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Supporting Information

Visible-Light Organophotoredox-Mediated Intermolecular Formal [4+2] Cycloadditions of Arylcyclobutylamines with Olefins

Zhengshan Luo, Zequn Xing, Rui Gao, Yufang Han, Jun Ren, and Zhongwen Wang*

State Key Laboratory of Elemento-Organic Chemistry, Frontiers Science Center for New Organic Matter, Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, 94# Weijin Road, Tianjin 300071, China
E-mail: wzwrj@nankai.edu.cn

Table of Contents

1. General Information

1.1 General reaction setup and analytical methods

All reactions were carried out under an atmosphere of argon in flame-dried glassware. The solvents used were purified by distillation over standard drying agents and were stored over molecular sieves and transferred under argon. Technical solvents used for aqueous workup and for column chromatography [dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), petroleum ether (PE), methanol (MeOH), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *n*-hexane (hexane)] were distilled prior to use.
Flash chromatography was performed on silica gel (200~300 or 300~400 mesh) with the indicated eluent mixtures. Thin-layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV (λ = 254 and 365 nm) and/or by staining with a potassium permanganate solution ($KMnO_4$) followed by heat treatment.
The ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometers at ambient temperature, and spectrometer instruments in $CDCl_3$ and/or $(CD_3)_2SO$. NMR standards were used as follows, ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), ^{1}H: δ = 2.50 ppm ($(CD_3)_2SO$). ^{13}C NMR spectroscopy: δ = 77.16 ppm ($CDCl_3$), ^{13}C: δ = 39.52 ppm ($(CD_3)_2SO$). Chemical shifts (δ) are given in parts per million (ppm), are referenced to the residual solvent peaks, and are quoted to the nearest 0.01 ppm for ^{1}H NMR spectra and 0.1 ppm for ^{13}C NMR spectra. The following abbreviations for single multiplicities were used: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet , sex = sextet, sept = septet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dp = doublet of pentets, td = triplet of doublets and furthermore as combinations. Coupling constants (J_{HH}) are reported in Hz and are quoted to the nearest 0.1 Hz . The relative configuration of new compounds was established by HMBC, NOESY experiments, and X-ray crystallography. Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. High resolution mass spectroscopy (HRMS) were performed on Thermo Scientific Q Exactive combined quadrupole, Orbitrap mass spectrometer with ESI resource. Absorption spectra were recorded on a JASCO V-570 UV/Vis spectrometer. Cyclic voltammetry was performed on a Shanghai Chenhua T-660M electrochemical analyzer. The voltammetric cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. Stern-Volmer quenching experiments were conducted on a FS5 Spectrofluoromete and equipped with a 1 cm quartz cell using MeCN as the solvent. The diffraction data for the compound were obtained on Bruker D8 Venture and Rigaku 007 Saturn 70 diffractometer system using a MoKα radiation (λα = 0.71073 Å). The crystallographic figures were generated using the Diamond Version 4.6.8 software.

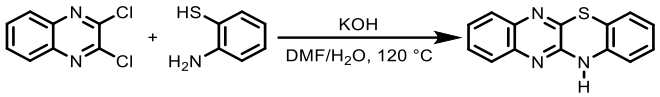
1.2 Photoredox catalysis reaction setup

The catalyst is synthesized according to the published procedure.[1] Blue LED lamp (18 W, λmax = 420 nm) as ordinary light source. At room temperature and argon atmosphere, in a 50 mL quartz photoreaction tube (diameter = 2 cm), the distance from the light source to the irradiation container was 2 cm, and photochemical experiments were performed. The sample is placed in the center of a magnetic stirrer and the solvent used in the photochemical reaction is dry in an ultrasonic bath under continuous argon flow for 5 minutes. The LED manufacturer is Shenzhen Shining Lighting Co., Ltd., single bead LED model is PAR38, overall LED lamp model is BG-Z14318-420, Voltage is 220 V and power is 18 W. The wavelength range is 415~420nm. The electric fan is used to help the reaction system dissipate heat to eliminate the influence of thermal reaction. The electric fan manufacturer is China Cixi Jiyang Electrical Appliance Co., Ltd., with a voltage of 220 V and a power of 5 W.

Figure S1. Photoredox reaction setup.

2. Synthesis of Catalyst

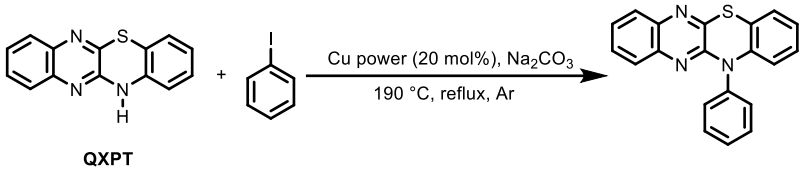
12H-benzo [5,6] [1,4] thiazine [2,3-*b*] quinoxaline (QXPT)



In a 50 mL single-necked flask, 2-aminobenzenethiol (335 μL, 3.13 mmol, 1.25 equiv) was added to a mixed solvents of water and DMF (v/v, 5 mL/15 mL). After the solid was dissolved, a solution of KOH (350 mg, 6.25 mmol, 2.5 equiv) and 2,3-dichloroquinoxaline (498 mg, 2.5 mmol, 1.0 equiv) in DMF (6 mL) were added, and the mixture was heated to 120 °C at oil bath and refluxed for 6 h (TLC). The reaction was quenched by adding ice water, and the solid was filtered, washed with water (50 mL) for three times, and dried in vacuo to afford a yellow solid product **QXPT** (590 mg, 94% yield).

QXPT was known compound, which can be synthesized according to the reported methods, spectral data correspond to those described in the reference.[1a]

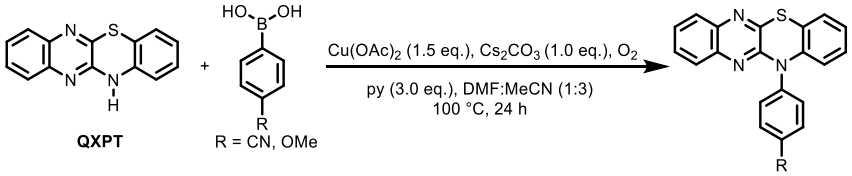
12-Phenyl-12H-benzo [5,6] [1,4] thiazino[2,3-*b*] quinoxaline (QXPT-NPh)



A mixture of 12H-benzo[5,6][1,4]thiazine [2,3-*b*]quinoxaline (**QXPT**) (1 g, 4 mmol), Na_2CO_3 (848 mg, 8 mmol) and copper powder (51 mg, 20 mol%) was heated to reflux (oil bath = 190 °C) in iodobenzene (20 mL) until 12H-benzo[5,6][1,4]thiazine[2,3-*b*]quinoxaline disappears. The reaction mixture was cooled to room temperature, and the unreacted substituted iodobenzene was distilled off under reduced pressure. Then absolute ethanol was added and the mixture was heated and filtered after the product was dissolved. The filtrate was cooled to give a solid which was recrystallized to afford **QXPT-NPh** as a yellow solid (1.18 g, 90% yield).

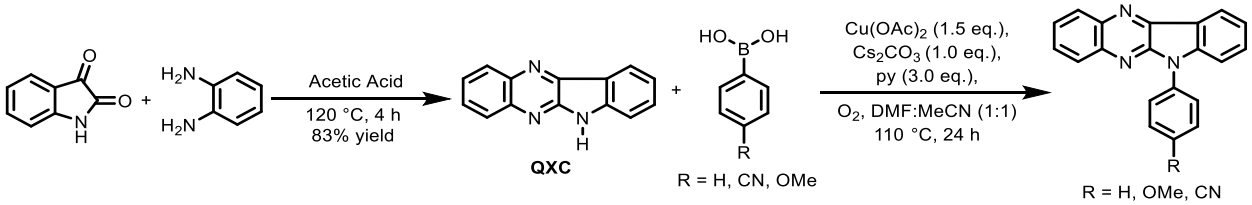
QXPT-NPh was known compound, which can be synthesized according to the reported methods, spectral data correspond to those described in the reference.[1b]

2.1 General Procedure 1 (GP1): synthesis of QXPT-NPhCN and QXPT-NPhOMe



In a 100 mL two-necked flask, **QXPT** (4 mmol, 1.0 equiv) and substituted phenylboronic acid (6 mmol, 1.5 equiv) were dissolved in a mixed solvent of anhydrous DMF and anhydrous acetonitrile (v/v, 15 mL/45 mL). Anhydrous copper acetate (6 mmol, 1.5 equiv), cesium carbonate (4 mmol, 1.0 equiv) and pyridine (12 mmol, 3.0 equiv) were added to the mixture. Under oxygen, the mixture was stirred at 100 °C oil bath for 24 hours. The reaction was cooled to room temperature and quenched with saturated NH_4Cl solution. An appropriate amount of water was added and extracted for three times with ethyl acetate. The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (EtOAc:PE = 1:40) to afford the product.

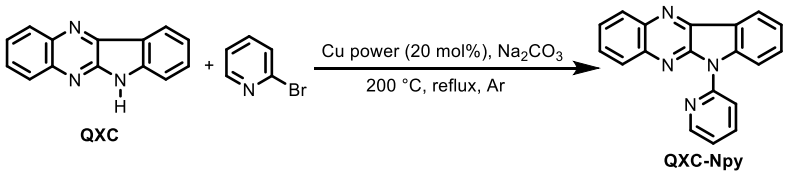
2.2 General Procedure 2 (GP2): synthesis of QXC-NPh、QXC-NPhCN、QXC-NPhOMe and QXC-Npy



6H-indolo[2,3-*b*]quinoxaline (QXC): This compound was synthesized according to the reported procedure with a minor modifications.[2] In a 100 mL round-bottomed flask, isatin (0.10 g, 0.68 mmol, 1.0 equiv) and o-phenylenediamine (0.80 g, 0.74 mmol, 1.1 equiv) were

dissolved in 10 ml of acetic acid, and the reaction mixture was refluxed at 120 °C oil bath for 4 h. After cooling to room temperature, the mixture continued to cool in an ice bath. The precipitated product was filtered and was washed with ice water. The obtained crude product was dried and recrystallized using DMF-MeOH (1:1) to obtain a yellow solid (837 mg, 83% yield). The spectral data correspond to those described in the reference.[3]

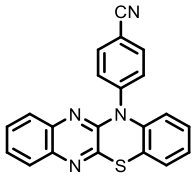
In a 100 mL two-necked flask, 6H-indolo[2,3-*b*]quinoxaline (**QXC**) (4 mmol, 1.0 equiv) and substituted phenylboronic acid (6 mmol, 1.5 equiv) were dissolved in a mixed solvent of anhydrous DMF and anhydrous acetonitrile (v/v, 22.5 mL/22.5 mL). Anhydrous copper acetate (6 mmol, 1.5 equiv), cesium carbonate (4 mmol, 1.0 equiv) and pyridine (12 mmol, 3.0 equiv) were adde to the mixture. The mixture was stirred at 110 °C oil bath for 24 h under oxygen. The reaction mixture was cooled to room temperature and quenched with saturated NH_4Cl solution, an appropriate amount of water was added and extracted for three times with ethyl acetate. The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography (EtOAc:PE = 1:20) to afford the product.



QXC **QXC-Npy**

A mixture of 6H-indolo[2,3-*b*]quinoxaline (**QXC**) (876 mg, 4 mmol), Na_2CO_3 (848 mg, 8 mmol) and copper powder (51 mg, 20 mol%) was heated to reflux (oil bath = 200 °C) in 2-bromopyridine (20 mL) until **QXC** disappears. The reaction mixture was cooled to room temperature, and the unreacted substituted iodobenzene was distilled off under reduced pressure. Then absolute ethanol was added and the mixture was heated and filtered after the product was dissolved. The filtrate was cooled to give a solid which was recrystallized to afford **QXC-Npy** as a yellow solid (734 mg, 62% yield).

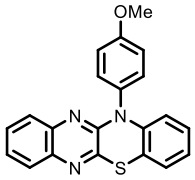
M.p.: 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 8.53 – 8.42 (m, 3H), 8.35 – 8.26 (m, 1H), 8.15 – 8.08 (m, 1H), 8.05 – 7.96 (m, 1H), 7.79 – 7.65 (m, 3H), 7.46 (td, *J* = 7.6, 1.0 Hz, 1H), 7.32 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 148.6, 145.2, 143.6, 140.9, 140.2, 140.1, 138.4, 131.4, 129.4, 129.1, 128.4, 127.1, 122.9, 122.3, 121.5, 120.7, 119.7, 114.4.. HRMS (ESI, m/z) calcd for $C_{20}H_{13}N_4$ $[M+H]^+$: 297.1140, found: 297.1136.



QXPT-NPhCN

4-(12H-benzo[5,6][1,4]thiazino[2,3-*b*]quinoxalin-12-yl) benzonitrile (QXPT-NPhCN). Following **GP1** with (4-cyanophenyl) boronic acid (882 mg, 6 mmol, 1.5 equiv), the product was isolated by column chromatography on silica gel (EtOAc:PE = 1:40) to obtain a yellow solid (887 mg, 63% yield).

M.p.: 228-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.19 (m, 3H), 7.00 – 6.93 (m, 1H), 6.84 – 6.78 (m, 2H), 5.98 (dt, *J* = 5.0, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 145.2, 143.7, 139.8, 139.7, 139.3, 134.1, 131.8, 129.3, 127.6, 127.2, 127.1, 127.0, 126.9, 123.7, 118.3, 118.3, 117.7, 112.3. HRMS (ESI, m/z) calcd for $C_{21}H_{13}N_4S$ $[M+H]^+$: 353.0861, found: 353.0856.



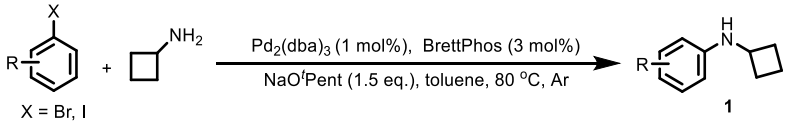
QXPT-NPhOMe

12-(4-Methoxyphenyl)-12H-benzo[5,6][1,4]thiazino[2,3-*b*]quinoxaline (QXPT-NPhOMe). Following **GP1** with (4-methoxyphenyl) boronic acid (912 mg, 6 mmol, 1.5 equiv), the product was isolated by column chromatography on silica gel (EtOAc:PE = 1:40) to obtain a yellow solid (957 mg, 67% yield).

M.p.: 230-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.28 – 7.16 (m, 5H), 7.08 – 7.01 (m, 2H), 6.98 – 6.93 (m, 1H), 6.79 (tt, *J* = 7.3, 5.5 Hz, 2H), 6.14 – 6.07 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 145.7, 141.0, 140.0, 139.7, 132.0, 131.4, 128.9, 127.5, 127.4, 126.9, 126.6, 126.6, 123.0, 118.0, 117.7, 115.5, 55.6. HRMS (ESI, m/z) calcd for $C_{21}H_{16}N_3OS$ $[M+H]^+$: 358.1014, found: 358.1009.

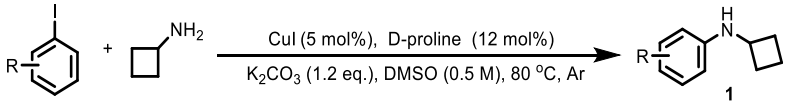
3. Synthesis of Substrates

3.1 General Procedure 3 (GP3): preparation of *N*-arylcyclobutanamine 1[4]



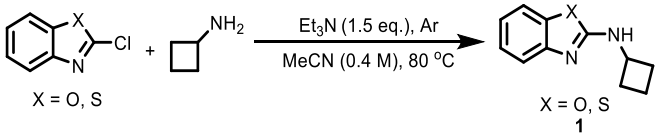
0.01 mmol of $Pd_2(dba)_3$ and 0.03 mmol of BrettPhos were added to an oven-dried round-bottomed flask, and 1.5 mmol of NaO^{t}Pent was added, under argon protection. Then 1 mmol of aromatic halide, 1.5 mmol of cyclobutanamine and 5 mL of toluene were added to the reaction mixture and heated at 80 °C oil bath for 18 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, filtered through a short pad of silica gel, and concentrated in vacuo. Purification by silica gel flash chromatography gave **1**.

3.2 General Procedure 4 (GP4): preparation of *N*-aylcyclobutanamine 1[5]

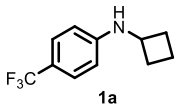


0.05 mmol of CuI and 0.12 mmol of D-proline were added to an oven-dried round-bottomed flask, and 1.2 mmol of K_2CO_3 was added, under argon protection. Then 1 mmol of aromatic iodides, 1.5 mmol of cyclobutanamine and 2.0 mL of DMSO were added to the reaction mixture and heated at 80 °C oil bath for 24 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, filtered through a short pad of silica gel, and concentrated in vacuo. Purification by silica gel flash chromatography gave **1**.

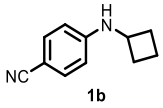
3.3 General Procedure 5 (GP5): preparation of *N*-arylcyclobutanamine 1



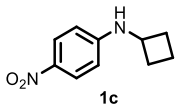
1 mmol aomatic chlorides and 1.5 mmol of cyclobutanamine were added to an oven-dried round-bottomed flask. Then, under argon protection, 1.5 mmol of triethylamine (Et_3N) and 2.5 mL of MeCN were added to the reaction mixture and heated at 80 °C oil bath for 24 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, filtered through a short pad of silica gel, and concentrated in vacuo. Purification by silica gel flash chromatography gave **1**.



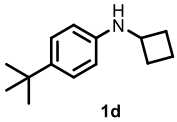
4-trifluoromethyl-*N*-cyclobutylaniline (1a). Following **GP4** with 1-iodo-4-(trifluoromethyl)benzene (2.25 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:50) as a yellowish oil (2.97 g, 92%). The spectral data correspond to those described in the reference.[4]



4-cyano-*N*-cyclobutylaniline (1b). Following **GP4** with 1-cyano-4-iodobenzene (3.5 g, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc: PE = 1:20) as a gray solid (1.78 g, 69%).
M.p.: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 6.53 – 6.45 (m, 2H), 4.55 (d, *J* = 6.1 Hz, 1H), 3.96 – 3.87 (m, 1H), 2.50 – 2.35 (m, 2H), 1.95 – 1.74 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 133.7, 120.7, 112.3, 98.3, 48.2, 30.8, 15.3. HRMS (ESI, m/z) calcd for $C_{11}H_{13}N_2$ $[M+H]^+$: 173.1079, found: 173.1074.

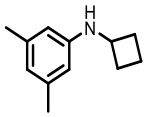


***N*-cyclobutyl-4-nitroaniline (1c)**. Following **GP4** with 1-iodo-4-nitrobenzene (3.81 g, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:10) as a yellow solid (1.58 g, 55%). The spectral data correspond to those described in the literature.[6]



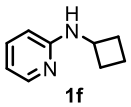
1d

***4-tert*-butyl-*N*-cyclobutylaniline (1d)**. Following **GP3** with 4-*tert*-butyl-bromobenzene (2.61 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:50) as a yellowish oil (2.90 g, 95%). The spectral data correspond to those described in the reference.[4]



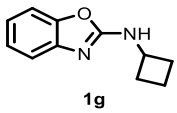
1e

3,5-dimethyl-*N*-cyclobutylaniline (1e). Following **GP3** with 1-iodo-3,5-dimethylbenzene (2.21 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:50) as a colorless oil (2.50 g, 95%). The spectral data correspond to those described in the reference.[4]



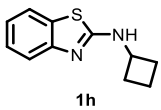
1f

***N*-cyclobutyl-2-pyridinamine (1f)**. Following **GP3** with 2-bromopyridine (1.42 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:5) as a light yellow solid (1.44 g, 65%). The spectral data correspond to those described in the reference.[4]



1g

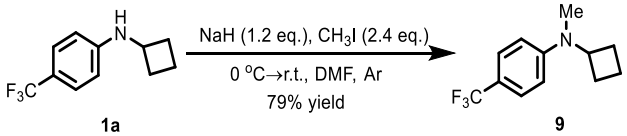
***N*-cyclobutylbenzo[*d*]oxazol-2-amine (1g)**. Following **GP5** with 2-chlorobenzo[*d*]oxazole (1.74 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:5) as a yellowish oil (2.76 g, 98%).
M.p.: 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 4.37 (p, *J* = 8.3 Hz, 1H), 2.47 (dtt, *J* = 12.7, 7.6, 2.6 Hz, 2H), 2.06 (pd, *J* = 9.2, 2.7 Hz, 2H), 1.85 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 148.4, 142.9, 123.9, 120.5, 115.8, 108.8, 48.1, 31.5, 15.0. HRMS (ESI, m/z) calcd for $C_{11}H_{13}N_2O$ $[M+H]^+$: 189.1028, found: 189.1024.



1h

***N*-cyclobutylbenzo[*d*]thiazol-2-amine (1h)**. Following **GP5** with 2-chlorobenzo[*d*]thiazole (1.22 mL, 15 mmol, 1.0 equiv), the product was isolated after column chromatography on silica gel (EtOAc:PE = 1:5) as a yellowish oil (949 mg, 31%).
M.p.: 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.10 – 7.01 (m, 1H), 4.09 (p, *J* = 7.9 Hz, 1H), 2.47 (dtt, *J* = 12.9, 7.3, 2.7 Hz, 2H), 2.00 (ddt, *J* = 11.8, 9.0, 6.1 Hz, 2H), 1.84 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 152.4, 130.4, 125.9, 121.3, 120.9, 118.5, 50.7, 31.1, 15.0. HRMS (ESI, m/z) calcd for $C_{11}H_{13}N_2S$ $[M+H]^+$: 205.0799, found: 205.0795.

***N*-cyclopropyl-*N*-methylaniline (9)**



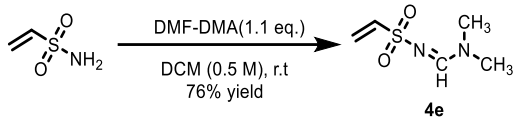
1a 9

The secondary amine **4-trifluoromethyl-*N*-cyclobutylaniline (1a)** (1.29 g, 6 mmol, 1.0 equiv) was mixed with NaH (288 mg, 7.2 mmol, 1.2 equiv) in DMF (20 mL) and stirred at room temperature for 10 min. The iodomethane (0.90mL, 14.4 mmol, 2.4 equiv) was added.

The resulting mixture was stirred overnight and quenched with brine and extracted with ether. The organic layer was concentrated in vacuo and separated by flash chromatography on silica gel (PE:EtOAc = 50:1) gave the **9** as a pale yellow oil (1.09 g, 79% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 4.13 – 4.00 (m, 1H), 2.88 (d, *J* = 1.0 Hz, 3H), 2.33 – 2.21 (m, 2H), 2.18 – 2.03 (m, 2H), 1.79 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 126.3 (q, *J* = 4.0 Hz), 123.9, 118.1 (q, *J* = 32.3 Hz), 112.9, 54.5, 33.4, 29.1, 14.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.91. HRMS (ESI, m/z) calcd for $C_{12}H_{15}F_3N$ $[M+H]^+$: 230.1157, found: 230.1152.

3.4 Synthesis of Olefins

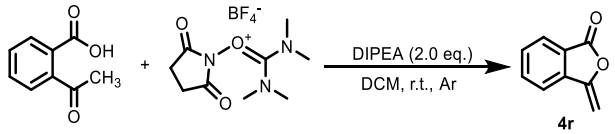
*3.4.1 Preparation of N,N-dimethyl-N'-(vinylsulfonyl) formimidamide (**4e**)*



4e

The vinylsulfonamide (3.0 g, 28 mmol 1.0 equiv) was mixed with *N,N*-dimethylformamide dimethyl acetal (DMF-DMA) (4.18 mL, 30.81 mmol, 1.1 equiv) in DCM (56 Ml, 0.5 M) and stirred at room temperature for 3 h. Then, the reaction mixture was quenched with brine and extracted with DCM. The organic layer was concentrated in vacuo and separated by flash chromatography on silica gel (PE:EtOAc = 1:20) gave the **4e** as a pale yellow oil (3.44 g, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 6.61 (dd, *J* = 16.6, 9.9 Hz, 1H), 6.24 – 6.16 (m, 1H), 5.81 (t, *J* = 8.3 Hz, 1H), 3.18 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 138.0, 123.4, 41.4, 35.4. HRMS (ESI, m/z) calcd for $C_5H_{11}N_2O_2S$ $[M+H]^+$: 163.0541, found: 163.0536.

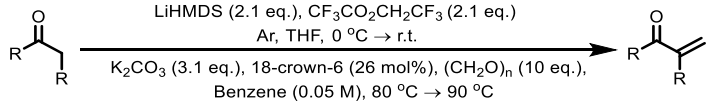
*3.4.2 Preparation of N,N-dimethyl-N'-(vinylsulfonyl) formimidamide (**4r**)*



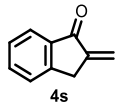
4r

Typical procedure for the synthesis of (*Z*)-3-ylidenephthalide **4r**. To a solution of 2-acetyl-benzoic acid (164 mg, 1.0 mmol) and O-(N-succinimidyl)-*N,N,N',N'*-tetramethyl uronium BF_4 (TSTU) (301 mg, 1.0 mmol) in DCM (5.0 mL) was added DIPEA (348 μL, 2.0 mmol). The reaction was allowed to stir at room temperature for 6 h. Then, the reaction mixture was poured into water (10 mL), extracted using EtOAc (3 ~10 mL). The combined organic layers were washed by brine with water (3~10 mL) and $NaHCO_3$ aqueous (3 ~10 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation to yield (*Z*)-3-ylidenephthalide **4r** as a white solid (122mg, 0.84 mmol, 84%). The spectral data correspond to those described in the reference.[7]

3.4.3 General Procedure 6 (GP6): preparation of exocyclic terminal olefins[8]



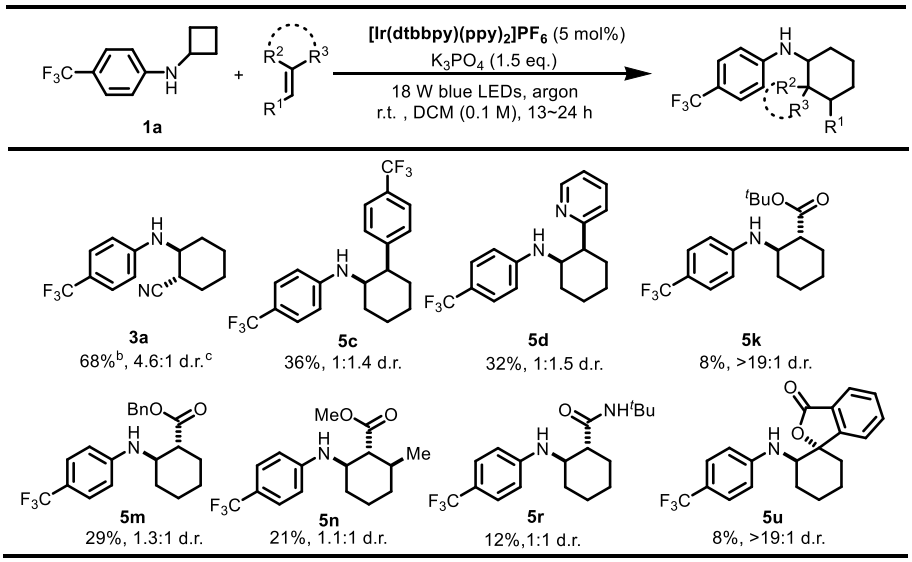
To a solution of LiHMDS at 0 °C (0.65 mL, 0.6 M in THF) was added a solution of substituted ketone (0.19 mmol, 1.0 equiv) in THF (1.0 mL). The reaction mixture was allowed to warm to room temperature for over 20 minutes, then $CF_3CO_2CH_2CF_3$ (0.41 mmol, 2.1 equiv) was added. After an additional 20 minutes at room temperature, saturated aqueous NH_4Cl (5 mL) was added and the resulting mixture was extracted with EtOAc (3~5 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Without purification, the crude mixture was immediately dissolved in benzene (3.8 mL, 0.05 M) and K_2CO_3 (82 mg, 0.59 mmol, 3.1 equiv), 18-crown-6 (13 mg, 0.05 mmol, 26 mol%), and paraformaldehyde (200 mg, 6.59 mmol, 10.0 equiv) were added in. The reaction mixture was heated to 80 °C for 2 hours and then to reflux (oil bath = 90 °C) for 4 hours. The mixture was cooled to room temperature, saturated aqueous NH_4Cl (10 mL) was added, and the resulting mixture was extracted with EtOAc (3 x 10 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. SiO_2 flash chromatography gave the product.


4s

2-Methylene-2,3-dihydro-1H-inden-1-one (8e). Following **GP6** with 2,3-dihydro-1H-inden-1-one (2.56 g, 19 mmol, 1.0 equiv.), product was isolated by column chromatography on silica gel (EtOAc:PE = 1:30) as a reddish-brown oil (1.20 g, 44%). The spectral data correspond to those described in the reference.[9]

4. Optimization of Reaction Conditions

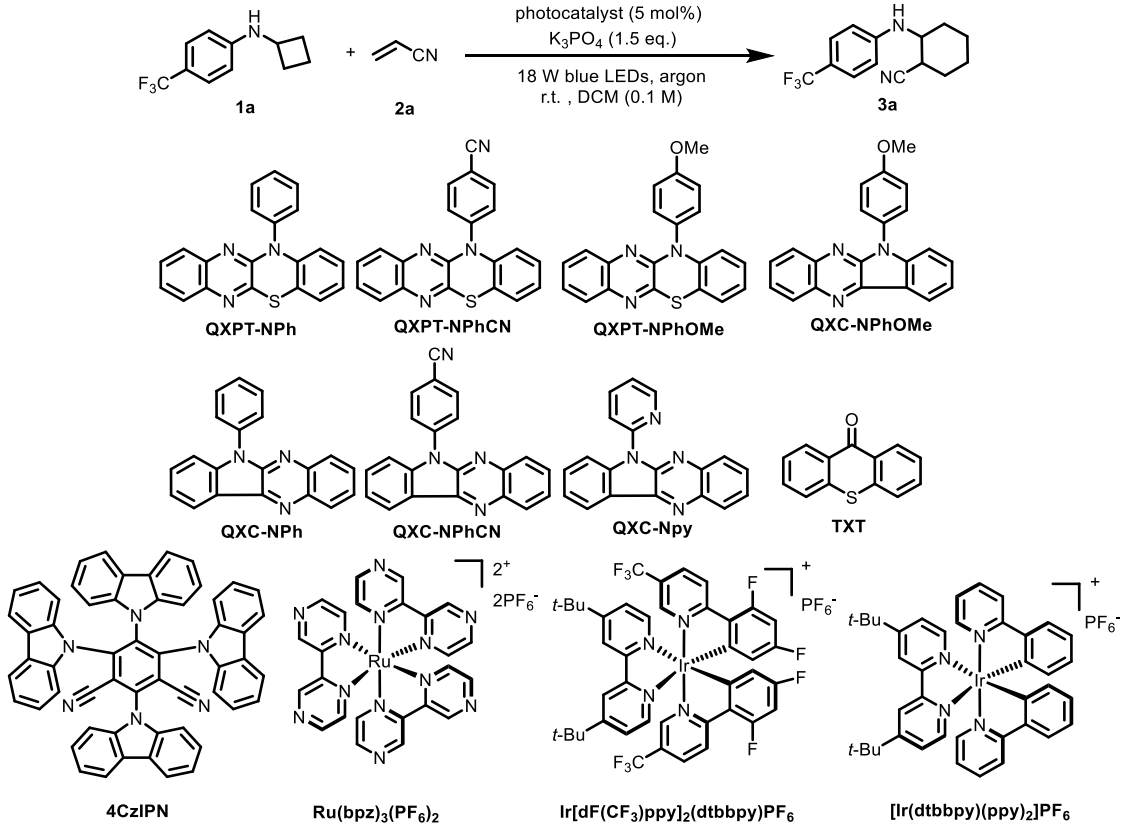
Table S1. $[Ir(dtbbpy)(ppy)_2]PF_6$ substrate scope of application [a]



[a]Unless otherwise noted, all reactions were performed with **1a** (0.75 mmol), **olefins** (2.25 mmol), K_3PO_4 (1.13 mmol) and photocatalyst (0.0375 mmol) in dry DCM (7.5 mL, 0.1 M) under irradiation of 18 W blue LEDs (420 nm), r.t., argon. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^1H NMR analysis of the crude reaction mixture and d.r. refers to trans/cis.

When $[Ir(dtbbpy)(ppy)_2]PF_6$ was used as photocatalyst, cycloaddition product **3a** was obtained from **1a** and acrylonitrile **2a** in 68% yield (4.6:1 d.r.). When other olefins were tried, although the reaction could occur, the cycloaddition product yield was generally low (12%~36%), and 1a was severely photodegraded. It indicates that the universality of $[Ir(dtbbpy)(ppy)_2]PF_6$ in this reaction system is not good. Therefore, we have to consider other photocatalysts.

Table S2. Optimization of photocatalysts for [4+2] cycloaddition reaction[a]

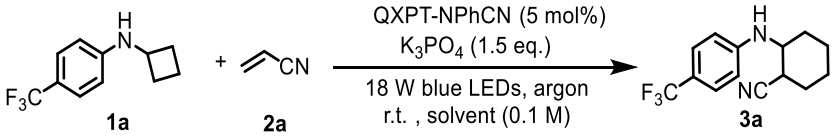


Entry	photocatalyst	λ (nm)	t (h)	yield (%)[b]	d.r.[c]

1	$[Ir(dtbbpy)(ppy)_2]PF_6$	420	13	68	4.6.:1
2	QXPT-NPh	420	13	62	2.5:1
3	**QXPT-NPhCN**	**420**	**13**	**64**	**1.9:1**
4	QXPT-NPhOMe	395	15	48	3.1:1
5	QXC-NPhOMe	395	15	47	2.8:1
6	QXC-NPh	395	15	61	2.2:1
7	QXC-NPhCN	395	15	62	2.1:1
8	QXC-Npy	395	15	61	1.9:1
9	TXT	395	15	30	>19:1
10	4CzIPN	420	22	22	6.2:1
11	$[Ru(bpz)_3](PF_6)_2$	420	22	15	>19:1
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	420	22	52	>19:1

[a]Unless otherwise noted, all reactions were performed with **1a** (0.75 mmol), **2a** (2.25 mmol), K_3PO_4 (1.13 mmol) and photocatalyst (0.0375 mmol) in dry DCM (7.5 mL, 0.1 M) under irradiation of 18 W blue LEDs (420 nm), r.t., argon. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture and d.r. refers to trans/cis.[d]Without K_3PO_4.

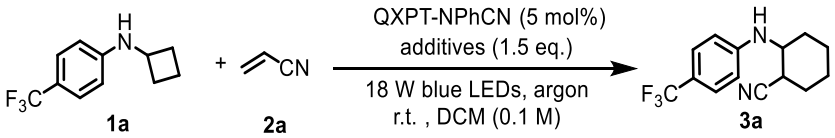
Table S3. Optimization of the solvents[a]



Entry	solvent	t (h)	yield (%)[b]	d.r.[c]
1	Toluene	15	56	2.6:1
2	MeOH	12	11	3.6:1
3	MeCN	20	44	3.6:1
4	THF	12	45	2.3:1
5	DCE	12	48	2.5:1
6	DCM	13	64	1.9:1
7	DMF	12	50	2.2:1
8	DMSO	20	43	1.5:1

[a]Unless otherwise specified, all reactions were performed with **1a** (0.75 mmol), **2a** (2.25 mmol), K_3PO_4 (1.13 mmol) and **QXPT-NPhCN** (0.0375 mmol) in solvent (7.5 mL, 0.1 M) in the presence of 18 W blue LEDs (λ = 420 nm) at room temperature under argon. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^{1}H NMR analysis and d.r. refers to trans/cis.

Table S4. Optimization of the additives[a]

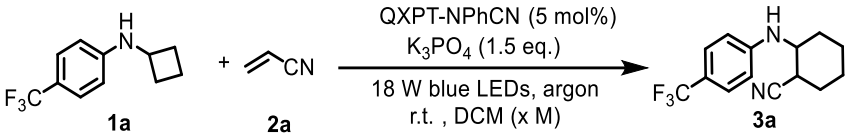


Entry	additives	yield (%)[b]	d.r.[c]
1	DIPEA	0	
2	DMAP	18	3.1:1
3	KOH	42	3.9:1

4	Cs_2CO_3	45	4.3:1
5	K_2CO_3	46	4.5:1
6	KOAc	48	4.9:1
7	KF	52	3.8:1
8	Na_3PO_4	58	2.2:1
9	K_3PO_4	64	1.9:1
10	K_2HPO_4	58	2.3:1
11	KCl	43	2.2:1

[a]Unless otherwise noted, all reactions were performed with **1a** (0.75 mmol), **2a** (2.25 mmol), addieives (1.13 mmol) and **QXPT-NPhCN** (0.0375 mmol) in dry DCM (7.5 mL, 0.1 M) under irradiation of 18 W blue LEDs (420 nm), r.t., argon, 13 h. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture and d.r. refers to trans/cis.

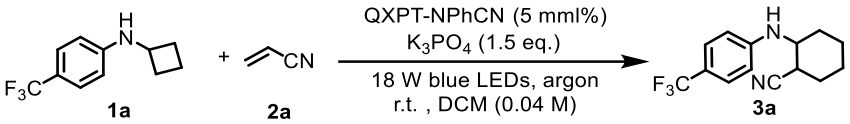
Table S5. Optimization of the concentration[a]



Entry	concentration (x M)	yield (%)[b]	d.r.[c]
1	0.2	59	2.9:1
2	0.1	64	1.9:1
3	0.08	64	2.7:1
4	0.06	65	3.0:1
5	0.04	71	2.5:1
6	0.02	65	2.7:1

[a]Unless otherwise specified, all reactions were performed with **1a** (0.75 mmol), **2a** (2.25 mmol), K_3PO_4 (1.13 mmol) and **QXPT-NPhCN** (0.0375 mmol) in DCM under the presence of 18 W blue LEDs (λ = 420 nm) at room temperature, argon, 13 h. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^{1}H NMR analysis and d.r. refers to trans/cis.

Table S6. Control experiments for [4+2] cycloaddition reaction[a]

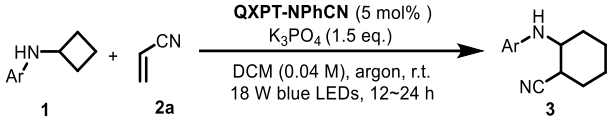


Entry	variation from the standard conditions	yield (%)[b]	d.r.[c]
1	none	71	2.5:1
2	without QXPT-NPhCN	20	3.2:1
3	without K_3PO_4	43	3.2:1
4	without QXPT-NPhCN and K_3PO_4	19	3.5:1
5	without light	0	
6	under air	22	>19:1

[a]Reaction conditions: **1a** (0.75 mmol), **2a** (2.25 mmol), K_3PO_4 (1.13 mmol), K_3PO_4 (1.13 mmol) and **QXPT-NPhCN** (0.0375 mmol) in DCM (18.75 mL, 0.04 M) under the presence of 18 W blue LEDs (λ = 420 nm) at room temperature, argon, 13 h. [b]Combined yields of the two isomers after column chromatography. [c]Determined by ^{1}H NMR analysis and d.r. refers to trans/cis.

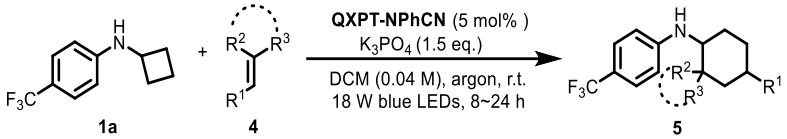
5. General Experiment Procedures

5.1 General Procedure 7 (GP7): [4+2] cycloaddition of arylcyclobutylamines with acrylonitrile



For **3a**–**3h**: A dried 50 mL quartz photoreaction tube was charged with **1** (0.75 mmol, 1.0 equiv), **2a** (2.25 mmol, 3.0 equiv), **QXPT-NPhCN** (0.0375 mmol, 0.05 equiv), and dry toluene (18.75 mL), vaccum/argon for three times. Under irradiation of 18 W blue LEDs (λ = 420 nm), the reaction mixture was stirred for 12~24 hour at room temperature under argon atmosphere. The solvent was evaporated to dryness under reduced pressure, and the reaction mixture was loaded directly onto a short silica gel column, followed by gradient elution with PE/EtOAc (10/1-1/1 ratio). The solvent was removed in *vacuo* to give the products **3a**–**3h**.

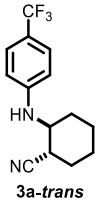
5.2 General Procedure 8 (GP8): [4+2] cycloaddition of 4-trifluoromethyl-*N*-cyclobutylaniline with olefins



For **5a**–**5d**: A dried 50 mL quartz photoreaction tube was charged with **1a** (0.75 mmol, 1.0 equiv), **4** (1.13 mmol, 1.5 equiv), **QXPT-NPhCN** (0.0375 mmol, 0.05 equiv), and dry DCM (18.75 mL), vaccum/argon for three times. Under irradiation of 18 W blue LEDs (λ = 420 nm), the reaction mixture was stirred for 8~24 hours at room temperature under argon atmosphere. The solvent was evaporated to dryness under reduced pressure, and the reaction mixture was loaded directly onto a short silica gel column, followed by gradient elution with PE/EtOAc (100/1-50/1 ratio). The solvent was removed in *vacuo* to give the products **5a**–**5d**.
For **5e**-**5w**: A dried 50 mL quartz photoreaction tube was charged with **1a** (0.9 mmol, 1.2 equiv), **4** (0.75 mmol, 1.0 equiv), **QXPT-NPhCN** (0.0375 mmol, 0.05 equiv), and dry DCM (18.75 mL), vaccum/argon for three times. Under irradiation of 18 W blue LEDs (λ = 420 nm), the reaction mixture was stirred for 8~24 hours at room temperature under argon atmosphere. The solvent was evaporated to dryness under reduced pressure, and the reaction mixture was loaded directly onto a short silica gel column, followed by gradient elution with PE/EtOAc (50/1-1/1 ratio). The solvent was removed in *vacuo* to give the products **5e**-**5w**.

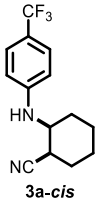
6. Characterization Data of Products

Following **GP7** with 4-trifluoromethyl-*N*-cyclobutylaniline **1a** (161 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol) and dry DCM (18.75 mL), cycloadduct **3a** was obtained after silica gel column chromatography (EtOAc: PE = 1:5) as a separable mixture of two diastereoisomers (*trans*:*cis* = 2.5:1).



3a-*trans*

Data for **3a-*trans*:** White solid (102 mg, 51%), m.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.20 (s, 1H), 3.52 – 3.45 (m, 1H), 3.34 (q, *J* = 3.5 Hz, 1H), 2.16 – 2.05 (m, 1H), 2.03 – 1.95 (m, 1H), 1.91 (dq, *J* = 14.5, 3.5, 2.9 Hz, 1H), 1.72 (ddt, *J* = 8.5, 5.5, 2.6 Hz, 1H), 1.63 (qd, *J* = 12.8, 12.2, 2.7 Hz, 3H), 1.43 (tt, *J* = 12.2, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 127.0 (q, *J* = 3.0 Hz), 126.2, 123.5, 120.0 (q, *J* = 32.3 Hz), 112.7, 51.8, 33.6, 29.5, 27.6, 24.8, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.15. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}F_3N_2$ $[M+H]^+$: 269.1266, found: 269.1260.

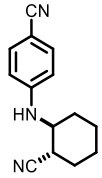


3a-*cis*

Data for **3a-*cis***: Yellow solid (40.8 mg, 20%), m.p.: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.63 (d, *J* = 9.5 Hz, 1H), 2.57 (td, *J* = 9.2, 3.8 Hz, 1H), 2.23 – 2.06 (m, 2H), 1.76 (dtd, *J* = 13.5, 9.9,

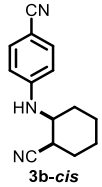
5.7 Hz, 3H), 1.47 (tdd, *J* = 12.7, 6.3, 2.9 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.29 (p, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 126.9 (q, *J* = 4.0 Hz), 126.2, 121.2, 120.0 (q, *J* = 32.3 Hz), 112.7, 52.8, 34.7, 31.7, 28.3, 23.8, 23.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.15. HRMS (ESI, m/z) calcd $C_{14}H_{16}F_3N_2$ $[M+H]^+$: 269.1266, found: 269.1260.

Following **GP7** with 4-cyano-*N*-cyclobutylaniline **1b** (129 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3b** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.5:1).



3b-*trans*

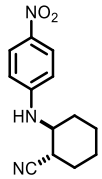
Data for **3b-*trans***: Light yellow oil (78 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 1H), 3.61 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.57 (td, *J* = 9.8, 3.9 Hz, 1H), 2.17 – 2.11 (m, 2H), 1.80 – 1.70 (m, 3H), 1.44 (ddd, *J* = 13.5, 10.7, 3.0 Hz, 1H), 1.38 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 133.9, 121.0, 120.3, 113.0, 99.7, 52.7, 34.9, 31.8, 28.6, 23.8, 23.5. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3$ $[M+H]^+$: 226.1344, found: 226.1341.



3b-*cis*

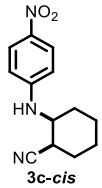
Data for **3b-*cis***: Light yellow oil (52 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 1H), 3.54 – 3.42 (m, 1H), 3.32 (d, *J* = 4.1 Hz, 1H), 2.11 (dd, *J* = 10.1, 5.1 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.75 (dd, *J* = 10.1, 4.3 Hz, 1H), 1.70 – 1.58 (m, 3H), 1.42 (dddd, *J* = 16.6, 12.8, 8.1, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 134.0, 120.1, 119.4, 112.9, 100.0, 51.5, 33.6, 29.4, 27.6, 24.7, 21.4.. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3$ $[M+H]^+$: 226.1344, found: 226.1341.

Following **GP7** with *N*-cyclobutyl-4-nitroaniline **1c** (144 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3c** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.7:1).



3c-*trans*

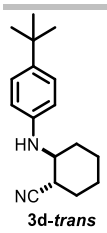
Data for **3c-*trans***: Yellow oil (76 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.59 – 6.52 (m, 2H), 4.58 (d, *J* = 8.8 Hz, 1H), 3.62 (qd, *J* = 9.2, 3.8 Hz, 1H), 2.53 (td, *J* = 9.9, 3.8 Hz, 1H), 2.11 (dp, *J* = 12.3, 4.0 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.71 – 1.63 (m, 1H), 1.42 (qt, *J* = 13.5, 3.9 Hz, 1H), 1.33 – 1.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 138.7, 126.5, 120.8, 111.9, 53.0, 35.0, 31.9, 28.7, 23.8, 23.6. HRMS (ESI, *m/z*) calcd for $C_{13}H_{16}N_3O_2$ $[M+H]^+$: 246.1243, found: 246.1237.



3c-*cis*

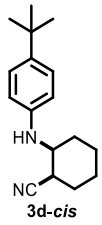
Data for **3c-*cis***: Yellow oil (44 mg, 24%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 6.60 – 6.53 (m, 2H), 4.70 (d, *J* = 8.7 Hz, 1H), 3.56 (ddt, *J* = 12.4, 8.5, 4.0 Hz, 1H), 3.35 (t, *J* = 4.1 Hz, 1H), 2.14 (dq, *J* = 12.4, 2.6 Hz, 1H), 2.07 – 1.93 (m, 2H), 1.81 – 1.73 (m, 1H), 1.71 – 1.60 (m, 3H), 1.45 (ddq, *J* = 17.9, 8.8, 5.0, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 139.0, 126.6, 119.3, 111.8, 51.8, 33.7, 29.4, 27.7, 24.7, 21.4. HRMS (ESI, *m/z*) calcd for $C_{13}H_{16}N_3O_2$ $[M+H]^+$: 246.1243, found: 246.1237.

Following **GP7** with 4-*tert*-butyl-*N*-cyclobutylaniline **1d** (152 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3d** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a separable mixture of two diastereoisomers (*trans*:*cis* = 2.5:1).



3d-*trans*

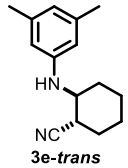
Data for **3d-*trans***: Yellow oil (79 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.64 – 6.58 (m, 2H), 3.58 (dq, *J* = 8.0, 3.8 Hz, 2H), 2.63 (td, *J* = 8.1, 3.8 Hz, 1H), 2.19 (ddd, *J* = 13.0, 7.2, 3.6 Hz, 1H), 2.05 (ddd, *J* = 12.2, 6.7, 3.5 Hz, 1H), 1.72 (ttd, *J* = 16.7, 6.7, 3.0 Hz, 3H), 1.48 (td, *J* = 9.3, 4.6 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.3, 126.3, 121.6, 113.6, 53.1, 34.0, 31.6, 31.6, 31.4, 27.6, 23.6, 22.9. HRMS (ESI, *m/z*) calcd for $C_{17}H_{25}N_2$ $[M+H]^+$: 257.2018, found: 257.2013.



3d-*cis*

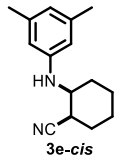
Data for **3d-*cis***: Red brown oil (31 mg, 16%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.1 Hz, 2H), 3.85 (s, 1H), 3.41 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.35 (s, 1H), 2.06 (d, *J* = 11.6 Hz, 1H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.90 (d, *J* = 13.4 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.60 (s, 2H), 1.58 – 1.52 (m, 1H), 1.46 – 1.39 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.4, 126.4, 120.0, 113.7, 52.6, 34.0, 31.6, 29.8, 27.8, 25.1, 22.8, 21.7. HRMS (ESI, *m/z*) calcd for $C_{17}H_{25}N_2$ $[M+H]^+$: 257.2018, found: 257.2013.

Following **GP7** with 3,5-dimethyl-*N*-cyclobutylaniline **1e** (131 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3e** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.5:1).



3e-*trans*

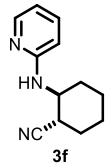
Data for **3e-*trans***: Red brown solid (82 mg, 48%), m.p.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 6.31 (s, 2H), 3.62 (td, *J* = 8.0, 4.0 Hz, 2H), 2.64 (td, *J* = 8.2, 3.9 Hz, 1H), 2.27 (s, 6H), 2.21 (dd, *J* = 10.4, 2.9 Hz, 1H), 2.05 (q, *J* = 4.0 Hz, 1H), 1.74 (dddd, *J* = 24.3, 13.1, 7.2, 3.5 Hz, 3H), 1.51 (tdt, *J* = 9.9, 6.3, 2.6 Hz, 1H), 1.46 – 1.38 (m, 1H), 1.37 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 139.1, 121.6, 120.5, 111.6, 52.7, 33.9, 31.2, 27.5, 23.5, 22.8, 21.5. HRMS (ESI, *m/z*) calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1705, found: 229.1701.



3e-*cis*

Data for **3e-*cis***: Red brown solid (55 mg, 32%), m.p.: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 6.26 (s, 2H), 3.68 (s, 1H), 3.44 (dt, *J* = 11.6, 4.0 Hz, 1H), 3.36 (q, *J* = 3.2 Hz, 1H), 2.25 (s, 6H), 2.09 (d, *J* = 3.1 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.91 (dq, *J* = 14.3, 3.0 Hz, 1H), 1.75 – 1.70 (m, 1H), 1.65 – 1.53 (m, 3H), 1.47 – 1.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 139.2, 120.4, 119.9, 111.7, 52.2, 33.8, 29.7, 27.7, 24.9, 21.6, 21.5. HRMS (ESI, *m/z*) calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1705, found: 229.1701.

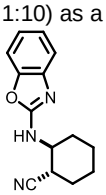
Following **GP7** with *N*-cyclobutyl-2-pyridinamine **1f** (111 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3f** was obtained after silica gel column chromatography (EtOAc:PE = 1:5) as a single diastereoisomer (*trans*:*cis* > 19:1).



3f

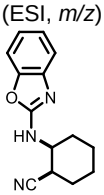
Data for **3f**: Yellow solid (81 mg, 54%), m.p.: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 5.1 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 6.64 – 6.56 (m, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 8.6 Hz, 1H), 4.08 (qd, *J* = 8.5, 3.8 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.24 – 2.01 (m, 2H), 1.74 (qd, *J* = 11.0, 5.5 Hz, 3H), 1.50 (tt, *J* = 9.9, 5.7 Hz, 1H), 1.44 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 147.7, 137.8, 121.5, 113.6, 108.1, 50.8, 34.5, 31.6, 29.8, 28.1, 23.7. HRMS (ESI, *m/z*) calcd for $C_{12}H_{16}N_3$ $[M+H]^+$:202.1344, found: 202.1339.

Following **GP7** with *N*-cyclobutylbenzo[*d*]oxazol-2-amine **1g** (141 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3g** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.3:1).



3g-*trans*

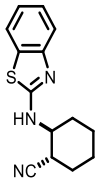
Data for **3g-*trans***: Light yellow solid (43 mg, 24%), m.p.: 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.23 – 7.14 (m, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.05 (s, 1H), 4.00 (td, *J* = 9.5, 3.9 Hz, 1H), 2.85 (td, *J* = 9.9, 3.9 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.15 (ddd, *J* = 17.0, 7.3, 3.4 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.76 – 1.65 (m, 1H), 1.63 – 1.47 (m, 2H), 1.35 (d, *J* = 12.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 148.5, 142.5, 124.2, 121.4, 120.7, 116.4, 109.1, 53.3, 34.8, 31.8, 29.8, 28.5, 23.8. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3O$ $[M+H]^+$: 242.1293, found: 242.1288.



3g-*cis*

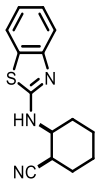
Data for **3g-*cis***: Light yellow solid (33 mg, 18%), m.p.: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 5.39 (s, 1H), 3.94 (dt, *J* = 12.1, 4.2 Hz, 1H), 3.66 (d, *J* = 4.3 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.92 (dt, *J* = 10.6, 3.6 Hz, 1H), 1.75 (dt, *J* = 14.1, 3.9 Hz, 2H), 1.72 – 1.66 (m, 1H), 1.64 – 1.55 (m, 1H), 1.44 (qt, *J* = 12.8, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 148.6, 142.4, 124.3, 121.6, 119.8, 116.7, 109.2, 52.3, 34.0, 29.2, 27.5, 24.7, 21.4. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3O$ $[M+H]^+$: 242.1293, found: 242.1288.

Following **GP7** with *N*-cyclobutylbenzo[*d*]thiazol-2-amine **1h** (153 mg, 0.75 mmol), acrylonitrile (148 μL, 2.25 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **3h** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a single diastereoisomer (*trans*:*cis* =1.1:1).



3h-*trans*

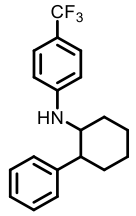
Data for **3h-*trans***: Yellow solid (43 mg, 22%), m.p.: 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 15.6, 8.0 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.28 – 5.15 (m, 1H), 2.87 (d, *J* = 10.4 Hz, 1H), 2.33 (d, *J* = 8.8 Hz, 2H), 2.14 (d, *J* = 12.2 Hz, 1H), 1.97 (t, *J* = 10.2 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.58 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 139.3, 127.1, 126.2, 123.5, 120.7, 120.4, 113.4, 66.7, 53.6, 41.4, 33.9, 25.0, 24.4. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3S$ $[M+H]^+$: 258.1065, found: 258.1057.



3h-*cis*

Data for **3h-*cis***: Yellow solid (40 mg, 21%), m.p.: 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 11.8, 8.0 Hz, 2H), 7.22 (dd, *J* = 16.4, 8.6 Hz, 1H), 7.05 (q, *J* = 7.6, 6.7 Hz, 1H), 5.82 (s, 1H), 3.90 (q, *J* = 5.8, 4.4 Hz, 1H), 2.78 (dt, *J* = 14.0, 8.2 Hz, 1H), 2.17 (d, *J* = 10.5 Hz, 1H), 2.11 – 1.96 (m, 1H), 1.68 (q, *J* = 10.9, 10.0 Hz, 3H), 1.46 (q, *J* = 9.8 Hz, 2H), 1.28 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 152.1, 130.6, 126.2, 122.2, 121.0, 120.9, 119.3, 55.1, 38.5, 34.2, 31.4, 28.1, 23.6. HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_3S$ $[M+H]^+$: 258.1065, found: 258.1057.

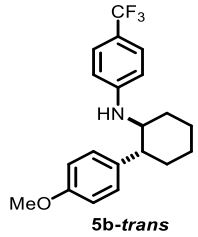
Following **GP8** with 4-trifluoromethyl-*N*-cyclobutylaniline **1a** (161 mg, 0.75 mmol), styrene **4a** (130 μL, 1.13 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol) and dry DCM (18.75 mL), cycloadduct **5a** was obtained after silica gel column chromatography (EtOAc: PE = 1:100) as an inseparable mixture of two diastereoisomers (1:1 d.r.).



5a

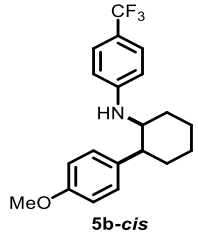
Data for **5a**: Yellow oil (81.4 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of diastereomers) δ 7.37 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.21 (m, 7H), 7.17 (d, *J* = 7.5 Hz, 5H), 6.52 (d, *J* = 8.3 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 4H), 3.92 (p, *J* = 8.0, 7.0 Hz, 1H), 3.78 (s, 1H), 3.66 (s, 1H), 3.46 (td, *J* = 10.8, 3.7 Hz, 2H), 2.51 (td, *J* = 11.3, 3.6 Hz, 2H), 2.46 – 2.33 (m, 2H), 1.97 (dq, *J* = 12.8, 3.1 Hz, 2H), 1.85 (tdd, *J* = 12.9, 7.9, 4.4 Hz, 5H), 1.58 (qd, *J* = 12.9, 3.5 Hz, 2H), 1.51 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, a mixture of diastereomers) δ 150.1, 143.7, 128.9 (q, *J* = 3.0 Hz), 128.7 (q, *J* = 4.0 Hz), 127.6, 127.4, 126.7, 126.5, 123.8, 121.1, 120.9, 118.0 (q, *J* = 33.3 Hz), 112.2, 111.9, 56.2, 56.0, 51.3, 51.3, 49.1, 48.6, 35.8, 33.7, 33.5, 26.5, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$, a mixture of diastereomers) δ -60.97, -60.91. HRMS (ESI, m/z) calcd $C_{19}H_{21}F_3N$ $[M+H]^+$: 320.1626, found: 320.1619.

Following **GP8** with 4-trifluoromethyl-*N*-cyclobutylaniline **1a** (161 mg, 0.75 mmol), 4-methoxystyrene **4b** (142 μL, 1.13mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5b** was obtained after silica gel column chromatography (EtOAc:PE = 1:100) as a separable mixture of two diastereoisomers (*cis*:*trans* = 1.8:1).



5b-*trans*

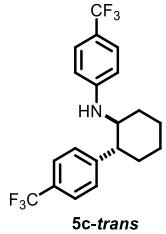
Data for **5b-*trans***: Yellow oil (24 mg, 9%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.16 – 7.11 (m, 2H), 6.82 – 6.76 (m, 2H), 6.38 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 1H), 3.83 (p, *J* = 3.4, 2.9 Hz, 1H), 3.74 (s, 3H), 3.01 – 2.92 (m, 1H), 2.09 – 2.02 (m, 1H), 1.95 – 1.88 (m, 1H), 1.88 – 1.77 (m, 2H), 1.69 – 1.56 (m, 2H), 1.55 – 1.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 150.4, 135.5, 128.5, 126.5 (q, *J* = 4.0 Hz), 123.8, 118.3 (q, *J* = 32.3 Hz), 114.0, 112.3, 55.3, 53.3, 45.3, 32.1, 30.2, 26.1, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.92. HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}F_3NO$ $[M+H]^+$: 350.1732, found: 350.1725.



5b-*cis*

Data for **5b-*cis***: Yellow oil (44 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 2H), 3.95 – 3.80 (m, 1H), 3.74 (s, 3H), 3.39 (td, *J* = 10.8, 3.7 Hz, 1H), 2.46 (td, *J* = 11.3, 3.5 Hz, 1H), 2.41 – 2.33 (m, 1H), 1.99 – 1.91 (m, 1H), 1.82 (d, *J* = 11.8 Hz, 2H), 1.55 (qd, *J* = 13.1, 3.9 Hz, 2H), 1.47 – 1.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 150.2, 135.8, 128.3, 126.5 (q, *J* = 3.0 Hz), 123.8, 118.3 (q, *J* = 32.3 Hz), 114.2, 112.0, 56.4, 55.3, 50.4, 36.0, 33.6, 26.5, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.89. HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}F_3NO$ $[M+H]^+$: 350.1732, found: 350.1725.

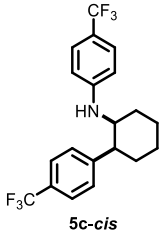
Following **GP8** with 4-trifluoromethyl-*N*-cyclobutylaniline **1a** (161 mg, 0.75 mmol), 1-(trifluoromethyl)-4-vinylbenzene **4c** (177 μL, 1.13 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5c** was obtained after silica gel column chromatography (EtOAc:PE = 1:100) as a separable mixture of two diastereoisomers (*cis*:*trans* = 1.4:1).



5c-*trans*

Data for **5c-*trans***: Light yellow oil (67 mg, 23%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 4H), 6.42 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 1H), 3.53 (td, *J* = 10.8, 3.7 Hz, 1H), 2.59 (td, *J* = 11.2, 3.6 Hz, 1H), 2.38 (dd, *J* = 13.8, 3.9 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.92 – 1.81 (m, 2H), 1.59 (td, *J* = 12.7, 3.4 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.47 – 1.38 (m, 1H), 1.20 (td, *J* = 13.1, 12.4, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 148.0, 128.85, 127.8, 126.7 (q, *J* = 4.0 Hz), 125.7 (q, *J* = 4.0 Hz), 118.8 (q, *J* = 33.3 Hz),

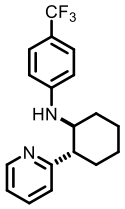
112.1, 55.8, 51.3, 35.7, 33.5, 26.3, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.03, -62.42. HRMS (ESI, *m/z*) calcd for $C_{20}H_{20}F_6N$ $[M+H]^+$: 388.1500, found: 388.1493.



5c-*cis*

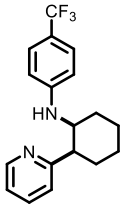
Data for **5c-*cis***: Light yellow oil (93 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.37 (d, *J* = 8.5 Hz, 2H), 3.99 (s, 1H), 3.93 (q, *J* = 3.4 Hz, 1H), 3.12 – 3.03 (m, 1H), 2.08 (dq, *J* = 13.4, 3.5, 2.9 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.90 (dd, *J* = 8.2, 3.1 Hz, 2H), 1.69 (ddt, *J* = 24.1, 10.2, 3.9 Hz, 2H), 1.53 (tt, *J* = 12.2, 4.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.7, 129.0, 128.0, 126.6 (q, *J* = 3.0 Hz), 125.4 (q, *J* = 4.0 Hz), 118.8 (q, *J* = 32.3 Hz), 112.3, 53.0, 46.2, 30.4, 25.8, 25.6, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.08, -62.43. HRMS (ESI, *m/z*) calcd for $C_{20}H_{20}F_6N$ $[M+H]^+$: 388.1500, found: 388.1493.

Following **GP8** with 4-trifluoromethyl-*N*-cyclobutylaniline **1a** (161 mg, 0.75 mmol), 2-vinylpyridine **4d** (121 μL, 1.13 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5d** was obtained after silica gel column chromatography (EtOAc:PE = 1:30) as a separable mixture of two diastereoisomers (*cis*:*trans* = 1.5:1).



5d-*trans*

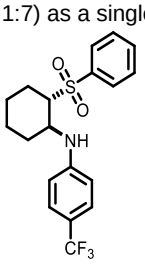
Data for **5d-*trans***: Gray solid (51 mg, 21%), m.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.0 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 2H), 4.02 (s, 1H), 3.62 (td, *J* = 10.7, 3.8 Hz, 1H), 2.70 (td, *J* = 11.4, 3.7 Hz, 1H), 2.33 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.91 – 1.83 (m, 2H), 1.74 (td, *J* = 12.7, 3.2 Hz, 1H), 1.46 (dddd, *J* = 31.4, 13.4, 8.5, 3.8 Hz, 2H), 1.38 – 1.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 150.1, 149.1, 136.9, 126.5 (q, *J* = 4.0 Hz), 123.8, 122.0, 121.9, 117.8 (q, *J* = 32.3 Hz), 111.9, 56.1, 53.1, 33.7, 33.1, 26.0, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.90. HRMS (ESI, *m/z*) calcd for $C_{18}H_{20}F_3N_2$ $[M+H]^+$:321.1579, found: 321.1573.



5d-*cis*

Data for **5d-*cis***: Gray solid (76 mg, 32%), m.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.38 (d, *J* = 8.3 Hz, 2H), 5.12 (s, 1H), 3.79 (d, *J* = 5.1 Hz, 1H), 3.05 (dt, *J* = 11.9, 3.7 Hz, 1H), 2.14 – 1.99 (m, 2H), 1.77 (ddq, *J* = 21.9, 12.8, 4.0 Hz, 2H), 1.60 – 1.48 (m, 3H), 1.39 (ddd, *J* = 19.8, 9.9, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 150.7, 148.8, 136.8, 126.5 (q, *J* = 4.0 Hz), 123.8, 122.7, 121.7, 117.8 (q, *J* =31.3 Hz), 112.2, 52.9, 47.7, 30.0, 26.1, 25.4, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.89. HRMS (ESI, *m/z*) calcd for $C_{18}H_{20}F_3N_2$ $[M+H]^+$:321.1579, found: 321.1573.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), phenyl vinyl sulfone **4e** (126 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5e** was obtained after silica gel column chromatography (EtOAc:PE = 1:7) as a single diastereoisomer (*trans:cis* >19:1).

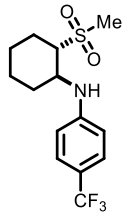


5e

Data for **5e**: Yellow solid (147 mg, 51%), m.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.43 (d, *J* = 8.3 Hz, 2H), 4.46 (s, 1H), 3.39 (t, *J* = 9.2 Hz, 1H), 3.10 (td, *J* = 10.3,

3.8 Hz, 1H), 2.30 (ddt, *J* = 19.7, 10.9, 4.2 Hz, 2H), 1.92 (dt, *J* = 9.4, 4.7 Hz, 1H), 1.71 (dq, *J* = 9.2, 4.9, 4.3 Hz, 1H), 1.53 (td, *J* = 14.6, 13.1, 9.4 Hz, 1H), 1.44 – 1.35 (m, 1H), 1.34 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 137.9, 133.9, 129.0, 126.8 (q, *J* = 3.0 Hz), 126.4, 123.7, 119.5 (q, *J* = 32.3 Hz), 112.2, 66.8, 52.1, 32.8, 26.1, 24.5, 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.01. HRMS (ESI, *m/z*) calcd for $C_{19}H_{21}F_3NO_2S$ $[M+H]^+$: 384.1245, found 384.1241.

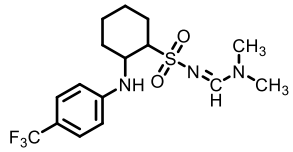
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), (methylsulfonyl)ethene **4f** (68 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5f** was obtained after silica gel column chromatography (EtOAc:PE = 1:3) as a single diastereoisomer (*trans:cis* >19:1).



5f

Data for **5f**: Red brown oil (89 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 4.22 (s, 1H), 3.71 (s, 1H), 2.96 (d, *J* = 6.4 Hz, 1H), 2.93 (s, 3H), 2.48 – 2.40 (m, 1H), 2.26 (dt, *J* = 12.9, 4.1 Hz, 1H), 1.97 (dq, *J* = 12.0, 4.4, 3.9 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.61 (qd, *J* = 12.4, 3.8 Hz, 1H), 1.42 (d, *J* = 6.4 Hz, 1H), 1.39 – 1.33 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 126.9 (q, *J* = 4.0 Hz), 123.4, 120.1 (q, *J* = 33.3 Hz), 113.2, 66.5, 53.4, 41.5, 33.7, 24.8, 24.5, 24.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.20. HRMS (ESI, *m/z*) calcd for $C_{14}H_{19}F_3NO_2S$ $[M+H]^+$: 322.1089, found 322.1084.

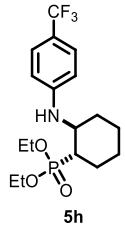
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *N*,*N*-dimethyl-*N'*-(vinylsulfonyl)formimidamide **4g** (122 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5g** was obtained after silica gel column chromatography (EtOAc:PE = 1:1) as an inseparable mixture of two diastereoisomers (2.6:1 d.r.).



5g

Data for **5g**: Reddish-brown oil (94 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of diastereomers) δ 7.61 (s, 1H), 7.59 (s, 0.38H), 7.39 (dd, *J* = 8.7, 4.0 Hz, 2.76H), 6.61 (s, 0.76H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.87 (s, 1H), 4.85 (s, 0.38H), 3.34 (td, *J* = 10.4, 3.9 Hz, 1H), 3.28 – 3.22 (m, 0.38H), 2.96 (ddd, *J* = 12.0, 10.0, 3.8 Hz, 1H), 2.90 (d, *J* = 4.5 Hz, 4.14H), 2.60 (d, *J* = 4.9 Hz, 4.14H), 2.53 – 2.45 (m, 1H), 2.28 (d, *J* = 3.5 Hz, 0.38H), 2.22 (dd, *J* = 14.1, 3.9 Hz, 1H), 2.04 (d, *J* = 6.1 Hz, 0.38H), 1.96 (s, 0.38H), 1.90 (dd, *J* = 12.8, 9.1 Hz, 1.38H), 1.84 (d, *J* = 3.9 Hz, 0.38H), 1.80 – 1.73 (m, 1H), 1.71 – 1.61 (m, 1H), 1.56 (tt, *J* = 10.8, 5.7 Hz, 1H), 1.49 – 1.44 (m, 0.38H), 1.39 (ddt, *J* = 18.8, 9.1, 3.1 Hz, 2H), 1.32 (d, *J* = 2.8 Hz, 0.76H), 1.28 (d, *J* = 3.6 Hz, 0.38H). ^{13}C NMR (101 MHz, $CDCl_3$, a mixture of diastereomers) δ 160.4, 159.5, 149.9, 149.5, 130.2, 129.0, 126.8 (q, *J* = 4.0 Hz), 126.3, 123.6, 118.8 (q, *J* = 33.3 Hz), 111.8, 111.6, 64.7, 62.1, 54.0, 50.3, 49.0, 40.9, 37.9, 35.2, 33.3, 29.8, 27.5, 25.0, 24.6, 24.3, 21.4, 19.8. ^{19}F NMR (376 MHz, $CDCl_3$, a mixture of diastereomers) δ -60.98, -60.99. HRMS (ESI, *m/z*) calcd for $C_{16}H_{22}F_3N_2O_2S$ $[M+H]^+$: 378.1463, found: 378.1458.

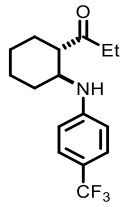
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), diethyl vinylphosphonate **4h** (119 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5h** was obtained after silica gel column chromatography (EtOAc:PE = 1:3) as a single diastereoisomer (*trans*:*cis* >19:1).



5h

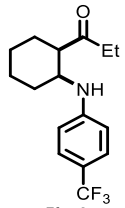
Data for **5h**: Yellow oil (137 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.80 (s, 1H), 4.11 – 3.93 (m, 4H), 3.46 – 3.39 (m, 1H), 2.34 – 2.26 (m, 1H), 2.18 – 2.08 (m, 1H), 1.95 – 1.85 (m, 1H), 1.85 – 1.74 (m, 2H), 1.53 (tdt, *J* = 12.0, 5.7, 3.0 Hz, 1H), 1.47 – 1.40 (m, 1H), 1.40 – 1.33 (m, 1H), 1.32 (s, 1H), 1.30 – 1.23 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 135.7, 126.6 (q, *J* = 4.0 Hz), 118.7 (q, *J* = 32.3 Hz), 112.1, 62.1 (td, *J* = 7.1, 6.1, 7.1 Hz), 52.6 (d, *J* = 5.1 Hz) , 42.1, 41.7, 33.6 (d, *J* = 14.1 Hz), 26.5 (d, *J* = 5.1 Hz), 25.5 (d, *J* = 14.1 Hz), 24.4, 16.5 (q, *J* = 4.0 Hz), 16.5 (t, *J* = 6.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.92. HRMS (ESI, *m/z*) calcd for $C_{17}H_{26}F_3NO_3P$ $[M+H]^+$: 380.1602, found: 380.1597.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), pent-1-en-3-one **4i** (77 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5i** was obtained after silica gel column chromatography (EtOAc:PE = 1:20) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.2:1).



5i-*trans*

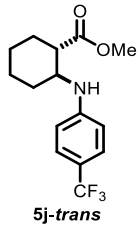
Data for **5i-*trans***: Light yellow oil (53 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.47 (s, 1H), 3.83 (dt, *J* = 7.6, 3.6 Hz, 1H), 2.89 (dt, *J* = 8.5, 4.4 Hz, 1H), 2.53 – 2.31 (m, 2H), 2.04 (tt, *J* = 9.6, 4.6 Hz, 1H), 1.90 (dtd, *J* = 17.0, 8.3, 3.4 Hz, 1H), 1.73 (ddt, *J* = 14.0, 7.6, 4.2 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.52 (ddt, *J* = 11.7, 7.3, 3.7 Hz, 1H), 1.47 – 1.37 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 149.6, 126.8 (q, *J* = 3.0 Hz), 123.7, 118.6 (q, *J* = 32.3 Hz), 112.4, 51.1, 50.8, 34.4, 28.9, 24.9, 23.3, 22.5, 7.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.98. HRMS (ESI, *m/z*) calcd for $C_{16}H_{21}F_3NO$ $[M+H]^+$: 300.1575, found: 300.1572.



5i-*cis*

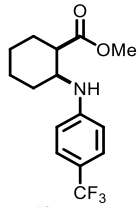
Data for **5i-*cis***: Light yellow oil (44 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 1H), 3.63 (td, *J* = 10.8, 4.0 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.46 – 2.37 (m, 2H), 2.21 – 2.12 (m, 1H), 1.91 – 1.83 (m, 1H), 1.79 (dt, *J* = 14.1, 3.5 Hz, 2H), 1.50 (qd, *J* = 12.7, 3.2 Hz, 1H), 1.36 (ddd, *J* = 12.9, 10.0, 3.8 Hz, 1H), 1.29 (dd, *J* = 5.3, 3.7 Hz, 1H), 1.15 – 1.06 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8, 149.7, 126.7 (q, *J* = 4.0 Hz), 123.7, 119.0 (q, *J* = 33.3 Hz), 112.7, 57.4, 53.4, 35.2, 33.0, 29.3, 25.0, 24.9, 7.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.02. HRMS (ESI, *m/z*) calcd for $C_{16}H_{21}F_3NO$ $[M+H]^+$: 300.1575, found: 300.1572.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), methyl acrylate **4j** (68 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5j** was obtained after silica gel column chromatography (EtOAc:PE = 1:20) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.3:1).



5j-*trans*

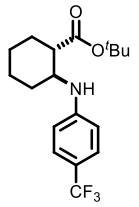
Data for **5j-*trans***: Light yellow oil (73 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 1H), 3.58 (s, 3H), 2.31 (ddd, *J* = 11.6, 10.2, 3.7 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.02 – 1.93 (m, 1H), 1.83 – 1.75 (m, 2H), 1.72 – 1.58 (m, 2H), 1.43 (d, *J* = 3.1 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 1H), 1.11 (tdd, *J* = 13.0, 10.8, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 149.7, 126.7 (q, *J* = 4.0 Hz), 123.7, 119.2 (q, *J* = 32.3 Hz), 112.6, 53.7, 52.0, 50.8, 32.9, 29.8, 29.1, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.04. HRMS (ESI, *m/z*) calcd for $C_{15}H_{19}F_3NO_2$ $[M+H]^+$: 302.1368, found: 302.1362.



5j-*cis*

Data for **5j-*cis***: Light yellow oil (56 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.67 (s, 1H), 3.78 (dd, *J* = 7.9, 3.9 Hz, 1H), 3.64 (s, 3H), 2.86 (dt, *J* = 8.0, 4.3 Hz, 1H), 2.01 (ddd, *J* = 10.5, 8.6, 4.9 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.76 – 1.66 (m, 2H), 1.65 – 1.58 (m, 1H), 1.54 – 1.46 (m, 2H), 1.43 (q, *J* = 2.8, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 149.7, 126.8 (q, *J* = 3.0 Hz), 123.7, 118.9 (q, *J* = 33.3 Hz), 112.5, 51.8, 51.1, 44.6, 29.0, 26.1, 23.2, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.98. HRMS (ESI, *m/z*) calcd for $C_{15}H_{19}F_3NO_2$ $[M+H]^+$: 302.1368, found: 302.1362.

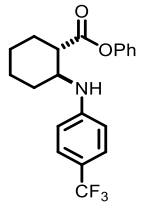
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *tert*-butyl acrylate **4k** (77 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5k** was obtained after silica gel column chromatography (EtOAc:PE = 1:40) as a single diastereoisomer (*trans*:*cis* > 19:1).



5k

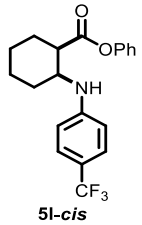
Data for **5k**: Gray oil (98 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.2 Hz, 2H), 3.97 – 3.87 (m, 1H), 3.59 – 3.49 (m, 1H), 2.17 (q, *J* = 11.5 Hz, 2H), 1.97 (d, *J* = 13.6 Hz, 1H), 1.77 (d, *J* = 12.6 Hz, 2H), 1.70 – 1.60 (m, 1H), 1.60 – 1.46 (m, 1H), 1.45 – 1.37 (m, 1H), 1.33 (d, *J* = 2.9 Hz, 9H), 1.10 (q, *J* = 12.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 149.8, 126.7 (q, *J* = 4.0 Hz), 118.9 (q, *J* = 32.3 Hz), 112.3, 80.8, 53.9, 52.1, 32.9, 29.1, 28.1, 24.8, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.95. HRMS (ESI, *m/z*) calcd for $C_{18}H_{25}F_3NO_2$ $[M+H]^+$: 344.1837, found: 344.1832.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), phenyl acrylate **4l** (77 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5l** was obtained after silica gel column chromatography (EtOAc:PE = 1:30) as a separable mixture of two diastereoisomers (*trans*:*cis* = 3:1).



5l-*trans*

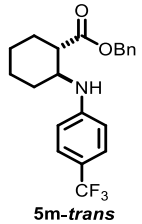
Data for **5l-*trans***: Yellow oil (87 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 1H), 3.98 (d, *J* = 7.6 Hz, 1H), 3.13 (dt, *J* = 8.2, 4.4 Hz, 1H), 2.14 (dtd, *J* = 15.1, 7.6, 3.5 Hz, 1H), 1.96 (dtd, *J* = 10.4, 7.7, 7.2, 3.0 Hz, 1H), 1.86 (ddt, *J* = 13.1, 8.3, 4.2 Hz, 1H), 1.79 – 1.60 (m, 3H), 1.54 (ddt, *J* = 14.6, 8.5, 3.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 150.6, 149.7, 129.6, 126.9 (q, *J* = 4.0 Hz), 126.1, 121.6, 119.2 (q, *J* = 32.3 Hz), 112.7, 51.1, 44.9, 29.0, 25.9, 23.3, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.00. HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}F_3NO_2$ $[M+H]^+$: 364.1524, found: 364.1518.



5l-*cis*

Data for **5l-*cis***: Yellow oil (29 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.24 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.80 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 1H), 3.77 (td, *J* = 10.7, 3.9 Hz, 1H), 2.53 (td, *J* = 10.8, 10.3, 3.6 Hz, 1H), 2.26 – 2.12 (m, 2H), 1.89 – 1.73 (m, 3H), 1.51 – 1.41 (m, 1H), 1.34 (tt, *J* = 13.8, 3.8 Hz, 1H), 1.17 (td, *J* = 13.0, 12.1, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 150.7, 149.7, 129.5, 126.9 (q, *J* = 4.0 Hz), 126.0, 121.6, 119.4 (q, *J* = 32.3 Hz), 112.7, 54.0, 51.2, 33.0, 29.1, 24.9, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.05. HRMS (ESI, *m/z*) calcd for $C_{20}H_{21}F_3NO_2$ $[M+H]^+$: 364.1524, found: 364.1518.

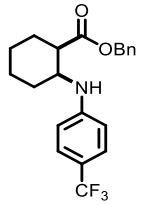
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), benzyl acrylate **4m** (119 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5m** was obtained after silica gel column chromatography (EtOAc:PE = 1:30) as a separable mixture of two diastereoisomers (*trans*:*cis* = 1.3:1).



5m-*trans*

Data for **5m-*trans***: Yellow solid (72 mg, 25%). m.p.: 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 4.9 Hz, 3H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.55 (d, *J* = 8.1 Hz, 2H), 5.08 – 4.95 (m, 2H), 3.85 (s, 1H), 3.62 (t, *J* = 11.0 Hz, 1H), 2.35 (t, *J* = 11.3 Hz, 1H), 2.16 (d, *J* = 13.3 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.78 (d, *J* = 12.7 Hz, 2H), 1.71 – 1.60 (m, 1H), 1.40 (q, *J* = 16.4, 14.6 Hz, 1H), 1.27 (d, *J* = 11.5 Hz, 1H), 1.09 (q, *J* = 12.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 149.5, 135.7, 128.5, 128.2, 128.2, 126.6 (q,

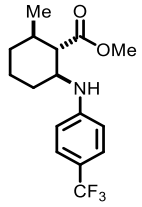
J = 4.0 Hz), 123.6, 118.7 (q, *J* = 33.3 Hz), 112.4, 66.5, 53.6, 50.9, 32.8, 29.0, 24.7, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.98. HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}F_3NO_2$ $[M+H]^+$: 378.1681, found: 378.1678.



5m-*cis*

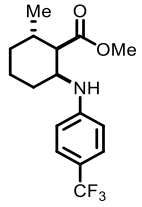
Data for **5m-*cis***: Yellow solid (55 mg, 20%). m.p.: 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 3H), 7.22 (d, *J* = 7.3 Hz, 2H), 6.54 (d, *J* = 8.2 Hz, 2H), 5.07 (q, *J* = 12.5 Hz, 2H), 4.56 (s, 1H), 3.84 (s, 1H), 2.90 (d, *J* = 7.9 Hz, 1H), 1.99 (q, *J* = 12.6, 8.6 Hz, 1H), 1.88 (d, *J* = 10.0 Hz, 1H), 1.74 (d, *J* = 13.2 Hz, 1H), 1.61 (q, *J* = 21.5, 17.0 Hz, 3H), 1.44 (t, *J* = 9.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 149.6, 135.9, 128.7, 128.4, 128.2, 126.8 (q, *J* = 3.03 Hz), 123.8, 119.0 (q, *J* = 33.3 Hz), 112.5, 66.4, 51.0, 44.8, 29.0, 25.7, 23.3, 22.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.95. HRMS (ESI, *m/z*) calcd for $C_{21}H_{23}F_3NO_2$ $[M+H]^+$: 378.1681, found: 378.1678.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), methyl-but-2-enoate **4n** (81 µL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5n** was obtained after silica gel column chromatography (EtOAc:PE = 1:40) as a separable mixture of two diastereoisomers (*trans*:*cis* = 2.9:1).



5n-*trans*

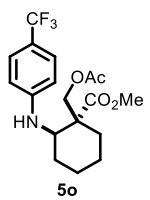
Data for **5n-*trans***: Yellow oil (69 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.47 (s, 1H), 3.83 (dt, *J* = 7.6, 3.6 Hz, 1H), 2.89 (dt, *J* = 8.5, 4.4 Hz, 1H), 2.53 – 2.31 (m, 2H), 2.04 (tt, *J* = 9.6, 4.6 Hz, 1H), 1.90 (dtd, *J* = 17.0, 8.3, 3.4 Hz, 1H), 1.73 (ddt, *J* = 14.0, 7.6, 4.2 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.52 (ddt, *J* = 11.7, 7.3, 3.7 Hz, 1H), 1.47 – 1.37 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 149.7, 126.6 (q, *J* = 4.0 Hz), 123.6, 118.5 (q, *J* = 33.3 Hz), 112.2, 52.8, 51.7, 49.7, 32.9, 29.7, 28.9, 20.7, 19.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.00. HRMS (ESI, *m/z*) calcd for $C_{16}H_{21}F_3NO_2$ $[M+H]^+$: 316.1524, found: 316.1517.



5n-*cis*

Data for **5n-*cis***: Yellow oil (24 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.3 Hz, 2H), 3.76 (s, 1H), 3.73 – 3.63 (m, 1H), 3.58 (s, 3H), 2.22 – 2.14 (m, 1H), 1.94 (t, *J* = 10.6 Hz, 1H), 1.79 (tdd, *J* = 13.6, 9.7, 5.6 Hz, 3H), 1.43 (qt, *J* = 13.8, 6.7 Hz, 1H), 1.09 – 0.96 (m, 2H), 0.92 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 149.7, 126.7 (q, *J* = 4.0 Hz), 123.7, 118.9 (q, *J* = 32.3 Hz), 112.6, 58.8, 54.4, 51.8, 35.2, 33.7, 32.7, 24.3, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.02. HRMS (ESI, *m/z*) calcd for $C_{16}H_{21}F_3NO_2$ $[M+H]^+$: 316.1524, found: 316.1517.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), methyl-2-(acetoxymethyl)acrylate **4o** (115 µL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5o** was obtained after silica gel column chromatography (EtOAc:PE = 1:20) as a single diastereoisomer (*trans*:*cis* > 19:1).

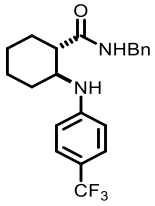


5o

Data for **5o**: Yellow oil (100.8 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 4.38 – 4.27 (m, 2H), 4.26 – 4.19 (m, 1H), 4.18 (s, 1H), 3.68 (s, 3H), 2.03 (d, *J* = 7.6 Hz, 3H), 2.02 – 1.98 (m, 1H), 1.79 (tt, *J* = 7.7, 3.3 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.58 – 1.54 (m, 2H), 1.54 (s, 1H), 1.49 – 1.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 170.6, 149.9, 126.7 (q, *J* =

4.0 Hz), 126.3, 123.6, 118.9 (q, *J* = 32.3 Hz), 114.2, 112.6, 65.7, 52.4, 52.0, 50.7, 28.5, 28.0, 21.9, 21.5, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.04. HRMS (ESI, m/z) calcd $C_{18}H_{22}F_3NNaO_4$ $[M+Na]^+$: 396.1399, found: 396.1393.

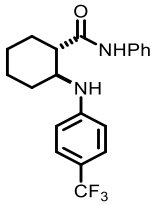
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *N*-benzylacrylamide **4p** (118 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5p** was obtained after silica gel column chromatography (EtOAc:PE = 1:1) as a single diastereoisomer (*trans*:*cis* > 19:1).



5p

Data for **5p**: Light yellow soliid (96 mg, 35%). m.p.: 182-184 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.14 (t, *J* = 6.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.13 (dd, *J* = 8.1, 4.6 Hz, 5H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.05 (d, *J* = 9.2 Hz, 1H), 4.28 (dd, *J* = 15.5, 6.3 Hz, 1H), 4.14 (dd, *J* = 15.5, 5.6 Hz, 1H), 3.58 (qd, *J* = 10.5, 3.8 Hz, 1H), 2.26 (td, *J* = 11.2, 3.6 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.83 (d, *J* = 13.0 Hz, 1H), 1.70 (d, *J* = 12.1 Hz, 2H), 1.54 (qd, *J* = 12.9, 3.2 Hz, 1H), 1.42 – 1.29 (m, 1H), 1.26 – 1.12 (m, 2H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 173.8, 151.0, 139.4, 128.0, 126.8, 126.4, 126.1 (q, *J* = 3.0 Hz), 124.1, 114.8 (q, *J* = 32.3 Hz), 111.6, 52.0, 50.7, 41.8, 32.1, 29.5, 24.7, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.75. HRMS (ESI, *m/z*) calcd for $C_{21}H_{24}F_3N_2O$ $[M+H]^+$: 377.1841, found: 377.1835.

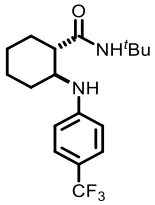
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *N*-phenylacrylamide **4q** (110 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5q** was obtained after silica gel column chromatography (EtOAc:PE = 1:1) as a single diastereoisomer (*trans*:*cis* > 19:1).



5q

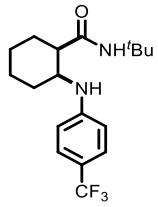
Data for **5q**: Light yellow soliid (33 mg, 12%). m.p.: 170-172 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.72 (s, 1H), 7.55 – 7.49 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.17 (m, 2H), 7.02 – 6.94 (m, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.07 (d, *J* = 9.2 Hz, 1H), 3.61 (qd, *J* = 10.5, 3.8 Hz, 1H), 2.40 (ddd, *J* = 11.9, 10.2, 3.6 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.93 (d, *J* = 13.3 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.54 (qd, *J* = 12.8, 3.4 Hz, 1H), 1.44 – 1.32 (m, 1H), 1.24 – 1.20 (m, 1H), 1.16 – 1.06 (m, 1H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 173.1, 151.6, 139.7, 129.1, 126.5 (q, *J* = 4.0 Hz), 124.5, 123.4, 119.7 (q, *J* = 30.3 Hz), 115.4, (q, *J* = 32.3 Hz), 112.2, 52.4, 52.3, 51.7, 32.4, 30.6, 25.5. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ -60.81. HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}F_3N_2O$ $[M+H]^+$: 363.1684, found: 363.1378.

Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *N*-(tert-butyl) acrylamide **4r** (94 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5r** was obtained after silica gel column chromatography (EtOAc:PE = 1:1) as a separable mixture of two diastereoisomers (*trans:cis*= 2.2:1).



5r-*trans*

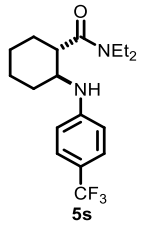
Data for **5r-*trans***: Light yellow solid (56 mg, 22%). m.p.: 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 5.40 (s, 1H), 3.91 (s, 1H), 3.50 (s, 1H), 2.18 – 2.11 (m, 1H), 1.93 (d, *J* = 13.9 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 2H), 1.67 – 1.55 (m, 1H), 1.37 (dd, *J* = 13.5, 10.8 Hz, 2H), 1.28 (d, *J* = 2.2 Hz, 1H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 150.0, 126.7 (q, *J* = 4.0 Hz), 123.8, 119.1 (q, *J* = 33.3 Hz), 112.7, 54.3, 53.9, 51.2, 33.8, 29.6, 28.8, 25.1, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.96. HRMS (ESI, *m/z*) calcd for $C_{18}H_{26}F_3N_2O$ $[M+H]^+$: 343.1997, found: 343.1993.



5r-*cis*

Data for **5r-*cis***: Light yellow solid (26 mg, 10%). m.p.: 193-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.45 (s, 1H), 4.81 (s, 1H), 3.67 (dt, *J* = 7.1, 3.5 Hz, 1H), 2.52 (td, *J* = 7.5, 6.9, 3.6 Hz, 1H), 2.09 – 1.97 (m, 1H), 1.89 – 1.78 (m, 1H), 1.76 – 1.67 (m, 2H), 1.67 – 1.62 (m, 1H), 1.61 – 1.50 (m, 1H), 1.47 – 1.39 (m, 2H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 150.1, 126.8 (q, *J* = 3.0 Hz), 123.8, 118.9 (q, *J* = 31.3 Hz), 112.8, 52.0, 51.2, 46.2, 33.1, 28.9, 26.6, 23.3, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.96. HRMS (ESI, *m/z*) calcd for $C_{18}H_{26}F_3N_2O$ $[M+H]^+$: 343.1997, found: 343.1993.

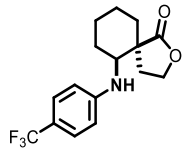
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), *N,N*-diethylacrylamide **4s** (106 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5s** was obtained after silica gel column chromatography (EtOAc:PE = 1:3) as a single diastereoisomer (*trans*:*cis* > 19:1).



5s

Data for **5s**: Light yellow soliid (121 mg, 47%). m.p.: 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.77 (td, *J* = 10.7, 4.1 Hz, 1H), 3.59 (s, 1H), 3.44 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.32 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.27 – 3.13 (m, 2H), 2.47 (td, *J* = 10.8, 10.4, 3.5 Hz, 1H), 2.13 (dt, *J* = 11.7, 3.7 Hz, 1H), 1.79 (tt, *J* = 11.3, 5.8 Hz, 3H), 1.73 – 1.64 (m, 1H), 1.42 (qt, *J* = 12.9, 3.2 Hz, 1H), 1.30 – 1.19 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 150.1, 126.5 (q, *J* = 4.0 Hz), 123.8, 118.6 (q, *J* = 32.3 Hz), 112.9, 54.4, 47.6, 42.0, 40.6, 33.9, 30.0, 25.3, 25.1, 15.2, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.94. HRMS (ESI, *m/z*) calcd for $C_{18}H_{26}F_3N_2O$ $[M+H]^+$: 343.1997, found: 343.1991.

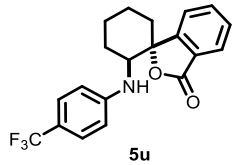
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), 3-methylenedihydrofuran-2(3H)-one **4t** (69 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5t** was obtained after silica gel column chromatography (EtOAc:PE = 1:5) as a single diastereoisomer (> 19:1 d.r.).



5t

Data for **5t**: Red oil (122 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.35 – 4.20 (m, 2H), 4.02 (d, *J* = 9.5 Hz, 1H), 3.42 (td, *J* = 10.0, 4.1 Hz, 1H), 2.60 (dt, *J* = 12.5, 9.1 Hz, 1H), 2.23 – 2.08 (m, 2H), 1.92 (ddd, *J* = 12.8, 6.6, 3.8 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.75 – 1.62 (m, 2H), 1.61 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 150.4, 126.9 (q, *J* = 4.0 Hz), 119.6 (q, *J* = 33.3 Hz), 112.4, 65.4, 55.3, 47.7, 34.6, 32.1, 28.7, 24.8, 22.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.12. HRMS (ESI, *m/z*) calcd for $C_{16}H_{19}F_3NO_2$ $[M+H]^+$: 314.1368, found: 314.1363.

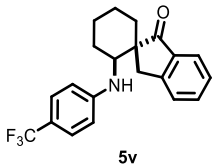
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), 3-methyleneisobenzofuran-1(3H)-one **4u** (110 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5u** was obtained after silica gel column chromatography (EtOAc:PE = 1:5) as a single diastereoisomer (> 19:1 d.r.).



5u

Data for **5u**: Light yellow solid (114 mg, 42%). m.p.: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (dt, *J* = 7.4, 3.6 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 2H), 3.83 (d, *J* = 8.6 Hz, 1H), 3.75 (s, 1H), 2.15 – 2.07 (m, 1H), 2.01 (ddd, *J* = 15.5, 9.0, 4.4 Hz, 2H), 1.92 (dq, *J* = 14.4, 2.9 Hz, 1H), 1.81 (tt, *J* = 9.6, 3.3 Hz, 2H), 1.77 – 1.66 (m, 1H), 1.58 (ddd, *J* = 17.0, 10.5, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 152.4, 149.4, 134.3, 129.5, 126.5 (q, *J* = 4.0 Hz), 126.3, 125.8, 123.5, 194.9, 119.5 (q, *J* = 32.3 Hz), 112.6, 88.8, 56.5, 37.2, 30.4, 25.1, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.18. HRMS (ESI, *m/z*) calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$: 362.1368, found: 362.1365.

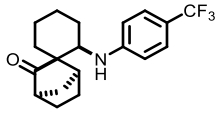
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), 2-methylene-2,3-dihydro-1H-inden-1-one **4v** (108 mg, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5v** was obtained after silica gel column chromatography (EtOAc:PE = 1:10) as a single diastereoisomer (> 19:1 d.r.).



5v

Data for **5v**: Yellow oil (108 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.59 (td, *J* = 7.4, 1.2 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, 2H), 6.54 (d, *J* = 8.5 Hz, 2H), 3.90 (dd, *J* = 12.0, 3.8 Hz, 1H), 3.48 (s, 1H), 3.19 (d, *J* = 17.6 Hz, 1H), 3.03 (d, *J* = 17.6 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.89 – 1.80 (m, 2H), 1.77 (dd, *J* = 8.1, 3.9 Hz, 1H), 1.58 – 1.48 (m, 2H), 1.47 – 1.39 (m, 1H), 1.36 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 152.8, 149.7, 136.9, 135.1, 127.8, 126.5 (q, *J* = 4.0 Hz), 124.5, 119.5 (q, *J* = 32.3 Hz), 113.2, 56.0, 55.2, 35.1, 34.0, 30.9, 25.2, 22.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.12. HRMS (ESI, *m/z*) calcd for $C_{21}H_{21}F_3NO$ $[M+H]^+$: 360.1575, found: 360.1570.

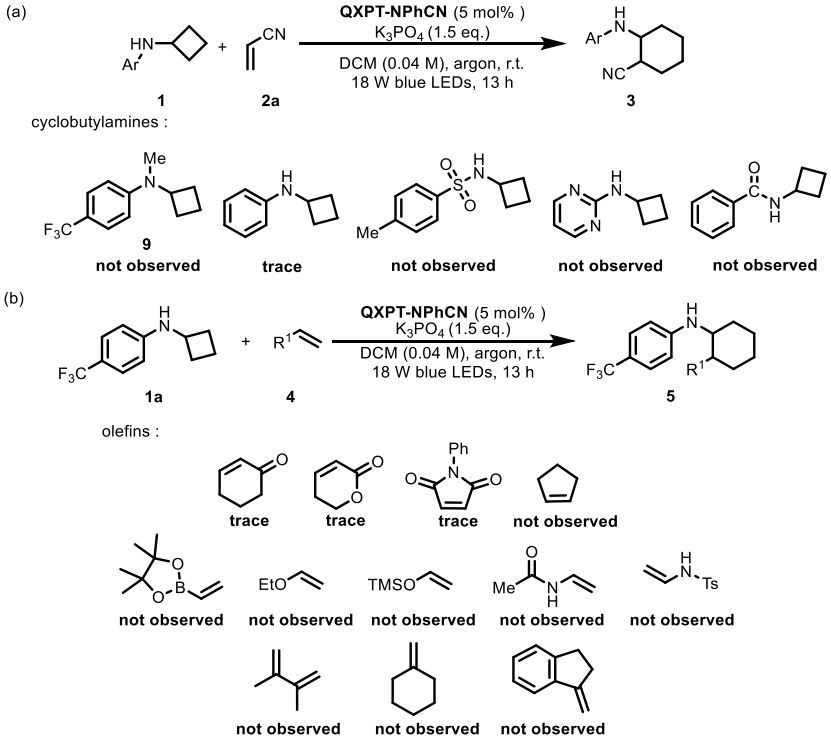
Following **GP8** with 4-*tert*-butyl-*N*-cyclobutylaniline **1a** (194 mg, 0.9 mmol), 3-methylenebicyclo [2.2.1] heptan-2-one **4w** (94 μL, 0.75 mmol), **QXPT-NPhCN** (13.2 mg, 0.0375 mmol), and dry DCM (18.75 mL), cycloadduct **5w** was obtained after silica gel column chromatography (EtOAc:PE = 1:20) as a single diastereoisomer (> 19:1 d.r.).



5w

Data for **5w**: Yellow solid (139 mg, 55%). m.p.: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.3 Hz, 2H), 5.15 (s, 1H), 3.55 (d, *J* = 3.7 Hz, 1H), 2.71 (d, *J* = 3.8 Hz, 1H), 2.53 (d, *J* = 5.2 Hz, 1H), 2.05 – 1.95 (m, 2H), 1.86 (dt, *J* = 14.9, 3.6 Hz, 1H), 1.77 (tt, *J* = 12.0, 3.3 Hz, 2H), 1.69 (dt, *J* = 12.5, 5.0 Hz, 1H), 1.64 – 1.56 (m, 4H), 1.44 (ddd, *J* = 14.1, 11.0, 4.4 Hz, 3H), 1.21 (dd, *J* = 12.7, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 150.5, 126.6 (q, *J* = 3.0 Hz), 123.8, 118.2 (q, *J* = 32.3 Hz), 112.2, 53.5, 51.8, 50.2, 42.2, 35.3, 26.6, 26.1, 25.4, 22.4, 21.8, 19.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.89. HRMS (ESI, *m/z*) calcd for $C_{19}H_{23}F_3NO$ $[M+H]^+$: 338.1732, found: 338.1728.

7. Limitations of substrates



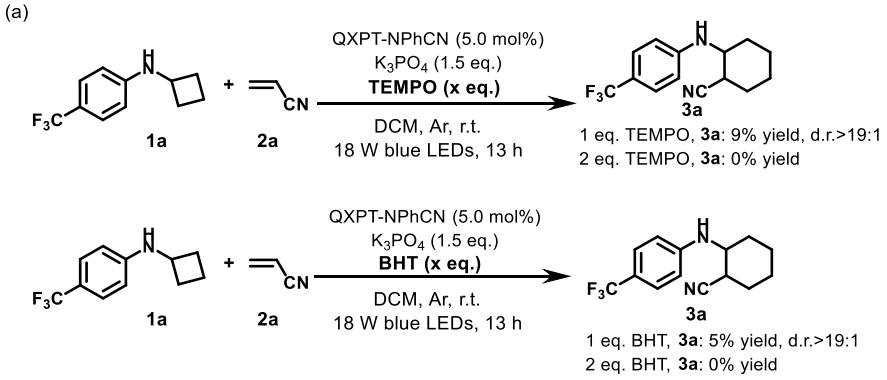
Scheme S1. Selected unsuccessful cyclobutylamine and olefin substrates.

The scheme S1 lists cyclobutylamine and olefin partners that have not been successfully tested or have low yields. For these substrates shown in Scheme S1, crude ^{1}H NMR analysis was performed after 13 h of illumination according to the 0.75 mmol ratio of **GP7** and **GP8**. The unconsumed starting materials were returned alone or degradation was observed in the crude reaction mixture (Scheme S1a). The reactivity of intracyclic olefins is poor. Olefin ketones, ene esters and ene amides can only obtain trace products. Intracyclic alkyl olefins, electron-rich group substituted olefins, conjugated diene and exocyclic alkyl olefins could not react (Scheme S1b).

8. Mechanistic Studies

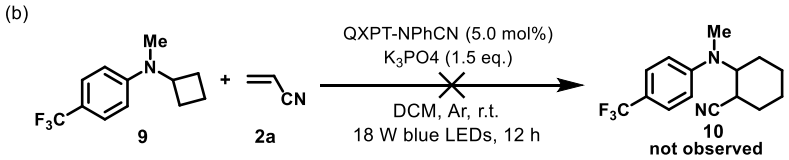
8.1 Radical Inhibition Experiment

In the reaction of **1a** and **2a** in the presence of **QXPT-NPhCN** (5.0 mol%), different equivalents of free radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine oxide) and antioxidant BHT (2,6-di-tert-butyl-4-methylphenol) were added, and the mixture was stirred for 13 hours under the irradiation of 18 W blue LED. When TEMPO is 1.0 eq., the **3a** is 9% yield and >19:1 d.r.. When TEMPO is 2.0 eq., the **3a** is 0% yield. When BHT was 2.0 eq., the **3a** is 5% yield and >19:1 d.r. . When BHT is 2.0 eq., the desired product **3a** was not observed (Scheme S2). These two experiments indicate that the reaction is carried out through a free radical pathway.



Scheme S2. Radical inhibition experiment.

Under standard reaction conditions, *N*-cyclobutyl-*N*-methyl-4-trifluoromethylaniline (**9**) did not react with **2a** (Scheme S3). This experiment shows that the N-H of trifluoromethylcyclobutanamine **1a** may be essential for the generation of carbon radicals through the ring opening of cyclobutane.



Scheme S3. Study on the reactivity of tertiary arylcyclobutylamine.

8.2 Emission Quenching Experiments

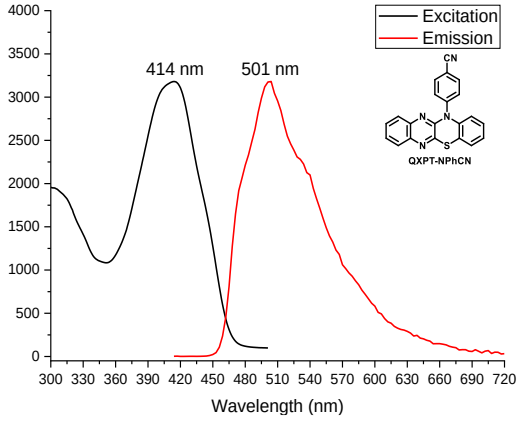


Figure S2. Excitation and emission spectra of **QXPT-NPhCN** in DMF.

Emission intensities were recorded on a spectrofluorometer. The **QXPT-NPhCN** solution was excited at 414 nm and the emission intensity at 501 nm was observed (Figure S2). A solution of **QXPT-NPhCN** (5.0×10^{-4} M) in DMF was added to the appropriate amount of quencher in 10.0 mL volumetric flask under argon. Transfer 3.0 mL of this solution to a quartz cell and collect the emission spectrum of the sample (Figure S3-S5).

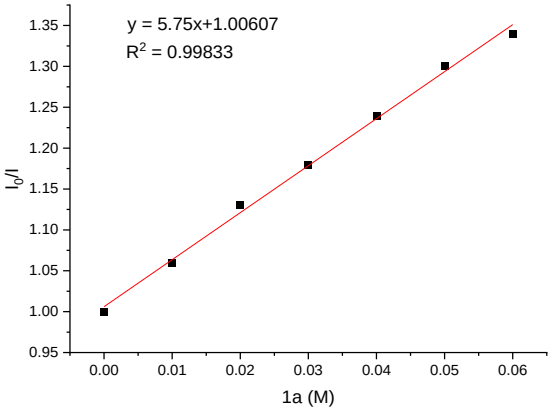


Figure S3. Stern–Volmer quenching experiment of **QXPT-NPhCN** and **1a**.

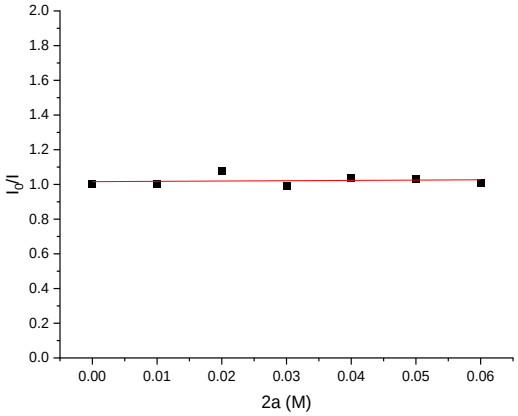


Figure S4. Stern–Volmer quenching experiment of **QXPT-NPhCN** and **2a.**

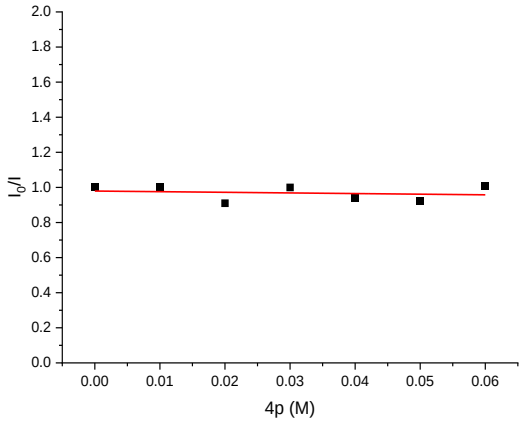


Figure S5. Stern–Volmer quenching experiment of **QXPT-NPhCN** and **4p**.

