(7)
C(10)-C(9)-C(12)	119.5(7)
C(8)-C(9)-C(12)	120.0(7)
C(11)-C(10)-C(9)	118.7(7)
C(11)-C(10)-H(10)	120.7
C(9)-C(10)-H(10)	120.7
C(10)-C(11)-C(6)	122.0(6)
C(10)-C(11)-H(11)	119.0
C(6)-C(11)-H(11)	119.0
N(2)-C(12)-C(9)	178.7(10)
C(14)-C(13)-C(1)	113.0(12)
C(14)-C(13)-H(13A)	109.0
C(1)-C(13)-H(13A)	109.0
C(14)-C(13)-H(13B)	109.0
C(1)-C(13)-H(13B)	109.0
H(13A)-C(13)-H(13B)	107.8
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16A)-C(15A)-C(2)	112(4)
C(16A)-C(15A)-H(15A)	109.2
C(2)-C(15A)-H(15A)	109.2
C(16A)-C(15A)-H(15B)	109.2
C(2)-C(15A)-H(15B)	109.2
H(15A)-C(15A)-H(15B)	107.9
C(16B)-C(15B)-C(2)	113.4(8)
C(16B)-C(15B)-H(15C)	108.9
C(2)-C(15B)-H(15C)	108.9
C(16B)-C(15B)-H(15D)	108.9
C(2)-C(15B)-H(15D)	108.9
H(15C)-C(15B)-H(15D)	107.7
C(15A)-C(16A)-H(16A)	109.5
C(15A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16B)	109.5
C(15A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(15B)-C(16B)-H(16D)	109.5
C(15B)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16E)	109.5
C(15B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
C(3)-C(17)-H(17A)	109.5
C(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(20A)-C(19B)-C(18)	117.7(8)
C(20A)-C(19B)-H(19B)	121.2

C(18)-C(19B)-H(19B)	121.2
C(19B)-C(20A)-C(21A)	121.4(8)
C(19B)-C(20A)-H(20A)	119.3
C(21A)-C(20A)-H(20A)	119.3
C(22A)-C(21A)-C(20A)	120.4(9)
C(22A)-C(21A)-H(21A)	119.8
C(20A)-C(21A)-H(21A)	119.8
C(23A)-C(22A)-C(21A)	119.6(9)
C(23A)-C(22A)-H(22A)	120.2
C(21A)-C(22A)-H(22A)	120.2
C(22A)-C(23A)-C(18)	118.9(8)
C(22A)-C(23A)-H(23A)	120.6
C(18)-C(23A)-H(23A)	120.6
C(18)-C(23B)-C(22B)	120.0
C(18)-C(23B)-H(23B)	120.0
C(22B)-C(23B)-H(23B)	120.0
C(23B)-C(18)-C(19A)	120.0
C(19B)-C(18)-C(23A)	122.0(7)
C(23B)-C(18)-N(1)	109.0(13)
C(19A)-C(18)-N(1)	128.7(14)
C(19B)-C(18)-N(1)	120.7(6)
C(23A)-C(18)-N(1)	117.0(5)
C(20B)-C(19A)-C(18)	120.0
C(20B)-C(19A)-H(19A)	120.0
C(18)-C(19A)-H(19A)	120.0
C(19A)-C(20B)-C(21B)	120.0
C(19A)-C(20B)-H(20B)	120.0
C(21B)-C(20B)-H(20B)	120.0
C(20B)-C(21B)-C(22B)	120.0
C(20B)-C(21B)-H(21B)	120.0
C(22B)-C(21B)-H(21B)	120.0
C(21B)-C(22B)-C(23B)	120.0
C(21B)-C(22B)-H(22B)	120.0
C(23B)-C(22B)-H(22B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S34. Anisotropic displacement parameters (Å2x 103) for 007b-20020. The anisotropic displacement factor exponent takes the form: -2π2[h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	38(1)	30(1)	69(1)	1(1)	-10(1)	-2(1)
O(1)	61(3)	35(2)	72(3)	10(2)	-18(2)	1(2)
O(2)	36(2)	34(2)	68(3)	2(2)	-12(2)	-9(2)
O(3)	33(2)	39(2)	93(3)	-14(2)	5(2)	2(2)
O(4)	48(2)	52(2)	74(3)	17(2)	-5(2)	-13(2)
O(5)	74(3)	57(3)	49(3)	4(2)	-5(2)	-6(2)
O(6)	55(3)	37(2)	71(3)	-13(2)	-7(2)	2(2)
O(7)	55(3)	35(2)	69(3)	11(2)	-12(2)	0(2)
O(8)	42(2)	55(2)	63(3)	-16(2)	-5(2)	-4(2)
O(9)	41(2)	61(3)	63(3)	-7(2)	4(2)	-9(2)
N(3)	46(3)	41(3)	55(3)	9(2)	0(2)	1(2)
N(4)	40(3)	31(2)	63(3)	-3(2)	-10(2)	0(2)
N(5)	43(3)	40(3)	54(3)	0(2)	-6(2)	-3(2)
C(24)	26(3)	32(3)	57(3)	7(3)	-8(2)	

						-4(2)
C(25)	32(3)	35(3)	48(3)	2(2)	-7(2)	1(2)
C(26)	34(3)	41(3)	53(3)	-2(3)	-7(2)	2(2)
C(27)	37(3)	27(3)	54(3)	-5(2)	-12(3)	3(2)
C(28)	29(3)	32(3)	51(3)	3(2)	-3(2)	-5(2)
C(29)	30(3)	36(3)	50(3)	-3(3)	-6(2)	1(2)
N(1)	53(3)	47(3)	61(3)	2(2)	0(2)	-4(2)
N(2)	88(5)	89(5)	151(7)	-37(5)	-27(5)	3(4)
C(1)	51(4)	62(4)	89(5)	-8(4)	1(3)	-15(3)
C(2)	86(5)	49(4)	85(5)	-6(4)	-9(4)	-5(4)
C(3)	91(6)	78(5)	70(5)	-3(4)	6(4)	-14(5)
C(4)	65(4)	73(5)	82(5)	16(4)	3(4)	-5(4)
C(5)	47(3)	53(4)	58(4)	11(3)	4(3)	4(3)
C(6)	45(3)	54(4)	73(4)	15(3)	-5(3)	-9(3)
C(7)	57(4)	55(4)	76(5)	11(3)	-13(3)	0(3)
C(8)	68(5)	60(4)	84(5)	13(4)	-24(4)	7(4)
C(9)	69(5)	65(5)	93(6)	2(4)	-16(4)	7(4)
C(10)	71(5)	54(4)	112(6)	10(4)	-32(4)	-8(4)

C(11)	59(4)	66(4)	77(5)	21(4)	-18(4)	-9(3)
C(12)	73(5)	64(5)	116(7)	-23(5)	-27(5)	13(4)
C(13)	53(6)	310(19)	211(13)	-180(14)	38(7)	-30(8)
C(14)	97(9)	214(15)	269(18)	-114(14)	24(10)	-62(9)
C(15A)	86(6)	65(6)	85(8)	-18(7)	2(7)	-4(5)
C(15B)	86(6)	65(6)	85(8)	-18(7)	2(7)	-4(5)
C(16A)	100(9)	113(9)	143(10)	-57(8)	-42(8)	29(7)
C(16B)	100(9)	113(9)	143(10)	-57(8)	-42(8)	29(7)
C(17)	101(7)	121(8)	120(8)	-33(6)	39(6)	-15(6)
C(19B)	52(4)	54(4)	70(5)	13(4)	4(4)	3(4)
C(20A)	102(8)	67(5)	111(8)	23(5)	38(6)	32(5)
C(21A)	167(13)	61(6)	132(10)	-5(7)	60(9)	33(7)
C(22A)	180(13)	75(7)	91(7)	-11(6)	30(8)	29(7)
C(23A)	88(7)	63(5)	59(5)	0(4)	1(4)	7(5)
C(23B)	88(7)	63(5)	59(5)	0(4)	1(4)	7(5)
C(18)	54(4)	53(4)	68(4)	7(3)	4(3)	8(3)
C(19A)	52(4)	54(4)	70(5)	13(4)	4(4)	3(4)
C(20B)	102(8)	67(5)	111(8)	23(5)	38(6)	

	32(5)				
C(21B)	167(13)	61(6)	132(10)	-5(7)	60(9)
	33(7)				
C(22B)	180(13)	75(7)	91(7)	-11(6)	30(8)
	29(7)				

Table S35. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for 007b-20020.

	x	y	z	U(eq)
H(26)	6529	5779	6462	51
H(28)	8237	5982	4423	45
H(1)	8362	2829	6718	65
H(1A)	9928	2546	8086	81
H(2B)	7719	3650	7839	88
H(2A)	7801	3706	7883	88
H(3)	7330	2810	9048	95
H(4A)	7132	1947	8289	88
H(4B)	5252	2199	8242	88
H(5)	5965	2888	7225	63
H(7)	5011	2598	6025	76
H(8)	3790	1815	5223	86
H(10)	4879	302	6668	96
H(11)	6035	1096	7480	82
H(13A)	10202	3708	7067	229
H(13B)	11478	3571	7743	229
H(14A)	12126	2565	7171	290
H(14B)	12695	3245	6781	290
H(14C)	11098	2845	6468	290
H(15A)	9322	3349	9486	94
H(15B)	10148	3959	9059	94
H(15C)	9896	4125	8422	94
H(15D)	8556	4042	9030	94

H(16A)	7981	4501	9056	180
H(16B)	8549	4263	9865	180
H(16C)	7064	3883	9431	180
H(16D)	9938	3096	9492	180
H(16E)	11150	3735	9496	180
H(16F)	11269	3167	8878	180
H(17A)	4821	3518	8204	170
H(17B)	5735	3830	8921	170
H(17C)	4610	3169	8983	170
H(19B)	9707	1497	7929	71
H(20A)	10608	456	7493	111
H(21A)	10520	222	6241	142
H(22A)	9464	1021	5399	137
H(23A)	8604	2083	5815	84
H(23B)	9710	2401	6002	84
H(19A)	8810	1212	7744	71
H(20B)	10697	413	7343	111
H(21B)	12091	608	6272	142
H(22B)	11597	1602	5601	137

Table S36. Torsion angles [°] for 007b-20020.

O(2)-S(1)-C(24)-C(25)	93.2(4)
O(3)-S(1)-C(24)-C(25)	-145.4(4)
O(1)-S(1)-C(24)-C(25)	-27.1(5)
O(2)-S(1)-C(24)-C(29)	-97.3(4)
O(3)-S(1)-C(24)-C(29)	24.1(5)
O(1)-S(1)-C(24)-C(29)	142.3(4)
C(29)-C(24)-C(25)-C(26)	-2.7(7)
S(1)-C(24)-C(25)-C(26)	167.5(4)
C(29)-C(24)-C(25)-N(3)	176.6(4)
S(1)-C(24)-C(25)-N(3)	-13.2(7)
O(5)-N(3)-C(25)-C(26)	-46.8(6)

O(4)-N(3)-C(25)-C(26)	130.0(5)
O(5)-N(3)-C(25)-C(24)	133.8(5)
O(4)-N(3)-C(25)-C(24)	-49.4(7)
C(24)-C(25)-C(26)-C(27)	0.6(8)
N(3)-C(25)-C(26)-C(27)	-178.7(4)
C(25)-C(26)-C(27)-C(28)	1.3(7)
C(25)-C(26)-C(27)-N(4)	-179.4(4)
O(7)-N(4)-C(27)-C(28)	13.2(7)
O(6)-N(4)-C(27)-C(28)	-167.0(4)
O(7)-N(4)-C(27)-C(26)	-166.2(5)
O(6)-N(4)-C(27)-C(26)	13.7(7)
C(26)-C(27)-C(28)-C(29)	-0.8(7)
N(4)-C(27)-C(28)-C(29)	179.8(4)
C(25)-C(24)-C(29)-C(28)	3.3(7)
S(1)-C(24)-C(29)-C(28)	-167.3(4)
C(25)-C(24)-C(29)-N(5)	-175.3(4)
S(1)-C(24)-C(29)-N(5)	14.2(6)
C(27)-C(28)-C(29)-C(24)	-1.7(7)
C(27)-C(28)-C(29)-N(5)	177.0(4)
O(9)-N(5)-C(29)-C(24)	-124.8(5)
O(8)-N(5)-C(29)-C(24)	59.0(6)
O(9)-N(5)-C(29)-C(28)	56.5(6)
O(8)-N(5)-C(29)-C(28)	-119.7(5)
C(18)-N(1)-C(1)-C(2)	-154.5(6)
C(5)-N(1)-C(1)-C(2)	-24.8(7)
C(18)-N(1)-C(1)-C(13)	85.1(8)
C(5)-N(1)-C(1)-C(13)	-145.1(7)
N(1)-C(1)-C(2)-C(3)	58.1(8)
C(13)-C(1)-C(2)-C(3)	176.9(7)
N(1)-C(1)-C(2)-C(15B)	-170.3(7)
C(13)-C(1)-C(2)-C(15B)	-51.5(10)
N(1)-C(1)-C(2)-C(15A)	167(2)
C(13)-C(1)-C(2)-C(15A)	-74(2)
C(1)-C(2)-C(3)-C(4)	-26.4(9)
C(15B)-C(2)-C(3)-C(4)	-156.1(7)

C(15A)-C(2)-C(3)-C(4)	-152.0(18)
C(1)-C(2)-C(3)-C(17)	-152.5(7)
C(15B)-C(2)-C(3)-C(17)	77.8(9)
C(15A)-C(2)-C(3)-C(17)	81.9(19)
C(2)-C(3)-C(4)-C(5)	-36.0(9)
C(17)-C(3)-C(4)-C(5)	91.1(8)
C(3)-C(4)-C(5)-C(6)	-165.6(6)
C(3)-C(4)-C(5)-N(1)	68.7(7)
C(18)-N(1)-C(5)-C(4)	95.2(6)
C(1)-N(1)-C(5)-C(4)	-35.7(7)
C(18)-N(1)-C(5)-C(6)	-34.0(6)
C(1)-N(1)-C(5)-C(6)	-164.9(5)
C(4)-C(5)-C(6)-C(7)	147.7(6)
N(1)-C(5)-C(6)-C(7)	-87.1(7)
C(4)-C(5)-C(6)-C(11)	-34.1(9)
N(1)-C(5)-C(6)-C(11)	91.1(7)
C(11)-C(6)-C(7)-C(8)	-0.6(10)
C(5)-C(6)-C(7)-C(8)	177.7(6)
C(6)-C(7)-C(8)-C(9)	-0.4(11)
C(7)-C(8)-C(9)-C(10)	0.5(12)
C(7)-C(8)-C(9)-C(12)	178.8(7)
C(8)-C(9)-C(10)-C(11)	0.4(12)
C(12)-C(9)-C(10)-C(11)	-177.9(7)
C(9)-C(10)-C(11)-C(6)	-1.4(12)
C(7)-C(6)-C(11)-C(10)	1.5(11)
C(5)-C(6)-C(11)-C(10)	-176.7(7)
C(2)-C(1)-C(13)-C(14)	-176.6(11)
N(1)-C(1)-C(13)-C(14)	-55.4(13)
C(1)-C(2)-C(15B)-C(16B)	-53.1(13)
C(3)-C(2)-C(15B)-C(16B)	77.8(12)
C(18)-C(19B)-C(20A)-C(21A)	-0.3(16)
C(19B)-C(20A)-C(21A)-C(22A)	-1(2)
C(20A)-C(21A)-C(22A)-C(23A)	1(2)
C(21A)-C(22A)-C(23A)-C(18)	-1.2(17)
C(22B)-C(23B)-C(18)-C(19A)	0.0

C(22B)-C(23B)-C(18)-N(1)	164.0(19)
C(20A)-C(19B)-C(18)-C(23A)	0.6(12)
C(20A)-C(19B)-C(18)-N(1)	174.3(8)
C(22A)-C(23A)-C(18)-C(19B)	0.2(13)
C(22A)-C(23A)-C(18)-N(1)	-173.8(9)
C(1)-N(1)-C(18)-C(23B)	-99(2)
C(5)-N(1)-C(18)-C(23B)	131(2)
C(1)-N(1)-C(18)-C(19A)	63(3)
C(5)-N(1)-C(18)-C(19A)	-66(3)
C(1)-N(1)-C(18)-C(19B)	47.1(8)
C(5)-N(1)-C(18)-C(19B)	-82.6(7)
C(1)-N(1)-C(18)-C(23A)	-138.9(7)
C(5)-N(1)-C(18)-C(23A)	91.4(7)
C(23B)-C(18)-C(19A)-C(20B)	0.0
N(1)-C(18)-C(19A)-C(20B)	-161(2)
C(18)-C(19A)-C(20B)-C(21B)	0.0
C(19A)-C(20B)-C(21B)-C(22B)	0.0
C(20B)-C(21B)-C(22B)-C(23B)	0.0
C(18)-C(23B)-C(22B)-C(21B)	0.0

Symmetry transformations used to generate equivalent atoms:

Table S37. Hydrogen bonds for 007b-20020 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)	1.00	1.93	2.911(6)	167.4

Symmetry transformations used to generate equivalent atoms:

Product 2z

Crystal Growth
2z (10 mg) and picrylsulfonic acid dihydrate (0.9 equiv) were dissolved in a mixture of toluene (0.25 mL) and DCM (0.25 mL) in a 1-dram vial. Methanol was added dropwise addition until complete dissolution occurred. A few drops of hexanes were added until the cloud point was reached. Single crystals suitable for X-ray diffraction grew at room temperature over 3-5 days.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007c-20017. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H1, which was found in the difference map and freely refined. The toluene crystallized near the inversion center. The best refinement was obtained by suppressing the special position constraints and placing a whole model of toluene near the observed electron density (see Guzei, I. A. (2014). J. Appl. Crystallogr. 47, 806-809). The model was then allowed to freely refine at half occupancy. The full numbering scheme of compound 007c-20017 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1989520 (007c-20017) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

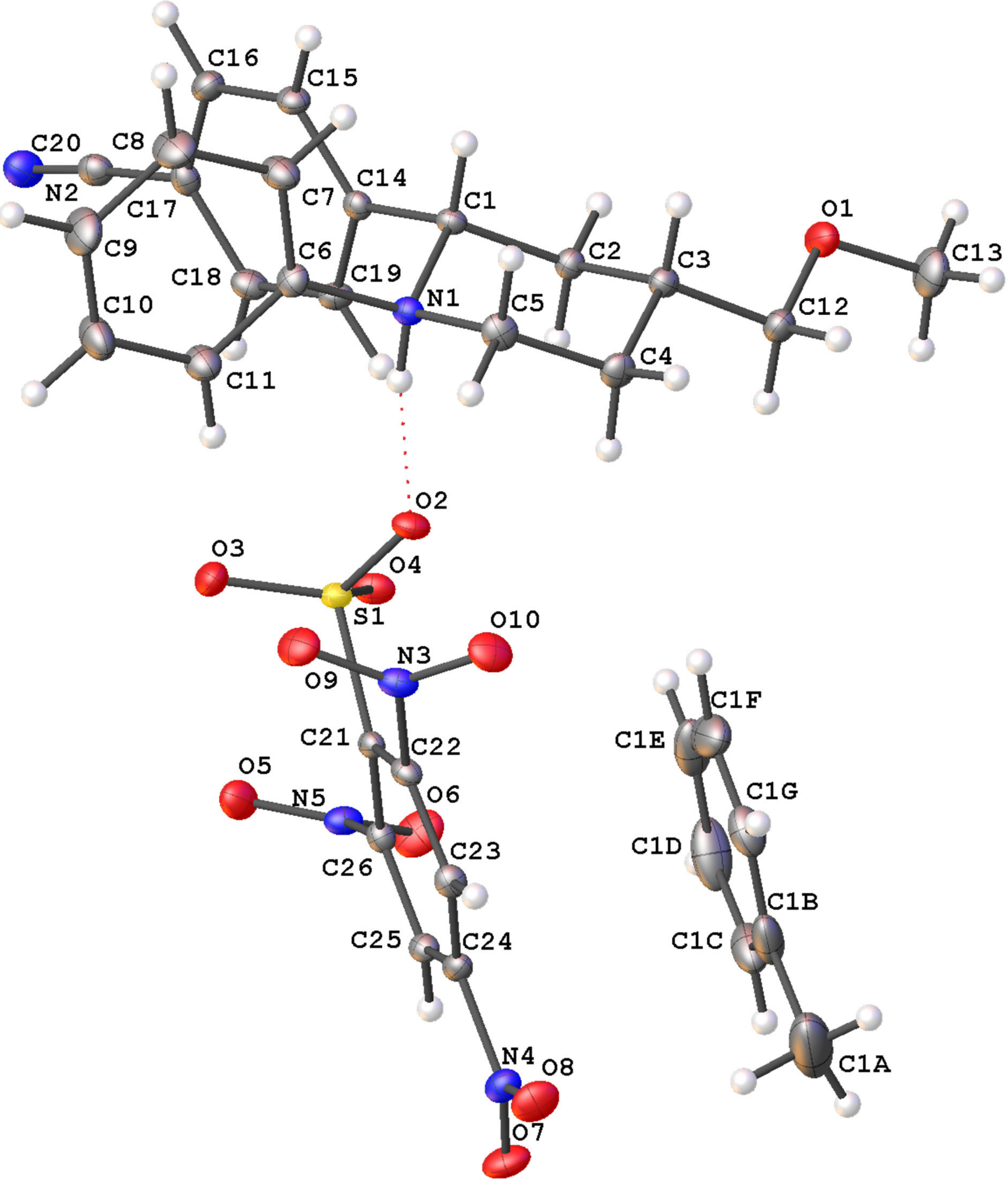


Figure S14. The complete numbering scheme of 007c-20017 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S38. Crystal data and structure refinement for 007c-20017.

Identification code	007c-20017	
Empirical formula	C29.50 H29 N5 O10 S	
Formula weight	645.64	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9495(3) Å	α= 81.734(2)°.
	b = 9.6147(3) Å	β= 86.081(2)°.
	c = 18.2756(5) Å	γ = 75.200(3)°.
Volume	1503.77(8) Å3	
Z	2	
Density (calculated)	1.426 Mg/m3	
Absorption coefficient	0.175 mm-1	
F(000)	674	
Crystal size	0.200 x 0.200 x 0.040 mm3	
Crystal color and habit	Colorless Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.943 to 27.482°.	
Index ranges	-10<=h<=11, -12<=k<=12, -23<=l<=23	
Reflections collected	35175	
Independent reflections	6892 [R(int) = 0.0248]	
Observed reflections (I > 2sigma(I))	6140	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.55232	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	6892 / 0 / 448	
Goodness-of-fit on F2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0813	
R indices (all data)	R1 = 0.0361, wR2 = 0.0837	
Largest diff. peak and hole	0.387 and -0.432 e.Å-3	

Table S39. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for 007c-20017. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	6086(1)	4451(1)	3281(1)	12(1)
O(2)	7665(1)	4521(1)	3040(1)	16(1)
N(3)	8332(1)	5136(1)	4341(1)	15(1)
O(3)	4997(1)	5846(1)	3226(1)	20(1)
O(4)	5601(1)	3337(1)	2978(1)	18(1)
N(4)	7300(1)	1755(1)	6460(1)	16(1)
N(5)	4275(1)	2445(1)	4261(1)	15(1)
O(5)	3129(1)	3426(1)	4102(1)	21(1)
O(6)	4449(1)	1177(1)	4172(1)	26(1)
O(7)	6527(1)	923(1)	6736(1)	22(1)
O(8)	8337(1)	2038(1)	6770(1)	23(1)
O(9)	7612(1)	6401(1)	4187(1)	22(1)
O(10)	9736(1)	4681(1)	4268(1)	22(1)
C(21)	6316(1)	3793(1)	4256(1)	11(1)
C(22)	7439(1)	4082(1)	4664(1)	13(1)
C(23)	7798(1)	3432(1)	5378(1)	14(1)
C(24)	6965(1)	2465(1)	5698(1)	13(1)
C(25)	5826(1)	2124(1)	5336(1)	12(1)
C(26)	5527(1)	2809(1)	4624(1)	12(1)
O(1)	12316(1)	1287(1)	1213(1)	20(1)
N(1)	9138(1)	6136(1)	2020(1)	12(1)
C(1)	9196(1)	5494(1)	1296(1)	11(1)
C(2)	9911(1)	3857(1)	1437(1)	13(1)
N(2)	1771(1)	7080(1)	63(1)	20(1)
C(3)	11527(1)	3489(1)	1749(1)	13(1)
C(4)	11449(1)	4162(1)	2465(1)	16(1)
C(5)	10727(1)	5783(1)	2349(1)	16(1)
C(6)	8447(1)	7723(1)	1957(1)	14(1)
C(7)	9089(2)	8650(1)	1451(1)	20(1)
C(8)	8493(2)	10140(1)	1433(1)	25(1)
C(9)	7284(2)	10678(1)	1916(1)	27(1)

C(10)	6653(2)	9733(1)	2413(1)	26(1)
C(11)	7232(2)	8235(1)	2436(1)	19(1)
C(12)	12196(1)	1861(1)	1894(1)	17(1)
C(13)	12952(2)	-236(1)	1296(1)	28(1)
C(14)	7581(1)	5861(1)	999(1)	12(1)
C(15)	7188(1)	6851(1)	363(1)	14(1)
C(16)	5706(1)	7172(1)	92(1)	16(1)
C(17)	4606(1)	6514(1)	470(1)	14(1)
C(18)	4991(1)	5517(1)	1107(1)	15(1)
C(19)	6479(1)	5186(1)	1359(1)	14(1)
C(20)	3039(1)	6840(1)	223(1)	16(1)
C(1A)	11096(5)	-626(5)	6365(2)	60(1)
C(1B)	10444(7)	-254(8)	5588(3)	29(1)
C(1C)	9346(10)	-886(9)	5383(4)	31(2)
C(1D)	8771(12)	-544(11)	4689(5)	39(2)
C(1E)	9302(8)	412(8)	4180(3)	34(1)
C(1F)	10426(13)	1054(11)	4371(4)	32(2)
C(1G)	10974(9)	738(10)	5071(4)	26(2)

Table S40. Bond lengths [Å] and angles [°] for 007c-20017.

S(1)-O(3)	1.4378(9)
S(1)-O(4)	1.4431(8)
S(1)-O(2)	1.4659(9)
S(1)-C(21)	1.8089(11)
N(3)-O(9)	1.2247(13)
N(3)-O(10)	1.2255(13)
N(3)-C(22)	1.4798(14)
N(4)-O(7)	1.2215(13)
N(4)-O(8)	1.2253(13)
N(4)-C(24)	1.4744(14)
N(5)-O(6)	1.2217(13)
N(5)-O(5)	1.2228(13)

N(5)-C(26)	1.4783(14)
C(21)-C(26)	1.3932(15)
C(21)-C(22)	1.3960(15)
C(22)-C(23)	1.3842(15)
C(23)-C(24)	1.3796(16)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3813(16)
C(25)-C(26)	1.3823(15)
C(25)-H(25)	0.9500
O(1)-C(13)	1.4191(14)
O(1)-C(12)	1.4196(14)
N(1)-C(6)	1.4829(14)
N(1)-C(5)	1.5204(14)
N(1)-C(1)	1.5314(13)
N(1)-H(1)	0.895(16)
C(1)-C(14)	1.5165(15)
C(1)-C(2)	1.5310(14)
C(1)-H(1A)	1.0000
C(2)-C(3)	1.5286(15)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
N(2)-C(20)	1.1482(16)
C(3)-C(12)	1.5174(15)
C(3)-C(4)	1.5311(15)
C(3)-H(3)	1.0000
C(4)-C(5)	1.5165(16)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(11)	1.3828(17)
C(6)-C(7)	1.3904(16)
C(7)-C(8)	1.3910(17)
C(7)-H(7)	0.9500
C(8)-C(9)	1.391(2)

C(8)-H(8)	0.9500
C(9)-C(10)	1.3872(19)
C(9)-H(9)	0.9500
C(10)-C(11)	1.3964(17)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(19)	1.3938(16)
C(14)-C(15)	1.3950(15)
C(15)-C(16)	1.3917(16)
C(15)-H(15)	0.9500
C(16)-C(17)	1.3948(16)
C(16)-H(16)	0.9500
C(17)-C(18)	1.3986(16)
C(17)-C(20)	1.4456(16)
C(18)-C(19)	1.3827(16)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(1A)-C(1B)	1.531(6)
C(1A)-H(1AA)	0.9800
C(1A)-H(1AB)	0.9800
C(1A)-H(1AC)	0.9800
C(1B)-C(1C)	1.378(13)
C(1B)-C(1G)	1.392(14)
C(1C)-C(1D)	1.364(7)
C(1C)-H(1C)	0.9500
C(1D)-C(1E)	1.362(16)
C(1D)-H(1D)	0.9500
C(1E)-C(1F)	1.394(16)
C(1E)-H(1E)	0.9500
C(1F)-C(1G)	1.366(6)

C(1F)-H(1F)	0.9500
C(1G)-H(1G)	0.9500
O(3)-S(1)-O(4)	115.44(5)
O(3)-S(1)-O(2)	113.53(5)
O(4)-S(1)-O(2)	112.63(5)
O(3)-S(1)-C(21)	107.16(5)
O(4)-S(1)-C(21)	104.82(5)
O(2)-S(1)-C(21)	101.70(5)
O(9)-N(3)-O(10)	125.24(10)
O(9)-N(3)-C(22)	117.33(10)
O(10)-N(3)-C(22)	117.41(10)
O(7)-N(4)-O(8)	124.71(10)
O(7)-N(4)-C(24)	117.65(10)
O(8)-N(4)-C(24)	117.65(10)
O(6)-N(5)-O(5)	125.52(10)
O(6)-N(5)-C(26)	117.17(9)
O(5)-N(5)-C(26)	117.24(9)
C(26)-C(21)-C(22)	115.19(10)
C(26)-C(21)-S(1)	122.05(8)
C(22)-C(21)-S(1)	122.23(8)
C(23)-C(22)-C(21)	123.82(10)
C(23)-C(22)-N(3)	115.70(10)
C(21)-C(22)-N(3)	120.47(10)
C(24)-C(23)-C(22)	117.06(10)
C(24)-C(23)-H(23)	121.5
C(22)-C(23)-H(23)	121.5
C(23)-C(24)-C(25)	122.90(10)
C(23)-C(24)-N(4)	118.93(10)
C(25)-C(24)-N(4)	118.17(10)
C(24)-C(25)-C(26)	117.12(10)
C(24)-C(25)-H(25)	121.4
C(26)-C(25)-H(25)	121.4
C(25)-C(26)-C(21)	123.89(10)
C(25)-C(26)-N(5)	115.57(10)

C(21)-C(26)-N(5)	120.53(9)
C(13)-O(1)-C(12)	112.25(9)
C(6)-N(1)-C(5)	109.66(8)
C(6)-N(1)-C(1)	114.12(8)
C(5)-N(1)-C(1)	111.58(8)
C(6)-N(1)-H(1)	107.9(9)
C(5)-N(1)-H(1)	106.4(9)
C(1)-N(1)-H(1)	106.8(9)
C(14)-C(1)-C(2)	112.65(9)
C(14)-C(1)-N(1)	109.30(8)
C(2)-C(1)-N(1)	108.98(8)
C(14)-C(1)-H(1A)	108.6
C(2)-C(1)-H(1A)	108.6
N(1)-C(1)-H(1A)	108.6
C(3)-C(2)-C(1)	112.56(9)
C(3)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2A)	109.1
C(3)-C(2)-H(2B)	109.1
C(1)-C(2)-H(2B)	109.1
H(2A)-C(2)-H(2B)	107.8
C(12)-C(3)-C(2)	111.40(9)
C(12)-C(3)-C(4)	110.13(9)
C(2)-C(3)-C(4)	109.36(9)
C(12)-C(3)-H(3)	108.6
C(2)-C(3)-H(3)	108.6
C(4)-C(3)-H(3)	108.6
C(5)-C(4)-C(3)	111.70(9)
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4B)	109.3
C(3)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	107.9
C(4)-C(5)-N(1)	111.78(9)
C(4)-C(5)-H(5A)	109.3
N(1)-C(5)-H(5A)	109.3

C(4)-C(5)-H(5B)	109.3
N(1)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	107.9
C(11)-C(6)-C(7)	122.08(11)
C(11)-C(6)-N(1)	118.45(10)
C(7)-C(6)-N(1)	119.37(10)
C(6)-C(7)-C(8)	118.66(11)
C(6)-C(7)-H(7)	120.7
C(8)-C(7)-H(7)	120.7
C(9)-C(8)-C(7)	120.18(12)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.24(12)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	120.32(12)
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-H(10)	119.8
C(6)-C(11)-C(10)	118.52(11)
C(6)-C(11)-H(11)	120.7
C(10)-C(11)-H(11)	120.7
O(1)-C(12)-C(3)	108.44(9)
O(1)-C(12)-H(12A)	110.0
C(3)-C(12)-H(12A)	110.0
O(1)-C(12)-H(12B)	110.0
C(3)-C(12)-H(12B)	110.0
H(12A)-C(12)-H(12B)	108.4
O(1)-C(13)-H(13A)	109.5
O(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	119.44(10)
C(19)-C(14)-C(1)	119.64(10)

C(15)-C(14)-C(1)	120.91(10)
C(16)-C(15)-C(14)	120.40(11)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	119.39(10)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
C(16)-C(17)-C(18)	120.57(10)
C(16)-C(17)-C(20)	121.53(10)
C(18)-C(17)-C(20)	117.90(10)
C(19)-C(18)-C(17)	119.29(11)
C(19)-C(18)-H(18)	120.4
C(17)-C(18)-H(18)	120.4
C(18)-C(19)-C(14)	120.86(10)
C(18)-C(19)-H(19)	119.6
C(14)-C(19)-H(19)	119.6
N(2)-C(20)-C(17)	176.56(12)
C(1B)-C(1A)-H(1AA)	109.5
C(1B)-C(1A)-H(1AB)	109.5
H(1AA)-C(1A)-H(1AB)	109.5
C(1B)-C(1A)-H(1AC)	109.5
H(1AA)-C(1A)-H(1AC)	109.5
H(1AB)-C(1A)-H(1AC)	109.5
C(1C)-C(1B)-C(1G)	118.7(5)
C(1C)-C(1B)-C(1A)	121.6(6)
C(1G)-C(1B)-C(1A)	119.7(6)
C(1D)-C(1C)-C(1B)	121.1(7)
C(1D)-C(1C)-H(1C)	119.5
C(1B)-C(1C)-H(1C)	119.5
C(1E)-C(1D)-C(1C)	120.3(9)
C(1E)-C(1D)-H(1D)	119.8
C(1C)-C(1D)-H(1D)	119.8
C(1D)-C(1E)-C(1F)	119.7(5)
C(1D)-C(1E)-H(1E)	120.1
C(1F)-C(1E)-H(1E)	120.1

C(1G)-C(1F)-C(1E)	119.9(8)
C(1G)-C(1F)-H(1F)	120.0
C(1E)-C(1F)-H(1F)	120.0
C(1F)-C(1G)-C(1B)	120.2(7)
C(1F)-C(1G)-H(1G)	119.9
C(1B)-C(1G)-H(1G)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S41. Anisotropic displacement parameters (Å2x 103) for 007c-20017. The anisotropic displacement factor exponent takes the form: -2π2[h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	14(1)	12(1)	10(1)	-1(1)	1(1)	-4(1)
O(2)	17(1)	20(1)	12(1)	-1(1)	3(1)	-7(1)
N(3)	18(1)	18(1)	12(1)	-4(1)	1(1)	-10(1)
O(3)	22(1)	16(1)	18(1)	1(1)	1(1)	0(1)
O(4)	23(1)	21(1)	12(1)	-4(1)	0(1)	-10(1)
N(4)	21(1)	14(1)	14(1)	-1(1)	-3(1)	-5(1)
N(5)	17(1)	18(1)	12(1)	-1(1)	-1(1)	-9(1)
O(5)	14(1)	28(1)	20(1)	-3(1)	-3(1)	-4(1)
O(6)	36(1)	18(1)	30(1)	-2(1)	-9(1)	-15(1)
O(7)	32(1)	20(1)	18(1)	4(1)	-3(1)	-13(1)

O(8)	28(1)	26(1)	19(1)	-1(1)	-9(1)	-11(1)
O(9)	29(1)	14(1)	24(1)	-1(1)	2(1)	-10(1)
O(10)	15(1)	29(1)	24(1)	-3(1)	1(1)	-12(1)
C(21)	12(1)	10(1)	11(1)	-2(1)	1(1)	-2(1)
C(22)	13(1)	12(1)	14(1)	-3(1)	3(1)	-5(1)
C(23)	14(1)	15(1)	14(1)	-4(1)	-1(1)	-4(1)
C(24)	16(1)	12(1)	11(1)	-2(1)	0(1)	-2(1)
C(25)	14(1)	10(1)	13(1)	-2(1)	1(1)	-4(1)
C(26)	12(1)	12(1)	13(1)	-4(1)	0(1)	-3(1)
O(1)	28(1)	13(1)	17(1)	-3(1)	2(1)	-1(1)
N(1)	14(1)	11(1)	11(1)	-3(1)	1(1)	-5(1)
C(1)	13(1)	12(1)	10(1)	-2(1)	1(1)	-5(1)
C(2)	13(1)	12(1)	13(1)	-2(1)	-1(1)	-3(1)
N(2)	18(1)	25(1)	18(1)	-3(1)	-2(1)	-6(1)
C(3)	13(1)	14(1)	13(1)	-2(1)	-1(1)	-3(1)
C(4)	18(1)	18(1)	14(1)	-3(1)	-4(1)	-4(1)
C(5)	16(1)	19(1)	17(1)	-6(1)	-3(1)	-6(1)
C(6)	17(1)	11(1)	16(1)	-3(1)	-1(1)	

						-5(1)
C(7)	23(1)	16(1)	20(1)	-4(1)	6(1)	-8(1)
C(8)	32(1)	15(1)	28(1)	0(1)	6(1)	-10(1)
C(9)	31(1)	12(1)	38(1)	-4(1)	4(1)	-4(1)
C(10)	25(1)	18(1)	33(1)	-7(1)	9(1)	-3(1)
C(11)	21(1)	16(1)	22(1)	-2(1)	4(1)	-7(1)
C(12)	19(1)	16(1)	15(1)	-1(1)	-2(1)	-1(1)
C(13)	32(1)	15(1)	34(1)	-7(1)	-3(1)	0(1)
C(14)	13(1)	12(1)	11(1)	-4(1)	0(1)	-3(1)
C(15)	16(1)	14(1)	14(1)	-1(1)	2(1)	-5(1)
C(16)	18(1)	14(1)	13(1)	-1(1)	-2(1)	-3(1)
C(17)	13(1)	15(1)	14(1)	-6(1)	0(1)	-2(1)
C(18)	16(1)	18(1)	14(1)	-3(1)	2(1)	-8(1)
C(19)	17(1)	16(1)	11(1)	-1(1)	0(1)	-6(1)
C(20)	19(1)	16(1)	13(1)	-4(1)	0(1)	-5(1)
C(1A)	50(2)	71(3)	39(2)	-17(2)	-9(2)	27(2)
C(1B)	21(2)	35(2)	26(3)	-13(2)	-5(2)	9(2)
C(1C)	24(3)	19(3)	47(6)	-3(4)	11(4)	-5(2)

C(1D)	18(3)	35(4)	70(7)	-25(4)	-7(3)	-4(2)
C(1E)	29(3)	40(3)	29(3)	-17(3)	-14(2)	11(2)
C(1F)	40(4)	17(2)	32(4)	-1(2)	8(3)	0(2)
C(1G)	18(4)	25(3)	37(4)	-11(3)	3(3)	-5(2)

Table S42. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for 007c-20017.

	x	y	z	U(eq)
H(23)	8583	3644	5635	17
H(25)	5272	1449	5567	15
H(1A)	9872	5943	927	14
H(2A)	9229	3401	1789	15
H(2B)	9971	3444	966	15
H(3)	12219	3917	1381	16
H(4A)	10832	3691	2846	20
H(4B)	12506	3981	2648	20
H(5A)	11412	6268	2014	20
H(5B)	10634	6166	2829	20
H(7)	9918	8274	1124	23
H(8)	8913	10791	1089	30
H(9)	6889	11696	1906	33
H(10)	5823	10108	2740	31
H(11)	6801	7582	2774	23
H(12A)	13229	1648	2108	20
H(12B)	11515	1412	2250	20
H(13A)	12967	-592	818	41
H(13B)	12318	-711	1657	41
H(13C)	14009	-458	1470	41

H(15)	7937	7309	113	17
H(16)	5445	7832	-346	19
H(18)	4239	5072	1363	18
H(19)	6754	4489	1783	17
H(1)	8552(17)	5700(16)	2344(8)	18(4)
H(1AA)	10589	141	6665	90
H(1AB)	12211	-706	6331	90
H(1AC)	10904	-1552	6597	90
H(1C)	8982	-1571	5729	37
H(1D)	7998	-975	4561	47
H(1E)	8907	641	3696	41
H(1F)	10811	1710	4016	38
H(1G)	11718	1197	5205	31

Table S43. Torsion angles [°] for 007c-20017.

O(3)-S(1)-C(21)-C(26)	98.48(10)
O(4)-S(1)-C(21)-C(26)	-24.67(10)
O(2)-S(1)-C(21)-C(26)	-142.14(9)
O(3)-S(1)-C(21)-C(22)	-90.31(10)
O(4)-S(1)-C(21)-C(22)	146.54(9)
O(2)-S(1)-C(21)-C(22)	29.07(10)
C(26)-C(21)-C(22)-C(23)	1.39(16)
S(1)-C(21)-C(22)-C(23)	-170.38(9)
C(26)-C(21)-C(22)-N(3)	-178.52(9)
S(1)-C(21)-C(22)-N(3)	9.71(14)
O(9)-N(3)-C(22)-C(23)	-116.48(11)
O(10)-N(3)-C(22)-C(23)	61.73(13)
O(9)-N(3)-C(22)-C(21)	63.44(14)
O(10)-N(3)-C(22)-C(21)	-118.35(12)
C(21)-C(22)-C(23)-C(24)	-1.10(17)
N(3)-C(22)-C(23)-C(24)	178.81(10)
C(22)-C(23)-C(24)-C(25)	0.60(17)

C(22)-C(23)-C(24)-N(4)	-179.56(10)
O(7)-N(4)-C(24)-C(23)	178.69(10)
O(8)-N(4)-C(24)-C(23)	-1.56(15)
O(7)-N(4)-C(24)-C(25)	-1.46(15)
O(8)-N(4)-C(24)-C(25)	178.30(10)
C(23)-C(24)-C(25)-C(26)	-0.46(16)
N(4)-C(24)-C(25)-C(26)	179.69(9)
C(24)-C(25)-C(26)-C(21)	0.81(16)
C(24)-C(25)-C(26)-N(5)	-178.55(9)
C(22)-C(21)-C(26)-C(25)	-1.24(16)
S(1)-C(21)-C(26)-C(25)	170.55(9)
C(22)-C(21)-C(26)-N(5)	178.09(9)
S(1)-C(21)-C(26)-N(5)	-10.12(14)
O(6)-N(5)-C(26)-C(25)	-61.18(13)
O(5)-N(5)-C(26)-C(25)	116.14(11)
O(6)-N(5)-C(26)-C(21)	119.43(12)
O(5)-N(5)-C(26)-C(21)	-63.25(14)
C(6)-N(1)-C(1)-C(14)	-55.78(12)
C(5)-N(1)-C(1)-C(14)	179.22(9)
C(6)-N(1)-C(1)-C(2)	-179.28(9)
C(5)-N(1)-C(1)-C(2)	55.72(11)
C(14)-C(1)-C(2)-C(3)	-178.96(9)
N(1)-C(1)-C(2)-C(3)	-57.48(11)
C(1)-C(2)-C(3)-C(12)	179.15(9)
C(1)-C(2)-C(3)-C(4)	57.18(12)
C(12)-C(3)-C(4)-C(5)	-177.78(10)
C(2)-C(3)-C(4)-C(5)	-55.05(12)
C(3)-C(4)-C(5)-N(1)	55.25(13)
C(6)-N(1)-C(5)-C(4)	176.84(9)
C(1)-N(1)-C(5)-C(4)	-55.71(12)
C(5)-N(1)-C(6)-C(11)	-107.93(12)
C(1)-N(1)-C(6)-C(11)	126.05(11)
C(5)-N(1)-C(6)-C(7)	68.47(13)
C(1)-N(1)-C(6)-C(7)	-57.54(14)
C(11)-C(6)-C(7)-C(8)	0.50(19)

N(1)-C(6)-C(7)-C(8)	-175.77(11)
C(6)-C(7)-C(8)-C(9)	0.3(2)
C(7)-C(8)-C(9)-C(10)	-0.8(2)
C(8)-C(9)-C(10)-C(11)	0.4(2)
C(7)-C(6)-C(11)-C(10)	-0.83(19)
N(1)-C(6)-C(11)-C(10)	175.47(11)
C(9)-C(10)-C(11)-C(6)	0.4(2)
C(13)-O(1)-C(12)-C(3)	179.34(10)
C(2)-C(3)-C(12)-O(1)	61.15(12)
C(4)-C(3)-C(12)-O(1)	-177.32(9)
C(2)-C(1)-C(14)-C(19)	50.17(13)
N(1)-C(1)-C(14)-C(19)	-71.13(12)
C(2)-C(1)-C(14)-C(15)	-128.86(11)
N(1)-C(1)-C(14)-C(15)	109.84(11)
C(19)-C(14)-C(15)-C(16)	0.47(16)
C(1)-C(14)-C(15)-C(16)	179.51(10)
C(14)-C(15)-C(16)-C(17)	1.17(17)
C(15)-C(16)-C(17)-C(18)	-1.36(17)
C(15)-C(16)-C(17)-C(20)	178.31(10)
C(16)-C(17)-C(18)-C(19)	-0.09(17)
C(20)-C(17)-C(18)-C(19)	-179.78(10)
C(17)-C(18)-C(19)-C(14)	1.76(17)
C(15)-C(14)-C(19)-C(18)	-1.96(16)
C(1)-C(14)-C(19)-C(18)	178.99(10)
C(1G)-C(1B)-C(1C)-C(1D)	-0.6(10)
C(1A)-C(1B)-C(1C)-C(1D)	179.9(7)
C(1B)-C(1C)-C(1D)-C(1E)	1.4(12)
C(1C)-C(1D)-C(1E)-C(1F)	-0.6(12)
C(1D)-C(1E)-C(1F)-C(1G)	-1.0(13)
C(1E)-C(1F)-C(1G)-C(1B)	1.8(12)
C(1C)-C(1B)-C(1G)-C(1F)	-1.0(9)
C(1A)-C(1B)-C(1G)-C(1F)	178.5(7)

Symmetry transformations used to generate equivalent atoms:

Table S44. Hydrogen bonds for 007c-20017 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)	0.895(16)	1.855(16)	2.7399(13)	169.5(14)

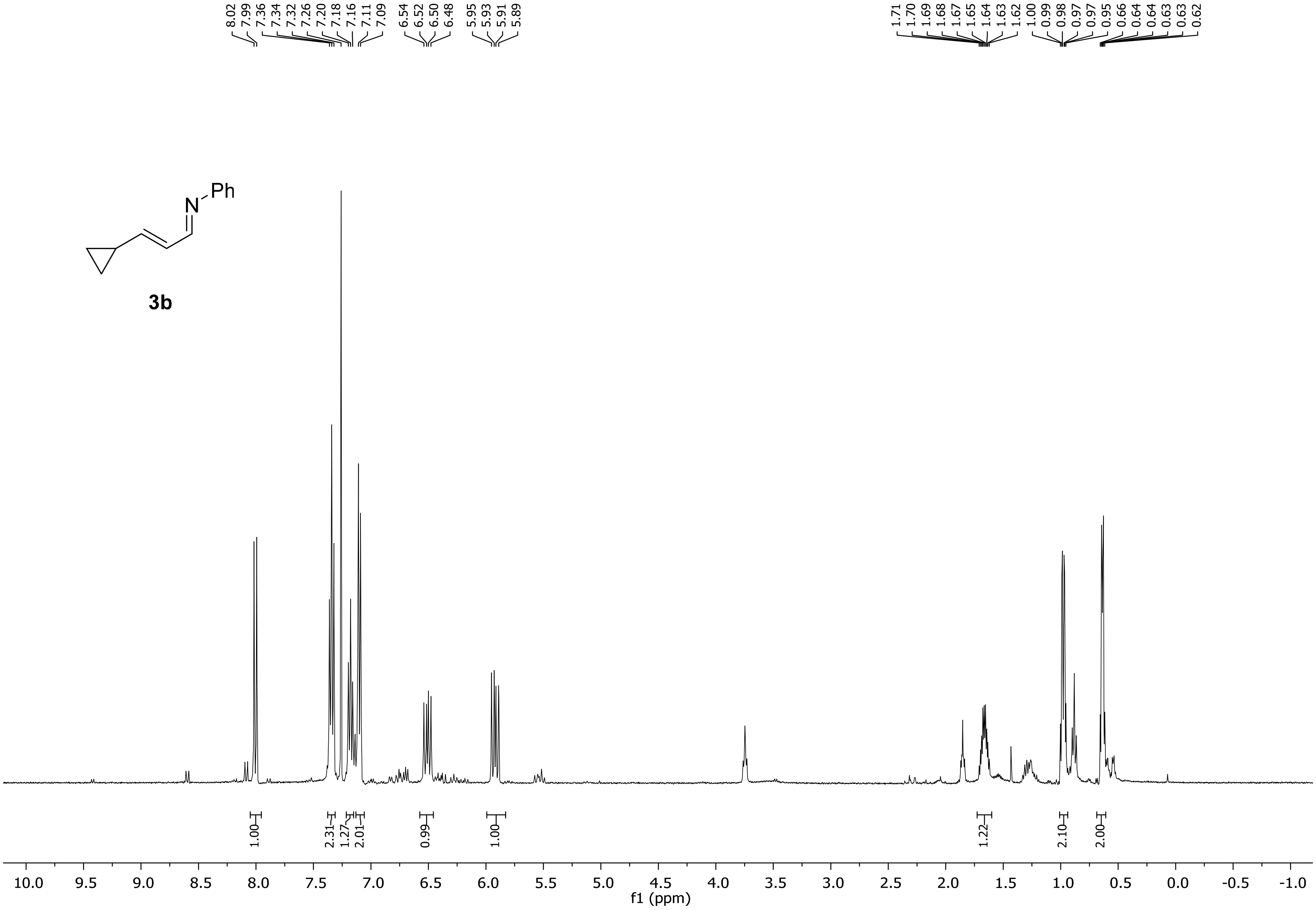
Symmetry transformations used to generate equivalent atoms:

References

1. Jiang, J.; Spies, J. A.; Swierk, J. R.; Matula, A. J.; Regan, K. P.; Romano, N.; Brennan, B. J.; Crabtree, R. H.; Batista, V. S.; Schmuttenmaer, C. A.; Brudvig, G. W. Direct Interfacial Electron Transfer from High-Potential Porphyrins into Semiconductor Surfaces: A Comparison of Linkers and Anchoring Groups. *J. Phys. Chem. C.* **2018,** *122,* 13529.
2. Hood, T. S.; Huehls, C. B.; Yang, J. A modular approach to α,β-unsaturated *N*-aryl ketonitrones. *Tetrahedron Lett.* **2012**, *53*, 4679.
3. Walker, M. M.; Chen, S.; Mercado, B. Q.; Houk, K. N.; Ellman, J. A. Formation of Aminocyclopentadienes from Silyldihydropyridines: Ring Contractions Driven by Anion Stabilization. *Angew. Chem. Int. Ed.* **2018,** *57,* 6605.
4. Niu, Z.; Zhang, W.; Lan, P. C.; Aguila, B.; Ma, S. Promoting Frustrated Lewis Pairs for Heterogeneous Chemoselective Hydrogenation via the Tailored Pore Environment within Metal–Organic Frameworks. *Angew. Chem. Int. Ed.* **2019**, *58*, 7420.
5. Feringa, B. L.; Jansen, J. F. G. A. A New Synthesis of Imines via Grignard- and Cuprate Additions to *N*-Trimethylsilylformamides. *Synthesis* **1988**, 184.
6. Lu, B.; Li, C.; Zhang, L. Gold-Catalyzed Highly Regioselective Oxidation of C−C Triple Bonds without Acid Additives: Propargyl Moieties as Masked α,β-Unsaturated Carbonyls. *J. Am. Chem. Soc.* **2010,** *132,* 14070.
7. Duttwyler, S.; Chen, S.; Takase, M. K.; Wiberg, K. B.; Bergman, R. G.; Ellman, J. A. Proton Donor Acidity Controls Selectivity in Nonaromatic Nitrogen Heterocycle Synthesis. *Science* **2013,** *339,* 678.
8. Liang, T.; Nguyen, K. D.; Zhang, W.; Krische, M. J. Enantioselective Ruthenium-Catalyzed Carbonyl Allylation via Alkyne–Alcohol C–C Bond-Forming Transfer Hydrogenation: Allene Hydrometalation vs Oxidative Coupling. *J. Am. Chem. Soc.* **2015,** *137,* 3161.
9. Maiti, D.; Fors, B. P.; Henderson, J. L.; Nakamura, Y.; Buchwald, S. L. Palladium-catalyzed coupling of functionalized primary and secondary amines with aryl and heteroaryl halides: two ligands suffice in most cases. *Chem. Sci.* **2011,** *2,* 57.
10. McNally, A.; Prier, C. K.; MacMillan, D. W. C. Discovery of an α-Amino C–H Arylation Reaction Using the Strategy of Accelerated Serendipity. *Science* **2011,** *334,* 1114.
11. Pitre, S. P.; McTiernan, C. D.; Vine, W.; DiPucchio, R.; Grenier, M.; Scaiano, J. C. Visible-Light Actinometry and Intermittent Illumination as Convenient Tools to Study Ru(bpy)$_3$Cl$_2$ Mediated Photoredox Transformations. *Sci. Rep.* **2015,** *5,* 16397.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian Inc.: Wallingford, CT, **2009**.
13. Chai, J. D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.
14. (a) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures,

and Electronic Properties of Molecules in Solution With the C-PCM Solvation Model. *J. Comput. Chem.* **2003**, *24*, 669. (c) Takano, Y.; Houk, K. N. Benchmarking the Conductor-like Polarizable Continuum Model (CPCM) for Aqueous Solvation Free Energies of Neutral and Ionic Organic Molecules. *J. Chem. Theory Comput.* **2005**, *1*, 70.

15. Bootsma, A. N.; Wheeler, S. Popular Integration Grids Can Result in Large Errors in DFT-Computed Free Energies. *ChemRxiv.* **2019**, Preprint.
16. Grimme, S., Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. Eur. J.* **2012**, *18*, 9955.
17. Legault, C. Y. CYLview, 1.0b; Université de Sherbrooke, **2009**; http://www.cylview.org.

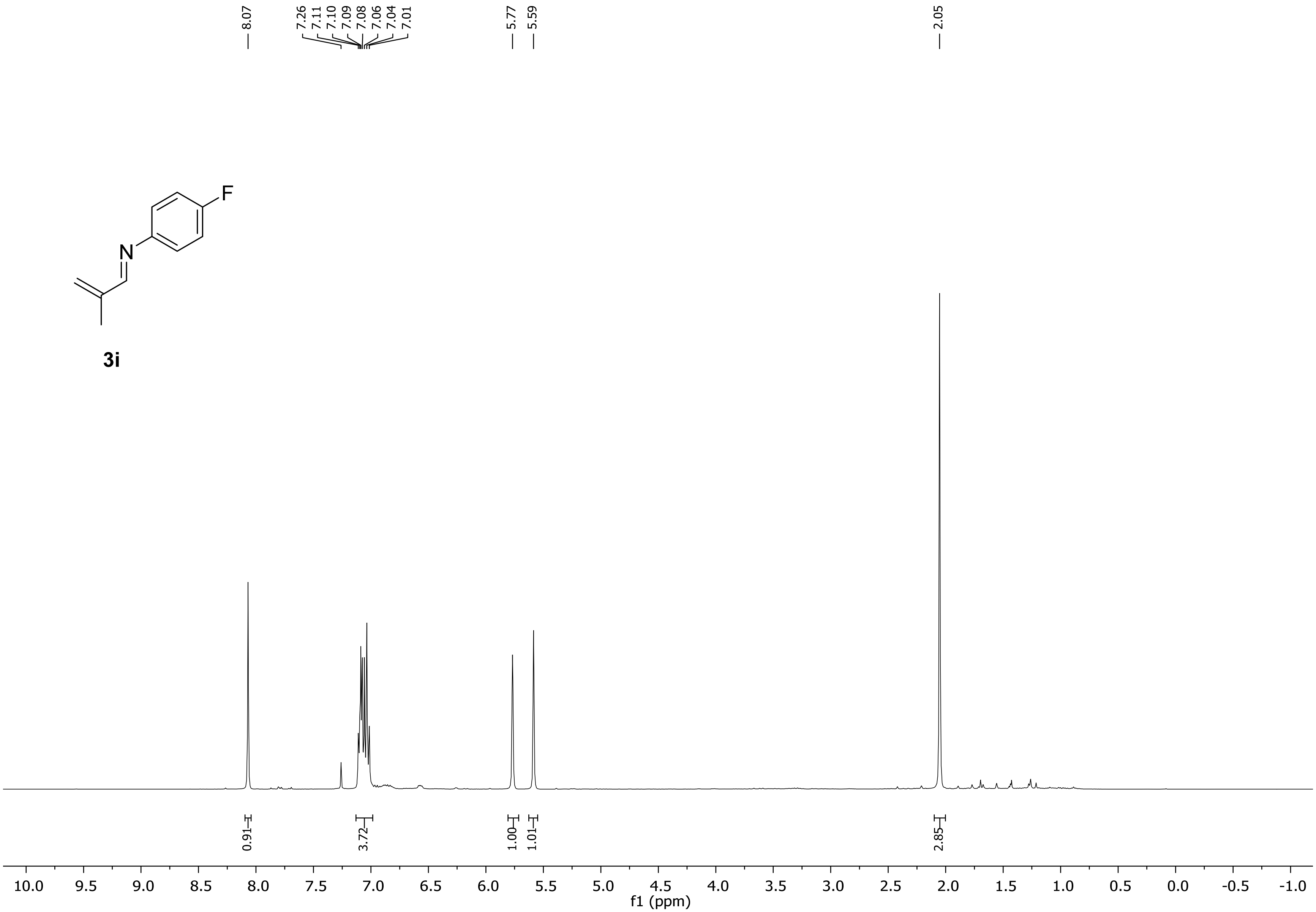

N
Ph

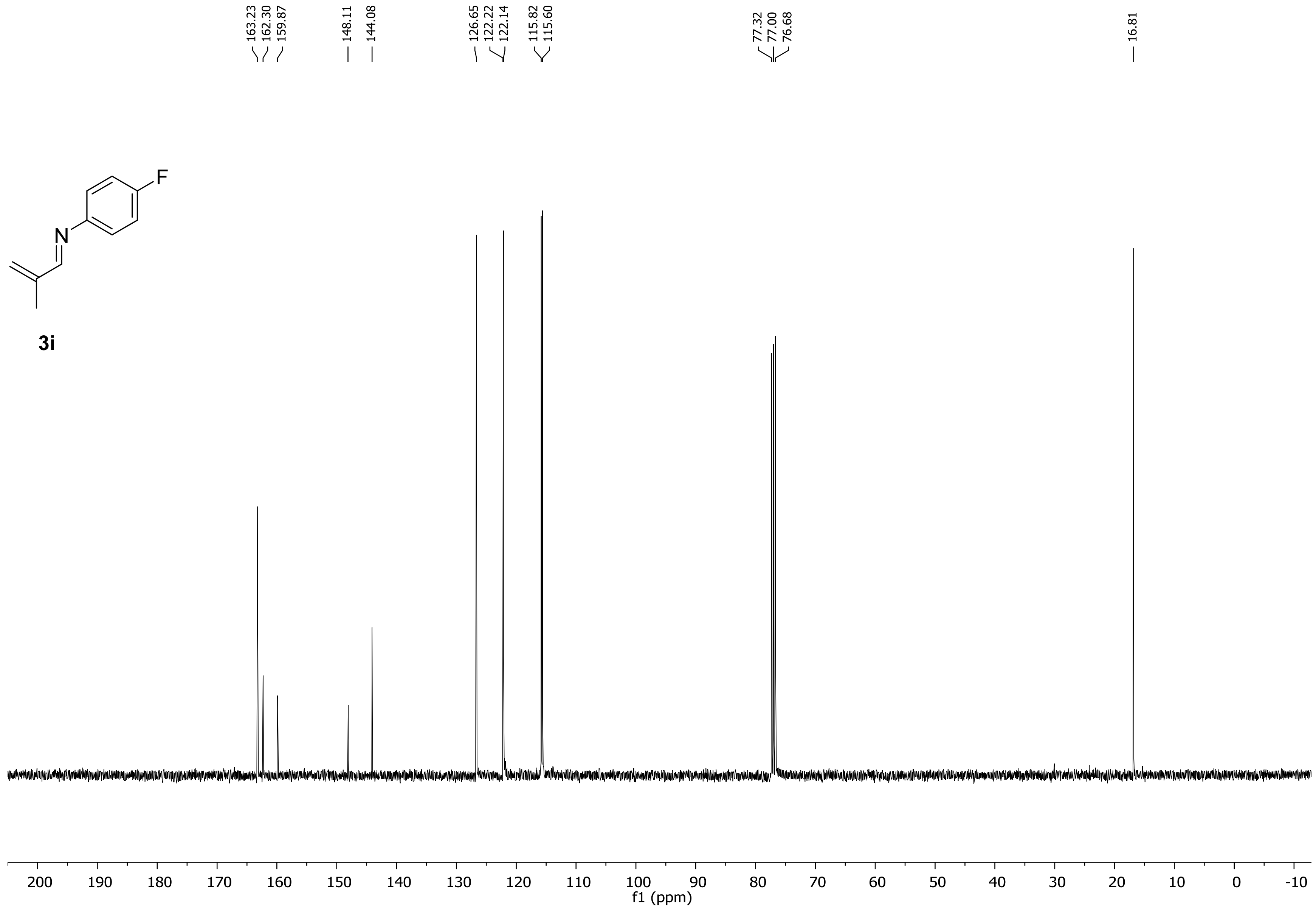
3b

8.02
7.99
7.36
7.34
7.32
7.26
7.20
7.18
7.16
7.11
7.09
6.54
6.52
6.50
6.48
5.95
5.93
5.91
5.89
1.71
1.70
1.69
1.68
1.67
1.65
1.64
1.63
1.62
1.00
0.99
0.98
0.97
0.97
0.95
0.66
0.64
0.64
0.63
0.62
1.00
2.31
1.27
2.01
0.99
1.00
1.22
2.10
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

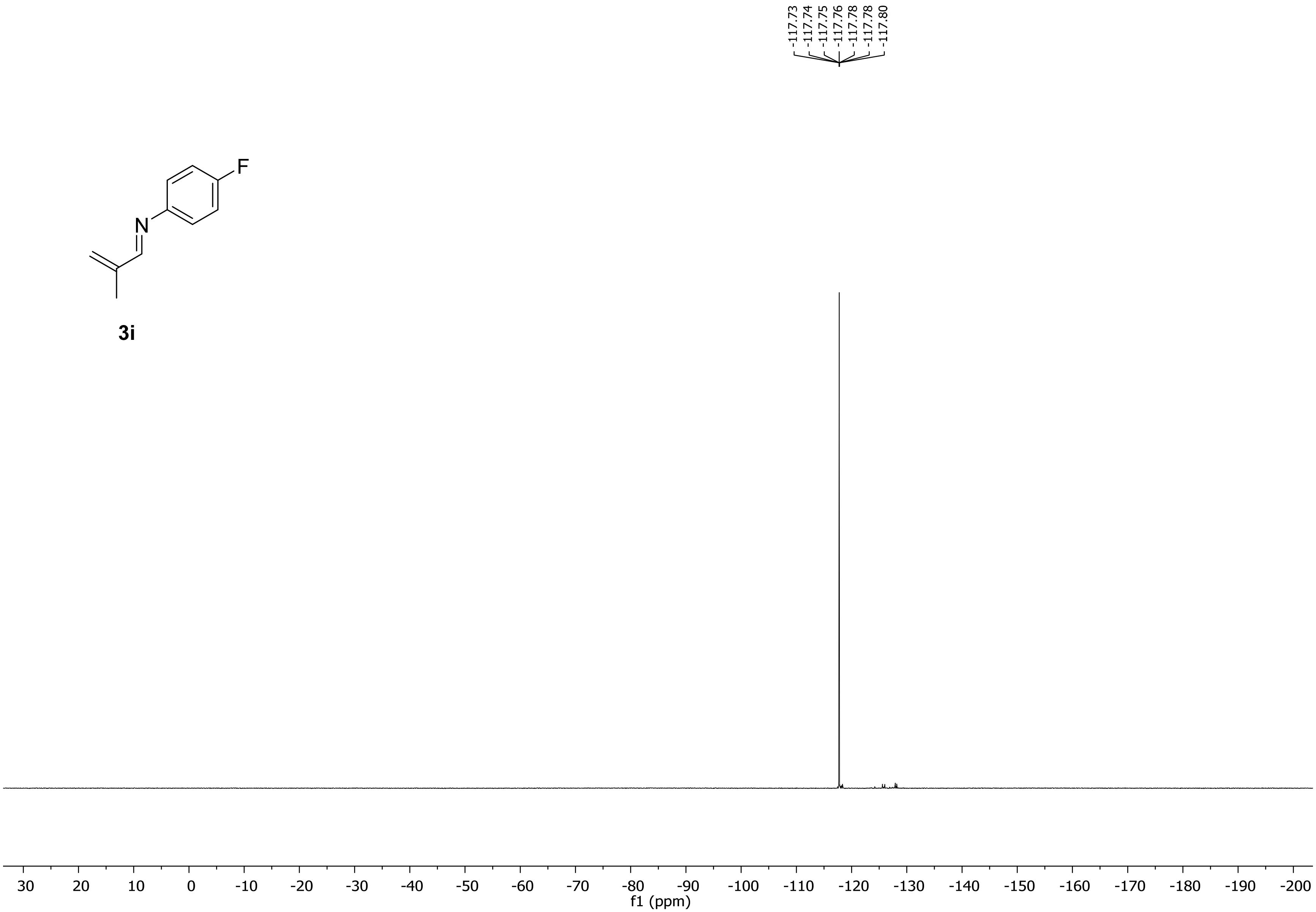
F
N

3i


8.07
7.26
7.11
7.10
7.09
7.08
7.06
7.04
7.01
5.77
5.59
2.05
0.91
3.72
1.00
1.01
2.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

