Supporting Information

PIDA/I_2-mediated photo-induced aerobic *N*-acylation of sulfoximines with methylarenes

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1. General information:

All the reagents were commercial grade and purified according to the established procedures. All the reactions were carried out in oven-dried glassware. The highest commercial quality reagents were purchased and were used without further purification unless otherwise stated. All the cinnamic acids used in this protocol were commercially purchased from Sigma Aldrich and BLD Pharma. Reactions were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel plates ($60F_{254}$) visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Solvents were removed using a rotary evaporator under reduced pressure. Column chromatography was performed to purify the crude product on silica gel 60−120 mesh using a mixture of hexane and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [^1H, $^{13}C\{1H\}$ NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform ($CDCl_3$). ^1H, $^{13}C\{^1H\}$ were recorded in 400 (100), 500 (125) or 600 (150) MHz spectrometers and were calibrated using tetramethylsilane or residual undeuterated solvent for ^1H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm or $CHCl_3$: 7.260 ppm for ^1H NMR and 77.230 ppm for $^{13}C\{1H\}$. ^{19}F NMR was calibrated without any internal standard in $CDCl_3$ in a 370, 471 or 565 MHz spectrometer. The chemical shifts are quoted in δ units, parts per million (ppm). ^1H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), integration and coupling constant(s) J in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded in neat and reported in the frequency of absorption (cm^{-1}).

2. Light Information and Reaction Setup:

Philips 2 x 10 W white LEDs (flux = 46mW/cm^2) bulb was used as the light source for this light-induced reaction, and no filter was used. Borosilicate round bottom glass was used as the reaction vessel. The distance from the light source to the irradiation vessel was ~3-5 cm. A regular fan was used to ventilate the area to maintain the room temperature (25−30 ^oC). The reaction setup for this photochemical strategy is shown below (Fig. S1).

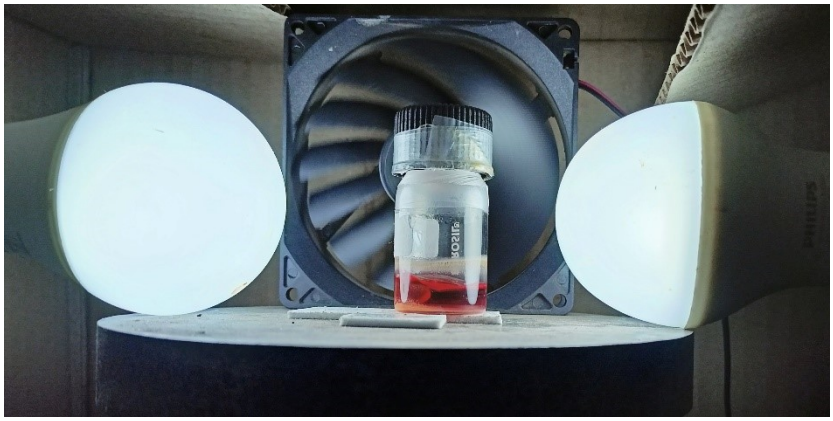


Fig. S1 Photochemical Reaction Set-up.

3. Crystallographic Information:

Crystallographic information of *N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide* (1a):

(i) Sample Preparation: The single crystal of compound **1a** was prepared by the slow evaporation method for which 25 mg of the compound (**1a**) was dissolved in 1 mL of DCM in a clean and dry 10 mL glass vial. MeOH (0.5 mL) was added to this solution slowly with a dropper. The mouth of the glass vial was covered with a cap having a small hole and kept for slow evaporation at room temperature. Crystals of **1a** were obtained after approximately 3-4 days as a transparent block-shaped crystal.

(ii) Data Collection: Diffraction data were collected at 292 K with MoKα radiation (λ = 0.71073 Ǻ) using a Bruker Nonius SMART APEX CCD diffractometer equipped with graphite monochromator and Apex CD camera. The SMART software was used for data collection and for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT[1,2] software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-973 software. All the non-H atoms were refined in the anisotropic approximation against F2 of all reflections.[3]

(iii) Crystallographic description of *N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1a):

$C_{14}H_{13}NO_2S$, colourless block shaped crystal; crystal dimensions 0.06 x 0.05 x 0.05 mm, M_r = 259.312, Triclinic space group P -1; a = 5.8219 (4) Å, b = 8.6182 (5) Å, c = 13.5458 (8) Å, α = 81.096 (2) °, β = 88.255 (2)°, γ = 73.391 (2)°, V = 643.38 (7) Å^3, Z = 2, ρ_{calcd} = 1.339 g/cm^3, μ = 0.244 mm^{-1}, F(000)= 272.0, reflection collected / unique = 3160 / 2525, refinement method

= full-matrix least-squares on F^2, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0552, wR_2 = 0.1069, R indices (all data): R_1 = 0.0769, wR_2 = 0.1180, goodness of fit = 1.139. **CCDC**-2302382 for *N*-(methyl(oxo)(phenyl)-λ^6-sulfaneylidene)benzamide (**1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

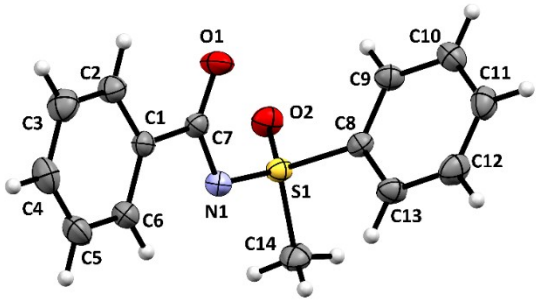


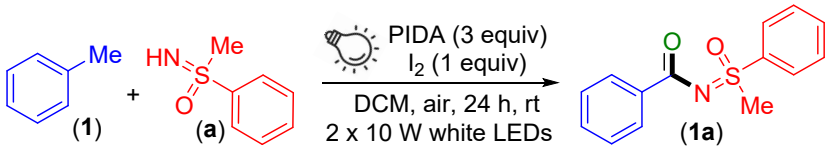
Fig. S2 ORTEP diagram of ***N*-(methyl(oxo)(phenyl)-λ^6-sulfaneylidene)benzamide** (**1a**) with 30% ellipsoid probability (CCDC 2302382).

4. Optimization of Reaction Conditions

Inspired by this, extensive optimization studies involving the selection of different reaction conditions were carried out. Initially, different oxidant systems such as only PIDA, only I_2, and *N*-iodosuccinimide (NIS), were screened. However, in all three cases the anticipated product, **1a** was not formed at all (Table S1, entries 2-4). Further, a trace amount of product was obtained when a 3:1 combination of NIS: I_2 was used (Table S1, entry 5). Next, to optimize the loading of PIDA and I_2, reactions were performed with different concentrations of PIDA: I_2 (Table S1, entries 6-7). Decreasing the loading of PIDA to 1 equiv and 2 equiv was detrimental for the reaction whereas increasing it to 5 equiv had no major impact on the reaction (Table S1, entry 6). Further, changing the concentration of I_2 to 0.5 equiv lowered the product yield whereas increasing it to 2 equiv made no significant difference in the product formation (Table S1, entry 7). Thus, all further reactions were conducted with the original condition using PIDA: I_2 in a ratio of 3:1. Next, to check the effect of solvent in the given transformation, different solvents such as DCE, CH_3CN, DMSO, DMF, EtOH, and 1,2-dioxane were screened. However, except for DCE (71%) and CH_3CN (54%), the reaction did not proceed at all for other solvents (Table S1, entries 8-9). To check the effect of wavelength and intensity of light, the standard reaction was carried out in 4 x 5 W blue (448 nm) and green (534 nm) LEDs. Both the lights failed to improve the reaction yield (Table S1, entries 10 and 11). Hence, the optimized condition for this reaction is the use of *NH*-sulfoximine (1 equiv), toluene (5 equiv), PIDA (3 equiv), I_2 (1

equiv) in DCM (3 mL) in open air at room temperature under 2 x 10 W white LEDs (46 mW/cm^2).

Table S1. Optimization of the Reaction Conditions[a,b]



entry	variation from optimal conditions[a]	yield (%)[b]
1.	None	86
2.	Only PIDA (3 equiv)	N.D.
3.	Only I_2 (1 equiv)	N.D.
4.	NIS (1 equiv)	N.D.
5.	NIS and I_2 (3:1)	trace
6.	PIDA (1 equiv), (2 equiv), (5 equiv)	42, 67, 87
7.	I_2 (0.5 equiv), (2 equiv)	61, 85
8.	CH_3CN, DCE instead of DCM	54, 71
9.	DMSO, THF, EtOH, 1,2-dioxane instead of DCM	N.D.
10.	4 x 5 W blue LEDs	78
11.	4 x 5 W green LEDs	37

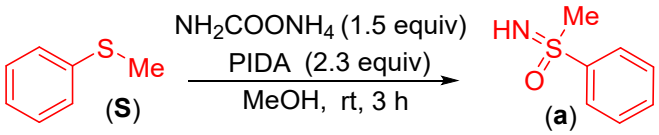
[a]Reaction condition: **a** (0.4 mmol), **1** (2.0 mmol), PIDA (1.2 mmol), I_2 (0.4 mmol) in DCM (3 mL) in open air for 24 h in 2 x 10 W white LED's. [b]Isolated pure product. N.D. = not detected.

5. General Procedures:

5A. Procedure for the Synthesis of NH-Sulfoximine (a)[4]

All the substrates were prepared according to the previously reported literature procedure.[4] In an oven-dried 50 mL round bottom flask, methylphenylsulfide **S** (5 mmol, 1 equiv, 620 mg), ammonium carbamate (7.5 mmol, 1.5 equiv, 585 mg) and phenyliodo diacetate (PIDA) (11.5 mmol, 2.3 equiv, 3.7 g) in 15 mL methanol were taken and stirred at room temperature for 3 hours. After the disappearance of the sulfides, as indicated by TLC, the

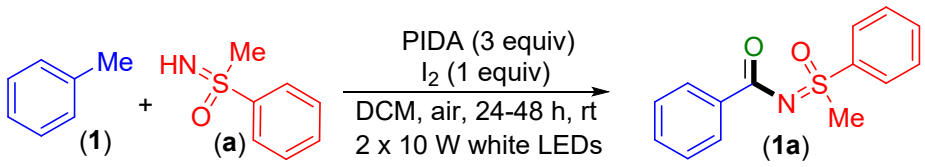
reaction was stopped and the solvent was evaporated under reduced pressure. The compound was purified by column chromatography and separated in 1:2 ratio of EtOAc:hexane to result in the product *S*-phenyl-*S*-methyl-sulfoximine (**a**) in 690 mg, 89% yield (Scheme S1).



Scheme S1 Preparation of *NH*-sulfoximines (**a**).

5B. Procedure for the Synthesis of *N*-Acylsulfoximine (1a)

NH-sulfoximine (**a**) (0.4 mmol, 1 equiv, 62 mg), toluene (**1**) (2 mmol, 5 equiv, 184 mg), and phenyliododiacetate (PIDA) (1.2 mmol, 3 equiv, 386 mg), molecular iodine I_2 (0.4 mmol, 1 equiv, 102 mg) in 3 mL of DCM were added to an oven-dried 10 mL borosilicate vial and stirred in open air at room temperature, approximately at a distance of ~3−5 cm from two 10 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was added ethyl acetate (25 mL) and washed with 5% aqueous $Na_2S_2O_3$ (1 x 10 mL) solution followed by saturated brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, and then the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using (1:4) mixture of ethyl acetate in hexane to afford the *N*-acyl sulfoximine (**1a**) in 82% yield. The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S2).

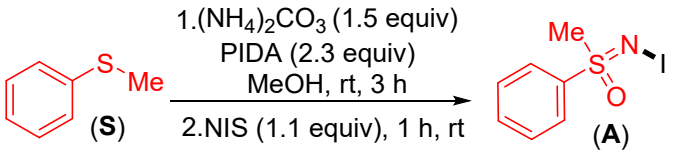


Scheme S2 Preparation of *N*-acyl sulfoximines (**1a**).

5C. Procedure for the Synthesis of Intermediate A.[5]

Intermediate **A** was prepared according to the previously reported literature procedure.[5] In an oven-dried 10 mL round bottom flask, methylphenylsulfide **S** (1 mmol, 1equiv, 124 mg), ammonium carbonate (1.5 mmol, 1.5 equiv, 117 mg) and phenyliodo diacetate (PIDA) (2.3 mmol, 2.3 equiv, 741 mg) in 5 mL methanol were taken and stirred at room temperature for 1 hour. Then, 1.1 equiv of NIS (1.1 mmol, 248 mg) was added, and the stirring was continued

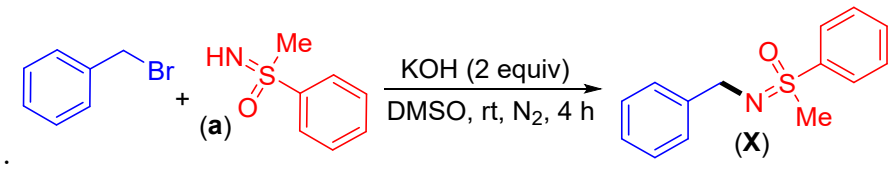
for another 1 hour. After the completion of the reaction as indicated by TLC, the reaction was stopped and the precipitate was collected by vacuum filtration using a Büchner funnel, washed with a small amount of MeOH, and dried under reduced pressure (vacuum pump) to obtain pure product *N*-iodo-*S*-phenyl-*S*-methyl sulfoximine **A** in 83% yield (233 mg). The identity and purity of the product was confirmed by spectroscopic analysis and literature reports (Scheme S3).



Scheme S3 Preparation of *N*-iodo-*S*-phenyl-*S*-methyl sulfoximine (**A**).

5D. Procedure for the Synthesis of (Benzylimino)(methyl)(phenyl)-λ⁶-sulfanone X.[6]

A 25 mL oven-dried round bottom flask was charged with a magnetic stir- bar, S-phenyl-S-methylsulfoximine **a** (2 mmol, 1 equiv, 310 mg) and KOH (4 mmol, 2 equiv, 224 mg) were added. Maintaining an atmosphere of nitrogen, anhydrous DMSO (4 mL) was added to the reaction mixture followed by a dropwise addition of benzylbromide (3.0 mmol, 1.5 equiv, 513 mg). The resultant reaction mixture was further stirred at room temperature and the progress of the reaction was monitored by TLC. Once all the sulfoximine was consumed, the reaction mixture was added ethyl acetate (25 mL) and washed with saturated brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, and then the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using (4:1) ethyl acetate in hexane to afford the *N*-benzylsulfoximine (**X**) in 87% yield. The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S2).



Scheme S4 Preparation of intermediate **X**.

6. Mechanistic investigations:

(a) Radical-trapping experiment:

NH-sulfoximine (**a**) (0.4 mmol, 1 equiv, 62 mg), toluene (**1**) (2 mmol, 5 equiv, 184 mg), phenyliododiacetate (PIDA) (1.2 mmol, 3 equiv, 386 mg), molecular iodine I_2 (0.4 mmol, 1 equiv, 102 mg), and 1,1-dephenylethylene (0.4 mmol, 1 equiv, 72 mg) in 3 mL of DCM were added to an oven-dried 10 mL borosilicate vial and stirred in aopen air at room temperature, approximately at a distance of ~3−5 cm from two 10 W white LED bulbs. A small aliquot of the reaction mixture was withdrawn at approximately 12 h and diluted with acetonitrile (1 mL) and subjected to HRMS. The HRMS analysis of this reaction aliquot shows HRMS values corresponding to diphenylethylene-sulfoximine adduct (**a''**). This observation infers the possible involvement of *N*-centered sulfoximine radical in the reaction (Fig. S3).

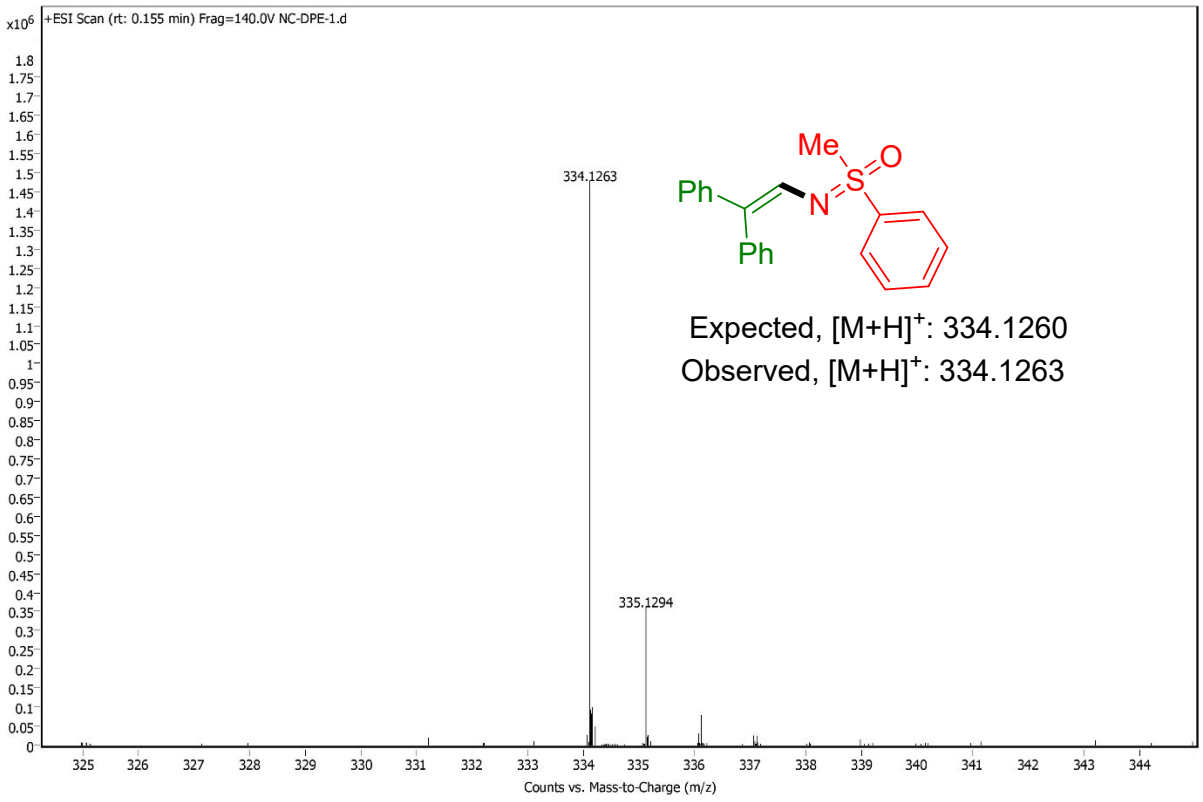
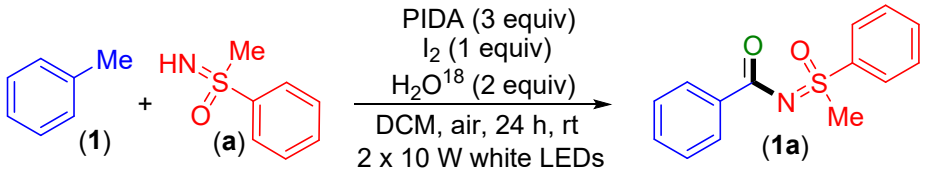


Fig. S3 HRMS analysis of diphenylethylene-sulfoximine adduct (**a''**).

(b) *H_2O^{18}-labelling experiment*

NH-sulfoximine (**a**) (1 mmol, 1 equiv, 155 mg), toluene (**1**) (5 mmol, 5 equiv, 460 mg), phenyliododiacetate (PIDA) (3 mmol, 3 equiv, 966 mg), molecular iodine I_2 (1 mmol, 1 equiv, 254 mg) and H_2O^{18} (2 mmol, 2 equiv, 40 mg) in 4 mL of DCM were added to an oven-dried 10 mL borosilicate vial and stirred in open air at room temperature, approximately at a distance

of ~3−5 cm from two 10 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the mixture was admixed with 20 mL ethyl acetate and sequentially washed with 5% aqueous $Na_2S_2O_3$ (1 x 10 mL) and brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (4:1) as eluent to afford *N*-acylsulfoximine (**1a**) in 85% yield. To confirm the origin of the carbonyl oxygen present in the product, the isolated product was subjected to ^{13}C NMR and HRMS analysis. However, in the HRMS, there was only one peak for O^{16} labelled product {$[M + H]^+$ calculated for $C_{14}H_{13}NO_2S$, 260.0740, found 260.0741} and no peak was found for O^{18} labelled product . Similarly, the single peak at 174.5 in the ^{13}C NMR analysis suggested no presence of O^{18} in the product. Both these observations rule out the involvement of moisture as the source of carbonyl oxygen.



Scheme S5 H_2O^{18} labelling experiment.

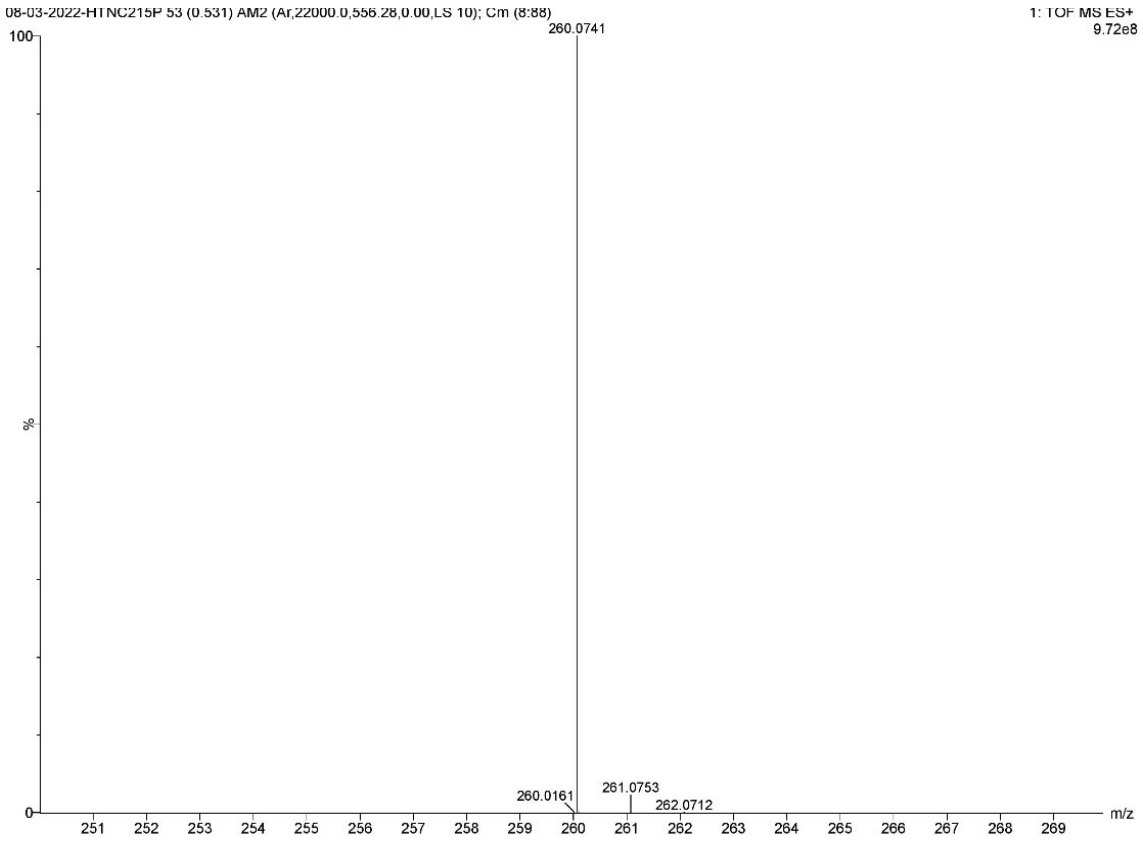


Fig. S4 HRMS of *N*-acylsulfoximines (**1a**).

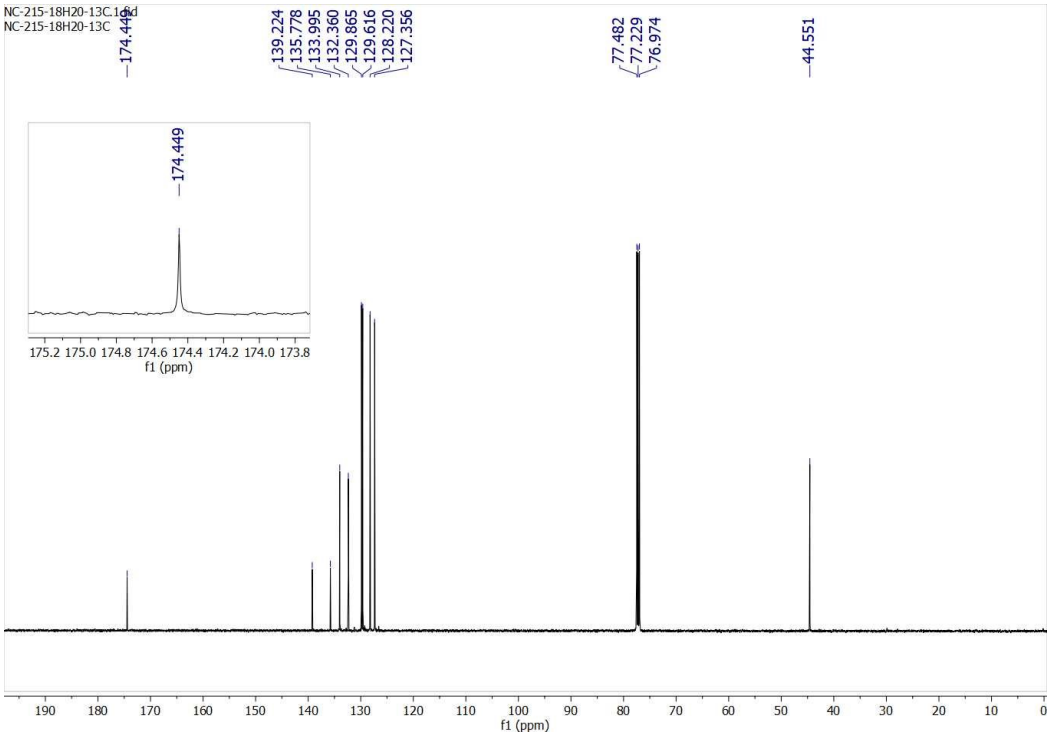
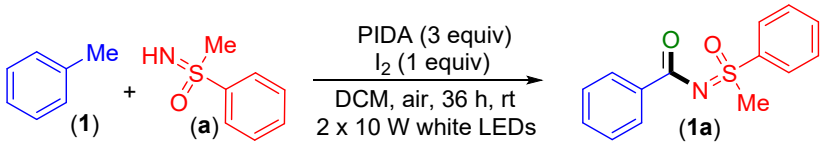


Fig. S5 ^{13}C NMR of *N*-acylsulfoximines (**1a**).

7. Scale-up Reaction Procedure:

NH-sulfoximine (**a**) (5 mmol, 1 equiv, 775 mg), toluene (**1**) (25 mmol, 5 equiv, 2.3 g), phenyliododiacetate (PIDA) (15 mmol, 3 equiv, 4.98 g), and molecular iodine I_2 (5 mmol, 1 equiv, 1.27 g) in 15 mL of DCM were added to an oven-dried 25 mL borosilicate vial and stirred in open air at room temperature, approximately at a distance of ~3−5 cm from two 10 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was added ethyl acetate (50 mL) and washed with 5% aqueous $Na_2S_2O_3$ (1 x 25 mL) solution followed by saturated brine solution (1 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4, and then the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using (4:1) ethyl acetate in hexane to afford the *N*-acylsulfoximine (**1a**) in 63% yield. The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S5).

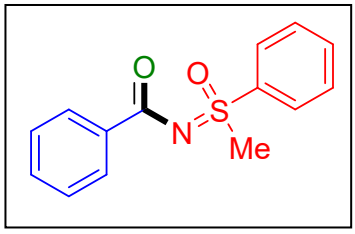


Scheme S6 Scale up reaction condition for the synthesis of *N*-acyl sulfoximines (**1a**).

8. Spectral Data

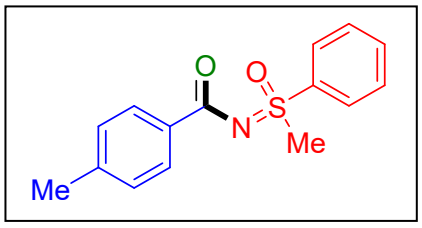
Compounds **13a**, **15a**, **1c**, and **1p** are newly synthesized and their full characterization data (^{1}H NMR, ^{13}C NMR, IR, HRMS and melting point) is provided. The other synthesized compounds are previously reported and hence only ^{1}H and ^{13}C NMR data are provided which are in accordance with the previously reported data. The related references are cited herein.

N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1a)[7,8]



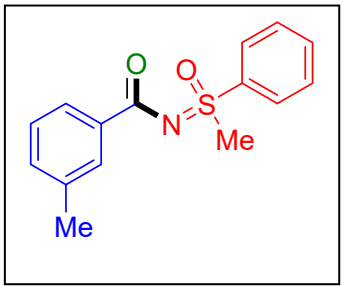
As yellow solid (89 mg, 86% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 7.5 Hz), 8.06 (d, 2H, J = 8.0 Hz), 7.69 (t, 1H, J = 7.5 Hz), 7.62 (t, 2H, J = 7.5 Hz), 7.51 (t, 1H, J = 7.3 Hz), 7.41 (t, 2H, J = 7.5 Hz), 3.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.5, 139.3, 135.8, 134.0, 132.4, 129.9, 129.6, 128.2, 127.4, 44.6.

4-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (2a)[7,8]



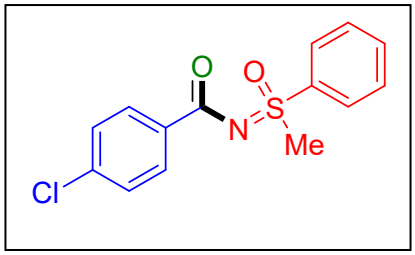
As dark brown solid (90 mg, 82% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.06 (d, 4H, J = 6.5 Hz), 7.68 (t, 1H, J = 7.5 Hz), 7.61 (t, 2H, J = 7.8 Hz), 7.21 (d, 2H, J = 8.0 Hz), 3.46 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.5, 142.9, 139.4, 133.9, 133.1, 129.9, 129.7, 129.0, 127.4, 44.6, 21.8.

3-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (3a) [7,8]



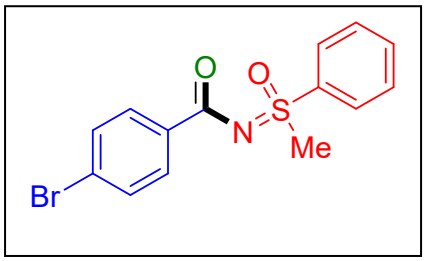
As light brown solid (86 mg, 79% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.06 (d, 2H, J = 7.5 Hz), 7.97 (d, 2H, J = 8.5 Hz), 7.69 (t, 1H, J = 7.3 Hz,), 7.62 (t, 2H, J = 7.8 Hz), 7.33–7.29 (m, 2H), 3.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.7, 139.3, 137.9, 135.7, 134.0, 133.2, 130.2, 129.9, 128.2, 127.4, 126.8, 44.6, 21.5.

4-Chloro-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (4a)[7,8]



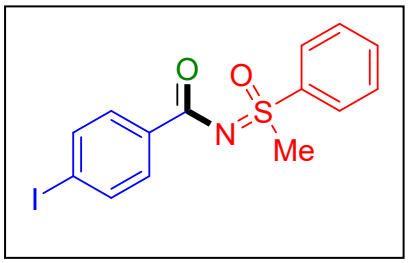
As brown solid (98 mg, 84% yield); purified over a column of silica gel (27% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.10 (d, 2H, J = 8.5 Hz), 8.04 (d, 2H, J = 7.5 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.62 (t, 2H, J = 7.8 Hz), 7.38 (d, 2H, J = 8.5 Hz), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.5, 139.0, 138.7, 134.3, 134.1, 131.1, 129.9, 128.5, 127.3, 44.6.

4-Bromo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (5a)[7,8]



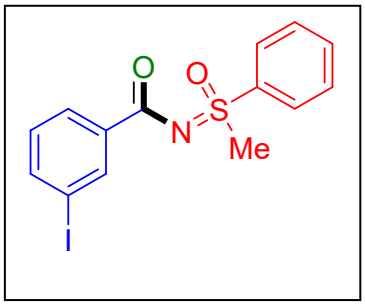
As yellow solid (109 mg, 81% yield); purified over a column of silica gel (27% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03 (t, 4H, J = 8.8 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.62 (t, 2H, J = 7.5 Hz), 7.54 (d, 2H, J = 8.5 Hz), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.6, 139.0, 134.7, 134.1, 131.5, 131.3, 129.9, 127.4, 127.3, 44.6.

4-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (6a)[7,8]



As pale yellow solid (115 mg, 75% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04 (d, 2H, J = 7.5 Hz), 7.87 (d, 2H, J = 8.5 Hz), 7.76 (d, 2H, J = 8.5 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.62 (t, 2H J = 7.8 Hz), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 173.8, 139.0, 137.5, 135.3, 134.1, 131.3, 129.9, 127.3, 100.0, 44.6.

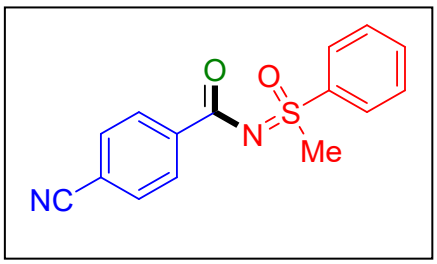
3-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (7a)[9]



As brown solid (111 mg, 72% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.51 (s, 1H), 8.11 (d, 1H, J = 7.5 Hz), 8.04 (d, 2H, J = 8.5 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.70 (t, 1H, J = 7.0 Hz), 7.63 (t, 2H, J = 7.5 Hz), 7.15 (t, 1H, J = 7.8 Hz), 3.46 (s, 3H); ^{13}C

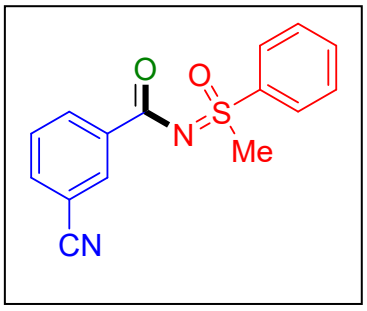
NMR (125 MHz, $CDCl_3$): δ (ppm) 172.8, 141.1, 139.0, 138.7, 137.8, 134.1, 130.0, 129.9, 128.8, 127.4, 93.9, 44.6.

4-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (8a)[7,9]



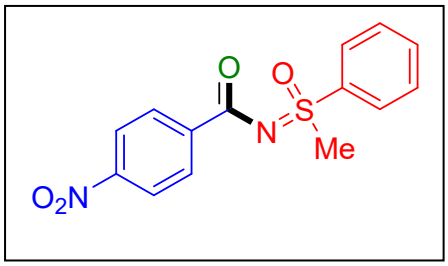
As brown gummy (88 mg, 78% yield);); purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.24 (d, 2H, J = 8.0 Hz), 8.04 (d, 2H, J = 7.5 Hz), 7.73–7.69 (m, 3H), 7.64 (t, 2H, J = 7.8 Hz), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 172.6, 139.7, 138.7, 134.3, 132.1, 130.1, 130.0, 127.3, 118.7, 115.6, 44.6.

3-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (9a)[7]



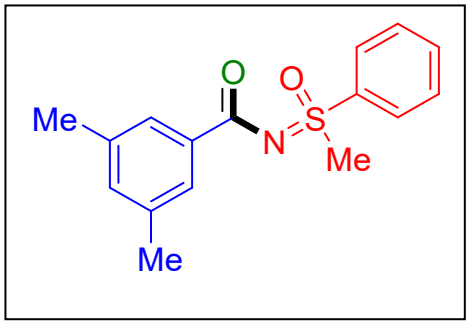
As brown gummy (83 mg, 73% yield); purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.47 (s, 1H), 8.36 (d, 1H, J = 8.0 Hz), 8.05 (d, 2H, J = 8.0 Hz), 7.78 (d, 1H, J = 7.5 Hz), 7.72 (t, 1H, J = 7.5 Hz), 7.65 (t, 2H, J = 7.8 Hz), 7.53 (t, 1H, J = 7.8 Hz), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 172.1, 138.7, 137.1, 135.3, 134.4, 133.7, 133.5, 130.1, 129.3, 127.3, 118.6, 112.6, 44.6.

N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-nitrobenzamide (10a)[7,8]



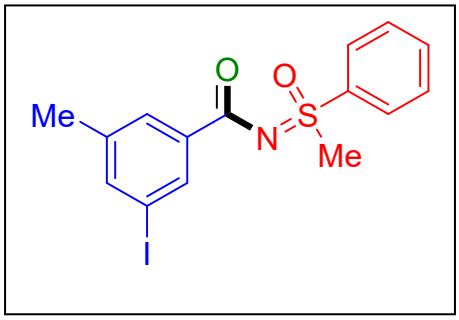
As dark brown solid (83 mg, 68% yield); purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (d, 2H J = 9.2 Hz), 8.24 (d, 2H, J = 8.8 Hz), 8.05 (d, 2H, J = 7.6 Hz), 7.73 (t, 1H, J = 7.4 Hz), 7.65 (t, 2H, J = 7.6 Hz), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 172.3, 150.2, 141.2, 138.5, 134.4, 130.6, 130.1, 127.3, 123.4, 44.5.

3,5-Dimethyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (11a)[7]



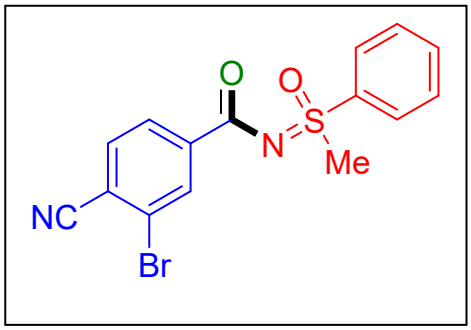
As pale yellow solid (77 mg, 67% yield); purified over a column of silica gel (22% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05 (d, 2H, J = 7.5 Hz), 7.78 (s, 2H), 7.68 (t, 1H, J = 7.5 Hz), 7.61 (t, 2H, J = 7.5 Hz), 7.15 (s, 1H), 3.46 (s, 3H), 2.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.9, 139.4, 137.8, 135.7, 134.1, 133.9, 129.9, 128.1, 127.4, 44.6, 21.4.

3-Iodo-5-methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (12a)[8]

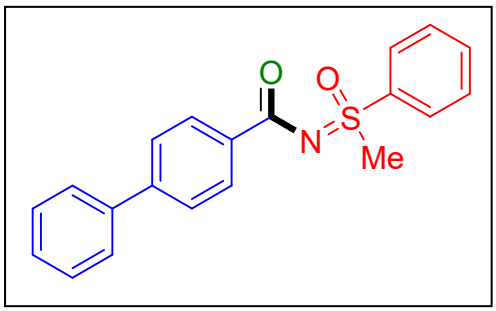


As orange solid (105 mg, 66% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 8.03 (d, 2H, J = 8.0 Hz), 7.90 (s, 1H), 7.71–7.67 (m, 2H), 7.62 (t, 2H, J = 7.8 Hz), 3.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 173.0, 141.7, 140.2, 138.9, 137.5, 135.7, 134.1, 129.9, 129.5, 127.3, 93.9, 44.6, 21.1.

3-Bromo-4-cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (13a)

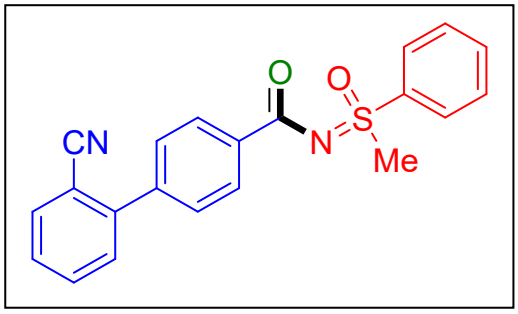


As brown solid (91 mg, 63% yield); m.p. 119–121 °C; purified over a column of silica gel (28% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 8.16 (dd, 1H, J_1 = 8.0, J_2 = 1.5 Hz,), 8.03 (d, 2H, J = 7.6 Hz), 7.73–7.63 (m, 4H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 171.2, 140.9, 138.4, 134.5, 134.2, 134.0, 130.1, 128.4, 127.3, 125.3, 118.7, 117.1, 44.6; IR (neat, cm^{-1}): 3101, 2915, 2850, 2233, 1732, 1623, 1549, 1445, 1379, 1285, 1213, 1089; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}BrN_2O_2S$ 362.9797; Found 362.9799.