It can be seen from the fluorescence quenching test that the substrate 4-trifluoromethylphenylcyclobutanamine (**1a**) can significantly quench the photocatalyst **QXPT-NPhCN**, showing a clear linear relationship: y = 5.75x + 1.00607, R^2 = 0.99833. Different types of olefins, such as acrylonitrile (**2a**) and *N*-benzyl acrylamide (**4p**), could not quench **QXPT-NPhCN**.Therefore, it was proved that substrate **1a** preferentially reacted with the excited state of **QXPT-NPhCN** during the reaction (Figure S3-S5).

8.3 Cyclic Voltammetry Measurement

Cyclic voltammetry was performed on a Shanghai Chenhua T-660M electrochemical analyzer. CV measurements were performed with the three-electrode CHI660E potentiostation by using a glassy carbon working electrode, a platinum wire counter electrode, saturated KCl Ag/AgCl as a reference electrode. The voltammograms were taken in a dry MeCN solution ([*n*-Bu_4NBF_4] = 0.1 M, [substrate] = 1 mM in MeCN), each measurement was conducted at 0.1 V/s at room temperature under nitrogen atmosphere without stirring. The obtained potentials were calibrated to the saturated calomel electrode (SCE) scale with a ferrocene/ferrocenium ion couple.[10] The obtained potential is half of the sum of the potentials of the adjacent peaks and troughs of the cyclic voltammetry curve (half-wave potential).[11] The polishing material is deer skin, the Al_2O_3 powder (particle size 0.3 μm) is placed on the deer skin wetted by distilled water, the surface of the glassy carbon electrode and the platinum wire electrode is polished, and then washed with distilled water, followed by ultrasonic cleaning with acetone and ethanol for 10 min, and finally washed with distilled water.

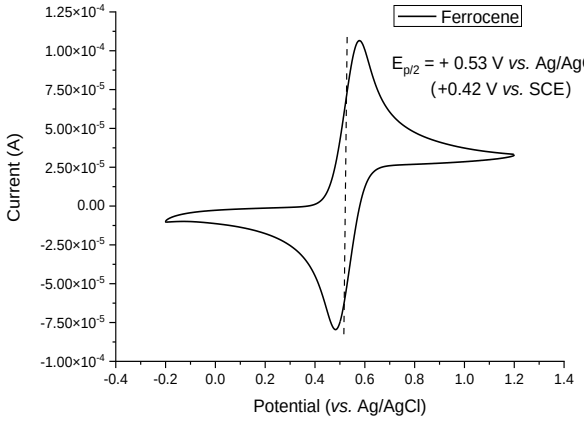


Figure S6. Cyclic voltammogram of Ferrocene in MeCN (IUPAC). CV conditions: Ferrocene (1 mM) in *n*-Bu_4NBF_4 (0.1 M in MeCN). *n*-Bu_4NBF_4 was used as the supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode, saturated KCl Ag/AgCl reference electrode. Starting point: (1.2 V, 3.32E-05 A). Initial scan direction: negative. Initial potential = 1.2 V, Scan rate = 0.1 V/s.

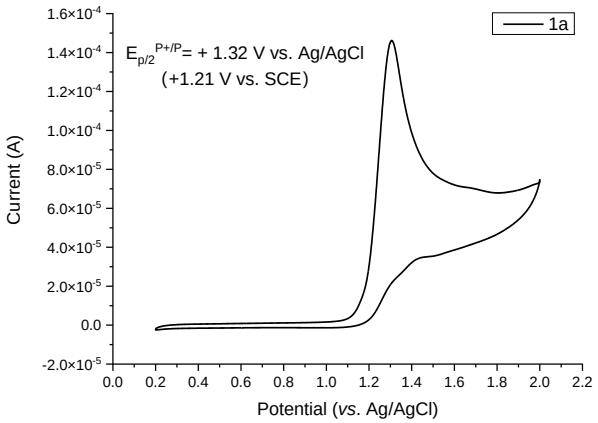


Figure S7. Cyclic voltammogram of **1a** in MeCN (IUPAC). CV conditions: **1a** (1 mM) in *n*-Bu_4NBF_4 (0.1 M in MeCN). *n*-Bu_4NBF_4 was used as the supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode, saturated KCl Ag/AgCl reference electrode. Starting point (P^+/P): (2.0 V, 7.49E-05 A), Initial scan direction: negative. Initial potential = 2.0 V, Scan rate = 0.1 V/s.

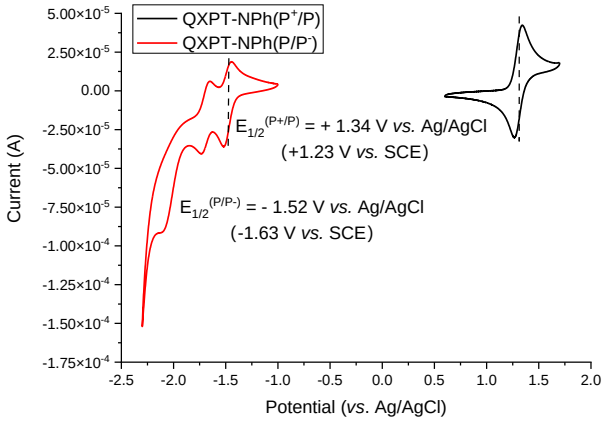


Figure S8. Cyclic voltammogram of **QXPT-NPhCN** in MeCN (IUPAC). CV conditions: **QXPT-NPhCN** (1 mM) in *n*-Bu_4NBF_4 (0.1 M in MeCN). *n*-Bu_4NBF_4 was used as the supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode, saturated KCl Ag/AgCl reference electrode. Starting point (P/P^-): (-1.0 V, 4.399E-06 A), Initial scan direction: negative. Starting point (P^+/P): (1.7 V,1.823E-05 A), Initial scan direction: negative. Initial potential (P/P^-) = -1.0 V, Scan rate = 0.1 V/s. Initial potential (P^+/P) = 1.7 V, Scan rate = 0.1 V/s.

The oxidation peak potential of **1a** was measured to be 1.21 V *vs.* SCE, which was more positive than the reduction potential of photoexcited **QXPT-NPhCN** ($E_{1/2}^{(P*/P-)}$ = + 0.85 V *vs.* SCE). Although thermodynamically unfavorable, such SET processes have been reported as long as there is an overlap between the oxidation (or reduction) peak potential of **1a** and the redox potential of the excited state of the photocatalyst.[12] In addition, the SET process is more likely to be completed if it is followed by an irreversible chemical reaction.[12]

Table S7. Redox potential and photophysical properties of common visible light photocatalysts

Photocatalyst	Emission λ_{max}(nm)[b]	E_{S_1} (V)[c]	$E_{1/2}^{(P*/P-)}$(V)[c,e,g]	$E_{1/2}^{(P/P-)}$(V)[d]	$E_{1/2}^{(P+/P*)}$(V)[c,f,g]	$E_{1/2}^{(P+/P)}$(V)[d]
QXPT-NPhCN	501	2.48	(+0.85)	-1.63	(**-1.25**)	+1.23
4CzIPN[13]	535	2.32	+1.35 (+1.11)	-1.21	-1.04 (-0.80)	+1.52
[Ir(dtbbpy)(ppy)$_2$]PF$_6$[14]	581	2.13	+0.66 (+0.62)	-1.51	-0.96 (-0.92)	+1.21
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$[14]	470	2.64	+1.21 (+1.21)	-1.37	-0.89 (-0.95)	+1.69
[Ru(bpz)$_3$](PF$_6$)$_2$[14]	591	2.10	+1.45 (+1.30)	-0.80	-0.26 (-0.24)	+1.86

[a]UV-vis.absorption spectra obtained in DMF; [b]Emission wavelength measured using fluorescence spectroscopy in DMF; [c]Singlet energy is estimated by the maximum wavelength emitted, E_{S_1}=1240/λ; [d]Cyclic voltammetry, Ar atmosphere, voltammetry obtained in dry MeCN solution

([*n*-Bu_4NBF_4] = 0.1 M, [photocatalyst] = 1 mM in MeCN, withKCl Ag/AgCl as the reference electrode); [e]Singlet energy (estimated from the maximum emission wavelength) and $E_{1/2}$ to calculate the singlet excited state reduction potential ($E^*_{1/2}{}^{P/P^-} = E_{1/2}{}^{P/P^-} + E_{S_1}$); [f]Calculate the singlet excited oxidation potential ($E^*_{1/2}{}^{P+/P} = E_{1/2}{}^{P+/P} - E_{S_1}$) using singlet energy (estimated from the maximum emission wavelength) and $E_{1/2}$. [g]In parentheses is the estimated value.

As can be seen from Table S7, compared with other common visible light photocatalysts, **QXPT-NPhCN** has the lowest oxidation potential in the excited state ($E_{1/2}{}^{(P+/P^*)}$ = -1.25 V *vs.* SCE), which means that in the excited state, the free radical anion **QXPT-NPhCN**$^{\cdot-}$ is very easy to lose electrons back to the ground state. Therefore, this may be an important reason why **QXPT-NPhCN** is superior to other photocatalysts in this reaction system.

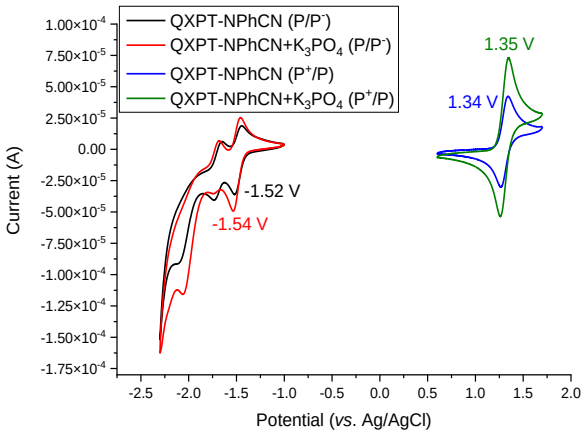
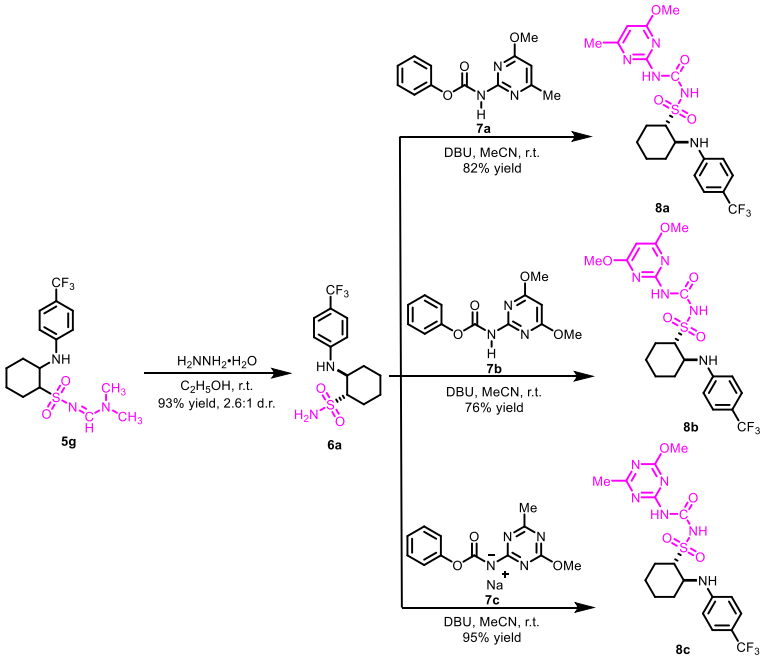


Figure S9. Cyclic voltammetric curves of mixture of **QXPT-NPhCN** and **K_3PO_4** (1:1.5, in MeCN) (IUPAC).

In the cyclic voltammogram of the mixture of photocatalyst **QXPT-NPhCN** and K_3PO_4 (1:1.5), no new local maximum was observed except for the peak of **QXPT-NPhCN**, and the addition of K_3PO_4 had no significant effect on the potential of the original oxidation peak and reduction peak of **QXPT-NPhCN**. This experiment shows that there is no interaction between **QXPT-NPhCN** and K_3PO_4 in the mixture (Figure S9).

Note: Due to the particularly poor solubility of potassium phosphate, we employed ultrasonic vibration and agitation to promote its micro-dissolution.

9. Synthetic applications



Scheme S4. Product derivatizations.

Compound **5g** (500 mg, 1.33 mmol, 1.0 equiv) was placed in 13.3 mL ethanol, and *N, N*-dimethylformamide dimethyl acetal (DMF-DMA) (485 μL, 7.98 mmol, 6.0 equiv) was added under stirring at room temperature. When **5g** completely disappeared, the reaction solution was concentrated under reduced pressure, slowly added water to quench the reaction, and extracted with DCM (20 mL × 3).

The organic phase was collected, washed with saturated salt water, and dried with anhydrous Na_2SO_4. The organic solution was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (PE : EtOAc = 1 : 1) to obtain a pair of diastereomers (93%, 2.6 : 1 dr), and the main product was **6a** (288 mg, 67% yield).

Compound **6a** (100 mg, 0.31 mmol, 1.0 equiv) was placed in 10 mL MeCN, and then compound **7a**[15] (122 mg, 0.47 mmol, 1.5 equiv) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) (72 μL, 0.47 mmol, 1.5 equiv) were added, protected by argon, stirred at room temperature, and monitored by TLC. After 10 h of reaction, the organic solution was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (PE: EtOAc = 1:100) to obtain white solid compound **8a** (124 mg, 82 % yield).

Compound **6a** (100 mg, 0.31 mmol, 1.0 equiv) was placed in 10 mL MeCN, and then compound **7b**[15] (129 mg, 0.47 mmol, 1.5 equiv) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) (72 μL, 0.47 mmol, 1.5 equiv) were added. The reaction was monitored by TLC. After 10 h of reaction, the organic solution was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (PE: EtOAc = 1:100) to obtain white solid compound **8b** (119 mg, 76 % yield).

Compound **6a** (100 mg, 0.31 mmol, 1.0 equiv) was placed in 10 mL MeCN, followed by the addition of sodium salt **7c**[15] (133mg, 0.47 mmol, 1.5 equiv) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) (72 μL, 0.47 mmol, 1.5 equiv) were added. The reaction was monitored by TLC. After 10 h of reaction, the organic solution was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (PE: EtOAc = 1:100) to obtain light yellow solid compound **8c** (144 mg, 95 % yield).

Data for **6a**: Reddish-brown oil (288 mg, 67 % yield). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 6.77 (s, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.27 (d, *J* = 8.2 Hz, 1H), 3.83 (dq, *J* = 8.6, 5.6, 4.1 Hz, 1H), 2.99 (td, *J* = 7.4, 4.6 Hz, 1H), 2.07 (ddt, *J* = 18.1, 13.7, 5.6 Hz, 2H), 1.76 (m, 2H), 1.71 – 1.62 (m, 1H), 1.45 – 1.36 (m, 2H), 1.34 – 1.26 (m, 1H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 150.3, 126.2 (q, *J* = 3.0 Hz), 124.0, 115.6 (q, *J* = 31.3 Hz), 112.0, 63.0, 49.4, 29.6, 24.6, 22.6, 22.0. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ -58.98. HRMS (ESI, *m/z*) calcd for $C_{13}H_{18}F_3N_2O_2S$ $[M+H]^+$: 323.1041, found: 323.1038.

Data for **8a**: White solid (124 mg, 82 % yield), m.p.: 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 1H), 8.00 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.45 (d, *J* = 8.3 Hz, 2H), 6.03 (s, 1H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.85 (s, 1H), 3.83 – 3.76 (m, 1H), 3.71 (s, 3H), 2.44 (d, *J* = 13.4 Hz, 1H), 2.12 (d, *J* = 20.5 Hz, 1H), 2.04 (s, 3H), 1.88 (d, *J* = 10.6 Hz, 1H), 1.73 (d, *J* = 9.5 Hz, 2H), 1.32 (d, *J* = 14.7 Hz, 1H), 1.29 – 1.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 151.0, 149.2, 126.4 (q, *J* = 4.0 Hz), 126.1, 123.4, 118.9 (q, *J* = 32.3 Hz), 112.0, 111.8, 101.8, 64.3, 54.2, 52.0, 34.1, 25.6, 24.6, 24.6, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.21. HRMS (ESI, *m/z*) calcd for $C_{20}H_{25}F_3N_5O_4S$ $[M+H]^+$: 488.1579, found: 488.1574.

Data for **8b**: White solid (119 mg, 76 % yield), m.p.: 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (d, *J* = 5.2 Hz, 1H), 7.61 (s, 1H), 7.29 – 7.22 (m, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 6.96 – 6.83 (m, 1H), 6.54 (dd, *J* = 16.0, 8.3 Hz, 2H), 5.61 (s, 1H), 4.09 (d, *J* = 9.5 Hz, 1H), 3.95 – 3.84 (m, 1H), 3.83 – 3.58 (m, 6H), 2.55 – 2.47 (m, 1H), 2.15 (d, *J* = 13.7 Hz, 1H), 1.95 (d, *J* = 10.8 Hz, 1H), 1.81 (m, 2H), 1.58 (d, *J* = 8.3 Hz, 1H), 1.35 (dd, *J* = 23.4, 12.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 150.5, 148.9, 141.6, 129.8, 126.6 (q, *J* = 4.0 Hz), 120.7, 119.4 (q, *J* = 31.3 Hz), 115.5, 111.8, 85.2, 64.5, 54.6, 51.9, 48.7, 34.2, 25.7, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.26. HRMS (ESI, *m/z*) calcd for $C_{20}H_{24}F_3N_5NaO_5S$ $[M+Na]^+$: 526.1348, found: 526.1342.

Data for **8c**: Light yellow solid (144 mg, 95 % yield), m.p.: 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.36 (s, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.13 (dd, *J* = 8.1, 5.5 Hz, 1H), 3.92 (s, 3H), 3.86 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.78 (td, *J* = 11.3, 10.5, 3.8 Hz, 1H), 2.50 (dd, *J* = 13.6, 3.7 Hz, 1H), 2.28 (s, 3H), 2.17 – 2.10 (m, 1H), 2.00 – 1.93 (m, 1H), 1.89 – 1.78 (m, 2H), 1.48 – 1.38 (m, 1H), 1.38 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 150.2, 149.2, 126.6 (q, *J* = 4.0 Hz), 126.0, 123.3, 119.3 (q, *J* = 33.3 Hz), 112.1, 64.5, 55.6, 52.2, 34.3, 25.4, 25.1, 24.6, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.35. HRMS (ESI, *m/z*) calcd for $C_{19}H_{24}F_3N_6O_4S$ $[M+H]^+$: 489.1532, found: 489.1530.

10. X-ray Crystallographic Details

10.1 Compound 3f

The preparation of crystal **3f**: A light yellow sheet-shaped crystal of **3f** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **3f** in a 25 mL round bottom flask with the solvent of dichlorometan and *n*-hexane（V:V = 3:1） at room temperature. The X-ray intensity data was measured on a Bruker D8 Venture single crystal diffractometer (Mo). The details of the structure and crystal data details of **3f** are given in Figure S10 and Table S8.

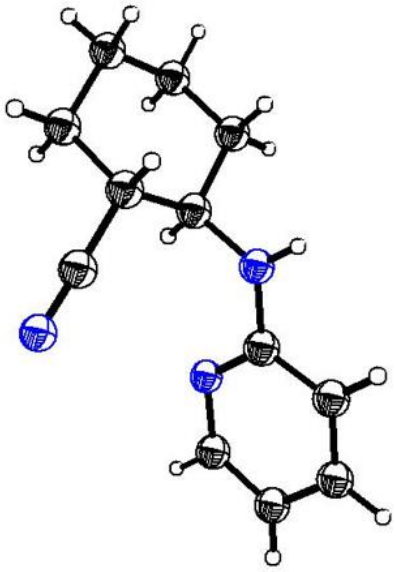


Figure S10. The Crystal parameters of **3f** wherein thermal ellipsoid is drawn at 50% probability (**CCDC No. 2236343**).

Table S8. Crystal data and structure refinement for **3f**

Identification code	**3f**
Empirical formula	$C_{12}H_{15}N_3$
Formula weight	201.27
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.2123(4)
b/Å	8.7897(3)
c/Å	30.3416(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2190.17(16)
Z	8
ρcalcg/cm^3	1.221
μ/mm^{-1}	0.075
F (000)	864.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.37 to 54.994
Index ranges	-10 ≤ h ≤ 9, -11 ≤ k ≤ 11, -33 ≤ l ≤ 39
Reflections collected	18586
Independent reflections	2511 [R_{int} = 0.0629, R_{sigma} = 0.0390]
Data/restraints/parameters	2511/0/136

Goodness-of-fit on F^2	1.154
Final R indexes [I>=2σ (I)]	R_1 = 0.0684, wR_2 = 0.1396
Final R indexes [all data]	R_1 = 0.0975, wR_2 = 0.1531
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.19

10.2 Compound 5p

The preparation of crystal **5p**: A light yellow sheet-shaped crystal of **5p** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **5p** in a 25 mL round bottom flask with the solvent of dichlorometan and *n*-hexane（V:V = 4:1） at room temperature. The X-ray intensity data was measured on a Bruker D8 Venture single crystal diffractometer (Mo). The details of the structure and crystal data details of **5p** are given in Figure S11 and Table S9.

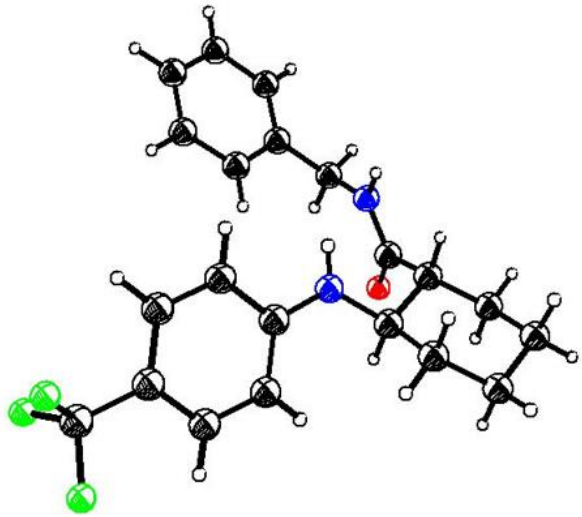


Figure S11. The Crystal parameters of **5p** wherein thermal ellipsoid is drawn at 50% probability (**CCDC No. 2236344**).

Table S9. Crystal data and structure refinement for **5p**

Identification code	**5p**
Empirical formula	$C_{21}H_{23}F_3N_2O$
Formula weight	376.41
Temperature/K	192.90
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3145(15)
b/Å	4.9401(6)
c/Å	33.363(4)
α/°	90
β/°	92.022(4)
γ/°	90
Volume/$Å^3$	1863.6(4)
Z	4
ρcalcg/cm^3	1.342
μ/mm^{-1}	0.103

F (000)	792.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 55.358
Index ranges	-8 ≤ h ≤ 14, -6 ≤ k ≤ 6, -43 ≤ l ≤ 43
Reflections collected	12894
Independent reflections	4357 [R_{int} = 0.0651, R_{sigma} = 0.0768]
Data/restraints/parameters	4357/0/244
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1408
Final R indexes [all data]	R_1 = 0.1407, wR_2 = 0.1758
Largest diff. peak/hole / e Å^{-3}	0.25/-0.33

10.3 Compound 5w

The preparation of crystal **5w**: A light yellow sheet-shaped crystal of **5w** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **5w** in a 25 mL round bottom flask with the solvent of dichlorometan and *n*-hexane（V:V = 4:1）at room temperature. The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer (Mo). The details of the structure and crystal data details of **5w** are given in Figure S12 and Table S10.

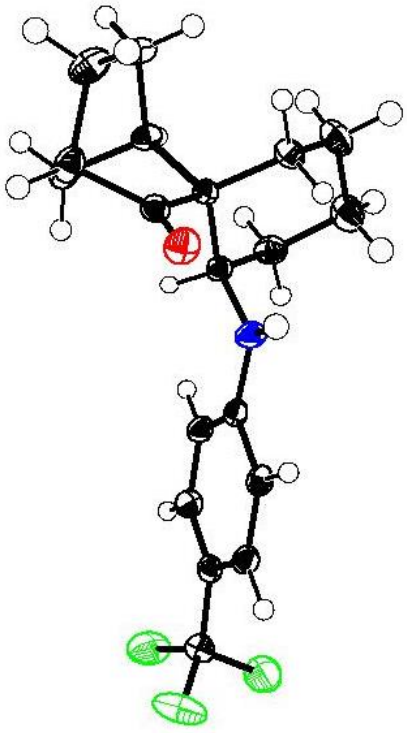


Figure S4. The Crystal parameters of **5w** wherein thermal ellipsoid is drawn at 50% probability (**CCDC No. 2234700**).

Table S10. Crystal data and structure refinement for **5w**

Identification code	**5w**
Empirical formula	$C_{19}H_{22}F_3NO$

Formula weight	337.37
Temperature/K	113.15
Crystal system	tetragonal
Space group	I-4
a/Å	13.5660(3)
b/Å	13.5660(3)
c/Å	18.1175(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3334.28(18)
Z	8
ρcalcg/cm^3	1.344
μ/mm^{-1}	0.105
F (000)	1424.0
Crystal size/mm^3	0.48 × 0.26 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.75 to 57.382
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -23 ≤ l ≤ 24
Reflections collected	21324
Independent reflections	4313 [R_{int} = 0.0485, R_{sigma} = 0.0333]
Data/restraints/parameters	4313/0/222
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0859
Largest diff. peak/hole / e Å^{-3}	0.21/-0.15
Flack parameter	0.2(3)

10.4 Compound 8a

The preparation of crystal **8a**: A light yellow sheet-shaped crystal of **8a** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **8a** in a 25 mL round bottom flask with the solvent of ethyl acetate at room temperature. The X-ray intensity data was measured on a Bruker D8 Venture single crystal diffractometer (Mo). The details of the structure and crystal data details of **8a** are given in Figure S13 and Table S11.

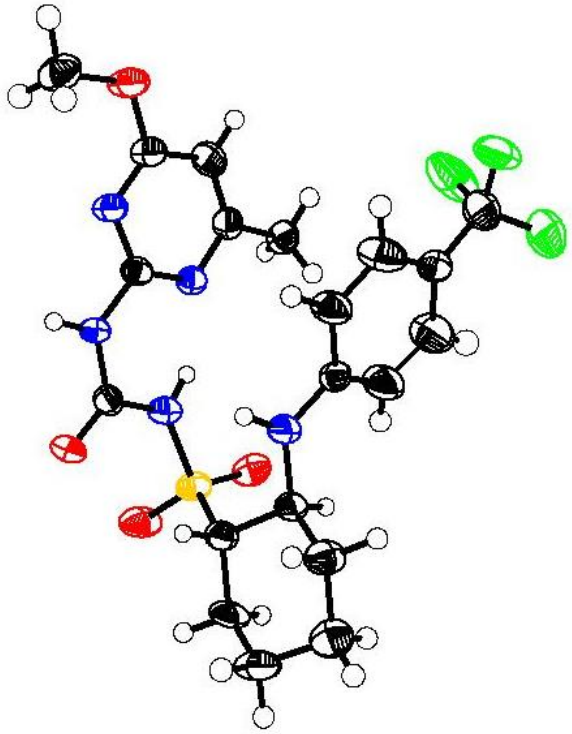


Figure S5. The Crystal parameters of **8a** wherein thermal ellipsoid is drawn at 50% probability (**CCDC No. 2236522**).

Table S11. Crystal data and structure refinement for **8a**

Identification code	**8a**
Empirical formula	$C_{20}H_{24}F_3N_5O_4S$
Formula weight	487.1501
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	11.1319(6)
b/Å	12.1324(6)
c/Å	12..4463(2)
α/°	68.619(2)
β/°	81.912(2)
γ/°	65.651(2)
Volume/Å^3	1425.95(13)
Z	2
ρcalcg/cm^3	1.341
μ/mm^{-1}	0.179
F (000)	604.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.514 to 55.04

Index ranges	$-14 \le h \le 11$, $-15 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	13282
Independent reflections	6477 [R_{int} = 0.0531, R_{sigma} = 0.0817]
Data/restraints/parameters	6477/0/356
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1884
Final R indexes [all data]	R_1 = 0.1261, wR_2 = 0.2266
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.35

11. References

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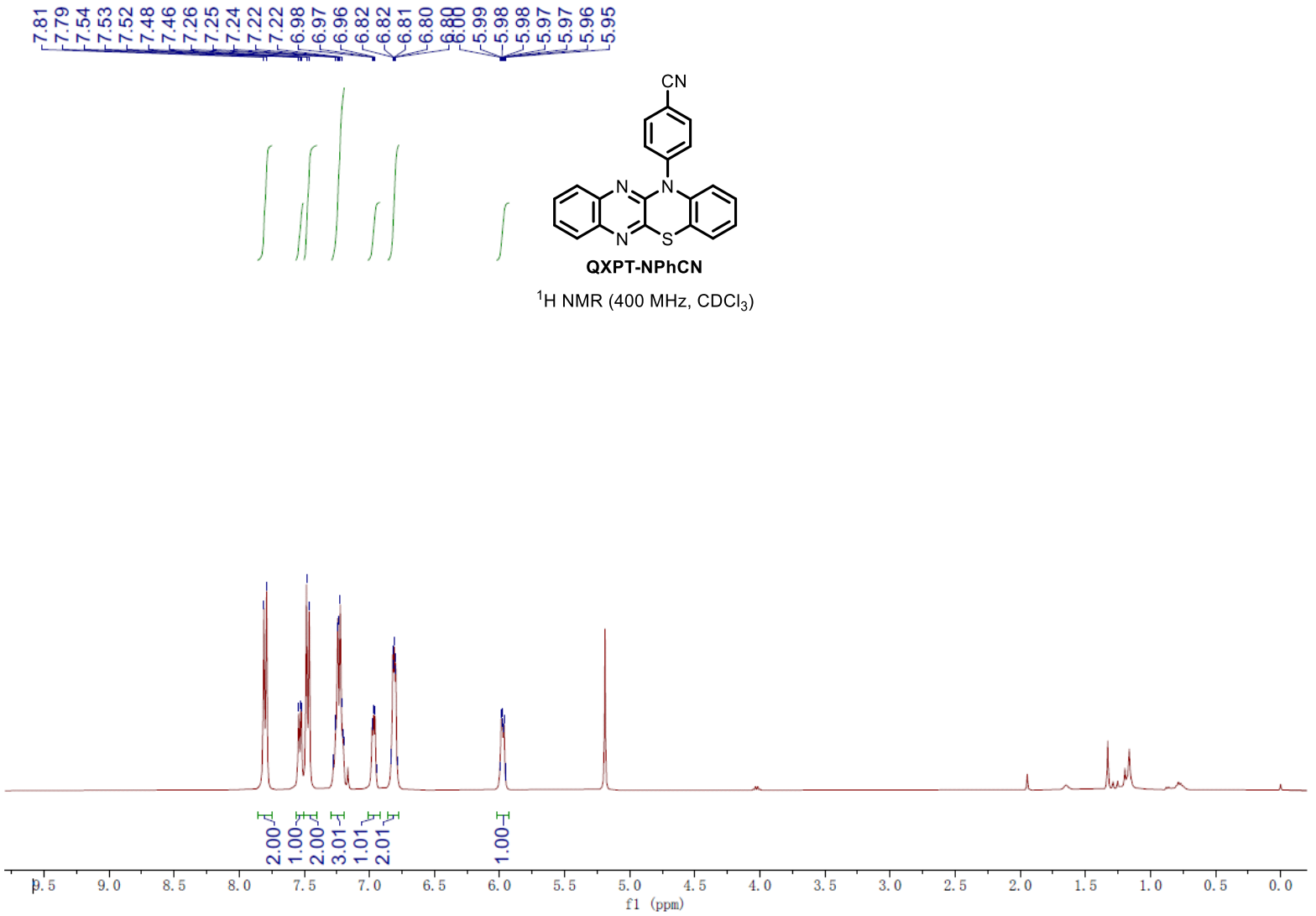
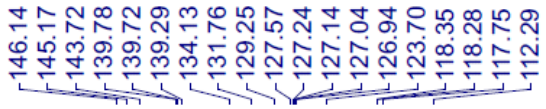
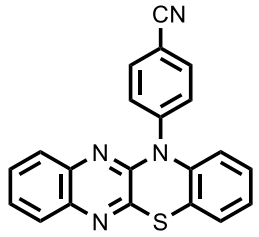
12. NMR Spectra of New Compounds

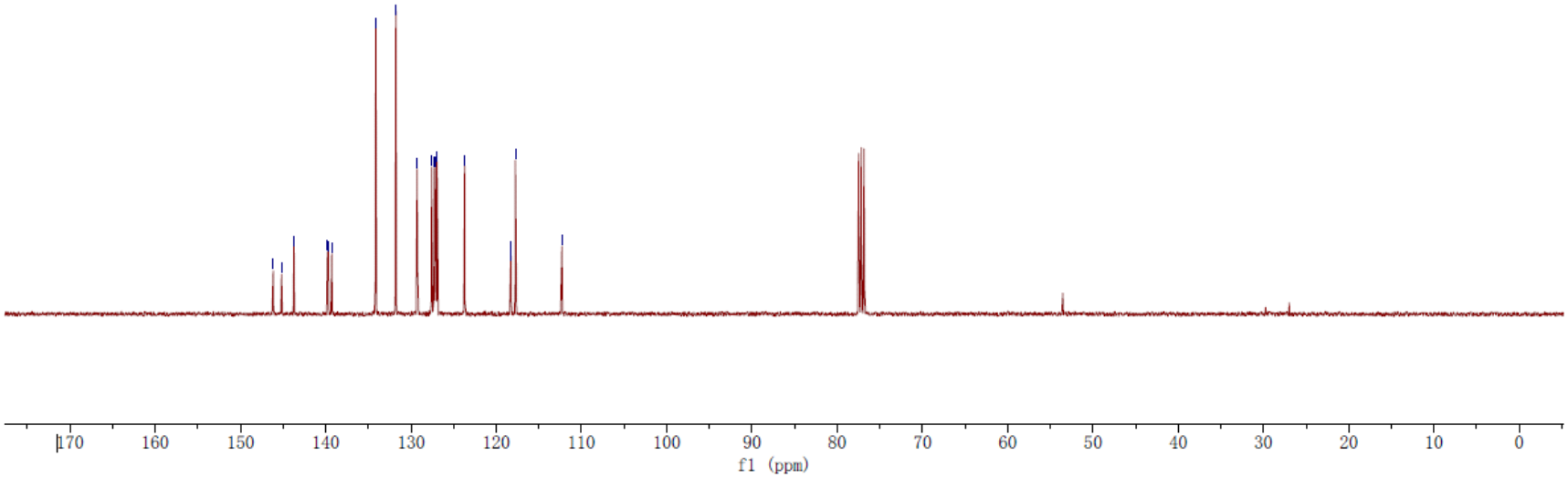


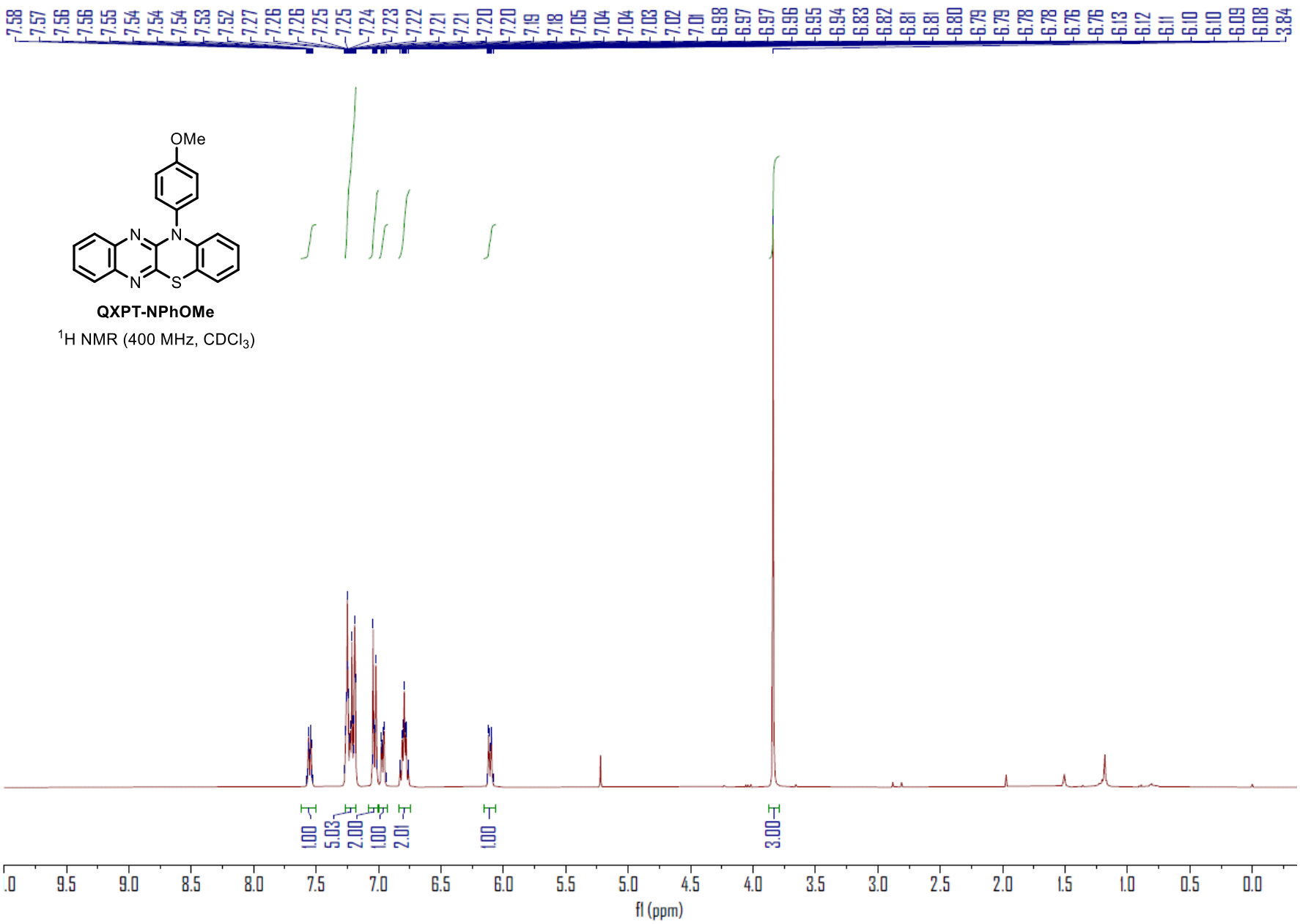


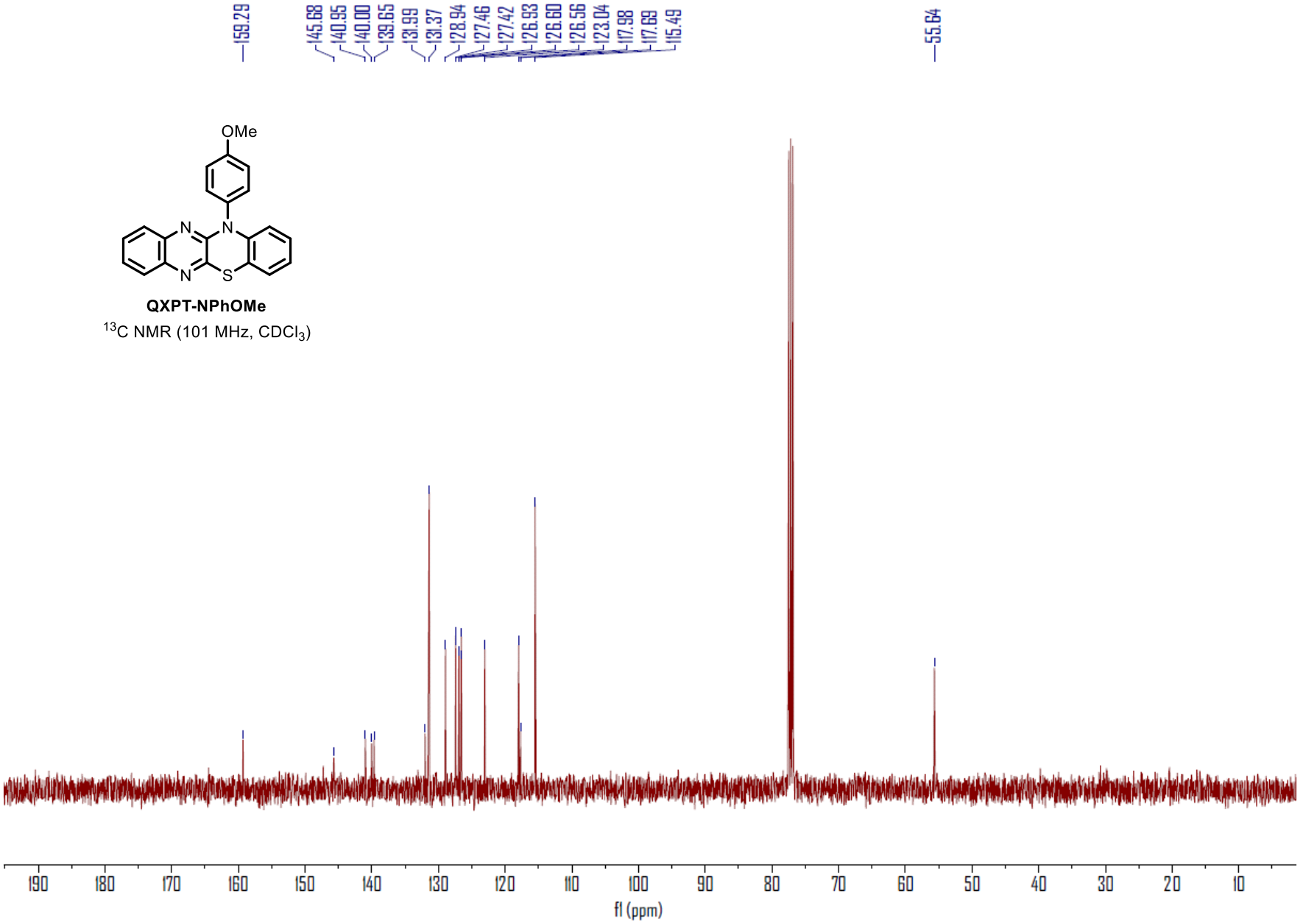


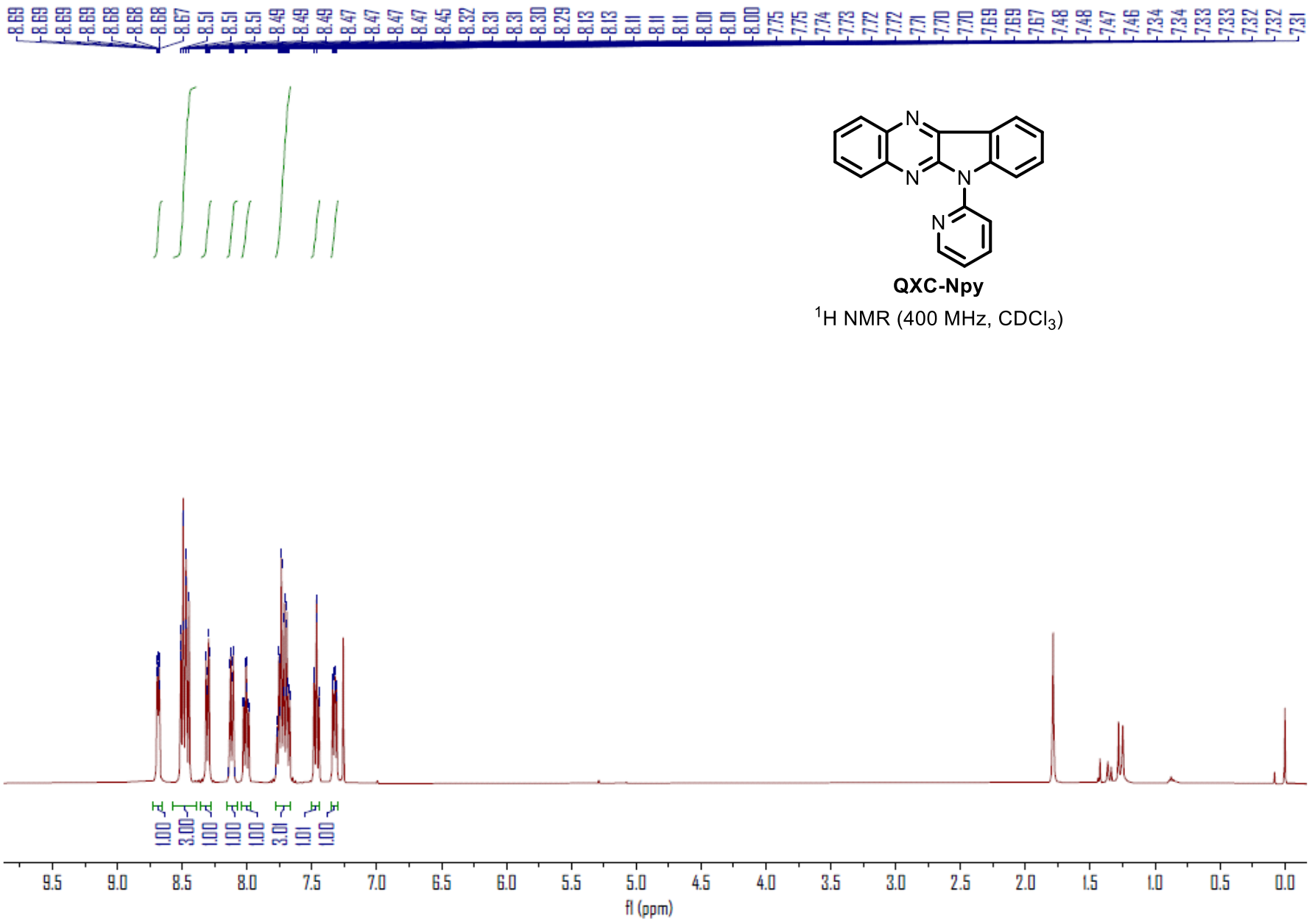
QXPT-NPhCN

^{13}C NMR (101 MHz, $CDCl_3$)



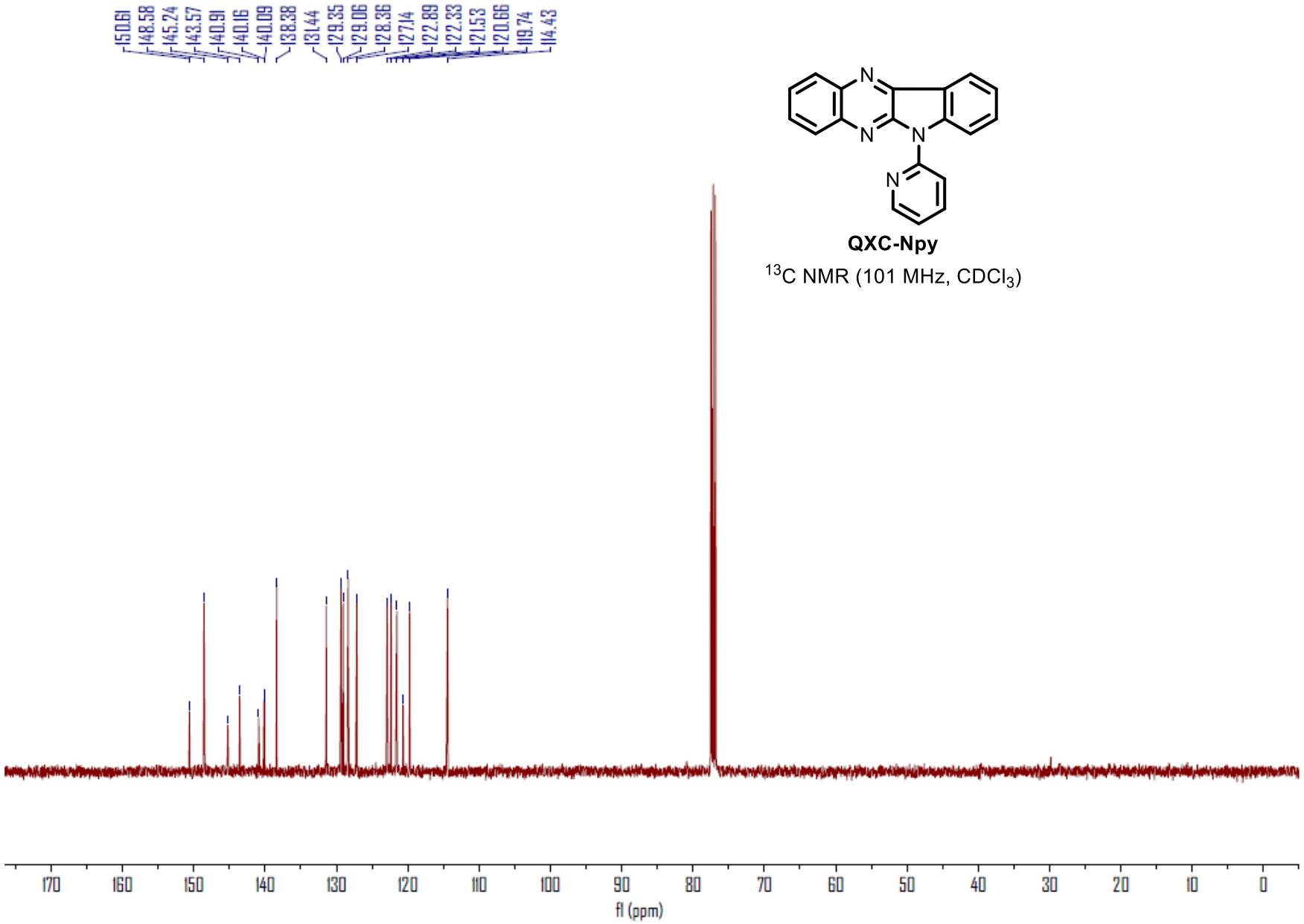

OMe
N
N
N
S
QXPT-NPhOMe
1H NMR (400 MHz, CDCl3)
7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.54 7.53 7.52 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.05 7.04 7.04 7.03 7.02 7.01 6.98 6.97 6.97 6.96 6.95 6.94 6.83 6.82 6.81 6.81 6.80 6.79 6.79 6.78 6.78 6.76 6.76 6.13 6.12 6.11 6.10 6.10 6.09 6.08 3.84
1.00
5.03
2.00
1.00
2.01
1.00
3.00
f1 (ppm)

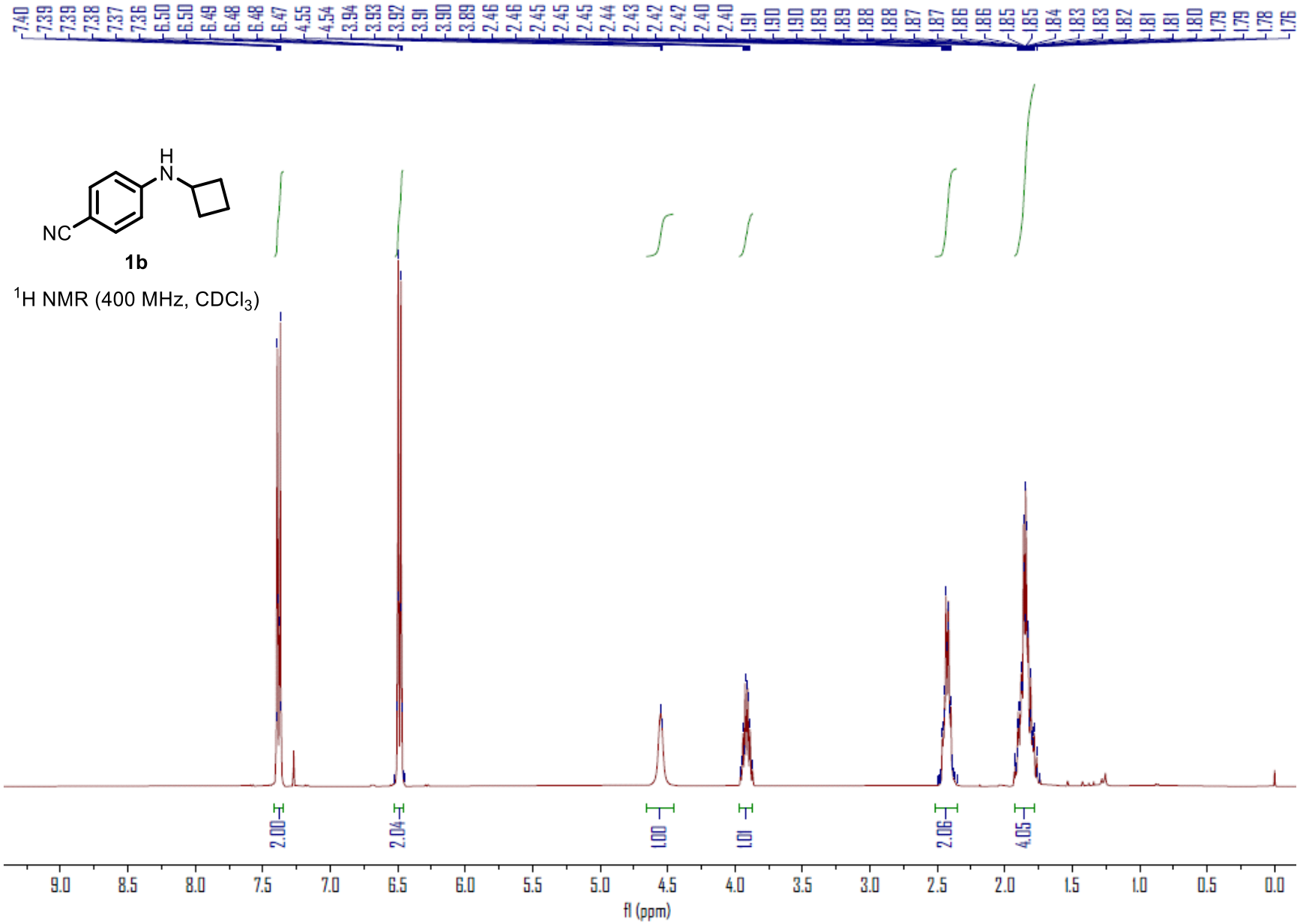

159.29
145.68
140.95
140.00
139.65
131.99
131.37
128.94
127.46
127.42
126.93
126.60
126.56
123.04
117.98
117.69
115.49
55.64
OMe
N
N
N
S
QXPT-NPhOMe
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

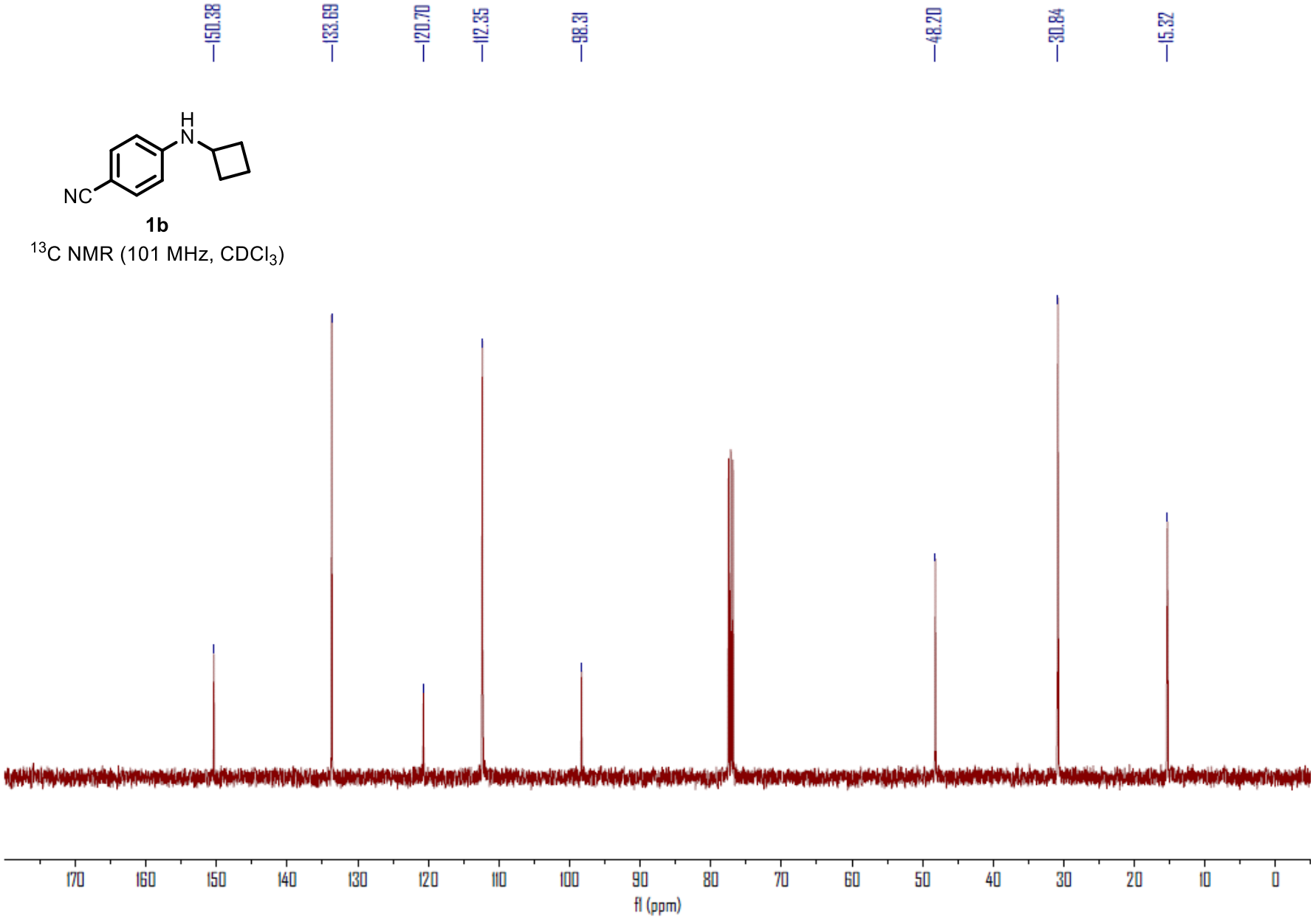


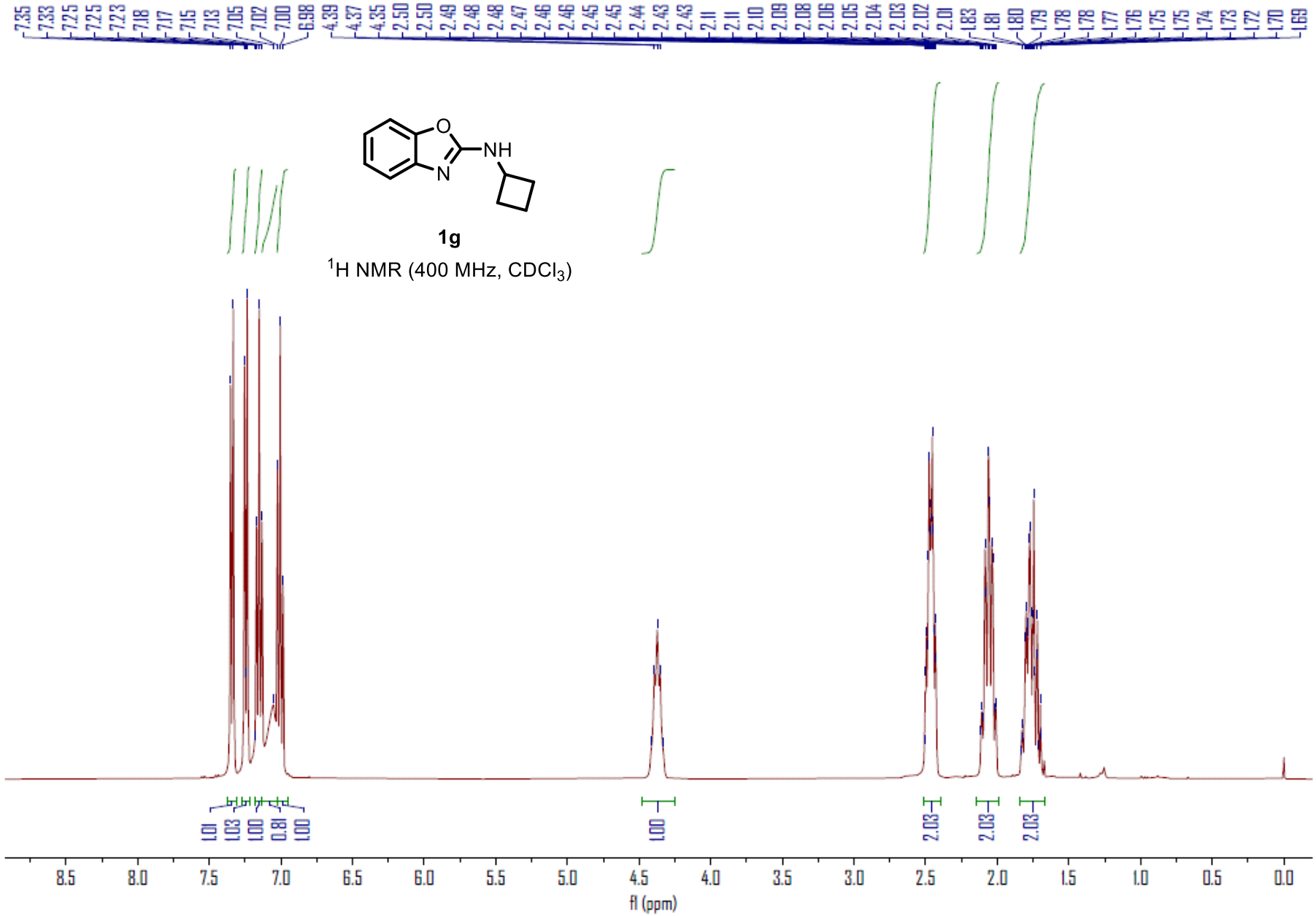
QXC-Npy

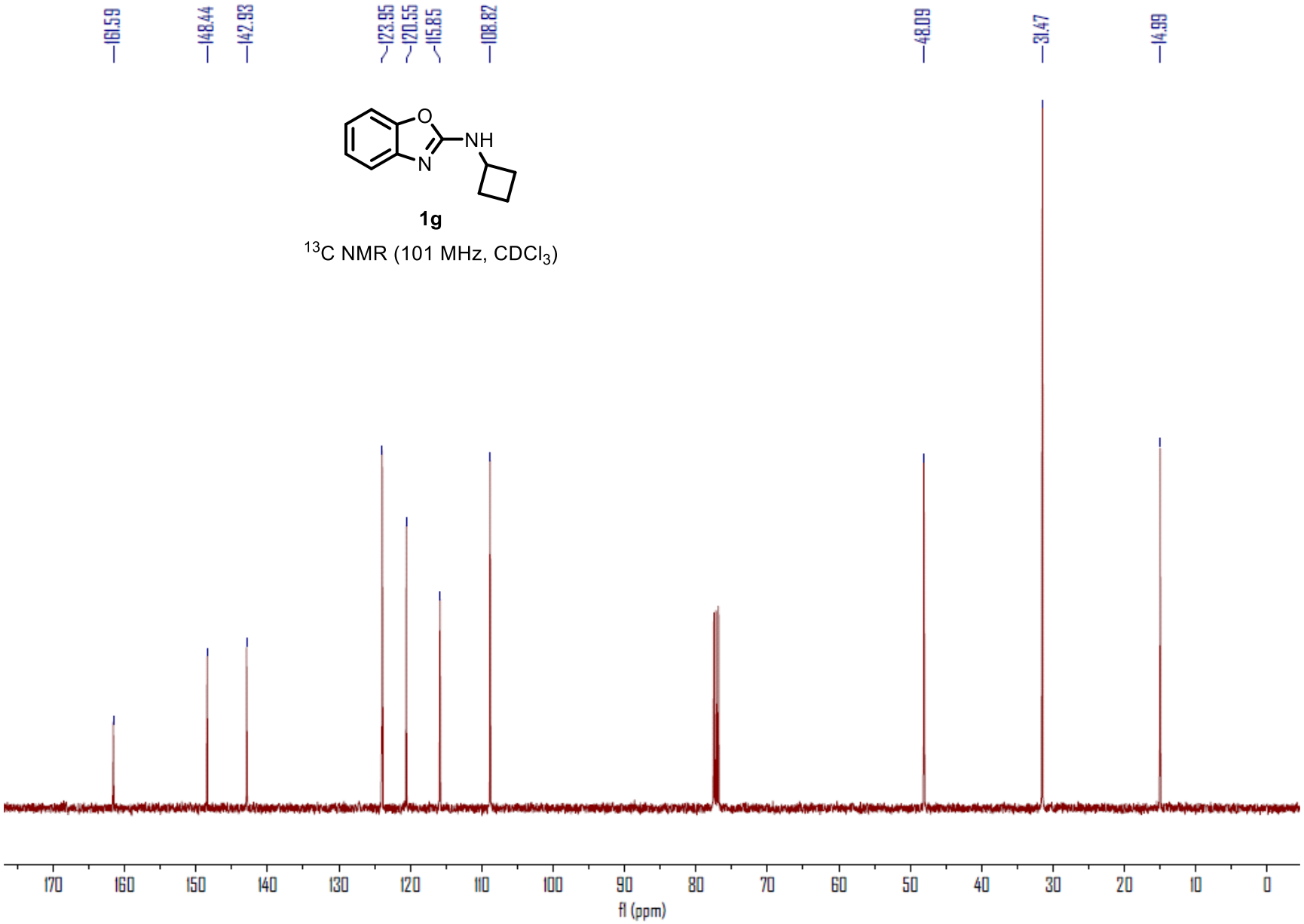
^{1}H NMR (400 MHz, $CDCl_3$)


150.61
148.58
145.24
143.57
140.91
140.16
140.09
138.38
131.44
129.35
129.06
128.36
127.14
122.89
122.33
121.53
120.66
119.74
114.43
N
N
N
N
QXC-Npy
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.40 7.39 7.39 7.38 7.37 7.36 6.50 6.50 6.49 6.48 6.48 6.47 4.55 4.54 3.94 3.93 3.92 3.91 3.90 3.89 2.46 2.46 2.45 2.45 2.45 2.44 2.43 2.42 2.42 2.40 2.40 1.91 1.90 1.90 1.89 1.89 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.81 1.81 1.80 1.79 1.79 1.78 1.76
NC
H
N
1b
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
2.04
1.00
1.01
2.06
4.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

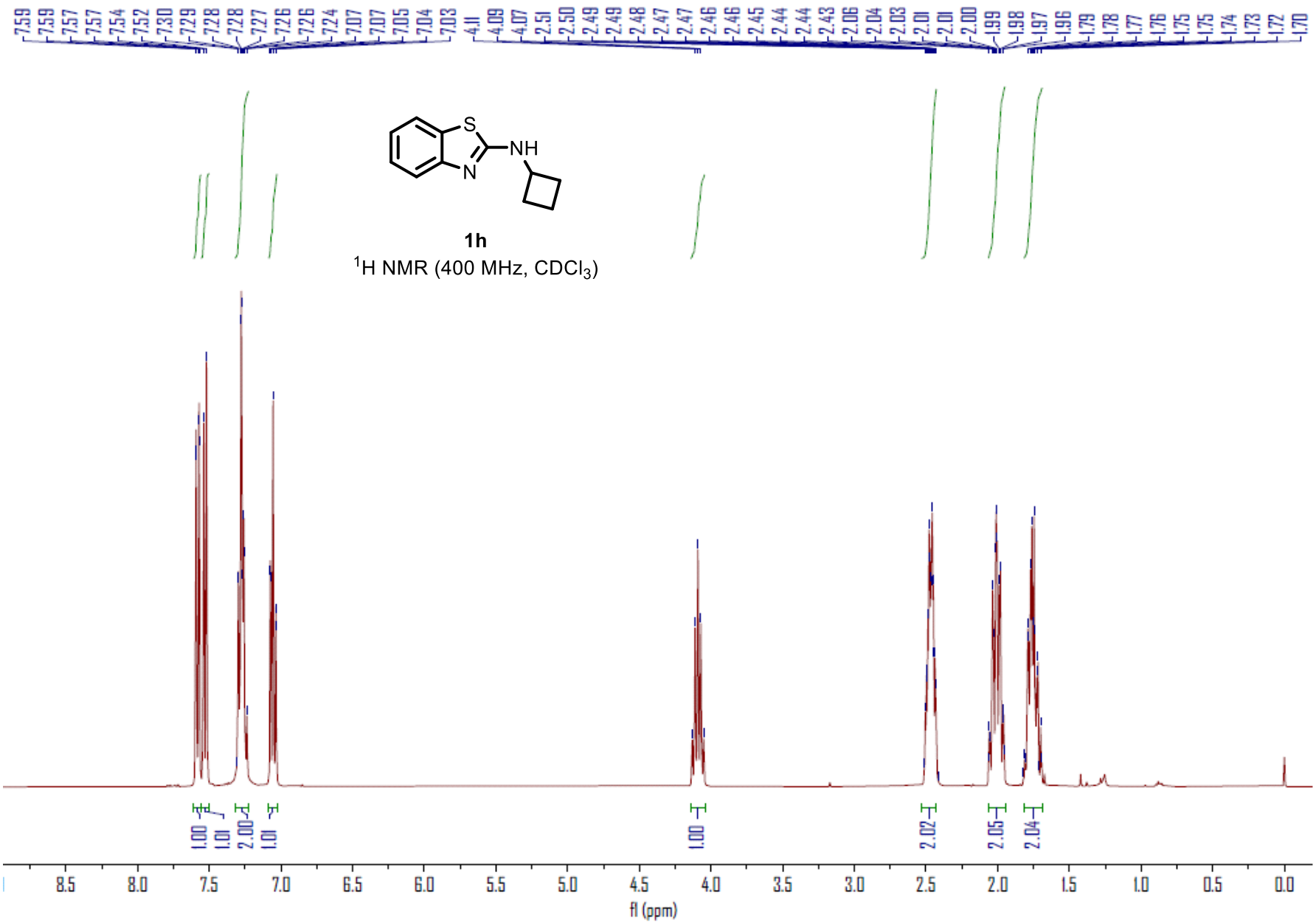

150.38
133.69
120.70
112.35
98.31
48.20
30.84
15.32
H
N
NC
1b
^{13}C NMR (101 MHz, $CDCl_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

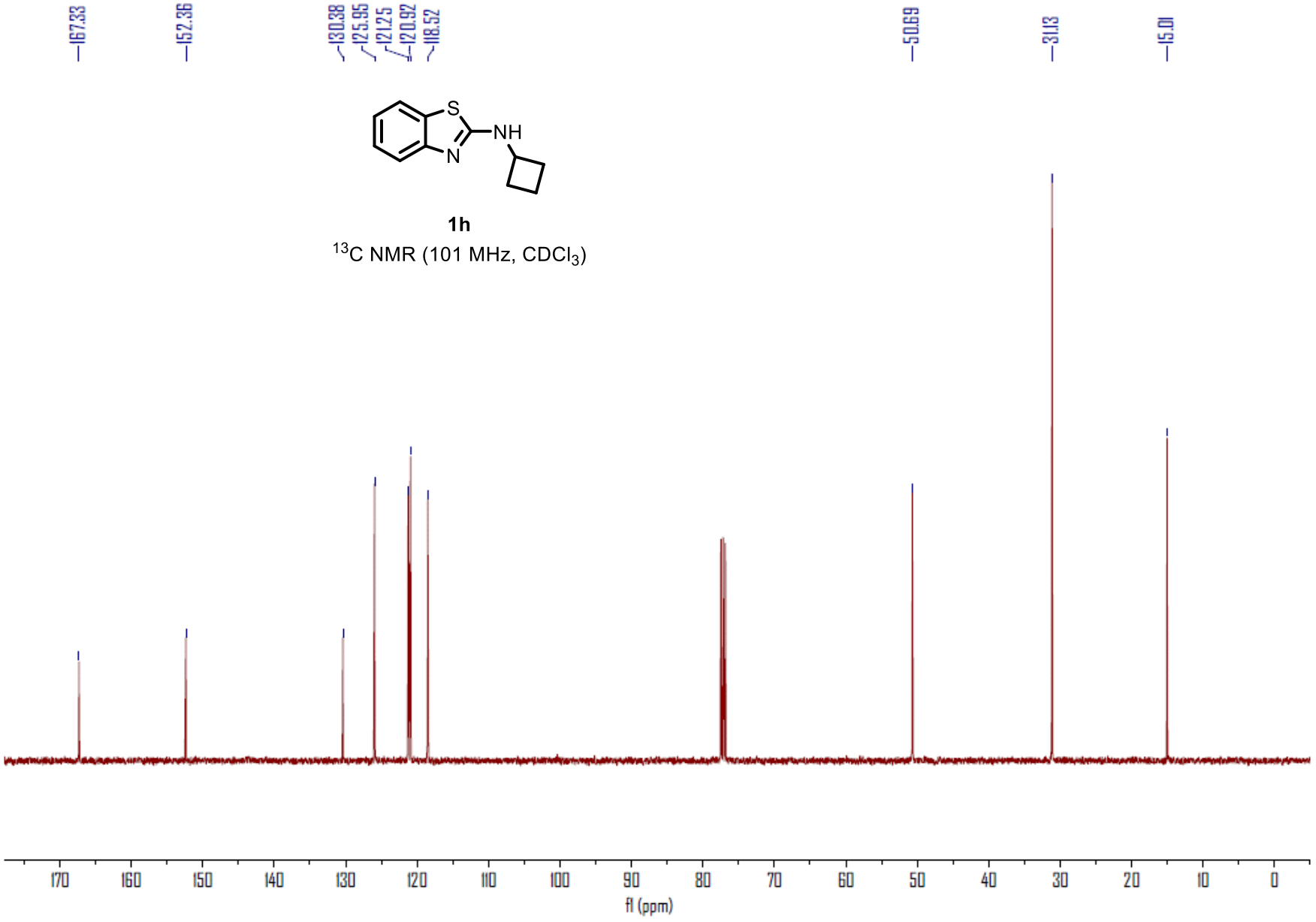

7.35 7.33 7.25 7.25 7.23 7.18 7.17 7.15 7.13 7.05 7.02 7.00 6.98
4.39 4.37 4.35 2.50 2.50 2.49 2.48 2.48 2.47 2.46 2.46 2.45 2.45 2.44 2.43 2.43 2.11 2.11 2.10 2.09 2.08 2.06 2.05 2.04 2.03 2.02 2.01 1.83 1.81 1.80 1.79 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.72 1.70 1.69
O
NH
N
1g
1H NMR (400 MHz, CDCl3)
1.01 1.03 1.00 0.81 1.00 1.00 2.03 2.03 2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



1g

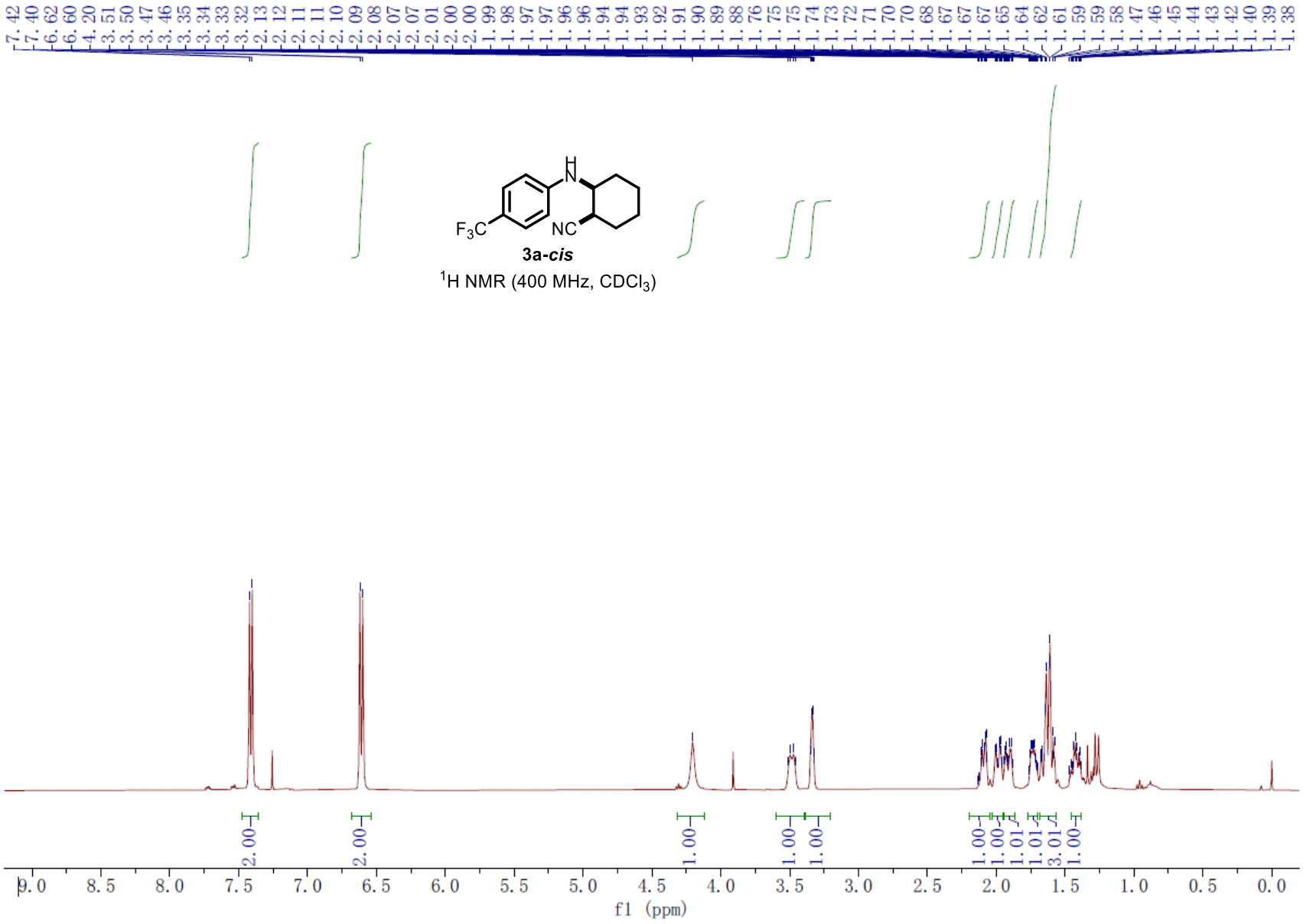
^{13}C NMR (101 MHz, $CDCl_3$)


7.59
7.59
7.57
7.57
7.54
7.52
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.07
7.07
7.05
7.04
7.03
4.11
4.09
4.07
2.51
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.46
2.45
2.44
2.44
2.43
2.06
2.04
2.03
2.01
2.01
2.00
1.99
1.98
1.97
1.96
1.79
1.78
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.70
S
NH
N
1h
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.00
1.01
1.00
2.02
2.05
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



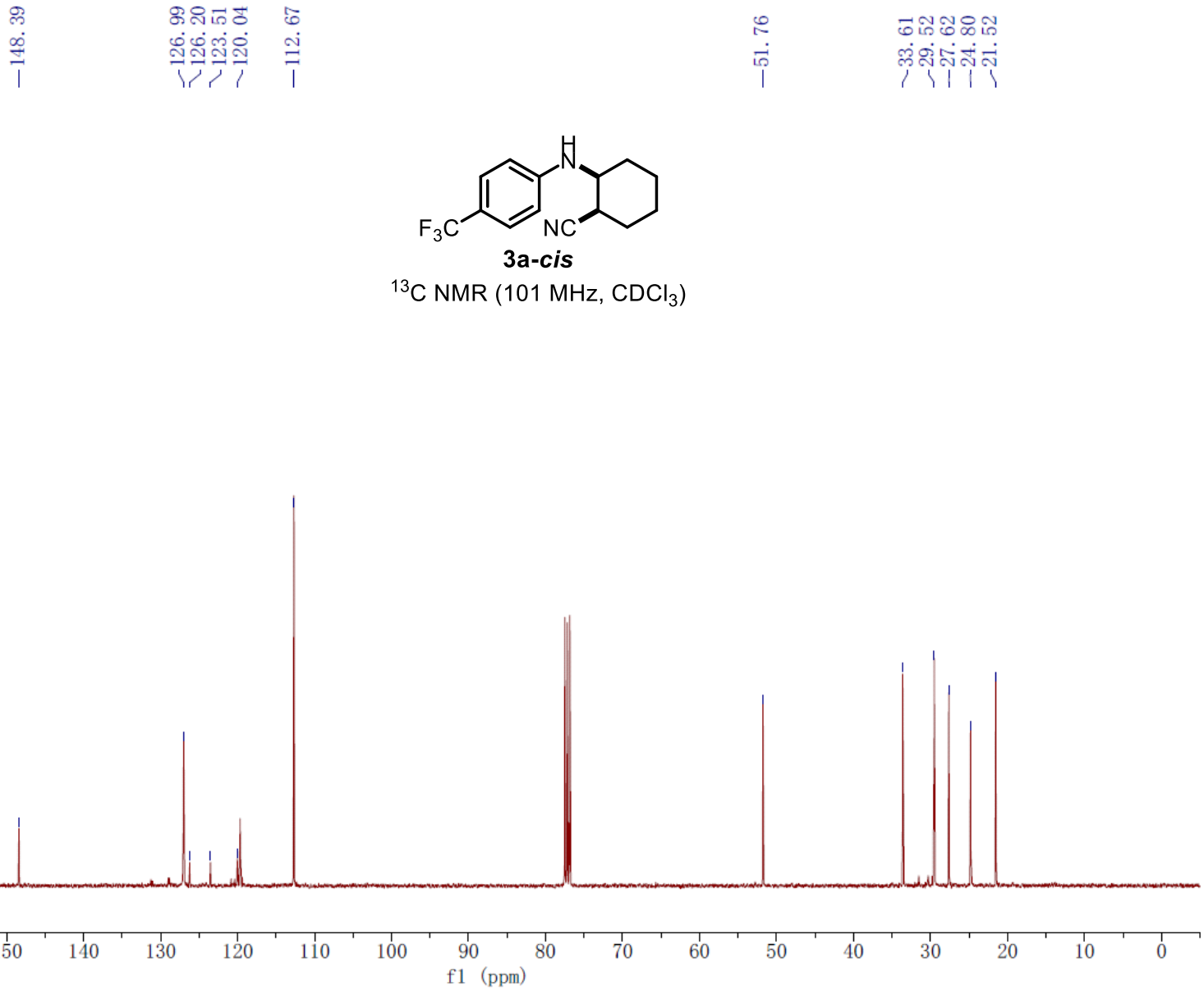
1h

^{13}C NMR (101 MHz, $CDCl_3$)



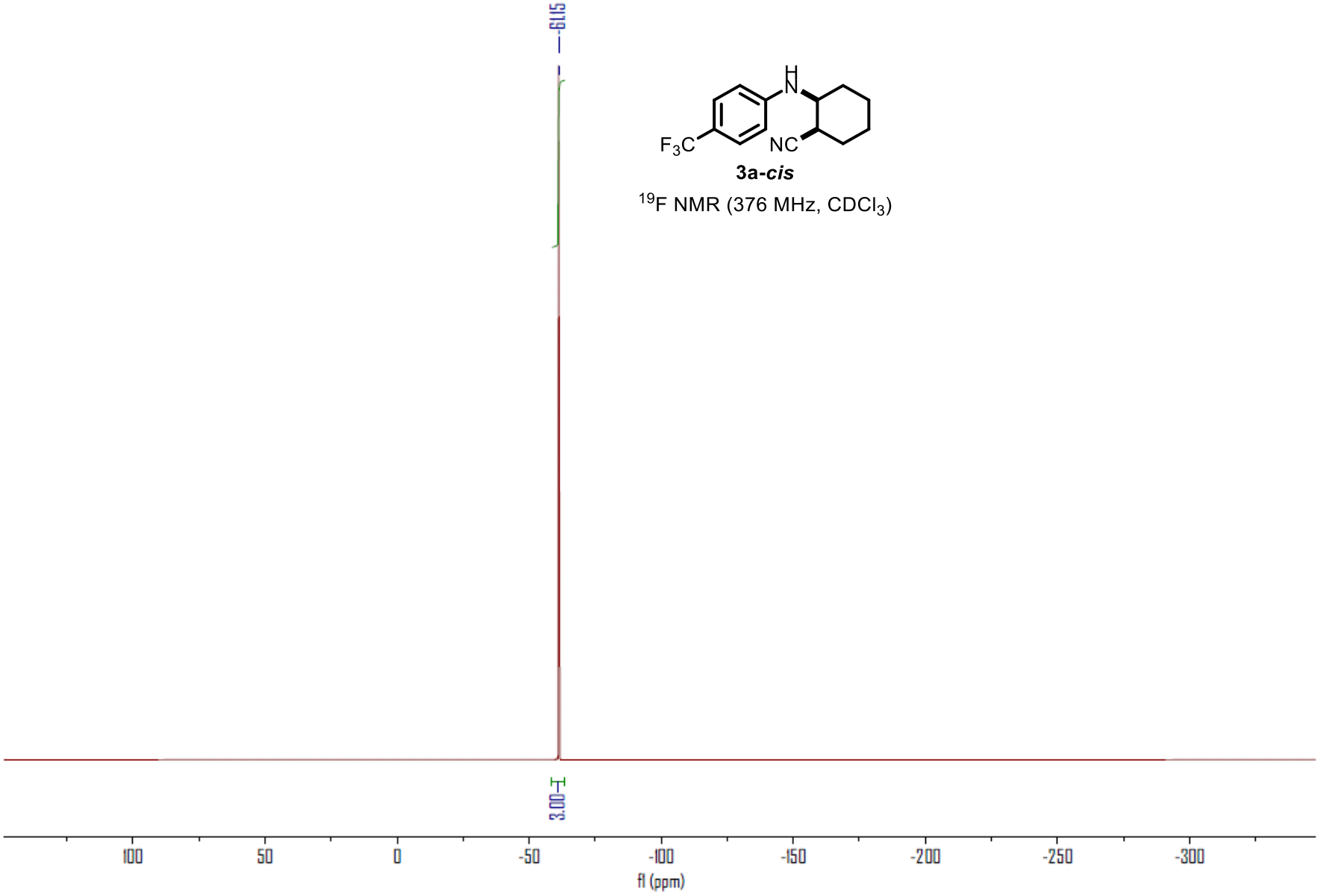
3a-*cis*

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



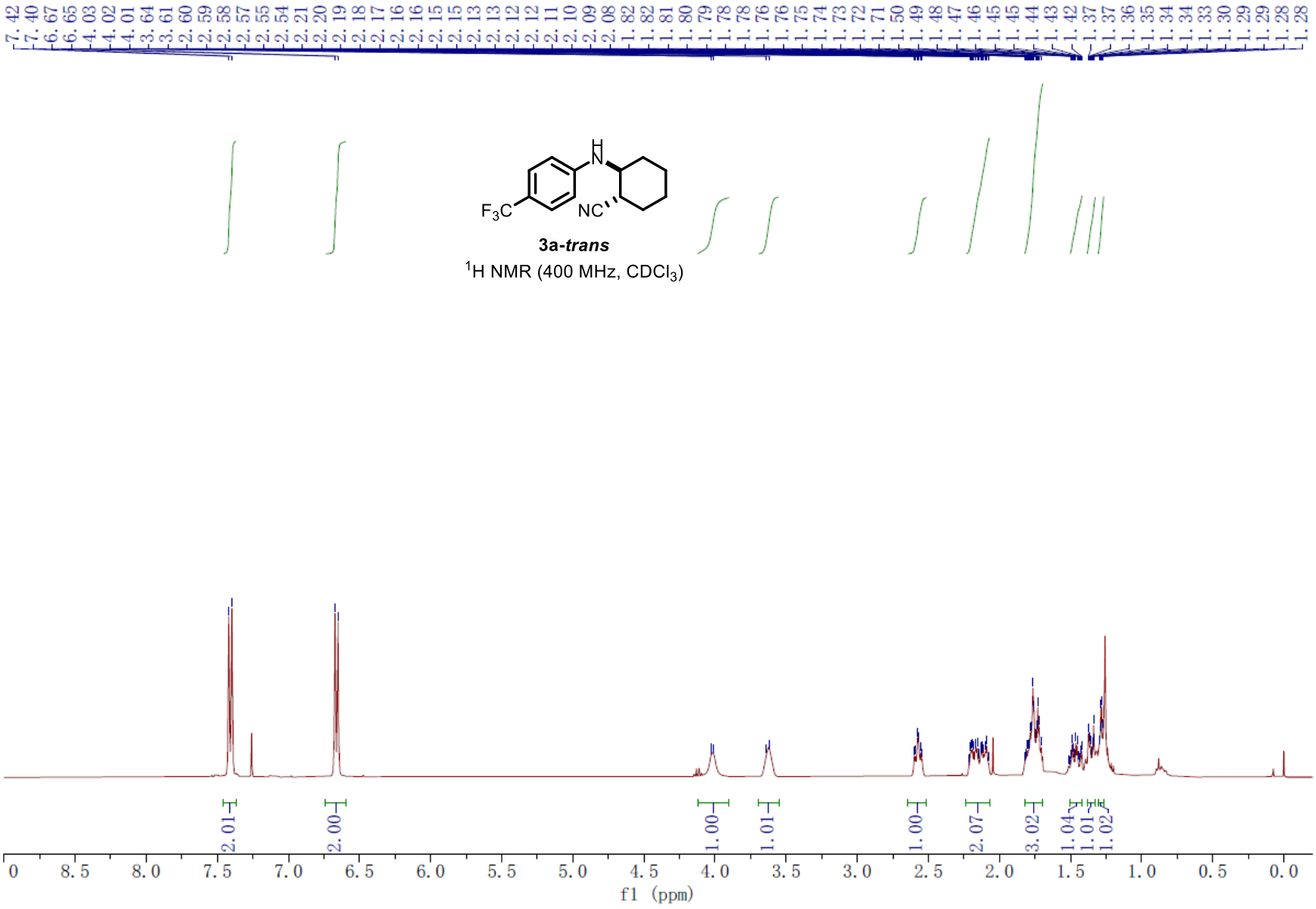
3a-*cis*

^{13}C NMR (101 MHz, $CDCl_3$)



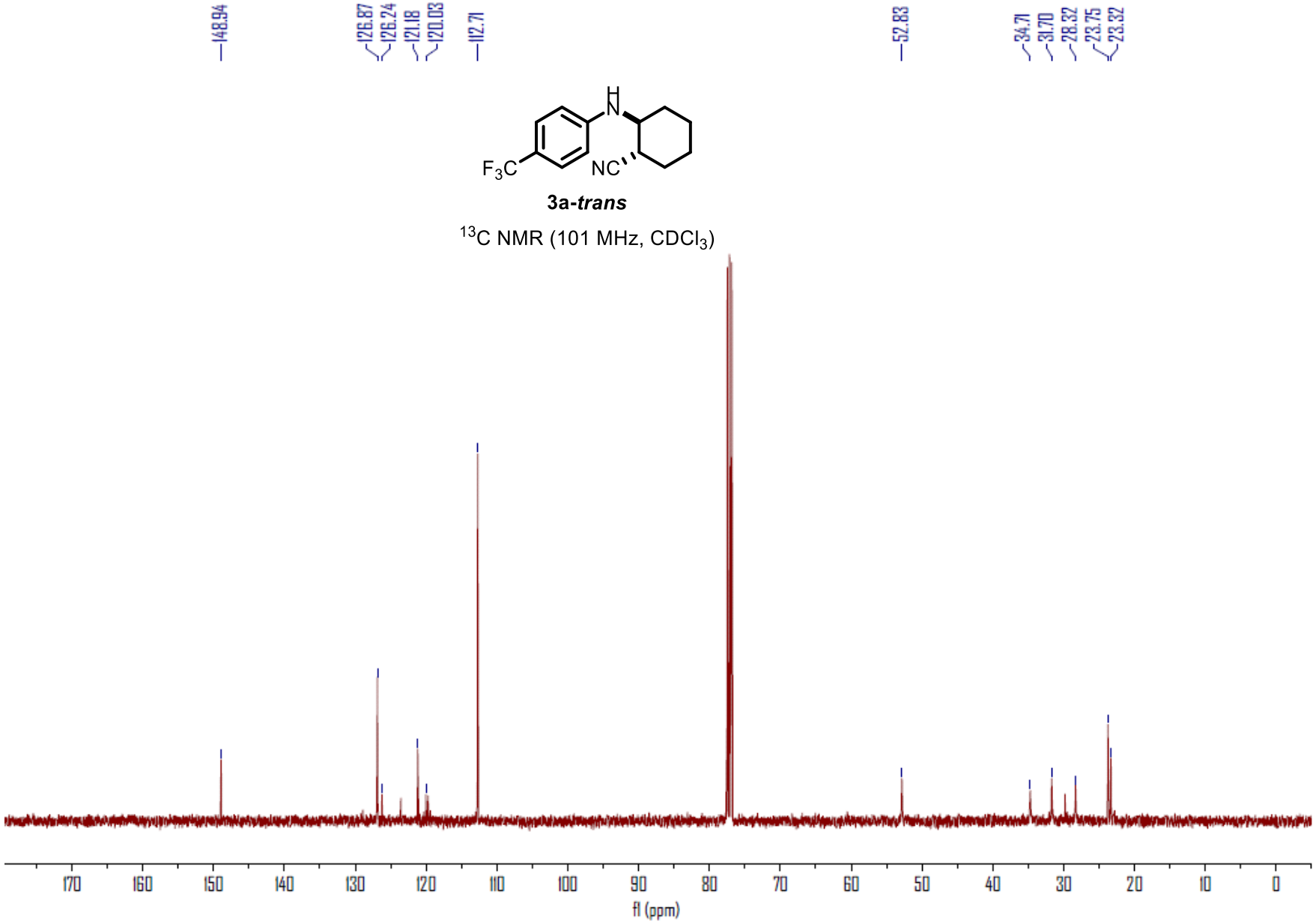
3a-*cis*

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



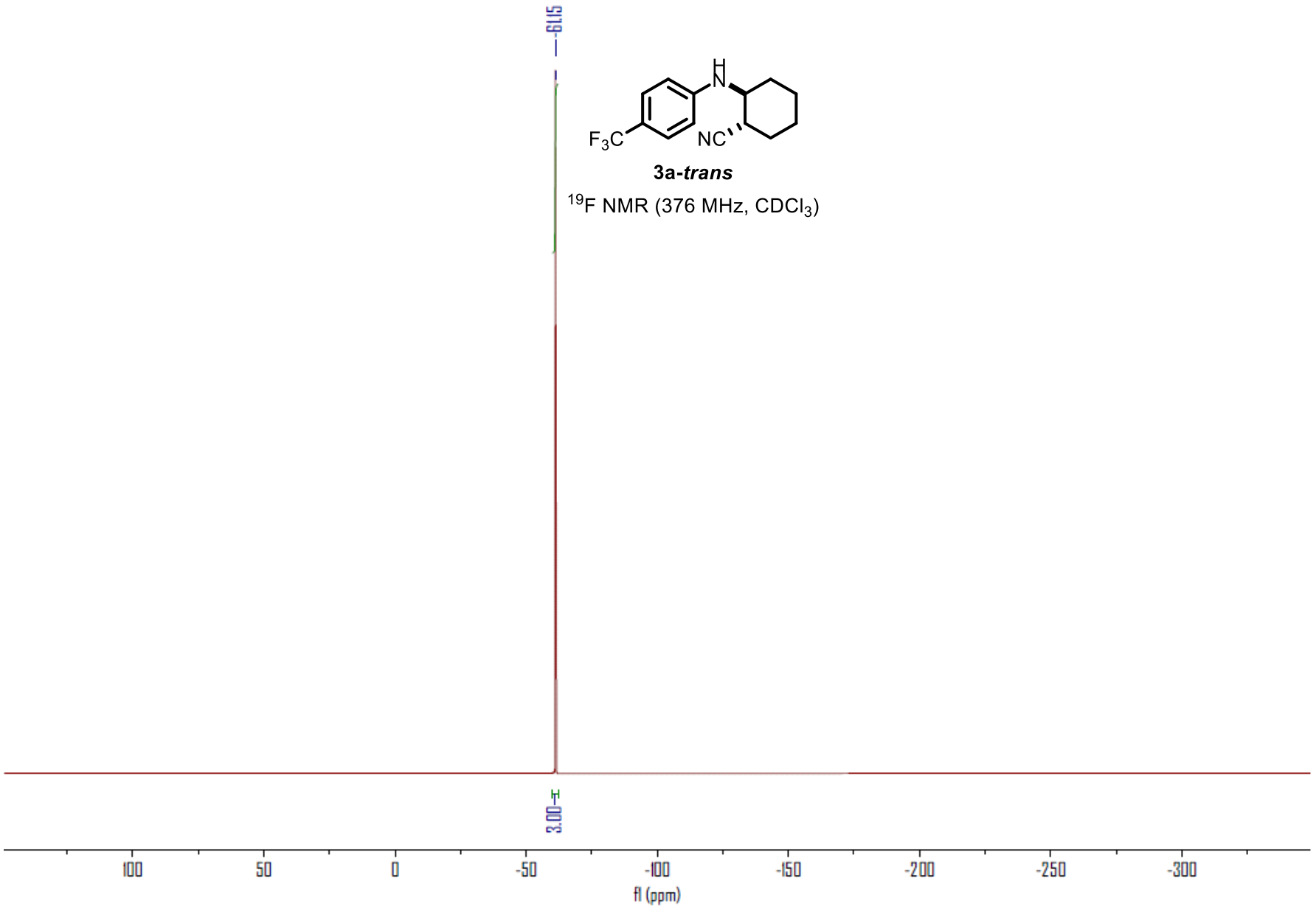
3a-*trans*

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



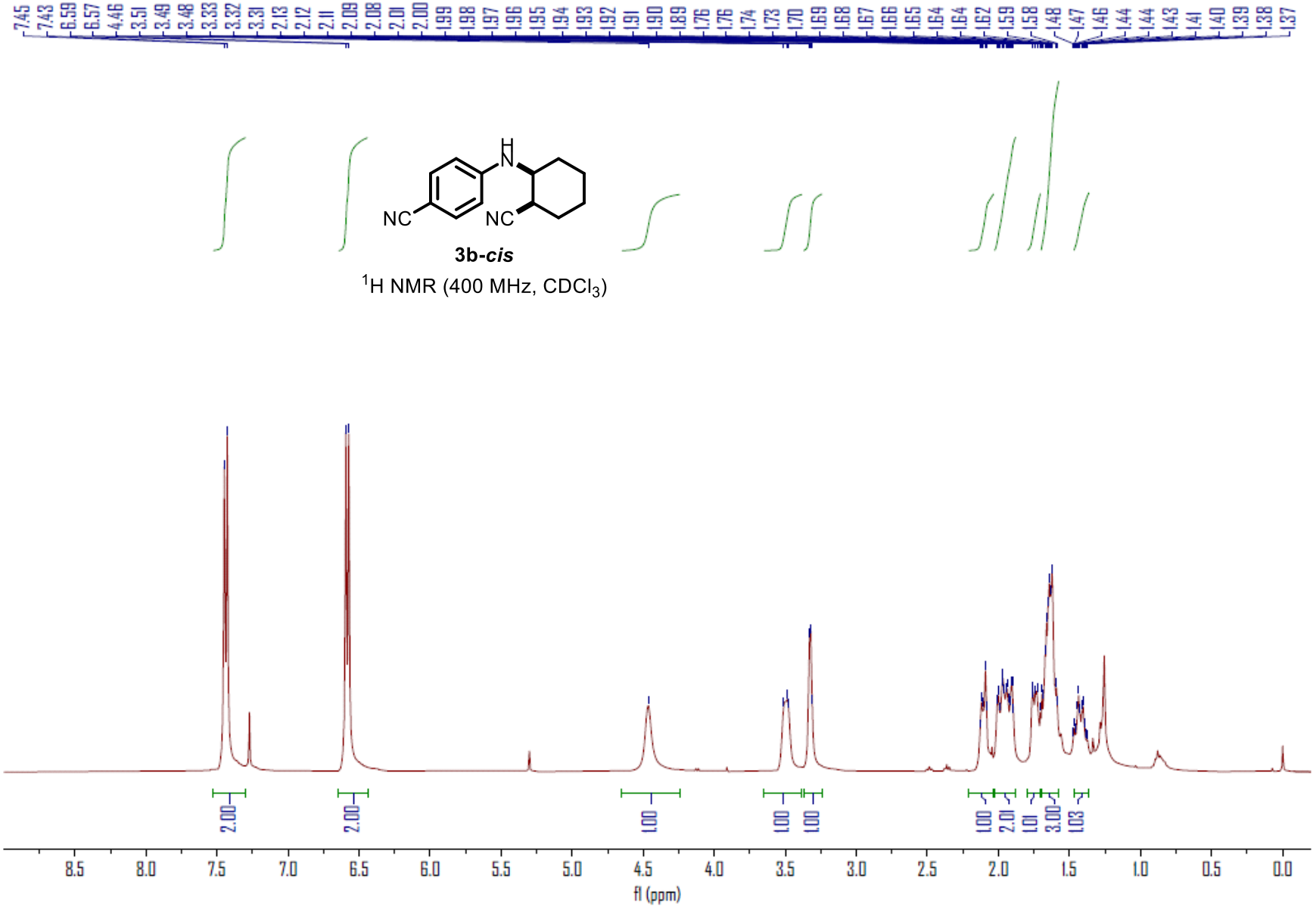
3a-*trans*

^{13}C NMR (101 MHz, $CDCl_3$)



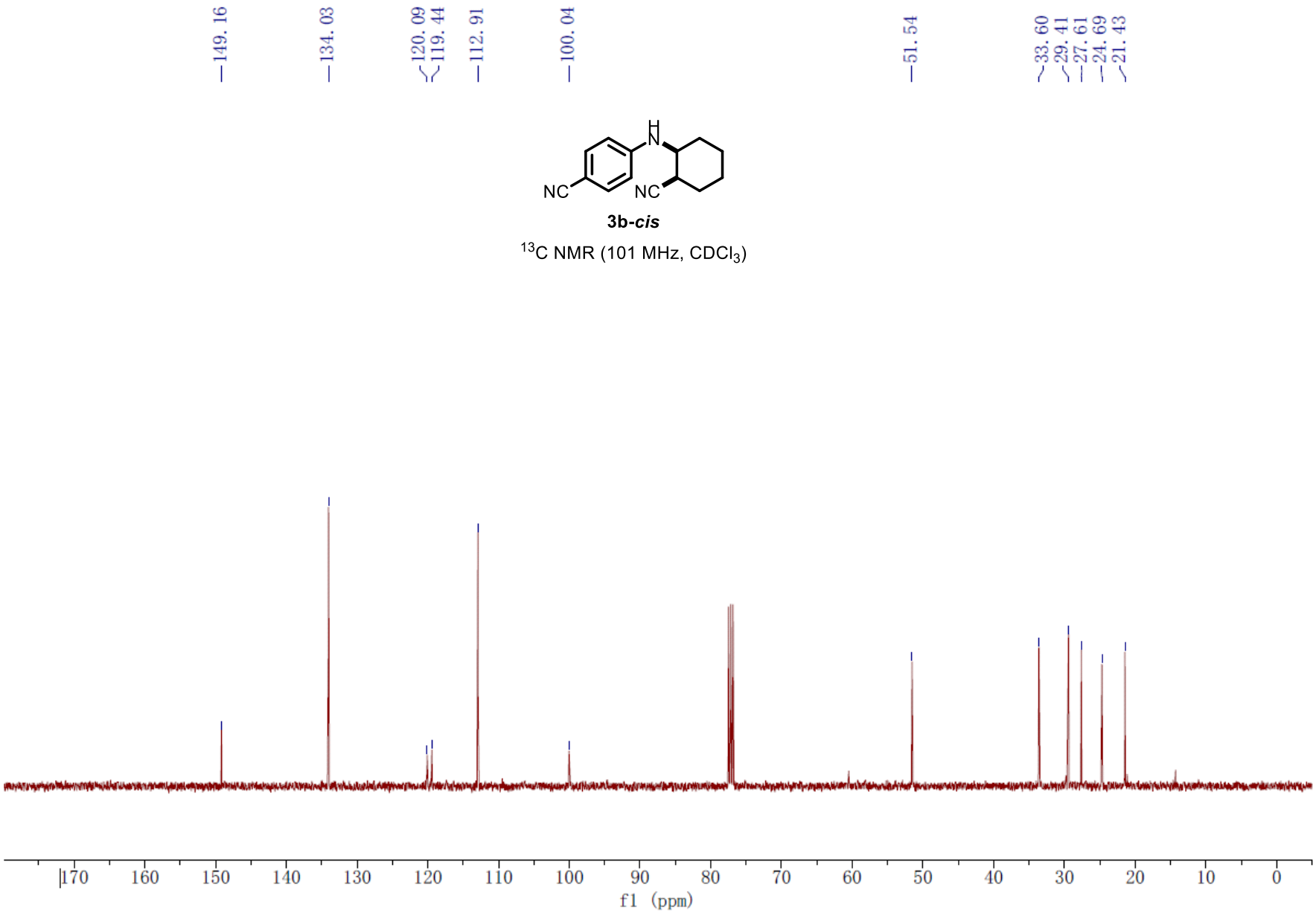
3a-*trans*

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



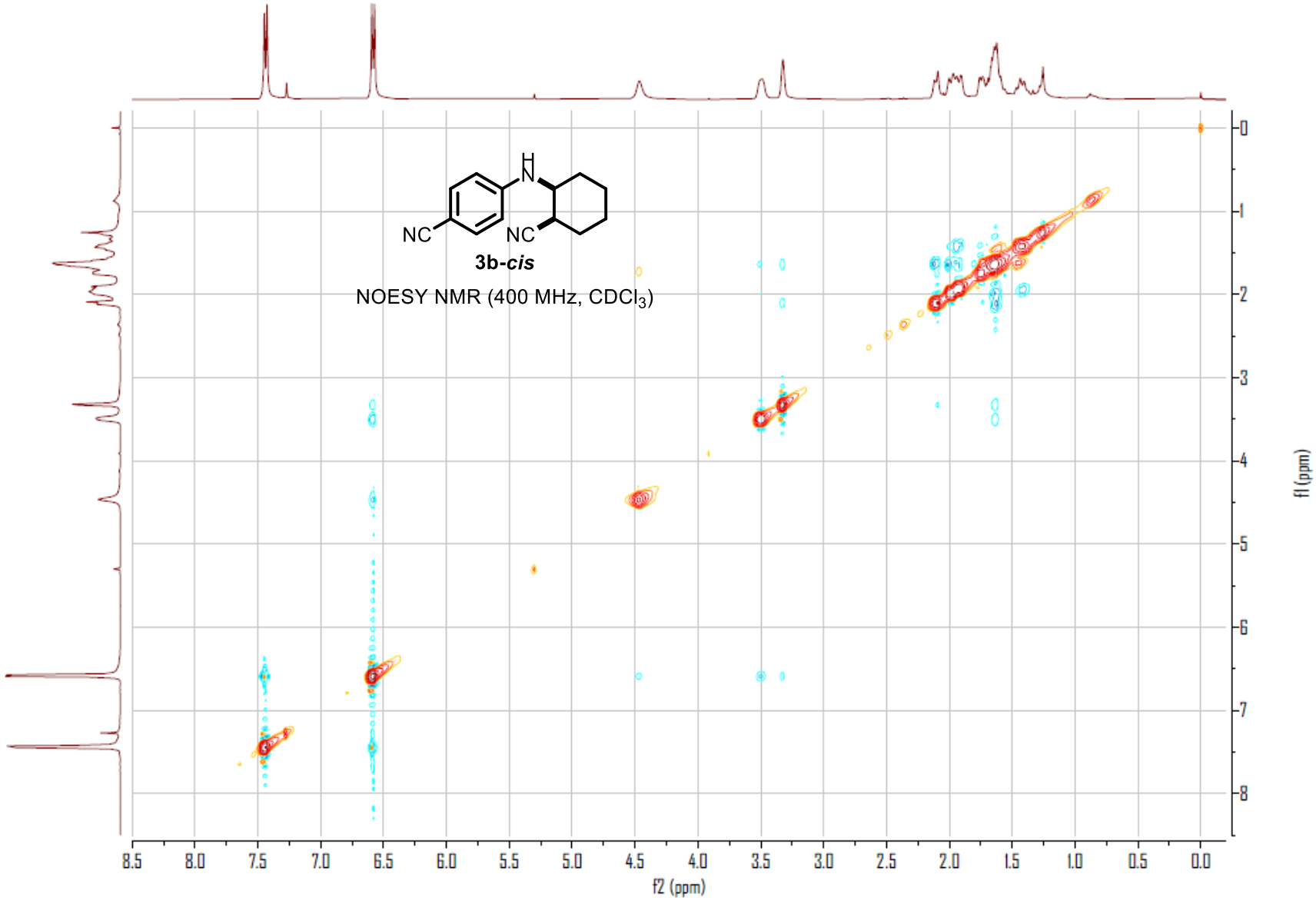
3b-*cis*

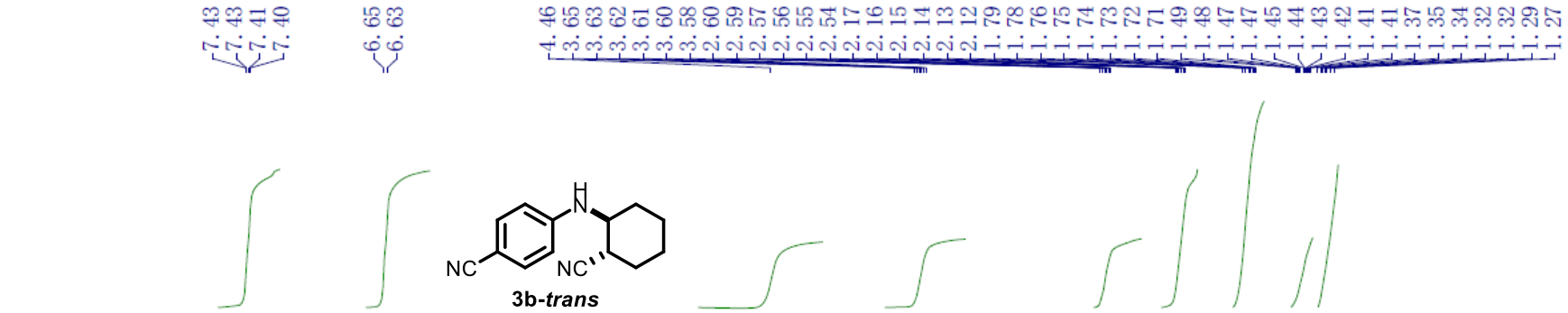
^{1}H NMR (400 MHz, $CDCl_3$)



