Supplementary Information (SI) for New Journal of Chemistry.

Regioselective Thionation at C-2 of *N*-Substituted Isatins: Overcoming Synthetic Paradigms

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SUPPORTING INFORMATION

General Information

All chemicals and solvents were of analytical grade and were purchased from commercial sources and used without further purification unless otherwise stipulated. Compound **2** (Lawesson's reagent) is commercially available. We emphasize, however, that the quality of the Lawesson reagent is paramount to obtaining the reported yield in a reproducible manner. We have used a recently bought bottle of commercial Lawesson reagent, and we have noticed that the use of older bottles of **2** could be detrimental to the yields. Compounds **1a-t** are known and were prepared according to reported procedures.[1, 2,3]

All reactions were performed under nitrogen atmosphere in oven-dried open-flask glassware with magnetic stirring unless otherwise noted. Reaction progress was monitored by analytical thin-layer chromatography (TLC) performed on Merck pre-coated silica gel 60 F254 (5-40 μm thickness) plates. The TLC plates were visualized with UV light (254 nm) and stained with potassium permanganate or sulfuric vanillin followed by heating. The reaction products were purified by flash column chromatography using silica gel (230-400 Mesh).

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solutions at room temperature, unless noted otherwise. ^1H NMR and proton-decoupled ^{13}C NMR spectra were acquired on a Bruker Avance 300 (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR), Bruker Avance 400 (400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR), Bruker Avance 500 (500 MHz for ^1H and 126 MHz for ^{13}C NMR), or Bruker Avance 600 (600 MHz for ^1H and 150 MHz for ^{13}C NMR). Chemical shifts (δ) were reported in ppm and the coupling constants (*J*) in Hertz (Hz). Signal multiplicity was assigned as singlet (s), doublet (d), double doublet (dd), double double doublet (ddd), triplet (t), quartet (qt), dq (double quartet), multiplet (m) and broad singlet (bs). High resolution mass spectrometry (HRMS) was performed using electrospray ionization (ESI) on a Thermo Scientific Q Exactive mass spectrometer. Melting points were obtained using a Gehaka equipment model PF 1500 FARMA and were corrected. The compounds were named according to IUPAC rules using the software MarvinSketch version 25.1.79.

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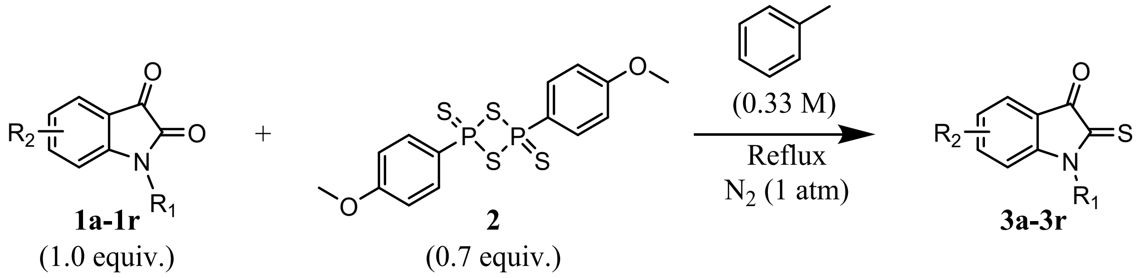
[1] J.-Y. Liang, H. Wang, Y.-L. Yang, S.-J. Shen and J.-X. Chen, *Tetrahedron Lett.*, 2017, **58**, 2636-2639

[2] J. Azizian, M. R. Mohammadizadeh, Z. Kazemizadeh, N. Karimi, A. A. Mohammadi, A. R. Karimi and A. Alizadeh, *Lett. Org. Chem.*, 2006, **3**, 56-57.

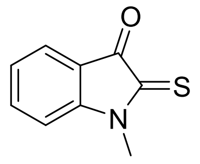
[3] Y. Liu, J. Xue, Z. Sun, D. Liu, Y. Xing and Y. Li, *Asian J. Org. Chem.* 2016, **5**, 43-47.

General Procedure for the Preparation of 2-sulfanylidene-2,3-dihydro-1*H*-indol-3-ones – compounds 3a-3p



In a 25 mL round-bottom flask, isatin **1** (1.0 equiv.) was dissolved in toluene (0.33 M). Lawesson's reagent (**2**, 0.7 equiv.) was added to the solution and the mixture was stirred under nitrogen atmosphere and reflux conditions. The reaction was monitored by thin layer chromatography (TLC) until complete conversion of starting materials or stagnation of the reaction. The reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/EtOAc) to furnish the corresponding thioisatin **3**.

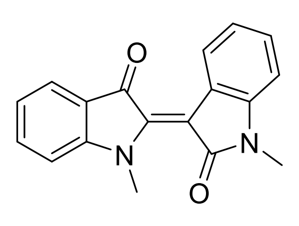
1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3a

Reaction of isatin **1a** (66.0 mg, 409.5 µmol), **2** (115.9 mg, 286.7 µmol) in toluene (1.2 mL) under reflux for 5 minutes afforded compound **3a** (58.2 mg, 80% yield). Red solid, mp 163-165 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.61 (td, *J* = 7.9, 1.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.2, 176.9, 151.8, 137.4, 126.9, 125.0, 119.5, 110.3, 31.2. HRMS (ESI+): *m/z* calcd for $C_9H_8NOS^+$ $[M + H]^+$ 178.0319, found 178,0319, error 1.12 ppm.

1,1'-dimethyl-[2,3'- biindolinylidene]-2',3'-dione[4]

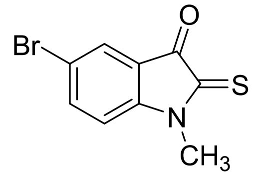


3a'

[This compound was isolated under the conditions of entry 10 of Table 1 – see main article].

Reaction of isatin **1a** (58.5 mg, 363.0 µmol), **2** (102.8 mg, 254.1 µmol) in toluene (1.2 mL) under reflux for 30 minutes afforded compounds **3a** (12.2 mg, 68.8 µmol) and **3a'** (2.1 mg, 4% yield). Data for compound **3a'**: purple solid, mp. 210–213 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 – 7.00 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.60 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 188.6, 166.9, 154.8, 143.2, 142.7, 136.7, 129.5, 125.1, 124.9, 122.5, 122.4, 122.0, 121.0, 111.2, 109.4, 107.8, 38.0, 26.4. HRMS (ESI+): *m/z* calcd for $C_{18}H_{14}N_2O_2^+$ [M + H]$^+$ 291.1128, found 291.1123, error: 1.72 ppm..

5-bromo-1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3b

Reaction of isatin **1b** (48.0 mg, 199.9 µmol), **2** (56.6 mg, 140.0 µmol) in toluene (0.6 mL) under reflux for 5 minutes afforded compound **3b** (23.7 mg, 46% yield). Red solid, mp 163-164 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.0 Hz, 1H), 7.71 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 185.5, 175.5, 150.60, 139.7, 129.7, 120.9, 118.2, 111.8, 31.3. HRMS (ESI+): *m/z* calcd for $C_9H_6BrNOS^+$ [M + H]$^+$ 255.9426, found 255.9424, error: 0.78 ppm.

5-methoxy-1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one

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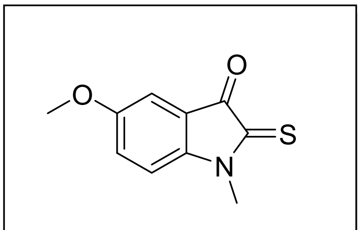
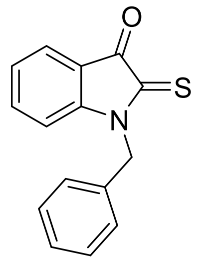
[4] M. A. Sukari and J. M. Vernon J. Chem. Soc., Perkin Trans. I 1983, 2219-2223.



3c

Reaction of isatin **1c** (21,3 mg, 111,3 μmol), **2** (31,5 mg, 77,9 μmol) in toluene (0,3 mL) under reflux for 5 minutes afforded compound **3c** (17,0 mg, 74% yield). Red solid, mp. 152-153 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 – 7.26 (m, 1H), 7.13 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 185.4, 177.0, 157.8, 145.7, 123.6, 120.3, 111.3, 111.2, 56.2, 31.4. HRMS (ESI+): *m/z* calcd for $C_{10}H_{10}NO_2S^+$ [M + H]$^+$ 208.0427, found 208.0425, error: 0.96 ppm.

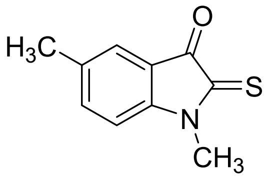
1-benzyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3d

Reaction of isatin **1d** (27.3 mg, 115.1 μmol), **2** (32.6 mg, 80.5 μmol) in toluene (0.4 mL) under reflux for 5 minutes afforded compound **3d** (19.6 mg, 67% yield). Red solid, mp. 193-196 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.49 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.18 (td, *J* = 7.5, 0.8 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.7, 176.8, 151.3, 137.4, 134.0, 129.2, 128.4, 127.4, 127.1, 125.0, 119.8, 111.3, 48.3. HRMS (ESI+): *m/z* calcd for $C_{10}H_{11}NO_2S^+$ [M + H]$^+$ 254.0634, found 254.0631, error: 1.18 ppm.

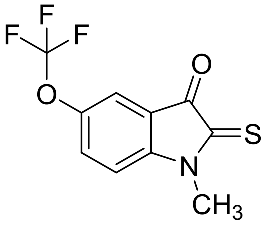
1,5-dimethyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3e

Reaction of isatin **1e** (40.0 mg, 228.3 µmol), **2** (64.6 mg, 159.8 µmol) in toluene (0.7 mL) under reflux for 5 minutes afforded compound **3e** (33.2 mg, 76% yield). Red solid, mp. 168-171 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 185.8, 177.1, 149.6, 137.7, 135.0, 127.3, 119.5, 110.0, 31.2, 20.7. HRMS (ESI+): *m/z* calcd for $C_{10}H_{10}NOS^{+}$ $[M + H]^{+}$ 192.0478, found 192.0473, error: 2.60 ppm.

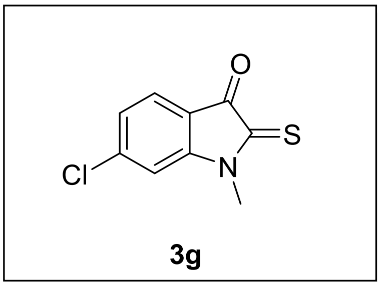
1-methyl-2-sulfanylidene-5-(trifluoromethoxy)-2,3-dihydro-1H-indol-3-one



3f

Reaction of isatin **1f** (101.0 mg, 412.0 µmol), **2** (116.6 mg, 288.4 µmol) in toluene (1.2 mL) under reflux for 5 minutes afforded compound **3f** (91.8 mg, 85% yield). brown solid, mp. 138-140 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.48 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 186.1 (s), 175.3 (s), 150.0 (s), 146.4 (q, $^{3}J_{C\text{-}F}$ = 2.3 Hz), 130.1 (s), 120,4 (q, $^{1}J_{C\text{–}F}$ = 259.2 Hz) 120.3 (s), 119.8 (s,), 111.1 (s), 31.3 (s). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -58.5 (s, 3F). HRMS (ESI+): *m/z* calcd for $C_{10}H_{7}F_{3}NO_{2}S^{+}$ $[M + H]^{+}$ 262.0144, found 262.0144, error: 0.0 ppm.

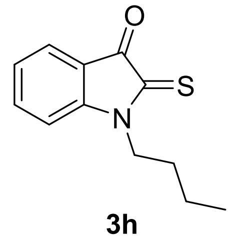
6-chloro-1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3g

Reaction of isatin **1g** (95.0 mg, 485.8 μmol), **2** (137.5 mg, 340.0 μmol) in toluene (1.5 mL) under reflux for 5 minutes afforded compound **3f** (41.0 mg, 40% yield). brown solid, mp. 95-98 °C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 186.2, 175.5, 152.7, 141.9, 127.2, 124.7, 117.9, 112.2, 31.6. HRMS (ESI+): *m/z* calcd for $C_{10}H_7NOS^+$ [M + H]$^+$ 211,9931, found 211.9928, error: 1.41 ppm.

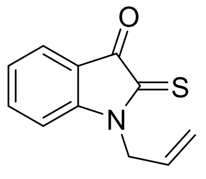
1-butyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3h

Reaction of isatin **1h** (120.0 mg, 590.4 μmol), **2** (167.16 mg, 413.3 μmol) in toluene (2.0 mL) under reflux for 5 minutes afforded compound **3h** (100.1 mg, 77% yield). Red brown wax. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 4.13 – 4.08 (m, 2H), 1.75 (q, *J*=7.4 Hz, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 185.7, 177.0, 151.4, 137.3, 127.01, 124.8, 119.7, 110.5, 44.6, 28.5, 20.4, 13.9. HRMS (ESI+): *m/z* calcd for $C_{10}H_7NOS^+$ [M + H]$^+$ 220.0791, found 220.0787, error: 1.82 ppm.

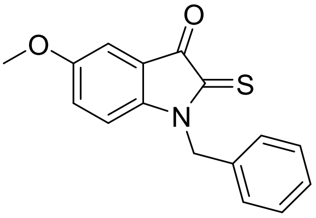
1-(prop-2-en-1-yl)-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3i

Reaction of isatin **1i** (110.0 mg, 587.6 μmol), **2** (166.4 mg, 411.3 μmol) in toluene (2.0 mL) under reflux for 5 minutes afforded compound **3i** (65.0 mg, 54% yield). Brown solid mp. 95-98 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (ddd, *J* = 7.4, 1.3, 0.6 Hz, 1H), 7.58 (td, *J* = 7.8, 1.3 Hz, 1H), 7.21 (td, *J* = 7.4, 0.6 Hz, 1H), 7.03 (dt, *J* = 7.8, 0.6 Hz, 1H), 5.87 (17.2, 10.5, 5.4 1H), 5.33 – 5.30 (m, 1H), 5.30 (t, *J* = 1.6 Hz, 1H), 4.79 (dt, *J* = 5.4, 1.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 186.1, 176.8, 151.3, 137.4, 129.0, 127.1, 125.0, 119.7, 119.2, 111.0, 46.9. HRMS (ESI+): *m/z* calcd for $C_{11}H_{10}NOS^+$ $[M + H]^+$ 204.0478, found 204.0476, error: 0.98 ppm.

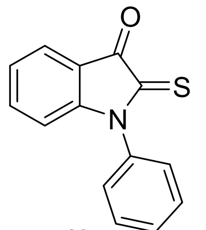
1-benzyl-5-methoxy-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3j

Reaction of isatin **1j** (111.0 mg, 415.3 μmol), **2** (117.6 mg, 290.7 μmol) in toluene (1.3 mL) under reflux for 5 minutes afforded compound **3j** (106.0 mg, 90% yield). black solid mp. 188 – 189 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.16 (m, 6H), 6.99 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 5.32 (s, 1H), 3.77 (s, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 185.8, 176.8, 157.6, 145.1, 133.9, 129.1, 128.2, 127.3, 123.7, 120.4, 112.1, 111.1, 56.0, 48.2. HRMS (ESI+): *m/z* calcd for $C_{16}H_{14}NO_2S^+$ $[M + H]^+$ 284.0740, found 284.0734, error: 2.11 ppm.

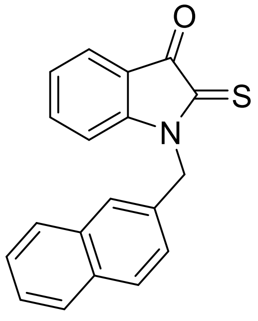
1-phenyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3k

Reaction of isatin **1k** (100.0 mg, 447.97 µmol), **2** (129.4 mg, 313.6 µmol) in toluene (1.4 mL) under reflux for 5 minutes afforded compound **3j** (59.0 mg, 55% yield). Orange solid mp. 168-170 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (ddd, *J* = 7.5, 1.4, 0.6 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.24 (td, *J* = 7.5, 0.6 Hz, 1H), 6.80 (dt, *J*= 8.0, 0.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 186.9, 176.4, 152.9, 137.3, 135.6, 130.3, 129.7, 127.2, 127.1, 125.2, 119.5, 111.6. HRMS (ESI+): *m/z* calcd for $C_{14}H_{10}NOS^+$ $[M + H]^+$ 240.0478, found 240.0476, error: 0.83 ppm.

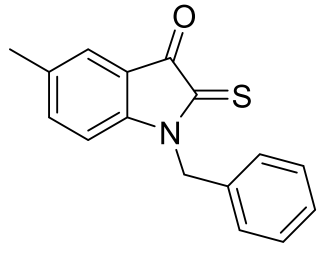
1-[(naphthalen-2-yl)methyl]-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3l

Reaction of isatin **1l** (100.0 mg, 348.05 µmol), **2** (98.5 mg, 243.6 µmol) in toluene (1.0 mL) under reflux for 5 minutes afforded compound **3l** (90.2 mg, 85% yield). Red solid mp. 205-208 °C. 1H NMR (600 MHz, Chloroform-d) δ 7.84 – 7.76 (m, 5H), 7.50 – 7.42 (m, 4H), 7.17 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 5.55 (s, 2H). 13C NMR (151 MHz, Chloroform-d) δ 186.8, 176.9, 151.4, 137.4, 133.4, 133.2, 131.4, 129.3, 128.0, 127.9, 127.1, 126.8, 126.5, 126.3, 125.1, 125.0, 119.8, 111.4, 48.6. HRMS (ESI+): *m/z* calcd for $C_{19}H_{14}NOS^+$ $[M + H]^+$ 304.0791, found 304.0788 error: 0.99 ppm

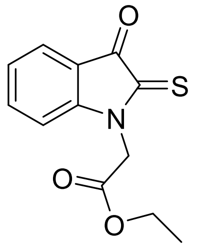
1-benzyl-5-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



3m

Reaction of isatin **1m** (102.0 mg, 405.9 µmol), **2** (114.9 mg, 284.1 µmol) in toluene (1.2 mL) under reflux for 5 minutes afforded compound **3m** (77.0 mg, 70% yield). Purple solid. 189-190 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.35 – 7.25 (m, 6H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.4, 177.0, 149.2, 137.7, 134.99, 134.0, 129.0, 128.2, 127.4, 127.3, 119.8, 111.0, 48.2, 20.7. HRMS (ESI+): *m/z* calcd for $C_{16}H_{14}NOS^+$ $[M + H]^+$ 268.0791, found 268.0788, error: 1.12 ppm.

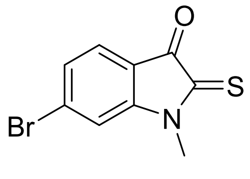
Ethyl 2-(3-oxo-2-tioxoindolin-1-il)acetate



3n

Reaction of isatin **1n** (96.0 mg, 411.6 µmol), **2** (116.5 mg, 288.1 µmol) in toluene (1.2 mL) under reflux for 5 minutes afforded compound **3n** (86.0 mg, 83% yield). Red solid. 205-206 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.8 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.59 (td, *J* = 8.0, 1.3 Hz, 1H), 7.21 (t, *J*=7.5, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.88 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.1, 176.5, 165.9, 151.0, 137.4, 127.2, 125.2, 119.6, 110.2, 62.4, 45.5, 14.2. HRMS (ESI+): *m/z* calcd for $C_{12}H_{12}NO_3S^+$ $[M + H]^+$ 250.0532, found 250.0530, error: 0.8 ppm

6-bromo-1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one

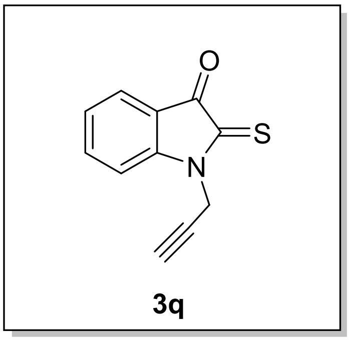


3p

Reaction of isatin **1p** (83.0 mg, 354.7 µmol), **2** (97.9 mg, 242.0 µmol) in toluene (1.0 mL) under reflux for 5 minutes afforded compound **3p** (36.0 mg, 40% yield). Red solid. 156-158 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.85 (d, *J*=7,8 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, DMSO-

d$_6$) δ 186.6, 175.4, 148.2, 142.8, 126.6, 125.6, 122.6, 104.1, 34.8. HRMS (ESI+): *m/z* calcd for $C_9H_6BrNOS^+$ [M + H]$^+$ 255.9426, found 255.9424, error: 0.78 ppm.

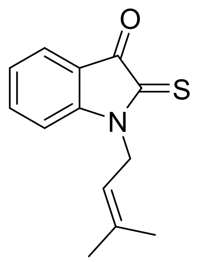
3-(prop-2-yn-1-yl)-2-sulfanylidene-2,3-dihydro-1H-inden-1-one



3q

Reaction of isatin **1q** (101.0 mg, 545.4 μmol), **2** (154.4 mg, 381.8 μmol) in toluene (1.8 mL) under reflux for 5 minutes afforded compound **3q** (64.0 mg, 58% yield). Red solid. 161-163 °C. ^{1}H NMR (600 MHz, DMSO-d6) δ 7.79 – 7.75 (m, 2H), 7.48 (d, J = 7.9 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 5.03 (d, J = 2.5 Hz, 2H), 3.38 (s, 1H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 185.3, 176.2, 149.8, 137.7, 126.4, 125.3, 119.1, 111.9, 75.7 (d, *J* = 126.9 Hz), 33.7. HRMS (ESI+): *m/z* calcd for $C_{11}H_8NO_3S^+$ [M + H]$^+$ 202.0321, found 202.0322, error: 0.46 ppm

3-(3-methylbut-2-en-1-yl)-2-sulfanylidene-2,3-dihydro-1H-inden-1-one

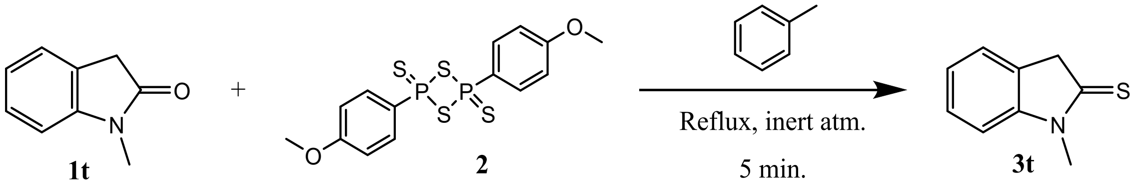


3r

Reaction of isatin **1r** (101.0 mg, 469.2 μmol), **2** (132.8 mg, 328.4 μmol) in toluene (1.6 mL) under reflux for 5 minutes afforded compound **3r** (32.0 mg, 30% yield). Red solid. 147-148 °C. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.73-7.70 (m, 2H), 7.29-7.27 (m, 1H), 5.19 (t, 6.5 Hz, 1H), 4.77 (d, *J* = 6.5 Hz, 1H), 1.83 (s, 1H), 1.70 (s, 1H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 184.7, 176.8, 150.6, 137.7, 137.6, 126.2, 125.0, 119.2, 116.3, 111.7, 42.6, 25.3, 18.4. HRMS (ESI+): *m/z* calcd for $C_{13}H_{13}NOS^+$ [M + H]$^+$ 232,0790, found 232,0789, error: 0.69 ppm

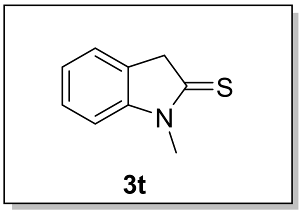
Synthesis and Characterization of Compound 3t

Compound **3t** was prepared according to the scheme shown below:



In a 25 mL round-bottom flask, 1-methyl-2-oxindole (**1t**) (100.0 mg, 679.4 µmol, 1.0 equiv.) was dissolved in toluene (2.0 ml, 0.3 M). Lawesson's reagent (193.3 mg, 475.6 µmol, 0.7 equiv.) was added to the solution and the mixture was stirred under reflux conditions and under nitrogen atmosphere. The reaction was monitored by thin layer chromatography (TLC) until complete conversion of starting materials or stagnation of the reaction. The solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/EtOAc) to furnish the corresponding compound **3t** (80.0 mg, 72%).

6-Bromo-1-methyl-2-sulfanylidene-2,3-dihydro-1H-indol-3-one



Yellowish solid, mp. 108-110°C (lit. 109-110)[5] 1H NMR (300 MHz, Chloroform-d) δ 7.37 – 7.24 (m, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.8 Hz, 0H), 4.08 (s, 1H), 3.61 (s, 1H). 13C NMR (75 MHz, Chloroform-d) δ 201.19, 146.68, 129.22, 128.08, 124.40, 124.02, 109.68, 49.11, 31.33.

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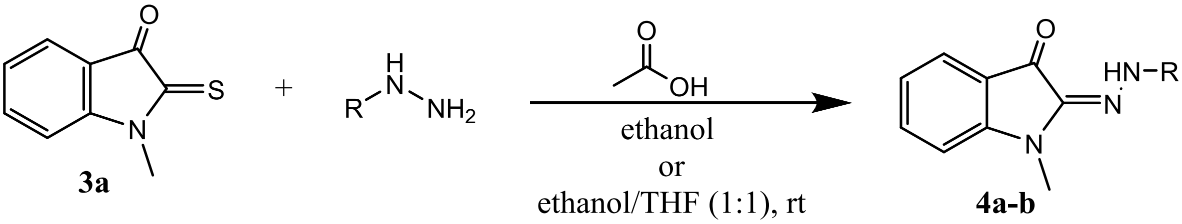
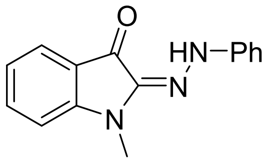
[5] Hino, Tohru, Chem. Ind., 1967, 275-276.

General Procedure for Synthesis of hydrazones 7a and 7b.



In a 25 mL round-bottom flask, compound **3a** (1.0 equiv.) was dissolved in ethanol (0.1 M, for the synthesis of **4a**) or a mixture of ethanol/THF (1:1; 0.1 M, for the synthesis of **4b**). Then phenylhydrazine (1.0 equiv., for the synthesis of **4a**) or benzoylhydrazide (1.0 equiv., for the synthesis of **4b**) was added to the solution together with glacial acetic acid (5% mol) and the mixture was stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC) until complete conversion of starting materials. The solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/EtOAc) to furnish hydrazone **4a** or **4b**.

1-Methyl-2-(2-phenylhydrazin-1-ylidene)-2,3-dihydro-1H-indol-3-one[6]



4a

Reaction of thioisatin **3a** (42.0 mg, 237.0 µmol), phenylhydrazine (26.4 mg, 237.0 µmol) and acetic acid (5% mol) in ethanol (2.4 mL) afforded compound **4a** (36.0 mg, 60% yield) after 5 minutes. Dark pink solid, mp. 111-112 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.40 (s, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.58 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.23 (d, J = 8.3 Hz, 1H), 6.98 – 6.90 (m, 2H), 3.37 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.5, 151.4, 143.1, 136.2, 135.2, 129.4, 124.0, 121.7, 118.9, 118.2, 113.4, 110.1, 27.5. HRMS (ESI+): *m/z* calcd for $C_{15}H_{14}N_3O^+$ [M + H]$^+$ 252.1131, found 280.1081, error: 0.79 ppm.

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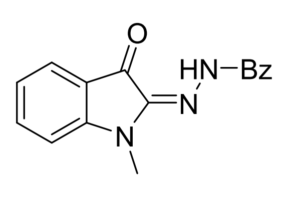
[6] T. Prabakar, P. Ambastha, R. Yadav, A. Samanta, M. K. Ravva, P. Munshi, S. Sen, *Adv. Synth. Catal.* 2025, **367**, e202500353.

N'-(1-Methyl-3-oxo-2,3-dihydro-1H-inden-2-ylidene)benzohydrazine[7]


4b

Reaction of thioisatin **3a** (60.0 mg, 338.5 µmol), (69.1 mg, 507.8 µmol), acetic acid (5% mol) in ethanol/THF (1:1 *v/v*, 1 mL) afforded compound **4b** (83.0 mg, 88% yield) after 1 hour. Dark pink solid, mp. 182-184 °C. ^{1}H NMR (300 MHz, Chloroform-d) δ 13.48 (s, 1H), 7.98 (d, J = 6.8 Hz, 1H), 7.66 (d, J = 7.7 Hz, 2H), 7.54 (dq, J = 14.4, 7.1 Hz, 4H), 7.00 – 6.84 (m, 2H), 3.40 (s, 1H). ^{13}C NMR (75 MHz, Chloroform-d) δ 182.1, 164.1, 154.0, 140.7, 138.4, 132.8, 132.4, 129.0, 127.7, 125.7, 120.6, 118.5, 109.7, 27.9. HRMS (ESI+): *m/z* calcd for $C_{16}H_{13}N_3O_2^+$ $[M + H]^+$ 280.1081, found 280.1078, error: 1.07 ppm.

NMR data for compound **4b** has already been reported in the literature. Comparison of the spectral data of **4b** obtained in this work and in the work of Shukla *et al.*[7] – see in Table S1 below – shows good agreement and corroborates the proposed structural elucidation.

Table S1: Comparison between the NMR data for **4b** reported in the literature (Shukla *et al.*) and obtained in this work.

σ (^{1}H) – ppm Literature[7]	**Multiplicity Literature[7]**	**σ (^{1}H) – ppm This work**	**Multiplicity This work**
13.49	s, 1H	13.48	s, 1H
7.98	d, *J* = 7.6 Hz, 2H	7.98	d, *J* = 7.6 Hz, 2H
7.68	d, *J* = 7.6 Hz, 1H	7.67	d, *J* = 7.6 Hz, 1H
7.60 – 7.49	m, 4H	7.59- 7.50	m, 4H
6.98 – 6.92	m, 2H	7.00-6.84	m, 2H
3.41	s, 3H	3.40	s, 3H
σ (^{13}C) – ppm Literature[6]		**σ (^{13}C) – ppm This work**	
182.1		182.1	
164.0		164.1	
153.9		154.0	
140.6		140.7	
138.4		138.4	
132.7		132.8	
132.4		132.4	
128.9		129.0	
127.6		127.7	

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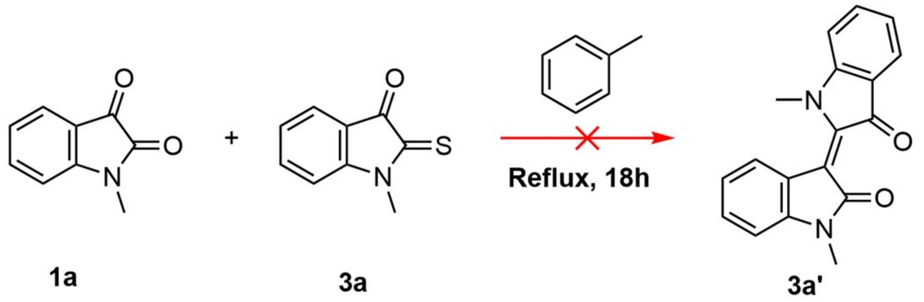
[7] G. Shukla; T. Alam, H. K. Srivastava, R. Kumar and B. K. Patel, *Org. Lett.*, 2019, **21**, 3543-3547.

125.7	125.7
120.5	120.6
118.4	118.5
109.6	109.7
27.8	27.9

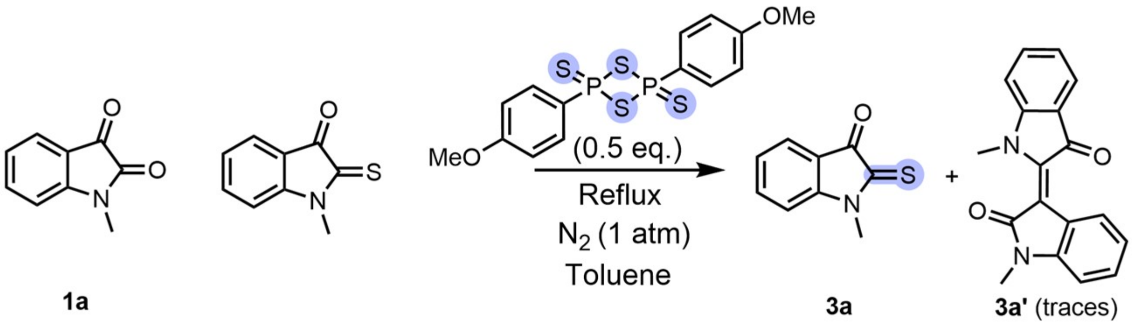
Control experiments

Control experiments were performed to evaluate the formation and stability of intermediates and byproducts that could be formed under the optimization of the reaction conditions. Firstly, an equimolar mixture of *N*-methylisatin (**1a**) and *N*-methyl-2-thioisatin (**3a**) was heated under reflux in toluene in the absence of additional reagents (Scheme S1). The reaction mixture was monitored by thin-layer chromatography (TLC) and GC/MS analysis for 18 hours. In both analyses, only the starting materials were detected, with no evidence of degradation or formation of new products. This result indicates that the formation of the C2–C3 dimer (**3a'**) does not occur spontaneously upon heating and that product **3a** is stable in high temperature without lawesson reagent in the mixture.