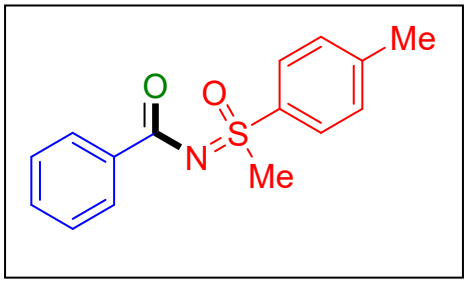
N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (14a)[7]

As pale yellow solid (95 mg, 71% yield); purified over a column of silica gel (22% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.24 (d, 2H, J = 8.4 Hz), 8.08 (d, 2H, J = 7.2 Hz), 7.70 (t, 1H, J = 7.2 Hz), 7.66–7.61 (m, 6H), 7.46 (t, 2H, J = 7.4 Hz), 7.38 (t, 1H, J = 7.2 Hz), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.3, 145.1, 140.6, 139.3, 134.7, 134.0, 130.2, 129.9, 129.1, 128.1, 127.5, 127.4, 127.0, 44.6;



2'-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (15a)

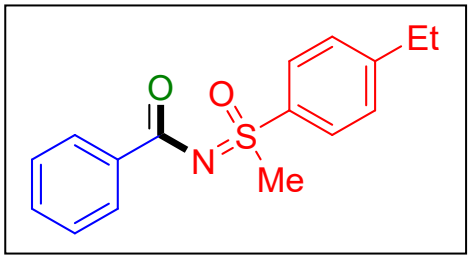
As brown solid (99 mg, 69% yield); m.p. 110–112 ^{o}C; purified over a column of silica gel (28% EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (d, 2H, J = 8.4 Hz), 8.08 (d, 2H, J = 8.0 Hz), 7.79 (d, 1H, J = 7.6 Hz), 7.73–7.65 (m, 3H), 7.64–7.60 (m, 3H), 7.54 (d, 1H, J = 7.2 Hz), 7.48 (t, 1H, J = 7.6 Hz), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 173.9, 144.9, 141.9, 139.0, 136.0, 134.1, 134.0, 133.1, 130.2, 130.1, 129.9, 128.8, 128.2, 127.4, 118.7, 111.5, 44.6; IR (neat, cm^{-1}): 3062, 3013, 2922, 2851, 2223, 1676, 1620, 1445, 1280, 1219, 1147, 1091; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O_2S$, 361.1005; Found 361.1015.



N-(Methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)benzamide (1b)[10]

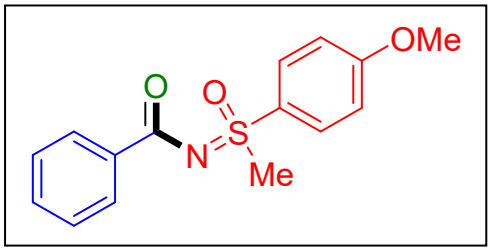
As pale-yellow solid (93 mg, 85% yield); purified over a column of silica gel (25% EtOAc in hexane) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 6.5 Hz), 7.93 (d, 2H J = 8.0 Hz), 7.50 (t, 1H, J = 7.5 Hz), 7.40 (t, 4H, J = 7.5 Hz), 3.45 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 145.1, 136.3, 136.0, 132.3, 130.5, 129.6, 128.2, 127.4, 44.7, 21.8.

N-((4-Ethylphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1c)



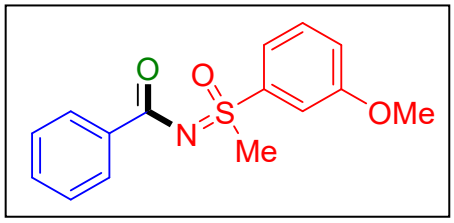
As brown solid (100 mg, 87% yield); m.p. 84–86 °C; purified over a column of silica gel (25% EtOAc in hexane) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 8.0 Hz), 7.96 (d, 2H, J = 8.0 Hz), 7.50 (t, 1H, J = 7.3 Hz), 7.43–7.39 (m, 4H), 3.46 (s, 3H), 2.75 (q, 2H, J = 7.6 Hz), 1.28 (t, 3H, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.5, 151.2, 136.3, 135.9, 132.3, 129.6, 129.4, 128.2, 127.5, 44.7, 29.1, 15.3; IR (neat, cm^{-1}): 3021, 2963, 2927, 1740, 1615, 1574, 1450, 1404, 1318, 1274, 1208, 1135; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2S$, 288.1053; Found 288.1065.

N-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1d)[8]



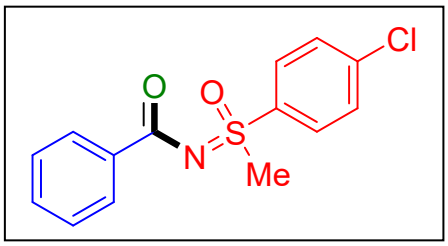
As brown solid (90 mg, 78% yield); purified over a column of silica gel (25% EtOAc in hexane) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 7.5 Hz), 7.98 (d, 2H, J = 9.0 Hz), 7.50 (t, 1H, J = 7.5 Hz), 7.40 (t, 2H, J = 7.5 Hz), 7.06 (d, 2H, J = 8.5 Hz), 3.88 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 164.1, 136.0, 132.2, 130.3, 129.6, 129.5, 128.2, 115.1, 55.9, 44.9.

N-((3-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1e)[13]



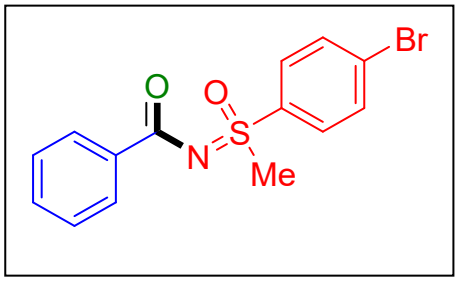
As orange solid (88 mg, 76% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 7.0 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.57 (s, 1H), 7.52–7.49 (m, 2H), 7.41 (t, 2H, J = 7.5 Hz), 7.19 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 3.88 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.5, 160.6, 140.5, 135.8, 132.4, 131.0, 129.6, 128.2, 120.3, 119.3, 112.3, 56.0, 44.6.

N-((4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1f)[8]



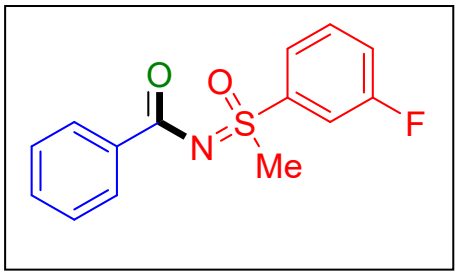
As brown solid (104 mg, 89% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.15 (d, 2H, J = 7.5 Hz), 7.99 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 8.0 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.42 (t, 2H, J = 7.8 Hz), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.4, 140.9, 137.7, 135.5, 132.6, 130.3, 129.7, 128.9, 128.3, 44.6.

N-((4-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1g)[8]



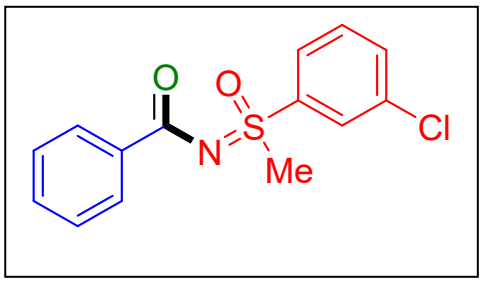
As brown solid (110 mg, 82% yield); purified over a column of silica gel (28% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.14 (d, 2H, J = 7.0 Hz), 7.91 (d, 2H, J = 8.0 Hz), 7.74 (d, 2H, J = 8.5 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.41 (t, 2H, J = 7.5 Hz), 3.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 138.3, 135.5, 133.2, 132.5, 129.6, 129.4, 128.9, 128.3, 44.6.

N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1h)[13]



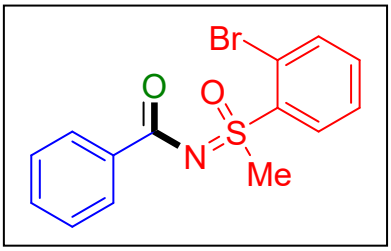
As brown solid (85 mg, 77% yield); purified over a column of silica gel (28% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (d, 2H, J = 6.8 Hz), 7.85 (d, 1H, J = 7.6 Hz), 7.79–7.76 (m, 1H), 7.64–7.58 (m, 1H), 7.52 (t, 1H, J = 7.4 Hz), 7.44–7.36 (m, 3H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.4, 162.9 (d, J = 251.5 Hz), 141.3 (d, J = 6.7 Hz), 135.4, 132.6, 131.8(d, J = 7.8 Hz), 129.7, 128.3, 123.2 (d, J = 3.3 Hz), 121.4 (d, J = 21.2 Hz), 115.0 (d, J = 24.9 Hz), 44.5; ^{19}F (471 MHz, $CDCl_3$): δ (ppm) -108.2.

N-((3-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1i)[10]



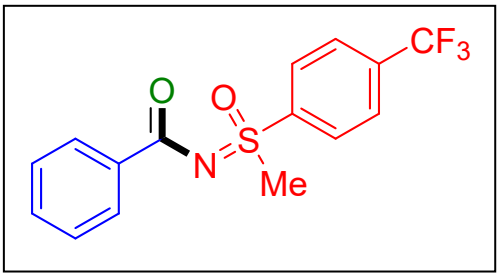
As brown solid (94 mg, 80% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.15 (d, 2H, J = 7.0 Hz), 8.04 (s, 1H), 7.93 (d, 1H, J = 8.0 Hz), 7.65 (d, 1H, J = 9.0 Hz), 7.57–7.51 (m, 2H), 7.42 (t, 2H, J = 7.8 Hz), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 141.1, 136.2, 135.5, 134.2, 132.6, 131.2, 129.7, 128.3, 127.5, 125.5, 44.6.

N-((2-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1j) [10]



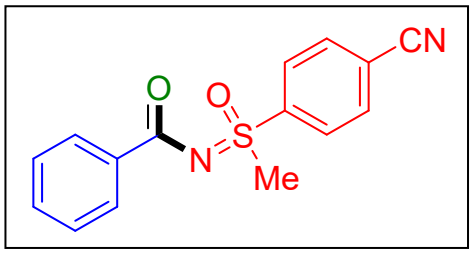
As dark brown solid (92 mg, 68% yield); purified over a column of silica gel (28% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.37 (d, 1H, J = 8.0 Hz), 8.14 (d, 2H, J = 7.5 Hz), 7.77 (d, 1H, J = 7.5 Hz), 7.62 (t, 1H, J = 7.8 Hz), 7.50 (t, 2H, J = 8.0 Hz), 7.39 (t, 2H, J = 7.5Hz), 3.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 173.9, 138.3, 135.9, 135.5, 134.9, 132.4, 132.1, 129.8, 128.7, 128.2, 119.7, 42.2.

N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)benzamide (1k) [11]



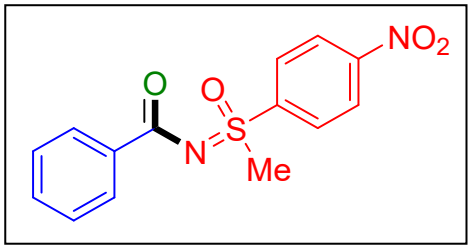
As yellow solid (85 mg, 65% yield); purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.19 (d, 2H, J = 8.5 Hz), 8.15 (d, 2H, J = 7.0 Hz), 7.88 (d, 2H, J = 8.5 Hz), 7.53 (t, 1H, J = 7.5 Hz), 7.42 (t, 2H, J = 7.5 Hz), 3.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.2, 142.9, 135.9, 135.7, 135.4, 135.1, 132.5, 129.5, 128.1, 127.9, 126.9 (q, J = 3.7 Hz), 124.2, 122.0, 44.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -63.2.

N-((4-Cyanophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1l)[11]



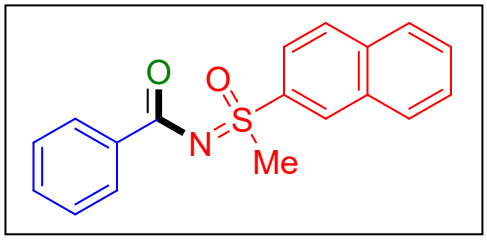
As brown solid (77 mg, 68% yield); purified over a column of silica gel (32% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.15 (d, 2H, J = 9.0 Hz), 8.11 (d, 2H, J = 7.0 Hz), 7.88 (d, 2H, J = 9.0 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.41 (t, 2H, J = 7.8 Hz), 3.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.3, 143.7, 135.0, 133.6, 132.8, 129.6, 128.3, 128.2, 117.7, 117.2, 44.1.

N-(Methyl(4-nitrophenyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1m) [8]



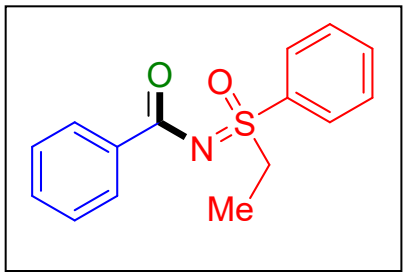
As pale yellow solid (89 mg, 73% yield); purified over a column of silica gel (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.44 (d, 2H, J = 9.0 Hz), 8.24 (d, 2H, J =9.0 Hz), 8.12 (d, 2H, J = 7.0 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.42 (t, 2H, J = 7.8 Hz), 3.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.3, 151.0, 145.3, 135.0, 132.9, 129.7, 128.9, 128.4, 125.1, 44.2.

N-(Methyl(naphthalen-2-yl)(oxo)-λ⁶-sulfaneylidene)benzamide (1n)[10]



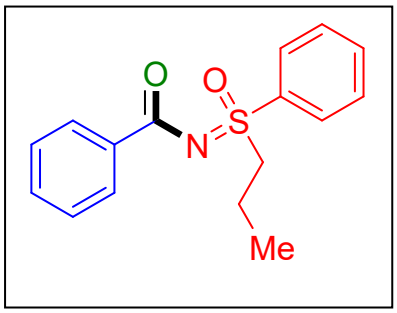
As pale yellow solid (88 mg, 71% yield); purified over a column of silica gel (27% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.66 (s, 1H), 8.20 (d, 2H, J = 7.0 Hz), 8.04 (t, 2H, J = 8.5 Hz), 7.96 (t, 2H, J = 8.3 Hz), 7.71–7.64 (m, 2H), 7.52 (t, 1H, J = 7.5 Hz), 7.43 (t, 2H, J = 7.5 Hz), 3.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.5, 136.0, 135.8, 135.6, 132.6, 132.4, 130.3, 129.7, 129.67, 129.4, 128.3, 128.2, 128.1, 121.8, 44.6.

N-(Ethyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1o)[12]



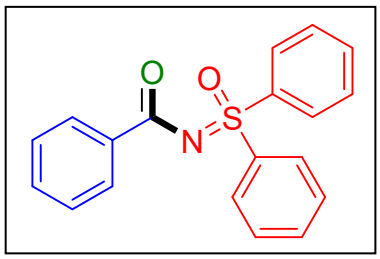
As brown solid (79 mg, 72% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.18 (d, 2H, J = 7.5 Hz), 8.01 (d, 2H, J = 7.5 Hz), 7.68 (t, 1H, J = 7.5 Hz), 7.61 (t, 2H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.5 Hz), 3.62 (q, 2H, J = 7.5 Hz), 1.32 (t, 3H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 136.9, 136.0, 133.9, 132.3, 129.8, 129.7, 128.24, 128.22, 50.9, 7.5.

N-(Oxo(phenyl)(propyl)-λ⁶-sulfaneylidene)benzamide (1p)



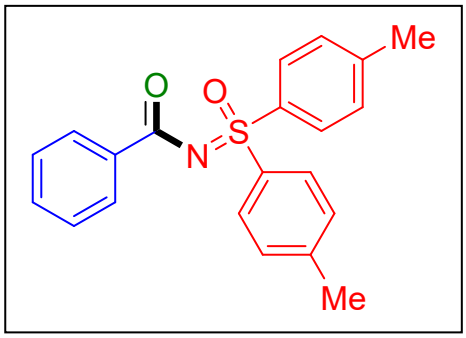
As dark brown solid (79 mg, 69% yield); m.p. 80–82 °C; purified over a column of silica gel (22% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, J = 7.5 Hz), 8.01 (d, 2H, J = 7.5 Hz), 7.67 (t, 1H J = 7.3 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.50 (t, 1H, J = 7.3 Hz), 7.41 (t, 2H, J = 7.8 Hz), 3.62–3.48 (m, 2H), 1.88–1.69 (m, 2H), 1.01 (t, 3H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.4, 137.5, 136.0, 133.9, 132.3, 129.8, 129.6, 128.2, 128.1, 57.9, 16.5, 12.9; IR (neat, cm^{-1}): 3059, 2968, 2930, 2876, 1714, 1620, 1575, 1447, 1313, 1275, 1193, 1132, 1086, 929; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2S$, 288.1053; Found 288.1070.

N-(Oxodiphenyl-λ⁶-sulfaneylidene)benzamide (1q) [9]



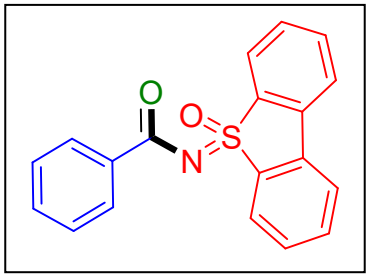
As brown solid (81 mg, 63% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, 2H, J = 6.8 Hz), 8.09–8.06 (m, 4H), 7.59–7.52 (m, 7H), 7.44 (t, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.1, 140.1, 136.0, 133.5, 132.4, 129.75, 129.73, 128.3, 127.8.

N-(Oxodi-p-tolyl-λ⁶-sulfaneylidene)benzamide (1r)[13]



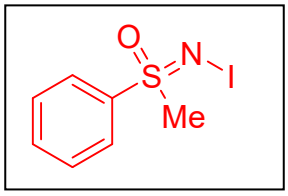
As brown gummy (96 mg, 69% yield); purified over a column of silica gel (18% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.24 (d, 2H, J = 7.5 Hz), 7.93 (d, 4H, J = 8.0 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.31 (d, 4H, J = 8.5 Hz), 2.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 174.1, 144.3, 137.3, 136.2, 132.3, 130.4, 129.7, 128.2, 127.7, 21.7.

N-(5-Oxido-5λ⁴-dibenzo[b,d]thiophen-5-ylidene)benzamide (1s)[10]



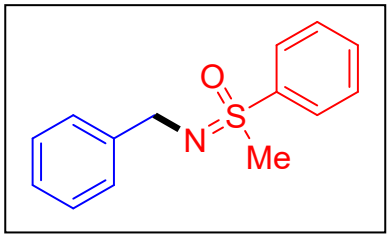
As white solid (82 mg, 64% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (d, 2H, J = 7.6 Hz), 8.13 (d, 2H, J = 6.8 Hz), 7.85 (d, 2H, J = 7.6 Hz), 7.70 (t, 2H, J = 7.6 Hz), 7.59 (t, 2H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.2 Hz), 7.37 (t, 2H, J = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 175.3, 137.4, 135.3, 134.6, 133.3, 132.5, 130.8, 129.8, 128.2, 125.8, 121.9.

***(Iodoimino)(methyl)(phenyl)-λ⁶-sulfanone* (A):**



As white solid (233 mg, 83% yield); ^{1}H NMR (600 MHz, $CDCl_3$); δ (ppm) 7.85 (d, 2H, J = 7.2 Hz), 7.68 (t, 1H, J = 7.8 Hz), 7.60 (t, 2H, J = 7.8 Hz), 3.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 140.1, 133.9, 129.8, 128.5, 42.9.

(Benzylimino)(methyl)(phenyl)-λ⁶-sulfanone (X):



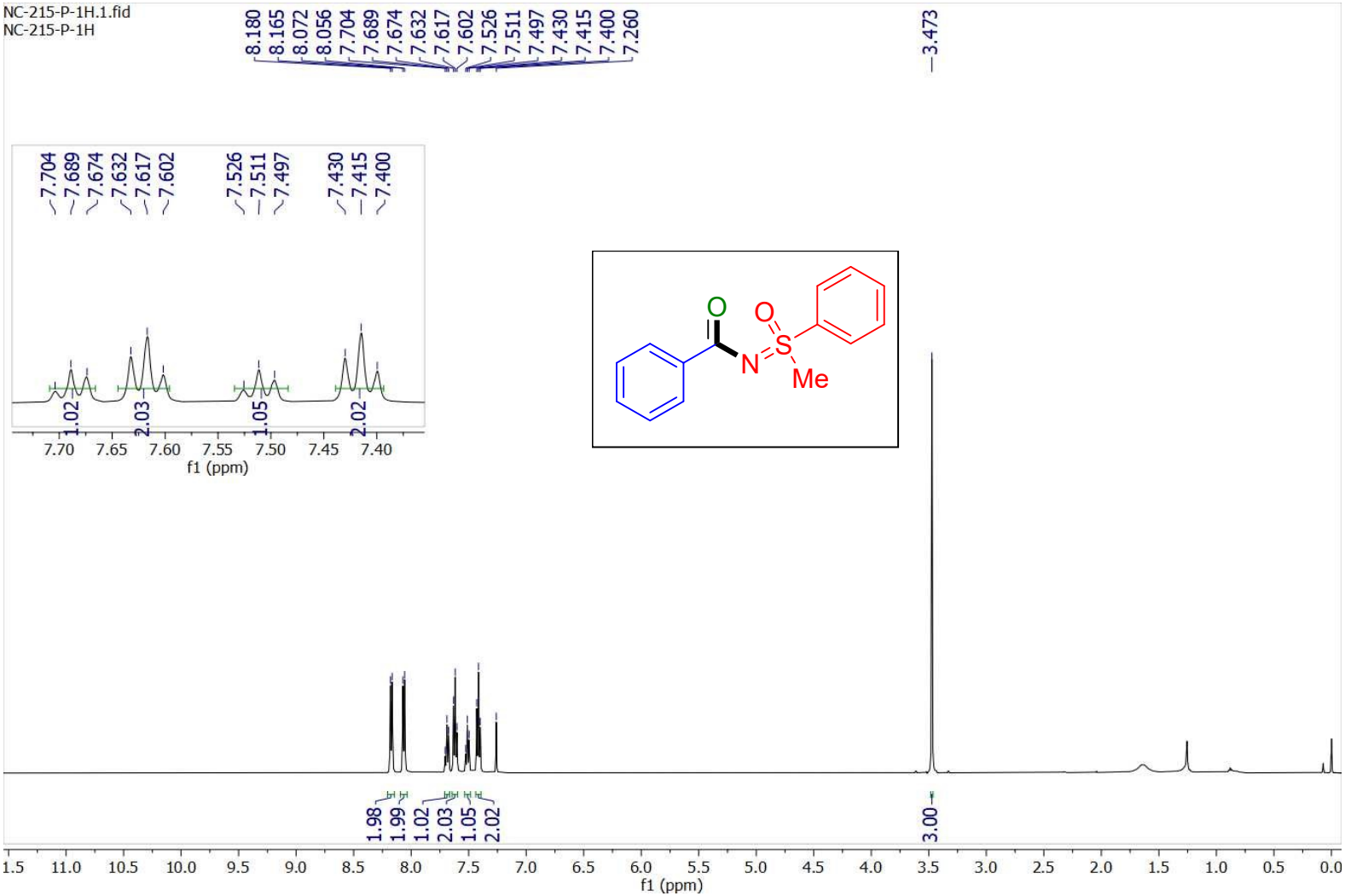
As yellow gummy (426 mg, 87% yield); purified over a column of silica gel (25% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.94 (d, 2H, J = 7.0 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.56 (t, 2H, J = 7.5 Hz), 7.35 (d, 2H, J = 7.5 Hz), 7.29 (t, 2H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.3 Hz), 4.20 (d, 1H, J = 14.0 Hz), 3.98 (d, 1H, J = 14.5 Hz), 3.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.4, 139.7, 133.1, 129.7, 128.9, 128.5, 127.8, 126.8, 47.6, 45.5.

9. References:

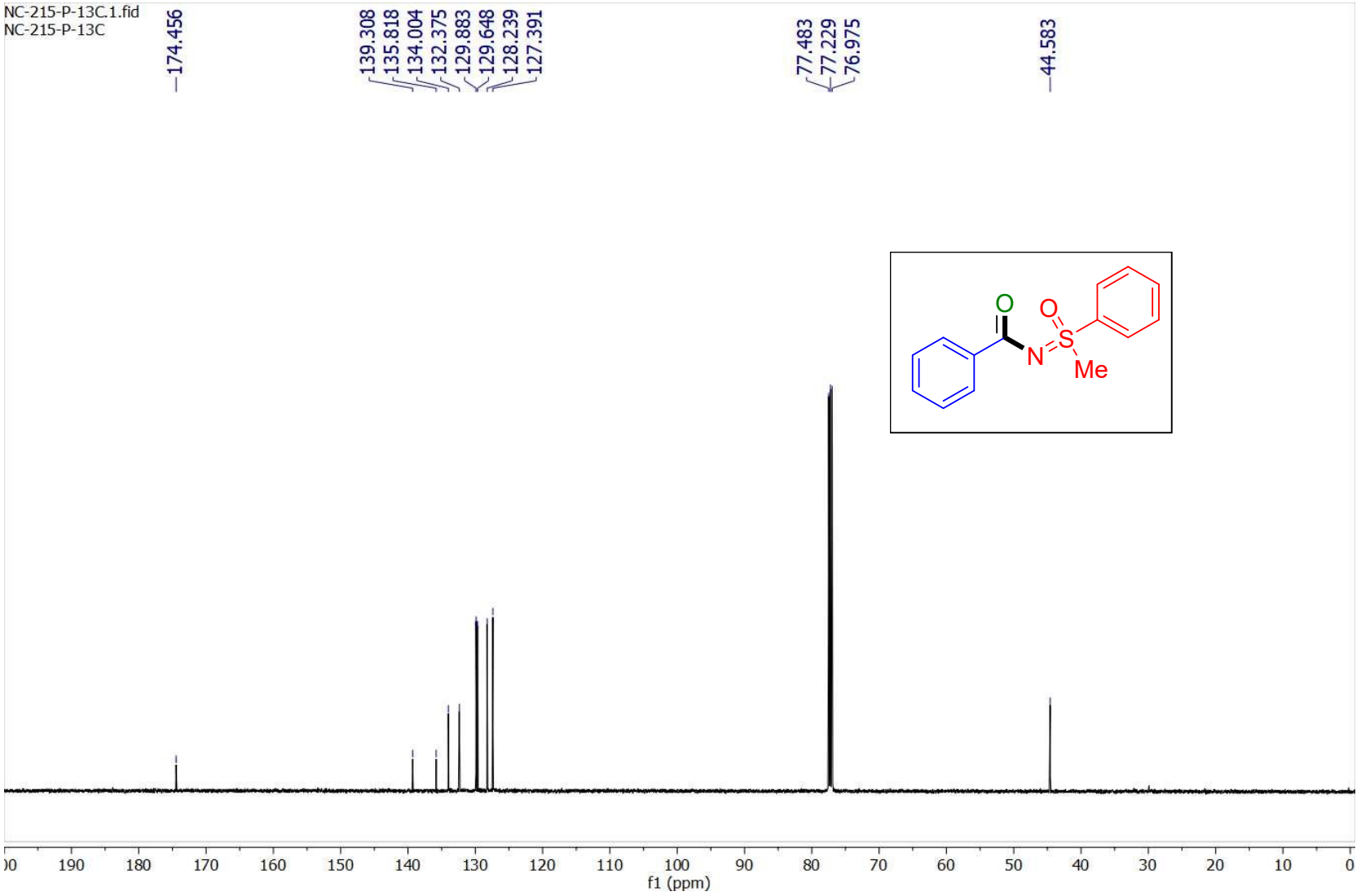
1. G. M. Sheldrick, SADABS, 1996, based on the method described in: R. H. Blessing, Acta Crystallogr. 1995, A51, 33–38.
2. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
3. G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112–122.
4. Chakraborty, N.; Rajbongshi, K. K.; Dahiya, A.; Das, B.; Vaishnani, A.; Patel, B. K. *Chem. Commun.,* **2023**, *59* (19), 2779–2782.
5. Zupanc, A.; Jereb, M. *J. Org. Chem*., **2021**, *86*, 5991−6000.
6. Hendriks, C. M. M.; Bohmann, R. A.; Bohlem, M.; Bolm, C. *Adv. Synth. Catal.*, **2014**, *356*, 1847–1852.
7. Zhao, Z.; Wang, T.; Yuan, L.; Jia, X.; Zhao, J. *RSC Adv.*, **2015**, *5*, 75386–75389.
8. Priebbenow, D. L.; Bolm, C. *Org. Lett.*, **2014**, *16*, 1650–1652
9. Zou, Y.; Xiao, J.; Peng, Z.; Dong, W.; An, D. *Chem. Commun.*, **2015**, *51*, 14889–14892.
10. Tu, Y.; Zhang, D.; Shi, P.; Wang, C.; Ma, D.; Bolm, C. *Org. Biomol. Chem.*, **2021**, *19*, 8096–8101.
11. Guo, S.-R.; Kumar, P. S.; Yuan, Y.-Q.; Yang, M.-H. *Tetrahedron Lett.*, **2017**, *58*, 2681–2684.
12. Sekar, G.; Muneeswara, M.; Kotha, S. *Synthesis*, **2016**, *48*, 1541–1549.
13. Alam, T.; Patel, B. K. *Chem. Eur. J.*, DOI:10.1002/chem.202303444.

10. Spectra of all Compounds

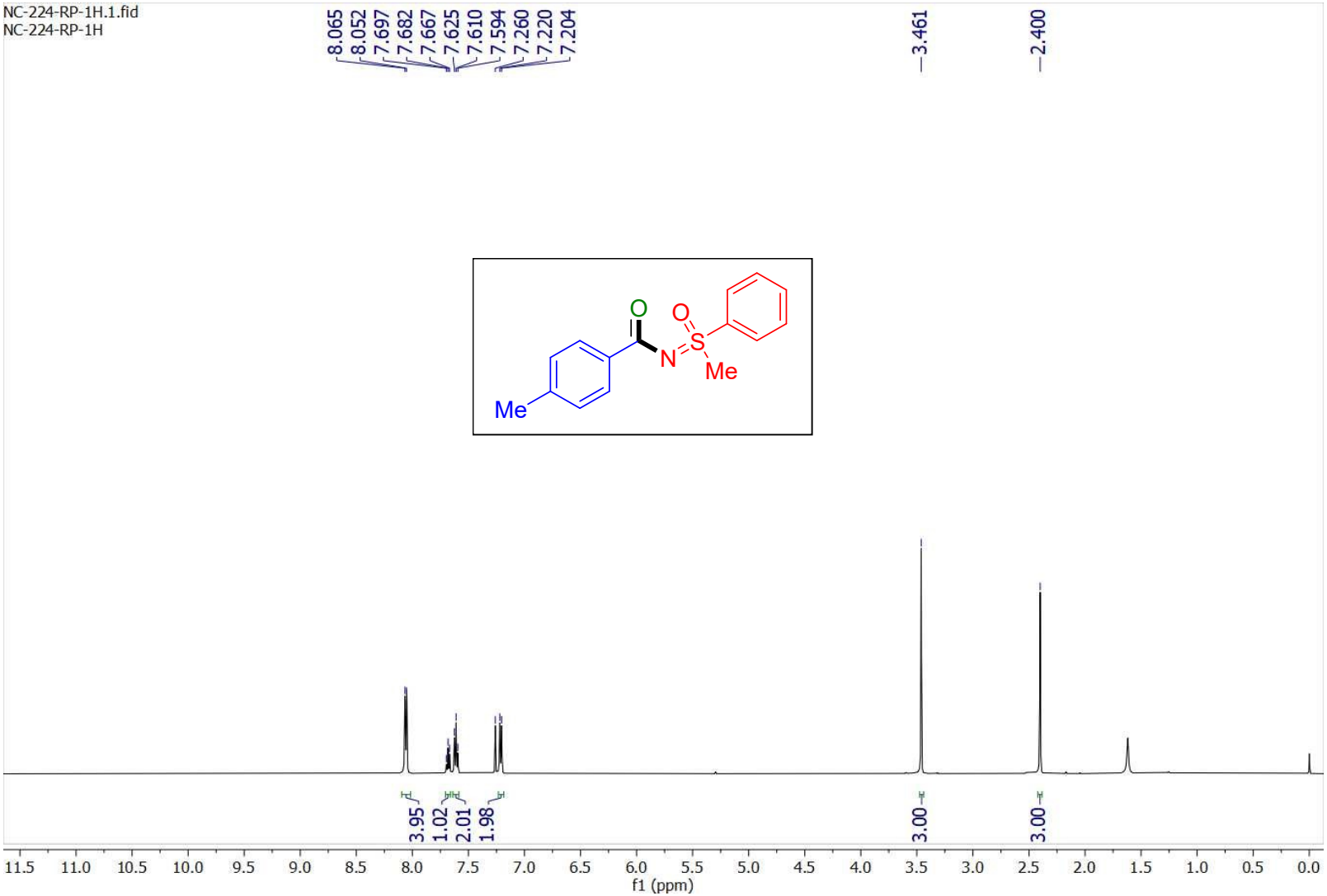
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



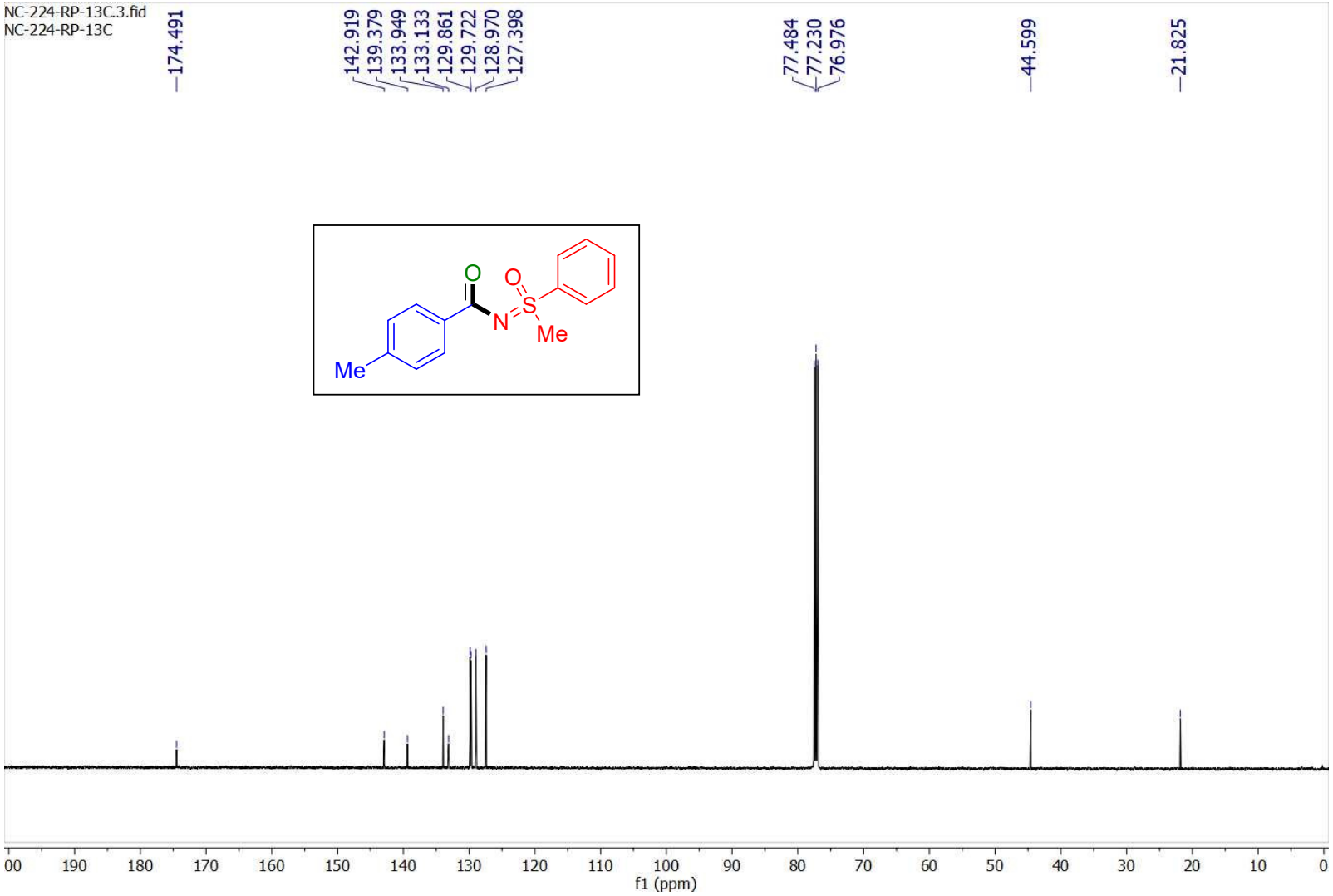
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



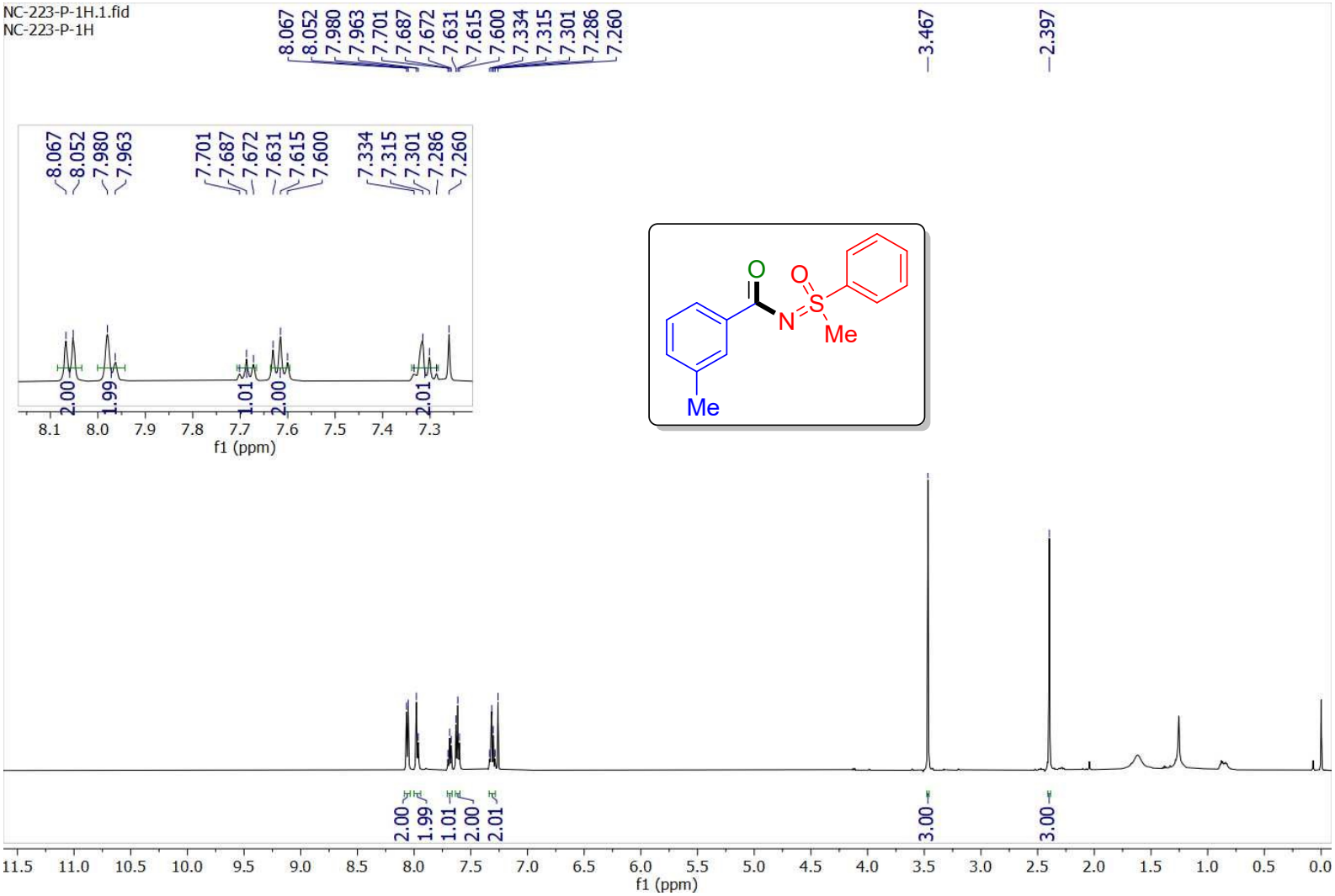
***4-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (2a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



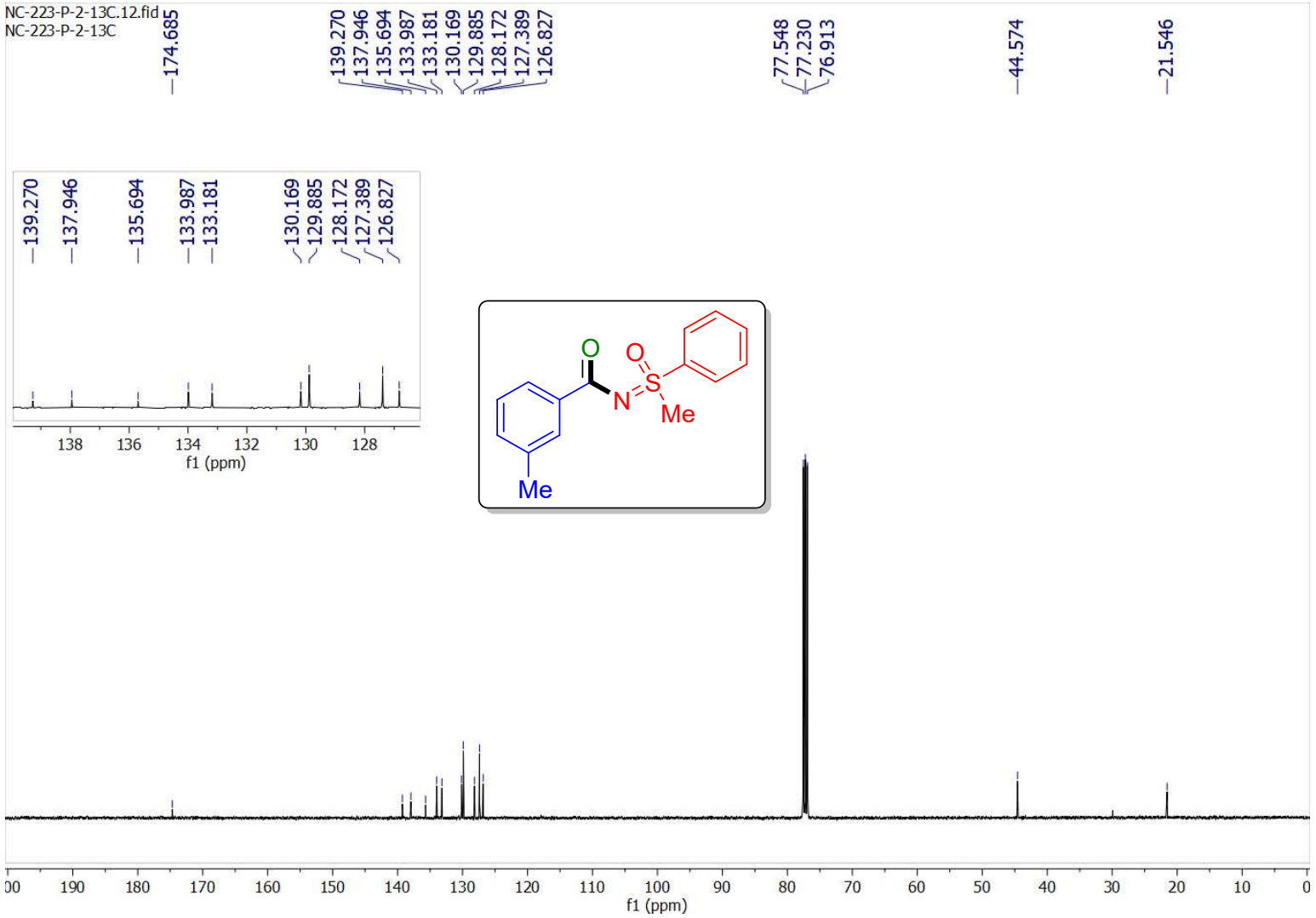
***4-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (2a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