3b-*cis*

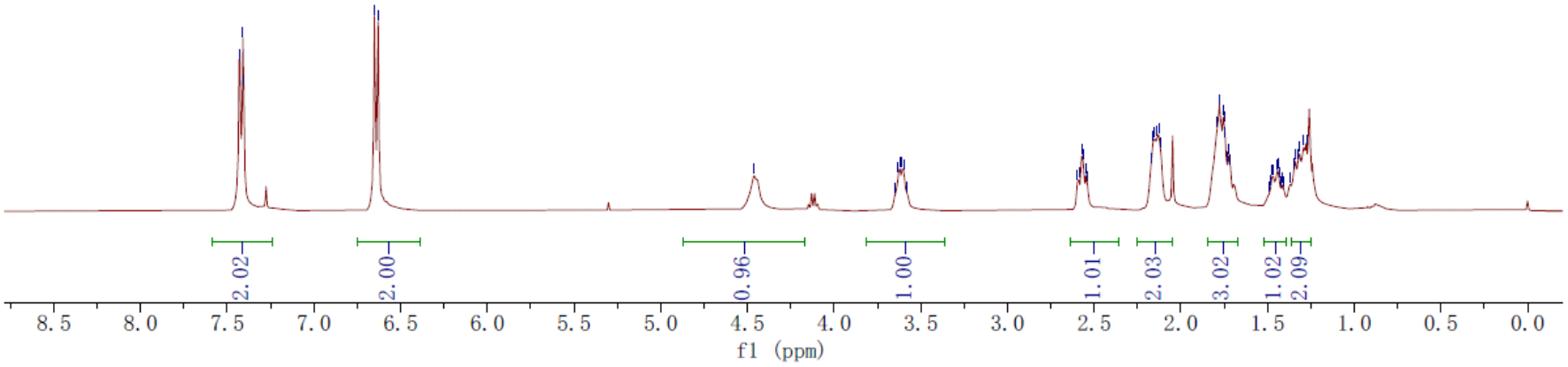
^{13}C NMR (101 MHz, $CDCl_3$)

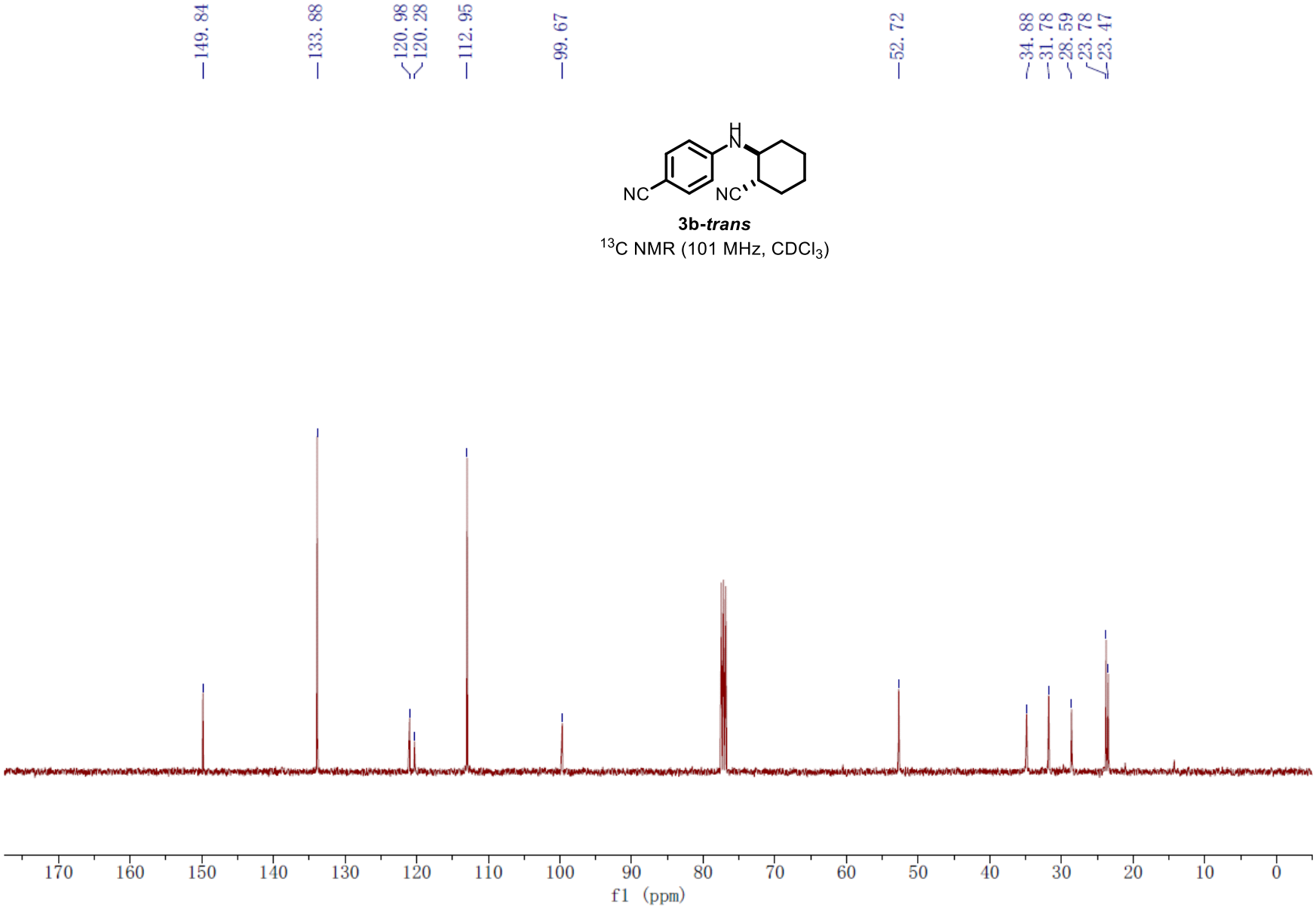

NC
NC
H
N
3b-*cis*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)



3b-*trans*

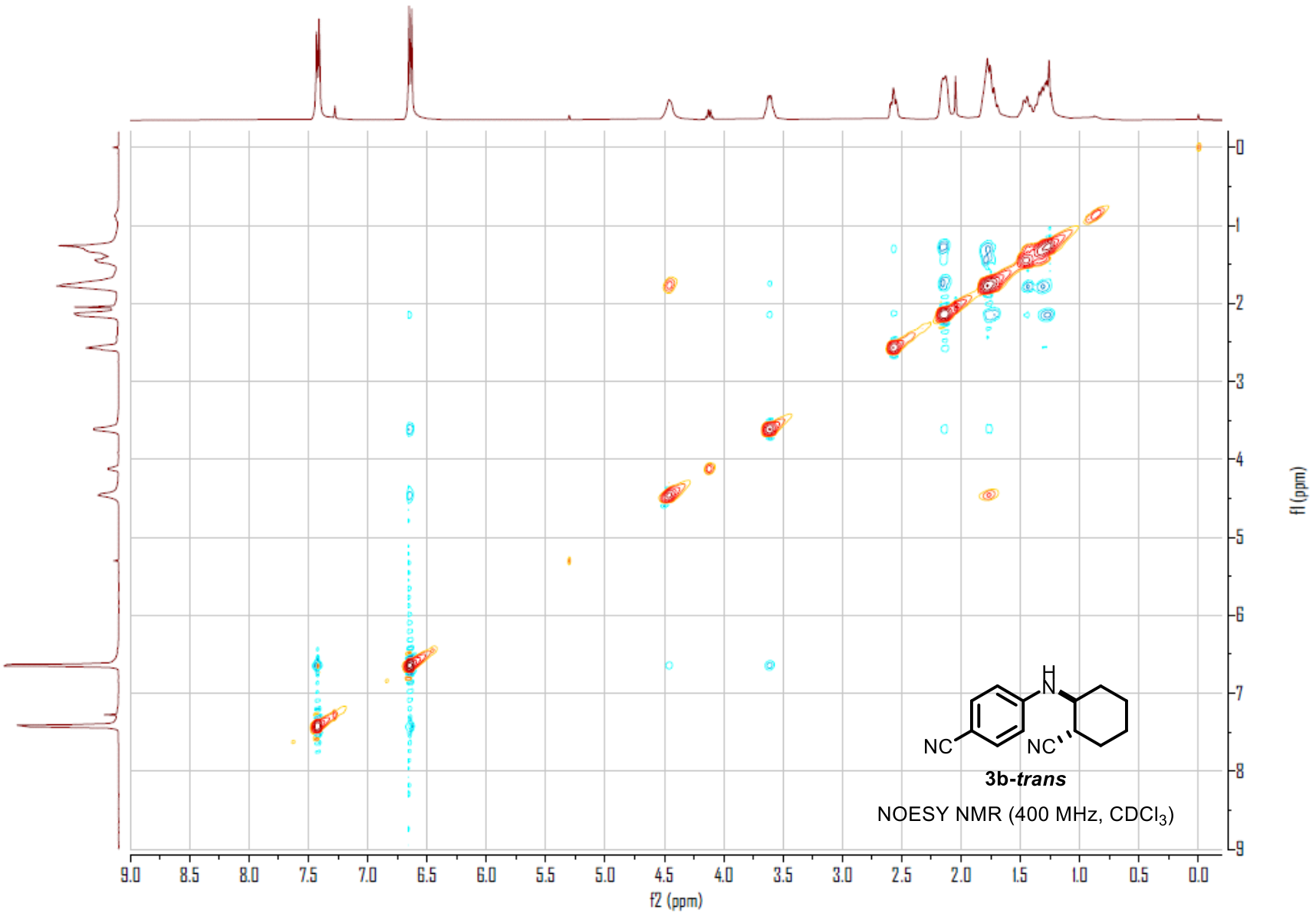
^{1}H NMR (400 MHz, $CDCl_3$)





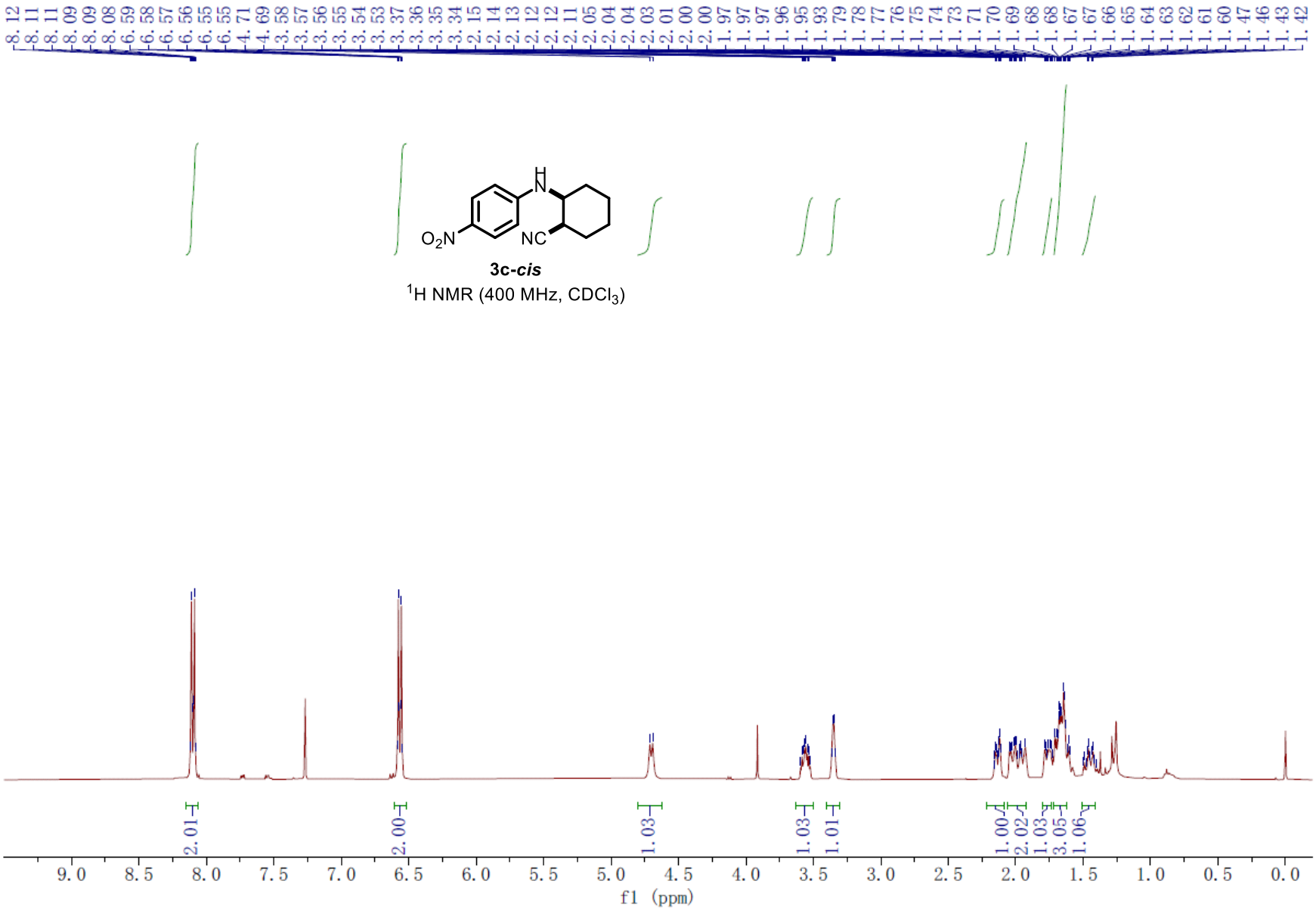
3b-*trans*

^{13}C NMR (101 MHz, $CDCl_3$)



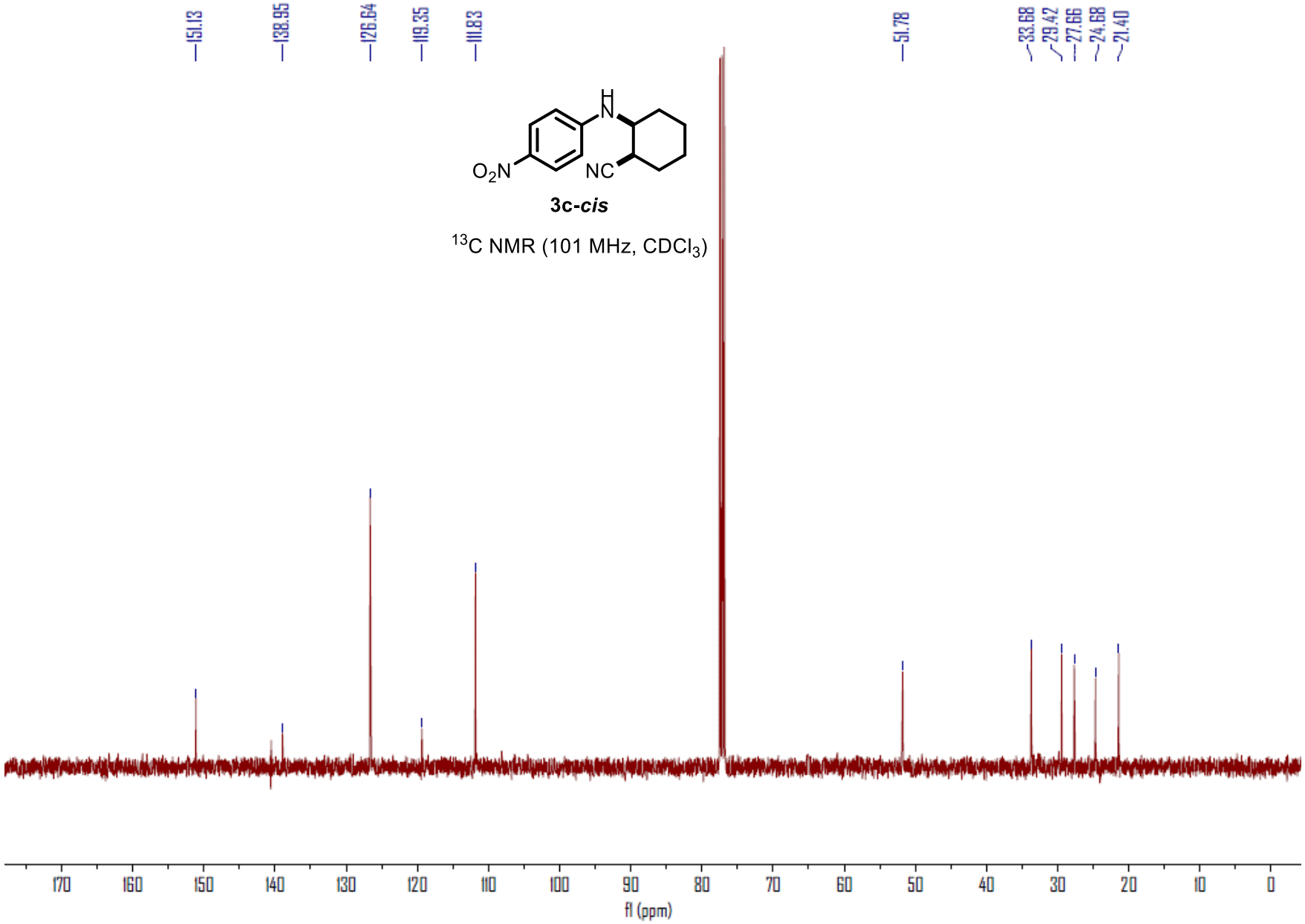
3b-*trans*

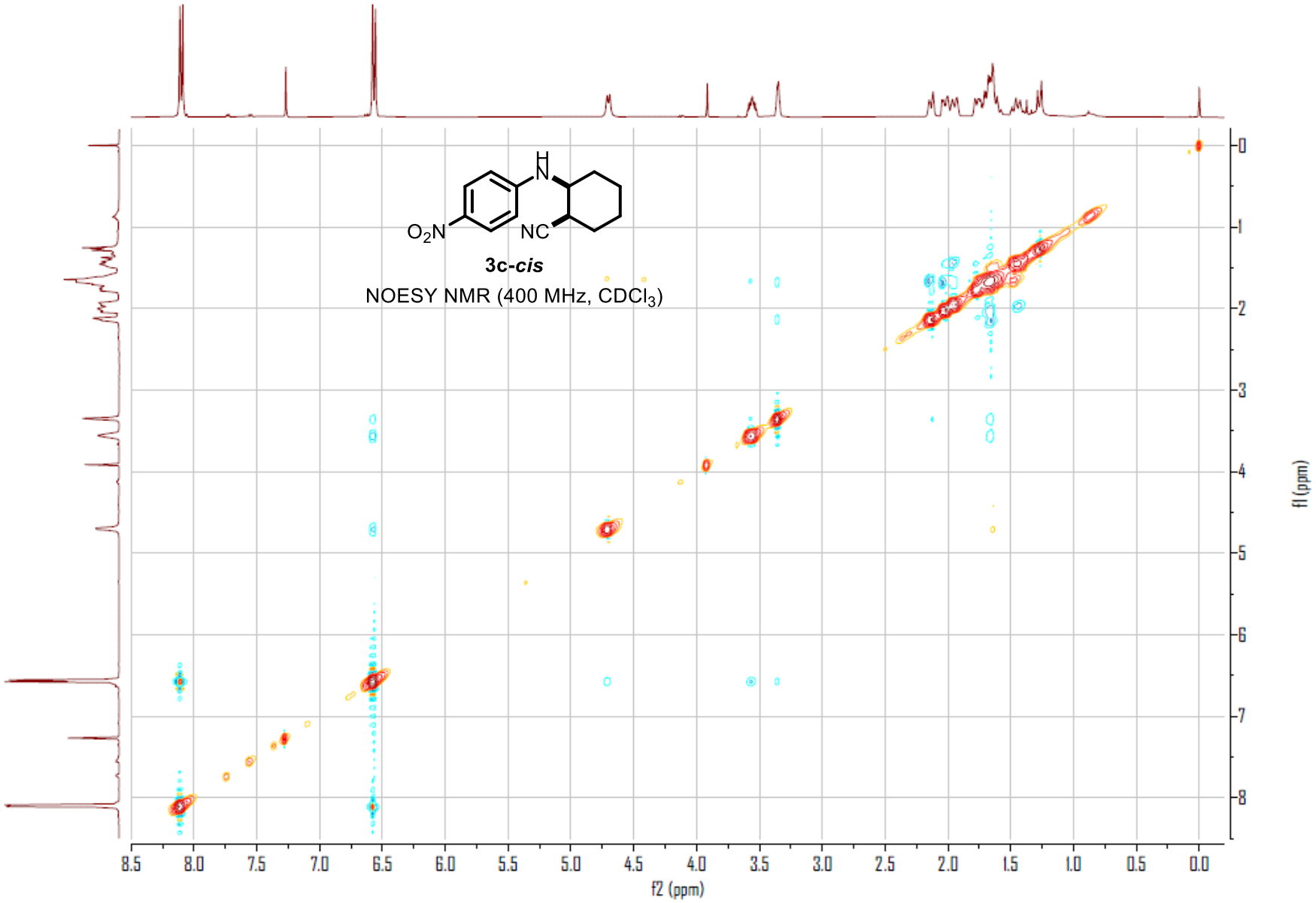
NOESY NMR (400 MHz, $CDCl_3$)

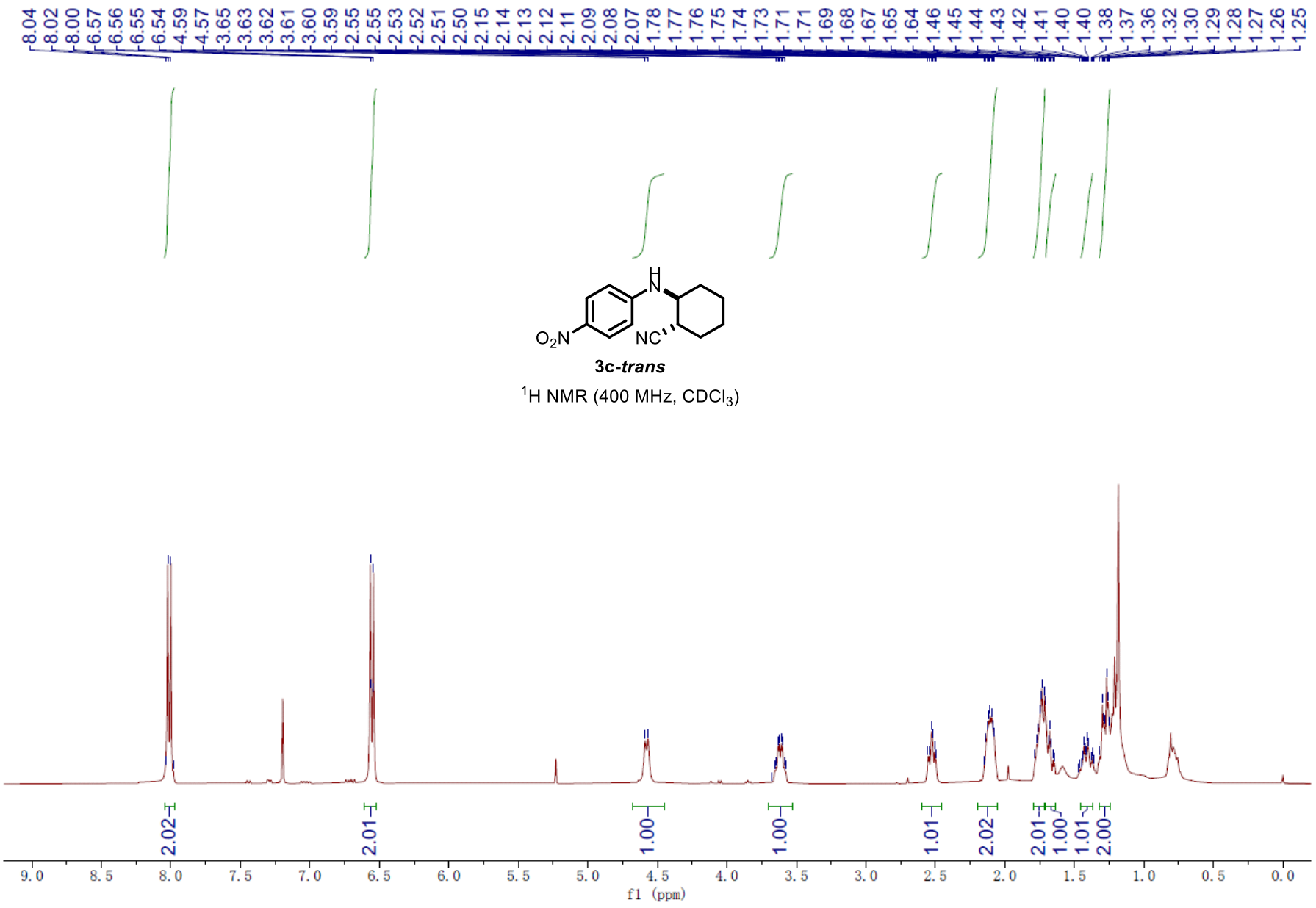


3c-*cis*

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

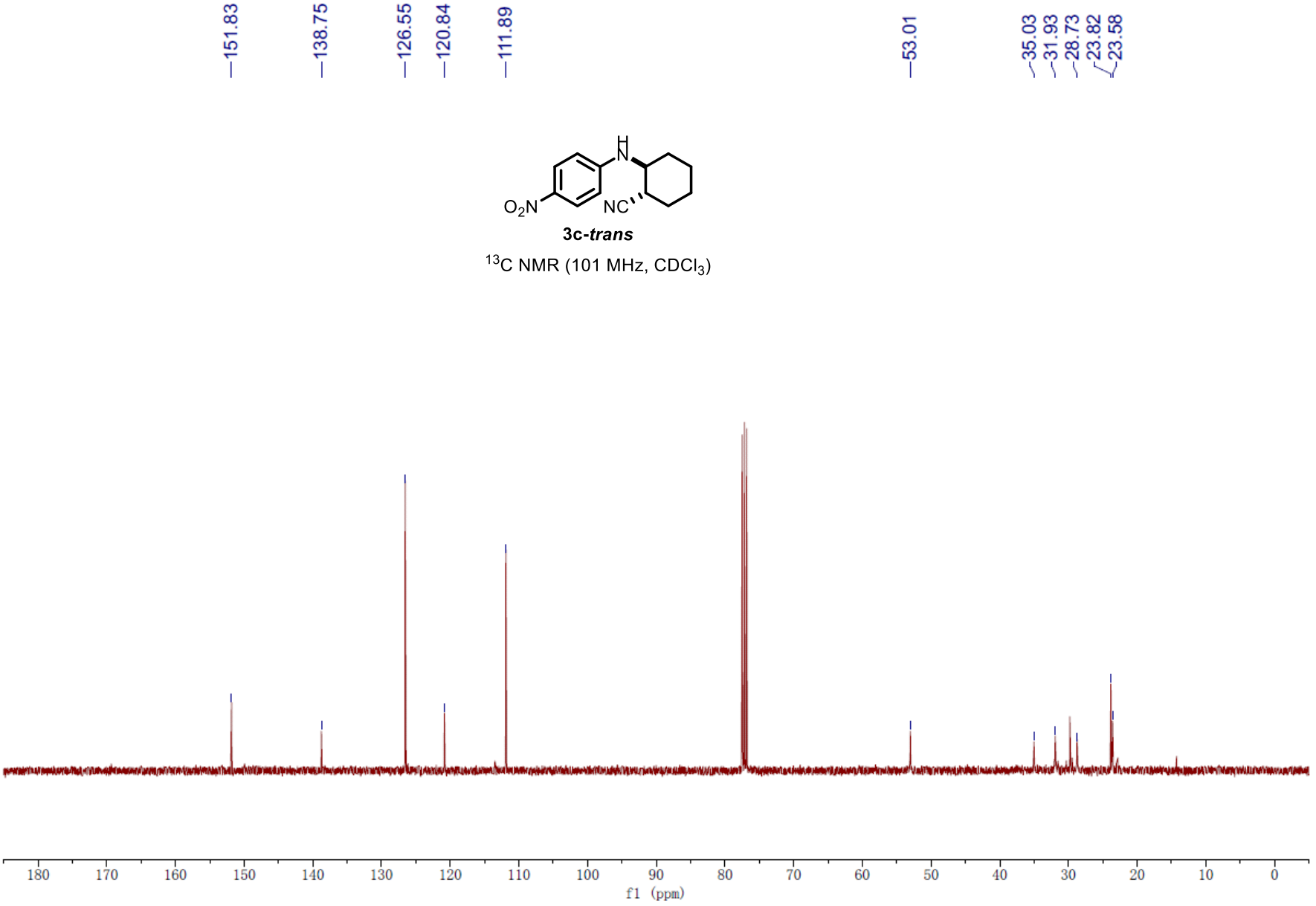

151.13
138.95
126.64
119.35
111.83
51.78
33.68
29.42
27.66
24.68
21.40
O2N
NC
H
N
3c-cis
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3c-*cis*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)



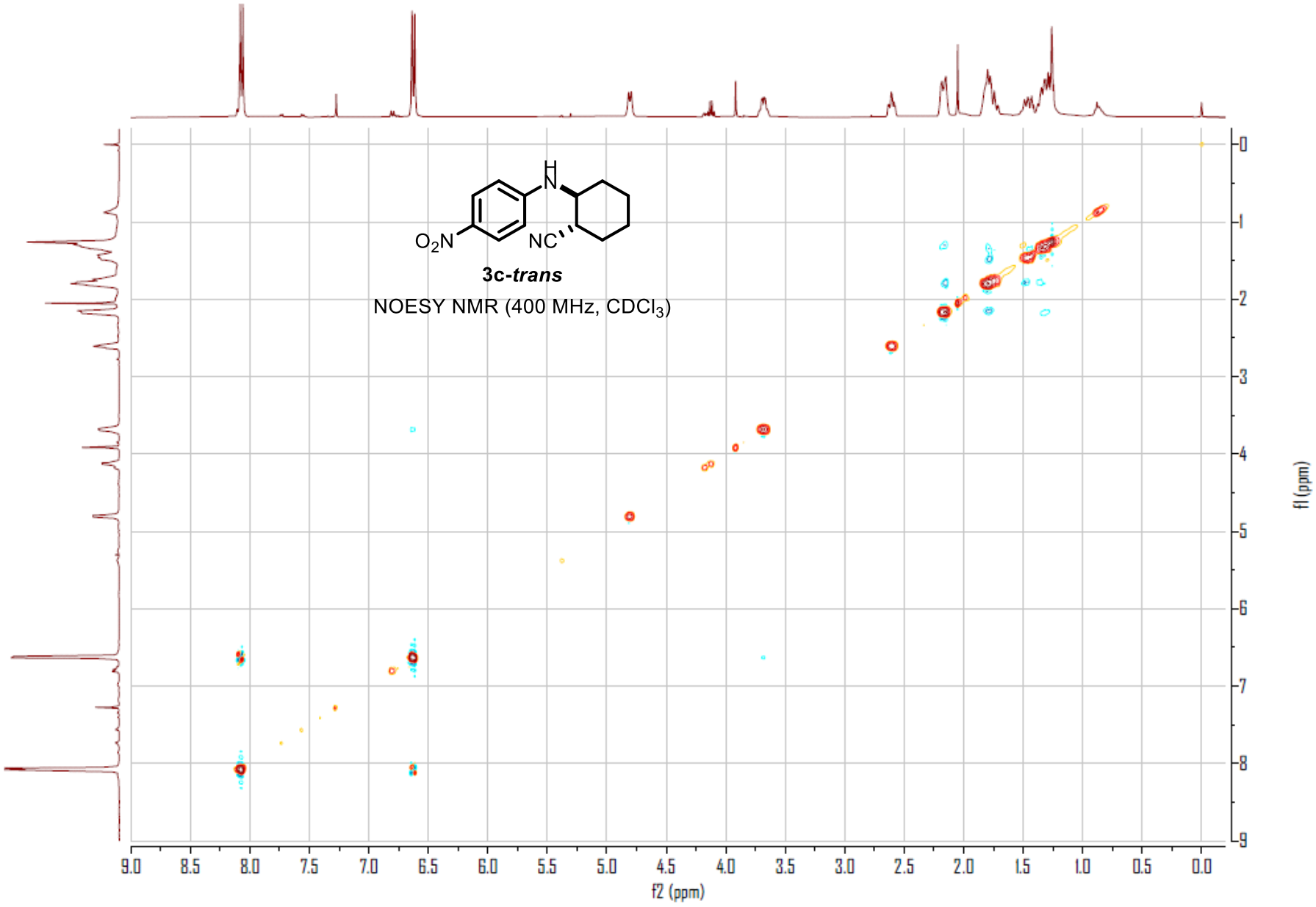
3c-*trans*

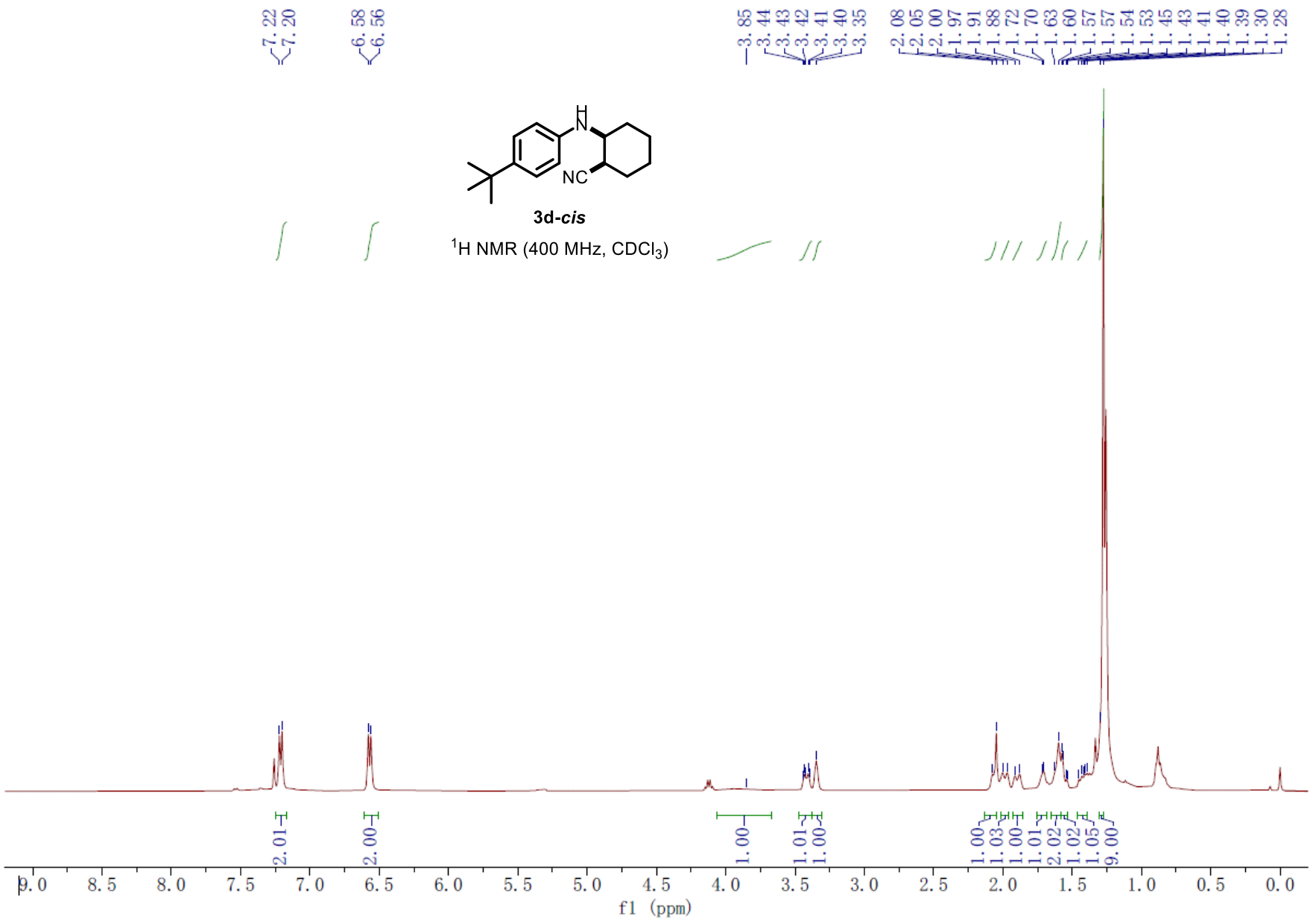
^{1}H NMR (400 MHz, $CDCl_3$)

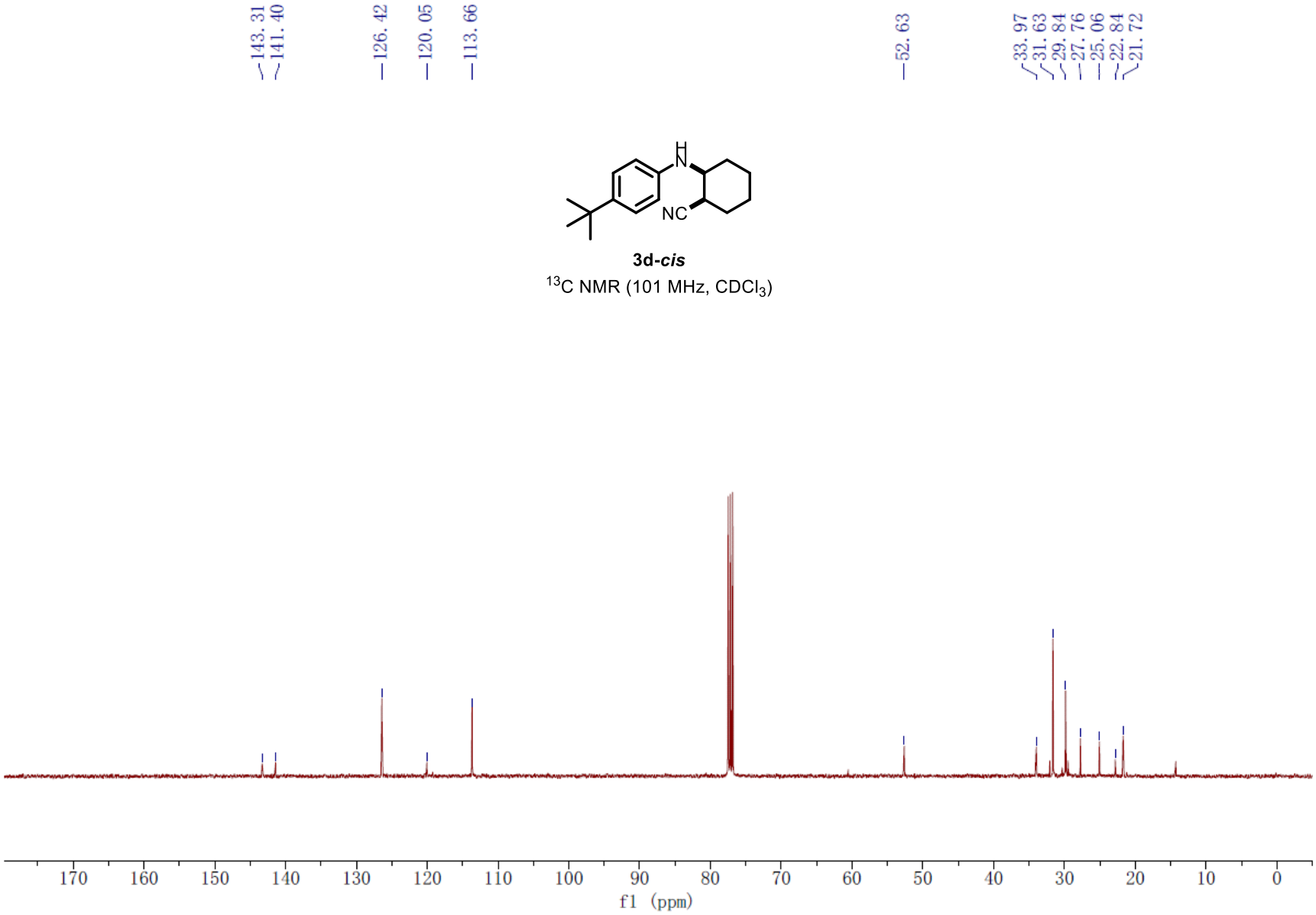


3c-*trans*

^{13}C NMR (101 MHz, $CDCl_3$)

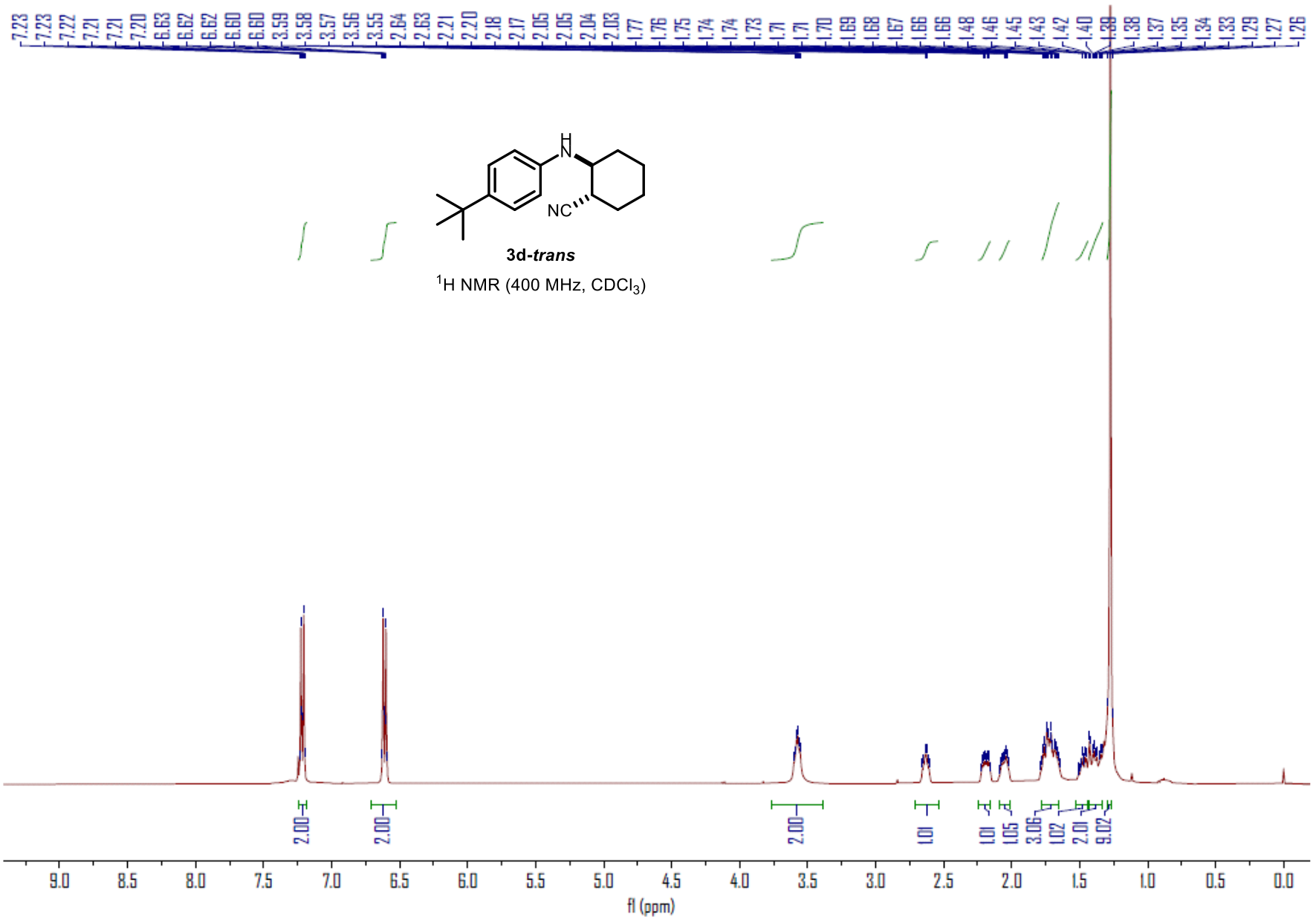

O2N
NC
H
N
3c-trans
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


7.22
7.20
6.58
6.56
3.85
3.44
3.43
3.42
3.41
3.40
3.35
2.08
2.05
2.00
1.97
1.91
1.88
1.72
1.70
1.63
1.60
1.57
1.57
1.54
1.53
1.45
1.43
1.41
1.40
1.39
1.30
1.28
H
N
NC
3d-cis
1H NMR (400 MHz, CDCl3)
2.01
2.00
1.00
1.01
1.00
1.00
1.03
1.00
1.01
2.02
1.02
1.05
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



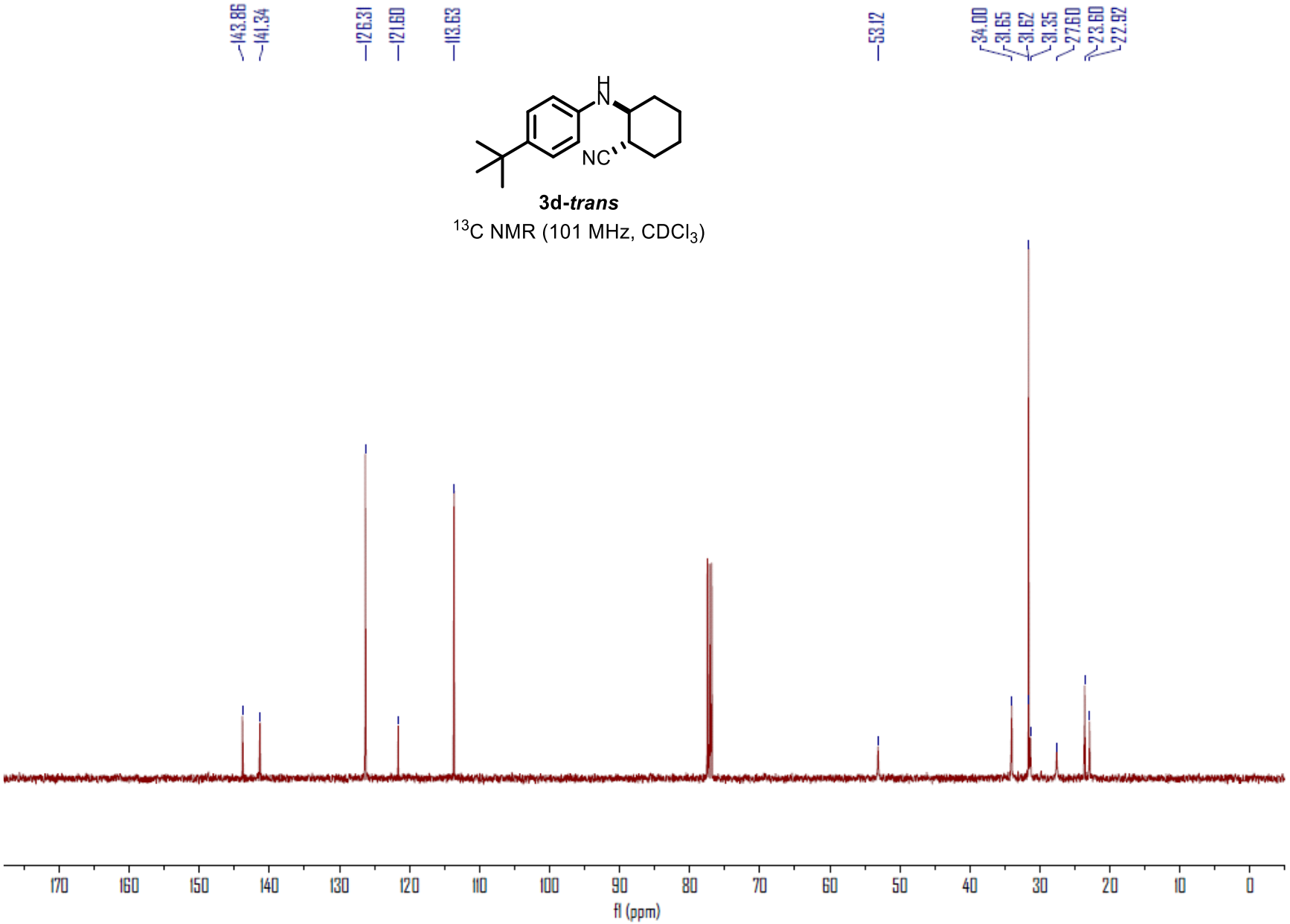
3d-*cis*

^{13}C NMR (101 MHz, $CDCl_3$)



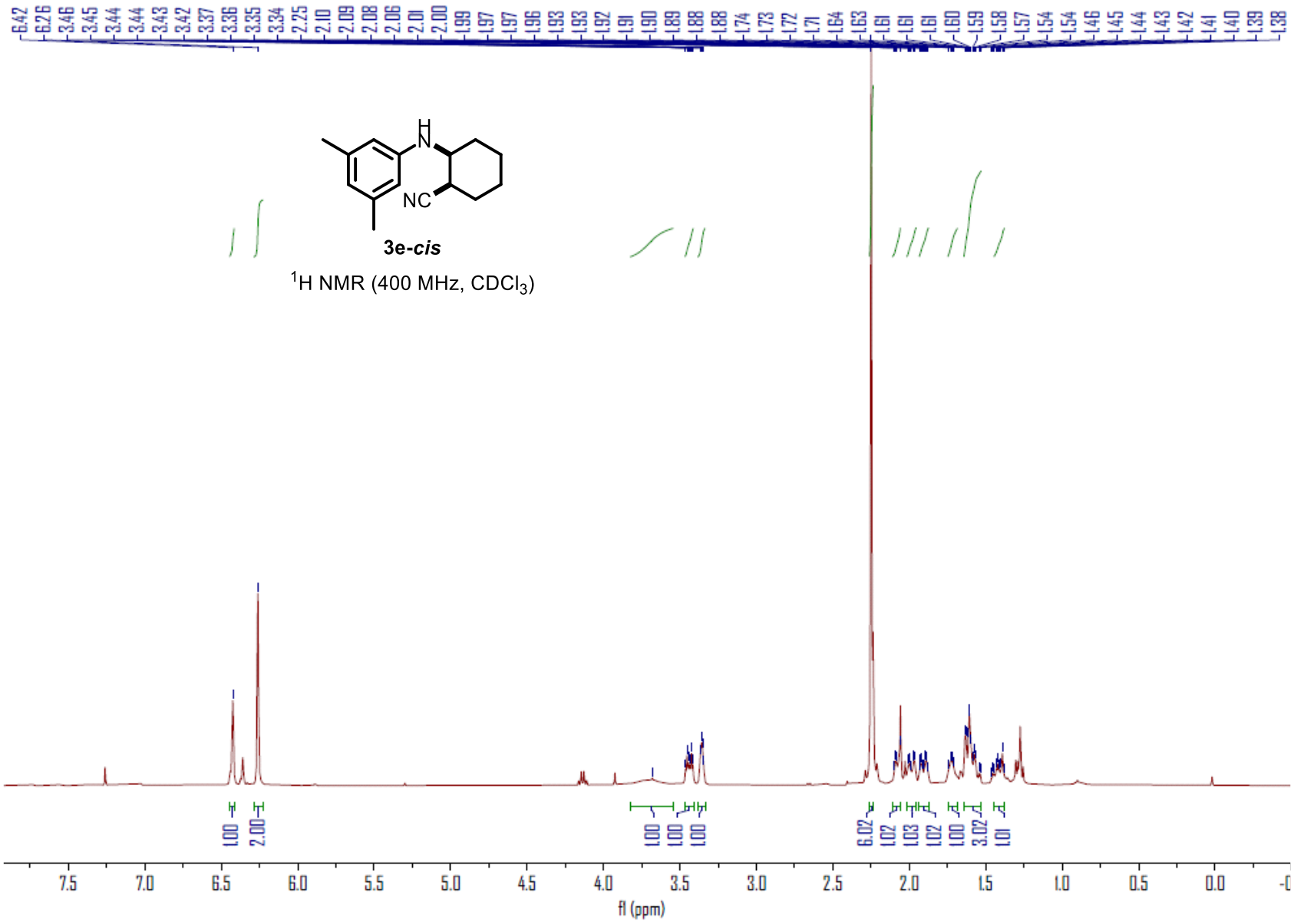
3d-*trans*

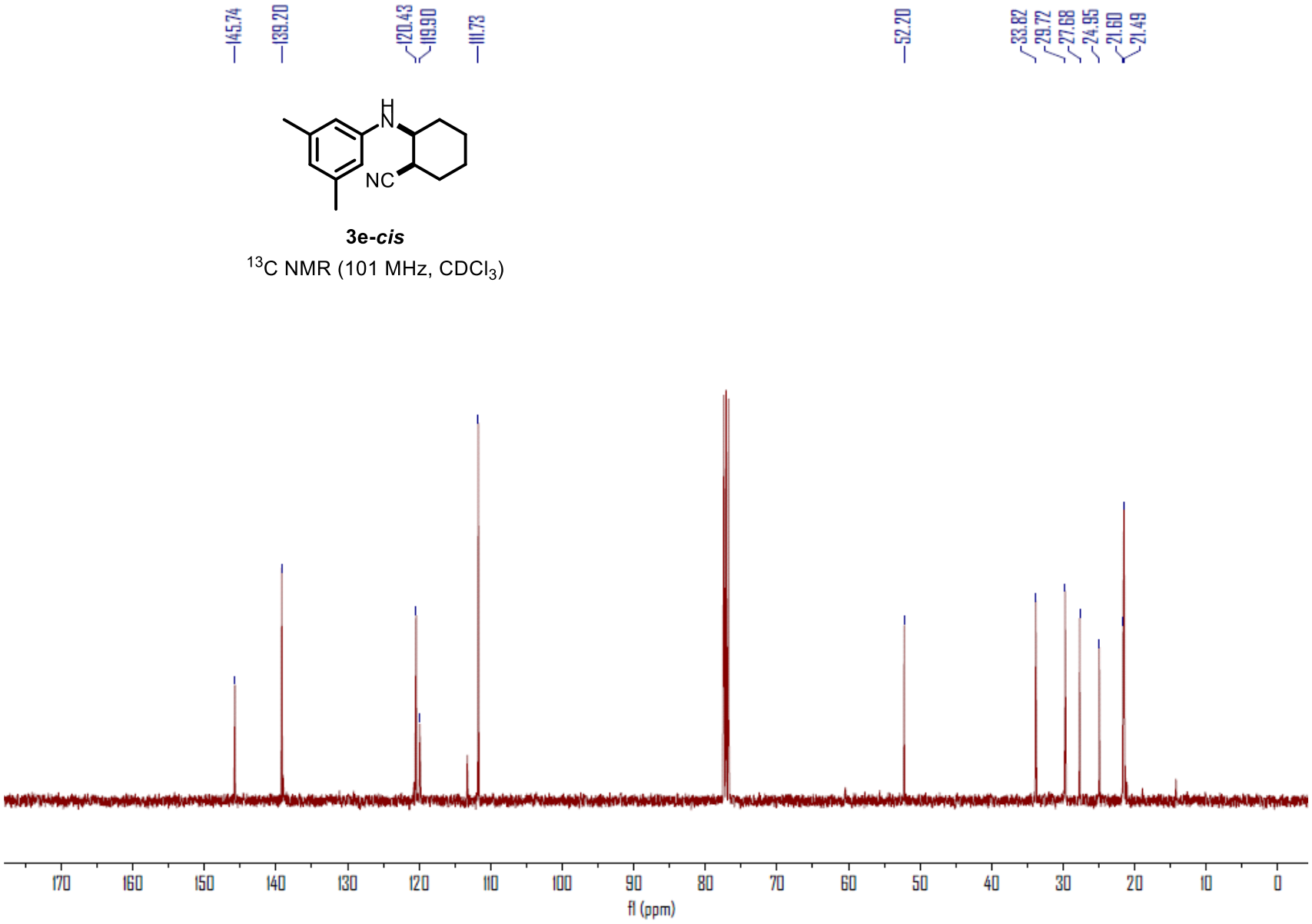
^{1}H NMR (400 MHz, $CDCl_3$)



3d-*trans*

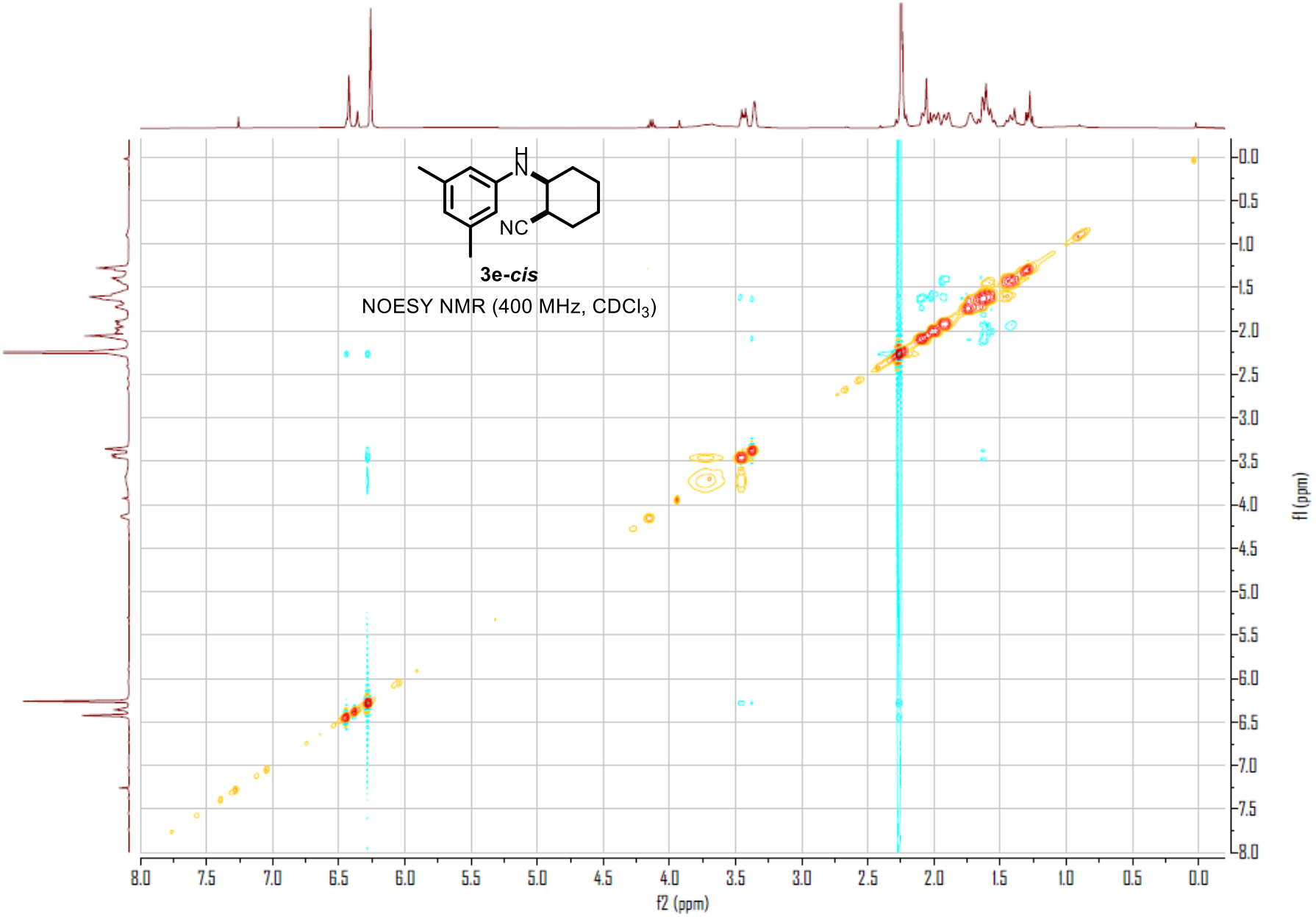
^{13}C NMR (101 MHz, $CDCl_3$)

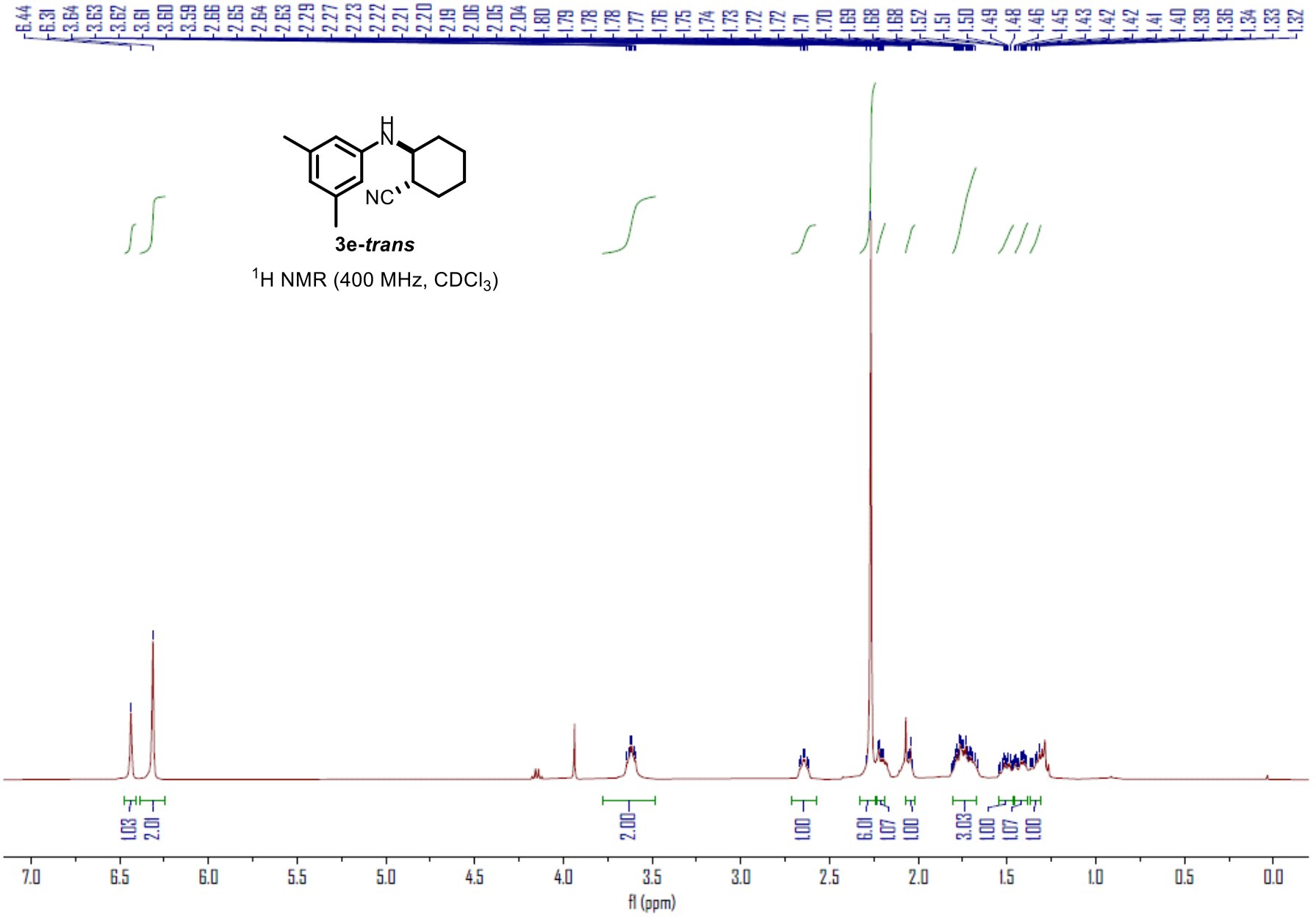

6.42
6.26
3.46
3.45
3.44
3.44
3.43
3.42
3.37
3.36
3.35
3.34
2.25
2.10
2.09
2.08
2.06
2.01
2.00
1.99
1.97
1.97
1.96
1.93
1.93
1.92
1.91
1.90
1.89
1.88
1.88
1.74
1.73
1.72
1.71
1.64
1.63
1.61
1.61
1.61
1.60
1.59
1.58
1.57
1.54
1.54
1.46
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
H
N
NC
3e-cis
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
1.00
1.00
6.02
1.02
1.03
1.02
1.00
3.02
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3e-*cis*

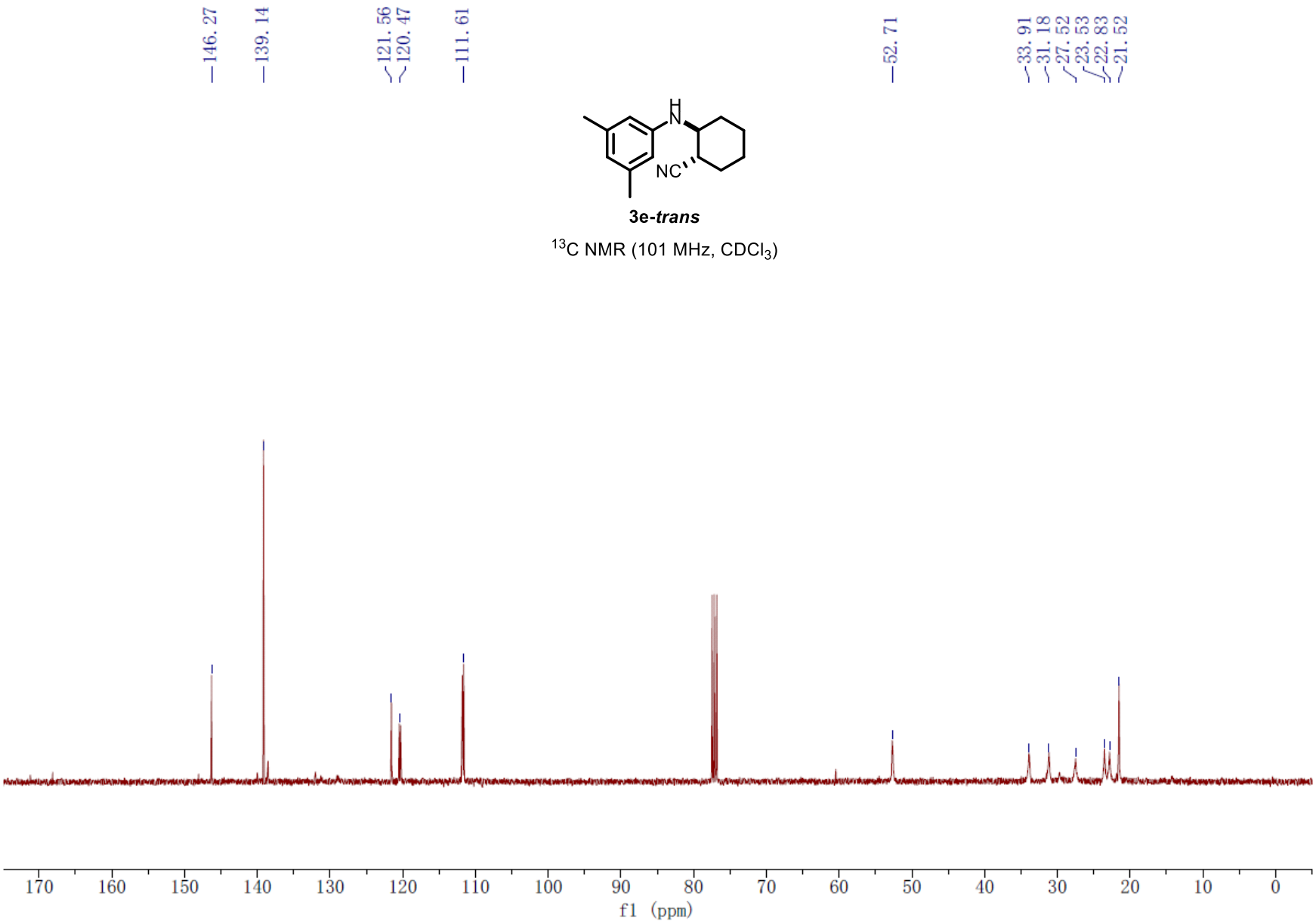
^{13}C NMR (101 MHz, $CDCl_3$)


H
N
NC
3e-*cis*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)



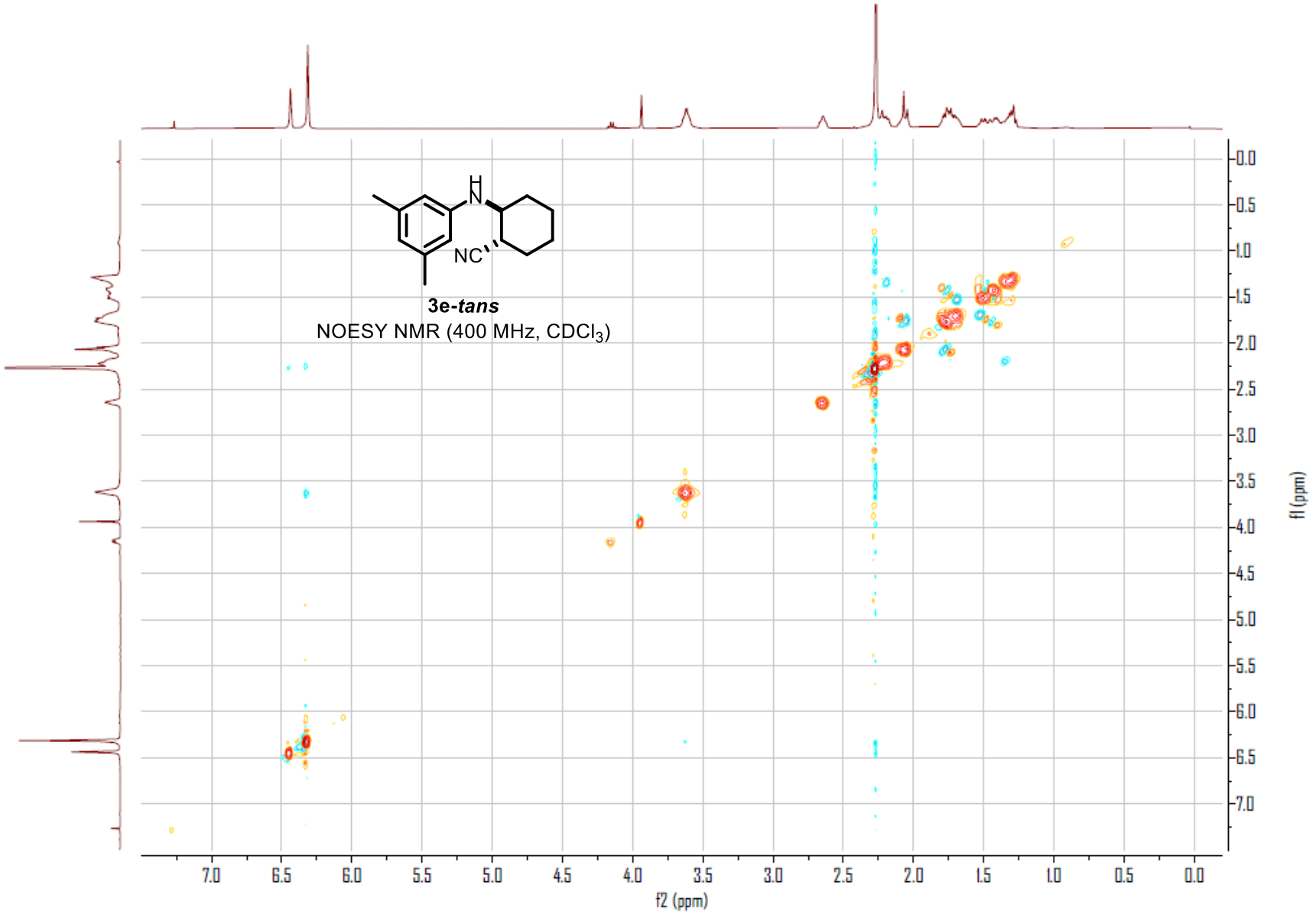
3e-*trans*

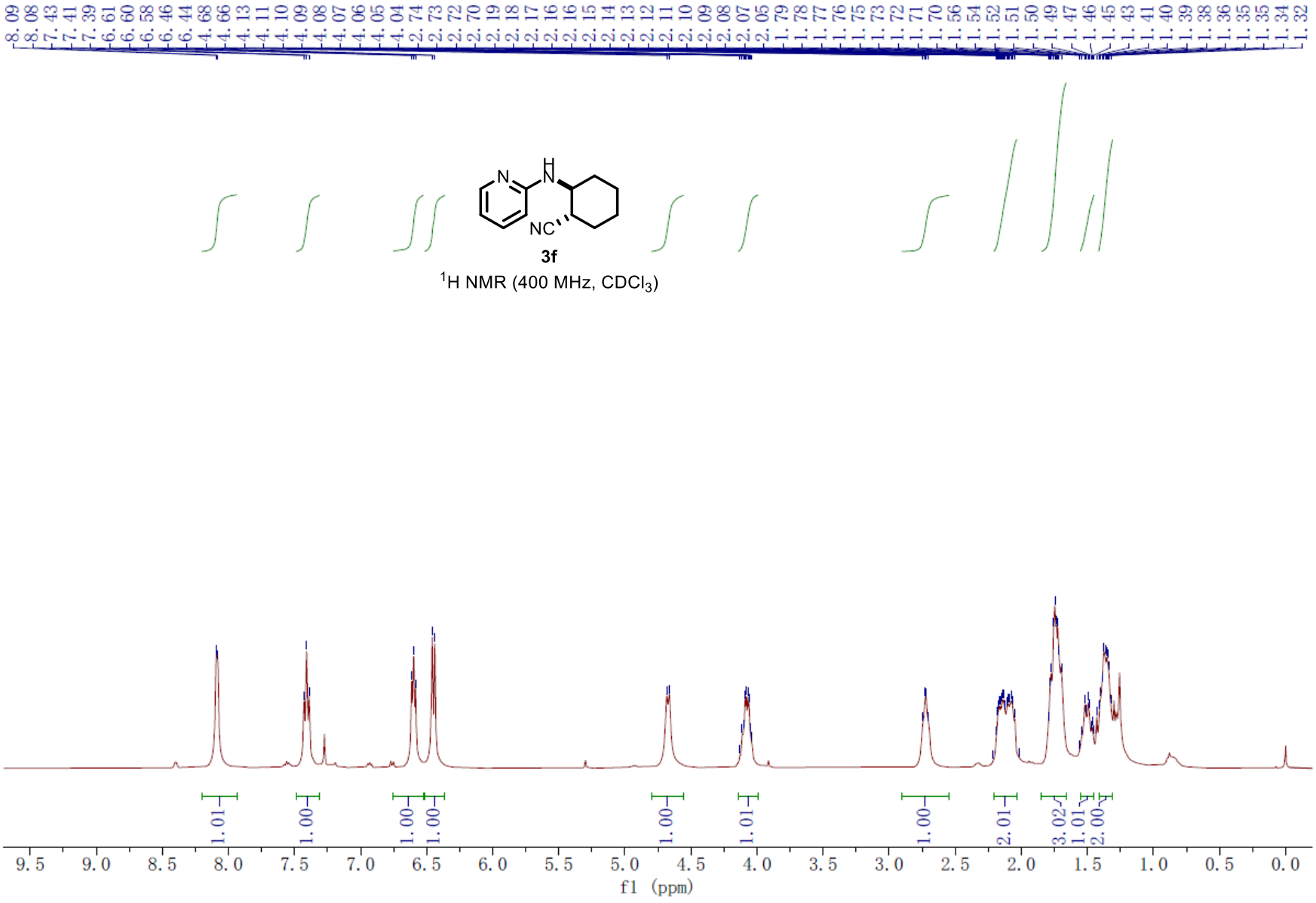
^{1}H NMR (400 MHz, $CDCl_3$)



3e-*trans*

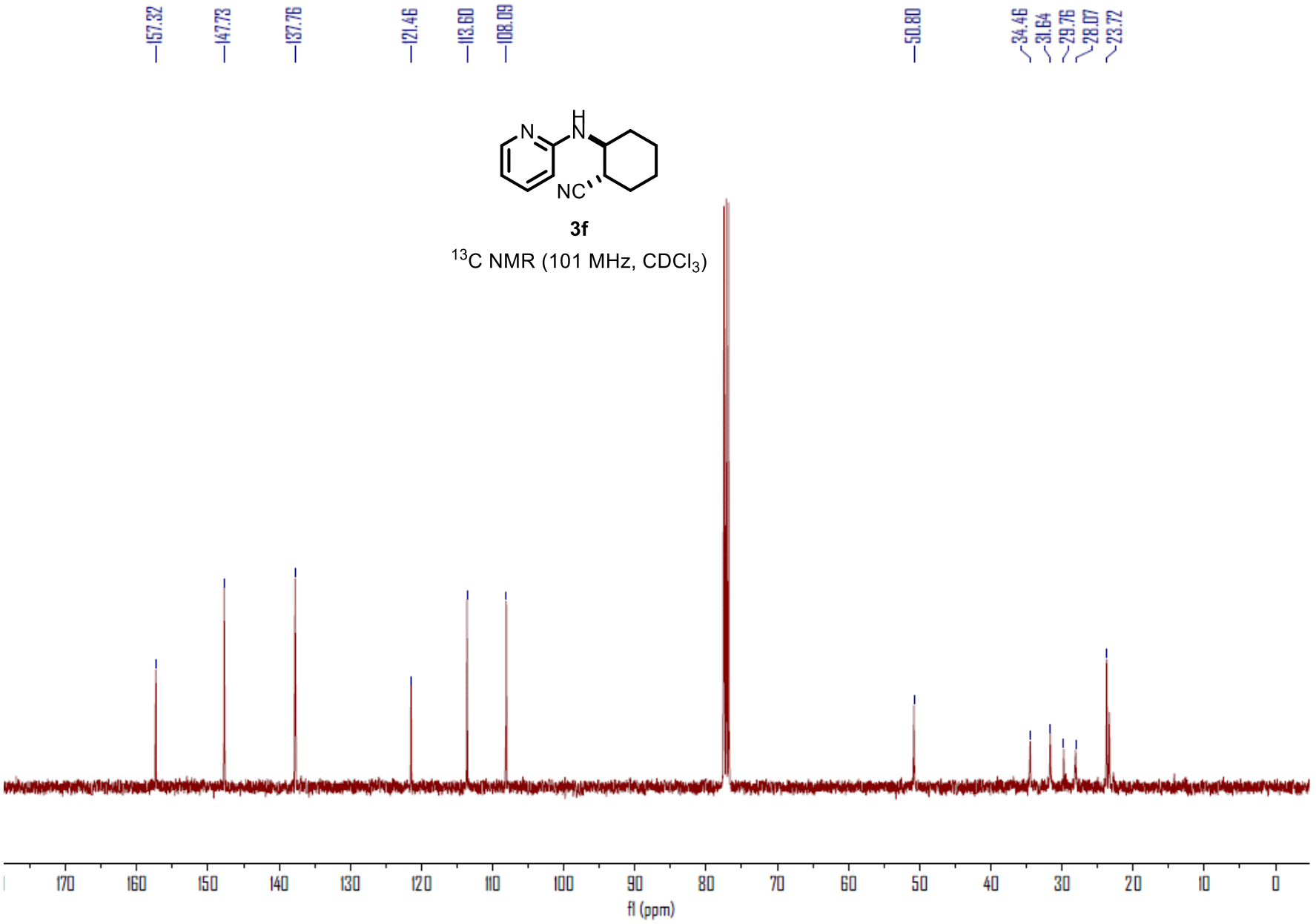
^{13}C NMR (101 MHz, $CDCl_3$)

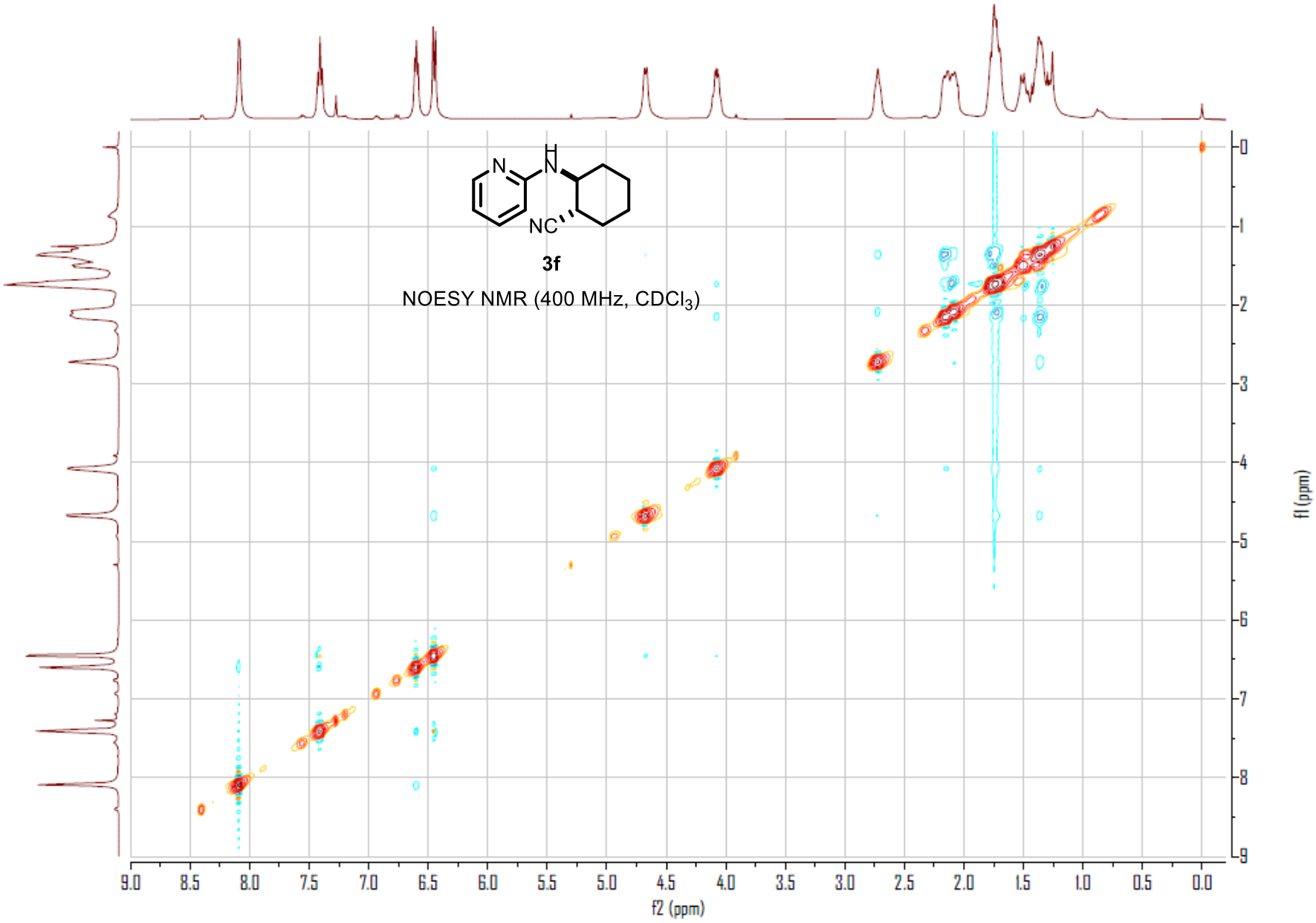

H
N
NC
3e-*tans*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)

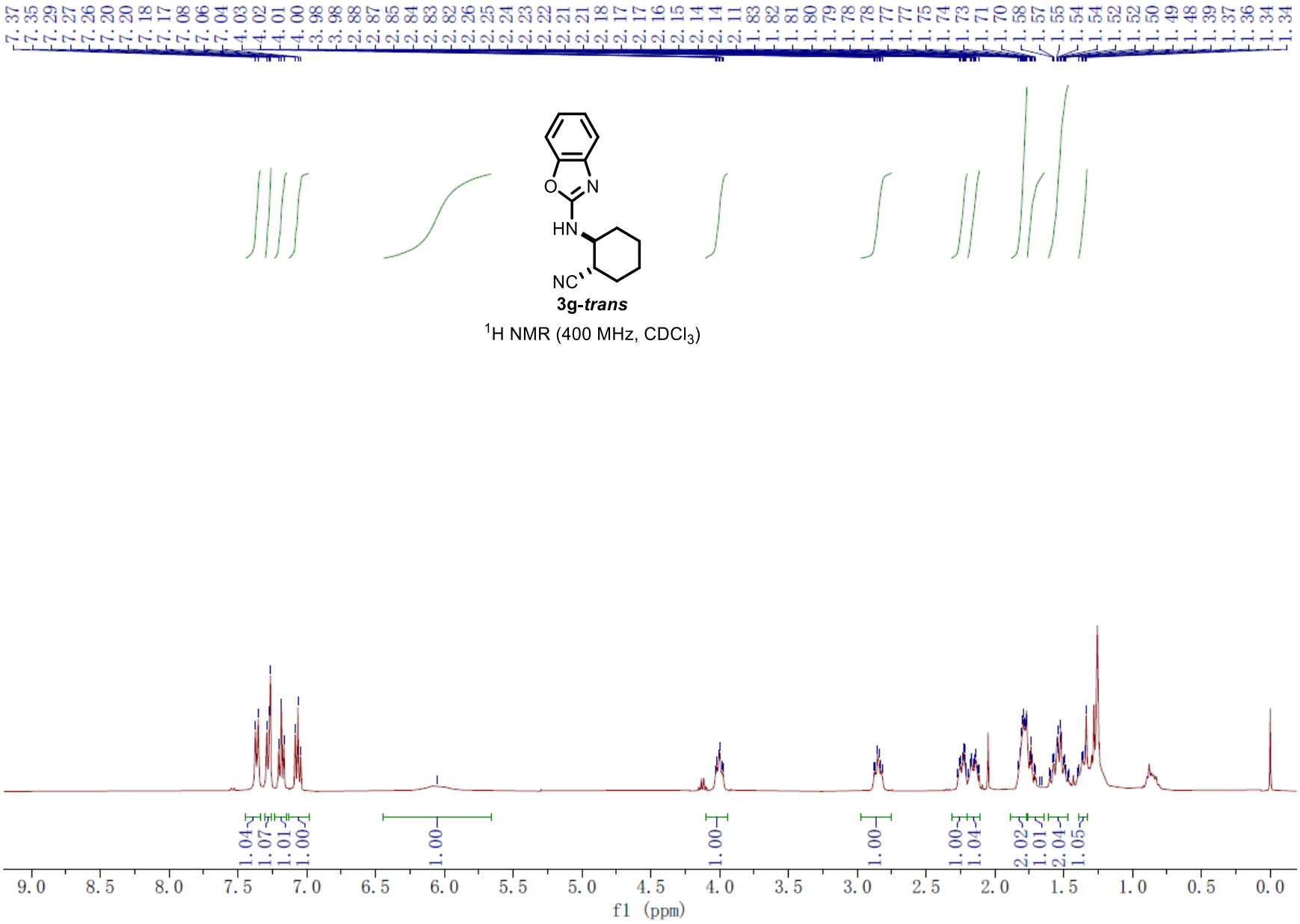


3f

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

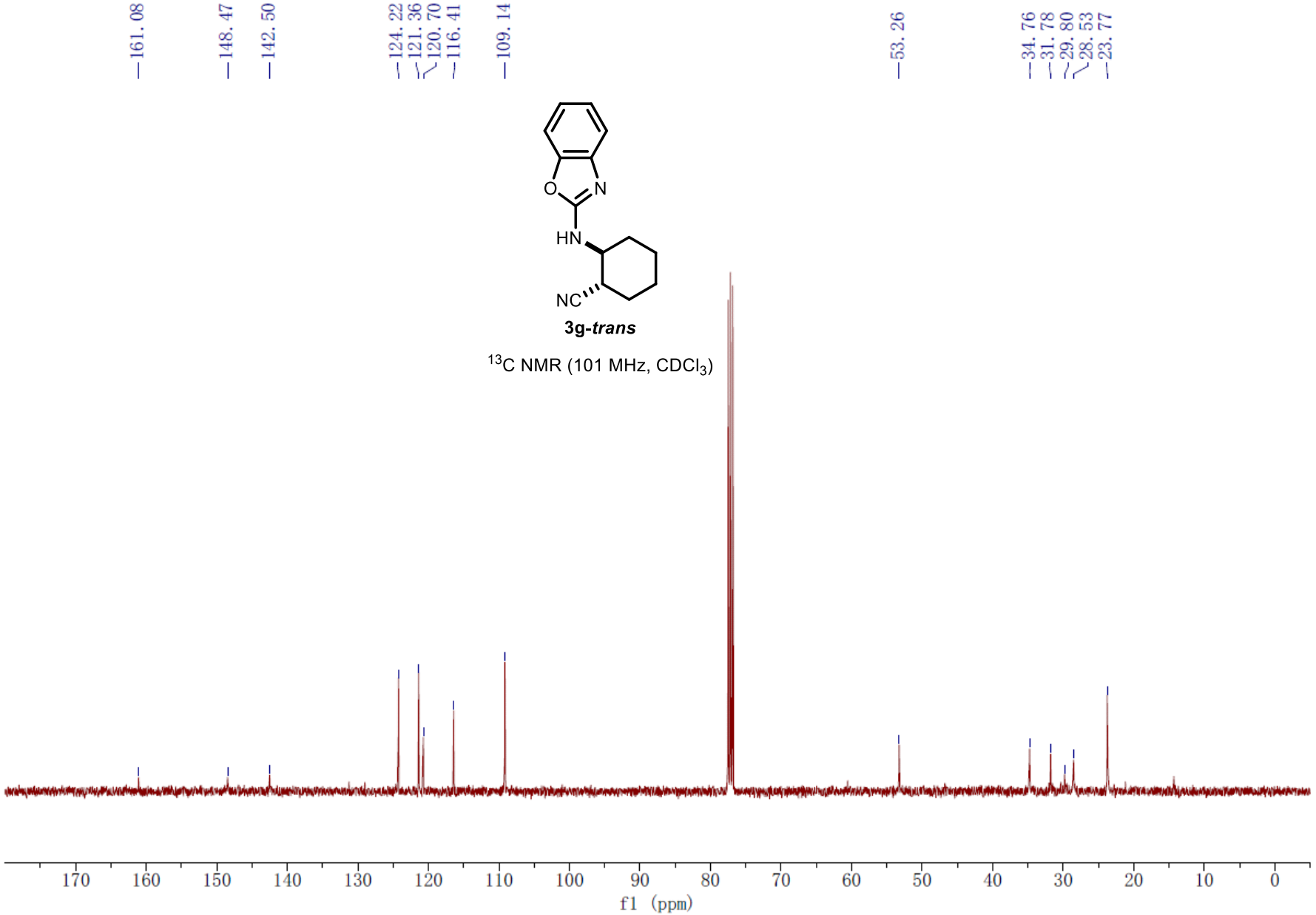

157.32
147.73
137.76
121.46
113.60
108.09
50.80
34.46
31.64
29.76
28.07
23.72
N
H
N
NC
3f
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

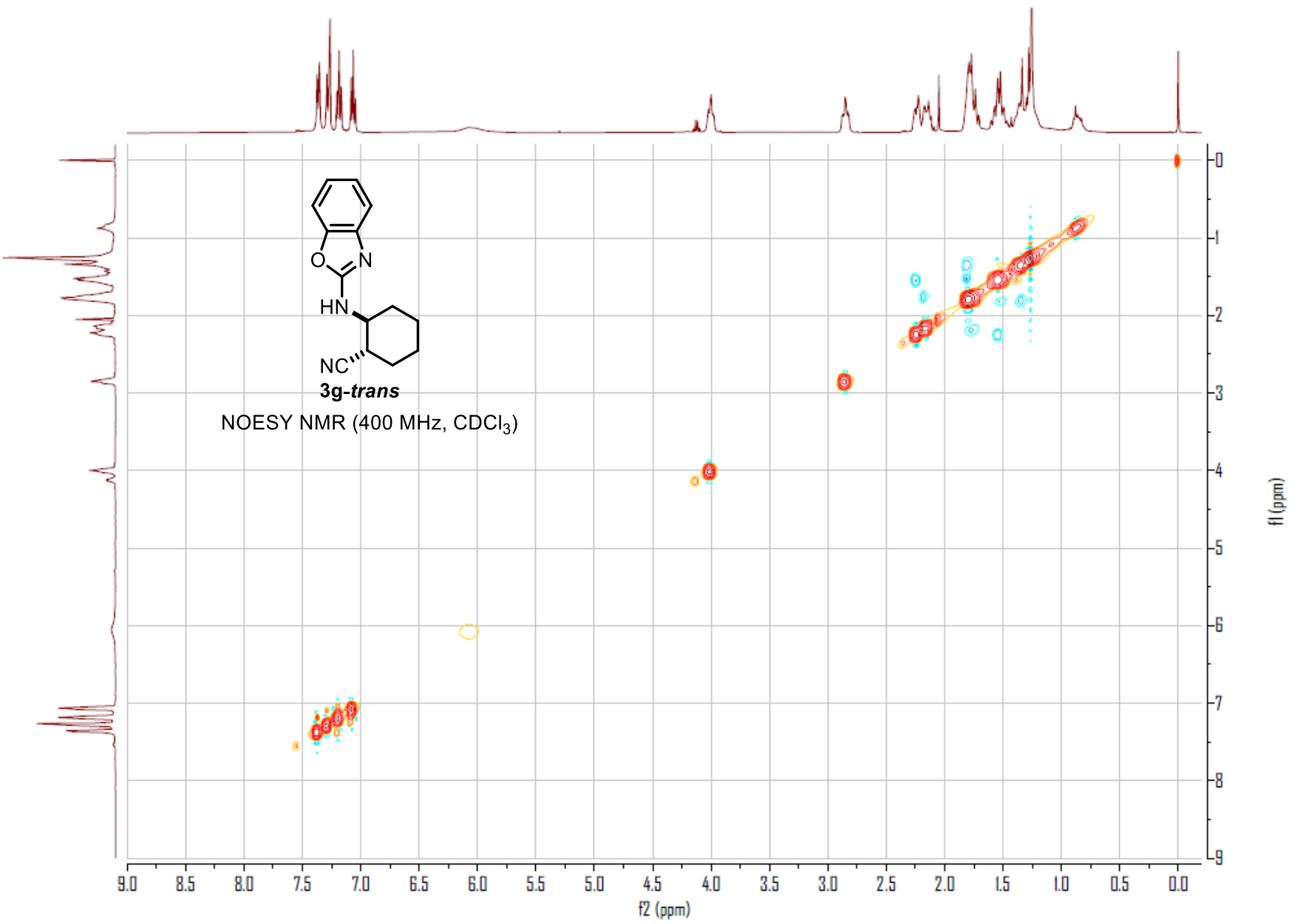

N
H
N
NC
3f
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

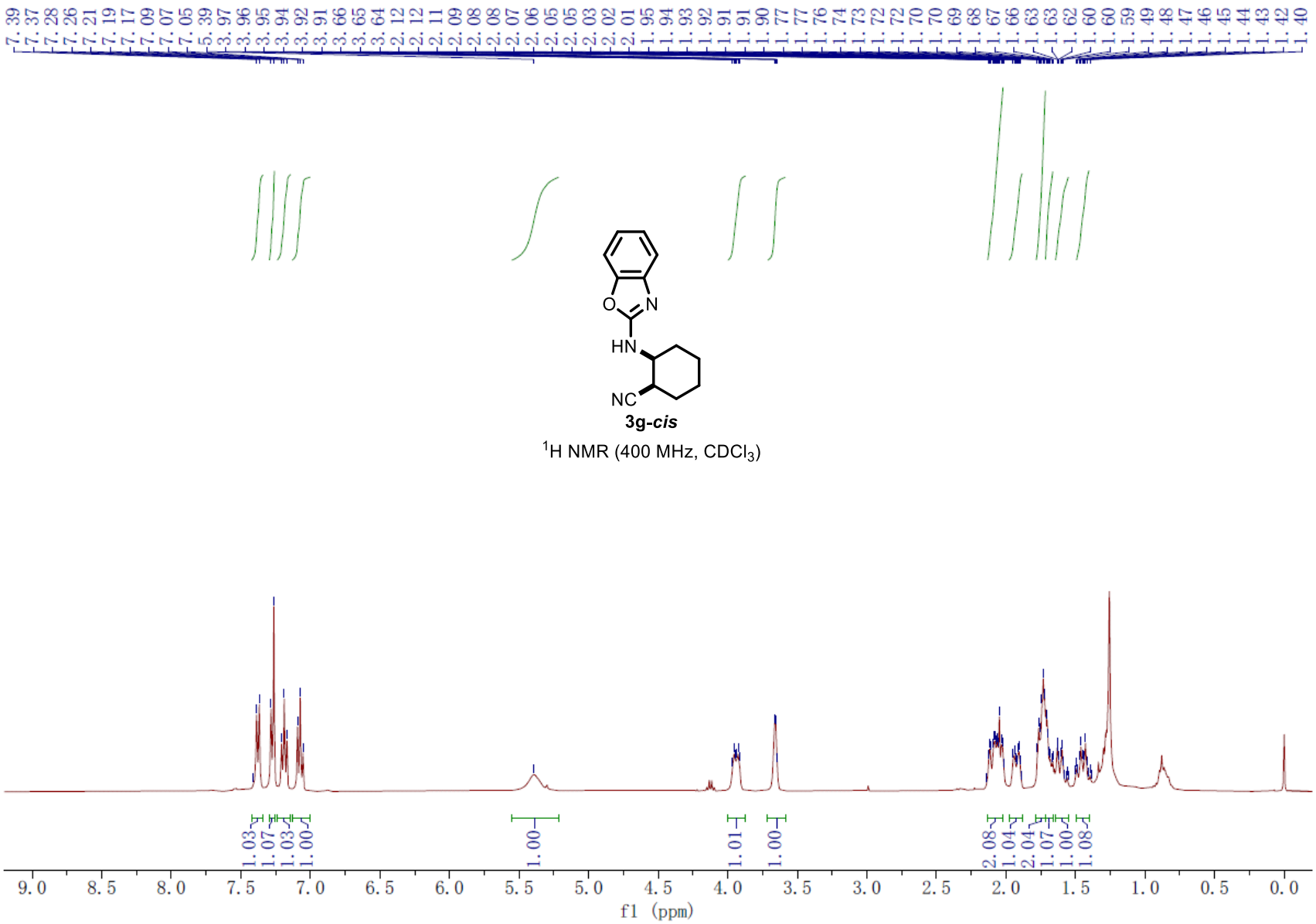


3g-*trans*

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

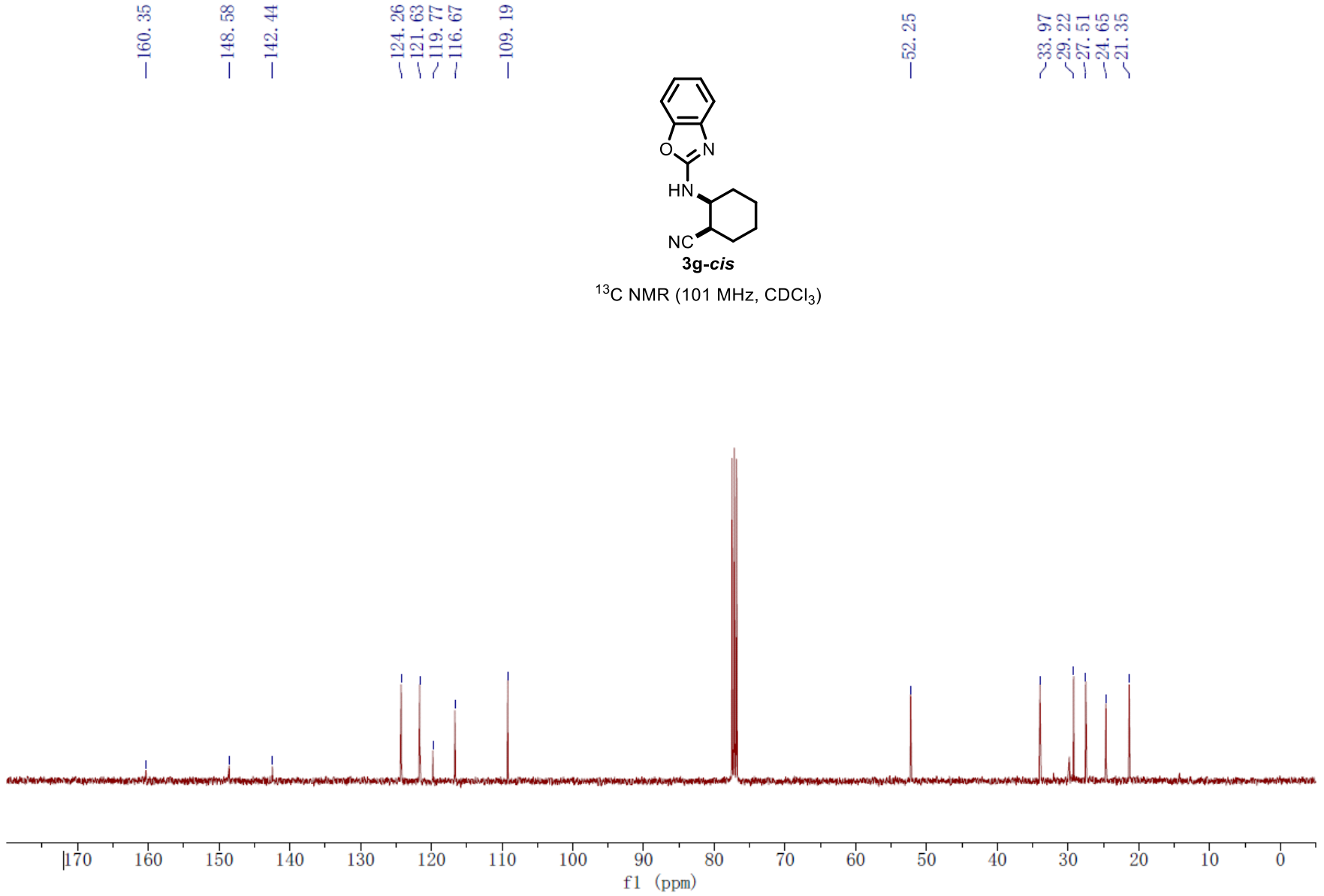

161.08
148.47
142.50
124.22
121.36
120.70
116.41
109.14
53.26
34.76
31.78
29.80
28.53
23.77
O
N
HN
NC
3g-trans
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
HN
NC
3g-*trans*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)