Scheme S1. Control experiment nº 1.

Additional time-dependent control experiments were conducted to evaluate the progression of the thionation process and the potential formation of byproducts under the reaction conditions. An equimolar mixture of *N*-methylisatin (**1a**) and *N*-methyl-2-thioisatin (**3a**) was treated with 0.5 equivalent of Lawesson's reagent in refluxing toluene (Scheme S2), and aliquots were withdrawn at different reaction times for analysis by thin-layer chromatography (TLC) and GC/MS.



Scheme S2. Control experiment nº 2.

After 5 min of reaction time, TLC analysis indicated complete consumption of *N*-methylisatin, the only observed compound corresponding to *N*-methyl-2-thioisatin. GC/MS analysis of the crude reaction mixture confirmed this observation, showing a major chromatographic peak corresponding to **3a** (98.011%), together with trace amounts of **1a** (1.157%). No significant signals attributable to dimeric products or other sulfur-containing byproducts were observed at this stage.

When the reaction was allowed to proceed for 1.5 h under the same conditions, TLC analysis still indicated complete consumption of *N*-methylisatin and predominant formation of *N*-methyl-2-thioisatin. The TLC plate showed slightly increased levels of minor impurities compared to the sample taken after 5 min, although these spots remained very weak in intensity relative to the major product, as shown in Figure S1.

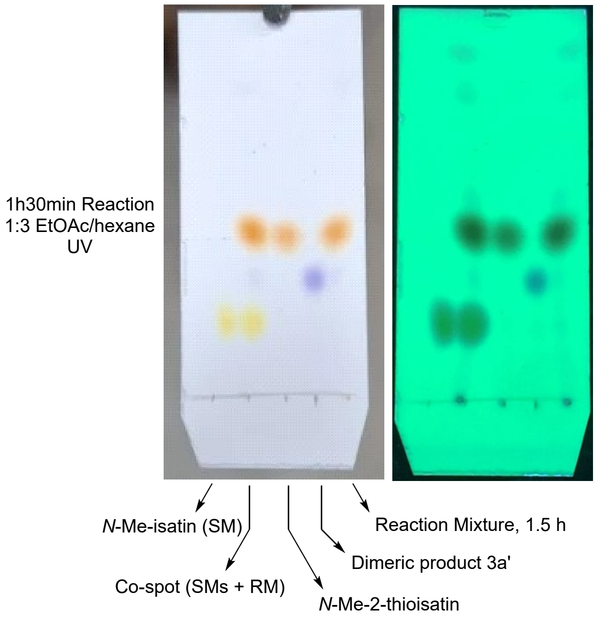


Figure S1: TLC plate showing spots of the starting material **1a**, product **3a**, dimeric product **3a'** and the reaction mixture.

GC/MS analysis of the 1.5 h reaction mixture aliquot revealed a major peak corresponding to *N*-methyl-2-thioisatin (98.326%), with only trace amounts of *N*-methylisatin remaining (0.409%). Additional minor peaks were assigned to sulfur allotropes, specifically S_6 (0.610%) and S_8 (0.655%). A signal corresponding to the C2–C3 dimer (*m/z* 290), was detected only very close to the chromatographic baseline and is therefore estimated to be below or near the detection limit under the analytical conditions employed. The isolated thionation product was recovered and quantified by quantitative NMR using 1,3,5-trimethoxybenzene as an internal standard, providing an estimated yield of 82%. It is noteworthy, however, that during the reaction a persistent solid residue was formed, which remained insoluble in hot toluene as well as in $CDCl_3$, and was not characterized.

Lastly, the stability of compound **3a** in the presence of LR was investigated. In this experiment, the thionated compound was treated with 0.4 equivalents of Lawesson's reagent in refluxing toluene. TLC monitoring of the reaction mixture, particularly after approximately 1h40min, revealed the appearance of new spots with higher Rf values relative to the starting material, indicating possible degradation of **3a** into unidentified by-products, as illustrated in Figure S2.

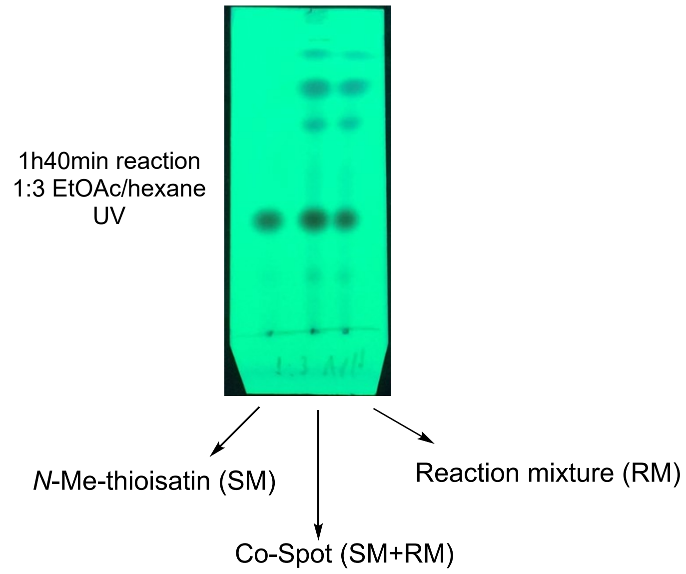


Figure S2. TLC showing product **3a**, co-spot, and the reaction mixture (**3a** + LR) after 1h40min under reflux (toluene). Visible degradation of **3a** is observed in the TLC plate.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra for compounds 3a-t and 4a-4b (only resonance signals associated with each compound have been integrated and/or assigned chemical shift values)

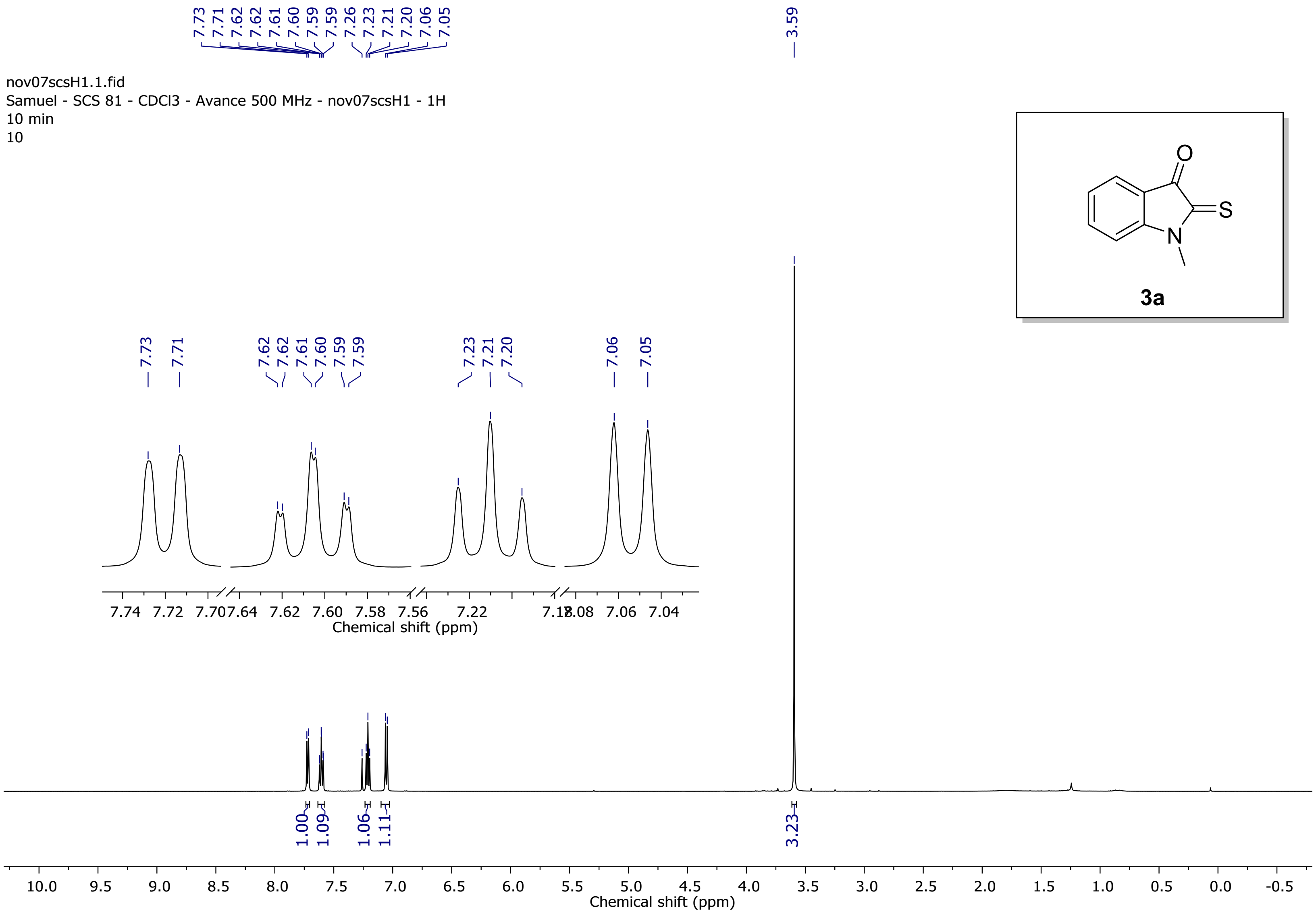
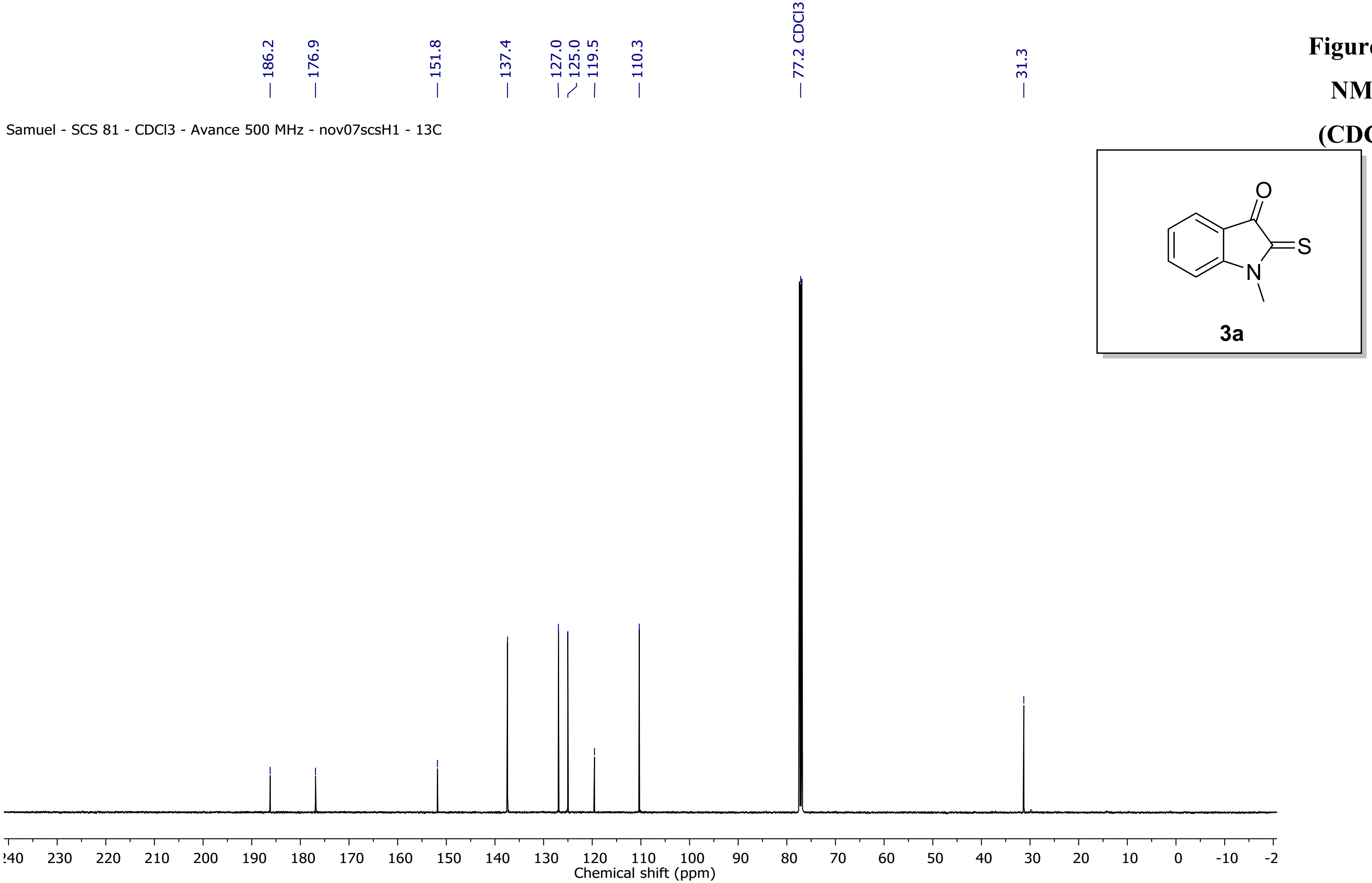
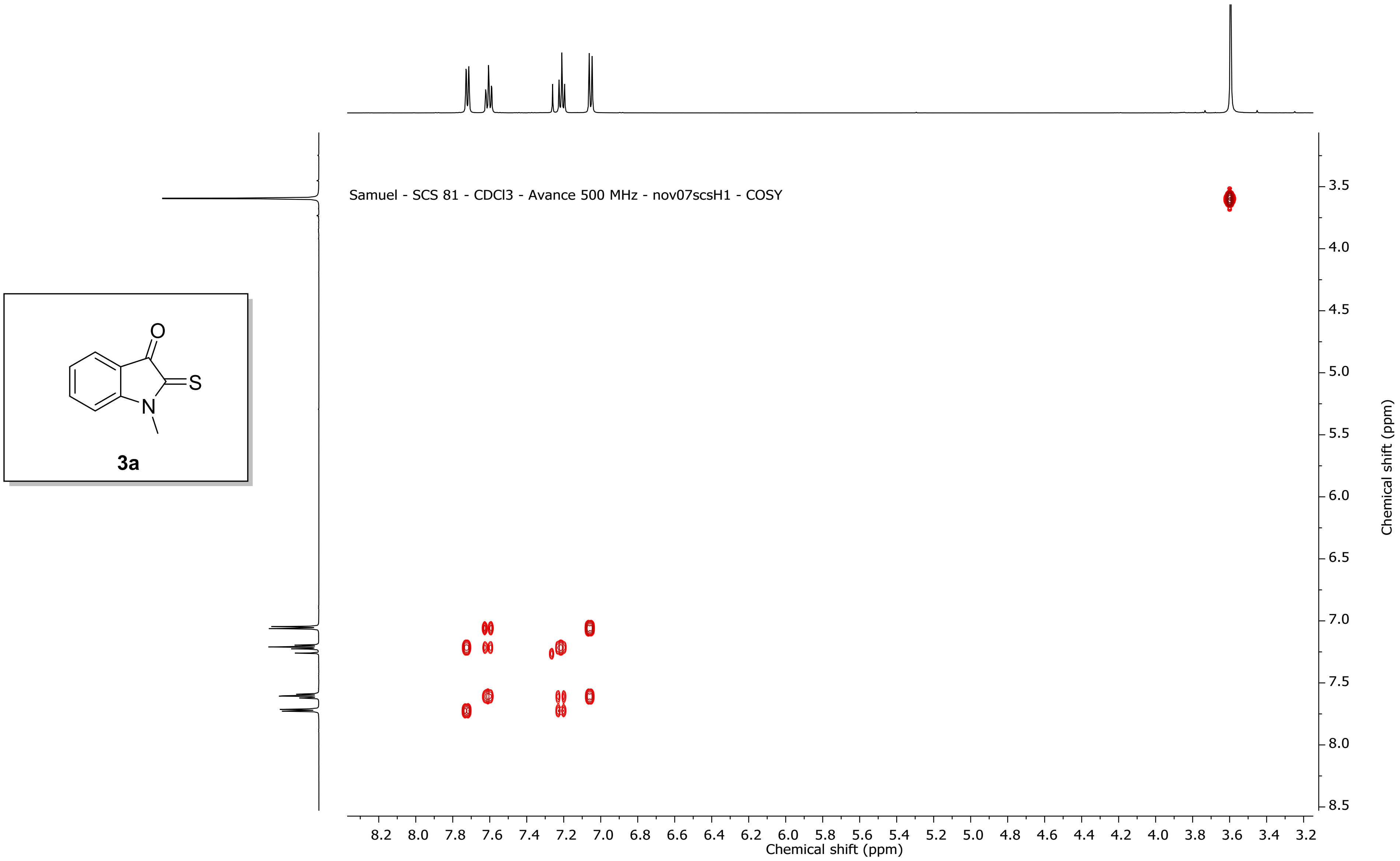


Figure S3. ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound 3a.

Figure S4 ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, 126 MHz) of compound 3a.

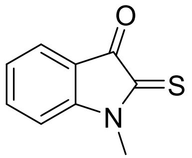




3a

Samuel - SCS 81 - CDCl3 - Avance 500 MHz - nov07scsH1 - COSY

Figure S5. Correlation map ^1H–^1H COSY ($CDCl_3$, 500 MHz) of compound 3a.


O
S
N

3a

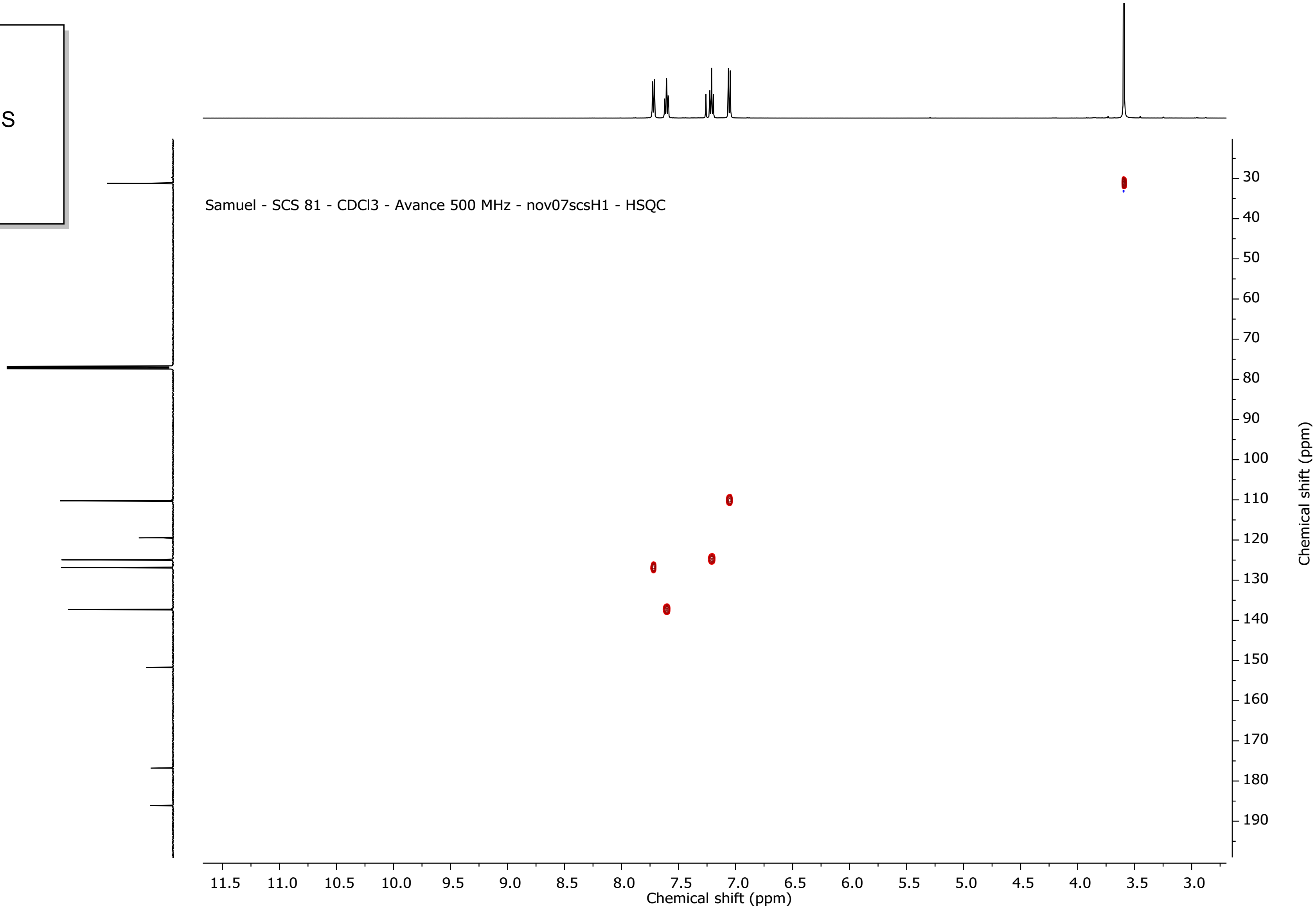

Samuel - SCS 81 - CDCl3 - Avance 500 MHz - nov07scsH1 - HSQC
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical shift (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
Chemical shift (ppm)

Figure S6. Correlation map ^{1}H–^{13}C HSQC ($CDCl_3$, 500 MHz) of compound 3a.

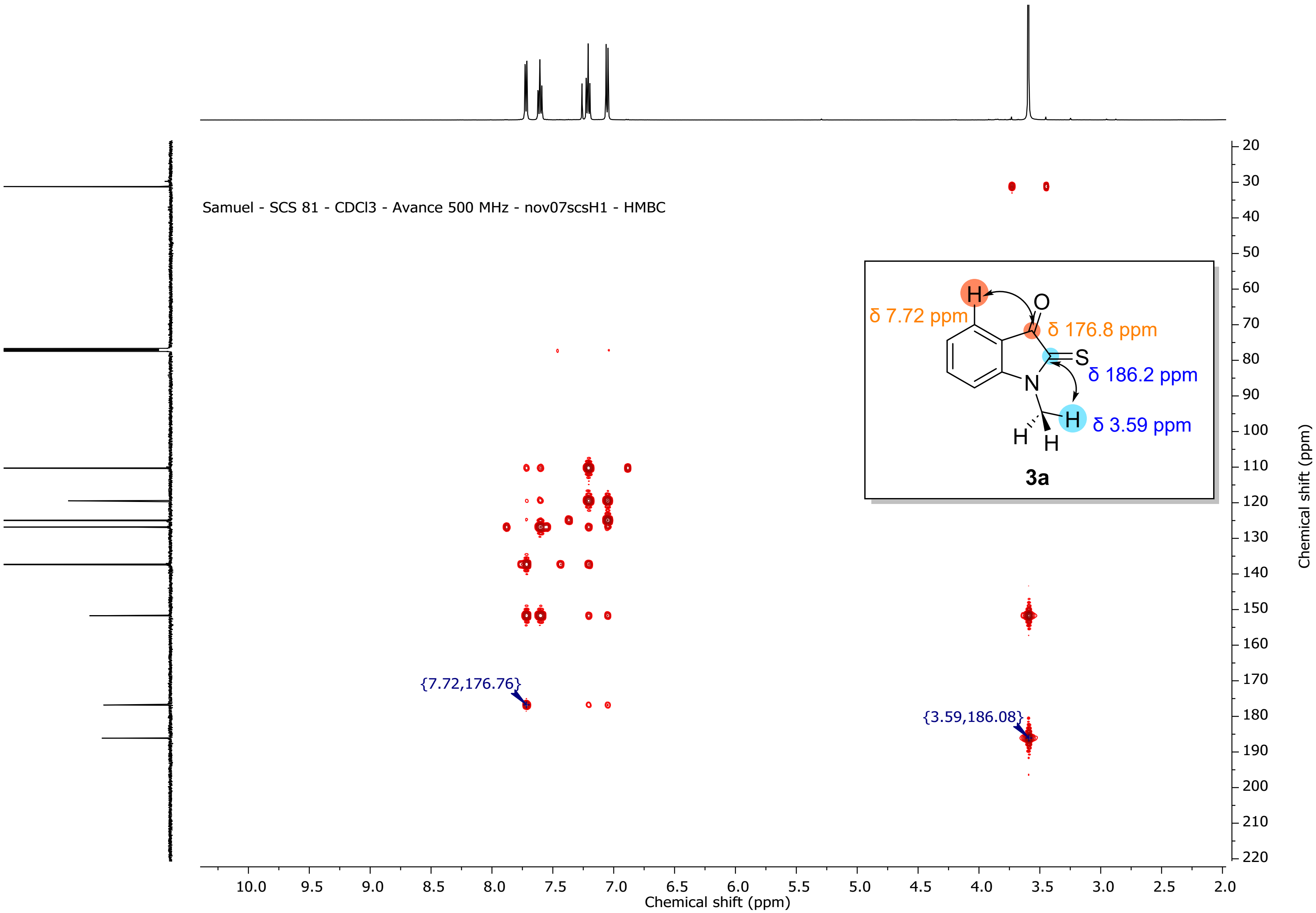

Samuel - SCS 81 - CDCl3 - Avance 500 MHz - nov07scsH1 - HMBC
δ 7.72 ppm
H
O
δ 176.8 ppm
S
δ 186.2 ppm
N
H
δ 3.59 ppm
H
H
3a
{7.72,176.76}
{3.59,186.08}
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical shift (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
Chemical shift (ppm)

Figure S7. Correlation map ^{1}H–^{13}C HMBC (CDCl$_3$, 500 MHz) of compound 3a.

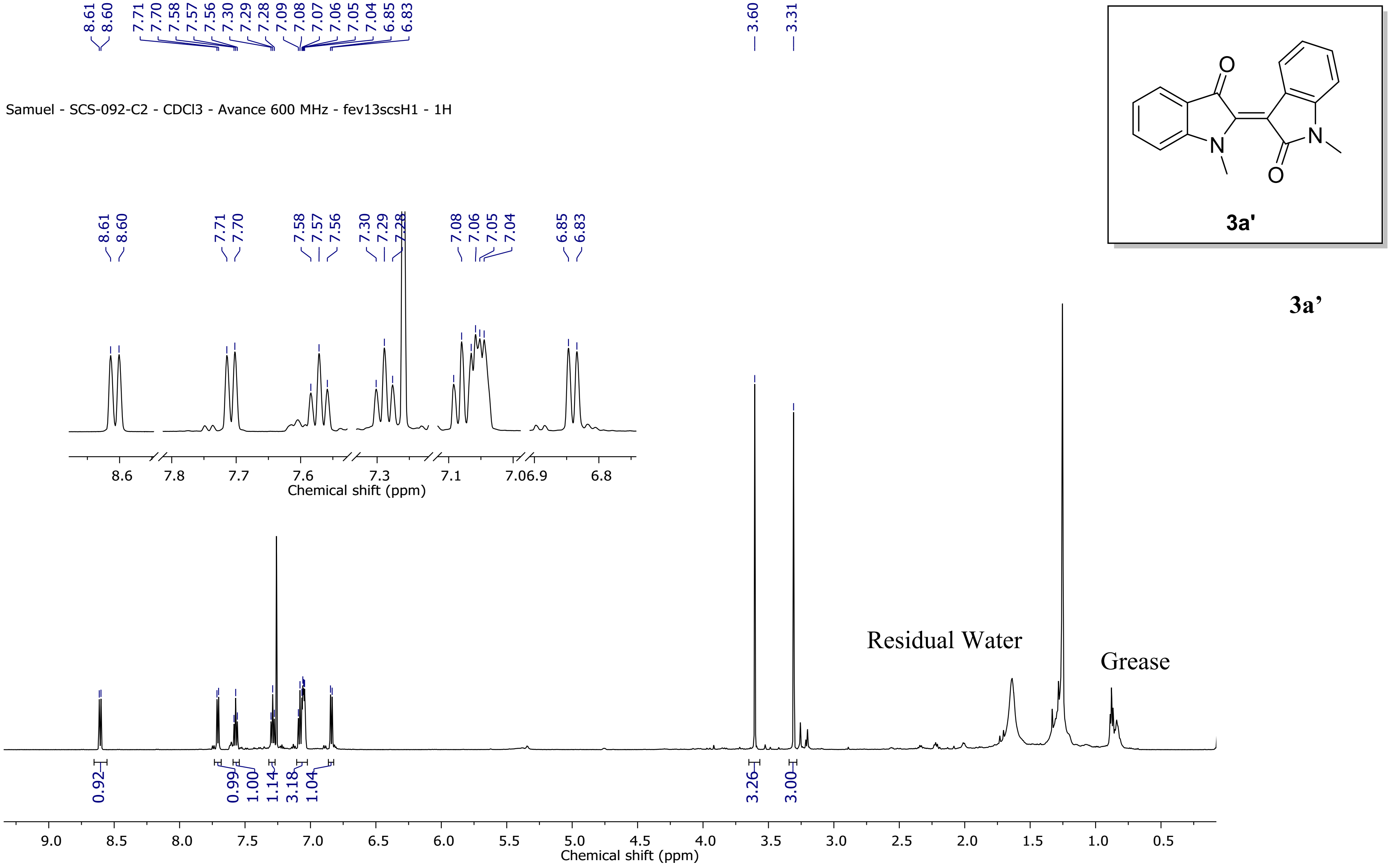


Figure S8. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of compound 3a’

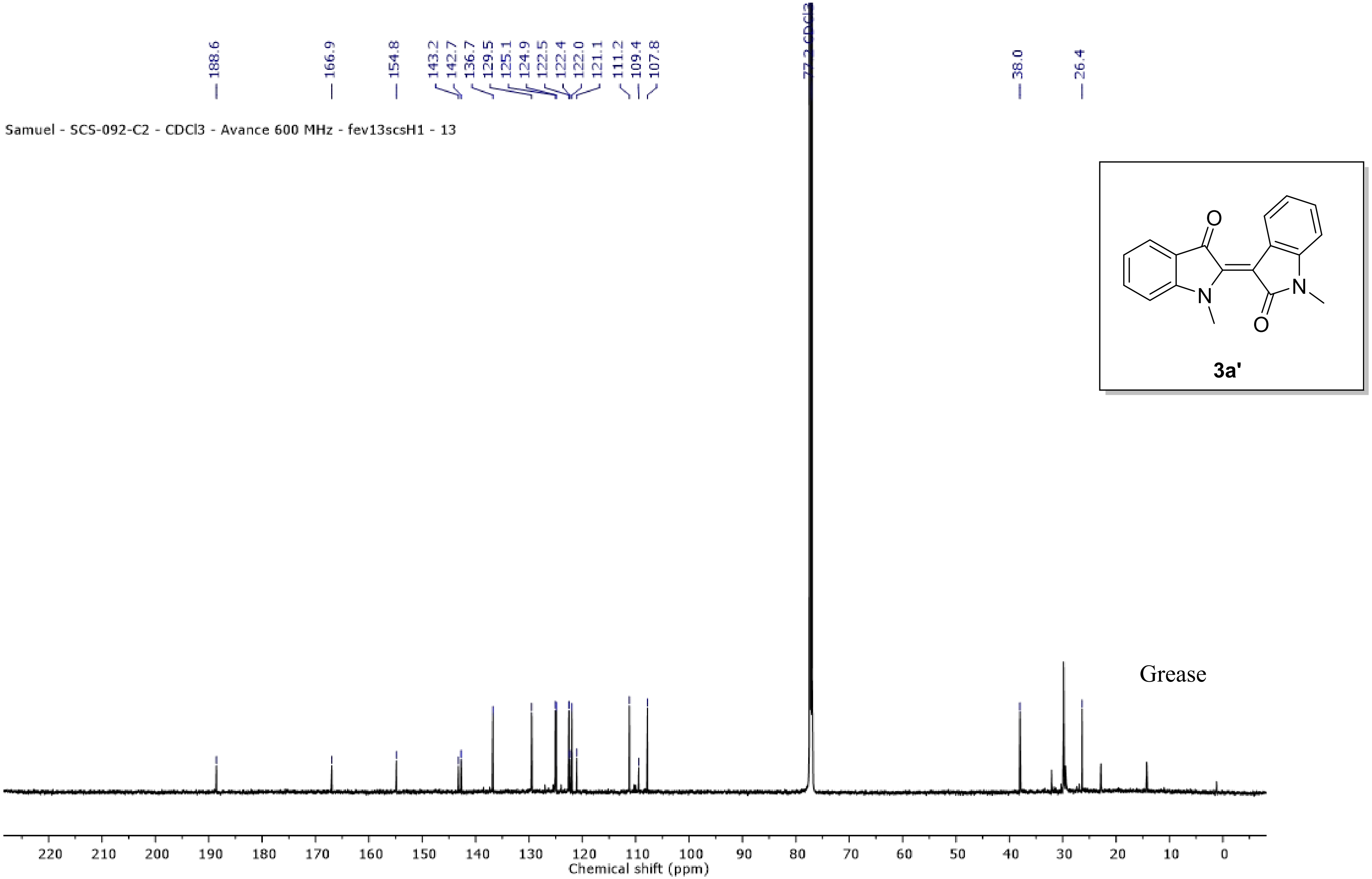

188.6
166.9
154.8
143.2
142.7
136.7
129.5
125.1
124.9
122.5
122.4
122.0
121.1
111.2
109.4
107.8
77.2 CDCl3
38.0
26.4
Samuel - SCS-092-C2 - CDCl3 - Avance 600 MHz - fev13scsH1 - 13
O
N
O
N
3a'
Grease
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S9. $^{13}C\{^{1}H\}$ **NMR spectrum ($CDCl_3$, 151 MHz) of compound 3a'.**