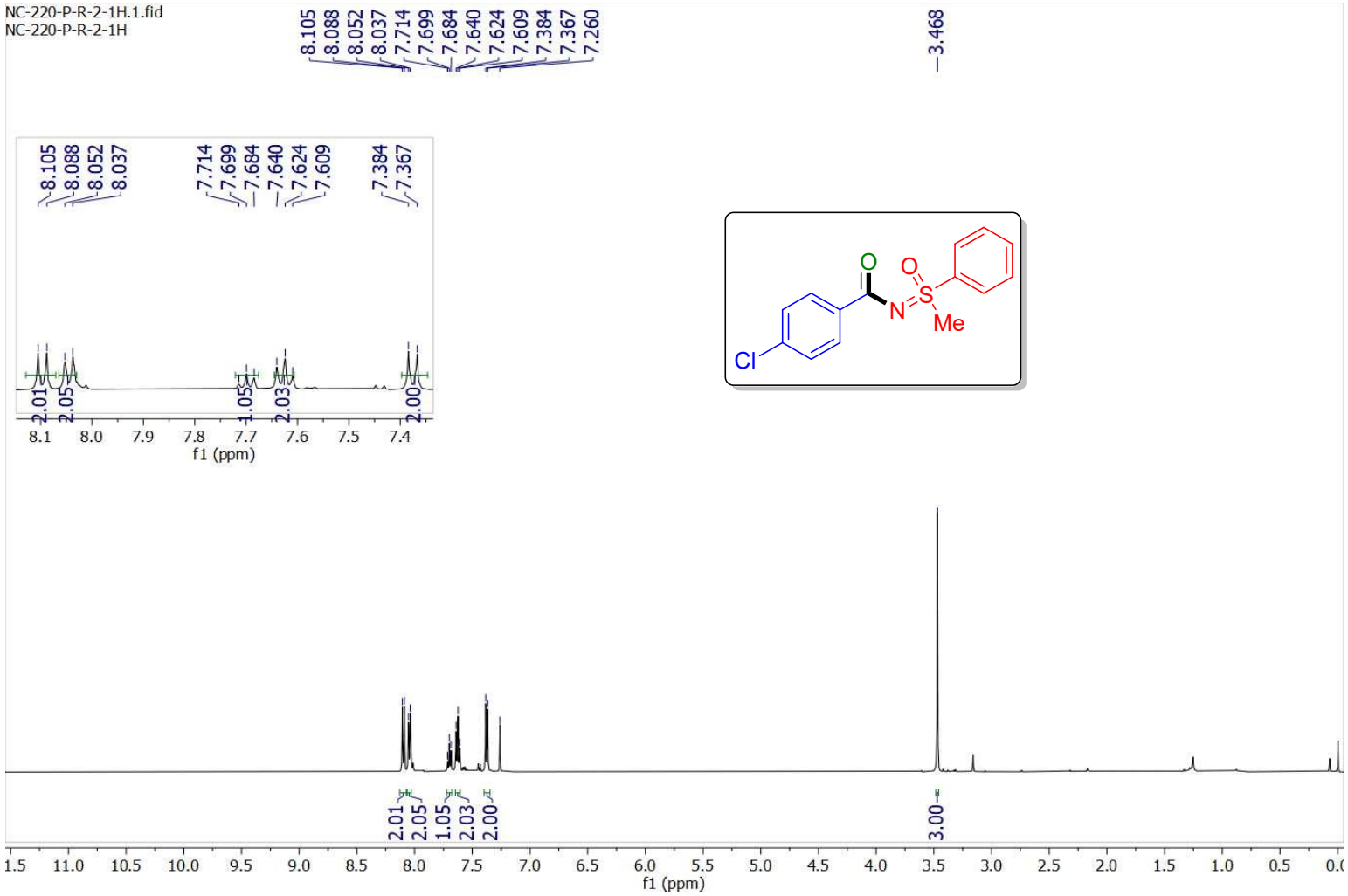
3-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (3a): **^{1}H NMR (500 MHz, $CDCl_3$)**



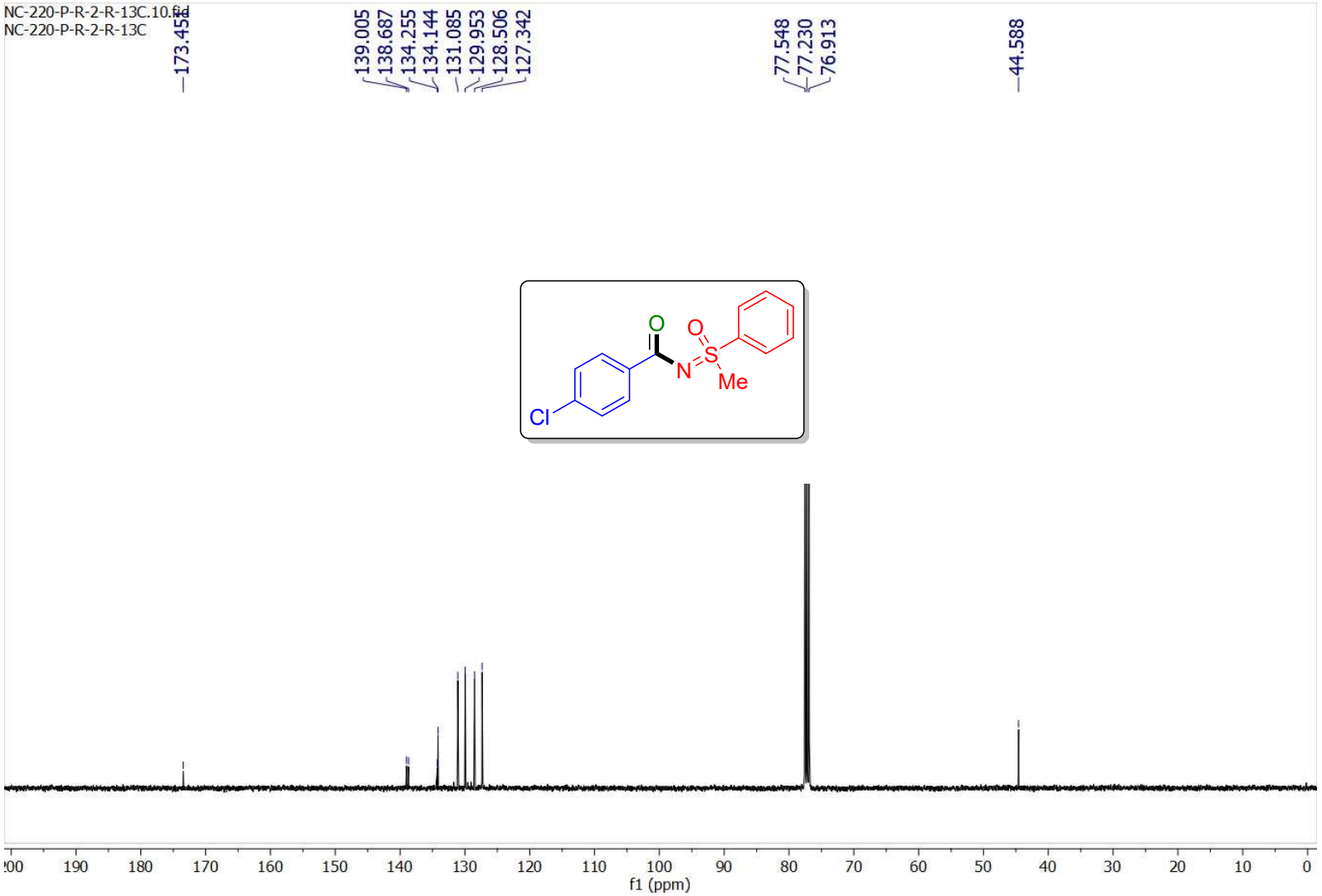
3-Methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (3a): **^{13}C NMR (100 MHz, $CDCl_3$)**



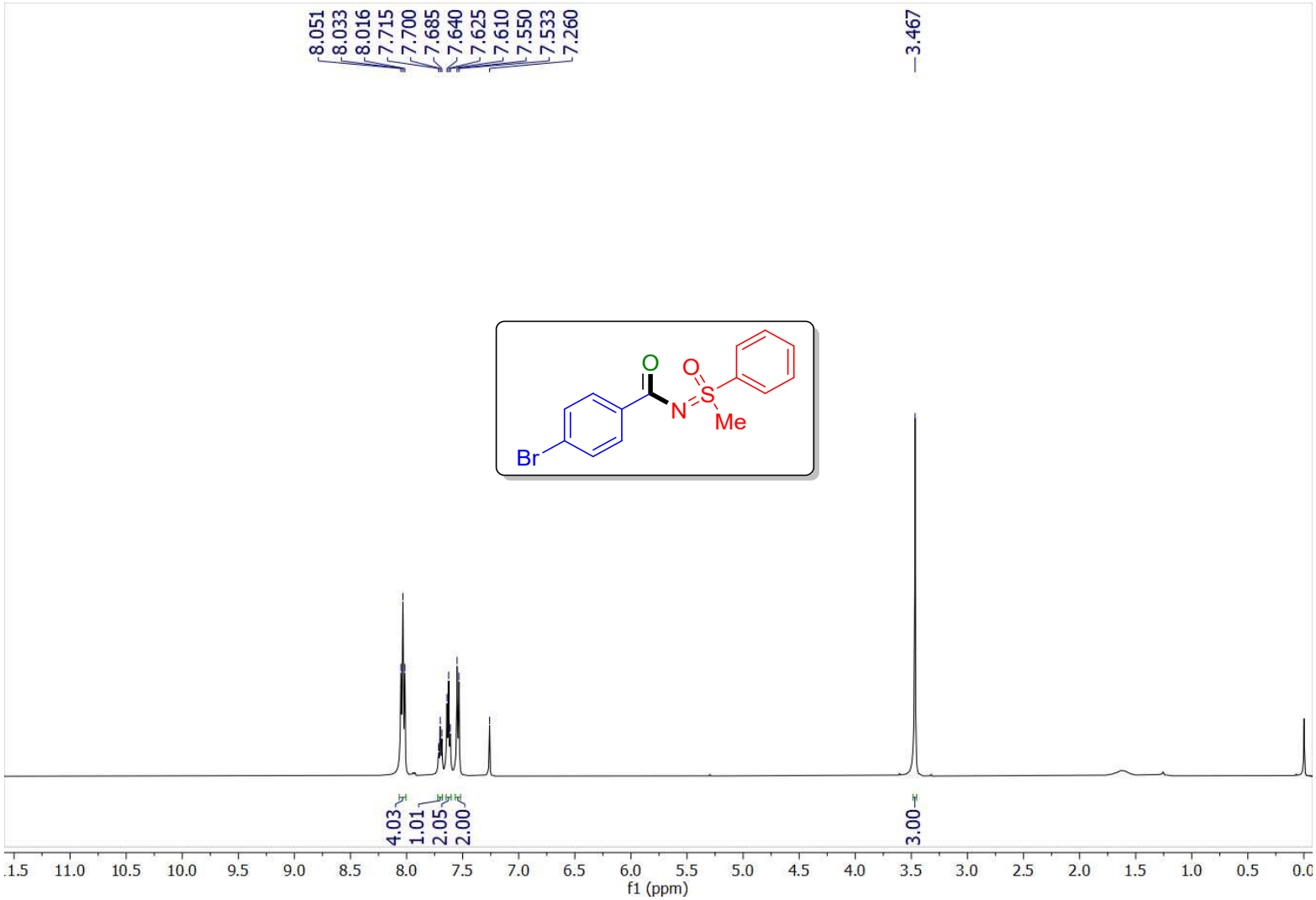
***4-Chloro-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (4a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



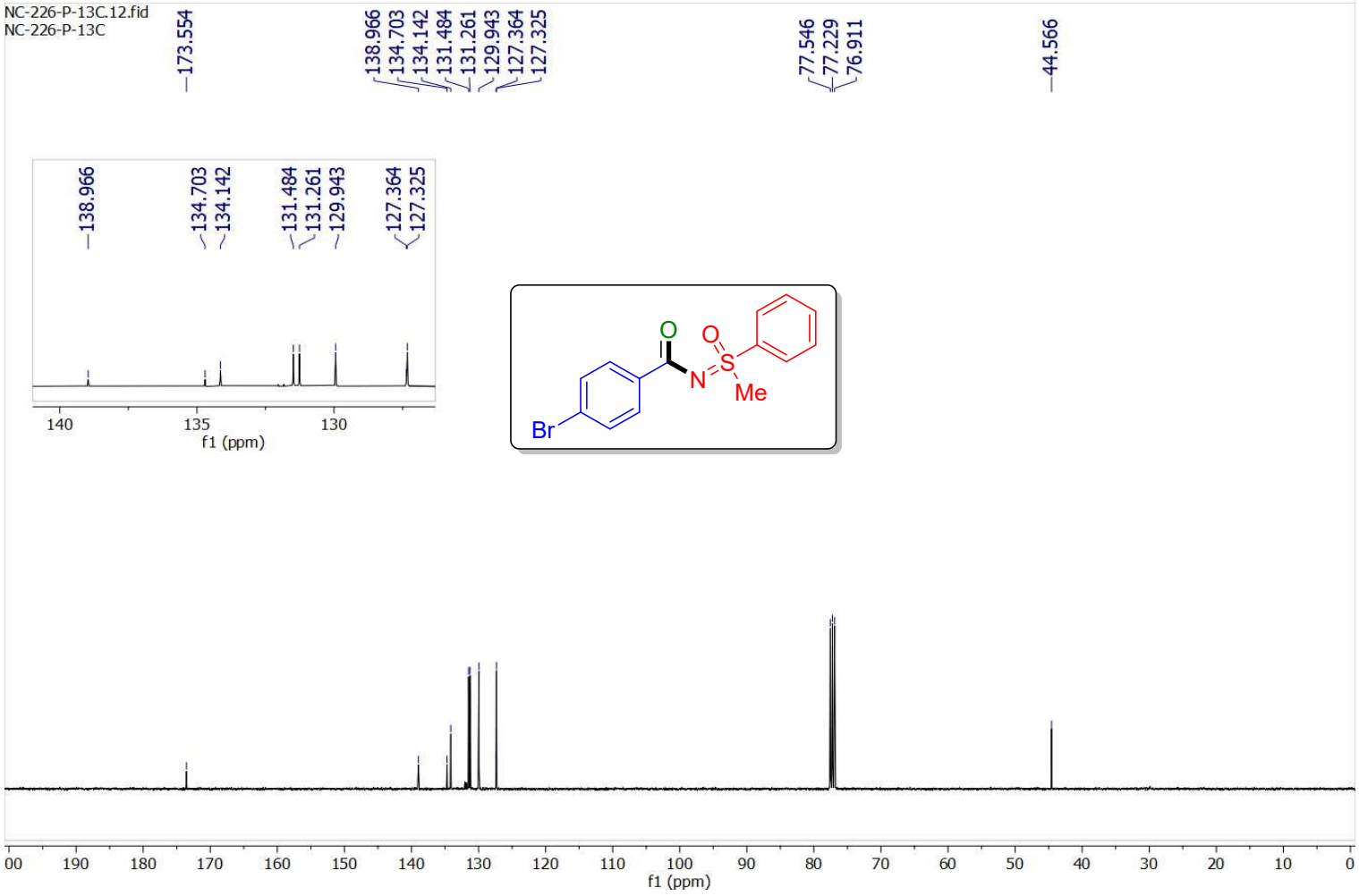
***4-Chloro-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (4a)*: ^{13}C NMR (100 MHz, $CDCl_3$)**



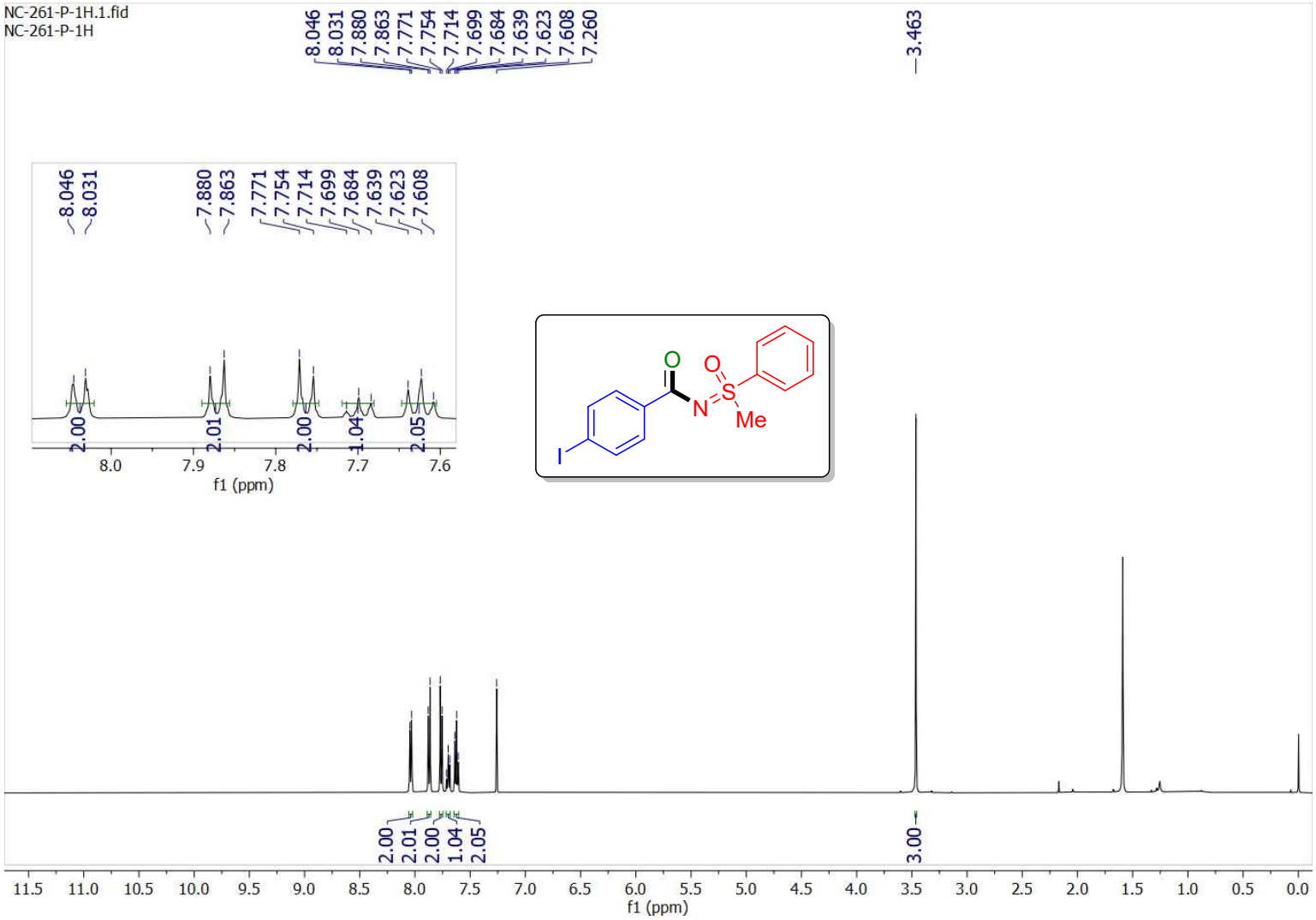
***4-Bromo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (5a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



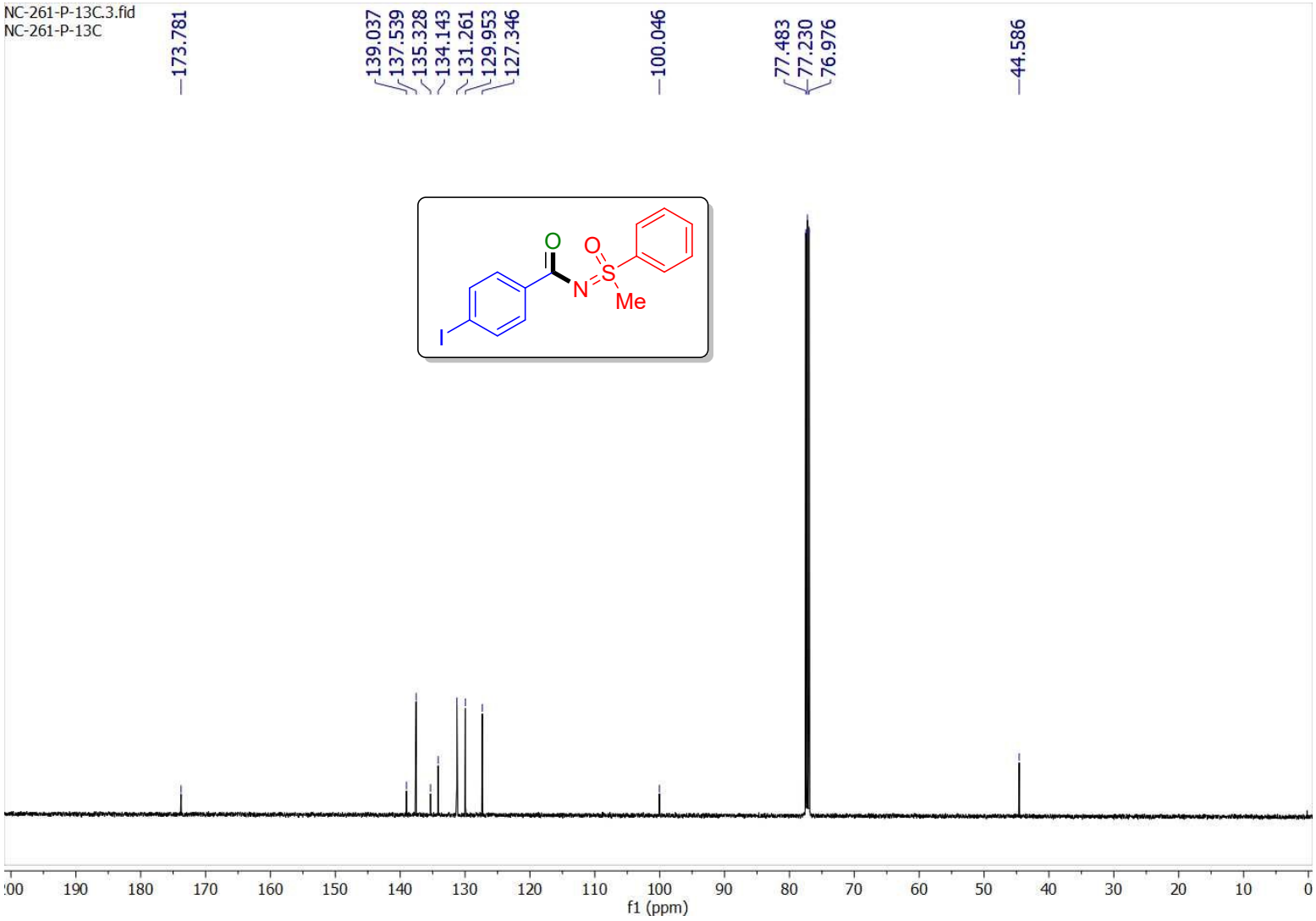
***4-Bromo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (5a)*: ^{13}C NMR (100 MHz, $CDCl_3$)**



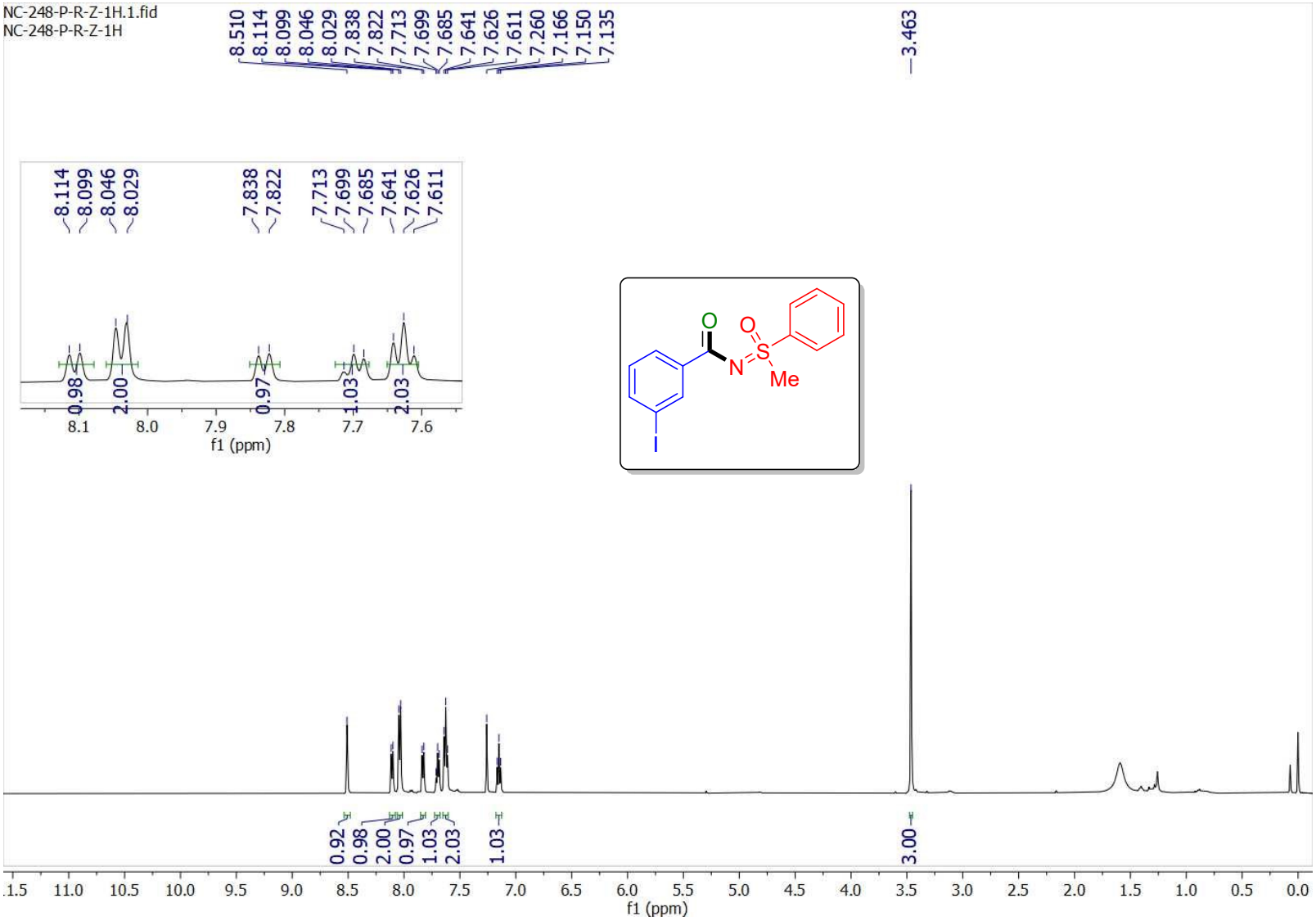
***4-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (6a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



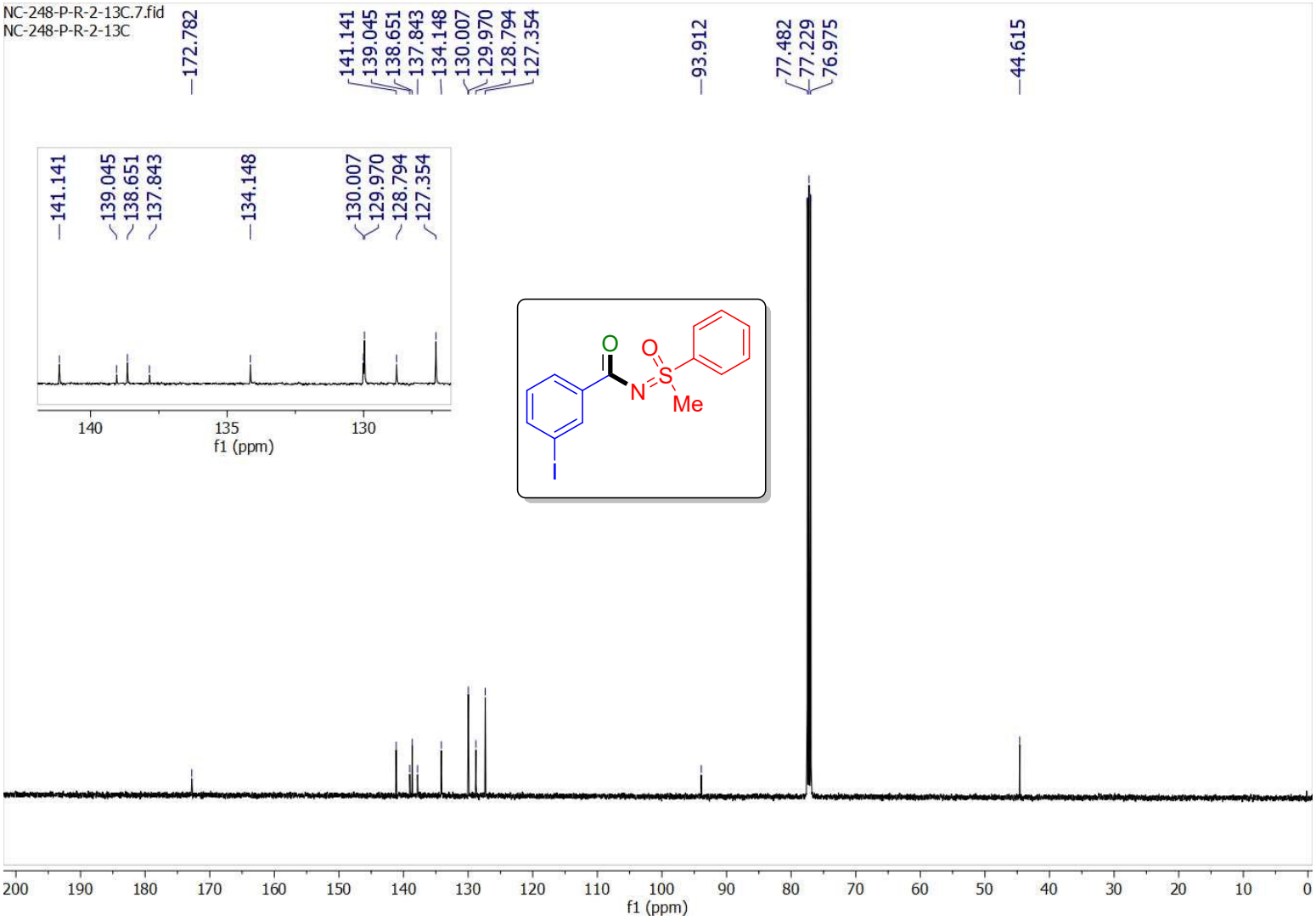
***4-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (6a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



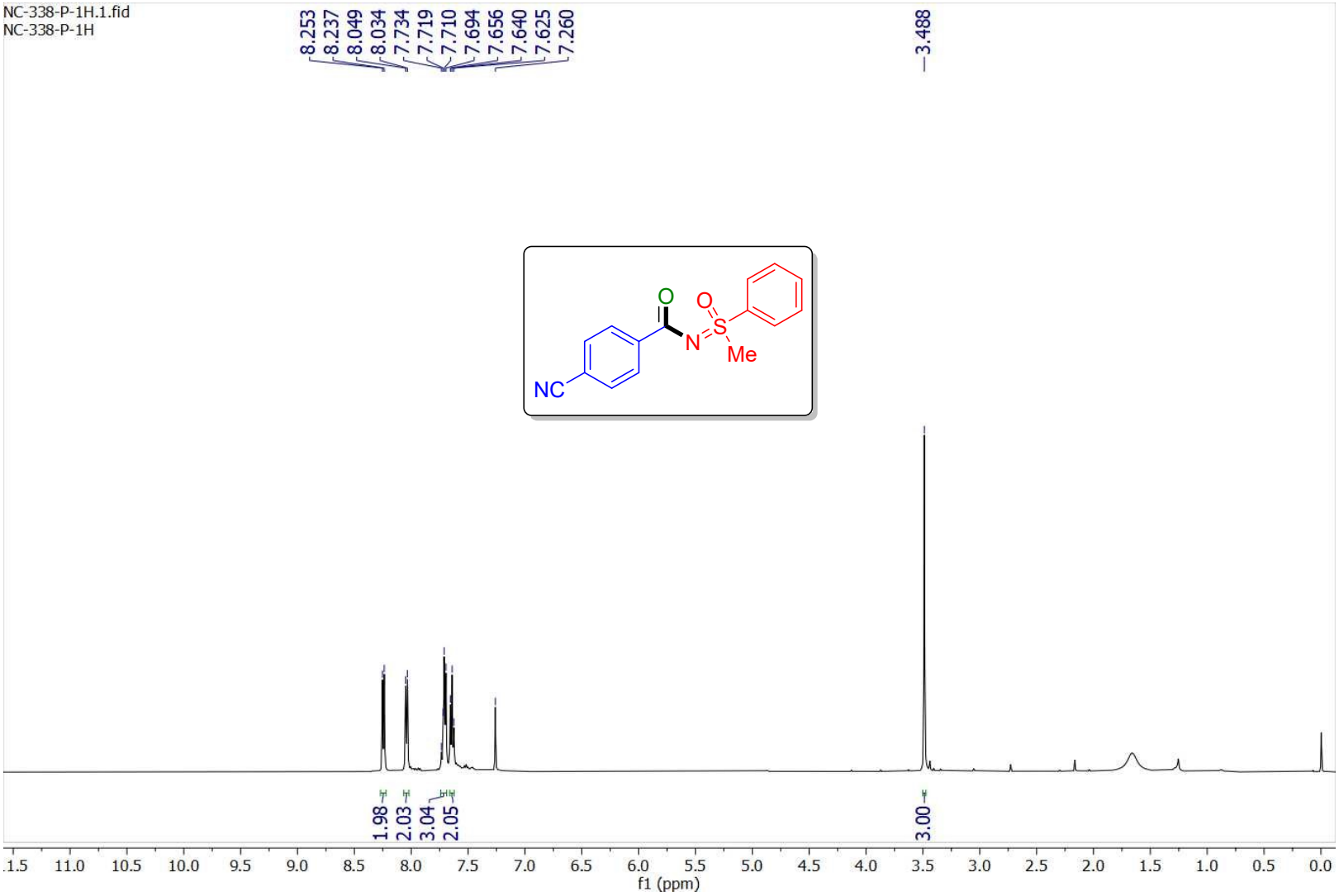
***3-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (7a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



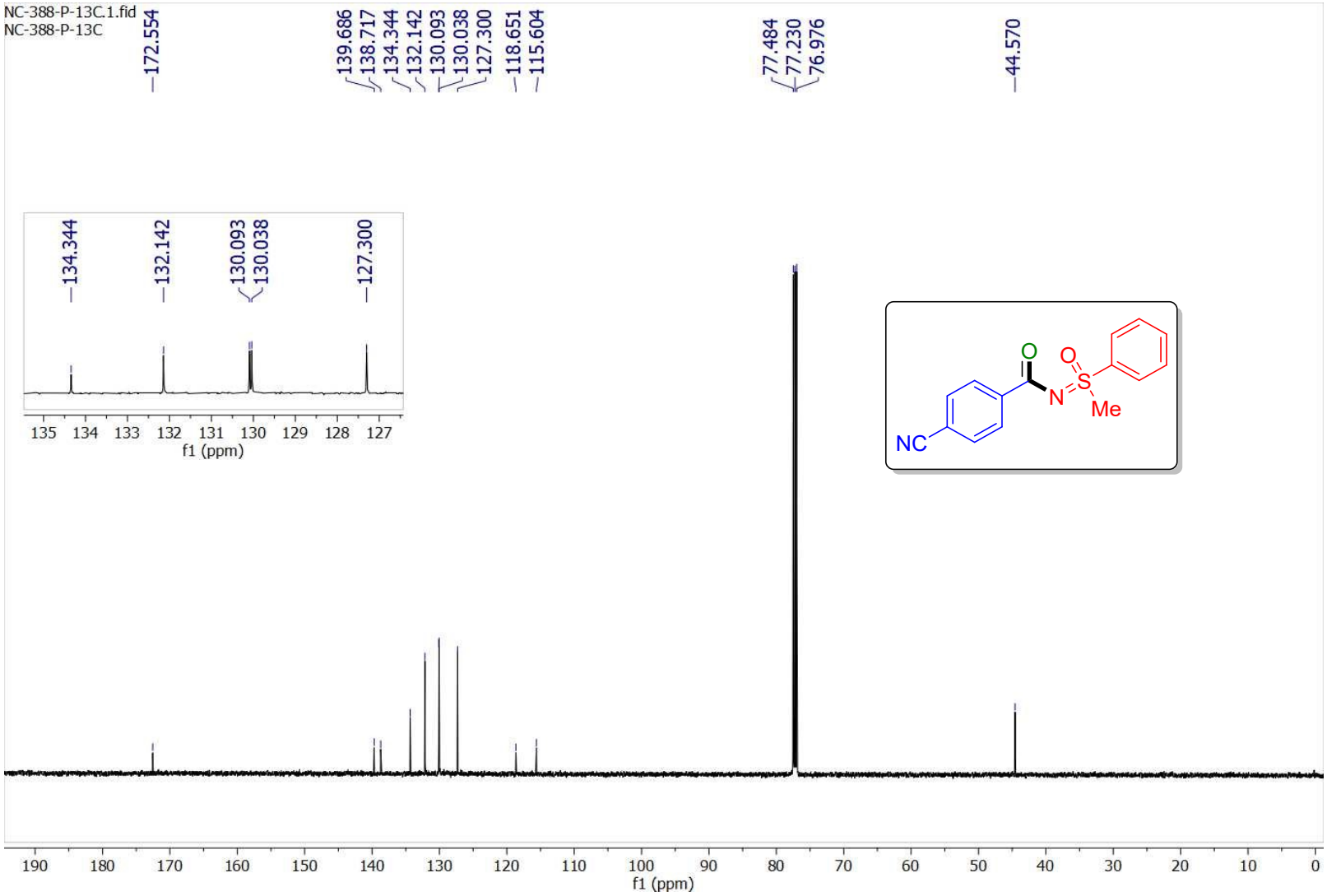
***3-Iodo-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (7a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



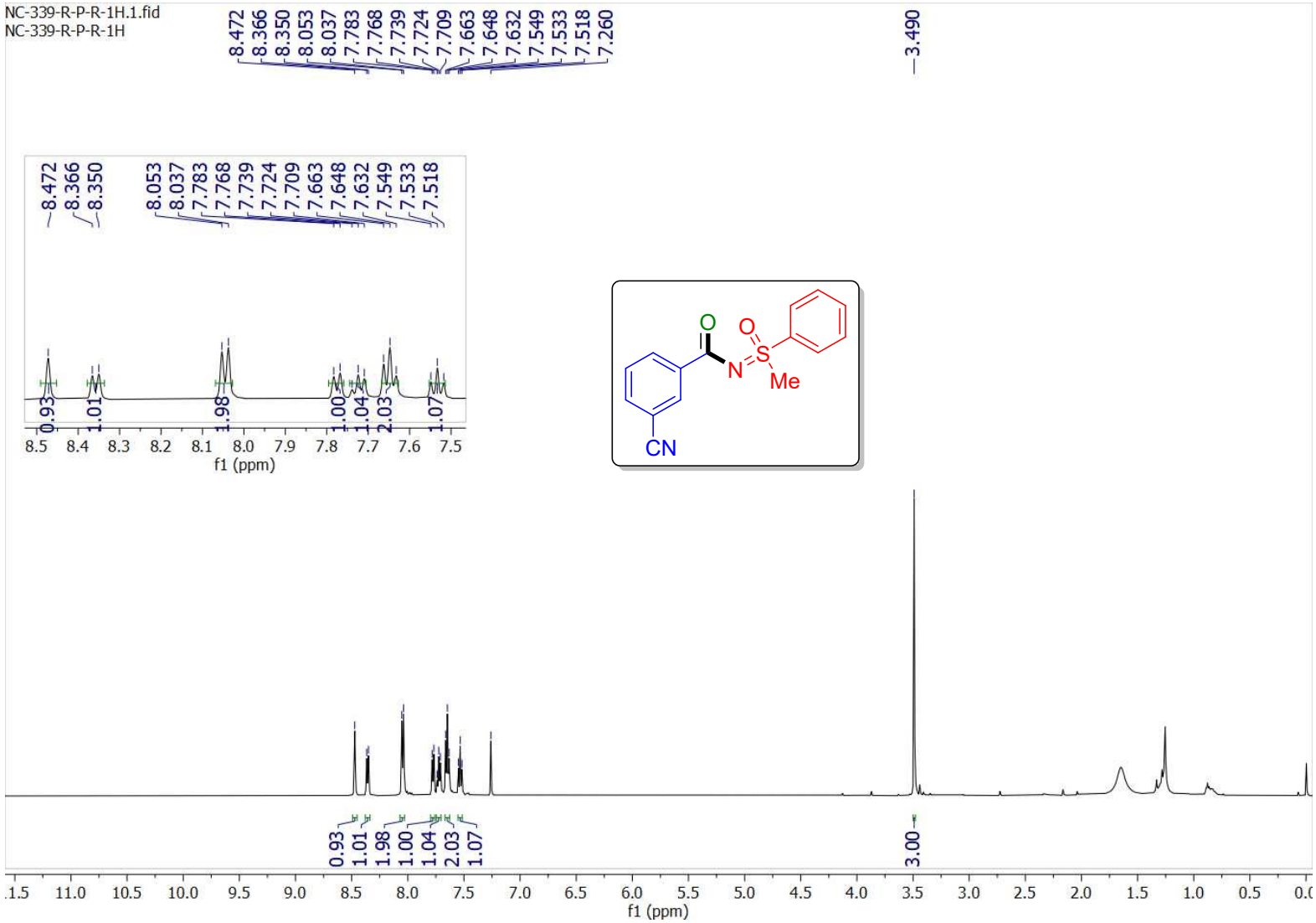
***4-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (8a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