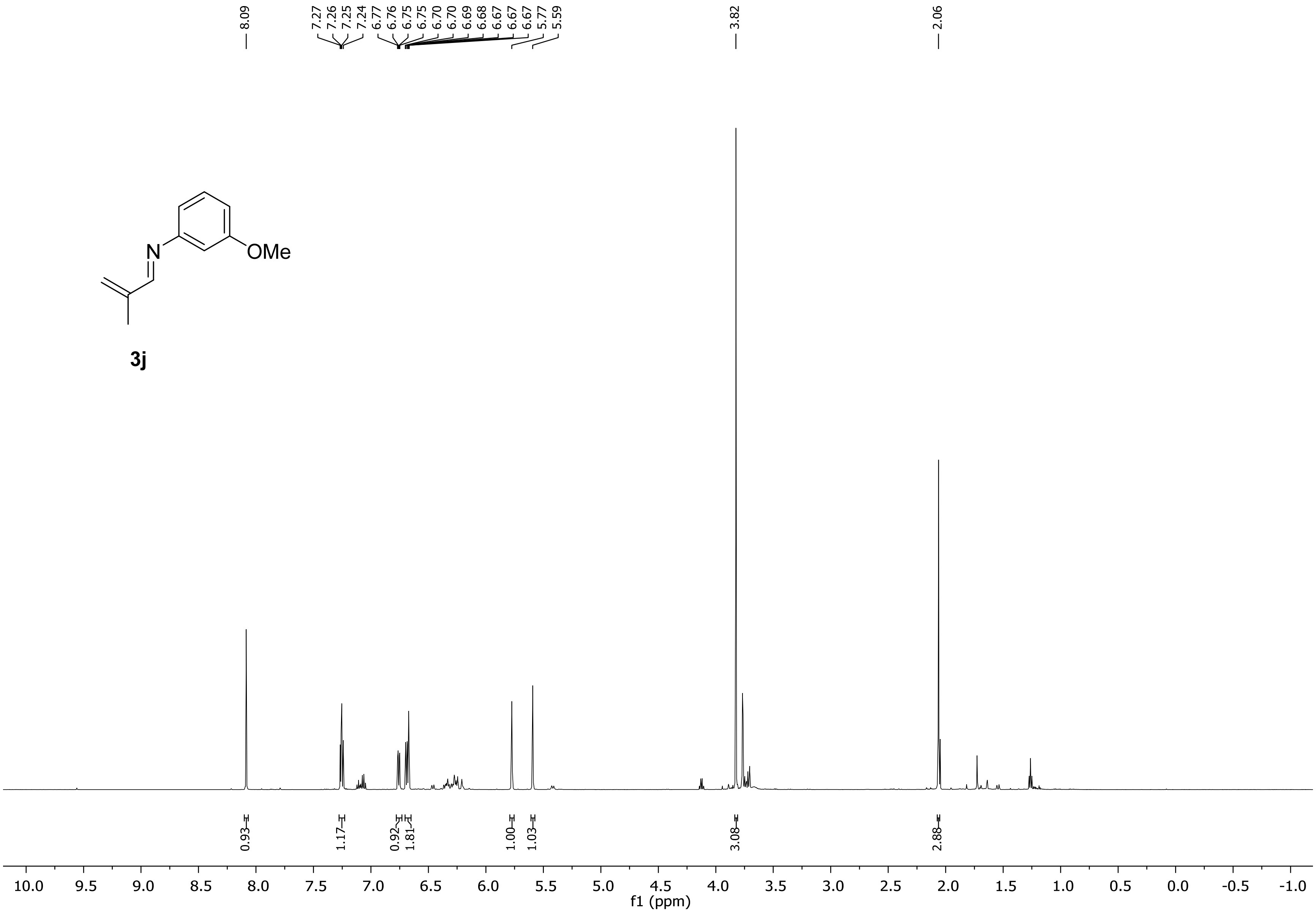

163.23
162.30
159.87
148.11
144.08
126.65
122.22
122.14
115.82
115.60
77.32
77.00
76.68
16.81
F
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

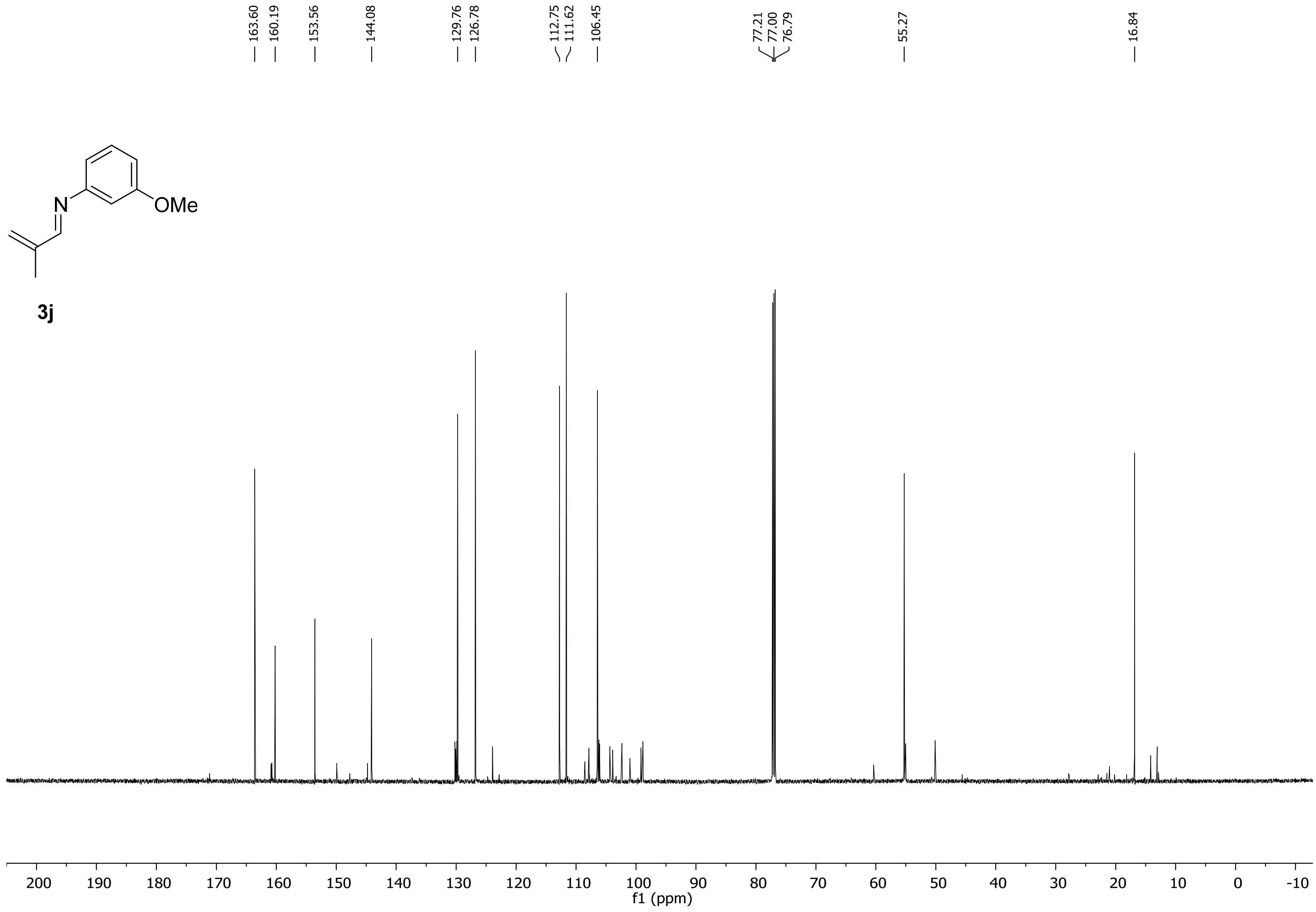
3i

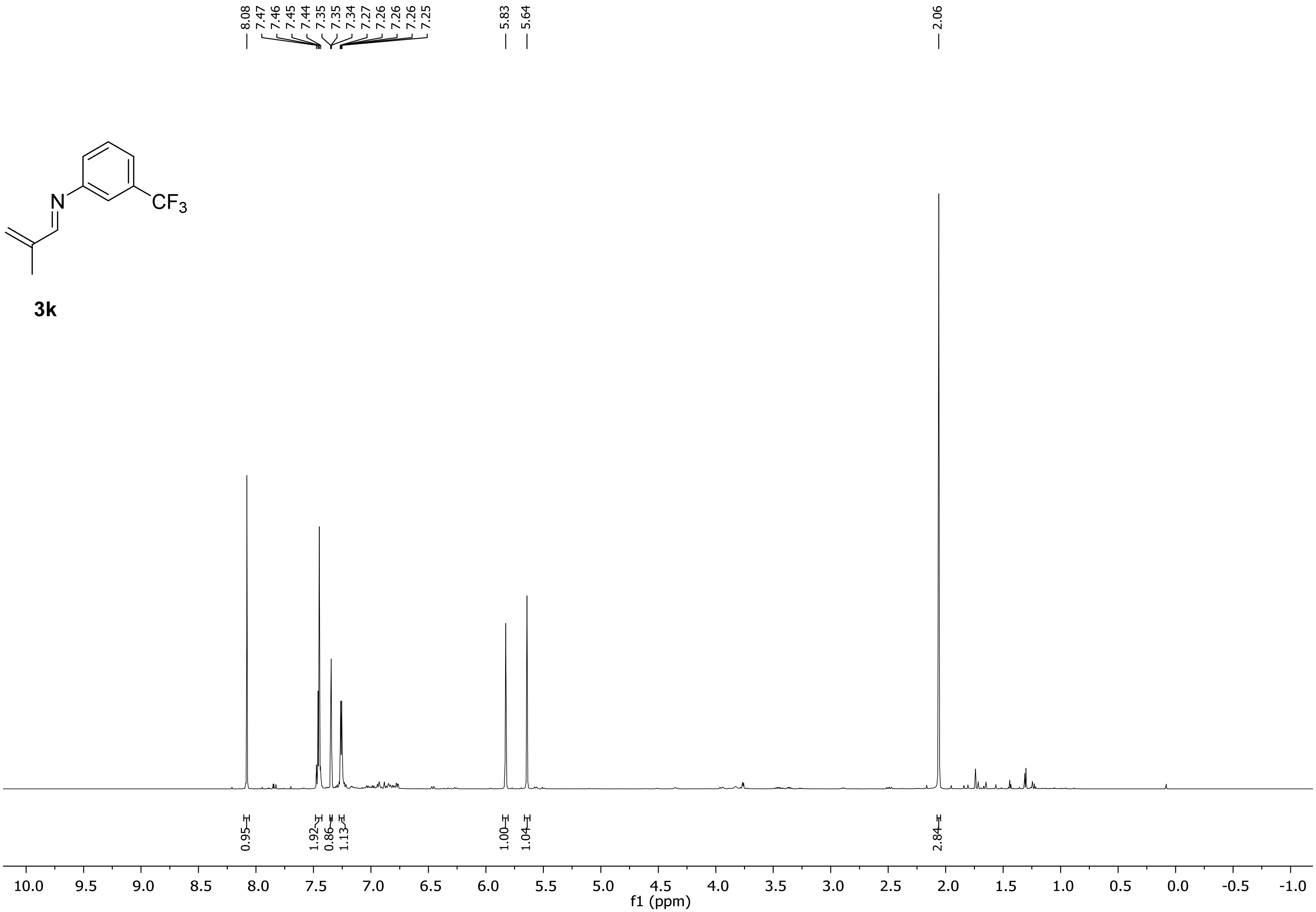


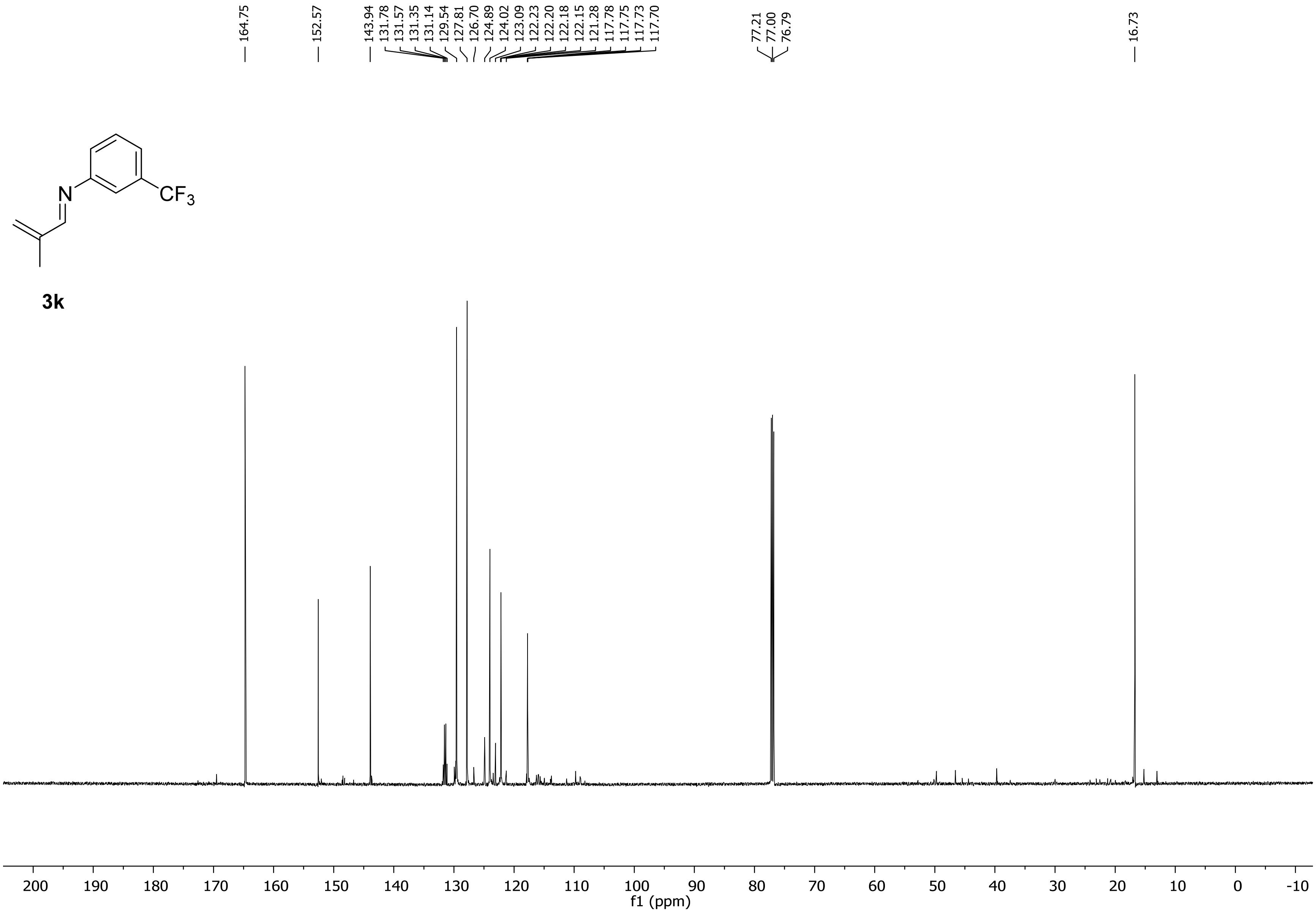
3i

-117.73
-117.74
-117.75
-117.76
-117.78
-117.78
-117.80
F
N
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

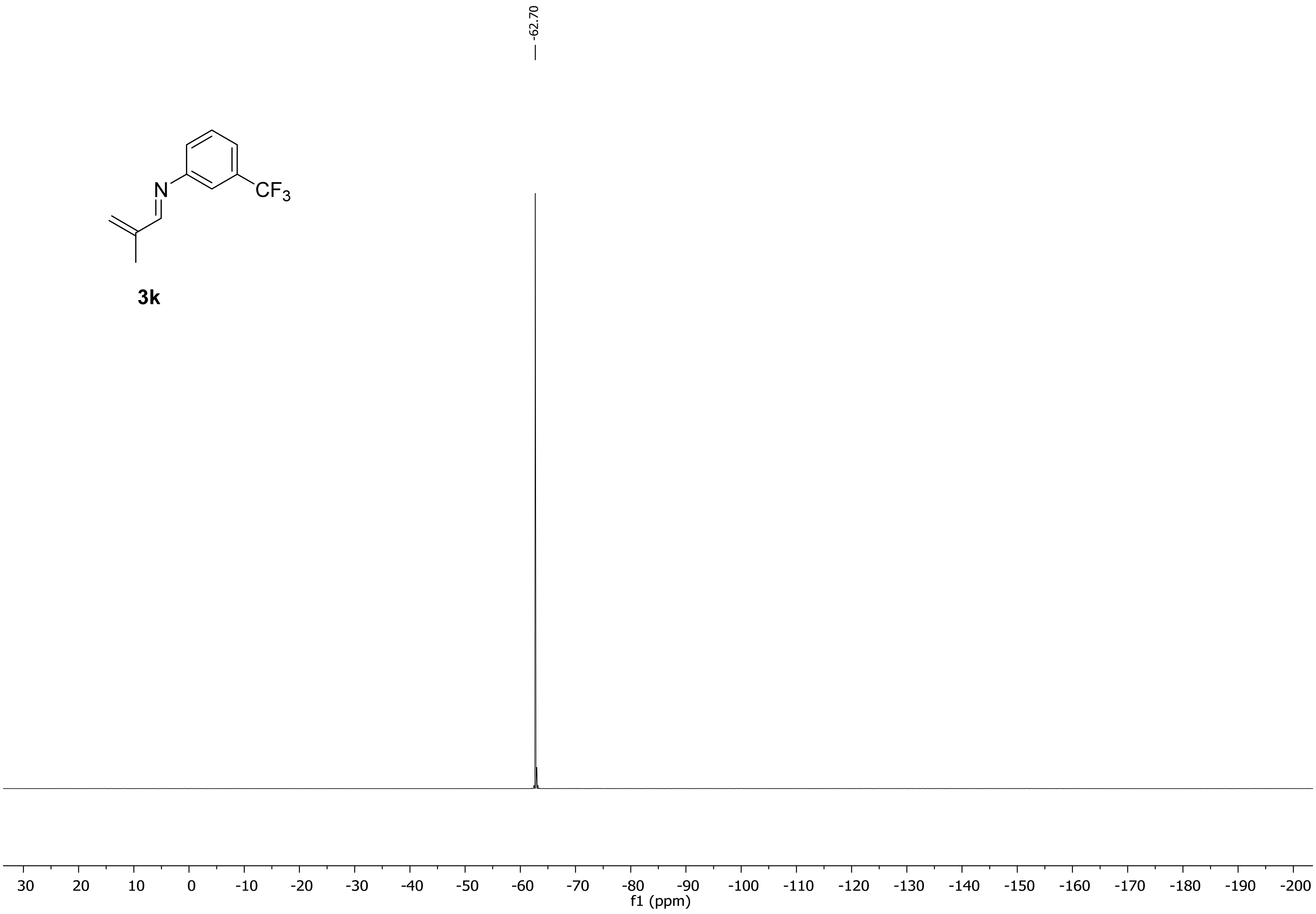

8.09
7.27
7.26
7.25
7.24
6.77
6.76
6.75
6.75
6.70
6.70
6.69
6.68
6.67
6.67
6.67
5.77
5.59
3.82
2.06
N
OMe
3j
0.93
1.17
0.92
1.81
1.00
1.03
3.08
2.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

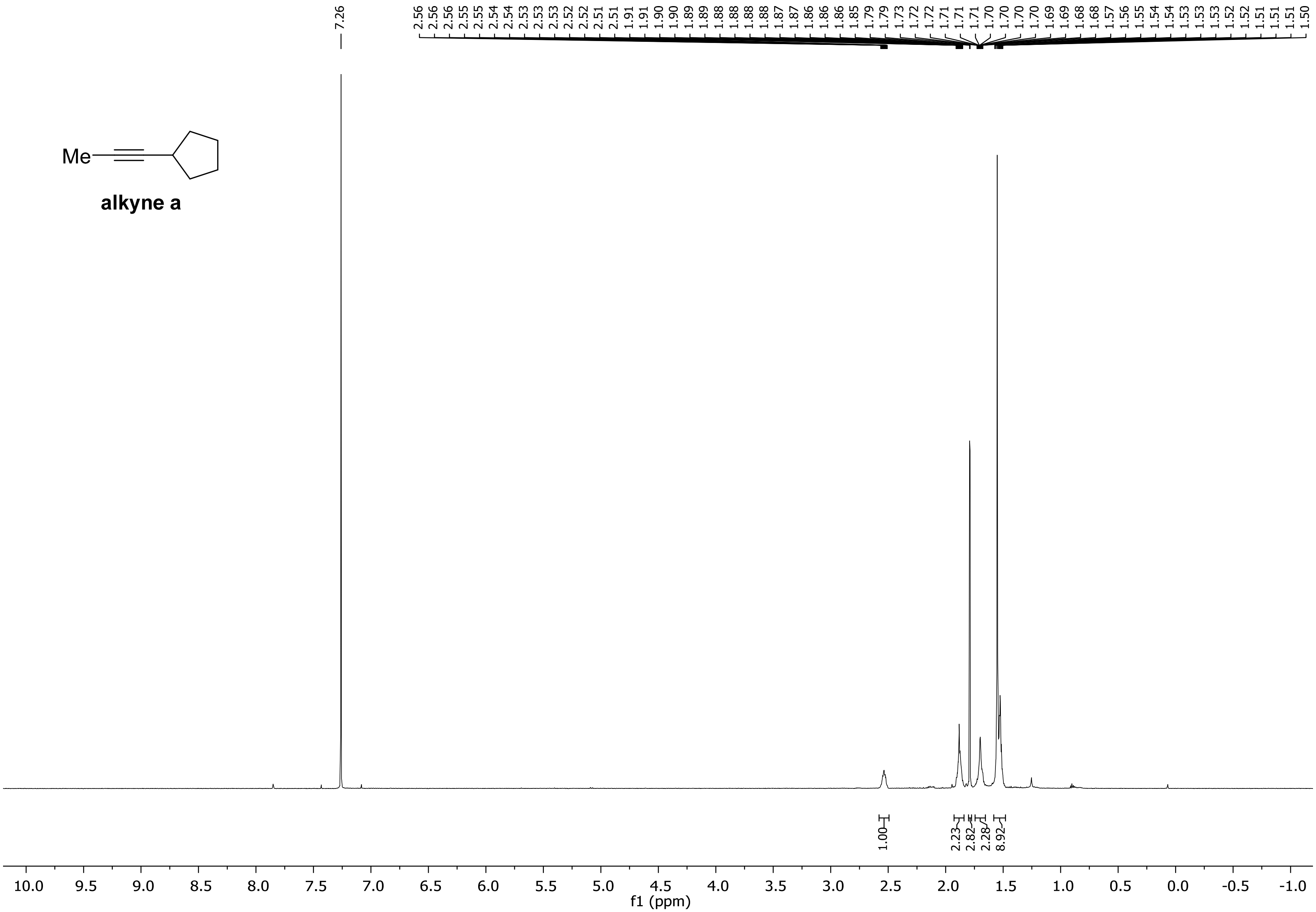

163.60
160.19
153.56
144.08
129.76
126.78
112.75
111.62
106.45
77.21
77.00
76.79
55.27
16.84
N
OMe
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

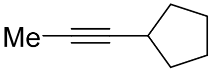

8.08
7.47
7.46
7.45
7.44
7.35
7.35
7.34
7.27
7.26
7.26
7.26
7.25
5.83
5.64
2.06
N
CF3
3k
0.95
1.92
0.86
1.13
1.00
1.04
2.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


3k

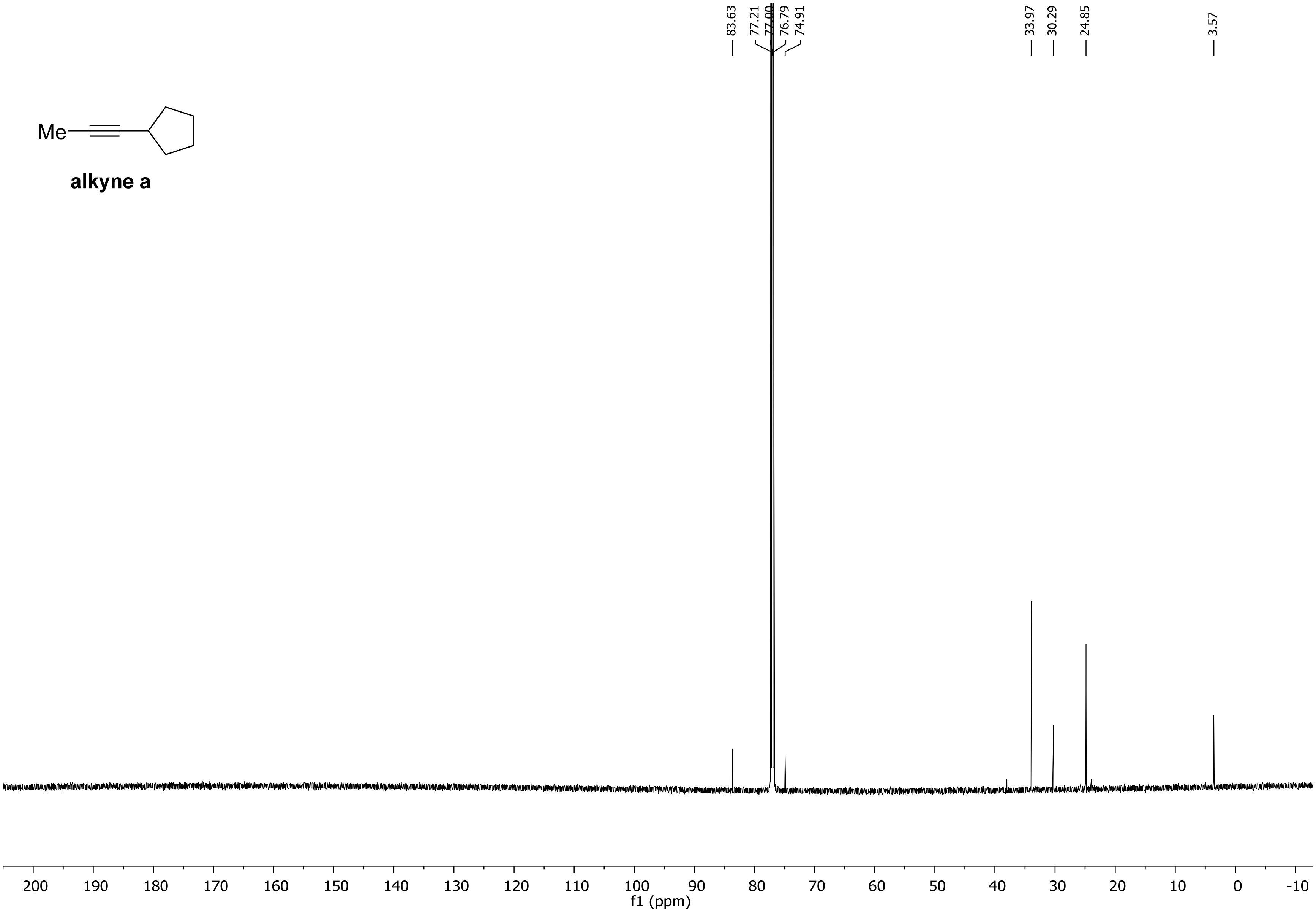
164.75
152.57
143.94
131.78
131.57
131.35
131.14
129.54
127.81
126.70
124.89
124.02
123.09
122.23
122.20
122.18
122.15
121.28
117.78
117.75
117.73
117.70
77.21
77.00
76.79
16.73
N
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

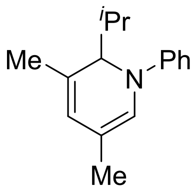

-62.70
N
CF3
3k
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


7.26
2.56
2.56
2.56
2.55
2.55
2.54
2.54
2.53
2.53
2.53
2.52
2.52
2.51
2.51
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.88
1.88
1.88
1.87
1.87
1.86
1.86
1.86
1.85
1.79
1.79
1.73
1.72
1.72
1.71
1.71
1.71
1.70
1.70
1.70
1.70
1.69
1.69
1.68
1.68
1.57
1.56
1.55
1.54
1.54
1.53
1.53
1.53
1.52
1.52
1.51
1.51
1.51
1.50
Me
alkyne a
1.00
2.23
2.82
2.28
8.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


Me

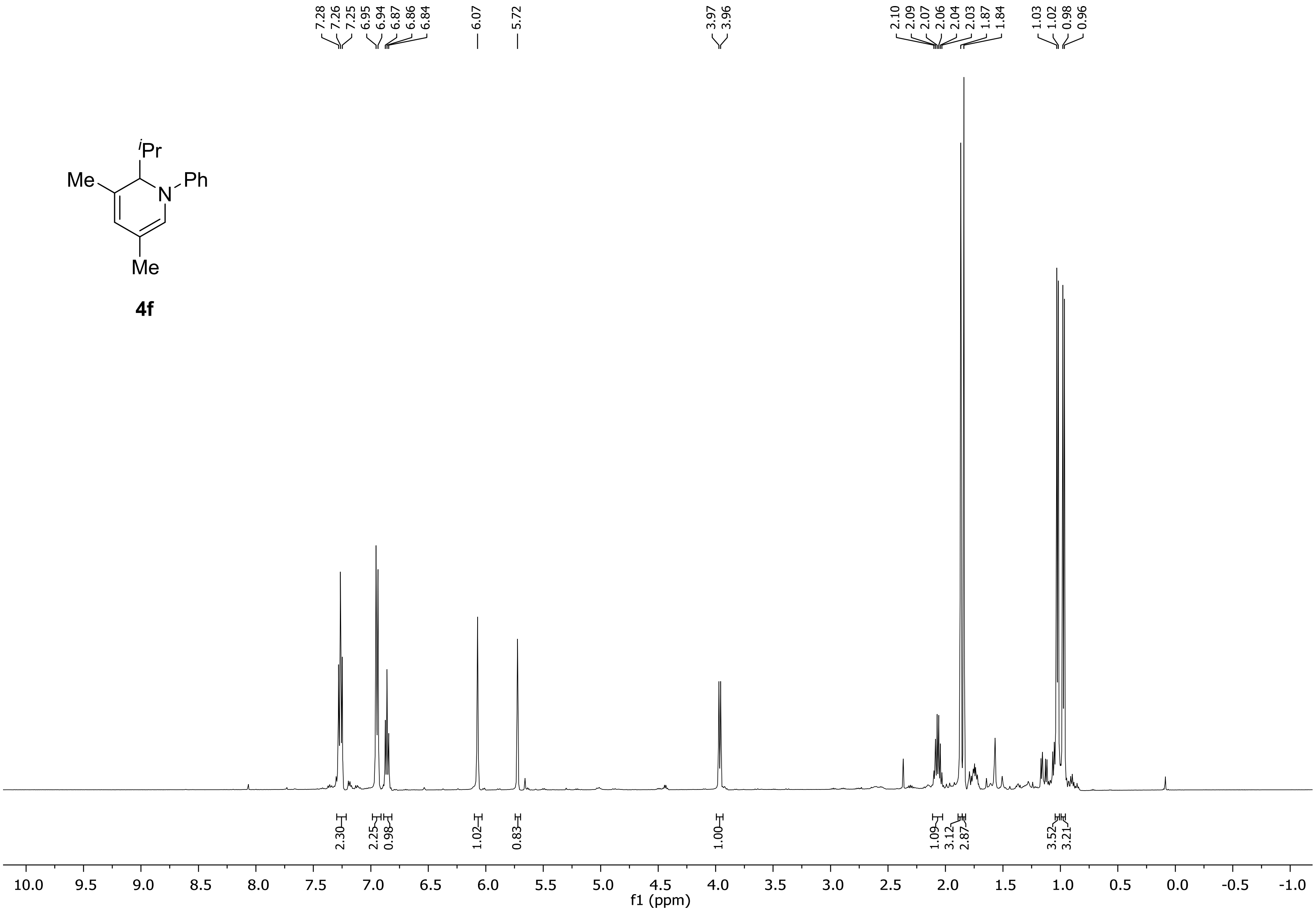
alkyne a


83.63
77.21
77.00
76.79
74.91
33.97
30.29
24.85
3.57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

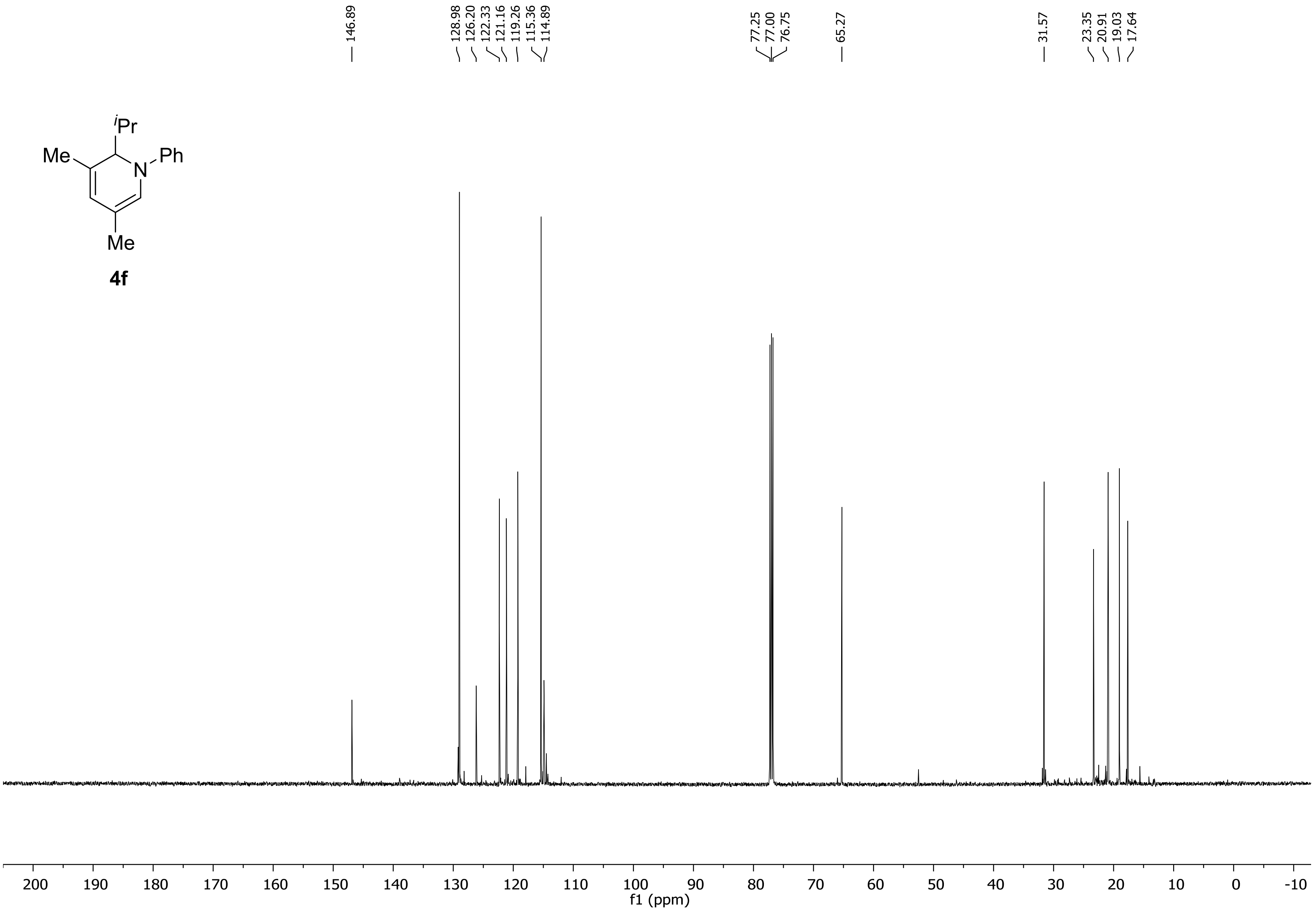


iPr
Me
N
Ph
Me

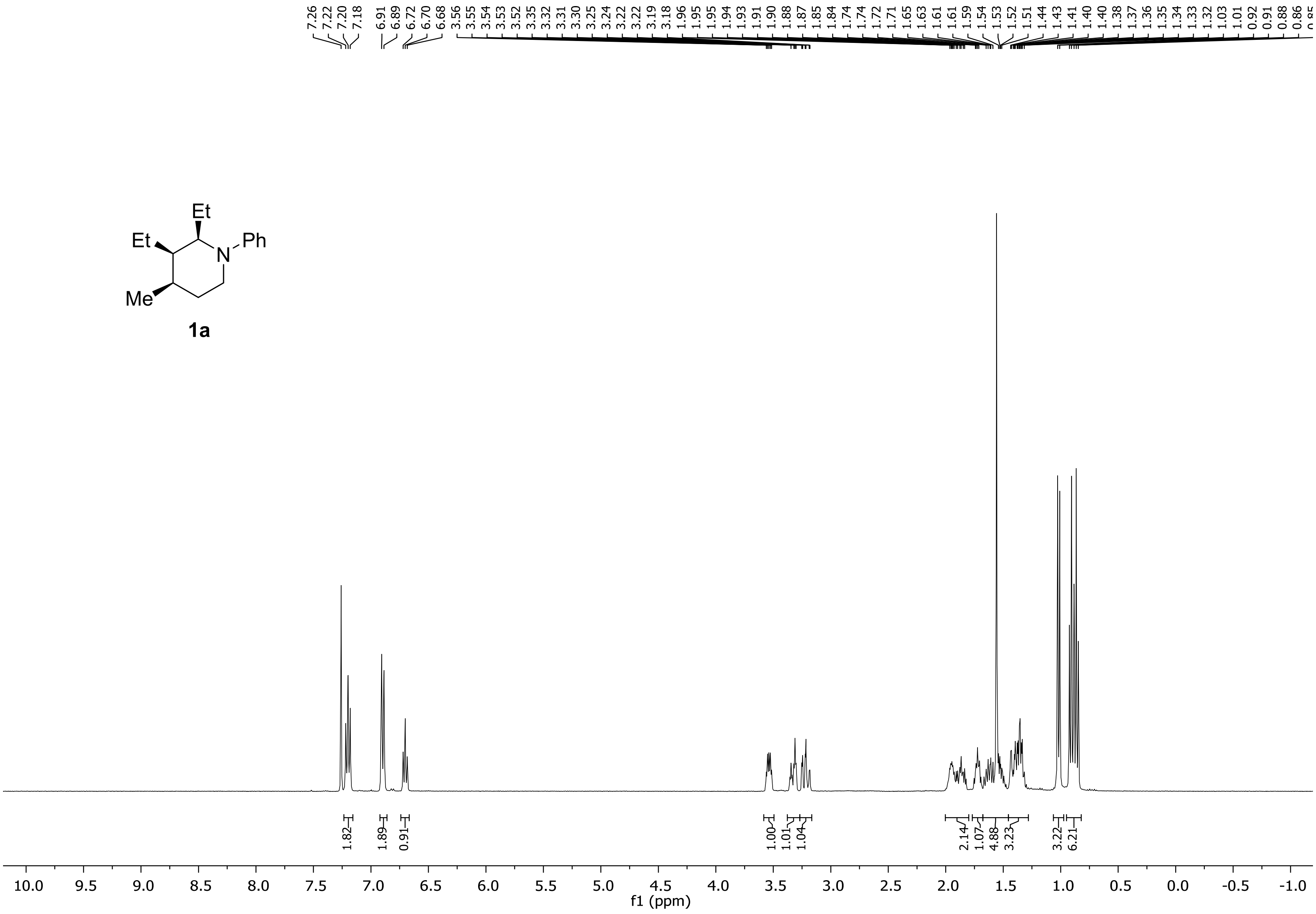
4f

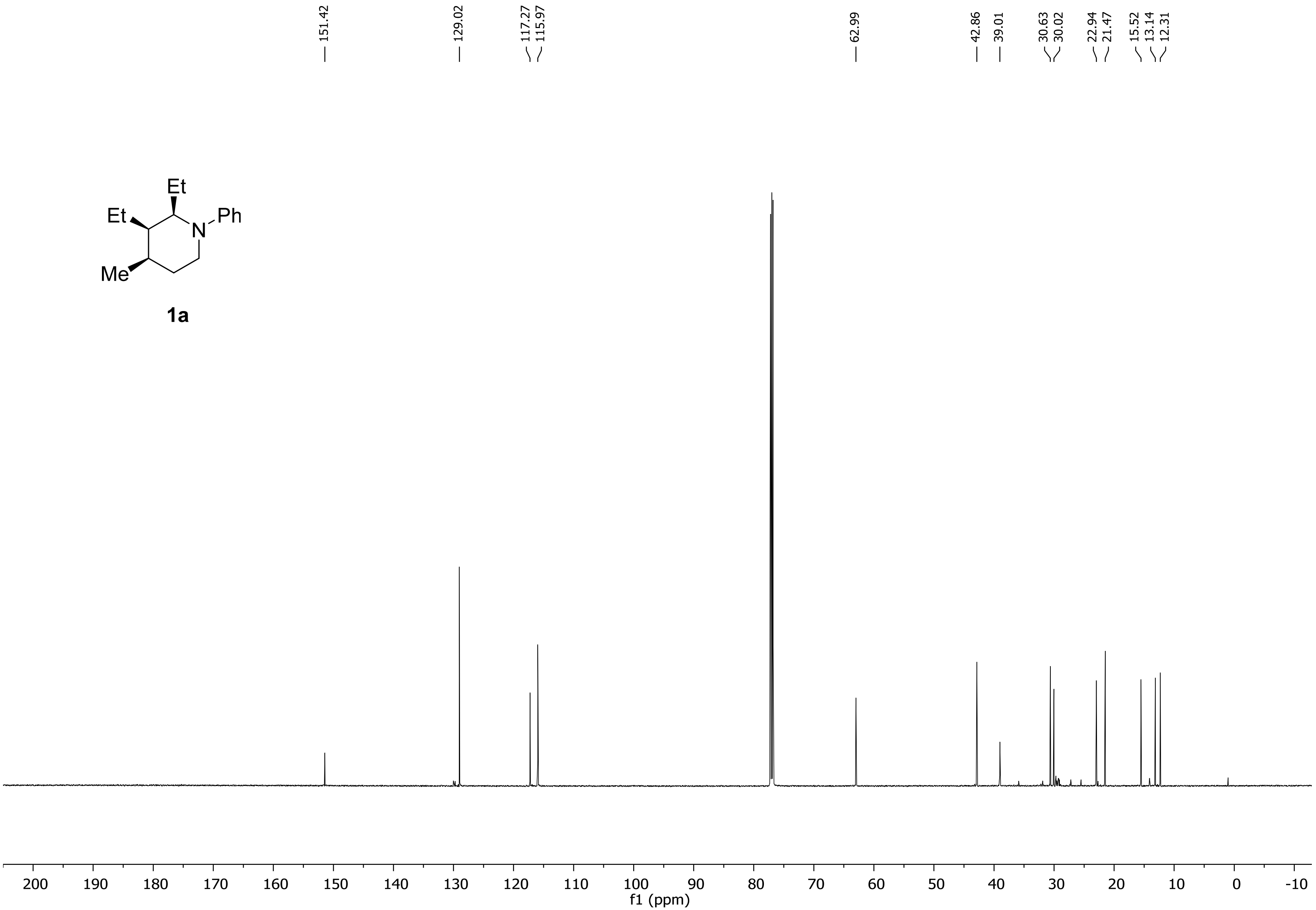


7.28
7.26
7.25
6.95
6.94
6.87
6.86
6.84
6.07
5.72
3.97
3.96
2.10
2.09
2.07
2.06
2.04
2.03
1.87
1.84
1.03
1.02
0.98
0.96
2.30
2.25
0.98
1.02
0.83
1.00
1.09
3.12
2.87
3.52
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

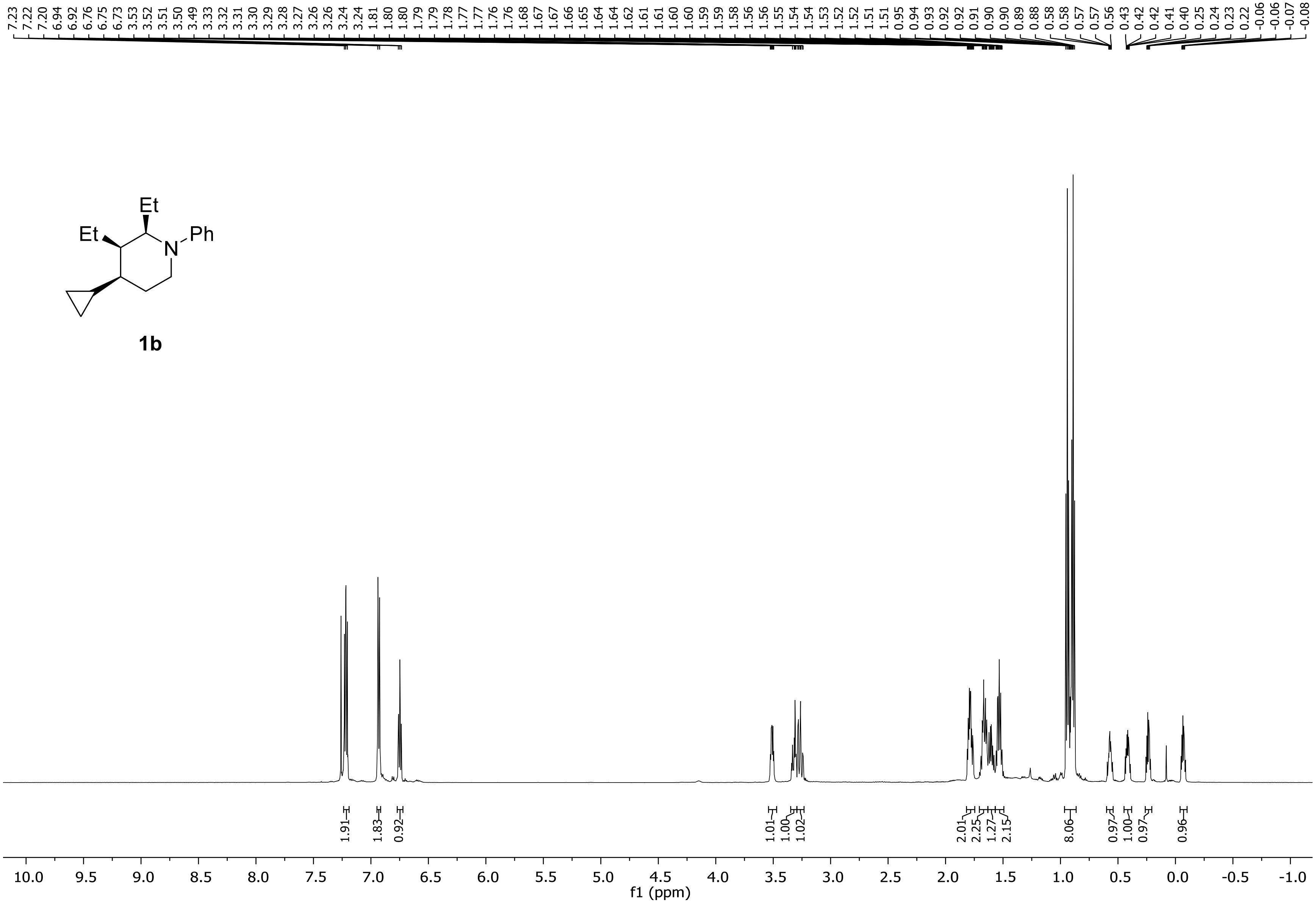

146.89
128.98
126.20
122.33
121.16
119.26
115.36
114.89
77.25
77.00
76.75
65.27
31.57
23.35
20.91
19.03
17.64
ⁱPr
Me
N
Ph
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4f

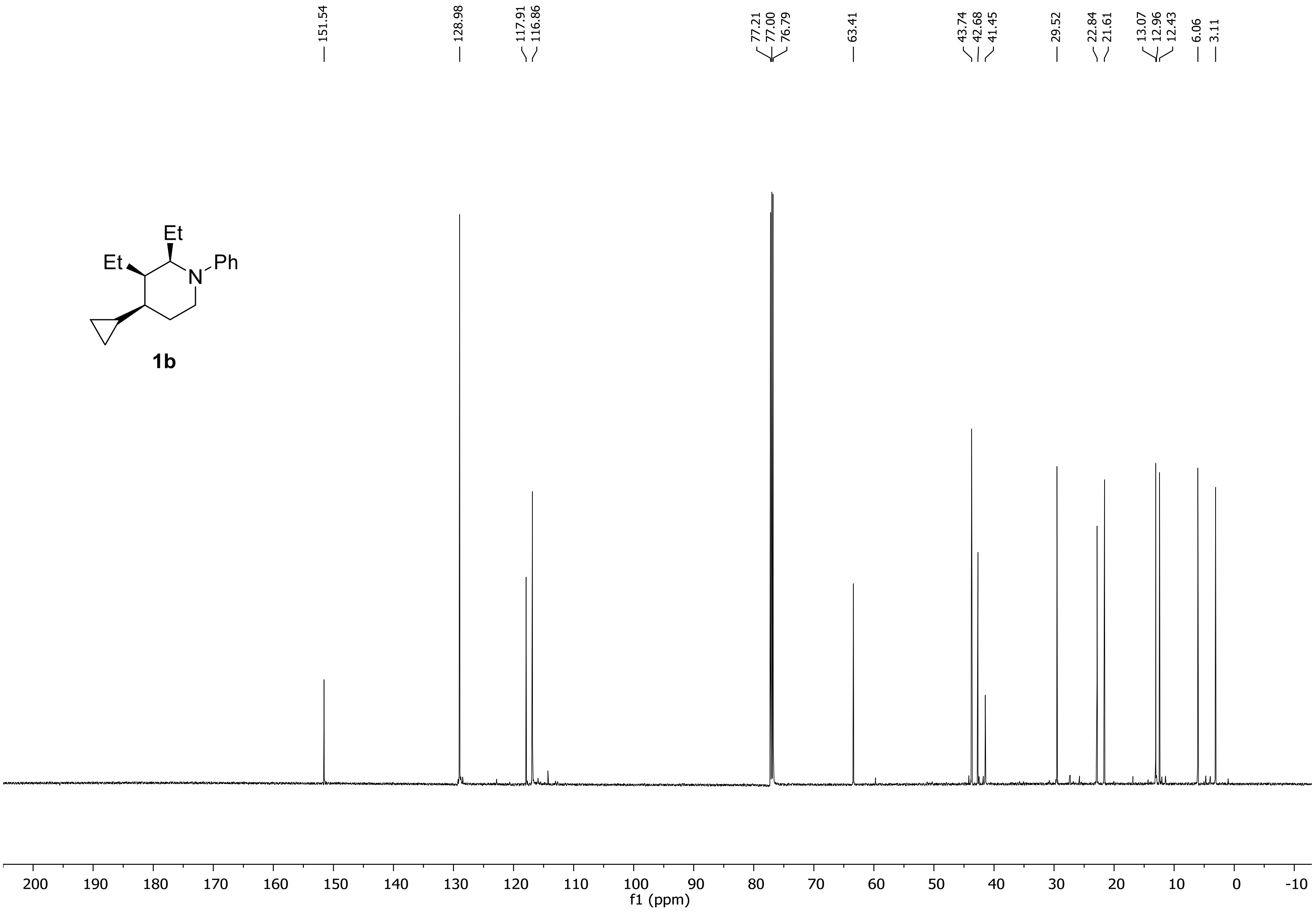

7.26
7.22
7.20
7.18
6.91
6.89
6.72
6.70
6.68
3.56
3.55
3.54
3.53
3.52
3.35
3.32
3.31
3.30
3.25
3.24
3.22
3.22
3.19
3.18
1.96
1.95
1.95
1.94
1.93
1.91
1.90
1.88
1.87
1.85
1.84
1.74
1.74
1.72
1.71
1.65
1.63
1.61
1.61
1.59
1.54
1.53
1.52
1.51
1.44
1.43
1.41
1.40
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.03
1.01
0.92
0.91
0.88
0.86
Et
Et
N
Ph
Me
1a
1.82
1.89
0.91
1.00
1.01
1.04
2.14
1.07
4.88
3.23
3.22
6.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


151.42
129.02
117.27
115.97
62.99
42.86
39.01
30.63
30.02
22.94
21.47
15.52
13.14
12.31
Et
Et
N
Ph
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

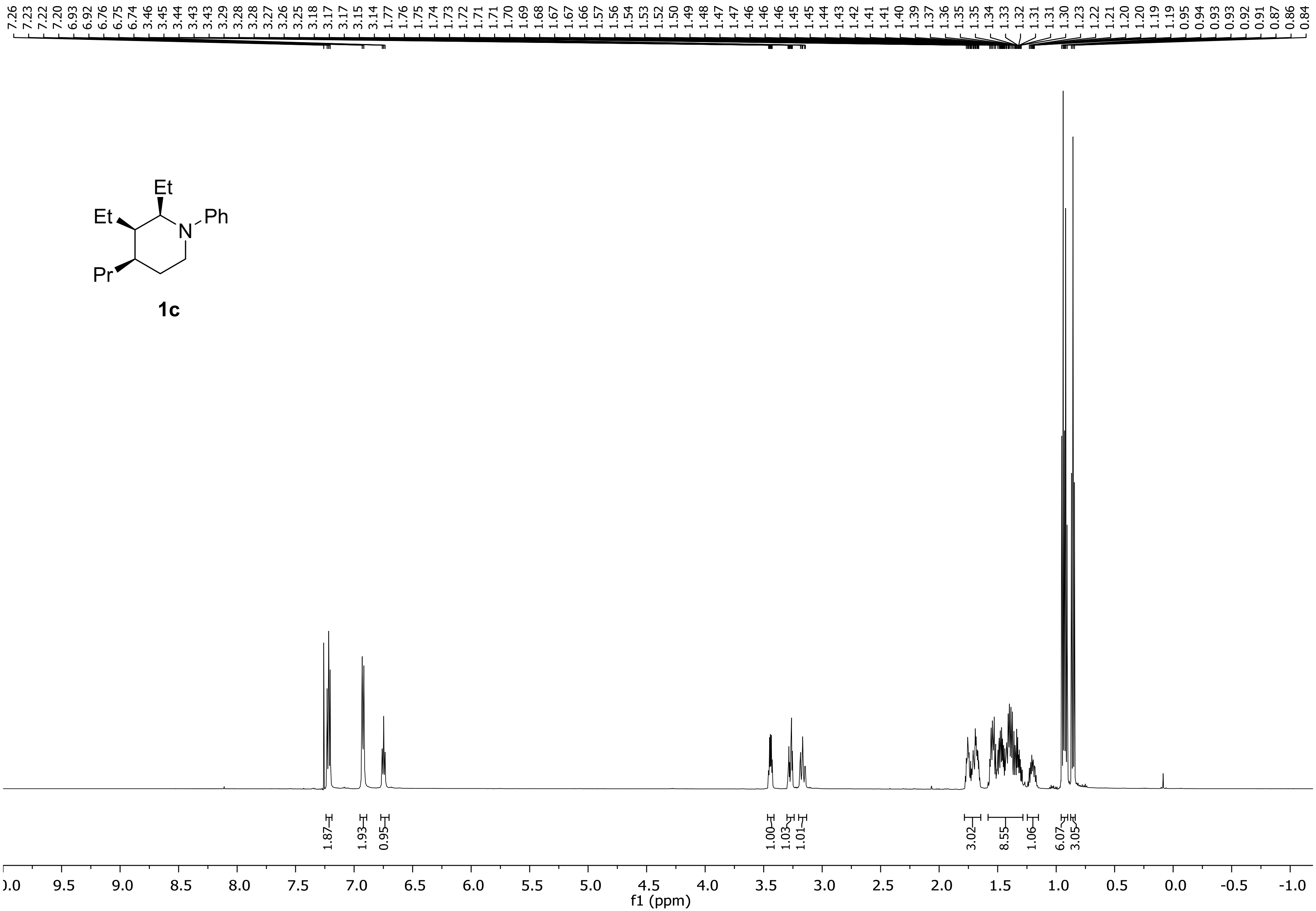
1a


7.23
7.22
7.20
6.94
6.92
6.76
6.75
6.73
3.53
3.52
3.51
3.50
3.49
3.33
3.32
3.31
3.30
3.29
3.28
3.27
3.26
3.26
3.24
3.24
1.81
1.80
1.80
1.79
1.79
1.78
1.77
1.77
1.76
1.68
1.67
1.67
1.66
1.65
1.64
1.64
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.58
1.56
1.56
1.55
1.54
1.54
1.53
1.52
1.52
1.51
1.51
0.95
0.94
0.93
0.92
0.92
0.91
0.90
0.90
0.89
0.88
0.58
0.58
0.57
0.57
0.56
0.43
0.42
0.42
0.41
0.40
0.25
0.24
0.23
0.22
-0.06
-0.06
-0.07
-0.08
Et
Et
N
Ph
1.91
1.83
0.92
1.01
1.00
1.02
2.01
2.25
1.27
2.15
8.06
0.97
1.00
0.97
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

1b

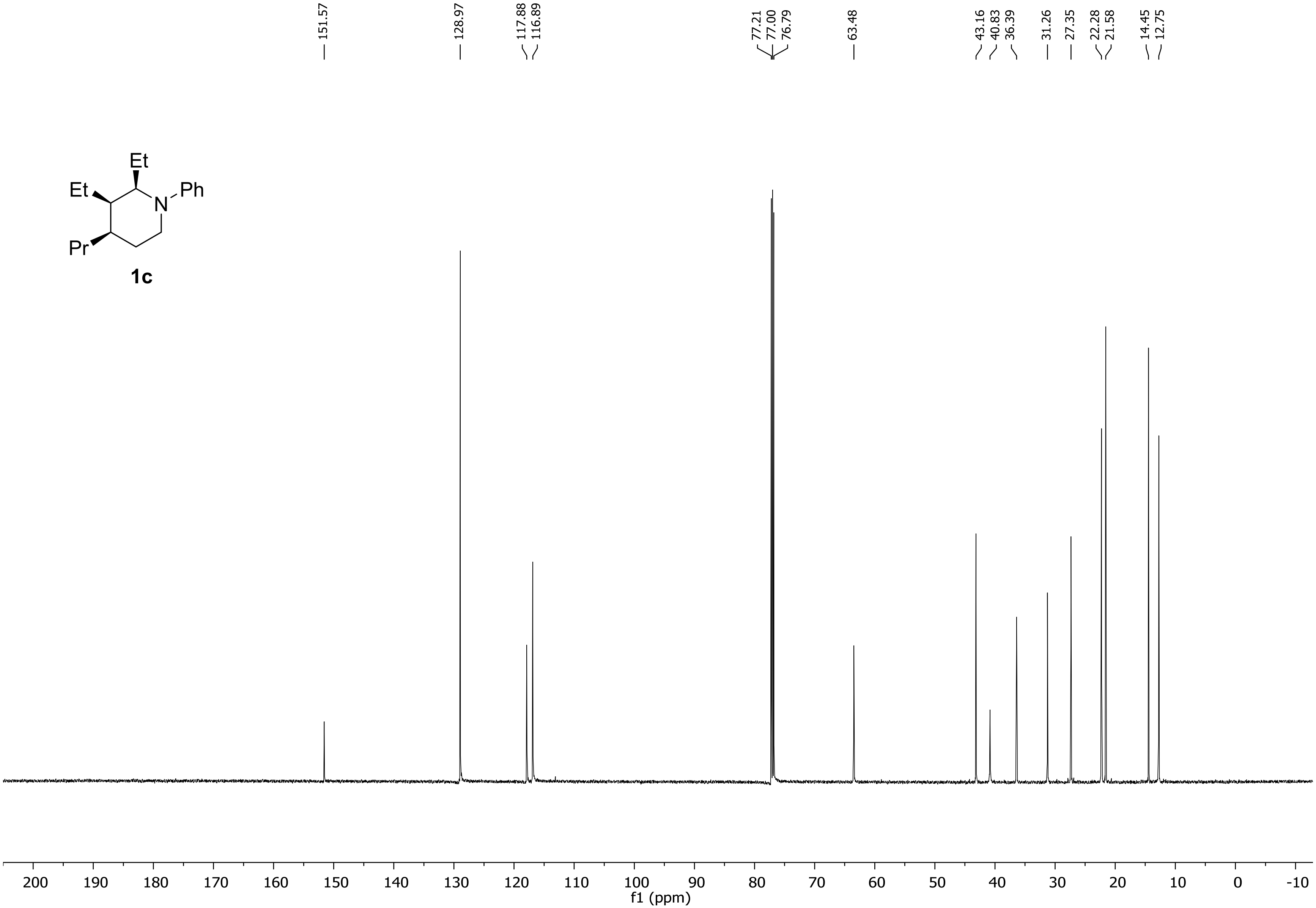

151.54
128.98
117.91
116.86
77.21
77.00
76.79
63.41
43.74
42.68
41.45
29.52
22.84
21.61
13.07
12.96
12.43
6.06
3.11
Et
Et
N
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1b



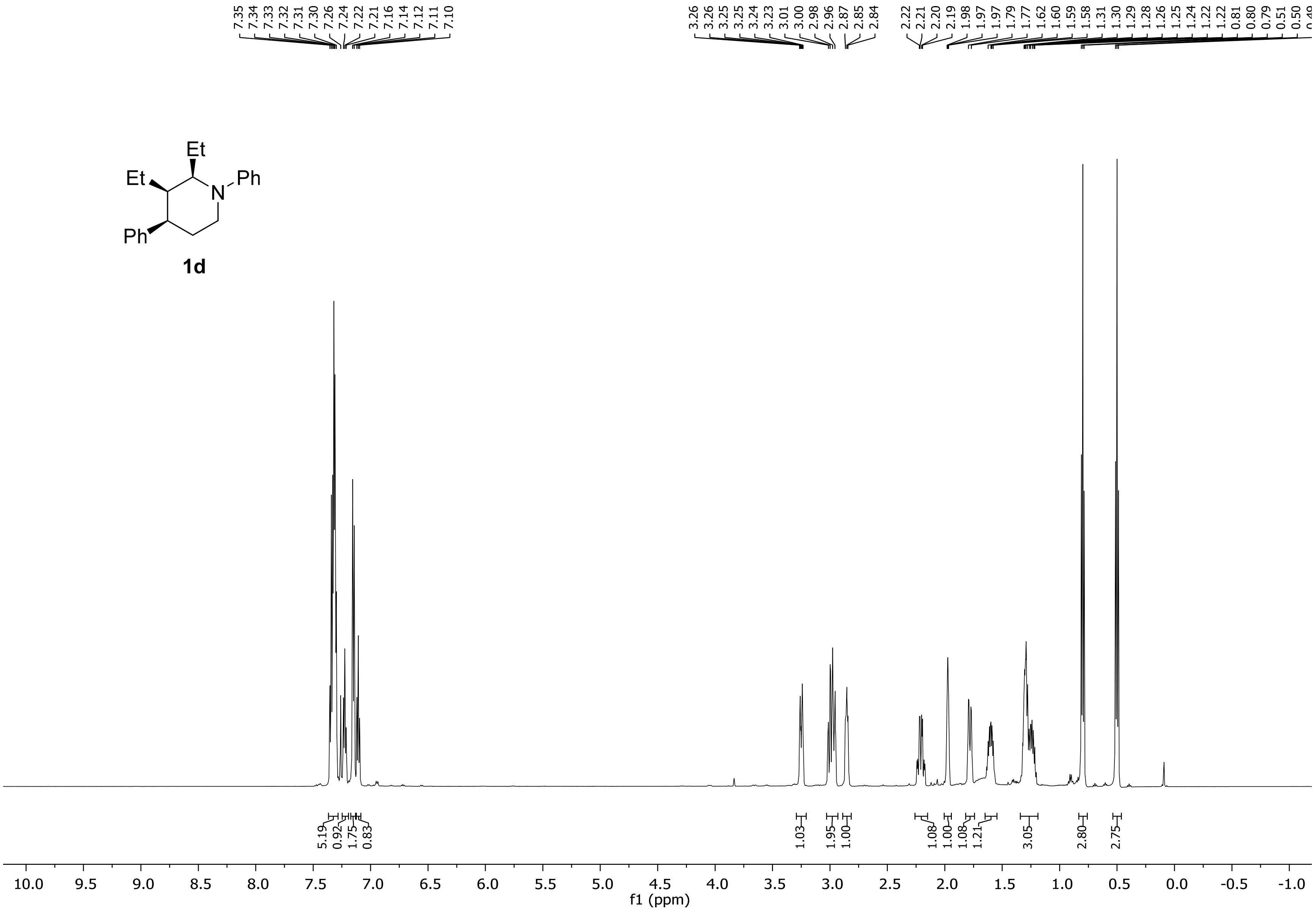
7.26
7.23
7.22
7.20
6.93
6.92
6.76
6.75
6.74
3.46
3.45
3.44
3.43
3.43
3.29
3.28
3.28
3.27
3.26
3.25
3.18
3.17
3.17
3.15
3.14
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.67
1.67
1.66
1.57
1.56
1.54
1.53
1.52
1.50
1.49
1.48
1.47
1.47
1.46
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.41
1.41
1.40
1.39
1.37
1.36
1.35
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.23
1.22
1.21
1.20
1.20
1.19
1.19
0.95
0.94
0.93
0.93
0.92
0.91
0.87
0.86
0.84
Et
Et
N
Ph
Pr
1.87
1.93
0.95
1.00
1.03
1.01
3.02
8.55
1.06
6.07
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

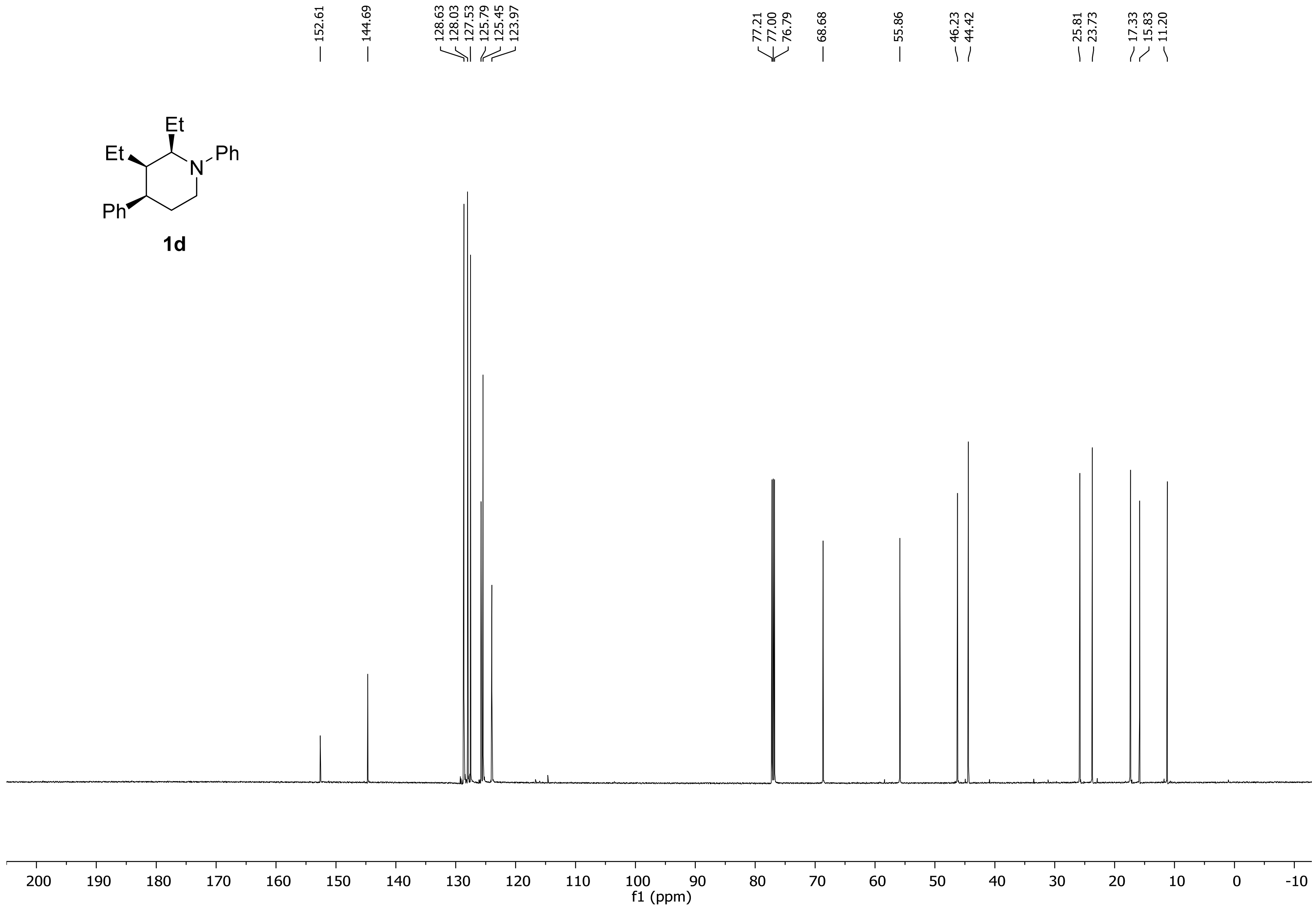
1c



1c

151.57
128.97
117.88
116.89
77.21
77.00
76.79
63.48
43.16
40.83
36.39
31.26
27.35
22.28
21.58
14.45
12.75
Et
Et
N
Ph
Pr
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