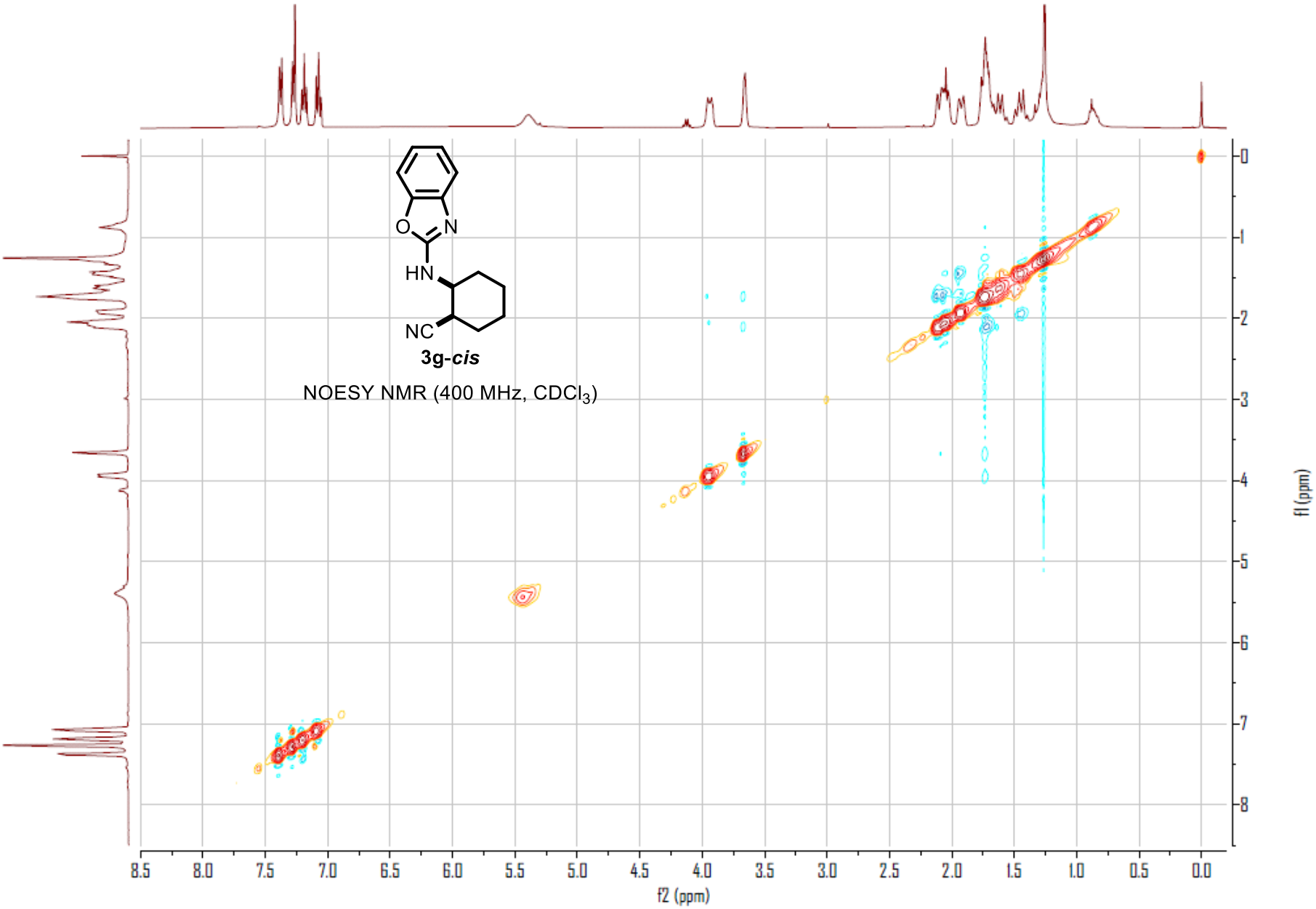
3g-*cis*

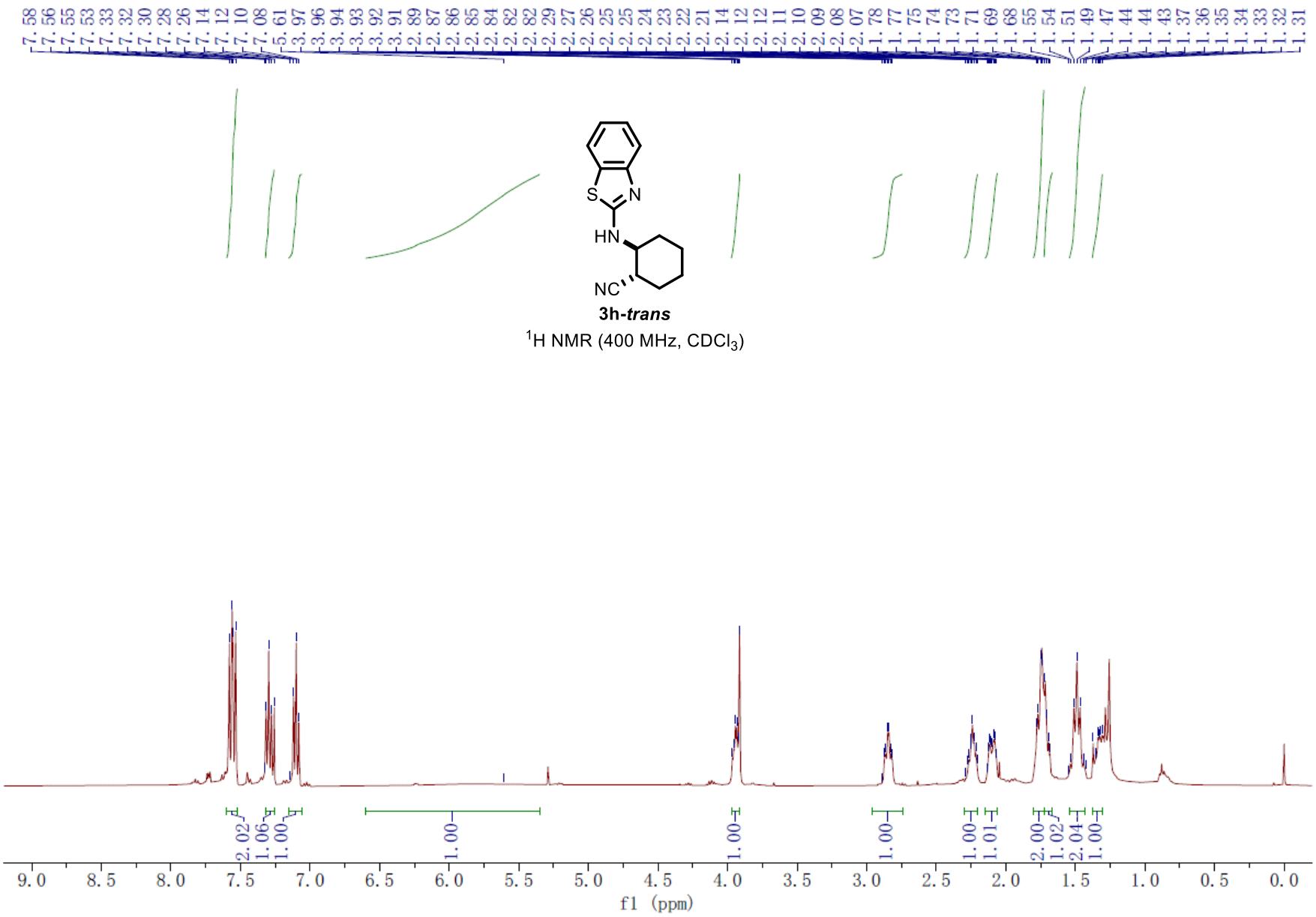
^{1}H NMR (400 MHz, $CDCl_3$)



3g-*cis*

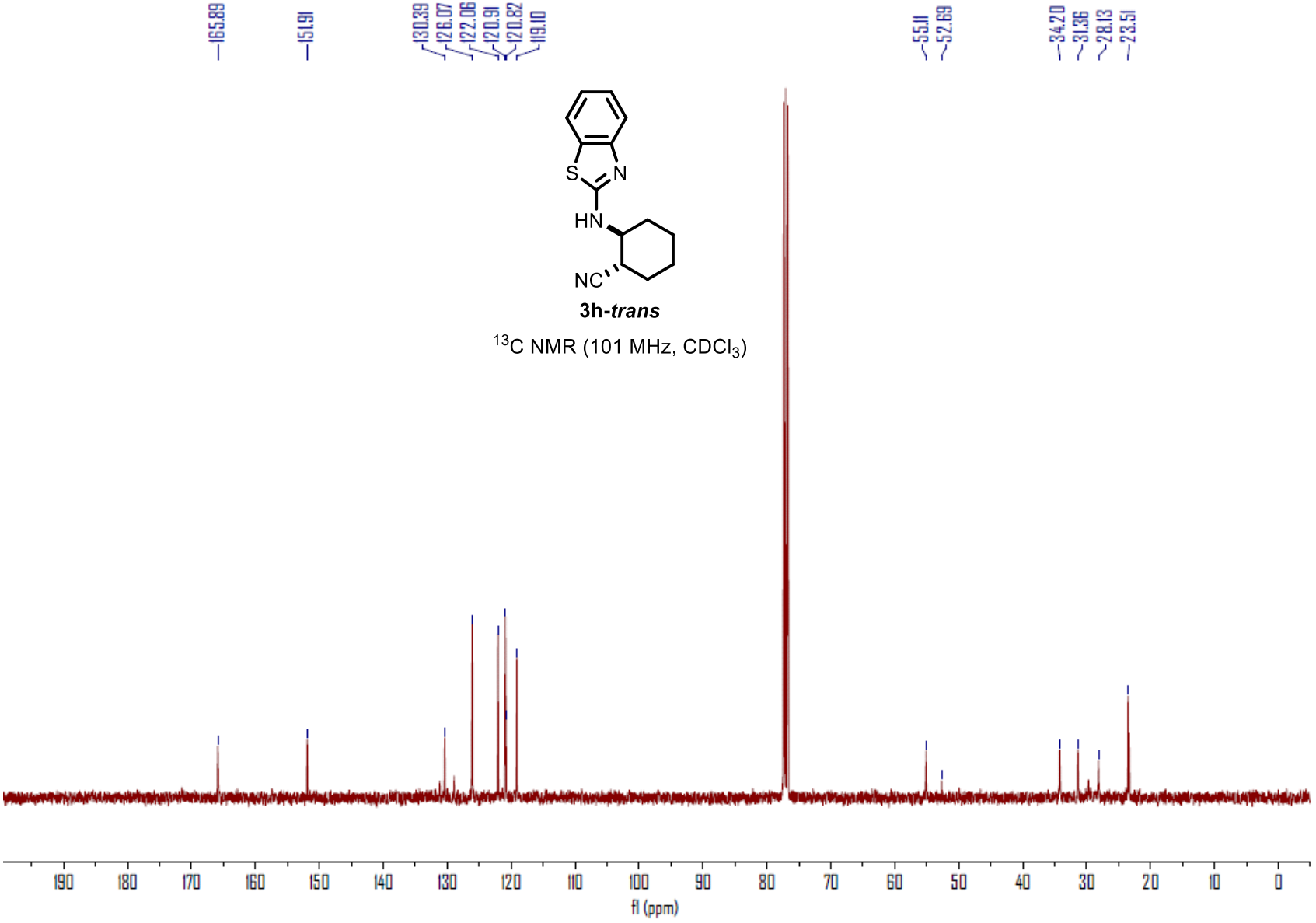
^{13}C NMR (101 MHz, $CDCl_3$)

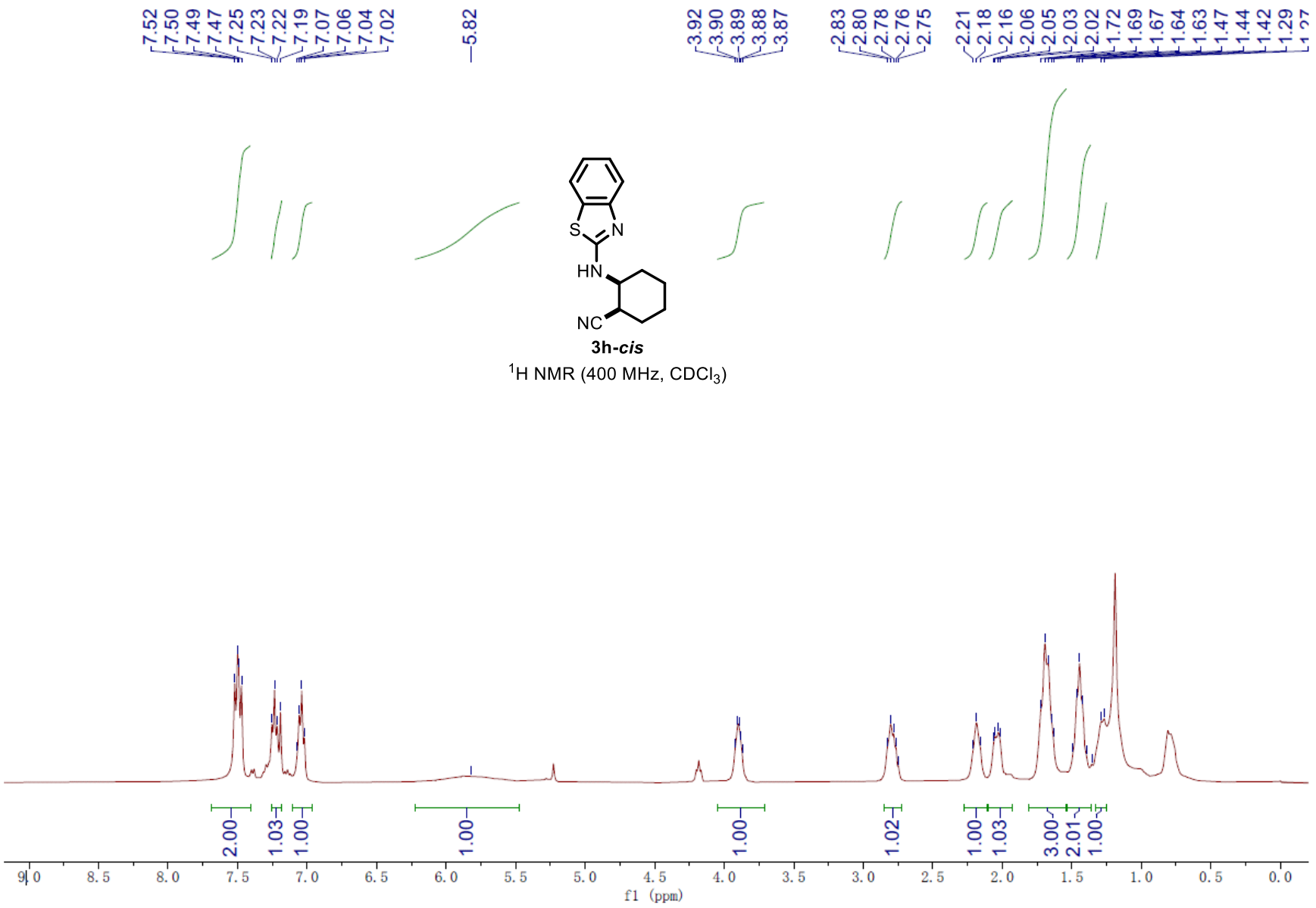

O
N
HN
NC
3g-*cis*
NOESY NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)



3h-*trans*

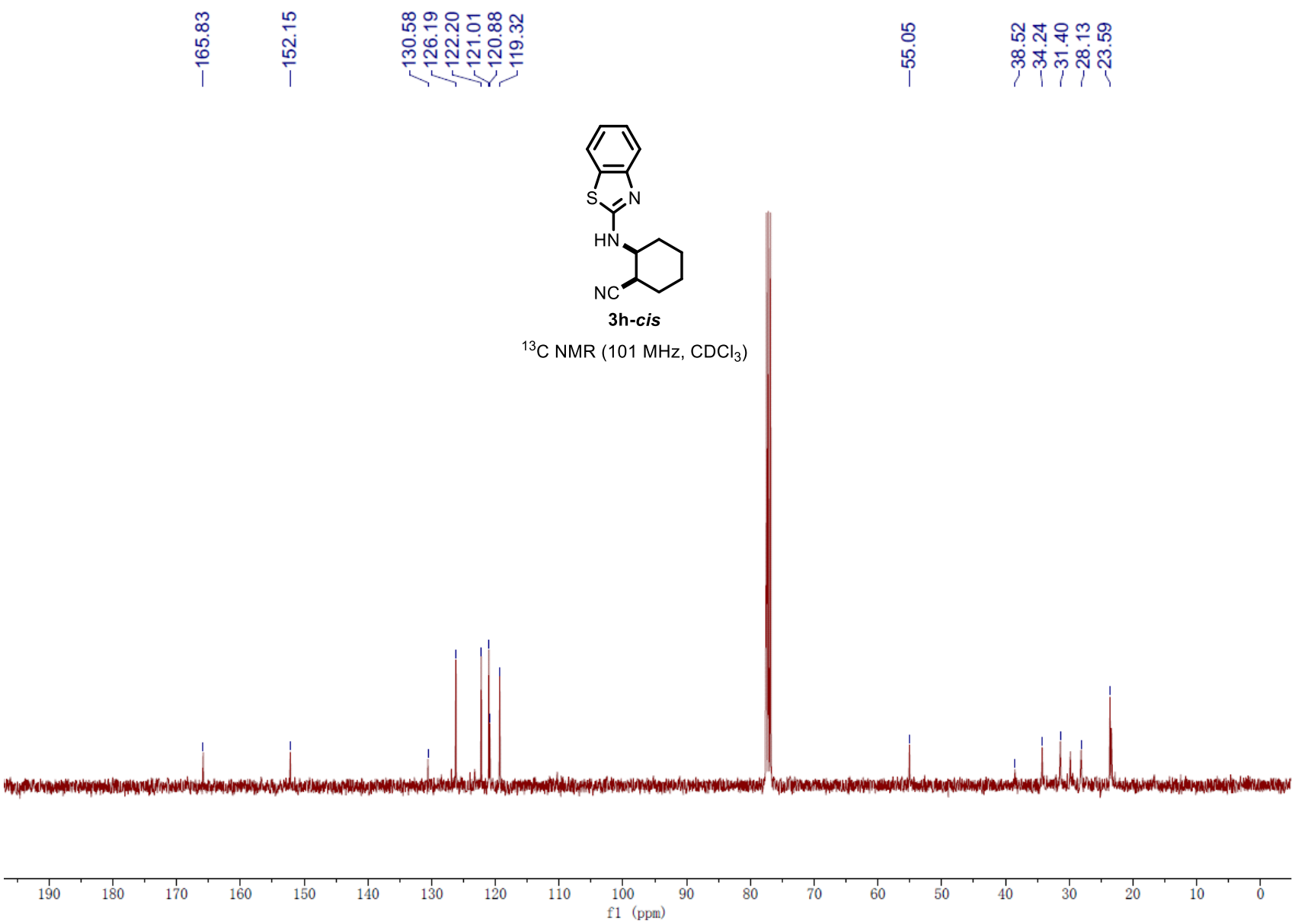
^{1}H NMR (400 MHz, $CDCl_3$)

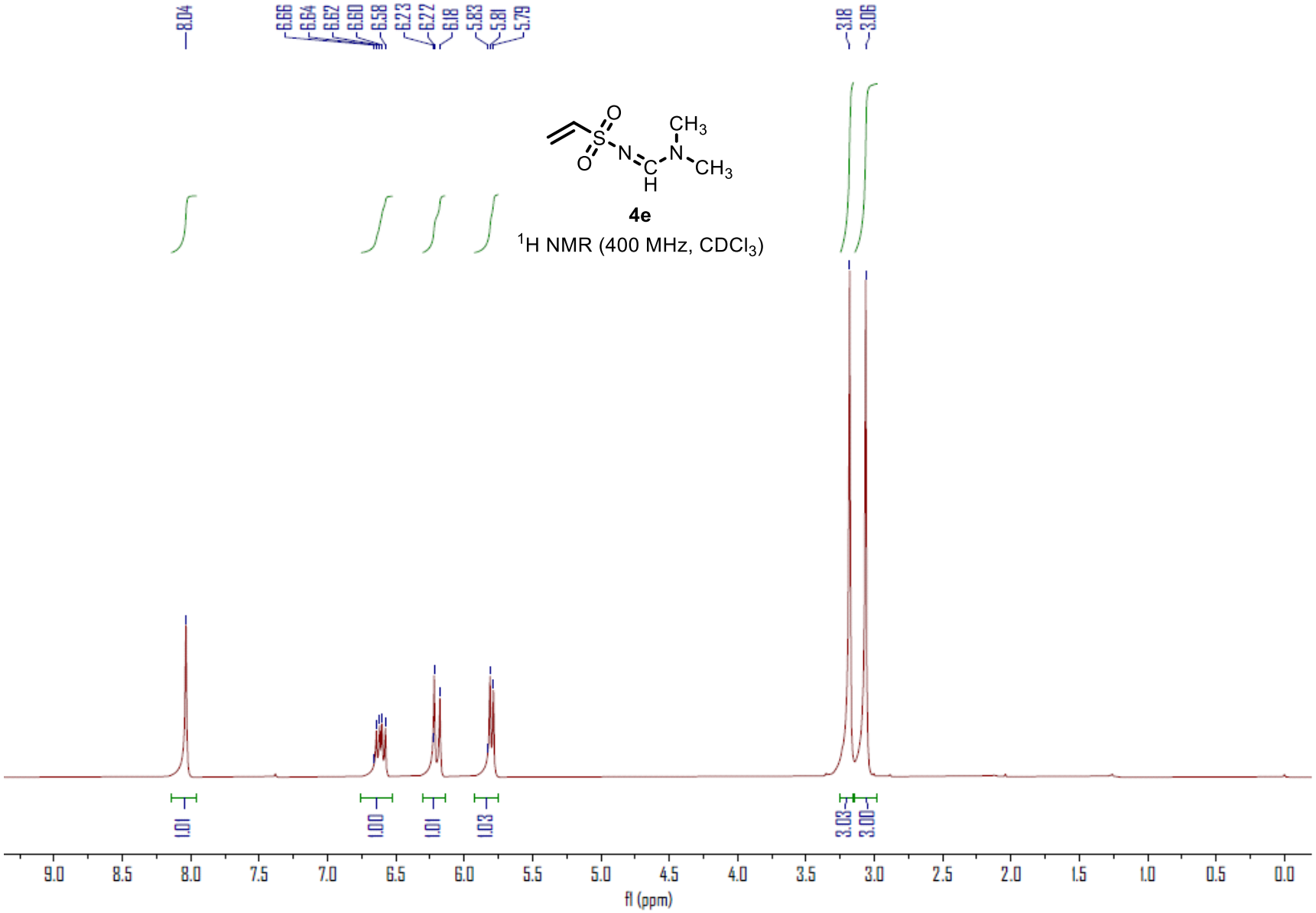

165.89
151.91
130.39
126.07
122.06
120.91
120.82
119.10
55.11
52.69
34.20
31.36
28.13
23.51
S
N
HN
NC
3h-trans
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

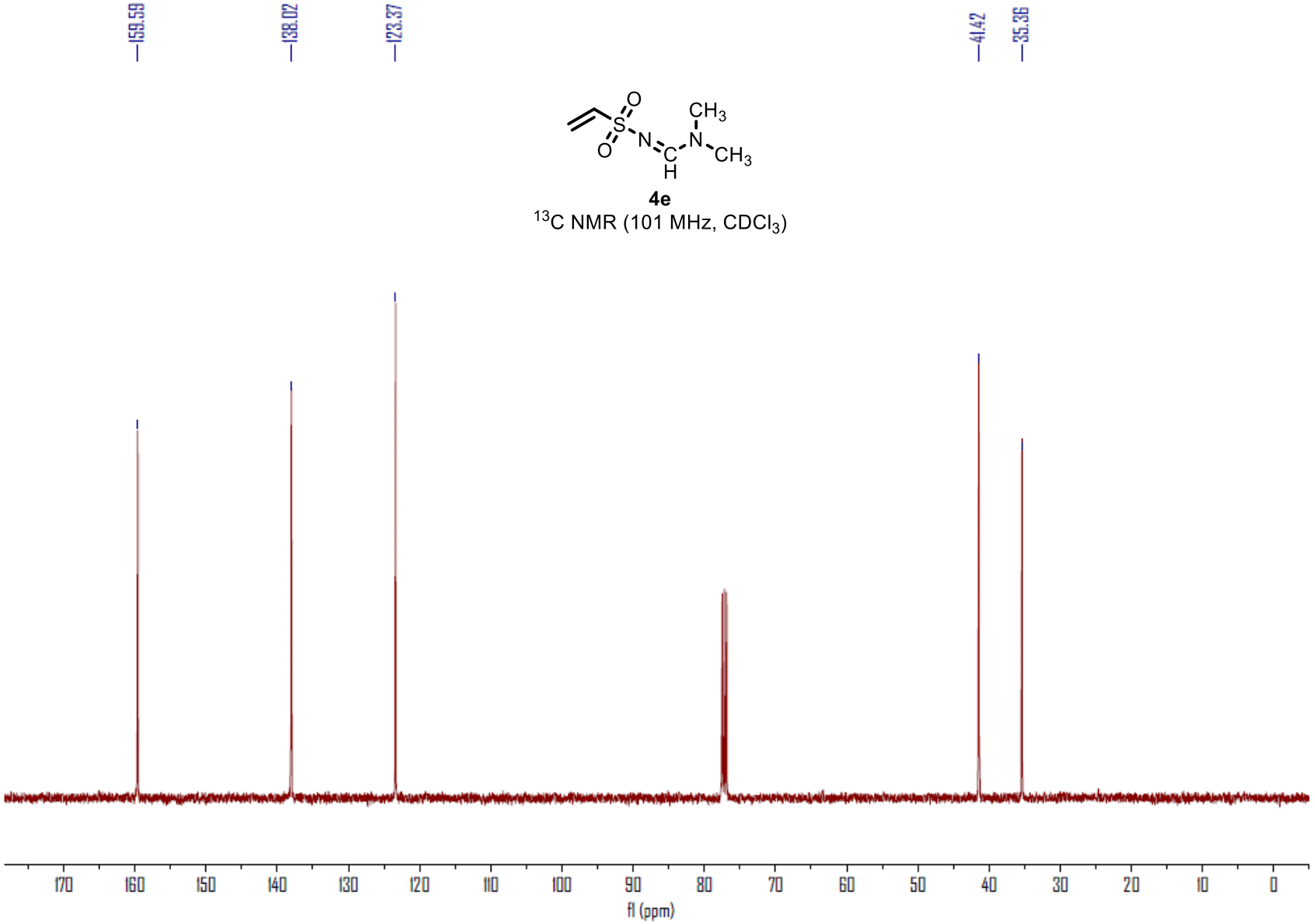


3h-*cis*

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

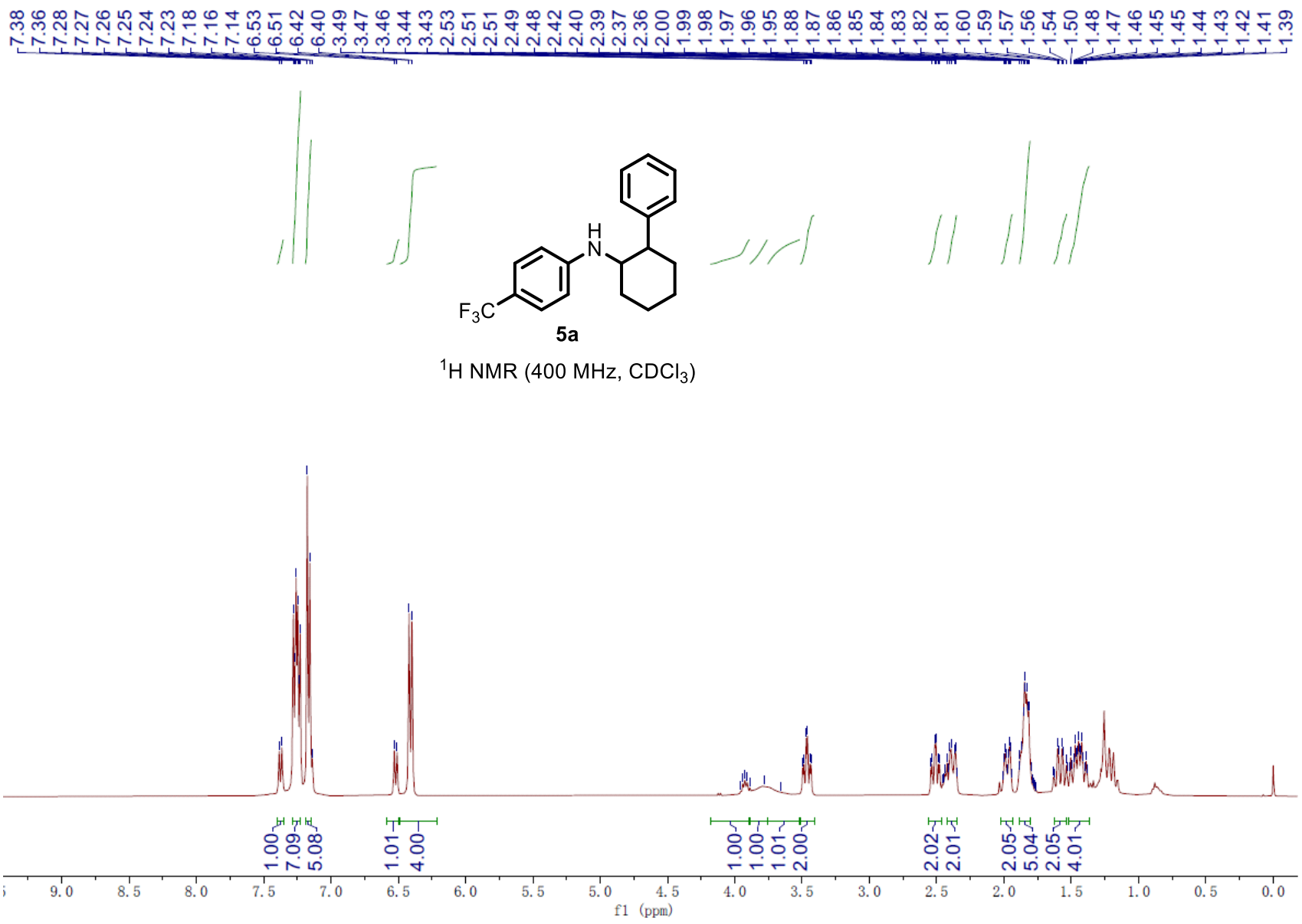

165.83
152.15
130.58
126.19
122.20
121.01
120.88
119.32
55.05
38.52
34.24
31.40
28.13
23.59
S
N
HN
NC
3h-cis
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.04
6.66
6.64
6.62
6.60
6.58
6.23
6.22
6.18
5.83
5.81
5.79
3.18
3.06
O
S
O
N
C
H
CH3
N
CH3
4e
1H NMR (400 MHz, CDCl3)
1.01
1.00
1.01
1.03
3.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

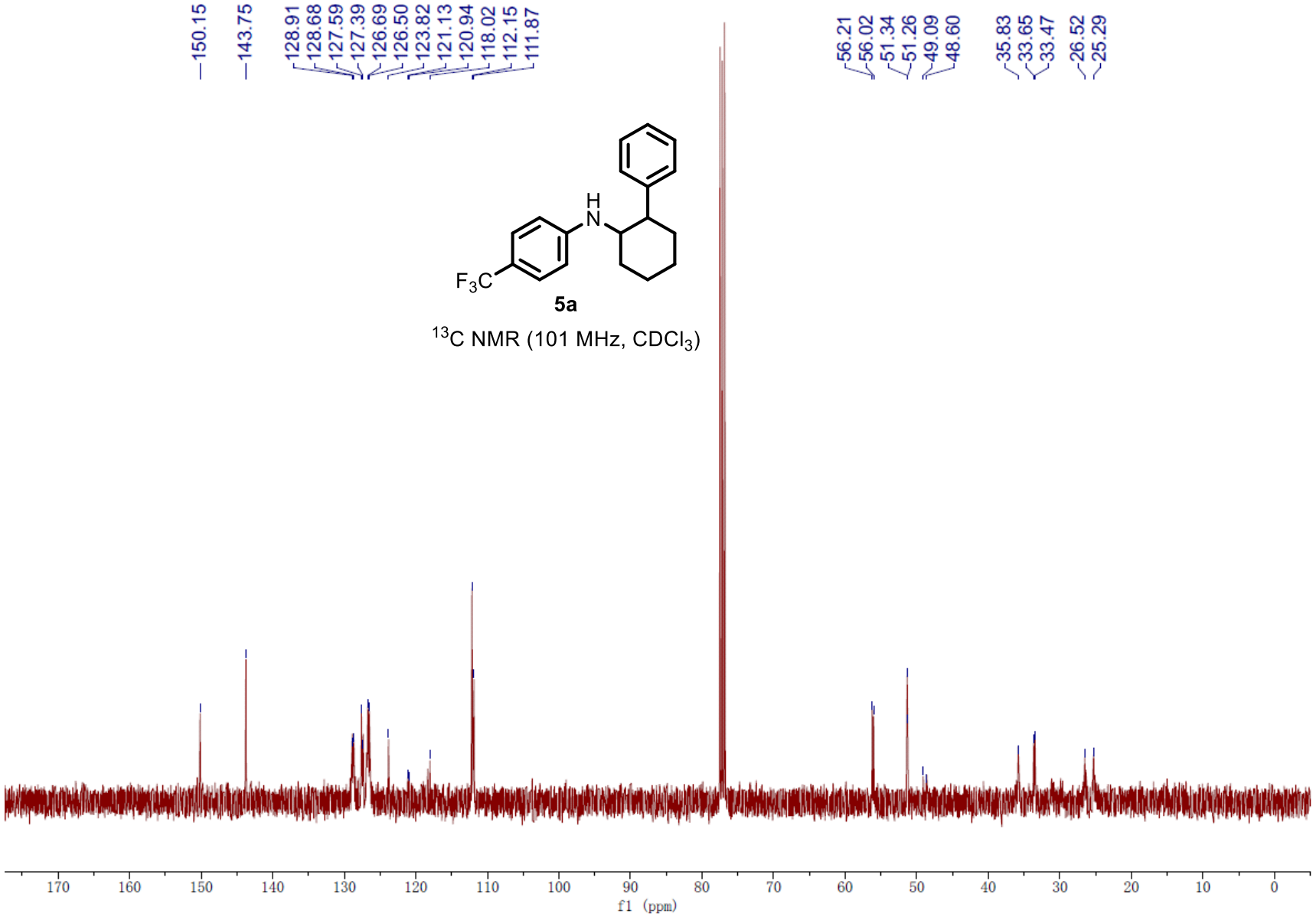


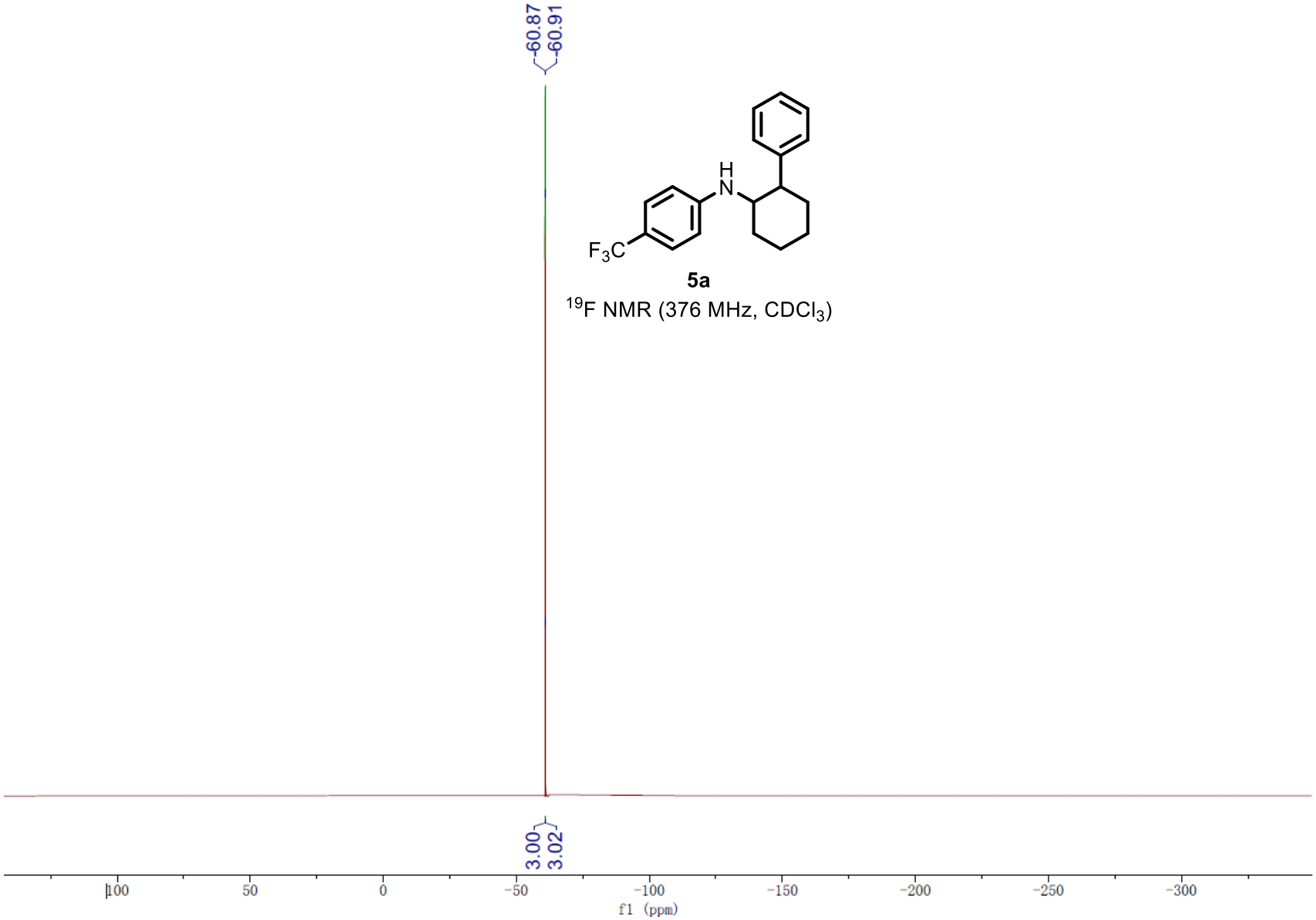
4e

^{13}C NMR (101 MHz, $CDCl_3$)



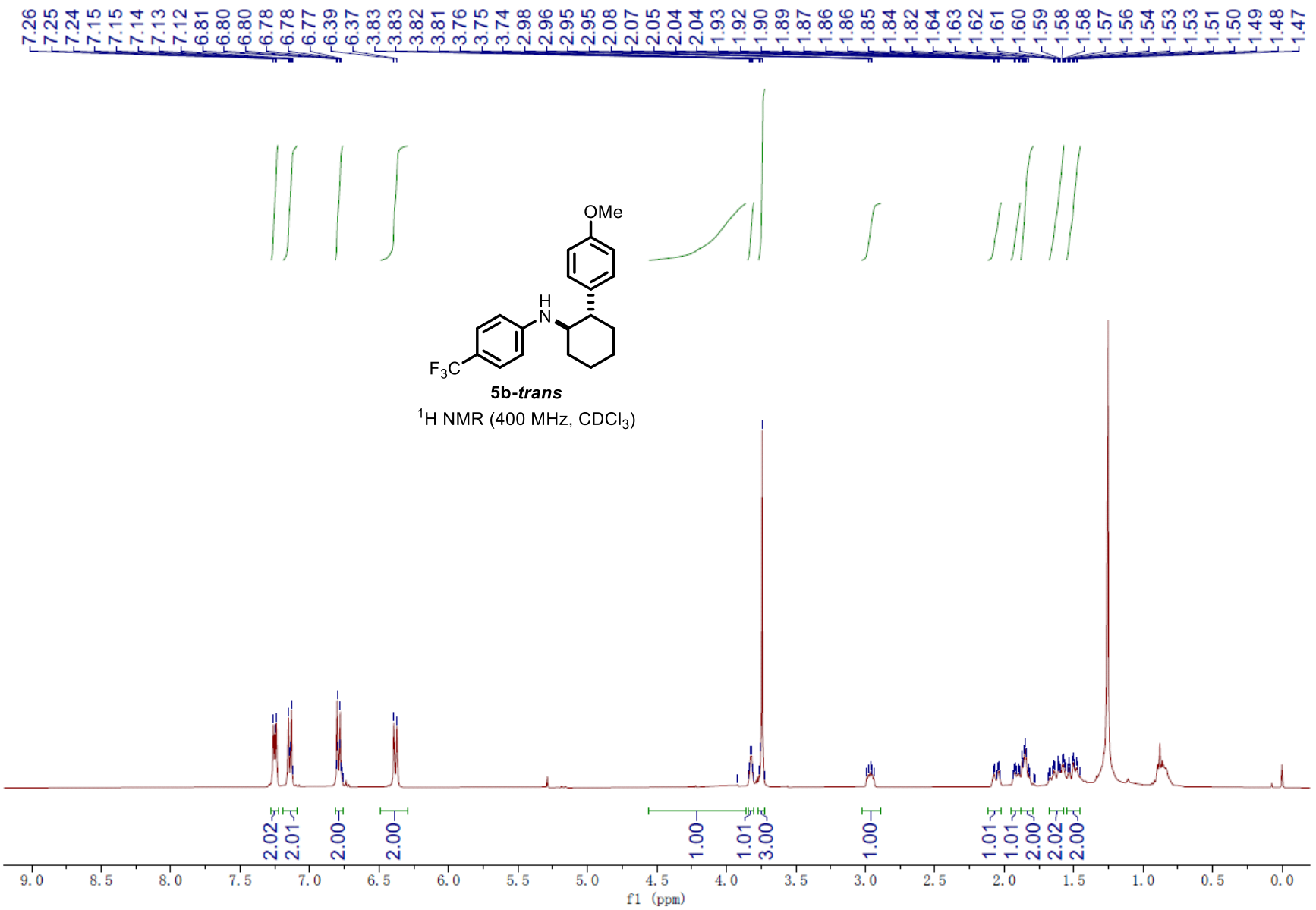
^{1}H NMR (400 MHz, $CDCl_3$)

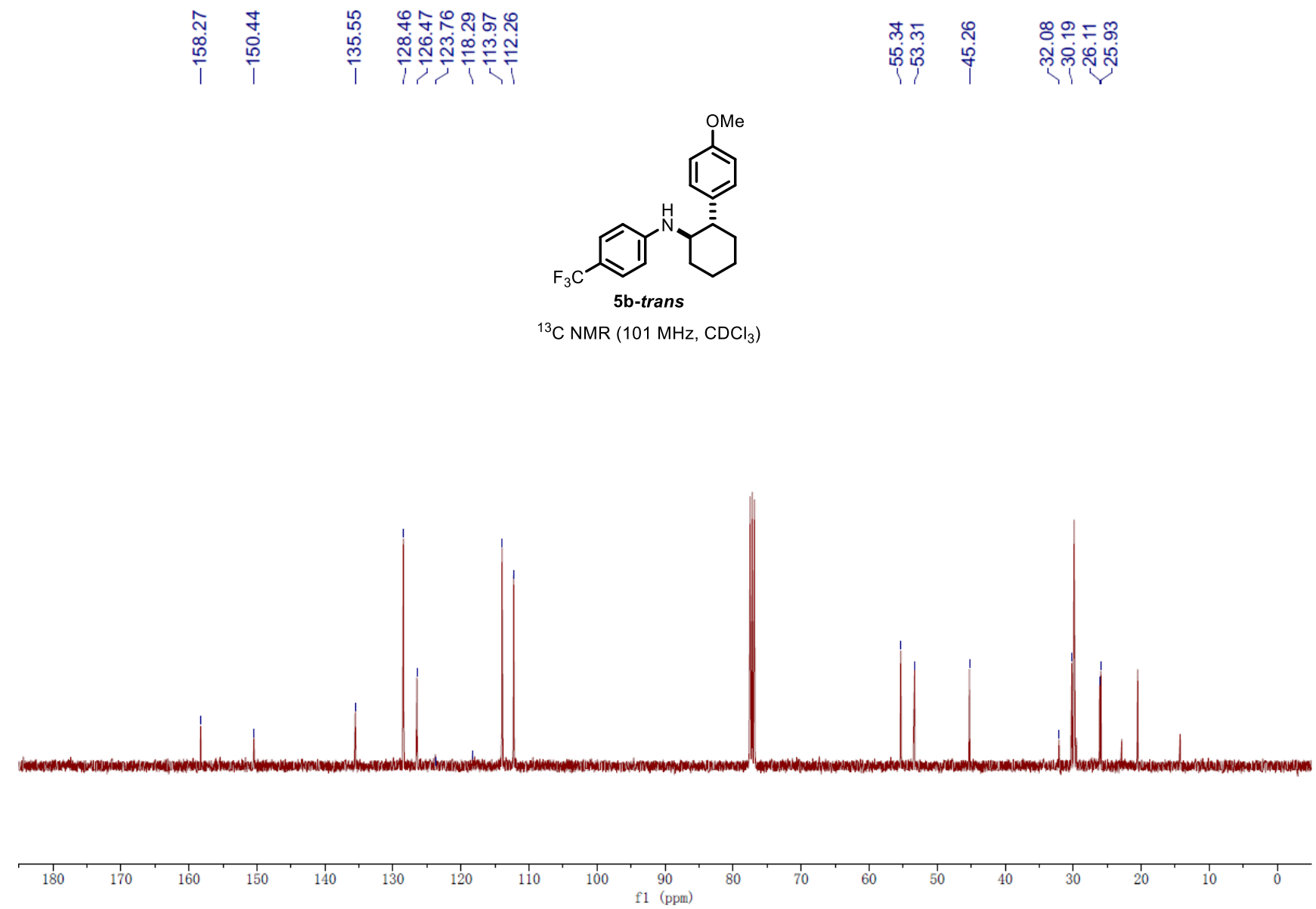

150.15
143.75
128.91
128.68
127.59
127.39
126.69
126.50
123.82
121.13
120.94
118.02
112.15
111.87
56.21
56.02
51.34
51.26
49.09
48.60
35.83
33.65
33.47
26.52
25.29
H
N
F3C
5a
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5a

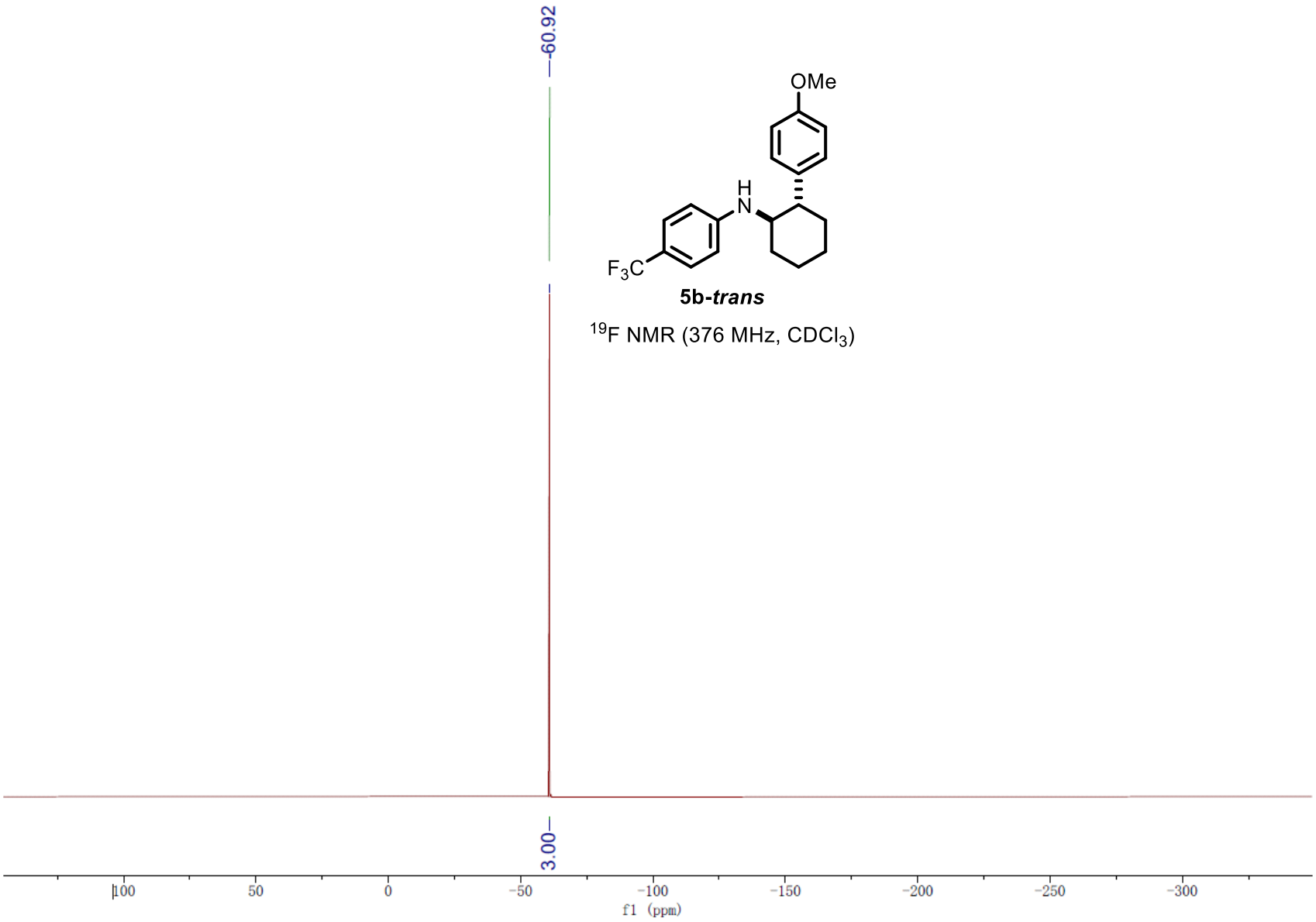
^{19}F NMR (376 MHz, $CDCl_3$)


7.26 7.25 7.24 7.15 7.15 7.14 7.13 7.12 6.81 6.80 6.80 6.78 6.78 6.77 6.39 6.37 3.83 3.83 3.82 3.81 3.76 3.75 3.74 2.98 2.96 2.95 2.95 2.08 2.07 2.05 2.04 2.04 1.93 1.92 1.90 1.89 1.87 1.86 1.86 1.85 1.84 1.82 1.64 1.63 1.62 1.61 1.60 1.59 1.58 1.58 1.57 1.56 1.54 1.53 1.53 1.51 1.50 1.49 1.48 1.47
OMe
H
N
F3C
5b-trans
1H NMR (400 MHz, CDCl3)
2.02 2.01 2.00 2.00 1.00 1.01 3.00 1.00 1.01 1.01 2.00 2.02 2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



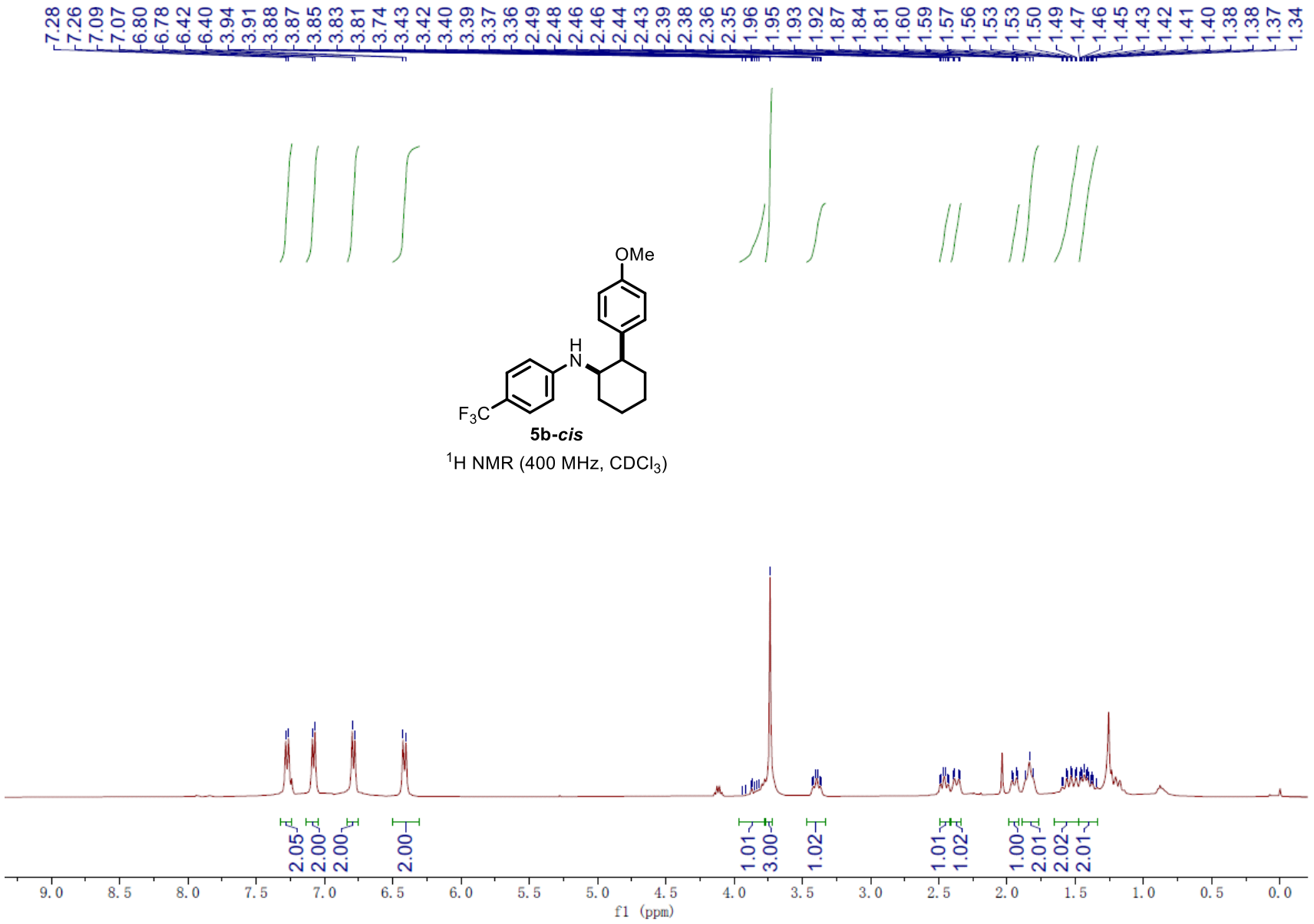
5b-*trans*

^{13}C NMR (101 MHz, $CDCl_3$)



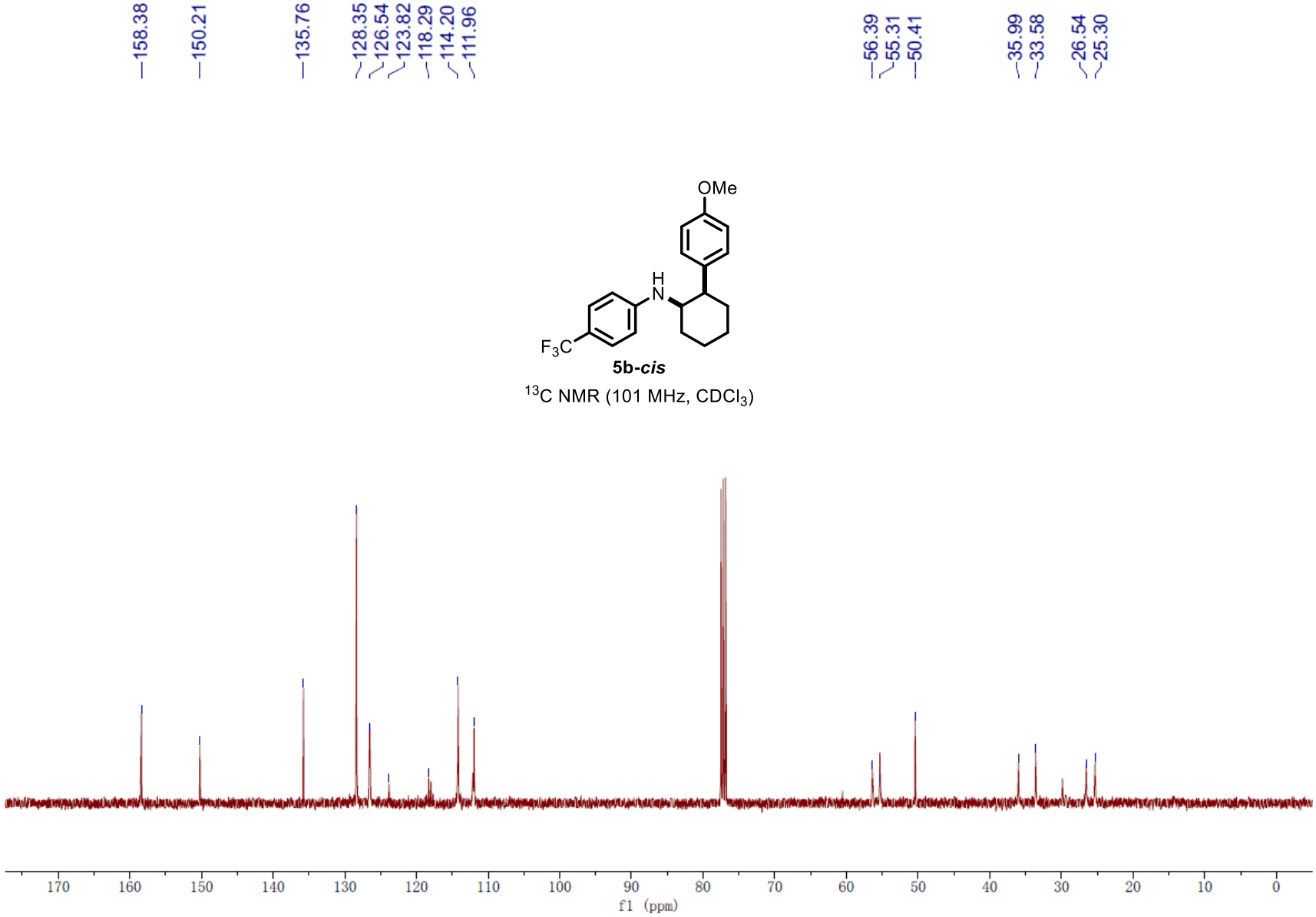
5b-*trans*

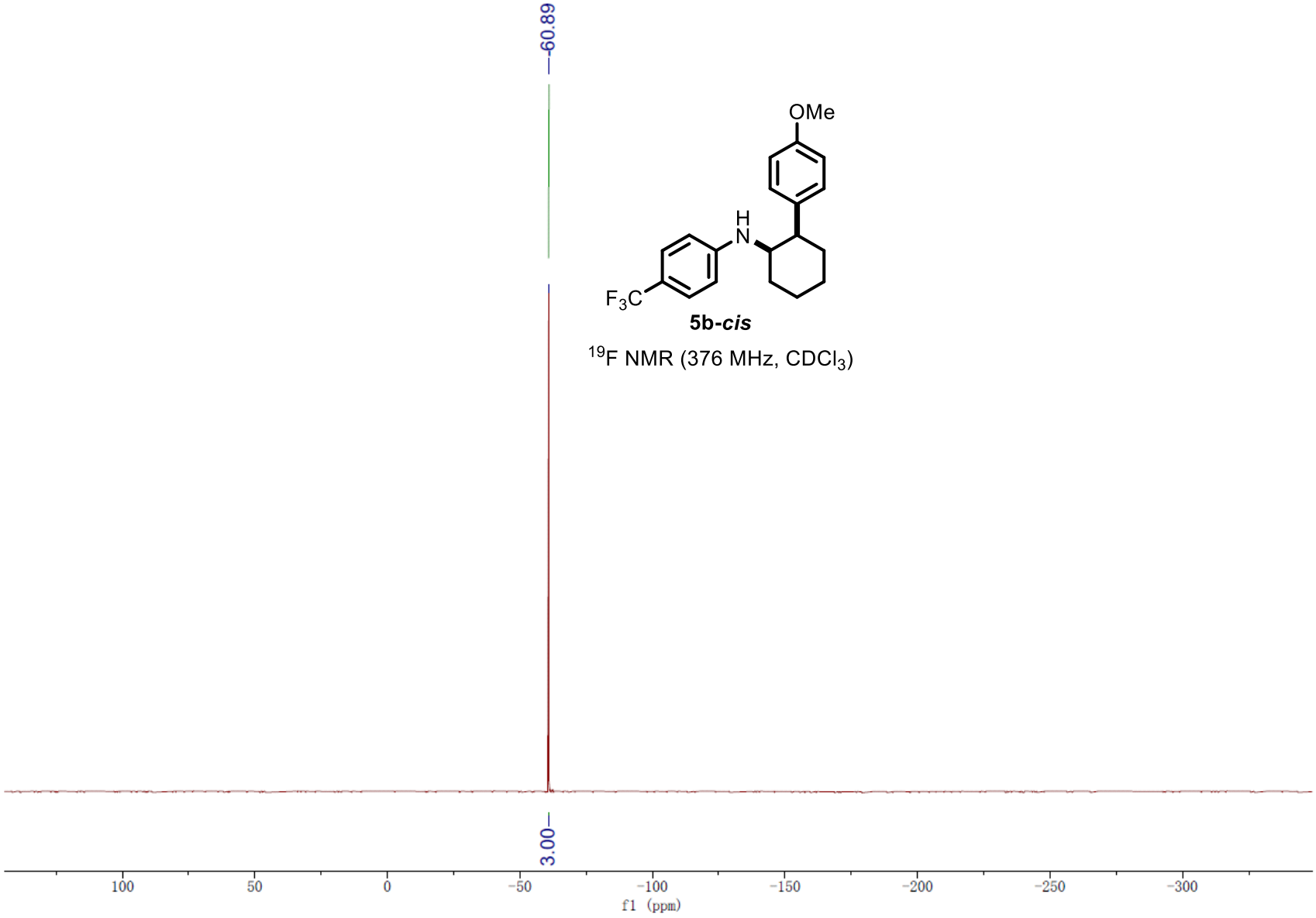
^{19}F NMR (376 MHz, $CDCl_3$)

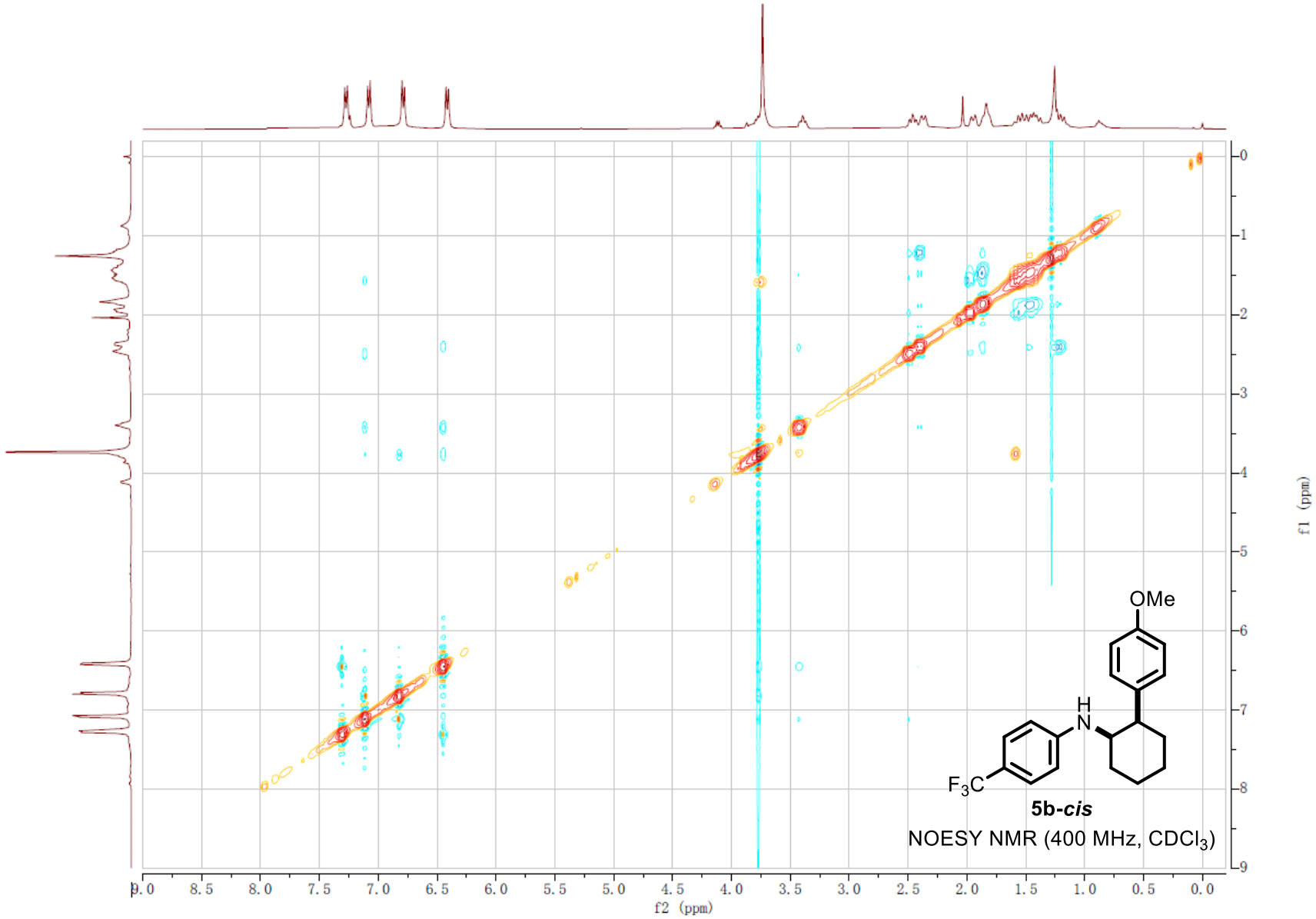


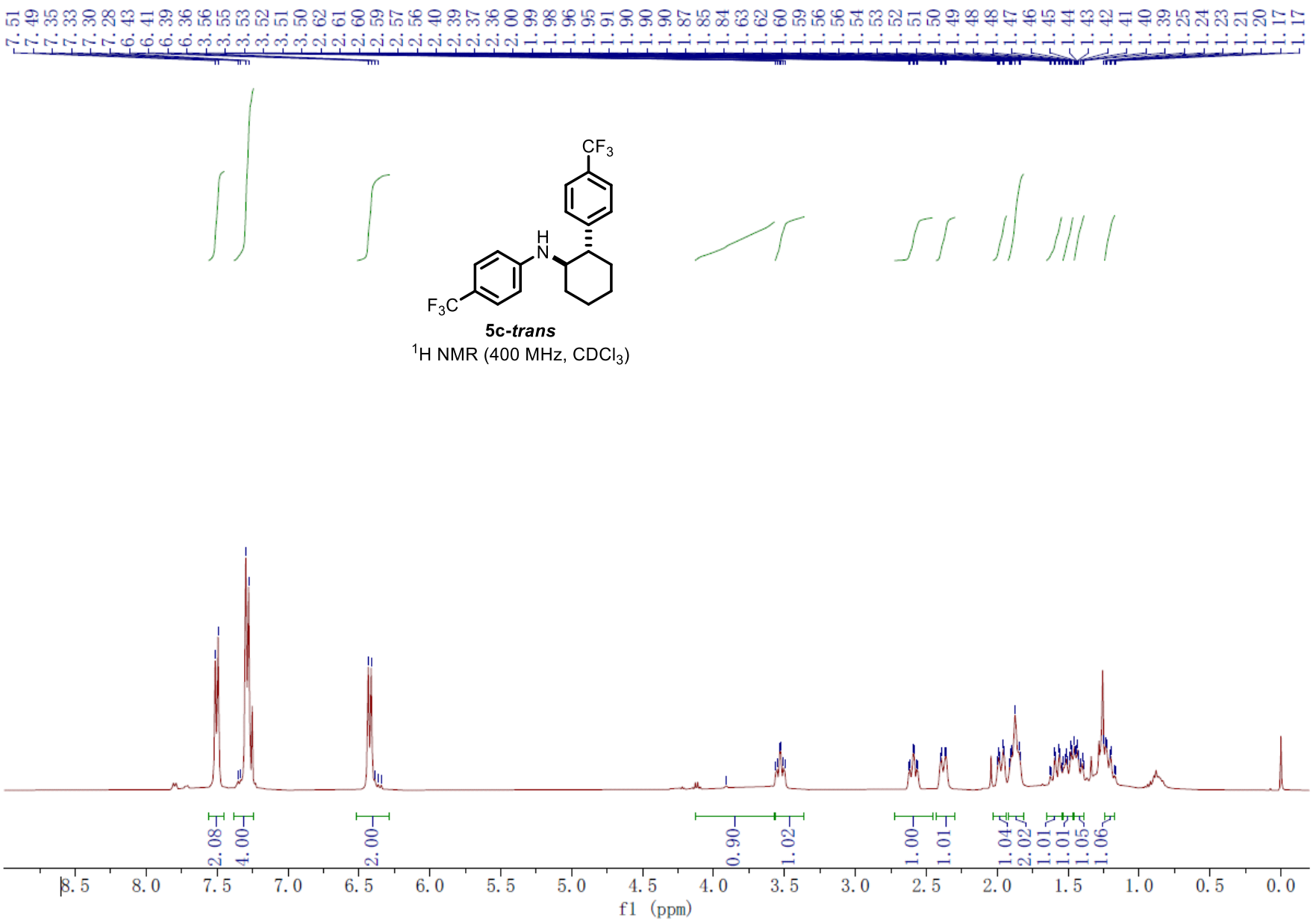
5b-*cis*

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


158.38
150.21
135.76
128.35
126.54
123.82
118.29
114.20
111.96
56.39
55.31
50.41
35.99
33.58
26.54
25.30
OMe
H
N
F3C
5b-cis
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

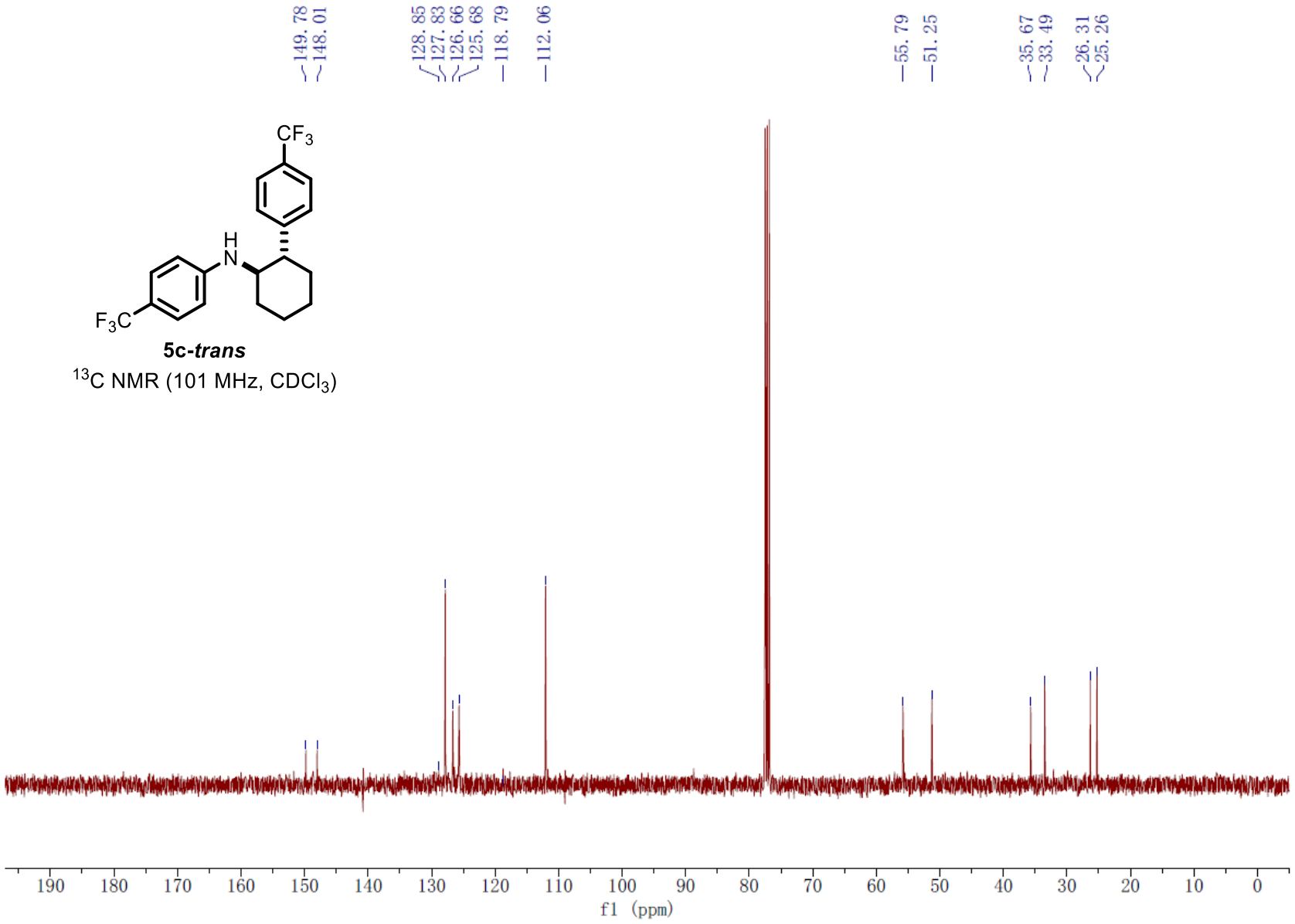

-60.89
OMe
H
N
F3C
5b-cis
19F NMR (376 MHz, CDCl3)
3.00
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


OMe
H
N
F3C
5b-cis
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



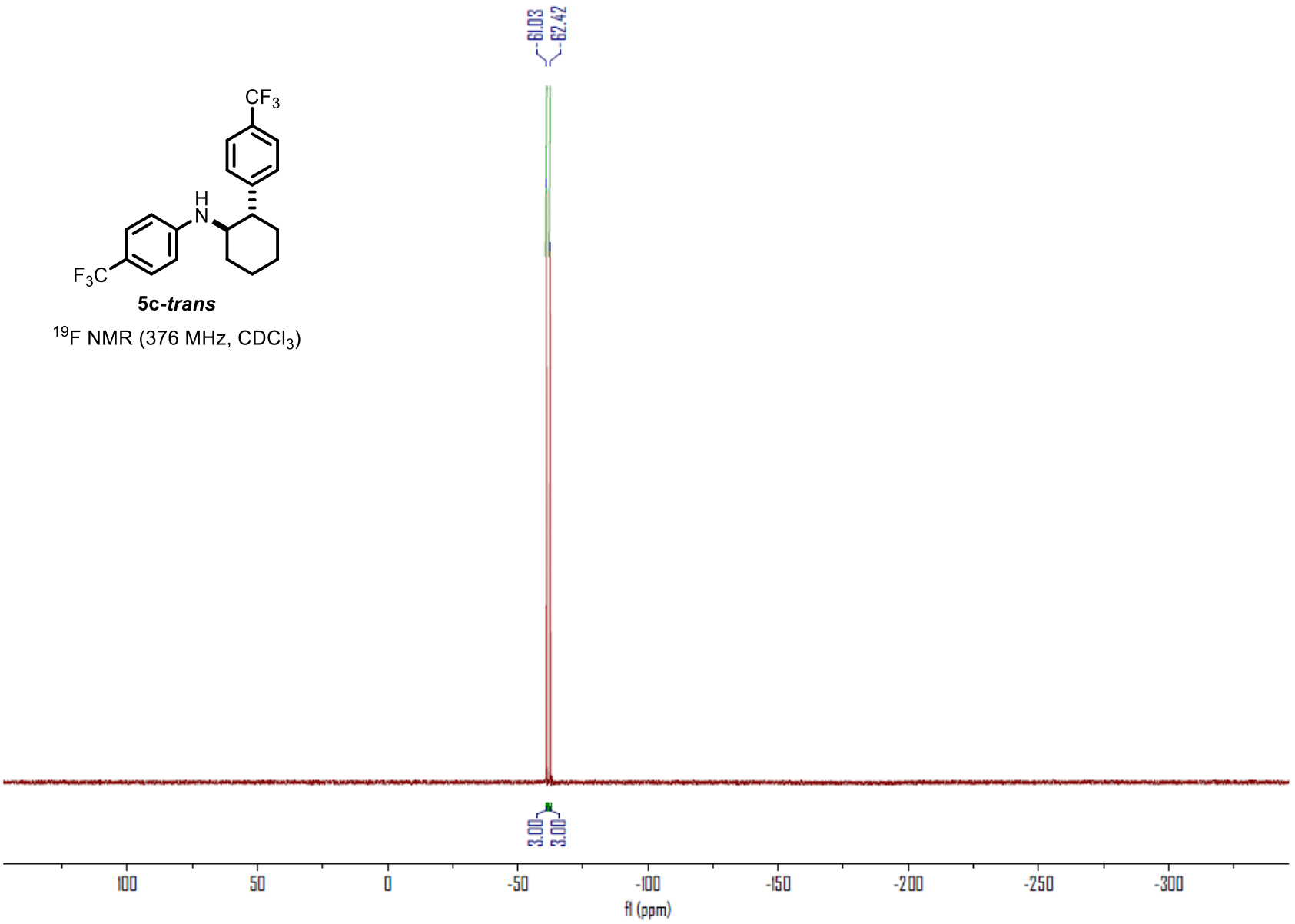
5c-*trans*

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



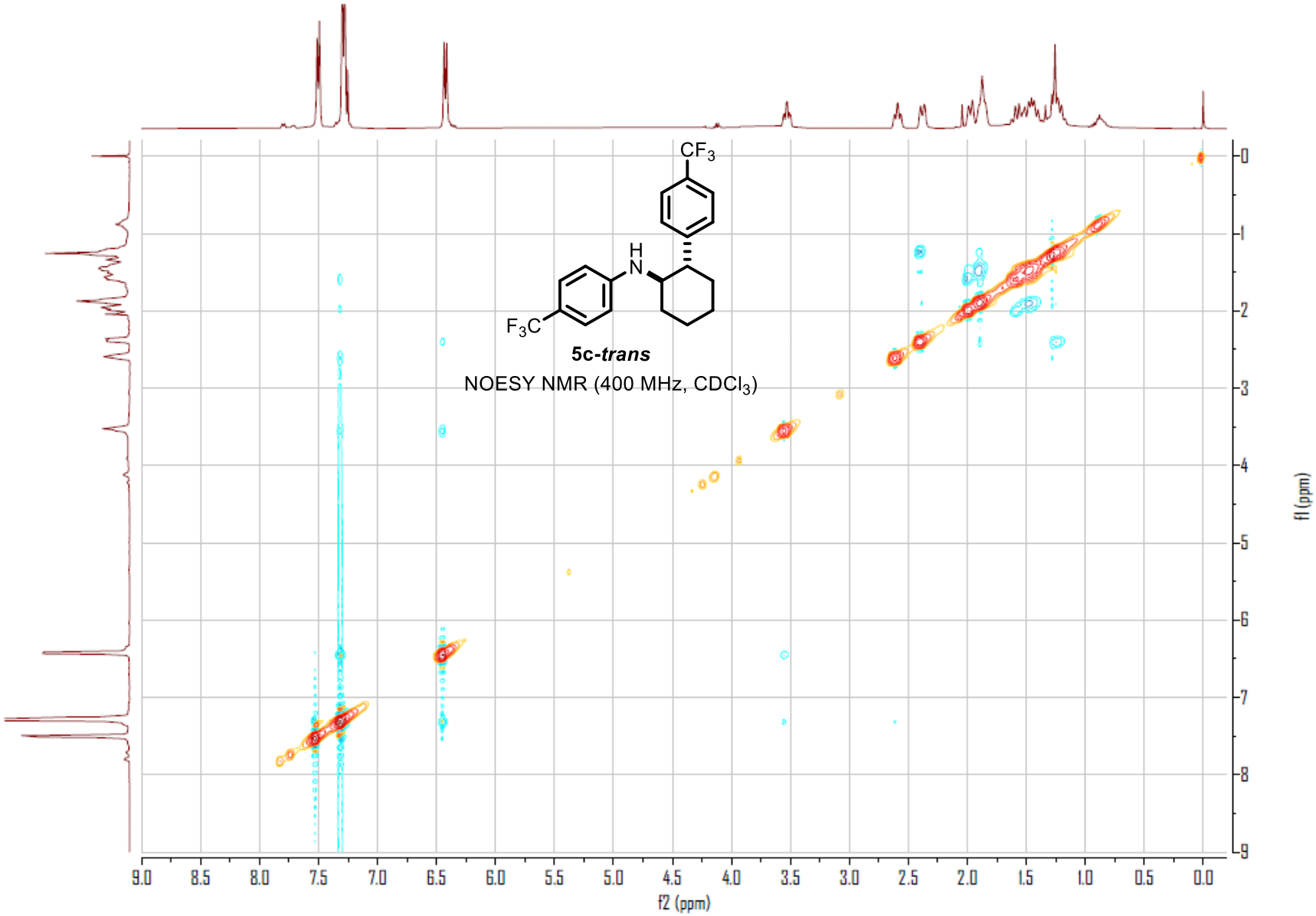
5c-*trans*

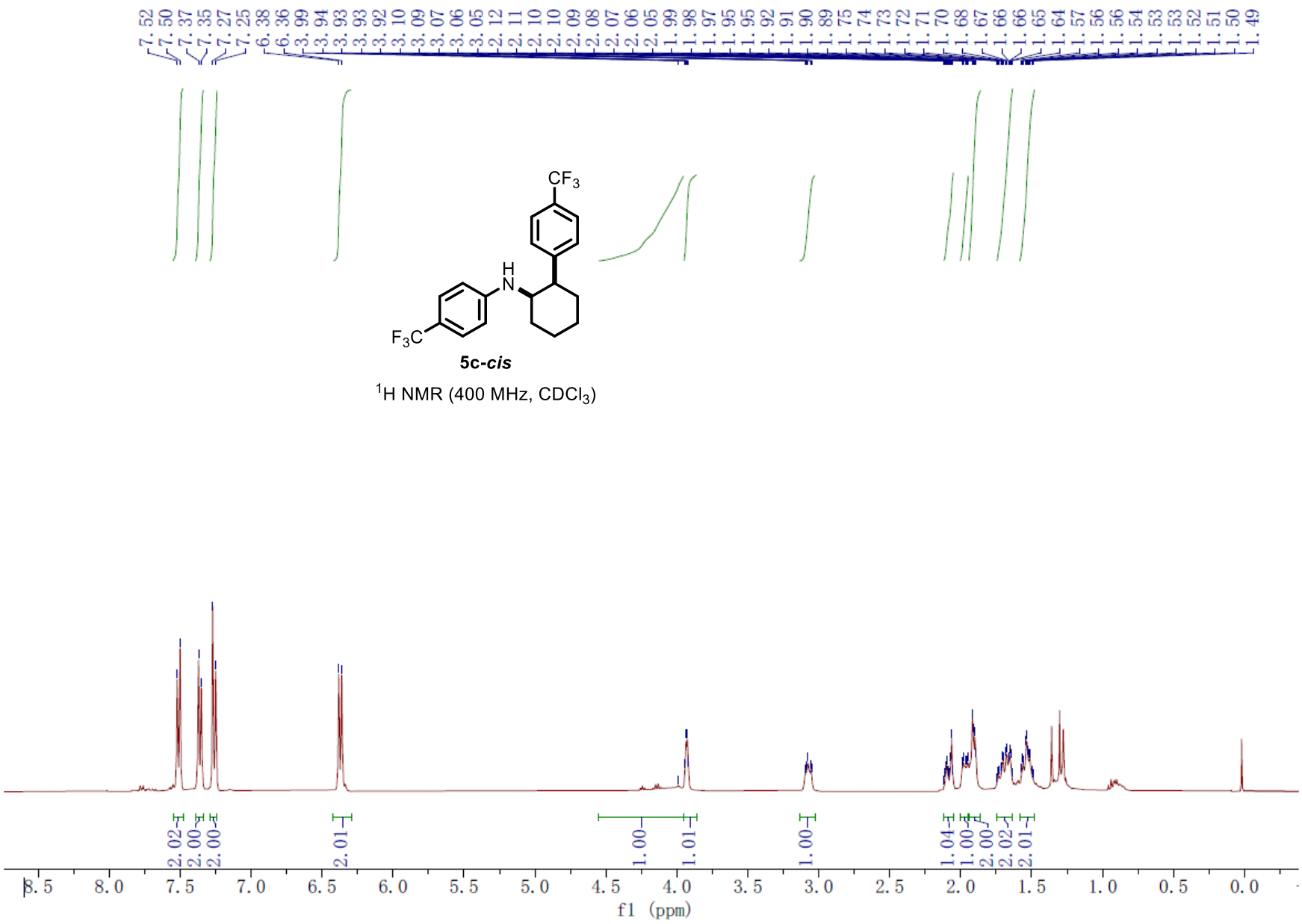
^{13}C NMR (101 MHz, $CDCl_3$)

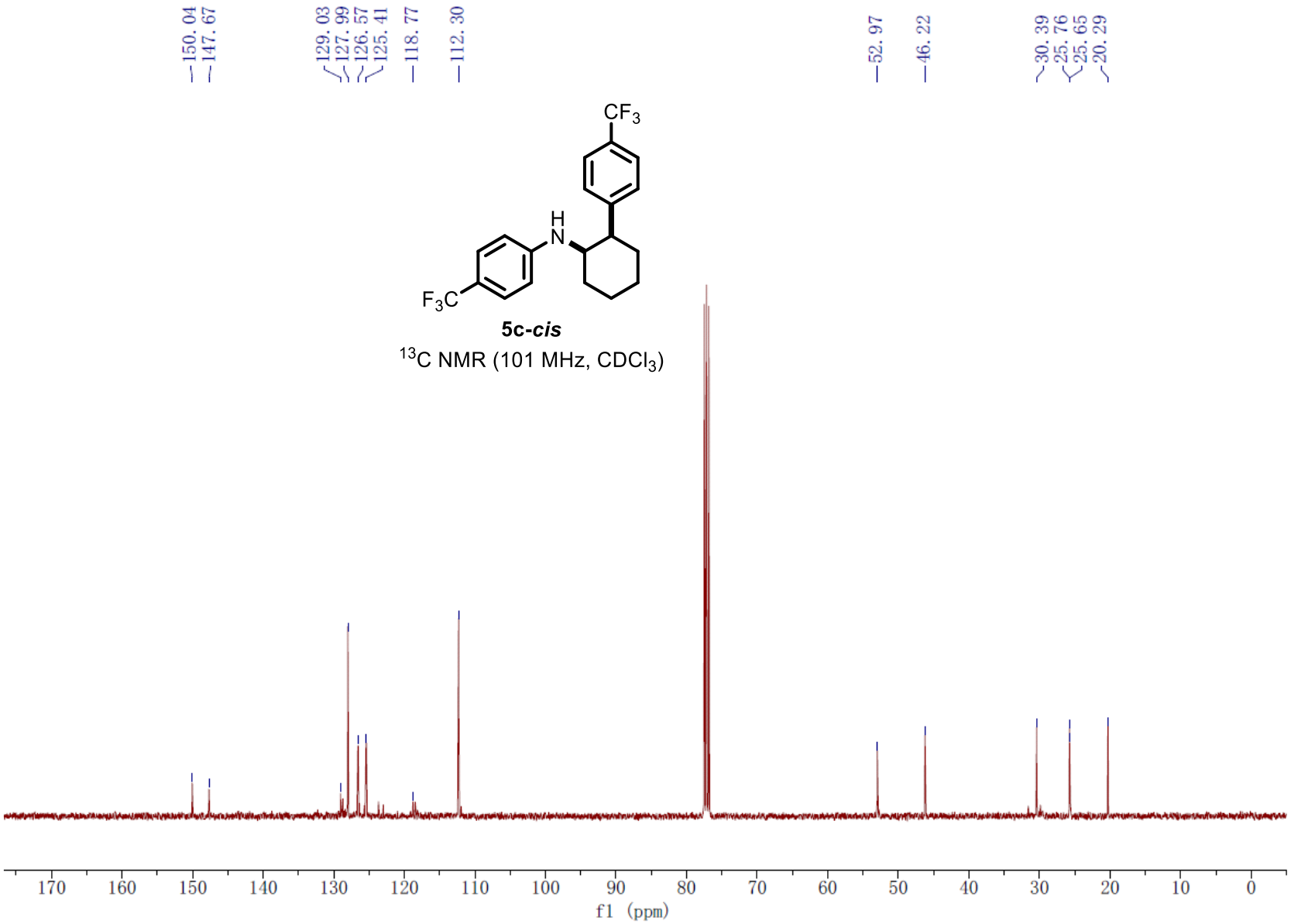


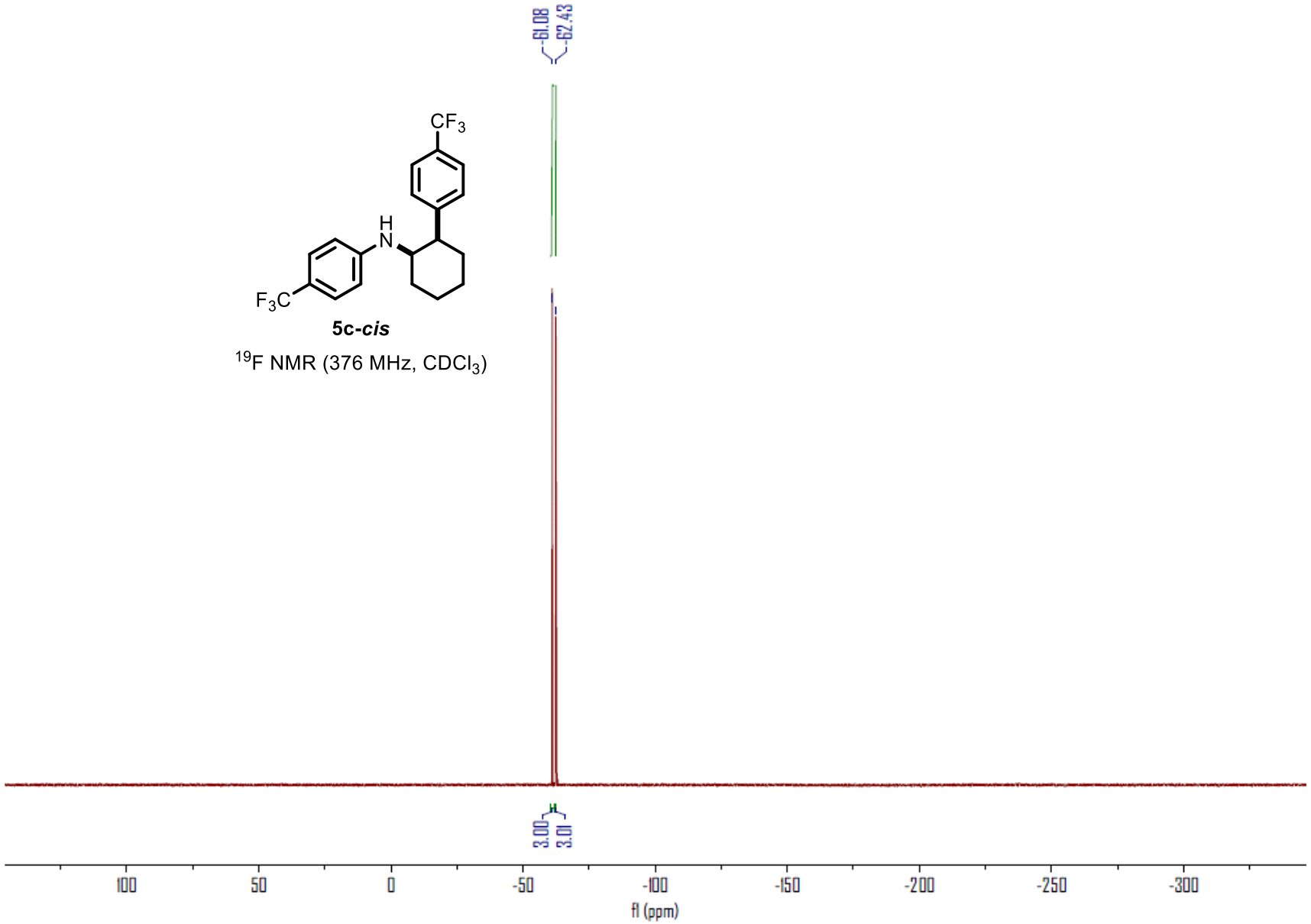
5c-*trans*

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


CF3
H
N
F3C
5c-trans
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

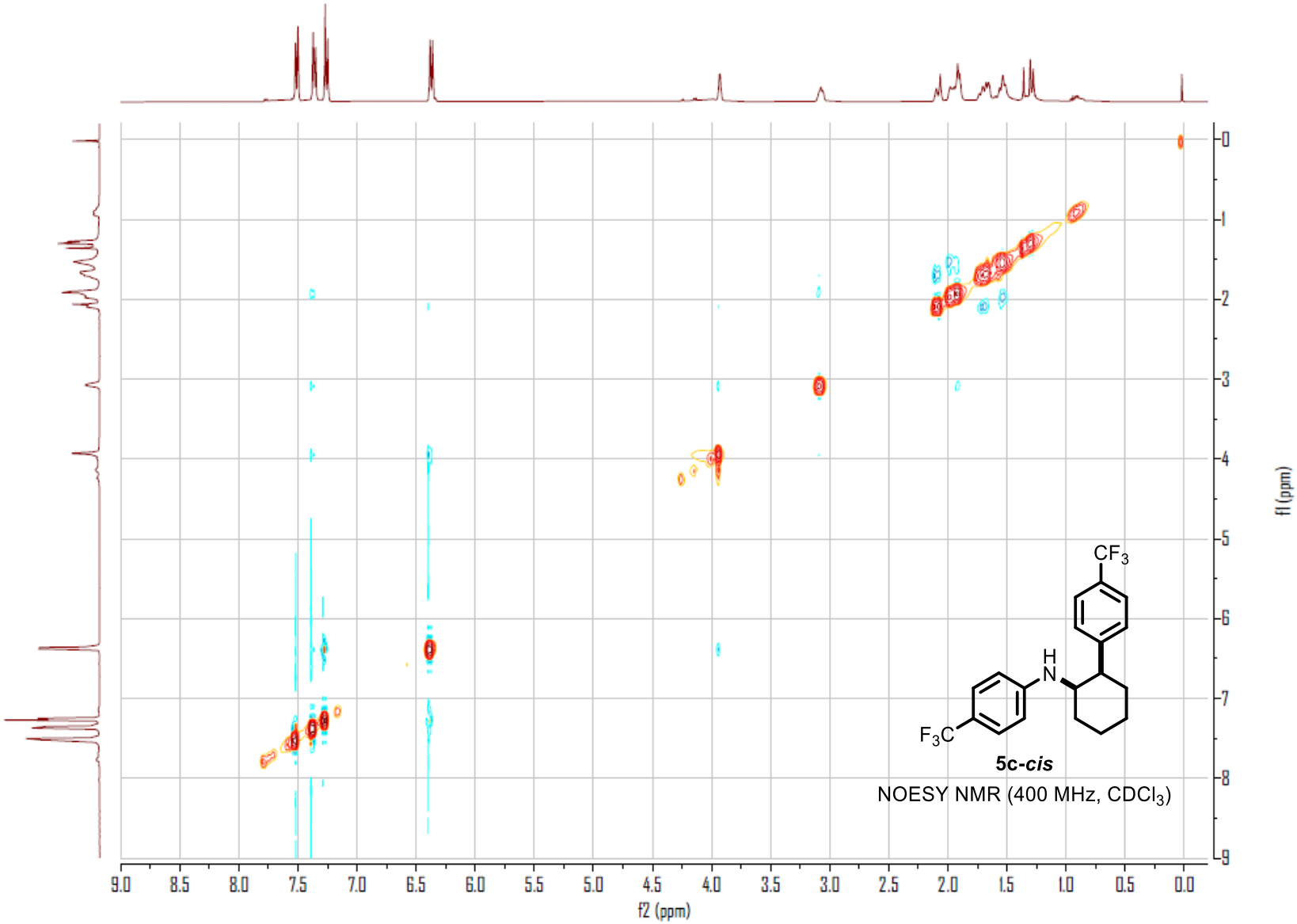

7.52 7.50 7.37 7.35 7.27 7.25 6.38 6.36 3.99 3.94 3.93 3.92 3.10 3.09 3.07 3.06 3.05 2.12 2.11 2.10 2.10 2.09 2.08 2.07 2.06 2.05 1.99 1.98 1.97 1.95 1.95 1.92 1.91 1.90 1.89 1.75 1.74 1.73 1.72 1.71 1.70 1.68 1.67 1.66 1.66 1.65 1.64 1.57 1.56 1.56 1.54 1.53 1.53 1.52 1.51 1.50 1.49
CF3
H
N
F3C
5c-cis
1H NMR (400 MHz, CDCl3)
2.02 2.00 2.00 2.01 1.00 1.01 1.00 1.04 1.00 2.00 2.02 2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

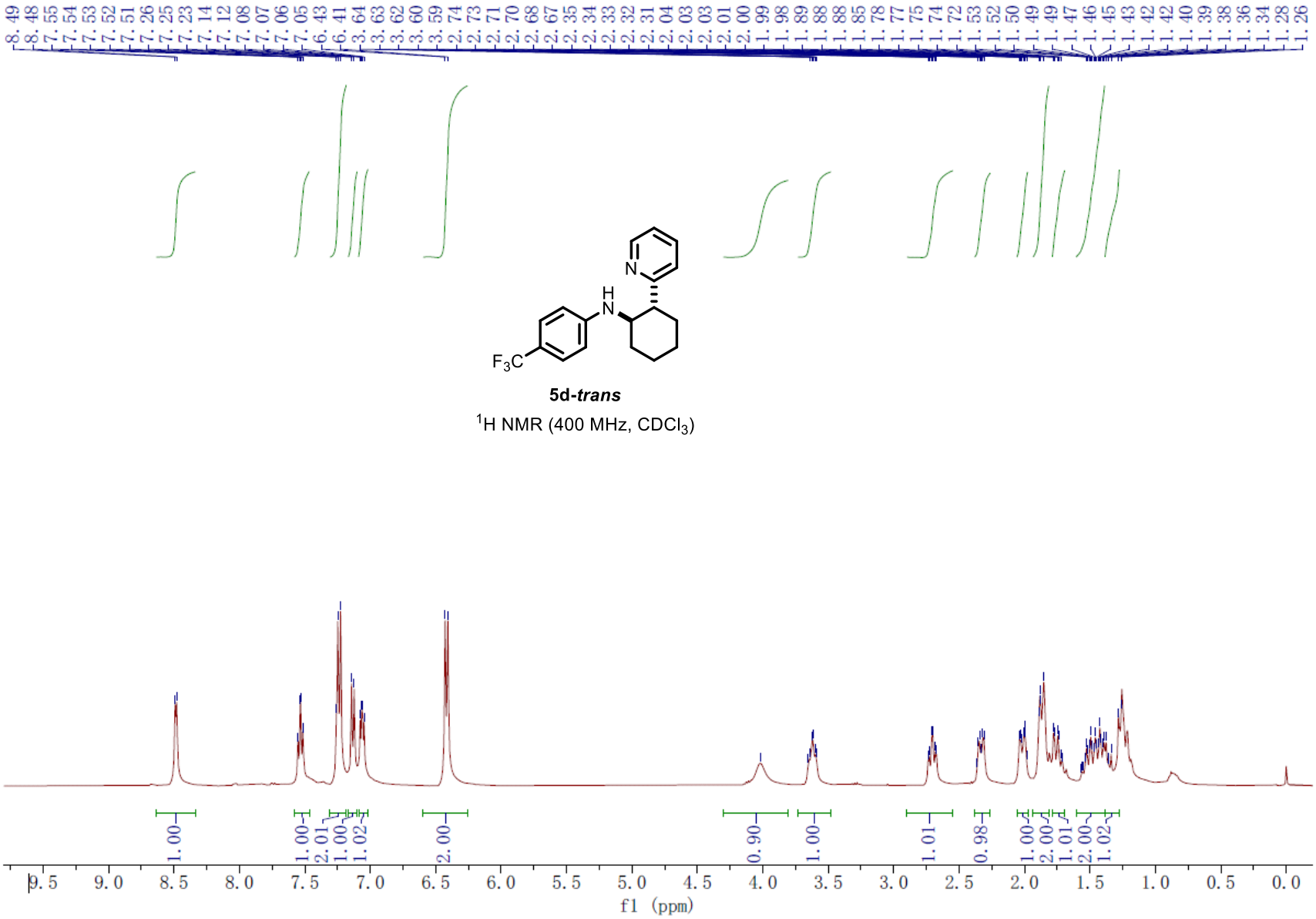

150.04
147.67
129.03
127.99
126.57
125.41
118.77
112.30
52.97
46.22
30.39
25.76
25.65
20.29
CF3
H
N
F3C
5c-cis
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5c-*cis*

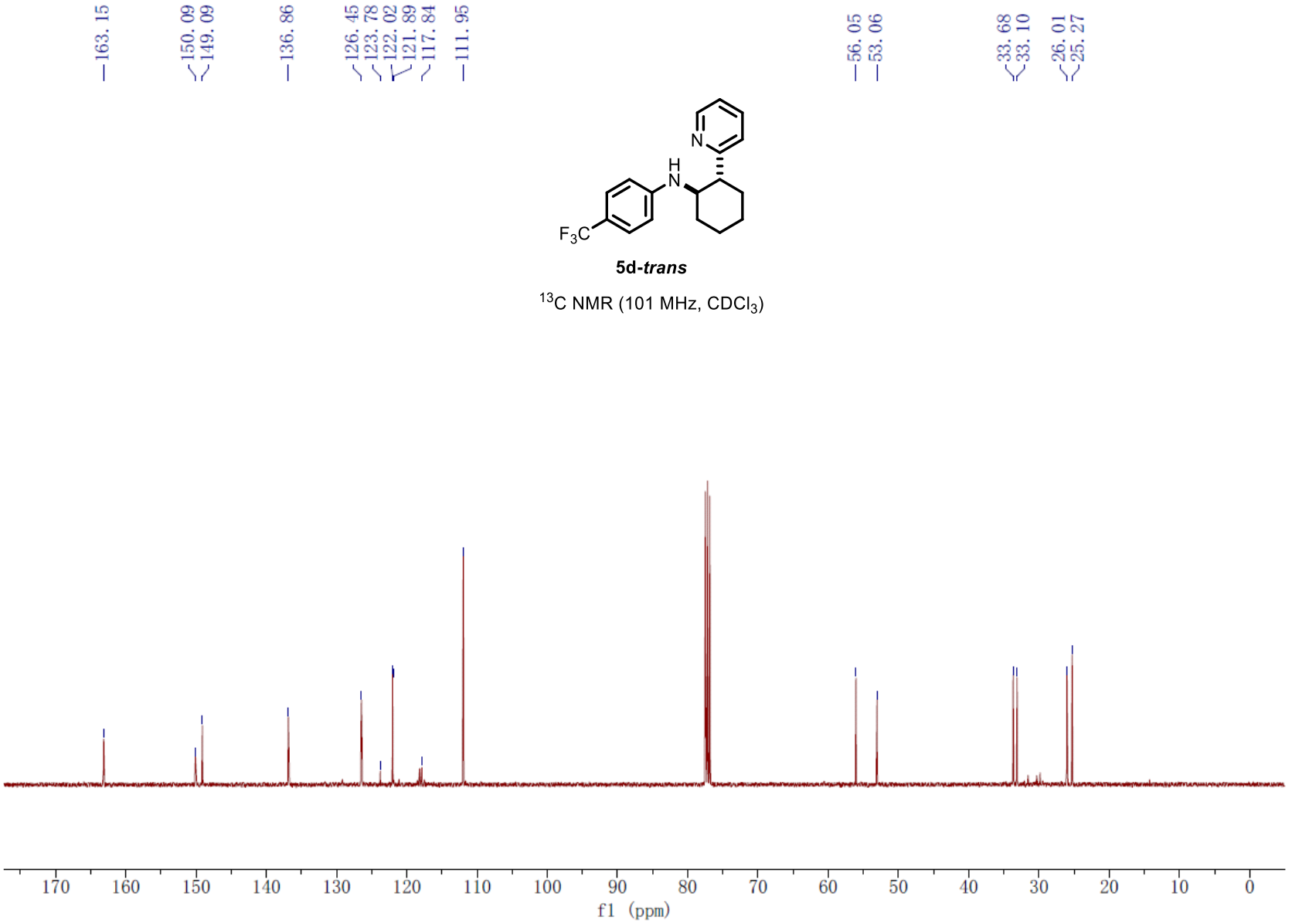
^{19}F NMR (376 MHz, $CDCl_3$)

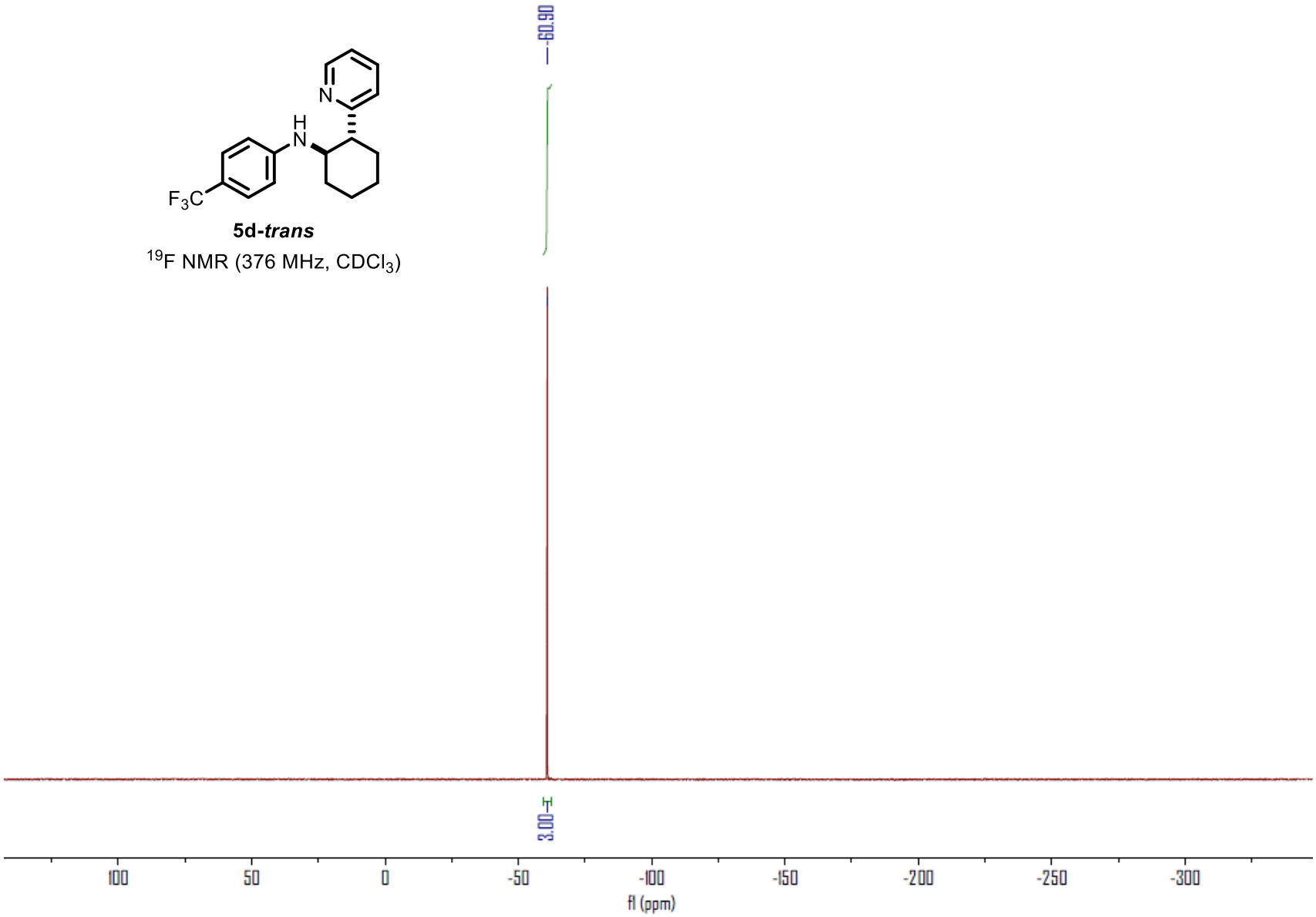

f2 (ppm)
f1 (ppm)
CF3
H
N
F3C
5c-cis
NOESY NMR (400 MHz, CDCl3)