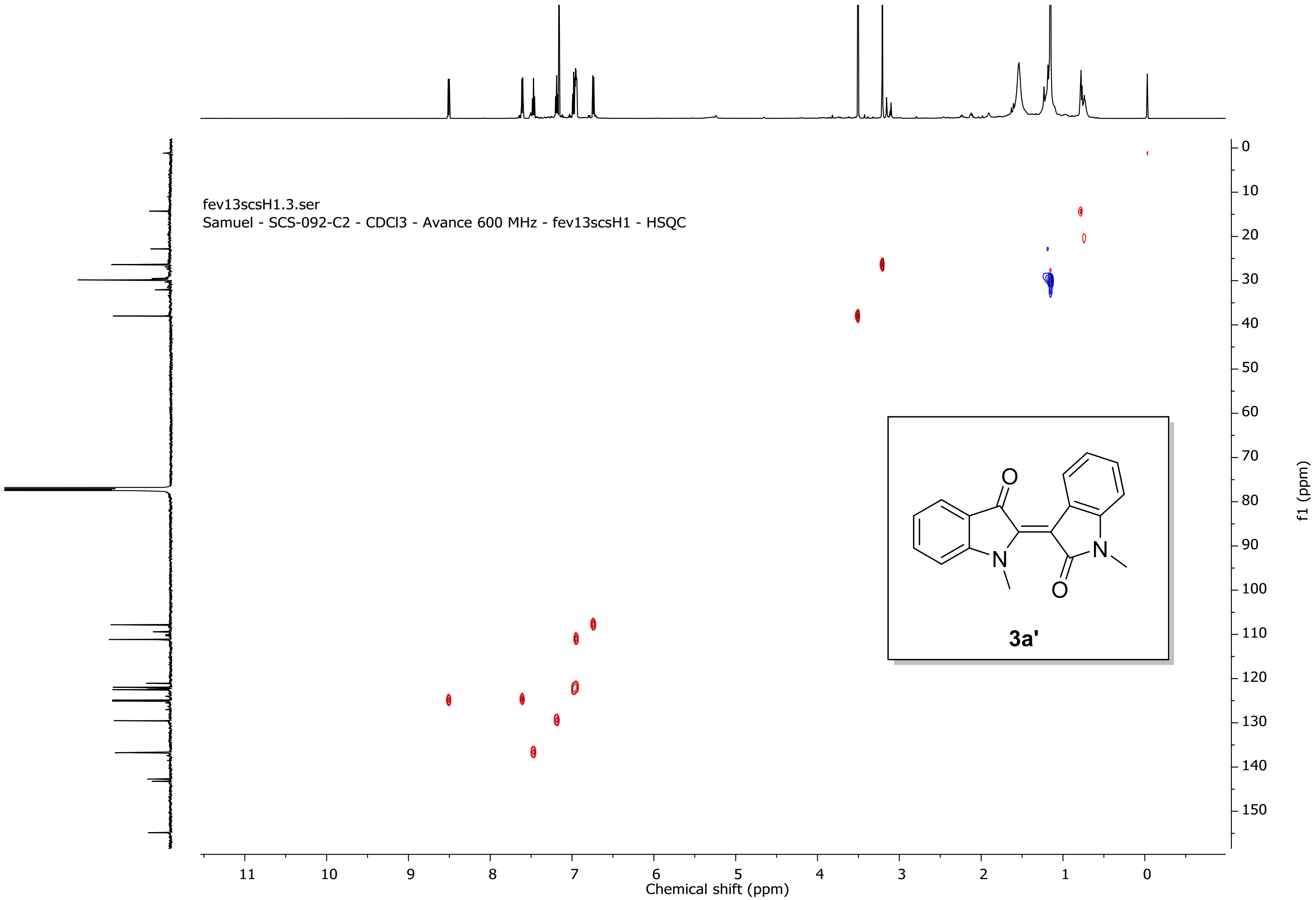


Figure S10. Correlation map ^{1}H–^{13}C HSQC ($CDCl_3$, 600 MHz) of compound 3a'.

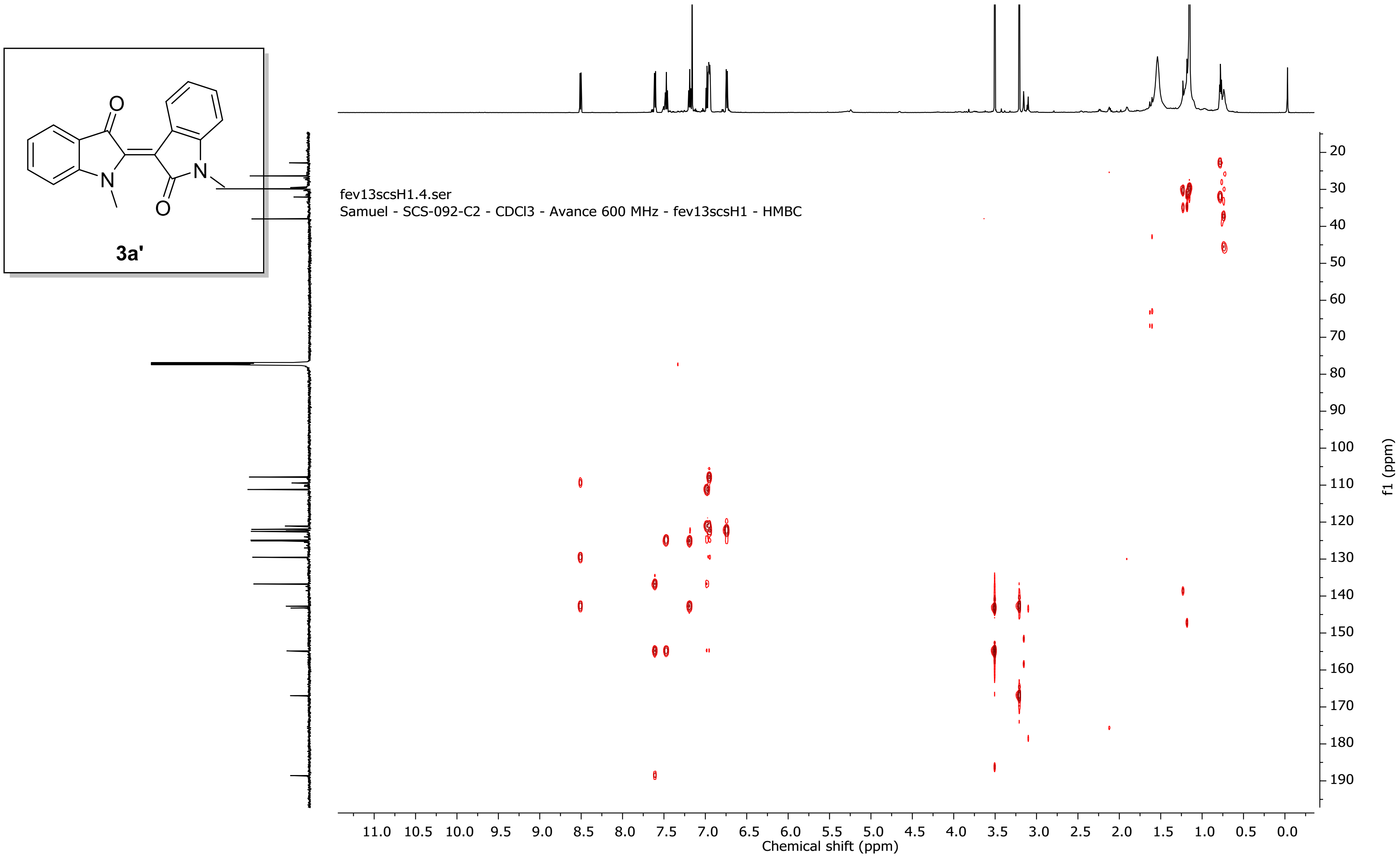
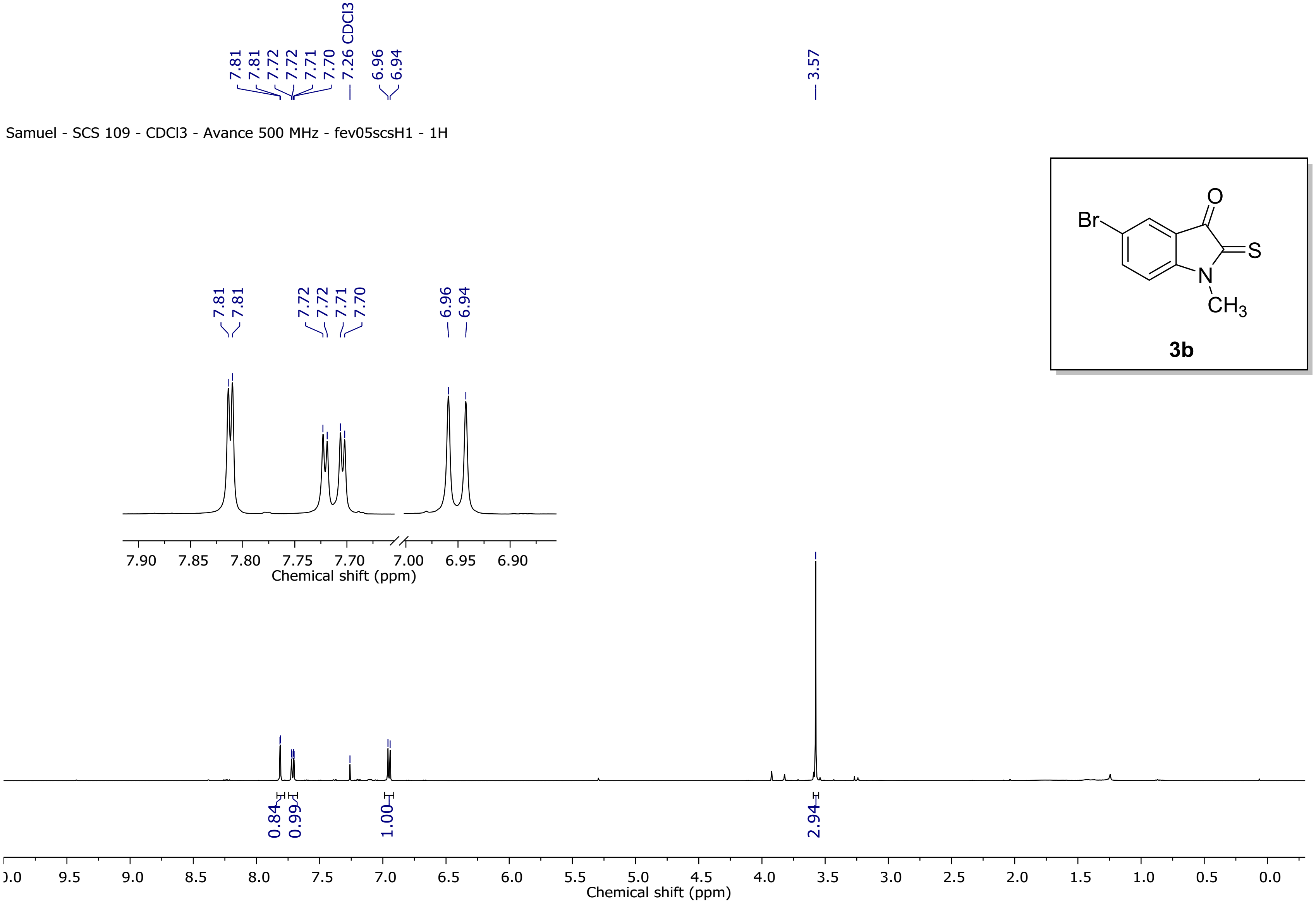


Figure S11. Correlation map ^1H–^{13}C HMBC ($CDCl_3$, 500 MHz) of compound **3a**.


7.81
7.81
7.72
7.72
7.71
7.70
7.26 CDCl3
6.96
6.94
3.57
Samuel - SCS 109 - CDCl3 - Avance 500 MHz - fev05scsH1 - 1H
7.90
7.85
7.80
7.75
7.70
7.00
6.95
6.90
Chemical shift (ppm)
0.84
0.99
1.00
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

Br
O
S
N
CH3

3b

Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **3b**.

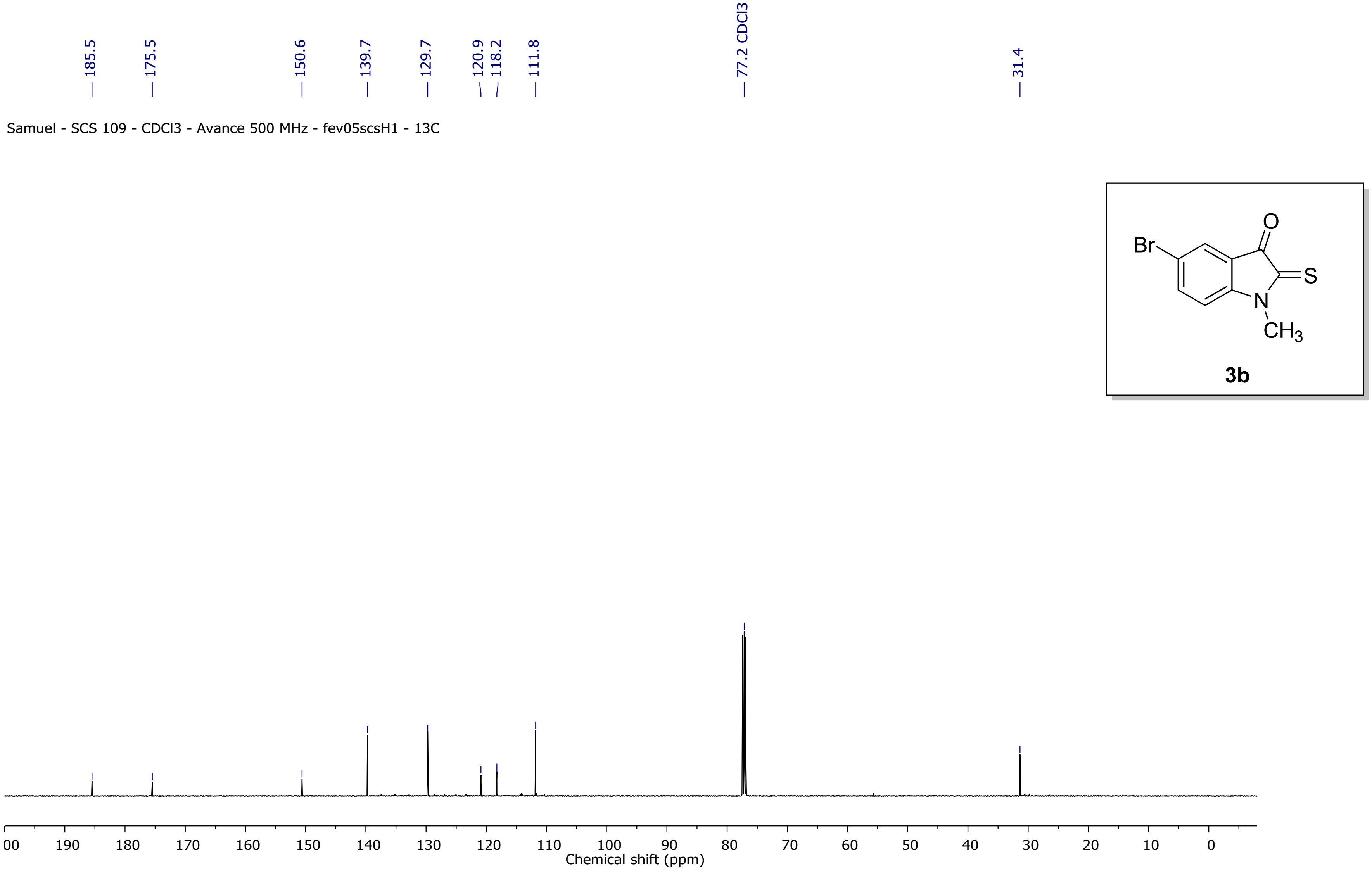

185.5
175.5
150.6
139.7
129.7
120.9
118.2
111.8
77.2 CDCl3
31.4
Samuel - SCS 109 - CDCl3 - Avance 500 MHz - fev05scsH1 - 13C
Br
O
S
N
CH3
3b
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S13. $^{13}C\{^1H\}$ **NMR spectrum ($CDCl_3$, 126 MHz) of compound 3b.**

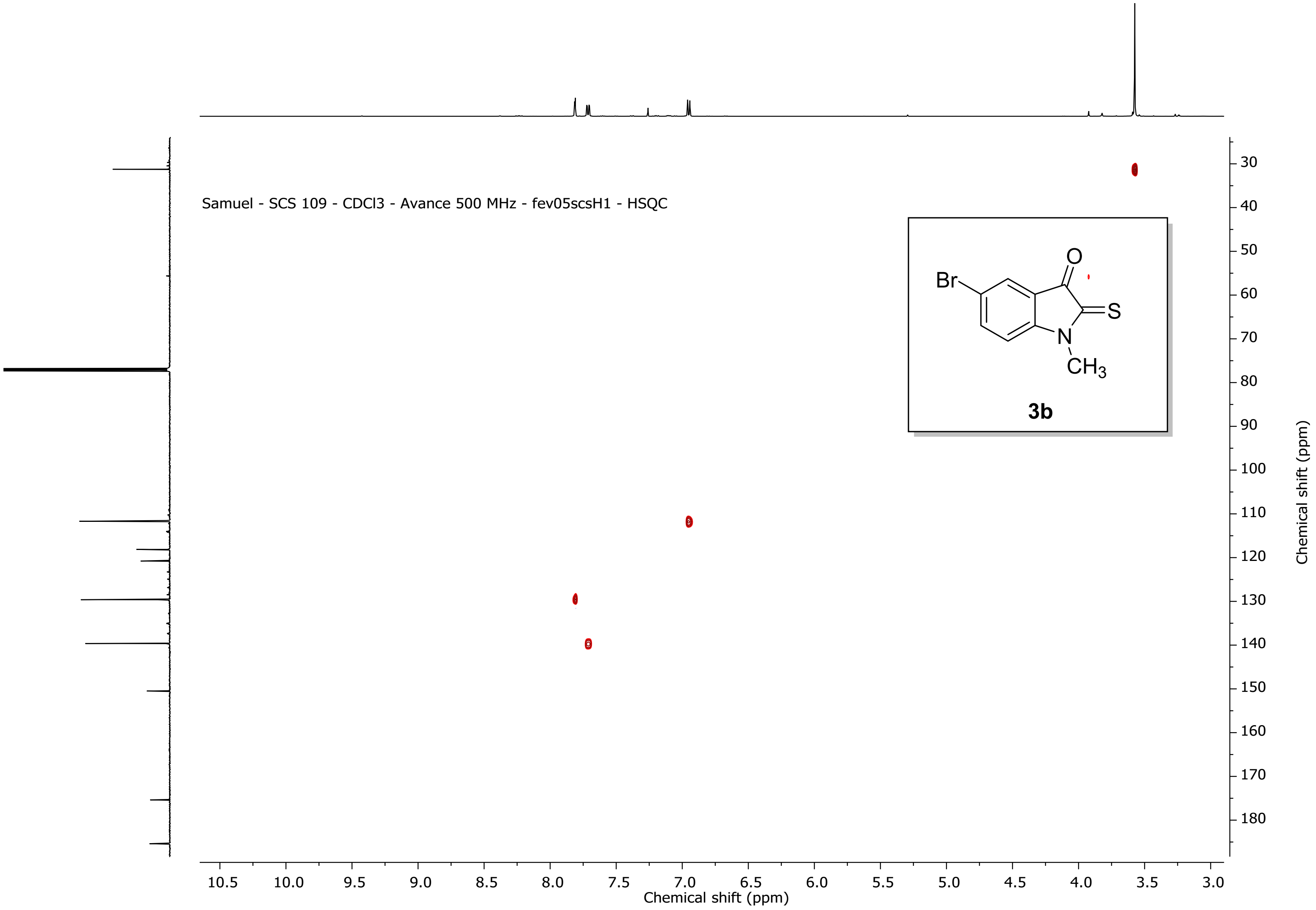

Samuel - SCS 109 - CDCl3 - Avance 500 MHz - fev05scsH1 - HSQC
Br
O
S
N
CH3
3b
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical shift (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Chemical shift (ppm)

Figure S14. Correlation map ^1H–^{13}C HSQC ($CDCl_3$, 500 MHz) of compound 3b.

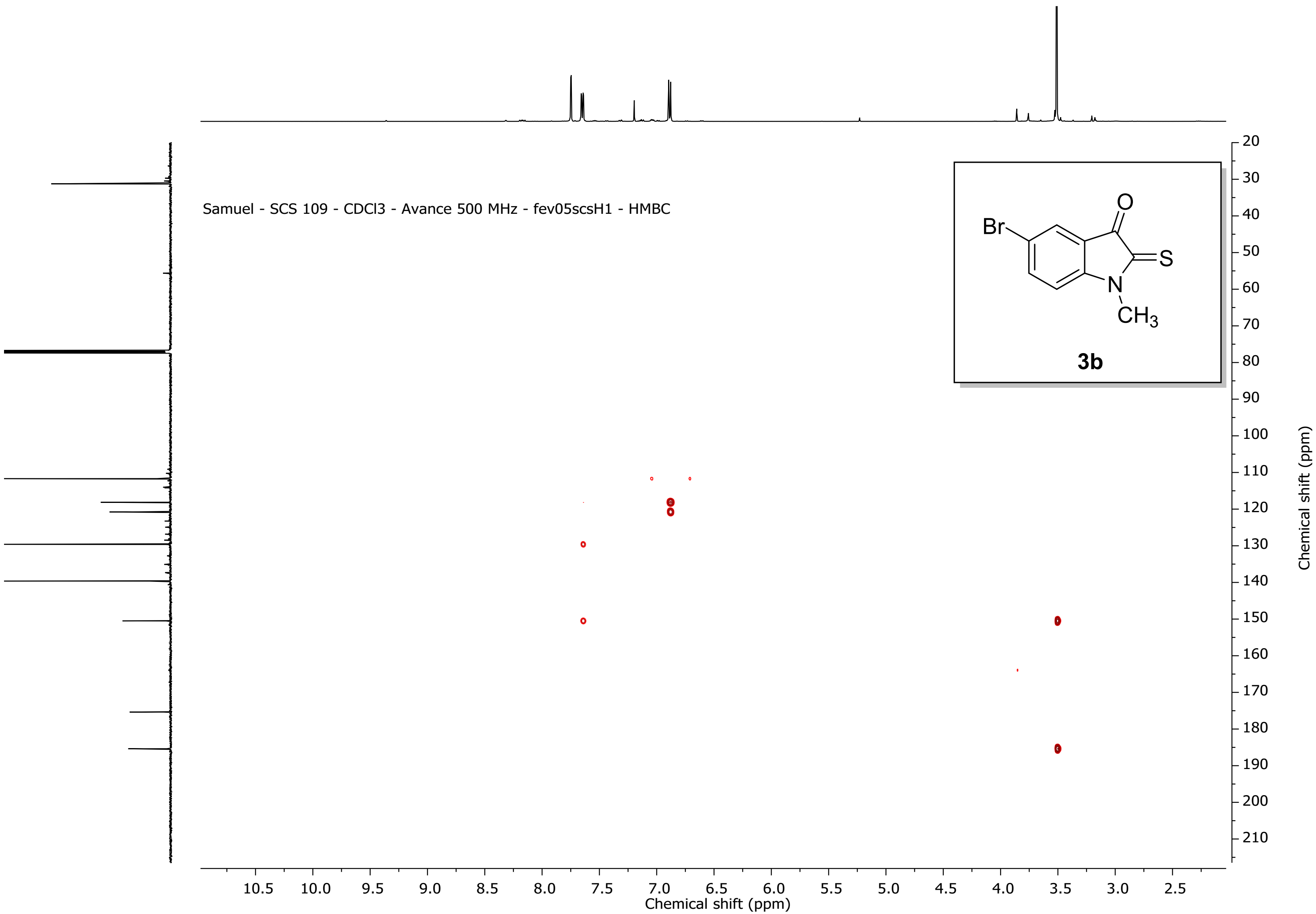
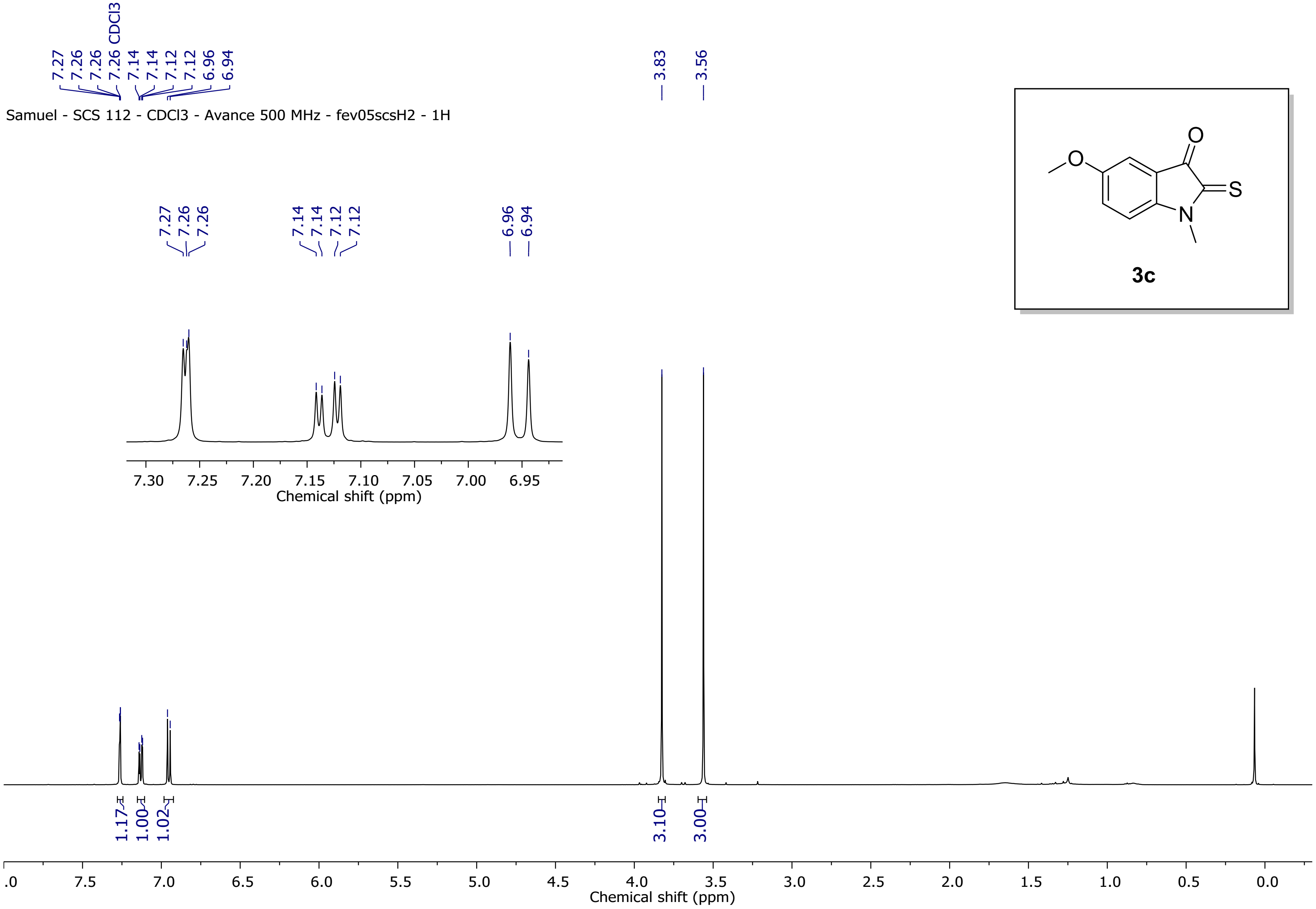


Figure S15. **Correlation map ^1H–^{13}C HMBC ($CDCl_3$, 500 MHz) of compound 3b.**


7.27
7.26
7.26
7.26 CDCl3
7.14
7.14
7.12
7.12
6.96
6.94
3.83
3.56
Samuel - SCS 112 - CDCl3 - Avance 500 MHz - fev05scsH2 - 1H
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
Chemical shift (ppm)
O
O
S
N
1.17
1.00
1.02
3.10
3.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

3c

Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound 3c.