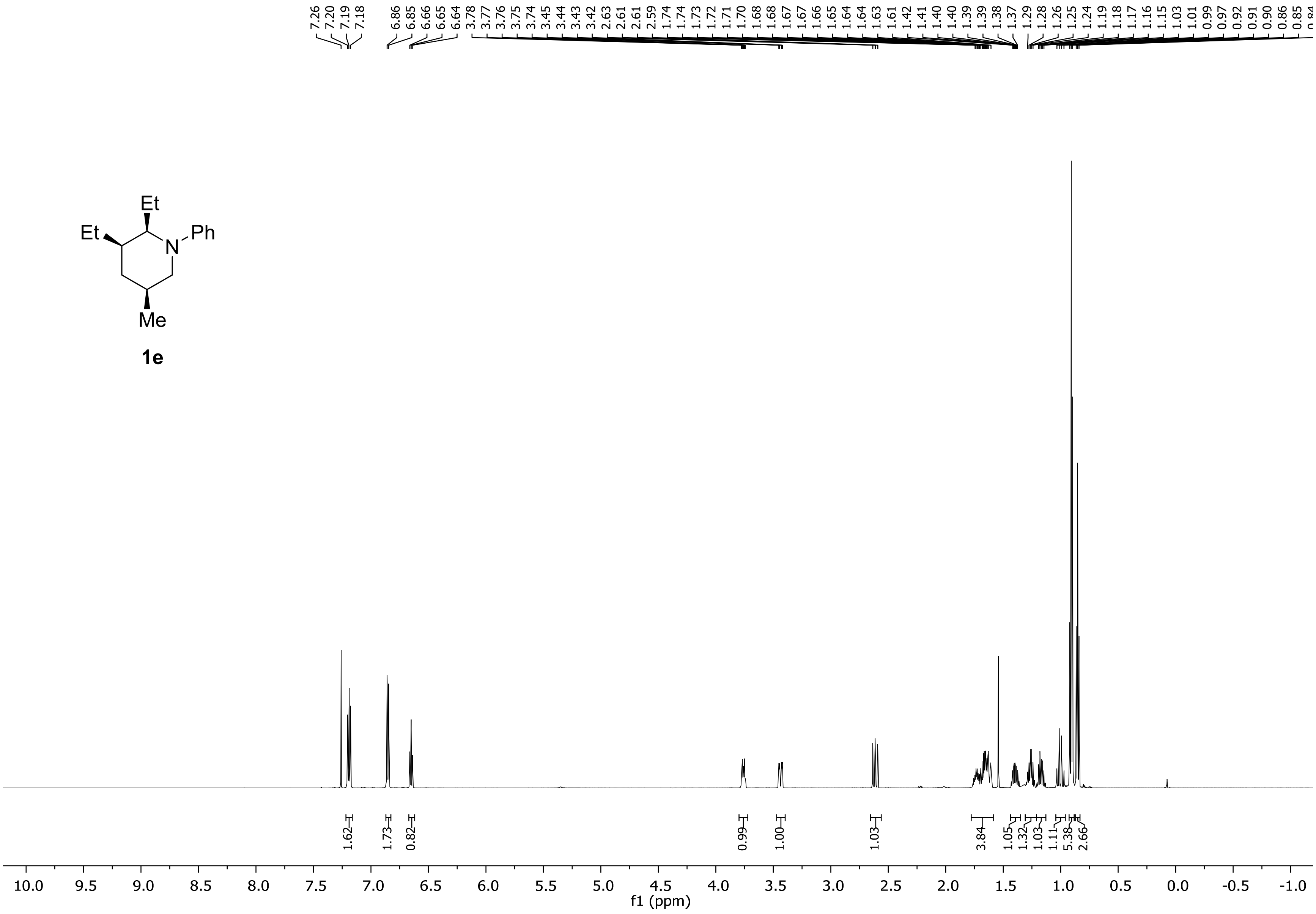

7.35
7.34
7.33
7.32
7.31
7.30
7.26
7.24
7.22
7.21
7.16
7.14
7.12
7.11
7.10
3.26
3.26
3.25
3.25
3.24
3.23
3.01
3.00
2.98
2.96
2.87
2.85
2.84
2.22
2.21
2.20
2.19
1.98
1.97
1.97
1.79
1.77
1.62
1.60
1.59
1.58
1.31
1.30
1.29
1.28
1.26
1.25
1.24
1.22
1.22
0.81
0.80
0.79
0.51
0.50
Et
Et
N
Ph
Ph
1d
5.19
0.92
1.75
0.83
1.03
1.95
1.00
1.08
1.00
1.08
1.21
3.05
2.80
2.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

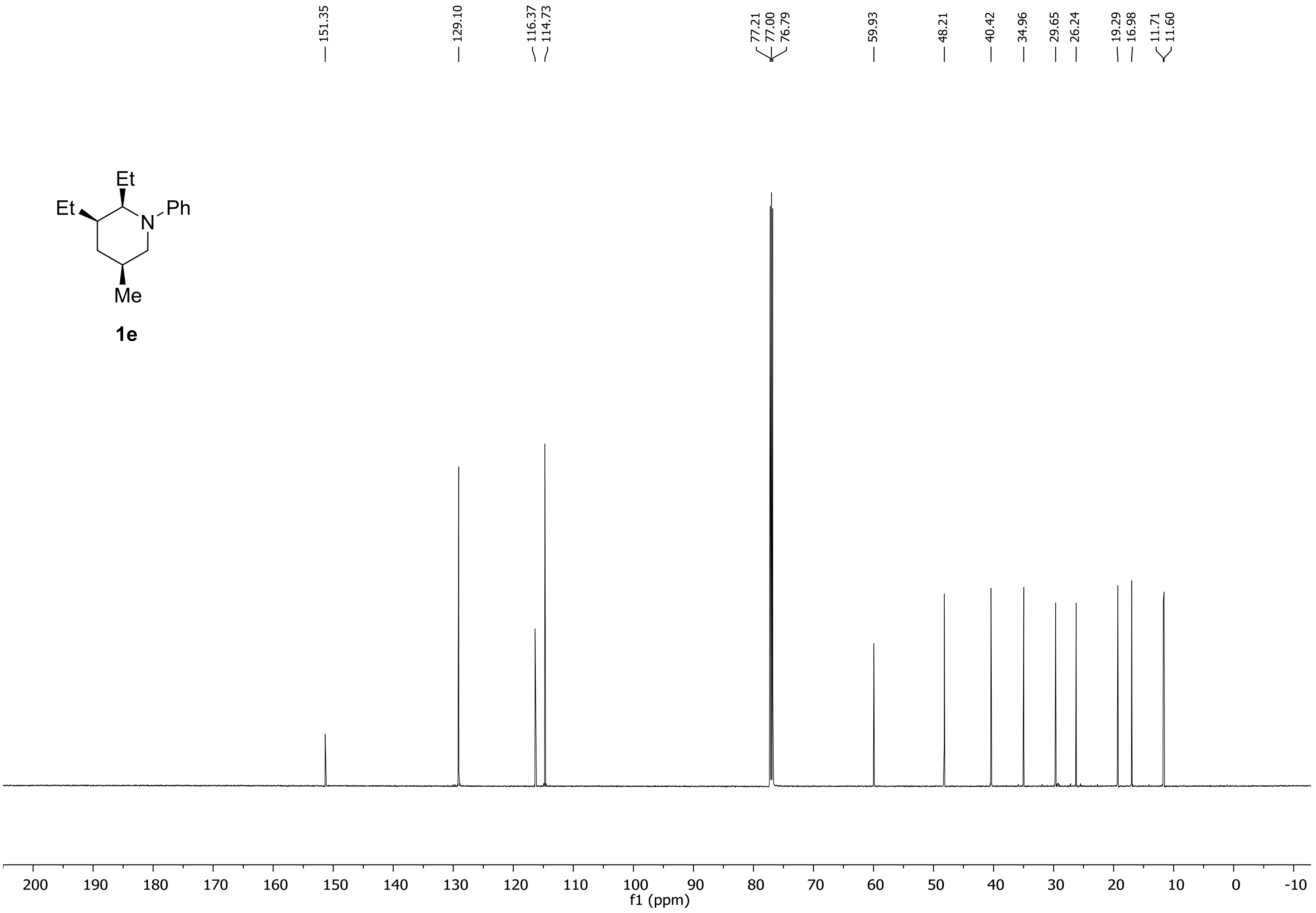

152.61
144.69
128.63
128.03
127.53
125.79
125.45
123.97
77.21
77.00
76.79
68.68
55.86
46.23
44.42
25.81
23.73
17.33
15.83
11.20
Et
Et
N
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1d

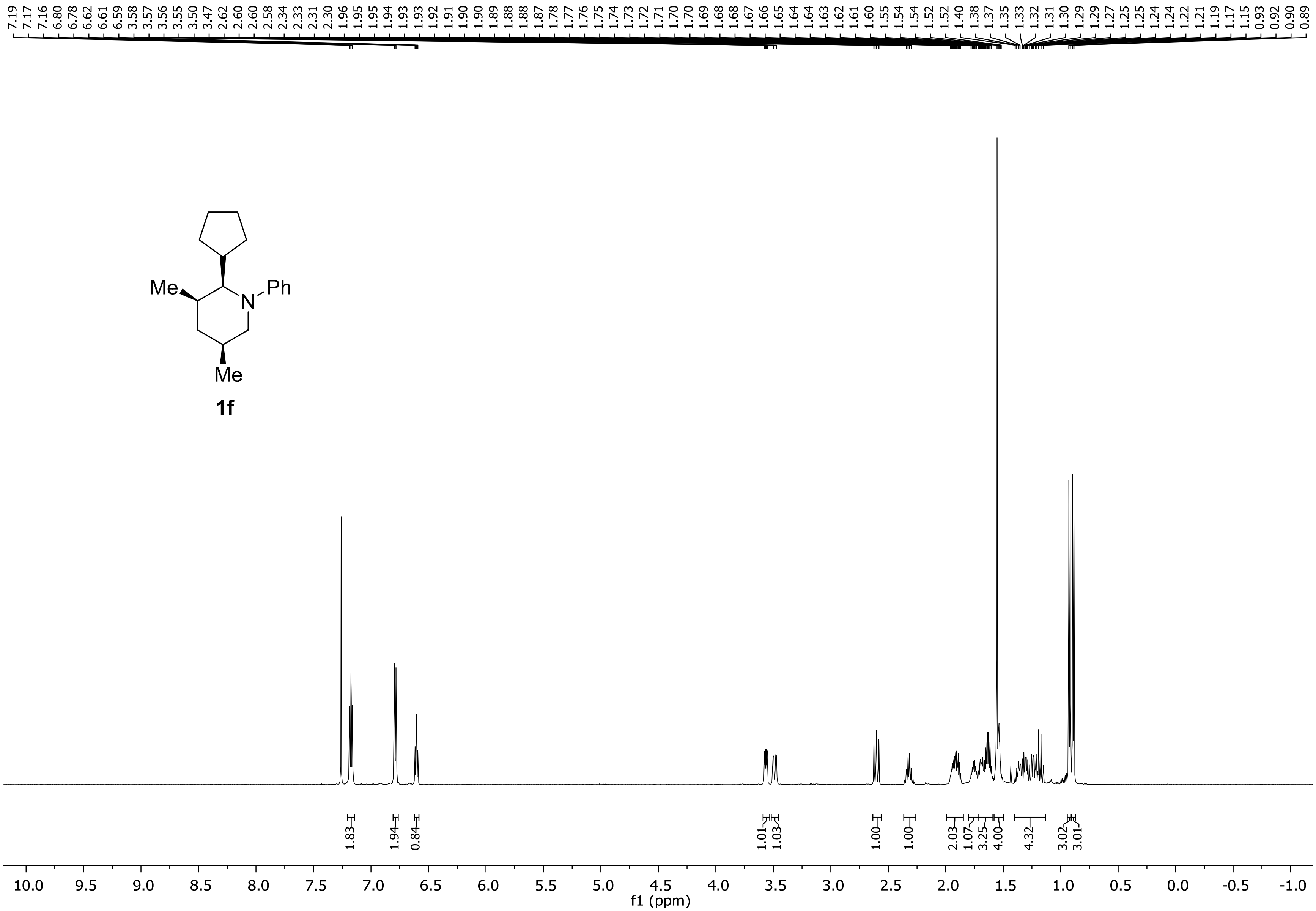
Et
Et
N
Ph
Me

1e

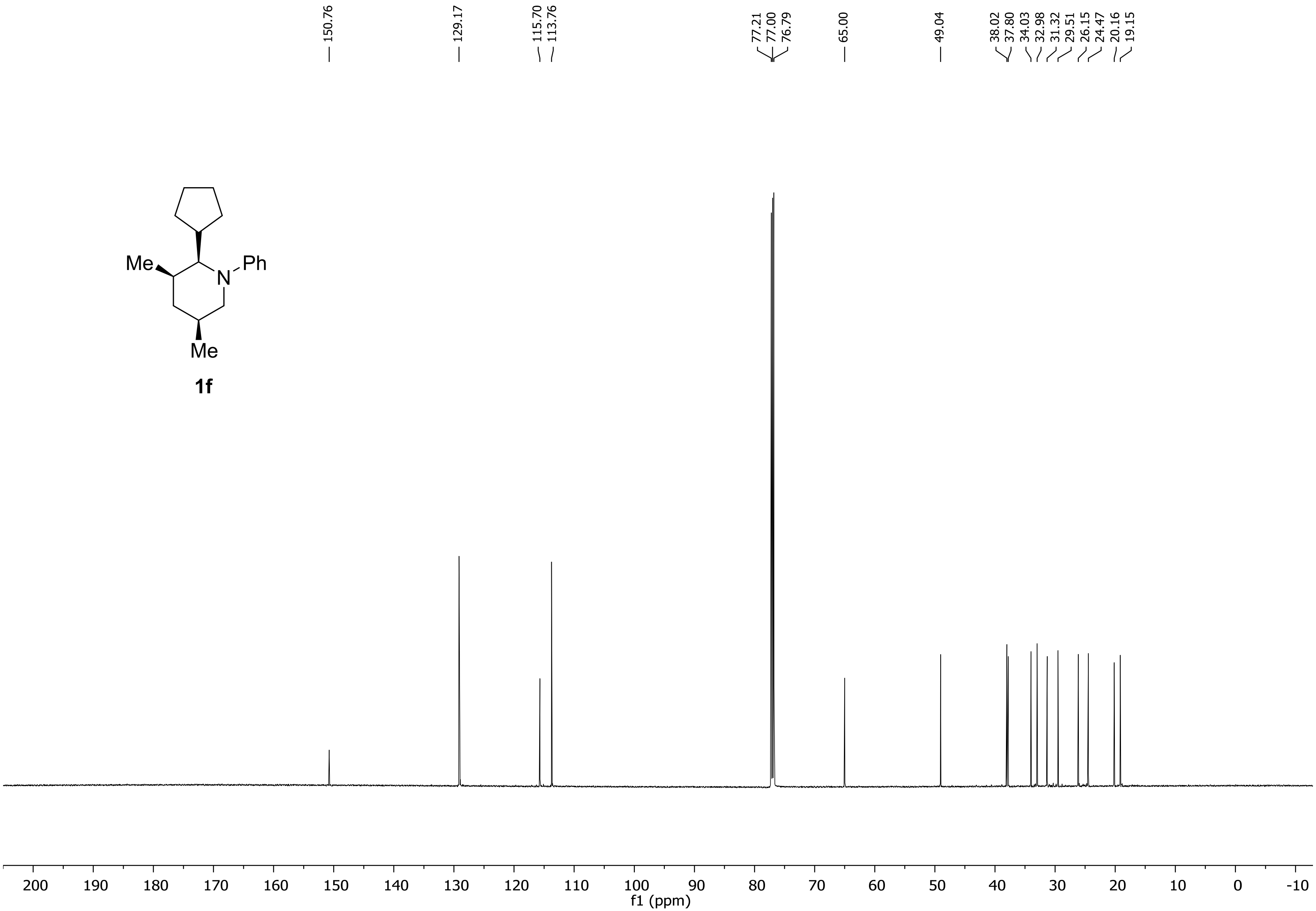

7.26
7.20
7.19
7.18
6.86
6.85
6.66
6.65
6.64
3.78
3.77
3.76
3.75
3.74
3.45
3.44
3.43
3.42
2.63
2.61
2.61
2.59
1.74
1.74
1.73
1.72
1.71
1.70
1.68
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.61
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.37
1.29
1.28
1.26
1.25
1.24
1.19
1.18
1.17
1.16
1.15
1.03
1.01
0.99
0.97
0.92
0.91
0.90
0.86
0.85
1.62
1.73
0.82
0.99
1.00
1.03
3.84
1.05
1.32
1.03
1.11
5.38
2.66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

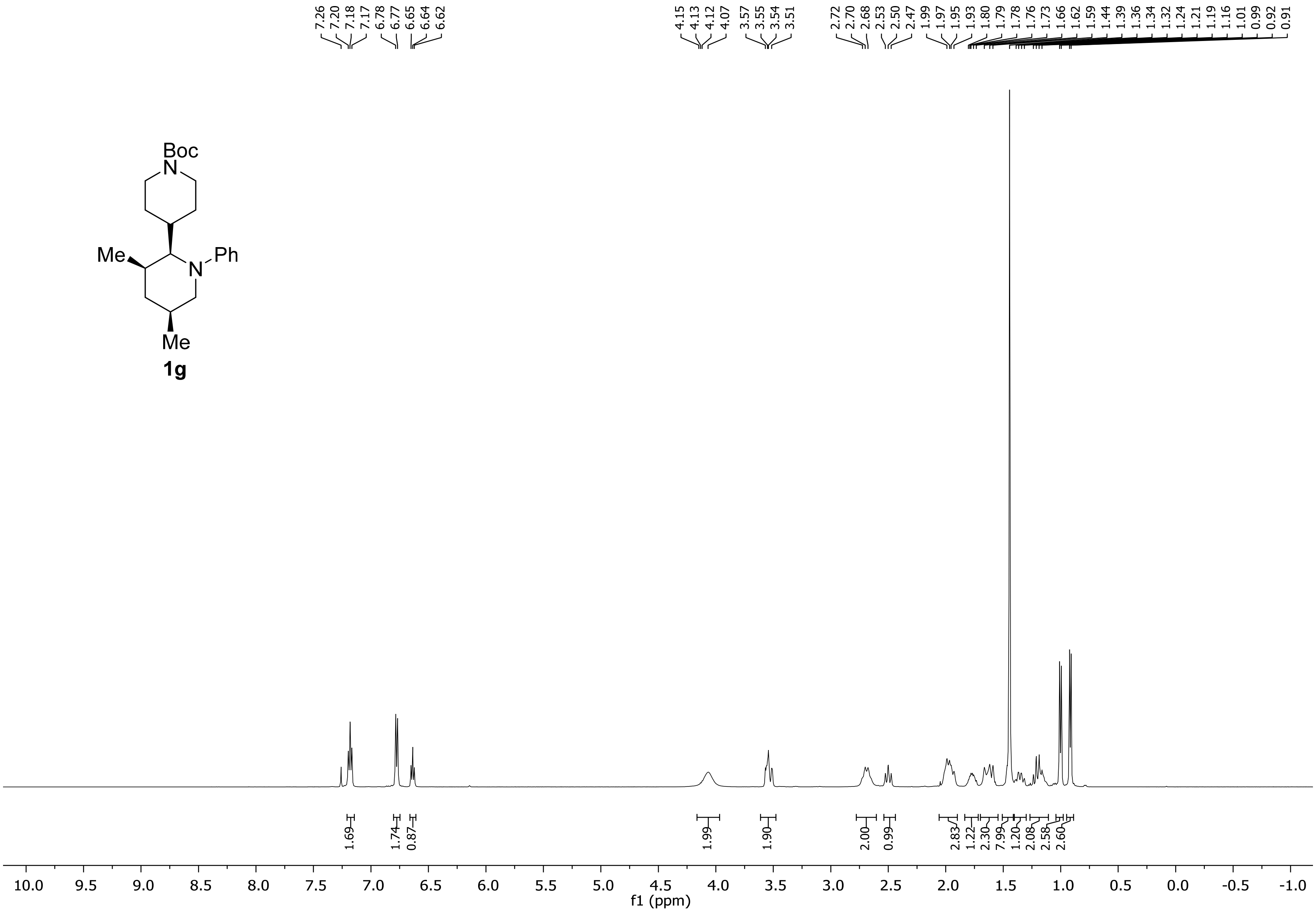

151.35
129.10
116.37
114.73
77.21
77.00
76.79
59.93
48.21
40.42
34.96
29.65
26.24
19.29
16.98
11.71
11.60
Et
Et
N
Ph
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1e

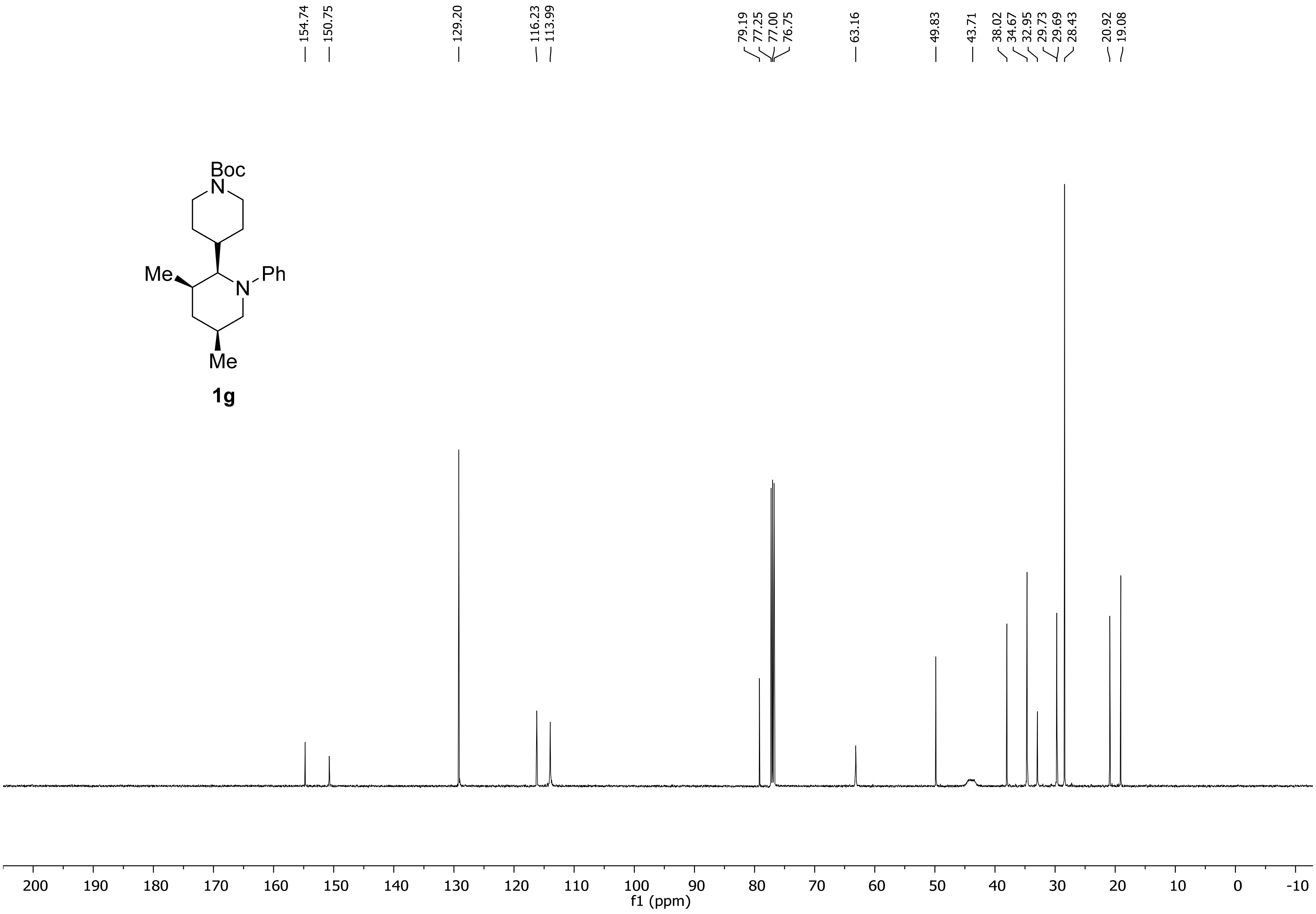

7.19
7.17
7.16
6.80
6.78
6.62
6.61
6.59
3.58
3.57
3.56
3.55
3.50
3.47
2.62
2.60
2.60
2.58
2.34
2.33
2.31
2.30
1.96
1.95
1.95
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.60
1.55
1.54
1.54
1.52
1.52
1.40
1.38
1.37
1.35
1.33
1.32
1.31
1.30
1.29
1.29
1.27
1.25
1.25
1.24
1.24
1.22
1.21
1.19
1.17
1.15
0.93
0.92
0.90
0.89
Me
N
Ph
Me
1.83
1.94
0.84
1.01
1.03
1.00
1.00
2.03
1.07
3.25
4.00
4.32
3.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

1f

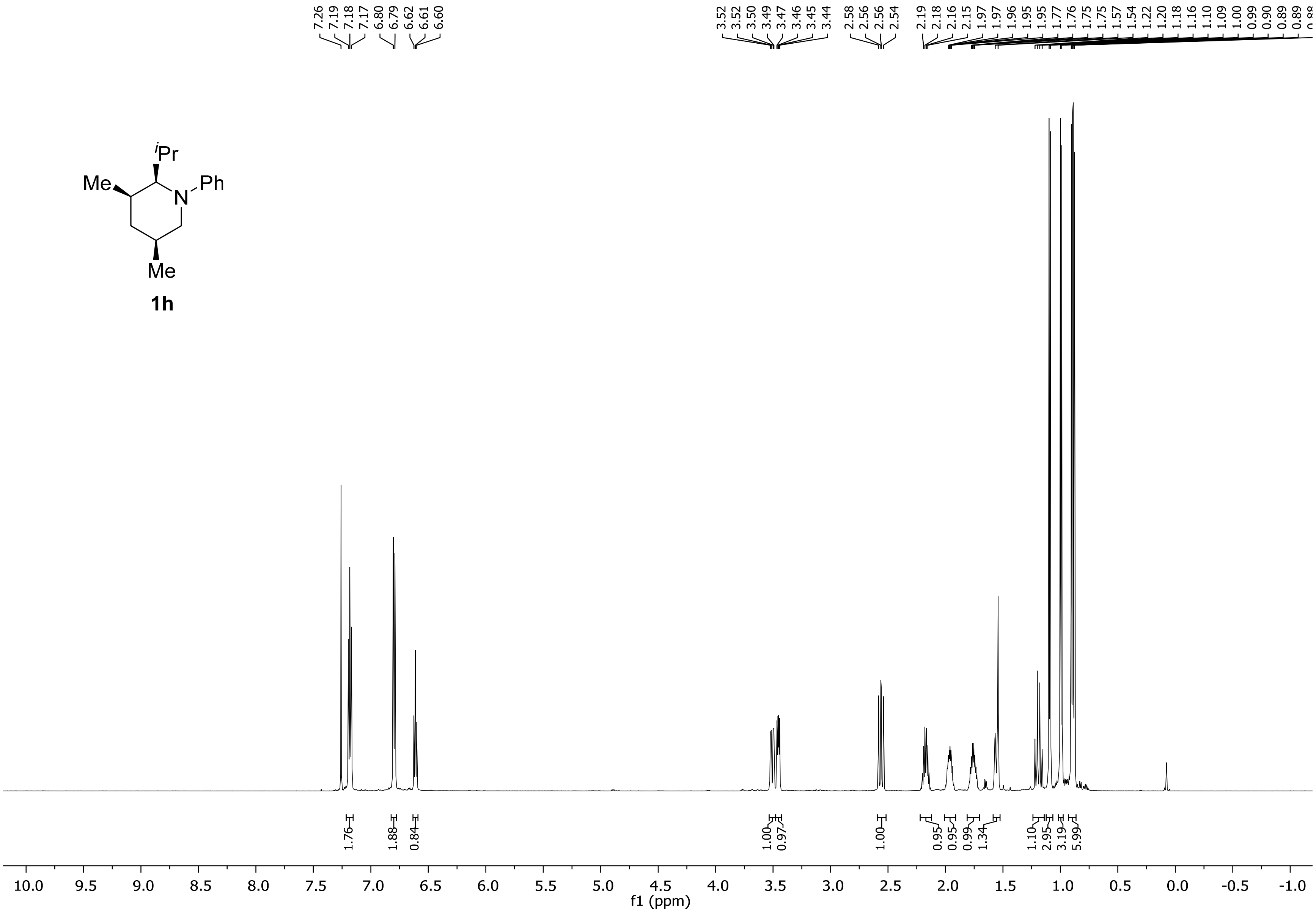

150.76
129.17
115.70
113.76
77.21
77.00
76.79
65.00
49.04
38.02
37.80
34.03
32.98
31.32
29.51
26.15
24.47
20.16
19.15
Me
N
Ph
Me
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
7.20
7.18
7.17
6.78
6.77
6.65
6.64
6.62
4.15
4.13
4.12
4.07
3.57
3.55
3.54
3.51
2.72
2.70
2.68
2.53
2.50
2.47
1.99
1.97
1.95
1.93
1.80
1.79
1.78
1.76
1.73
1.66
1.62
1.59
1.44
1.39
1.36
1.34
1.32
1.24
1.21
1.19
1.16
1.01
0.99
0.92
0.91
Boc
N
Me
N
Ph
Me
1.69
1.74
0.87
1.99
1.90
2.00
0.99
2.83
1.22
2.30
7.99
1.20
2.08
2.58
2.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

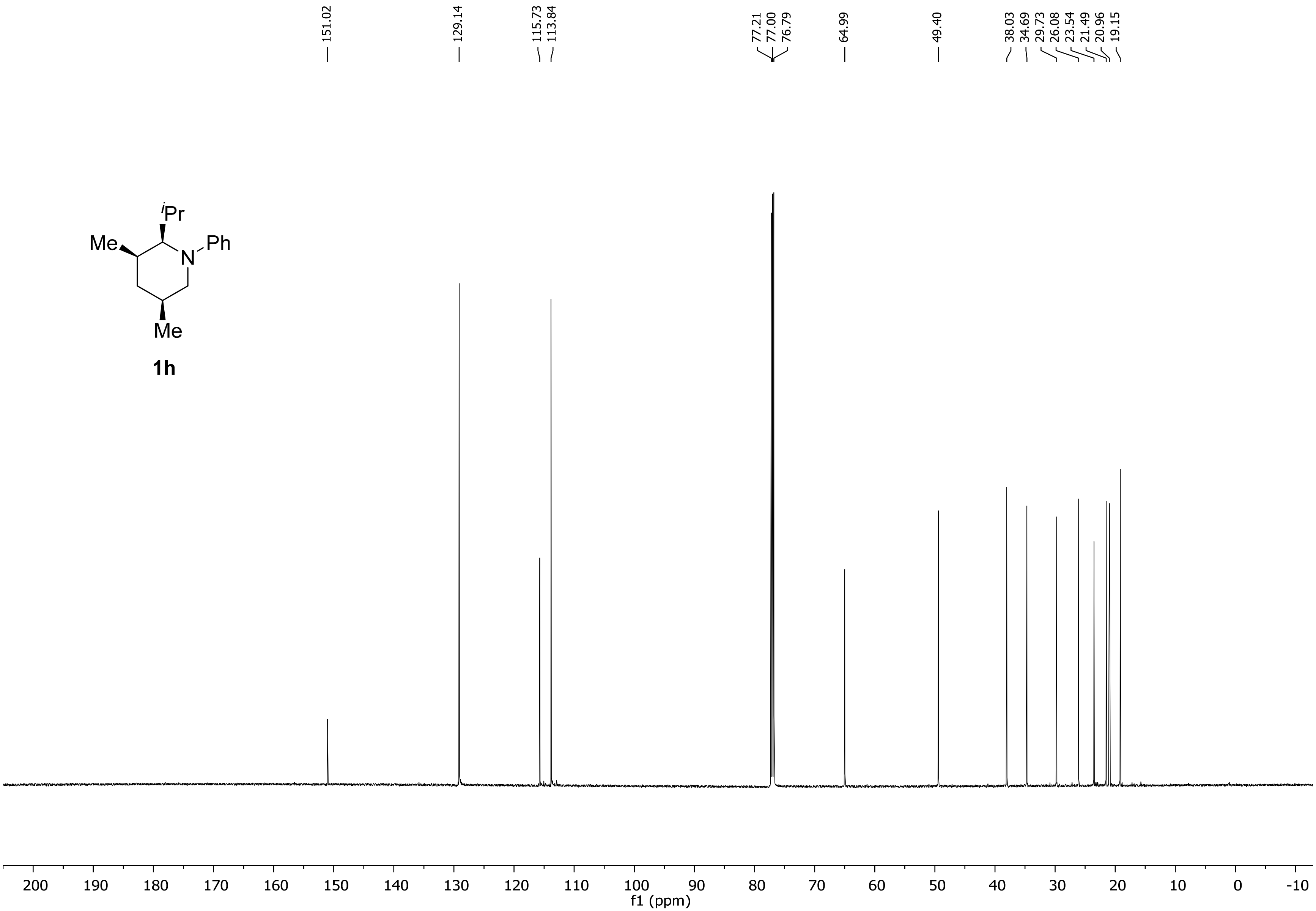
1g

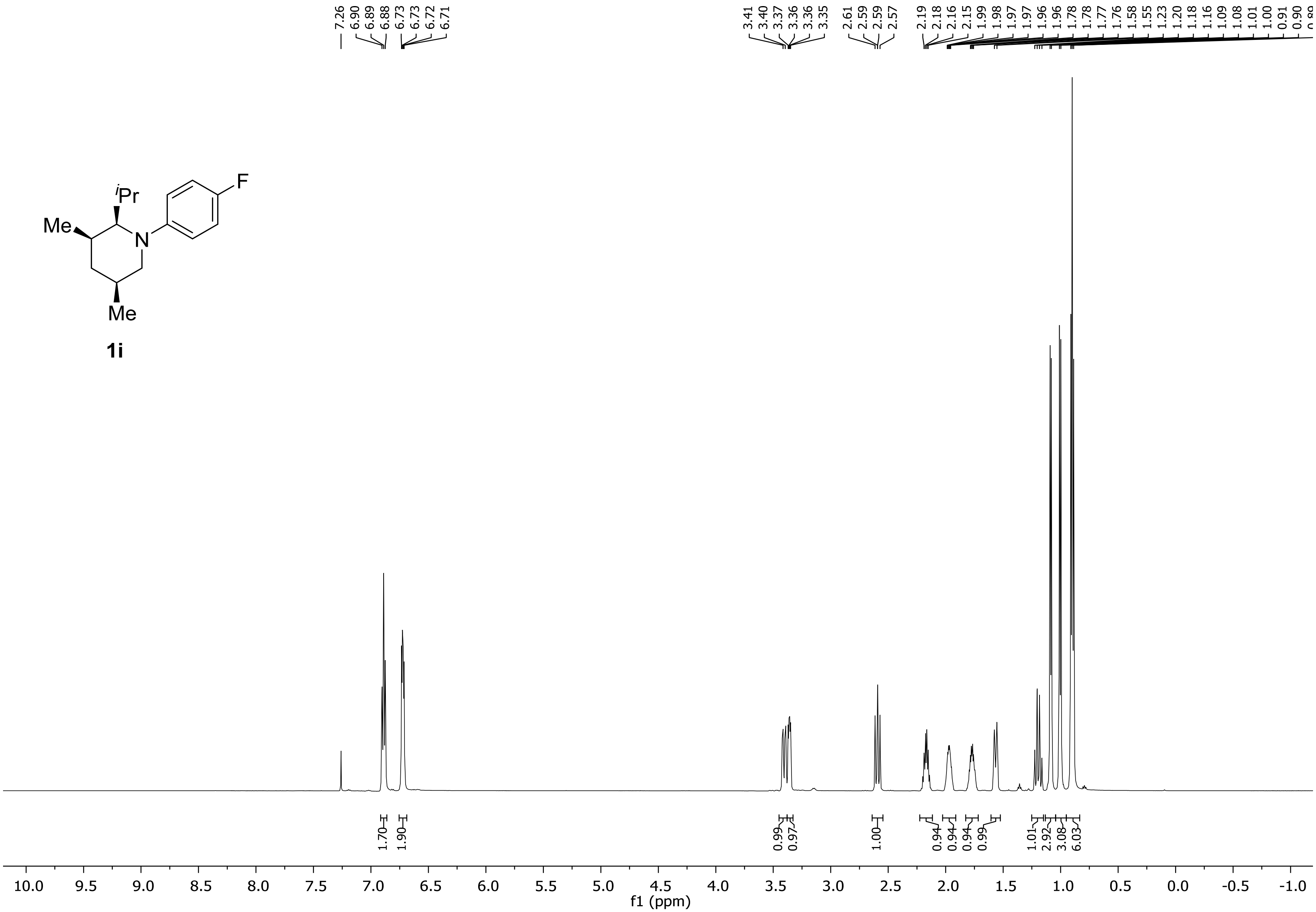

154.74
150.75
129.20
116.23
113.99
79.19
77.25
77.00
76.75
63.16
49.83
43.71
38.02
34.67
32.95
29.73
29.69
28.43
20.92
19.08
Boc
N
Me
N
Ph
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

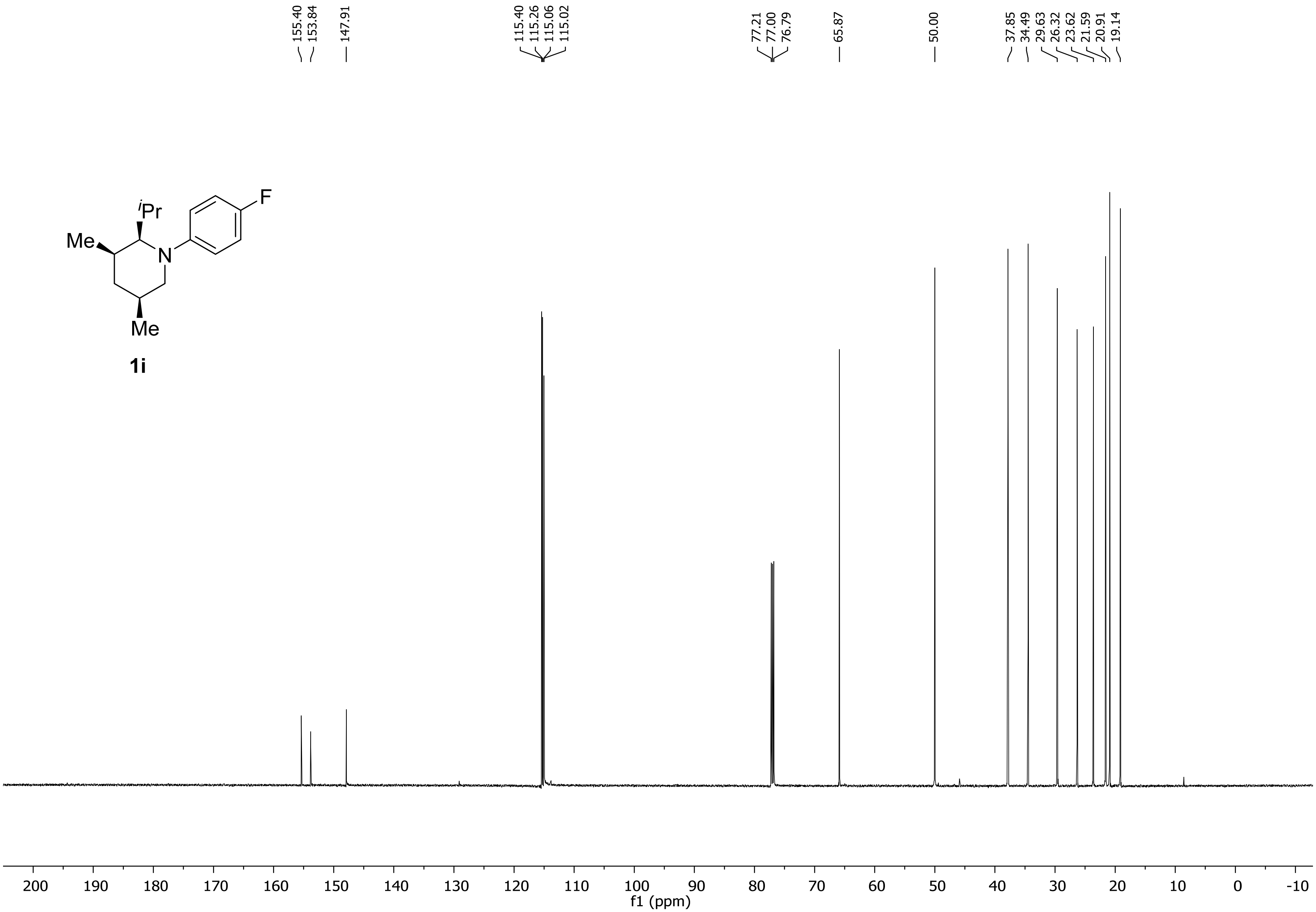
1g


7.26
7.19
7.18
7.17
6.80
6.79
6.62
6.61
6.60
3.52
3.52
3.50
3.49
3.47
3.46
3.45
3.44
2.58
2.56
2.56
2.54
2.19
2.18
2.16
2.15
1.97
1.97
1.96
1.95
1.95
1.77
1.76
1.75
1.75
1.57
1.54
1.22
1.20
1.18
1.16
1.10
1.09
1.00
0.99
0.90
0.89
iPr
Me
N
Ph
Me
1.76
1.88
0.84
1.00
0.97
1.00
0.95
0.95
0.99
1.34
1.10
2.95
3.19
5.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

1h

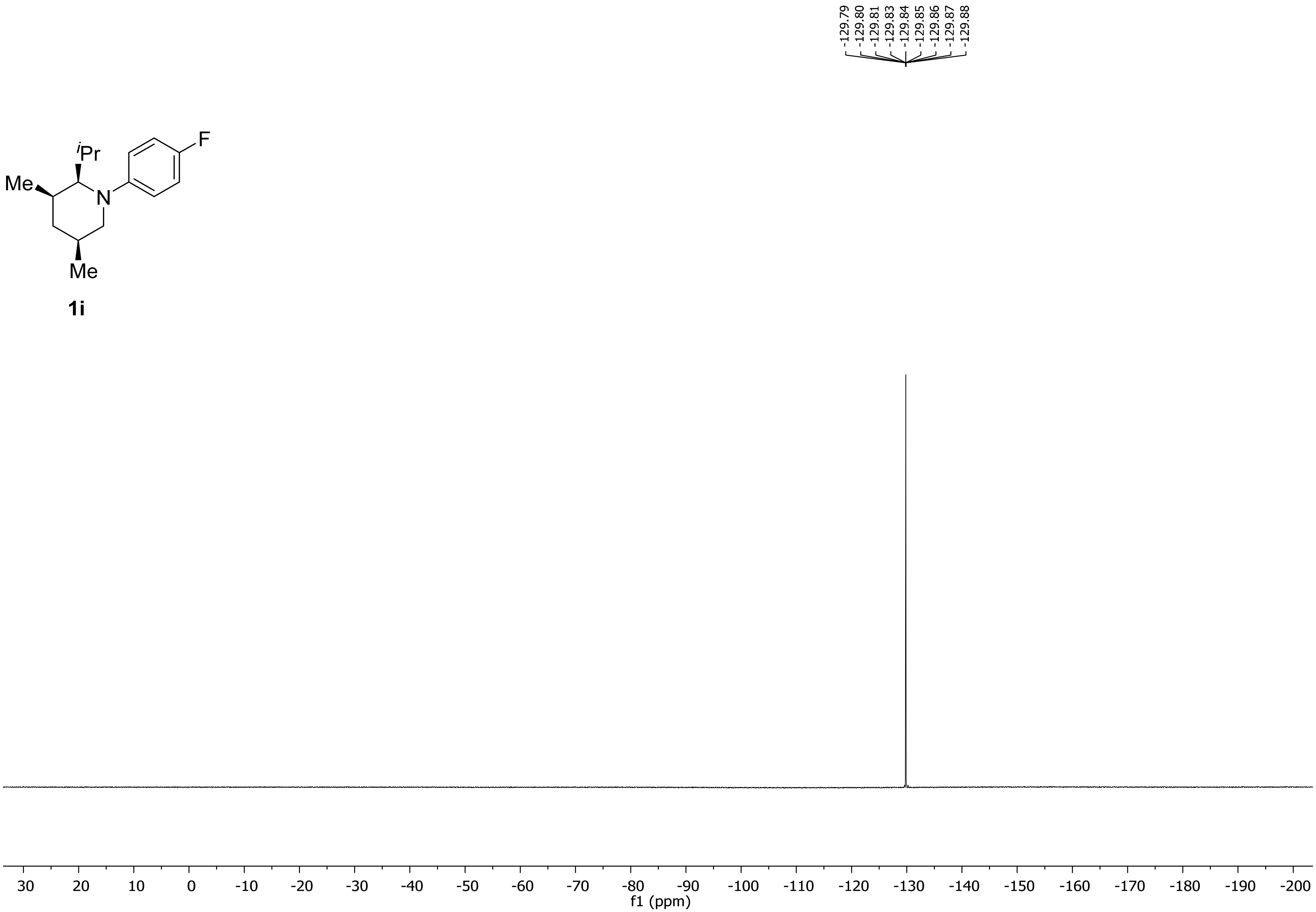

151.02
129.14
115.73
113.84
77.21
77.00
76.79
64.99
49.40
38.03
34.69
29.73
26.08
23.54
21.49
20.96
19.15
^{i}Pr
Me
N
Ph
Me
1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

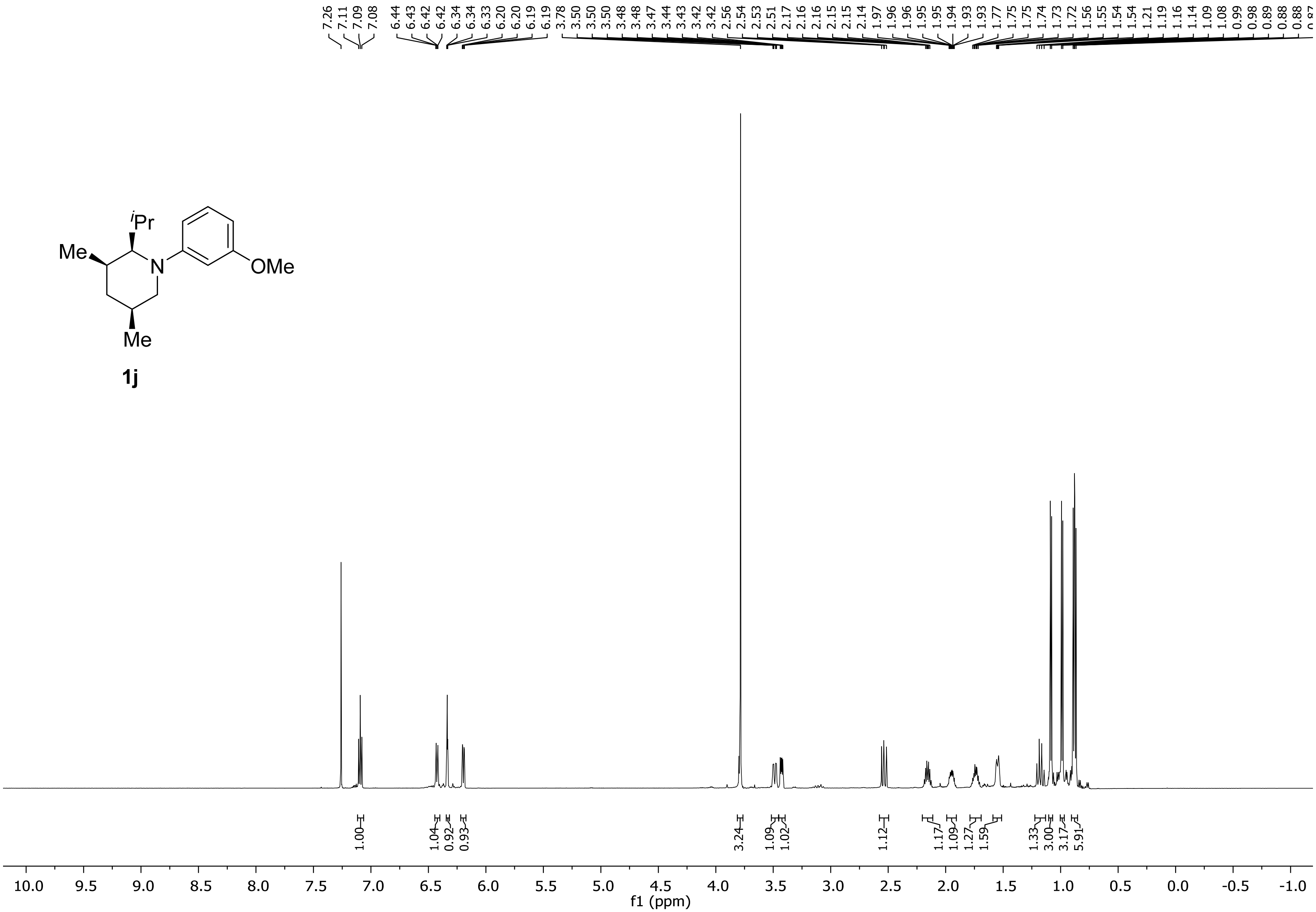

iPr
Me
N
F
Me
1i
7.26
6.90
6.89
6.88
6.73
6.73
6.72
6.71
3.41
3.40
3.37
3.36
3.36
3.35
2.61
2.59
2.59
2.57
2.19
2.18
2.16
2.15
1.99
1.98
1.97
1.97
1.96
1.96
1.78
1.77
1.76
1.58
1.55
1.23
1.20
1.18
1.16
1.09
1.08
1.01
1.00
0.91
0.90
1.70
1.90
0.99
0.97
1.00
0.94
0.94
0.94
0.99
1.01
2.92
3.08
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


155.40
153.84
147.91
115.40
115.26
115.06
115.02
77.21
77.00
76.79
65.87
50.00
37.85
34.49
29.63
26.32
23.62
21.59
20.91
19.14
ⁱPr
Me
N
F
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1i

1i

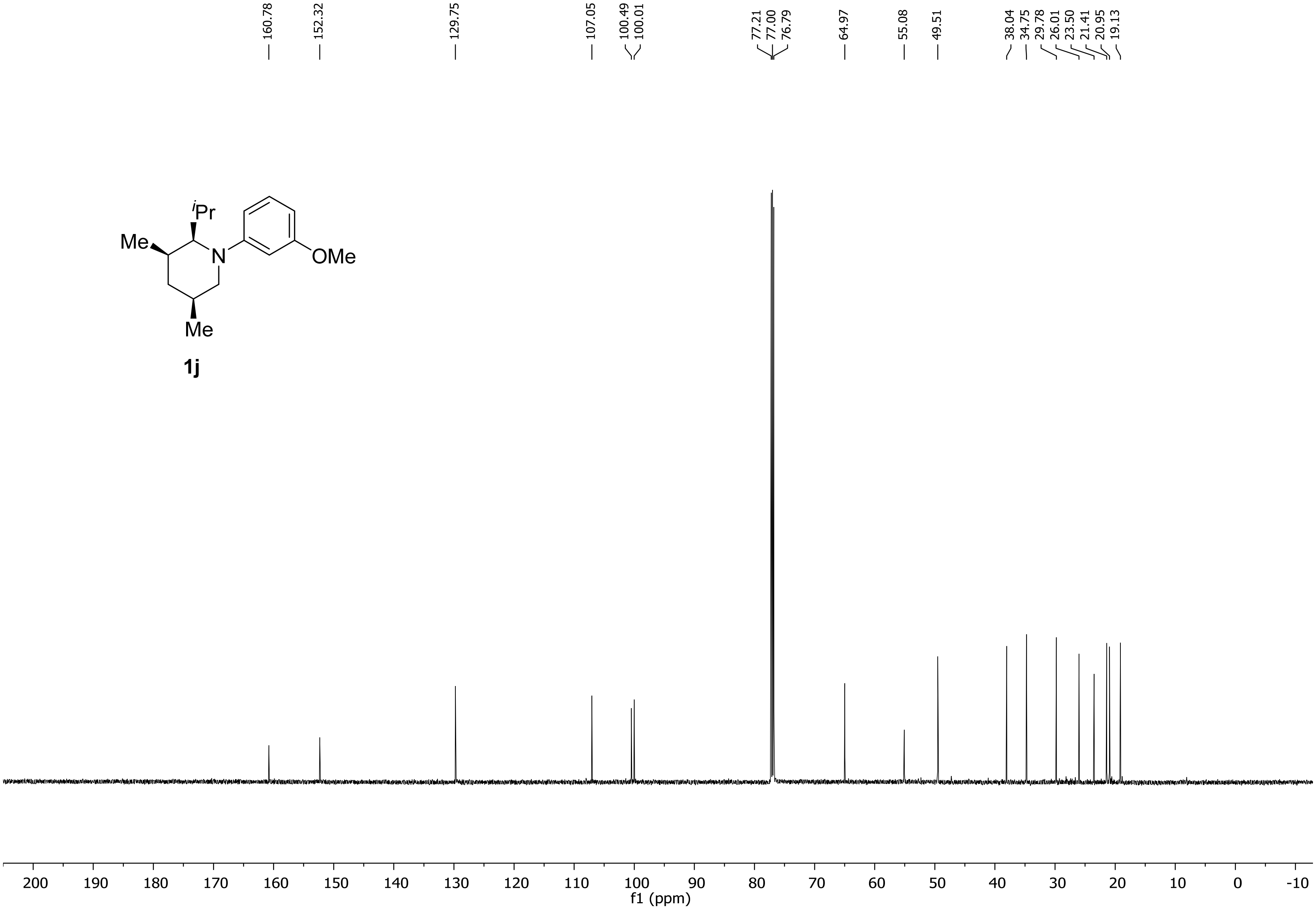

-129.79
-129.80
-129.81
-129.83
-129.84
-129.85
-129.86
-129.87
-129.88
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)



^{i}Pr
Me
N
OMe
Me

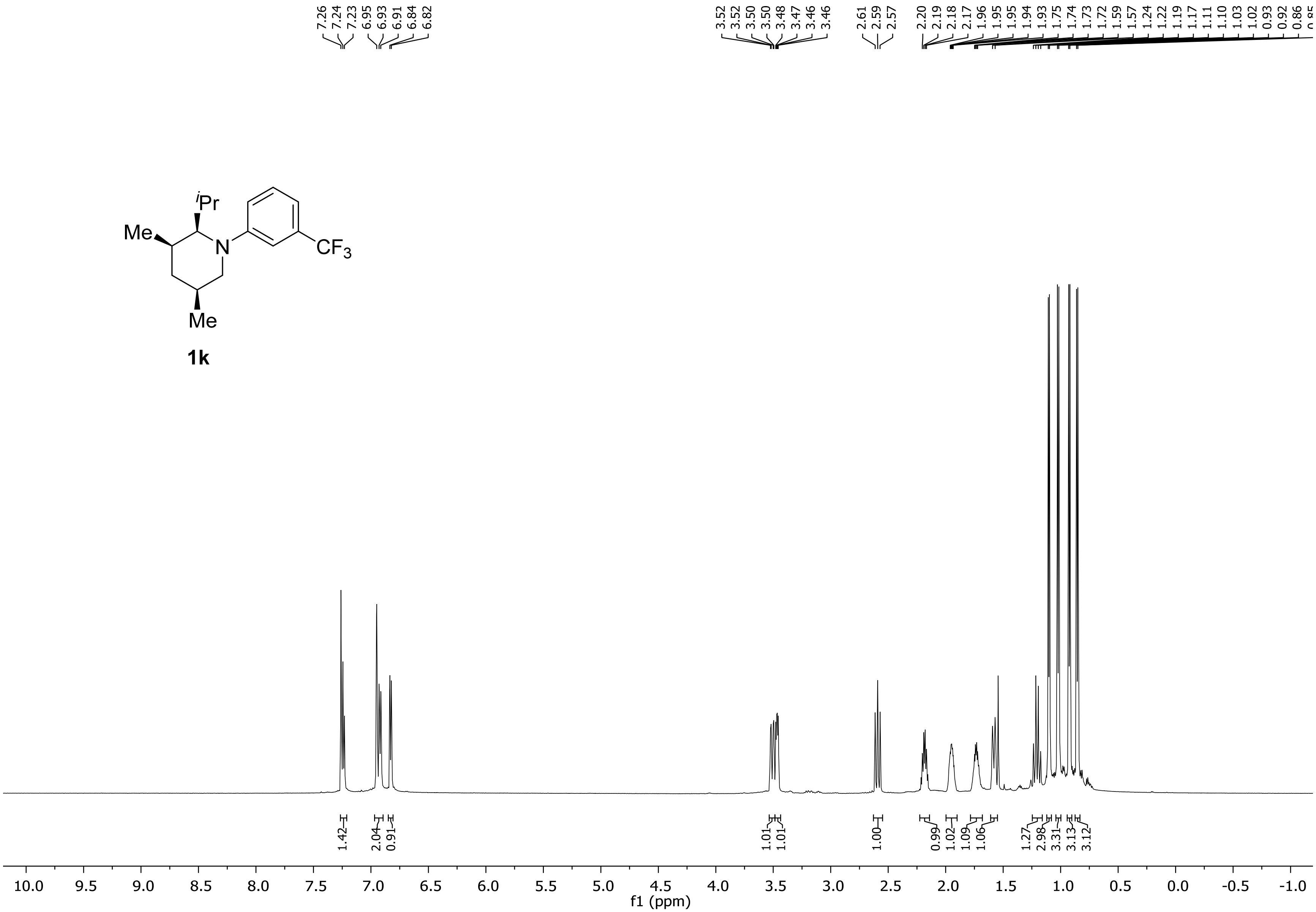
1j

7.26
7.11
7.09
7.08
6.44
6.43
6.42
6.42
6.34
6.34
6.33
6.20
6.20
6.19
6.19
3.78
3.50
3.50
3.50
3.48
3.47
3.44
3.43
3.42
3.42
2.56
2.54
2.53
2.51
2.17
2.16
2.16
2.15
2.15
2.14
1.97
1.96
1.95
1.95
1.94
1.93
1.93
1.77
1.75
1.75
1.74
1.73
1.72
1.56
1.55
1.54
1.54
1.21
1.19
1.16
1.14
1.09
1.08
0.99
0.98
0.89
0.88
0.88
1.00
1.04
0.92
0.93
3.24
1.09
1.02
1.12
1.17
1.09
1.27
1.59
1.33
3.00
3.17
5.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

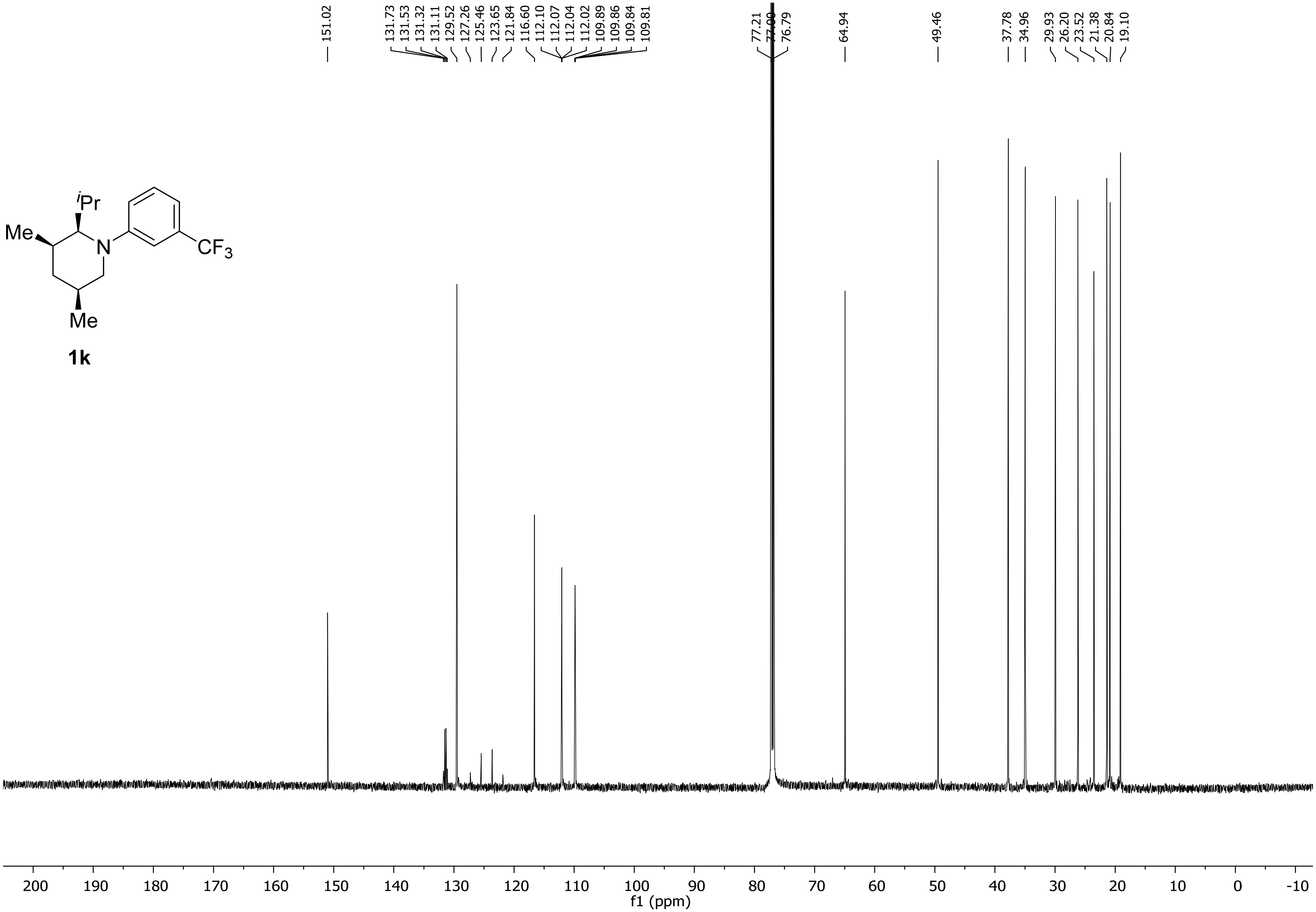

160.78
152.32
129.75
107.05
100.49
100.01
77.21
77.00
76.79
64.97
55.08
49.51
38.04
34.75
29.78
26.01
23.50
21.41
20.95
19.13
^{i}Pr
Me
N
OMe
Me
1j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

