

Supporting Information

NaI-mediated α -keto-acylation of *NH*-sulfoximines with aryl methyl ketones†

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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 (60F₂₅₄) visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na₂SO₄). 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, ¹³C{¹H} NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuteriochloroform (CDCl₃). ¹H, ¹³C{¹H} were recorded in 500 (125), or 600 (150) MHz spectrometers and were calibrated using tetramethylsilane or residual undeuterated solvent for ¹H NMR, deuteriochloroform for ¹³C NMR as an internal reference {Si(CH₃)₄: 0.00 ppm or CHCl₃: 7.260 ppm for ¹H NMR and 77.230 ppm for ¹³C{¹H}. ¹⁹F NMR was calibrated without any internal standard in CDCl₃ in a 470, 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.

2. Representative examples of bioactive sulfoximine derivatives

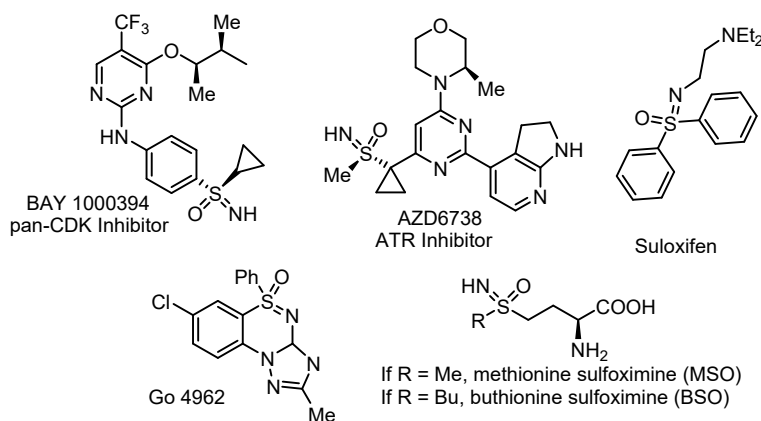
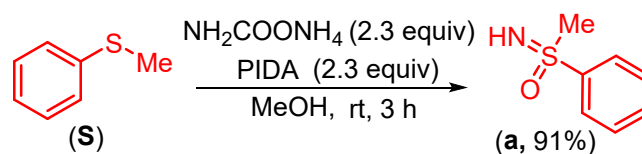


Figure S1 Some biologically relevant sulfoximines

3. General procedure:

3A. Procedure for the synthesis of starting substrates (a)¹

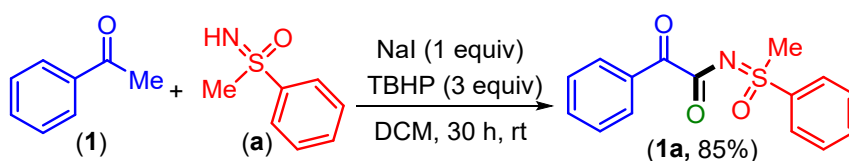
All the substrates were prepared according to the previously reported literature procedure. In an oven-dried 50 mL round bottom flask, methyl phenyl sulfide (**S**) (0.621 g, 1 equiv, 5 mmol), ammonium carbamate (0.897 g, 2.3 equiv, 11.5 mmol), and phenyliodo diacetate (PIDA) (3.704 g, 2.3 equiv, 11.5 mmol) in 10 mL methanol are taken and stirred at room temperature for 3 h. 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 using 50% ethyl acetate in hexane to result in the product *S*-phenyl-*S*-methyl-sulfoximine (**a**) in 705 mg, 91% yield (Scheme S1).



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

3B. Procedure for the synthesis of α -keto-*N*-acyl sulfoximines (**1a**)

To an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (**a**), (0.062 g, 1 equiv, 0.40 mmol), acetophenone (**1**) (0.072 g, 1.5 equiv, 0.60 mmol), NaI (0.060 g, 1 equiv, 0.40 mmol), aq TBHP (0.108 g, 115 μ L, 3 equiv, 1.2 mmol), and DCM (2 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 °C) for 30 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL). The organic layer was washed with saturated NaHCO₃ solution (1 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) solution followed by saturated brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using 25% ethyl acetate in hexane to afford the *N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (**1a**) in 85% yield (98 mg). The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S2).



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

4. Mechanistic investigations:

4A. ESI-MS of 2-iodo-1-phenylethanone (C) in the reaction mixture:

In an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (**a**), (0.039 g, 1 equiv, 0.25 mmol), acetophenone (**1**) (0.044 g, 1.5 equiv, 0.37 mmol), NaI (0.037 g, 1 equiv, 0.25 mmol), aq. TBHP (0.068 g, 72 μ L, 3 equiv, 0.75 mmol), and DCM (2 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 $^{\circ}$ C). A small aliquot of the reaction mixture was withdrawn at approximately 16 h, diluted with acetonitrile (1 mL), and subjected to ESI-MS. The ESI-MS analysis of this reaction aliquot shows ESI-MS values corresponding to 2-iodo-1-phenylethanone (**C**). This observation confirms the involvement of the 2-iodo-1-phenylethanone intermediate in the reaction. (Figure S2).

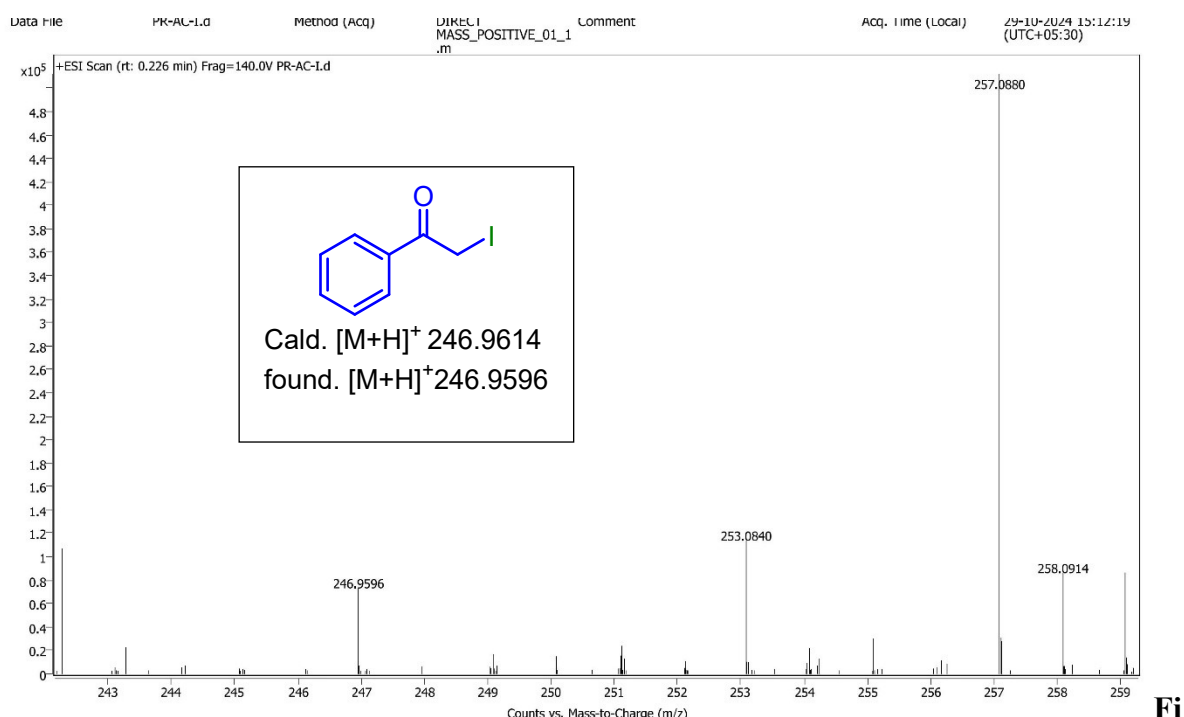


Figure S2 ESI-MS analysis of 2-iodo-1-phenylethanone intermediate (**C**)

4B. HRMS of intermediate (D) in the reaction mixture:

In an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (**a**), (0.039 g, 1 equiv, 0.25 mmol), acetophenone (**1**) (0.044 g, 1.5 equiv, 0.37 mmol), NaI (0.037 g, 1 equiv, 0.25 mmol), aq. TBHP (0.068 g, 72 μ L, 3 equiv, 0.75 mmol), and DCM (2 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 $^{\circ}$ C). A small aliquot of the reaction mixture was withdrawn at approximately 16 h, diluted with acetonitrile (1 mL), and subjected to HRMS. The HRMS analysis of this reaction aliquot shows HRMS values corresponding to intermediate (**D**). (Figure S3).

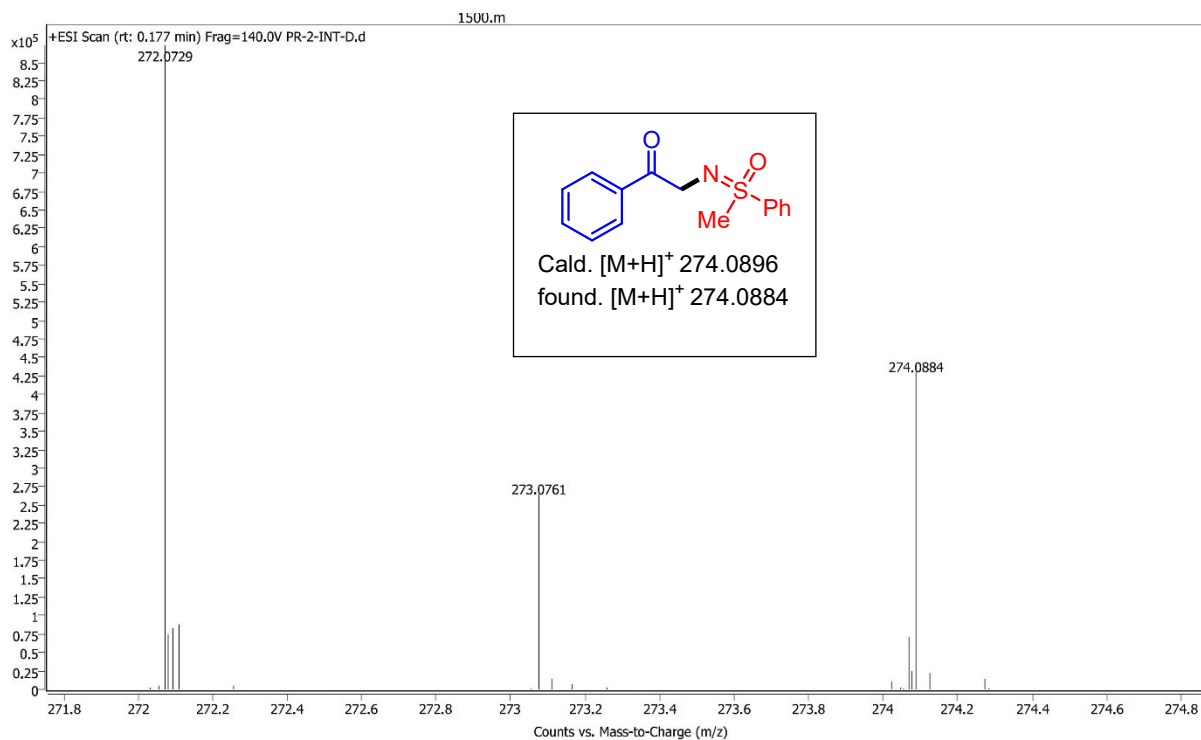


Figure S3 HRMS analysis of intermediate (D)

4C. HRMS of intermediate (F) in the reaction mixture:

In an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (**a**), (0.039 g, 1 equiv, 0.25 mmol), acetophenone (**1**) (0.044 g, 1.5 equiv, 0.37 mmol), NaI (0.037 g, 1 equiv, 0.25 mmol), aq. TBHP (0.068 g, 72 μ L, 3 equiv, 0.75 mmol), and DCM (2 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 °C). A small aliquot of the reaction mixture was withdrawn at approximately 16 h, diluted with acetonitrile (1 mL), and subjected to HRMS. The HRMS analysis of this reaction aliquot shows HRMS values corresponding to intermediate (F). (Figure S4).

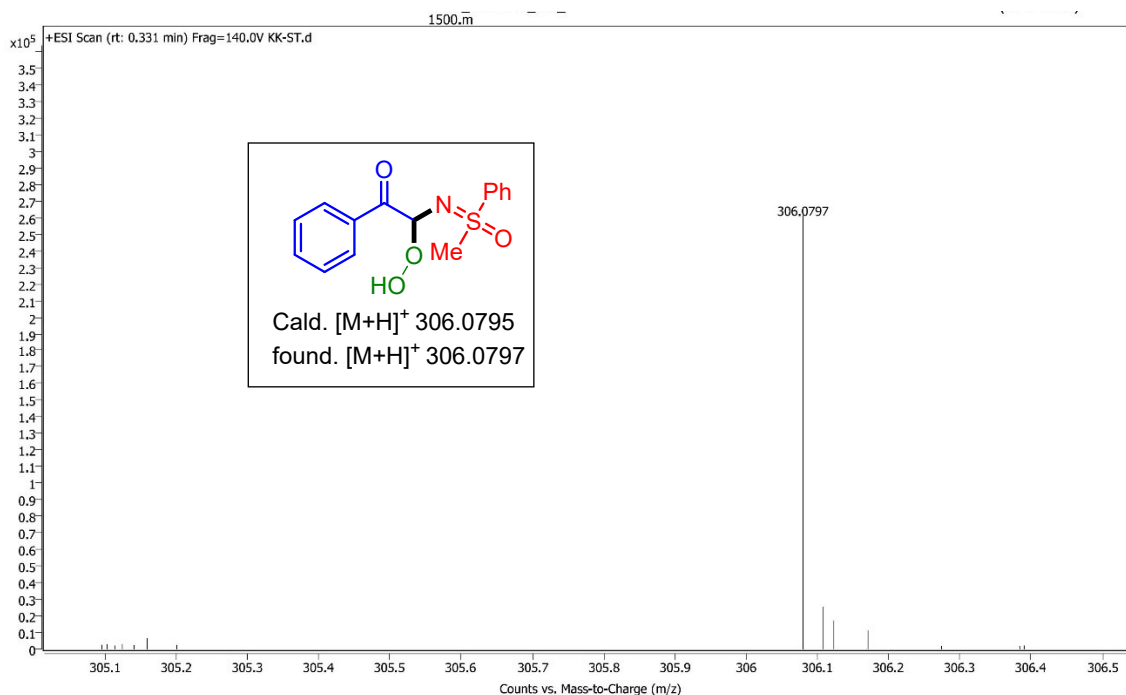
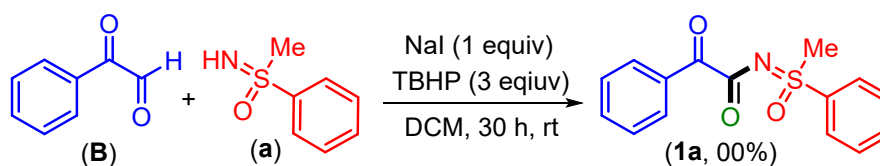


Figure S4 HRMS analysis of intermediate (F)

4D. Reaction with phenyl glyoxal (B) and *NH*-sulfoximine (a):

To an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (a), (0.062 g, 1 equiv, 0.40 mmol), phenyl glyoxal (B) (0.080 g, 1.5 equiv, 0.60 mmol), NaI (0.060 g, 1 equiv, 0.40 mmol), TBHP (0.108 g, 115 μ L, 3 equiv, 1.2 mmol), and DCM (2 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 $^{\circ}$ C) for 30 h. The reaction was monitored by TLC analysis and was allowed to stir for another 12 h. The failure in the formation of *N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1a) even after a prolonged time indicated phenyl glyoxal (B) did not involve in this transformation (Scheme S3).

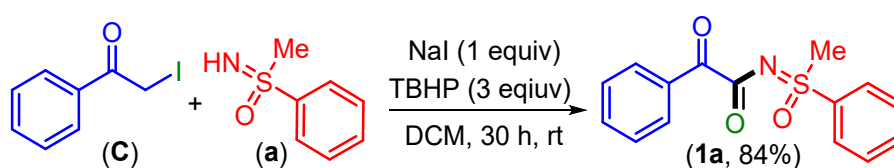


Scheme S3 Reaction with phenyl glyoxal (B)

4E. Reaction with 2-iodo-1-phenylethanone (C) and *NH*-sulfoximine (a):

To an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (a), (0.062 g, 1 equiv, 0.40 mmol), 2-iodo-1-phenylethanone (C) (0.147 g, 1.5 equiv, 0.60 mmol), NaI (0.060 g, 1 equiv, 0.40 mmol), TBHP (0.108 g, 115 μ L, 3 equiv, 1.2 mmol), and DCM (2 mL) in air were

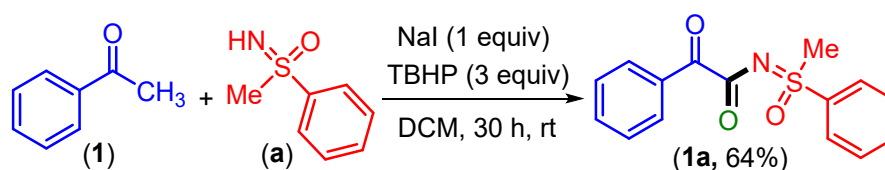
taken. After that, the reaction mixture was stirred at room temperature (25–30 °C) for 30 h. After completion of the reaction (monitored by TLC analysis) the reaction mixture was admixed with ethyl acetate (25 mL), and the organic layer was washed with saturated NaHCO₃ solution (1 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) solution followed by saturated brine solution (1 x 10 mL), and the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using 25% ethyl acetate in hexane to give pure *N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (**1a**), with 84% yield (96 mg) (Scheme S4). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S4 Reaction with 2-iodo-1-phenylethanone (C) and *NH*-sulfoximine (a)

5. Scale up reaction procedure:

In an oven-dried 10 mL round bottom flask, *NH*-sulfoximine (a), (0.775 g, 1 equiv, 5 mmol), acetophenone (1) (0.900 g, 1.5 equiv, 7.5 mmol), NaI (0.745 g, 1 equiv, 5 mmol), TBHP (1.35 g, 1.44 mL, 3 equiv, 15 mmol), and DCM (8 mL) in air were taken. After that, the reaction mixture was stirred at room temperature (25–30 °C) for 30 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL), and the organic layer was washed with saturated NaHCO₃ solution (1 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) solution followed by saturated brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using 25 % ethyl acetate in hexane to afford the α-keto-*N*-acyl sulfoximine (**1a**) in 64% yield (918 mg). The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S5).



Scheme S5 Scale up reaction conditions for the synthesis of (**1a**)

6. Crystallographic information:

Crystallographic information of *N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (**12a**):

(i) **Sample Preparation:** The single crystal of compound **12a** was prepared by the slow evaporation method for which 10 mg of the compound (**12a**) 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 **12a** were obtained after approximately 3-4 days as a transparent block-shaped crystal.

(ii) **Data Collection:** Diffraction data were collected at 292 K with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) 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^{2,3} 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 F^2 of all reflections.⁴

(iii) Crystallographic description of *N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (**12a**):

C₁₅H₁₂N₂O₅S, Yellow block shaped crystal; crystal dimensions 0.05 x 0.06 x 0.05 mm, $M_r = 332.33$, Triclinic, space group P -1; $a = 7.7745 (7)$, $b = 8.9918 (9)$, $c = 11.1848 (11) \text{ \AA}$, $\alpha = 84.052 (2)^\circ$, $\beta = 77.840 (2)^\circ$, $\gamma = 78.812 (2)^\circ$, $V = 748.22 (13) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.475 \text{ g/cm}^3$, $\mu = 0.244 \text{ mm}^{-1}$, $F(000) = 344.0$, reflection collected / unique = 2618 / 2273, refinement method = full-matrix least-squares on F^2 , final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0423$, $wR_2 = 0.1038$, R indices (all data): $R_1 = 0.0500$, $wR_2 = 0.1153$, goodness of fit = 0.985. **CCDC-2335021** for *N*-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (**12a**) 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.

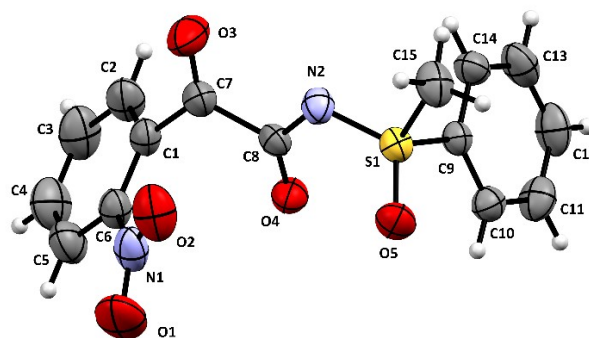
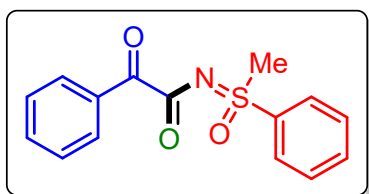


Figure S5 ORTEP diagram of *N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (**12a**) with 50% ellipsoid probability (CCDC 2335021)

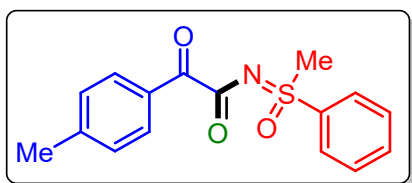
7. Spectral data

N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (**1a**):⁵



White solid (98 mg, 85% yield); m.p. 97–99 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.07 (d, 2H, J = 7.8 Hz), 8.04 (d, 2H, J = 7.2 Hz), 7.71 (t, 1H, J = 7.5 Hz), 7.63 (t, 2H, J = 7.8 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.46 (t, 2H, J = 7.8 Hz), 3.47 (s, 3H); ¹³C {¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.3, 173.4, 137.9, 134.6, 134.4, 132.9, 130.4, 130.1, 128.8, 127.4, 45.0; IR (neat, cm⁻¹): 2925, 2853, 1681, 1632, 1596, 1448, 1404, 1209, 1175; HRMS (ESI): calculated for C₁₅H₁₄NO₃S [M + H]⁺: 288.0689, found 288.0686.

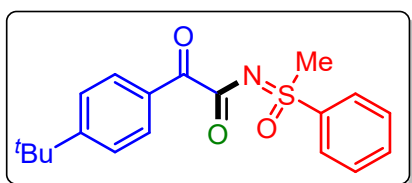
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(*p*-tolyl)acetamide (**2a**):⁵



Pale yellow solid (99 mg, 82% yield); m.p. 148–150 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.08 (d, 2H, J = 7.2 Hz), 7.95 (d, 2H, J = 7.8 Hz), 7.72 (t, 1H, J = 7.2 Hz), 7.64 (t, 2H, J = 7.8 Hz), 7.27 (s, 1H), 7.26 (s,

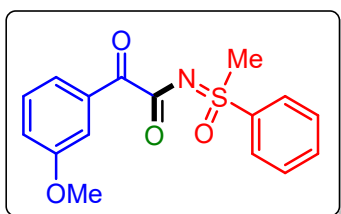
1H), 3.48 (s, 3H), 2.41 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.1, 173.7, 145.6, 138.0, 134.6, 130.6, 130.5, 130.1, 129.6, 127.4, 45.1, 22.1; IR (neat, cm^{-1}): 3016, 2925, 1677, 1630, 1604, 1447, 1332, 1214, 1205; HRMS (ESI): calculated for $\text{C}_{16}\text{H}_{16}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 302.0845, found 302.0849.

2-(4-(tert-butyl)phenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (3a):



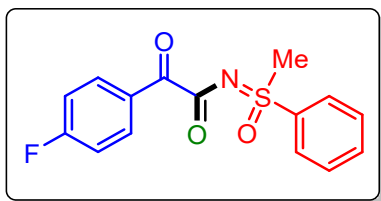
Yellow solid (101 mg, 74% yield); m.p. 104–106 °C. purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.07 (d, 2H, $J = 7.8$ Hz), 7.98 (d, 2H, $J = 8.4$ Hz), 7.72 (t, 1H, $J = 7.2$ Hz), 7.64 (t, 2H, $J = 7.8$ Hz), 7.48 (d, 2H, $J = 8.4$ Hz), 3.47 (s, 3H), 1.33 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.1, 173.7, 158.4, 138.0, 134.6, 130.4, 130.3, 130.1, 127.4, 125.9, 45.1, 35.5, 31.2; IR (neat, cm^{-1}): 2965, 2319, 1686, 1632, 1455, 1325, 1261, 1224, 1104; HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 344.1315, found 344.1307.

2-(3-Methoxyphenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (4a):⁵



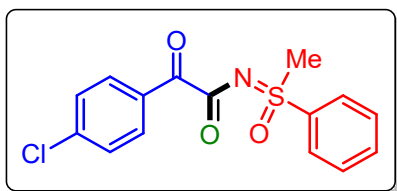
Yellow solid (99 mg, 78% yield); m.p. 66–68 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.08 (d, 2H, $J = 7.2$ Hz), 7.73 (t, 1H, $J = 7.5$ Hz), 7.66–7.62 (m, 3H), 7.56 (s, 1H), 7.37 (t, 1H, $J = 8.1$ Hz), 7.15 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 2.1$ Hz), 3.84 (s, 3H), 3.48 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.2, 173.5, 160.0, 138.0, 134.7, 134.2, 130.1, 129.9, 127.4, 123.6, 121.6, 113.4, 55.7, 45.1; IR (neat, cm^{-1}): 3008, 2927, 2840, 1682, 1631, 1595, 1448, 1323, 1248; HRMS (ESI): calculated for $\text{C}_{16}\text{H}_{16}\text{NO}_4\text{S}$ $[\text{M} + \text{H}]^+$: 318.0795 found 318.0797.

2-(4-Fluorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (5a):⁵



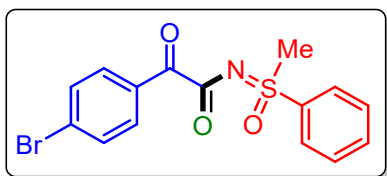
Light yellow solid (90 mg, 74% yield); m.p. 123–125 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.10–8.06 (m, 4H), 7.73 (t, 1H, J = 7.5 Hz), 7.65 (t, 2H, J = 7.8 Hz), 7.14 (t, 2H, J = 8.7 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 188.6, 173.1, 166.7 (d, J = 255.3 Hz), 137.9, 134.7, 133.2 (d, J = 9.6 Hz), 130.2, 129.5 (d, J = 2.8 Hz), 127.4, 116.2 (d, J = 21.9 Hz), 45.1; ¹⁹F NMR (565 MHz, CDCl₃): δ (ppm) –102.7; IR (neat, cm^{–1}): 2925, 1683, 1632, 1597, 1505, 1447, 1332, 1206, 1152; HRMS (ESI): calculated for C₁₅H₁₃FN₂O₃S [M + H]⁺: 306.0595, found 306.0596.

2-(4-Chlorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (6a):⁵



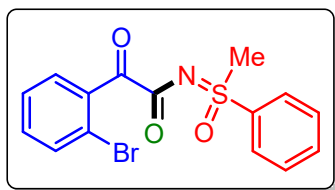
Pale yellow solid, (112 mg, 87% yield); m.p. 134–136 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.07 (d, 2H, J = 7.2 Hz), 8.00 (d, 2H, J = 8.4 Hz), 7.73 (t, 1H, J = 7.5 Hz), 7.65 (t, 2H, J = 7.8 Hz), 7.44 (d, 2H, J = 8.4 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 189.0, 172.8, 141.0, 137.8, 134.7, 131.8, 131.4, 130.2, 129.3, 127.4, 45.1; IR (neat, cm^{–1}): 3017, 2924, 2852, 1683, 1632, 1584, 1446, 1328, 1204; HRMS (ESI): calculated for C₁₅H₁₂ClN₂O₃SN_a [M + Na]⁺: 344.0119, found 344.0122.

2-(4-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (7a):⁵



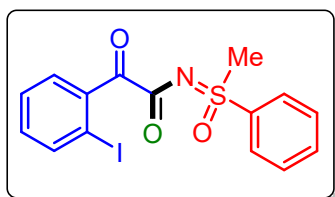
White solid (132 mg, 90% yield); m.p. 137–139 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.06 (d, 2H, $J = 7.2$ Hz), 7.92 (d, 2H, $J = 8.4$ Hz), 7.73 (t, 1H, $J = 7.2$ Hz), 7.65 (t, 2H, $J = 7.8$ Hz), 7.61 (d, 2H, $J = 8.4$ Hz), 3.48 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 189.1, 172.8, 137.8, 134.7, 132.2, 132.1, 131.8, 130.2, 129.9, 127.4, 45.1; IR (neat, cm^{-1}): 3016, 2920, 2850, 1685, 1632, 1584, 1328, 1206, 1173; HRMS (ESI): calculated for $\text{C}_{15}\text{H}_{13}\text{BrNO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 365.9794, found 365.9792; $[\text{M} + \text{H} + 2]^+$ found: 367.9771.

2-(2-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (8a):⁵



White solid (123 mg, 84% yield); m.p. 106–108 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.04 (d, 2H, $J = 7.8$ Hz), 7.70 (t, 1H, $J = 7.5$ Hz), 7.67 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz), 7.63–7.58 (m, 3H), 7.40–7.37 (m, 1H), 7.36–7.33 (m, 1H), 3.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 191.2, 170.8, 137.8, 136.7, 134.6, 133.7, 133.3, 132.0, 130.0, 127.6, 127.4, 121.4, 44.4; IR (neat, cm^{-1}): 3059, 2927, 1691, 1634, 1436, 1207, 1086, 982, 821; HRMS (ESI): calculated for $\text{C}_{15}\text{H}_{13}\text{BrNO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 365.9794, found: 365.9800; $[\text{M} + \text{H} + 2]^+$ found: 367.9781.

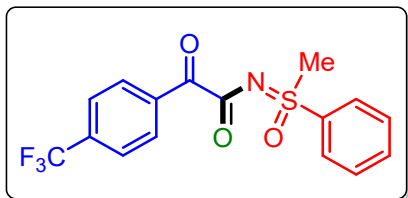
2-(2-Iodophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (9a):⁶



Yellow gummy liquid (132 mg, 80% yield); purified over a column of silica gel (28% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.05 (d, 2H, $J = 7.8$ Hz), 7.93 (d, 1H, $J = 7.8$ Hz), 7.71 (t, 1H, $J = 7.5$ Hz), 7.64–7.61 (m, 3H), 7.43 (t, 1H, $J = 7.5$ Hz), 7.17 (t, 1H, $J = 7.8$ Hz), 3.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 191.6, 170.4, 140.8, 139.0, 137.8, 134.6, 133.2, 132.2, 130.0, 128.2, 127.4, 93.0, 44.5; IR (neat, cm^{-1}): 3020, 2925, 1690,

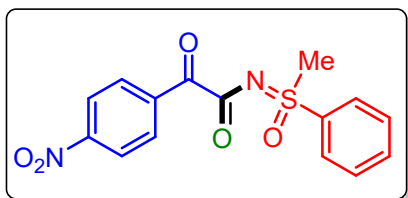
1629, 1433, 1312, 1203, 1094, 987; HRMS (ESI): calculated for $C_{15}H_{13}INO_3S$ $[M + H]^+$: 413.9655, found: 413.9658.

N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl)acetamide (10a):⁷

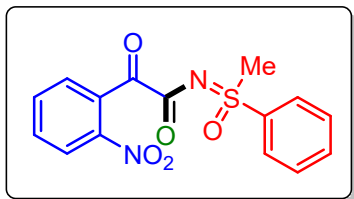


White solid (102 mg, 72% yield); m.p. 121–123 °C; purified over a column of silica gel (30% ethyl acetate in hexane); 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 2H, $J = 8.4$ Hz), 8.07 (d, 2H, $J = 7.8$ Hz), 7.73 (t, 3H, $J = 6.9$ Hz), 7.66 (t, 2H, $J = 7.8$ Hz), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 189.0, 172.4, 137.7, 135.8, 135.5, 135.3, 134.8, 130.7, 130.2, 127.3, 125.8 (q, $J = 3.7$ Hz), 45.0; ^{19}F NMR (565 MHz, $CDCl_3$): δ (ppm) –63.3; IR (neat, cm^{-1}): 2953, 2925, 2854, 1693, 1637, 1581, 1449, 1325, 1210; HRMS (ESI): calculated for $C_{16}H_{13}F_3NO_3S$ $[M + H]^+$: 356.0563, found 356.0553.

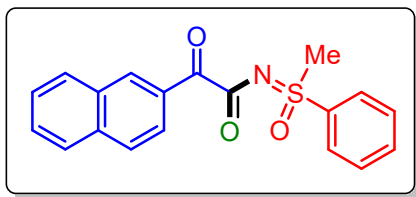
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(4-nitrophenyl)-2-oxoacetamide (11a):⁸



Yellow solid (104 mg, 78% yield); m.p. 136–138 °C; purified over a column of silica gel (28% ethyl acetate in hexane); 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.30 (d, 2H, $J = 9.0$ Hz), 8.23 (d, 2H, $J = 9.0$ Hz), 8.07 (d, 2H, $J = 7.8$ Hz), 7.75 (t, 1H, $J = 7.2$ Hz), 7.67 (t, 2H, $J = 8.1$ Hz), 3.50 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 188.2, 171.8, 151.0, 137.7, 137.5, 134.9, 131.5, 130.2, 127.3, 123.9, 45.0; IR (neat, cm^{-1}): 3110, 3021, 2928, 1693, 1631, 1604, 1526, 1447, 1345; HRMS (ESI): calculated for $C_{15}H_{12}N_2O_5S$ $[M + Na]^+$: 355.0359, found 355.0323.

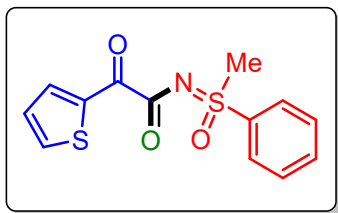
***N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (12a):⁹**

Yellow gummy solid (100 mg, 75% yield); m.p. 105–107 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.09 (d, 1H, J = 8.4 Hz), 7.99 (d, 2H, J = 7.8 Hz), 7.74 (t, 1H, J = 7.5 Hz), 7.69 (t, 1H, J = 7.5 Hz), 7.64–7.59 (m, 4H), 3.42 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 188.6, 167.7, 147.9, 137.4, 134.7, 134.6, 134.4, 131.7, 130.2, 130.0, 127.4, 123.7, 44.3; IR (neat, cm⁻¹): 3025, 2928, 1713, 1640, 1523, 1336, 1211, 1092, 979; HRMS (ESI): calculated for C₁₅H₁₃N₂O₅S [M + H]⁺: 333.0540, found: 333.0540.

***N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(naphthalen-2-yl)-2-oxoacetamide (13a):⁵**

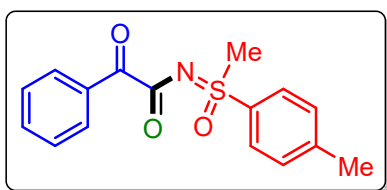
Pale yellow solid (101 mg, 75% yield); m.p. 142–143 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.60 (s, 1H); 8.11 (d, 2H, J = 7.2 Hz), 8.08 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.8 Hz), 7.95 (d, 1H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 7.8 Hz), 7.74 (t, 1H, J = 7.5 Hz), 7.66 (t, 2H, J = 7.8 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.54 (t, 1H, J = 7.5 Hz), 3.50 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.3, 173.6, 138.0, 136.4, 134.7, 133.7, 132.6, 130.2, 130.1, 129.3, 128.8, 128.0, 127.5, 127.1, 124.6, 45.1; IR (neat, cm⁻¹): 2920, 2848, 1676, 1628, 1445, 1327, 1250, 1176, 1091; HRMS (ESI): calculated for C₁₉H₁₅NO₃S [M + Na]⁺: 360.0665, found 360.0637.