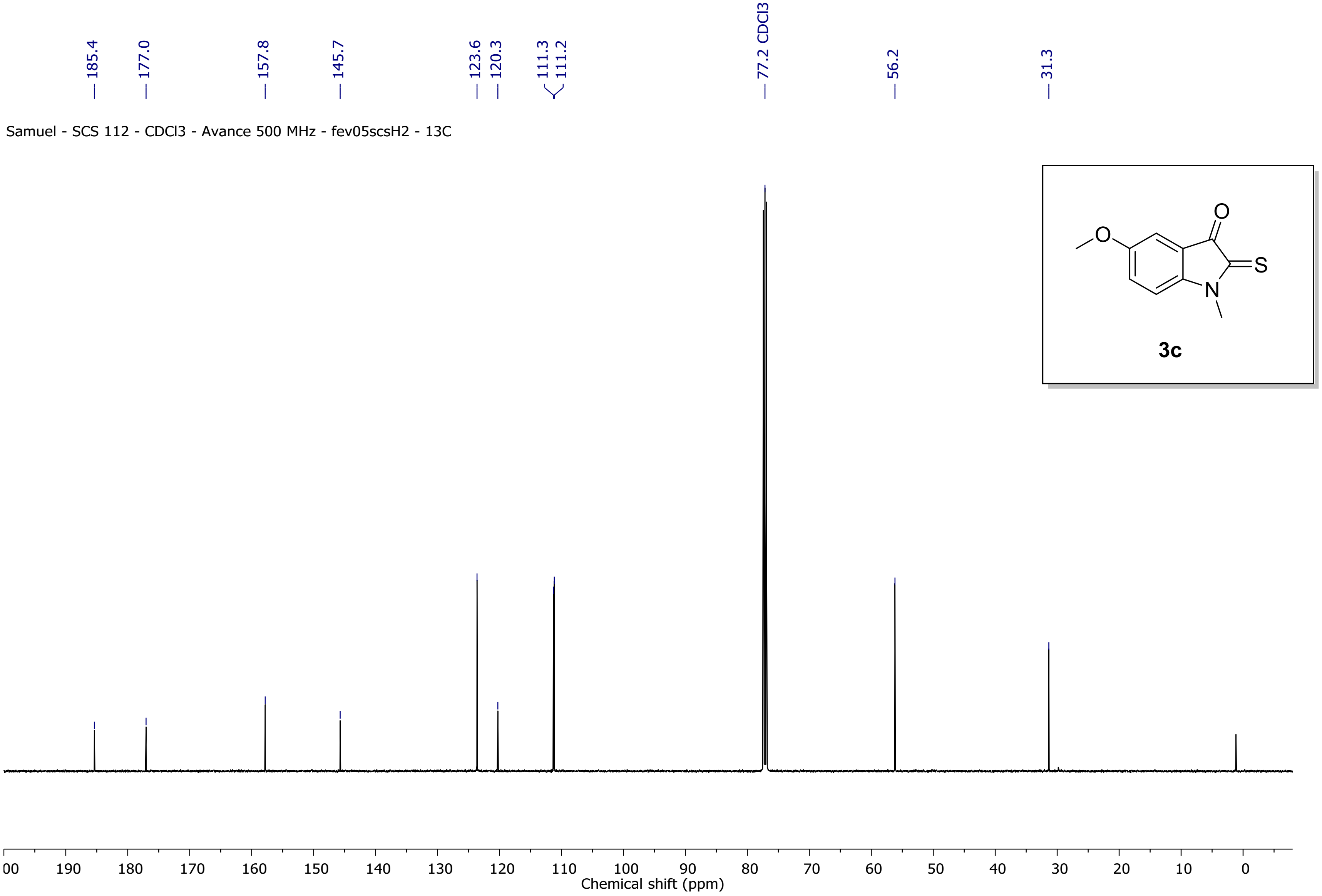

185.4
177.0
157.8
145.7
123.6
120.3
111.3
111.2
77.2 CDCl3
56.2
31.3
Samuel - SCS 112 - CDCl3 - Avance 500 MHz - fev05scsH2 - 13C
O
O
S
N
3c
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S17. $^{13}C\{^{1}H\}$ **NMR spectrum (**$CDCl_3$**, 126 MHz) of compound 3c.**

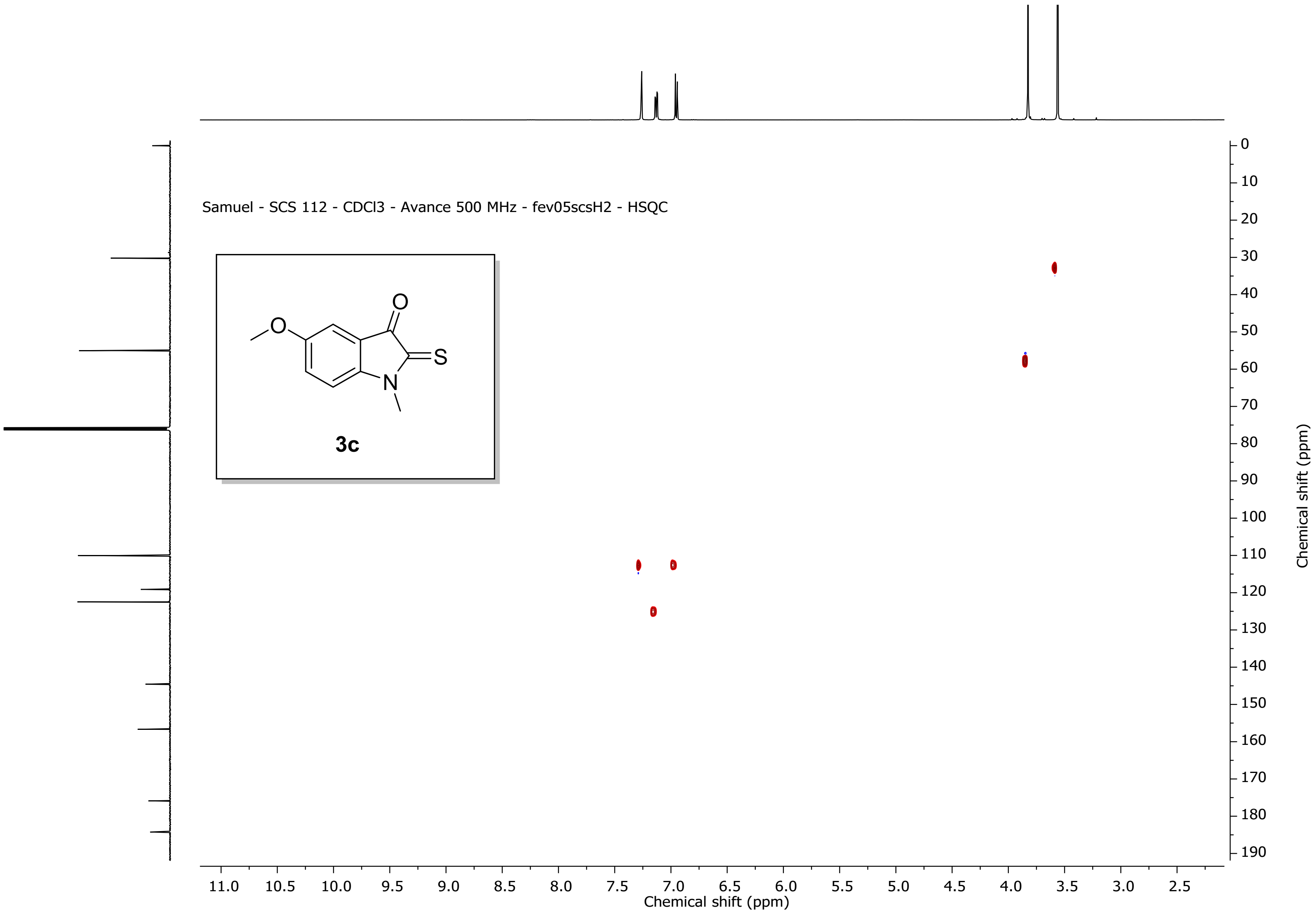


Figure S18. Correlation map ^{1}H–^{13}C HSQC (CDCl$_3$, 500 MHz) of compound 3c.

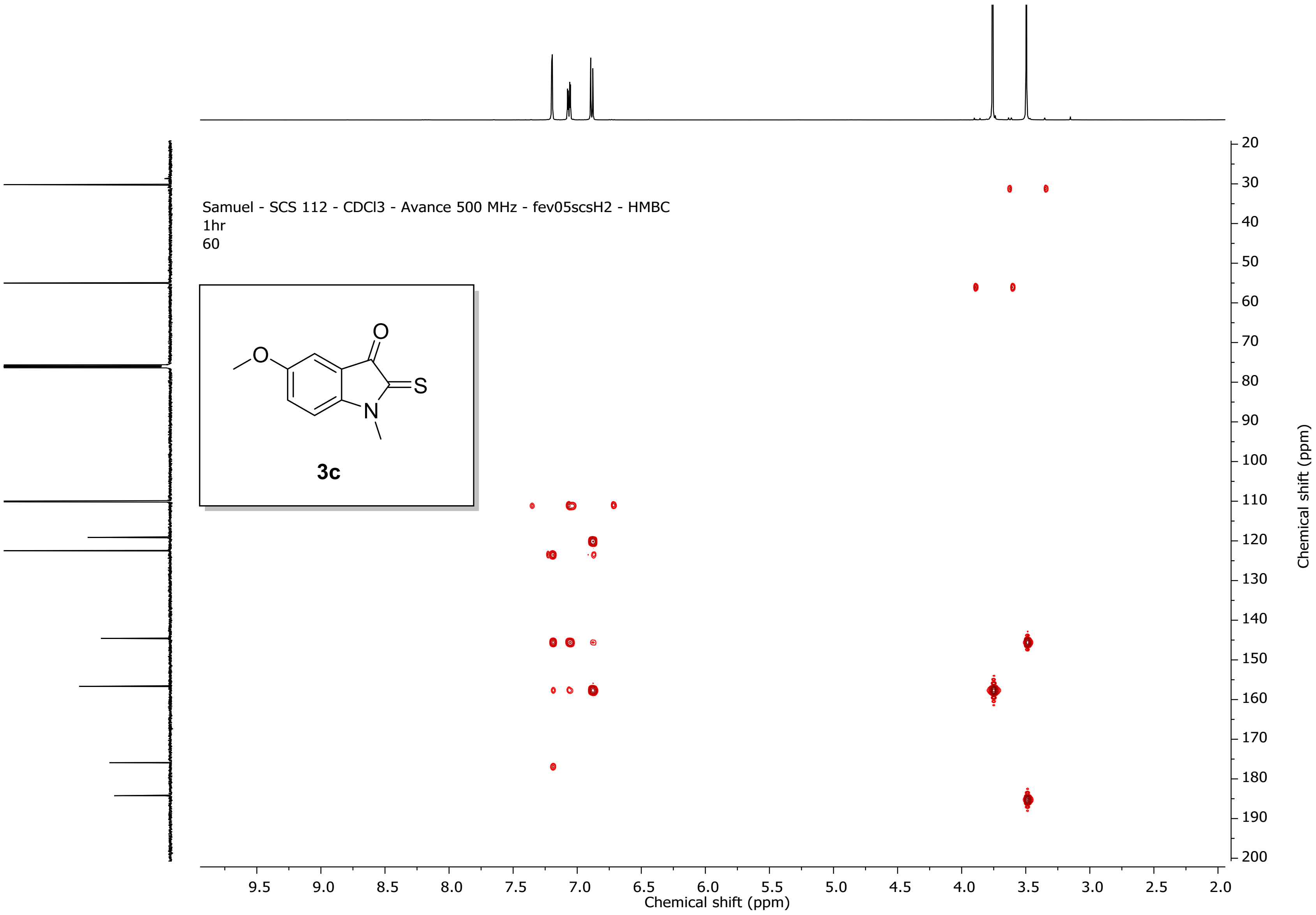

Samuel - SCS 112 - CDCl3 - Avance 500 MHz - fev05scsH2 - HMBC
1hr
60
O
O
S
N
3c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical shift (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Chemical shift (ppm)

Figure S19. Correlation map ^{1}H–^{13}C HMBC (CDCl$_3$, 500 MHz) of compound 3c.

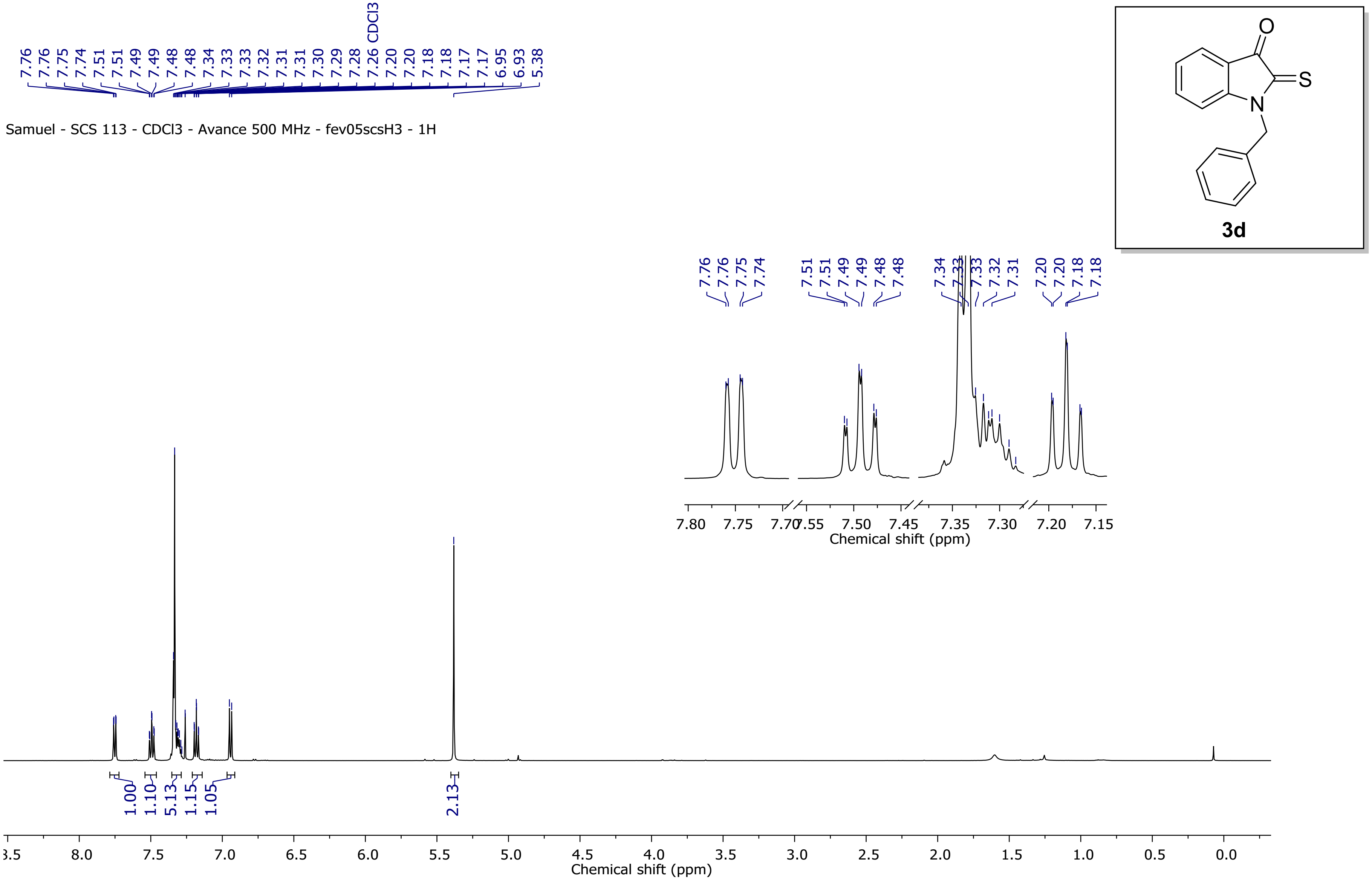

7.76 7.76 7.75 7.74 7.51 7.49 7.49 7.48 7.48 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.26 CDCl3 7.20 7.20 7.18 7.18 7.17 7.17 6.95 6.93 5.38
Samuel - SCS 113 - CDCl3 - Avance 500 MHz - fev05scsH3 - 1H
O
S
N
3d
7.76 7.76 7.75 7.74 7.51 7.51 7.49 7.49 7.48 7.48 7.34 7.33 7.33 7.32 7.31 7.20 7.20 7.18 7.18
7.80 7.75 7.70 7.55 7.50 7.45 7.35 7.30 7.20 7.15
Chemical shift (ppm)
1.00 1.10 5.13 1.15 1.05 2.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

Figure S20. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound 3d.

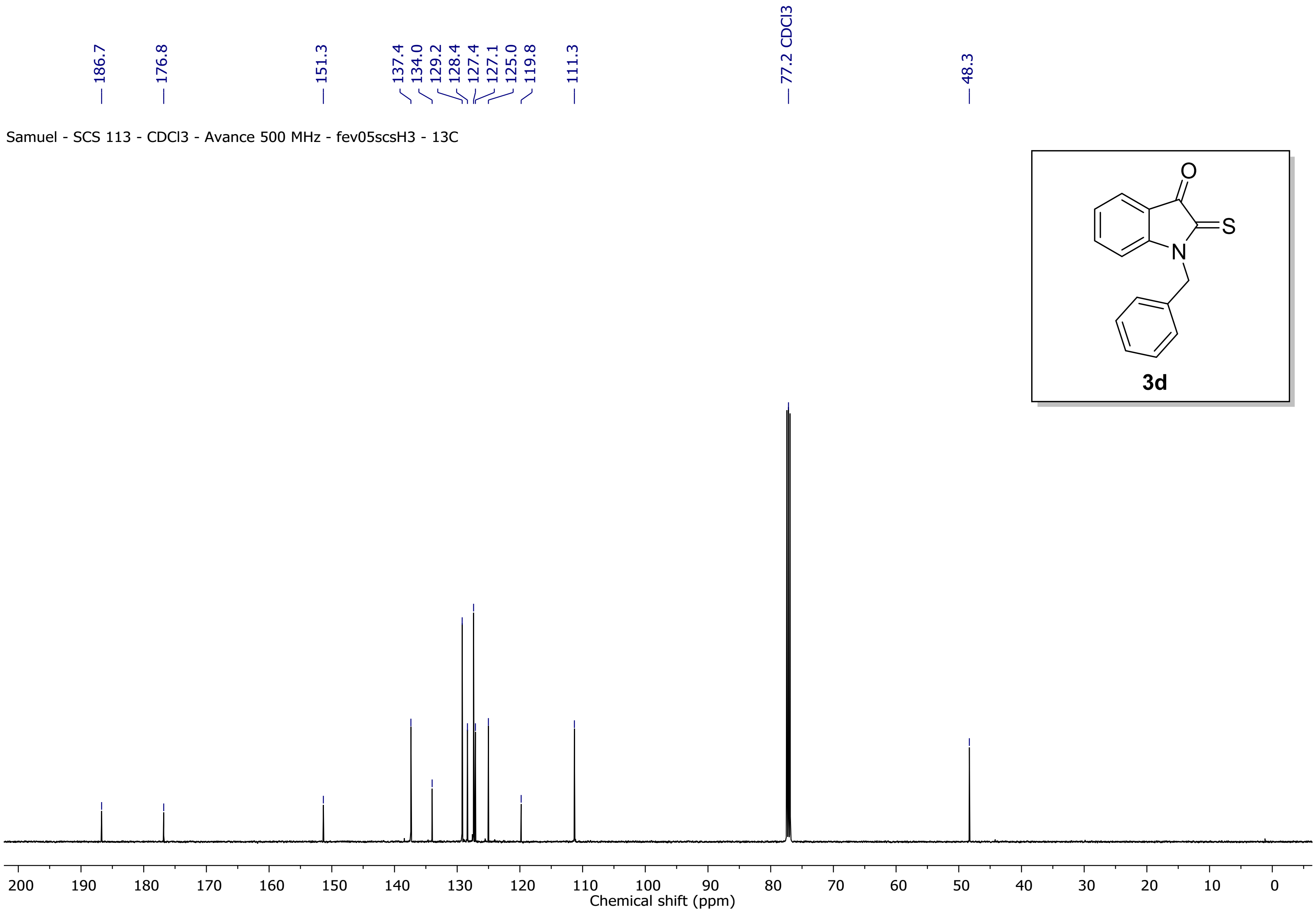

186.7
176.8
151.3
137.4
134.0
129.2
128.4
127.4
127.1
125.0
119.8
111.3
77.2 CDCl3
48.3
Samuel - SCS 113 - CDCl3 - Avance 500 MHz - fev05scsH3 - 13C
O
S
N
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S21. $^{13}C\{^1H\}$ NMR spectrum (CDCl$_3$, 126 MHz) of compound 3d.

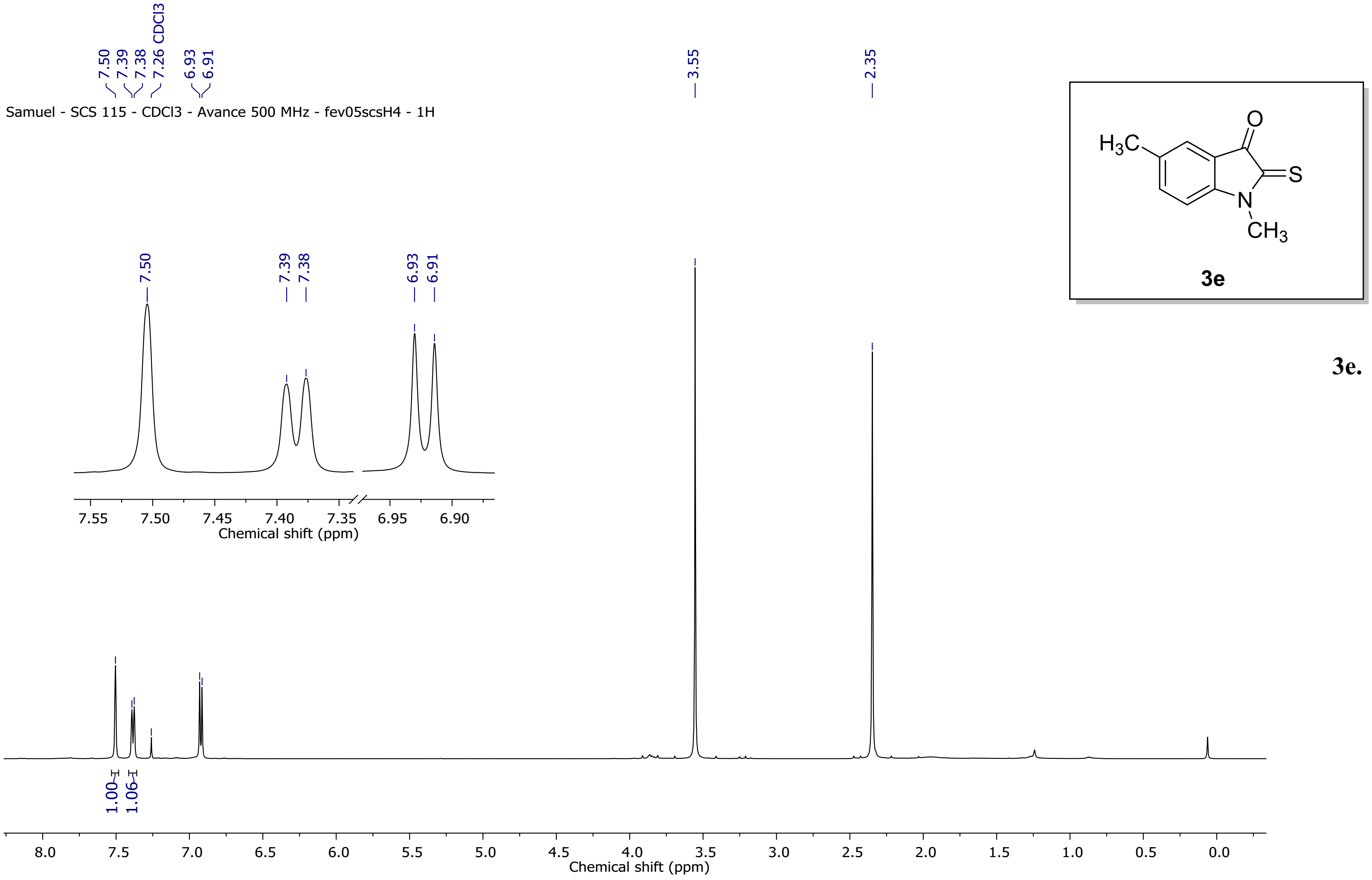


Figure S22. ^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of compound 3e.

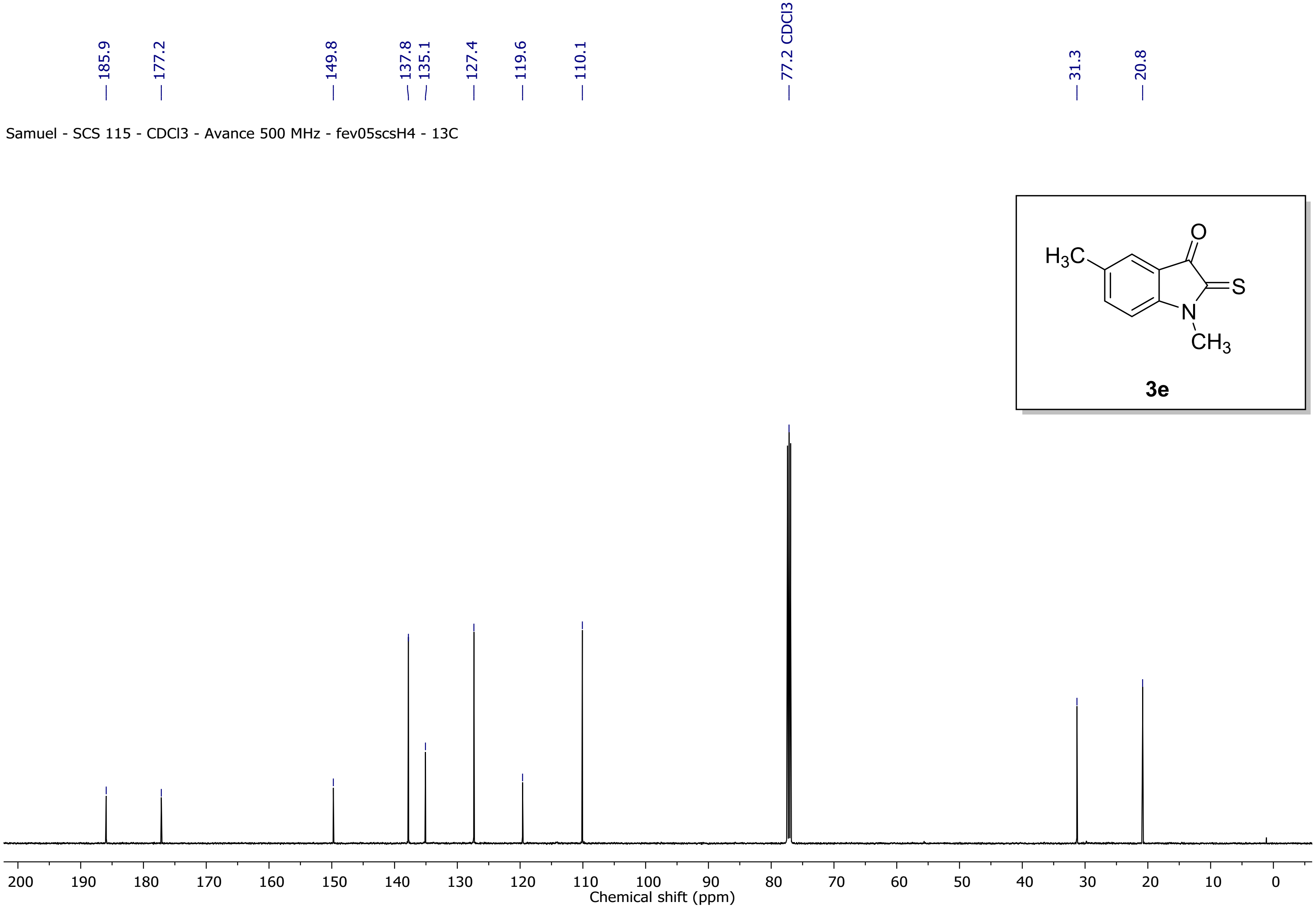

185.9
177.2
149.8
137.8
135.1
127.4
119.6
110.1
77.2 CDCl3
31.3
20.8
Samuel - SCS 115 - CDCl3 - Avance 500 MHz - fev05scsH4 - 13C
H3C
O
S
N
CH3
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S23. $^{13}C\{^1H\}$ **NMR spectrum ($CDCl_3$, 126 MHz) of compound 3e.**

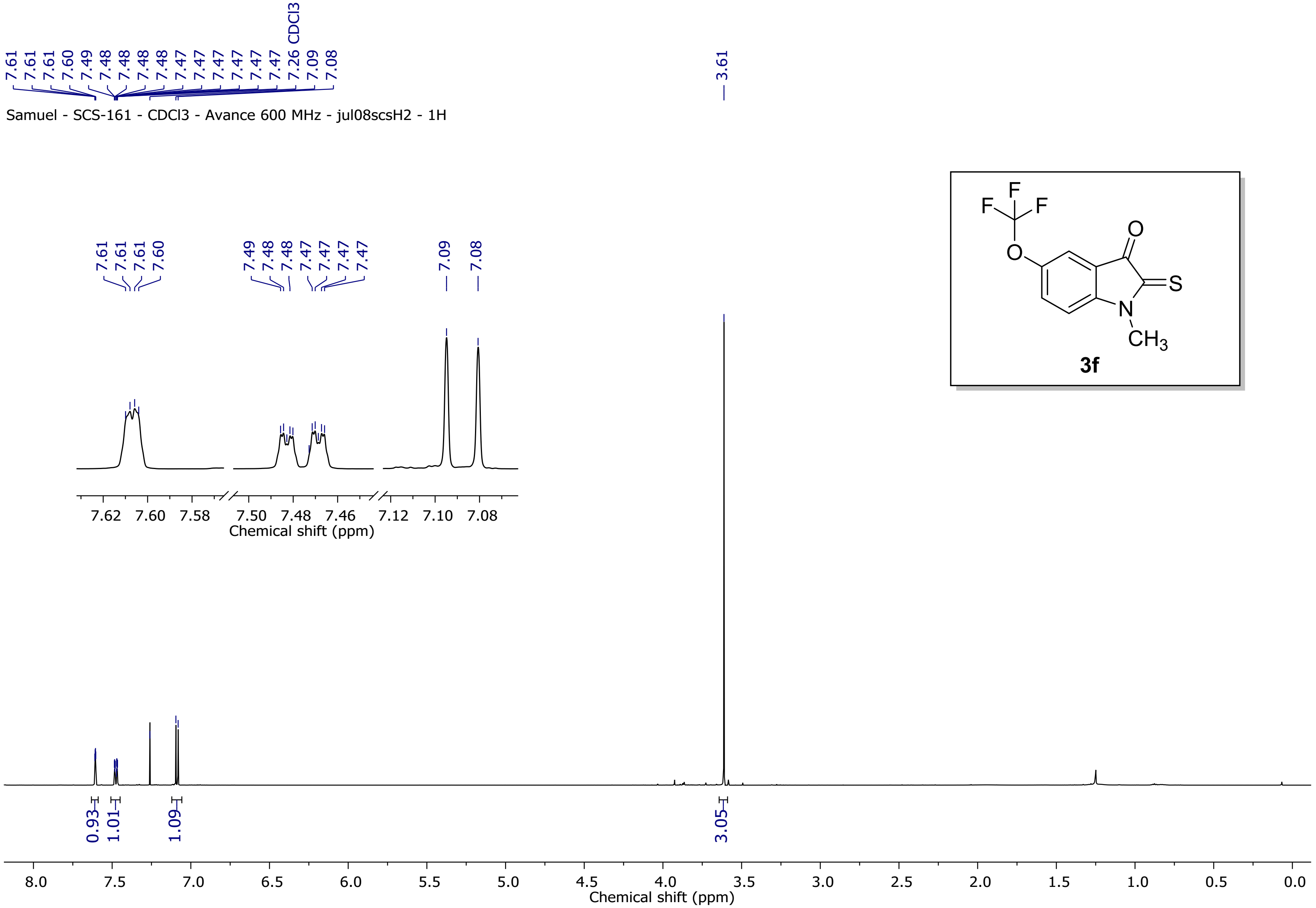

7.61
7.61
7.61
7.60
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.47
7.47
7.26 CDCl3
7.09
7.08
3.61
Samuel - SCS-161 - CDCl3 - Avance 600 MHz - jul08scsH2 - 1H
7.61
7.61
7.61
7.60
7.49
7.48
7.48
7.47
7.47
7.47
7.47
7.09
7.08
7.62
7.60
7.58
7.50
7.48
7.46
7.12
7.10
7.08
Chemical shift (ppm)
F
F
F
O
O
S
N
CH3
3f
0.93
1.01
1.09
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

Figure S24. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of compound 3f.