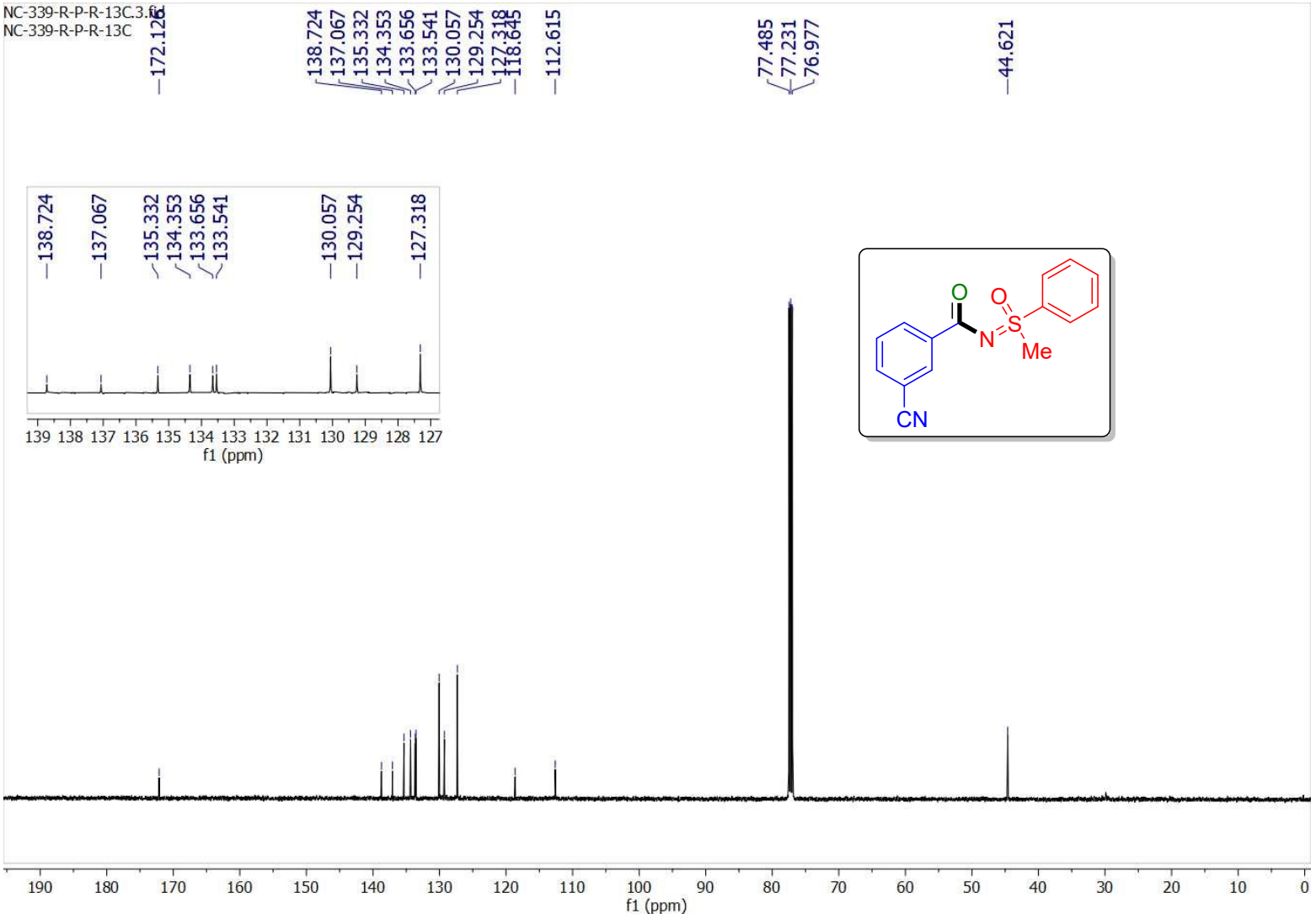
***4-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (8a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



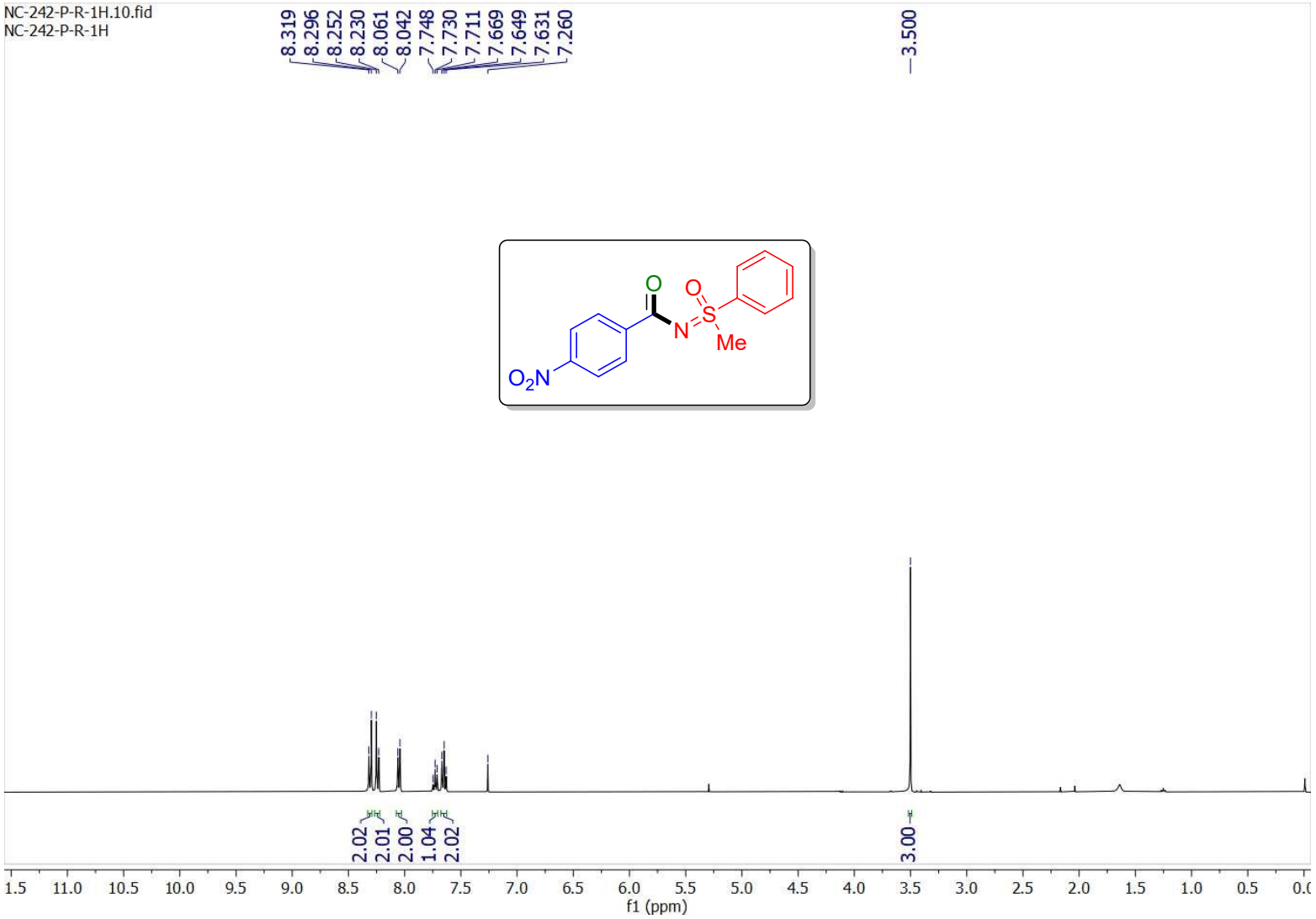
***3-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (9a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



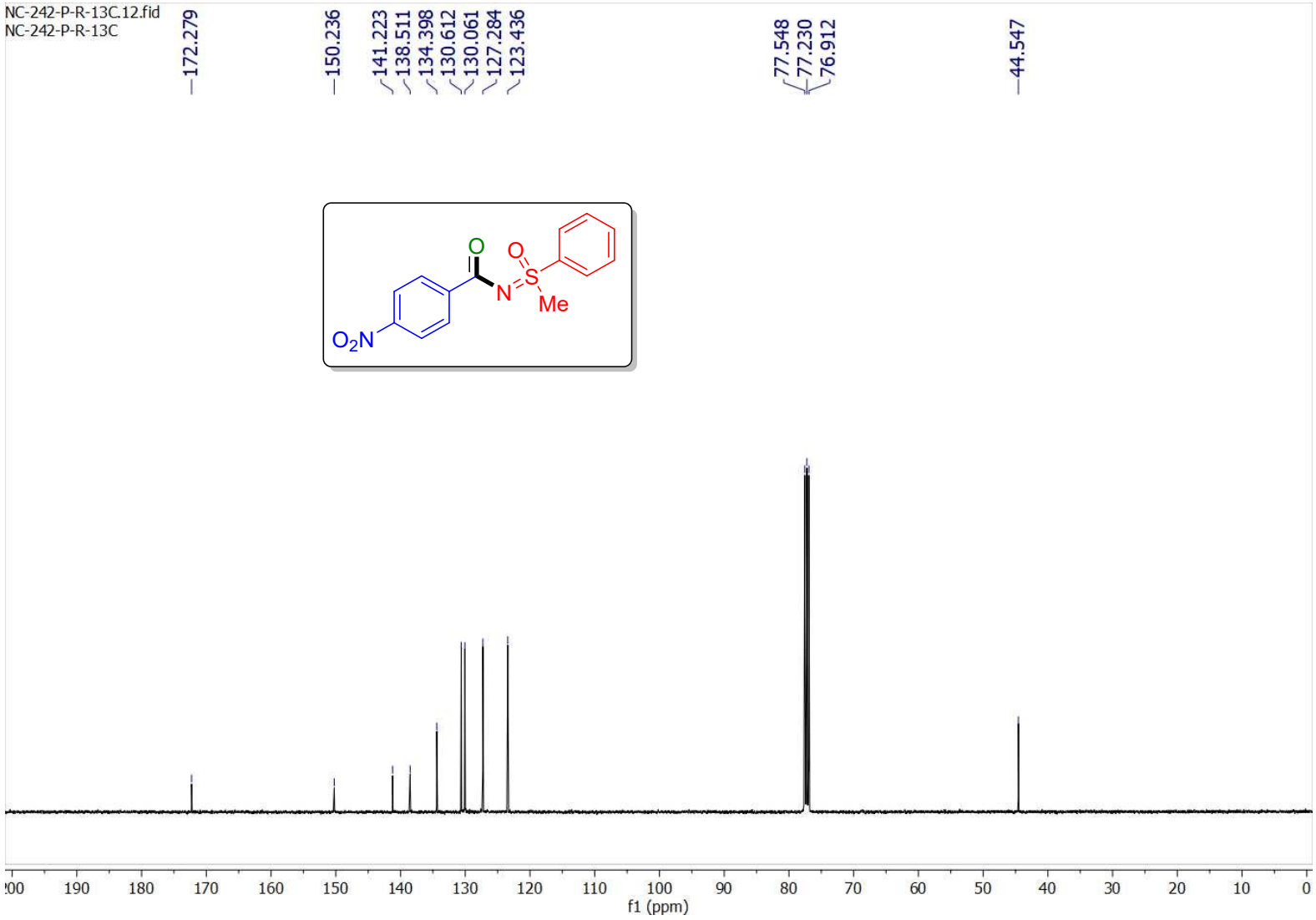
***3-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (9a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



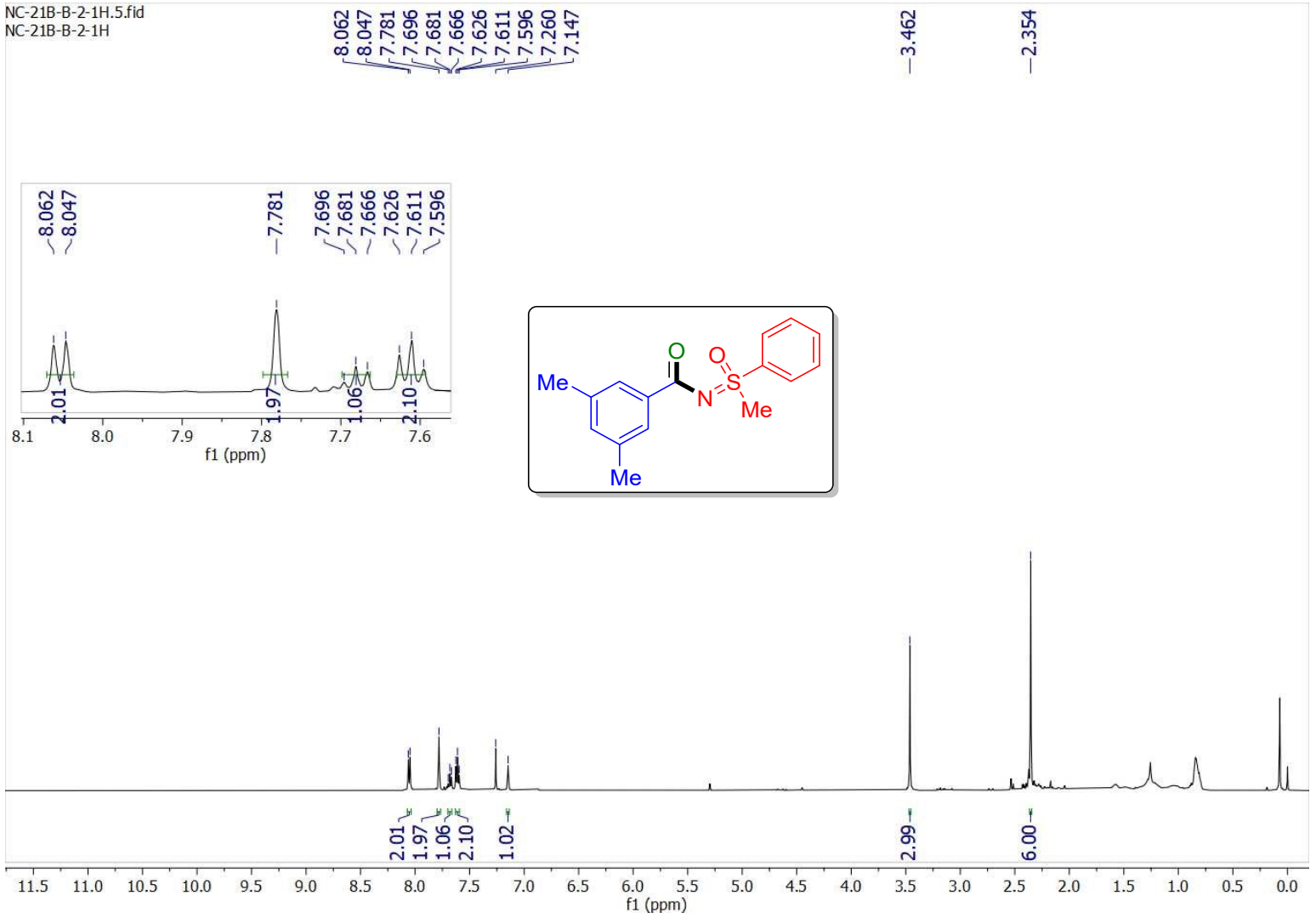
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-nitrobenzamide (10a)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



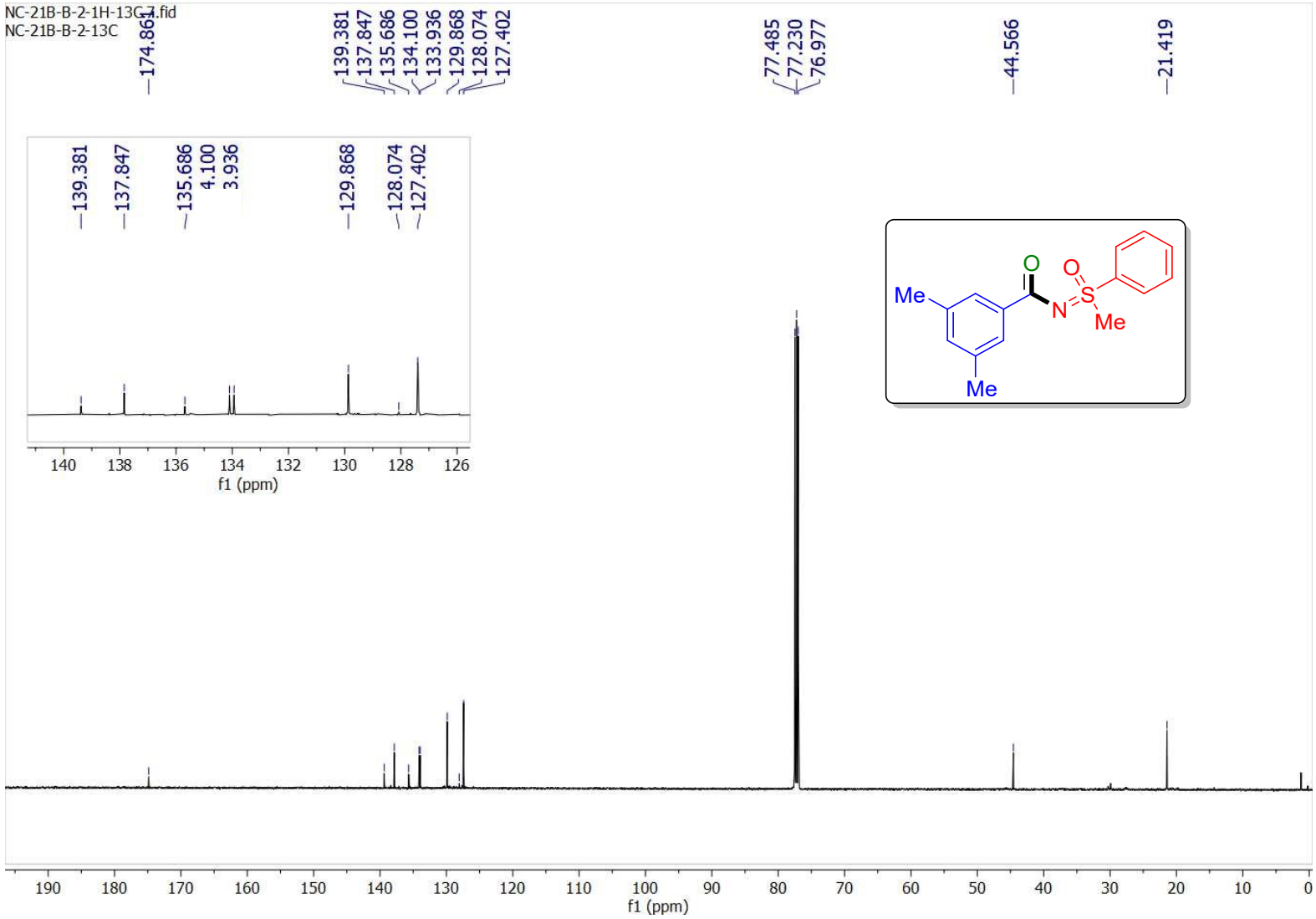
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-nitrobenzamide (10a)*: ^{13}C NMR (100 MHz, $CDCl_3$)**



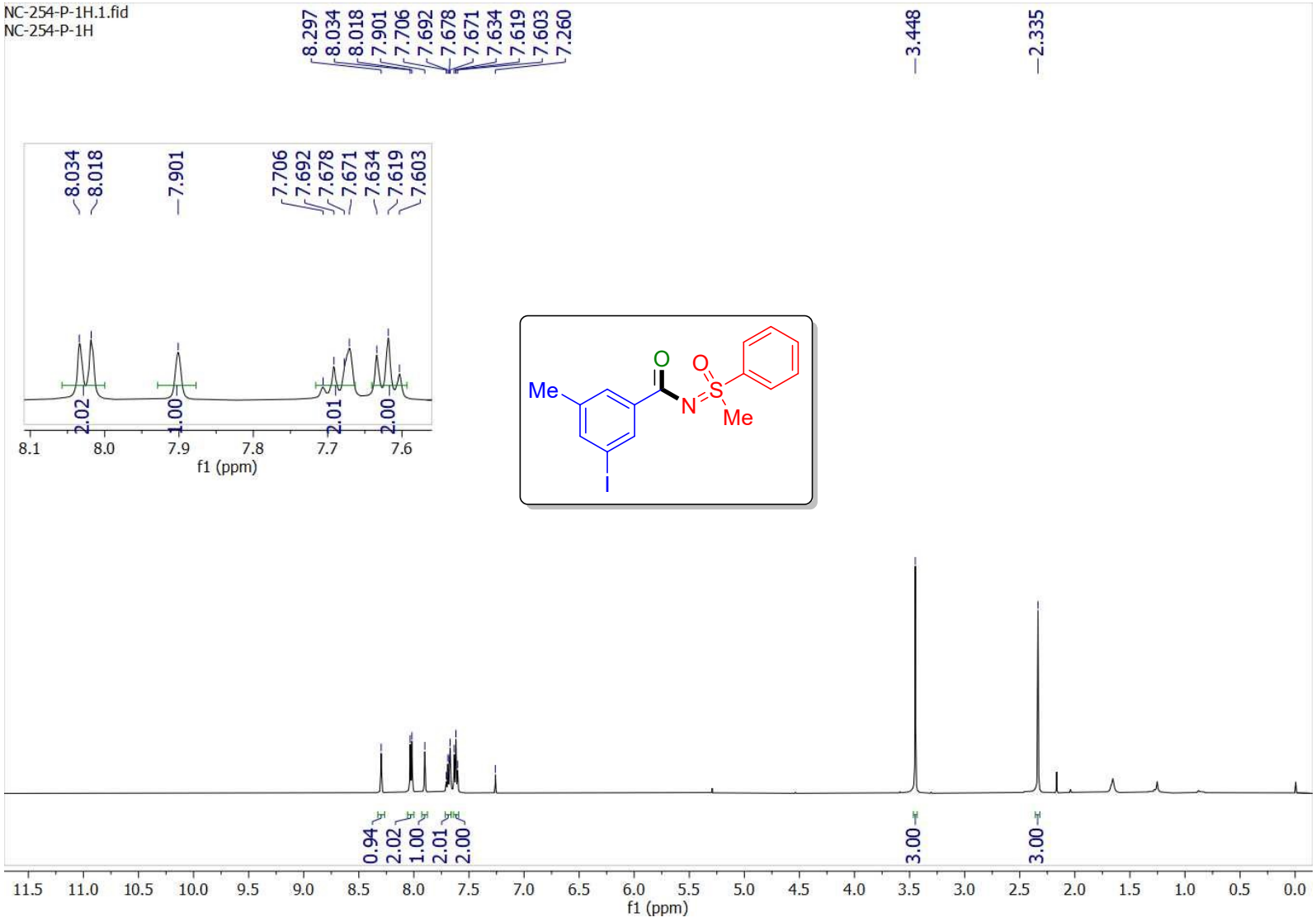
***3,5-Dimethyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (11a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



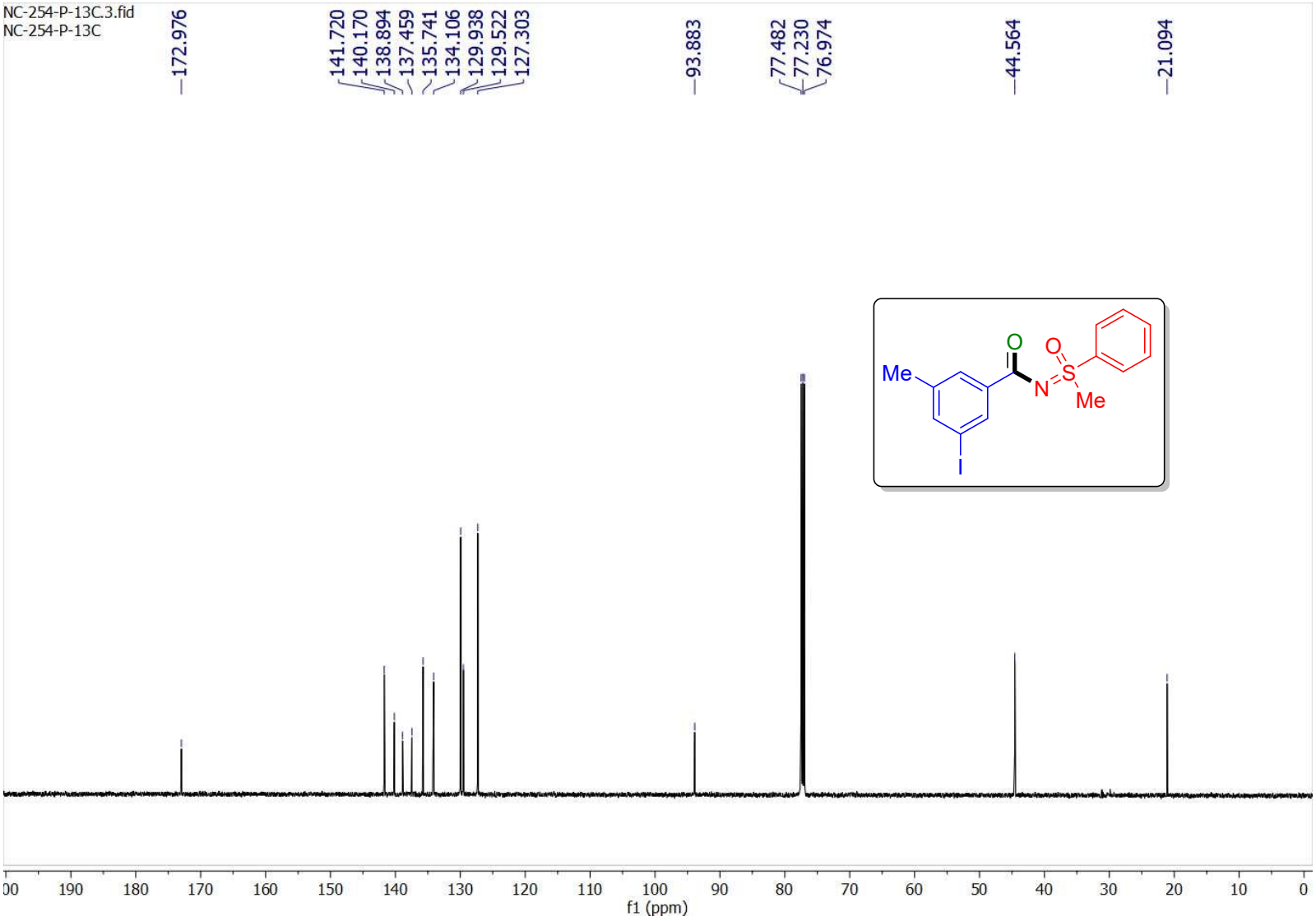
***3,5-Dimethyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (11a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



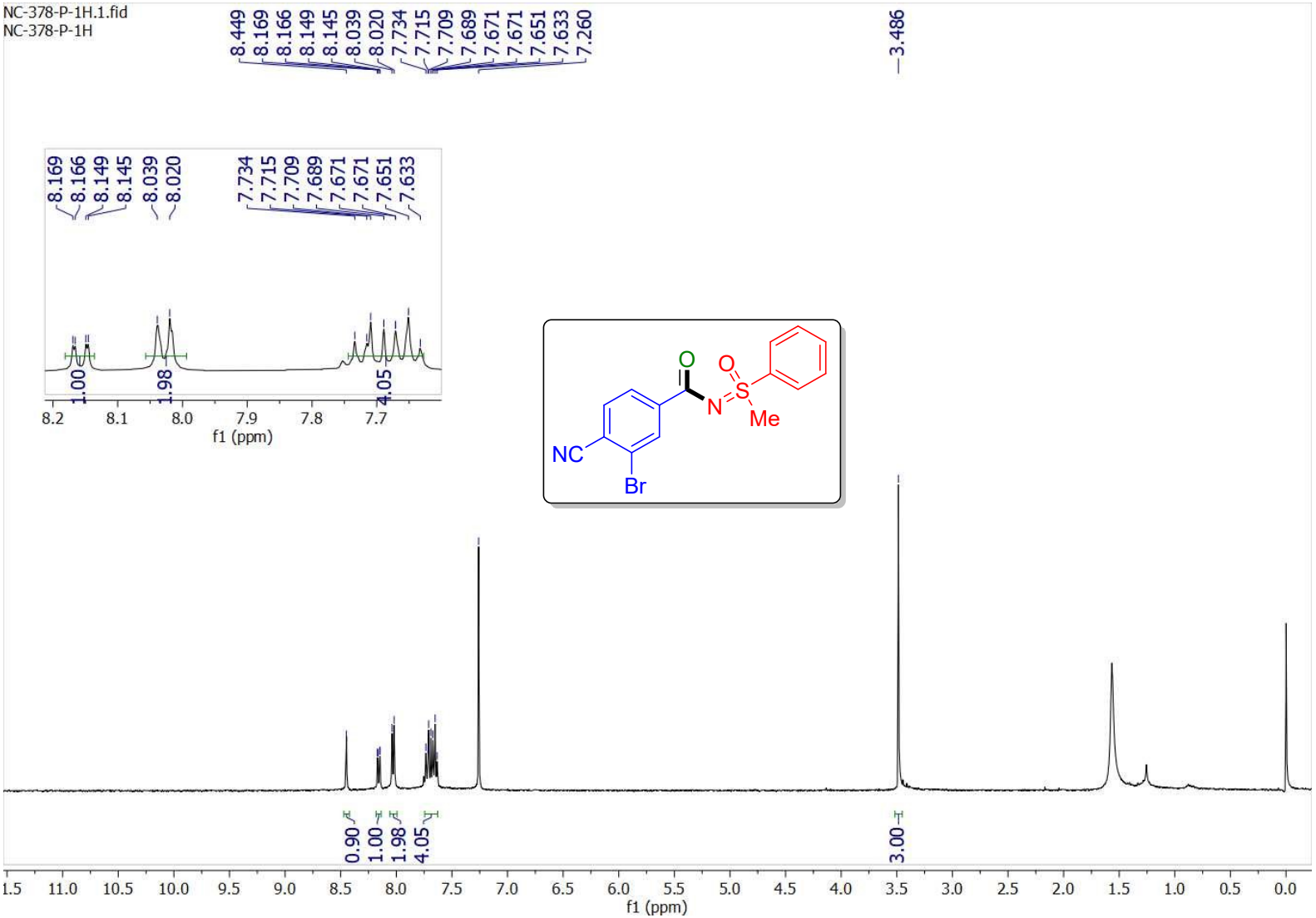
***3-Iodo-5-methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (12a)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



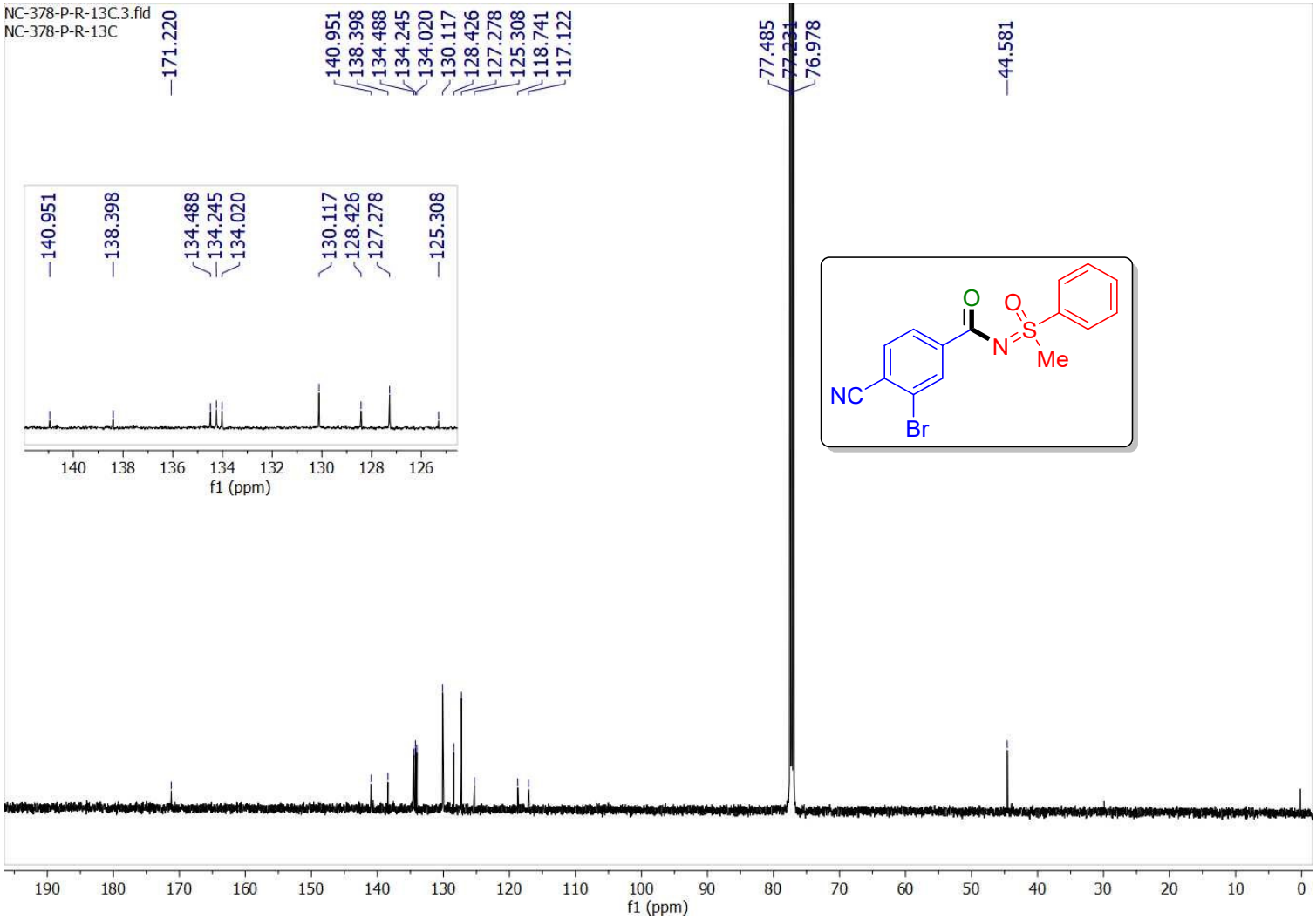
***3-Iodo-5-methyl-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (12a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



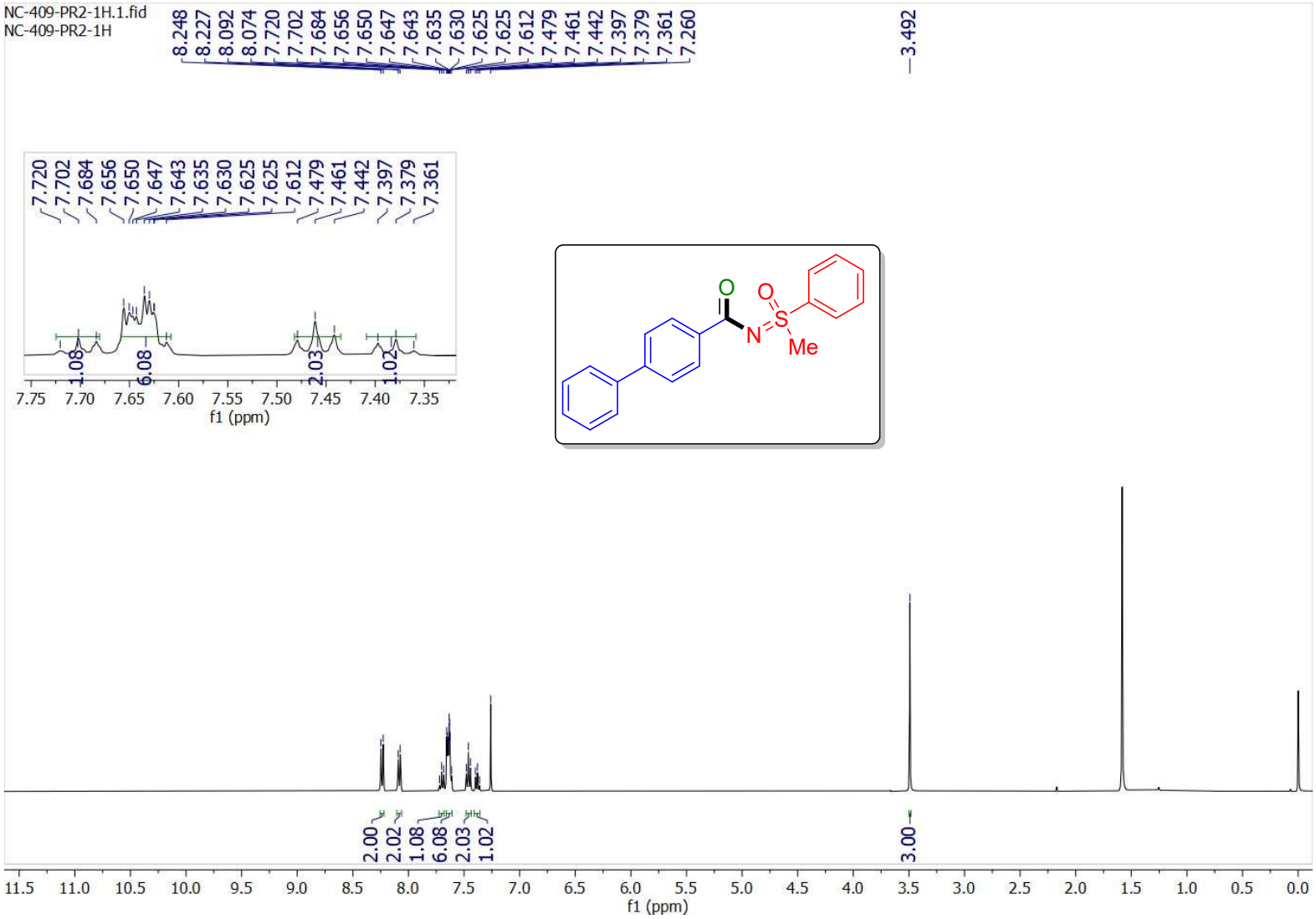
***3-Bromo-4-cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (13a)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



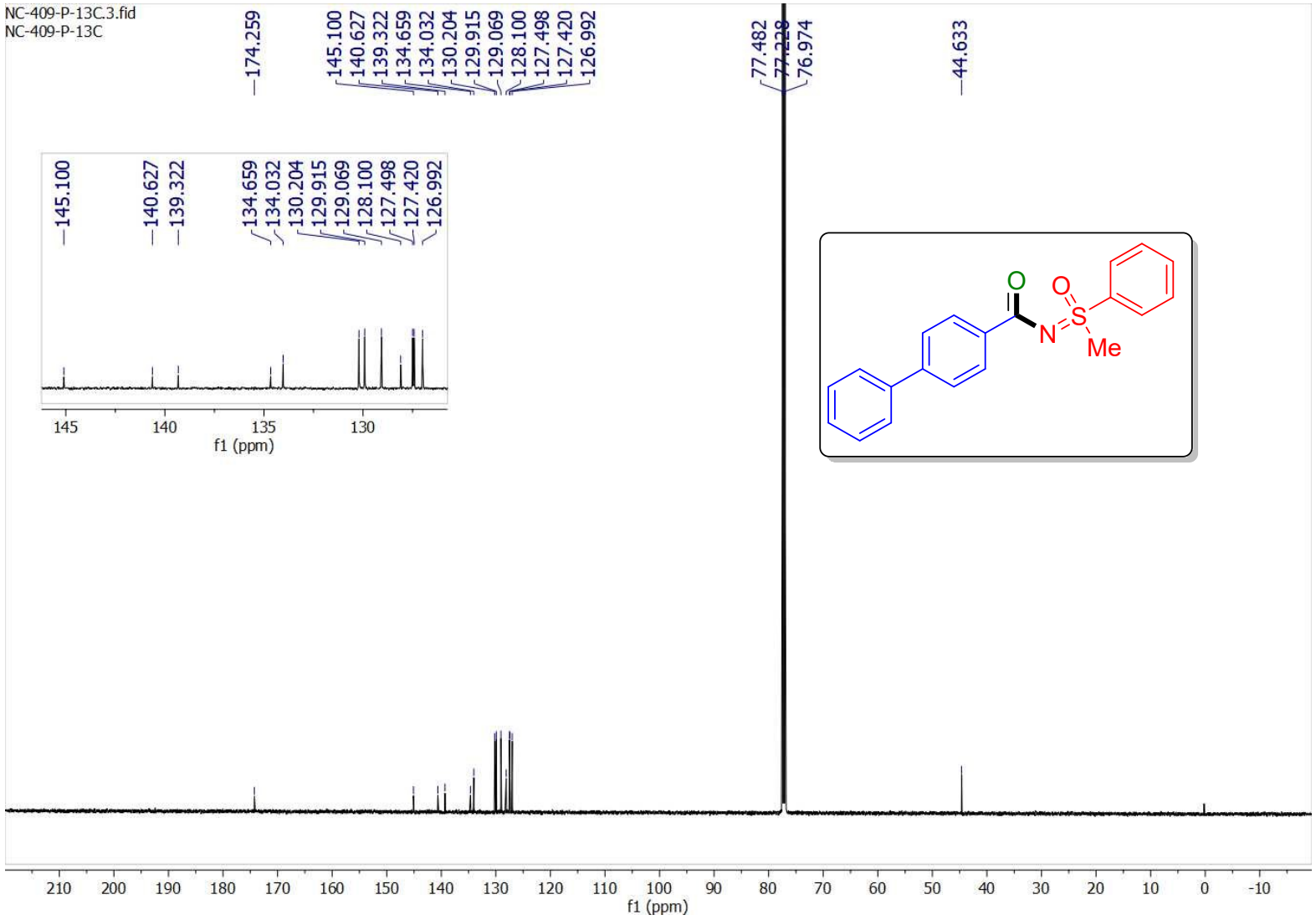
***3-Bromo-4-cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (13a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