***N*-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(thiophen-2-yl)acetamide (14a):⁵**



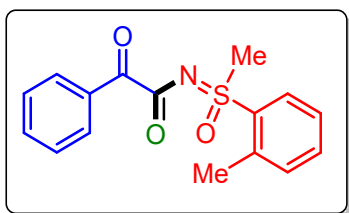
Brown solid (82 mg, 70% yield); m.p. 106–108 °C; purified over a column of silica gel (35% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08–8.05 (m, 3H), 7.72 (t, 2H, J = 7.0 Hz), 7.64 (t, 2H, J = 7.7 Hz), 7.13 (t, 1H, J = 4.2 Hz), 3.47 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 181.0, 170.9, 139.3, 137.8, 137.1, 136.7, 134.6, 130.1, 128.5, 127.4, 44.9; IR (neat, cm⁻¹): 3094, 2848, 1684, 1636, 1510, 1447, 1408, 1216, 1090; HRMS (ESI): calculated for C₁₃H₁₂NO₃S₂ [M + H]⁺: 294.0253, found 294.0254.

***N*-(Methyl(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1b):⁵**



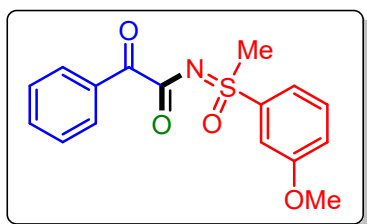
White solid (96 mg, 80% yield); m.p. 118–120 °C; purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.04 (d, 2H, J = 7.2 Hz), 7.94 (d, 2H, J = 8.4 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.46 (t, 2H, J = 7.8 Hz), 7.42 (d, 2H, J = 7.8 Hz), 3.45 (s, 3H), 2.46 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.4, 173.5, 145.9, 134.7, 134.4, 133.0, 130.7, 130.4, 128.8, 127.4, 45.2, 21.9; IR (neat, cm⁻¹): 2962, 2850, 1683, 1634, 1595, 1451, 1401, 1331, 1208; HRMS (ESI): calculated for C₁₆H₁₅NO₃SNa [M + Na]⁺: 324.0665, found 324.0644.

***N*-(Methyl(oxo)(*o*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1c):⁷**



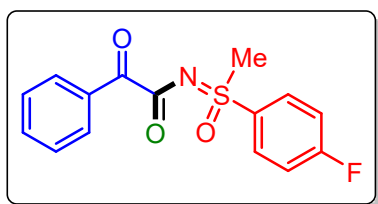
Gummy liquid (94 mg, 78% yield); purified over a column of silica gel (28% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.17 (d, 1H, $J = 8.4$ Hz), 8.05 (d, 2H, $J = 7.2$ Hz), 7.60–7.57 (m, 2H), 7.47 (t, 3H, $J = 7.5$ Hz), 7.40 (d, 1H, $J = 7.8$ Hz), 3.49 (s, 3H), 2.76 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.4, 173.1, 137.6, 135.9, 134.5, 134.4, 133.7, 132.9, 130.4, 129.4, 128.9, 127.5, 43.8, 20.8; IR (neat, cm^{-1}): 2927, 2850, 1730, 1681, 1630, 1453, 1317, 1214, 1032, 972; HRMS (ESI): calculated for $\text{C}_{16}\text{H}_{16}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 302.0845, found 302.0842.

N-((3-Methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1d):⁷



Viscous solid (94 mg, 74% yield); purified over a column of silica gel (30% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.05 (d, 2H, $J = 6.6$ Hz), 7.63–7.58 (m, 2H), 7.56–7.52 (m, 2H), 7.47 (t, 2H, $J = 7.8$ Hz), 7.23 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz), 3.89 (s, 3H), 3.46 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.4, 173.5, 160.7, 139.0, 134.5, 132.9, 131.2, 130.4, 128.9, 121.2, 119.3, 111.8, 56.1, 45.1; IR (neat, cm^{-1}): 3016, 2926, 2837, 1680, 1633, 1595, 1480, 1424, 1208; HRMS (ESI): calculated for $\text{C}_{16}\text{H}_{16}\text{NO}_4\text{S}$ $[\text{M} + \text{H}]^+$: 318.0795, found 318.0790.

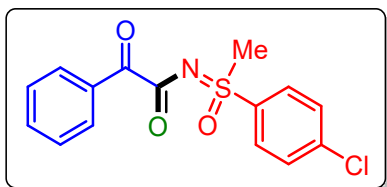
N-((4-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1e):⁷



Light yellow solid (88 mg, 72% yield); m.p. 108–110 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.11–8.08 (m, 2H), 8.04 (d, 2H, $J = 7.8$ Hz), 7.60 (t, 1H, $J = 7.2$ Hz), 7.47 (t, 2H, $J = 7.5$ Hz), 7.32 (t, 2H, $J = 8.4$ Hz), 3.48 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.2, 173.4, 166.4 (d, $J = 256.6$ Hz), 134.5, 133.7 (d, $J = 3.3$ Hz), 132.8, 130.4, 130.3, 128.9, 117.6 (d, $J = 22.9$ Hz), 45.2; ^{19}F NMR

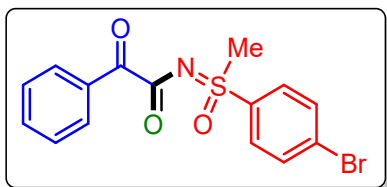
(565 MHz, CDCl₃): δ (ppm) –101.8; IR (neat, cm⁻¹): 3054, 2959, 2852, 1682, 1633, 1590, 1493, 1375, 1263; HRMS (ESI): calculated for C₁₅H₁₃FNO₃S [M + H]⁺: 306.0595; found 306.0596.

N-((4-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1f):⁵

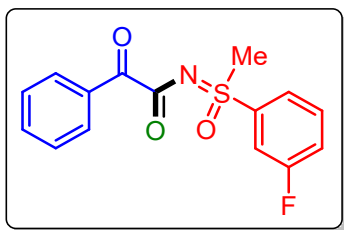


White solid (112 mg, 87% yield); m.p. 138–140 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.03–8.00 (m, 4H), 7.61 (t, 3H, *J* = 8.4 Hz), 7.47 (t, 2H, *J* = 7.8 Hz), 3.47 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.2, 173.3, 141.6, 136.3, 134.5, 132.8, 130.5, 130.4, 128.9, 128.9, 45.1; IR (neat, cm⁻¹): 2962, 2923, 2862, 1684, 1635, 1591, 1475, 1370, 1262, 1206; HRMS (ESI): calculated for C₁₅H₁₂ClNO₃S [M + Na]⁺: 344.0119, found: 344.0107.

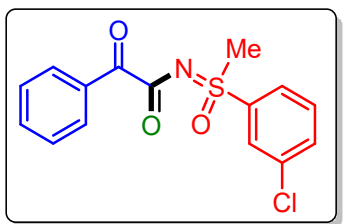
N-((4-Bromophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1g):⁵



White solid (124 mg, 85% yield); m.p. 108–110 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.04 (d, 2H, *J* = 7.8 Hz), 7.93 (d, 2H, *J* = 9.0 Hz), 7.78 (d, 2H, *J* = 8.4 Hz), 7.60 (t, 1H, *J* = 8.1 Hz), 7.47 (t, 2H, *J* = 7.5 Hz), 3.47 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.1, 173.3, 136.9, 134.5, 133.5, 132.8, 130.4, 130.2, 128.9, 128.9, 45.0; IR (neat, cm⁻¹): 2922, 1683, 1632, 1570, 1445, 1382, 1330, 1207, 1172; HRMS (ESI): calculated for C₁₅H₁₃BrNO₃S [M + H]⁺: 365.9794, found: 365.9758; [M + H + 2]⁺ found: 367.9734.

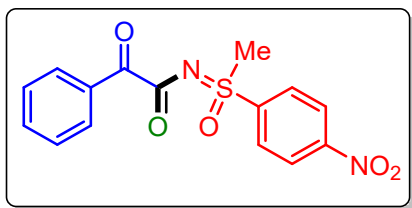
N-((3-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1h):⁷

Light yellow solid (85 mg, 70% yield); m.p. 108–110 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.04 (d, 2H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.4 Hz), 7.80 (d, 1H, J = 7.8 Hz), 7.66–7.59 (m, 2H), 7.48 (t, 2H, J = 7.8 Hz), 7.44–7.41 (m, 1H), 3.49 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.1, 173.3, 163.0 (d, J = 252.4 Hz), 139.9 (d, J = 6.7 Hz), 134.6, 132.8, 132.0 (d, J = 7.6 Hz), 130.4, 128.9, 123.2, (d, J = 3.7 Hz), 122.1 (d, J = 21.1 Hz), 115.1 (d, J = 25.2 Hz), 44.9; ¹⁹F NMR (565 MHz, CDCl₃): δ (ppm) –107.4; IR (neat, cm^{–1}): 3070, 3021, 2927, 1682, 1633, 1594, 1478, 1331, 1206; HRMS (ESI): calculated for C₁₅H₁₂FNO₃SNa [M + Na]⁺: 328.0414, found 328.0405.

N-((3-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1i):⁷

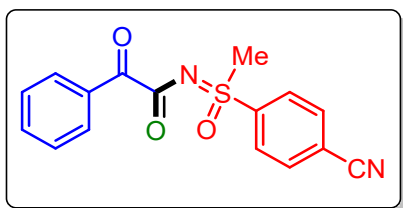
Yellow gummy solid (105 mg, 82% yield); purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.05 (t, 3H, J = 9.0 Hz), 7.96 (d, 1H, J = 7.8 Hz), 7.69 (d, 1H, J = 7.8 Hz), 7.62–7.58 (m, 2H), 7.48 (t, 2H, J = 7.8 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 190.1, 173.3, 139.7, 136.5, 134.9, 134.6, 132.8, 131.4, 130.4, 128.9, 127.6, 125.5, 45.0; IR (neat, cm^{–1}): 3054, 2926, 2853, 1684, 1637, 1572, 1371, 1267, 1243, 1206; HRMS (ESI): calculated for C₁₅H₁₃ClNO₃S [M + H]⁺: 322.0299, found 322.0299.

***N*-(Methyl(4-nitrophenyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1j):**⁷



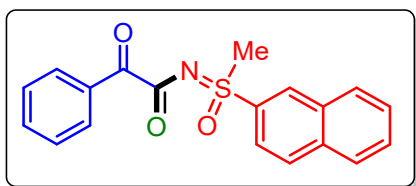
Light yellow solid (104 mg, 78% yield); m.p. 122–124 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.48 (d, 2H, J = 9.0 Hz), 8.29 (d, 2H, J = 9.0 Hz), 8.03 (d, 2H, J = 7.8 Hz), 7.62 (t, 1H, J = 7.2 Hz), 7.48 (t, 2H, J = 7.8 Hz), 3.51 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 189.8, 173.2, 151.4, 143.8, 134.7, 132.6, 130.4, 129.1, 129.0, 125.3, 44.7; IR (neat, cm⁻¹): 3055, 1681, 1633, 1531, 1333, 1261, 1210, 1094, 1011; HRMS (ESI): calculated for C₁₅H₁₂N₂O₅SNa [M + Na]⁺: 355.0359, found 355.0352.

***N*-(4-Cyanophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1k):**⁷



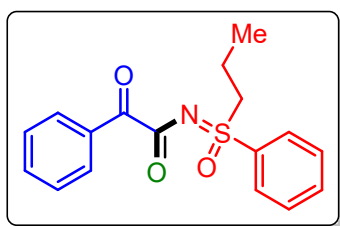
Light yellow solid (87 mg, 70% yield); m.p. 142–144 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.21 (d, 2H, J = 9.0 Hz), 8.02 (d, 2H, J = 7.2 Hz), 7.95 (d, 2H, J = 8.4 Hz), 7.62 (t, 1H, J = 7.5 Hz), 7.48 (t, 2H, J = 7.5 Hz), 3.49 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 189.8, 173.2, 142.4, 134.7, 133.8, 132.7, 130.4, 129.0, 128.3, 118.5, 117.0, 44.7; IR (neat, cm⁻¹): 3056, 1681, 1638, 1414, 1263, 1208, 1091, 1014, 974; HRMS (ESI): calculated for C₁₆H₁₃N₂O₃S [M + H]⁺: 313.0641, found 313.0639.

***N*-(Methyl(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1l):**



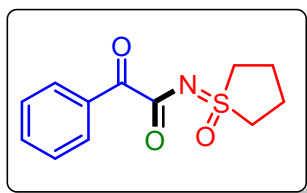
Light yellow solid (102 mg, 76% yield); m.p. 134–136 °C; purified over a column of silica gel (28% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.68 (s, 1H), 8.06 (t, 3H, $J = 8.1$ Hz), 8.03 (d, 1H, $J = 7.8$ Hz), 7.97–7.94 (m, 2H), 7.71 (t, 1H, $J = 7.2$ Hz), 7.71 (t, 1H, $J = 7.2$ Hz), 7.66 (t, 1H, $J = 7.2$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 7.46 (t, 2H, $J = 7.5$ Hz), 3.54 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.4, 173.5, 135.7, 134.4, 134.4, 132.9, 132.4, 130.6, 130.4, 130.0, 129.7, 128.8, 128.4, 128.3, 121.4, 45.1; IR (neat, cm^{-1}): 3056, 2978, 2301, 1683, 1636, 1424, 1264, 1211, 725; HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{16}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 338.0845, found 338.0850.

2-Oxo-N-(oxo(phenyl)(propyl)- λ^6 -sulfaneylidene)-2-phenylacetamide (1m):⁷



Yellow liquid (91 mg, 72% yield); purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.04 (t, 4H, $J = 8.5$ Hz), 7.72 (t, 1H, $J = 7.2$ Hz), 7.65–7.57 (m, 3H), 7.46 (t, 2H, $J = 7.7$ Hz), 3.61–3.55 (m, 1H), 3.49–3.43 (m, 1H), 1.86–1.69 (m, 2H), 1.00 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 190.5, 173.6, 136.2, 134.5, 134.4, 133.0, 130.4, 130.0, 128.8, 128.1, 58.3, 16.2, 12.8; IR (neat, cm^{-1}): 3064, 2920, 2852, 1684, 1632, 1445, 1326, 1274, 1206; HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 316.1002, found 316.1007.

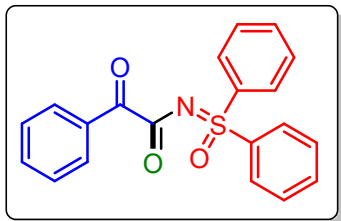
N-(1-Oxidotetrahydro-1 λ^6 -thiophen-1-ylidene)-2-oxo-2-phenylacetamide (1n):⁵



Light yellow solid (70 mg, 70% yield); m.p. 145–147 °C; purified over a column of silica gel (30% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.06 (d, 2H, $J = 7.2$ Hz), 7.61 (t, 1H, $J = 7.2$ Hz), 7.49 (t, 2H, $J = 7.8$ Hz), 3.76–3.72 (m, 2H), 3.45–3.40 (m, 2H), 2.43–2.33 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.5, 174.0, 134.5, 133.0,

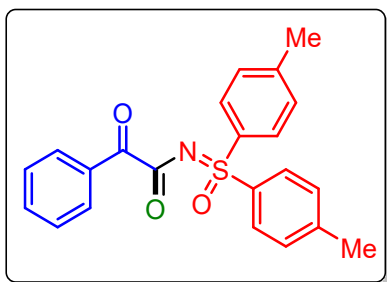
130.4, 128.9, 53.5, 23.9; IR (neat, cm^{-1}): 2953, 1680, 1623, 1596, 1581, 1445, 1338, 1306, 1210; HRMS (ESI): calculated for $\text{C}_{12}\text{H}_{14}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 252.0689, found 252.0687

2-Oxo-N-(oxodiphenyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1o):⁵



Light yellow solid (109 mg, 78% yield); m.p. 81–83 °C; purified over a column of silica gel (22% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.08 (t, 6H, $J = 7.8$ Hz), 7.63–7.58 (m, 3H), 7.56 (t, 4H, $J = 7.8$ Hz), 7.46 (t, 2H, $J = 7.8$ Hz); ^{13}C $\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.3, 173.4, 139.1, 134.4, 134.1, 133.0, 130.5, 129.9, 128.9, 127.8; IR (neat, cm^{-1}): 1683, 1635, 1592, 1583, 1446, 1327, 1304, 1226, 1206; HRMS (ESI): calculated for $\text{C}_{20}\text{H}_{16}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 350.0845, found 350.0848.

2-Oxo-N-(oxodi-*p*-tolyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1p):



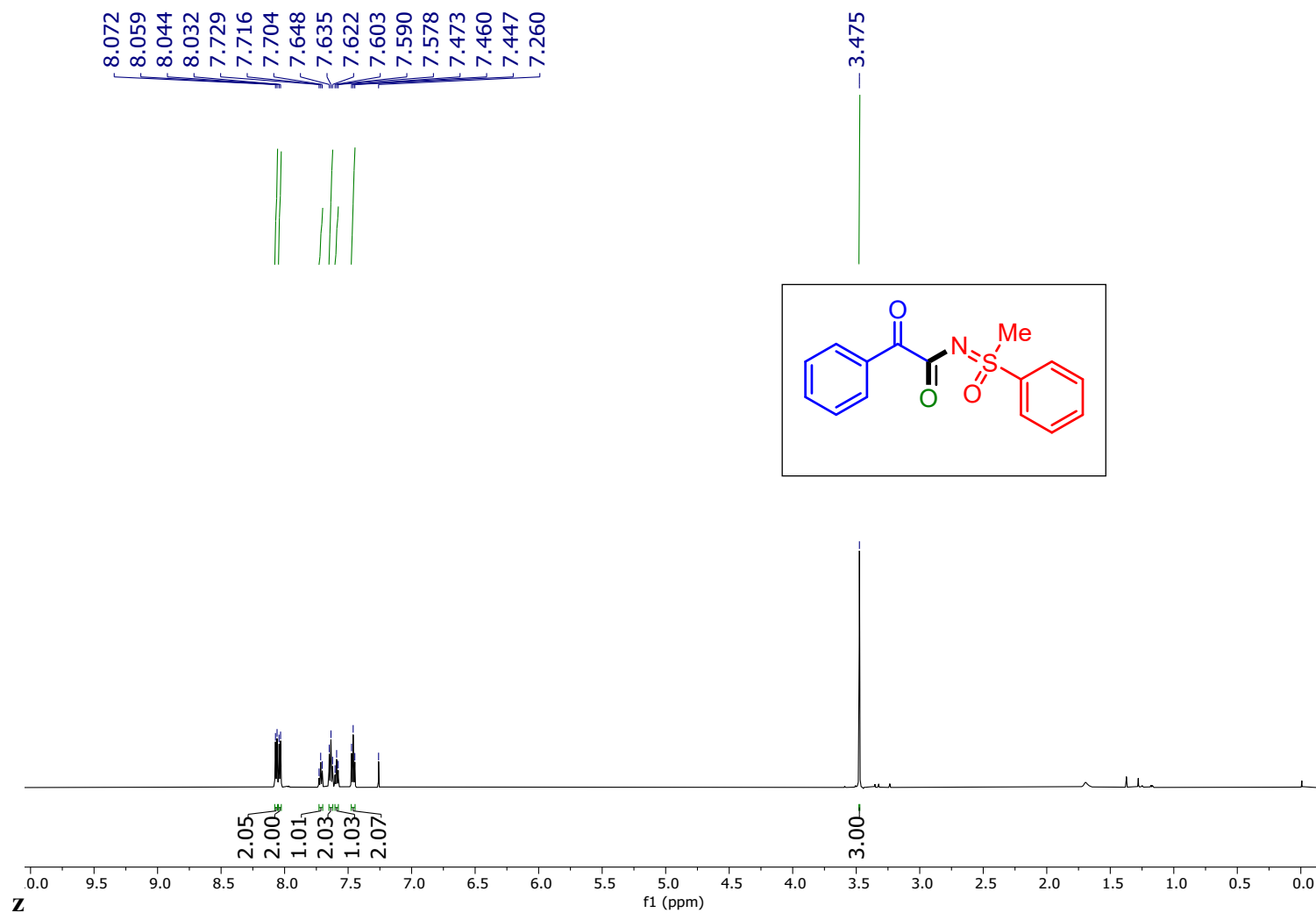
Light yellow solid (113 mg, 75% yield); m.p. 109–111 °C; purified over a column of silica gel (25% ethyl acetate in hexane); ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.07 (d, 2H, $J = 7.2$ Hz), 7.93 (d, 4H, $J = 8.4$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 7.46 (t, 2H, $J = 7.8$ Hz), 7.33 (d, 4H, $J = 8.4$ Hz), 2.40 (s, 6H); ^{13}C $\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) 190.5, 173.4, 145.1, 136.2, 134.3, 133.1, 130.5, 130.4, 128.8, 127.7, 21.8; IR (neat, cm^{-1}): 3051, 2926, 1920, 1681, 1636, 1448, 1307, 1203, 1092; HRMS (ESI): calculated for $\text{C}_{22}\text{H}_{20}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 378.1158, found 378.1158.

8. References:

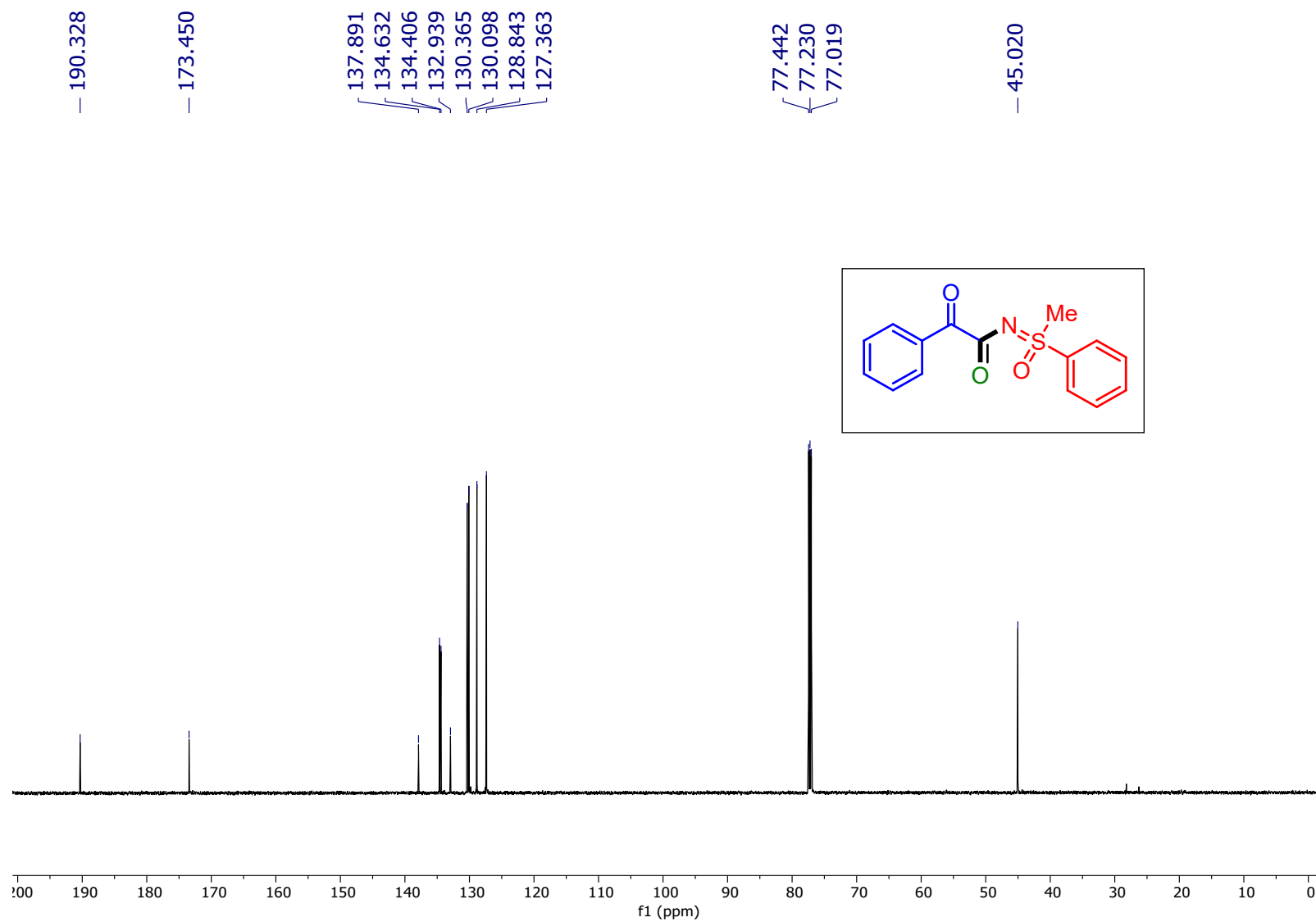
1. A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, *Chem. Commun.*, 2017, **53**, 348–351.
2. G. M. Sheldrick, SADABS, 1996, based on the method described in: R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33–38.
3. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
4. G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112–122.
5. C. Bolm and H. Cheng, *Synlett*, 2015, **27**, 769–772.
6. C. Wang, D. Ma, Y. Tu and C. Bolm, *Org. Lett.*, 2020, **22**, 8937–8940.
7. C. Kang, M. Li, W. Huang, S. Wang, M. Peng, L. Zhao, G. Jiang and F. Ji, *Green Chem.*, 2023, **25**, 8838–8844.
8. S. Baranwal, S. Gupta and J. Kandasamy, *Asian J. Org. Chem.*, 2021, **10**, 1835–1845.
9. Y. Zou, Z. Peng, W. Dong and D. An, *European J. Org. Chem.*, 2015, **2015**, 4913–4921.

9. Spectra of all compounds

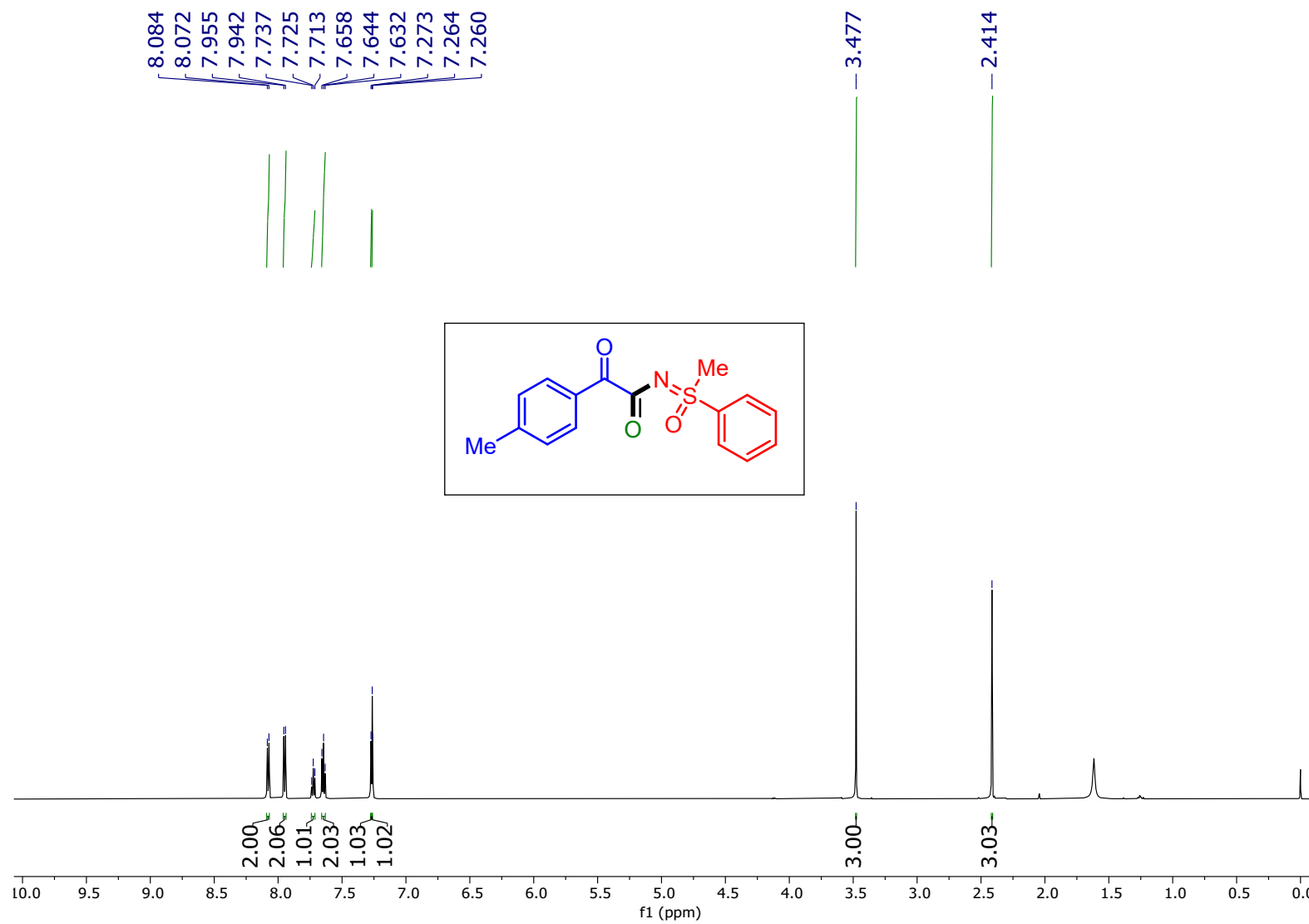
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1a): ^1H NMR (600 MHz, CDCl_3)



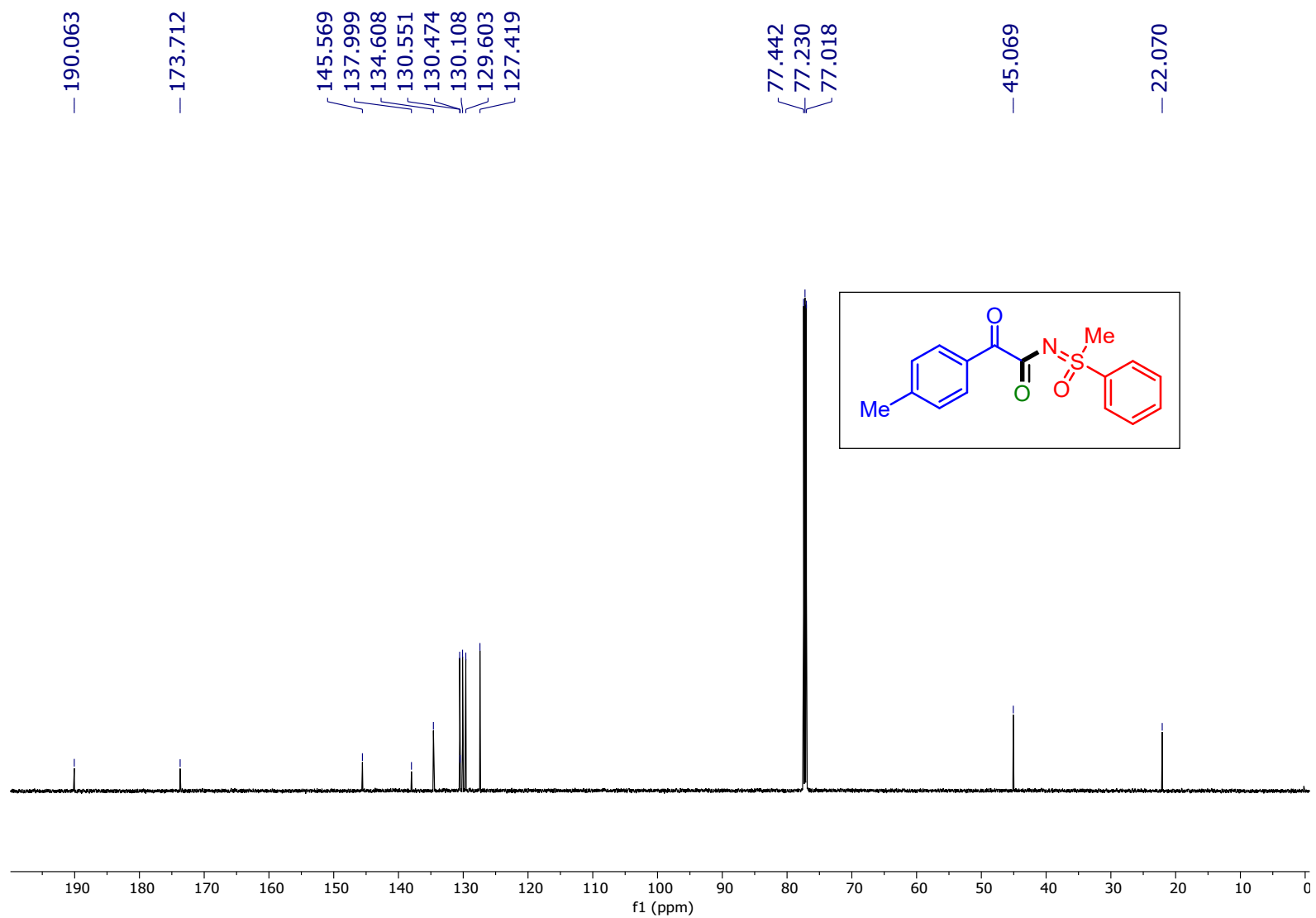
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



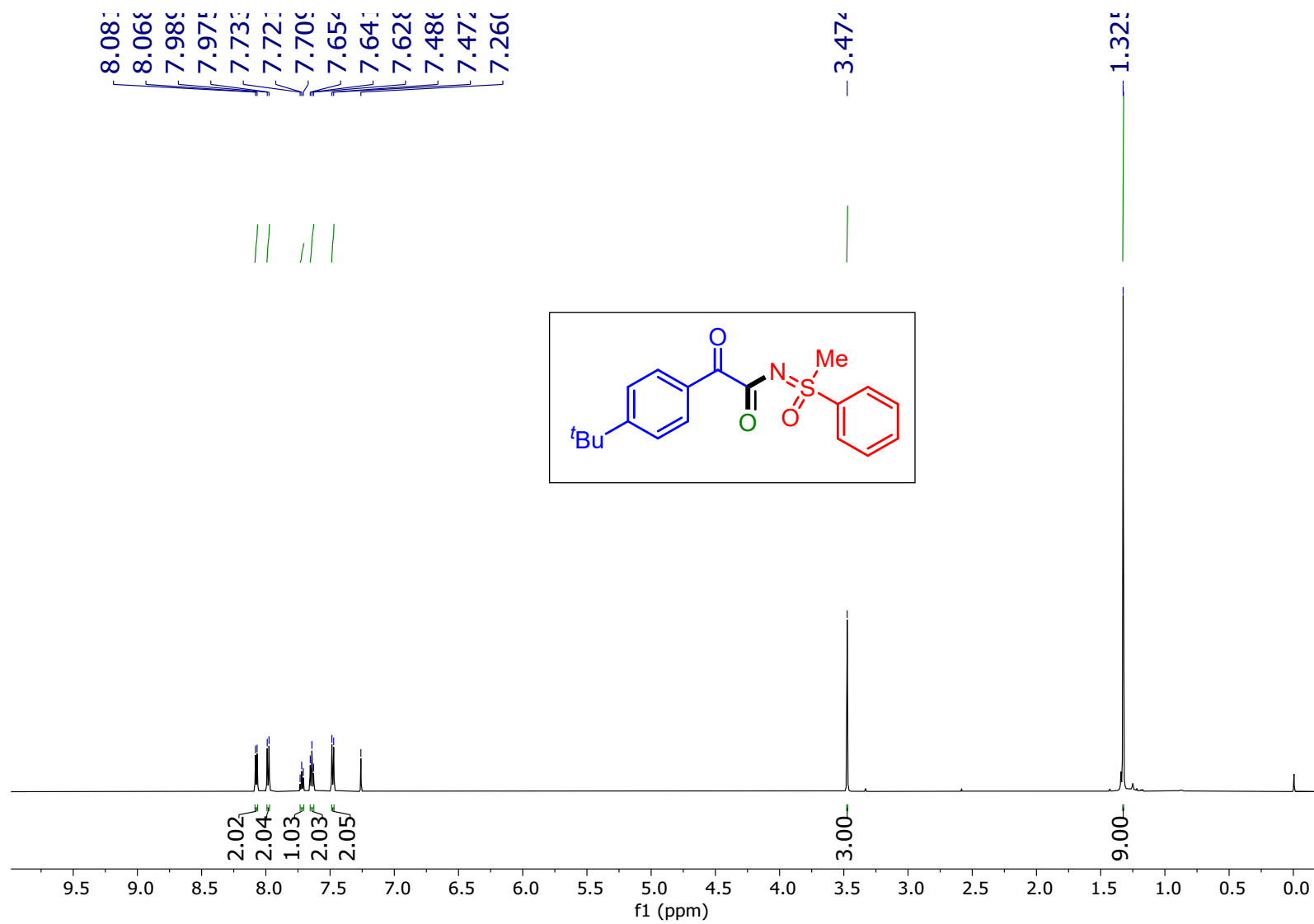
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(*p*-tolyl)acetamide (2a): ^1H NMR (600 MHz, CDCl_3)