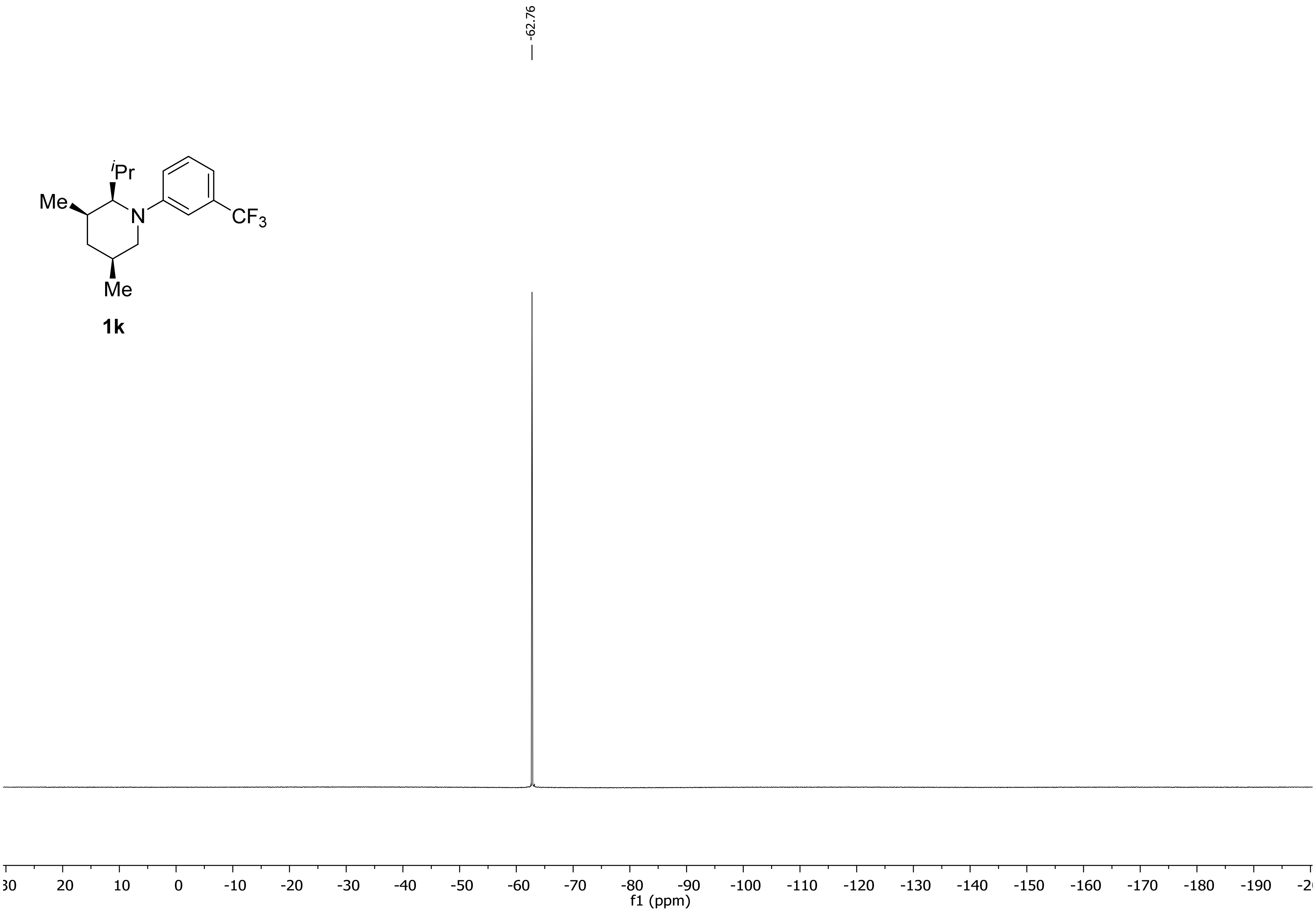
^{i}Pr
Me
N
CF$_3$
Me

1k



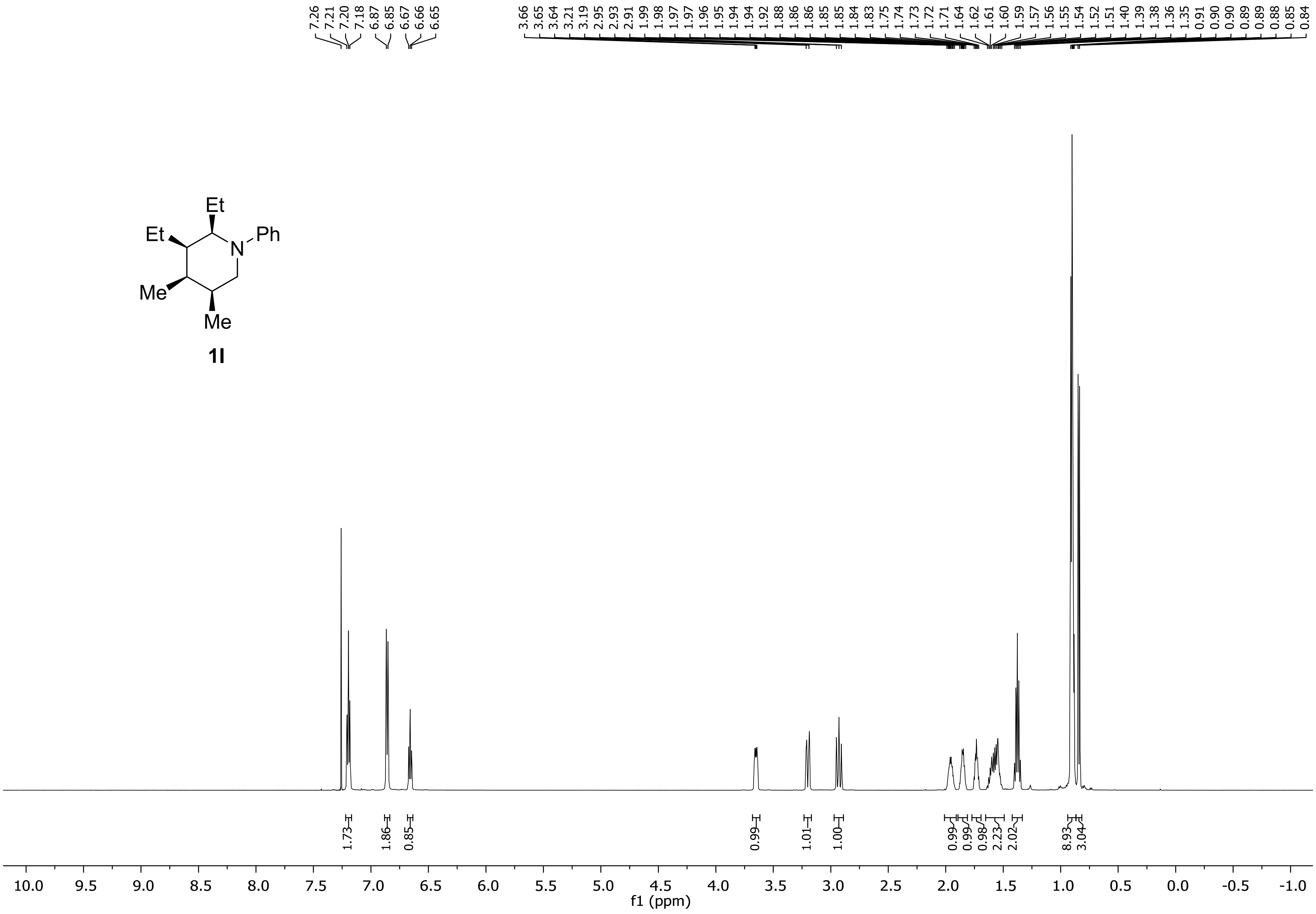
7.26
7.24
7.23
6.95
6.93
6.91
6.84
6.82
3.52
3.52
3.50
3.50
3.48
3.47
3.46
3.46
2.61
2.59
2.57
2.20
2.19
2.18
2.17
1.96
1.95
1.95
1.94
1.93
1.75
1.74
1.73
1.72
1.59
1.57
1.24
1.22
1.19
1.17
1.11
1.10
1.03
1.02
0.93
0.92
0.86
1.42
2.04
0.91
1.01
1.01
1.00
0.99
1.02
1.09
1.06
1.27
2.98
3.31
3.13
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


151.02
131.73
131.53
131.32
131.11
129.52
127.26
125.46
123.65
121.84
116.60
112.10
112.07
112.04
112.02
109.89
109.86
109.84
109.81
77.21
77.00
76.79
64.94
49.46
37.78
34.96
29.93
26.20
23.52
21.38
20.84
19.10
iPr
Me
N
CF3
Me
1k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

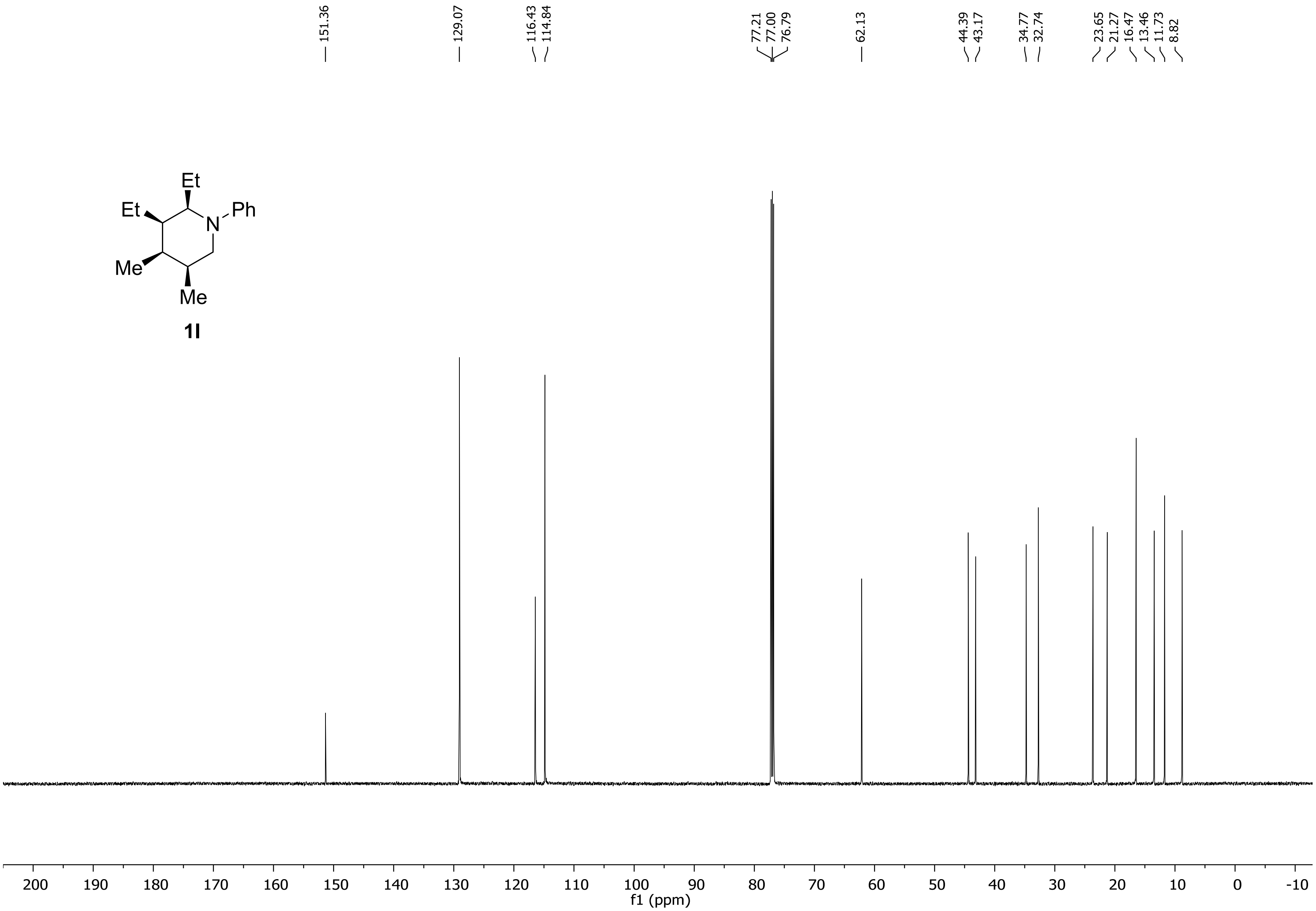


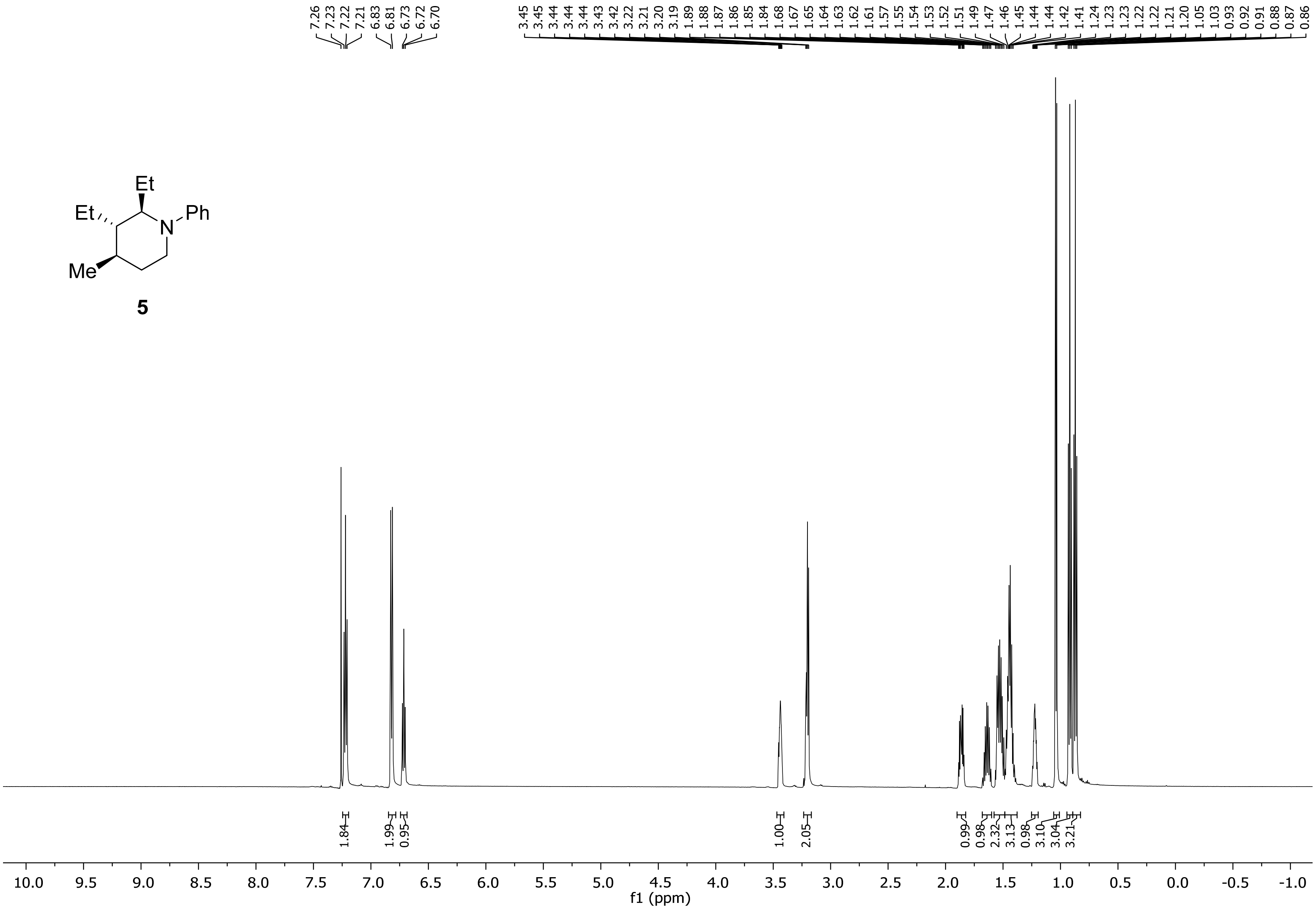
1k

-62.76
iPr
Me
N
CF3
Me
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

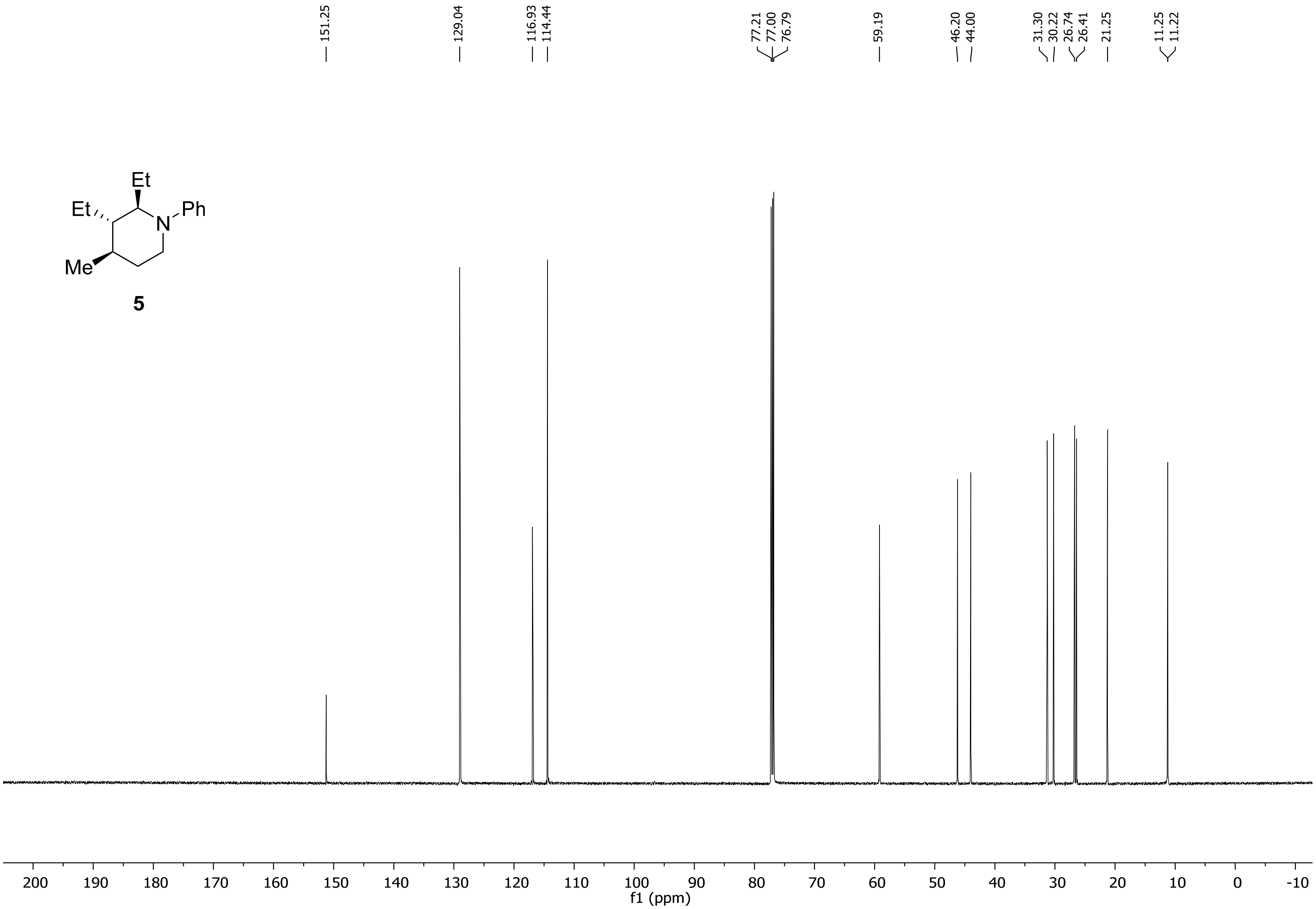

7.26
7.21
7.20
7.18
6.87
6.85
6.67
6.66
6.65
3.66
3.65
3.64
3.21
3.19
2.95
2.93
2.91
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.94
1.92
1.88
1.86
1.86
1.85
1.85
1.84
1.83
1.75
1.74
1.73
1.72
1.71
1.64
1.62
1.61
1.60
1.59
1.57
1.56
1.55
1.54
1.52
1.51
1.40
1.39
1.38
1.36
1.35
0.91
0.90
0.89
0.89
0.88
0.85
0.84
Et
Et
N
Ph
Me
Me
1.73
1.86
0.85
0.99
1.01
1.00
0.99
0.99
0.98
2.23
2.02
8.93
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

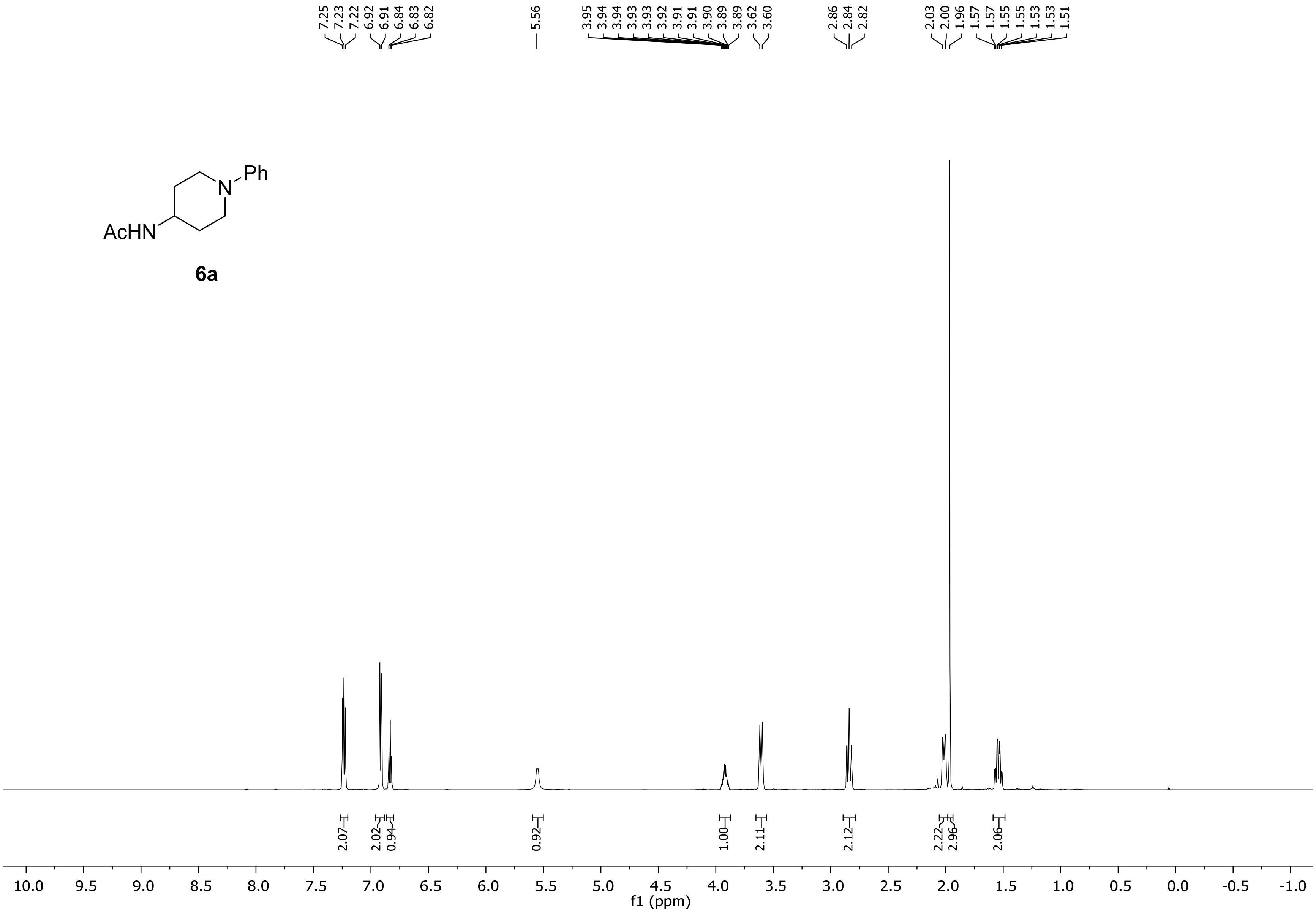
1l


151.36
129.07
116.43
114.84
77.21
77.00
76.79
62.13
44.39
43.17
34.77
32.74
23.65
21.27
16.47
13.46
11.73
8.82
Et
Et
N
Ph
Me
Me
1l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

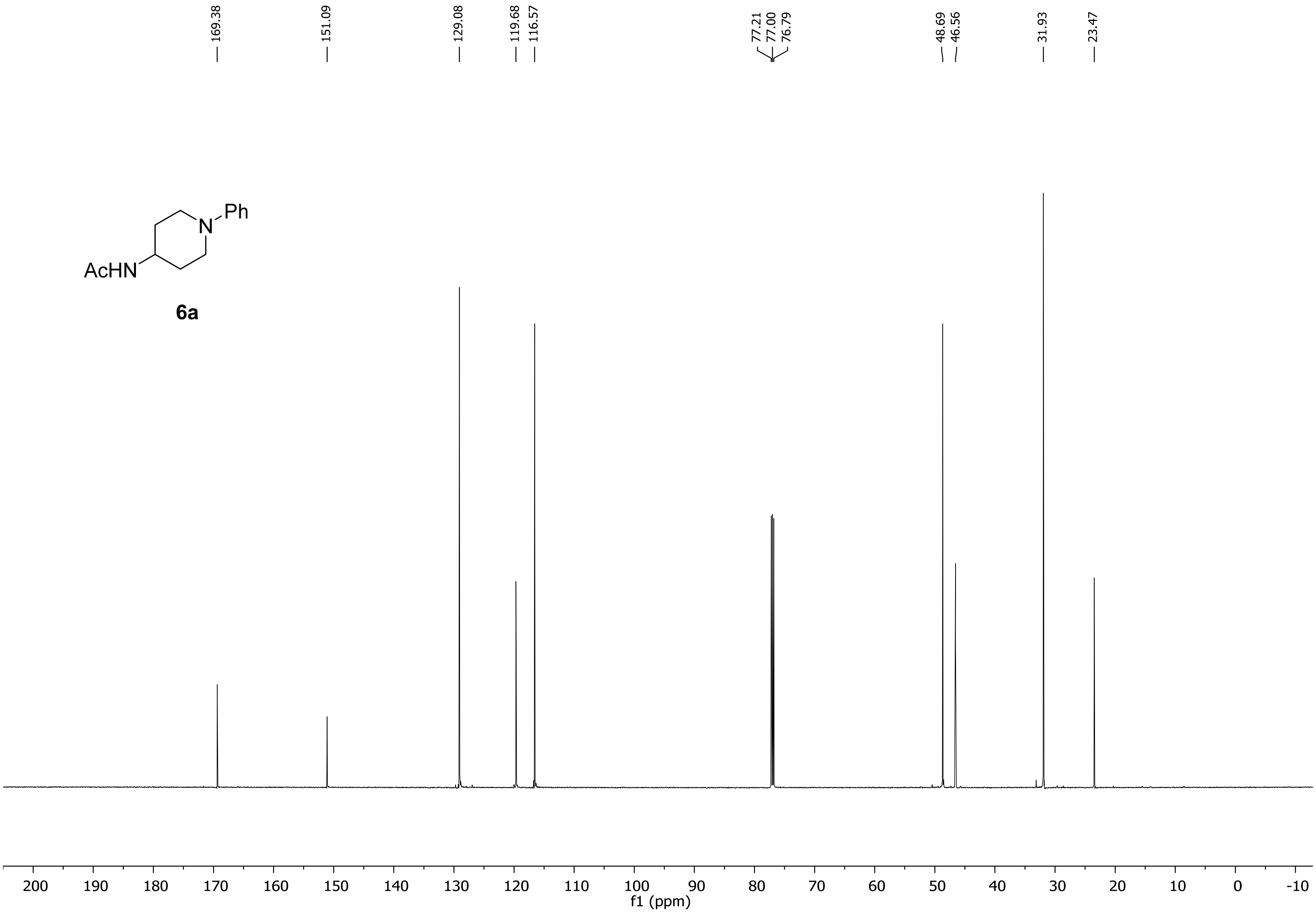

7.26
7.23
7.22
7.21
6.83
6.81
6.73
6.72
6.70
3.45
3.45
3.44
3.44
3.44
3.43
3.42
3.22
3.21
3.20
3.19
1.89
1.88
1.87
1.86
1.85
1.84
1.68
1.67
1.65
1.64
1.63
1.62
1.61
1.57
1.55
1.54
1.53
1.52
1.51
1.49
1.47
1.46
1.45
1.44
1.44
1.42
1.41
1.24
1.23
1.23
1.22
1.22
1.21
1.20
1.05
1.03
0.93
0.92
0.91
0.88
0.87
0.86
Et
Et
N
Ph
Me
5
1.84
1.99
0.95
1.00
2.05
0.99
0.98
2.32
3.13
0.98
3.10
3.04
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

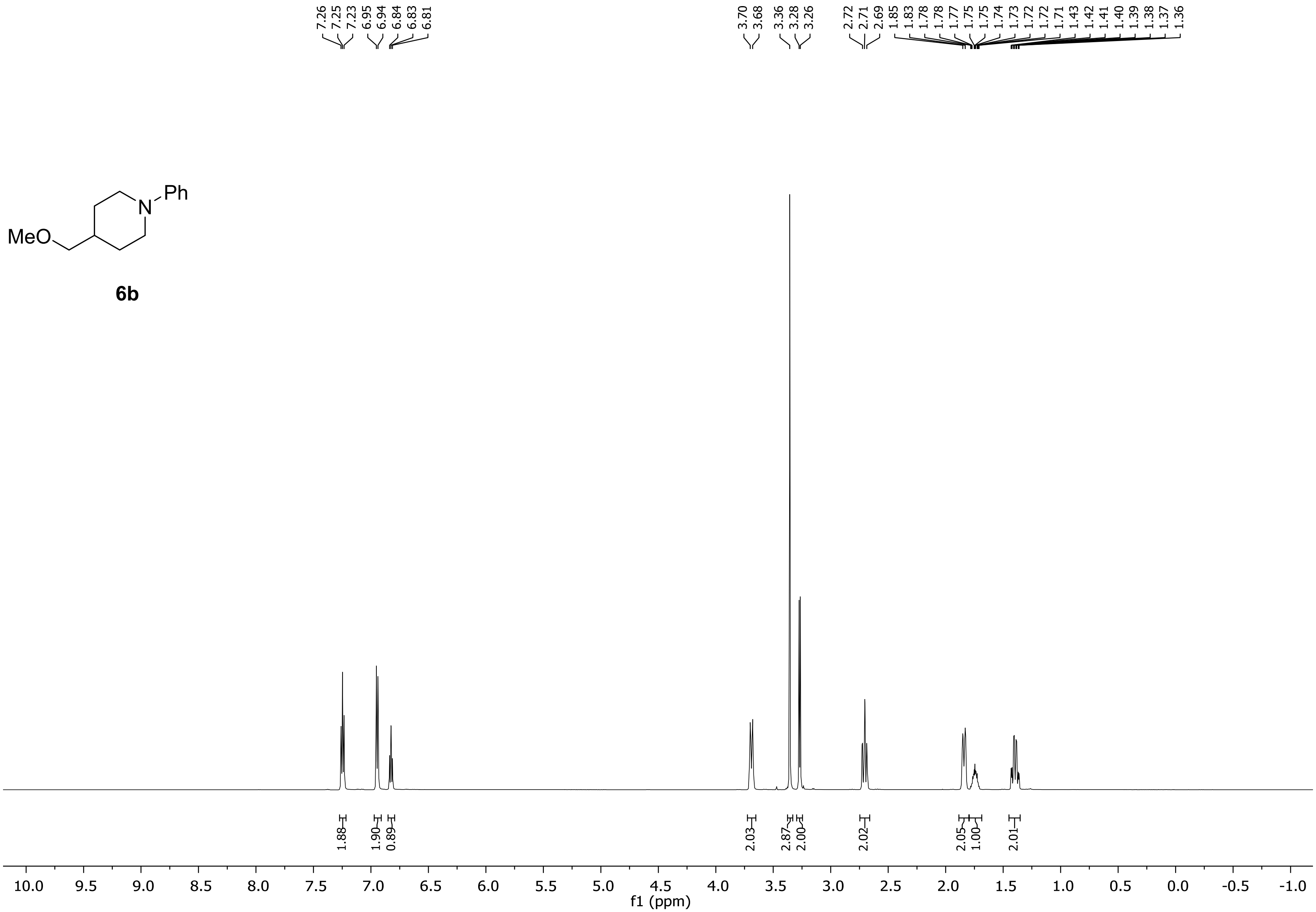
5

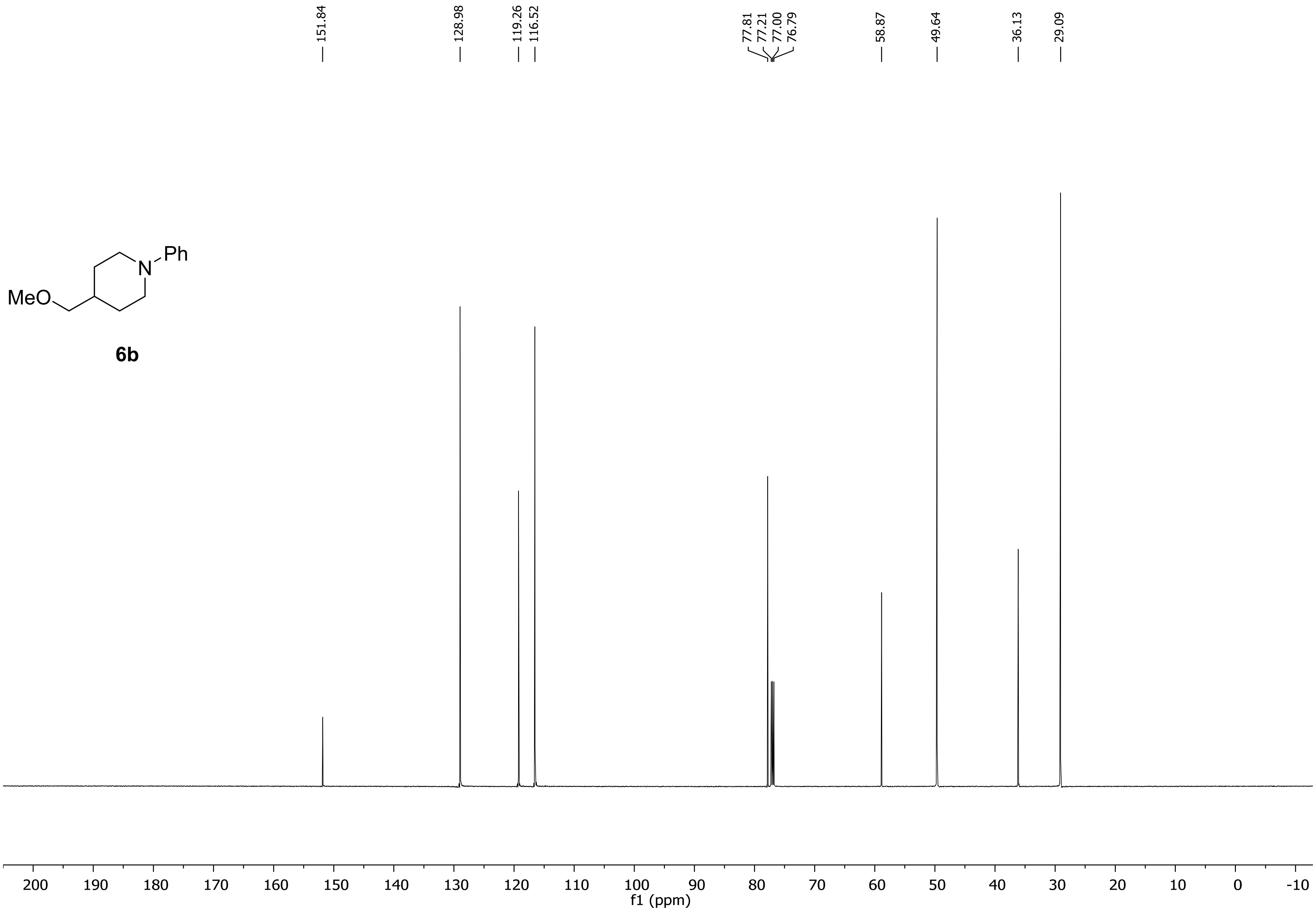

151.25
129.04
116.93
114.44
77.21
77.00
76.79
59.19
46.20
44.00
31.30
30.22
26.74
26.41
21.25
11.25
11.22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

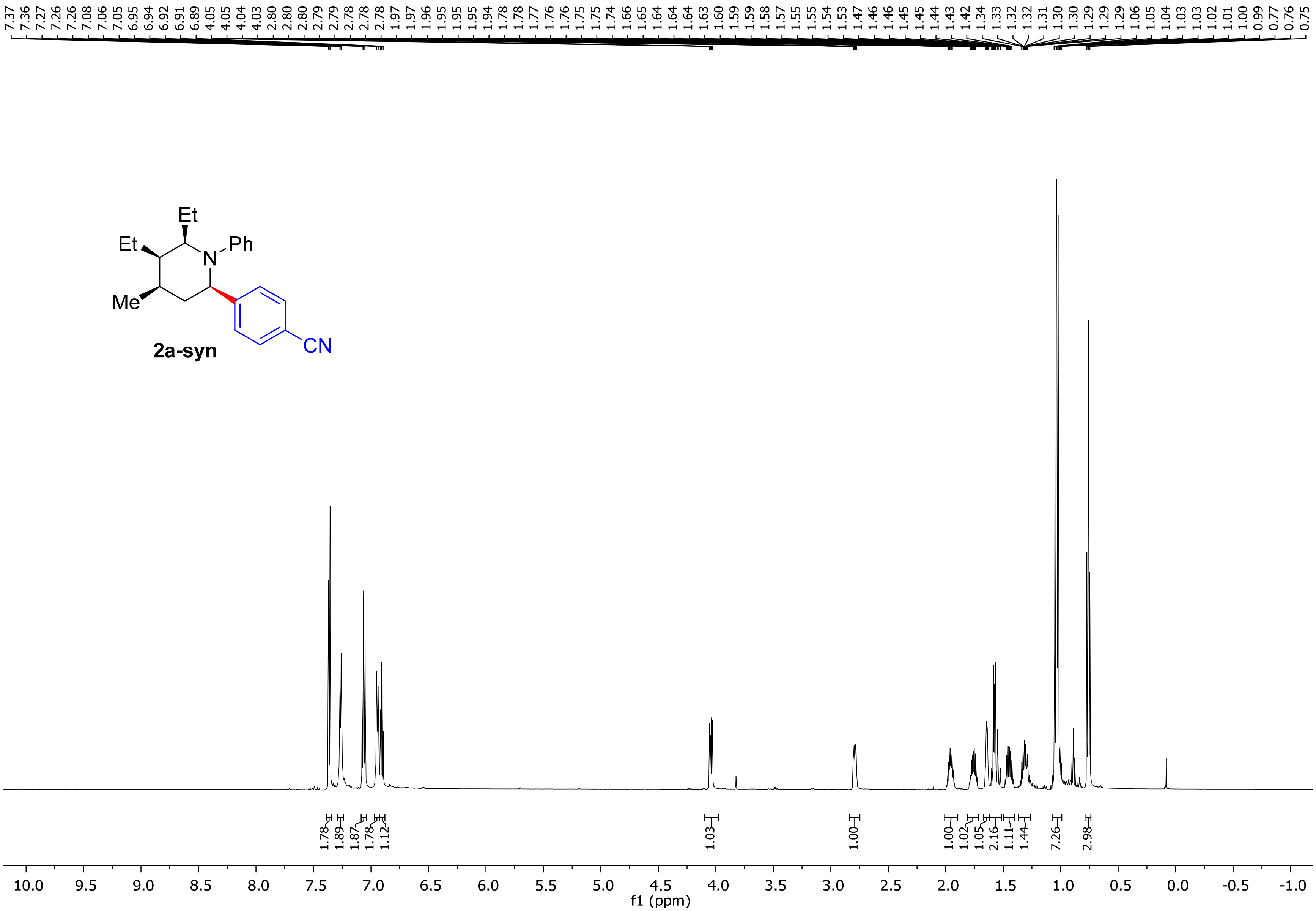

7.25
7.23
7.22
6.92
6.91
6.84
6.83
6.82
5.56
3.95
3.94
3.94
3.93
3.93
3.92
3.91
3.91
3.90
3.89
3.89
3.62
3.60
2.86
2.84
2.82
2.03
2.00
1.96
1.57
1.57
1.55
1.55
1.53
1.53
1.51
Ph
N
AcHN
2.07
2.02
0.94
0.92
1.00
2.11
2.12
2.22
2.96
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

6a

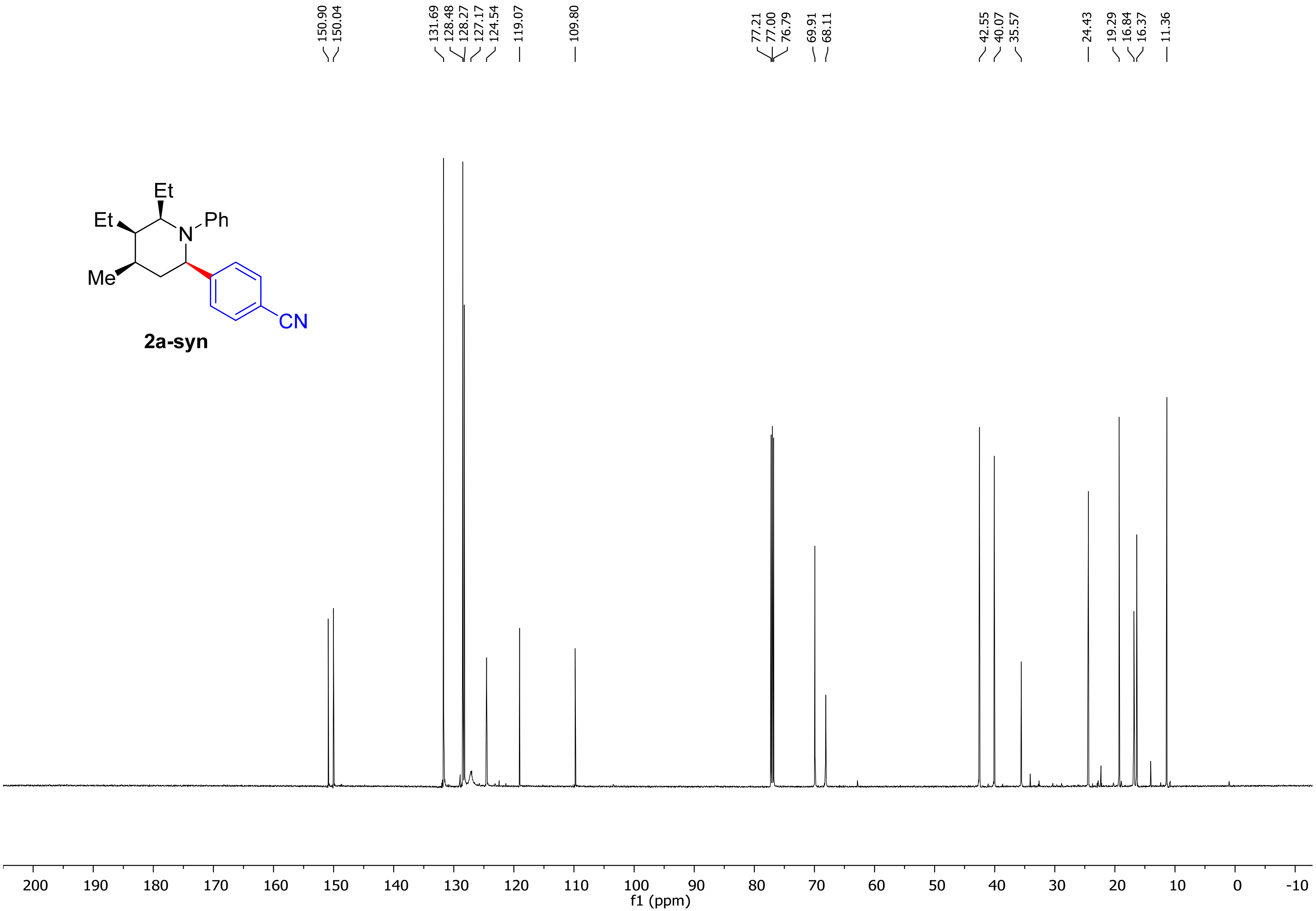

169.38
151.09
129.08
119.68
116.57
77.21
77.00
76.79
48.69
46.56
31.93
23.47
Ph
N
AcHN
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
N
Ph
6b
7.26
7.25
7.23
6.95
6.94
6.84
6.83
6.81
3.70
3.68
3.36
3.28
3.26
2.72
2.71
2.69
1.85
1.83
1.78
1.78
1.77
1.75
1.75
1.74
1.73
1.72
1.72
1.71
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.88
1.90
0.89
2.03
2.87
2.00
2.02
2.05
1.00
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

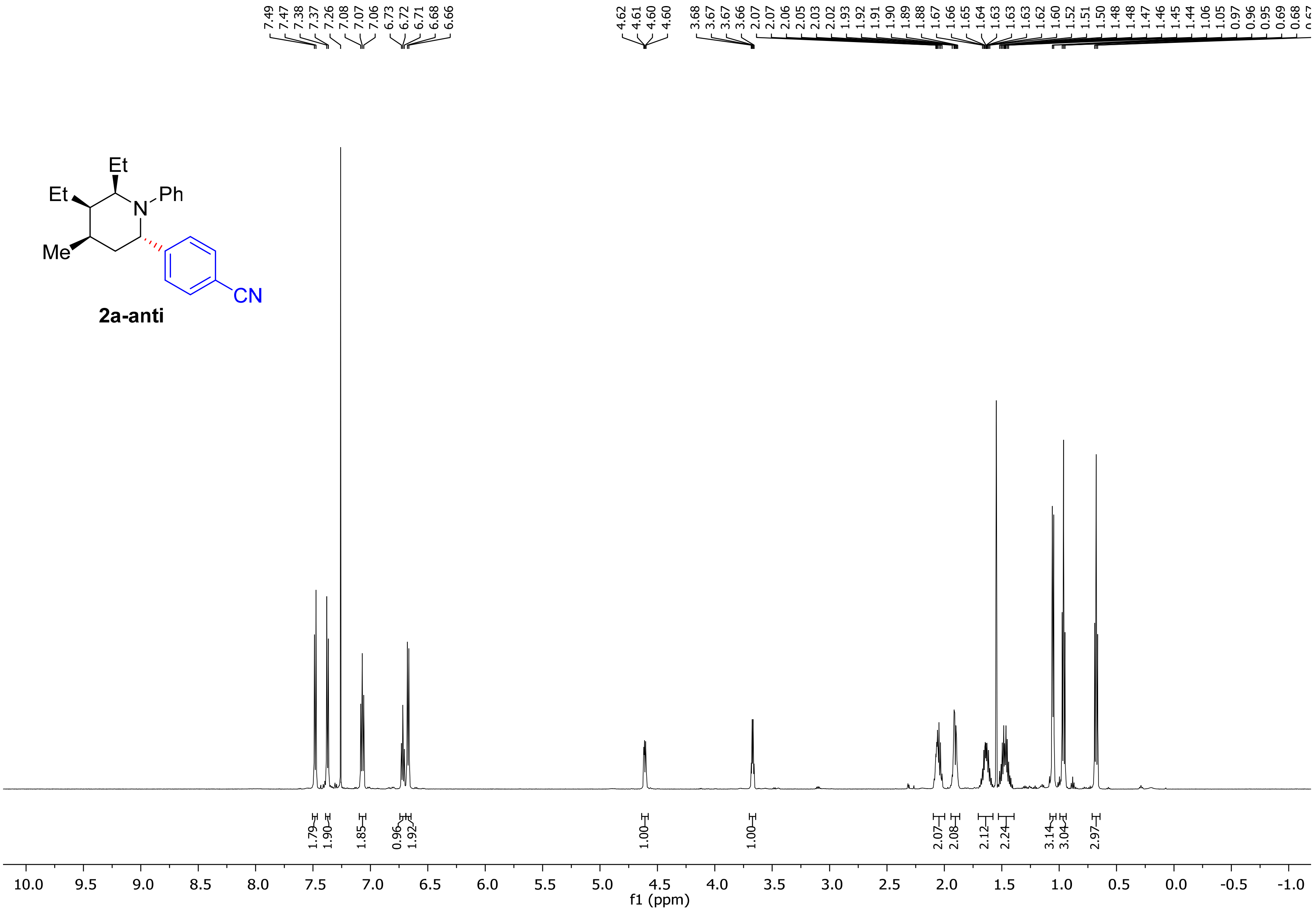

151.84
128.98
119.26
116.52
77.81
77.21
77.00
76.79
58.87
49.64
36.13
29.09
MeO
N
Ph
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.37
7.36
7.27
7.26
7.08
7.06
7.05
6.95
6.94
6.92
6.91
6.89
4.05
4.05
4.04
4.03
2.80
2.80
2.79
2.79
2.78
2.78
2.78
1.97
1.97
1.96
1.95
1.95
1.95
1.94
1.78
1.78
1.77
1.76
1.75
1.75
1.74
1.66
1.65
1.64
1.64
1.64
1.63
1.60
1.59
1.59
1.58
1.57
1.55
1.55
1.54
1.53
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.34
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.29
1.29
1.06
1.05
1.04
1.03
1.03
1.02
1.01
1.00
0.99
0.77
0.76
0.75
Et
Et
N
Ph
Me
CN
1.78
1.89
1.87
1.78
1.12
1.03
1.00
1.00
1.02
1.05
2.16
1.11
1.44
7.26
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

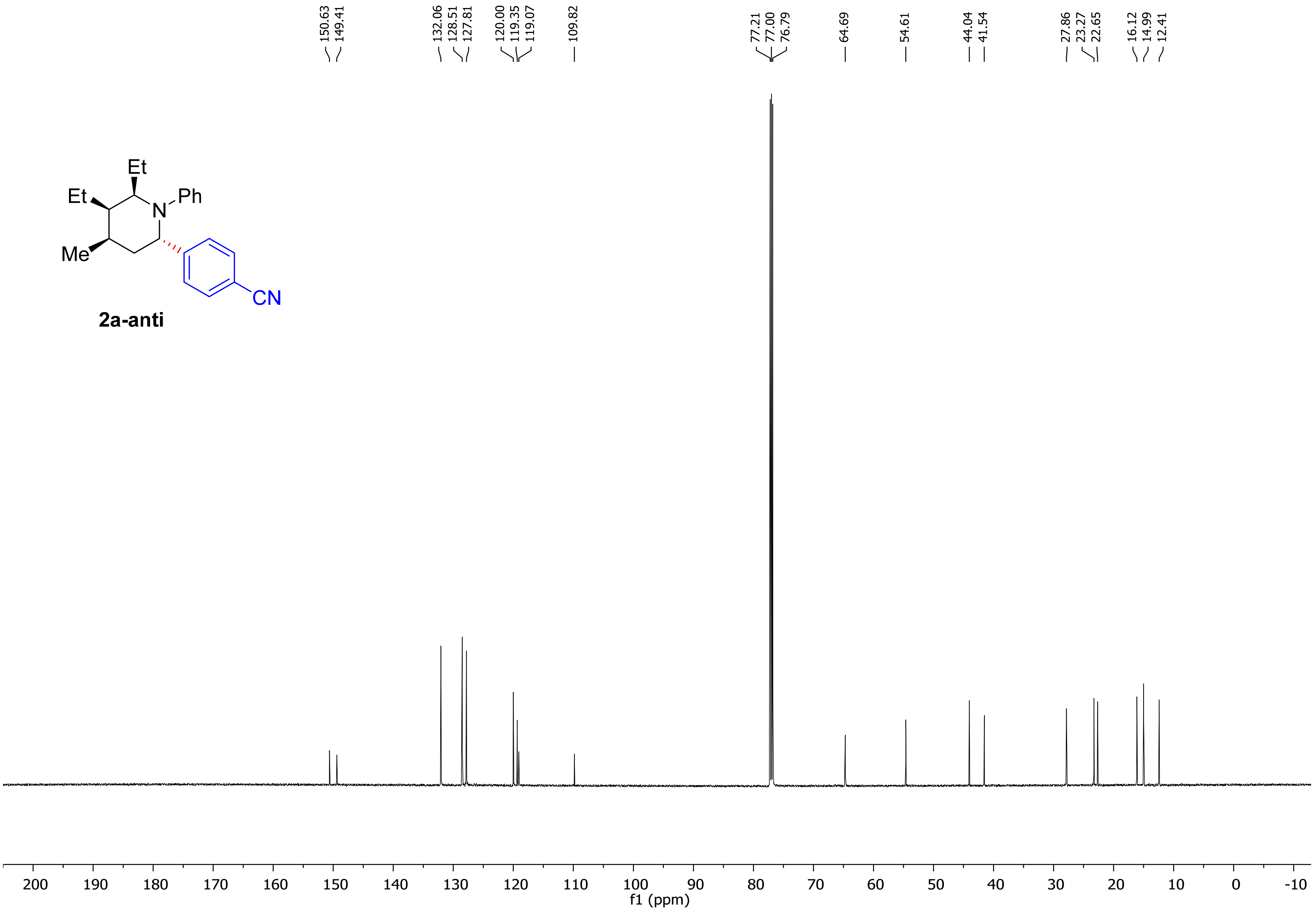
2a-syn


150.90
150.04
131.69
128.48
128.27
127.17
124.54
119.07
109.80
77.21
77.00
76.79
69.91
68.11
42.55
40.07
35.57
24.43
19.29
16.84
16.37
11.36
Et
Et
N
Ph
Me
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2a-syn

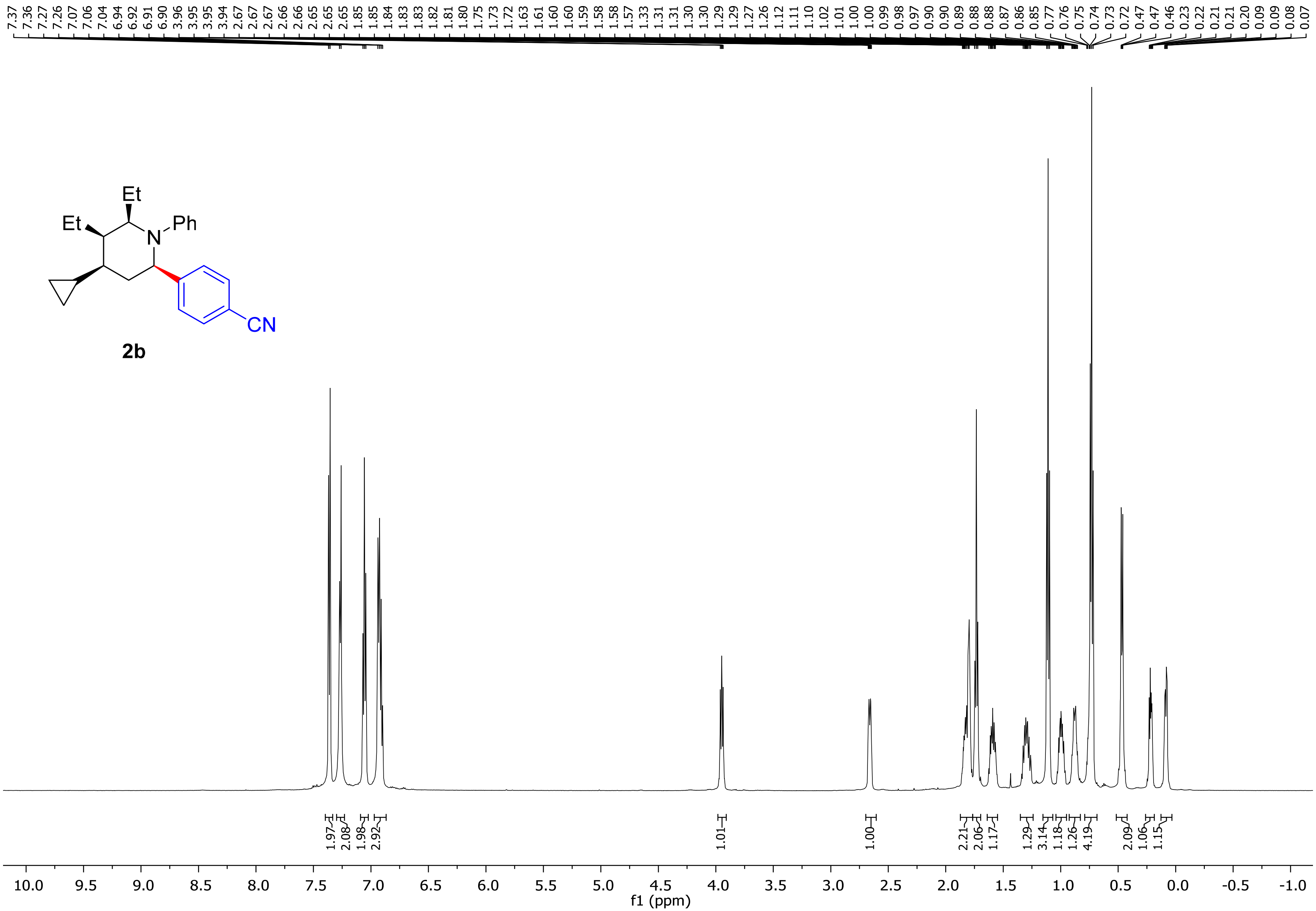

7.49
7.47
7.38
7.37
7.26
7.08
7.07
7.06
6.73
6.72
6.71
6.68
6.66
4.62
4.61
4.60
4.60
3.68
3.67
3.67
3.66
2.07
2.07
2.06
2.05
2.03
2.02
1.93
1.92
1.91
1.90
1.89
1.88
1.67
1.66
1.65
1.64
1.63
1.63
1.63
1.62
1.60
1.52
1.51
1.50
1.48
1.48
1.47
1.46
1.45
1.44
1.06
1.05
0.97
0.96
0.95
0.69
0.68
Et
Et
N
Ph
Me
CN
1.79
1.90
1.85
0.96
1.92
1.00
1.00
2.07
2.08
2.12
2.24
3.14
3.04
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2a-anti

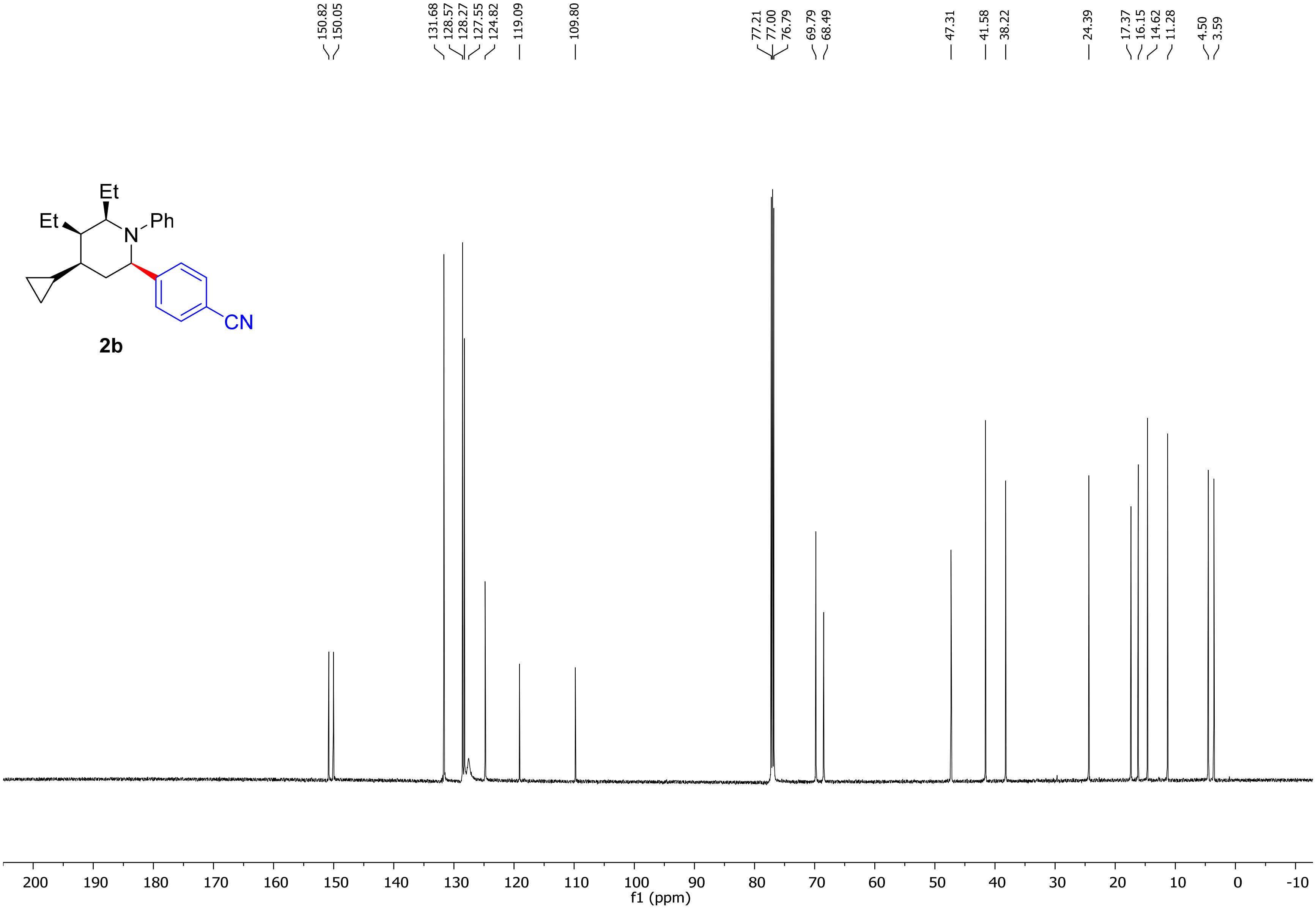


2a-anti

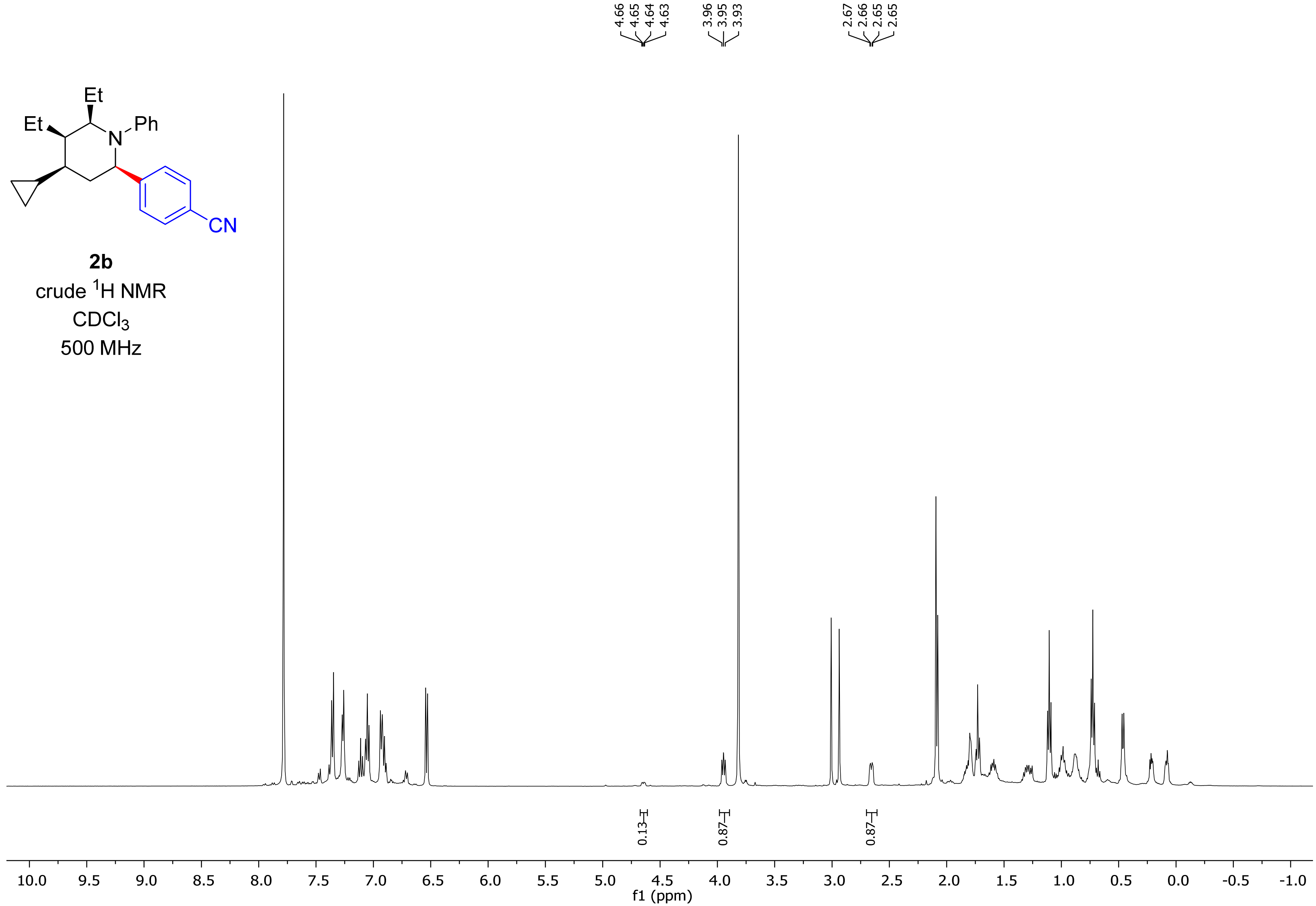
150.63
149.41
132.06
128.51
127.81
120.00
119.35
119.07
109.82
77.21
77.00
76.79
64.69
54.61
44.04
41.54
27.86
23.27
22.65
16.12
14.99
12.41
Et
Et
N
Ph
Me
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.37
7.36
7.27
7.26
7.07
7.06
7.04
6.94
6.92
6.91
6.90
3.96
3.95
3.95
3.94
2.67
2.67
2.67
2.66
2.66
2.65
2.65
1.85
1.85
1.84
1.83
1.83
1.82
1.81
1.80
1.75
1.73
1.72
1.63
1.61
1.60
1.59
1.58
1.58
1.57
1.33
1.31
1.31
1.30
1.30
1.29
1.29
1.27
1.26
1.12
1.11
1.10
1.02
1.01
1.00
1.00
0.99
0.98
0.97
0.90
0.89
0.88
0.88
0.87
0.86
0.85
0.77
0.76
0.75
0.74
0.73
0.72
0.47
0.47
0.46
0.23
0.22
0.21
0.20
0.09
0.08
0.07
Et
Et
N
Ph
CN
1.97
2.08
1.98
2.92
1.01
1.00
2.21
2.06
1.17
1.29
3.14
1.18
1.26
4.19
2.09
1.06
1.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2b



2b
150.82
150.05
131.68
128.57
128.27
127.55
124.82
119.09
109.80
77.21
77.00
76.79
69.79
68.49
47.31
41.58
38.22
24.39
17.37
16.15
14.62
11.28
4.50
3.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

