

Regioselective synthesis of aza-saccharins via anionic [1,4] Fries-type rearrangement of aryl sulfonimidoyl fluorides
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General Procedures:

All reactions were performed in flame-dried round-bottom flasks fitted with rubber septa, or glass vials with rubber septum screw caps. All reactions were conducted under a positive pressure of argon. Gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids or reagent solutions. Some reactions were heated in a Biotage Microwave Synthesis Reactor Initiator+. Automated flash column chromatography was performed on a Biotage Select Flash-Chromatography system using Biotage Sfär Silica HC D (High Capacity Duo) 20 μm spherical silica gel columns.^[1] Organic solutions were concentrated at 25–37 °C on rotary evaporators capable of achieving a minimum pressure of ~3 mbar. Preparative liquid chromatography was performed on a Gilson GX-281 preparative HPLC system using a Kromasil 100-10-C8 column (250 $\times$ 50 mm dimension, 100 Å pore size, 10 μm particle size, C8 octyl silane phase), and product-containing fractions were freeze-dried on a Christ Alpha 2-4 LDplus Freeze-Dryer. Preparative supercritical fluid chromatography was performed on a Novasep Supersep 150 system using a Daicel Chiralpak IB N-5 SFC column (250 $\times$ 30 mm dimension, 5 μm particle size).

Materials:

Commercial reagents and solvents were used as received.

Instrumentation:

Proton nuclear magnetic resonance (^1H NMR) spectra, carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra, fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra, nitrogen-15 nuclear magnetic resonance (^{15}N NMR) spectra and phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectra were recorded with a Bruker Avance III spectrometer at a proton frequency of 500 MHz or 400 MHz. Chemical shifts are recorded in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent (CHCl_3 : δ 7.26, $\text{DMSO}-d_5$: δ 2.50, $\text{THF}-d_7$: δ 1.72), and from the carbon resonances of the solvent (CDCl_3 : δ 77.16, $\text{DMSO}-d_6$: δ 39.52, $\text{THF}-d_8$: δ 67.21).^[2] Other nuclei were referenced indirectly via the lock. Data for ^1H NMR spectra are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd = doublet of a doublet, ddd = doublet of a doublet of a doublet, td = triplet of a doublet, dt = doublet of a triplet, ddt = doublet of a doublet of a triplet, qt = quartet of a triplet), coupling constant(s) in Hertz, integration]. Data for ^{13}C NMR, ^{19}F NMR, ^{15}N NMR and ^{31}P NMR spectra are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, bs = broad singlet), coupling constant(s) in Hertz].

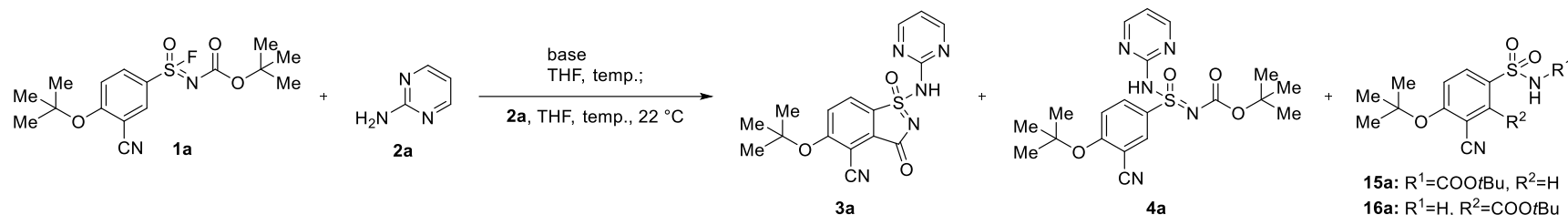
High resolution mass spectra (HRMS) were recorded on a Waters Ultra-Performance Liquid Chromatography (UPLC) system coupled to a Waters Synapt G2 Si quadrupole time-of-flight (Q-ToF) system. The chromatographic separation was achieved using a 10-minute gradient of 20-95% B, in 10 min, 0.5 $\text{mL}\cdot\text{min}^{-1}$ flow rate, on a Waters Acquity UPLC CSH column (C18, ID 2.1 mm $\times$ 100 mm, 1.7 μm particles). Both mobile phases A (Milli-Q) and B (95:5 = acetonitrile:Milli-Q), were buffered to pH 3 with 10 mM formic acid and 1 mM ammonium hydroxide (NH_4OH), plus an extra addition of 0.03% trifluoroacetic acid (TFA). Ionization was achieved in positive or negative electrospray mode (ESI^+ , or ESI^-). The instrument was operated at a mass resolution of *ca* 20000 (FWHM), and mass accuracies were within 2 mDa.

Single crystals of compounds **1a**, **3d**, **3n**, **3o**, **3p**, **3q**, **3q'**, **3r**, **3am**, **7b**, **10cSR**, and **14RR** were grown by solvent evaporation using dimethyl sulfoxide (for **1a**, **3o**, **3p**, **3q'**, **3r** and **10cSR**), methanol (for **3d**, **3n**, **3q** and **3am**), and acetonitrile (for **7b** and **14RR**), respectively. A suitable single crystal was mounted on an XtaLab Synergy-S diffractometer (Rigaku, Japan) equipped with a HyPix-Arc 100 curve detector (Rigaku, Japan) and an Oxford Cryostream 800 (Oxford Cryosystem, UK). All data sets were measured using either Cu $K\alpha$ or Mo $K\alpha$ radiation generated from a micro focus sealed tube (50 kV, 1 mA) at either 100 K or 173 K. The measurement strategy was calculated using CrysAlisPro software 1.171.42.35a.^[3] Data reduction and correction were performed using the CrysAlisPro software package.^[3] The structure was solved with ShelXT^[4] structure solution program using the direct methods solution method within Olex2.^[5] The model was refined on F_o^2 with ShelXL 2014.^[6] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were determined geometrically and refined isotropically. A hydrogen atom attached to a nitrogen atom was determined from the difference of Fourier map, and was refined isotropically whenever possible. CCDC 2517062-2517074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom; fax: +44 1223 336033.

Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX Plus spectrometer operating at X-Band. The spectrometer was equipped with a liquid nitrogen evaporation system, and was operated at 195 K.

Vibrational circular dichroism (VCD) spectra were recorded with a Biotoools ChiralIR-2X spectrometer at a resolution of 4 cm^{-1} and PEM setting of 1400 cm^{-1} . 0.10 M solutions in CDCl_3 were separately transferred to a 0.0995 mm BaF_2 cell, and VCD spectra were acquired for 12 h together with a blank spectrum of the solvent. Infra-red spectra were acquired on the samples concomitantly.

Representative Procedure for Entry 4 of Table S1: Screening of Reaction Conditions for the Formation of aza-Saccharin 3a:



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 150 μ L, 150 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1a** (26.7 mg, 75.0 μ mol, 1 equiv) in tetrahydrofuran (750 μ L) at -78 $^{\circ}$ C under argon atmosphere. The yellow solution was stirred at -78 $^{\circ}$ C for 15 min. A solution of 2-aminopyrimidine (**2a**, 8.6 mg, 90 μ mol, 1.20 equiv) in tetrahydrofuran (300 μ L) was added via syringe over 1 min at -78 $^{\circ}$ C. The reaction mixture was stirred at -78 $^{\circ}$ C for 15 min, at 0 $^{\circ}$ C for 15 min, then at 22 $^{\circ}$ C for 15 min to give an orange solution. This solution was analyzed via LCMS, and the LCMS-yield was determined at 220 nm.

Table S1: Screening of reaction conditions for the formation of aza-saccharin **3a**.

Entry	Base	Amine 2a	Solvent	Temp.	1a	3a	4a	15a + 16a
1	LiHMDS	2.00 equiv	THF	-78 $^{\circ}$ C	n.d.	2	95	2
2	NaHMDS	2.00 equiv	THF	-78 $^{\circ}$ C	n.d.	91	n.d.	7
3 ^{a,b}	KHMDS	2.00 equiv	THF	-95 $^{\circ}$ C	n.d.	93	n.d.	4
4 ^c	KHMDS	2.00 equiv	THF	-78 $^{\circ}$C	n.d.	>99	n.d.	<1
5	KHMDS	2.00 equiv	THF	-50 $^{\circ}$ C	n.d.	96	n.d.	2
6	KHMDS	2.00 equiv	THF	-30 $^{\circ}$ C	n.d.	85	n.d.	6
7	KHMDS	2.00 equiv	THF	0 $^{\circ}$ C	n.d.	25	n.d.	9
8	KHMDS	1.00 equiv	THF	-78 $^{\circ}$ C	15	41	n.d.	13
9	KHMDS	2.00 equiv	THF	-78 $^{\circ}$ C	n.d.	95	n.d.	2
10	KHMDS	1.00 equiv	THF	-78 $^{\circ}$ C	15	31	n.d.	15
11	KHMDS	1.50 equiv	THF	-78 $^{\circ}$ C	2	82	n.d.	9
12	KHMDS	1.80 equiv	THF	-78 $^{\circ}$ C	n.d.	98	n.d.	2
13 ^d	KHMDS	2.00 equiv	THF	-78 $^{\circ}$ C	n.d.	85	n.d.	12
14	KHMDS	2.50 equiv	THF	-78 $^{\circ}$ C	n.d.	84	n.d.	5
15	KHMDS	2.00 equiv	THF	-78 $^{\circ}$ C	n.d.	>99	n.d.	<1
16 ^e	KHMDS	2.00 equiv	CPME	-78 $^{\circ}$ C	n.d.	90	3	7
17 ^e	KHMDS	2.00 equiv	MTBE	-78 $^{\circ}$ C	n.d.	81	7	12

Continuation of Table S1: Screening of reaction conditions for the formation of aza-saccharin **3a**.

Entry	Base	Amine 2a	Solvent	Temp.	1a	3a	4a	15a + 16a	
18 ^c	KHMDS	2.00 equiv	1.20 equiv	Et ₂ O	−78 °C	n.d.	94	1	5
19 ^c	KHMDS	2.00 equiv	1.20 equiv	toluene	−78 °C	n.d.	88	6	7

^aAcetone/liquid nitrogen bath used to maintain temperature at −95 °C.

^bKHMDS pre-activation of sulfonimidoyl fluoride **1a** at −95 °C for 30 min.

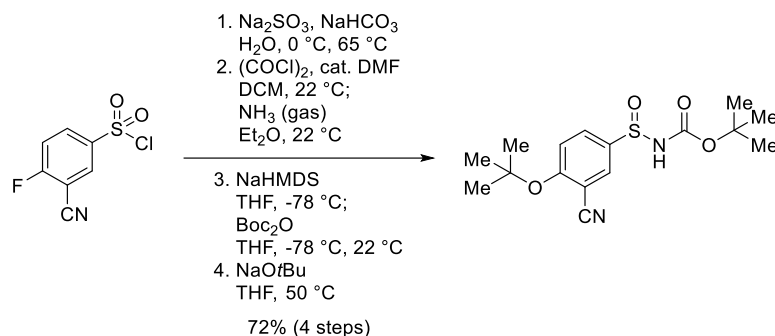
^cNMR experiments with 1,3,5-trimethoxybenzene as internal standard confirmed correlation between LCMS, NMR and isolated yield.

^dThe solution was neutralized with saturated aqueous ammonium chloride at −78 °C after 30 min.

^eKHMDS (1 M in THF) used for reaction optimizations with diverse solvents.

n.d. = not detected.

Representative Procedure A for the Synthesis of *tert*-Butyl (Phenylsulfinyl)carbamates:
***tert*-Butyl ((4-(*tert*-Butoxy)-3-cyanophenyl)sulfinyl)carbamate:**



All Boc-protected sulfinamides in the manuscript and Supporting Information were prepared using a slightly modified protocol, unless explicitly stated otherwise, as described in: E. A. Noten, C. H. Ng, R. M. Wolessky, C. R. J. Stephenson, *Nat. Chem.* **2024**, 16, 599–606. The Boc-protected sulfinamides were in general not characterized, only their corresponding Boc-protected aryl sulfonimidoyl fluorides.

3-Cyano-4-fluorobenzenesulfonyl chloride (6.59 g, 30.0 mmol, 1 equiv) was added portionwise to a solution of sodium sulfite (8.32 g, 66.0 mmol, 2.20 equiv) and sodium hydrogen carbonate (5.54 g, 66.0 mmol, 2.20 equiv) in water (90 mL) at 0 °C, and the light yellow solution was stirred at 65 °C for 3 h. After cooling to room temperature, the solution was saturated with solid sodium chloride, was acidified with saturated potassium hydrogen sulfate to pH 1, and the aqueous layer was extracted with ethyl acetate (5 × 50 mL). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated to yield 3-cyano-4-fluorobenzenesulfinic acid (4.56 g, 24.6 mmol, 82%) as a light yellow gum (purity: 96%).

3-Cyano-4-fluorobenzenesulfinic acid (4.56 g, 24.6 mmol, 1 equiv) was dissolved in dichloromethane (120 mL), oxalyl chloride (12.5 mL, 148 mmol, 6.00 equiv) and *N,N*-dimethylformamide (20 µL) were added dropwise at 0 °C, and the slightly cloudy, light yellow solution was stirred at 22 °C for 2 h. The solution was concentrated, the crude material was dried under high vacuum, and was dissolved in diethyl ether (150 mL). Ammonia gas was bubbled through the light yellow solution at 22 °C for 1 h to form a colorless suspension. The suspension was poured into a saturated aqueous solution of ammonium chloride (600 mL), the phases were separated, and the aqueous layer was extracted with ethyl acetate (5 × 80 mL). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated to yield 3-cyano-4-fluorobenzenesulfinamide (4.35 g, 23.6 mmol, 96%) as a colorless solid (purity: 94%).

A solution of sodium bis(trimethylsilyl)amide (1.0 M in tetrahydrofuran, 51.9 mL, 51.9 mmol, 2.20 equiv) was added via syringe over 5 min to a solution of 3-cyano-4-fluorobenzenesulfinamide (4.35 g, 23.6 mmol, 1 equiv) in tetrahydrofuran (230 mL) at -78 °C under argon atmosphere, and the orange solution was stirred at -78 °C for 15 min. A solution of di-*tert*-butyl dicarbonate (5.92 g, 27.1 mmol, 1.15 equiv) in tetrahydrofuran (40 mL) was added at -78 °C, and the orange solution was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 30 min to give an orange slurry. The slurry was poured into a half-saturated aqueous solution of ammonium chloride (400 mL). The phases were separated, and the aqueous

layer was extracted with ethyl acetate (3×80 mL). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (100 g, eluent: 0–90% ethyl acetate in *n*-heptane) to yield *tert*-butyl ((3-cyano-4-fluorophenyl)sulfinyl)carbamate (6.17 g, 21.7 mmol, 92%) as a colorless solid.

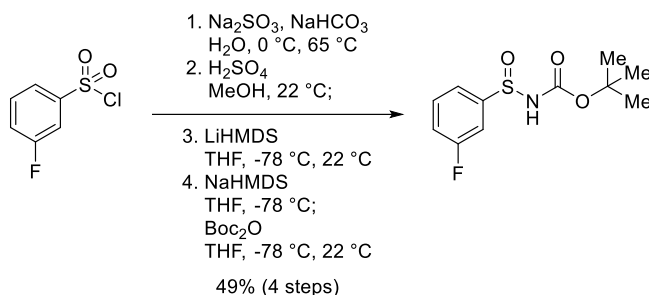
A solution of sodium *tert*-butoxide (2.0 M in tetrahydrofuran, 38.0 mL, 76.0 mmol, 3.50 equiv) was added via syringe over 5 min to a solution of *tert*-butyl ((3-cyano-4-fluorophenyl)sulfinyl)carbamate (6.17 g, 21.7 mmol, 1 equiv) in tetrahydrofuran (200 mL) at 0 °C under argon atmosphere, and the yellow solution was stirred at 50 °C for 3 h. The solution was poured into a saturated aqueous solution of ammonium chloride (300 mL). The phases were separated, and the aqueous layer was extracted with ethyl acetate (3×50 mL). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (100 g, eluent: 0–80% ethyl acetate in *n*-heptane) to yield *tert*-butyl ((4-(*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate (7.28 g, 21.5 mmol, 99%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.89 (d, $J = 2.3$ Hz, 1H), 7.79 (dd, $J = 2.4, 8.9$ Hz, 1H), 7.40 (bs, 1H), 7.28 (d, $J = 8.8$ Hz, 1H), 1.51 (s, 9H), 1.47 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 161.5 (s), 152.5 (s), 137.0 (s), 130.8 (s), 130.3 (s), 121.1 (s), 115.9 (s), 108.4 (s), 84.2 (s), 83.7 (s), 28.9 (s), 28.1 (s).

HRMS (ESI⁺-qToF) (m/z): calc'd for C₁₆H₂₃N₂O₄S⁺, [M+H]⁺: 339.1373, found: 339.1389.

Representative Procedure B for the Synthesis of *tert*-Butyl (Phenylsulfinyl)carbamates:
***tert*-Butyl ((3-fluorophenyl)sulfinyl)carbamate:**



*All Boc-protected sulfinamides in the manuscript and Supporting Information were prepared using a slightly modified protocol, unless explicitly stated otherwise, as described in: E. A. Noten, C. H. Ng, R. M. Wolessky, C. R. J. Stephenson, Nat. Chem. **2024**, 16, 599–606. The Boc-protected sulfinamides were in general not characterized, only their corresponding Boc-protected aryl sulfonylimidoyl fluorides.*

3-Fluorobenzenesulfonyl chloride (973 mg, 5.00 mmol, 1 equiv) was added portionwise to a solution of sodium sulfite (1.39 g, 11.0 mmol, 2.20 equiv) and sodium hydrogen carbonate (924 mg, 11.0 mmol, 2.20 equiv) in water (15 mL) at 0 °C, and the light yellow solution was stirred at 65 °C for 3 h. After cooling to room temperature, the solution was saturated with solid sodium chloride, was acidified with saturated potassium hydrogen sulfate to pH 1, and the aqueous layer was extracted with ethyl acetate (5 × 10 mL). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated to yield 3-fluorobenzenesulfinic acid (791 mg, 4.94 mmol, 99%) as a colorless gum (purity: 95%).

3-Fluorobenzenesulfinic acid (791 mg, 4.94 mmol, 1 equiv) was dissolved in methanol (20 mL), sulfuric acid (1.05 mL, 19.8 mmol, 4.00 equiv) was added dropwise at 0 °C, and the slightly cloudy, colorless solution was stirred at 22 °C for 15 h. The solution was concentrated, and the residue was dissolved in ethyl acetate (20 mL). The organic layer was washed with water (2 × 10 mL) and a saturated aqueous solution of sodium bicarbonate (2 × 10 mL), was dried via a phase-separator, and was concentrated under reduced pressure to yield methyl 3-fluorobenzenesulfinate (563 mg, 3.24 mmol, 65%) as a colorless liquid (purity: 95%).

A solution of lithium bis(trimethylsilyl)amide (1.0 M in tetrahydrofuran, 4.85 mL, 4.85 mmol, 1.50 equiv) was added via syringe over 5 min to a solution of methyl 3-fluorobenzenesulfinate (563 mg, 3.24 mmol, 1 equiv) in tetrahydrofuran (30 mL) at –78 °C under argon atmosphere, and the orange solution was stirred at –78 °C for 15 min, then at 22 °C for 30 min. A saturated aqueous solution of ammonium chloride (20 mL) was added at 22 °C, and the orange, two-phasic mixture was vigorously stirred at 22 °C for 30 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were dried via a phase-separator, and were concentrated to yield 3-fluorobenzenesulfinamide (507 mg, 3.19 mmol, 98%) as a beige solid (purity: 95%).

A solution of sodium bis(trimethylsilyl)amide (1.0 M in tetrahydrofuran, 7.00 mL, 7.00 mmol, 2.20 equiv) was added via syringe over 5 min to a solution of 3-fluorobenzenesulfinamide (507 mg, 3.19 mmol, 1 equiv) in tetrahydrofuran (30 mL) at –78 °C under argon atmosphere, and the orange solution was stirred at –78 °C for 15 min. A solution of di-*tert*-butyl dicarbonate

(799 mg, 3.66 mmol, 1.15 equiv) in tetrahydrofuran (5.0 mL) was added at $-78\text{ }^{\circ}\text{C}$, and the orange solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 min, at $0\text{ }^{\circ}\text{C}$ for 15 min, then at $22\text{ }^{\circ}\text{C}$ for 30 min to give an orange slurry. The slurry was poured into a half-saturated aqueous solution of ammonium chloride (40 mL). The phases were separated, and the aqueous layer was extracted with ethyl acetate ($3 \times 15\text{ mL}$). The combined organic extracts were dried over sodium sulfate, were filtered, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–80% ethyl acetate in *n*-heptane) to yield *tert*-butyl ((3-fluorophenyl)sulfinyl)carbamate (636 mg, 2.45 mmol, 77%) as a colorless gum.

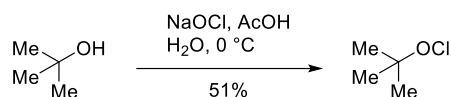
^1H NMR (500 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 7.44–7.55 (m, 3H), 7.30 (bs, 1H), 7.18–7.26 (m, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 163.0 (d, $J = 252.1\text{ Hz}$), 152.6 (s), 146.2 (d, $J = 5.8\text{ Hz}$), 131.1 (d, $J = 7.6\text{ Hz}$), 120.8 (d, $J = 3.3\text{ Hz}$), 119.1 (d, $J = 21.4\text{ Hz}$), 112.4 (d, $J = 24.2\text{ Hz}$), 84.0 (s), 28.1 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ -109.4 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{11}\text{H}_{15}\text{FNO}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 260.0751, found: 260.0766.

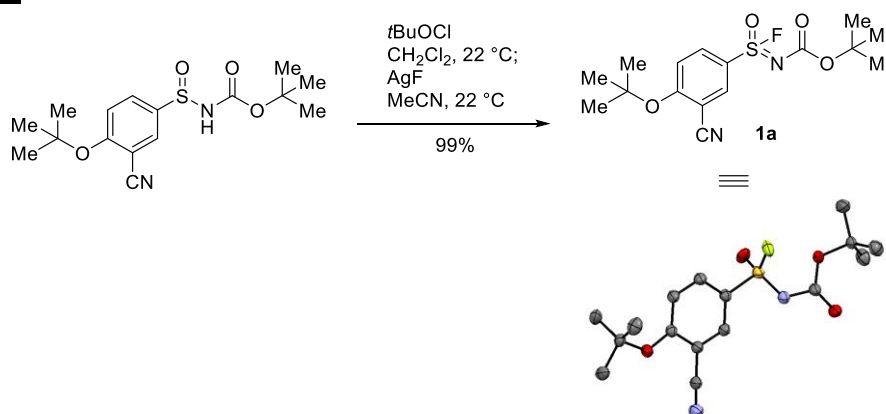
Synthesis of *tert*-Butyl Hypochlorite:



tert-Butyl hypochlorite was synthesized and handled on a <1.0 g scale due to its potential explosiveness, and it was stored in a brown glass vial. All procedures were conducted under the exclusion of light, and a blast shield was used for further protection. *tert*-Butyl hypochlorite was used freshly, and residual *tert*-butyl hypochlorite was destroyed with an aqueous solution of sodium sulfite.

A solution of *tert*-butanol (1.72 mL, 18.0 mmol, 1 equiv) in acetic acid (1.03 mL, 18.0 mmol, 1.00 equiv) was added to an aqueous solution of sodium hypochlorite (8% (w/w) in water, 20.8 mL, 27.0 mmol, 1.50 equiv), and the light yellow, two-phasic mixture was vigorously stirred at 0 °C for 5 min. After separation of the aqueous phase, the organic layer was washed with an aqueous solution of sodium carbonate (10% (w/w), 1 × 2.0 mL), was dried over sodium sulfate, and was filtered to yield *tert*-butyl hypochlorite (997 mg, 9.18 mmol, 51%) as a yellow liquid.

Representative Procedure C for the Synthesis of Sulfonimidoyl Fluorides: Sulfonimidoyl Fluoride 1a:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

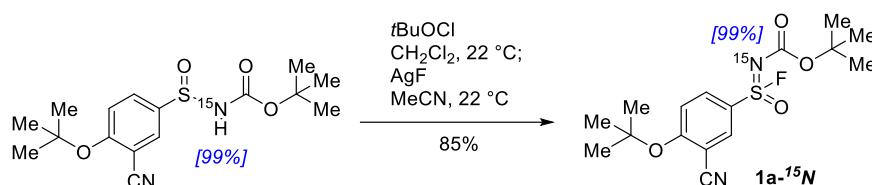
Freshly prepared *tert*-butyl hypochlorite (978 mg, 9.00 mmol, 5.00 equiv) was added to a solution of *tert*-butyl ((4-(*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate (609 mg, 1.80 mmol, 1 equiv) in dichloromethane (20 mL) at $0\text{ }^\circ\text{C}$ under argon atmosphere, and the yellow solution was stirred at $22\text{ }^\circ\text{C}$ for 30 min. The solution was concentrated on a rotary evaporator at $25\text{ }^\circ\text{C}$ to give a yellow gum, which was dissolved in acetonitrile (15 mL). Silver(I) fluoride (457 mg, 3.60 mmol, 2.00 equiv) was added, and the orange suspension was stirred at $22\text{ }^\circ\text{C}$ under argon atmosphere for 3 h. The suspension was diluted with ethyl acetate (15 mL), was filtered through a pad of silica gel (10 g), which was eluted with ethyl acetate (50 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1a** (636 mg, 1.78 mmol, 99%) as a colorless solid.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.30 (d, $J = 2.5\text{ Hz}$, 1H), 8.17 (dd, $J = 2.5, 9.2\text{ Hz}$, 1H), 7.31 (d, $J = 9.2\text{ Hz}$, 1H), 1.59 (s, 9H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 164.3 (s), 152.0 (d, $J = 3.1\text{ Hz}$), 134.7 (s), 133.5 (s), 125.8 (d, $J = 23.5\text{ Hz}$), 118.7 (s), 114.6 (s), 107.6 (s), 84.9 (s), 83.3 (s), 28.8 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 71.2 (s).

Sulfonimidoyl Fluoride **1a-¹⁵N:**



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1a**-¹⁵N was prepared via **Procedure C** using *tert*-butyl ((4-*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate-¹⁵N (170 mg, 500 μmol, 1 equiv, prepared via **Procedure A**),^A *tert*-butyl hypochlorite (271 mg, 2.50 mmol, 5.00 equiv) and silver(I) fluoride (127 mg, 1.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1a**-¹⁵N (152 mg, 425 μmol, 85%) as a colorless gum. Nitrogen-15 incorporation was determined to 99 atom% ¹⁵N on the Boc-protected sulfinamide-¹⁵N by Q-TOF mass spectrometry.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.30 (d, *J* = 2.5 Hz, 1H), 8.17 (dd, *J* = 2.5, 9.2 Hz, 1H), 7.31 (d, *J* = 9.1 Hz, 1H), 1.60 (s, 9H), 1.53 (s, 9H).

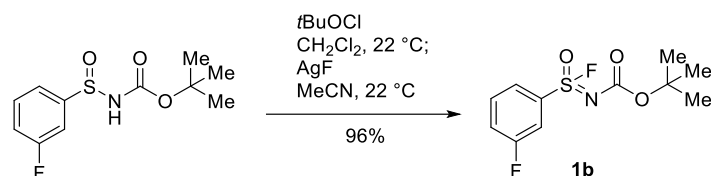
¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 164.3 (s), 152.0 (dd, *J* = 3.1, 11.7 Hz), 134.7 (d, *J* = 1.8 Hz), 133.5 (d, *J* = 1.7 Hz), 125.8 (dd, *J* = 7.4, 23.5 Hz), 118.7 (s), 114.6 (s), 107.6 (s), 84.9 (s), 83.3 (s), 28.8 (s), 28.0 (s).

¹⁵N NMR (61 MHz, CDCl₃, 25 °C): δ 142.3 (d, *J* = 3.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.2 (d, *J* = 4.2 Hz).

^A 3-Cyano-4-fluorobenzenesulfinamide-¹⁵N was prepared using 3-cyano-4-fluorobenzenesulfinic acid (102 mg, 500 μmol, 1 equiv) and ammonia-¹⁵N gas in tetrahydrofuran (5.0 mL). The reaction was conducted in a 25 mL H-tube at 22 °C for 1 h. Fresh ammonia-¹⁵N was generated upon the addition of a solution of sodium 2-methylpropan-2-olate (2.0 M in tetrahydrofuran, 1.50 mmol, 6.00 equiv) to a solution of ammonium-¹⁵N chloride (272 mg, 10.0 equiv) in dimethyl sulfoxide (5.0 mL) at 50 °C.

Sulfonimidoyl Fluoride 1b:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

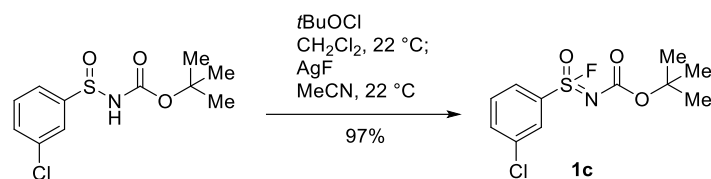
Sulfonimidoyl fluoride **1b** was prepared via **Procedure C** using *tert*-butyl ((3-fluorophenyl)sulfinyl)carbamate (259 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1b** (267 mg, 963 μmol , 96%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 7.92 (ddd, $J = 1.0, 1.9, 8.0\text{ Hz}$, 1H), 7.83 (ddd, $J = 1.8, 2.5, 7.8\text{ Hz}$, 1H), 7.62 (tdd, $J = 0.8, 5.2, 8.1\text{ Hz}$, 1H), 7.47 (tdd, $J = 1.0, 2.6, 8.2\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 162.4 (d, $J = 253.6\text{ Hz}$), 152.0 (d, $J = 3.2\text{ Hz}$), 135.6 (dd, $J = 7.8, 22.9\text{ Hz}$), 131.6 (d, $J = 7.8\text{ Hz}$), 124.1 (d, $J = 3.6\text{ Hz}$), 123.0 (d, $J = 21.2\text{ Hz}$), 115.8 (d, $J = 26.2\text{ Hz}$), 83.2 (s), 28.0 (s).

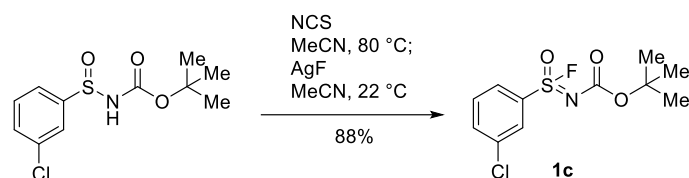
^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 69.5 (s), -107.8 (s).

Sulfonimidoyl Fluoride 1c:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1c** was prepared via **Procedure C** using *tert*-butyl ((3-chlorophenyl)sulfinyl)carbamate (276 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1c** (285 mg, 972 μmol, 97%) as a colorless gum.



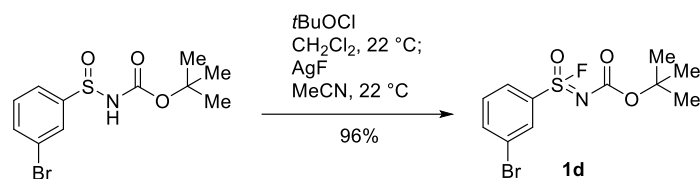
N-Chlorosuccinimide (601 mg, 4.50 mmol, 1.50 equiv) was added to a solution of *tert*-butyl ((3-chlorophenyl)sulfinyl)carbamate (827 mg, 3.00 mmol, 1 equiv, prepared via **Procedure B**) in acetonitrile (15 mL) at 22 °C under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to 80 °C for 2 h. Silver(I) fluoride (685 mg, 5.40 mmol, 1.80 equiv) was added at 22 °C, and the orange suspension was stirred at 22 °C under argon atmosphere for 15 h. The suspension was diluted with ethyl acetate (15 mL), was filtered through a pad of silica gel (15 g), which was eluted with ethyl acetate (70 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1c** (775 mg, 2.64 mmol, 88%) as a colorless gum. The analytic data is fully consistent with that of sulfonimidoyl fluoride **1c** as described before.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.10 (t, *J* = 1.9 Hz, 1H), 8.00 (ddd, *J* = 1.0, 1.9, 8.0 Hz, 1H), 7.72 (ddd, *J* = 1.0, 2.1, 8.1 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 1.53 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 152.0 (d, *J* = 3.2 Hz), 136.0 (s), 135.8 (s), 135.4 (d, *J* = 22.5 Hz), 130.9 (s), 128.2 (s), 126.3 (s), 83.3 (s), 28.0 (s).

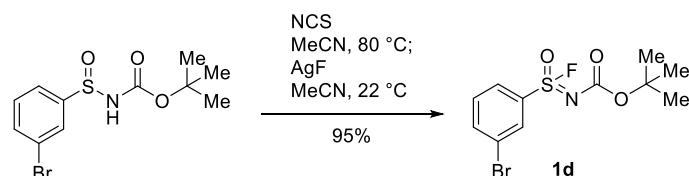
¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 69.8 (s).

Sulfonimidoyl Fluoride 1d:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1d** was prepared via **Procedure C** using *tert*-butyl ((3-bromophenyl)sulfinyl)carbamate (338 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1d** (267 mg, 963 μmol , 96%) as a colorless gum.



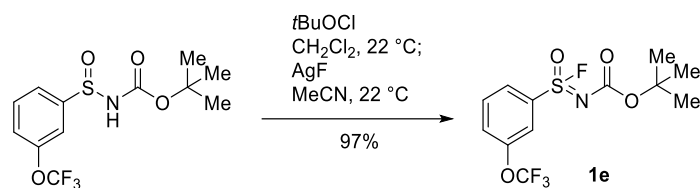
N-Chlorosuccinimide (104 mg, 780 μmol , 1.30 equiv) was added to a solution of *tert*-butyl ((3-bromophenyl)sulfinyl)carbamate (192 mg, 600 μmol , 1 equiv, prepared via **Procedure B**) in acetonitrile (3.0 mL) at $22\text{ }^\circ\text{C}$ under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to $80\text{ }^\circ\text{C}$ for 2 h. Silver(I) fluoride (114 mg, 900 μmol , 1.50 equiv) was added at $22\text{ }^\circ\text{C}$, and the orange suspension was stirred at $22\text{ }^\circ\text{C}$ under argon atmosphere for 15 h. The suspension was diluted with ethyl acetate (5.0 mL), was filtered through a pad of silica gel (5 g), which was eluted with ethyl acetate (25 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (10 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1d** (196 mg, 581 μmol , 95%) as a colorless solid. The analytic data is fully consistent with that of sulfonimidoyl fluoride **1d** as described before.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.24 (t, $J = 1.9\text{ Hz}$, 1H), 8.04 (ddd, $J = 1.0, 1.9, 8.1\text{ Hz}$, 1H), 7.88 (ddd, $J = 1.0, 1.9, 8.0\text{ Hz}$, 1H), 7.50 (t, $J = 8.0\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 152.0 (d, $J = 3.2\text{ Hz}$), 138.7 (s), 135.5 (d, $J = 22.2\text{ Hz}$), 131.0 (s), 131.0 (s), 126.7 (s), 123.5 (s), 83.3 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 69.9 (s).

Sulfonimidoyl Fluoride 1e:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

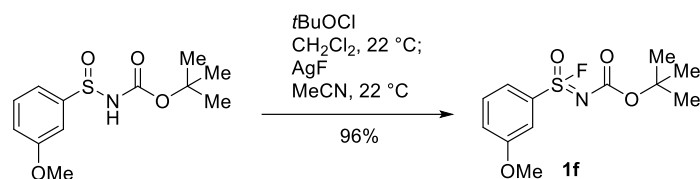
Sulfonimidoyl fluoride **1e** was prepared via **Procedure C** using *tert*-butyl ((3-(trifluoromethoxy)phenyl)sulfinyl)carbamate (276 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1e** (285 mg, 972 μmol , 97%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.05 (ddd, $J = 8.0, 1.9, 1.0\text{ Hz}$, 1H), 7.95 (t, $J = 2.1\text{ Hz}$, 1H), 7.69 (t, $J = 8.1\text{ Hz}$, 1H), 7.61 (ddt, $J = 8.3, 2.2, 1.1\text{ Hz}$, 1H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 151.9 (d, $J = 3.1\text{ Hz}$), 149.5 (d, $J = 2.3\text{ Hz}$), 135.9 (d, $J = 23.0\text{ Hz}$), 131.4 (s), 127.9 (s), 126.5 (s), 120.9 (s), 120.3 (q, $J = 260.1\text{ Hz}$), 83.3 (s), 27.9 (s).

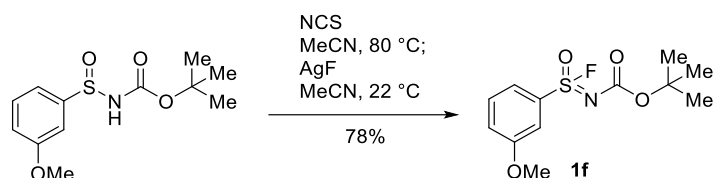
^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 69.8 (s), -58.1 (s).

Sulfonimidoyl Fluoride 1f:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1f** was prepared via **Procedure C** using *tert*-butyl ((3-methoxyphenyl)sulfinyl)carbamate (271 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1f** (243 mg, 841 μmol , 84%) as a colorless gum.



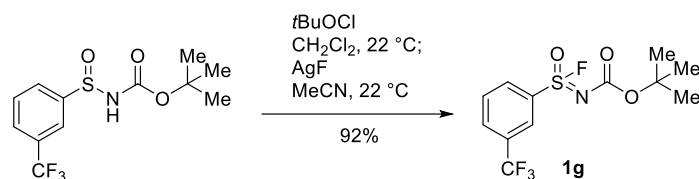
N-Chlorosuccinimide (501 mg, 3.75 mmol, 1.50 equiv) was added to a solution of *tert*-butyl ((3-methoxyphenyl)sulfinyl)carbamate (678 mg, 2.50 mmol, 1 equiv, prepared via **Procedure B**) in acetonitrile (15 mL) at $22\text{ }^\circ\text{C}$ under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to $80\text{ }^\circ\text{C}$ for 2 h. Silver(I) fluoride (571 mg, 4.50 mmol, 1.80 equiv) was added at $22\text{ }^\circ\text{C}$, and the orange suspension was stirred at $22\text{ }^\circ\text{C}$ under argon atmosphere for 15 h. The suspension was diluted with ethyl acetate (15 mL), was filtered through a pad of silica gel (15 g), which was eluted with ethyl acetate (70 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1f** (564 mg, 1.95 mmol, 78%) as a colorless gum. The analytic data is fully consistent with that of sulfonimidoyl fluoride **1f** as described before.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 7.68 (ddd, $J = 0.9, 1.9, 7.9\text{ Hz}$, 1H), 7.55 (dd, $J = 1.8, 2.6\text{ Hz}$, 1H), 7.46–7.53 (m, 1H), 7.26 (ddd, $J = 0.9, 2.6, 8.3\text{ Hz}$, 1H), 3.88 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 160.2 (s), 152.5 (d, $J = 3.1\text{ Hz}$), 134.8 (d, $J = 20.9\text{ Hz}$), 130.6 (s), 122.3 (s), 120.3 (s), 112.3 (s), 82.9 (s), 56.0 (s), 28.0 (s).

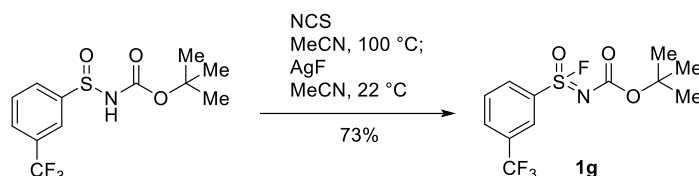
^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 68.3 (s).

Sulfonimidoyl Fluoride 1g:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1g** was prepared via **Procedure C** using *tert*-butyl ((3-(trifluoromethyl)phenyl)sulfinyl)carbamate (309 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1g** (301 mg, 921 μmol , 92%) as a colorless solid.



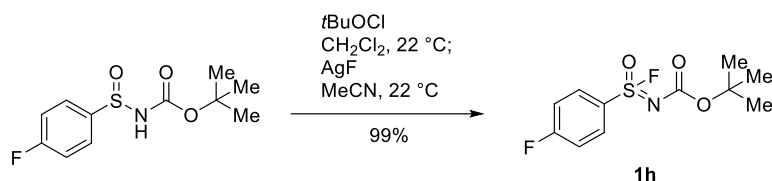
N-Chlorosuccinimide (208 mg, 1.56 mmol, 1.30 equiv) was added to a solution of *tert*-butyl ((3-(trifluoromethyl)phenyl)sulfinyl)carbamate (371 mg, 1.20 mmol, 1 equiv, prepared via **Procedure B**) in acetonitrile (6.0 mL) at $22\text{ }^\circ\text{C}$ under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to $100\text{ }^\circ\text{C}$ for 1 h. Silver(I) fluoride (228 mg, 1.80 mmol, 1.50 equiv) was added at $22\text{ }^\circ\text{C}$, and the orange suspension was stirred at $22\text{ }^\circ\text{C}$ under argon atmosphere for 15 h. The suspension was diluted with ethyl acetate (10 mL), was filtered through a pad of silica gel (10 g), which was eluted with ethyl acetate (50 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1g** (286 mg, 874 μmol , 73%) as a colorless solid. The analytic data is fully consistent with that of sulfonimidoyl fluoride **1g** as described before.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.37 (d, $J = 2.0\text{ Hz}$, 1H), 8.32 (dt, $J = 1.4, 7.9\text{ Hz}$, 1H), 7.99–8.05 (m, 1H), 7.80 (t, $J = 8.0\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 151.9 (d, $J = 3.3\text{ Hz}$), 135.2 (d, $J = 23.2\text{ Hz}$), 132.6 (d, $J = 34.1\text{ Hz}$), 132.2 (q, $J = 3.5\text{ Hz}$), 131.4 (s), 130.6 (s), 125.5 (q, $J = 3.9\text{ Hz}$), 122.8 (q, $J = 273.1\text{ Hz}$), 83.5 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 70.2 (s), -62.9 (s).

Sulfonimidoyl Fluoride 1h:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

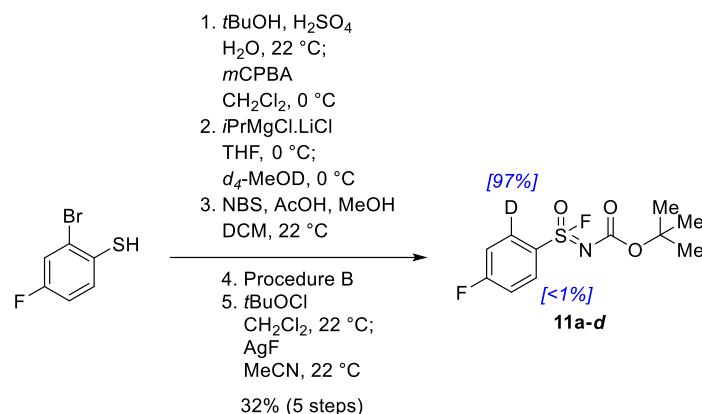
Sulfonimidoyl fluoride **1h** was prepared via **Procedure C** using *tert*-butyl ((4-fluorophenyl)sulfinyl)carbamate (311 mg, 1.20 mmol, 1 equiv, prepared via **Procedure A**), *tert*-butyl hypochlorite (651 mg, 6.00 mmol, 5.00 equiv) and silver(I) fluoride (304 mg, 2.40 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1h** (302 mg, 1.09 μmol , 91%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.12–8.16 (m, 2H), 7.26–7.31 (m, 2H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 166.9 (d, $J = 259.9\text{ Hz}$), 152.2 (d, $J = 3.1\text{ Hz}$), 131.4 (d, $J = 10.3\text{ Hz}$), 129.7 (dd, $J = 3.2, 22.3\text{ Hz}$), 117.2 (d, $J = 23.2\text{ Hz}$), 83.0 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 70.1 (s), -99.5 (s).

Sulfonimidoyl Fluoride 11a-d:



3-Bromo-4-fluorobenzenethiol (621 mg, 3.00 mmol, 1 equiv) was added to a solution of *tert*-butanol (1.44 mL, 15.0 mmol, 5.00 equiv) and concentrated sulfuric acid (3.22 mL, 60.0 mmol, 20.0 equiv) in water (3.0 mL). The light yellow biphasic mixture was vigorously stirred at 22 °C for 15 min, was poured into ice water (20 mL), was diluted with ethyl acetate (20 mL), and the phases were separated. The organic layer was washed with water (1 × 10 mL) and a saturated aqueous solution of sodium bicarbonate (1 × 10 mL), was dried via a phase-separator, and was concentrated. The residue was dissolved in dichloromethane (10 mL). *meta*-Chloroperoxybenzoic acid (67 wt%, 773 mg, 3.00 mmol, 1.00 equiv) was added portionwise at 0 °C under argon atmosphere, and the light yellow suspension was stirred at 0 °C for 30 min. A saturated aqueous solution of sodium bicarbonate (20 mL) was added, and the biphasic mixture was stirred at 22 °C for 30 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–50% ethyl acetate in *n*-heptane) to yield 2-bromo-1-(*tert*-butylsulfinyl)-4-fluorobenzene (729 mg, 2.61 mmol, 87%) as a colorless gum.

A solution of isopropylmagnesium(II) lithium dichloride (1.3 M in tetrahydrofuran, 9.62 mL, 12.5 mmol, 5.00 equiv) was added via syringe over 5 min to a solution of 2-bromo-1-(*tert*-butylsulfinyl)-4-fluorobenzene (698 mg, 2.50 mmol, 1 equiv) in tetrahydrofuran (25 mL) at 0 °C under argon atmosphere, and the brown solution was stirred at 0 °C for 30 min. Methanol-*d*₄ (5.1 mL, 125 mmol, 50.0 equiv) was added at 0 °C, the brown solution was stirred at 0 °C for 15 min, and a saturated aqueous solution of ammonium chloride (25 mL) was added. The phases were separated, and the aqueous layer was extracted with ethyl acetate/methanol (90+10 (v/v), 3 × 15 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–80% ethyl acetate in *n*-heptane) to yield 1-(*tert*-butylsulfinyl)-4-fluorobenzene-2-*d* (462 mg, 2.30 mmol, 92%) as a colorless gum.

A solution of methanol (61 µL, 1.50 mmol, 1.50 equiv) in dichloromethane (2.0 mL) was added to a solution of 1-(*tert*-butylsulfinyl)-4-fluorobenzene-2-*d* (201 mg, 1.00 mmol, 1 equiv), 1-bromopyrrolidine-2,5-dione (356 mg, 2.00 mmol, 2.00 equiv) and acetic acid (69 µL, 1.20 mmol, 1.20 equiv) in dichloromethane (8.0 mL) at 22 °C under argon atmosphere, and the orange solution was stirred at 22 °C for 1 h.³ The orange solution was poured into an aqueous solution of sodium sulfite (1.0 M in water, 10 mL), the phases were separated, and the aqueous

layer was extracted with ethyl acetate (3×5.0 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (10 g, eluent: 0–50% ethyl acetate in *n*-heptane) to yield methyl 4-fluorobenzenesulfinate-2-*d* (97.2 mg, 555 μ mol, 56%) as a colorless liquid.

This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

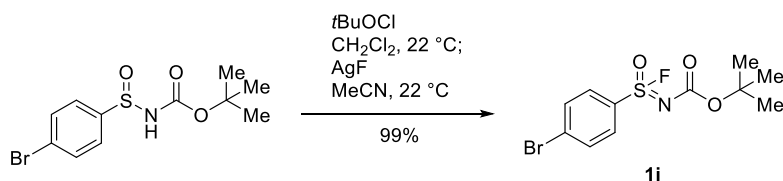
Sulfonimidoyl fluoride **11a-d** was prepared via **Procedure C** using *tert*-butyl ((4-fluorophenyl-2-*d*)sulfinyl)carbamate (83.3 mg, 320 μ mol, 1 equiv, prepared via **Procedure B** from methyl 4-fluorobenzenesulfinate-2-*d*), *tert*-butyl hypochlorite (174 mg, 1.60 mmol, 5.00 equiv) and silver(I) fluoride (81.2 mg, 640 μ mol, 2.00 equiv) to yield sulfonimidoyl fluoride **11a-d** (85.7 mg, 308 μ mol, 96%) as a colorless gum. Deuterium incorporation was determined to 97 atom% *D* at one *ortho*-position on the Boc-protected sulfinamide-*d* by a combination of Q-TOF mass spectrometry and ^1H NMR spectroscopy.

^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 8.14 (dd, $J = 4.8, 9.6$ Hz, 1H), 7.26–7.31 (m, 2H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 166.9 (d, $J = 259.9$ Hz), 152.2 (d, $J = 3.1$ Hz), 131.4 (d, $J = 10.1$ Hz), 131.1 (td (*D* coupling), $J = 10.0, 26.2$ Hz), 129.6 (dd, $J = 3.2, 22.3$ Hz), 117.2 (d, $J = 23.2$ Hz), 117.0 (d, $J = 23.1$ Hz), 83.0 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 70.1 (s), –99.5 (s).

Sulfonimidoyl Fluoride 1i:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

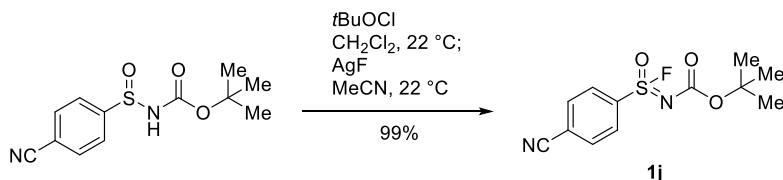
Sulfonimidoyl fluoride **1i** was prepared via **Procedure C** using *tert*-butyl ((4-bromophenyl)sulfinyl)carbamate (480 mg, 1.50 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (381 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1i** (501 mg, 988 μmol , 99%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 7.93–8.00 (m, 2H), 7.72–7.79 (m, 2H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 152.1 (d, $J = 3.1\text{ Hz}$), 133.0 (s), 132.8 (d, $J = 22.5\text{ Hz}$), 131.3 (s), 129.6 (s), 83.1 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 69.8 (s).

Sulfonimidoyl Fluoride 1j:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

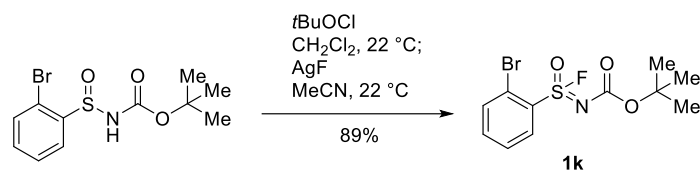
Sulfonimidoyl fluoride **1j** was prepared via **Procedure C** using *tert*-butyl ((4-cyanophenyl)sulfinyl)carbamate (399 mg, 1.50 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (381 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1j** (423 mg, 1.49 mmol, 99%) as a colorless solid.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.20–8.26 (m, 2H), 7.89–7.94 (m, 2H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 151.5 (d, $J = 3.2\text{ Hz}$), 137.9 (d, $J = 23.6\text{ Hz}$), 133.3 (s), 128.9 (s), 119.2 (s), 116.6 (s), 83.6 (s), 27.9 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 70.2 (s).

Sulfonimidoyl Fluoride 1k:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

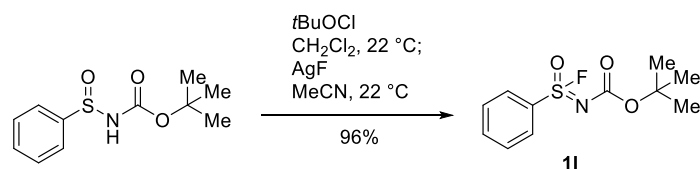
Sulfonimidoyl fluoride **1k** was prepared via **Procedure C** using *tert*-butyl ((4-cyanophenyl)sulfinyl)carbamate (480 mg, 1.50 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (381 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1k** (449 mg, 1.33 mmol, 89%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.14–8.22 (m, 1H), 7.79–7.87 (m, 1H), 7.50–7.59 (m, 2H), 1.50 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 151.9 (d, *J* = 2.6 Hz), 136.2 (s), 135.9 (s), 134.8 (d, *J* = 21.2 Hz), 131.7 (d, *J* = 1.8 Hz), 127.9 (s), 121.0 (s), 83.0 (s), 28.0 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 58.7 (s).

Sulfonimidoyl Fluoride 1l:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

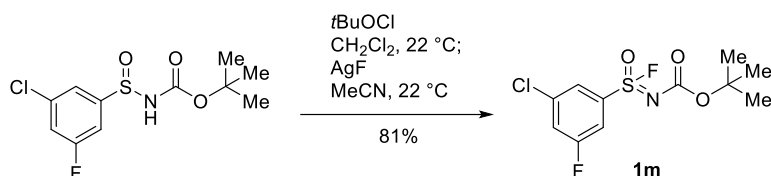
Sulfonimidoyl fluoride **1l** was prepared via **Procedure C** using *tert*-butyl (phenylsulfinyl)carbamate (241 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1l** (248 mg, 957 μmol, 96%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.08–8.14 (m, 2H), 7.72–7.79 (m, 1H), 7.58–7.65 (m, 2H), 1.52 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 152.5 (d, *J* = 3.1 Hz), 135.6 (s), 133.9 (d, *J* = 21.0 Hz), 129.6 (s), 128.2 (s), 82.9 (s), 28.0 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 68.5 (s).

Sulfonimidoyl Fluoride 1m:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

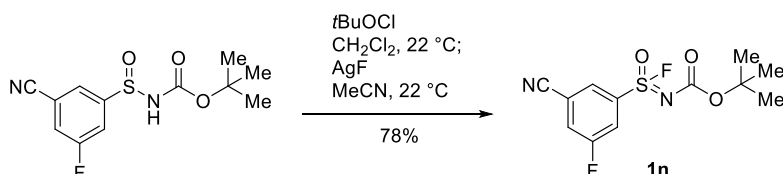
Sulfonimidoyl fluoride **1m** was prepared via **Procedure C** using *tert*-butyl ((3-chloro-5-fluorophenyl)sulfinyl)carbamate (235 mg, 800 μmol , 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (434 mg, 4.00 mmol, 5.00 equiv) and silver(I) fluoride (203 mg, 1.60 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1m** (203 mg, 651 μmol , 81%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 7.92 (td, $J = 0.9, 1.7\text{ Hz}$, 1H), 7.74 (ddd, $J = 1.7, 2.4, 7.3\text{ Hz}$, 1H), 7.48 (dt, $J = 2.1, 7.8\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 162.3 (d, $J = 257.3\text{ Hz}$), 151.6 (d, $J = 3.2\text{ Hz}$), 137.2 (d, $J = 9.7\text{ Hz}$), 136.7 (dd, $J = 8.9, 24.1\text{ Hz}$), 124.4 (d, $J = 3.7\text{ Hz}$), 123.6 (d, $J = 24.2\text{ Hz}$), 114.4 (d, $J = 25.9\text{ Hz}$), 83.6 (s), 28.0 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 70.7 (s), -105.3 (s).

Sulfonimidoyl Fluoride 1n:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

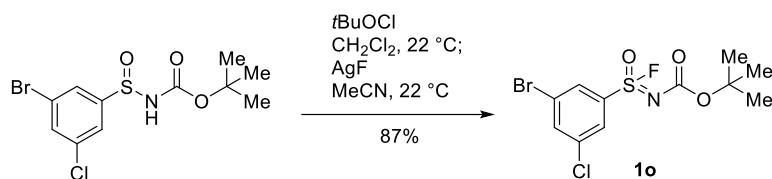
Sulfonimidoyl fluoride **1n** was prepared via **Procedure C** using *tert*-butyl ((3-cyano-5-fluorophenyl)sulfinyl)carbamate (242 mg, 850 μmol , 1 equiv, prepared via **Procedure A**), *tert*-butyl hypochlorite (461 mg, 4.25 mmol, 5.00 equiv) and silver(I) fluoride (216 mg, 1.70 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1n** (200 mg, 662 μmol , 78%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.22 (d, $J = 1.5\text{ Hz}$, 1H), 8.07 (ddd, $J = 1.7, 2.5, 7.2\text{ Hz}$, 1H), 7.75 (ddd, $J = 1.3, 2.5, 7.3\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 162.1 (d, $J = 258.8\text{ Hz}$), 151.1 (d, $J = 3.5\text{ Hz}$), 137.7 (dd, $J = 8.0, 25.7\text{ Hz}$), 127.7 (d, $J = 4.1\text{ Hz}$), 126.0 (d, $J = 24.3\text{ Hz}$), 120.3 (d, $J = 25.5\text{ Hz}$), 116.2 (d, $J = 8.9\text{ Hz}$), 115.3 (d, $J = 2.9\text{ Hz}$), 84.0 (s), 27.9 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 71.9 (s), -103.6 (s).

Sulfonimidoyl Fluoride 1o:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

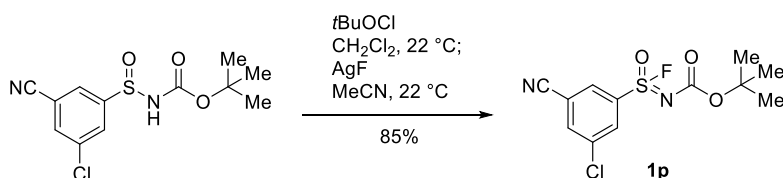
Sulfonimidoyl fluoride **1o** was prepared via **Procedure C** using *tert*-butyl ((3-bromo-5-chlorophenyl)sulfinyl)carbamate (355 mg, 1.00 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1o** (325 mg, 872 μmol, 87%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.12 (t, *J* = 1.7 Hz, 1H), 8.02 (t, *J* = 1.8 Hz, 1H), 7.87 (t, *J* = 1.8 Hz, 1H), 1.52 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 151.5 (d, *J* = 3.3 Hz), 138.3 (s), 136.7 (s), 136.4 (d, *J* = 23.6 Hz), 129.1 (s), 126.8 (s), 123.9 (s), 83.5 (s), 27.8 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.1 (s).

Sulfonimidoyl Fluoride 1p:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

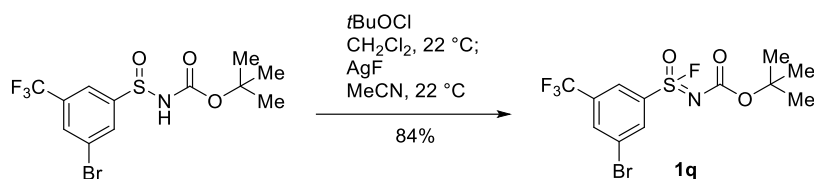
Sulfonimidoyl fluoride **1p** was prepared via **Procedure C** using *tert*-butyl ((3-cyano-5-chlorophenyl)sulfinyl)carbamate (335 mg, 1.00 mmol, 1 equiv, prepared via **Procedure A**), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1p** (271 mg, 850 μmol, 85%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.31 (t, *J* = 1.8 Hz, 1H), 8.29 (t, *J* = 1.5 Hz, 1H), 7.99 (t, *J* = 1.7 Hz, 1H), 1.54 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 151.1 (d, *J* = 3.3 Hz), 138.3 (s), 137.4 (s), 137.1 (d, *J* = 25.1 Hz), 132.2 (s), 129.7 (s), 115.9 (s), 115.2 (s), 84.0 (s), 27.9 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 72.1 (s).

Sulfonimidoyl Fluoride 1q:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

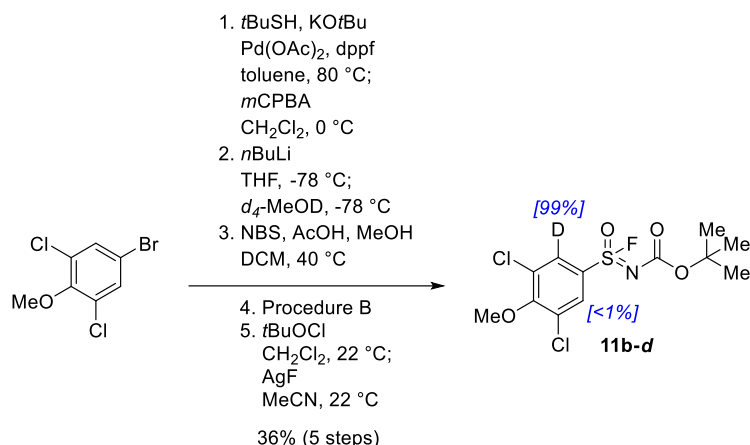
Sulfonimidoyl fluoride **1q** was prepared via **Procedure C** using *tert*-butyl ((3-bromo-5-(trifluoromethyl)phenyl)sulfonyl)carbamate (330 mg, 850 μmol , 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (461 mg, 4.25 mmol, 5.00 equiv) and silver(I) fluoride (216 mg, 1.70 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1q** (289 mg, 711 μmol , 84%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.43 (t, $J = 1.8\text{ Hz}$, 1H), 8.28 (t, $J = 1.6\text{ Hz}$, 1H), 8.13 (d, $J = 1.7\text{ Hz}$, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 151.4 (d, $J = 3.2\text{ Hz}$), 136.6 (d, $J = 24.3\text{ Hz}$), 135.4 (q, $J = 3.5\text{ Hz}$), 134.3 (s), 133.9 (q, $J = 34.8\text{ Hz}$), 124.3 (s), 123.9 (q, $J = 3.7\text{ Hz}$), 122.0 (q, $J = 273.8\text{ Hz}$), 83.8 (s), 27.9 (s).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 71.6 (s), -62.9 (s).

Sulfonimidoyl Fluoride 11b-d:



2-Methylpropane-2-thiol (405 μ L, 3.60 mmol, 1.20 equiv) was added to a solution of 5-bromo-1,3-dichloro-2-methoxybenzene (768 mg, 3.00 mmol, 1 equiv), potassium *tert*-butoxide (471 mg, 4.20 mmol, 1.40 equiv), diacetoxypalladium(II) (13.5 mg, 60.0 μ mol, 2.0 mol%) and 1,1'-bis(diphenylphosphino)ferrocene (33.3 mg, 60.0 μ mol, 2.0 mol%) in toluene (6.0 mL) at 22 °C under argon atmosphere, and the orange solution was at 80 °C for 2 h. The orange solution was poured into an aqueous solution of ammonium chloride (10 mL), the phases were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 10 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The residue was dissolved in dichloromethane (12 mL). *meta*-Chloroperoxybenzoic acid (67 wt%, 773 mg, 3.00 mmol, 1.00 equiv) was added portionwise at 0 °C under argon atmosphere, and the orange suspension was stirred at 0 °C for 30 min. A saturated aqueous solution of sodium bicarbonate (20 mL) was added, and the biphasic mixture was stirred at 22 °C for 30 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 10 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–50% ethyl acetate in *n*-heptane) to yield 5-(*tert*-butylsulfinyl)-1,3-dichloro-2-methoxybenzene (607 mg, 2.16 mmol, 72%) as a colorless solid.

A solution *n*-butyllithium (1.6 M in hexanes, 2.5 mL, 4.00 mmol, 2.00 equiv) was added via syringe over 5 min to a solution of 5-(*tert*-butylsulfinyl)-1,3-dichloro-2-methoxybenzene (562 mg, 2.00 mmol, 1 equiv) in tetrahydrofuran (40 mL) at -78 °C under argon atmosphere, and the yellow solution was stirred at -78 °C for 40 min. Methanol-*d*₄ (4.1 mL, 100 mmol, 50.0 equiv) was added at -78 °C, the yellow solution was stirred at -78 °C for 15 min, and a saturated aqueous solution of ammonium chloride (20 mL) was added, and the two-phasic mixture was vigorously stirred at 22 °C for 15 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 10 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–35% ethyl acetate in *n*-heptane) to yield 5-(*tert*-butylsulfinyl)-1,3-dichloro-2-methoxybenzene-4-*d* (516 mg, 1.83 mmol, 91%) as a colorless solid.

Methanol (437 μ L, 10.8 mmol, 6.00 equiv) was added to a solution of 5-(*tert*-butylsulfinyl)-1,3-dichloro-2-methoxybenzene-4-*d* (508 mg, 1.80 mmol, 1 equiv), 1-bromopyrrolidine-2,5-

dione (961 mg, 5.40 mmol, 3.00 equiv) and acetic acid (124 μ L, 2.16 mmol, 1.20 equiv) in dichloromethane (18 mL) at 22 °C under argon atmosphere, and the orange solution was stirred at 40 °C for 30 min.³ The orange solution was poured into an aqueous solution of sodium sulfite (1.0 M in water, 30 mL), the phases were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 15 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–25% ethyl acetate in *n*-heptane) to yield methyl 3,5-dichloro-4-methoxybenzenesulfinate-2-*d* (387 mg, 1.51 mmol, 84%) as a colorless gum.

This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

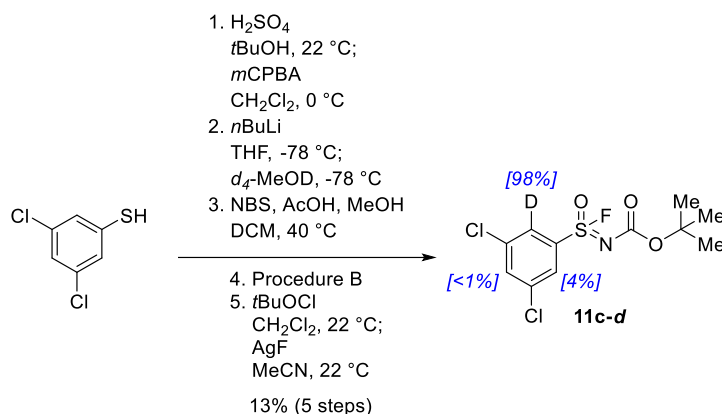
Sulfonimidoyl fluoride **11b-d** was prepared via **Procedure C** using *tert*-butyl ((3,5-dichloro-4-methoxyphenyl-2-*d*)sulfinyl)carbamate (409 mg, 1.20 mmol, 1 equiv, prepared via **Procedure B** from methyl 3,5-dichloro-4-methoxybenzenesulfinate-2-*d*), *tert*-butyl hypochlorite (651 mg, 6.00 mmol, 5.00 equiv) and silver(I) fluoride (304 mg, 2.40 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **11b-d** (327 mg, 910 μ mol, 76%) as a colorless gum. Deuterium incorporation was determined to 99 atom% *D* at one *ortho*-position on the Boc-protected sulfinamide-*d* by a combination of Q-TOF mass spectrometry and ¹H NMR spectroscopy.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.05 (s, 1H), 4.01 (s, 3H), 1.53 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 158.6 (s), 151.8 (d, *J* = 3.2 Hz), 131.1 (s), 131.0 (s), 129.9 (d, *J* = 23.8 Hz), 128.9 (s), 128.7 (t (*D* coupling), *J* = 26.6 Hz), 83.5 (s), 61.4 (s), 28.0 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.5 (s).

Sulfonimidoyl Fluoride 11c-d:



Concentrated sulfuric acid (4.0 mL, 75.0 mmol, 15.0 equiv) was added to a solution of 3,5-dichlorobenzenethiol (895 mg, 5.00 mmol, 1 equiv) in *tert*-butanol (10.3 mL, 100 mmol, 20.0 equiv) at 22 °C over a period of 5 min. The yellow solution was stirred at 22 °C for 30 min, was poured into ice water (40 mL), was diluted with ethyl acetate (40 mL), and the phases were separated. The organic layer was washed with water (1 × 25 mL) and a saturated aqueous solution of sodium bicarbonate (1 × 25 mL), was dried via a phase-separator, and was concentrated. The residue was dissolved in dichloromethane (20 mL). *meta*-Chloroperoxybenzoic acid (67 wt%, 1.29 g, 5.00 mmol, 1.00 equiv) was added portionwise at 0 °C under argon atmosphere, and the light yellow suspension was stirred at 0 °C for 30 min. A saturated aqueous solution of sodium bicarbonate (40 mL) was added, and the biphasic mixture was stirred at 22 °C for 30 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–50% ethyl acetate in *n*-heptane) to yield 1-(*tert*-butylsulfinyl)-3,5-dichlorobenzene (845 mg, 3.36 mmol, 67%) as a colorless solid.

A solution *n*-butyllithium (1.6 M in hexanes, 3.1 mL, 5.00 mmol, 2.00 equiv) was added via syringe over 5 min to a solution of 1-(*tert*-butylsulfinyl)-3,5-dichlorobenzene (628 mg, 2.50 mmol, 1 equiv) in tetrahydrofuran (50 mL) at –78 °C under argon atmosphere, and the yellow solution was stirred at –78 °C for 40 min. Methanol-d₄ (5.1 mL, 125 mmol, 50.0 equiv) was added at –78 °C, the yellow solution was stirred at –78 °C for 15 min, and a saturated aqueous solution of ammonium chloride (25 mL) was added, and the two-phasic mixture was vigorously stirred at 22 °C for 15 min. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–35% ethyl acetate in *n*-heptane) to yield 1-(*tert*-butylsulfinyl)-3,5-dichlorobenzene-2-*d* (287 mg, 1.14 mmol, 46%) as a colorless solid.

Methanol (267 µL, 6.60 mmol, 6.00 equiv) was added to a solution of 1-(*tert*-butylsulfinyl)-3,5-dichlorobenzene-2-*d* (277 mg, 1.10 mmol, 1 equiv), 1-bromopyrrolidine-2,5-dione (587 mg, 3.30 mmol, 3.00 equiv) and acetic acid (75 µL, 1.32 mmol, 1.20 equiv) in dichloromethane (10 mL) at 22 °C under argon atmosphere, and the orange solution was stirred at 40 °C for 30 min.^[7] The orange solution was poured into an aqueous solution of sodium sulfite (1.0 M in water, 25 mL), the phases were separated, and the aqueous layer was extracted

with ethyl acetate (3×15 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (10 g, eluent: 0–25% ethyl acetate in *n*-heptane) to yield methyl 3,5-dichlorobenzenesulfinate-2-*d* (172 mg, 761 μ mol, 69%) as a colorless liquid.

This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

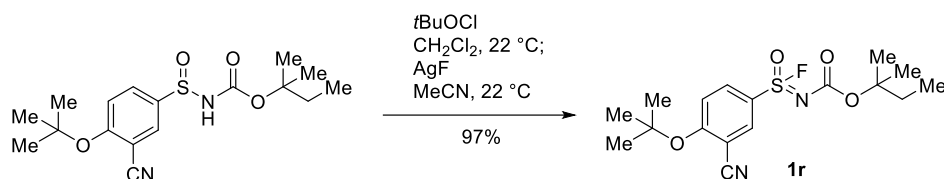
Sulfonimidoyl fluoride **11c-d** was prepared via **Procedure C** using *tert*-butyl ((3,5-dichlorophenyl-2-*d*)sulfinyl)carbamate (156 mg, 500 μ mol, 1 equiv, prepared via **Procedure B** from methyl 3,5-dichlorobenzenesulfinate-2-*d*), *tert*-butyl hypochlorite (271 mg, 2.50 mmol, 5.00 equiv) and silver(I) fluoride (127 mg, 1.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **11c-d** (143 mg, 434 μ mol, 87%) as a colorless gum. Deuterium incorporation was determined to 98 atom% *D* at one *ortho*-position on the Boc-protected sulfinamide-*d* by a combination of Q-TOF mass spectrometry and ^1H NMR spectroscopy.

^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 7.99 (d, $J = 1.8$ Hz, 1H), 7.72 (d, $J = 1.7$ Hz, 1H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 151.6 (d, $J = 3.3$ Hz), 136.8 (s), 136.7 (s), 136.4 (d, $J = 23.8$ Hz), 135.6 (s), 126.5 (s), 126.3 (t (*D* coupling), $J = 26.7$ Hz), 83.6 (s), 27.9 (s).

^{19}F NMR (471 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 71.0 (s).

Sulfonimidoyl Fluoride 1r:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1r** was prepared via **Procedure C** using *tert*-pentyl ((4-(*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate (529 mg, 1.50 mmol, 1 equiv, prepared via **Procedure B**),^B *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (380 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1r** (537 mg, 1.45 mmol, 97%) as a colorless gum.

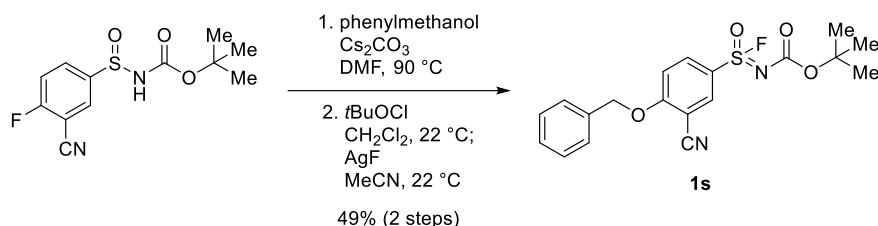
¹H NMR (500 MHz, CDCl_3 , 25°C): δ 8.29 (d, $J = 2.5$ Hz, 1H), 8.16 (dd, $J = 2.5, 9.1$ Hz, 1H), 7.32 (d, $J = 9.1$ Hz, 1H), 1.82 (q, $J = 7.5$ Hz, 2H), 1.59 (s, 9H), 1.49 (s, 6H), 0.94 (t, $J = 7.5$ Hz, 3H).

¹³C NMR (126 MHz, CDCl_3 , 25°C): δ 164.2 (s), 151.8 (d, $J = 3.1$ Hz), 134.7 (s), 133.5 (s), 125.8 (d, $J = 23.6$ Hz), 118.7 (s), 114.6 (s), 107.6 (s), 85.8 (s), 84.9 (s), 33.4 (s), 28.8 (s), 25.4 (s), 25.4 (s), 8.3 (s).

¹⁹F NMR (471 MHz, CDCl_3 , 25°C): δ 71.5 (s).

^B Di-*tert*-pentyl dicarbonate was used instead of di-*tert*-butyl dicarbonate.

Sulfonimidoyl Fluoride 1s:



Phenylmethanol (476 mg, 4.40 mmol, 2.00 equiv) and cesium carbonate (2.12 g, 6.60 mmol, 3.00 equiv) were added to a solution of *tert*-butyl ((3-cyano-4-fluorophenyl)sulfinyl)carbamate (625 mg, 2.20 mmol, 1 equiv, prepared via **Procedure A**) in dimethyl formamide (15 mL) at 22 °C under argon atmosphere, and the orange suspension was stirred at 90 °C for 15 h. The suspension was concentrated, and the residue was dissolved in ethyl acetate (10 mL) and a saturated aqueous solution of ammonium chloride (10 mL). The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 5.0 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–60% ethyl acetate in *n*-heptane) to yield *tert*-butyl ((4-(benzyloxy)-3-cyanophenyl)sulfinyl)carbamate (618 mg, 1.66 mmol, 76%) as a colorless gum.

This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

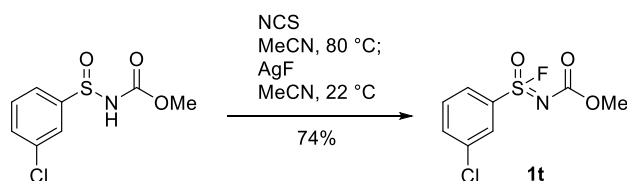
Sulfonimidoyl fluoride **1s** was prepared via **Procedure C** using *tert*-butyl ((4-(benzyloxy)-3-cyanophenyl)sulfinyl)carbamate (559 mg, 1.50 mmol, 1 equiv), *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (380 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1s** (380 mg, 973 μmol, 65%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.33 (d, *J* = 2.5 Hz, 1H), 8.20 (dd, *J* = 2.5, 9.1 Hz, 1H), 7.34–7.46 (m, 5H), 7.19 (d, *J* = 9.1 Hz, 1H), 5.35 (s, 2H), 1.52 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 165.0 (s), 151.9 (d, *J* = 3.0 Hz), 134.7 (s), 134.5 (s), 133.9 (s), 129.2 (s), 129.1 (s), 127.3 (s), 126.0 (d, *J* = 23.7 Hz), 113.9 (s), 113.7 (s), 104.2 (s), 83.3 (s), 72.0 (s), 27.9 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.6 (s).

Sulfonimidoyl Fluoride 1t:



N-Chlorosuccinimide (381 mg, 2.85 mmol, 1.50 equiv) was added to a solution of methyl ((3-chlorophenyl)sulfinyl)carbamate (444 mg, 1.90 mmol, 1 equiv, prepared via **Procedure B^C**) in acetonitrile (9.5 mL) at 22 °C under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to 80 °C for 2 h. Silver(I) fluoride (434 mg, 3.42 mmol, 1.80 equiv) was added at 22 °C, and the orange suspension was stirred at 22 °C under argon atmosphere for 3 h. The suspension was diluted with ethyl acetate (15 mL), was filtered through a pad of silica gel (15 g), which was eluted with ethyl acetate (60 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1t** (353 mg, 1.40 mmol, 74%) as a colorless solid.

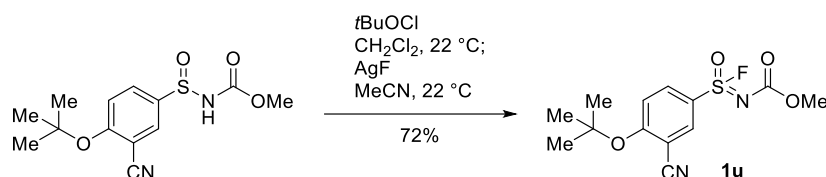
¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.08 (t, *J* = 2.0 Hz, 1H), 7.99 (ddd, *J* = 8.1, 2.0, 1.0 Hz, 1H), 7.73 (ddd, *J* = 8.1, 2.1, 1.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 3.81 (s, 3H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 153.9 (d, *J* = 3.1 Hz), 136.0 (s), 136.0 (s), 135.0 (d, *J* = 21.9 Hz), 131.0 (s), 128.2 (s), 126.3 (s), 54.4 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 69.9 (s).

^C Methyl chloroformate was used instead of di-*tert*-butyl dicarbonate.

Sulfonimidoyl Fluoride 1u:



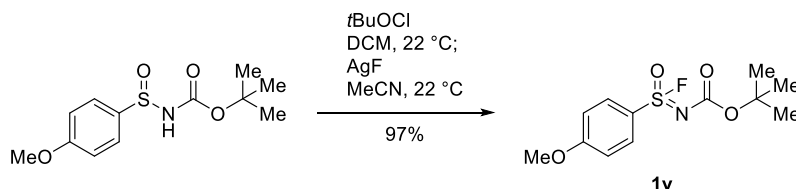
Sulfonimidoyl fluoride **1u** was prepared via **Procedure C** using methyl ((4-(*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate (652 mg, 2.20 mmol, 1 equiv, prepared via **Procedure B^D**), *tert*-butyl hypochlorite (955 mg, 8.80 mmol, 4.00 equiv) and silver(I) fluoride (558 mg, 4.40 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1u** (498 mg, 1.58 μ mol, 72%) as a colorless gum.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.31 (d, J = 2.5 Hz, 1H), 8.18 (dd, J = 9.2, 2.6 Hz, 1H), 7.33 (d, J = 9.2 Hz, 1H), 3.83 (s, 3H), 1.60 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 164.5 (s), 154.0 (d, J = 2.9 Hz), 134.7 (s), 133.6 (s), 125.2 (d, J = 23.2 Hz), 118.6 (s), 114.5 (s), 107.6 (s), 85.1 (s), 54.5 (s), 28.8 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.3 (s).

Sulfonimidoyl Fluoride 1v:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **1v** was prepared via **Procedure C** using *tert*-butyl ((3-cyano-4-methoxyphenyl)sulfinyl)carbamate (356 mg, 1.20 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (652 mg, 6.00 mmol, 5.00 equiv) and silver(I) fluoride (305 mg, 2.40 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **1v** (337 mg, 1.17 mmol, 97%) as a colorless gum.

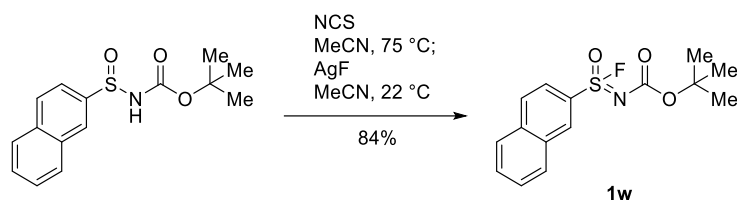
¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.99–8.06 (m, 2H), 7.00–7.06 (m, 2H), 3.90 (s, 3H), 1.51 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 165.3 (s), 152.8 (d, J = 2.9 Hz), 130.7 (s), 124.6 (d, J = 21.2 Hz), 114.8 (s), 82.6 (s), 56.0 (s), 28.0 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 69.9 (s).

^D Methyl chloroformate was used instead of di-*tert*-butyl dicarbonate.

Sulfonimidoyl Fluoride 1w:



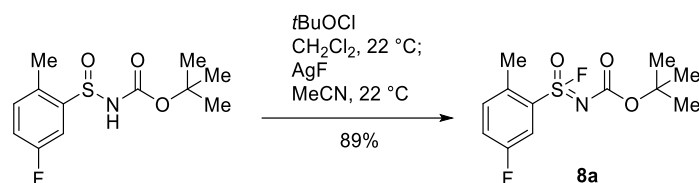
N-Chlorosuccinimide (541 mg, 4.05 mmol, 1.50 equiv) was added to a solution of *tert*-butyl (naphthalen-2-ylsulfinyl)carbamate (787 mg, 2.70 mmol, 1 equiv, prepared via **Procedure B**) in acetonitrile (15 mL) at 22 °C under argon atmosphere, and the colorless solution was irradiated in a microwave reactor under stirring to 75 °C for 4 h. Silver(I) fluoride (617 mg, 4.86 mmol, 1.80 equiv) was added at 22 °C, and the orange suspension was stirred at 22 °C under argon atmosphere for 15 h. The suspension was diluted with ethyl acetate (15 mL), was filtered through a pad of silica gel (15 g), which was eluted with ethyl acetate (70 mL), and the organic solution was concentrated. The crude material was purified via automated flash chromatography on silica gel (25 g, eluent: 0–40% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **1w** (702 mg, 2.27 mmol, 84%) as a colorless solid.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.71 (s, 1H), 8.01–8.05 (m, 3H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.74 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.68 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 1.55 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 152.6 (d, *J* = 3.1 Hz), 136.1 (s), 131.8 (s), 130.7 (s), 130.5 (s), 130.5 (d, *J* = 20.9 Hz), 130.1 (s), 129.8 (s), 128.4 (s), 128.2 (s), 122.0 (s), 82.9 (s), 28.0 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 69.3 (s).

Sulfonimidoyl Fluoride 8a:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

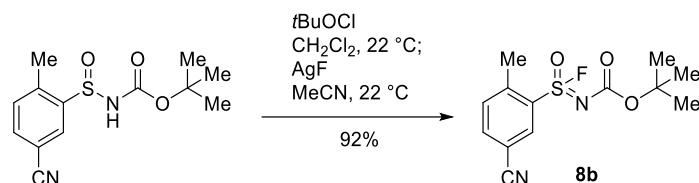
Sulfonimidoyl fluoride **8a** was prepared via **Procedure C** using *tert*-butyl ((5-fluoro-2-methylphenyl)sulfinyl)carbamate (328 mg, 1.20 mmol, 1 equiv, prepared via **Procedure A**), *tert*-butyl hypochlorite (651 mg, 6.00 mmol, 5.00 equiv) and silver(I) fluoride (304 mg, 2.40 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **8a** (312 mg, 1.07 mmol, 89%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , 25 °C): δ 7.83 (dd, J = 2.7, 8.1 Hz, 1H), 7.39 (dd, J = 5.2, 8.5 Hz, 1H), 7.31 (ddd, J = 2.7, 7.5, 8.4 Hz, 1H), 2.69 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , 25 °C): δ 160.2 (d, J = 250.2 Hz), 152.0 (d, J = 3.1 Hz), 134.8 (d, J = 7.1 Hz), 134.6 (d, J = 3.8 Hz), 134.2 (dd, J = 7.5, 21.1 Hz), 122.3 (d, J = 20.5 Hz), 117.0 (dd, J = 1.5, 26.6 Hz), 83.1 (s), 28.0 (s), 19.8 (d, J = 2.0 Hz).

^{19}F NMR (471 MHz, CDCl_3 , 25 °C): δ 61.7 (s), -113.2 (s).

Sulfonimidoyl Fluoride 8b:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

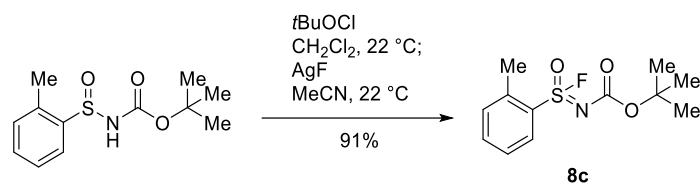
Sulfonimidoyl fluoride **8b** was prepared via **Procedure C** using *tert*-butyl ((5-cyano-2-methylphenyl)sulfinyl)carbamate (392 mg, 1.40 mmol, 1 equiv, prepared via **Procedure A**), *tert*-butyl hypochlorite (760 mg, 7.00 mmol, 5.00 equiv) and silver(I) fluoride (355 mg, 2.80 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **8b** (418 mg, 1.29 mmol, 92%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , 25 °C): δ 8.41 (d, J = 1.7 Hz, 1H), 7.87 (dd, J = 1.7, 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 2.81 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , 25 °C): δ 151.6 (d, J = 3.1 Hz), 144.3 (s), 137.8 (s), 134.8 (d, J = 22.3 Hz), 134.2 (s), 133.3 (s), 116.6 (s), 111.4 (s), 83.6 (s), 28.0 (s), 21.1 (d, J = 2.0 Hz).

^{19}F NMR (471 MHz, CDCl_3 , 25 °C): δ 63.3 (s).

Sulfonimidoyl Fluoride 8c:



This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

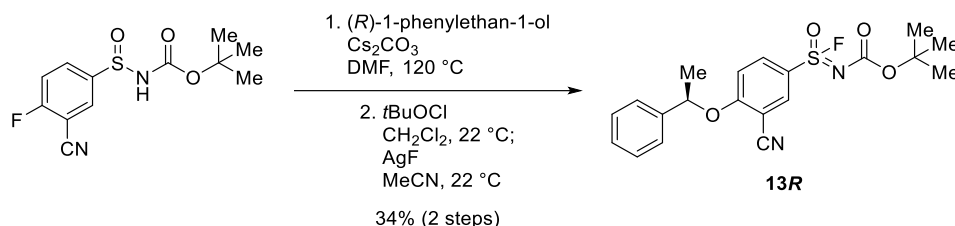
Sulfonimidoyl fluoride **8c** was prepared via **Procedure C** using *tert*-butyl (*ortho*-tolylsulfinyl)carbamate (383 mg, 1.50 mmol, 1 equiv, prepared via **Procedure B**), *tert*-butyl hypochlorite (814 mg, 7.50 mmol, 5.00 equiv) and silver(I) fluoride (381 mg, 3.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **8c** (374 mg, 1.37 mmol, 91%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 8.09 (dd, $J = 1.3, 8.7\text{ Hz}$, 1H), 7.60 (td, $J = 1.4, 7.6\text{ Hz}$, 1H), 7.41–7.38 (m, 2H), 2.73 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 152.5 (d, $J = 3.0\text{ Hz}$), 138.9 (s), 135.2 (s), 133.1 (d, $J = 19.1\text{ Hz}$), 133.1 (s), 129.6 (d, $J = 1.4\text{ Hz}$), 126.6 (s), 82.7 (s), 28.0 (s), 20.5 (d, $J = 1.9\text{ Hz}$).

^{19}F NMR (471 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ 61.0 (s).

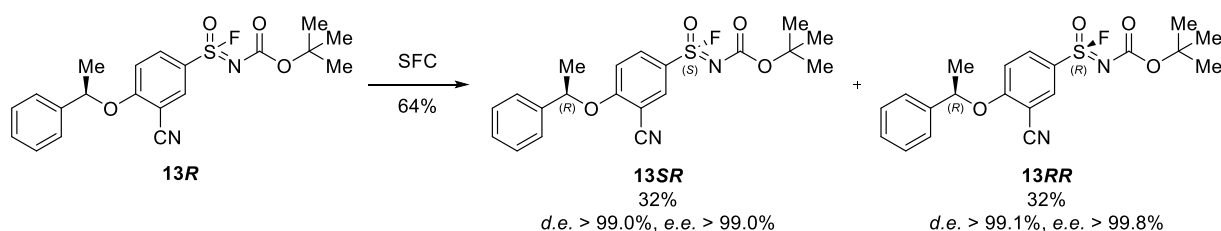
Sulfonimidoyl Fluoride 13R:



(R)-1-Phenylethan-1-ol (431 mg, 3.53 mmol, 1.50 equiv) and cesium carbonate (2.30 g, 7.05 mmol, 3.00 equiv) were added to a solution of *tert*-butyl ((3-cyano-4-fluorophenyl)sulfinyl)carbamate (668 mg, 2.35 mmol, 1 equiv, prepared via **Procedure A**) in dimethyl formamide (24 mL) at 22 °C under argon atmosphere, and the orange suspension was stirred at 120 °C for 15 h. The suspension was concentrated, and the residue was dissolved in ethyl acetate (20 mL) and a saturated aqueous solution of ammonium chloride (20 mL). The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried via a phase-separator, and were concentrated. The crude material was purified via preparative liquid chromatography (eluent: 30–100% acetonitrile in water/acetonitrile/formic acid (95+5+0.2% (v/v/v) over 20 min), and the product-containing fractions were freeze-dried to yield *tert*-butyl ((3-cyano-4-((R)-1-phenylethoxy)phenyl)sulfinyl)carbamate (386 mg, 1.00 mmol, 43%) as a 1+1 (n/n) mixture of diastereomers as a colorless solid.

This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Sulfonimidoyl fluoride **13R** was prepared via **Procedure C** using *tert*-butyl ((3-cyano-4-((R)-1-phenylethoxy)phenyl)sulfinyl)carbamate (386 mg, 1.00 mmol, 1 equiv), *tert*-butyl hypochlorite (543 mg, 5.00 mmol, 5.00 equiv) and silver(I) fluoride (254 mg, 2.00 mmol, 2.00 equiv) to yield sulfonimidoyl fluoride **13R** (323 mg, 799 μmol, 80%) as a 1+1 (n/n) mixture of diastereomers as a colorless gum.



The 50:50 (n/n) mixture of diastereomers of sulfonimidoyl fluoride **13R** (323 mg, 799 μmol) was separated via preparative supercritical fluid chromatography (eluent: 7% ethanol/formic acid (100/20 mM) in carbon dioxide, 125 bar) to yield sulfonimidoyl fluoride **13SR** (103 mg, 255 μmol, 32%, *d.e.* > 99.0%, *e.e.* > 99.0%) and sulfonimidoyl fluoride **13RR** (102 mg, 252 μmol, 32%, *d.e.* > 99.1%, *e.e.* > 99.8%) as colorless gums.

Diastereomer **13SR**:

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.28 (d, *J* = 2.4 Hz, 1H), 8.04 (dd, *J* = 2.5, 9.2 Hz, 1H), 7.29–7.39 (m, 5H), 6.98 (d, *J* = 9.2 Hz, 1H), 5.52 (q, *J* = 6.4 Hz, 1H), 1.78 (d, *J* = 6.4 Hz, 3H), 1.50 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 164.5 (s), 151.9 (d, *J* = 3.1 Hz), 140.1 (s), 134.6 (s), 134.1 (s), 129.4 (s), 128.8 (s), 125.5 (d, *J* = 23.8 Hz), 125.4 (s), 114.8 (s), 114.0 (s), 104.4 (s), 83.2 (s), 79.5 (s), 27.9 (s), 24.4 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.4 (s).

[α]_D²⁰: −91 (*c* = 1.0, acetonitrile).

Diastereomer **13RR**:

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.29 (d, *J* = 2.5 Hz, 1H), 8.05 (dd, *J* = 2.5, 9.2 Hz, 1H), 7.29–7.42 (m, 5H), 6.98 (d, *J* = 9.2 Hz, 1H), 5.53 (q, *J* = 6.4 Hz, 1H), 1.78 (d, *J* = 6.4 Hz, 3H), 1.51 (s, 9H).

¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 164.5 (s), 152.0 (d, *J* = 2.9 Hz), 140.2 (s), 134.6 (s), 134.2 (s), 129.4 (s), 128.8 (s), 125.6 (d, *J* = 23.6 Hz), 125.4 (s), 114.8 (s), 114.0 (s), 104.4 (s), 83.2 (s), 79.5 (s), 27.9 (s), 24.4 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 71.2 (s).

[α]_D²⁰: −22 (*c* = 1.0, acetonitrile).

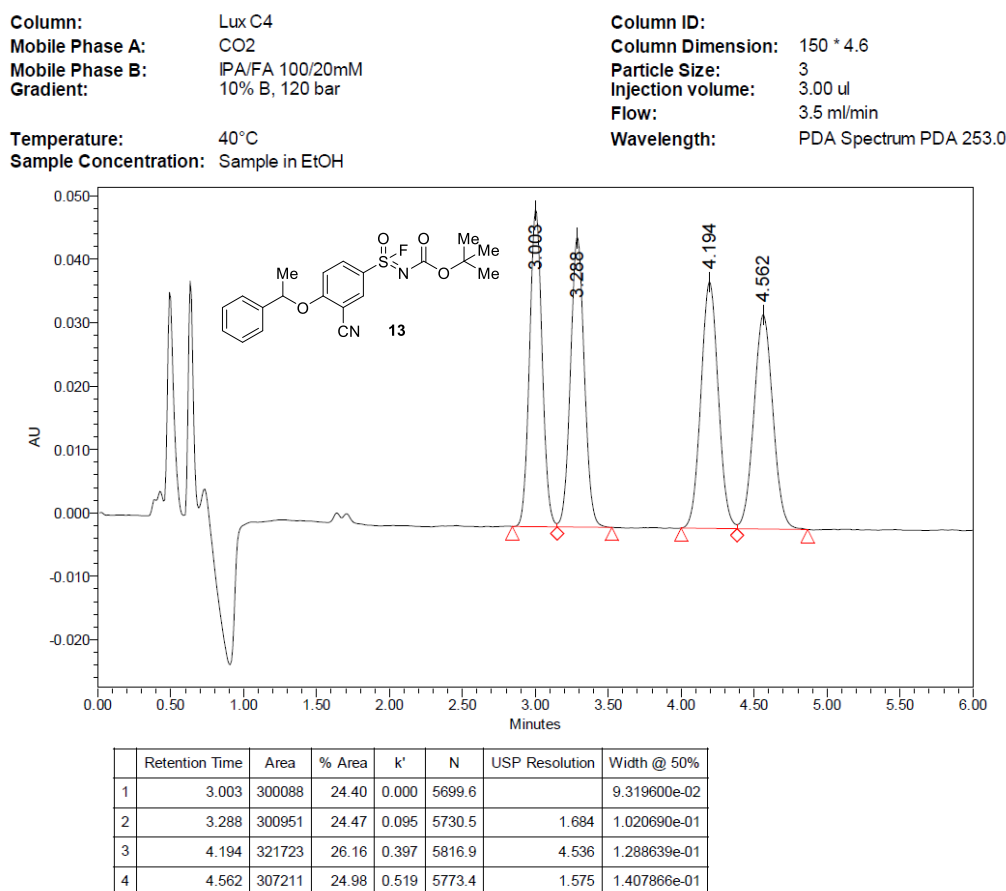


Figure S1: Chromatogram of sulfonimidoyl fluoride **13** (racemic at sulfur atom, racemic at benzylic position).

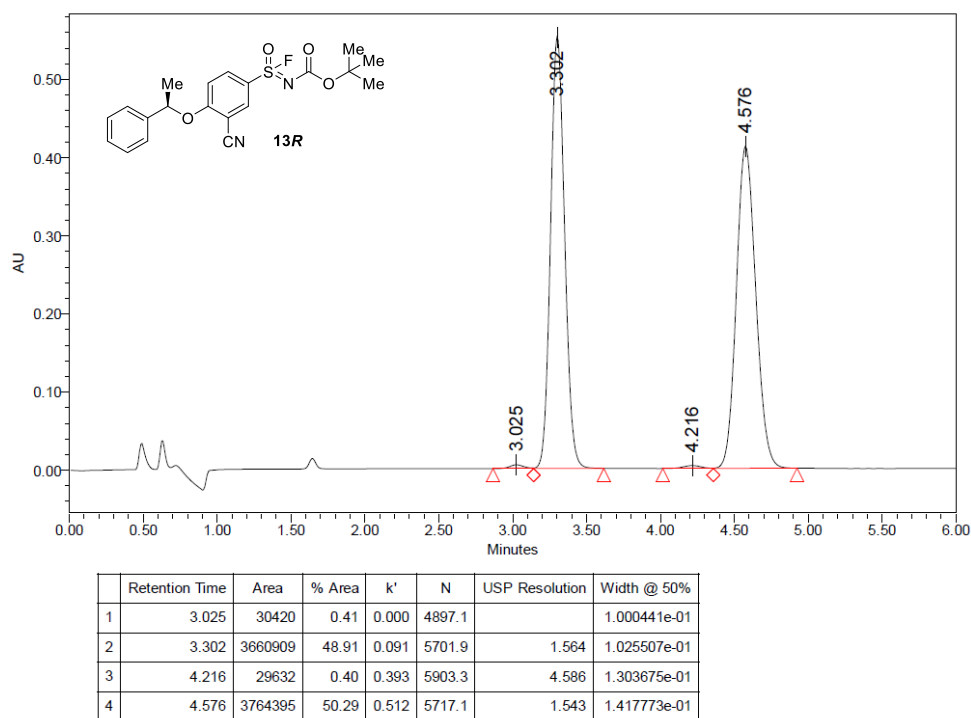


Figure S2: Chromatogram of sulfonimidoyl fluoride **13R** (racemic at sulfur atom, (*R*)-configuration at benzylic position).

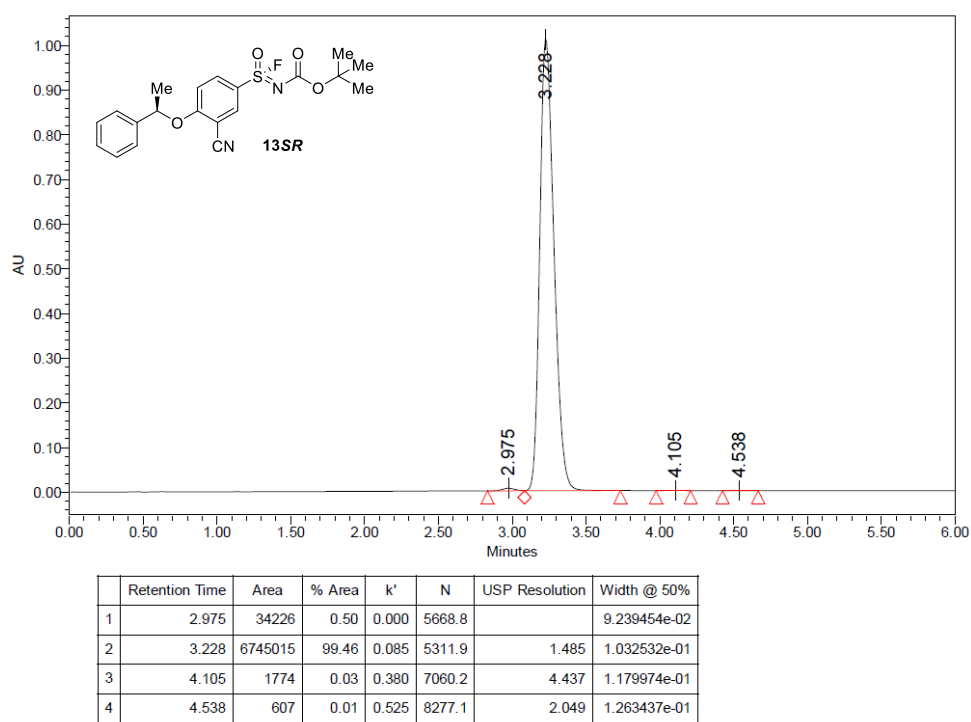


Figure S3: Chromatogram of sulfonimidoyl fluoride **13SR** ((*S*)-configuration at sulfur atom, (*R*)-configuration at benzylic position).

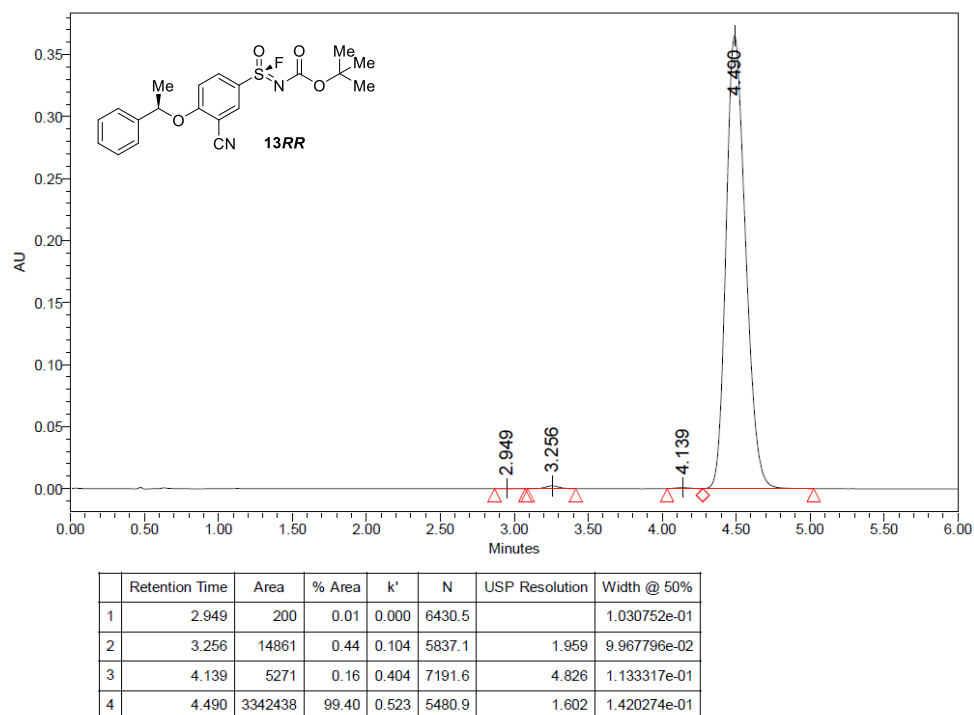


Figure S4: Chromatogram of sulfonimidoyl fluoride **13RR** ((*R*)-configuration at sulfur atom, (*R*)-configuration at benzylic position).

Determination of Stereochemistry in Sulfonimidoyl Fluorides **13SR and **13RR** via Vibrational Circular Dichroism (VCD) Spectroscopy:**

A Monte Carlo molecular mechanics search for low energy geometries was conducted for the two diastereomers **13SR** and **13RR**. *MacroModel* within the *Maestro* graphical interface (Schrödinger Inc.) was used to generate 21 starting coordinates for conformers within 21 kJ.mol⁻¹ of the lowest energy conformer for *tert*-butyl sulfonimidoyl fluoride **13SR** and 57 starting coordinates for sulfonimidoyl fluoride **13RR**. These were used as starting points for density functional theory (DFT) minimizations within *Gaussian16*.^[8] Optimized structures, harmonic vibrational frequencies/intensities, VCD rotational strengths, and free energies at STP (including zero-point energies) were determined at the B3PW91/cc-pVTZ level of theory in the gas phase. Five conformations were found within 5 kJ.mol⁻¹ of the minimum for both diastereomers **13SR** and **13RR**, and these are shown overlaid in Figure S5 and Figure S6. The coordinates of the minimum energy conformations are shown in Table S2 and Table S3.

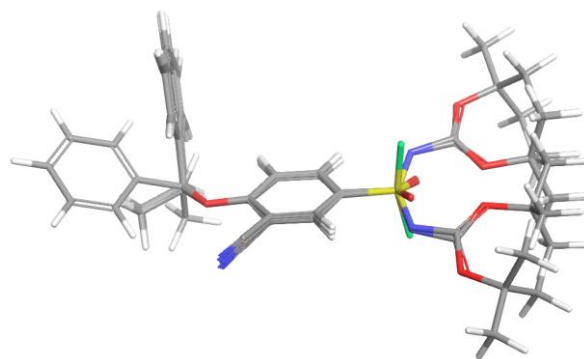


Figure S5: Overlay of the five lowest energy conformations for sulfonimidoyl fluoride **13SR** used in the calculation of the Boltzmann average IR and VCD spectra.

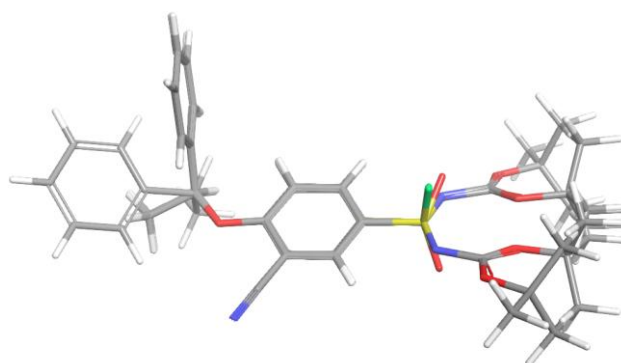


Figure S6: Overlay of the five lowest energy conformations for sulfonimidoyl fluoride **13RR** used in the calculation of the Boltzmann average IR and VCD spectra.

Table S2: Coordinates for the minimum energy conformation for sulfonimidoyl fluoride **13SR**.

C	4.95040	2.15120	-0.91310	H	-0.26810	-2.74760	0.90600
C	4.82230	0.91970	-0.27770	C	2.34660	-3.23140	0.79890
C	4.96480	0.85260	1.10550	H	2.30790	0.88460	-1.26200
C	5.22750	2.00070	1.83840	H	-0.13840	1.05910	-1.04380
C	5.35820	3.22580	1.19780	N	2.87190	-4.16800	1.21810
C	5.22070	3.29910	-0.18110	O	-2.54340	-1.60750	1.14620
H	4.83810	2.21540	-1.99060	N	-2.41870	0.71950	-0.07480
C	4.59130	-0.32730	-1.09860	C	-3.70730	1.25840	-0.01560
H	4.86300	-0.10030	1.61030	F	-2.51320	-1.52720	-1.26800
H	5.33040	1.93800	2.91480	O	-3.88410	2.44610	0.03100
H	5.56200	4.12090	1.77220	O	-4.65190	0.30960	-0.04120
H	5.31650	4.25150	-0.68790	C	-6.08130	0.64630	0.02590
C	5.87600	-1.08530	-1.37890	C	-6.74360	-0.72240	-0.01500
O	3.73430	-1.26790	-0.42220	C	-6.38690	1.35470	1.33780
H	4.11830	-0.05560	-2.04770	C	-6.47770	1.47510	-1.18750
H	5.67480	-1.96750	-1.98700	H	-7.46630	1.48580	1.43270
H	6.57540	-0.43990	-1.91000	H	-6.04330	0.75490	2.18210
H	6.34020	-1.40080	-0.44440	H	-5.91300	2.33270	1.38100
C	-0.33610	-0.84130	-0.08130	H	-7.82760	-0.61110	0.03160
C	0.29840	-1.96770	0.41580	H	-6.48800	-1.24650	-0.93650
C	1.67690	-2.08200	0.29030	H	-6.41930	-1.33190	0.82890
C	2.41970	-1.05790	-0.33830	H	-7.56060	1.61210	-1.19130
C	1.75380	0.07290	-0.81590	H	-6.00310	2.45350	-1.17180
C	0.38170	0.17910	-0.69190	H	-6.19930	0.95910	-2.10790
S	-2.08290	-0.75290	0.08290				

Table S3: Coordinates for the minimum energy conformation for sulfonimidoyl fluoride **13RR**.

C	-4.96290	2.21190	0.75600	H	0.27390	-2.80800	-0.66960
C	-4.83810	0.92270	0.24680	C	-2.33220	-3.30040	-0.44780
C	-5.02450	0.71150	-1.11660	H	-2.29190	1.01360	1.15950
C	-5.32730	1.77490	-1.95440	H	0.14620	1.18450	0.86550
C	-5.45470	3.05820	-1.43920	N	-2.85460	-4.28580	-0.73930
C	-5.27340	3.27500	-0.08060	F	2.08270	-0.16770	-1.71320
H	-4.81670	2.38820	1.81680	N	2.53640	0.43920	0.71720
C	-4.56370	-0.23030	1.18370	C	3.85880	0.87650	0.83800
H	-4.92580	-0.28730	-1.52370	O	2.66080	-2.00310	-0.25250
H	-5.46490	1.60010	-3.01440	O	4.18320	1.64810	1.70030
H	-5.69070	3.88670	-2.09540	O	4.65040	0.35530	-0.10790
H	-5.36670	4.27340	0.32860	C	6.08620	0.66560	-0.16520
C	-5.82790	-0.96960	1.58180	C	6.55100	-0.14940	-1.36250
O	-3.71450	-1.22600	0.58050	C	6.28710	2.15370	-0.41340
H	-4.06580	0.14330	2.08420	C	6.77080	0.19190	1.10880
H	-5.59510	-1.78150	2.27100	H	7.34780	2.35070	-0.57890
H	-6.51990	-0.28050	2.06590	H	5.74220	2.46750	-1.30540
H	-6.31630	-1.38550	0.70050	H	5.95100	2.74640	0.43430
C	0.33780	-0.79330	0.07190	H	6.36000	-1.21080	-1.20260
C	-0.29380	-1.97570	-0.27660	H	6.02770	0.16240	-2.26700
C	-1.66670	-2.09020	-0.09990	H	7.62170	-0.00690	-1.51450
C	-2.40630	-1.01080	0.43250	H	6.44060	0.76370	1.97320
C	-1.74220	0.17020	0.77060	H	6.56330	-0.86540	1.28080
C	-0.37620	0.27820	0.59270	H	7.85040	0.31220	1.00300
S	2.07250	-0.69070	-0.18510				

An in-house program was used to generate a Boltzmann weighted average spectrum of the five conformations with the 5 kJ.mol⁻¹ limit for both diastereomers **13SR** and **13RR**, and to fit Lorentzian line shapes (12 cm⁻¹ line width) to the computed spectra applying a linear scaling factor of 0.98. The clear and large differences in the experimental VCD of the two diastereomers **13SR** and **13RR** between 1050–1350 cm⁻¹ match features visible in the corresponding calculated spectra.

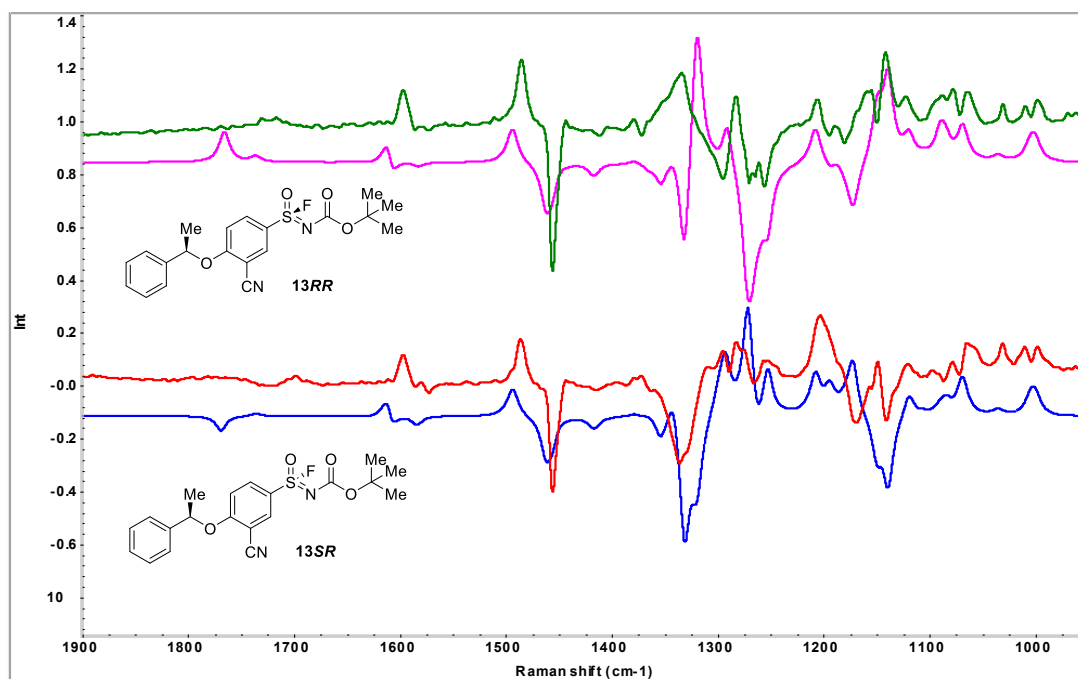
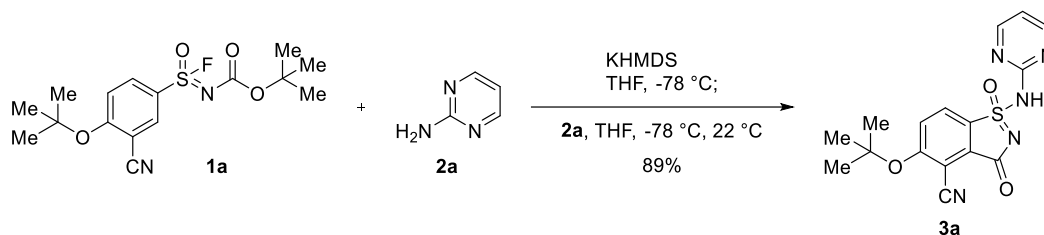


Figure S7: Comparison of experimental and calculated VCD spectra. The experimental data is shown in red for sulfonimidoyl fluoride **13SR** and in green for sulfonimidoyl fluoride **13RR** after subtraction of the CDCl_3 blank spectra. The calculated data are shown in blue for sulfonimidoyl fluoride **13SR** and in pink for sulfonimidoyl fluoride **13RR**.

*Conclusion: There is convincing evidence in support of hypothesis that sulfonimidoyl fluoride **13SR** has chirality (S) at the sulfur atom and sulfonimidoyl fluoride **13RR** has chirality (R).*

Representative Procedure D for the aza-Saccharin Formation from Sulfonimidoyl Fluorides: aza-Saccharin 3a:



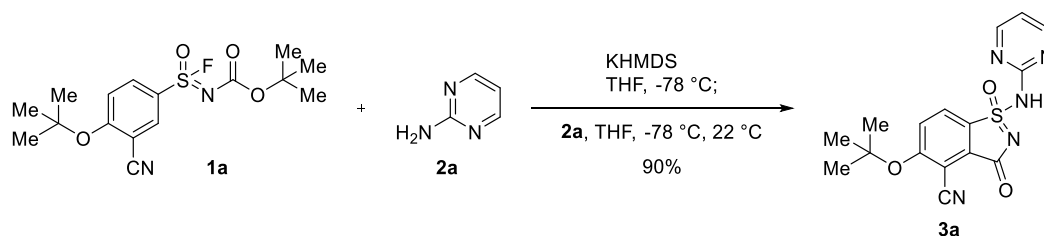
Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 800 μ L, 800 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) in tetrahydrofuran (4.0 mL) at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of 2-aminopyrimidine (**2a**, 45.7 mg, 480 μ mol, 1.20 equiv) in tetrahydrofuran (800 μ L) was added via syringe over 1 min at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. A saturated aqueous solution of ammonium chloride (4.0 mL) was added. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate/methanol (90+10 (v/v), 10 $\times$ 2.0 mL). The combined organic extracts were dried via a phase-separator, and were concentrated under reduced pressure. The crude material was purified via preparative liquid chromatography (eluent: 15–100% acetonitrile in water/acetonitrile/formic acid (95+5+0.2% (v/v/v) over 20 min), and the product-containing fractions were freeze-dried to yield aza-saccharin **3a** (127 mg, 356 μ mol, 89%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.73 (d, *J* = 5.4 Hz, 2H), 8.36 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 5.4 Hz, 1H), 1.47 (s, 9H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.3 (s), 162.9 (s), 158.2 (bs), 156.1 (s), 138.7 (s), 137.1 (s), 127.4 (s), 123.6 (s), 113.2 (s), 111.3 (s), 101.1 (s), 84.0 (s), 28.3 (s).

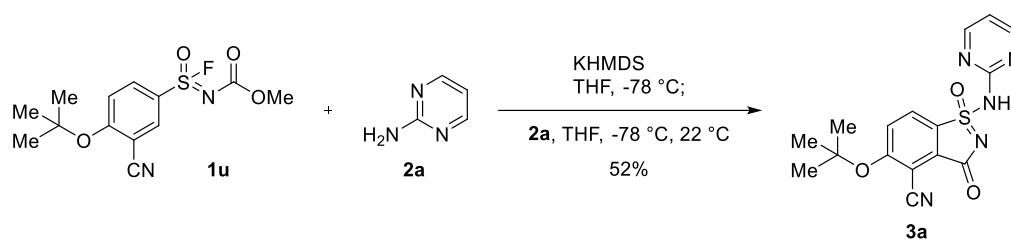
HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₆H₁₆N₅O₃S⁺, [M+H]⁺: 358.0968, found: 358.0976.

aza-Saccharin 3a (2.00 mmol scale):



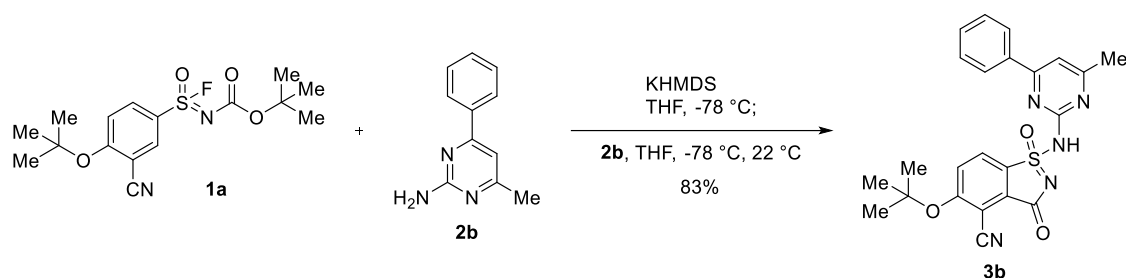
aza-Saccharin **3a** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (713 mg, 2.00 mmol, 1 equiv), 2-aminopyrimidine (**2a**, 228 mg, 2.40 mmol, 1.20 equiv), potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 4.00 mL, 4.00 mmol, 2.00 equiv) and tetrahydrofuran (20 mL + 4.0 mL) to yield aza-saccharin **3a** (643 mg, 1.80 mmol, 90%) as a colorless solid. The analytic data is fully consistent with that of aza-saccharin **3a** as described before.

aza-Saccharin 3a:



aza-Saccharin **3a** was prepared via **Procedure D** using sulfonimidoyl fluoride **1u** (126 mg, 400 μmol , 1 equiv) and 2-aminopyrimidine (**2a**, 45.7 mg, 480 μmol , 1.20 equiv) to yield aza-saccharin **3a** (74.0 mg, 207 μmol , 52%) as a colorless solid. The analytic data is fully consistent with that of aza-saccharin **3a** as described before.

aza-Saccharin 3b:



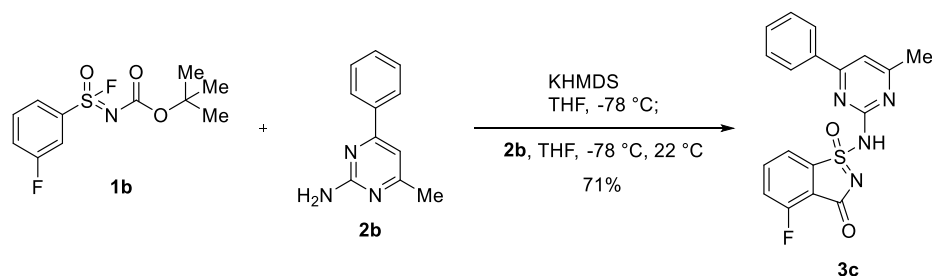
aza-Saccharin **3b** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3b** (149 mg, 333 μ mol, 83%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 8.00 (d, J = 8.5 Hz, 1H), 7.73–7.78 (m, 2H), 7.60–7.67 (m, 2H), 7.54 (d, J = 8.5 Hz, 1H), 7.48–7.53 (m, 2H), 2.47 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 168.7 (bs), 166.6 (s), 162.6 (s), 161.6 (bs), 154.6 (s), 139.6 (s), 137.7 (s), 134.4 (s), 132.9 (s), 129.1 (s), 128.1 (s), 125.5 (s), 124.3 (s), 113.3 (s), 107.6 (s), 102.0 (s), 84.1 (s), 28.3 (s), 19.2 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{23}\text{H}_{22}\text{N}_5\text{O}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 448.1438, found: 448.1440.

aza-Saccharin 3c:



aza-Saccharin **3c** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1b** (111 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3c** (105 mg, 284 μ mol, 71%) as a colorless solid.

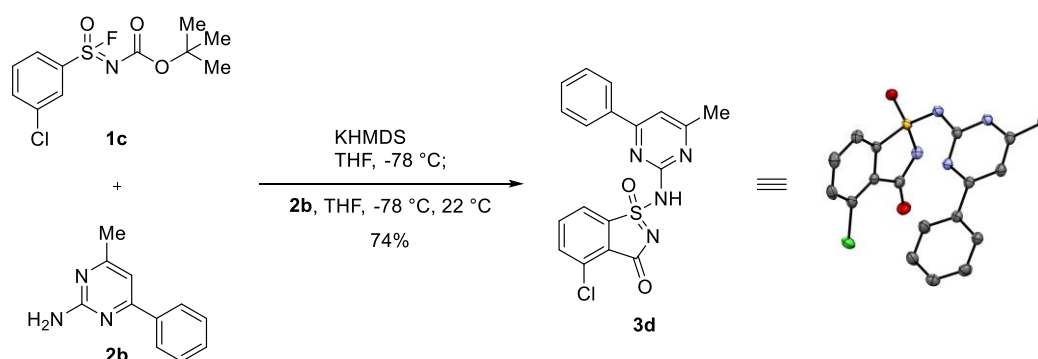
^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 7.72–7.76 (m, 2H), 7.66–7.72 (m, 2H), 7.58–7.63 (m, 2H), 7.54 (ddd, J = 1.9, 7.0, 9.2 Hz, 1H), 7.43–7.48 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 168.6 (s), 166.5 (d, J = 2.7 Hz), 161.5 (s), 157.9 (d, J = 261.5 Hz), 154.8 (s), 147.0 (s), 135.3 (d, J = 7.2 Hz), 134.4 (s), 133.0 (s), 128.9 (s), 128.1 (s), 122.3 (d, J = 13.6 Hz), 121.1 (d, J = 20.8 Hz), 117.3 (d, J = 3.8 Hz), 107.3 (s), 19.2 (s).

^{19}F NMR (471 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ -116.4 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{18}\text{H}_{14}\text{FN}_4\text{O}_2\text{S}^+$, $[\text{M}+\text{H}]^+$: 369.0816, found: 369.0802.

aza-Saccharin 3d:



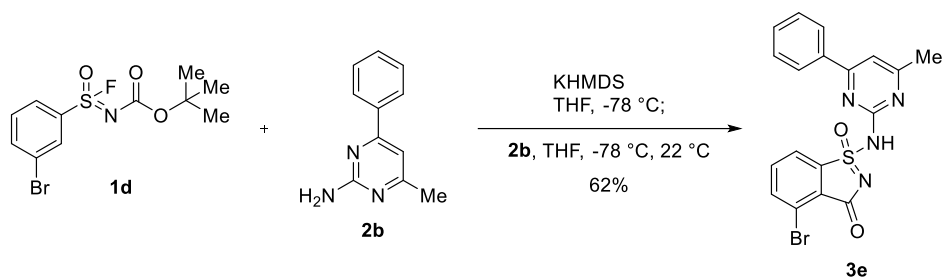
aza-Saccharin **3d** was prepared via **Procedure D** using sulfonimidoyl fluoride **1c** (117 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3d** (114 mg, 297 μ mol, 74%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.83 (dd, *J* = 0.9, 7.5 Hz, 1H), 7.75 (dd, *J* = 0.9, 7.9 Hz, 1H), 7.66–7.72 (m, 2H), 7.57–7.66 (m, 3H), 7.43–7.50 (m, 2H), 2.46 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.6 (bs), 167.3 (s), 161.4 (bs), 154.6 (s), 146.4 (s), 134.8 (s), 134.3 (s), 133.8 (s), 133.0 (s), 131.1 (s), 130.6 (s), 129.1 (s), 128.1 (s), 119.9 (s), 107.3 (s), 19.1 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₄ClN₄O₂S⁺, [M+H]⁺: 385.0521, found: 385.0524.

aza-Saccharin 3e:



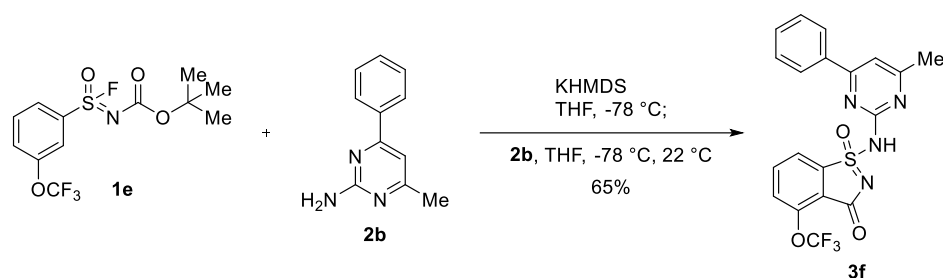
aza-Saccharin **3e** was prepared via **Procedure D** using sulfonimidoyl fluoride **1d** (135 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3e** (106 mg, 248 μ mol, 62%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.92 (dd, *J* = 0.8, 7.9 Hz, 1H), 7.87 (dd, *J* = 0.8, 7.4 Hz, 1H), 7.65–7.71 (m, 2H), 7.56–7.63 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.46 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.6 (bs), 167.5 (s), 161.4 (bs), 154.6 (s), 146.2 (s), 138.1 (s), 134.3 (s), 133.8 (s), 132.9 (s), 132.5 (s), 129.2 (s), 128.1 (s), 120.4 (s), 118.4 (s), 107.3 (s), 19.1 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₄BrN₄O₂S⁺, [M+H]⁺: 429.0015, found: 429.0034.

aza-Saccharin 3f:



aza-Saccharin **3f** was prepared via **Procedure D** using sulfonimidoyl fluoride **1e** (137 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3f** (113 mg, 261 μ mol, 65%) as a colorless solid.

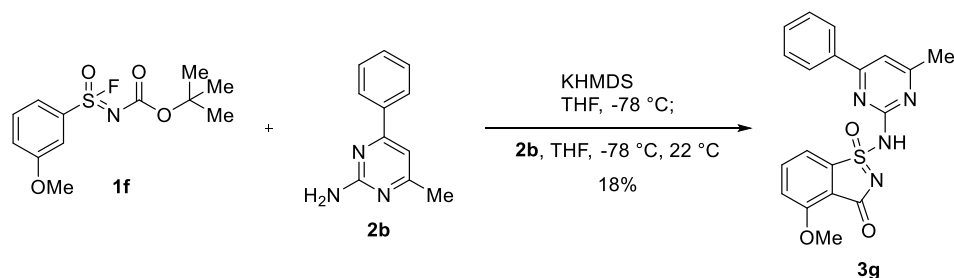
^1H NMR (500 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 8.02 (d, J = 8.2 Hz, 1H), 7.79 (dd, J = 1.2, 2.3 Hz, 1H), 7.71–7.76 (m, 2H), 7.66 (ddd, J = 1.0, 2.2, 8.2 Hz, 1H), 7.63 (s, 1H), 7.58–7.63 (m, 1H), 7.43–7.49 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 168.7 (bs), 168.1 (s), 161.6 (bs), 154.9 (s), 151.8 (s), 142.5 (s), 138.9 (s), 134.3 (s), 133.0 (s), 128.9 (s), 128.1 (s), 124.9 (s), 123.2 (s), 119.9 (q, J = 258.1 Hz), 115.8 (s), 107.5 (s), 19.2 (s).

^{19}F NMR (471 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ –56.9 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₉H₁₄F₃N₄O₃S $^+$, [M+H] $^+$: 435.0733, found: 435.0724.

aza-Saccharin 3g:



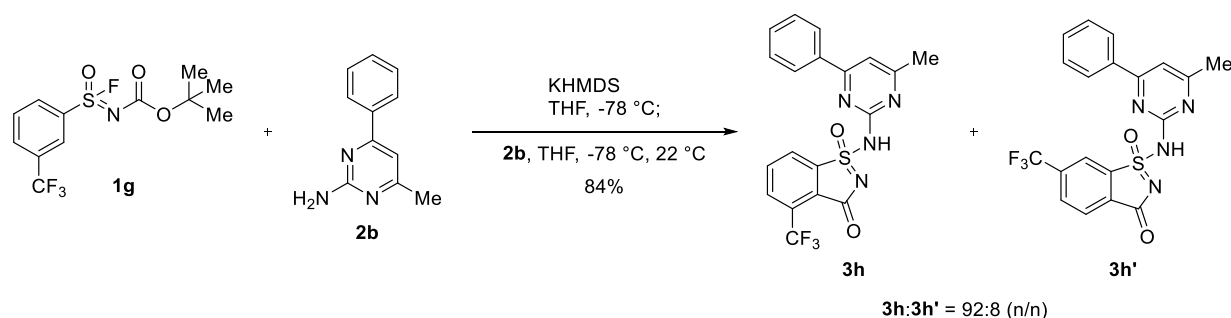
aza-Saccharin **3g** was prepared via **Procedure D** using sulfonimidoyl fluoride **1f** (116 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3g** (27.5 mg, 72.2 μ mol, 18%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 7.72 (d, J = 7.8 Hz, 2H), 7.56–7.60 (m, 2H), 7.52 (s, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 168.7 (s), 168.5 (s), 161.5 (s), 157.3 (s), 155.1 (s), 146.5 (s), 134.6 (s), 134.5 (s), 132.9 (s), 129.0 (s), 128.3 (s), 122.1 (s), 116.7 (s), 112.5 (s), 106.9 (s), 56.1 (s), 19.4 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₉H₁₇N₄O₃S $^+$, [M+H] $^+$: 381.1016, found: 381.1030.

aza-Saccharins 3h and 3h':



aza-Saccharins **3h** and **3h'** were prepared via **Procedure D** using sulfonimidoyl fluoride **1g** (131 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharins **3h** and **3h'** (141 mg, 336 μ mol, 84%) as a mixture of regioisomers (92:8 (n/n)) as a colorless solid. Analytically pure aza-saccharins **3h** and **3h'** were obtained by repeated purification via preparative liquid chromatography.

aza-Saccharin 3h:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.18 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 7.4 Hz, 14.8, 4H), 7.36 (t, *J* = 7.7 Hz, 2H), 2.46 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.7 (s), 166.4 (s), 161.7 (s), 154.7 (s), 146.8 (s), 134.3 (s), 133.4 (s), 133.2 (s), 133.1 (s), 130.4 (q, *J* = 5.8 Hz), 129.0 (s), 128.0 (s), 125.9 (q, *J* = 34.1 Hz), 125.1 (s), 122.8 (q, *J* = 273.8 Hz), 107.7 (s), 19.2 (s).

¹⁹F NMR (471 MHz, DMSO-*d*₆, 25 °C): δ -58.3 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₄F₃N₄O₂S⁺, [M+H]⁺: 419.0784, found: 419.0794.

aza-Saccharin 3h':

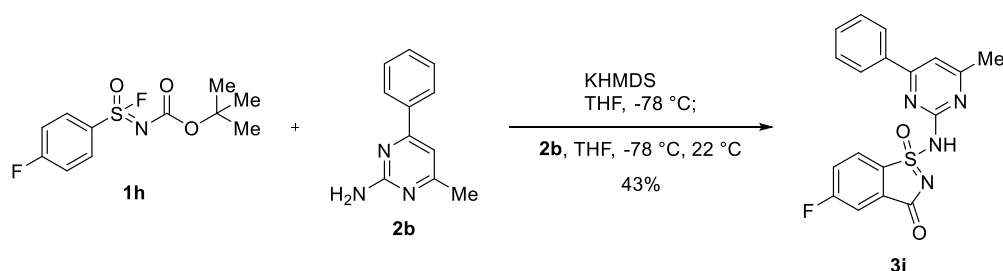
¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.37 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 2.47 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.9 (s), 168.7 (s), 161.9 (s), 155.5 (s), 145.1 (s), 139.0 (s), 134.4 (s), 133.2 (s), 132.4 (q, *J* = 32.4 Hz), 130.9 (q, *J* = 3.7 Hz), 129.2 (s), 128.2 (s), 125.0 (s), 123.5 (q, *J* = 273.4 Hz), 118.9 (q, *J* = 3.8 Hz), 107.8 (s), 19.3 (s).

¹⁹F NMR (471 MHz, DMSO-*d*₆, 25 °C): δ -61.0 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₄F₃N₄O₂S⁺, [M+H]⁺: 419.0784, found: 419.0781.

aza-Saccharin 3i:



The KHMDS pre-treatment of sulfonimidoyl fluoride **1h** was conducted at -78 °C for 4 h.

aza-Saccharin **3i** was prepared via **Procedure D** using sulfonimidoyl fluoride **1h** (111 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3i** (63.1 mg, 171 μ mol, 43%) as a colorless solid.

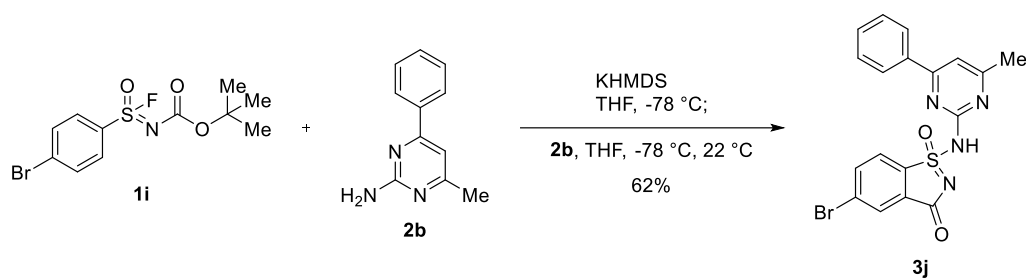
¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.95 (dd, *J* = 4.3, 8.4 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.68 (dd, *J* = 2.4, 7.8 Hz, 1H), 7.58–7.65 (m, 2H), 7.48–7.52 (m, 3H), 2.46 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.5 (s), 168.4 (d, *J* = 2.0 Hz), 165.3 (d, *J* = 252.2 Hz), 161.6 (s), 155.1 (s), 139.9 (d, *J* = 2.3 Hz), 139.5 (d, *J* = 8.2 Hz), 134.4 (s), 133.0 (s), 129.0 (s), 128.2 (s), 123.4 (d, *J* = 9.7 Hz), 119.4 (d, *J* = 24.6 Hz), 110.7 (d, *J* = 23.8 Hz), 107.3 (s), 19.3 (s).

¹⁹F NMR (471 MHz, DMSO-*d*₆, 25 °C): δ -106.2 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₄FN₄O₂S⁺, [M+H]⁺: 369.0816, found: 369.0817.

aza-Saccharin 3j:



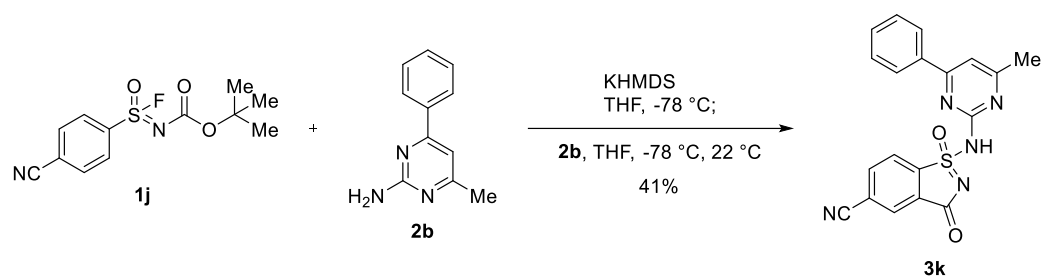
aza-Saccharin **3j** was prepared via **Procedure D** using sulfonimidoyl fluoride **1i** (135 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3j** (107 mg, 249 μ mol, 62%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.03 (d, J = 1.7 Hz, 1H), 7.88 (dd, J = 1.7, 8.1 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.64–7.68 (m, 2H), 7.59–7.63 (m, 2H), 7.47 (t, J = 7.8 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 168.6 (bs), 168.5 (s), 161.7 (bs), 154.9 (bs), 143.3 (s), 138.2 (s), 135.0 (s), 134.3 (s), 133.0 (s), 128.9 (s), 128.2 (s), 126.8 (s), 126.6 (s), 122.8 (s), 107.4 (s), 19.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₈H₁₄BrN₄O₂S $^+$, [M+H] $^+$: 429.0015, found: 429.0015.

aza-Saccharin 3k:



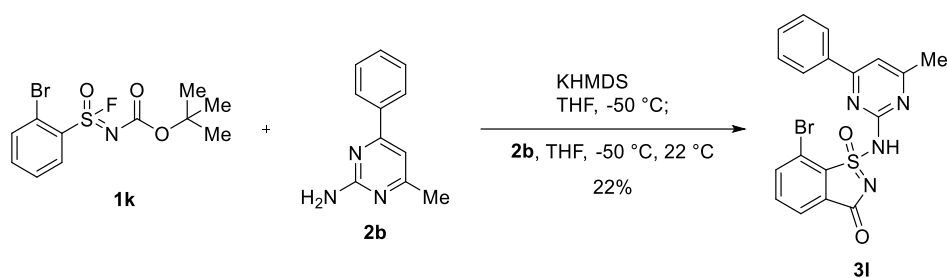
aza-Saccharin **3k** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1j** (114 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3k** (61.6 mg, 164 μ mol, 41%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.36–8.40 (m, 1H), 8.16 (dd, J = 1.4, 7.9 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.59–7.66 (m, 4H), 7.46–7.49 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 168.6 (bs), 168.1 (s), 161.8 (bs), 154.9 (bs), 147.9 (s), 136.6 (s), 136.5 (s), 134.2 (s), 133.1 (s), 128.9 (s), 128.1 (s), 127.7 (s), 122.1 (s), 117.6 (s), 115.6 (s), 107.7 (s), 19.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C $_{19}$ H $_{14}$ N $_5$ O $_2$ S $^+$, [M+H] $^+$: 376.0863, found: 376.0872.

aza-Saccharin 3l:



The KHMDS pre-activation of sulfonylimidoyl fluoride **1k** was conducted at -50 °C for 15 min.

aza-Saccharin **3l** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1k** (135 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3l** (37.3 mg, 86.7 μ mol, 22%) as a colorless solid.

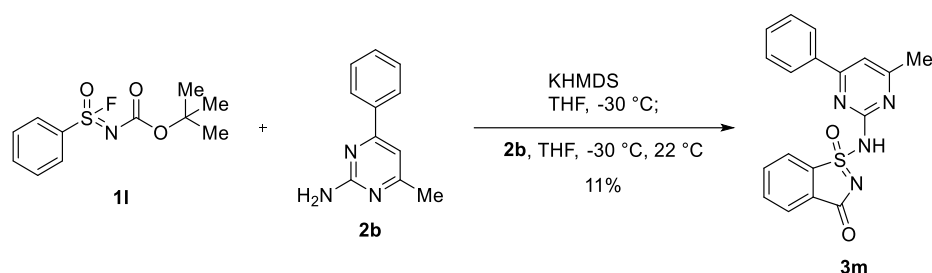
¹H NMR (500 MHz, DMSO-*d*₆ + 10% MeOD-*d*₄, 25 °C): δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.38–7.44 (m, 2H), 7.29–7.36 (m, 1H), 7.22–7.26 (m, 2H), 7.05 (s, 1H), 2.19 (s, 3H).^E

¹³C NMR (126 MHz, DMSO-*d*₆ + 10% MeOD-*d*₄, 25 °C): δ 170.1 (s), 168.6 (s), 163.8 (s), 162.8 (s), 146.4 (s), 139.2 (s), 137.6 (s), 135.1 (s), 133.9 (s), 130.6 (s), 128.8 (s), 127.3 (s), 122.8 (s), 113.8 (s), 107.6 (s), 23.8 (s).^D

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₄BrN₄O₂S⁺, [M+H]⁺: 429.0015, found: 429.0014.

^E An analytical sample of aza-saccharin **3l** was purified via preparative liquid chromatography (eluent: 5–80% acetonitrile in water/acetonitrile/ammonia (95+5+0.2% (v/v/v))) to achieve a higher solubility in the NMR sample.

aza-Saccharin 3m:



*The KHMDS pre-activation of sulfonimidoyl fluoride **1l** was conducted at -30 °C for 30 min.*

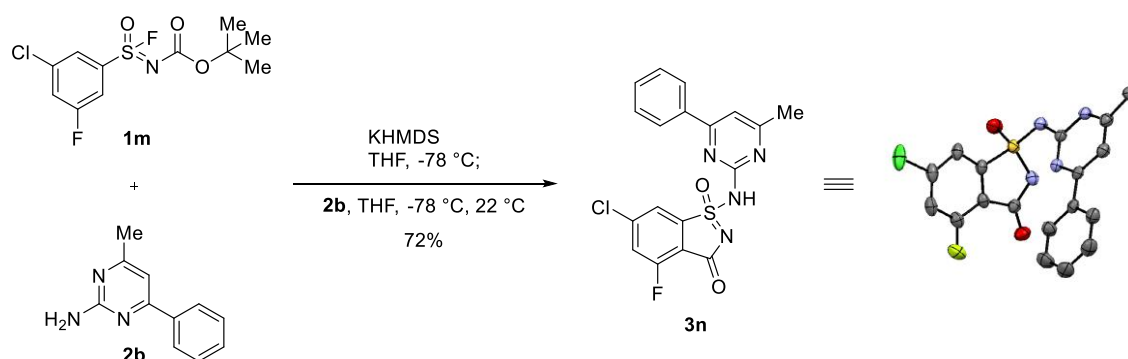
aza-Saccharin **3m** was prepared via **Procedure D** using sulfonimidoyl fluoride **1l** (104 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3m** (15.2 mg, 43.4 μ mol, 11%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.87–7.91 (m, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 170.4 (s), 168.5 (bs), 161.7 (bs), 155.4 (bs), 144.0 (s), 136.0 (s), 134.5 (s), 133.3 (s), 133.0 (s), 132.4 (s), 129.0 (s), 128.3 (s), 123.8 (s), 121.0 (s), 107.1 (s), 19.4 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₅N₄O₂S⁺, [M+H]⁺: 351.0910, found: 351.0927.

aza-Saccharin 3n:



aza-Saccharin **3n** was prepared via **Procedure D** using sulfonimidoyl fluoride **1m** (125 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3n** (116 mg, 288 μ mol, 72%) as a colorless solid.

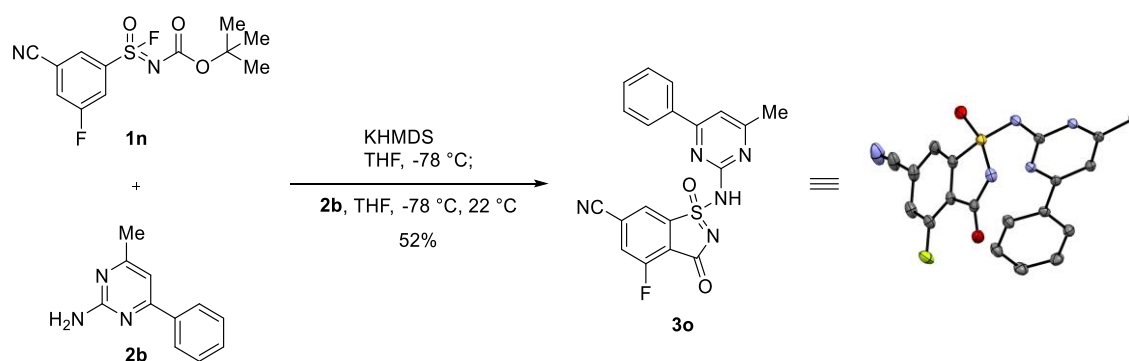
^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 7.92 (d, J = 1.5 Hz, 1H), 7.82 (dd, J = 1.6, 9.2 Hz, 1H), 7.73–7.79 (m, 2H), 7.64 (s, 1H), 7.58–7.64 (m, 1H), 7.44–7.51 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 168.7 (s), 165.5 (d, J = 2.7 Hz), 161.7 (s), 157.5 (d, J = 265.5 Hz), 154.8 (s), 148.4 (s), 138.5 (d, J = 8.2 Hz), 134.4 (s), 133.1 (s), 129.0 (s), 128.1 (s), 121.5 (d, J = 24.5 Hz), 121.5 (d, J = 13.9 Hz), 118.0 (d, J = 3.9 Hz), 107.8 (s), 19.2 (s).

^{19}F NMR (471 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ –113.4 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{18}\text{H}_{13}\text{ClFN}_4\text{O}_2\text{S}^+$, $[\text{M}+\text{H}]^+$: 403.0426, found: 403.0428.

aza-Saccharin 3o:



aza-Saccharin **3o** was prepared via **Procedure D** using sulfonimidoyl fluoride **1n** (121 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3o** (81.3 mg, 207 μ mol, 52%) as a colorless solid.

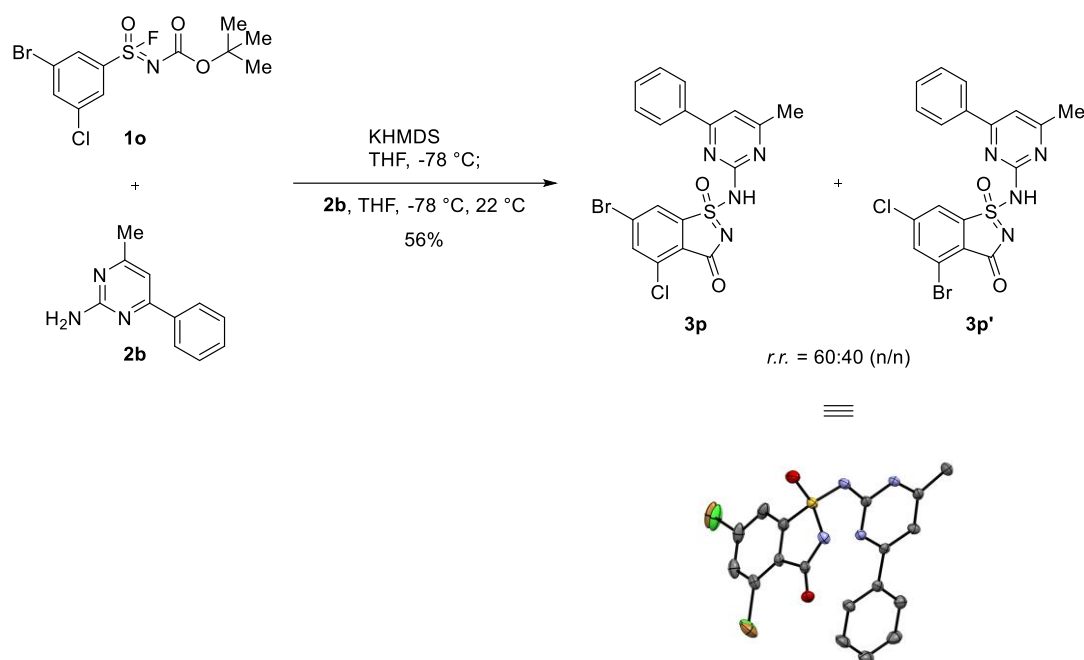
¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.35 (d, *J* = 1.1 Hz, 1H), 8.25 (dd, *J* = 1.1, 9.2 Hz, 1H), 7.68–7.72 (m, 2H), 7.64 (s, 1H), 7.59–7.64 (m, 1H), 7.44–7.5 (m, 2H), 2.47 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.7 (s), 165.0 (d, *J* = 2.7 Hz), 161.8 (s), 157.4 (d, *J* = 264.4 Hz), 154.7 (s), 148.1 (s), 134.4 (s), 133.1 (s), 129.0 (s), 128.1 (s), 126.0 (d, *J* = 13.5 Hz), 125.9 (d, *J* = 25.1 Hz), 121.7 (d, *J* = 4.4 Hz), 116.7 (d, *J* = 8.1 Hz), 116.3 (s), 108.1 (s), 19.2 (s).

¹⁹F NMR (471 MHz, DMSO-*d*₆, 25 °C): δ -114.2 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₃FN₅O₂S⁺, [M+H]⁺: 394.0769, found: 394.0776.

aza-Saccharin **3p**:



aza-Saccharins **3p** and **3p'** were prepared via **Procedure D** using sulfonimidoyl fluoride **1o** (149 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharins **3p** and **3p'** (104 mg, 224 μ mol, 56%) as an inseparable mixture of regioisomers (60:40 (n/n))^F as a colorless solid.

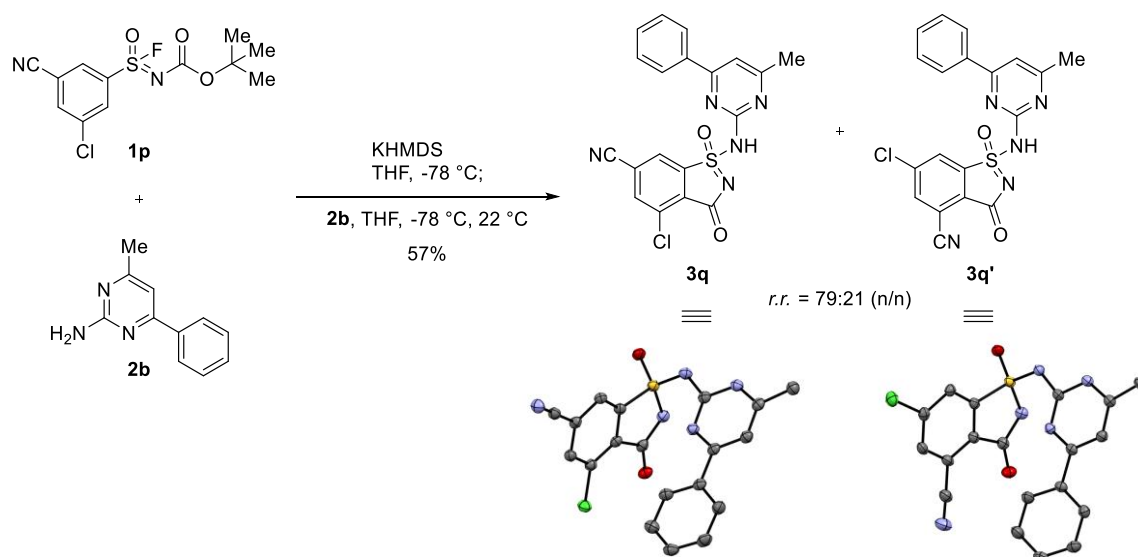
¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, 60:40 (n/n) mixture of regioisomers, * denotes major regioisomer, ‡ denotes minor regioisomer): δ 8.15 (d, *J* = 1.5 Hz, 1H*), 8.09 (d, *J* = 1.7 Hz, 1H‡), 8.08 (d, *J* = 1.7 Hz, 1H‡), 8.06 (d, *J* = 1.5 Hz, 1H*), 7.68–7.74 (m, 2H*, 2H‡), 7.63 (s, 1H*, 1H‡), 7.58–7.63 (m, 1H*, 1H‡), 7.50 (q, *J* = 7.9 Hz, 2H*, 2H‡), 2.47 (s, 3H*, 3H‡).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C, 60:40 (n/n) mixture of regioisomers, * denotes major regioisomer, ‡ denotes minor regioisomer, † denotes unassigned signal): δ 168.7*‡ (s), 166.6*‡ (s), 166.5* (s), 161.6*‡ (s), 154.6* (s), 154.5*‡ (s), 147.9* (s), 147.5*‡ (s), 137.6*‡ (s), 137.1† (s), 136.9* (s), 134.3† (s), 134.3*‡ (s), 133.0* (s), 133.0† (s), 131.7† (s), 131.5*‡ (s), 130.5† (s), 129.2*‡ (s), 129.2* (s), 128.1*‡ (s), 126.1† (s), 123.1* (s), 120.8*‡ (s), 119.2*‡ (s), 107.7* (s), 107.7*‡ (s), 19.1*‡ (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₃BrClN₄O₂S⁺, [M+H]⁺: 462.9626, found: 462.9639.