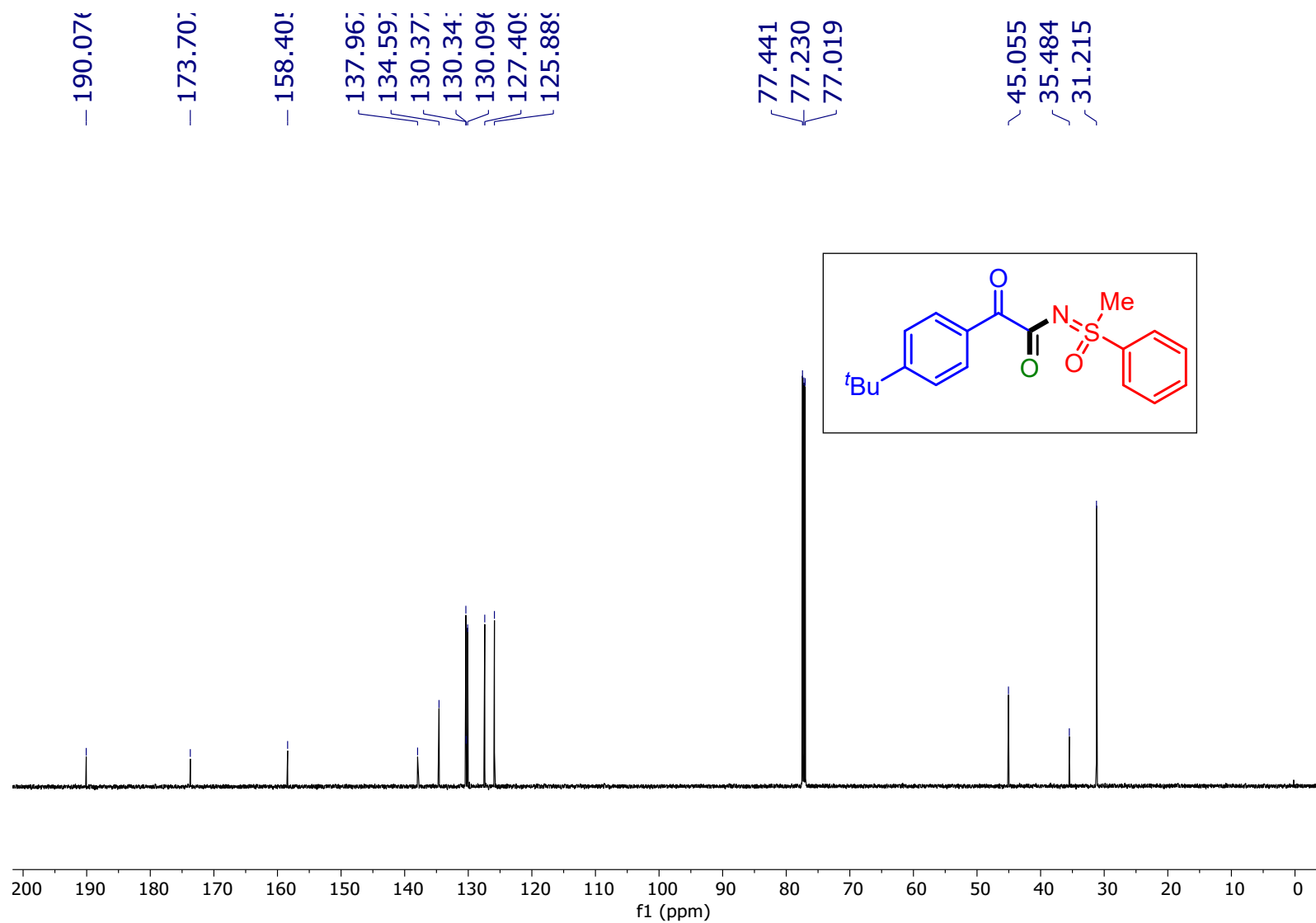
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(*p*-tolyl)acetamide (2a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



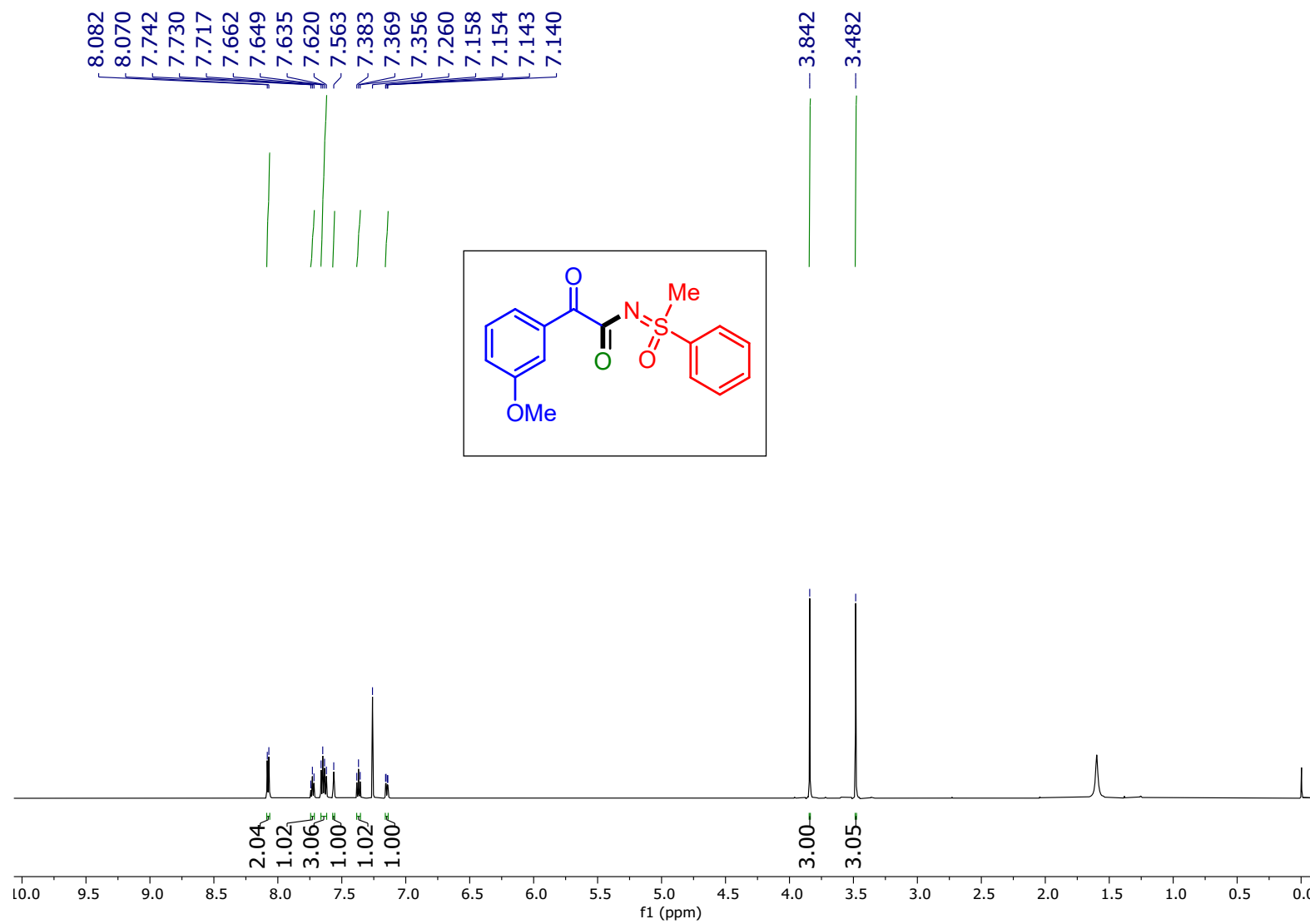
2-(4-(tert-butyl)phenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (3a): ^1H NMR (600 MHz, CDCl_3)



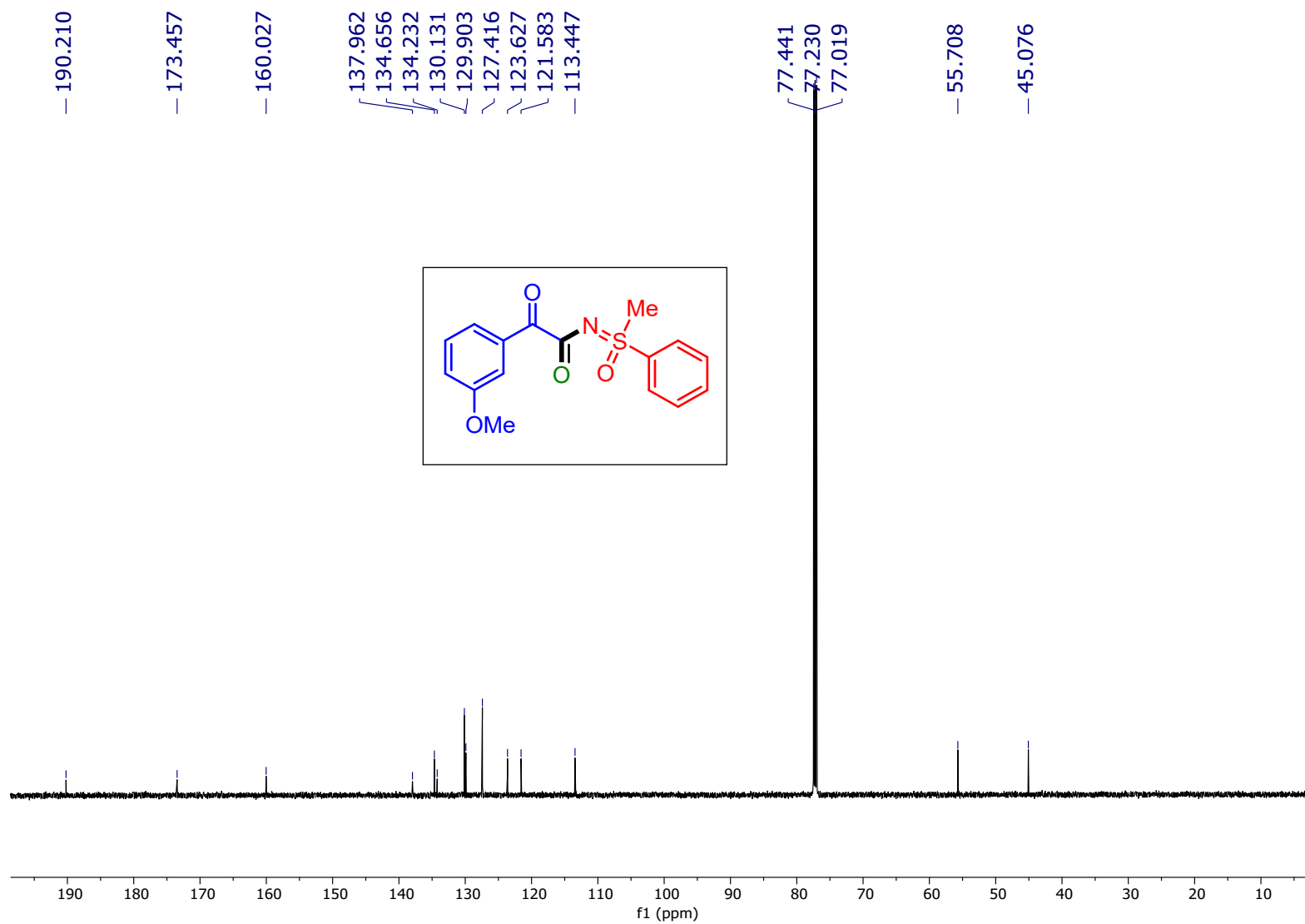
2-(4-(*tert*-butyl)phenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (3a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



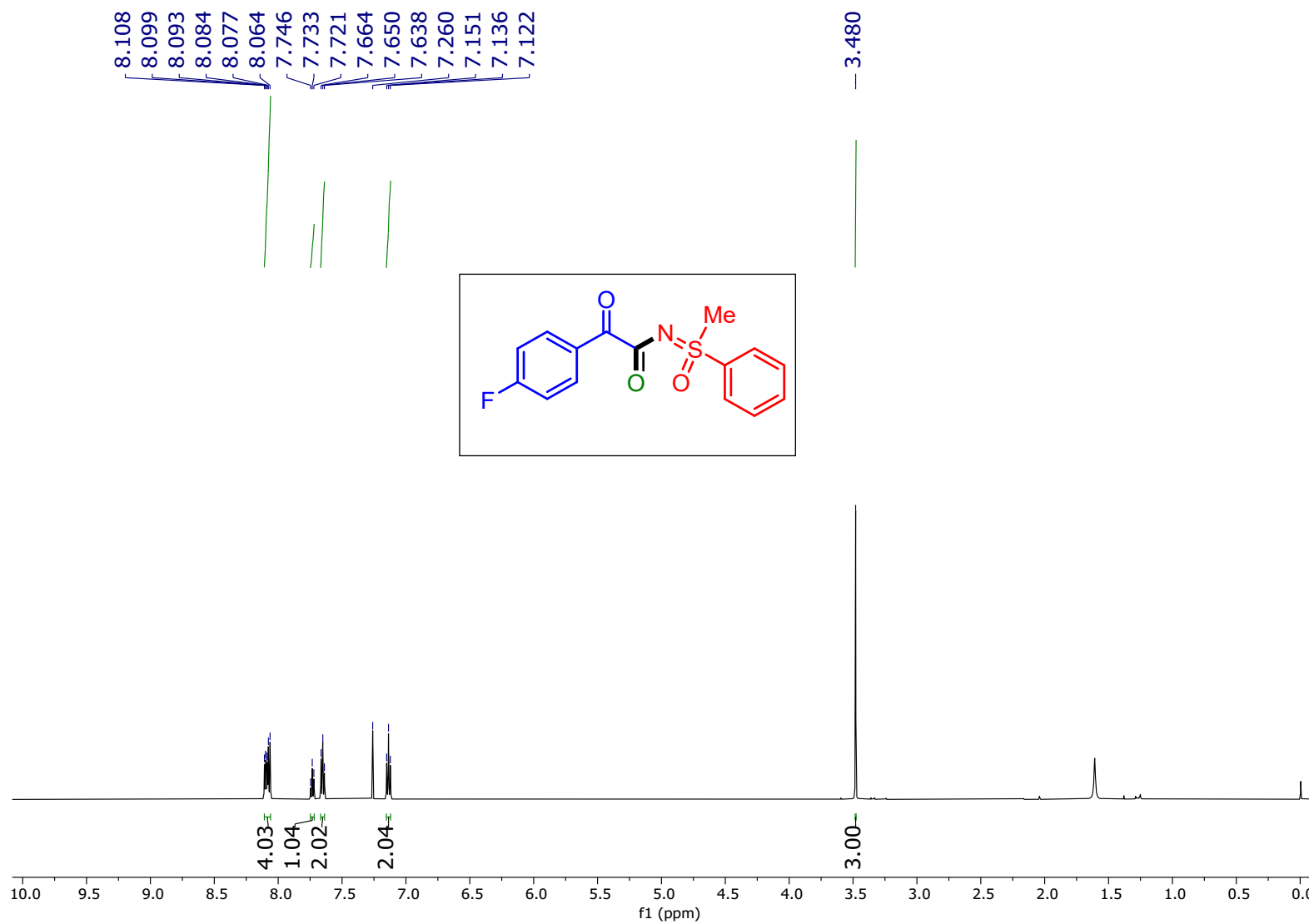
2-(3-Methoxyphenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (4a): ^1H NMR (600 MHz, CDCl_3)



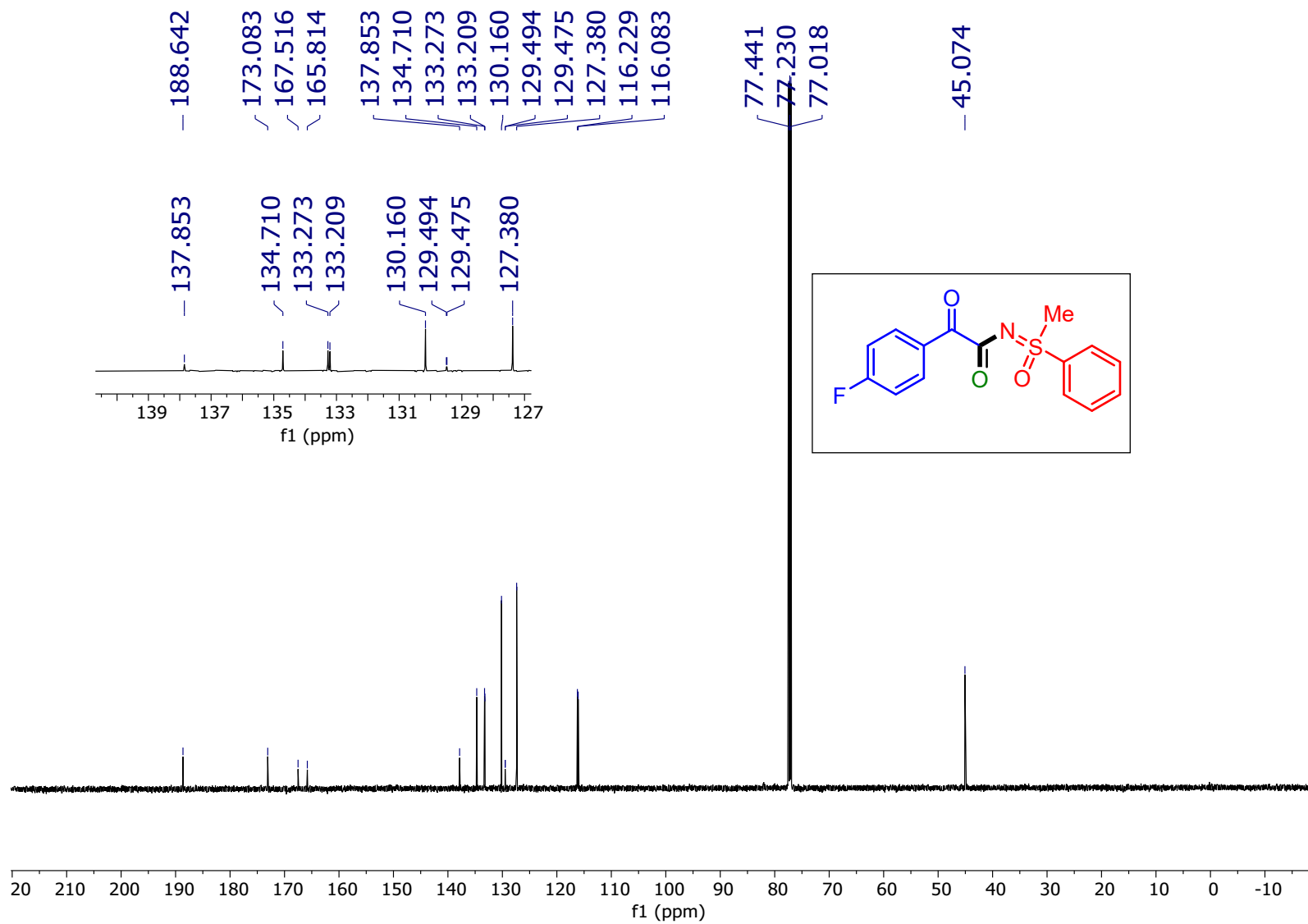
2-(3-Methoxyphenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (4a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



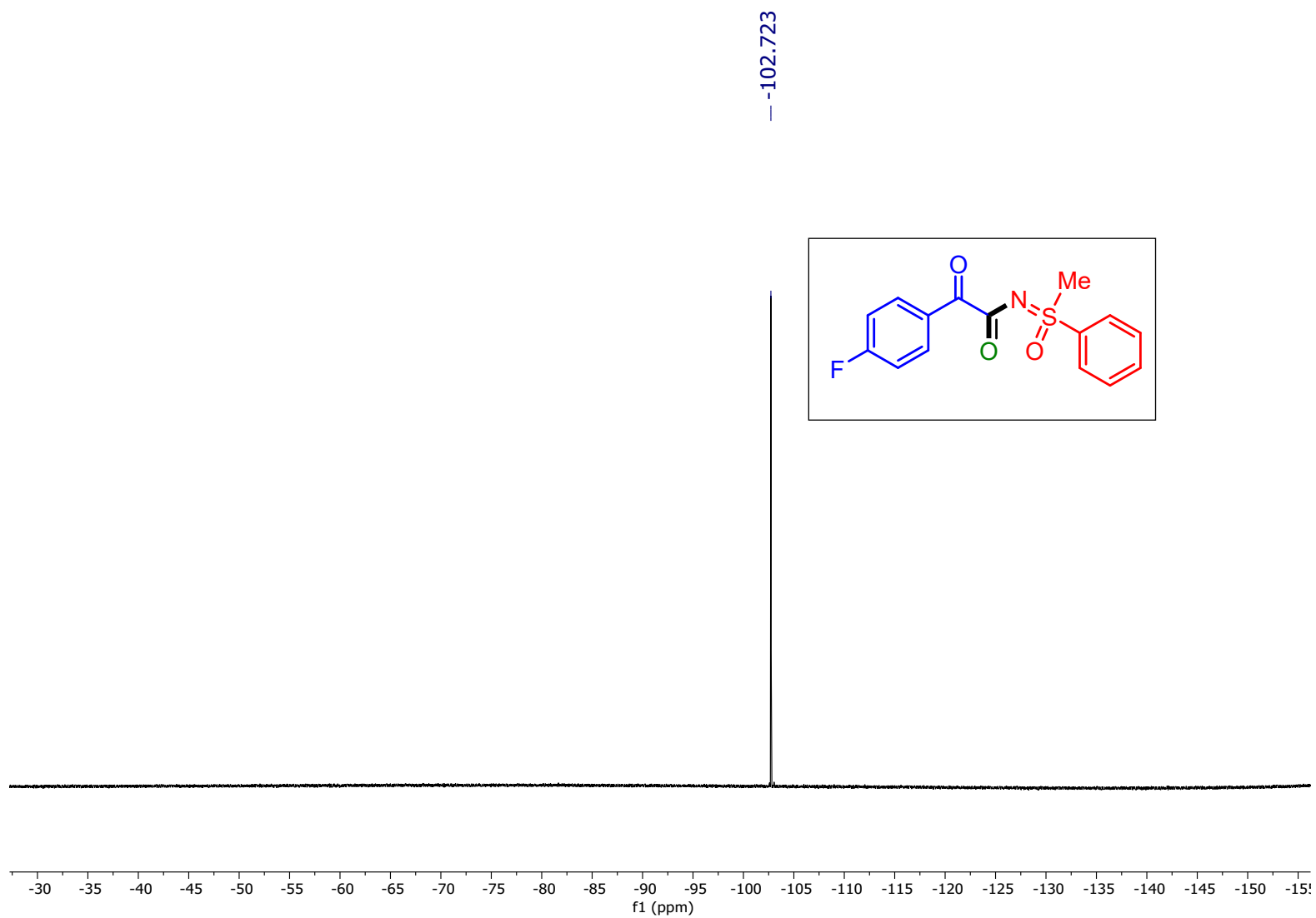
2-(4-Fluorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (5a): ^1H NMR (600 MHz, CDCl_3)



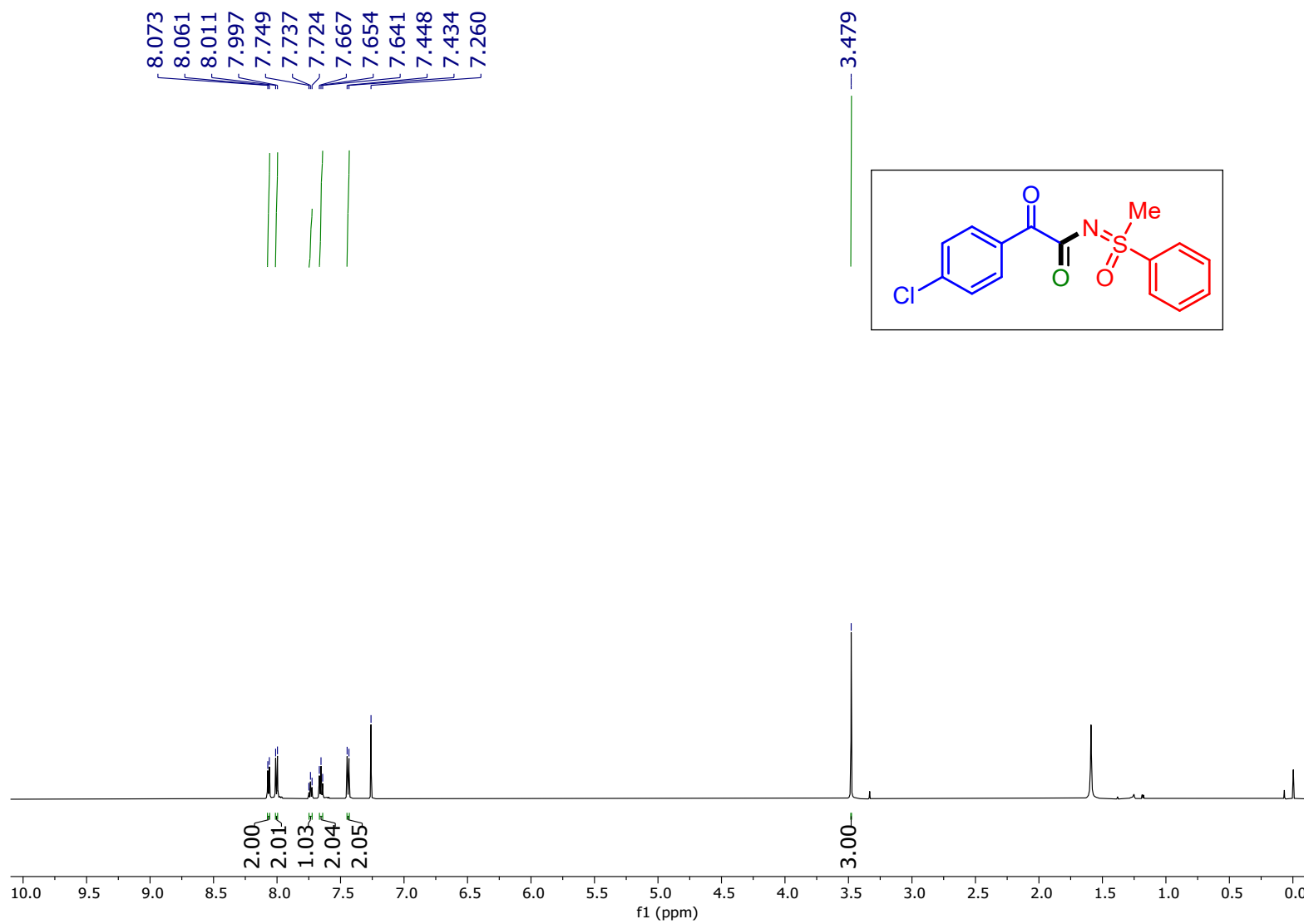
2-(4-Fluorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (5a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



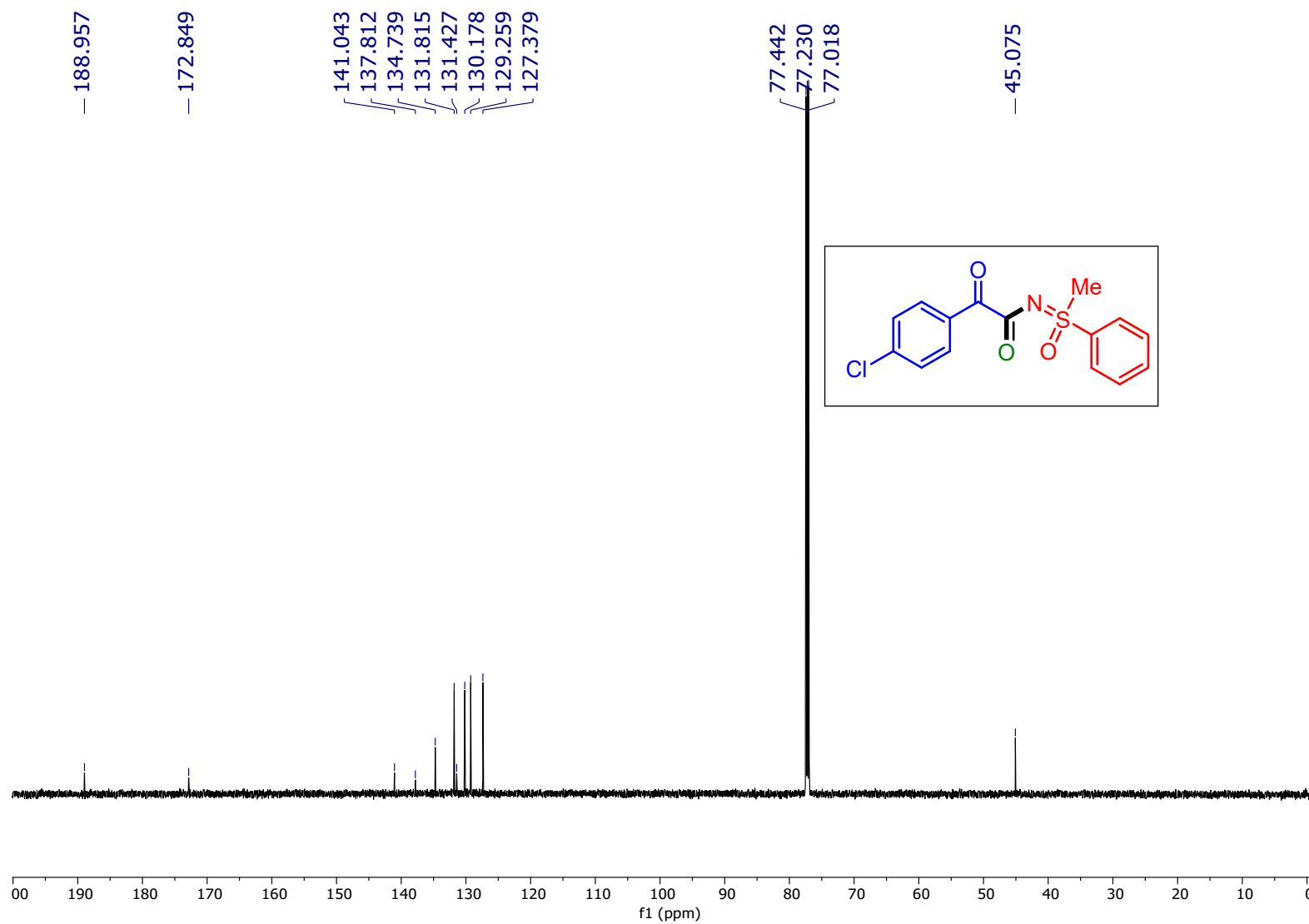
2-(4-Fluorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (5a): ^{19}F NMR (565 MHz, CDCl_3)



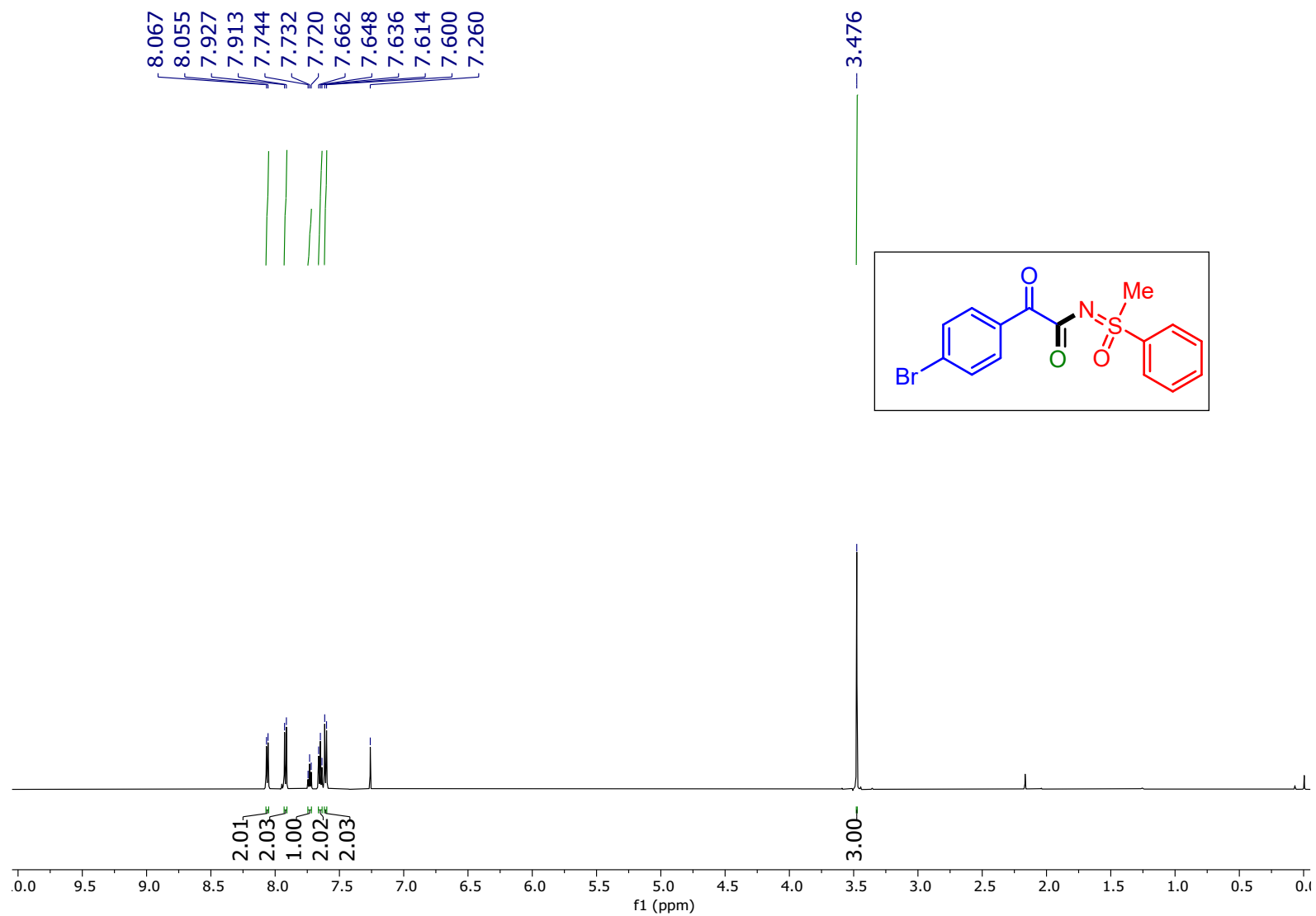
2-(4-Chlorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (6a): ^1H NMR (600 MHz, CDCl_3)