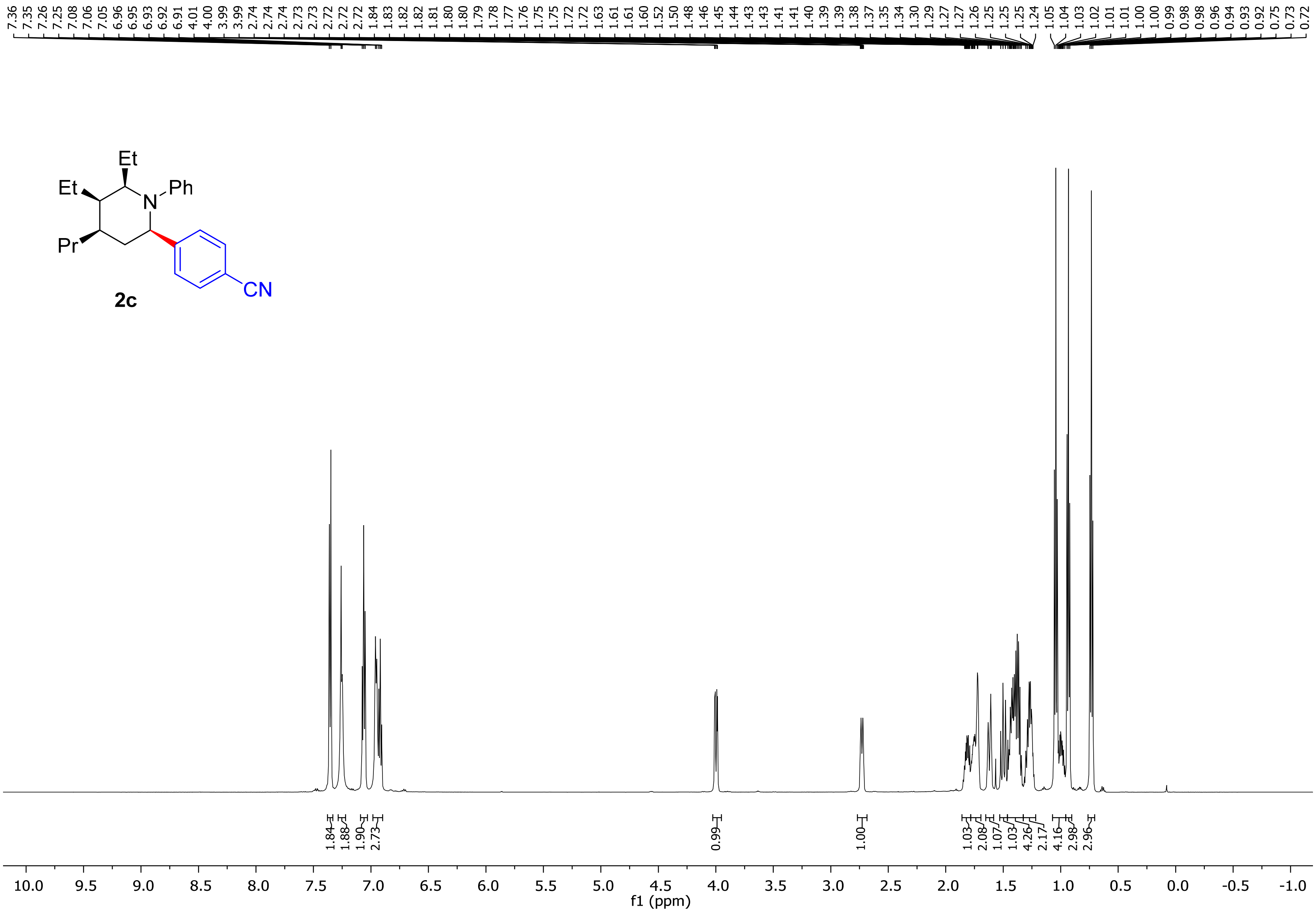


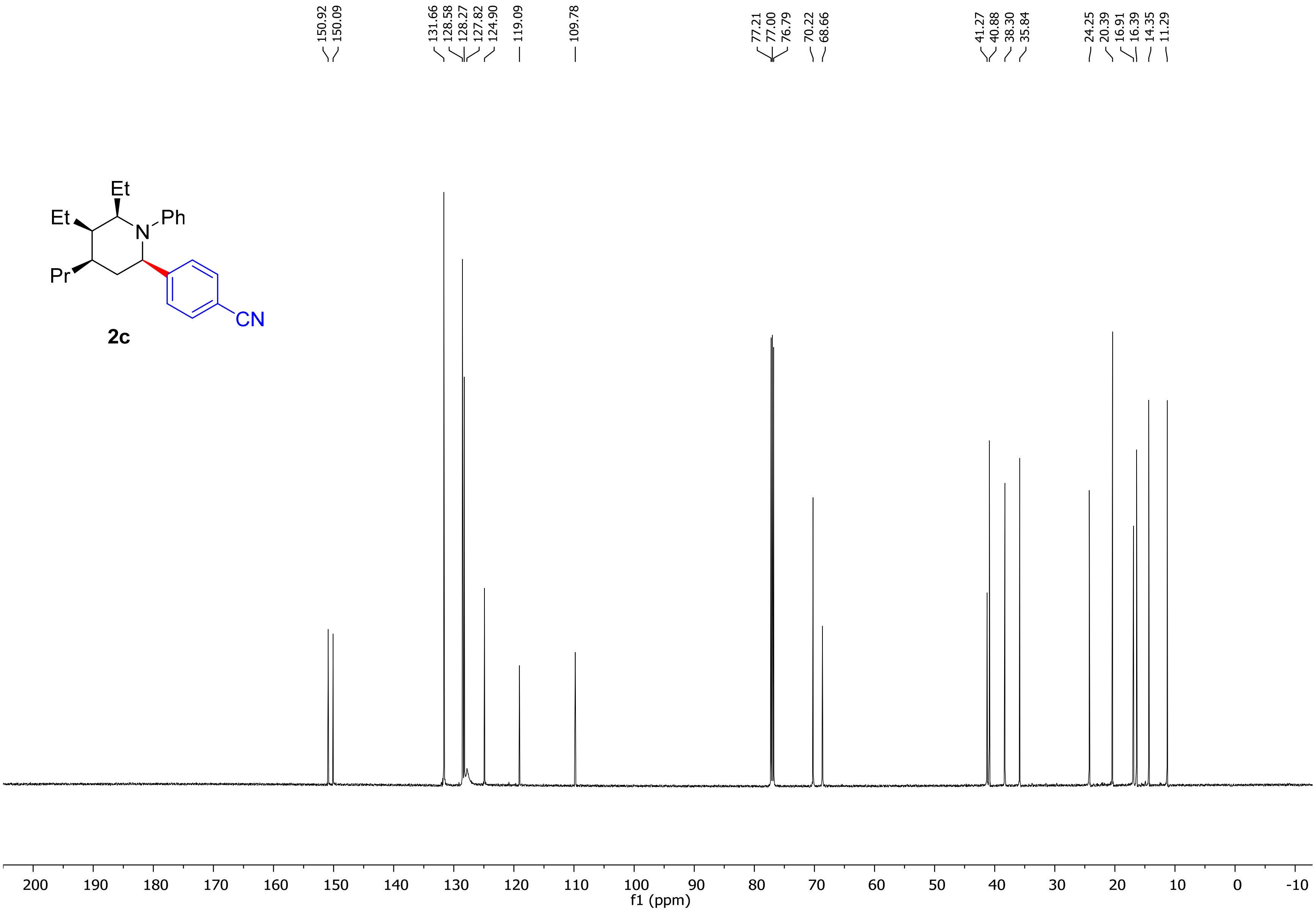
2b

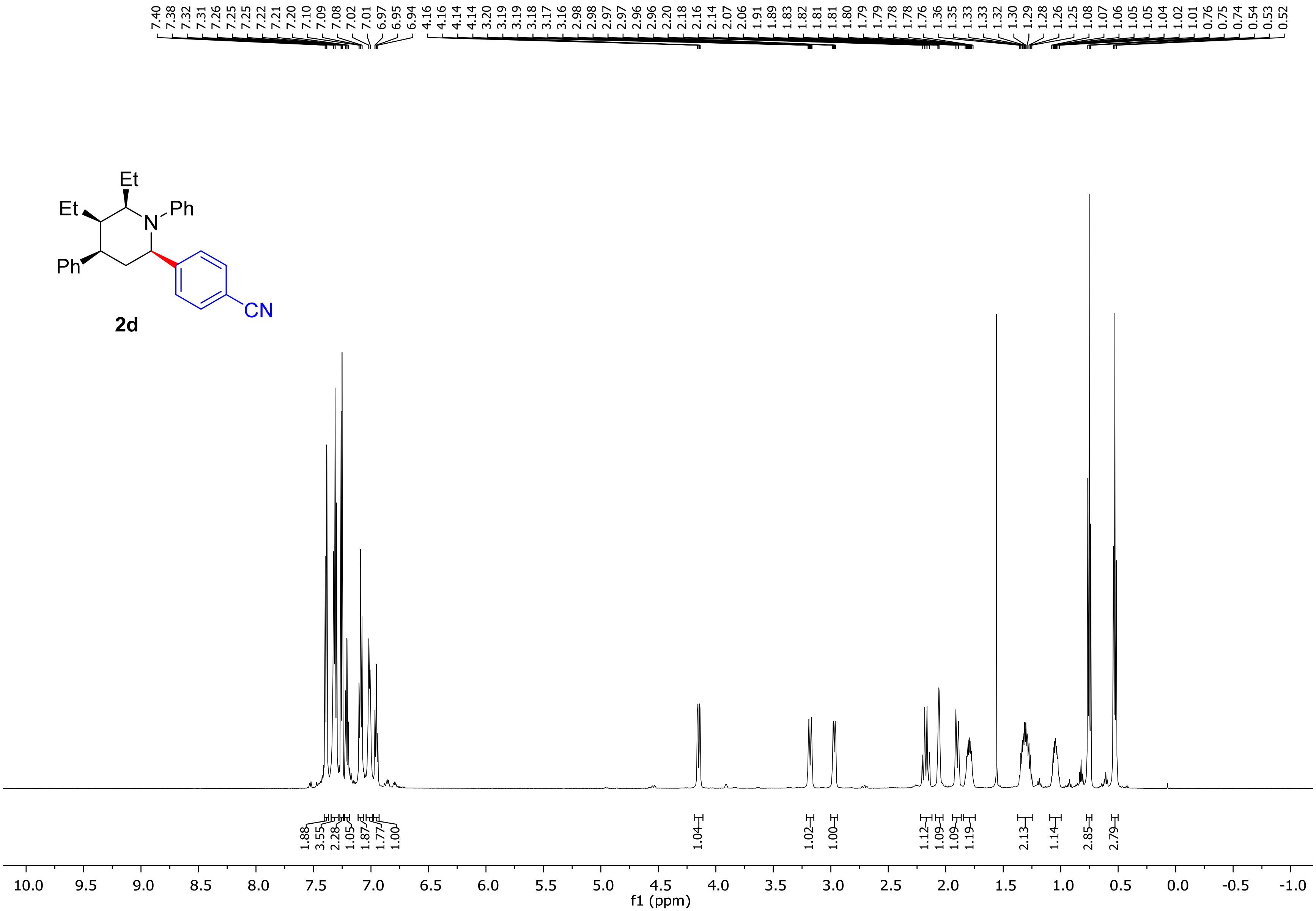
crude ^{1}H NMR

$CDCl_3$

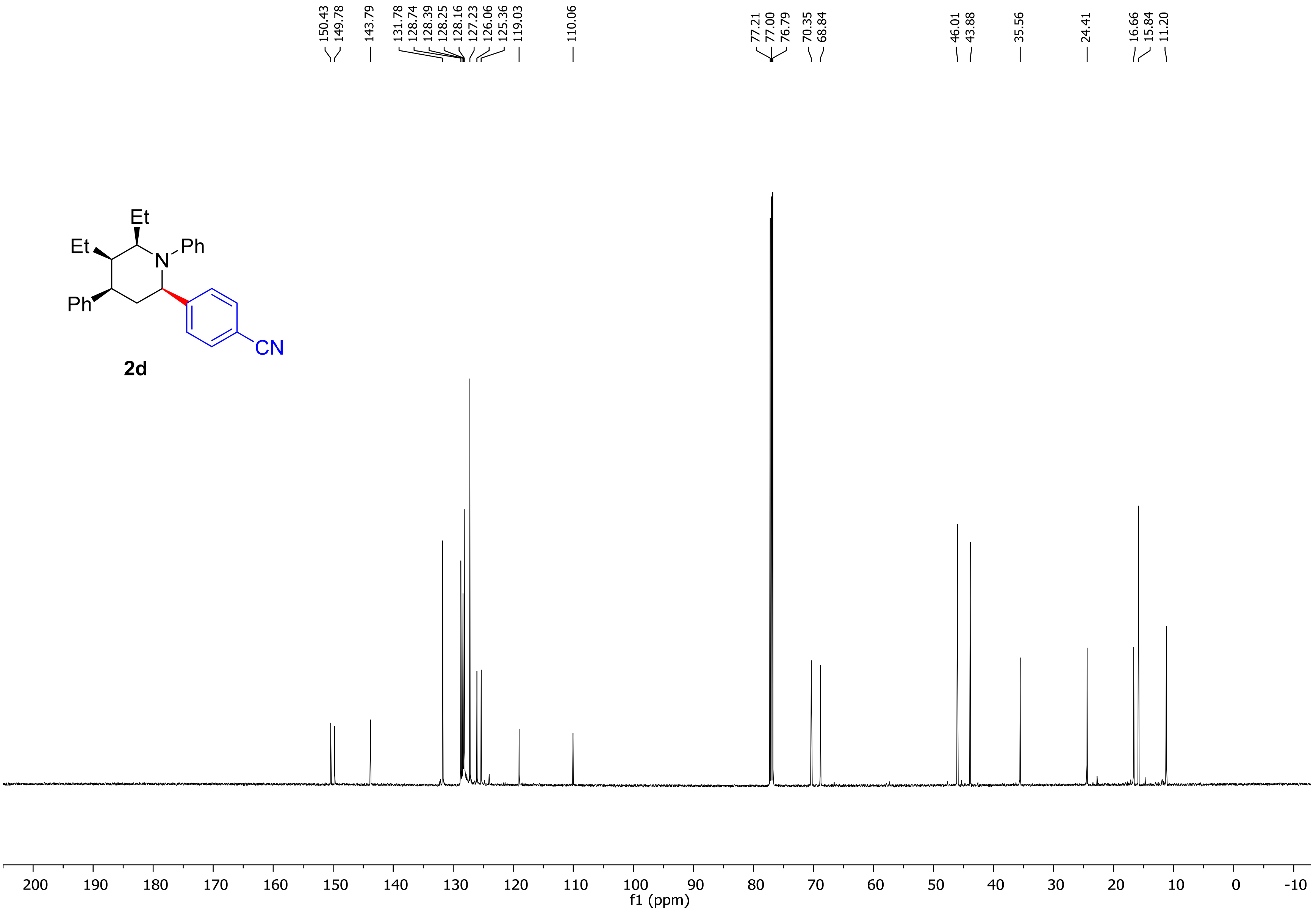
500 MHz


7.36
7.35
7.26
7.25
7.08
7.06
7.05
6.96
6.95
6.93
6.92
6.91
4.01
4.00
3.99
3.99
2.74
2.74
2.74
2.73
2.73
2.72
2.72
2.72
2.72
1.84
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.78
1.77
1.76
1.75
1.75
1.72
1.72
1.63
1.61
1.61
1.60
1.52
1.50
1.48
1.46
1.45
1.44
1.43
1.43
1.41
1.41
1.40
1.39
1.39
1.38
1.37
1.35
1.34
1.30
1.29
1.27
1.27
1.26
1.25
1.25
1.25
1.24
1.05
1.04
1.03
1.02
1.01
1.01
1.00
1.00
0.99
0.98
0.98
0.96
0.94
0.93
0.92
0.75
0.73
0.72
Et
Et
N
Ph
Pr
CN
2c
1.84
1.88
1.90
2.73
0.99
1.00
1.03
2.08
1.07
1.03
4.26
2.17
4.16
2.98
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

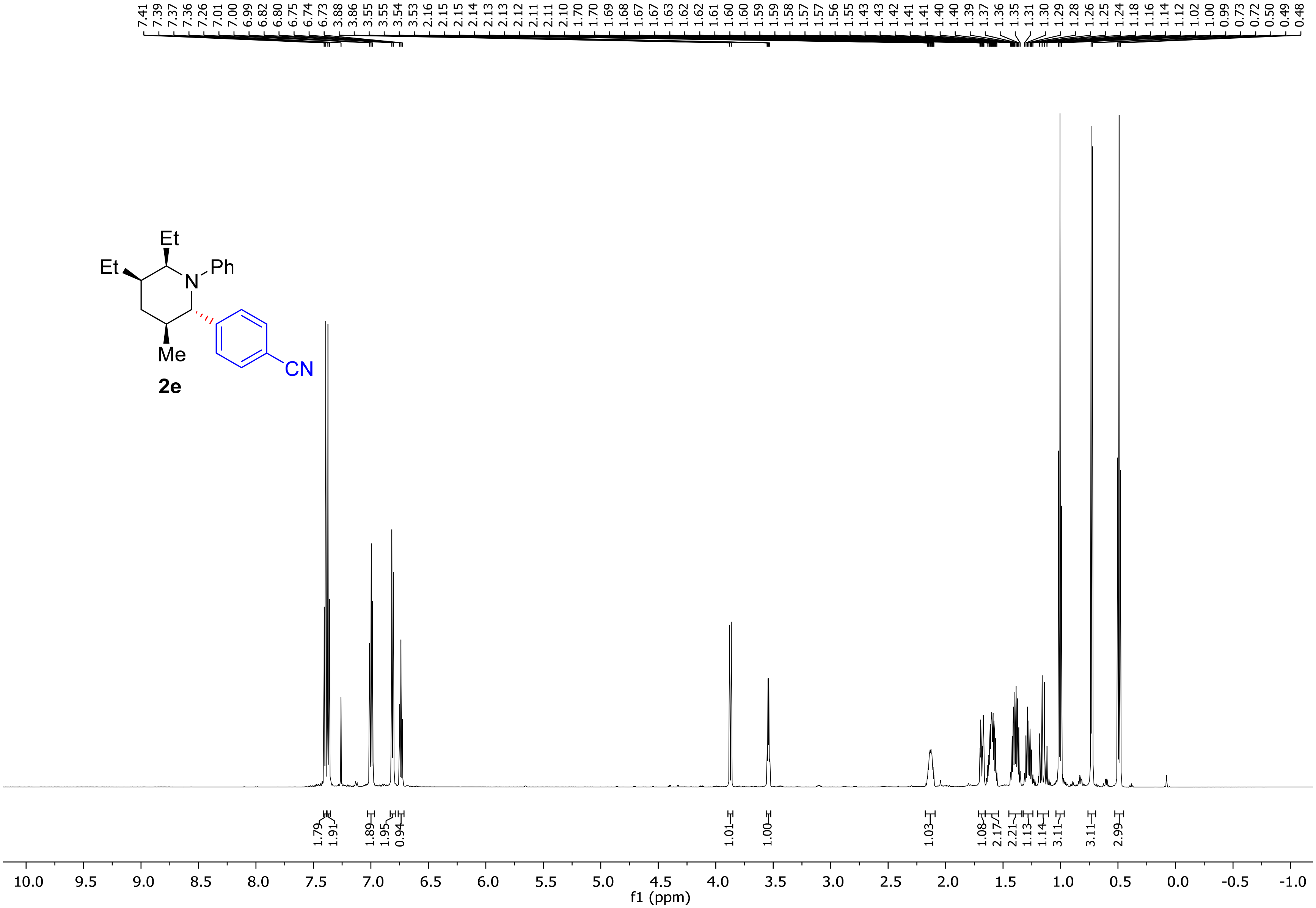

150.92
150.09
131.66
128.58
128.27
127.82
124.90
119.09
109.78
77.21
77.00
76.79
70.22
68.66
41.27
40.88
38.30
35.84
24.25
20.39
16.91
16.39
14.35
11.29
Et
Et
N
Ph
Pr
CN
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

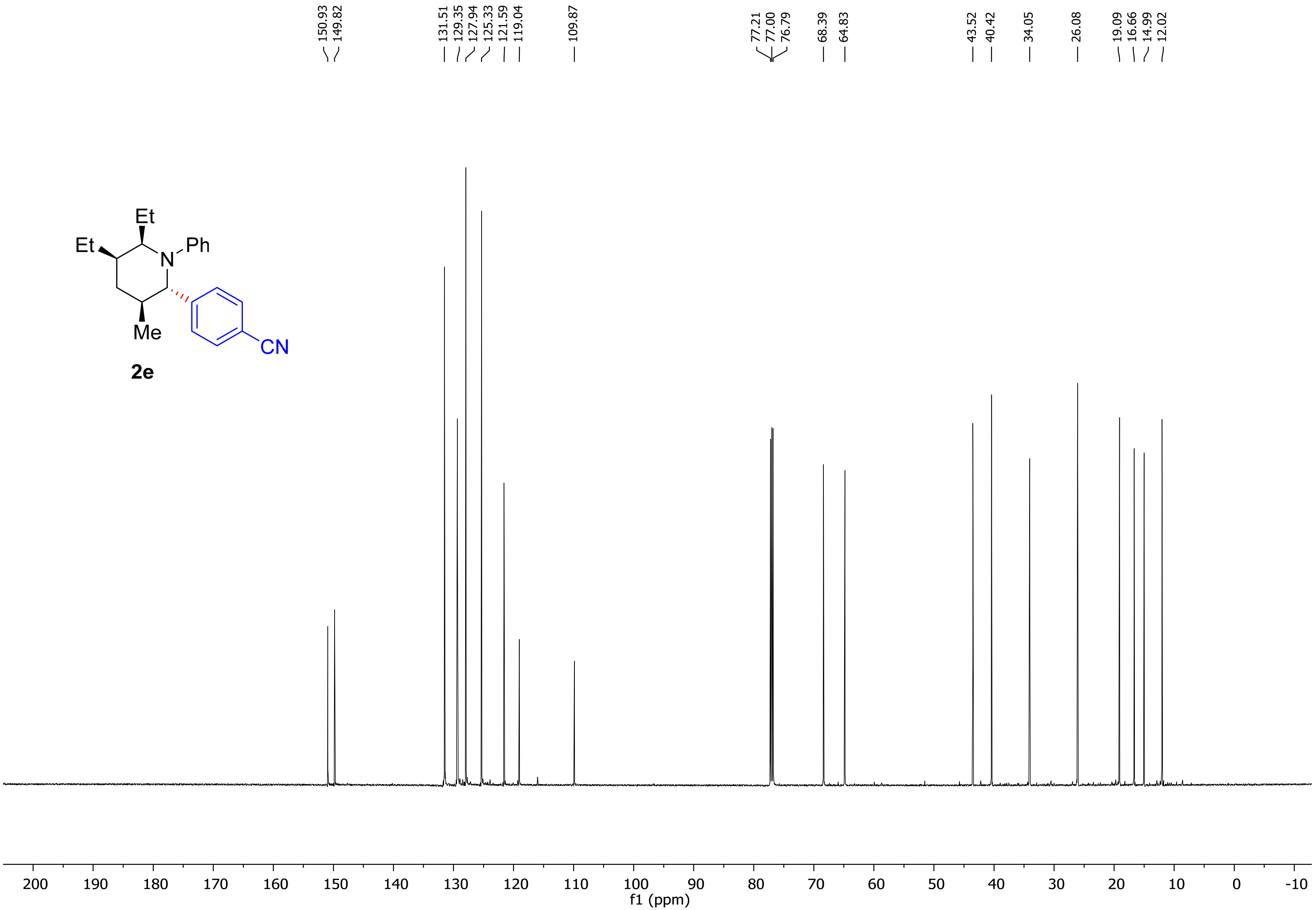

7.40
7.38
7.32
7.31
7.26
7.25
7.25
7.22
7.21
7.20
7.10
7.09
7.08
7.02
7.01
6.97
6.95
6.94
4.16
4.16
4.14
4.14
3.20
3.19
3.19
3.18
3.17
3.16
2.98
2.98
2.97
2.97
2.96
2.96
2.20
2.18
2.16
2.14
2.07
2.06
1.91
1.89
1.83
1.82
1.81
1.81
1.80
1.79
1.79
1.78
1.78
1.76
1.36
1.35
1.33
1.33
1.32
1.30
1.29
1.28
1.26
1.25
1.08
1.07
1.06
1.05
1.05
1.04
1.02
1.01
0.76
0.75
0.74
0.54
0.53
0.52
Et
Et
N
Ph
Ph
CN
1.88
3.55
2.28
1.05
1.87
1.77
1.00
1.04
1.02
1.00
1.12
1.09
1.09
1.19
2.13
1.14
2.85
2.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

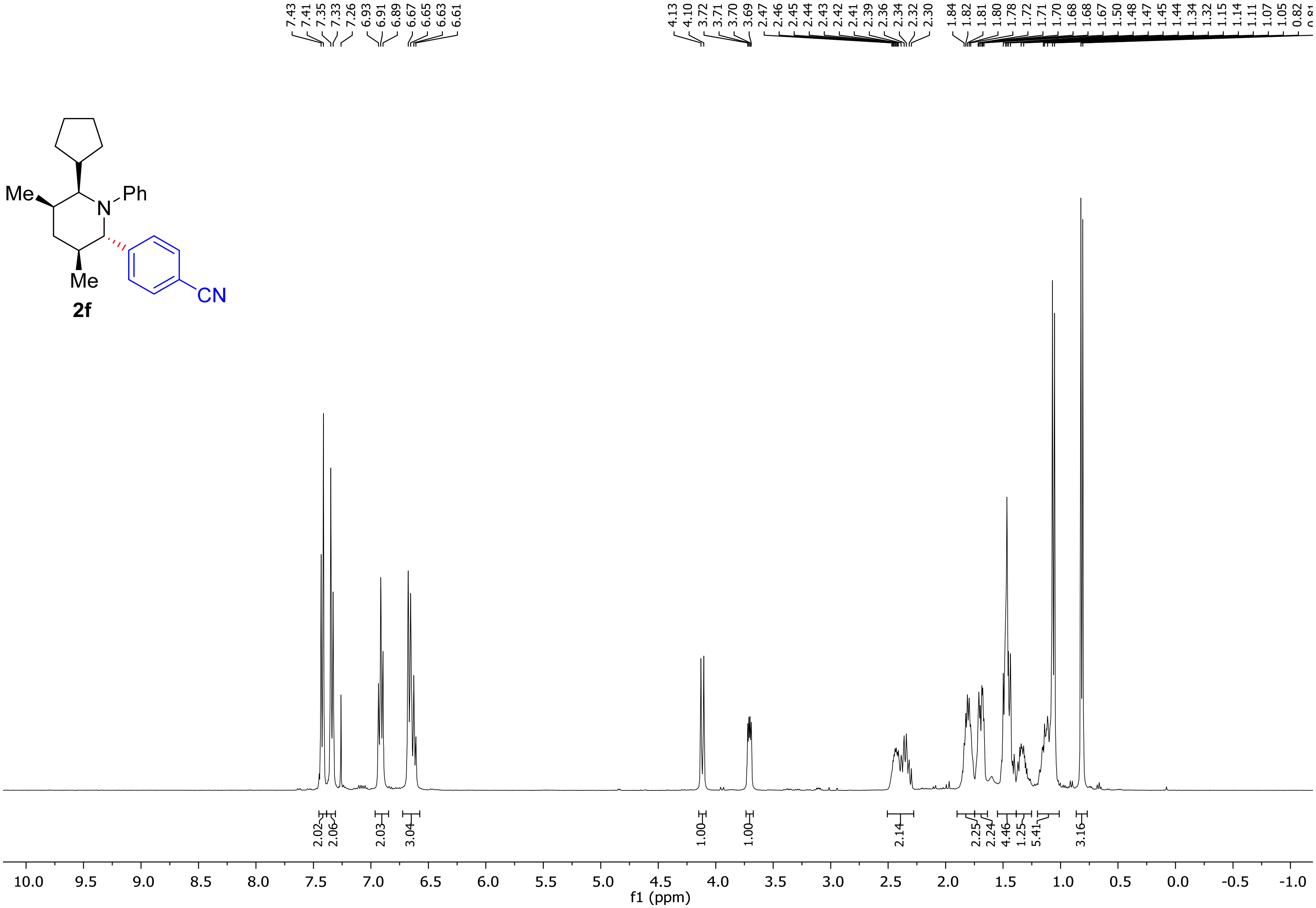
2d


2d

150.43
149.78
143.79
131.78
128.74
128.39
128.25
128.16
127.23
126.06
125.36
119.03
110.06
77.21
77.00
76.79
70.35
68.84
46.01
43.88
35.56
24.41
16.66
15.84
11.20
Et
Et
N
Ph
Ph
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.41
7.39
7.37
7.36
7.26
7.01
7.00
6.99
6.82
6.80
6.75
6.74
6.73
3.88
3.86
3.55
3.55
3.54
3.53
2.16
2.15
2.15
2.14
2.13
2.13
2.12
2.11
2.11
2.10
1.70
1.69
1.68
1.67
1.67
1.63
1.62
1.62
1.61
1.60
1.60
1.59
1.59
1.58
1.57
1.57
1.56
1.55
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.39
1.37
1.36
1.35
1.31
1.30
1.29
1.28
1.26
1.25
1.24
1.18
1.16
1.14
1.12
1.02
1.00
0.99
0.73
0.72
0.50
0.49
0.48
Et
Et
N
Ph
Me
CN
2e
1.79
1.91
1.89
1.95
0.94
1.01
1.00
1.03
1.08
2.17
2.21
1.13
1.14
3.11
3.11
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

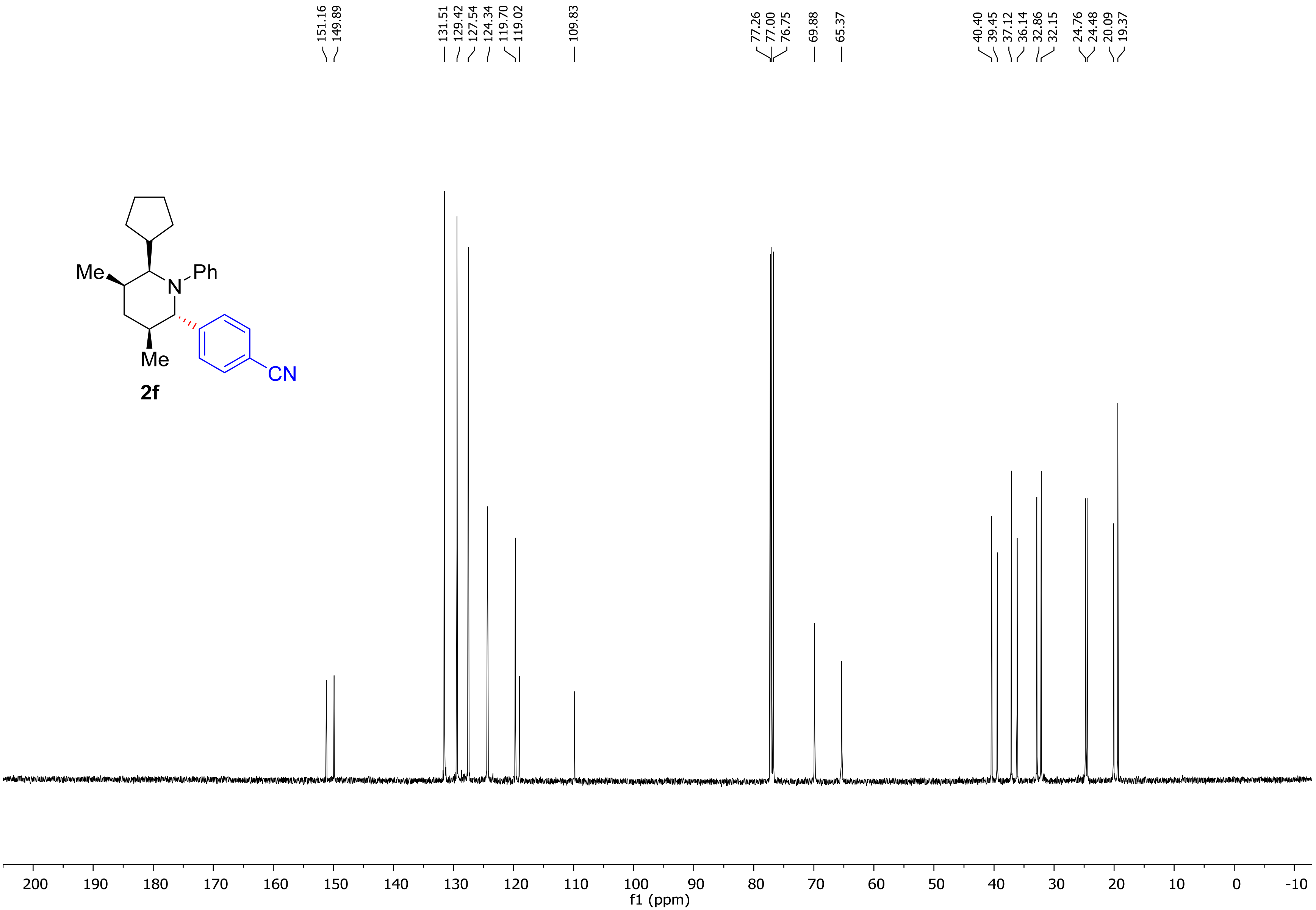

150.93
149.82
131.51
129.35
127.94
125.33
121.59
119.04
109.87
77.21
77.00
76.79
68.39
64.83
43.52
40.42
34.05
26.08
19.09
16.66
14.99
12.02
Et
Et
N
Ph
Me
CN
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

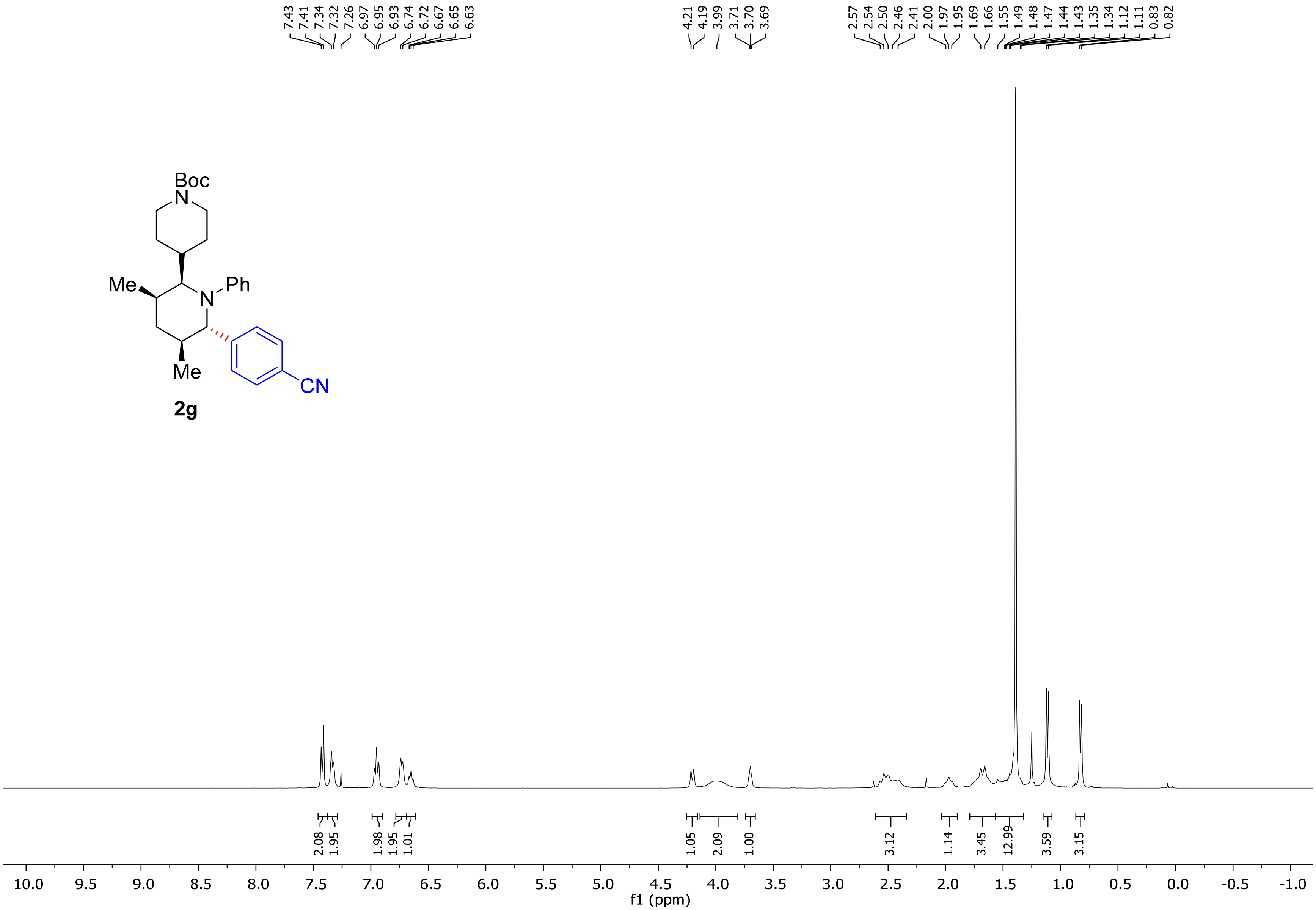


Me
N
Ph
Me
CN

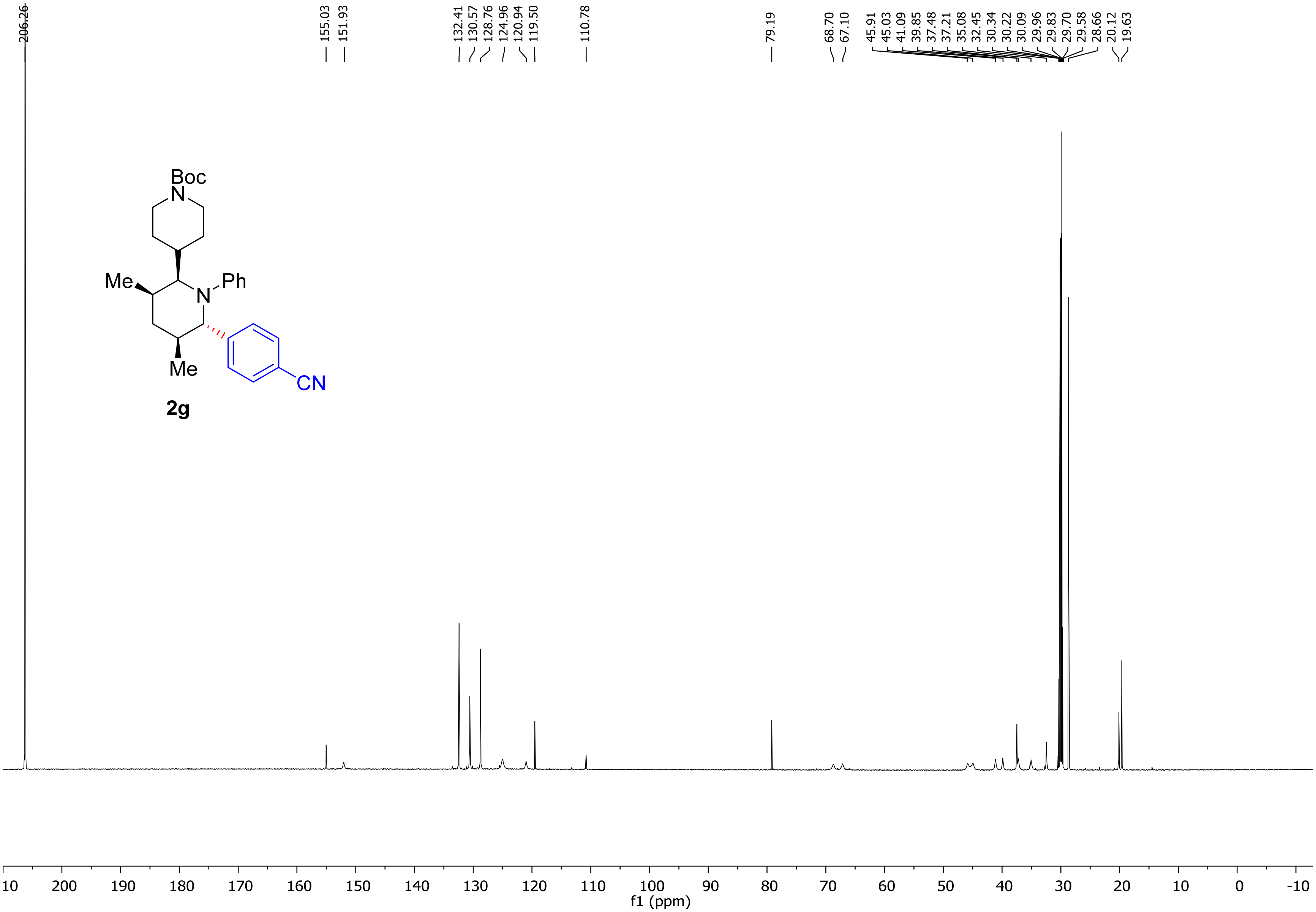
2f

7.43
7.41
7.35
7.33
7.26
6.93
6.91
6.89
6.67
6.65
6.63
6.61
4.13
4.10
3.72
3.71
3.70
3.69
2.47
2.46
2.45
2.44
2.43
2.42
2.41
2.39
2.36
2.34
2.32
2.30
1.84
1.82
1.81
1.80
1.78
1.72
1.71
1.70
1.68
1.67
1.50
1.48
1.47
1.45
1.44
1.34
1.32
1.15
1.14
1.11
1.07
1.05
0.82
2.02
2.06
2.03
3.04
1.00
1.00
2.14
2.25
2.24
4.46
1.25
5.41
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

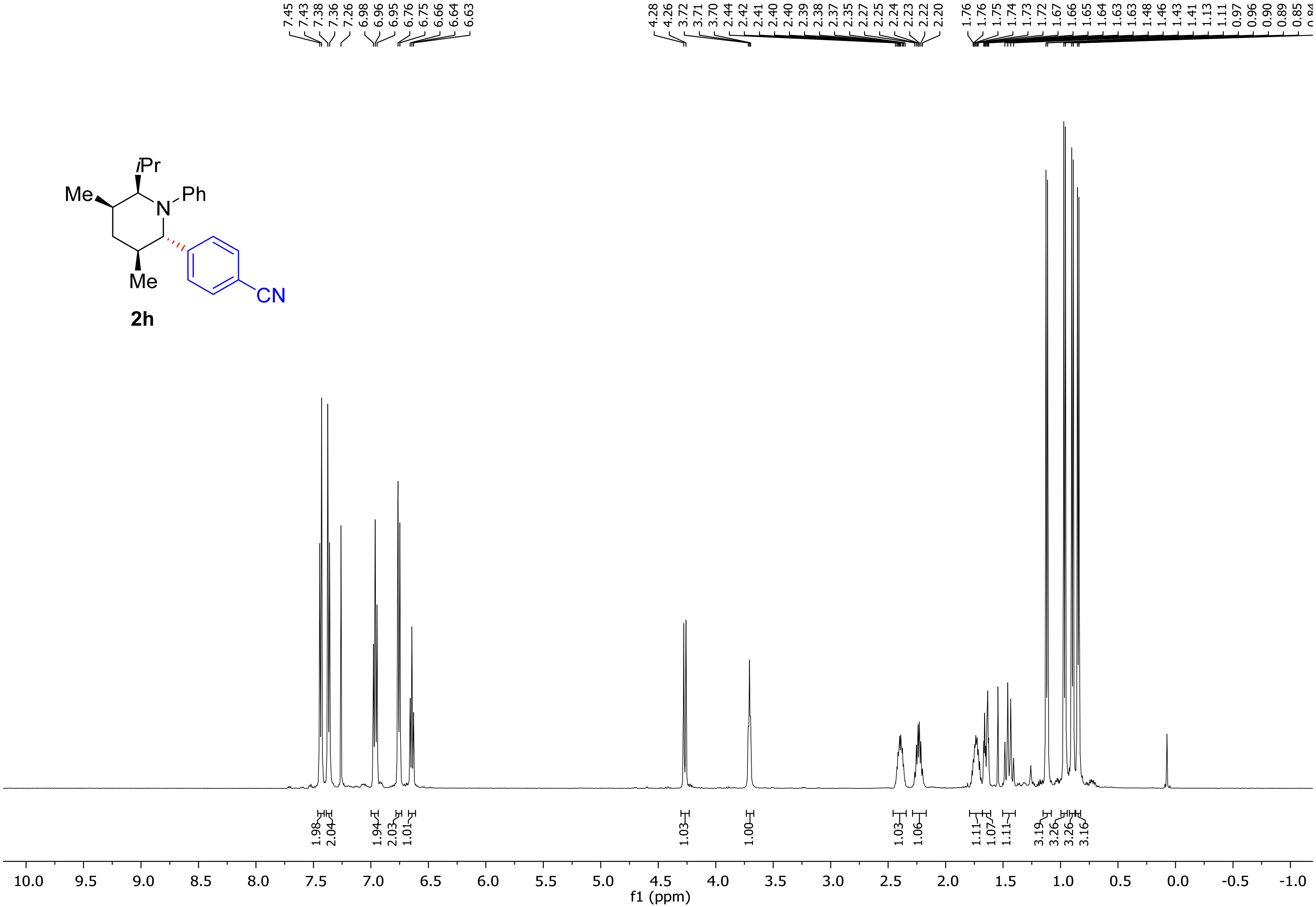

151.16
149.89
131.51
129.42
127.54
124.34
119.70
119.02
109.83
77.26
77.00
76.75
69.88
65.37
40.40
39.45
37.12
36.14
32.86
32.15
24.76
24.48
20.09
19.37
Me
N
Ph
Me
CN
2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.43
7.41
7.34
7.32
7.26
6.97
6.95
6.93
6.74
6.72
6.67
6.65
6.63
4.21
4.19
3.99
3.71
3.70
3.69
2.57
2.54
2.50
2.46
2.41
2.00
1.97
1.95
1.69
1.66
1.55
1.49
1.48
1.47
1.44
1.43
1.35
1.34
1.12
1.11
0.83
0.82
Boc
N
Me
N
Ph
Me
CN
2.08
1.95
1.98
1.95
1.01
1.05
2.09
1.00
3.12
1.14
3.45
12.99
3.59
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2g


206.26
155.03
151.93
132.41
130.57
128.76
124.96
120.94
119.50
110.78
79.19
68.70
67.10
45.91
45.03
41.09
39.85
37.48
37.21
35.08
32.45
30.34
30.22
30.09
29.96
29.83
29.70
29.58
28.66
20.12
19.63
Boc
N
Me
N
Ph
Me
CN
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

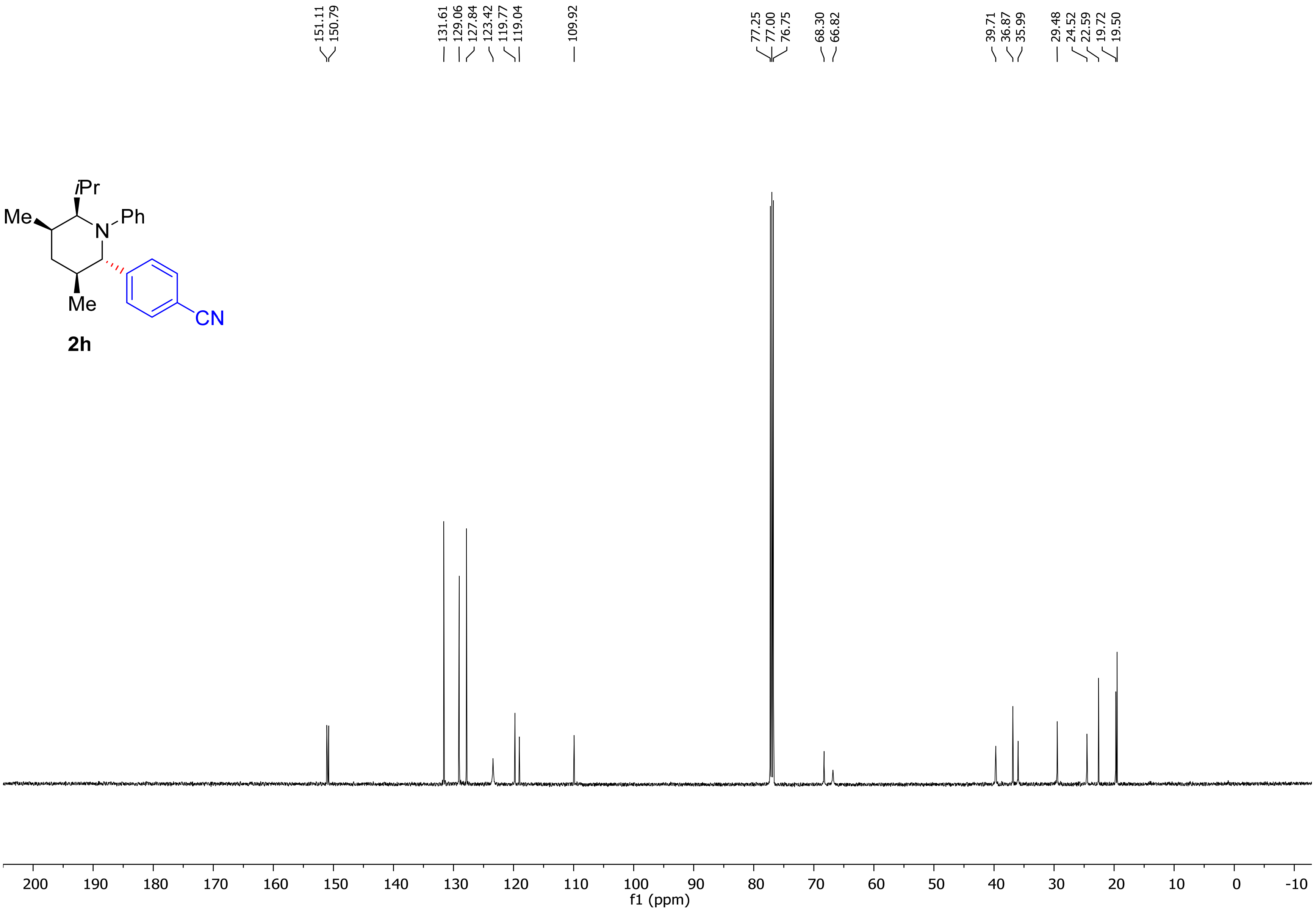
2g



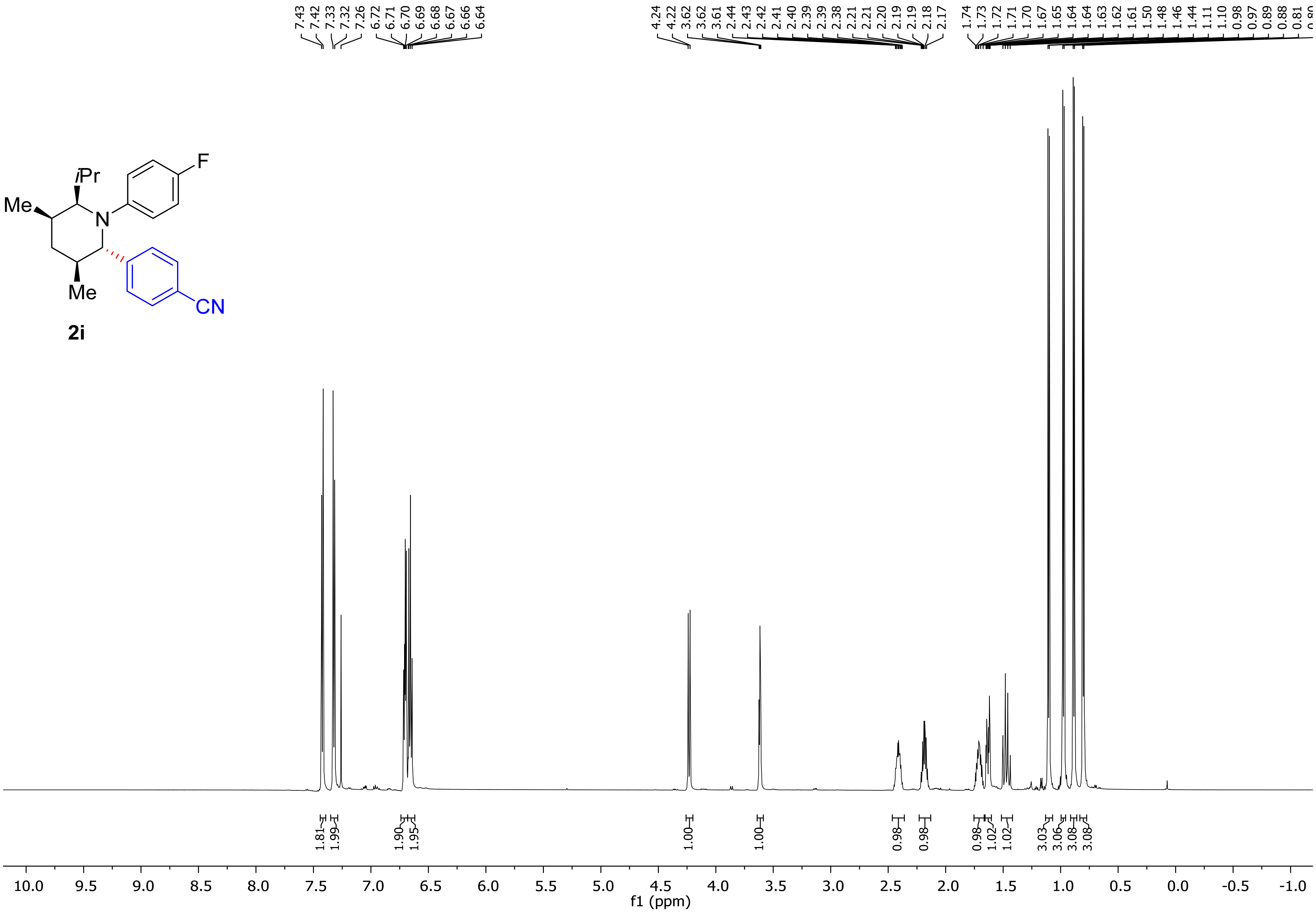
iPr
Me
N
Ph
Me
CN

2h

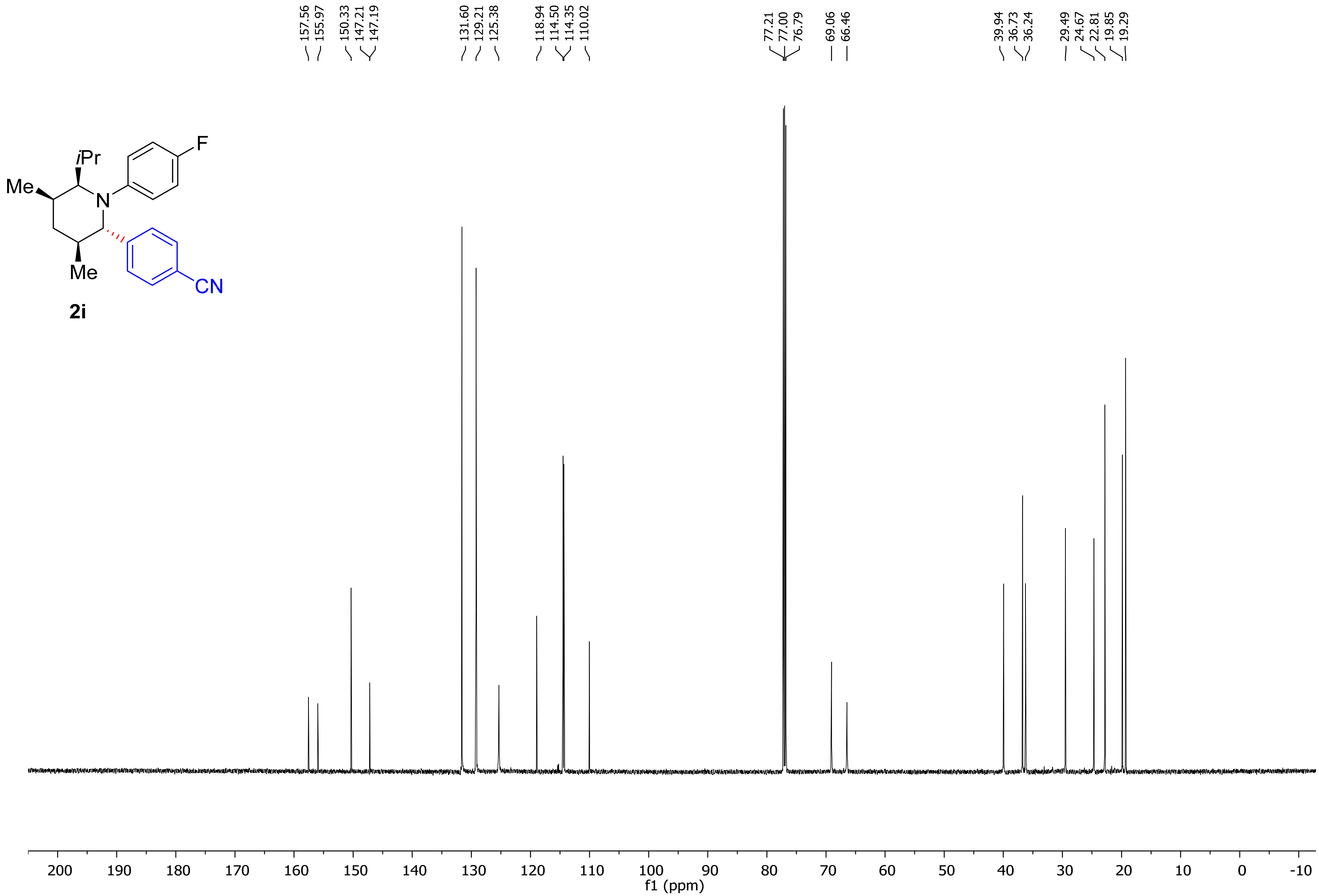
7.45
7.43
7.38
7.36
7.26
6.98
6.96
6.95
6.76
6.75
6.66
6.64
6.63
4.28
4.26
3.72
3.71
3.70
2.44
2.42
2.41
2.40
2.40
2.39
2.38
2.37
2.35
2.27
2.25
2.24
2.23
2.22
2.20
1.76
1.76
1.75
1.74
1.73
1.72
1.67
1.66
1.65
1.64
1.63
1.63
1.48
1.46
1.43
1.41
1.13
1.11
0.97
0.96
0.90
0.89
0.85
1.98
2.04
1.94
2.03
1.01
1.03
1.00
1.03
1.06
1.11
1.07
1.11
3.19
3.26
3.26
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

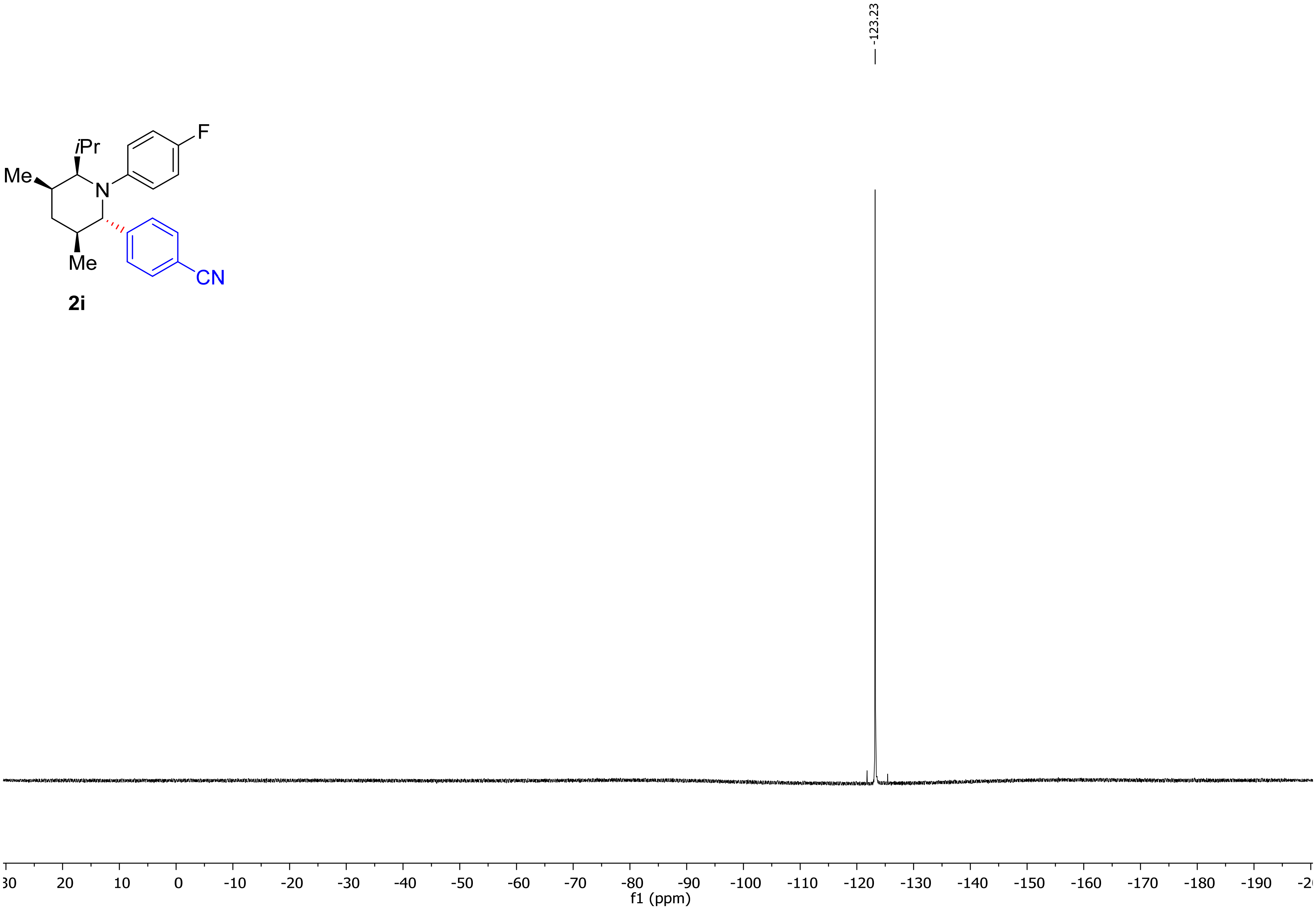

151.11
150.79
131.61
129.06
127.84
123.42
119.77
119.04
109.92
77.25
77.00
76.75
68.30
66.82
39.71
36.87
35.99
29.48
24.52
22.59
19.72
19.50
*i*Pr
Me
N
Ph
Me
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2h

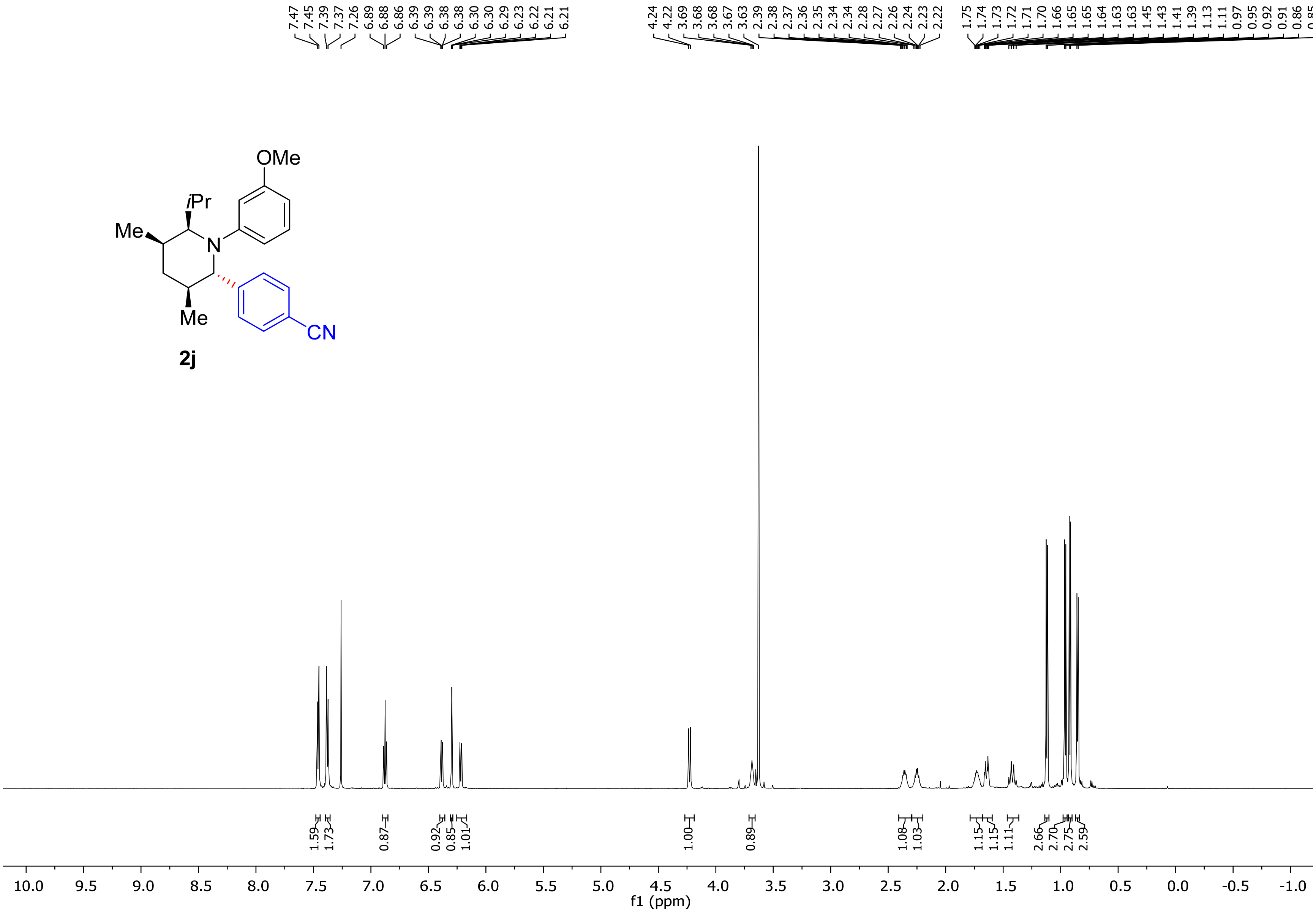

7.43
7.42
7.33
7.32
7.26
6.72
6.71
6.70
6.69
6.68
6.67
6.66
6.64
4.24
4.22
3.62
3.61
2.44
2.43
2.42
2.41
2.40
2.39
2.39
2.38
2.21
2.21
2.20
2.19
2.19
2.18
2.17
1.74
1.73
1.72
1.71
1.70
1.67
1.65
1.64
1.64
1.63
1.62
1.61
1.50
1.48
1.46
1.44
1.11
1.10
0.98
0.97
0.89
0.88
0.81
0.8
iPr
F
Me
N
Me
CN
1.81
1.99
1.90
1.95
1.00
1.00
0.98
0.98
0.98
1.02
1.02
3.03
3.06
3.08
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2i


157.56
155.97
150.33
147.21
147.19
131.60
129.21
125.38
118.94
114.50
114.35
110.02
77.21
77.00
76.79
69.06
66.46
39.94
36.73
36.24
29.49
24.67
22.81
19.85
19.29
iPr
F
Me
N
Me
CN
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