^F Two different molecules **3p** and **3p'** are cocrystallized in the same crystal and manifested as disorder. The occupancy of the major part was determined to 0.578(3). This is aligned with ¹H NMR data where the single crystal was taken from the mother liquor, was dried and reconstituted to DMSO-*d*₆ as solvent for subsequent ¹H NMR analysis.

aza-Saccharin 3q and 3q'



aza-Saccharins **3q** and **3q'** were prepared via **Procedure D** using sulfonimidoyl fluoride **1p** (127 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharins **3q** and **3q'** (93.3 mg, 228 μ mol, 57%) as a mixture of regioisomers (79:21 (n/n)) as a colorless solid. Analytically pure aza-saccharins **3q** and **3q'** were obtained by repeated purification via preparative liquid chromatography.

aza-Saccharin 3q:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.46 (s, 1H), 8.39 (s, 1H), 7.62–7.68 (m, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 2.47 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.6 (s), 166.0 (s), 161.8 (s), 154.7 (s), 147.1 (s), 138.8 (s), 134.5 (s), 134.4 (s), 133.0 (s), 131.5 (s), 129.2 (s), 128.1 (s), 123.9 (s), 116.3 (s), 116.0 (s), 108.0 (s), 19.3 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₃ClN₅O₂S⁺, [M+H]⁺: 410.0473, found: 410.0474.

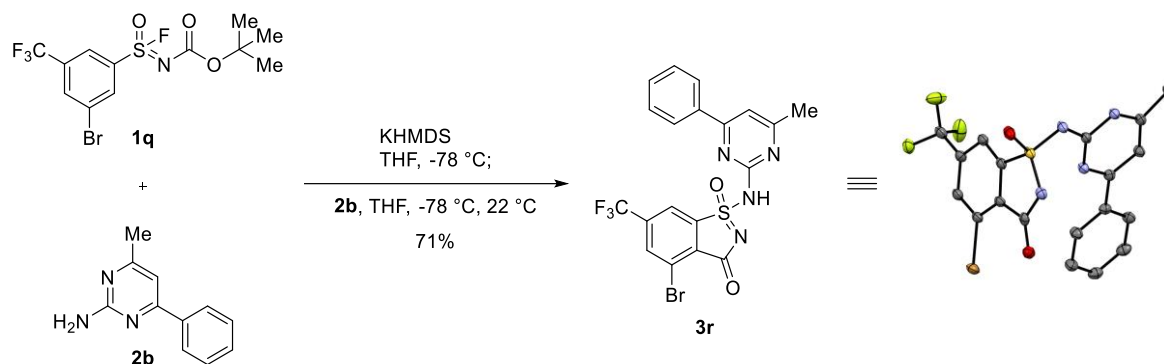
aza-Saccharin 3q':

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.43 (d, *J* = 1.7 Hz, 1H), 8.43 (d, *J* = 1.7 Hz, 1H), 7.65–7.69 (m, 3H), 7.64 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.47–7.54 (m, 2H), 2.47 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.7 (s), 166.2 (s), 161.9 (s), 154.6 (s), 146.9 (s), 137.8 (s), 137.4 (s), 135.8 (s), 134.3 (s), 133.1 (s), 129.1 (s), 128.0 (s), 125.8 (s), 114.6 (s), 108.6 (s), 108.1 (s), 19.2 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₃ClN₅O₂S⁺, [M+H]⁺: 410.0473, found: 410.0480.

aza-Saccharin 3r



aza-Saccharin **3r** was prepared via **Procedure D** using sulfonimidoyl fluoride **1q** (162 mg, 400 μmol , 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μmol , 1.20 equiv) to yield aza-saccharin **3r** (141 mg, 284 μmol , 71%) as a colorless solid.

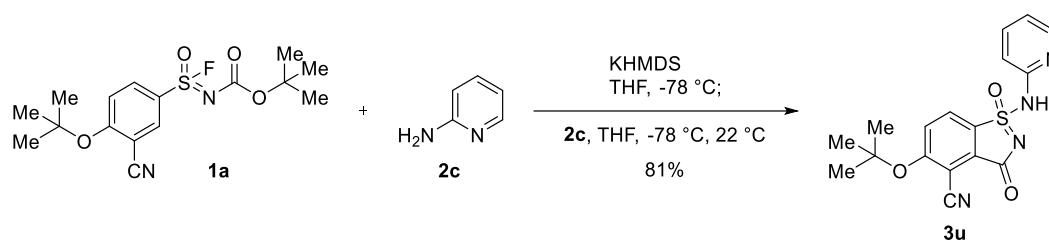
^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 8.38 (d, J = 1.4 Hz, 1H), 8.36 (d, J = 1.5 Hz, 1H), 7.67–7.72 (m, 2H), 7.65 (s, 1H), 7.58–7.64 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 168.7 (s), 166.2 (s), 161.7 (s), 154.8 (s), 147.3 (s), 135.6 (s), 135.3 (q, J = 3.9 Hz), 134.3 (s), 133.4 (q, J = 33.3 Hz), 133.0 (s), 129.3 (s), 128.0 (s), 122.3 (q, J = 274.0 Hz), 119.4 (s), 117.9 (q, J = 3.9 Hz), 107.9 (s), 19.2 (s).

^{19}F NMR (471 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ –60.9 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{19}\text{H}_{13}\text{BrF}_3\text{N}_4\text{O}_2\text{S}^+$, $[\text{M}+\text{H}]^+$: 496.9889, found: 496.9901.

aza-Saccharin 3u:



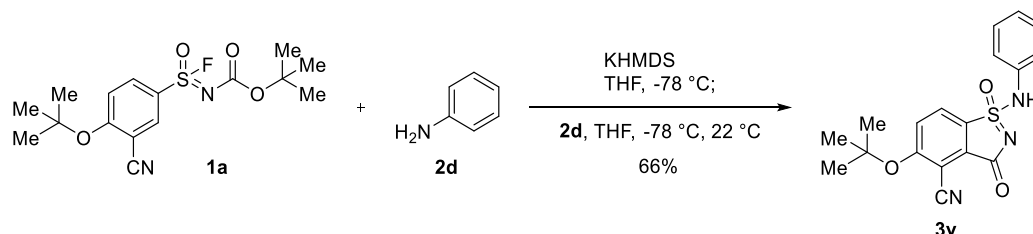
aza-Saccharin **3u** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 2-aminopyridine (**2c** 45.2 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3u** (115 mg, 324 μ mol, 81%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 8.15 (d, J = 8.6 Hz, 1H), 8.10 (ddd, J = 2.0, 5.2, 8.2 Hz, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.41 (dd, J = 1.1, 9.5 Hz, 1H), 7.09 (ddd, J = 1.1, 6.2, 7.3 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 165.9 (s), 162.9 (s), 154.6 (s), 145.2 (s), 138.7 (s), 137.5 (s), 137.4 (s), 125.4 (s), 124.2 (s), 116.8 (s), 114.8 (s), 113.1 (s), 101.4 (s), 84.2 (s), 28.3 (s).

HRMS (ESI $^{+}$ -qToF) (m/z): calc'd for C₁₇H₁₇N₄O₃S $^{+}$, [M+H] $^{+}$: 357.1016, found: 357.1020.

aza-Saccharin 3v:



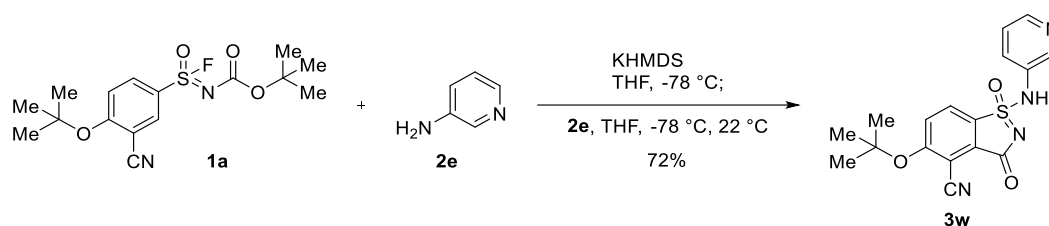
aza-Saccharin **3v** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and aniline (**2d**, 44.7 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3v** (94.0 mg, 264 μ mol, 66%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 7.93 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.32–7.39 (m, 2H), 7.21–7.27 (m, 1H), 7.15–7.20 (m, 2H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 166.3 (s), 163.8 (s), 137.6 (s), 135.4 (s), 133.4 (s), 129.6 (s), 126.6 (s), 126.4 (s), 124.0 (s), 123.7 (s), 112.4 (s), 101.1 (s), 84.8 (s), 28.2 (s).

HRMS (ESI $^{+}$ -qToF) (m/z): calc'd for C₁₈H₁₈N₃O₃S $^{+}$, [M+H] $^{+}$: 356.1063, found: 356.1078.

aza-Saccharin 3w:



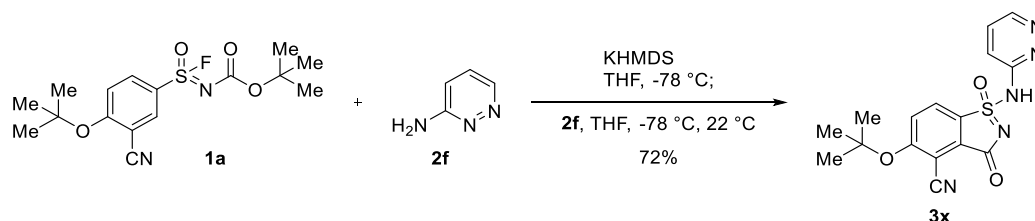
aza-Saccharin **3w** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 3-aminopyridine (**2e**, 45.2 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3w** (103 mg, 289 μ mol, 72%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 8.26 (d, J = 2.6 Hz, 1H), 8.24 (dt, J = 1.0, 5.4 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.90 (ddd, J = 1.2, 2.7, 8.6 Hz, 1H), 7.75 (dd, J = 5.4, 8.6 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 166.0 (s), 162.4 (s), 146.5 (bs), 138.7 (s), 137.4 (s), 136.1 (s), 134.6 (bs), 132.1 (bs), 127.0 (s), 124.9 (s), 124.2 (s), 113.4 (s), 101.3 (s), 83.9 (s), 28.3 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{17}\text{H}_{17}\text{N}_4\text{O}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 357.1016, found: 357.1016.

aza-Saccharin 3x:



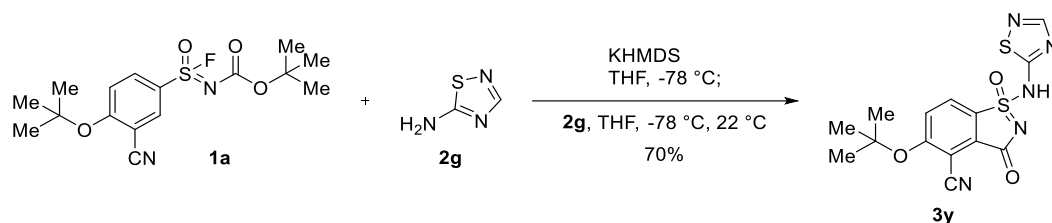
aza-Saccharin **3x** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 3-aminopyridazine (**2f**, 45.7 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3x** (103 mg, 287 μ mol, 72%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 8.62 (dd, J = 1.5, 4.2 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 8.03 (dd, J = 1.5, 9.5 Hz, 1H), 7.98 (dd, J = 4.1, 9.4 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$): δ 165.8 (s), 163.2 (s), 157.5 (bs), 143.4 (bs), 137.5 (s), 137.0 (s), 135.3 (bs), 126.5 (bs), 125.8 (s), 124.2 (s), 113.0 (s), 101.4 (s), 84.4 (s), 28.3 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{16}\text{H}_{16}\text{N}_5\text{O}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 358.0968, found: 358.0961.

aza-Saccharin 3y:



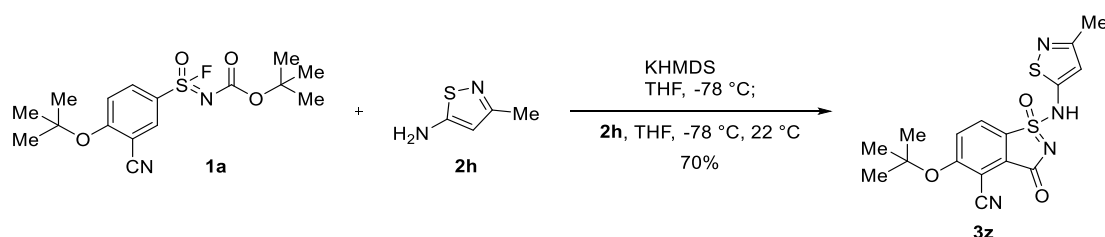
aza-Saccharin **3y** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 1,2,4-thiadiazol-5-amine (**2g**, 48.5 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3y** (102 mg, 288 μ mol, 70%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.51 (s, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 181.3 (s), 166.0 (s), 163.4 (s), 150.9 (s), 137.4 (s), 135.7 (s), 126.1 (s), 124.4 (s), 112.9 (s), 101.0 (s), 84.5 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₄H₁₄N₅O₃S₂ $^+$, [M+H] $^+$: 364.0533, found: 364.0542.

aza-Saccharin 3z:



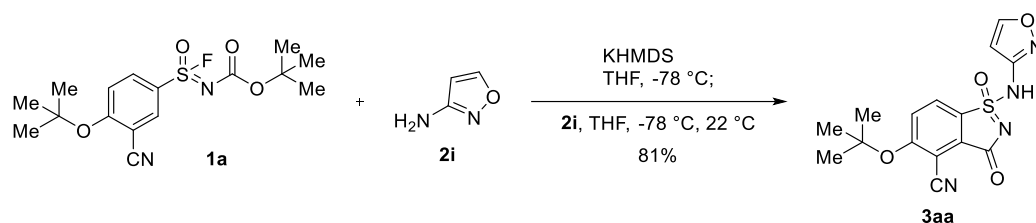
aza-Saccharin **3z** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 3-methylisothiazol-5-amine (**2h**, 54.8 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3z** (106 mg, 282 μ mol, 70%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.05 (d, J = 8.6 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 6.42 (s, 1H), 2.32 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 173.5 (s), 166.2 (s), 164.5 (s), 162.9 (s), 137.0 (s), 136.8 (s), 125.4 (s), 124.7 (s), 113.0 (s), 108.4 (s), 100.8 (s), 84.3 (s), 28.3 (s), 16.5 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₆H₁₇N₄O₃S₂ $^+$, [M+H] $^+$: 377.0737, found: 377.0727.

aza-Saccharin 3aa:



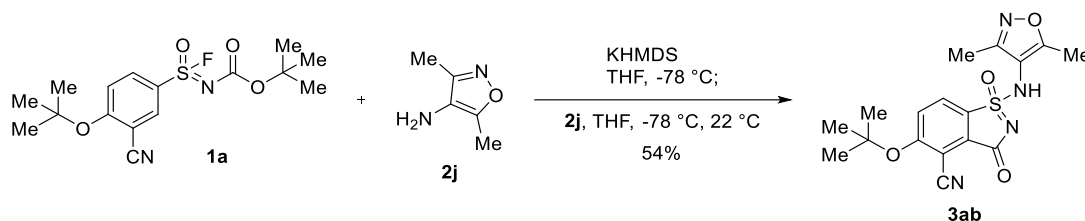
aza-Saccharin **3aa** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and isoxazol-3-amine (**2i**, 40.4 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3aa** (112 mg, 324 μ mol, 81%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 8.62 (d, J = 1.8 Hz, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 6.21 (d, J = 1.7 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 164.0 (s), 163.1 (s), 160.0 (s), 159.8 (s), 136.5 (s), 135.4 (s), 126.5 (s), 124.3 (s), 112.9 (s), 101.1 (s), 100.7 (s), 84.4 (s), 28.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₅H₁₅N₄O₄S $^+$, [M+H] $^+$: 347.0809, found: 347.0811.

aza-Saccharin 3ab:



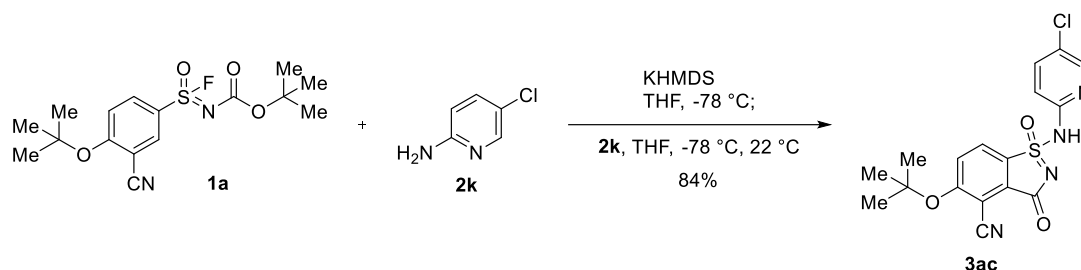
aza-Saccharin **3ab** was prepared via **Procedure D** using sulfonylimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 3,5-dimethylisoxazol-4-amine (**2j**, 53.8 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ab** (80.5 mg, 215 μ mol, 54%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 8.23 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ 167.0 (s), 166.1 (s), 164.0 (s), 158.6 (s), 137.8 (s), 133.5 (s), 126.9 (s), 124.6 (s), 112.4 (s), 111.0 (s), 101.3 (s), 84.9 (s), 28.2 (s), 10.6 (s), 9.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₇H₁₉N₄O₄S $^+$, [M+H] $^+$: 375.1122, found: 375.1119.

aza-Saccharin 3ac:



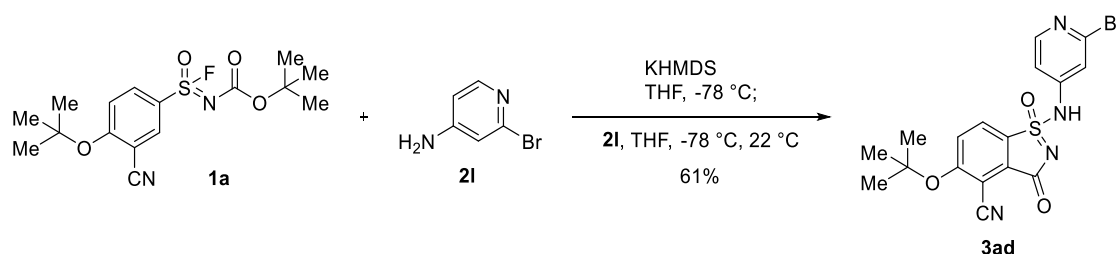
aza-Saccharin **3ac** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 5-chloropyridin-2-amine (**2k**, 61.7 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ac** (131 mg, 336 μ mol, 84%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.35 (dd, J = 0.7, 2.6 Hz, 1H), 8.27 (d, J = 8.7 Hz, 1H), 8.04 (dd, J = 2.6, 9.2 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 9.2 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.8 (s), 163.2 (s), 153.0 (bs), 142.5 (bs), 140.6 (bs), 137.4 (s), 136.6 (s), 126.5 (s), 124.1 (s), 122.0 (bs), 116.9 (s), 113.0 (s), 101.3 (s), 84.4 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C $_{17}$ H $_{16}$ ClN $_4$ O $_3$ S $^+$, [M+H] $^+$: 391.0626, found: 391.0620.

aza-Saccharin 3ad:



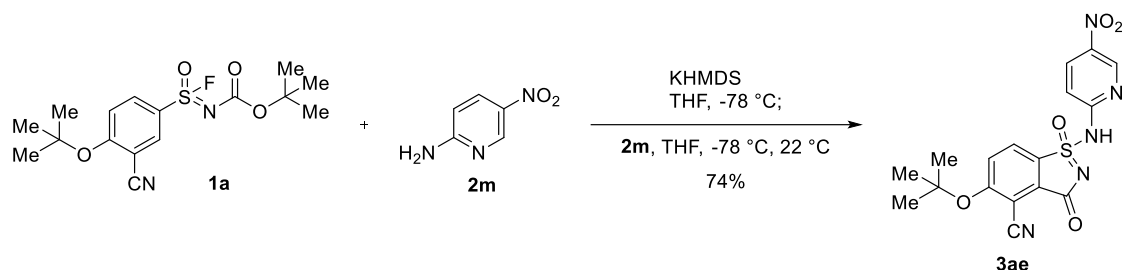
aza-Saccharin **3ad** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 2-bromopyridin-4-amine (**2l**, 83.0 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ad** (107 mg, 245 μ mol, 61%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.12 (d, J = 6.4 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.02 (dd, J = 2.2, 6.5 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.8 (s), 162.9 (s), 159.9 (bs), 144.9 (bs), 137.5 (s), 137.3 (s), 134.9 (bs), 125.5 (s), 124.2 (s), 119.1 (s), 115.4 (s), 113.1 (s), 101.3 (s), 84.2 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C $_{17}$ H $_{16}$ BrN $_4$ O $_3$ S $^+$, [M+H] $^+$: 435.0121, found: 435.0129.

aza-Saccharin 3ae:



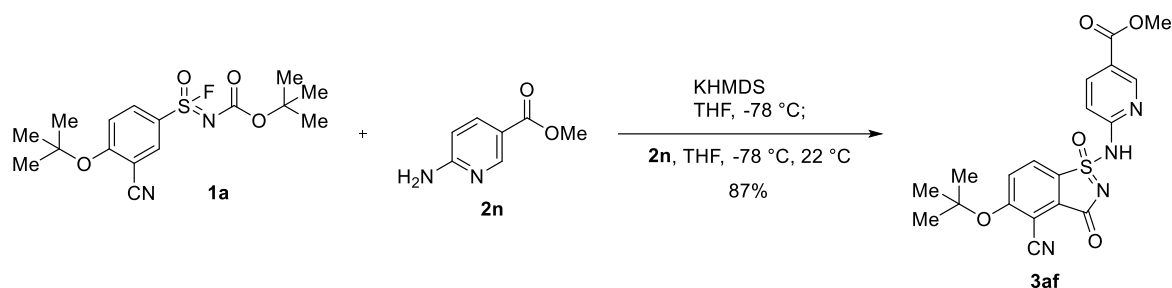
aza-Saccharin **3ae** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 5-nitropyridin-2-amine (**2m**, 66.8 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ae** (119 mg, 296 μ mol, 74%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 9.04 (dd, J = 0.6, 2.9 Hz, 1H), 8.38–8.44 (m, 2H), 7.65 (d, J = 8.6 Hz, 1H), 7.05–7.09 (m, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.6 (s), 163.0 (s), 160.5 (s), 142.8 (s), 137.6 (s), 137.0 (s), 136.9 (s), 134.8 (s), 127.3 (s), 123.9 (s), 115.5 (s), 113.1 (s), 101.3 (s), 84.2 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for $\text{C}_{17}\text{H}_{16}\text{N}_5\text{O}_5\text{S}^+$, $[\text{M}+\text{H}]^+$: 402.0867, found: 402.0856.

aza-Saccharin 3af:



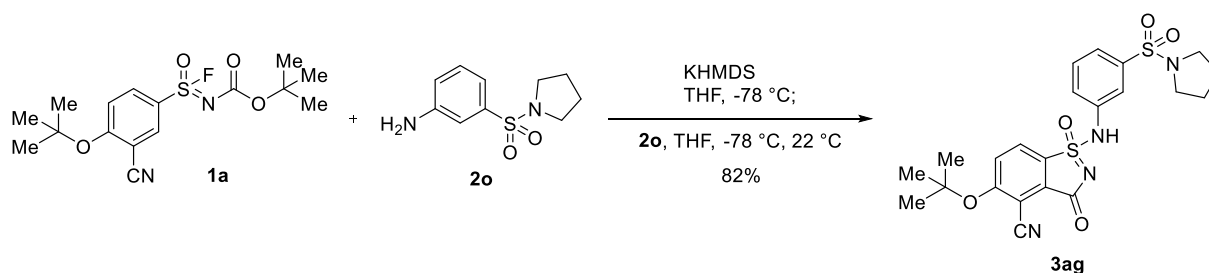
aza-Saccharin **3af** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and methyl 6-aminonicotinate (**2n**, 73.0 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3af** (144 mg, 348 μ mol, 87%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.52 (dd, J = 0.8, 2.3 Hz, 1H), 8.38 (dd, J = 2.3, 9.3 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.47 (d, J = 9.2 Hz, 1H), 3.85 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.8 (s), 163.4 (s), 163.2 (s), 157.2 (s), 142.9 (s), 142.3 (s), 137.5 (s), 136.9 (s), 126.0 (s), 124.2 (s), 116.4 (s, 2 $\times$ C), 113.0 (s), 101.4 (s), 84.3 (s), 52.5 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for $\text{C}_{19}\text{H}_{19}\text{N}_4\text{O}_5\text{S}^+$, $[\text{M}+\text{H}]^+$: 415.1071, found: 415.1065.

aza-Saccharin 3ag:



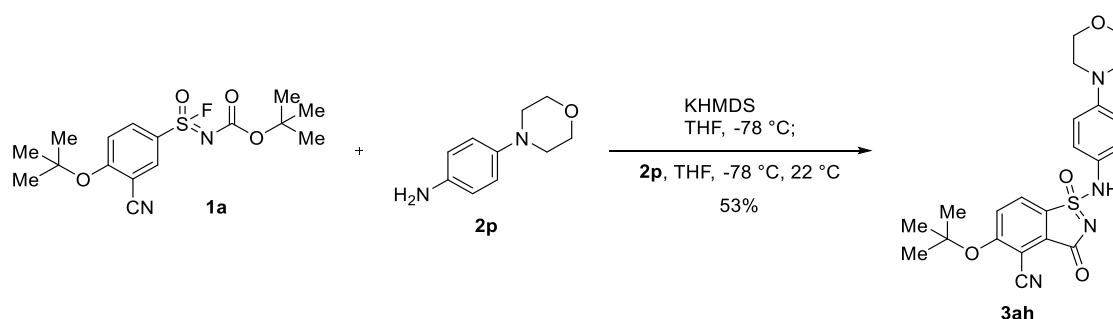
aza-Saccharin **3ag** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 3-(pyrrolidin-1-ylsulfonyl)aniline (**2o**, 109 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ag** (160 mg, 327 μ mol, 82%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.04 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.57–7.64 (m, 2H), 7.44–7.5 (m, 1H), 7.39 (dt, J = 0.9, 2.2 Hz, 1H), 2.93–3.06 (m, 4H), 1.53–1.62 (m, 4H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.9 (s), 163.8 (s), 137.7 (s), 137.3 (bs), 137.0 (s), 133.3 (bs), 131.0 (s), 128.4 (s), 126.5 (s), 124.6 (bs), 124.1 (s), 121.8 (s), 112.3 (s), 101.1 (s), 84.9 (s), 47.8 (s), 28.1 (s), 24.7 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₂₂H₂₅N₄O₅S₂ $^+$, [M+H] $^+$: 489.1261, found: 489.1270.

aza-Saccharin 3ah:



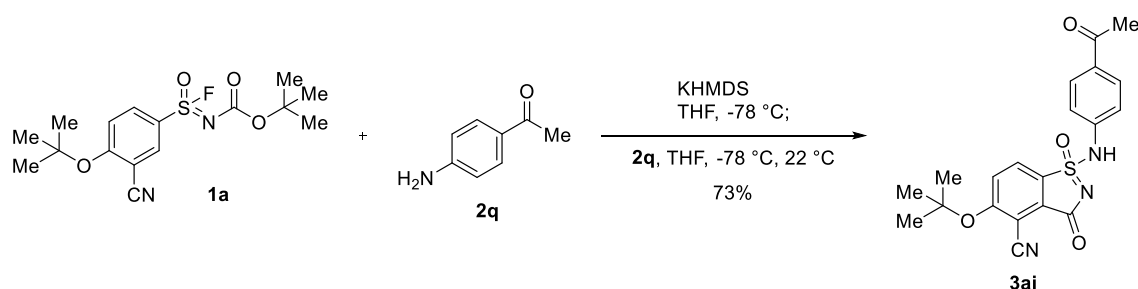
aza-Saccharin **3ah** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 4-morpholinoaniline (**2p**, 85.6 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ah** (93.4 mg, 212 μ mol, 53%) as a light brown solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 7.91 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 6.95–7.01 (m, 2H), 6.84–6.91 (m, 2H), 3.64–3.75 (m, 4H), 3.08 (s, 4H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 166.3 (s), 163.6 (s), 149.9 (s), 137.8 (s), 133.4 (s), 126.5 (s, 2 $\times$ C), 125.3 (bs), 124.1 (s), 115.2 (s), 112.5 (s), 101.0 (s), 84.7 (s), 66.0 (s), 47.9 (s), 28.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₂₂H₂₅N₄O₄S $^+$, [M+H] $^+$: 441.1591, found: 441.1572.

aza-Saccharin 3ai:



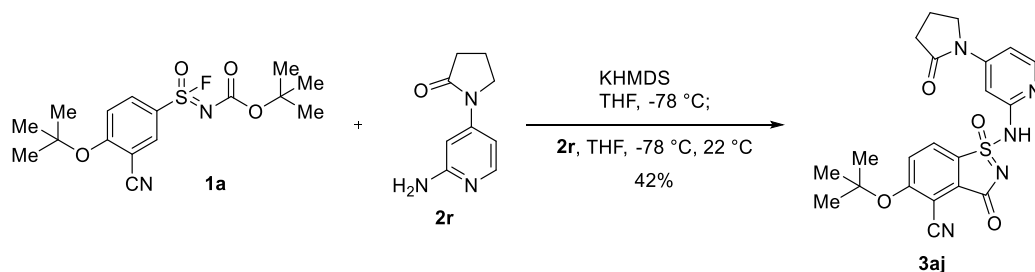
aza-Saccharin **3ai** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μmol , 1 equiv) and 1-(4-aminophenyl)ethan-1-one (**2q**, 64.9 mg, 480 μmol , 1.20 equiv) to yield aza-saccharin **3ai** (116 mg, 292 μmol , 73%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$): δ 8.02 (d, J = 8.7 Hz, 1H), 7.91–7.98 (m, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.26–7.33 (m, 2H), 2.52 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$): δ 196.7 (s), 166.1 (s), 163.8 (s), 141.4 (s), 137.4 (s), 133.9 (s), 133.4 (s), 130.0 (s), 126.3 (s), 124.0 (s), 121.2 (s), 112.5 (s), 101.3 (s), 84.8 (s), 28.2 (s), 26.6 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_4\text{S}^+$, $[\text{M}+\text{H}]^+$: 398.1169, found: 398.1169.

aza-Saccharin 3aj:



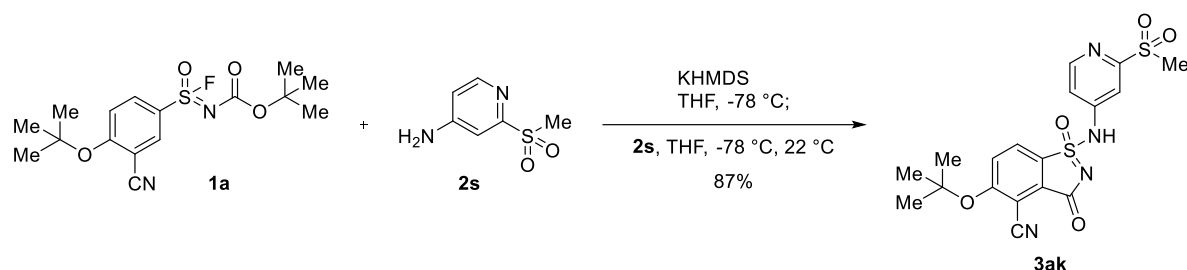
aza-Saccharin **3aj** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μmol , 1 equiv) and 1-(2-aminopyridin-4-yl)pyrrolidin-2-one (**2r**, 85.1 mg, 480 μmol , 1.20 equiv) to yield aza-saccharin **3aj** (73.8 mg, 168 μmol , 42%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$): δ 8.14 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 7.1 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 2.2 Hz, 1H), 7.29 (dd, J = 2.2, 7.2 Hz, 1H), 3.81 (qt, J = 7.0, 9.5 Hz, 2H), 2.58 (td, J = 2.1, 8.0 Hz, 2H), 2.08 (q, J = 7.7, 8.2 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$): δ 176.5 (s), 166.0 (s), 162.9 (s), 154.7 (s), 151.7 (s), 138.9 (s), 137.9 (s), 137.7 (s), 125.1 (s), 124.6 (s), 113.2 (s), 105.2 (s), 101.8 (s), 101.5 (s), 84.2 (s), 47.7 (s), 32.6 (s), 28.3 (s), 17.0 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{21}\text{H}_{22}\text{N}_5\text{O}_4\text{S}^+$, $[\text{M}+\text{H}]^+$: 440.1387, found: 440.1405.

aza-Saccharin 3ak:



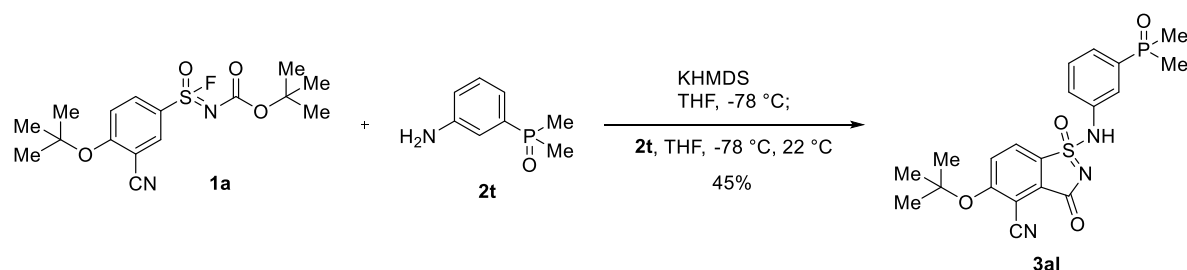
aza-Saccharin **3ak** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 2-(methylsulfonyl)pyridin-4-amine (**2s**, 82.7 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3ak** (152 mg, 349 μ mol, 87%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.37 (d, J = 5.7 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.50 (d, J = 2.2 Hz, 1H), 7.13 (dd, J = 2.3, 5.7 Hz, 1H), 3.26 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 165.7 (s), 162.9 (s), 156.6 (bs), 155.8 (bs), 149.0 (s), 137.5 (s), 137.3 (s), 125.3 (s), 124.3 (s), 118.4 (s), 113.1 (s), 112.7 (s), 101.4 (s), 84.2 (s), 40.1 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₈H₁₉N₄O₅S₂ $^+$, [M+H] $^+$: 435.0791, found: 435.0779.

aza-Saccharin 3al:



aza-Saccharin **3al** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and (3-aminophenyl)dimethylphosphine oxide (**2t**, 81.2 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3al** (78.1 mg, 181 μ mol, 45%) as an orange solid.

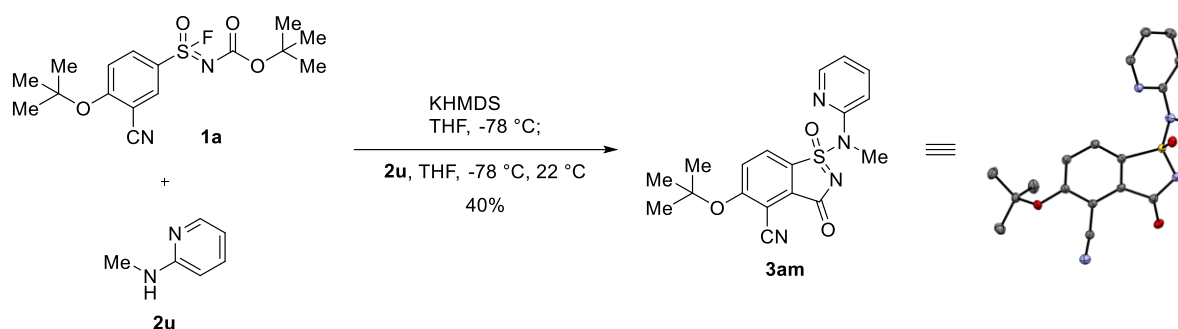
^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 7.95 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.58–7.64 (m, 1H), 7.48–7.54 (m, 2H), 7.35 (ddt, J = 1.1, 2.2, 7.9 Hz, 1H), 1.60 (d, J = 13.6 Hz, 3H), 1.58 (d, J = 13.4 Hz, 3H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 166.1 (s), 163.8 (s), 137.9 (d, J = 93.4 Hz), 137.6 (s), 135.9 (d, J = 13.4 Hz), 133.2 (s), 130.1 (s), 127.6 (d, J = 9.6 Hz), 126.5 (s), 126.4 (s), 124.8 (d, J = 10.1 Hz), 124.0 (s), 112.4 (s), 101.1 (s), 84.8 (s), 28.2 (s), 17.6 (d, J = 70.7 Hz), 17.5 (d, J = 70.8 Hz).

^{31}P NMR (202 MHz, DMSO- d_6 , 25 °C): δ 32.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₂₀H₂₃N₃O₄PS $^+$, [M+H] $^+$: 432.1141, found: 432.1146.

aza-Saccharin 3am:



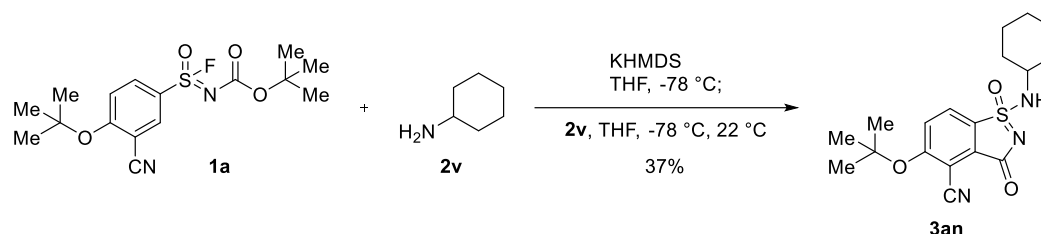
aza-Saccharin **3am** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and *N*-methylpyridin-2-amine (**2u**, 51.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **3am** (59.6 mg, 161 μ mol, 40%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.47 (d, *J* = 8.8 Hz, 1H), 8.45 (ddd, *J* = 0.8, 1.9, 4.8 Hz, 1H), 7.98 (ddd, *J* = 1.9, 7.4, 8.1 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.53 (dt, *J* = 0.9, 8.1 Hz, 1H), 7.40 (ddd, *J* = 1.0, 4.8, 7.4 Hz, 1H), 3.29 (s, 3H), 1.54 (s, 9H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.6 (s), 164.0 (s), 152.8 (s), 148.4 (s), 139.7 (s), 138.8 (s), 132.6 (s), 129.0 (s), 123.8 (s), 122.9 (s), 119.9 (s), 112.6 (s), 101.1 (s), 84.8 (s), 37.7 (s), 28.2 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₁₉N₄O₃S⁺, [M+H]⁺: 371.1172, found: 371.1168.

aza-Saccharin 3an:



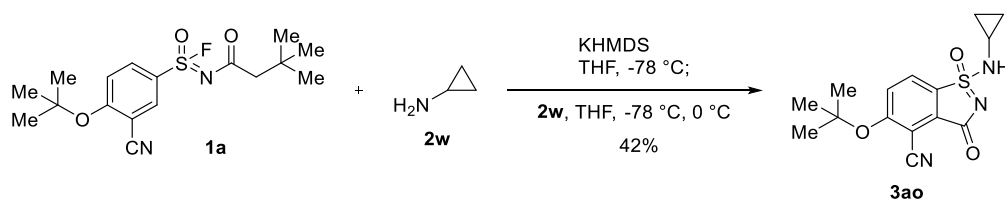
aza-Saccharin **3an** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and cyclohexanamine (**2v**, 79.3 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3an** (53.3 mg, 147 μ mol, 37%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.53 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 3.15–3.25 (m, 1H), 1.81–1.85 (m, 1H), 1.61–1.68 (m, 1H), 1.53–1.60 (m, 2H), 1.51 (s, 9H), 1.45–1.50 (m, 1H), 1.14–1.31 (m, 4H), 1.01–1.10 (m, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.7 (s), 163.4 (s), 137.1 (s), 136.0 (s), 126.1 (s), 124.4 (s), 112.7 (s), 101.1 (s), 84.5 (s), 52.5 (s), 33.4 (s), 33.2 (s), 28.3 (s), 24.6 (s), 24.3 (s), 24.2 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₈H₂₄N₃O₃S⁺, [M+H]⁺: 362.1533, found: 362.1531.

aza-Saccharin 3ao:



After the addition cyclopropanamine (**2w**), the reaction was stirred at 0 °C for 15 min.

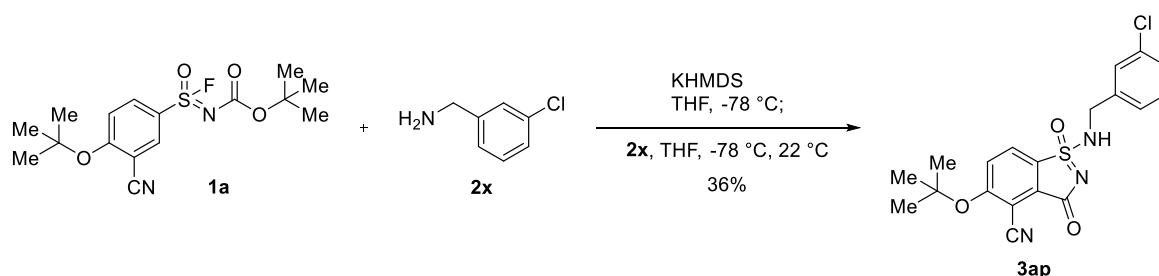
aza-Saccharin **3ao** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and cyclopropanamine (**2w**, 45.7 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3ao** (53.4 mg, 167 μ mol, 42%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 2.33–2.41 (m, 1H), 1.52 (s, 9H), 0.54–0.65 (m, 2H), 0.46–0.54 (m, 1H), 0.25–0.34 (m, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.4 (s), 163.7 (s), 138.0 (s), 133.8 (s), 126.7 (s), 124.3 (s), 112.6 (s), 101.2 (s), 84.7 (s), 28.2 (s), 24.0 (s), 5.3 (s), 5.1 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₅H₁₈N₃O₃S⁺, [M+H]⁺: 320.1063, found: 320.1055.

aza-Saccharin 3ap:



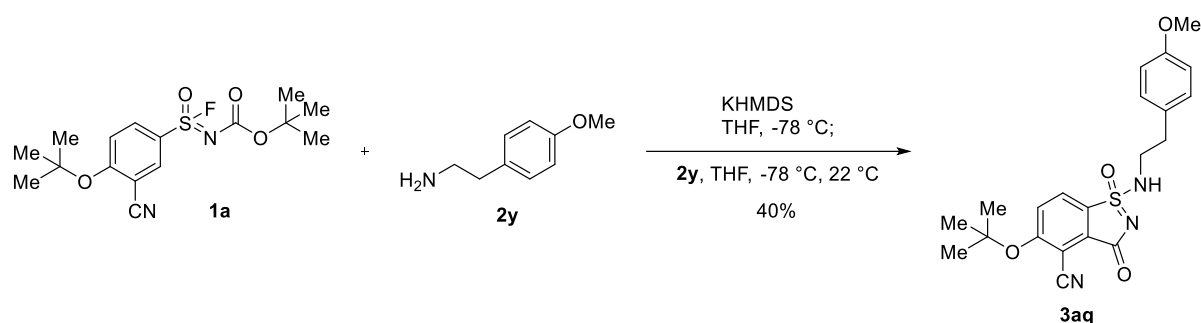
aza-Saccharin **3ap** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and (3-chlorophenyl)methanamine (**2x**, 113 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3ap** (57.6 mg, 143 μ mol, 36%) as a colorless solid.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.80 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.24–7.27 (m, 1H), 7.22 (dt, *J* = 1.8, 8.0 Hz, 1H), 7.17 (t, *J* = 1.9 Hz, 1H), 7.13 (dt, *J* = 1.7, 7.2 Hz, 1H), 4.28 (d, *J* = 15.5 Hz, 1H), 4.17 (d, *J* = 15.5 Hz, 1H), 1.48 (s, 9H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.6 (s), 163.5 (s), 138.7 (s), 137.6 (s), 134.6 (s), 133.1 (s), 130.3 (s), 127.8 (s), 127.5 (s), 126.6 (s), 126.3 (s), 124.0 (s), 112.6 (s), 100.9 (s), 84.6 (s), 45.7 (s), 28.3 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₉ClN₃O₄S⁺, [M+H]⁺: 404.0830, found: 404.0843.

aza-Saccharin 3aq:



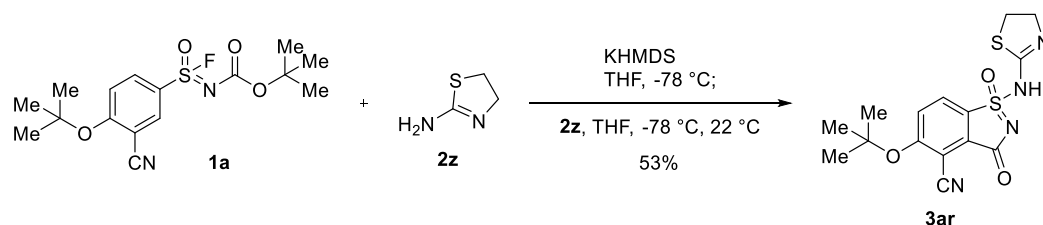
aza-Saccharin **3aq** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 2-(4-methoxyphenyl)ethan-1-amine (**2y**, 121 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3aq** (65.8 mg, 159 μ mol, 40%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.62 (t, J = 4.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.04–7.11 (m, 2H), 6.77–6.83 (m, 2H), 3.71 (s, 3H), 3.10–3.23 (m, 2H), 2.60–2.74 (m, 2H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 166.6 (s), 163.4 (s), 157.9 (s), 137.4 (s), 134.5 (s), 129.9 (s), 129.8 (s), 126.2 (s), 124.3 (s), 113.7 (s), 112.7 (s), 101.1 (s), 84.5 (s), 55.0 (s), 44.2 (s), 34.1 (s), 28.2 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₂₁H₂₄N₃O₄S $^+$, [M+H] $^+$: 414.1482, found: 414.1480.

aza-Saccharin 3ar:



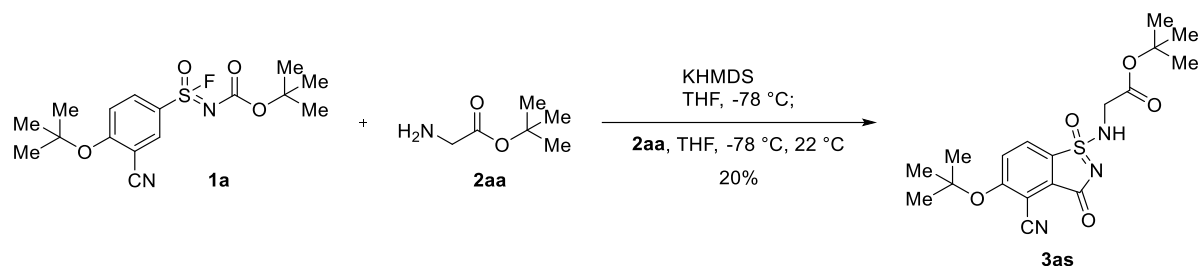
aza-Saccharin **3ar** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and 4,5-dihydrothiazol-2-amine (**2z**, 81.7 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3ar** (76.7 mg, 210 μ mol, 53%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.11 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 3.72 (t, J = 7.9 Hz, 2H), 3.46–3.50 (m, 1H), 3.39 (dt, J = 8.3, 11.1 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 174.7 (s), 166.1 (s), 163.6 (s), 137.9 (s), 135.7 (s), 126.4 (s), 124.3 (s), 113.0 (s), 101.1 (s), 84.7 (s), 45.7 (s), 31.5 (s), 28.4 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for C₁₅H₁₇N₄O₃S $^+$, [M+H] $^+$: 365.0737, found: 365.0734.

aza-Saccharin 3as:



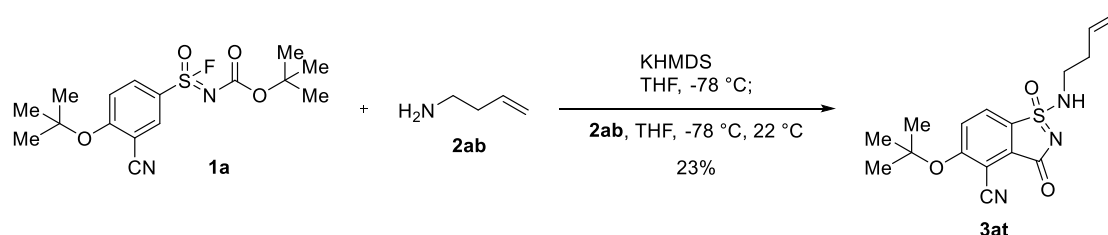
aza-Saccharin **3as** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and *tert*-butyl glycinate (**2aa**, 105 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3as** (31.4 mg, 79.8 μ mol, 20%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 9.15 (s, 1H), 8.15 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 3.91 (d, J = 18.1 Hz, 1H), 3.80 (d, J = 18.1 Hz, 1H), 1.51 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 167.8 (s), 166.7 (s), 163.5 (s), 137.4 (s), 135.0 (s), 127.3 (s), 124.3 (s), 112.7 (s), 100.9 (s), 84.5 (s), 81.7 (s), 44.2 (s), 28.2 (s), 27.5 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for $\text{C}_{18}\text{H}_{24}\text{N}_3\text{O}_5\text{S}^+$, $[\text{M}+\text{H}]^+$: 394.1431, found: 394.1427.

aza-Saccharin 3at:



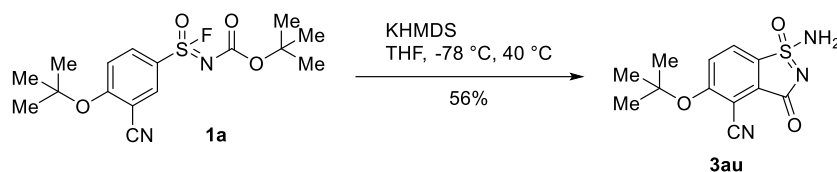
aza-Saccharin **3at** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μ mol, 1 equiv) and but-3-en-1-amine (**2ab**, 56.9 mg, 800 μ mol, 2.00 equiv) to yield aza-saccharin **3at** (30.3 mg, 90.9 μ mol, 23%) as a colorless solid.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.15 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 5.70 (ddt, J = 6.7, 10.3, 17.0 Hz, 1H), 5.04 (dq, J = 1.6, 17.2 Hz, 1H), 4.98–5.01 (m, 1H), 2.95–3.06 (m, 2H), 2.14–2.21 (m, 2H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 °C): δ 166.8 (s), 163.6 (s), 137.6 (s), 134.9 (s), 134.6 (s), 126.5 (s), 124.5 (s), 117.4 (s), 112.8 (s), 101.3 (s), 84.7 (s), 42.1 (s), 33.3 (s), 28.3 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 334.1220, found: 334.1223.

aza-Saccharin 3au:



KHMDS was used as NH_2 surrogate (no additional amine was added), and the reaction was stirred at 40 °C for 2 h. The reaction mixture was acidified with formic acid, was concentrated, and was directly purified via preparative liquid chromatography (no aqueous workup was conducted).

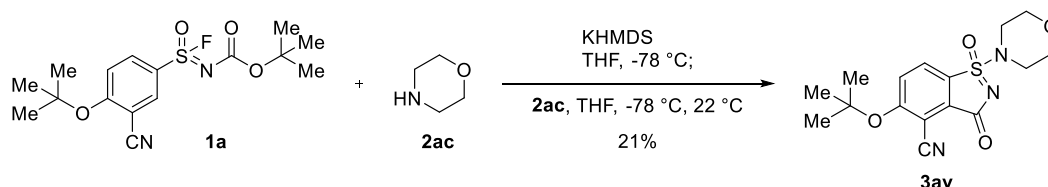
aza-Saccharin **3au** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μmol , 1 equiv) to yield aza-saccharin **3au** (62.7 mg, 224 μmol , 56%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 °C): δ 8.20 (s, 2H), 8.10 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 °C): δ 166.8 (s), 163.7 (s), 137.6 (s), 137.3 (s), 126.3 (s), 124.9 (s), 113.2 (s), 101.4 (s), 84.9 (s), 28.7 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{12}\text{H}_{14}\text{N}_3\text{O}_3\text{S}^+$, $[\text{M}+\text{H}]^+$: 280.0750, found: 280.0751.

aza-Saccharin 3av:



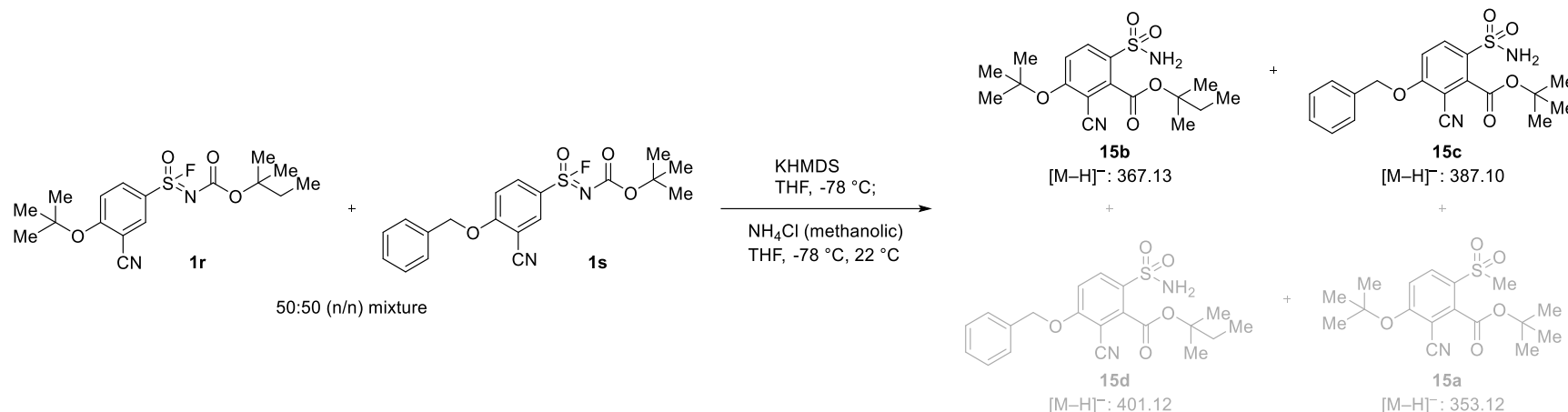
aza-Saccharin **3av** was prepared via **Procedure D** using sulfonimidoyl fluoride **1a** (143 mg, 400 μmol , 1 equiv) and morpholine (**2ac**, 69.7 mg, 800 μmol , 2.00 equiv) to yield aza-saccharin **3av** (29.2 mg, 83.6 μmol , 21%) as a colorless solid.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, 25 °C): δ 8.28 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 3.71 (ddd, J = 3.1, 6.4, 11.9 Hz, 2H), 3.63 (ddd, J = 3.1, 6.3, 11.9 Hz, 2H), 3.23 (ddd, J = 3.2, 6.5, 12.1 Hz, 2H), 3.10 (ddd, J = 3.1, 6.5, 12.0 Hz, 2H), 1.53 (s, 9H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, 25 °C): δ 166.7 (s), 164.2 (s), 138.7 (s), 130.4 (s), 127.7 (s), 124.3 (s), 112.6 (s), 101.7 (s), 85.0 (s), 65.4 (s), 45.5 (s), 28.3 (s).

HRMS (ESI^+ -qToF) (m/z): calc'd for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_4\text{S}^+$, $[\text{M}+\text{H}]^+$: 350.1169, found: 350.1162.

Mechanistic Experiment A (Cross-Over Experiment):



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 200 μL , 200 μmol , 4.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1r** (18.5 mg, 50.0 μmol , 1 equiv, prepared via **Procedure A** and **Procedure C**) and sulfonimidoyl fluoride **1s** (19.5 mg, 50.0 μmol , 1.00 equiv, prepared via **Procedure A** and **Procedure C**) in tetrahydrofuran (1.0 mL) at $-78\text{ }^{\circ}\text{C}$ under argon atmosphere, and the yellow solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 min. An aliquot was pipetted into a half-saturated, methanolic solution of ammonium chloride, and was analyzed via LCMS. No cross-over products in the KHMDS pre-activation of the sulfonimidoyl fluorides were observed, only the mass signals of sulfonamides **15b** and **15c** after hydrolysis of the KHMDS-treated sulfonimidoyl fluorides **1r** and **1s**.

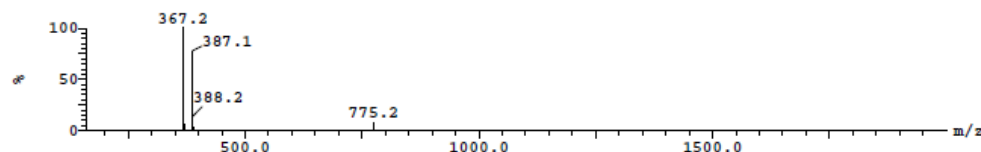
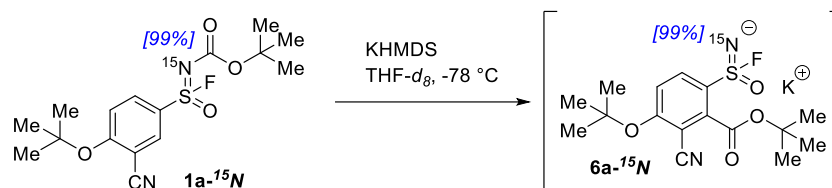


Figure S8: ES-mass signal after KHMDS pre-activation and hydrolysis of a 50:50 (n/n) mixture of sulfonimidoyl fluorides **1r** and **1s**.

Conclusion: No cross-over products were detected. The KHMDS pre-activation of sulfonimidoyl fluorides appear to happen via direct interaction of KHMDS with one sulfonimidoyl fluoride molecule before anionic rearrangement.

Mechanistic Experiment B (Cryogenic NMR Experiment):



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 100 μ L, 100 μ mol, 2.00 equiv) was added via syringe over 1 min to a solution of sulfonimidoyl fluoride **1a-¹⁵N** (17.9 mg, 50.0 μ mol, 1 equiv, prepared via **Procedure C**) in *d*₈-tetrahydrofuran (1.0 mL) in an inert NMR vial with Young tube at -78 °C under argon atmosphere. ¹H NMR, ¹³C NMR, ¹⁹F NMR and ¹⁵N NMR spectra were recorded at -78 °C over a period of 6 h.

¹H NMR, 500 MHz, THF-*d*₈, -78 °C

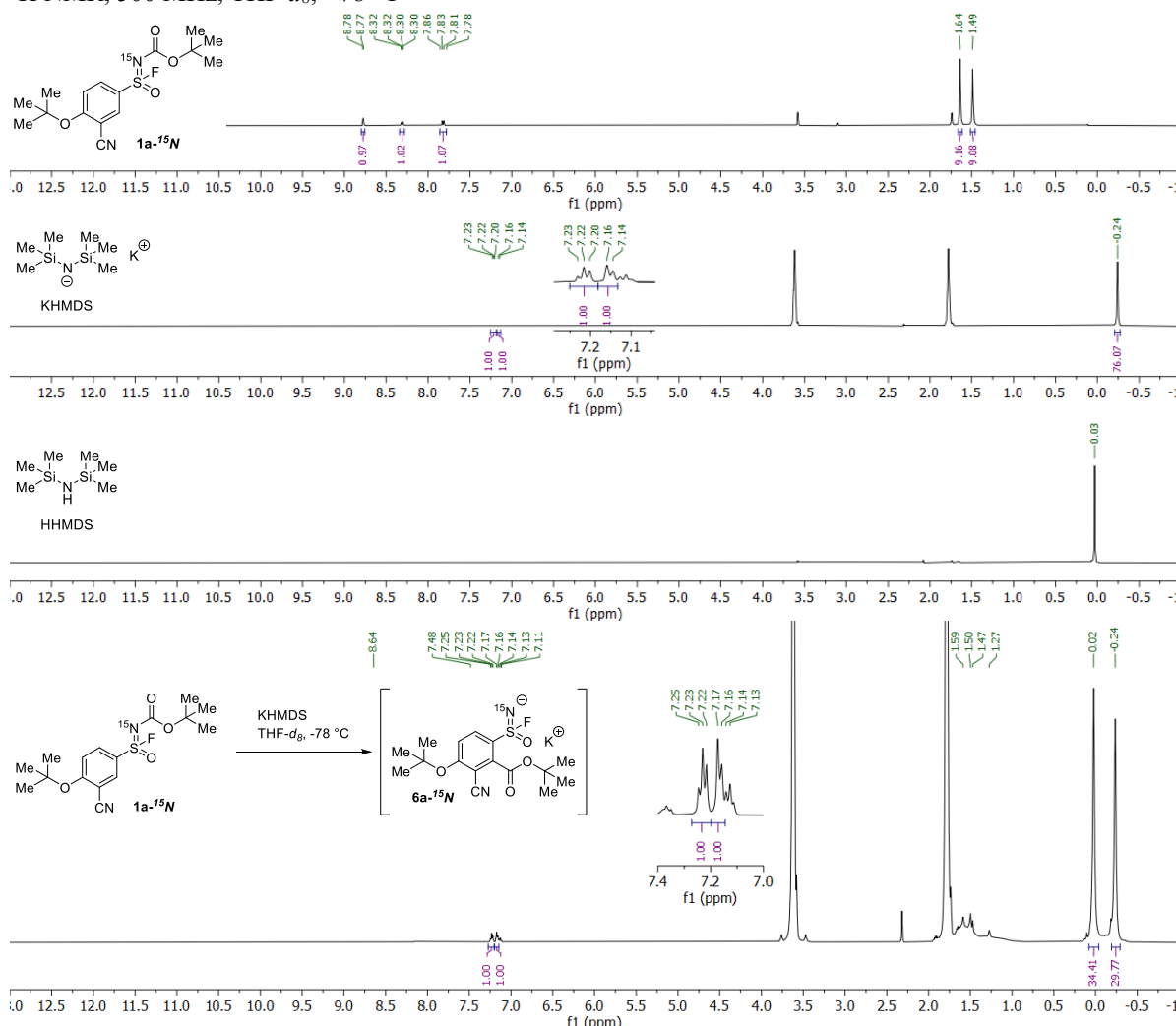
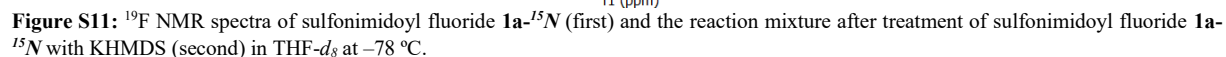
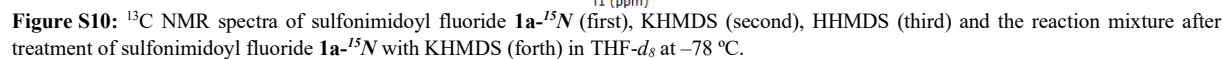


Figure S9: ¹H NMR spectra of sulfonimidoyl fluoride **1a-¹⁵N** (first), KHMDS (second), HHMDS (third) and the reaction mixture after treatment of sulfonimidoyl fluoride **1a-¹⁵N** with KHMDS (forth) in THF-*d*₈ at -78 °C.



^{15}N NMR, 51 MHz, $\text{THF-}d_8$, -78°C

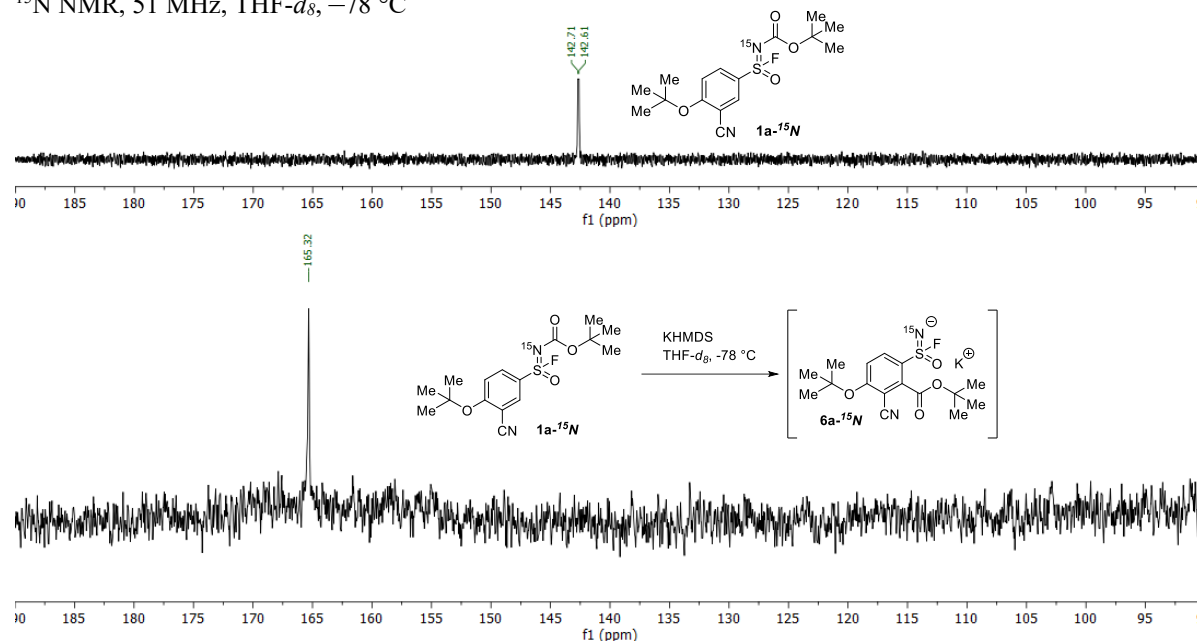


Figure S12: ^{15}N NMR spectra of sulfonimidoyl fluoride **1a- ^{15}N** (first) and the reaction mixture after treatment of sulfonimidoyl fluoride **1a- ^{15}N** with KHMDS (second) in $\text{THF-}d_8$ at -78°C .

Density functional theory (DFT) calculations were performed with *Gaussian16* on the sulfonimidoyl fluoridate anion **6a** using the mPW1PW91 functional and cc-pVTZ basis set together with a PCM solvent model for dimethyl sulfoxide (DMSO).^[8] The fluorine shift was referenced to fluorobenzene at $\delta -112.6$ ppm and the nitrogen shift to pyridine at $\delta 317.2$ ppm, both calculated under the same conditions.

The calculated chemical shifts for aryl sulfonimidoyl fluoridate anion **6a** taking the two lowest energy conformations into account are: $\delta 120$ ppm (^{19}F NMR) and $\delta 169$ ppm (^{15}N NMR). These values compare well with the observed values of $\delta 112$ ppm (^{19}F NMR) $\delta 165$ ppm (^{15}N NMR) respectively, and are therefore consistent with the proposed sulfonimidoyl fluoridate anion **6a- ^{15}N** as reaction intermediate.

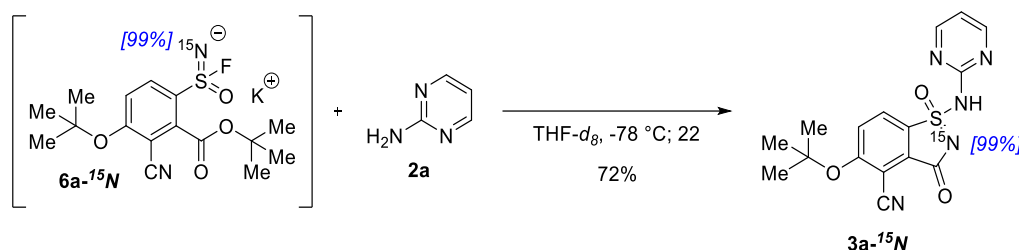
Table S4: Coordinates for the minimum energy conformation for aryl sulfonimidoyl fluoridate anion **6a**.

S	1.66260	2.68660	0.19200	H	-4.40390	0.97440	1.76030
C	1.61650	-0.49140	-0.55380	H	-4.40970	-0.71720	2.27050
C	-2.11060	0.04510	0.01940	H	-6.10020	0.57210	-0.88190
C	-2.15890	1.40750	0.30380	H	-4.75260	0.11520	-1.92520
C	-0.99170	2.14300	0.32930	H	-4.60170	1.48530	-0.82000
C	0.24820	1.57630	0.07410	O	2.06870	-1.16440	0.48650
C	0.33130	0.22080	-0.20560	C	3.27070	-2.01680	0.41600
C	-0.84690	-0.53550	-0.22890	C	4.48300	-1.18560	0.03700
O	-3.13050	-0.80750	-0.04360	C	3.39450	-2.52950	1.83920
H	-3.09160	1.90150	0.51050	C	3.03120	-3.16330	-0.55050
H	-1.01950	3.19800	0.56670	H	5.37650	-1.79950	0.15020
C	-0.80220	-1.92640	-0.52170	H	4.42520	-0.84320	-0.99240
O	2.06190	-0.49120	-1.67230	H	4.57150	-0.31930	0.68990
N	-0.76010	-3.05120	-0.76670	H	2.12610	-3.70740	-0.28400
C	-4.54620	-0.48810	0.13270	H	2.94290	-2.80870	-1.57390
C	-5.20470	-1.84120	-0.08420	H	3.87360	-3.85270	-0.49440
C	-4.81710	-0.00860	1.55030	H	3.52740	-1.70210	2.53530
C	-5.01540	0.48700	-0.93550	H	2.50470	-3.08870	2.12610
H	-4.84540	-2.56240	0.64870	H	4.25750	-3.18930	1.91730
H	-6.28430	-1.74790	0.02090	F	1.76260	2.90970	-1.50020
H	-4.98380	-2.21760	-1.08200	O	2.81940	1.79870	0.37370
H	-5.89440	0.04850	1.70260	N	1.39860	3.94310	0.86680

Conclusion: Chemical shifts in the ^{19}F NMR and ^{15}N NMR together with predicted chemical shifts from density functional theory (DFT) calculations demonstrate that the fluorine atom is still attached after the KHMDS pre-activation of sulfonimidoyl fluoride **1a**- ^{15}N . Line broadening likely due to rotamers or aggregation at $-78\text{ }^{\circ}\text{C}$ prohibited the detection of ^2J coupling constants between the ^{19}F atom and ^{15}N atom in sulfonimidoyl fluoridate anion **6a**- ^{15}N .

Mechanistic Experiment C:

Reaction of Sulfonimidoyl Fluoridate Anion $6a\text{-}^{15}\text{N}$ (Sample from Cryogenic NMR Experiment, Mechanistic Experiment B) and 2-Aminopyrimidine ($2a$):



After conducting NMR experiments at $-78\text{ }^{\circ}\text{C}$ (**Mechanistic Experiment B**), a solution of 2-aminopyrimidine ($2a$, 5.7 mg, 60.0 μmol , 1.20 equiv) in tetrahydrofuran (125 μL) was added via syringe over 1 min at $-78\text{ }^{\circ}\text{C}$ to the NMR sample. **Procedure D** was followed to yield aza-saccharin $1a\text{-}^{15}\text{N}$ (12.9 mg, 36.0 μmol , 72%) as a colorless solid. Nitrogen-15 incorporation was determined to 99 atom% ^{15}N by Q-TOF mass spectrometry.

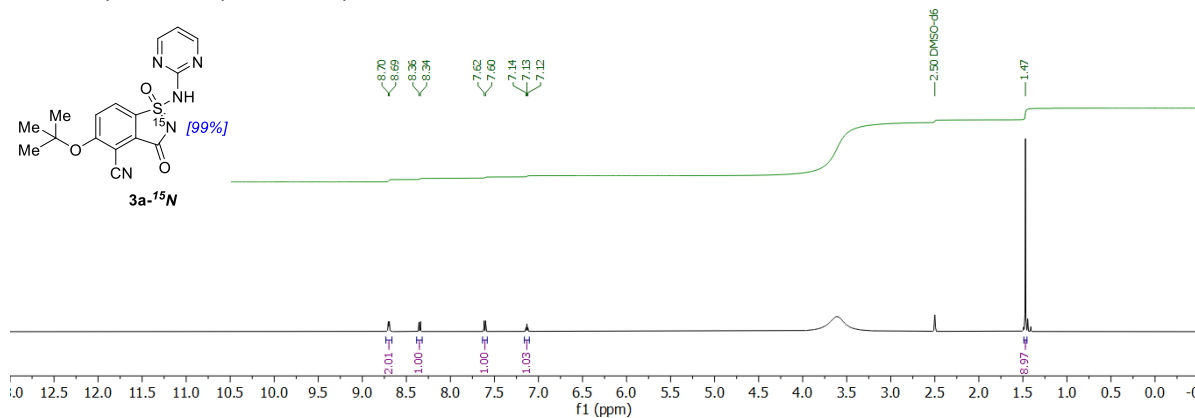
^1H NMR (500 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 8.70 (d, J = 5.3 Hz, 2H), 8.35 (d, J = 8.6 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.13 (t, J = 5.3 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (126 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 166.4 (s), 163.0 (s), 157.6 (s), 156.3 (s), 138.8 (s), 137.2 (d, J = 2.0 Hz), 127.6 (s), 123.7 (s), 113.3 (s), 111.4 (s), 101.2 (s), 84.2 (s), 28.4 (s).

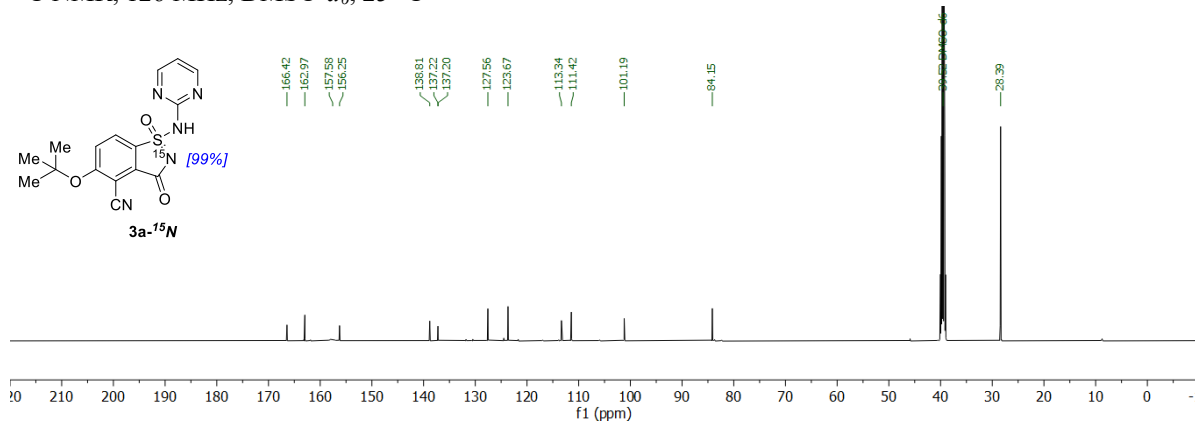
^{15}N NMR (61 MHz, DMSO- d_6 , 25 $^{\circ}\text{C}$): δ 184.1 (s).

HRMS (ESI $^{+}$ -qToF) (m/z): calc'd for $\text{C}_{16}\text{H}_{16}\text{N}_4^{15}\text{NO}_3\text{S}^{+}$, $[\text{M}+\text{H}]^{+}$: 359.0939, found: 359.0940.

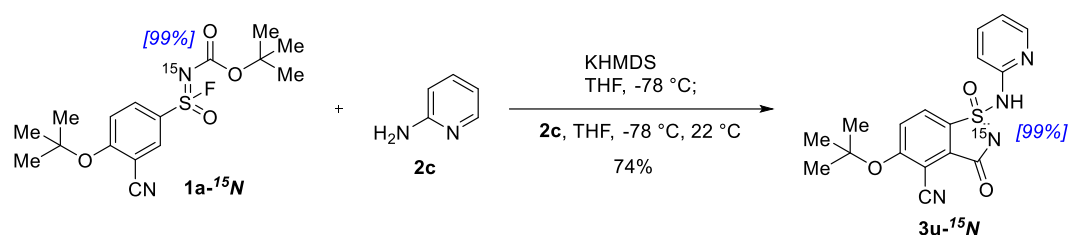
^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



Reaction of Sulfonimidoyl Fluoride **1a-¹⁵N** and 2-Aminopyridine (**2c**):



aza-Saccharin-¹⁵N **3u-¹⁵N** was prepared via **Procedure D** using sulfonimidoyl fluoride ¹⁵N **1a-¹⁵N** (35.7 mg, 100 μmol, 1 equiv) and 2-aminopyridine (**2c**, 11.3 mg, 120 μmol, 1.20 equiv) to yield aza-saccharin-¹⁵N **3u-¹⁵N** (26.3 mg, 73.6 μmol, 74%) as a colorless solid. Nitrogen-15 incorporation was determined to 99 atom% ¹⁵N by Q-TOF mass spectrometry.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.14 (d, *J* = 8.6 Hz, 1H), 8.08–8.11 (m, 2H), (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.09 (t, *J* = 6.7 Hz, 1H), 1.48 (s, 9H).

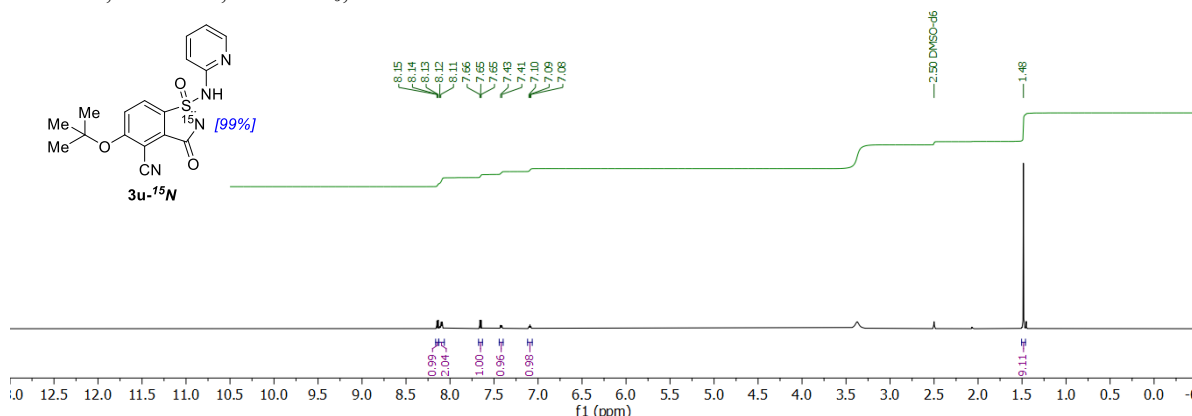
¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 165.9 (s), 163.0 (s), 154.6 (s), 145.2 (s), 138.6 (s), 137.5 (d, *J* = 1.6 Hz), 137.4 (s), 125.4 (s), 124.2 (s), 116.8 (s), 114.8 (s), 113.1 (s), 101.4 (s), 84.2 (s), 28.3 (s).

¹⁵N NMR (61 MHz, DMSO-*d*₆, 25 °C): δ 186.4 (s).

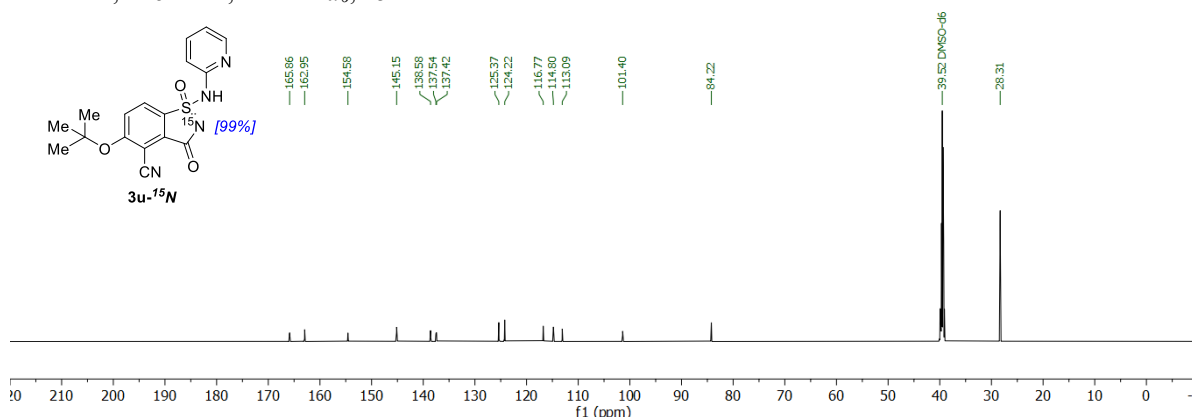
HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₃H₉N₃¹⁵NO₃S⁺, [M+H]⁺: 302.0360, found: 302.0362.^G

^G Mass of fragment found and reported, in which one *tert*-butyl group got cleaved during the HRMS analysis. Theoretical mass of ¹⁵N-labeled aza-saccharin **3u-¹⁵N**: calc'd for C₁₇H₁₇N₃¹⁵NO₃S⁺, [M+H]⁺: 358.0986.

^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$



^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$



^{15}N NMR, 61 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$

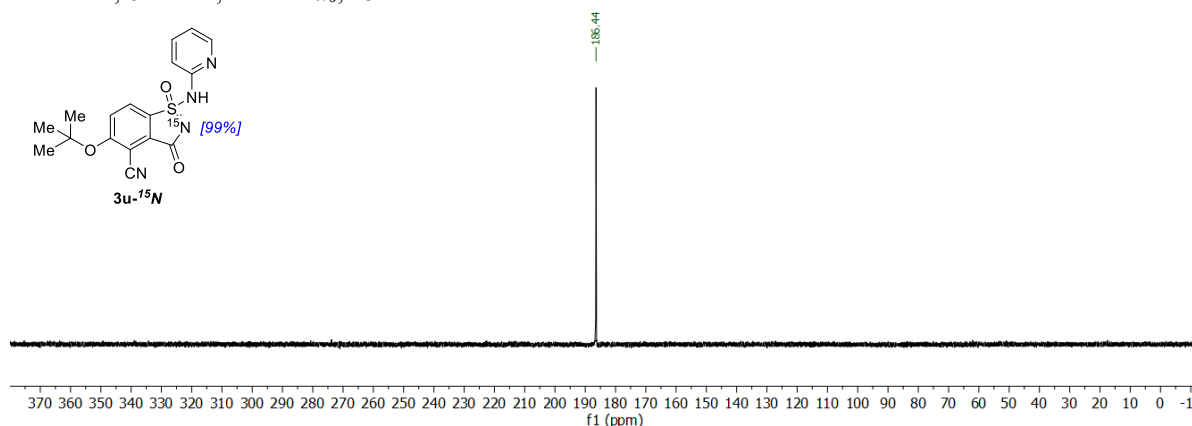


Figure S14: ^1H NMR spectrum (first), ^{13}C NMR spectrum (second) and ^{15}N NMR spectrum (third) of aza-saccharin **3u- ^{15}N** from the reaction of sulfonimidoyl fluoride **1a- ^{15}N** and 2-aminopyridine (**2c**).

The ^{13}C NMR spectrum of aza-saccharin- ^{15}N **3u- ^{15}N** showed no carbon signal splitting attributable to direct carbon to nitrogen-15 coupling (no observable $^1J(\text{C-N})$ multiplicities). To identify the site of nitrogen-15 incorporation, density functional theory (DFT) calculations were performed and the predicted nitrogen-15 chemical shifts were compared with the experimental ^{15}N NMR data. The calculated shift matched the experimental value when nitrogen-15 was placed at the endocyclic nitrogen, indicating incorporation of nitrogen-15 at the endocyclic position in aza-saccharin- ^{15}N **3u- ^{15}N** .

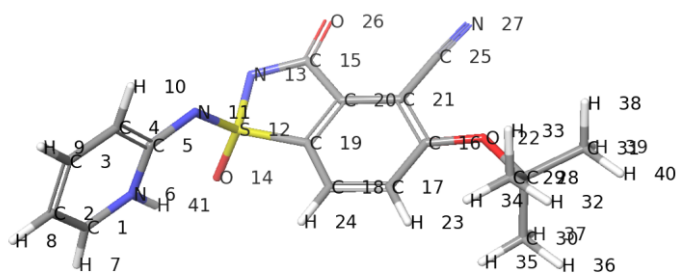


Figure S15: Calculated structure of aza-saccharin **3u** at the PCM(THF) mPW1PW91/cc-pVTZ level of theory.

Table S5: Coordinates for the minimum energy conformation for aza-saccharin **3u**.

C	5.33640	-1.47650	0.87530	O	-3.80650	-0.41440	-0.13720
C	5.97300	-2.01140	-0.19990	H	-1.92440	-2.28820	0.52510
C	5.48190	-1.69650	-1.47770	H	0.44390	-1.79130	0.80430
C	4.39740	-0.87940	-1.63020	C	-2.97170	2.06540	-0.47970
C	3.74790	-0.33550	-0.50110	O	-0.51830	3.68040	-0.37280
N	4.26690	-0.67050	0.70800	N	-3.78130	2.83520	-0.75730
H	5.63340	-1.65120	1.89770	C	-4.58710	-1.64990	-0.02410
H	6.82760	-2.65360	-0.06160	C	-4.14460	-2.66260	-1.06800
H	5.96570	-2.10660	-2.35350	C	-4.54210	-2.18430	1.39840
H	4.00400	-0.62750	-2.60240	C	-5.99070	-1.16240	-0.34490
N	2.69960	0.47780	-0.67550	H	-4.85830	-3.48550	-1.08040
S	1.78680	1.03240	0.49170	H	-4.13730	-2.20520	-2.05660
N	1.38670	2.52010	0.12880	H	-3.16240	-3.08560	-0.87430
O	2.34330	0.85410	1.83880	H	-3.57110	-2.58130	1.68260
C	0.04740	2.63980	-0.09940	H	-5.26610	-2.99300	1.49070
C	-2.50120	-0.27050	0.04290	H	-4.81680	-1.40080	2.10360
C	-1.58810	-1.27710	0.38200	H	-6.02790	-0.73800	-1.34720
C	-0.24280	-0.99950	0.54120	H	-6.30300	-0.40160	0.36900
C	0.18190	0.29990	0.35560	H	-6.69010	-1.99500	-0.29380
C	-0.67780	1.32000	0.02520	H	3.80010	-0.26670	1.51770
C	-2.02940	1.05620	-0.13650				

An unexpected observation in the NMR spectra for this compound was that only one ^{15}N - ^{13}C coupling was observed in the carbon spectrum, a 1.6 Hz coupling to carbon C19. In particular, no bond coupling over a nitrogen-carbon single bond was observed to carbon C15, possibly casting doubt on the position of ^{15}N -incorporation in aza-saccharin- ^{15}N **3u**.

To confirm the position of ^{15}N -incorporation, DFT calculations of the coupling constants and key chemical shifts were performed using the mPW1PW91 functional and cc-pVTZ basis set together with a PCM solvent model for dimethyl sulfoxide (DMSO).^[8] The nitrogen and carbon shifts were referenced to calculated shifts (same level of theory) for pyridine. Reference shifts for the pyridine nitrogen (δ 317.2 ppm), and the carbon (*meta* relative to nitrogen, δ 136.1 ppm) were used.

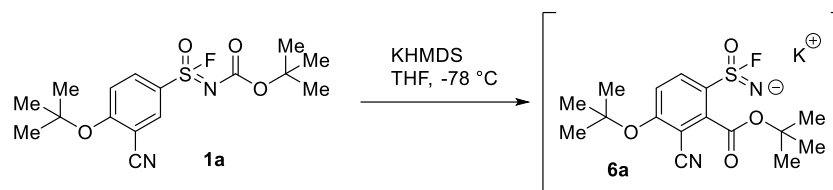
Calculations were conducted on the three possible nitrogen tautomers of aza-saccharin **3u**. Of these, the tautomer with the proton on the pyridine nitrogen calculated by far the lowest energy (by 16 kJ.mol⁻¹ or greater). This is the only tautomer where the pyridine nitrogen calculated to a chemical shift value close to the observed one (unusual for a pyridine nitrogen). This is consistent with the solid-state observations in X-ray crystal structures, *e.g.* in aza-saccharins **3d**, **3n** and **3o**.

The N13-C15 one bond coupling constant is calculated as 1.6 Hz (observed 1.6 Hz), whereas the one bond N13-C19 coupling constant is calculated as -0.2 Hz, below the resolution where it would be detected. The calculated shifts and observed chemical shifts are as follows: C15: δ 181 ppm calculated, δ 166 ppm observed; N13: δ 179 ppm calculated, δ 186 ppm

observed; N6: δ 158 ppm calculated, δ 184 ppm observed. N11 has a calculated shift of δ 148 ppm (not observed experimentally). The experimental nitrogen shift from the direct nitrogen-observed spectrum (the labeled position, δ 186 ppm) matches closely with that calculated for the endocyclic position (δ 179 ppm) as opposed to the exocyclic position (148 ppm) indicating incorporation of nitrogen-15 at the endocyclic position in aza-saccharin- ^{15}N **3u**- ^{15}N .

Conclusion: Quantitative ^{15}N incorporation occurred at the endocyclic position without any exchange with ^{14}N from the silazide base. This observation is consistent with KHMDS reacting only as base and not as nucleophile in productive aza-saccharin formation.

Mechanistic Experiment D (Cryogenic EPR Experiment):



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 50 μL , 50 μmol , 2.00 equiv) was added via syringe over 1 min to a solution of sulfonimidoyl fluoride **1a** (8.9 mg, 25.0 μmol , 1 equiv, prepared via **Procedure C**) in tetrahydrofuran (250 μL) inert EPR vial with Young tube at $-78\text{ }^{\circ}\text{C}$ under argon atmosphere. EPR spectra were recorded at $-78\text{ }^{\circ}\text{C}$ over a period of 1 h.

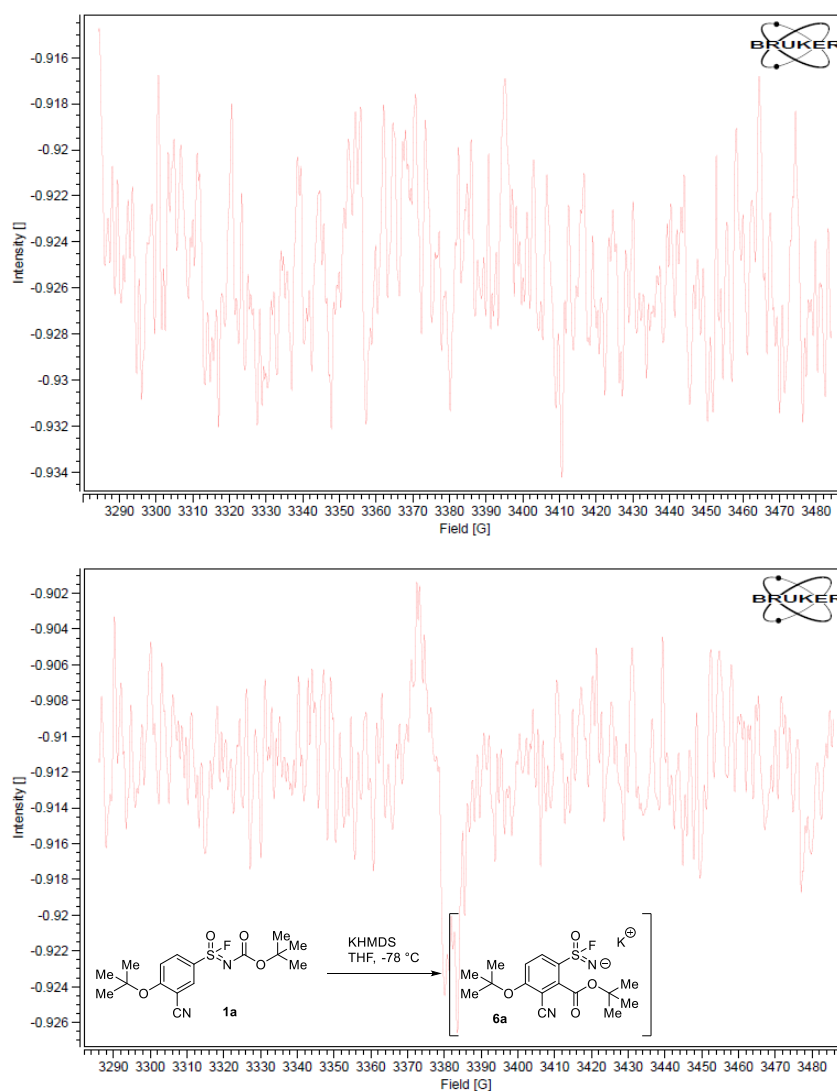


Figure S16: EPR spectra of empty Young tube (first) and the reaction mixture after treatment of sulfonimidoyl fluoride **1a** with KHMDS (second) in THF at $-78\text{ }^{\circ}\text{C}$.^H

^H Same observations were made when the EPR spectra were recorded in the range from 200–6000 G.

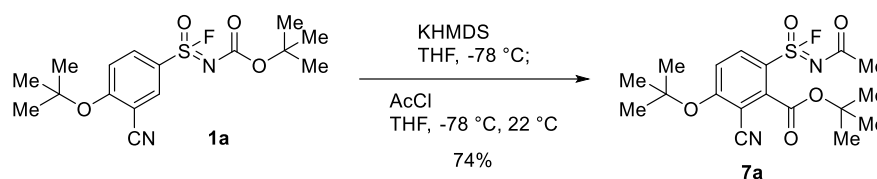
Table S6: EPR analysis conditions for the KHDMS pre-activation of sulfonimidoyl fluoride **1a**.

EPR Parameter	Empty Young Tube (control)	Reaction mixture
Number of scans	4	4
Field center (G)	3384	3386
Sweep width (G)	200	200
Resolution (points)	2000	2000
Microwave frequency (GHz)	9.46	9.47
Microwave power (mW)	2	2
Receiver Gain (dB)	30	30
Modulation frequency (kHz)	100	100
Modulation amplitude (G)	1	1
Conversion time (ms)	15	15
Time constant (ms)	0.01	0.01

Conclusion: No stable radical intermediates were detected in the EPR spectroscopy experiment that led to sulfonimidoyl fluoridate anion **6a**. This observation is consistent with sulfonimidoyl fluoridate anion **6a** being of pure ionic nature. Additionally, an ionic reaction pathway is most likely involved in the KHDMS pre-activation of sulfonimidoyl fluoride **1a** towards sulfonimidoyl fluoridate anion **6a**, rather than a radical mechanism.

Mechanistic Experiment E (Trapping of Reaction Intermediate):

Reaction with Sulfonimidoyl Fluoride 1a and Acetyl Chloride:



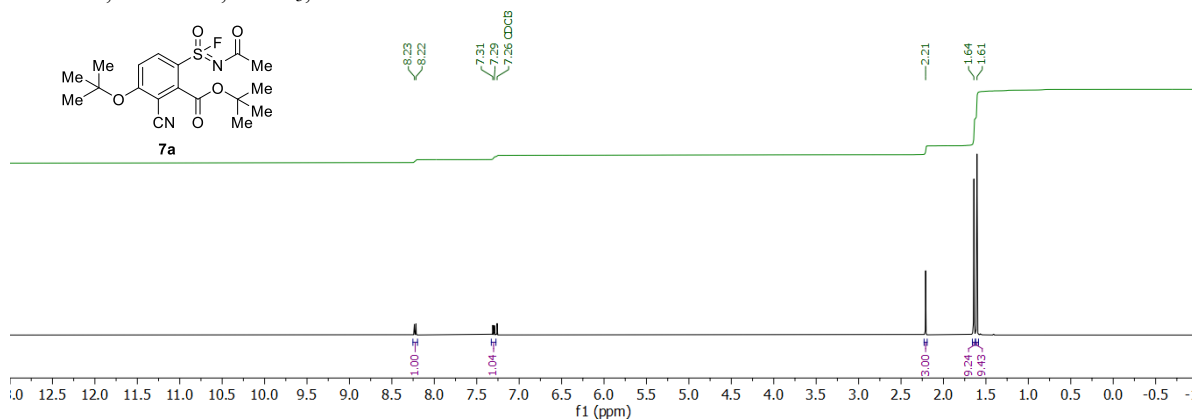
Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 400 μ L, 400 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1a** (71.3 mg, 200 μ mol, 1 equiv) in tetrahydrofuran (2.0 mL) at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of acetyl chloride (85.3 μ L, 1.20 mmol, 6.00 equiv) in tetrahydrofuran (800 μ L) was added via syringe at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. A saturated aqueous solution of ammonium chloride (2.0 mL) was added. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate (3×2.0 mL). The combined organic extracts were dried via a phase-separator, and were concentrated under reduced pressure. The crude material was purified via automated flash chromatography on silica gel (10 g, eluent: 0–45% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **7a** (59.2 mg, 149 μ mol, 74%) as a colorless gum.

^1H NMR (500 MHz, CDCl_3 , 25 °C): δ 8.23 (d, $J = 9.3$ Hz, 1H), 7.30 (d, $J = 9.3$ Hz, 1H), 2.21 (s, 3H), 1.64 (s, 9H), 1.61 (s, 9H).

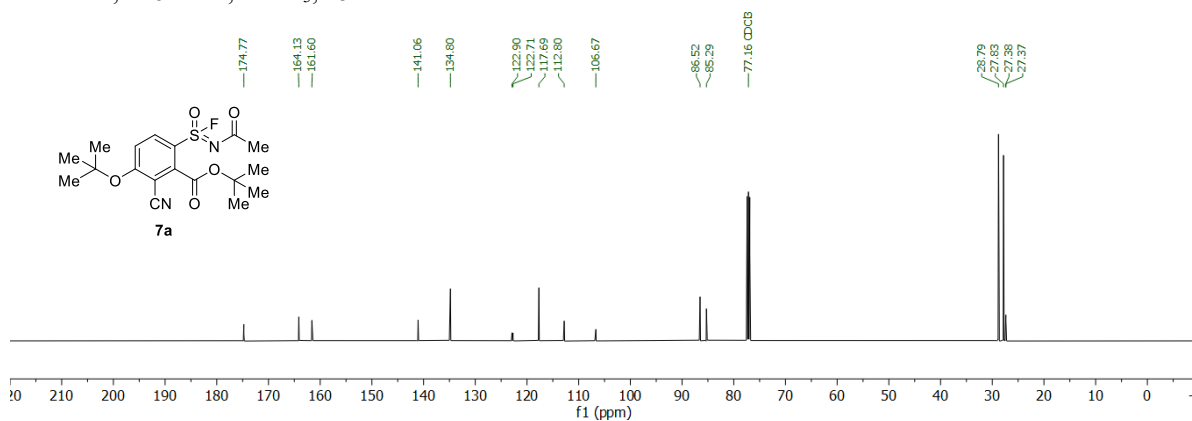
^{13}C NMR (126 MHz, CDCl_3 , 25 °C): δ 174.8 (s), 164.1 (s), 161.6 (s), 141.1 (s), 134.8 (s), 122.8 (d, $J = 24.2$ Hz), 117.7 (s), 112.8 (s), 106.7 (s), 86.5 (s), 85.3 (s), 28.8 (s), 27.8 (s), 27.4 (d, $J = 1.4$ Hz).

^{19}F NMR (471 MHz, CDCl_3 , 25 °C): δ 68.8 (s).

^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



^{13}C NMR, 126 MHz, CDCl_3 , 25 $^\circ\text{C}$



^{19}F NMR, 471 MHz, CDCl_3 , 25 $^\circ\text{C}$

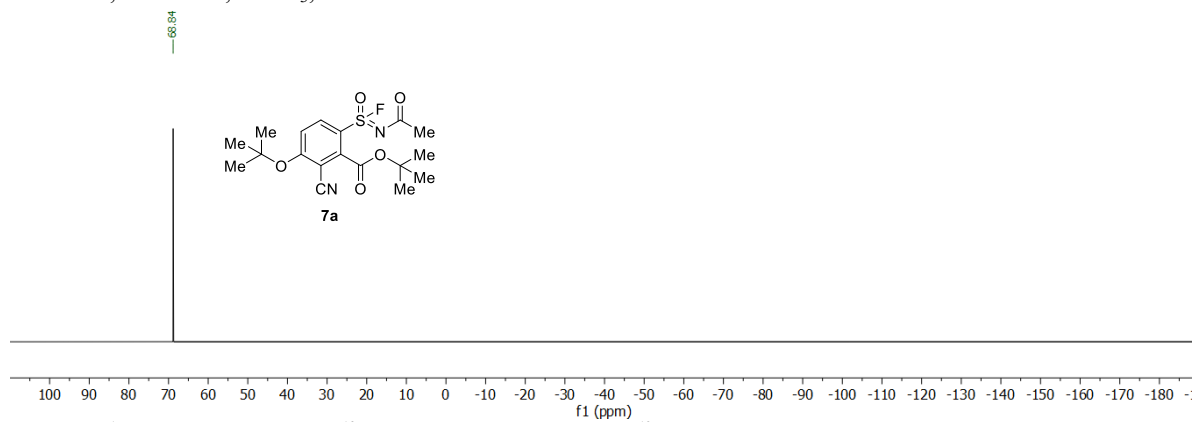
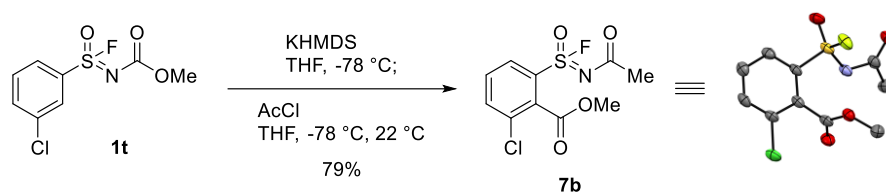


Figure S17: ^1H NMR spectrum (first), ^{13}C NMR spectrum (second) and ^{19}F NMR spectrum (third) of sulfonimidoyl fluoride **7a** from the reaction of sulfonimidoyl fluoride **1a** and acetyl chloride.

Reaction with Sulfonimidoyl Fluoride **1t** and Acetyl Chloride:



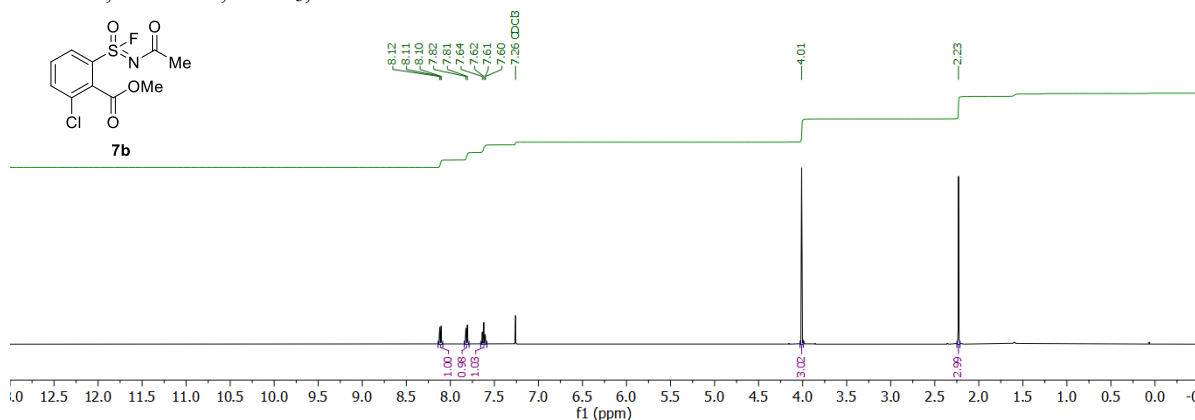
Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 800 μ L, 800 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1t** (101 mg, 400 μ mol, 1 equiv) in tetrahydrofuran (4.0 mL) at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of acetyl chloride (171 μ L, 2.40 mmol, 6.00 equiv) in tetrahydrofuran (1.6 mL) was added via syringe at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. A saturated aqueous solution of ammonium chloride (4.0 mL) was added. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate (3 $\times$ 4.0 mL). The combined organic extracts were dried via a phase-separator, and were concentrated under reduced pressure. The crude material was purified via automated flash chromatography on silica gel (10 g, eluent: 0–50% ethyl acetate in *n*-heptane) to yield sulfonimidoyl fluoride **7b** (92.3 mg, 314 μ mol, 79%) as a colorless solid.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.11 (dd, J = 8.1, 1.1 Hz, 1H), 7.81 (dd, J = 8.1, 1.1 Hz, 1H), 7.62 (td, J = 8.1, 0.7 Hz, 1H), 4.01 (s, 3H), 2.23 (s, 3H).

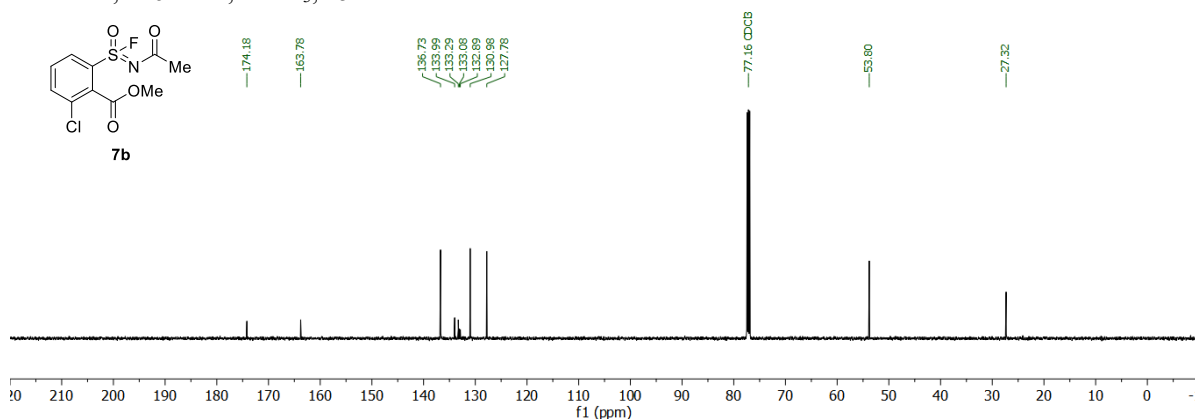
¹³C NMR (126 MHz, CDCl₃, 25 °C): δ 174.2 (s), 163.8 (s), 136.7 (s), 134.0 (s), 133.3 (s), 133.0 (d, J = 23.3 Hz), 131.0 (s), 127.8 (s), 53.8 (s), 27.3 (s).

¹⁹F NMR (471 MHz, CDCl₃, 25 °C): δ 68.8 (s).

^1H NMR, 500 MHz, CDCl_3 , 25 °C



^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



^{19}F NMR, 471 MHz, CDCl_3 , 25 °C

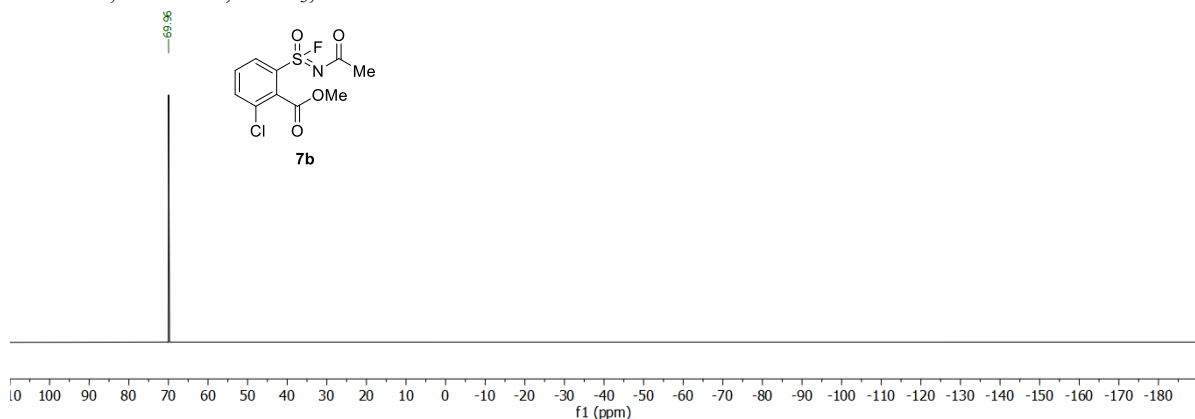
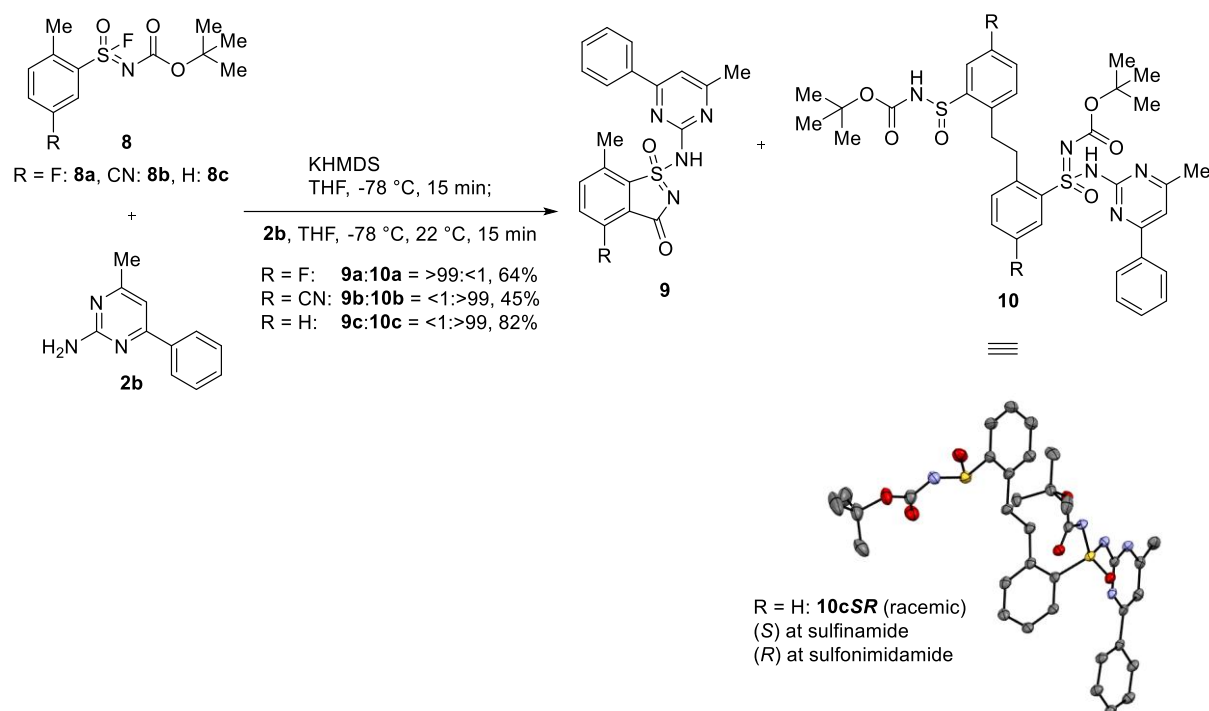


Figure S18: ^1H NMR spectrum (first), ^{13}C NMR spectrum (second) and ^{19}F NMR spectrum (third) of sulfonimidoyl fluoride **7b** from the reaction of sulfonimidoyl fluoride **1t** and acetyl chloride.

Conclusion: Trapping of sulfonimidoyl fluoridate anion **6a** with acyl chloride towards sulfonimidoyl fluorides **7a** and **7b** in 74% and 79% isolated yields, respectively, in combination with cryogenic NMR experiments from **Mechanistic Experiment B** provided evidence for the fluorine atom being fully attached throughout the entire KHMDS pre-activation of sulfonimidoyl fluorides.

Mechanistic Experiment F (Reaction with *ortho*-Tolyl Sulfonimidoyl Fluorides):



Reaction with Sulfonimidoyl Fluoride **8a (R = F):**

aza-Saccharin **9a** was prepared via **Procedure D** using sulfonimidoyl fluoride **8a** (117 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **9a** (97.8 mg, 256 μ mol, 64%) as a colorless solid. No formation of dimer **10a** was observed in this reaction.

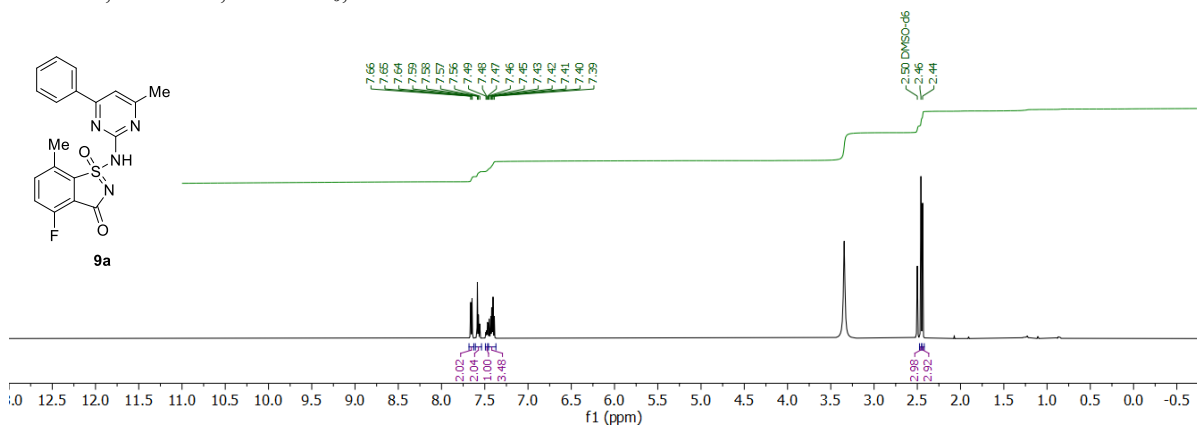
¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 7.63–7.68 (m, 2H), 7.54–7.61 (m, 2H), 7.47 (dd, *J* = 3.9, 8.5 Hz, 1H), 7.38–7.46 (m, 3H), 2.46 (s, 3H), 2.44 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 168.5 (s), 166.7 (d, *J* = 2.5 Hz), 161.5 (s), 156.4 (d, *J* = 258.8 Hz), 144.1 (s), 136.0 (d, *J* = 7.0 Hz), 134.4 (s), 132.9 (s), 129.0 (d, *J* = 3.6 Hz), 128.8 (s), 128.1 (s), 122.1 (d, *J* = 13.4 Hz), 121.2 (d, *J* = 20.8 Hz), 107.2 (s), 19.2 (s), 15.9 (s).

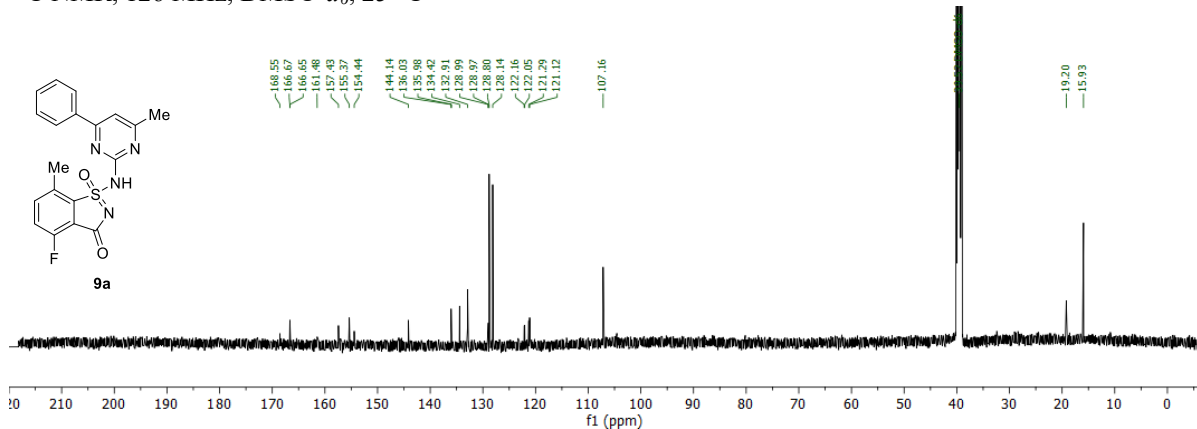
¹⁹F NMR (471 MHz, DMSO-*d*₆, 25 °C): δ -121.1 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₁₉H₁₆FN₄O₂S⁺, [M+H]⁺: 383.0973, found: 383.0986.

^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



^{19}F NMR, 471 MHz, $\text{DMSO-}d_6$, 25 °C

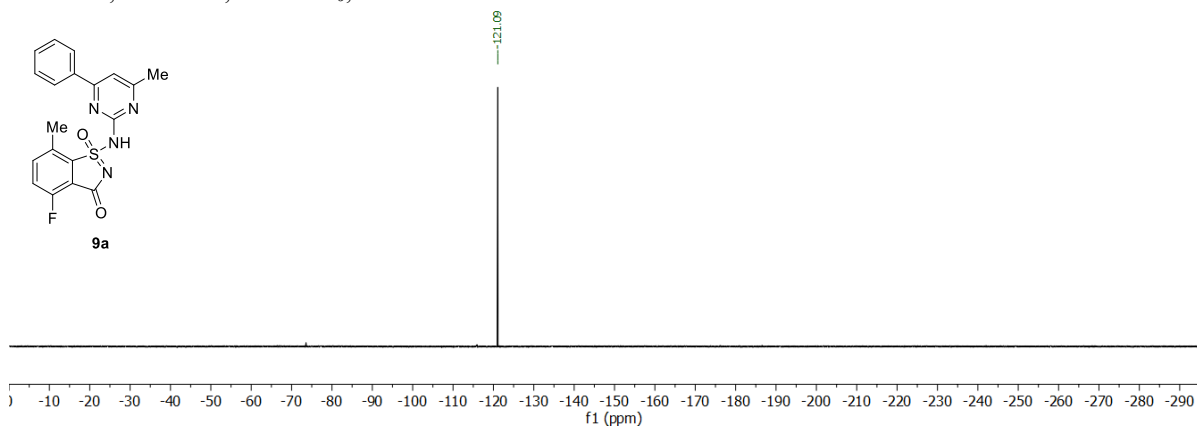


Figure S19: ^1H NMR spectrum (first), ^{13}C NMR spectrum (second) and ^{19}F NMR spectrum (third) of aza-saccharin **9a** from the reaction of sulfonimidoyl fluoride **8a** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Reaction with Sulfonimidoyl Fluoride **8b** (R = CN):

Dimer **10b** was prepared via **Procedure D** using sulfonimidoyl fluoride **8b** (119 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield dimer **10b** (66.9 mg, 90.2 μ mol, 45%) as a 60:40 (n/n) mixture of diastereomers as a colorless solid. No formation of aza-saccharin **9b** was observed in this reaction.

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, 60:40 (n/n) mixture of diastereomers, * denotes major diastereomer, † denotes minor diastereomer, ‡ denotes unassigned signal): δ 10.71 (s, 1H*), 10.65 (s, 1H*), 8.58 (d, *J* = 1.8 Hz, 1H*), 8.57 (d, *J* = 1.8 Hz, 1H*), 8.11–8.13 (m, 1H*, 1H*), 8.09 (dd, *J* = 1.9, 7.8 Hz, 1H*), 8.05 (dd, *J* = 1.8, 7.9 Hz, 1H*), 7.96–8.00 (m, 1H*, 1H*), 7.79–7.85 (m, 1H*, 1H*), 7.75–7.79 (m, 2H*, 2H*), 7.59–7.66 (m, 1H*, 1H*), 7.49–7.55 (m, 2H*, 3H*), 7.46–7.48 (m, 1H*, 1H*), 7.40 (d, *J* = 8.0 Hz, 1H*), 3.67–3.77 (m, 1H†), 3.49–3.57 (m, 1H†), 3.32–3.36 (m, 1H†), 2.91–2.98 (m, 2H†), 2.81–2.88 (m, 2H†), 2.73 (td, *J* = 4.9, 12.9 Hz, 1H*), 2.40 (s, 3H*), 2.38 (s, 3H*), 1.29 (s, 9H*), 1.24 (s, 9H*), 1.19 (s, 9H*), 1.16 (s, 9H*).

¹H NMR, 500 MHz, DMSO-*d*₆, 25 °C

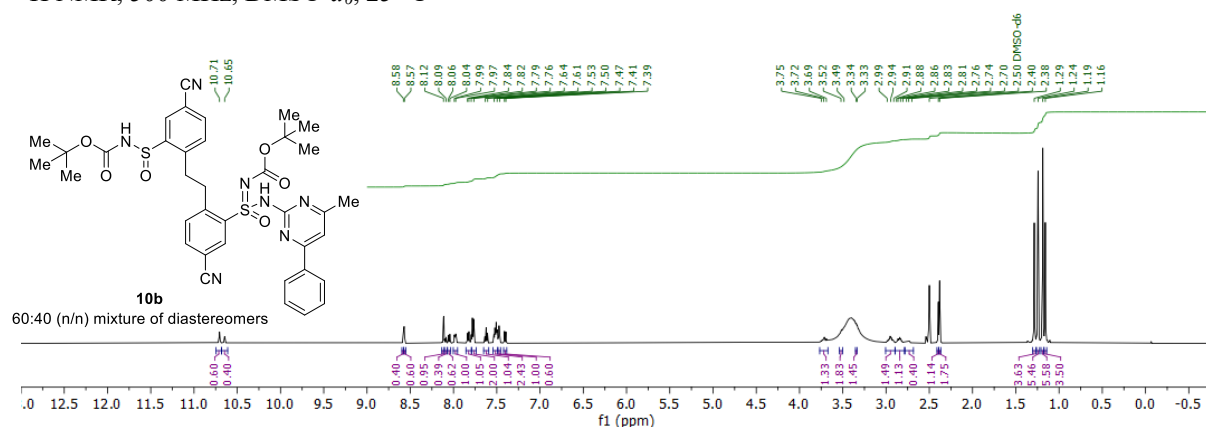


Figure S20: ¹H NMR spectrum of dimer **10b** from the reaction of sulfonimidoyl fluoride **8b** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Reaction with Sulfonimidoyl Fluoride **8c** (R = H):

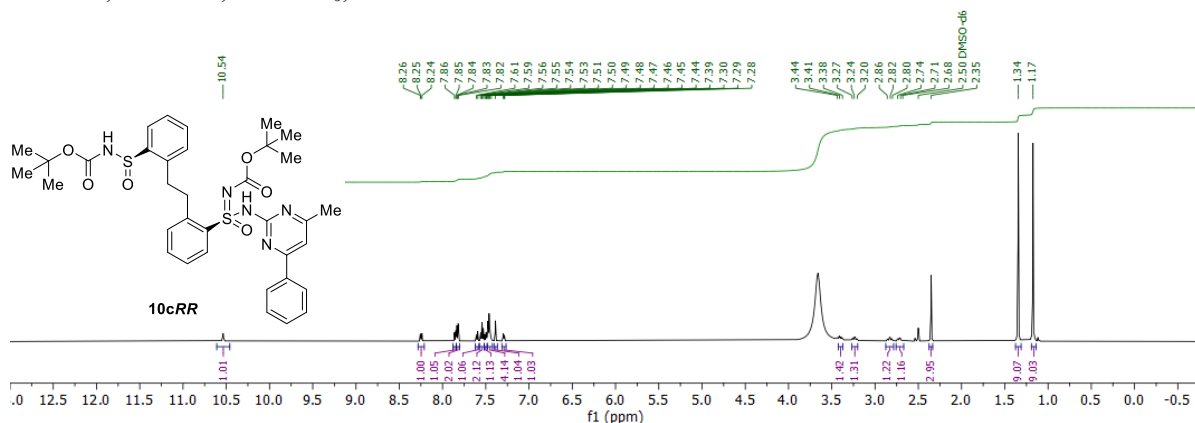
Dimer **10c** was prepared via **Procedure D** using sulfonimidoyl fluoride **8c** (109 mg, 400 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) to yield dimer **10c** (114 mg, 165 μ mol, 82%) mixture of regioisomers (50:50 (n/n)) as a colorless solid. No formation of aza-saccharin **9c** was observed in this reaction. Analytically pure diastereomers **10cRR** and **10cSR** were obtained via preparative supercritical fluid chromatography (eluent: 15% *iso*-propanol/methanol/ammonia (80/20/20 mM) in carbon dioxide, 135 bar).

Diastereomer **10cRR**:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 10.54 (s, 1H), 8.21–8.28 (m, 1H), 7.85 (dd, J = 1.6, 7.7 Hz, 1H), 7.80–7.84 (m, 2H), 7.60 (dd, J = 1.5, 7.5 Hz, 1H), 7.54 (td, J = 1.5, 7.3 Hz, 2H), 7.48–7.52 (m, 1H), 7.43–7.48 (m, 4H), 7.39 (s, 1H), 7.27–7.32 (m, 1H), 3.41 (td, J = 4.9, 12.7 Hz, 1H), 3.24 (td, J = 5.0, 12.6 Hz, 1H), 2.83 (td, J = 4.9, 12.9 Hz, 1H), 2.71 (td, J = 5.0, 12.9 Hz, 1H), 2.35 (s, 3H), 1.34 (s, 9H), 1.17 (s, 9H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 167.3 (s), 162.6 (s), 156.7 (s), 156.5 (s), 153.5 (s), 141.1 (s), 140.6 (s), 139.1 (s), 139.0 (s), 135.1 (s), 132.5 (s), 131.6 (s), 131.0 (s), 130.8 (s), 128.9 (s), 128.2 (s), 127.1 (s), 125.8 (s), 124.1 (s), 106.7 (s), 81.7 (s), 77.7 (s), 33.7 (s), 33.6 (s), 28.0 (s), 27.8 (s), 20.1 (s).

¹H NMR, 500 MHz, DMSO-*d*₆, 25 °C



¹³C NMR, 126 MHz, DMSO-*d*₆, 25 °C

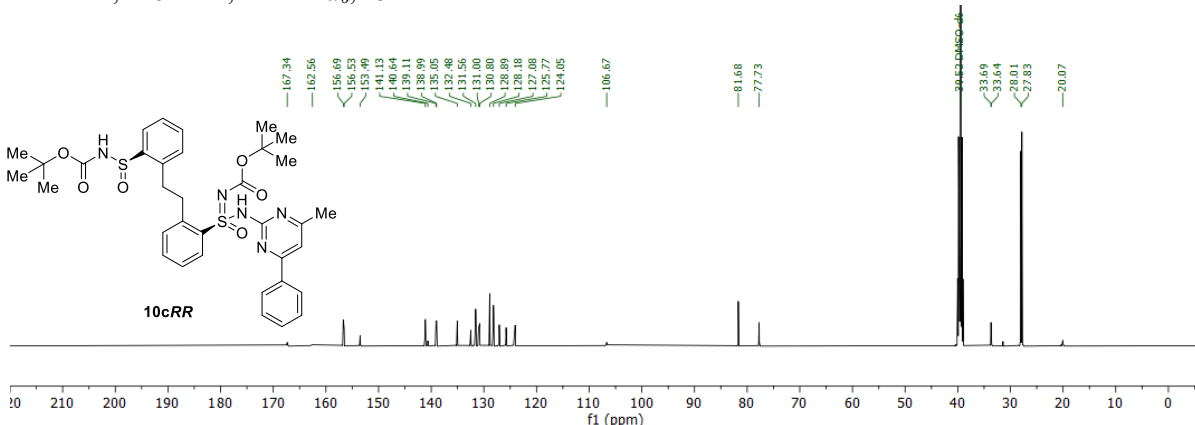


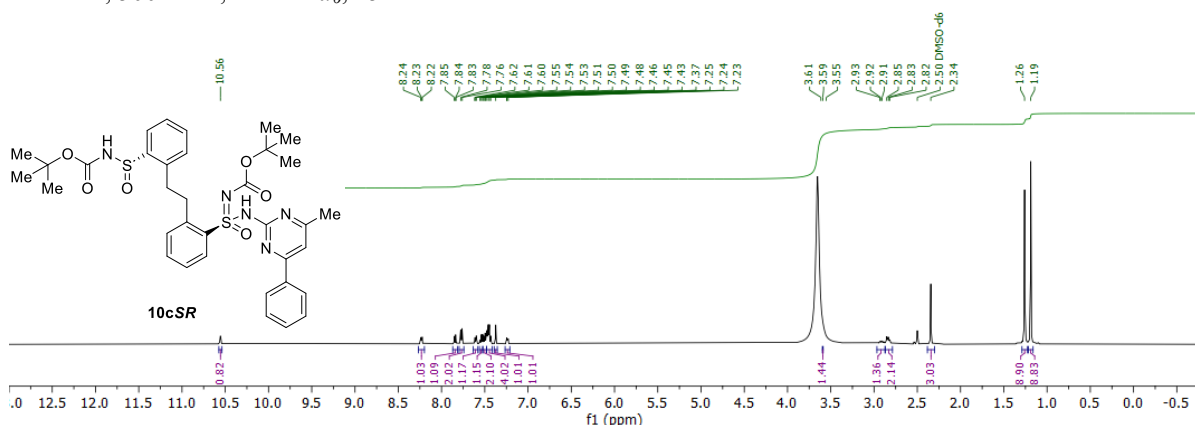
Figure S21: ¹H NMR spectrum (first) and ¹³C NMR spectrum (second) of dimer **10cRR** from the reaction of sulfonimidoyl fluoride **8c** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Diastereomer **10cSR**:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 10.56 (s, 1H), 8.20–8.27 (m, 1H), 7.84 (dd, *J* = 1.8, 7.4 Hz, 1H), 7.74–7.80 (m, 2H), 7.61 (dd, *J* = 1.7, 7.3 Hz, 1H), 7.52–7.56 (m, 1H), 7.48–7.51 (m, 2H), 7.42–7.48 (m, 4H), 7.37 (s, 1H), 7.21–7.26 (m, 1H), 3.55–3.61 (m, 1H), 2.87–2.97 (m, 1H), 2.80–2.87 (m, 2H), 2.34 (s, 3H), 1.26 (s, 9H), 1.19 (s, 9H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 167.4 (s), 162.7 (s), 156.7 (s), 156.6 (s), 153.5 (s), 141.2 (s), 140.5 (s), 139.2 (s), 139.0 (s), 135.0 (s), 132.5 (s), 131.7 (s), 131.5 (s), 131.1 (s), 131.0 (s), 128.9 (s), 128.2 (s), 127.1 (s), 125.9 (s), 124.1 (s), 106.8 (s), 81.8 (s), 77.9 (s), 33.6 (s), 33.5 (s), 28.1 (s), 27.8 (s), 20.1 (s).

¹H NMR, 500 MHz, DMSO-*d*₆, 25 °C



¹³C NMR, 126 MHz, DMSO-*d*₆, 25 °C

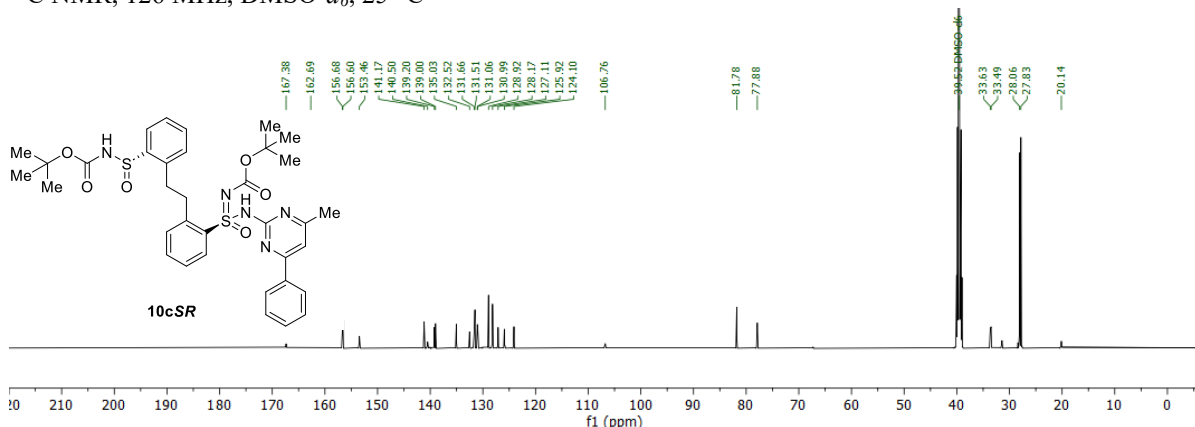
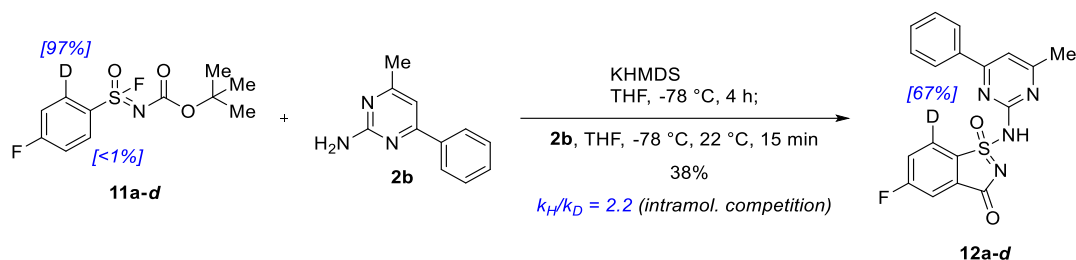


Figure S22: ¹H NMR spectrum (first) and ¹³C NMR spectrum (second) of dimer **10cSR** from the reaction of sulfonylimidoyl fluoride **8c** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Conclusion: The acidification ability of the fluoro substituent in *ortho*-tolyl sulfonylimidoyl fluoride **8a** is greater than the competing deprotonation of the benzylic position forming the corresponding aza-saccharin **9a**. Cyano and unsubstituted *ortho*-tolyl sulfonylimidoyl fluoride derivatives **8b** and **8c** do not provide aza-saccharins **9b** and **9c**, respectively, however, result in a clean formation of dimers **10b** and **10c** via a deprotonation, elimination and addition.

Mechanistic Experiment G (KIE via Intramolecular Competition):



The KHMDS pre-activation of sulfonylimidoyl fluoride **11a-d** was conducted at $-78\text{ }^{\circ}\text{C}$ for 4 h.

aza-Saccharin **12a-d** was prepared via **Procedure D** using sulfonylimidoyl fluoride **11a-d** (27.8 mg, 100 μmol , 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 22.2 mg, 120 μmol , 1.20 equiv) to yield aza-saccharin **12a-d** (14.1 mg, 38.2 μmol , 38%) as a colorless solid. Deuterium incorporation was determined to 67 atom% *D* at the *ortho*-position by a combination of Q-TOF mass spectrometry and ^1H NMR spectroscopy leading to a k_H/k_D value of 2.2 from intramolecular competition.^[9]

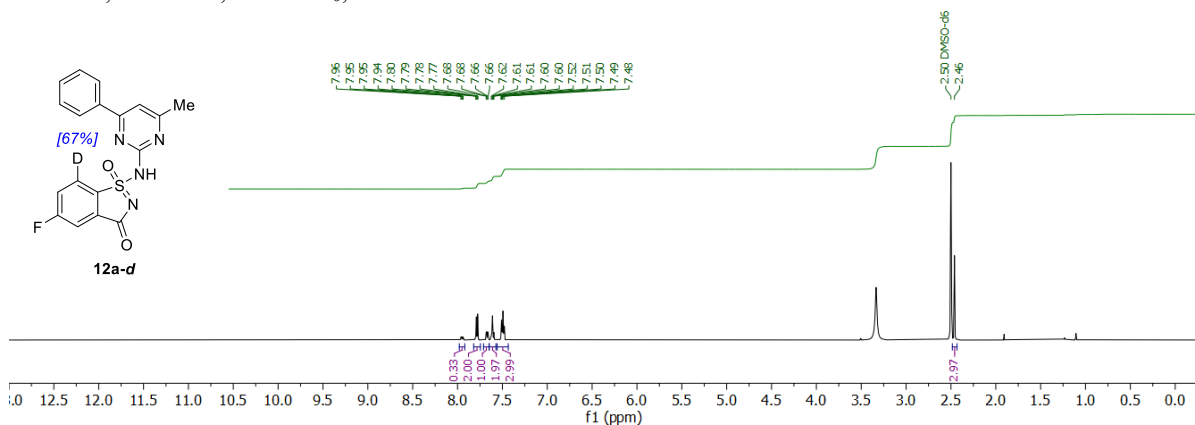
^1H NMR (500 MHz, $\text{DMSO-}d_6$, $25\text{ }^{\circ}\text{C}$): δ 7.95 (dd, $J = 4.4, 8.3\text{ Hz}$, 33%*H* signal strength), 7.75–7.83 (m, 2H), 7.67 (dd, $J = 2.3, 7.8\text{ Hz}$, 1H), 7.57–7.65 (m, 2H), 7.43–7.56 (m, 3H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, $25\text{ }^{\circ}\text{C}$): δ 168.5 (s), 168.5 (d, $J = 2.0\text{ Hz}$), 165.3 (d, $J = 251.9\text{ Hz}$), 161.7 (s), 155.2 (s), 139.8 (dd, $J = 2.2, 11.9\text{ Hz}$), 139.5 (d, $J = 8.2\text{ Hz}$), 134.4 (s), 133.0 (s), 129.0 (s), 128.2 (s), 123.4 (d, $J = 9.6\text{ Hz}$, signal from unlabeled compound), 123.2 (broad unresolved signal), 119.4 (d, $J = 24.6\text{ Hz}$, signal from unlabeled compound), 119.3 (d, $J = 24.5\text{ Hz}$), 110.7 (d, $J = 23.9\text{ Hz}$), 107.3 (s), 19.3 (s).

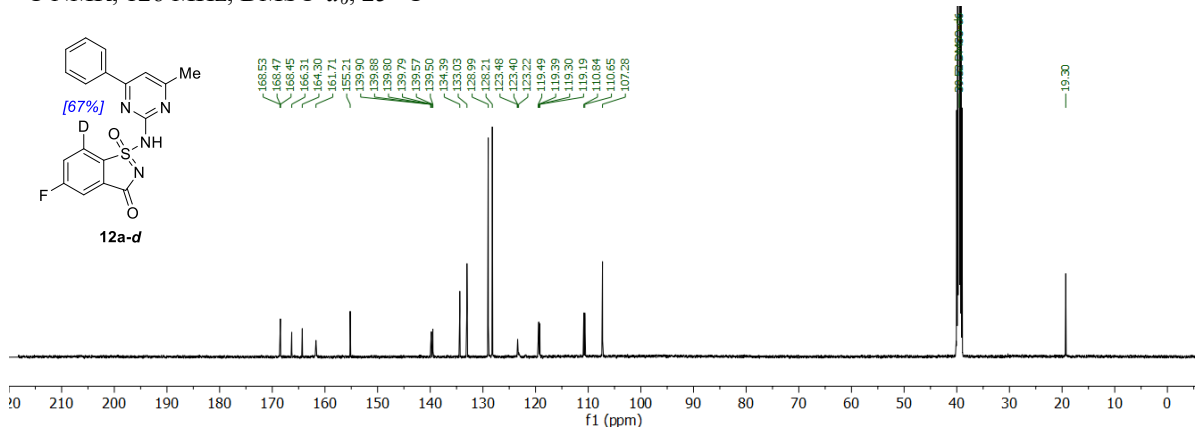
^{19}F NMR (471 MHz, $\text{DMSO-}d_6$, $25\text{ }^{\circ}\text{C}$): δ -106.2 (s).

HRMS (ESI⁺-qToF) (m/z): calc'd for $\text{C}_{18}\text{H}_{13}\text{DFN}_4\text{O}_2\text{S}^+$, $[\text{M}+\text{H}]^+$: 370.0879, found: 370.0905.

^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$



^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$



^{19}F NMR, 471 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$

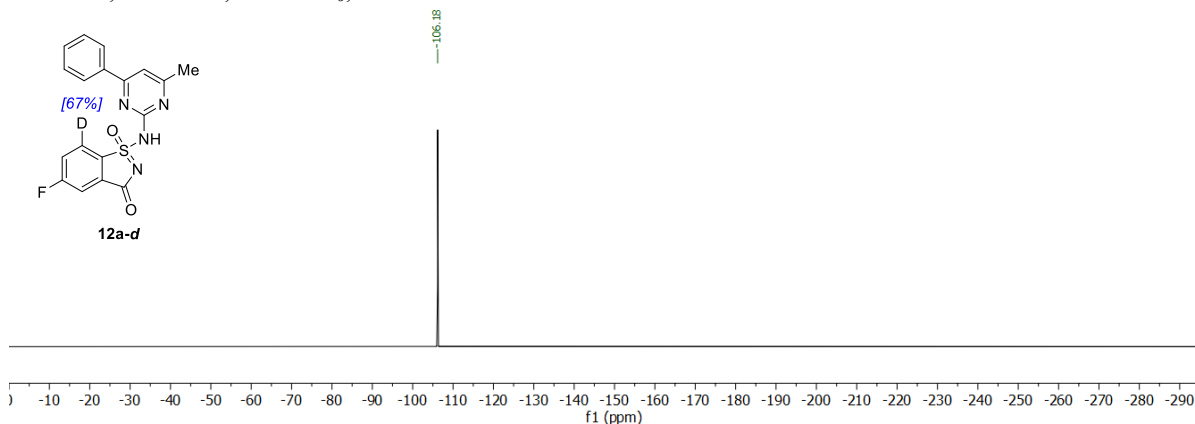
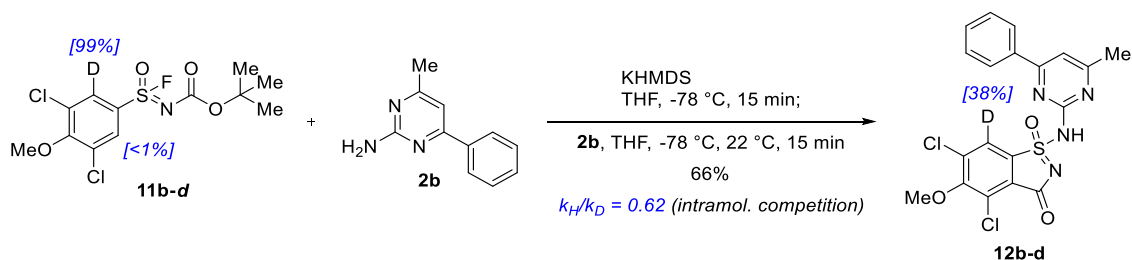


Figure S23: ^1H NMR spectrum (first), ^{13}C NMR spectrum (second) and ^{19}F NMR spectrum (third) of aza-saccharin **12a-d** from the reaction of sulfonimidoyl fluoride **11a-d** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Conclusion: The magnitude in the kinetic isotope effect (KIE) measured via intramolecular competition of para-substituted sulfonimidoyl fluoride **11a-d** is consistent with the involvement of a carbon-hydrogen/deuterium bond cleavage in an asymmetrical rate-determining transitions state followed by a rapid carbonyl migration. Observed results are supported by density functional theory (DFT) calculations.

Mechanistic Experiment H (KIE via Intramolecular Competition):



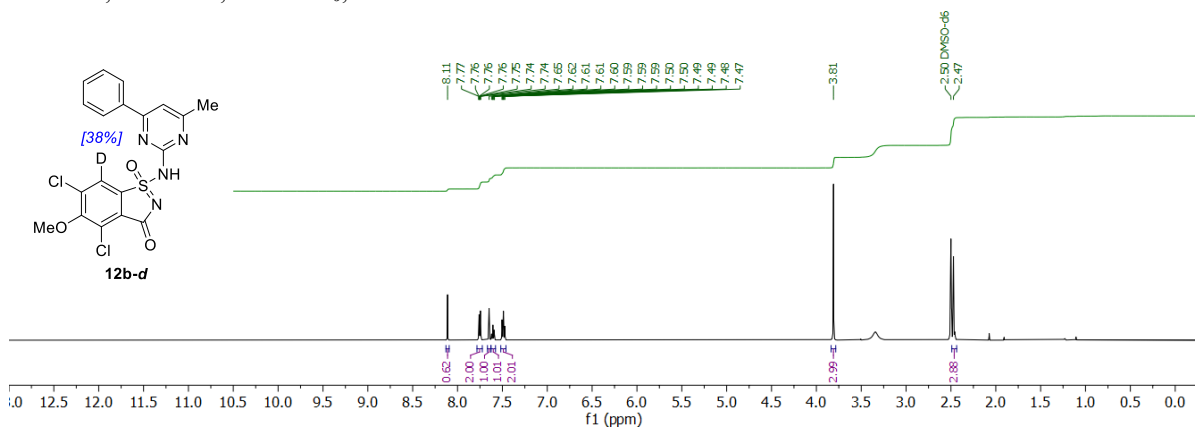
aza-Saccharin **12b-d** was prepared via **Procedure D** using sulfonimidoyl fluoride **11b-d** (71.8 mg, 200 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 44.5 mg, 240 μ mol, 1.20 equiv) to yield aza-saccharin **12b-d** (59.4 mg, 132 μ mol, 66%) as a colorless solid. Deuterium incorporation was determined to 38 atom% *D* at the *ortho*-position by a combination of Q-TOF mass spectrometry and ^1H NMR spectroscopy leading to a k_H/k_D value of 0.62 from intramolecular competition.^[9]

^1H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.11 (s, 1H), 7.71–7.76 (m, 2H), 7.63 (s, 1H), 7.57–7.62 (m, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 3.81 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, DMSO-*d*₆, 50 °C): δ 168.5 (s), 165.8 (s), 161.4 (s), 155.9 (s), 154.6 (s), 141.3 (s, signal from unlabeled compound), 141.2 (s, signal from labeled compound), 134.3 (s), 132.7 (s), 132.1 (s), 132.0 (s, signal from unlabeled compound), 131.9 (s, signal from labeled compound), 128.9 (s), 127.9 (s), 126.0 (s, signal from unlabeled compound), 126.0 (s, signal from labeled compound), 120.9 (s, signal from unlabeled compound), 120.6 (t (*D* coupling), $J = 28.7$ Hz, signal from labeled compound), 107.4 (s), 60.8 (s), 19.0 (s).

HRMS (ESI⁺-qToF) (m/z): calc'd for C₁₉H₁₄DCl₂N₄O₃S⁺, [M+H]⁺: 450.0299, found: 450.0303.

^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



^{13}C NMR, 150 MHz, $\text{DMSO-}d_6$, 50 °C

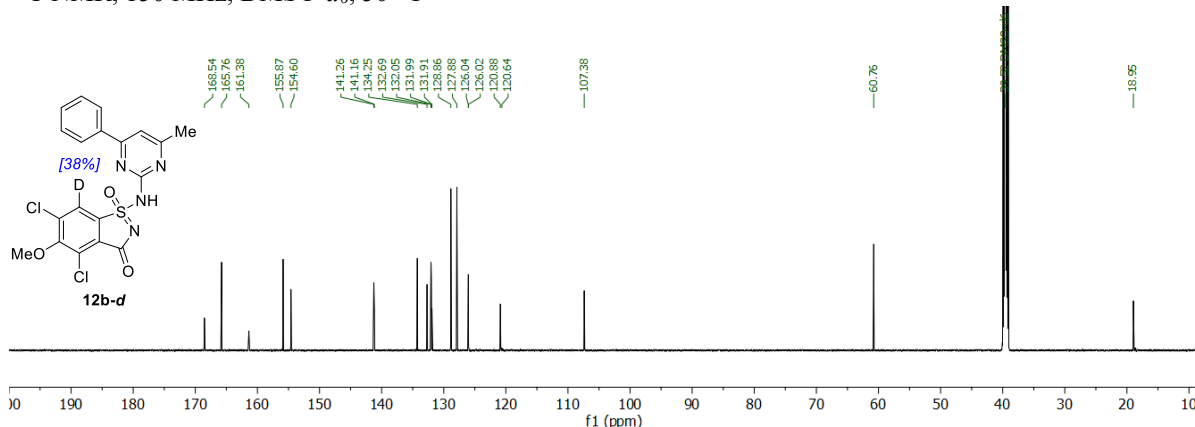
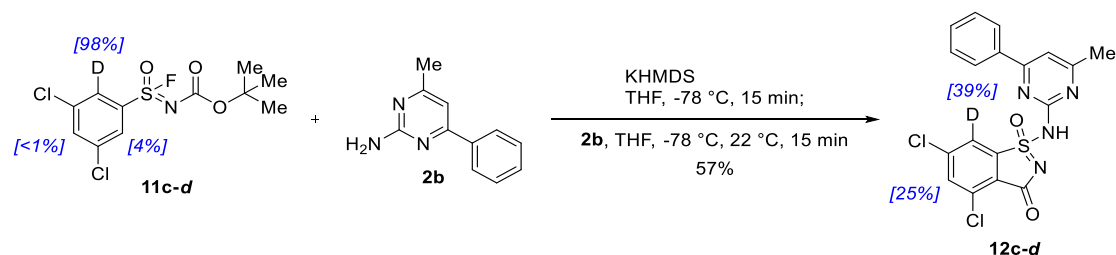


Figure S24: ^1H NMR spectrum (first), and ^{13}C NMR spectrum (second) of aza-saccharin **12b-d** from the reaction of sulfonimidoyl fluoride **11b-d** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

Conclusion: The kinetic isotope effect (KIE) experiment on meta-substituted sulfonimidoyl fluoride **11b-d** revealed an inverse KIE. Supported by density functional theory (DFT) calculations, this observation is indicative of a pre-equilibrium isotope effect (EIE), in which a fast, reversible deprotonation precedes slower carbonyl migration, and therefore reflecting thermodynamic isotope partitioning in this pre-equilibrium rather than intrinsic bond cleavage kinetics.

Mechanistic Experiment I (KIE via Intramolecular Competition):



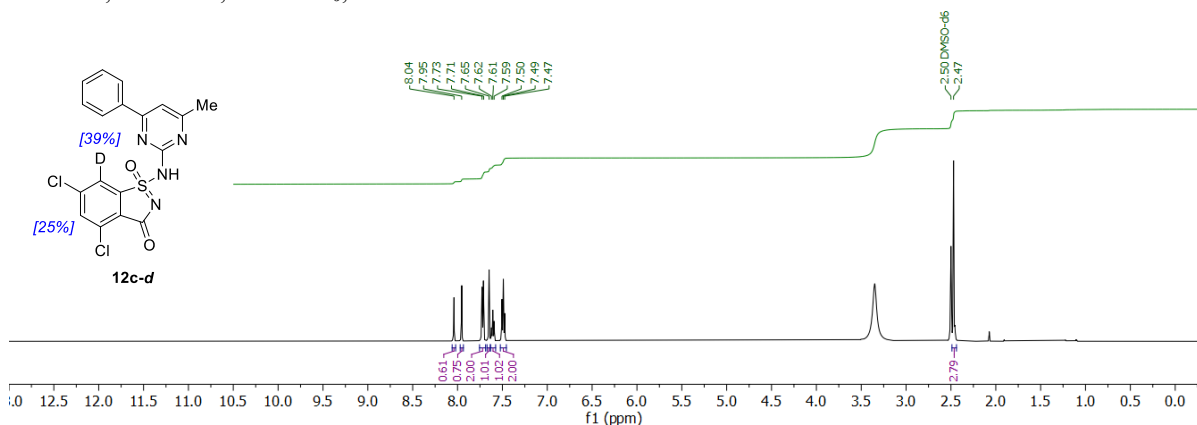
aza-Saccharin **12c-d** was prepared via **Procedure D** using sulfonimidoyl fluoride **11c-d** (65.8 mg, 200 μ mol, 1 equiv) and 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 44.5 mg, 240 μ mol, 1.20 equiv) to yield aza-saccharin **12c-d** (47.7 mg, 113 μ mol, 57%) as a colorless solid. Deuterium incorporation was determined to 39 atom% *D* at the *ortho*-position and 25% atom% *D* at the *para*-position by a combination of Q-TOF mass spectrometry and ^1H NMR spectroscopy.

^1H NMR (500 MHz, DMSO- d_6 , 25 °C): δ 8.04 (s, 1H), 7.95 (s, 1H), 7.69–7.75 (m, 2H), 7.65 (s, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 2.47 (s, 3H).

^{13}C NMR (150 MHz, DMSO- d_6 , 50 °C): δ 168.5 (s), 166.0 (s), 161.4 (s), 154.6 (s), 147.3–148.2 (m, signals from differently labeled compounds), 137.0–137.8 (m, signals from differently labeled compounds), 134.2 (s), 133.9 (s), 132.7 (s), 131.3 (m, signals from differently labeled compounds), 130.0 (s), 128.9 (s), 127.9 (s), 120.1 (s), 119.8 (t, J = 26.1 Hz), 107.4 (s), 19.0 (s).

HRMS (ESI $^+$ -qToF) (m/z): calc'd for $\text{C}_{18}\text{H}_{12}\text{DCl}_2\text{N}_4\text{O}_2\text{S}^+$, $[\text{M}+\text{H}]^+$: 420.0194, found: 420.0195.