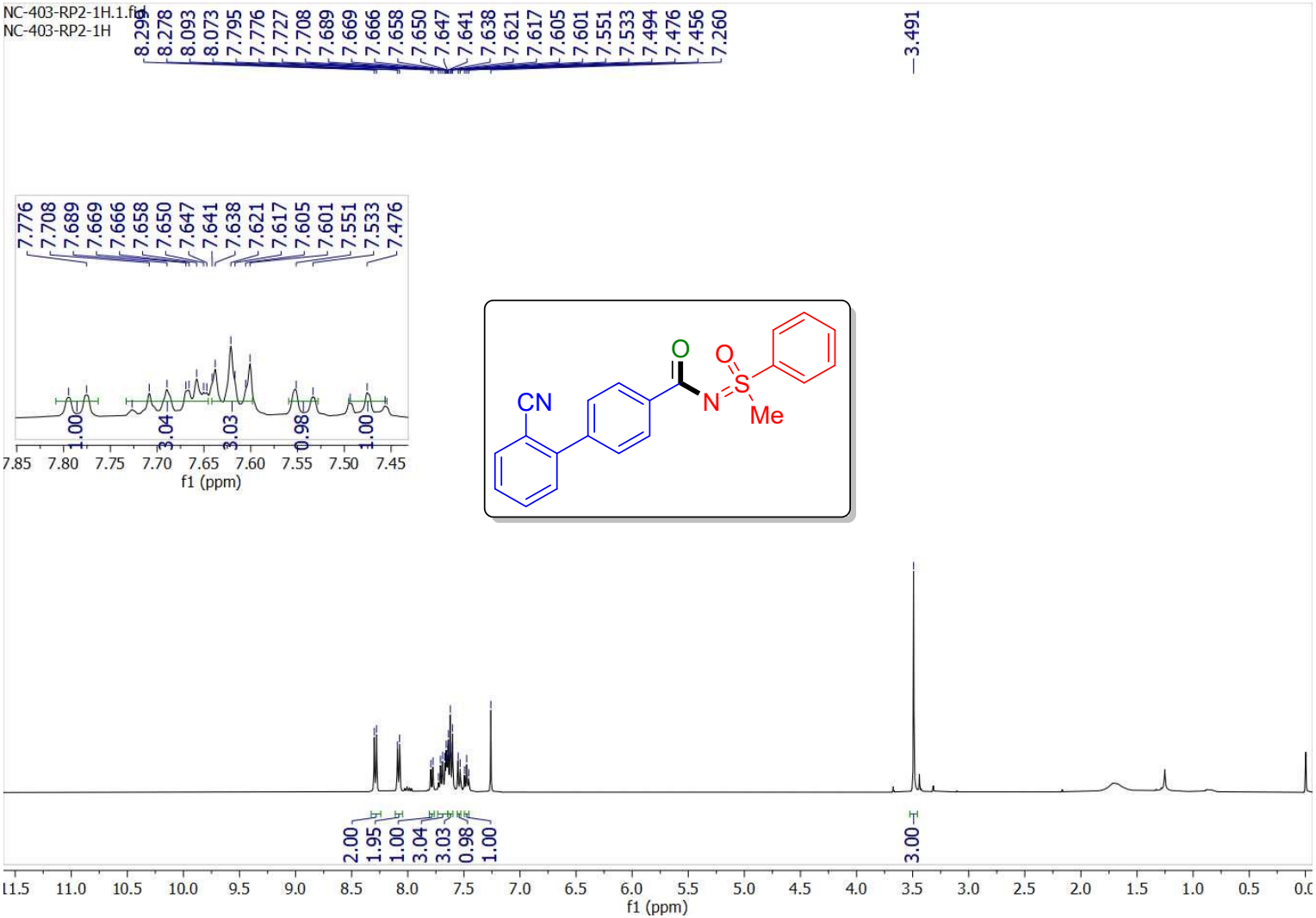
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (14a)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



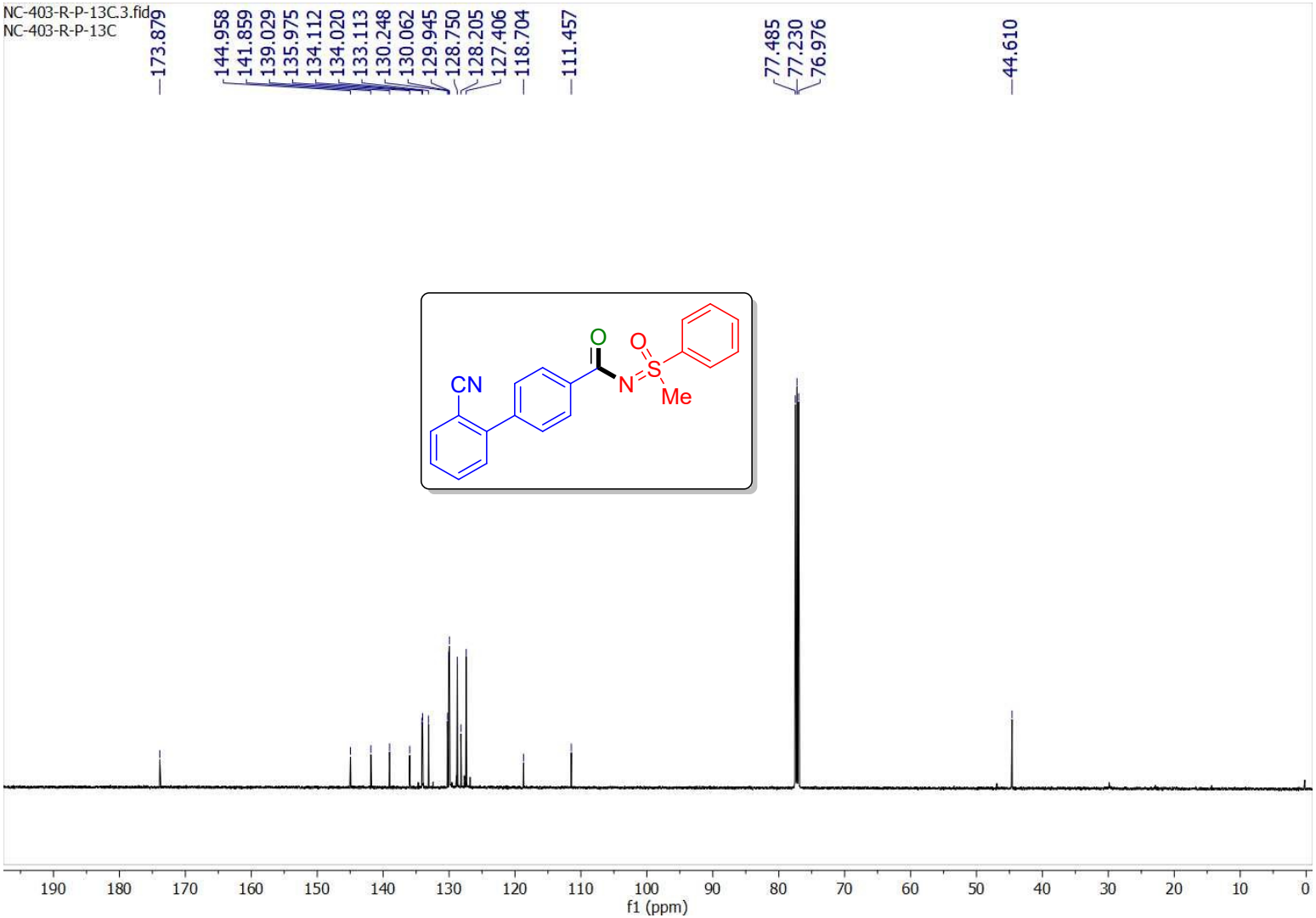
***N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (14a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



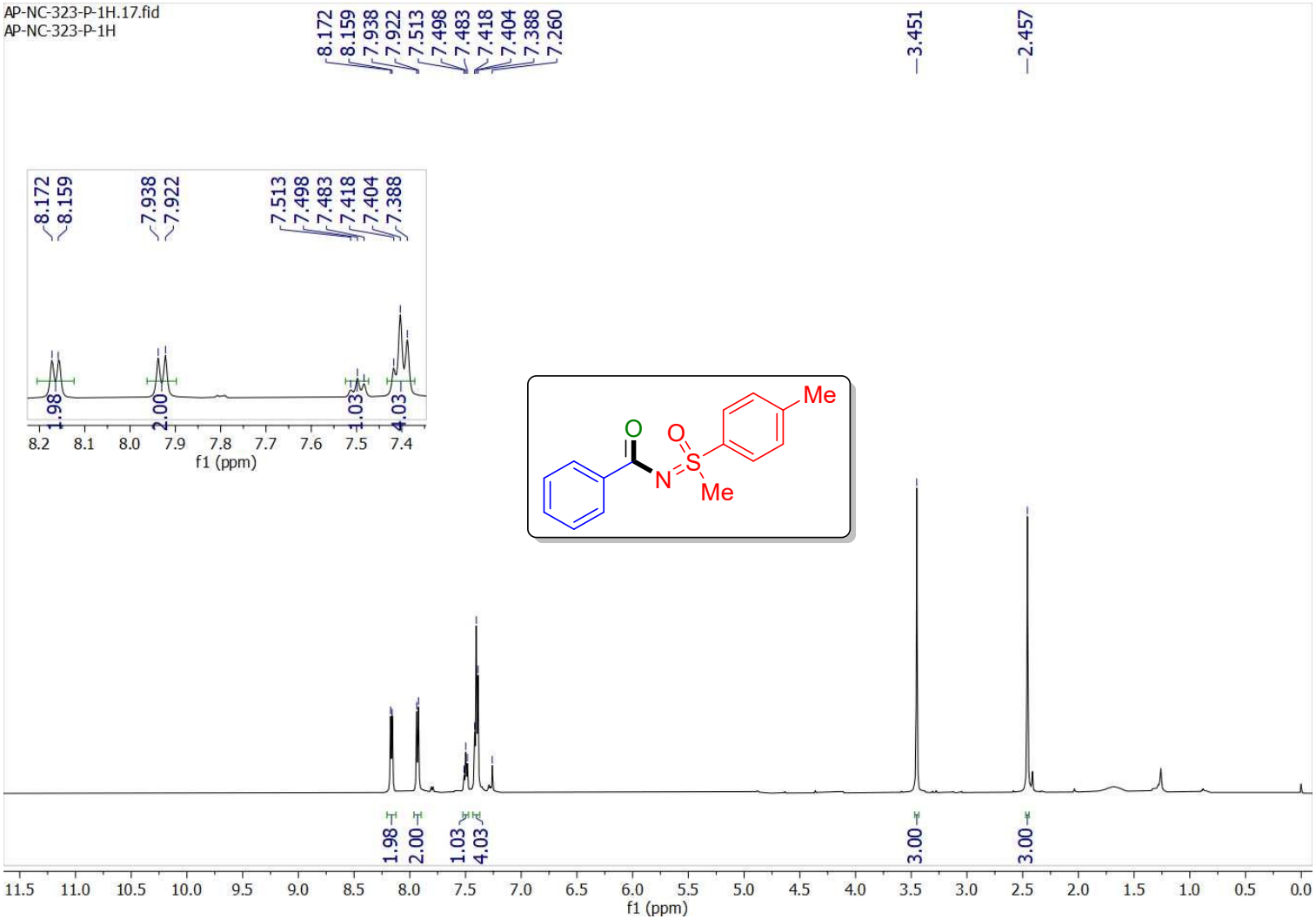
***2'-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (15a)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



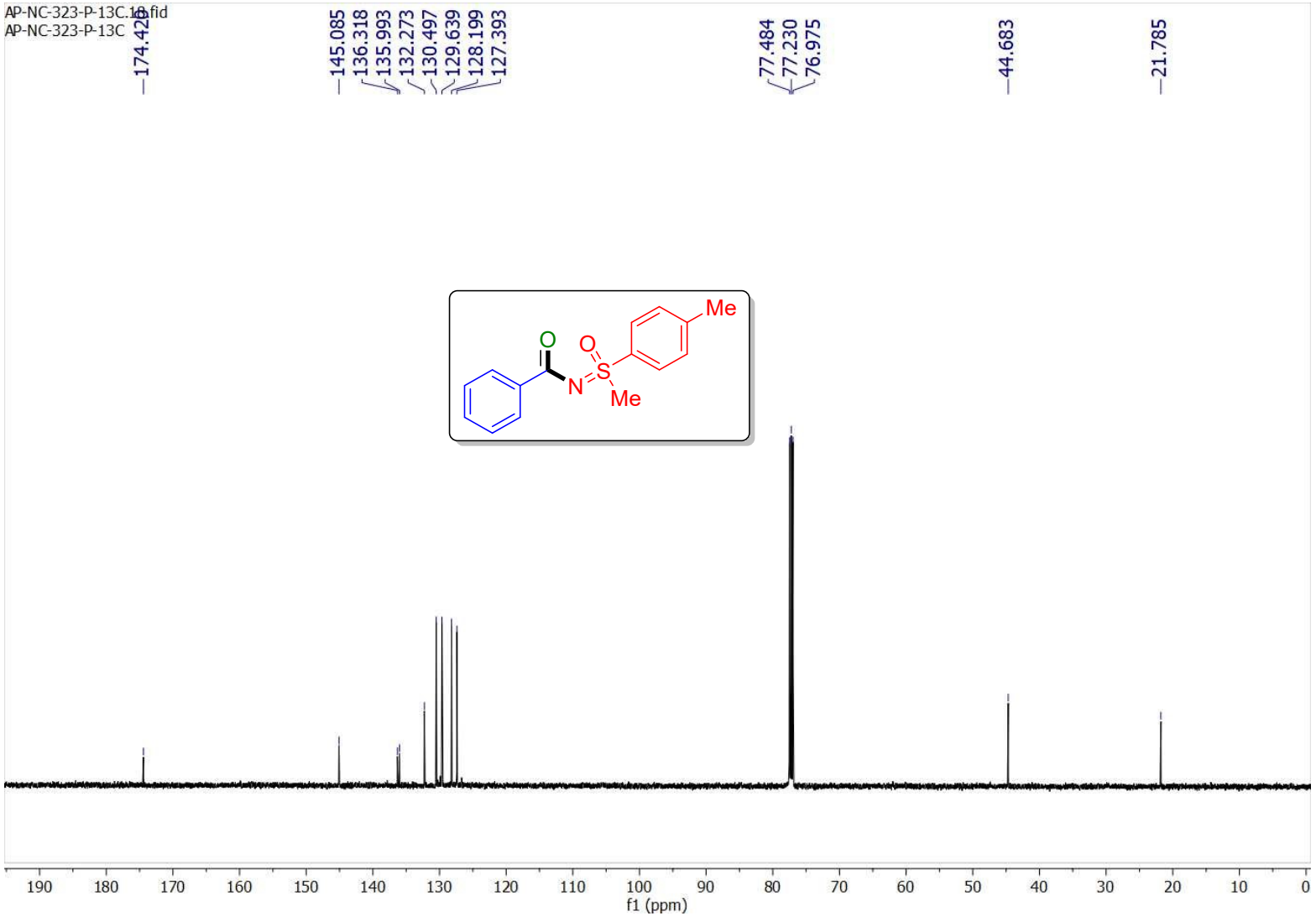
***2'-Cyano-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-[1,1'-biphenyl]-4-carboxamide (15a)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



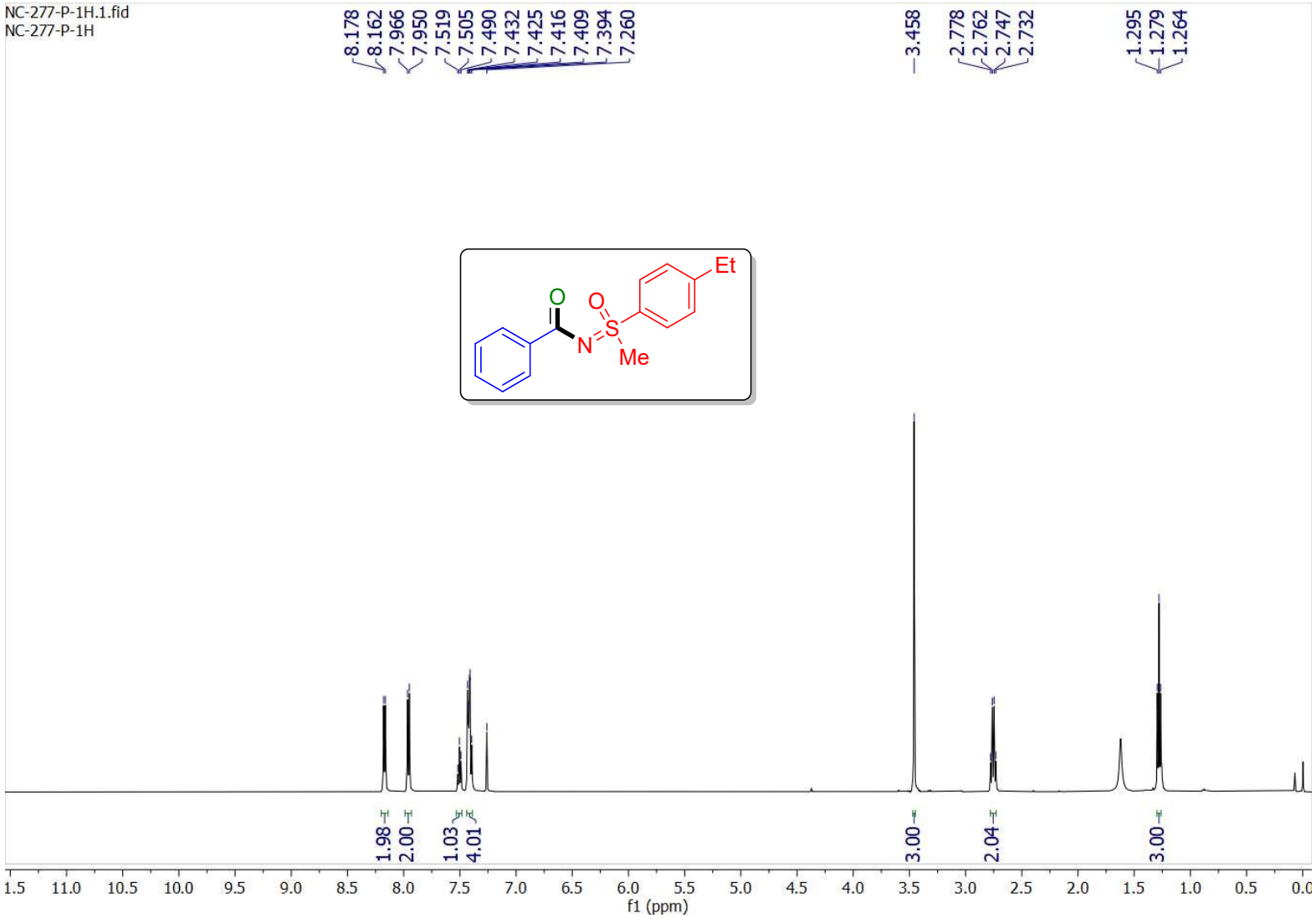
***N-(Methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)benzamide (1b)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



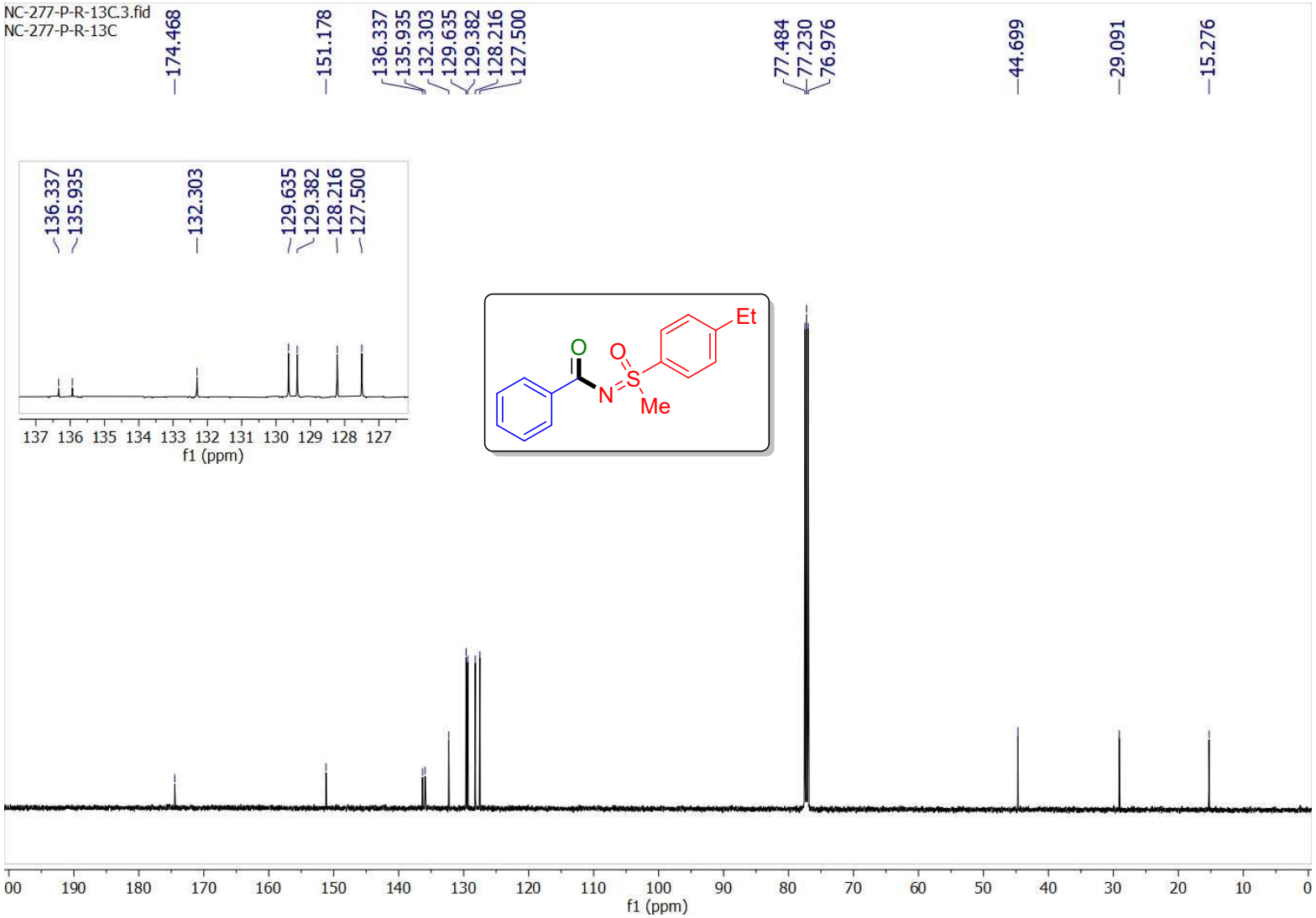
***N-(Methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)benzamide (1b)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



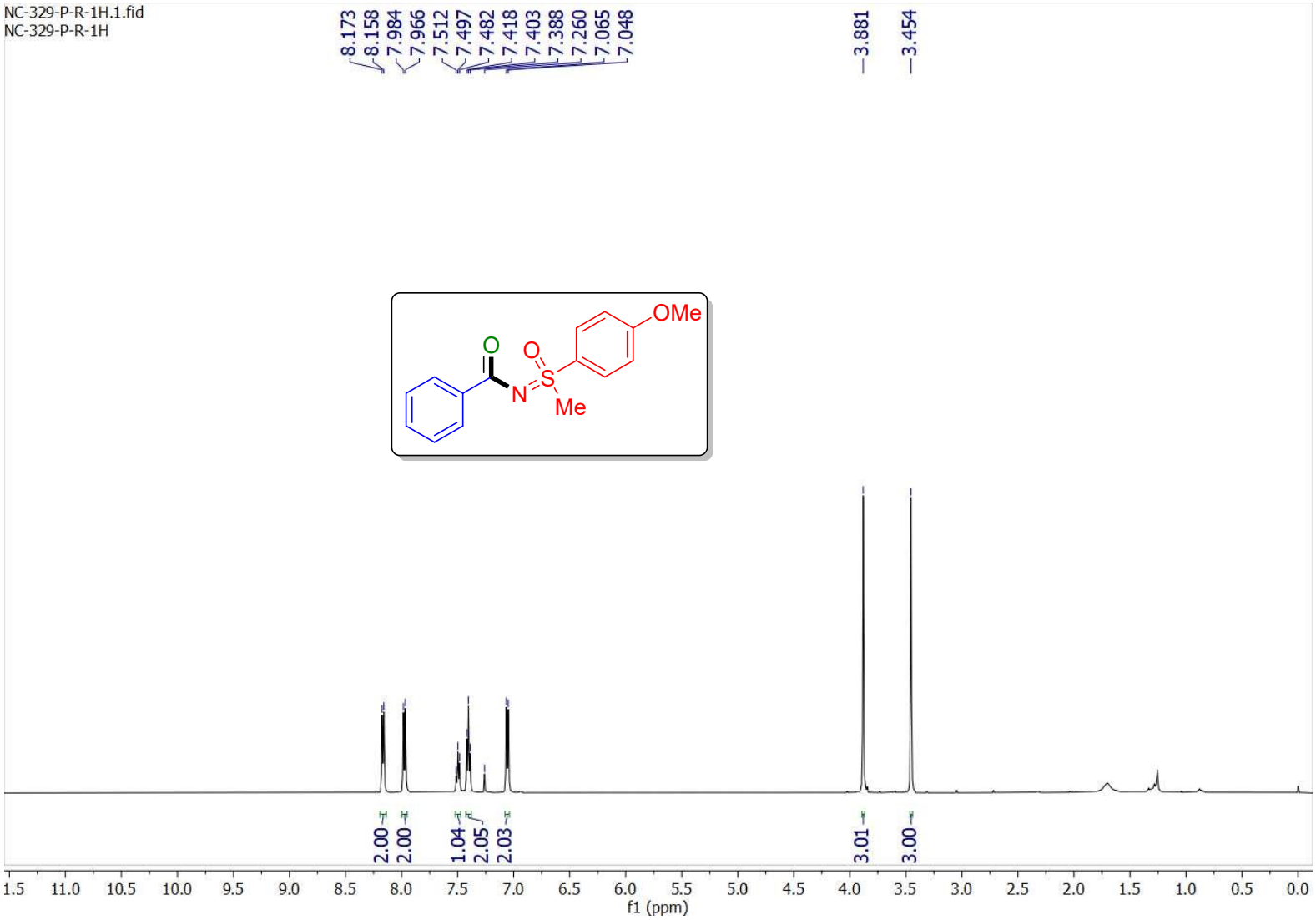
***N*-((4-Ethylphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)benzamide (1c)**: **^{1}H NMR (500 MHz, $CDCl_3$)**



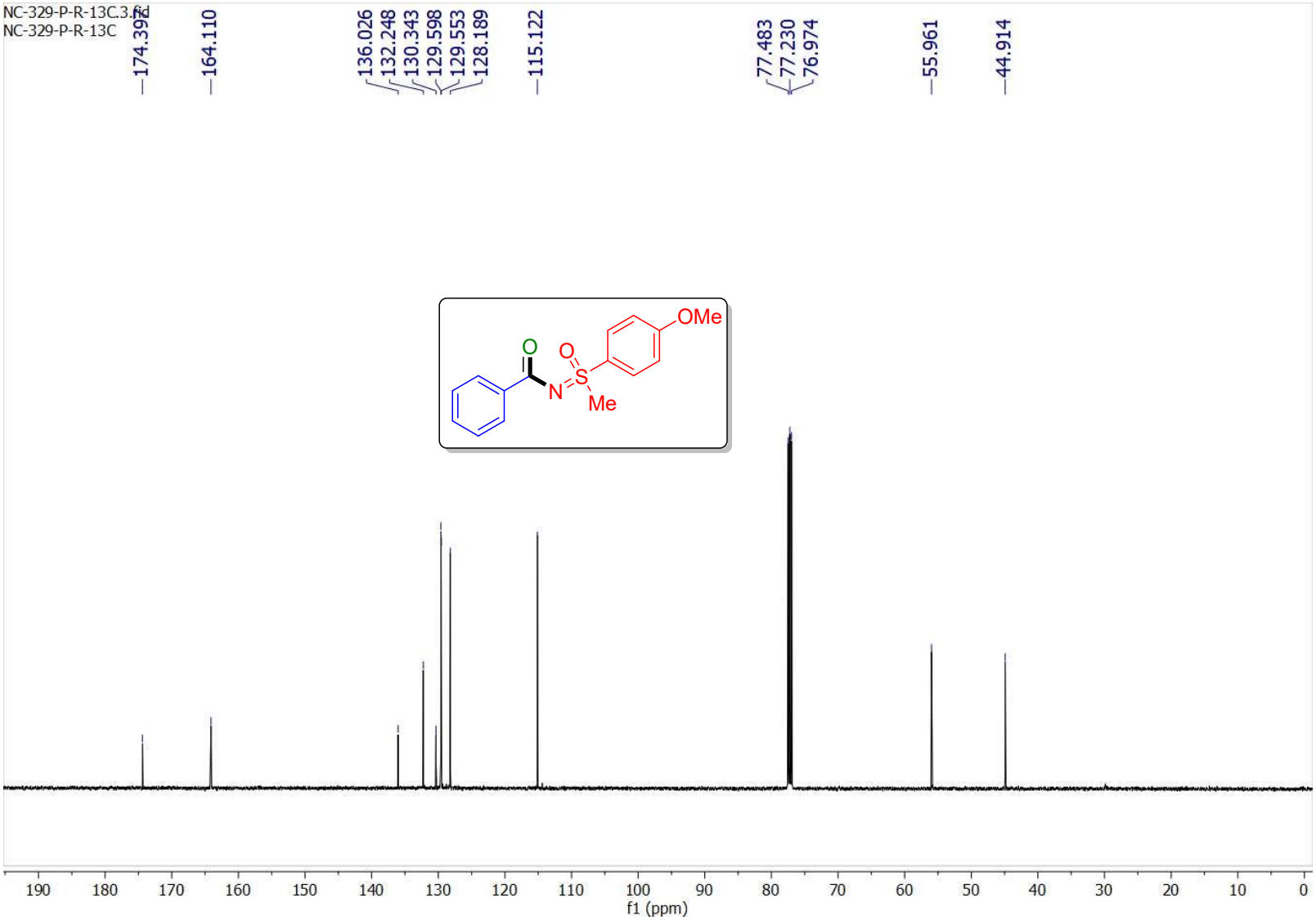
***N*-((4-Ethylphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)benzamide (1c)**: **^{13}C NMR (125 MHz, $CDCl_3$)**



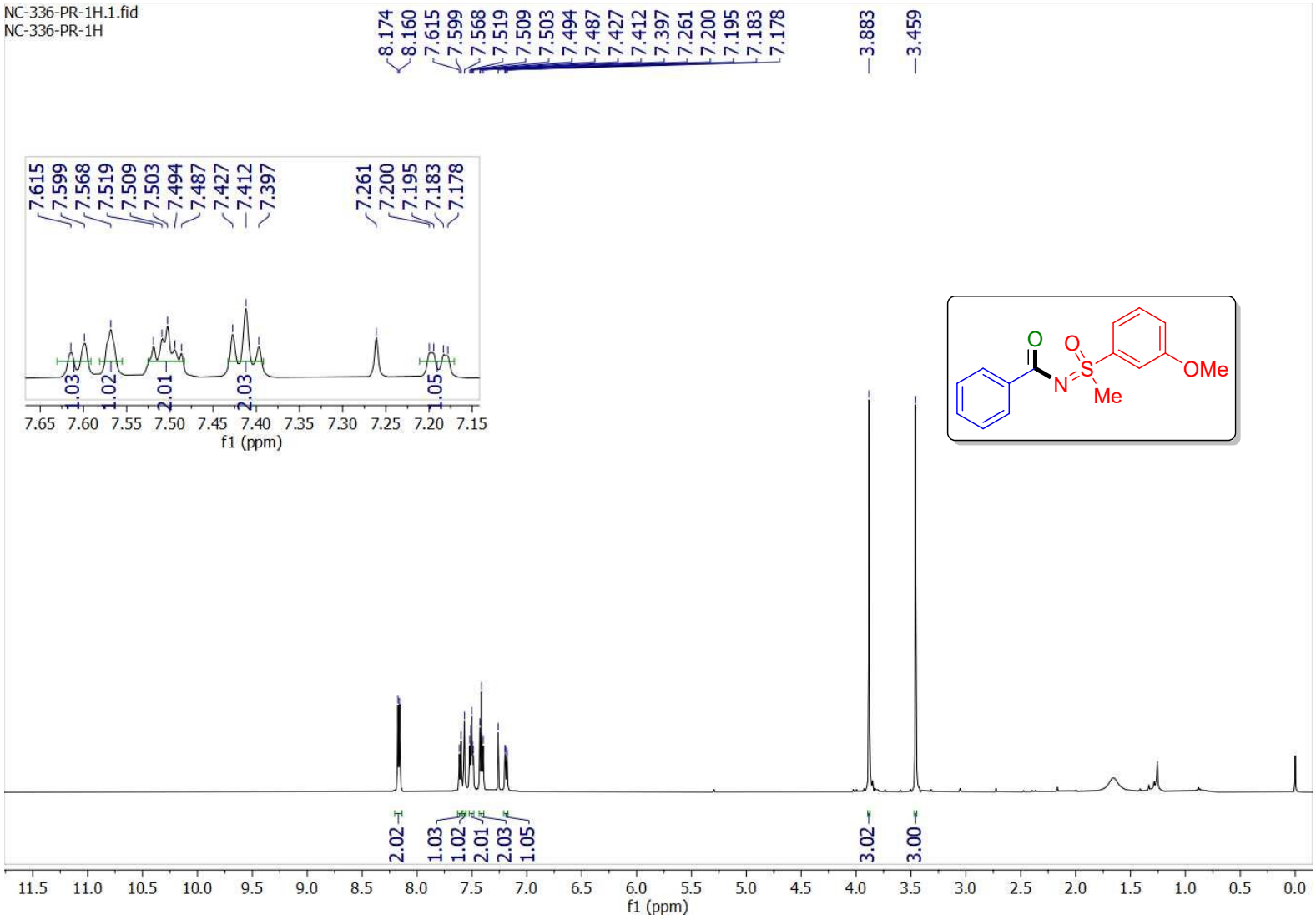
***N-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1d)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



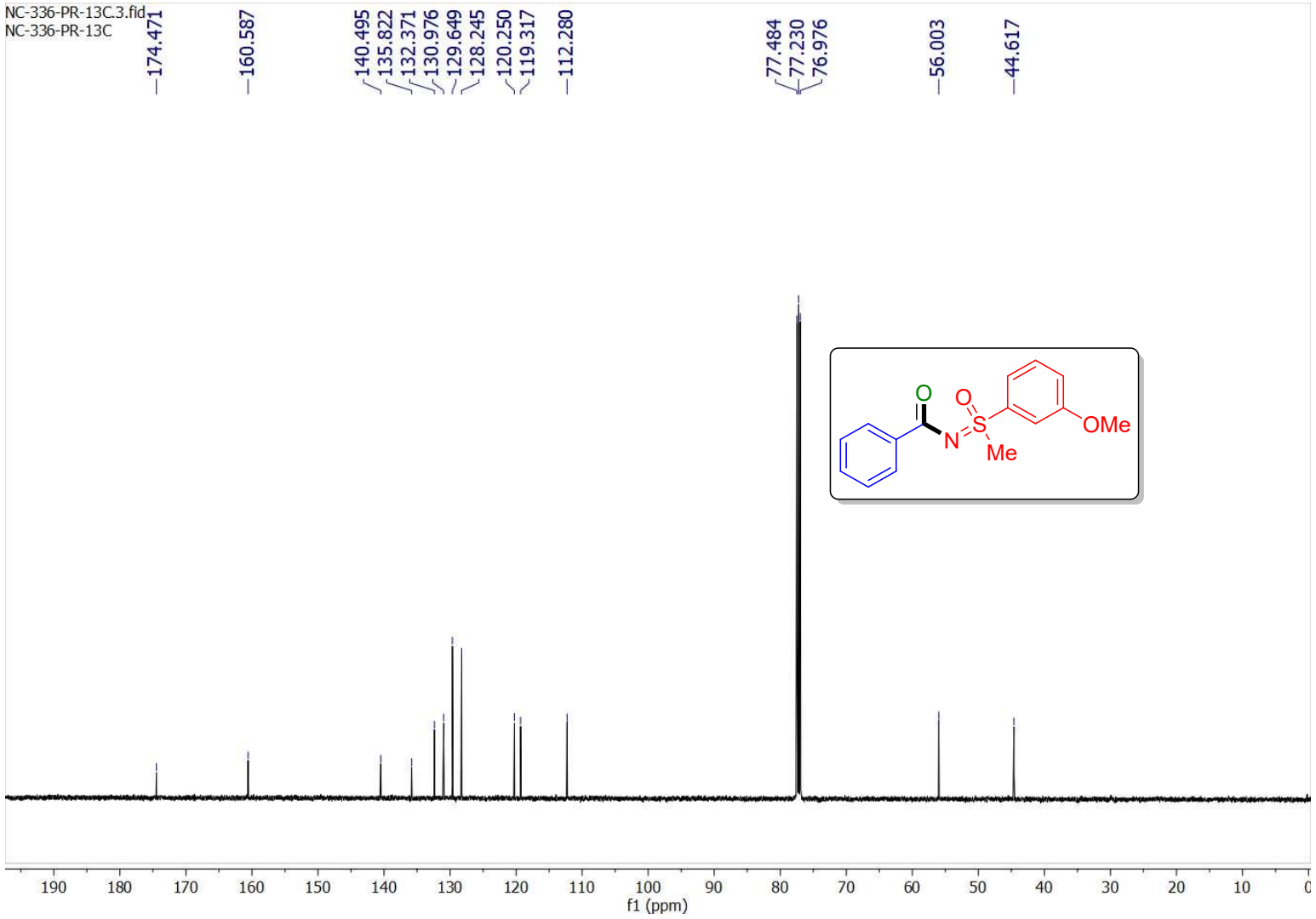
***N-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1d)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