5d-*trans*

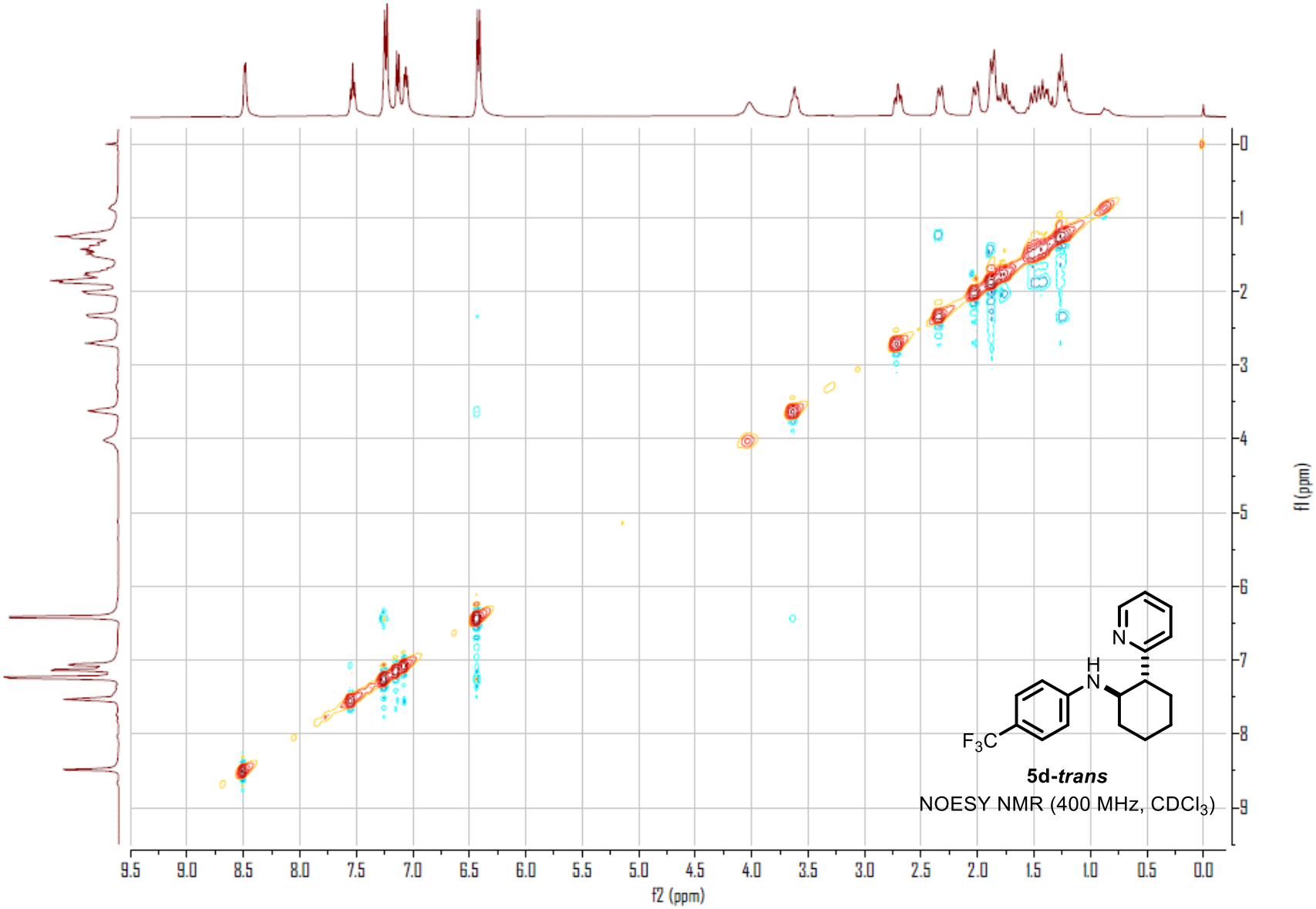
^{1}H NMR (400 MHz, $CDCl_3$)

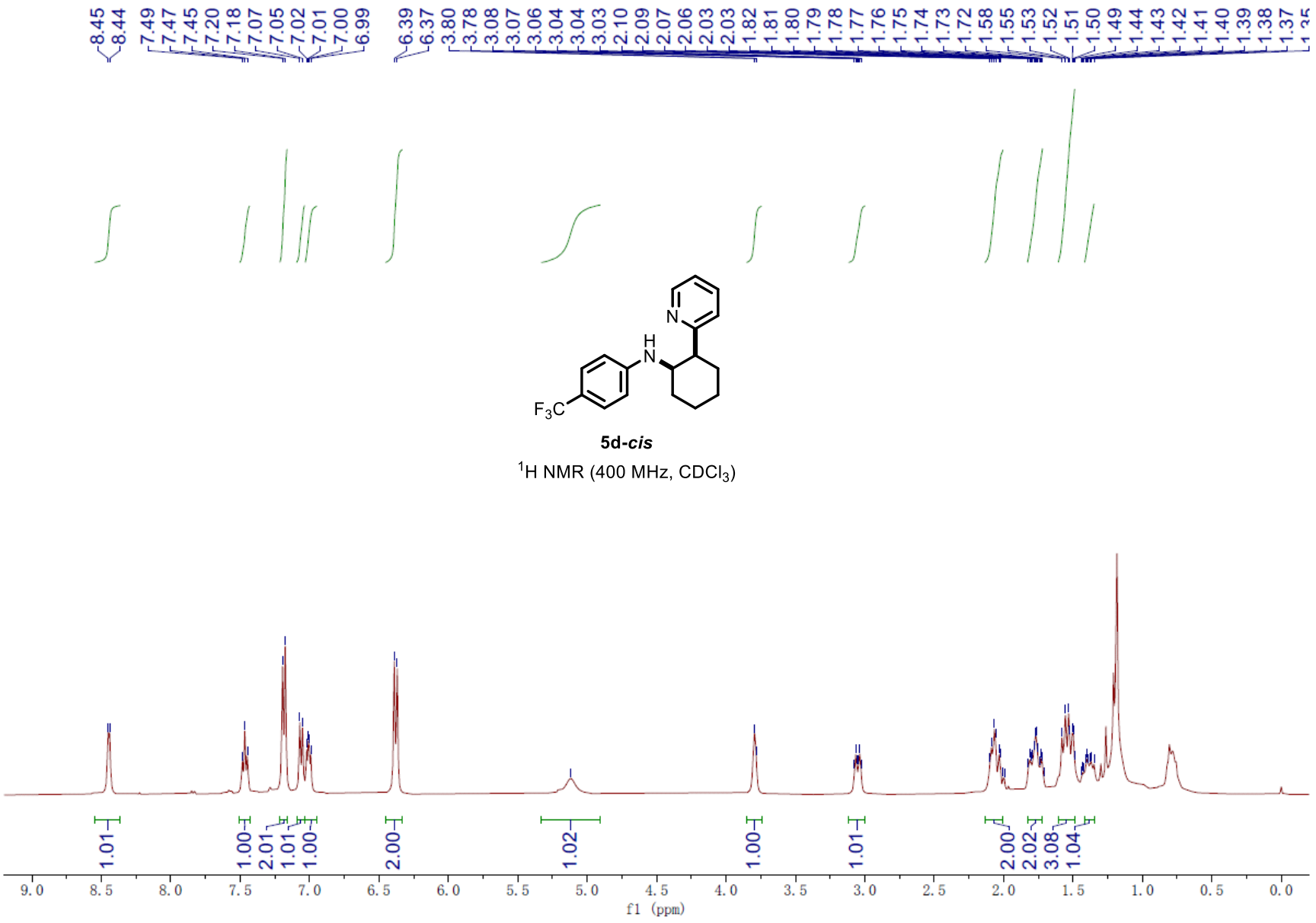

163.15
150.09
149.09
136.86
126.45
123.78
122.02
121.89
117.84
111.95
56.05
53.06
33.68
33.10
26.01
25.27
N
H
N
F3C
5d-trans
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5d-*trans*

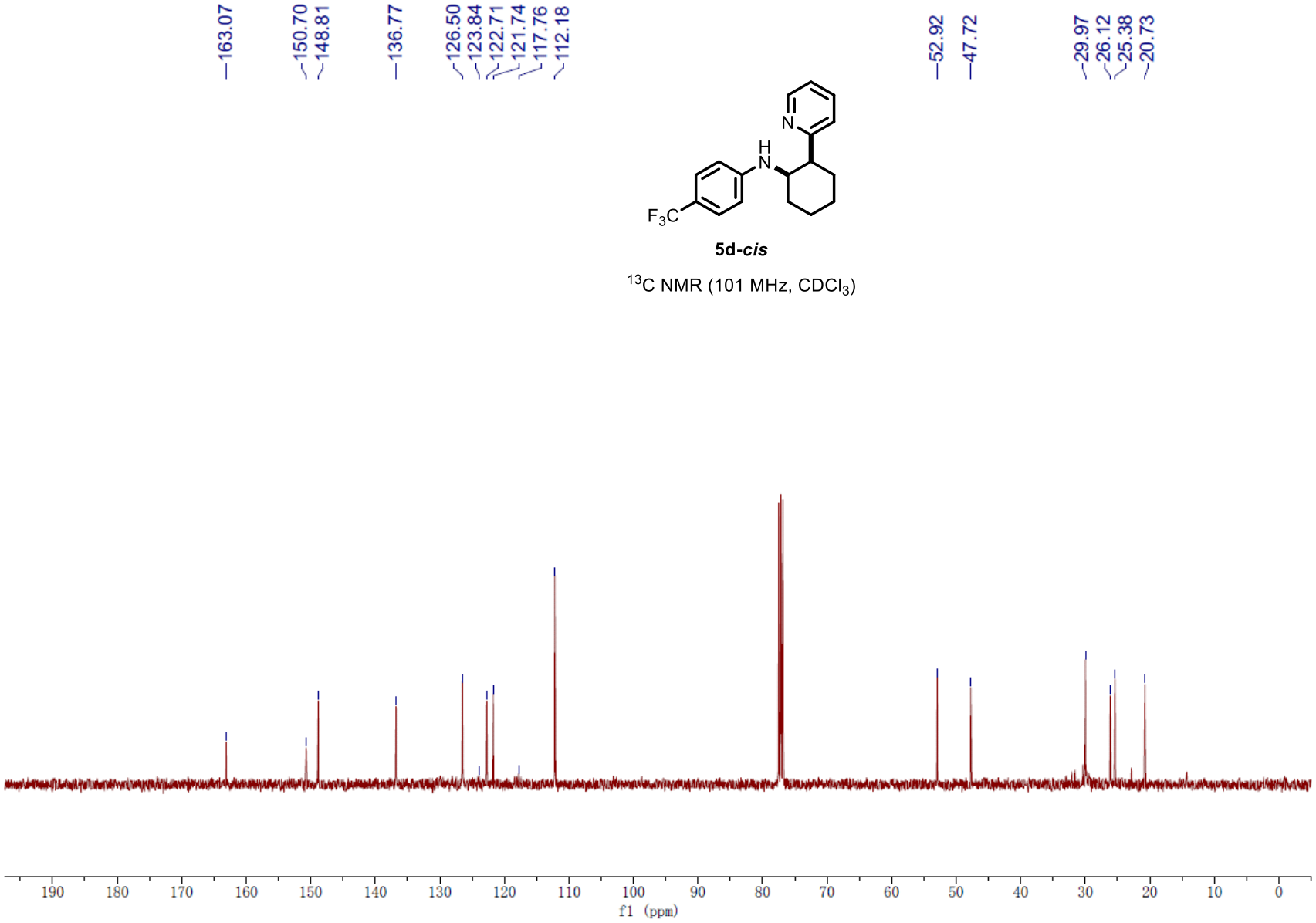
^{19}F NMR (376 MHz, $CDCl_3$)


f2 (ppm)
f1 (ppm)
N
H
N
F3C
5d-trans
NOESY NMR (400 MHz, CDCl3)



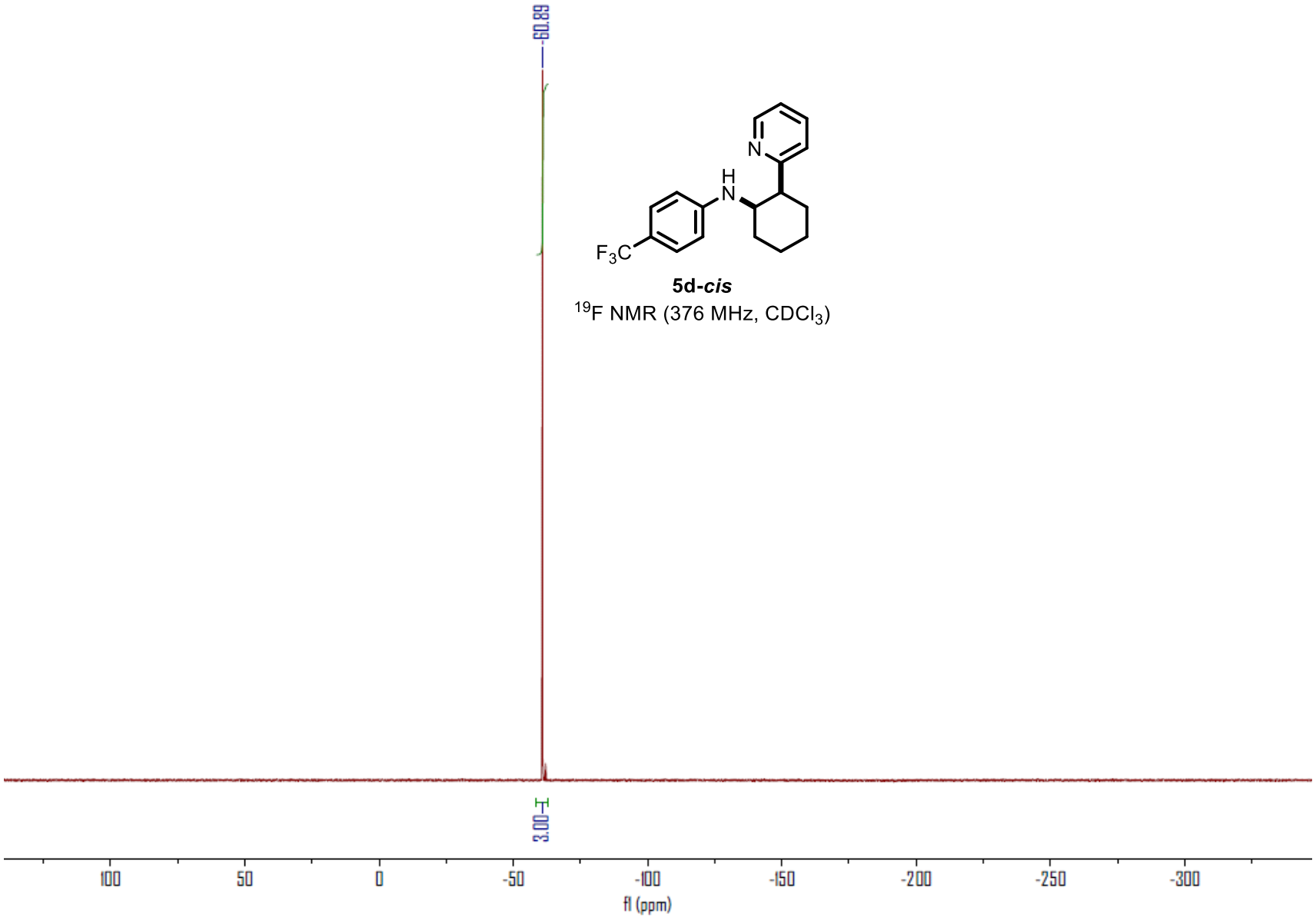
5d-*cis*

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



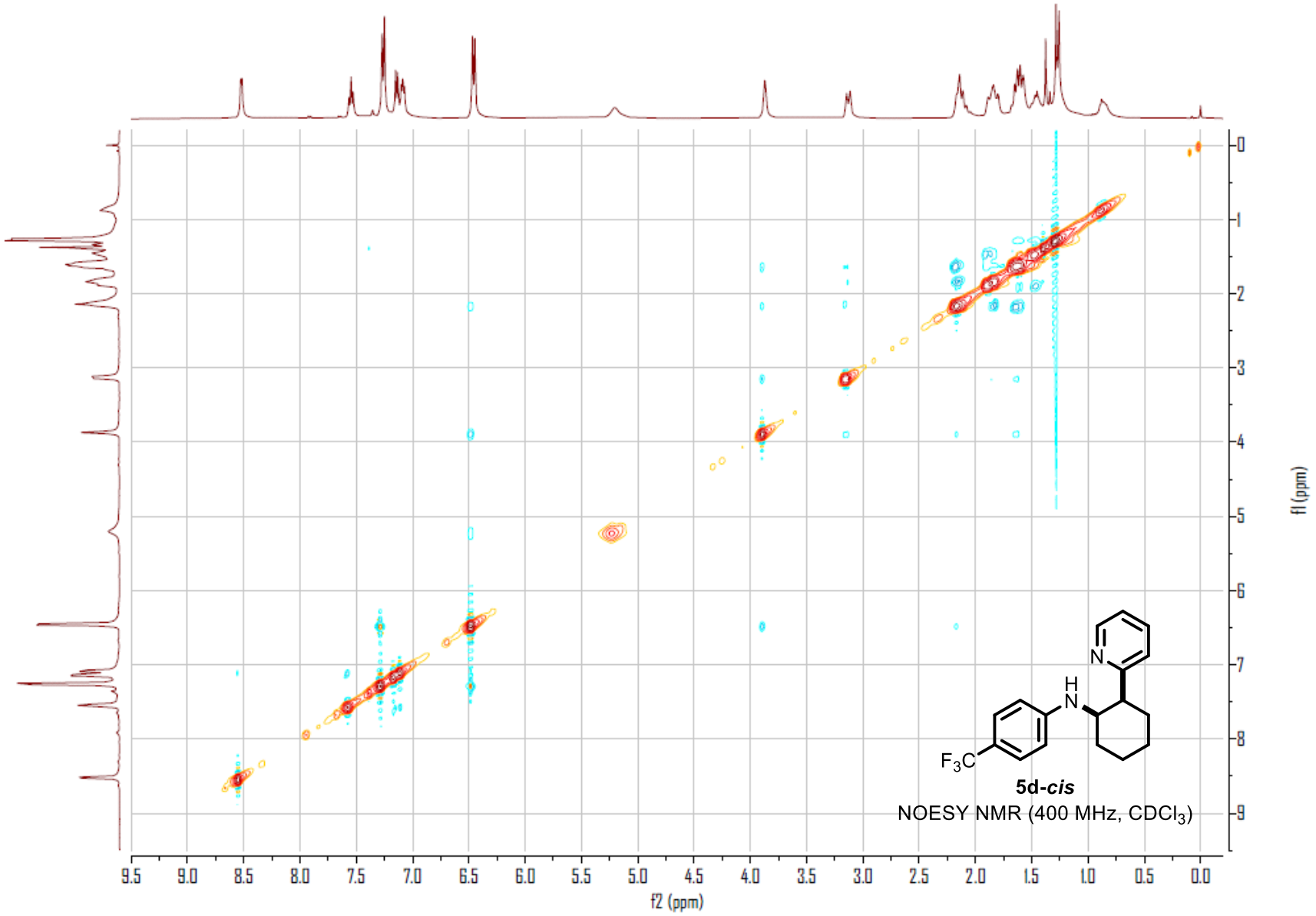
5d-*cis*

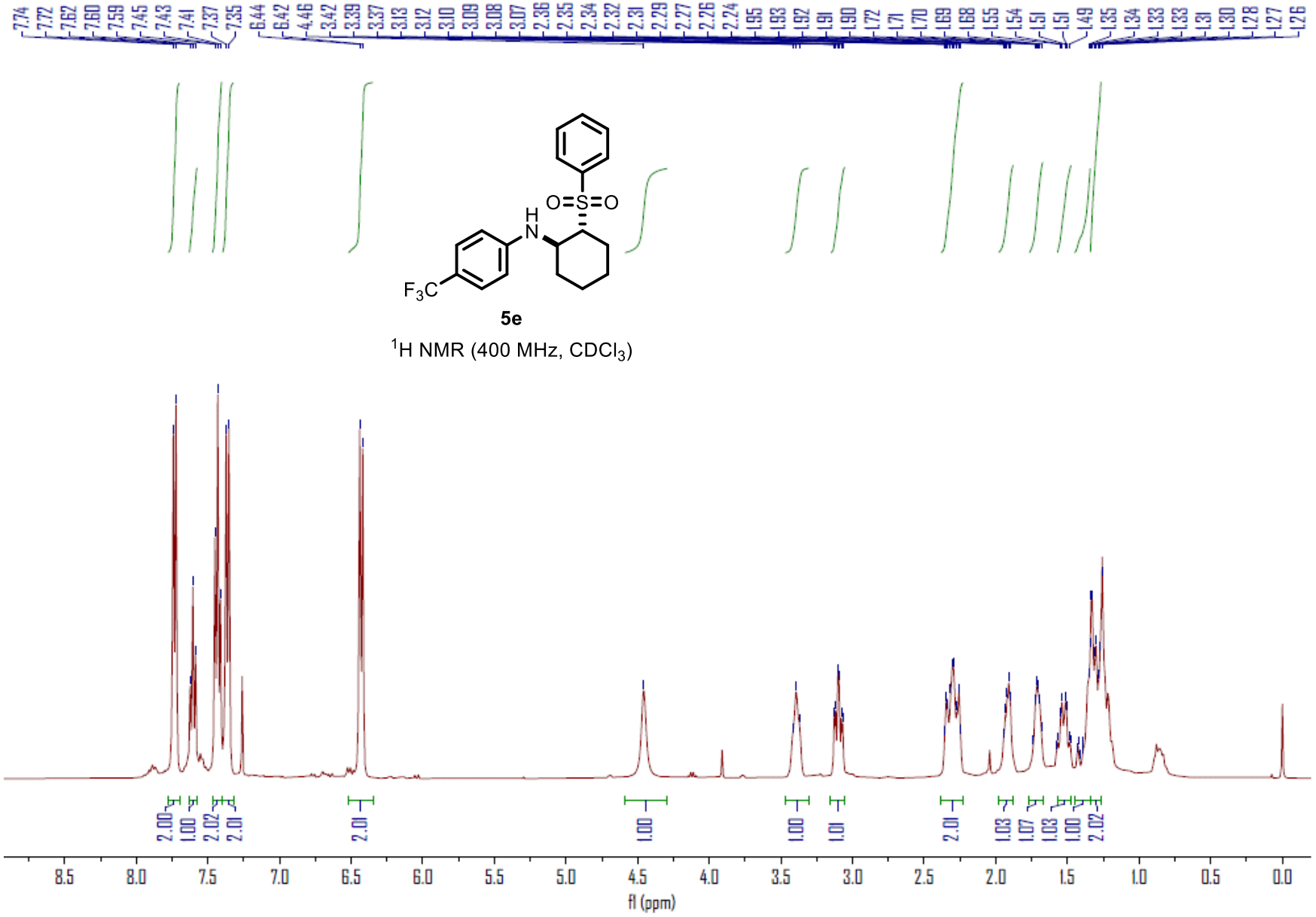
^{13}C NMR (101 MHz, $CDCl_3$)



5d-*cis*

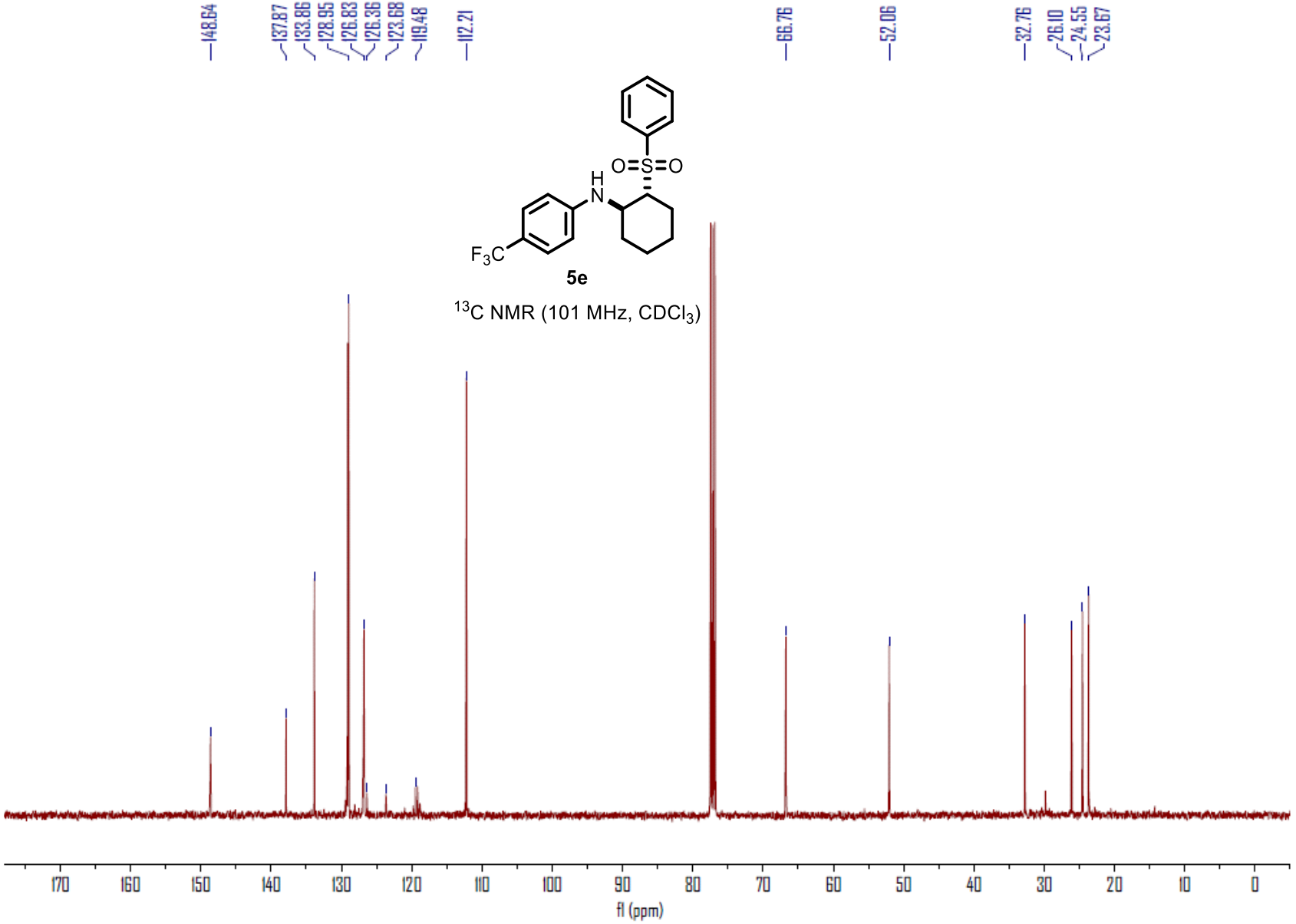
^{19}F NMR (376 MHz, $CDCl_3$)

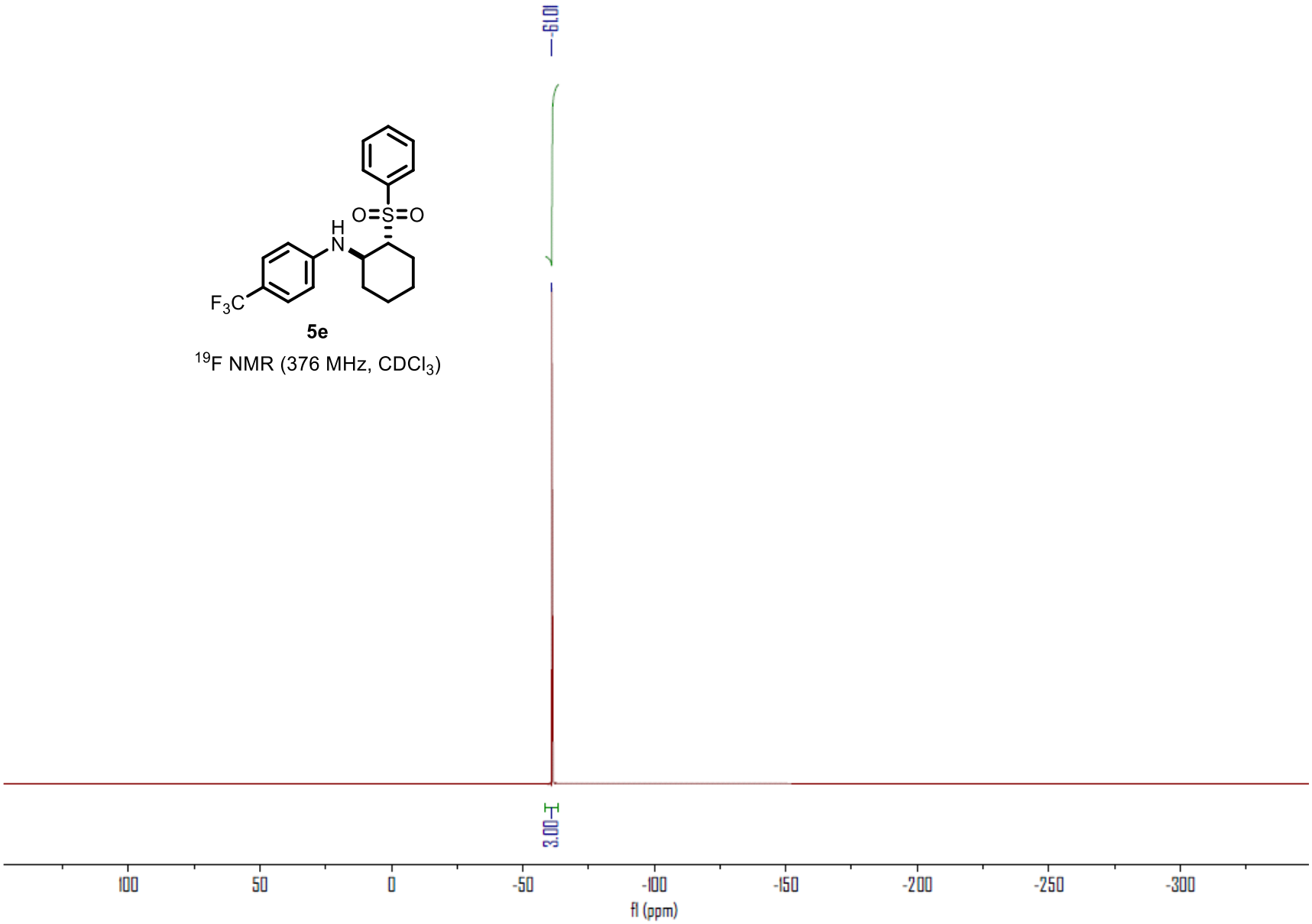

f2 (ppm)
f1 (ppm)
F3C
N
H
N
5d-cis
NOESY NMR (400 MHz, CDCl3)



5e

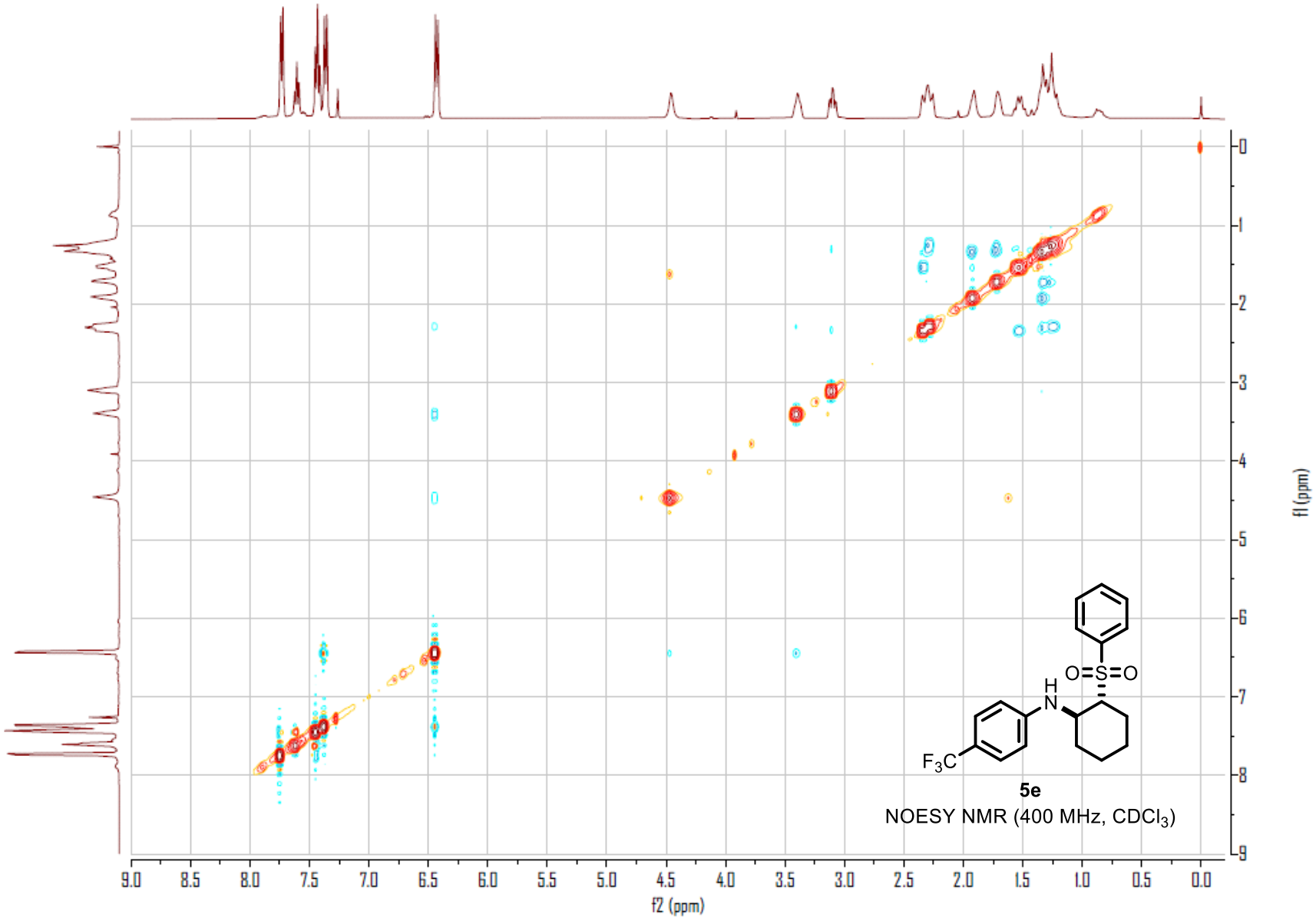
^{1}H NMR (400 MHz, $CDCl_3$)


148.64
137.87
133.86
128.95
126.83
126.36
123.68
119.48
112.21
66.76
52.06
32.76
26.10
24.55
23.67
O=S=O
H
N
F3C
5e
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



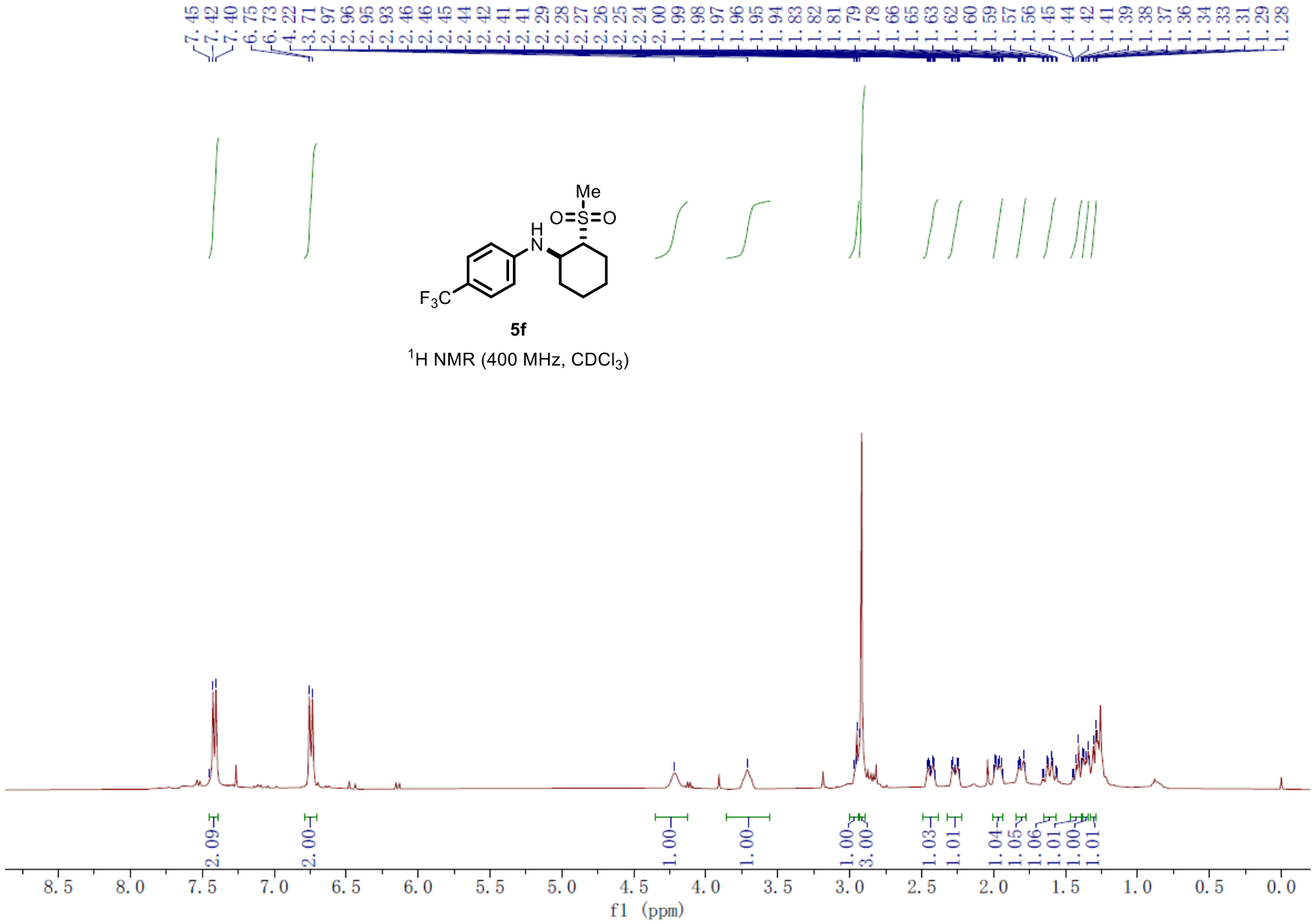
5e

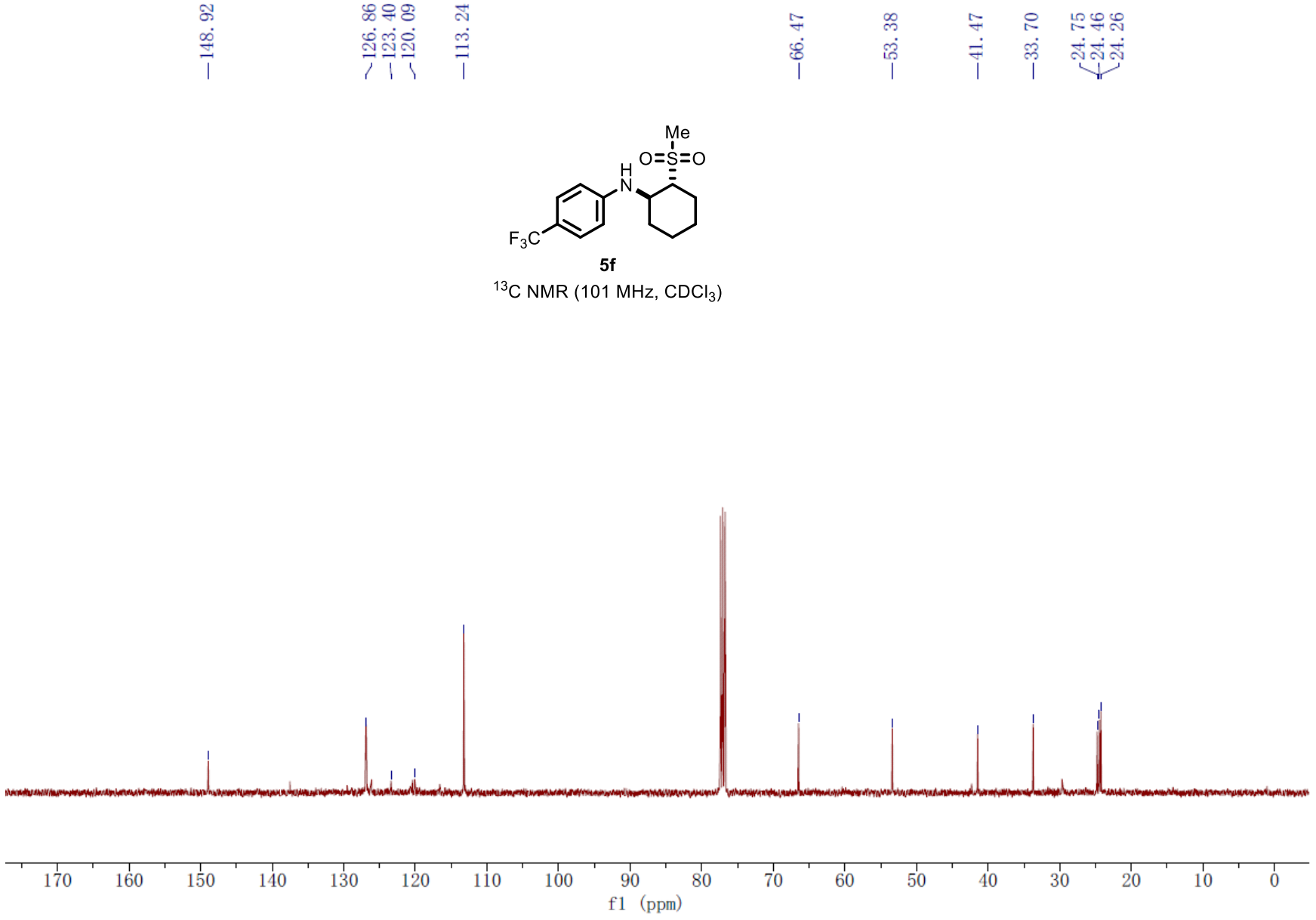
^{19}F NMR (376 MHz, $CDCl_3$)



5e

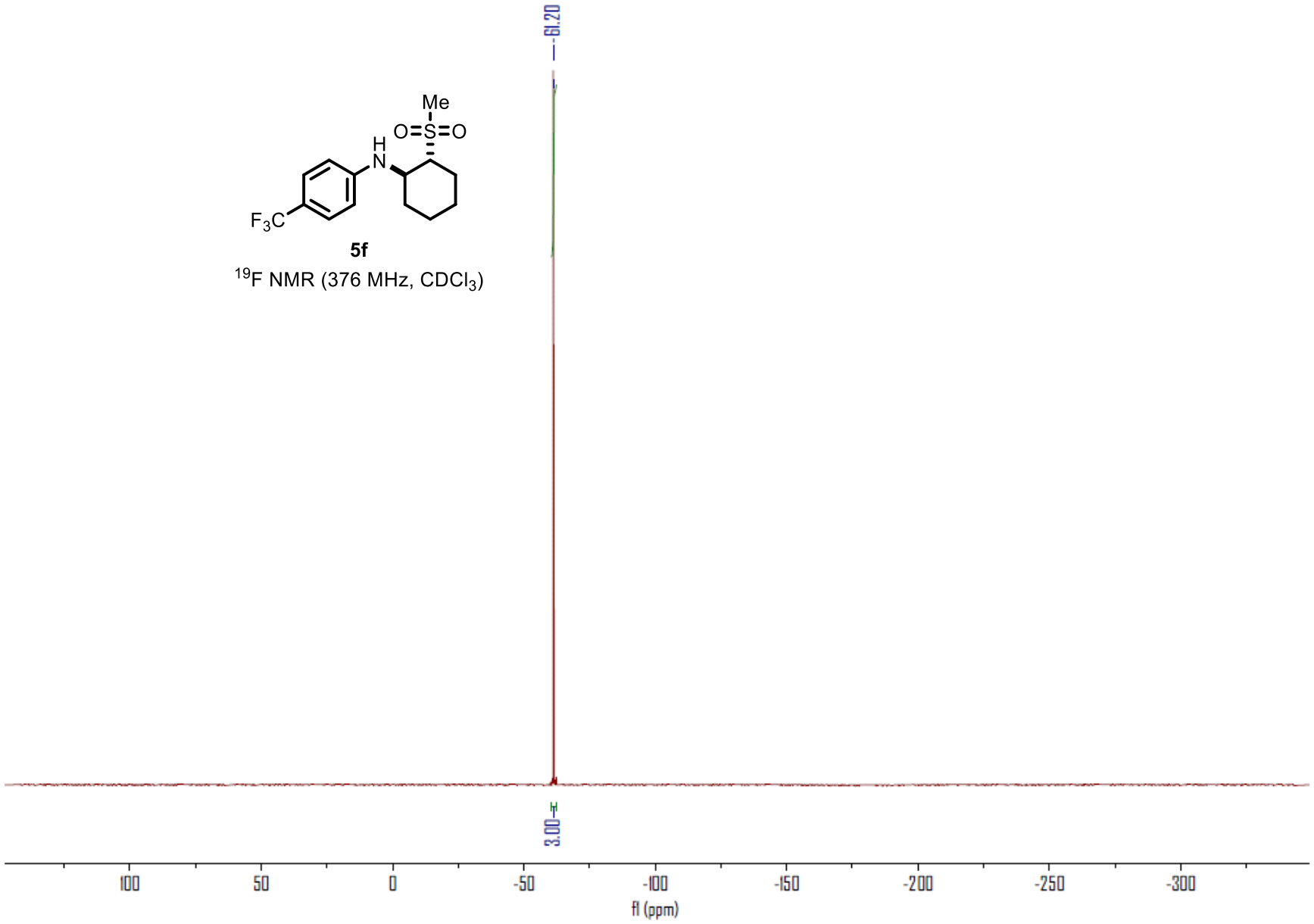
NOESY NMR (400 MHz, $CDCl_3$)

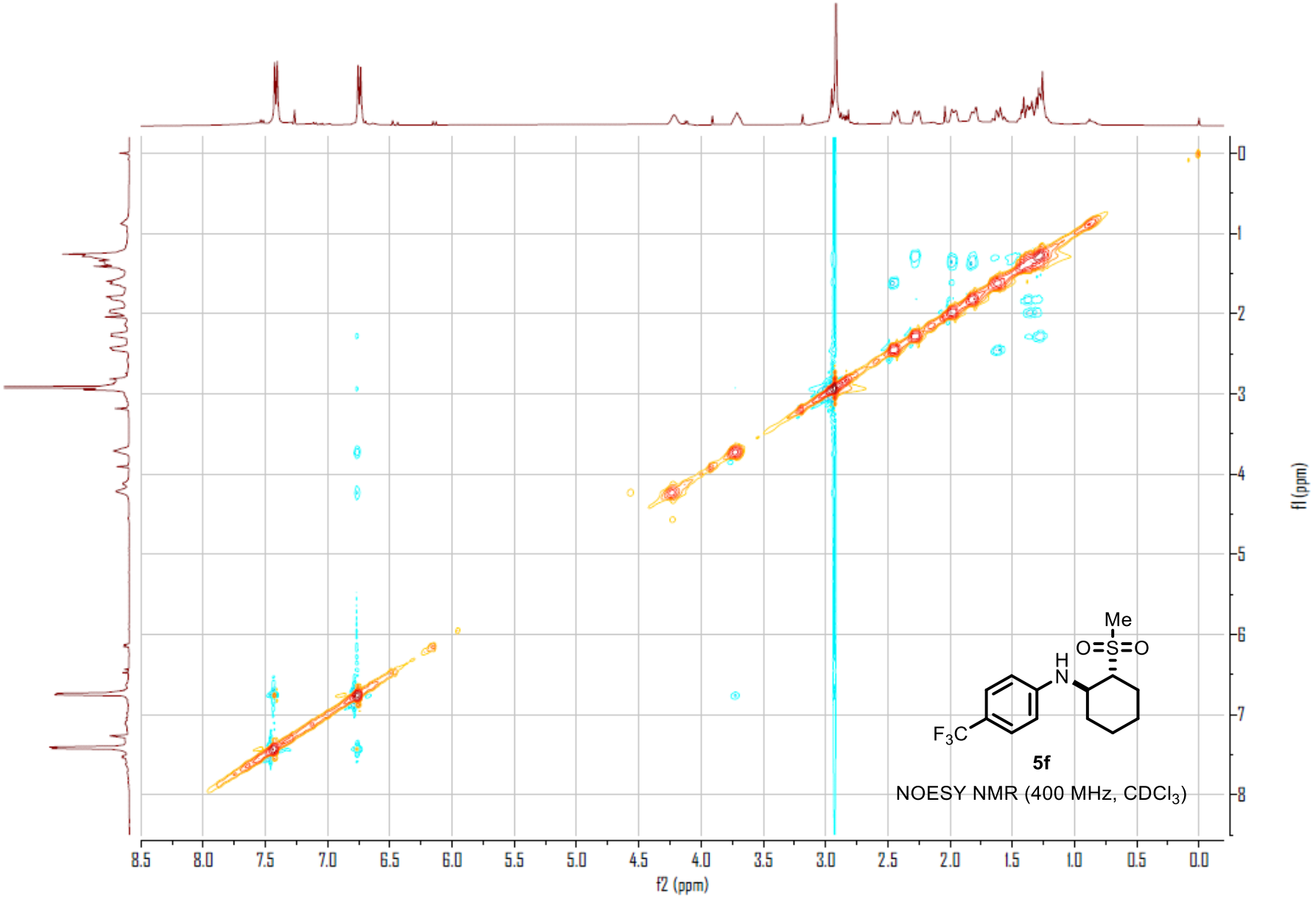

7.45 7.42 7.40 6.75 6.73 4.22 3.71 2.97 2.96 2.95 2.93 2.46 2.46 2.45 2.44 2.42 2.41 2.41 2.29 2.28 2.27 2.26 2.25 2.24 2.00 1.99 1.98 1.97 1.96 1.95 1.94 1.83 1.82 1.81 1.79 1.78 1.66 1.65 1.63 1.62 1.60 1.59 1.57 1.56 1.45 1.44 1.42 1.41 1.39 1.38 1.37 1.36 1.34 1.33 1.31 1.29 1.28
Me
O=S=O
H
N
F3C
5f
1H NMR (400 MHz, CDCl3)
2.09 2.00 1.00 1.00 1.00 3.00 1.03 1.01 1.04 1.05 1.06 1.01 1.00 1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

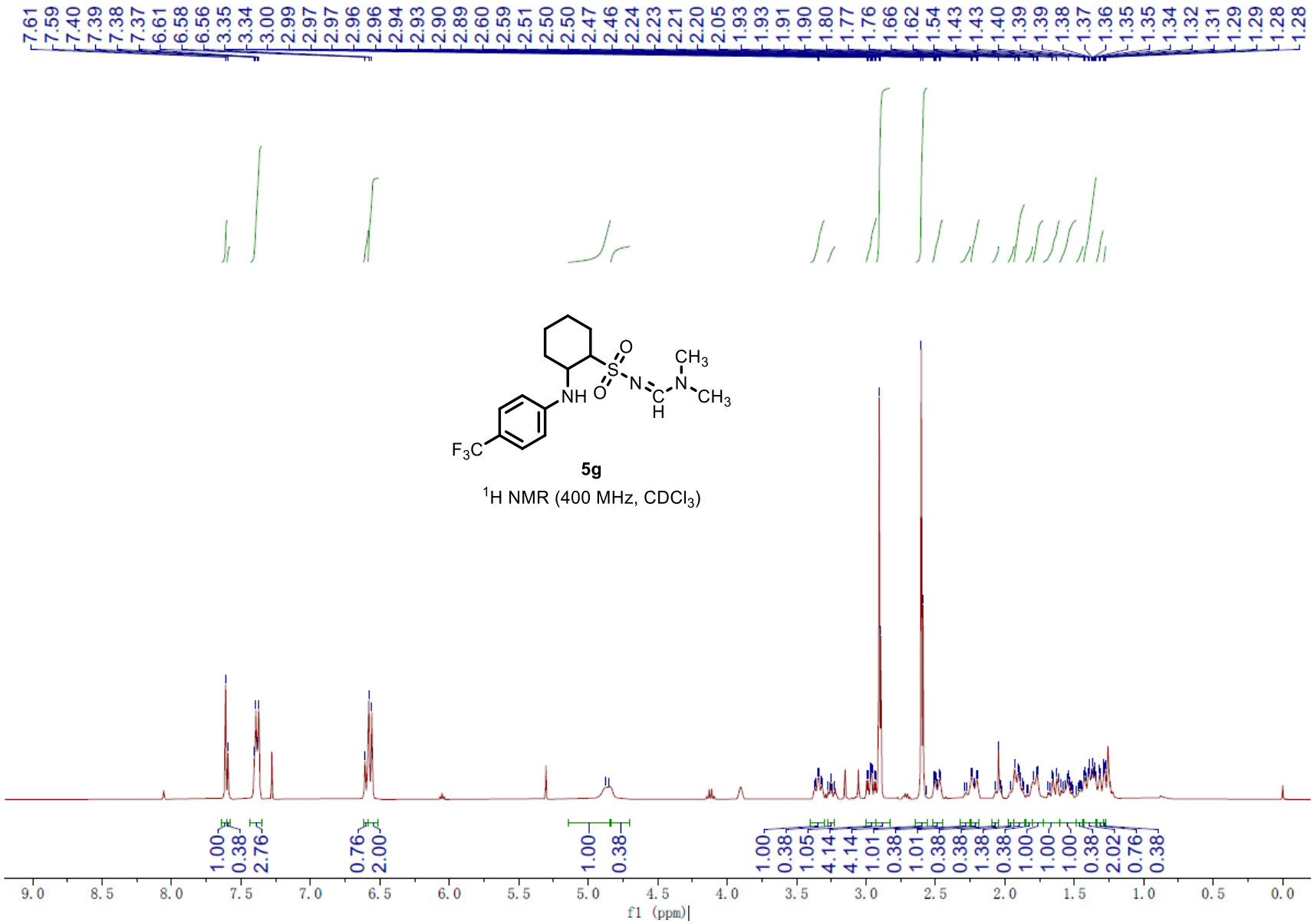


5f

^{13}C NMR (101 MHz, $CDCl_3$)

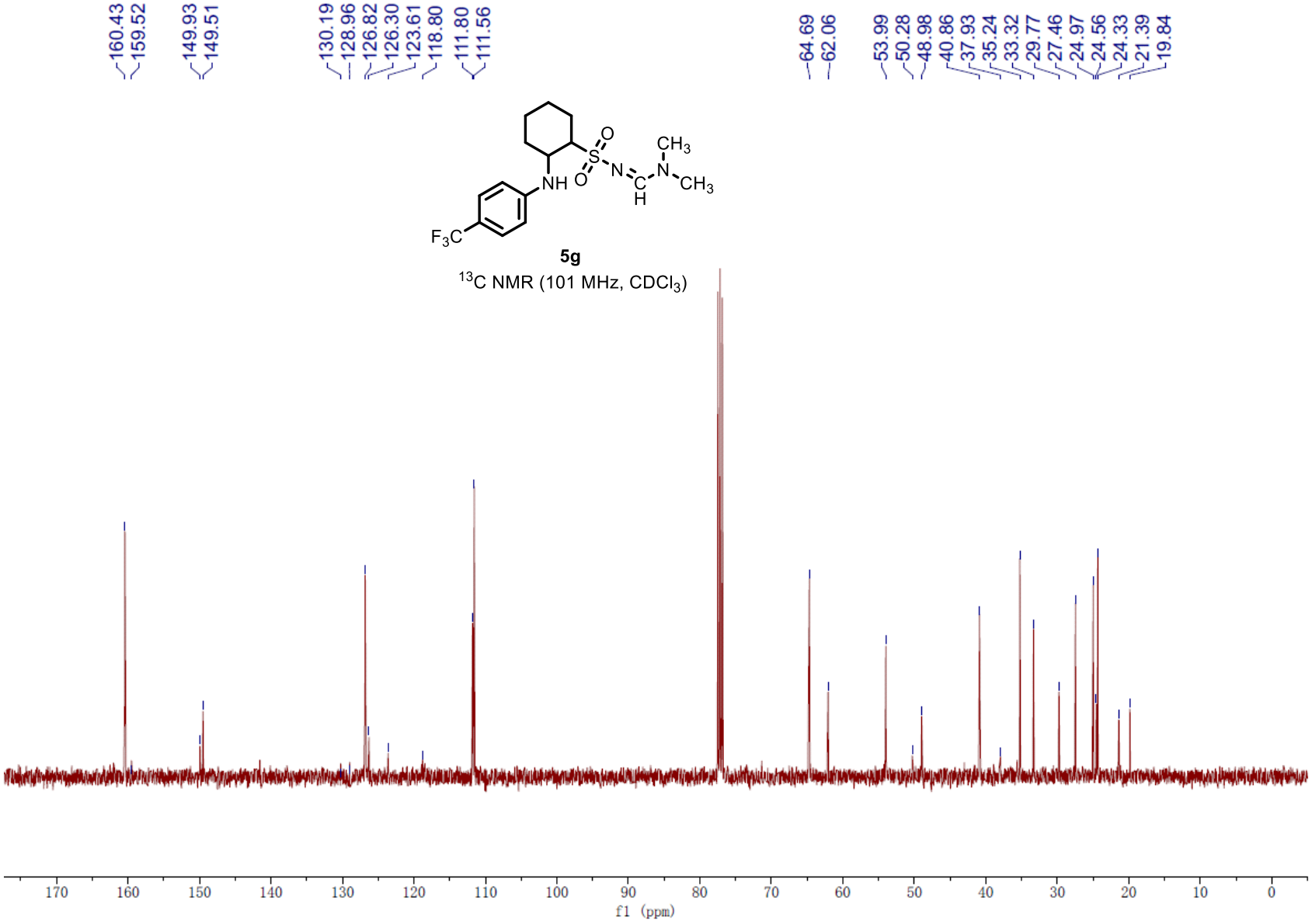

Me
O=S=O
H
N
F3C
5f
19F NMR (376 MHz, CDCl3)
-61.20
3.00
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


Me
O=S=O
H
N
F3C
5f
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



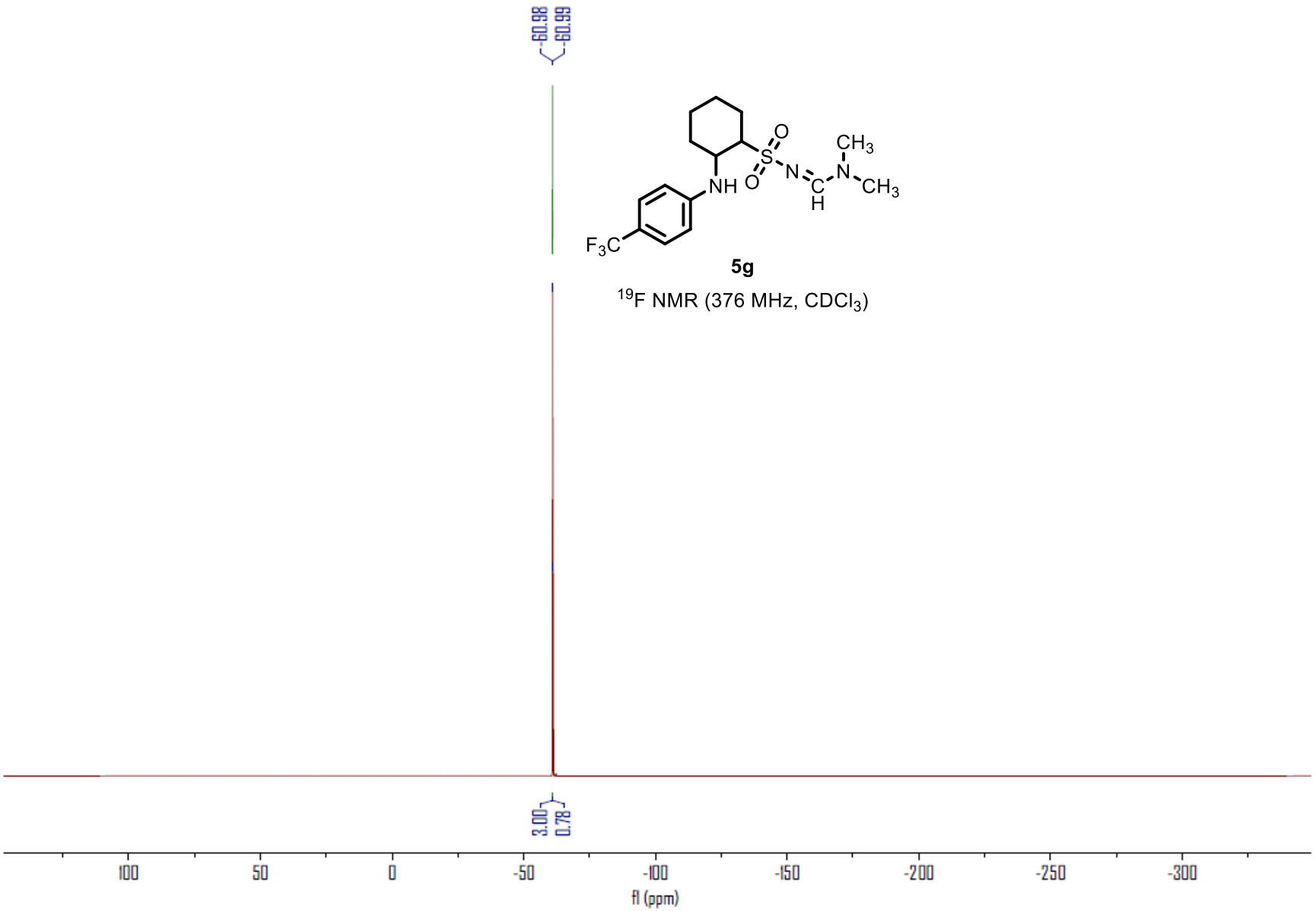
5g

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



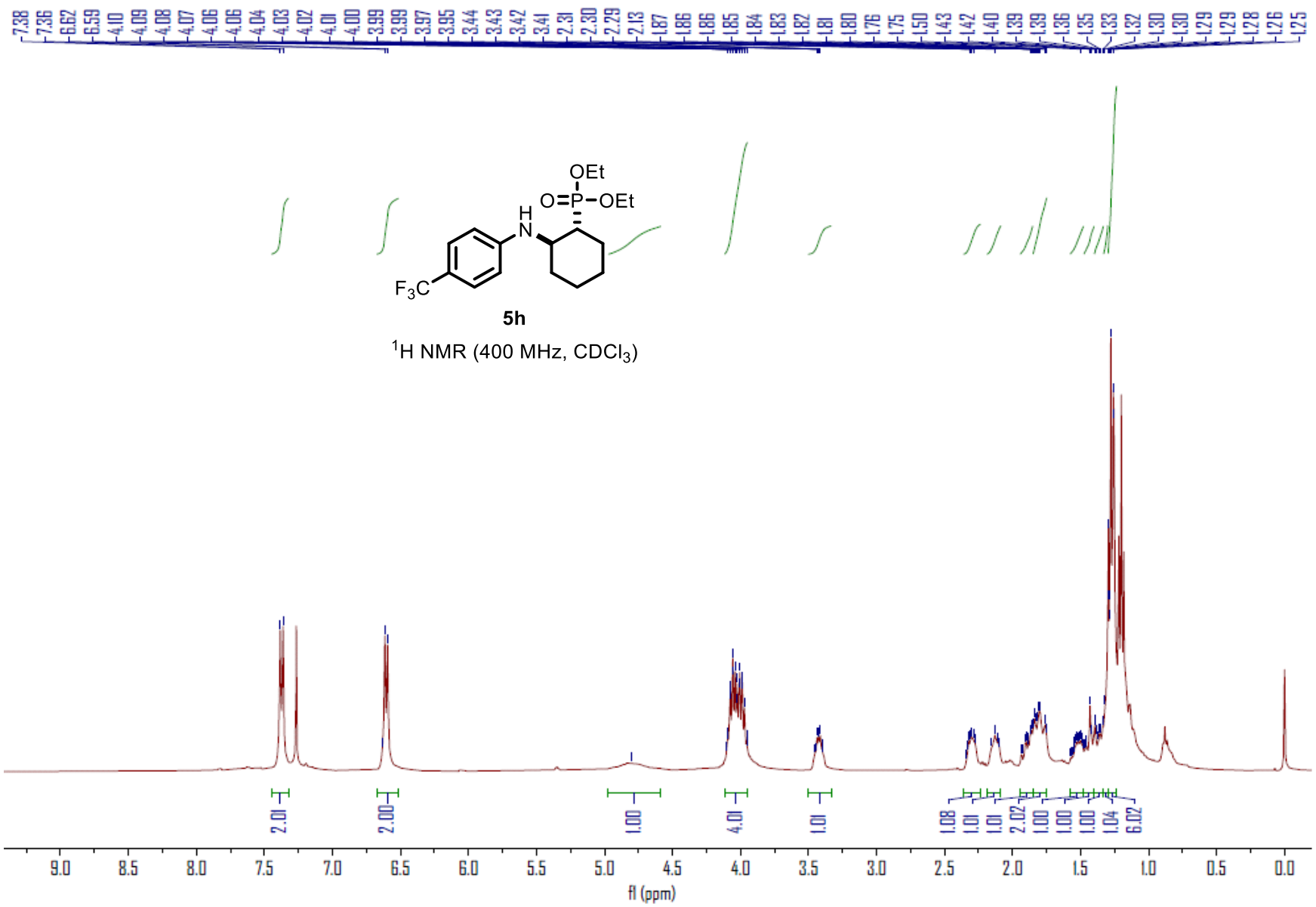
5g

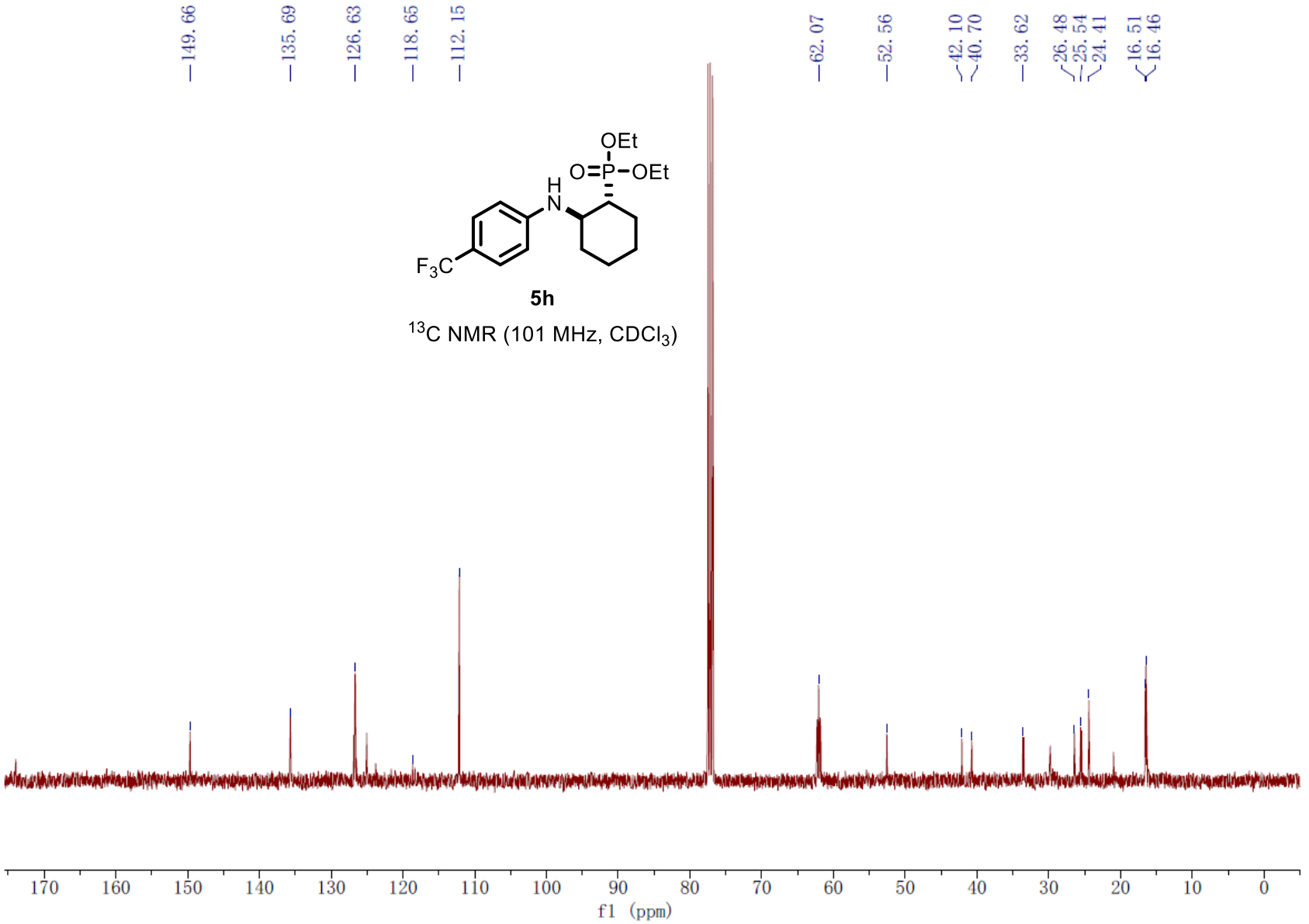
^{13}C NMR (101 MHz, $CDCl_3$)

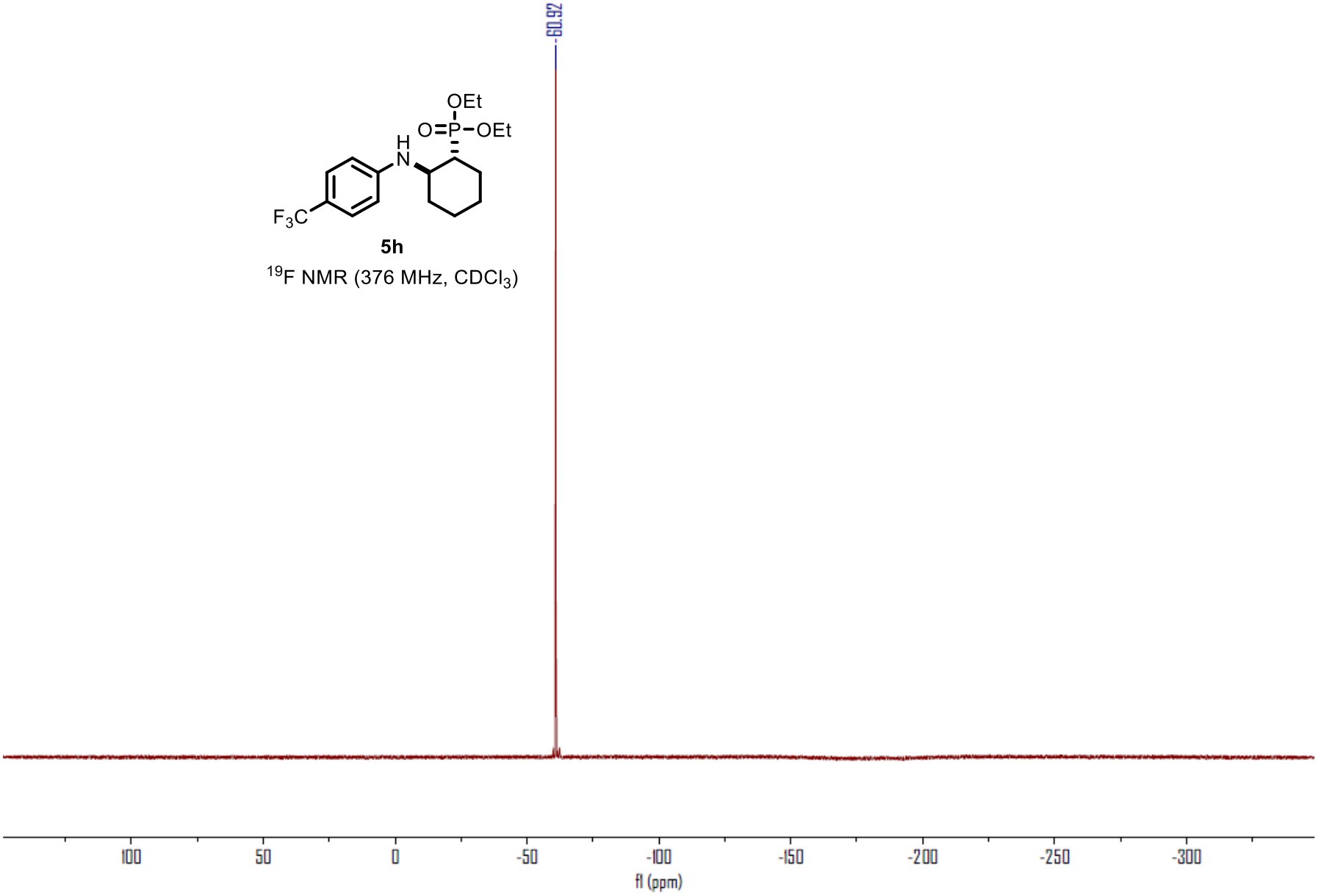


5g

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

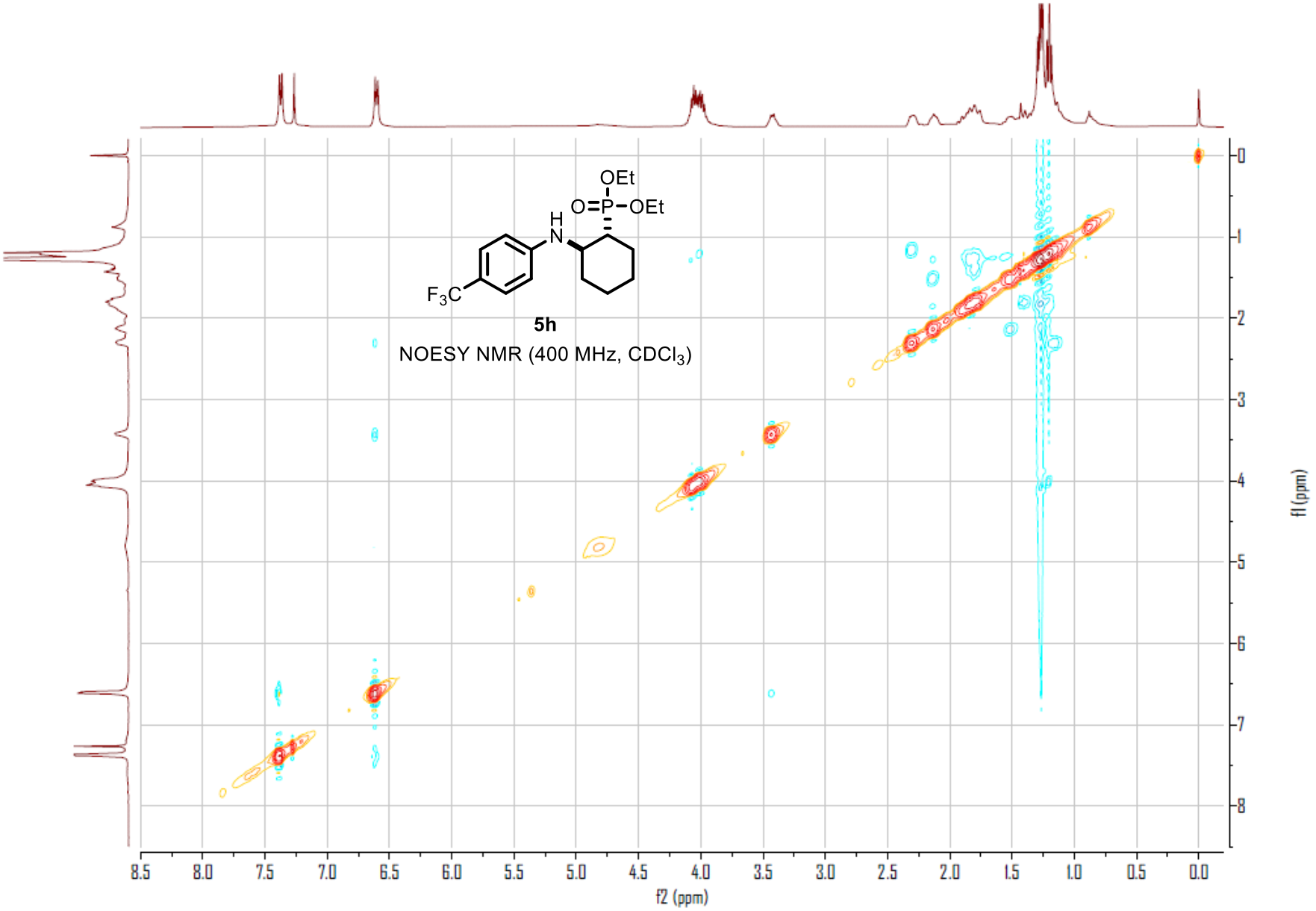

OEt
O=P–OEt
H
N
F3C
5h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

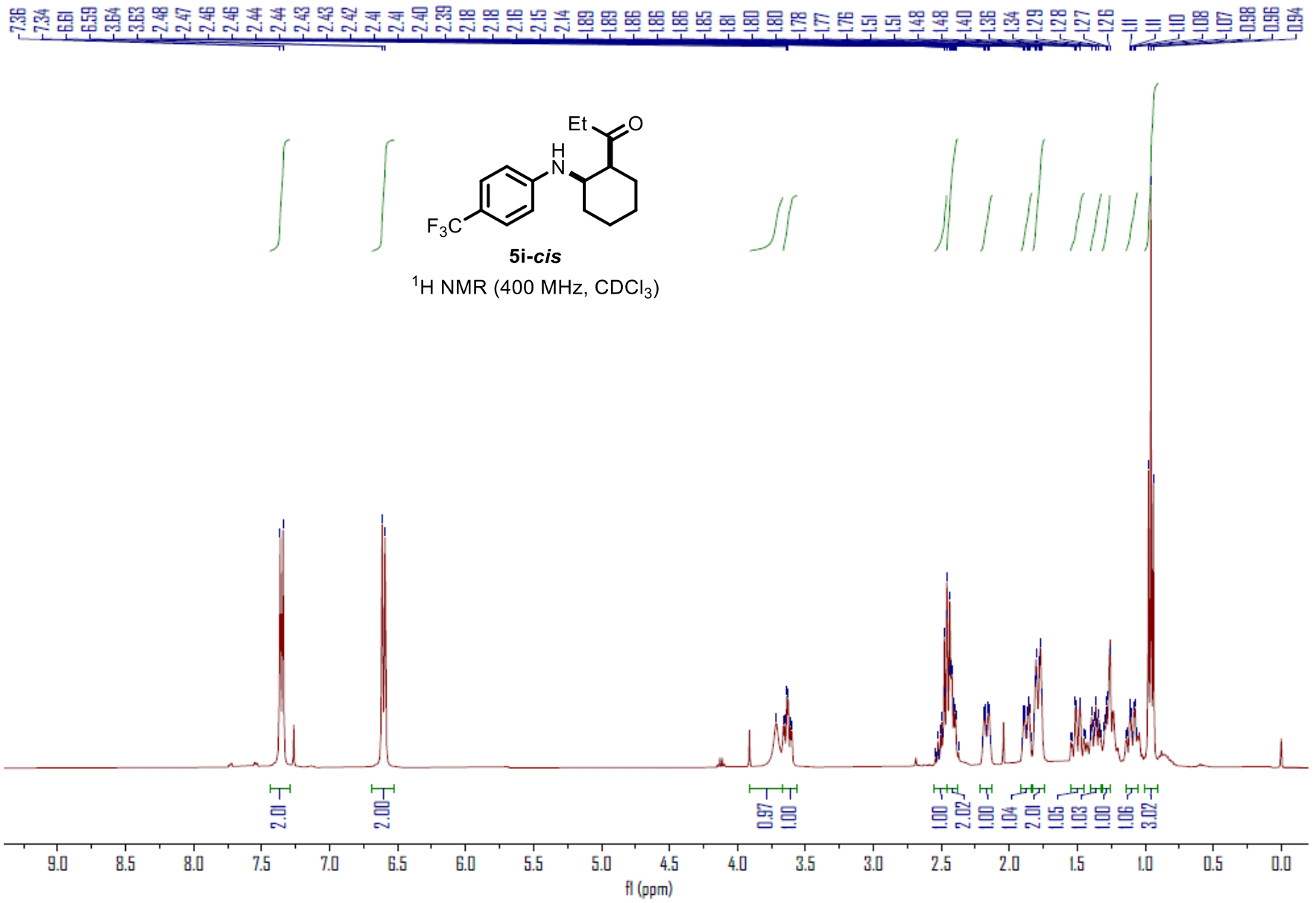

149.66
135.69
126.63
118.65
112.15
62.07
52.56
42.10
40.70
33.62
26.48
25.54
24.41
16.51
16.46
OEt
O=P-OEt
H
N
F3C
5h
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

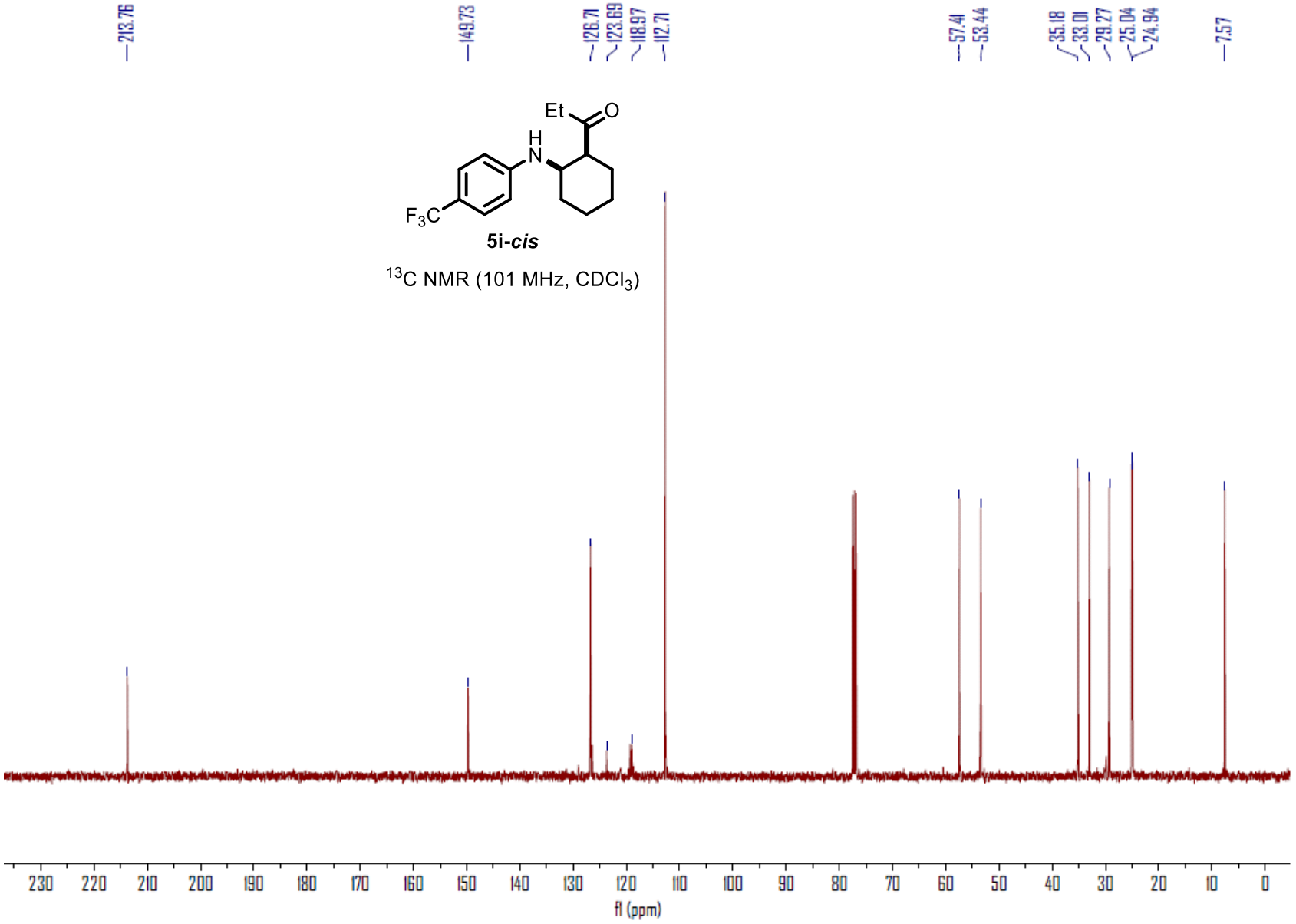


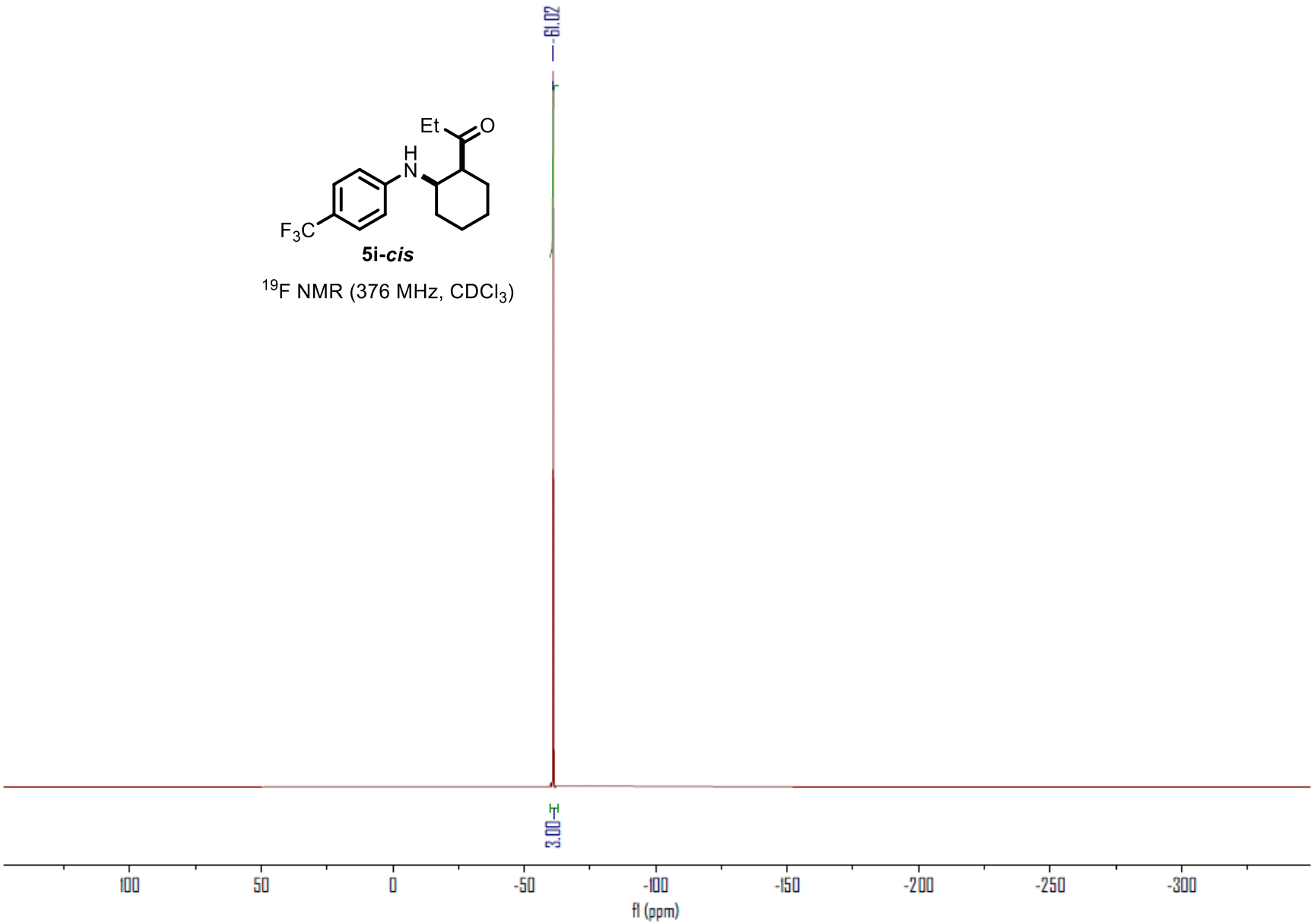
5h

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


OEt
O=P–OEt
H
N
F3C
5h
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

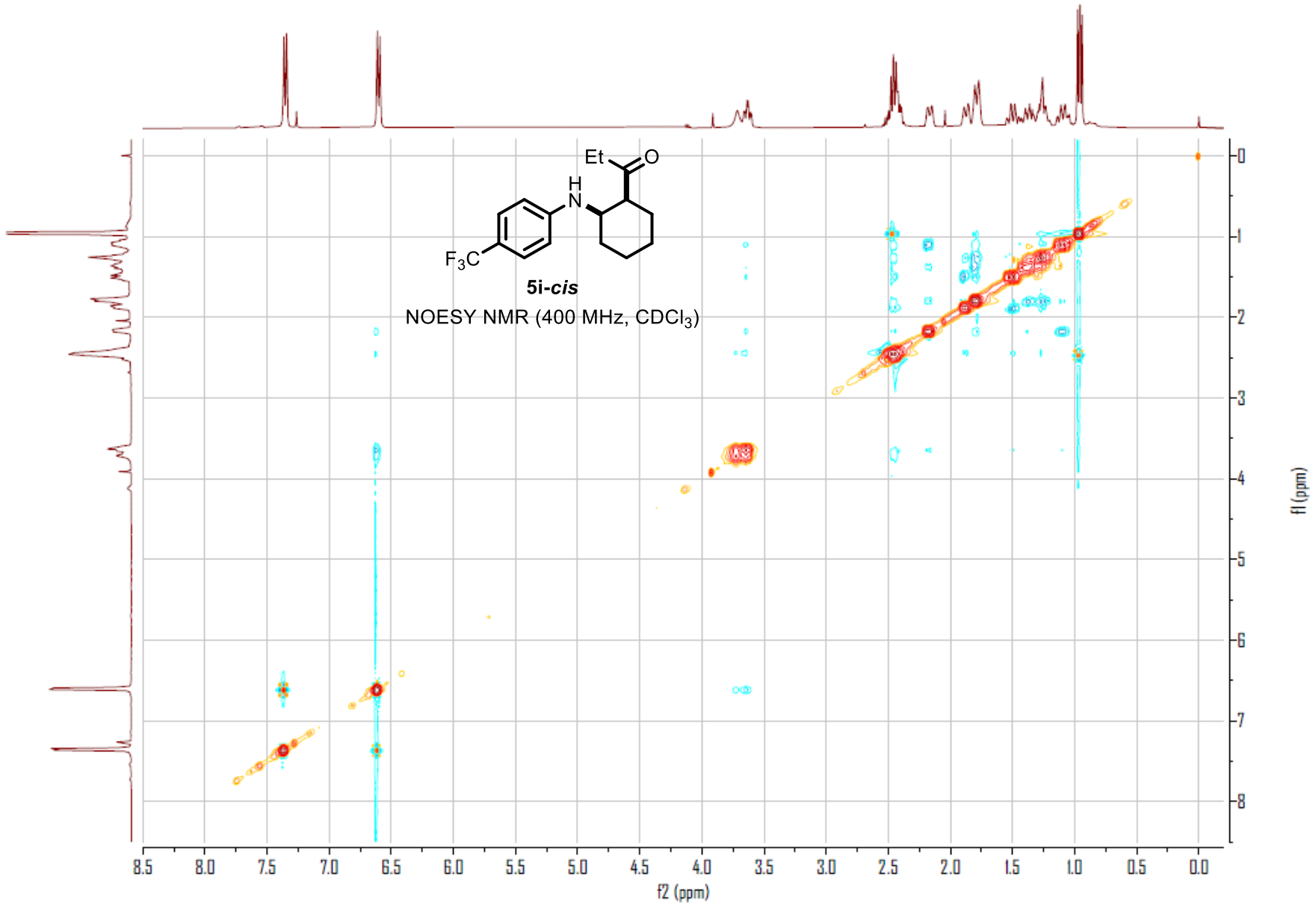

Et
O
H
N
F3C
5i-cis
1H NMR (400 MHz, CDCl3)
f1 (ppm)

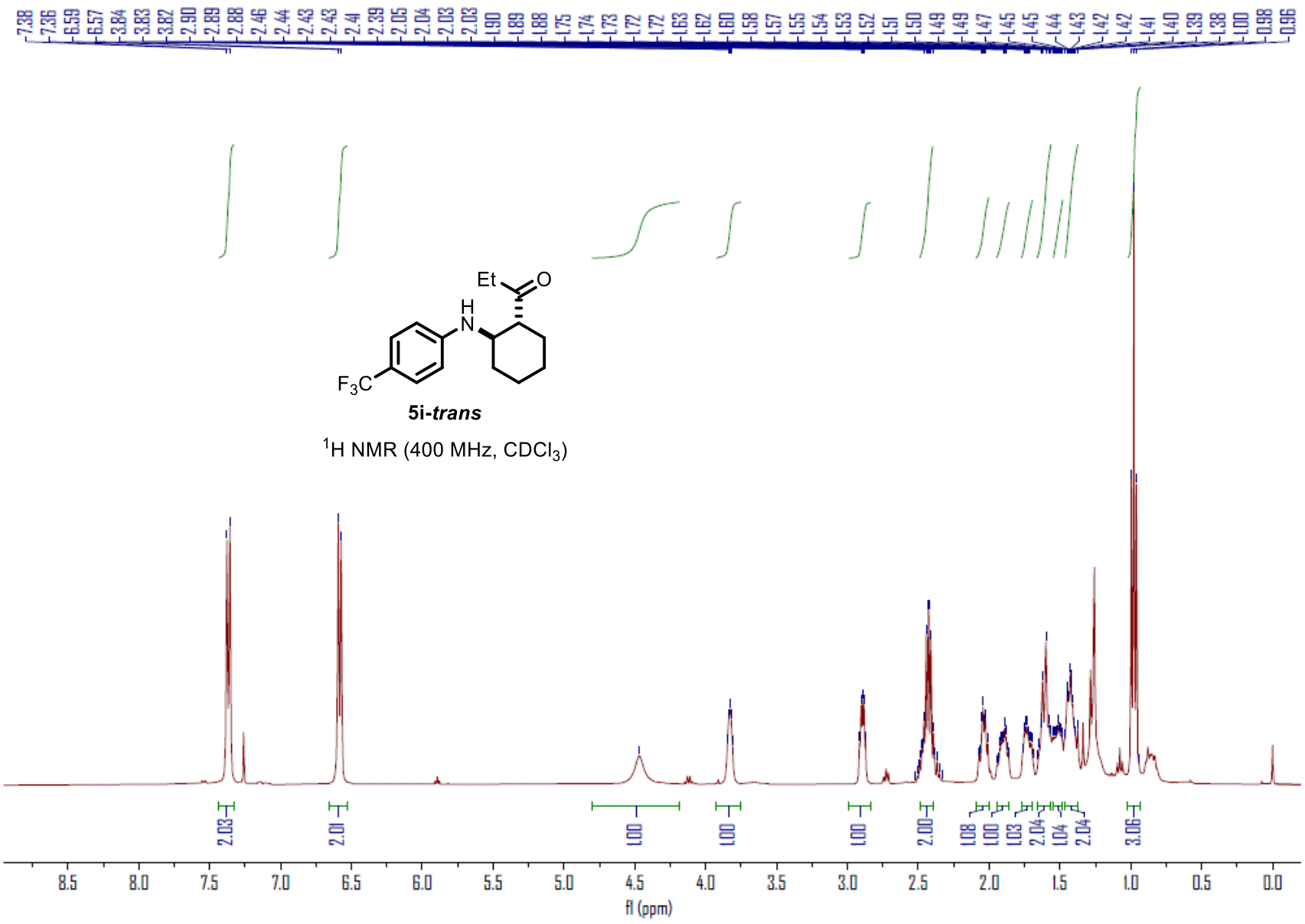

213.76
149.73
126.71
123.69
118.97
112.71
57.41
53.44
35.18
33.01
29.27
25.04
24.94
7.57
Et
O
H
N
F3C
5i-cis
13C NMR (101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5i-*cis*

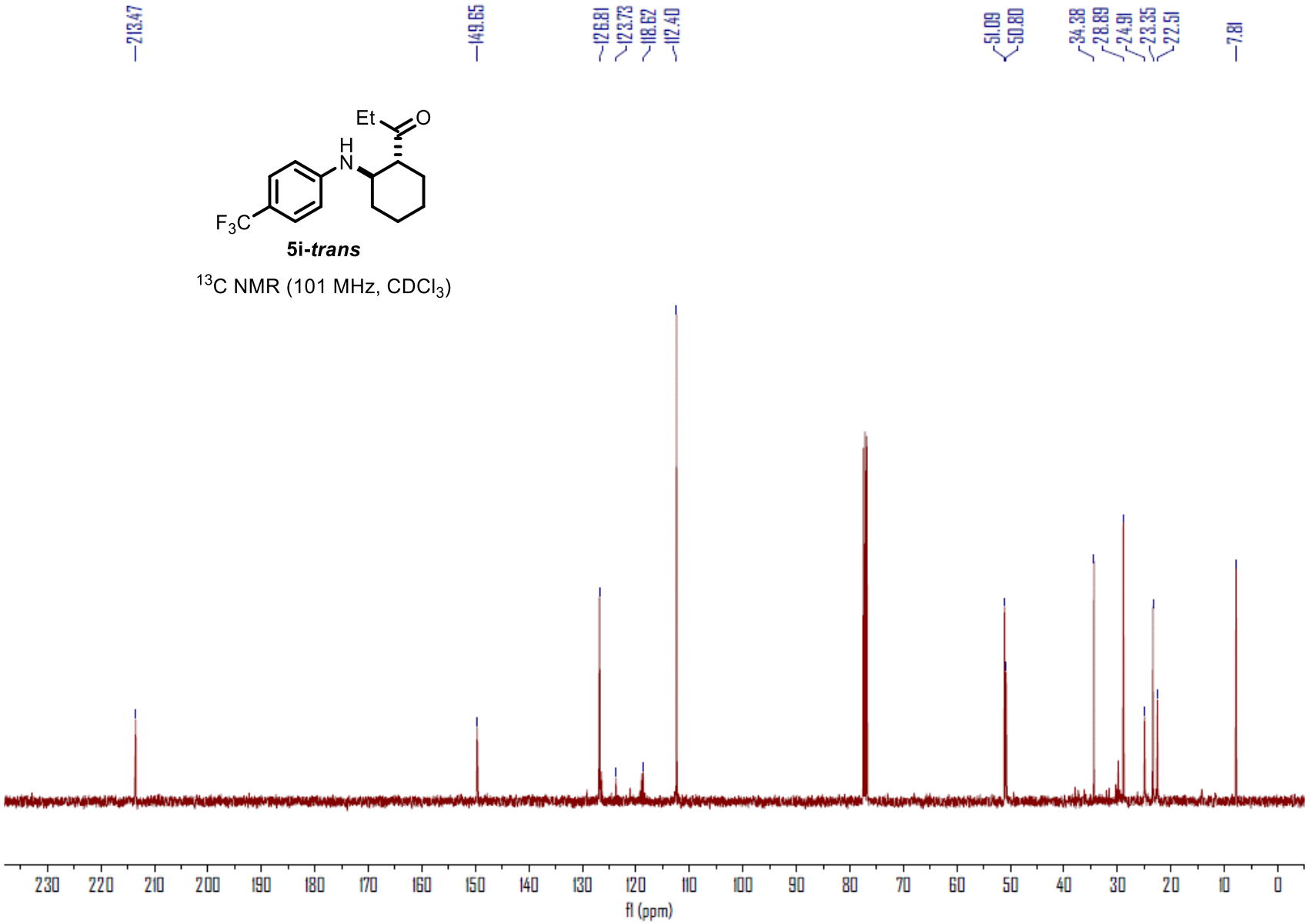
^{19}F NMR (376 MHz, $CDCl_3$)

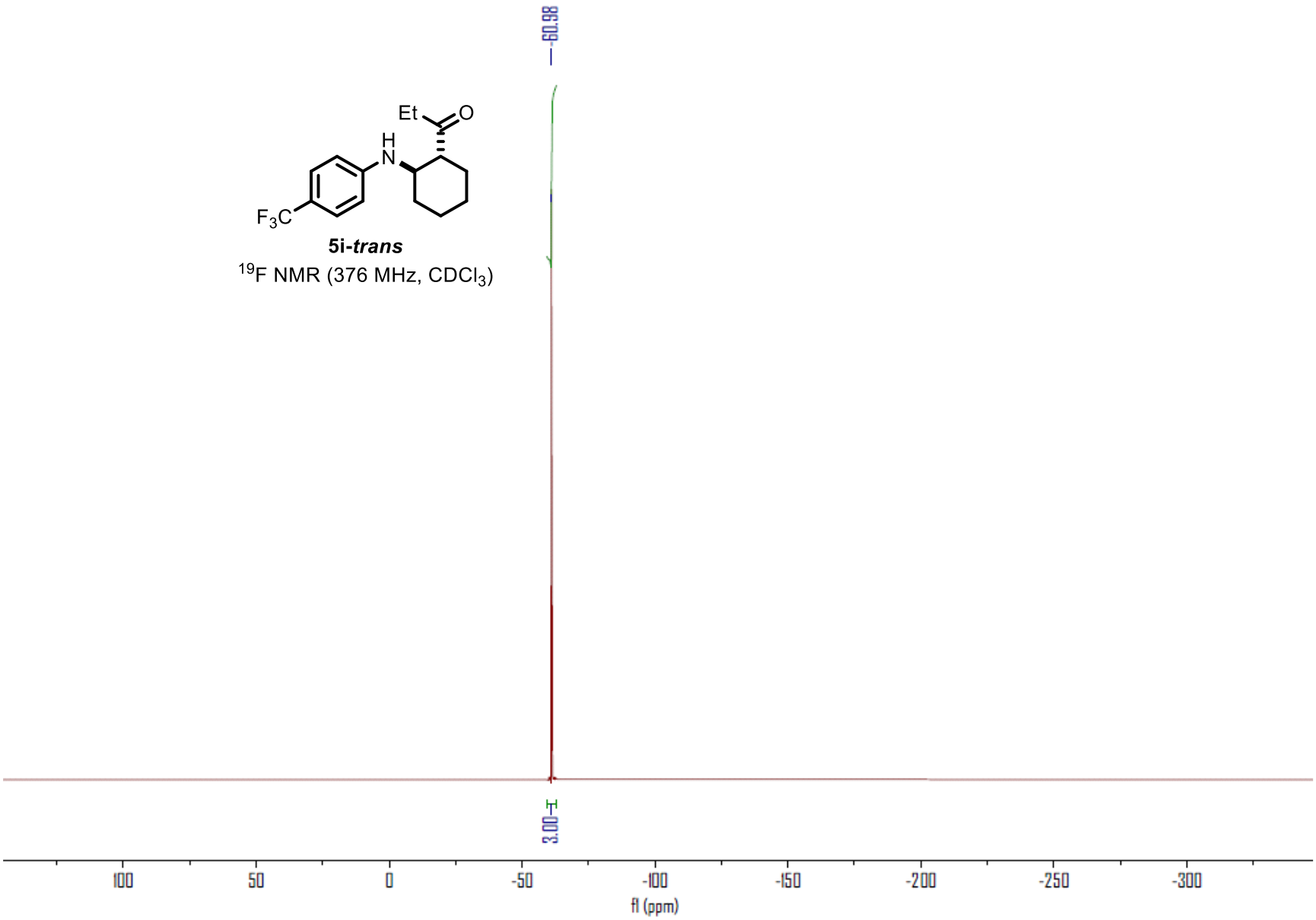

Et
O
H
N
F3C
5i-cis
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

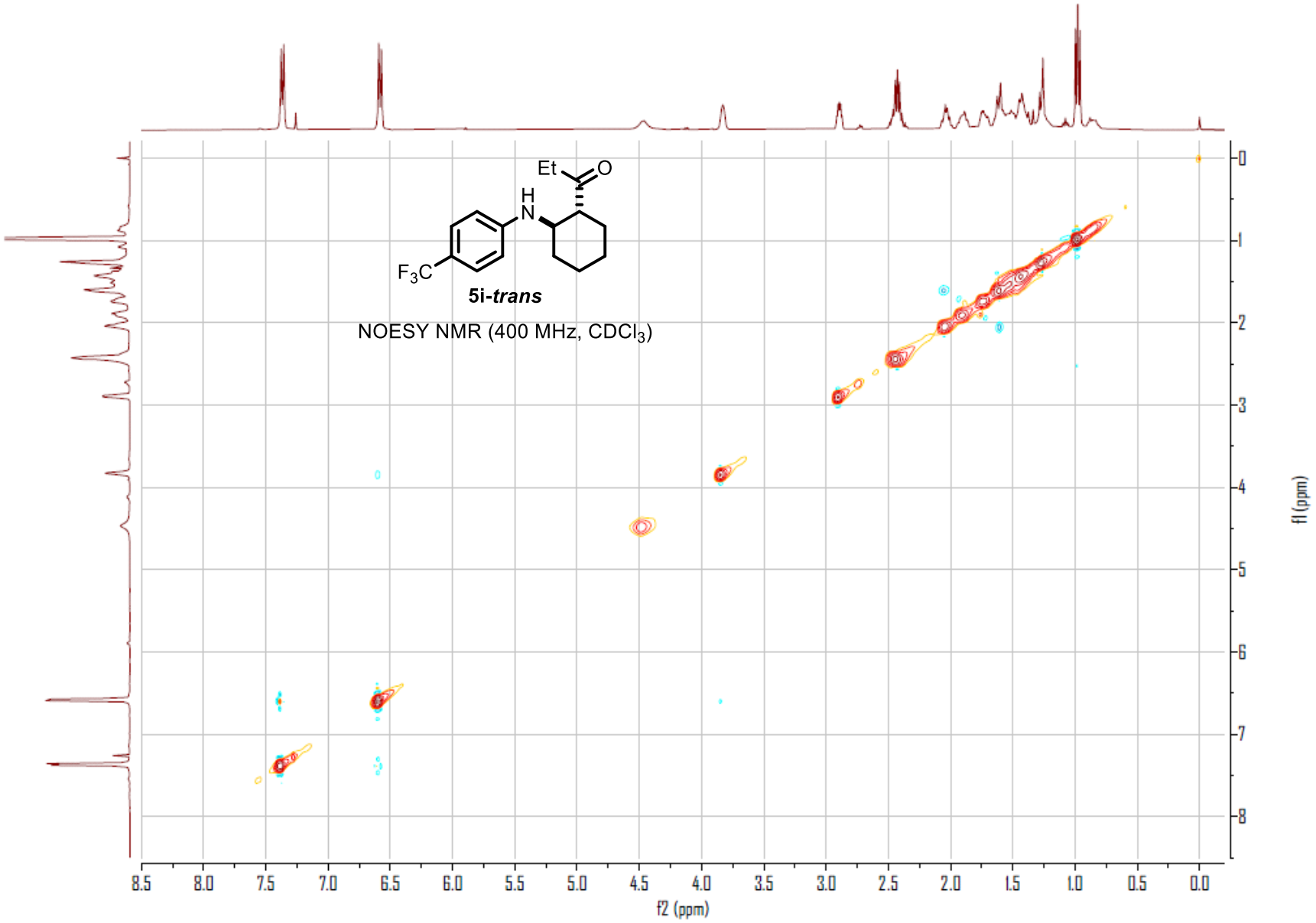


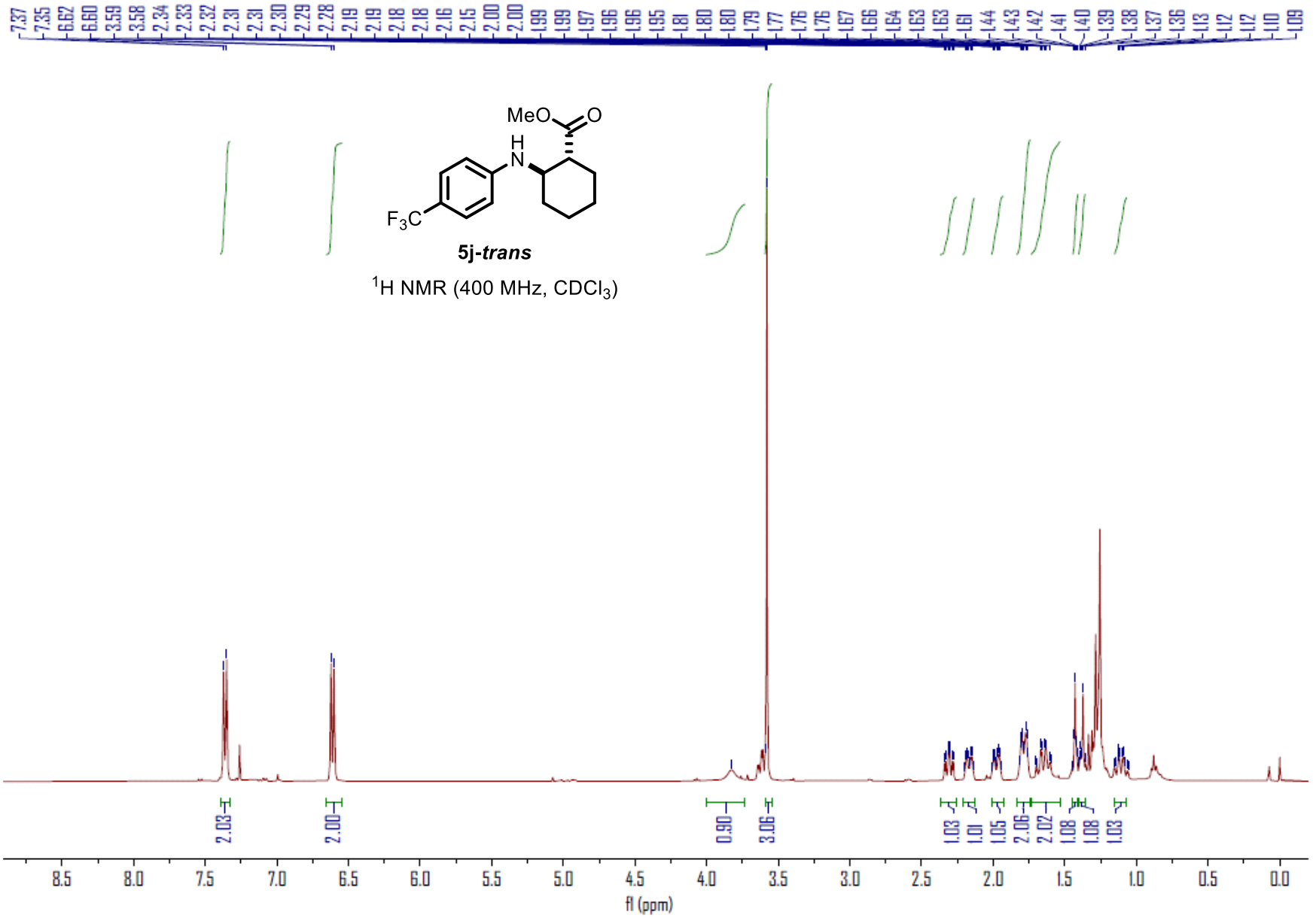
5i-*trans*

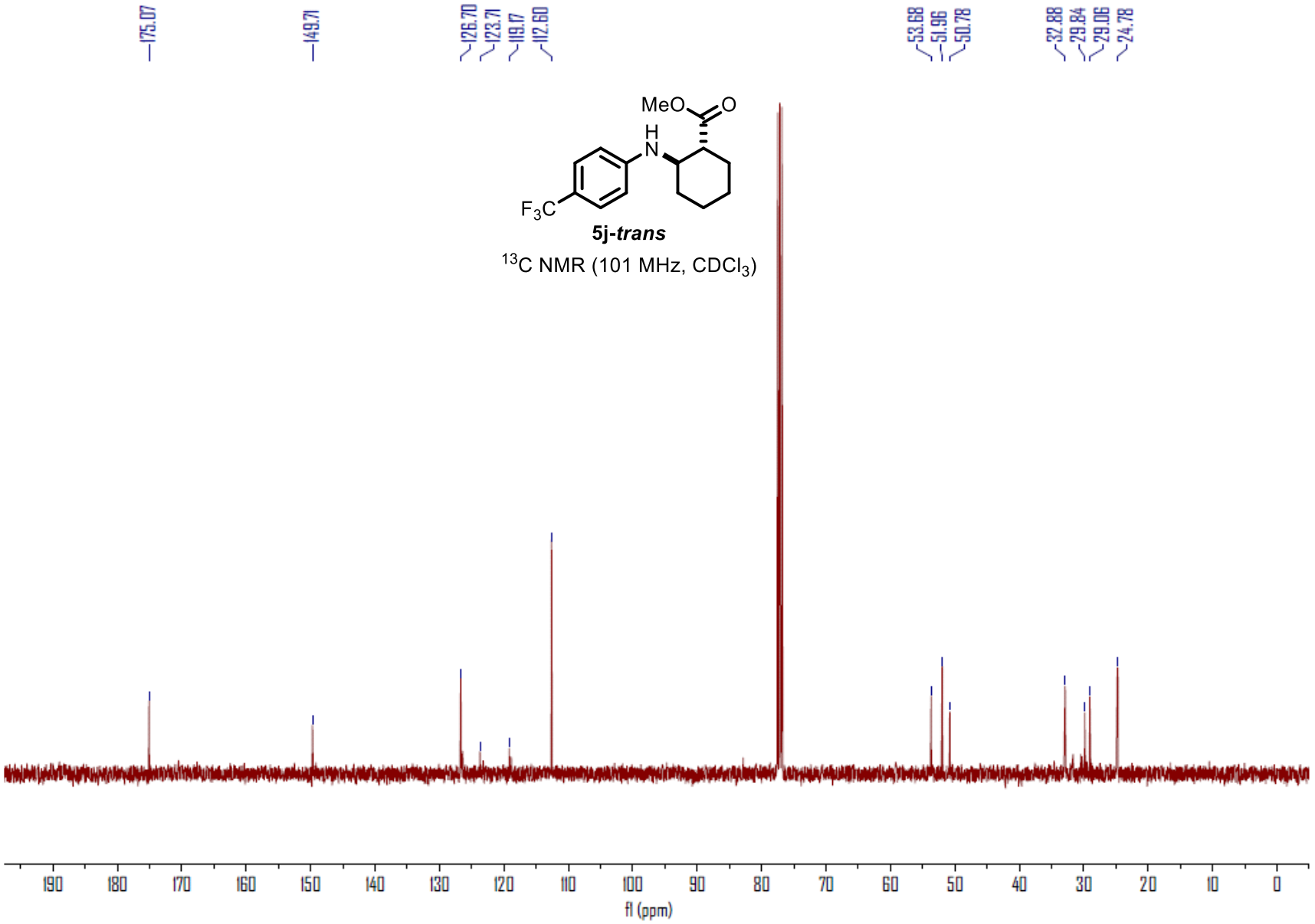
^{1}H NMR (400 MHz, $CDCl_3$)