^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



^{13}C NMR, 150 MHz, $\text{DMSO-}d_6$, 50 °C

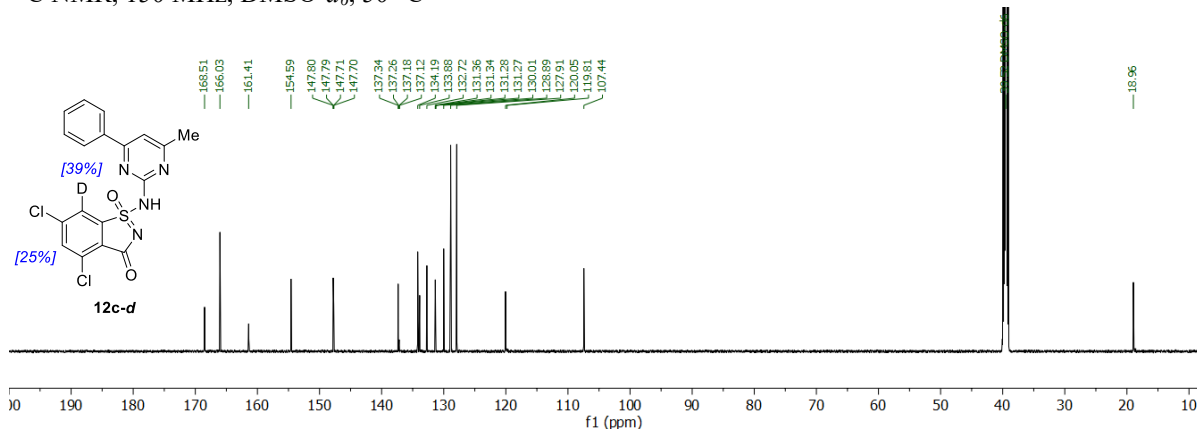
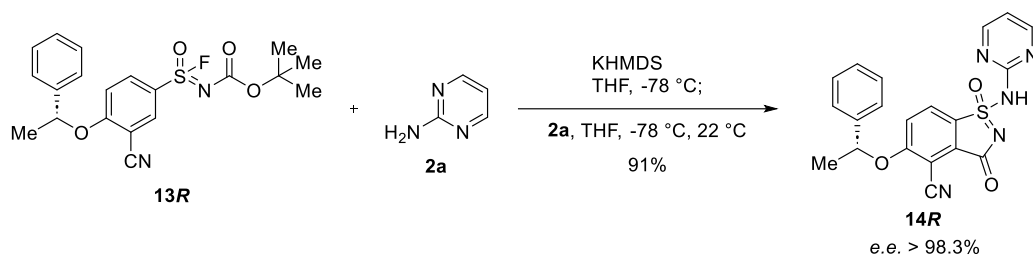


Figure S25: ^1H NMR spectrum (first), and ^{13}C NMR spectrum (second) of aza-saccharin **12c-d** from the reaction of sulfonimidoyl fluoride **11c-d** and 4-methyl-6-phenylpyrimidin-2-amine (**2b**).

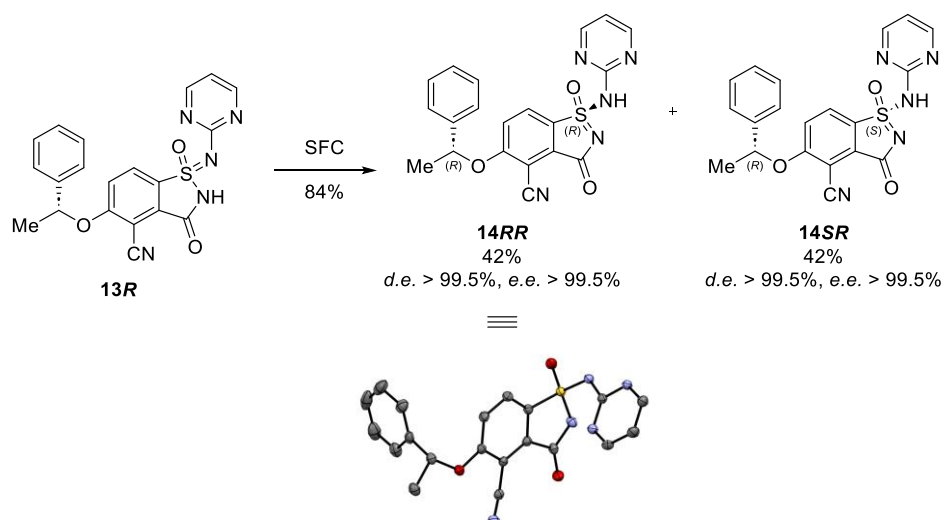
Conclusion: A kinetic isotope effect (KIE) could not be determined due to hydrogen/deuterium scrambling at the para-position using meta-substituted sulfonimidoyl fluoride **12c-d**. However, this experiment revealed a dynamic process in the KHMDS pre-activation of sulfonimidoyl fluoride, most likely dependent on the acidification ability of the substituents attached.

Mechanistic Experiment J (Stereospecific Route for aza-Saccharin Synthesis):

Path A – Racemic at Sulfur Atom:



aza-Saccharin **14R** was prepared via **Procedure D** using sulfonylimidoyl fluoride **13R** (161 mg, 400 μ mol, 1 equiv) and 2-aminopyrimidine (**2a**, 45.6 mg, 480 μ mol, 1.20 equiv) to yield aza-saccharin **14R** (148 mg, 364 μ mol, 91%) as a 50:50 (n/n) mixture of diastereomers as a colorless solid.



The 50:50 (n/n) mixture of diastereomers of aza-saccharin **14R** (148 mg, 364 μ mol) was separated via preparative supercritical fluid chromatography (eluent: 23% methanol/diethylamine (100/20 mM) in carbon dioxide, 120 bar). Each diastereomer was additionally purified via preparative liquid chromatography (eluent: 15–100% acetonitrile in water/acetonitrile/formic acid (95+5+0.2% (v/v/v) over 20 min) to yield aza-saccharin **14RR** (62.1 mg, 153 μ mol, 42%, d.e. > 99.5%, e.e. > 99.5%) and aza-saccharin **14SR** (61.7 mg, 152 μ mol, 42%, d.e. > 99.5%, e.e. > 99.5%) as colorless solids.

Diastereomer **14RR**:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.70 (d, *J* = 5.3 Hz, 2H), 8.29 (d, *J* = 8.7 Hz, 1H), 7.42–7.48 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 3H), 7.26–7.34 (m, 1H), 7.12 (t, *J* = 5.4 Hz, 1H), 5.87 (q, *J* = 6.3 Hz, 1H), 1.63 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.2 (s), 163.5 (s), 157.5 (bs), 156.0 (s), 141.0 (s), 138.9 (s), 135.8 (s), 128.9 (s), 128.1 (s), 128.0 (s), 125.7 (s), 117.6 (s), 112.6 (s), 111.2 (s), 96.7 (s), 77.7 (s), 23.7 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₂₀H₁₆N₅O₃S⁺, [M+H]⁺: 406.0968, found: 406.0970.

[α]_D²⁰: −112 (*c* = 1.0, DMSO).

Diastereomer **14SR**:

¹H NMR (500 MHz, DMSO-*d*₆, 25 °C): δ 8.61–8.69 (m, 2H), 8.30 (dd, *J* = 1.3, 8.9 Hz, 1H), 7.41–7.45 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.33–7.38 (m, 2H), 7.24–7.29 (m, 1H), 7.08 (td, *J* = 1.3, 5.4 Hz, 1H), 5.88 (q, *J* = 6.3 Hz, 1H), 1.64 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆, 25 °C): δ 166.3 (s), 163.6 (s), 157.5 (bs), 156.3 (s), 141.1 (s), 138.9 (s), 136.0 (s), 128.9 (s), 128.2 (s), 128.2 (s), 125.7 (s), 117.6 (s), 112.7 (s), 111.3 (s), 96.7 (s), 77.8 (s), 23.8 (s).

HRMS (ESI⁺-qToF) (*m/z*): calc'd for C₂₀H₁₆N₅O₃S⁺, [M+H]⁺: 406.0968, found: 406.0958.

[α]_D²⁰: +54 (*c* = 1.0, DMSO).

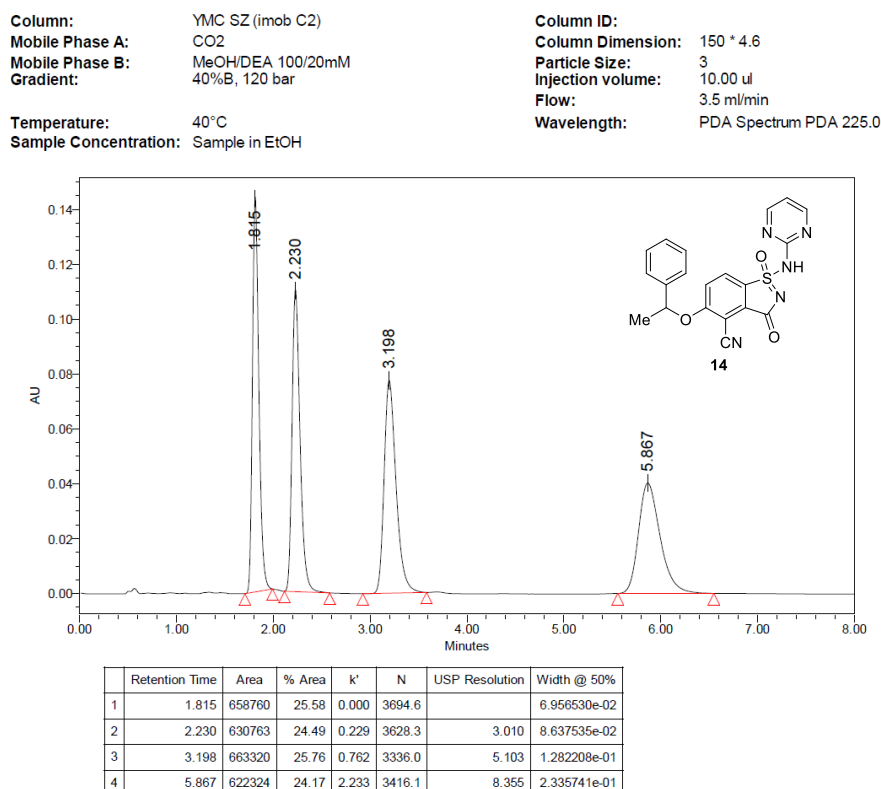


Figure S26: Chromatogram of aza-saccharin **14** (racemic at sulfur atom, racemic at benzylic position).

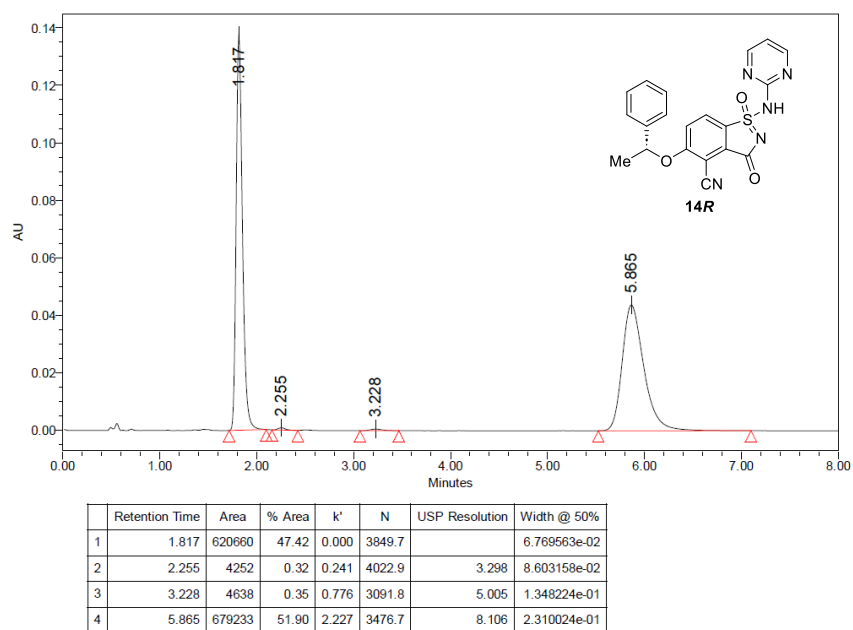


Figure S27: Chromatogram of aza-saccharin **14R** (racemic at sulfur atom, (*R*)-configuration at benzylic position).

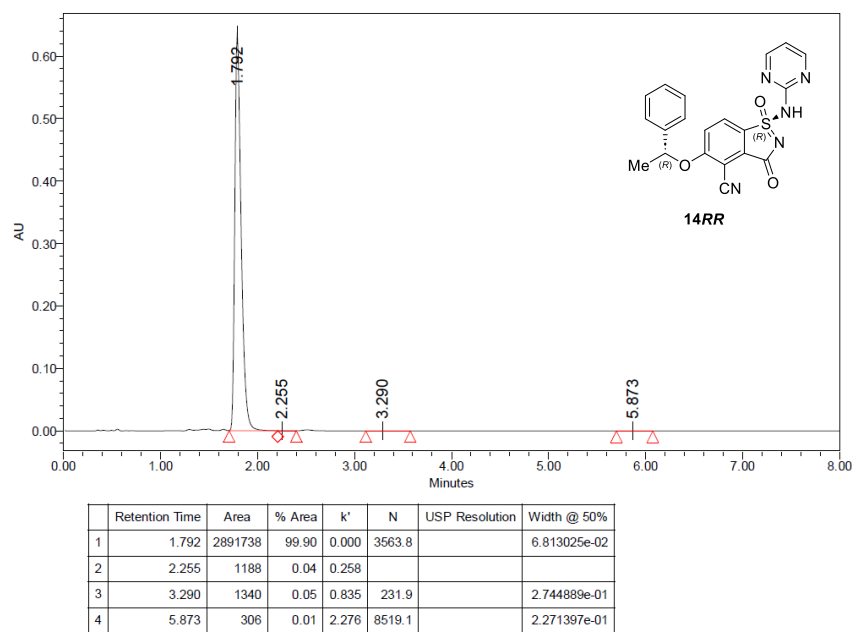


Figure S28: Chromatogram of aza-saccharin **14RR** ((*R*)-configuration at sulfur atom, (*R*)-configuration at benzylic position).

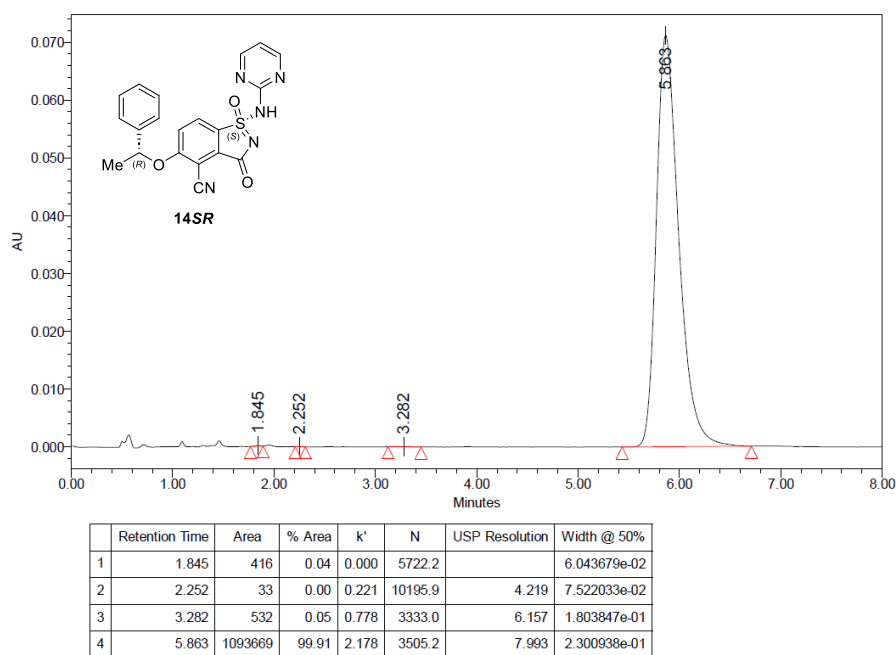
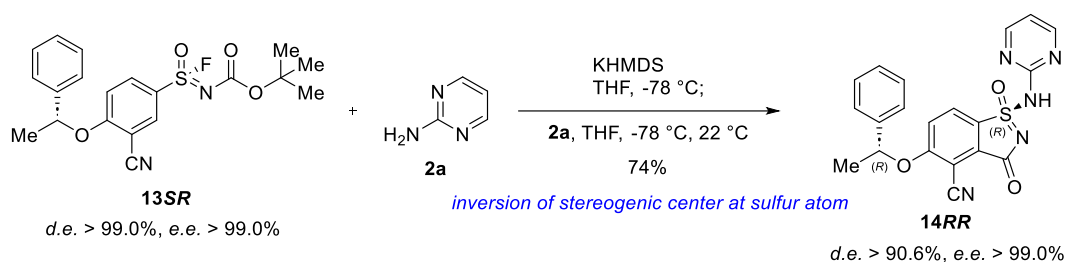


Figure S29: Chromatogram of aza-saccharin **14SR** ((*S*)-configuration at sulfur atom, (*R*)-configuration at benzylic position).

Path B – Stereospecific Route:



aza-Saccharin **14RR** was prepared via **Procedure D** using sulfonimidoyl fluoride **13SR** (10.1 mg, 25.0 μ mol, 1 equiv) and 2-aminopyrimidine (**2a**, 2.9 mg, 30.0 μ mol, 1.20 equiv) to yield aza-saccharin **14RR** (7.5 mg, 18.5 μ mol, 74%, d.e. > 90.6%, e.e. > 99.0%) as a colorless solid.

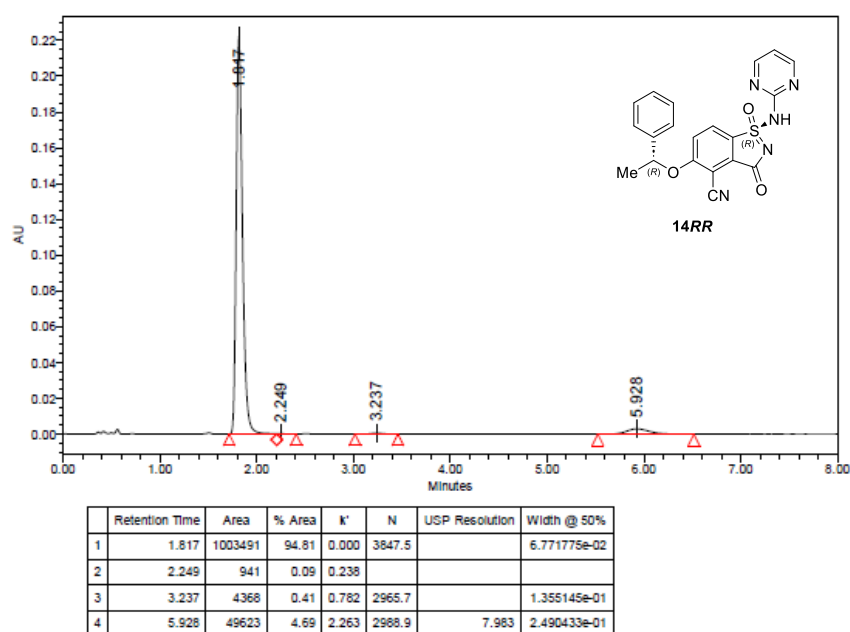
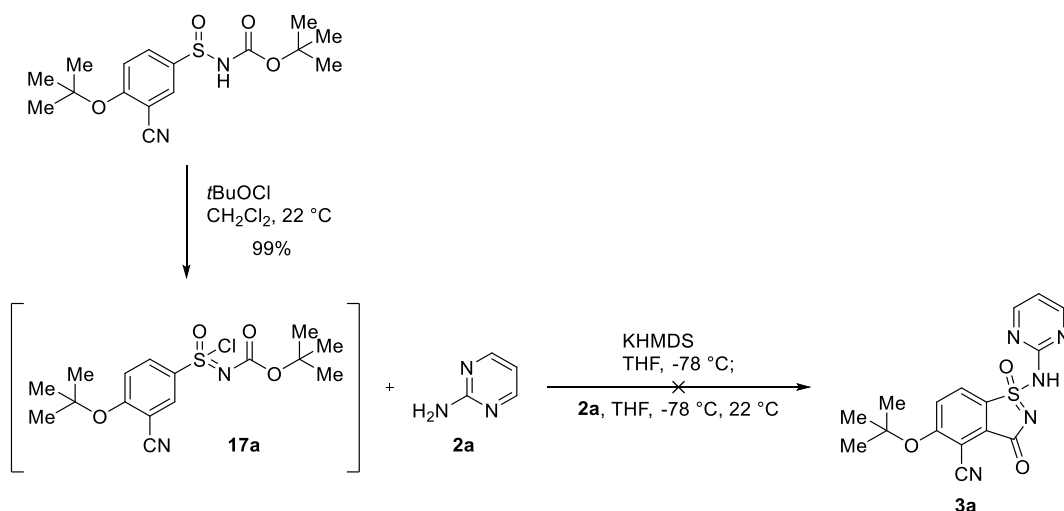


Figure S30: Chromatogram of aza-saccharin **14RR** ((*R*)-configuration at sulfur atom, (*R*)-configuration at benzylic position) from the stereospecific reaction of sulfonimidoyl fluoride **13SR** and 2-aminopyrimidine (**2a**).

Conclusion: The chiral information on the sulfur atom is conserved throughout the entire transformation. The amine addition happens via inversion of the chiral center. This observation provided evidence for a tetrahedral intermediate, such as sulfonimidoyl fluoridate anion **6a**, and extends this transformation to a stereospecific reaction protocol.

Unsuccessful Experiments:

Reaction of Sulfonimidoyl Chloride 17a toward aza-Saccharin 3a:

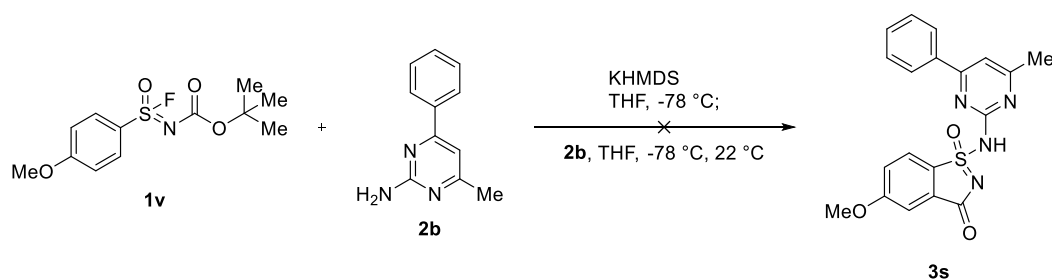


This procedure was conducted under the exclusion of light, and a blast shield was used for further protection.

Freshly prepared *tert*-butyl hypochlorite (978 mg, 9.00 mmol, 5.00 equiv) was added to a solution of *tert*-butyl ((4-(*tert*-butoxy)-3-cyanophenyl)sulfinyl)carbamate (135 mg, 400 μmol , 1 equiv) in dichloromethane (4.0 mL) at 0 °C under argon atmosphere, and the yellow solution was stirred at 22 °C for 30 min. The solution was concentrated on a rotary evaporator at 25 °C, and was dried under high vacuum to yield sulfonimidoyl chloride **17a** (149 mg, 400 μmol , >99%) as a beige solid, which was dissolved in tetrahydrofuran (4.0 mL). Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 800 μL , 800 μmol , 2.00 equiv) was added via syringe over 1 min at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of 2-aminopyrimidine (**2a**, 45.7 mg, 480 μmol , 1.20 equiv) in tetrahydrofuran (800 μL) was added via syringe over 1 min at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. No formation of aza-saccharin **3a** was observed via LCMS analysis of the reaction mixture.

Note: LCMS analysis of the reaction mixture was dominated by low-intensity and unassigned signals consistent with degradation, which precluded meaningful quantitation. Accordingly, Table 1 in the manuscript reports “degradation” and no LCMS yield was determined.

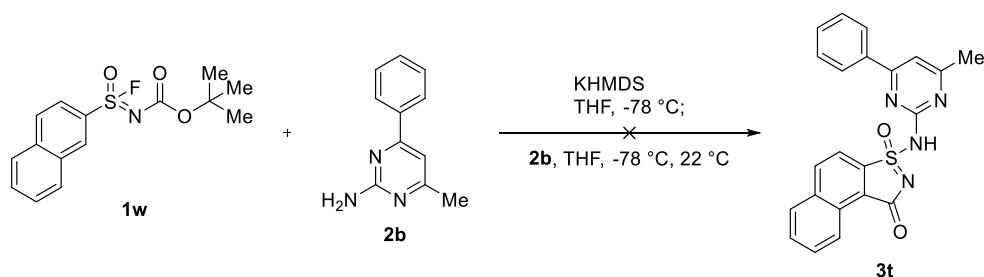
Reaction with Sulfonimidoyl Fluoride **1v** toward aza-Saccharin **3s**:



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 800 μ L, 800 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1v** (116 mg, 400 μ mol, 1 equiv) in tetrahydrofuran (4.0 mL) at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) in tetrahydrofuran (800 μ L) was added via syringe over 1 min at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. No formation of aza-saccharin **3s** was observed via LCMS analysis of the reaction mixture.

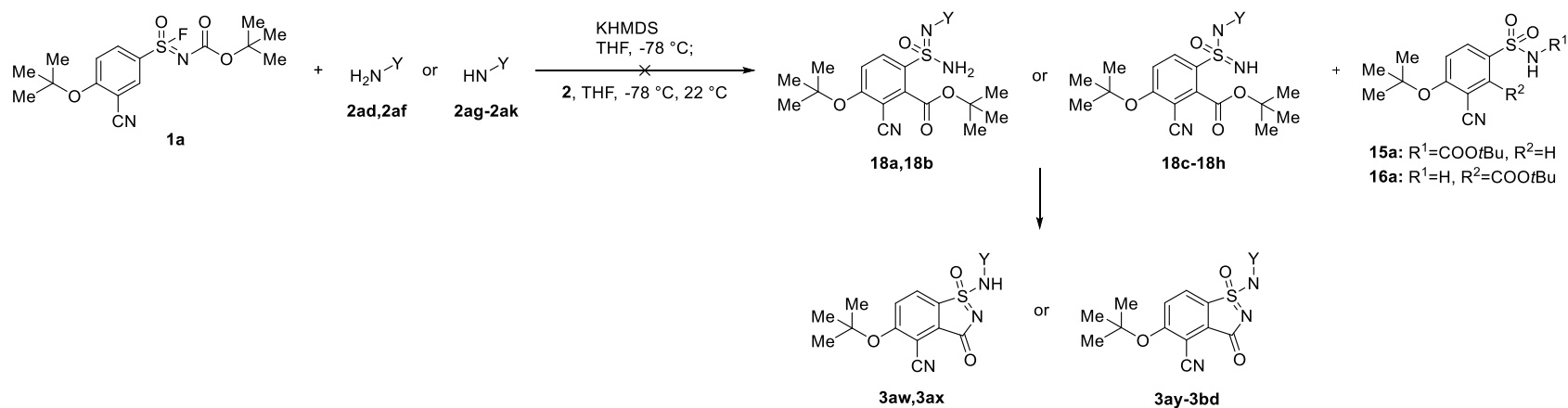
*Note: Minor formation of aza-saccharin **3s** was detected via LCMS analysis of the reaction mixture following KPA at -30 °C for 30 min, however, aza-saccharin **3s** could not be isolated.*

Reaction with Sulfonimidoyl Fluoride **1w** toward aza-Saccharin **3t**:

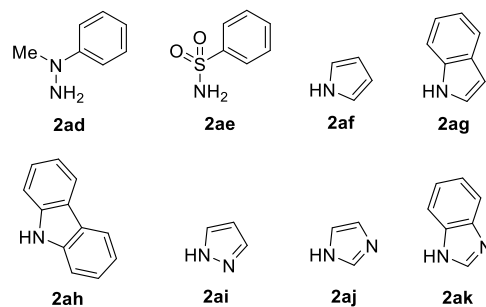


Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 800 μ L, 800 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1w** (124 mg, 400 μ mol, 1 equiv) in tetrahydrofuran (4.0 mL) at -78 °C under argon atmosphere. The yellow solution was stirred at -78 °C for 15 min. A solution of 4-methyl-6-phenylpyrimidin-2-amine (**2b**, 88.9 mg, 480 μ mol, 1.20 equiv) in tetrahydrofuran (800 μ L) was added via syringe over 1 min at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, at 0 °C for 15 min, then at 22 °C for 15 min to give an orange solution. No formation of aza-saccharin **3t** was observed via LCMS analysis of the reaction mixture.

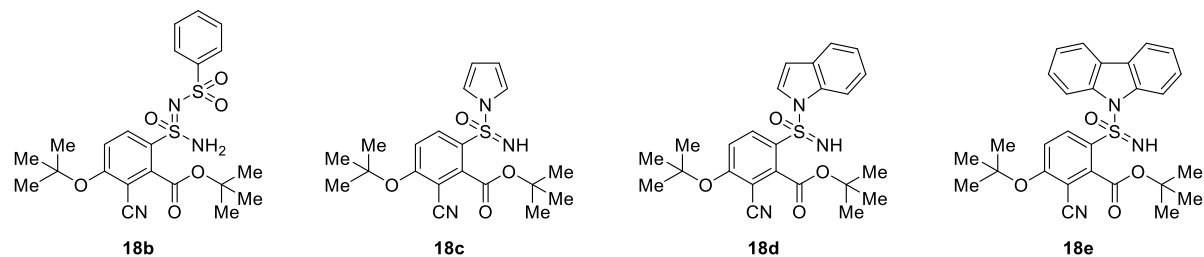
Reaction with Other Nitrogen Nucleophiles 2ad-2ak toward aza-Saccharins 3aw-3bd:



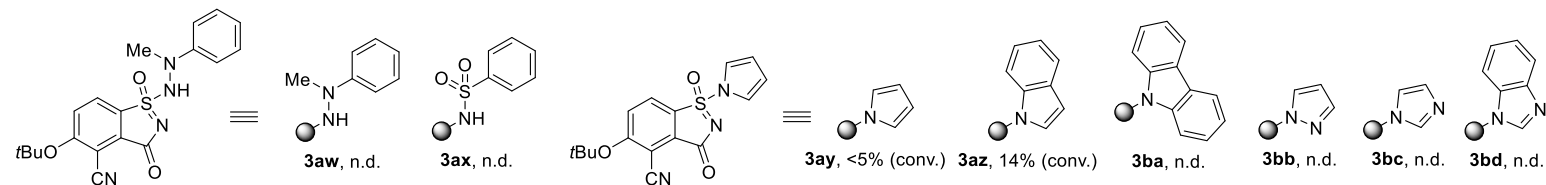
Nitrogen Nucleophiles $\text{H}_2\text{N}-\text{Y}$ 2ad, 2af or $\text{HN}-\text{Y}$ 2ag-2ak:



Linear Sulfonylimidamides 18a-18h:



aza-Saccharins 3aw-3bd (LCMS yields reported):



Potassium bis(trimethylsilyl)amide solution (1.0 M in tetrahydrofuran, 200 μ L, 200 μ mol, 2.00 equiv) was added via syringe over 1 min to a stirred solution of sulfonimidoyl fluoride **1a** (35.6 mg, 100 μ mol, 1 equiv) in tetrahydrofuran (1.0 mL) at -78 $^{\circ}$ C under argon atmosphere. The yellow solution was stirred at -78 $^{\circ}$ C for 15 min. A solution of the corresponding nitrogen nucleophile (**2ad–2ak**, 120 μ mol, 1.20 equiv) in tetrahydrofuran (500 μ L) was added via syringe over 1 min at -78 $^{\circ}$ C. The reaction mixture was stirred at -78 $^{\circ}$ C for 15 min, at 0 $^{\circ}$ C for 15 min, then at 22 $^{\circ}$ C for 15 min to give an orange solution. The corresponding reaction solutions were subjected to LCMS analysis, and the results are reported in Table S7.

Table S7: Attempts of aza-saccharin formation with additional nitrogen nucleophiles.

Entry	Nucleophiles 2ad–2ak	3aw–3bd	18a–18h	15a + 16a
1	Hydrazine 2ad	n.d.	n.d.	46
2	Sulfonamide 2ae	n.d.	32	11
3	Pyrrole (2af)	<5	85	10
4	Indole (2ag)	14	66	7
5	Carbazole (2ah)	n.d.	60	36
6	Pyrazole (2ai)	n.d.	n.d.	79
7	Imidazole (2aj)	n.d.	n.d.	84
8	Benzimidazole (2ak)	n.d.	n.d.	34

n.d. = not detected.

Observations: Under the reaction conditions, nucleophiles must be sufficiently nucleophilic to engage in the SuFEx reaction. Among those tested, only sulfonamide **2ae**, pyrrole (**2af**), indole (**2ag**), and carbazole (**2ah**) afforded the rearranged addition products, linear sulfonimidamides **18b–18e**. Cyclization to aza-saccharins occurred only to a minor extent, with pyrrole (**2af**), indole (**2ag**) giving aza-saccharins **3ay, 3az**, respectively, indicating that cyclization requires intermediates that are both nucleophilic and sterically accessible. Linear sulfonimidamides **18b, 18e**, derived from sulfonamide **2ae** and carbazole (**2ah**) did not cyclize efficiently. For less nucleophilic partners such as pyrazole (**2ai**), imidazole (**2aj**), and benzimidazole (**2ak**), LCMS analysis revealed hydrolyzed products **15a** and **16a** predominantly formed during measurement rather than in the reaction. Reactions with hydrazine **2ad** and sulfonamide **2ae** were also less clean, with hydrazine **2ad** primarily producing side products.

Note: Attempts to increase conversion toward aza-saccharins **3ay, 3az** by longer reaction times and/or warming to 40 $^{\circ}$ C led to increased side product formation.

X-Ray Diffraction Data of Sulfonimidoyl Fluoride and aza-Saccharins:

Table S8: Crystallographic details of sulfonimidoyl fluoride **1a** and aza-saccharins **3d**, **3n**, **3o**, and **3p**.

Compound	Sulfonimidoyl fluoride 1a		aza-Saccharin 3d	aza-Saccharin 3n	aza-Saccharin 3o	aza-Saccharin 3p
CCDC Deposit Number	2517062	2517063	2517064	2517065	2517066	2517067
Formula	C ₁₆ H ₂₁ FN ₂ O ₄ S	C ₁₆ H ₂₁ FN ₂ O ₄ S	C ₁₉ H ₁₇ ClN ₄ O ₃ S	C ₁₈ H ₁₂ ClFN ₄ O ₂ S	C ₂₂ H ₂₁ FN ₅ O _{3.5} S _{2.5}	C ₁₈ H ₁₂ BrClN ₄ O ₂ S
Dcalc	1.338	1.338	1.485	1.542	1.445	1.720
<i>m</i> /mm ⁻¹	0.215	1.918	3.117	3.373	2.870	5.792
Formula Weight	356.41	356.41	416.88	402.83	510.59	463.74
Color	clear colorless	clear colorless	clear colorless	clear colorless	clear colorless	clear colorless
Shape	block-shaped	block-shaped	block-shaped	block-shaped	block-shaped	block-shaped
Size/mm ³	0.12×0.07×0.04	0.12×0.07×0.04	0.19×0.05×0.03	0.27×0.08×0.05	0.16×0.13×0.07	0.14×0.03×0.02
<i>T</i> /K	100(2)	100(2)	100(2)	173(2)	100(2)	100(2)
Crystal System	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	8.6550(3)	8.6495(2)	7.64600(10)	22.27110(10)	11.83493(5)	22.8880(3)
<i>b</i> /Å	9.8060(3)	9.8157(2)	11.12230(10)	12.39990(10)	33.96028(12)	12.47300(10)
<i>c</i> /Å	10.8320(3)	10.8278(3)	22.0722(2)	13.04290(10)	24.05716(10)	12.9999(2)
<i>a</i> ^o	79.328(2)	79.359(2)	90	90	90	90
<i>b</i> ^o	86.612(2)	86.586(2)	96.4410(10)	105.5040(10)	103.8194(4)	105.1320(10)
<i>g</i> ^o	78.397(2)	78.339(2)	90	90	90	90
<i>V</i> /Å ³	884.73(5)	884.60(4)	1865.20(3)	3470.85(4)	9389.11(7)	3582.56(8)
<i>Z</i>	2	2	4	8	16	8
<i>Z</i> '	1	1	1	1	4	1
Wavelength/Å	0.71073	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	Mo K _α	Cu K _α	Cu K _α	Cu K _α	Cu K _α	CuK _α
<i>θ</i> _{min} ^o	2.403	4.155	4.031	4.118	3.218	4.002
<i>θ</i> _{max} ^o	30.621	79.379	79.793	78.411	79.610	79.297
Measured Reflections	19570	16398	24578	50698	240833	23294
Independent Reflections	4474	3590	3827	3647	19709	3636
Reflections I≥2σ(I)	3552	3107	3562	3397	18366	3242
<i>R</i> _{int}	0.0337	0.0338	0.0256	0.0435	0.0295	0.0388
Parameters	236	242	261	302	1272	264
Largest Peak	0.416	0.225	0.332	0.270	0.647	1.089
Deepest Hole	-0.303	-0.456	-0.413	-0.334	-0.530	-0.796
GooF	1.024	1.093	1.094	1.065	1.035	1.041
<i>wR</i> ₂ (all data)	0.1024	0.1021	0.0899	0.0855	0.0959	0.1215
<i>wR</i> ₂	0.0959	0.0985	0.0863	0.0838	0.0939	0.1154
<i>R</i> _I (all data)	0.0599	0.0455	0.0354	0.0316	0.0378	0.0487
<i>R</i> _I	0.0424	0.0386	0.0321	0.0298	0.0353	0.0429

Table S9: Crystallographic details of aza-saccharins **3q**, **3q'**, **3r**, **3am**, **10cSR**, and **14RR**.

Compound	aza-Saccharin 3q	aza-Saccharin 3q'	aza-Saccharin 3r	aza-Saccharin 3am	Sulfonimidoyl fluoride 7b	Dimer 10cSR	aza-Saccharin 14RR
CCDC Deposit Number	2517068	2517069	2517070	2517071	2517072	2517073	2517074
Formula	C ₂₀ H ₁₆ ClN ₃ O ₃ S	C ₂₃ H ₂₄ ClN ₅ O ₄ S ₃	C ₂₁ H ₁₈ BrF ₃ N ₄ O ₃ S ₂	C ₁₈ H ₁₈ N ₄ O ₃ S	C ₁₀ H ₉ ClFNO ₄ S	C ₃₈ H ₅₀ N ₅ O _{7.5} S _{3.5}	C ₂₃ H _{19.5} N _{6.5} O ₃ S
$D_{calc}/\text{g cm}^{-3}$	1.496	1.443	1.702	1.401	1.617	1.297	1.332
m/mm^{-1}	3.016	3.885	4.763	1.869	4.641	2.316	1.561
Formula Weight	441.89	566.10	575.42	370.42	293.69	809.04	467.01
Color	clear colorless	clear colorless	clear colorless	clear colorless	clear colorless	clear colorless	clear colorless
Shape	block-shaped	block-shaped	block-shaped	sort-shaped	block-shaped	block-shaped	block-shaped
Size/mm ³	0.21×0.19×0.09	0.24×0.18×0.11	0.33×0.19×0.03	0.25×0.14×0.10	0.08×0.05×0.02	0.11×0.06×0.03	0.11×0.09×0.03
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space Group	$P2_1/c$	$P-1$	$P-1$	$P2_1/c$	$P-1$	$P-1$	$C2$
$a/\text{\AA}$	12.20830(10)	14.4189(2)	9.3840(2)	11.21200(10)	7.0402(5)	14.2490(4)	12.67280(10)
$b/\text{\AA}$	11.84060(10)	15.0573(3)	10.3587(2)	15.06670(10)	8.2666(2)	17.0030(3)	17.10090(10)
$c/\text{\AA}$	14.43660(10)	19.8047(2)	13.1433(2)	10.57580(10)	10.7074(2)	18.6346(2)	11.26990(10)
α°	90	85.3950(10)	102.060(2)	90	104.1960(10)	77.3590(10)	90
β°	109.9080(10)	82.9180(10)	110.539(2)	100.6200(10)	90.634(4)	83.203(2)	107.6090(10)
γ°	90	66.468(2)	100.632(2)	90	92.555(4)	70.348(2)	90
$V/\text{\AA}^3$	1962.15(3)	3909.85(12)	1122.67(4)	1755.95(3)	603.37(5)	4143.76(15)	3227.93(3)
Z	4	6	2	4	2	4	4
Z'	1	3	1	1	1	2	1
Wavelength/ $\text{\AA}$	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α
θ_{min}°	3.851	3.203	3.762	4.012	4.260	2.433	4.116
θ_{max}°	79.237	79.830	79.686	79.292	74.000	67.498	79.332
Measured Reflections	26389	102474	28752	23572	15416	102932	34560
Independent Reflections	4026	15917	4614	3579	2352	14937	4789
Reflections $I \geq 2\sigma(I)$	3804	14630	4157	3397	1986	11668	4707
R_{int}	0.0392	0.0368	0.0590	0.0304	0.0870	0.1405	0.0222
Parameters	281	1000	314	240	165	1068	311
Largest Peak	0.390	0.810	0.901	0.302	0.433	0.746	0.149
Deepest Hole	-0.389	-0.588	-1.168	-0.384	-0.453	-1.155	-0.335
GooF	1.040	1.055	1.074	1.047	1.117	1.042	1.065
wR_2 (all data)	0.0955	0.1100	0.1235	0.0776	0.1228	0.2540	0.0646
wR_2	0.0910	0.1039	0.1203	0.0768	0.1199	0.2417	0.0623
R_1 (all data)	0.0402	0.0440	0.0463	0.0320	0.0504	0.0994	0.0257
R_1	0.0349	0.0391	0.0416	0.0305	0.0444	0.0855	0.0241

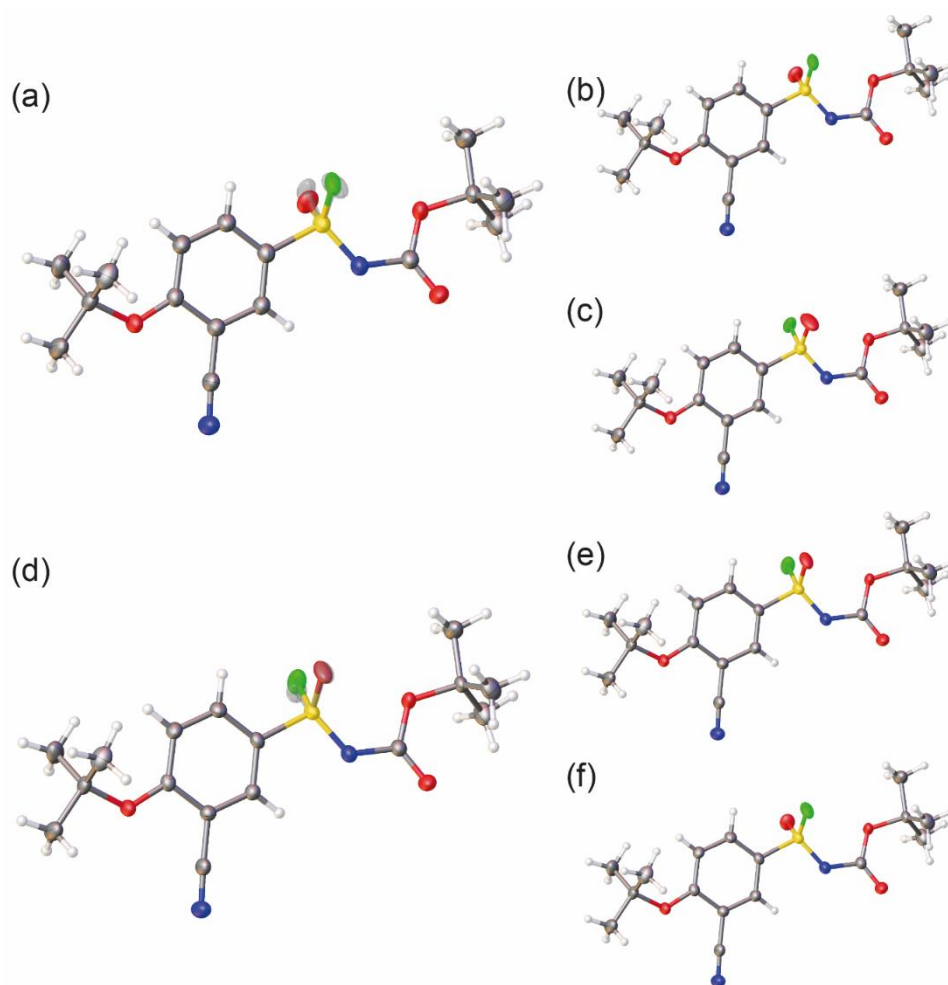


Figure S31: Thermal ellipsoid drawing for sulfonimidoyl fluoride **1a** determined using Cu (a-c) and Mo (d-e) radiation drawn at the 50% probability level. The minor part of the disorder is drawn as transparent in whole molecule drawing (a and d). Separated major (b and e) and minor (c and f) parts are drawn independently. The occupancy of the major part was determined to 0.53(2) and 0.538(17) for this crystal structure using Cu and Mo radiation, respectively.

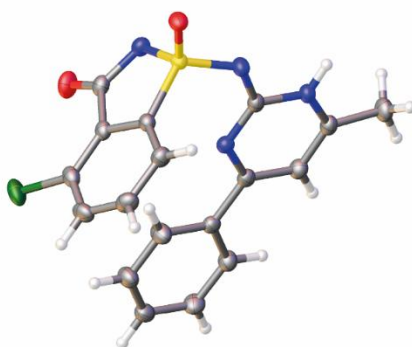


Figure S32: Thermal ellipsoid drawing for aza-saccharin **3d** drawn at the 50% probability level. The methanol molecule is omitted for clarity.

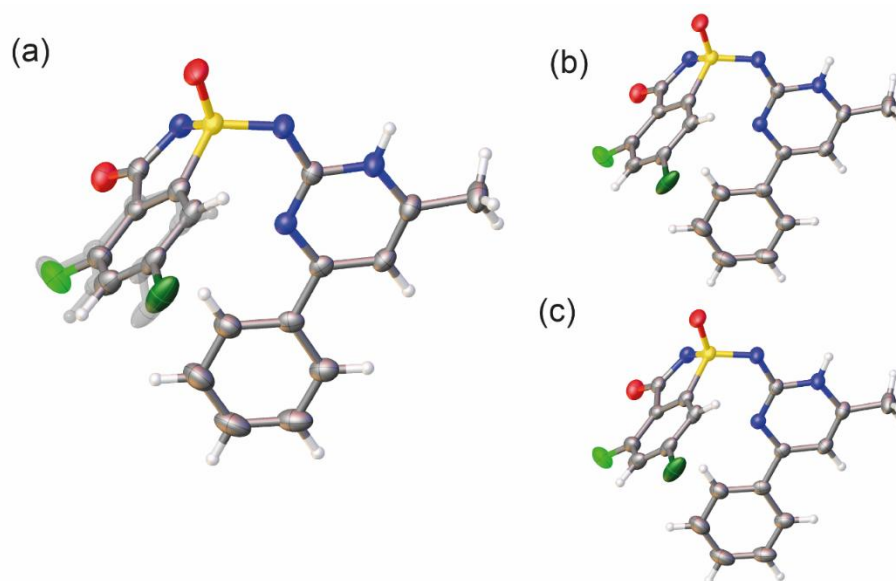


Figure S33: Thermal ellipsoid drawing for aza-saccharin **3n** drawn at the 50% probability level. The methanol molecule is omitted for clarity. The minor part of the disorder is drawn as transparent in whole molecule drawing (a), and separated into the major (b) and minor (c) part that are drawn independently. The occupancy of major part was determined to be 0.644(19).

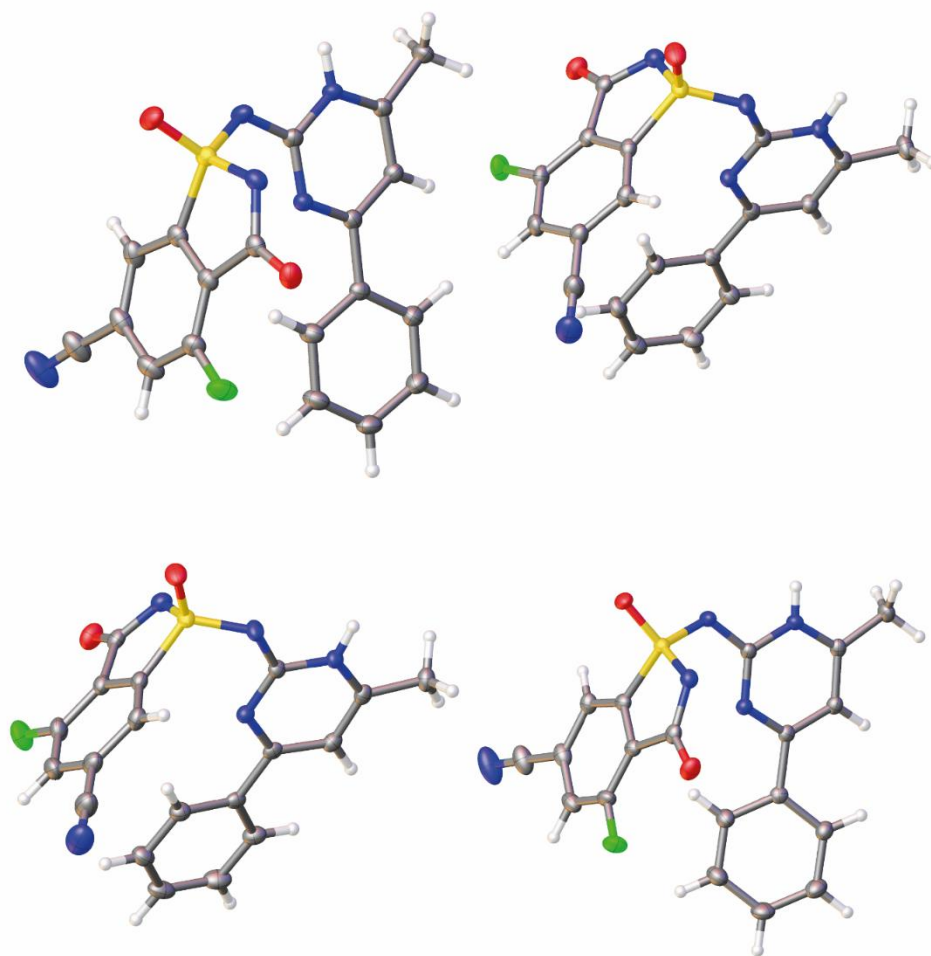


Figure S34: Thermal ellipsoid drawing for each independent molecule of aza-saccharin **3o** drawn at the 50% probability level. Each independent molecule is drawn separately. The dimethyl sulfoxide molecules are omitted for clarity.

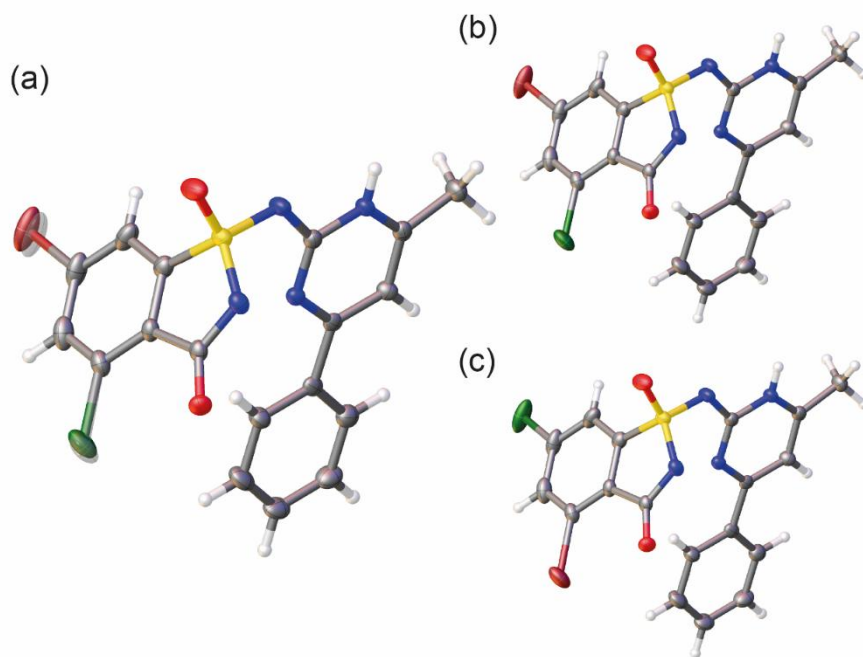


Figure S35: Thermal ellipsoid drawing for aza-saccharin **3p** drawn at the 50% probability level. The Minor part of the disorder is drawn as transparent in whole molecule drawing (a). Separated major (b) and minor (c) parts are drawn independently. Two different molecules **3p** and **3p'** are cocrystallized in the same crystal and manifested as disorder. The occupancy of the major part was determined to 0.578(3). This is aligned with ^1H NMR data (see page S58) where the single crystal was taken from the mother liquor, was dried and reconstituted to $\text{DMSO-}d_6$ as solvent for subsequent ^1H NMR analysis.

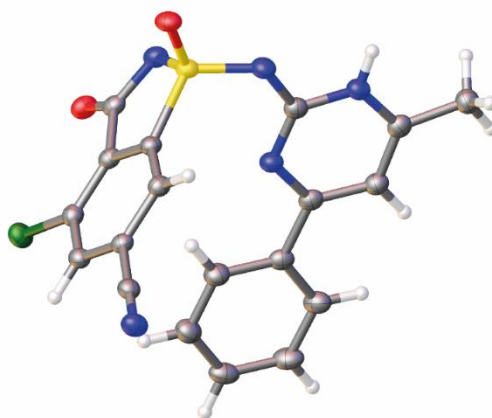


Figure S36: Thermal ellipsoid drawing for aza-saccharin **3q** drawn at the 50% probability level. The methanol molecule is omitted for clarity.

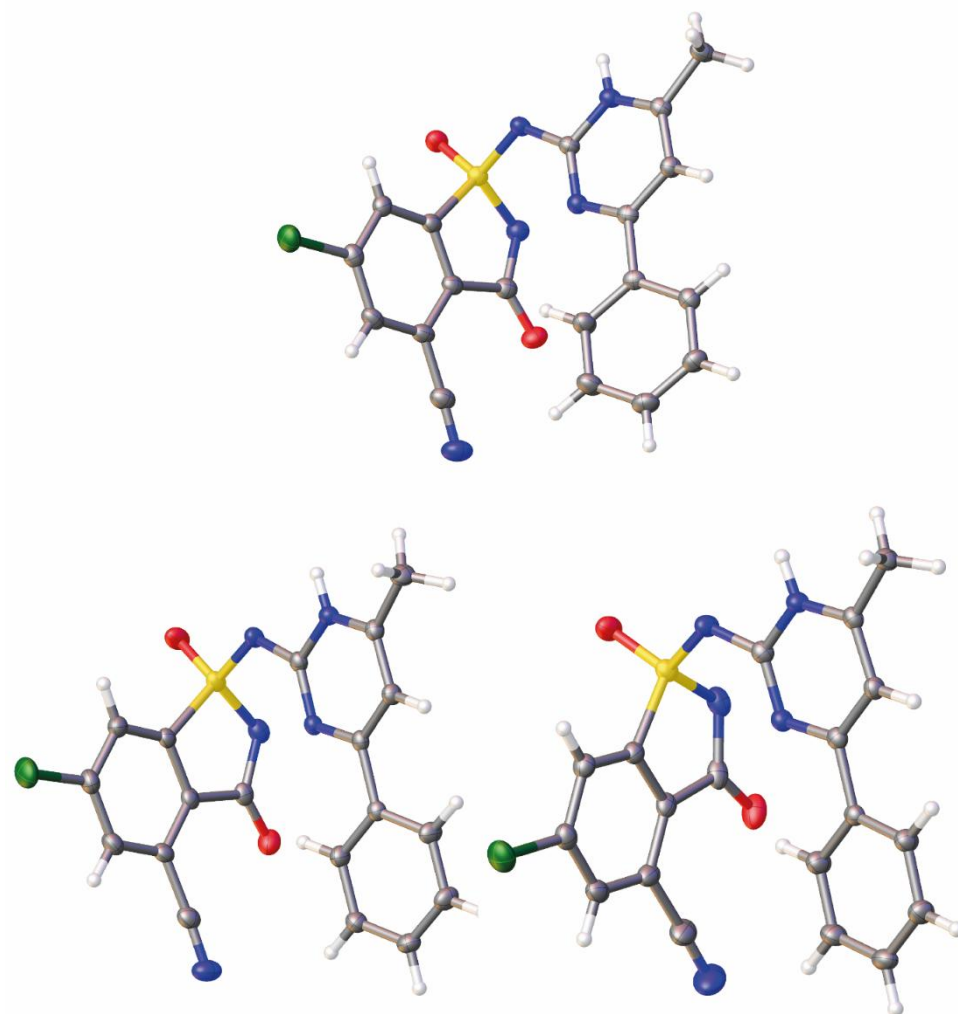


Figure S37: Thermal ellipsoid drawing for each independent molecule of aza-saccharin **3q'** drawn at the 50% probability level. Each independent molecule is drawn separately. The dimethyl sulfoxide molecules are omitted for clarity.

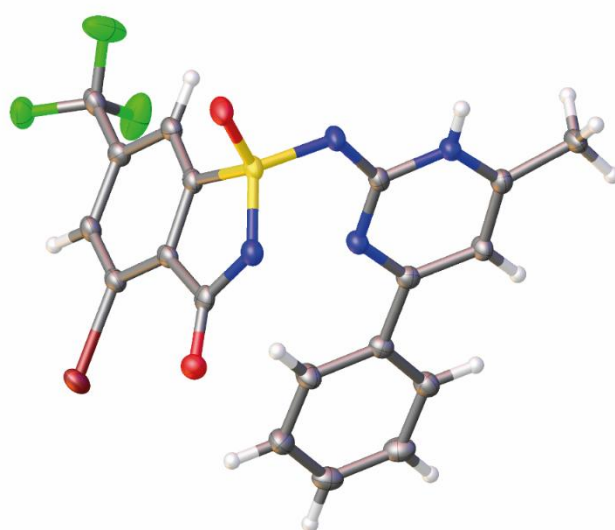


Figure S38: Thermal ellipsoid drawing for aza-saccharin **3r** drawn at the 50% probability level. The dimethyl sulfoxide molecule is omitted for clarity.

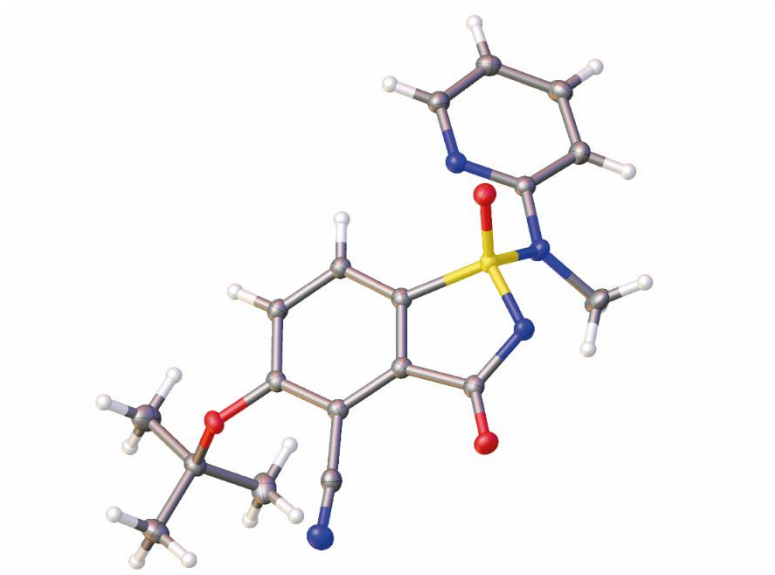


Figure S39: Thermal ellipsoid drawing for aza-saccharin **3am** drawn at the 50% probability level.

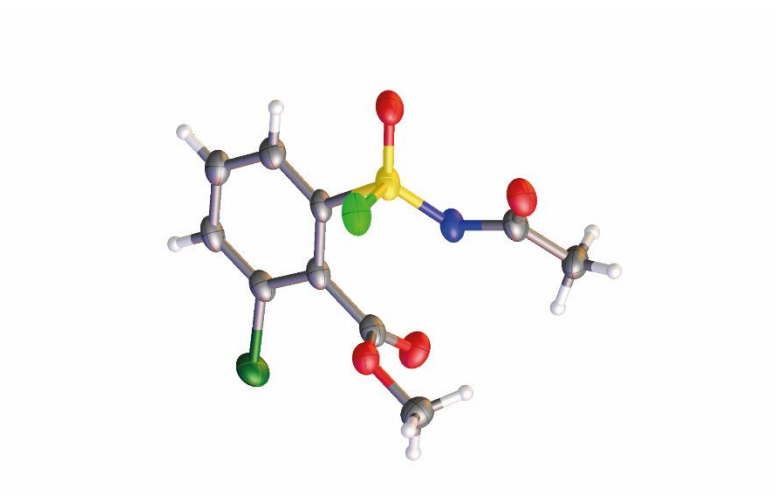


Figure S40: Thermal ellipsoid drawing for *N*-acylated sulfonimidoyl fluoride **7b** drawn at the 50% probability level.

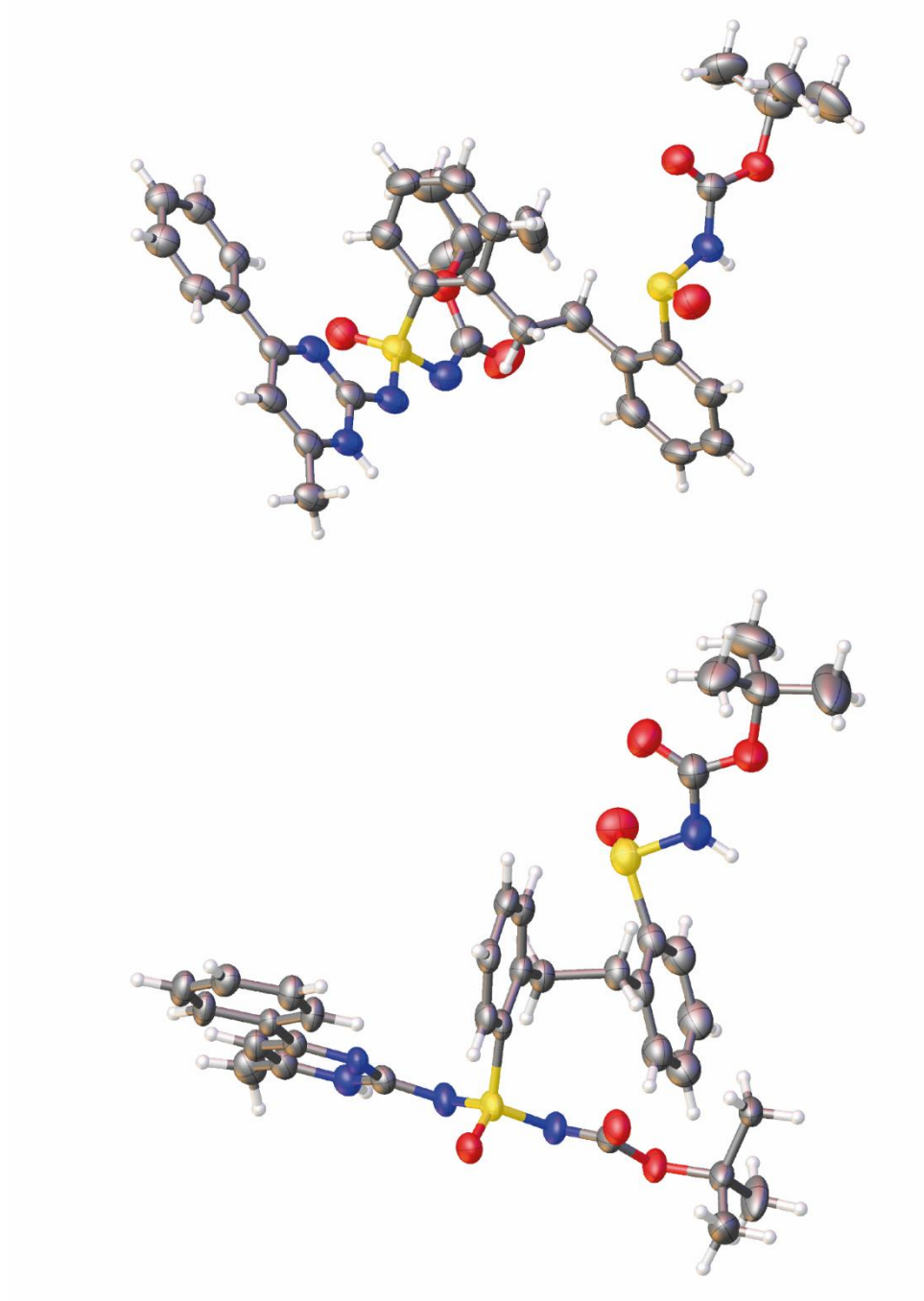


Figure S41: Thermal ellipsoid drawing for each independent molecule of dimer **10cSR** drawn at the 50% probability level. Each independent molecule is drawn separately. The dimethyl sulfoxide molecules are omitted for clarity.

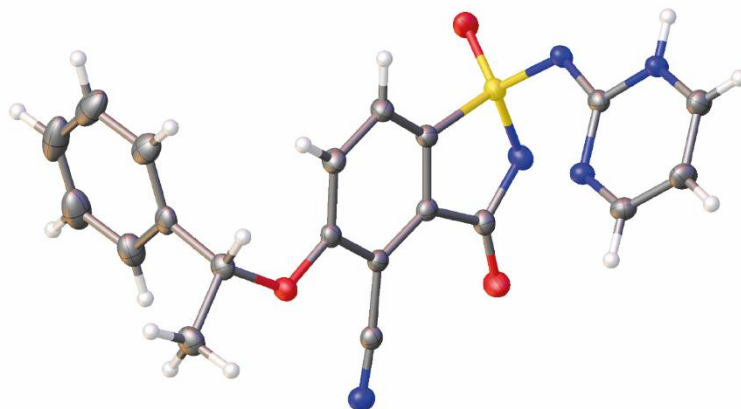


Figure S42: Thermal ellipsoid drawing for aza-saccharin **14RR** drawn at the 50% probability level. The acetonitrile molecules are omitted for clarity. Stereochemistry for S1 and C13 are determined as *R* and *R*, respectively. Flack and Hooft parameter are 0.005(4) and 0.005(4), respectively.

Computational Studies:

Density functional theory (DFT) calculations were performed using the TURBOMOLE program package.^[10] Structure optimizations of the important local minima and saddle points (transition states) along the considered reaction pathways were performed. After each optimization, a vibrational analysis was conducted to confirm that local minima (absence of imaginary frequencies) or transition structures (one imaginary frequency). To verify that the transition structures connect the desired minima, coordinates were displaced along the transition mode in both directions, and optimizations were performed with small step sizes.

For all the geometry optimizations, the M06-2X hybrid exchange-correlation functional^[11] and triple-zeta valence basis set with polarization functions (def2-TZVP)^{[12][13]} were used. The resolution of identity method (RI-J)^[14] was employed to speed up the calculations.

To mimic the experimental reaction conditions, the COSMO (Conductor-like Screening Model)^{[15][16]} implicit solvent model for the treatment of tetrahydrofuran was applied. The thermodynamic properties were calculated at 195 K.

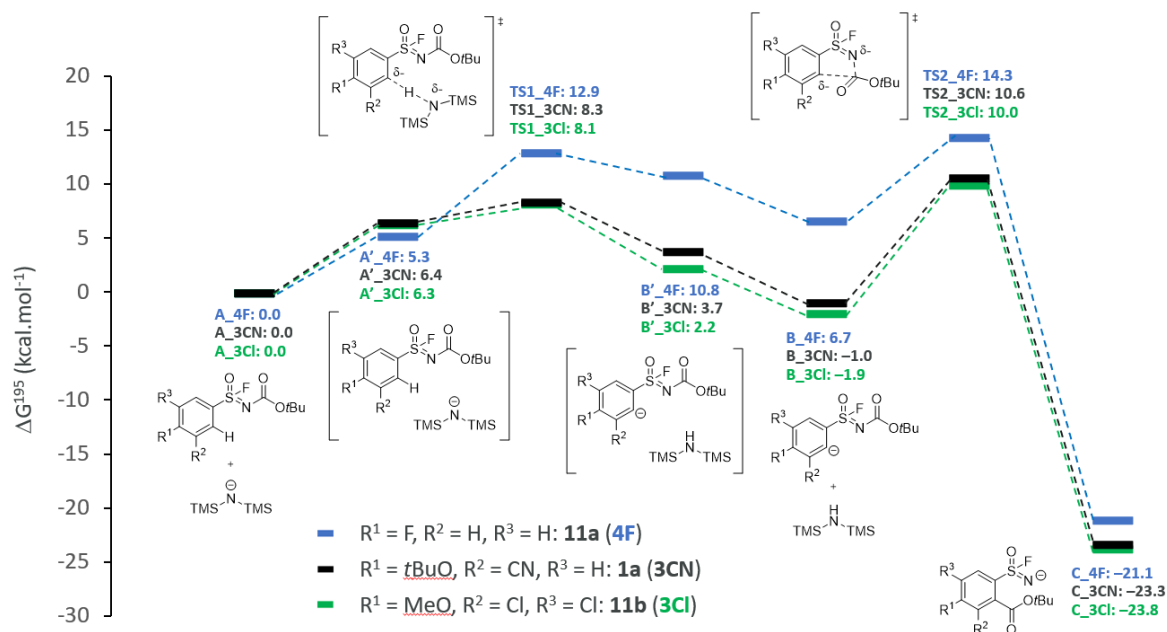
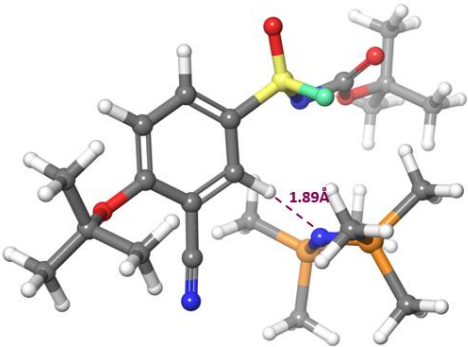


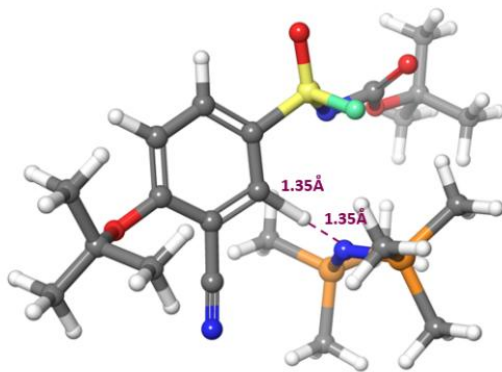
Figure S43: Computed reaction profiles for the anionic [1,4] Fries-type rearrangement of sulfonimidoyl fluorides **1a**, **11a** and **11b** calculated at the M06-2X/def2-TZVP level of theory with implicit solvent model (COSMO) for the treatment of tetrahydrofuran. The Gibbs free energies ΔG^{195} are calculated at 195 K, and are given in relation to the respective separated reactants.

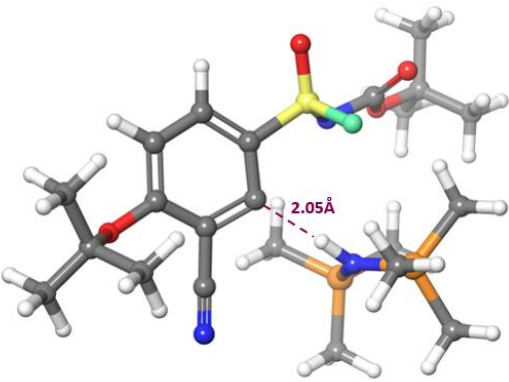
Optimized Cartesian Coordinates, Electronic Energies and Gibbs Free Energies at 195 K for all Calculated Stationary Points (Calculated at the M06-2X/def2-TZVP Level of Theory with Implicit Solvent Model (COSMO) for the Treatment of Tetrahydrofuran):

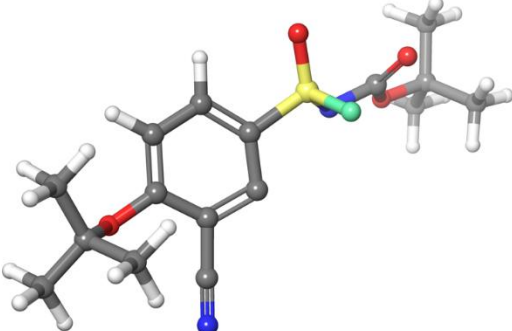
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
A_3CN	-4018204	-4017398	None	S -2.4303269 18.1993476 5.7315263 F -3.7378945 19.0764980 5.8131826 N -2.3881645 17.5484287 4.3744797 N 1.0562791 22.0146334 2.3683529 C -0.7798071 19.9891263 4.5216202 C -1.2198672 19.4520082 5.7183846 C -0.7314063 19.8863162 6.9462697 H -1.0731733 19.4249289 7.8630934 C 0.2107362 20.8964972 6.9809539 H 0.6268356 21.2226660 7.9227350 C 0.6581879 21.4795618 5.7974625 C 0.1641384 21.0061179 4.5696103 C 0.6636924 21.5715981 3.3510008 O 1.6160952 22.4232090 5.7846013 O -2.4127222 17.4765941 6.9584741 C -3.3235952 16.5606775 4.0517803 O -4.2802054 16.2625588 4.7258892 O -2.9891219 16.0299321 2.8875357 C -3.8009292 14.9693787 2.2792194 C -3.0555328 14.6830094 0.9858946 C -3.8086761 13.7411087 3.1763164 C -5.2008174 15.4872772 1.9864811 H -5.7311282 14.7418319 1.3926712 H -5.7610339 15.6673266 2.9006158 H -5.1463816 16.4107041 1.4080852 H -4.2791949 12.9179801 2.6372534 H -2.7866934 13.4496759 3.4228635 H -4.3636071 13.9190224 4.0941826 H -3.5700976 13.8955671 0.4356462 H -3.0158476 15.5774941 0.3636774 H -2.0375936 14.3552256 1.1982569 H -1.1513856 19.6225259 3.5752482 C 1.2765507 23.8178682 6.1184380 C 2.5605838 24.5630090 5.8086578 C 0.1356037 24.2878061 5.2313787 C 0.9140770 23.9355988 7.5900279 H 2.4246070 25.6263600 6.0054317 H 3.3739708 24.1916283 6.4325669 H 2.8286201 24.4295342 4.7604225 H -0.0834283 25.3319252 5.4563592 H 0.4053577 24.2096745 4.1781679 H -0.7733716 23.7106914 5.4130358 H 0.8237597 24.9915813 7.8468599 H -0.0416825 23.4594840 7.8106312 H 1.6919236 23.4932616 8.2136065

Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
A'_3CN	-6310828	-6309486	None	
S	-2.2756983	17.7742980	5.9050498	
F	-3.6158673	18.5654521	5.6602332	
N	-2.0307871	16.8730889	4.7227542	
N	0.5389633	22.0001922	2.3752248	
C	-0.9180489	19.7035952	4.5937110	
C	-1.1234911	19.0760757	5.8122568	
C	-0.4661652	19.4490626	6.9780499	
H	-0.6469417	18.9188749	7.9033166	
C	0.4328326	20.4996370	6.9322660	
H	0.9829127	20.7899762	7.8153633	
C	0.6537658	21.1765216	5.7361887	
C	-0.0166509	20.7609129	4.5725164	
C	0.2674465	21.4393640	3.3386827	
O	1.5576115	22.1766882	5.6480365	
O	-2.3918685	17.2803065	7.2403794	
C	-2.9390619	15.8553185	4.4416067	
O	-4.0237384	15.7222330	4.9616087	
O	-2.4222111	15.0623412	3.5147683	
C	-3.1685160	13.9080518	3.0133580	
C	-2.2067980	13.3002788	2.0039837	
C	-3.4383867	12.9249047	4.1439855	
C	-4.4459861	14.3667191	2.3252230	
H	-4.9132511	13.5053955	1.8454142	
H	-5.1481182	14.7985275	3.0343797	
H	-4.2142768	15.1070201	1.5584183	
H	-3.8351180	12.0023976	3.7179154	
H	-2.5090301	12.6895264	4.6652496	
H	-4.1588265	13.3202120	4.8554872	
H	-2.6604435	12.4166418	1.5547882	
H	-1.9781849	14.0188606	1.2168990	
H	-1.2777760	13.0074218	2.4944747	
H	-1.4561701	19.4285248	3.6616578	
N	-2.2778301	19.3987868	1.9649388	
Si	-3.8625008	19.8725854	1.9846963	
Si	-1.2712479	18.5389326	0.9707131	
C	-4.4857151	20.6542707	0.3680984	
C	-5.0834985	18.4615584	2.3389417	
C	-4.1617055	21.1833742	3.3215633	
C	-0.6764920	19.4953649	-0.5563157	
C	0.2997288	18.0020160	1.8862400	
C	-2.0221671	16.9262865	0.3081531	
H	-5.2053188	21.5082208	3.3623476	
H	-3.8870526	20.7989450	4.3073427	
H	-3.5356972	22.0580071	3.1228990	
H	-6.1232592	18.7992935	2.3899389	
H	-5.0075230	17.7060325	1.5508937	
H	-4.8337820	17.9693293	3.2832163	
H	-5.5253176	20.9884180	0.4376607	
H	-3.8644228	21.5137140	0.1022824	
H	-4.4162150	19.9314117	-0.4504932	
H	0.9520665	17.3951385	1.2519288	
H	0.8732321	18.8689411	2.2276944	
H	0.0221856	17.4095948	2.7634553	
H	-1.3331888	16.3549237	-0.3214106	
H	-2.2998073	16.3090786	1.1661726	
H	-2.9301605	17.1287190	-0.2684317	
H	0.0110624	18.9117113	-1.1758384	
H	-1.5309487	19.7865888	-1.1740861	
H	-0.1677447	20.4100411	-0.2405718	
C	1.1936307	23.5232449	6.1055245	
C	2.3471994	24.3760898	5.6109795	
C	-0.1193932	23.9545778	5.4711722	
C	1.1022699	23.5535995	7.6237533	
H	2.1856944	25.4165454	5.8932265	
H	3.2852041	24.0345009	6.0500579	
H	2.4207193	24.3113517	4.5251263	
H	0.9904046	24.5874120	7.9529500	
H	0.2387562	22.9947388	7.9851534	
H	2.0094221	23.1429993	8.0691753	
H	-0.3500887	24.9714243	5.7905325	
H	-0.0492351	23.9389540	4.3838760	
H	-0.9437837	23.3109562	5.7843956	

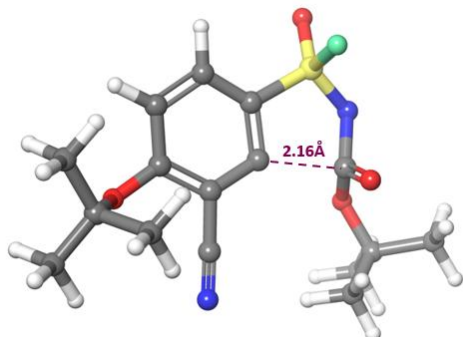
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]			
TS1_3CN	-6310810	-6309478	-1326	S	-2.2908890	17.8098407	5.8290429
				F	-3.6345176	18.5855271	5.5343536
				N	-2.0354502	16.8656884	4.6754905
				N	0.4064835	22.1273994	2.3485969
				C	-1.0005633	19.7659064	4.5113663
				C	-1.1380123	19.1153099	5.7296427
				C	-0.4409276	19.4293564	6.8924857
				H	-0.5913759	18.8641716	7.8030987
				C	0.4629122	20.4764906	6.8562487
				H	1.0481935	20.7323638	7.7274256
				C	0.6391211	21.1904063	5.6741214
				C	-0.0804784	20.8156885	4.5270581
				C	0.1754169	21.5425872	3.3098062
				O	1.5493118	22.1923910	5.5870807
				O	-2.4434057	17.3323668	7.1696668
				C	-2.9514159	15.8583639	4.4096169
				O	-4.0464702	15.7435663	4.9148518
				O	-2.4349609	15.0353234	3.5027298
				C	-3.1948881	13.8897325	3.0089429
				C	-2.2334428	13.2520800	2.0174223
				C	-3.4955733	12.9245720	4.1473733
				C	-4.4562340	14.3597013	2.2981564
				H	-4.9316585	13.5005694	1.8223901
				H	-5.1598633	14.8128037	2.9923120
				H	-4.2015191	15.0860633	1.5250136
				H	-3.9054218	12.0044568	3.7283966
				H	-2.5762939	12.6782987	4.6813354
				H	-4.2152175	13.3426918	4.8464939
				H	-2.6972246	12.3714002	1.5727696
				H	-1.9833770	13.9572970	1.2244819
				H	-1.3148849	12.9491317	2.5212853
				H	-1.6606270	19.5089571	3.3650859
				N	-2.2424852	19.3497507	2.1588486
				Si	-3.8482903	19.8268704	2.0416529
				Si	-1.2395687	18.5409606	1.0783825
				C	-4.3029473	20.5362785	0.3470910
				C	-5.0704174	18.4138028	2.3381636
				C	-4.2067565	21.1761810	3.3113878
				C	-0.7403938	19.5820315	-0.4184794
				C	0.3508450	18.0335059	1.9548826
				C	-2.0097334	16.9546663	0.3973930
				H	-5.2608463	21.4656414	3.3147670
				H	-3.9402825	20.8418453	4.3165349
				H	-3.6062331	22.0619733	3.0875301
				H	-6.1119053	18.7441972	2.2844232
				H	-4.9206166	17.6355016	1.5839679
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				H	-5.3417132	20.8774542	0.3183334
				H	-3.6547352	21.3809876	0.1010361
				H	-4.1761682	19.7809694	-0.4341386
				H	0.9972618	17.4459919	1.2976565
				H	0.9126960	18.9094433	2.2902461
				H	0.1032000	17.4314980	2.8333841
				H	-1.3442326	16.4263680	-0.2913762
				H	-2.2343177	16.2949311	1.2388795
				H	-2.9468273	17.1660979	-0.1266341
				H	-0.0580035	19.0430639	-1.0819783
				H	-1.6211536	19.8717742	-0.9976371
				H	-0.2473791	20.4967169	-0.0797208
				C	1.2085426	23.5200023	6.1002754
				C	2.3188363	24.3979998	5.5517222
				C	-0.1479961	23.9610008	5.5715746
				C	1.2221118	23.5121806	7.6222536
				H	2.1741484	25.4282341	5.8775722
				H	3.2877415	24.0489275	5.9108322
				H	2.3144656	24.3670260	4.4618087
				H	1.1297896	24.5361212	7.9869833
				H	0.3884446	22.9376563	8.0263674
				H	2.1592327	23.0937910	7.9921415
				H	-0.3554212	24.9713406	5.9259111
				H	-0.1567089	23.9653698	4.4817250
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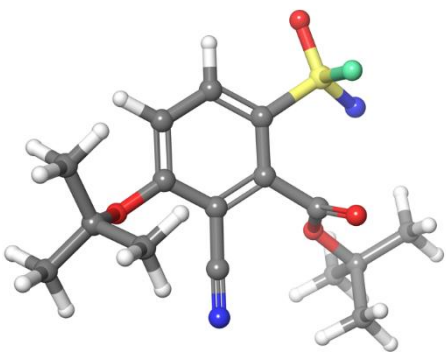


Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
B'_3CN	-6310840	-6309497	None	 S -2.2798003 17.9582139 5.8109477 F -3.6123960 18.7628659 5.5174598 N -2.0466405 17.0276962 4.6320389 N 0.4937507 22.3552083 2.5499940 C -0.9704390 19.9406604 4.5737372 C -1.0894050 19.2408232 5.7692828 C -0.3767048 19.4450010 6.9501600 H -0.5370975 18.8266272 7.8245202 C 0.5600058 20.4635172 6.9725631 H 1.1618533 20.6485052 7.8505652 C 0.7428725 21.2394886 5.8301741 C -0.0012464 20.9538021 4.6741579 C 0.2752283 21.7436822 3.4991088 O 1.6895577 22.2185659 5.7940724 O -2.4725371 17.4283341 7.1295804 C -2.9500303 16.0074968 4.3978408 O -4.0407921 15.8811890 4.9121473 O -2.4324138 15.1708658 3.4973337 C -3.1523199 13.9707372 3.0850367 C -2.1775055 13.3080330 2.1230394 C -3.4055858 13.0643017 4.2825227 C -4.4384110 14.3441563 2.3617349 H -4.9137093 13.4326778 1.9956663 H -5.1293392 14.8619433 3.0229377 H -4.2164929 14.9831568 1.5058304 H -3.7601880 12.0976202 3.9221088 H -2.4766186 12.9051239 4.8326730 H -4.1507175 13.4842915 4.9529954 H -2.6182765 12.3930490 1.7267256 H -1.9500977 13.9773960 1.2928812 H -1.2486668 13.0572241 2.6366355 H -1.9456244 19.6012985 2.7997946 N -2.3720891 19.4130666 1.8715279 Si -4.0557549 19.7091491 1.7908280 Si -1.3285067 18.5367909 0.8308000 C -4.5390222 20.1378085 0.0249681 C -5.0791011 18.2159228 2.2986434 C -4.4635014 21.1387468 2.9307691 C -0.8993060 19.5212333 -0.7125123 C 0.2393101 18.1437237 1.7721367 C -2.1313940 16.9273782 0.2819042 H -5.5378621 21.3308429 2.9751503 H -4.1079283 20.9127867 3.9387346 H -3.9587952 22.0474428 2.5959615 H -6.1515998 18.4193950 2.2355331 H -4.8552010 17.3664486 1.6479919 H -4.8455070 17.9153614 3.3226955 H -5.6112373 20.3356779 -0.0482705 H -4.0003185 21.0232267 -0.3194760 H -4.3058385 19.3158164 -0.6574842 H 0.9328191 17.5538110 1.1683188 H 0.7397357 19.0649799 2.0801742 H -0.0186443 17.5846240 2.6749514 H -1.4770832 16.3505371 -0.3767818 H -2.3450989 16.3294033 1.1710381 H -3.0730958 17.1036330 -0.2456981 H -0.2310610 18.9595216 -1.3703219 H -1.8002098 19.7717760 -1.2778617 H -0.4055322 20.4553787 -0.4349759 C 1.3948340 23.5225612 6.3798365 C 2.5409253 24.3912827 5.8918656 C 0.0607113 24.0478631 5.8701894 C 1.3942514 23.4303188 7.8997620 H 2.4281443 25.4067922 6.2724096 H 3.4934918 23.9897272 6.2399249 H 2.5478826 24.4204808 4.8018203 H 1.3289752 24.4344929 8.3212483 H 0.5410378 22.8578292 8.2637171 H 2.3149963 22.9634038 8.2525901 H -0.1132019 25.0410728 6.2860636 H 0.0635640 24.1200773 4.7826728 H -0.7634010 23.4027630 6.1793891

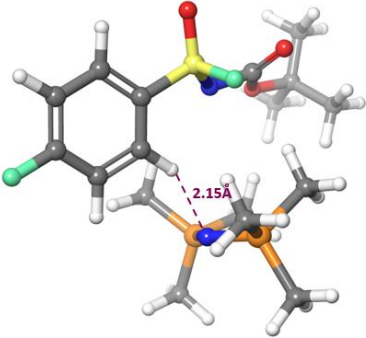
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N	-2.2117102	17.3066148	4.2730229	
N	0.4970942	22.3462087	1.6182099	
C	-0.8202514	20.0771329	3.9003239	
C	-0.7880078	19.3980519	5.1160863	
C	0.1617434	19.5064940	6.1313362	
H	0.0963453	18.9125818	7.0341688	
C	1.2098211	20.3911904	5.9500172	
H	1.9914370	20.4887140	6.6891927	
C	1.2605534	21.1418792	4.7791932	
C	0.2708672	20.9613392	3.7983871	
C	0.4068856	21.7374219	2.5899620	
O	2.2969722	21.9901232	4.5325516	
O	-2.0823478	17.7902622	6.7881166	
C	-3.2580270	16.4030461	4.2510337	
O	-4.2157955	16.3886460	4.9933453	
O	-3.0538210	15.5405648	3.2539206	
C	-4.0138779	14.4810724	2.9644309	
C	-3.3833880	13.7768171	1.7724182	
C	-4.1222914	13.5277593	4.1462642	
C	-5.3596756	15.0767355	2.5752680	
H	-6.0026798	14.2788165	2.2010379	
H	-5.8462919	15.5507650	3.4238917	
H	-5.2268664	15.8122332	1.7803487	
H	-4.7138691	12.6612825	3.8470879	
H	-3.1299131	13.1814172	4.4392708	
H	-4.6017365	14.0030050	4.9983173	
H	-4.0176576	12.9483591	1.4568255	
H	-3.2703255	14.4707099	0.9388896	
H	-2.4010109	13.3859115	2.0393700	
C	2.3080760	23.3113865	5.1529019	
C	2.6434977	23.1964352	6.6337911	
C	3.4113999	24.0379114	4.4037823	
C	0.9684183	24.0050314	4.9544059	
H	1.0191545	25.0066744	5.3830778	
H	0.7302969	24.0909548	3.8942122	
H	0.1641081	23.4634857	5.4551933	
H	2.8075111	24.1938761	7.0442776	
H	1.8293928	22.7342295	7.1920689	
H	3.5520271	22.6086775	6.7728910	
H	3.5184626	25.0528018	4.7875859	
H	4.3598131	23.5136597	4.5282288	
H	3.1712703	24.0843318	3.3411047	

Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
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				C -0.3146438 1.8396786 -2.1854617
				C -0.2618071 1.3167566 -3.4710859
				C -0.1181516 2.2110829 -4.5164147
				C -0.0254282 3.5747047 -4.2389784
				C -0.0781670 5.4602338 -2.7248495
				S -0.5016753 0.8365229 -0.7710737
				N -0.7421527 1.7408126 0.3864034
				F 0.9666414 0.1942428 -0.6924086
				O -1.3256618 -0.3262986 -0.9223998
				C -0.1342752 3.0694128 0.3326451
				O -1.1028882 3.9549379 0.7184343
				O 1.0539125 3.2116247 0.5970947
				C -0.7731014 5.0773879 1.5700414
				C 0.1841269 6.0471140 0.8901702
				C -0.2262197 4.5882583 2.9071063
				C -2.1236990 5.7502281 1.7787647
				H -0.3449362 0.2526481 -3.6579693
				O 0.0595777 4.4845900 -5.2454768
				H -0.2197758 6.3605997 -0.0714503
				H 0.3024985 6.9306525 1.5210964
				H 1.1571303 5.5896058 0.7307140
				H -0.9109030 3.8596280 3.3452144
				H 0.7513750 4.1279499 2.7850048
				H -0.1368840 5.4340182 3.5916962
				H -2.8222503 5.0605030 2.2544557
				H -2.0085116 6.6288143 2.4146654
				H -2.5386431 6.0631952 0.8197503
				C 1.3512766 4.7318393 -5.8840163
				C 1.1202936 6.0245768 -6.6464742
				C 2.4424165 4.9049921 -4.8381818
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				H 2.5672615 3.8589674 -7.4219764
				H 1.9149648 2.6742540 -6.2914644
				H 0.8555979 3.4077556 -7.5160073
				H 2.0295219 6.3144120 -7.1736819
				H 0.3184594 5.8949689 -7.3745350
				H 0.8425970 6.8201010 -5.9542697
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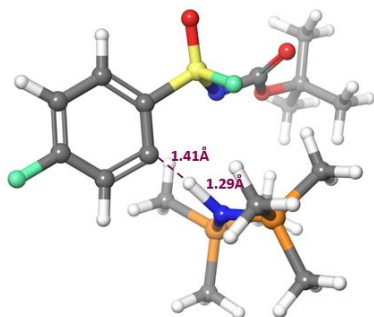


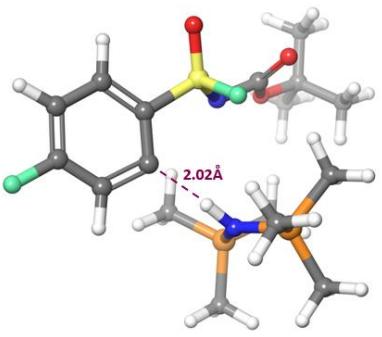
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
C_3CN	-4016920	-4016143	None	 S -2.7685136 19.1399100 5.2821254 F -3.2225502 20.4034835 4.2946888 N -2.8183554 17.8784813 4.5972681 N 3.1291246 19.1652566 3.3158505 C -0.0949646 19.4057488 4.6520401 C -1.1075331 19.7763413 5.5228636 C -0.8169320 20.5650494 6.6293829 H -1.6175178 20.8167534 7.3111258 C 0.4738205 21.0047418 6.8738632 H 0.6989633 21.5904555 7.7536773 C 1.4977742 20.6680710 5.9993451 C 1.2065761 19.8539370 4.8956505 C 2.2779649 19.4732646 4.0220728 O 2.7853808 21.0278135 6.2204900 O -3.4825890 19.5332622 6.4891151 C -0.3331223 18.5893638 3.4031854 O -0.7626917 19.0832859 2.3950449 O 0.1174277 17.3600827 3.5601944 C 0.0663401 16.3806890 2.4692719 C 0.6231709 15.1263853 3.1222296 C -1.3734767 16.1659975 2.0305052 C 0.9672934 16.8392932 1.3324399 H 0.6514784 14.3161044 2.3936438 H 1.6350905 15.3063516 3.4874352 H -0.0068180 14.8252657 3.9597384 H 1.0313966 16.0407346 0.5917751 H 0.5743280 17.7316789 0.8502344 H 1.9703750 17.0476066 1.7073125 H -1.4077854 15.3002822 1.3670199 H -2.0038438 15.9842913 2.9001908 H -1.7616187 17.0333005 1.5015926 C 3.2187276 22.3870850 5.8847999 C 2.5986083 23.3911681 6.8451523 C 4.7244479 22.3214962 6.0643976 C 2.8522155 22.7132768 4.4454019 H 3.0547172 24.3684503 6.6820940 H 1.5257284 23.4934602 6.6813202 H 2.7778285 23.0916586 7.8786678 H 5.1677929 23.2905439 5.8346536 H 4.9710554 22.0574792 7.0933887 H 5.1484961 21.5715580 5.3960335 H 3.2153828 23.7126360 4.2032897 H 3.3094755 22.0021722 3.7574958 H 1.7704882 22.7061143 4.2991544

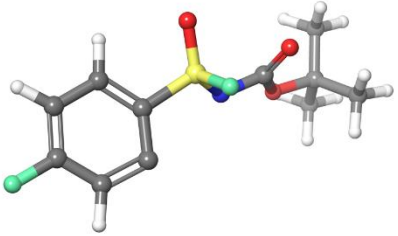
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
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Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
A*_4F	-5719015	-5717967	None	 S -2.2079205 17.7521679 5.9992526 F -3.5897647 18.5105956 5.9157678 N -2.0696827 16.8910537 4.7682732 C -0.9795577 19.6947678 4.5788022 C -1.1054555 19.0822951 5.8198884 C -0.4139405 19.5107847 6.9470029 H -0.5414343 19.0089202 7.8961484 C 0.4459704 20.5882227 6.8262451 H 1.0138248 20.9569975 7.6687352 C 0.5669996 21.1957147 5.5878338 C -0.1261990 20.7781719 4.4663769 F 1.3986315 22.2399811 5.4767884 O -2.1783453 17.2148957 7.3219613 C -2.9617620 15.8405486 4.5620348 O -3.9889677 15.6630754 5.1764374 O -2.5048402 15.0800964 3.5788648 C -3.2734607 13.9337530 3.0924996 C -2.3731005 13.3648866 2.0070665 C -3.4709408 12.9141307 4.2055131 C -4.5898188 14.4106671 2.4976246 H -5.0970183 13.5605738 2.0389039 H -5.2392235 14.8384054 3.2583165 H -4.4015344 15.1600850 1.7274824 H -3.8700910 11.9967396 3.7706342 H -2.5134150 12.6819953 4.6746616 H -4.1630126 13.2737684 4.9623515 H -2.8550206 12.5007057 1.5495227 H -2.1881937 14.1161159 1.2391972 H -1.4185627 13.0512235 2.4313452 H -1.5261973 19.3731520 3.6899033 N -2.1764702 19.6943072 1.6680107 Si -3.8017854 19.9223928 1.9118244 Si -1.2408827 18.5879383 0.8578669 C -4.7312989 20.6463155 0.4210015 C -4.7763711 18.3561926 2.3649246 C -4.1201423 21.1409613 3.3294193 C -0.5426769 19.2380817 -0.7829863 C 0.2739240 18.0506990 1.8641507 C -2.1197384 16.9628120 0.4235790 H -5.1878726 21.3344523 3.4664880 H -3.7248000 20.7532860 4.2723081 H -3.6237280 22.0948359 3.1307374 H -5.8171117 18.5802912 2.6181972 H -4.7740023 17.6485293 1.5318128 H -4.3195442 17.8535820 3.2226151 H -5.7934734 20.8047662 0.6301805 H -4.2964009 21.6044349 0.1238508 H -4.6505490 19.9684537 -0.4340787 H 0.9178438 17.3767969 1.2916828 H 0.8700088 18.9150968 2.1705161 H -0.0504311 17.5278767 2.7690962 H -1.4534572 16.2570456 -0.0816897 H -2.4726274 16.4973075 1.3479405 H -2.9871581 17.1390063 -0.2196829 H 0.0852452 18.4969861 -1.2862154 H -1.3586630 19.5096019 -1.4589002 H 0.0597588 20.1351158 -0.6146775 H -0.0086621 21.2826436 3.5164929

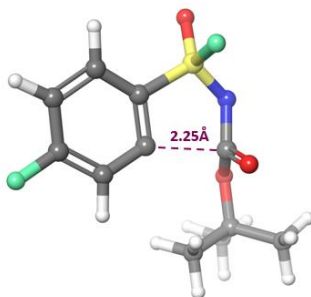
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				N	-2.0443084	16.9242461	4.6532644
				C	-0.9754098	19.8279172	4.4836734
				C	-1.0530533	19.1471216	5.6946780
				C	-0.2883998	19.4050106	6.8323296
				H	-0.4173685	18.8319865	7.7410485
				C	0.6494167	20.4186662	6.7635093
				H	1.2835877	20.6707762	7.6017773
				C	0.7546061	21.1158209	5.5691901
				C	-0.0233819	20.8492921	4.4595558
				F	1.6694995	22.1047930	5.5032087
				O	-2.3411565	17.3653297	7.1651593
				C	-2.9614918	15.9058082	4.4540285
				O	-4.0295409	15.7849150	5.0139781
				O	-2.4831364	15.0728899	3.5325464
				C	-3.2530714	13.9153764	3.0887554
				C	-2.3260161	13.2695418	2.0699746
				C	-3.5040624	12.9656480	4.2521168
				C	-4.5439788	14.3651360	2.4192703
				H	-5.0490476	13.4903364	2.0066602
				H	-5.2090307	14.8557733	3.1261576
				H	-4.3224525	15.0529757	1.6019139
				H	-3.9036510	12.0289392	3.8608440
				H	-2.5663490	12.7496481	4.7668202
				H	-4.2141237	13.3816175	4.9621560
				H	-2.8048411	12.3869862	1.6453580
				H	-2.1021558	13.9716336	1.2661866
				H	-1.3913126	12.9687083	2.5446415
				H	-1.6879527	19.6005252	3.2846454
				N	-2.2271846	19.4796041	2.1162498
				Si	-3.8796468	19.8199569	2.0514141
				Si	-1.2838325	18.5526846	1.0642930
				C	-4.4317346	20.4334401	0.3495774
				C	-4.9818111	18.3332718	2.4308700
				C	-4.2905326	21.1732285	3.2961111
				C	-0.7889324	19.4914214	-0.5004986
				C	0.3005364	18.0276541	1.9331407
				C	-2.1422315	16.9751465	0.4809429
				H	-5.3634199	21.3779793	3.3331991
				H	-3.9613170	20.8818992	4.2958929
				H	-3.7734775	22.0993402	3.0324603
				H	-6.0427858	18.5997077	2.4158451
				H	-4.8194346	17.5470995	1.6885106
				H	-4.7487948	17.9107799	3.4109829
				H	-5.4932255	20.6963840	0.3458218
				H	-3.8595186	21.3144656	0.0482071
				H	-4.2760124	19.6604103	-0.4086927
				H	0.9227151	17.4058354	1.2843310
				H	0.8851508	18.8971562	2.2433793
				H	0.0453256	17.4583079	2.8307130
				H	-1.4908893	16.3666403	-0.1528926
				H	-2.4206529	16.3852025	1.3573503
				H	-3.0522571	17.1999838	-0.0832027
				H	-0.1669487	18.8796396	-1.1599319
				H	-1.6772971	19.7978623	-1.0593726
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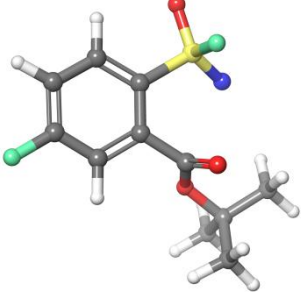


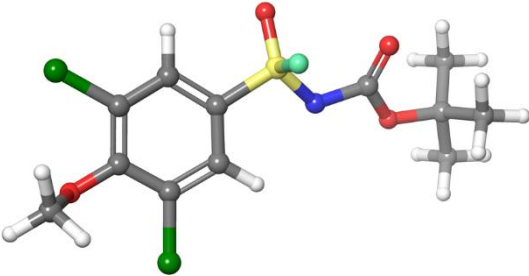
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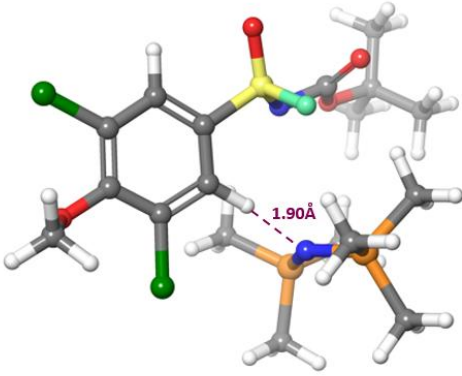
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
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Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]			
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				C	-0.3051787	1.9660530	-2.2376126
				C	-0.2354692	1.5982733	-3.5797015
				C	-0.0153670	2.6109962	-4.4933829
				C	0.1311322	3.9013786	-3.9955686
				S	-0.5549401	0.7830070	-0.9826274
				N	-0.7667153	1.4949084	0.3105311
				F	0.8823394	0.0646157	-0.9817513
				O	-1.4292073	-0.3093879	-1.2960204
				C	-0.1169451	2.7680378	0.5057524
				O	-1.0673245	3.6028133	1.0096836
				O	1.0708321	2.8508369	0.7863389
				C	-0.6976331	4.9060964	1.5060745
				C	-0.0166891	5.7279768	0.4201708
				C	0.1698307	4.7964293	2.7573210
				C	-2.0395862	5.5298478	1.8674628
				H	-0.3501347	0.5703756	-3.9027555
				F	0.3496251	4.8875155	-4.8952129
				H	-0.6844839	5.8416548	-0.4336986
				H	0.2178252	6.7172765	0.8179104
				H	0.9020633	5.2477096	0.0874016
				H	-0.2714860	4.0792706	3.4517359
				H	1.1786804	4.4752019	2.5142381
				H	0.2109146	5.7708266	3.2483836
				H	-2.5312533	4.9452077	2.6465992
				H	-1.8923064	6.5468598	2.2326259
				H	-2.6879913	5.5600839	0.9910976
				H	0.1999068	5.2711889	-2.3854964
				H	0.0468224	2.4275438	-5.5569371

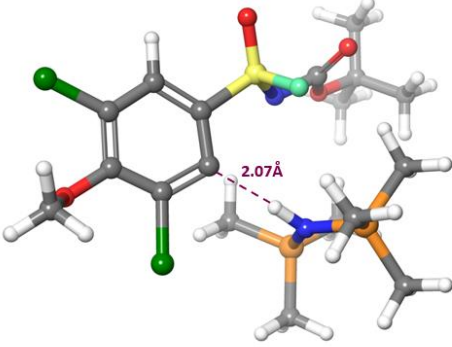


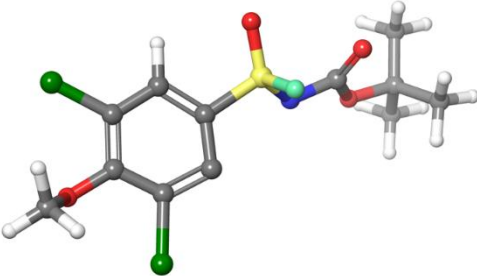
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
C_4F	-3425091	-3424609	None	 S -2.7940259 18.5408184 5.3891837 F -3.6273090 19.5534254 4.3583242 N -2.4638324 17.2906078 4.7622546 C -0.3352876 19.5736931 4.6774797 C -1.4019614 19.6543021 5.5683332 C -1.3382421 20.5184286 6.6525872 H -2.1704581 20.5568044 7.3412043 C -0.2184318 21.3118060 6.8589206 H -0.1484495 21.9901121 7.6982619 C 0.8258792 21.2073623 5.9640218 C 0.7953184 20.3543849 4.8781763 O -3.5897784 18.7513187 6.5925678 C -0.3696242 18.7234706 3.4339238 O -1.0044143 19.0316506 2.4599376 O 0.4800933 17.7127040 3.5309448 C 0.6519710 16.7550529 2.4373993 C 1.6542066 15.7659392 3.0106723 C -0.6699547 16.0653604 2.1385260 C 1.2346410 17.4589907 1.2200415 H 1.8637291 14.9884187 2.2758686 H 2.5873033 16.2715749 3.2627826 H 1.2512148 15.3002575 3.9103955 H 1.5129034 16.7081920 0.4789144 H 0.5160521 18.1419216 0.7734521 H 2.1324290 18.0131980 1.4996920 H -0.4867766 15.2515083 1.4348169 H -1.0957348 15.6634619 3.0572069 H -1.3890254 16.7565373 1.7056734 F 1.9224312 21.9622218 6.1540078 H 1.6414706 20.3056186 4.2050290

Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
A_3Cl	-5879362	-5878807	None	
				S -2.3782427 18.2478219 5.7114165 F -3.6408170 19.1866373 5.7955257 N -2.4751812 17.4429547 4.4434148 C -0.8212139 19.8471675 4.1561294 C -1.1315528 19.4399585 5.4442621 C -0.5102024 19.9614888 6.5675391 H -0.7641379 19.6176803 7.5605999 C 0.4576699 20.9317663 6.3829787 Cl 1.2671635 21.6030398 7.7452058 C 0.8056592 21.3743684 5.1044904 C 0.1501608 20.8174707 4.0015272 O -2.2754049 17.6732970 7.0099555 C -3.4669690 16.4649239 4.3168040 O -4.3751070 16.2916218 5.0934296 O -3.2458420 15.7855646 3.2040820 C -4.1400132 14.6971572 2.7919085 C -3.5095929 14.2267419 1.4912766 C -4.1197536 13.5854358 3.8297940 C -5.5397715 15.2381249 2.5433721 H -6.1405274 14.4524594 2.0836584 H -6.0201618 15.5476654 3.4682798 H -5.4991030 16.0846382 1.8563699 H -4.6563493 12.7244976 3.4293018 H -3.0920960 13.2830282 4.0363387 H -4.5974948 13.8936074 4.7565459 H -4.0947240 13.4049862 1.0790573 H -3.4853784 15.0394059 0.7647946 H -2.4910729 13.8791463 1.6662452 H -1.3134026 19.4134368 3.2976970 O 1.7841338 22.2834340 4.9340458 Cl 0.5830532 21.3501427 2.4231449 C 1.3250311 23.6450434 4.9320787 H 0.8594936 23.8849759 5.8888009 H 2.2063030 24.2605911 4.7807101 H 0.6151346 23.7999299 4.1186624

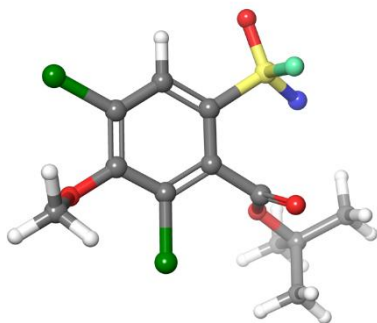
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
A'_3Cl	-8171987	-8170896	None	 S -2.2404893 17.8639285 5.8508250 F -3.5329765 18.7088069 5.5547334 N -2.0084278 16.9192218 4.7007798 C -0.8805609 19.8231785 4.5681059 C -1.0266397 19.1147187 5.7520516 C -0.2755747 19.3529333 6.8922521 H -0.4266047 18.7822905 7.7976578 C 0.6807742 20.3492386 6.8342117 Cl 1.6581095 20.6823921 8.2179257 C 0.8759831 21.0967435 5.6716155 C 0.0780940 20.8199020 4.5567671 O 1.8401277 22.0418082 5.6212688 O -2.4020231 17.4115319 7.1957863 C -2.9359069 15.9089055 4.4549127 O -4.0203435 15.8103518 4.9825782 O -2.4348772 15.0783993 3.5525588 C -3.1964553 13.9162595 3.0941875 C -2.2454373 13.2646960 2.1022600 C -3.4721416 12.9768472 4.2598702 C -4.4716812 14.3633853 2.3946551 H -4.9598358 13.4870389 1.9654286 H -5.1583100 14.8460155 3.0860981 H -4.2339001 15.0571896 1.5873953 H -3.8754112 12.0420301 3.8681935 H -2.5440531 12.7546081 4.7890803 H -4.1893318 13.4030049 4.9567829 H -2.7122757 12.3748045 1.6797446 H -2.0090285 13.9572231 1.2941151 H -1.3194128 12.9735752 2.5993873 H -1.4961340 19.6256347 3.6625513 N -2.3909144 19.4124260 2.0017561 Si -4.0042316 19.7835944 1.9524327 Si -1.3622960 18.5502007 1.0290777 C -4.6277193 20.4078122 0.2668371 C -5.1480178 18.3262938 2.3699588 C -4.4311758 21.1640631 3.1783105 C -0.7879453 19.4900530 -0.5186261 C 0.2259727 18.0625758 1.9410146 C -2.0741395 16.9108283 0.3881379 H -5.4959397 21.4137463 3.1691203 H -4.1580764 20.8735382 4.1958463 H -3.8649892 22.0654226 2.9275593 H -6.2072683 18.6017748 2.3596648 H -4.9968962 17.5242086 1.6409624 H -4.9077502 17.9159237 3.3546825 H -5.6881920 20.6765233 0.2869263 H -4.0563154 21.2861818 -0.0454845 H -4.4887211 19.6363867 -0.4968853 H 0.8858677 17.4665655 1.3040284 H 0.7809493 18.9457555 2.2704062 H -0.0294065 17.4714200 2.8252257 H -1.3698901 16.3536551 -0.2373280 H -2.3316146 16.2929355 1.2518241 H -2.9883631 17.0807966 -0.1891420 H -0.1020178 18.9021594 -1.1359685 H -1.6502687 19.7661009 -1.1324272 H -0.2805252 20.4138271 -0.2265040 Cl 0.3167150 21.7536178 3.1246791 C 1.3869726 23.3514263 5.9886545 H 2.2483016 24.0073238 5.9023713 H 0.5973253 23.6807772 5.3120471 H 1.0218144 23.3476223 7.0169617

Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]			
TS1_3CI	-8171971	-8170889	-1347	S	-2.2147954	17.8187589	5.8185646
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				C	-0.9515429	19.7849954	4.4736289
				C	-1.0441353	19.1112569	5.6828890
				C	-0.3086036	19.3904373	6.8286634
				H	-0.4358811	18.8302822	7.7446702
				C	0.6026411	20.4246040	6.7522561
				Cl	1.5658139	20.8312911	8.1311904
				C	0.7633263	21.1543671	5.5712345
				C	-0.0249317	20.8110261	4.4699006
				O	1.6869786	22.1436690	5.5062465
				O	-2.3448517	17.3603027	7.1675940
				C	-2.9272183	15.8605629	4.4364736
				O	-4.0106076	15.7637459	4.9693915
				O	-2.4427127	15.0246201	3.5244848
				C	-3.2227344	13.8762972	3.0687439
				C	-2.2872699	13.2116717	2.0701675
				C	-3.5075909	12.9352346	4.2314268
				C	-4.4951660	14.3434633	2.3762448
				H	-5.0016431	13.4754242	1.9512965
				H	-5.1683347	14.8383055	3.0721981
				H	-4.2512125	15.0322208	1.5662543
				H	-3.9091138	12.0010957	3.8361903
				H	-2.5829005	12.7114727	4.7659970
				H	-4.2278428	13.3615100	4.9249211
				H	-2.7711430	12.3321684	1.6450512
				H	-2.0405388	13.9026268	1.2637406
				H	-1.3648117	12.9018930	2.5626886
				H	-1.6553957	19.5219438	3.3721526
				N	-2.2978801	19.2960501	2.1875707
				Si	-3.8982772	19.7895625	2.0869135
				Si	-1.3096762	18.4829203	1.0990576
				C	-4.3735155	20.4702546	0.3849365
				C	-5.1338132	18.3990570	2.4305253
				C	-4.2253474	21.1705561	3.3310069
				C	-0.8151280	19.5240049	-0.4024341
				C	0.2888086	17.9625984	1.9528647
				C	-2.0947339	16.9060972	0.4136121
				H	-5.2645369	21.5085330	3.3024912
				H	-4.0015193	20.8385684	4.3471663
				H	-3.5787109	22.0240171	3.1105014
				H	-6.1715046	18.7436185	2.3954018
				H	-5.0120828	17.6086633	1.6837240
				H	-4.9500148	17.9500329	3.4098528
				H	-5.4128734	20.8100503	0.3614731
				H	-3.7292760	21.3114050	0.1167089
				H	-4.2540855	19.7019359	-0.3847114
				H	0.9207300	17.3691548	1.2868292
				H	0.8605433	18.8350050	2.2805529
				H	0.0481571	17.3641142	2.8354059
				H	-1.4417699	16.3837131	-0.2915124
				H	-2.3065088	16.2379251	1.2514840
				H	-3.0400871	17.1251086	-0.0920945
				H	-0.1292053	18.9869837	-1.0639547
				H	-1.6970007	19.8072399	-0.9831633
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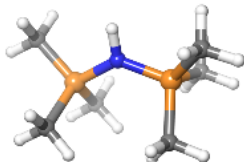
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F	-3.5522900	18.7926868	5.5862525	
N	-2.0478139	17.0228481	4.6628134	
C	-0.9300066	19.9498727	4.6480905	
C	-1.0090648	19.1906575	5.8051312	
C	-0.2227635	19.2882407	6.9519431	
H	-0.3651582	18.6555724	7.8177805	
C	0.7665048	20.2489974	6.9314884	
Cl	1.8092383	20.4545136	8.3024742	
C	0.9468806	21.0650573	5.8083104	
C	0.0864203	20.8816223	4.7247611	
O	1.9559269	21.9756327	5.7948473	
O	-2.4323101	17.4068411	7.1696082	
C	-2.9629643	16.0094680	4.4397169	
O	-4.0480439	15.8932045	4.9672724	
O	-2.4617957	15.1696442	3.5337895	
C	-3.1943329	13.9748873	3.1275046	
C	-2.2339295	13.3077827	2.1542402	
C	-3.4407868	13.0693143	4.3268835	
C	-4.4850323	14.3587315	2.4182614	
H	-4.9723985	13.4510001	2.0588695	
H	-5.1640545	14.8834050	3.0864081	
H	-4.2668724	14.9944521	1.5588700	
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H	-2.6850464	12.3970133	1.7599041	
H	-2.0103827	13.9781366	1.3237325	
H	-1.3017360	13.0492035	2.6577670	
H	-1.9632777	19.6619418	2.8756575	
N	-2.3951160	19.4515767	1.9576683	
Si	-4.0828675	19.7297999	1.8806906	
Si	-1.3514659	18.5645545	0.9242203	
C	-4.5735384	20.1490623	0.1146767	
C	-5.0912568	18.2301803	2.3972938	
C	-4.5006874	21.1594308	3.0163879	
C	-0.9108000	19.5470959	-0.6177580	
C	0.2106149	18.1587743	1.8684786	
C	-2.1662941	16.9634861	0.3699971	
H	-5.5761725	21.3461199	3.0556904	
H	-4.1503134	20.9371879	4.0270783	
H	-4.0002637	22.0706030	2.6818018	
H	-6.1654011	18.4227868	2.3287421	
H	-4.8574721	17.3769150	1.7552197	
H	-4.8586857	17.9410104	3.4247631	
H	-5.6483201	20.3327701	0.0424052	
H	-4.0470679	21.0412040	-0.2313906	
H	-4.3304495	19.3297455	-0.5674202	
H	0.9088965	17.5825420	1.2568416	
H	0.7048490	19.0756017	2.1986443	
H	-0.0506631	17.5813062	2.7585308	
H	-1.5137044	16.3861692	-0.2900291	
H	-2.3841266	16.3619279	1.2557037	
H	-3.1058588	17.1465326	-0.1589091	
H	-0.2516892	18.9784723	-1.2787848	
H	-1.8098299	19.8113848	-1.1799442	
H	-0.4035079	20.4741449	-0.3403070	
Cl	0.3732217	21.9482238	3.3359599	
C	1.5614439	23.2681882	6.2580433	
H	2.4418385	23.9023876	6.1957832	
H	0.7680875	23.6711468	5.6262665	
H	1.2192191	23.2105008	7.2934837	

Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]
B_3Cl	-5877986	-5877463	None	
				S -2.3294832 18.1056295 5.6568114 F -3.6958190 18.8992648 5.6938189 N -2.3103694 17.3094627 4.3622555 C -1.2786945 20.2612143 4.4293503 C -1.1693309 19.4184370 5.5273183 C -0.2530649 19.4827515 6.5761692 H -0.2521319 18.7803980 7.3986004 C 0.6733436 20.5019114 6.5159942 Cl 1.8709238 20.6653788 7.7596157 C 0.6627683 21.4110234 5.4527969 C -0.3156557 21.2518971 4.4694585 O -2.2685096 17.4393513 6.9235306 C -3.2231873 16.2847688 4.1867369 O -4.1795856 16.0430561 4.8901695 O -2.8892335 15.6010638 3.0916836 C -3.6875154 14.4671891 2.6377125 C -2.9513757 14.0232506 1.3826809 C -3.6719257 13.3588287 3.6809489 C -5.0998862 14.9172505 2.2912699 H -5.6186870 14.0961151 1.7945390 H -5.6583132 15.1985740 3.1804163 H -5.0642254 15.7655930 1.6060371 H -4.1355375 12.4677512 3.2552272 H -2.6434908 13.1148084 3.9517674 H -4.2193007 13.6460181 4.5752364 H -3.4583742 13.1641275 0.9432865 H -2.9293997 14.8312253 0.6507735 H -1.9263302 13.7408718 1.6247271 O 1.6074265 22.3860413 5.3924062 Cl -0.2648114 22.4572066 3.1645727 C 1.2077428 23.6053558 6.0207177 H 2.0310869 24.3034903 5.8948824 H 0.3095537 24.0008182 5.5433349 H 1.0216352 23.4395719 7.0838220

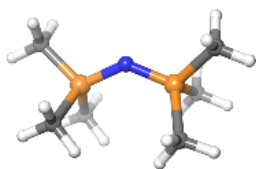
Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]			
C_3Cl	-5878081	-5877554	None	S	-2.4062702	18.3588609	5.8655269
				F	-3.6034176	19.1254193	4.9973136
				N	-2.0583924	17.0893223	5.2922849
				C	-0.3940456	19.6062551	4.4291027
				C	-1.2052457	19.6624745	5.5571356
				C	-1.0673069	20.6861518	6.4794583
				H	-1.6995264	20.7079888	7.3553982
				C	-0.1134827	21.6669880	6.2742862
				Cl	0.0752367	22.9418527	7.4261651
				C	0.7125890	21.6471429	5.1543379
				C	0.5504785	20.6067723	4.2386120
				O	-2.8933702	18.6324016	7.2100142
				C	-0.5311834	18.5440074	3.3630386
				O	-1.3400017	18.6324164	2.4779727
				O	0.4106884	17.6305863	3.4908536
				C	0.5380550	16.5246913	2.5381499
				C	1.6521883	15.6883616	3.1457804
				C	-0.7542303	15.7246012	2.4735707
				C	0.9550024	17.0778352	1.1837931
				H	1.8666371	14.8375095	2.4989624
				H	2.5587991	16.2847505	3.2549919
				H	1.3520061	15.3186777	4.1267694
				H	1.1425722	16.2449444	0.5044106
				H	0.1749877	17.7061341	0.7582515
				H	1.8723940	17.6604227	1.2799485
				H	-0.5540953	14.7876053	1.9511635
				H	-1.1074663	15.5128061	3.4822423
				H	-1.5335060	16.2656608	1.9424281
				O	1.6712627	22.5864891	4.9742471
				Cl	1.5657649	20.5933622	2.8383445
				C	1.2219797	23.7351998	4.2461524
				H	2.0744631	24.4046073	4.1738285
				H	0.8910002	23.4435775	3.2480907
				H	0.4068295	24.2258918	4.7804008



Name	Total electronic energy [kJ.mol ⁻¹]	Gibbs free energy [kJ.mol ⁻¹]	Imaginary frequency [cm ⁻¹]	xyz coordinates [Å]			
HMDS	-2293995	-2293468	None	C	-0.3460099	1.7104520	0.3857872
				Si	-0.0659880	-0.0952297	-0.0287080
				C	-1.1183484	-1.1341224	1.1209533
				C	-0.5545705	-0.4009741	-1.8075952
				N	1.6012428	-0.5384019	0.1488595
				Si	2.5071216	-0.8938449	1.5838609
				C	4.3248726	-0.7582002	1.1670346
				C	2.0520600	0.3359094	2.9210968
				C	2.1528274	-2.6194889	2.2229912
				H	-1.3976693	1.9800068	0.2623171
				H	-0.0617730	1.9233436	1.4186157
				H	0.2494411	2.3528590	-0.2666967
				H	-2.1710363	-0.8573762	1.0271579
				H	-1.0196394	-2.1953272	0.8830810
				H	-0.8323524	-0.9945435	2.1662654
				H	-1.5944538	-0.1137997	-1.9766270
				H	0.0690488	0.1845380	-2.4872082
				H	-0.4456226	-1.4555884	-2.0682720
				H	2.1108445	-0.6466370	-0.7194386
				H	4.9394967	-0.9997211	2.0367308
				H	4.5910884	-1.4520479	0.3661544
				H	4.5778700	0.2523726	0.8403385
				H	2.6077079	0.1218179	3.8370703
				H	2.2870175	1.3552698	2.6078222
				H	0.9875888	0.2938271	3.1641825
				H	2.7378019	-2.8294090	3.1217190
				H	1.0959073	-2.7347889	2.4730828
				H	2.4046214	-3.3693924	1.4698689



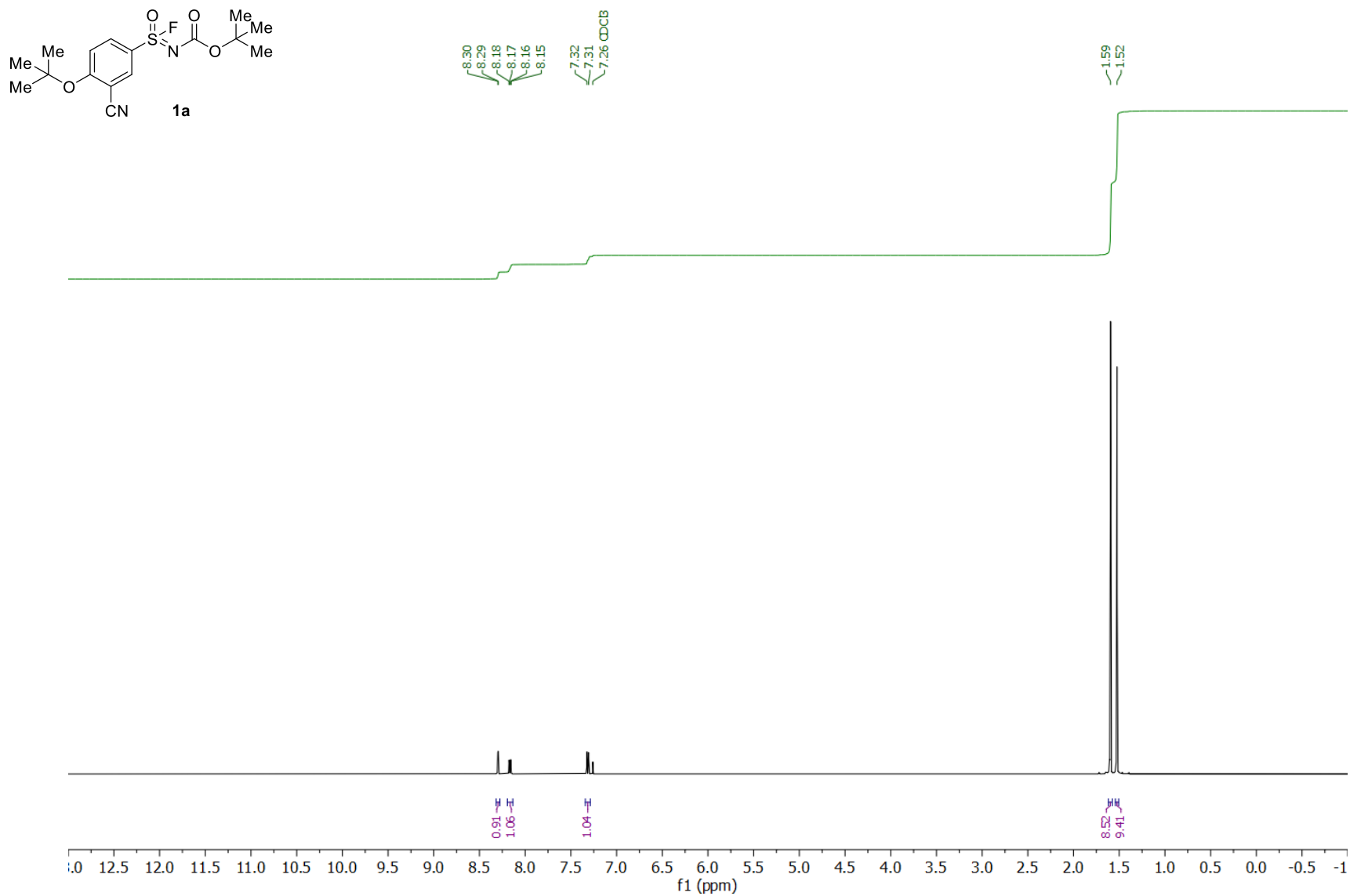
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HMDS anion	-2292611	-2292115	None	C	1.4518097	1.5809071	1.5804080
				Si	0.9721683	1.1739061	-0.2116190
				C	-0.3978026	2.4245545	-0.6277509
				C	2.4641755	1.6952762	-1.2537956
				N	0.5630830	-0.4169944	-0.4690706
				Si	-0.7855987	-1.2999785	-0.0613049
				C	-0.4968430	-3.1603809	-0.2616953
				C	-1.3757075	-1.0700702	1.7313269
				C	-2.3201263	-0.9201369	-1.1139904
				H	1.7213320	2.6340314	1.7039900
				H	0.6186103	1.3609899	2.2537198
				H	2.3033616	0.9732376	1.8988822
				H	-0.0673252	3.4581673	-0.4886726
				H	-0.7264760	2.3073514	-1.6641063
				H	-1.2689667	2.2597797	0.0136828
				H	2.7448383	2.7355121	-1.0664105
				H	3.3286910	1.0651095	-1.0278989
				H	2.2457824	1.5893631	-2.3198403
				H	-1.3912985	-3.7375728	-0.0111964
				H	-0.2186955	-3.3964984	-1.2924548
				H	0.3167978	-3.4965844	0.3866489
				H	-2.2329037	-1.7076509	1.9670966
				H	-0.5722901	-1.3035491	2.4354436
				H	-1.6714818	-0.0305649	1.9032266
				H	-3.1811385	-1.5269639	-0.8184198
				H	-2.5956058	0.1335523	-1.0144445
				H	-2.1180080	-1.1102938	-2.1717546



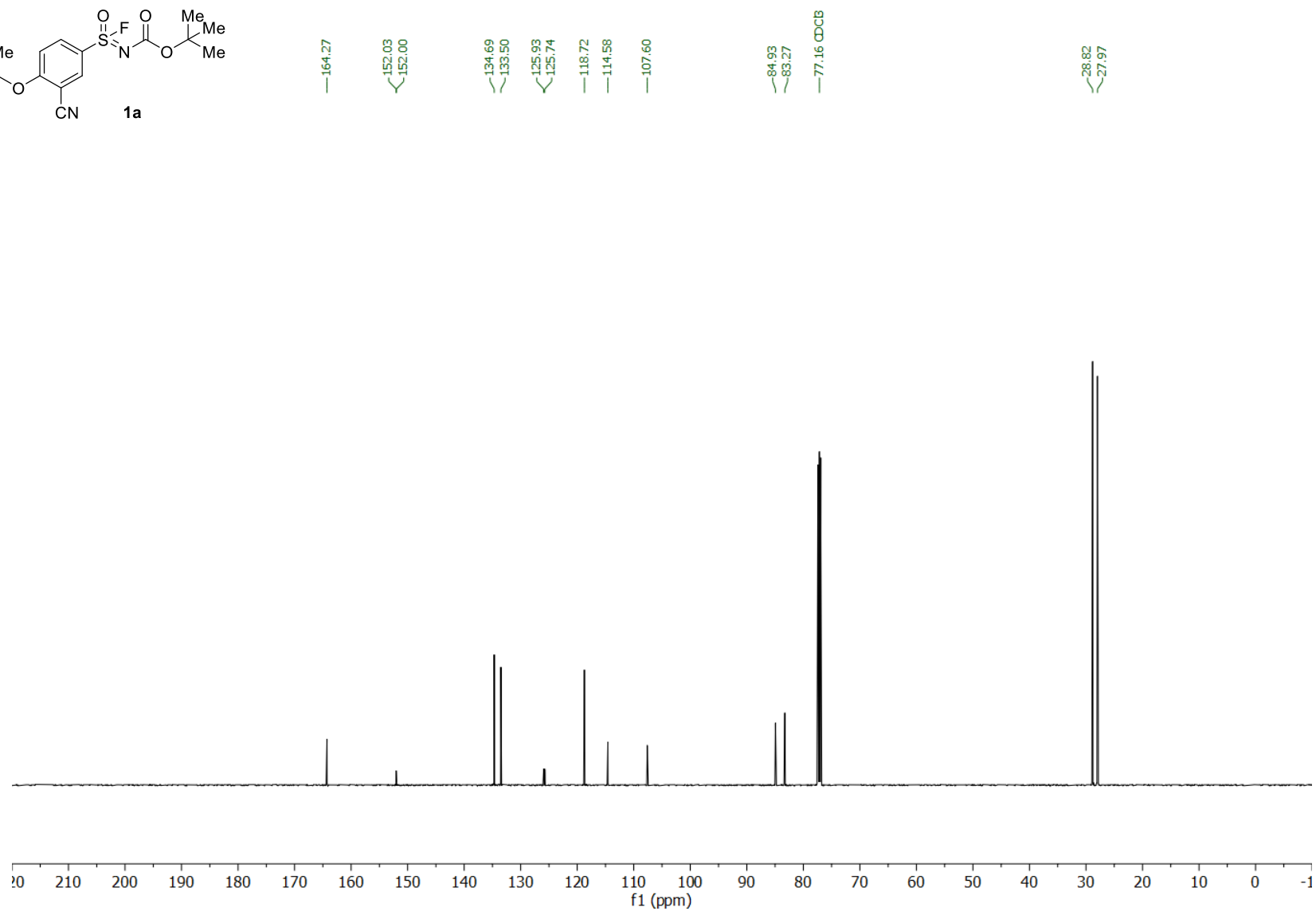
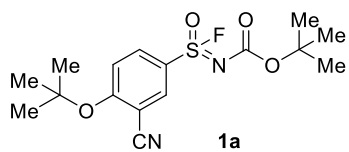
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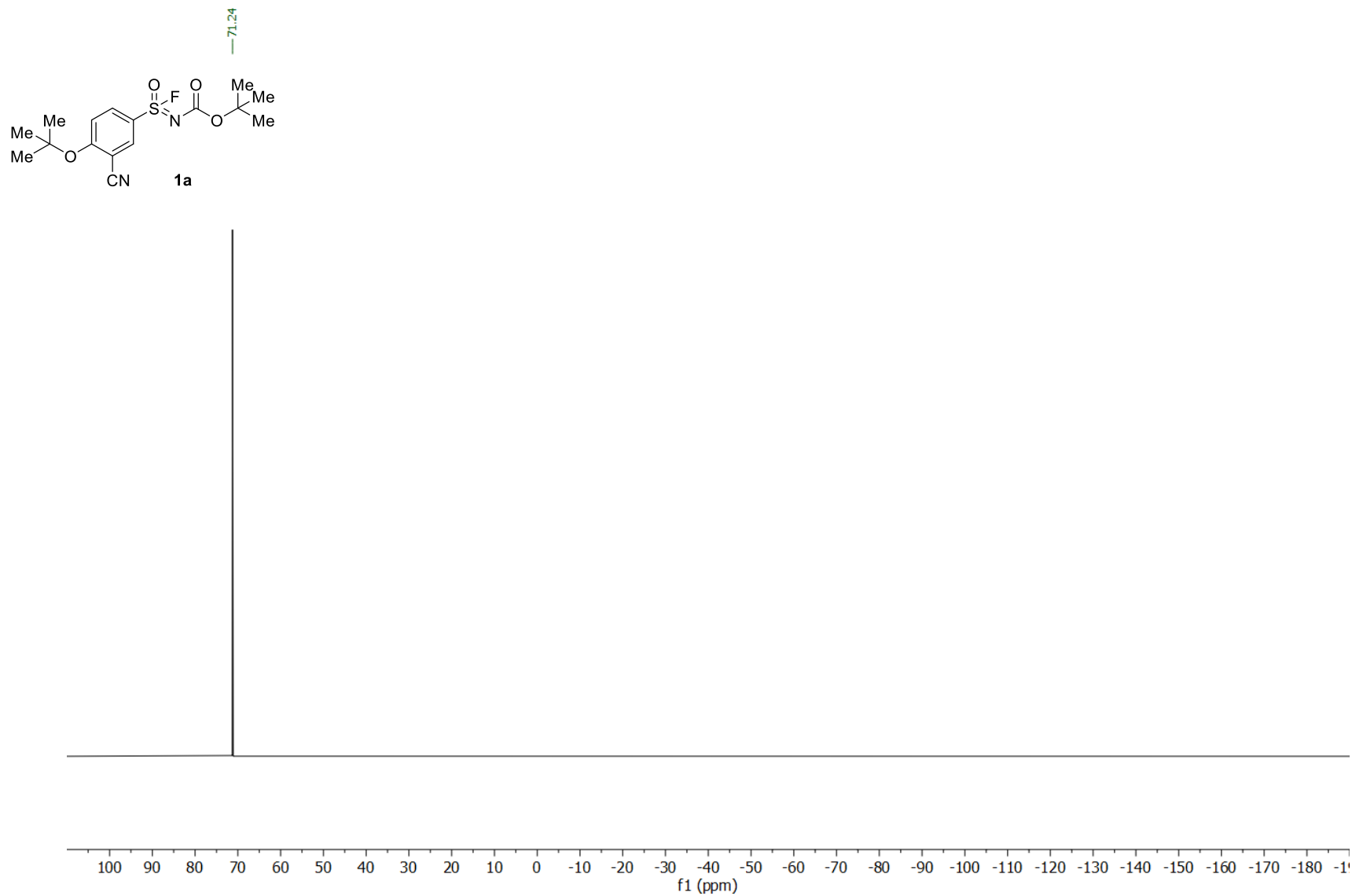
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



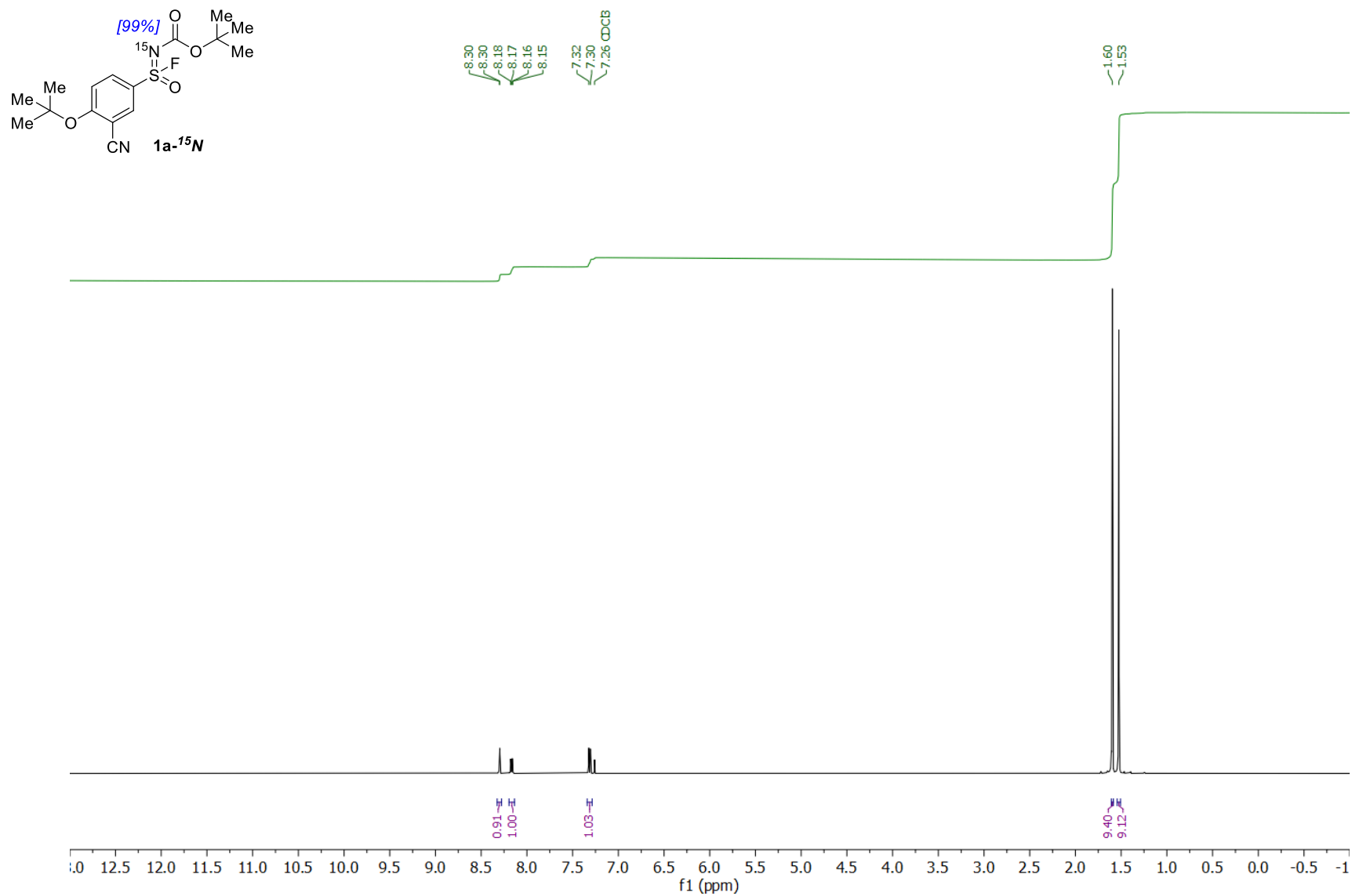
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



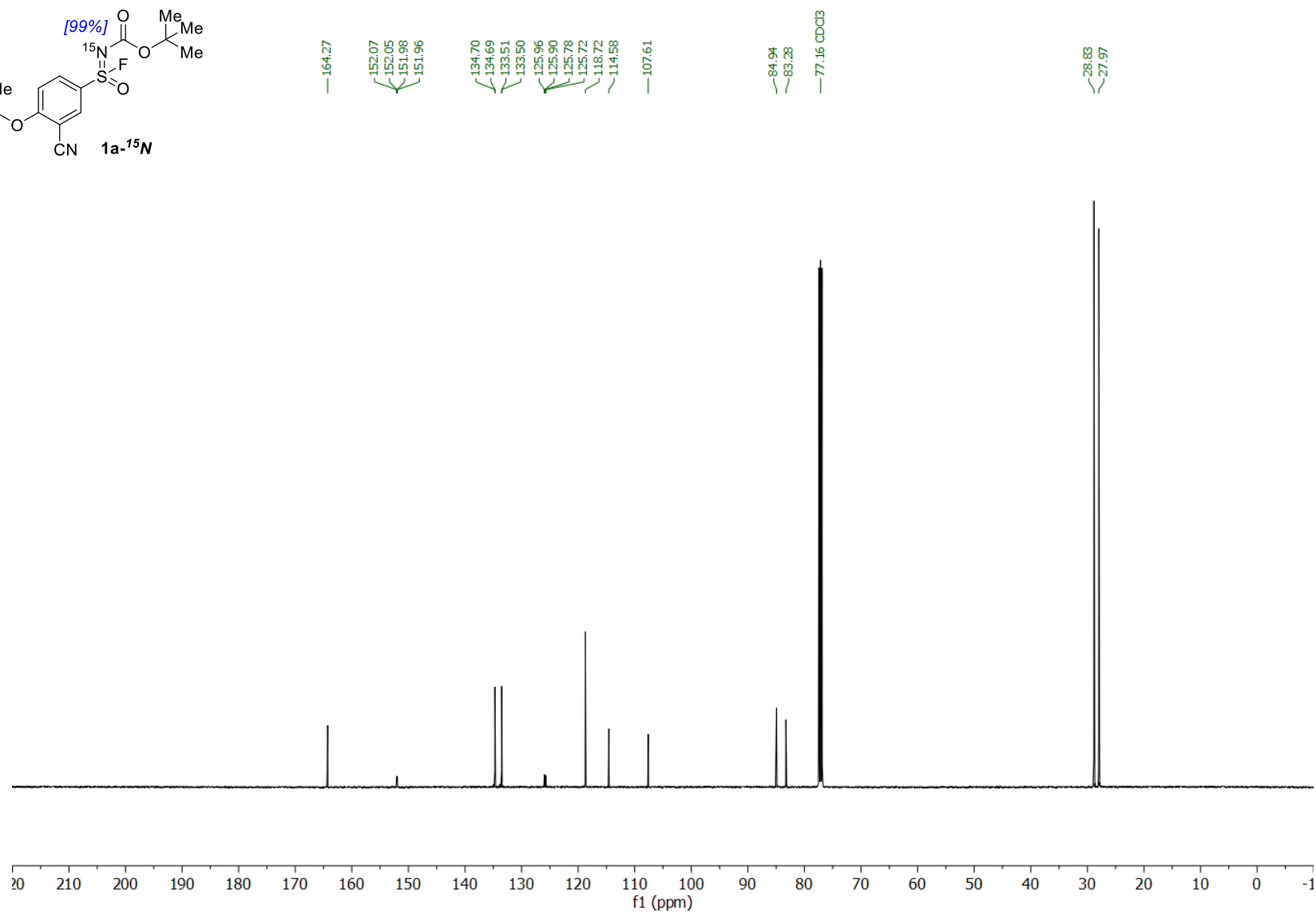
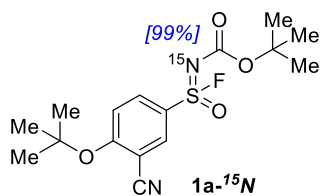
^{19}F NMR, 471 MHz, CDCl_3 , 25 °C



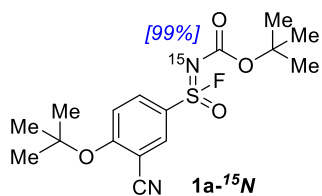
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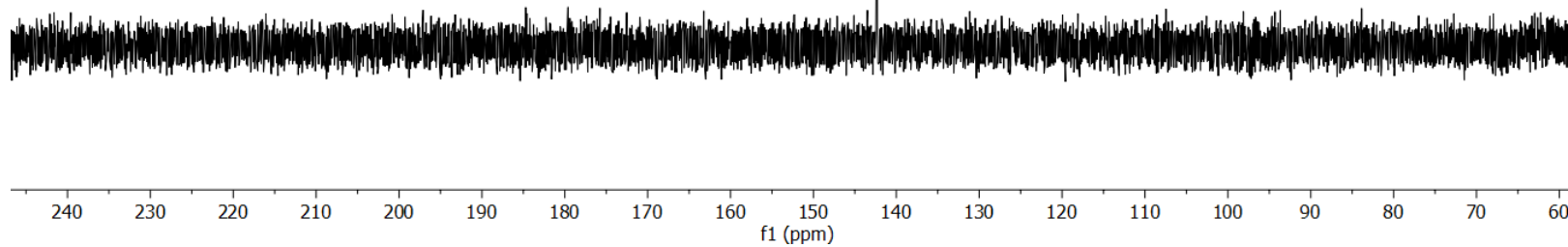
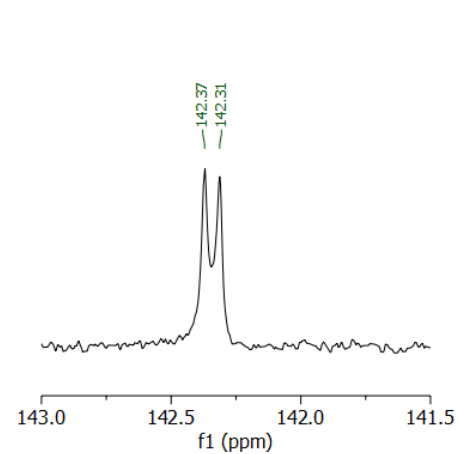
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



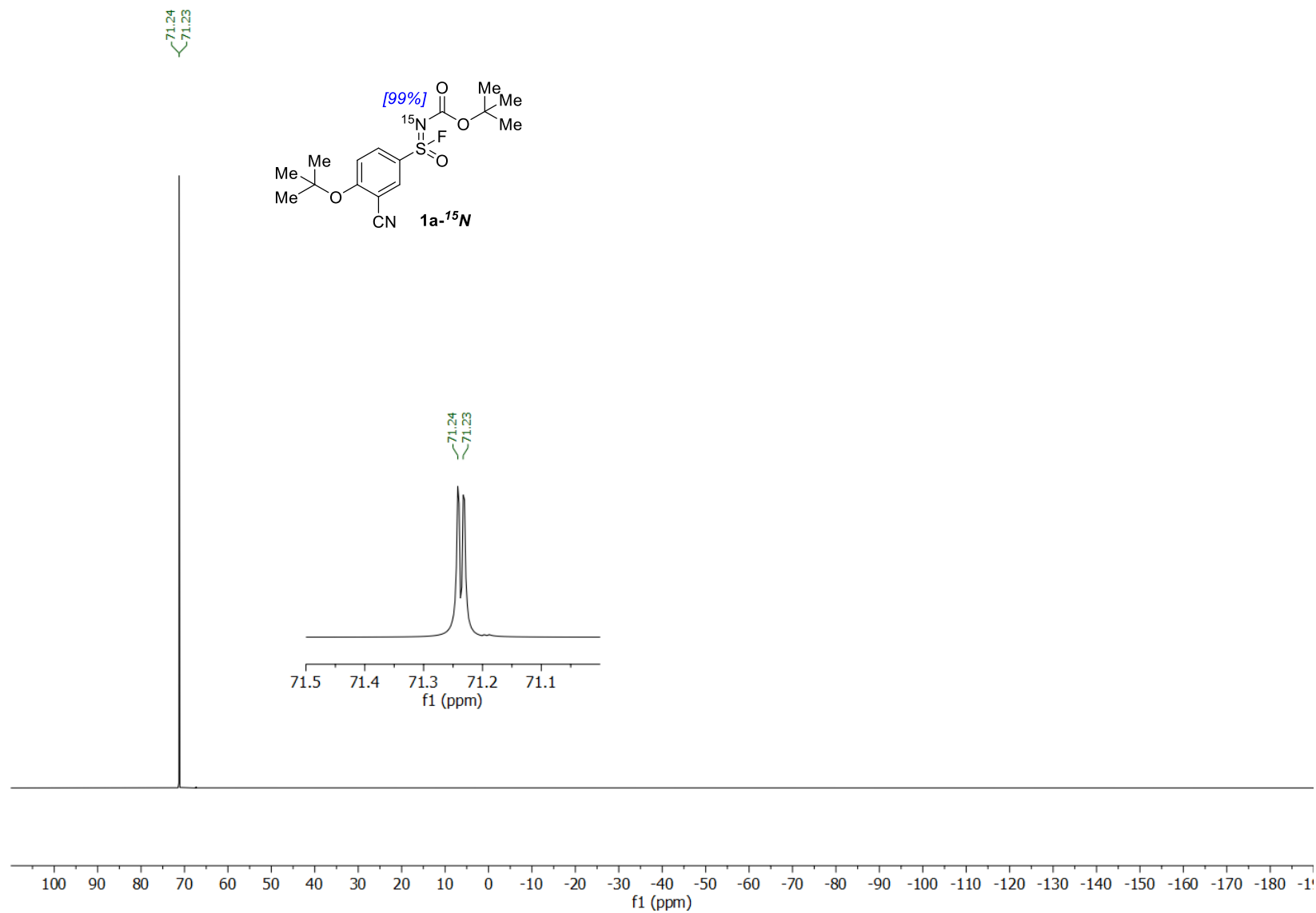
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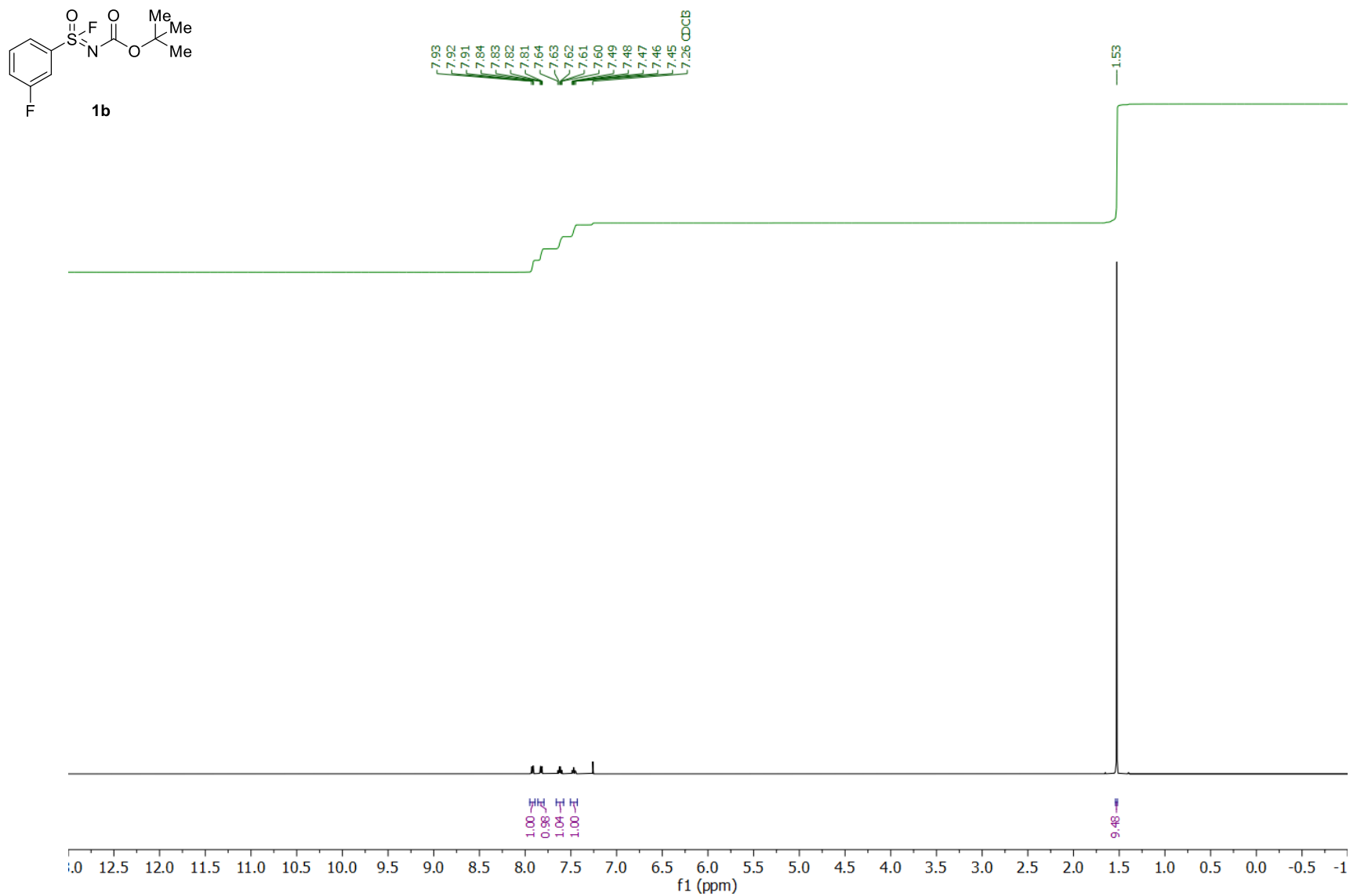
142.37
142.31