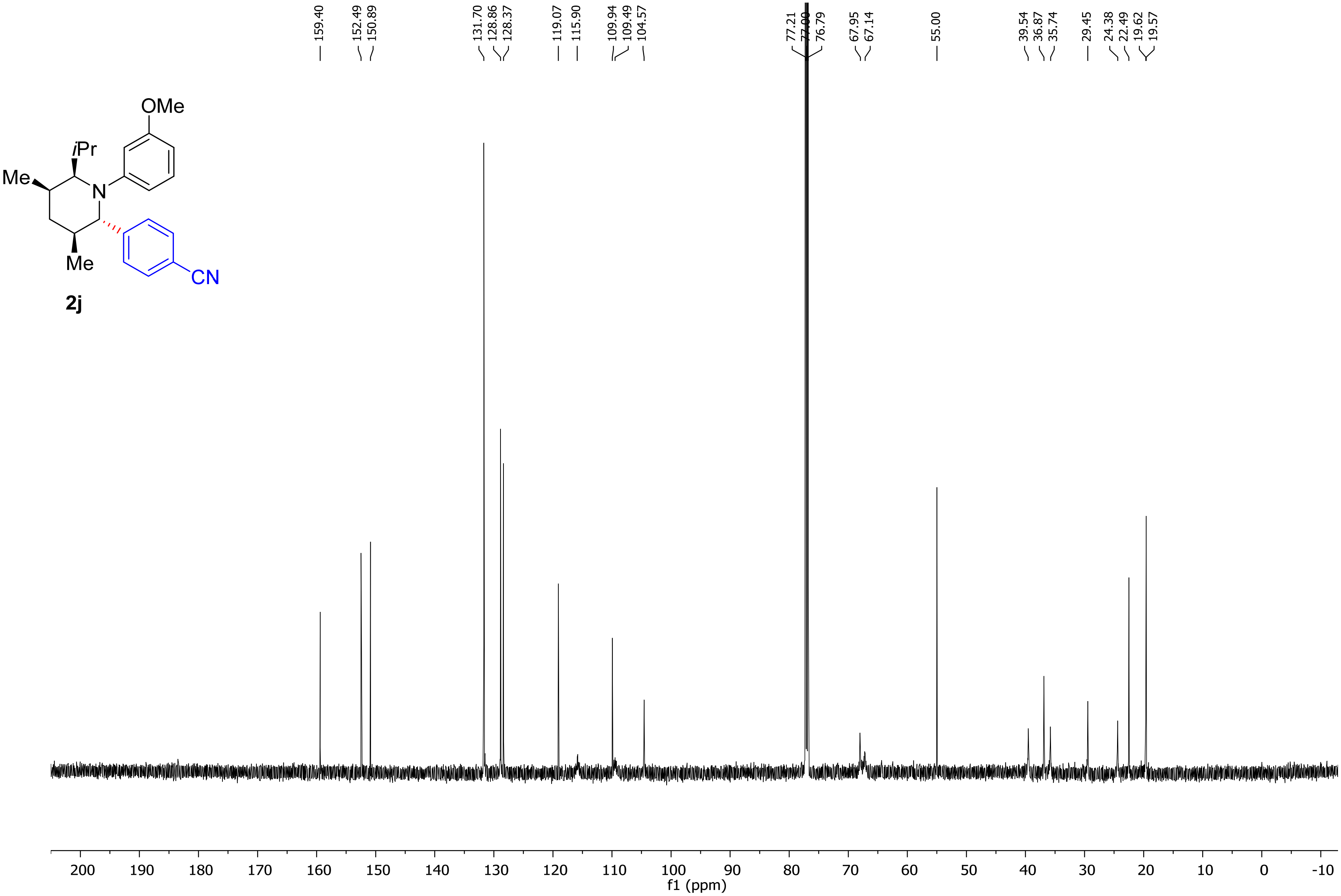


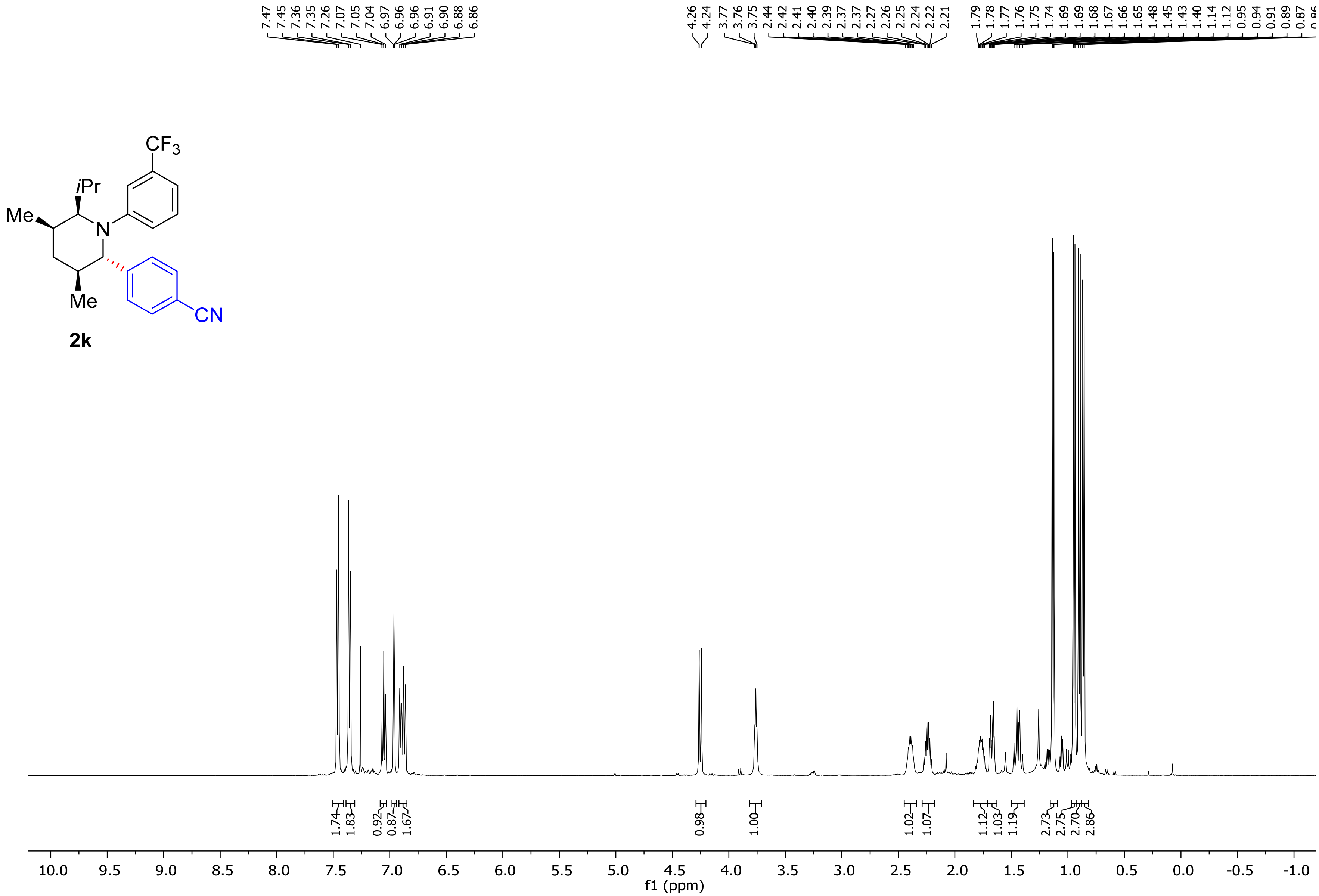
2i
-123.23
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.47
7.45
7.39
7.37
7.26
6.89
6.88
6.86
6.39
6.39
6.38
6.38
6.30
6.30
6.29
6.23
6.22
6.21
6.21
4.24
4.22
3.69
3.68
3.67
3.63
2.39
2.38
2.37
2.36
2.35
2.34
2.34
2.28
2.27
2.26
2.24
2.23
2.22
1.75
1.74
1.73
1.72
1.71
1.70
1.66
1.65
1.65
1.64
1.63
1.63
1.45
1.43
1.41
1.39
1.13
1.11
0.97
0.95
0.92
0.91
0.86
0.8
OMe
iPr
Me
N
Me
CN
2j
1.59
1.73
0.87
0.92
0.85
1.01
1.00
0.89
1.08
1.03
1.15
1.15
1.11
2.66
2.70
2.75
2.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

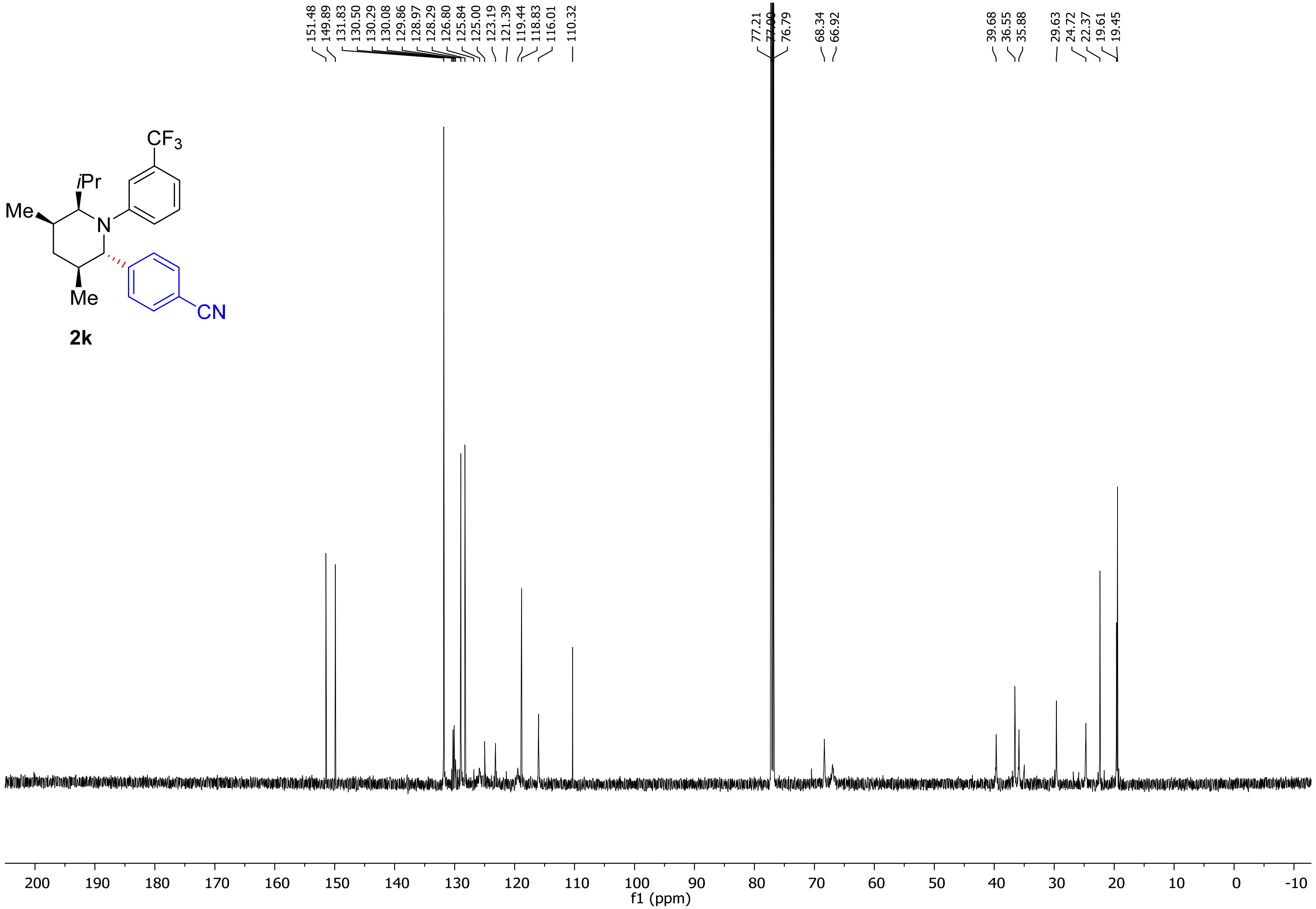
OMe
iPr
Me
N
Me
CN

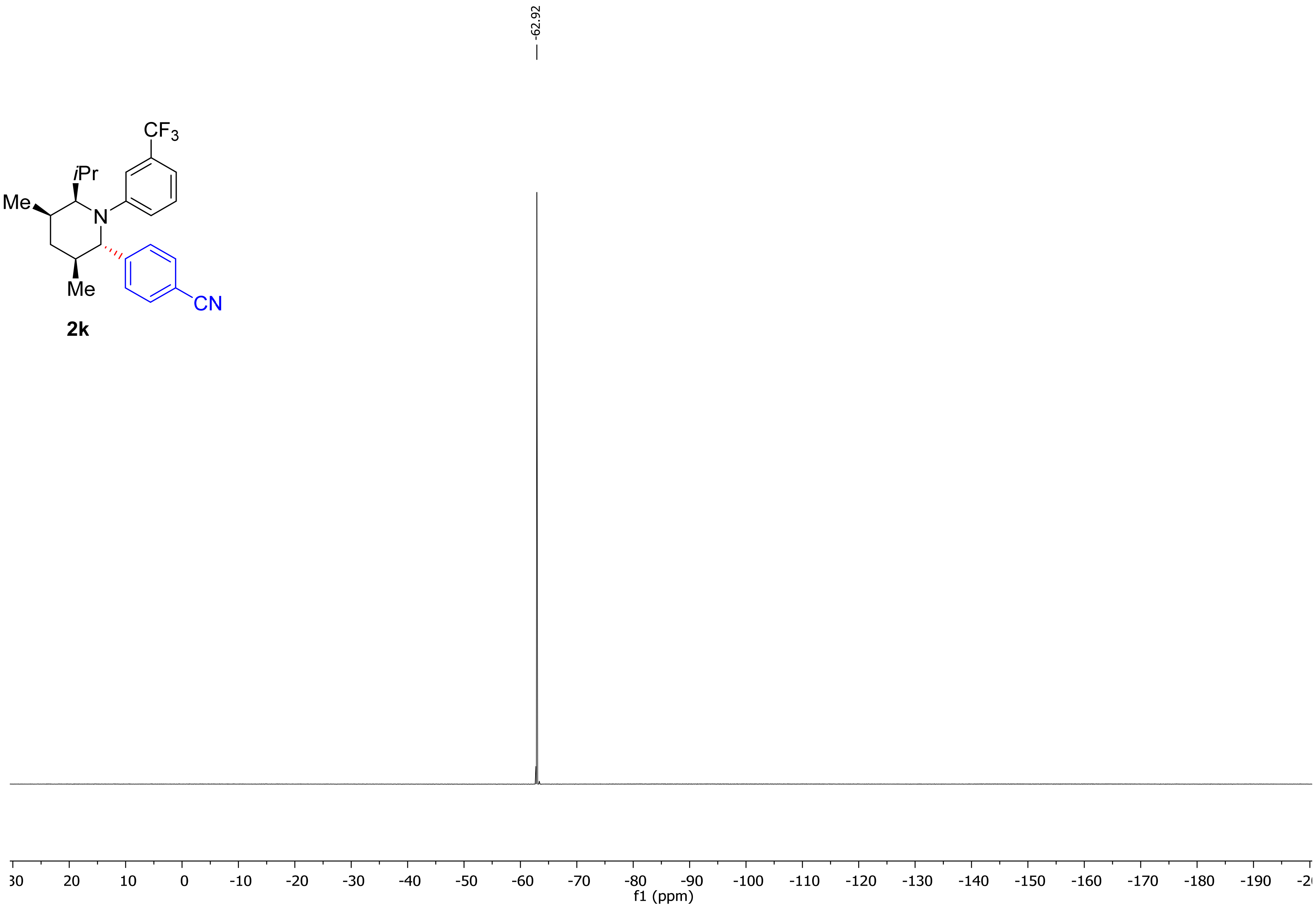
2j


159.40
152.49
150.89
131.70
128.86
128.37
119.07
115.90
109.94
109.49
104.57
77.21
77.00
76.79
67.95
67.14
55.00
39.54
36.87
35.74
29.45
24.38
22.49
19.62
19.57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

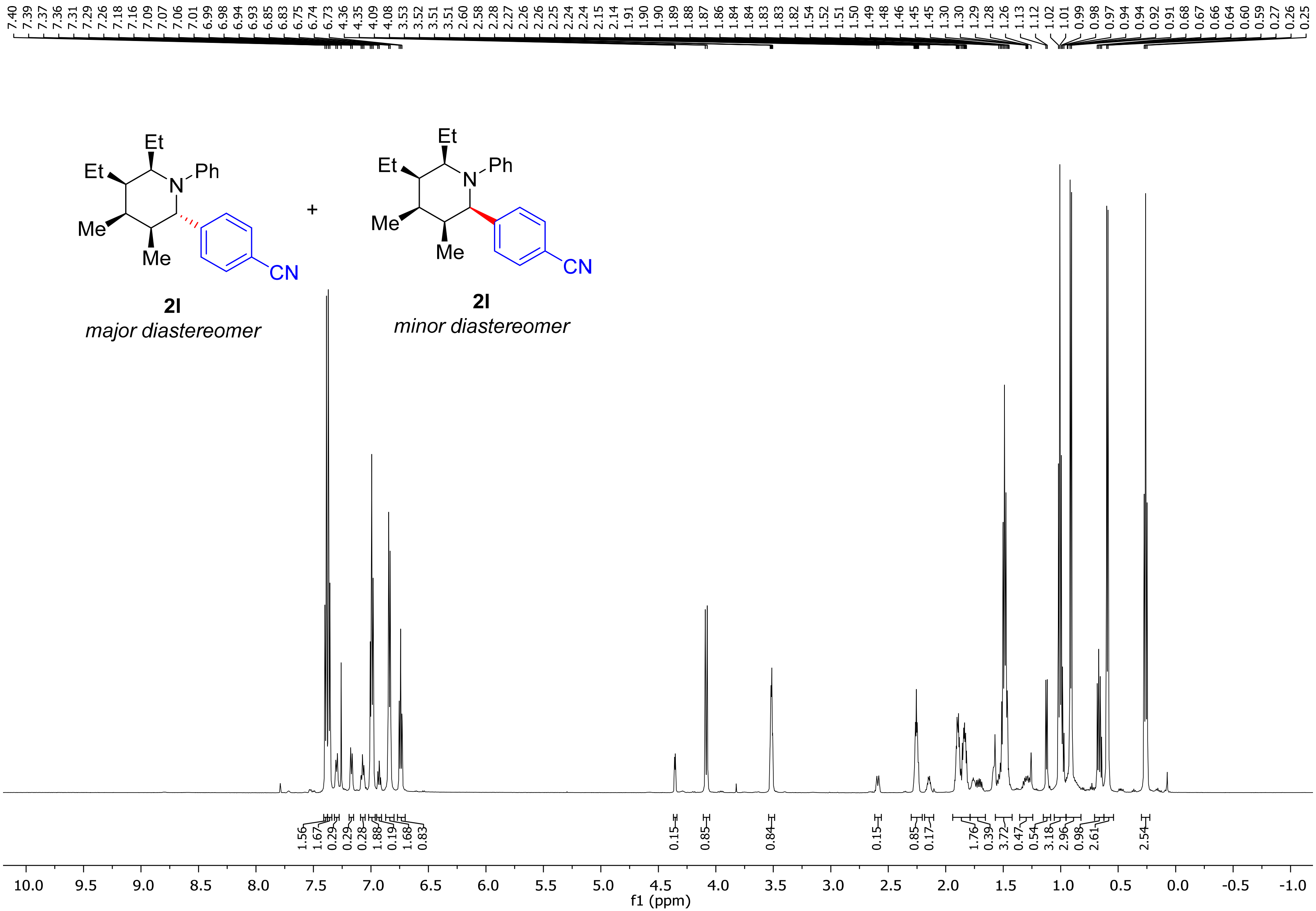

7.47
7.45
7.36
7.35
7.26
7.07
7.05
7.04
6.97
6.96
6.96
6.91
6.90
6.88
6.86
4.26
4.24
3.77
3.76
3.75
2.44
2.42
2.41
2.40
2.39
2.37
2.37
2.27
2.26
2.25
2.24
2.22
2.21
1.79
1.78
1.77
1.76
1.75
1.74
1.69
1.69
1.68
1.67
1.66
1.65
1.48
1.45
1.43
1.40
1.14
1.12
0.95
0.94
0.91
0.89
0.87
CF3
iPr
Me
N
Me
CN
1.74
1.83
0.92
0.87
1.67
0.98
1.00
1.02
1.07
1.12
1.03
1.19
2.73
2.75
2.70
2.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

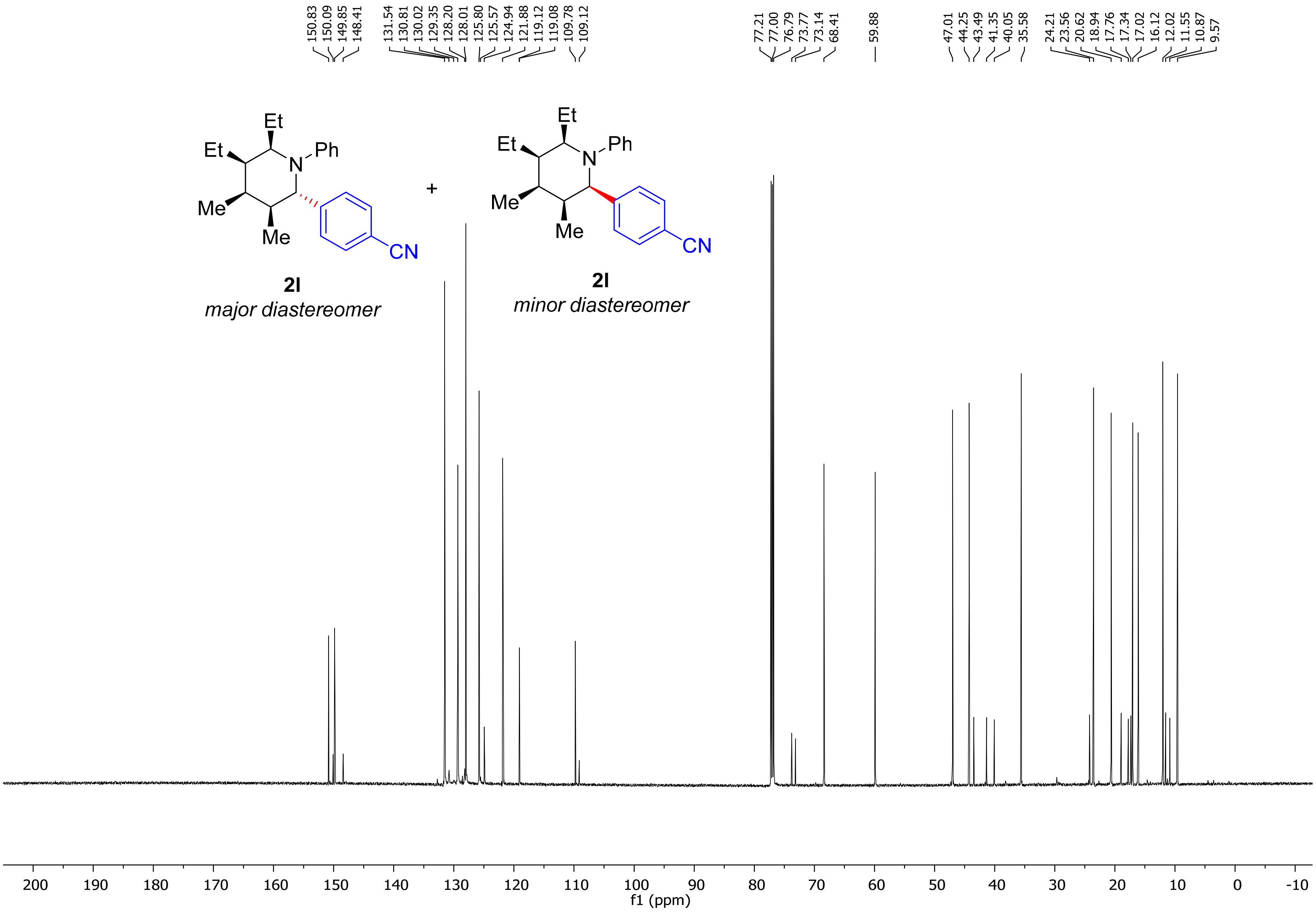
2k


151.48
149.89
131.83
130.50
130.29
130.08
129.86
128.97
128.29
126.80
125.84
125.00
123.19
121.39
119.44
118.83
116.01
110.32
77.21
77.00
76.79
68.34
66.92
39.68
36.55
35.88
29.63
24.72
22.37
19.61
19.45
CF3
iPr
Me
N
Me
CN
2k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-62.92
CF3
iPr
Me
N
Me
CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

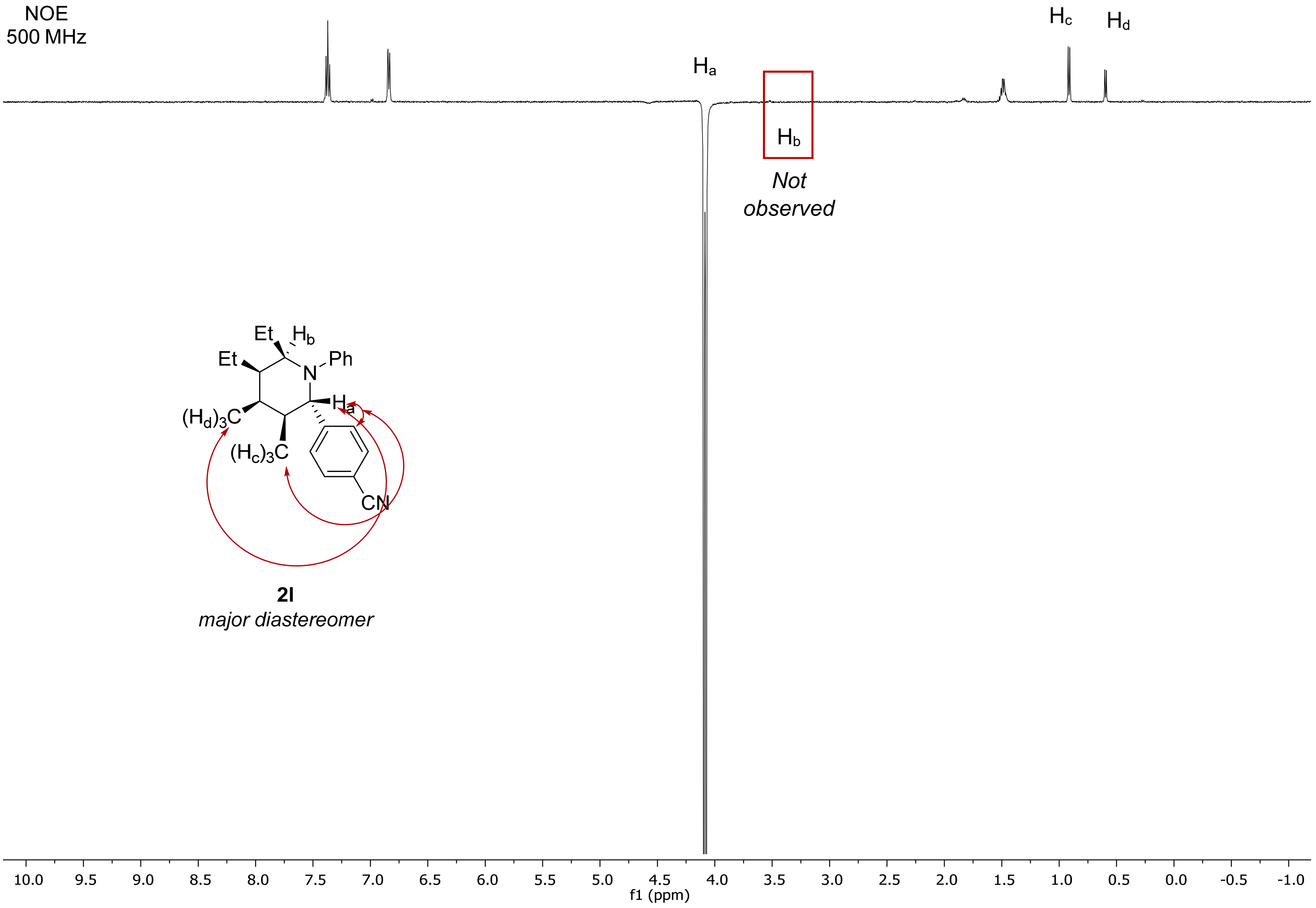
2k


7.40
7.39
7.37
7.36
7.31
7.29
7.26
7.18
7.16
7.09
7.07
7.06
7.01
6.99
6.98
6.94
6.93
6.85
6.83
6.75
6.74
6.73
4.36
4.35
4.09
4.08
3.53
3.52
3.51
3.51
2.60
2.58
2.28
2.27
2.26
2.26
2.25
2.24
2.24
2.15
2.14
1.91
1.90
1.90
1.89
1.88
1.87
1.86
1.84
1.84
1.83
1.83
1.82
1.54
1.52
1.51
1.50
1.49
1.48
1.46
1.45
1.45
1.30
1.30
1.29
1.28
1.26
1.13
1.12
1.02
1.01
0.99
0.98
0.97
0.94
0.94
0.92
0.91
0.68
0.67
0.66
0.64
0.60
0.59
0.27
0.26
0.25
Et
Et
N
Ph
Me
Me
CN
2l
major diastereomer
+
Et
Et
N
Ph
Me
Me
CN
2l
minor diastereomer
1.56
1.67
0.29
0.29
0.28
1.88
0.19
1.68
0.83
0.15
0.85
0.84
0.15
0.85
0.17
1.76
0.39
3.72
0.47
0.54
3.18
2.96
0.98
2.61
2.54
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

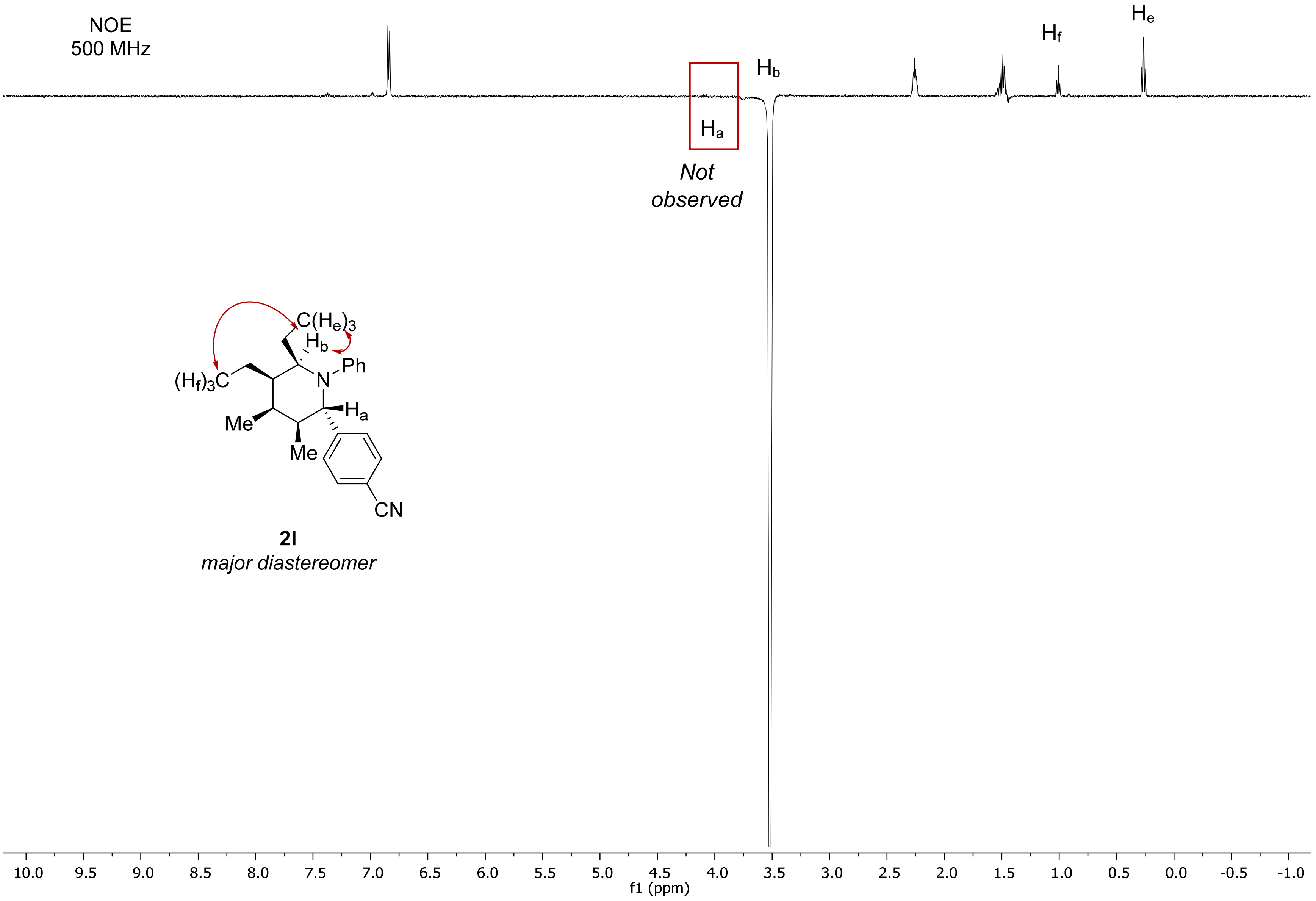


2l
major diastereomer

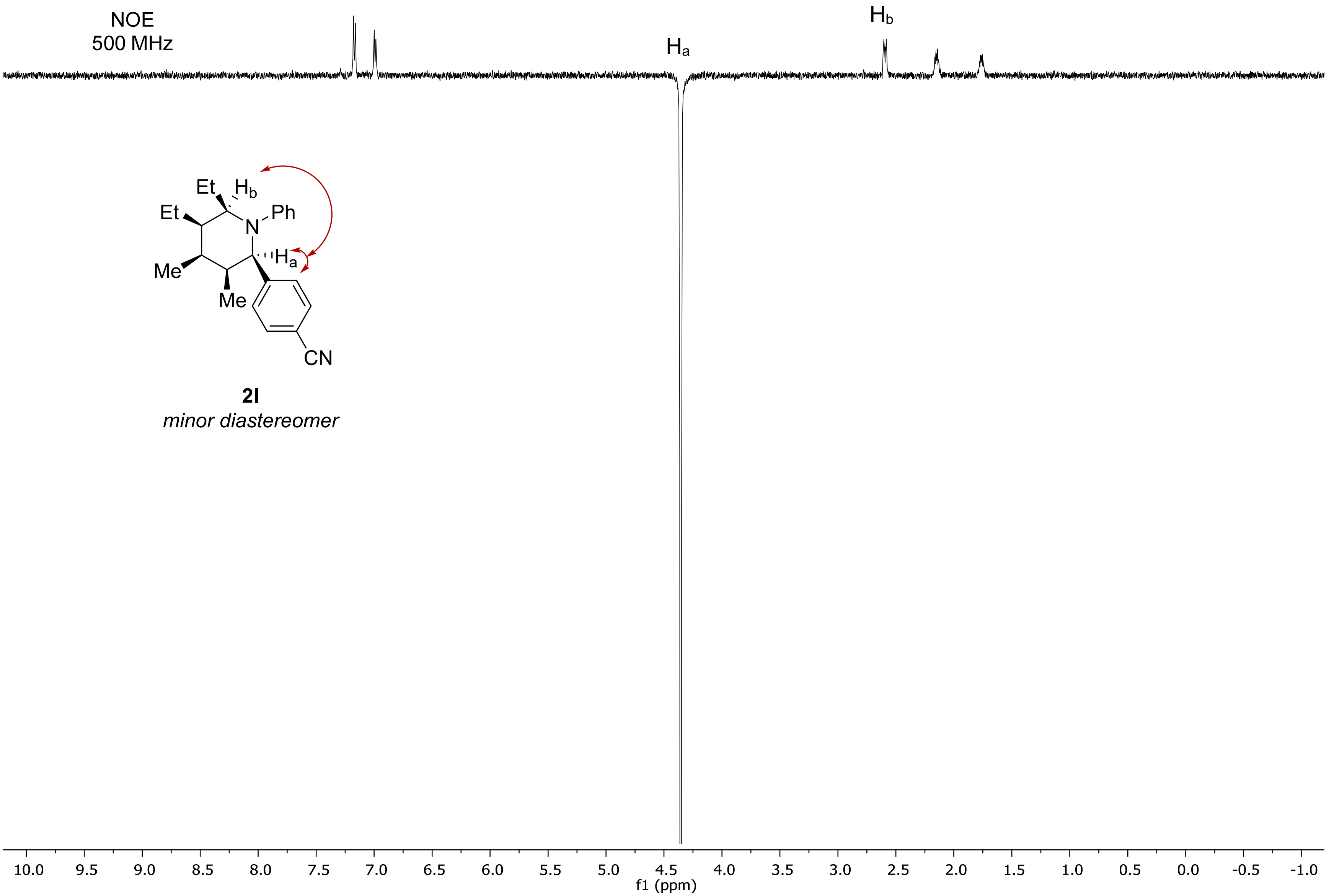
2l
minor diastereomer



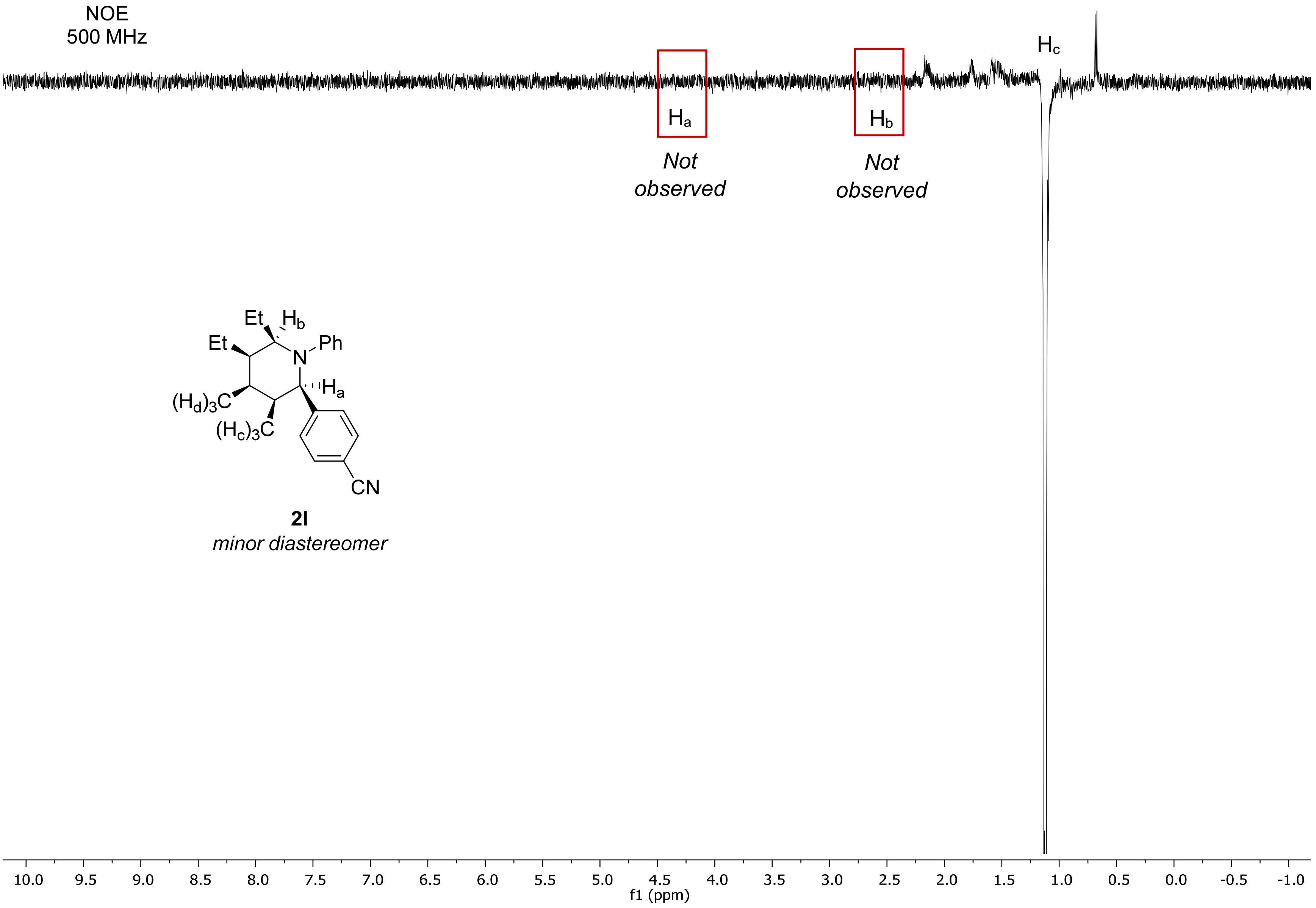
2l
major diastereomer



2l
major diastereomer

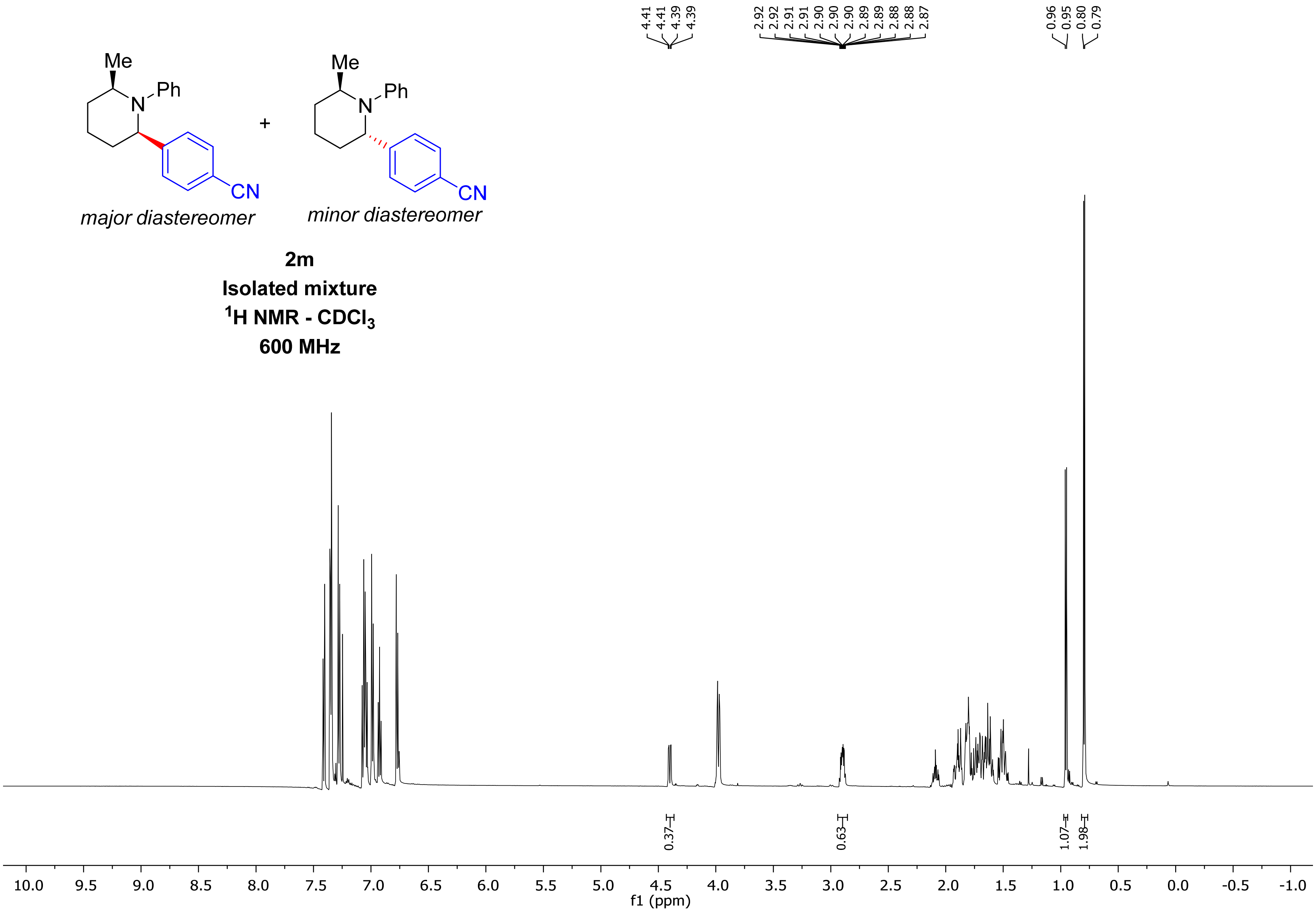


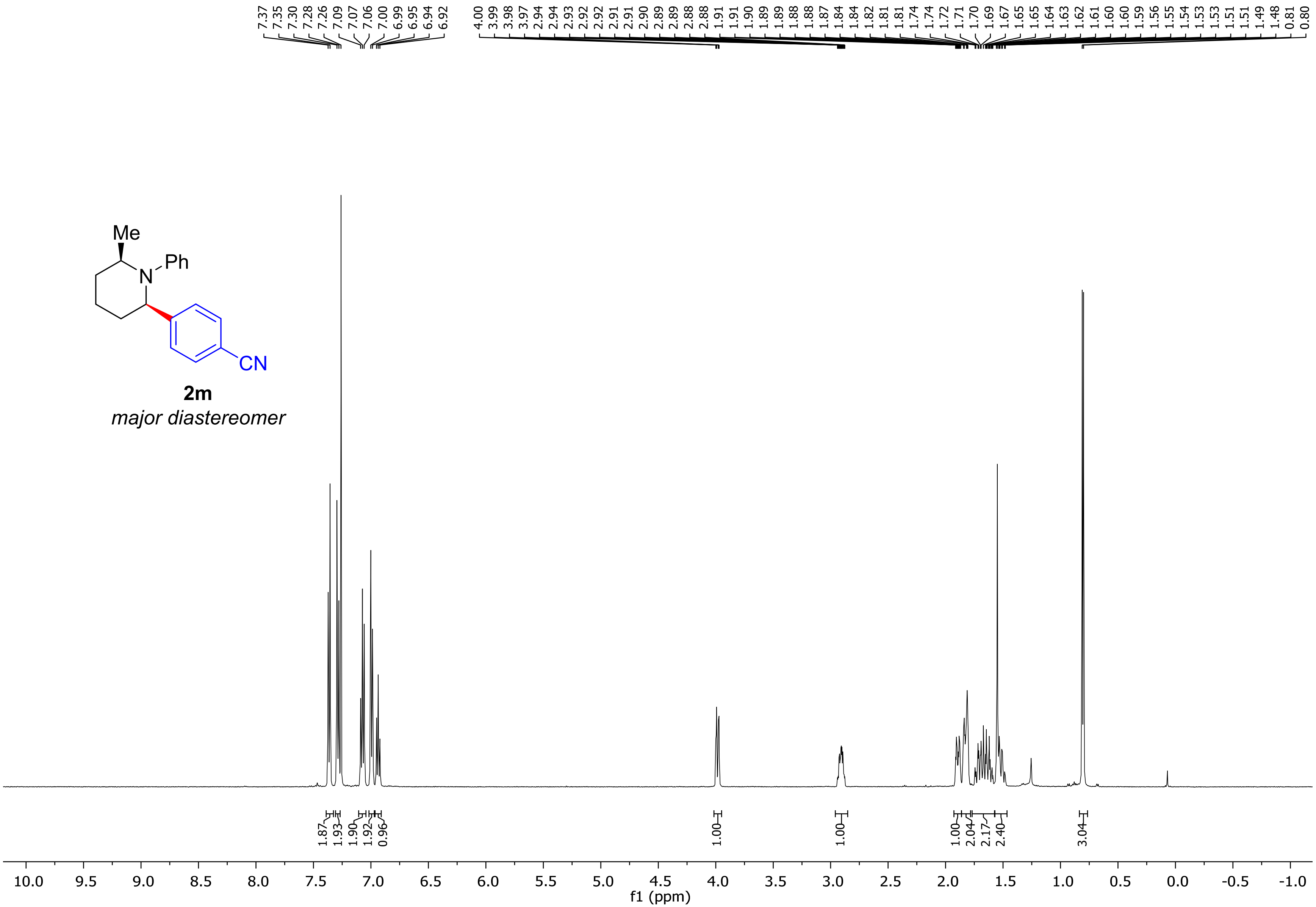
2l
minor diastereomer


NOE
500 MHz
Ha
Not observed
Hb
Not observed
Hc
Et
Hb
Et
N
Ph
(Hd)3C
Ha
(Hc)3C
CN
2l
minor diastereomer
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

major diastereomer *minor diastereomer*

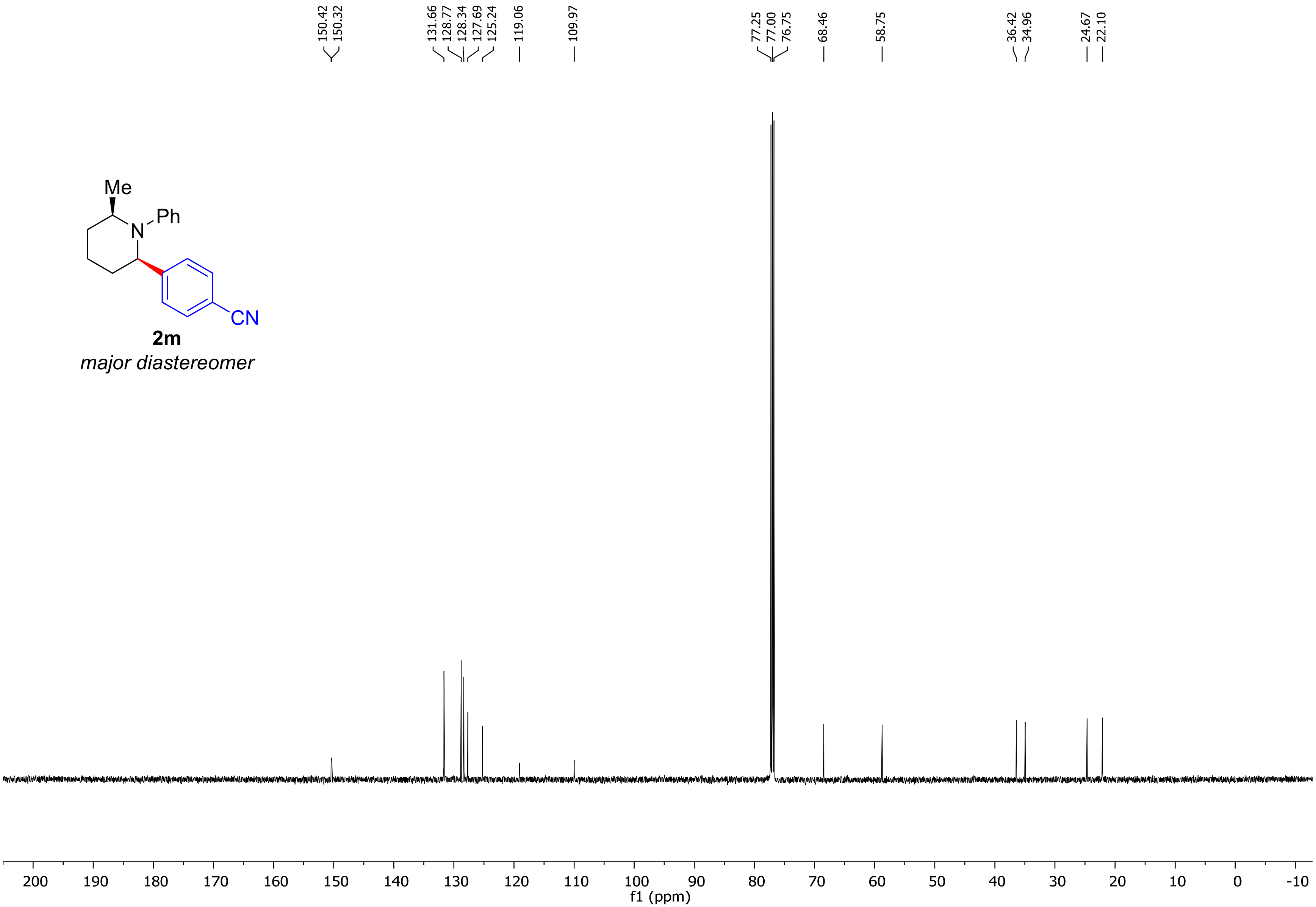
2m
Isolated mixture
^{1}H NMR - CDCl$_3$
600 MHz