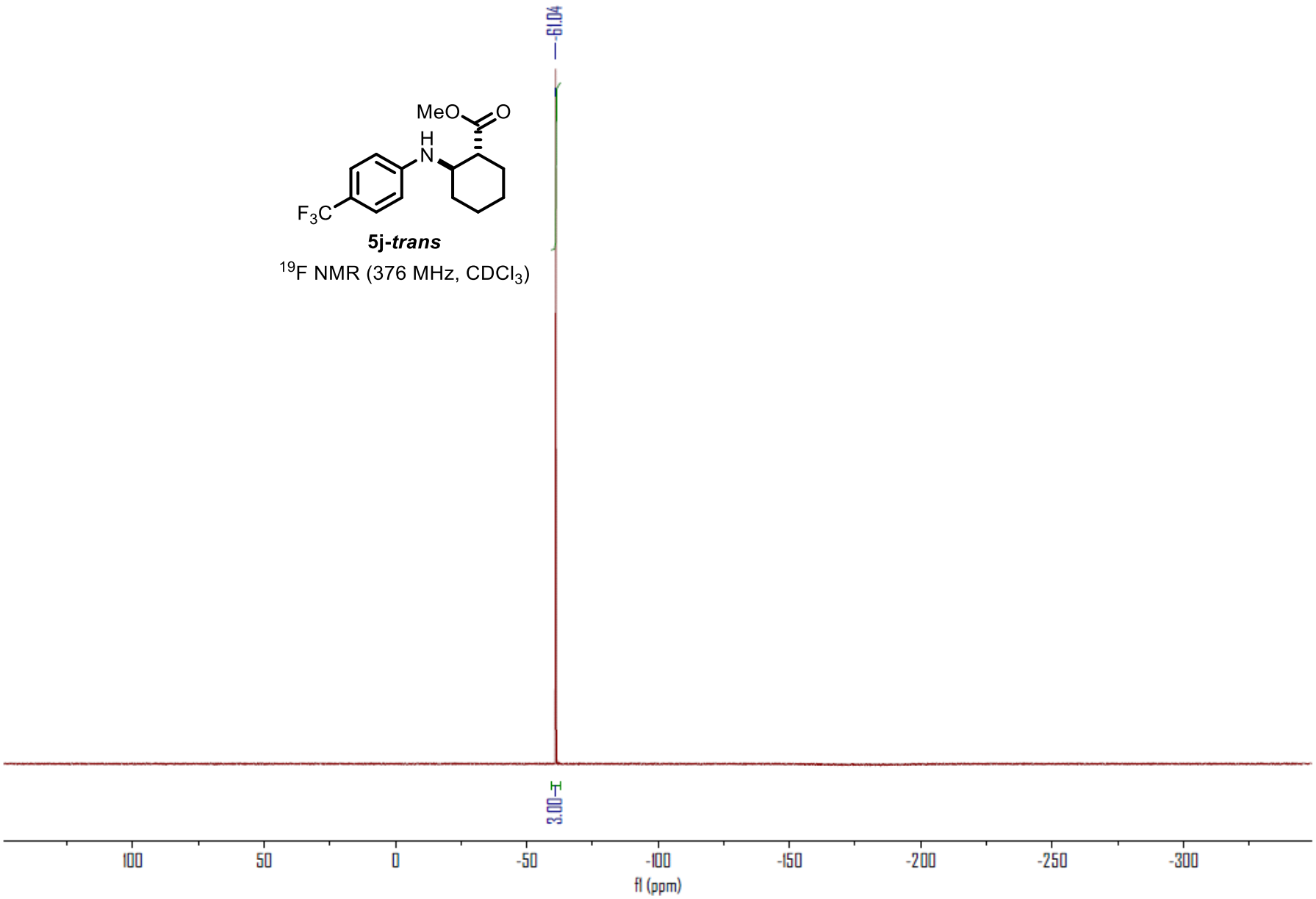

213.47
149.65
126.81
123.73
118.62
112.40
51.09
50.80
34.38
28.89
24.91
23.35
22.51
7.81
Et
O
H
N
F3C
5i-trans
13C NMR (101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Et
O
H
N
F3C
5i-trans
19F NMR (376 MHz, CDCl3)
-60.98
3.00
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


Et
O
H
N
F3C
5i-trans
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

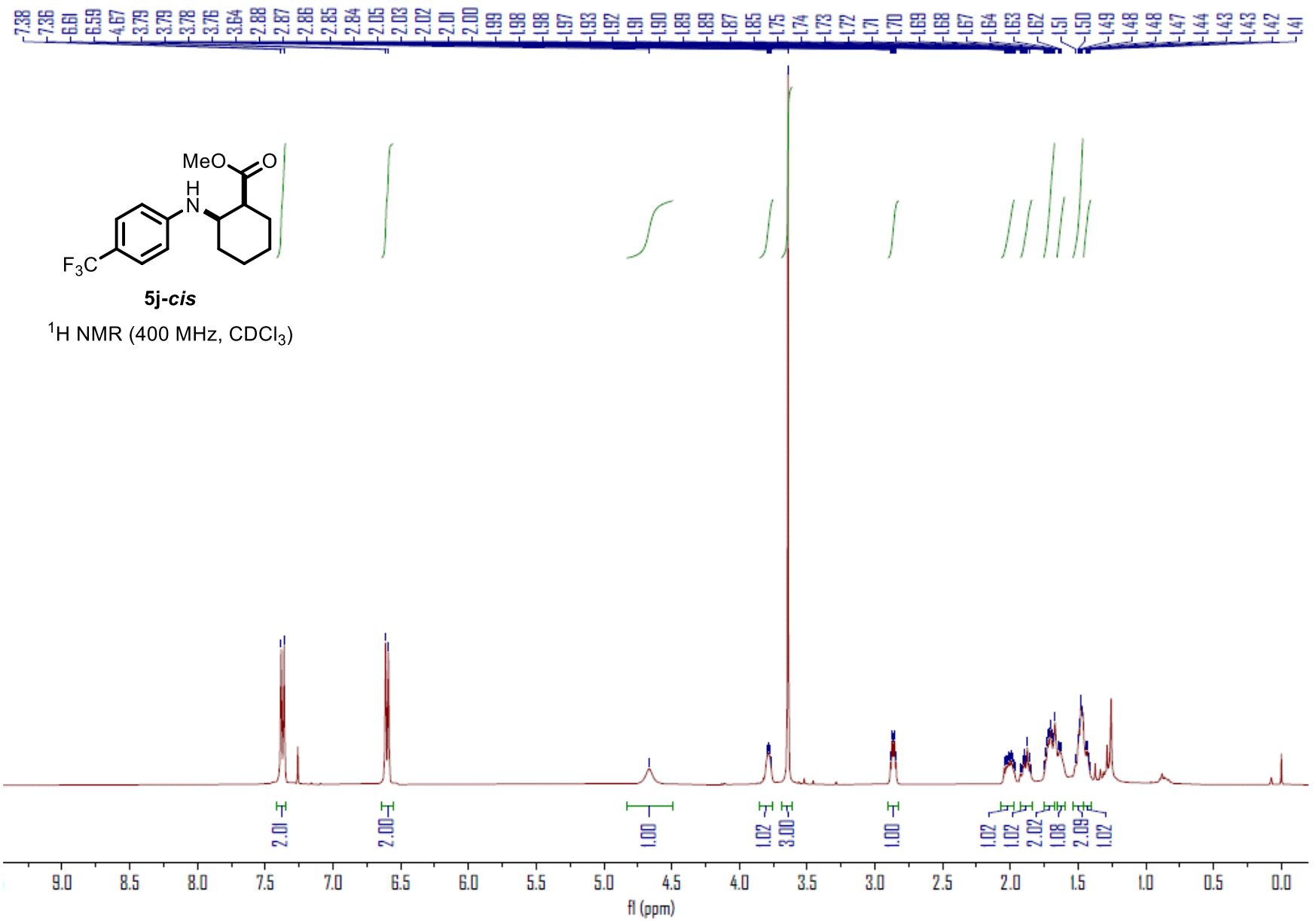

MeO
O
H
N
F3C
5j-trans
1H NMR (400 MHz, CDCl3)
f1 (ppm)

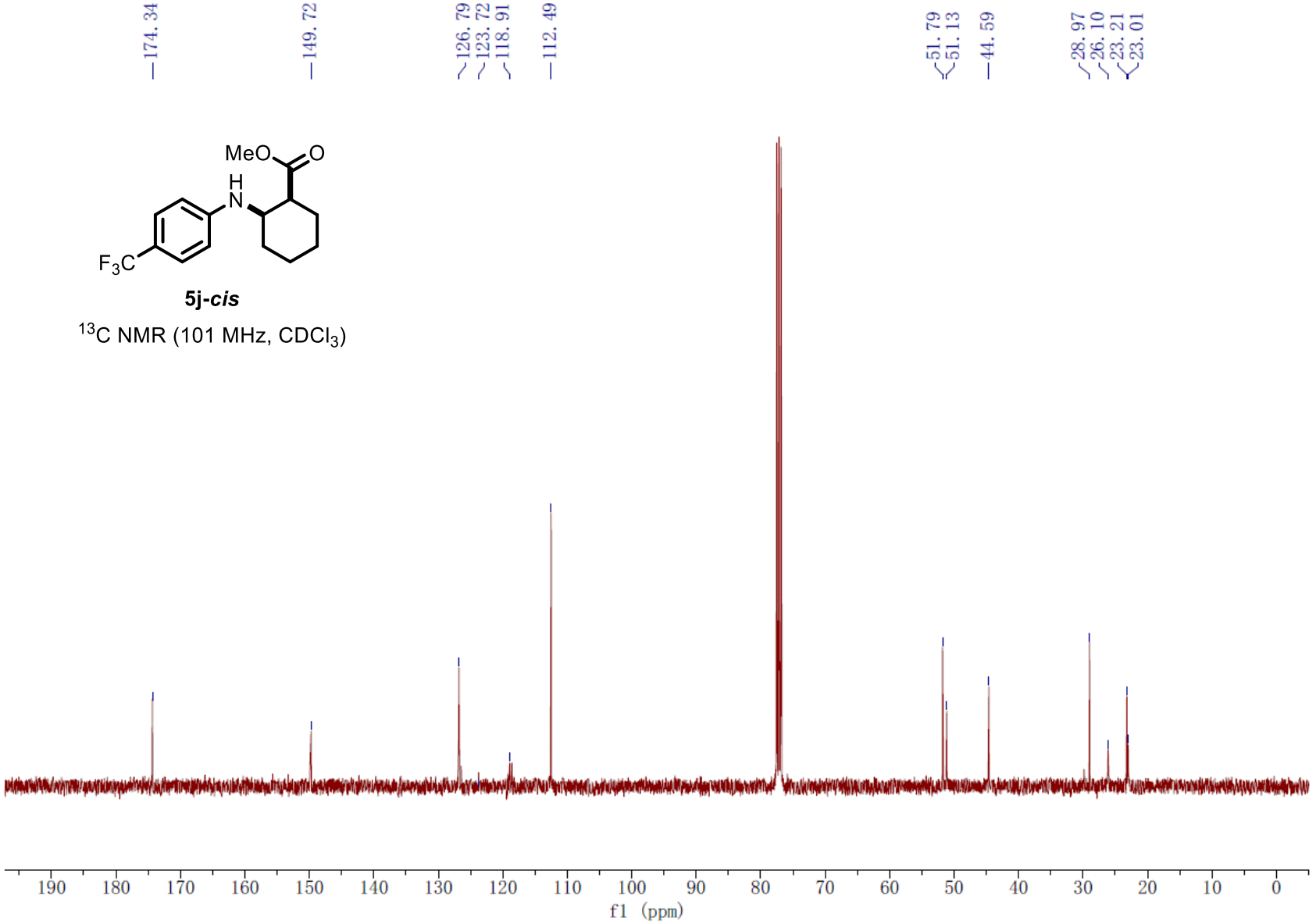

175.07
149.71
126.70
123.71
119.17
112.60
53.68
51.96
50.78
32.88
29.84
29.06
24.78
MeO
O
H
N
F3C
5j-trans
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

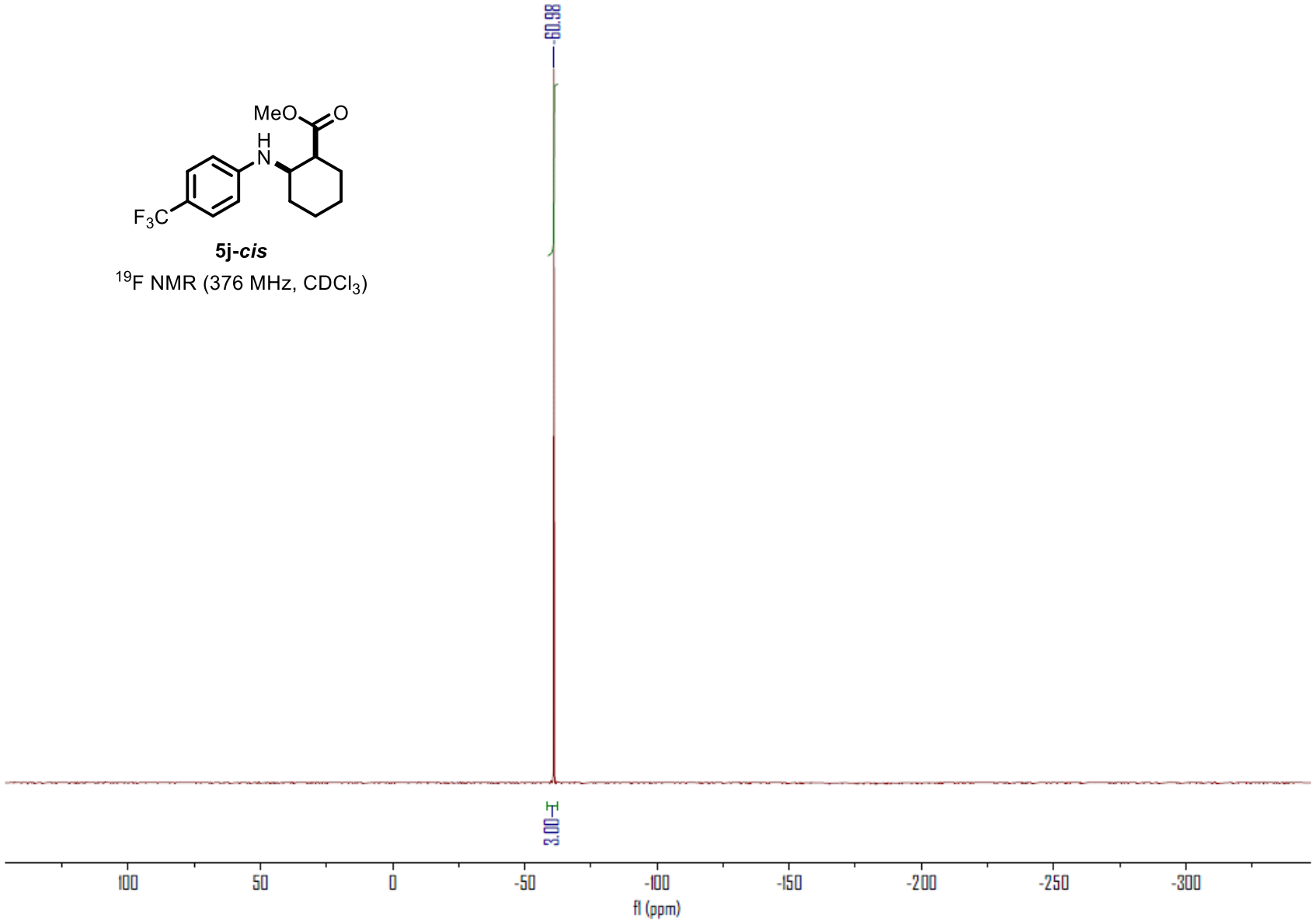


5j-*trans*

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

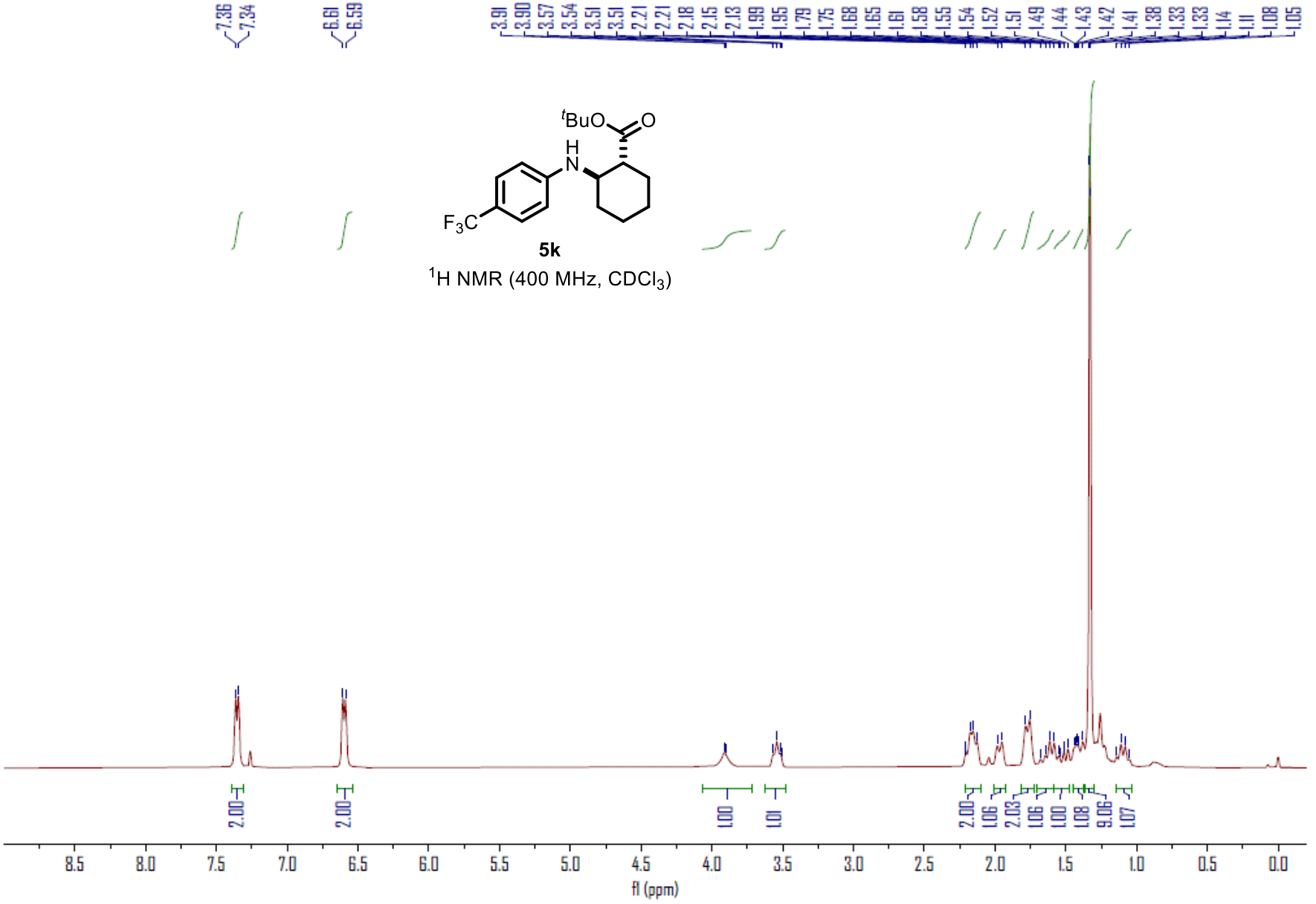

MeO
O
H
N
F3C
5j-cis
1H NMR (400 MHz, CDCl3)
f1 (ppm)

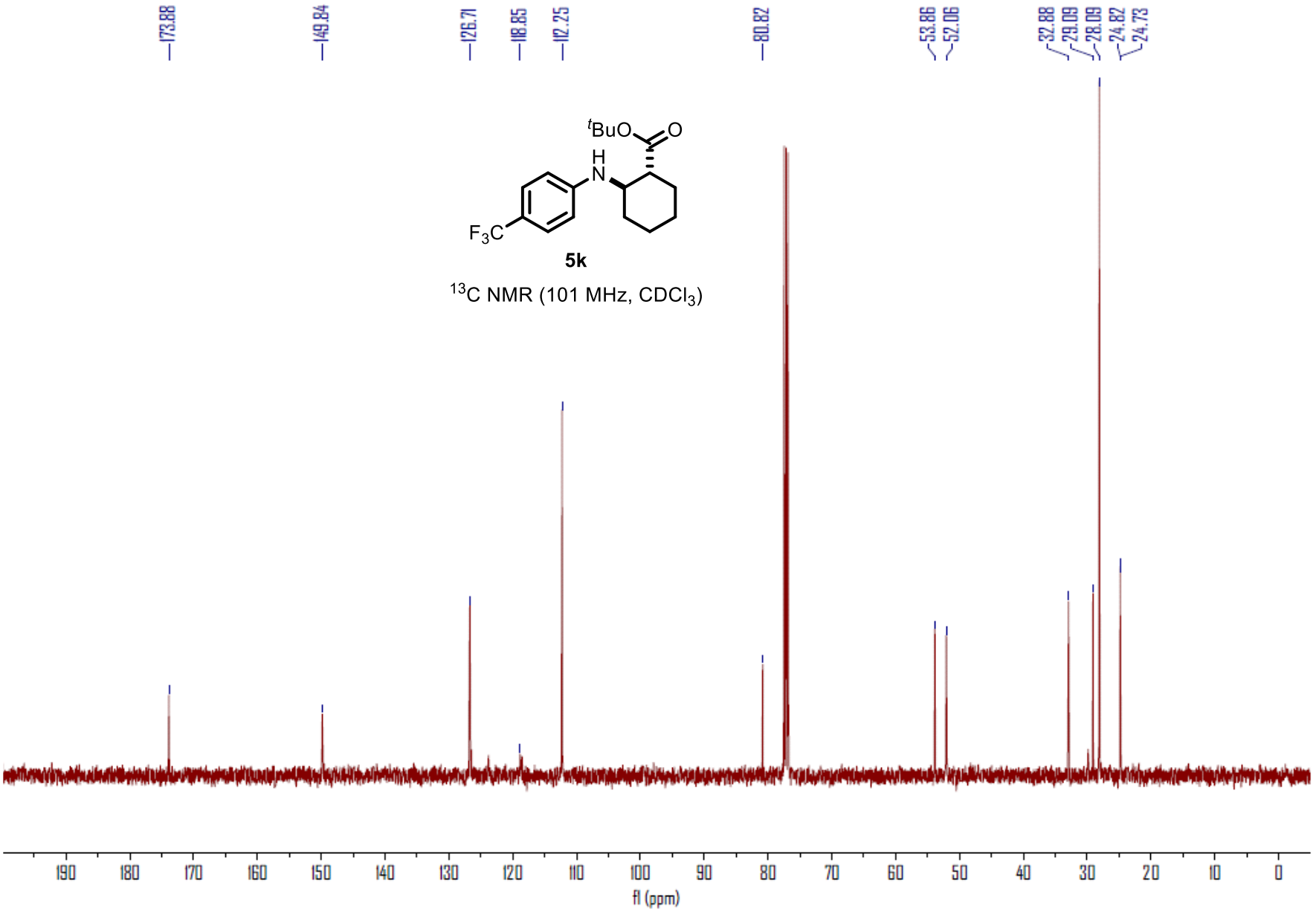

174.34
149.72
126.79
123.72
118.91
112.49
51.79
51.13
44.59
28.97
26.10
23.21
23.01
MeO
O
H
N
F3C
5j-cis
13C NMR (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

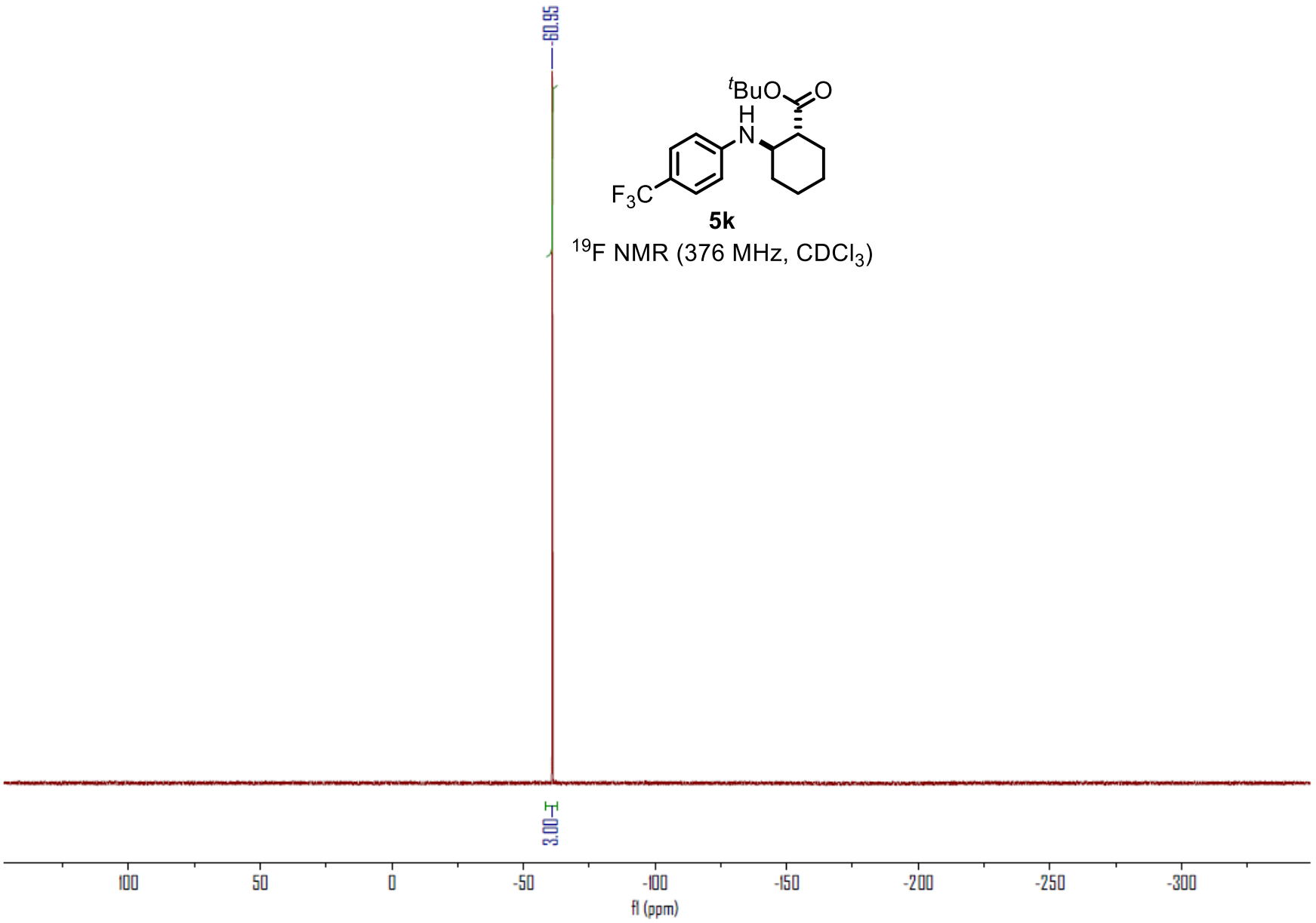


5j-*cis*

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

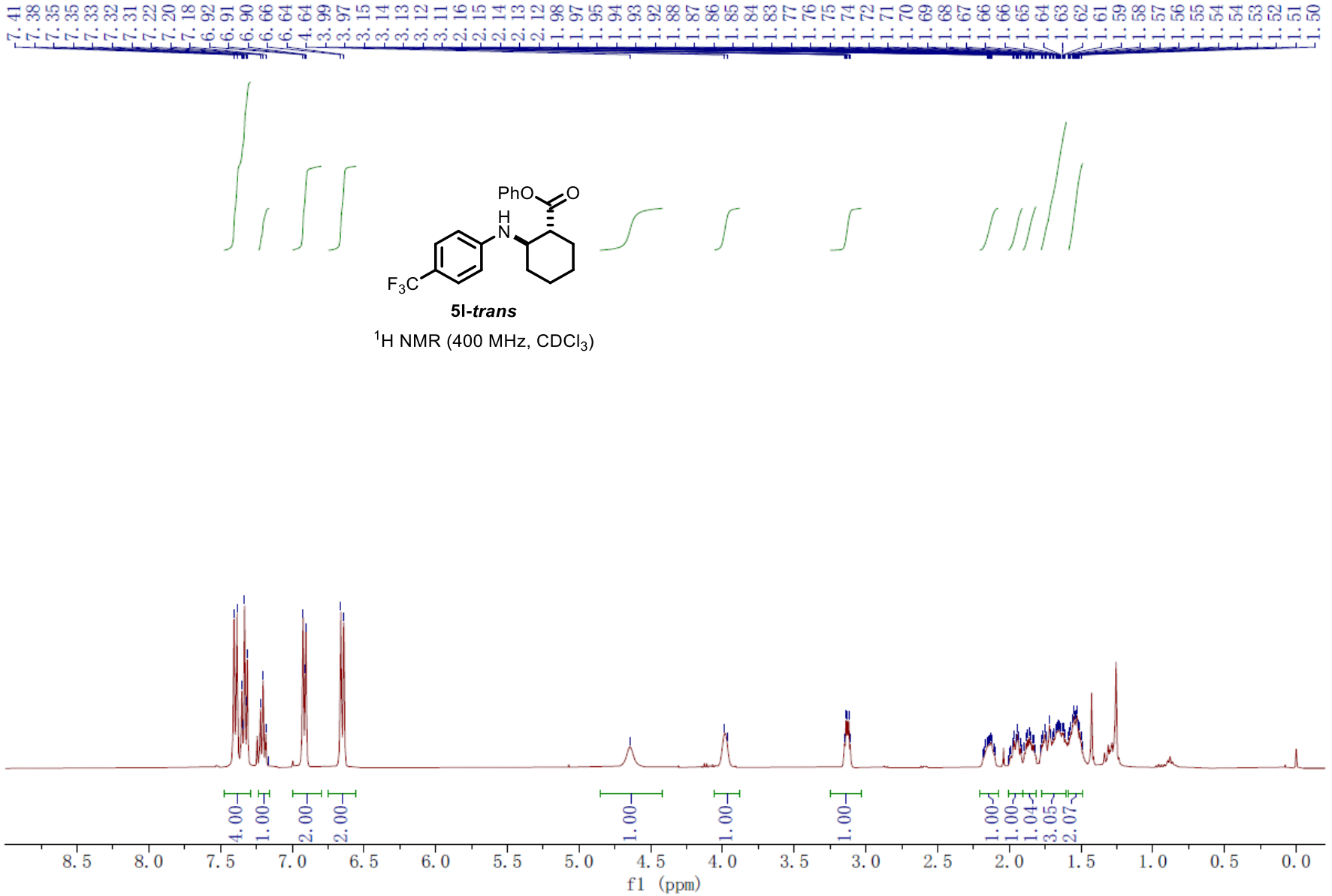

7.36
7.34
6.61
6.59
3.91
3.90
3.57
3.54
3.51
3.51
2.21
2.21
2.18
2.15
2.13
1.99
1.95
1.79
1.75
1.68
1.65
1.61
1.58
1.55
1.54
1.52
1.51
1.49
1.44
1.43
1.42
1.41
1.38
1.33
1.33
1.14
1.11
1.08
1.05
tBuO
O
H
N
F3C
5k
1H NMR (400 MHz, CDCl3)
2.00
2.00
1.00
1.01
2.00
1.06
2.03
1.06
1.00
1.08
9.06
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.88
149.84
126.71
118.85
112.25
80.82
53.86
52.06
32.88
29.09
28.09
24.82
24.73
tBuO
O
H
N
F3C
5k
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



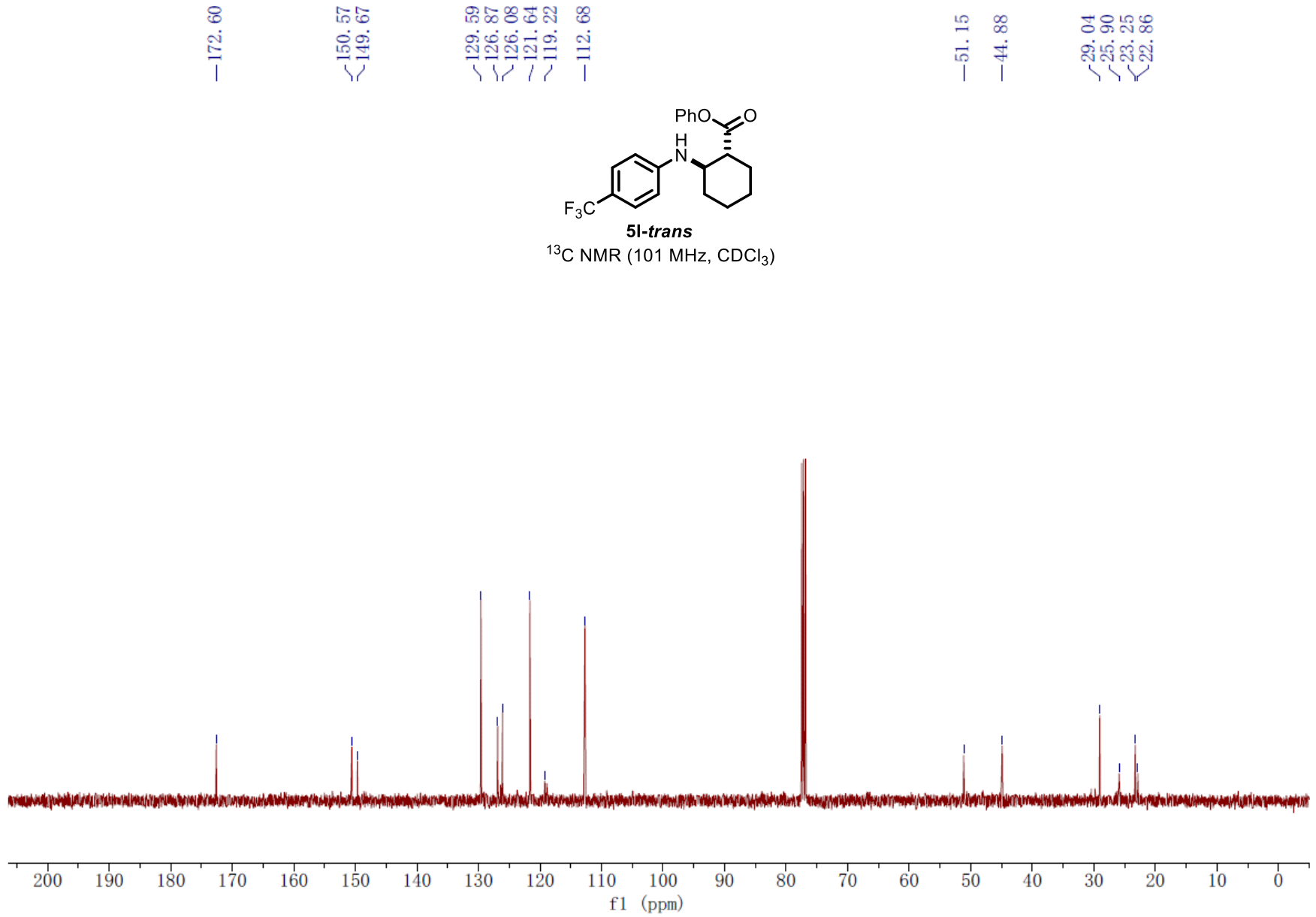
5k

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



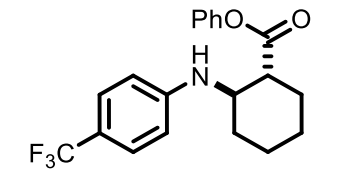
5l-*trans*

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



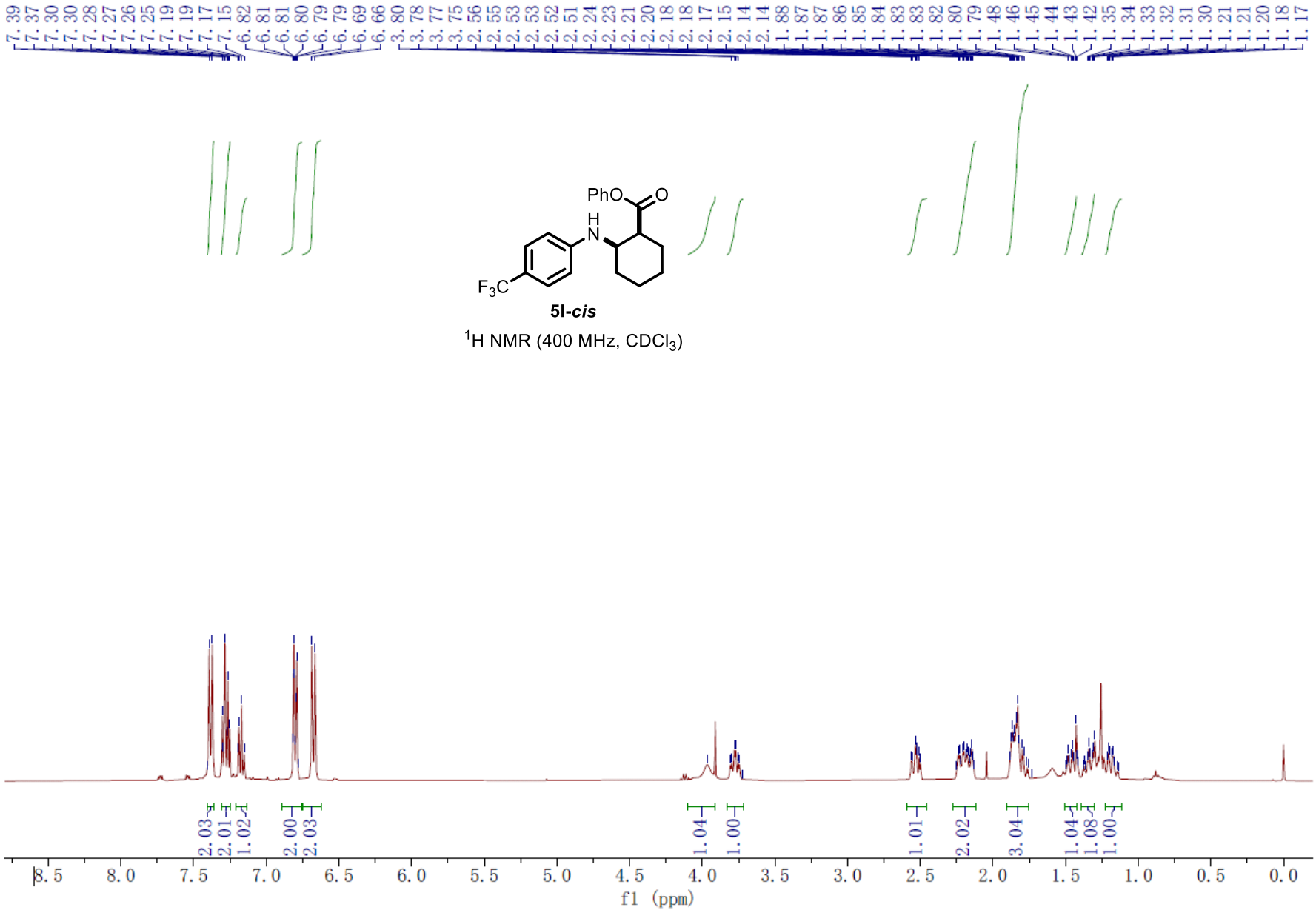
5l-*trans*

^{13}C NMR (101 MHz, $CDCl_3$)



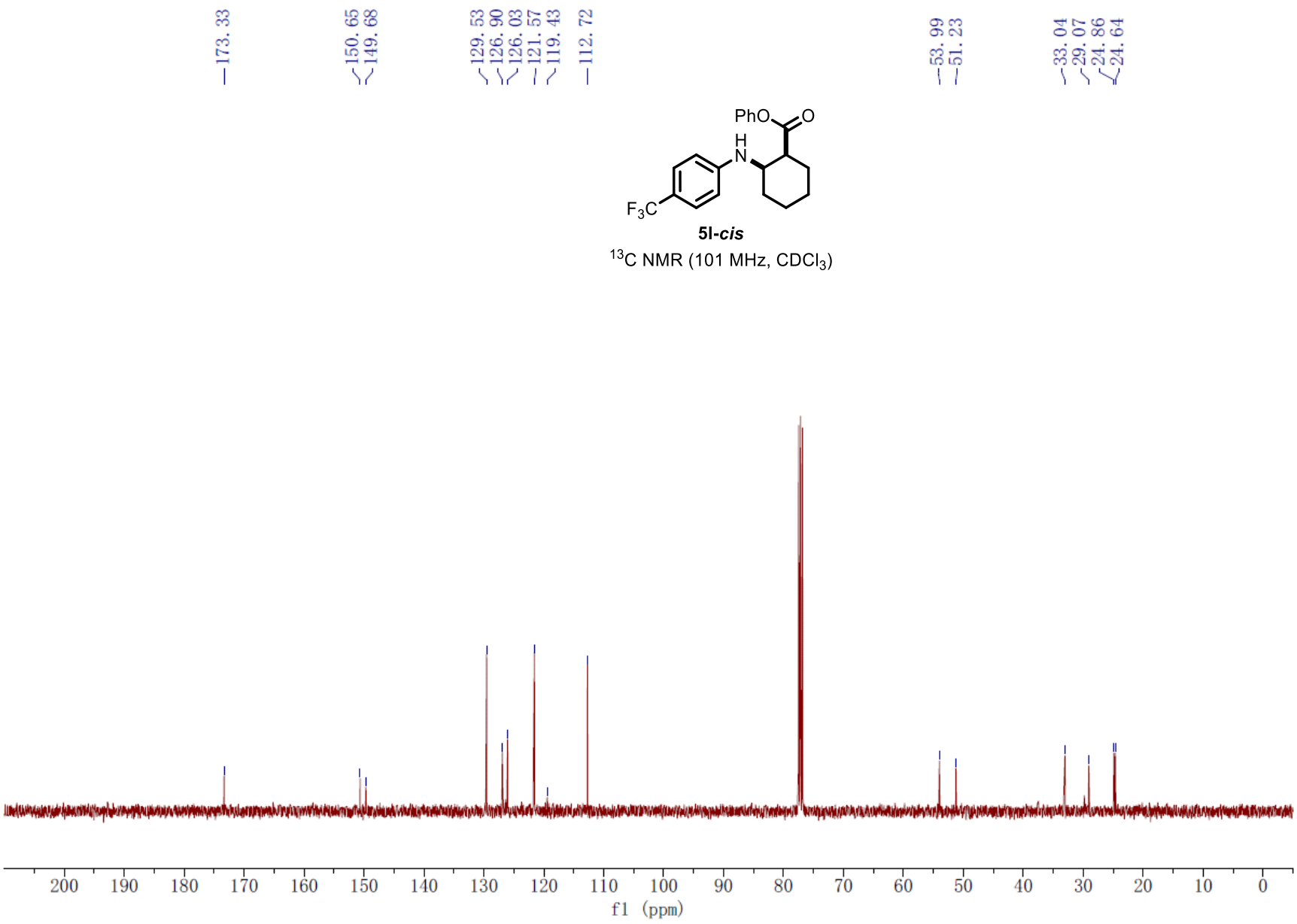
5l-*trans*

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



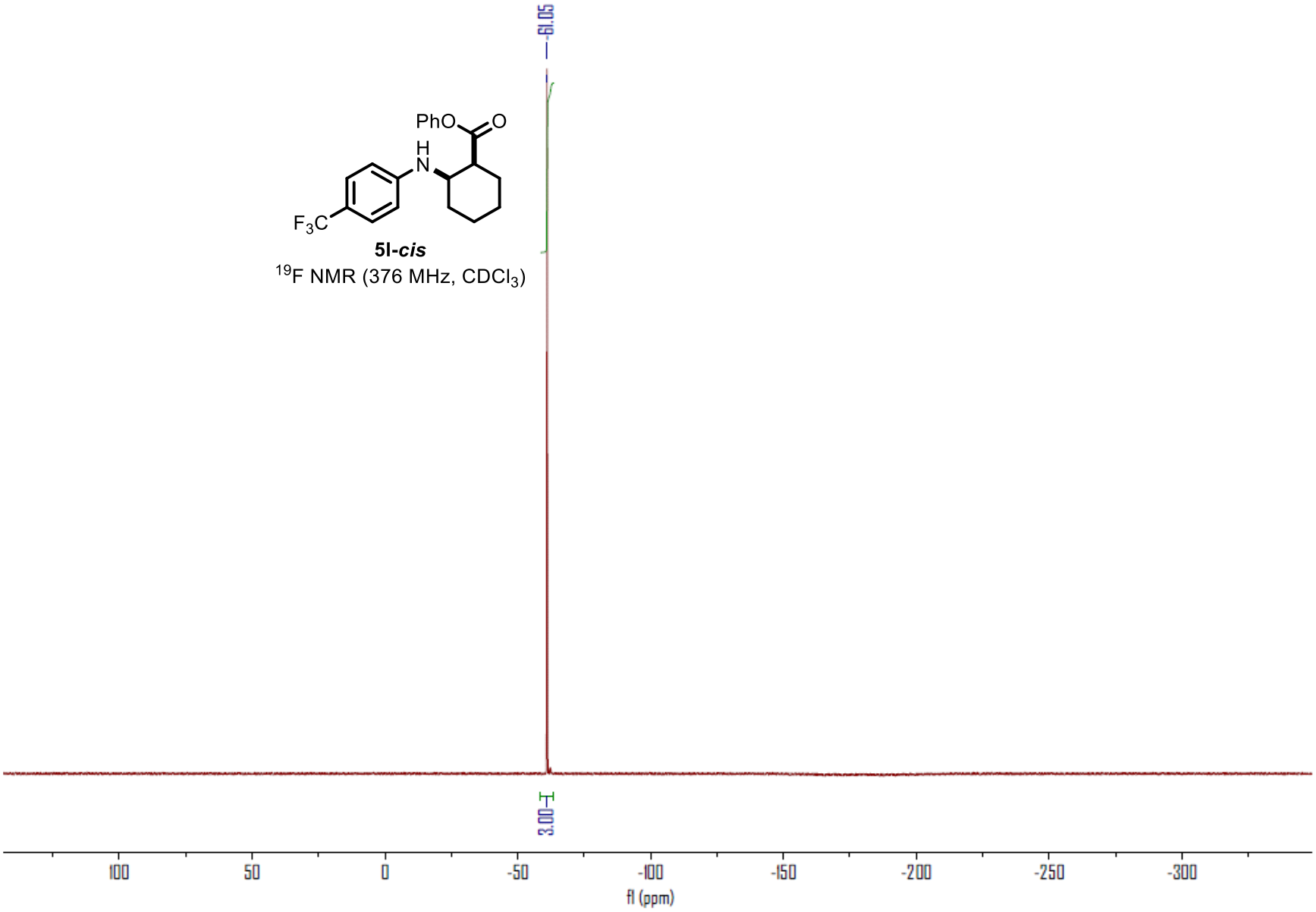
5l-*cis*

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



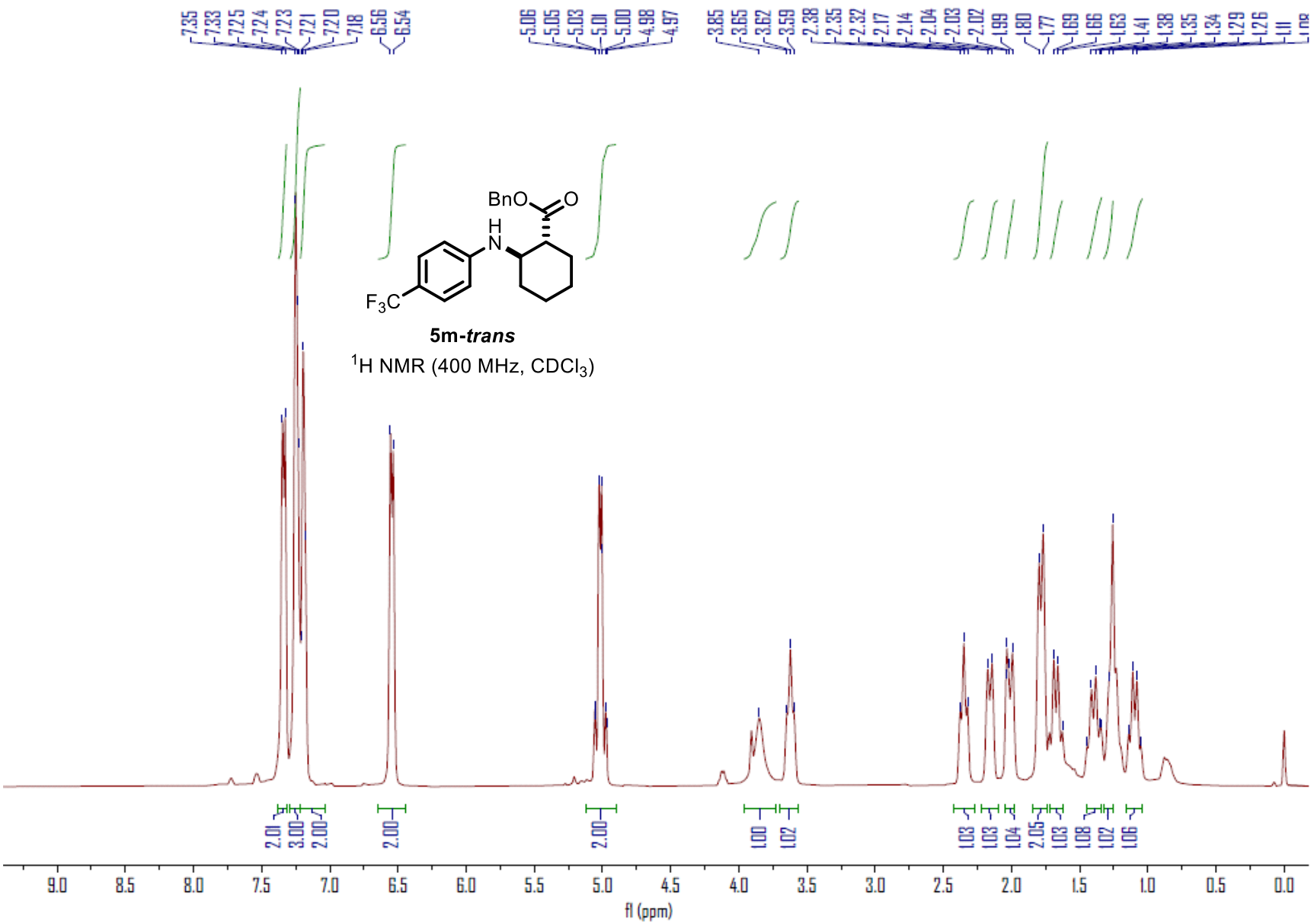
5l-*cis*

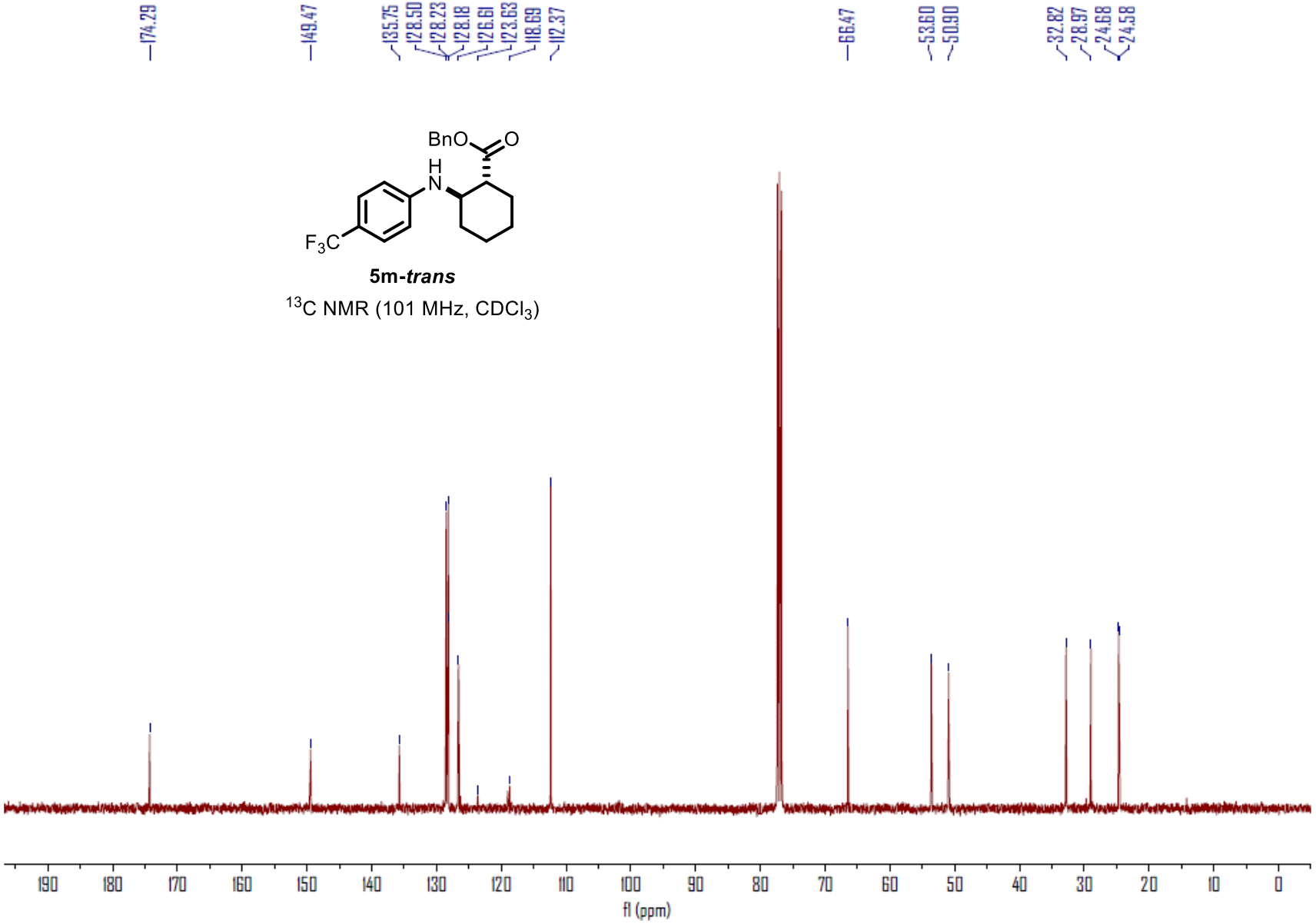
^{13}C NMR (101 MHz, $CDCl_3$)

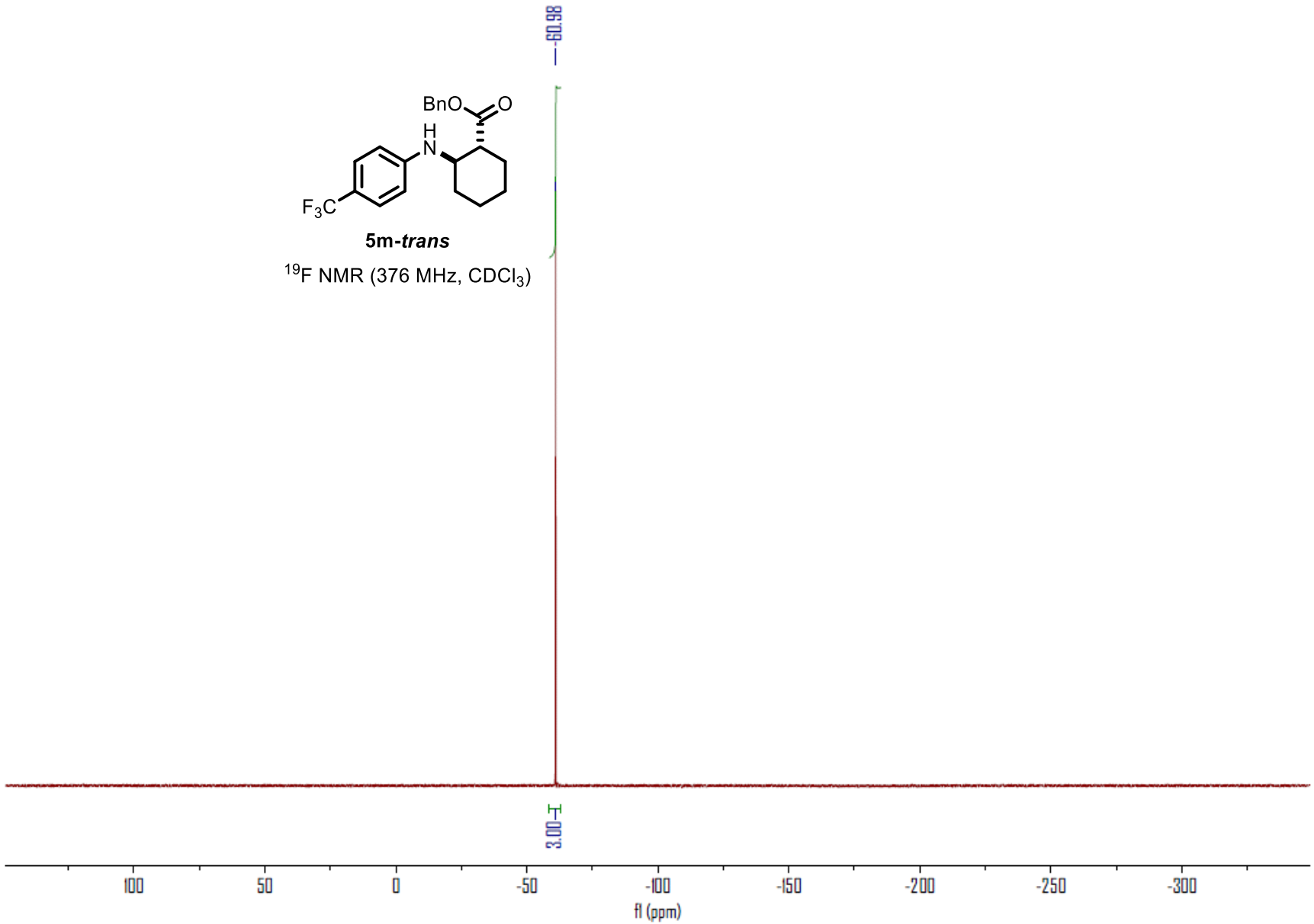


5l-*cis*

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

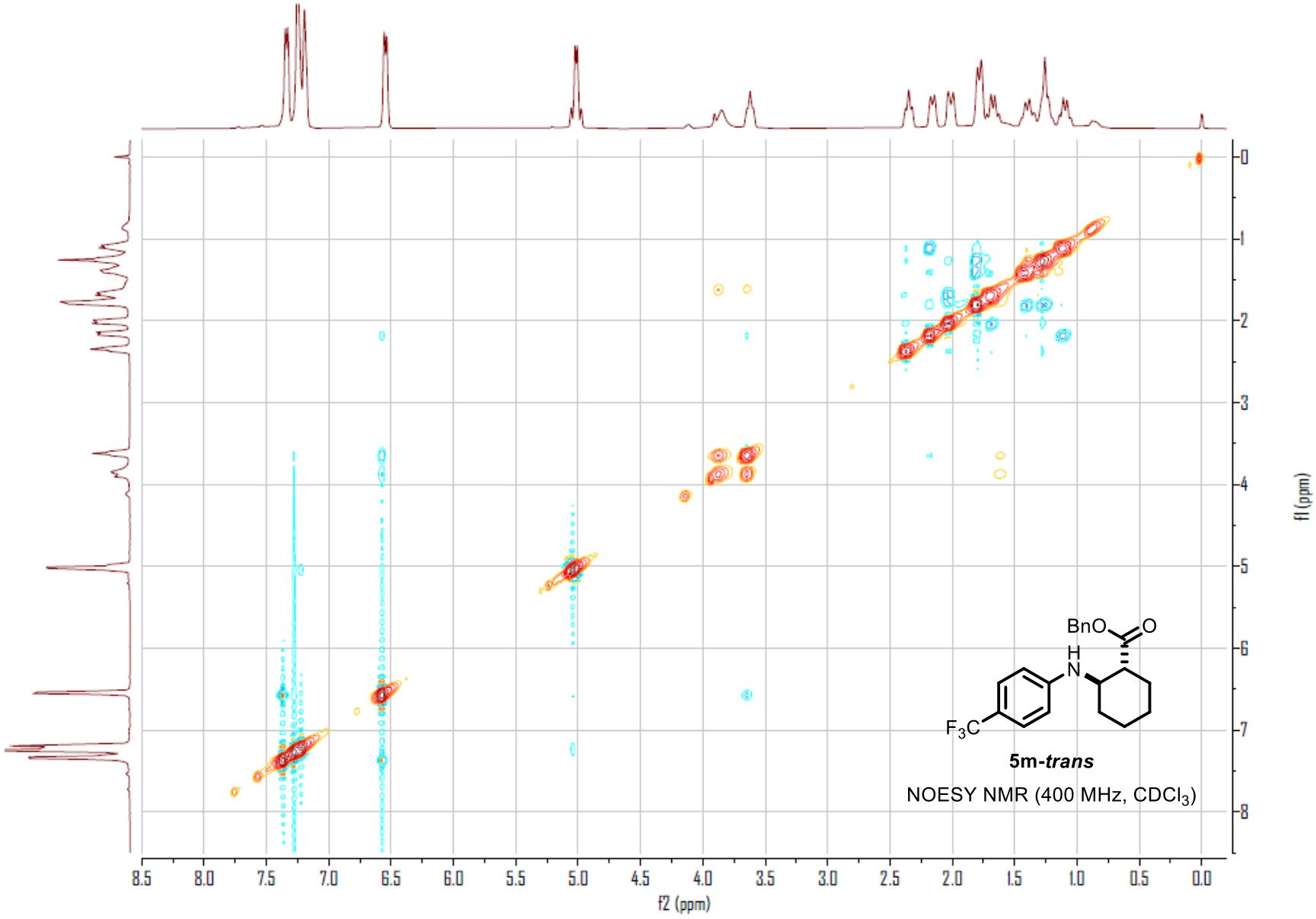

BnO
O
H
N
F3C
5m-trans
1H NMR (400 MHz, CDCl3)
f1 (ppm)

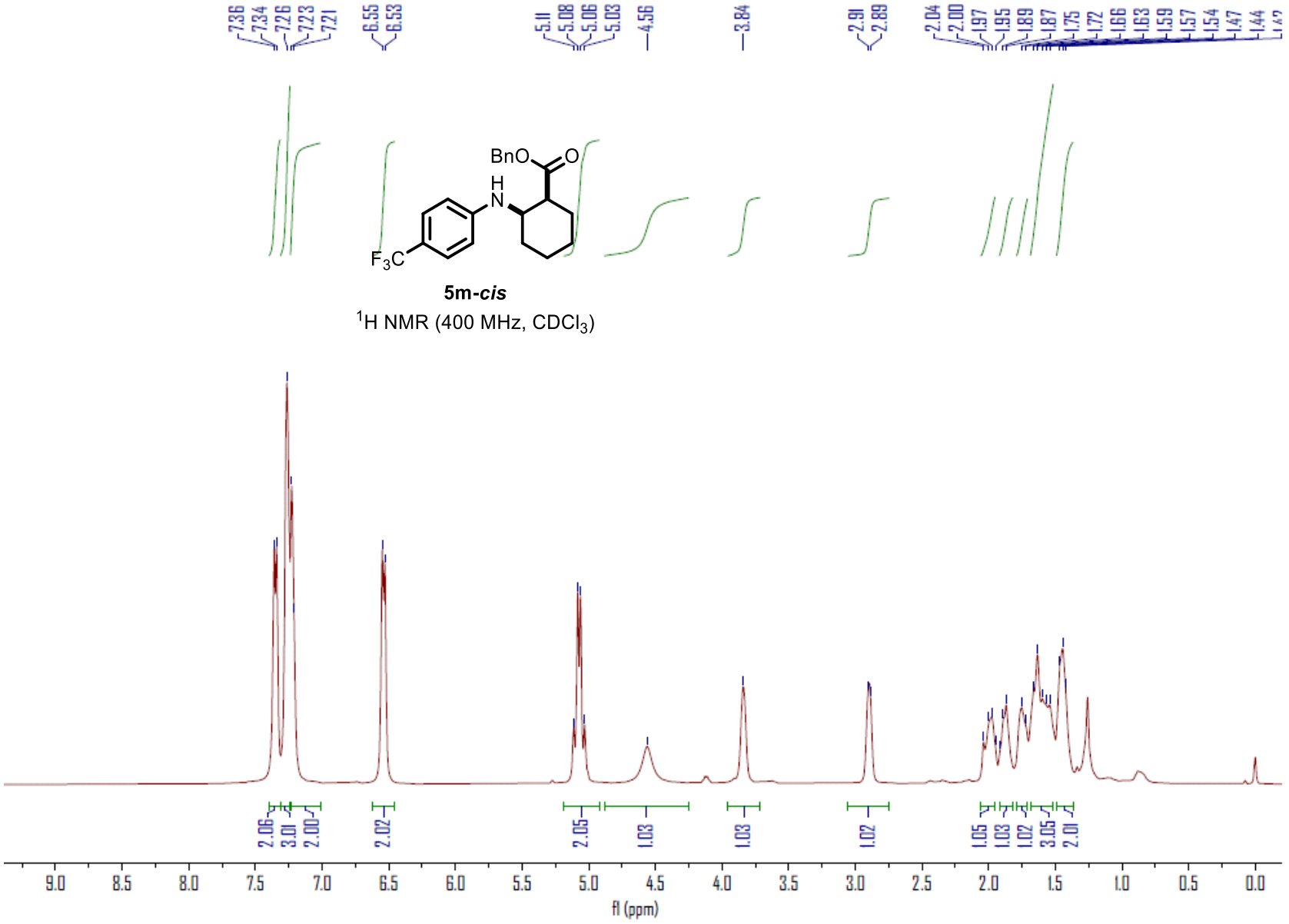

174.29
149.47
135.75
128.50
128.23
128.18
126.61
123.63
118.69
112.37
66.47
53.60
50.90
32.82
28.97
24.68
24.58
BnO
O
H
N
F3C
5m-trans
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5m-*trans*

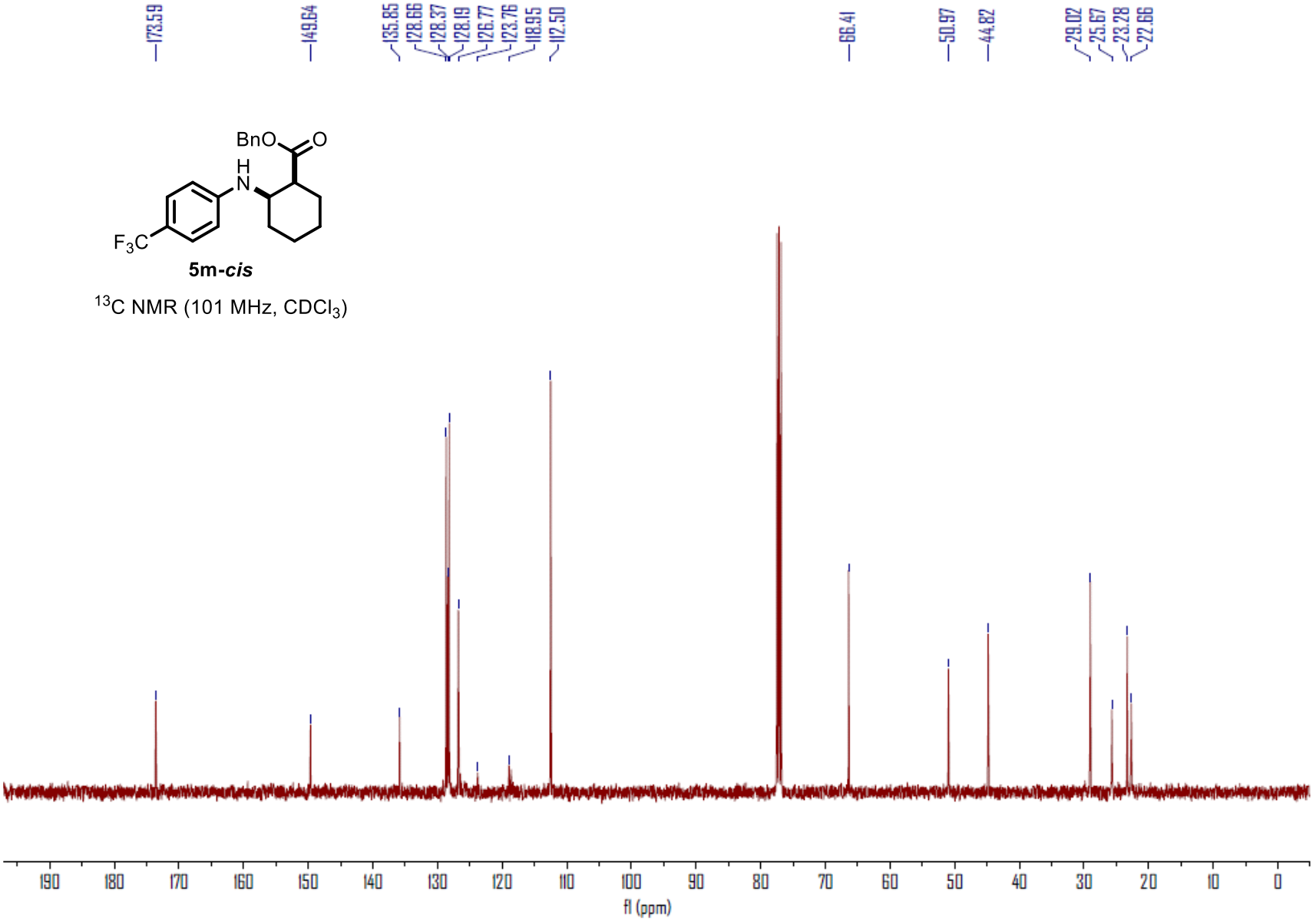
^{19}F NMR (376 MHz, $CDCl_3$)

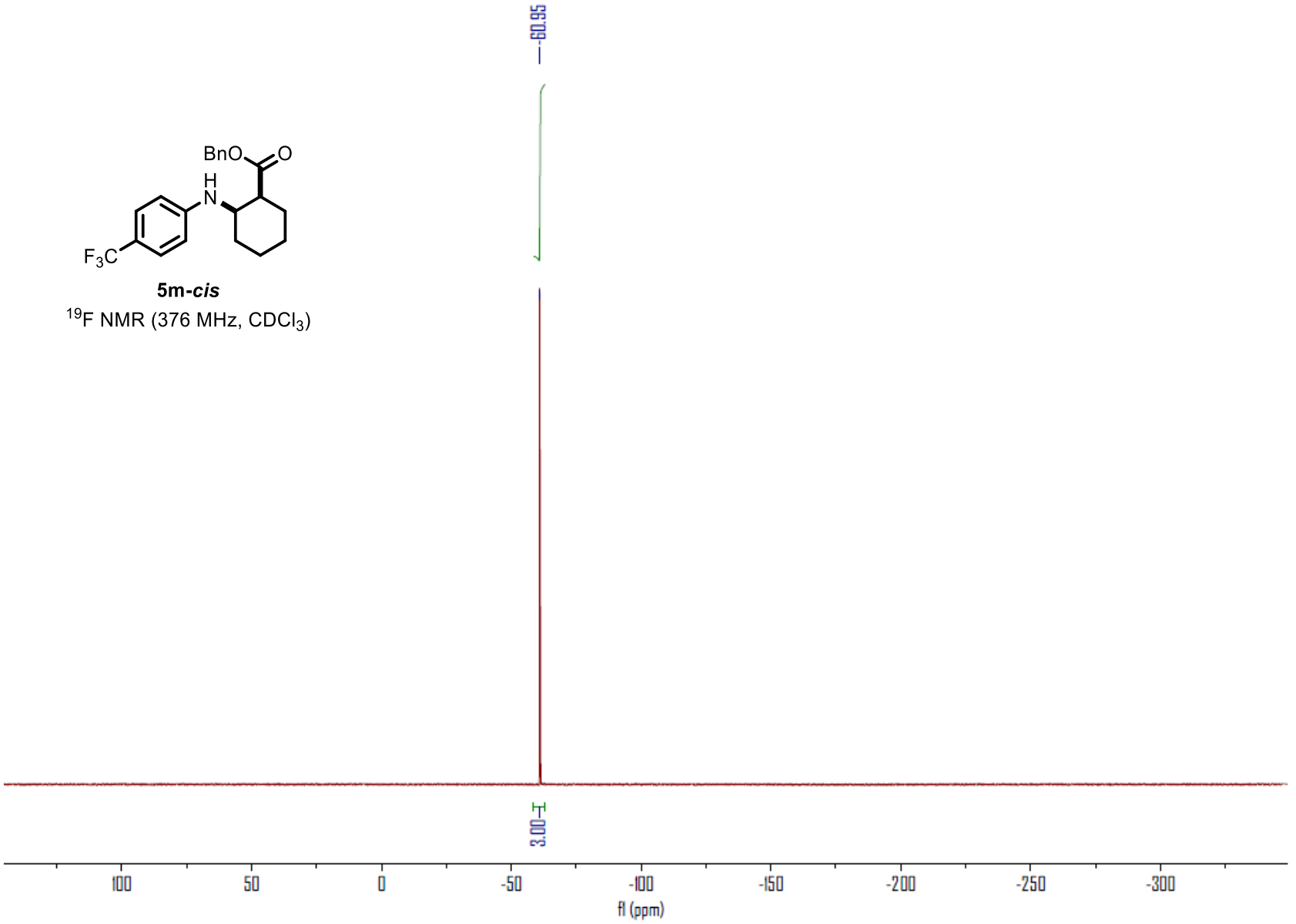

BnO
O
H
N
F3C
5m-trans
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



5m-*cis*

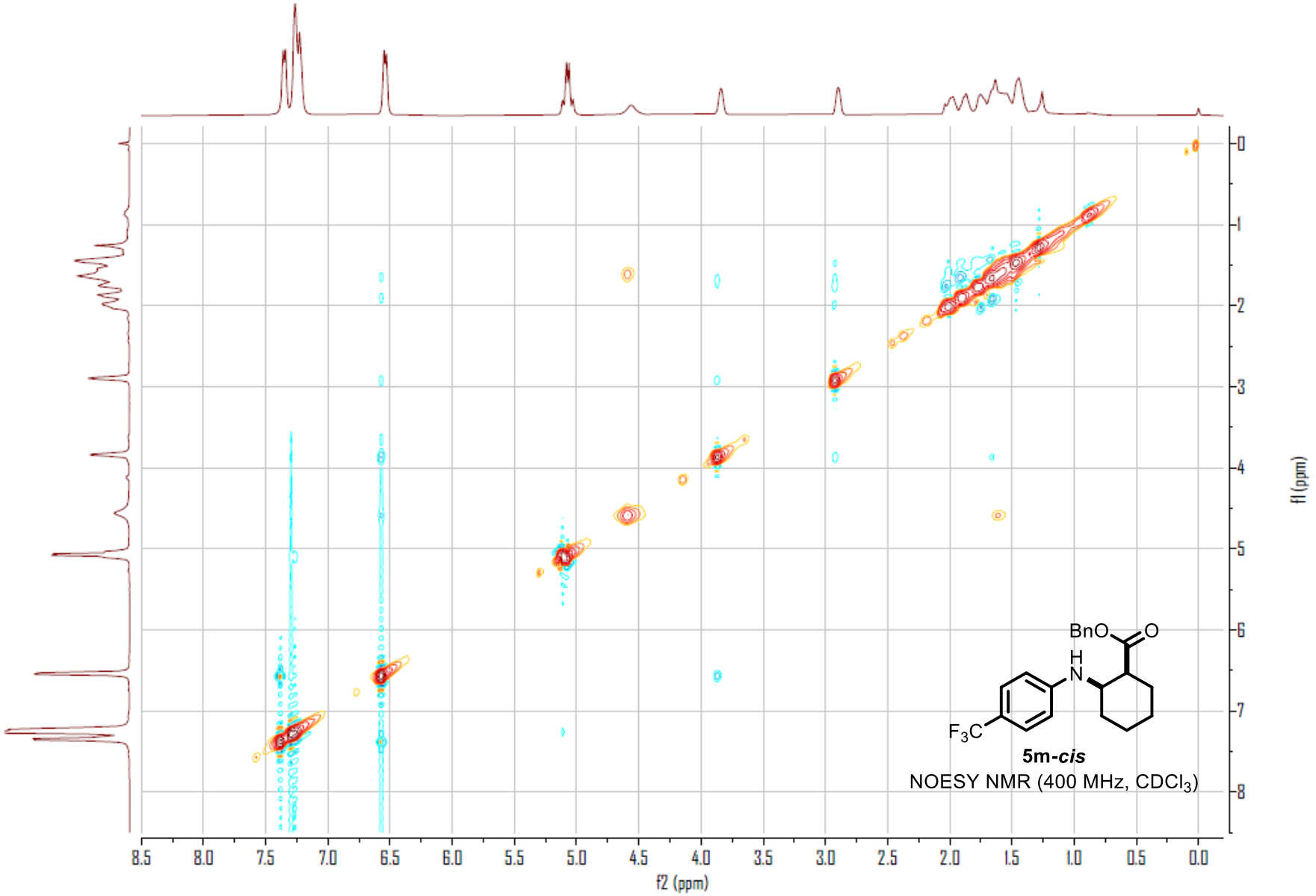
^{1}H NMR (400 MHz, $CDCl_3$)


173.59
149.64
135.85
128.66
128.37
128.19
126.77
123.76
118.95
112.50
66.41
50.97
44.82
29.02
25.67
23.28
22.66
BnO
O
H
N
F3C
5m-cis
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



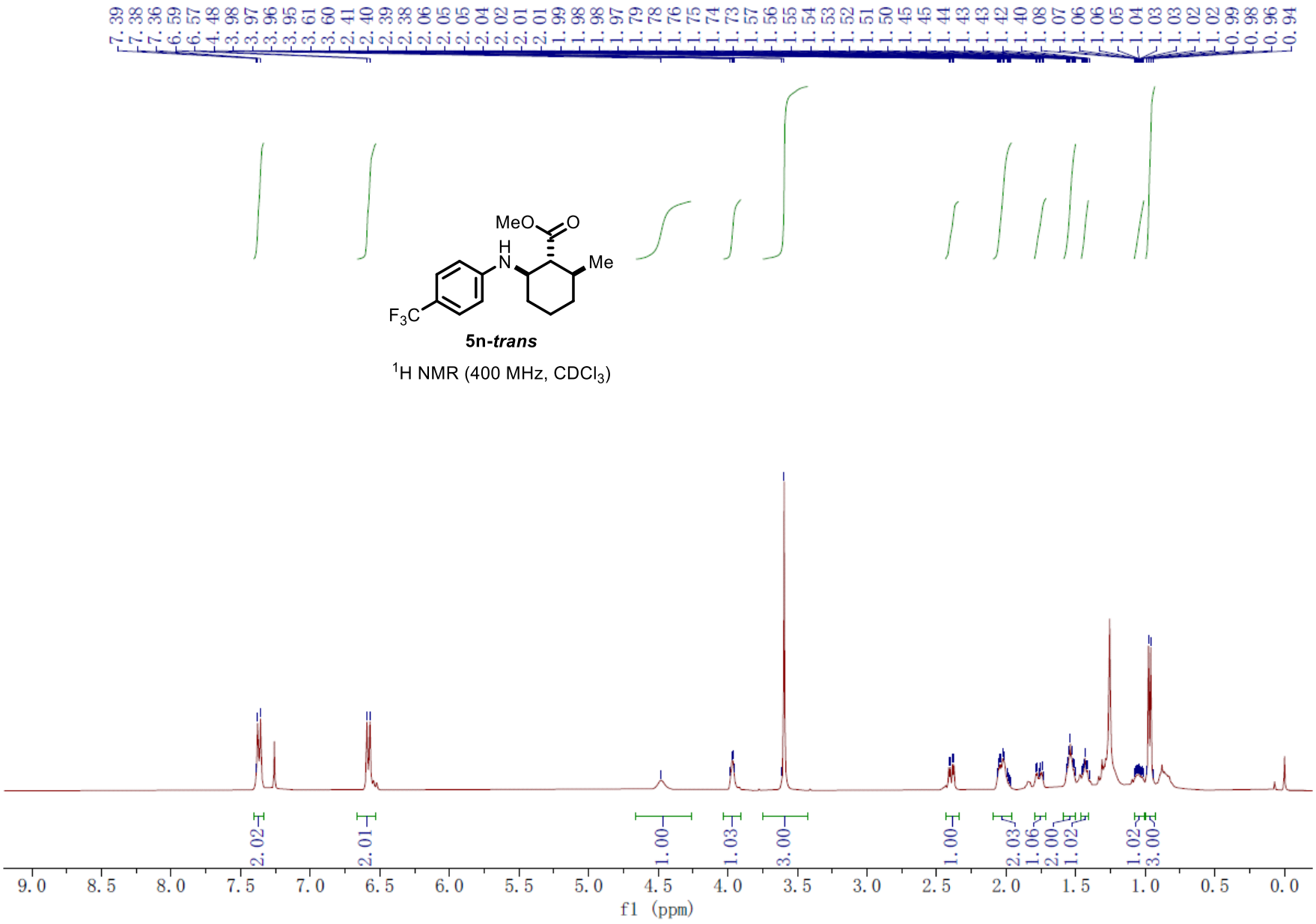
5m-*cis*

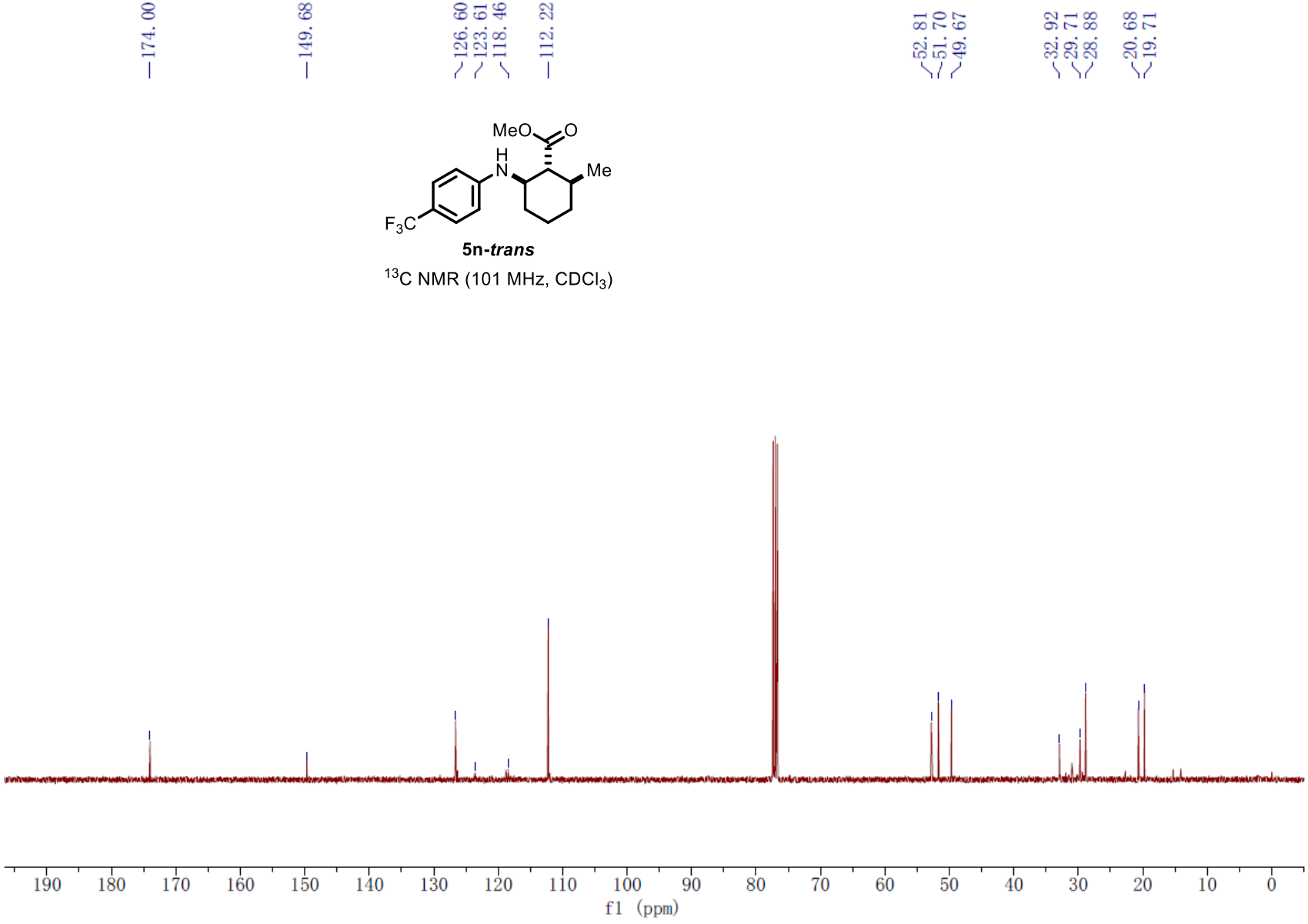
^{19}F NMR (376 MHz, $CDCl_3$)

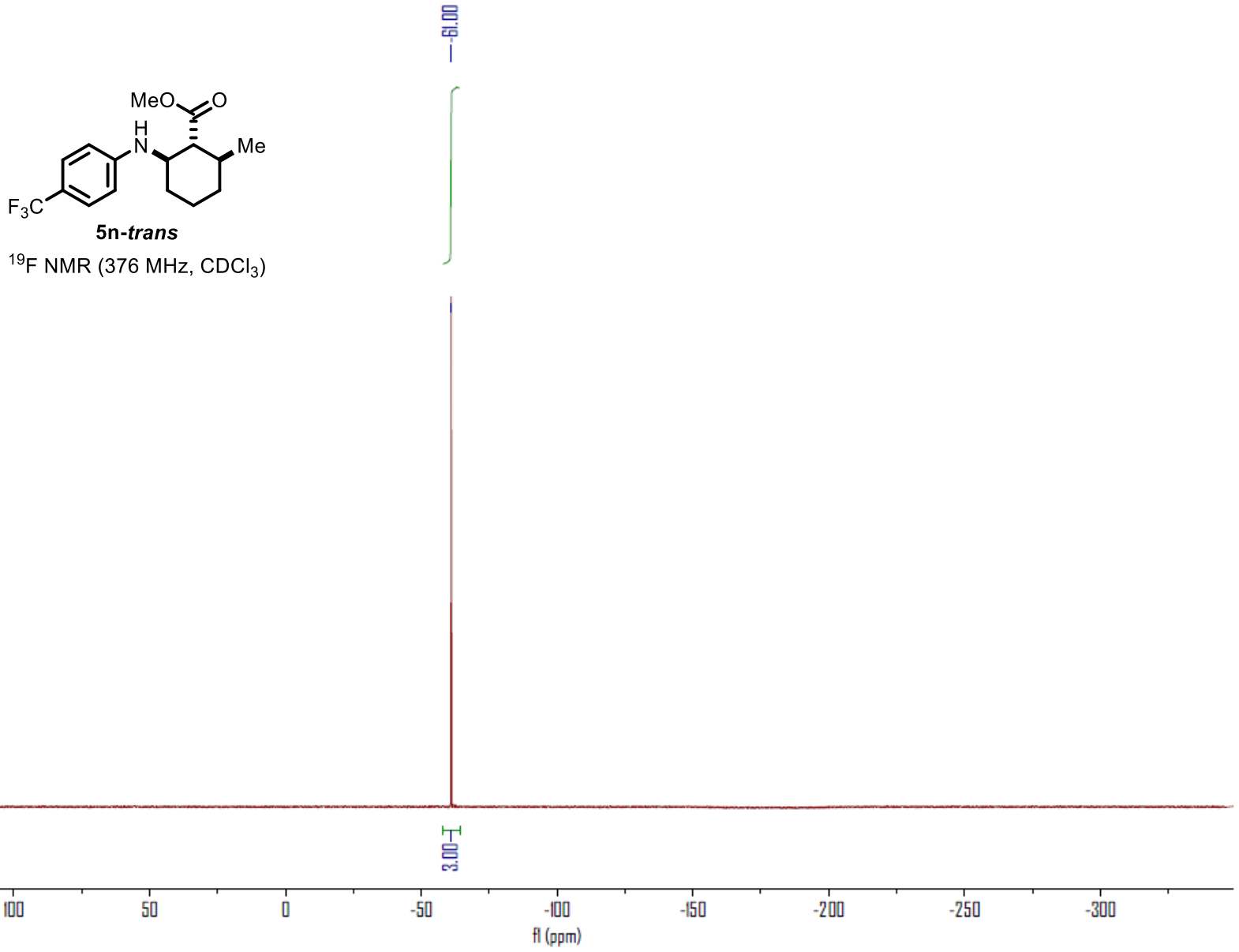


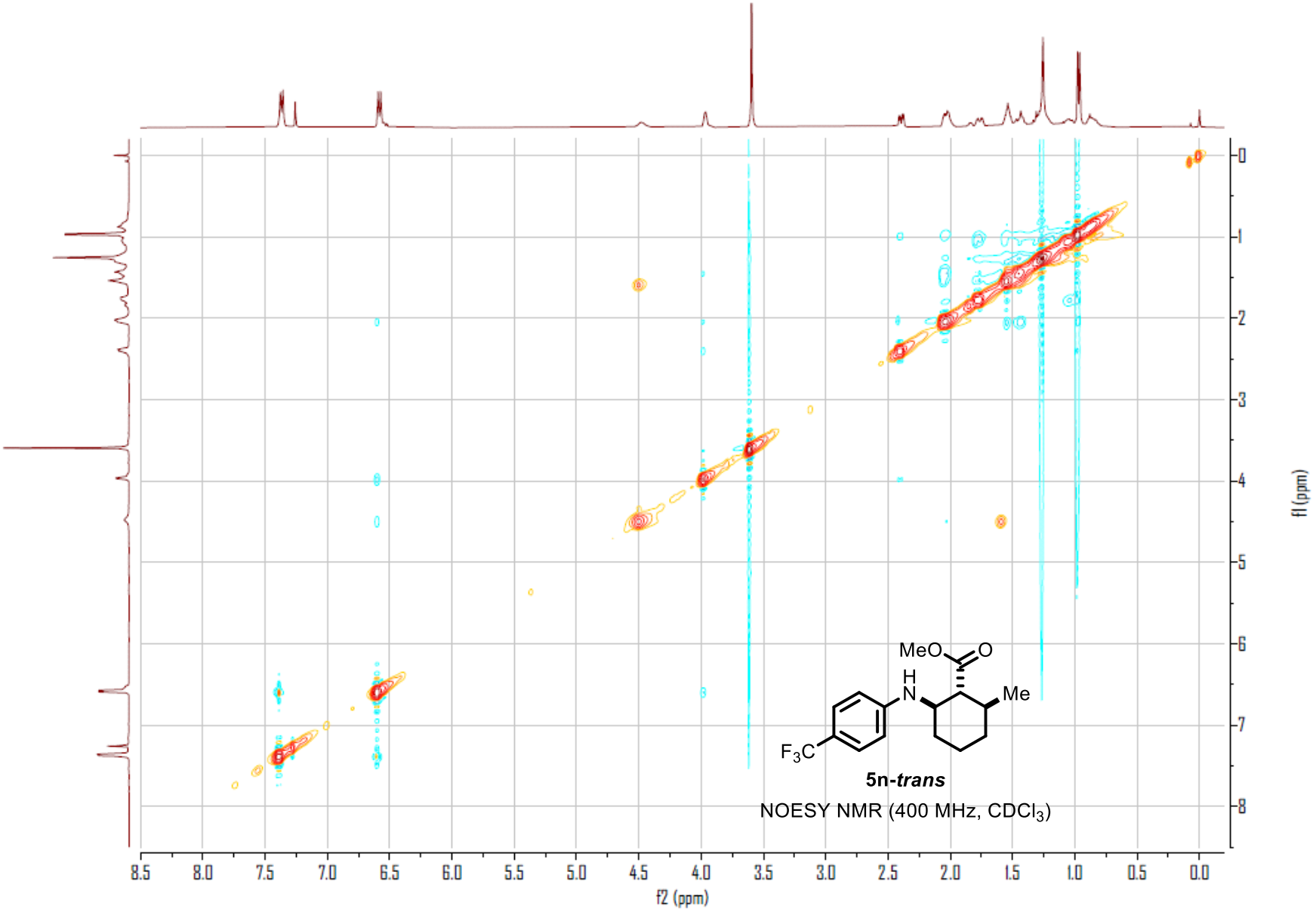
5m-*cis*

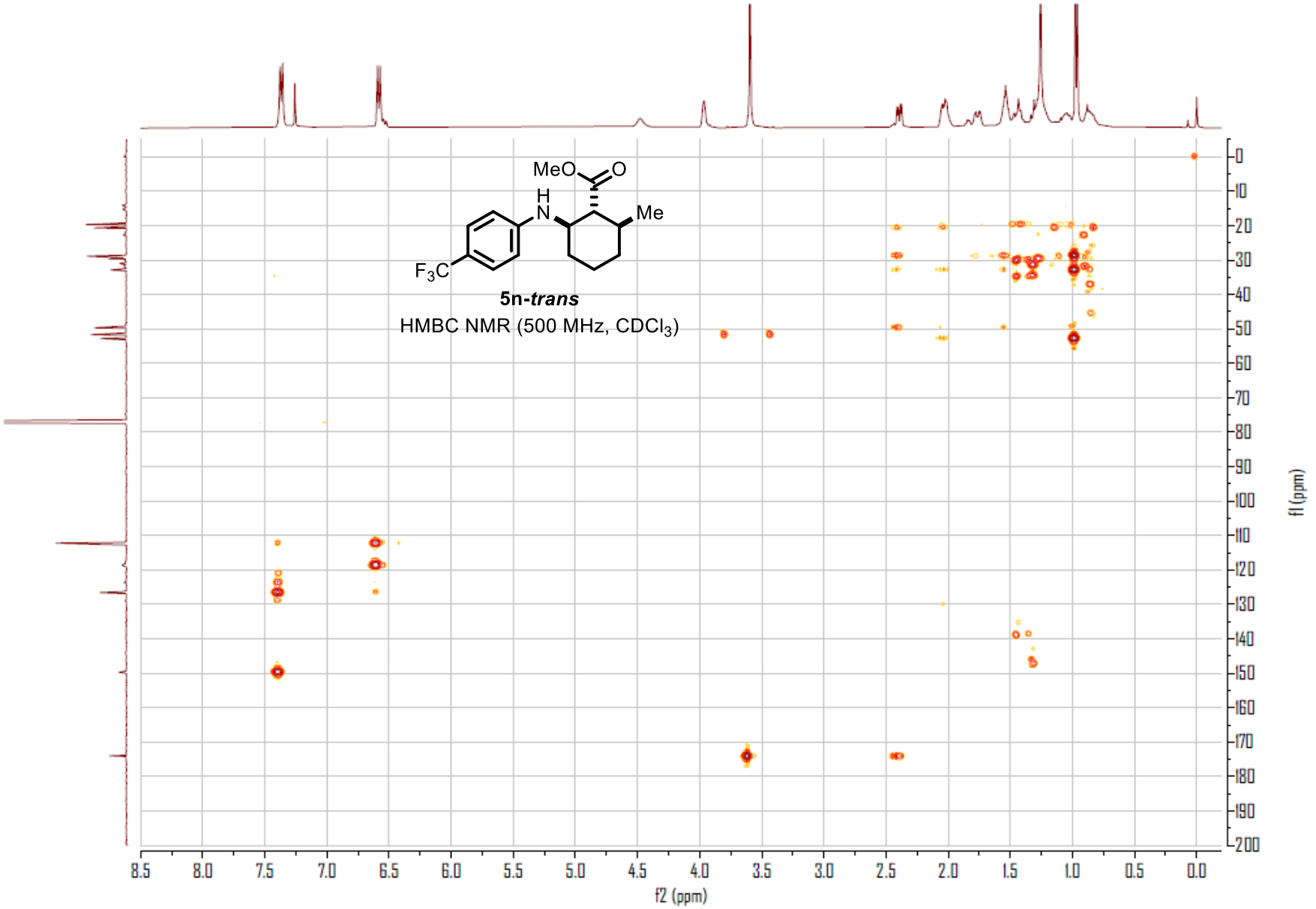
NOESY NMR (400 MHz, $CDCl_3$)

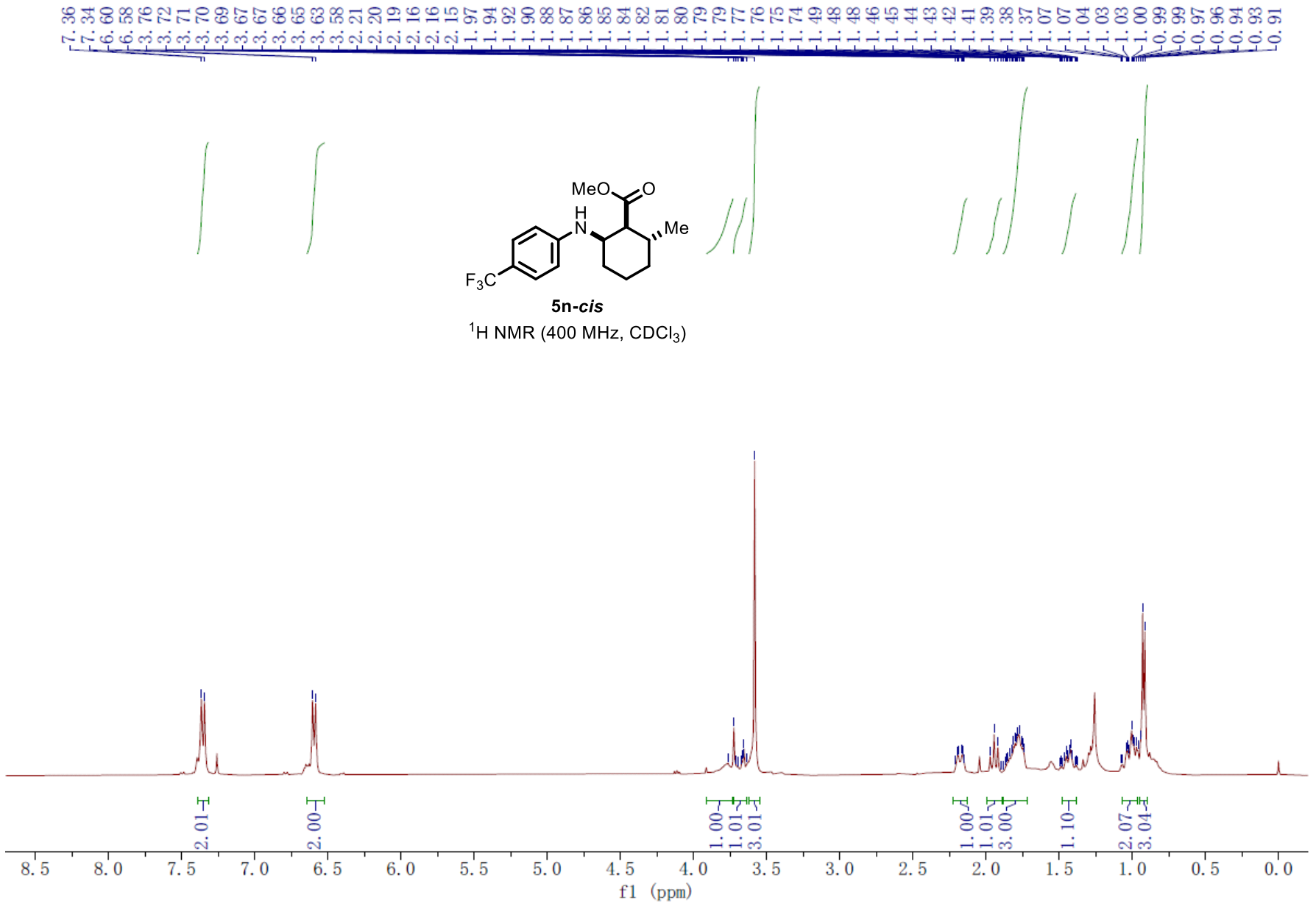

7.39 7.38 7.36 6.59 6.57 4.48 3.98 3.97 3.96 3.95 3.61 3.60 2.41 2.40 2.39 2.38 2.06 2.05 2.05 2.04 2.02 2.01 2.01 1.99 1.98 1.98 1.97 1.79 1.78 1.76 1.75 1.74 1.73 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.45 1.45 1.44 1.43 1.43 1.42 1.40 1.08 1.07 1.06 1.06 1.05 1.04 1.03 1.03 1.02 1.02 0.99 0.98 0.96 0.94
MeO
O
H
N
Me
F3C
5n-trans
1H NMR (400 MHz, CDCl3)
2.02
2.01
1.00
1.03
3.00
1.00
2.03
1.06
2.00
1.02
1.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