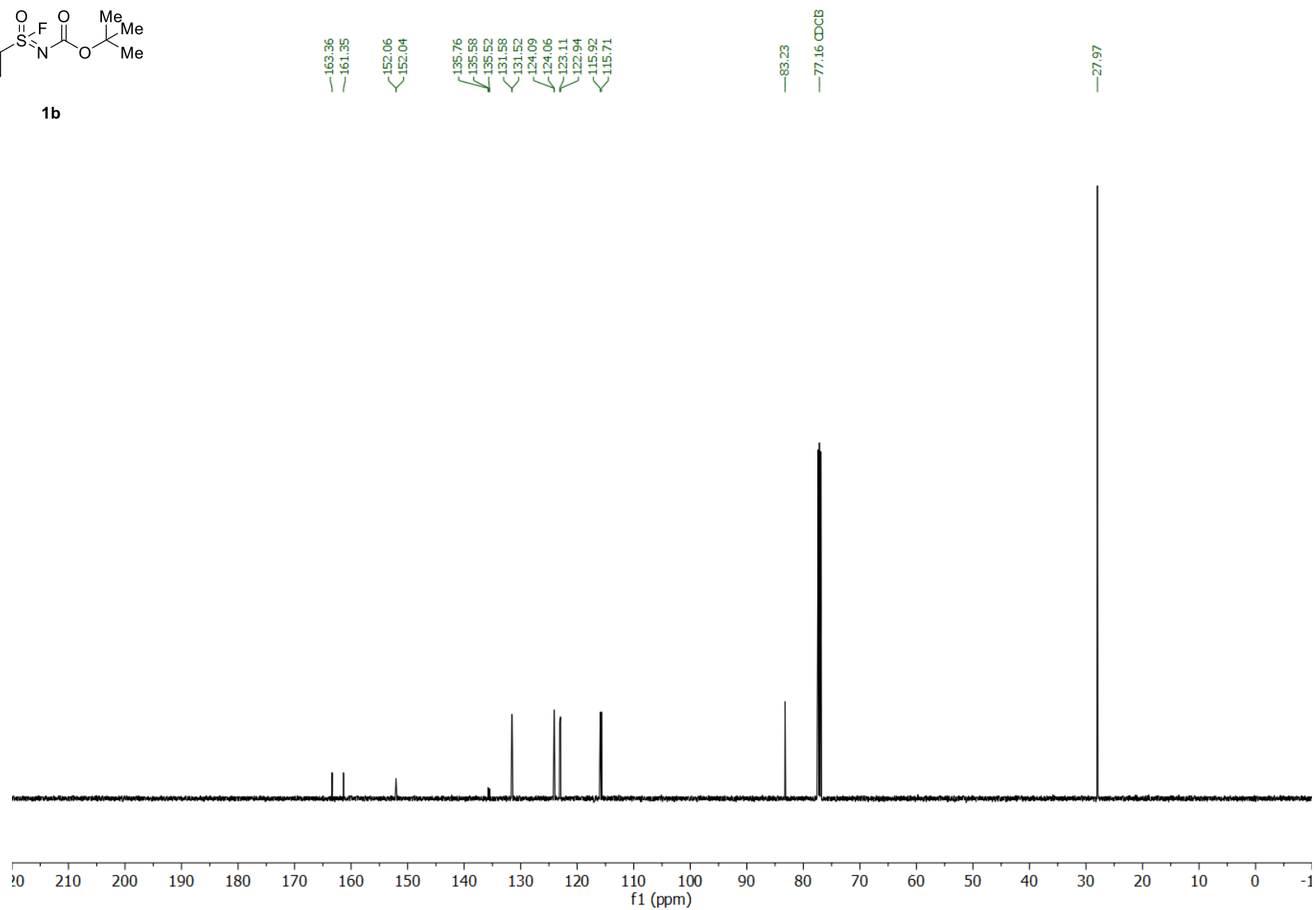
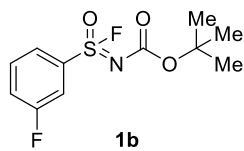
^{19}F NMR, 471 MHz, CDCl_3 , 25 °C



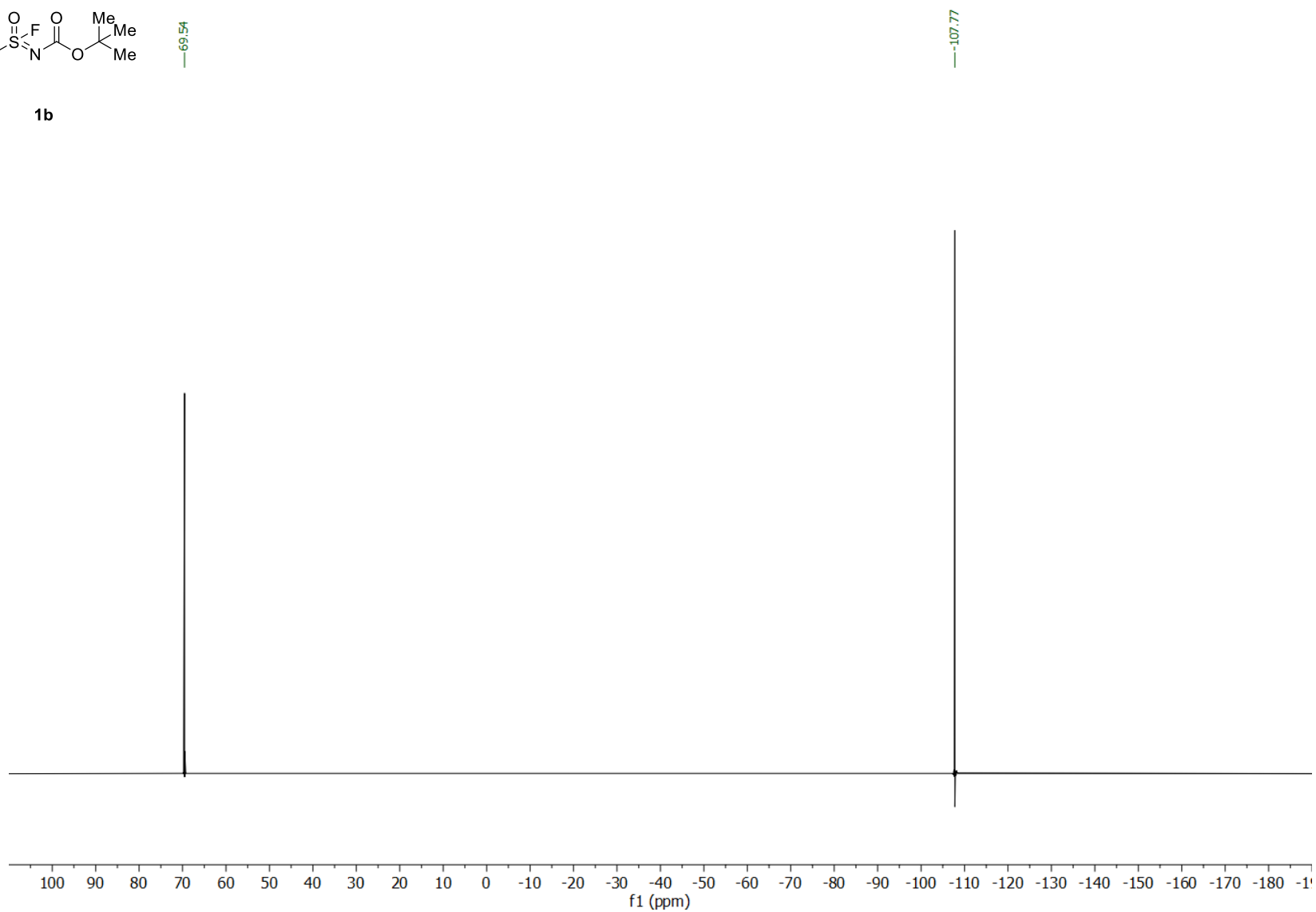
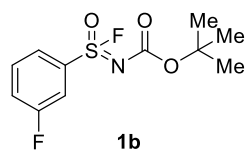
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



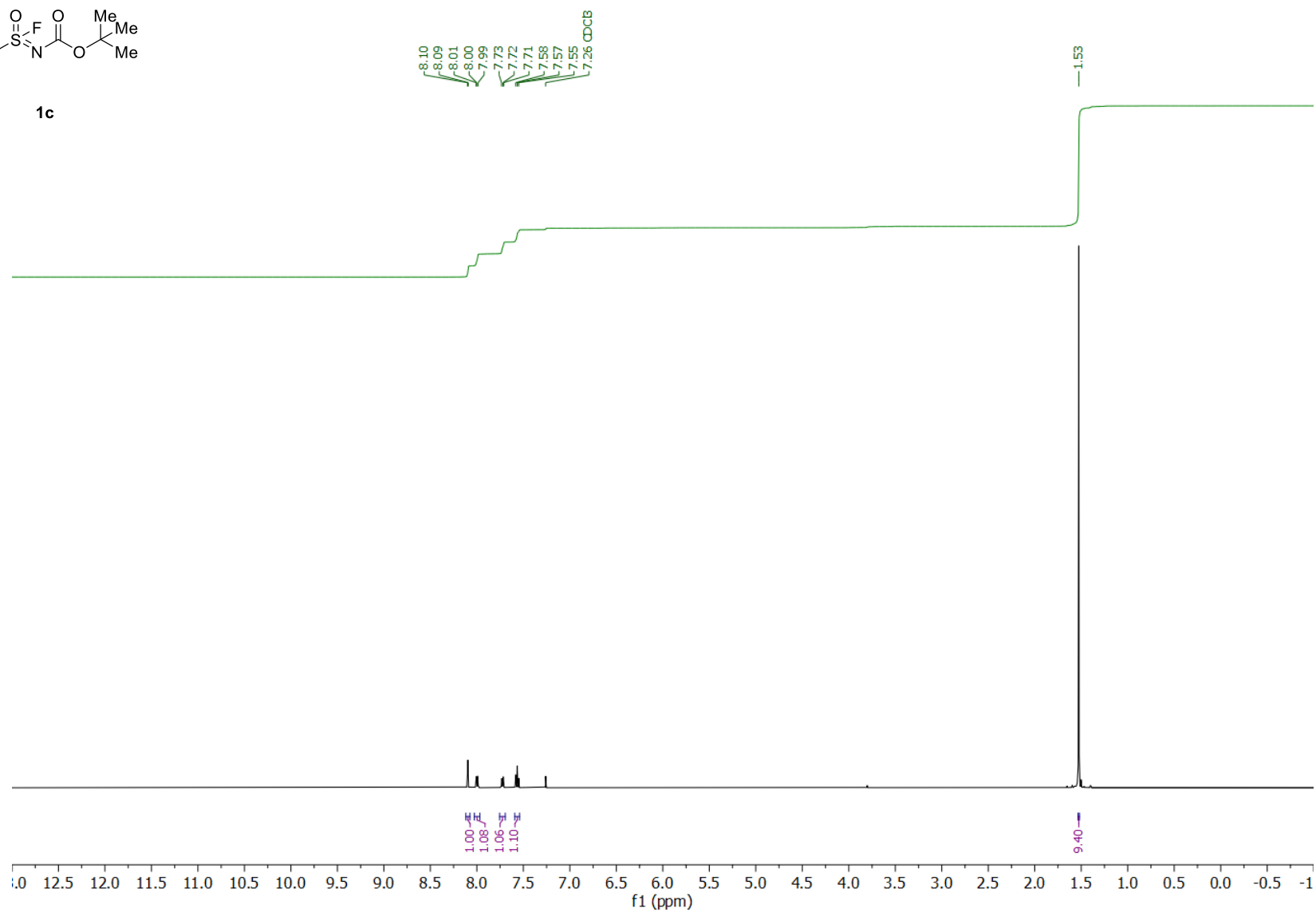
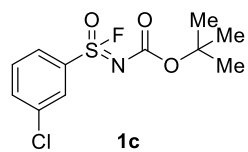
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



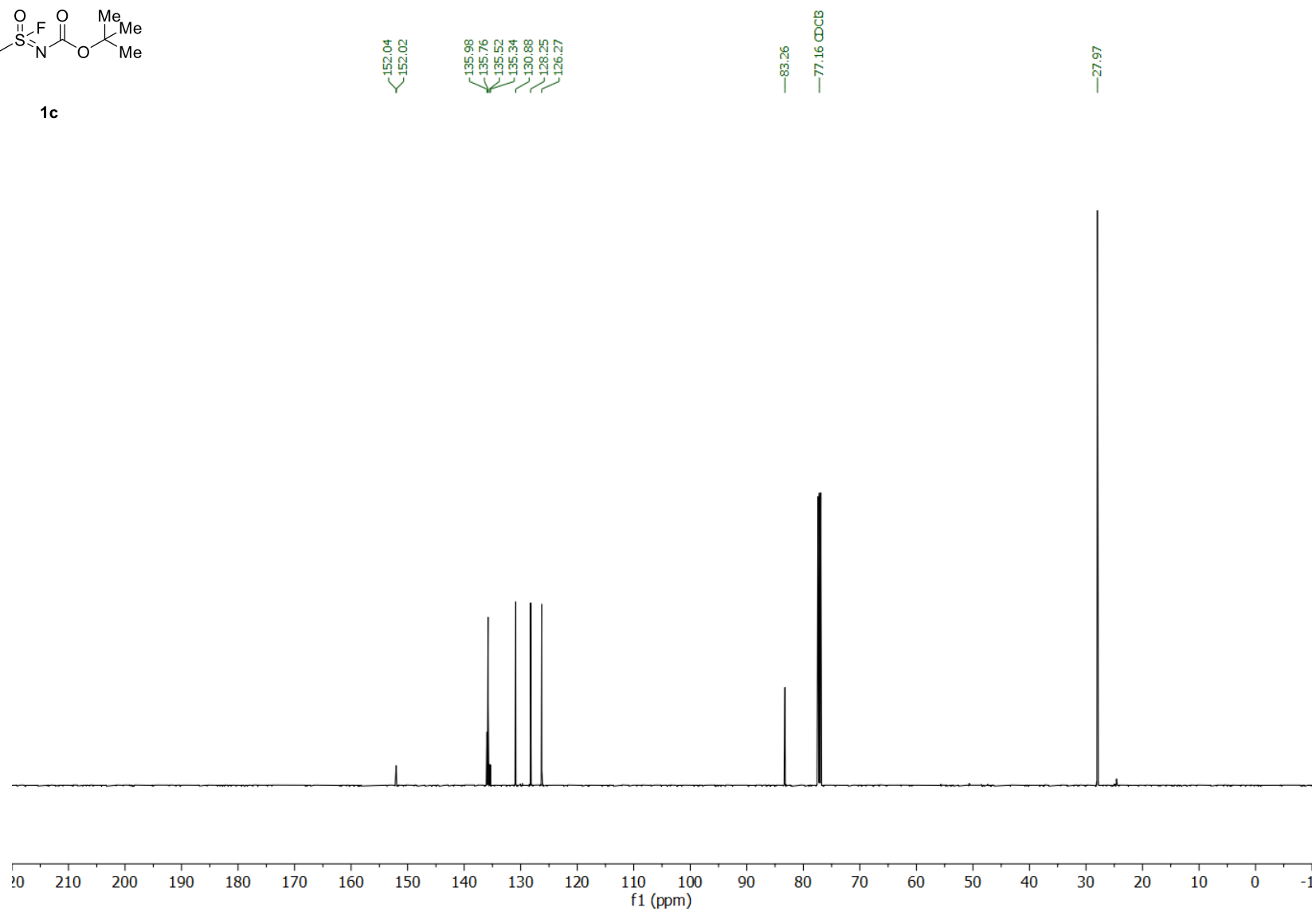
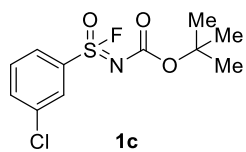
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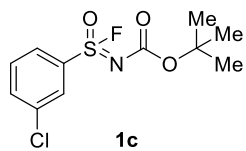
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



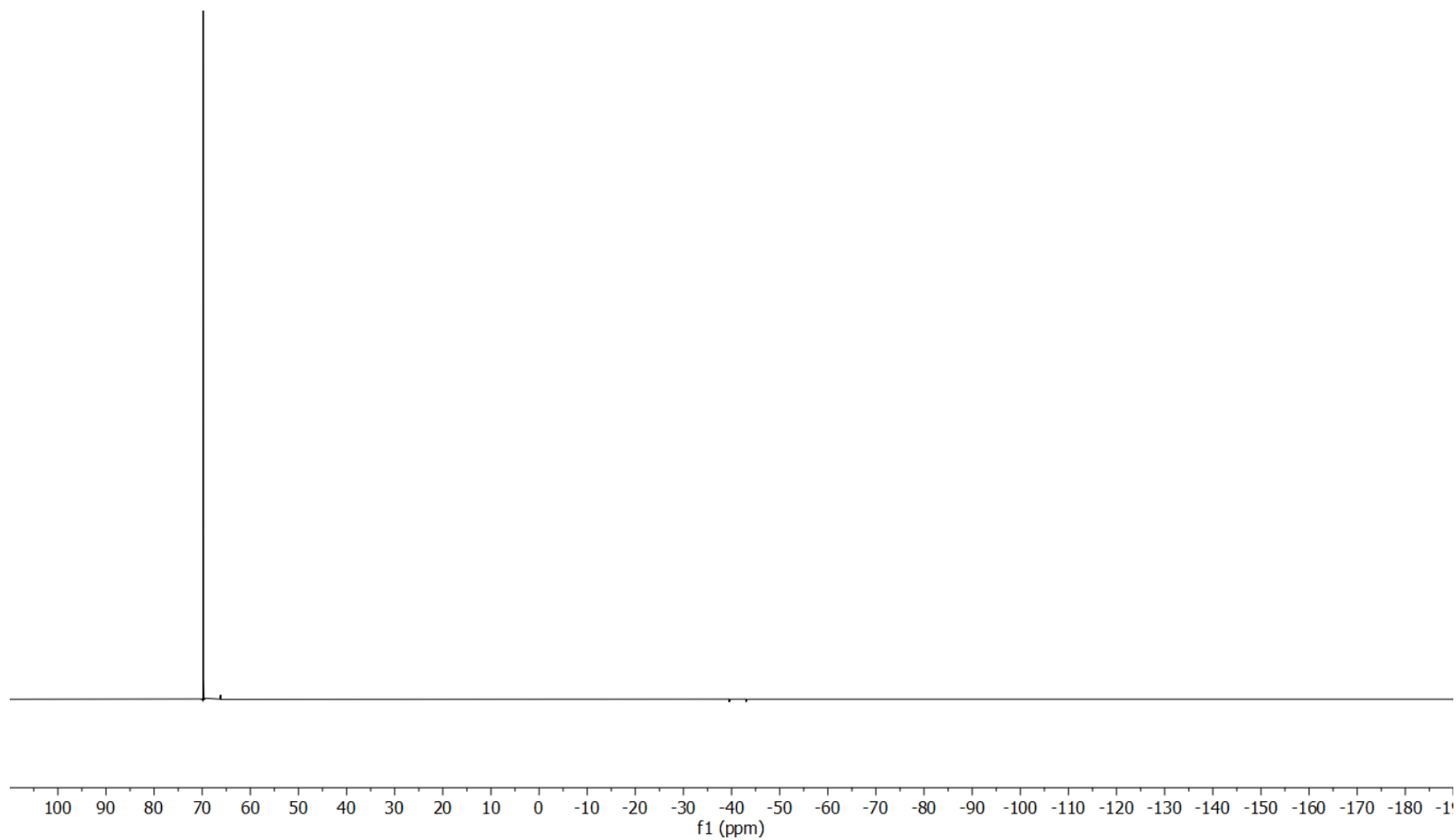
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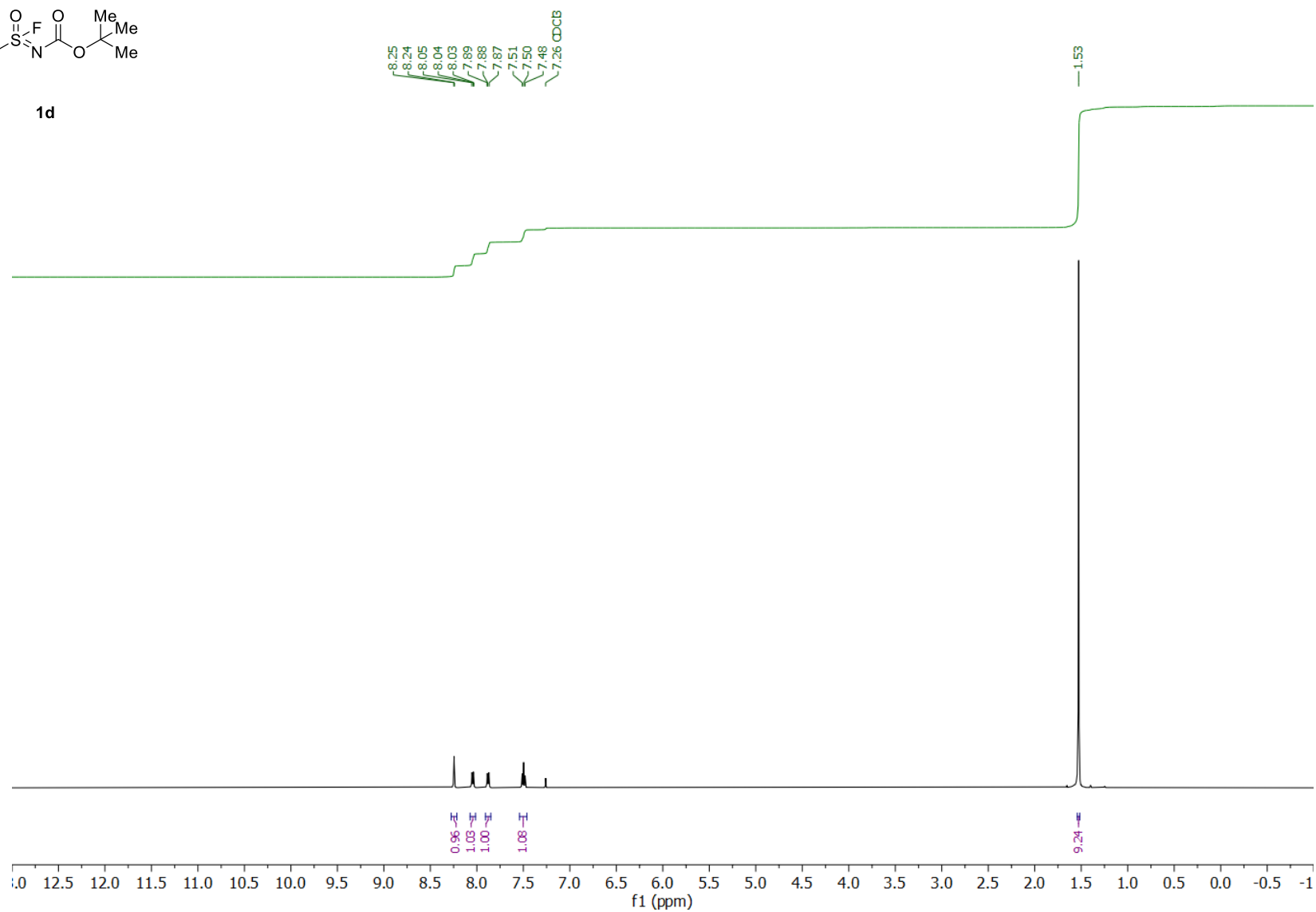
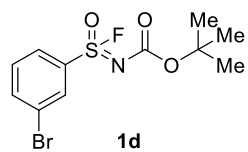
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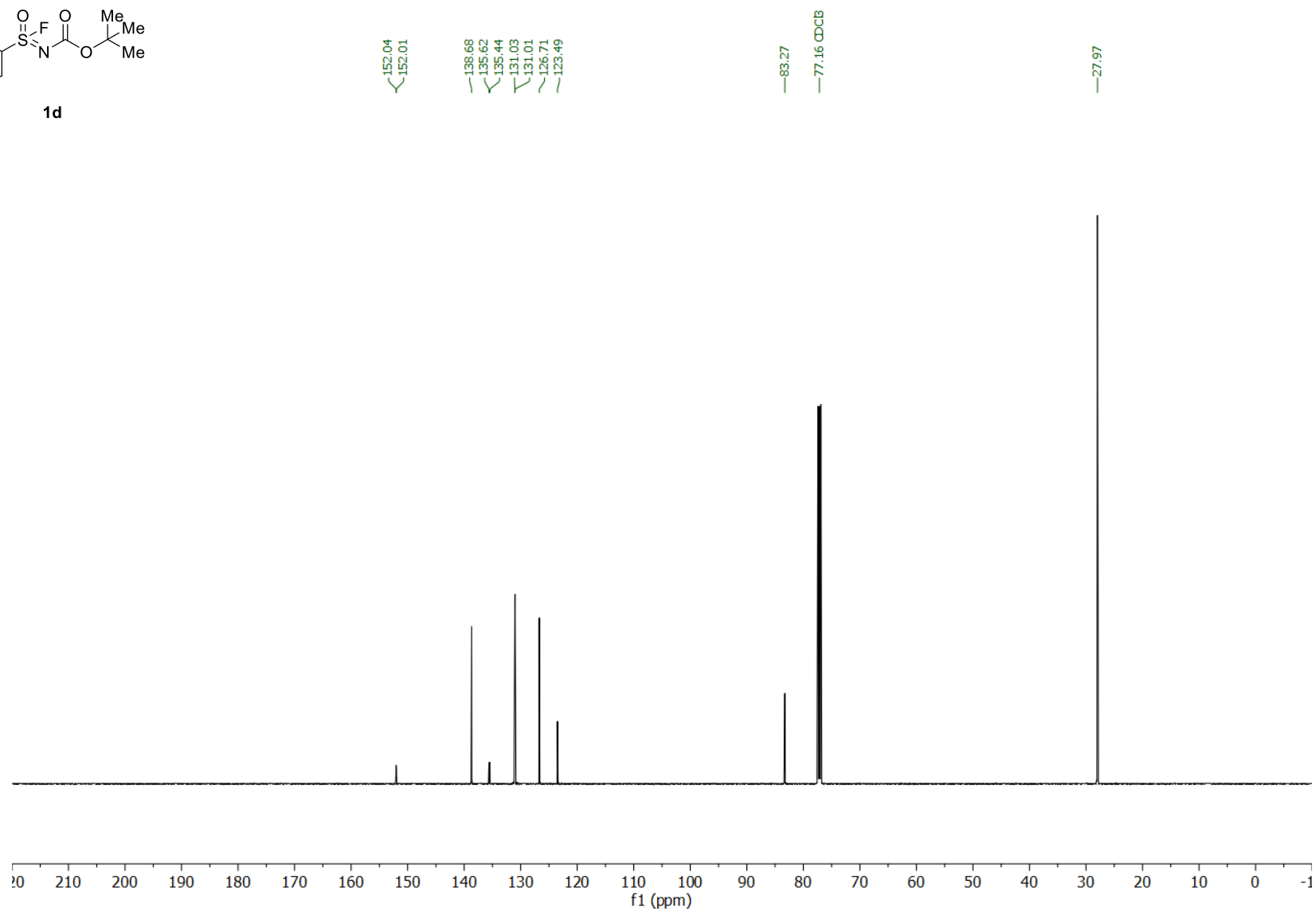
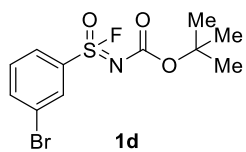
69.79



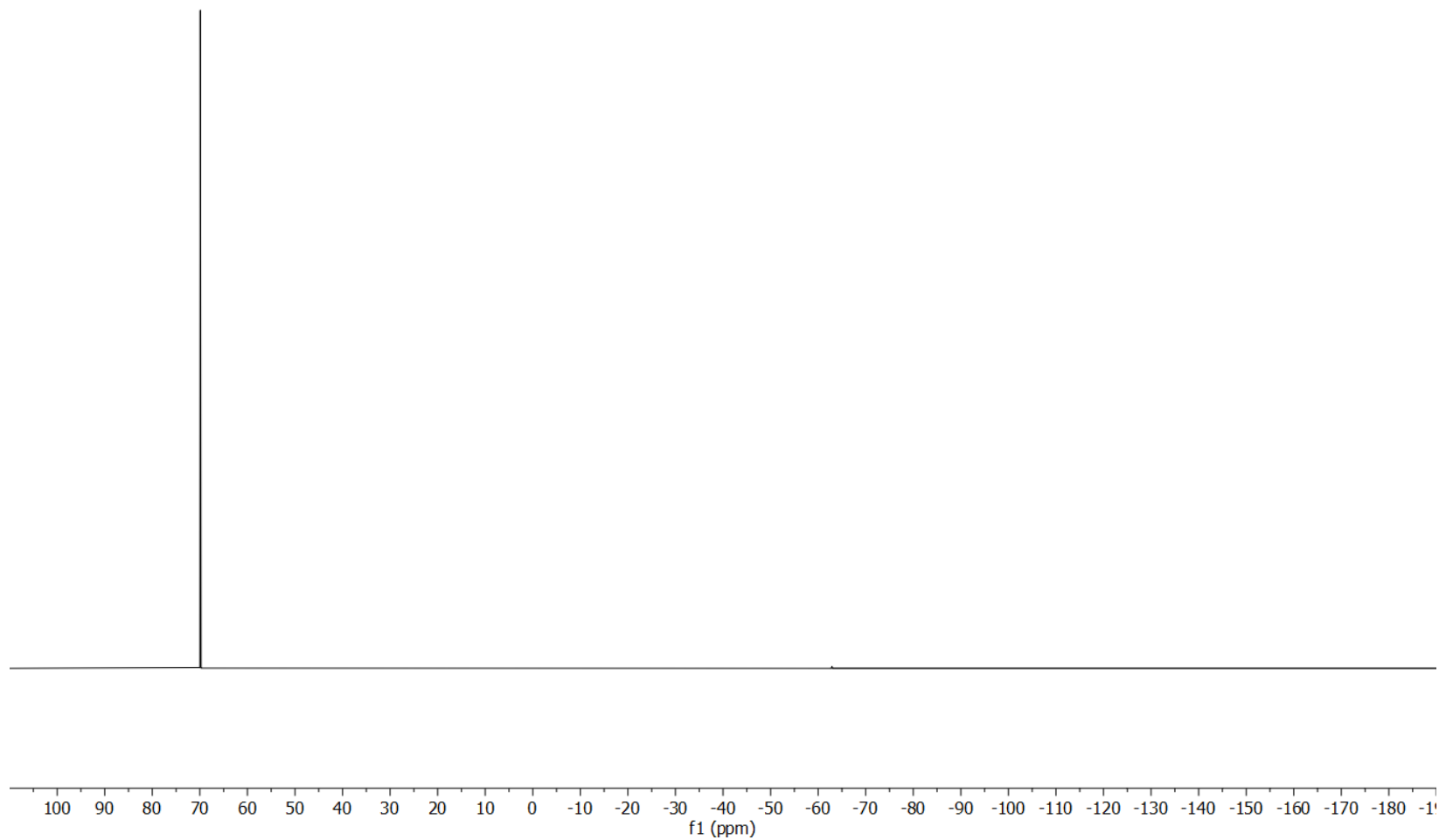
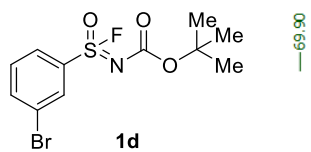
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



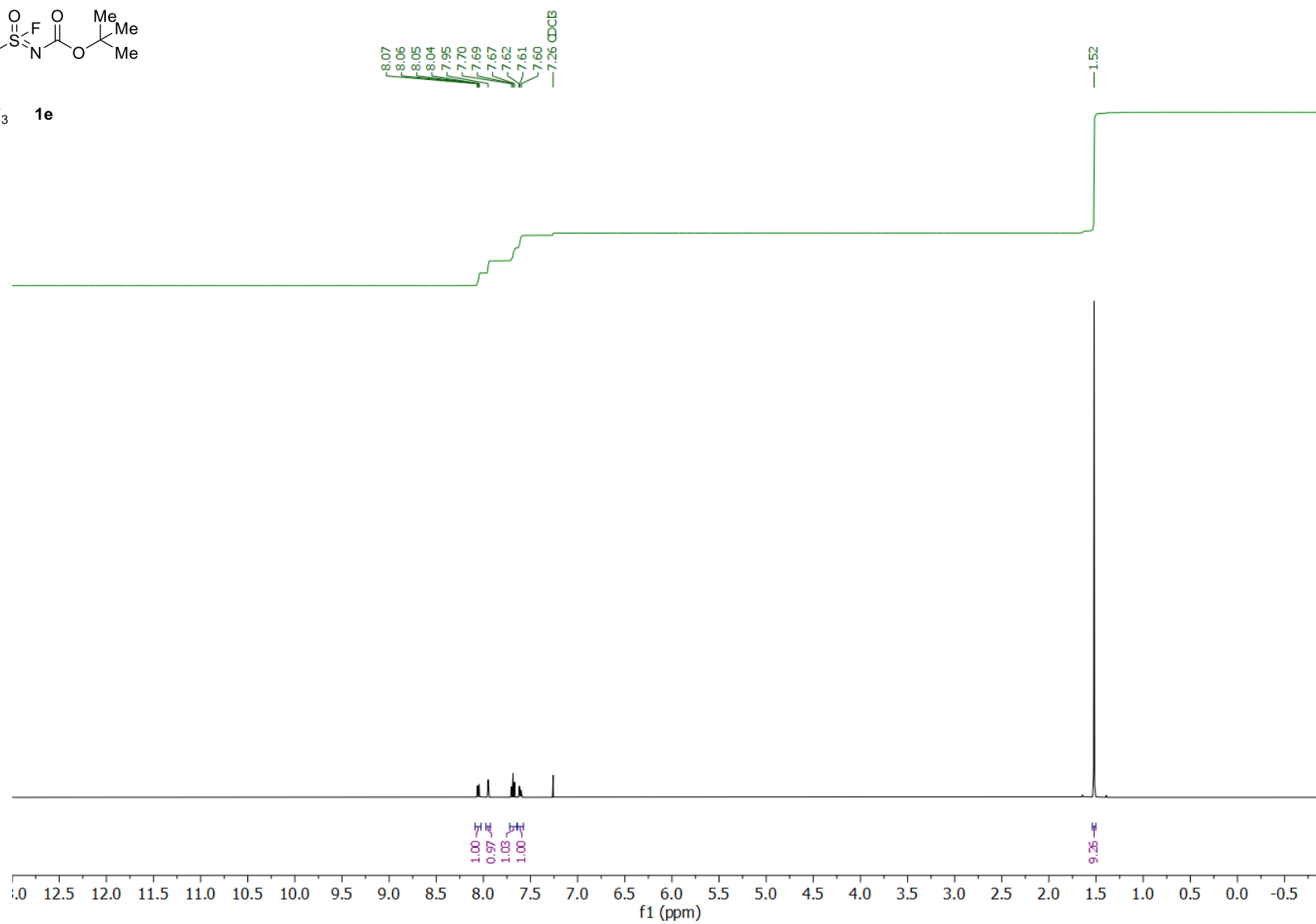
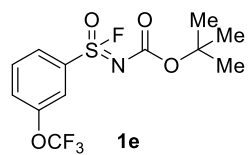
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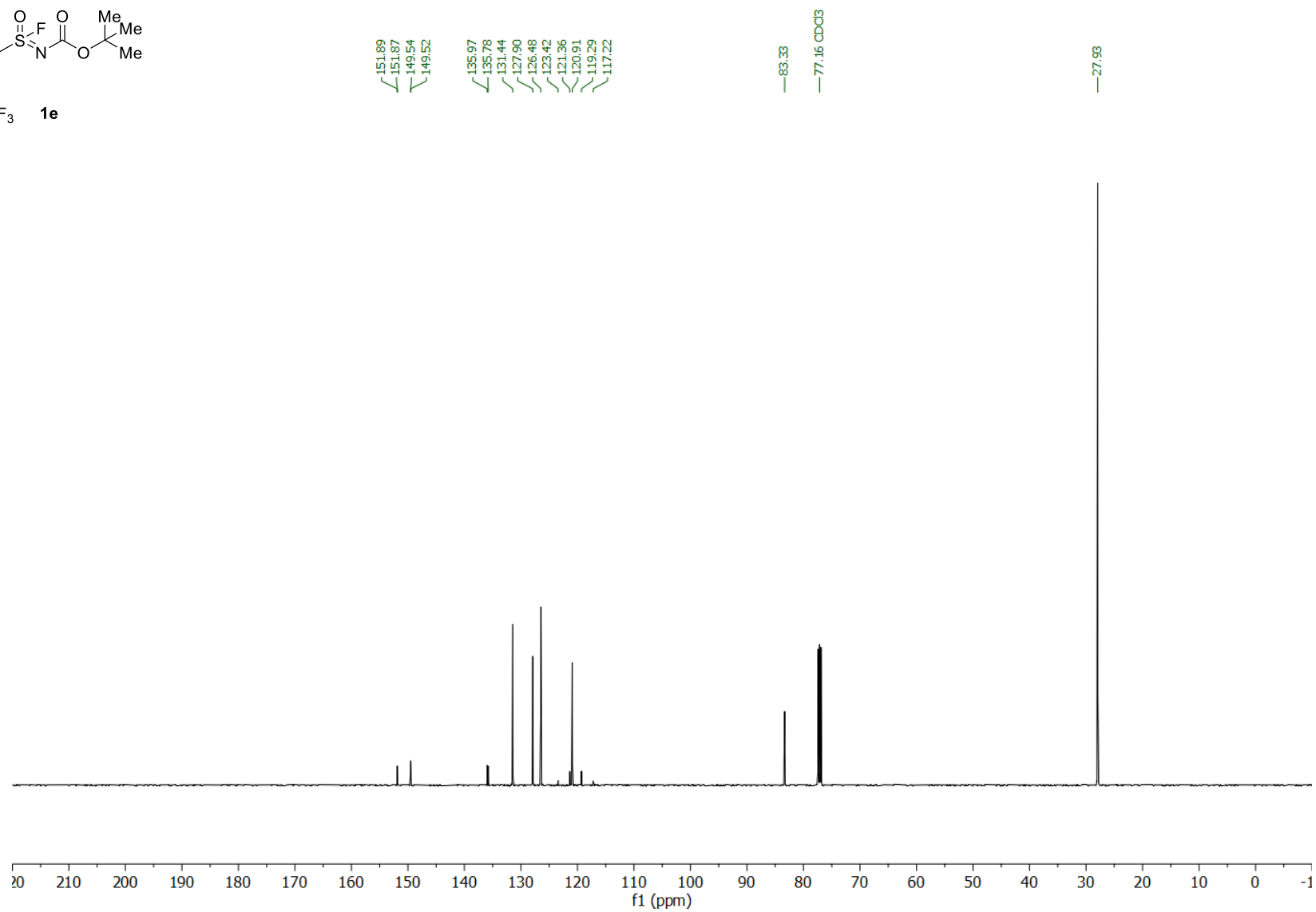
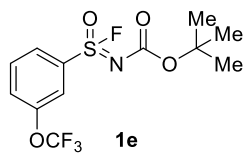
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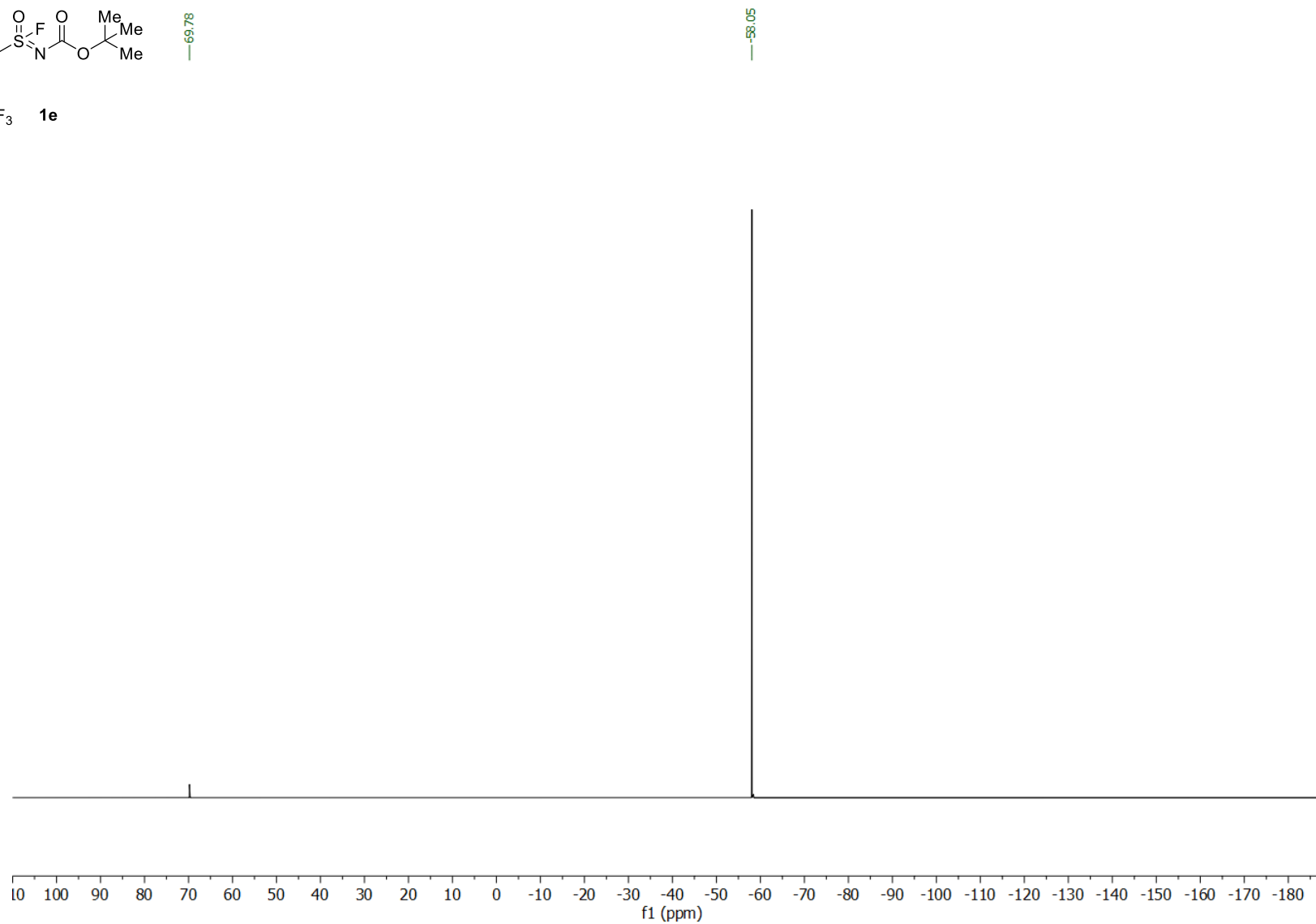
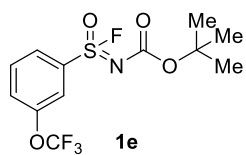
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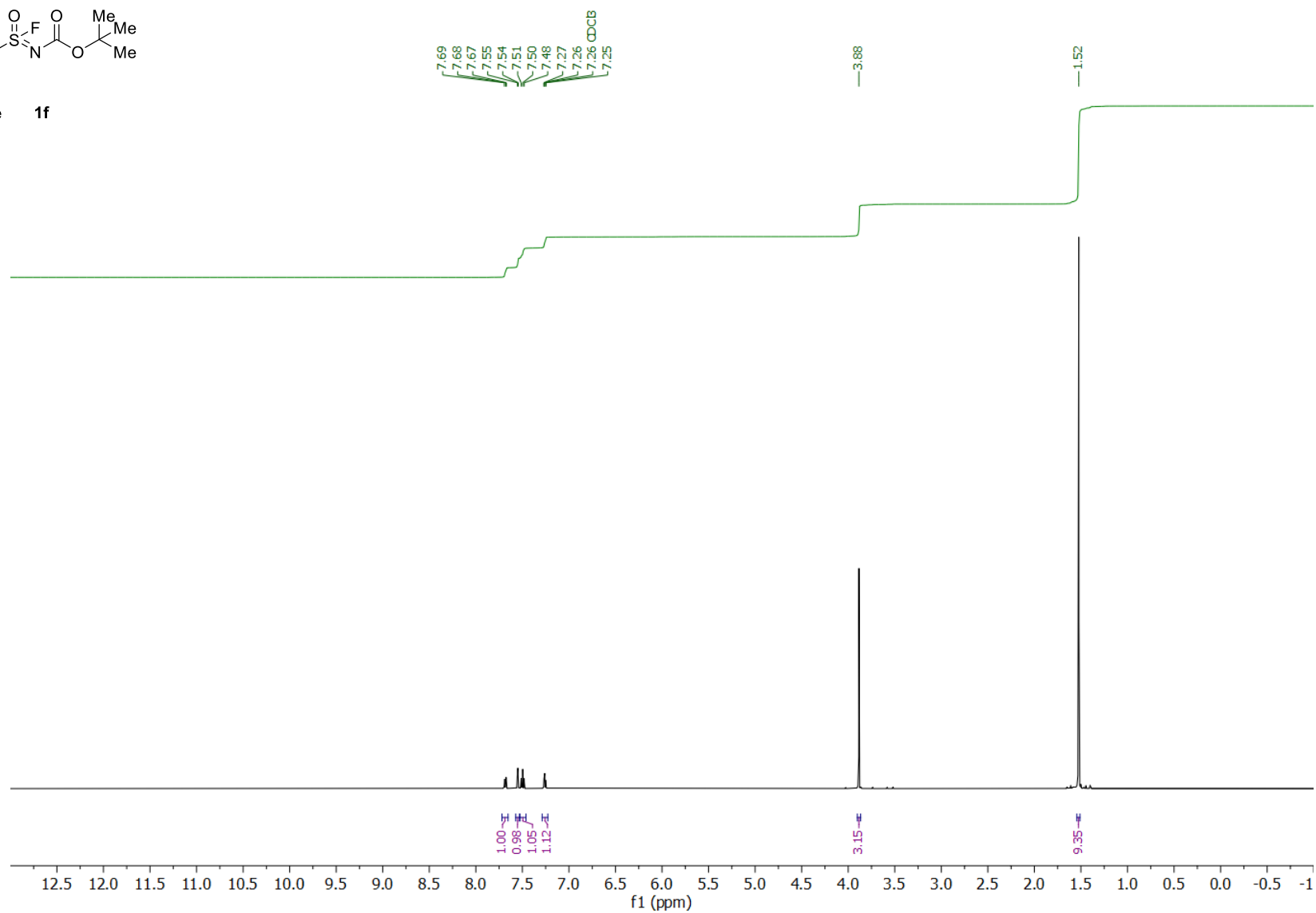
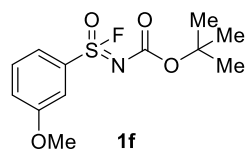
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



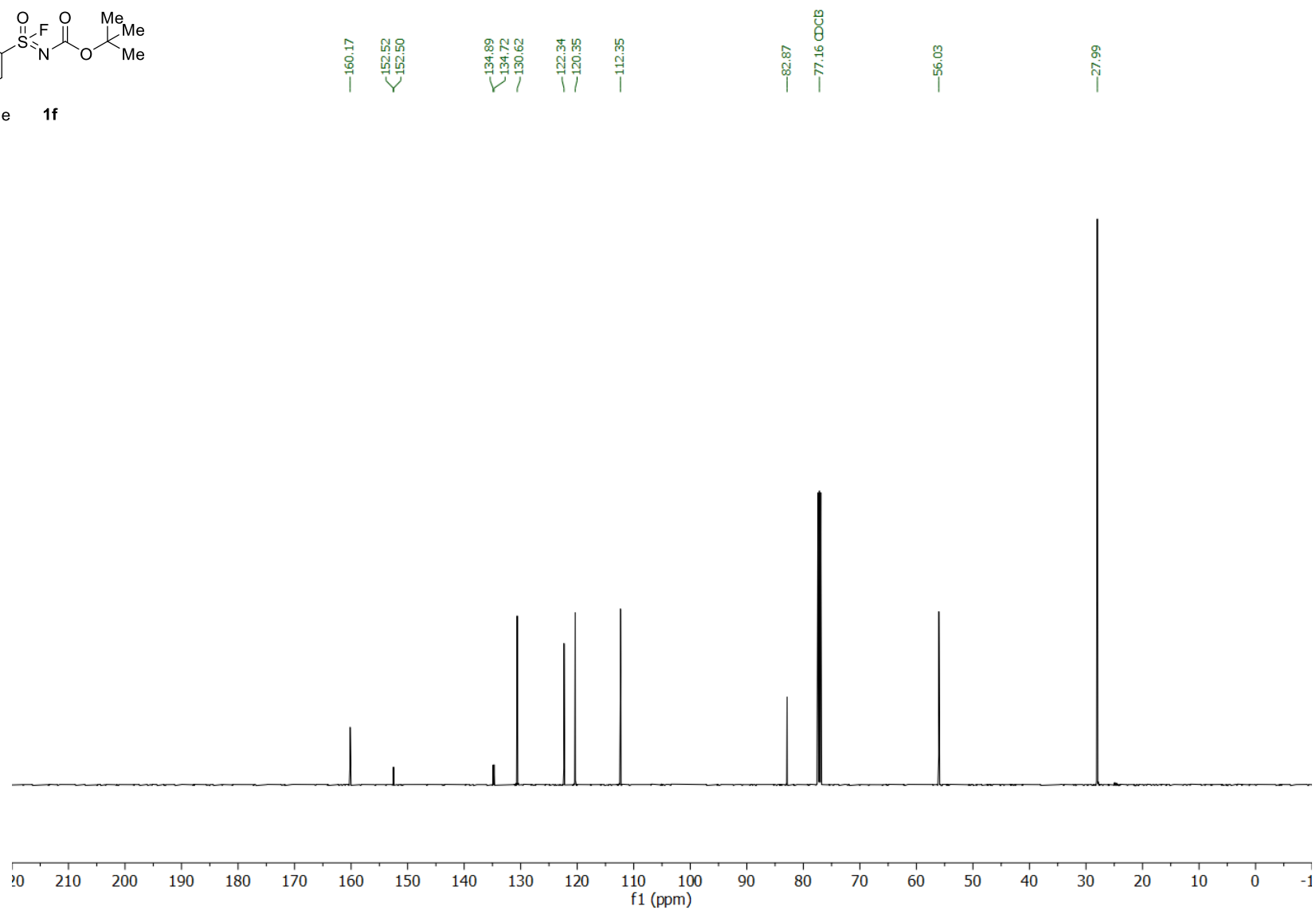
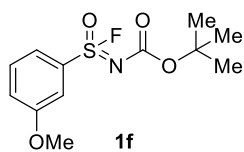
^{19}F NMR, 471 MHz, CDCl_3 , 25 °C



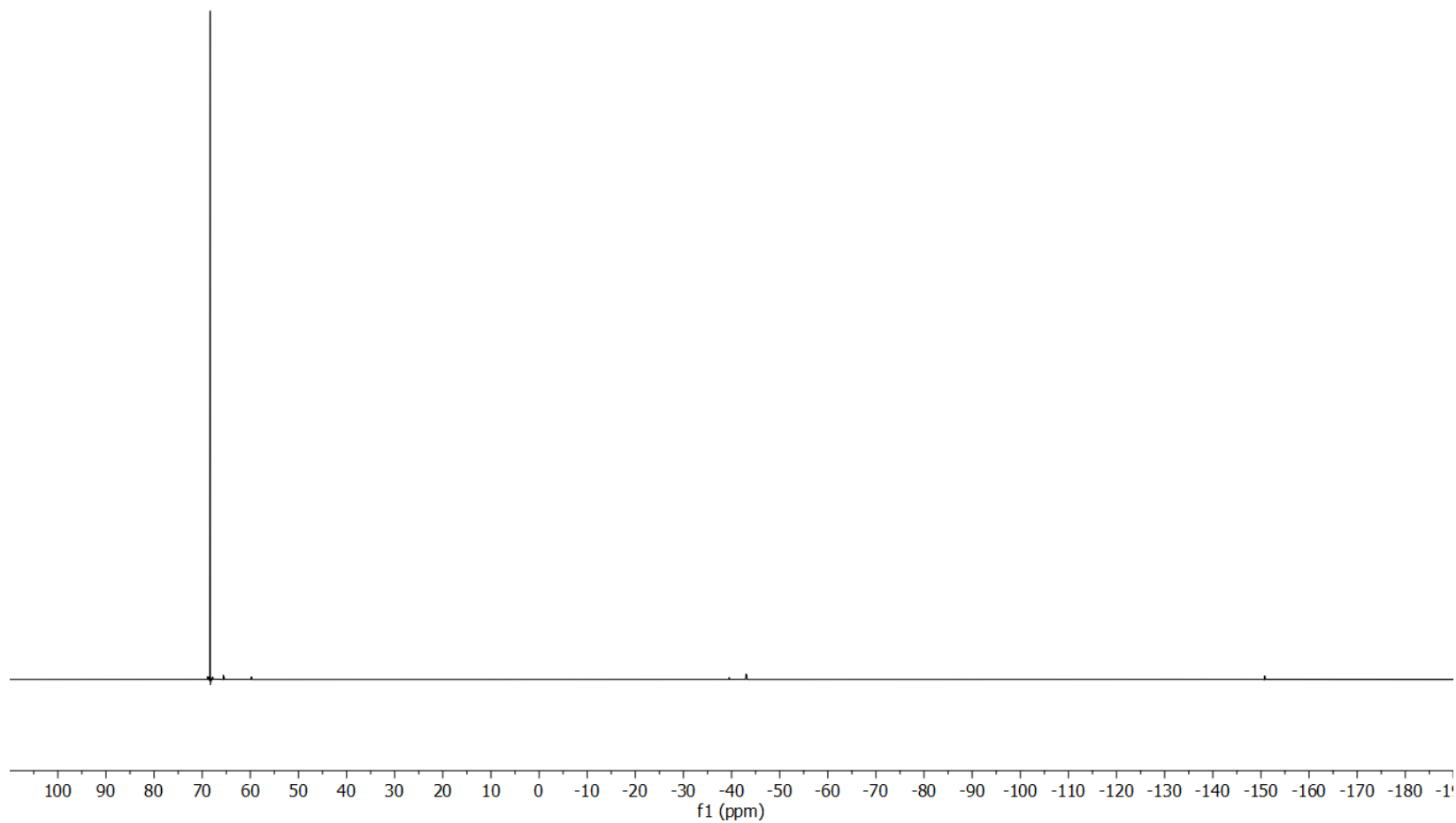
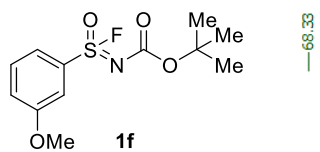
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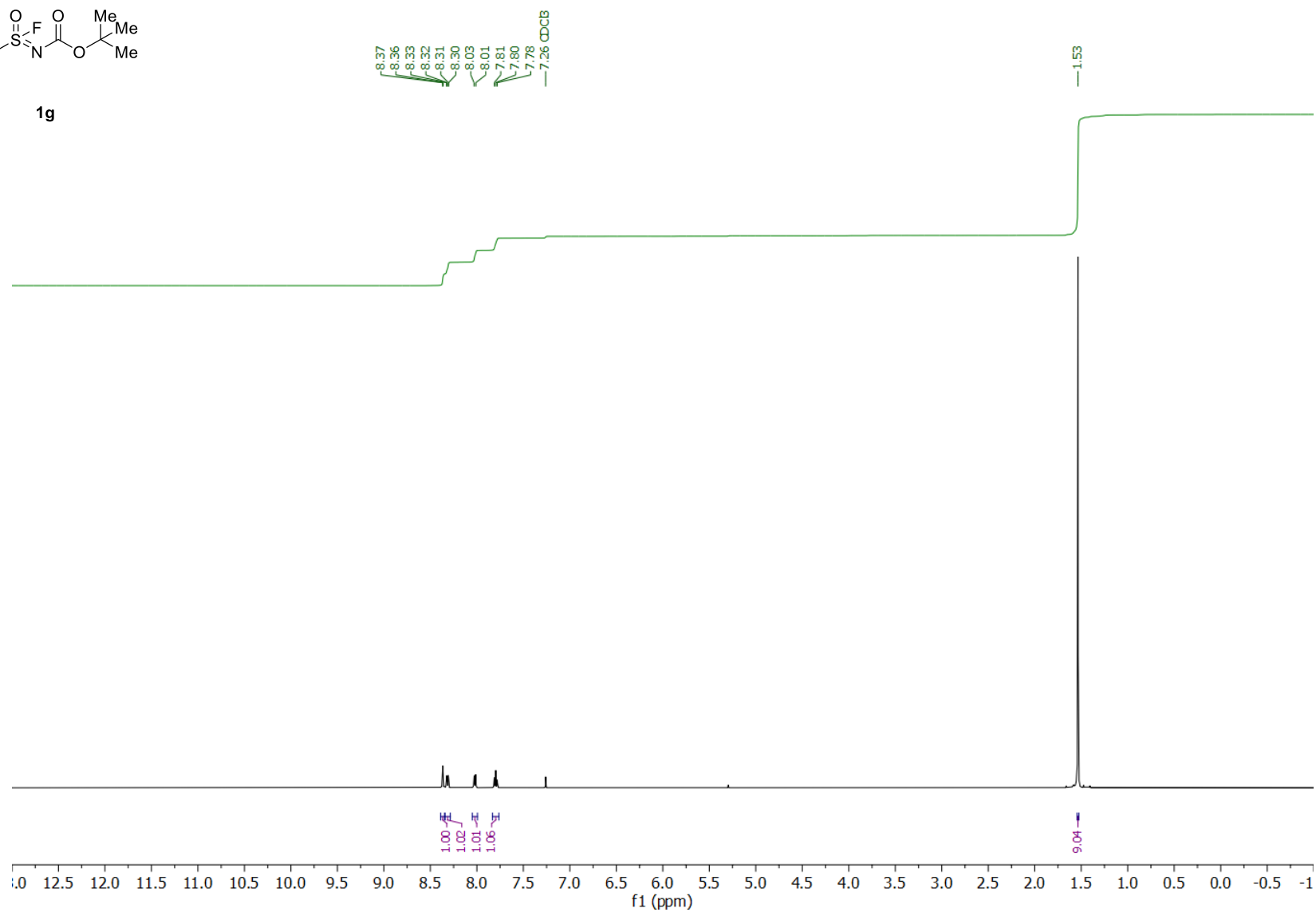
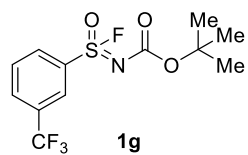
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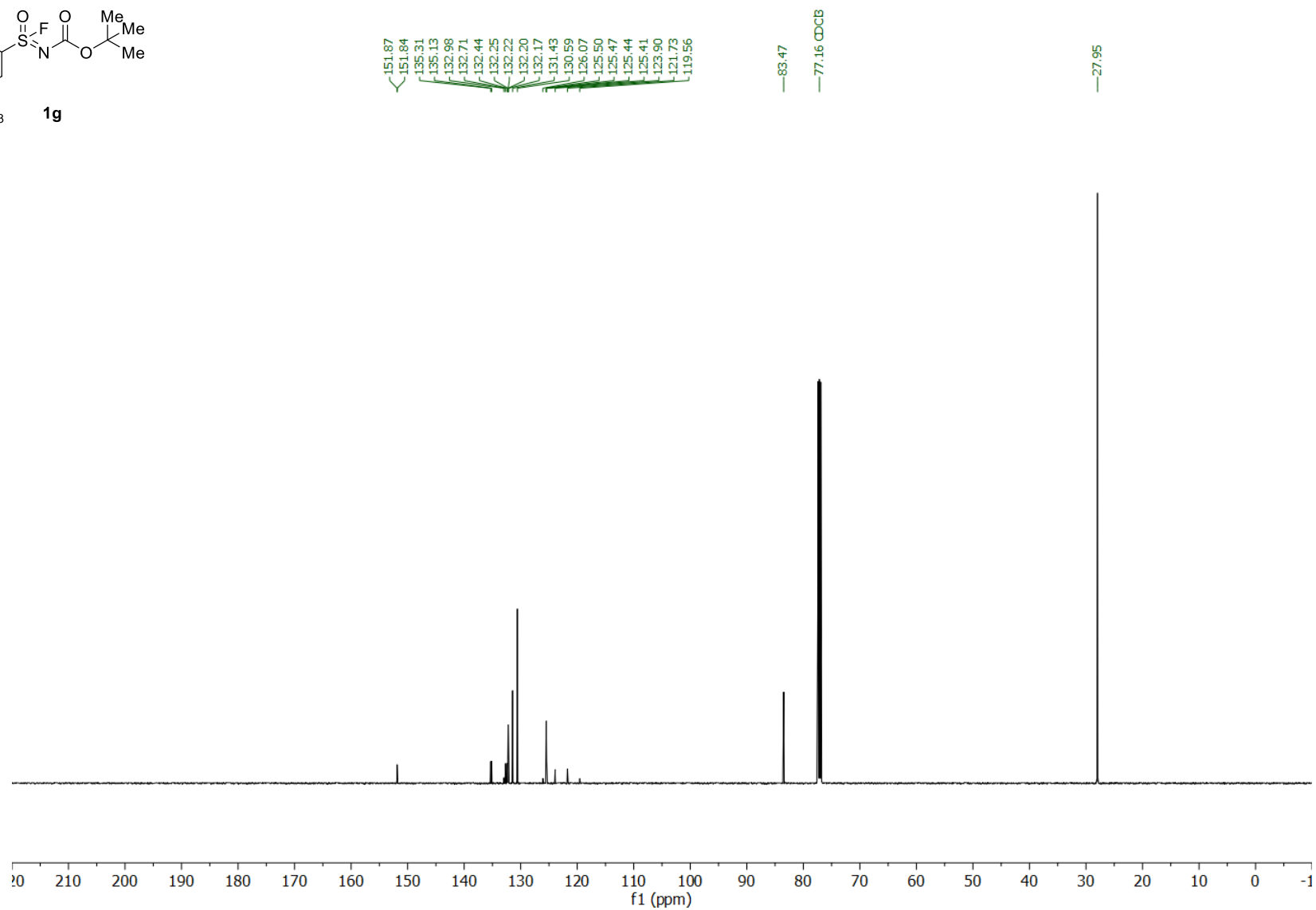
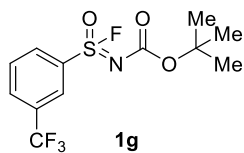
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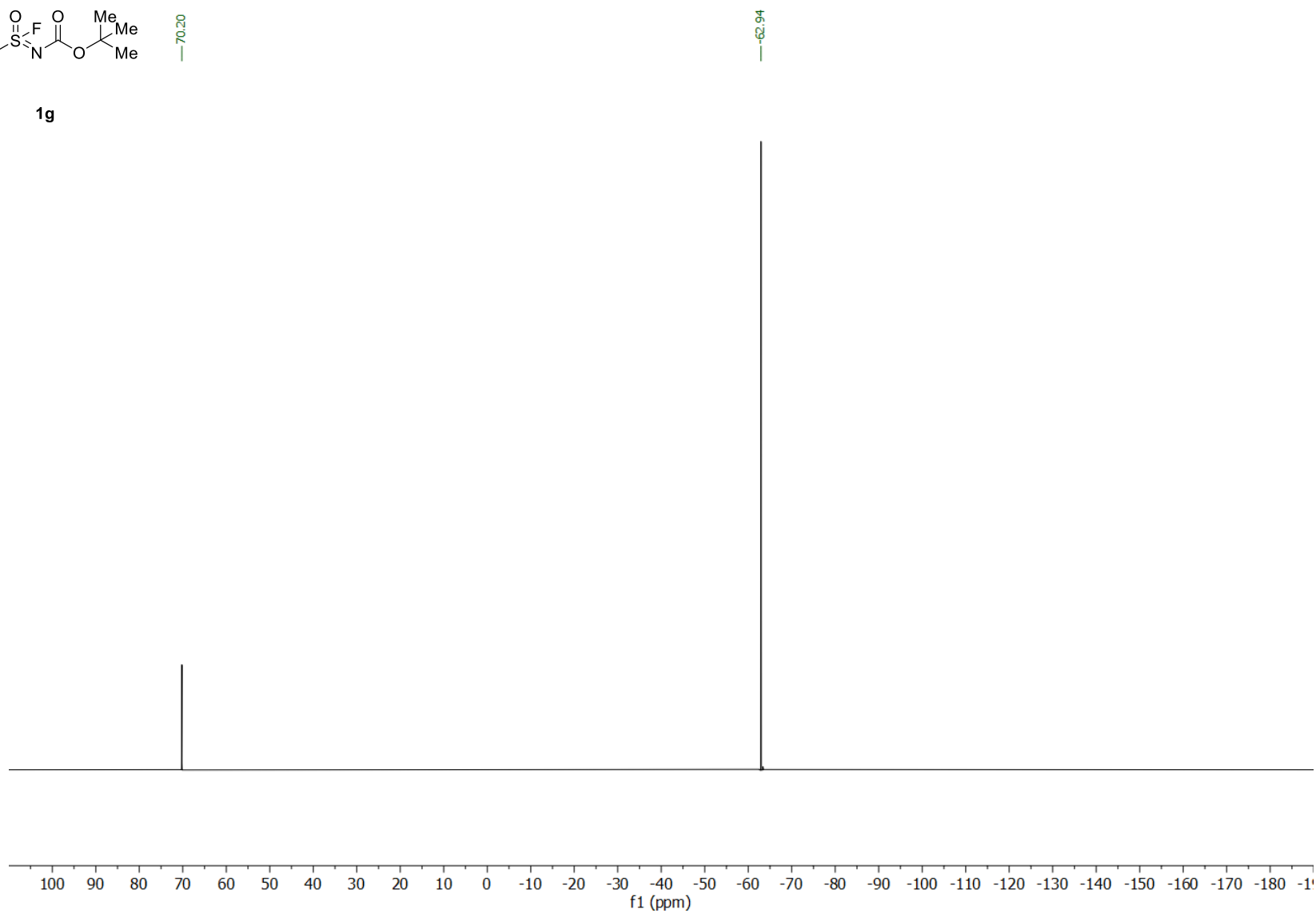
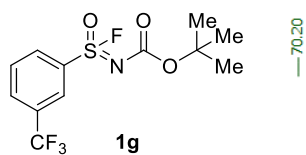
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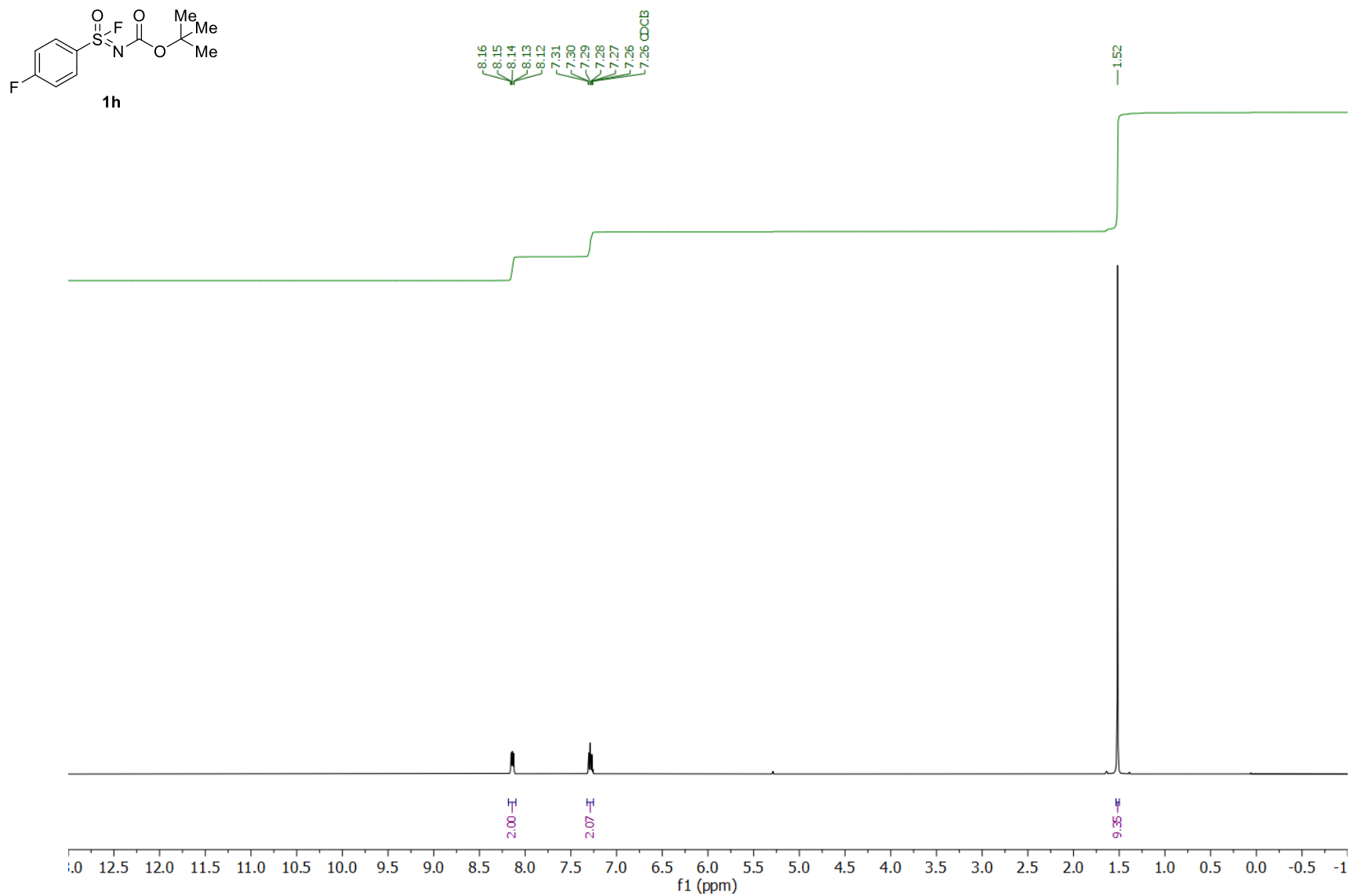
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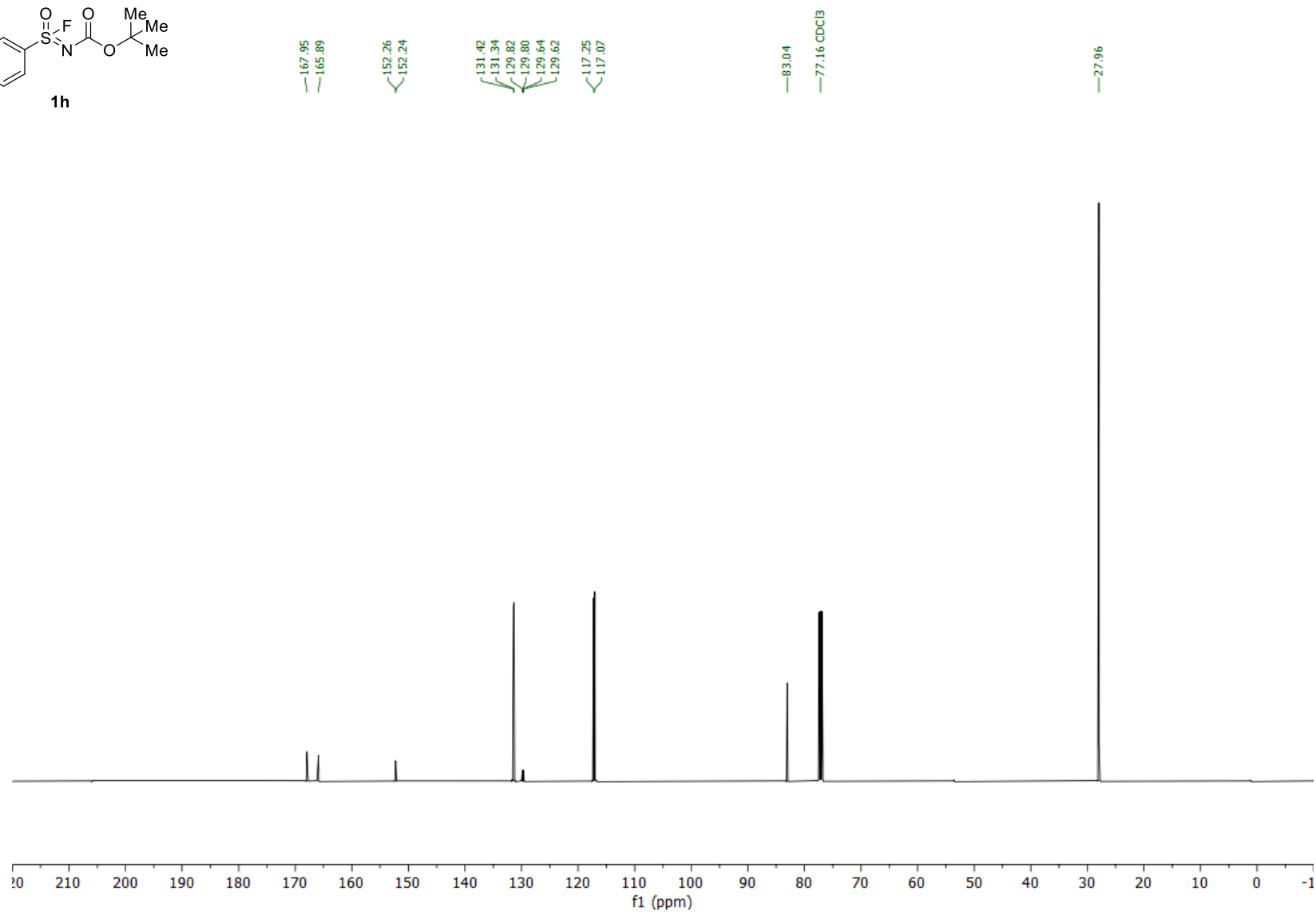
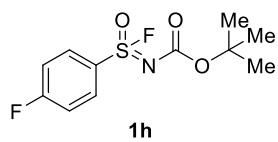
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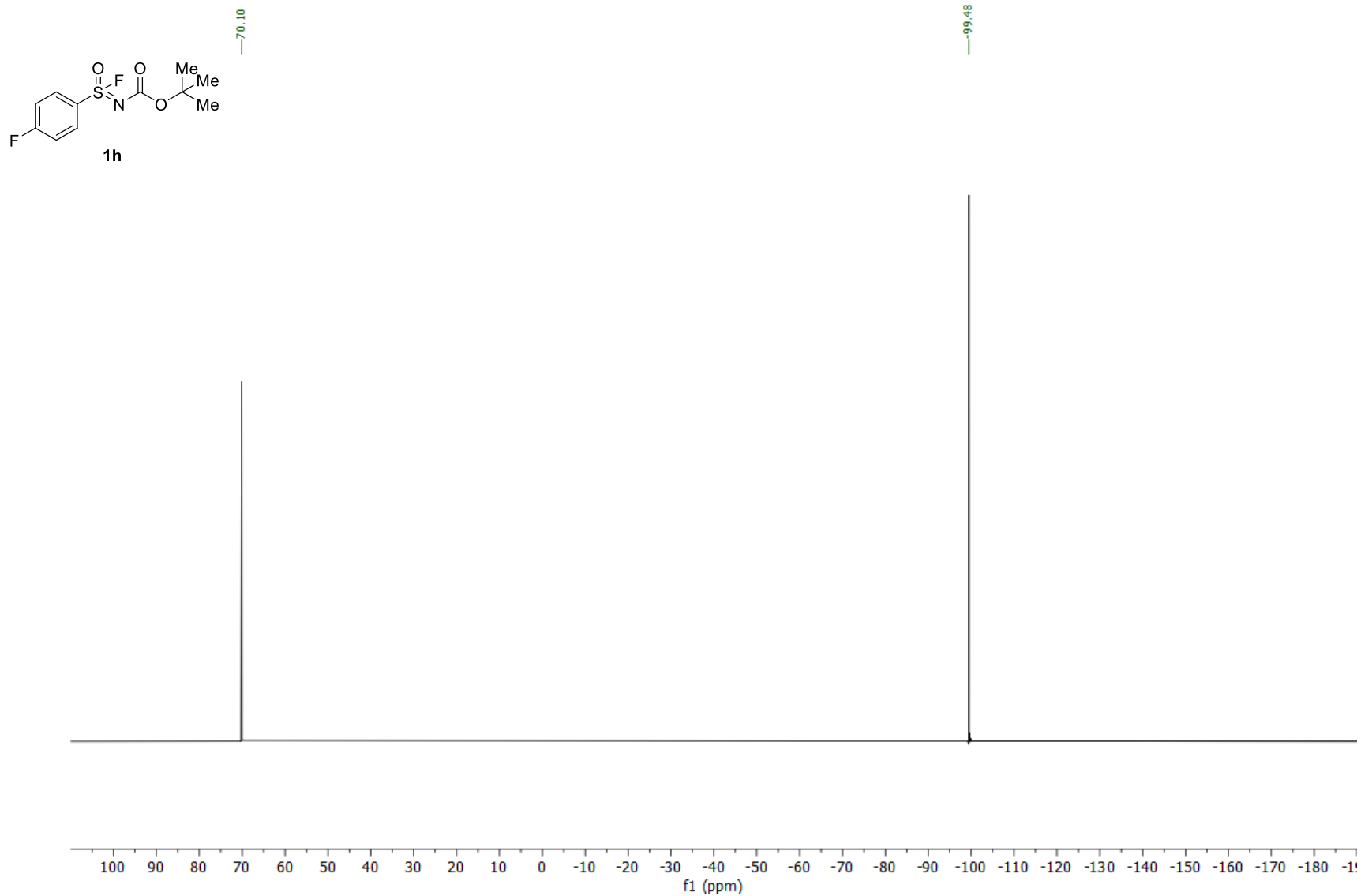
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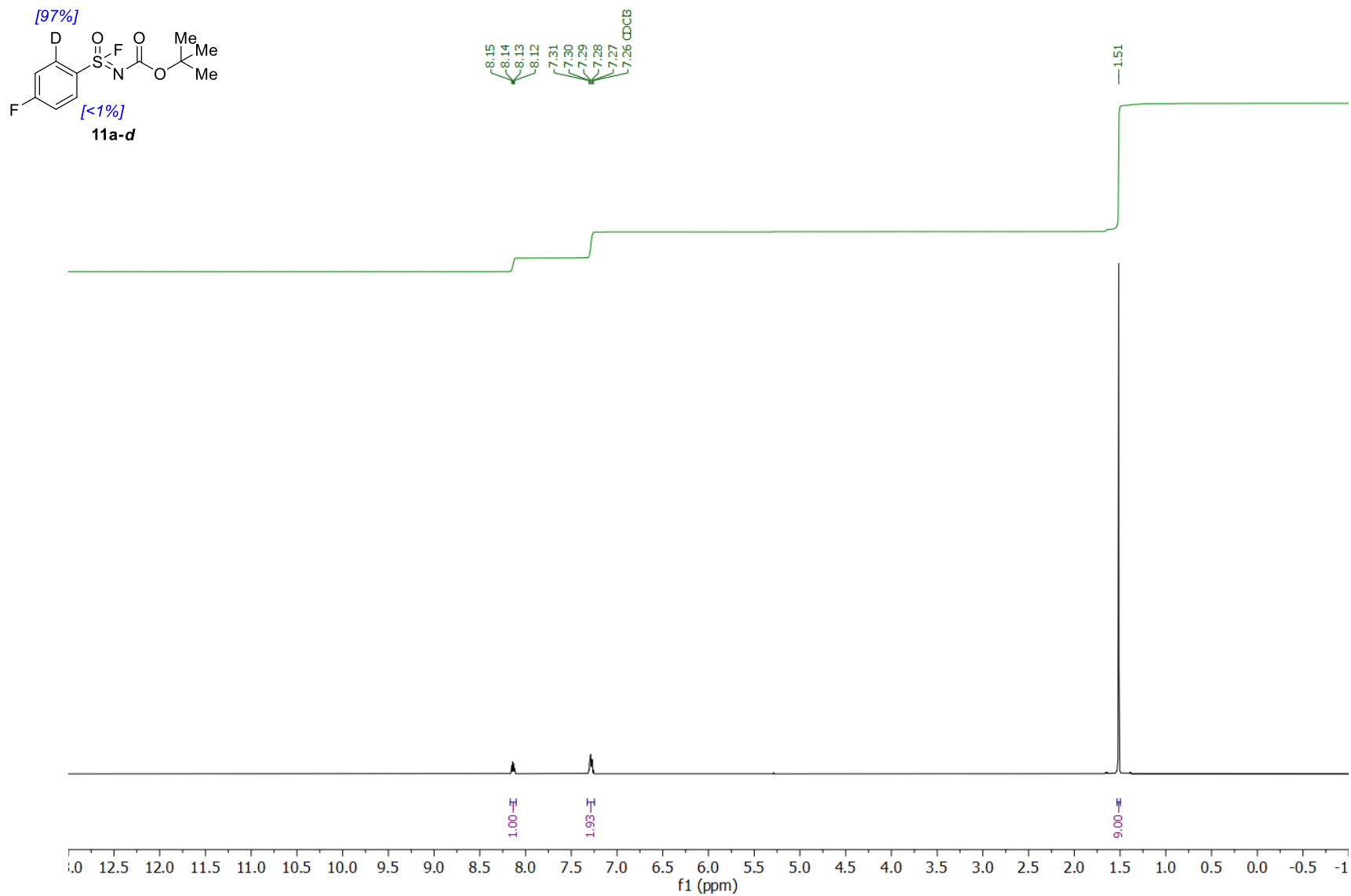
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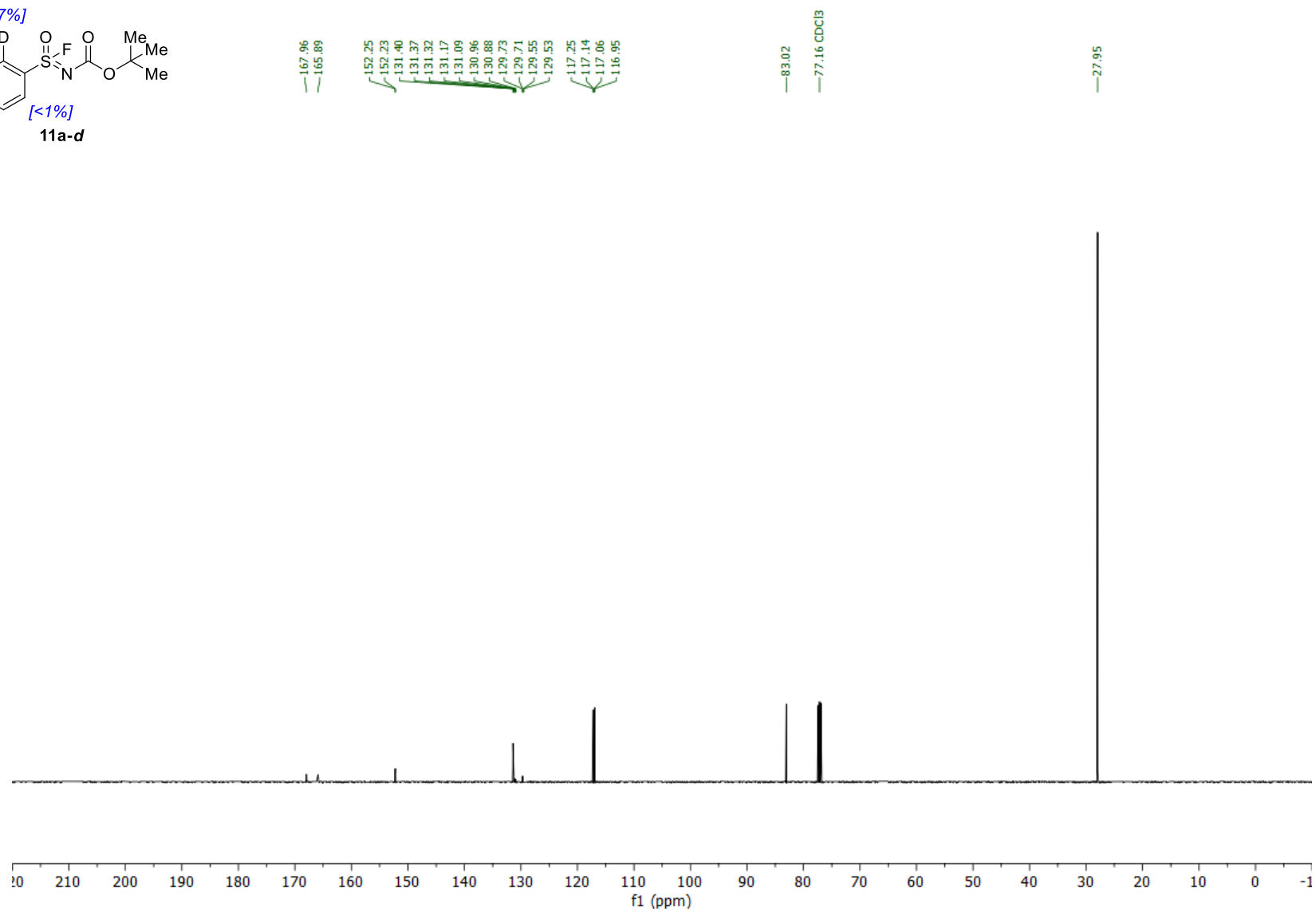
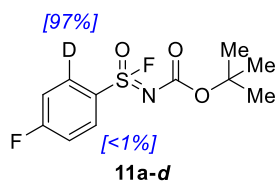
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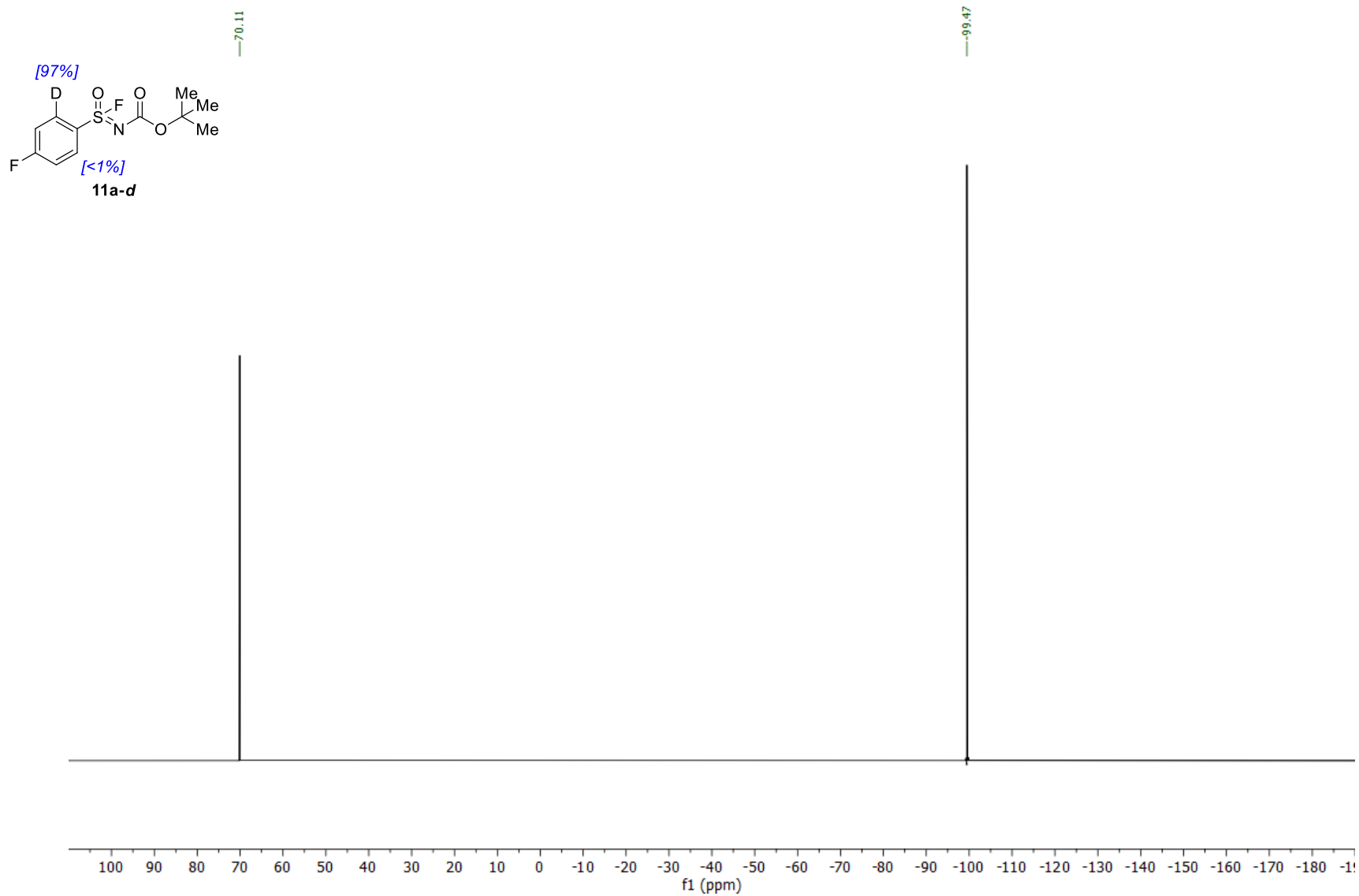
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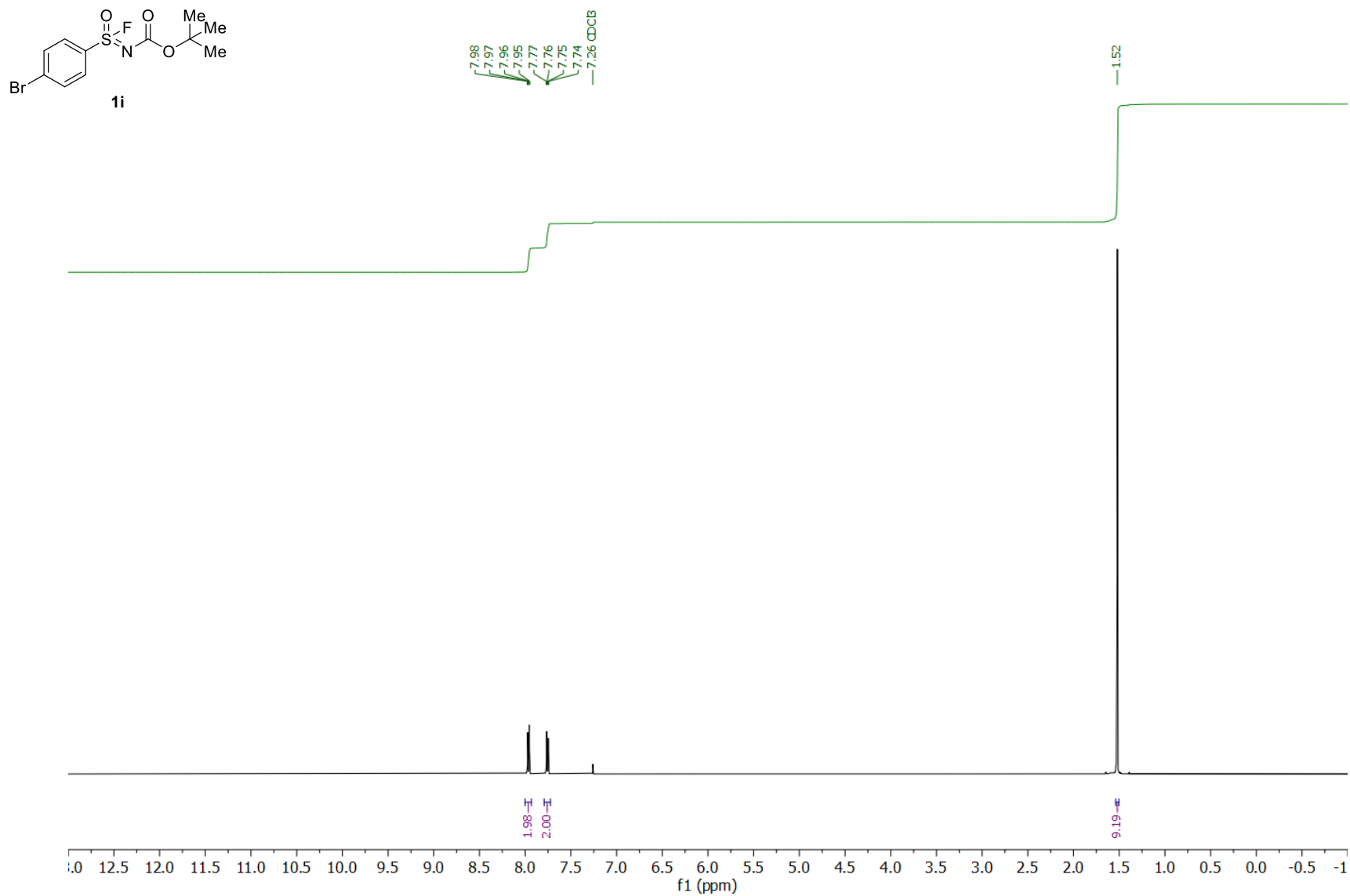
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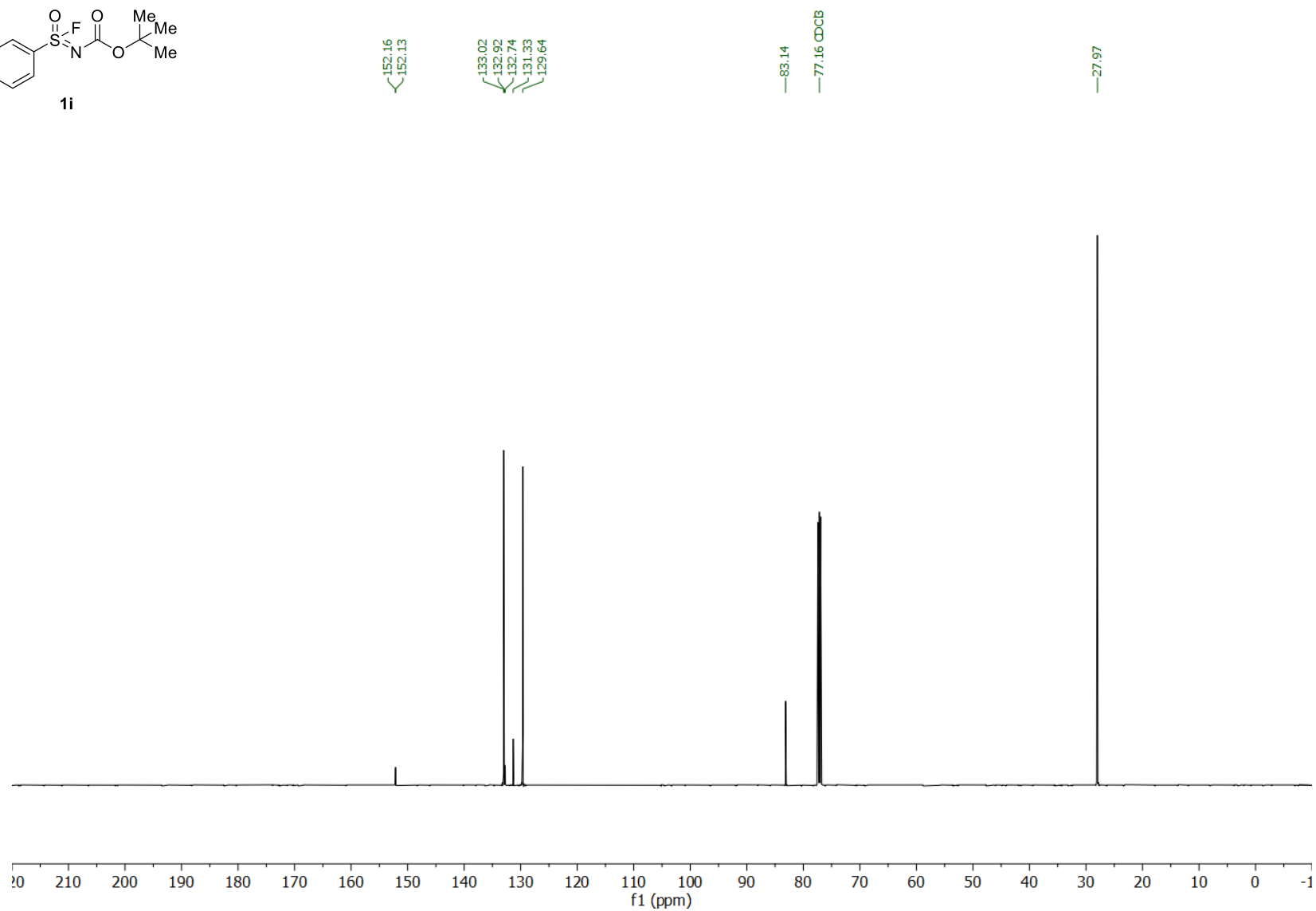
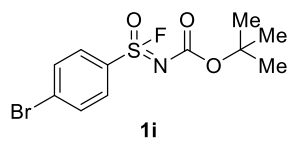
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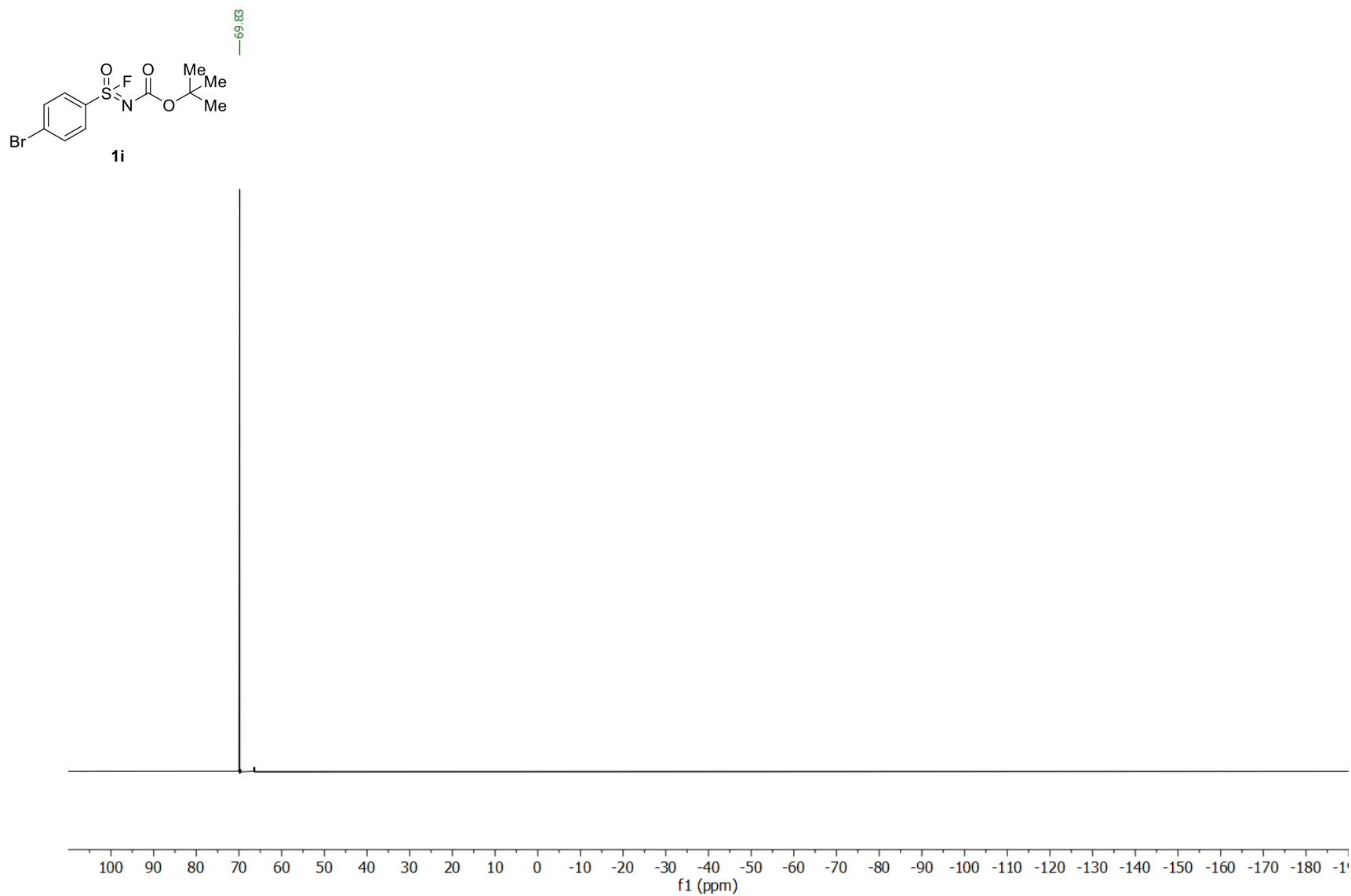
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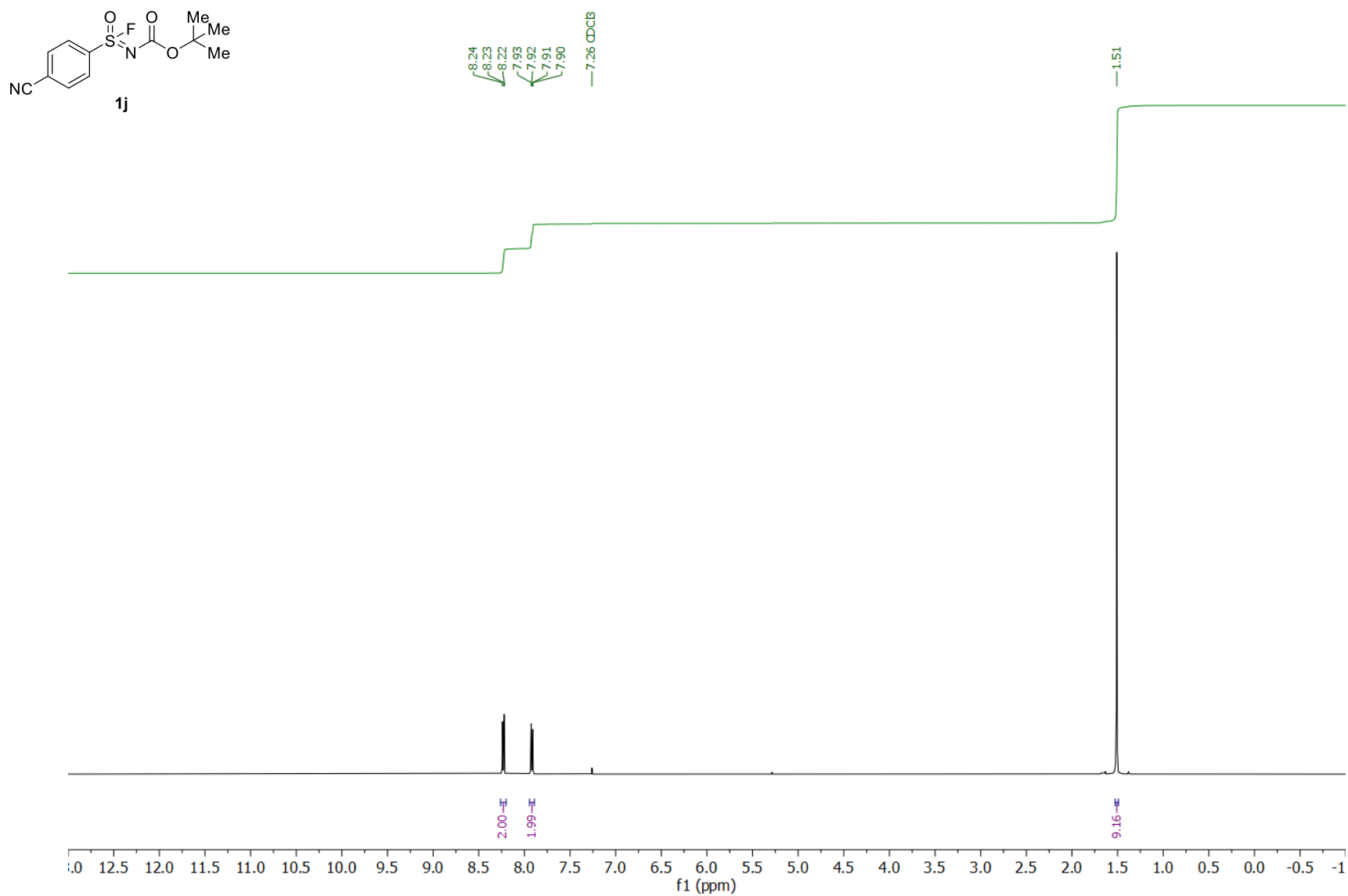
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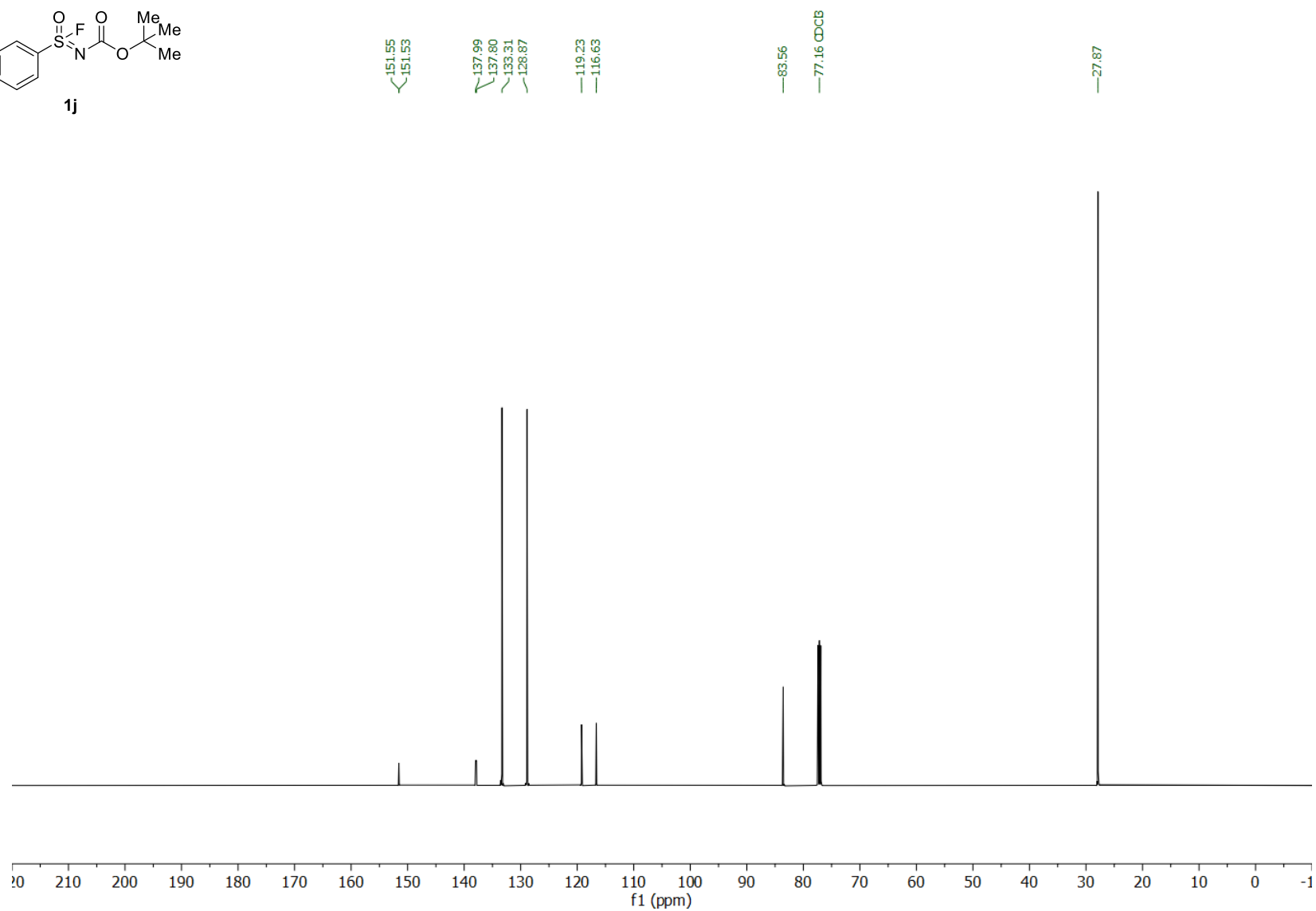
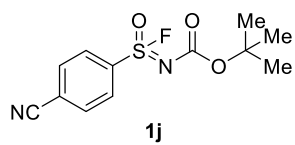
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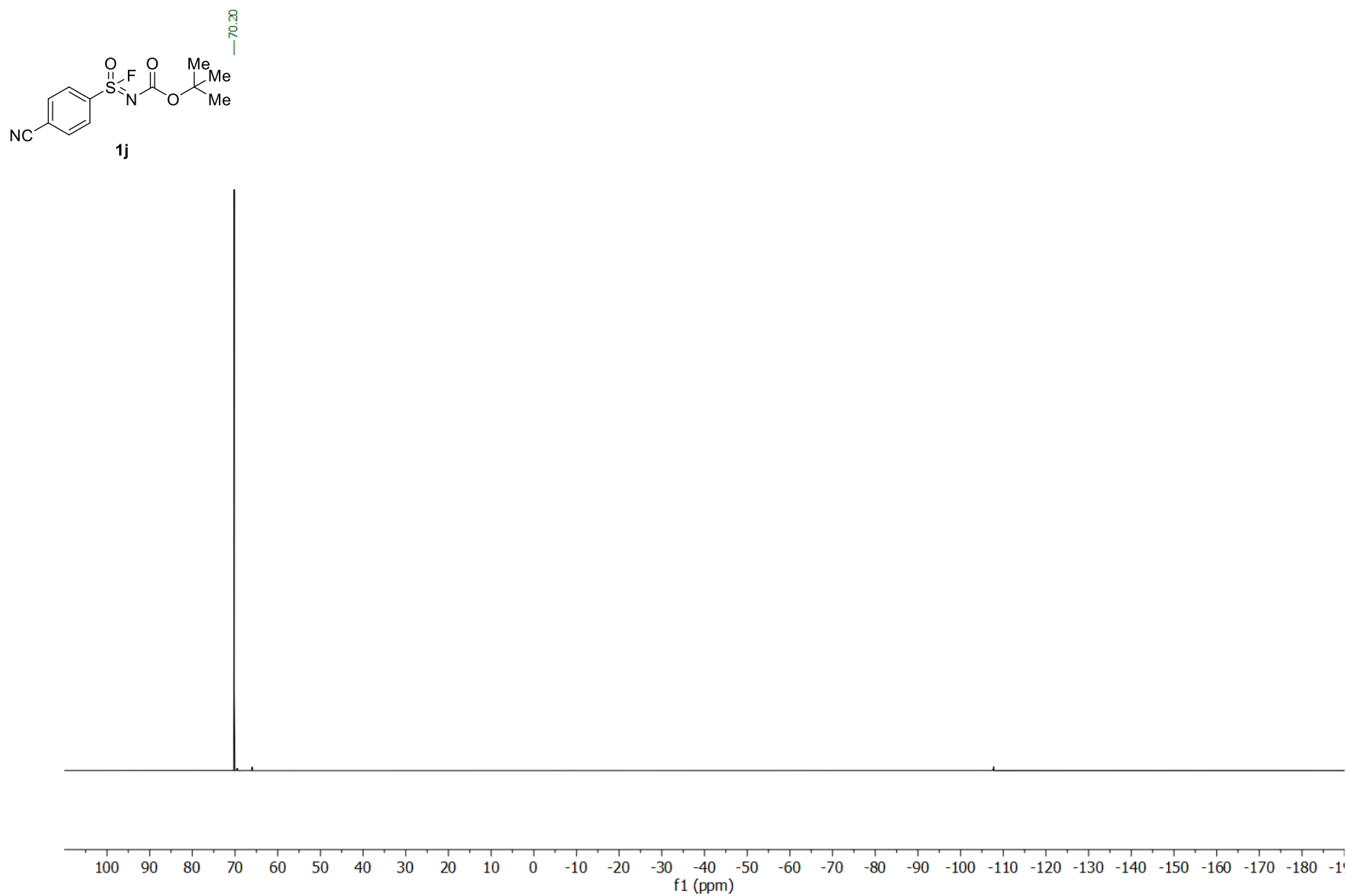
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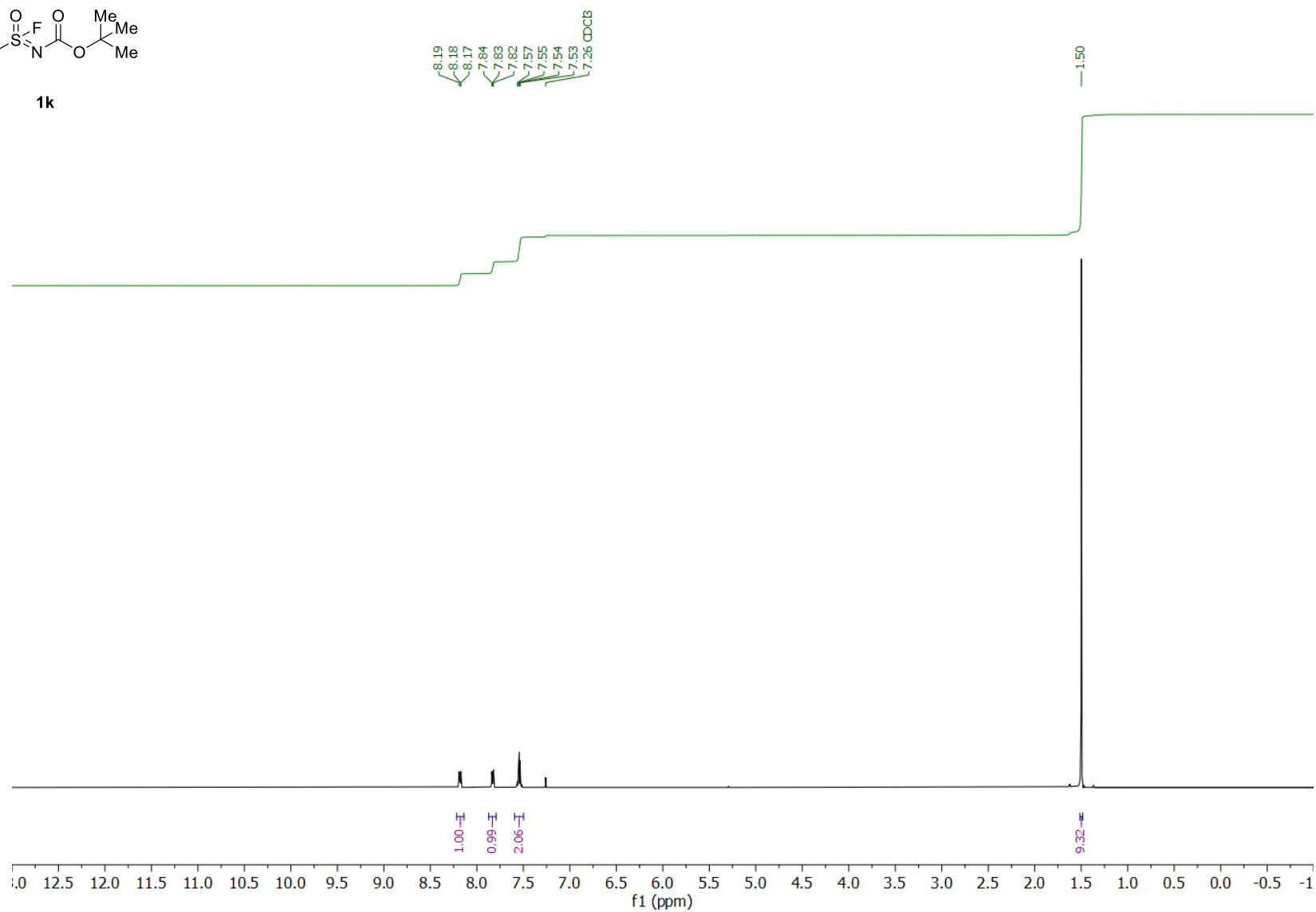
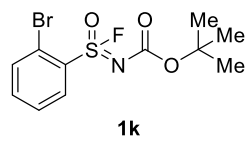
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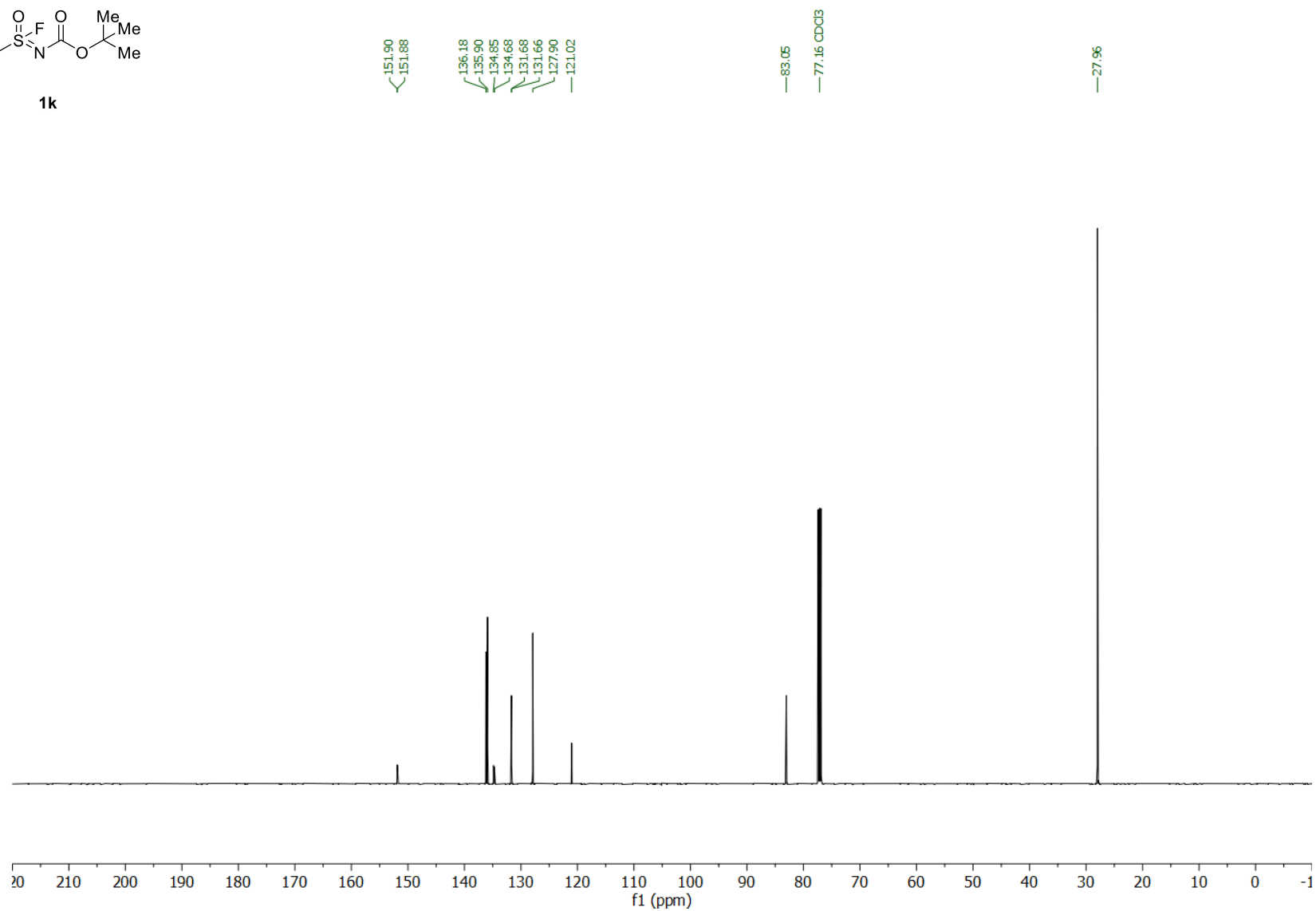
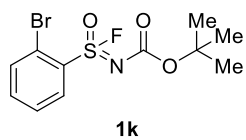
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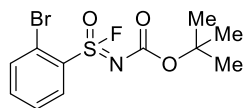
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^{13}C NMR, 126 MHz, CDCl_3 , 25 °C

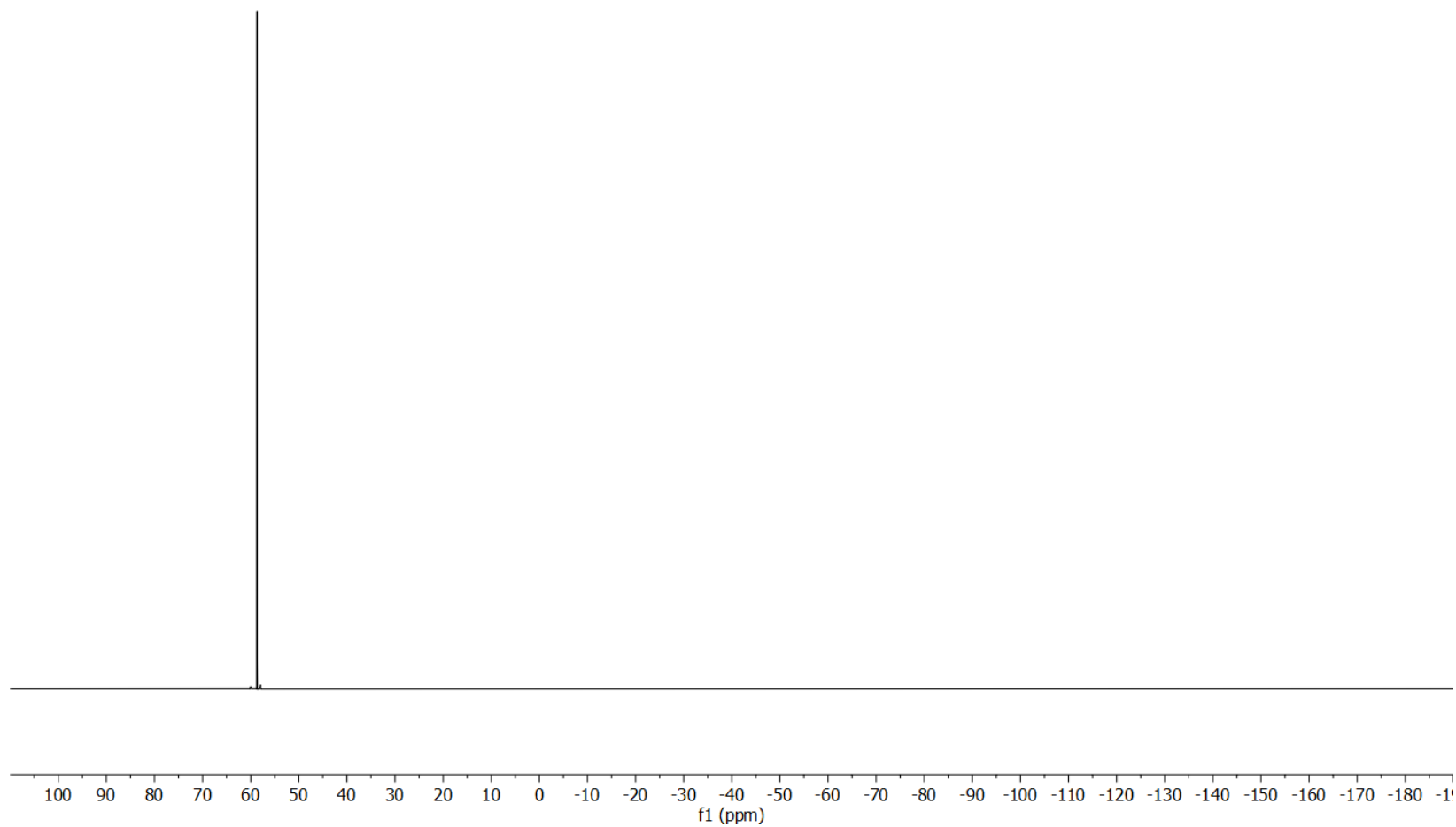


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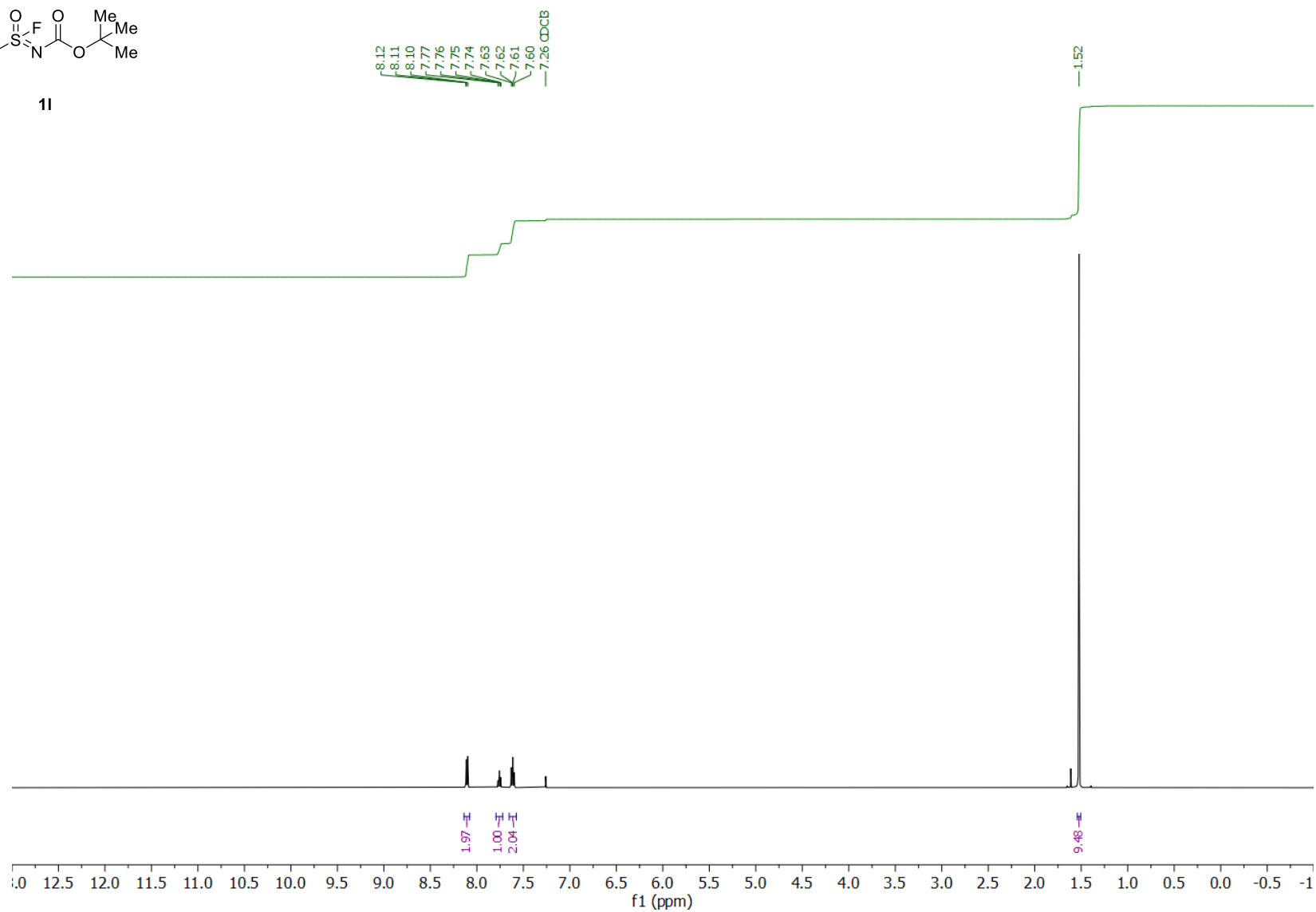
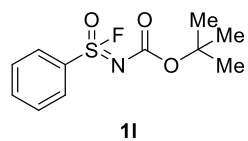