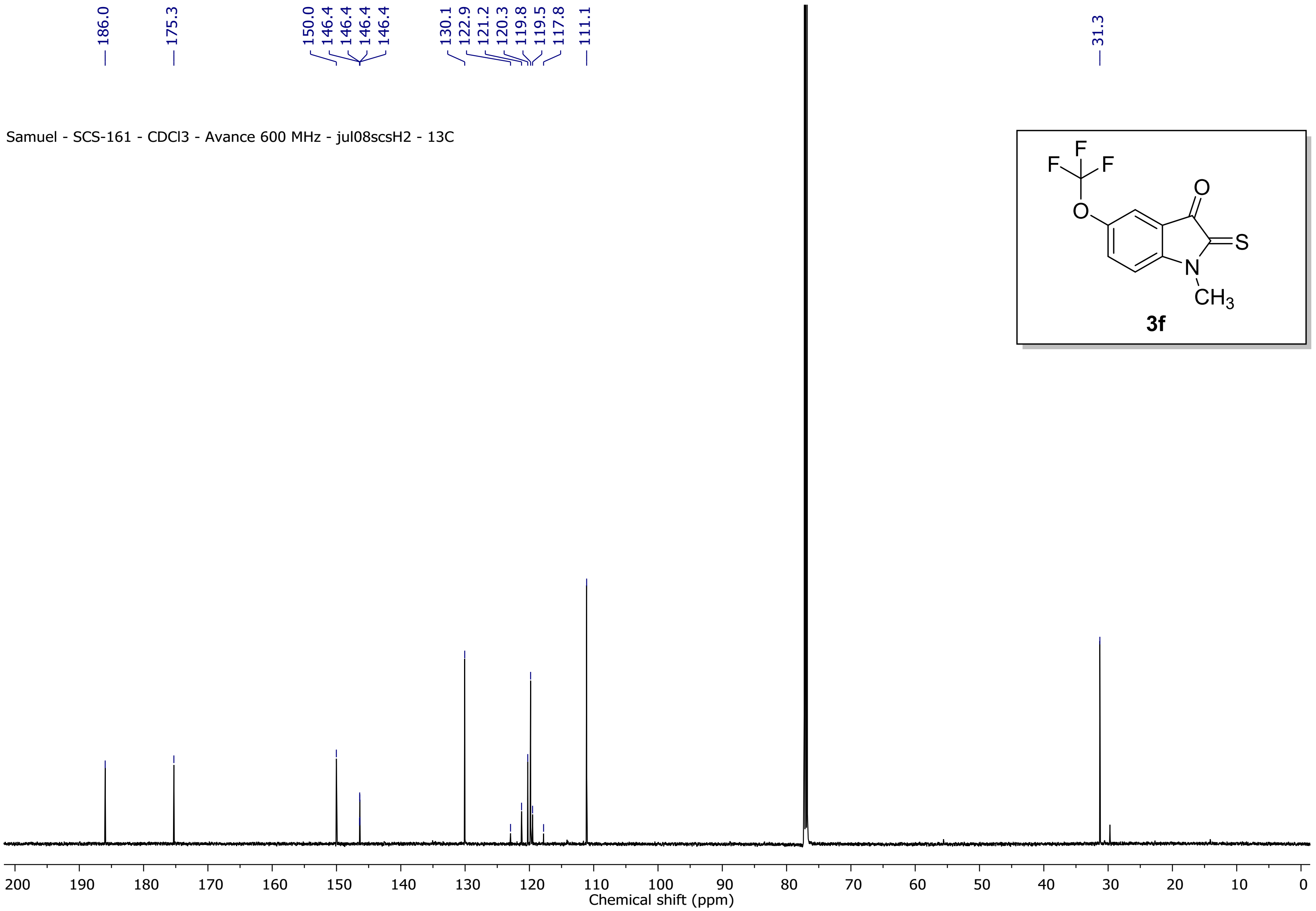

186.0
175.3
150.0
146.4
146.4
146.4
146.4
130.1
122.9
121.2
120.3
119.8
119.5
117.8
111.1
31.3
Samuel - SCS-161 - CDCl3 - Avance 600 MHz - jul08scsH2 - 13C
F
F
F
O
O
S
N
CH3
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S25. $^{13}C\{^1H\}$ **NMR spectrum ($CDCl_3$, 151 MHz) of compound 3f.**

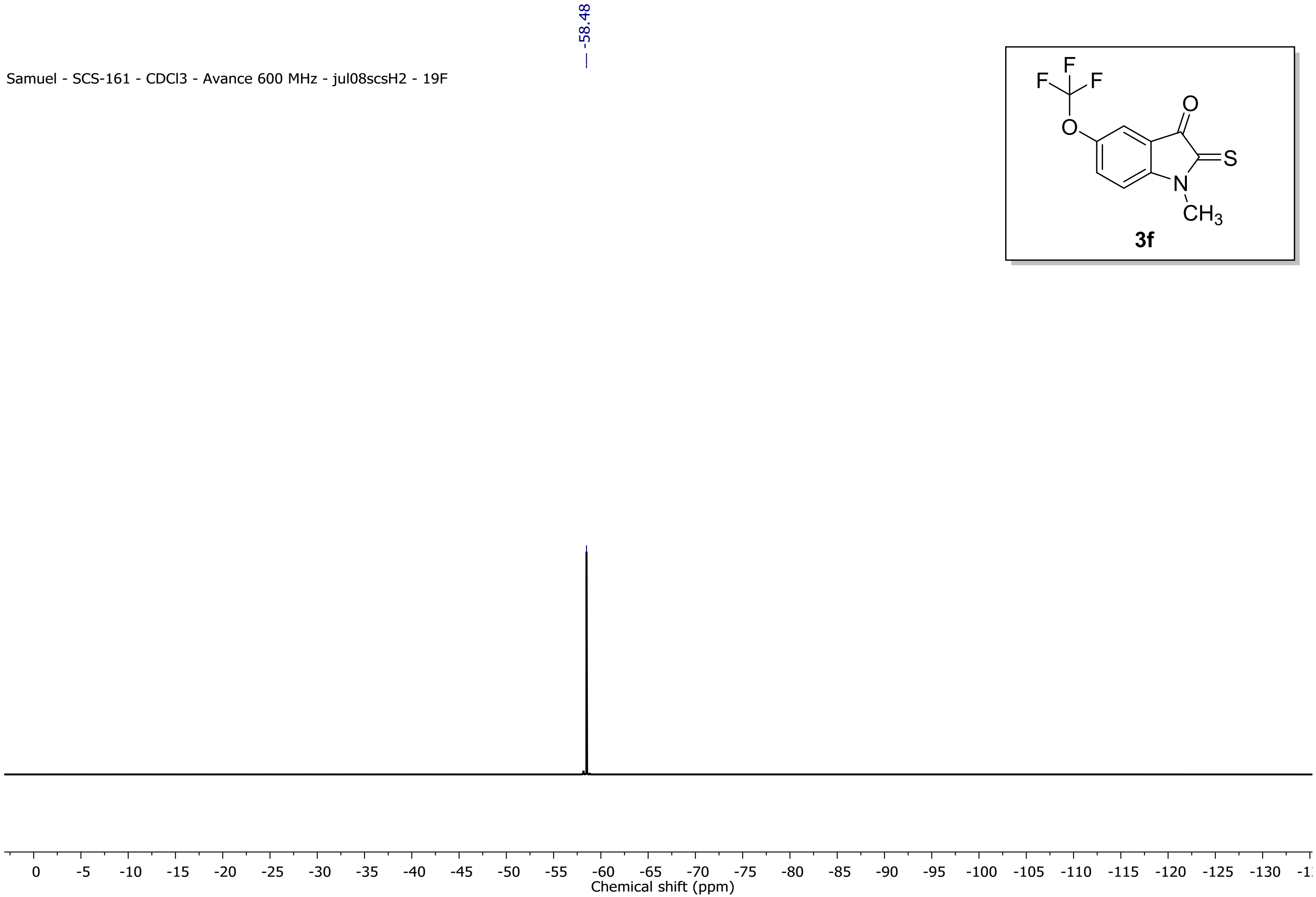

Samuel - SCS-161 - CDCl3 - Avance 600 MHz - jul08scsH2 - 19F
-58.48
F
F
F
O
O
S
N
CH3
3f
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
Chemical shift (ppm)

Figure S26. 19F NMR spectrum ($CDCl_3$, 565 MHz) of compound 3f.

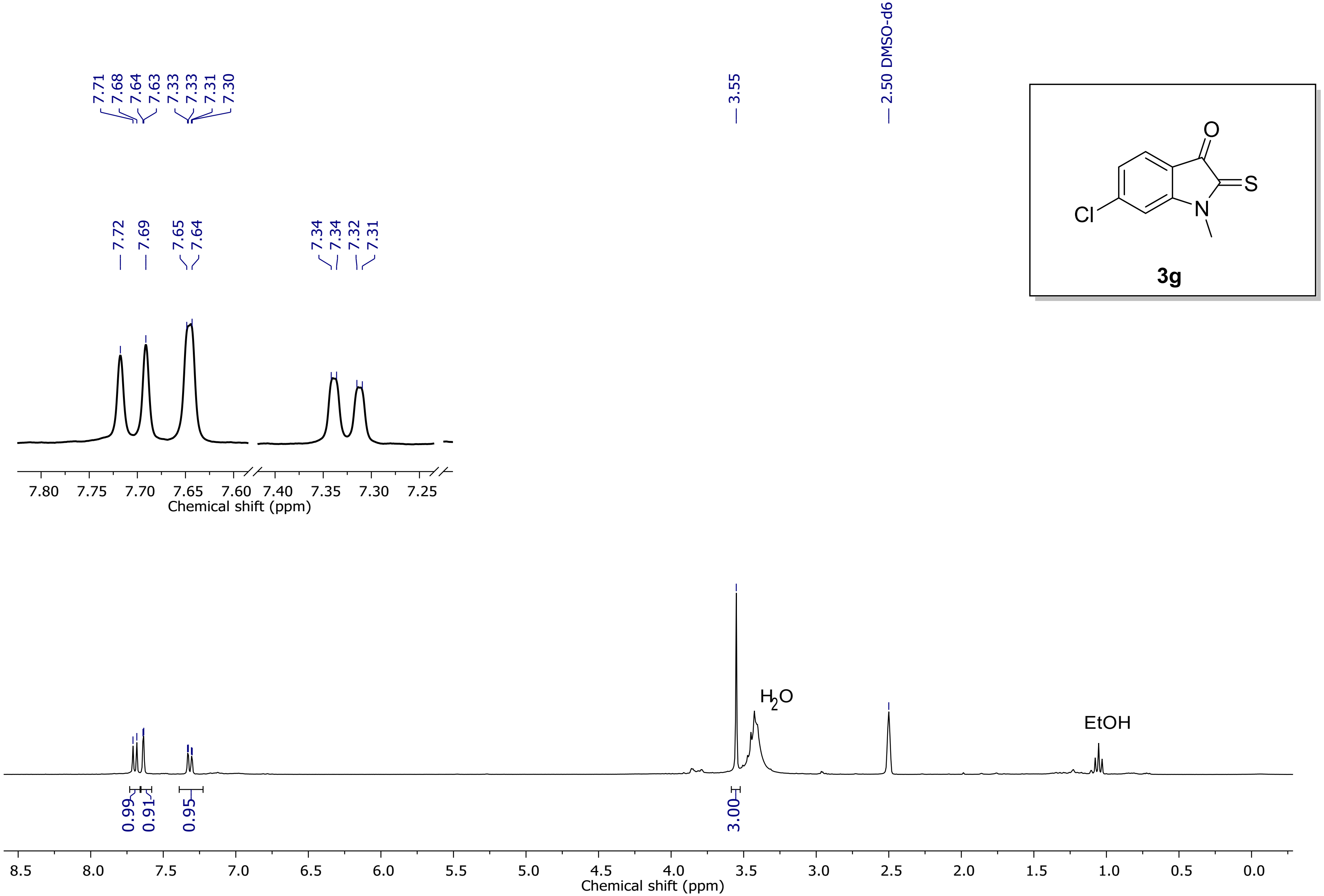

7.71
7.68
7.64
7.63
7.33
7.33
7.31
7.30
3.55
2.50 DMSO-d6
7.72
7.69
7.65
7.64
7.34
7.34
7.32
7.31
7.80 7.75 7.70 7.65 7.60 7.40 7.35 7.30 7.25
Chemical shift (ppm)
O
S
Cl
N
3g
H_2O
EtOH
0.99
0.91
0.95
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

Figure S27. ^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of compound 3g.

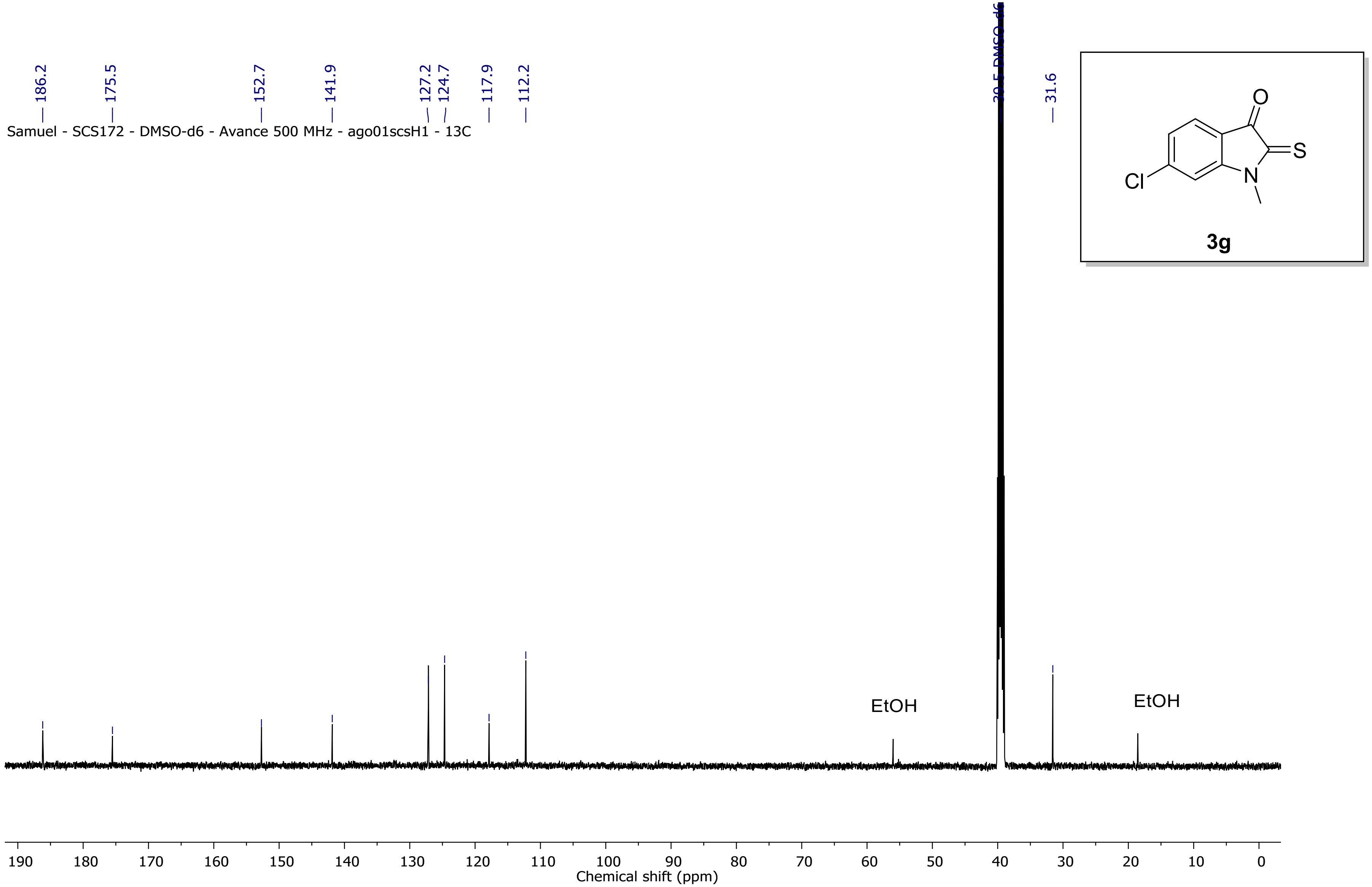

186.2
175.5
152.7
141.9
127.2
124.7
117.9
112.2
39.5 DMSO-d6
31.6
Samuel - SCS172 - DMSO-d6 - Avance 500 MHz - ago01scsH1 - 13C
EtOH
EtOH
O
S
Cl
N
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S28. ^{1}H NMR spectrum (CDCl$_3$, 126 MHz) of compound 3g.

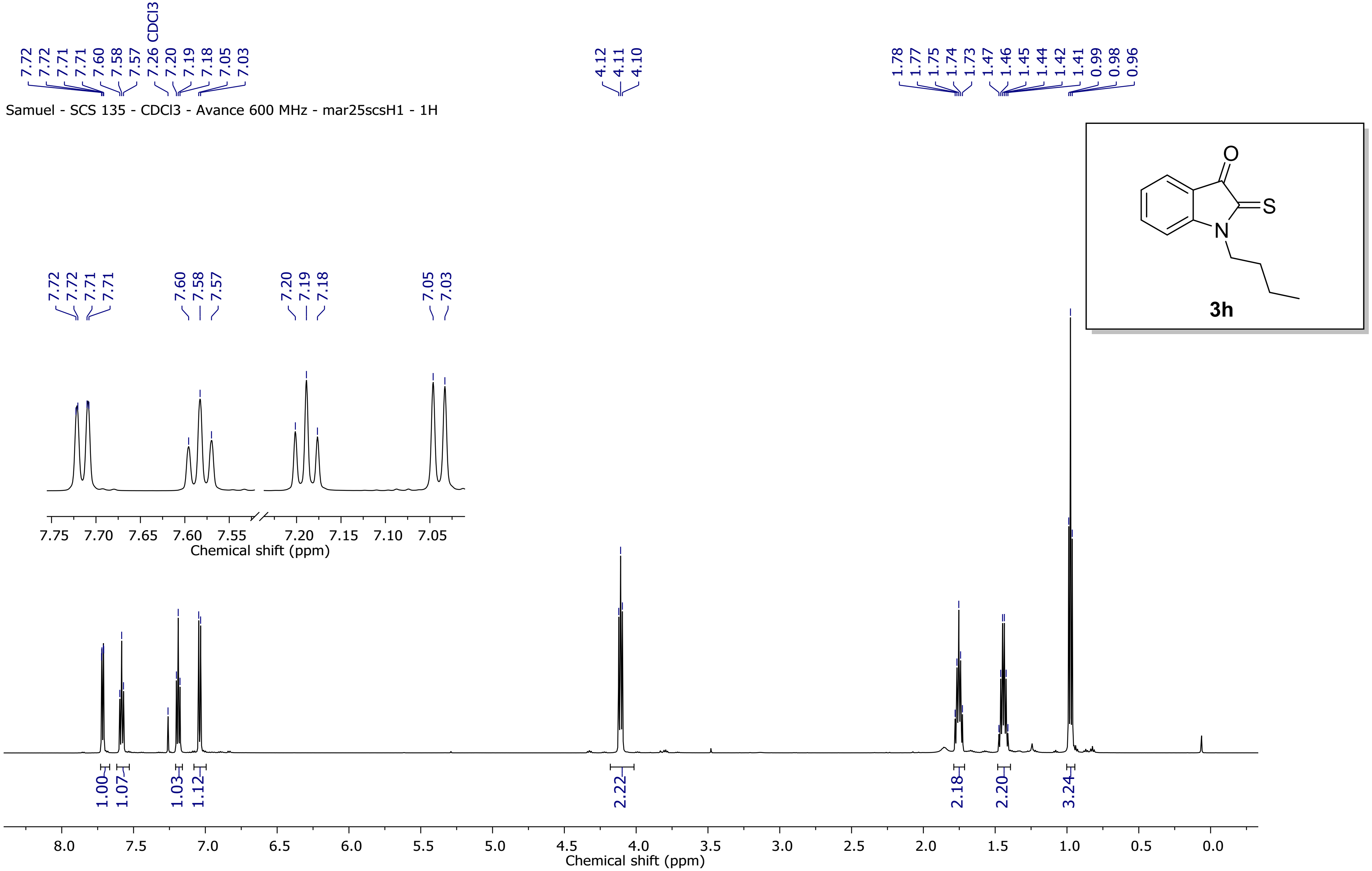

7.72
7.72
7.71
7.71
7.60
7.58
7.57
7.26 CDCl3
7.20
7.19
7.18
7.05
7.03
4.12
4.11
4.10
1.78
1.77
1.75
1.74
1.73
1.47
1.46
1.45
1.44
1.42
1.41
0.99
0.98
0.96
Samuel - SCS 135 - CDCl3 - Avance 600 MHz - mar25scsH1 - 1H
O
S
N
3h
7.75 7.70 7.65 7.60 7.55 7.20 7.15 7.10 7.05
Chemical shift (ppm)
1.00
1.07
1.03
1.12
2.22
2.18
2.20
3.24
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound 3h.

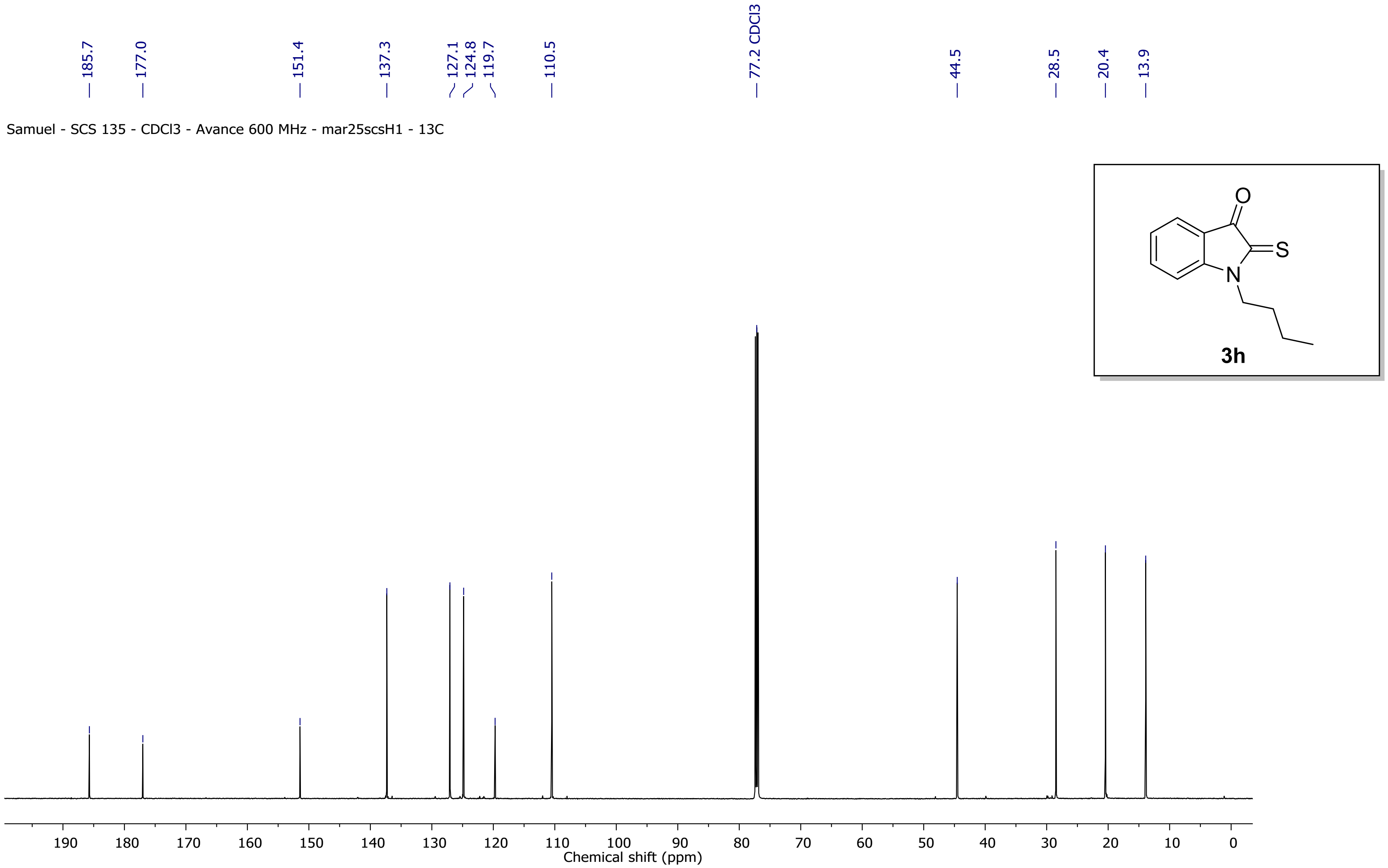


Figure S30. $^{13}C\{^{1}H\}$ **NMR spectrum ($CDCl_3$, 151 MHz) of compound 3h**

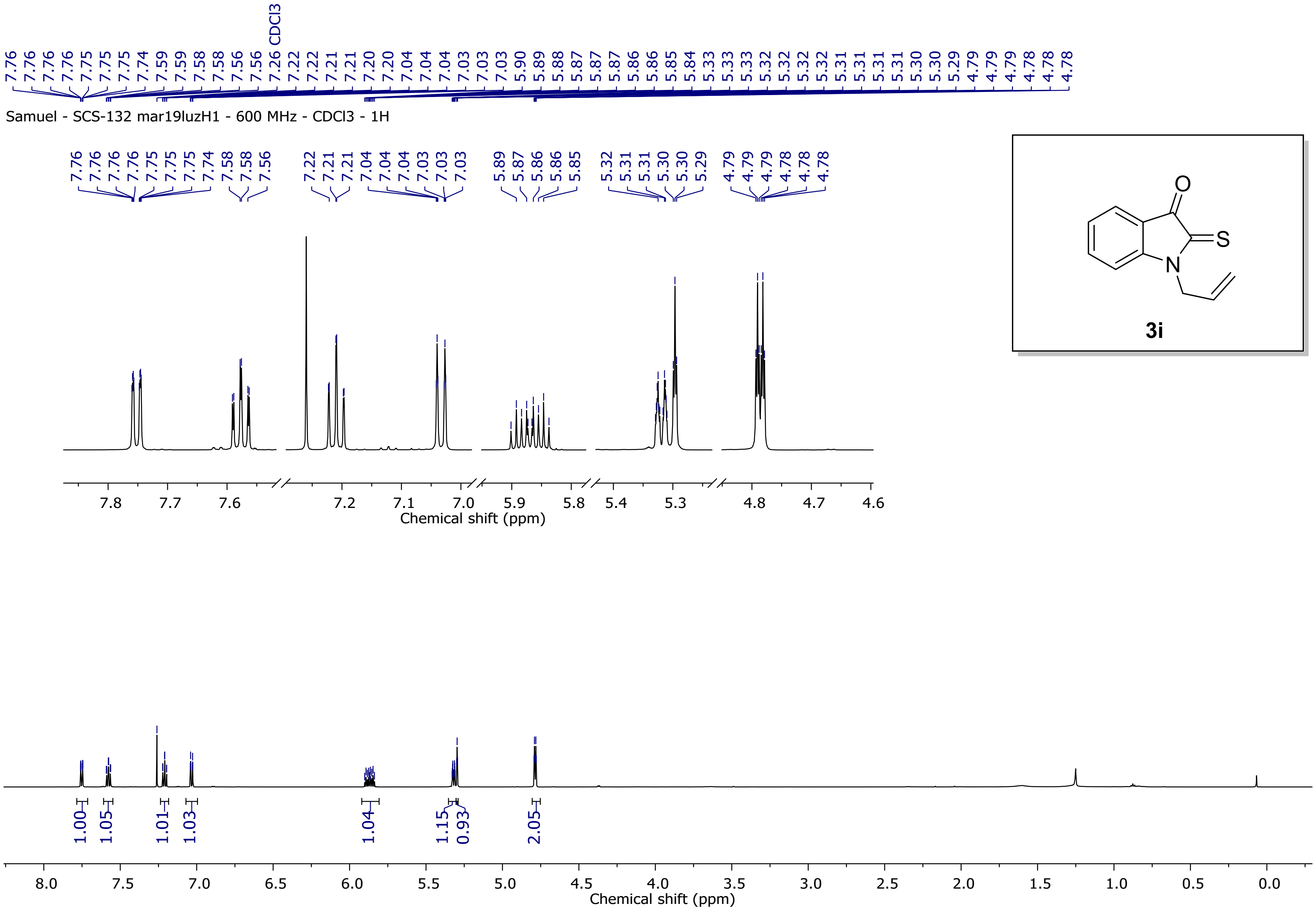

7.76 7.76 7.76 7.76 7.75 7.75 7.75 7.74 7.59 7.59 7.58 7.58 7.56 7.56 7.26 7.22 7.22 7.21 7.21 7.20 7.20 7.04 7.04 7.04 7.03 7.03 7.03 5.90 5.89 5.88 5.87 5.87 5.87 5.86 5.86 5.85 5.84 5.33 5.33 5.33 5.32 5.32 5.32 5.32 5.31 5.31 5.31 5.31 5.30 5.29 4.79 4.79 4.79 4.78 4.78 4.78
CDCl3
Samuel - SCS-132 mar19luzH1 - 600 MHz - CDCl3 - 1H
7.76 7.76 7.76 7.76 7.75 7.75 7.75 7.74 7.58 7.58 7.56
7.22 7.21 7.21 7.04 7.04 7.04 7.03 7.03 7.03
5.89 5.87 5.86 5.86 5.85
5.32 5.31 5.31 5.30 5.30 5.29
4.79 4.79 4.79 4.78 4.78 4.78
7.8 7.7 7.6 7.2 7.1 7.0 5.9 5.8 5.4 5.3 4.8 4.7 4.6
Chemical shift (ppm)
O
S
N
3i
1.00 1.05 1.01 1.03 1.04 1.15 0.93 2.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound 3i.

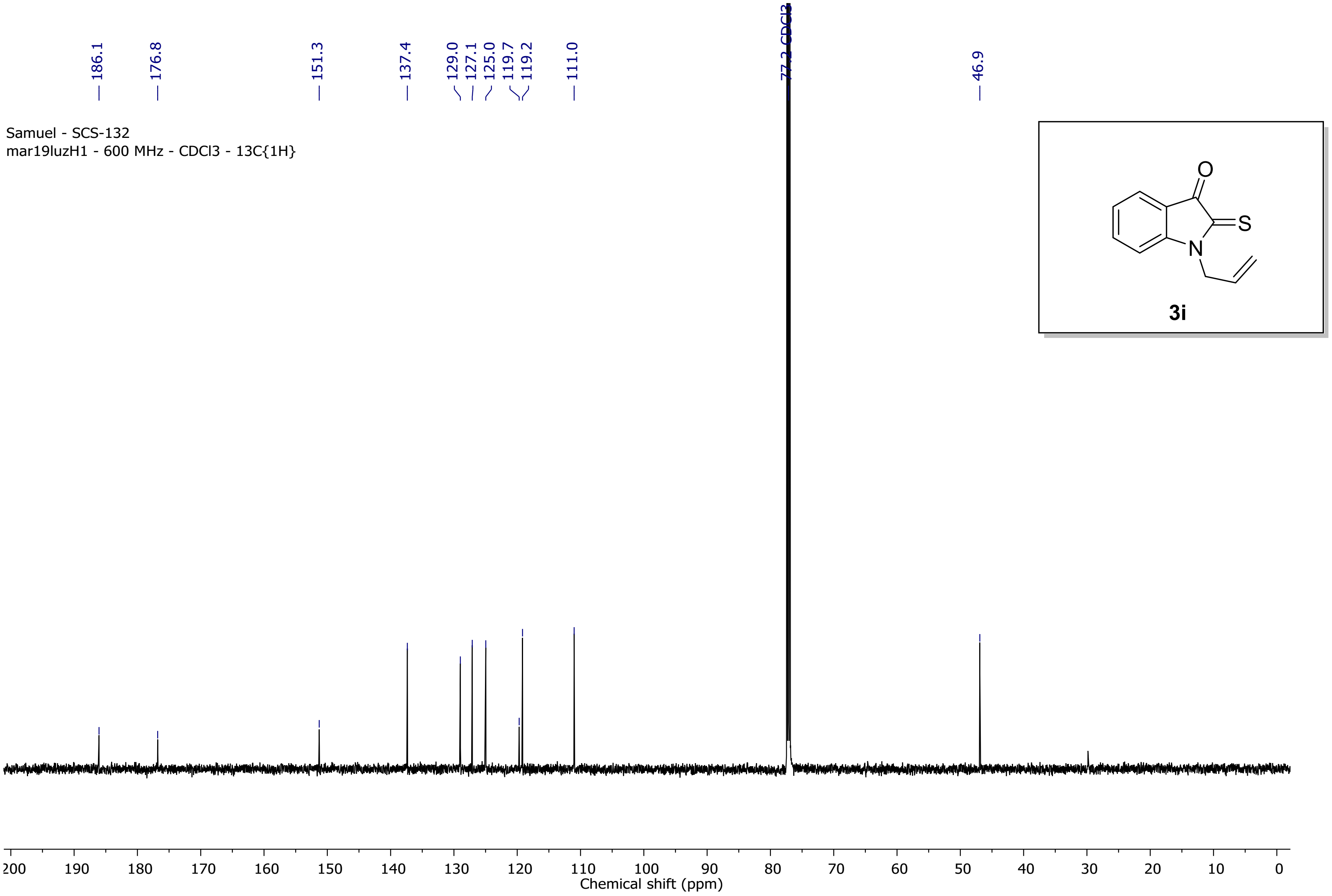
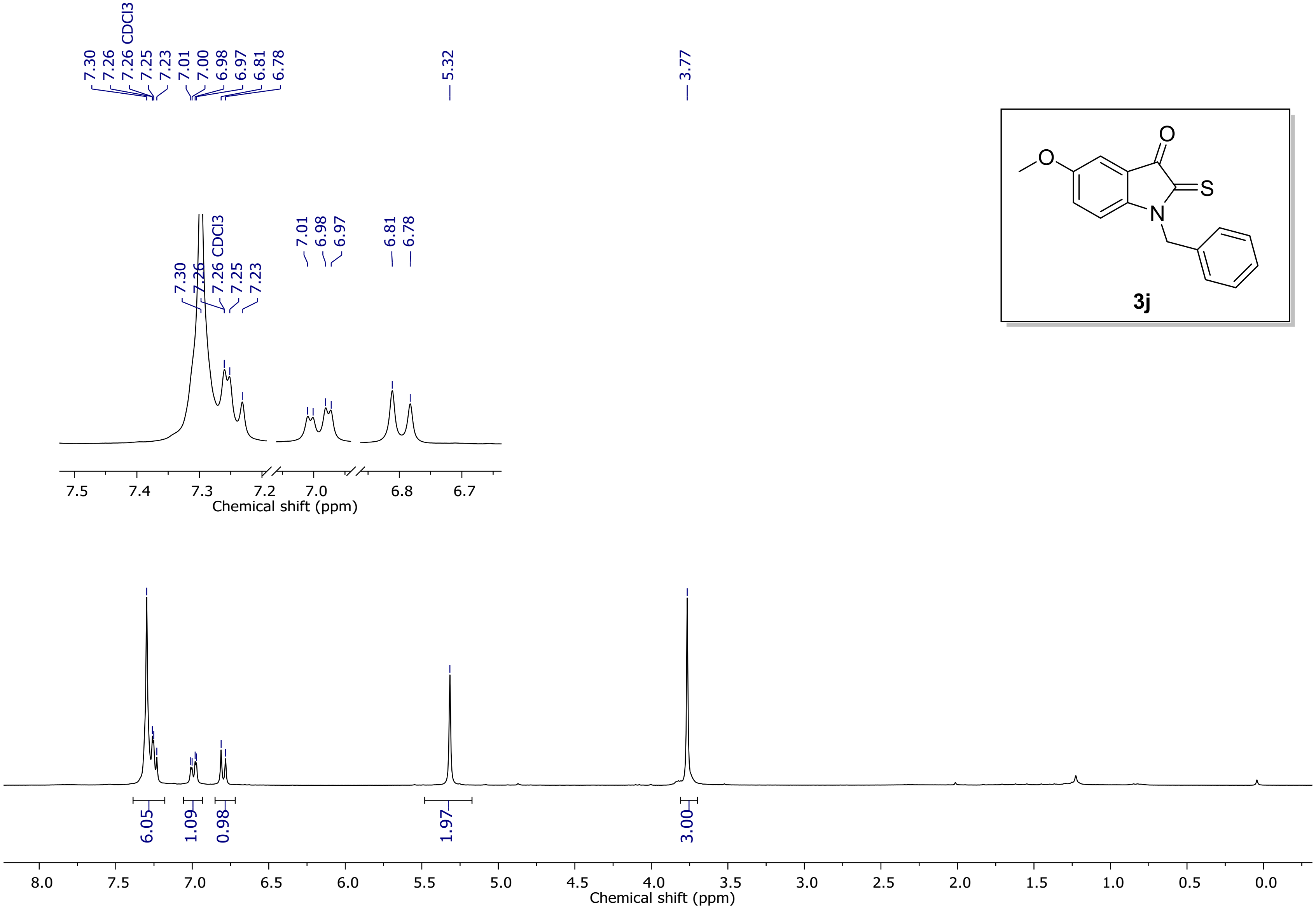

186.1
176.8
151.3
137.4
129.0
127.1
125.0
119.7
119.2
111.0
77.2 CDCl3
46.9
Samuel - SCS-132
mar19luzH1 - 600 MHz - CDCl3 - 13C{1H}
O
S
N
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S32. $^{13}C\{^{1}H\}$ **NMR spectrum ($CDCl_3$, 151 MHz) of compound 3i.**



3j

7.30
7.26
7.26 CDCl3
7.25
7.23
7.01
7.00
6.98
6.97
6.81
6.78
5.32
3.77
O
O
S
N
7.5
7.4
7.3
7.2
7.0
6.8
6.7
Chemical shift (ppm)
6.05
1.09
0.98
1.97
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound 3j.