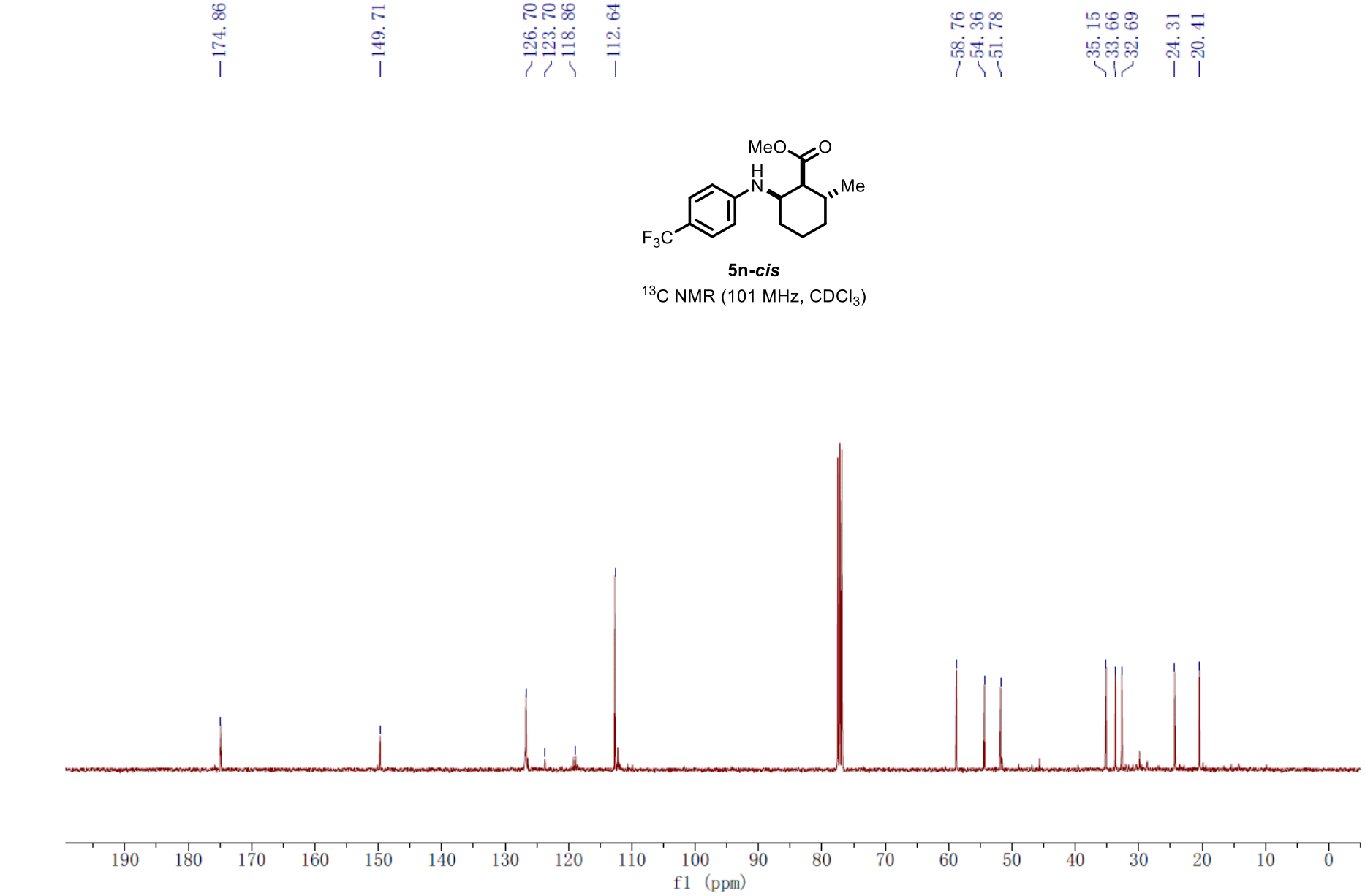

174.00
149.68
126.60
123.61
118.46
112.22
52.81
51.70
49.67
32.92
29.71
28.88
20.68
19.71
MeO
O
H
N
Me
F3C
5n-trans
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
H
N
Me
F3C
5n-trans
19F NMR (376 MHz, CDCl3)
-61.00
3.00
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


MeO
O
H
N
Me
F3C
5n-trans
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

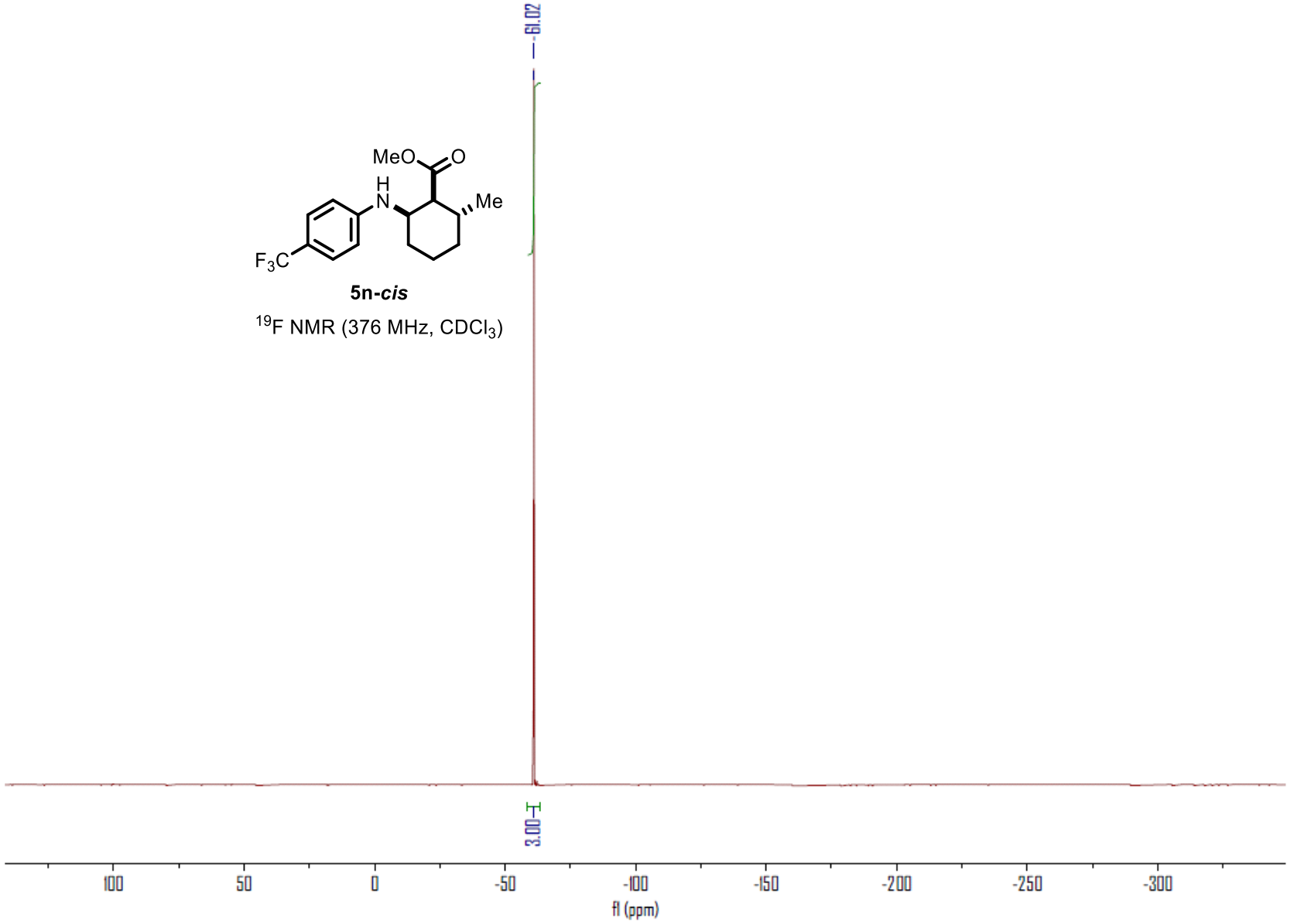

MeO
O
H
N
Me
F3C
5n-trans
HMBC NMR (500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


7.36
7.34
6.60
6.58
3.76
3.72
3.71
3.70
3.69
3.67
3.67
3.66
3.65
3.63
3.58
2.21
2.20
2.19
2.16
2.16
2.15
1.97
1.94
1.92
1.90
1.88
1.87
1.86
1.85
1.84
1.82
1.81
1.80
1.79
1.79
1.77
1.76
1.75
1.74
1.49
1.48
1.48
1.46
1.45
1.44
1.43
1.42
1.41
1.39
1.38
1.37
1.07
1.07
1.04
1.03
1.03
1.00
0.99
0.99
0.97
0.96
0.94
0.93
0.91
MeO
O
H
N
Me
F3C
5n-cis
1H NMR (400 MHz, CDCl3)
2.01
2.00
1.00
1.01
3.01
1.00
1.01
3.00
1.10
2.07
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



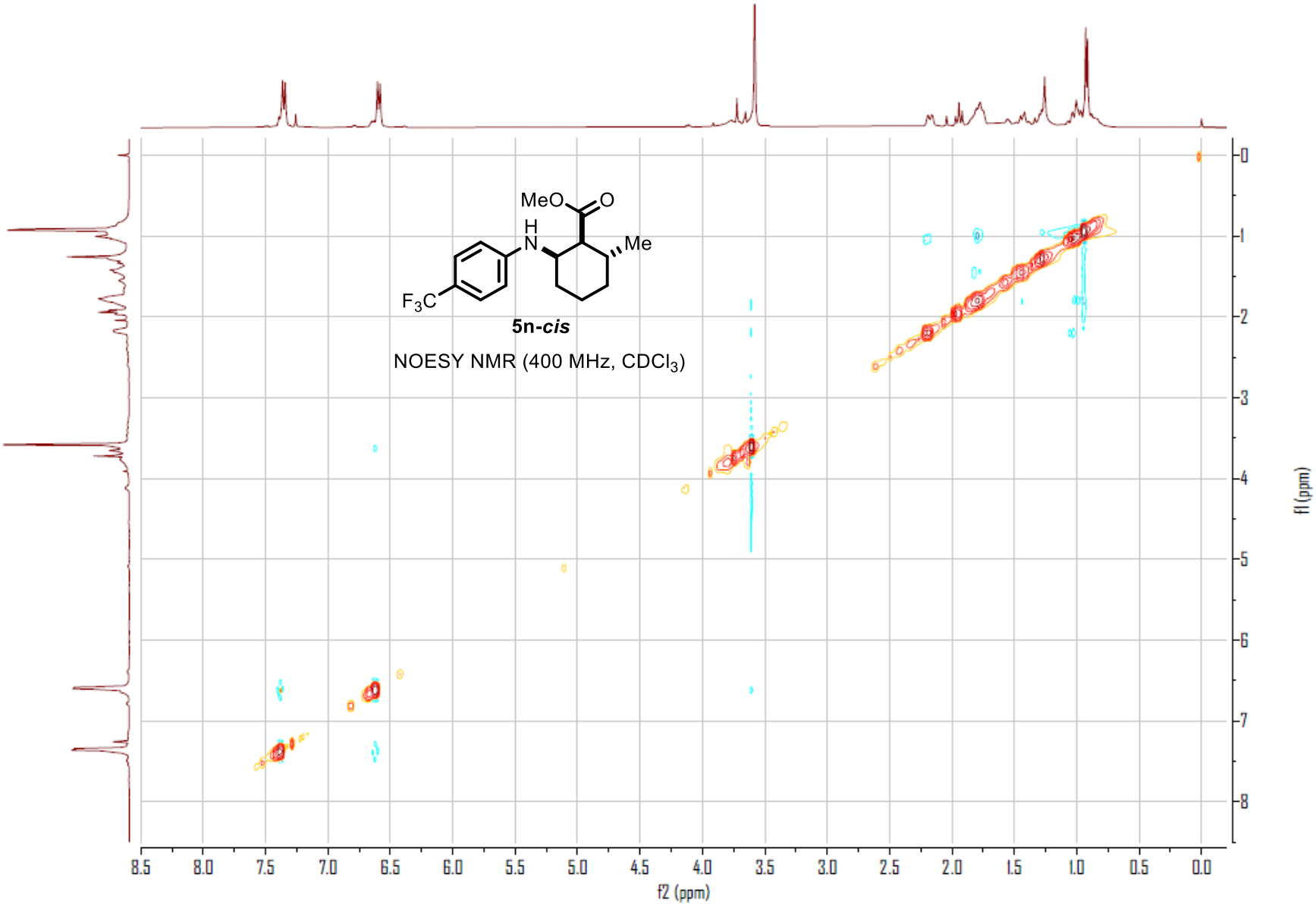
5n-*cis*

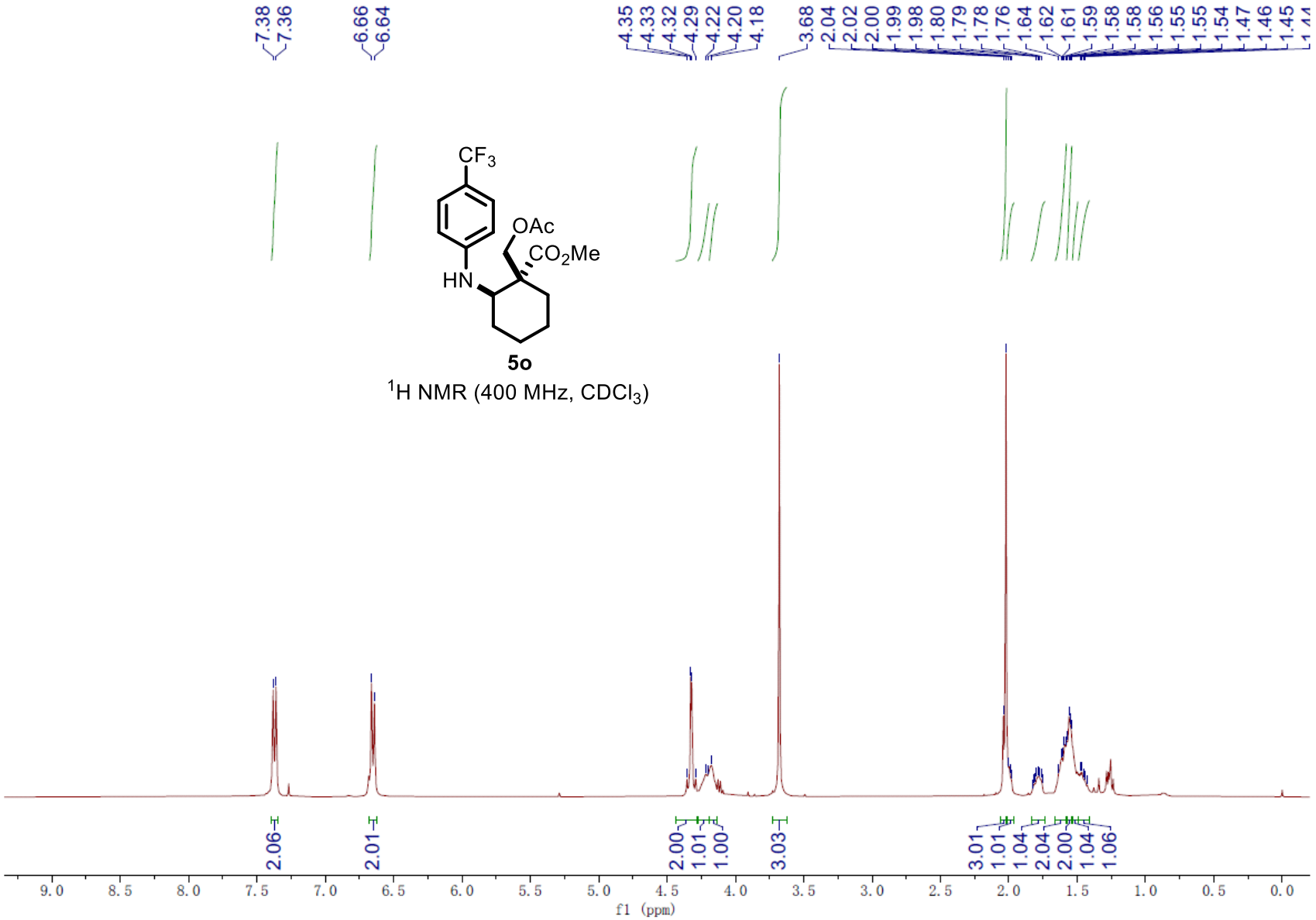
^{13}C NMR (101 MHz, $CDCl_3$)

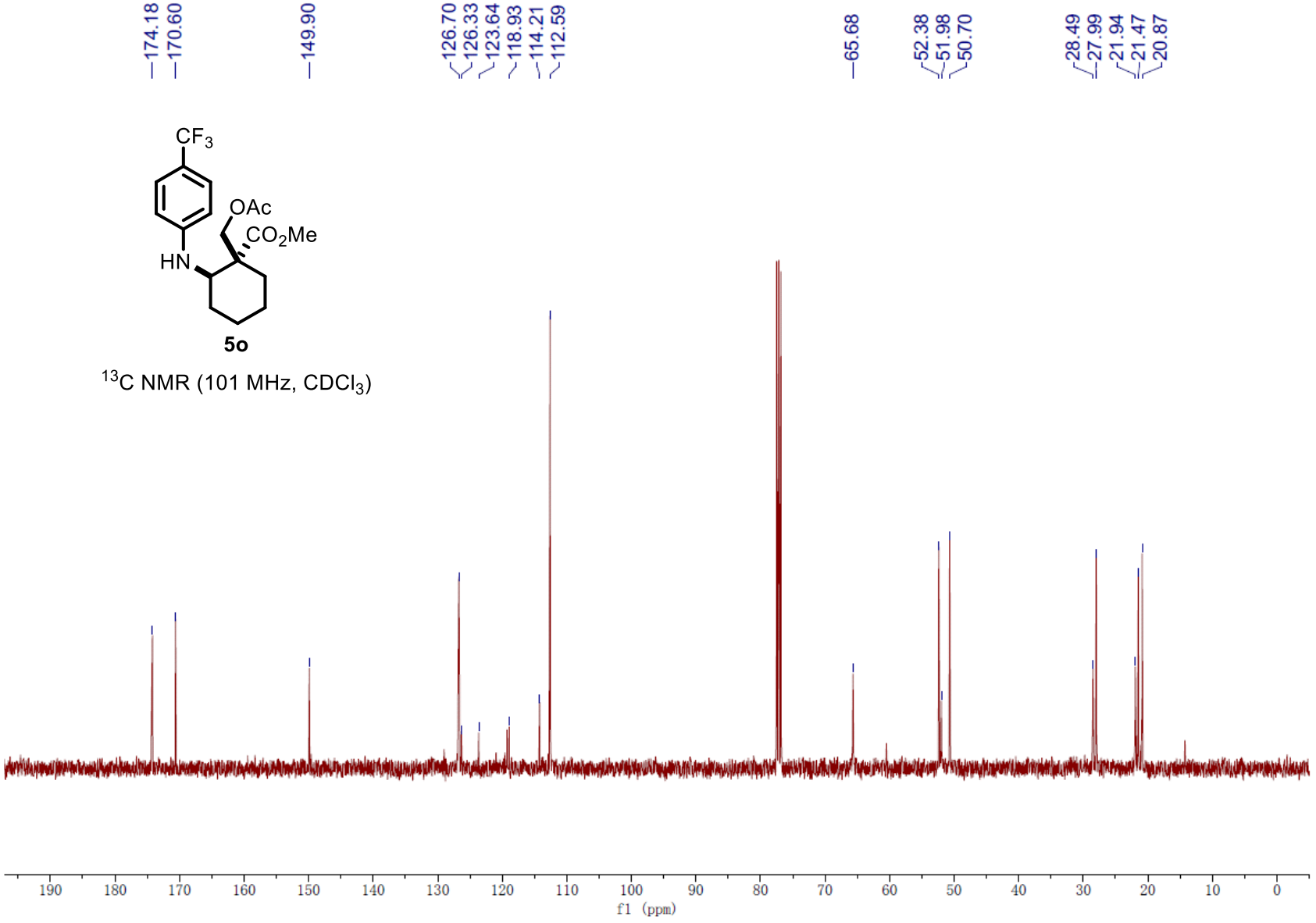


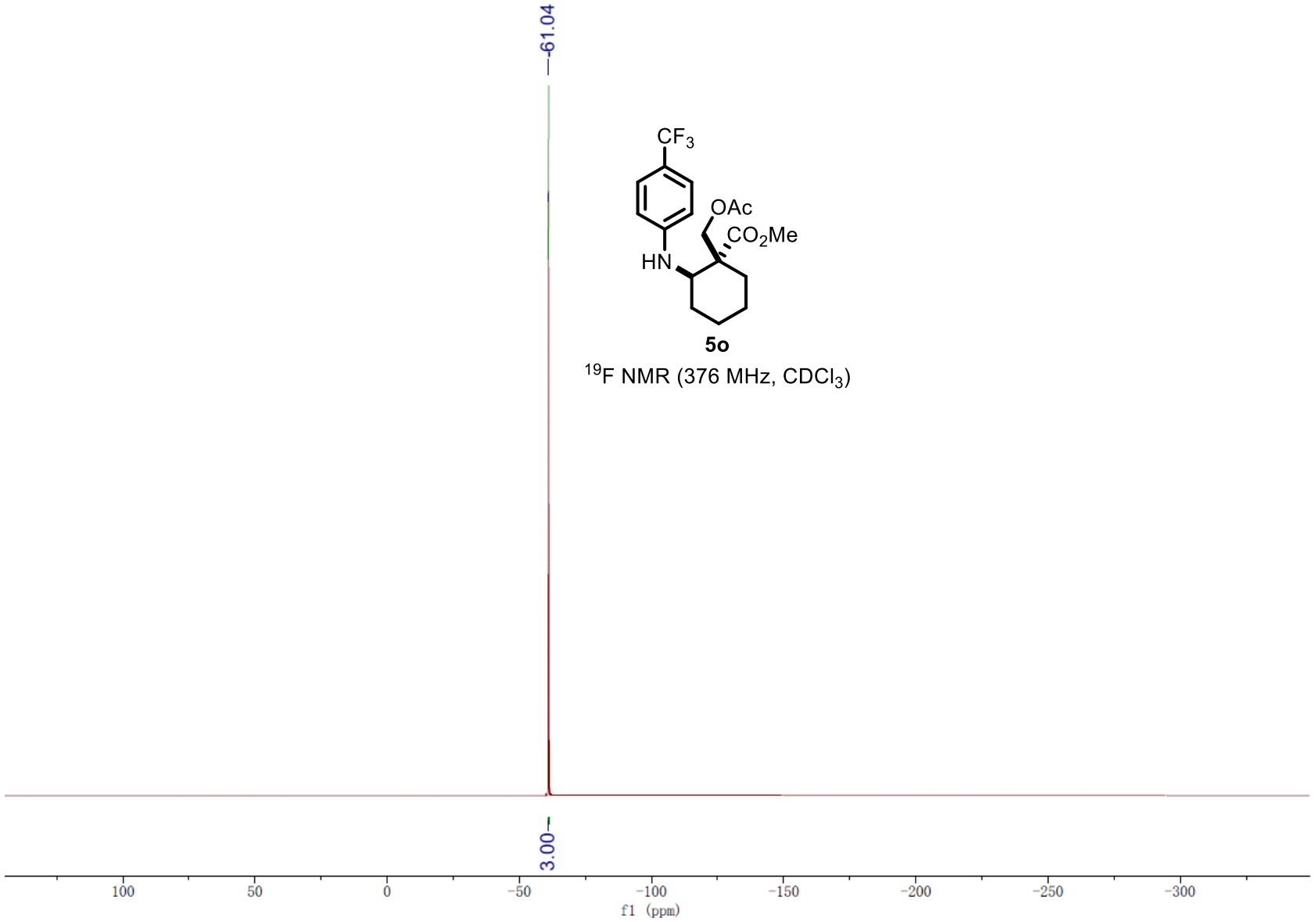
5n-*cis*

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


MeO
O
H
N
Me
F3C
5n-cis
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

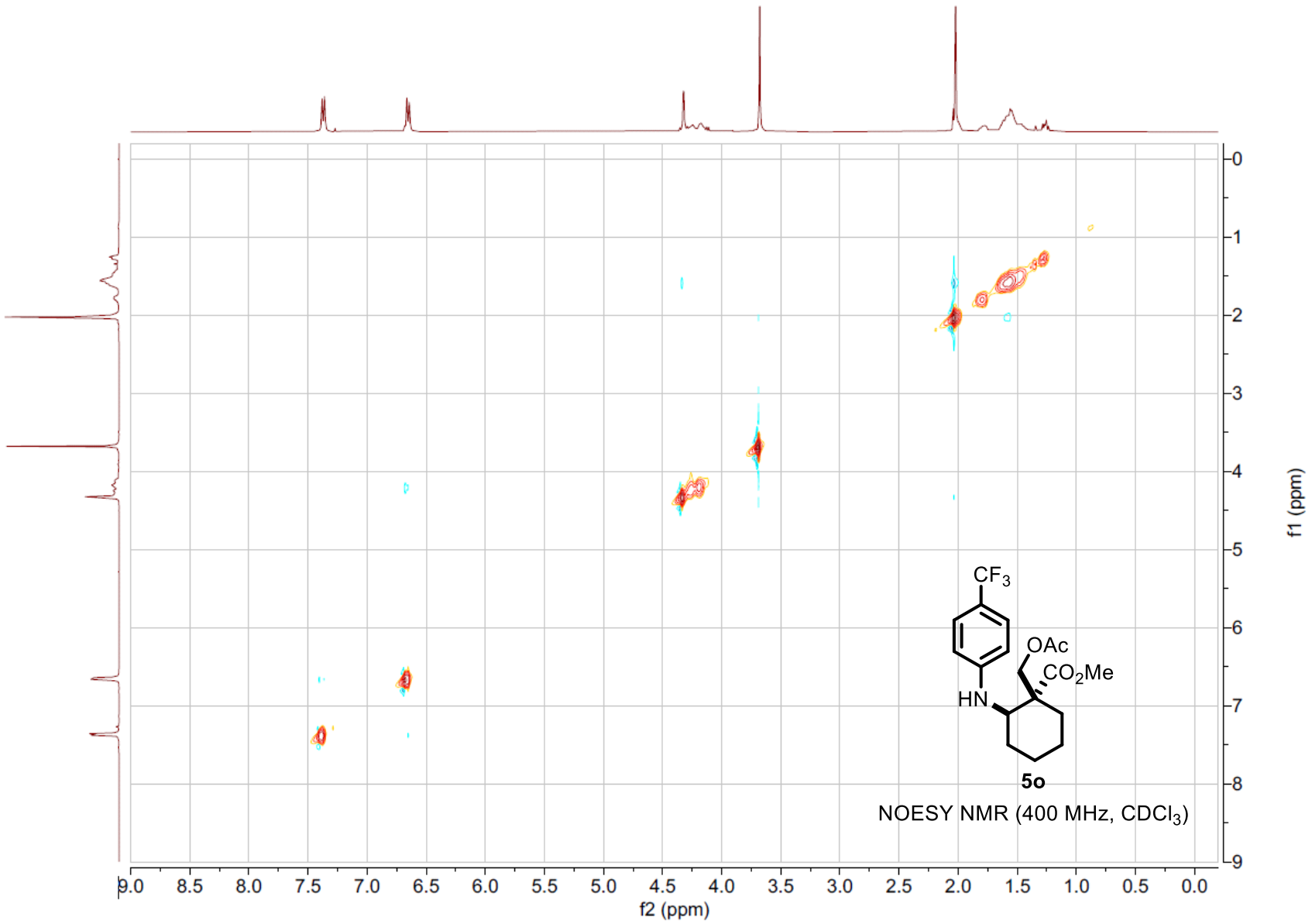

7.38
7.36
6.66
6.64
4.35
4.33
4.32
4.29
4.22
4.20
4.18
3.68
2.04
2.02
2.00
1.99
1.98
1.80
1.79
1.78
1.76
1.64
1.62
1.61
1.59
1.58
1.58
1.56
1.55
1.55
1.54
1.47
1.46
1.45
CF3
OAc
CO2Me
HN
5o
1H NMR (400 MHz, CDCl3)
2.06
2.01
2.00
1.01
1.00
3.03
3.01
1.01
1.04
2.04
2.00
1.04
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

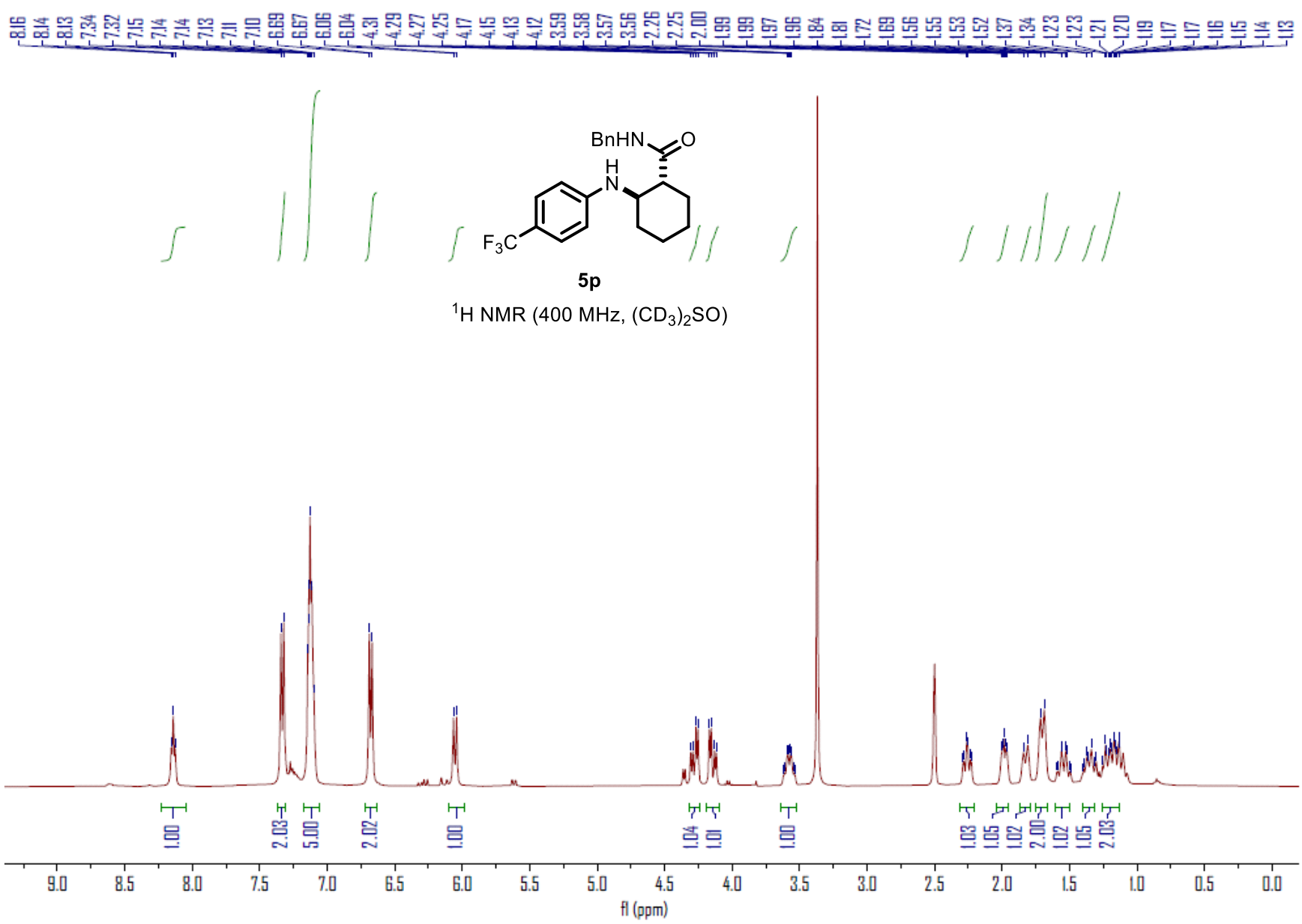

174.18
170.60
149.90
126.70
126.33
123.64
118.93
114.21
112.59
65.68
52.38
51.98
50.70
28.49
27.99
21.94
21.47
20.87
CF3
OAc
CO2Me
HN
5o
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

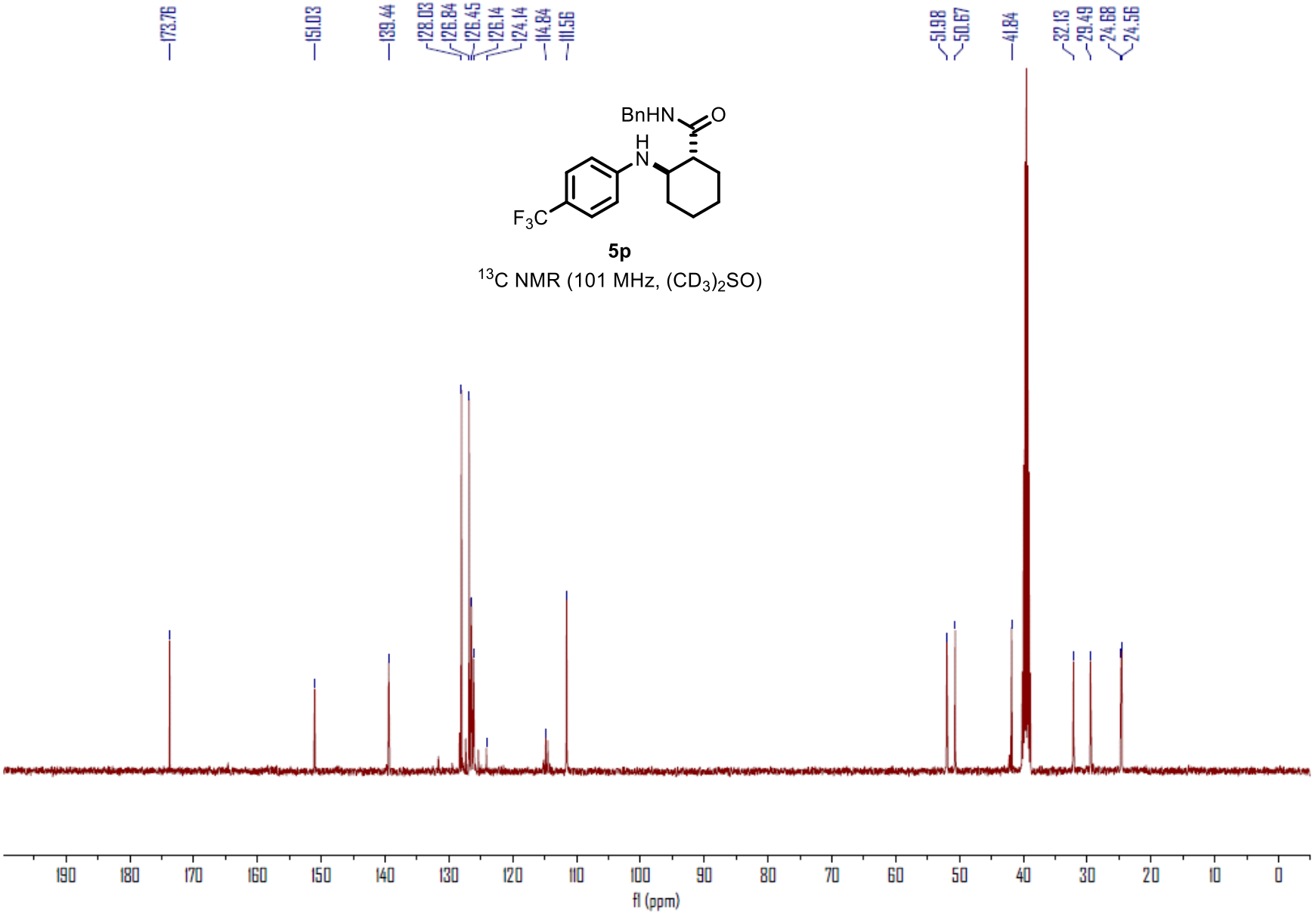


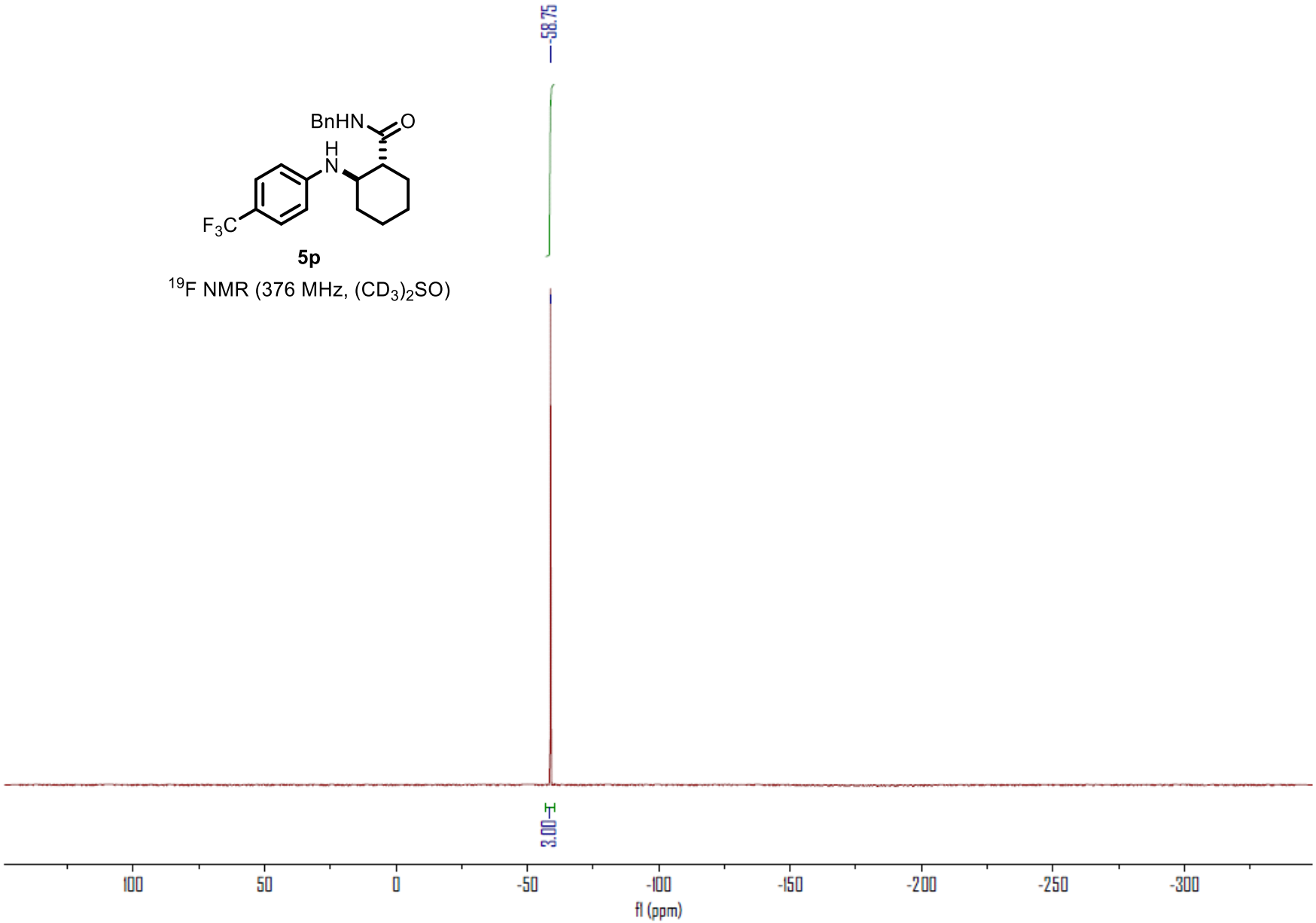
5o

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


f2 (ppm)
f1 (ppm)
CF3
OAc
CO2Me
HN
5o
NOESY NMR (400 MHz, CDCl3)

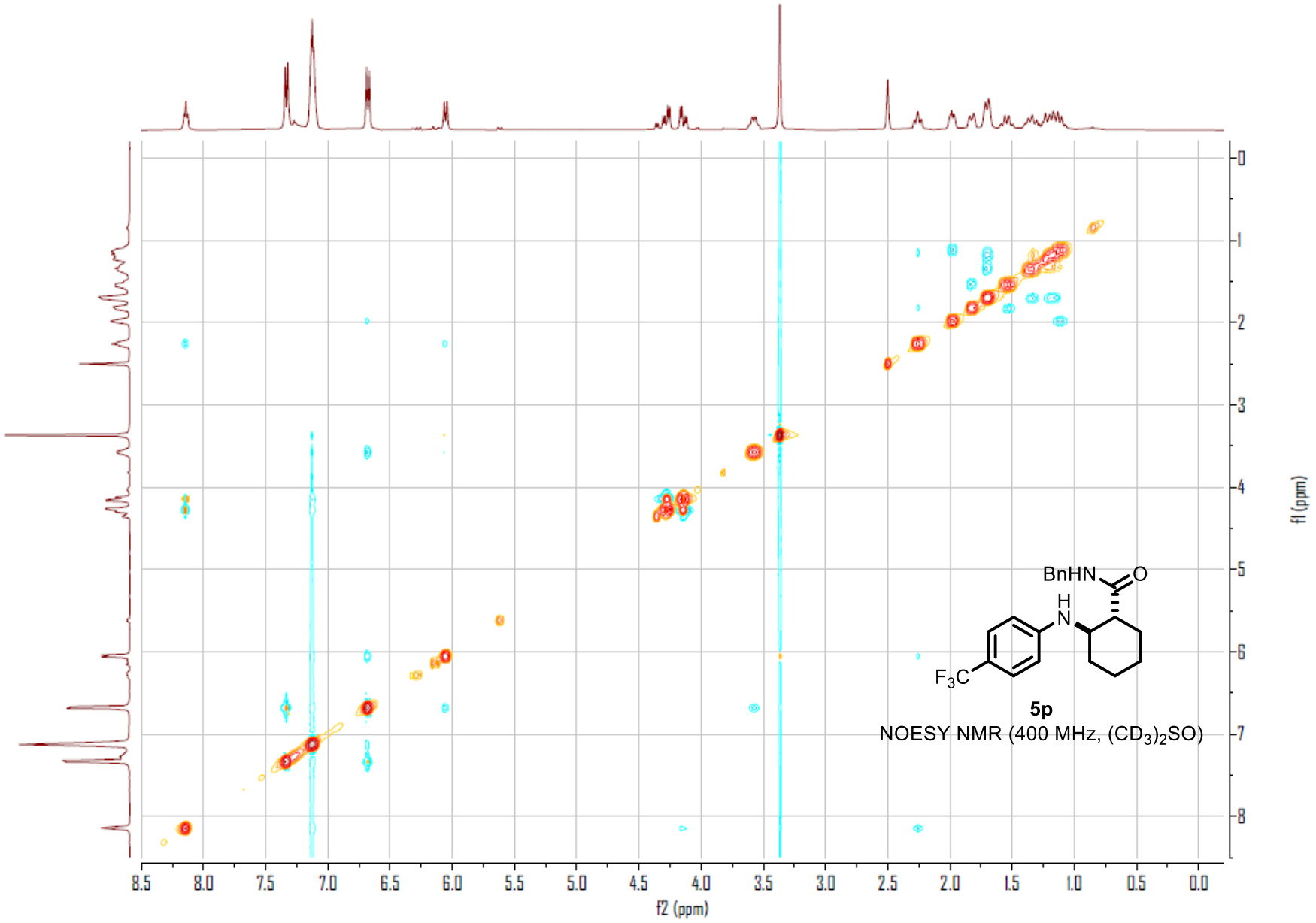

8.16
8.14
8.13
7.34
7.32
7.15
7.14
7.14
7.13
7.11
7.10
6.69
6.67
6.06
6.04
4.31
4.29
4.27
4.25
4.17
4.15
4.13
4.12
3.59
3.58
3.57
3.56
2.26
2.25
2.00
1.99
1.98
1.97
1.96
1.84
1.81
1.72
1.69
1.56
1.55
1.53
1.52
1.37
1.34
1.23
1.23
1.21
1.20
1.19
1.17
1.17
1.16
1.15
1.14
1.13
BnHN
O
H
N
F3C
5p
1H NMR (400 MHz, (CD3)2SO)
1.00
2.03
5.00
2.02
1.00
1.04
1.01
1.00
1.03
1.05
1.02
2.00
1.02
1.05
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

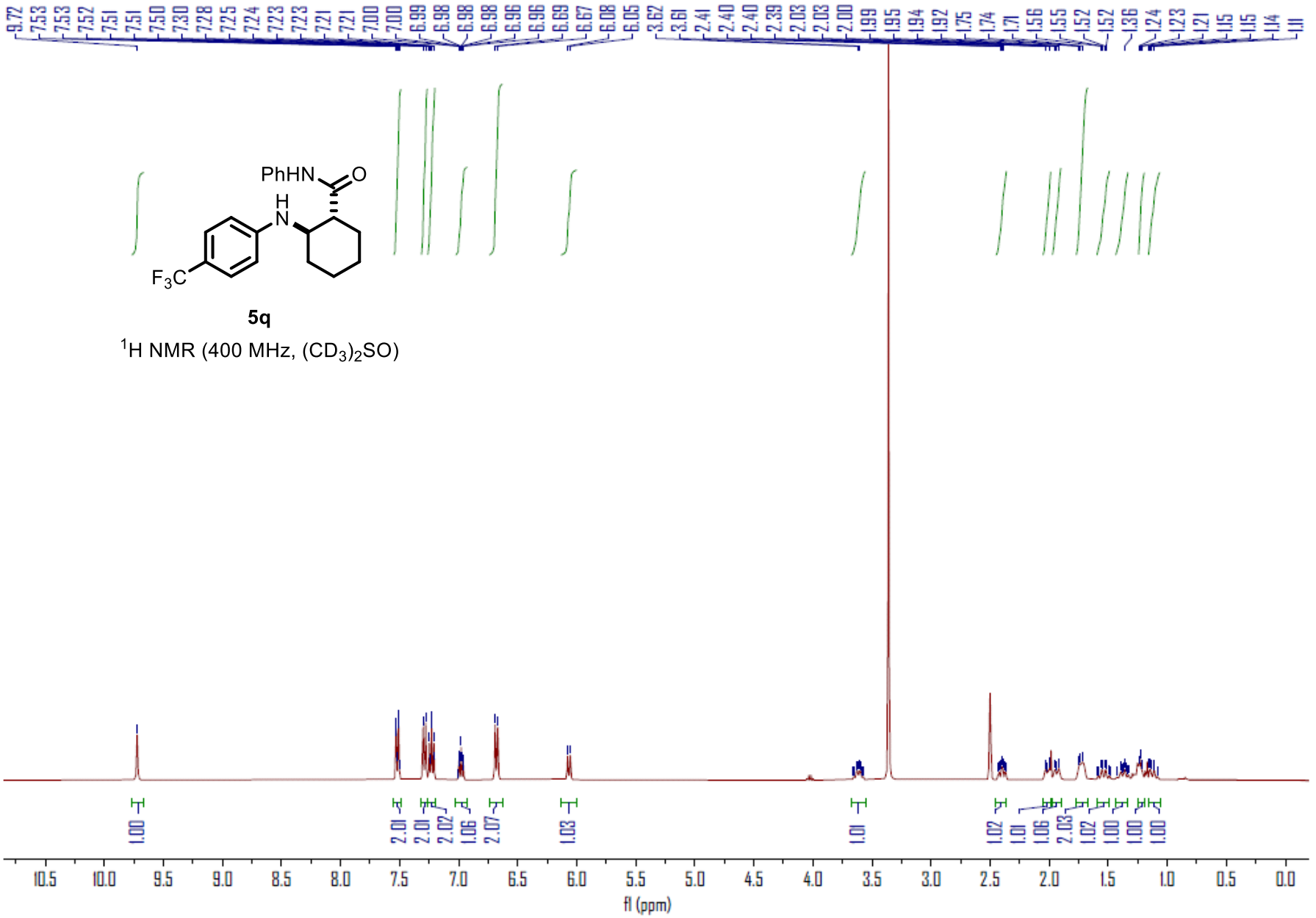

173.76
151.03
139.44
128.03
126.84
126.45
126.14
124.14
114.84
111.56
51.98
50.67
41.84
32.13
29.49
24.68
24.56
BnHN
O
H
N
F3C
5p
13C NMR (101 MHz, (CD3)2SO)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

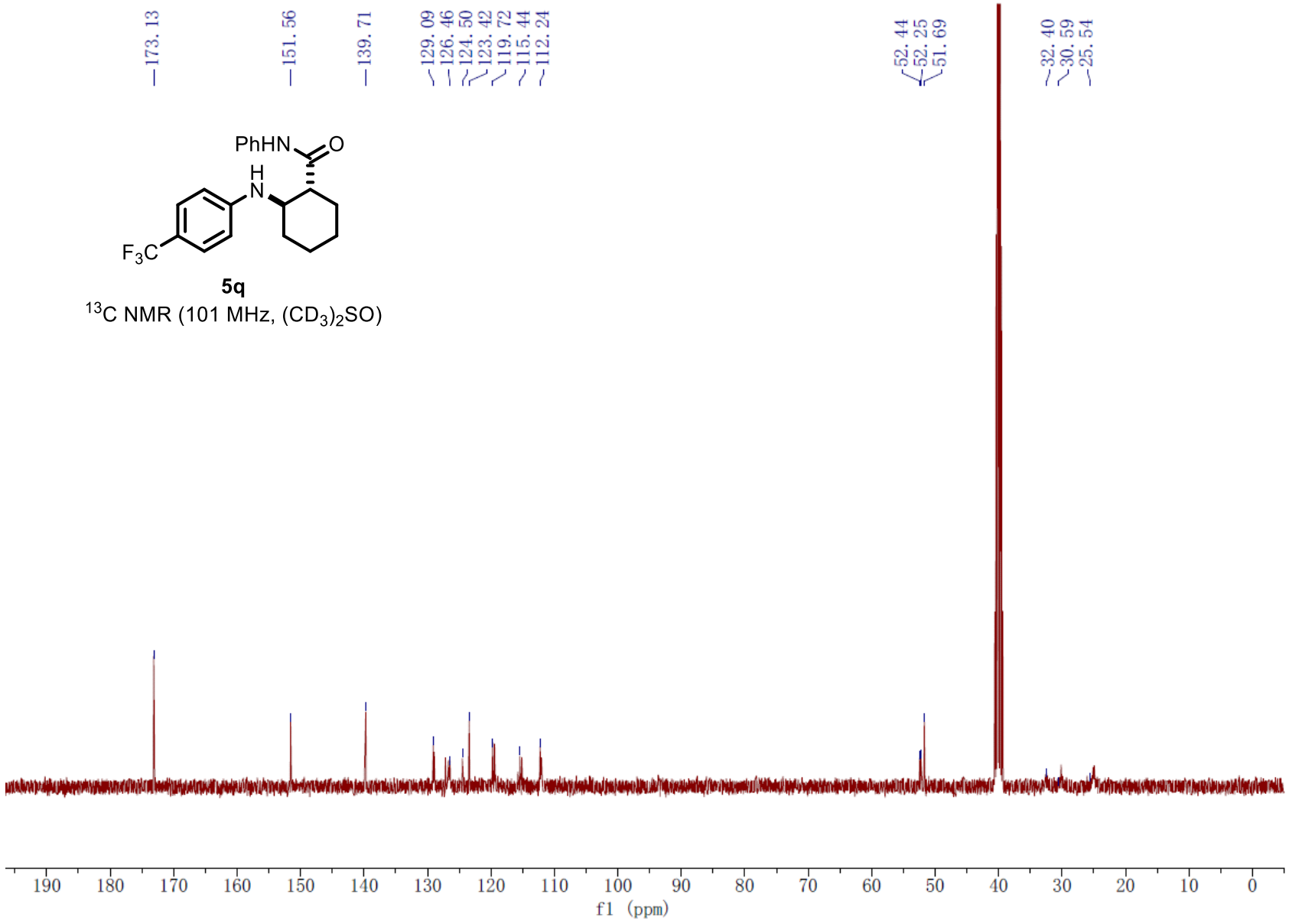


5p

^{19}F NMR (376 MHz, $(CD_3)_2SO$)

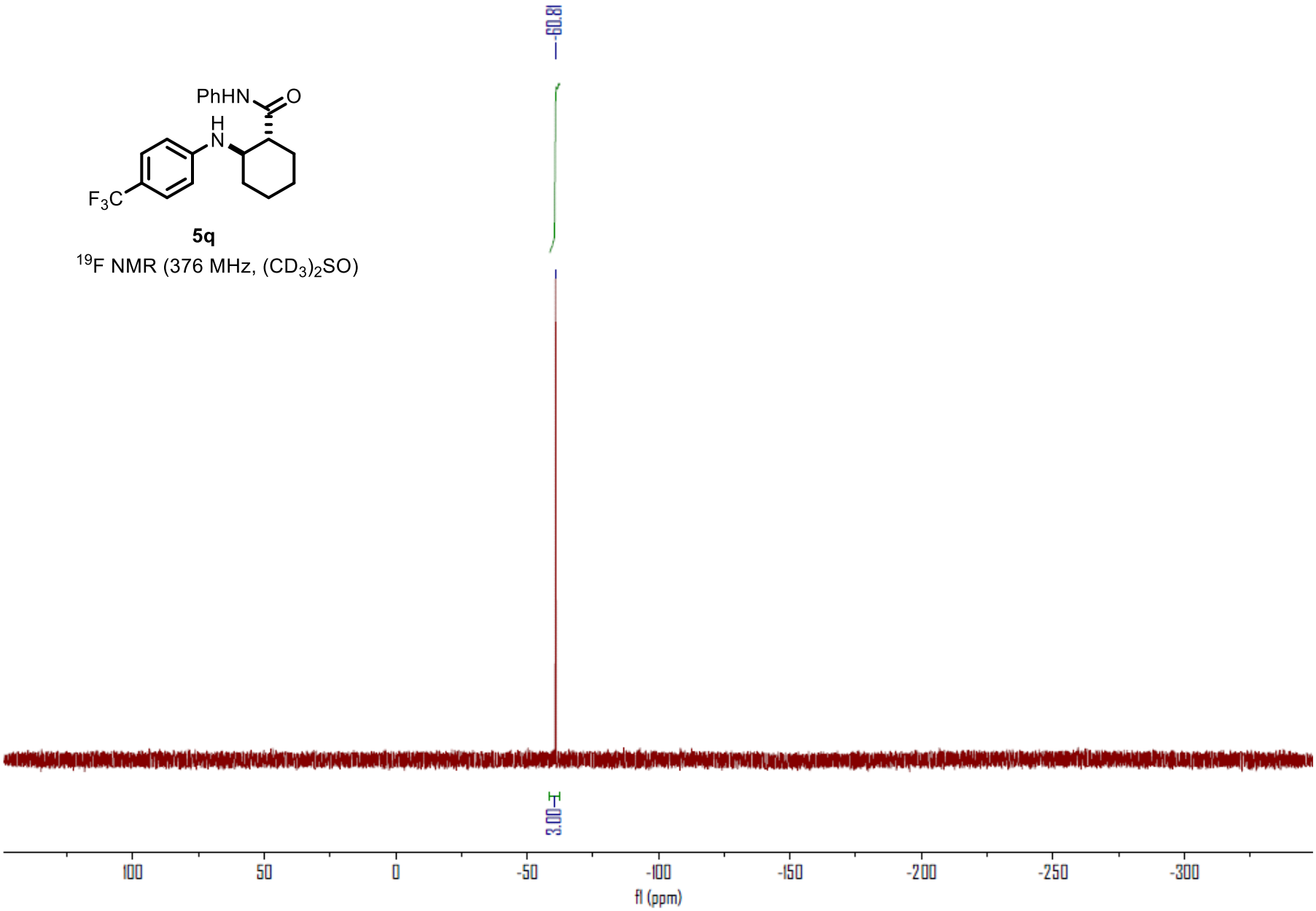

BnHN
O
H
N
F3C
5p
NOESY NMR (400 MHz, (CD3)2SO)
f2 (ppm)
f1 (ppm)


PhHN
O
H
N
F3C
5q
1H NMR (400 MHz, (CD3)2SO)
f1 (ppm)



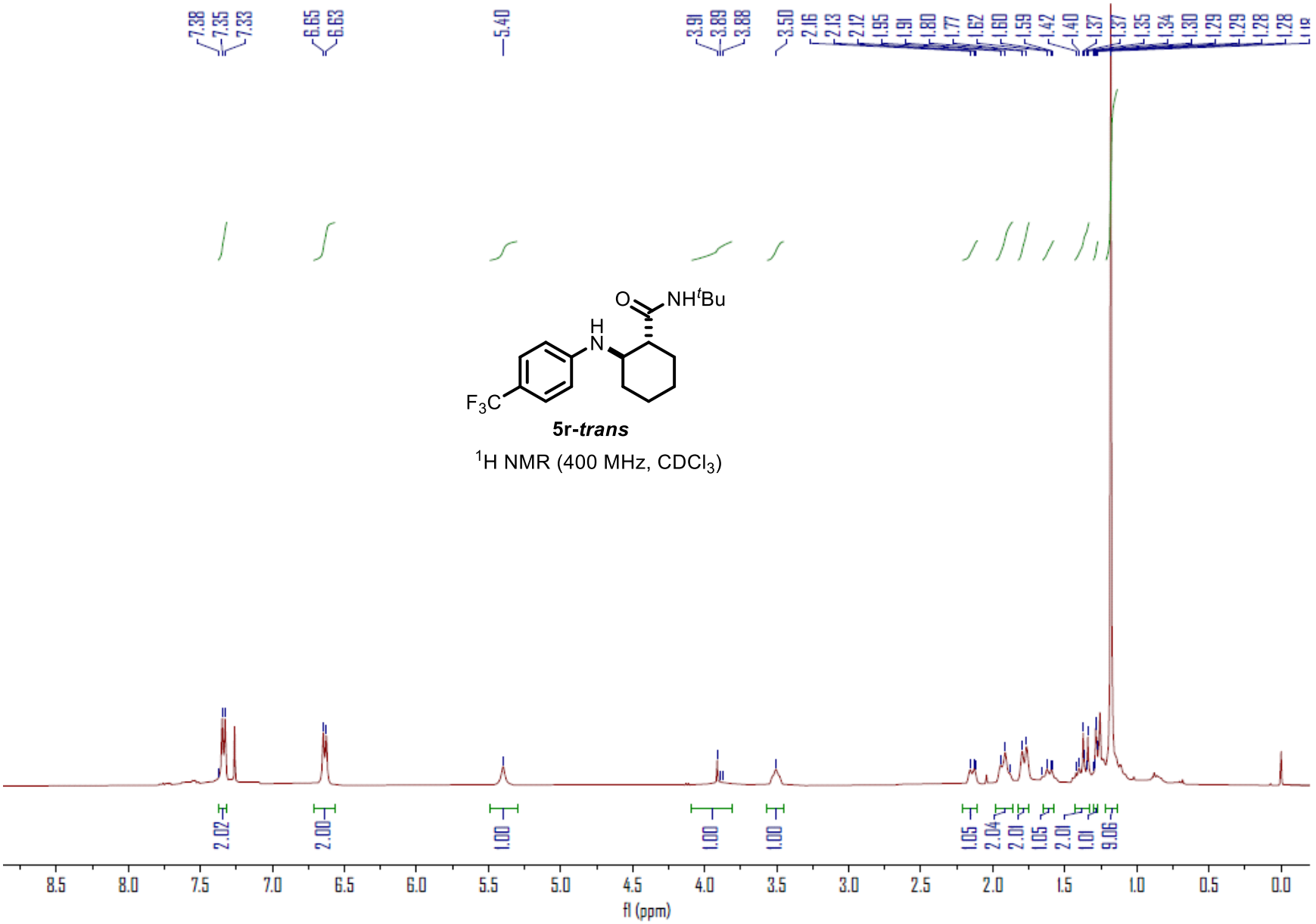
5q

^{13}C NMR (101 MHz, $(CD_3)_2SO$)



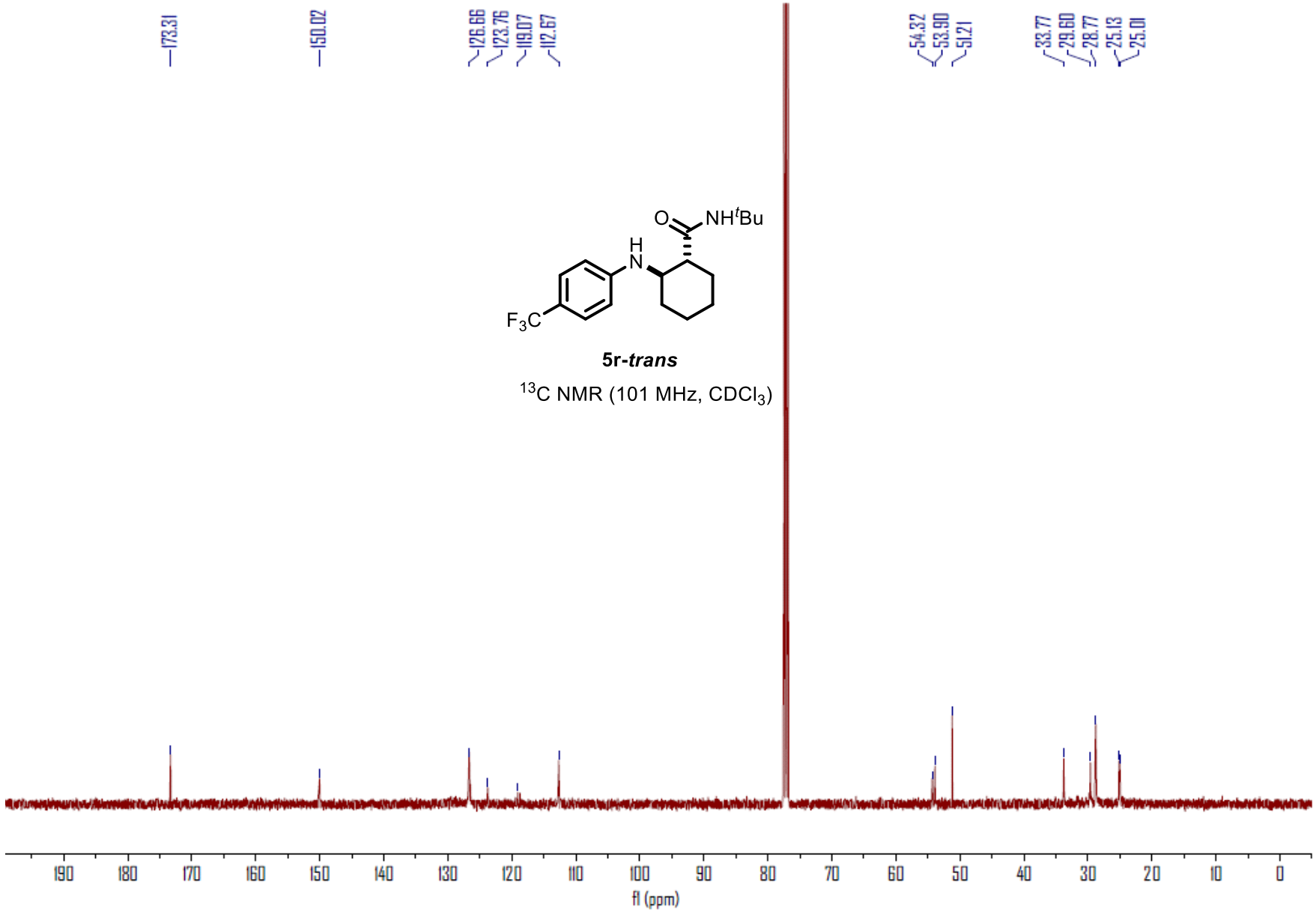
5q

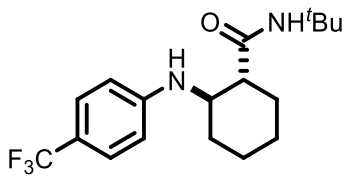
^{19}F NMR (376 MHz, $(CD_3)_2SO$)



5r-*trans*

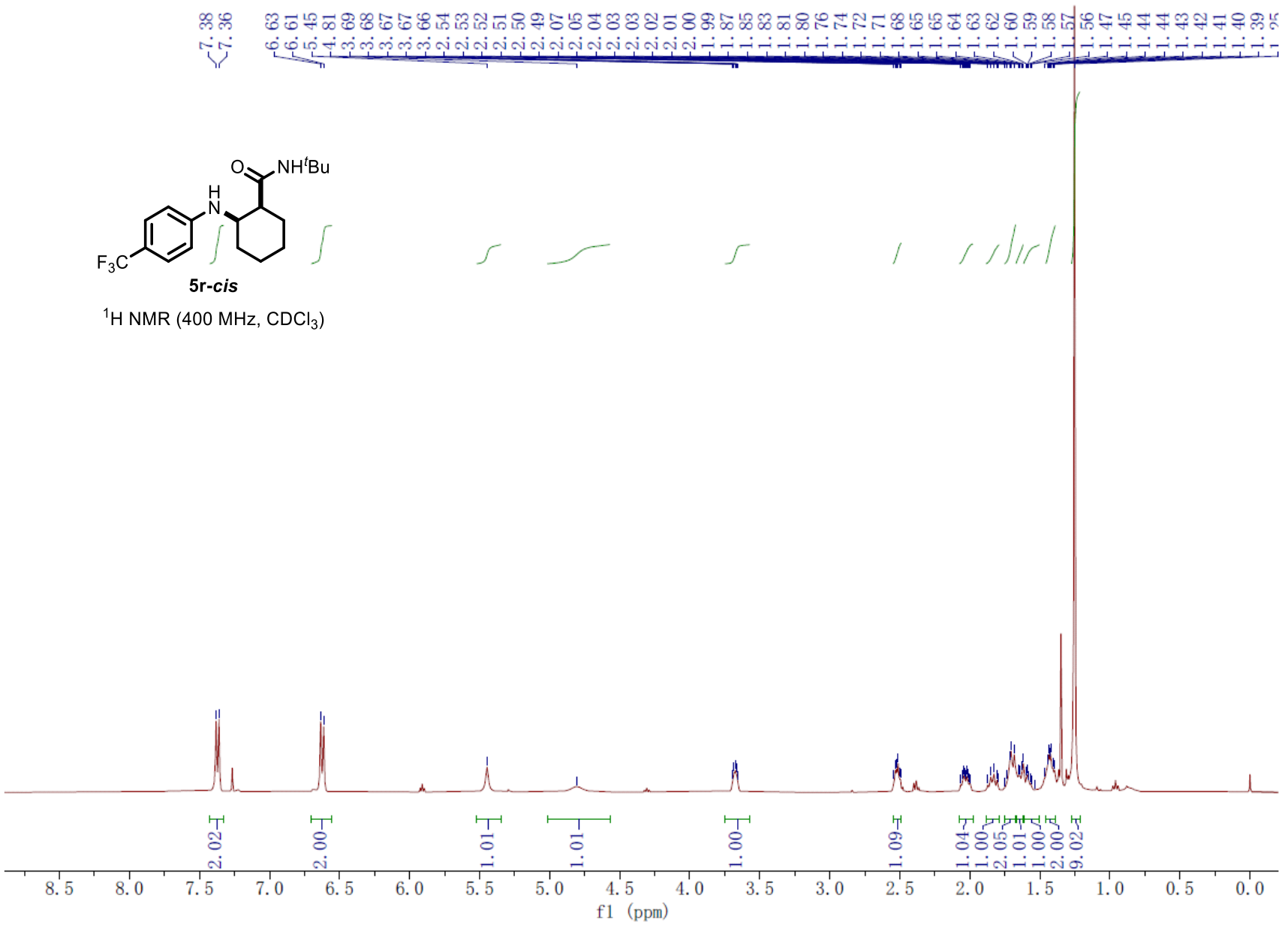
^{1}H NMR (400 MHz, $CDCl_3$)

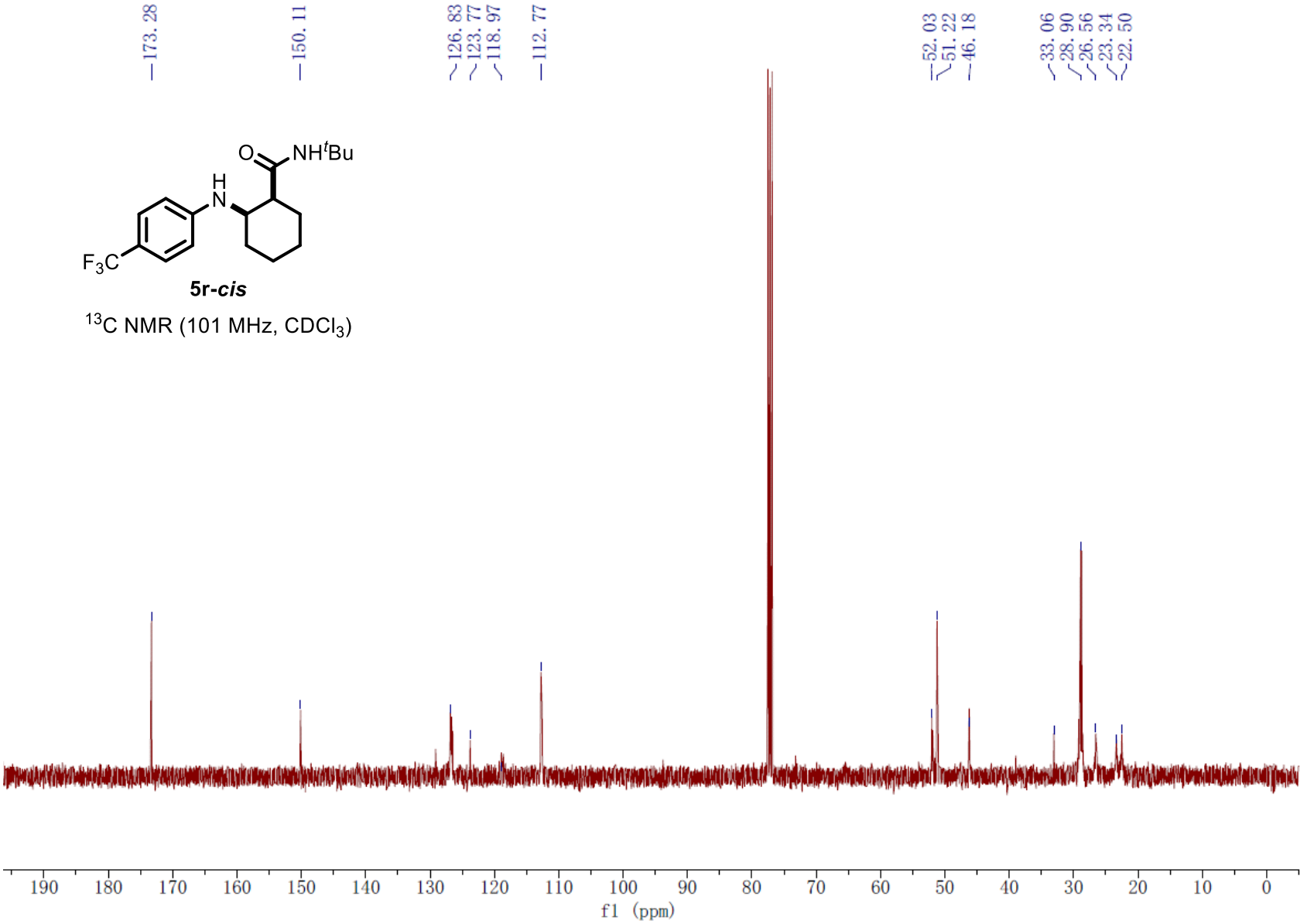

173.31
150.02
126.66
123.76
119.07
112.67
54.32
53.90
51.21
33.77
29.60
28.77
25.13
25.01
O
NH^{t}Bu
H
N
F$_3$C
5r-*trans*
^{13}C NMR (101 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5r-*trans*

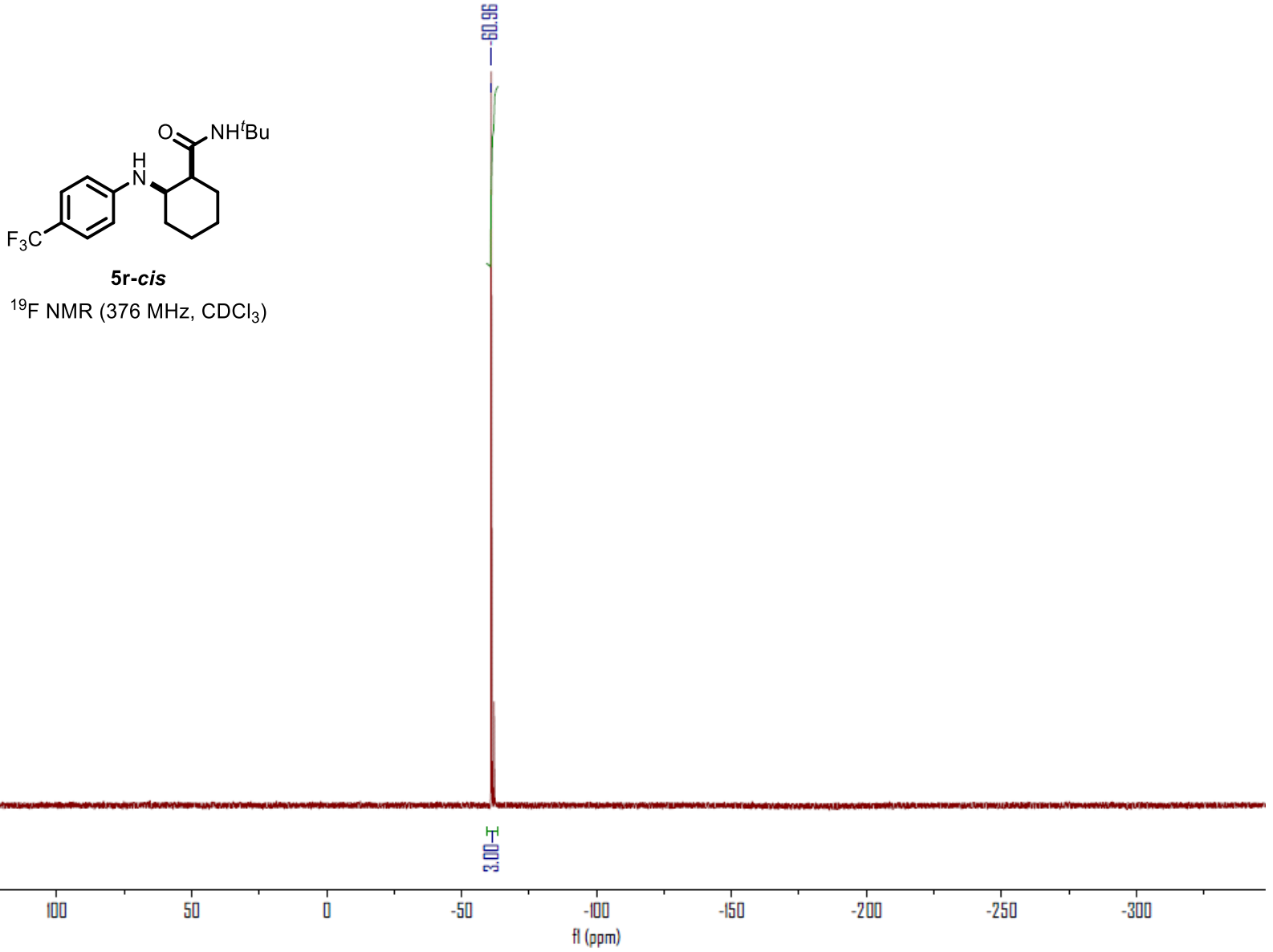
^{19}F NMR (376 MHz, $CDCl_3$)


O
NH^{t}Bu
H
N
F$_3$C
5r-*cis*
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)



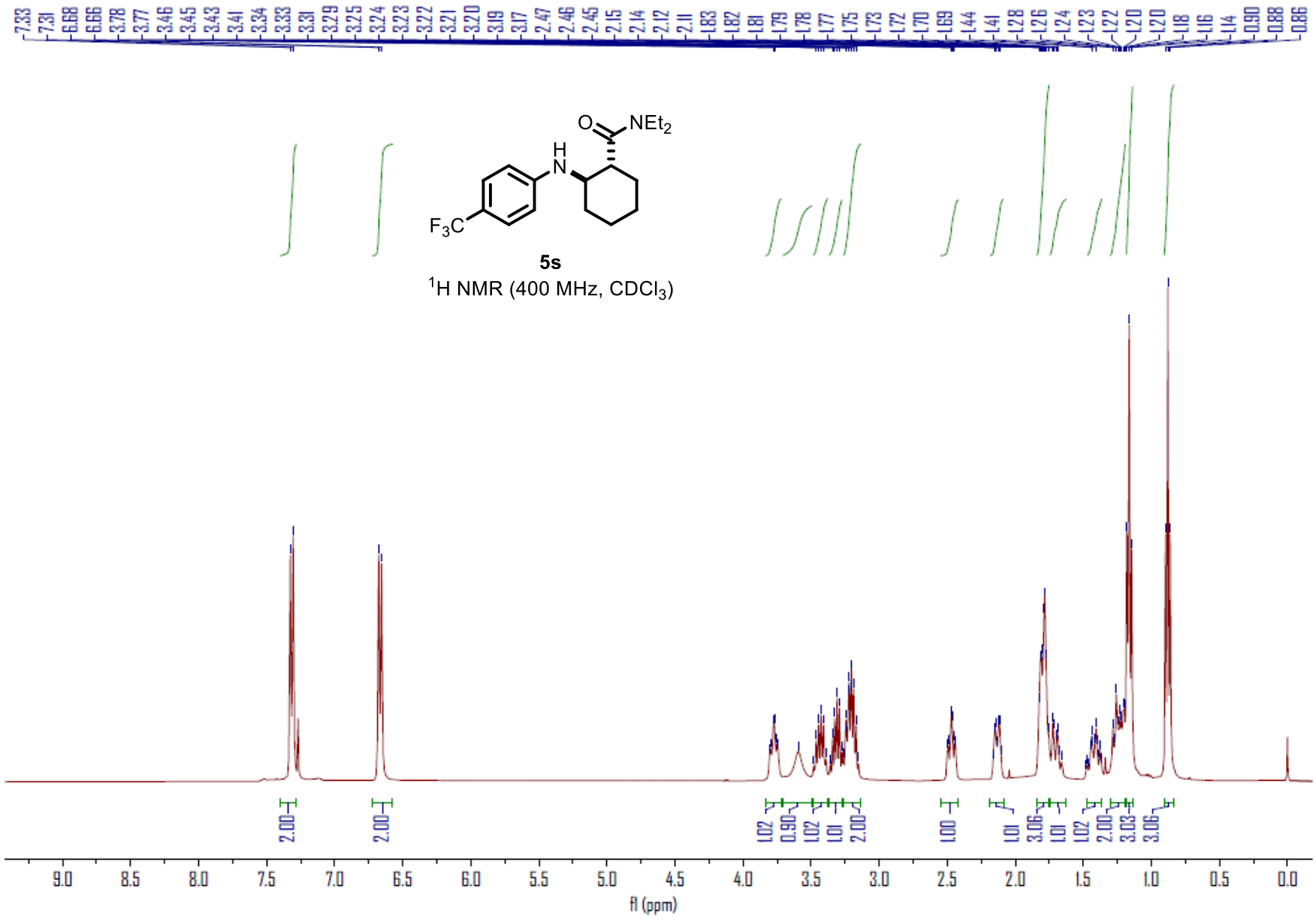
5r-*cis*

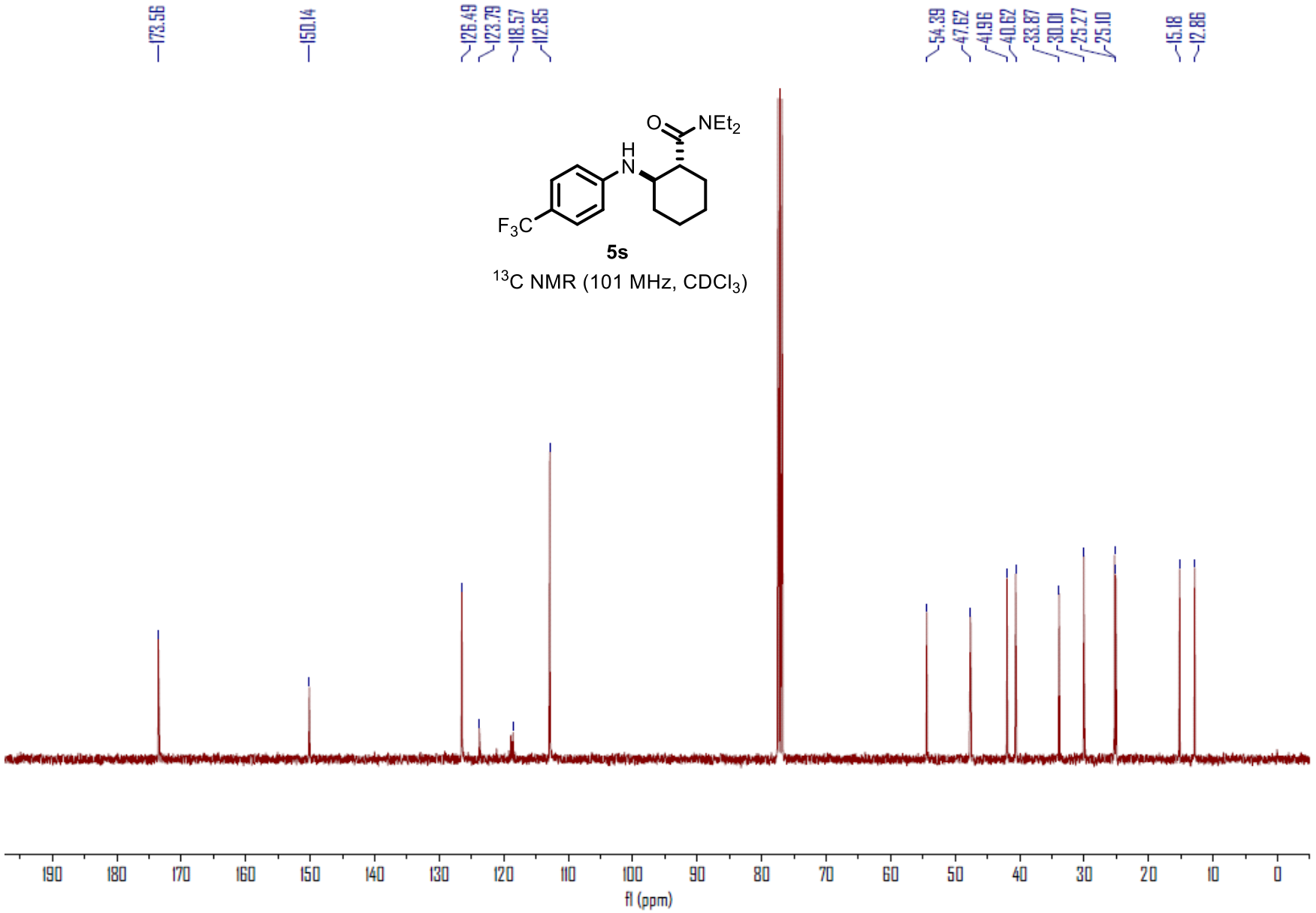
^{13}C NMR (101 MHz, $CDCl_3$)

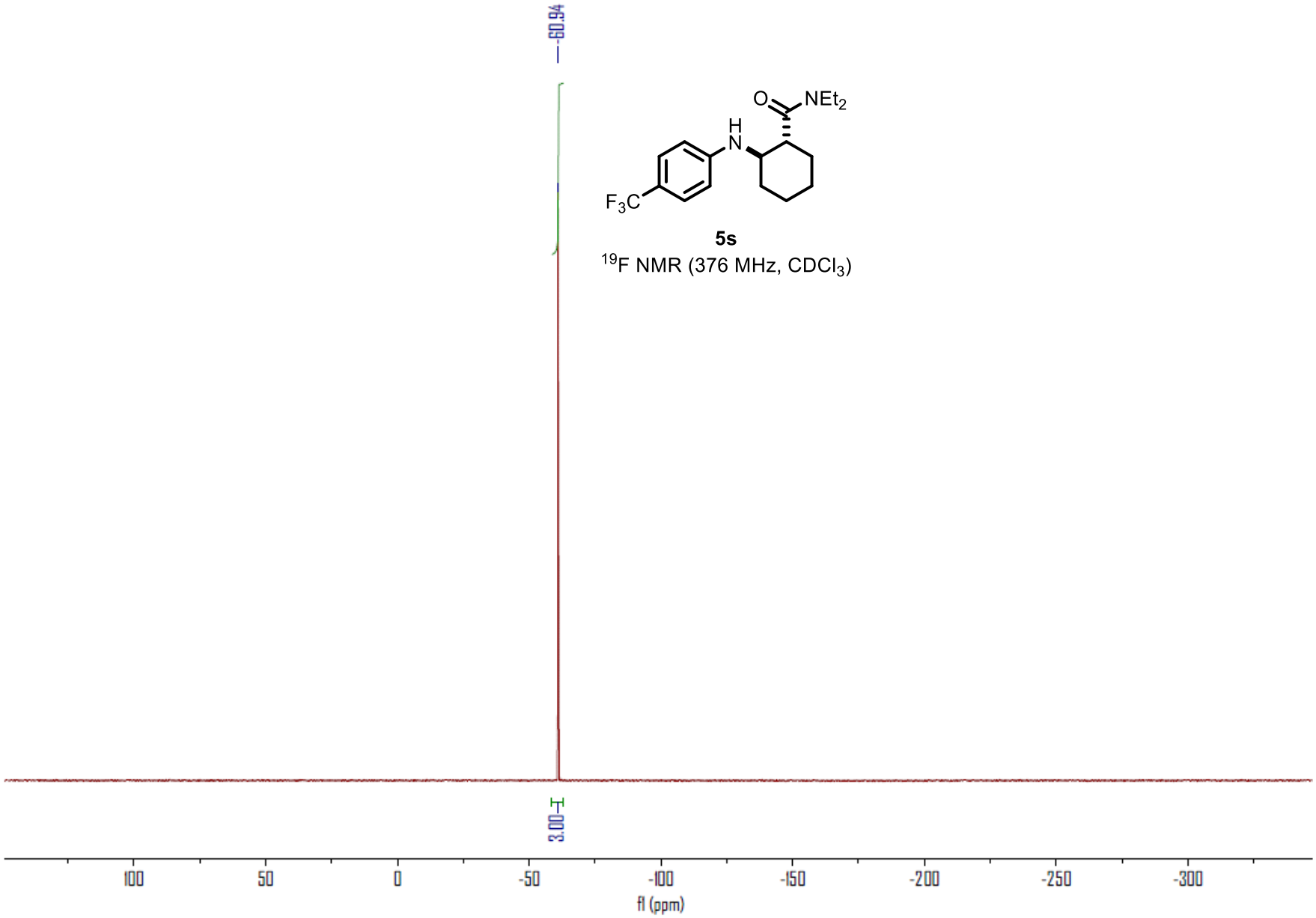


5r-*cis*

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

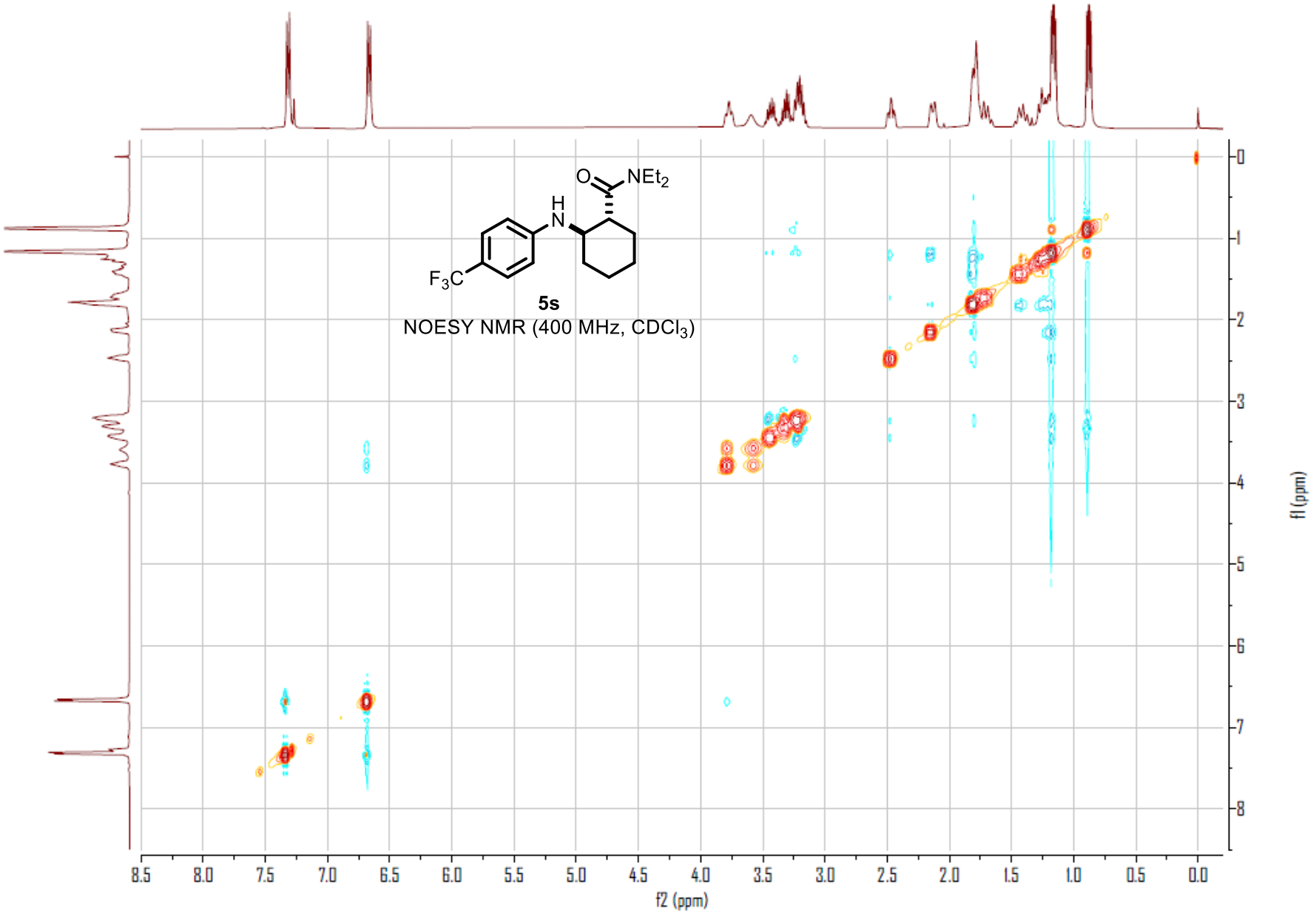

7.33
7.31
6.68
6.66
3.78
3.77
3.46
3.45
3.43
3.41
3.34
3.33
3.31
3.29
3.25
3.24
3.23
3.22
3.21
3.20
3.19
3.17
2.47
2.46
2.45
2.15
2.14
2.12
2.11
1.83
1.82
1.81
1.79
1.78
1.77
1.75
1.73
1.72
1.70
1.69
1.44
1.41
1.28
1.26
1.24
1.23
1.22
1.20
1.20
1.18
1.16
1.14
0.90
0.88
0.86
O
NEt2
H
N
F3C
5s
1H NMR (400 MHz, CDCl3)
2.00
2.00
1.02
0.90
1.02
1.01
2.00
1.00
1.01
3.06
1.01
1.02
2.00
3.03
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

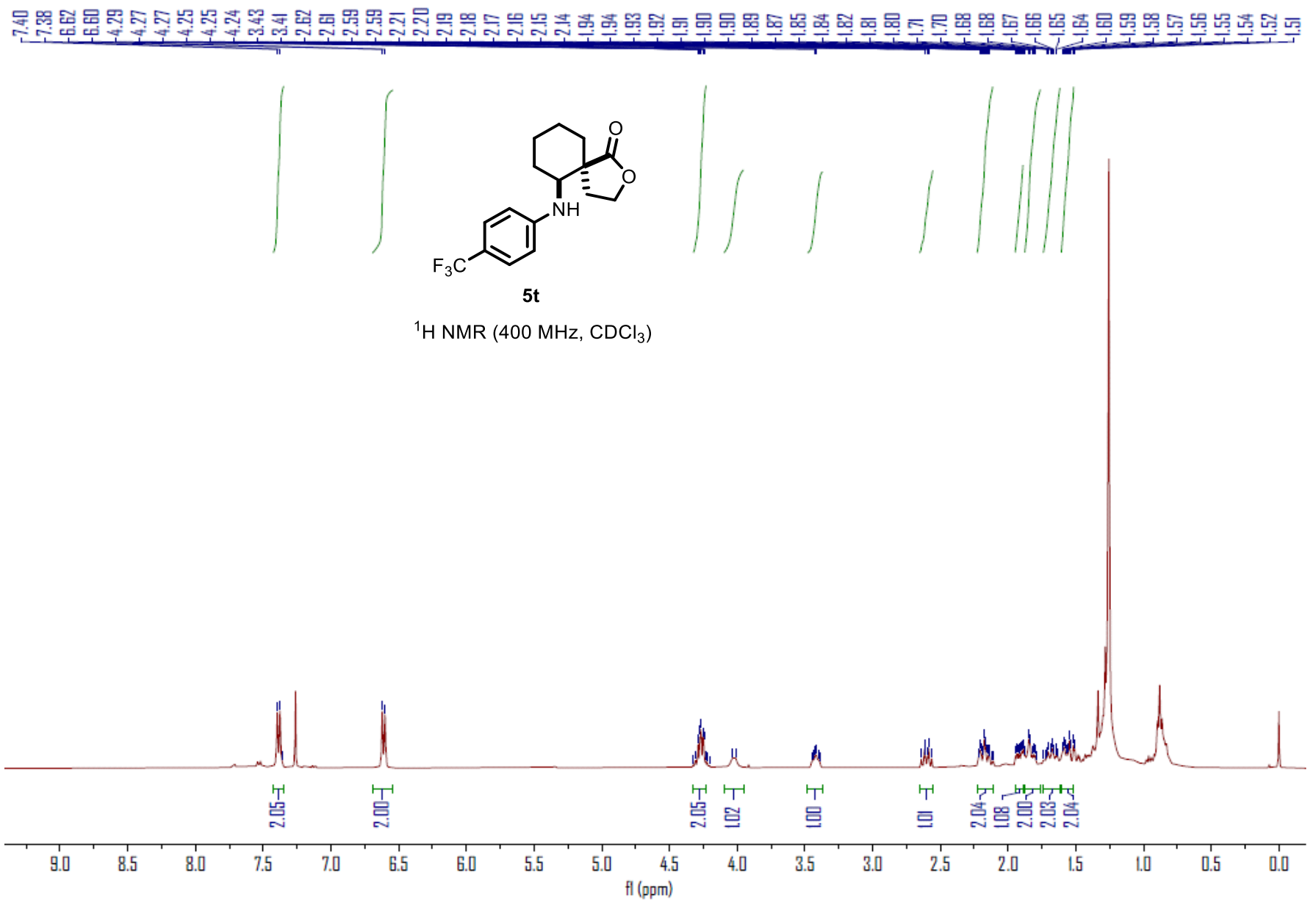

173.56
150.14
126.49
123.79
118.57
112.85
54.39
47.62
41.96
40.62
33.87
30.01
25.27
25.10
15.18
12.86
O
NEt2
H
N
F3C
5s
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5s

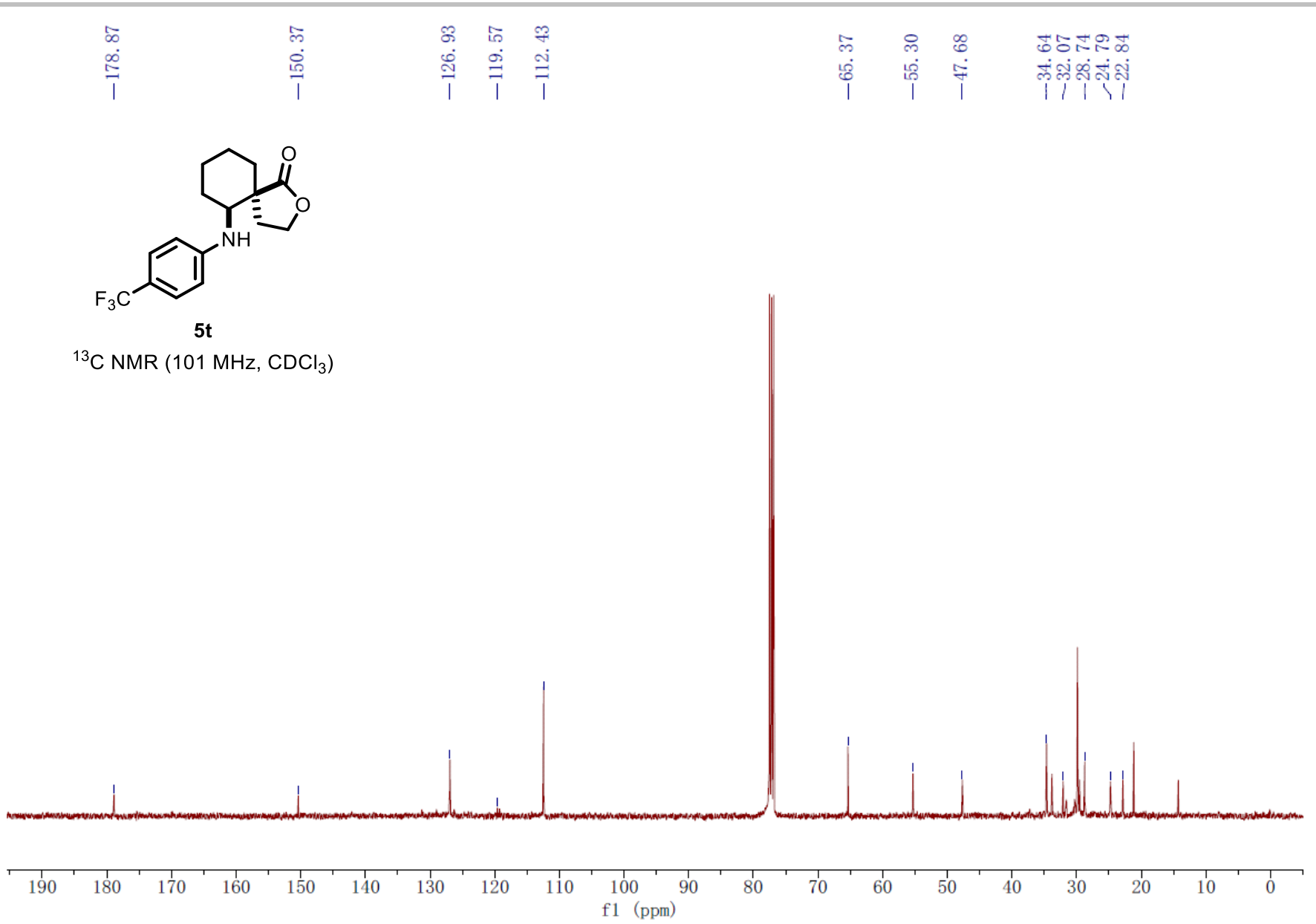
^{19}F NMR (376 MHz, $CDCl_3$)


O
NEt2
H
N
F3C
5s
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



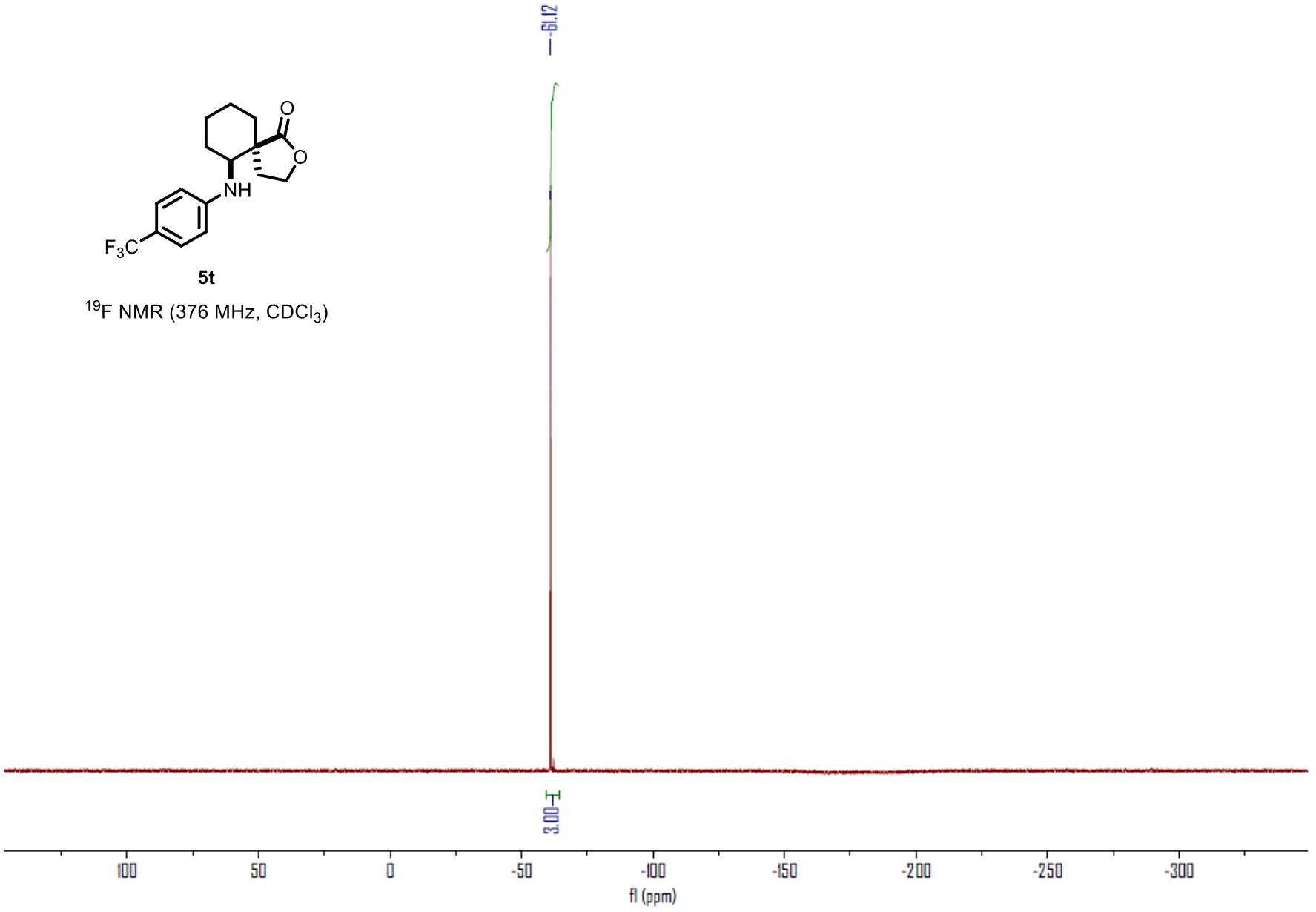
5t

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



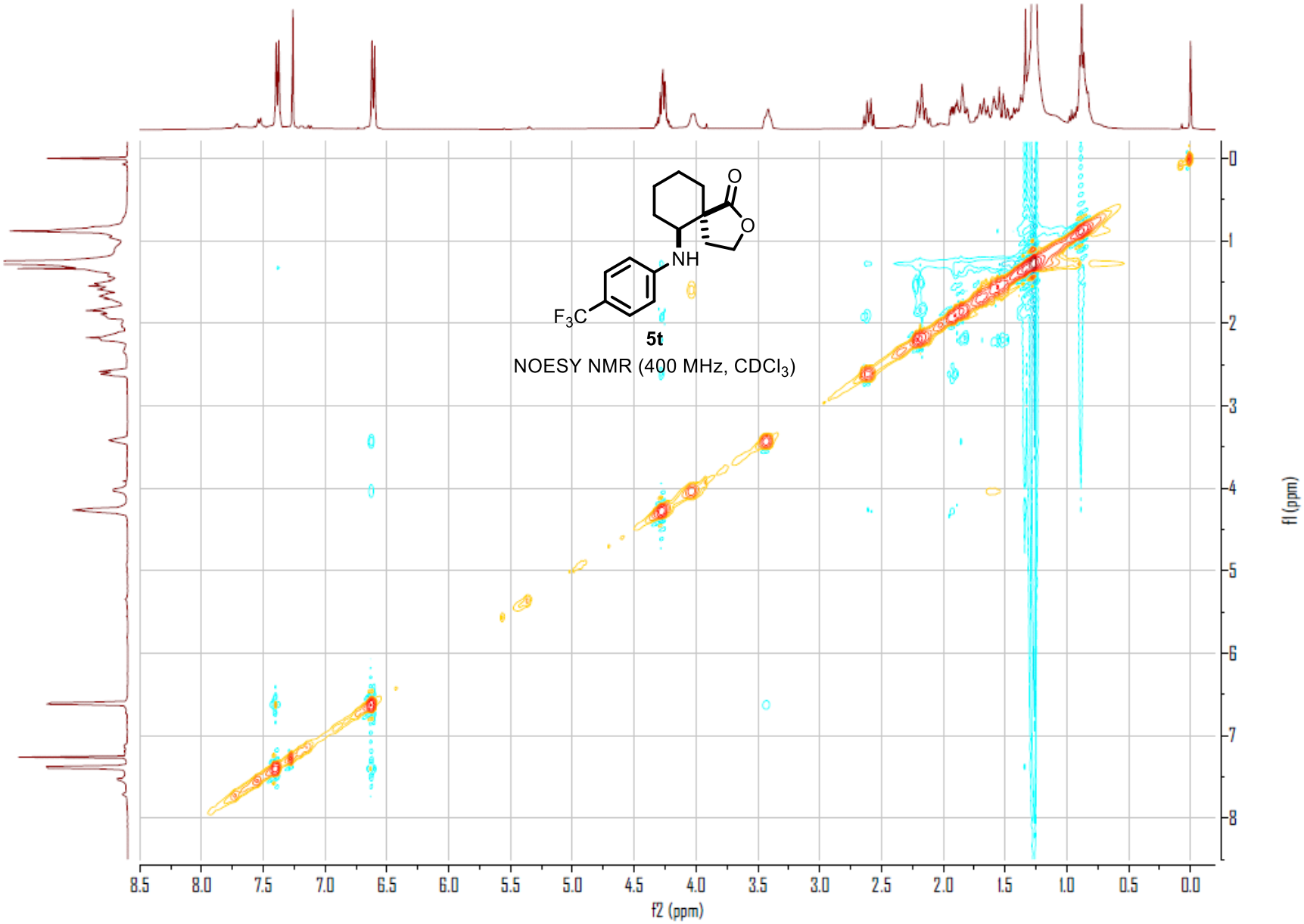
5t

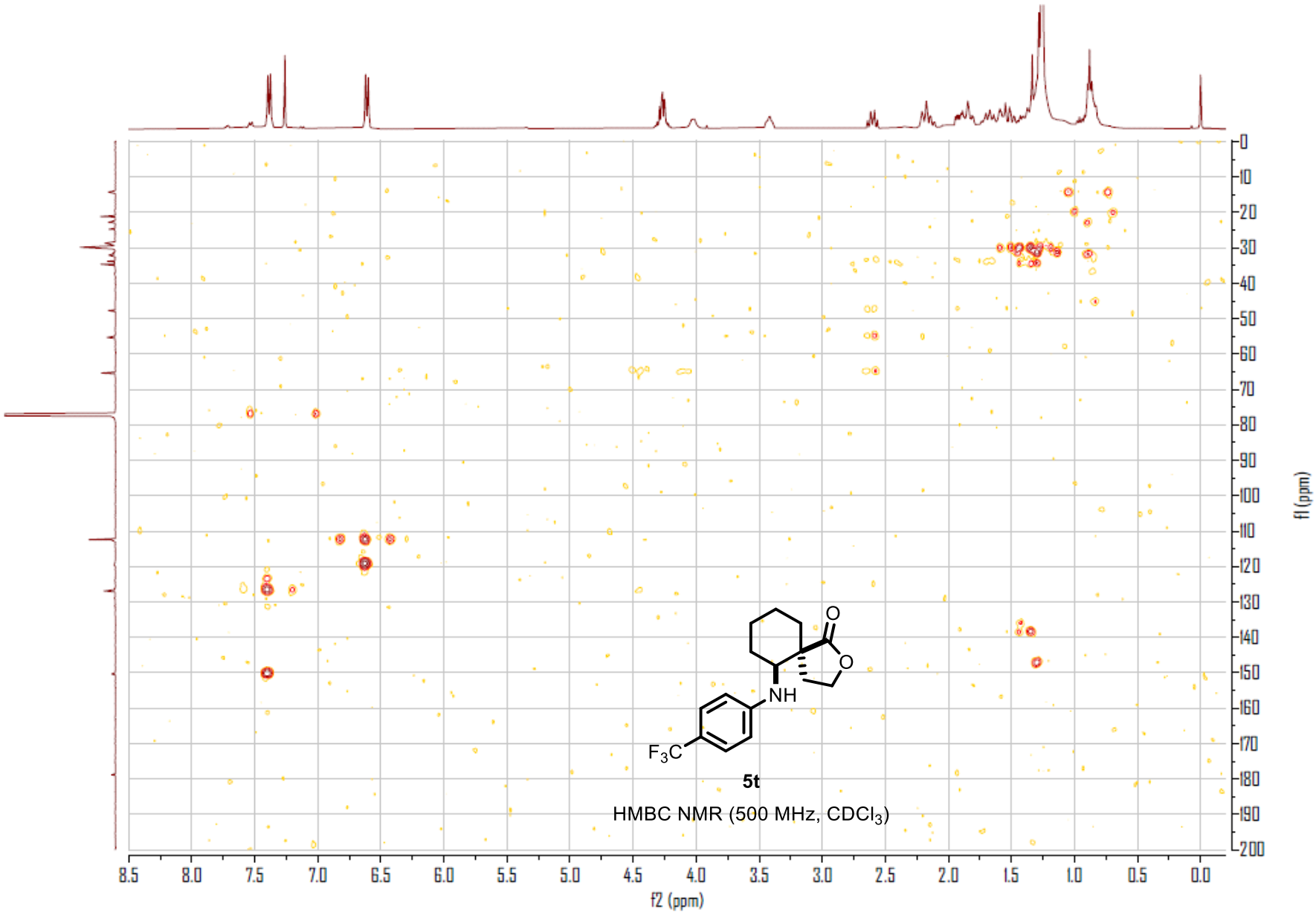
^{13}C NMR (101 MHz, $CDCl_3$)