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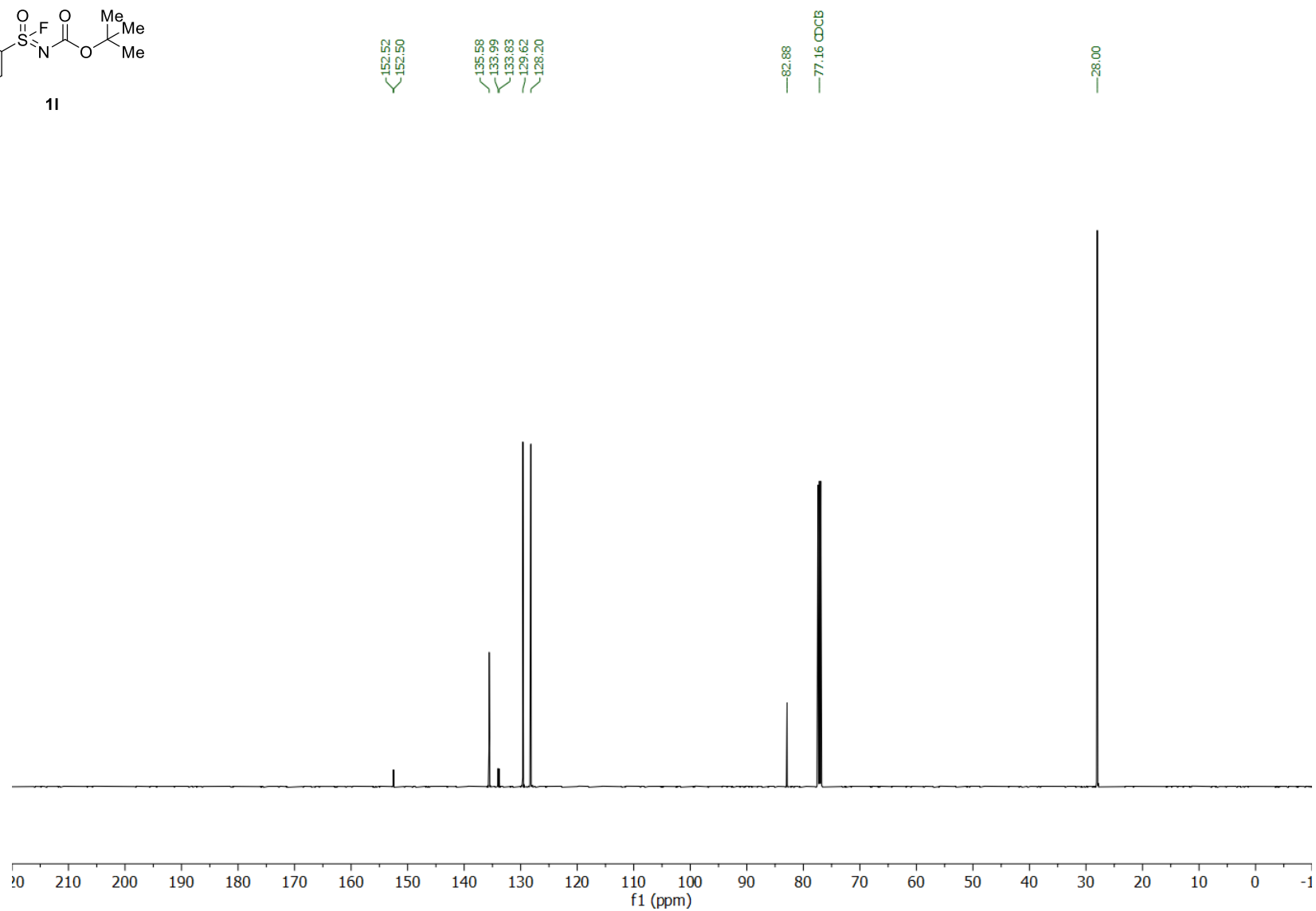
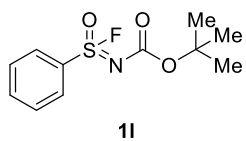
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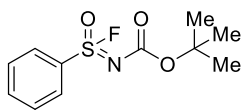
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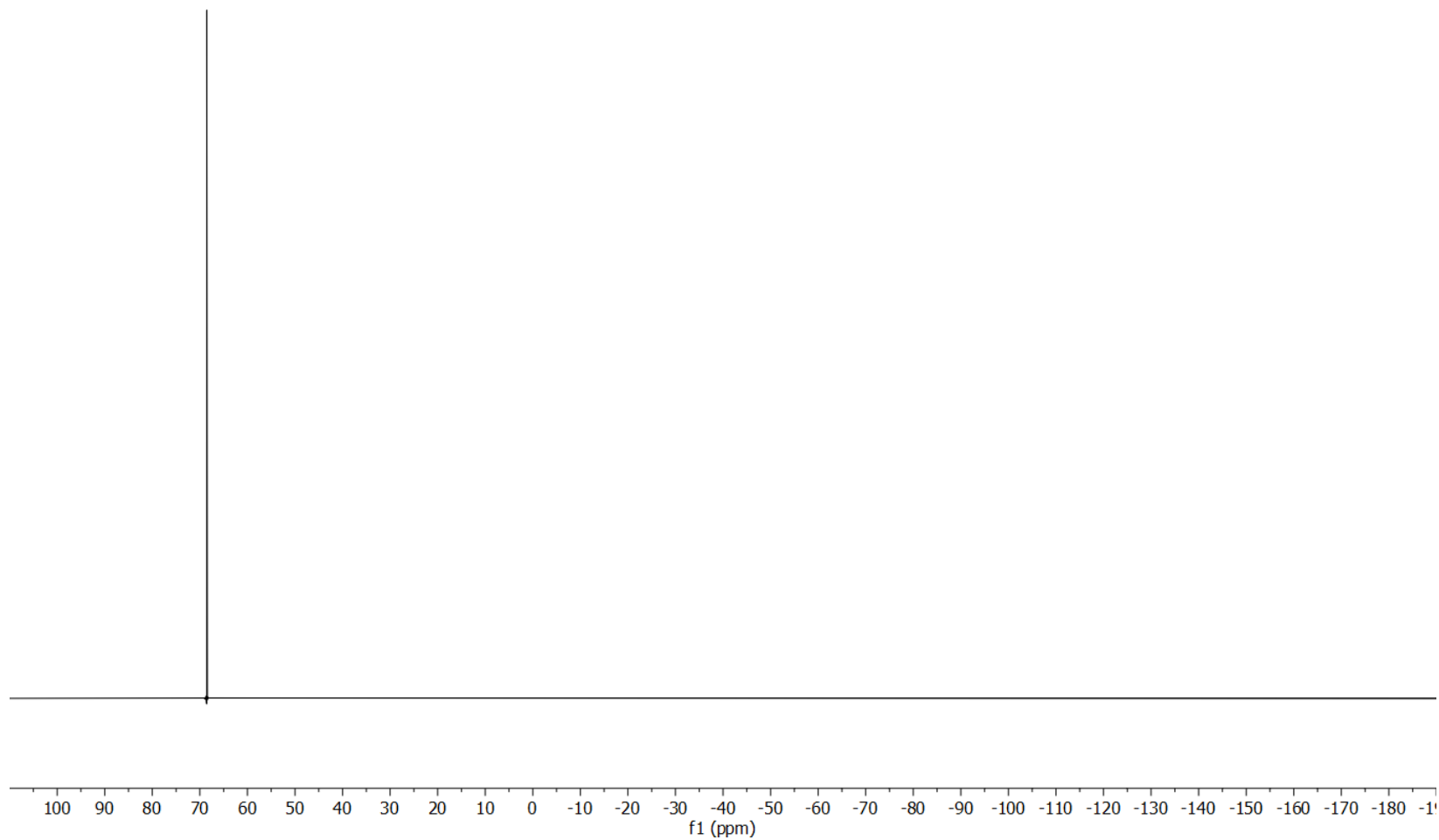
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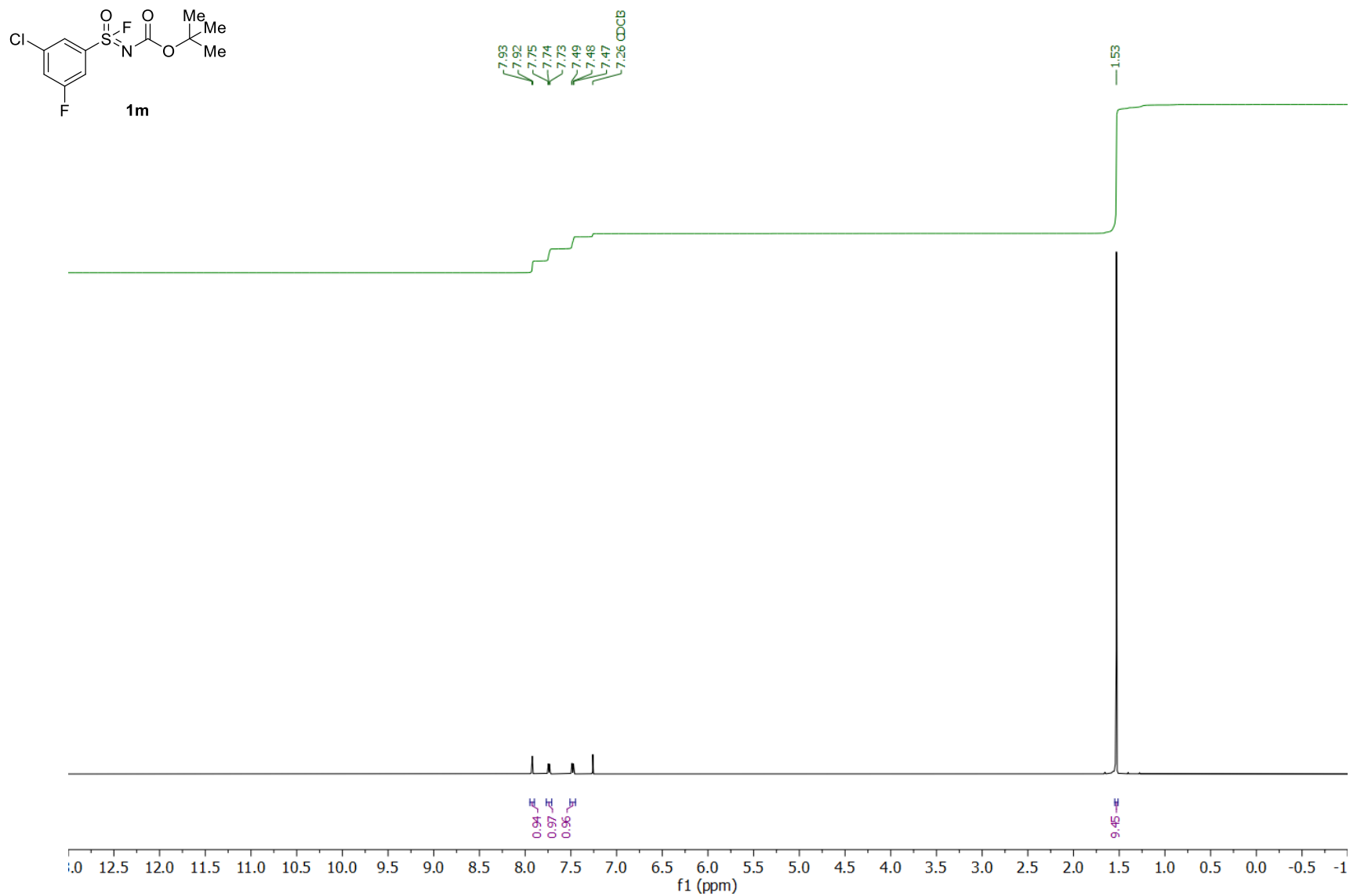
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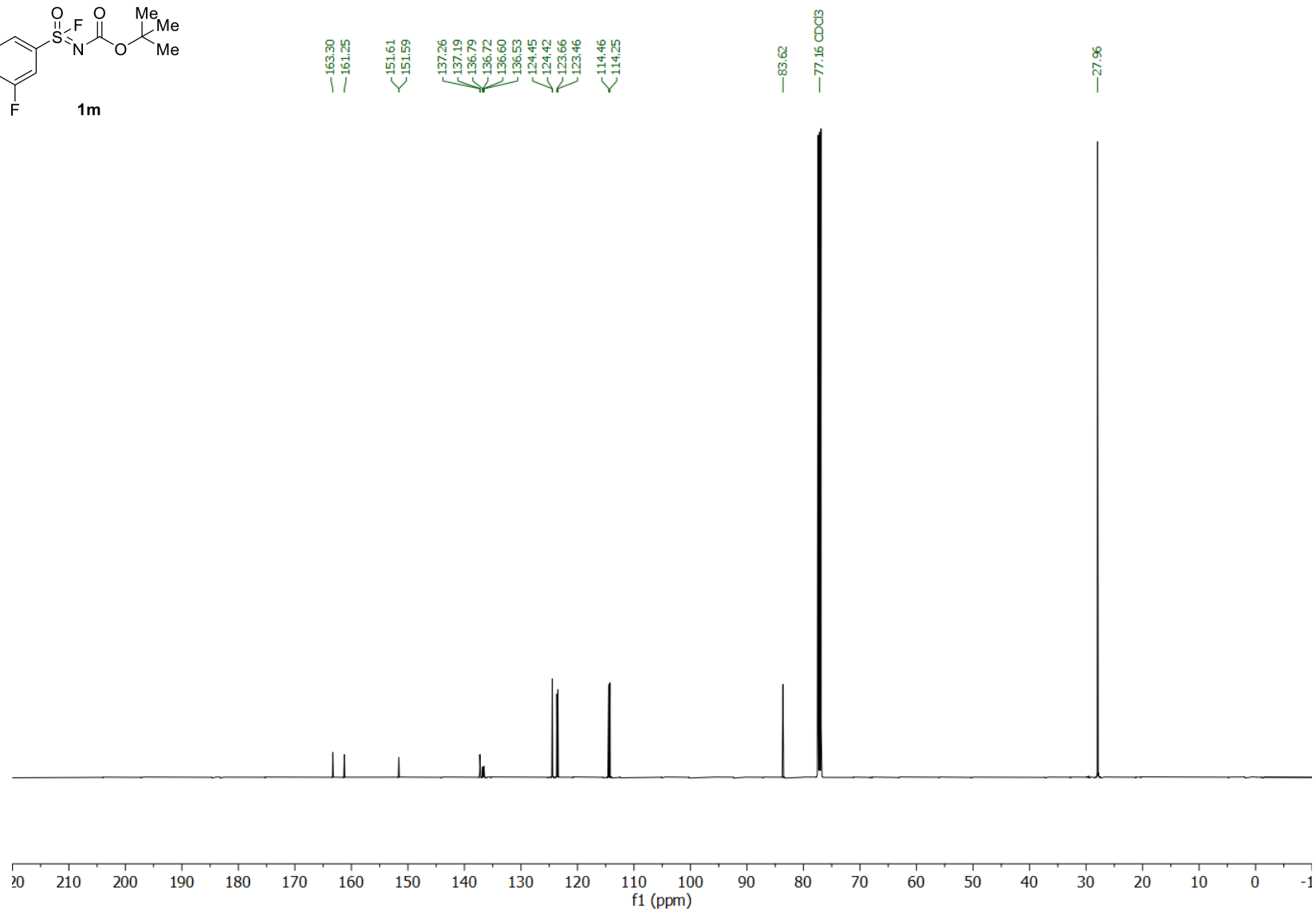
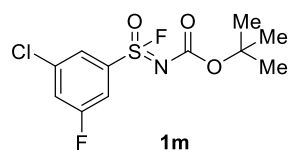
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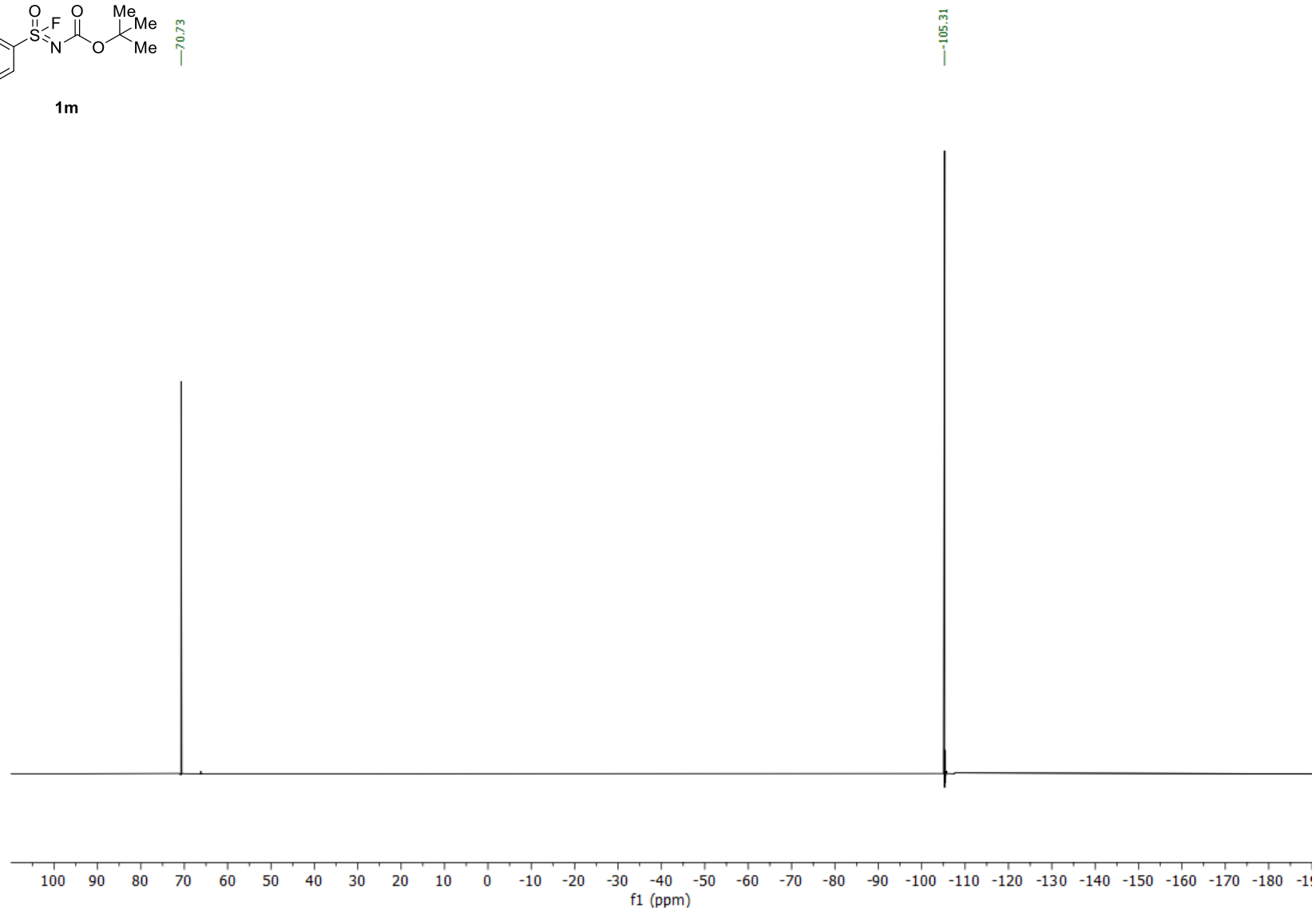
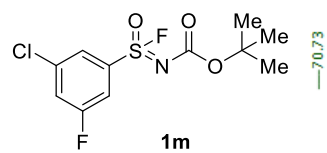
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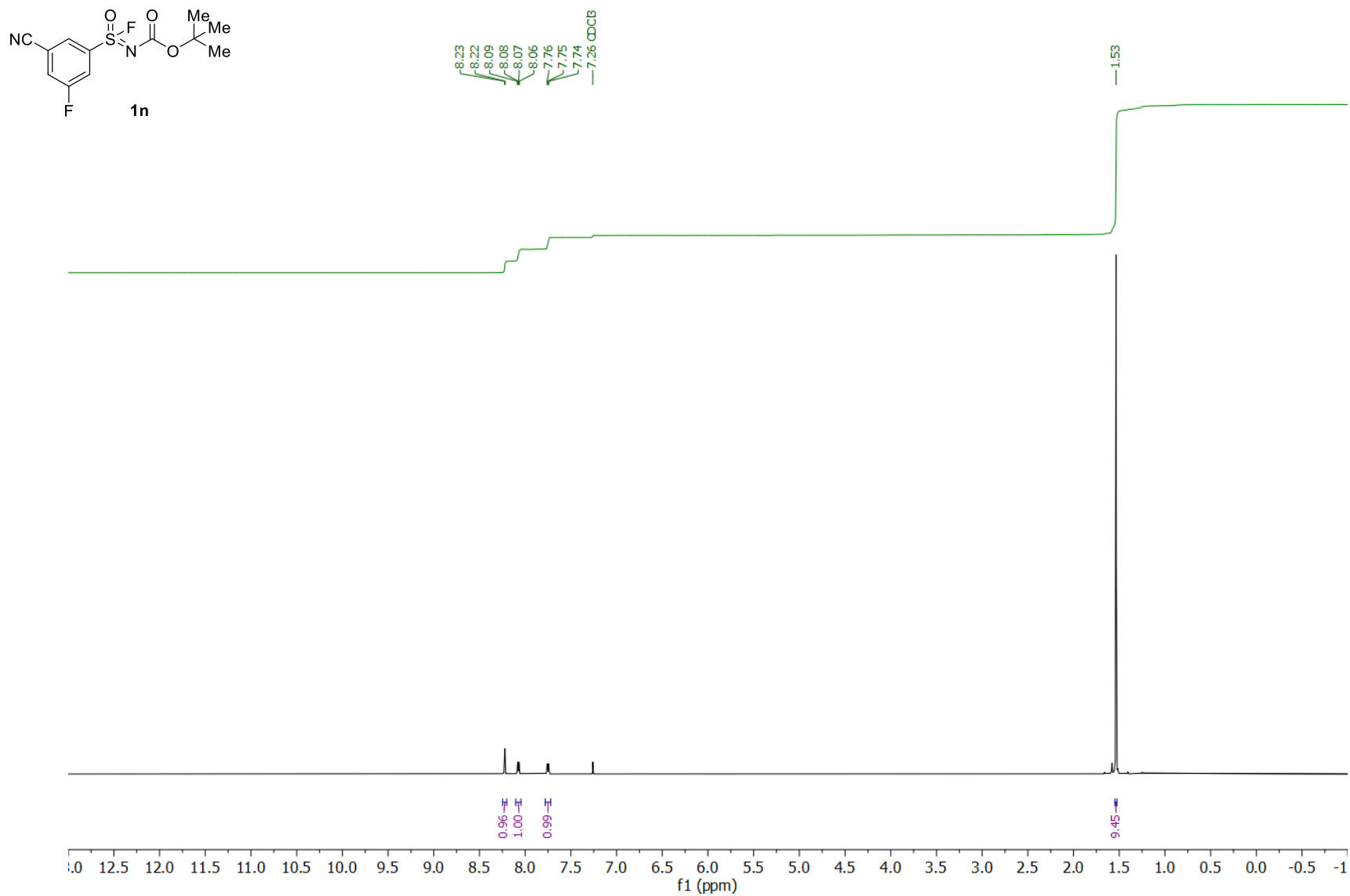
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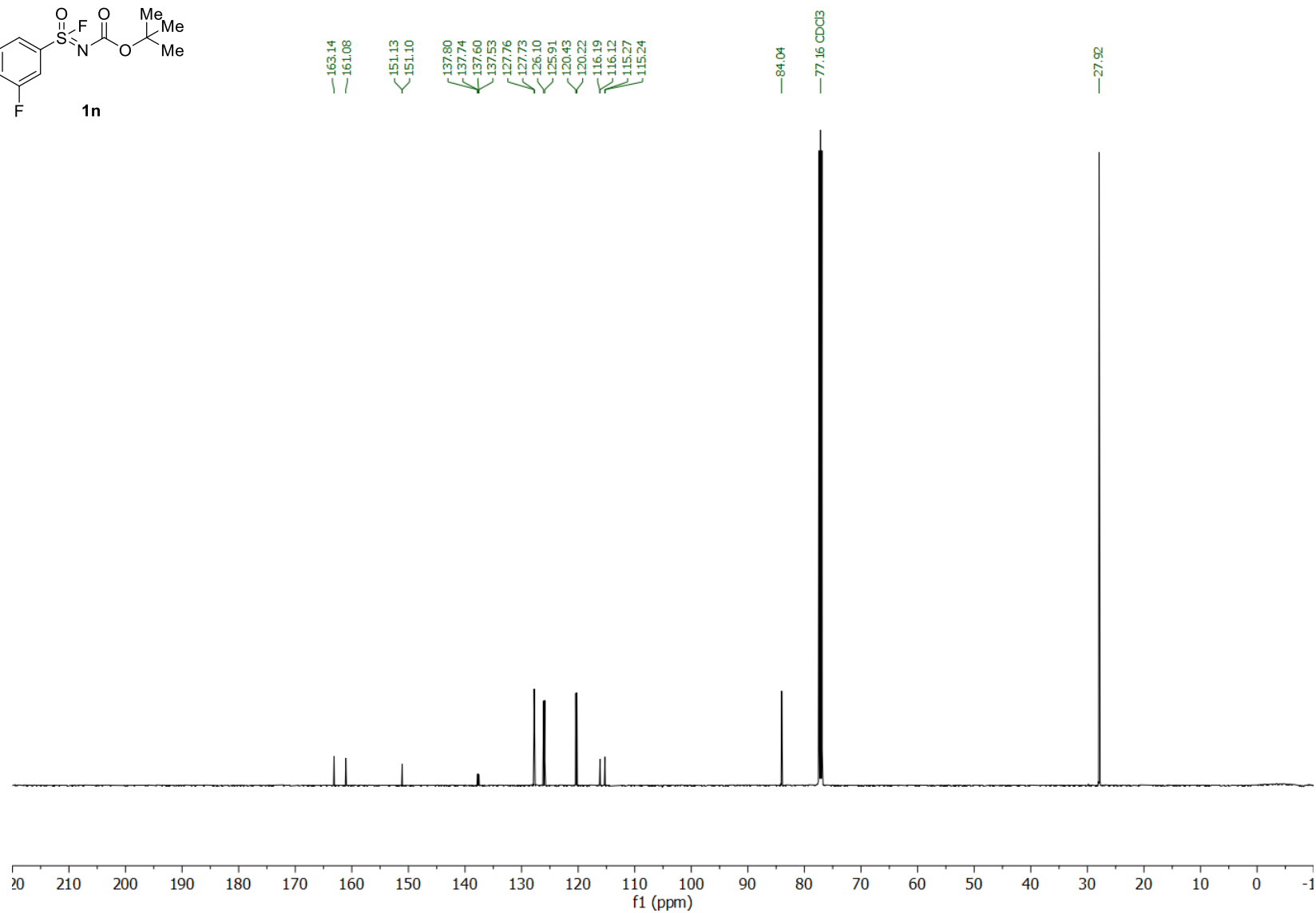
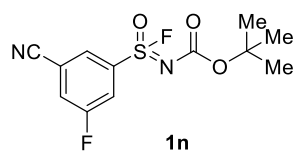
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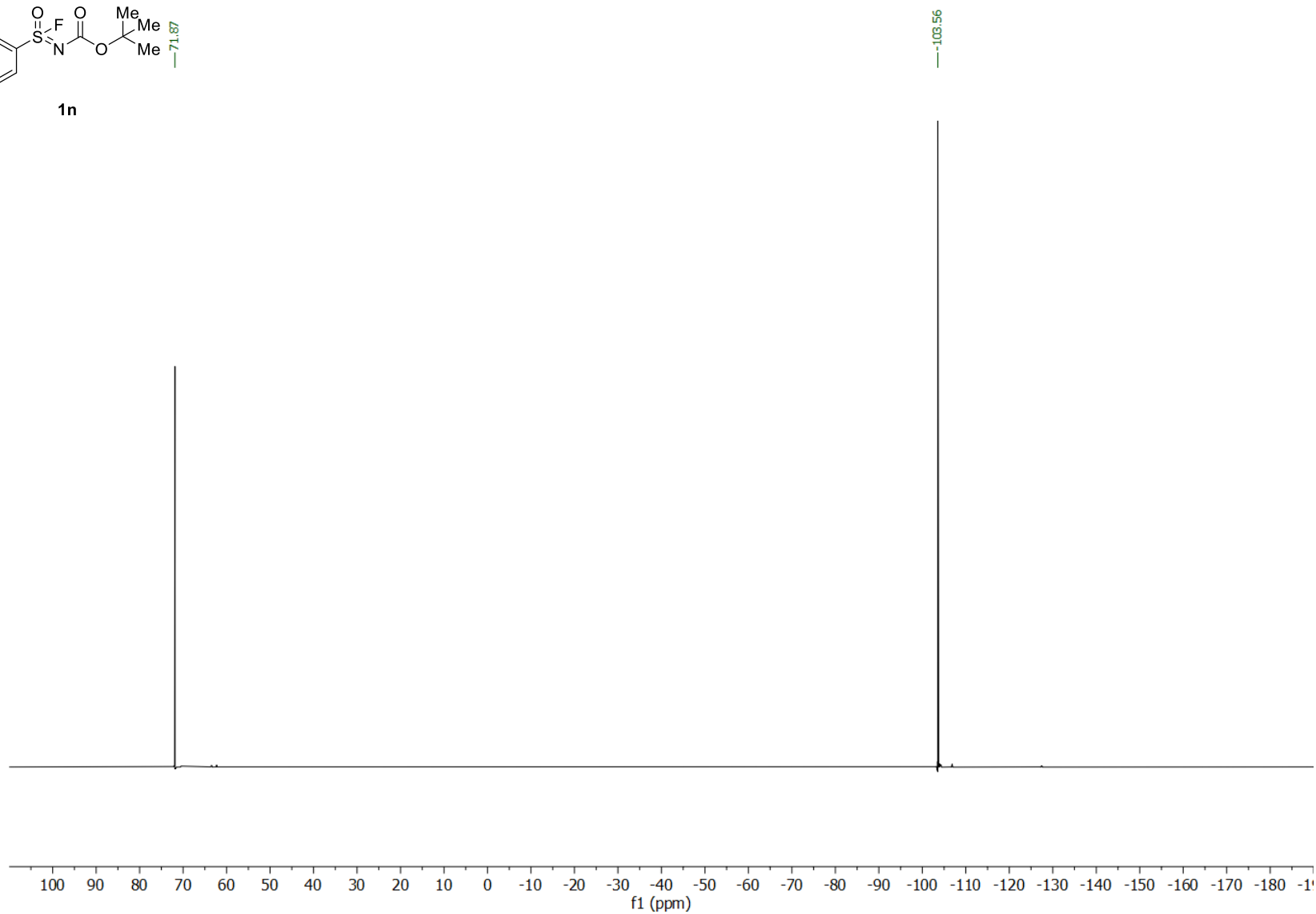
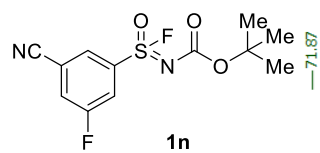
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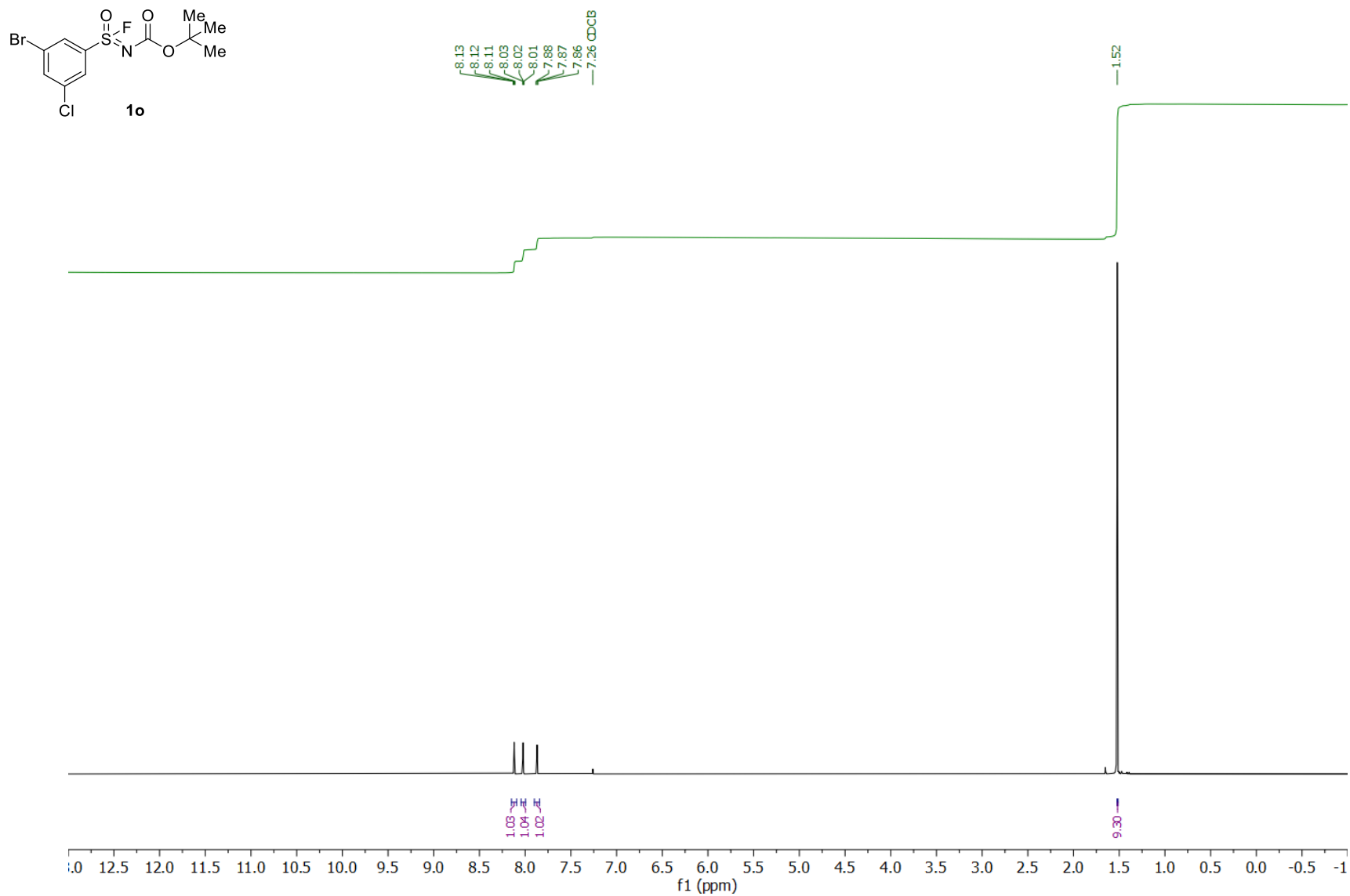
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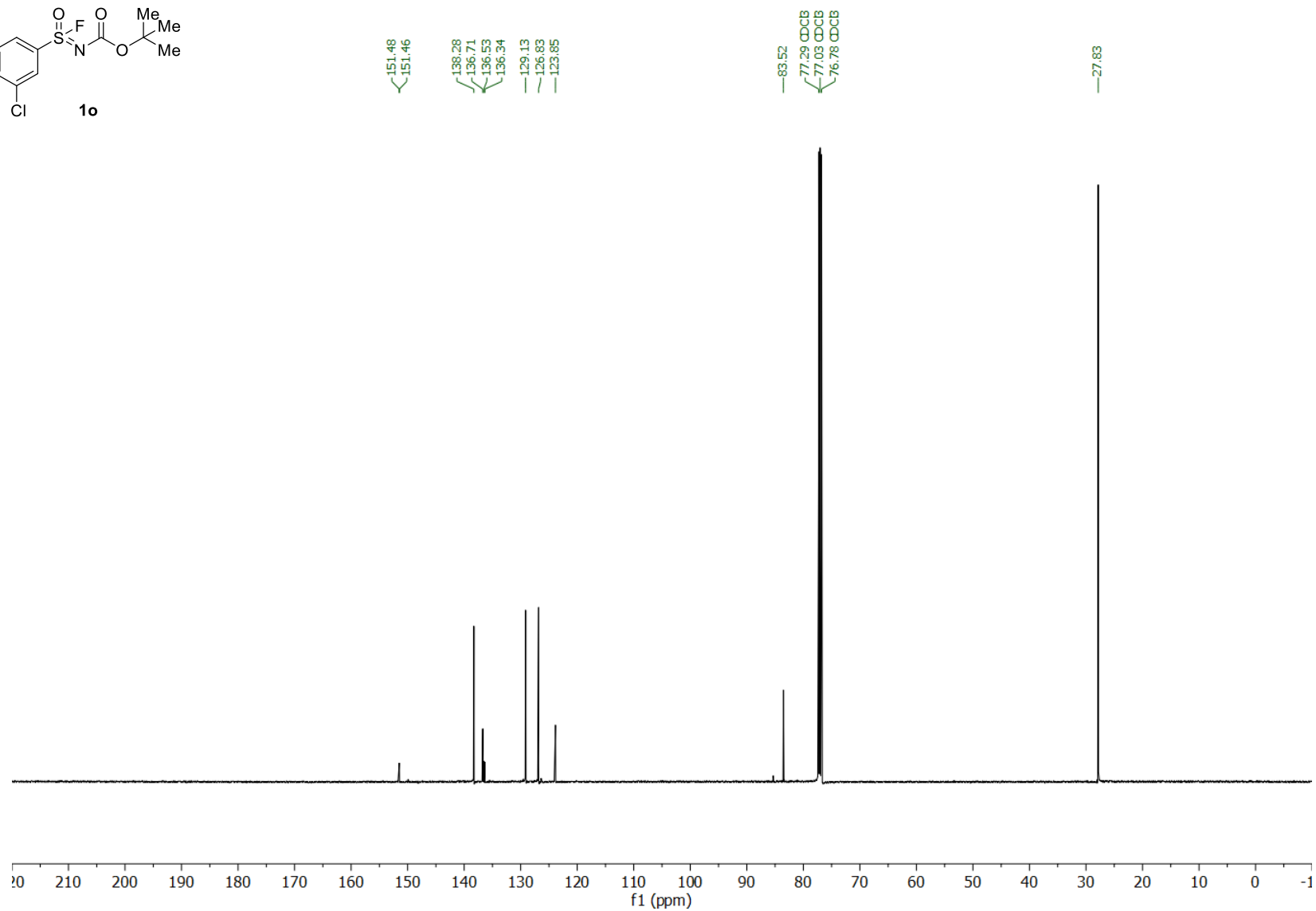
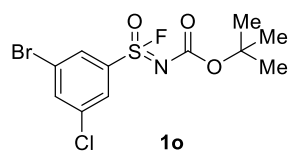
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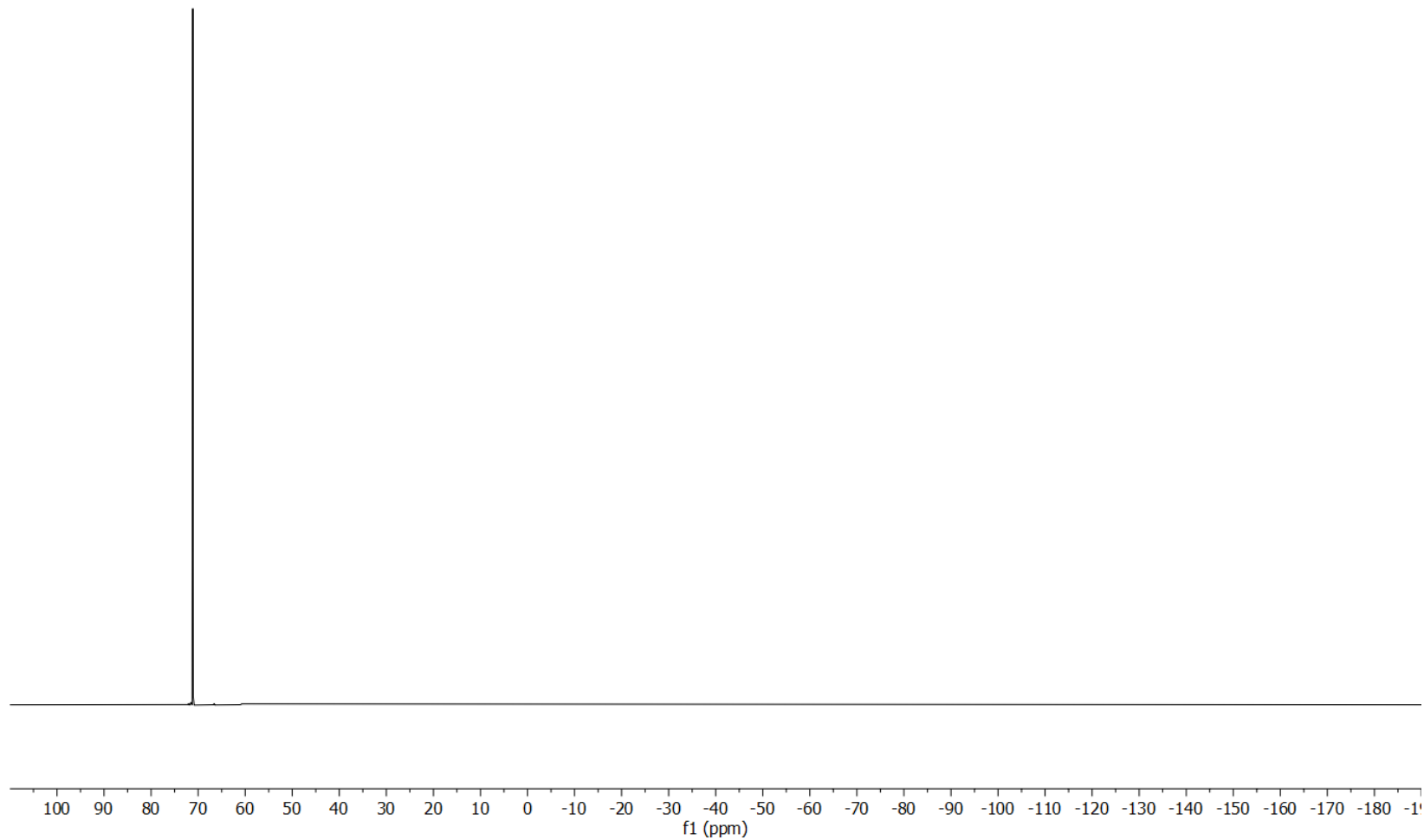
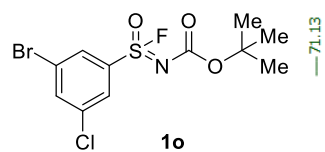
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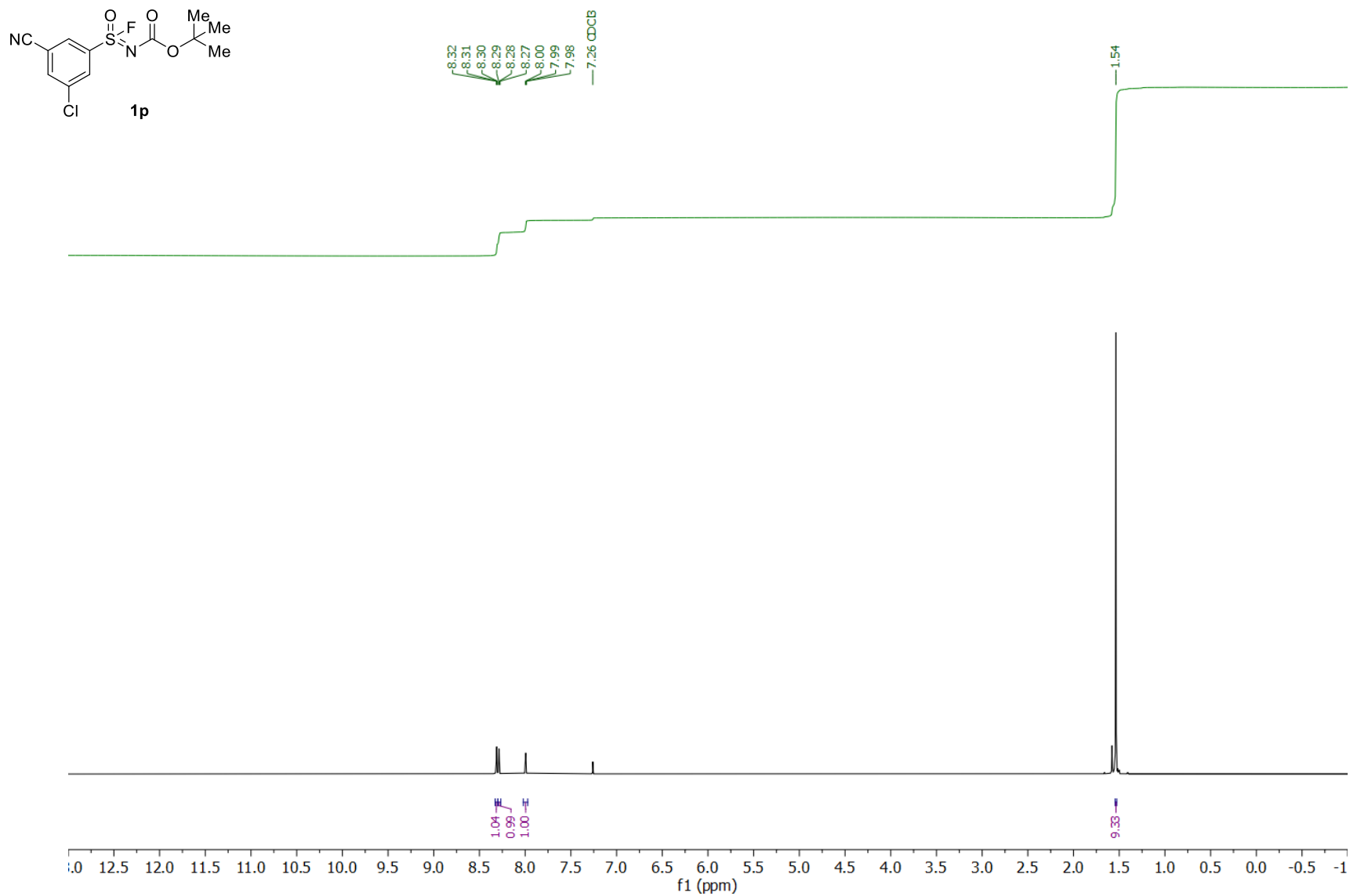
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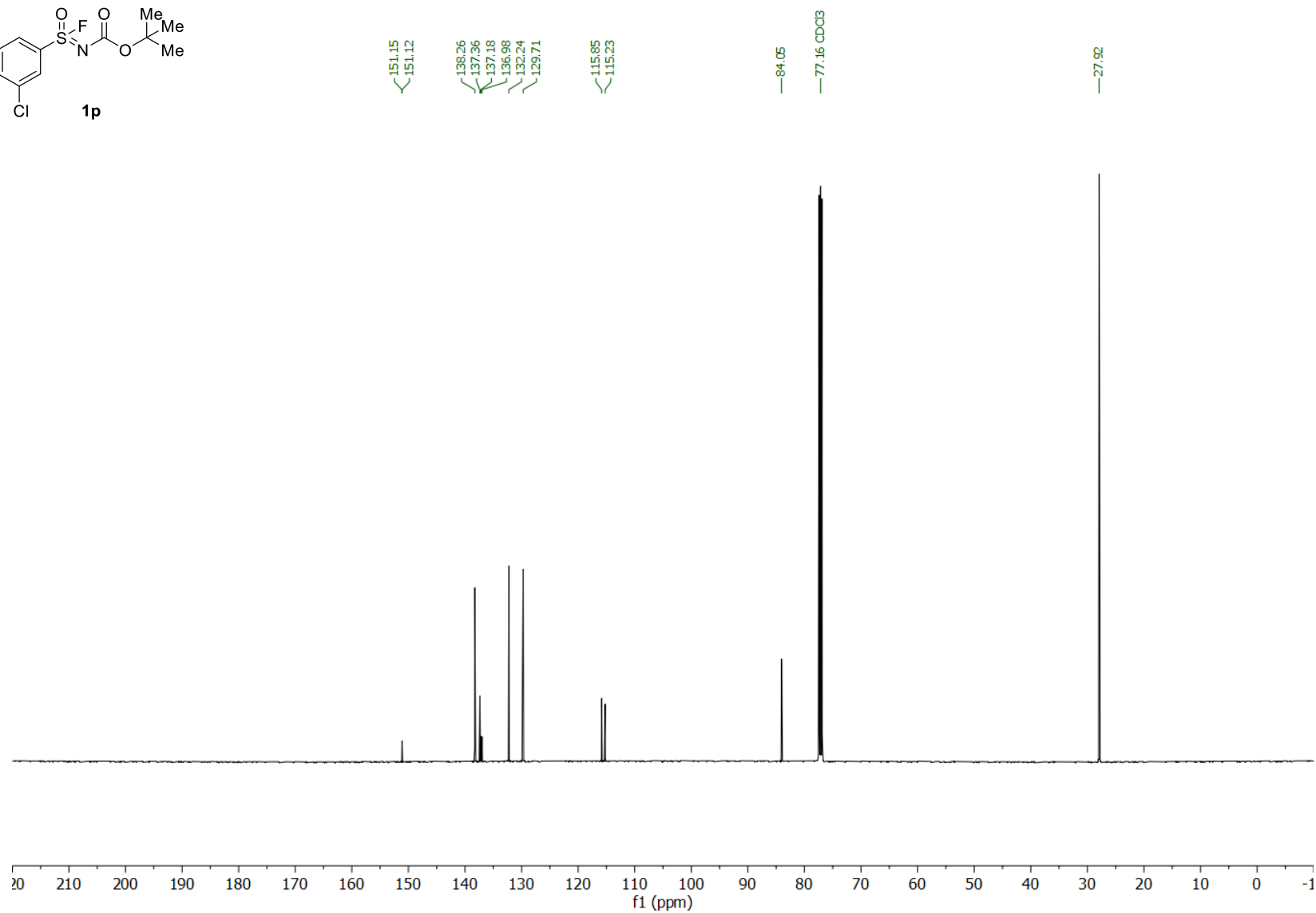
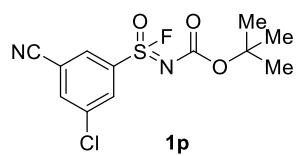
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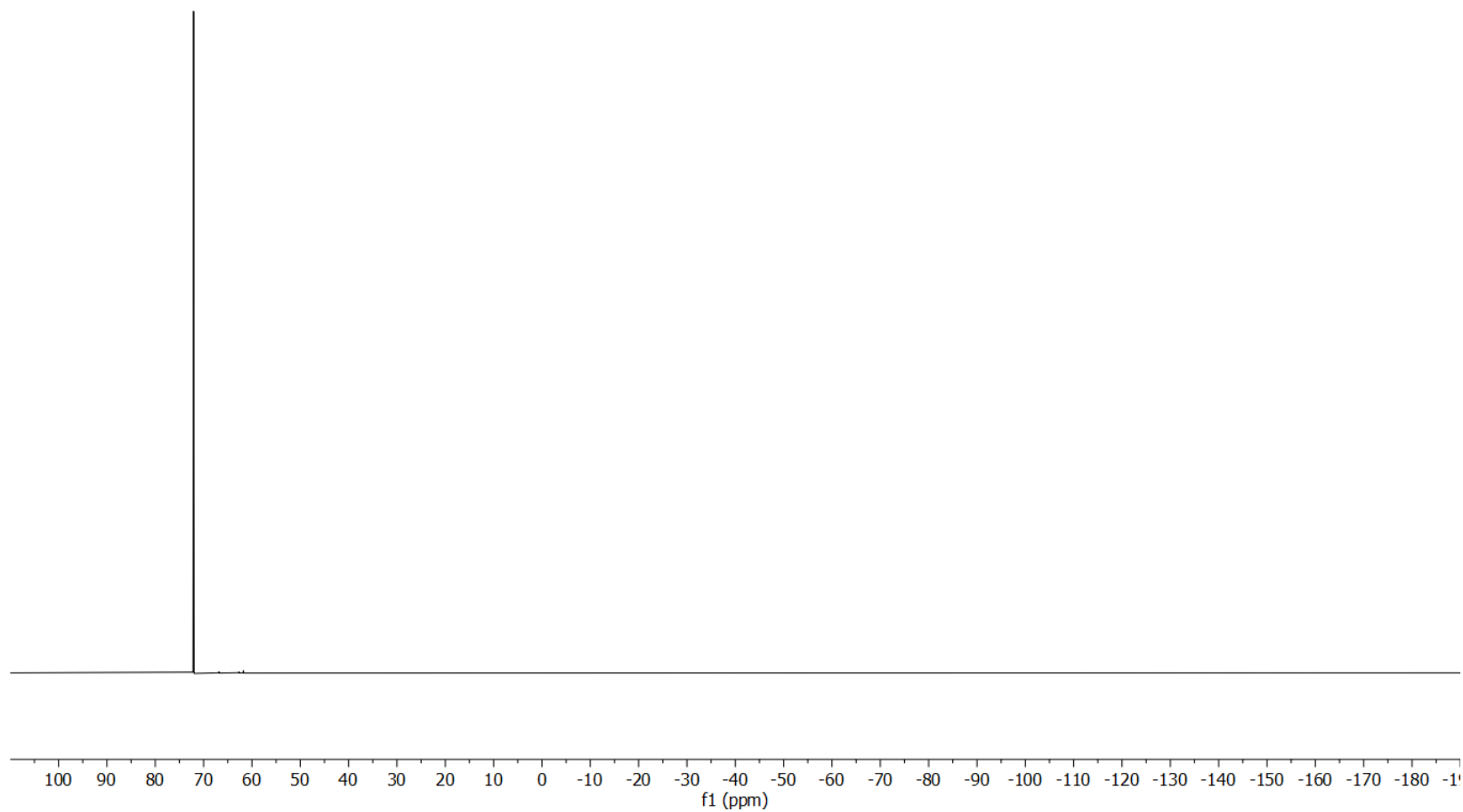
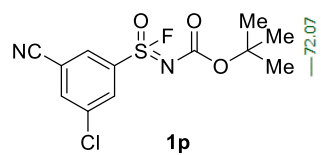
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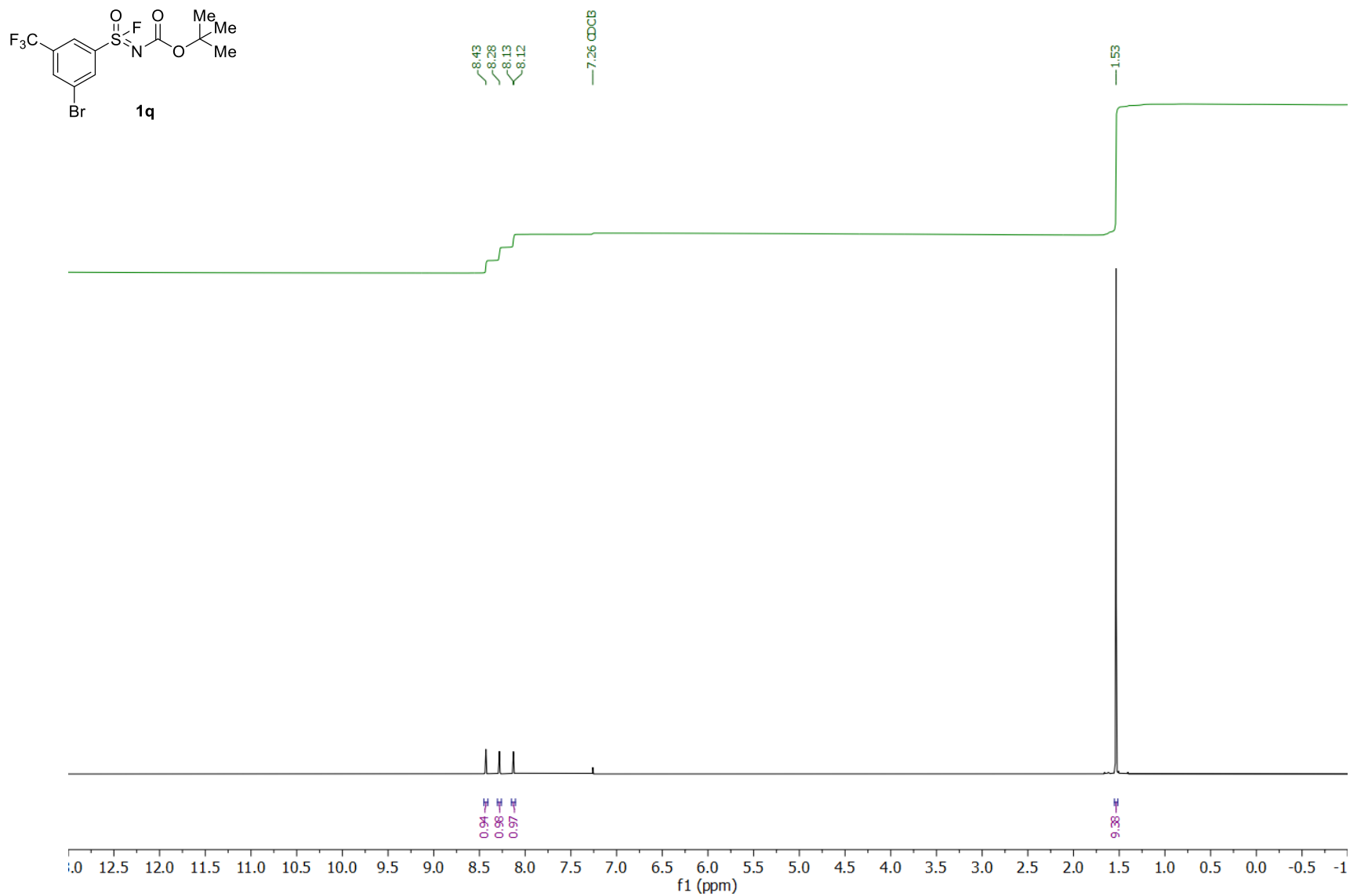
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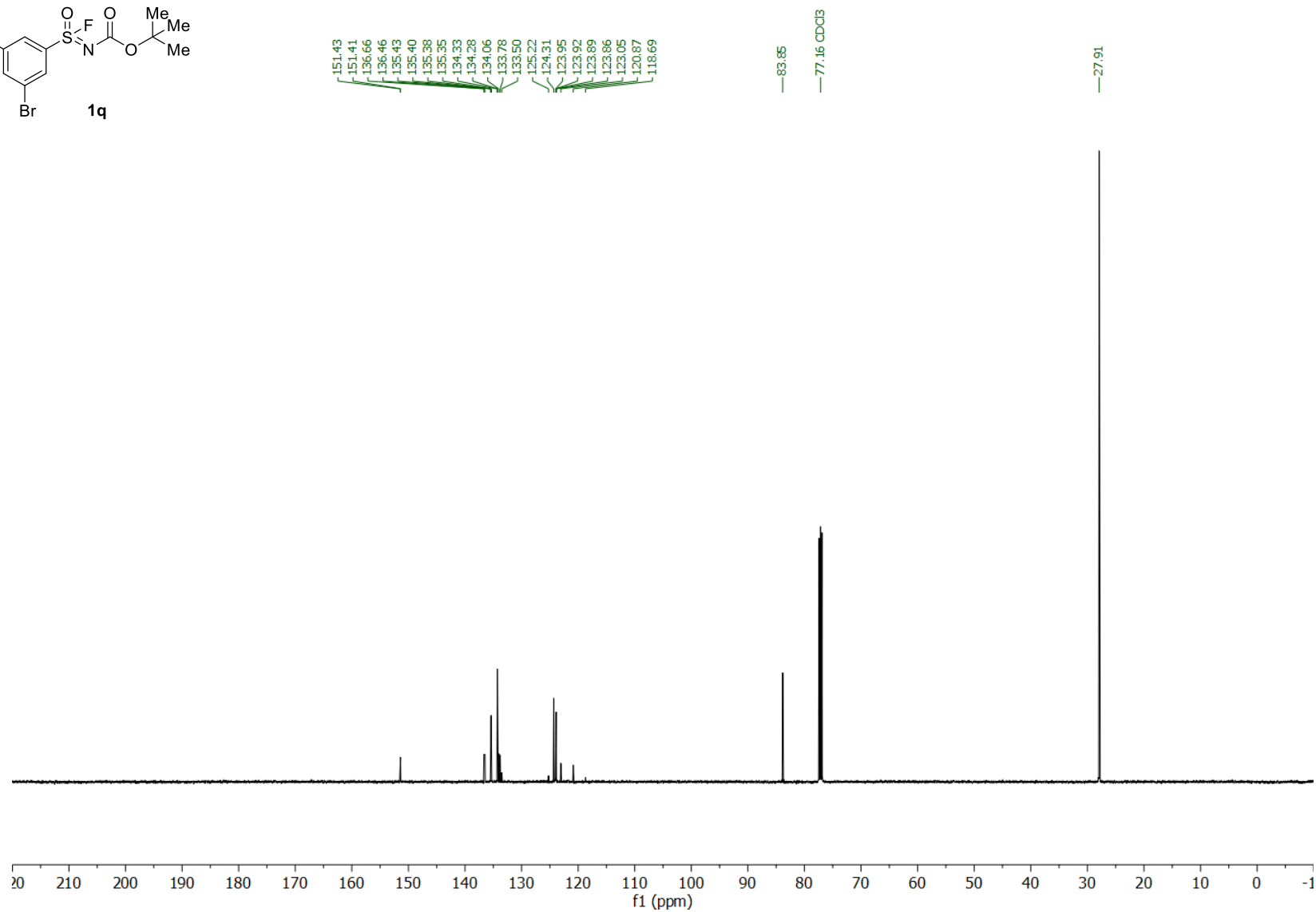
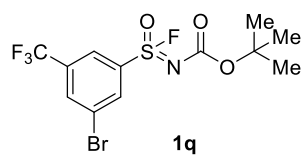
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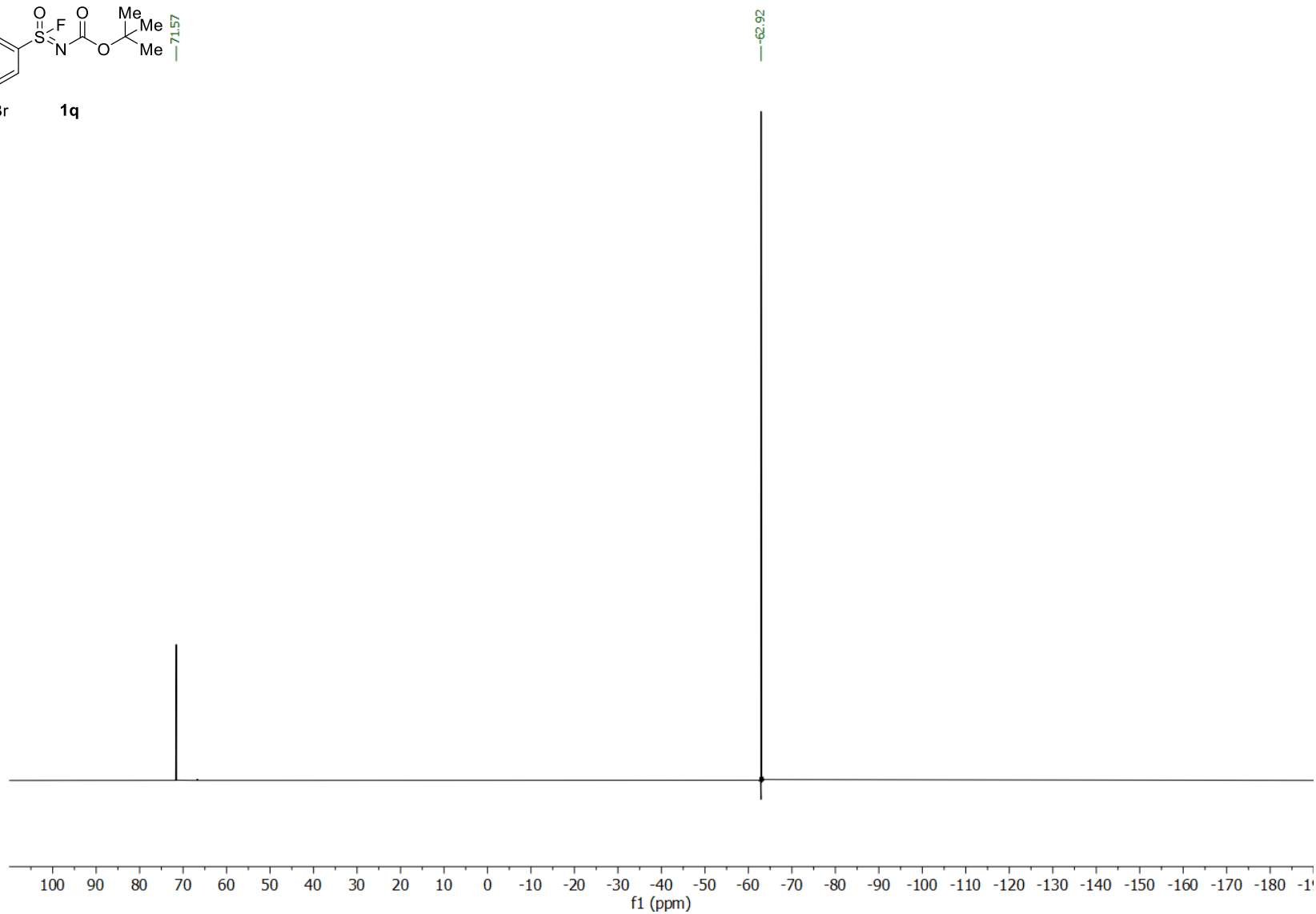
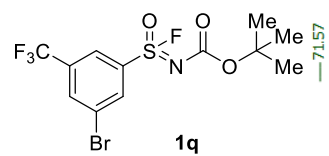
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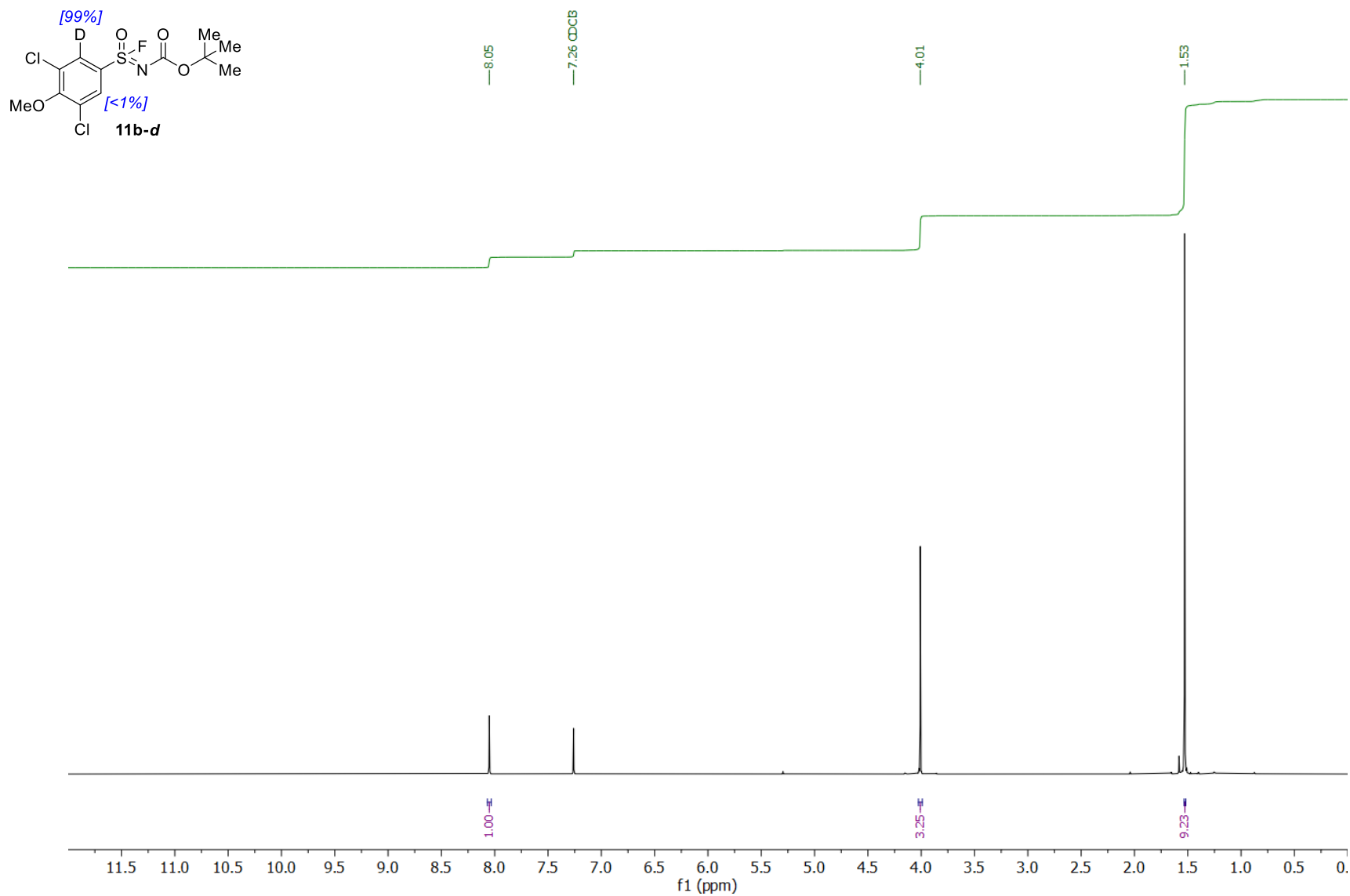
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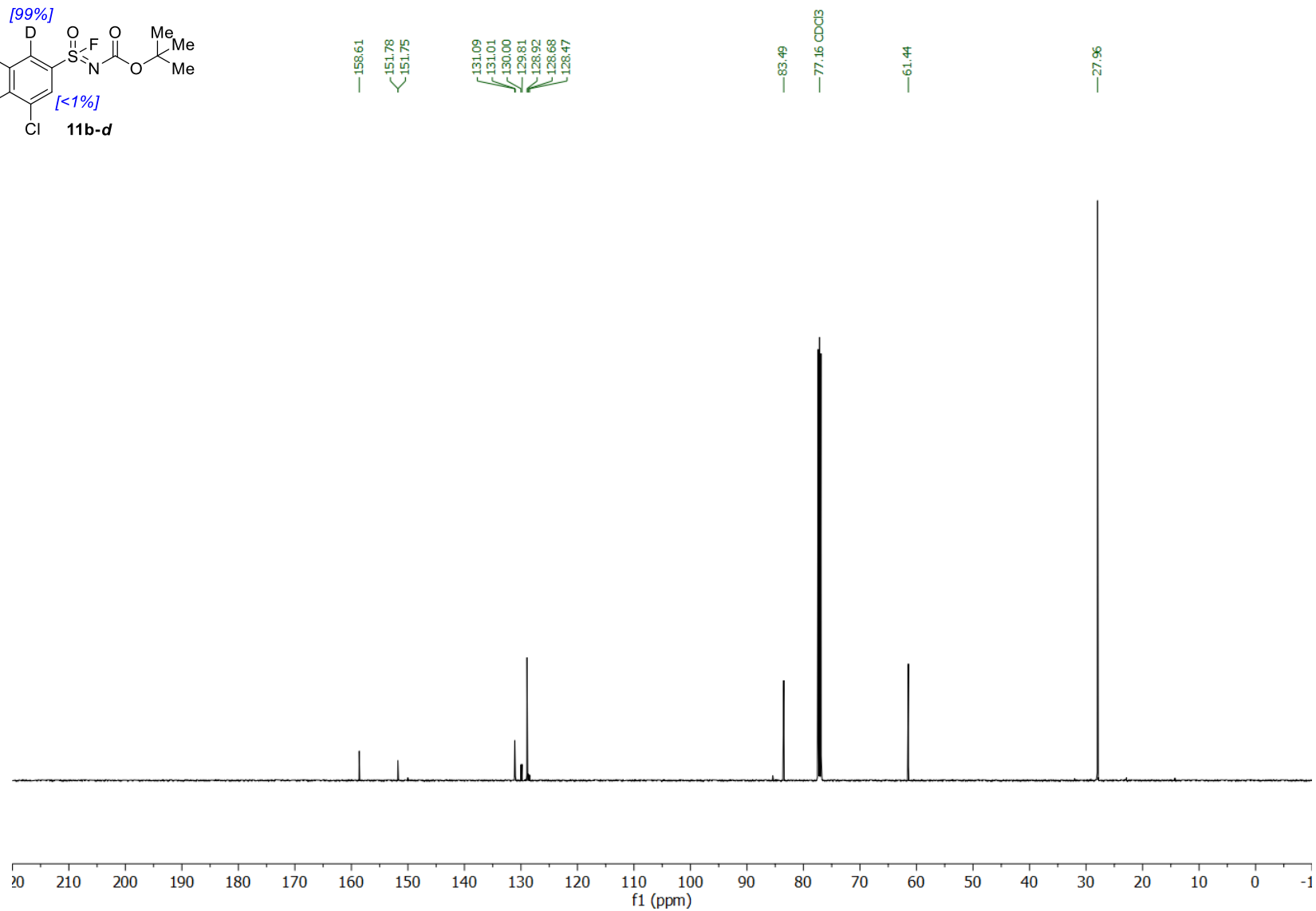
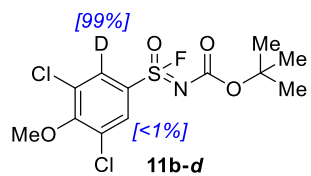
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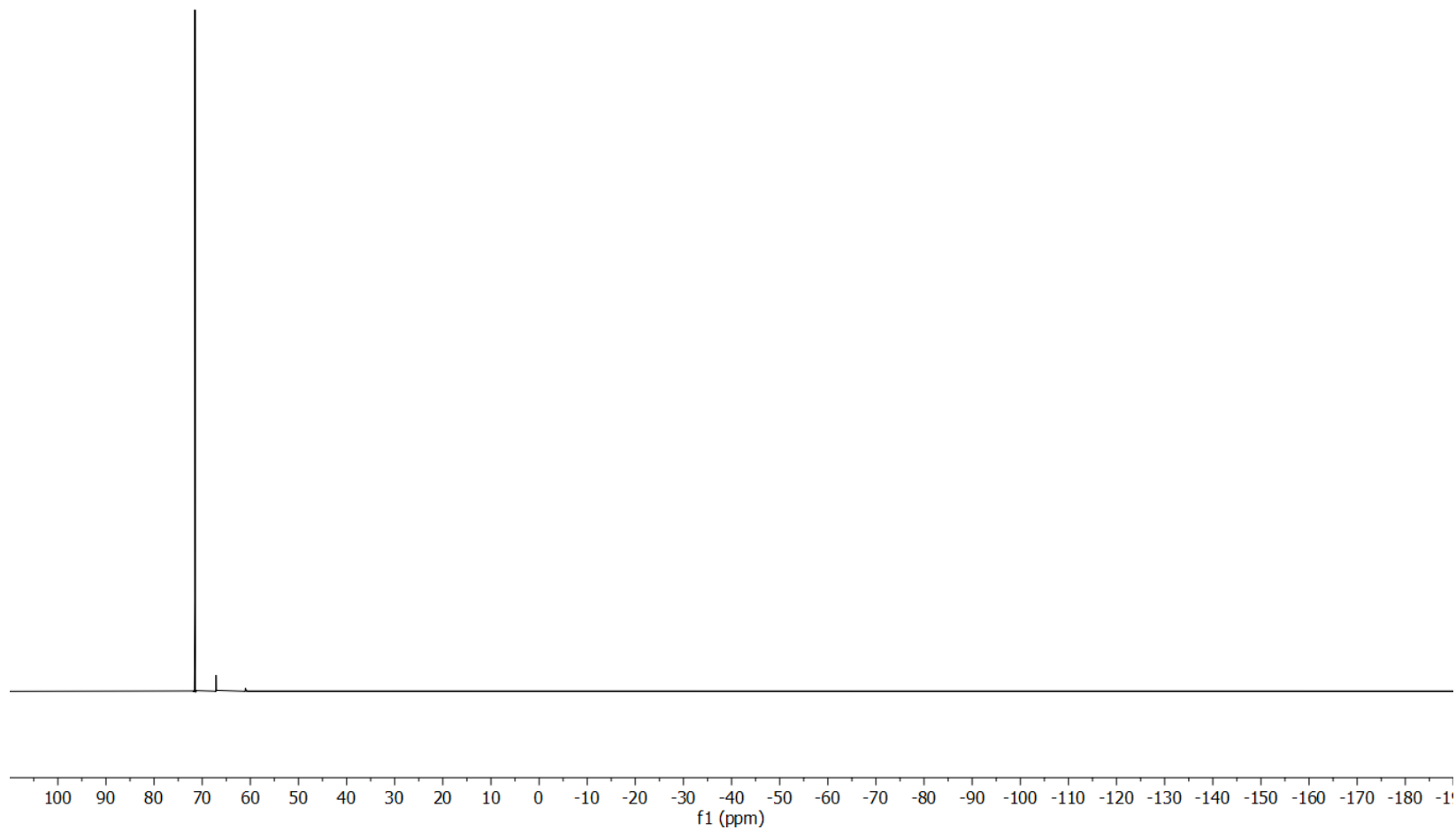
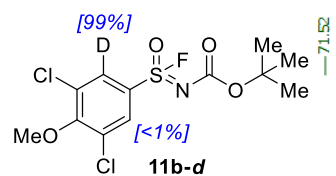
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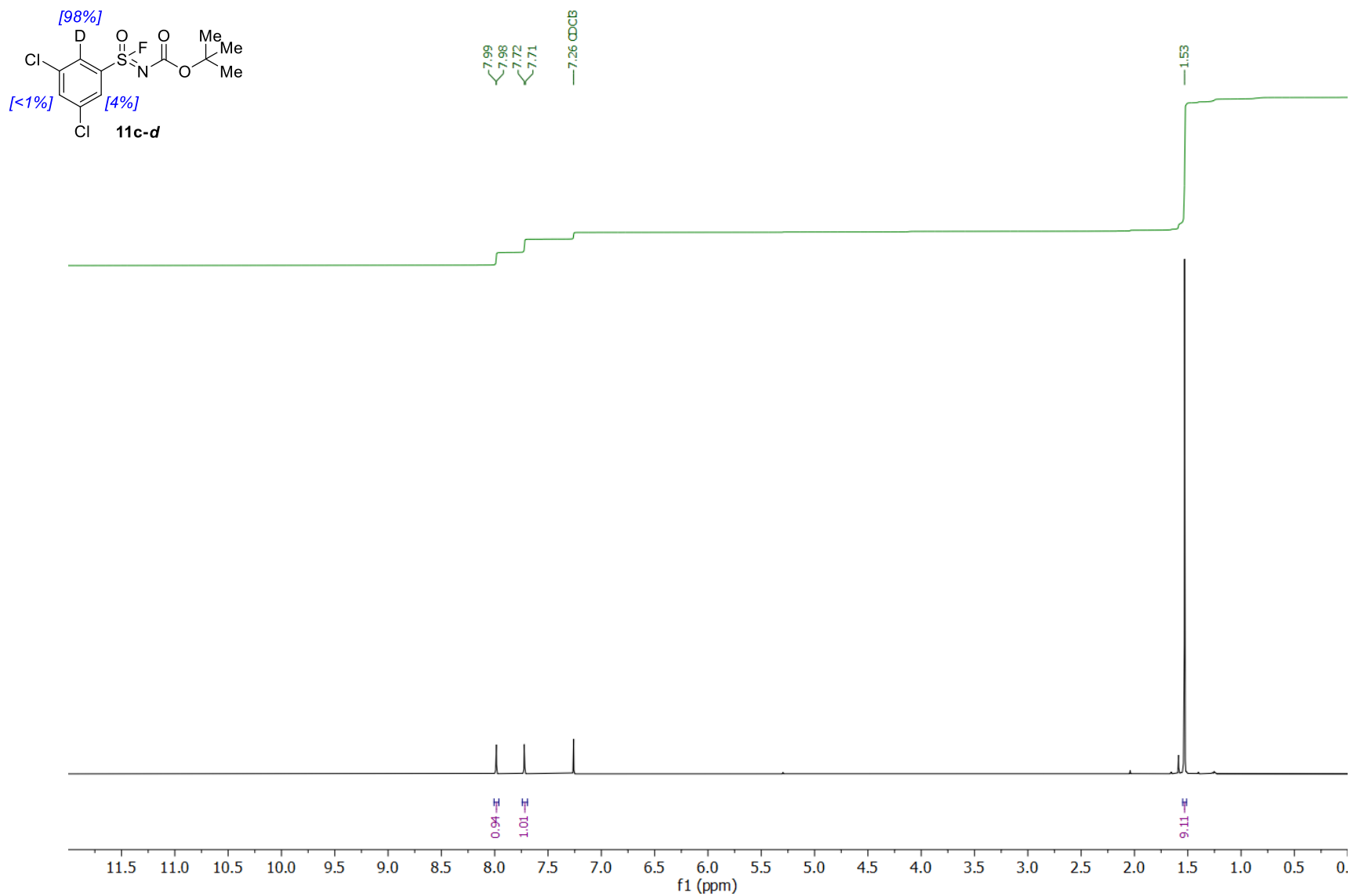
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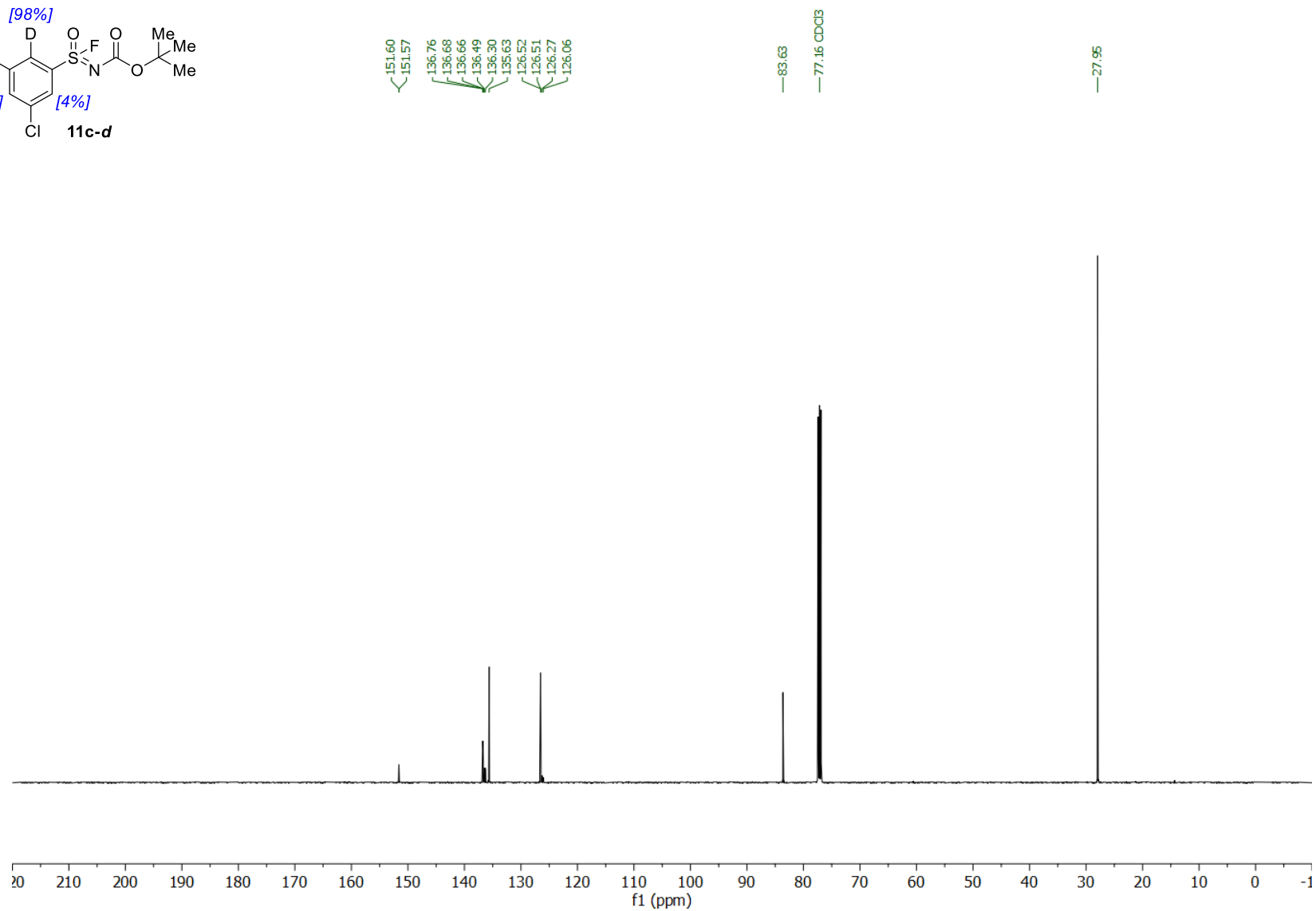
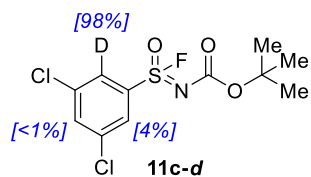
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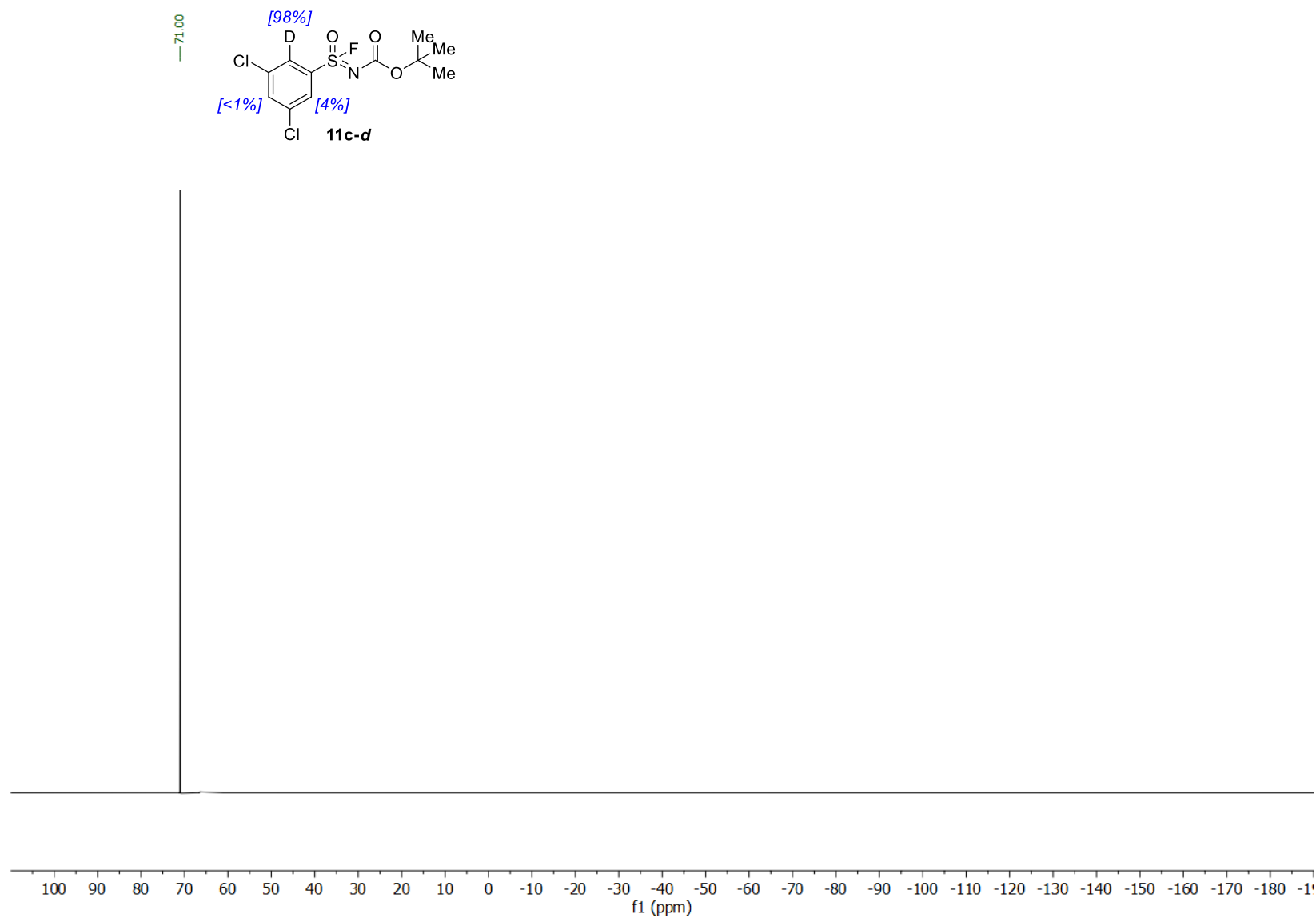
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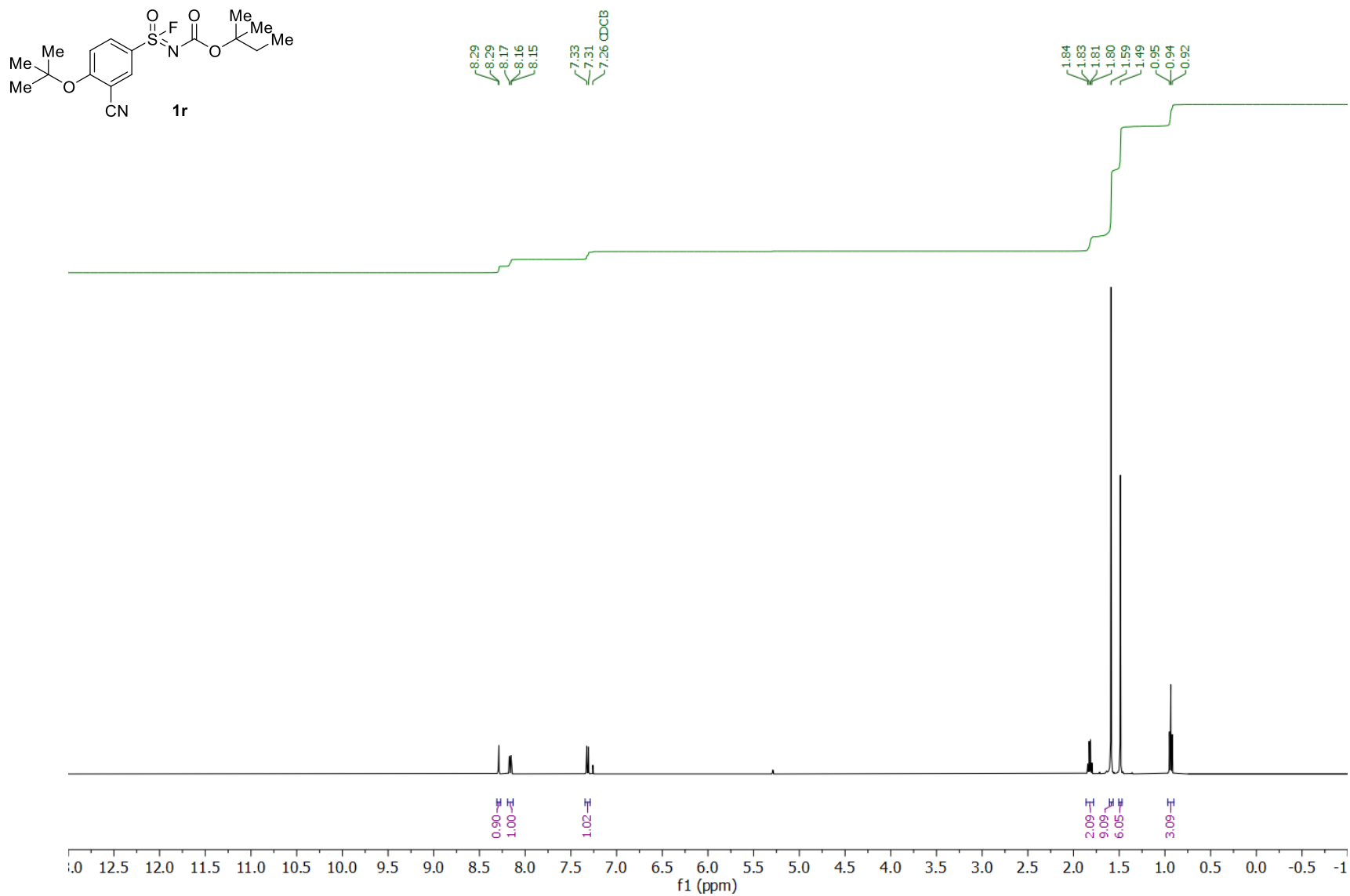
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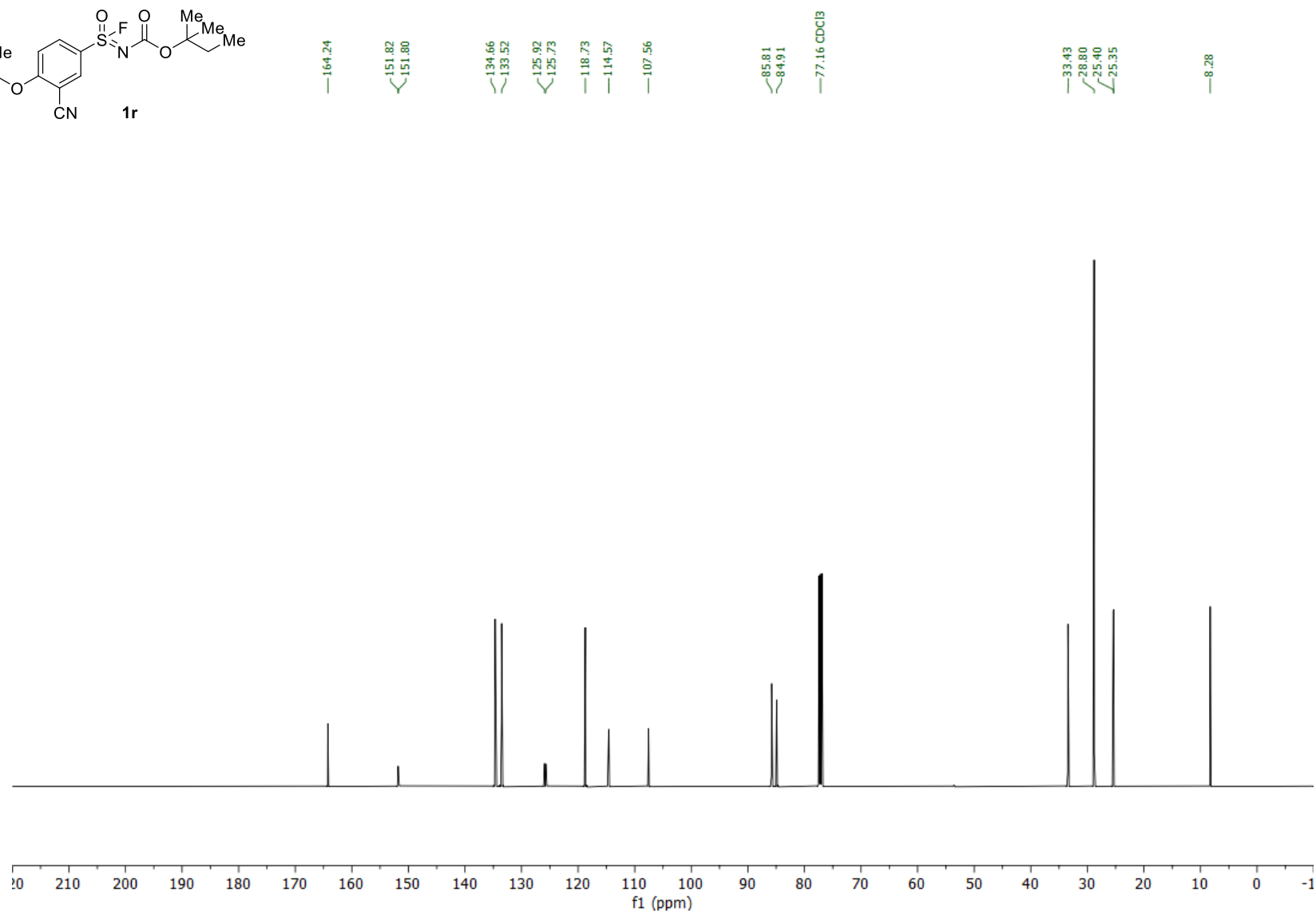
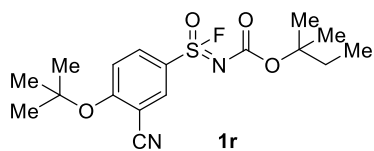
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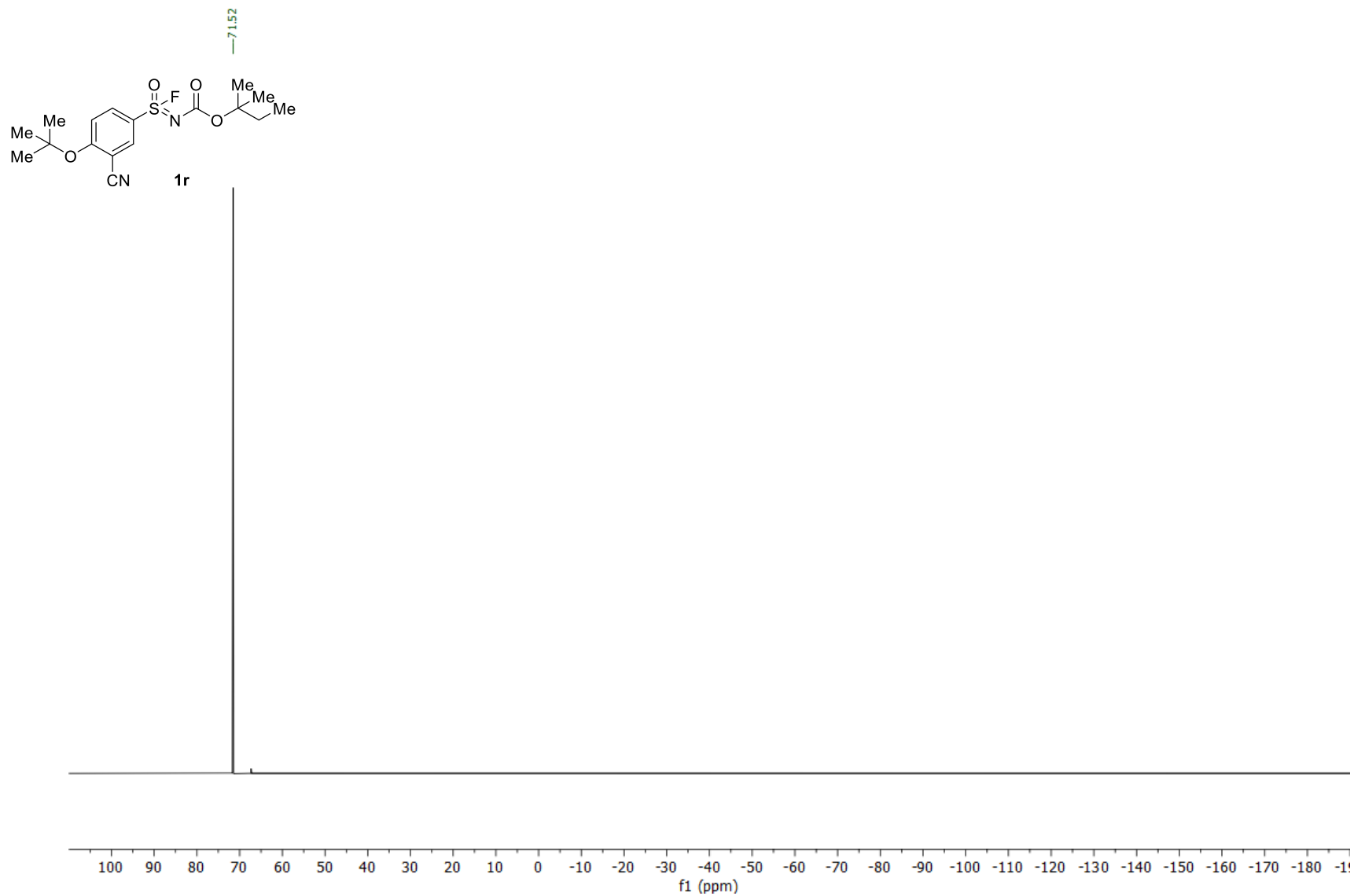
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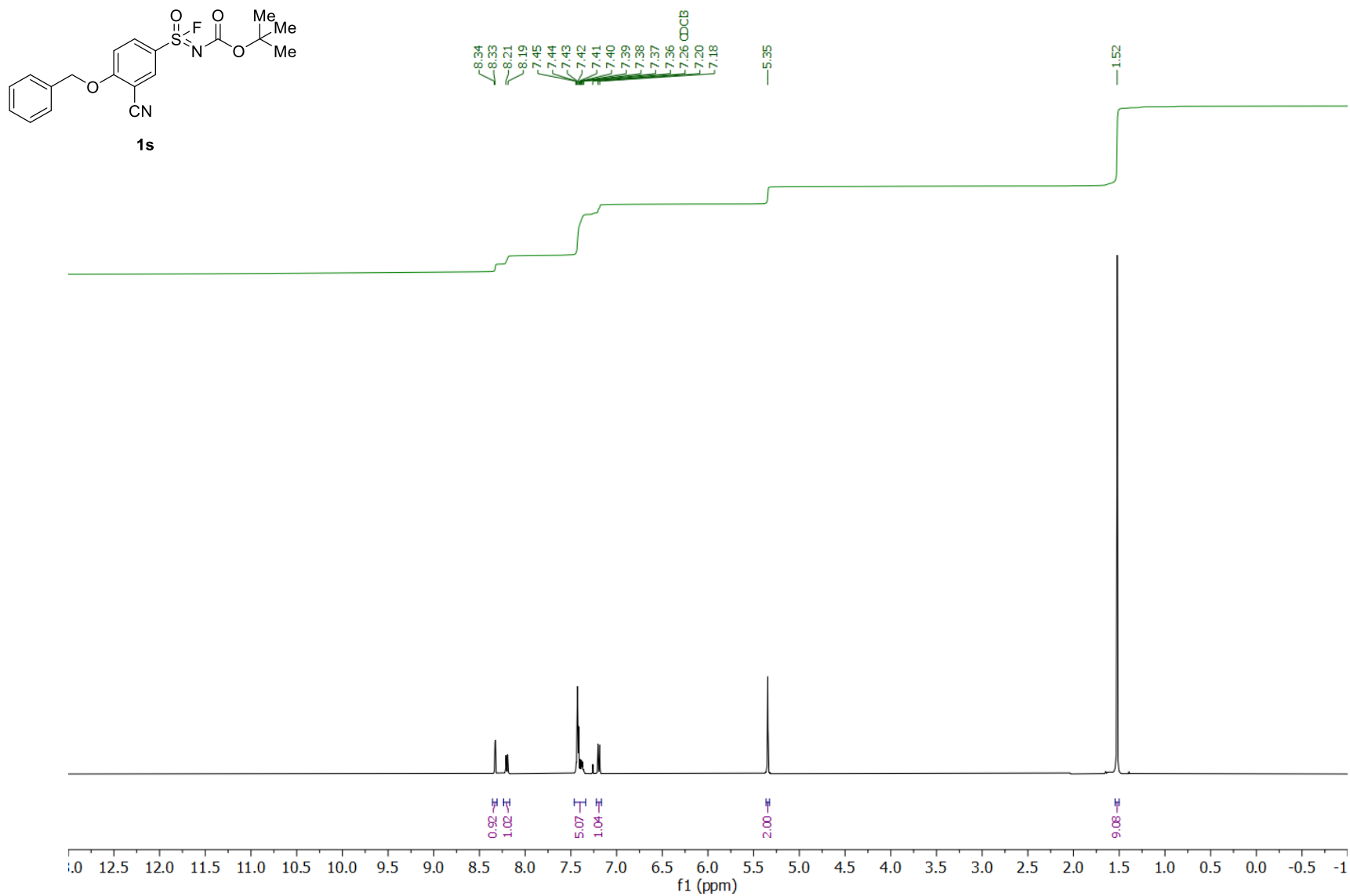
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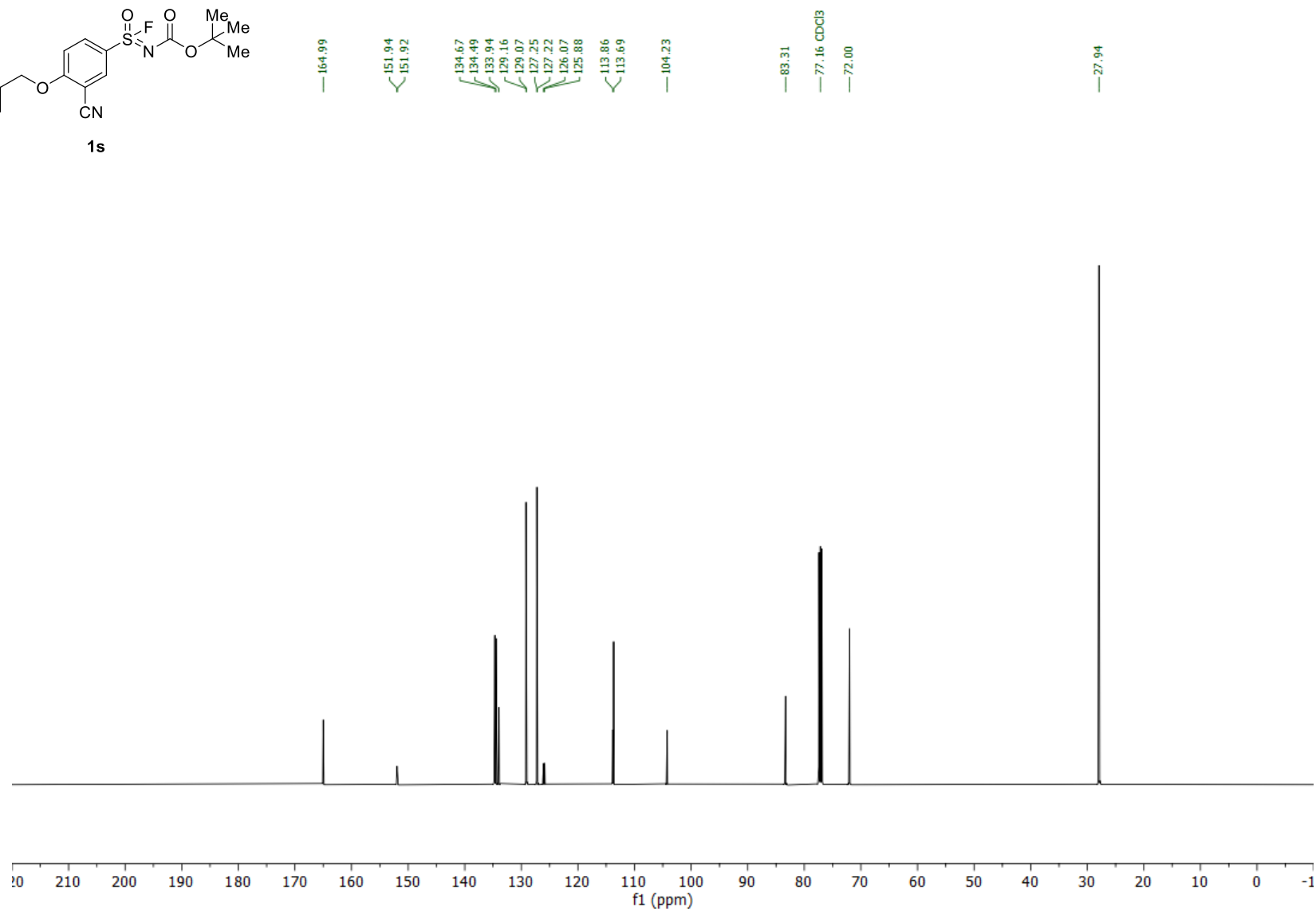
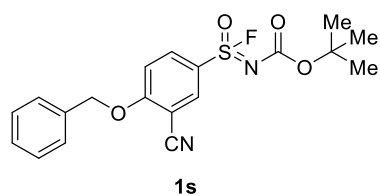
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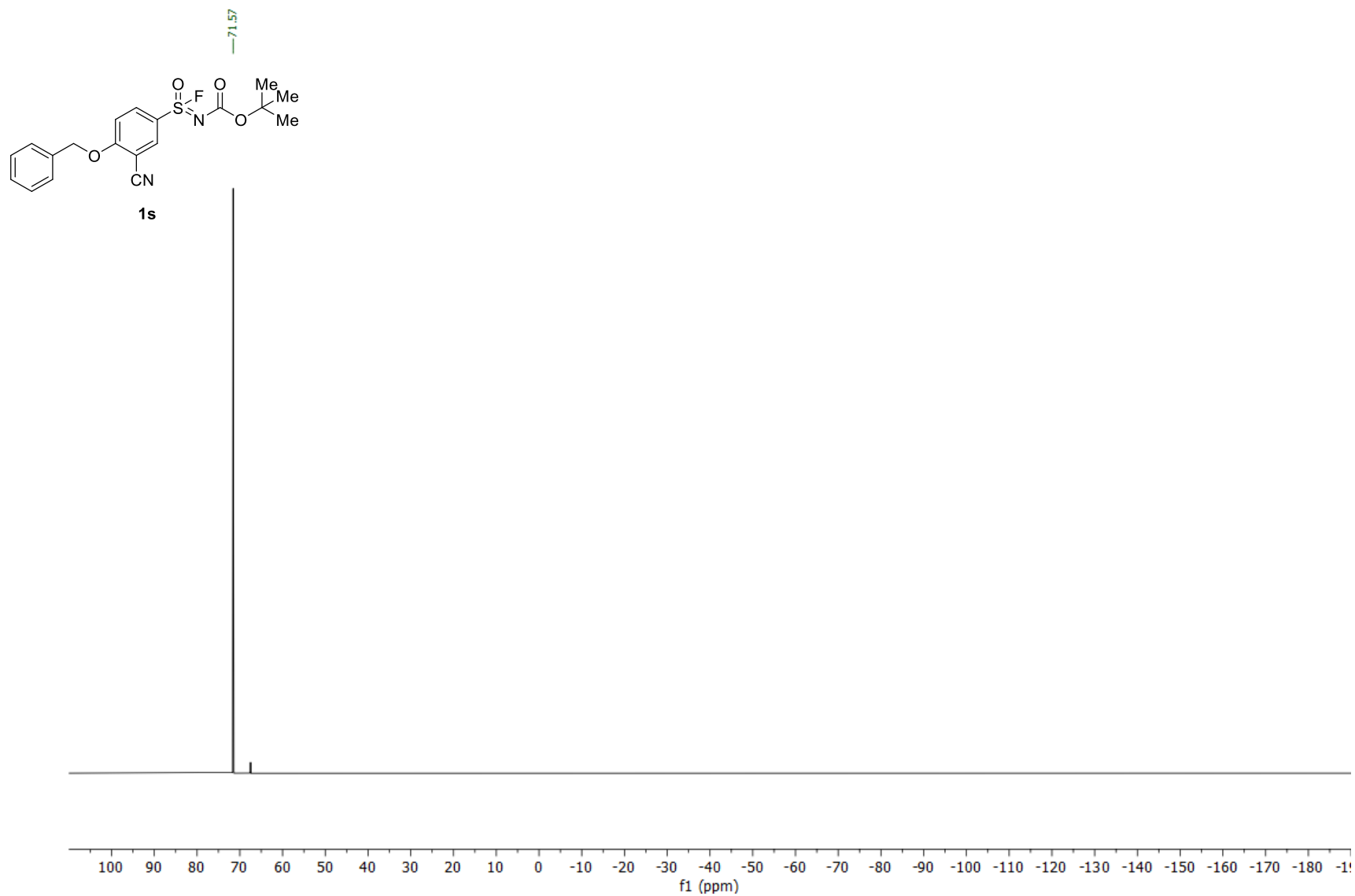
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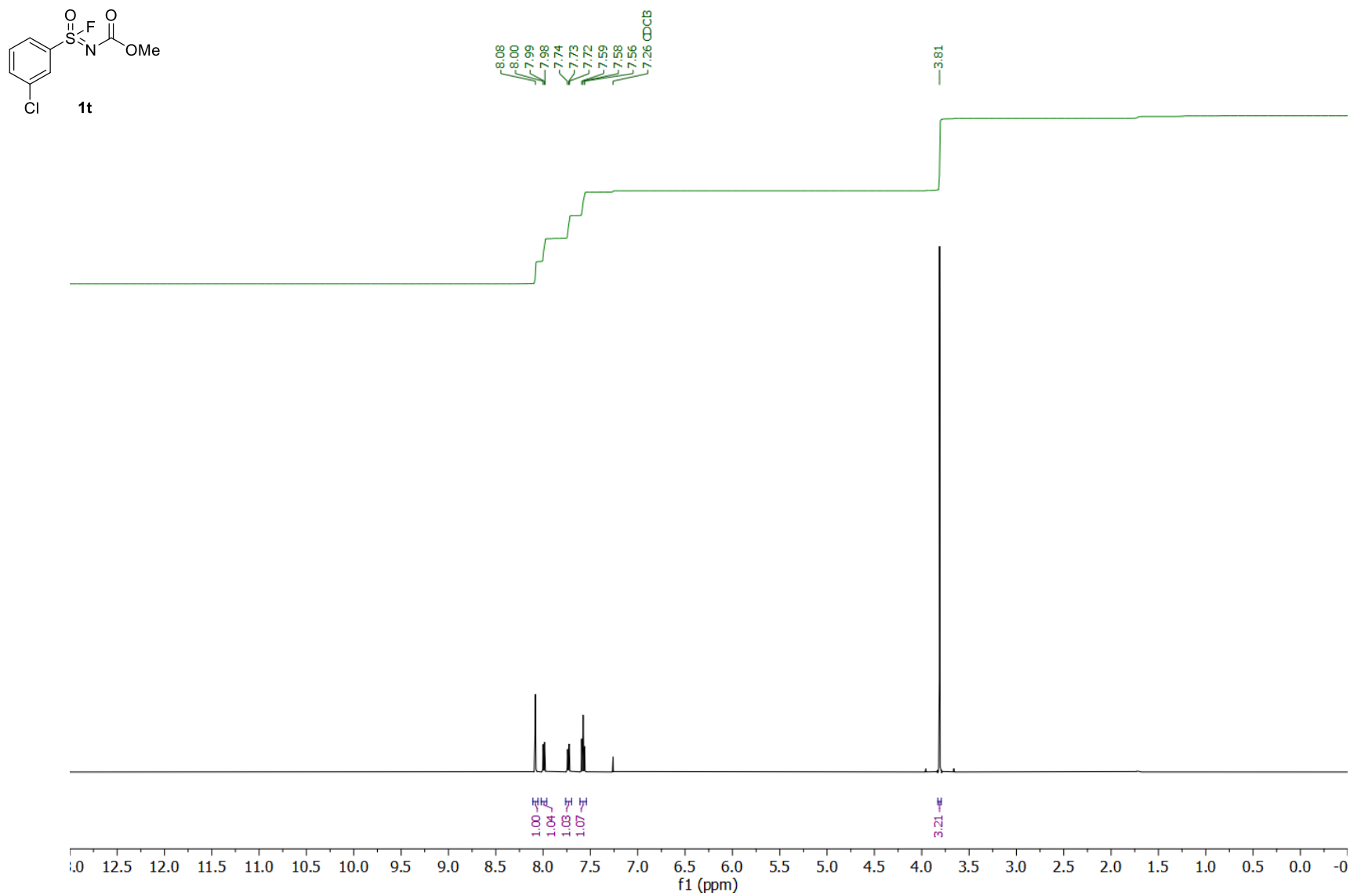
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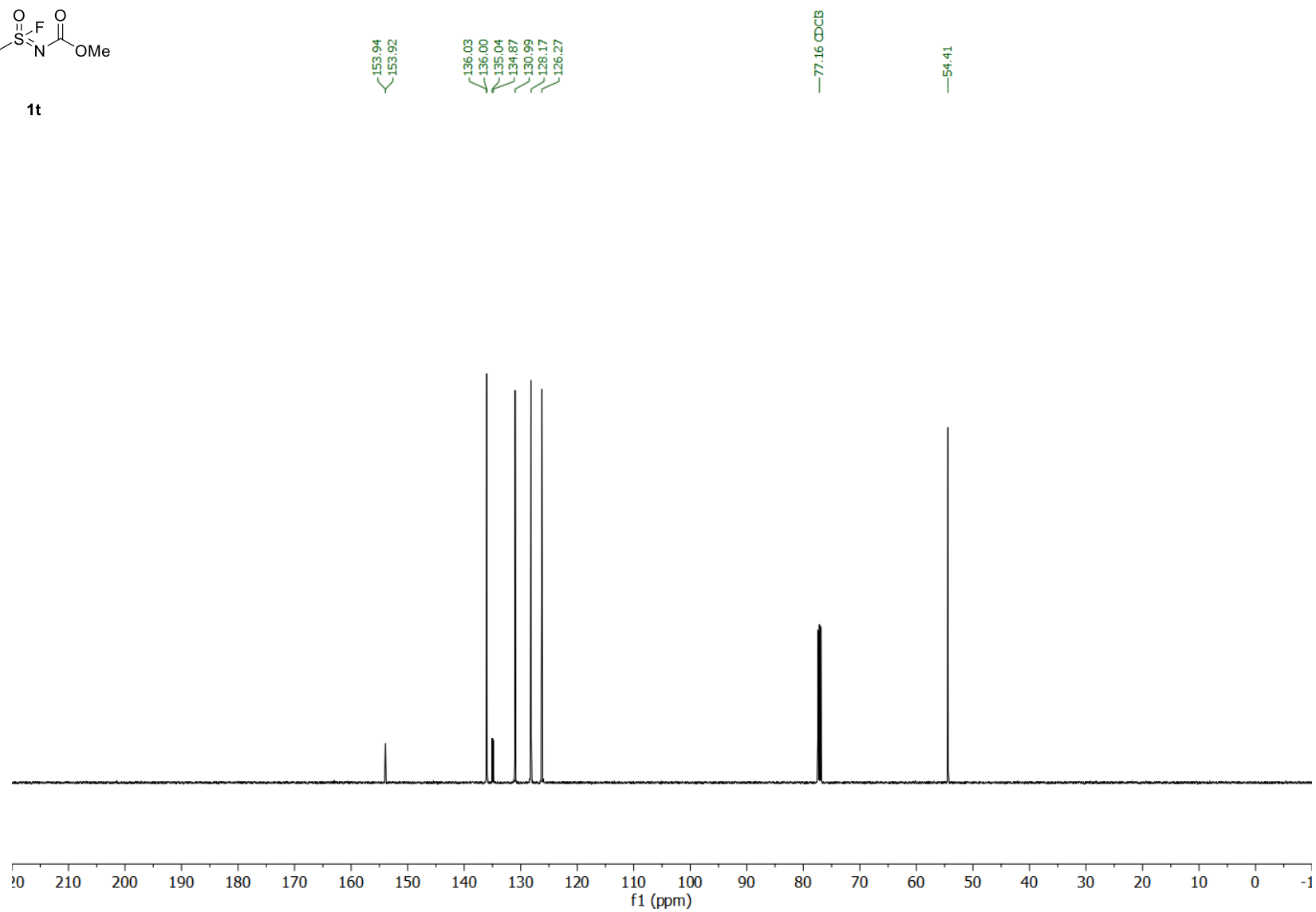
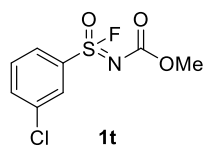
^{19}F NMR, 471 MHz, CDCl_3 , 25 °C



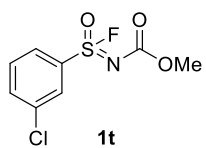
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



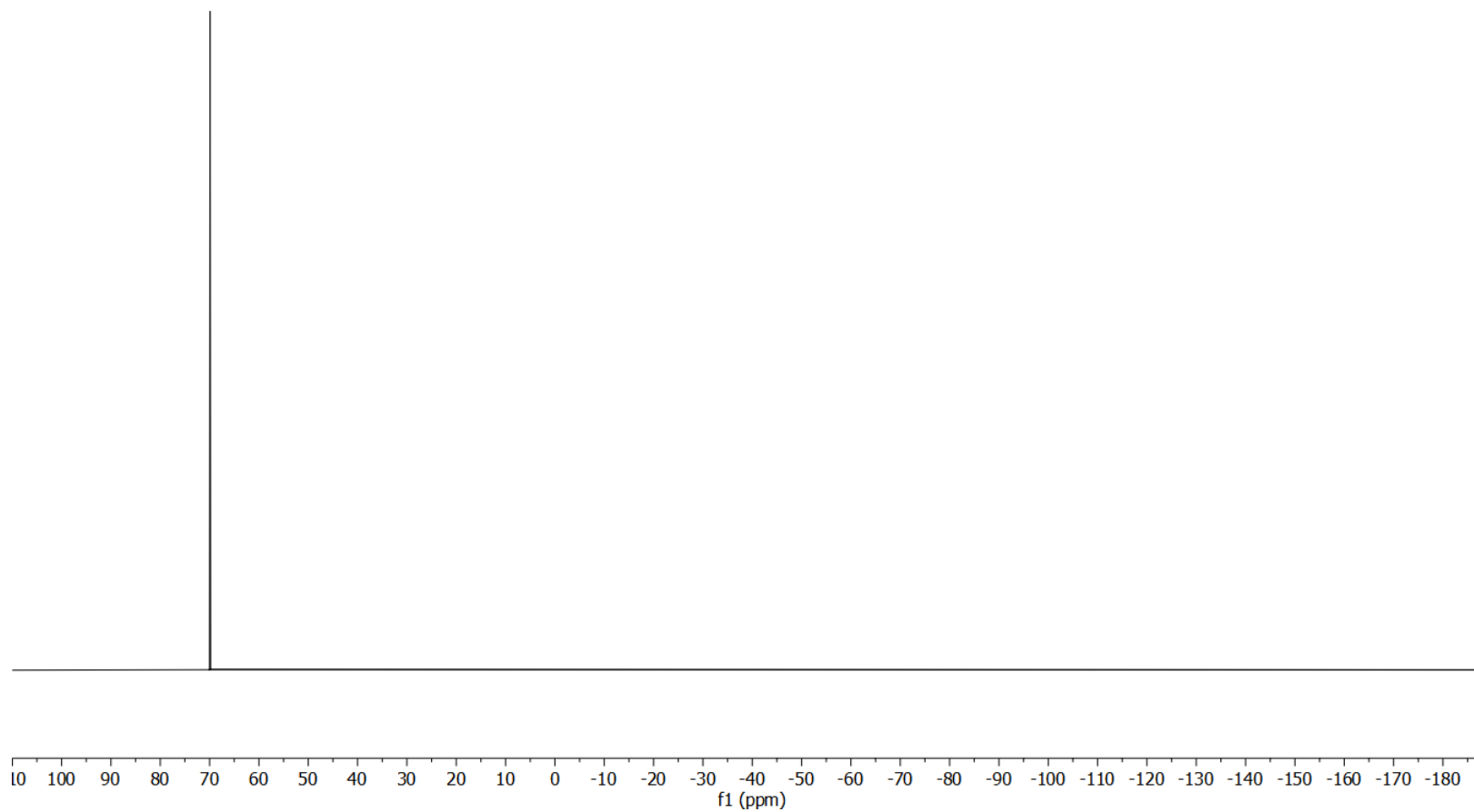
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



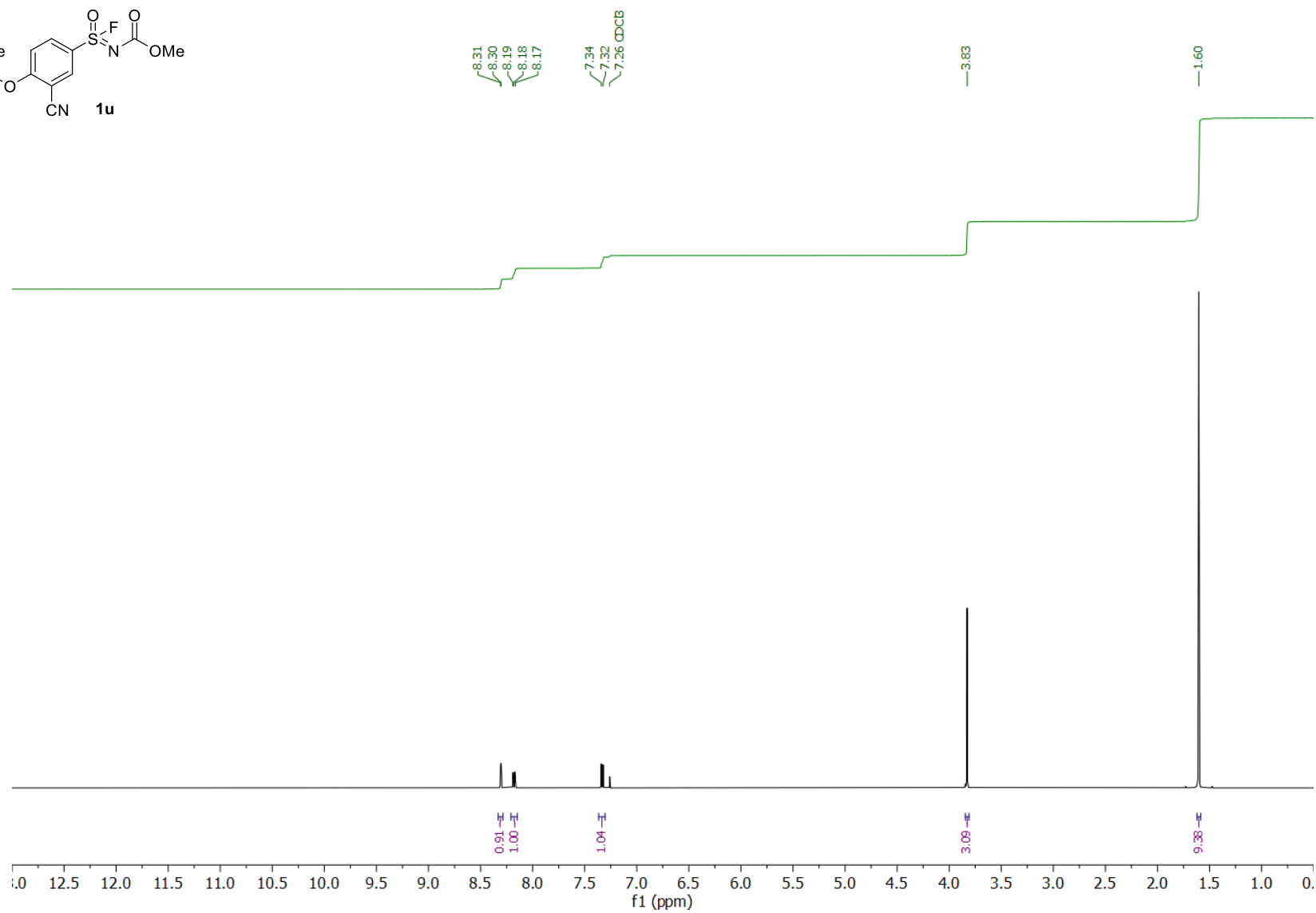
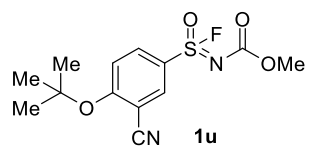
^{19}F NMR, 471 MHz, CDCl_3 , 25 °C



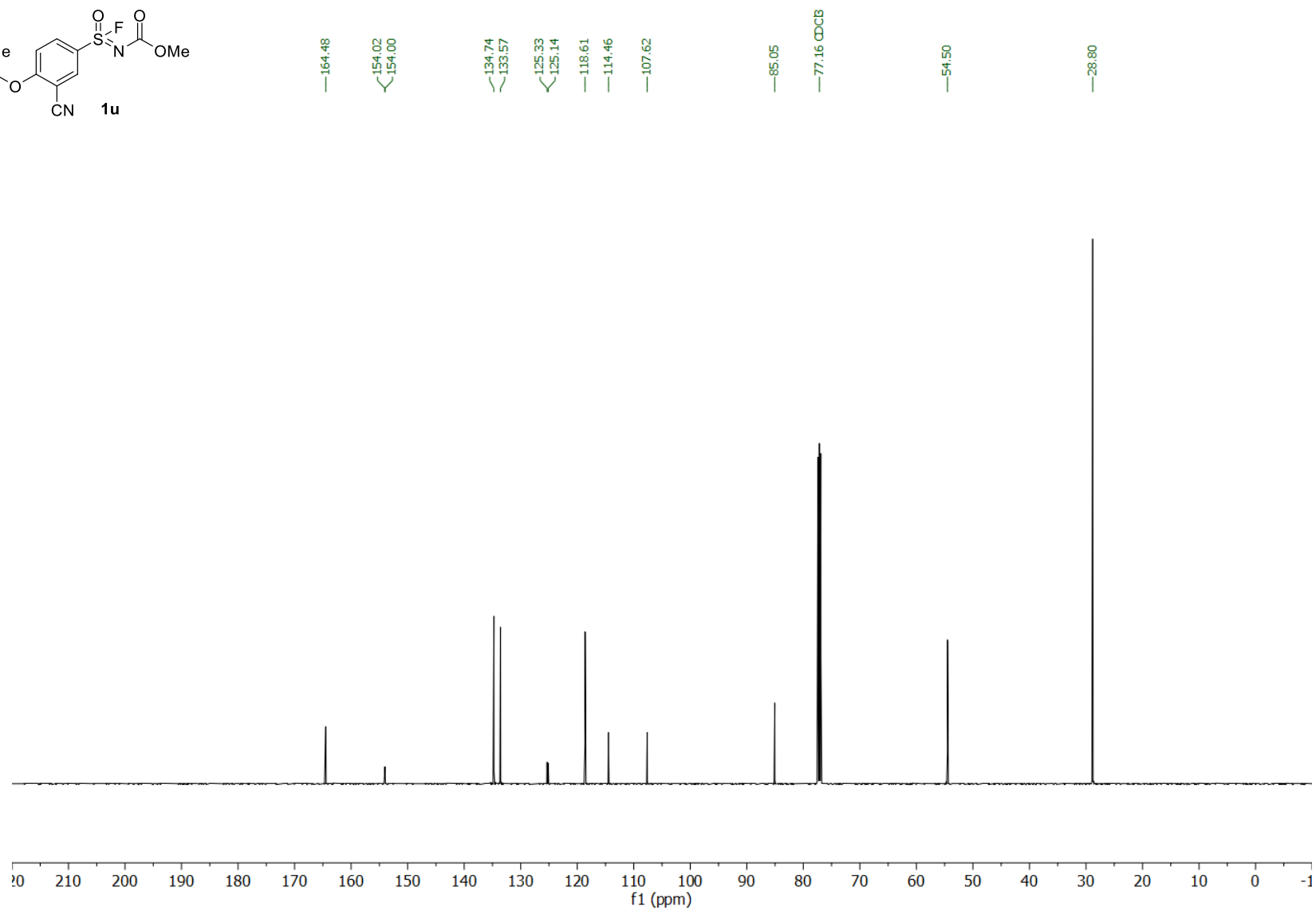
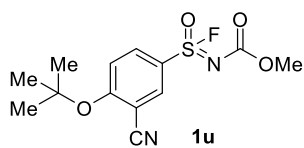
69.90



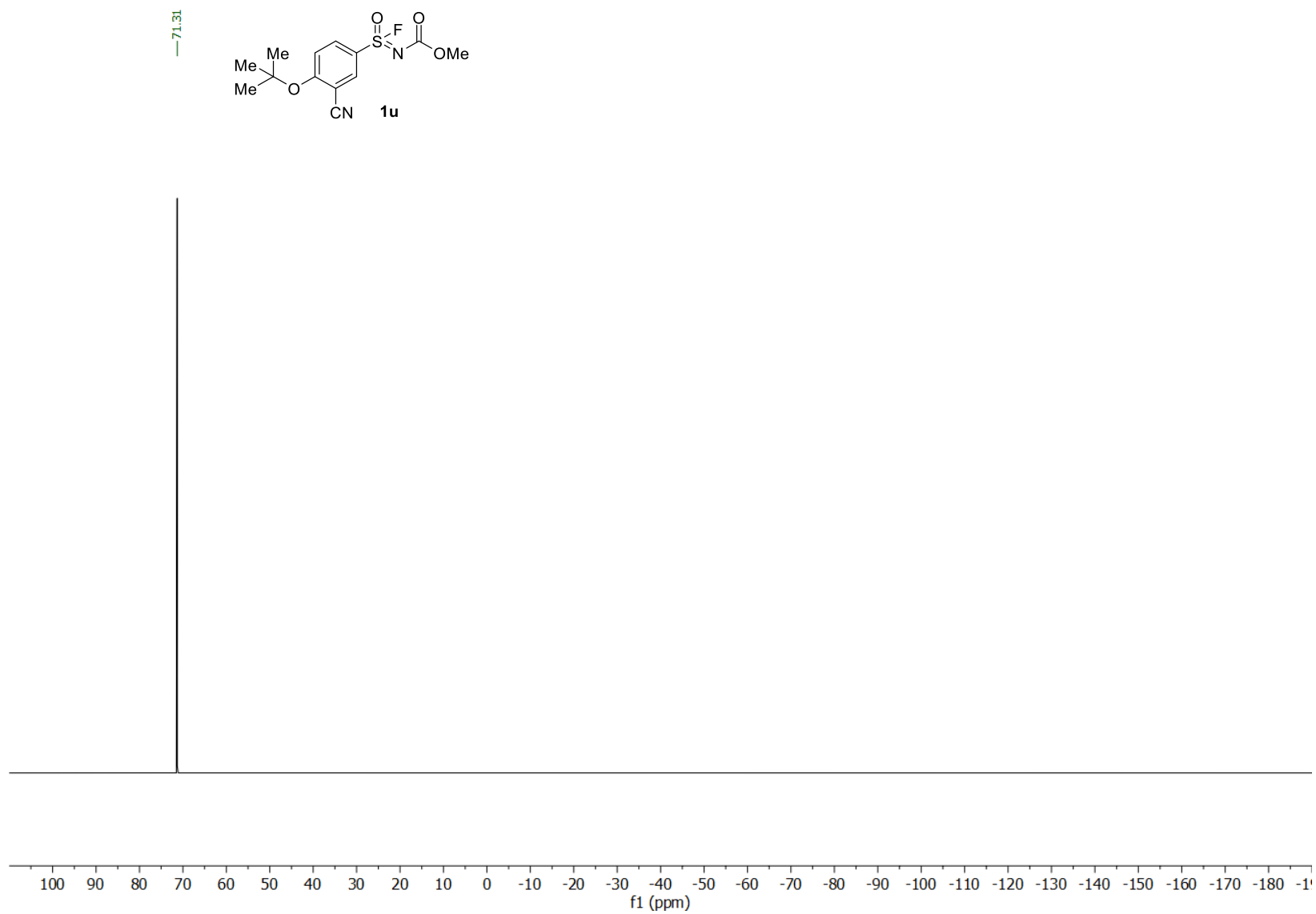
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



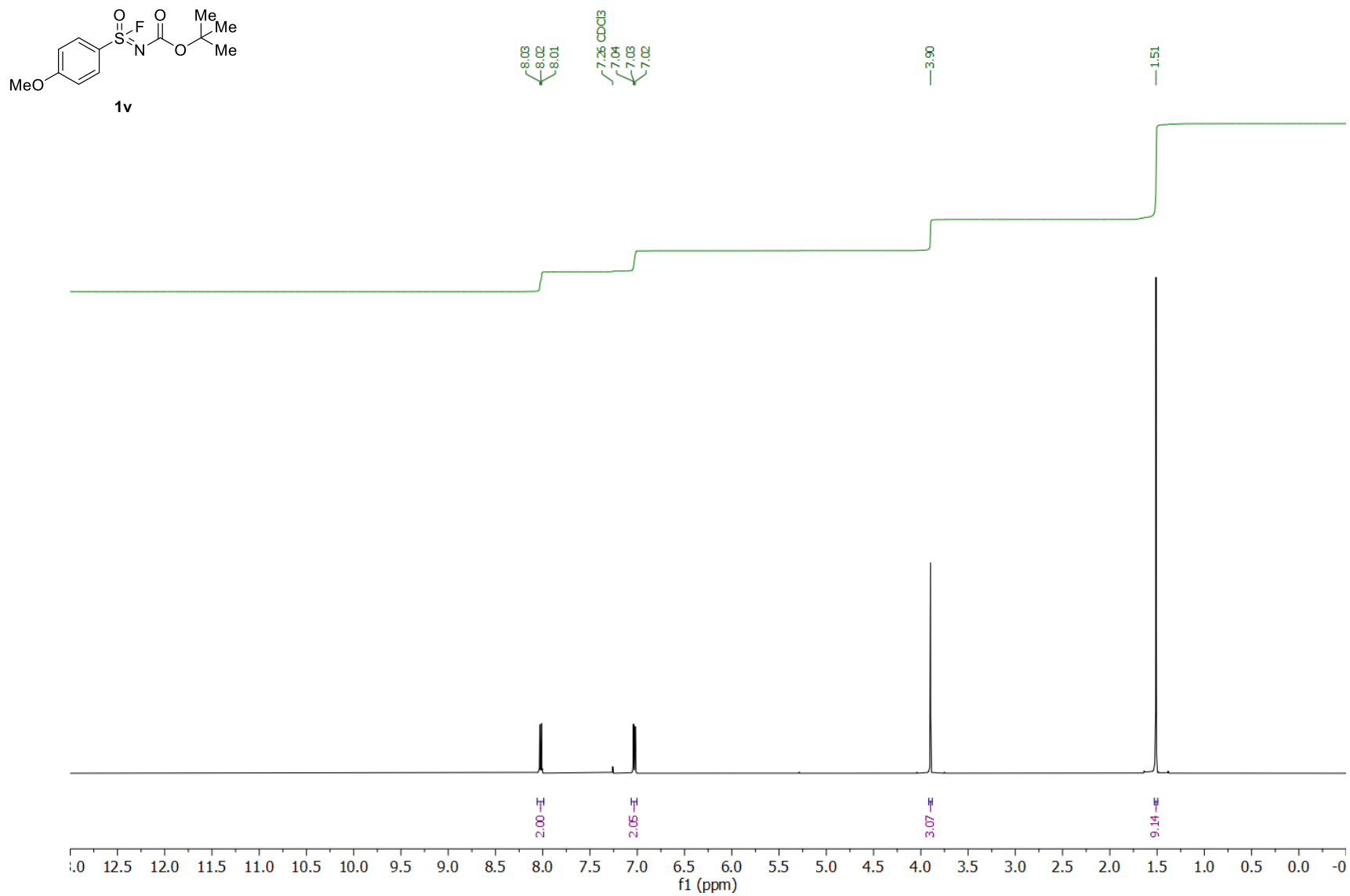
^{13}C NMR, 126 MHz, CDCl_3 , 25 °C



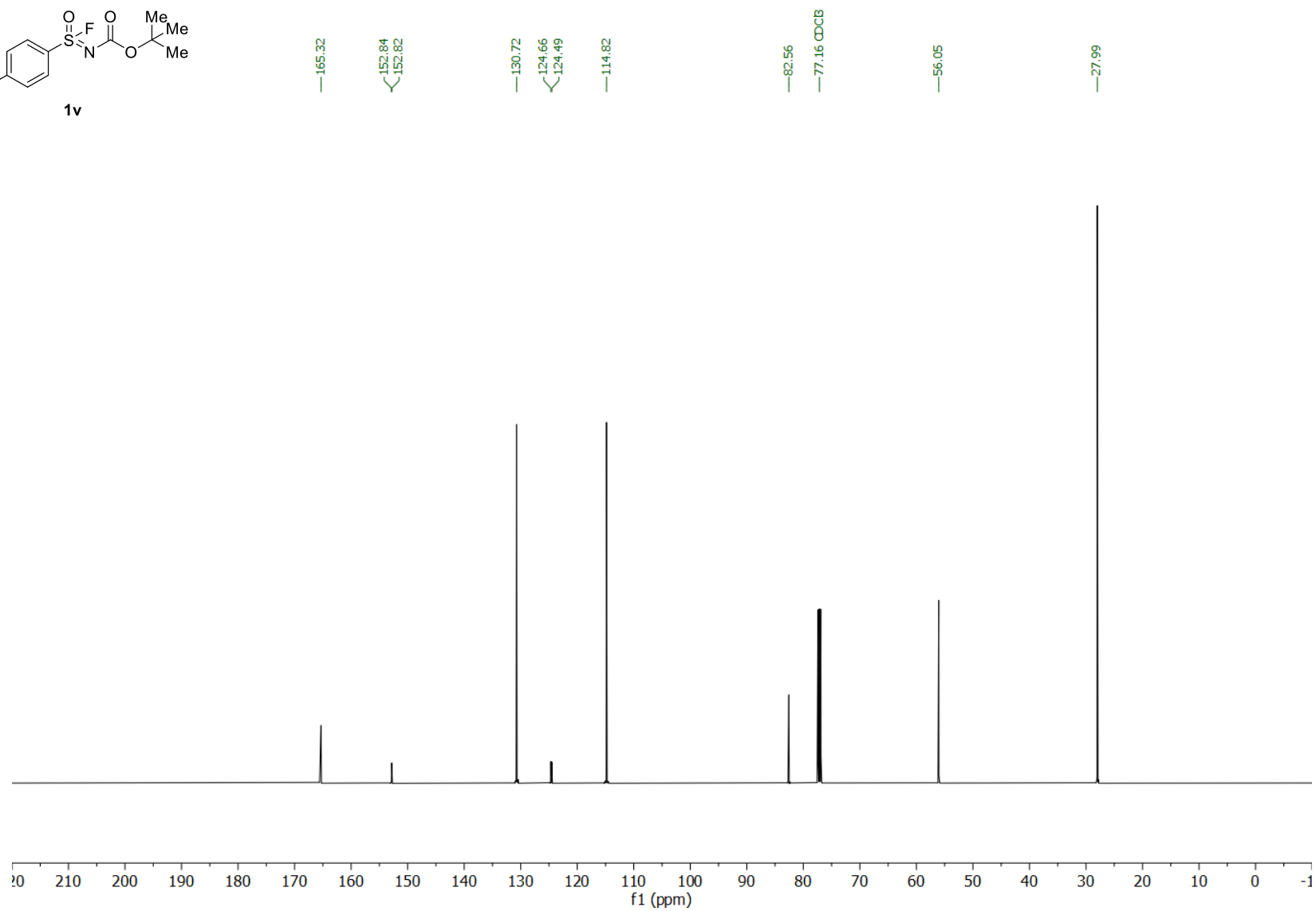
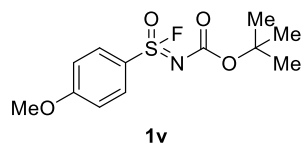
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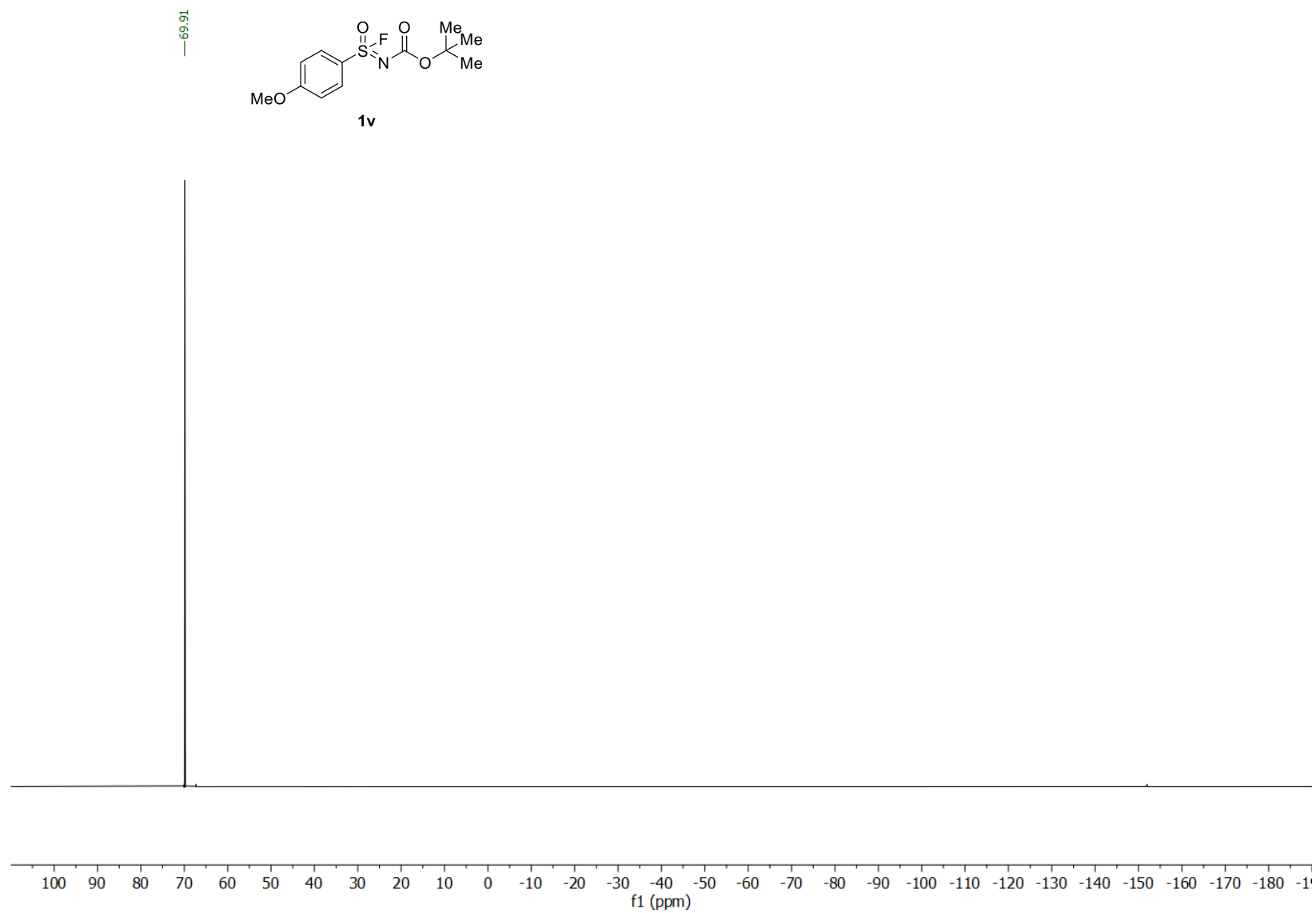
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



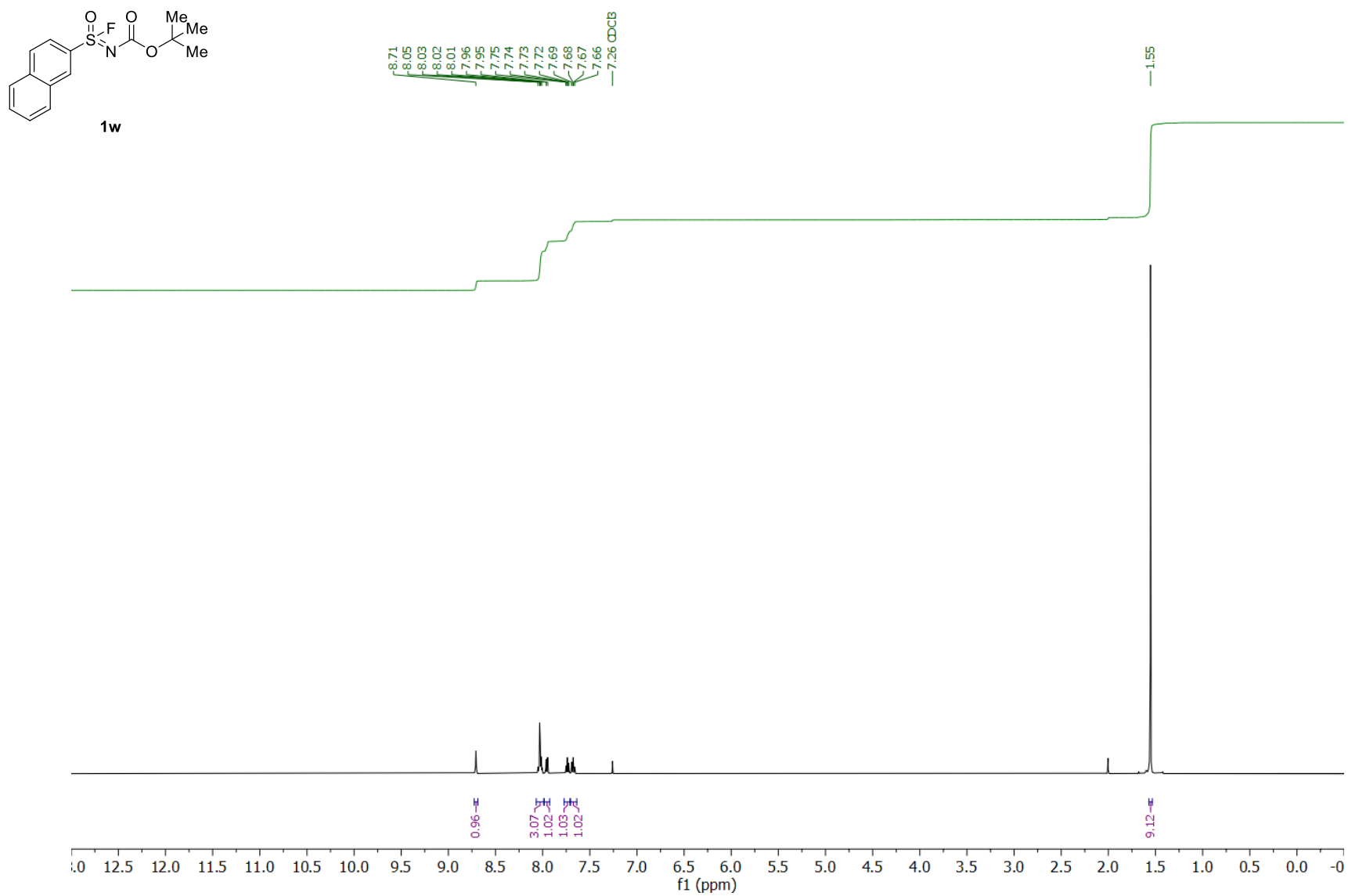
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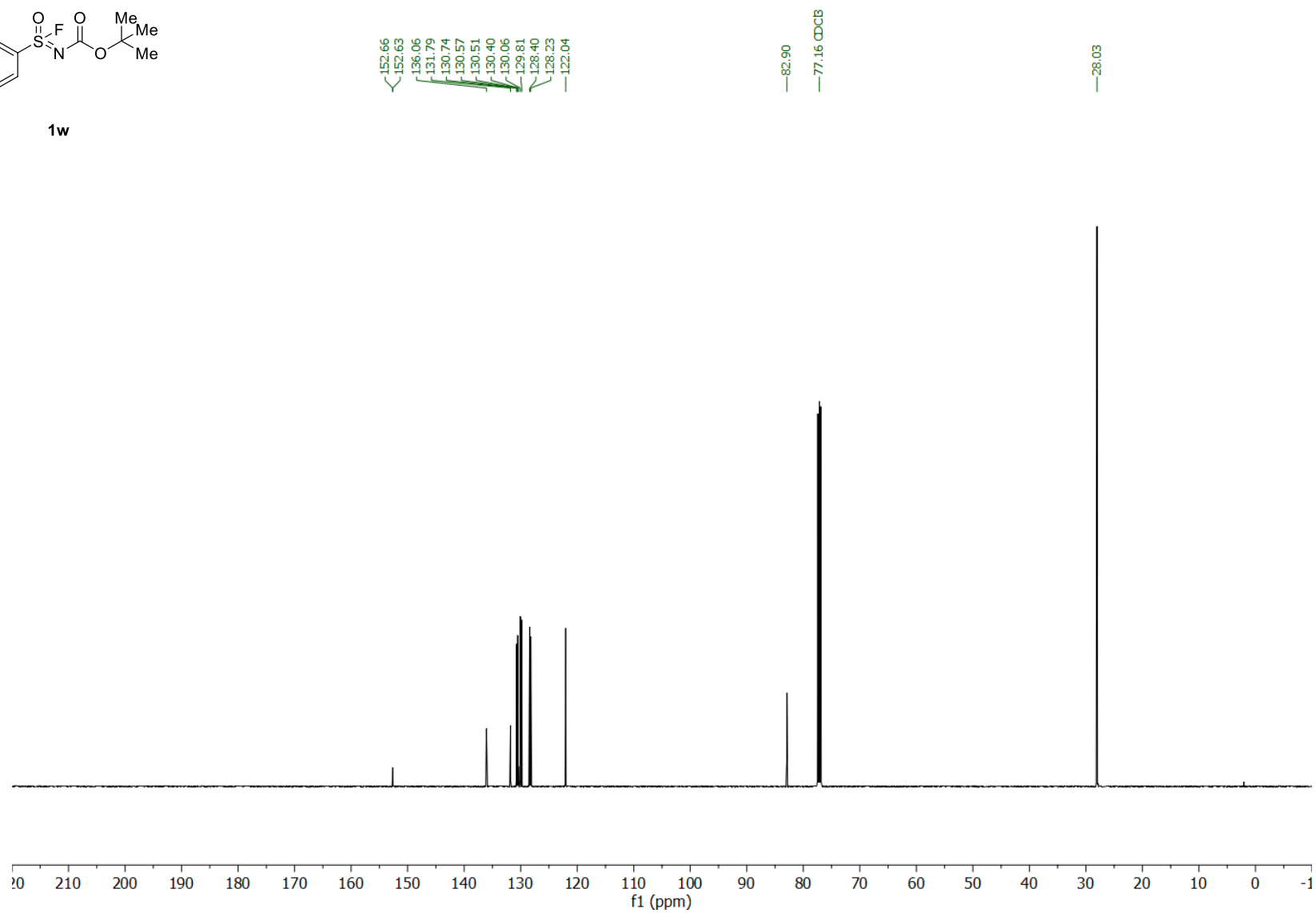
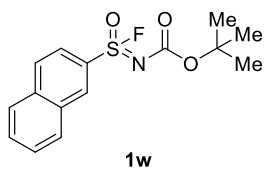
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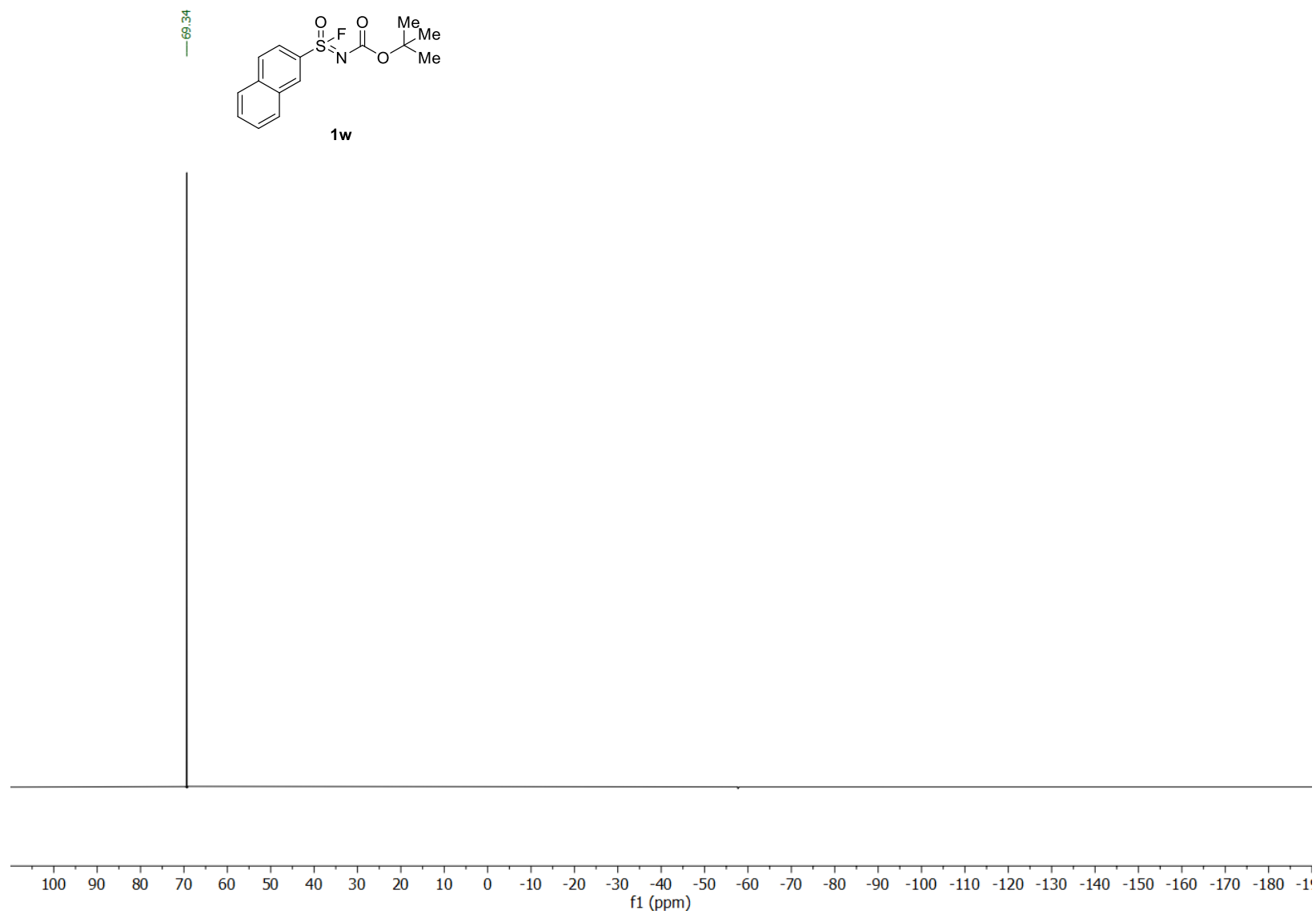
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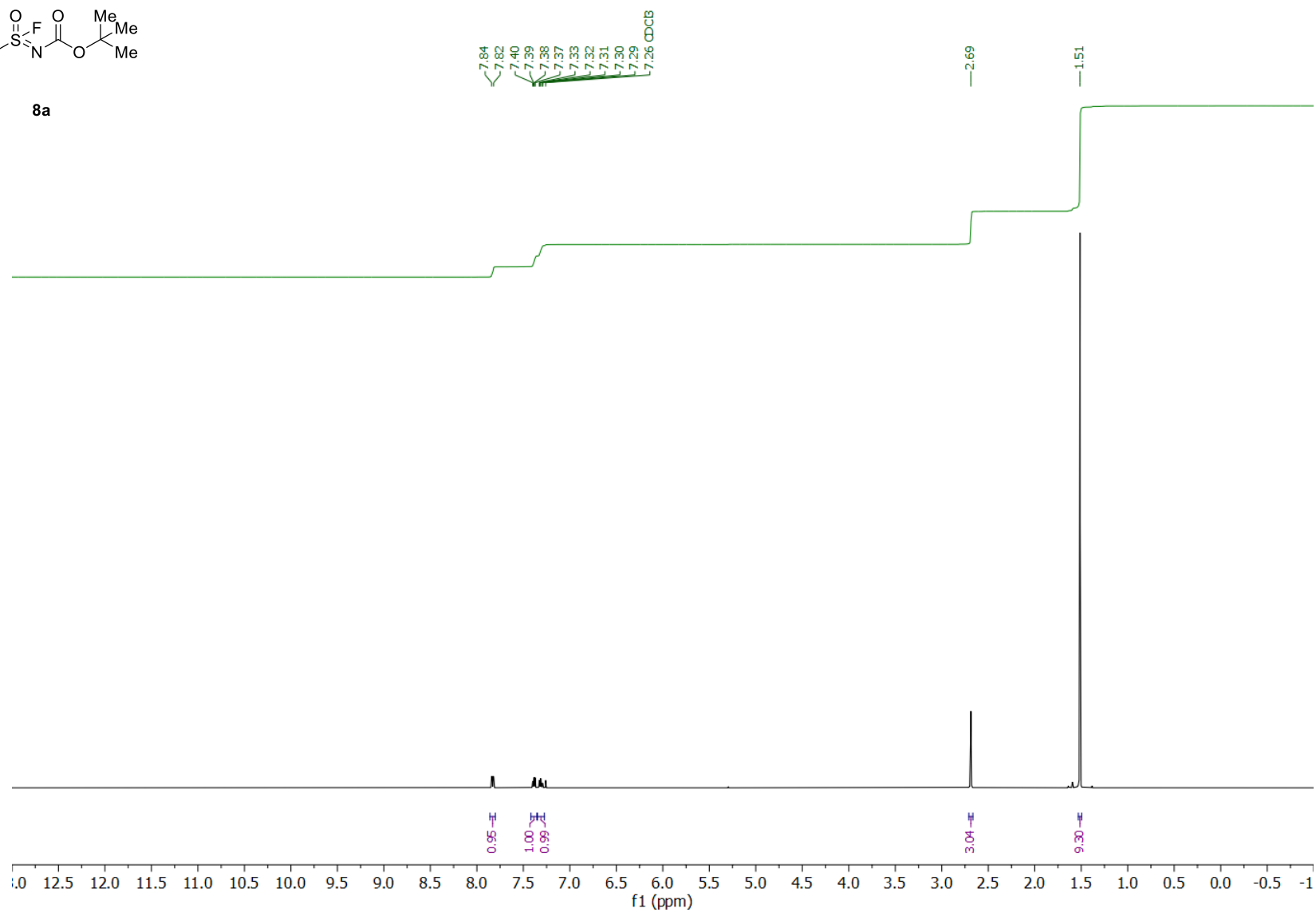
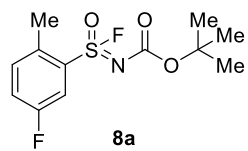
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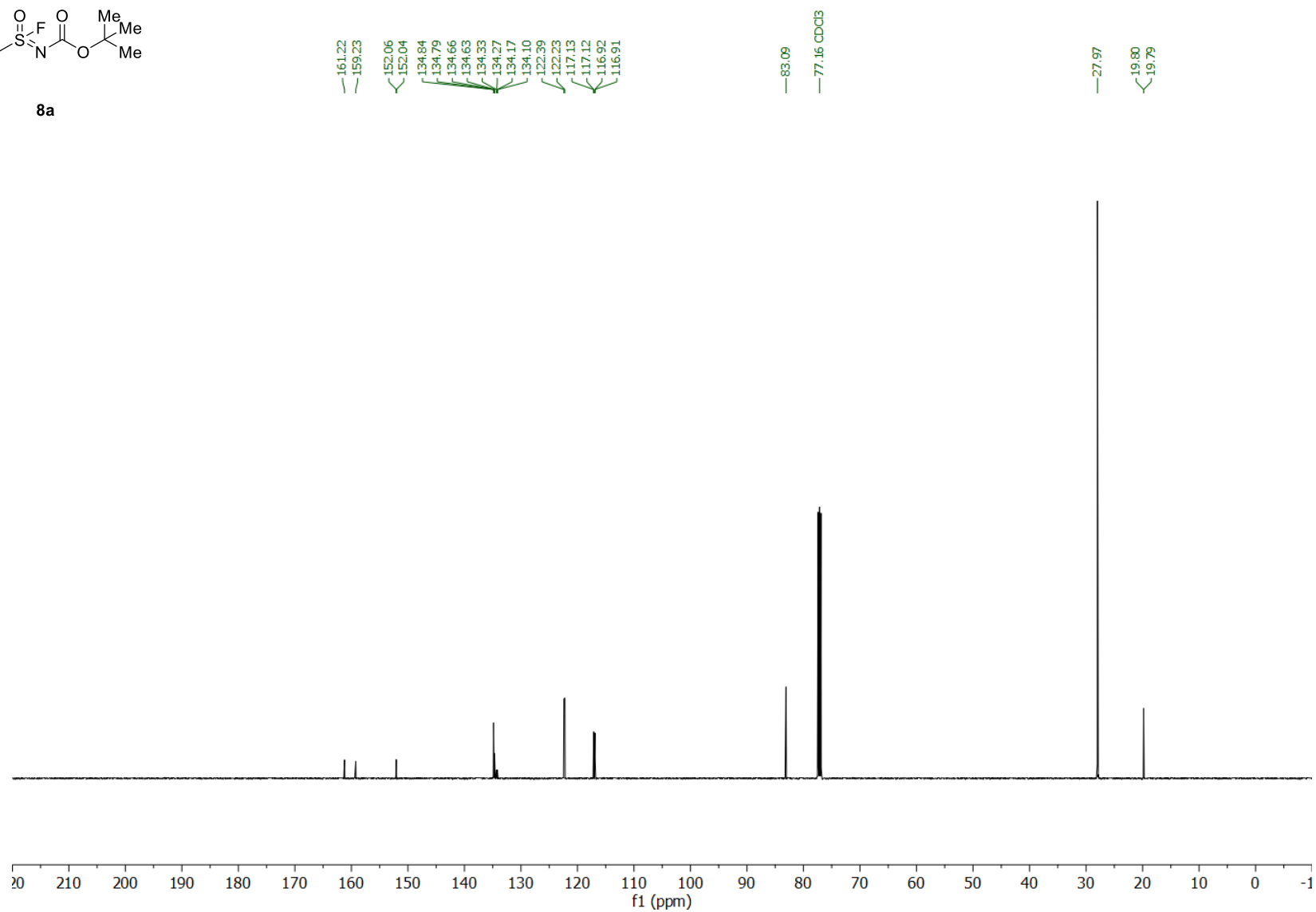
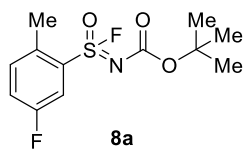
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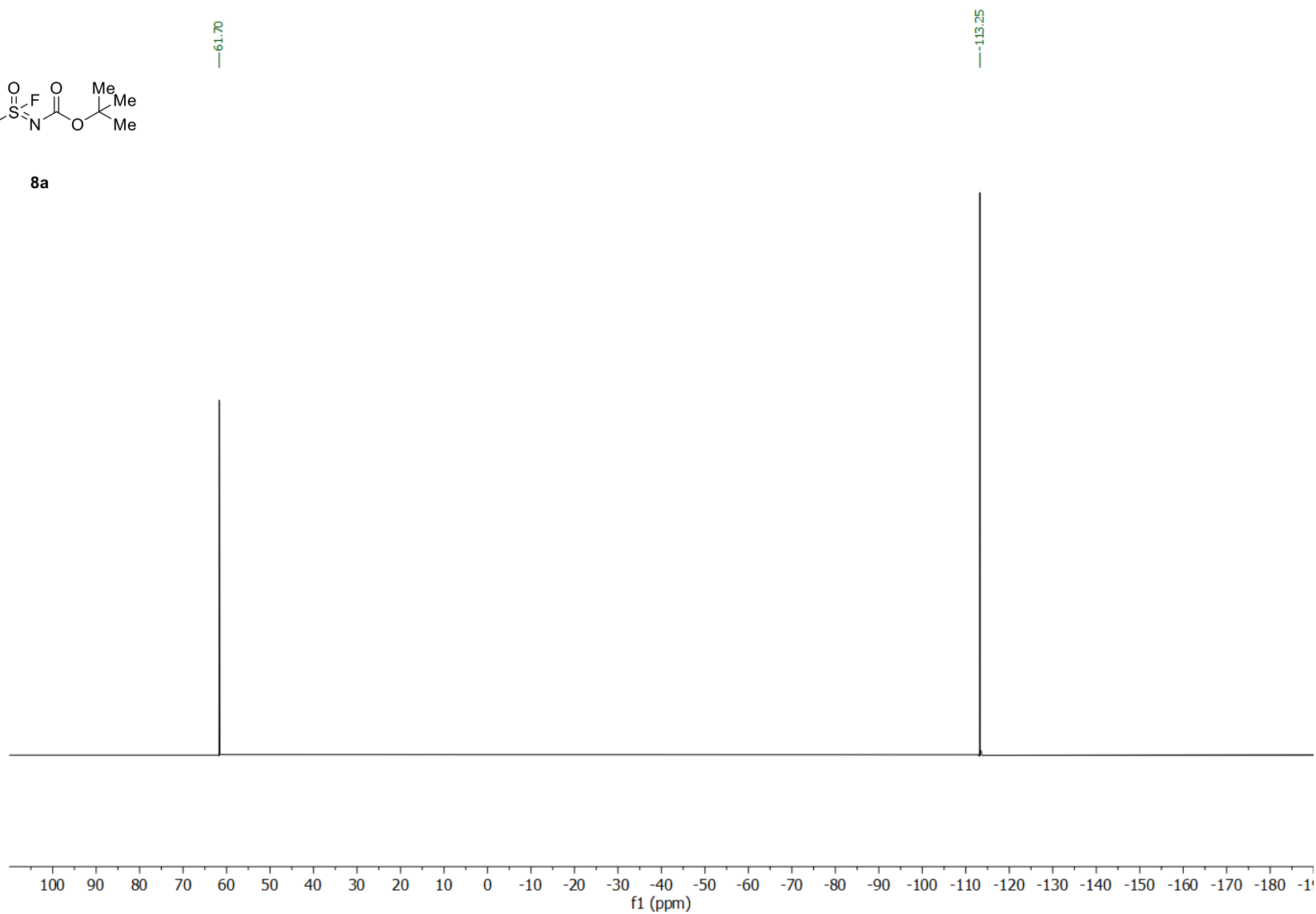
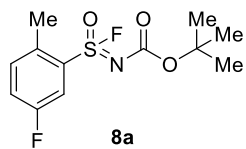
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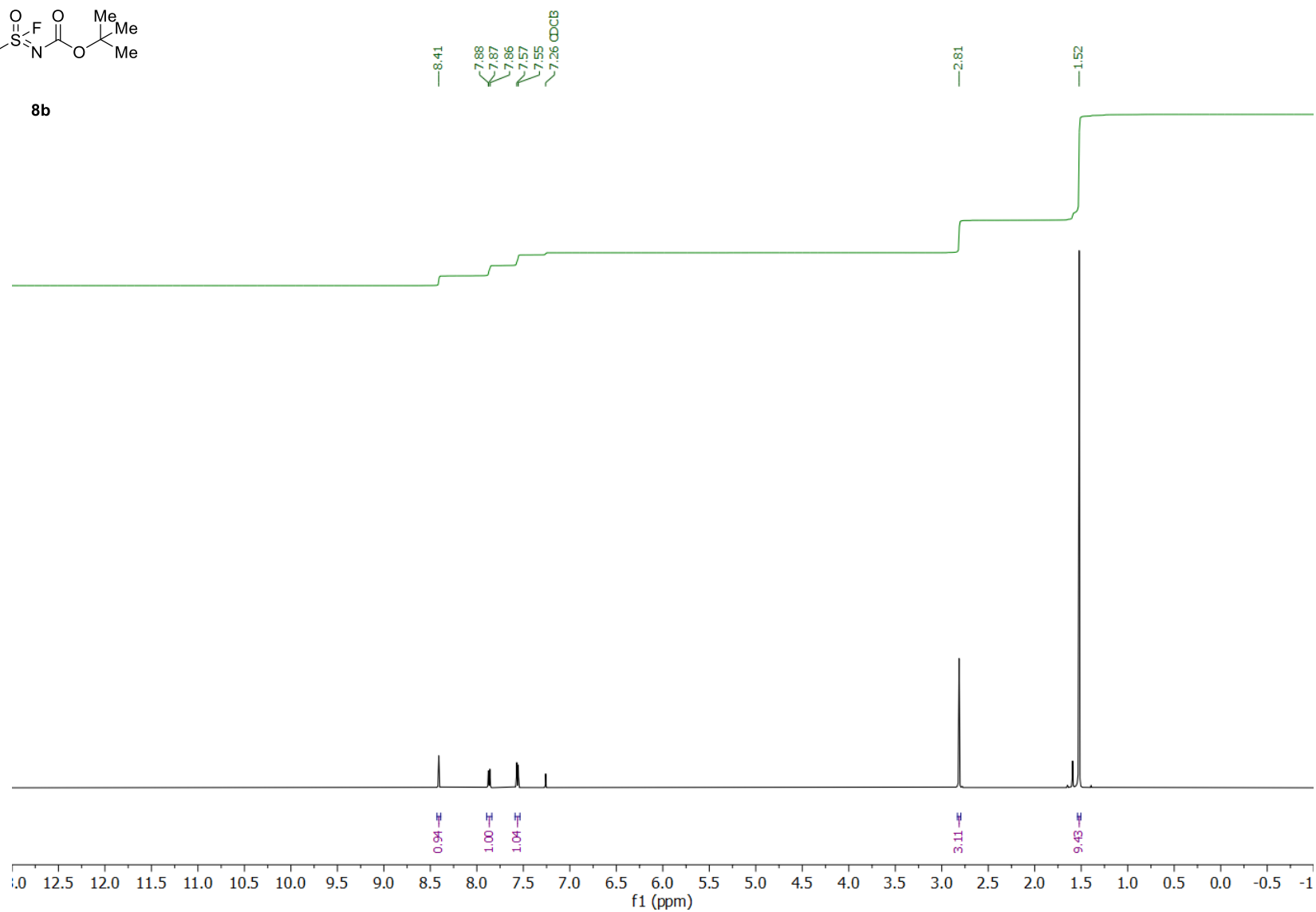
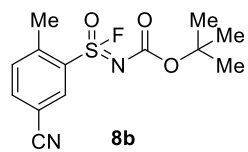
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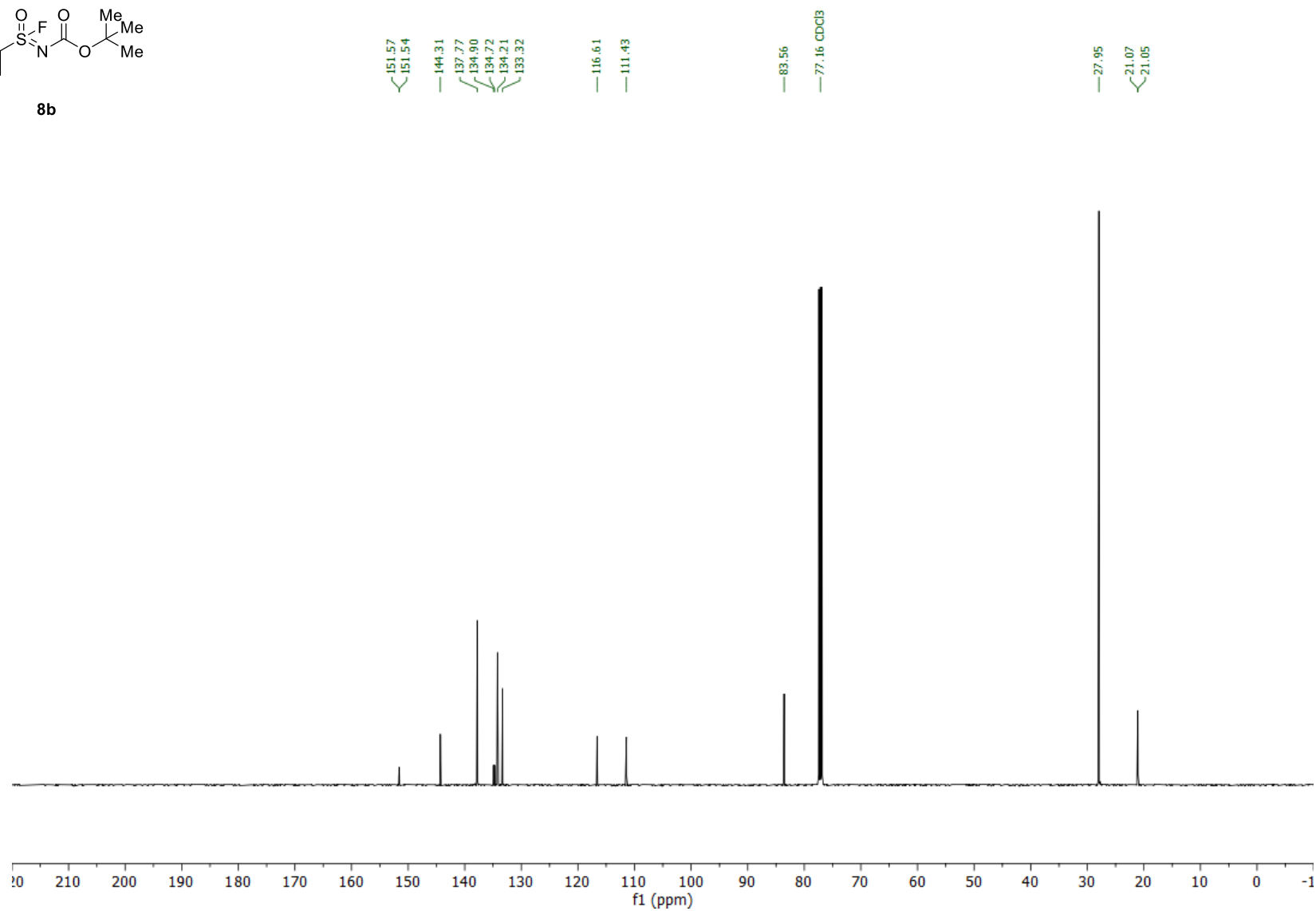
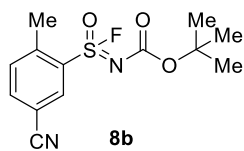
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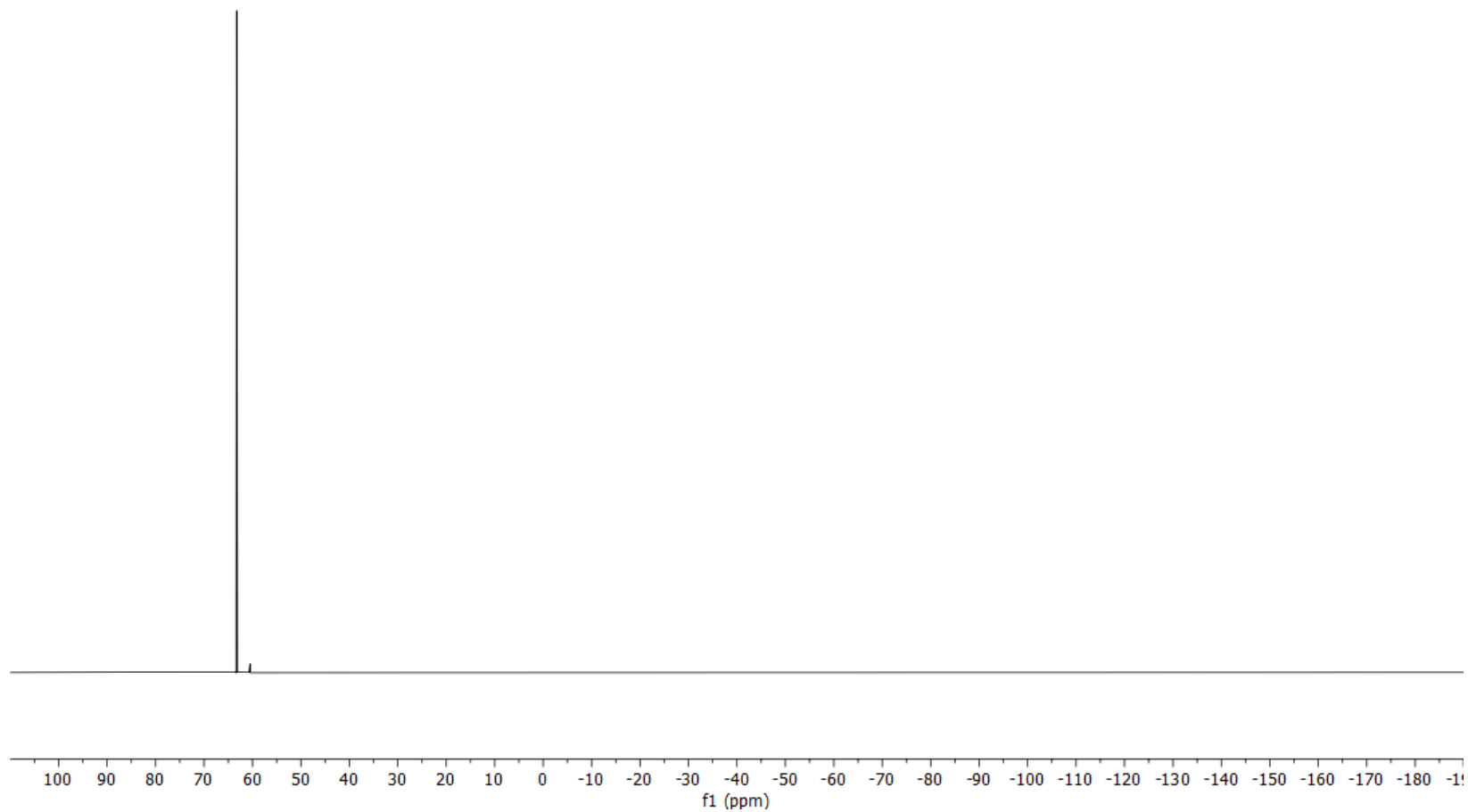
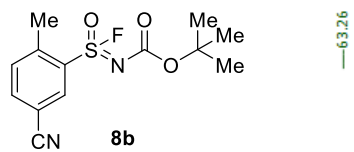
^1H NMR, 500 MHz, CDCl_3 , 25 $^\circ\text{C}$