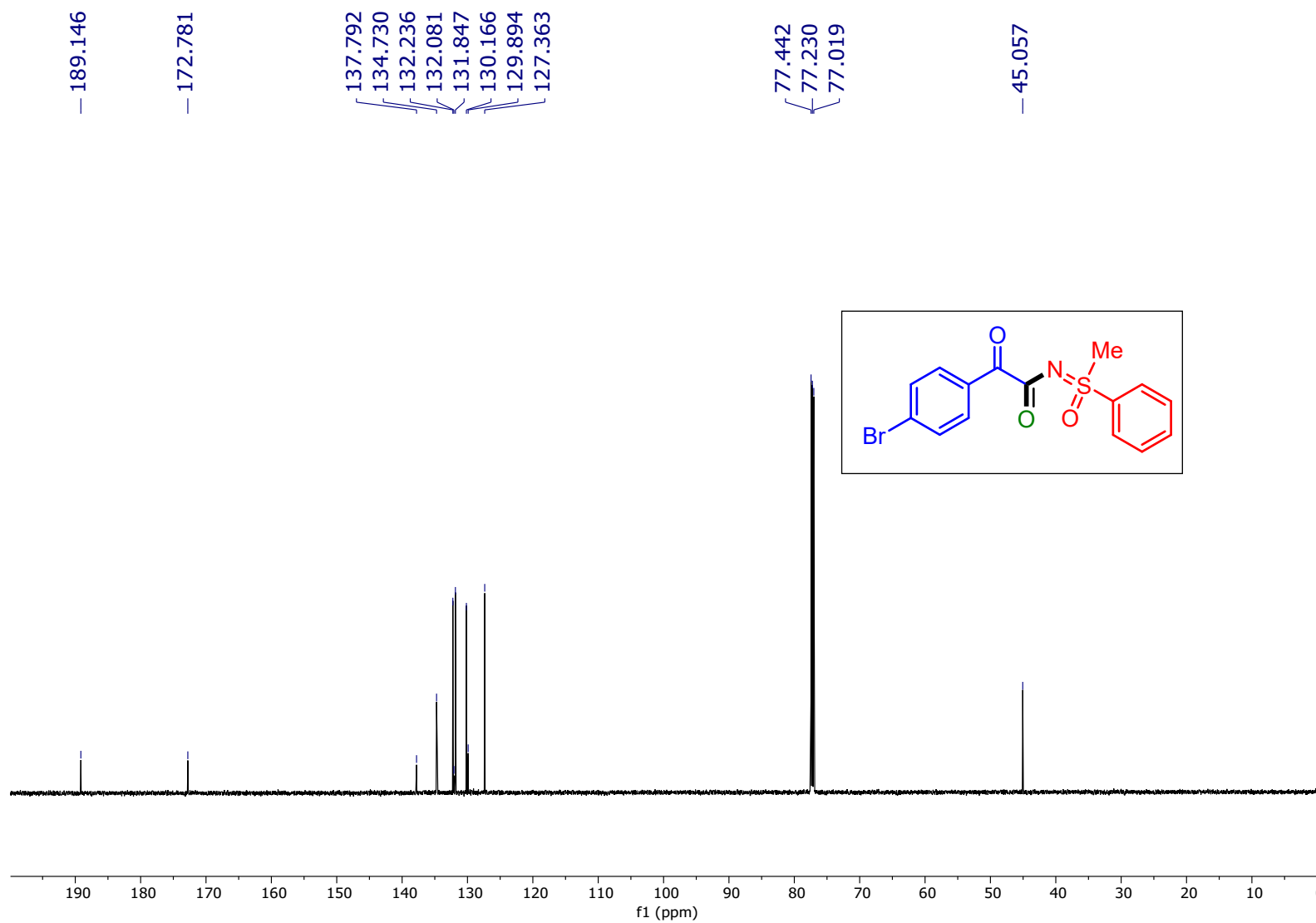
2-(4-Chlorophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (6a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



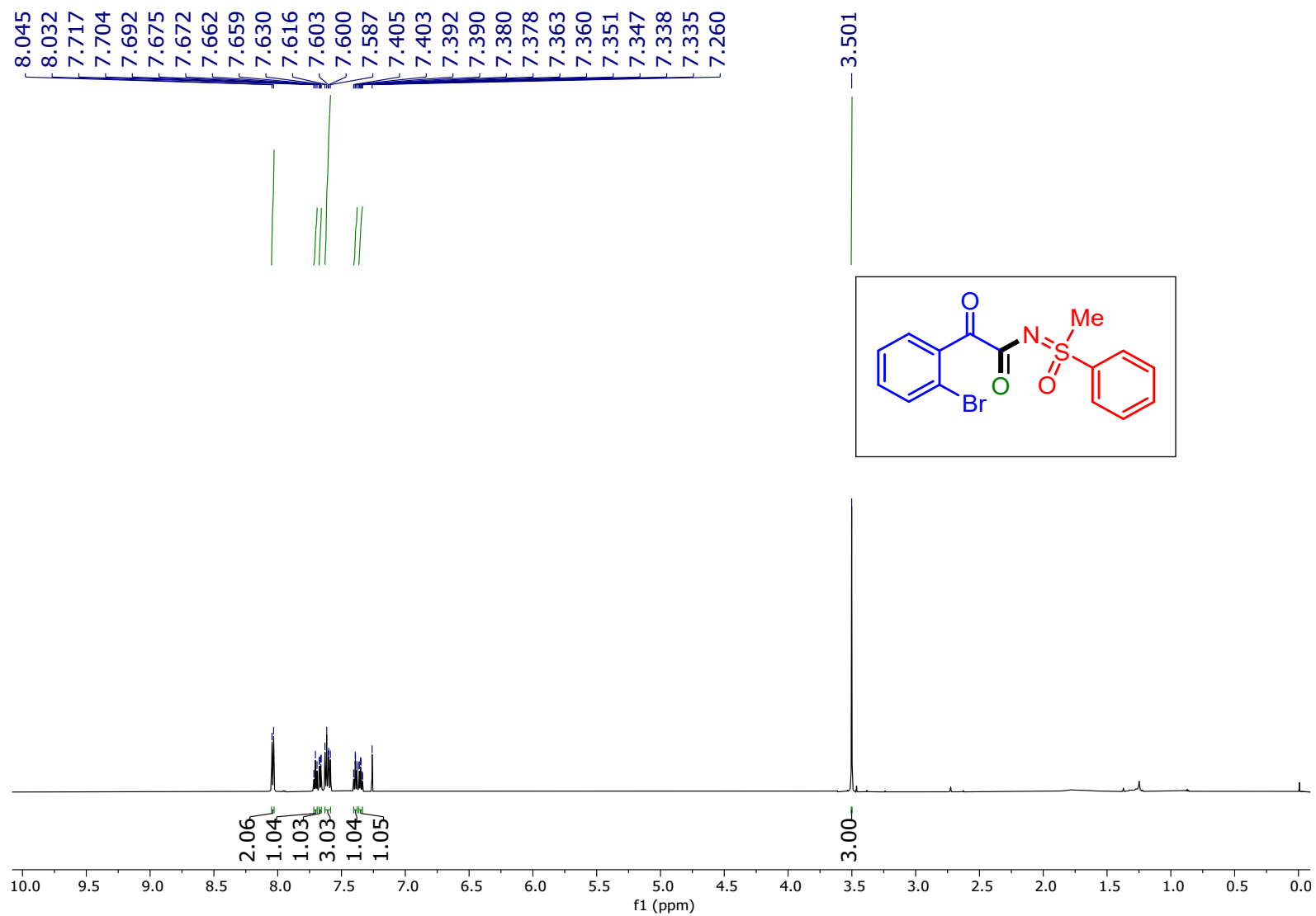
2-(4-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (7a): ^1H NMR (600 MHz, CDCl_3)



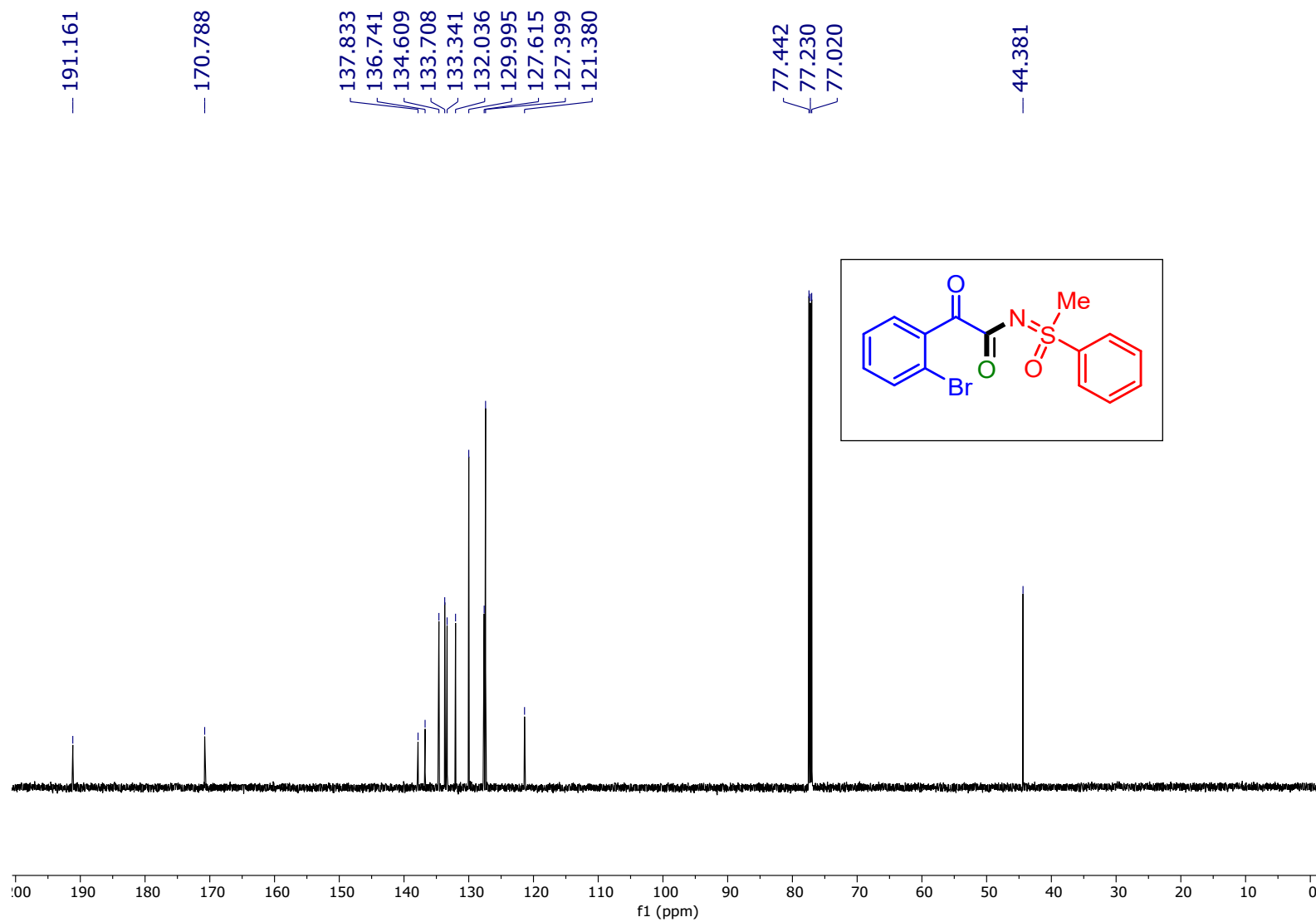
2-(4-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (7a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



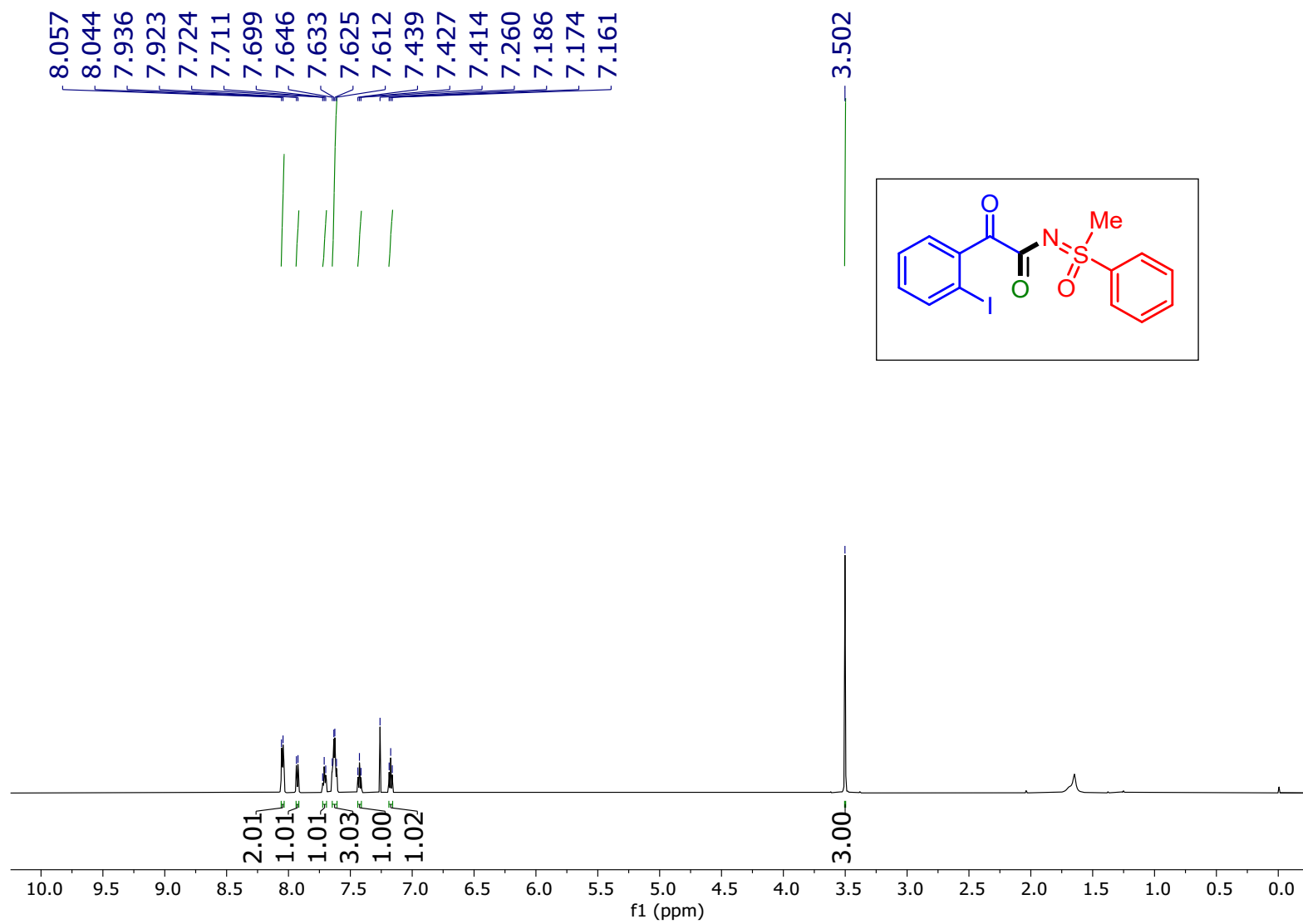
2-(2-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (8a): ^1H NMR (600 MHz, CDCl_3)



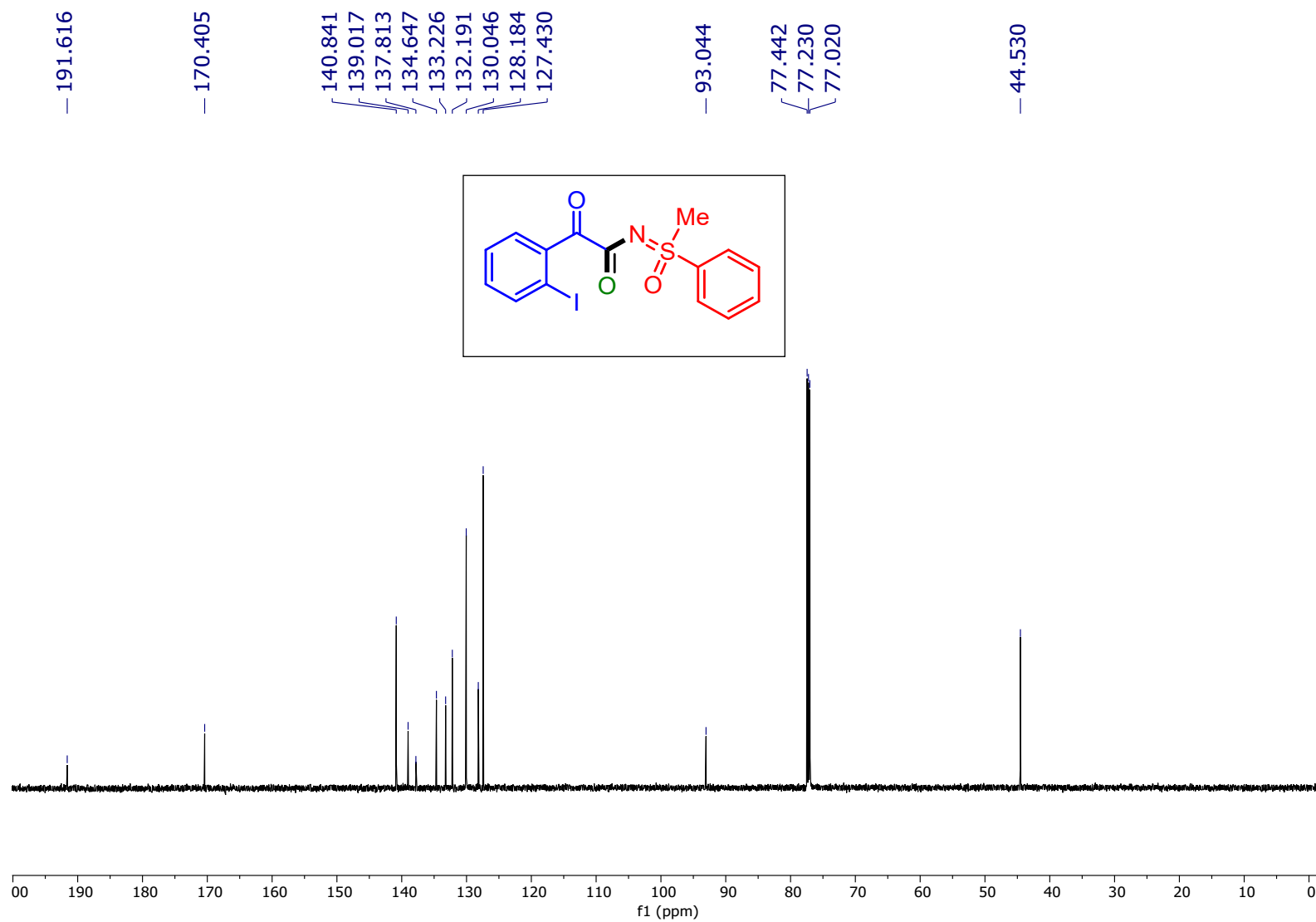
2-(2-Bromophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (8a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



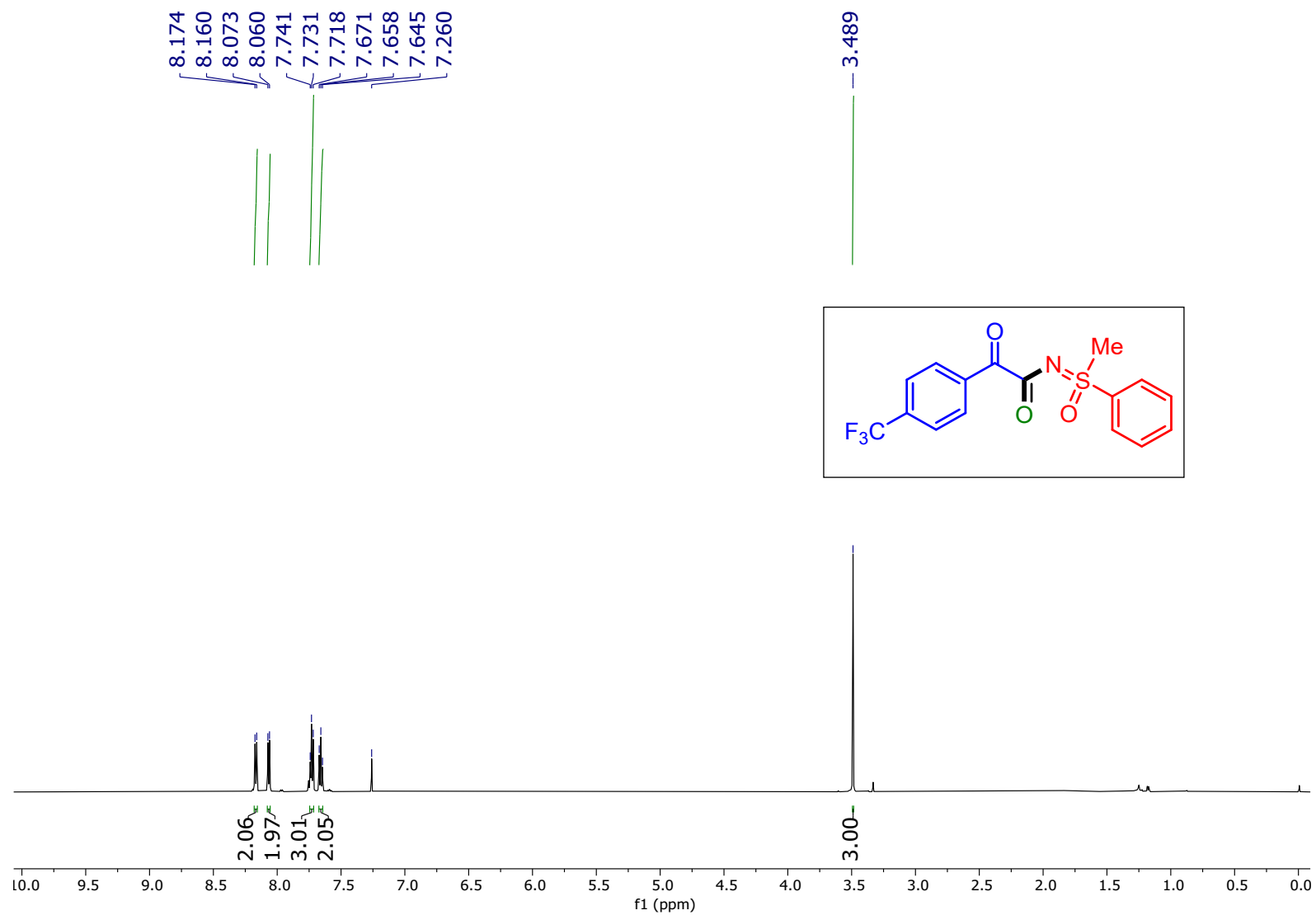
2-(2-Iodophenyl)-N-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (9a): ^1H NMR (600 MHz, CDCl_3)



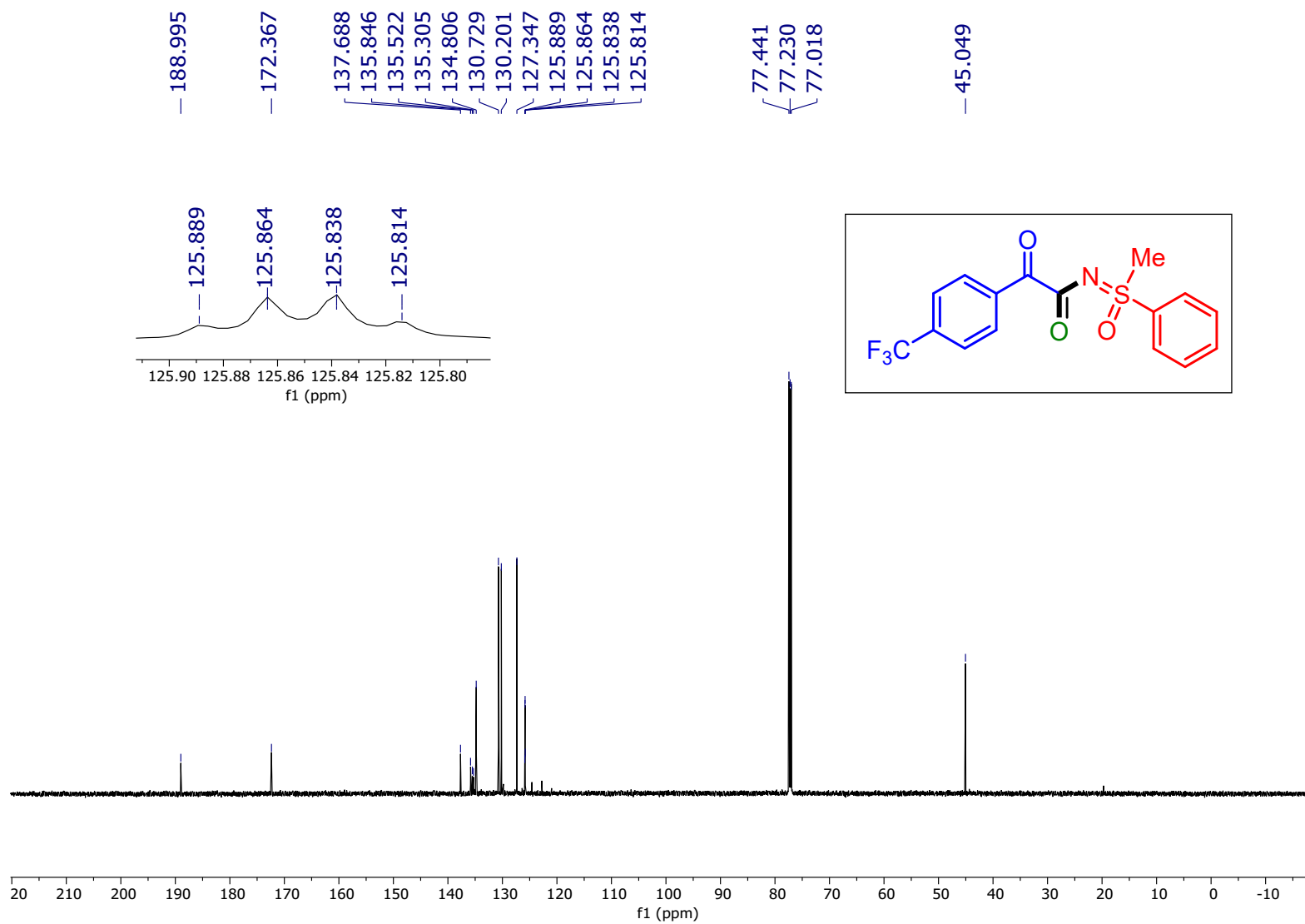
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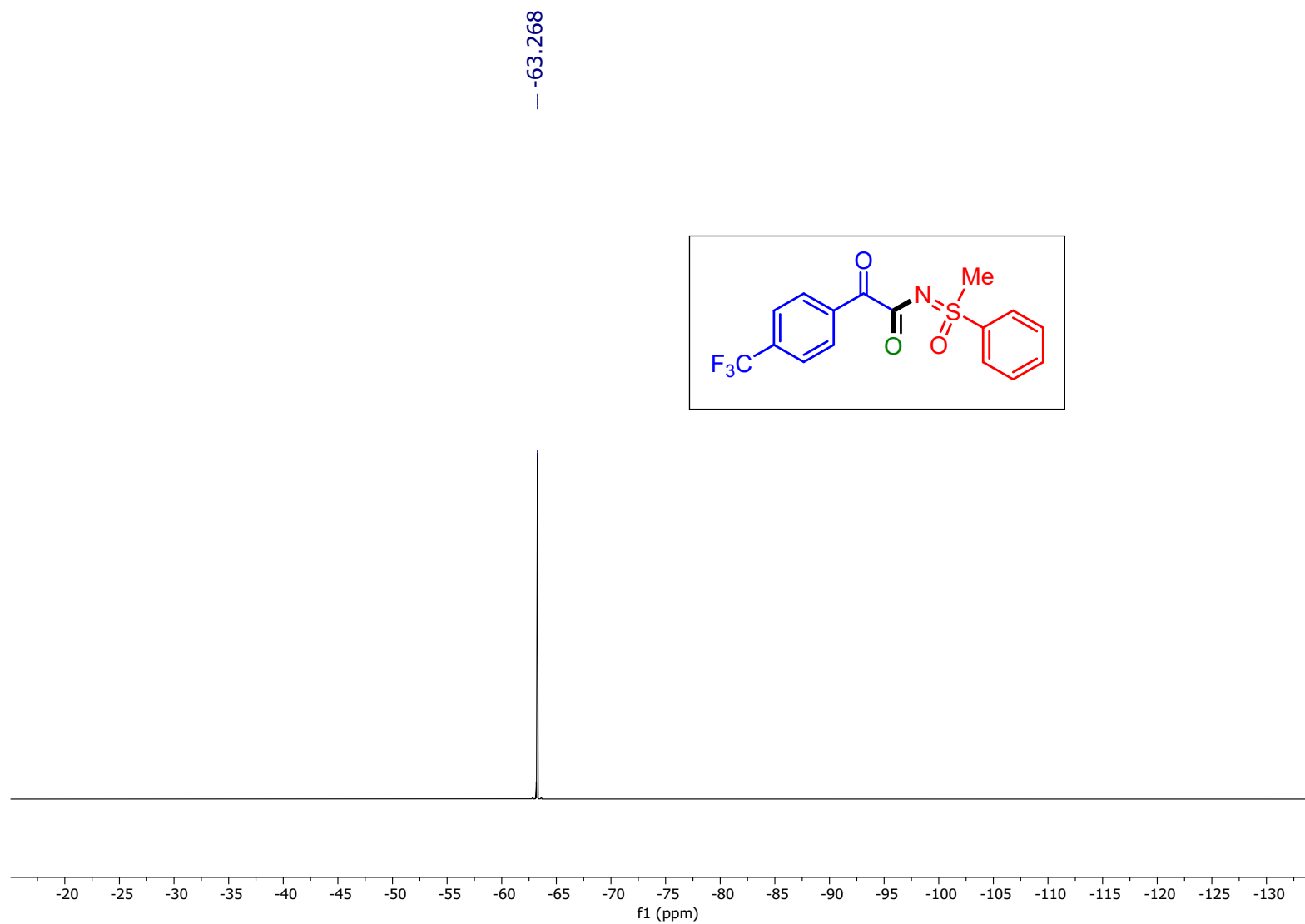
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (10a): ^1H NMR (600 MHz, CDCl_3)



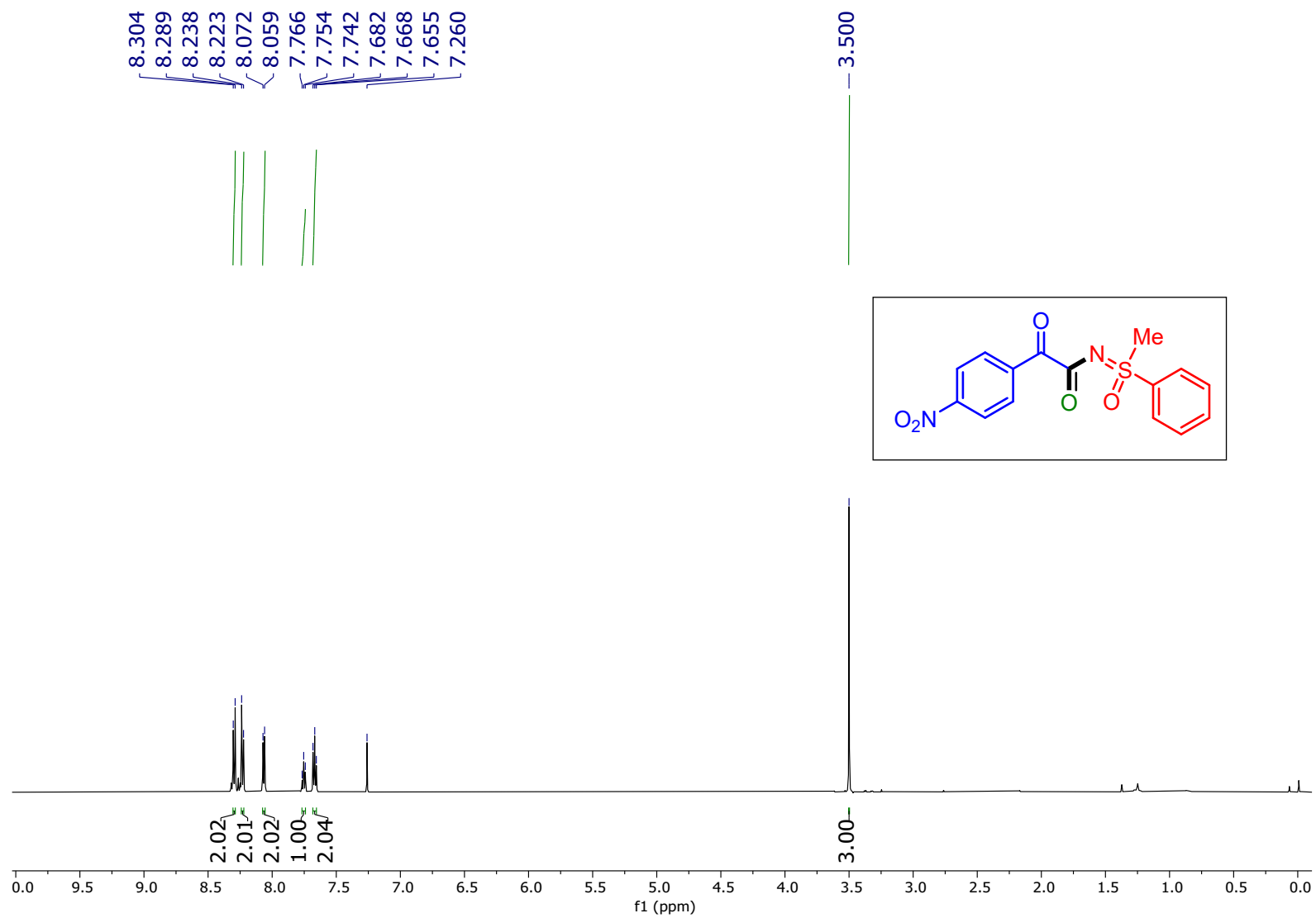
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (10a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



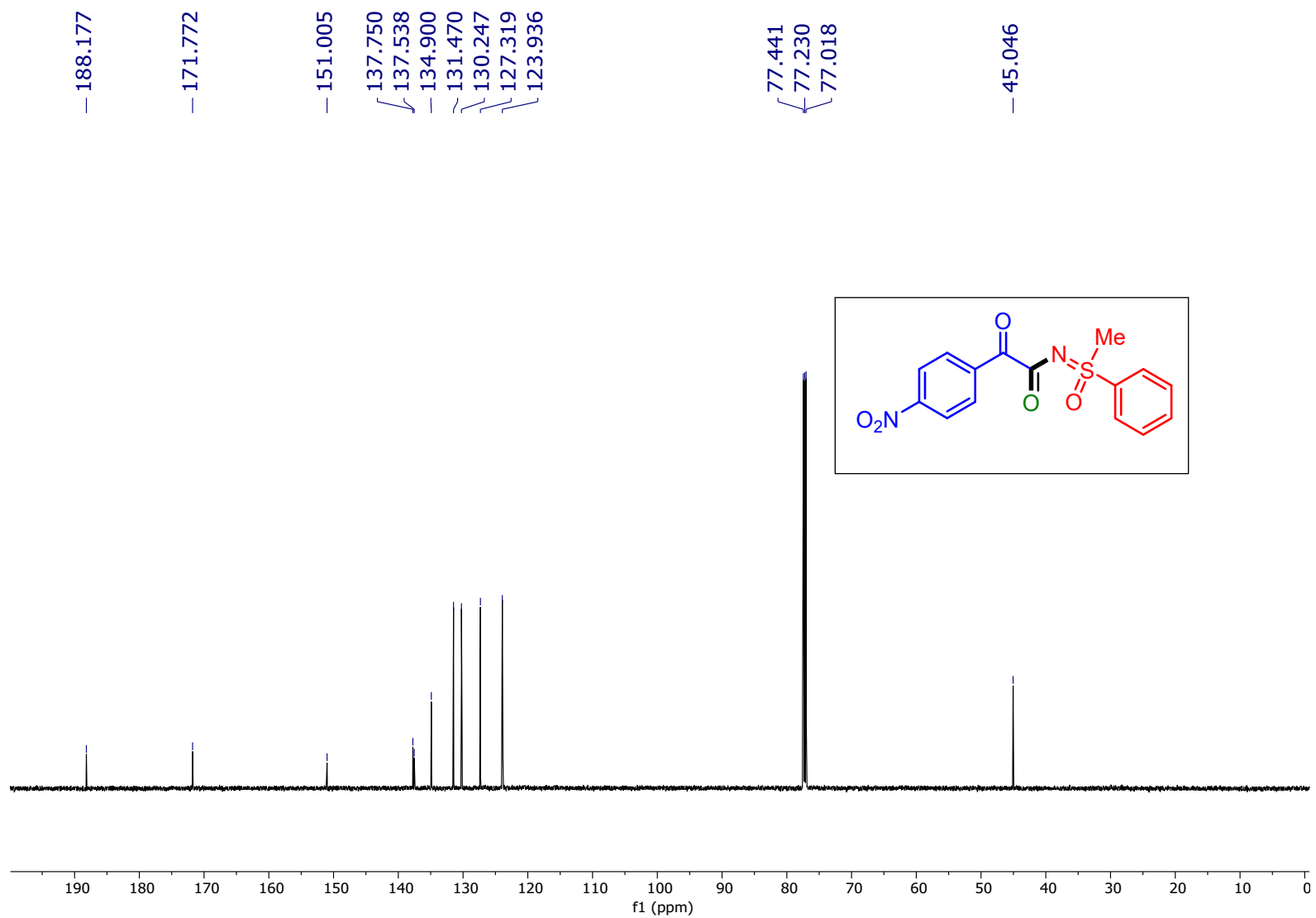
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (10a): ^{19}F NMR (565 MHz, CDCl_3)