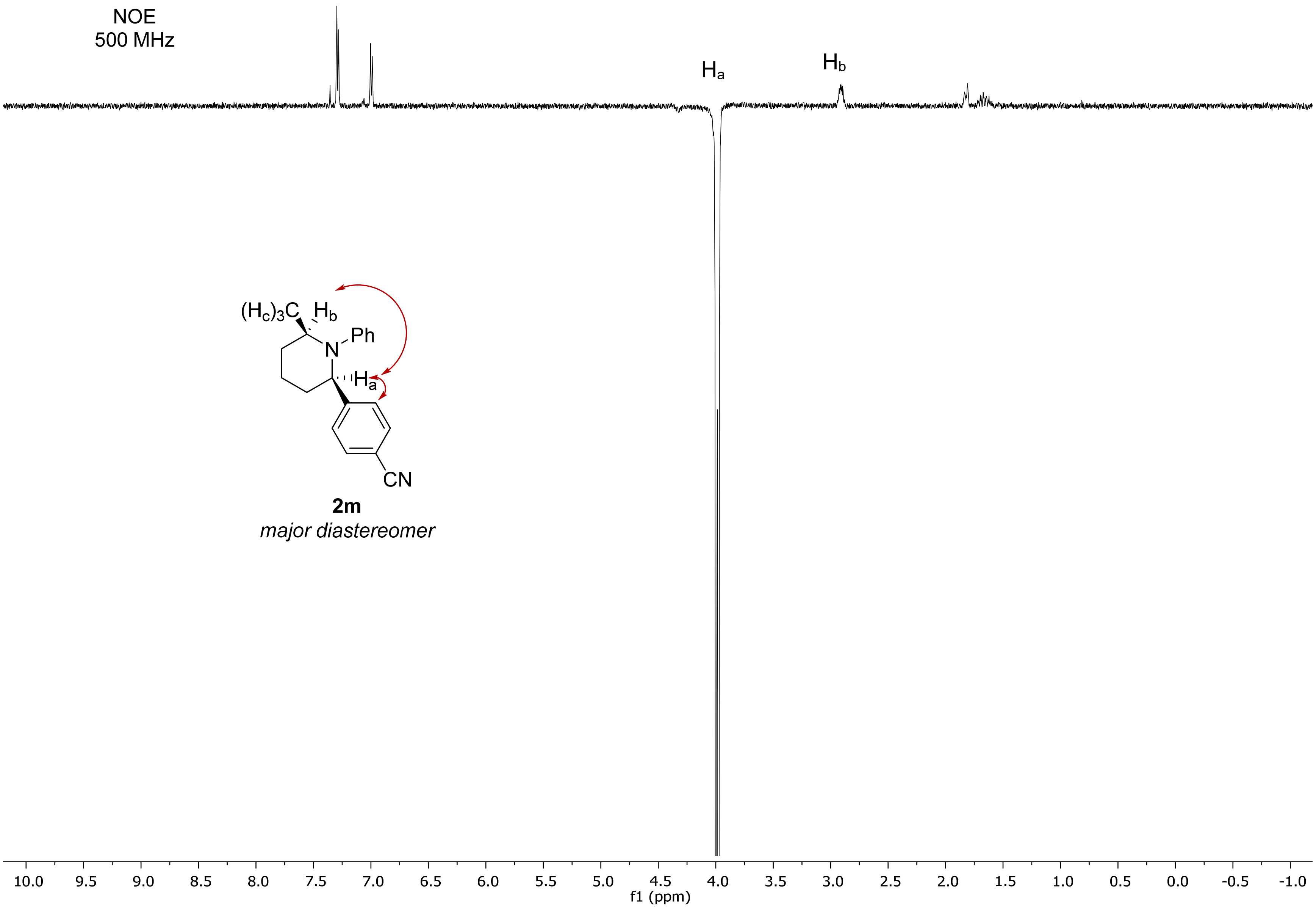
2m

major diastereomer



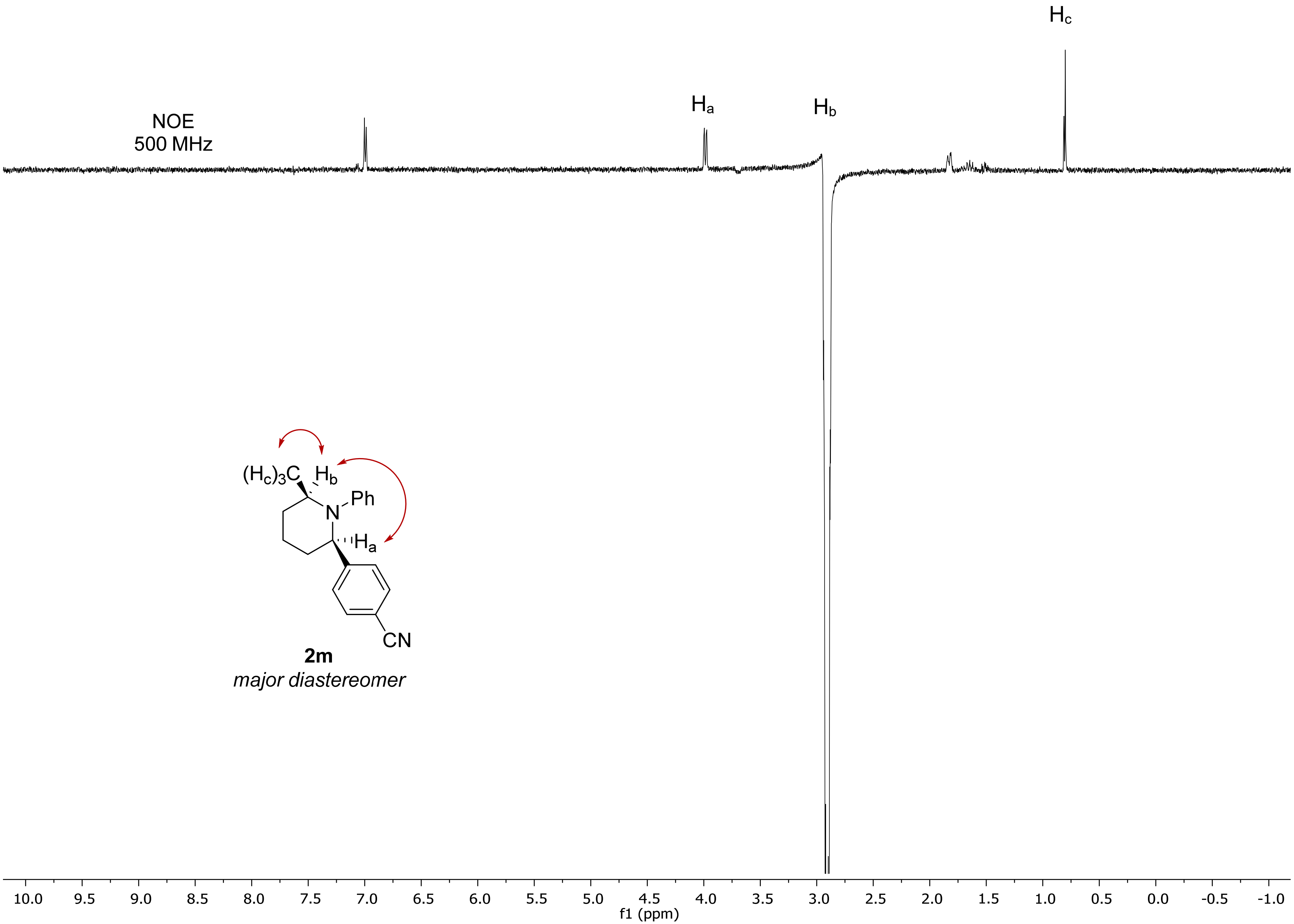
2m

major diastereomer



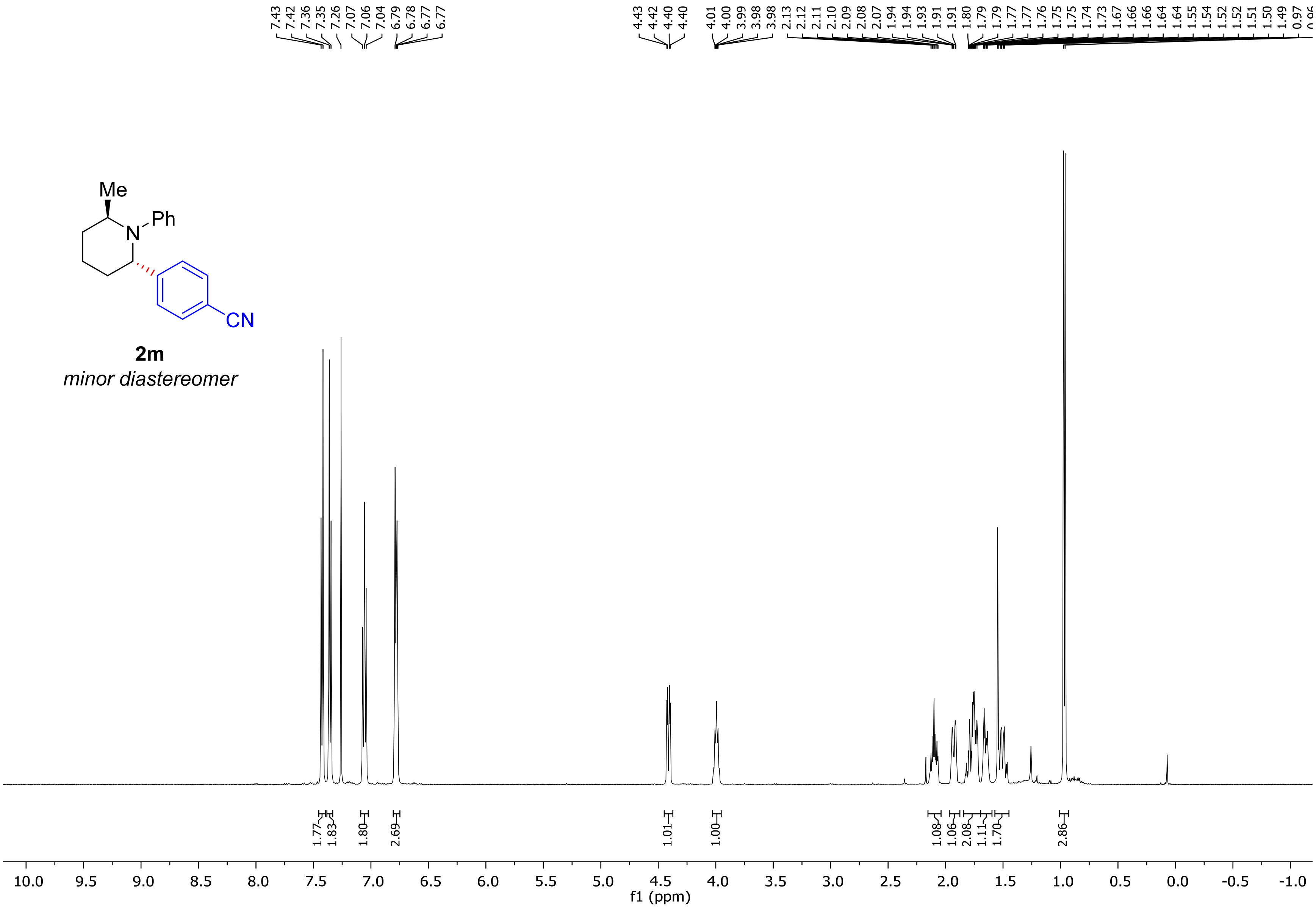
2m

major diastereomer



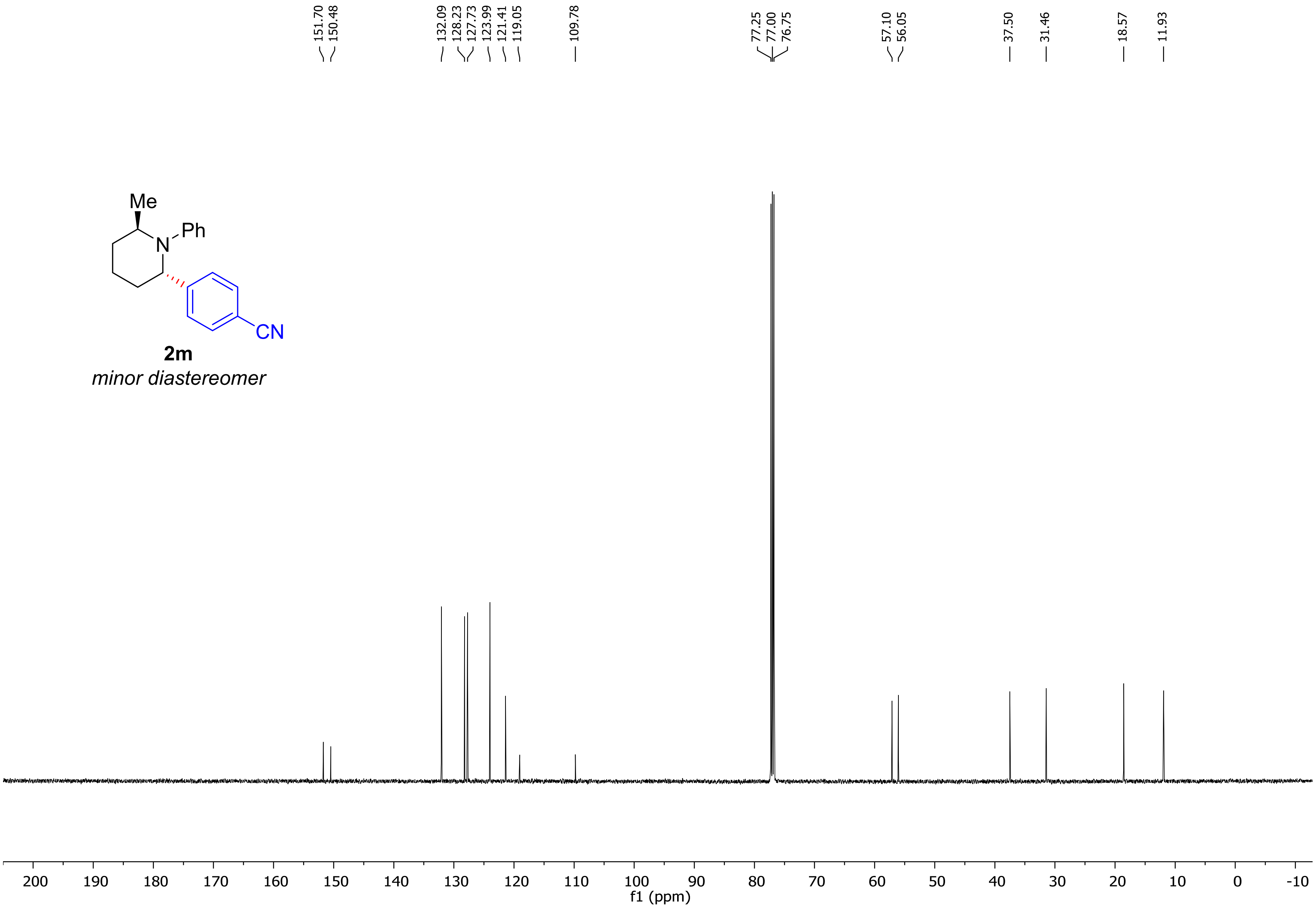
2m

major diastereomer



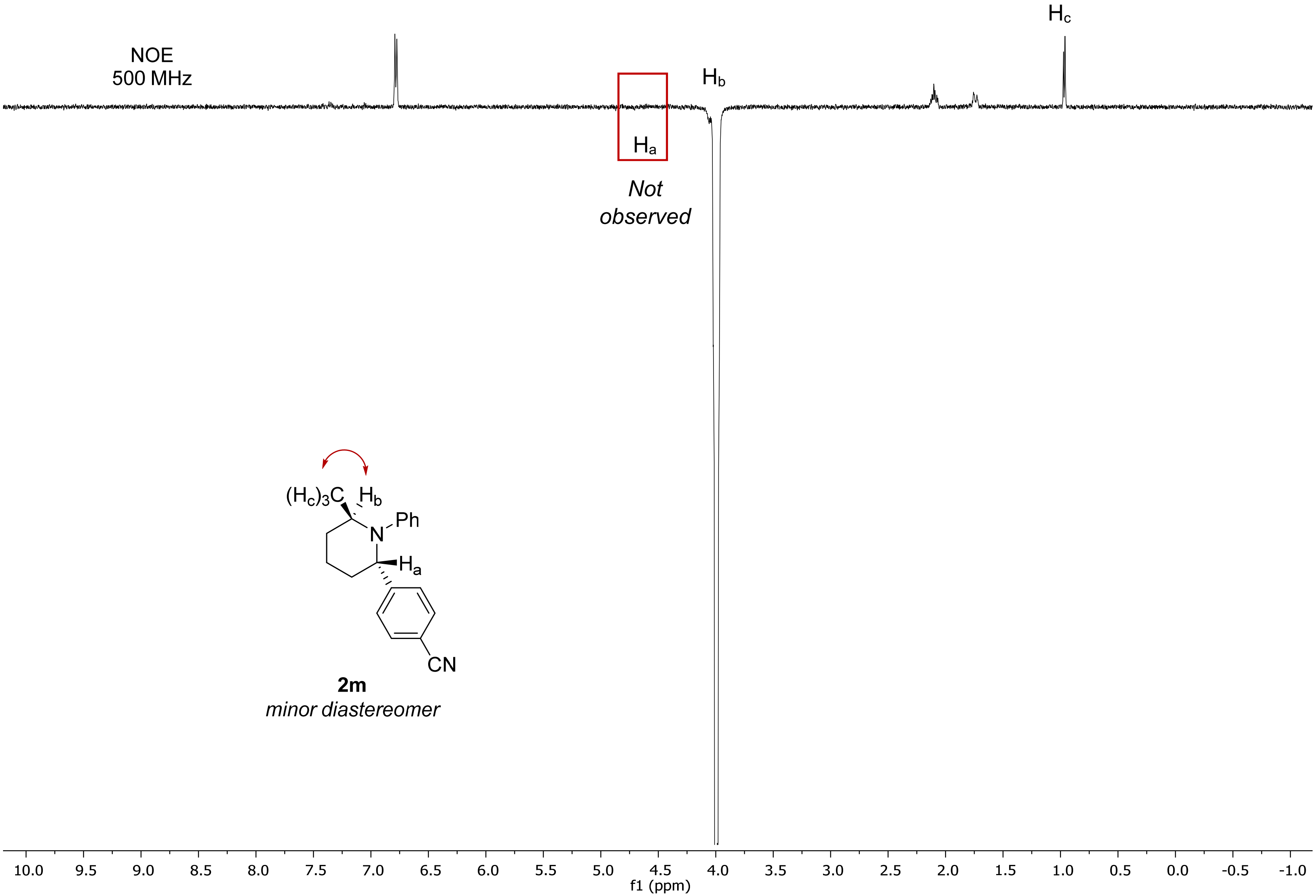
2m

minor diastereomer



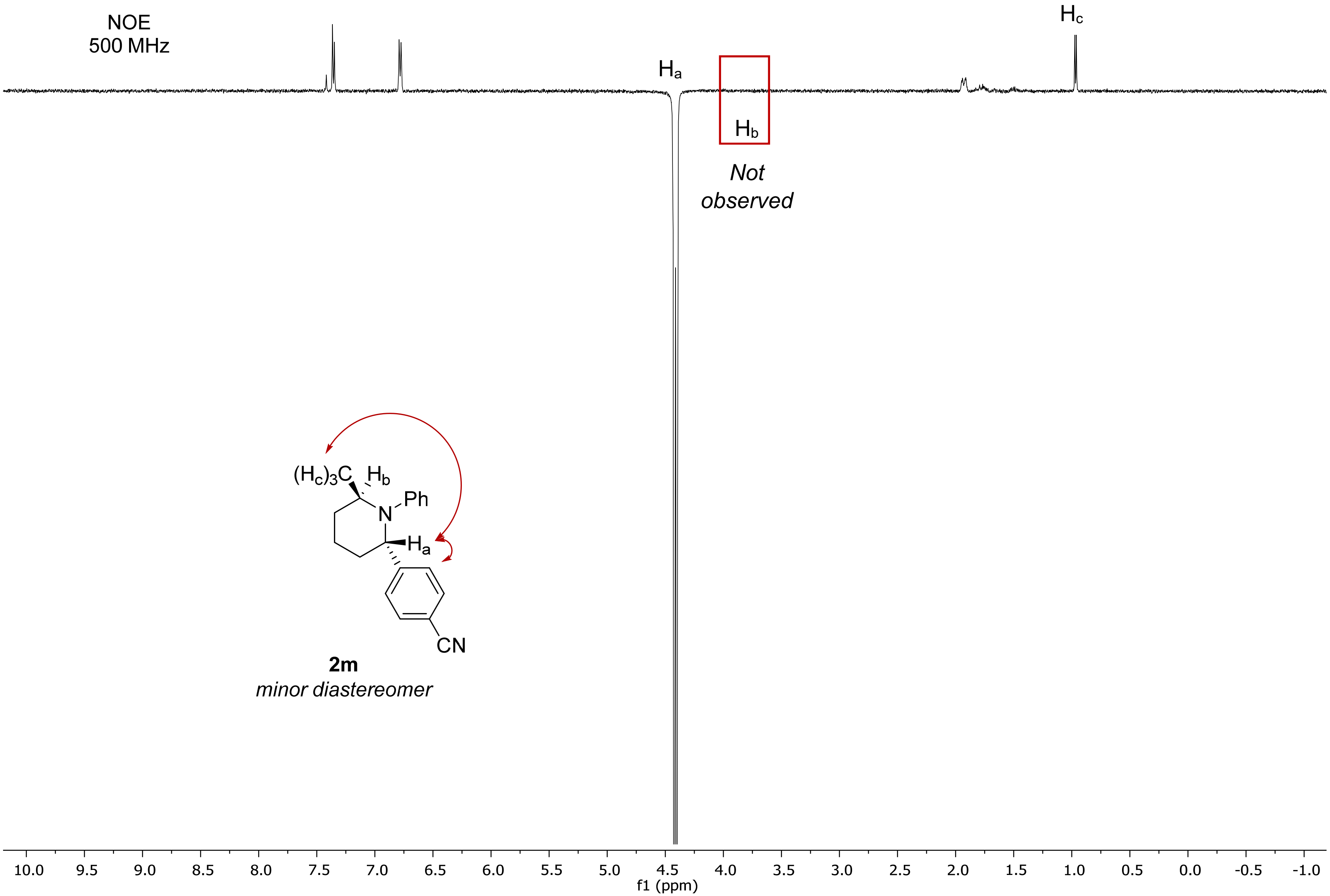
2m

minor diastereomer

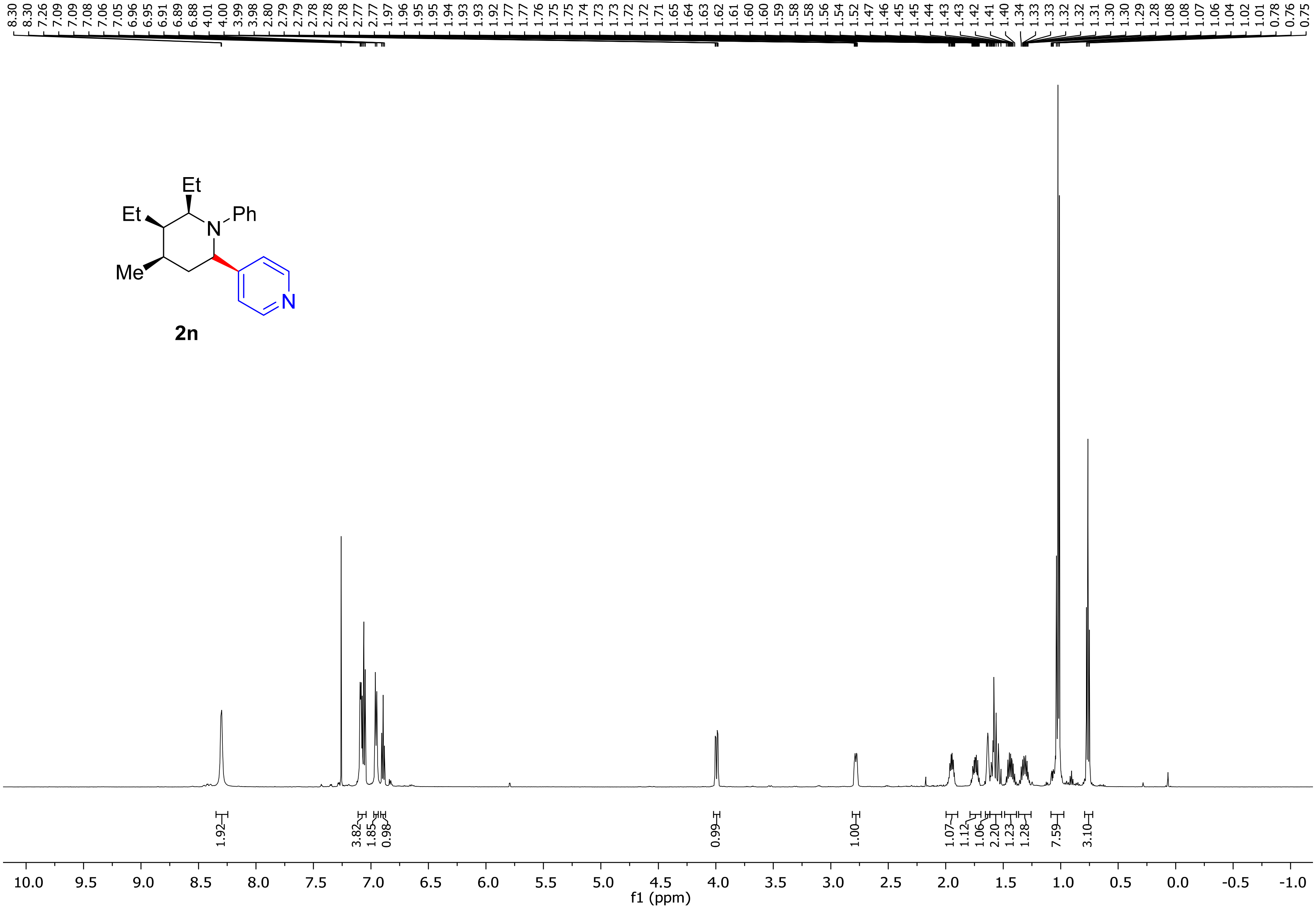


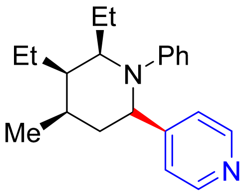
2m

minor diastereomer

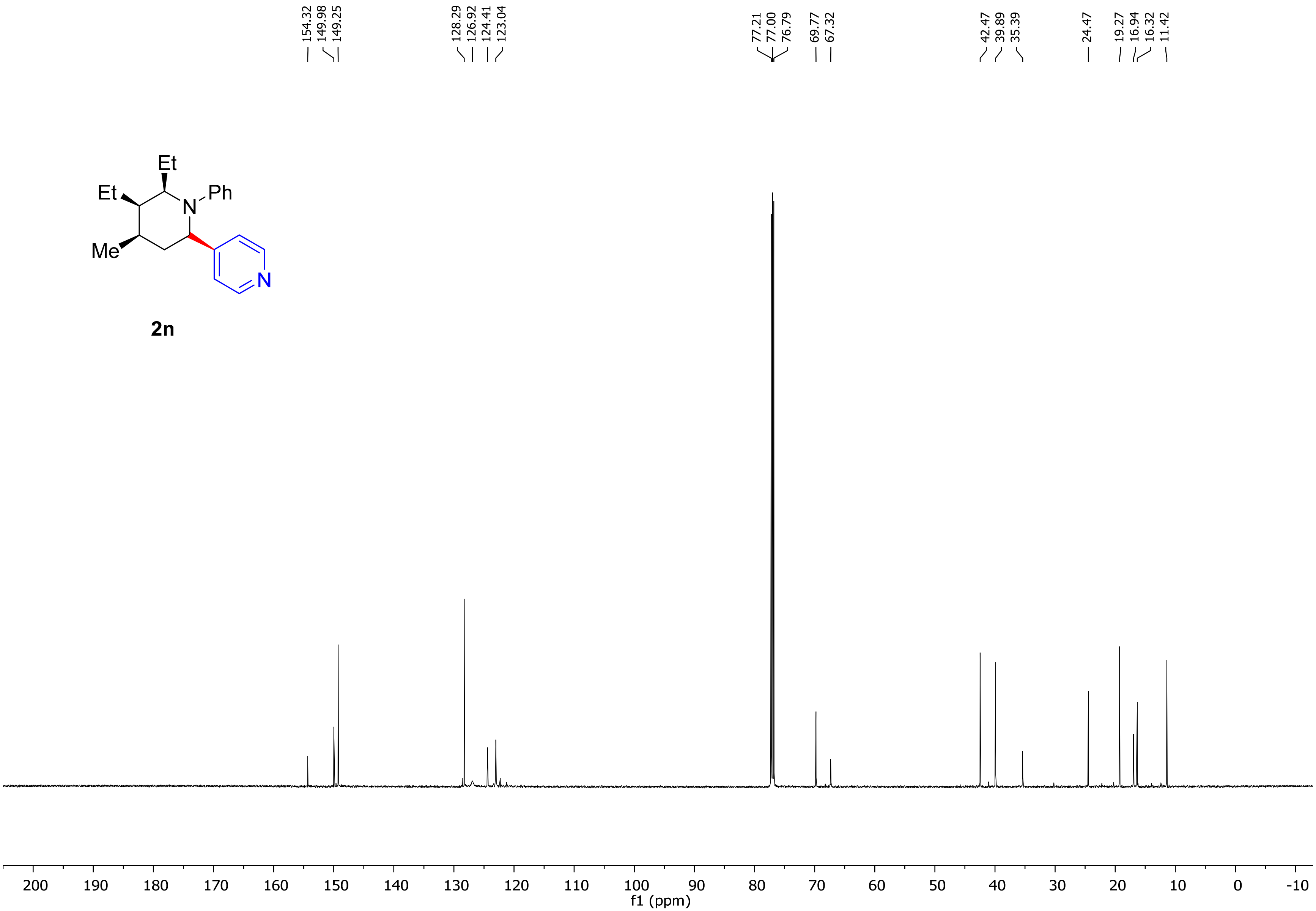


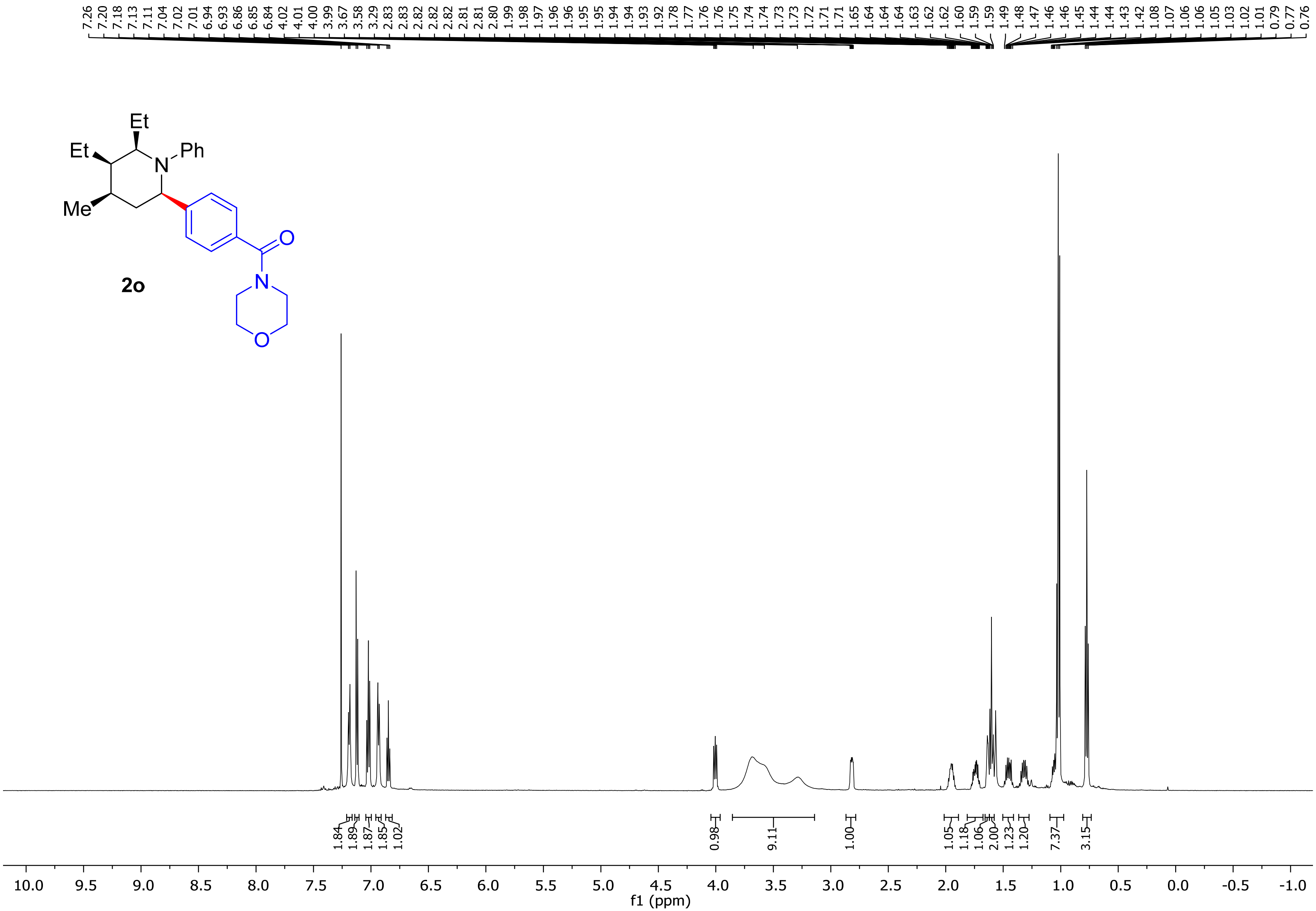
2m
minor diastereomer

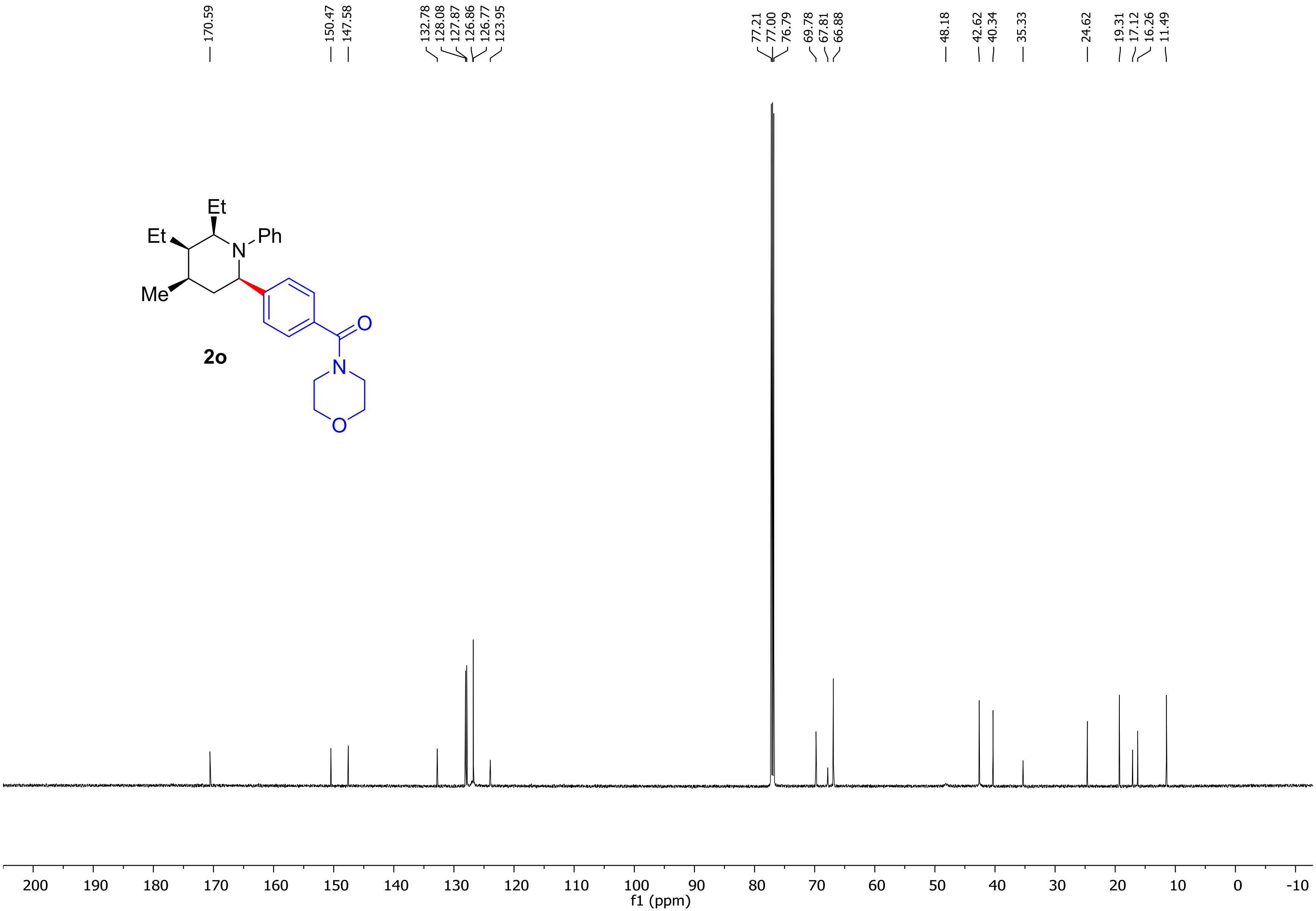

8.30
8.30
7.26
7.09
7.09
7.08
7.06
7.05
6.96
6.95
6.91
6.89
6.88
4.01
4.00
3.99
3.98
2.80
2.79
2.79
2.78
2.78
2.78
2.77
2.77
1.97
1.96
1.95
1.95
1.94
1.93
1.93
1.92
1.77
1.77
1.76
1.75
1.75
1.74
1.73
1.73
1.72
1.72
1.71
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.56
1.54
1.52
1.47
1.46
1.45
1.45
1.44
1.43
1.43
1.42
1.41
1.40
1.34
1.33
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.28
1.08
1.08
1.07
1.06
1.04
1.02
1.01
0.78
0.76
0.75
Et
Et
N
Ph
Me
N
2n
1.92
3.82
1.85
0.98
0.99
1.00
1.07
1.12
1.06
2.20
1.23
1.28
7.59
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

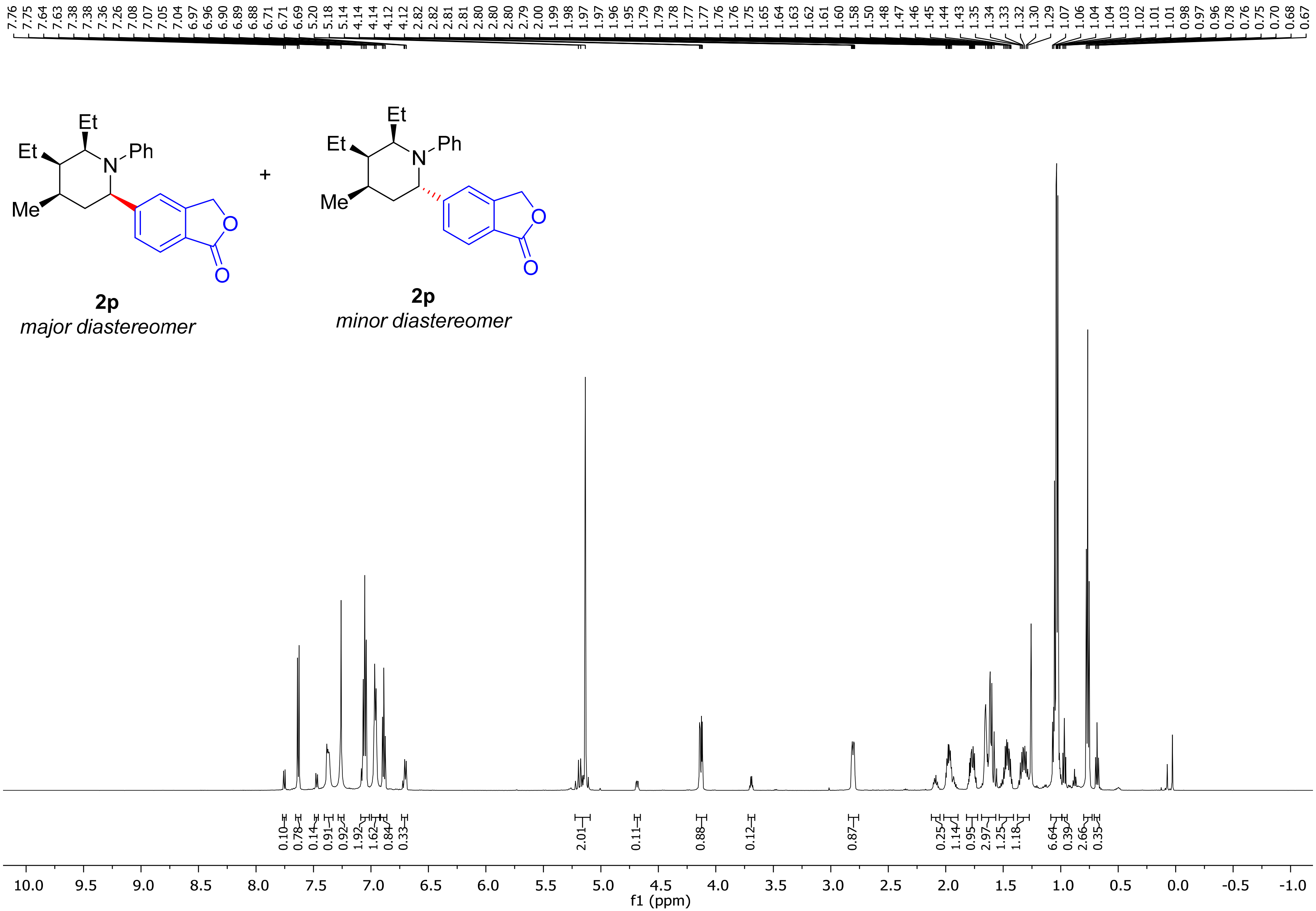

Et
Et
N
Ph
Me
N

2n


154.32
149.98
149.25
128.29
126.92
124.41
123.04
77.21
77.00
76.79
69.77
67.32
42.47
39.89
35.39
24.47
19.27
16.94
16.32
11.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
7.20
7.18
7.13
7.11
7.04
7.02
7.01
6.94
6.93
6.86
6.85
6.84
4.02
4.01
4.00
3.99
3.67
3.58
3.29
2.83
2.83
2.82
2.82
2.82
2.81
2.81
2.80
1.99
1.98
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.93
1.92
1.78
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.71
1.65
1.64
1.64
1.64
1.63
1.62
1.62
1.60
1.59
1.59
1.49
1.48
1.47
1.46
1.46
1.45
1.44
1.44
1.43
1.42
1.08
1.07
1.06
1.06
1.05
1.03
1.02
1.01
0.79
0.77
0.76
Et
Et
N
Ph
Me
O
N
O
2o
1.84
1.89
1.87
1.85
1.02
0.98
9.11
1.00
1.05
1.18
1.06
2.00
1.23
1.20
7.37
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

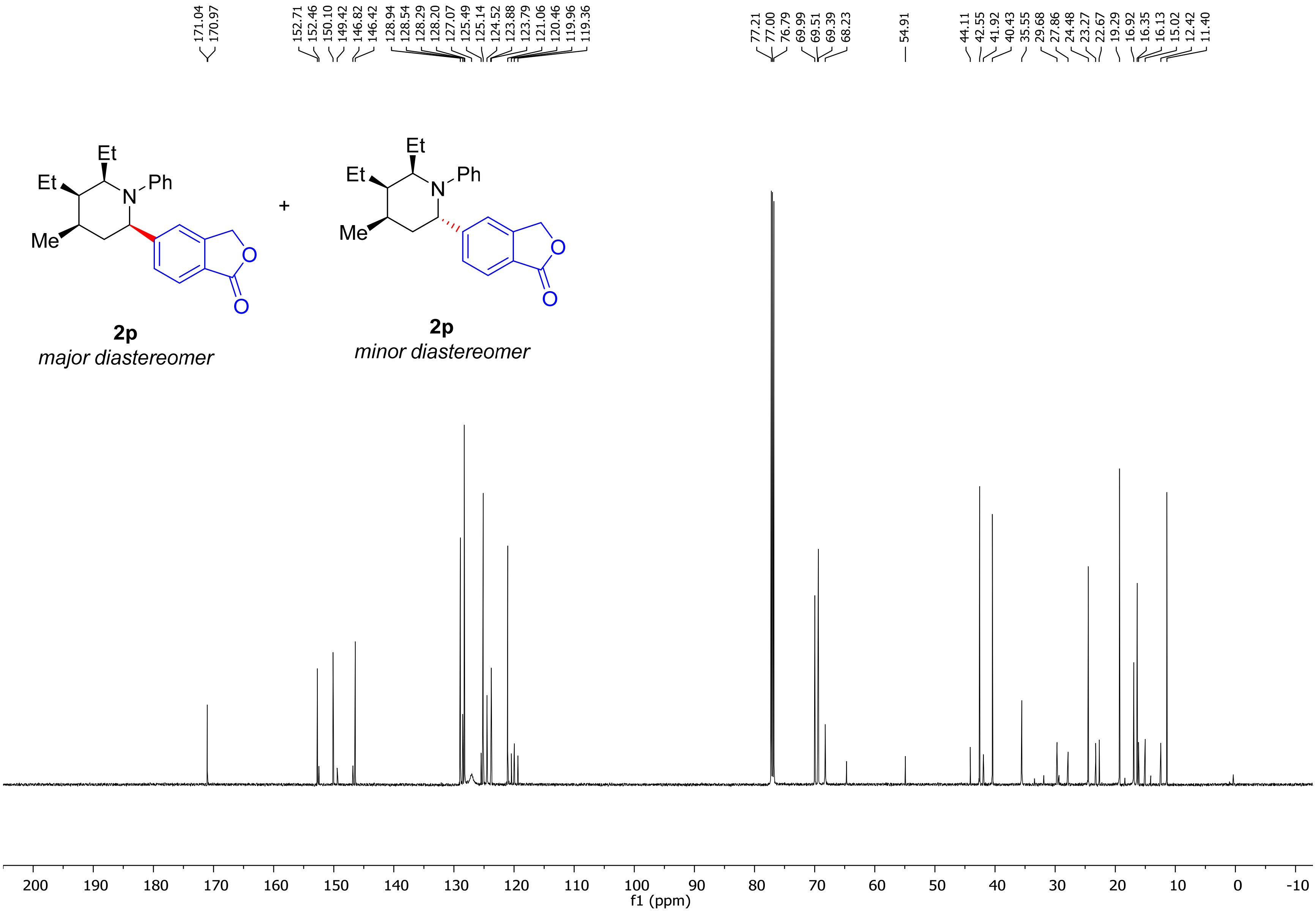

170.59
150.47
147.58
132.78
128.08
127.87
126.86
126.77
123.95
77.21
77.00
76.79
69.78
67.81
66.88
48.18
42.62
40.34
35.33
24.62
19.31
17.12
16.26
11.49
Et
Et
N
Ph
Me
O
N
O
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2p
major diastereomer

+

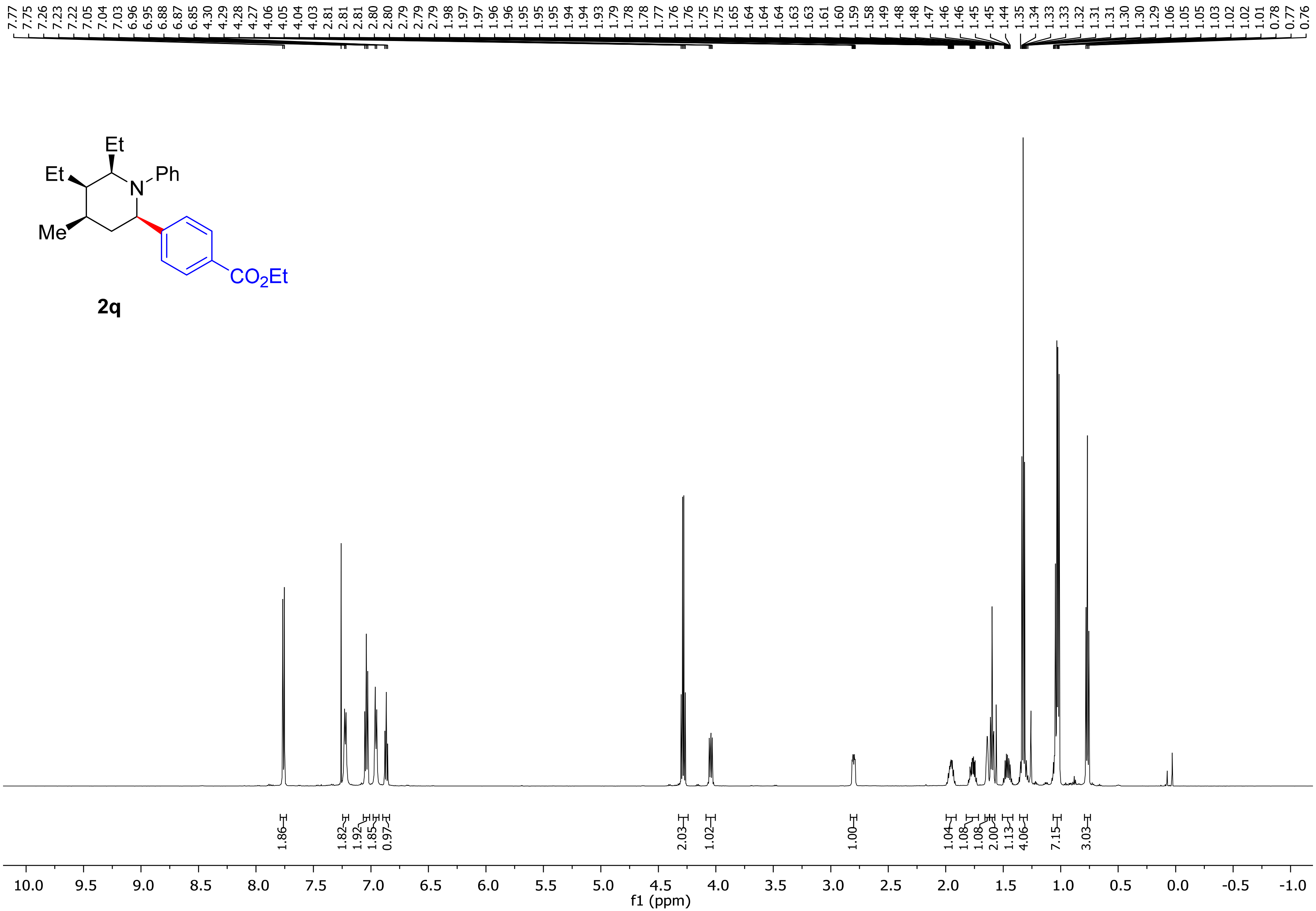
2p
minor diastereomer



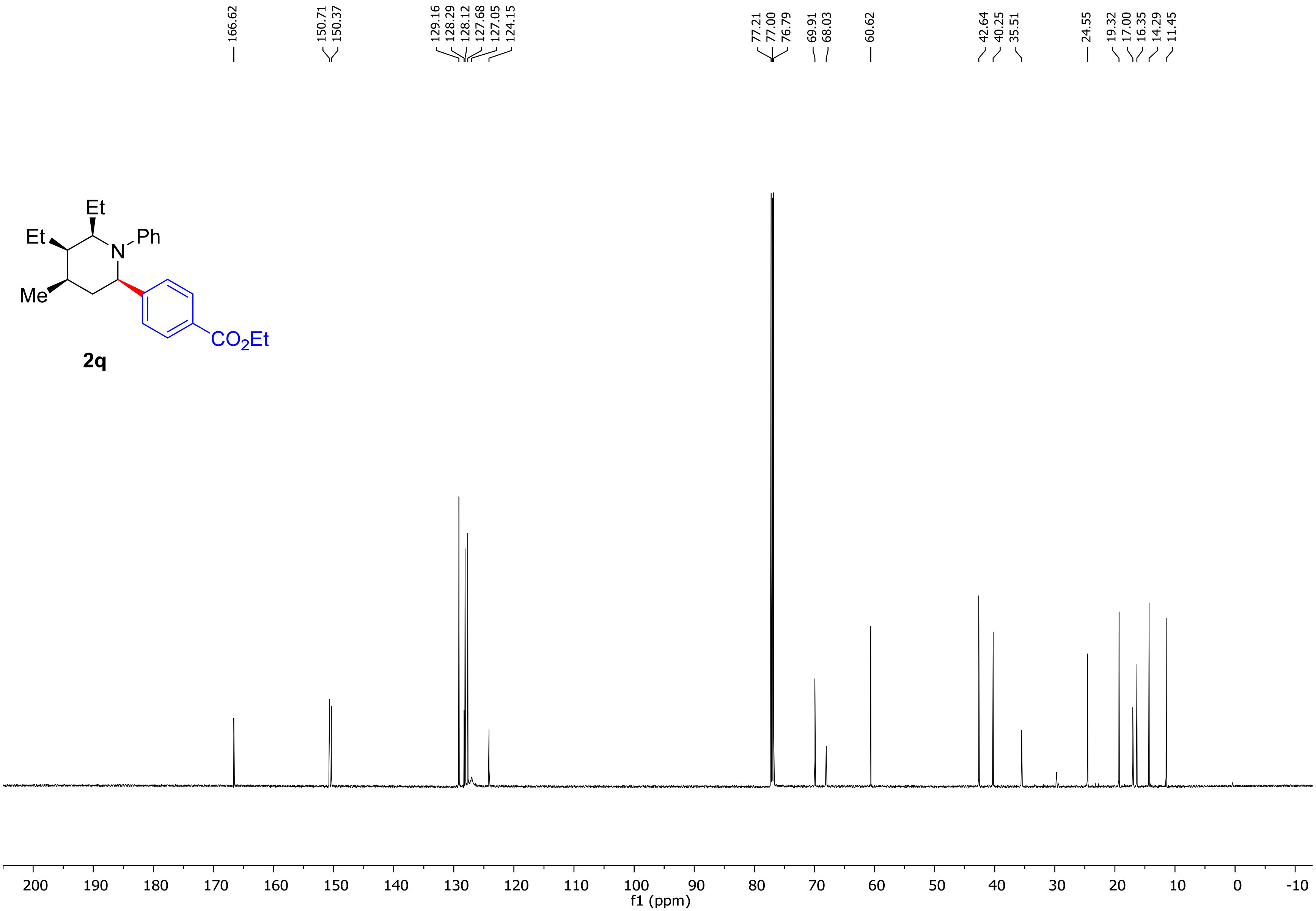
2p
major diastereomer

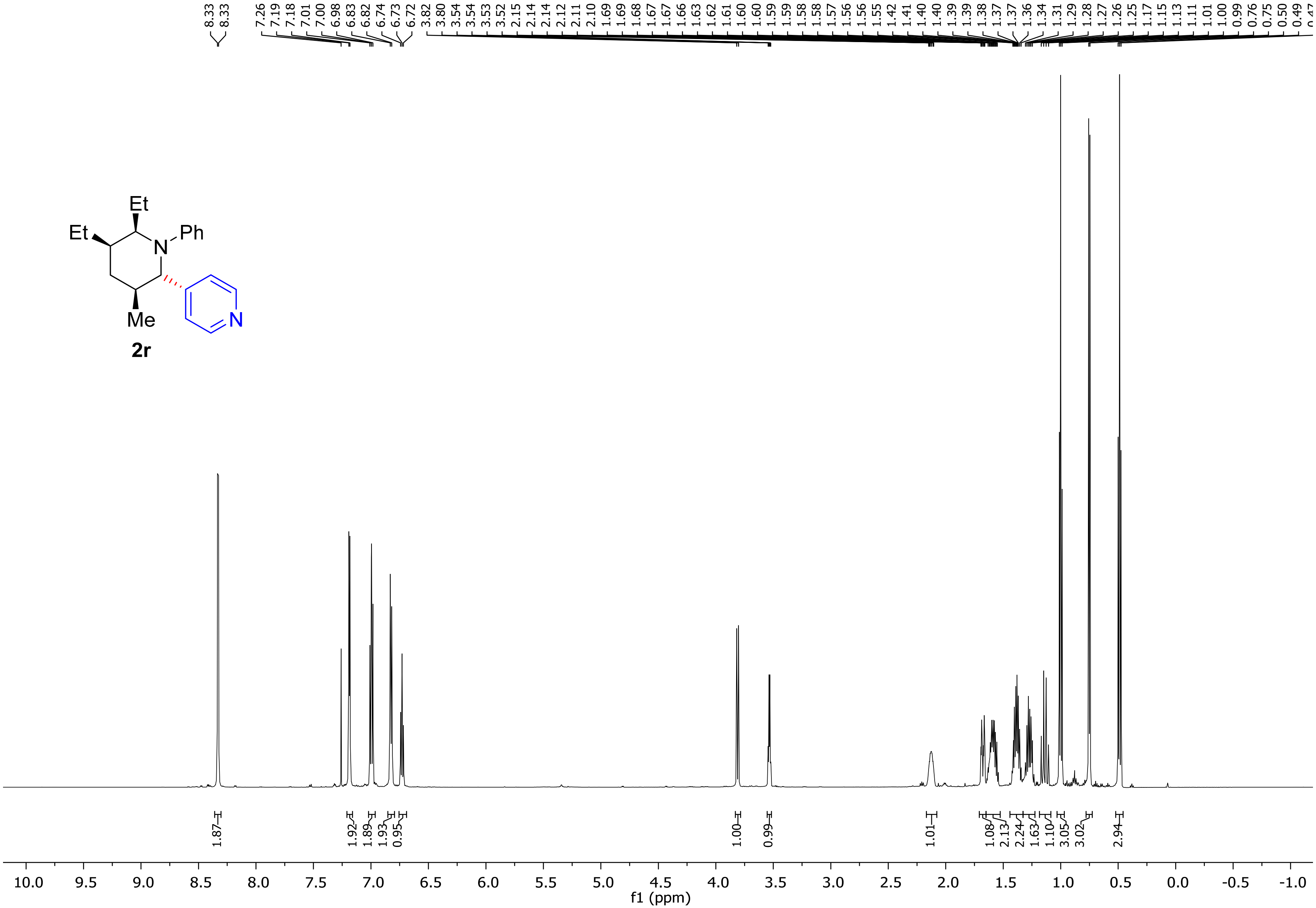
+

2p
minor diastereomer

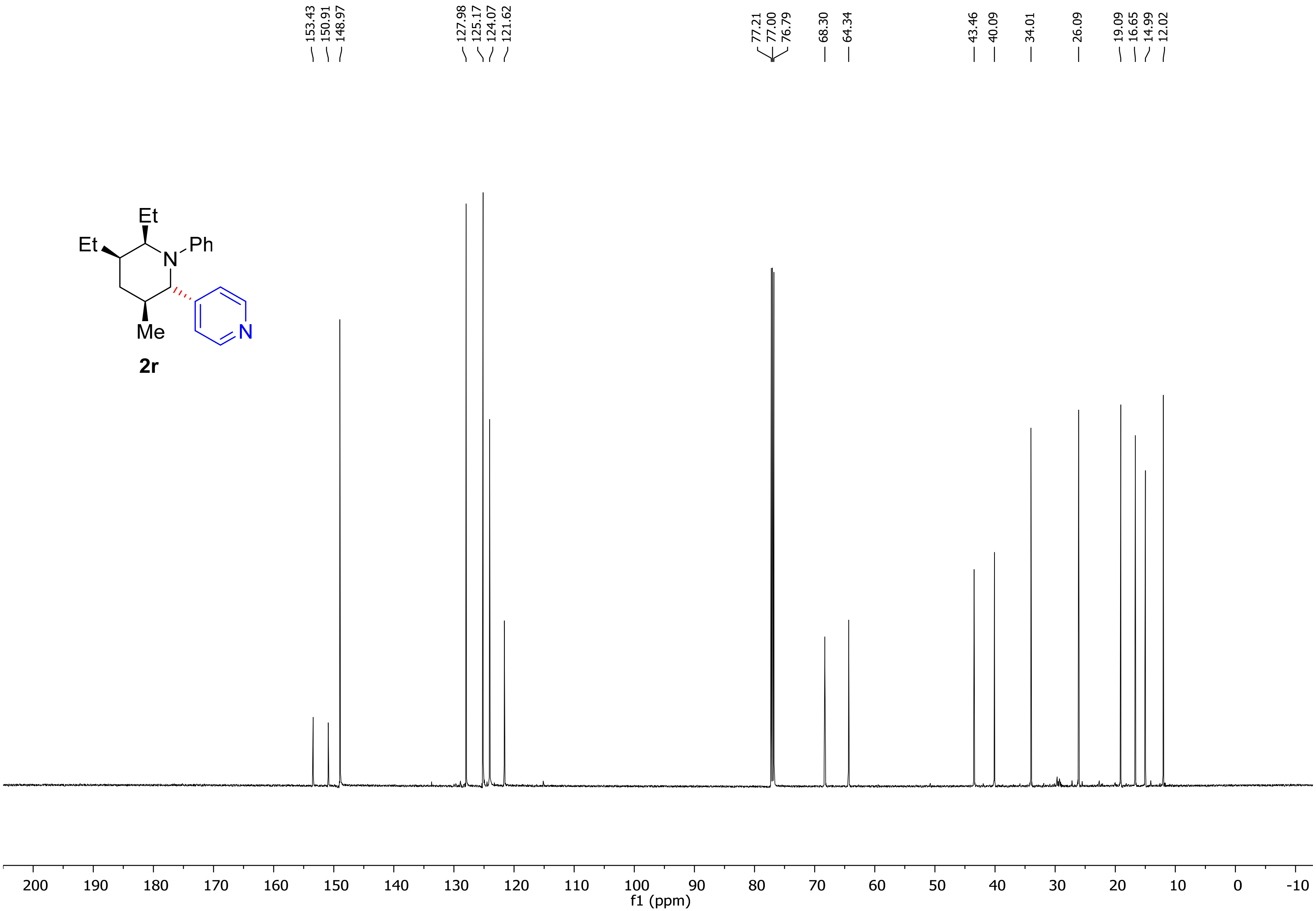

7.77
7.75
7.26
7.23
7.22
7.05
7.04
7.03
6.96
6.95
6.88
6.87
6.85
4.30
4.29
4.28
4.27
4.06
4.05
4.04
4.03
2.81
2.81
2.80
2.80
2.79
2.79
2.79
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.95
1.94
1.94
1.93
1.79
1.78
1.78
1.77
1.76
1.75
1.75
1.65
1.64
1.64
1.63
1.63
1.61
1.60
1.59
1.58
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.35
1.34
1.33
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.06
1.05
1.05
1.03
1.02
1.02
1.01
0.78
0.77
0.76
Et
Et
N
Ph
Me
CO_2Et
1.86
1.82
1.92
1.85
0.97
2.03
1.02
1.00
1.04
1.08
1.08
2.00
1.13
4.06
7.15
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

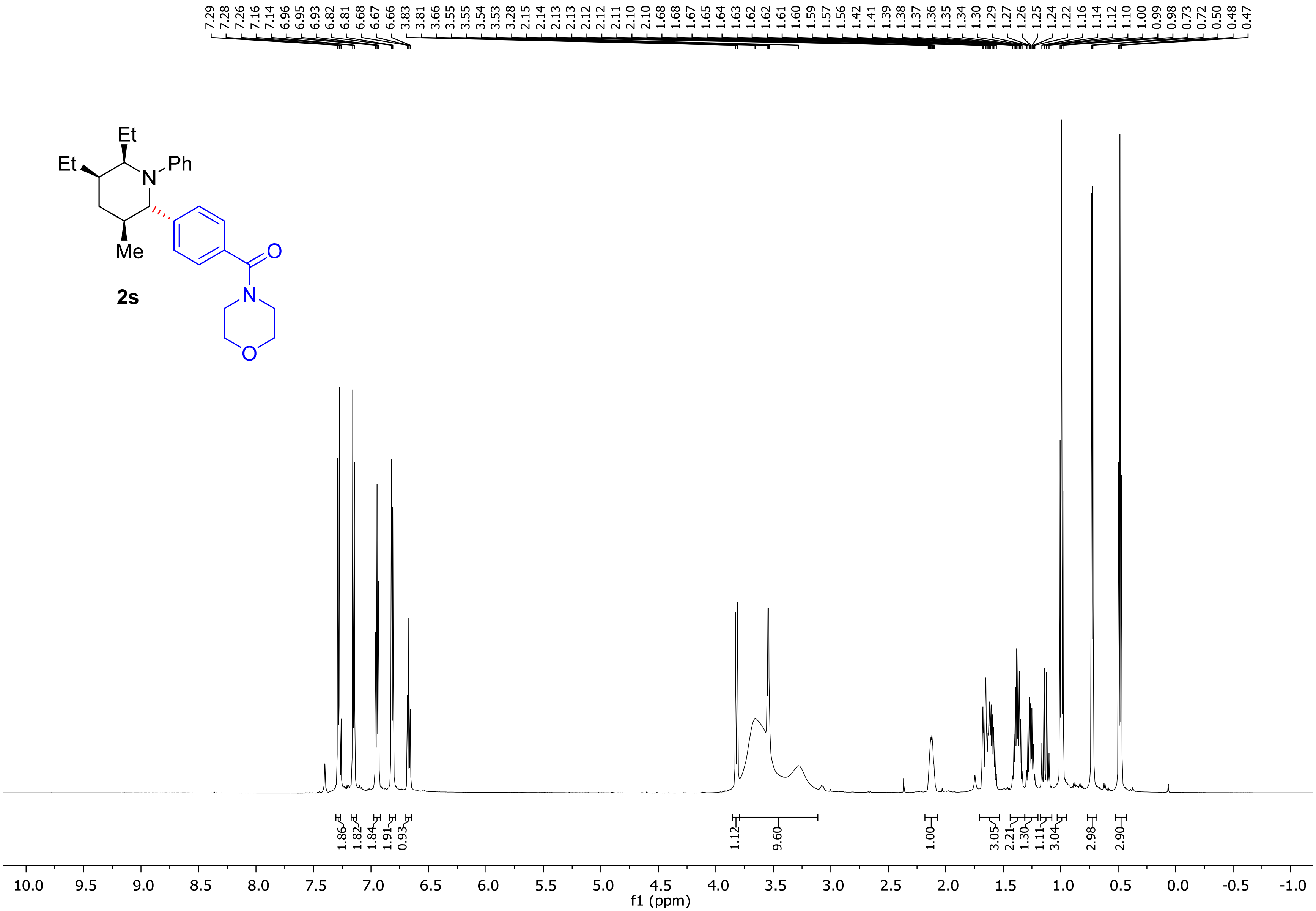
2q


166.62
150.71
150.37
129.16
128.29
128.12
127.68
127.05
124.15
77.21
77.00
76.79
69.91
68.03
60.62
42.64
40.25
35.51
24.55
19.32
17.00
16.35
14.29
11.45
Et
Et
N
Ph
Me
CO2Et
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

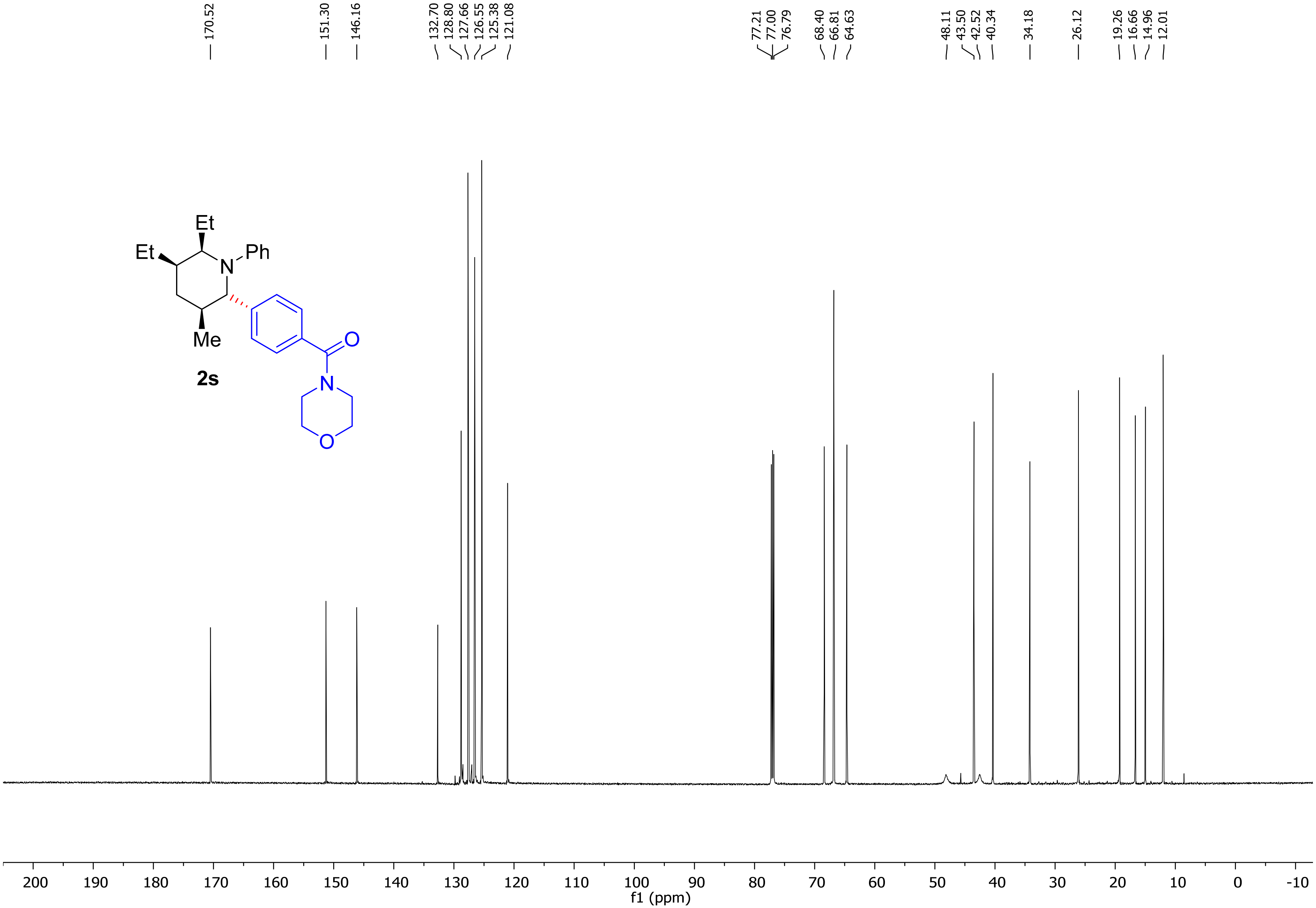

8.33
8.33
7.26
7.19
7.18
7.01
7.00
6.98
6.83
6.82
6.74
6.73
6.72
3.82
3.80
3.54
3.54
3.53
3.52
2.15
2.14
2.14
2.12
2.11
2.10
1.69
1.69
1.68
1.67
1.67
1.66
1.63
1.62
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.55
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.37
1.37
1.36
1.34
1.31
1.29
1.28
1.27
1.26
1.25
1.17
1.15
1.13
1.11
1.01
1.00
0.99
0.76
0.75
0.50
0.49
Et
Et
N
Ph
Me
N
1.87
1.92
1.89
1.93
0.95
1.00
0.99
1.01
1.08
2.13
2.24
1.63
1.10
3.05
3.02
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2r

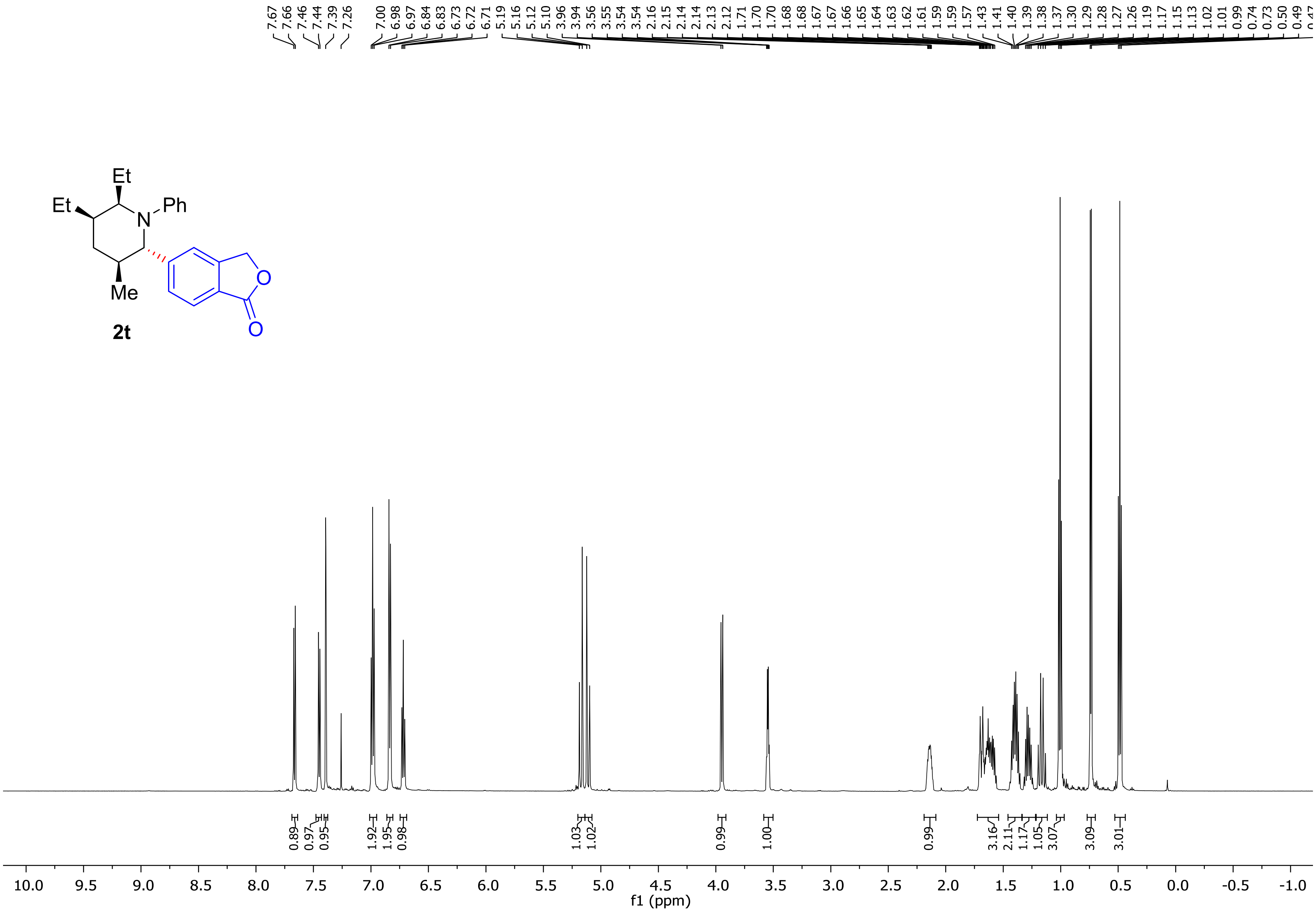

153.43
150.91
148.97
127.98
125.17
124.07
121.62
77.21
77.00
76.79
68.30
64.34
43.46
40.09
34.01
26.09
19.09
16.65
14.99
12.02
Et
Et
N
Ph
Me
N
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.29 7.28 7.26 7.16 7.14 6.96 6.95 6.93 6.82 6.81 6.68 6.67 6.66 3.83 3.81 3.66 3.55 3.55 3.54 3.53 3.28 2.15 2.14 2.13 2.13 2.12 2.12 2.11 2.10 2.10 1.68 1.68 1.67 1.65 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.57 1.56 1.42 1.41 1.39 1.38 1.37 1.36 1.35 1.34 1.30 1.29 1.27 1.26 1.25 1.24 1.22 1.16 1.14 1.12 1.10 1.00 0.99 0.98 0.73 0.72 0.50 0.48 0.47
Et
Et
N
Ph
Me
O
N
O
1.86
1.82
1.84
1.91
0.93
1.12
9.60
1.00
3.05
2.21
1.30
1.11
3.04
2.98
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

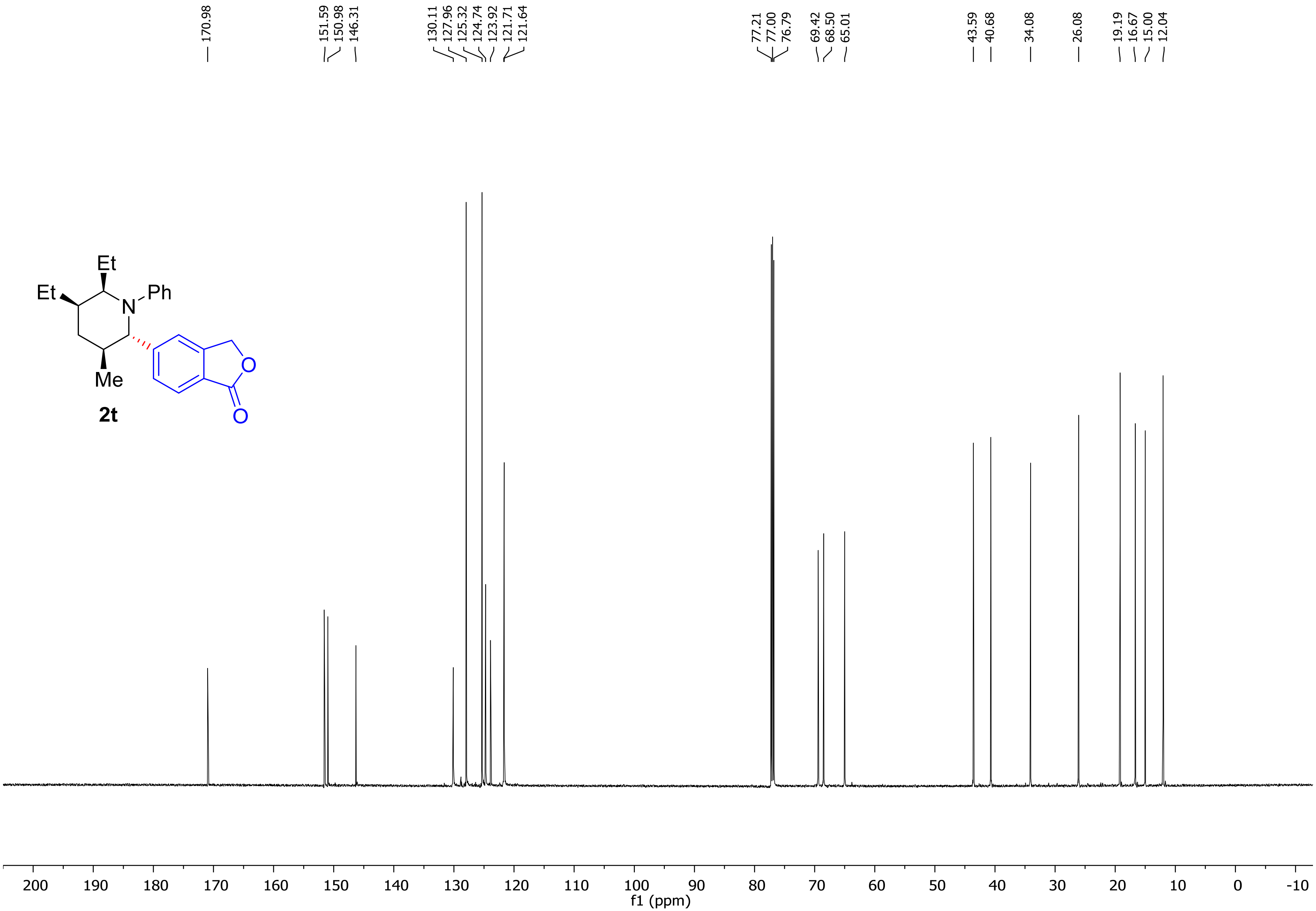
2s

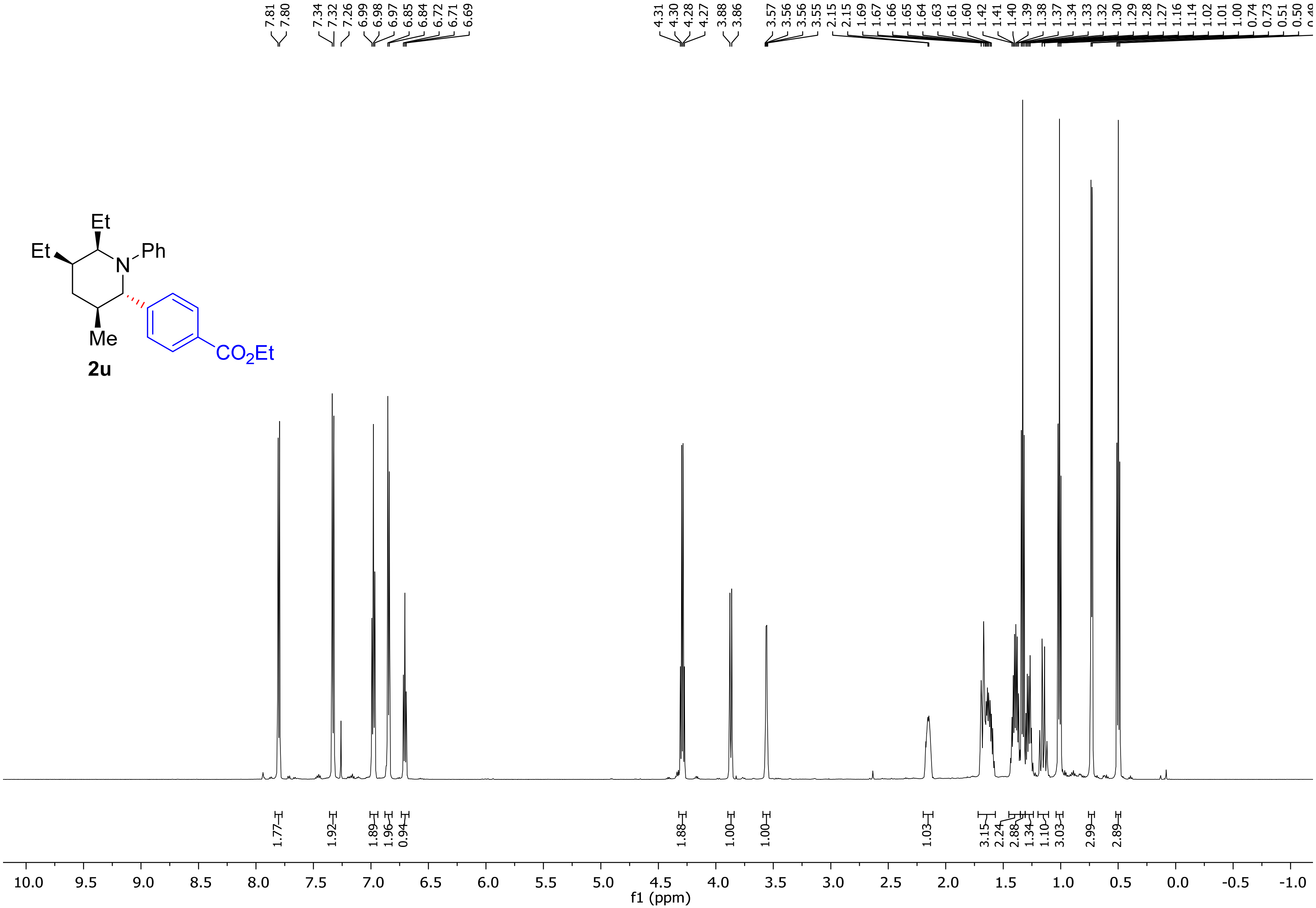

170.52
151.30
146.16
132.70
128.80
127.66
126.55
125.38
121.08
77.21
77.00
76.79
68.40
66.81
64.63
48.11
43.50
42.52
40.34
34.18
26.12
19.26
16.66
14.96
12.01
Et
Et
N
Ph
Me
O
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