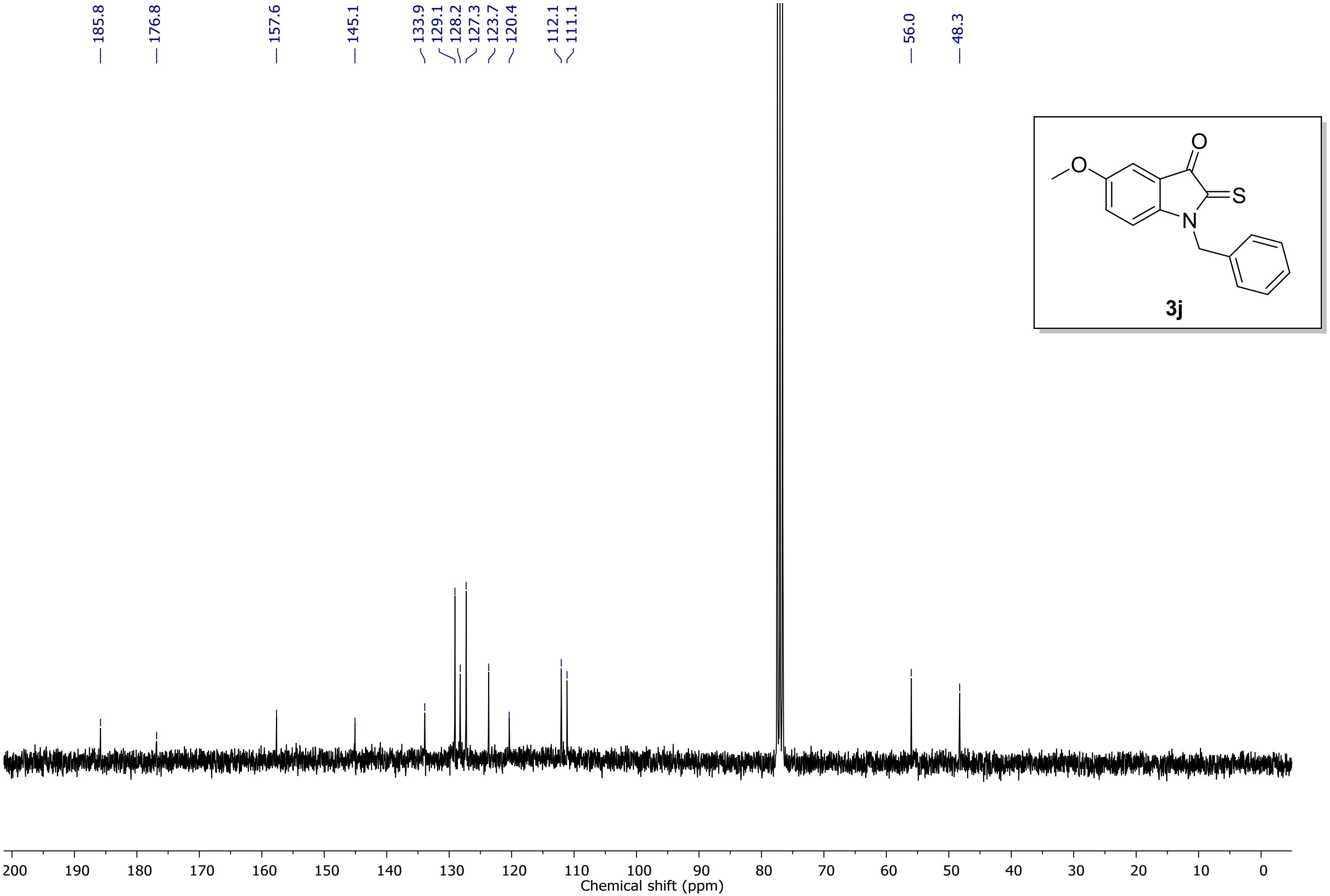

185.8
176.8
157.6
145.1
133.9
129.1
128.2
127.3
123.7
120.4
112.1
111.1
56.0
48.3
O
O
S
N
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S34. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of compound 3j.

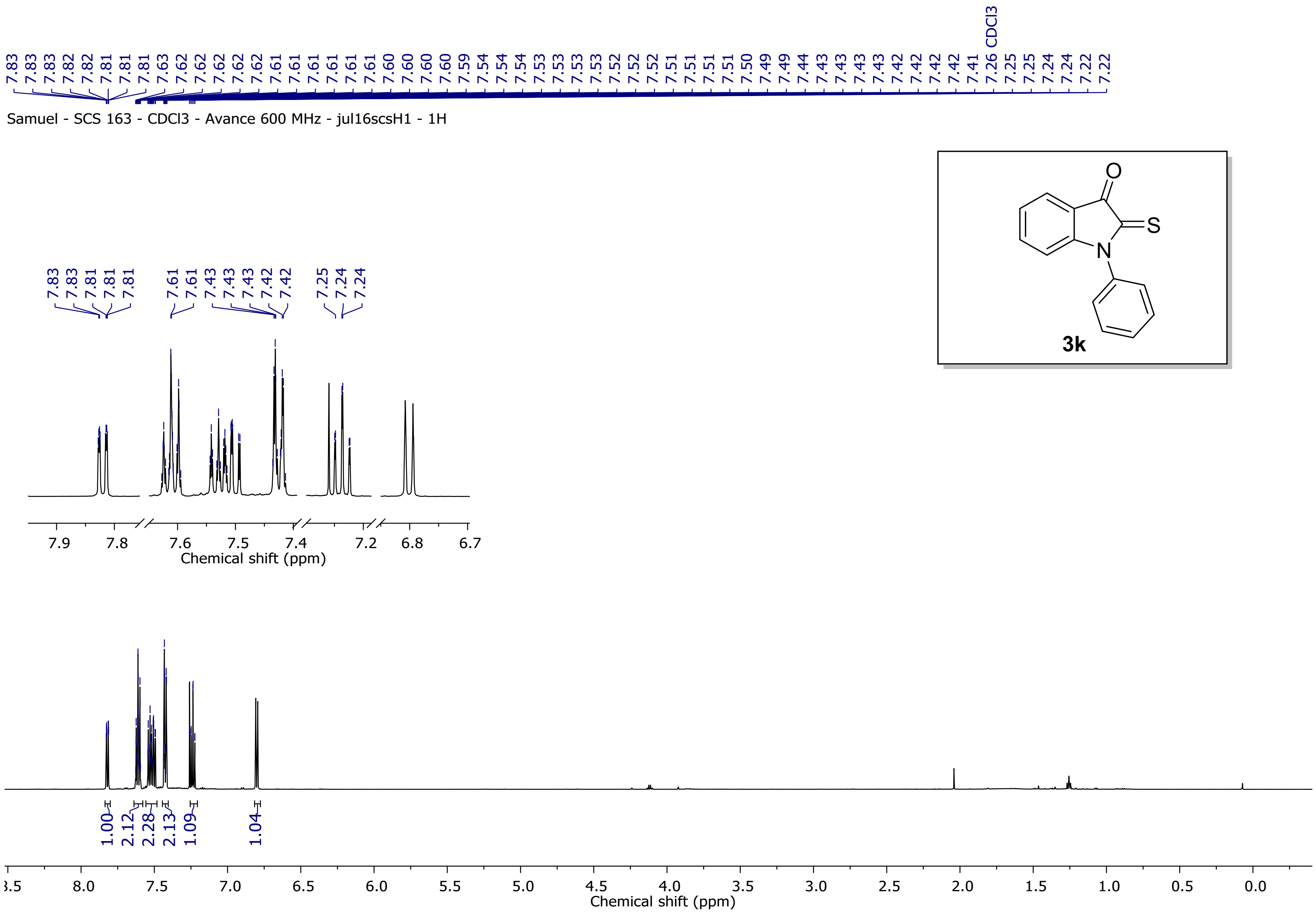

7.83 7.83 7.83 7.82 7.82 7.81 7.81 7.81 7.63 7.62 7.62 7.62 7.62 7.62 7.61 7.61 7.61 7.61 7.61 7.61 7.60 7.60 7.60 7.60 7.59 7.54 7.54 7.54 7.53 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.51 7.51 7.50 7.49 7.49 7.44 7.43 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.26 7.25 7.25 7.24 7.24 7.22 7.22
CDCl3
Samuel - SCS 163 - CDCl3 - Avance 600 MHz - jul16scsH1 - 1H
7.83 7.83 7.81 7.81 7.81
7.61 7.61
7.43 7.43 7.43 7.42 7.42
7.25 7.24 7.24
7.9 7.8 7.6 7.5 7.4 7.2 6.8 6.7
Chemical shift (ppm)
1.00 2.12 2.28 2.13 1.09 1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)
O
S
N
3k

Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound 3k.

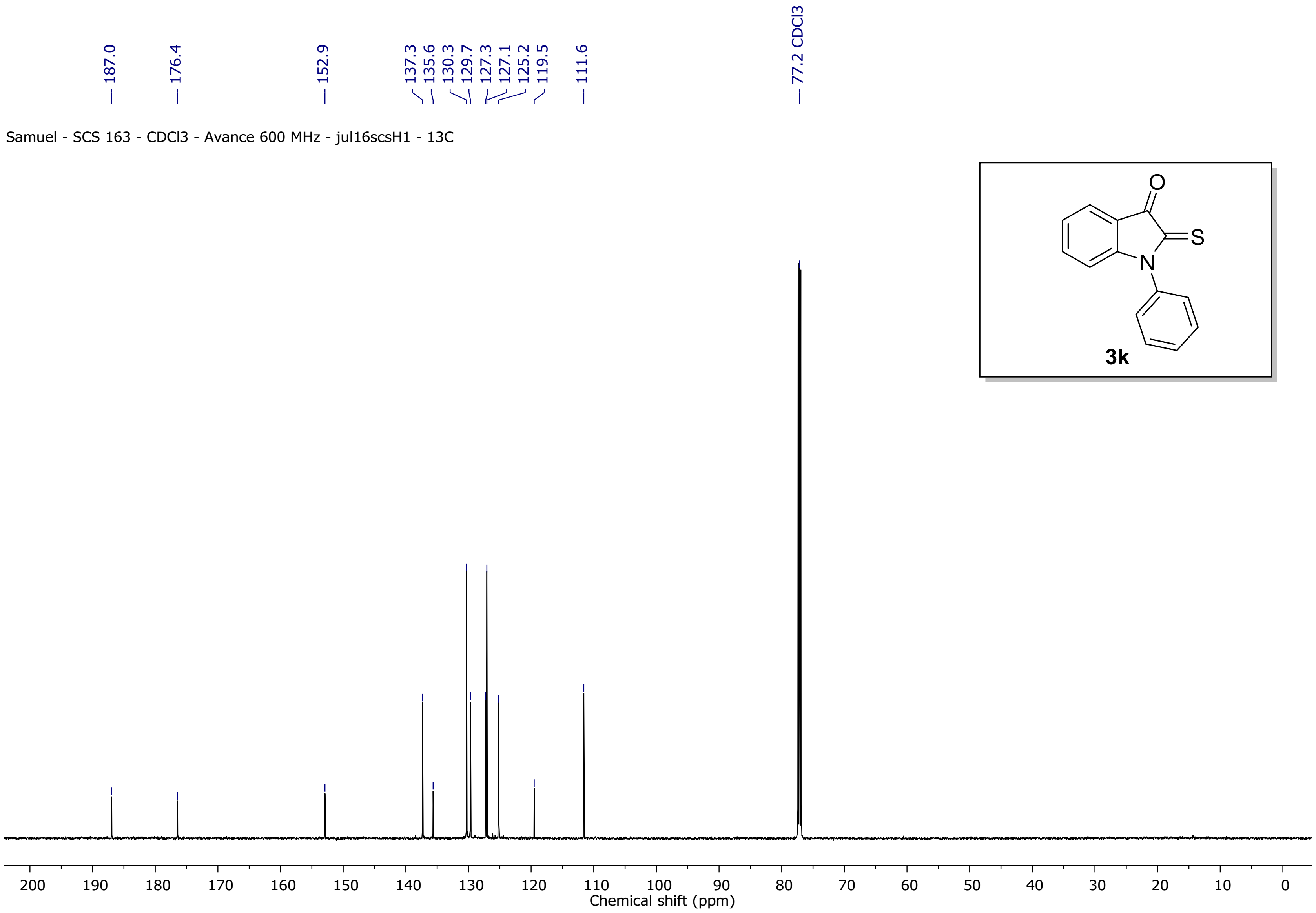
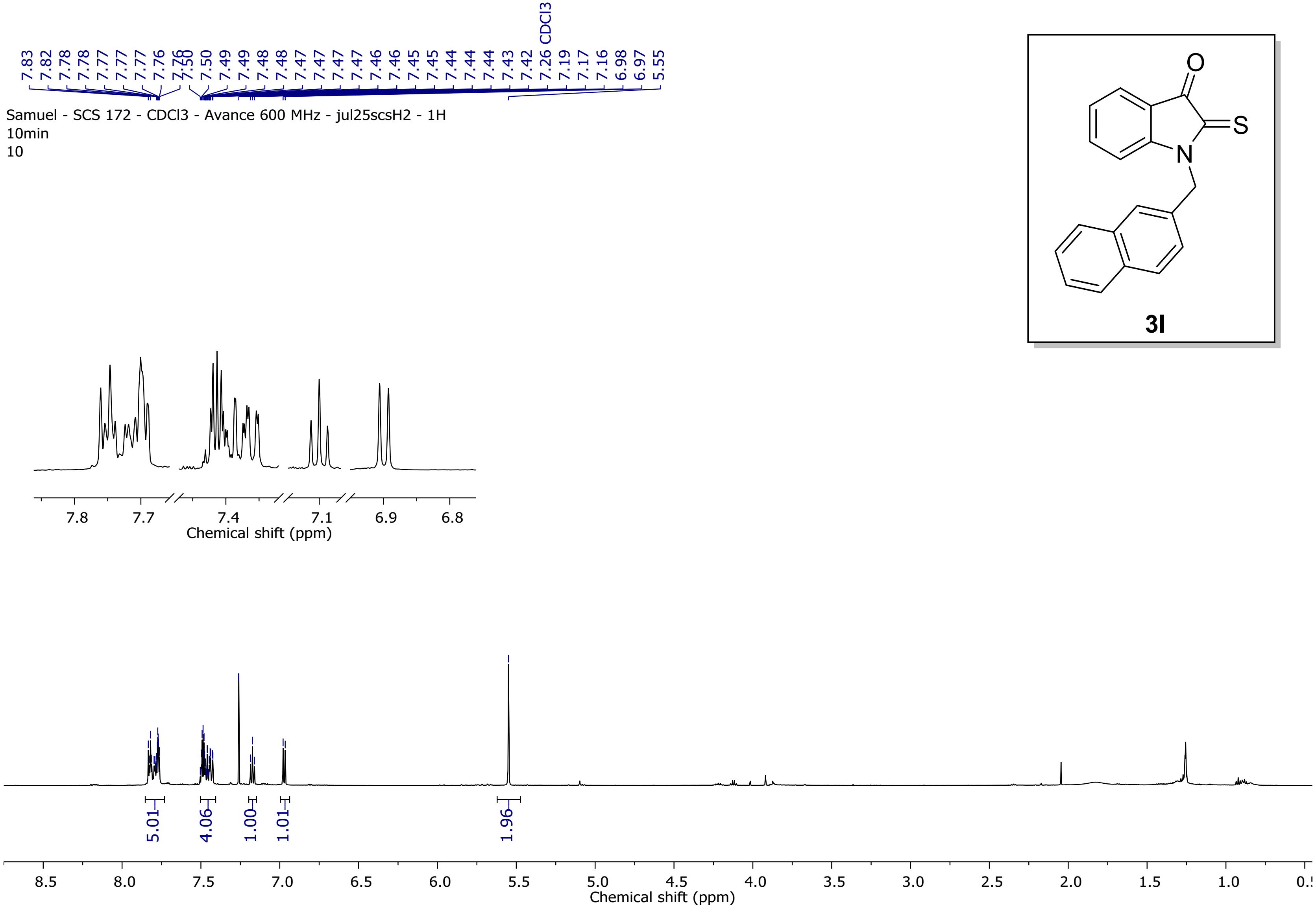

187.0
176.4
152.9
137.3
135.6
130.3
129.7
127.3
127.1
125.2
119.5
111.6
77.2 CDCl3
Samuel - SCS 163 - CDCl3 - Avance 600 MHz - jul16scsH1 - 13C
O
S
N
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of compound 3k.


7.83
7.82
7.78
7.78
7.77
7.77
7.77
7.76
7.76
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.42
7.26 CDCl3
7.19
7.17
7.16
6.98
6.97
5.55
Samuel - SCS 172 - CDCl3 - Avance 600 MHz - jul25scsH2 - 1H
10min
10
7.8
7.7
7.4
7.1
6.9
6.8
Chemical shift (ppm)
5.01
4.06
1.00
1.01
1.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical shift (ppm)

O
S
N

3l

Figure S37. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **3l**.

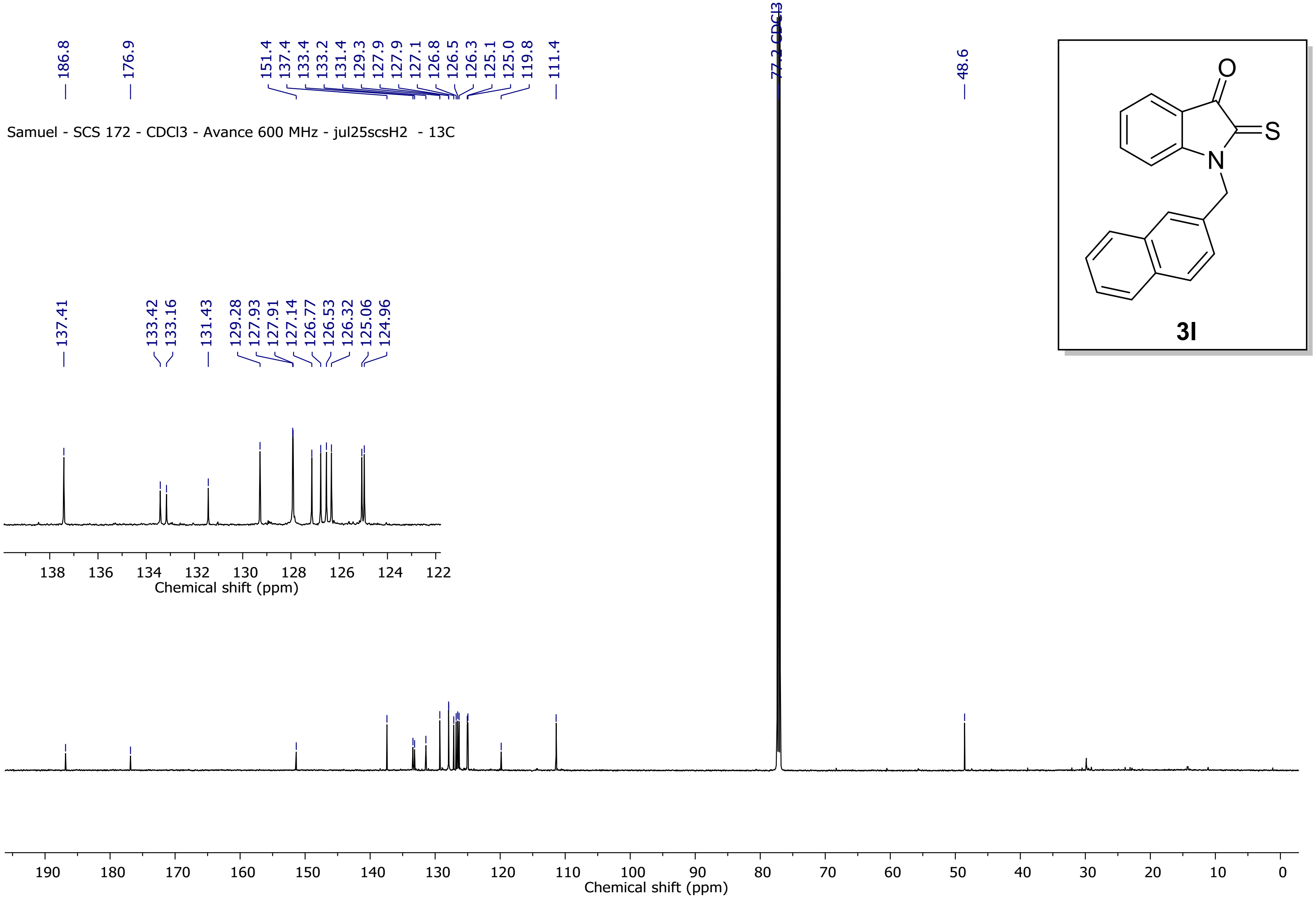
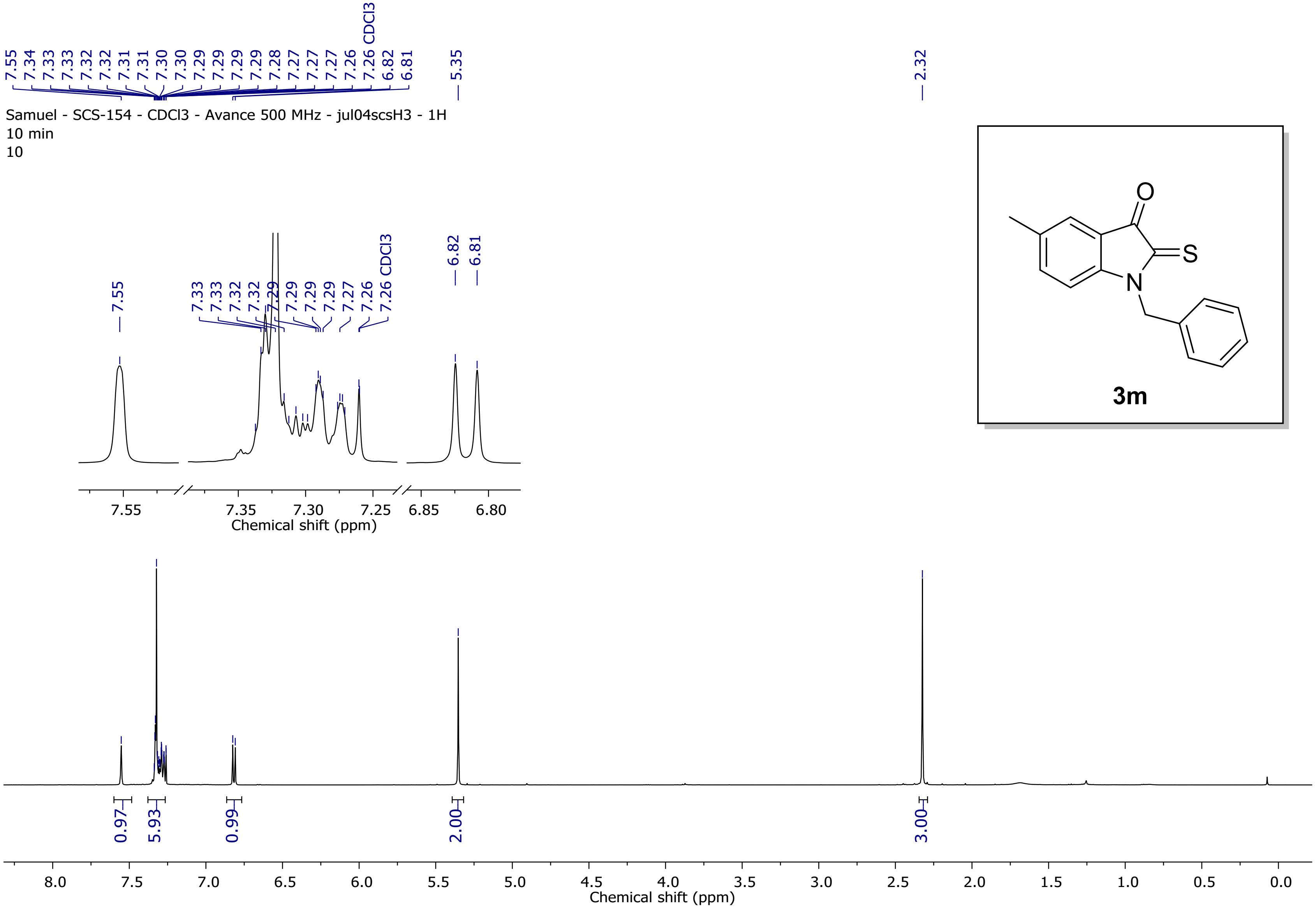


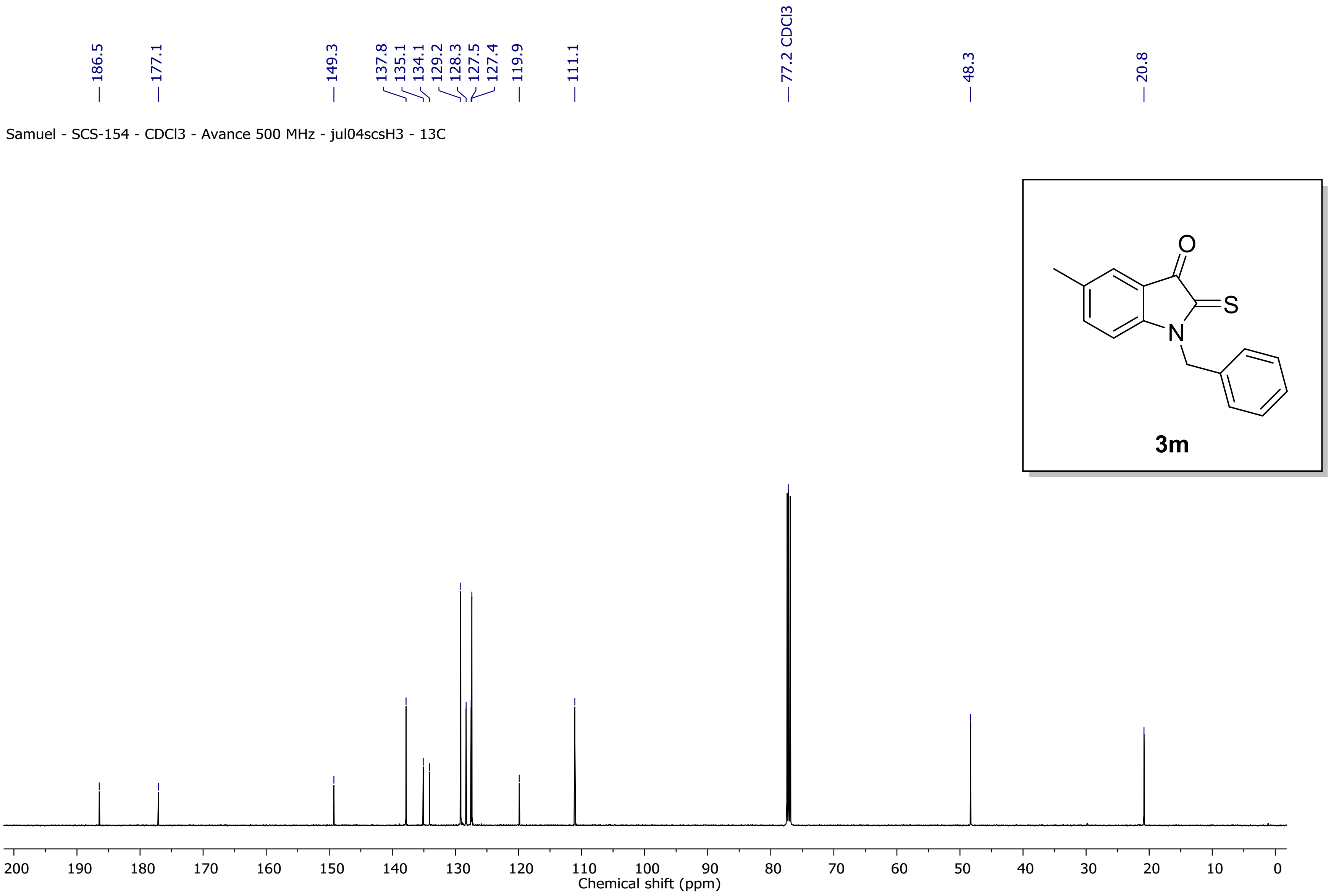
Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of compound 3l.