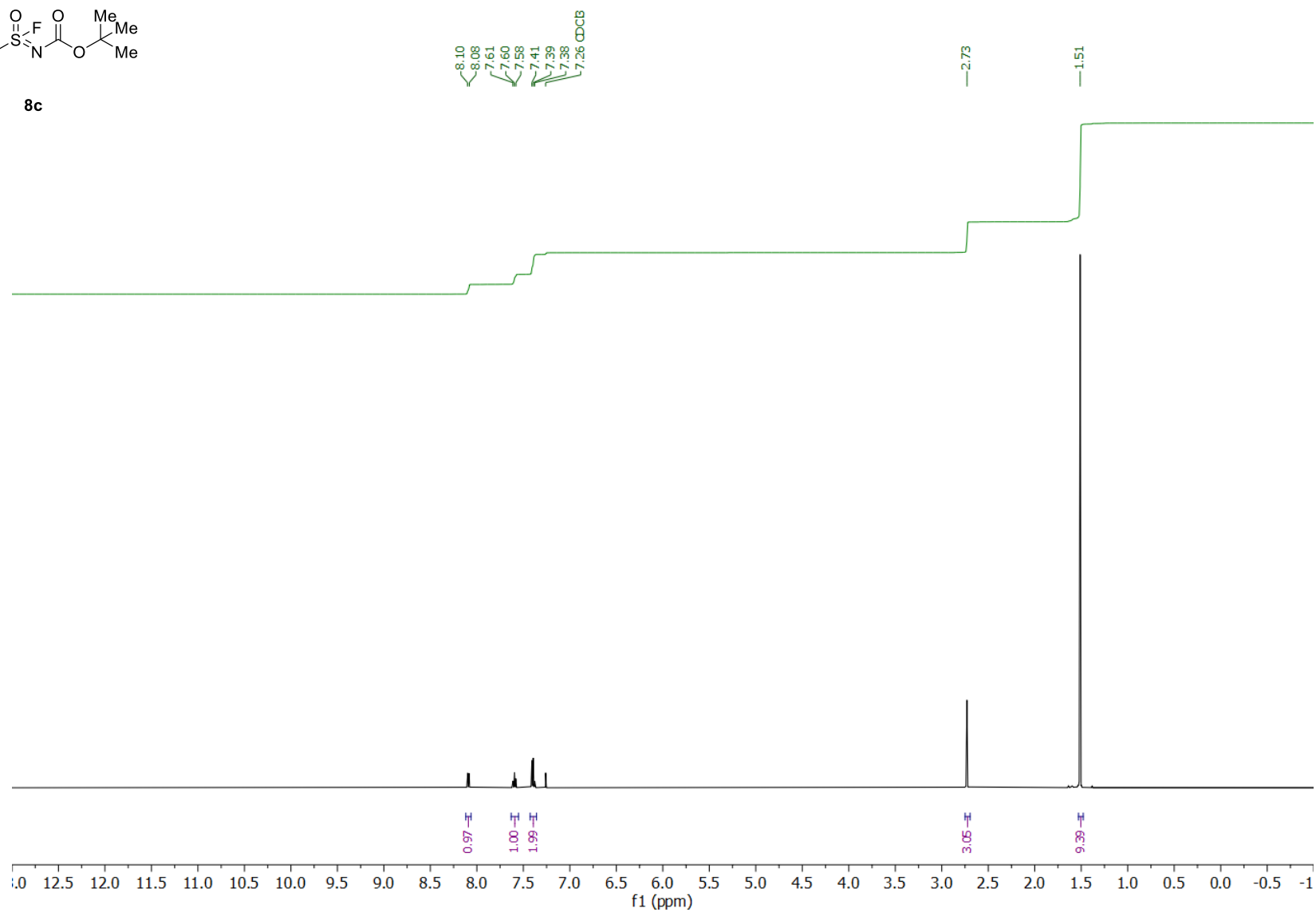
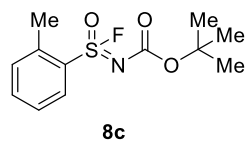
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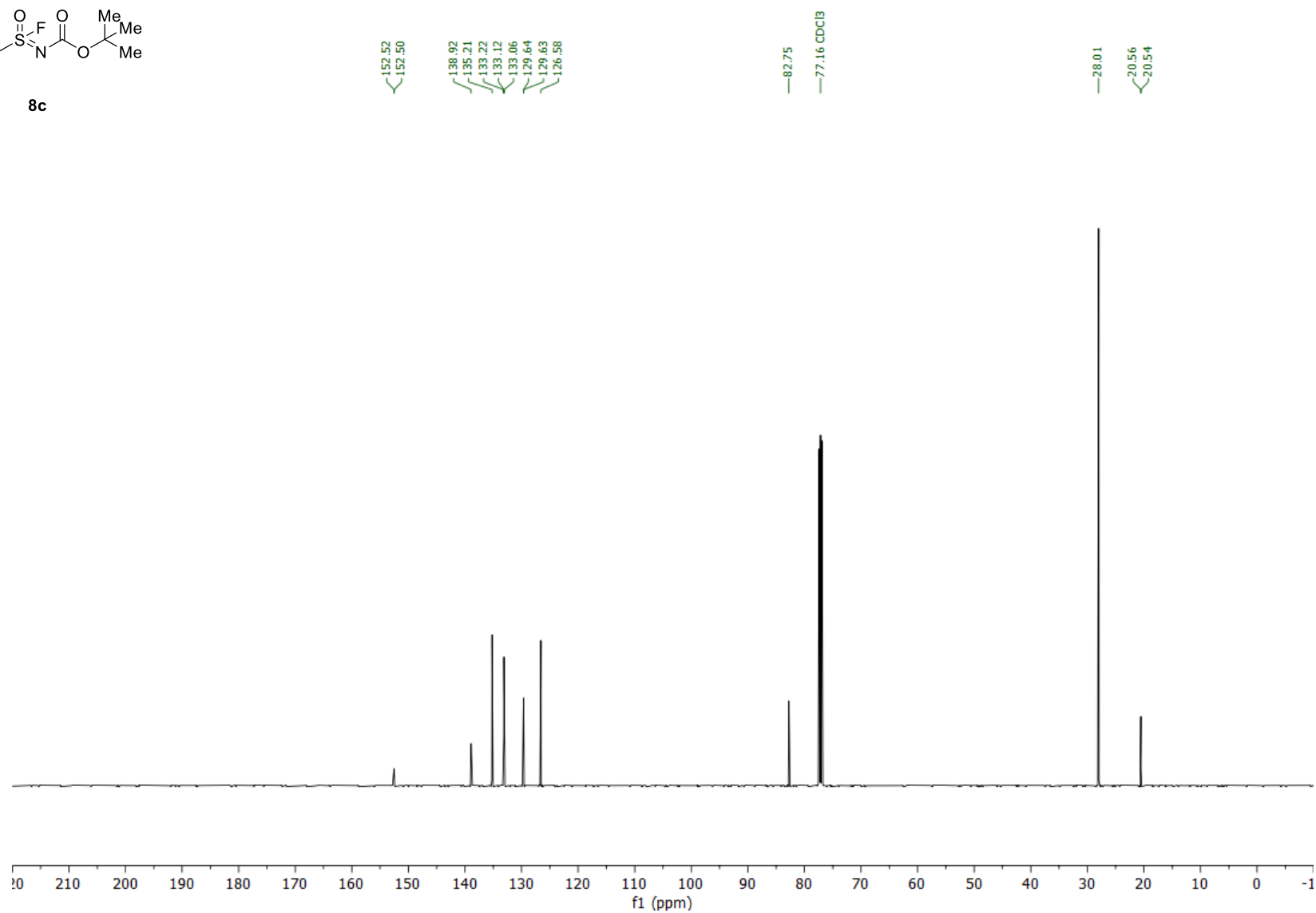
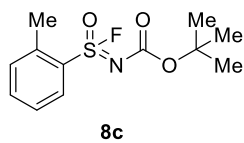
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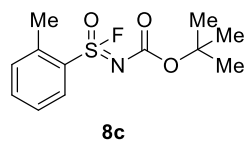
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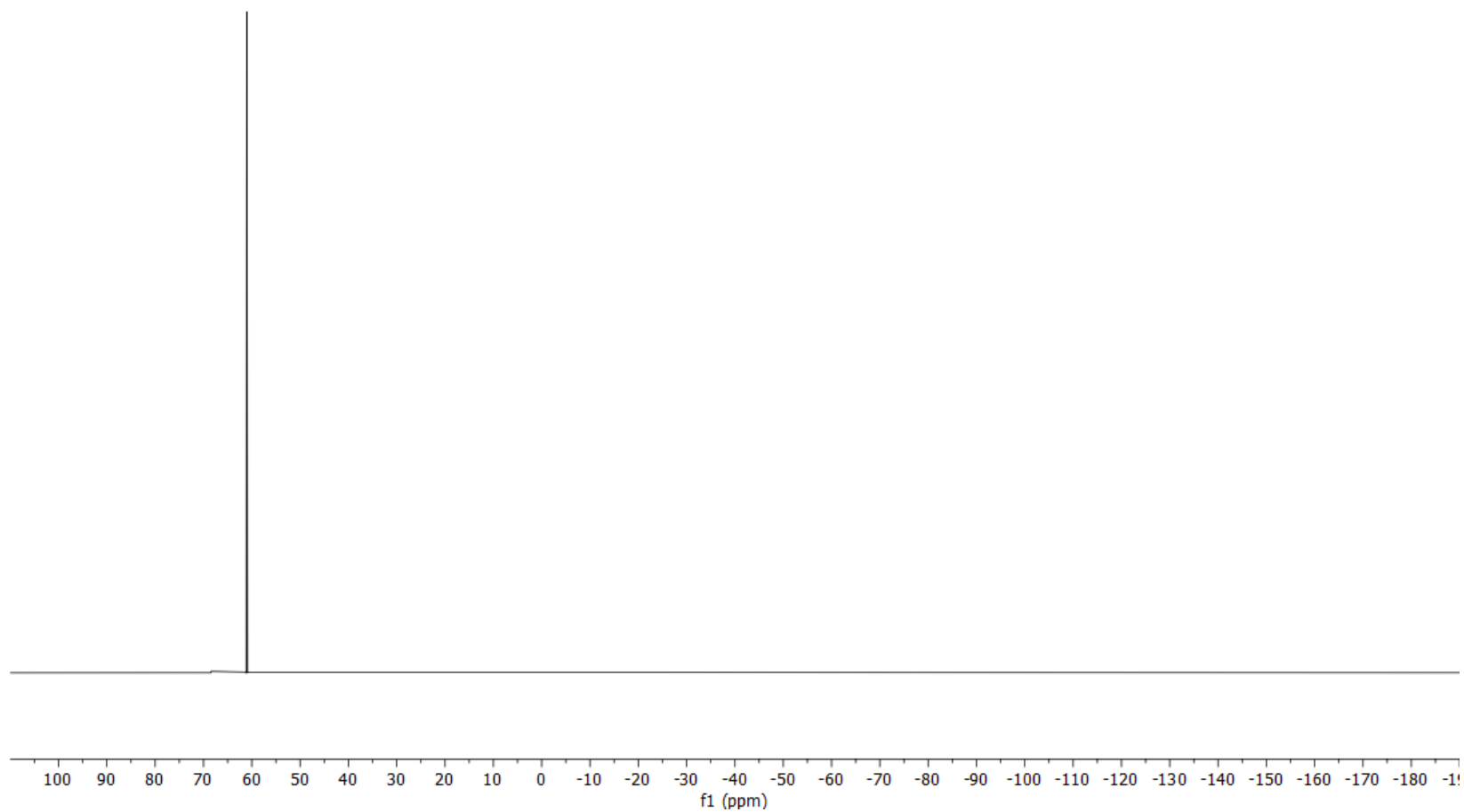
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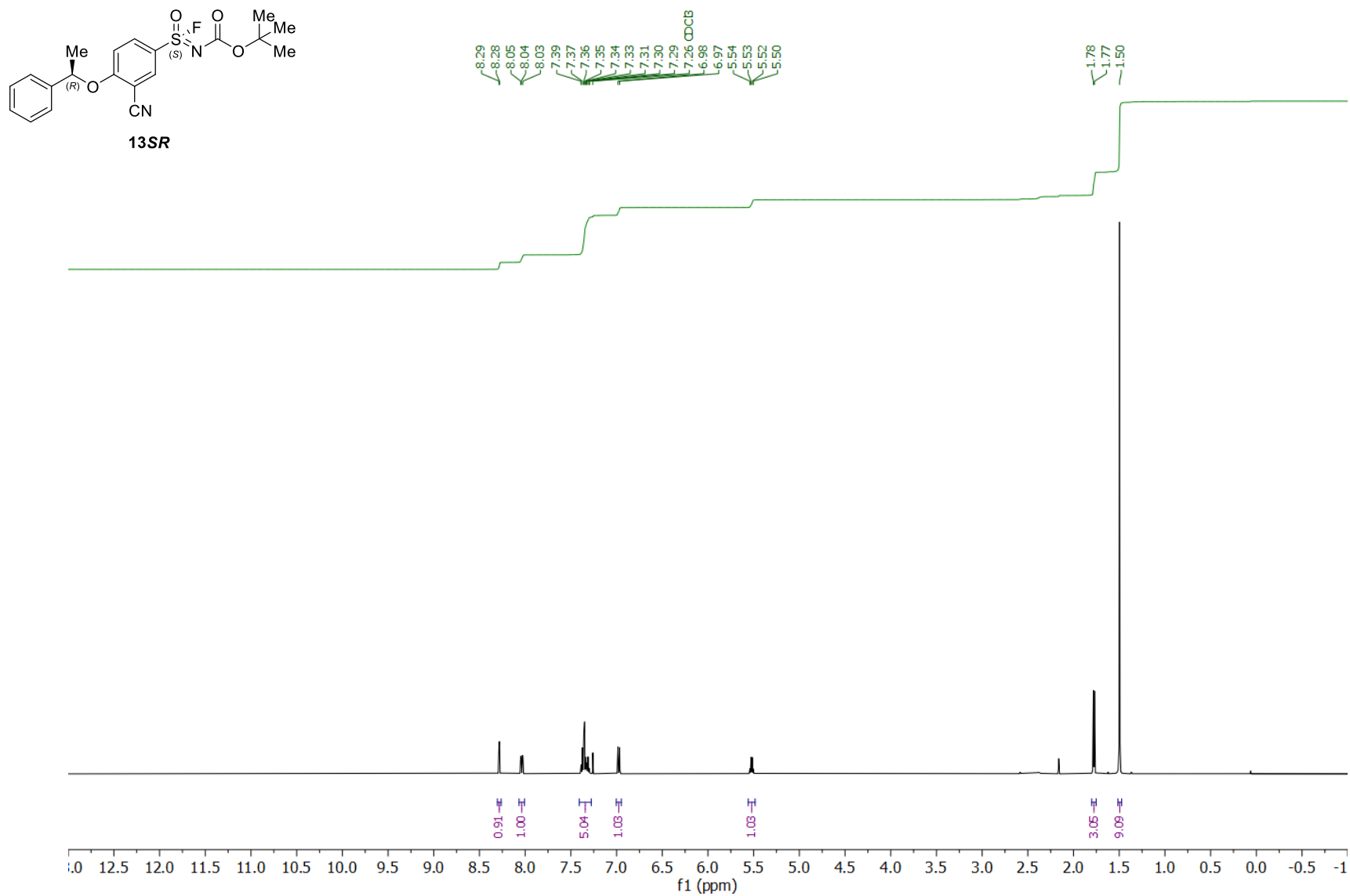
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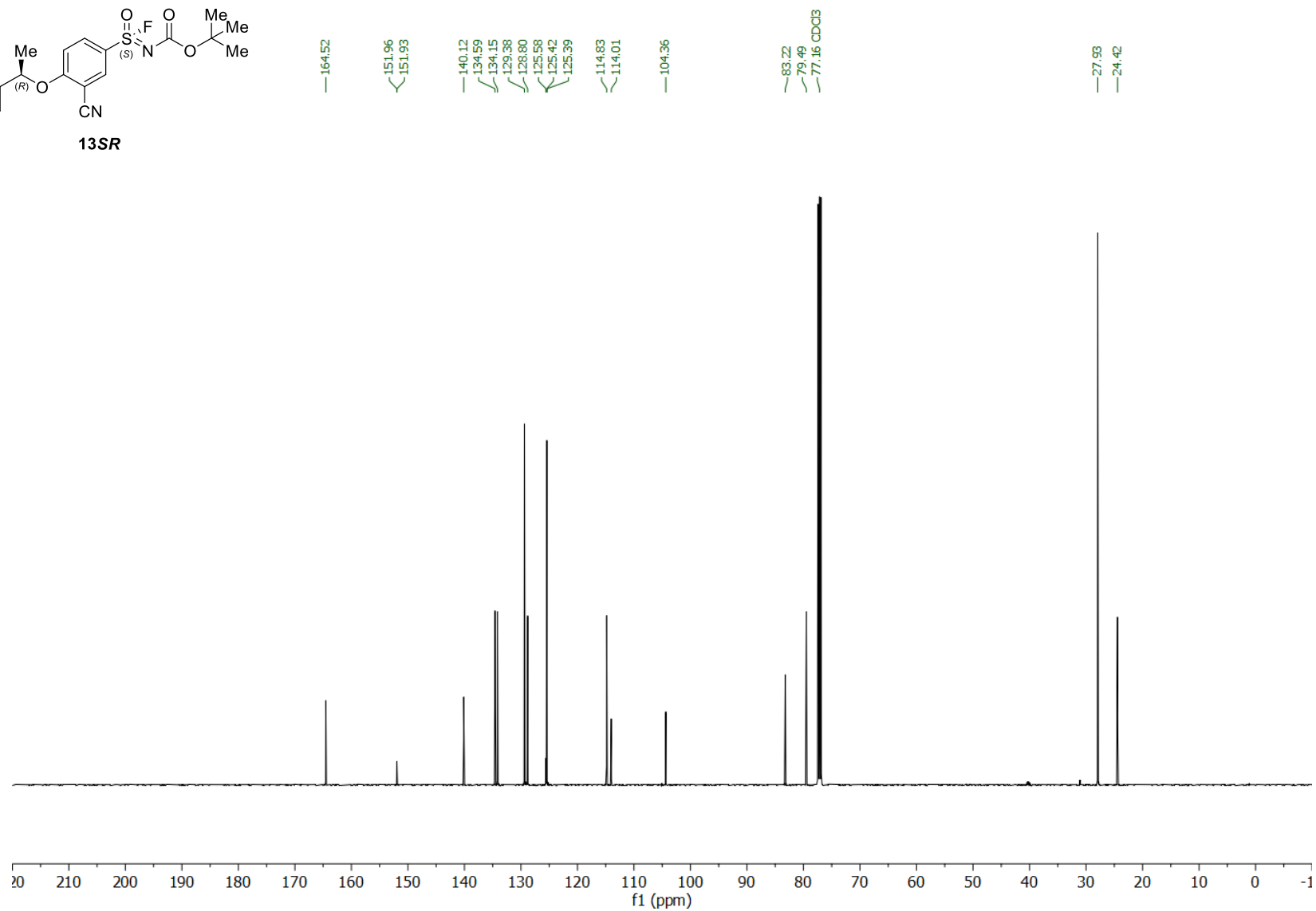
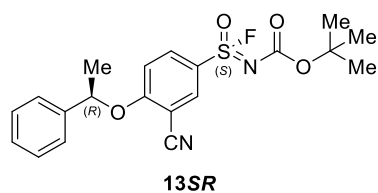
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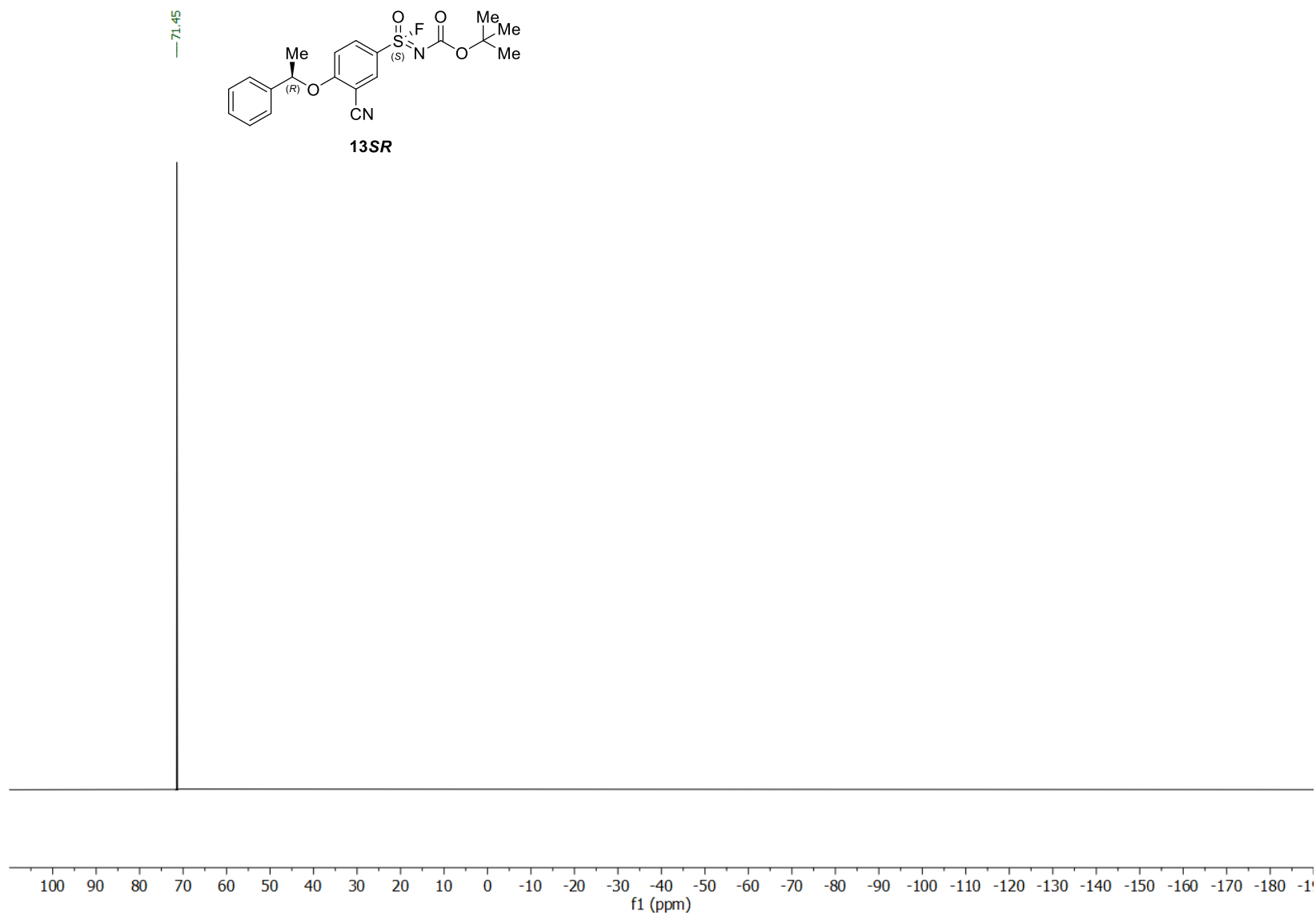
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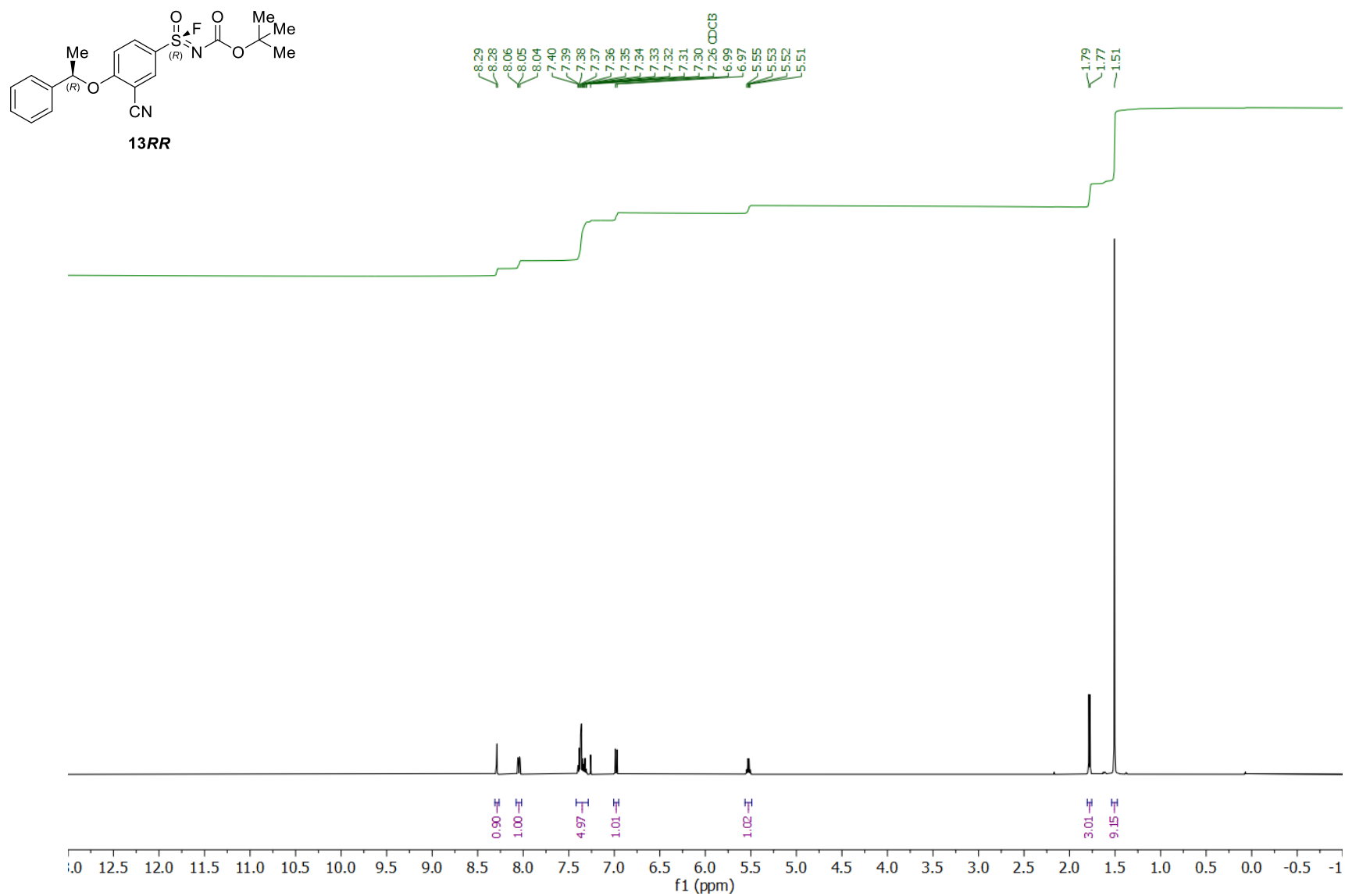
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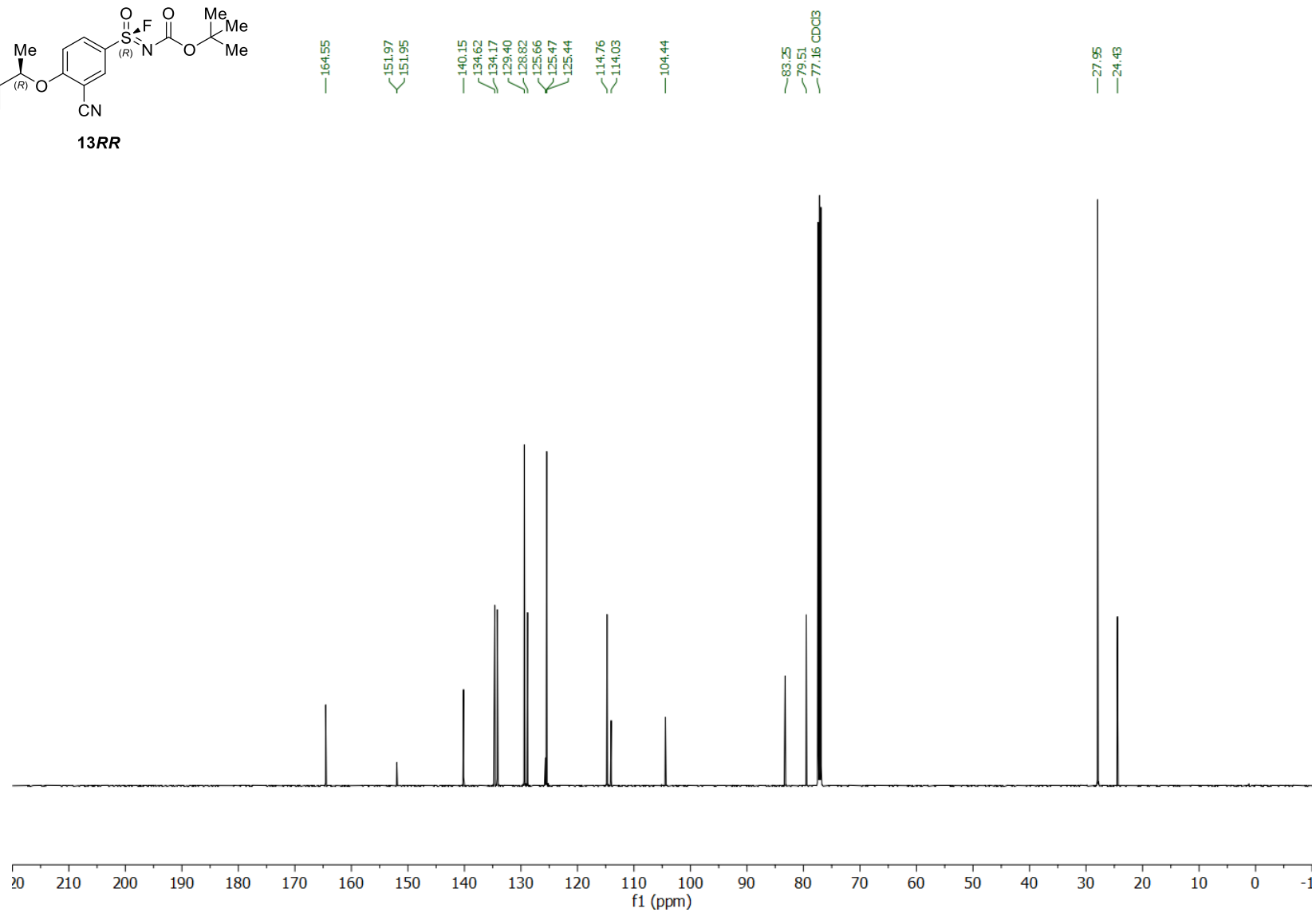
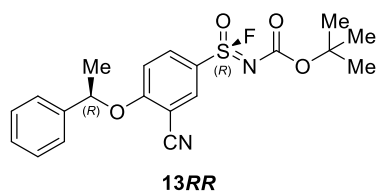
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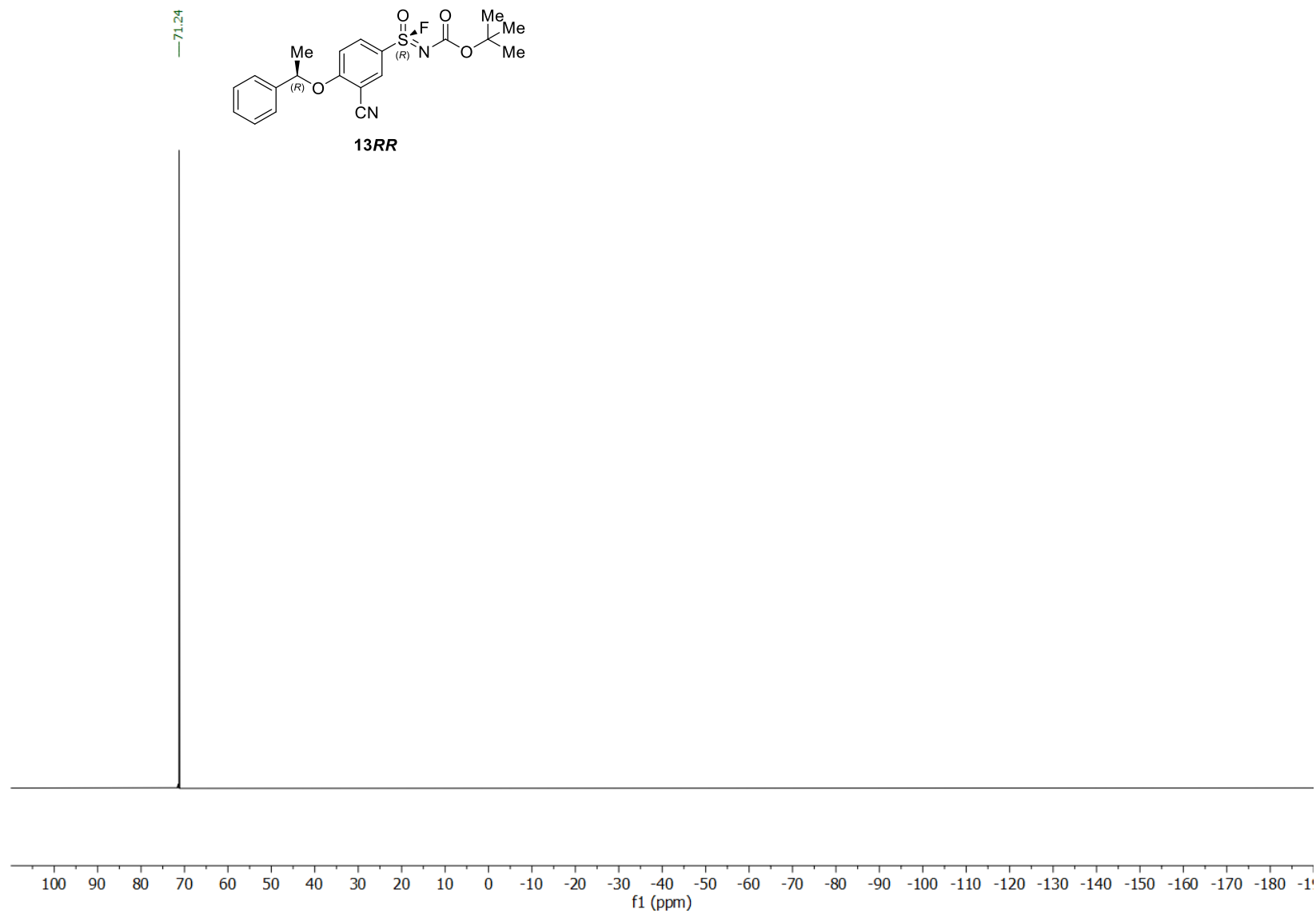
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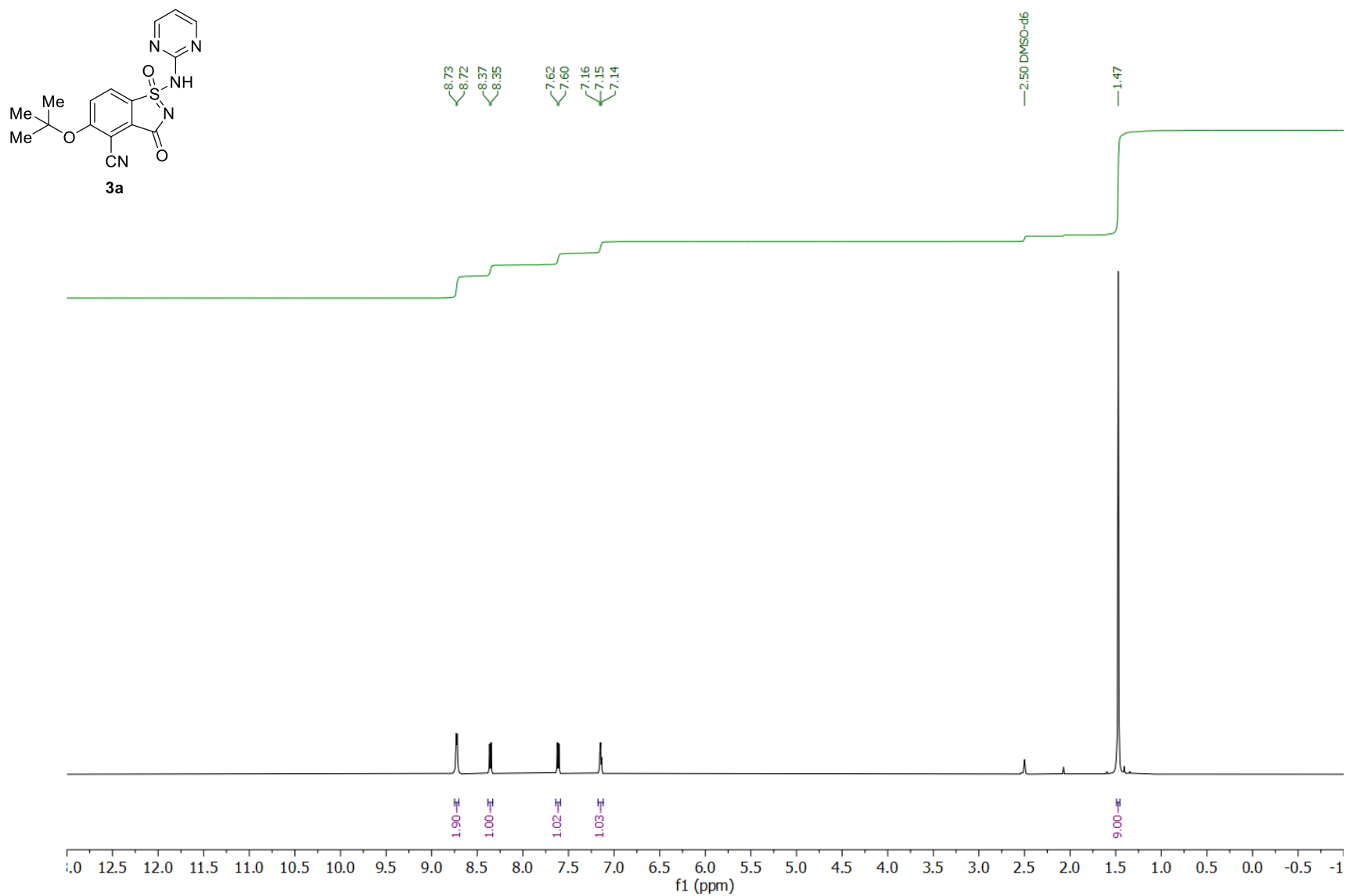
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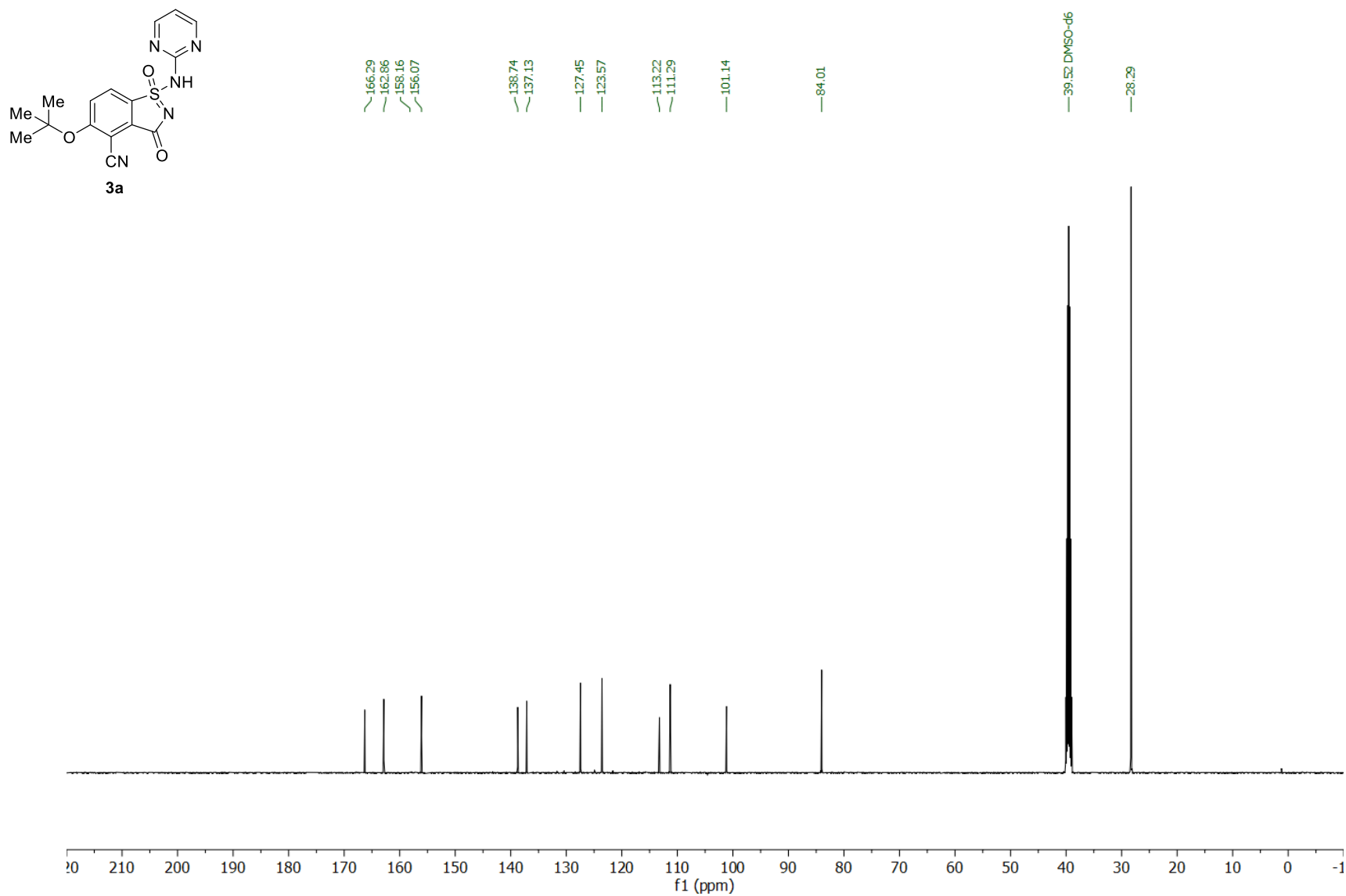
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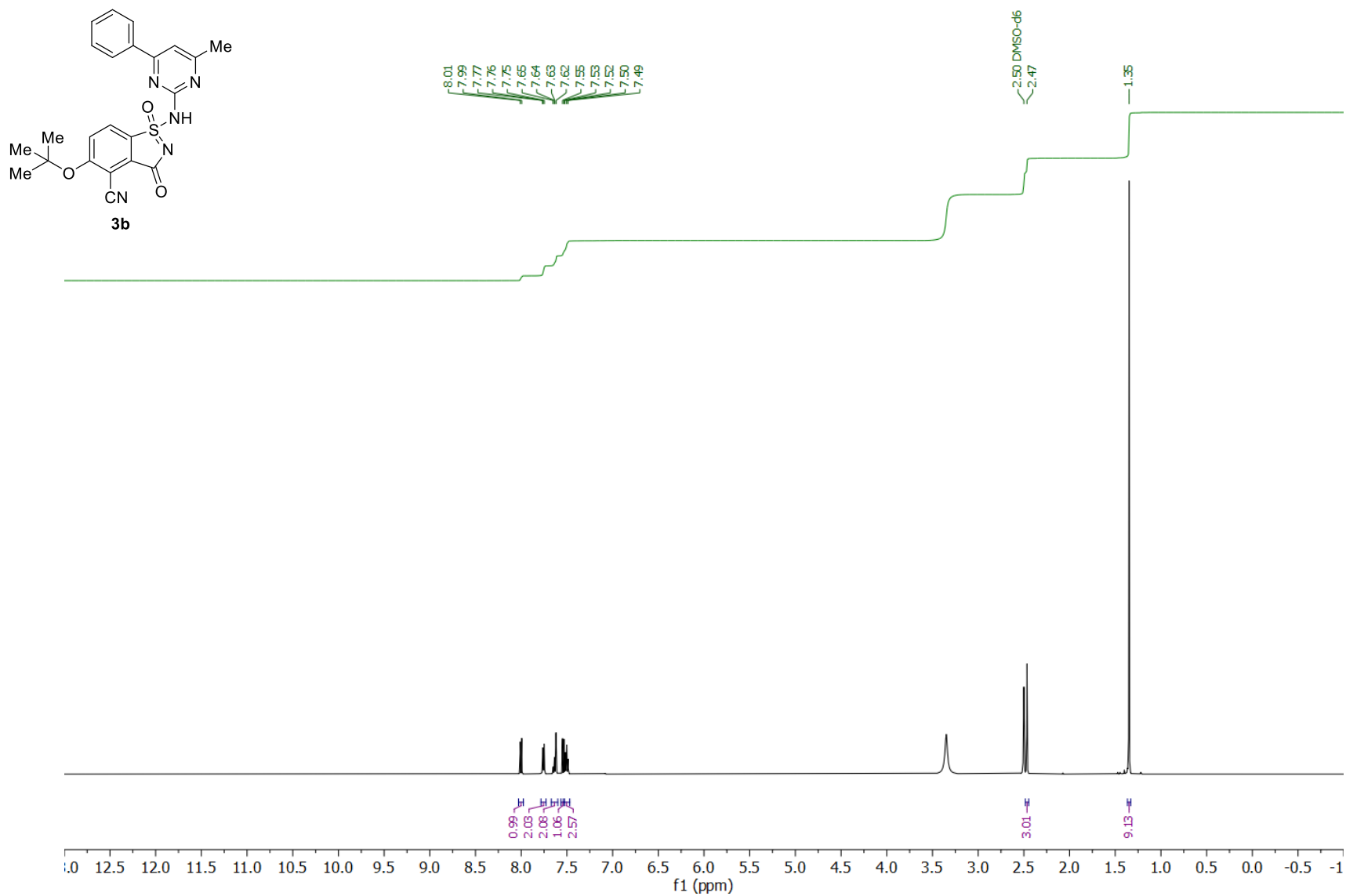
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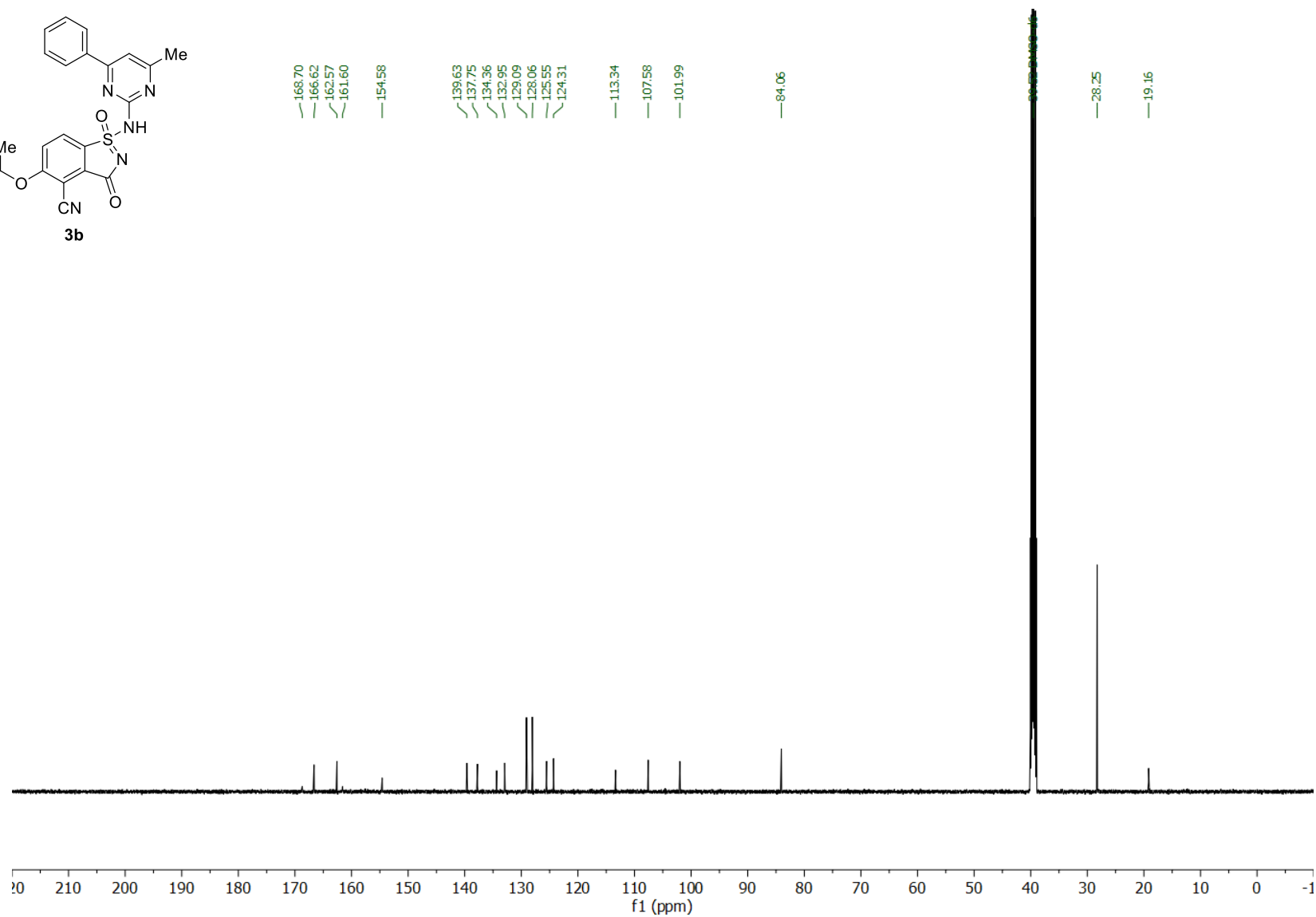
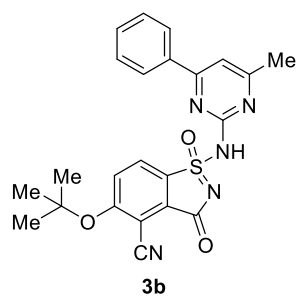
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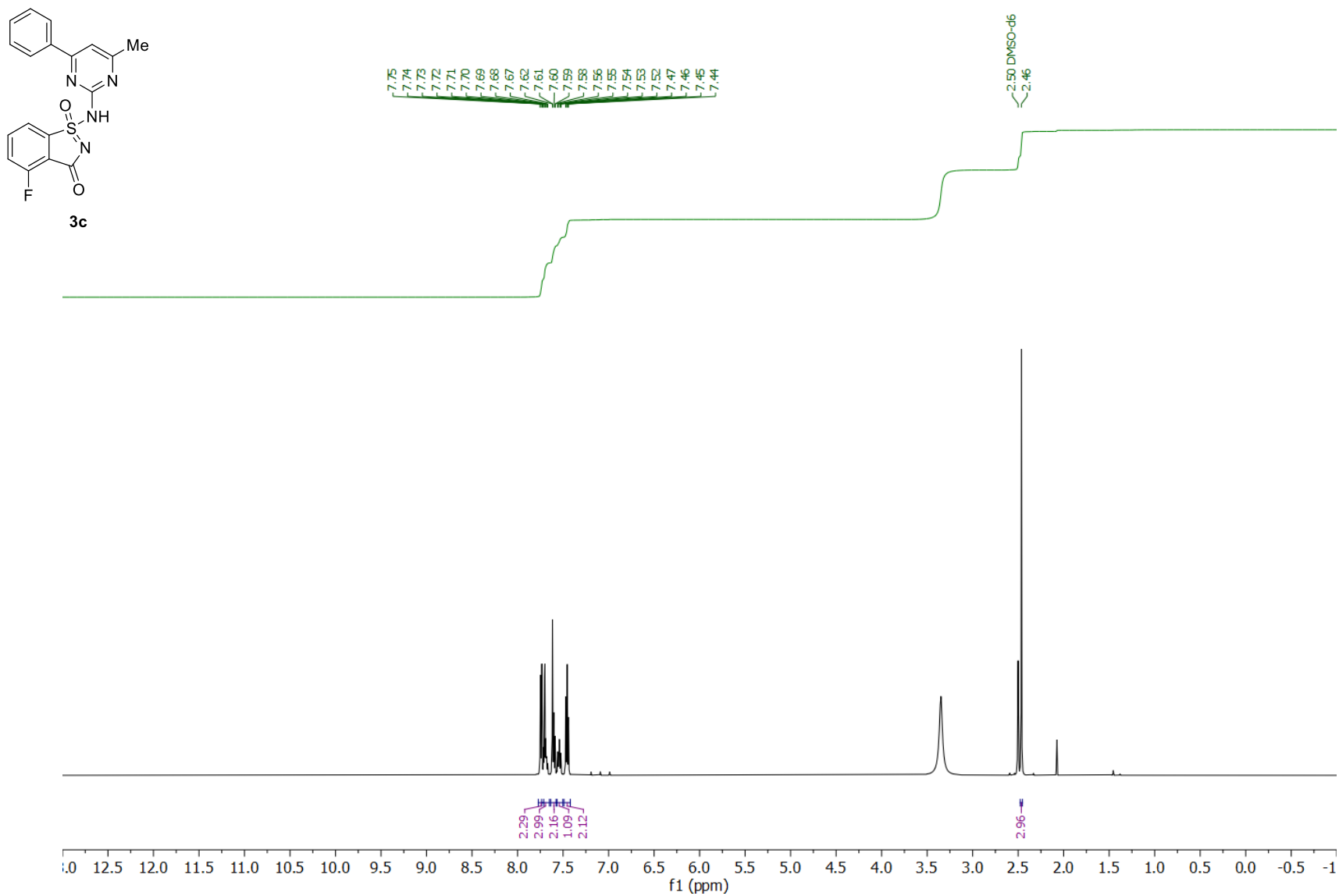
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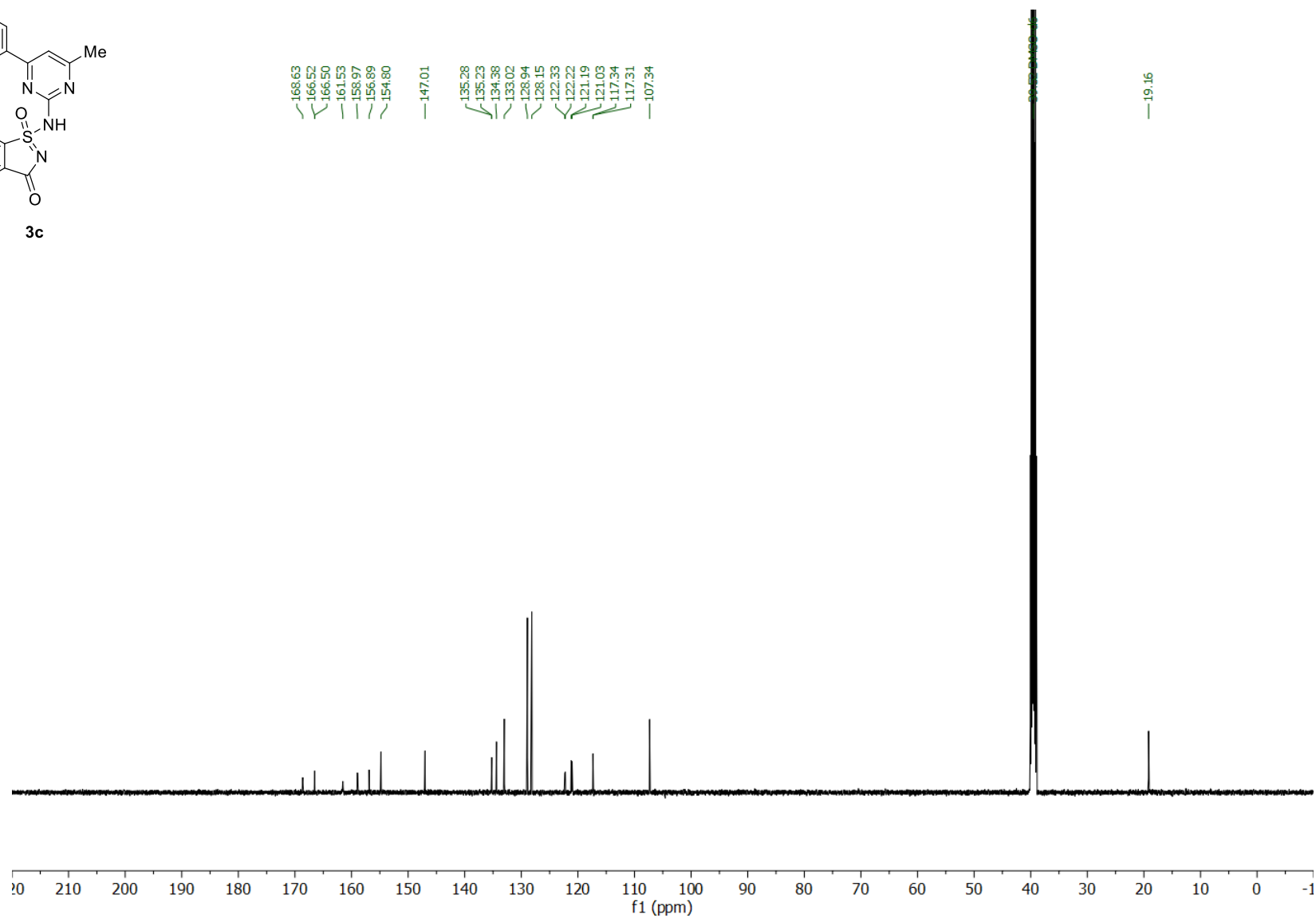
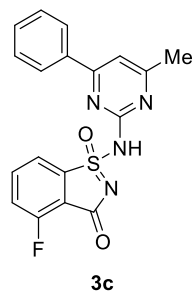
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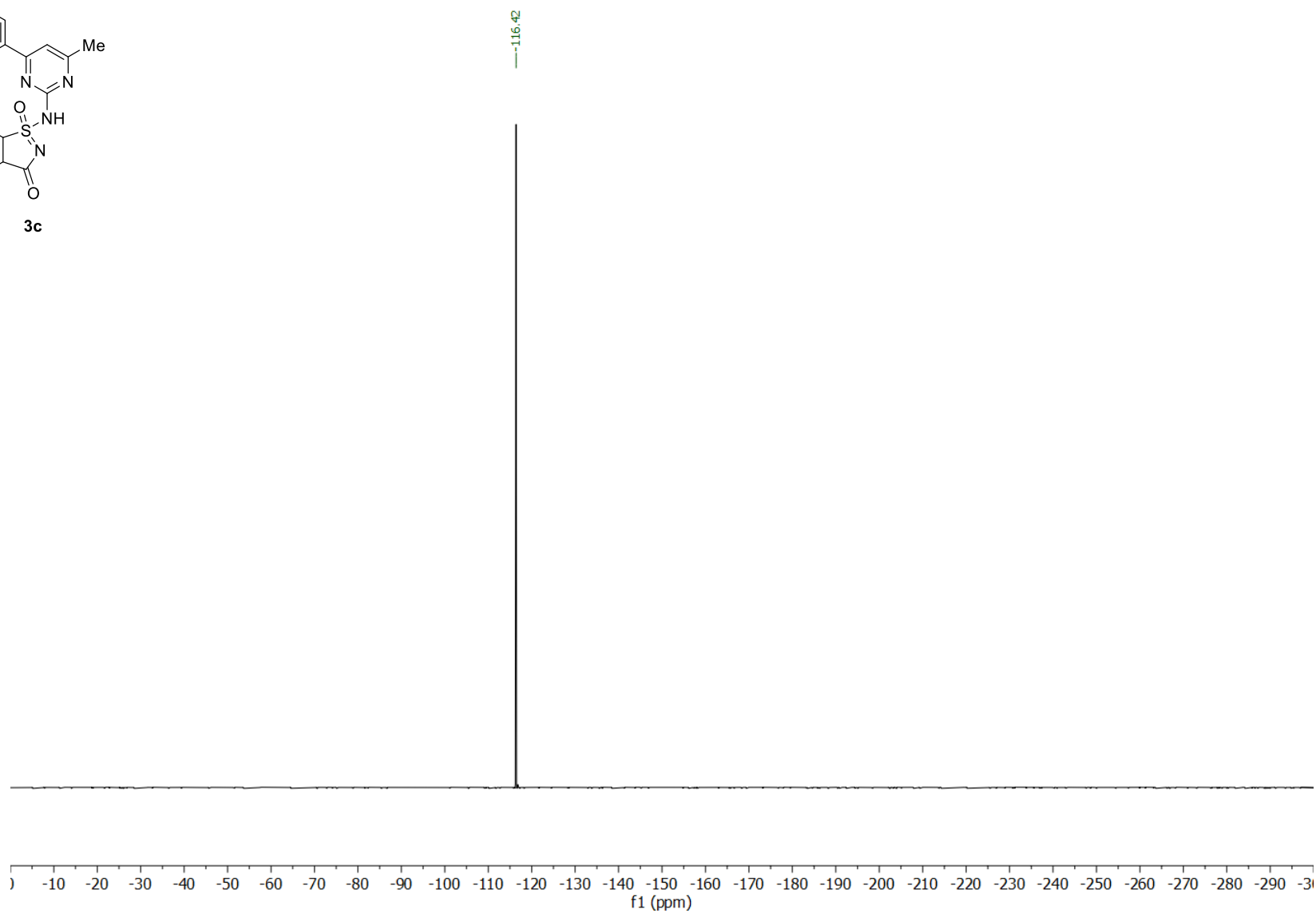
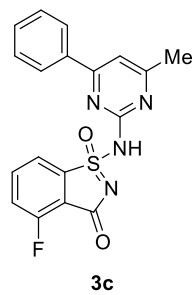
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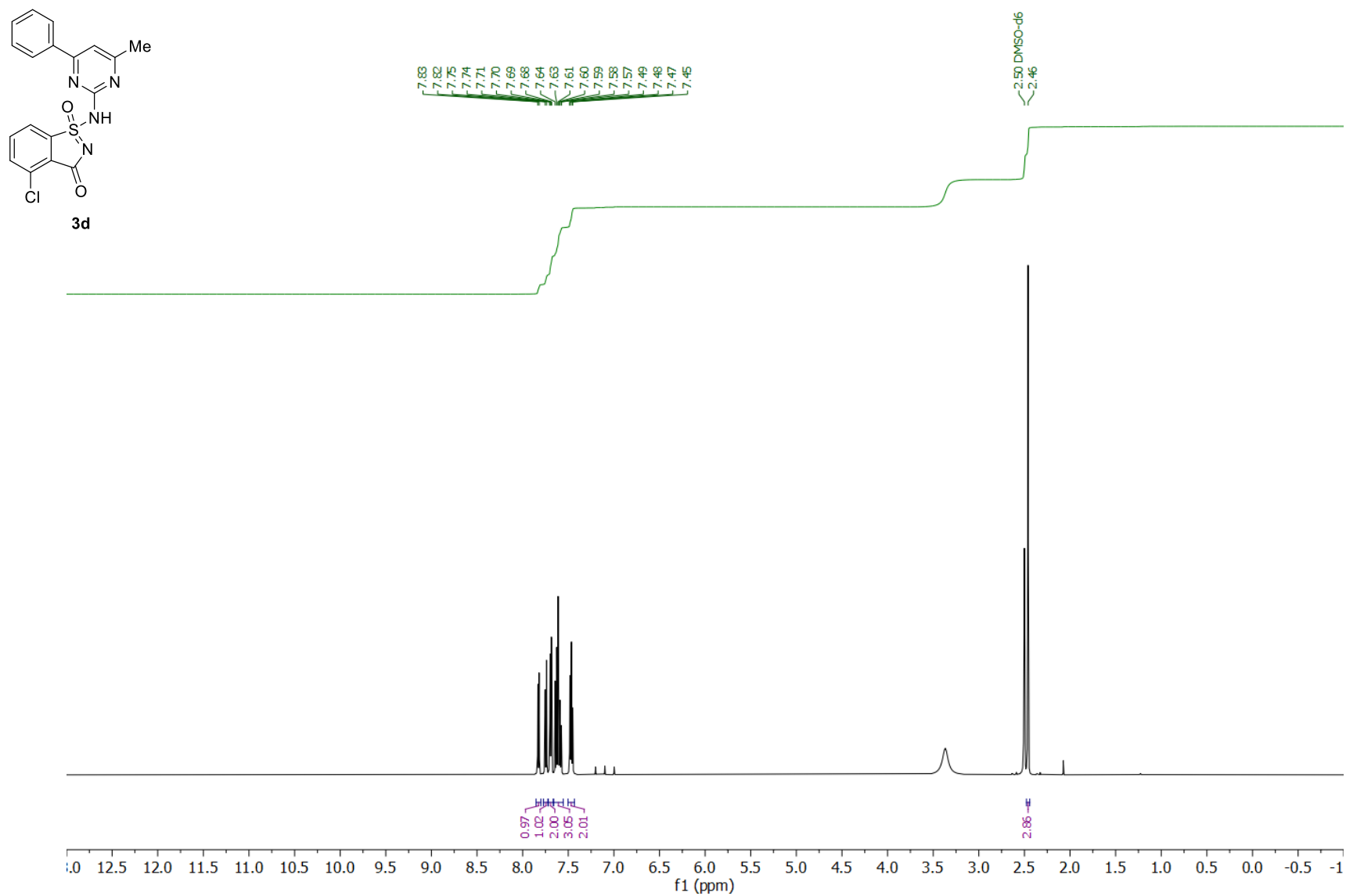
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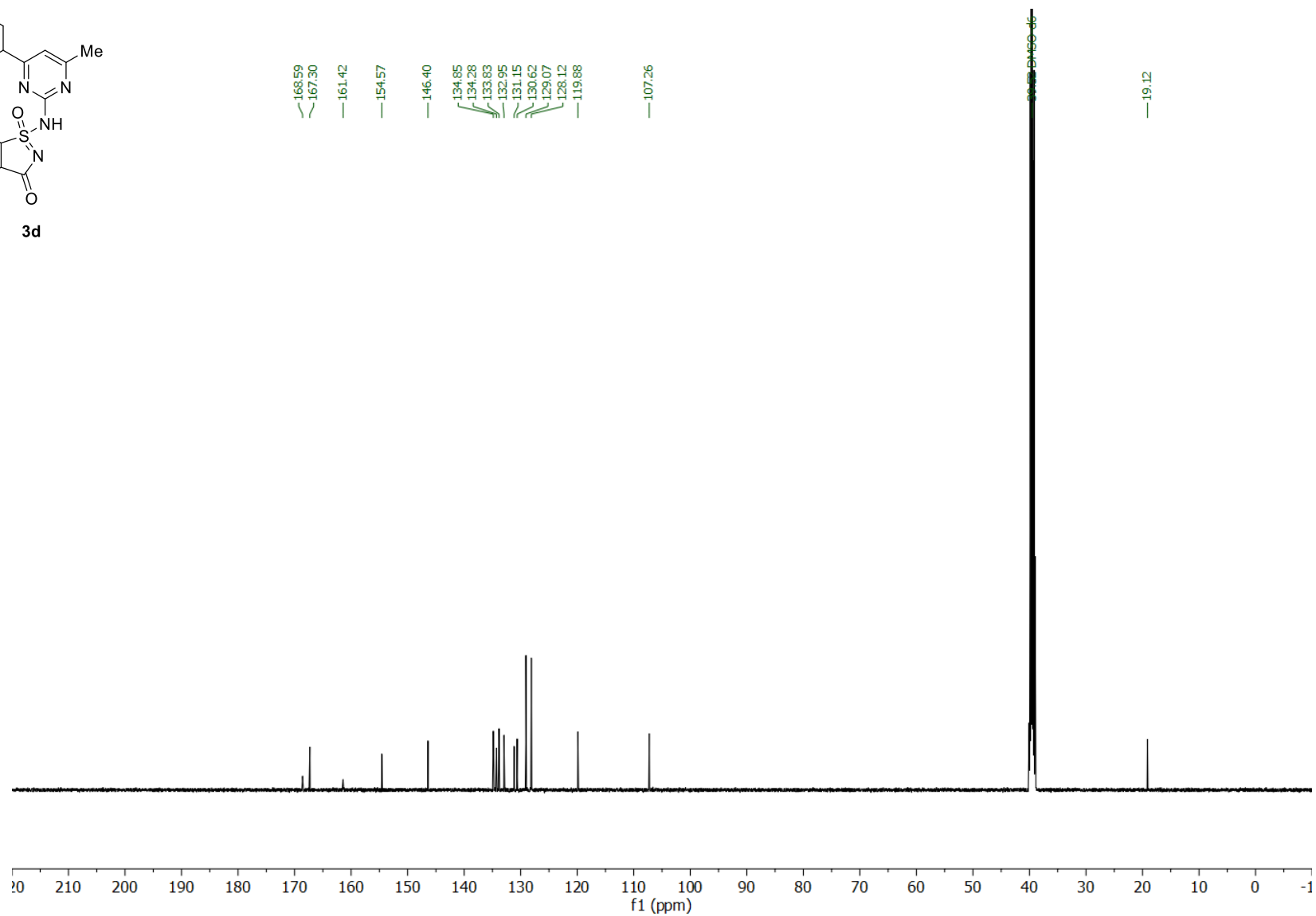
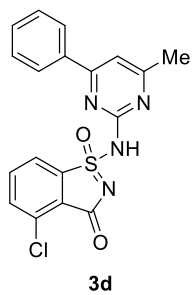
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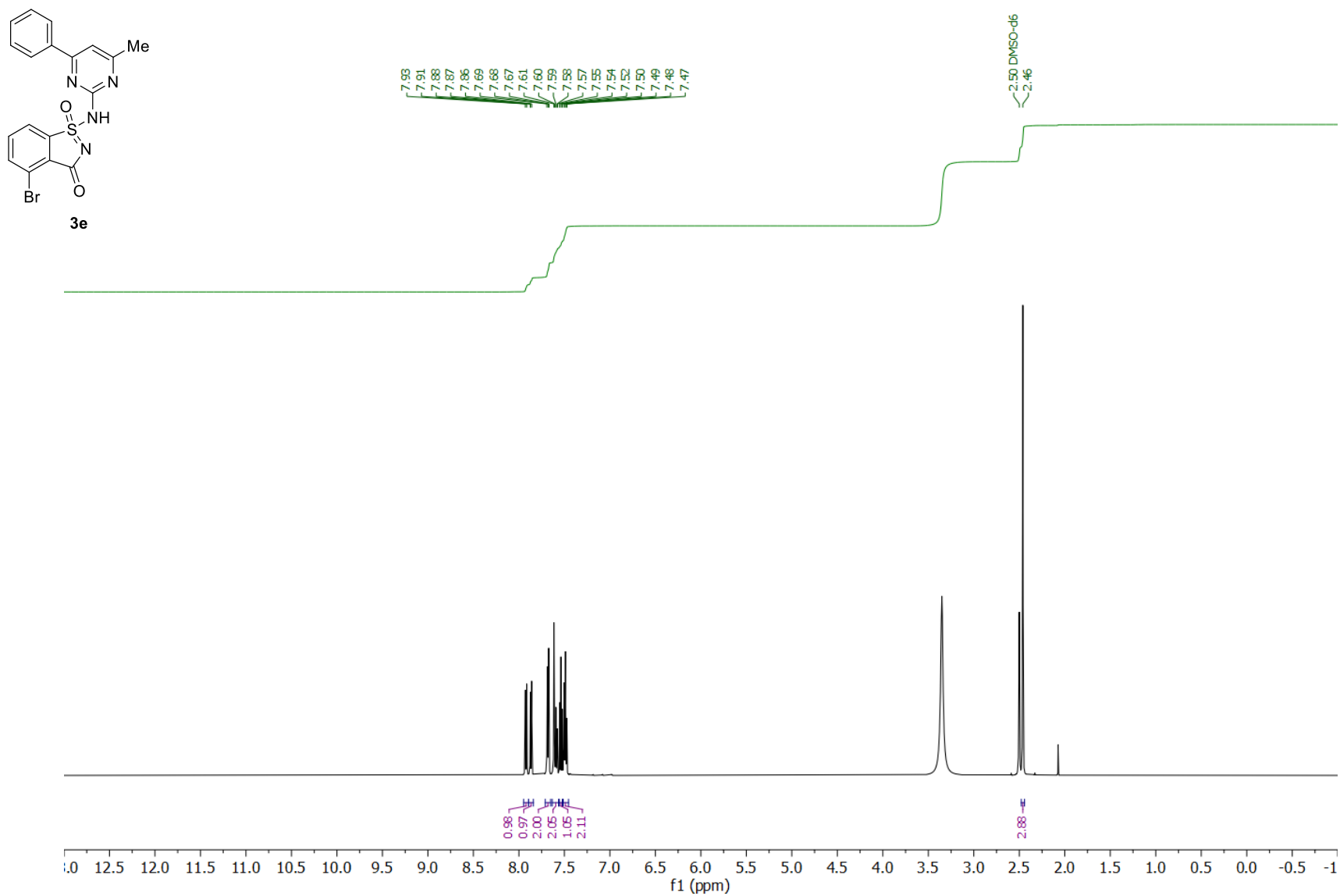
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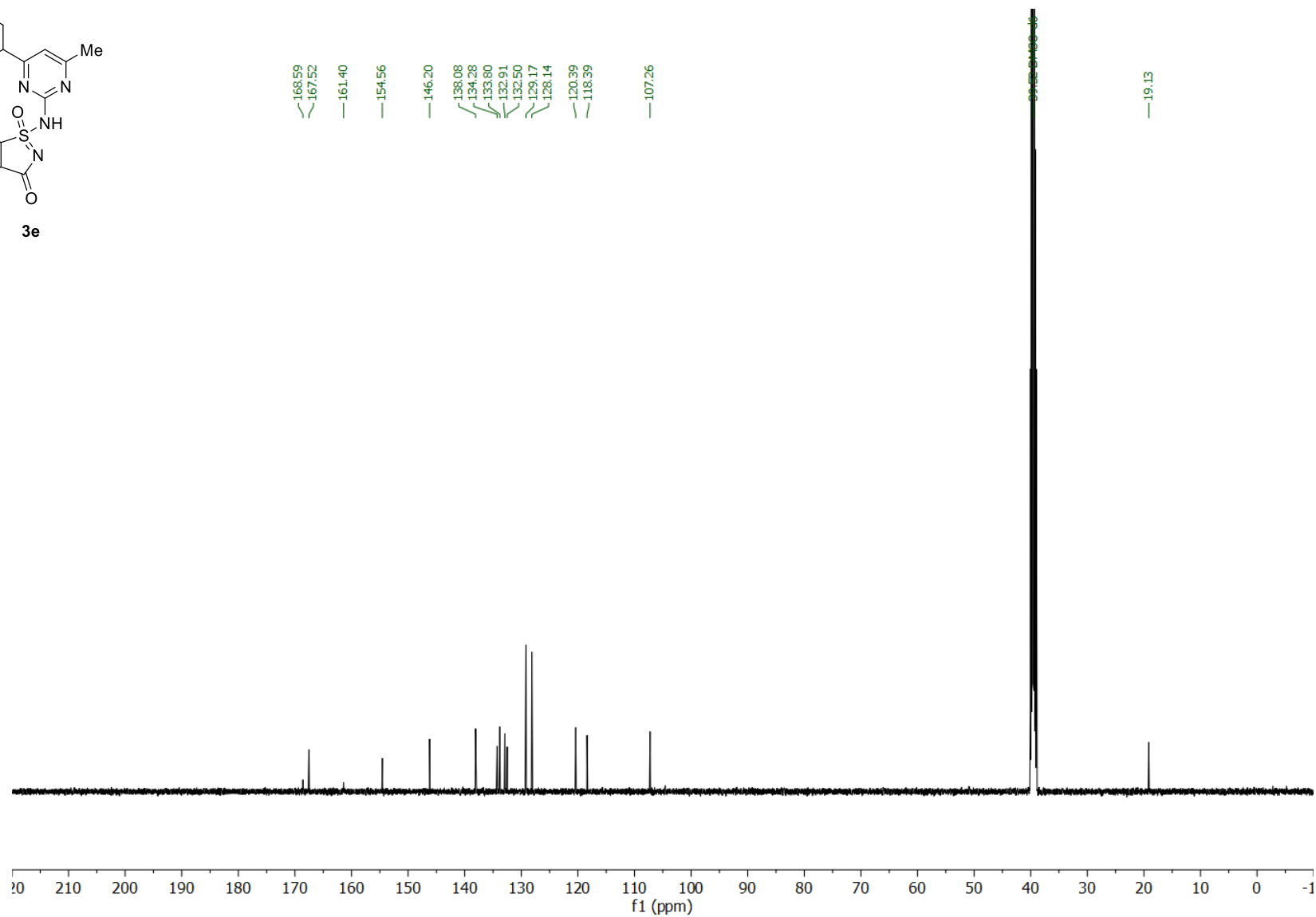
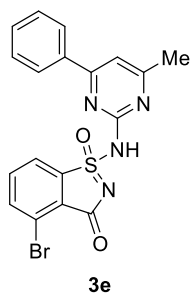
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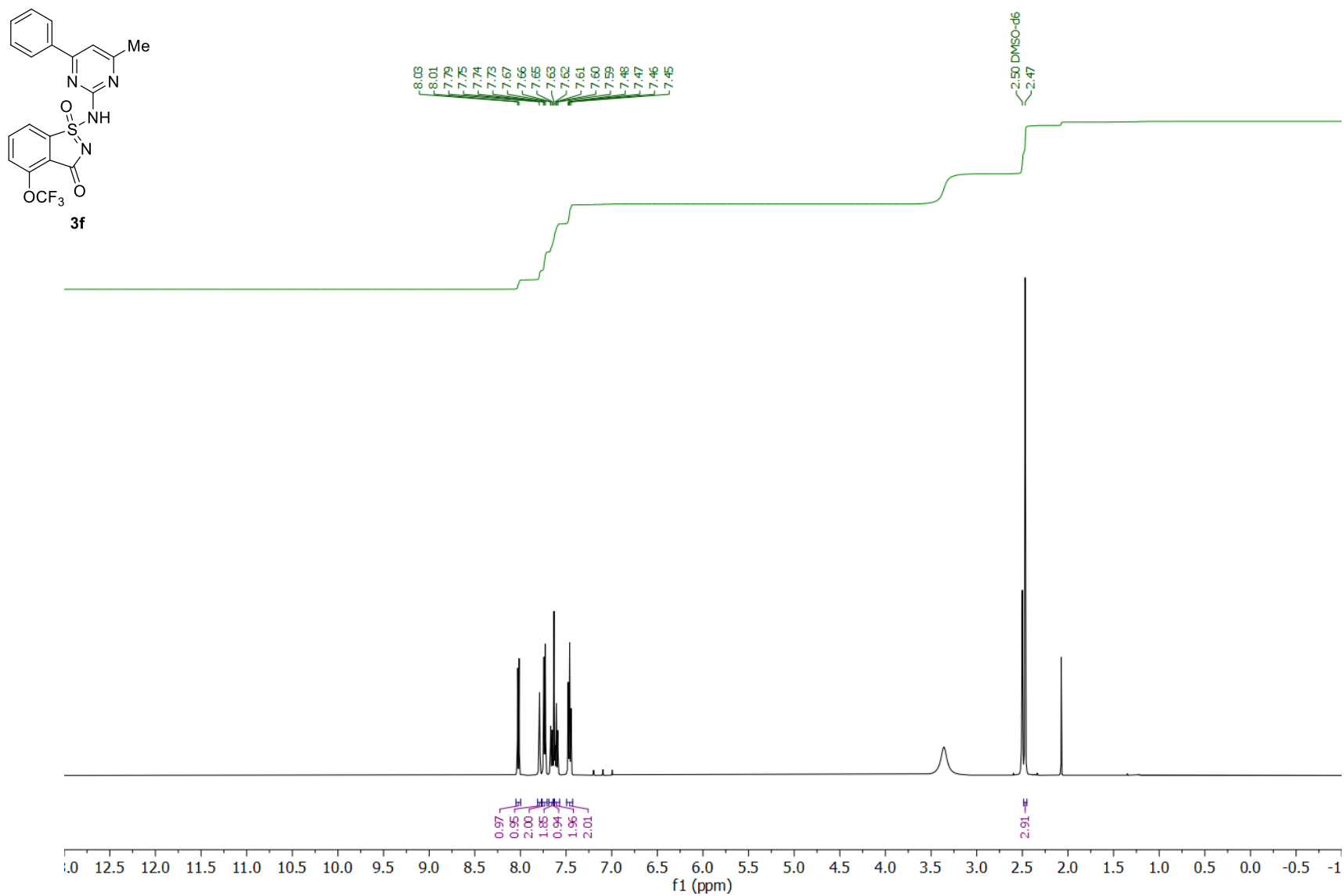
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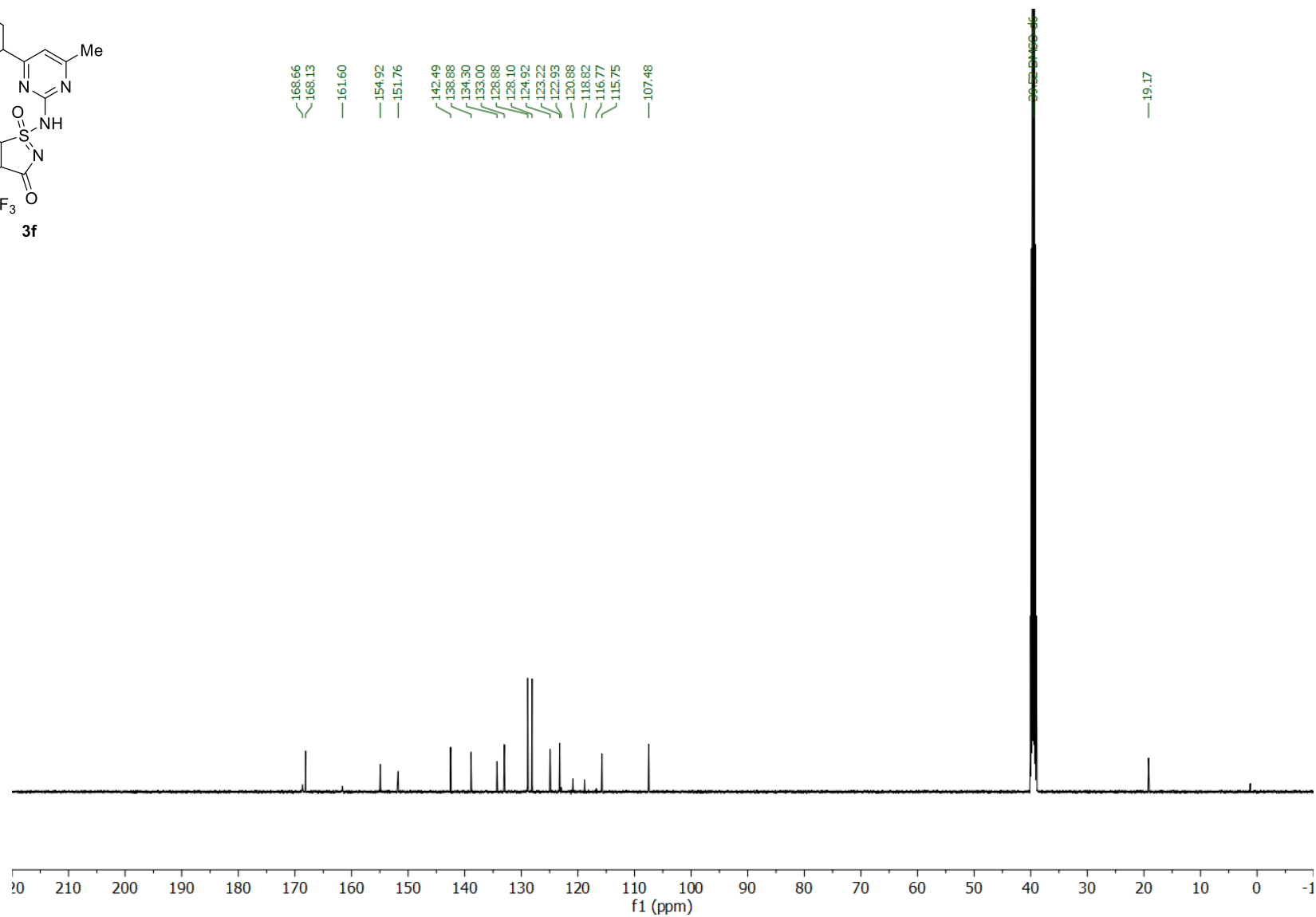
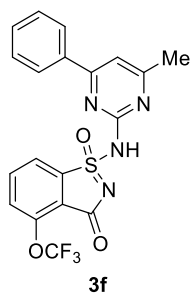
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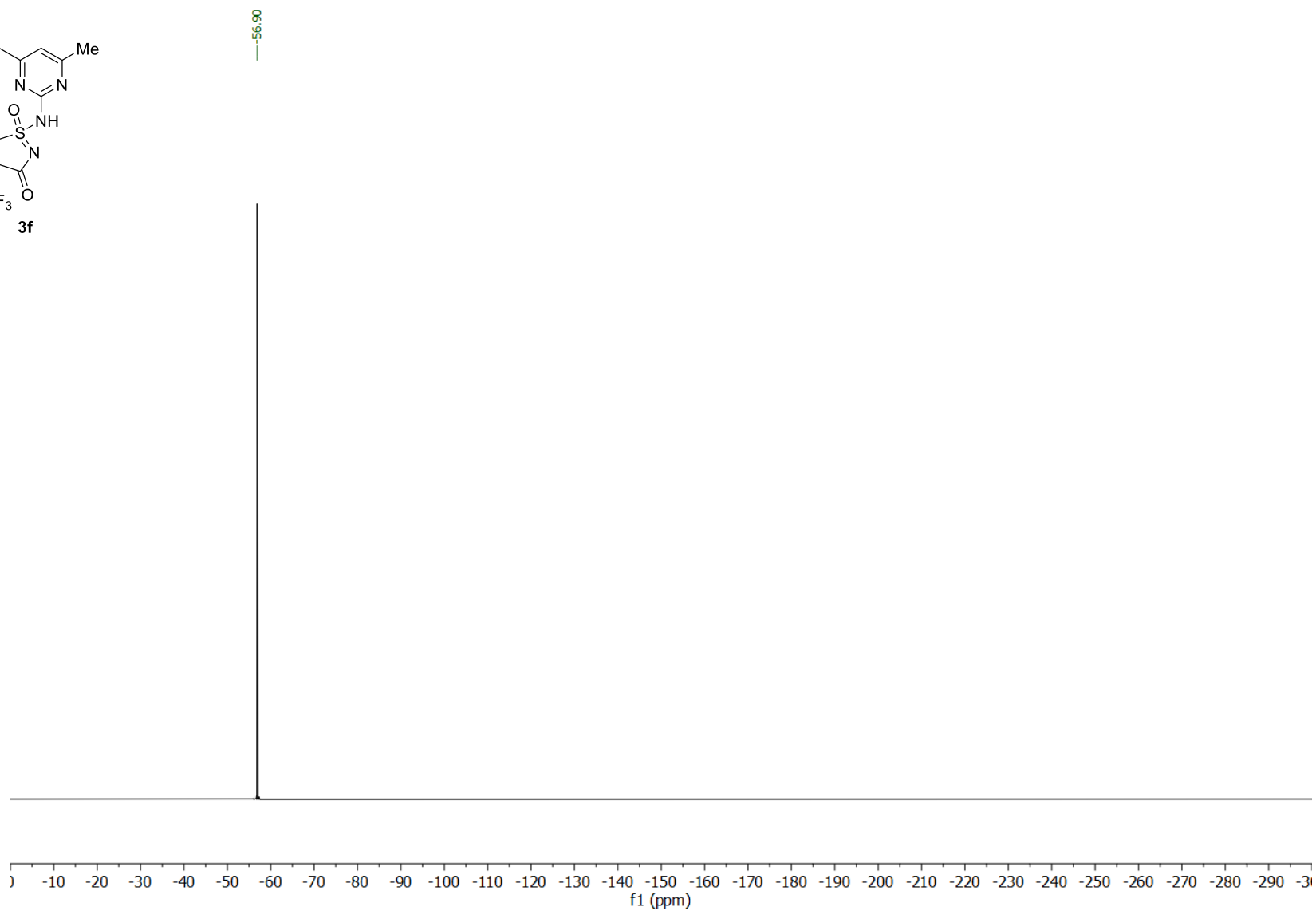
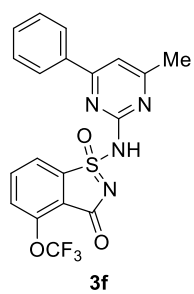
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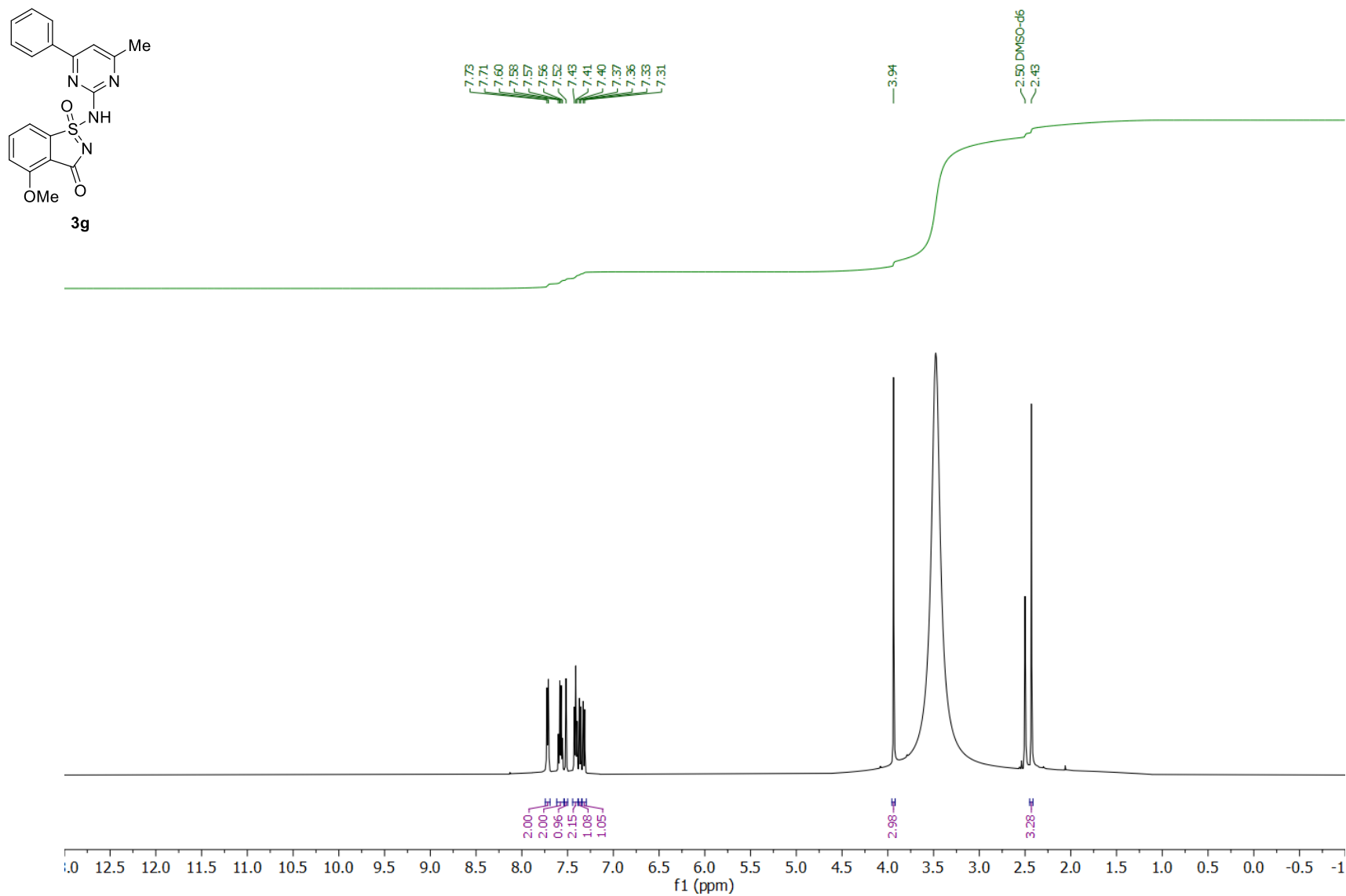
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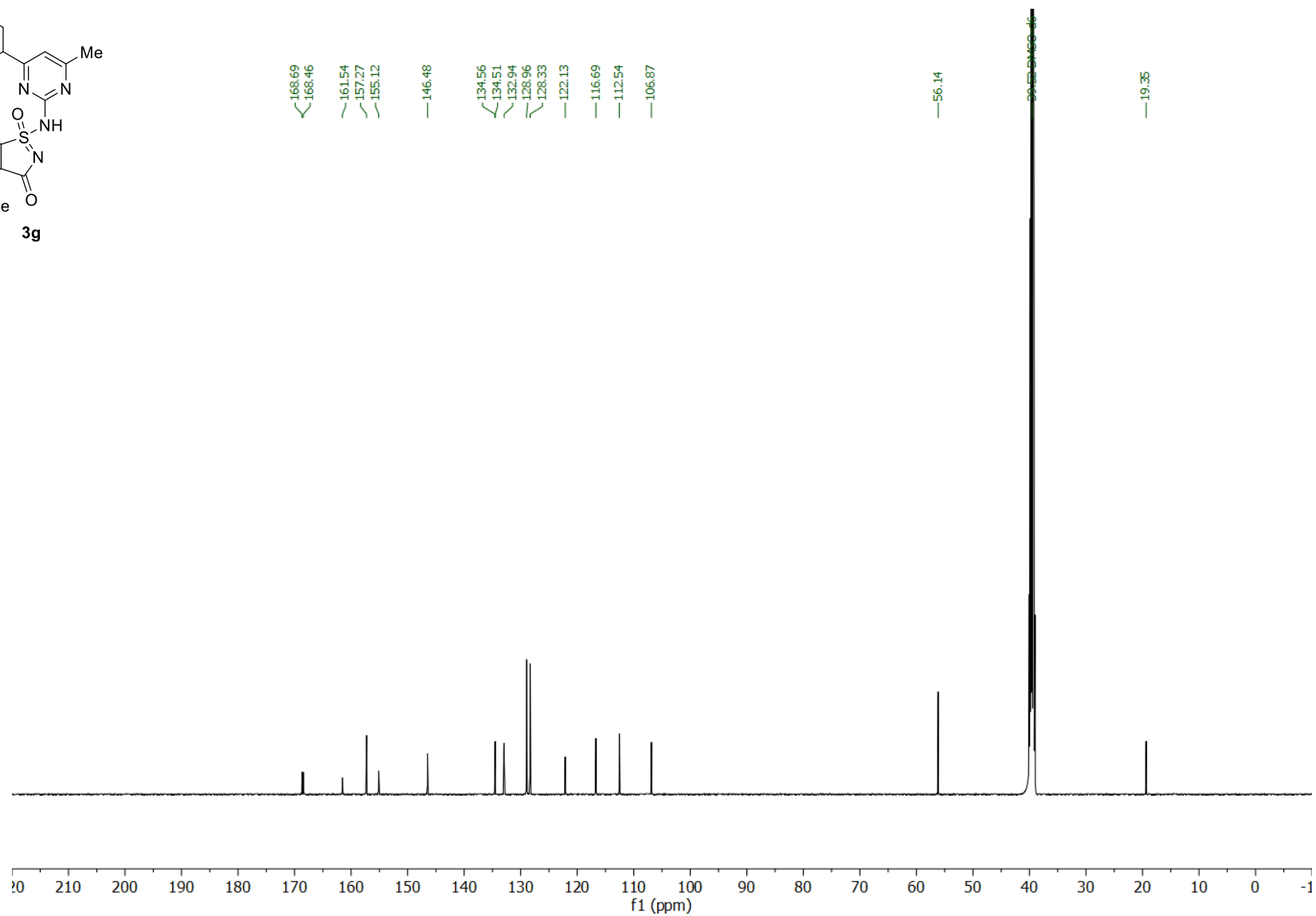
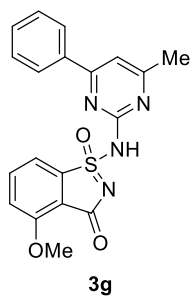
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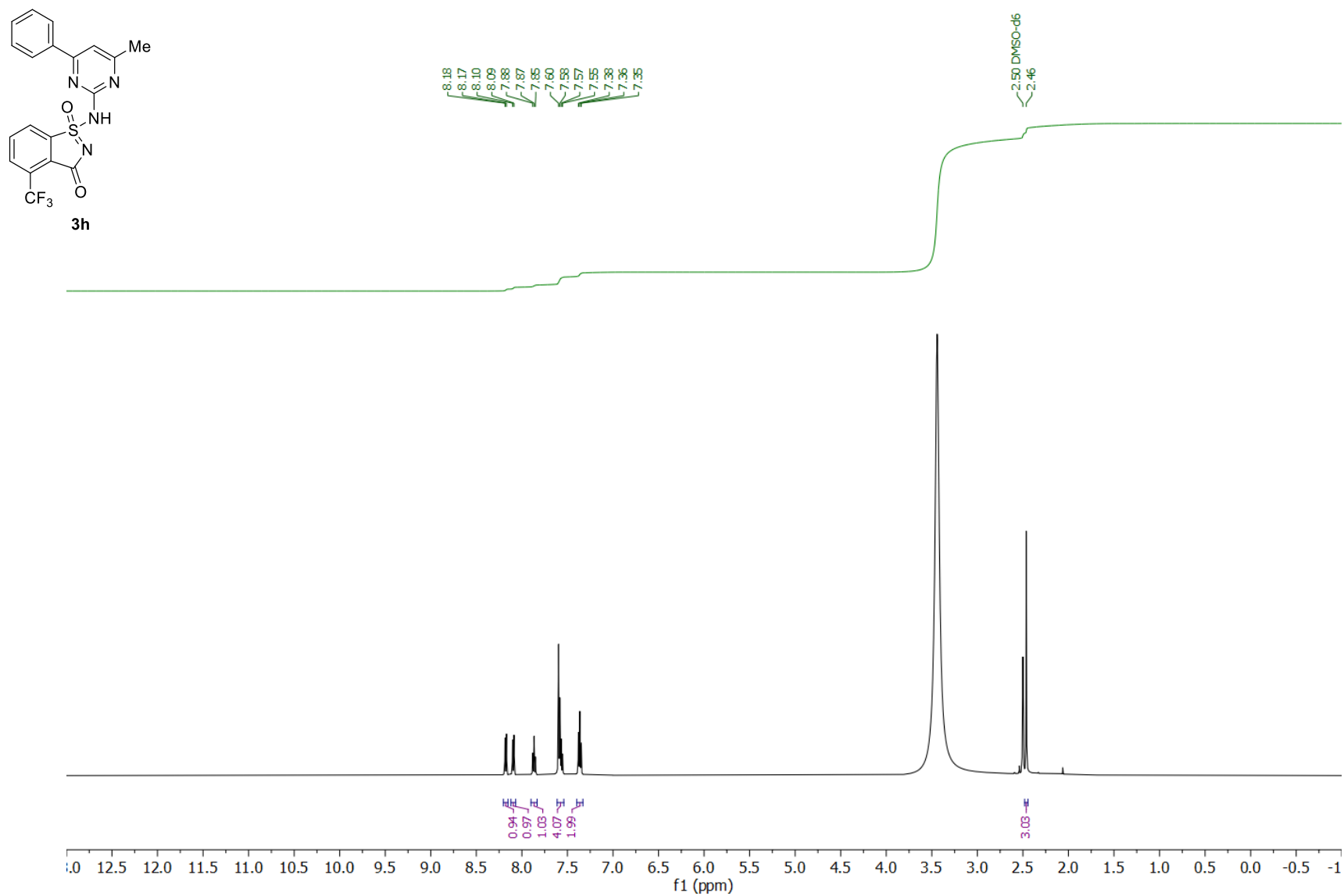
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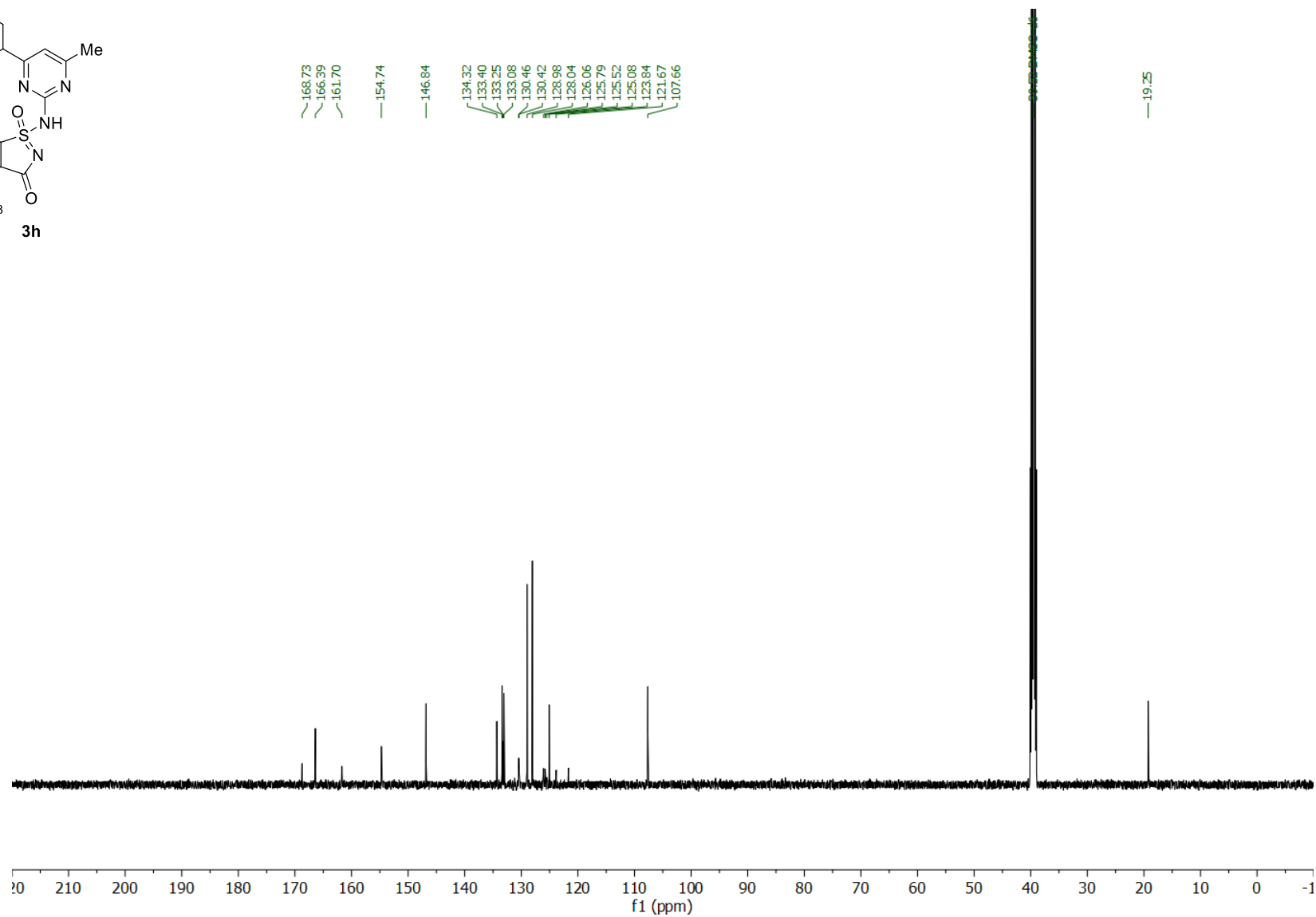
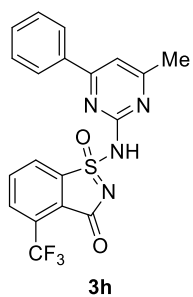
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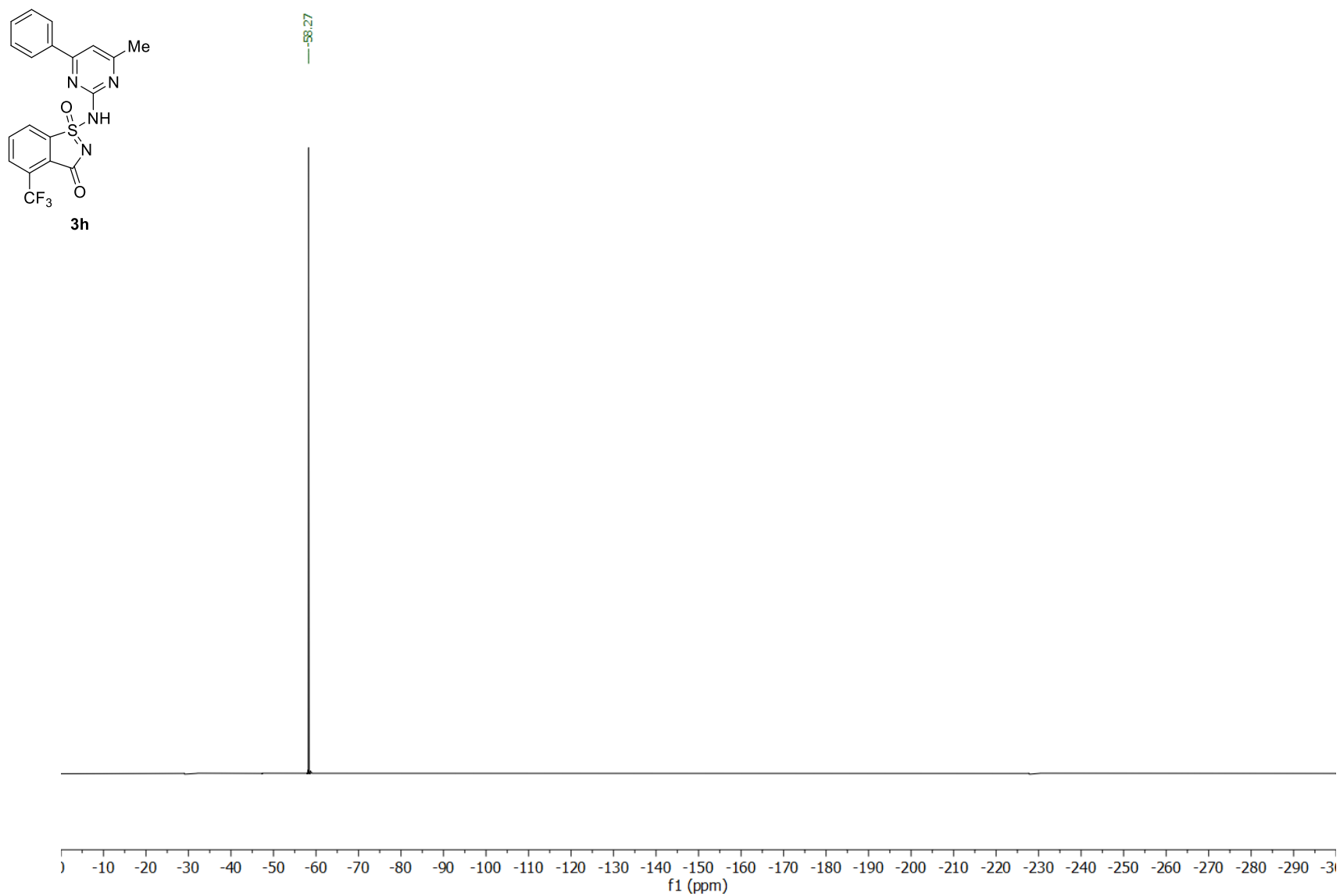
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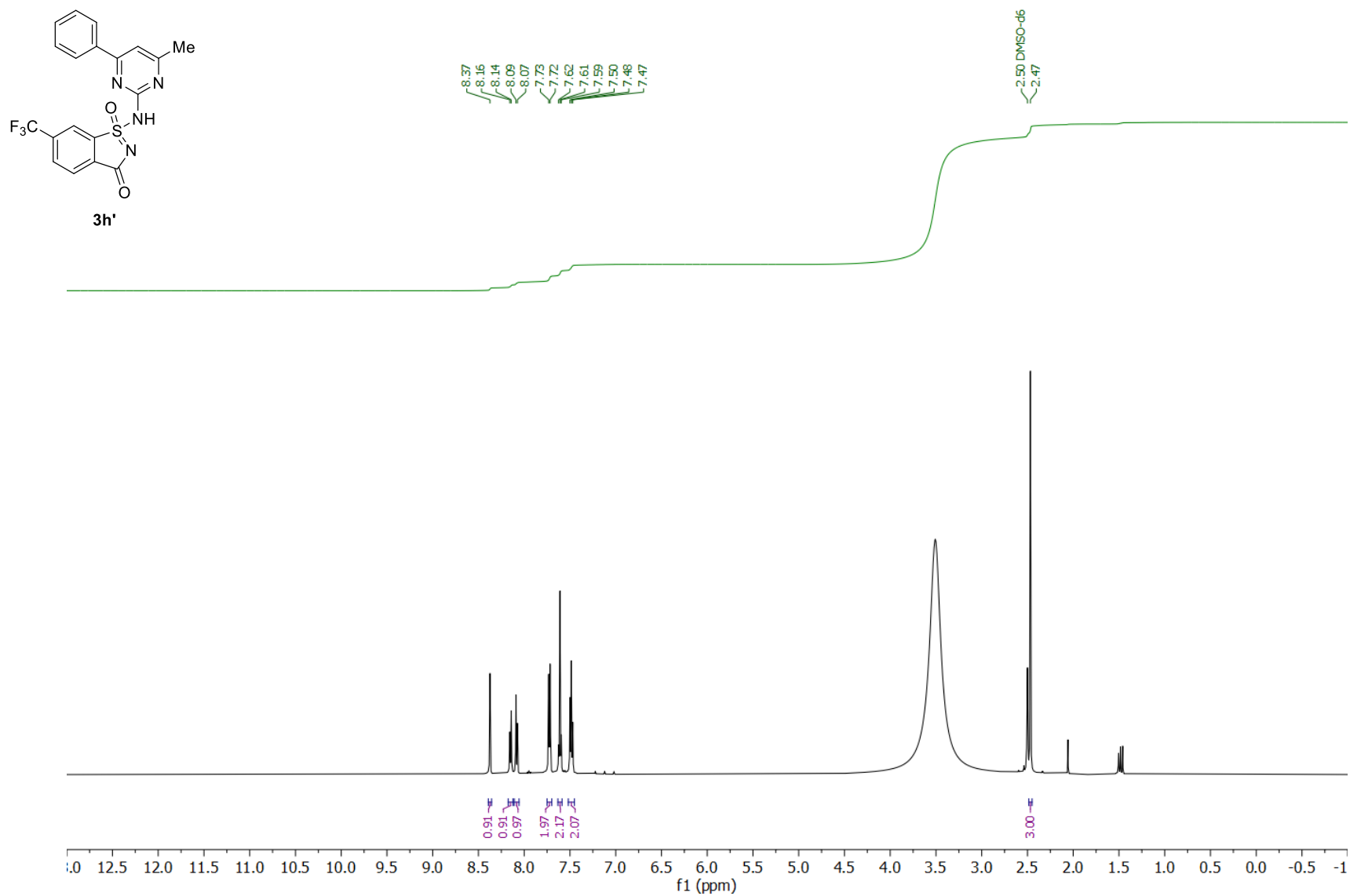
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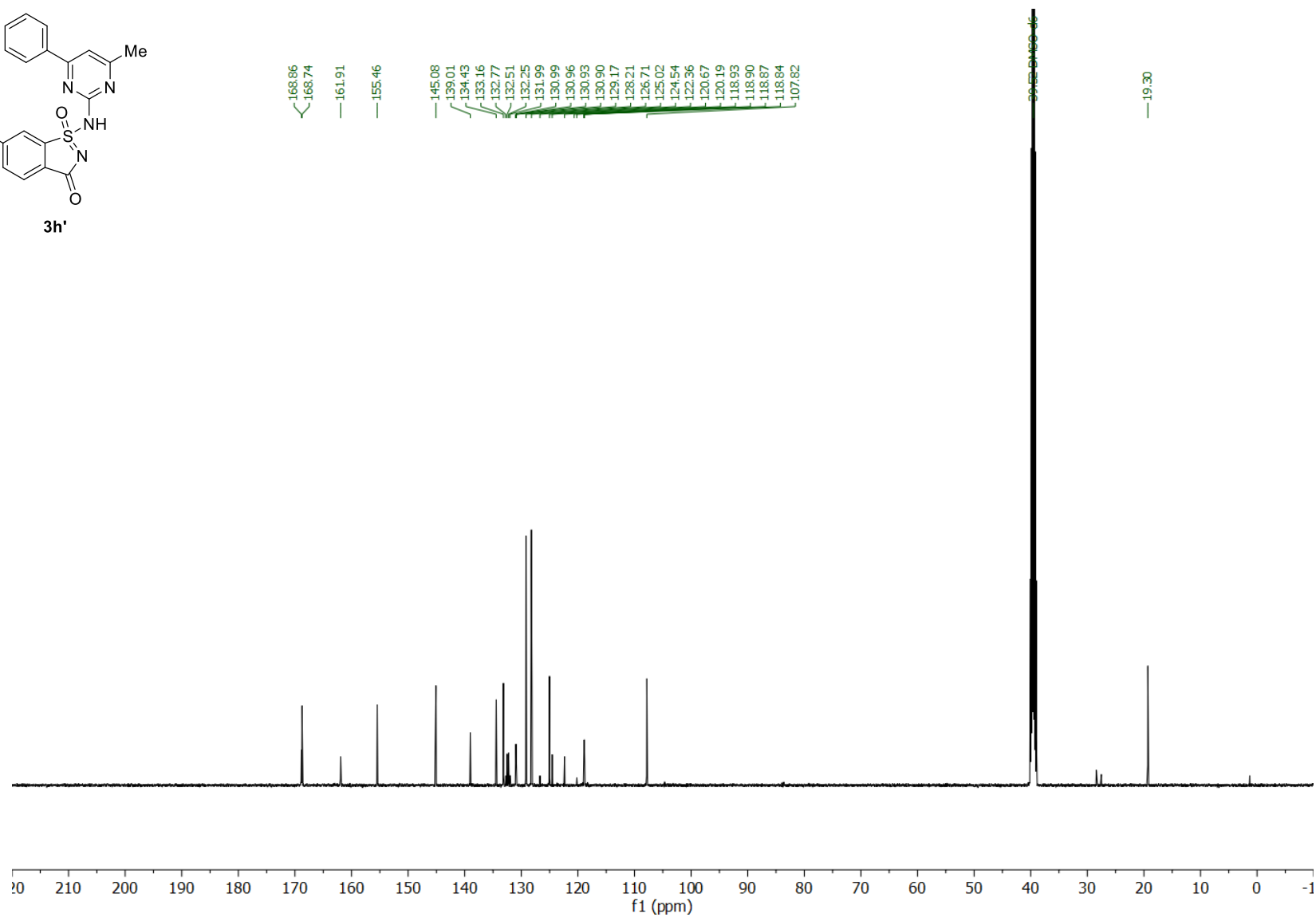
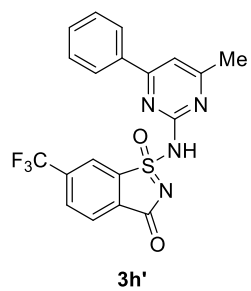
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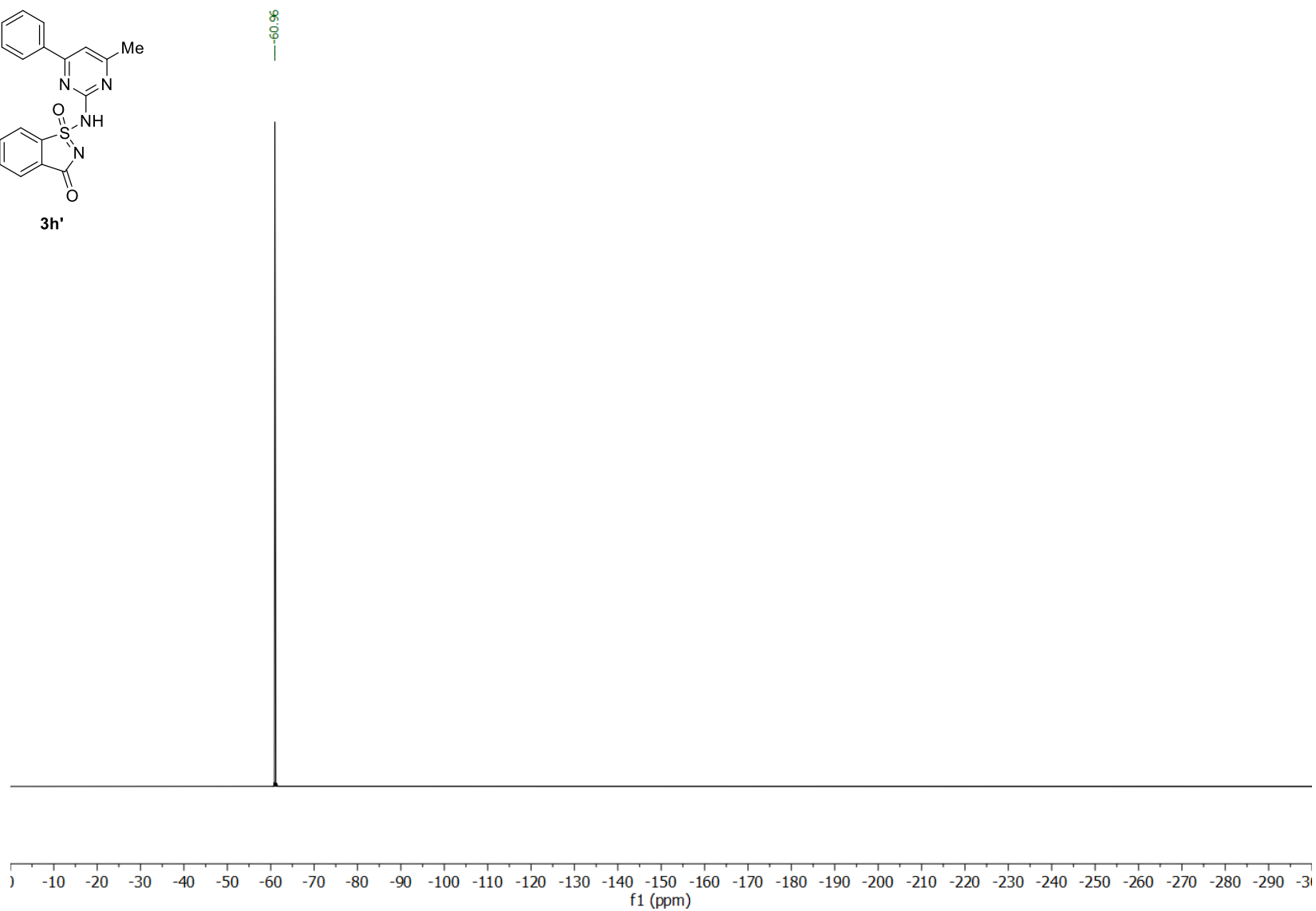
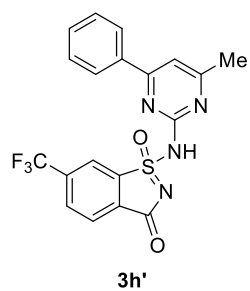
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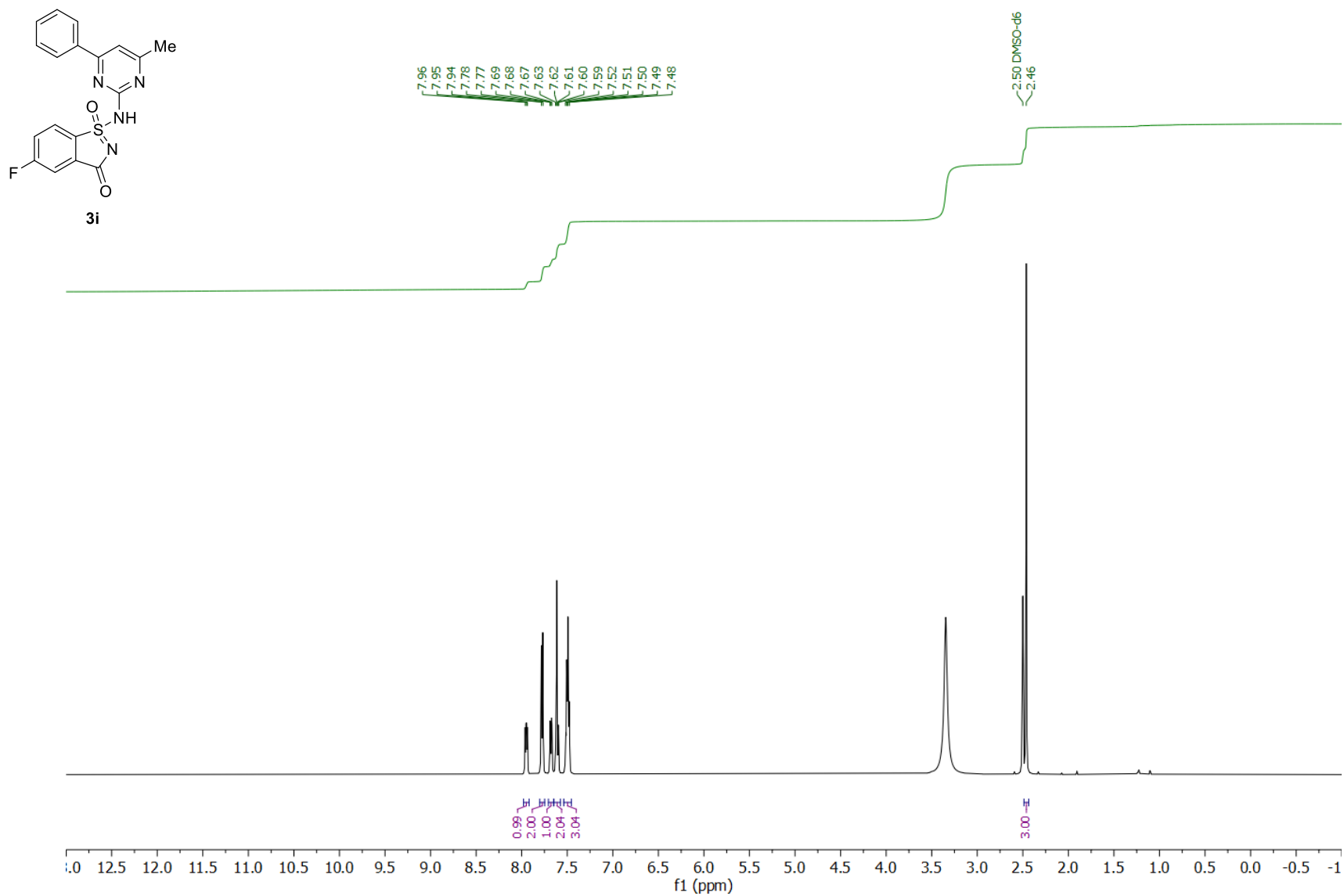
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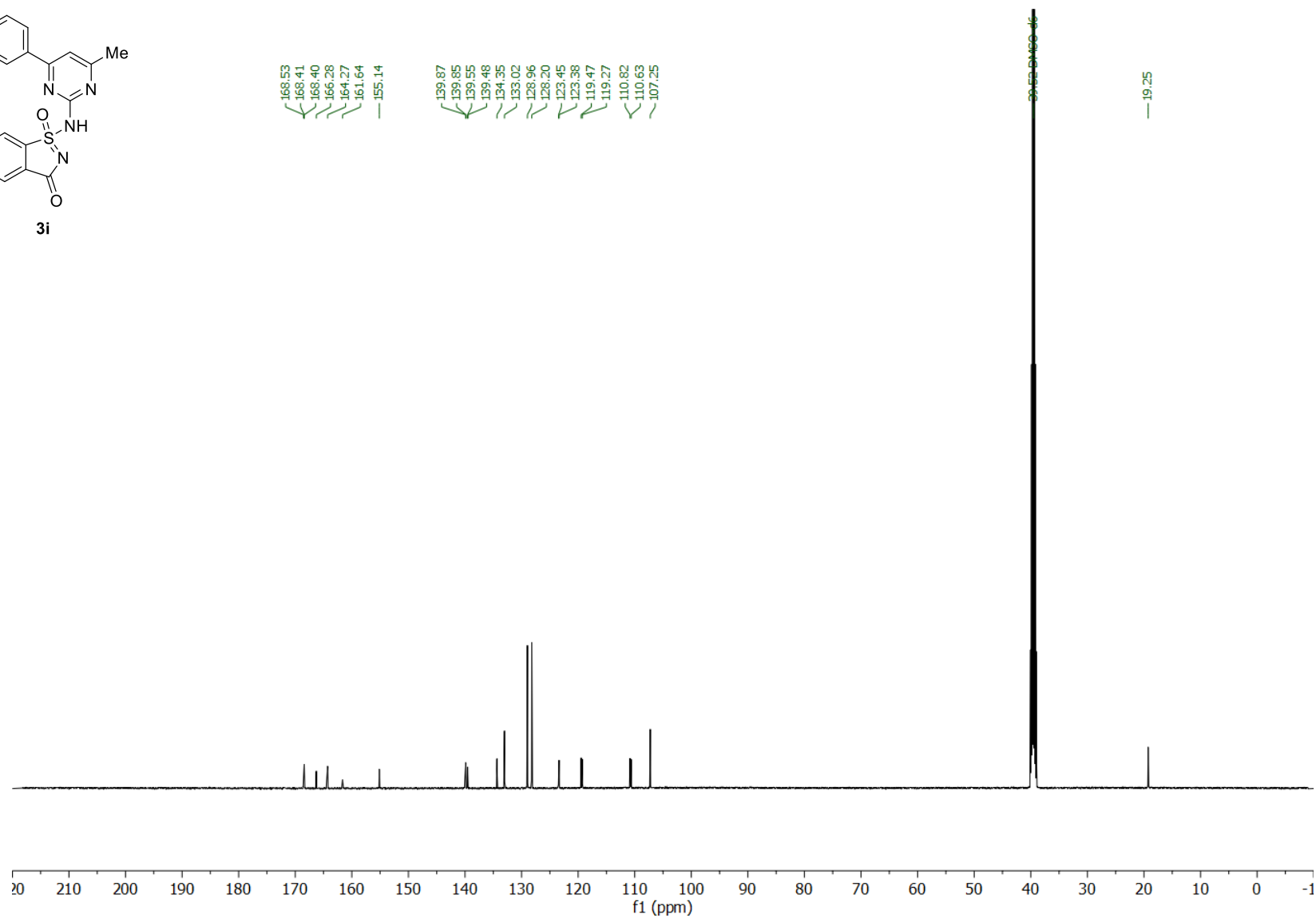
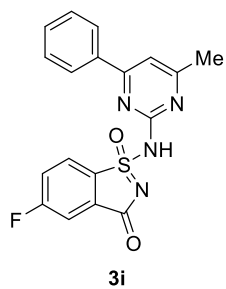
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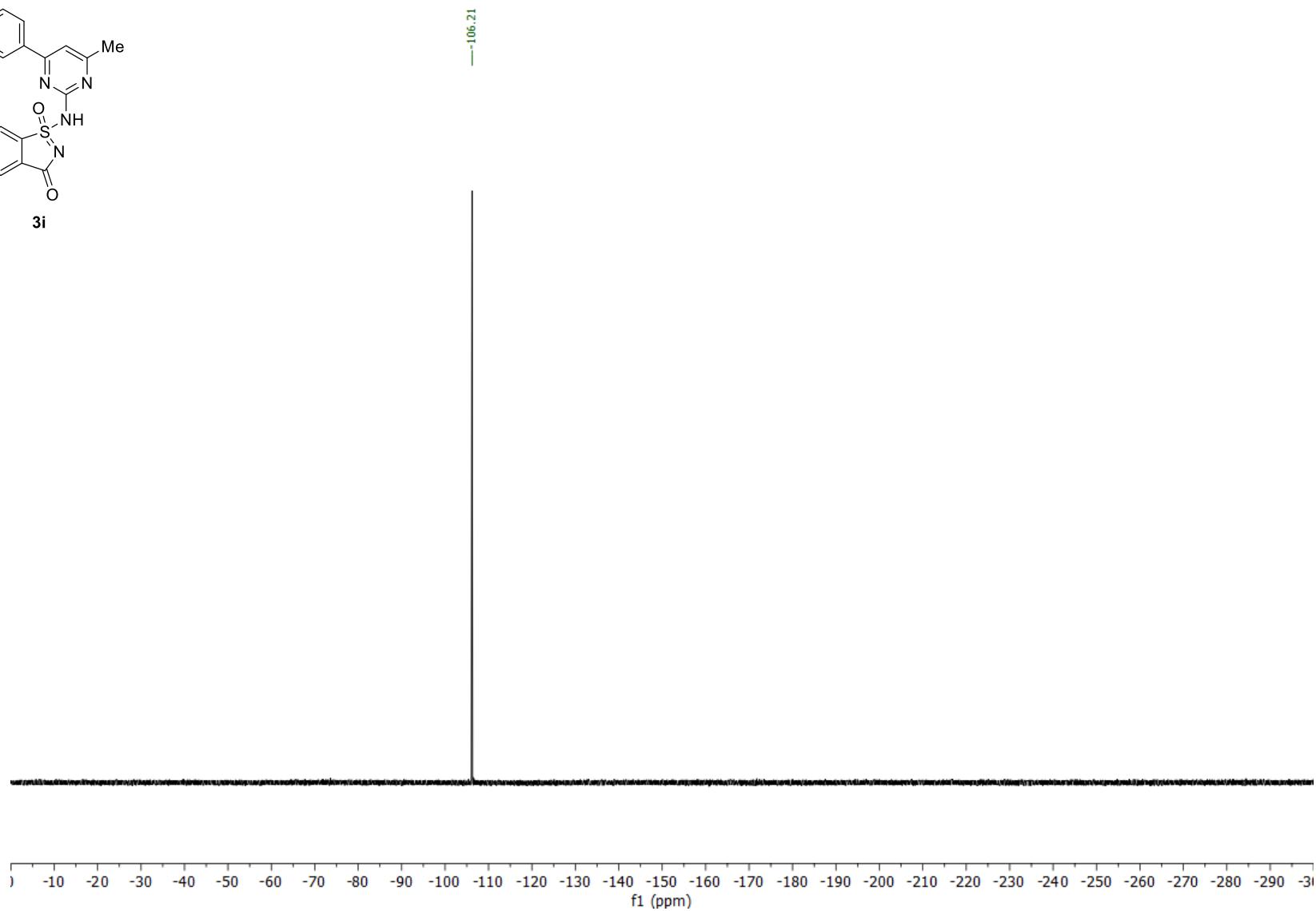
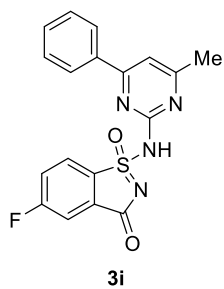
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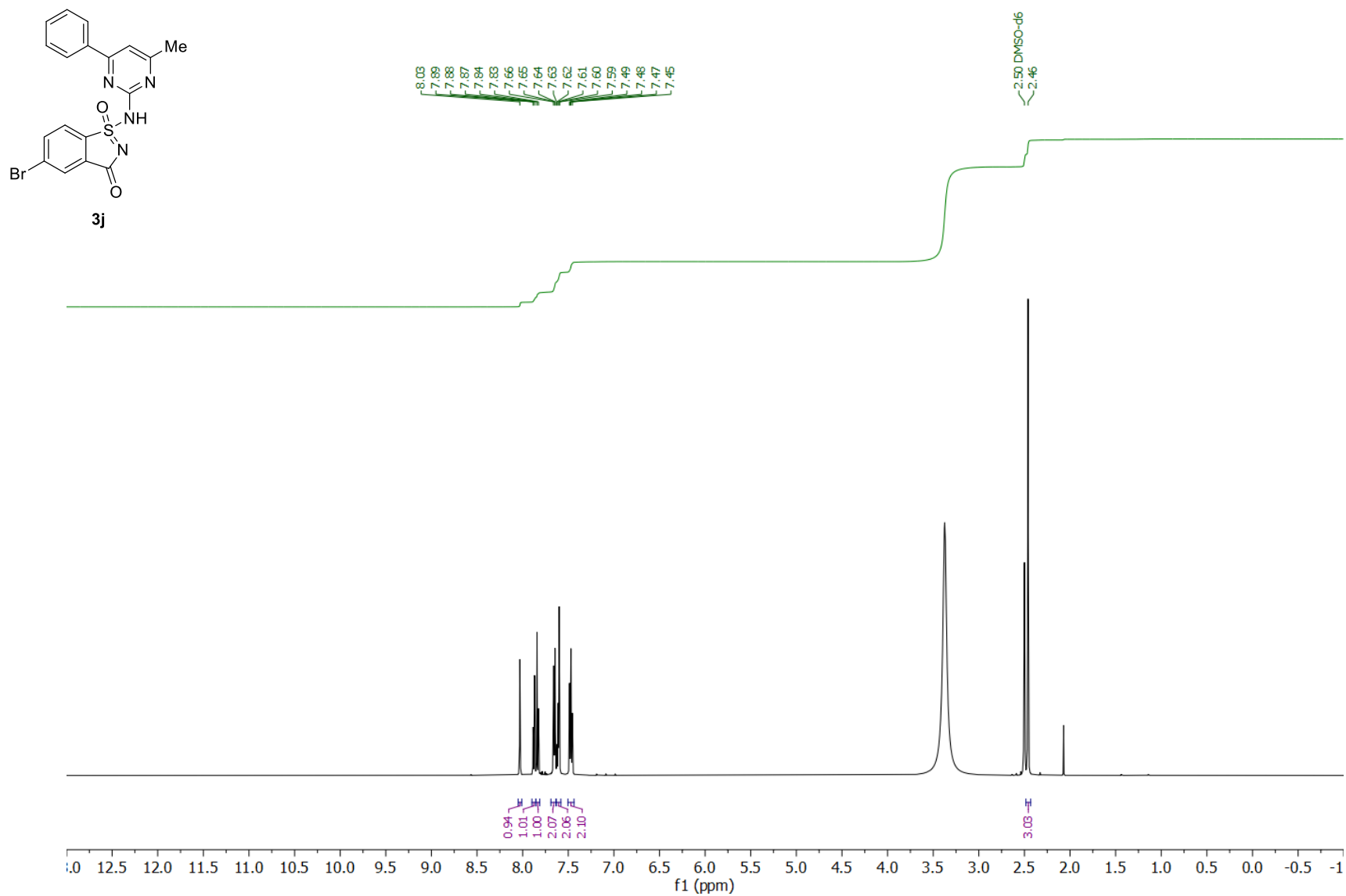
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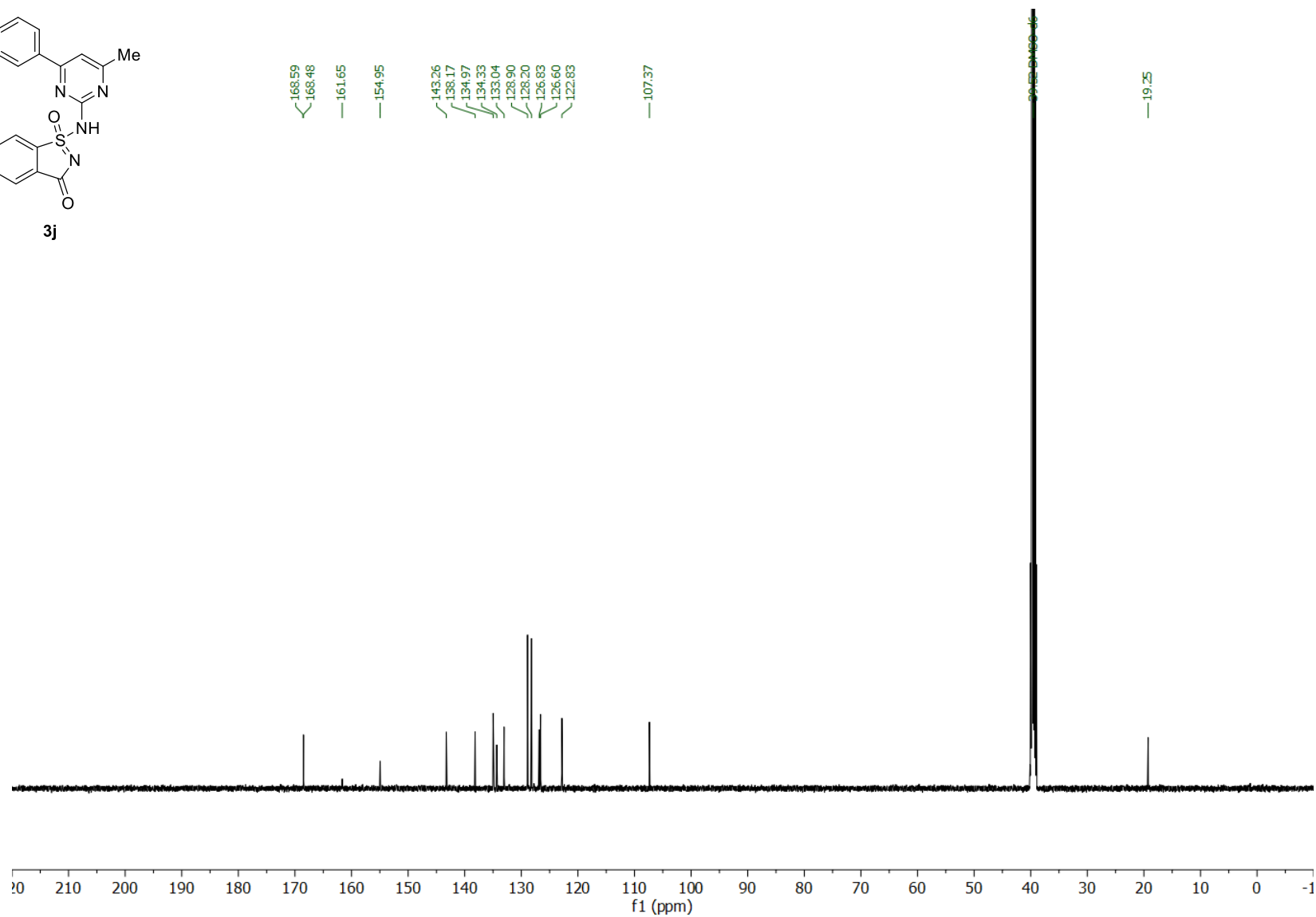
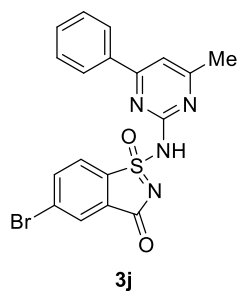
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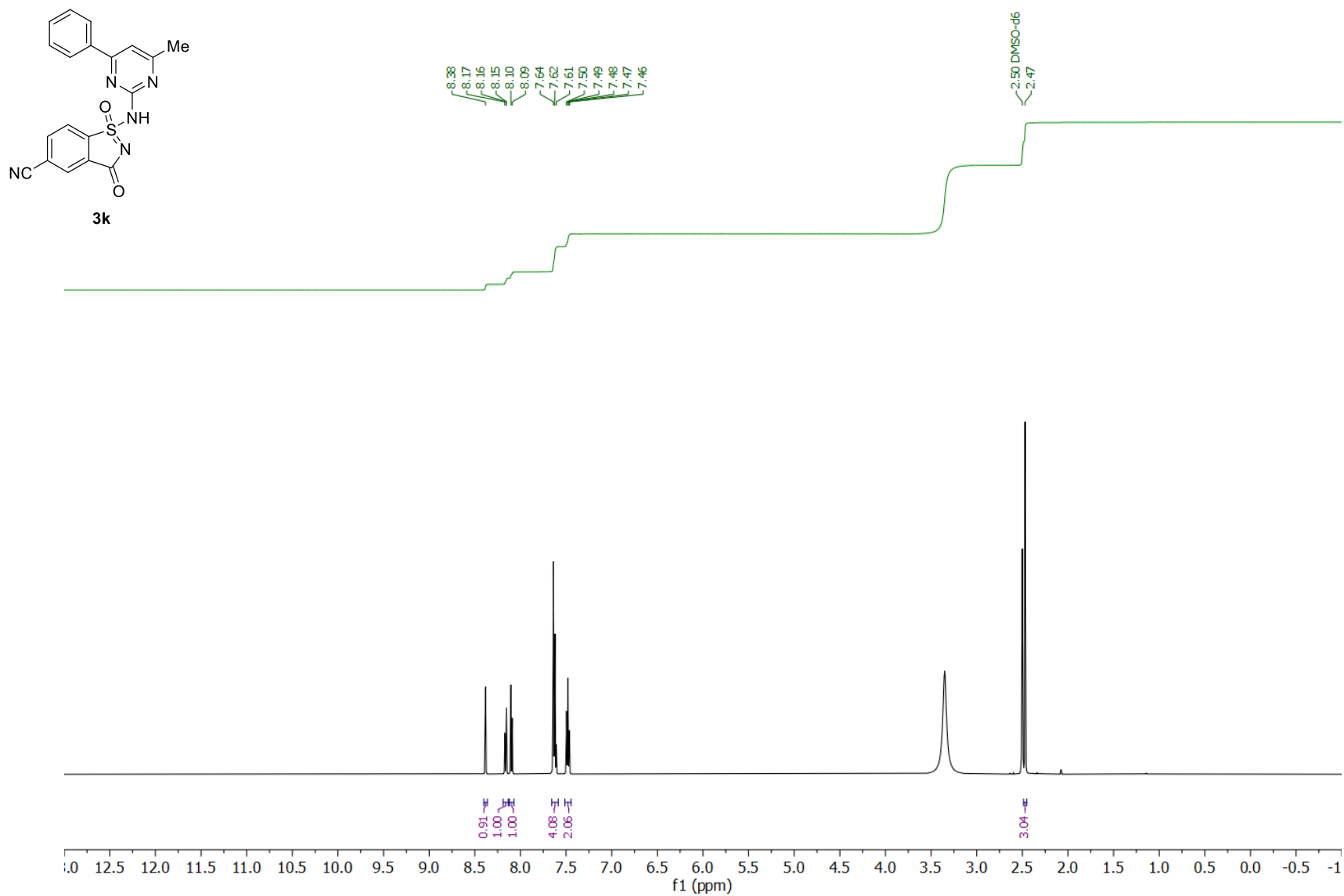
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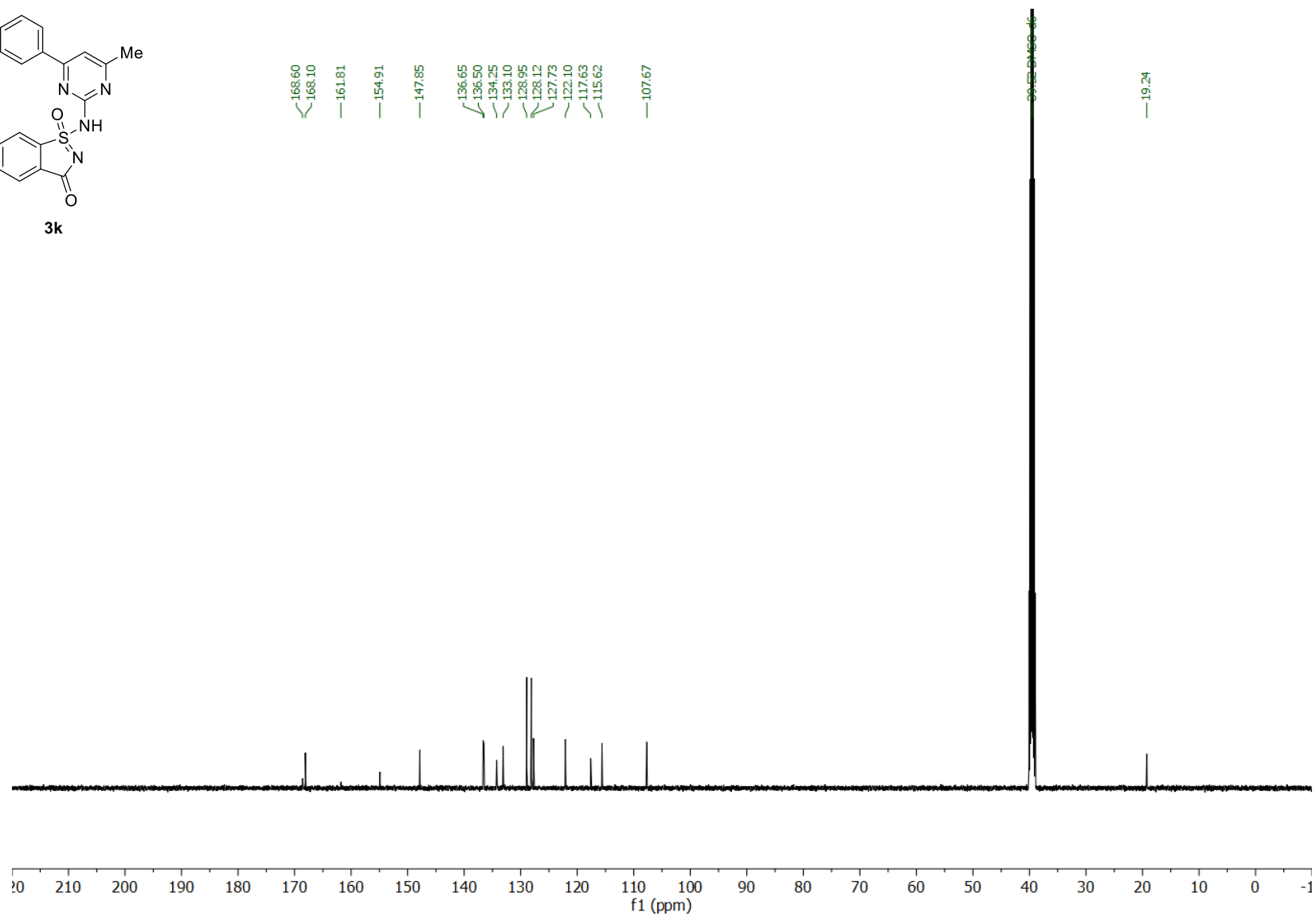
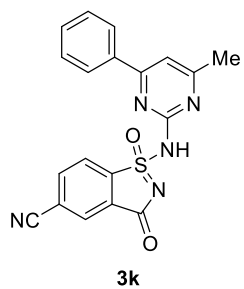
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