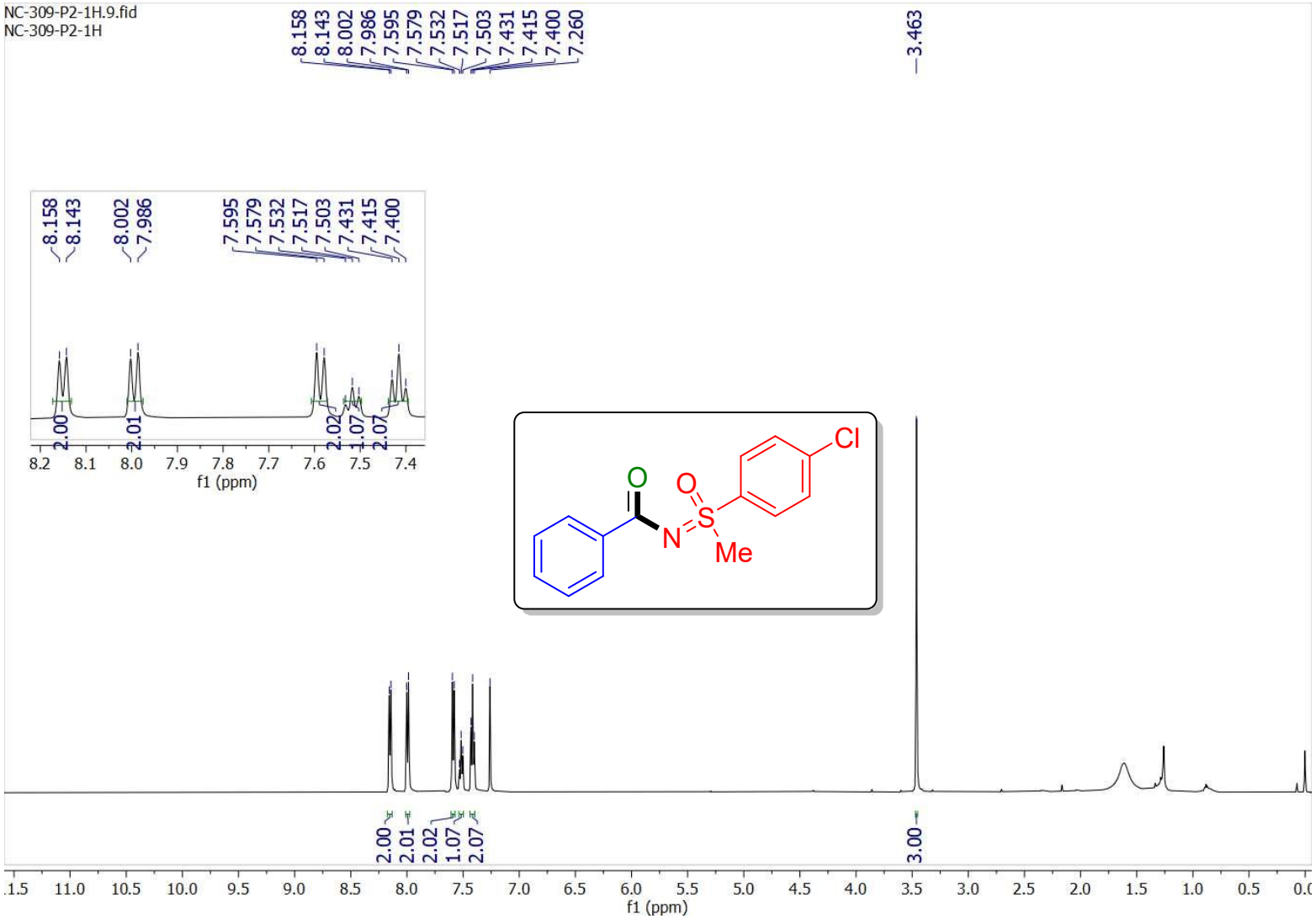
***N-((3-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1e)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



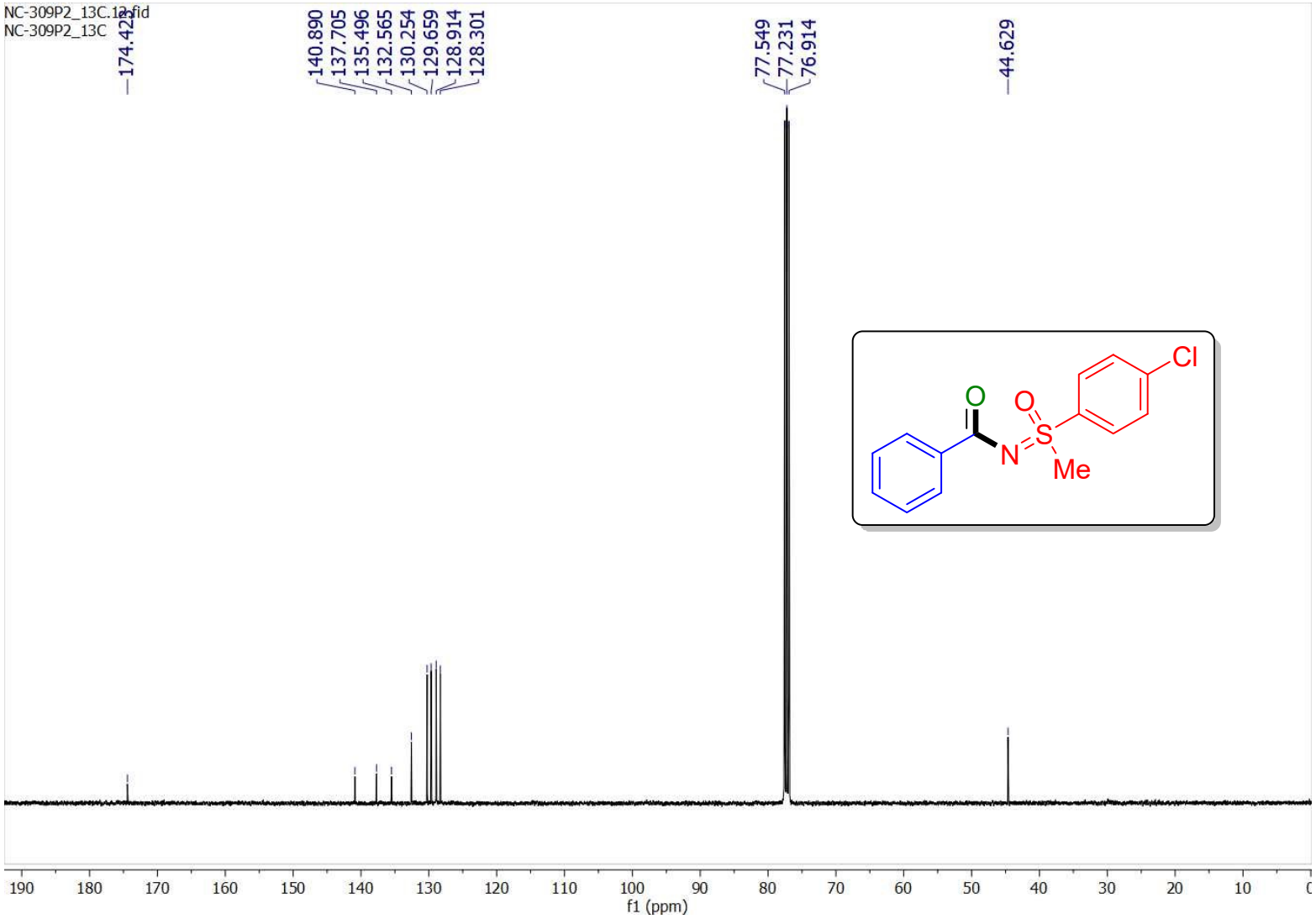
***N-((3-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1e)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



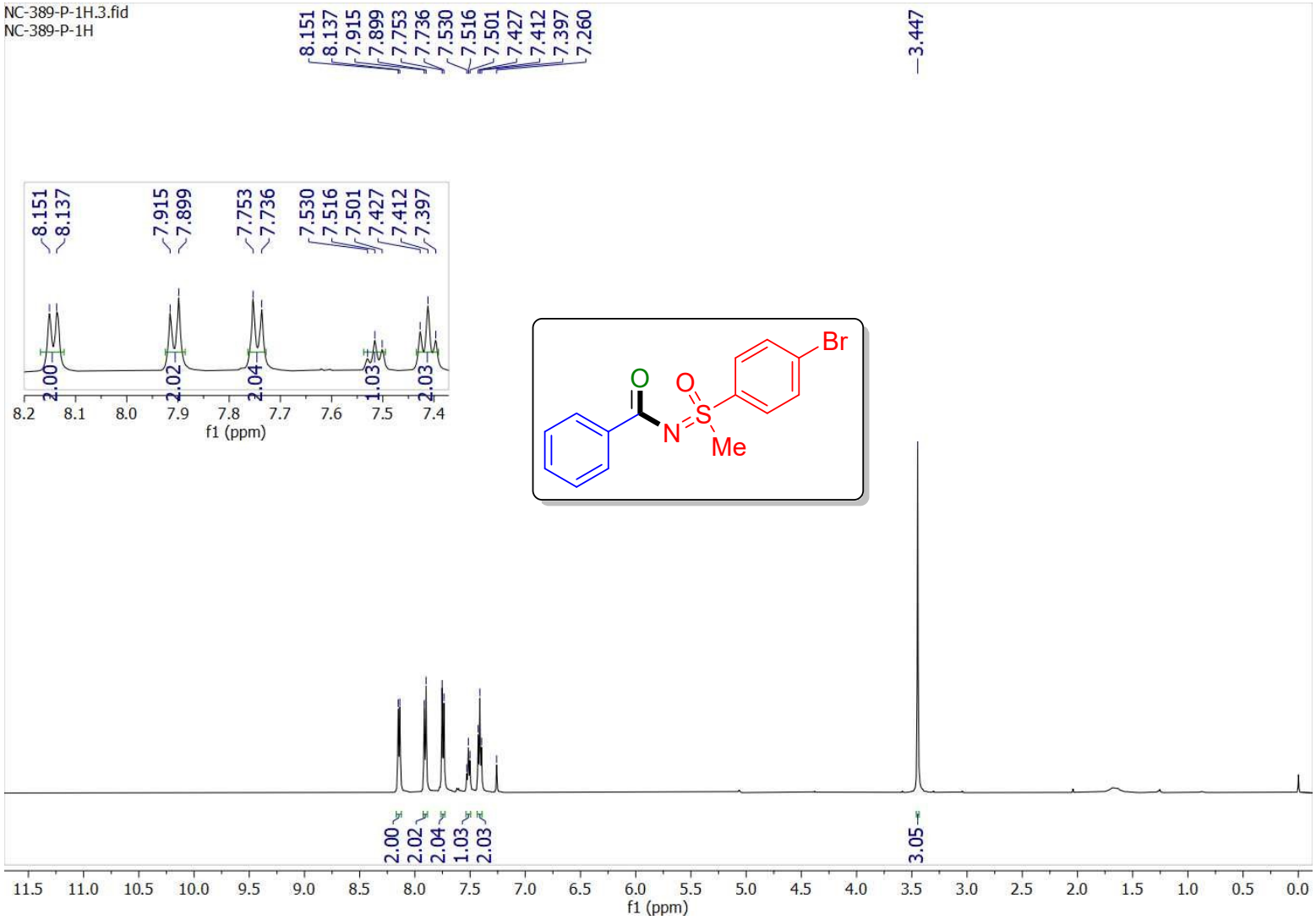
***N-((4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1f)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



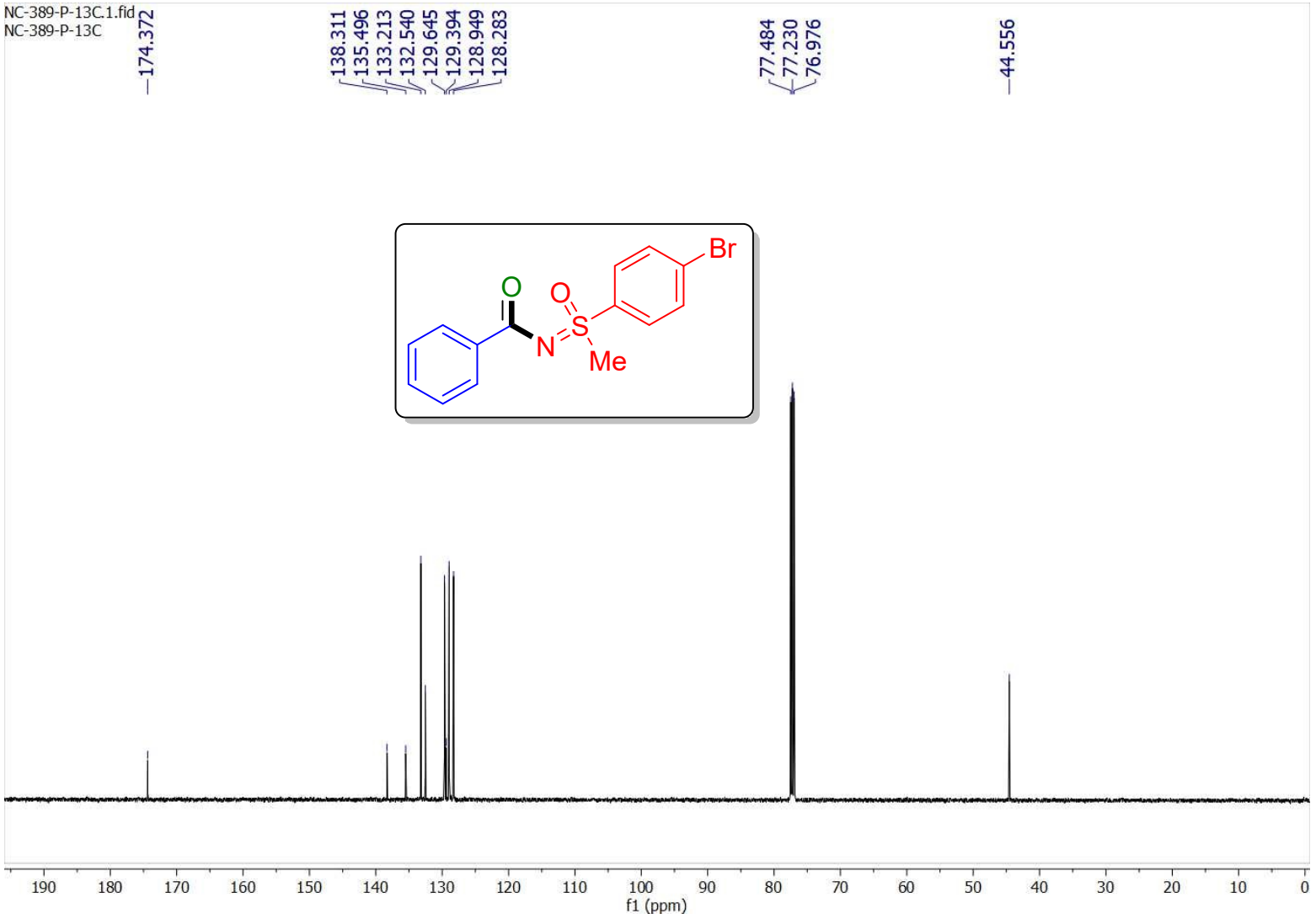
***N-((4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1f)*: ^{13}C NMR (100 MHz, $CDCl_3$)**



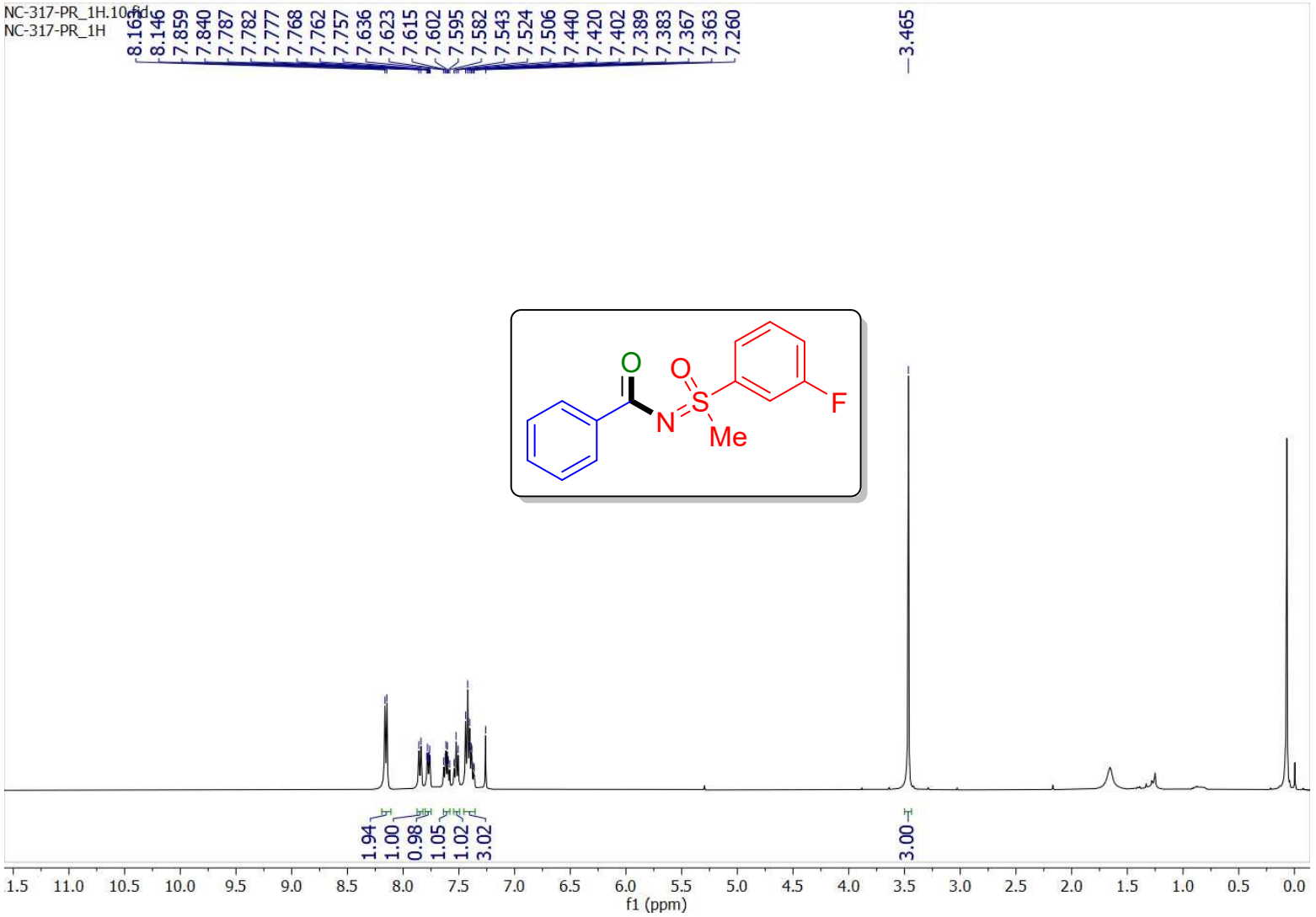
***N-((4-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1g)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



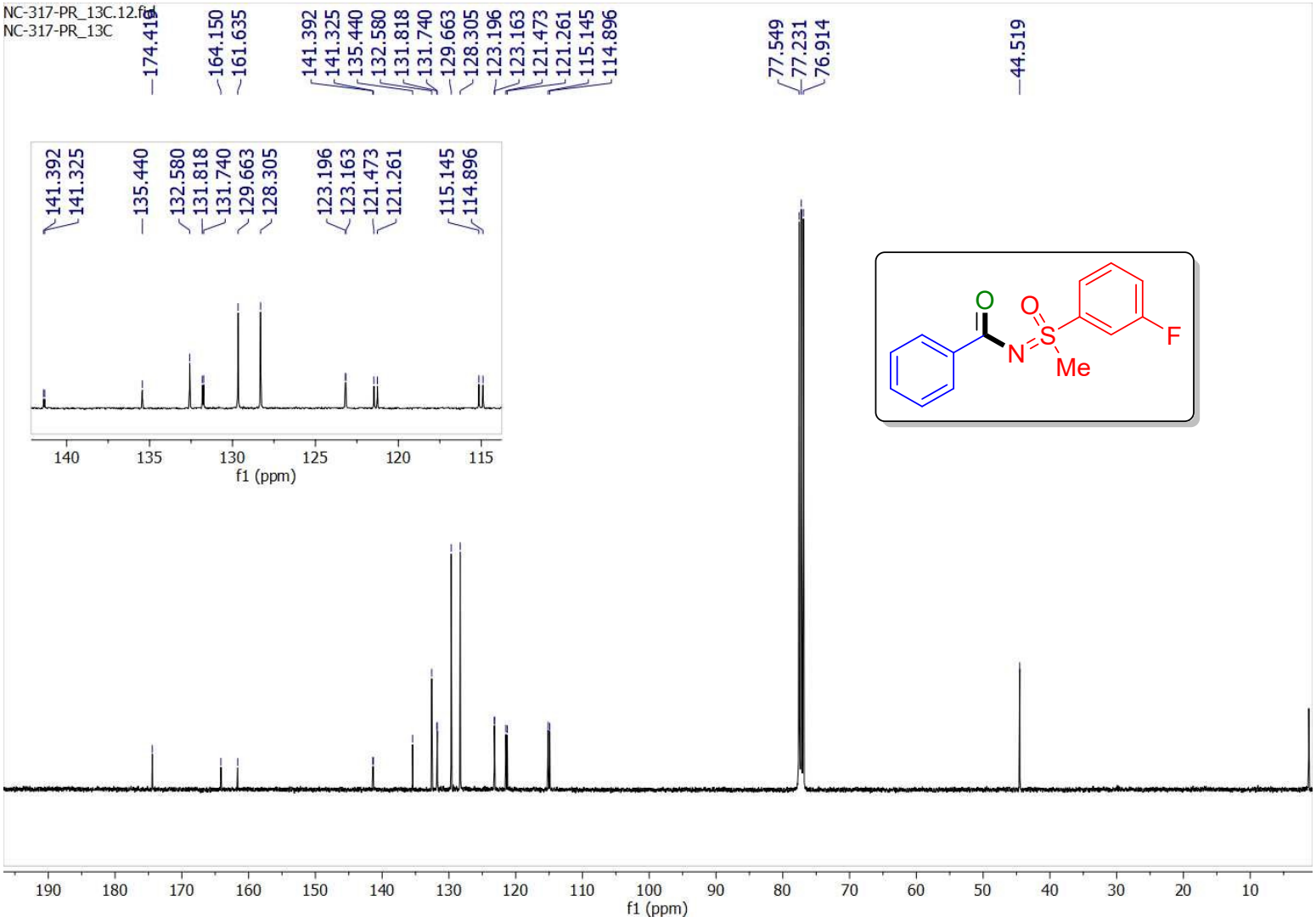
***N-((4-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1g)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



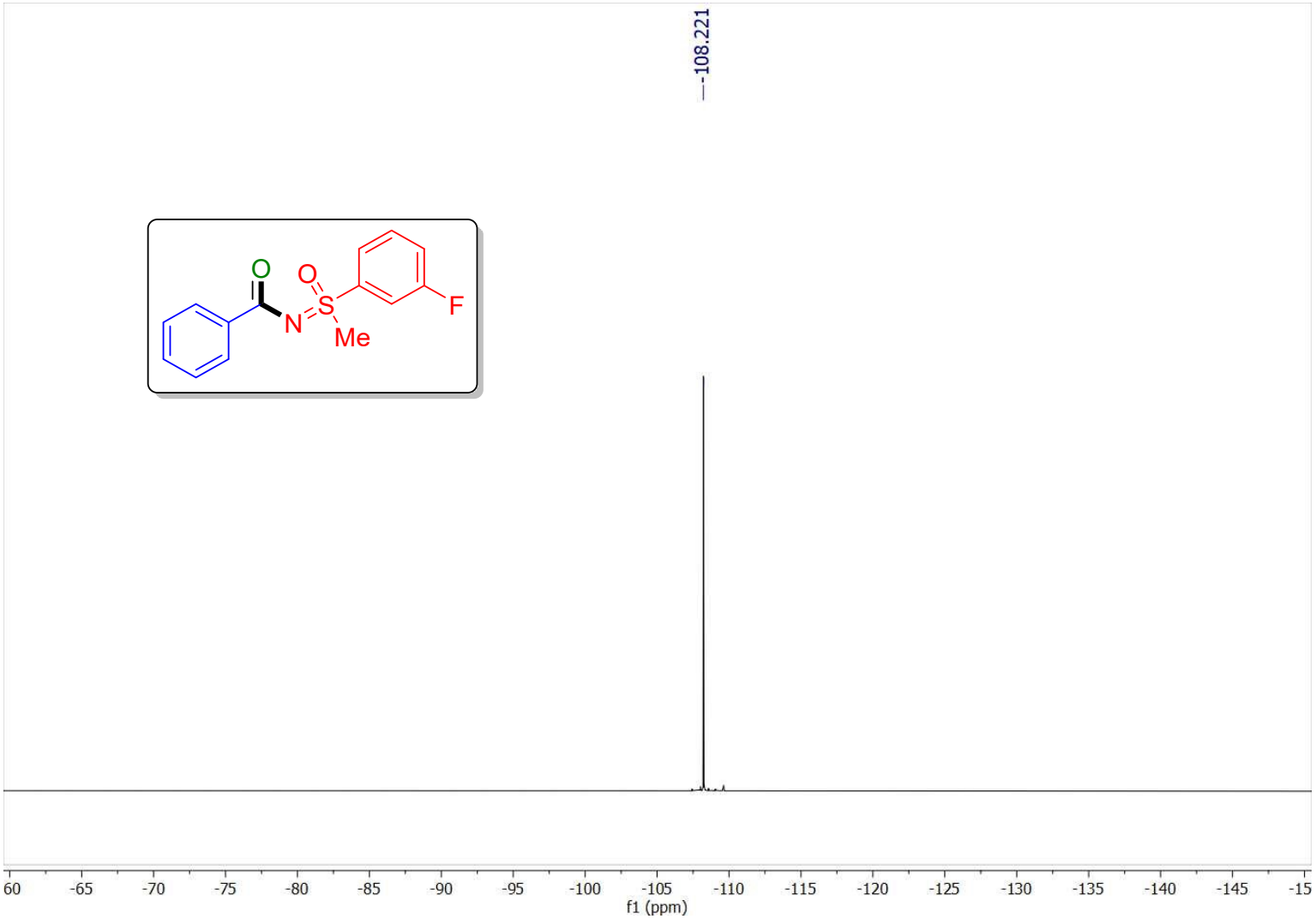
***N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1h)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



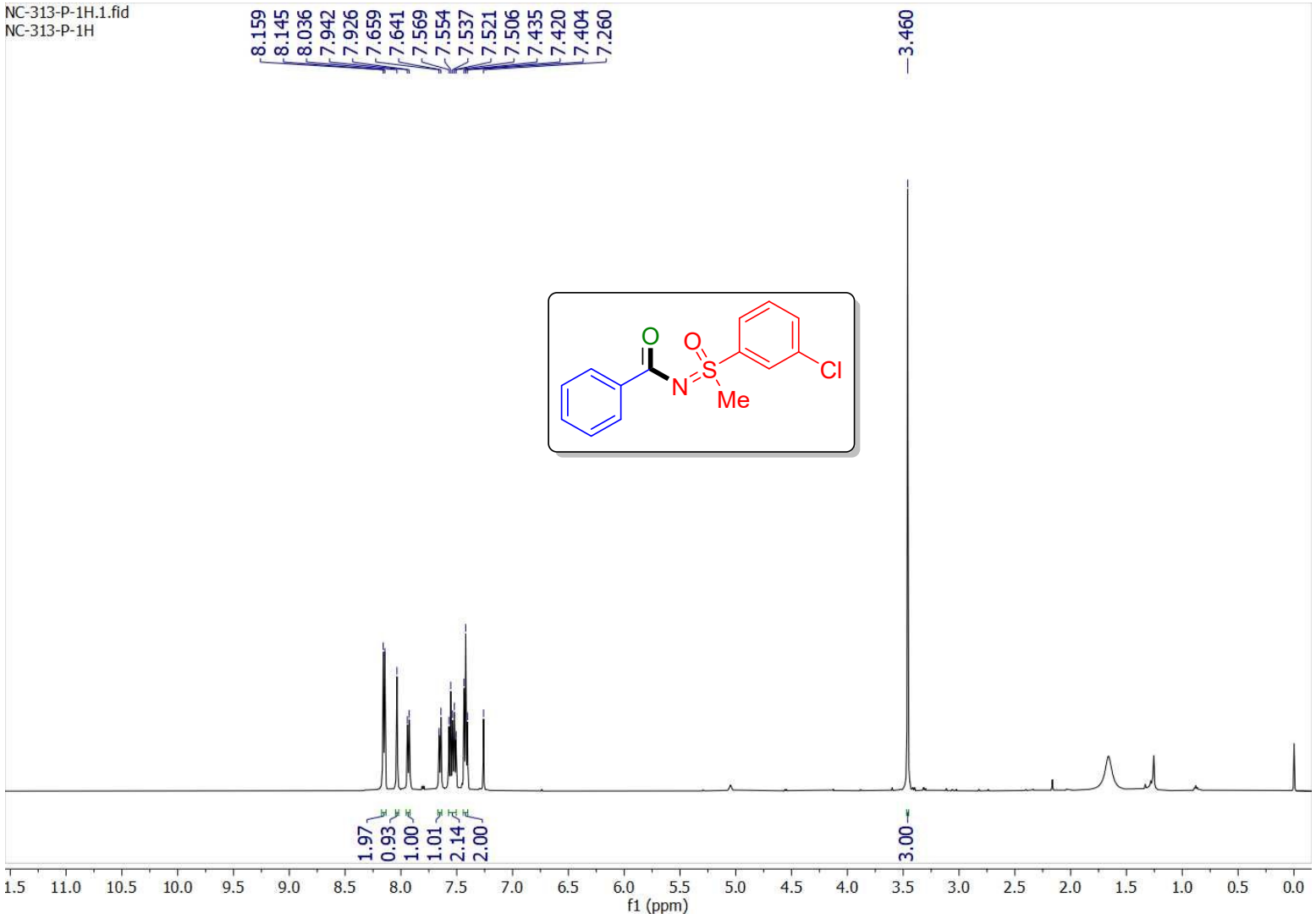
***N*-((3-Fluorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)benzamide (1h)**: **^{13}C NMR (100 MHz, $CDCl_3$)**



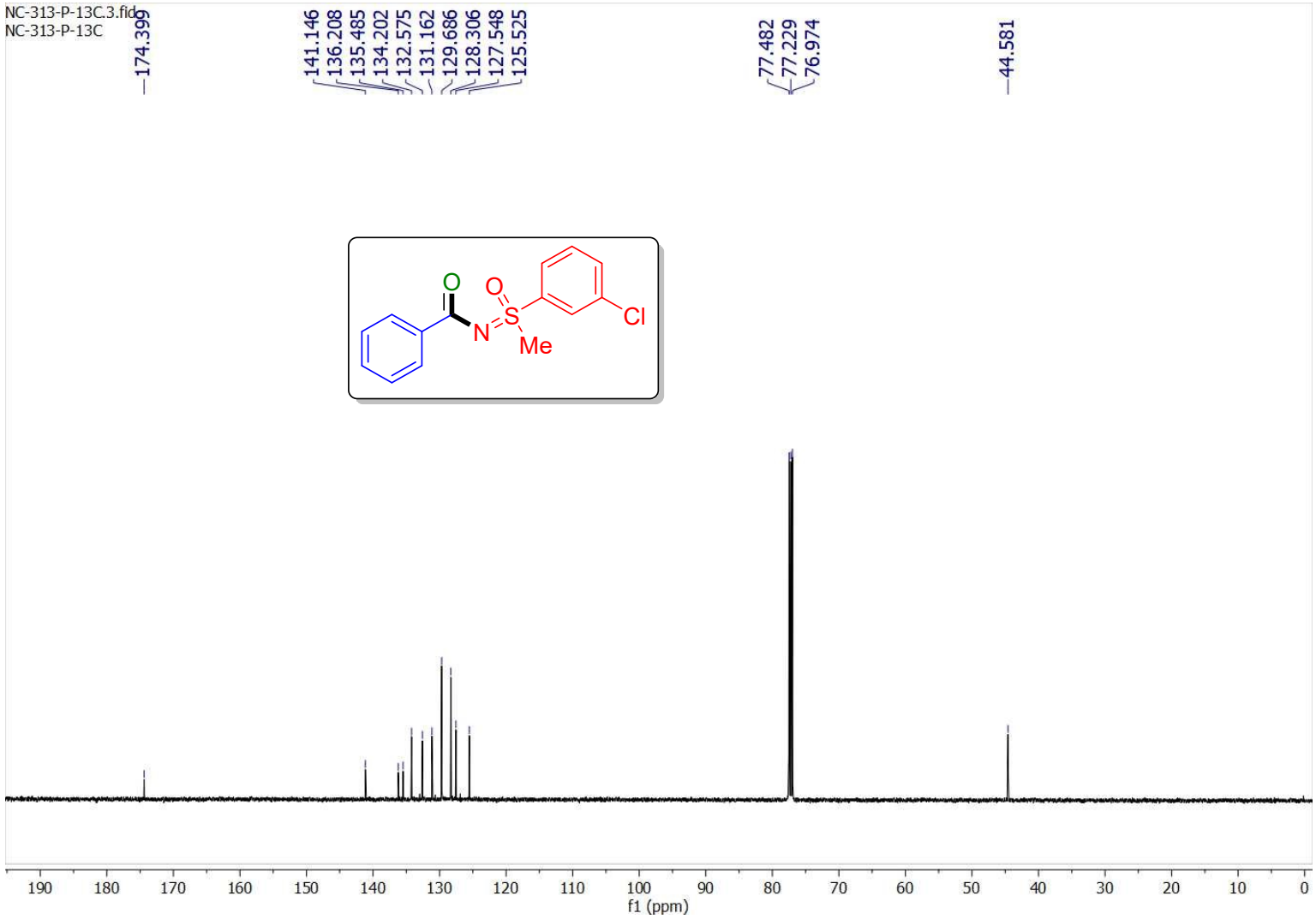
***N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1h)*: ^{19}F NMR (471 MHz, $CDCl_3$)**



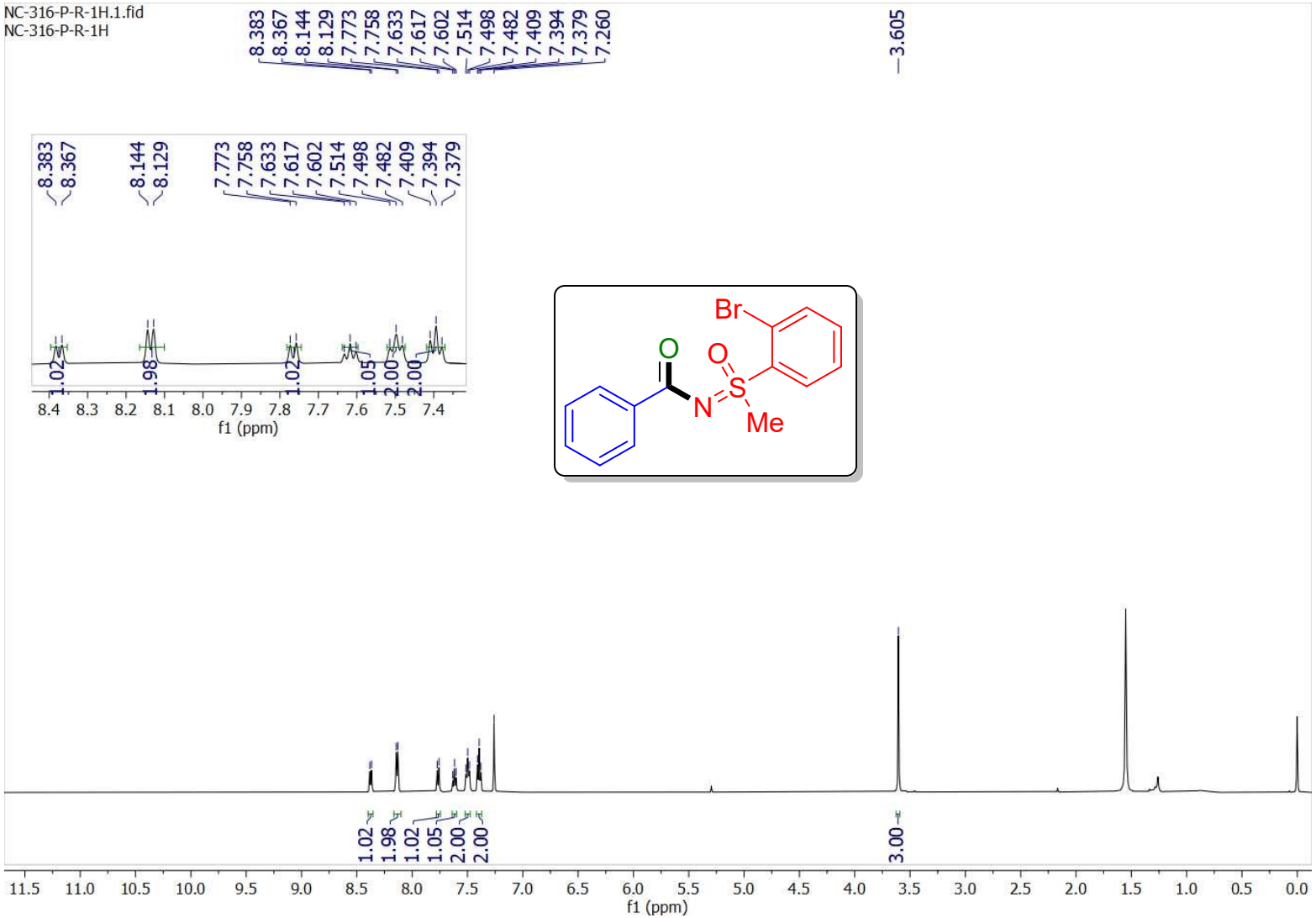
***N-((3-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1i)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



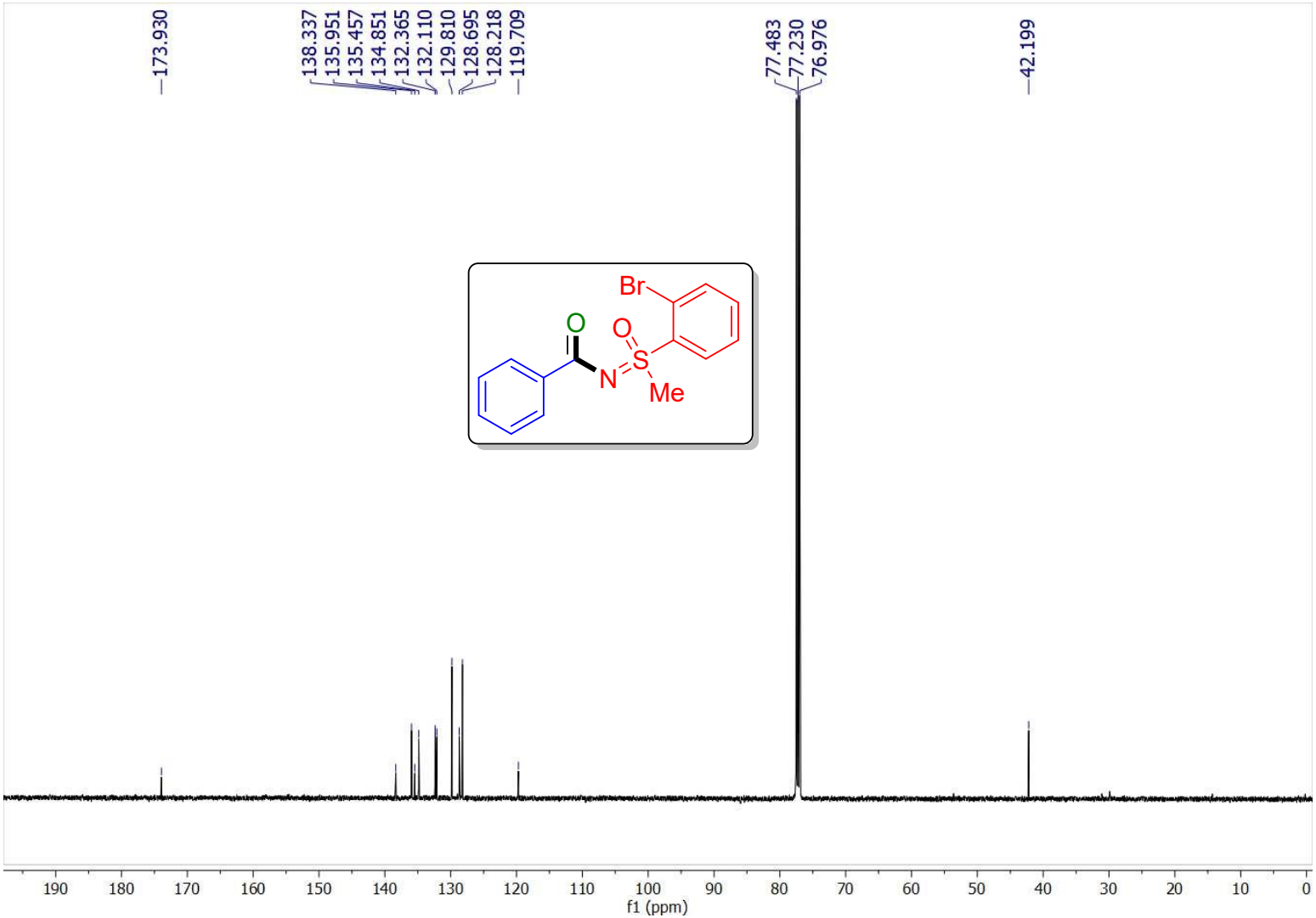
***N-((3-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1i)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