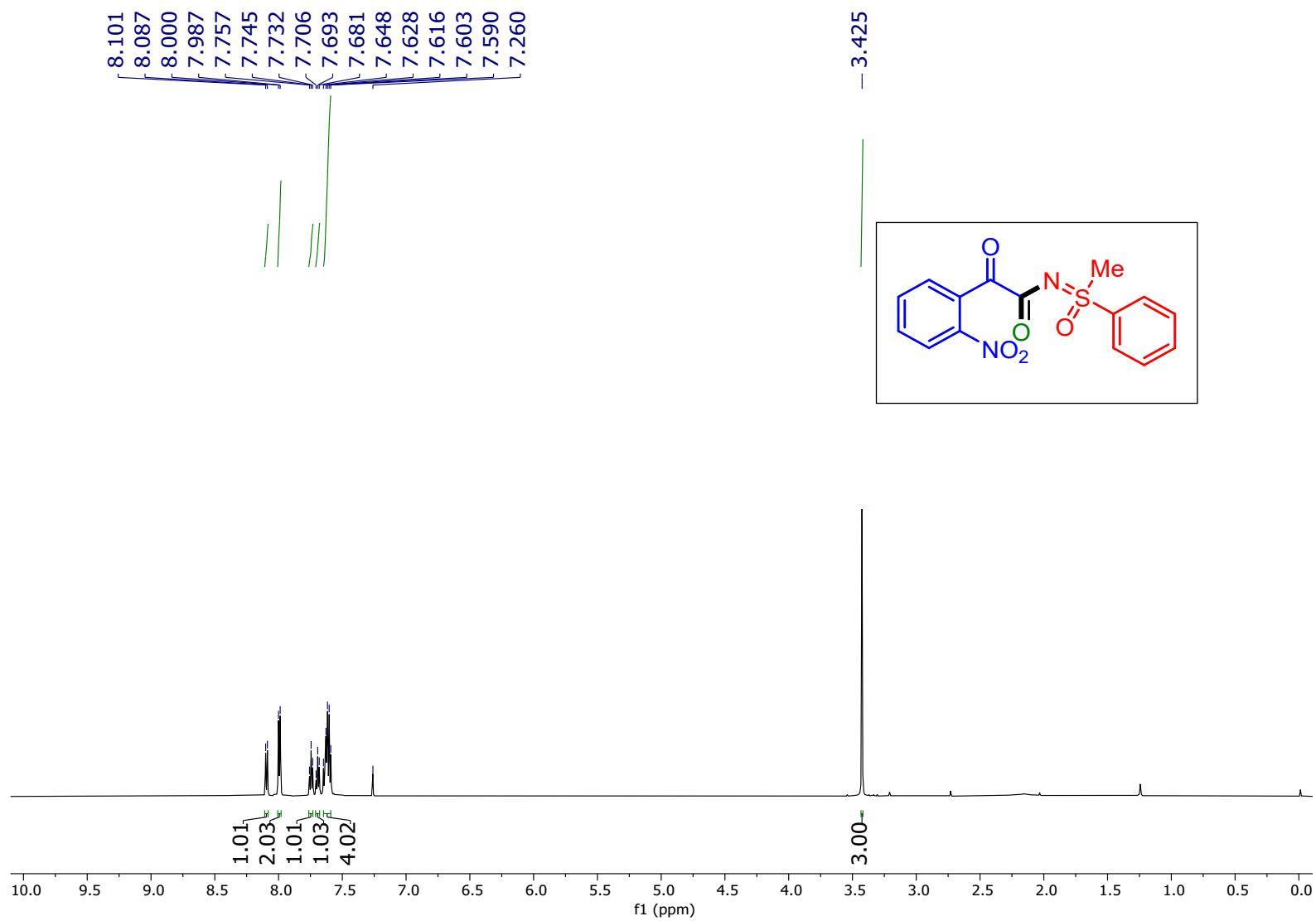
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(4-nitrophenyl)-2-oxoacetamide (11a): ^1H NMR (600 MHz, CDCl_3)



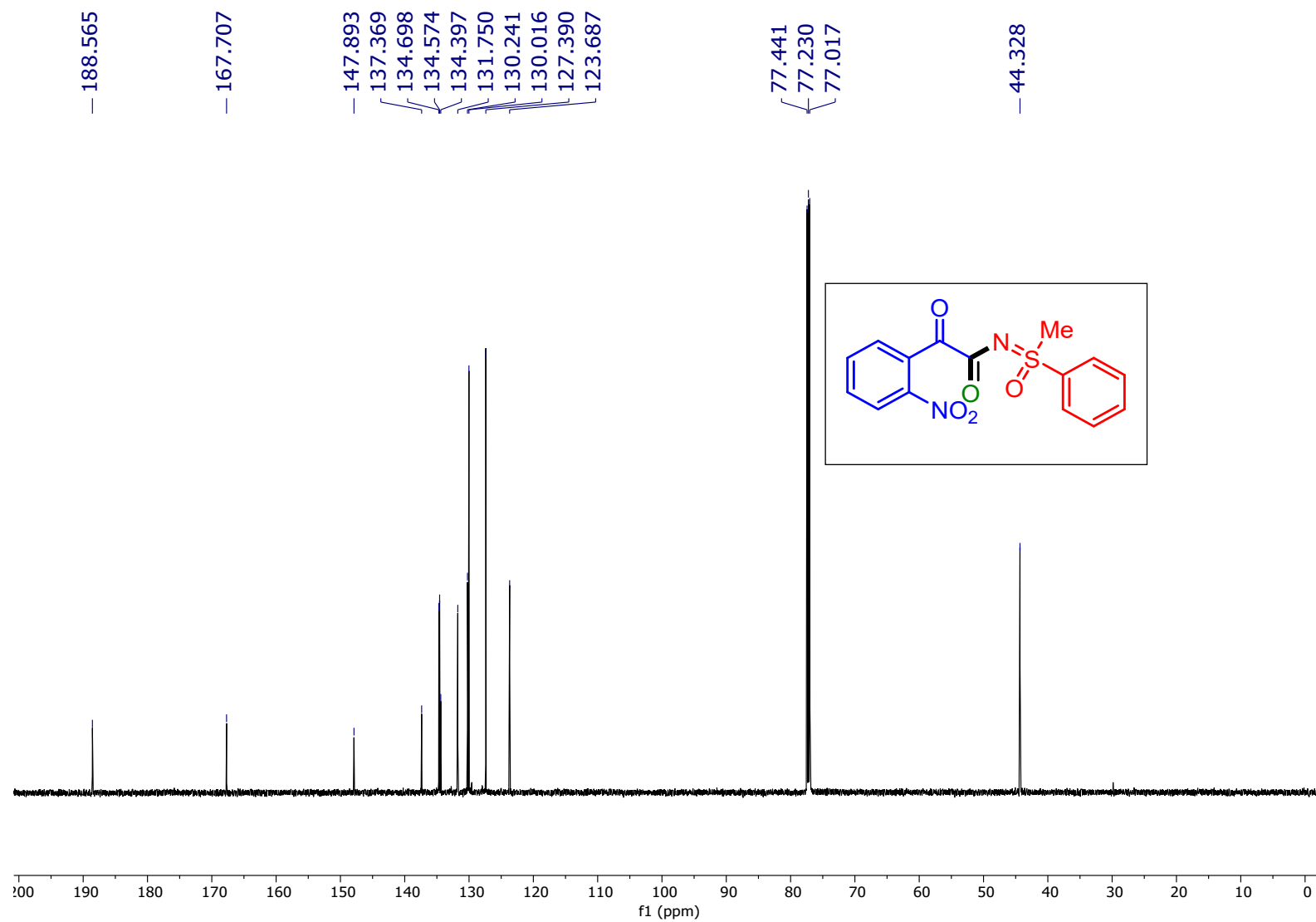
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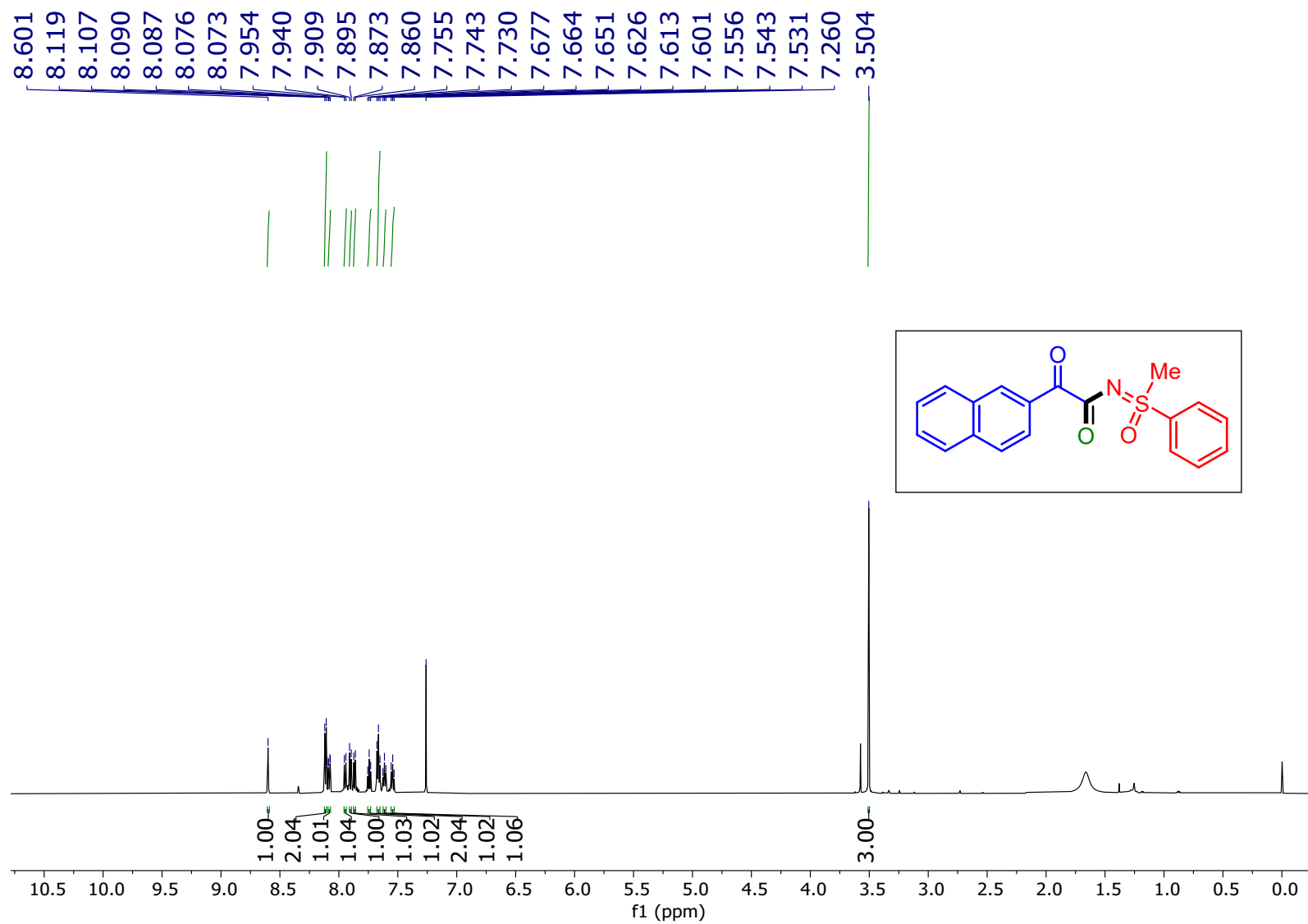
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (12a): ^1H NMR (600 MHz, CDCl_3)



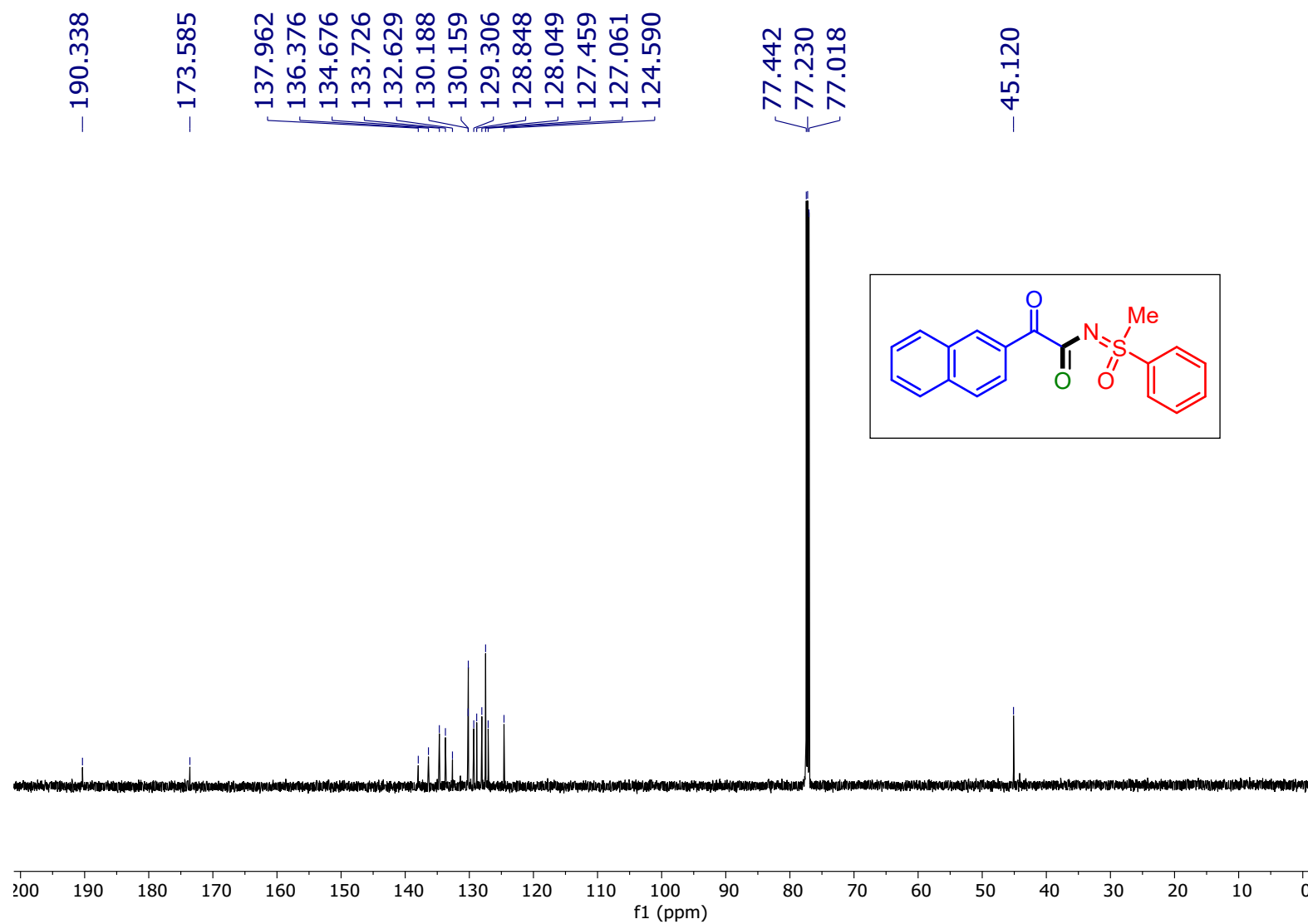
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(2-nitrophenyl)-2-oxoacetamide (12a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



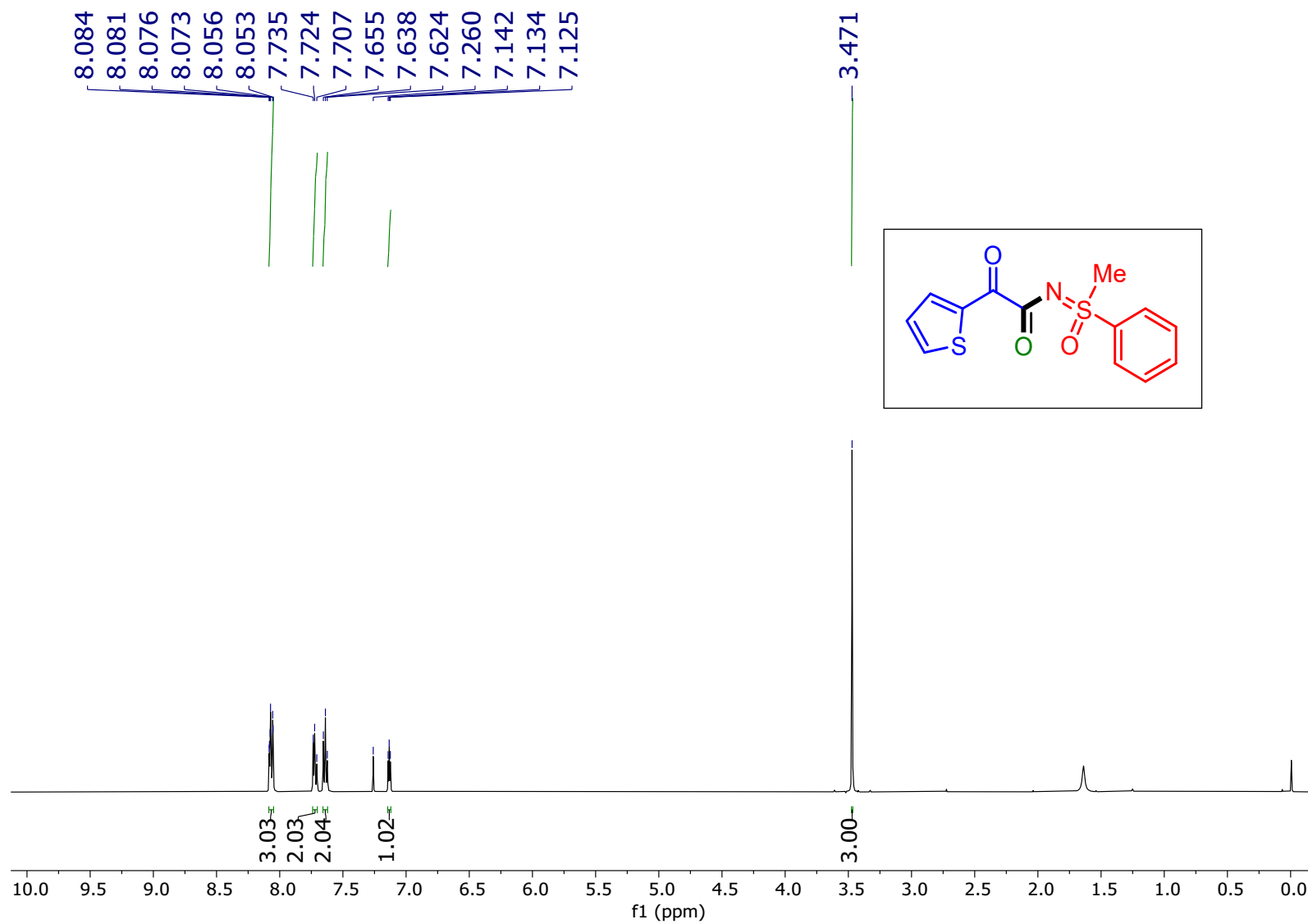
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(naphthalen-2-yl)-2-oxoacetamide (13a): ^1H NMR (600 MHz, CDCl_3)



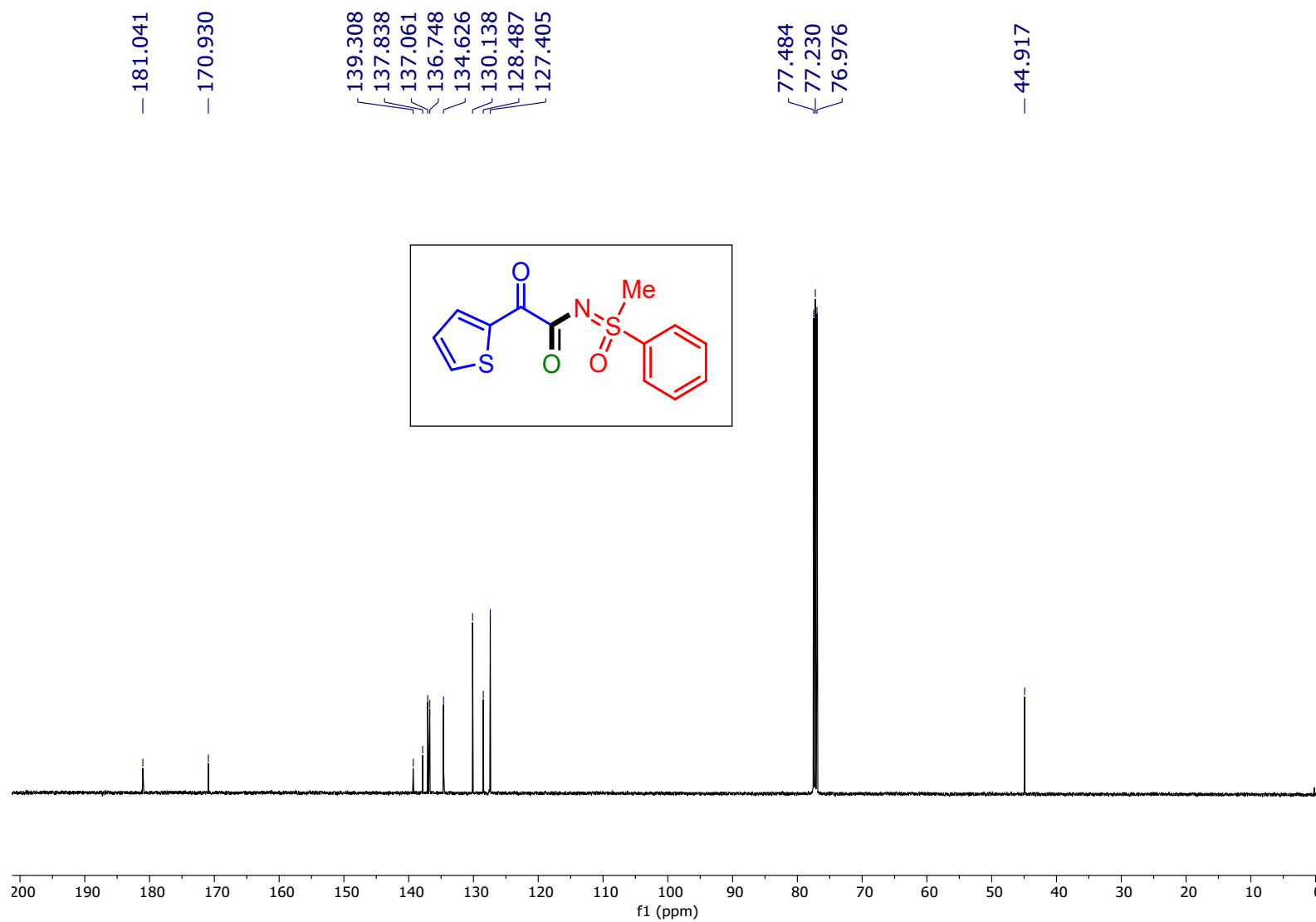
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(naphthalen-2-yl)-2-oxoacetamide (13a): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



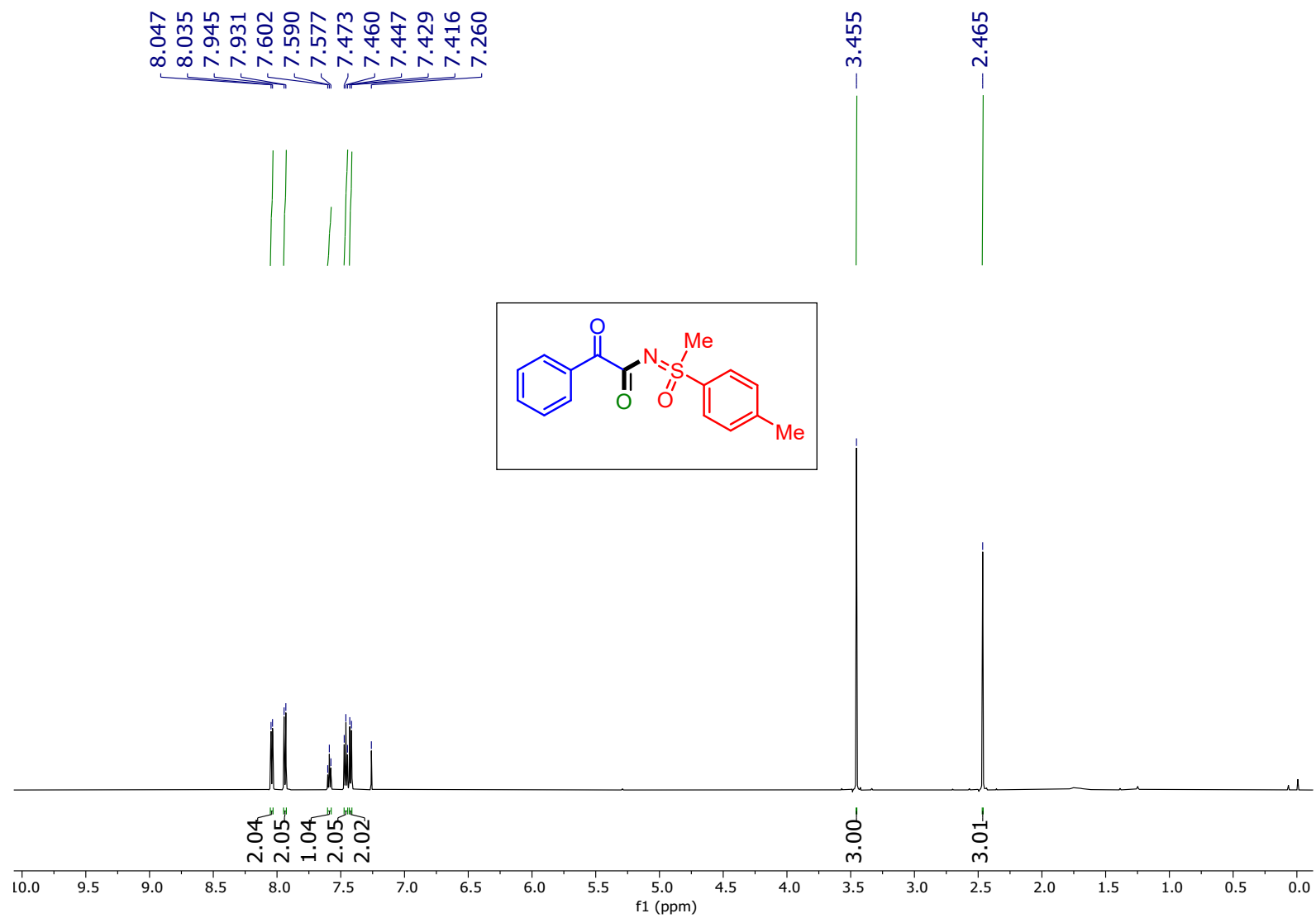
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(thiophen-2-yl)acetamide (14a): ^1H NMR (500 MHz, CDCl_3)



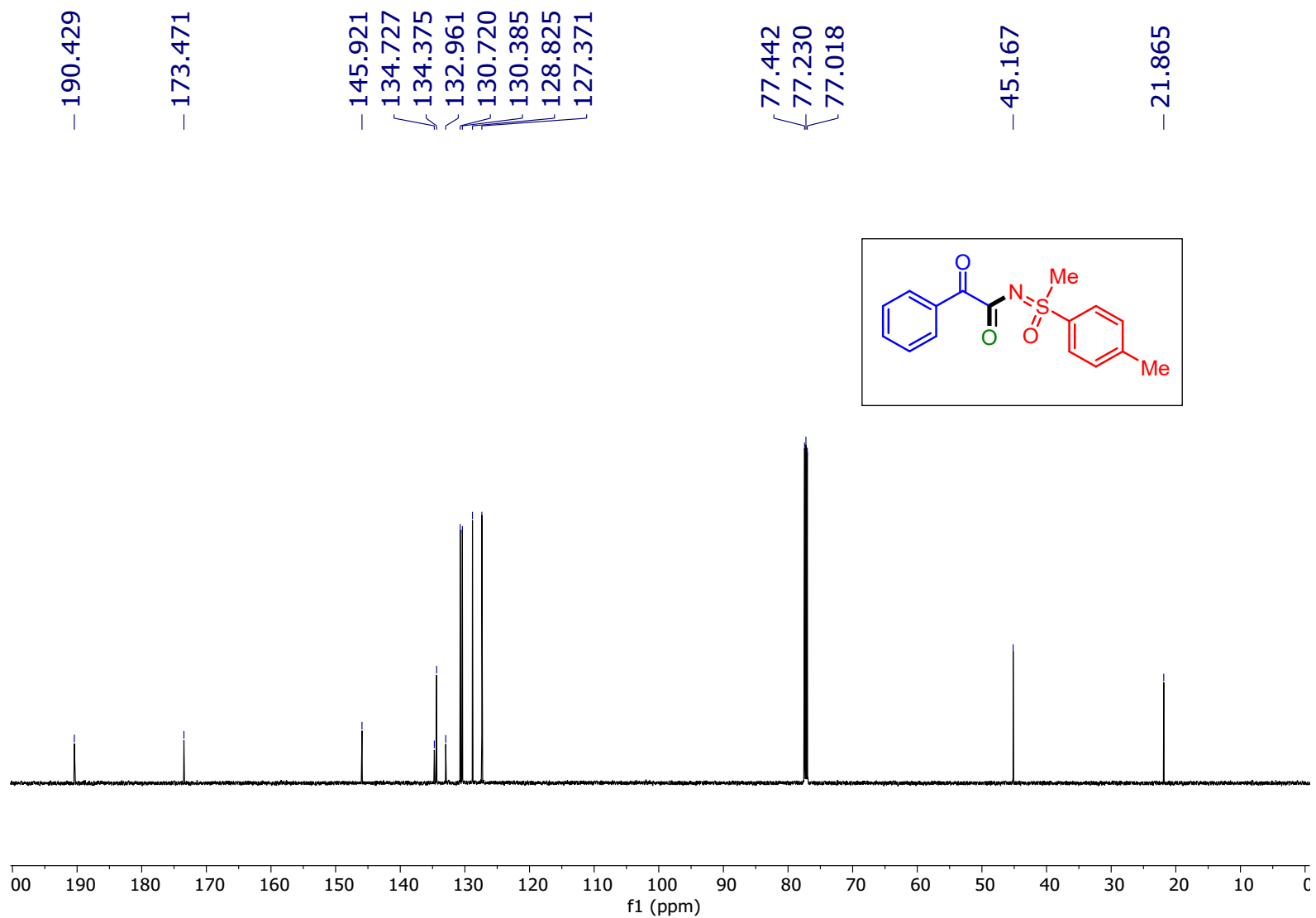
N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(thiophen-2-yl)acetamide (14a): $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



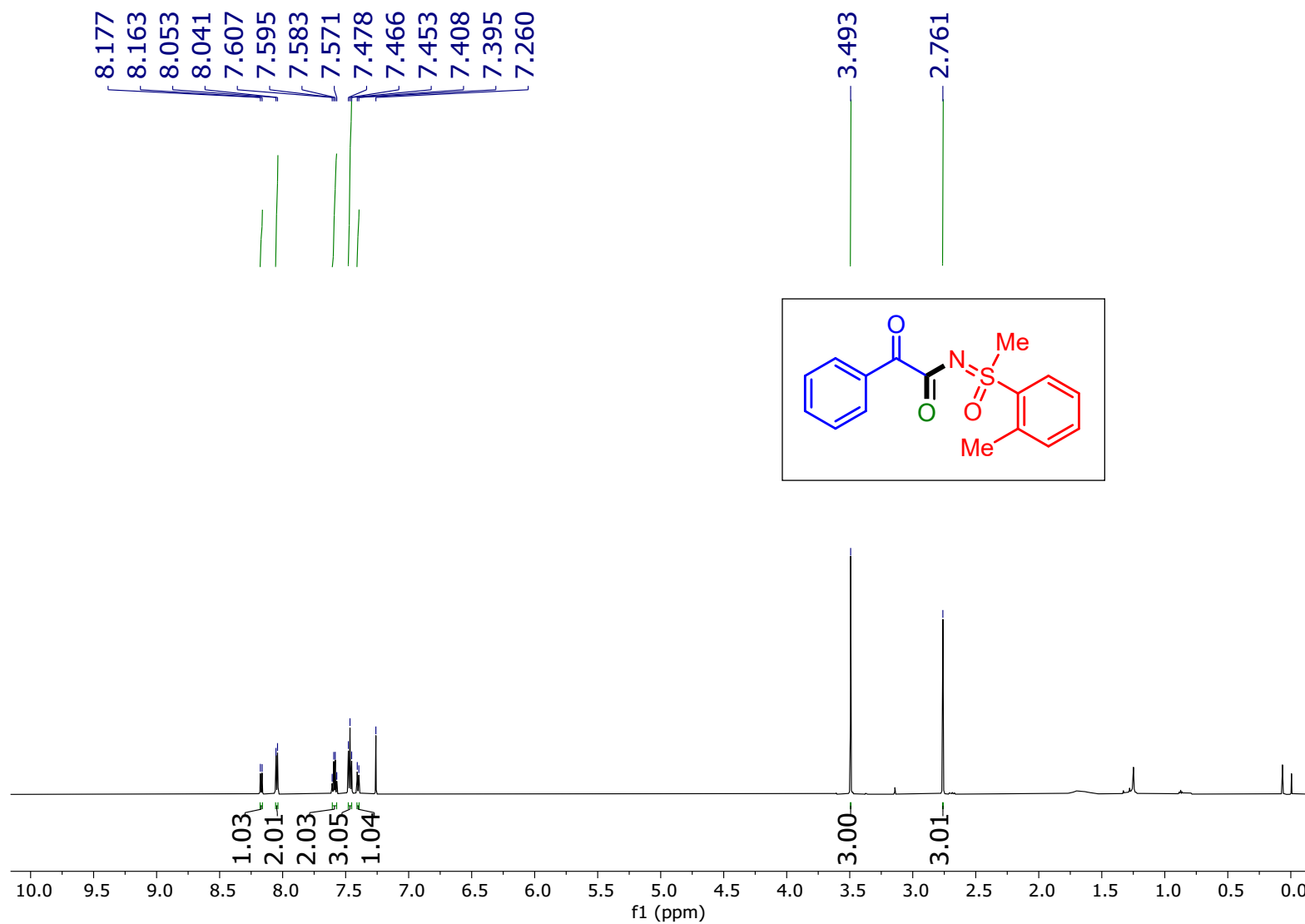
N-(Methyl(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1b): ^1H NMR (600 MHz, CDCl_3)