5t

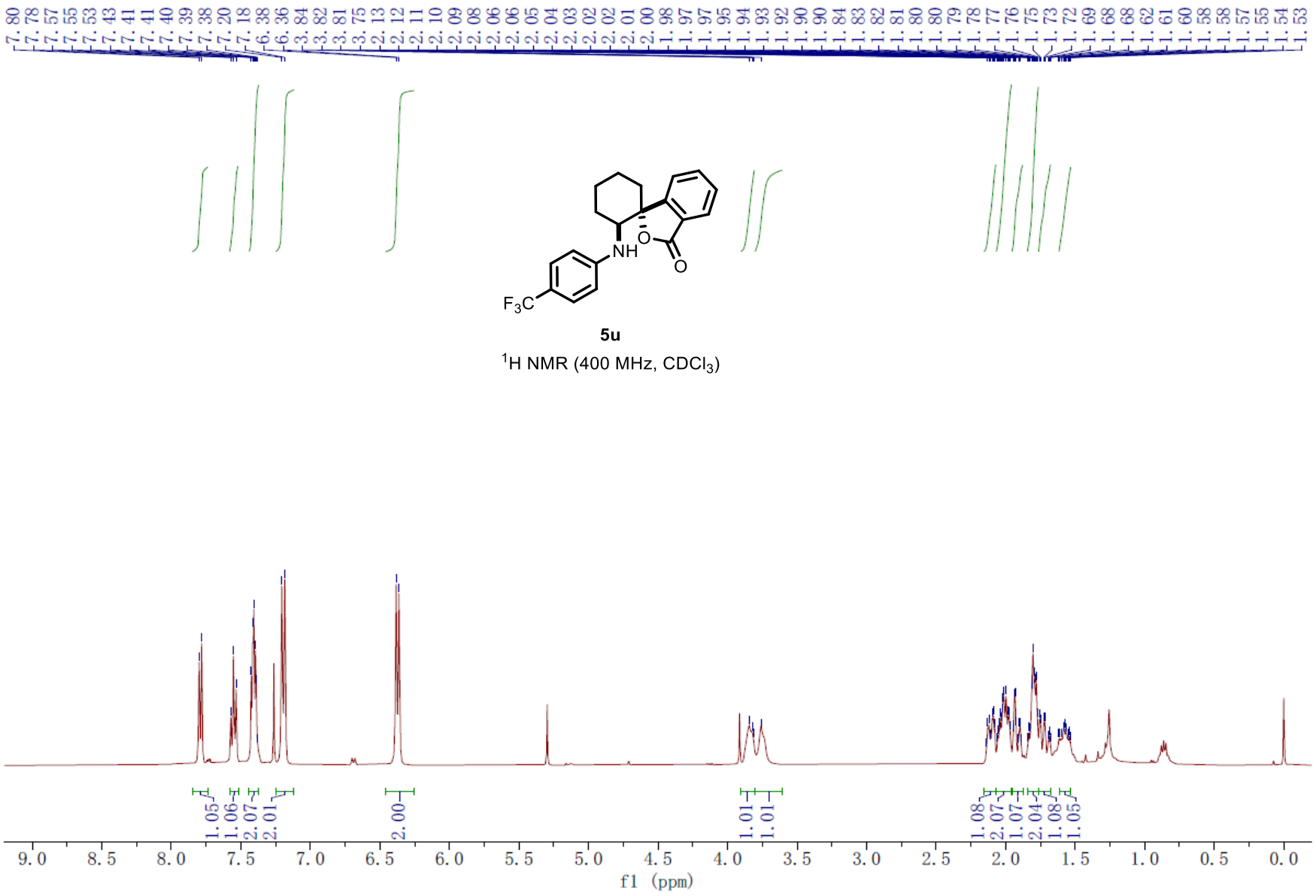
^{19}F NMR (376 MHz, $CDCl_3$)


O
O
NH
F3C
5t
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



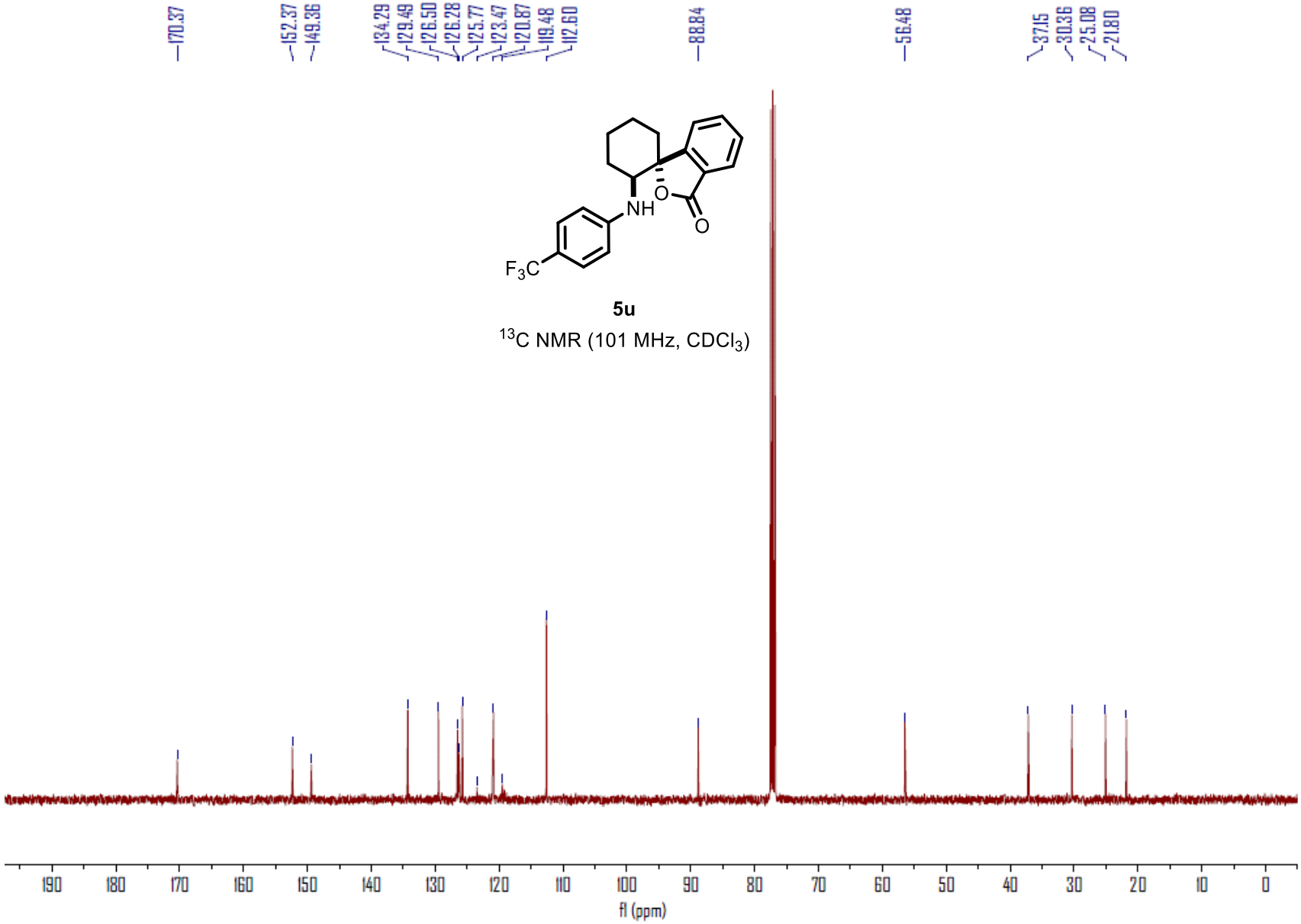
5t

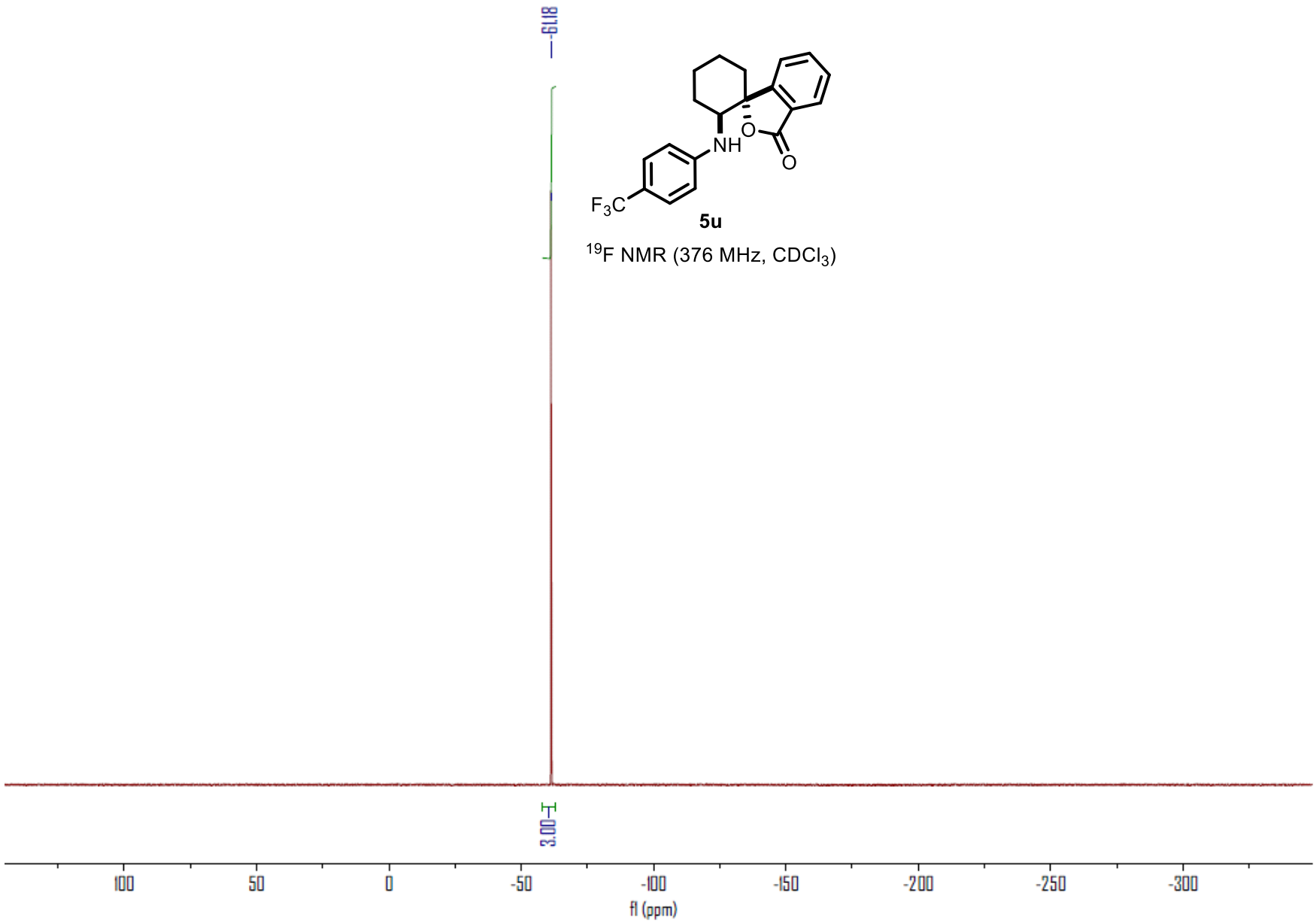
HMBC NMR (500 MHz, $CDCl_3$)



5u

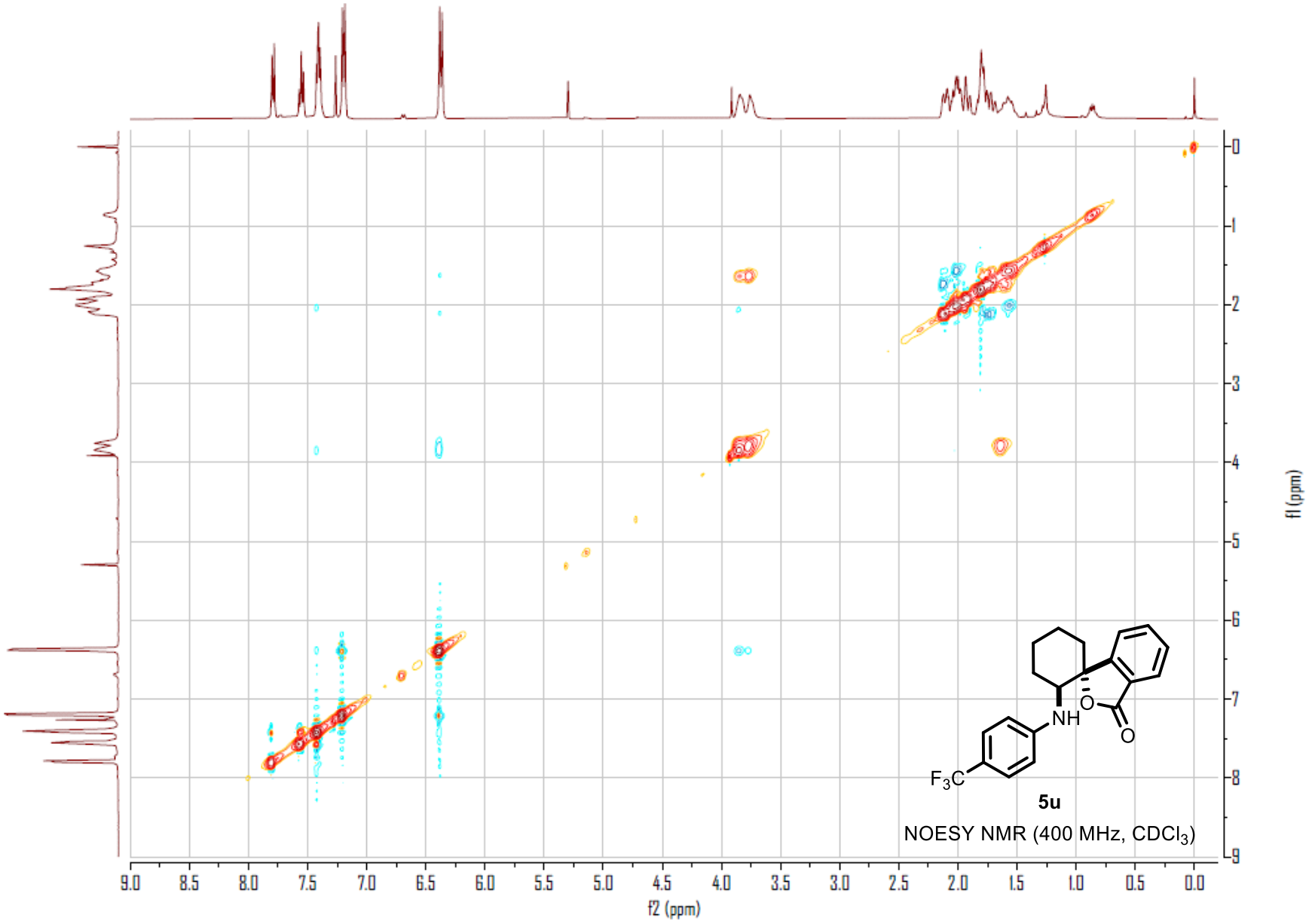
^{1}H NMR (400 MHz, $CDCl_3$)

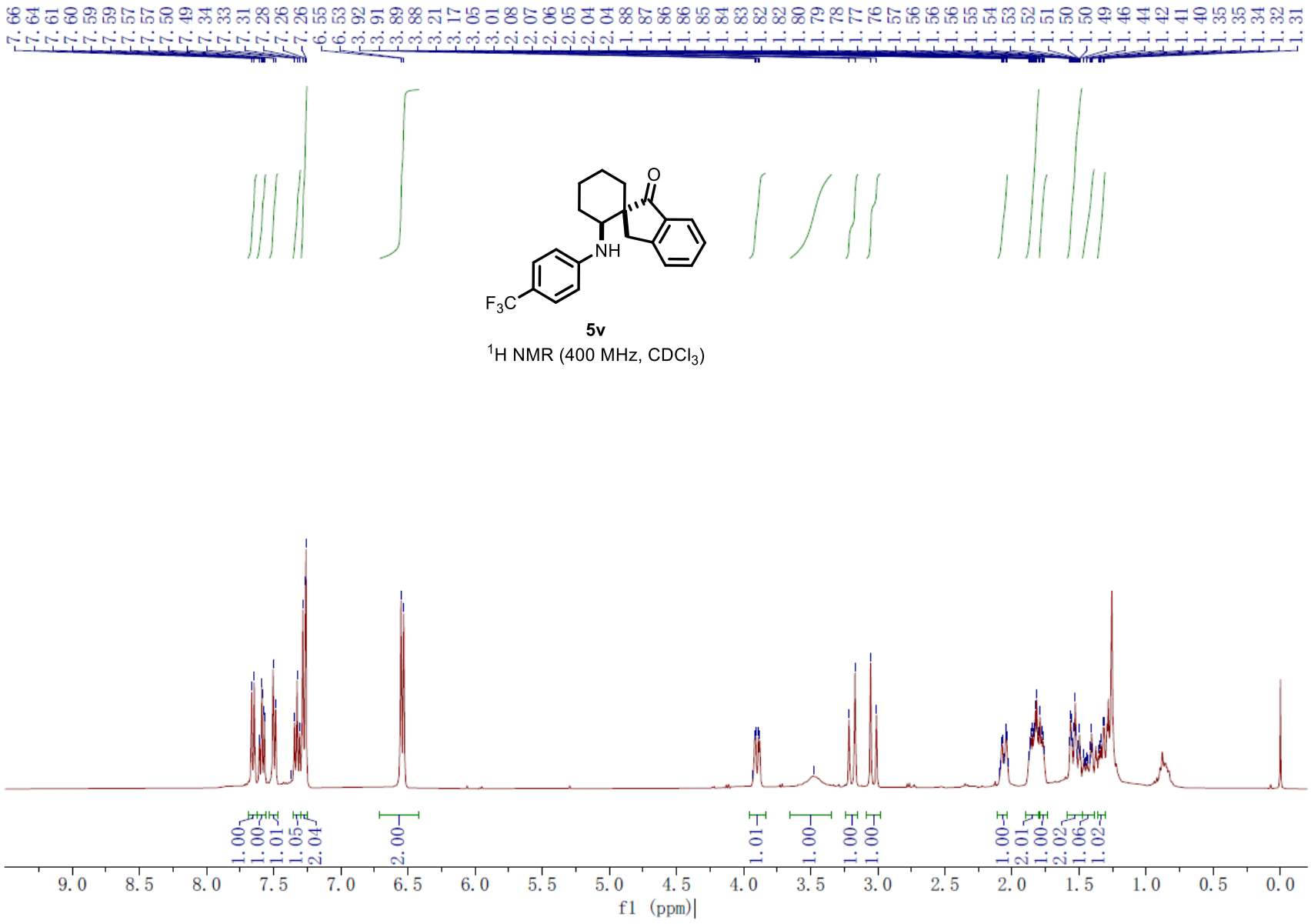

170.37
152.37
149.36
134.29
129.49
126.50
126.28
125.77
123.47
120.87
119.48
112.60
88.84
56.48
37.15
30.36
25.08
21.80
NH
O
O
F3C
5u
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5u

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

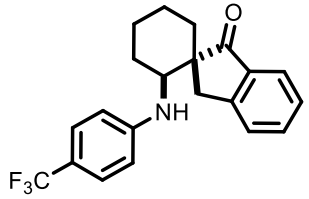

f2 (ppm)
f1 (ppm)
NH
O
O
F3C
5u
NOESY NMR (400 MHz, CDCl3)



5v

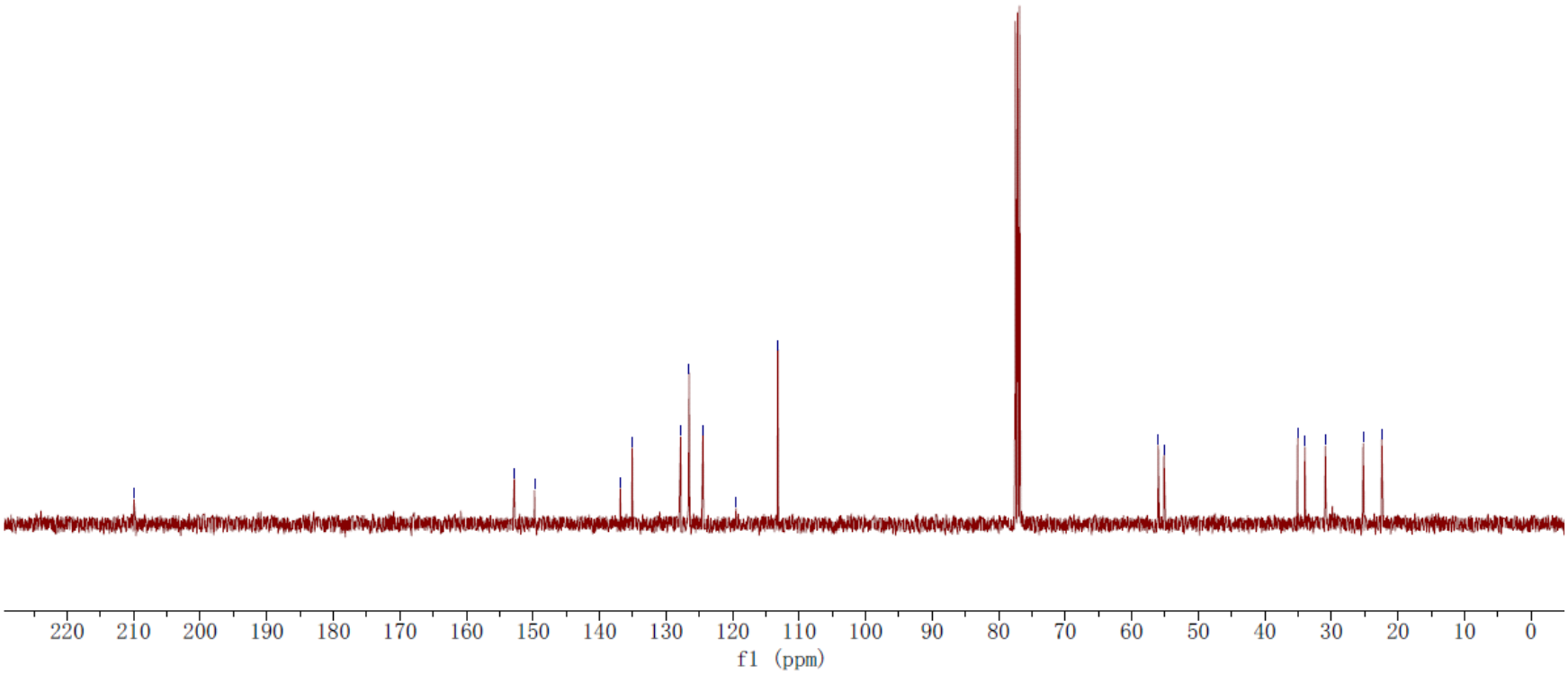
^{1}H NMR (400 MHz, $CDCl_3$)

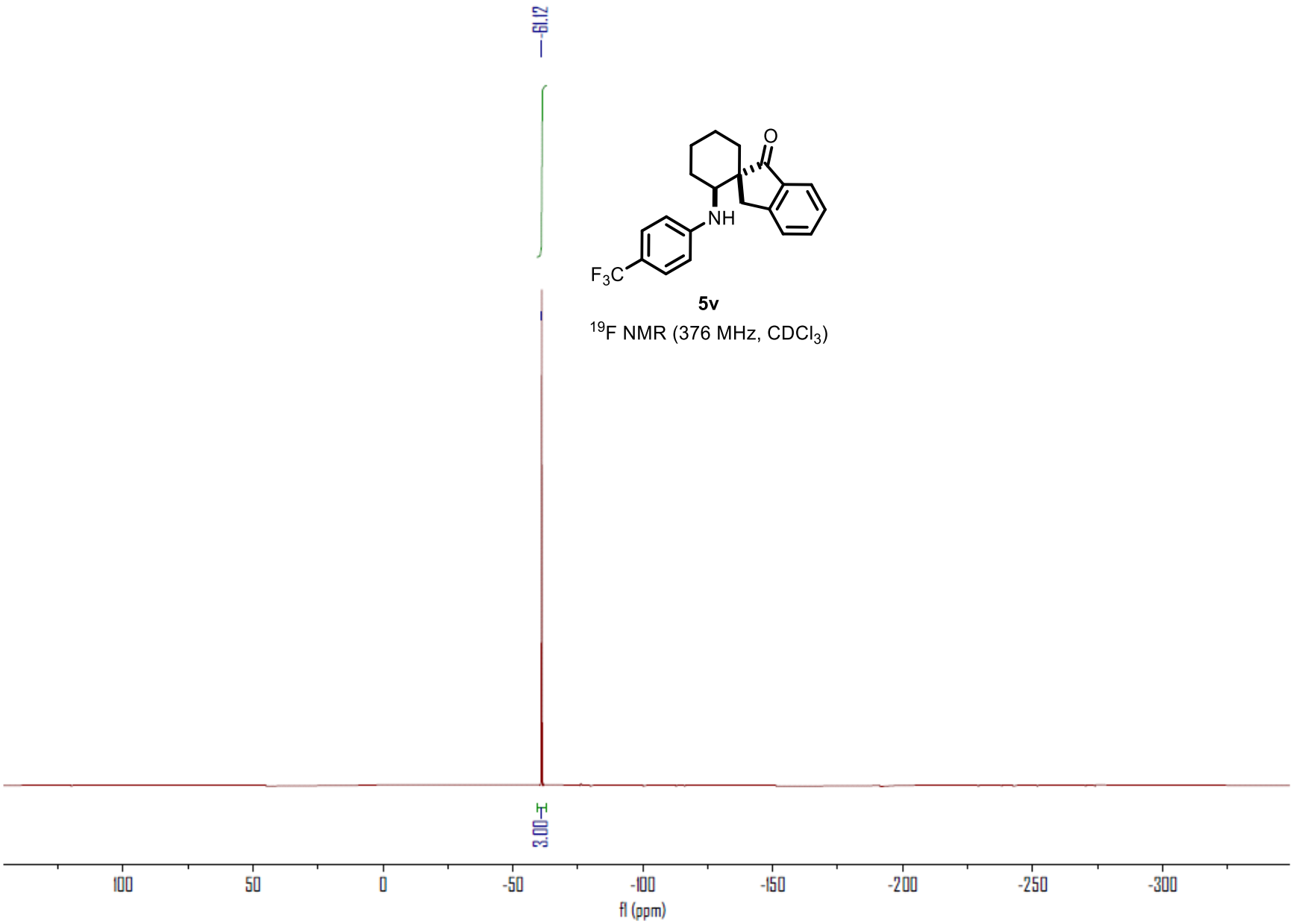
209.96
152.78
149.74
136.86
135.06
127.78
126.51
124.45
119.47
113.19
56.01
55.16
35.06
33.98
30.89
25.21
22.43



5v

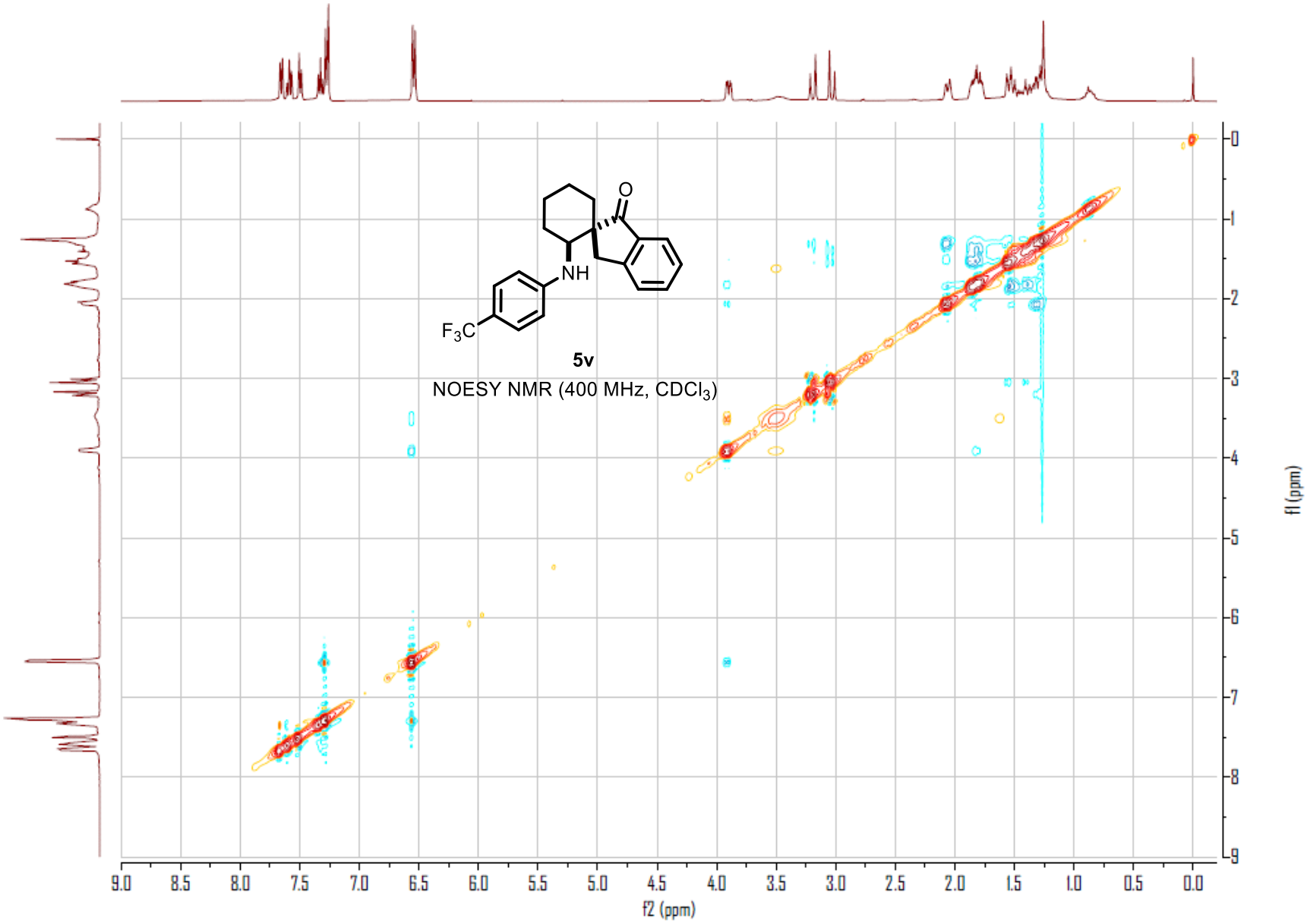
^{13}C NMR (101 MHz, $CDCl_3$)

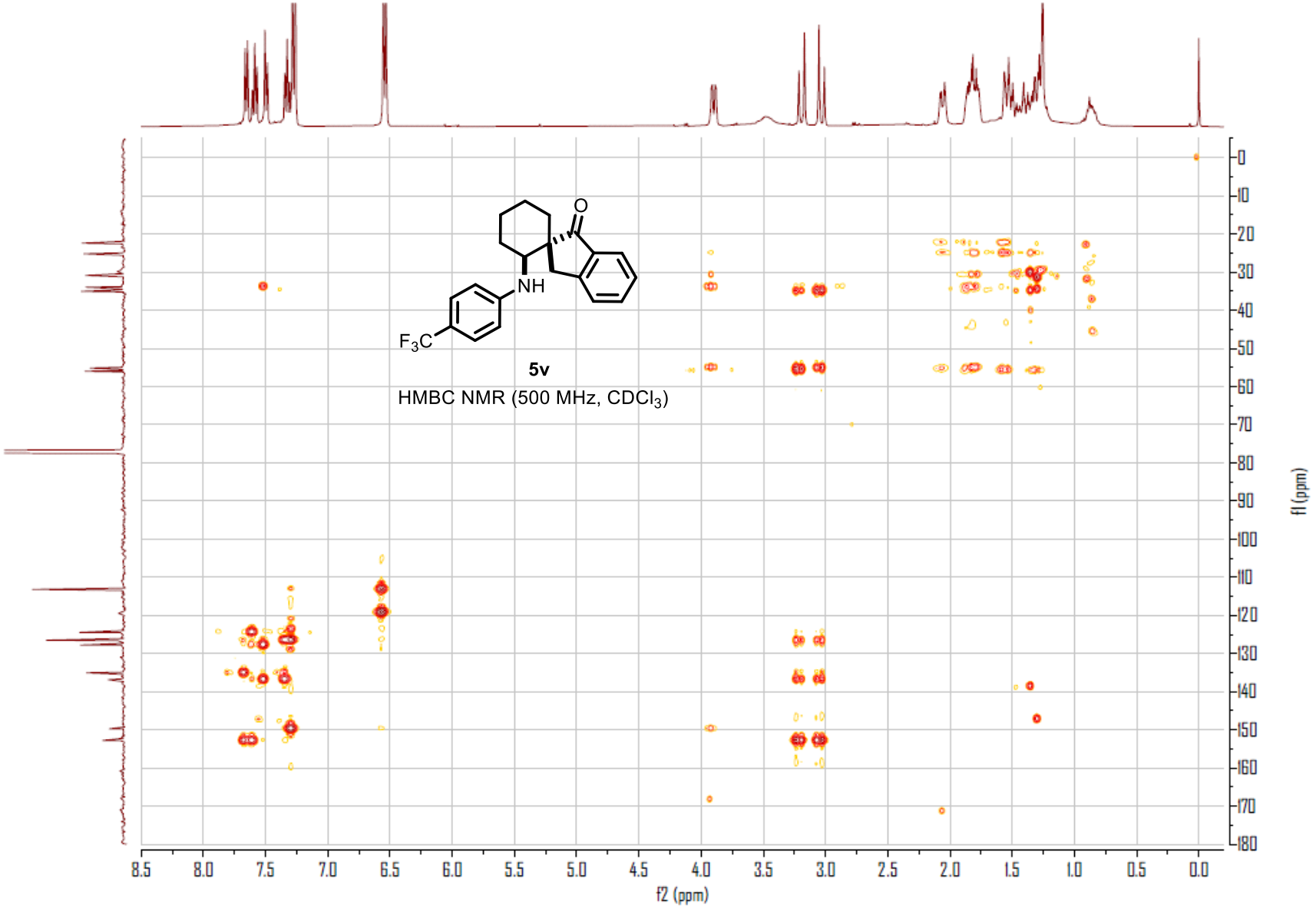


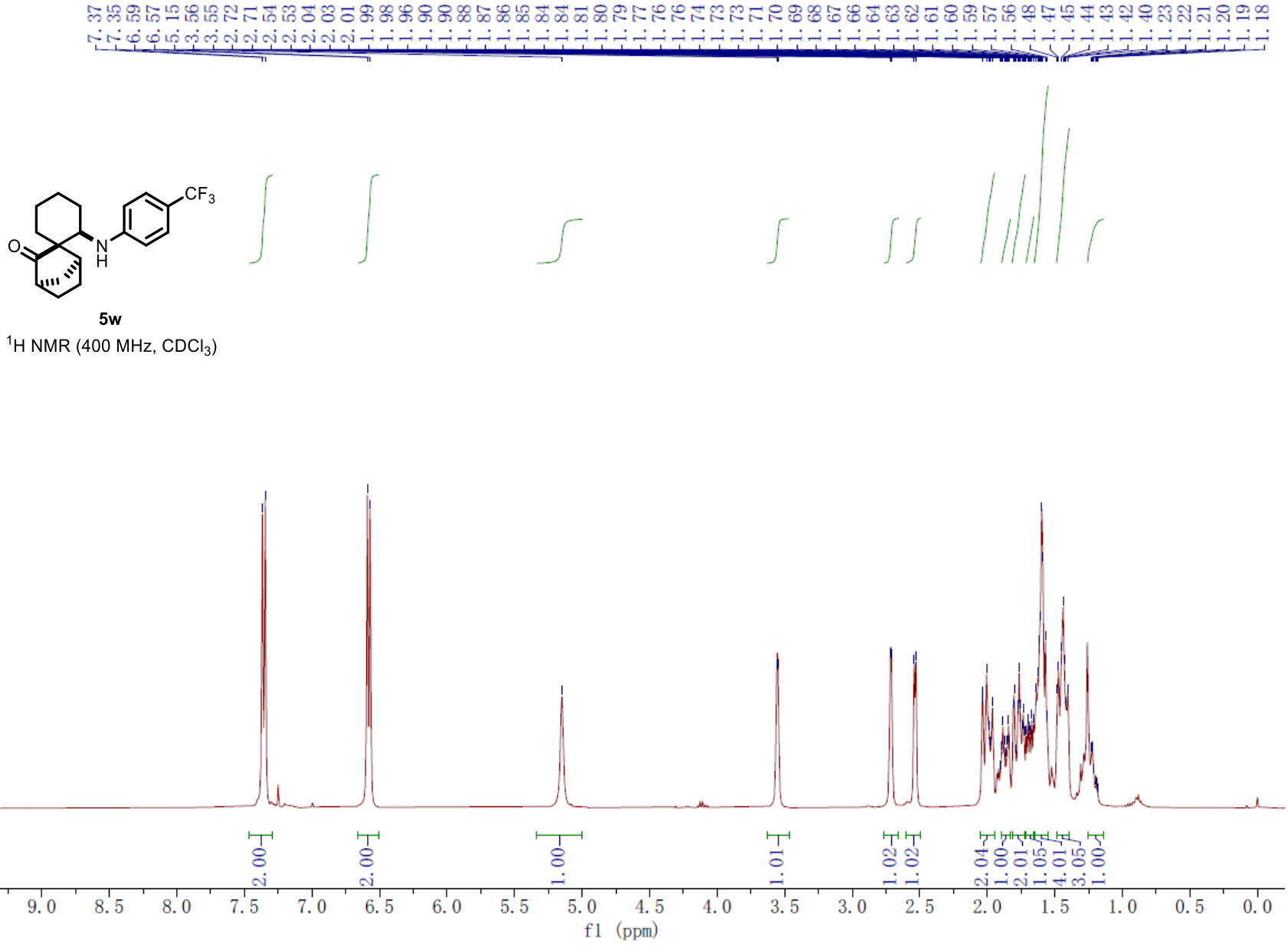


5v

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

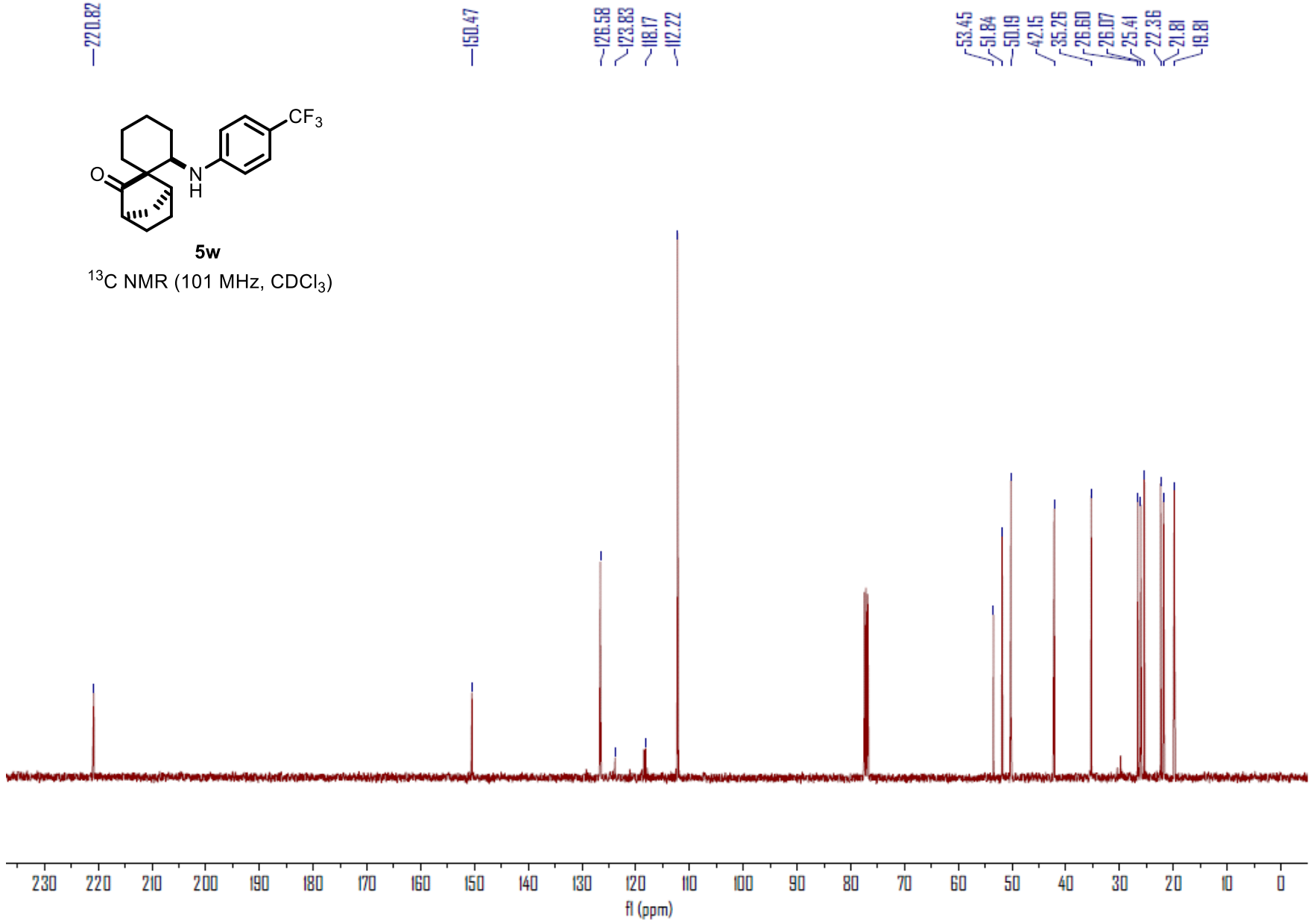

O
NH
F3C
5v
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


O
NH
F3C
5v
HMBC NMR (500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



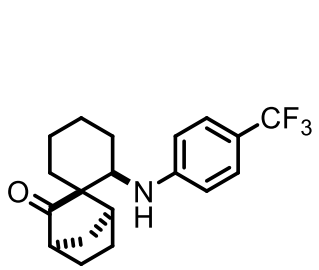
5w

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



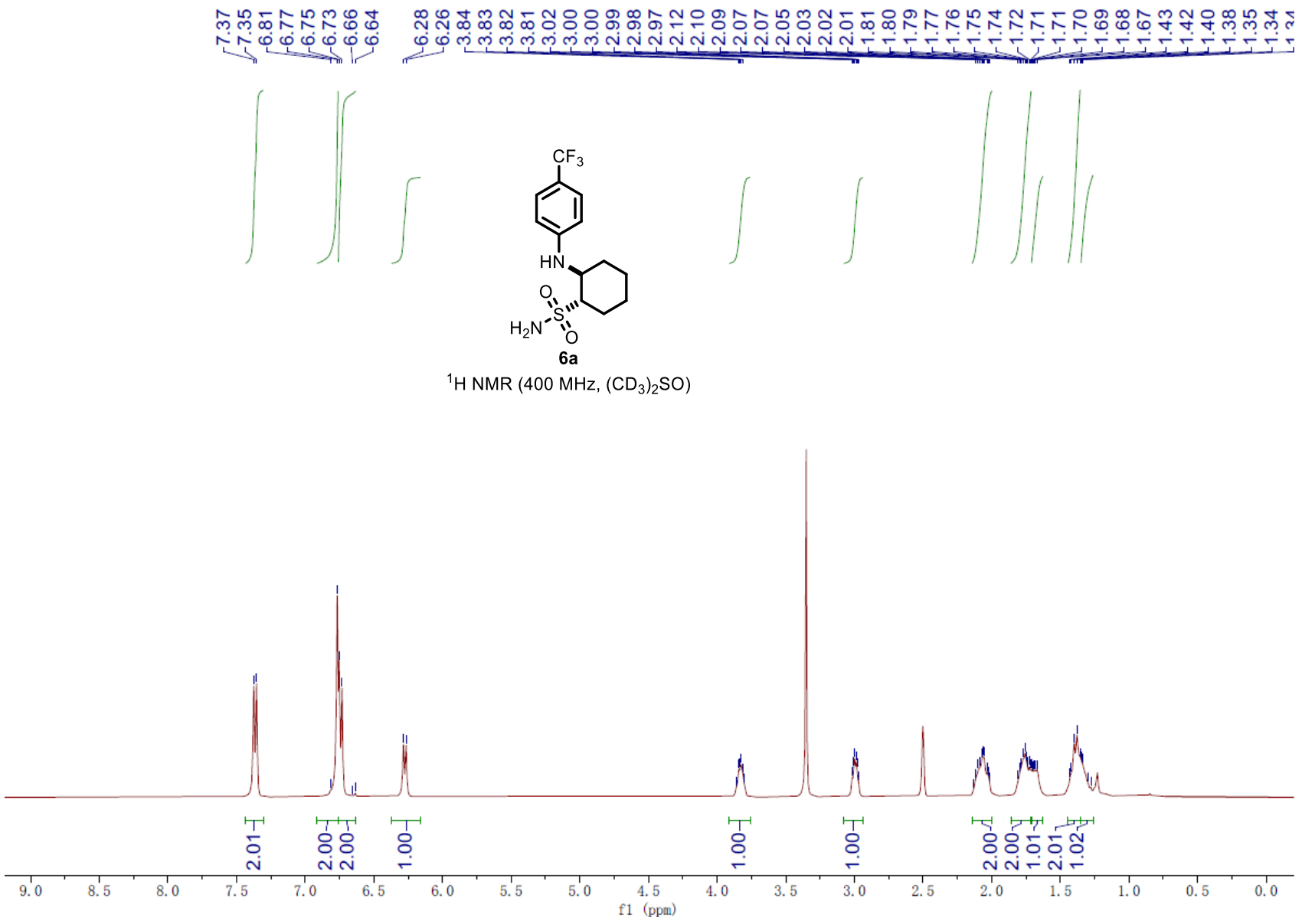
5w

^{13}C NMR (101 MHz, $CDCl_3$)



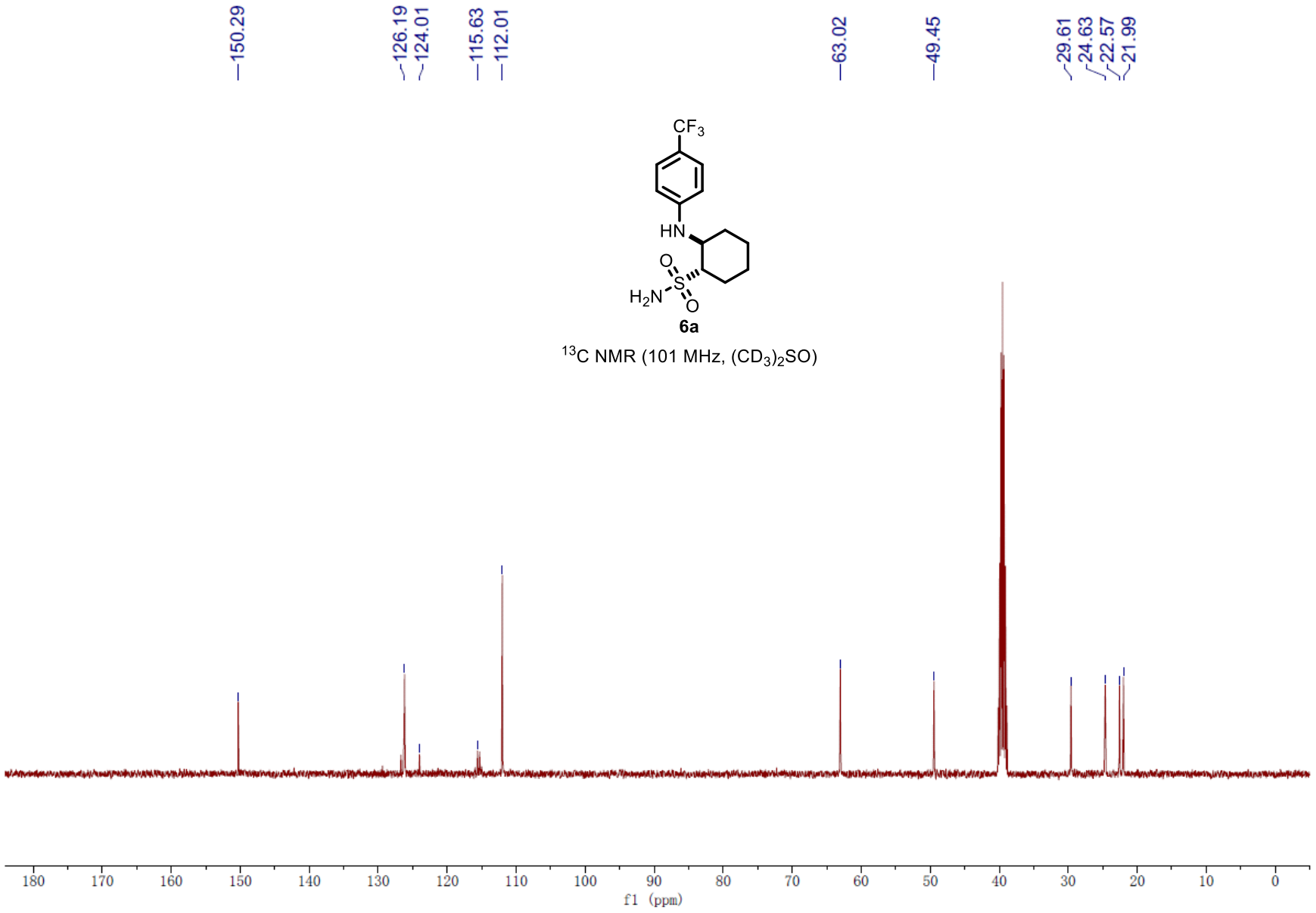
5w

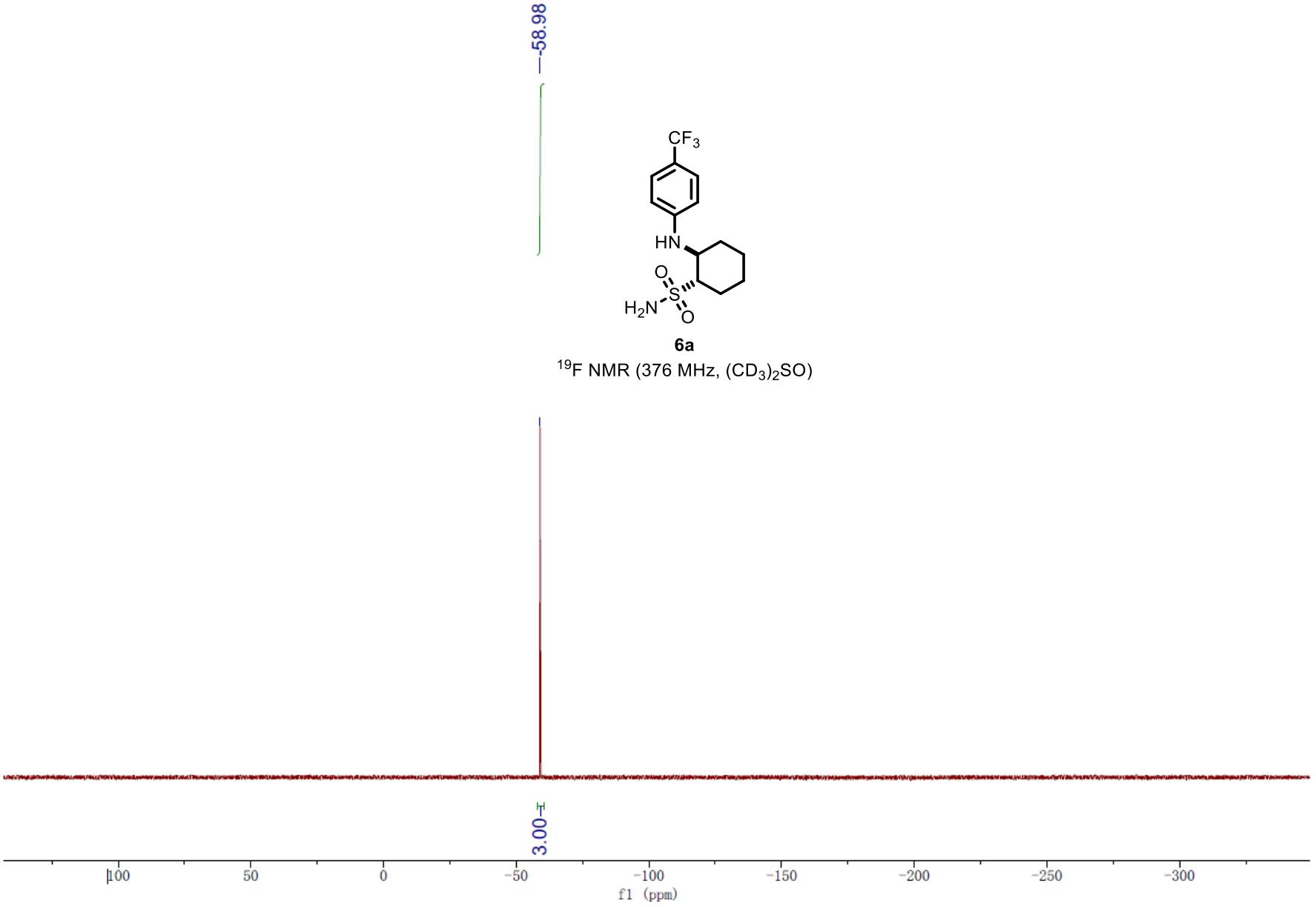
^{19}F NMR (376 MHz, $CDCl_3$)



6a

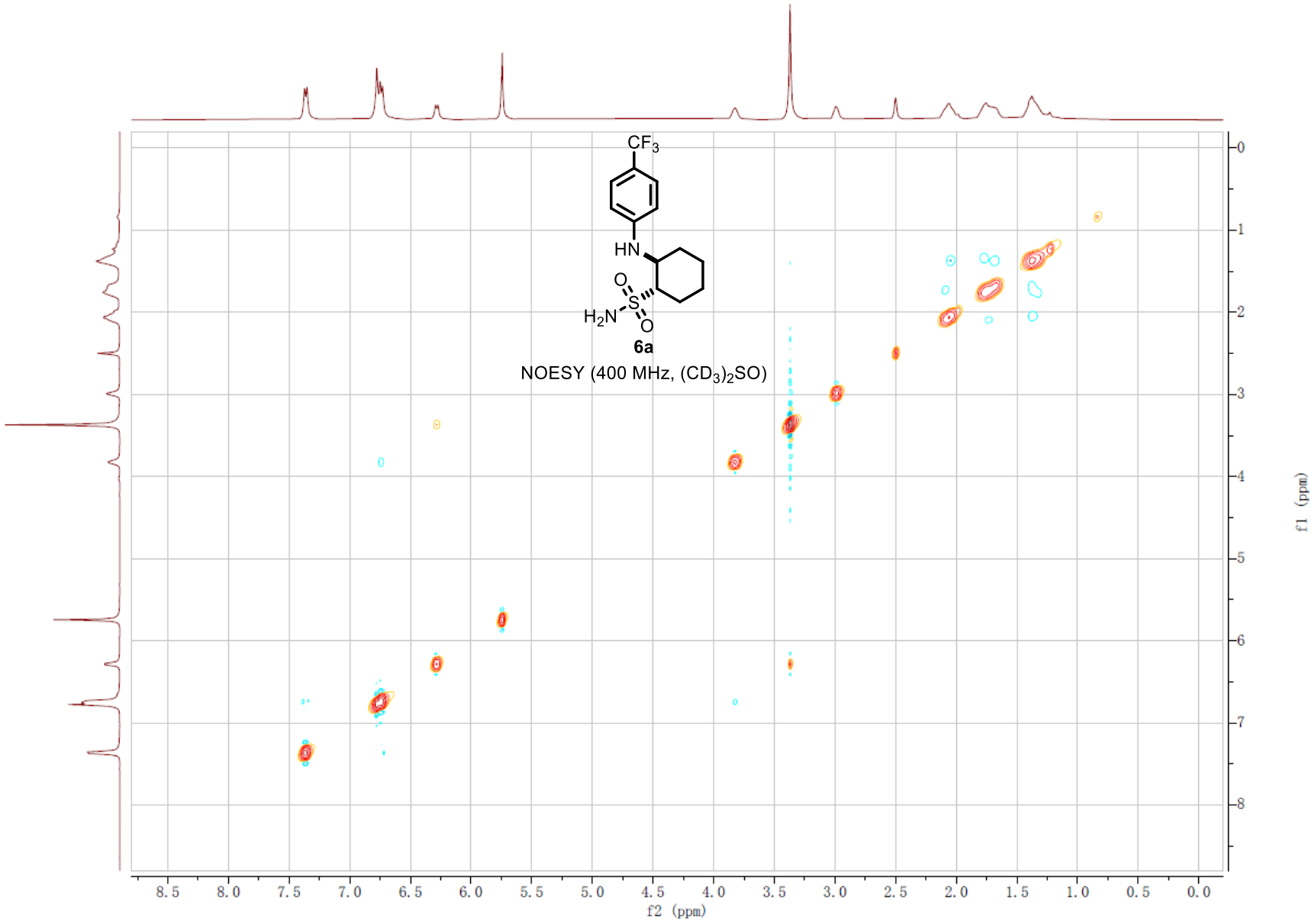
^{1}H NMR (400 MHz, $(CD_3)_2SO$)

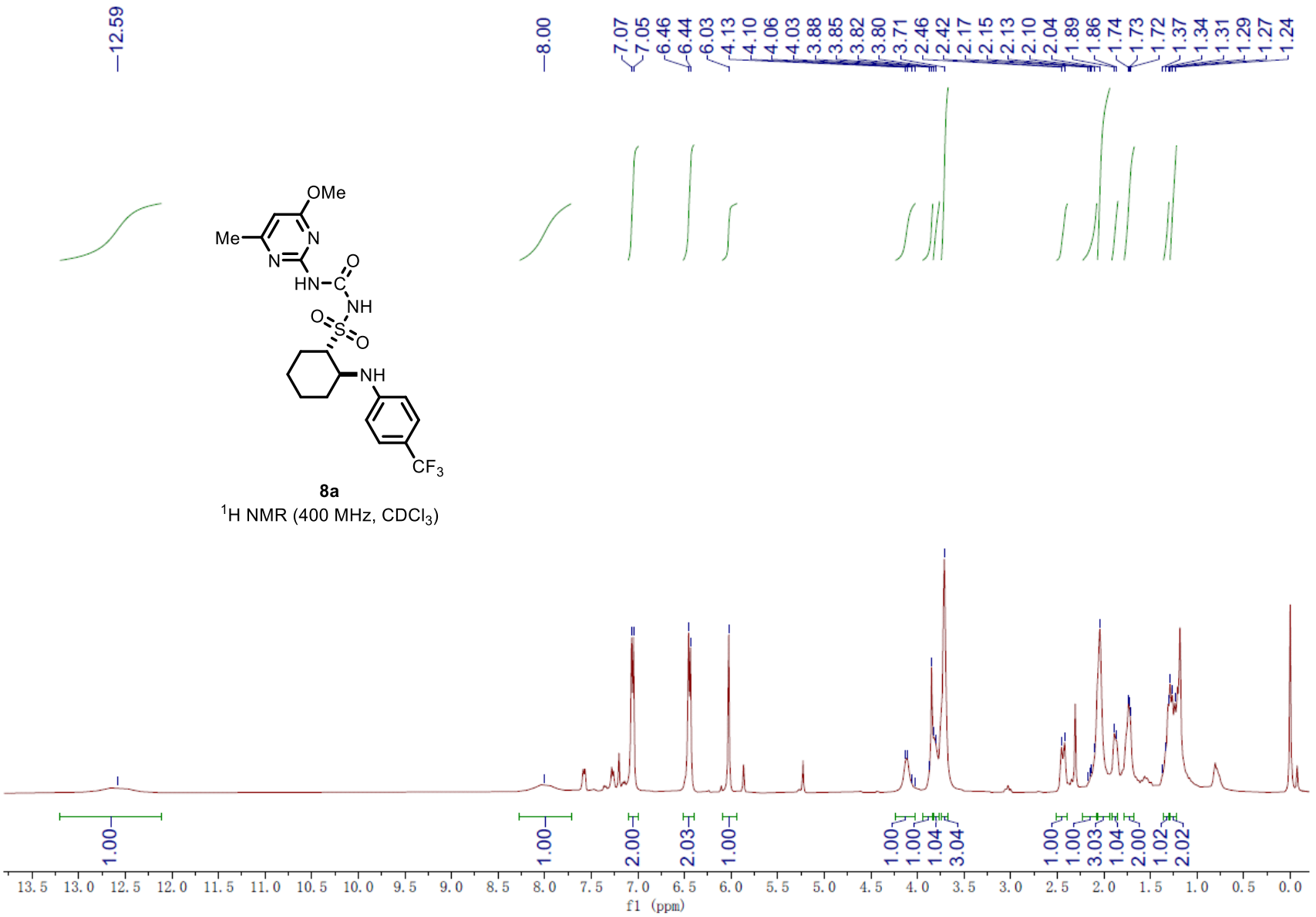

150.29
126.19
124.01
115.63
112.01
63.02
49.45
29.61
24.63
22.57
21.99
CF3
HN
O
S
H2N
O
6a
13C NMR (101 MHz, (CD3)2SO)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



6a

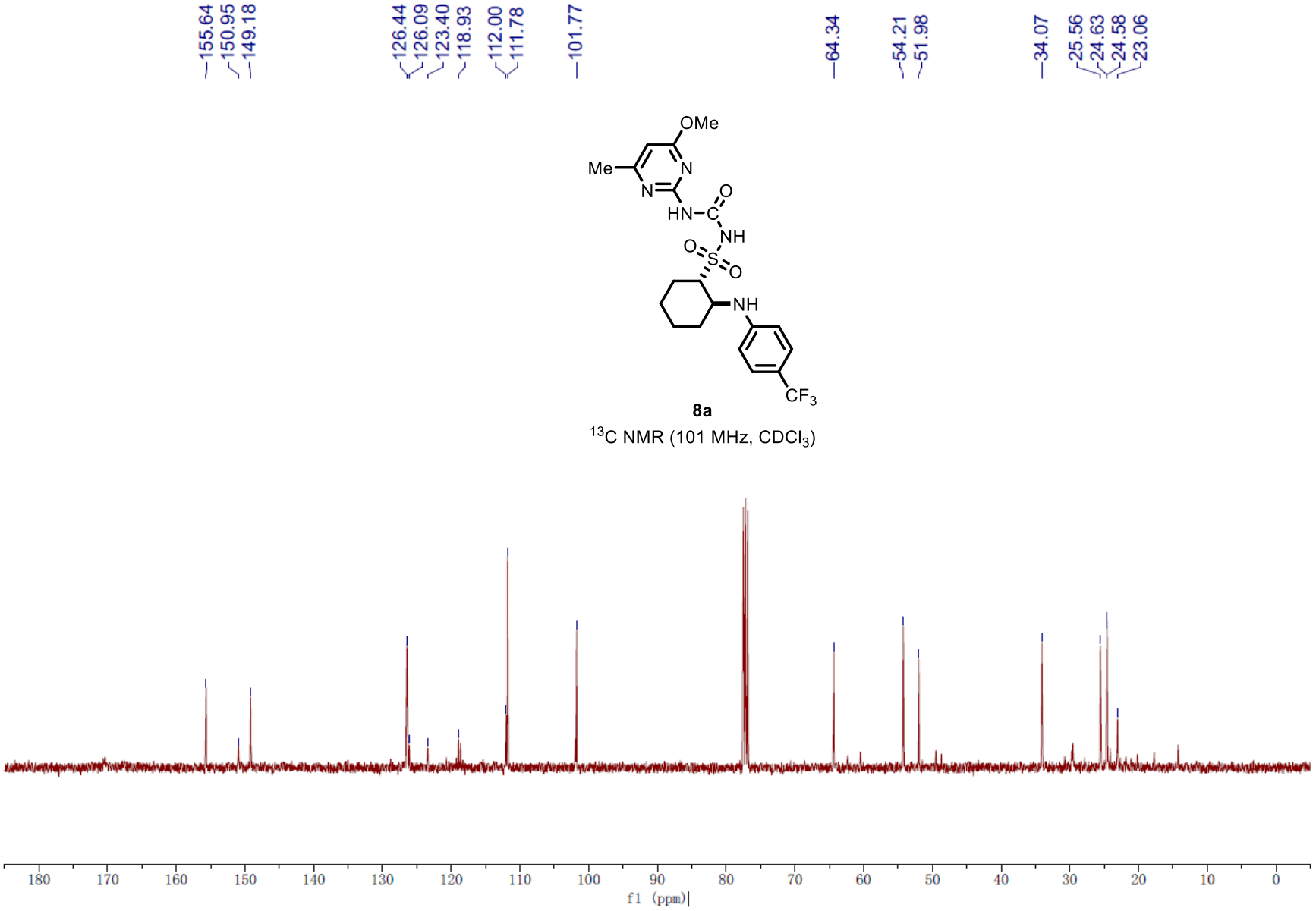
^{19}F NMR (376 MHz, $(CD_3)_2SO$)


CF3
HN
O
S
H2N
O
6a
NOESY (400 MHz, (CD3)2SO)
f2 (ppm)
f1 (ppm)



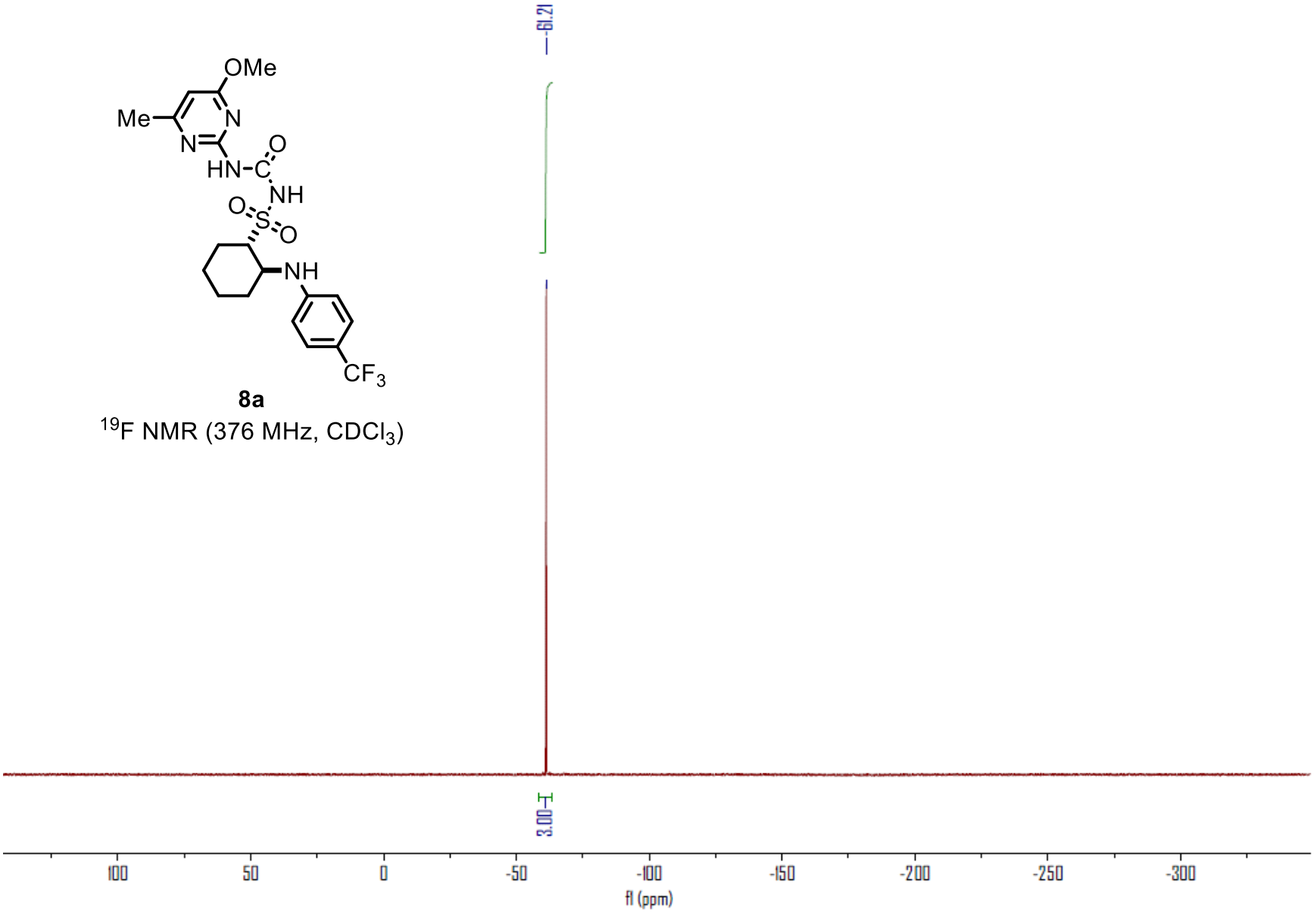
8a

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



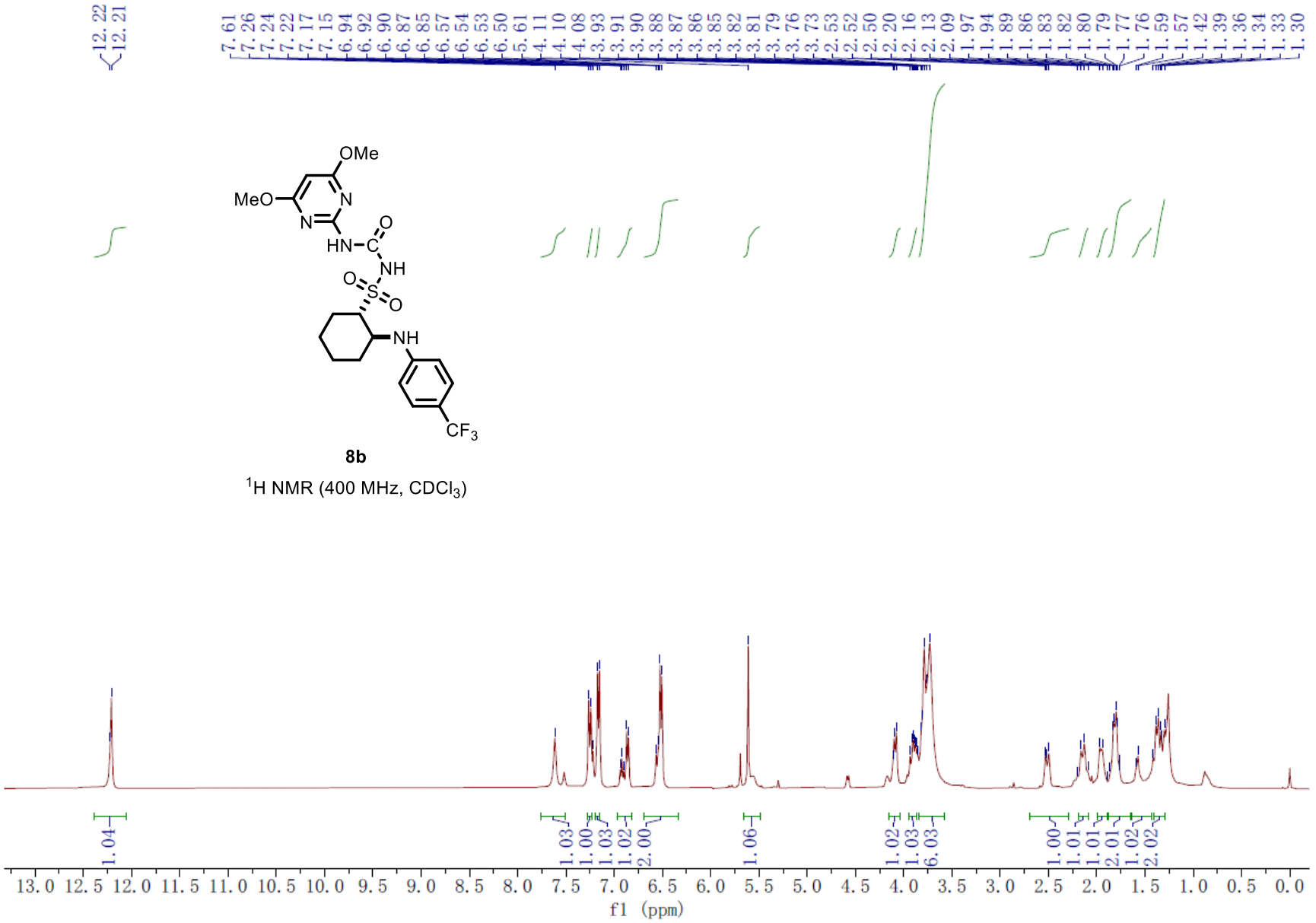
8a

^{13}C NMR (101 MHz, $CDCl_3$)



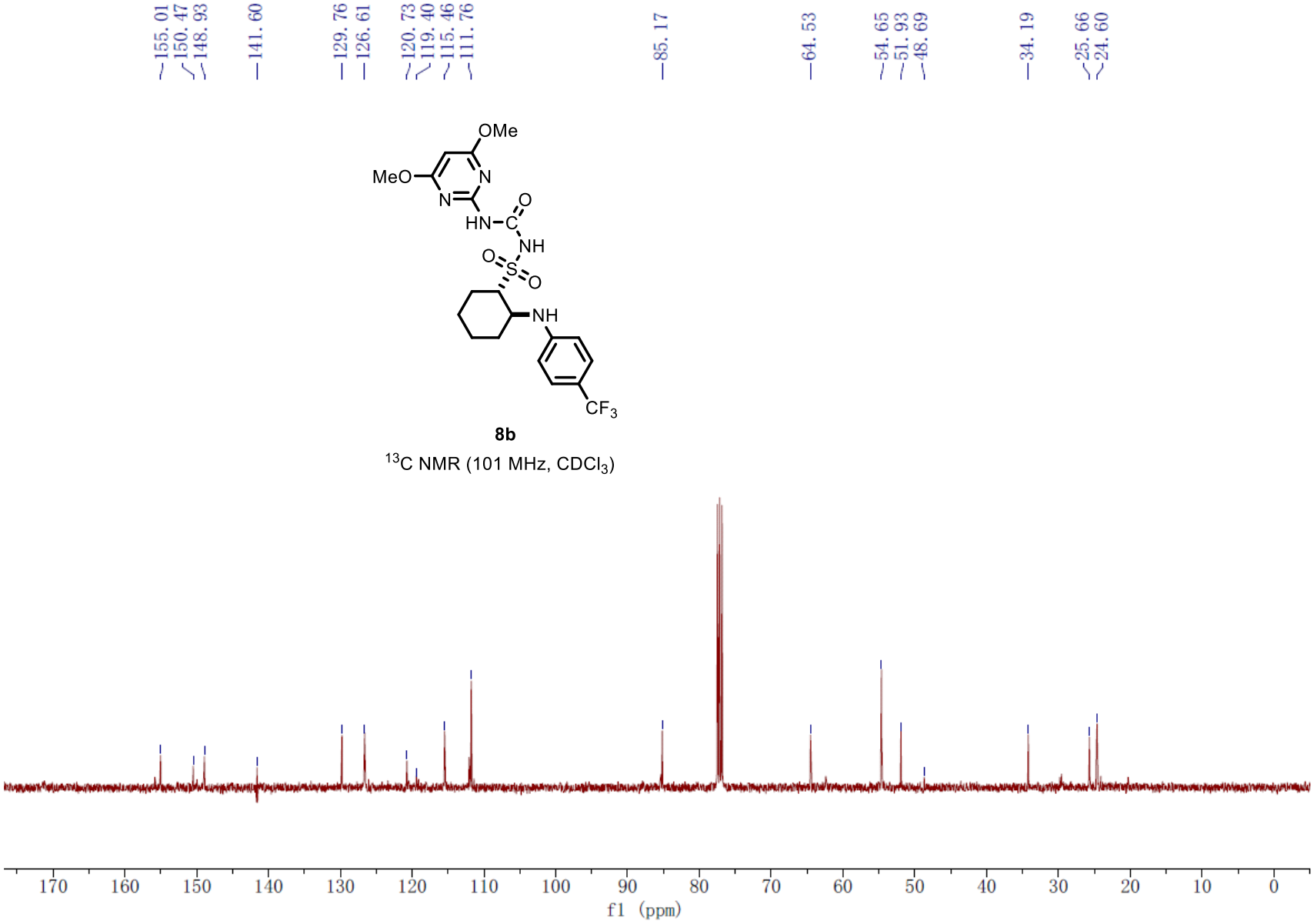
8a

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



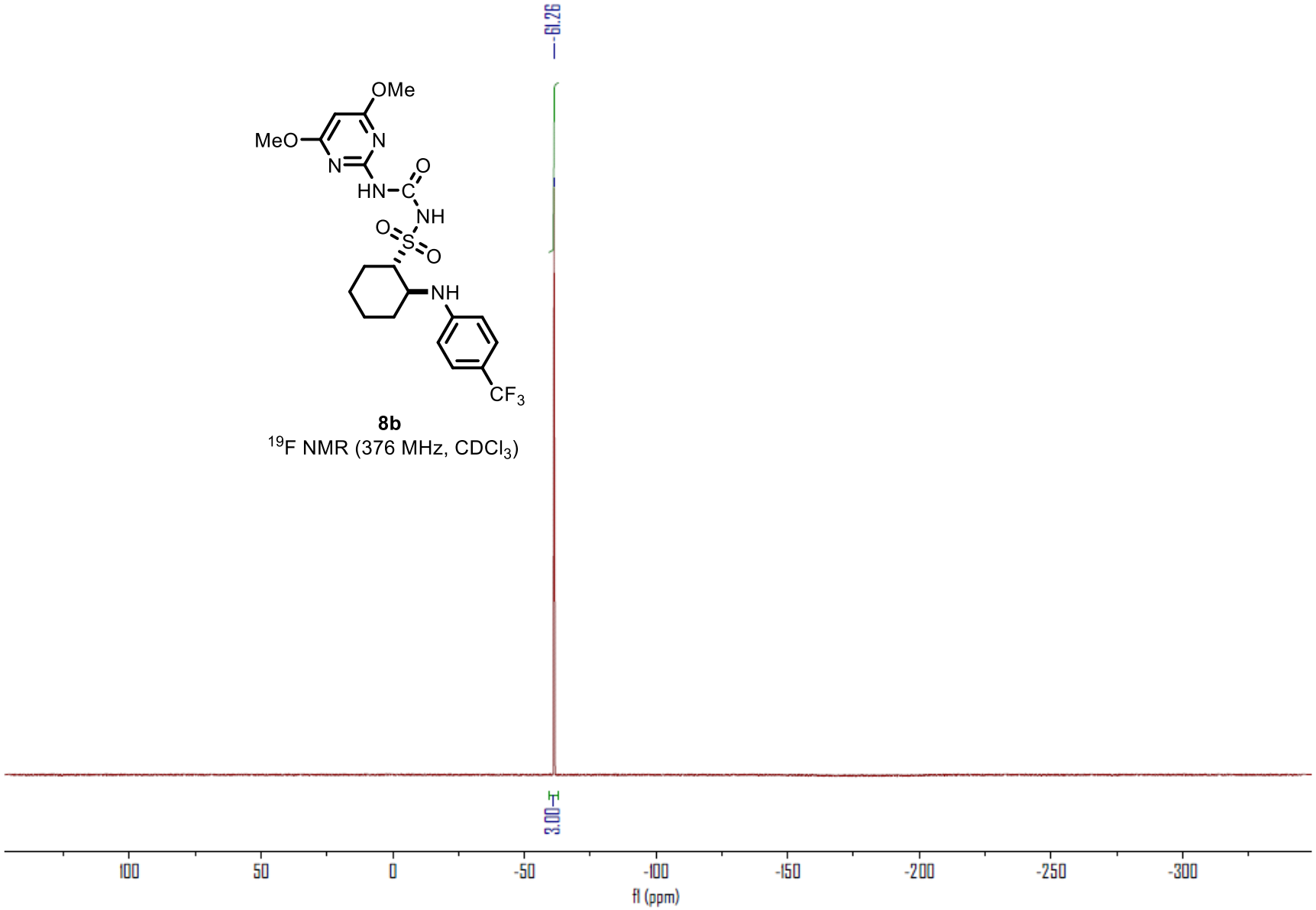
8b

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



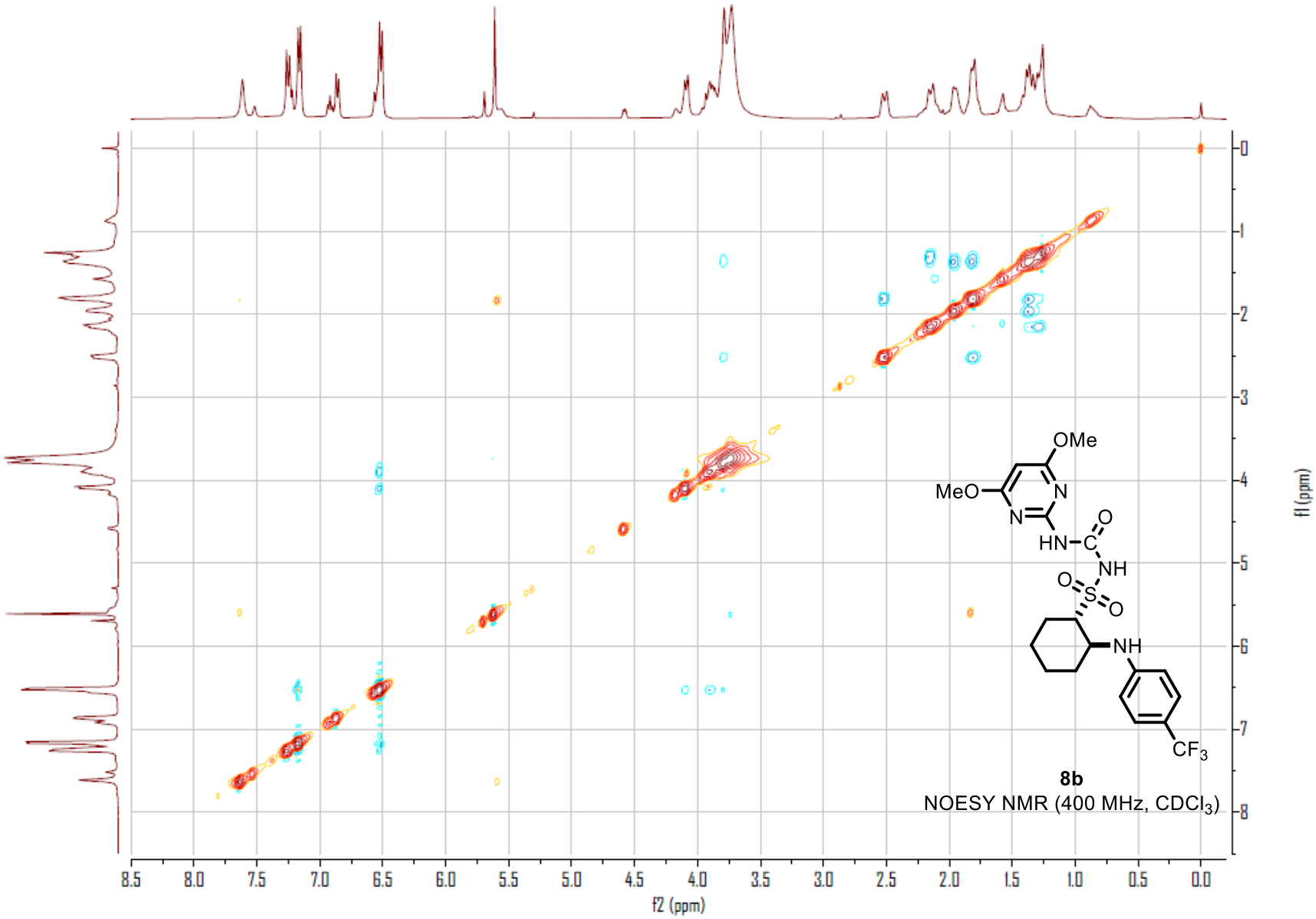
8b

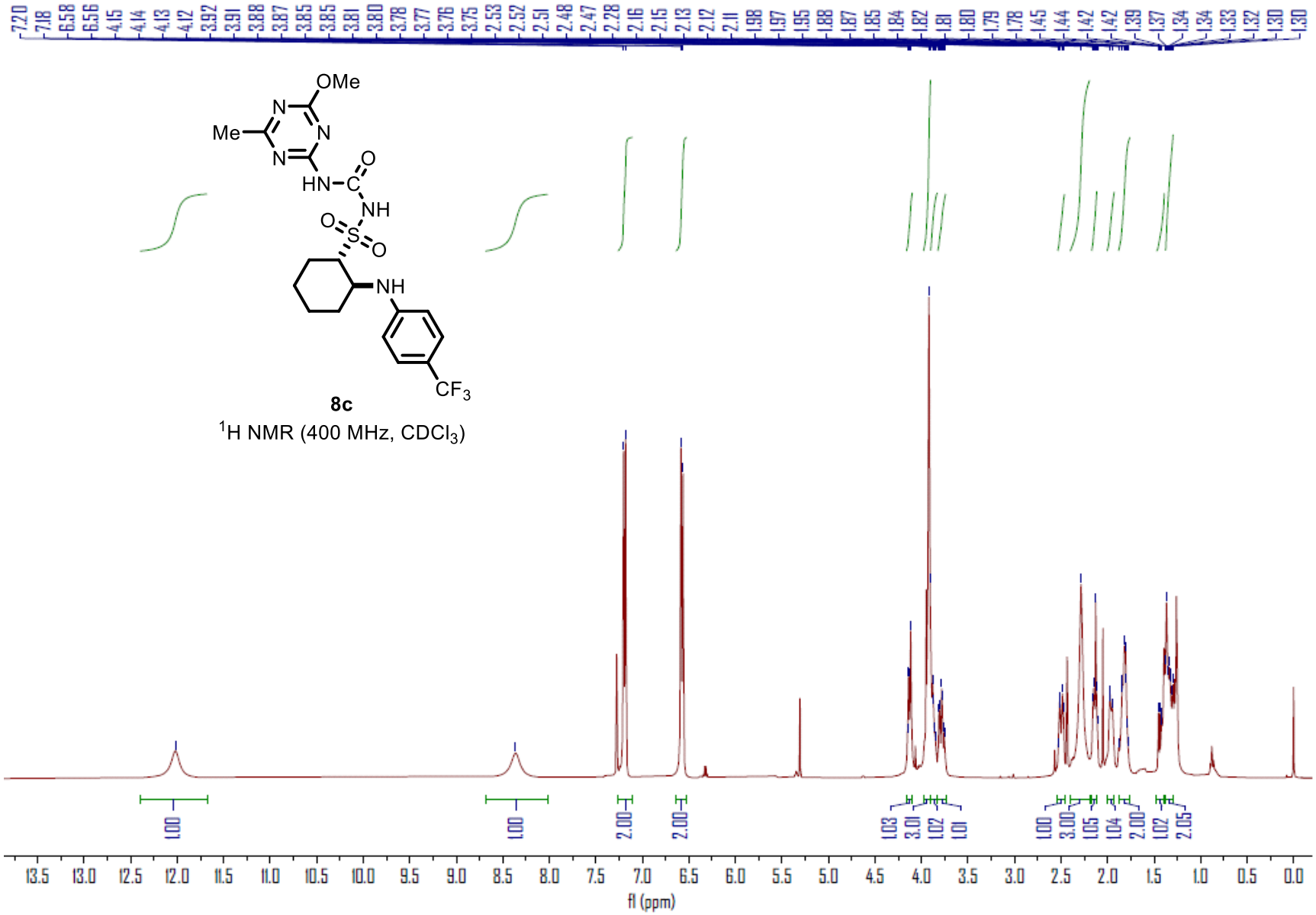
^{13}C NMR (101 MHz, $CDCl_3$)

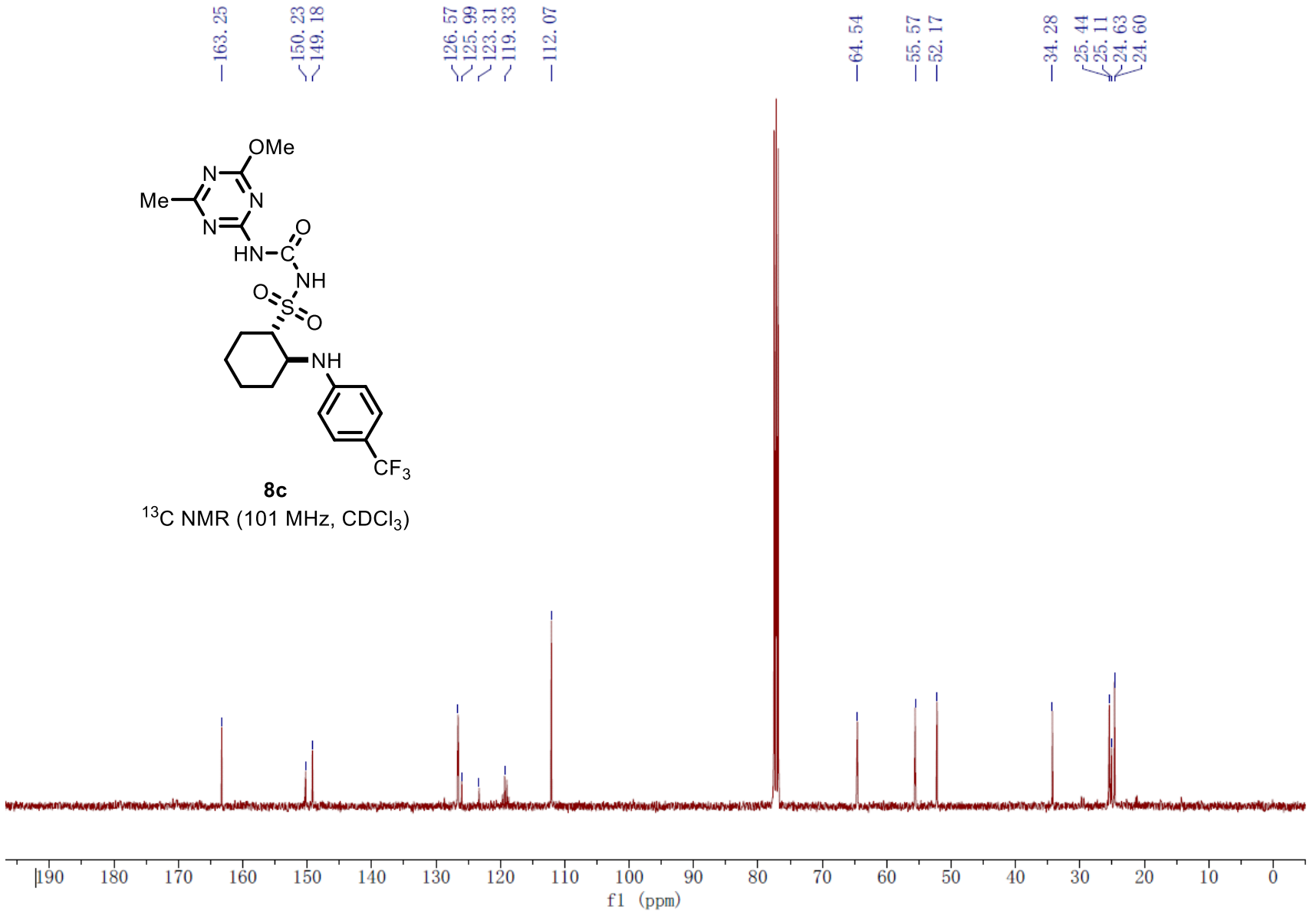


8b

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

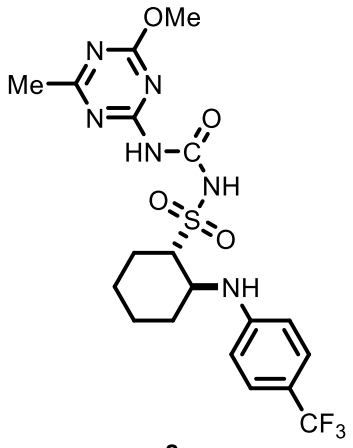

OMe
MeO
N
N
HN
C
O
NH
O
S
O
NH
CF3
8b
NOESY NMR (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8


OMe
N
Me
N
N
HN
C
O
NH
O
S
O
NH
CF3
8c
1H NMR (400 MHz, CDCl3)
fl (ppm)



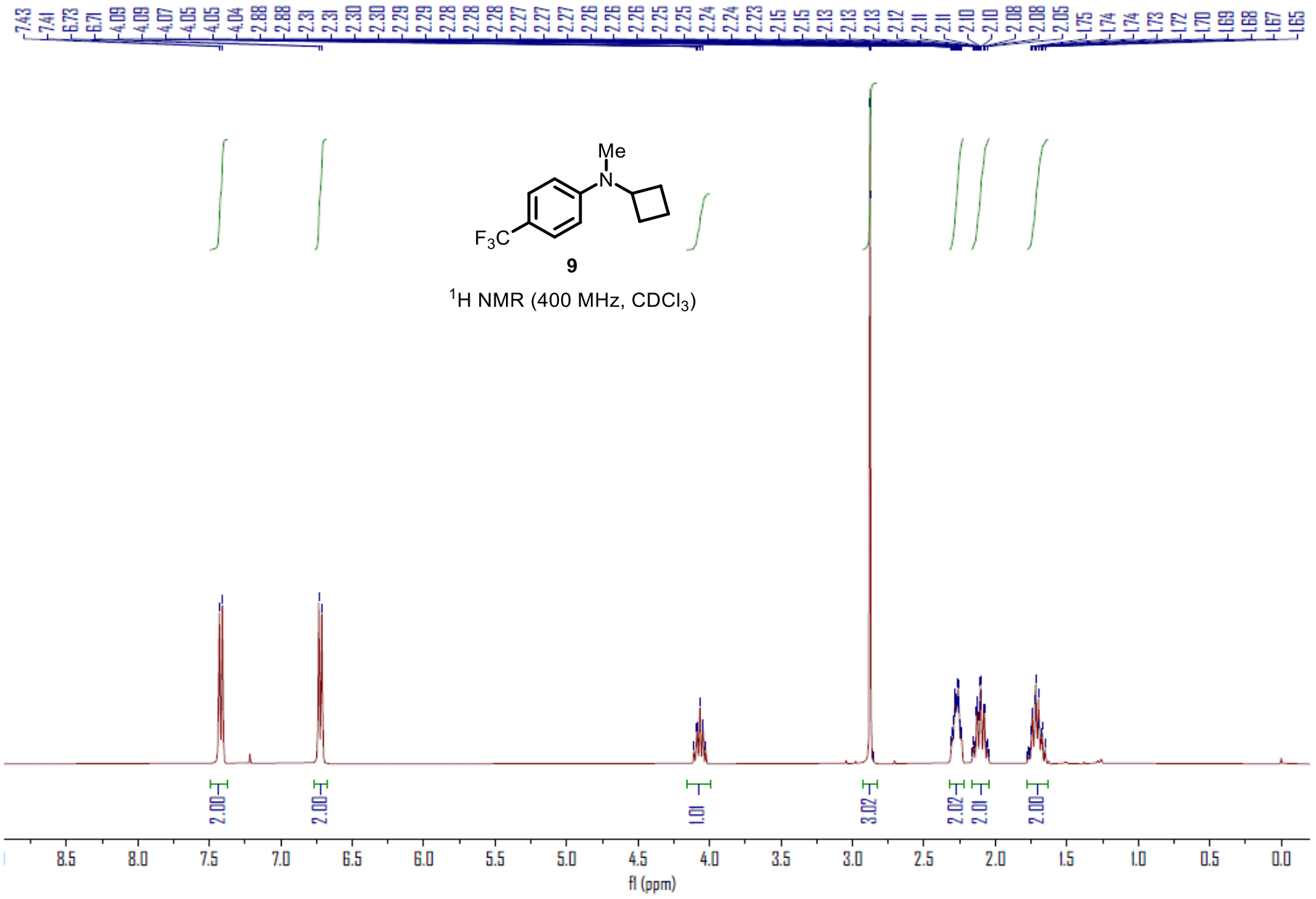
8c

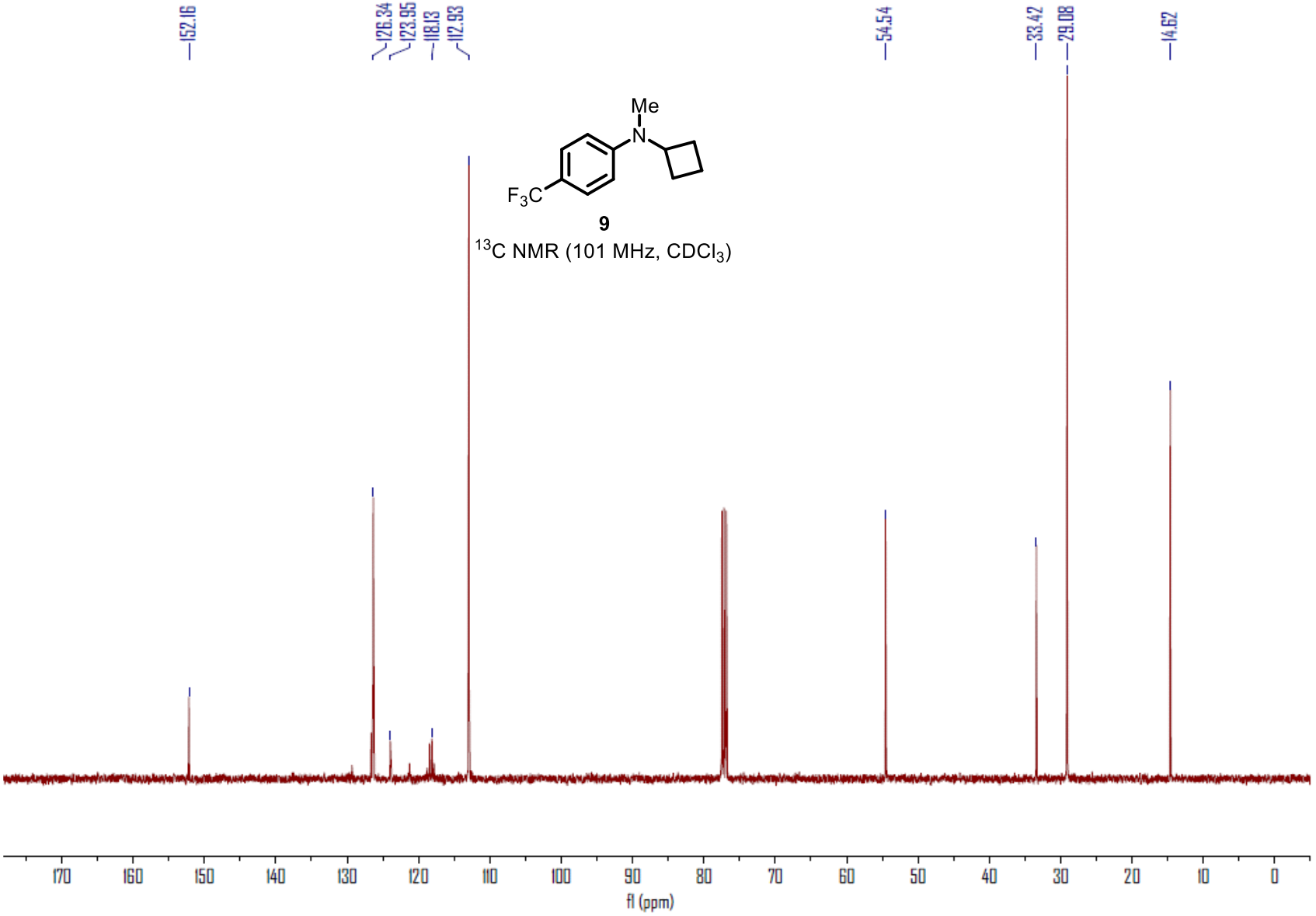
^{13}C NMR (101 MHz, $CDCl_3$)

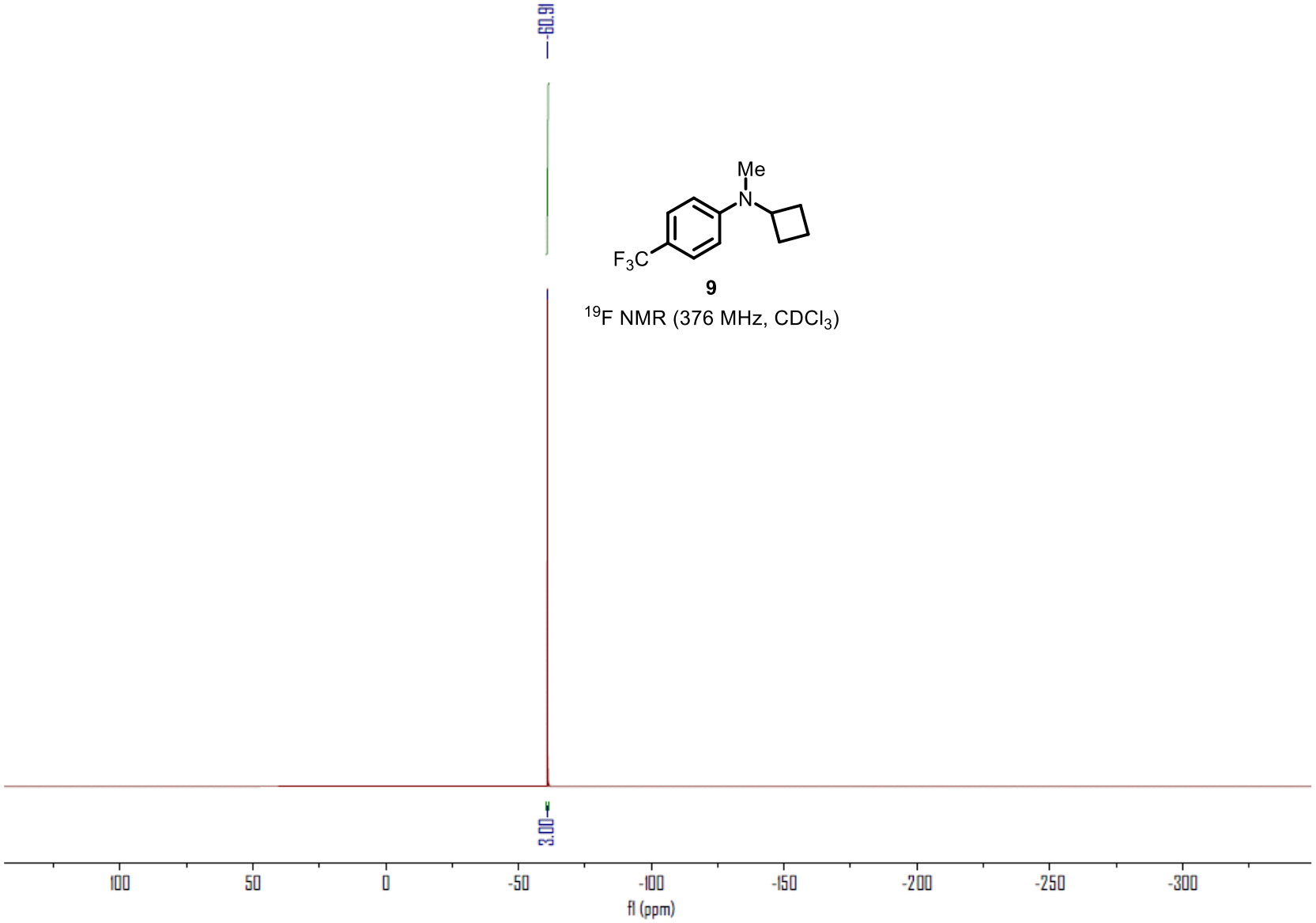


8c

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


Me
N
F3C
9
1H NMR (400 MHz, CDCl3)
2.00
2.00
1.01
3.02
2.02
2.01
2.00
f1 (ppm)


152.16
126.34
123.95
118.13
112.93
54.54
33.42
29.08
14.62
Me
N
F3C
9
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



9

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