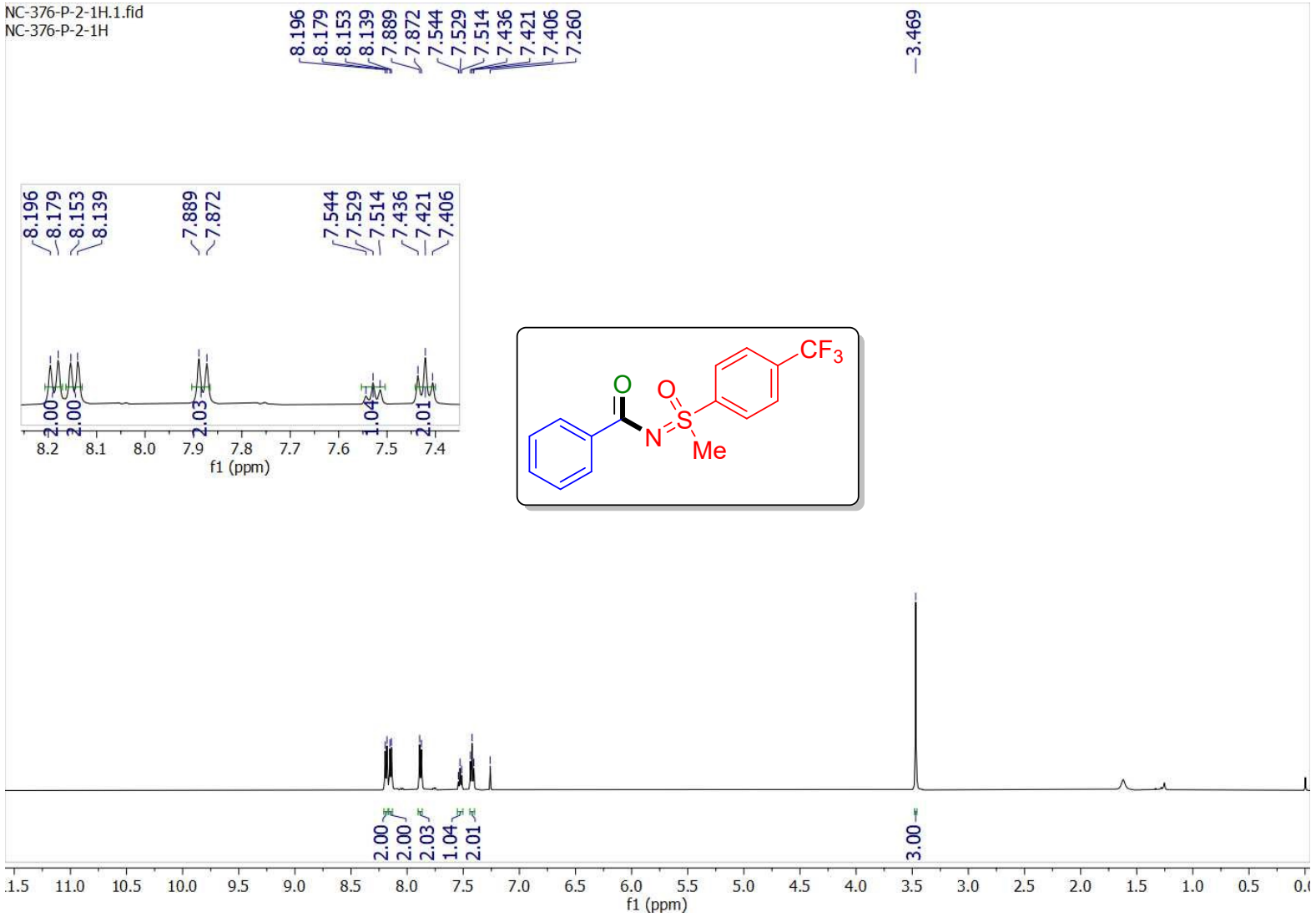
***N*-((2-Bromophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)benzamide (1j)**: **^{1}H NMR (500 MHz, $CDCl_3$)**



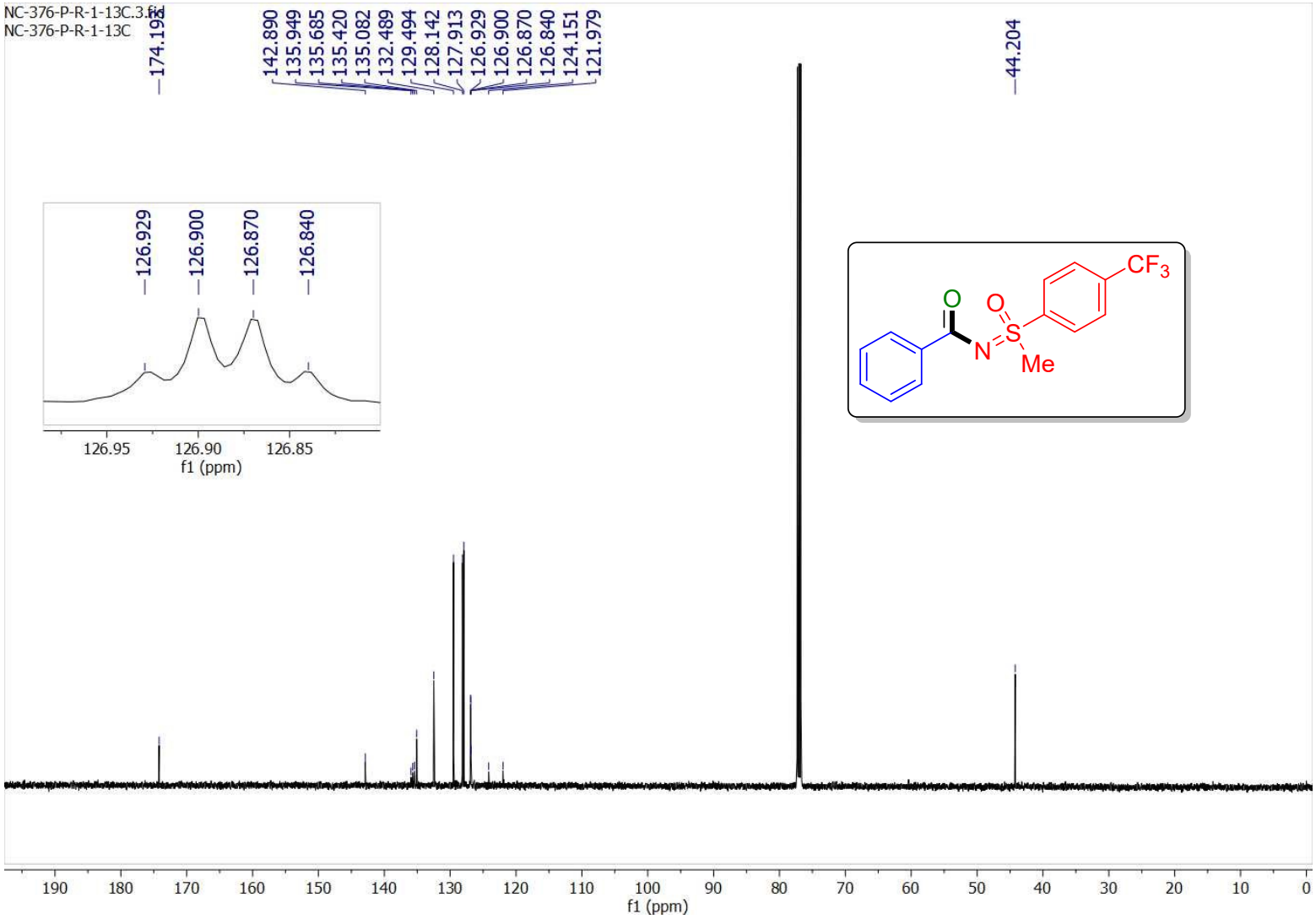
***N-((2-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1j)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



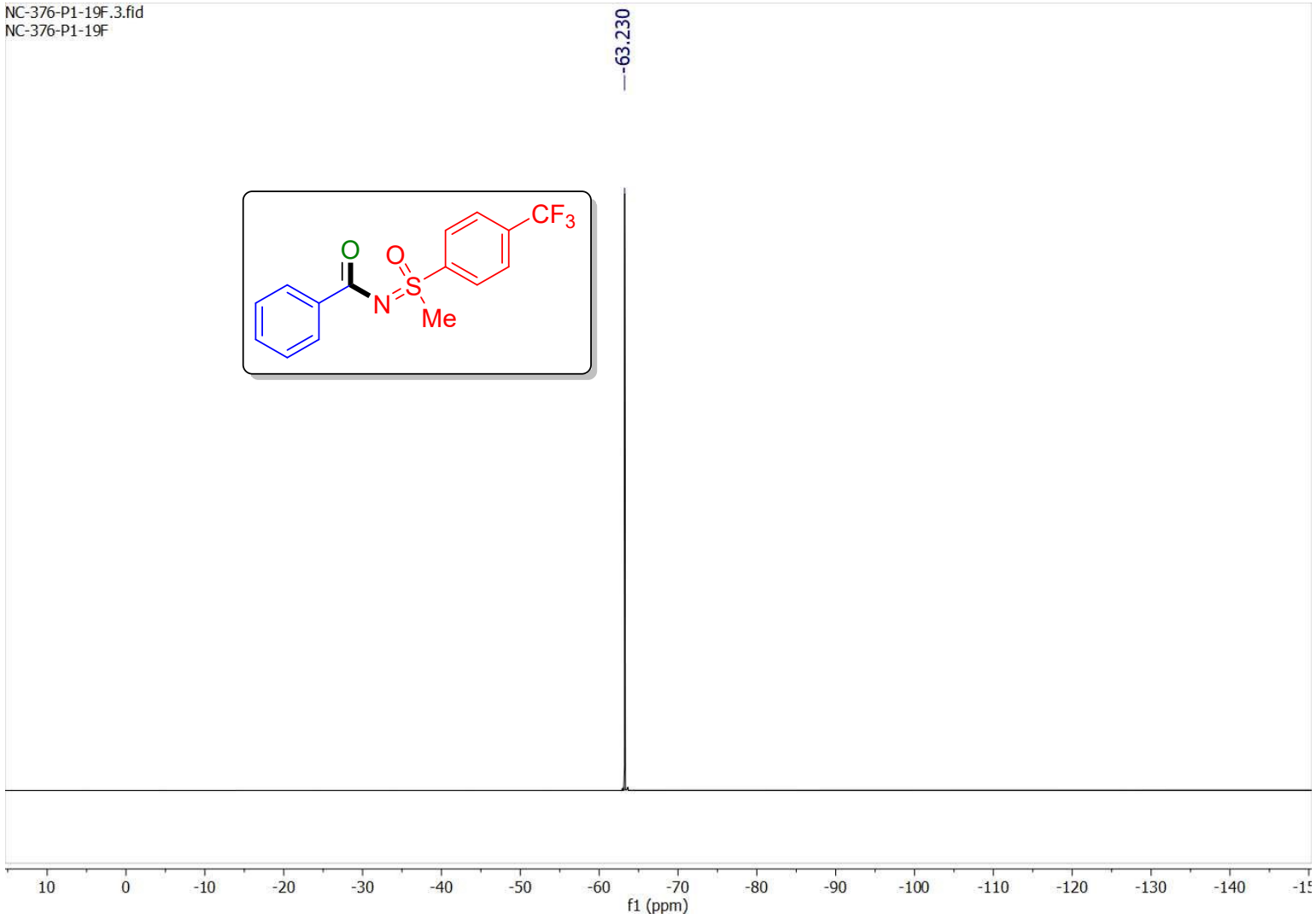
***N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)benzamide (1k)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



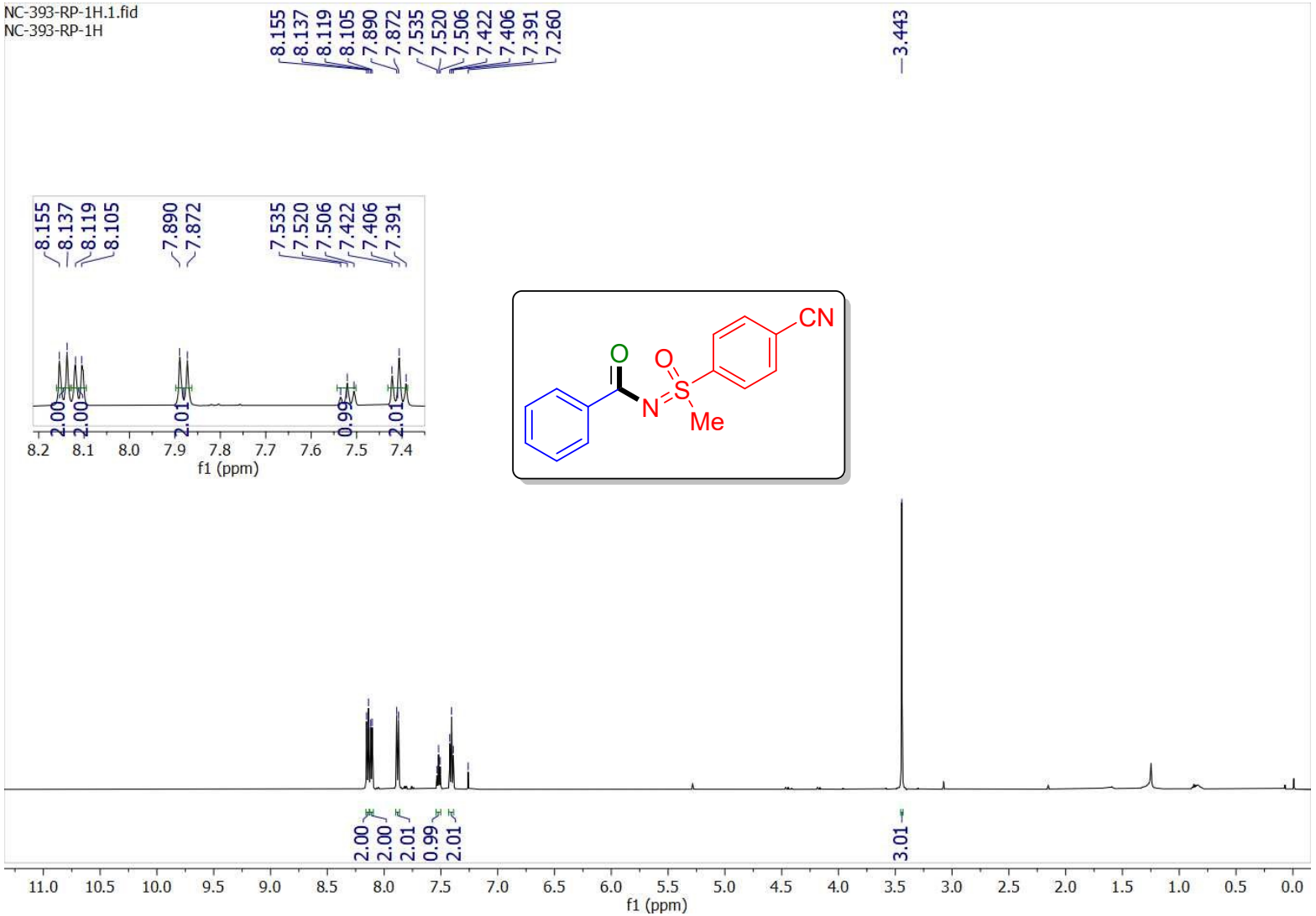
***N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)benzamide (1k)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



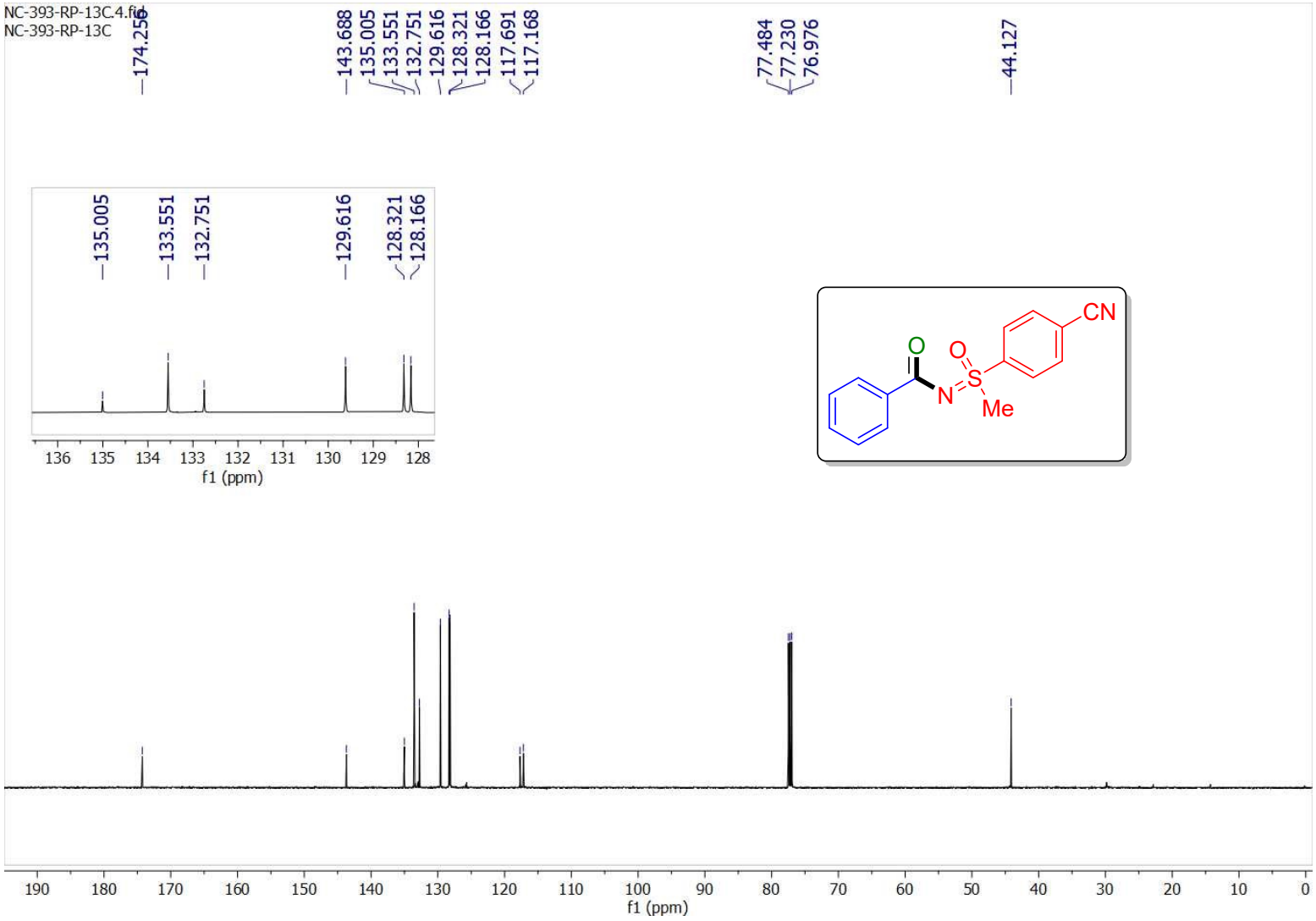
***N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)benzamide (1k)*: ^{19}F NMR (471 MHz, $CDCl_3$)**



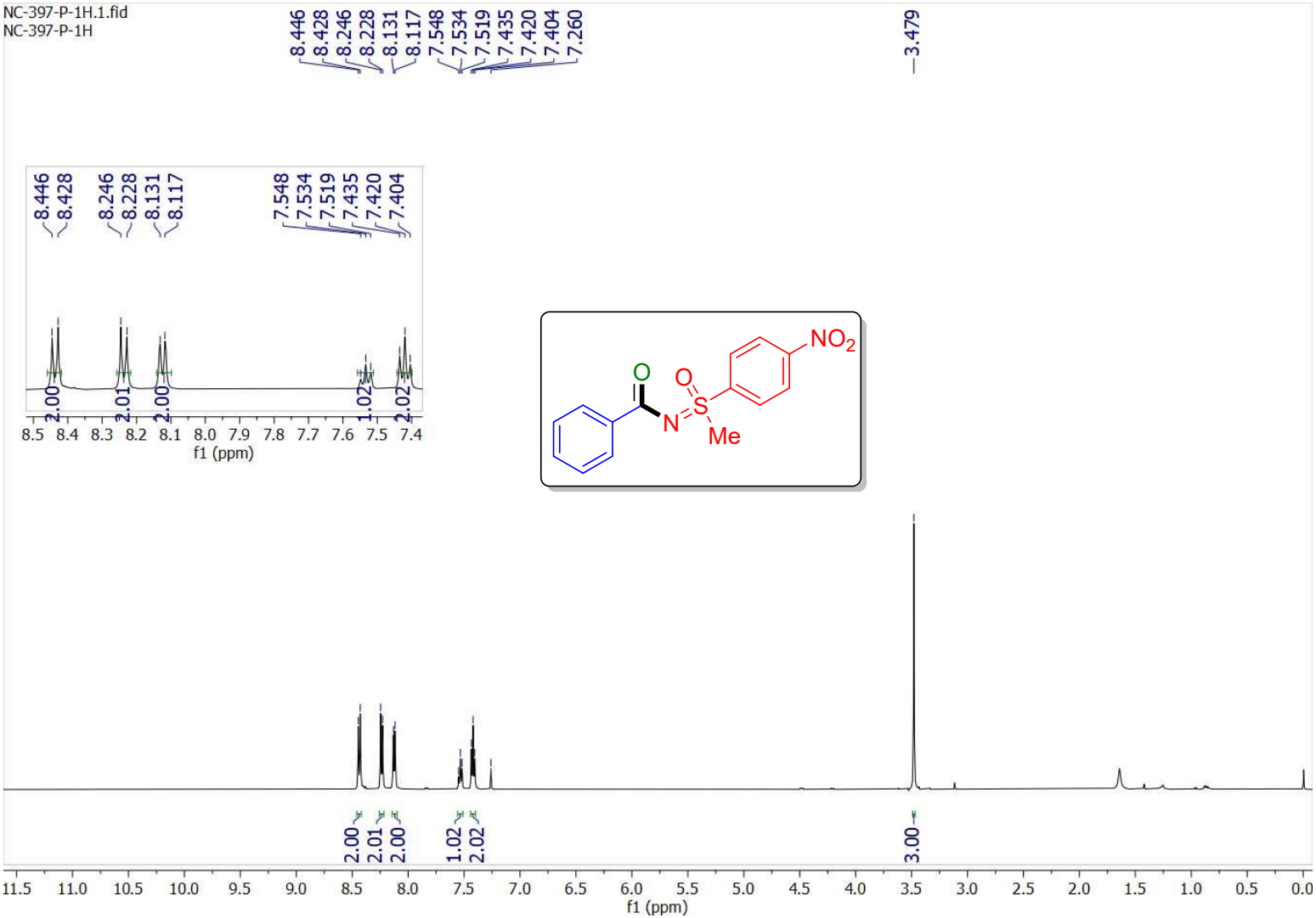
***N-((4-Cyanophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1l)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



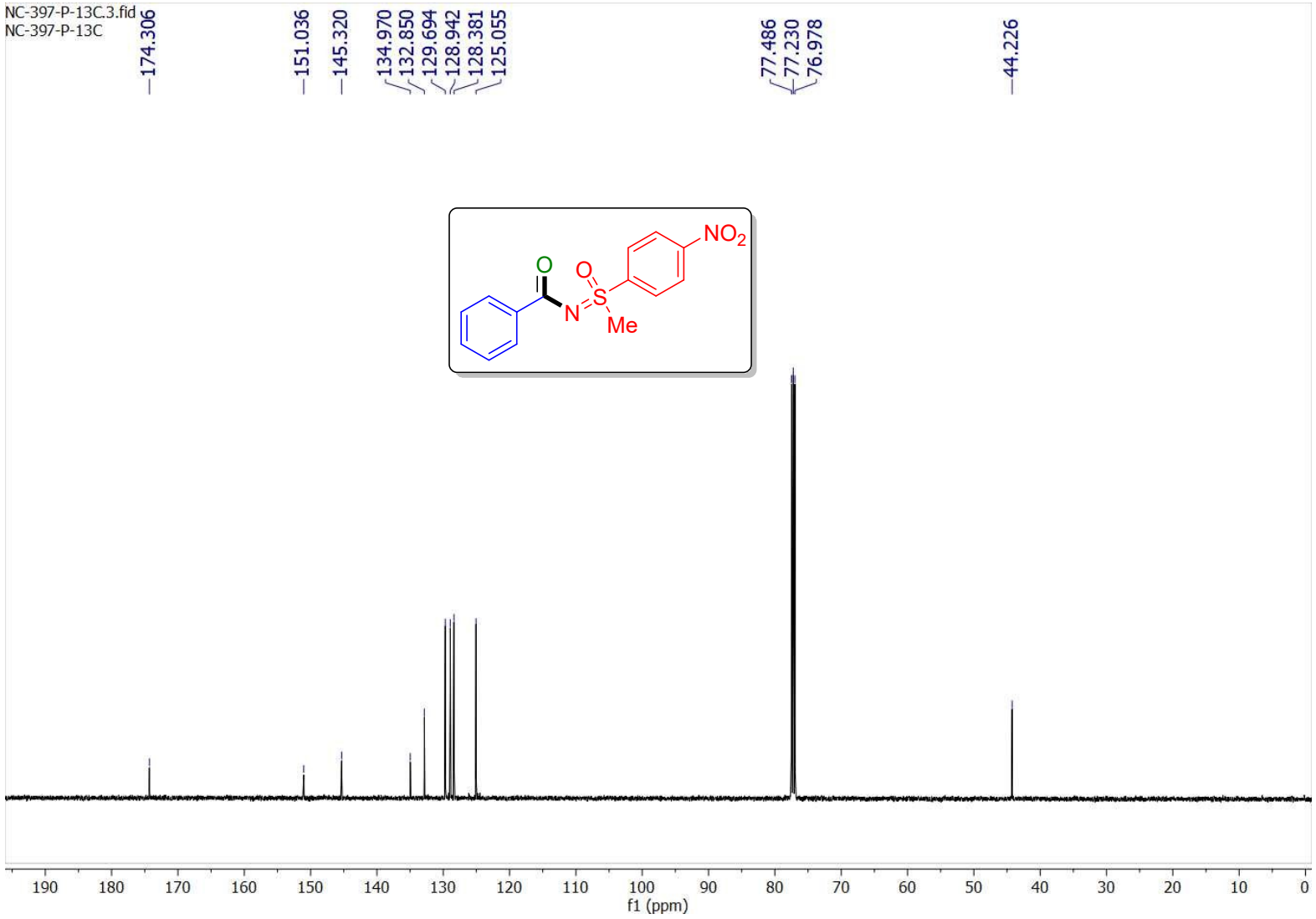
***N-((4-Cyanophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1l)*:^{13}C NMR (125 MHz, $CDCl_3$)**



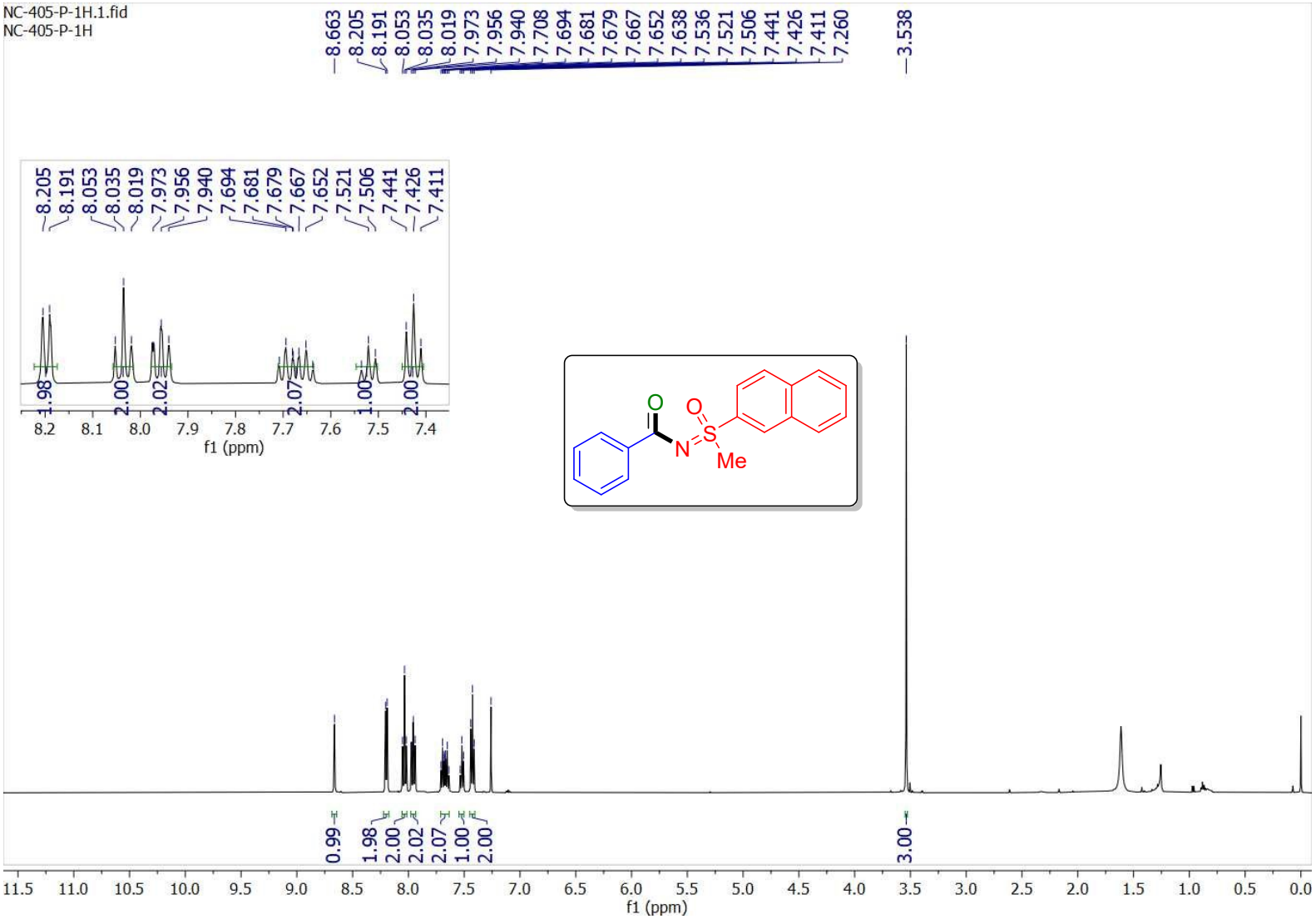
***N-(Methyl(4-nitrophenyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1m)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



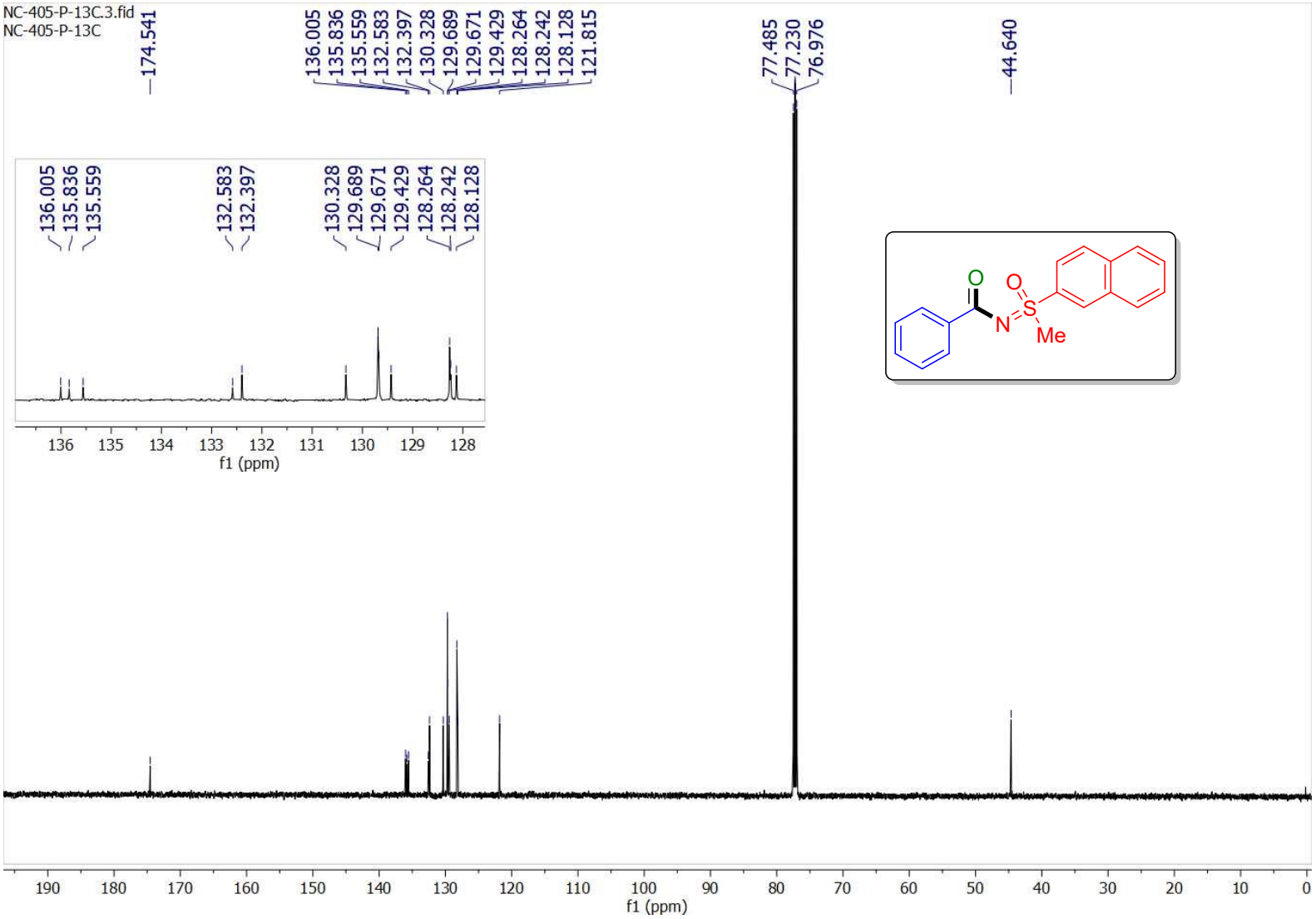
***N-(Methyl(4-nitrophenyl)(oxo)-λ⁶-sulfaneylidene)benzamide (1m)*: ^{13}CNMR (125 MHz, $CDCl_3$)**



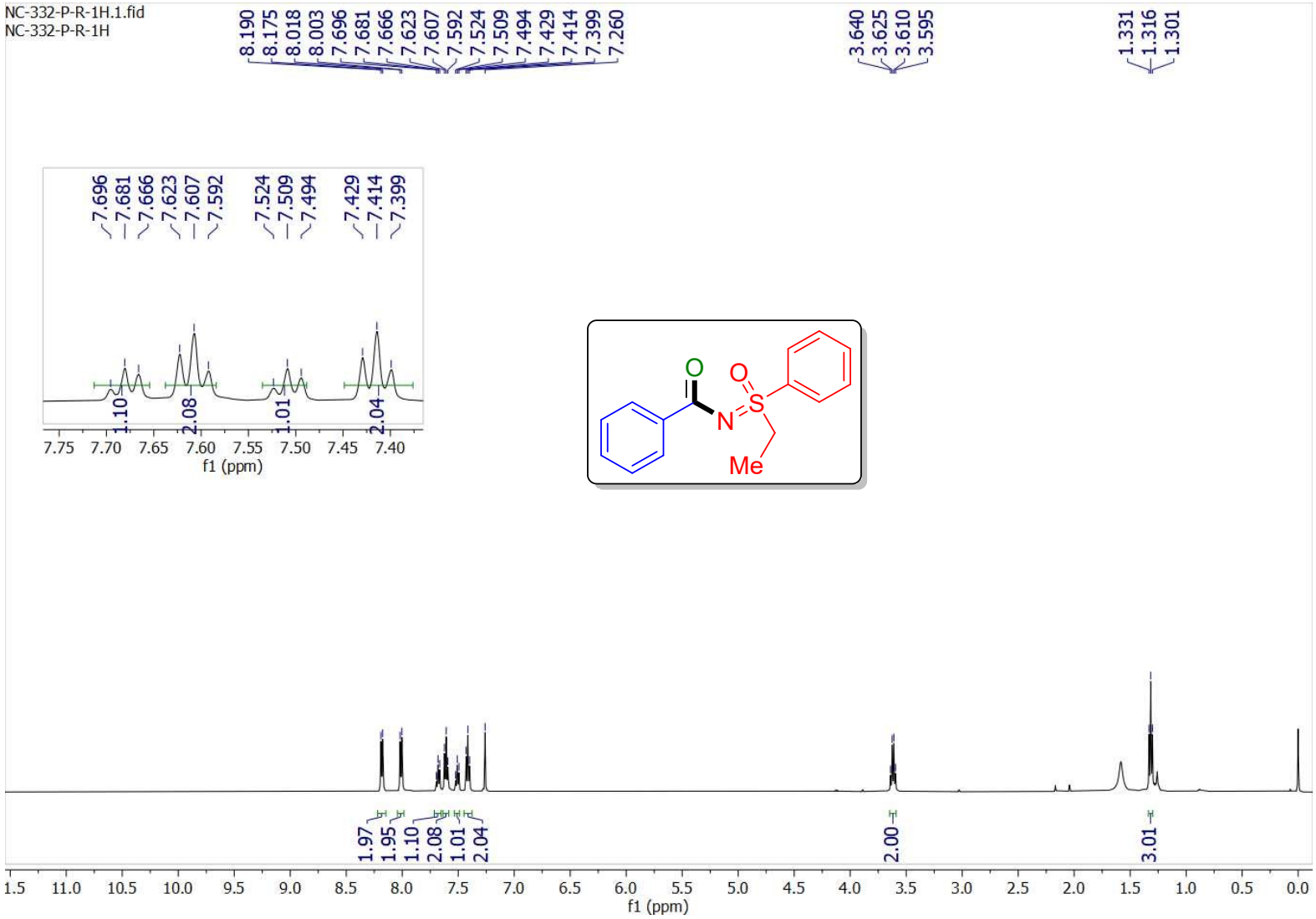
***N-(Methyl(naphthalen-2-yl)(oxo)-λ⁶-sulfaneylidene)benzamide (1n)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



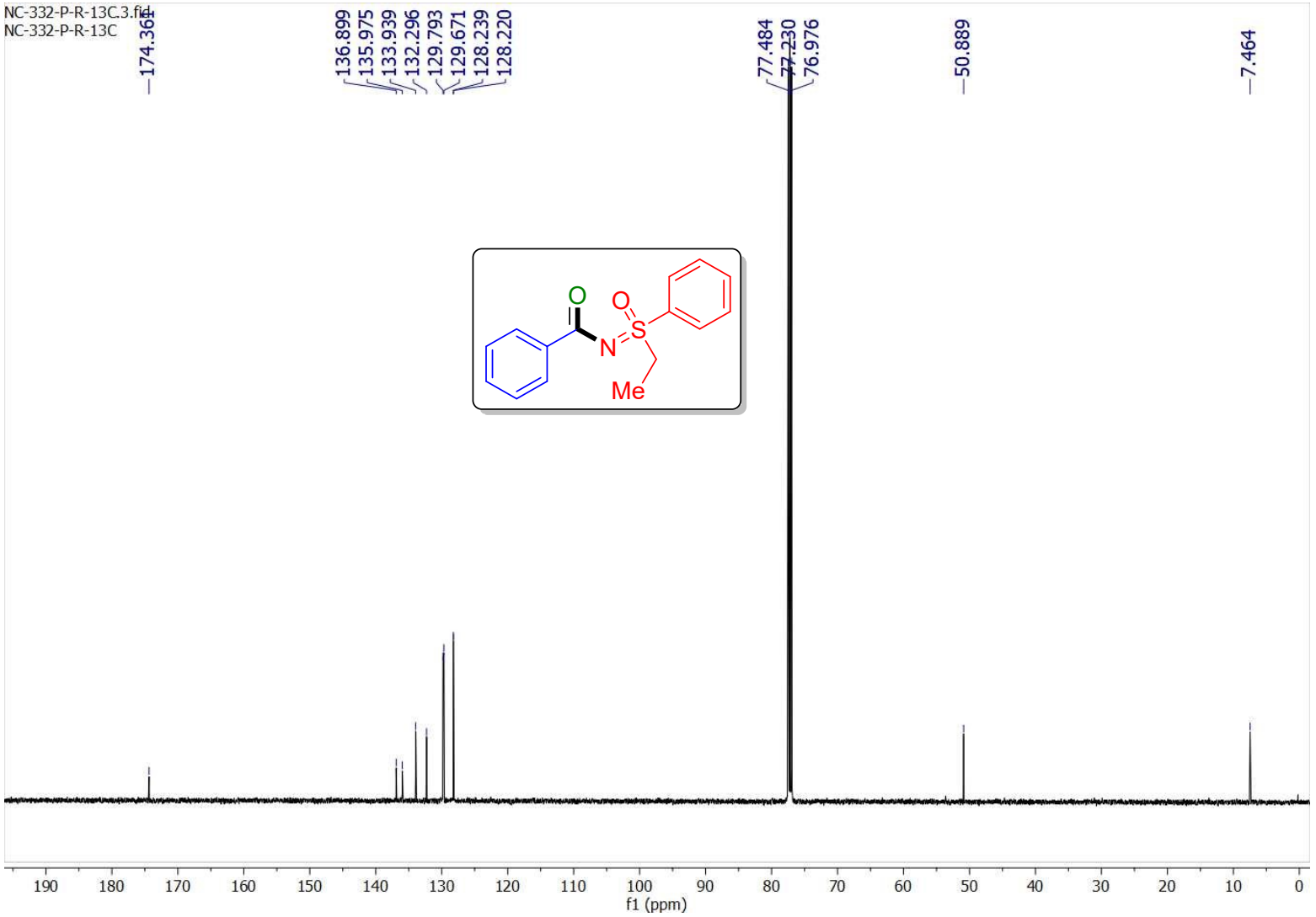
***N-(Methyl(naphthalen-2-yl)(oxo)-λ⁶-sulfaneylidene)benzamide (1n)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