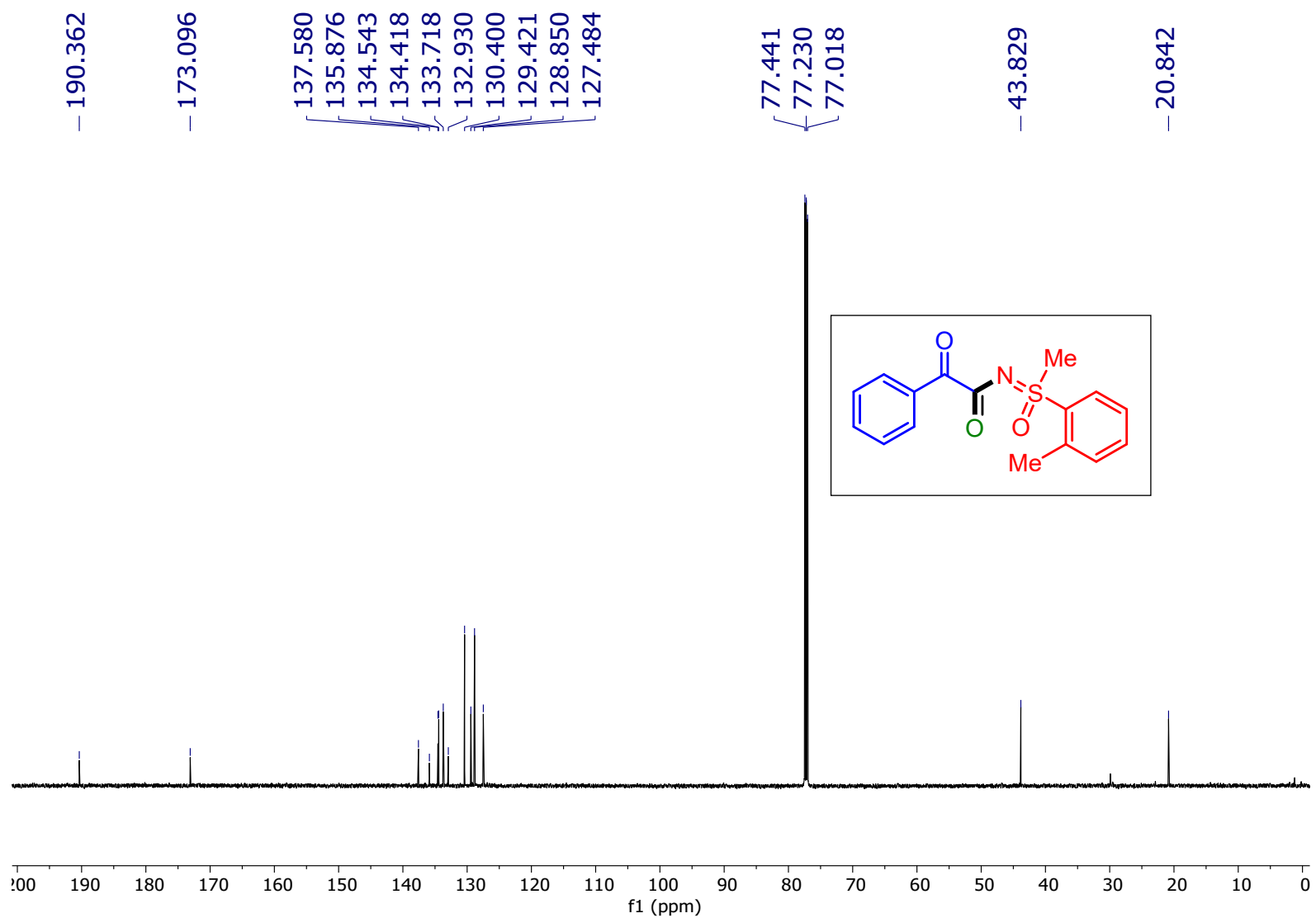
N-(Methyl(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1b): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



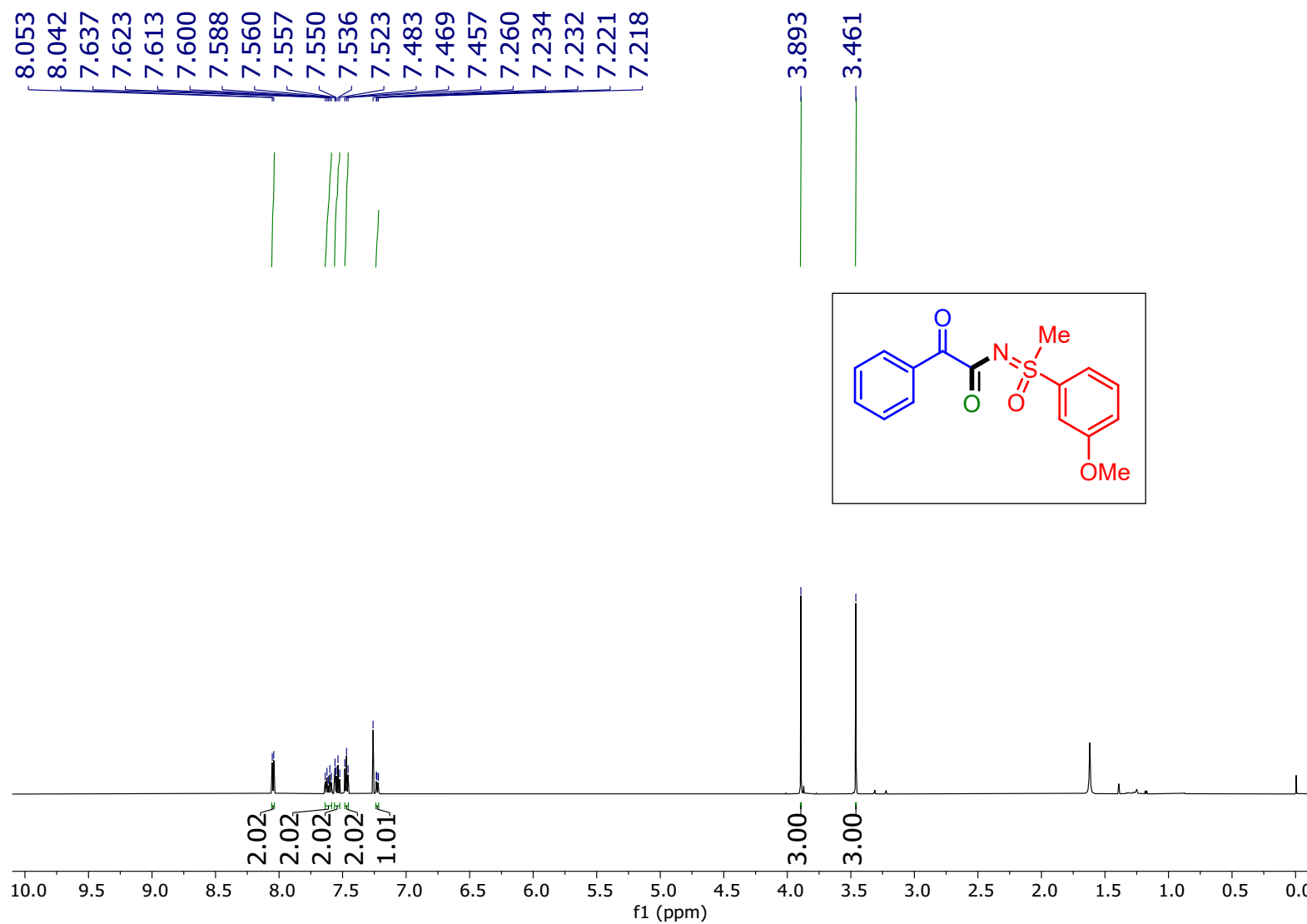
N-(Methyl(oxo)(*o*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1c): ^1H NMR (600 MHz, CDCl_3)



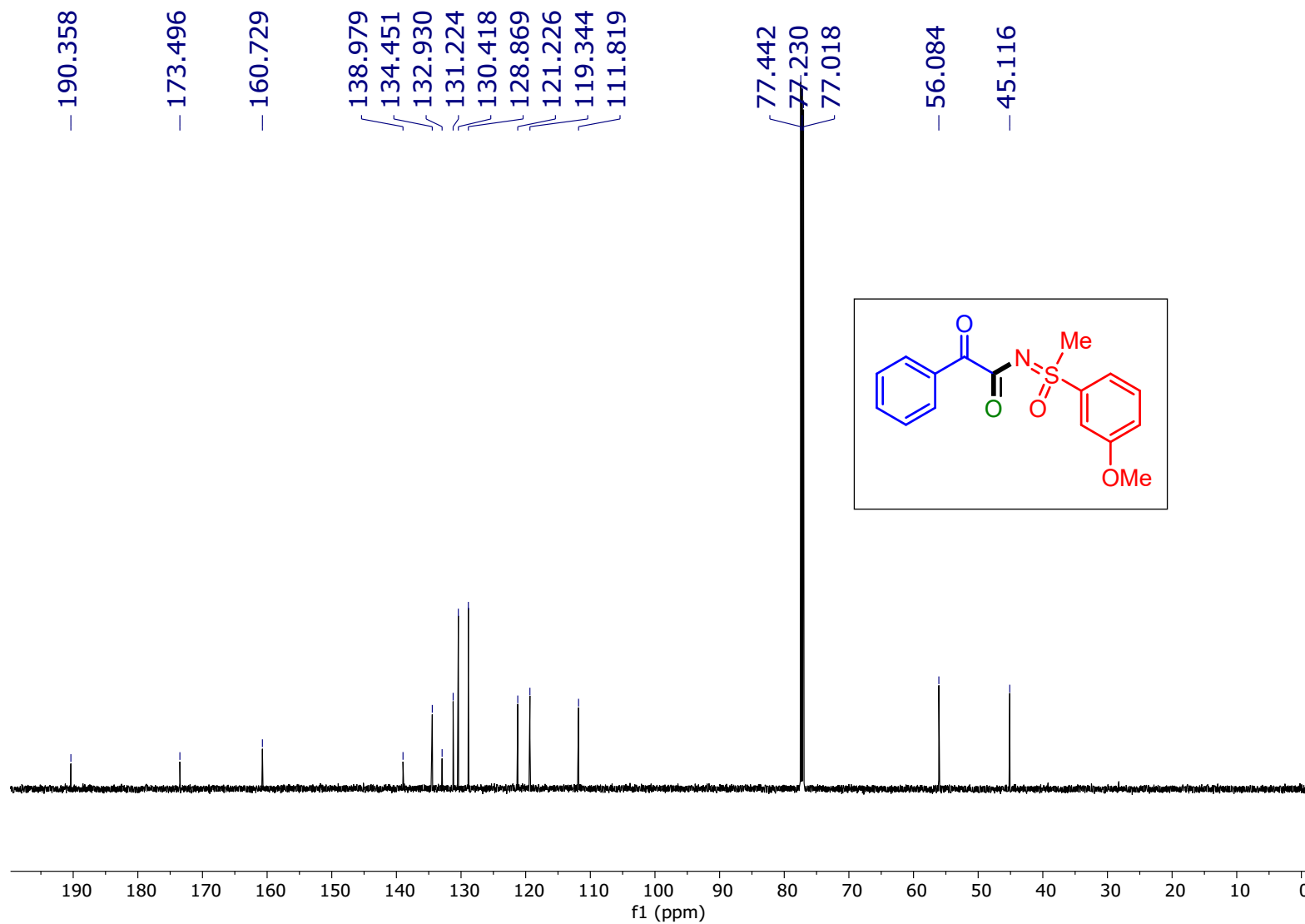
N-(Methyl(oxo)(*o*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1c): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



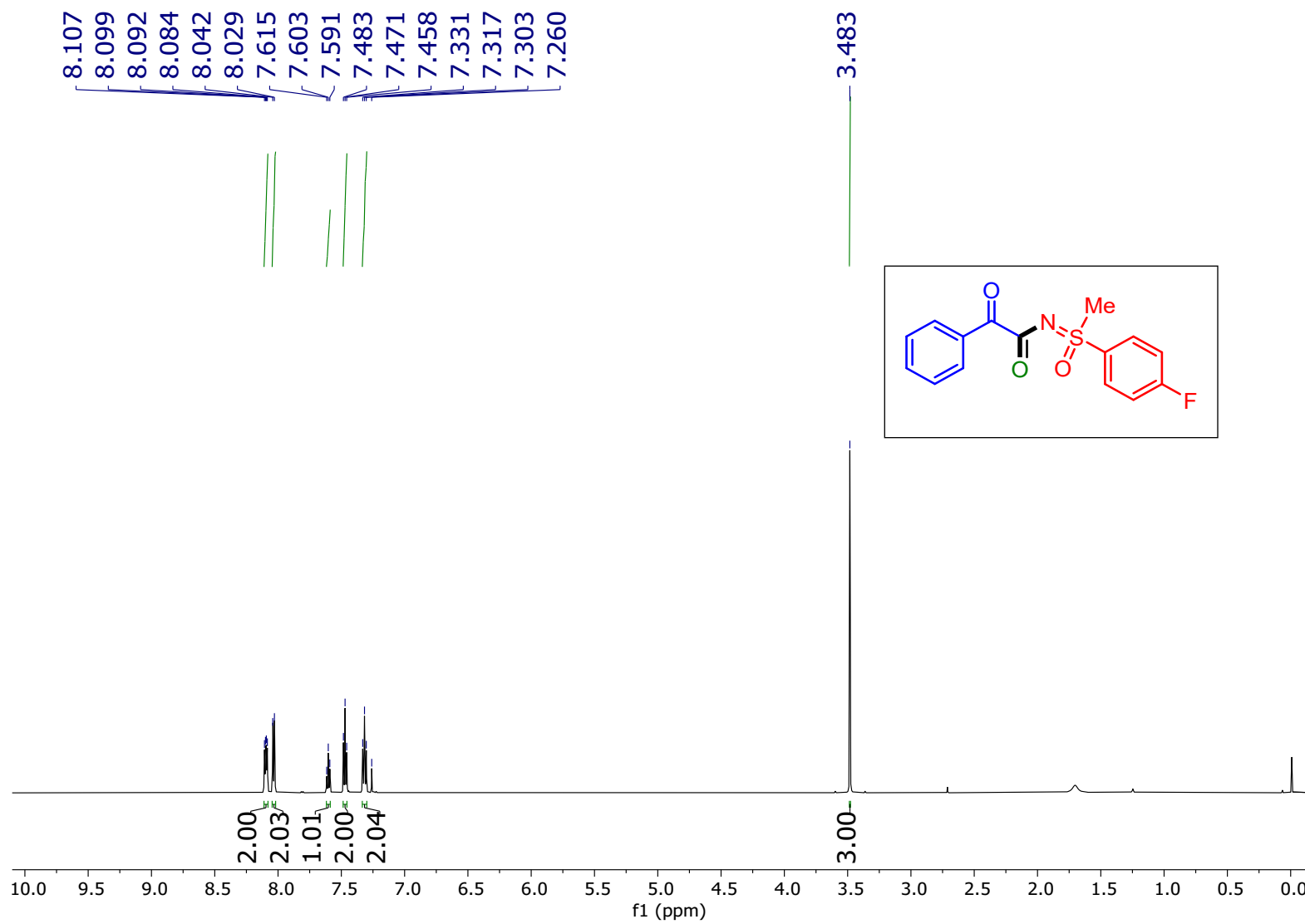
N-((3-Methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1d): ^1H NMR (600 MHz, CDCl_3)



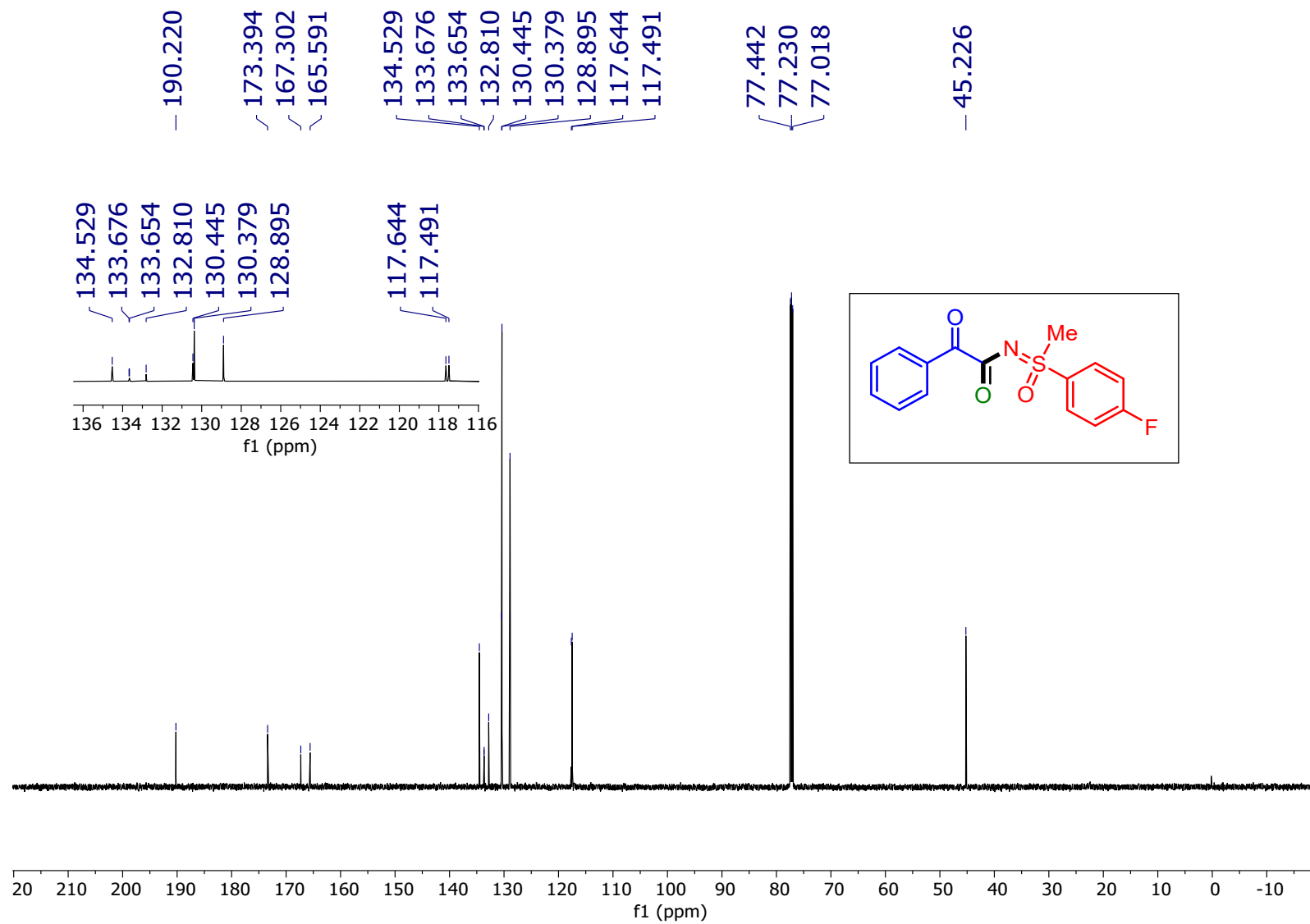
N-((3-Methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1d): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



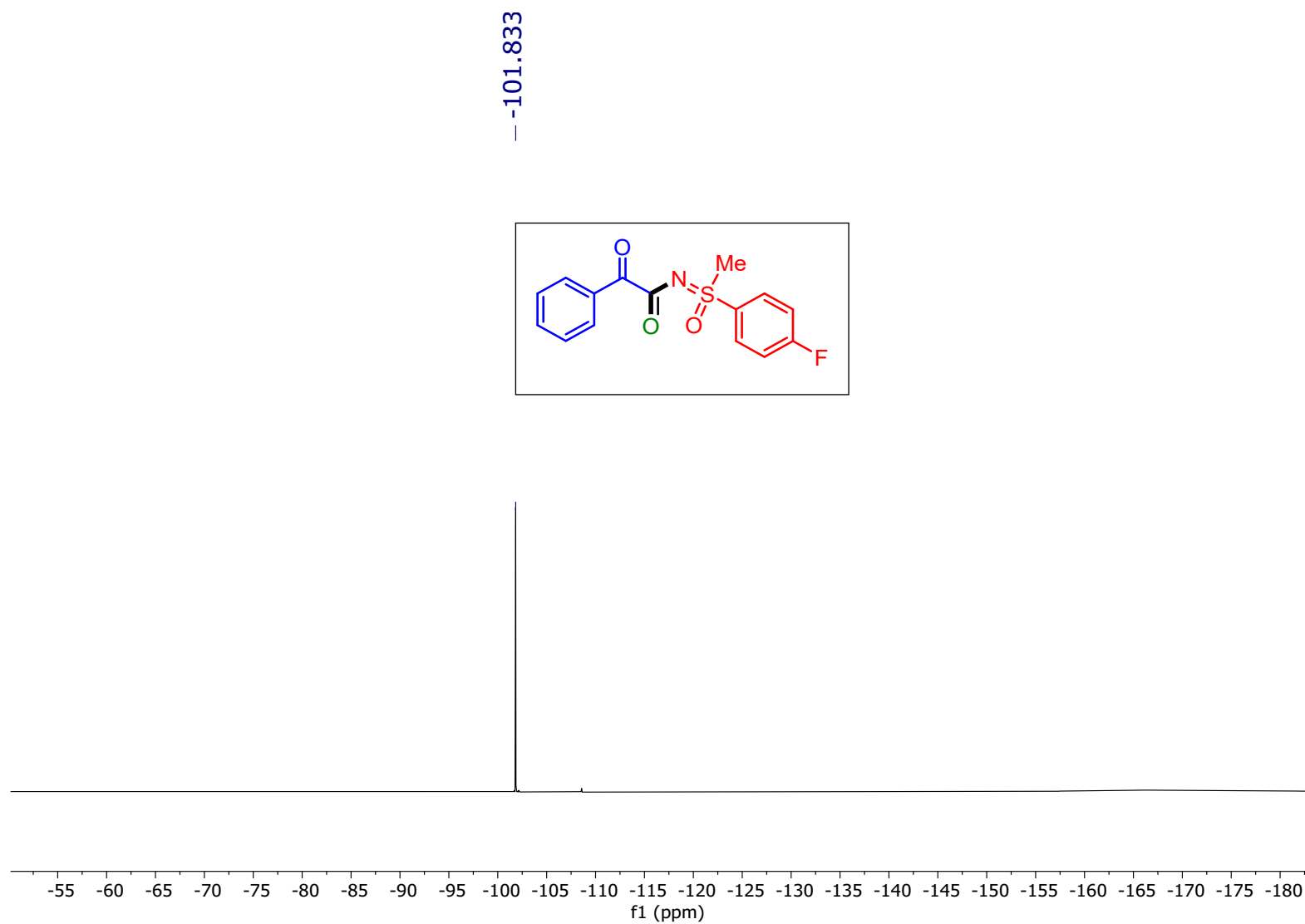
N-((4-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1e): ^1H NMR (600 MHz, CDCl_3)



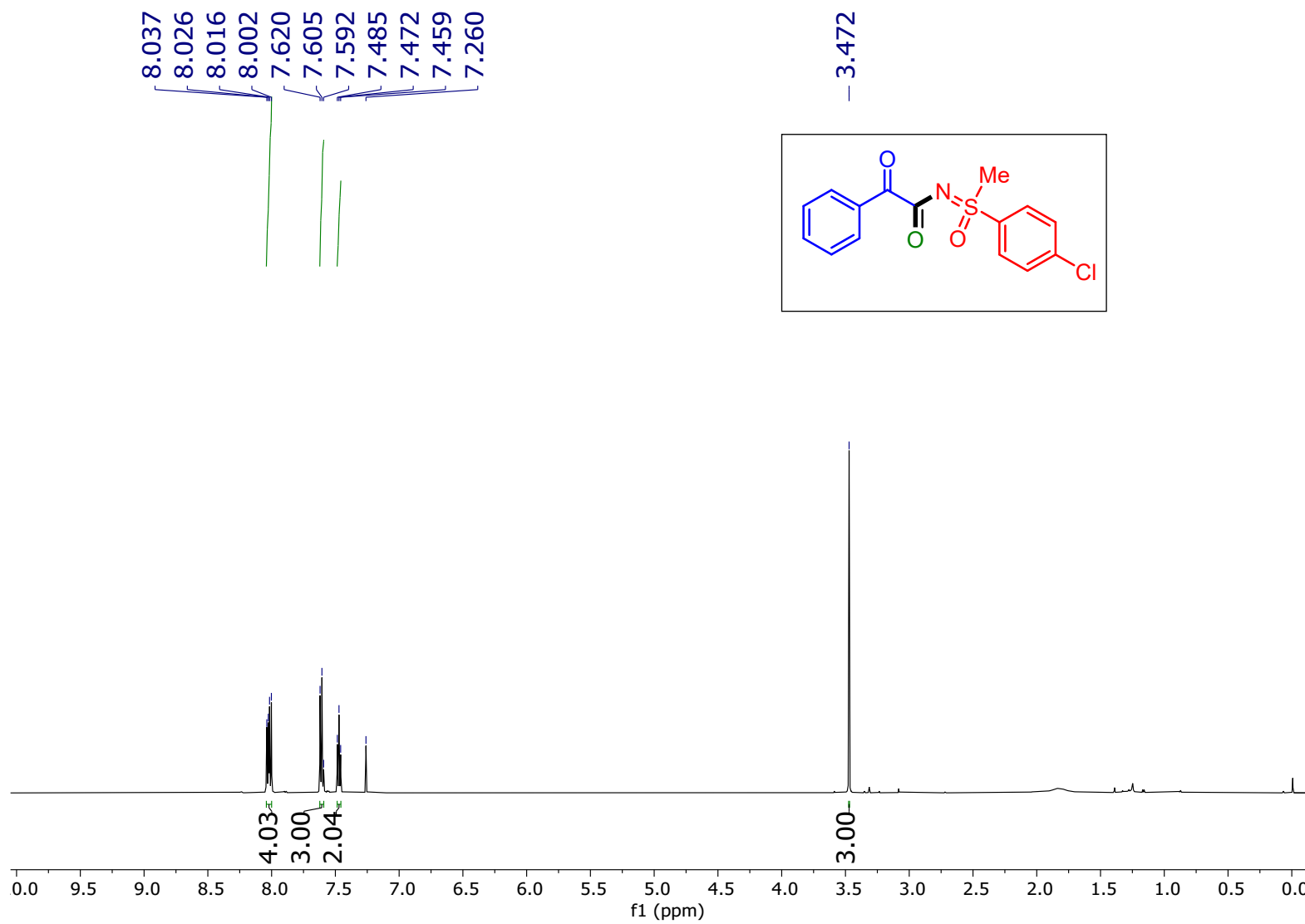
N-((4-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1e): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



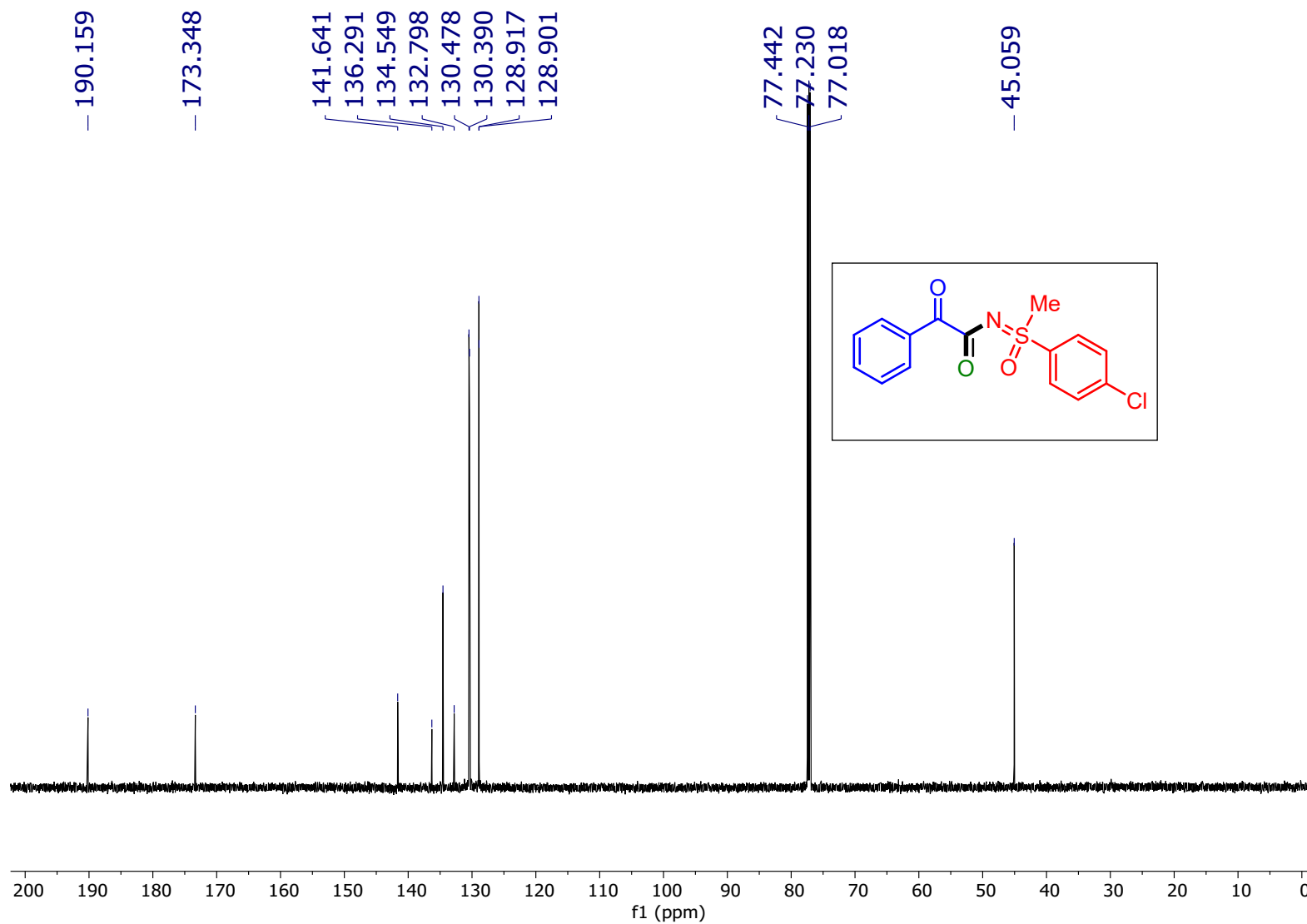
N-((4-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1e): ^{19}F NMR (565 MHz, CDCl_3)



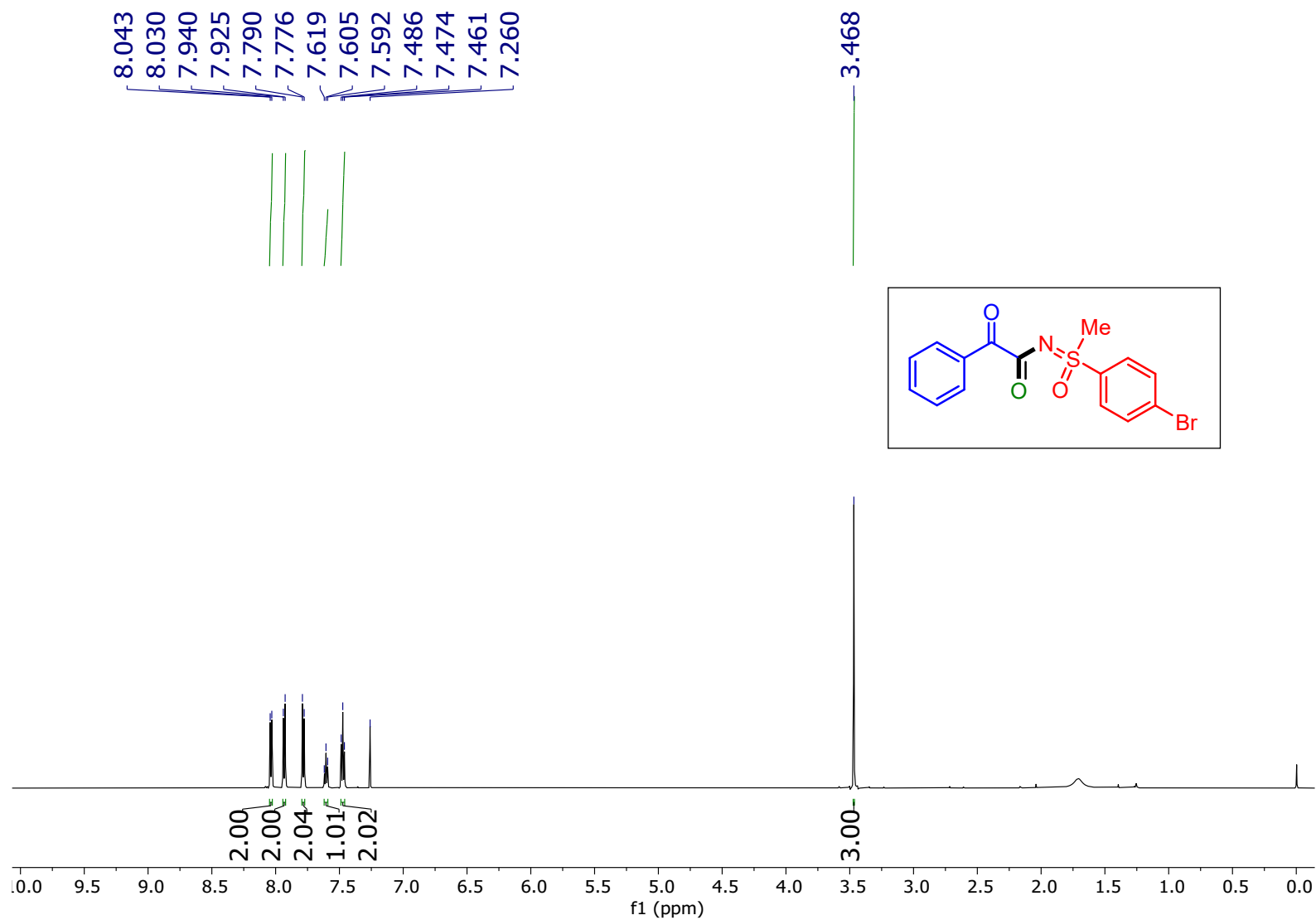
N-((4-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1f): ^1H NMR (600 MHz, CDCl_3)