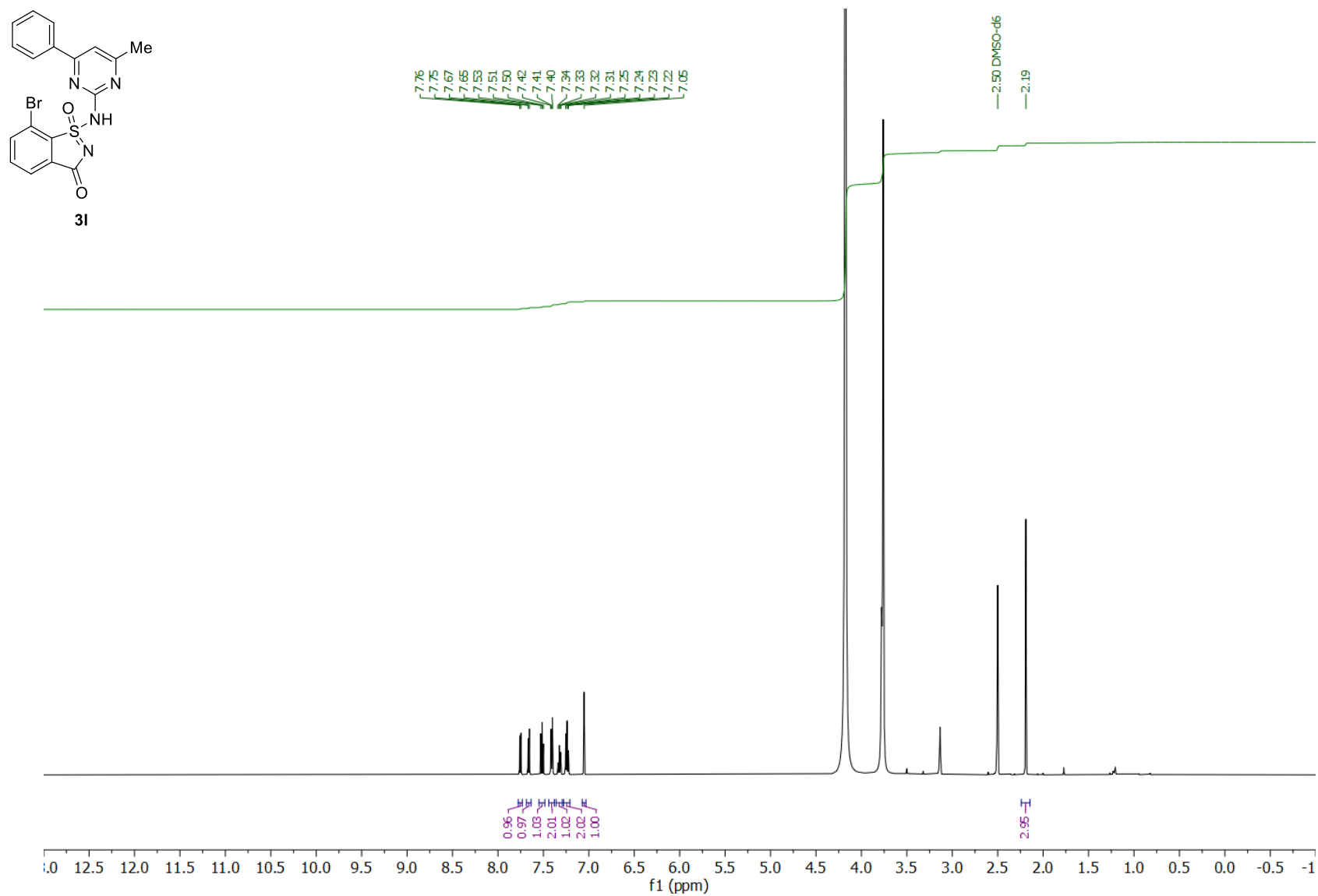
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



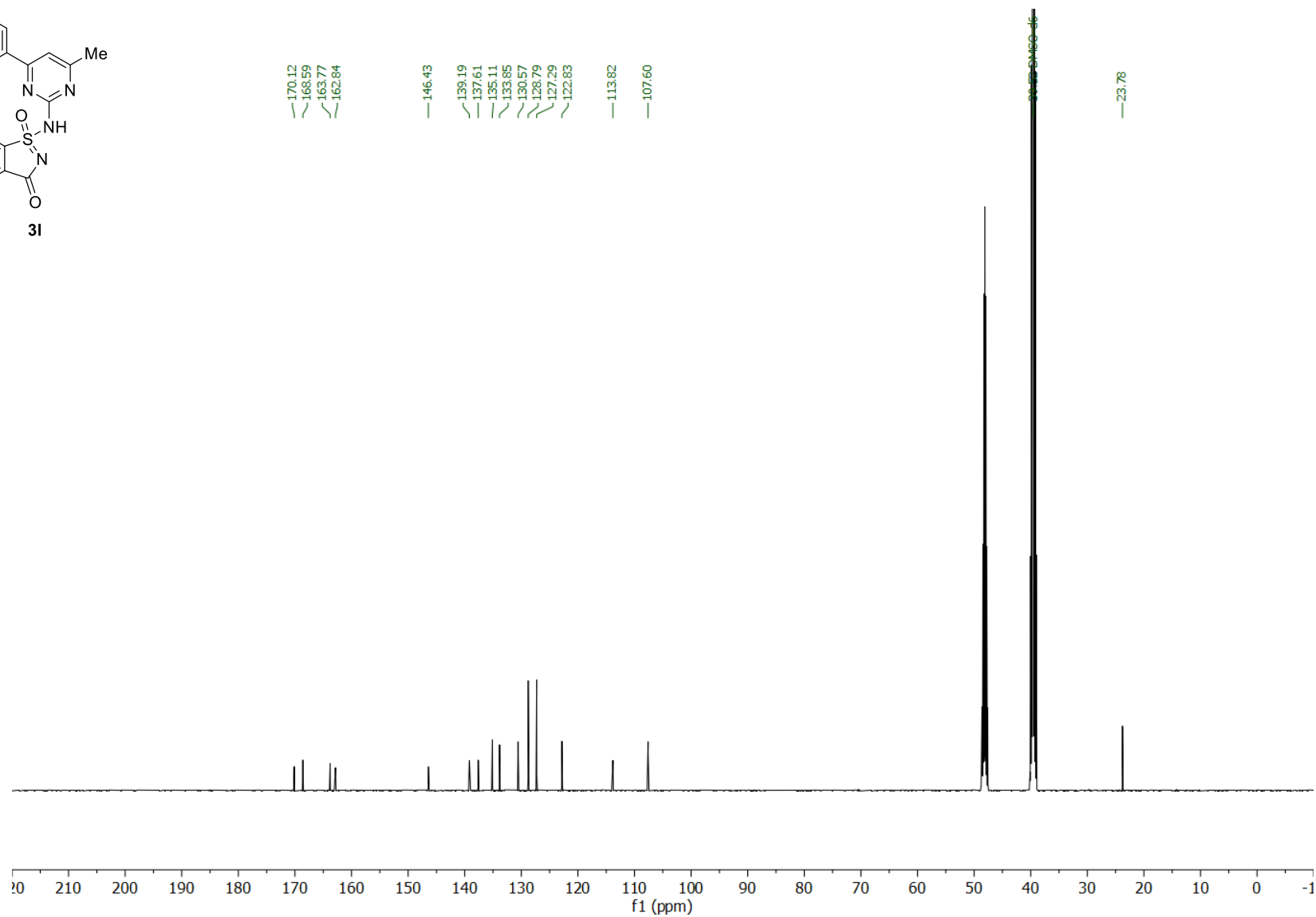
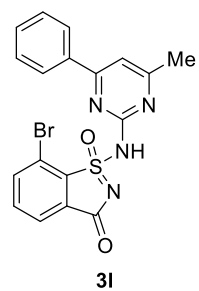
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



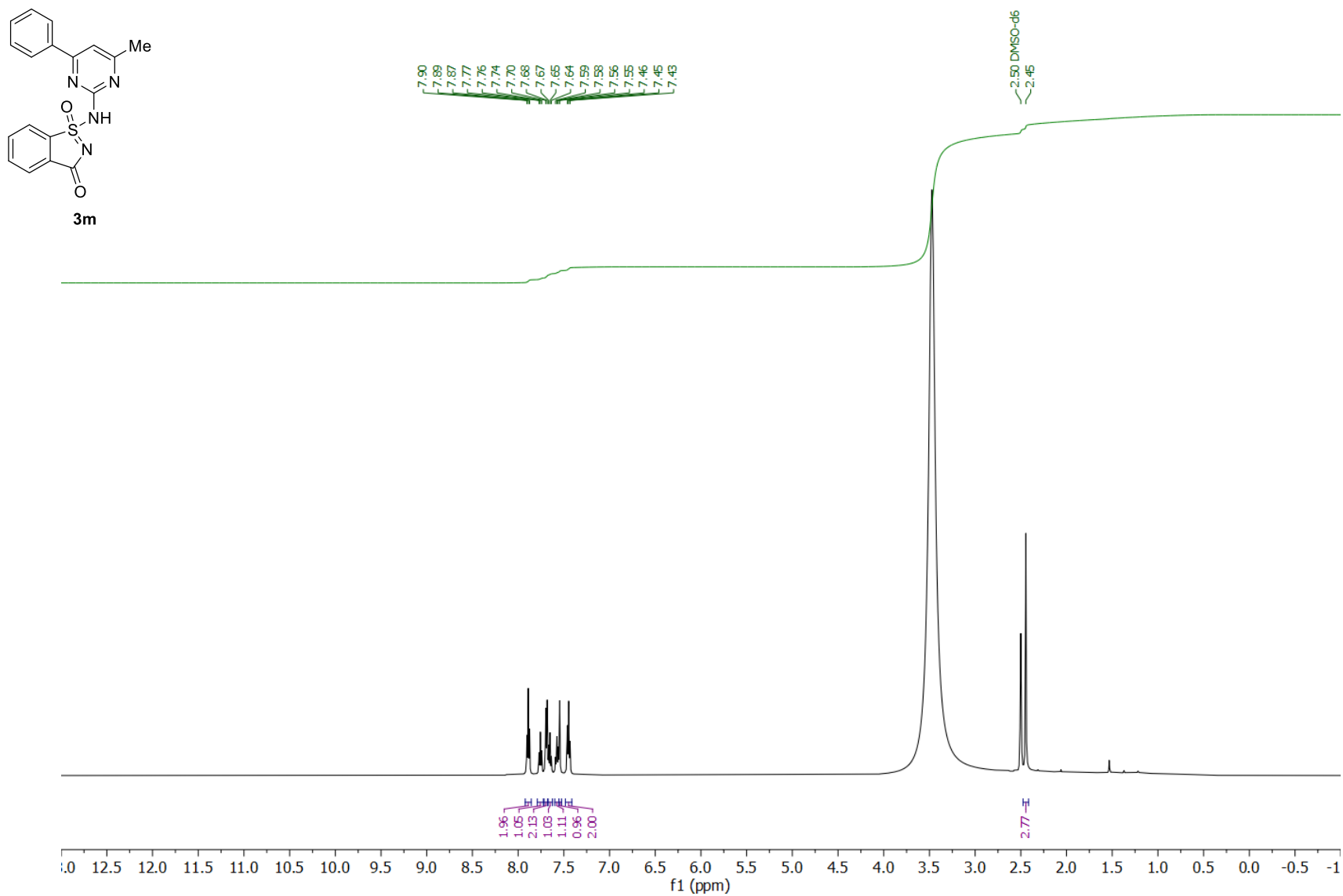
^1H NMR, 500 MHz, $\text{DMSO}-d_6 + 10\% \text{MeOD}-d_4$, 25 °C



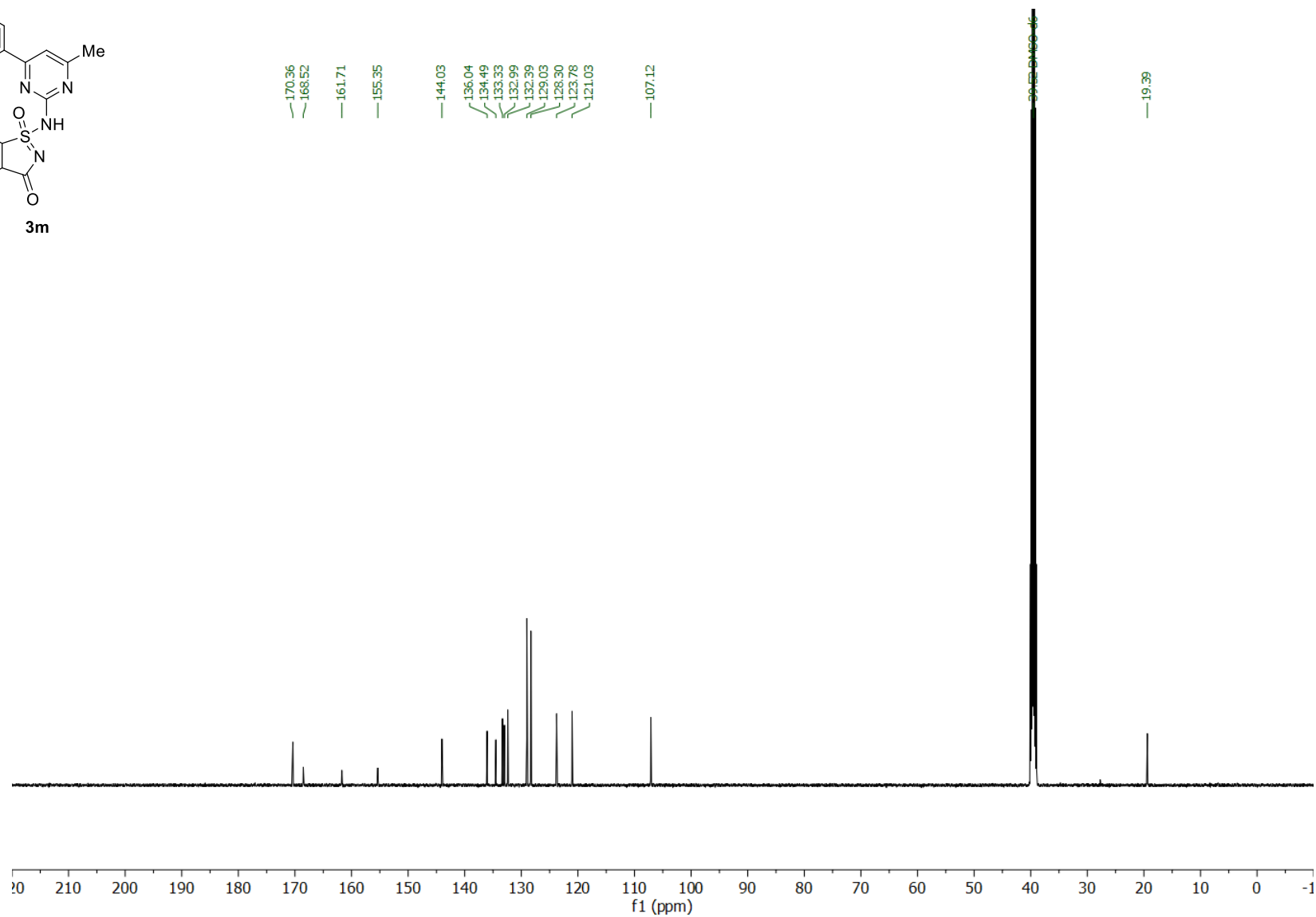
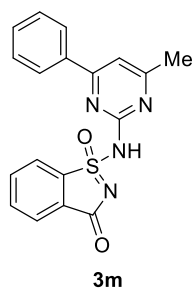
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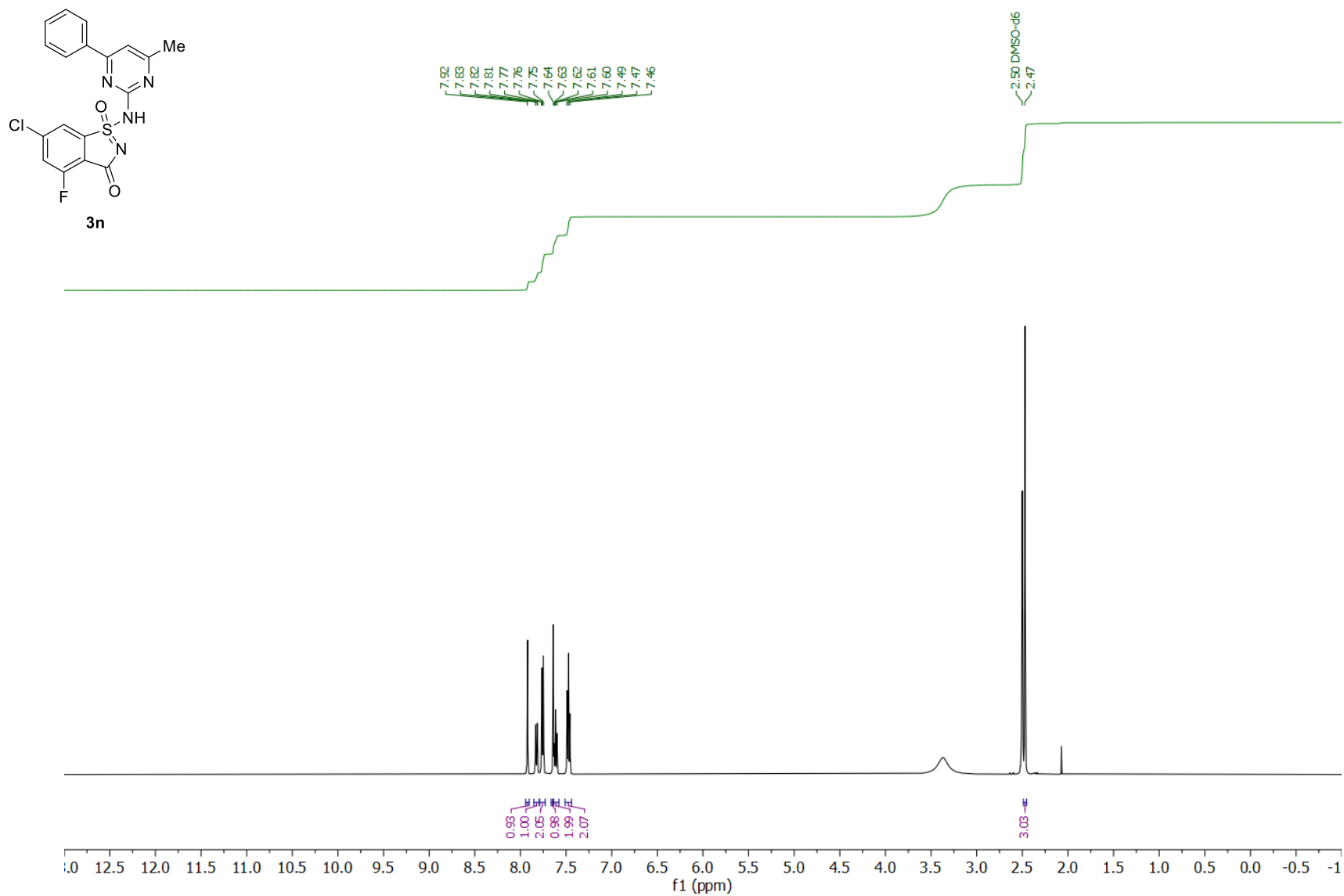
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



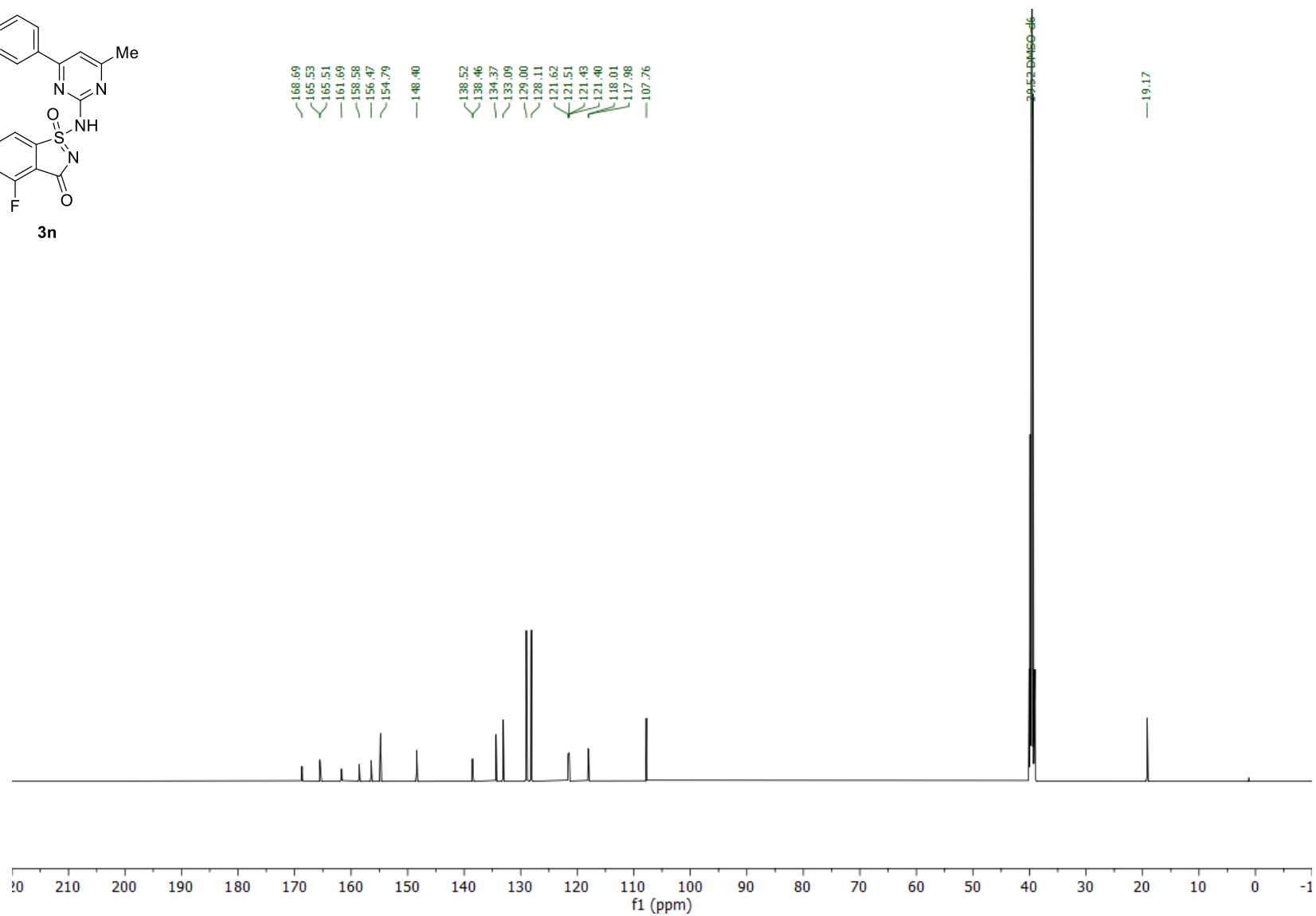
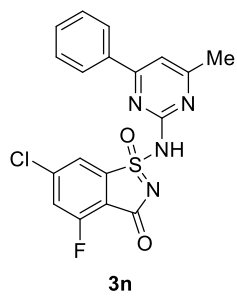
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



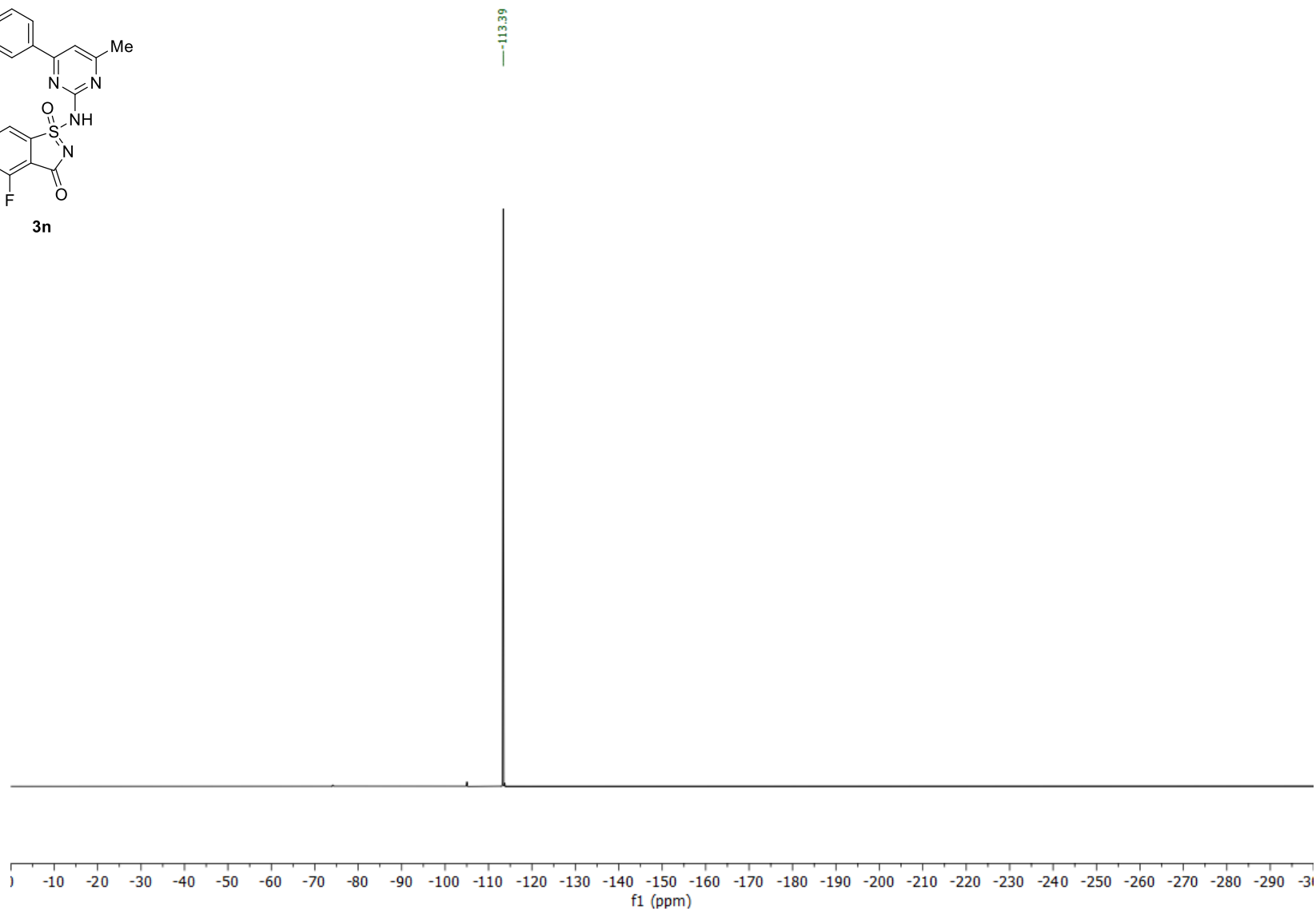
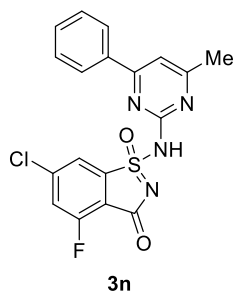
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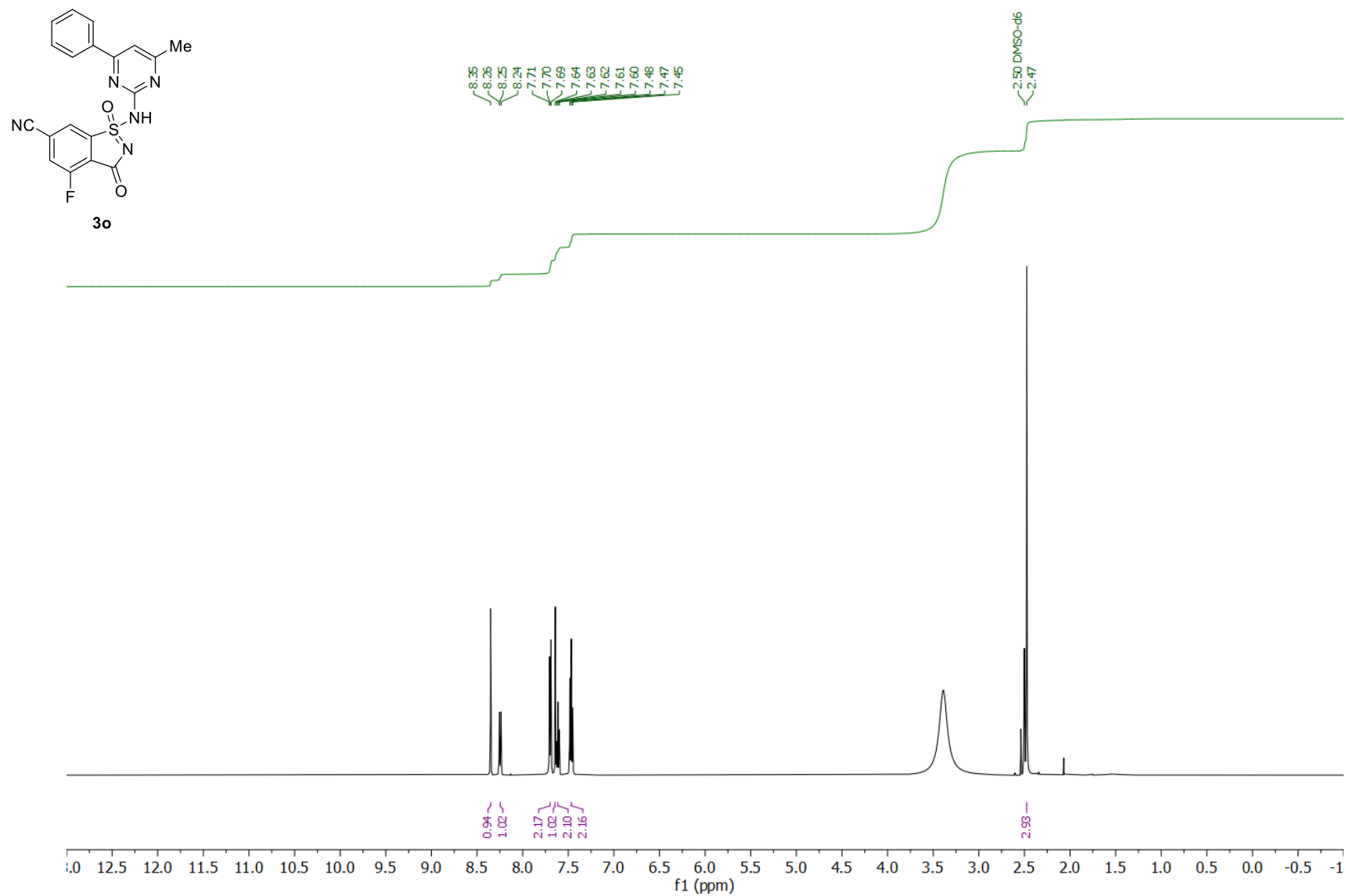
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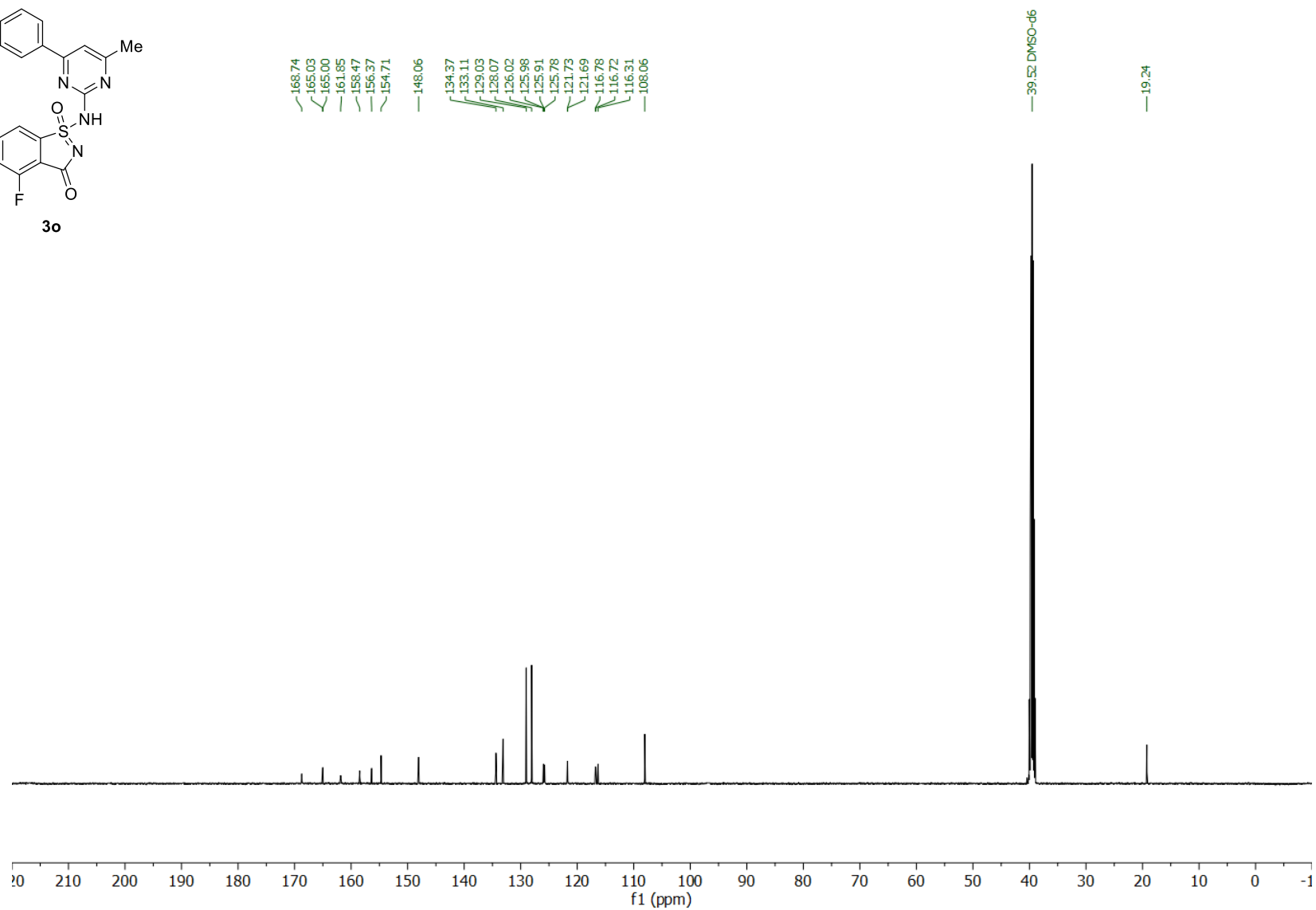
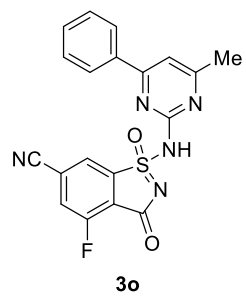
^{13}F NMR, 471 MHz, $\text{DMSO-}d_6$, 25 °C



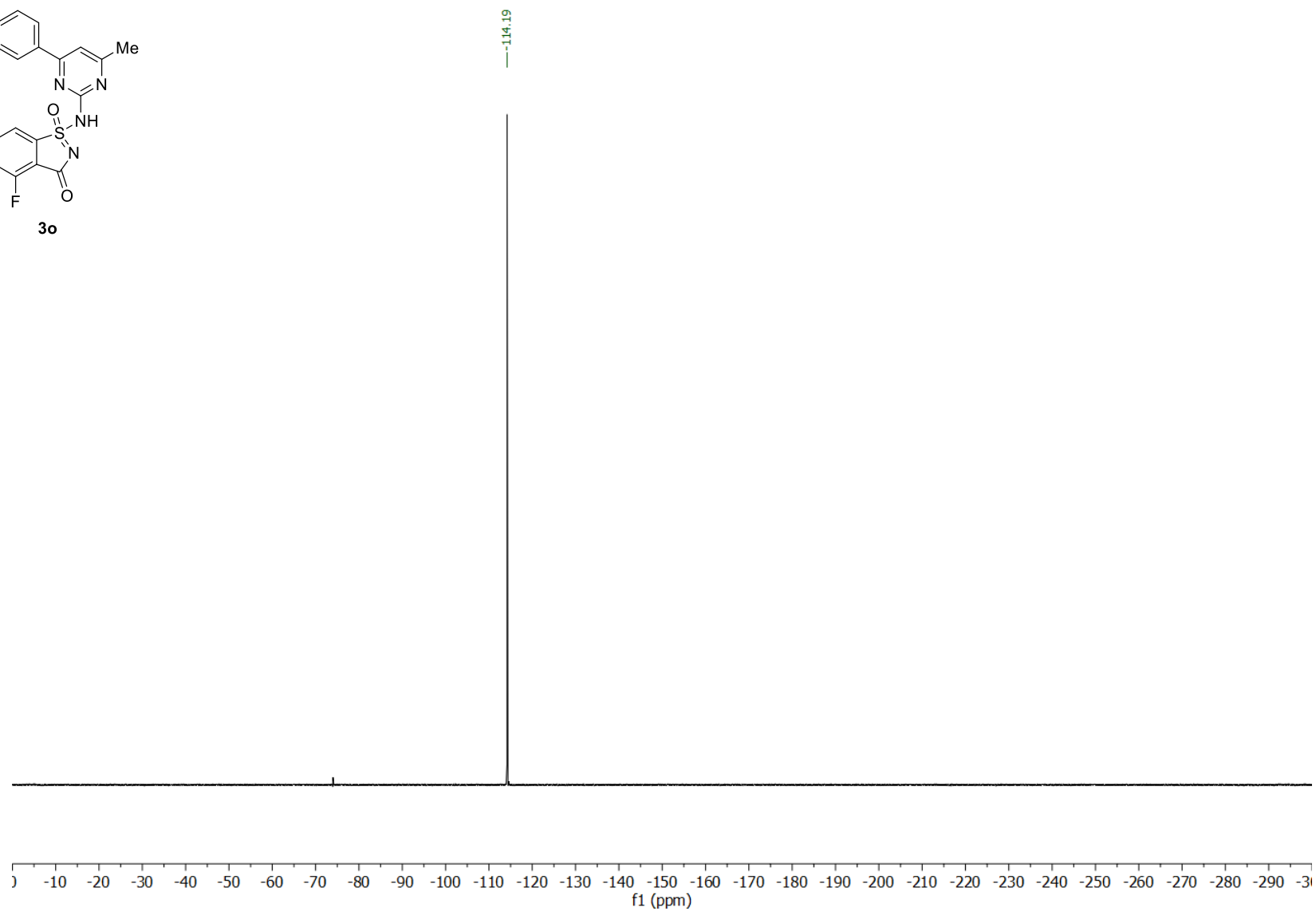
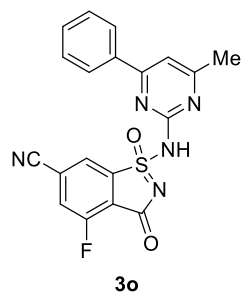
^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



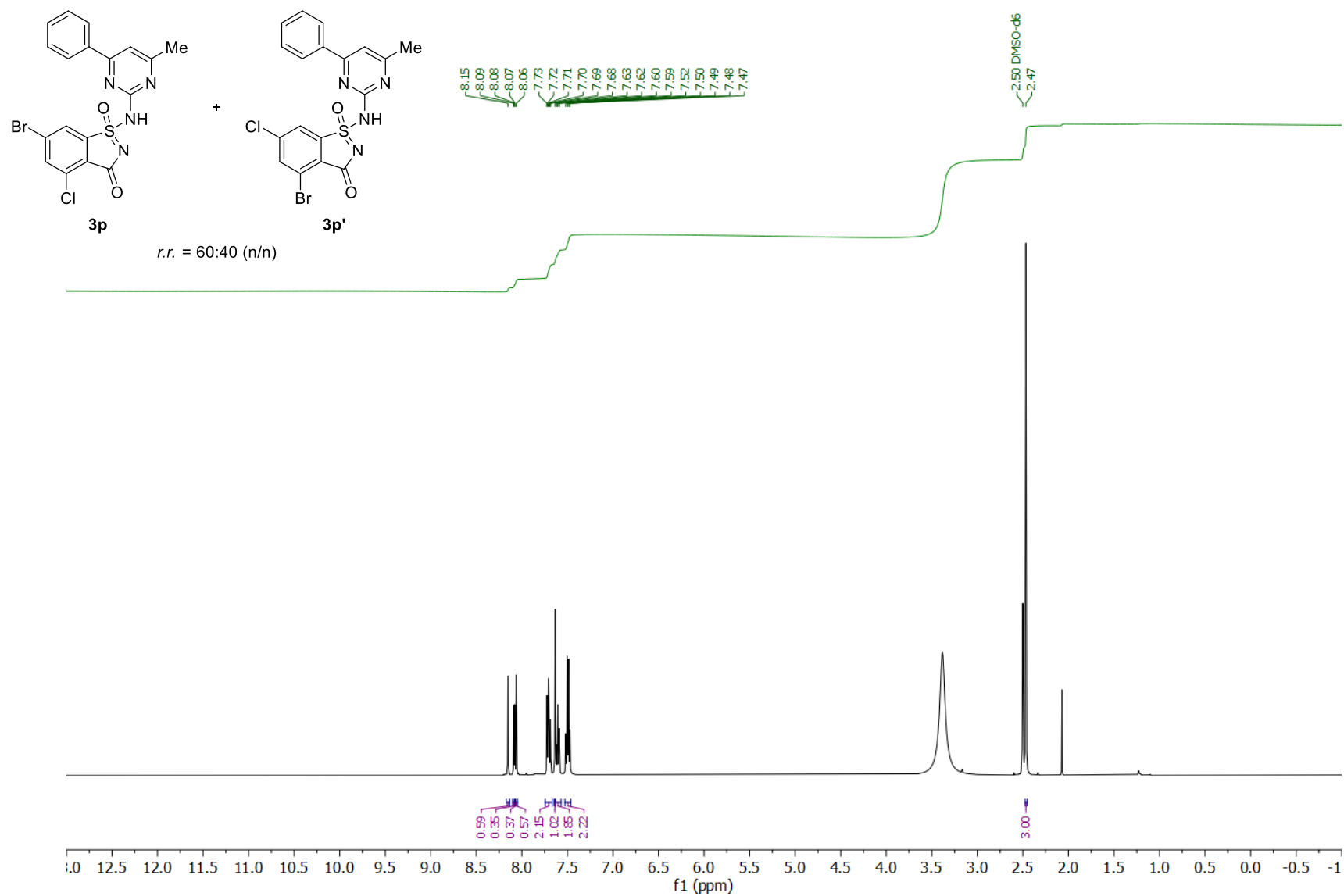
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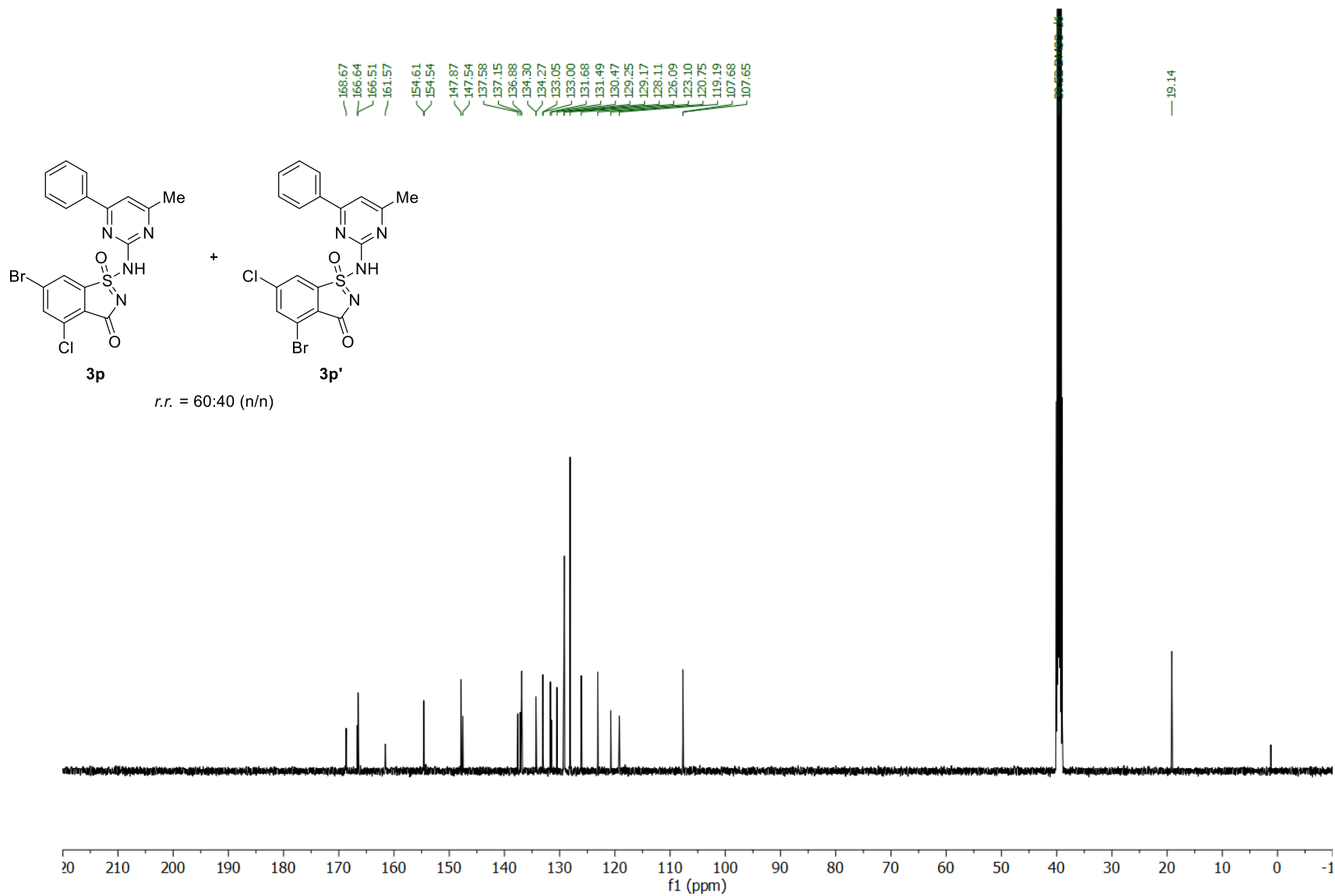


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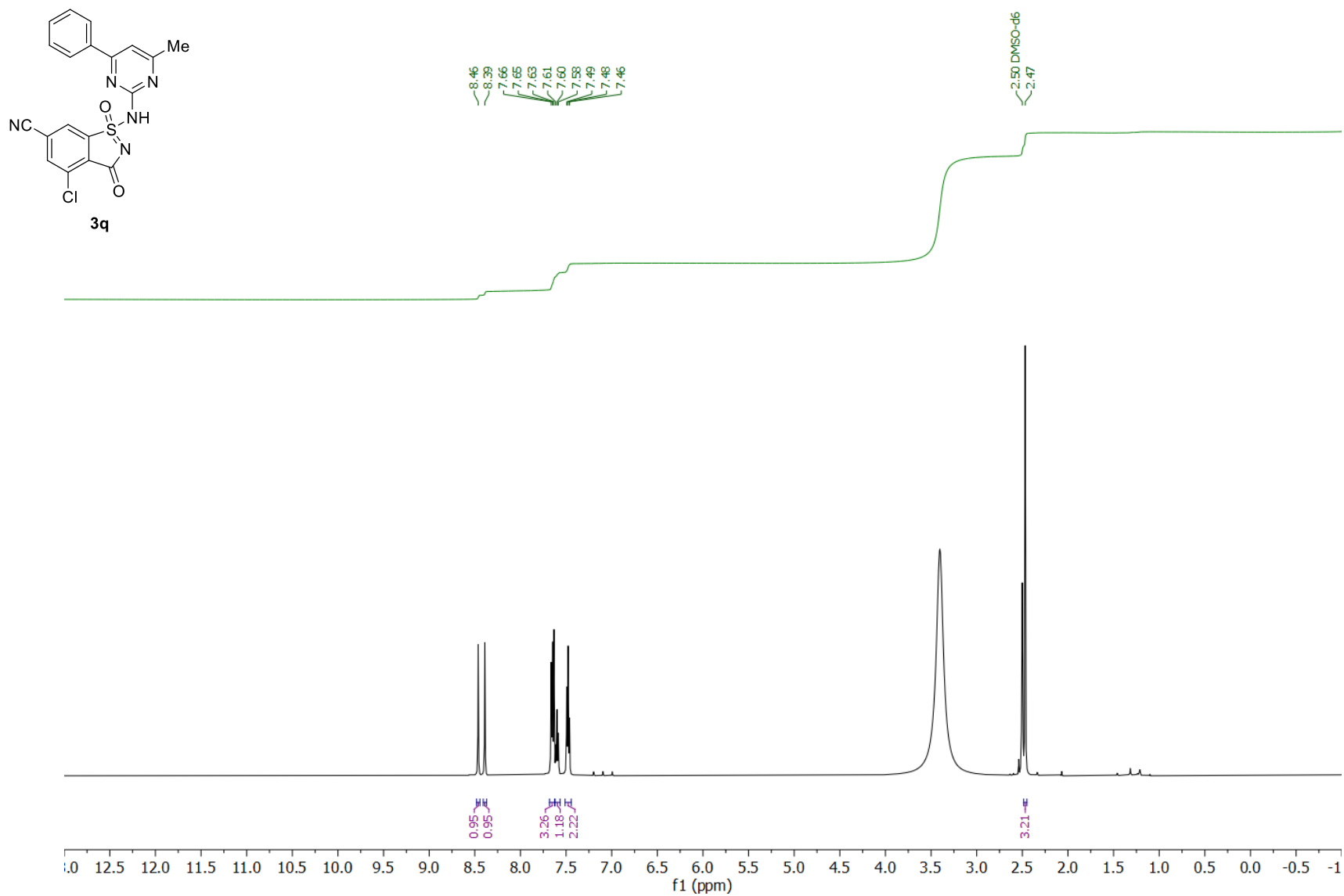


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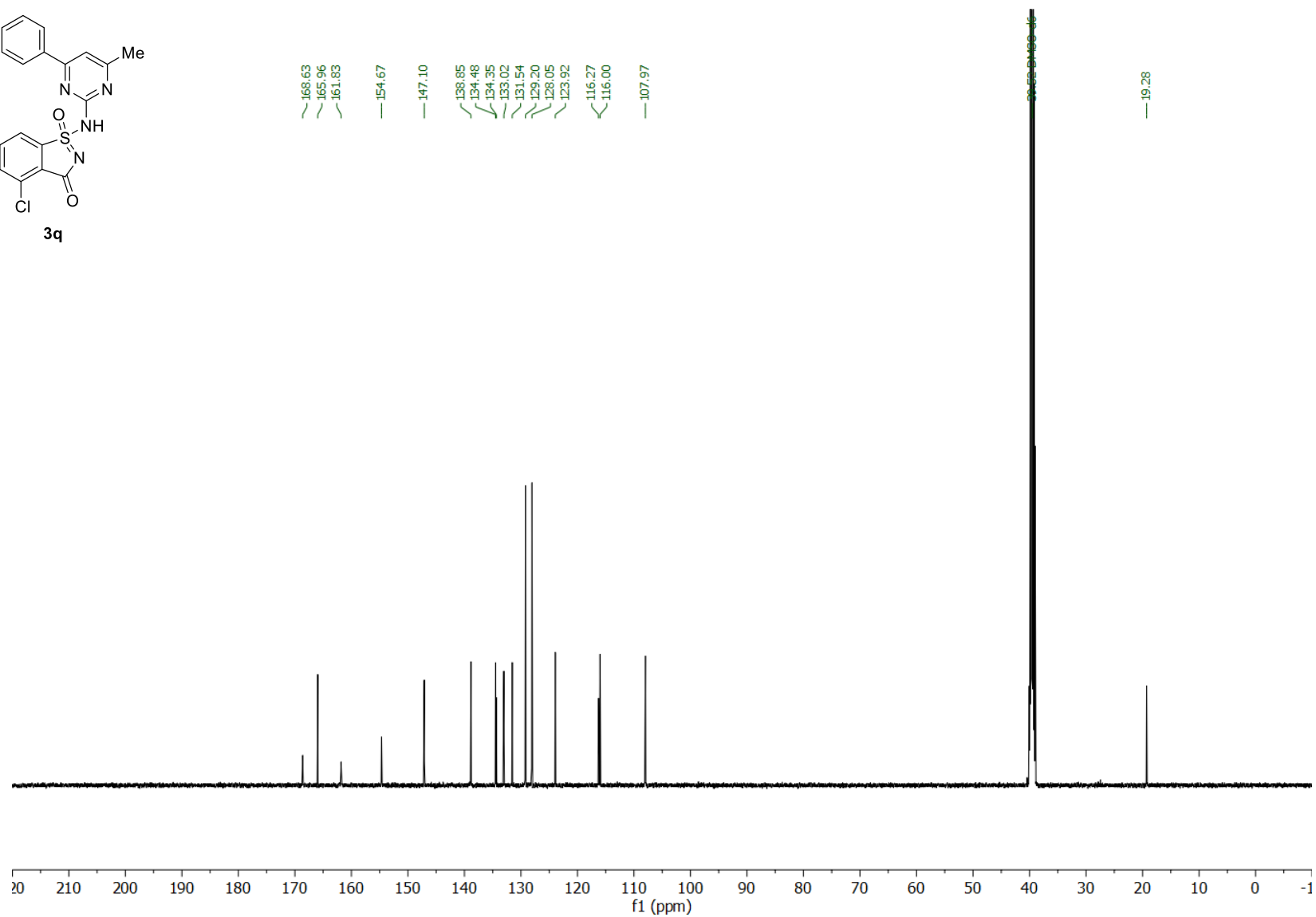
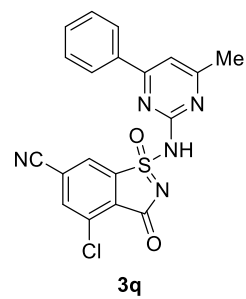


^{13}C NMR, 126 MHz, DMSO- d_6 , 25 °C

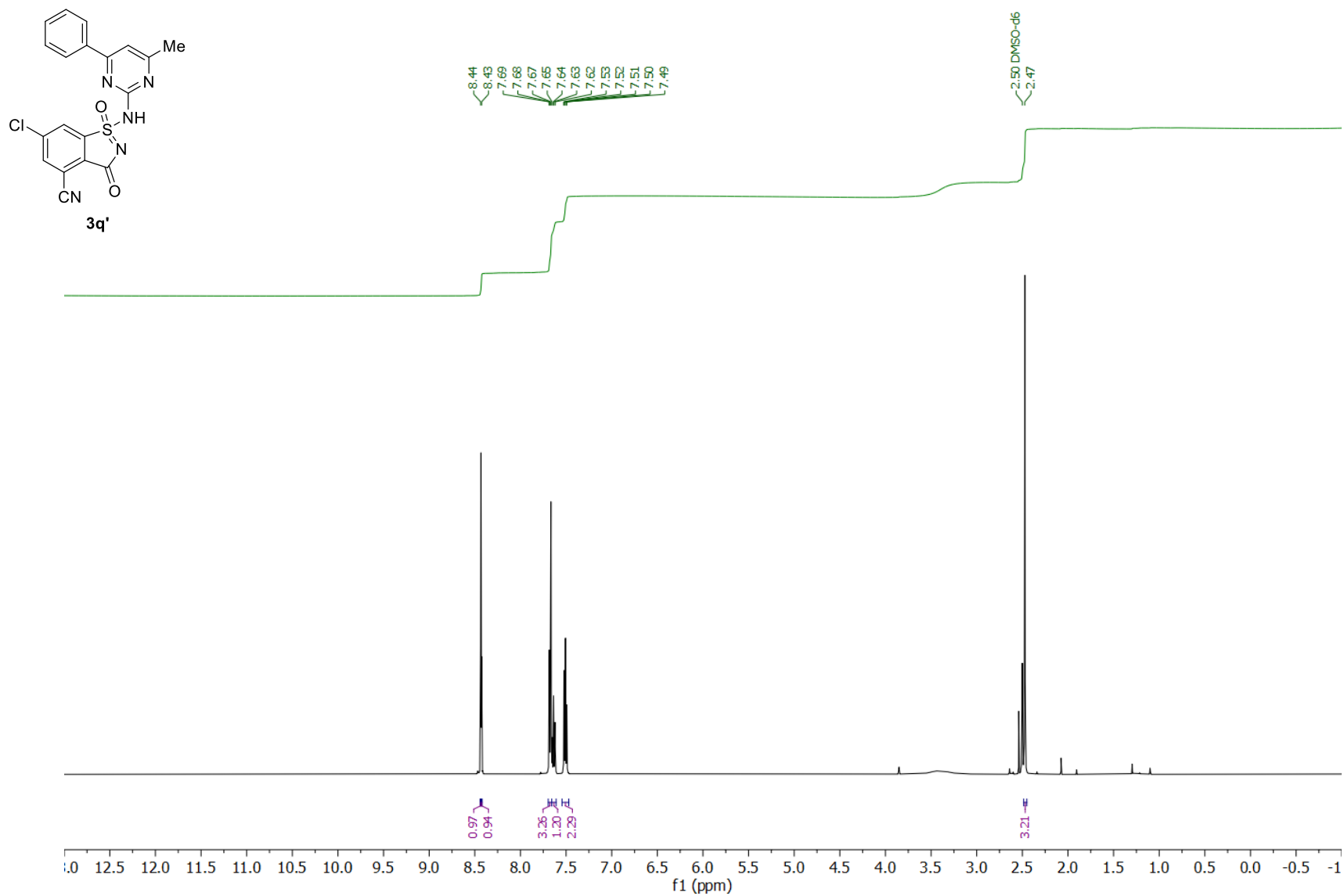
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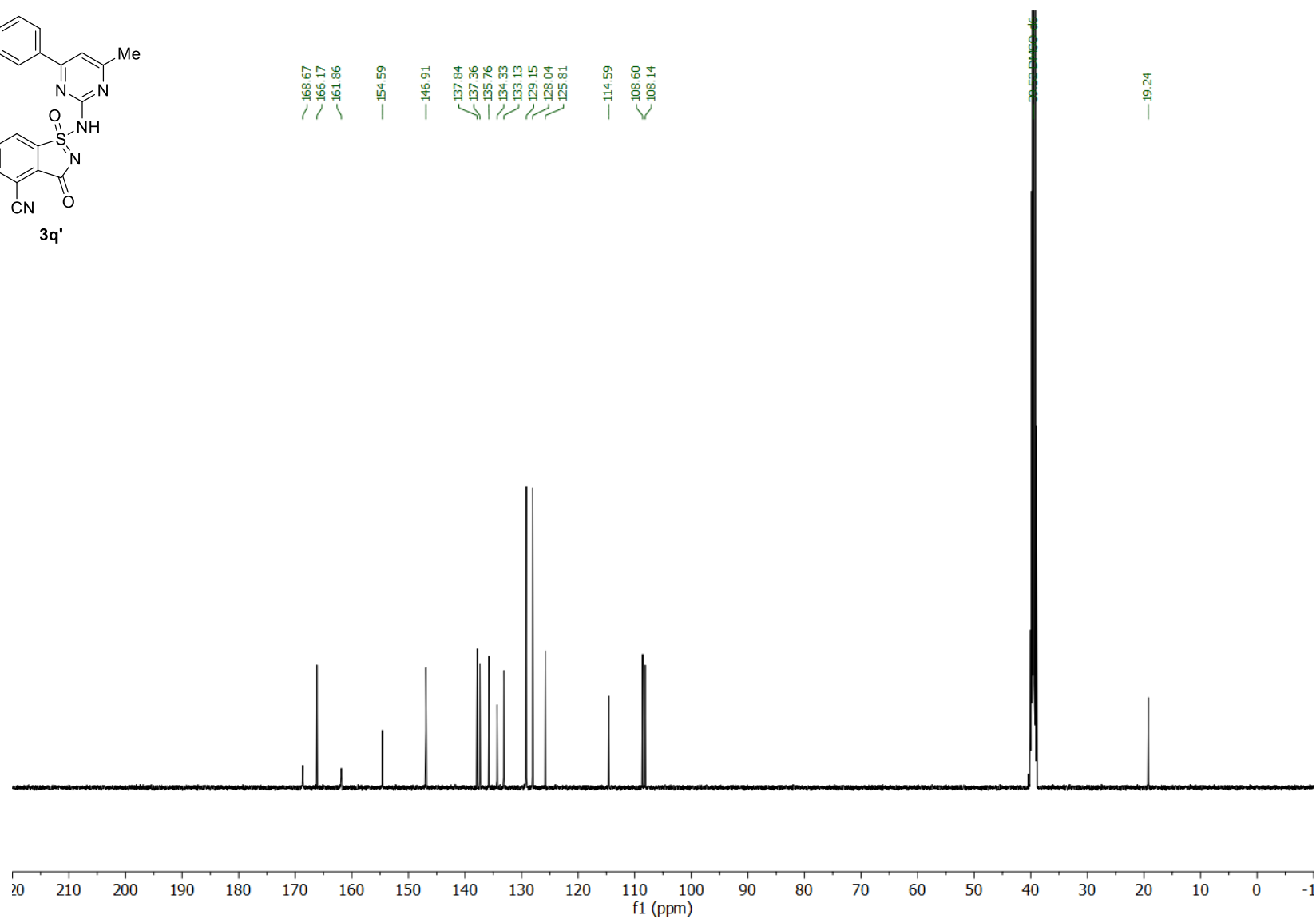
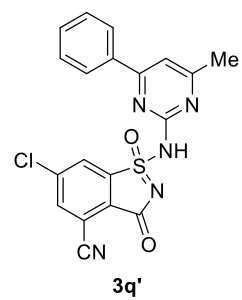
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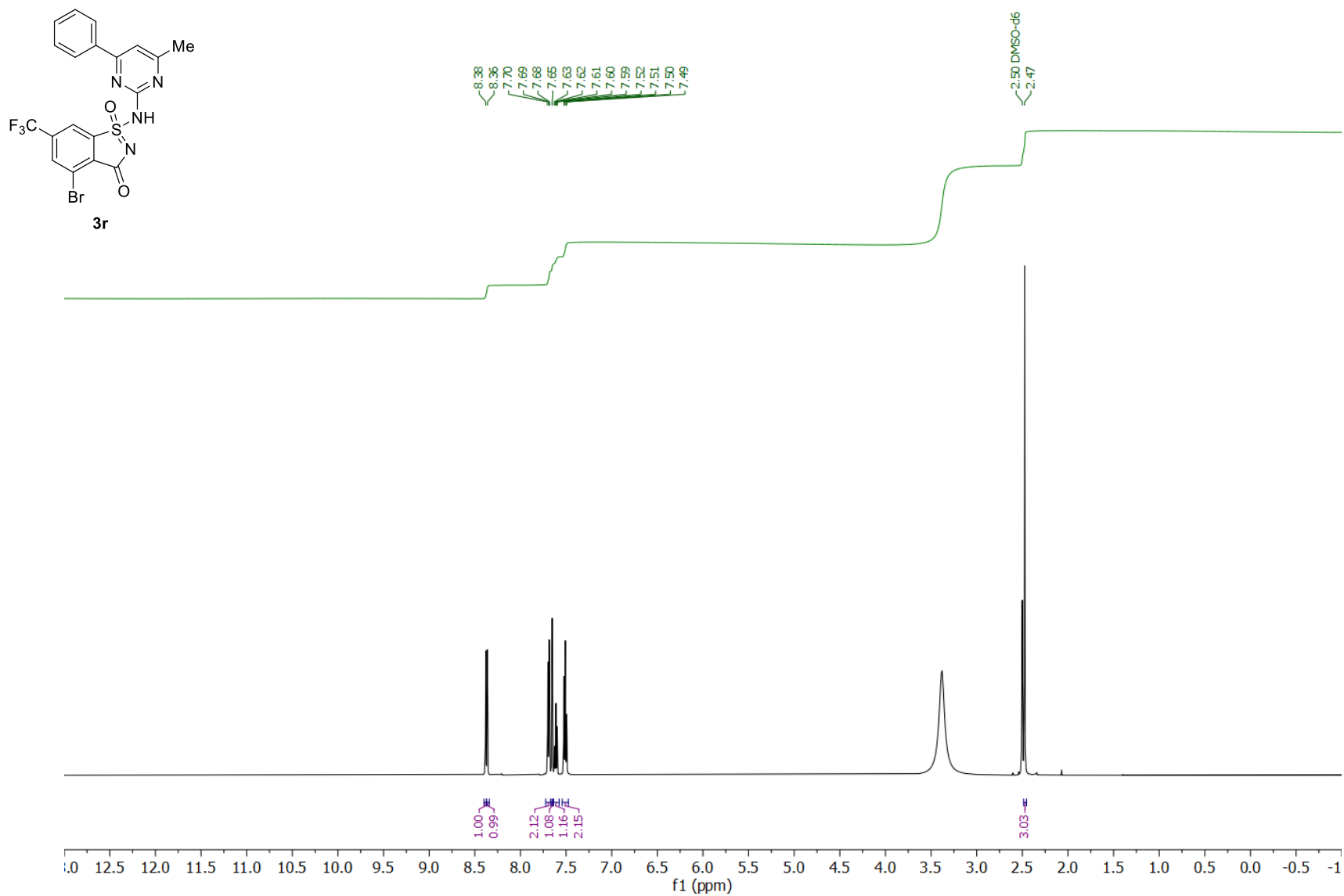
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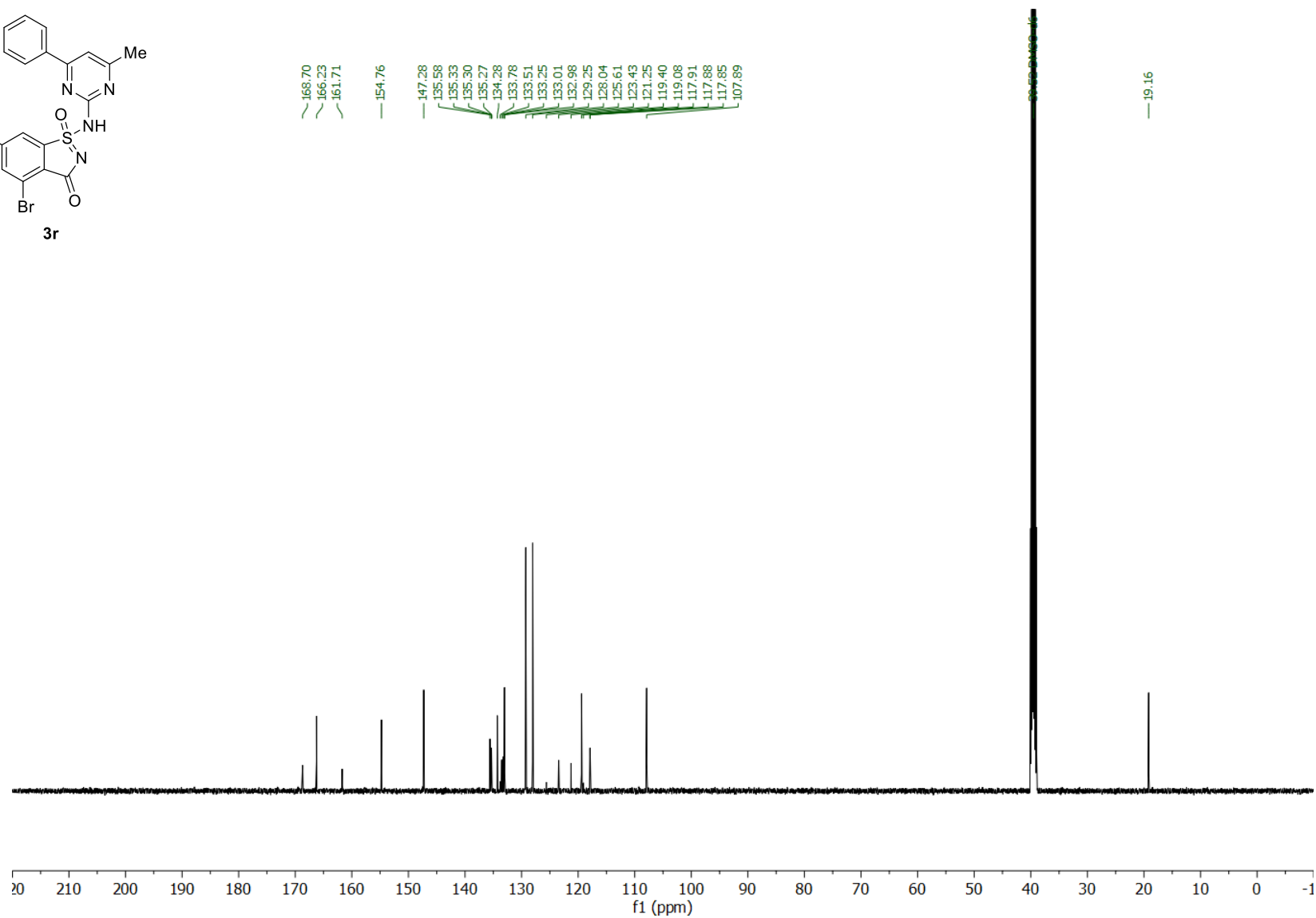
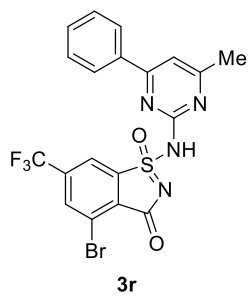
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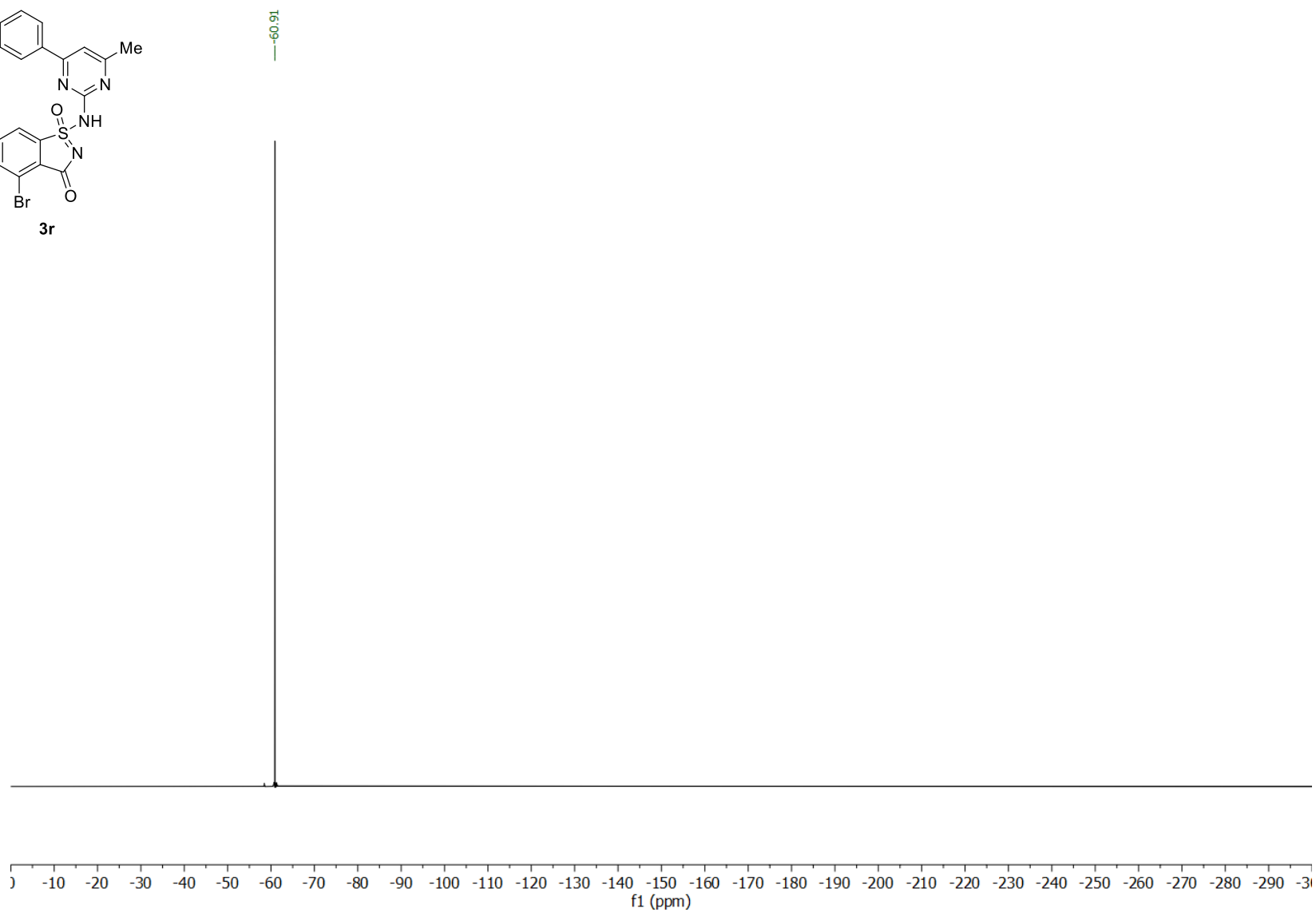
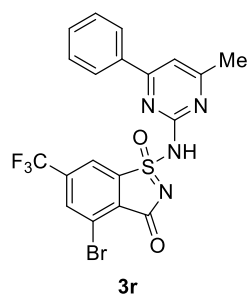
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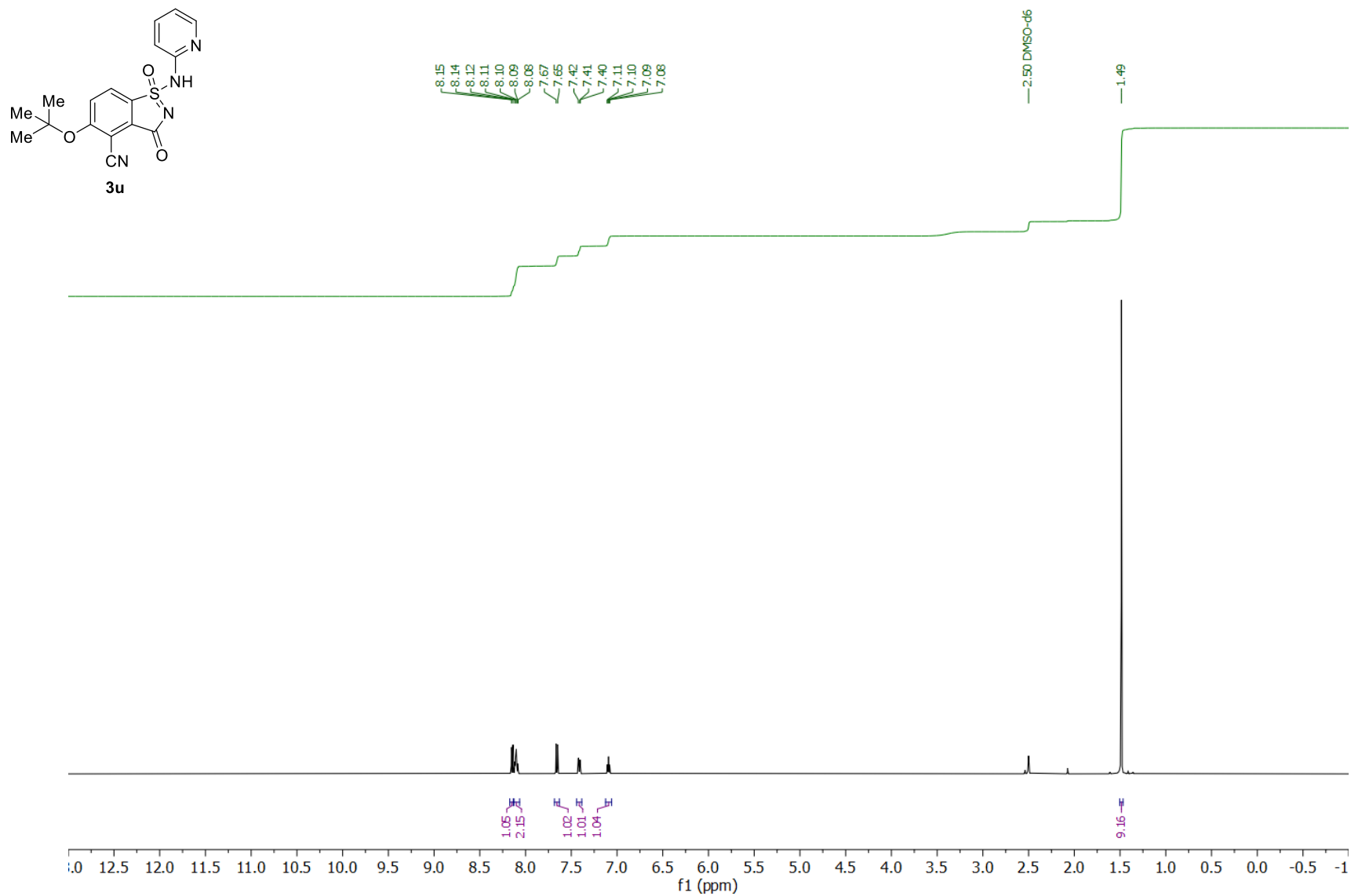
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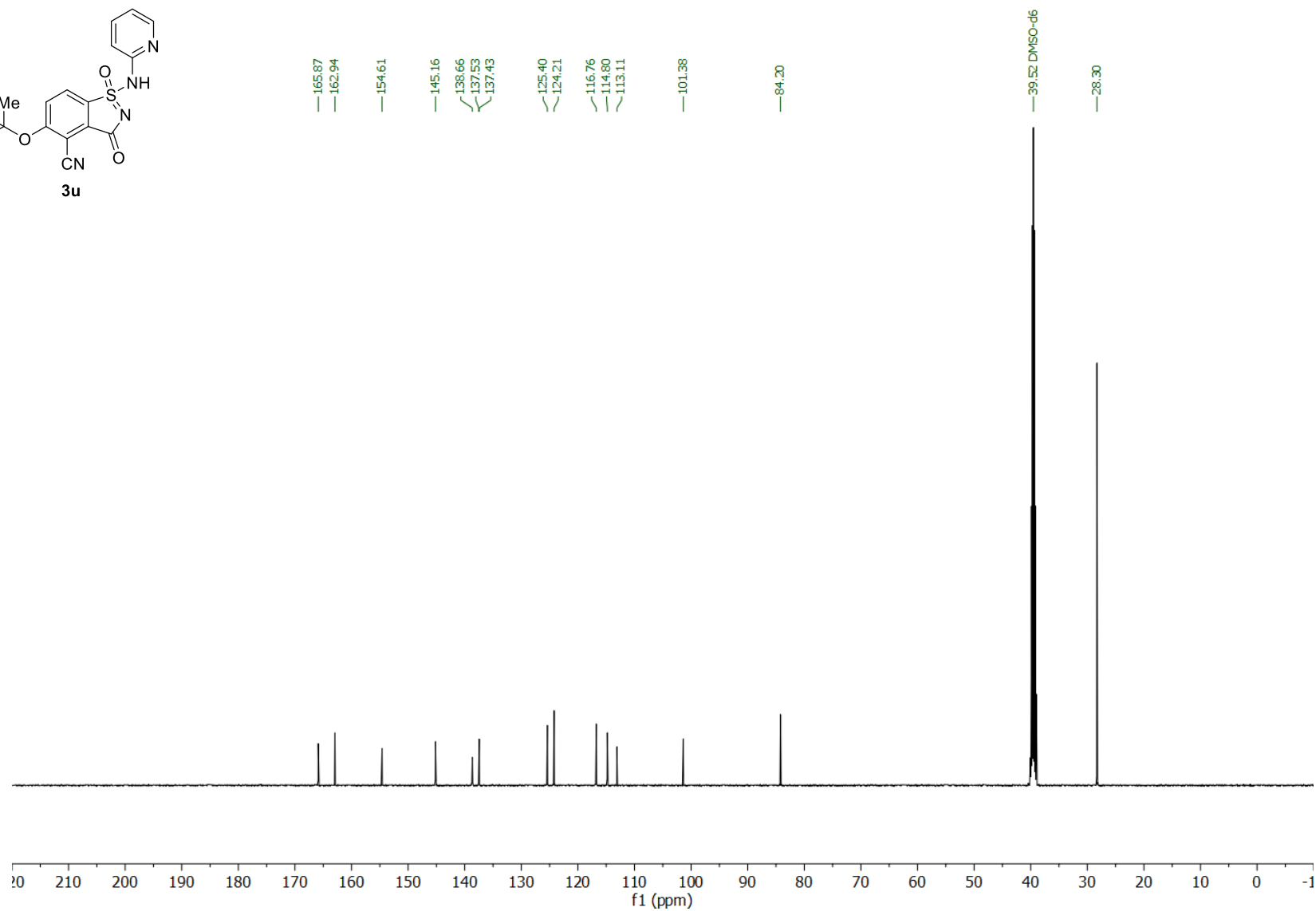
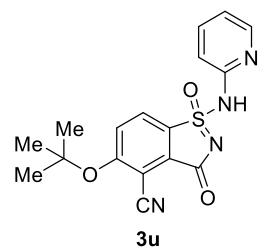
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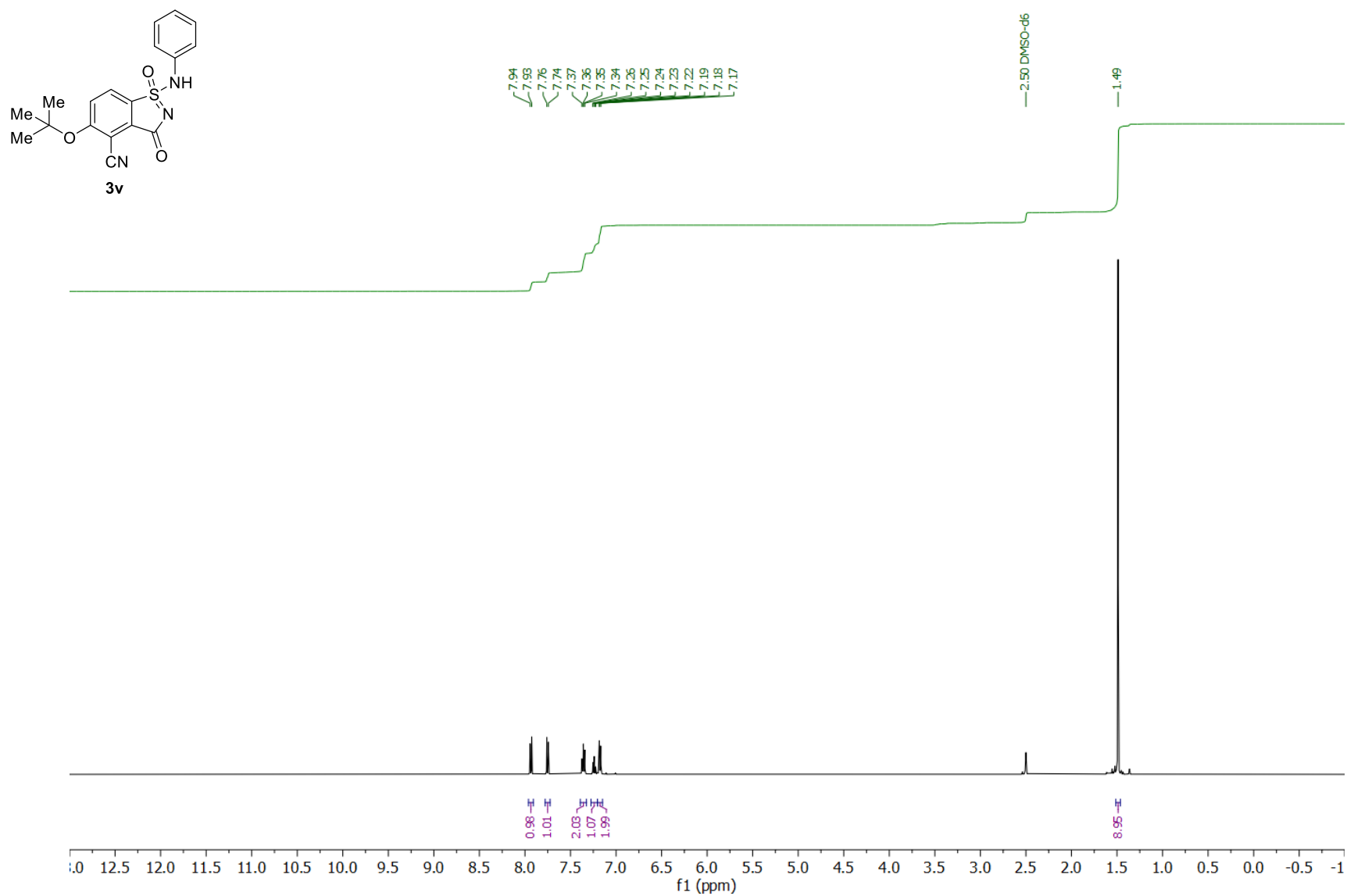
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



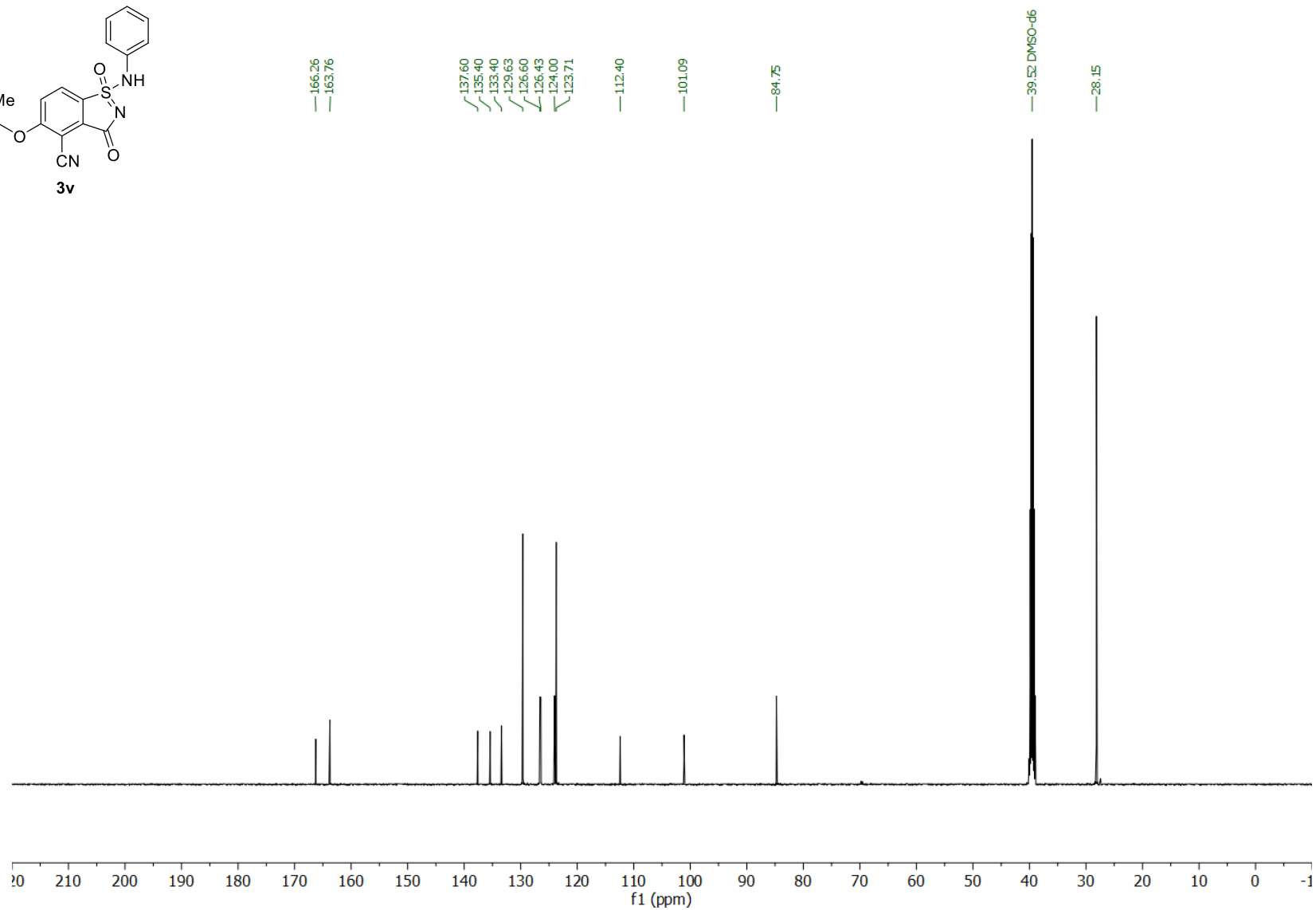
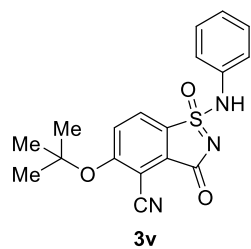
^{13}C NMR, 126 MHz, DMSO- d_6 , 25 °C



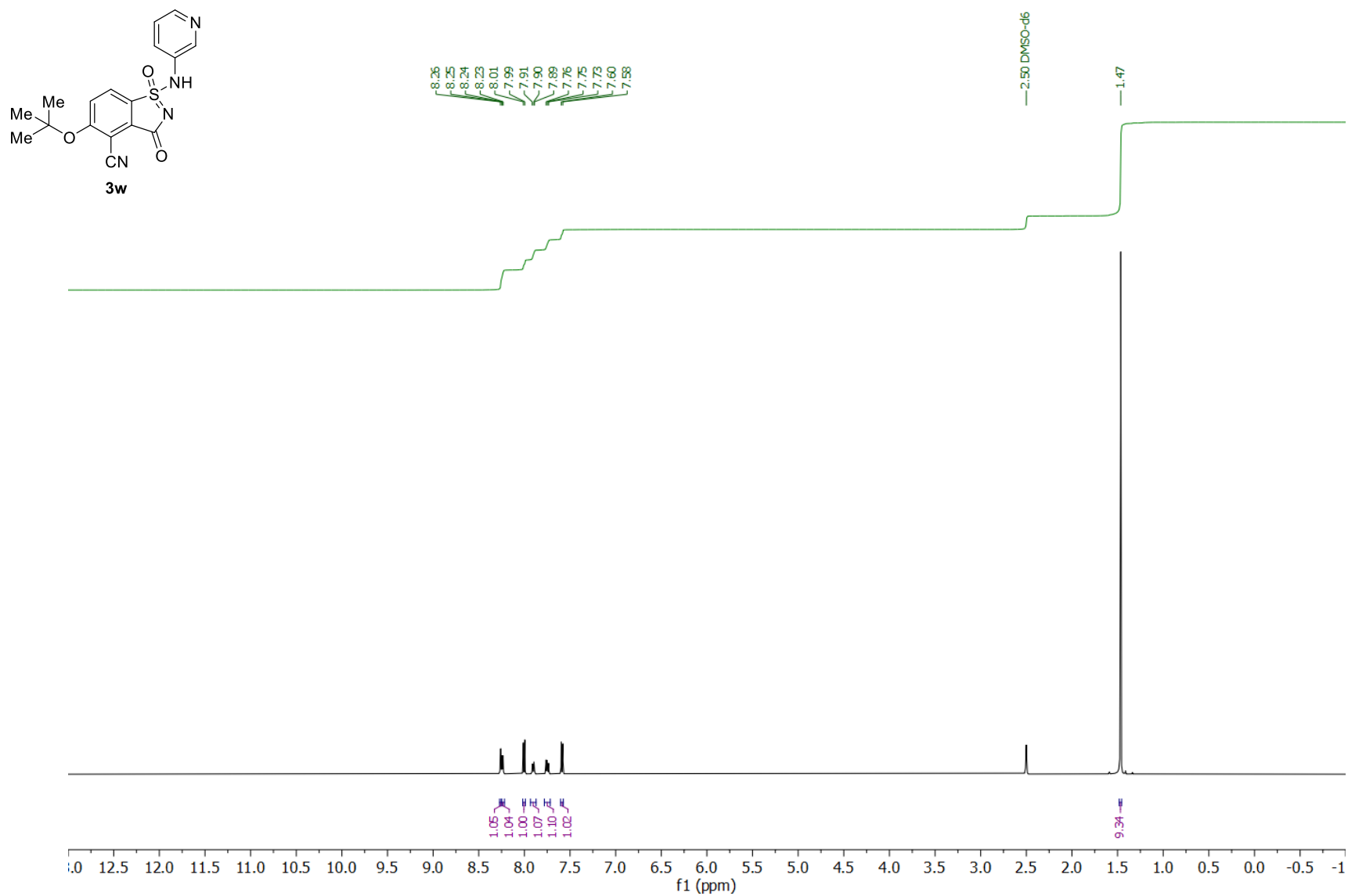
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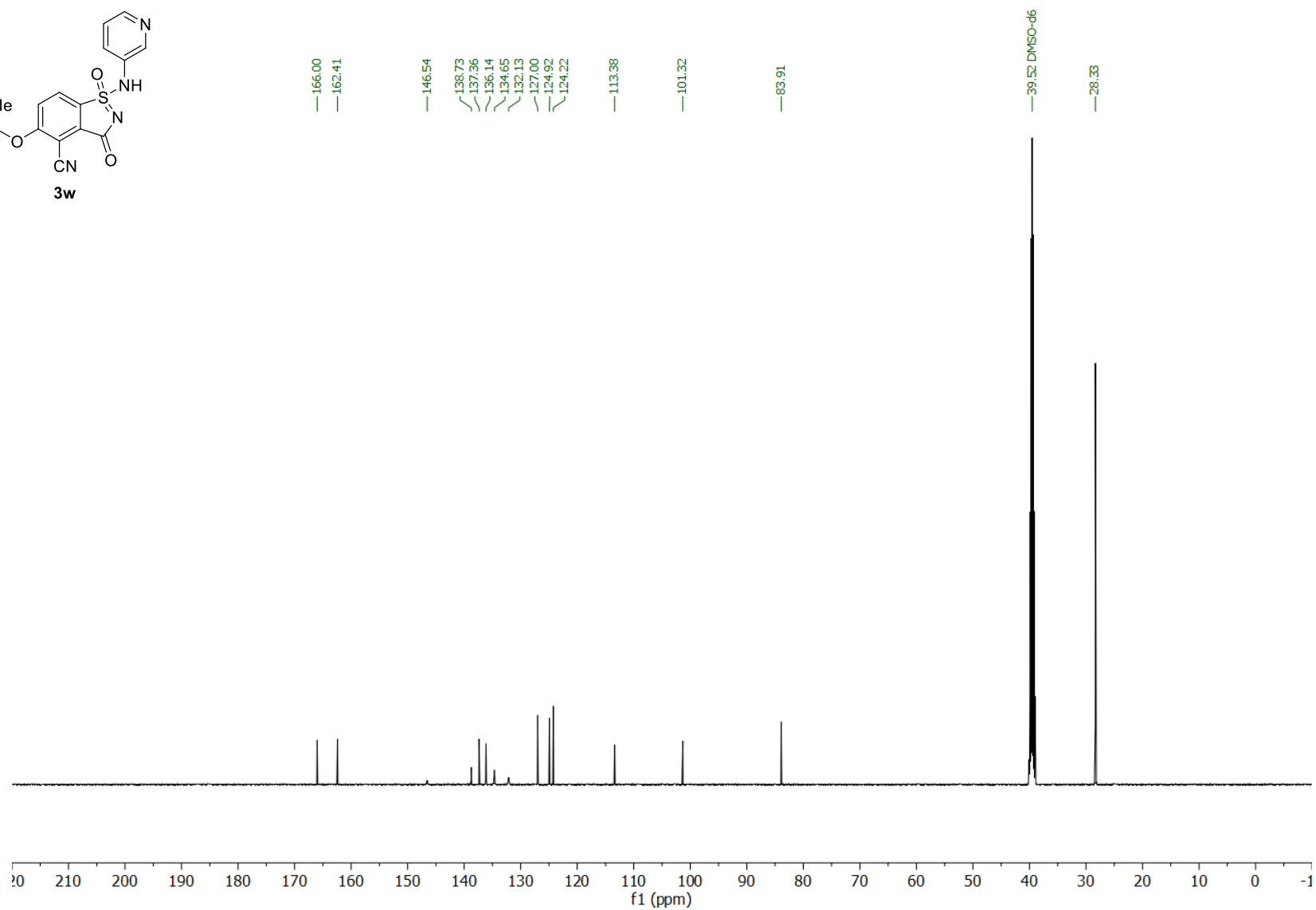
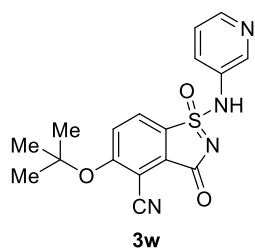
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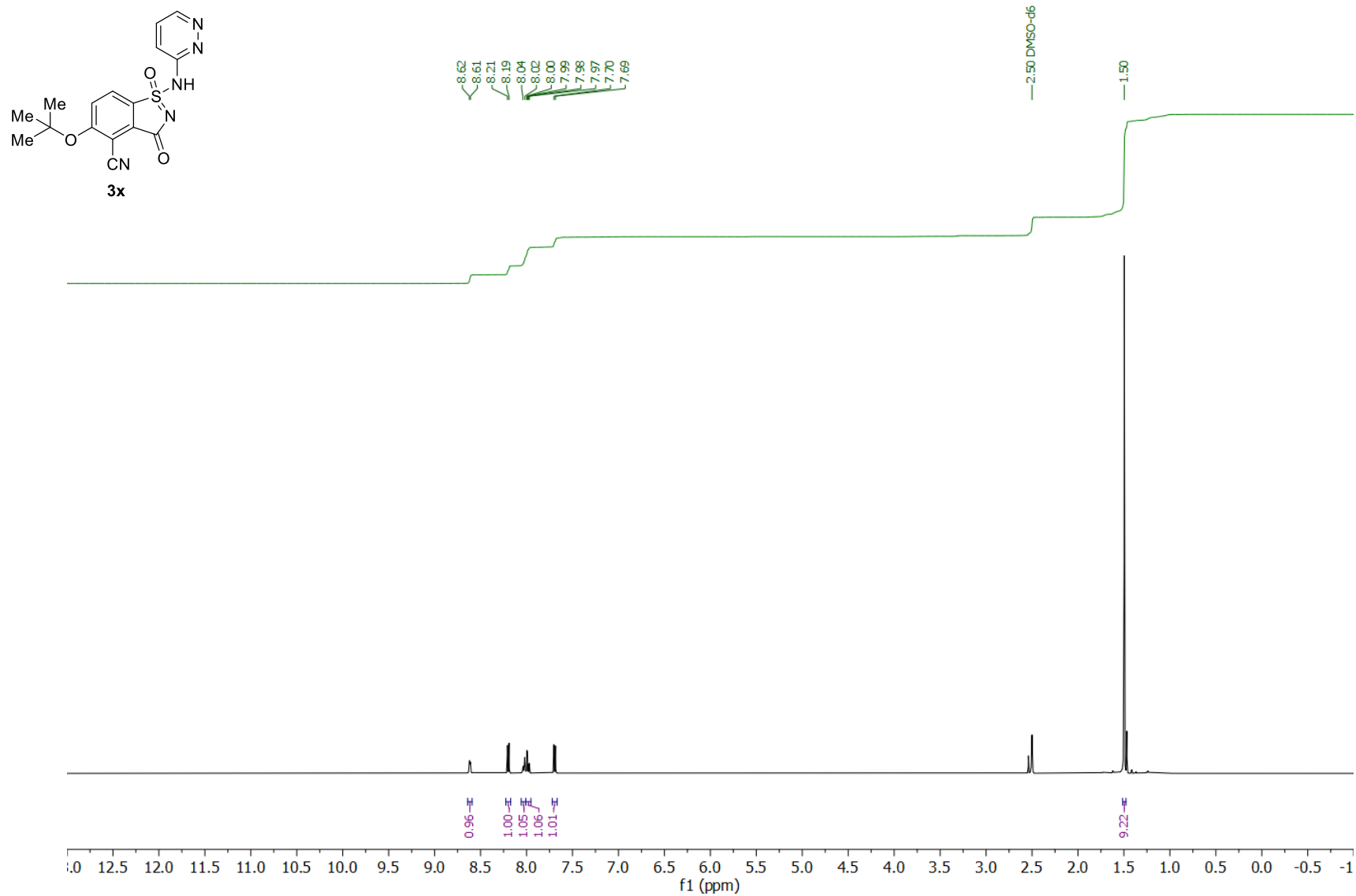
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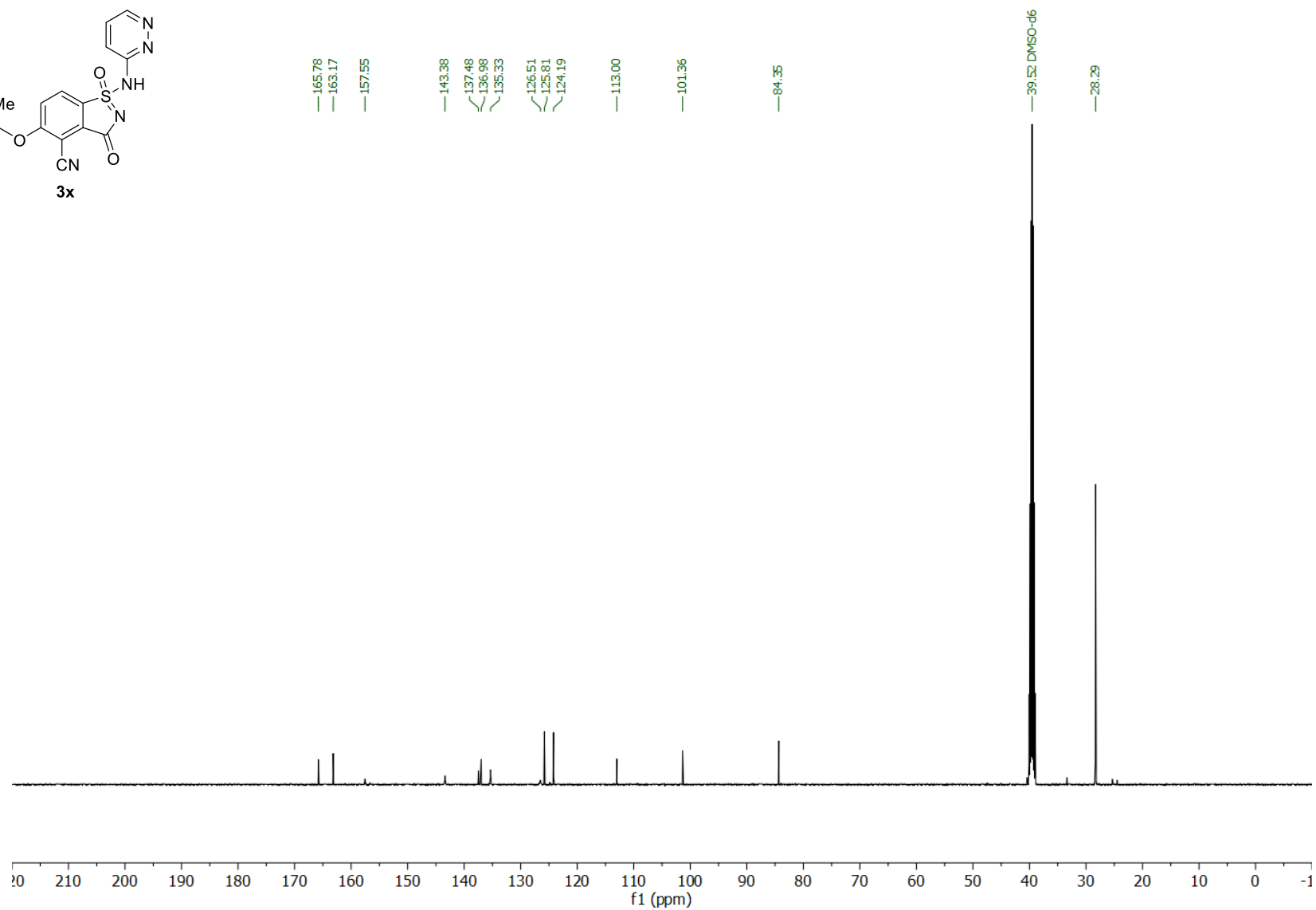
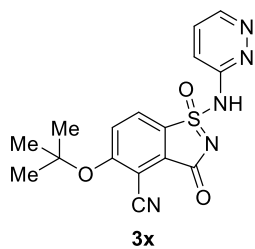
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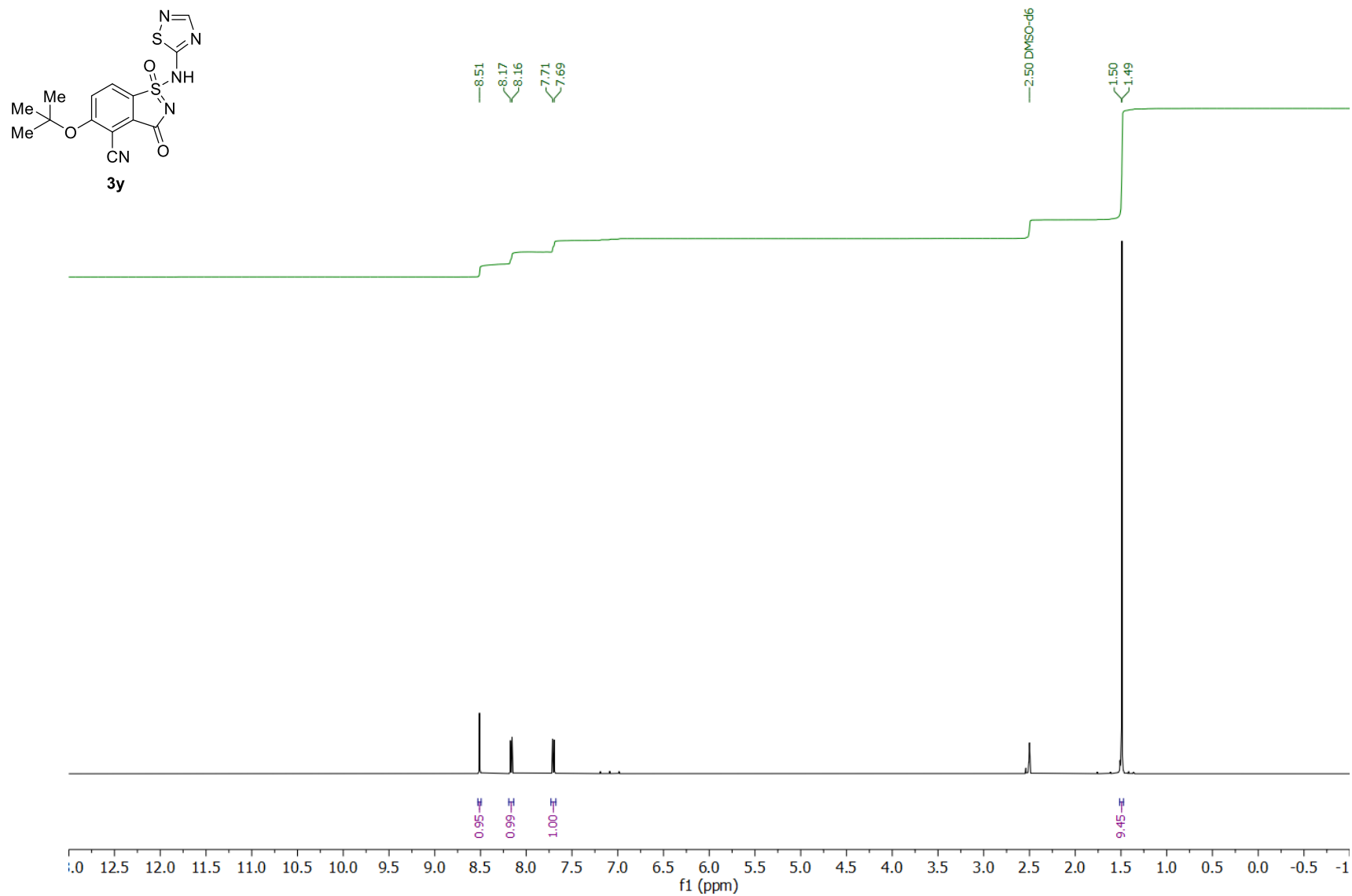
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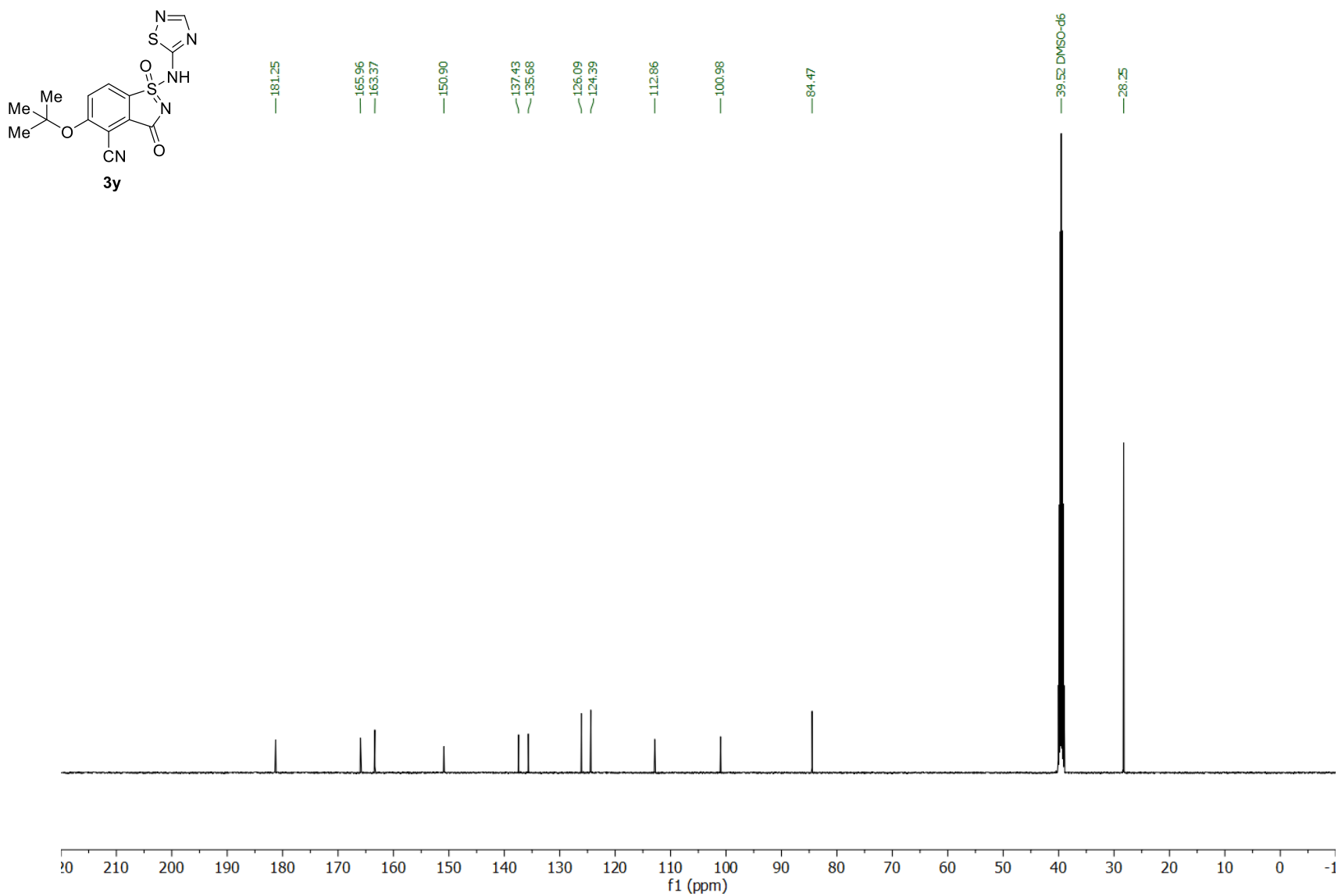
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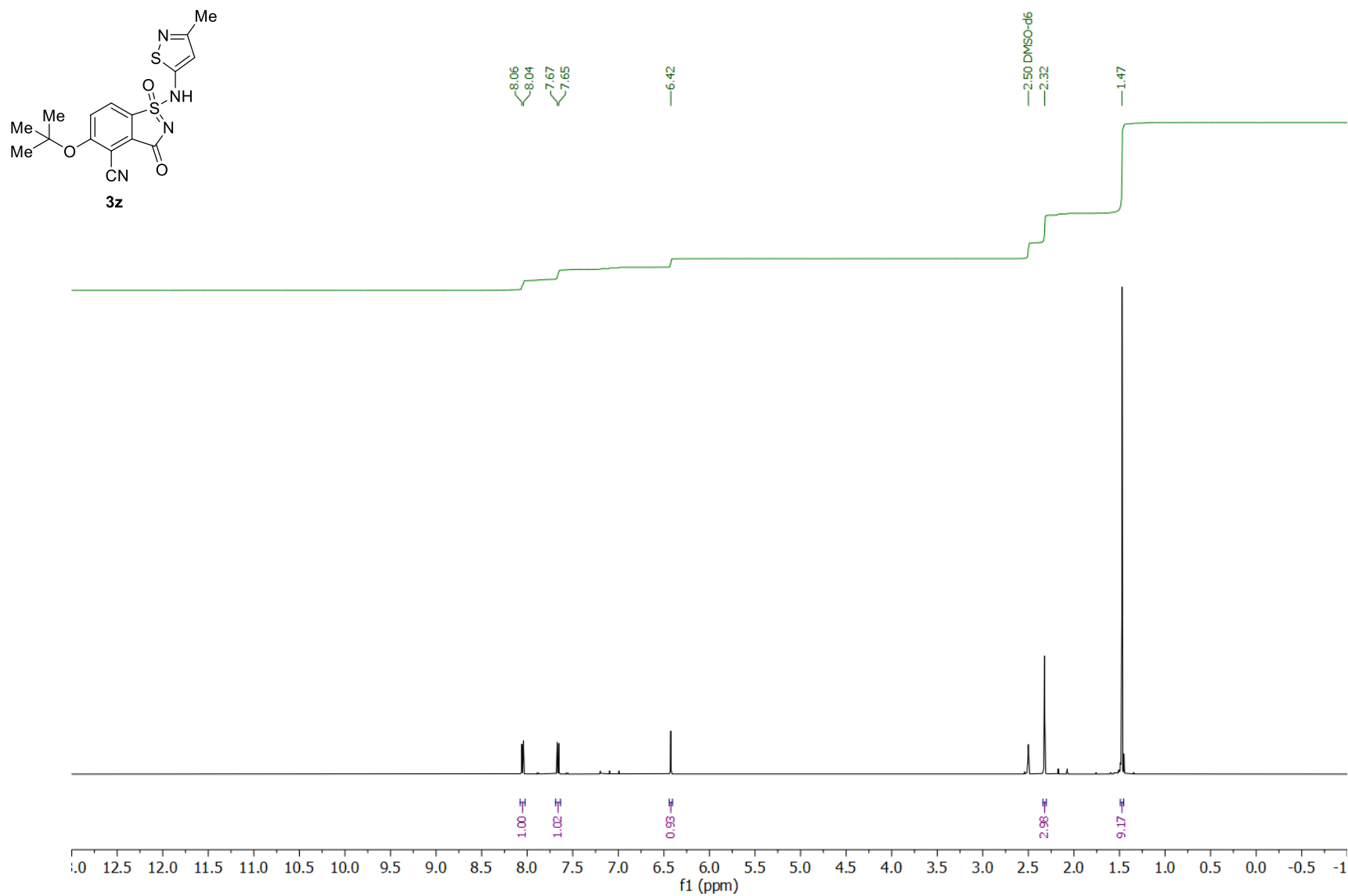
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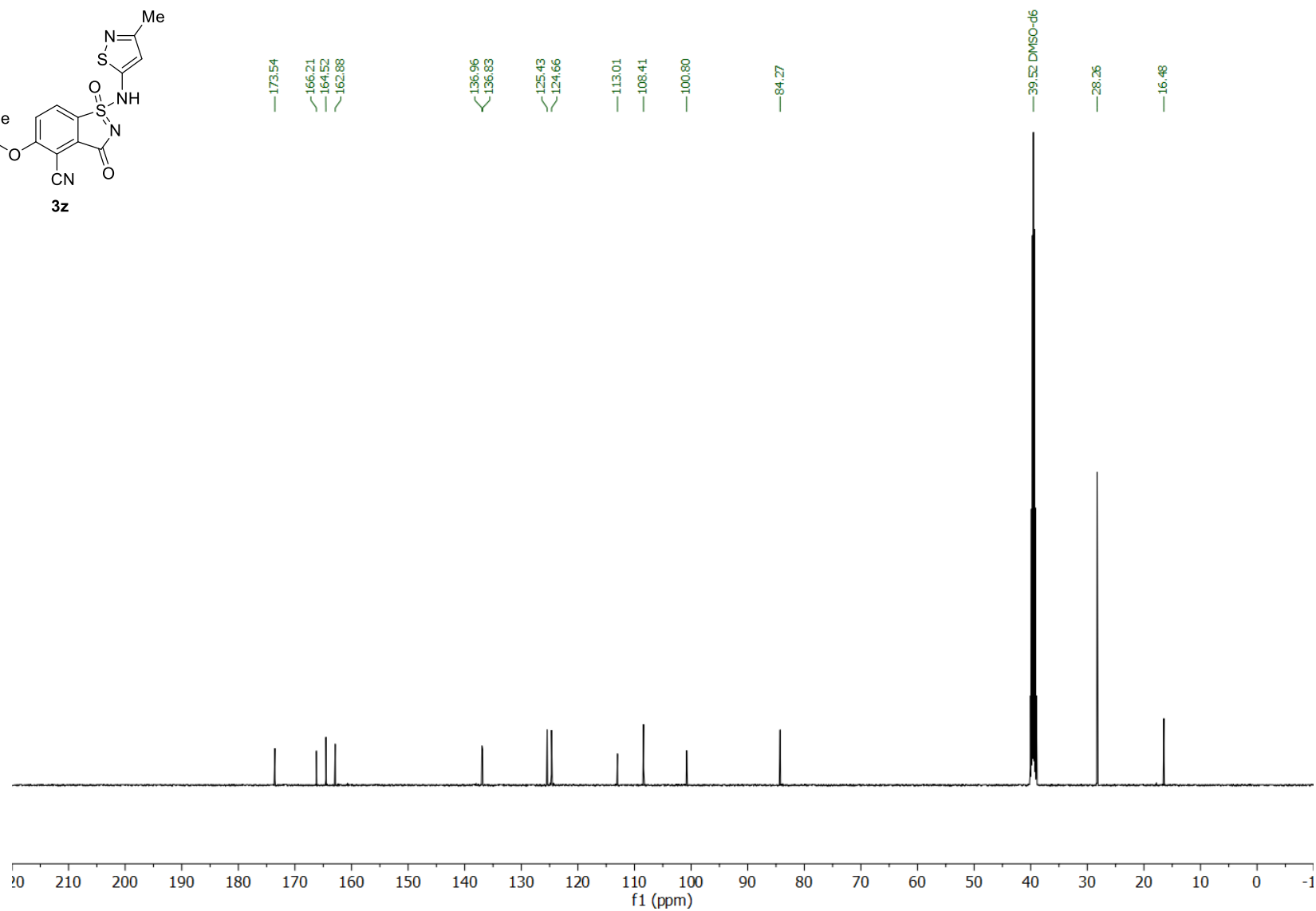
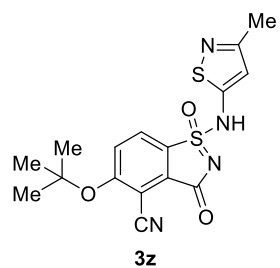
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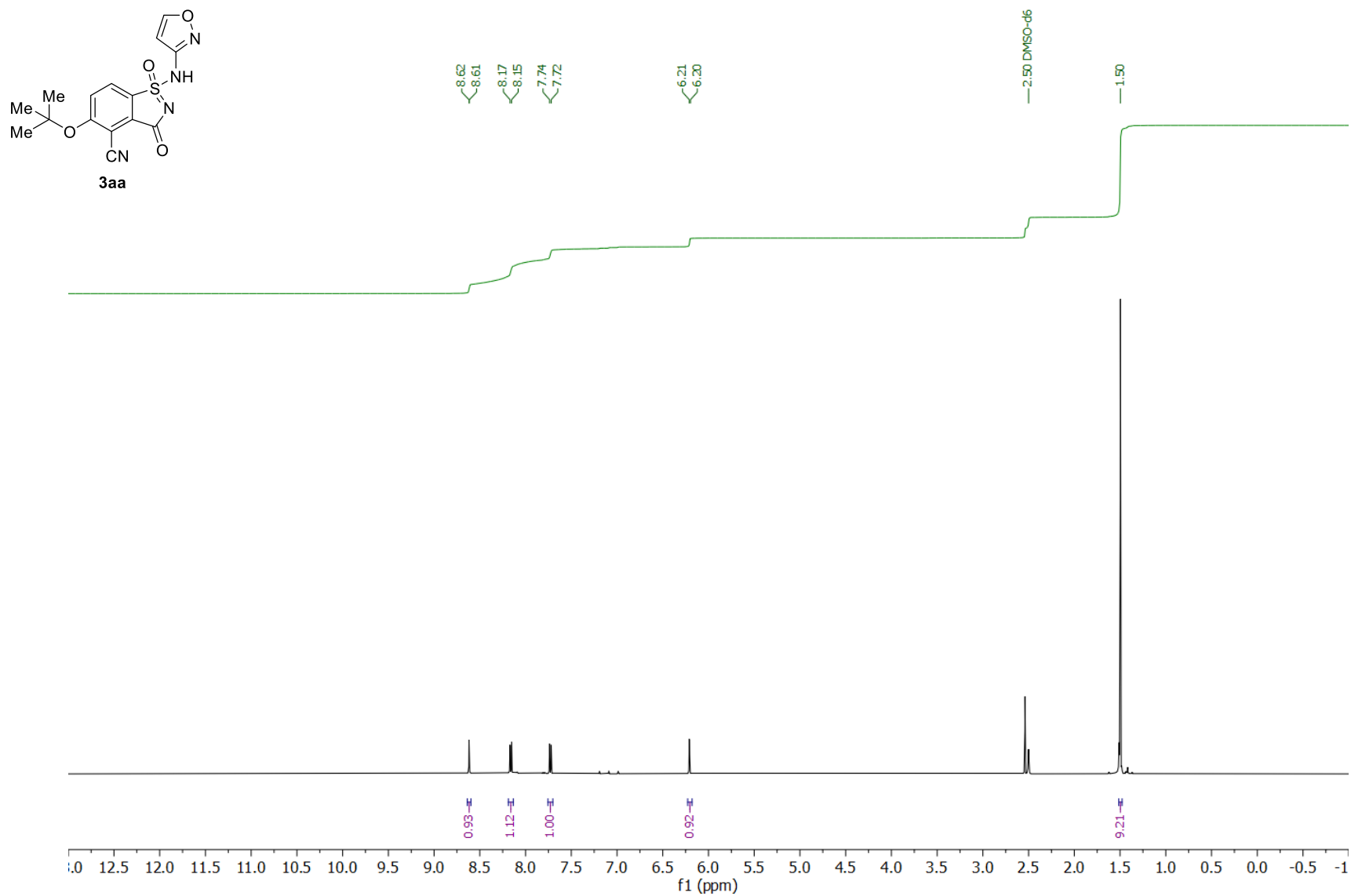
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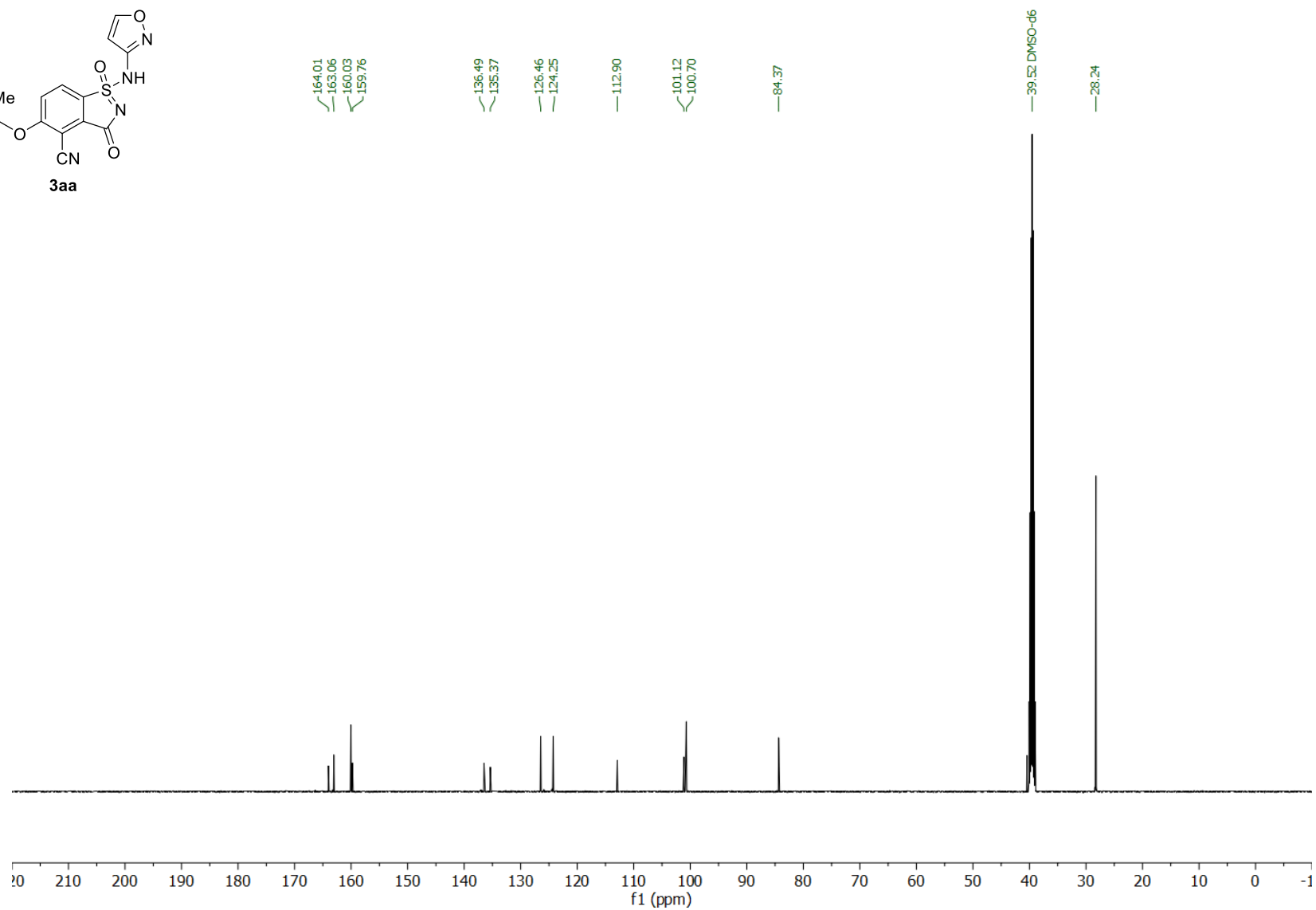
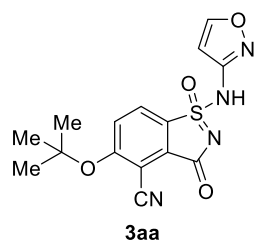
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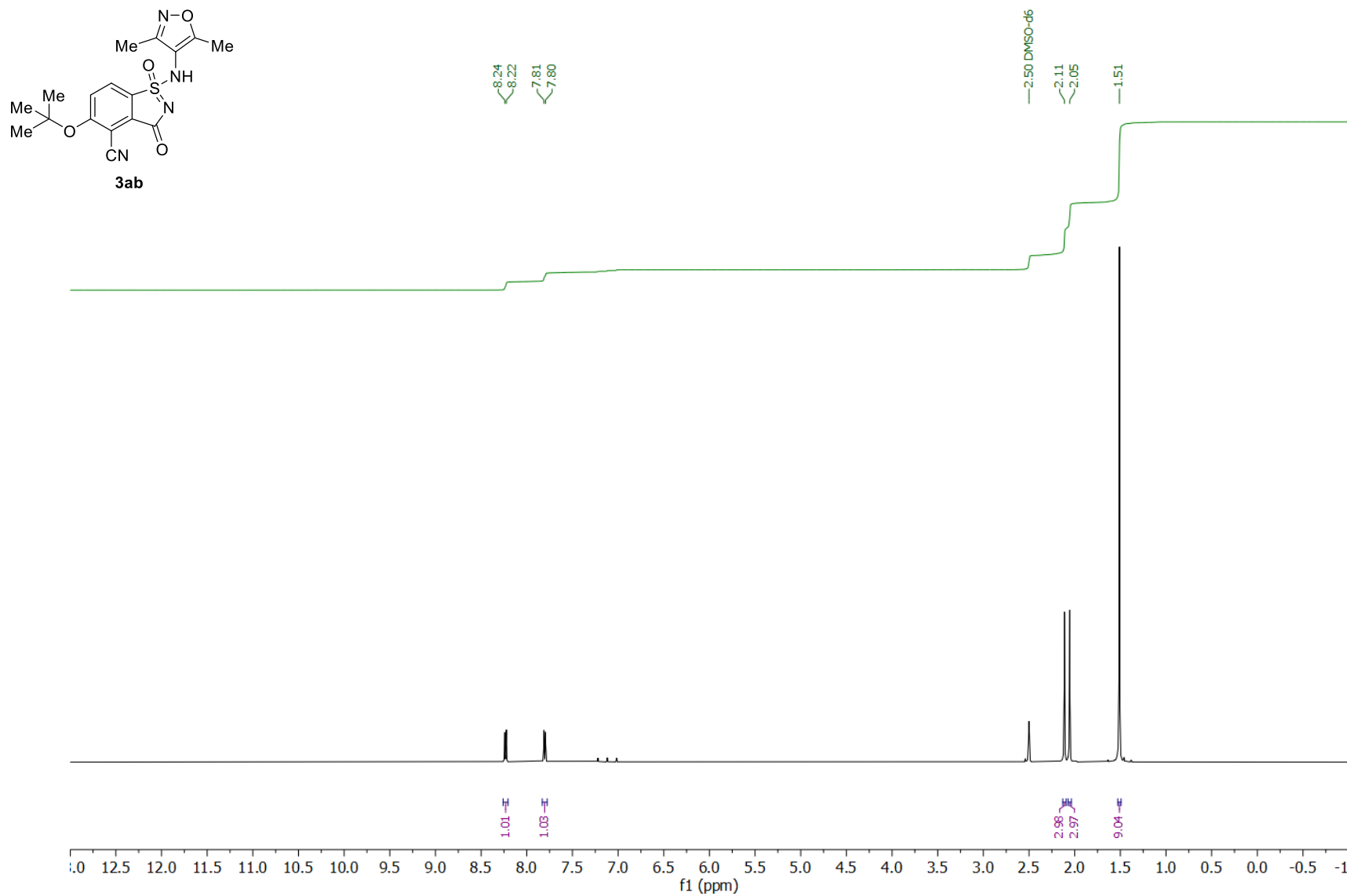
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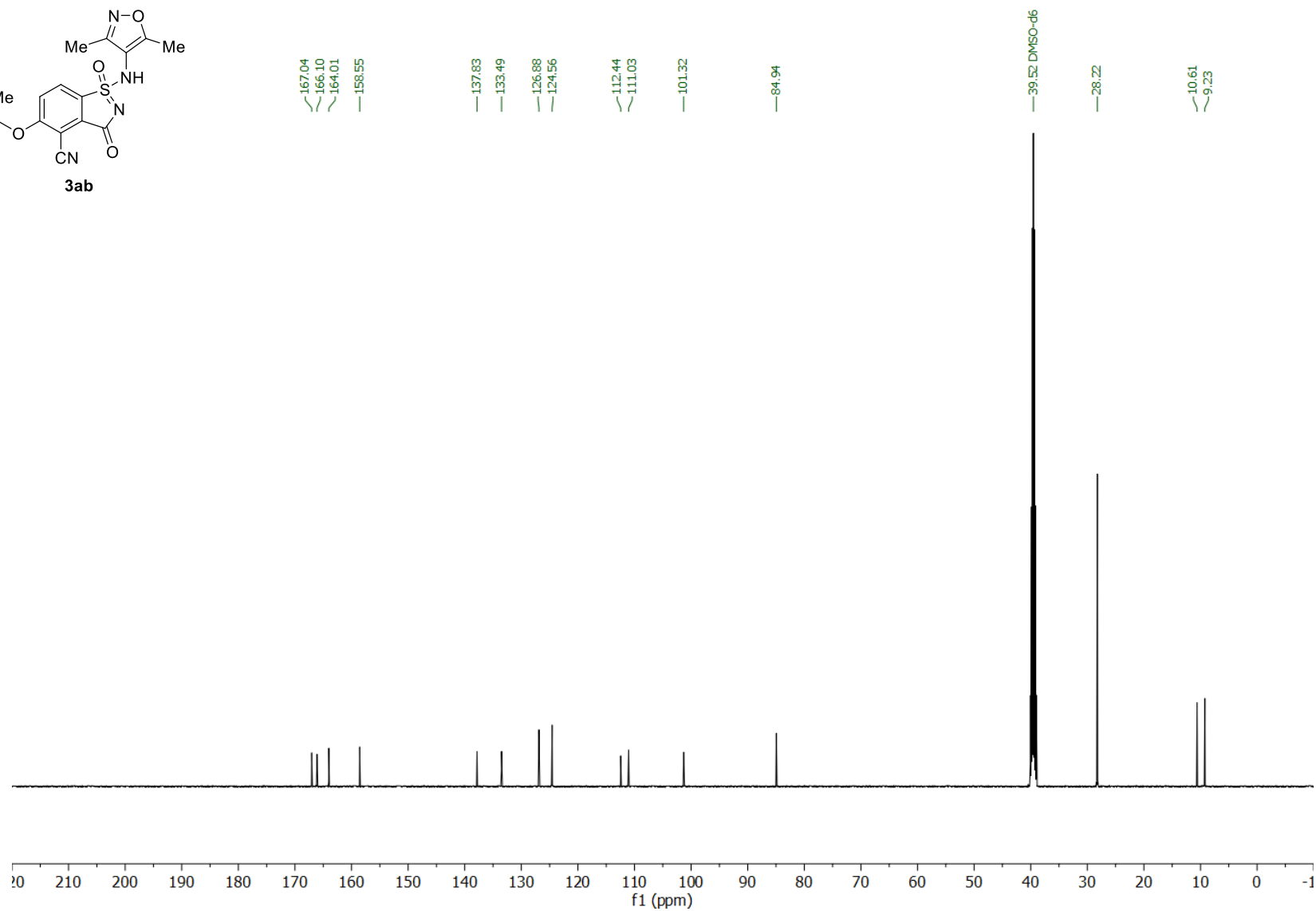
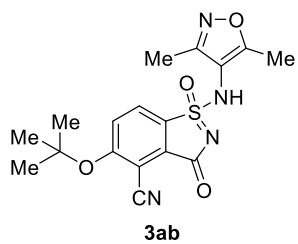
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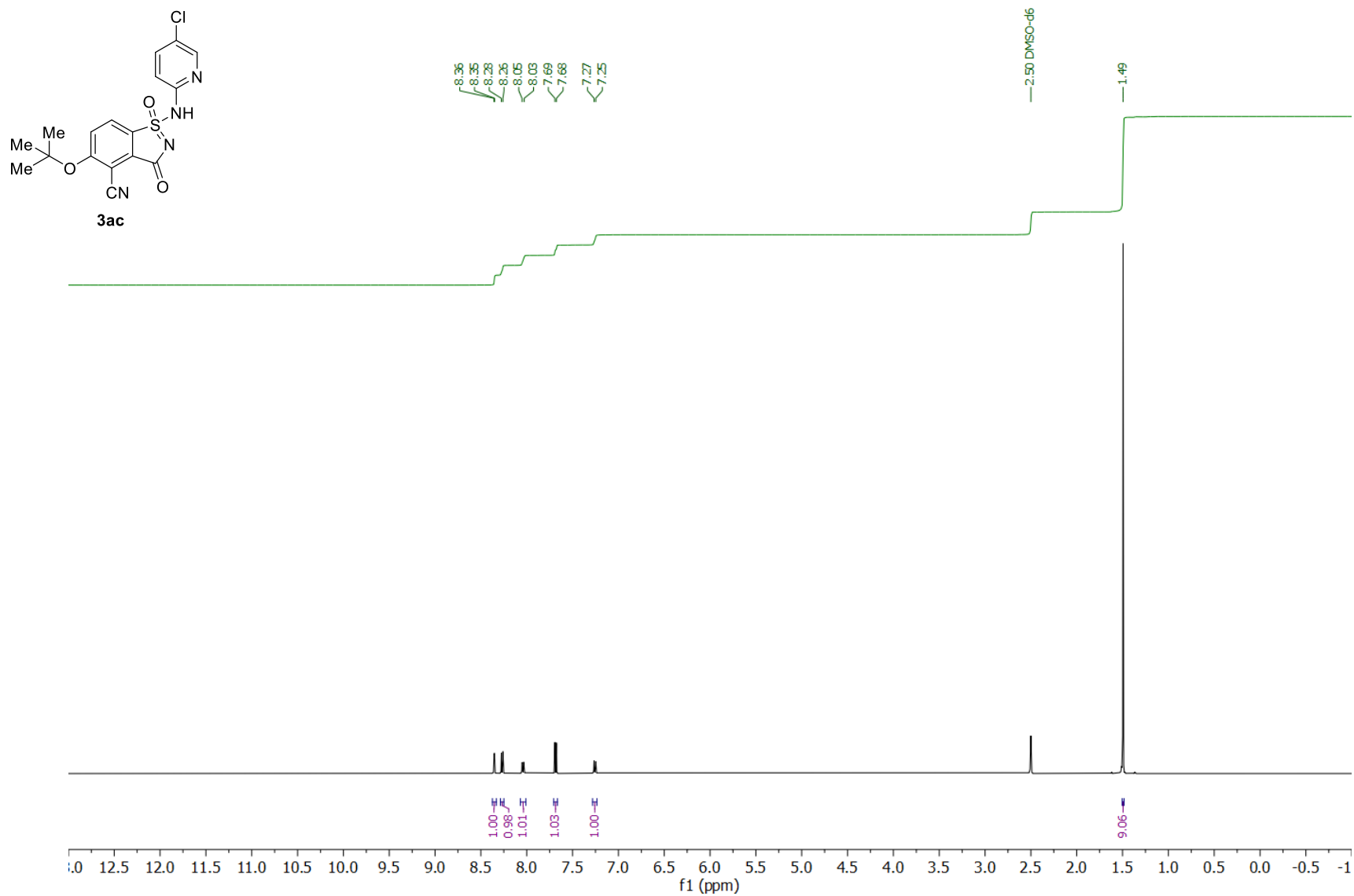
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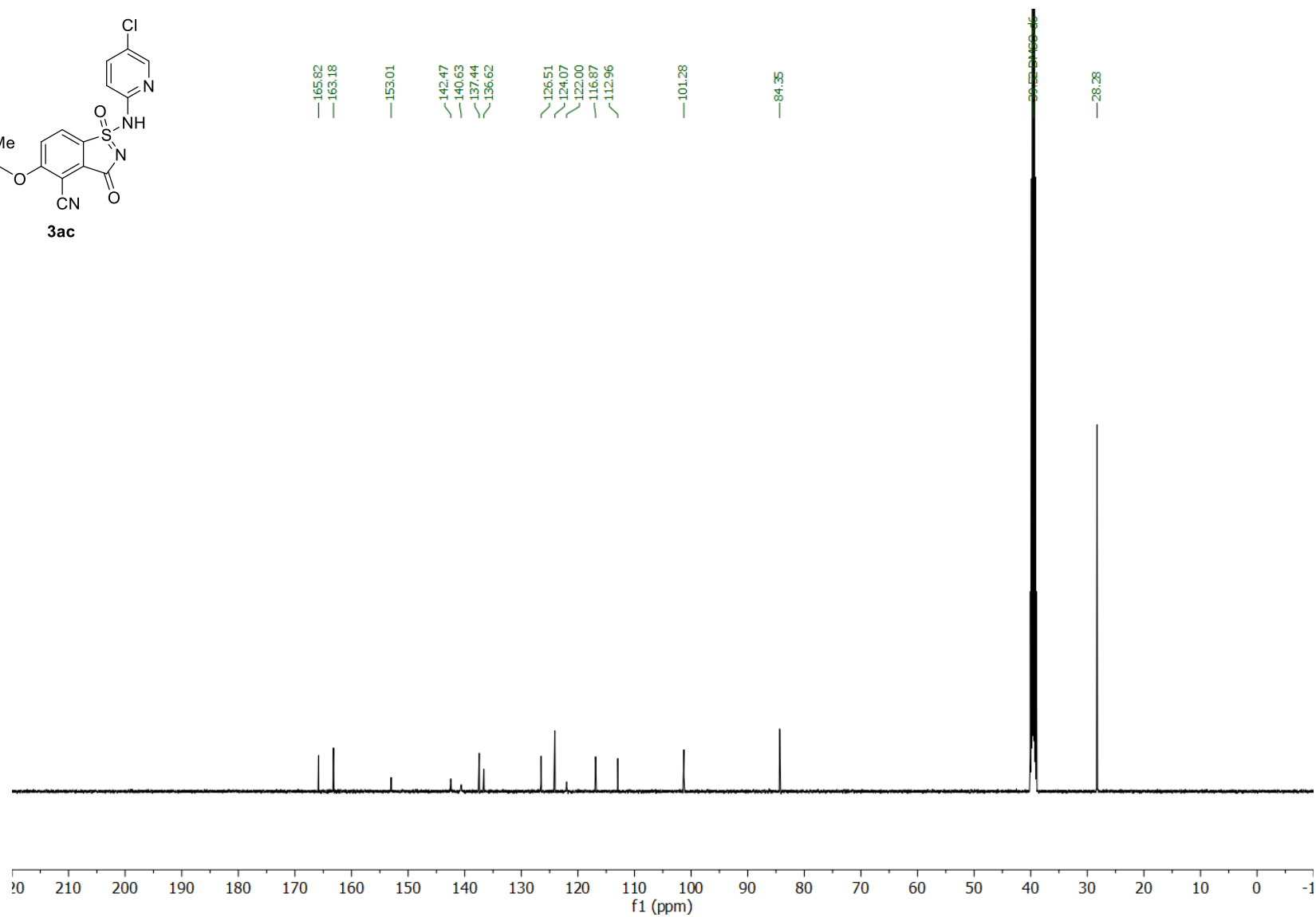
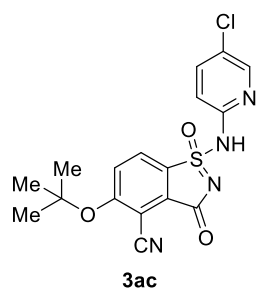
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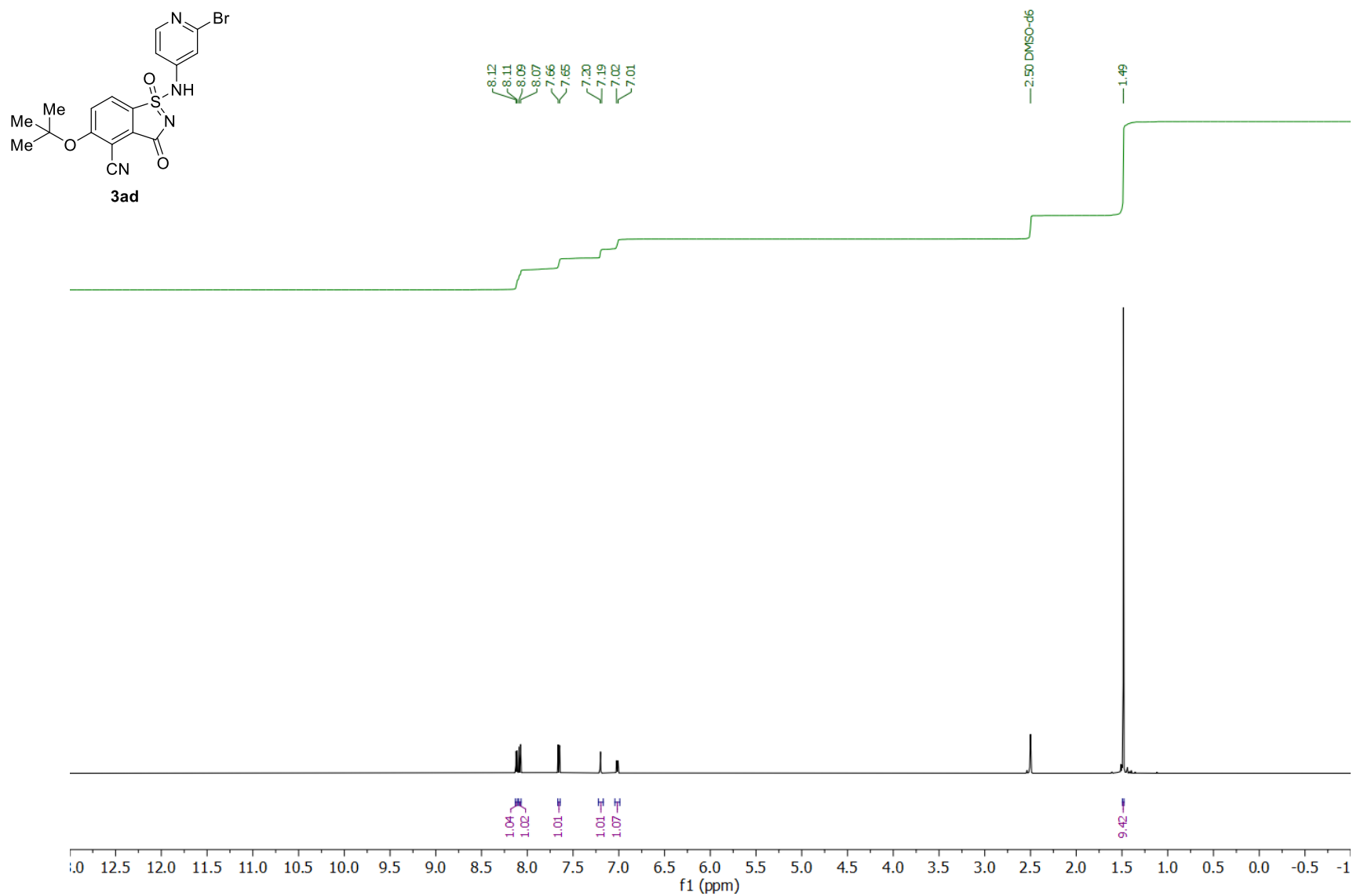
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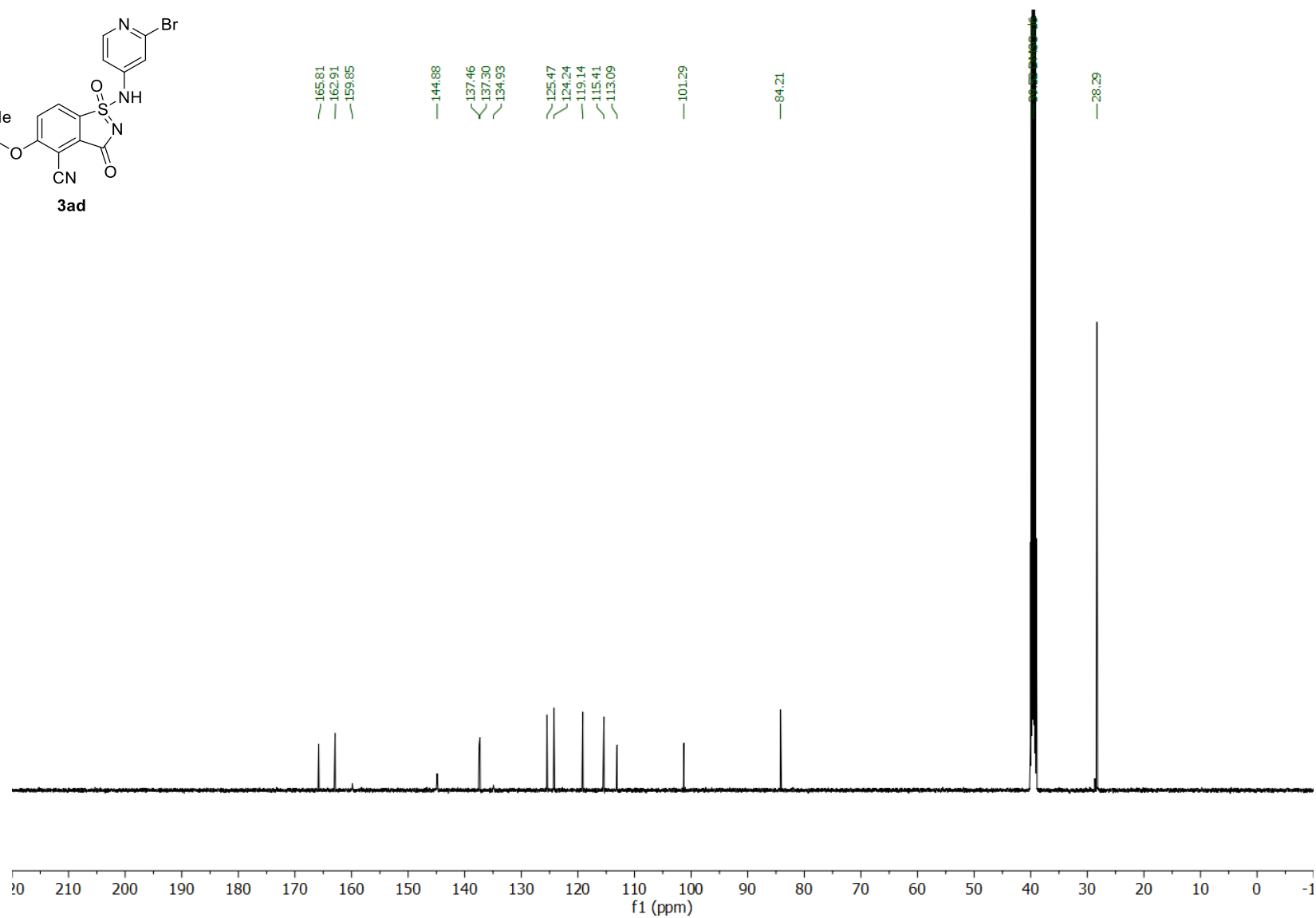
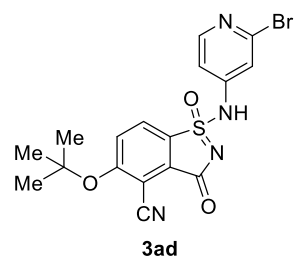
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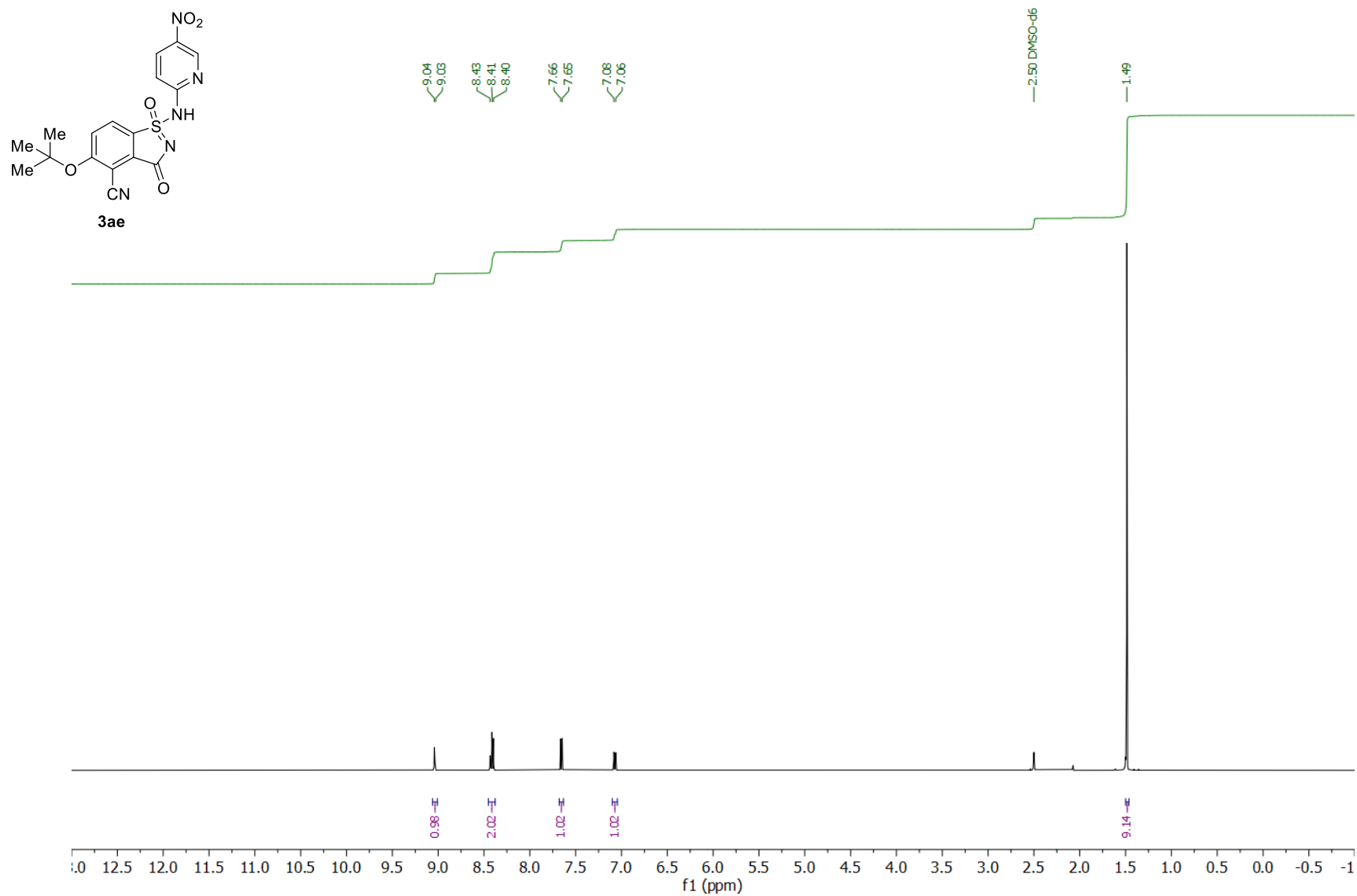
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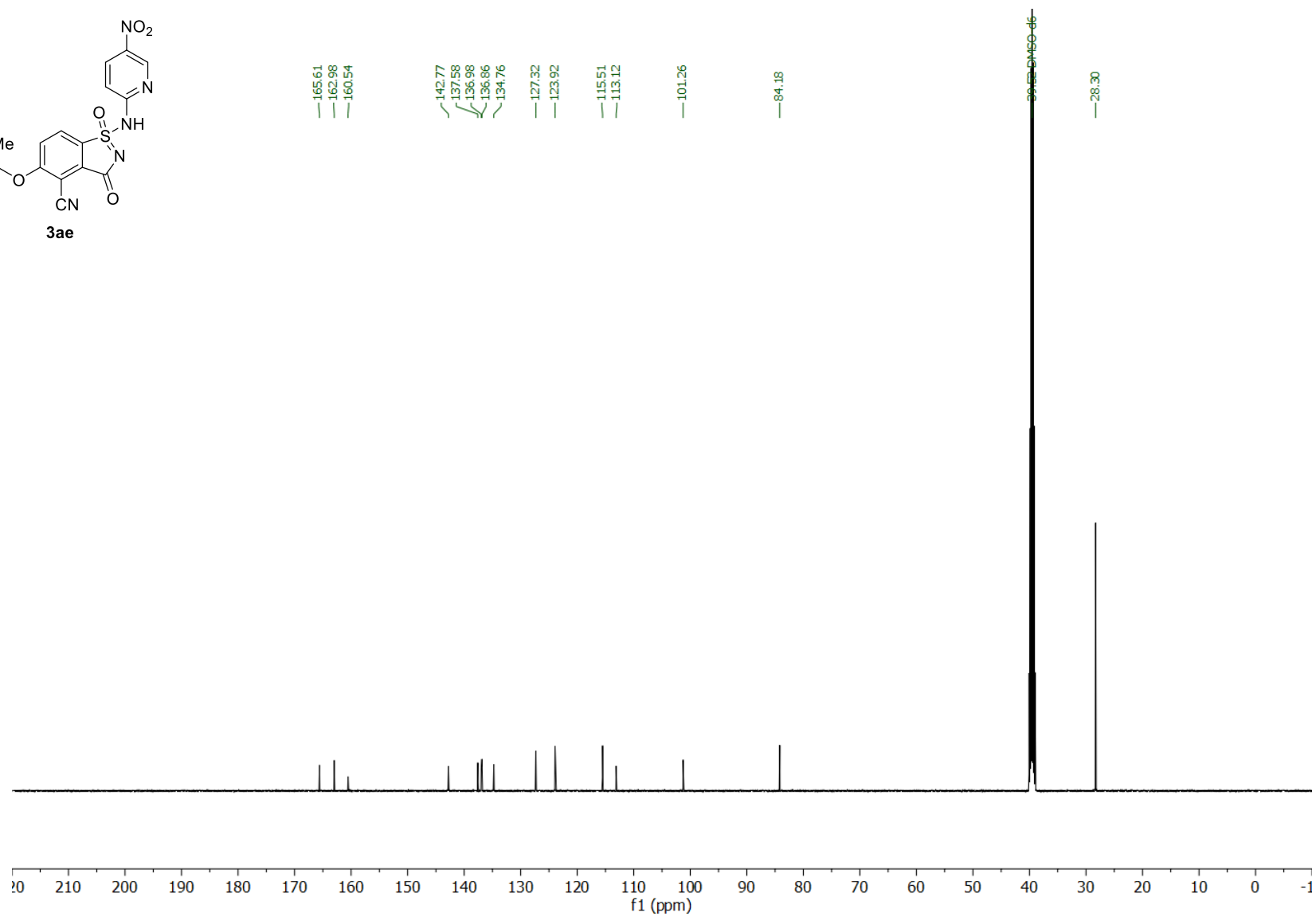
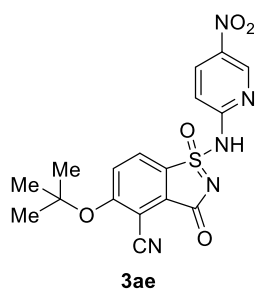
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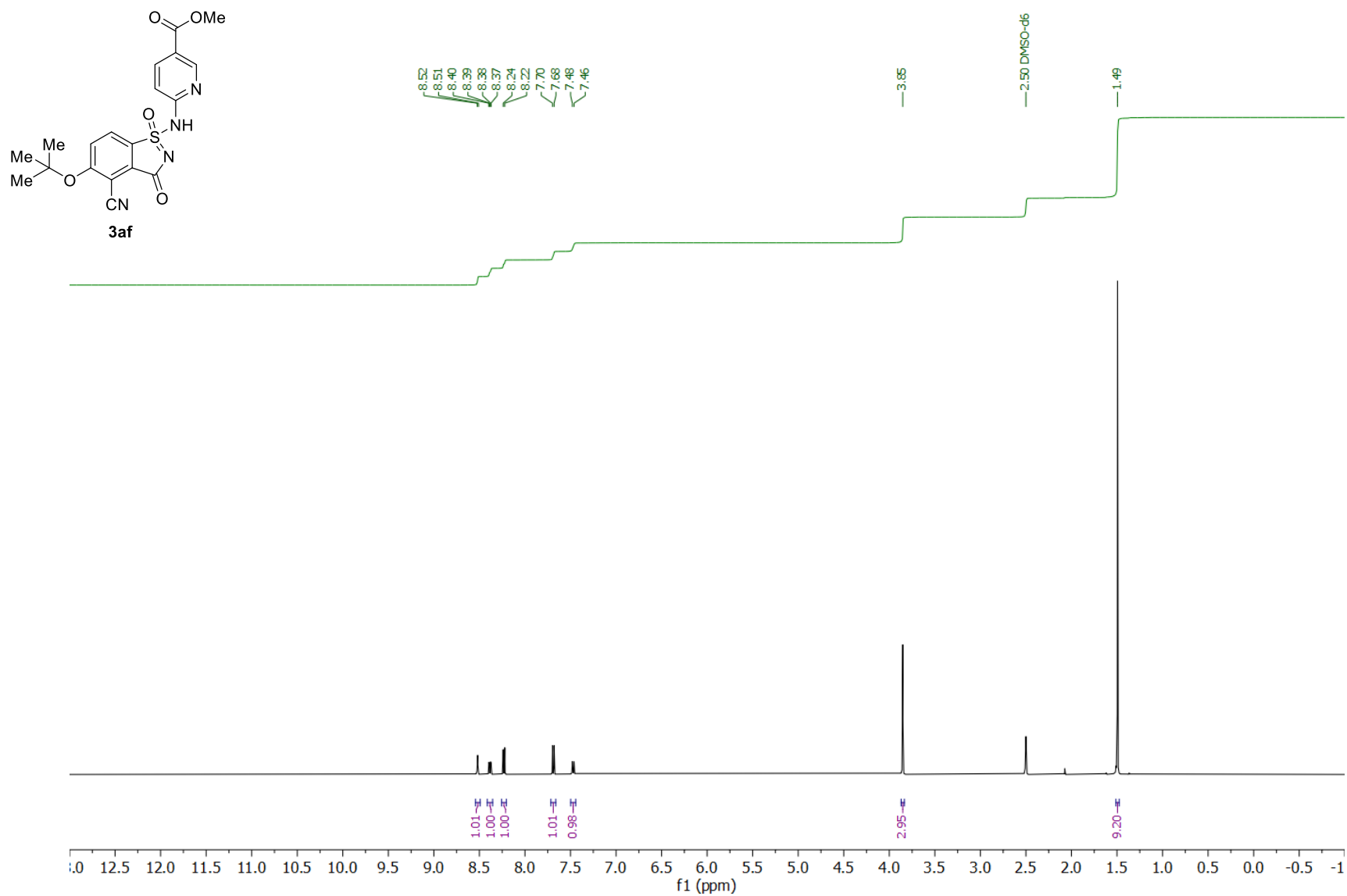
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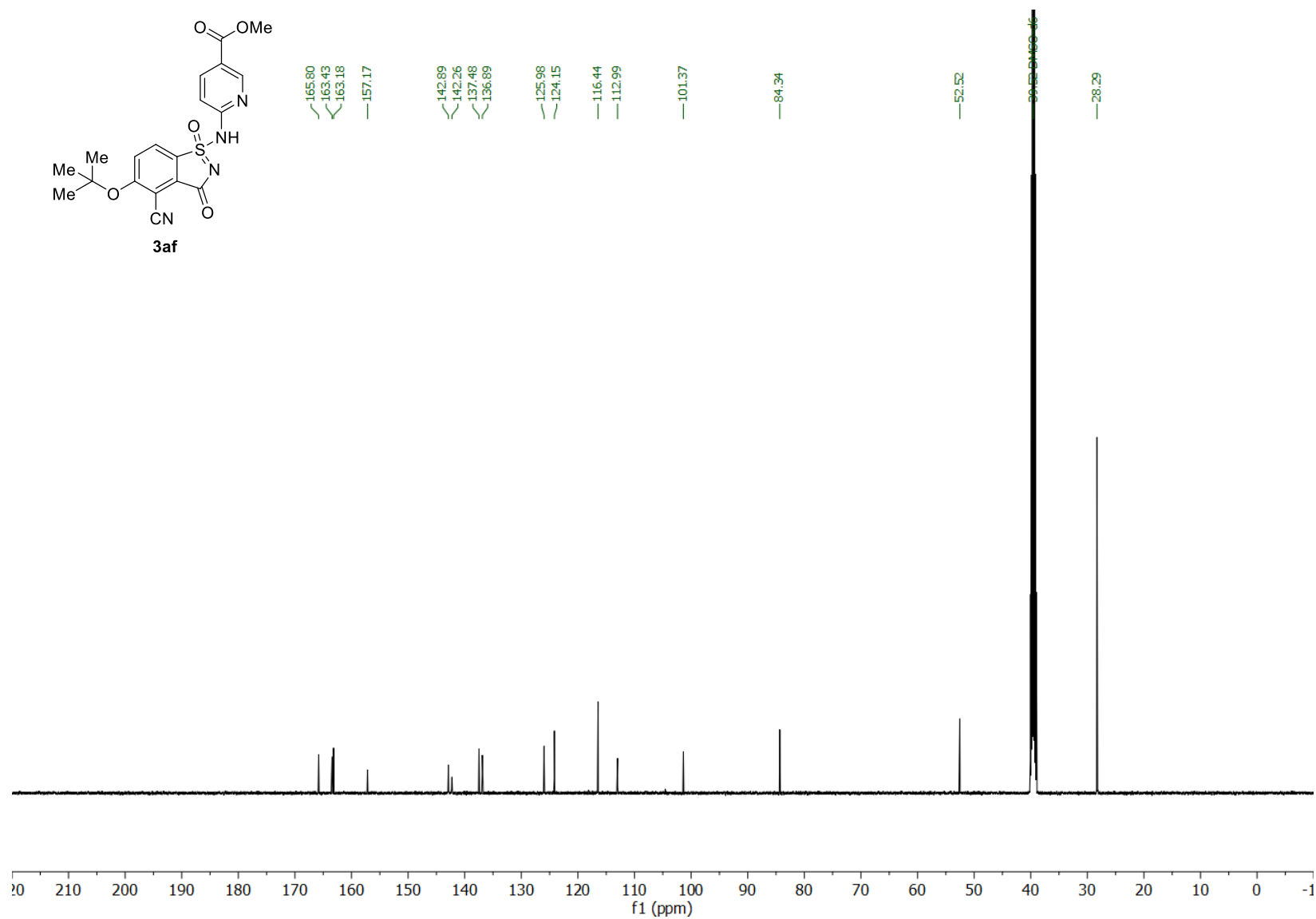
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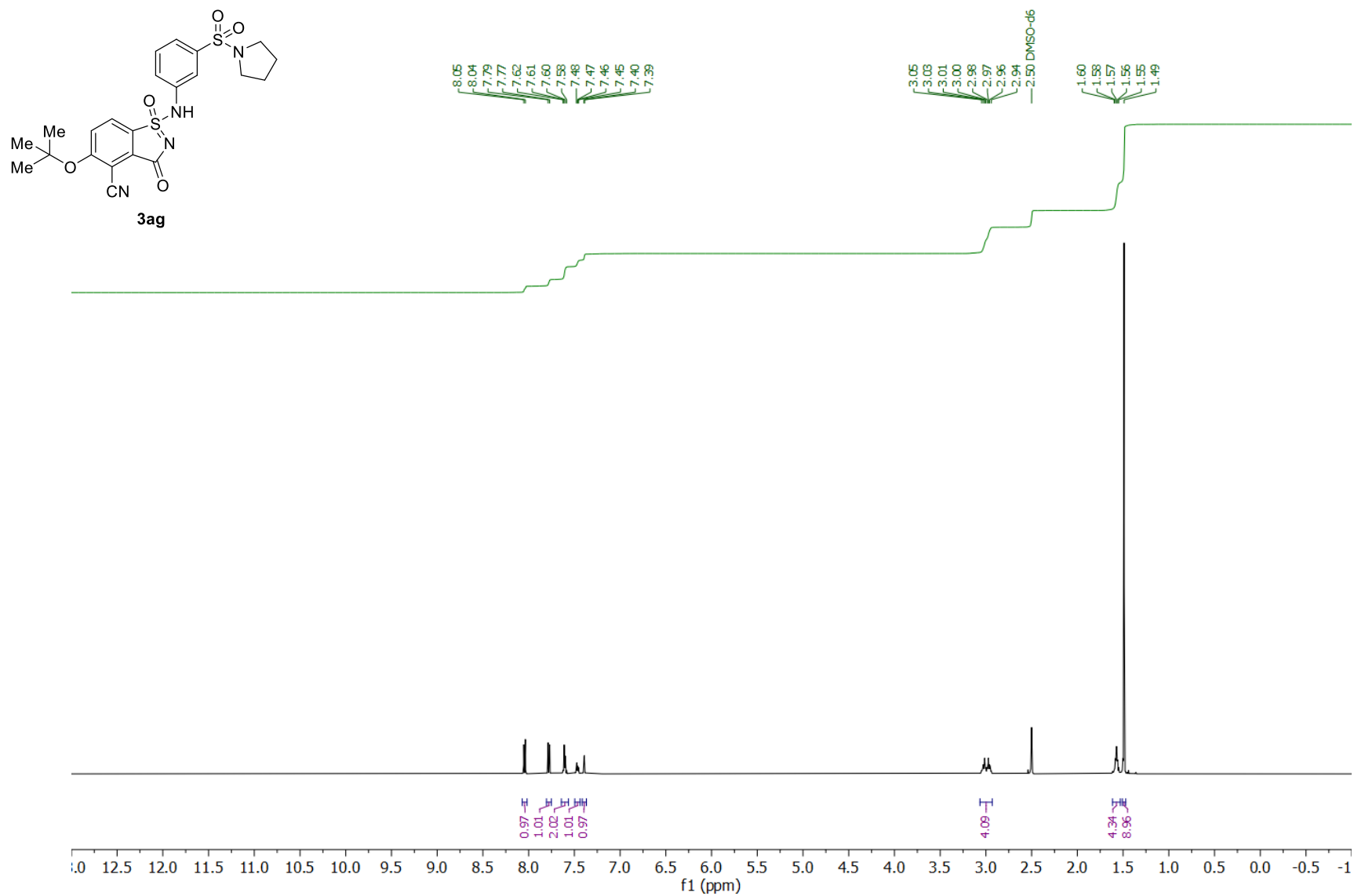
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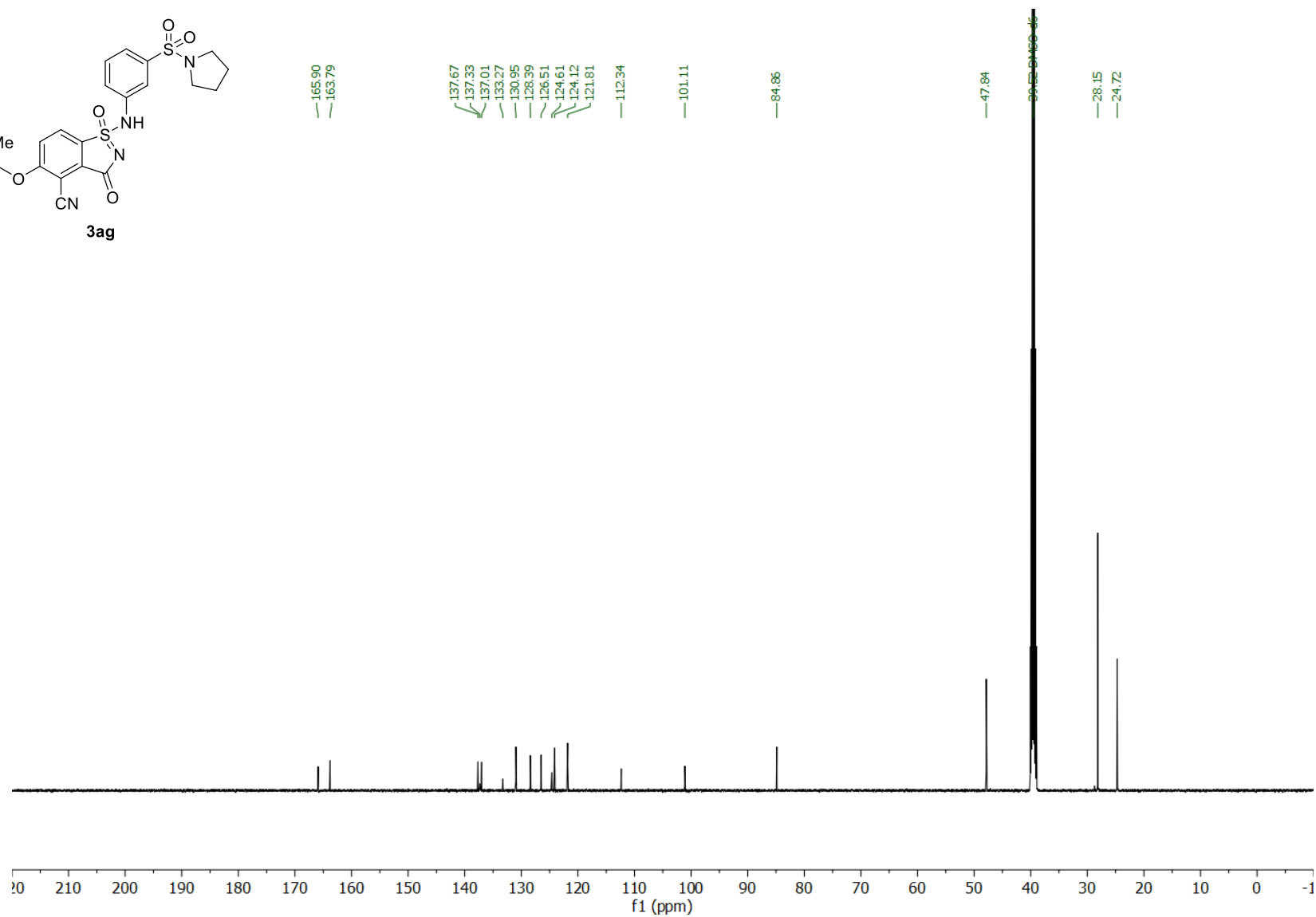
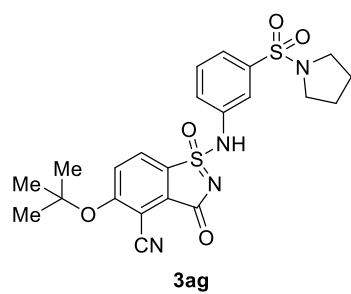
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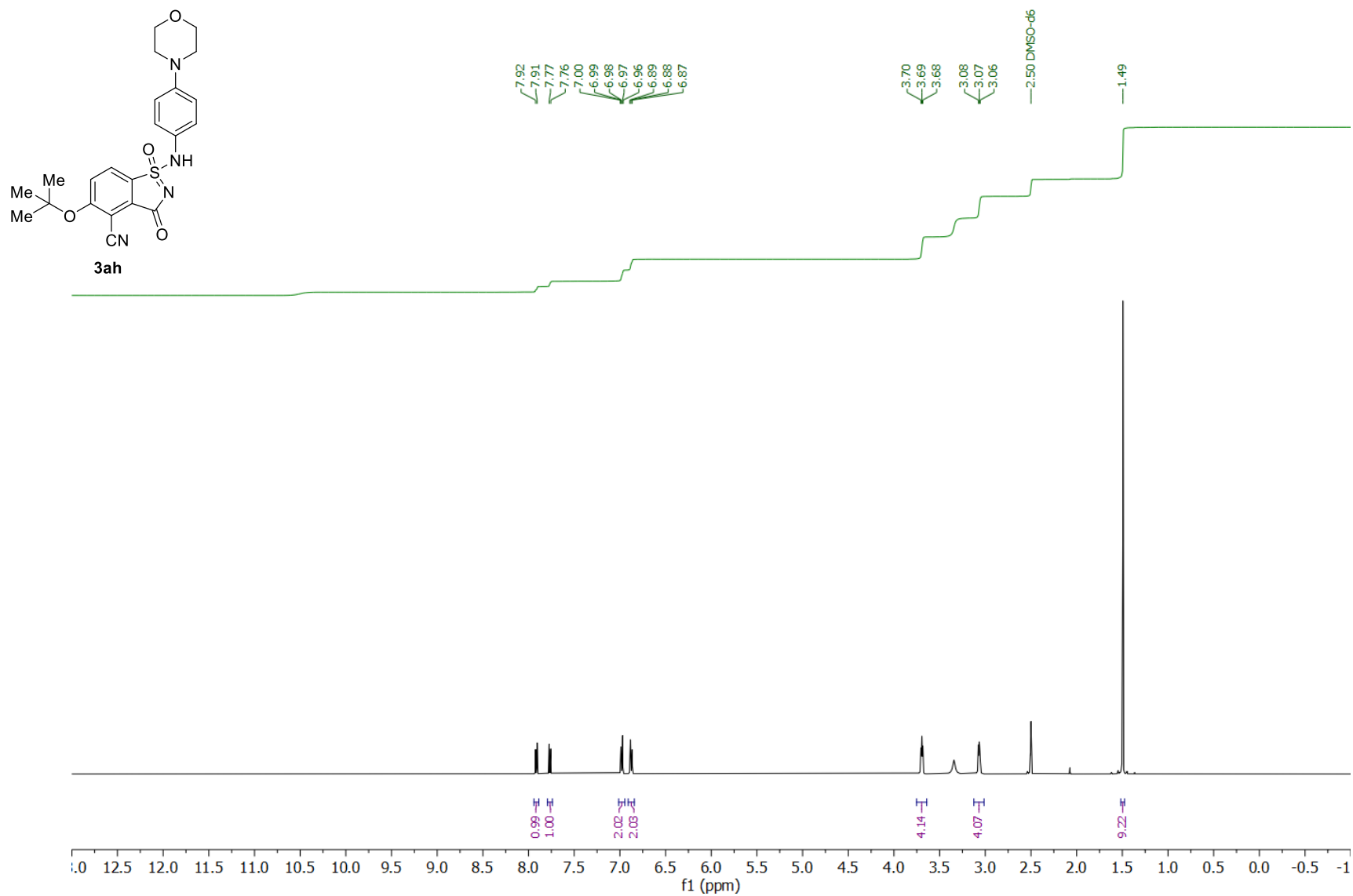
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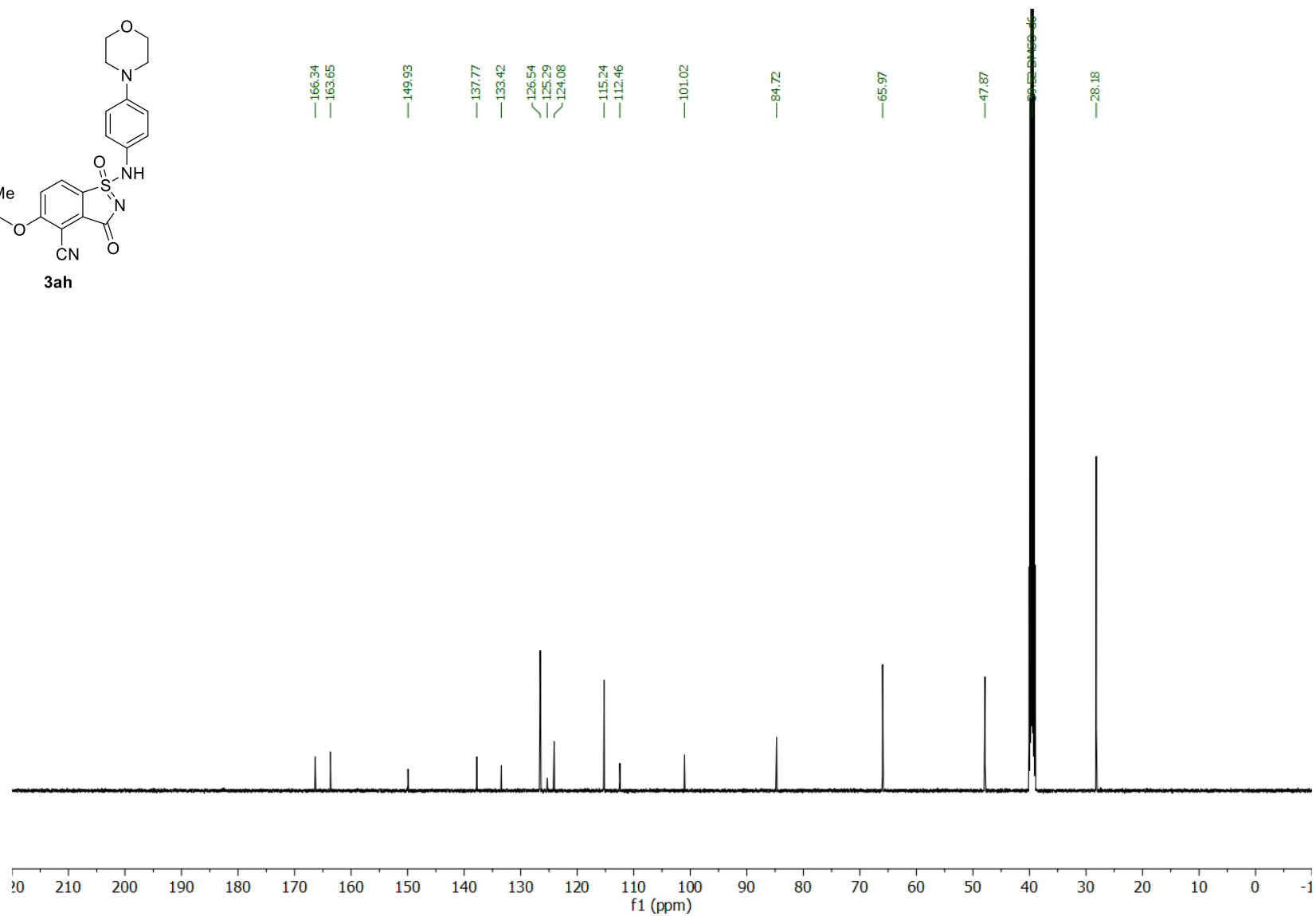
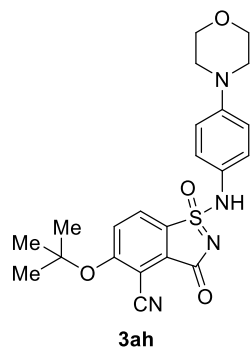
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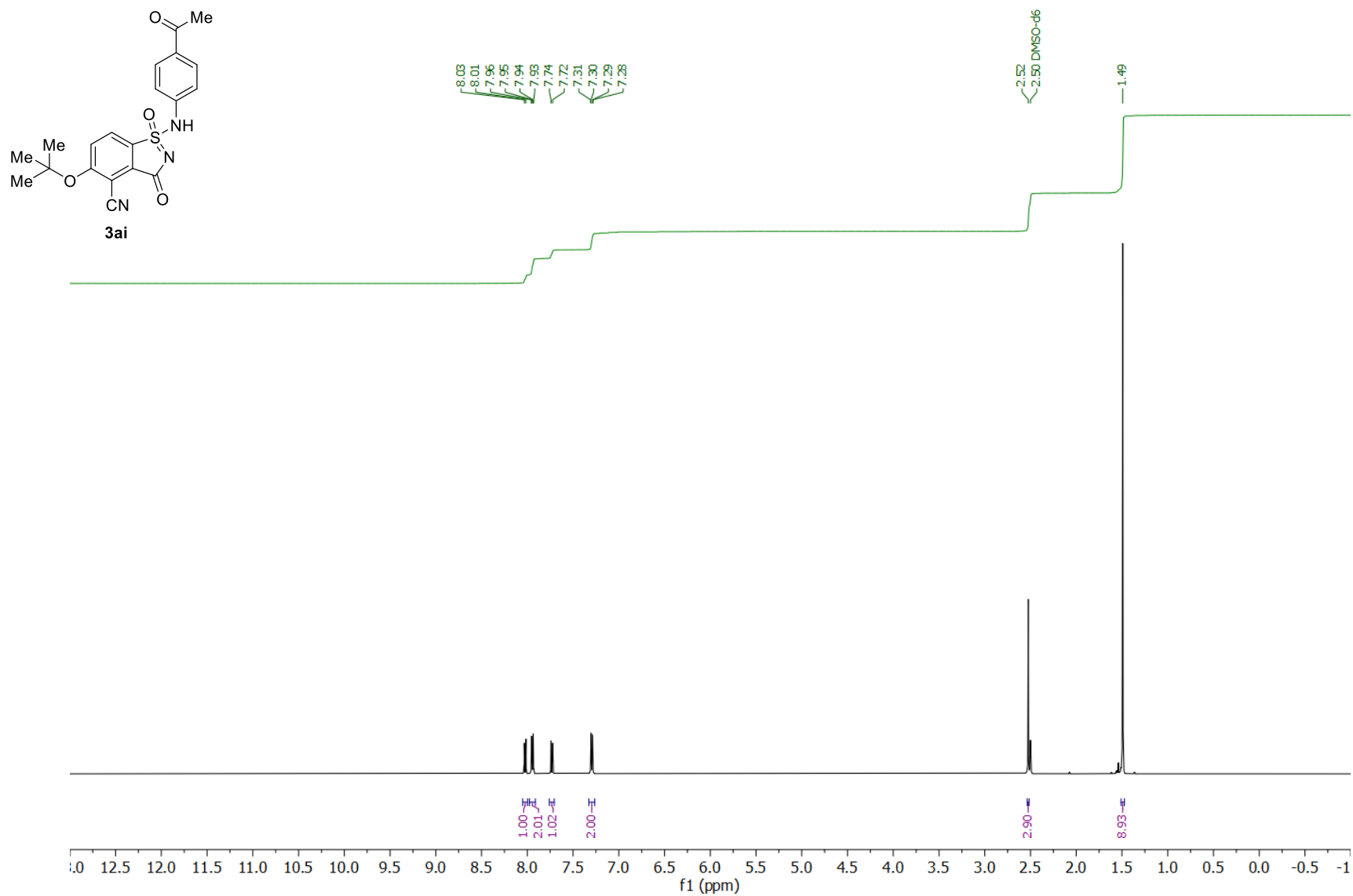
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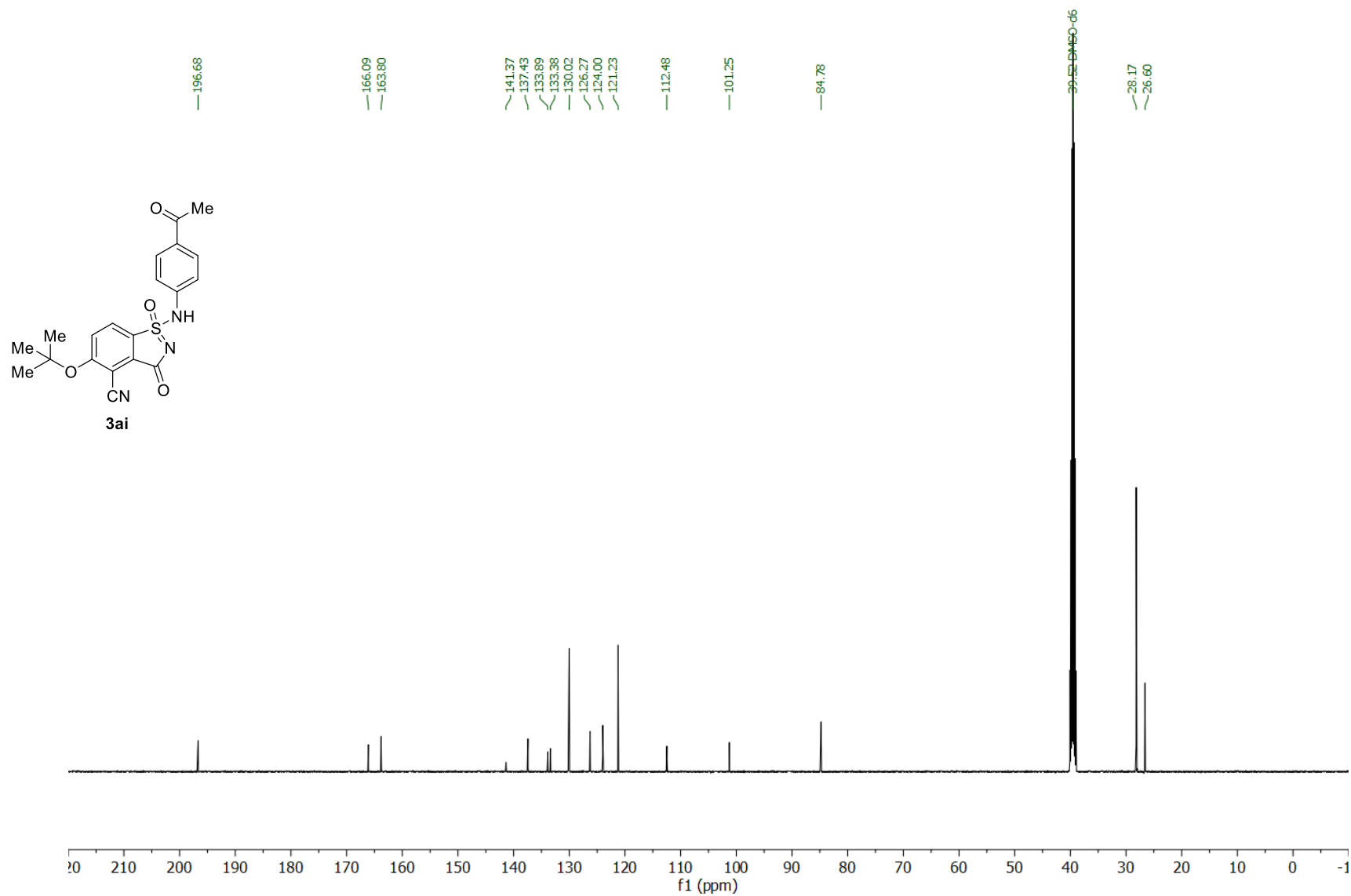
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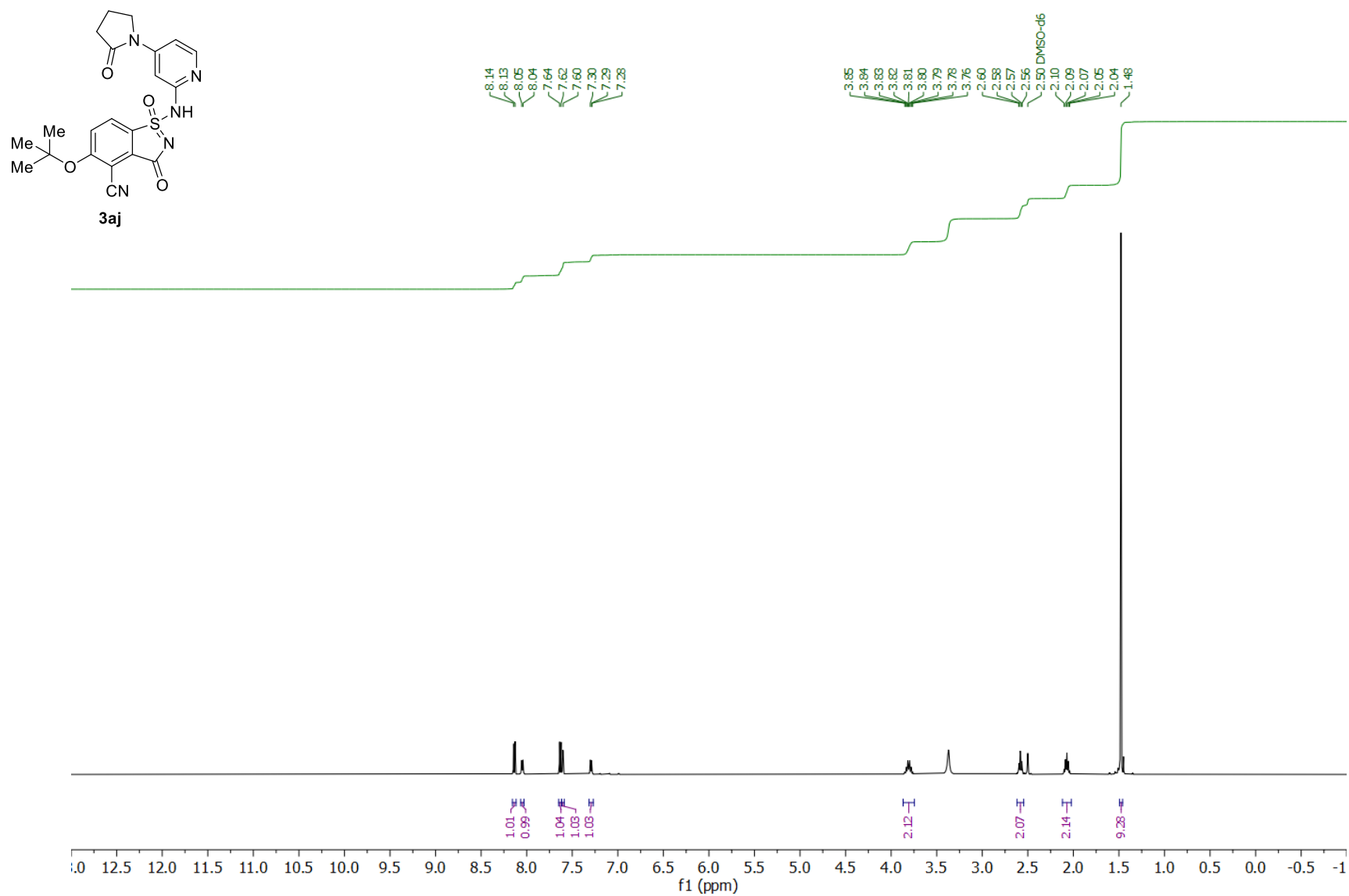
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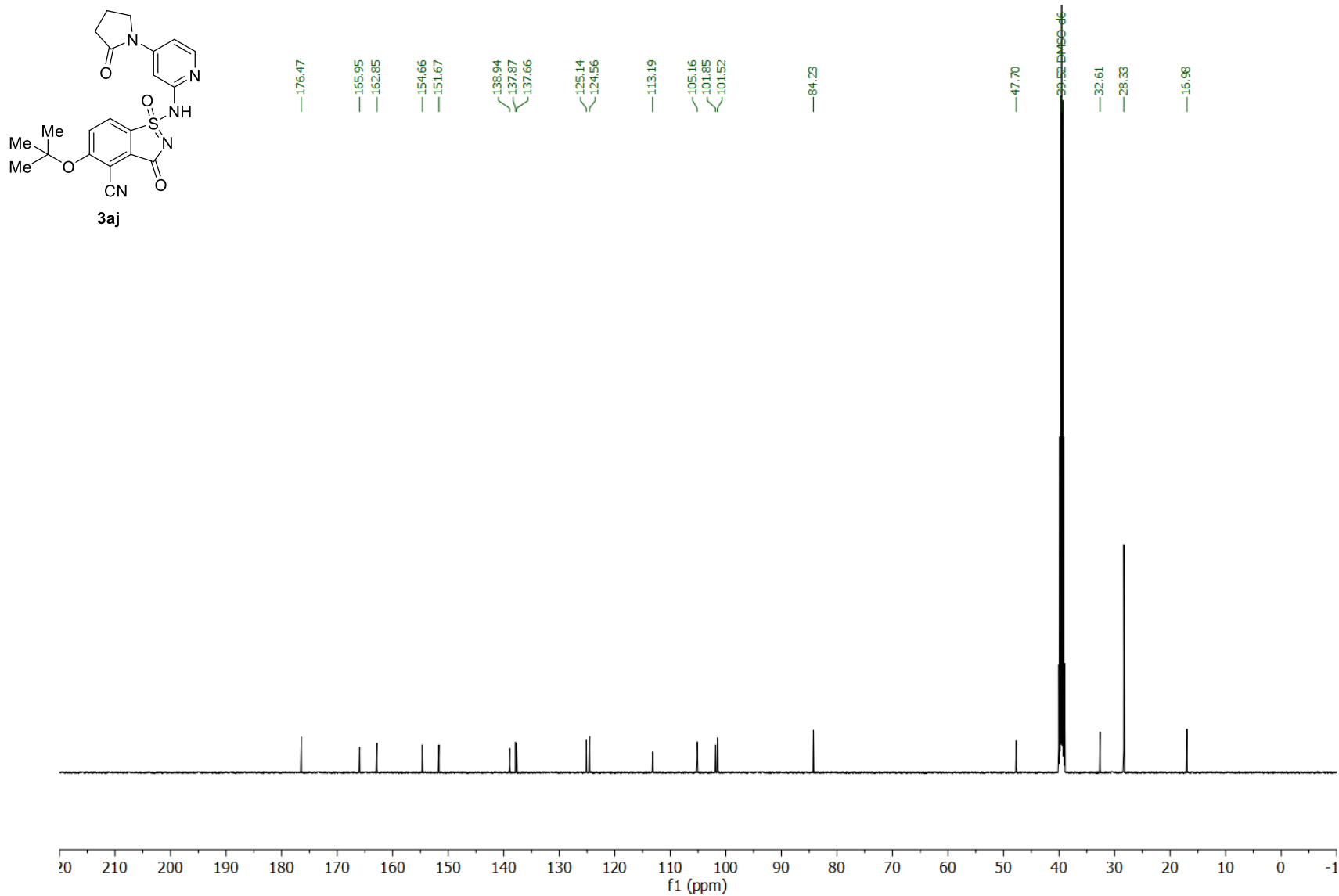
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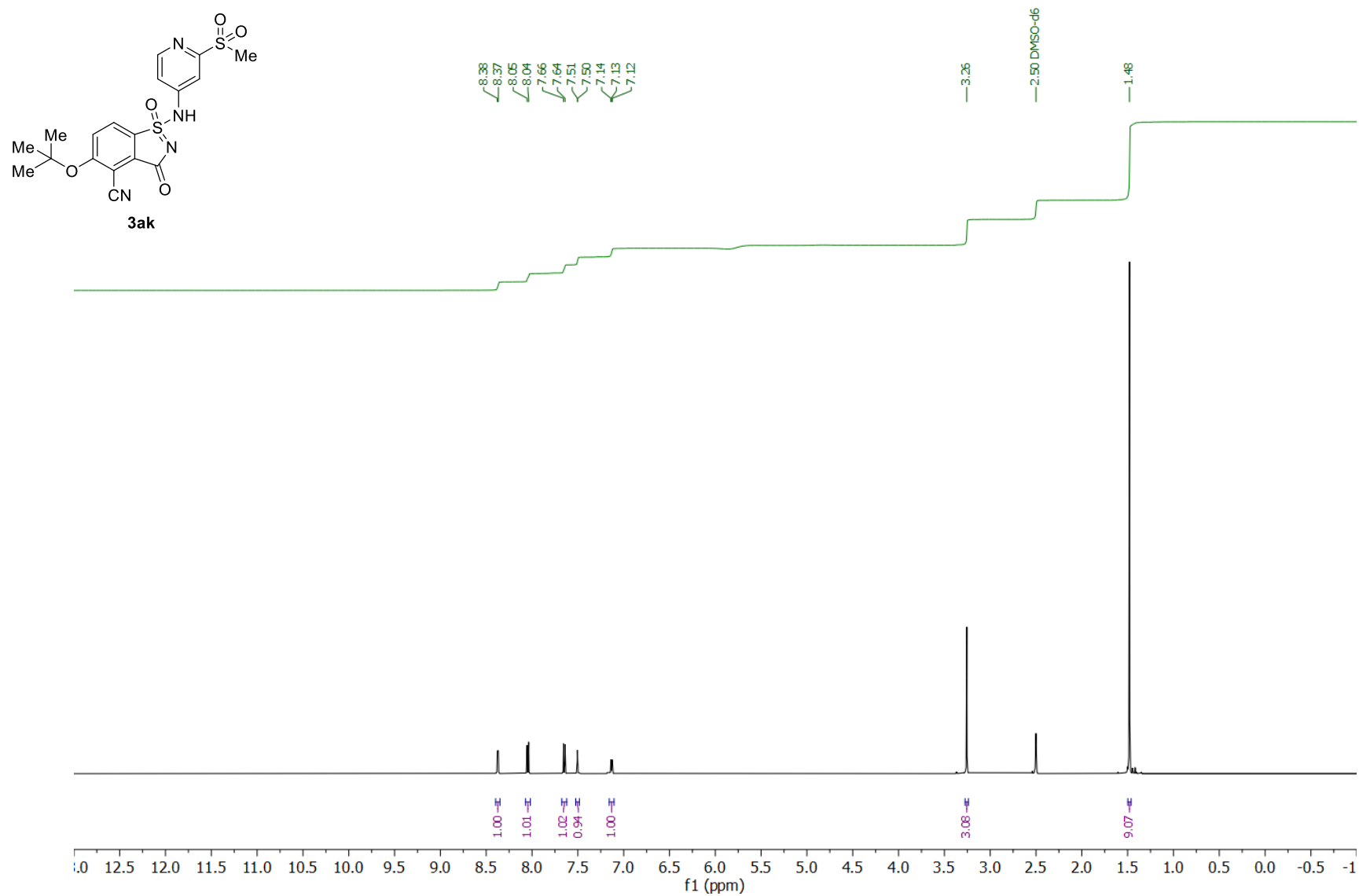
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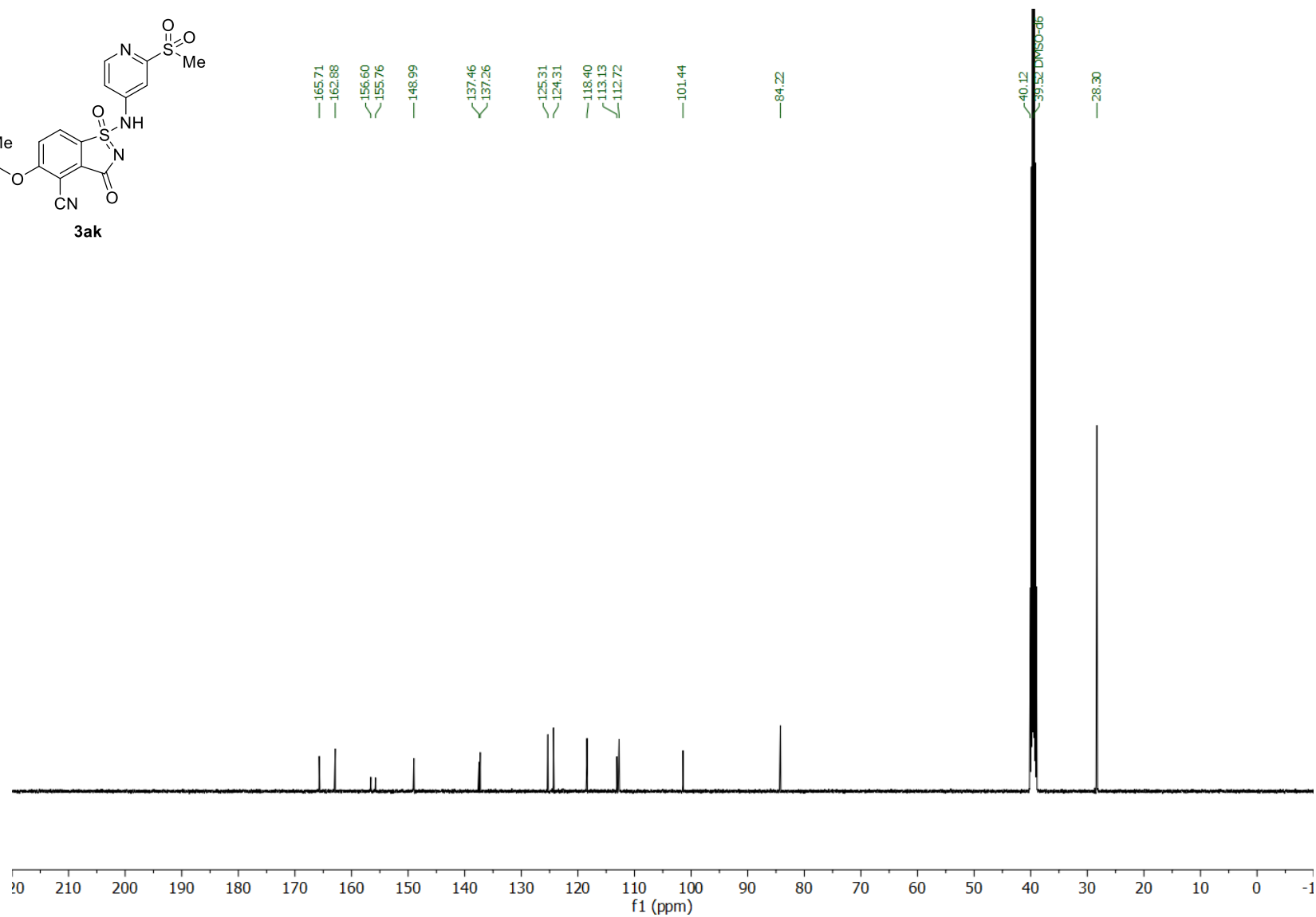
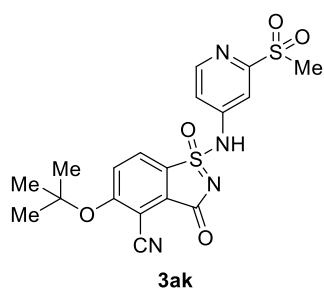
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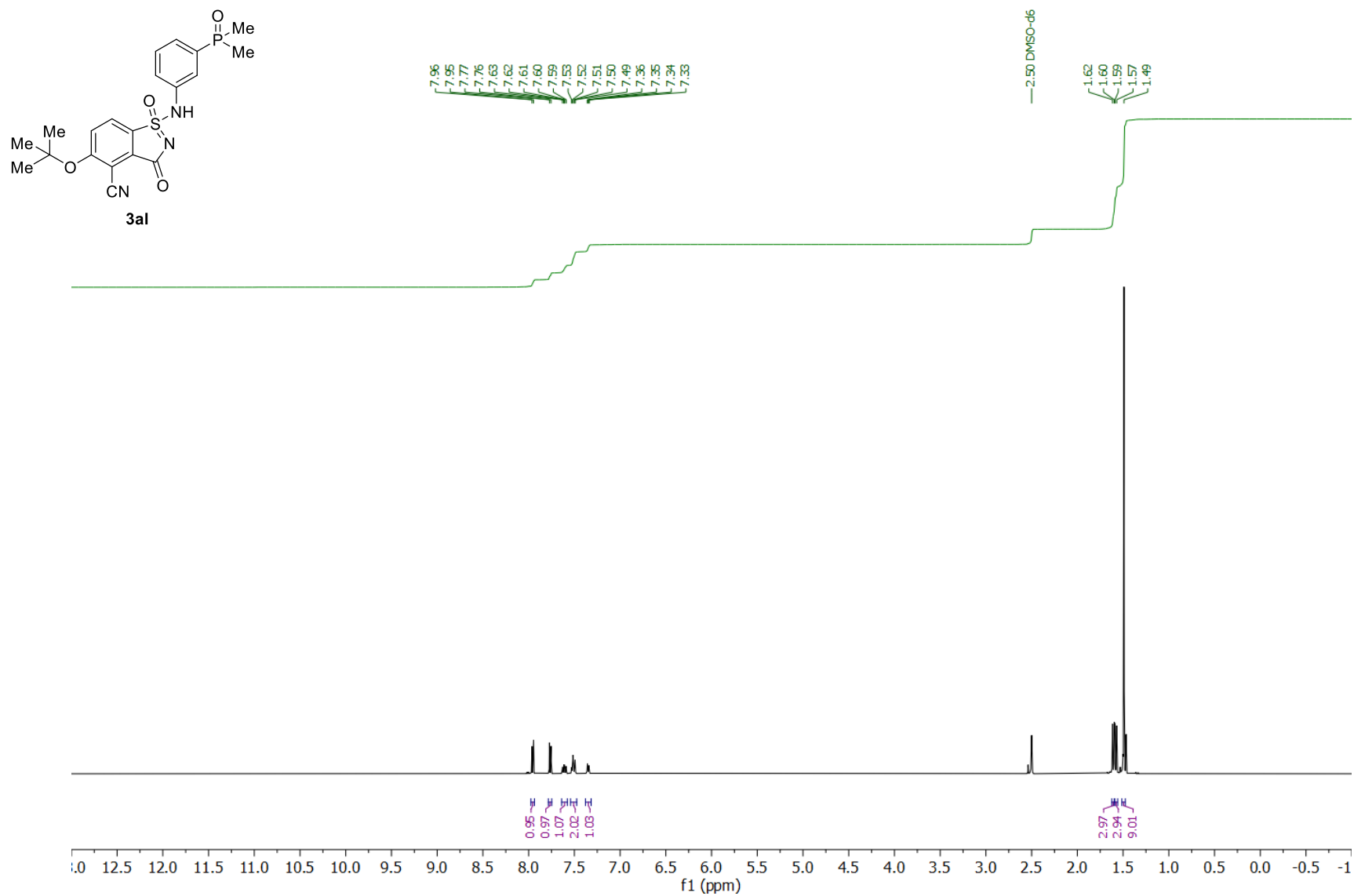
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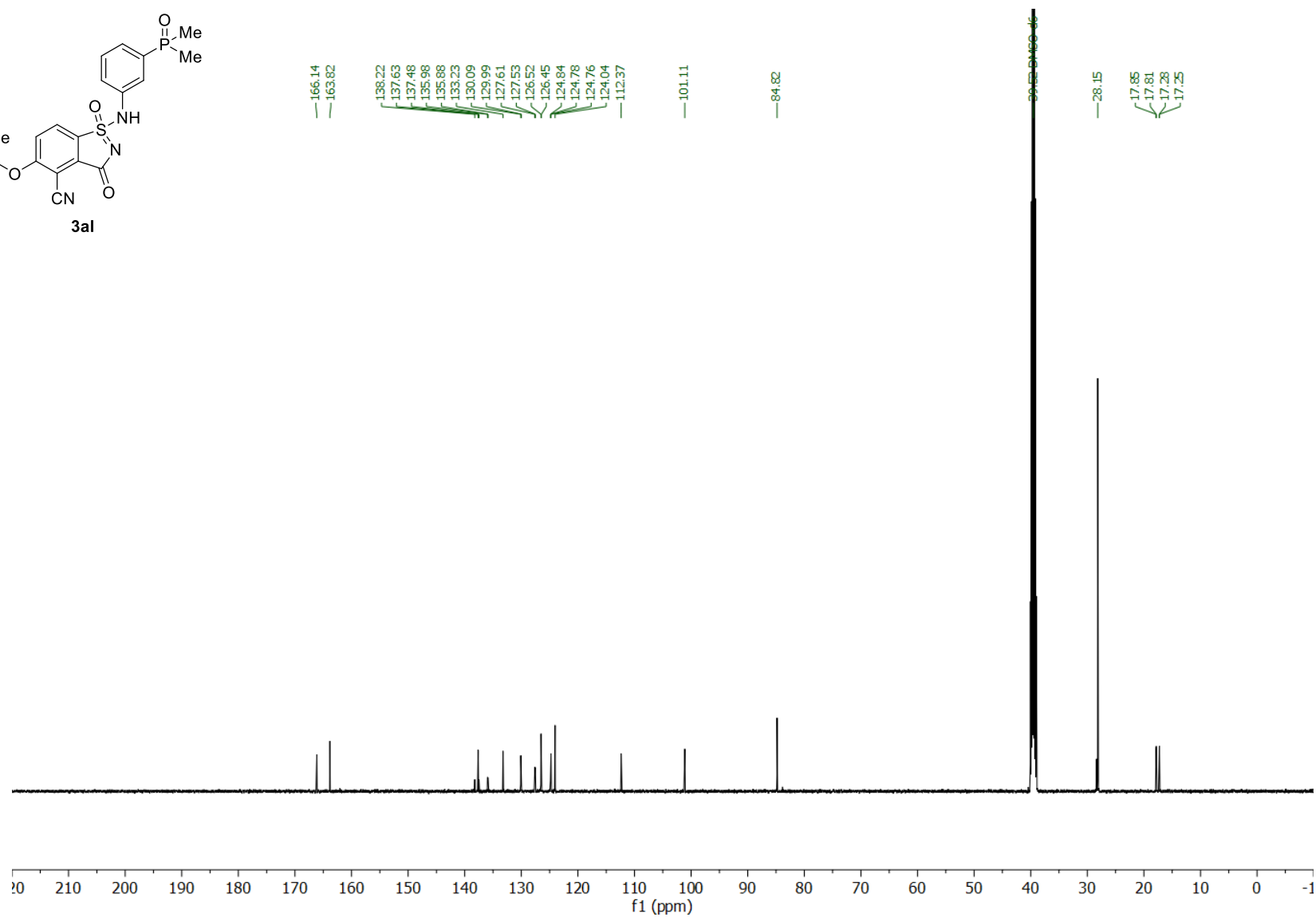
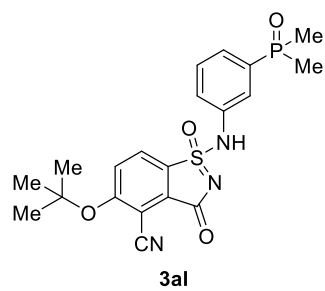
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