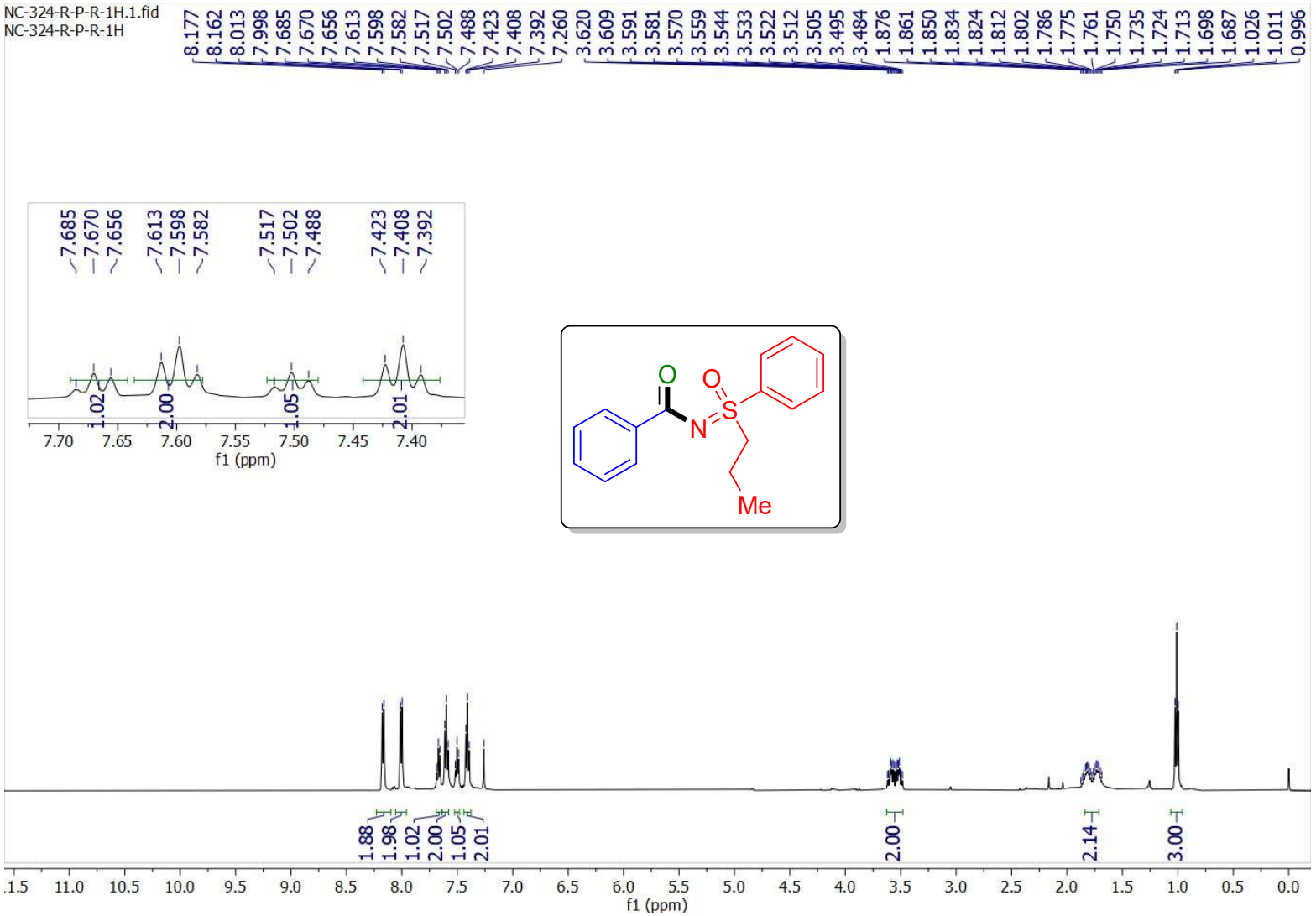
***N-(Ethyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1o)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



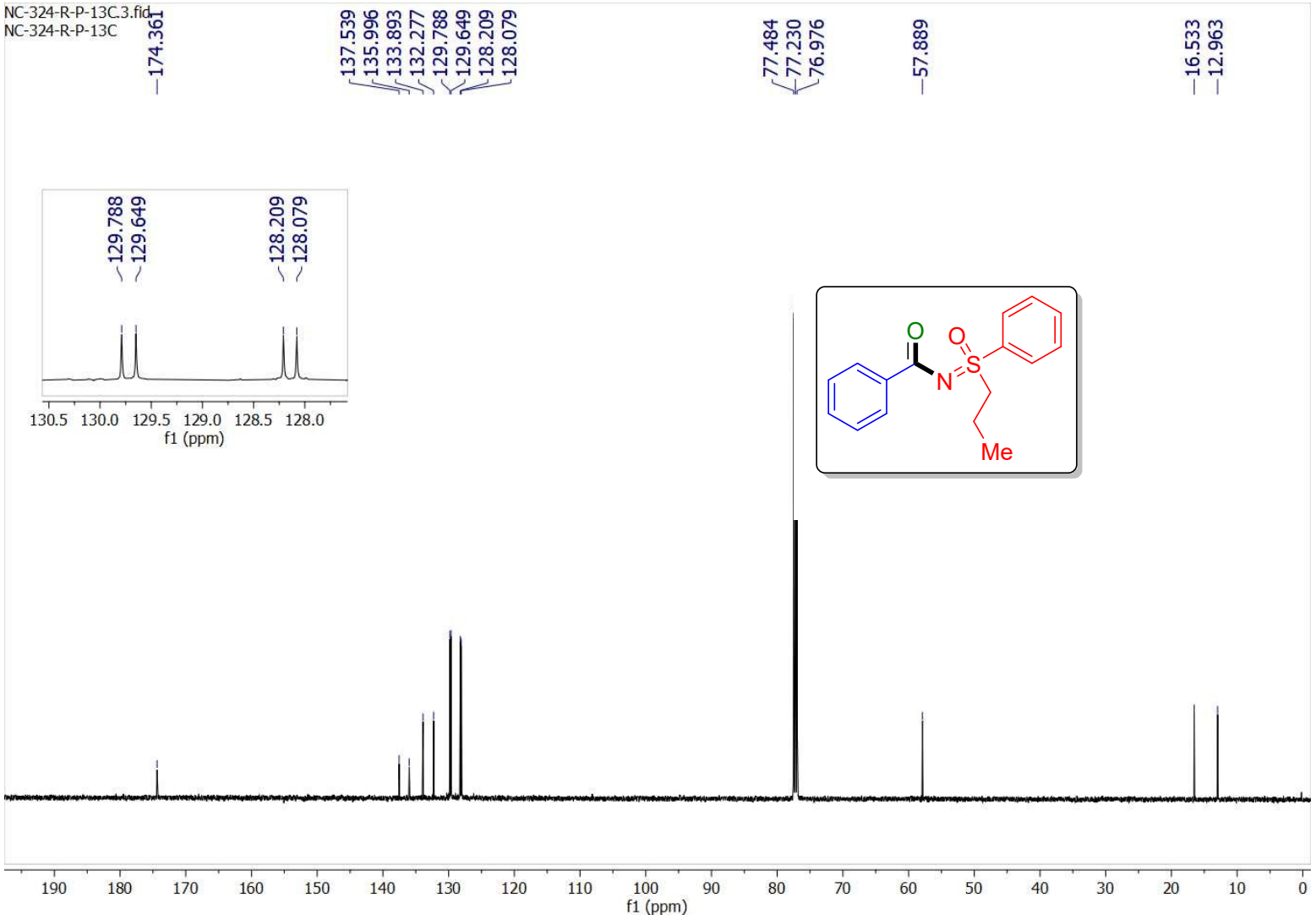
***N-(Ethyl(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (1o)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



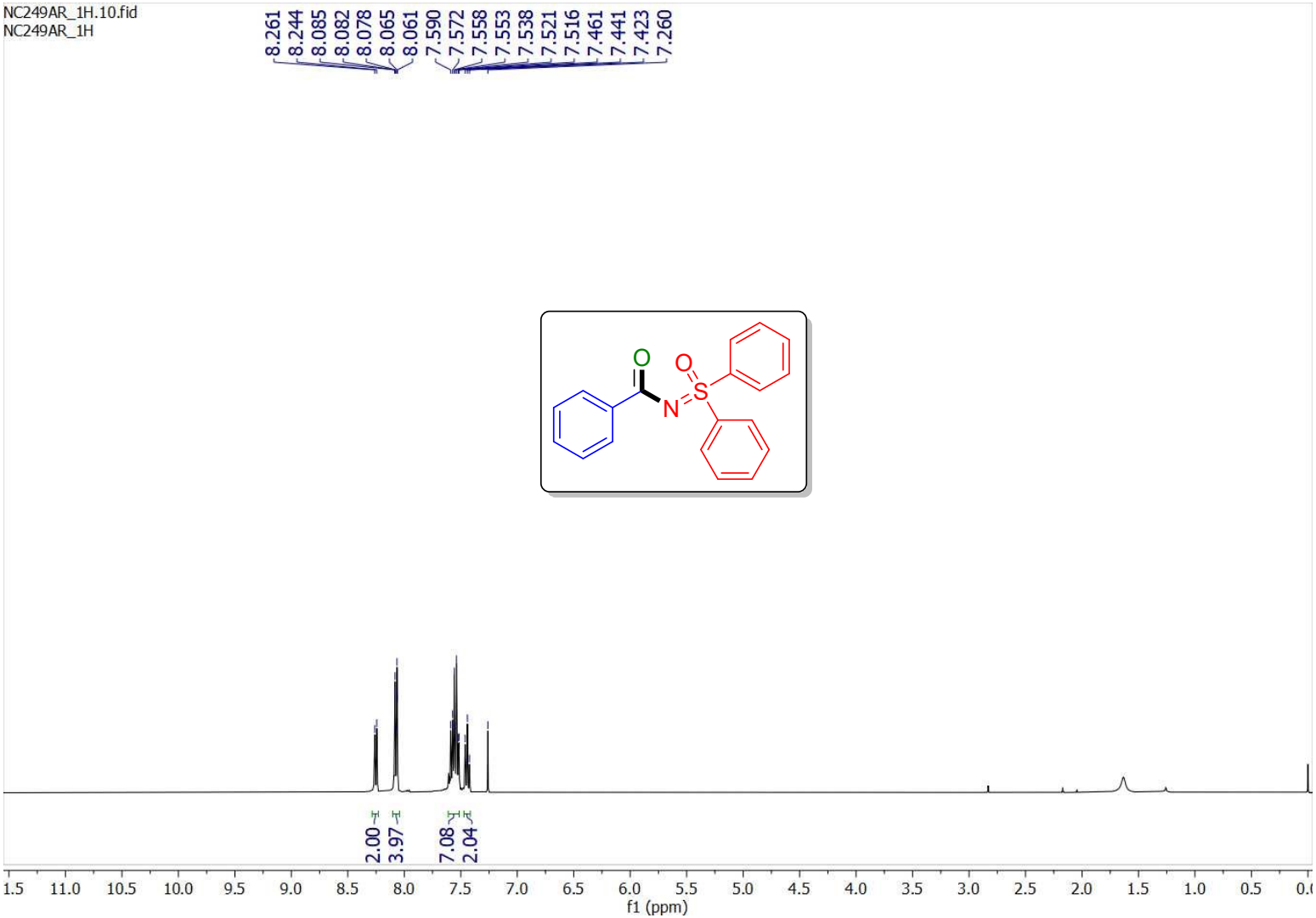
***N-(Oxo(phenyl)(propyl)-λ⁶-sulfaneylidene)benzamide (1p)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



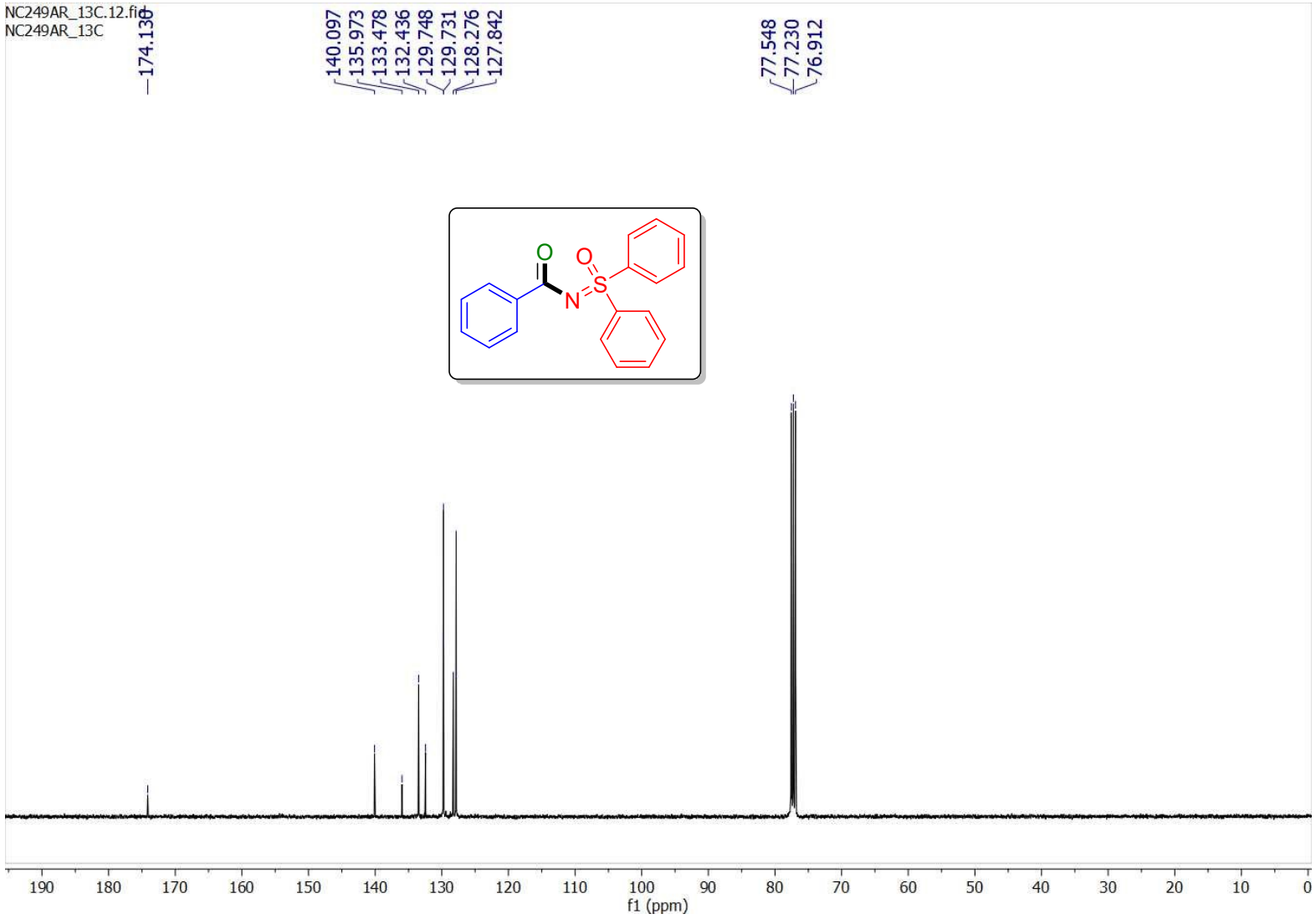
***N-(Oxo(phenyl)(propyl)-λ⁶-sulfaneylidene)benzamide (1p)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



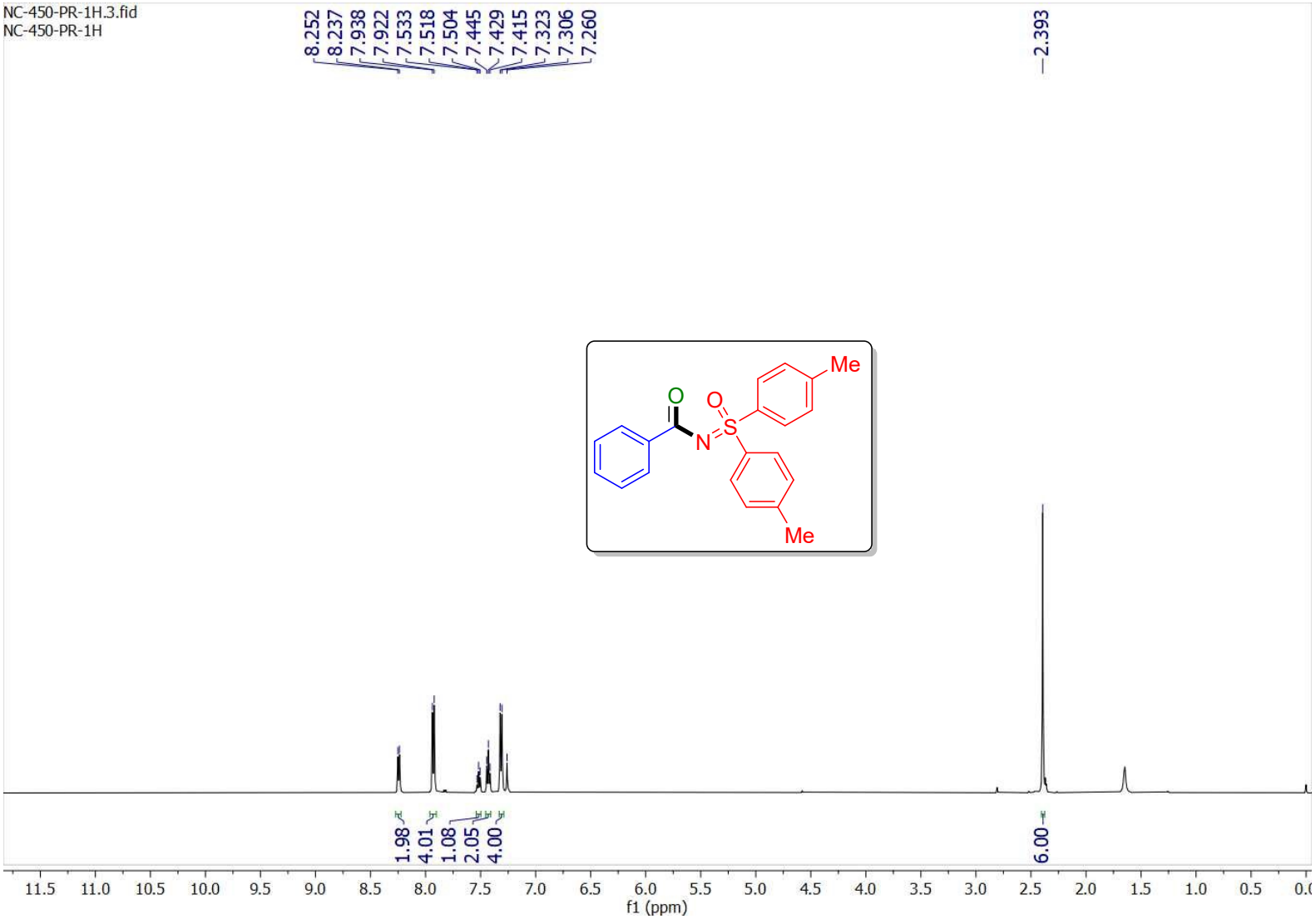
***N-(Oxodiphenyl-λ⁶-sulfaneylidene)benzamide (1q)*: ^{1}H NMR (400 MHz, $CDCl_3$)**



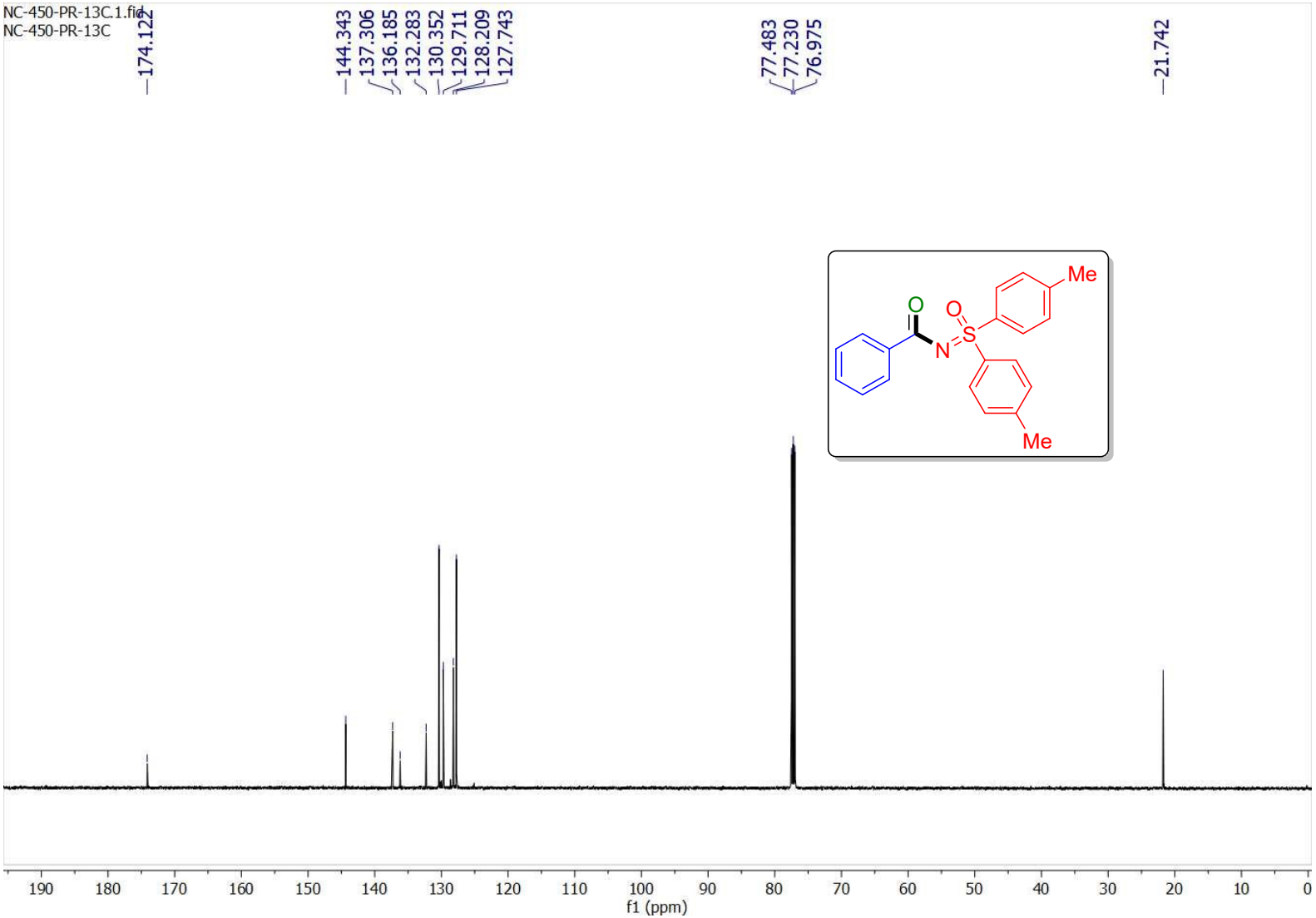
***N-(Oxodiphenyl-λ⁶-sulfaneylidene)benzamide (1q)*: ^{13}CNMR (100 MHz, $CDCl_3$)**



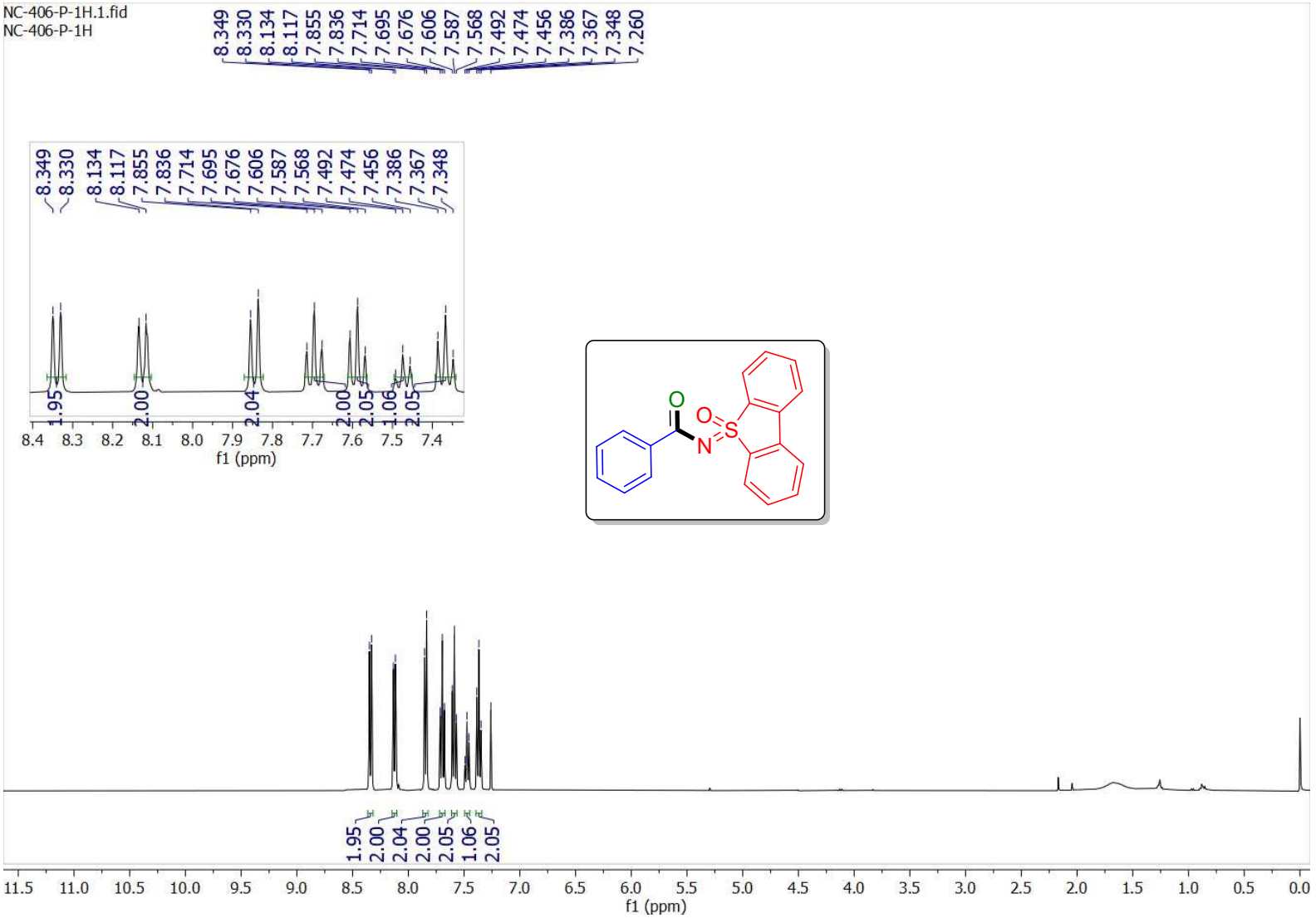
***N-(Oxodi-p-tolyl-λ⁶-sulfaneylidene)benzamide (1r)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



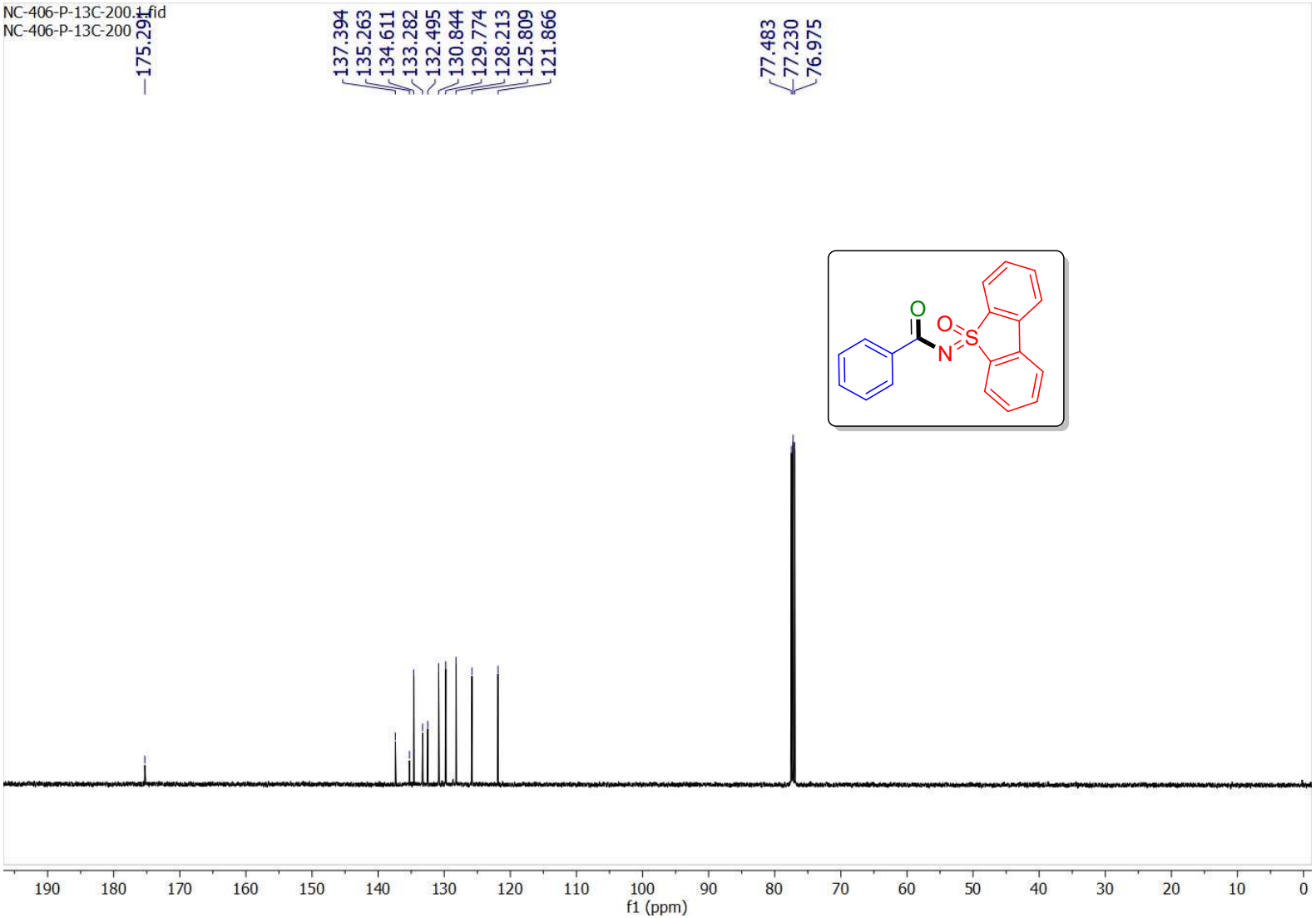
***N-(Oxodi-p-tolyl-λ⁶-sulfaneylidene)benzamide (1r)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



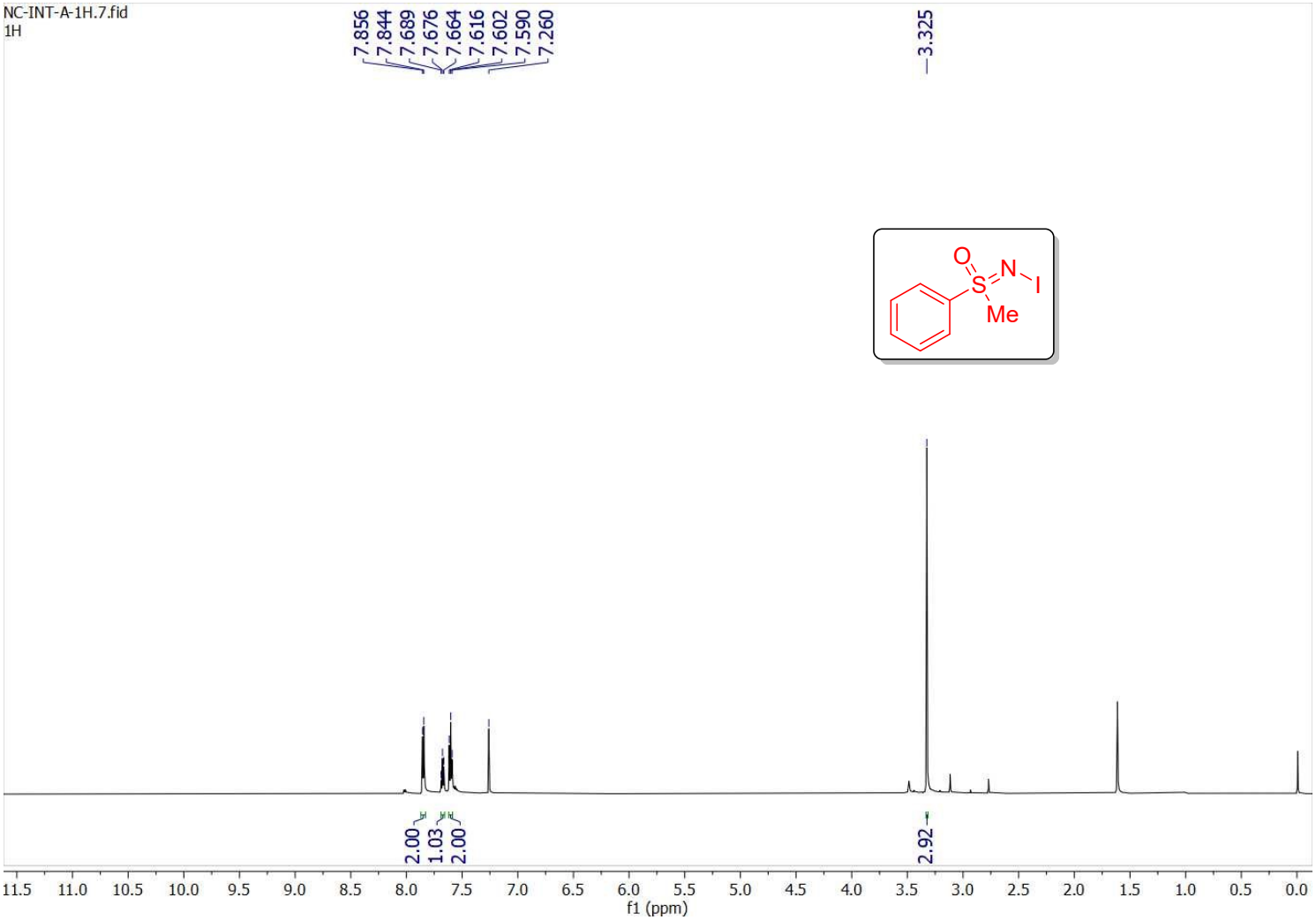
***N-(5-Oxido-5λ⁴-dibenzo[b,d]thiophen-5-ylidene)benzamide (1s)*: ^{1}H NMR (500 MHz, $CDCl_3$)**



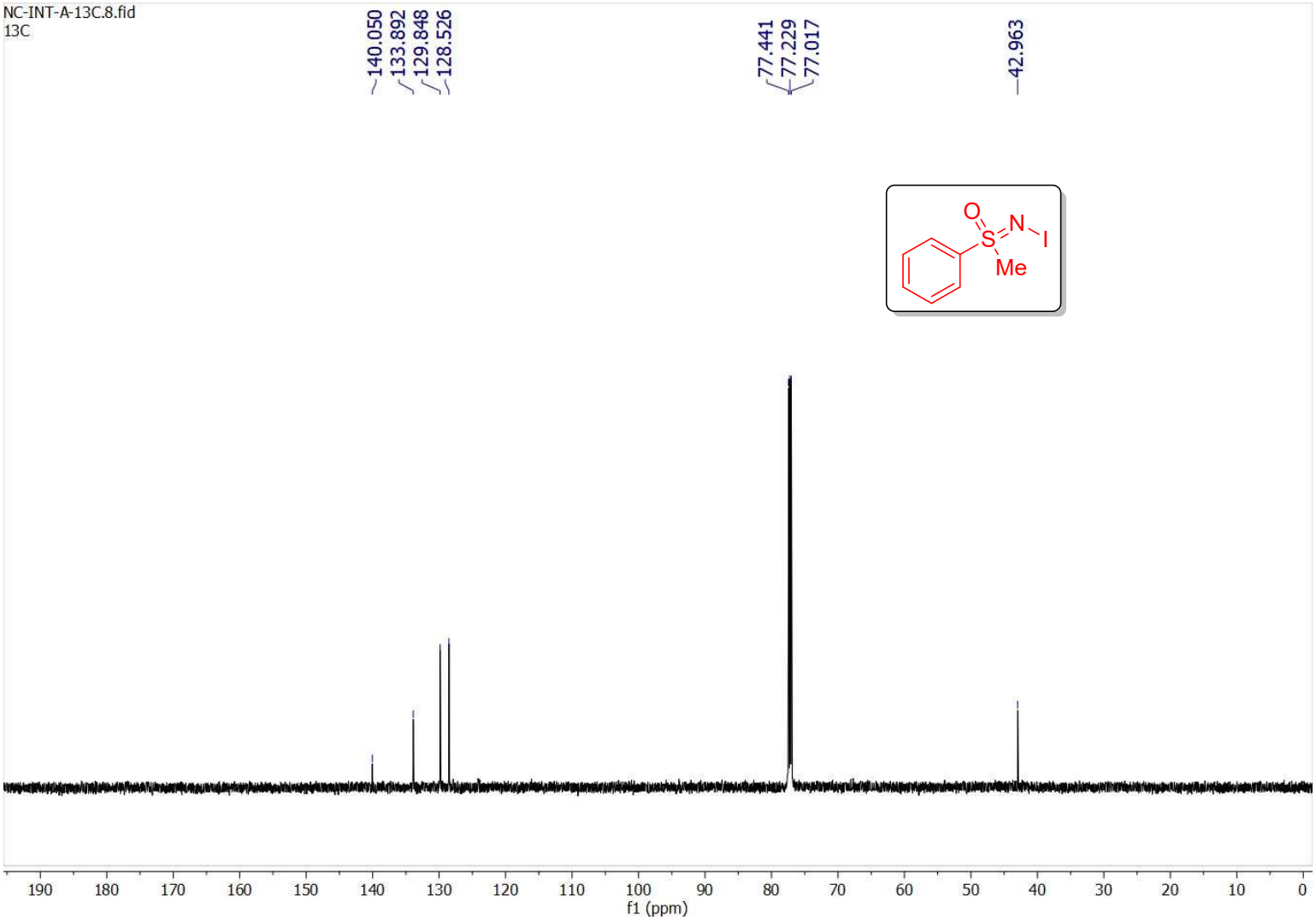
***N-(5-Oxido-5λ⁴-dibenzo[b,d]thiophen-5-ylidene)benzamide (1s)*: ^{13}C NMR (125 MHz, $CDCl_3$)**



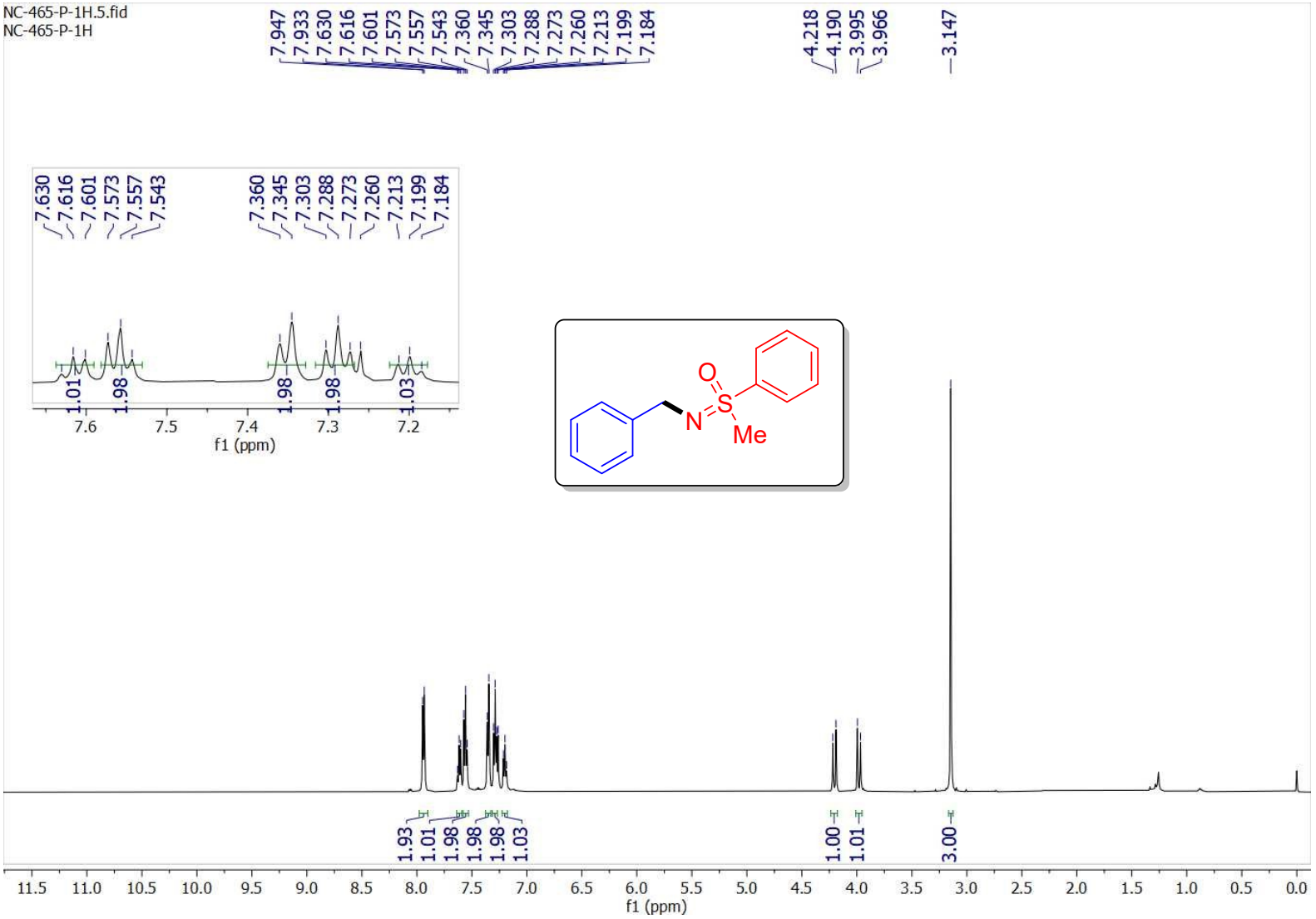
(Iodoimino)(methyl)(phenyl)- λ⁶-sulfanone *(A)*: ^{1}H NMR (400 MHz, $CDCl_3$)



(Iodoimino)(methyl)(phenyl)- λ⁶-sulfanone *(A)*: ^{13}C NMR (125 MHz, $CDCl_3$)



(Benzylimino)(methyl)(phenyl)-λ⁶-sulfanone (X): **^{1}H NMR (500 MHz, $CDCl_3$)**



(Benzylimino)(methyl)(phenyl)-λ⁶-sulfanone (X): **^{13}C NMR (125 MHz, $CDCl_3$)**