7.55
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.26 CDCl3
6.82
6.81
5.35
2.32
Samuel - SCS-154 - CDCl3 - Avance 500 MHz - jul04scsH3 - 1H
10 min
10
7.55
7.33
7.33
7.32
7.32
7.29
7.29
7.29
7.29
7.27
7.26
7.26 CDCl3
6.82
6.81
7.55
7.35
7.30
7.25
6.85
6.80
Chemical shift (ppm)
0.97
5.93
0.99
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

O
S
N

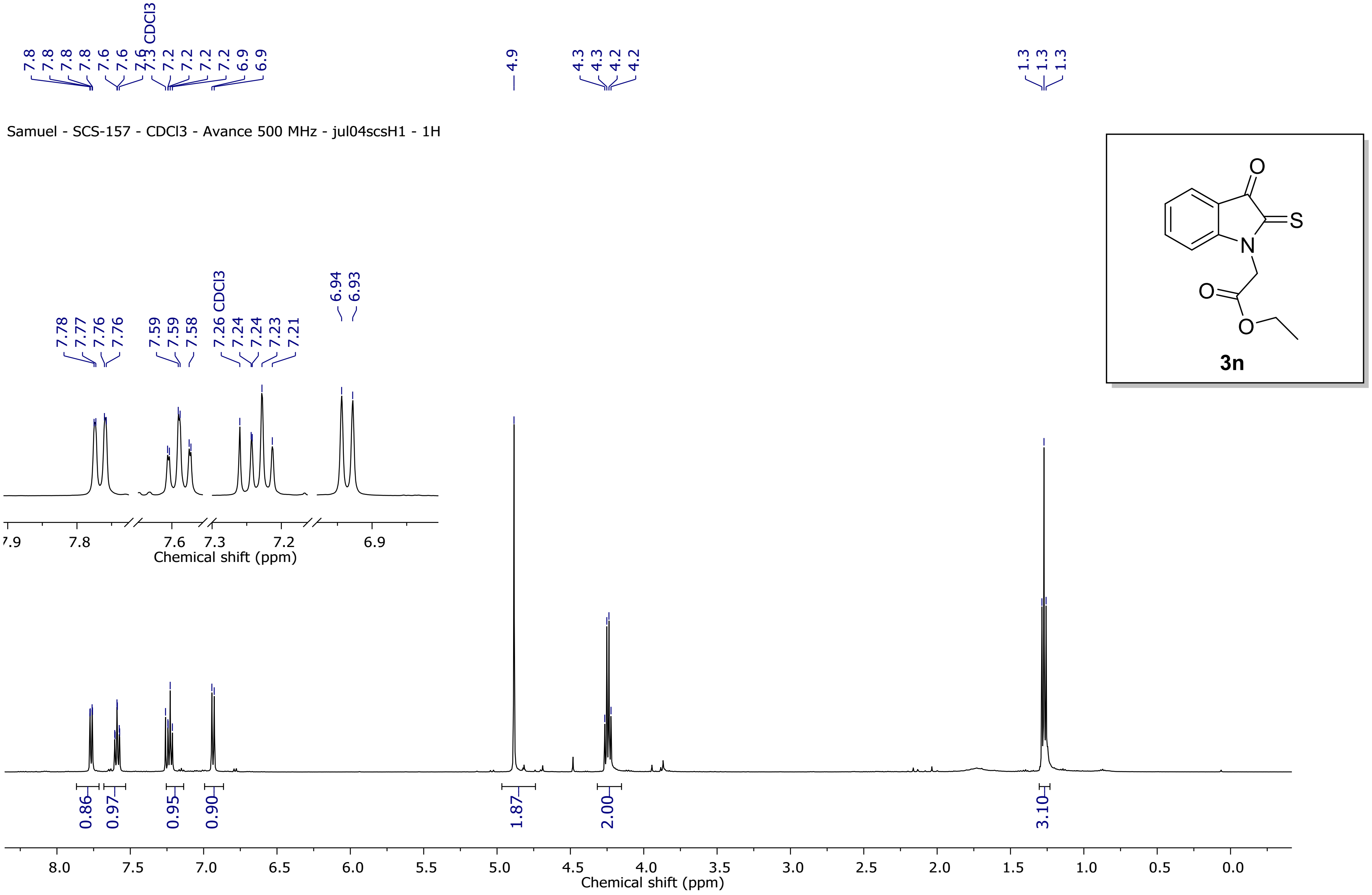
3m

Figure S39. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound 3m.


186.5
177.1
149.3
137.8
135.1
134.1
129.2
128.3
127.5
127.4
119.9
111.1
77.2 CDCl3
48.3
20.8
Samuel - SCS-154 - CDCl3 - Avance 500 MHz - jul04scsH3 - 13C
O
S
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

3m

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz) of compound 3m.


Samuel - SCS-157 - CDCl3 - Avance 500 MHz - jul04scsH1 - 1H

3n

Figure S41. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound 3n.

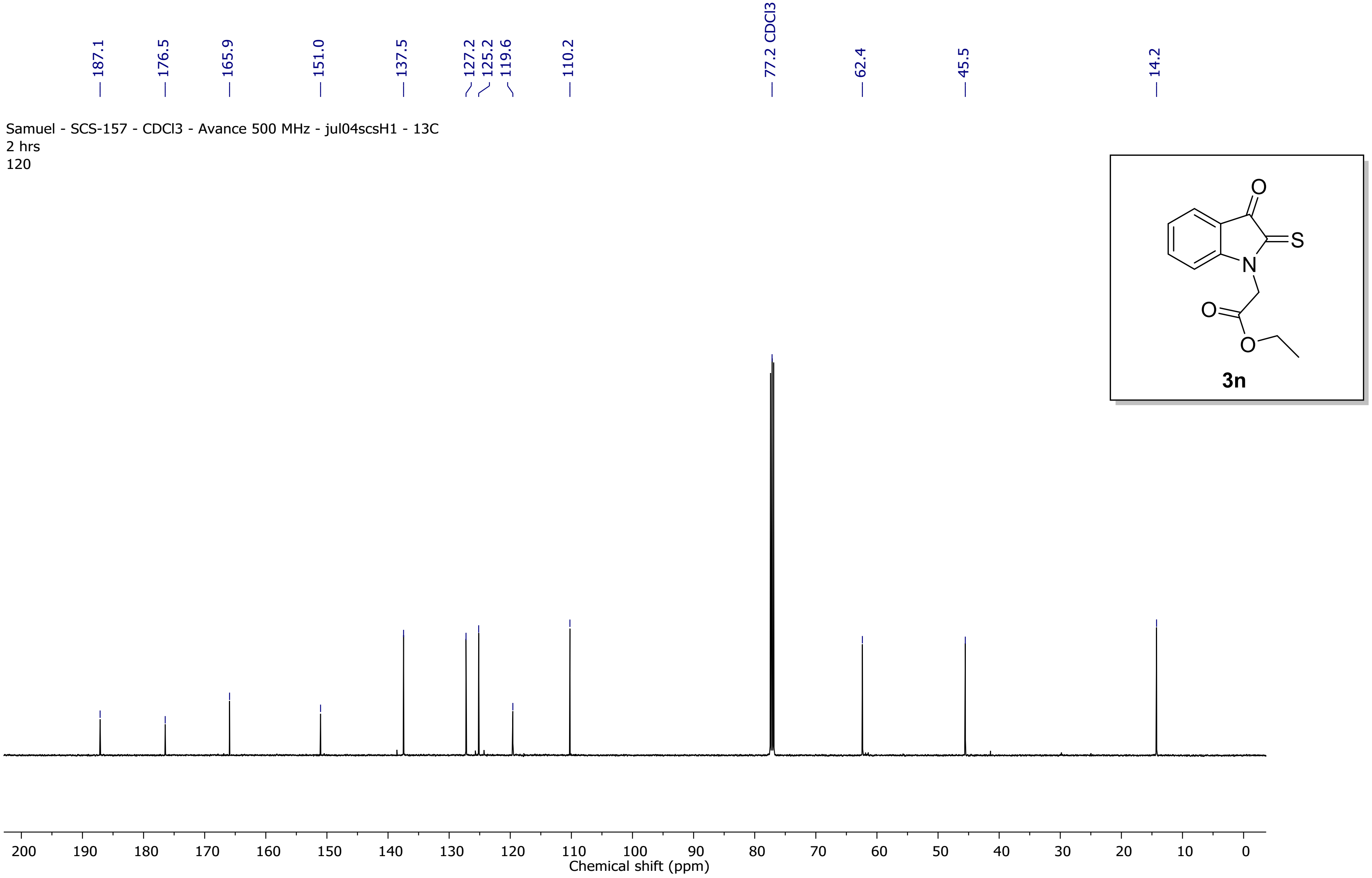

187.1
176.5
165.9
151.0
137.5
127.2
125.2
119.6
110.2
77.2 CDCl3
62.4
45.5
14.2
Samuel - SCS-157 - CDCl3 - Avance 500 MHz - jul04scsH1 - 13C
2 hrs
120
O
S
N
O
O
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S42. $^{13}C\{^1H\}$ **NMR spectrum ($CDCl_3$, 126 MHz) of compound 3n.**

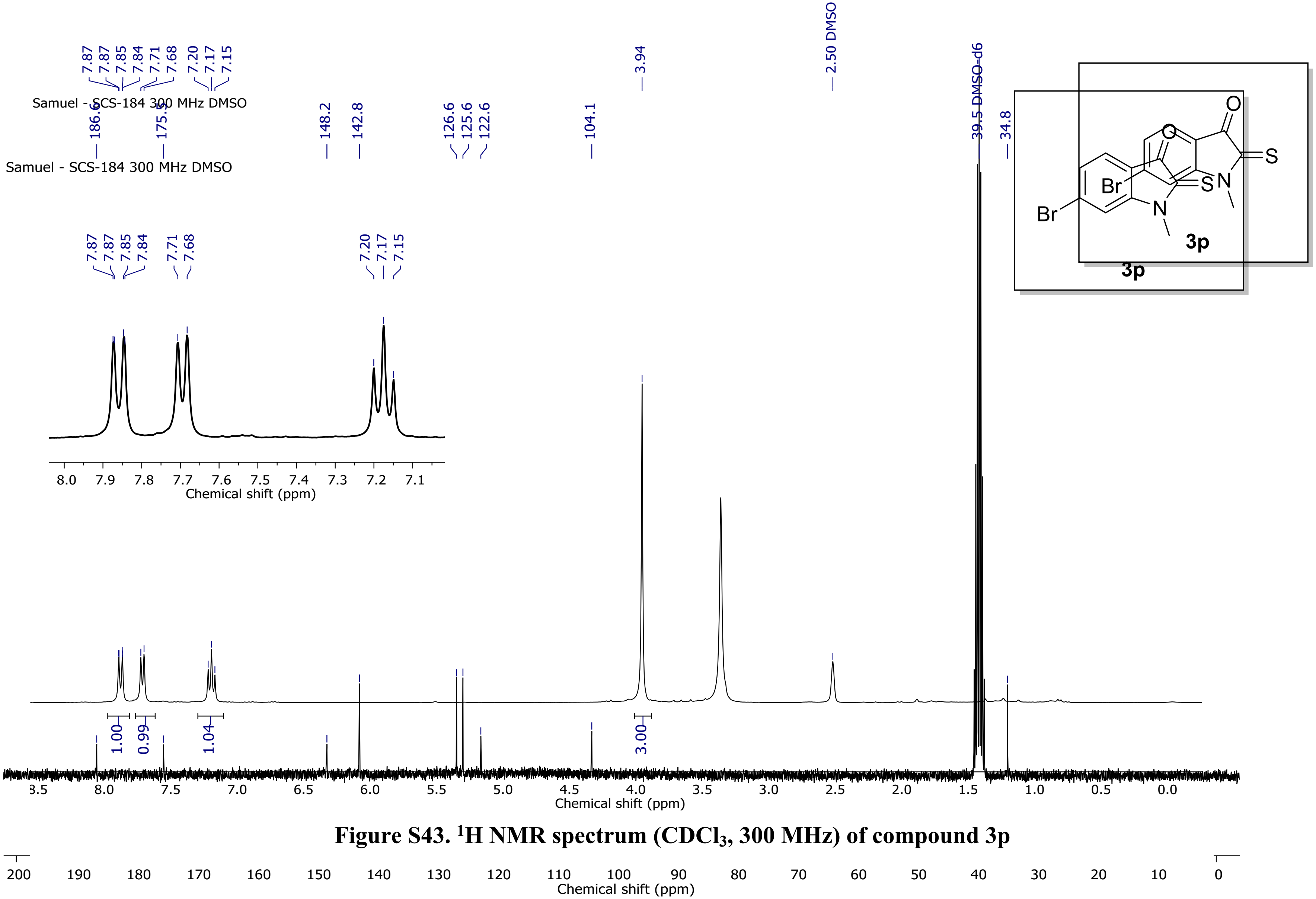


Figure S43. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **3p**

Figure S44. $^{13}C\{^{1}H\}$ **NMR spectrum ($CDCl_3$, 75 MHz) of compound 3p.**

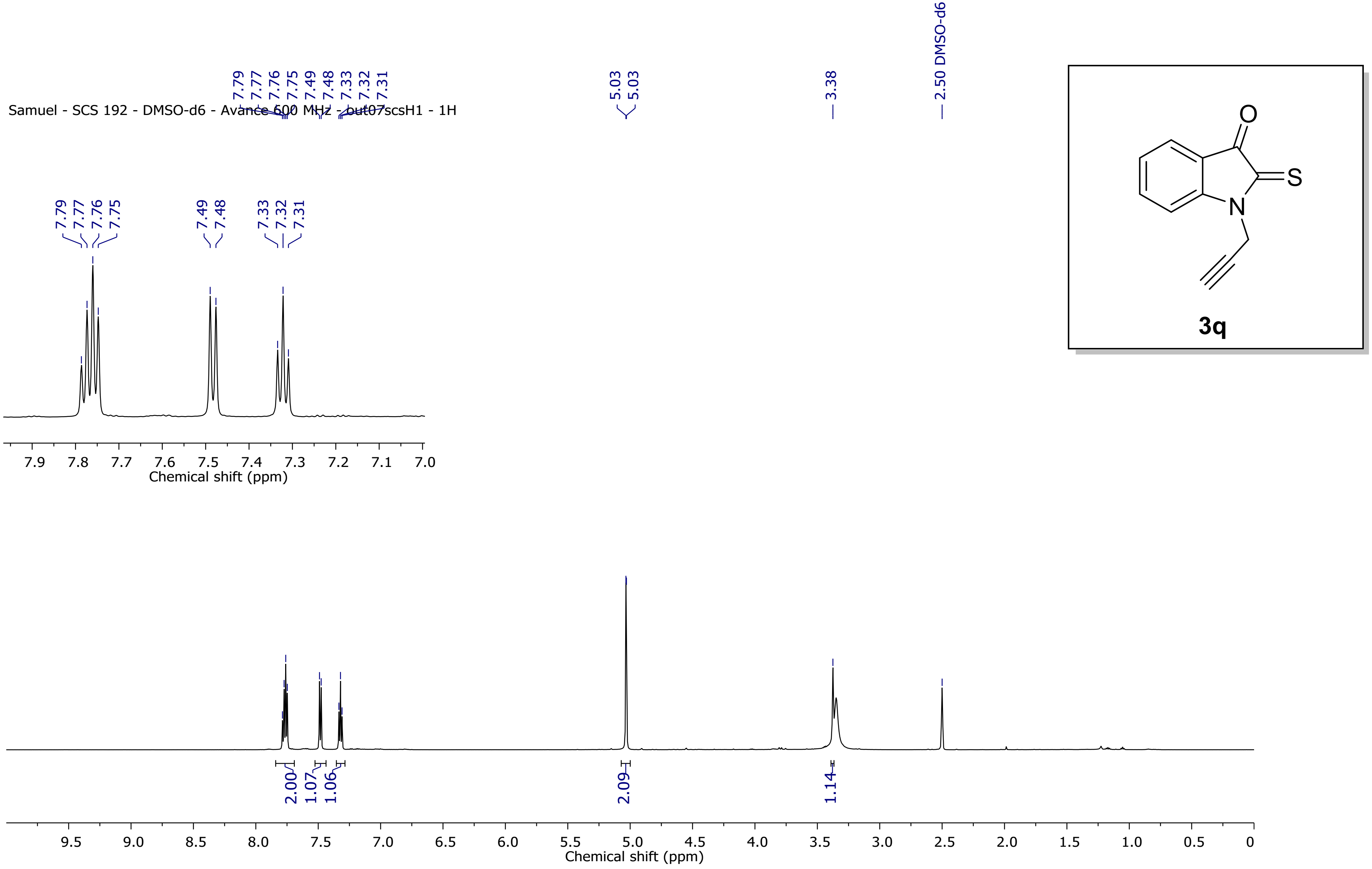
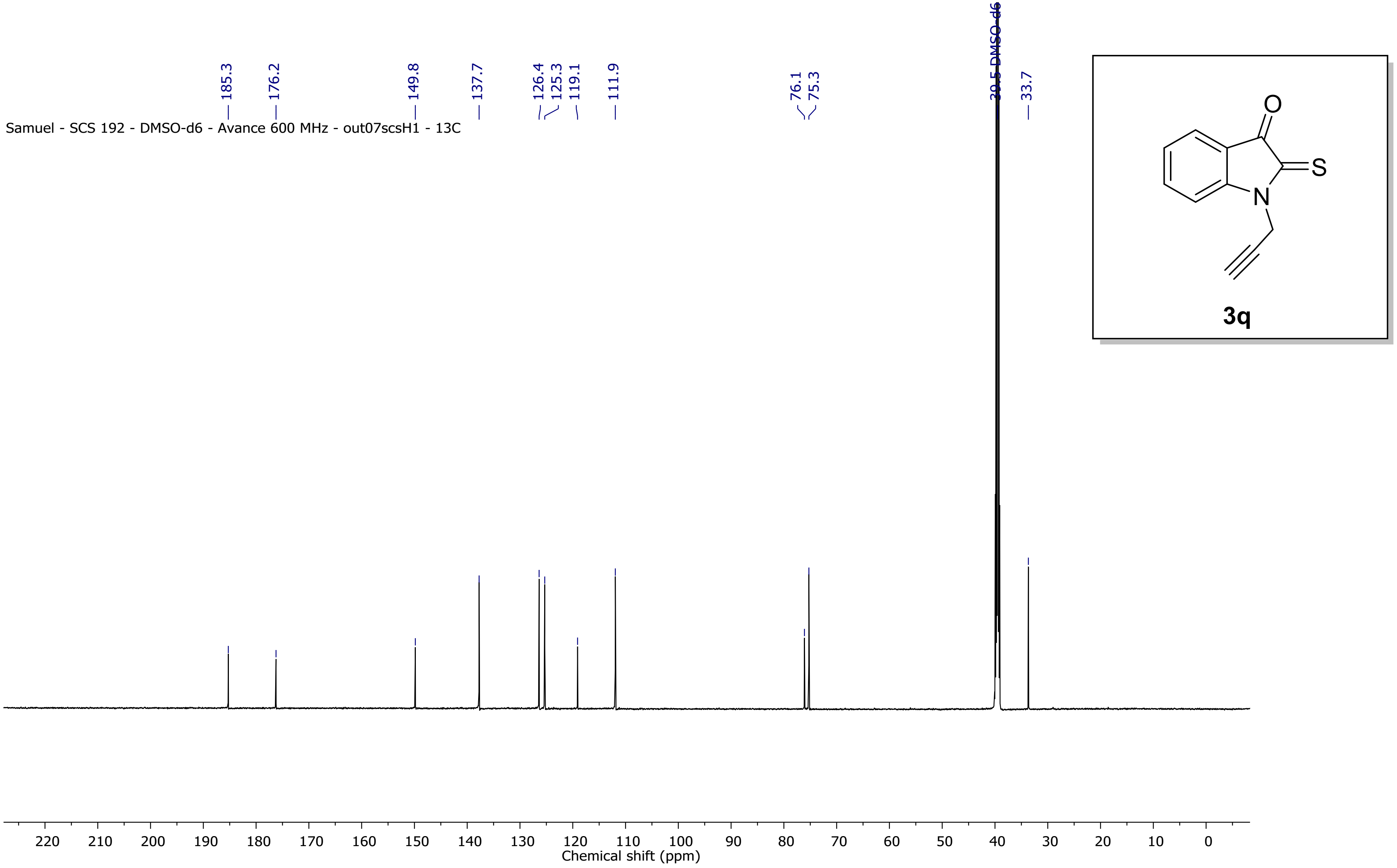

Samuel - SCS 192 - DMSO-d6 - Avance 600 MHz - but07scsH1 - 1H
7.79
7.77
7.76
7.75
7.49
7.48
7.33
7.32
7.31
5.03
5.03
3.38
2.50 DMSO-d6
2.00
1.07
1.06
2.09
1.14
Chemical shift (ppm)
O
S
N
3q

Figure S45. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of compound 3q.


Samuel - SCS 192 - DMSO-d6 - Avance 600 MHz - out07scsH1 - 13C
185.3
176.2
149.8
137.7
126.4
125.3
119.1
111.9
76.1
75.3
39.5 DMSO-d6
33.7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

O
S
N

3q

Figure S46. $^{13}C\{^1H\}$ **NMR spectrum ($CDCl_3$, 151 MHz) of compound 3q.**

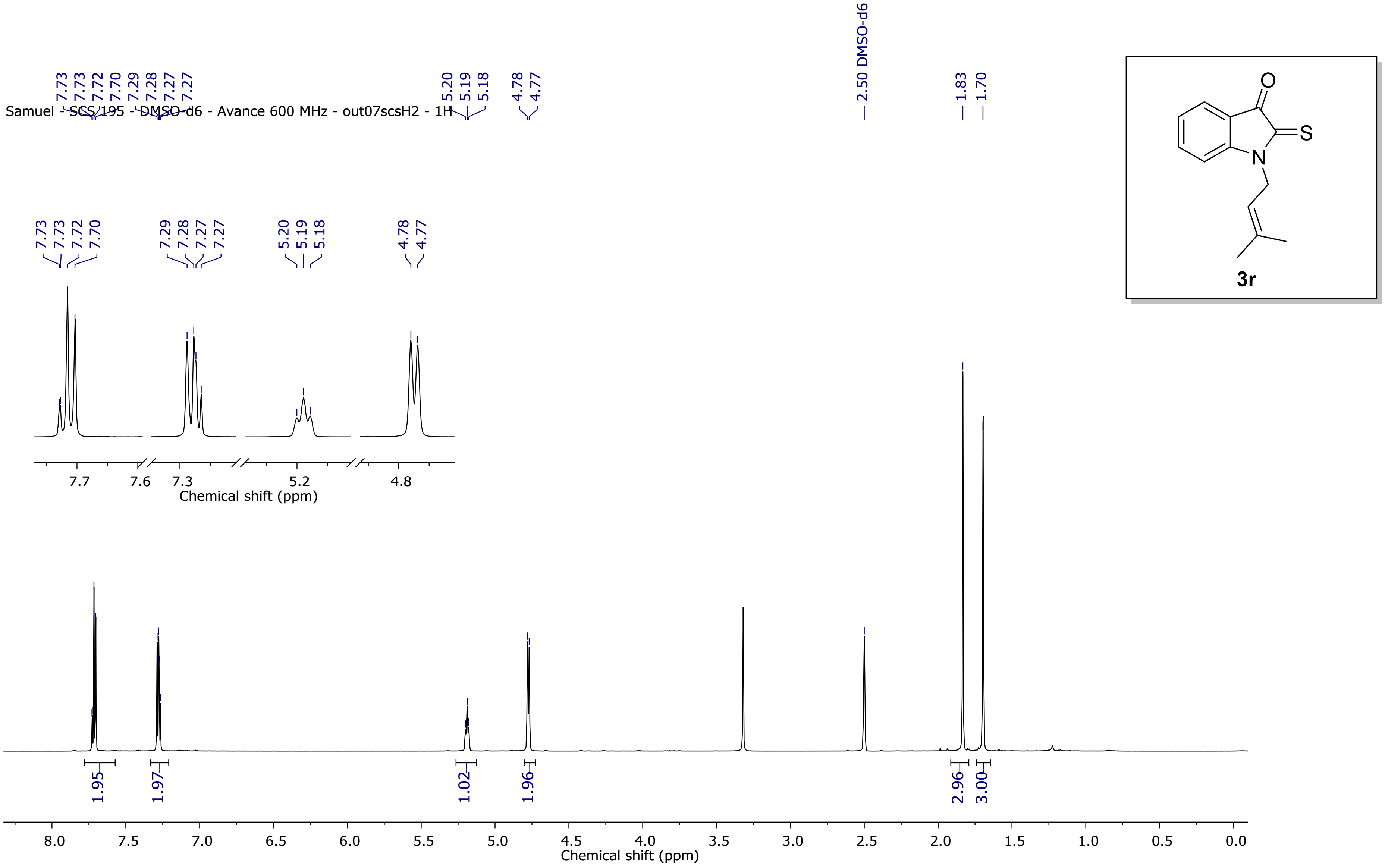

Samuel - SCS 195 - DMSO-d6 - Avance 600 MHz - out07scsH2 - 1H
7.73
7.73
7.72
7.70
7.29
7.28
7.27
7.27
5.20
5.19
5.18
4.78
4.77
2.50 DMSO-d6
1.83
1.70
7.7
7.6
7.3
5.2
4.8
Chemical shift (ppm)
1.95
1.97
1.02
1.96
2.96
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)
O
S
N
3r

Figure S47. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound 3r.

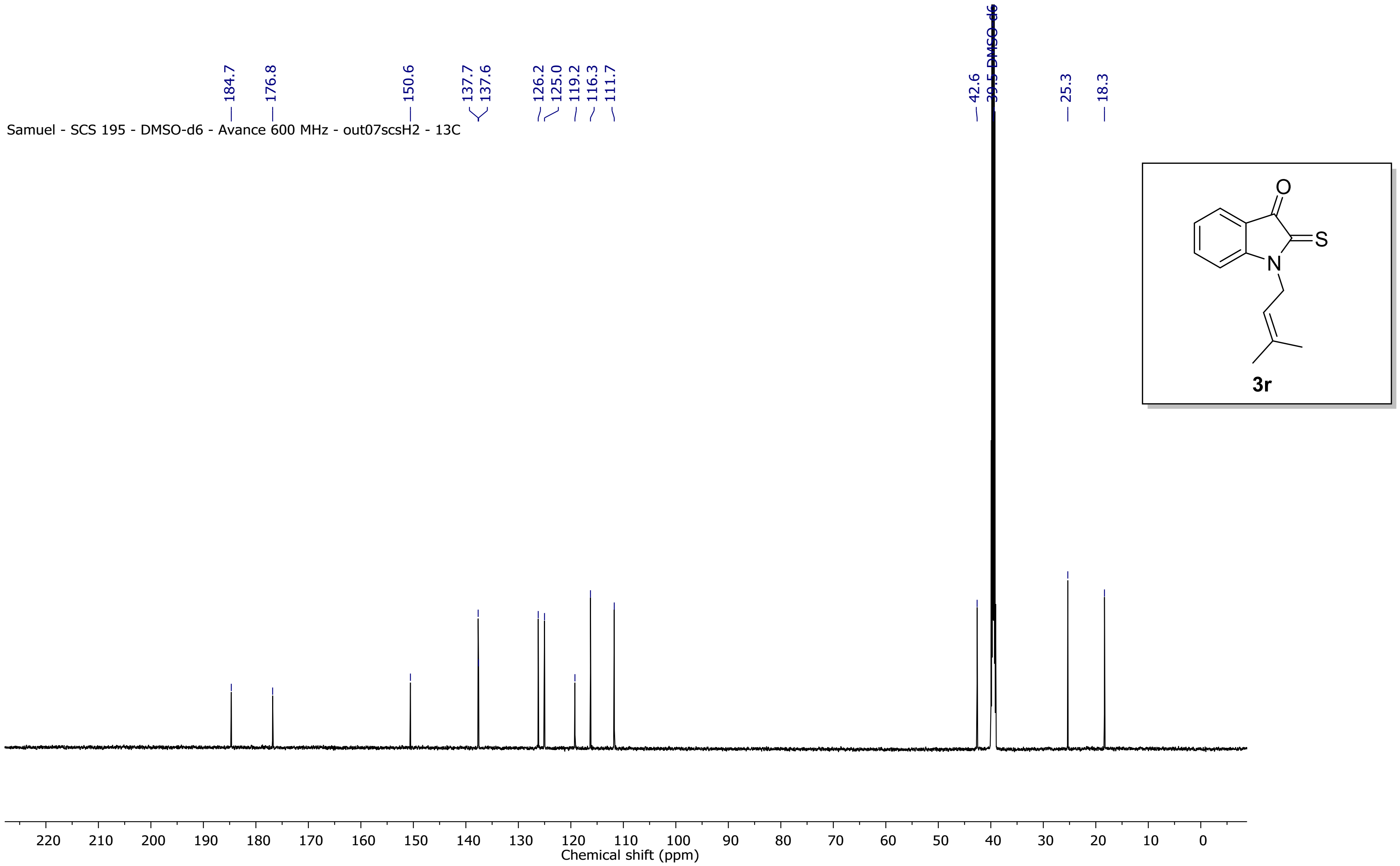

Samuel - SCS 195 - DMSO-d6 - Avance 600 MHz - out07scsH2 - 13C
184.7
176.8
150.6
137.7
137.6
126.2
125.0
119.2
116.3
111.7
42.6
39.5 DMSO-d6
25.3
18.3
O
S
N
3r
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S48. C{^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of compound 3r.

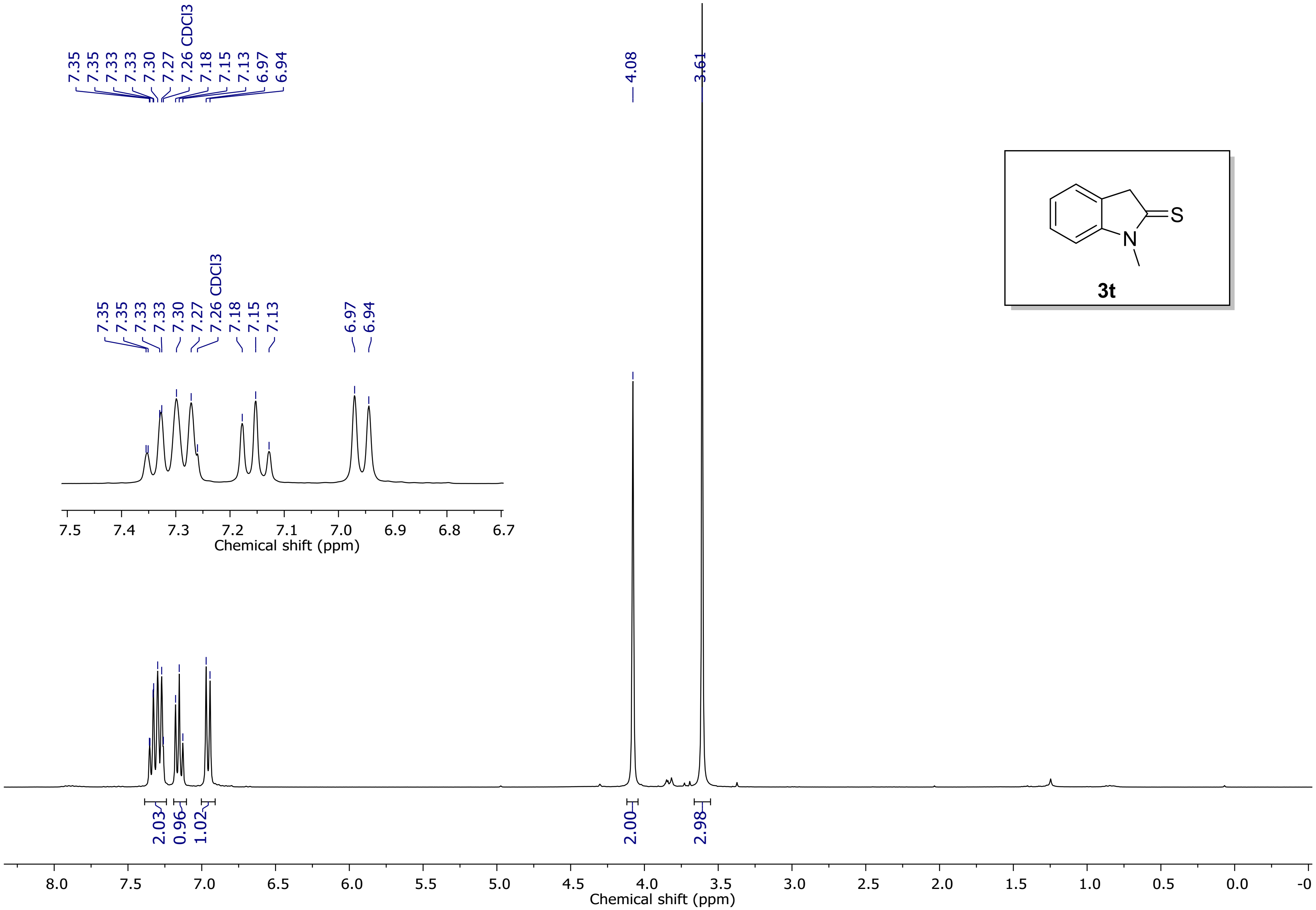

7.35
7.35
7.33
7.33
7.30
7.27
7.26 CDCl3
7.18
7.15
7.13
6.97
6.94
4.08
3.61
3t
S
N
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical shift (ppm)
2.03
0.96
1.02
2.00
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
Chemical shift (ppm)

Figure S49. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound 3t.