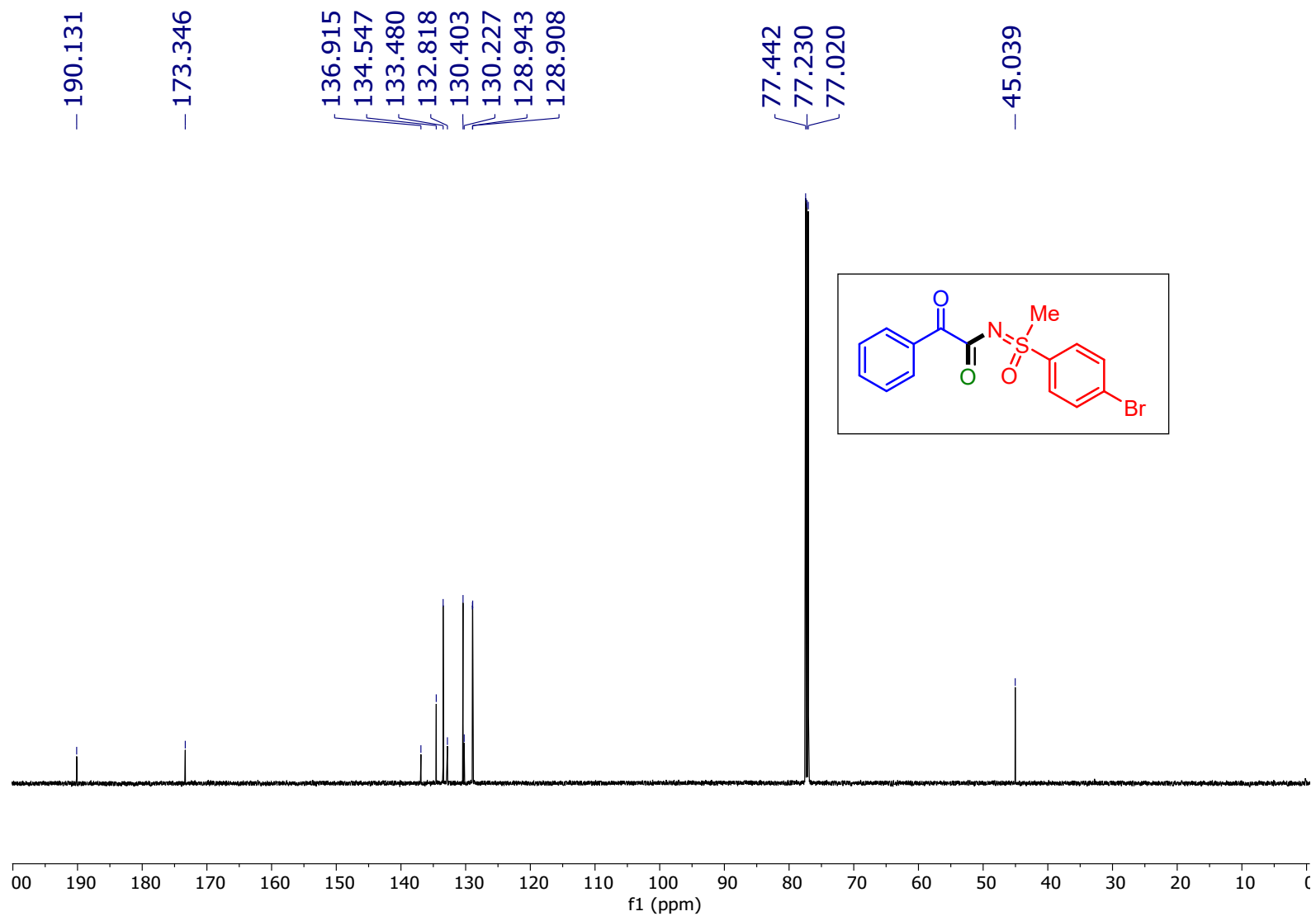
N-((4-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1f): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



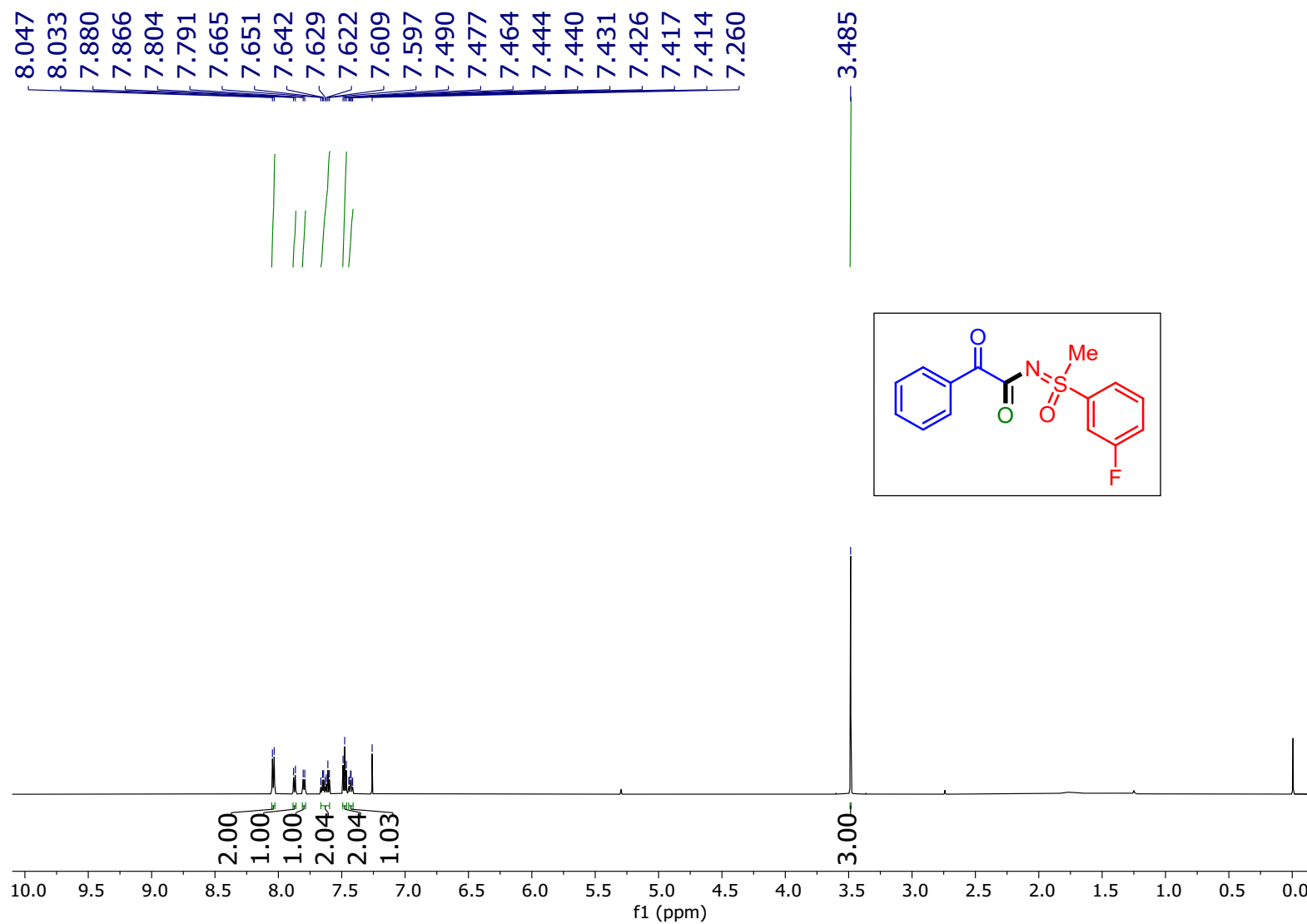
N-((4-Bromophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1g): ^1H NMR (600 MHz, CDCl_3)



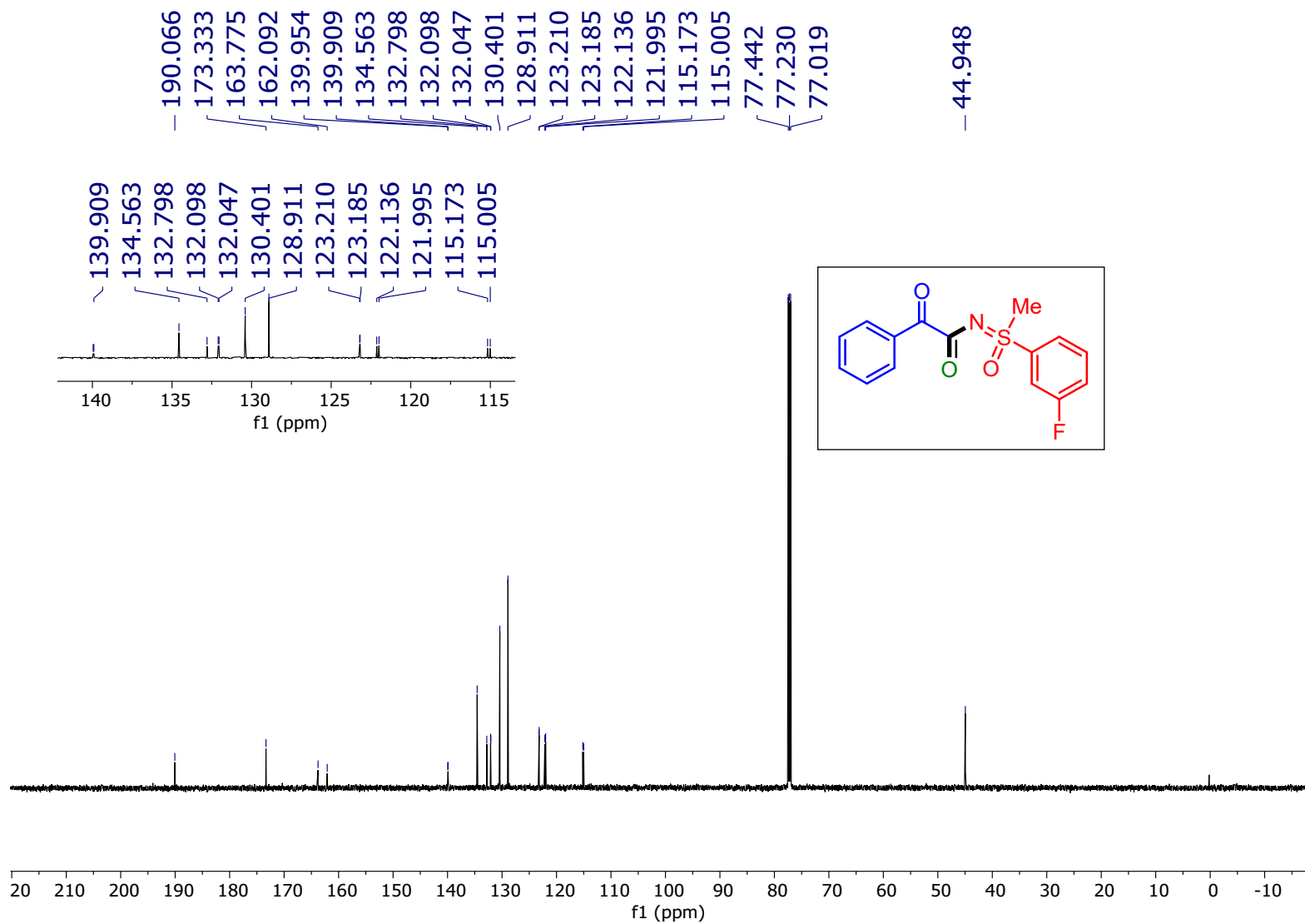
N-((4-Bromophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1g): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



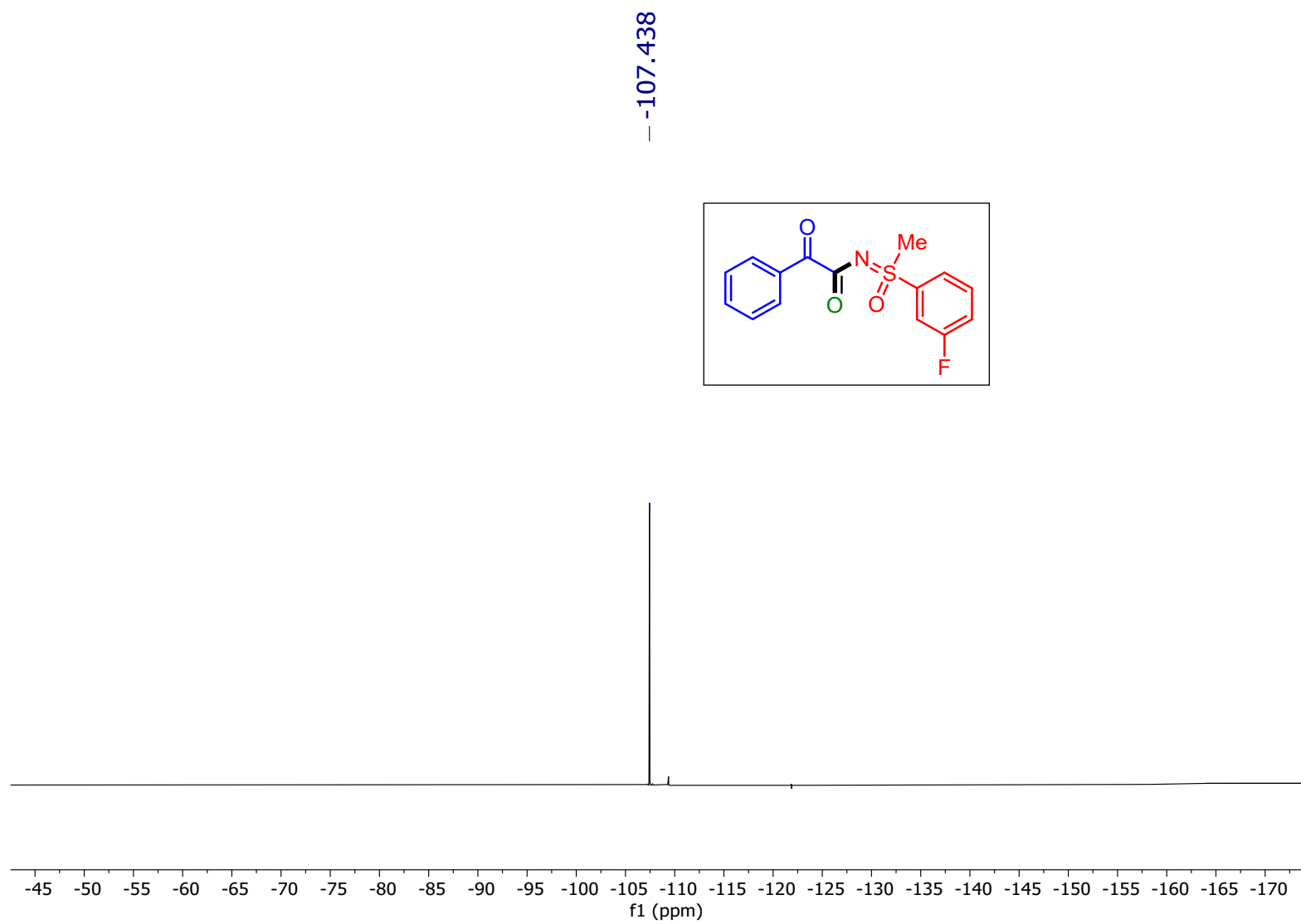
N-((3-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1h): ^1H NMR (600 MHz, CDCl_3)



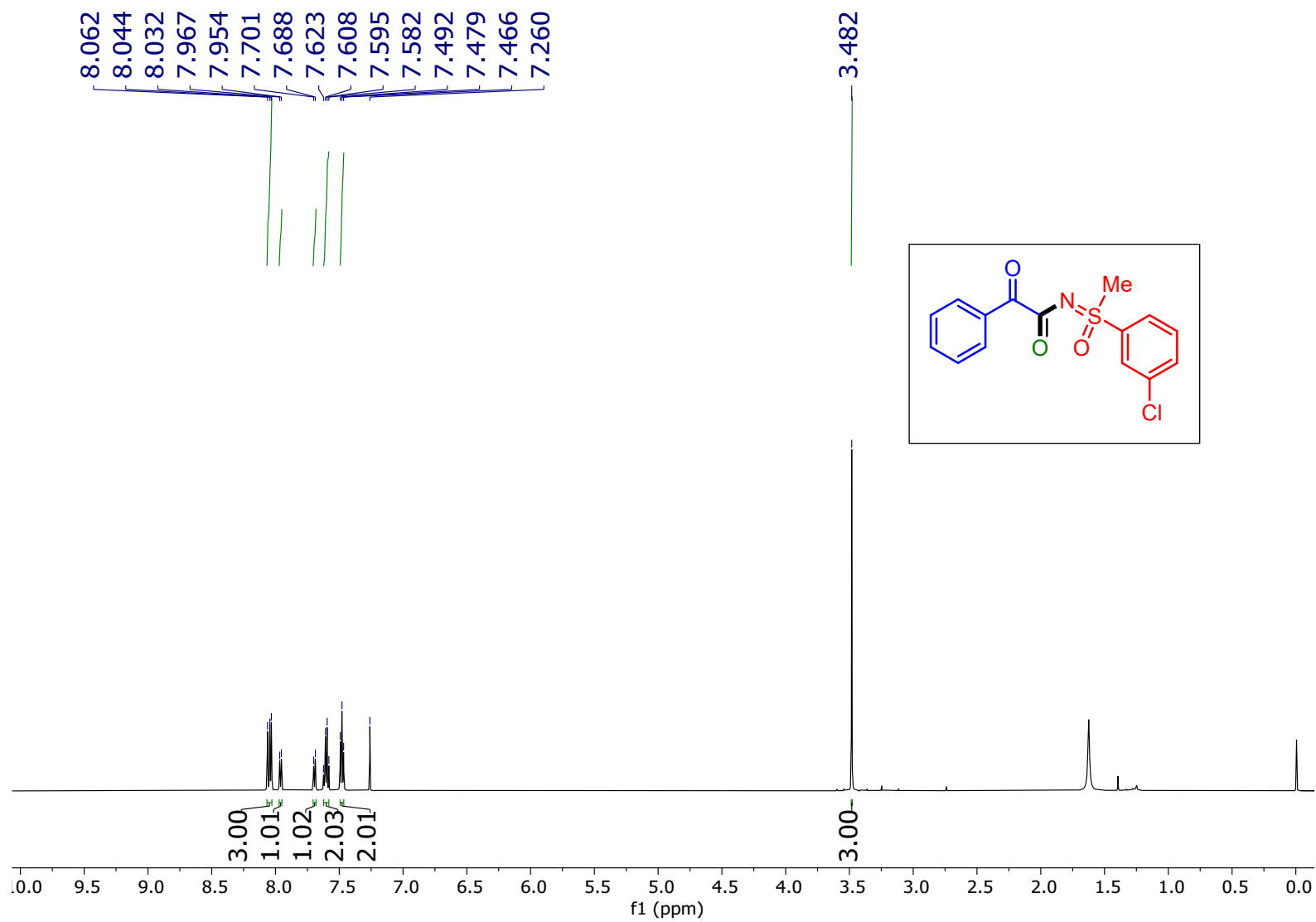
N-((3-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfanylidene)-2-oxo-2-phenylacetamide (1h): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



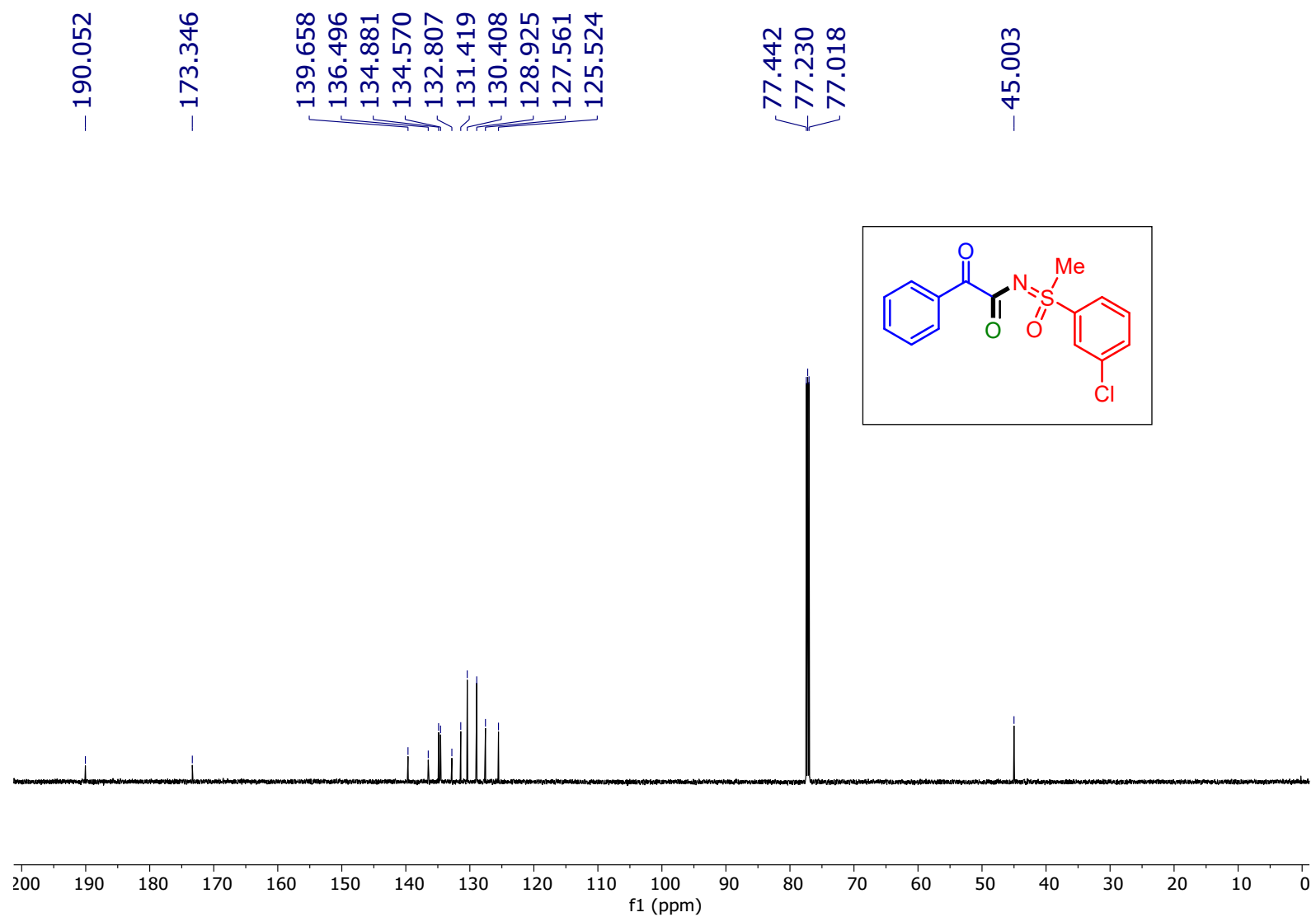
N-((3-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1h): ^{19}F NMR (565 MHz, CDCl_3)



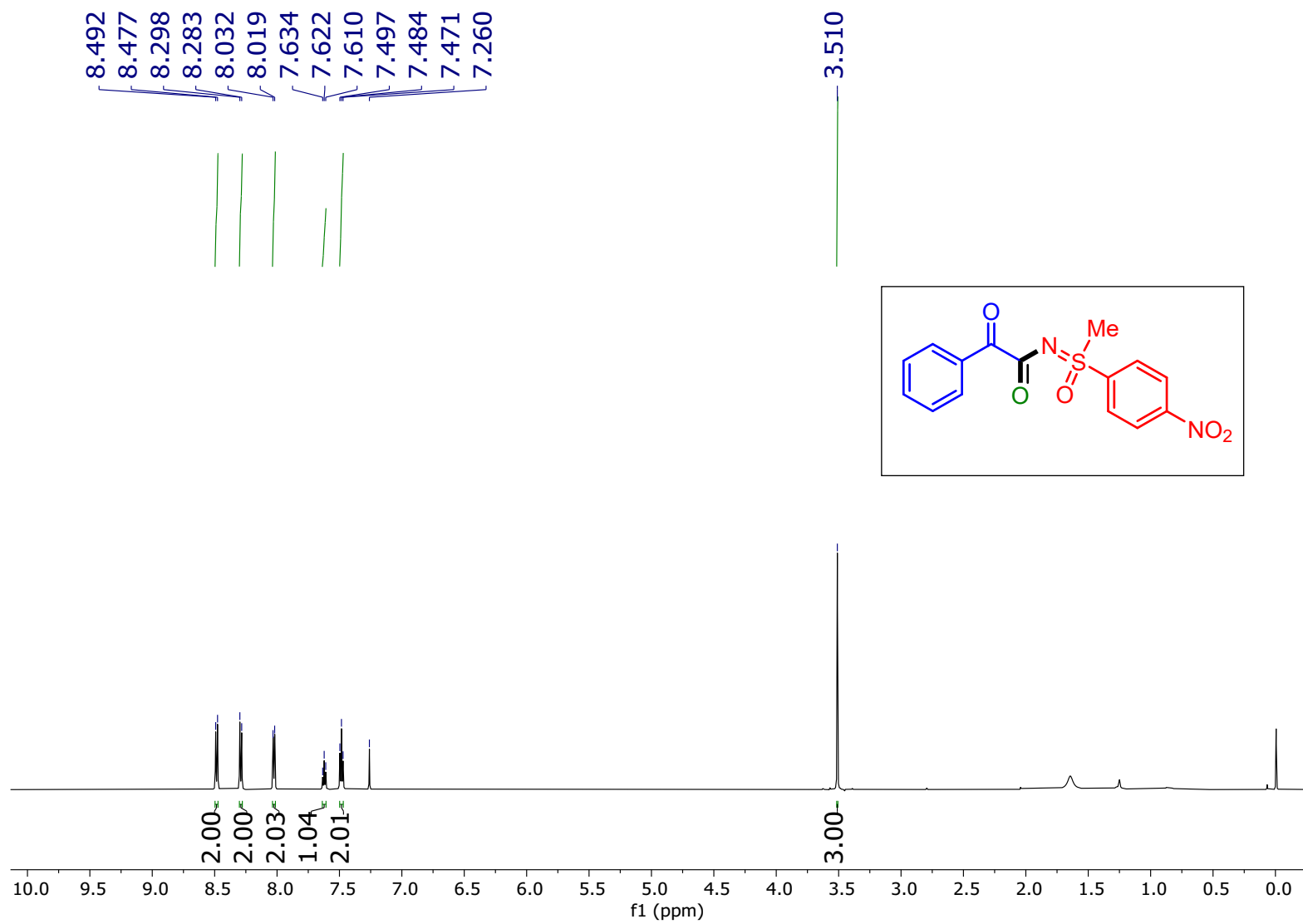
N-((3-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1i): ^1H NMR (600 MHz, CDCl_3)



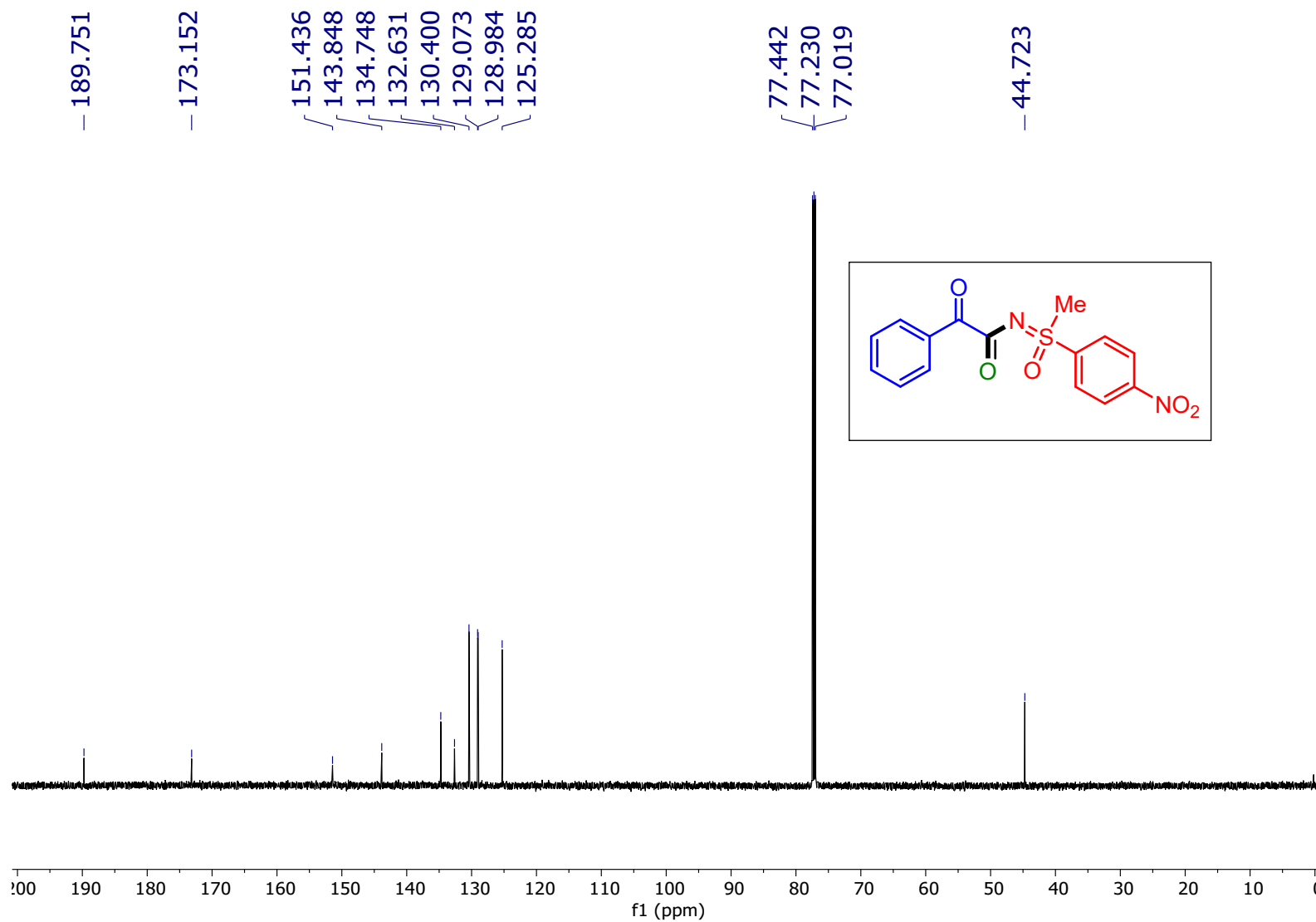
N-((3-Chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1i): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



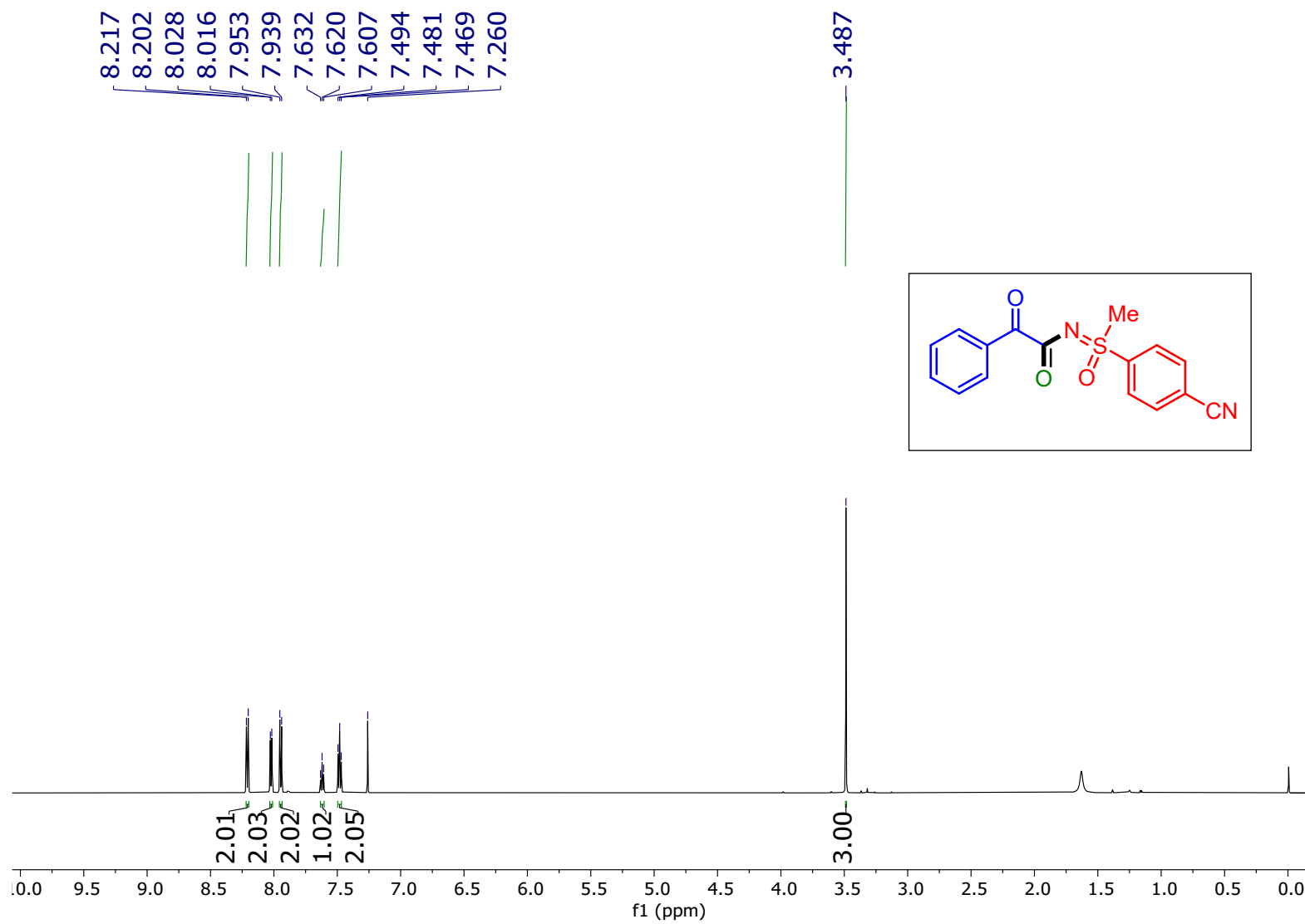
N-(Methyl(4-nitrophenyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1j): ^1H NMR (600 MHz, CDCl_3)



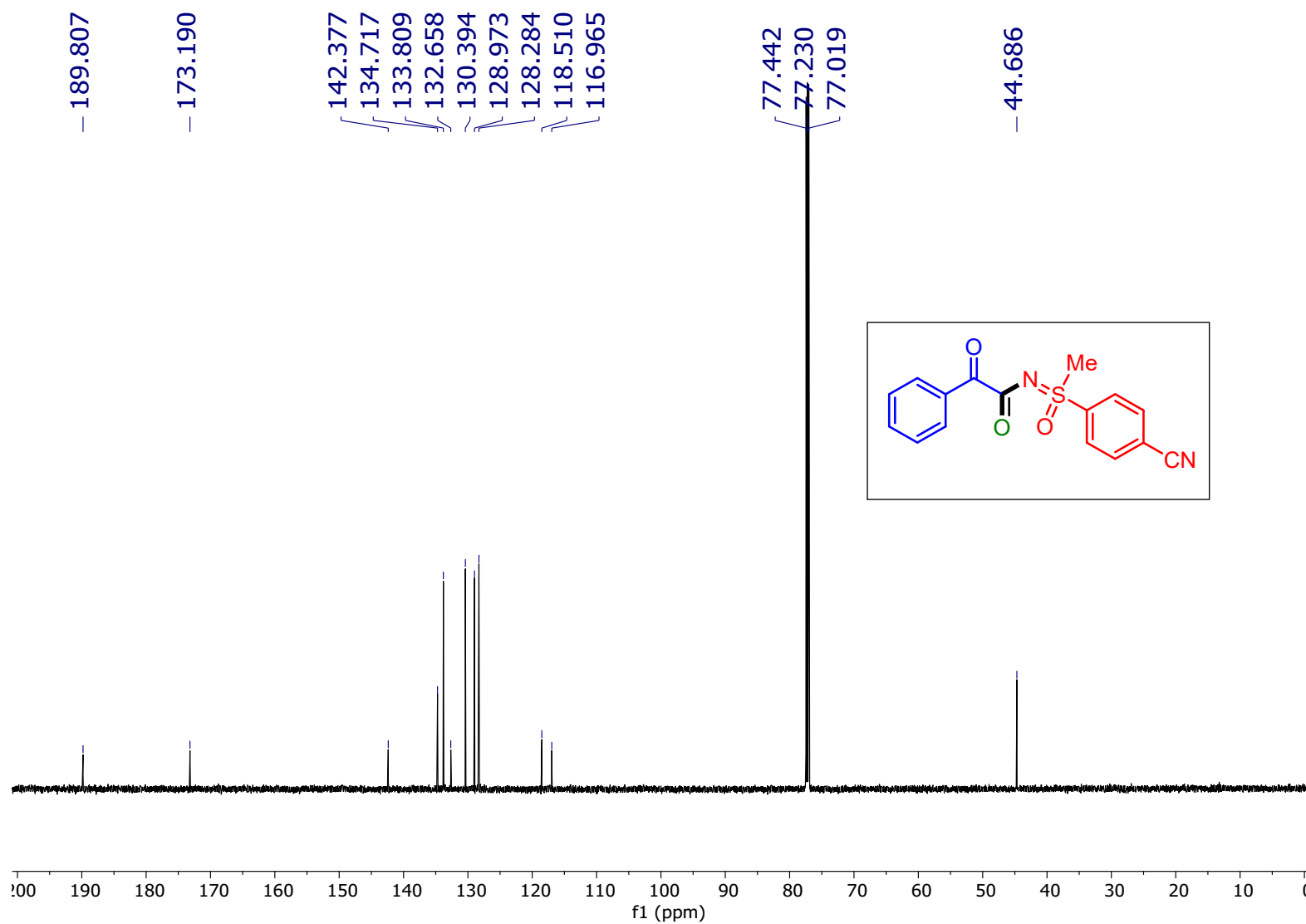
N-(Methyl(4-nitrophenyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1j): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