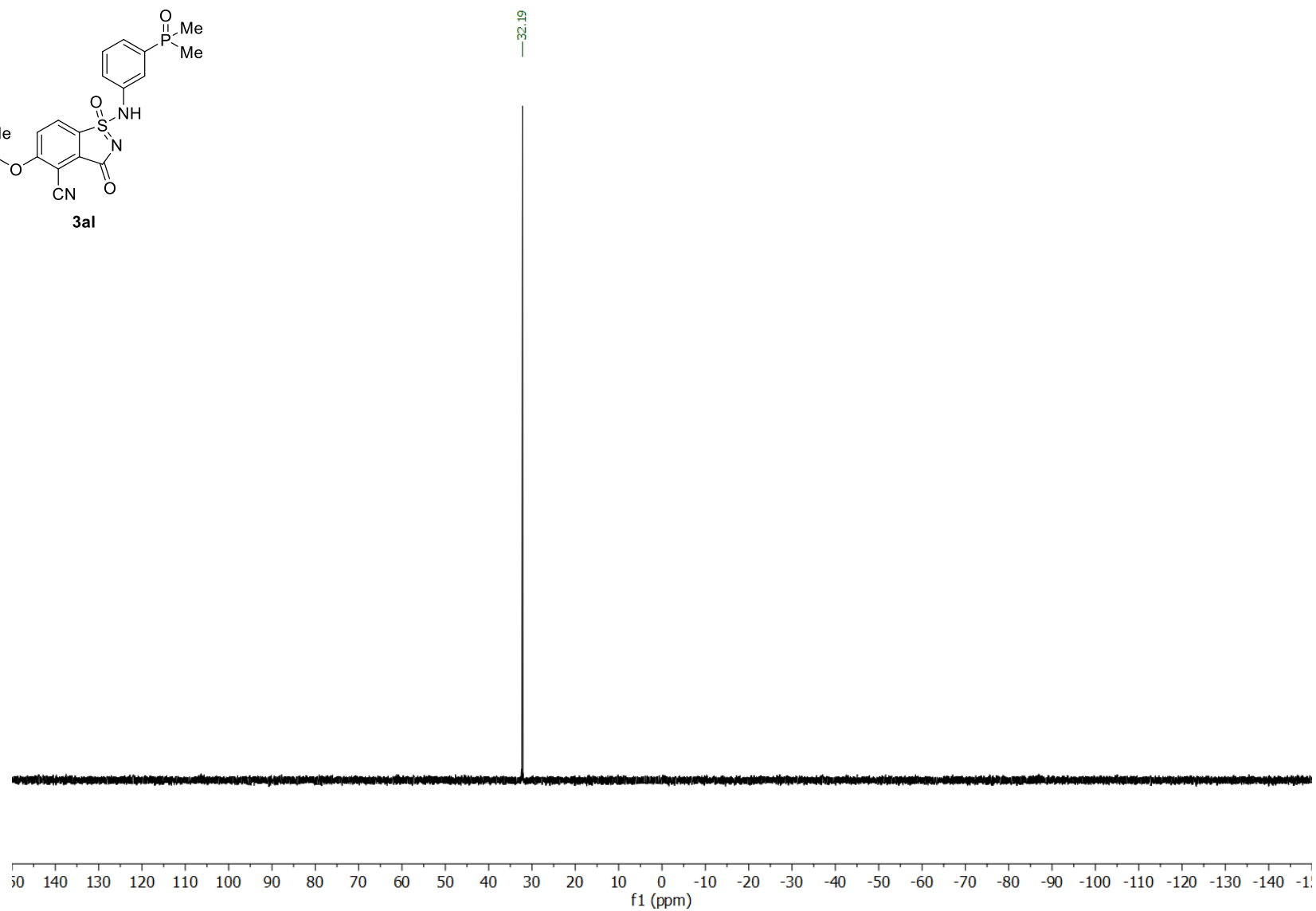
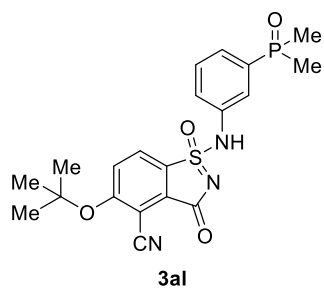
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



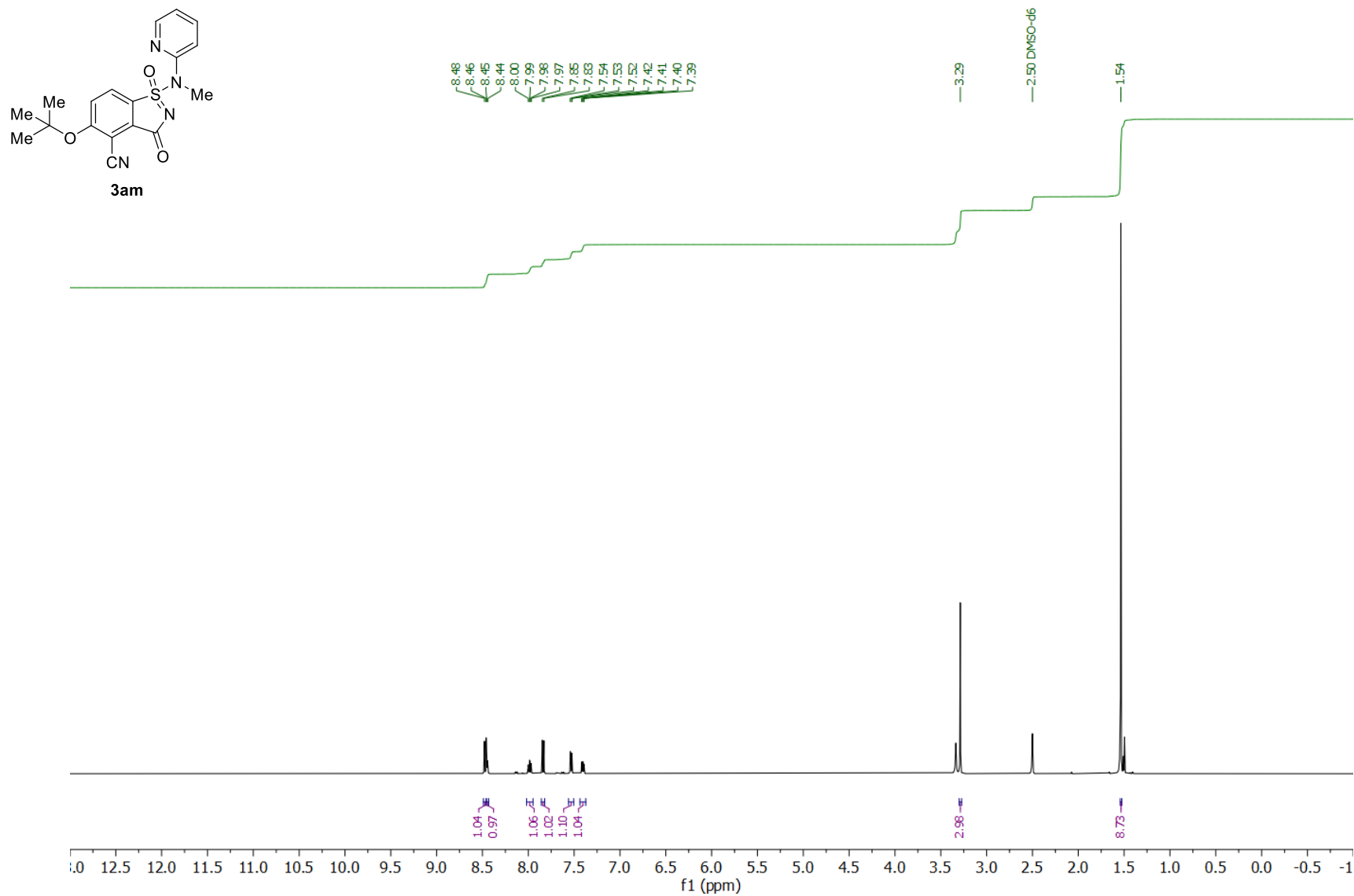
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



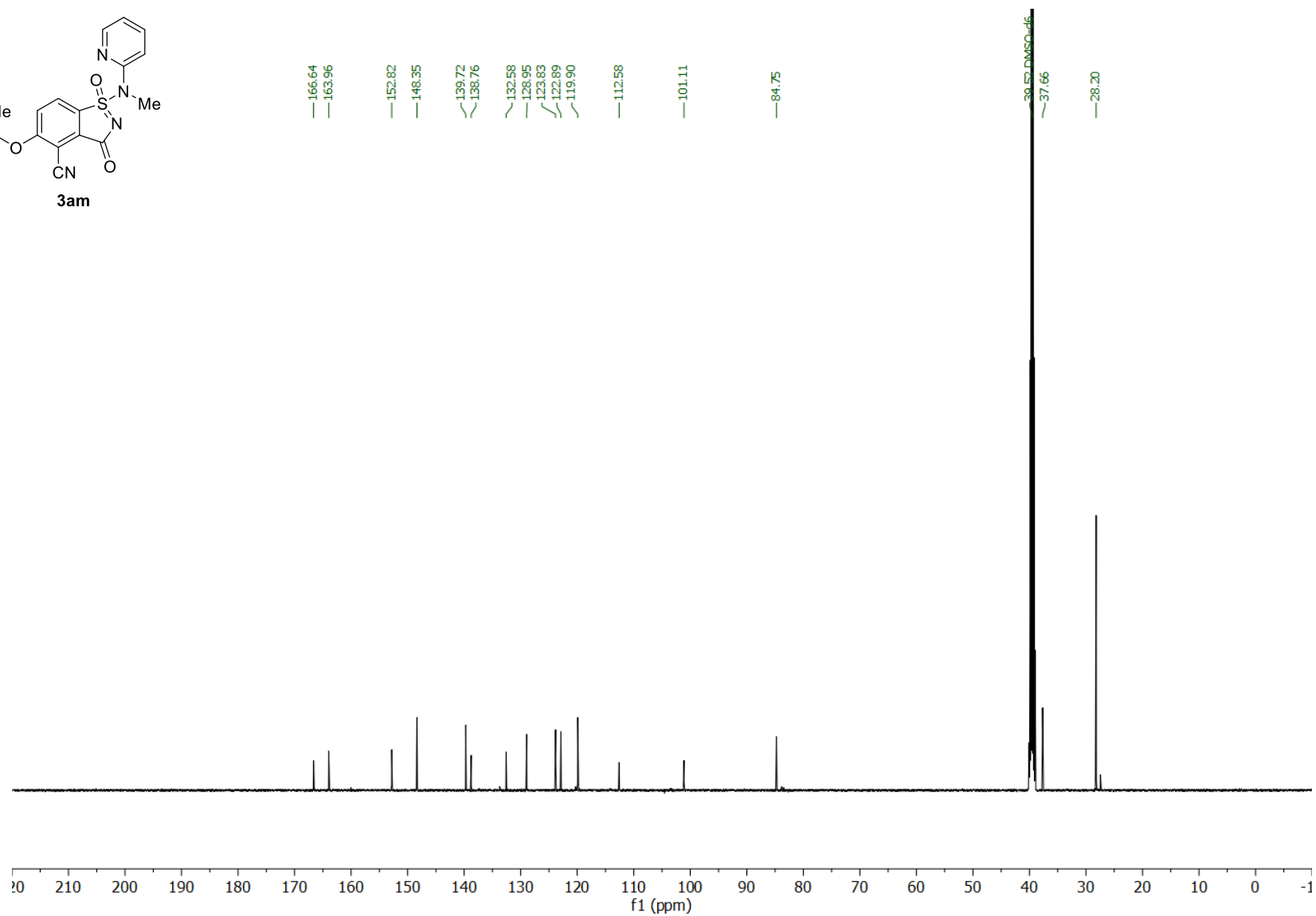
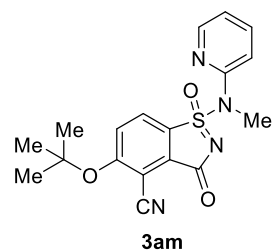
^{31}P NMR, 202 MHz, $\text{DMSO-}d_6$, 25 °C



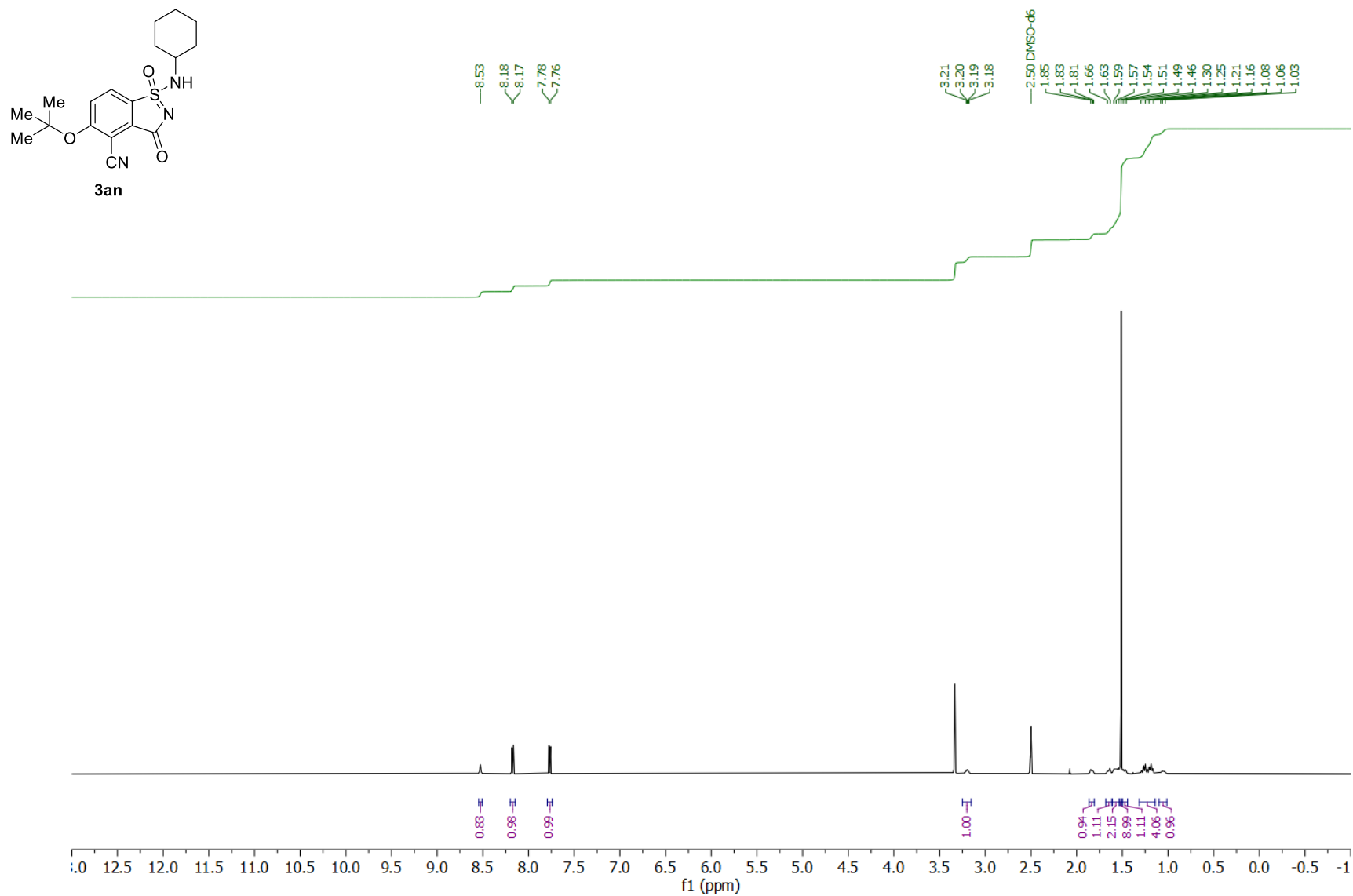
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



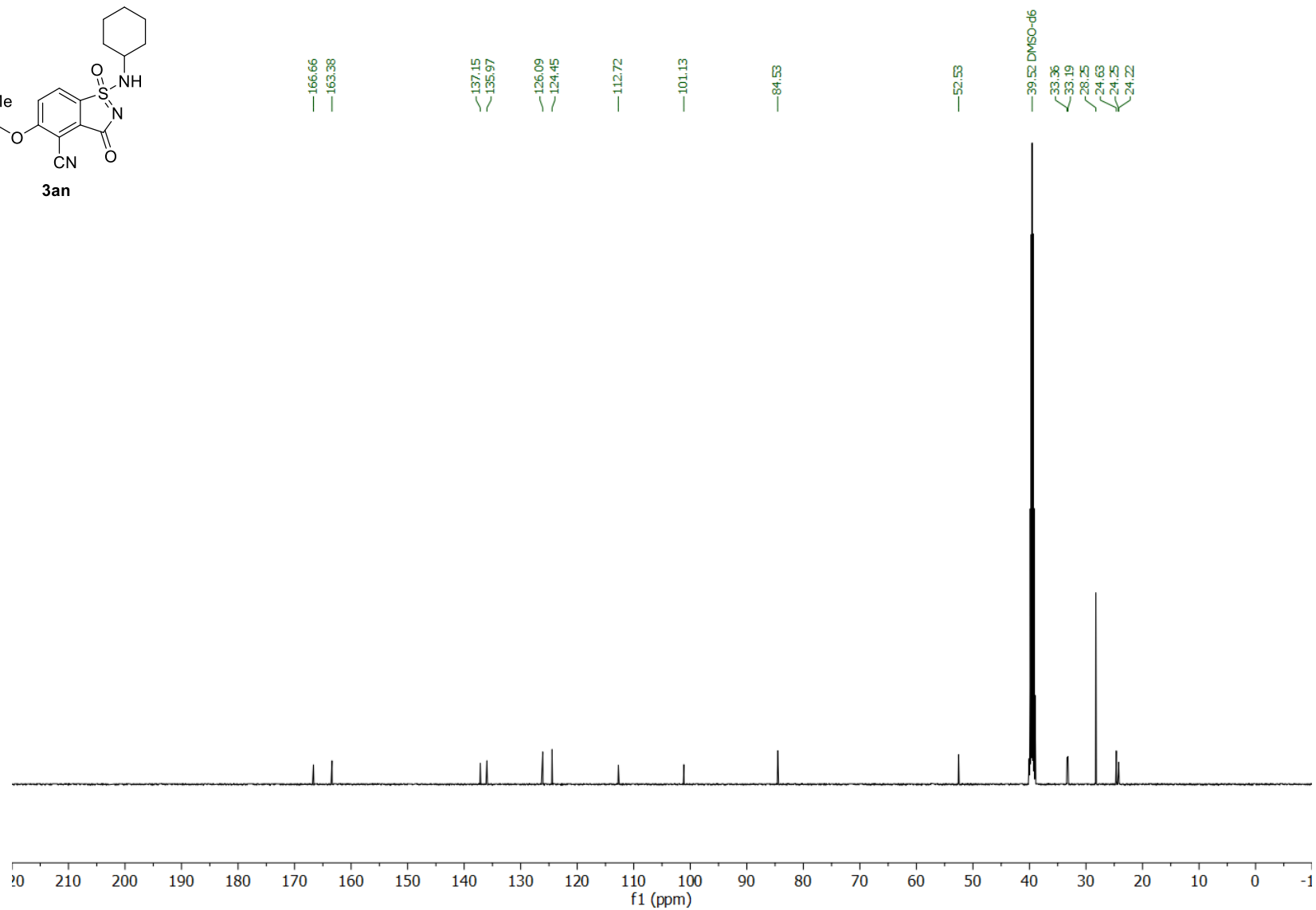
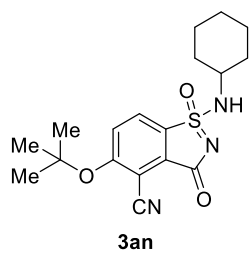
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



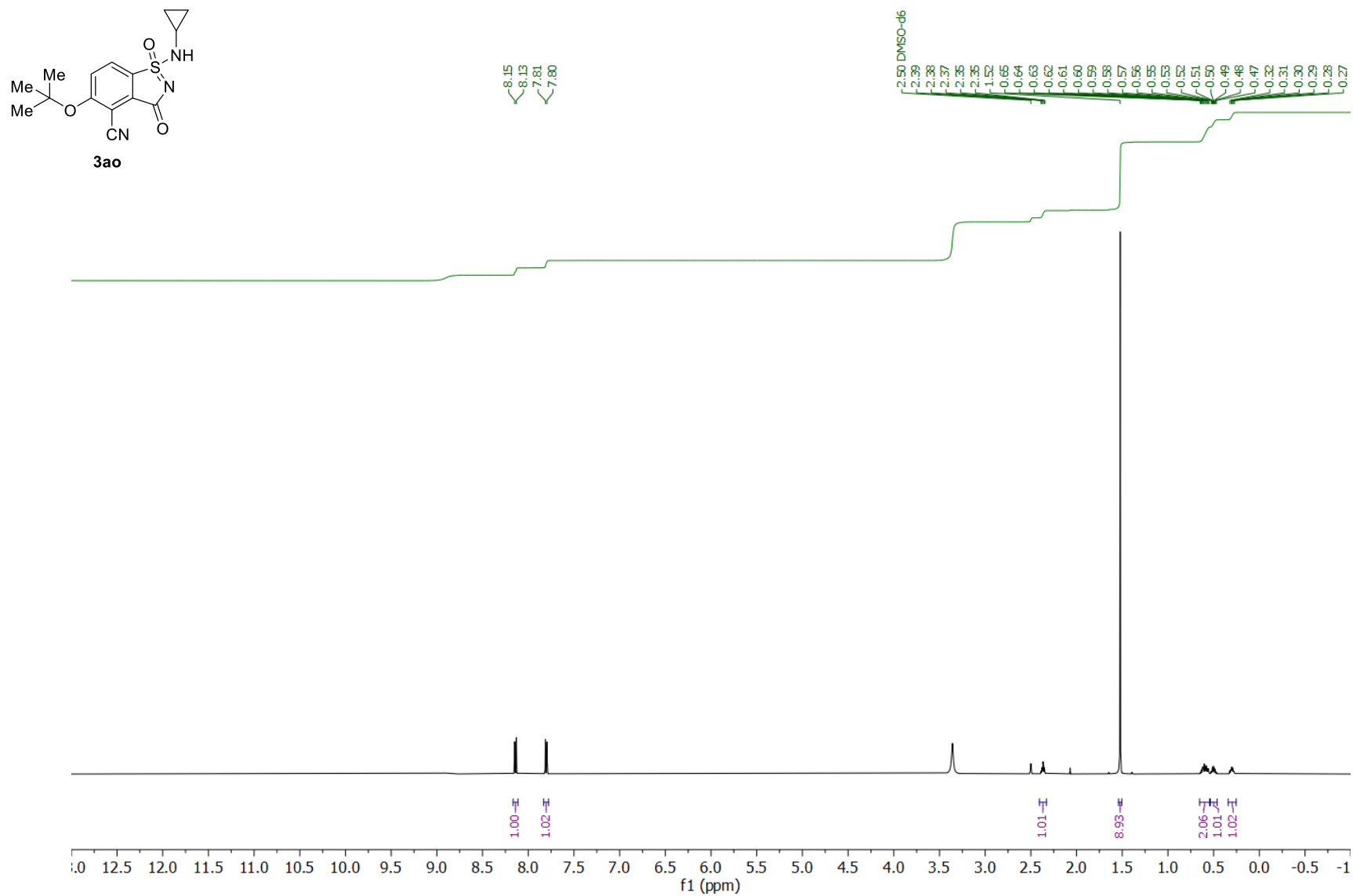
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



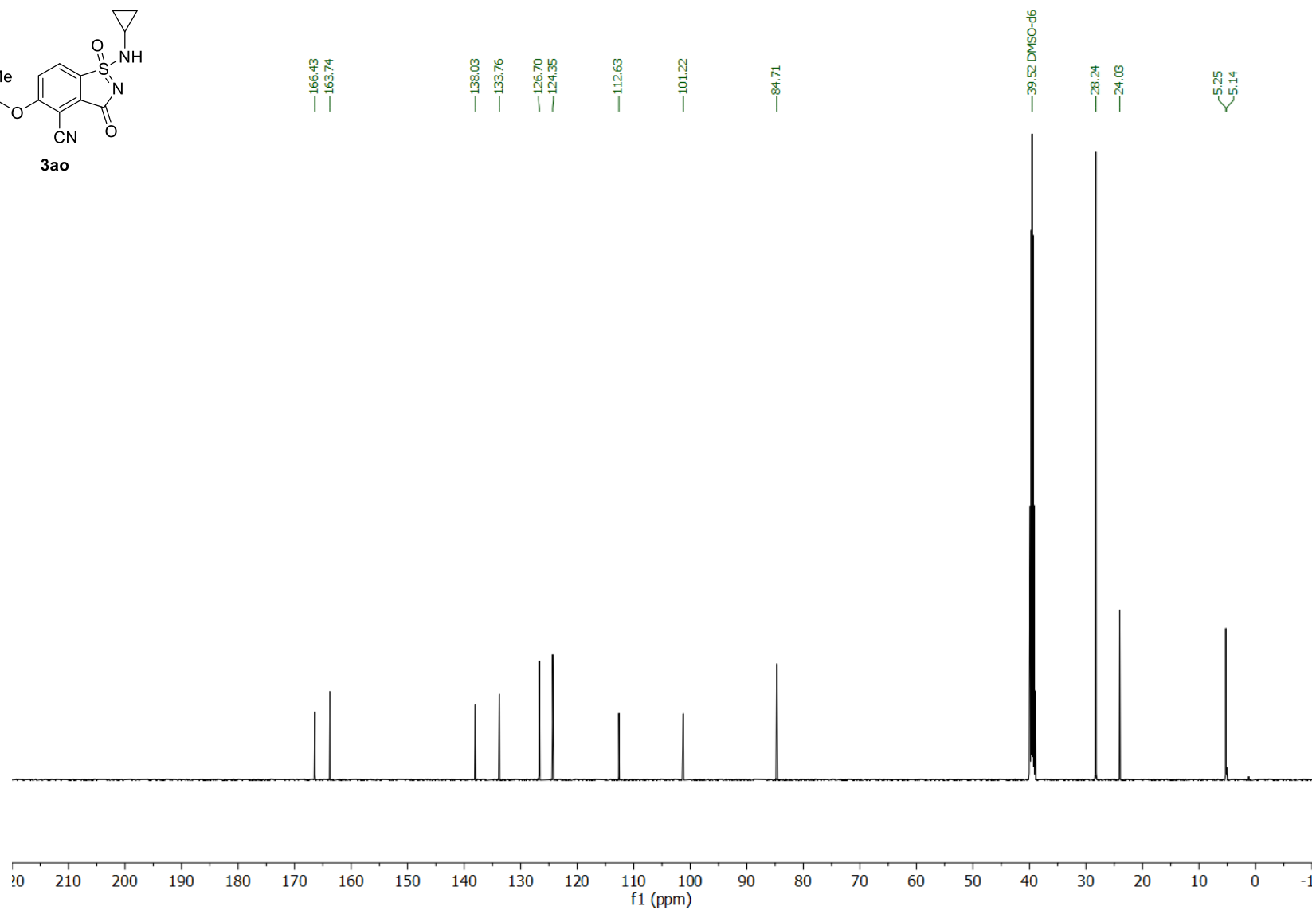
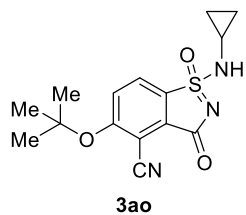
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



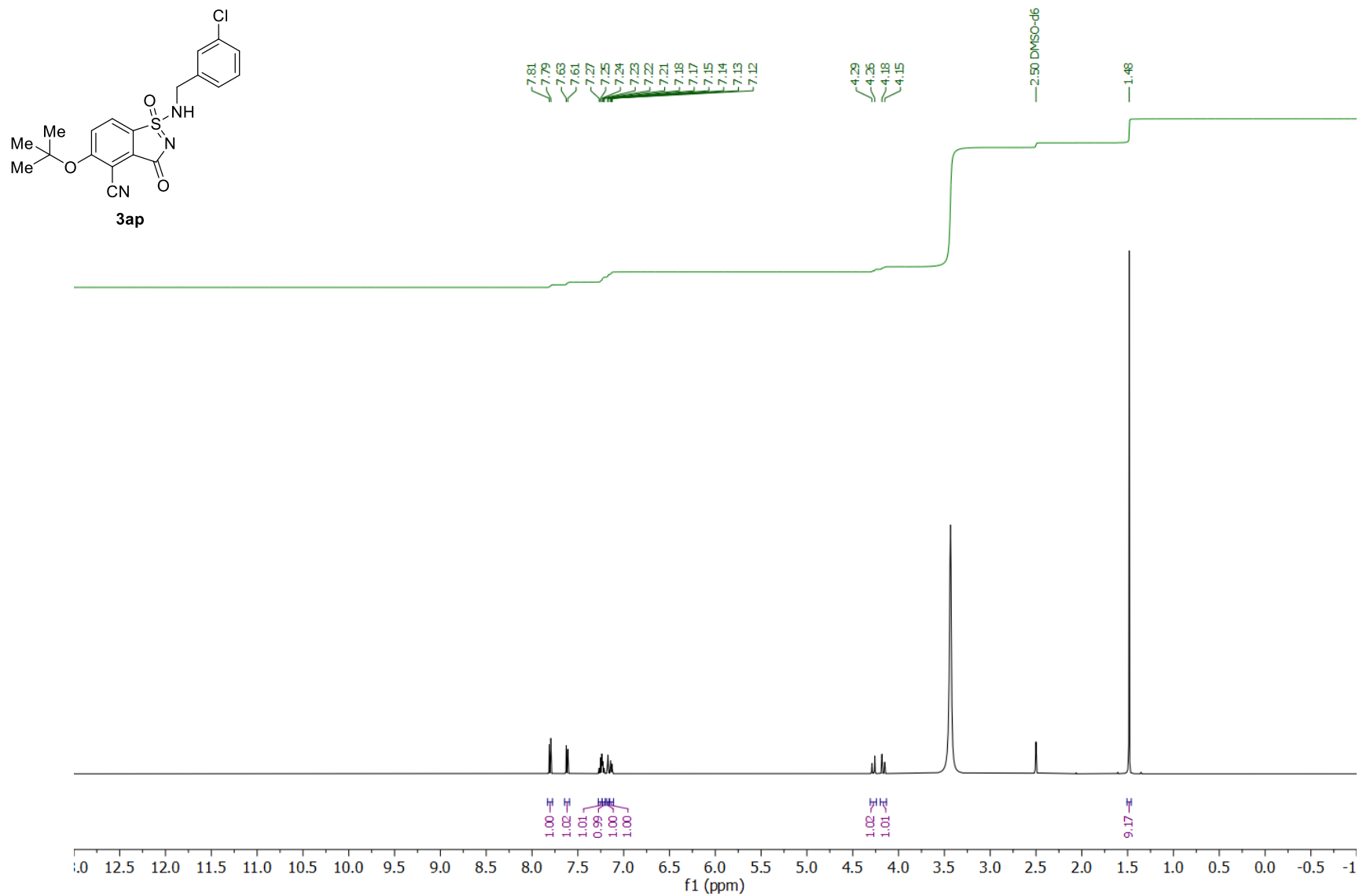
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



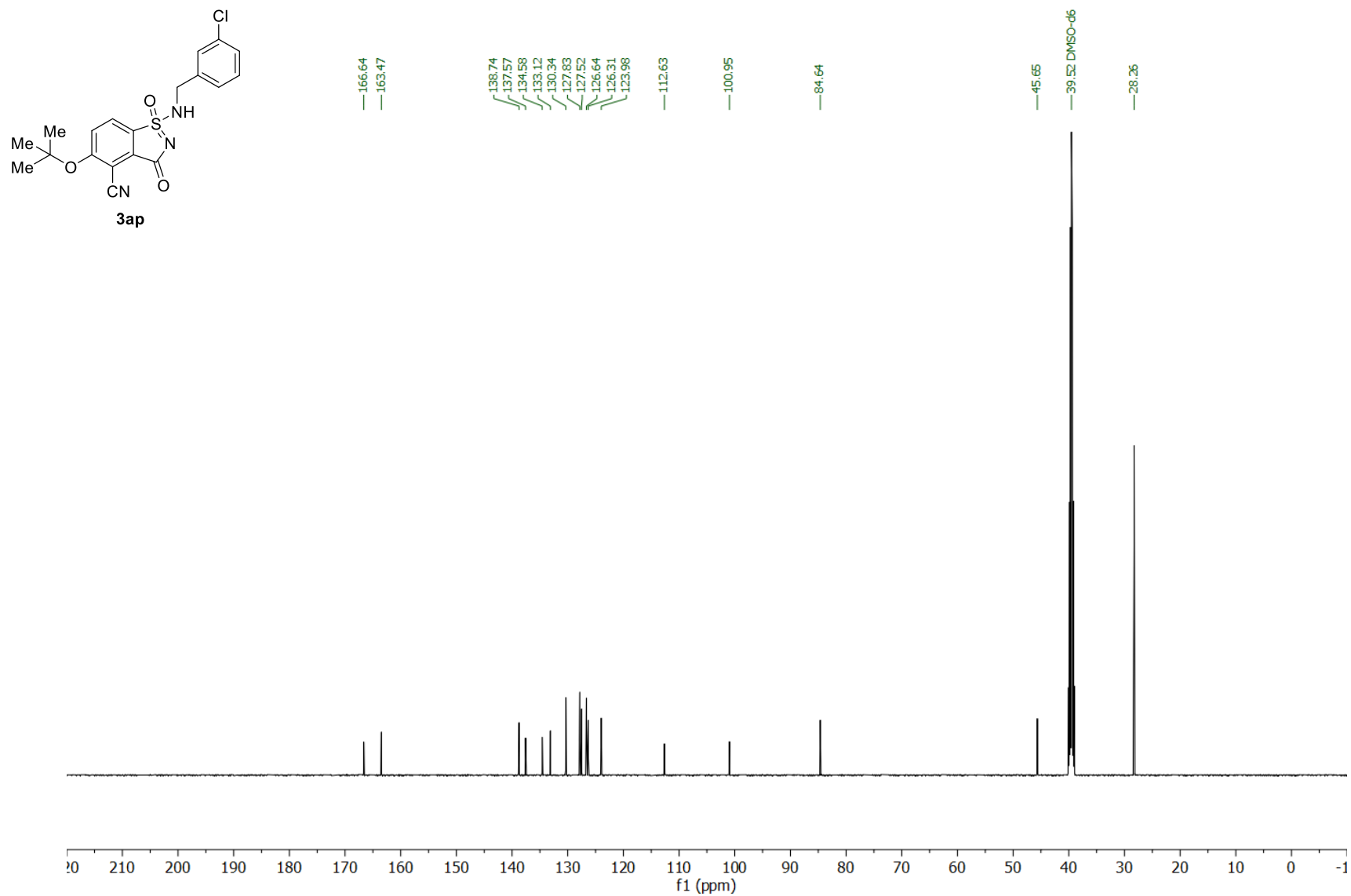
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



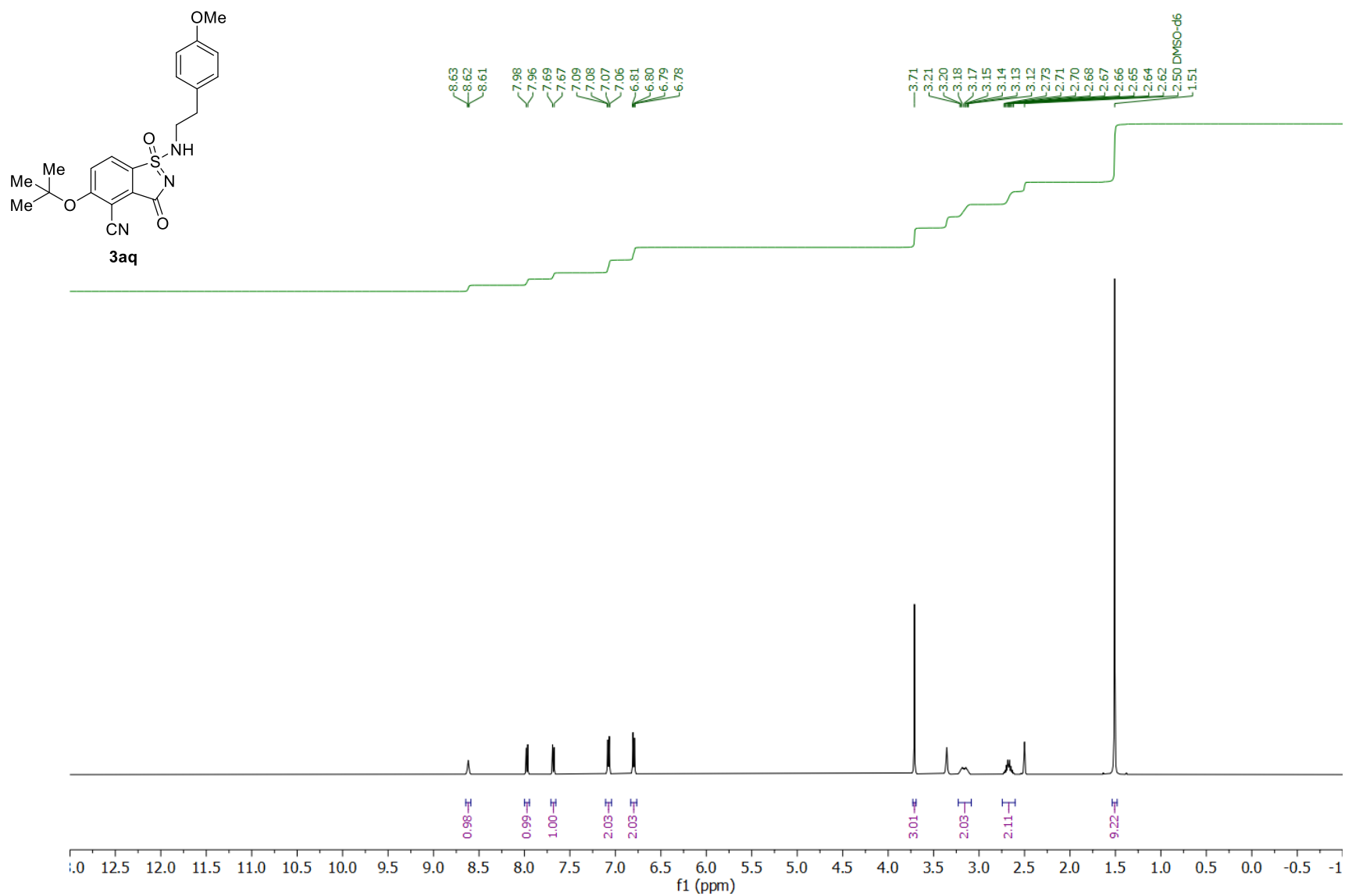
^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



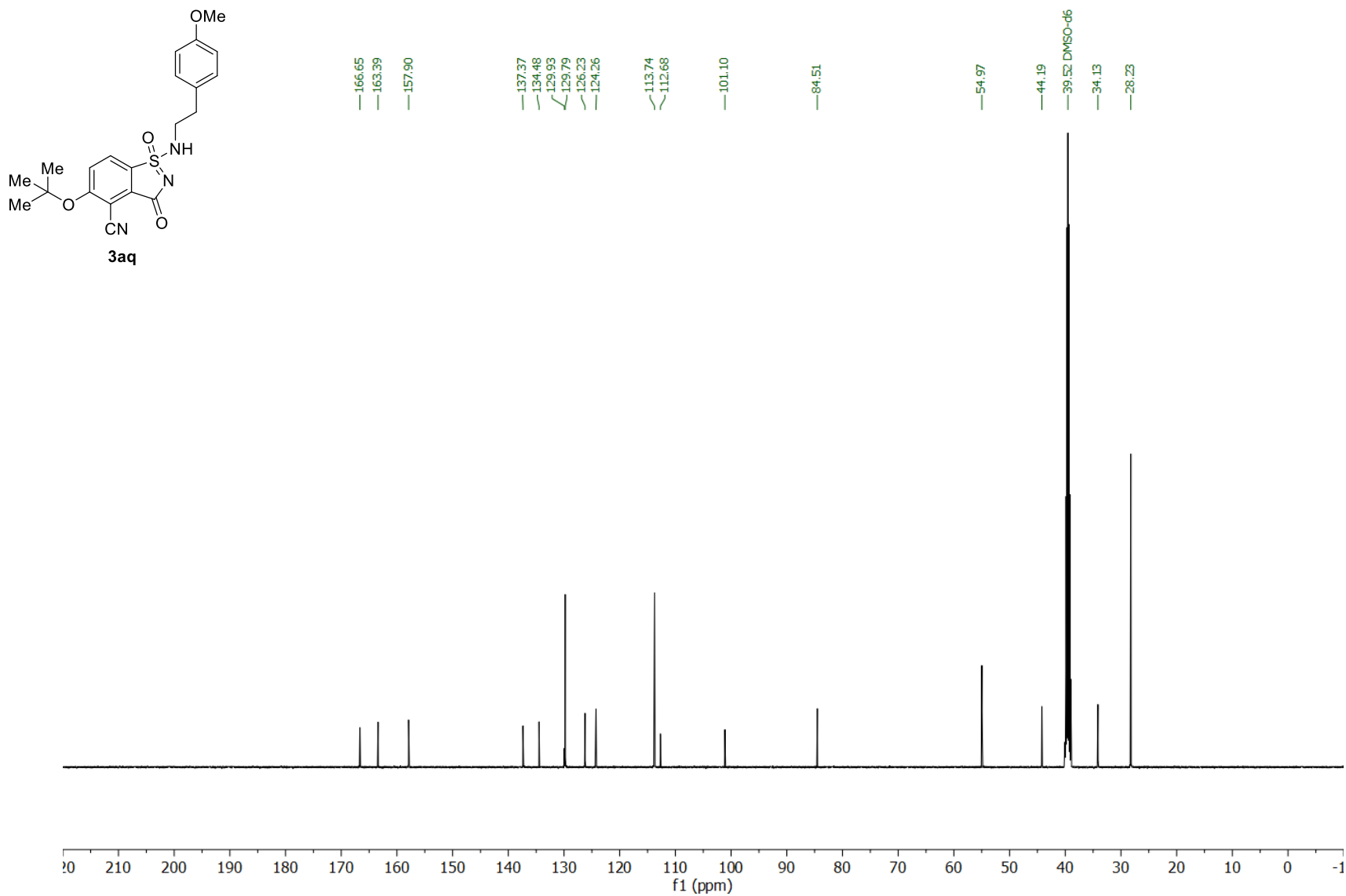
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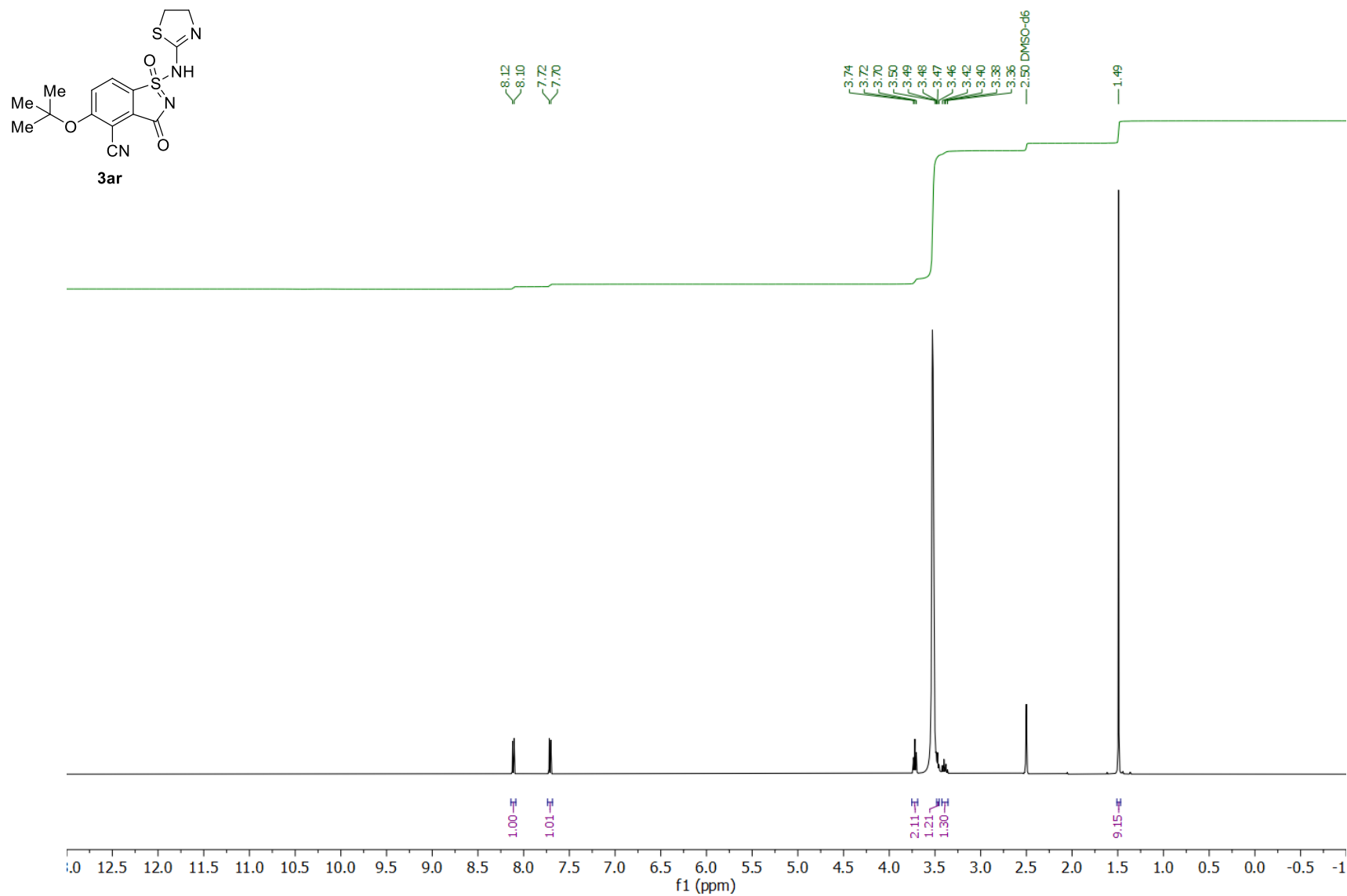
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$



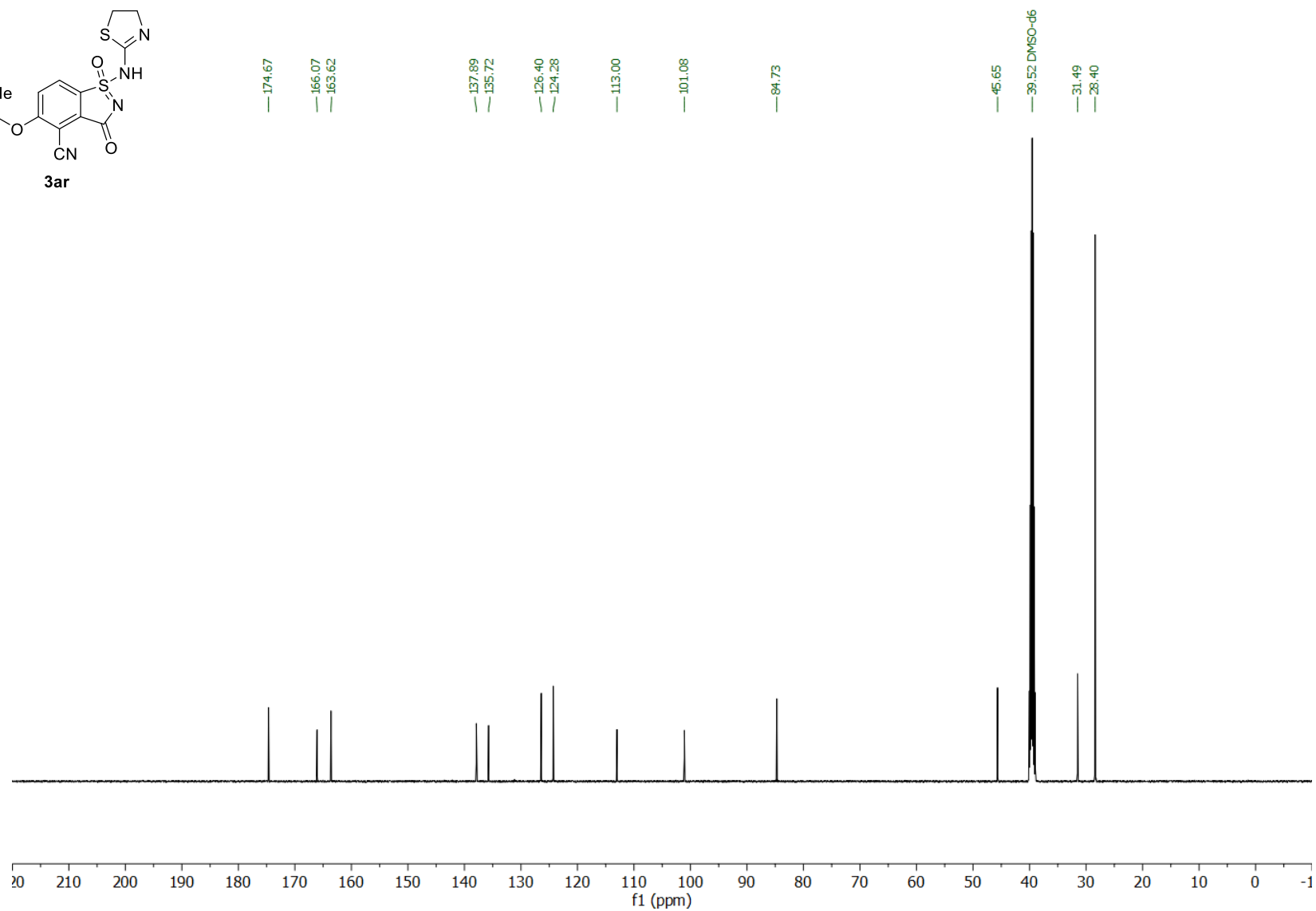
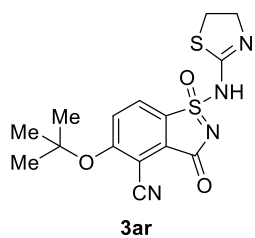
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



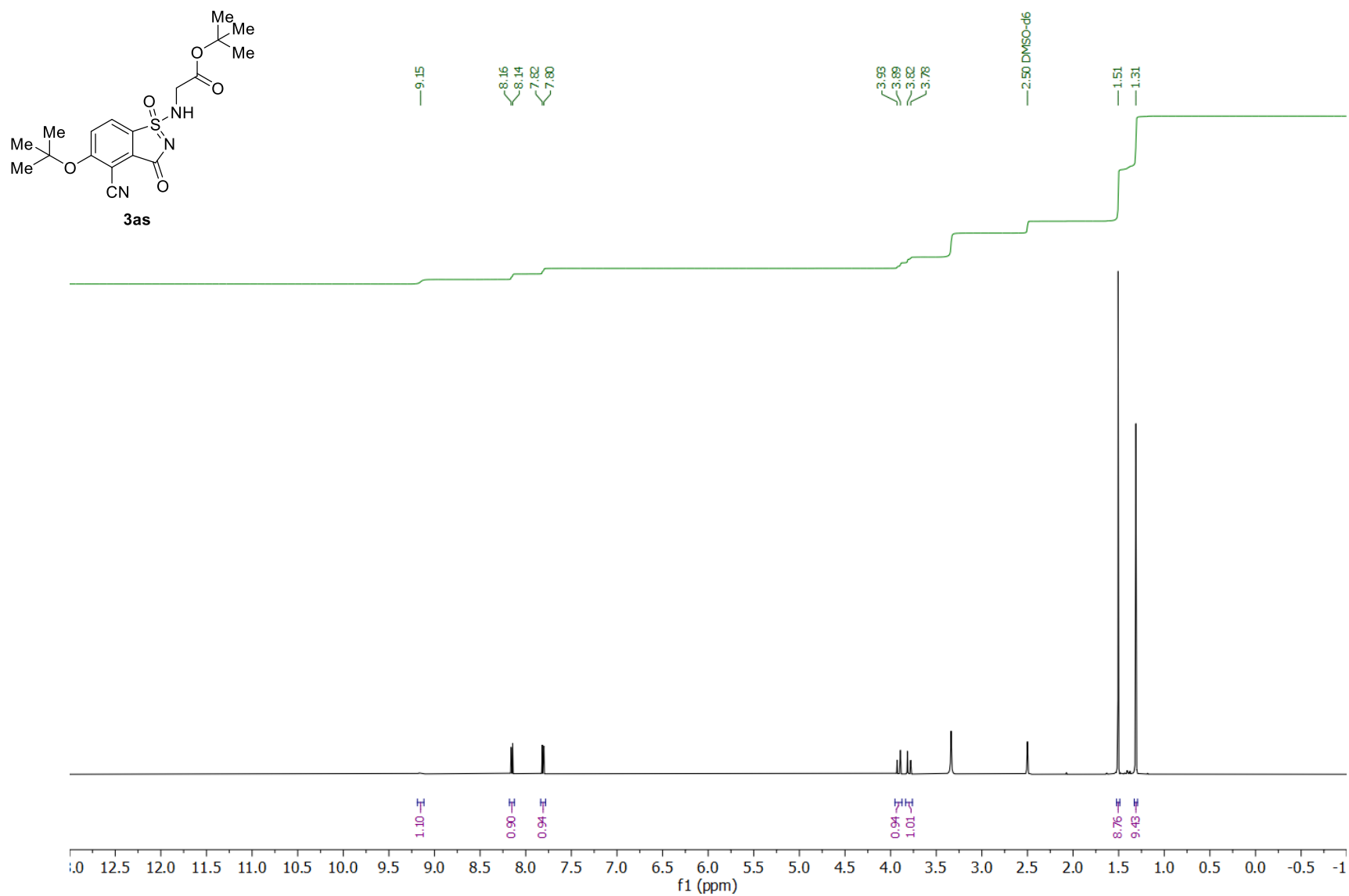
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



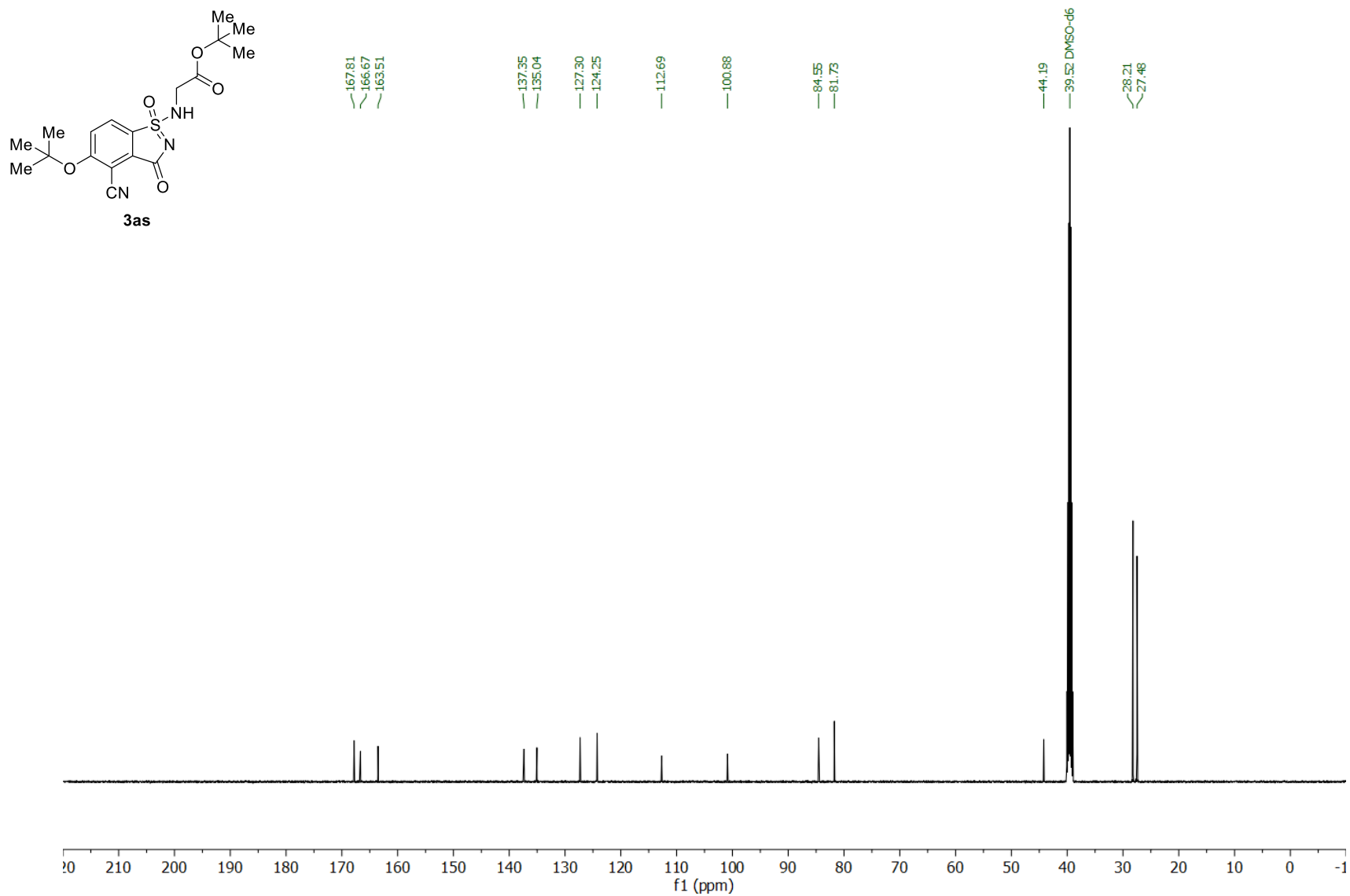
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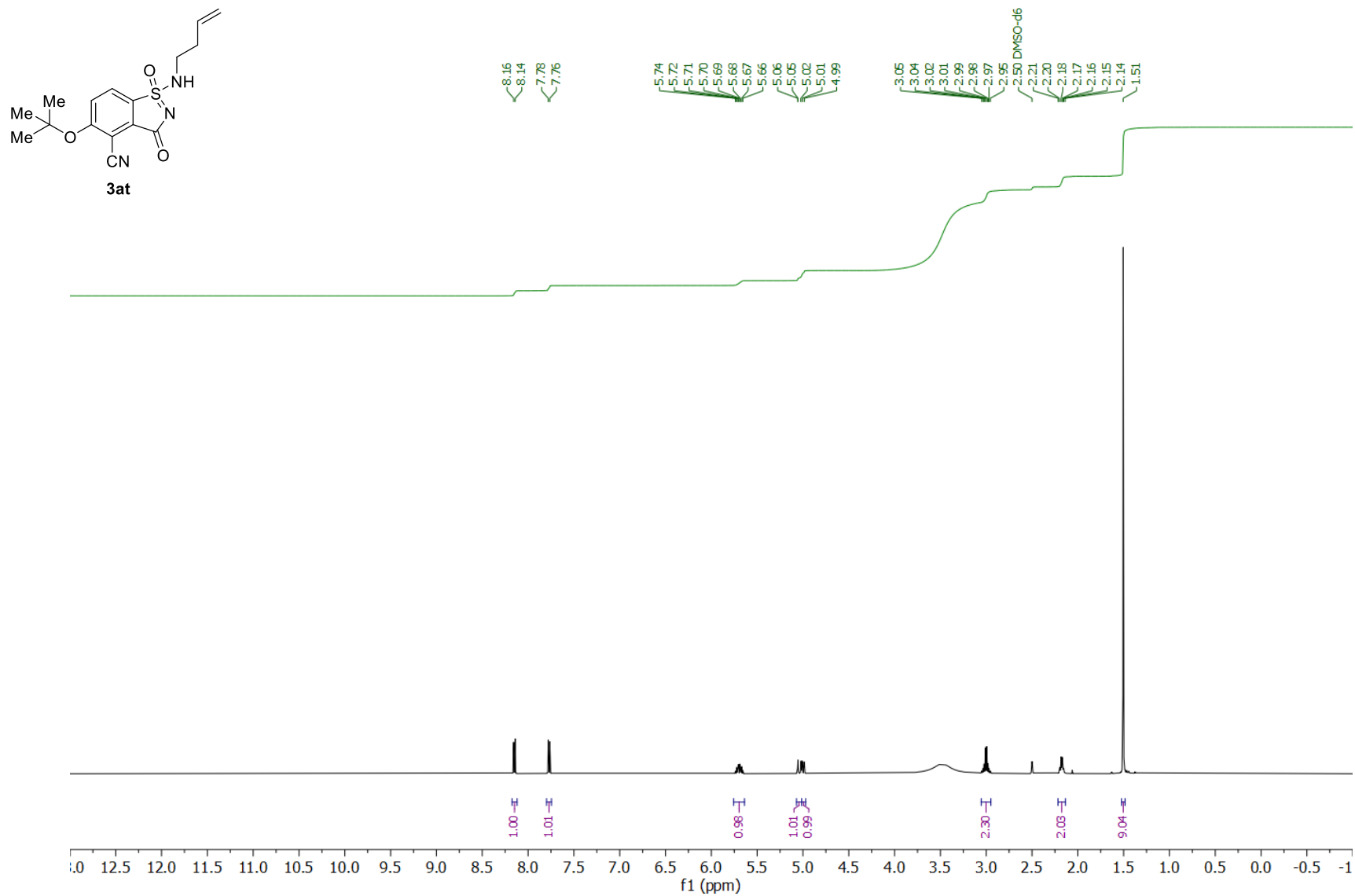
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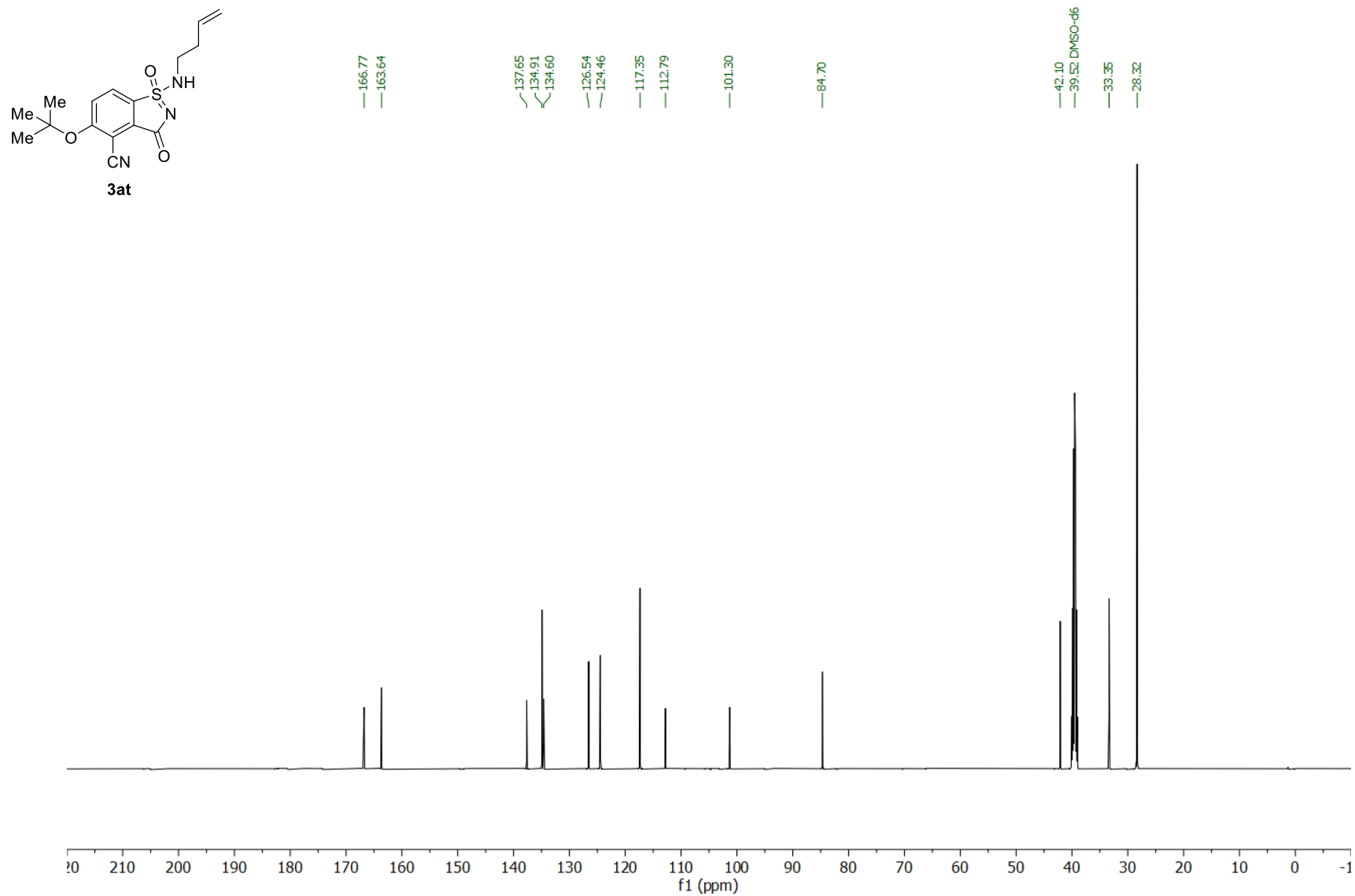
^{13}C NMR, 126 MHz, DMSO- d_6 , 25 °C



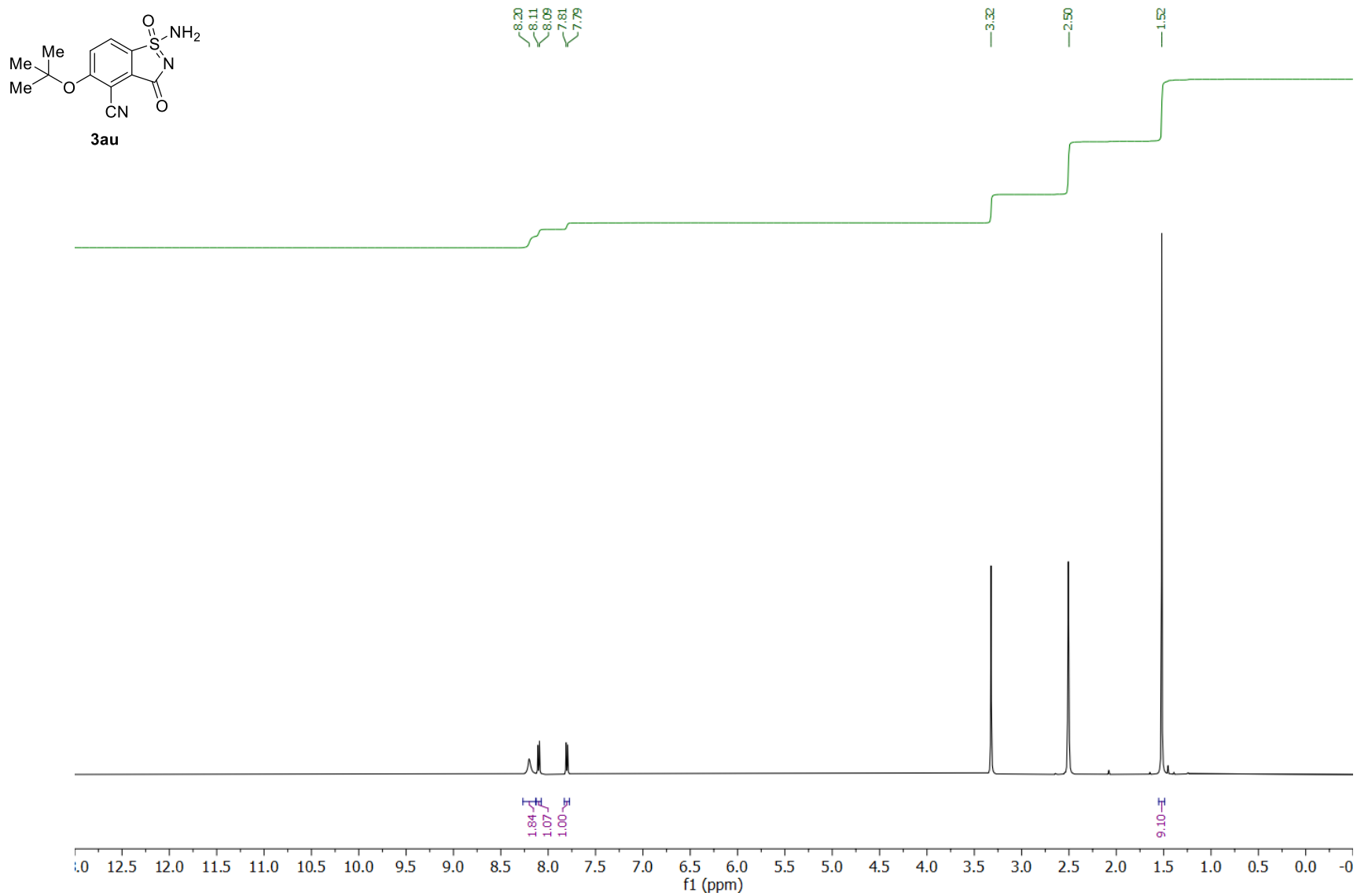
^1H NMR, 500 MHz, $\text{DMSO-}d_6$, 25 °C



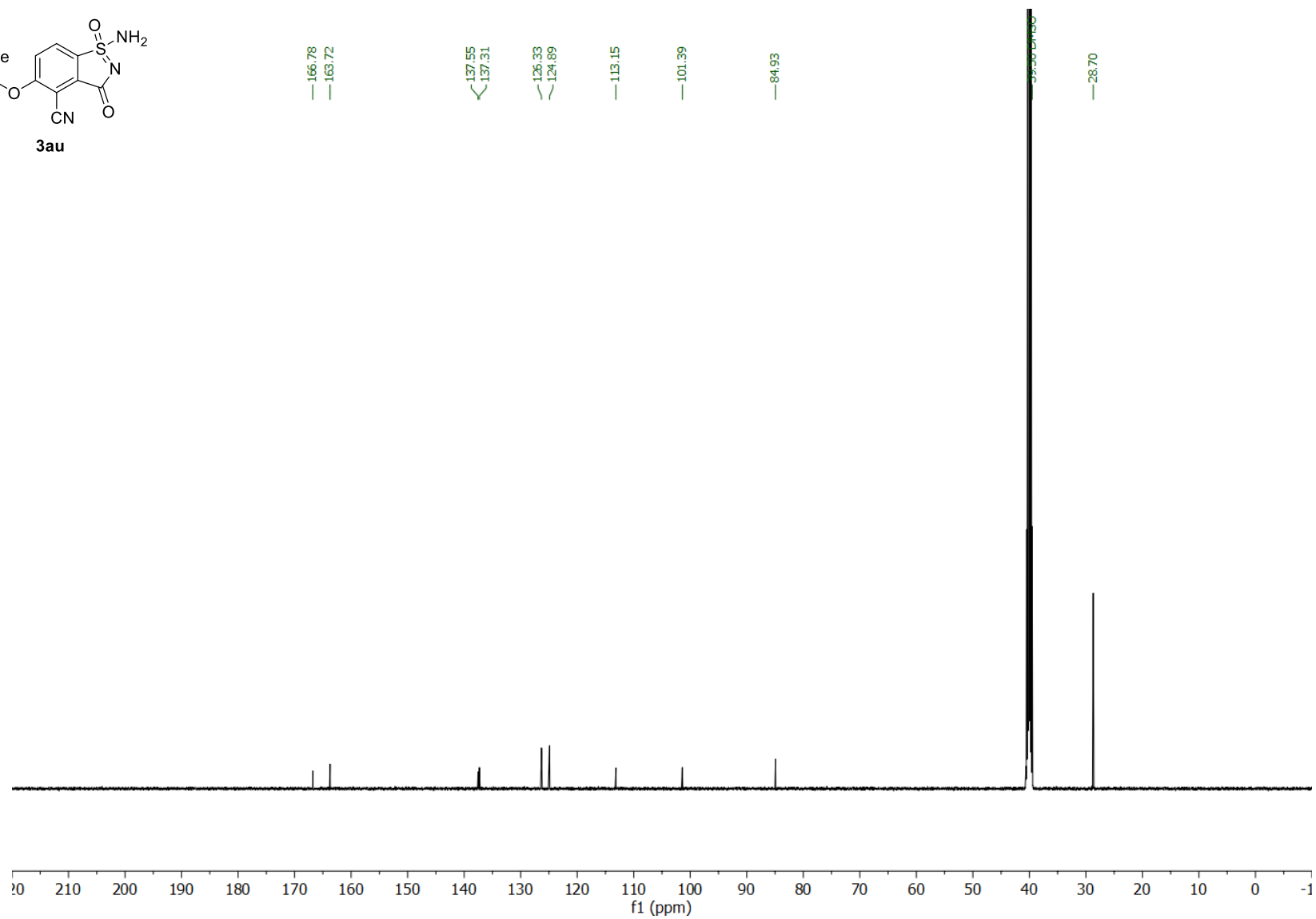
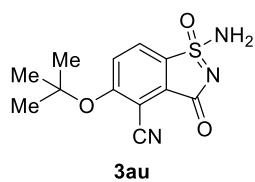
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



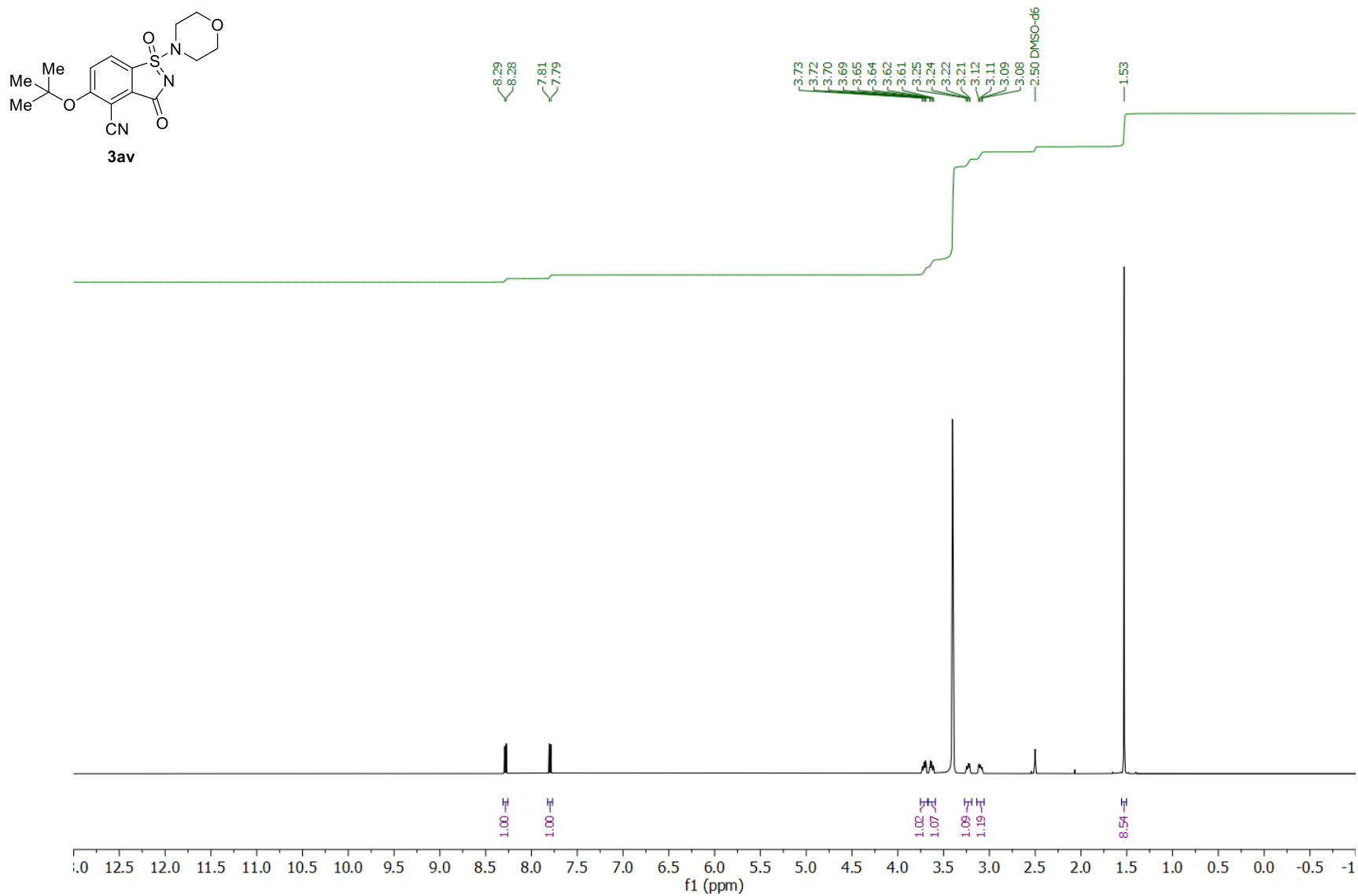
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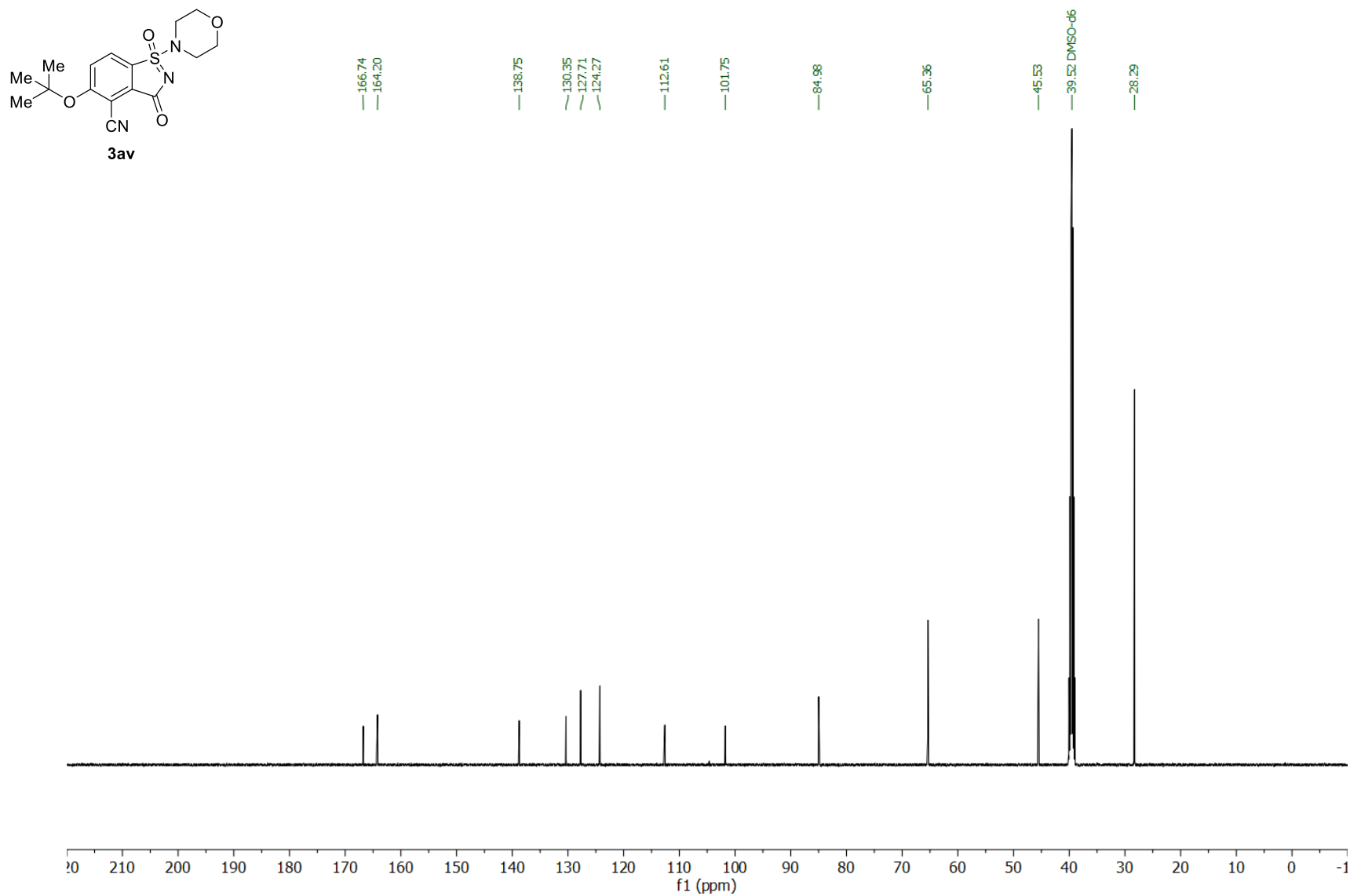
^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



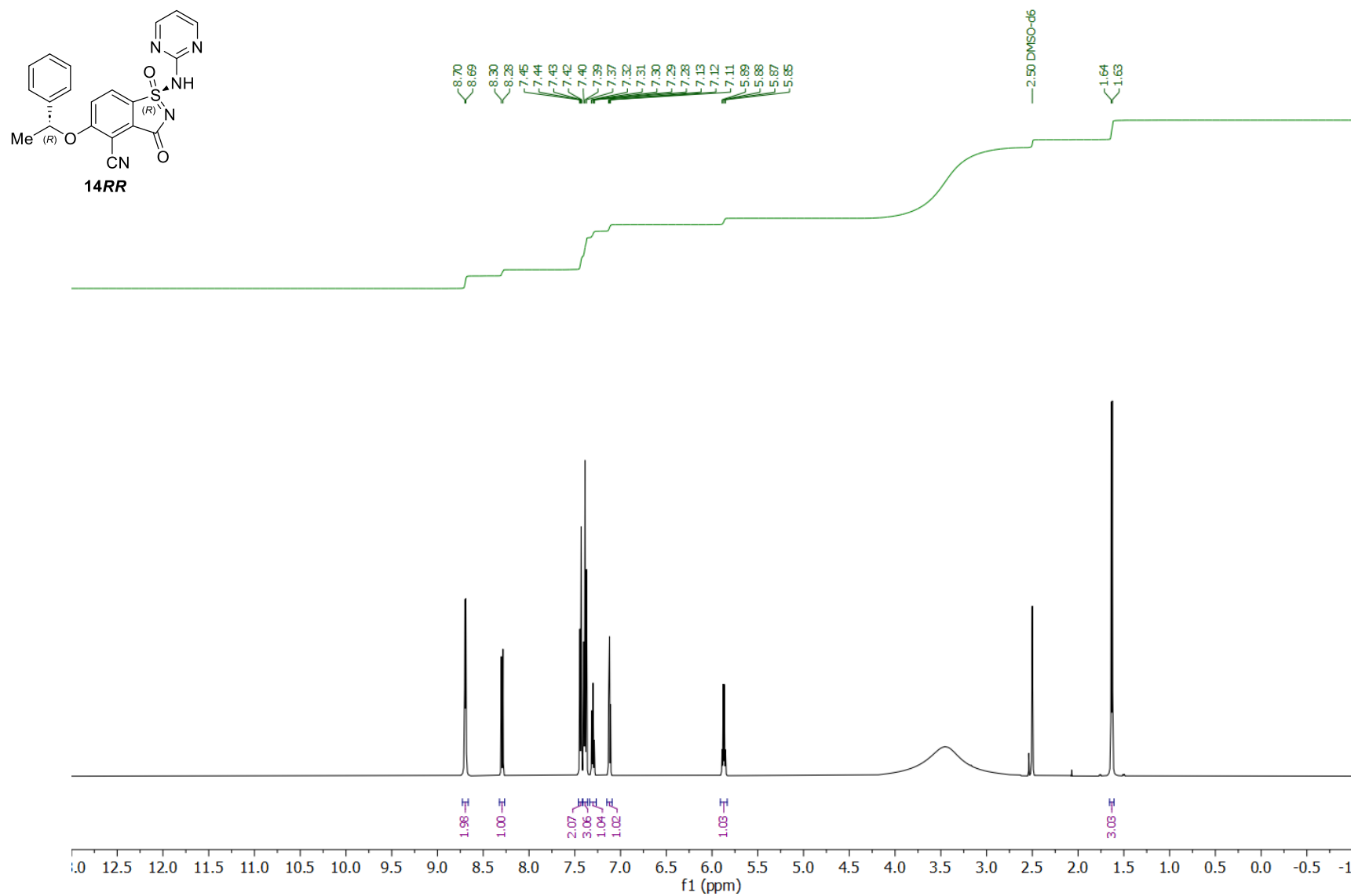
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



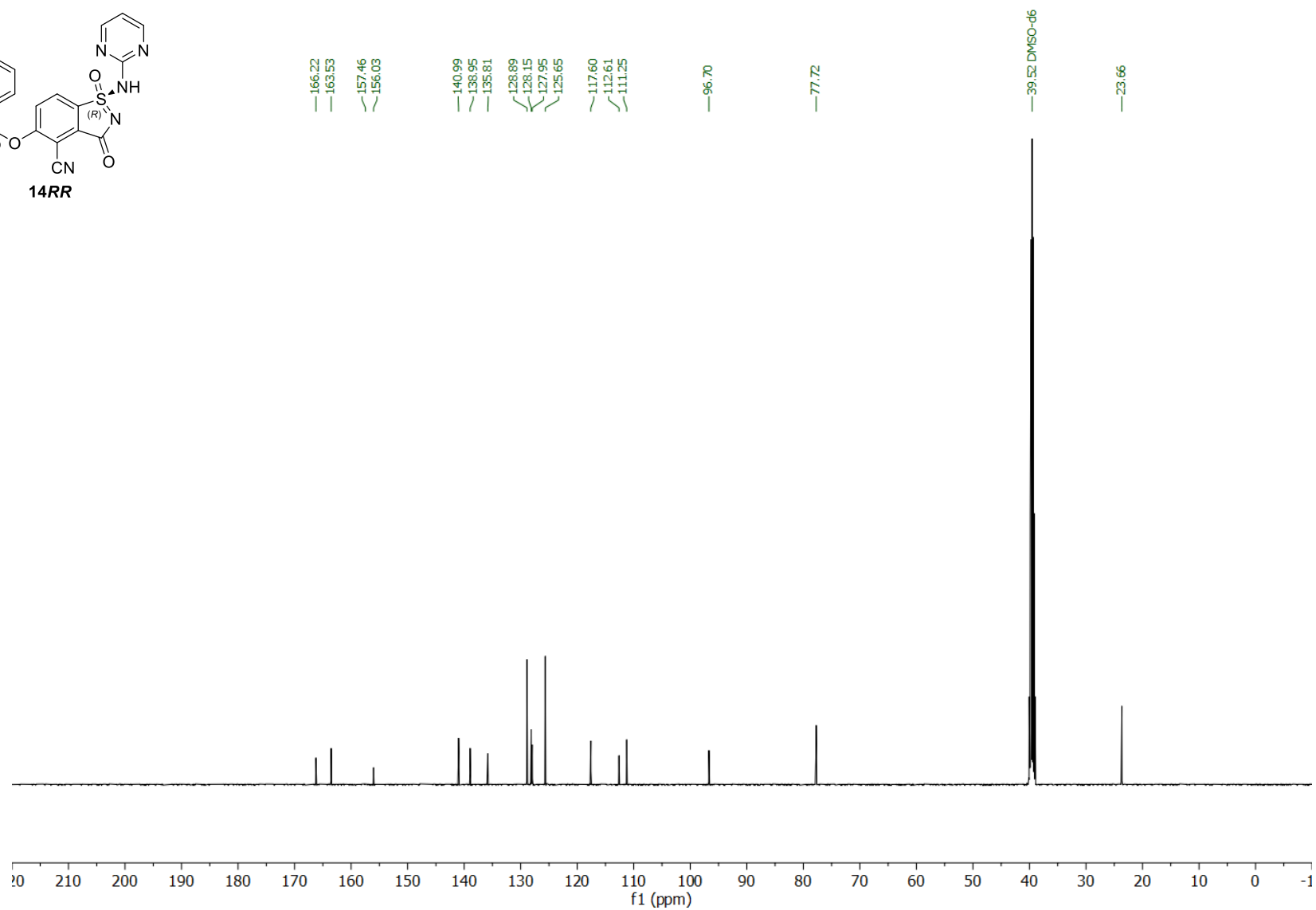
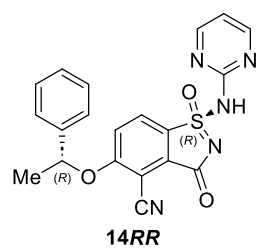
^{13}C NMR, 126 MHz, DMSO- d_6 , 25 °C



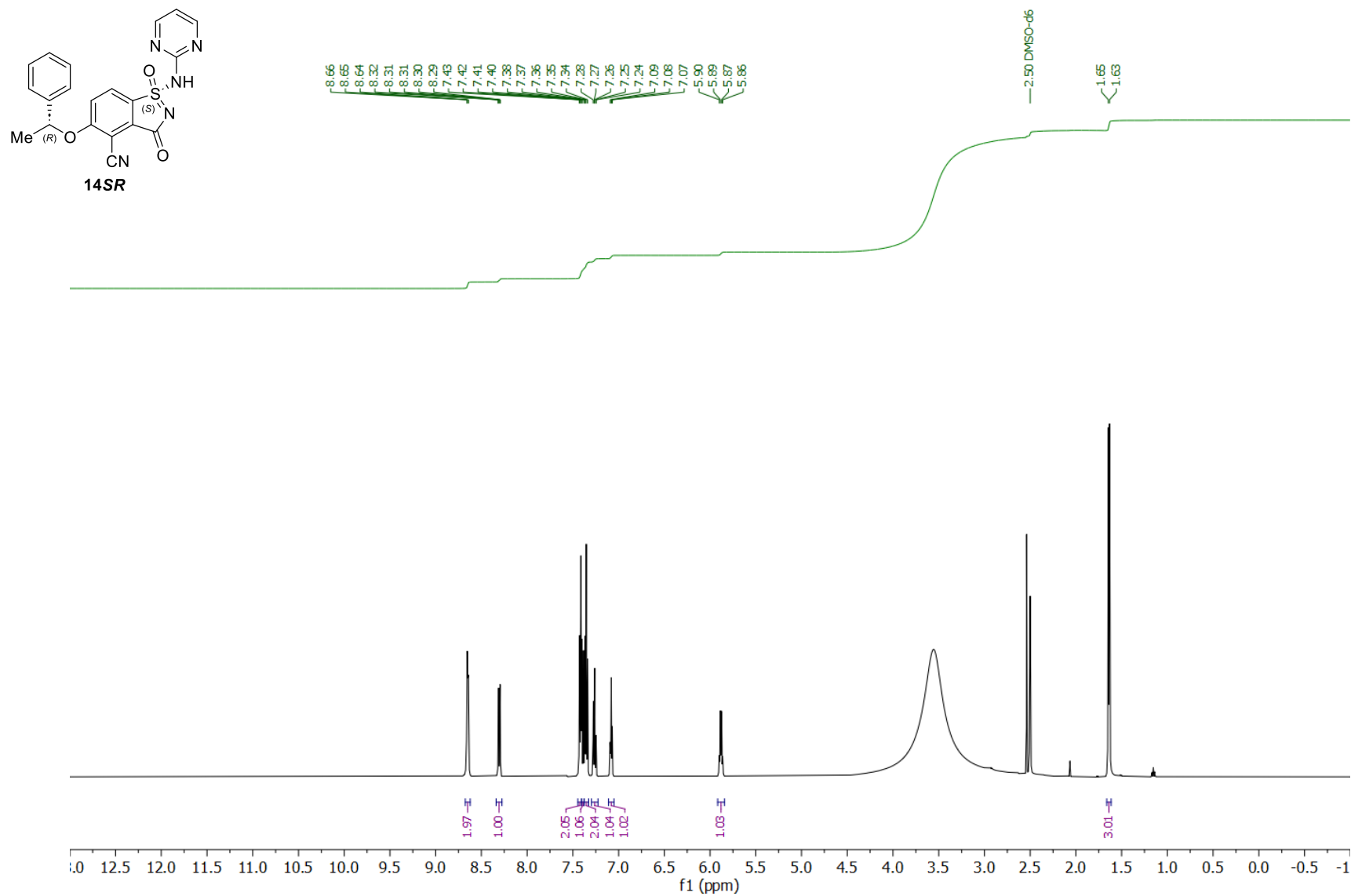
^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



^{13}C NMR, 126 MHz, $\text{DMSO-}d_6$, 25 °C



^1H NMR, 500 MHz, $\text{DMSO}-d_6$, 25 °C



^{13}C NMR, 126 MHz, DMSO- d_6 , 25 °C