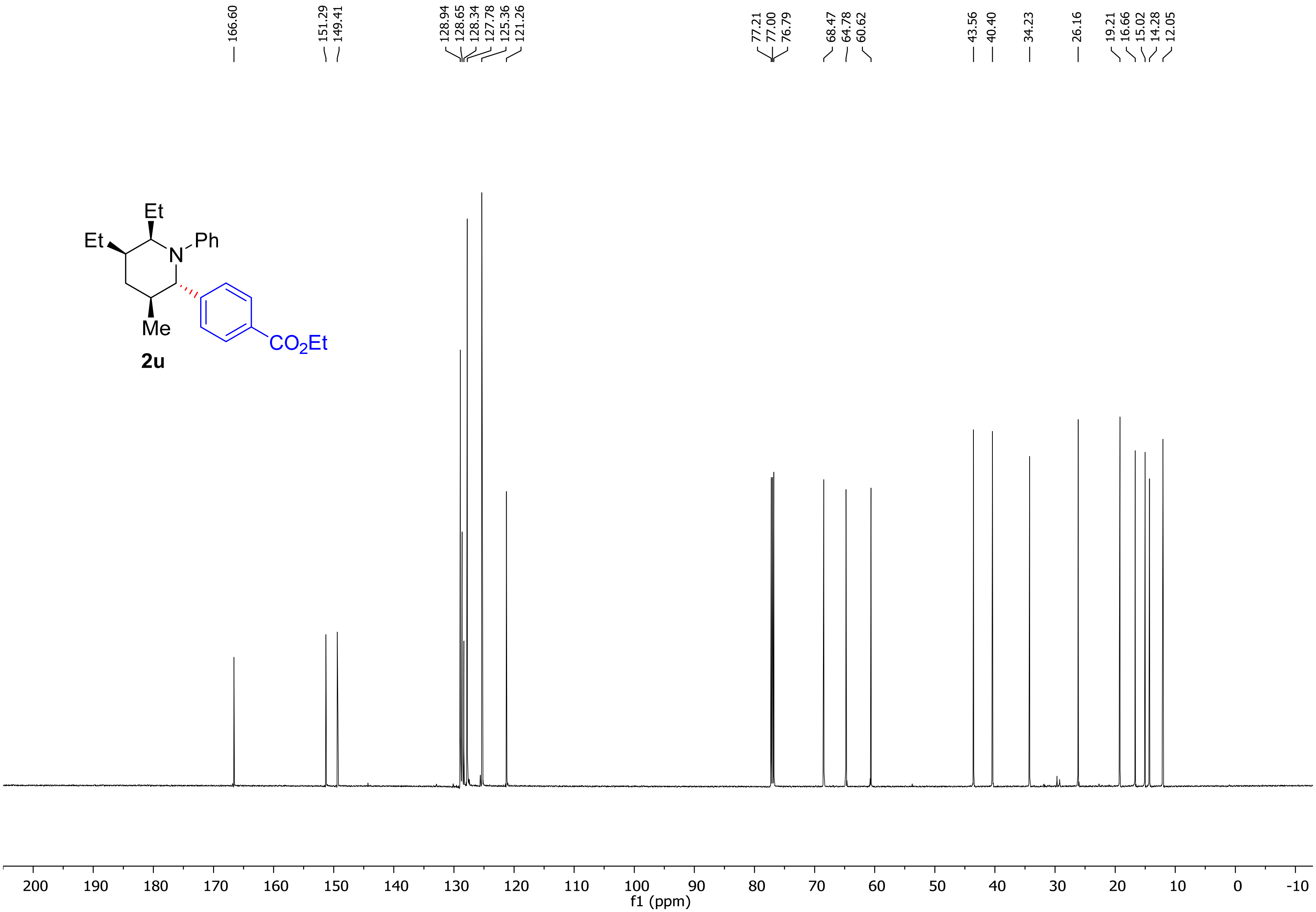
2s

7.67
7.66
7.46
7.44
7.39
7.26
7.00
6.98
6.97
6.84
6.83
6.73
6.72
6.71
5.19
5.16
5.12
5.10
3.96
3.94
3.56
3.55
3.54
3.54
2.16
2.15
2.14
2.14
2.13
2.12
1.71
1.70
1.68
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.59
1.59
1.57
1.43
1.41
1.40
1.39
1.38
1.37
1.30
1.29
1.28
1.27
1.26
1.19
1.17
1.15
1.13
1.02
1.01
0.99
0.74
0.73
0.50
0.49
0.4
Et
Et
N
Ph
Me
O
O
0.89
0.97
0.95
1.92
1.95
0.98
1.03
1.02
0.99
1.00
0.99
3.16
2.11
1.17
1.05
3.07
3.09
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

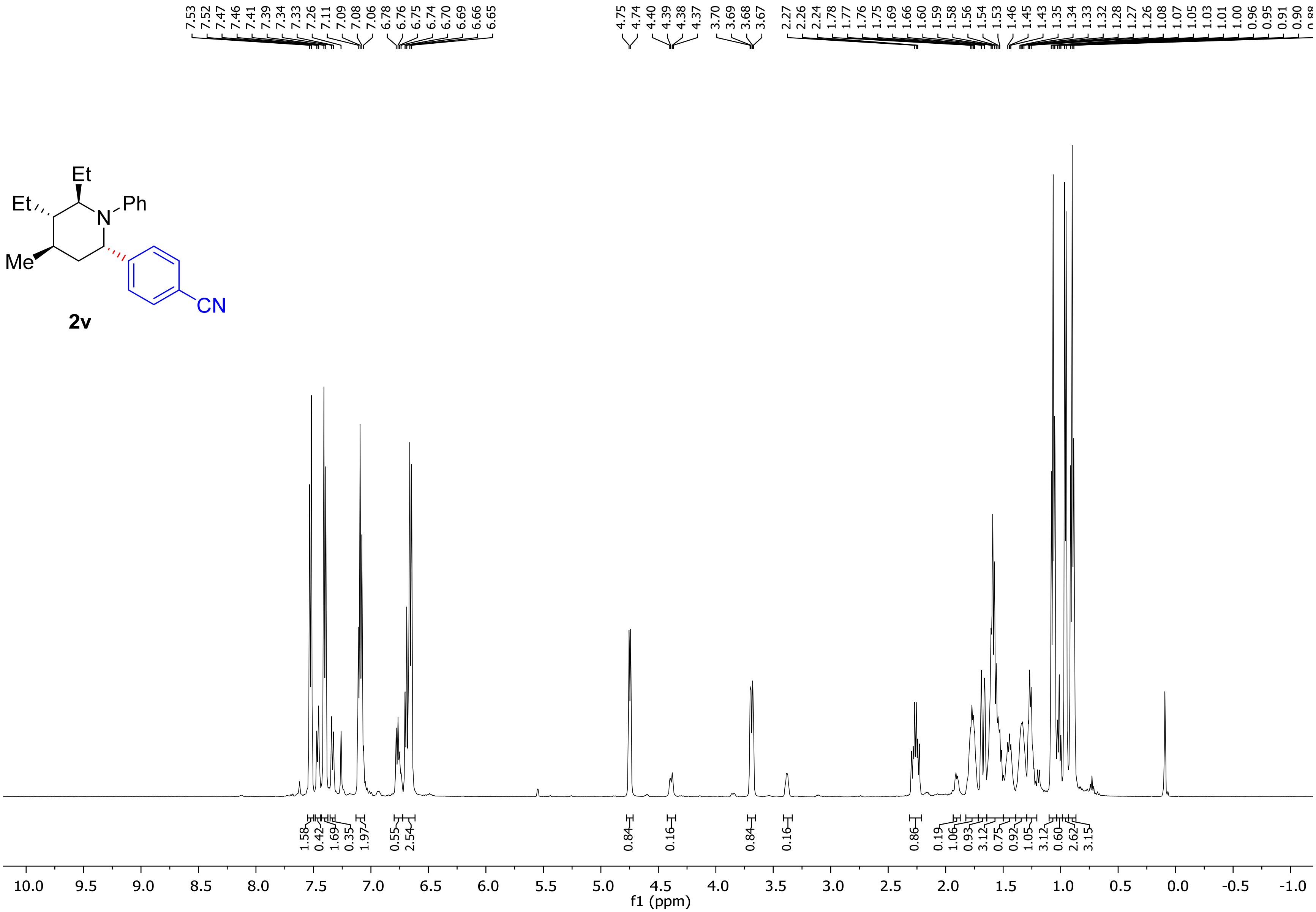
2t


170.98
151.59
150.98
146.31
130.11
127.96
125.32
124.74
123.92
121.71
121.64
77.21
77.00
76.79
69.42
68.50
65.01
43.59
40.68
34.08
26.08
19.19
16.67
15.00
12.04
Et
Et
N
Ph
Me
O
O
2t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

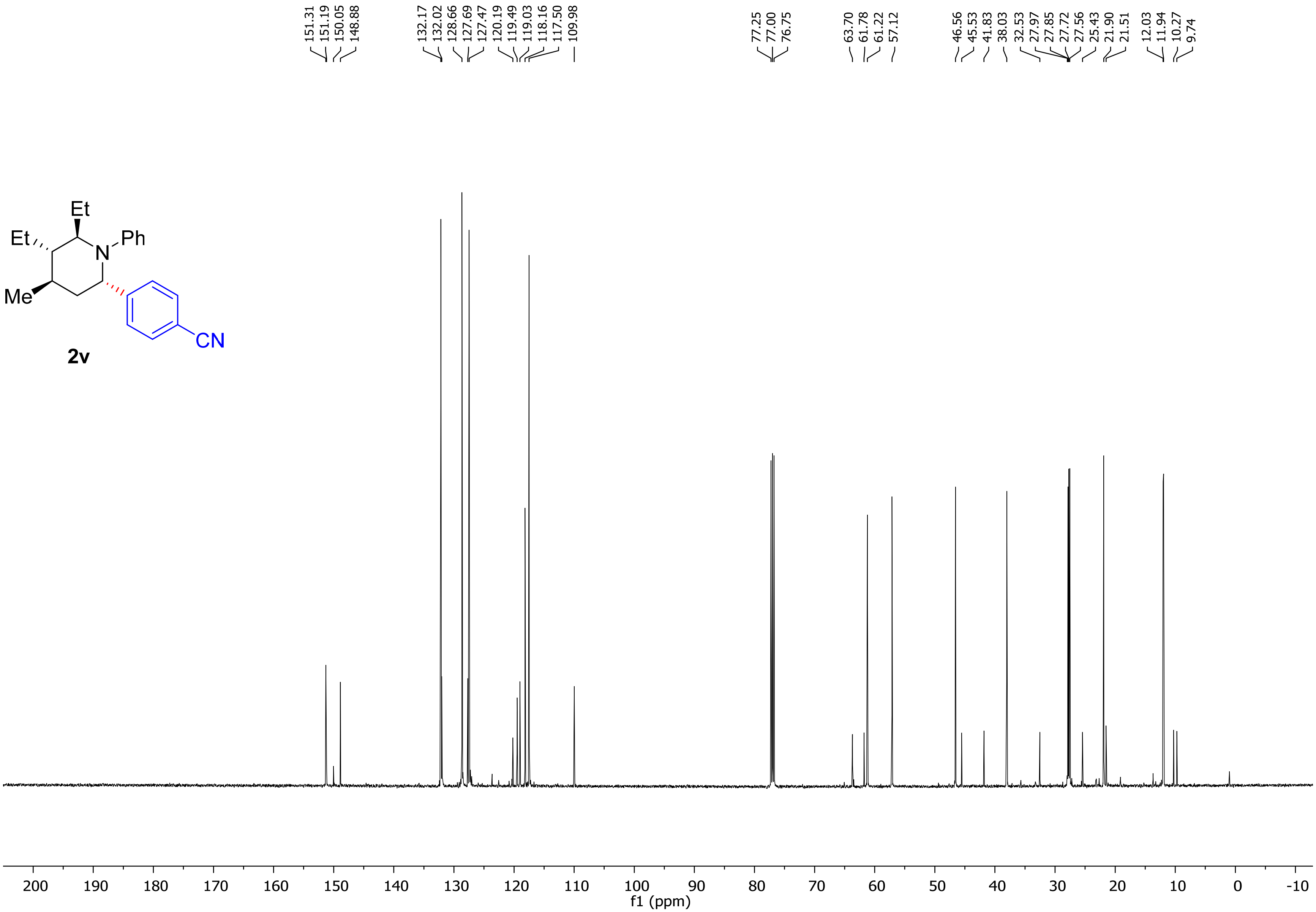

7.81
7.80
7.34
7.32
7.26
6.99
6.98
6.97
6.85
6.84
6.72
6.71
6.69
4.31
4.30
4.28
4.27
3.88
3.86
3.57
3.56
3.56
3.55
2.15
2.15
1.69
1.67
1.66
1.65
1.64
1.63
1.61
1.60
1.42
1.41
1.40
1.39
1.38
1.37
1.34
1.33
1.32
1.30
1.29
1.28
1.27
1.16
1.14
1.02
1.01
1.00
0.74
0.73
0.51
0.50
0.49
Et
Et
N
Ph
Me
CO2Et
2u
1.77
1.92
1.89
1.96
0.94
1.88
1.00
1.00
1.03
3.15
2.24
2.88
1.34
1.10
3.03
2.99
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


166.60
151.29
149.41
128.94
128.65
128.34
127.78
125.36
121.26
77.21
77.00
76.79
68.47
64.78
60.62
43.56
40.40
34.23
26.16
19.21
16.66
15.02
14.28
12.05
Et
Et
N
Ph
Me
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

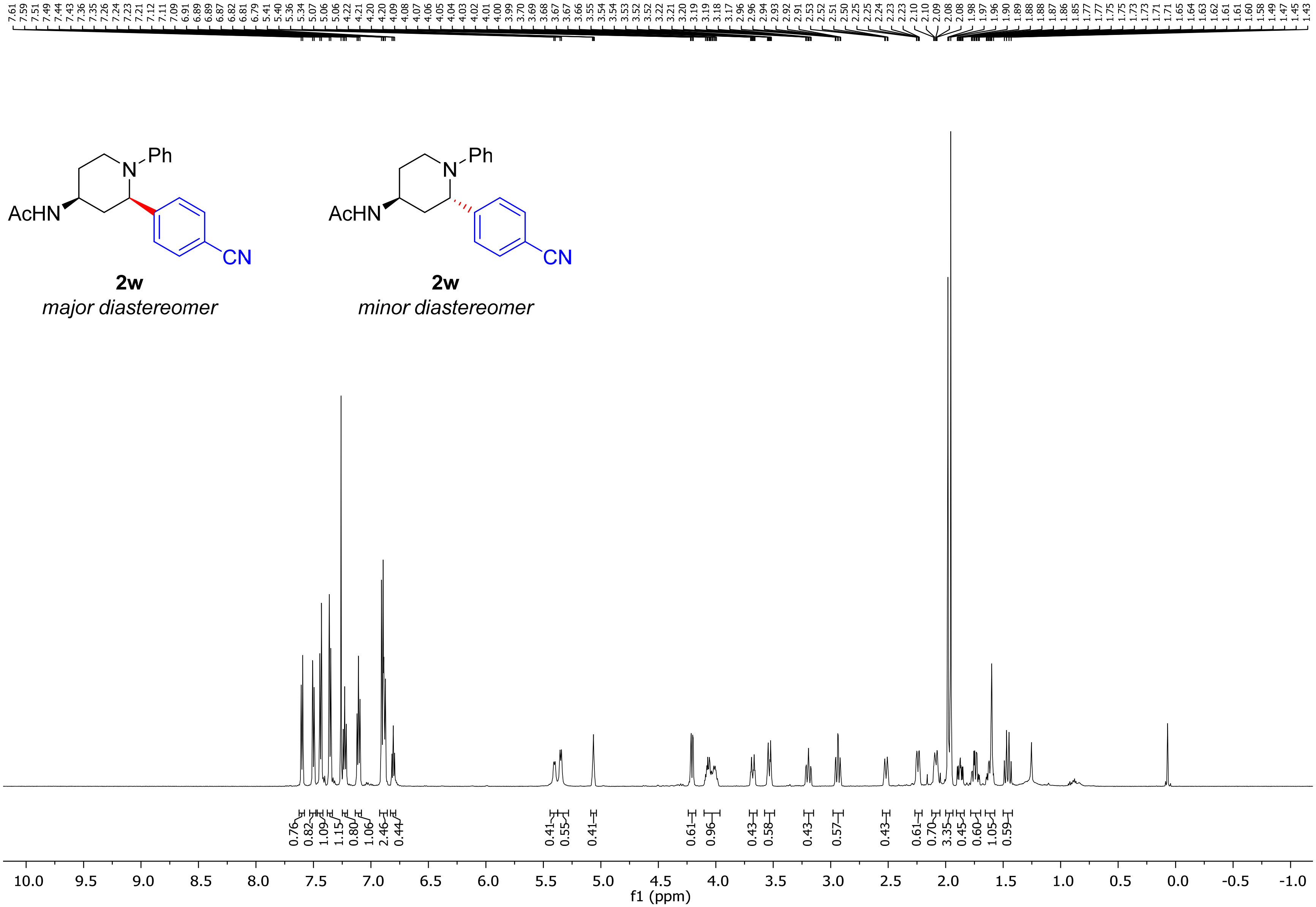
2u


7.53
7.52
7.47
7.46
7.41
7.39
7.34
7.33
7.26
7.11
7.09
7.08
7.06
6.78
6.76
6.75
6.74
6.70
6.69
6.66
6.65
4.75
4.74
4.40
4.39
4.38
4.37
3.70
3.69
3.68
3.67
2.27
2.26
2.24
1.78
1.77
1.76
1.75
1.69
1.66
1.60
1.59
1.58
1.56
1.54
1.53
1.46
1.45
1.43
1.35
1.34
1.33
1.32
1.28
1.27
1.26
1.08
1.07
1.05
1.03
1.01
1.00
0.96
0.95
0.91
0.90
0.88
Et
Et
N
Ph
Me
CN
1.58
0.42
1.69
0.35
1.97
0.55
2.54
0.84
0.16
0.84
0.16
0.86
0.19
1.06
0.93
3.12
0.75
0.92
1.05
3.12
0.60
2.62
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2v


151.31
151.19
150.05
148.88
132.17
132.02
128.66
127.69
127.47
120.19
119.49
119.03
118.16
117.50
109.98
77.25
77.00
76.75
63.70
61.78
61.22
57.12
46.56
45.53
41.83
38.03
32.53
27.97
27.85
27.72
27.56
25.43
21.90
21.51
12.03
11.94
10.27
9.74
Et
Et
N
Ph
Me
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2v

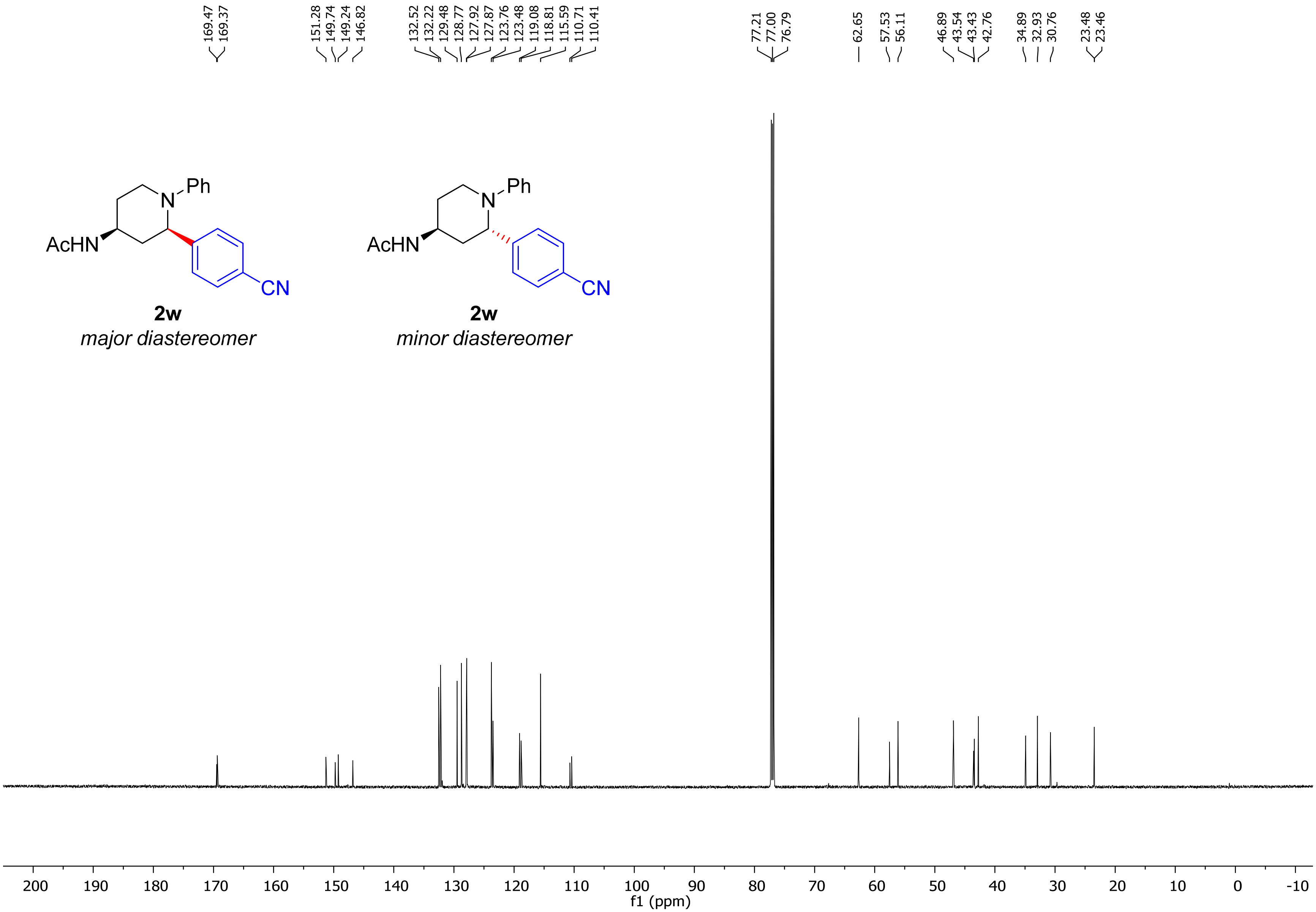


2w

major diastereomer

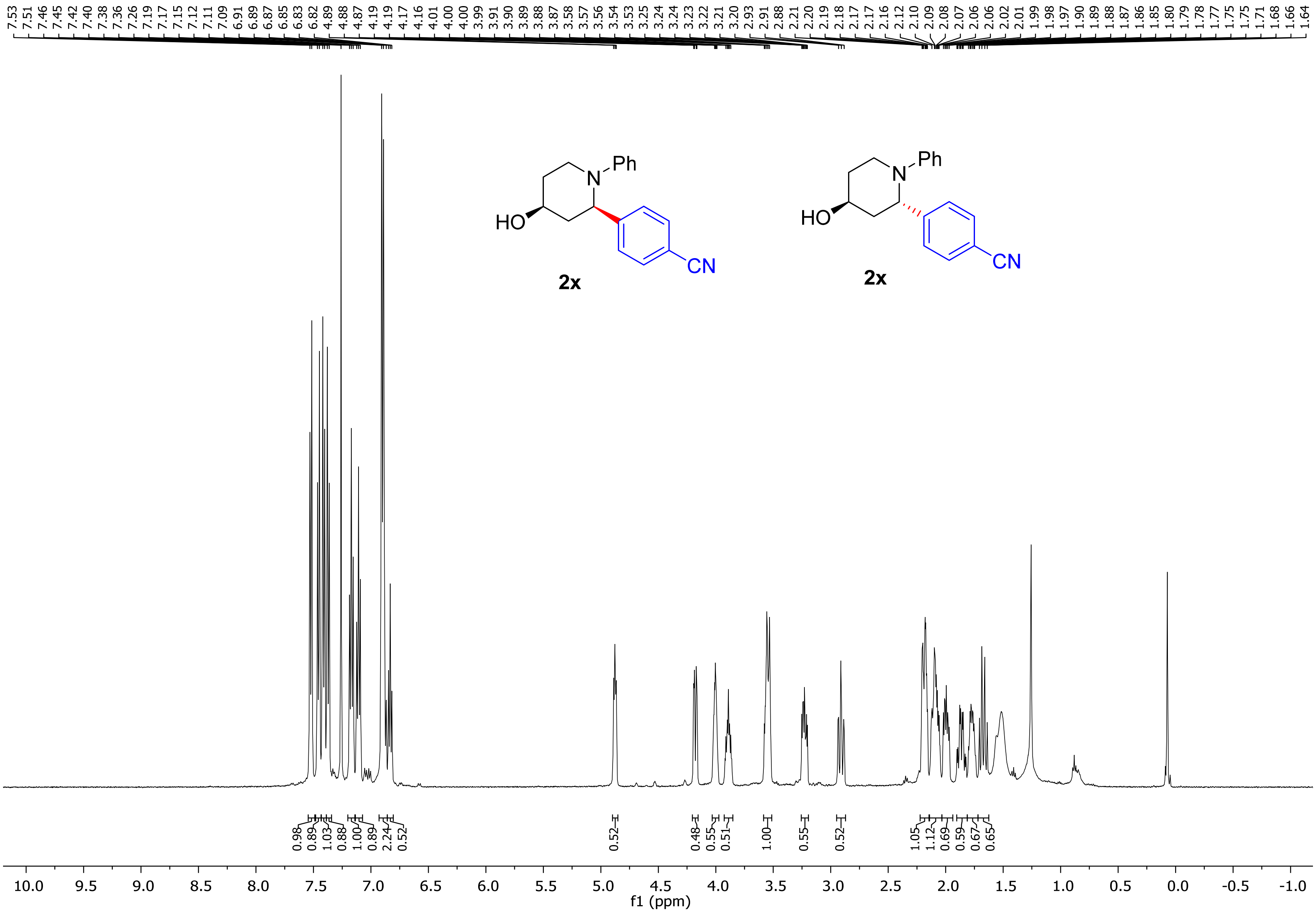
2w

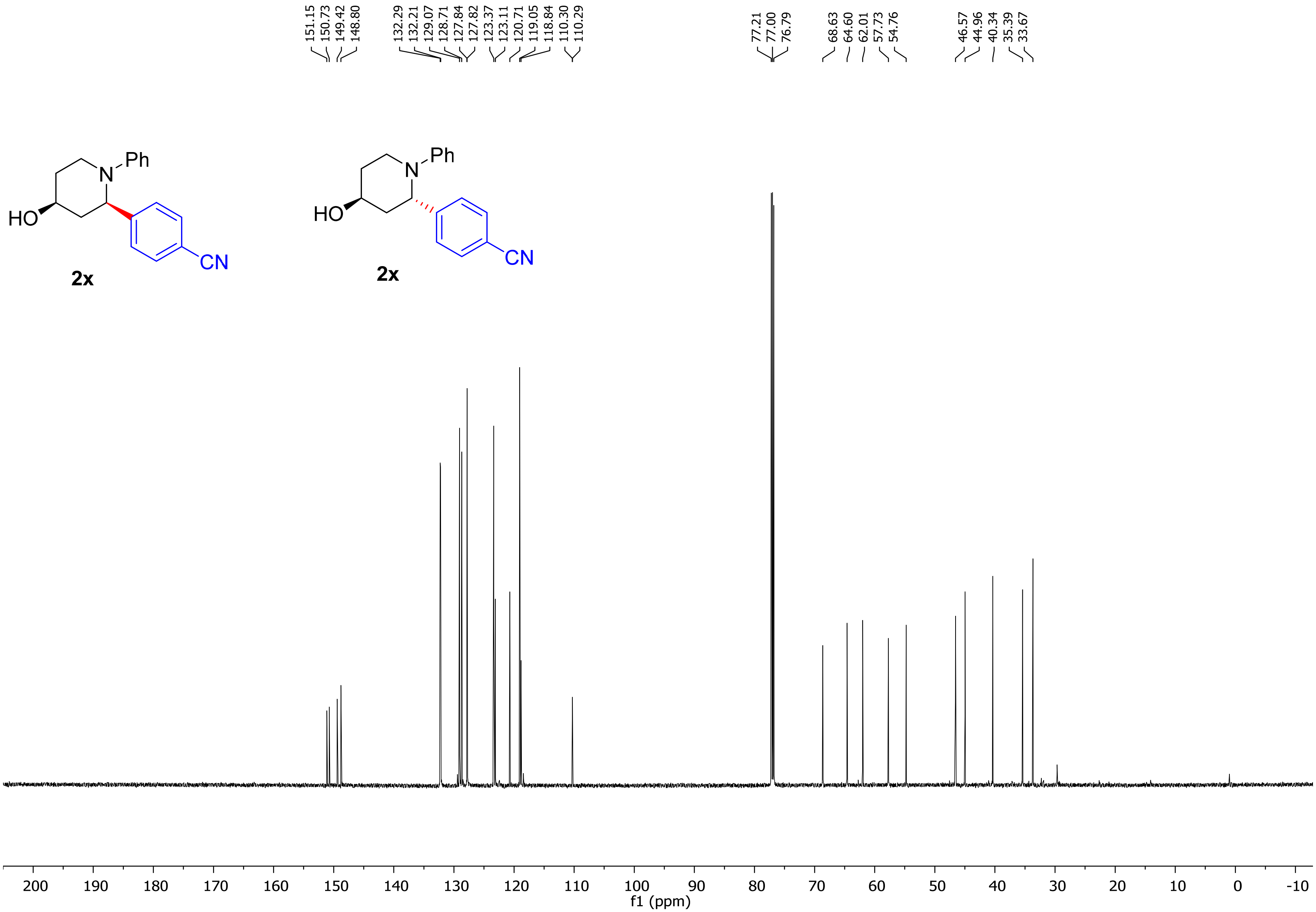
minor diastereomer



2w
major diastereomer

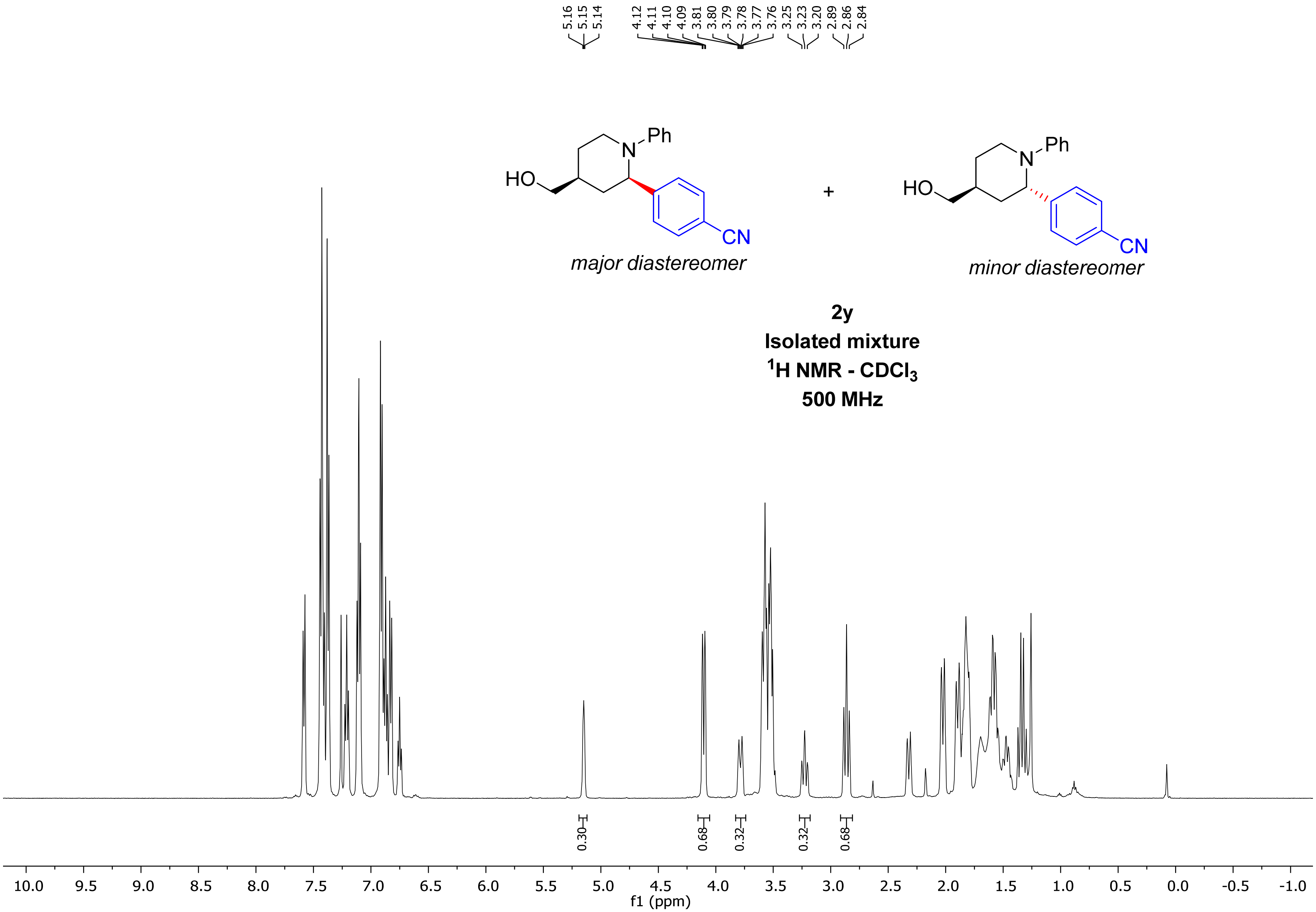
2w
minor diastereomer


7.53 7.51 7.46 7.45 7.42 7.40 7.38 7.36 7.26 7.19 7.17 7.15 7.12 7.11 7.09 6.91 6.89 6.87 6.85 6.83 6.82 4.89 4.88 4.87 4.19 4.19 4.17 4.16 4.01 4.00 3.99 3.91 3.90 3.89 3.88 3.87 3.58 3.57 3.56 3.54 3.53 3.25 3.24 3.24 3.23 3.22 3.21 3.20 2.93 2.91 2.88 2.21 2.20 2.19 2.18 2.17 2.17 2.16 2.12 2.10 2.09 2.08 2.07 2.06 2.06 2.02 2.01 1.99 1.98 1.97 1.90 1.89 1.88 1.87 1.86 1.85 1.80 1.79 1.78 1.77 1.75 1.75 1.71 1.68 1.66 1.64
N
Ph
HO
CN
2x
N
Ph
HO
CN
2x
0.98 0.89 1.03 0.88 1.00 0.89 2.24 0.52 0.52 0.48 0.55 0.51 1.00 0.55 0.52 1.05 1.12 0.69 0.59 0.67 0.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


151.15
150.73
149.42
148.80
132.29
132.21
129.07
128.71
127.84
127.82
123.37
123.11
120.71
119.05
118.84
110.30
110.29
77.21
77.00
76.79
68.63
64.60
62.01
57.73
54.76
46.57
44.96
40.34
35.39
33.67
Ph
N
HO
CN
Ph
N
HO
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2x

2x

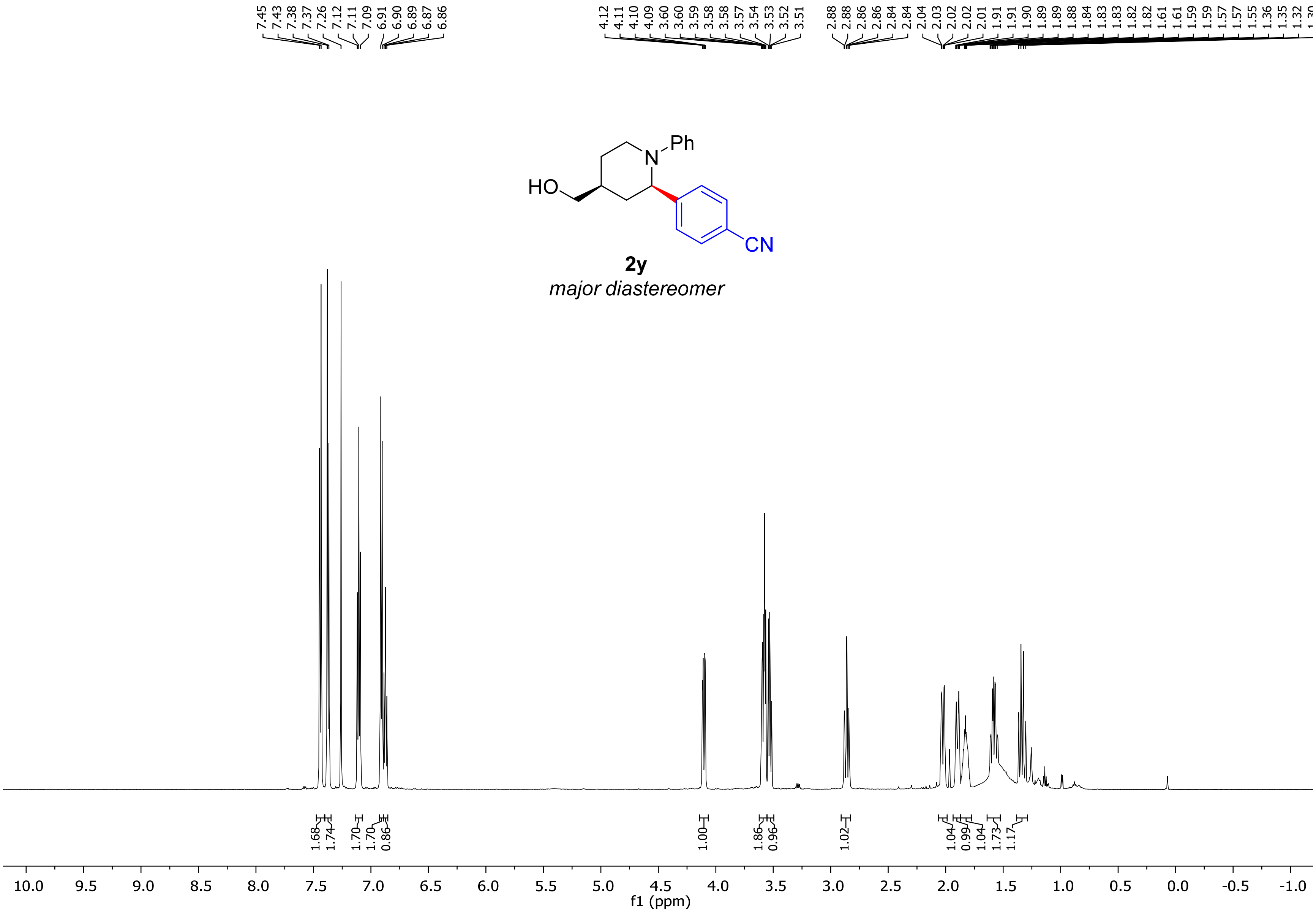


2y

Isolated mixture

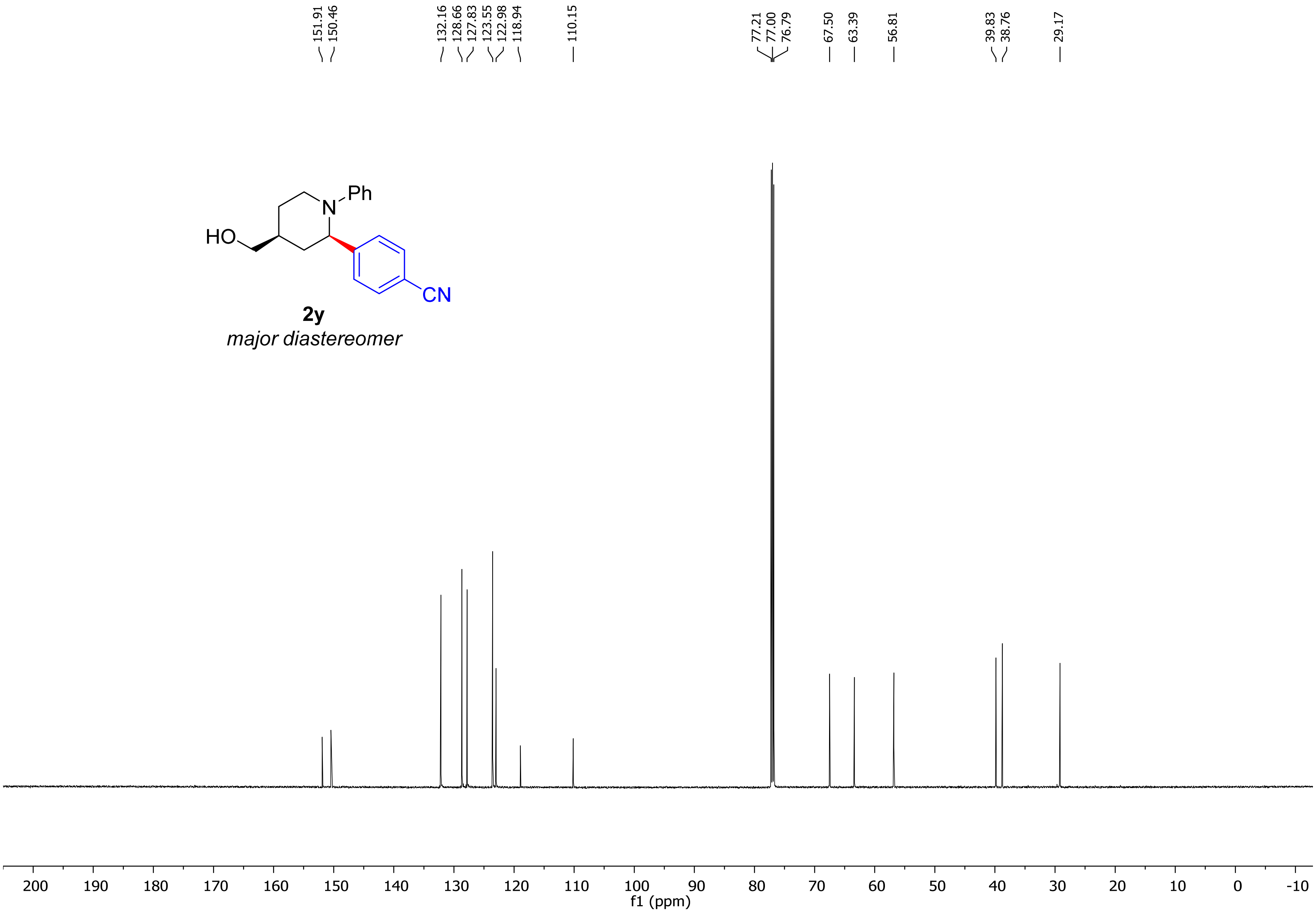
^{1}H NMR - CDCl$_3$

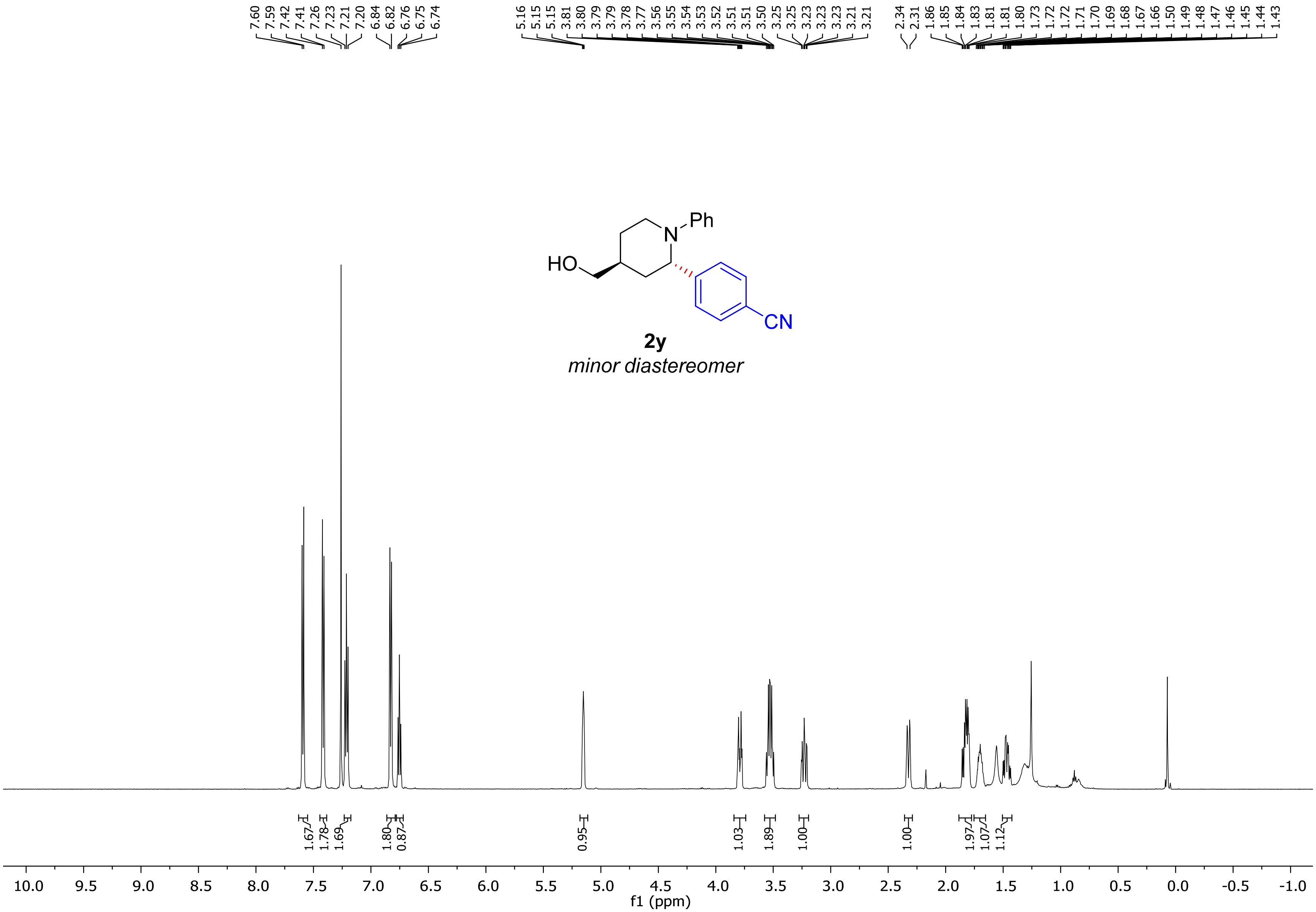
500 MHz



2y

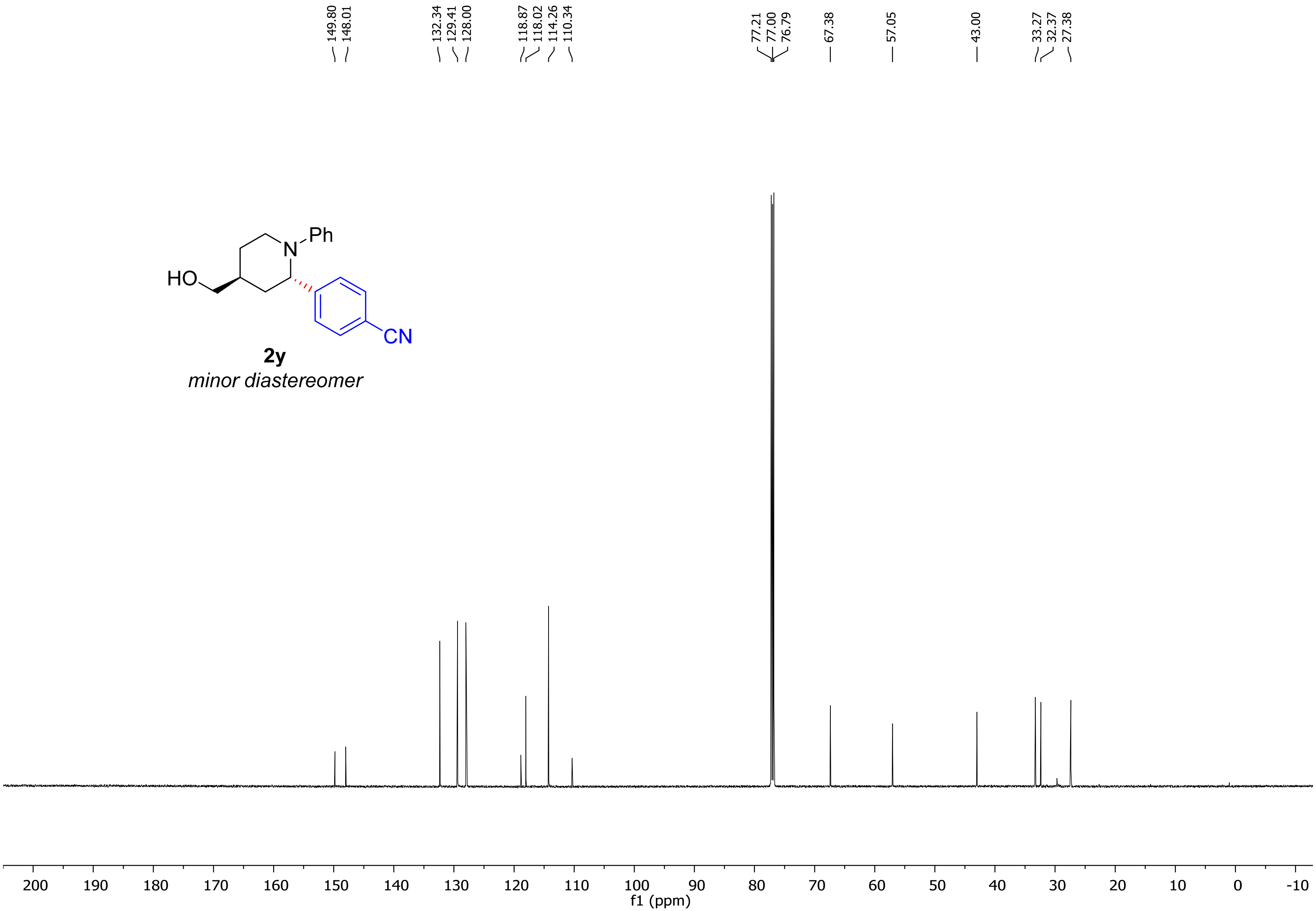
major diastereomer


2y
major diastereomer

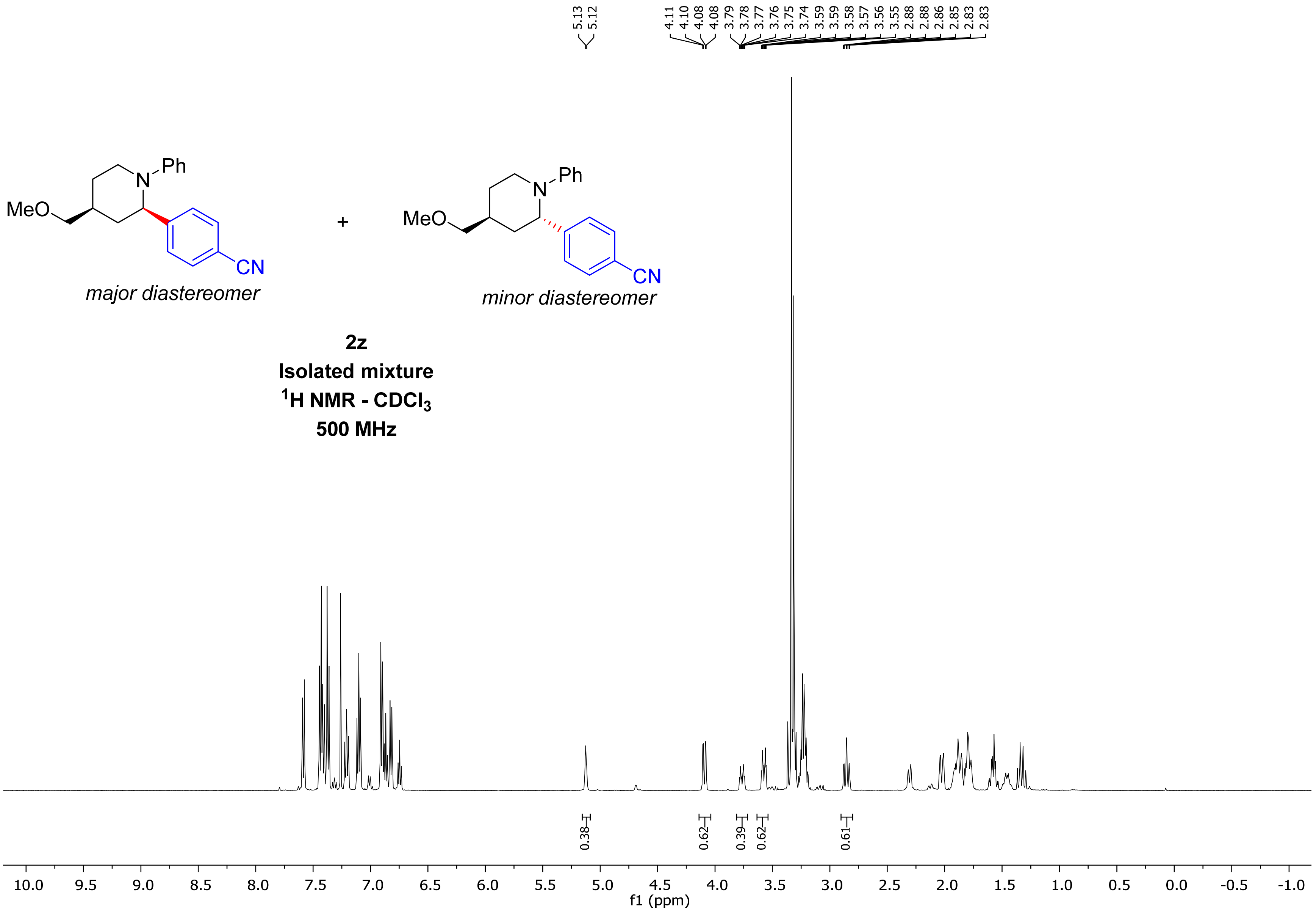


2y

minor diastereomer



2y
minor diastereomer



major diastereomer

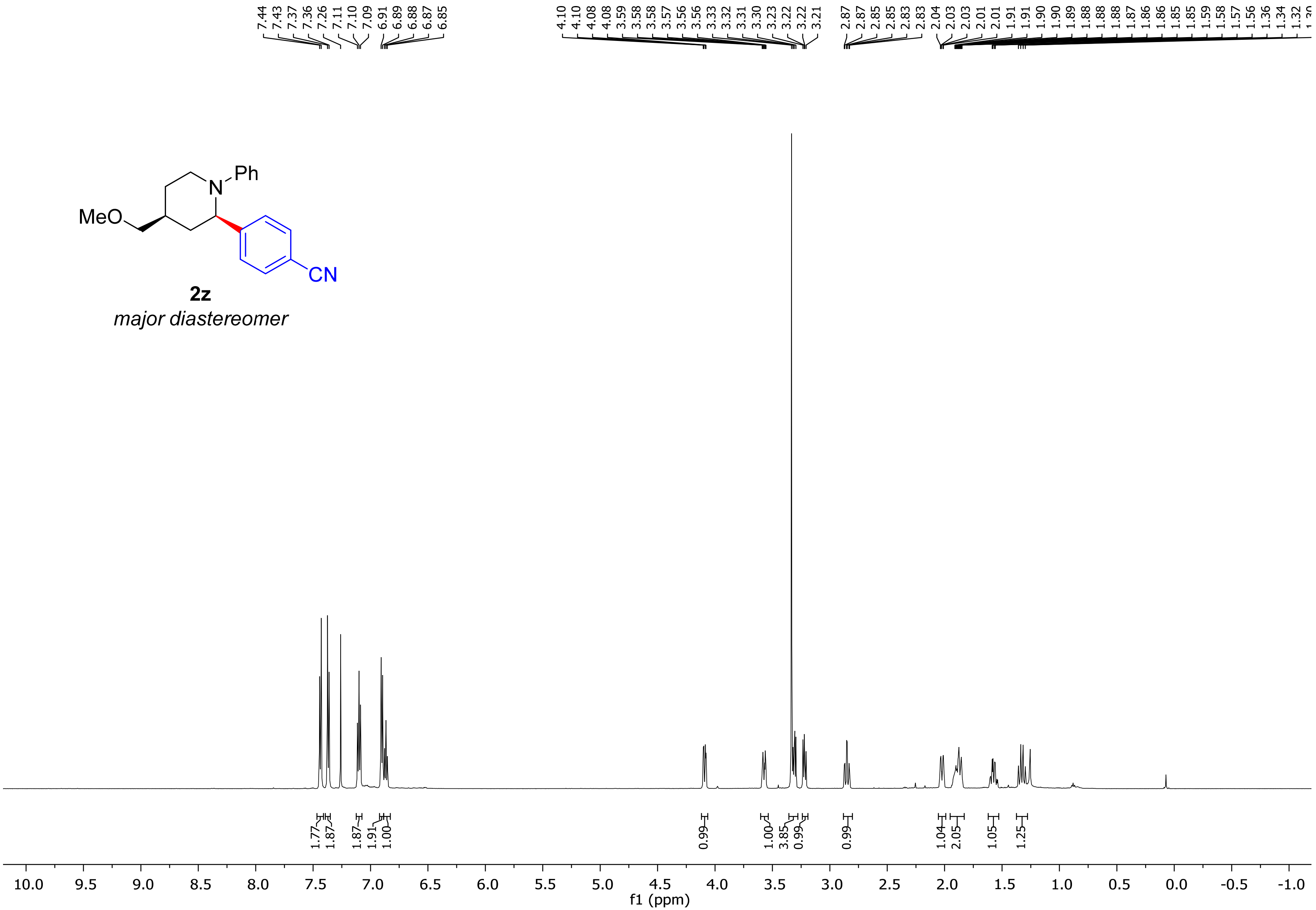
minor diastereomer

2z

Isolated mixture

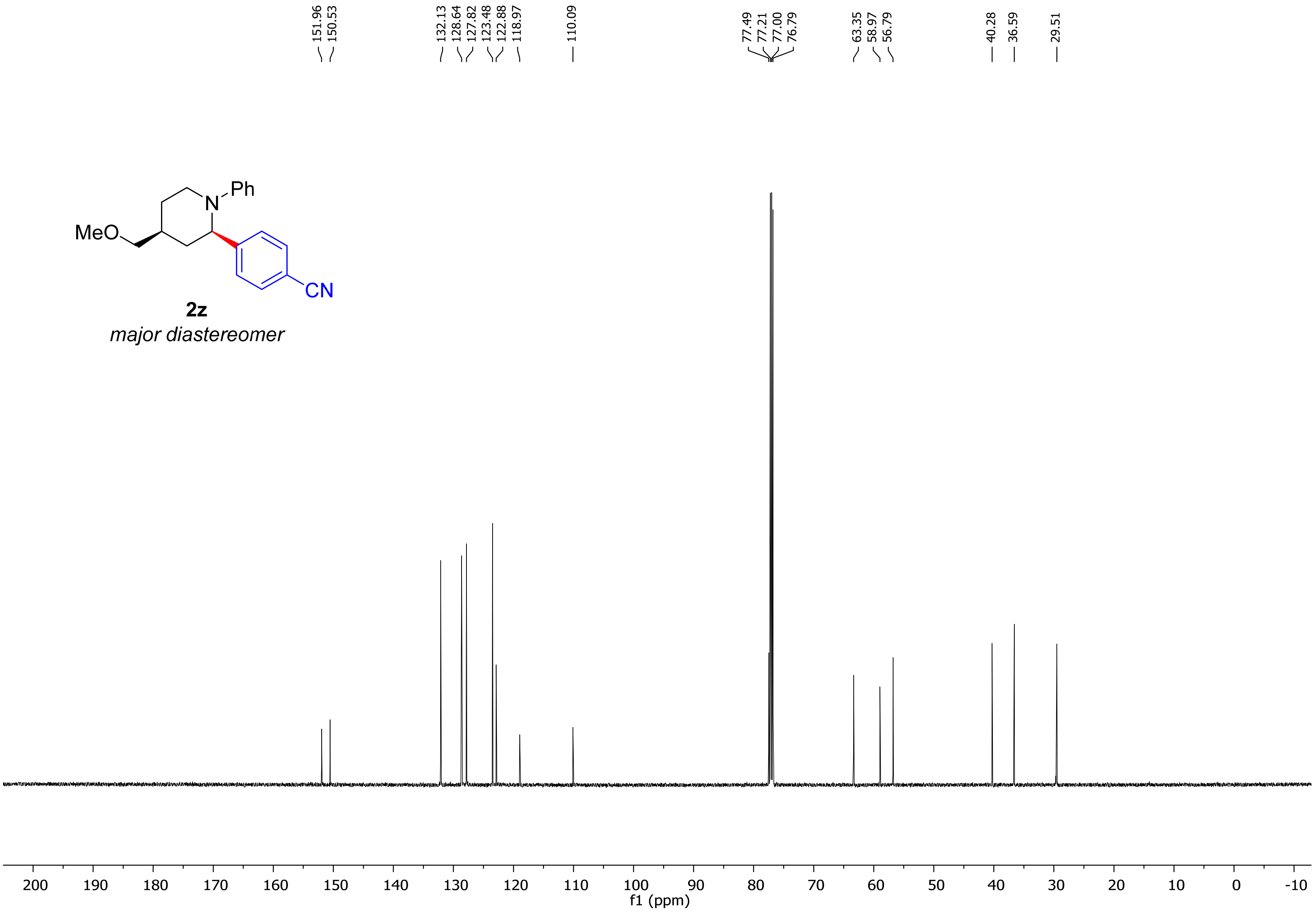
^{1}H NMR - $CDCl_3$

500 MHz



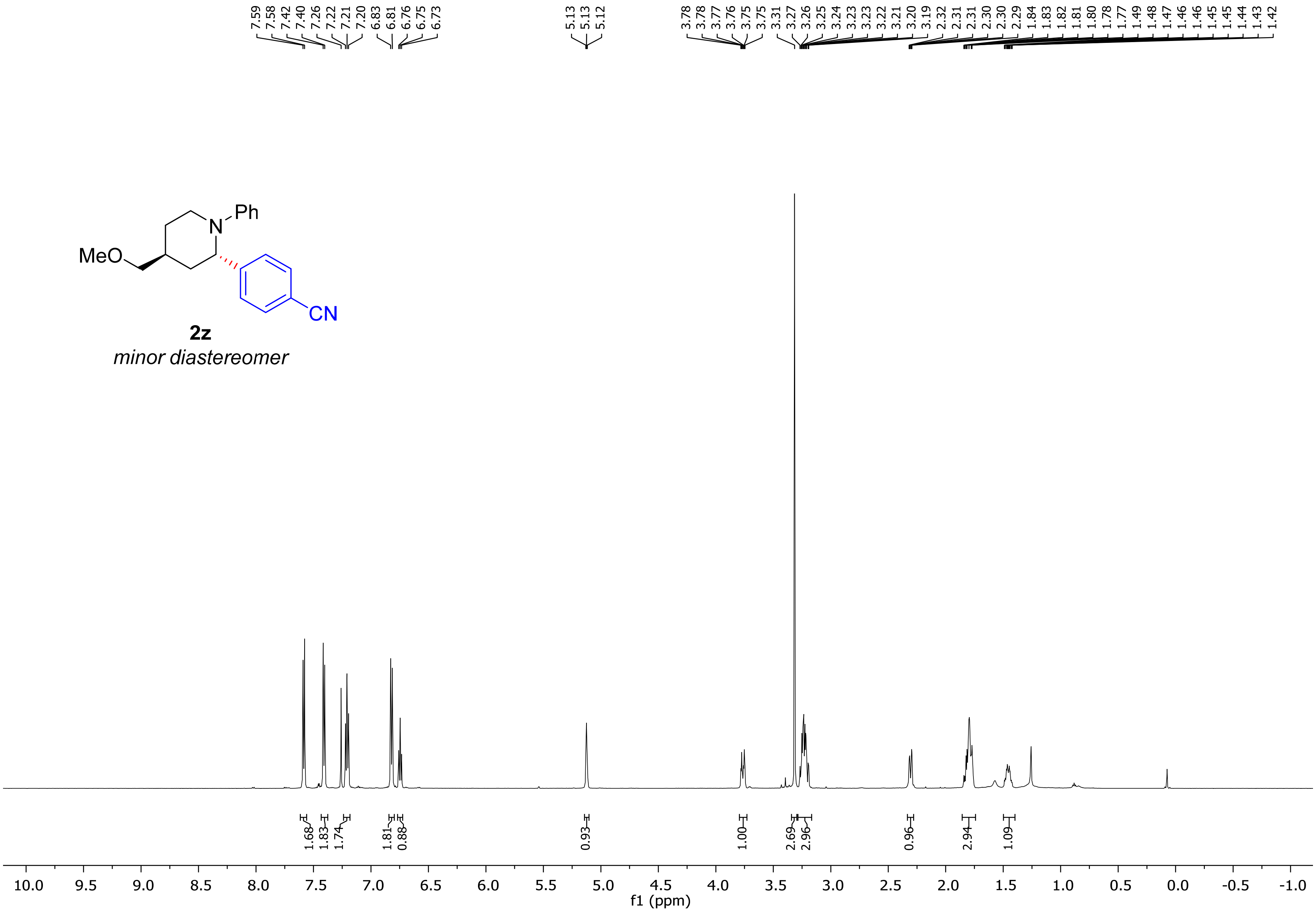
2z

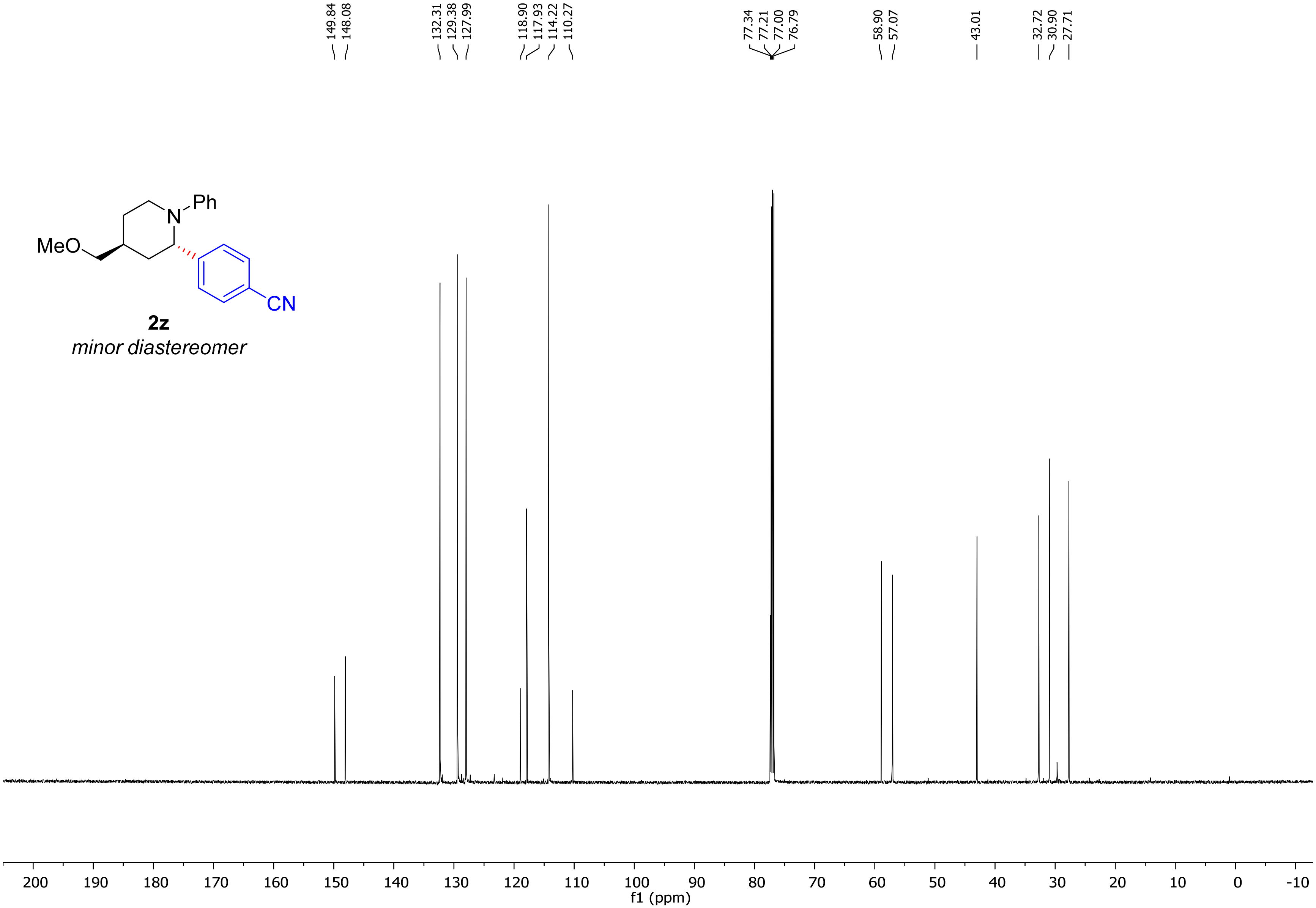
major diastereomer



2z

major diastereomer


2z
minor diastereomer


149.84
148.08
132.31
129.38
127.99
118.90
117.93
114.22
110.27
77.34
77.21
77.00
76.79
58.90
57.07
43.01
32.72
30.90
27.71
MeO
N
Ph
CN
2z
minor diastereomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)