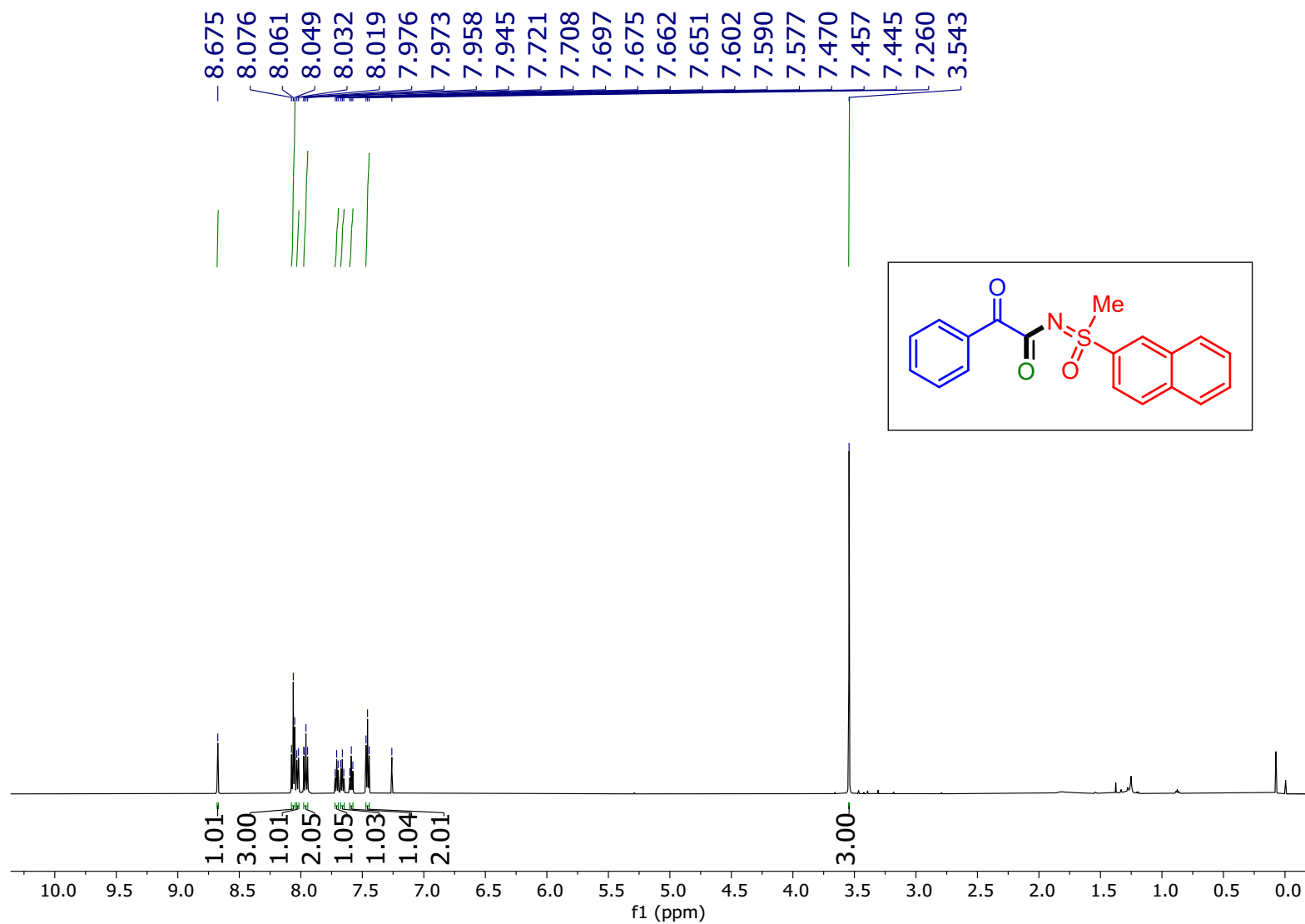
N-((4-Cyanophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1k): ^1H NMR (600 MHz, CDCl_3)



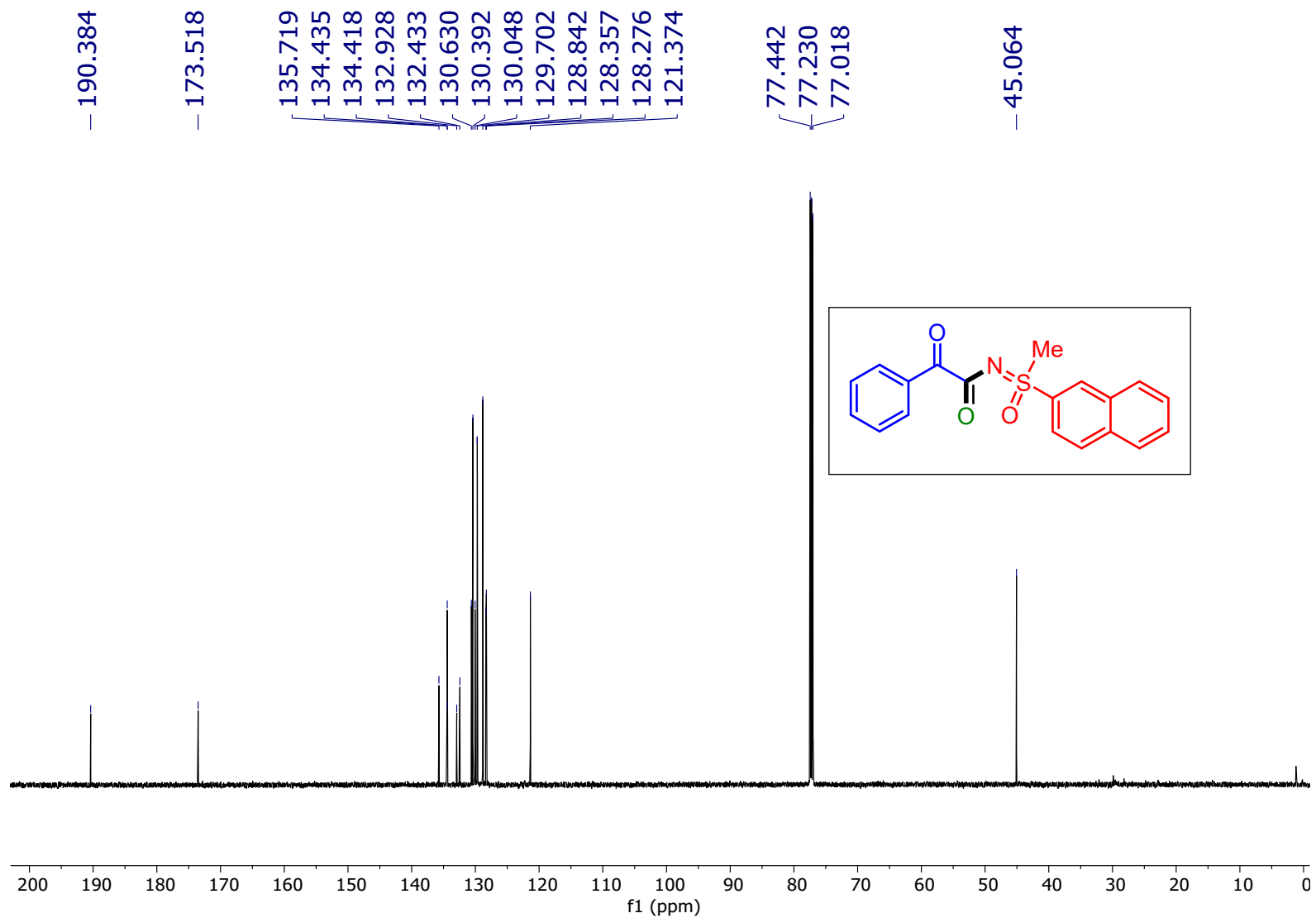
N-((4-Cyanophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1k): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



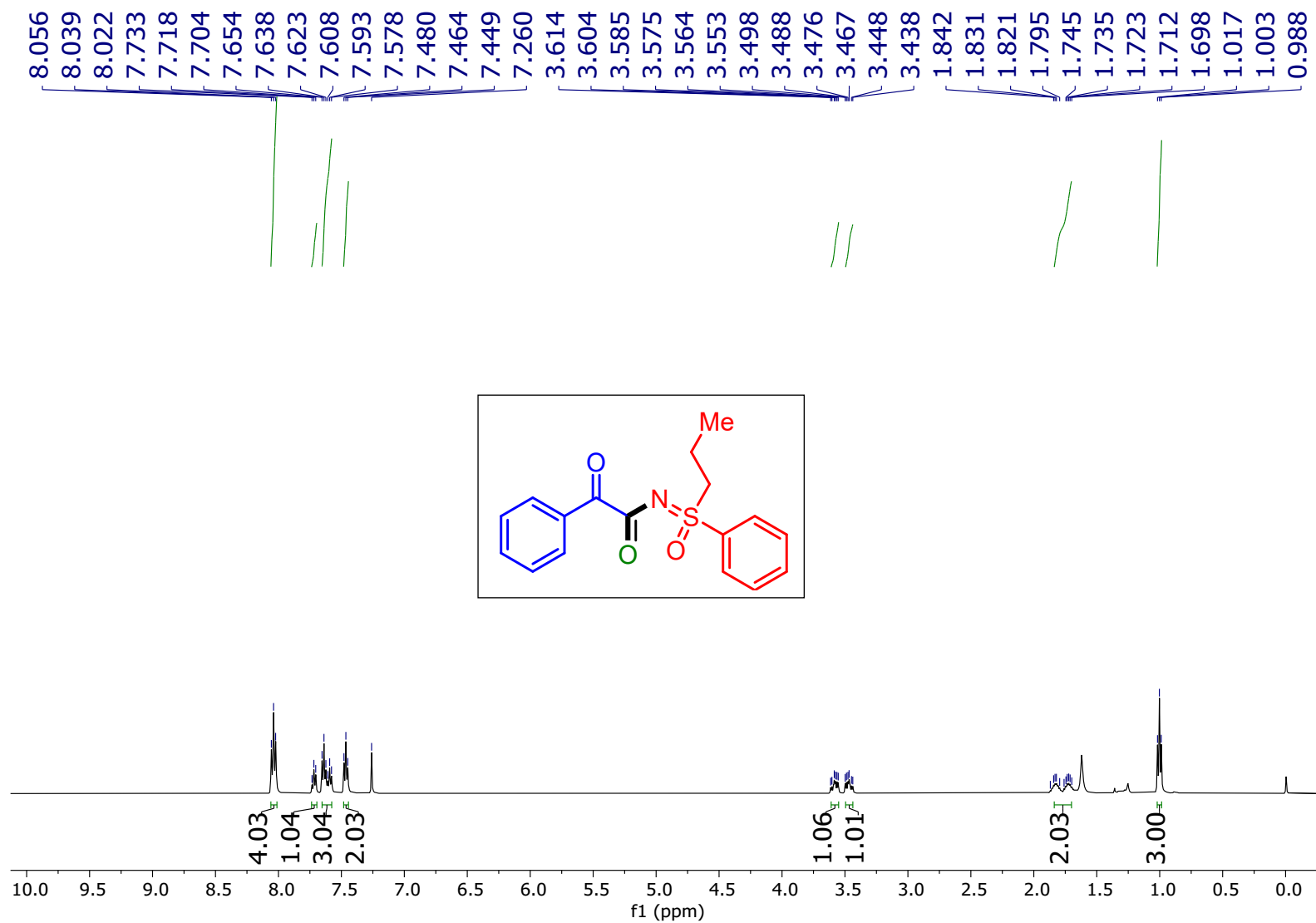
N-(Methyl(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (11): ^1H NMR (600 MHz, CDCl_3)



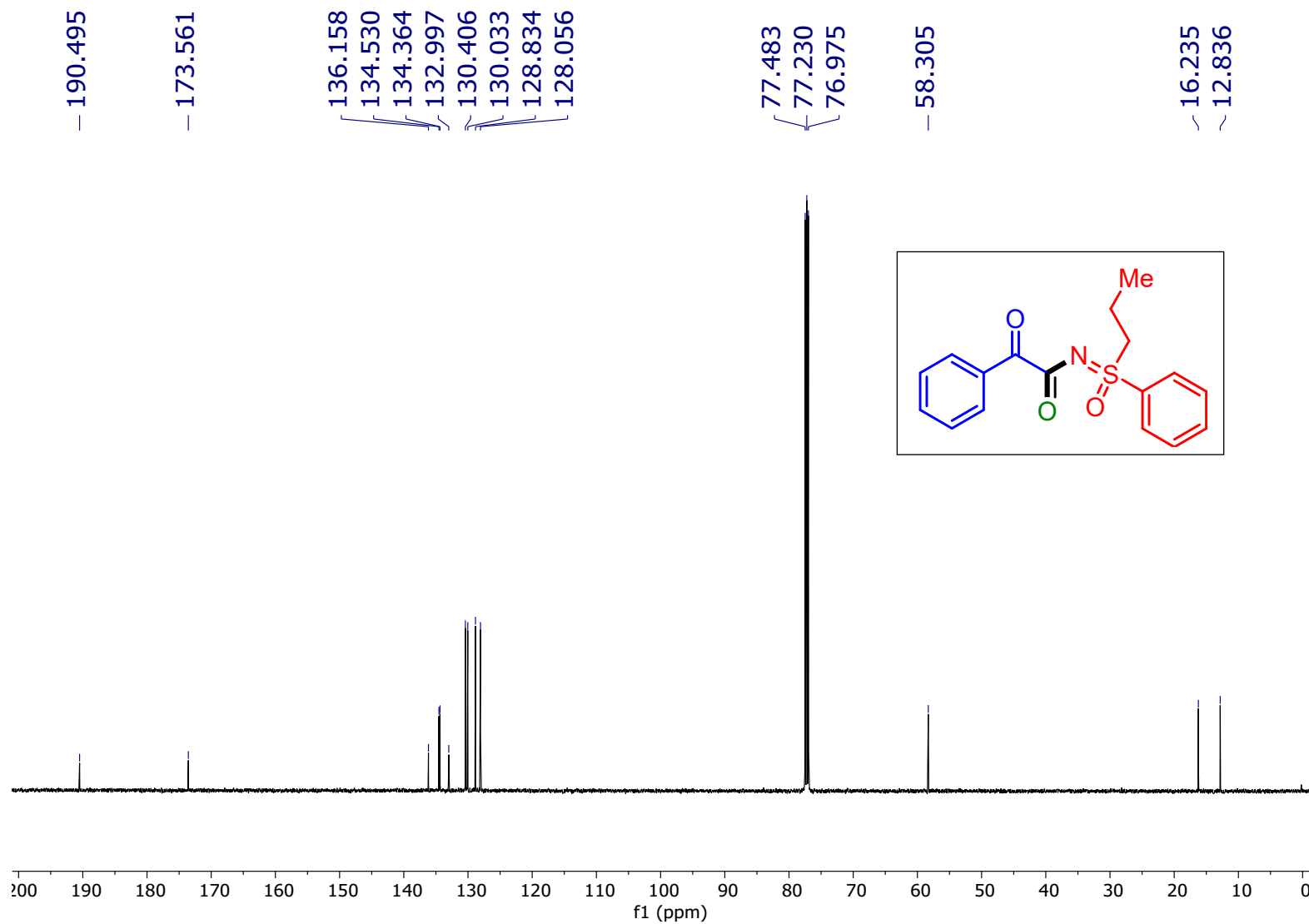
N-(Methyl(naphthalen-2-yl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (11): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



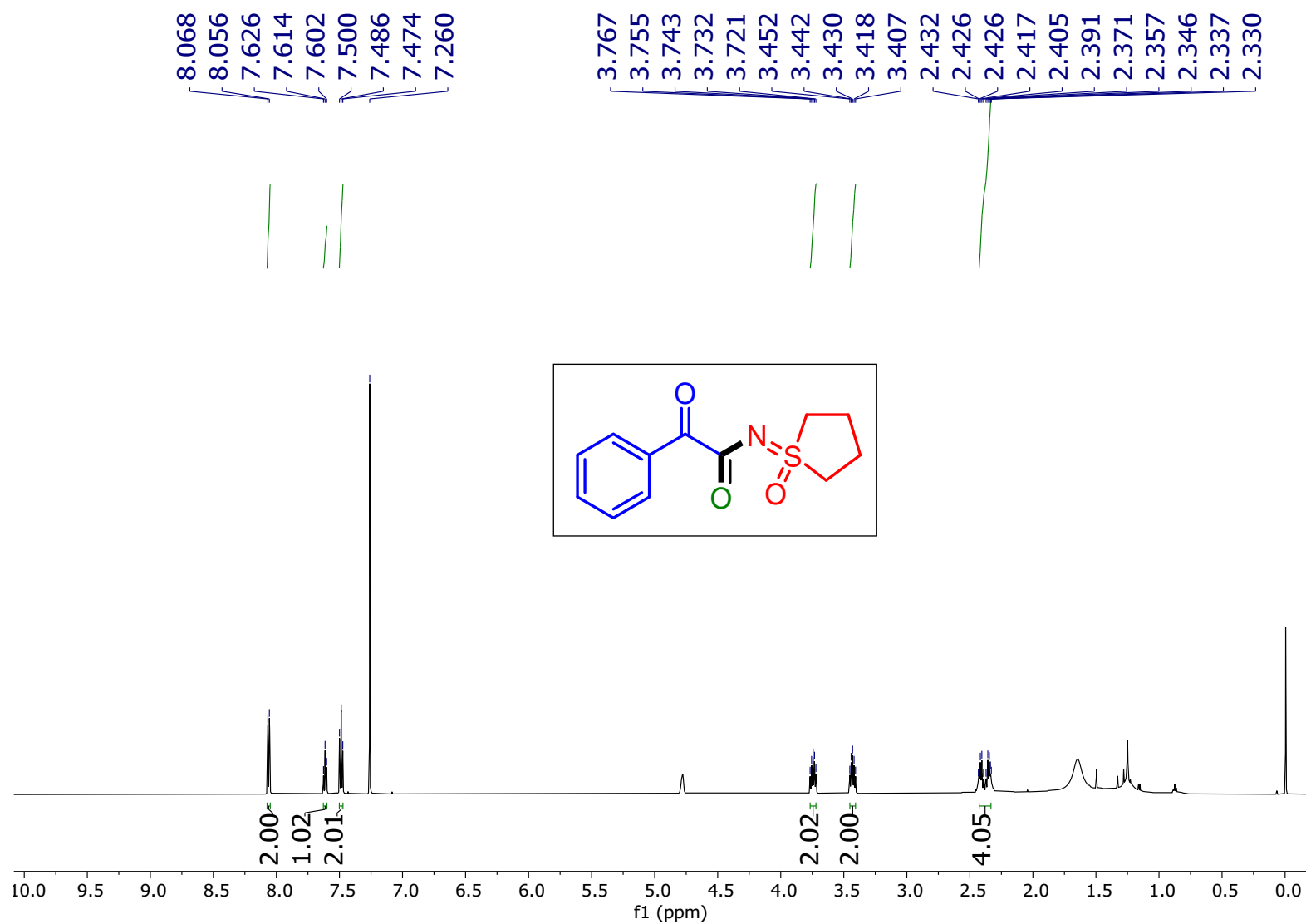
2-Oxo-N-(oxo(phenyl)(propyl)- λ^6 -sulfaneylidene)-2-phenylacetamide (1m): ^1H NMR (500 MHz, CDCl_3)



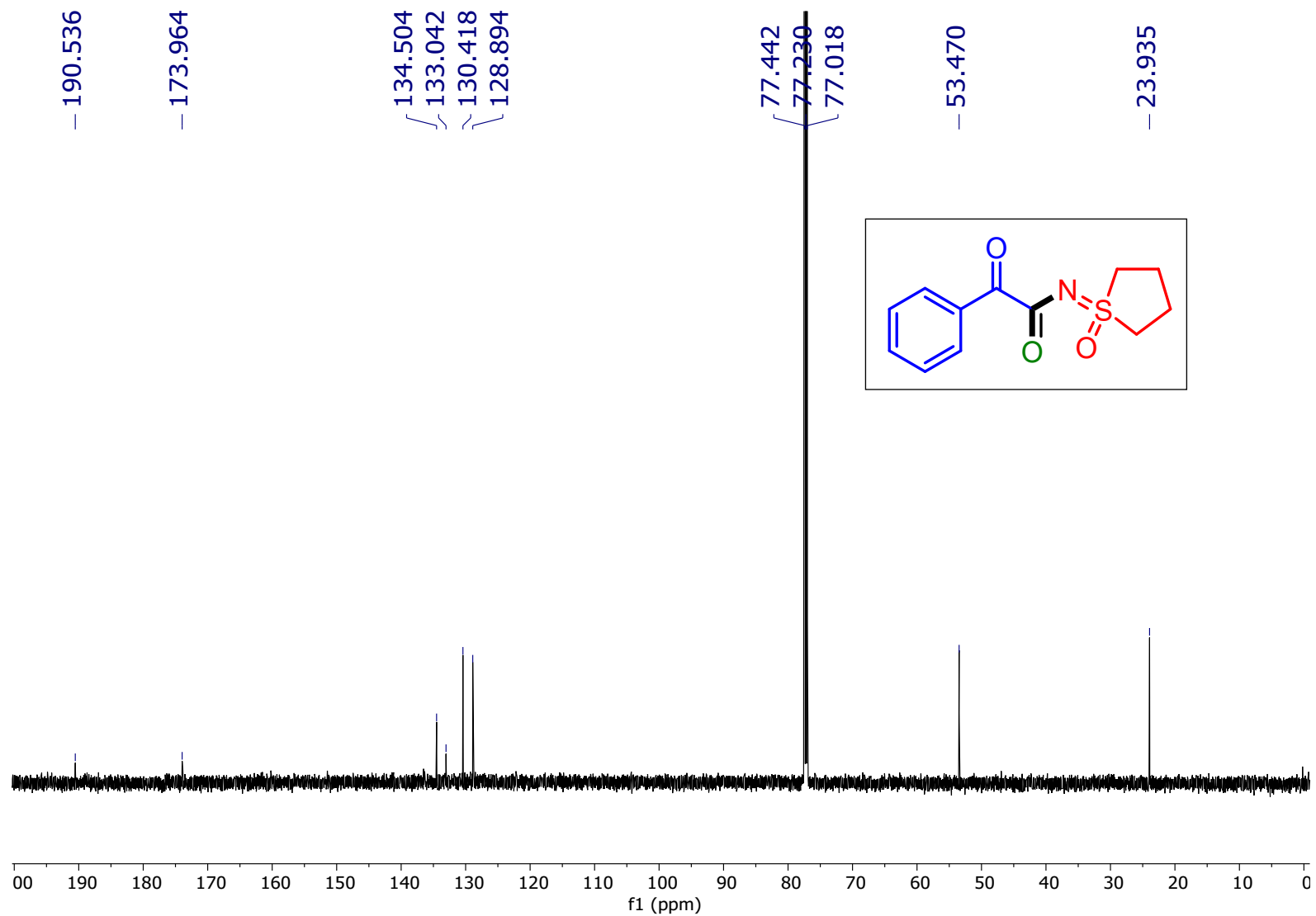
2-Oxo-N-(oxo(phenyl)(propyl)- λ^6 -sulfaneylidene)-2-phenylacetamide (1m): $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



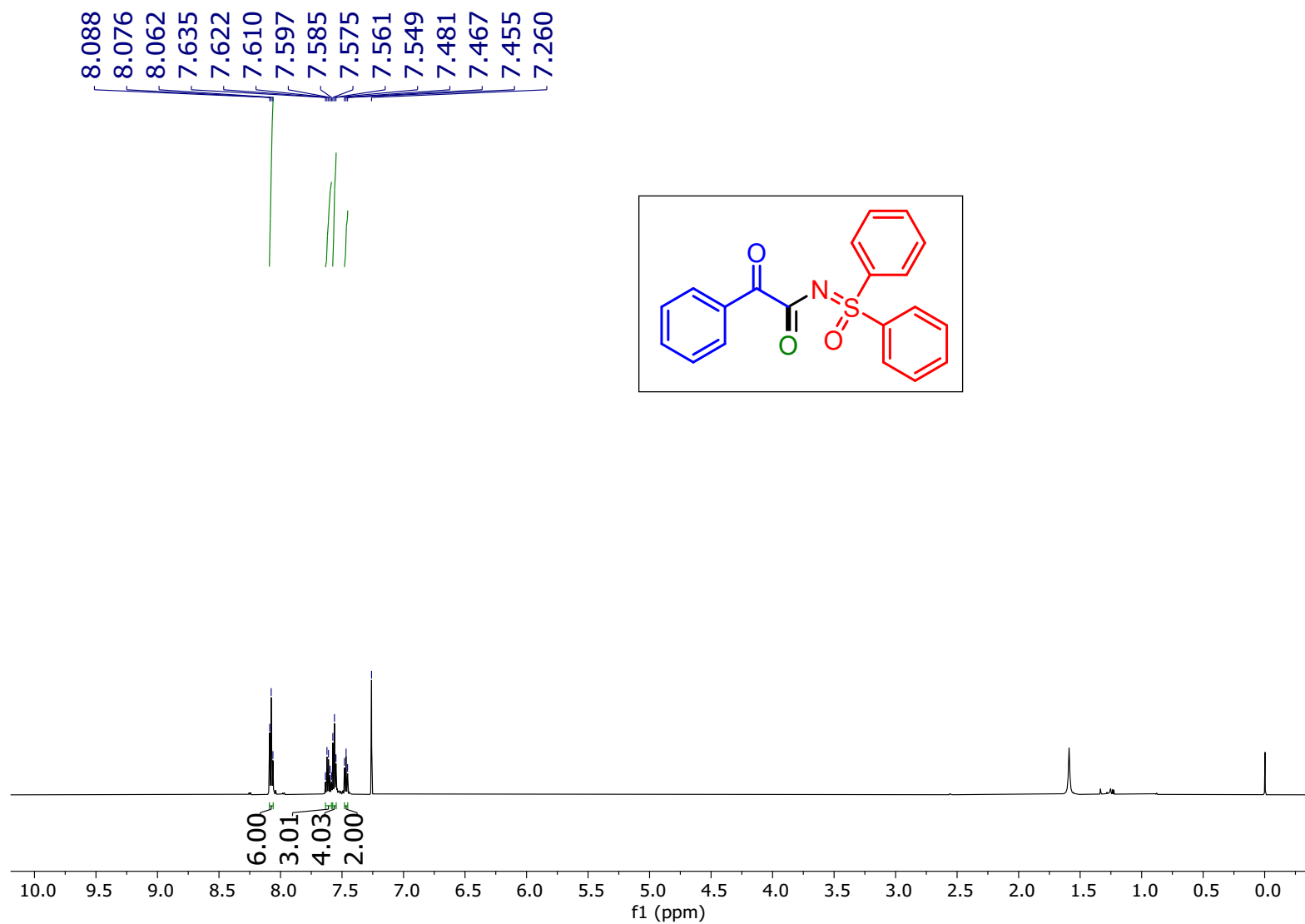
N-(1-Oxidotetrahydro-1 λ^6 -thiophen-1-ylidene)-2-oxo-2-phenylacetamide (1n): ^1H NMR (600 MHz, CDCl_3)



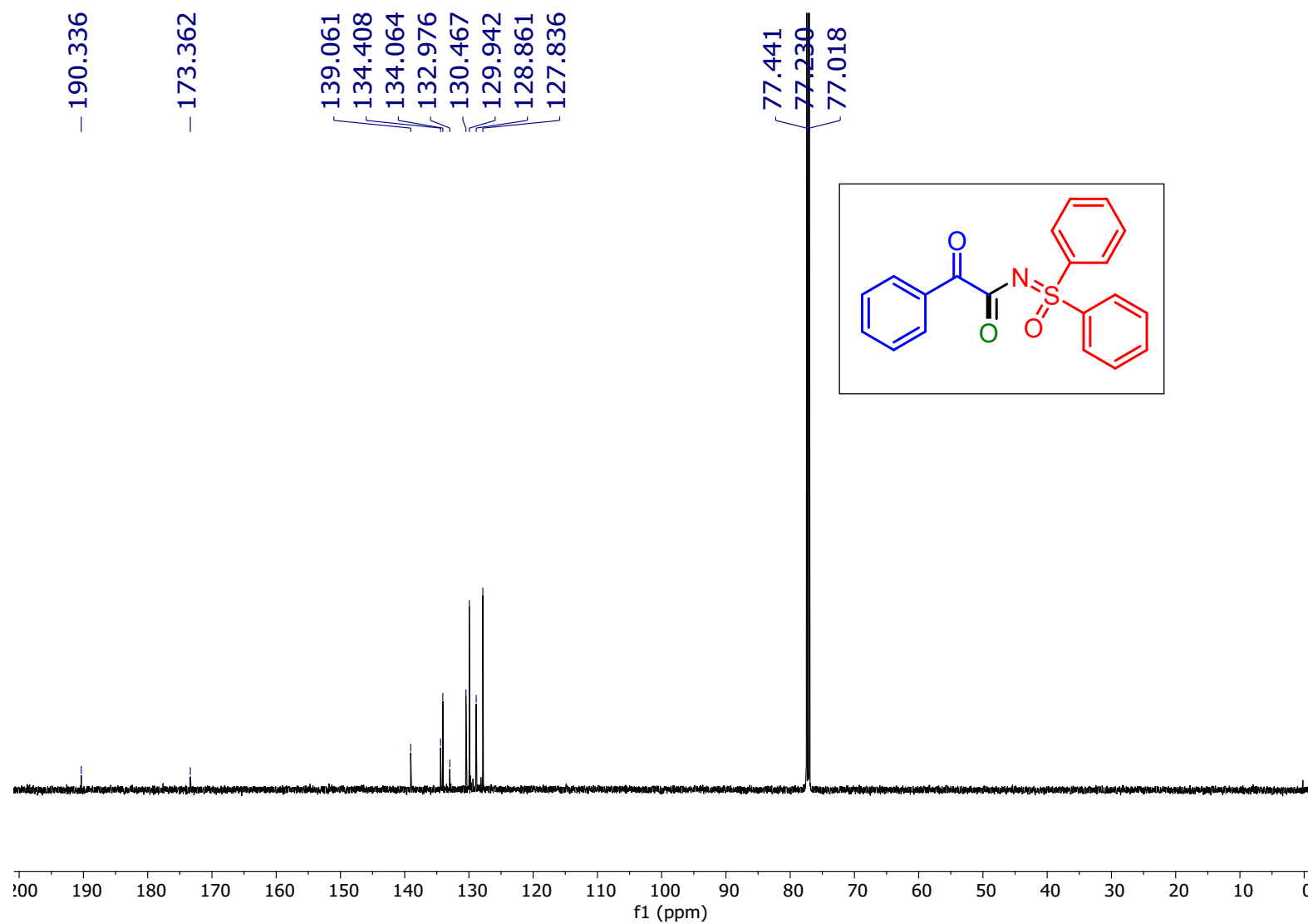
N-(1-Oxidotetrahydro-1 λ^6 -thiophen-1-ylidene)-2-oxo-2-phenylacetamide (1n): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



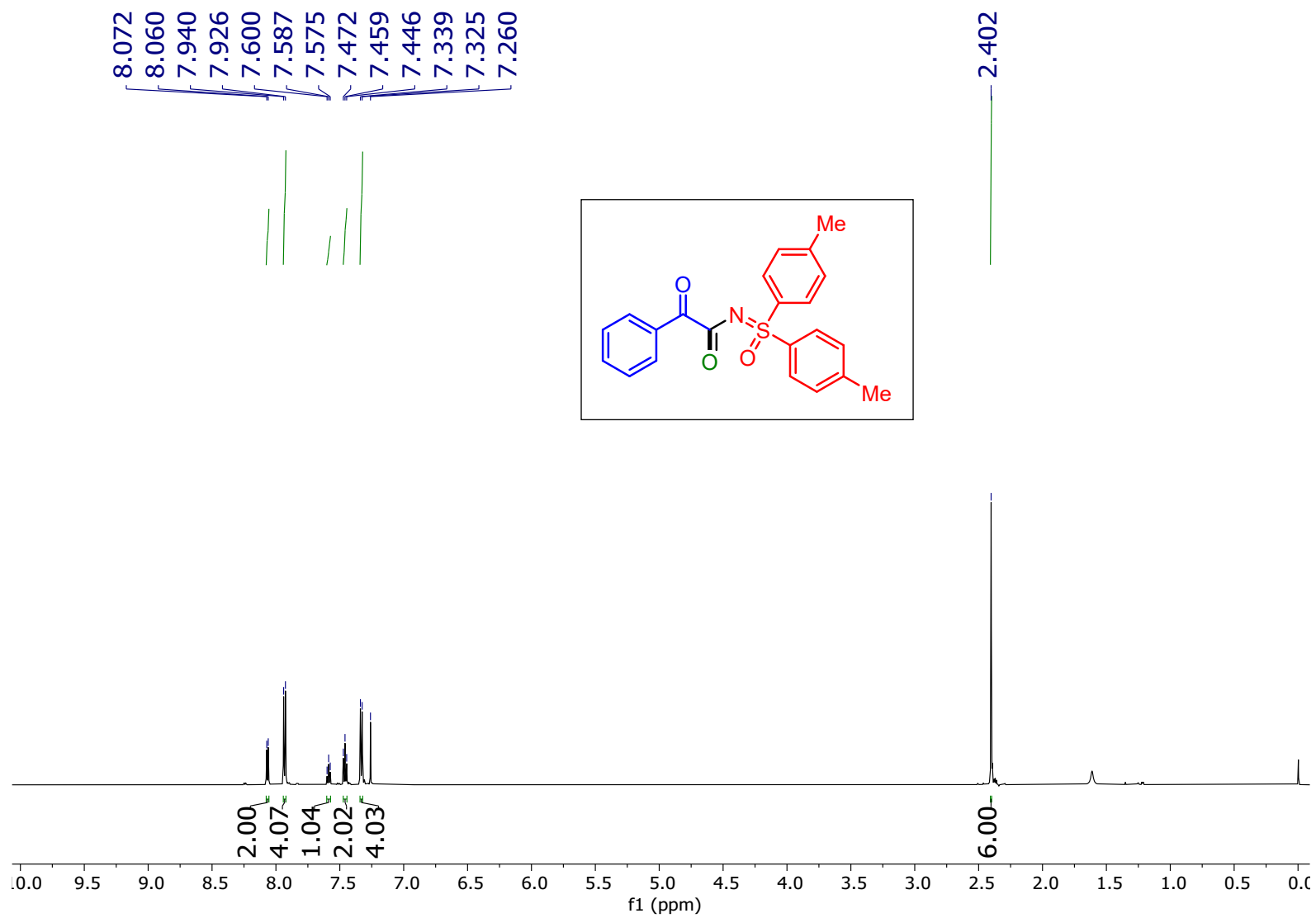
2-Oxo-N-(oxodiphenyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1o): ^1H NMR (600 MHz, CDCl_3)



2-Oxo-N-(oxodiphenyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1o): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



2-Oxo-N-(oxodi-*p*-tolyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1p): ^1H NMR (600 MHz, CDCl_3)



2-Oxo-N-(oxodi-*p*-tolyl- λ^6 -sulfaneylidene)-2-phenylacetamide (1p): $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