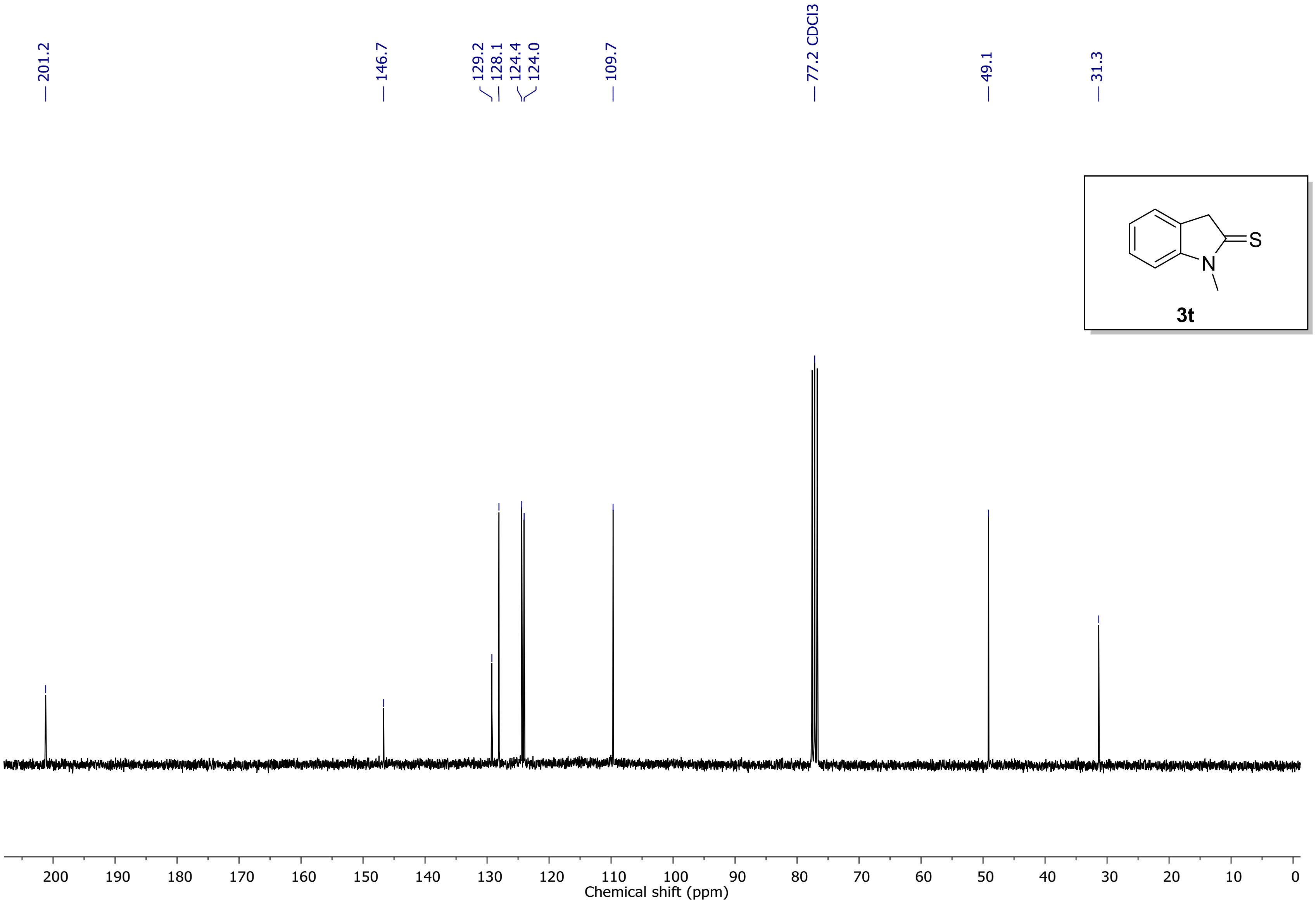
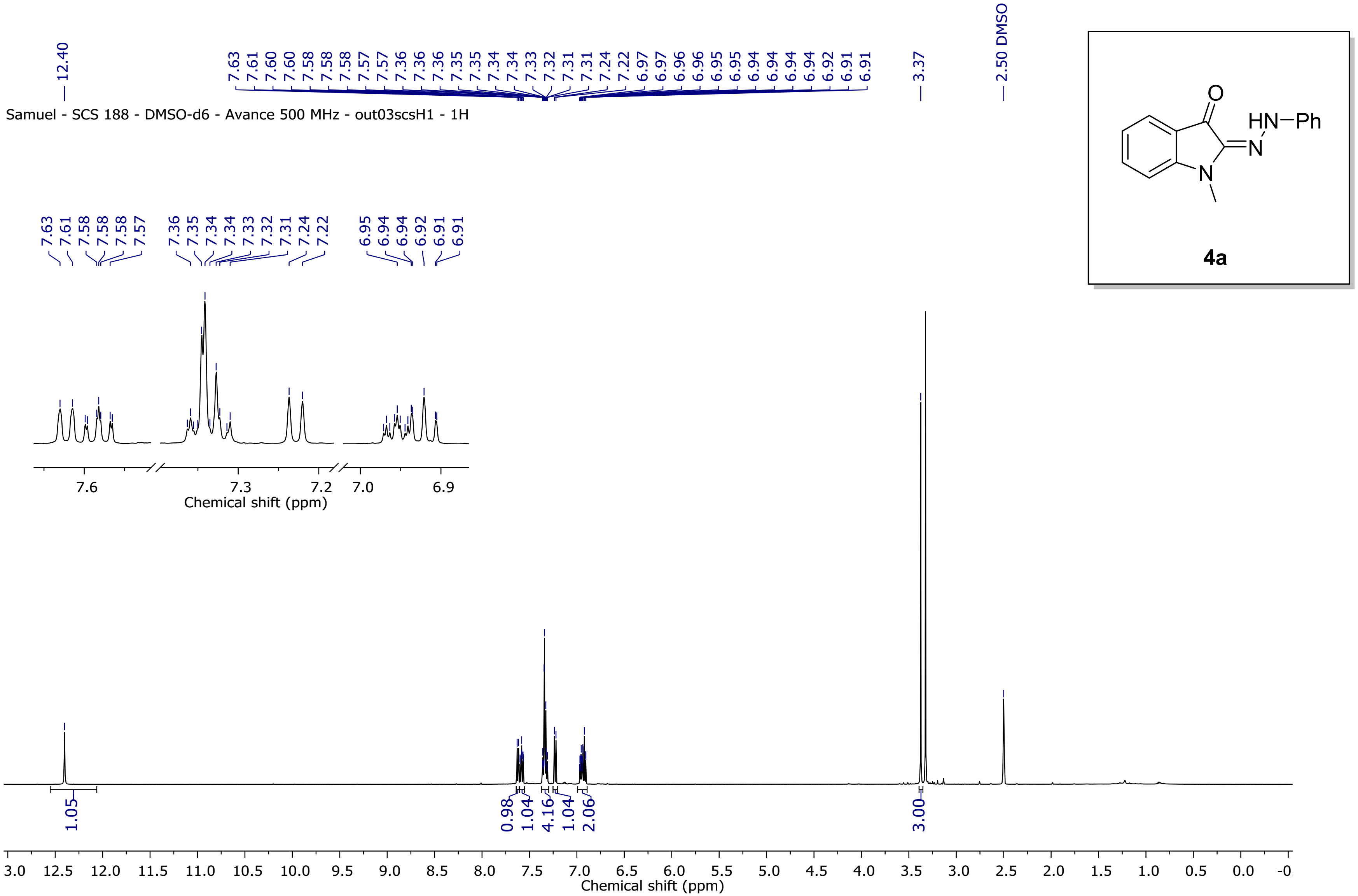

201.2
146.7
129.2
128.1
124.4
124.0
109.7
77.2 CDCl3
49.1
31.3
S
N
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S50. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of compound 3t.

Figure S51. ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound 4a.



4a

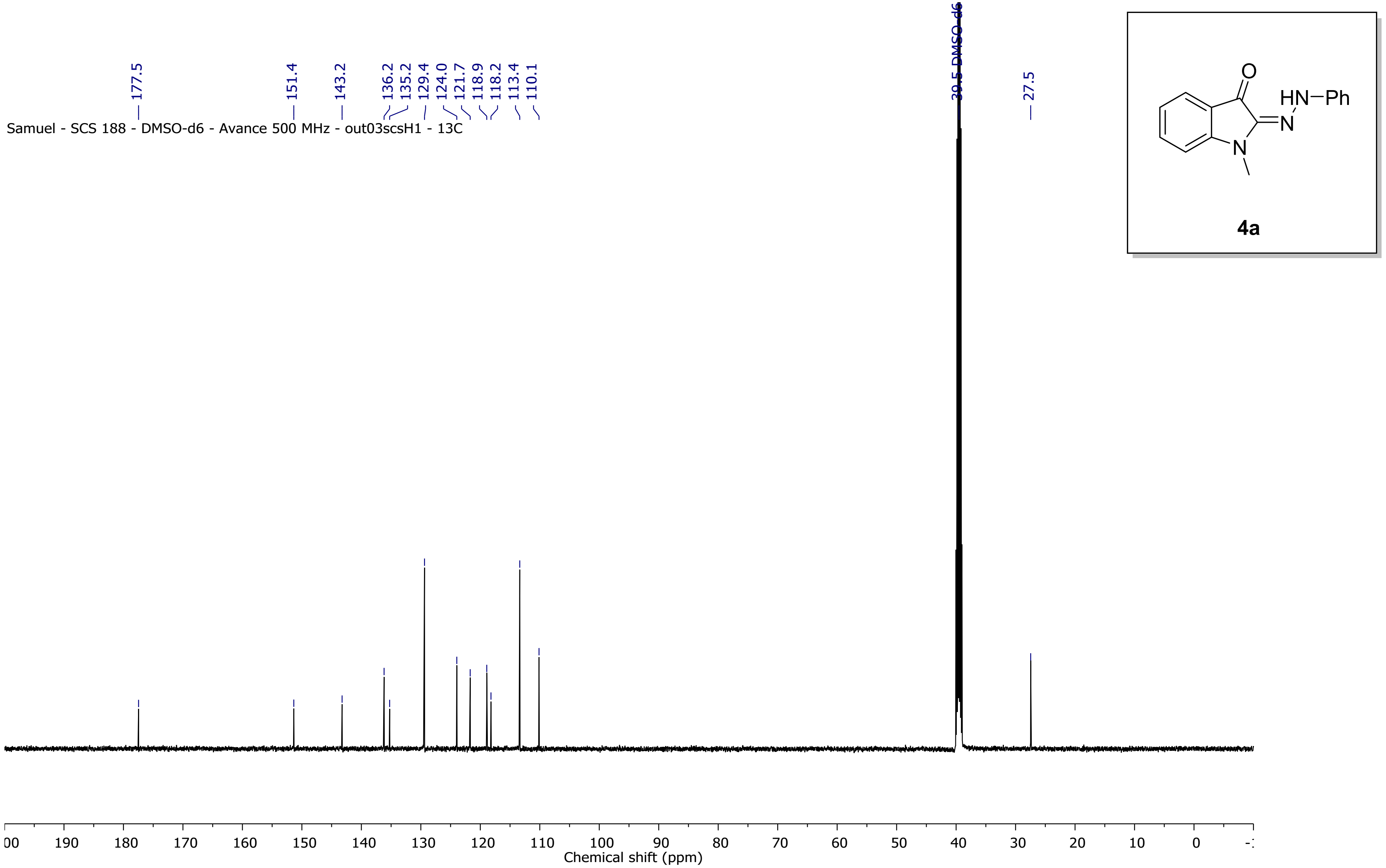

Samuel - SCS 188 - DMSO-d6 - Avance 500 MHz - out03scsH1 - 13C
177.5
151.4
143.2
136.2
135.2
129.4
124.0
121.7
118.9
118.2
113.4
110.1
39.5 DMSO-d6
27.5
O
HN−Ph
N
N
4a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

Figure S52. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 126 MHz) of compound 4a.

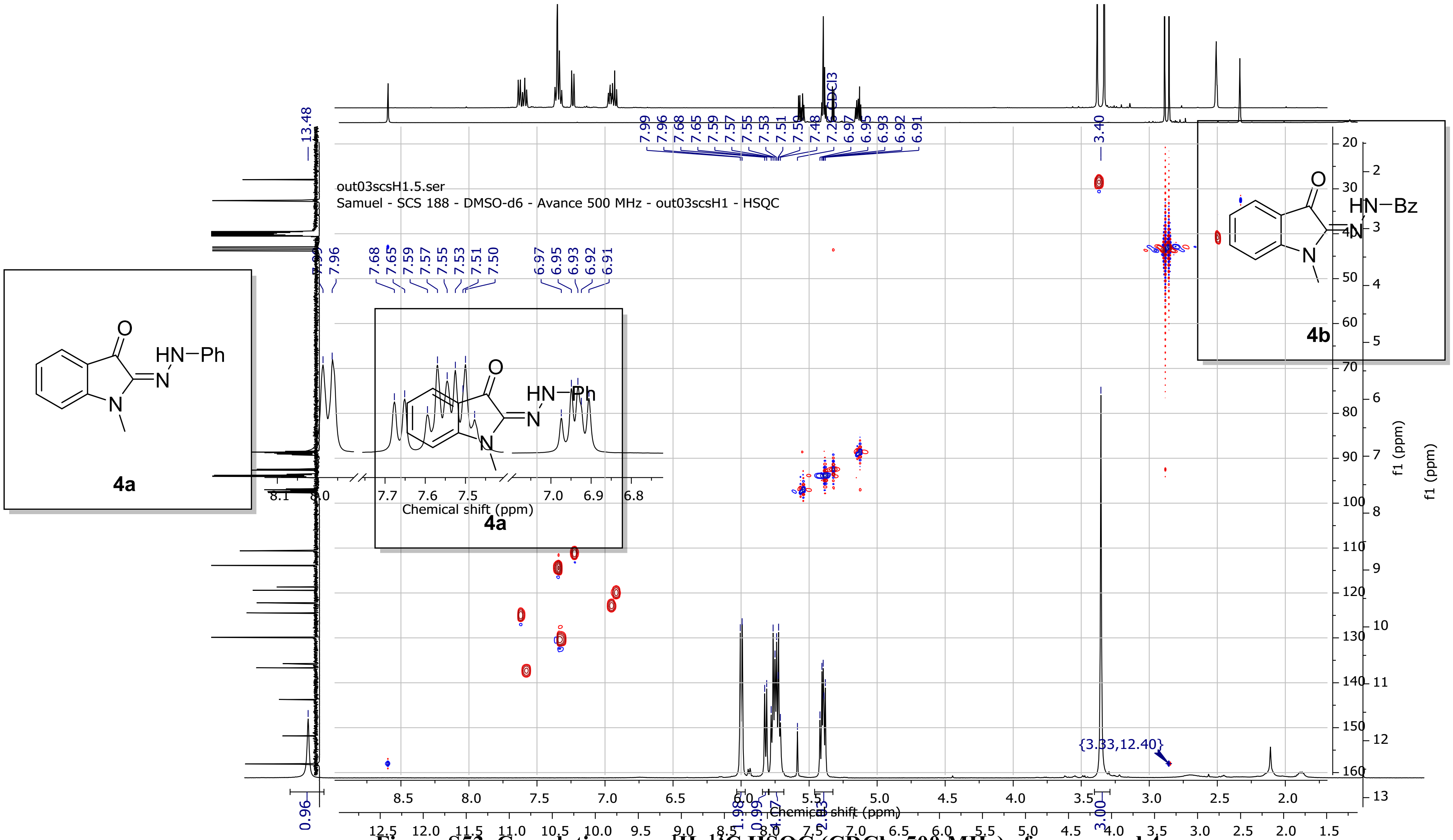
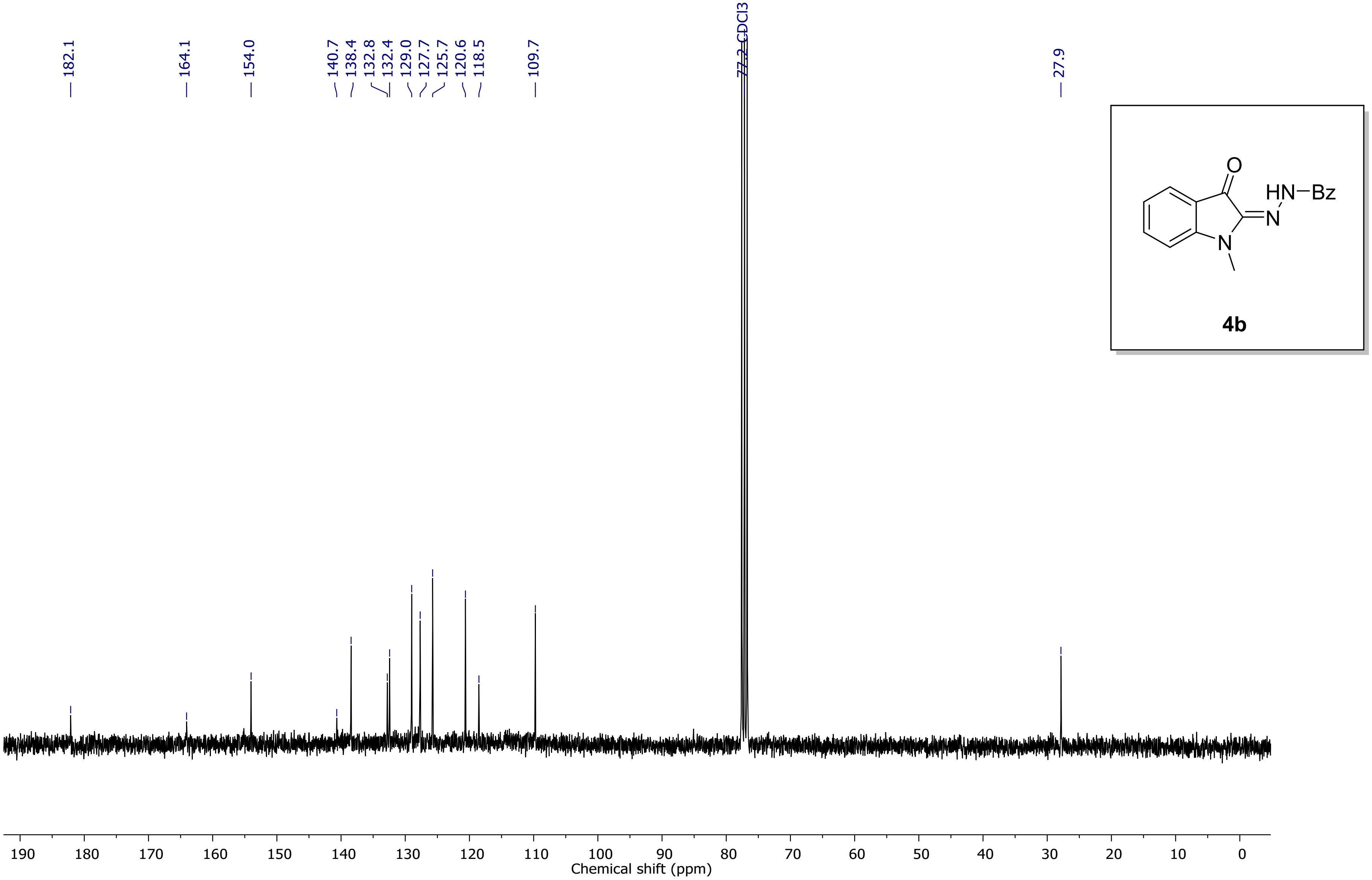


Figure S53. Correlation map ^1H–^{13}C HSQC ($CDCl_3$, 500 MHz) of compound 4a.

Figure S54. Correlation map ^1H– ^1H NOESY ($CDCl_3$, 500 MHz) of compound 4a.

Figure S55. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound 4b.


182.1
164.1
154.0
140.7
138.4
132.8
132.4
129.0
127.7
125.7
120.6
118.5
109.7
77.2 CDCl3
27.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

O
HN–Bz
N
N

4b

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of compound 4b.

Computational

The structure of compound **3a** and its C-3 thionated isomer (**5a**) were subjected to geometry optimization at two level of theory using the Gaussian 16 program[8]: B3LYP/6-31G* level in the gas phase and at the M06-2X/aug-cc-pVTZ level using the IEF-PCM[9] (integral equation formalism variant of the Polarizable Continuum Model) implicit solvent model with the parameters for CHCl3 (dielectric constant = 4.7113). The cartesian coordinates and Gibbs free energy of the optimized geometry of both compounds is presented in **Table S2** and **Table S3**, below.

The magnetic shielding constants (σ) were computed using the gauge including atomic orbitals (GIAO) method, at the mPW1PW91/6-311+G** level using the IEF-PCM (integral equation formalism variant of the Polarizable Continuum Model) implicit solvent model with the parameters for $CHCl_3$ (dielectric constant = 4.7113). The shielding tensors obtained from the NMR calculations of the structures optimized at the B3LYP/6-31G* were directly used in the DP4+ method as proposed by Sarotti *et al.*[10] and the results are available in a separate excel file, where "**isomer 2**" refers to **3a** and "**isomer 1**" to **5a**. A summary of the result is shown below in **Figure S57**.

The unscaled chemical shifts (δ_u) for the structures optimized at the M06-2X/aug-cc-pVTZ were computed using TMS as reference standard according to $\delta_u = \sigma_0 - \sigma^c$, where σ^c is the shielding tensor for the compound and σ_0 is the shielding tensor of TMS computed at the same level of theory employed for σ^c. The results are shown in **Tables 4, 5** and **6.** The plots of the experimental chemical shifts against the calculated unscaled chemical shifts are shown in **Figures S58** and S**59**.

---

[8] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[9] G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, **2010**, *132*, 114110

[10] N. Grimblat, M. M. Zanardi, A. M., J. Sarotti, *Org. Chem.* **2015**, *80*, 12526

Table S2. Cartesian coordinates and Gibbs free energy of the optimized geometry of 3a and 5a at the B3LYP/6-31G* level of theory in the gas phase.

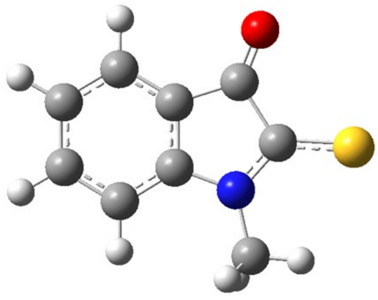
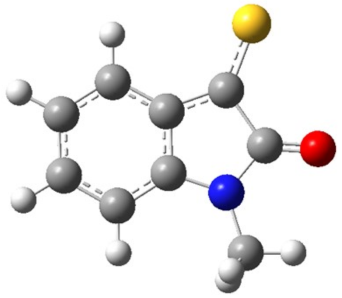
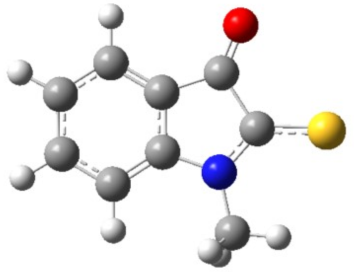
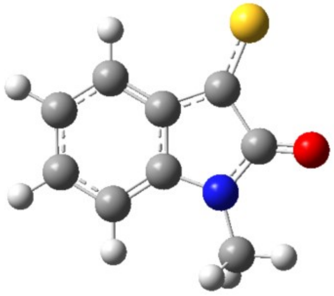
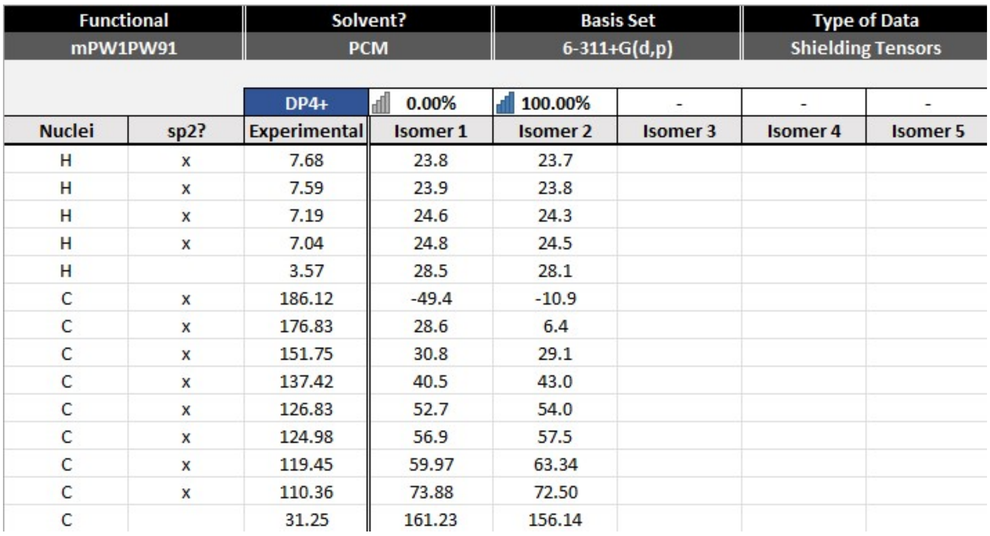
 **3a**				 **5a**			
C	3.22326200	-0.61007200	0.00001100	C	2.67973400	-1.42932200	0.00010600
C	3.10714600	0.78448700	0.00001100	C	3.09030300	-0.08906300	0.00011200
C	1.85900800	1.42484000	0.00000800	C	2.17027000	0.96798000	0.00007300
C	0.72971400	0.61516600	0.00000300	C	0.81867800	0.64350800	0.00002900
C	0.83491500	-0.78349500	0.00000200	C	0.38755900	-0.70638800	0.00002000
C	2.07550000	-1.40952100	0.00000600	C	1.32132100	-1.74447400	0.00005900
N	-0.62879000	1.00345300	-0.00000100	N	-0.28324500	1.49939800	-0.00001500
C	-1.46302800	-0.08204100	-0.00000500	C	-1.47203200	0.77054500	-0.00006300
C	-0.53629800	-1.32759300	-0.00000300	C	-1.05990300	-0.71623500	-0.00003400
C	-1.05090800	2.39235900	0.00000000	C	-0.23440200	2.94713300	-0.00002200
S	-3.10595200	-0.10997500	-0.00001100	O	-2.58838500	1.24194800	-0.00011500
O	-0.90377500	-2.48118500	-0.00000600	S	-2.11705000	-1.96182800	-0.00006300
H	4.20708500	-1.06895200	0.00001400	H	3.42273900	-2.22062200	0.00013700
H	4.00687900	1.39369200	0.00001500	H	4.15219500	0.14194800	0.00014600
H	1.79103600	2.50764900	0.00000800	H	2.50809700	1.99920600	0.00007400
H	2.13544600	-2.49392400	0.00000600	H	0.97594300	-2.77418200	0.00005200
H	-2.14108000	2.41348200	-0.00000500	H	-1.26513500	3.30543300	-0.00000100
H	-0.67414500	2.90408900	0.89279500	H	0.27981300	3.32199800	0.89265400
H	-0.67413700	2.90409200	-0.89279100	H	0.27977700	3.32199700	-0.89272100

Table S3. Cartesian coordinates and Gibbs free energy of the optimized geometry of 3a and 5a at the M06-2X/aug-cc-pVTZ level using the IEF-PCM implicit solvent model with the parameters for CHCl3 (dielectric constant = 4.7113).

 **3a**				 **5a**			
C	3.20304400	-0.61332100	-0.00000400	C	-2.65980100	-1.43191800	-0.00002000
C	3.08578300	0.77296900	0.00000900	C	-3.06798600	-0.10042200	0.00000000
C	1.84489500	1.41109000	0.00001400	C	-2.15425400	0.95300800	0.00000900
C	0.72814300	0.60116000	0.00000100	C	-0.81441900	0.62417500	0.00000600
C	0.83264600	-0.78728400	-0.00000300	C	-0.38662400	-0.71296400	-0.00001600
C	2.06403300	-1.41230300	-0.00000900	C	-1.30777000	-1.74763100	-0.00002900
N	-0.62599300	0.99556400	-0.00000400	N	0.28265500	1.48571600	0.00002500
C	-1.45478700	-0.06640600	0.00000500	C	1.45689600	0.77762700	-0.00003200
C	-0.53892400	-1.31804800	0.00000100	C	1.06021400	-0.71040500	-0.00001400
C	-1.02052000	2.38738600	-0.00001600	C	0.19248500	2.92749700	0.00004400
S	-3.08687400	-0.10677500	0.00000500	O	2.57142100	1.23483500	-0.00009100
O	-0.92476000	-2.45241300	0.00000000	S	2.12373000	-1.92130300	0.00004600
H	4.18316100	-1.06734900	-0.00001000	H	-3.40000700	-2.21848400	-0.00003400
H	3.98191300	1.37825500	0.00001700	H	-4.12529400	0.12721200	0.00000300

H	1.77234400	2.48899200	0.00002500	H	-2.48600000	1.98141900	0.00001300
H	2.12979900	-2.49177300	-0.00001700	H	-0.96617600	-2.77423500	-0.00004900
H	-2.10413900	2.43523800	-0.00005900	H	1.20341800	3.32363100	0.00081700
H	-0.62951600	2.88197000	0.88872800	H	-0.33336500	3.27449300	-0.88908300
H	-0.62944000	2.88196200	-0.88872700	H	-0.33466300	3.27432100	0.88845900

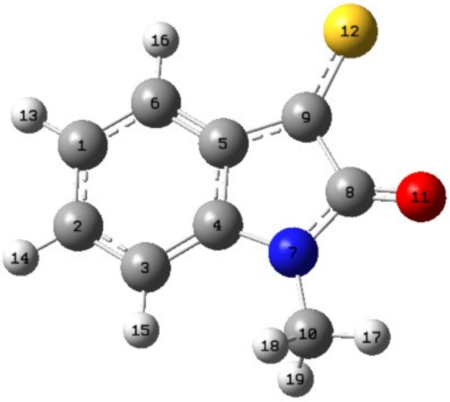


Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors

		DP4+	0.00%	100.00%	-	-	-
Nuclei	**sp2?**	**Experimental**	**Isomer 1**	**Isomer 2**	**Isomer 3**	**Isomer 4**	**Isomer 5**
H	x	7.68	23.8	23.7			
H	x	7.59	23.9	23.8			
H	x	7.19	24.6	24.3			
H	x	7.04	24.8	24.5			
H		3.57	28.5	28.1			
C	x	186.12	-49.4	-10.9			
C	x	176.83	28.6	6.4			
C	x	151.75	30.8	29.1			
C	x	137.42	40.5	43.0			
C	x	126.83	52.7	54.0			
C	x	124.98	56.9	57.5			
C	x	119.45	59.97	63.34			
C	x	110.36	73.88	72.50			
C		31.25	161.23	156.14			

Figure S57. Image from the DP4+ datasheet using the shielding tensors for 5a (Isomer 1) and 3a (Isomer 2). DP4+ results corroborates with the C-2 thionation. The shielding tensors are from the PCM/mPW1PW91/6-31+G**//B3LYP/6-31G* calculations.

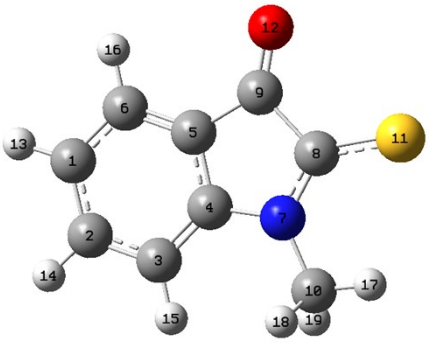
Table S4. Unscaled chemical shifts (δu) for **5a** optimized at the M06-2X/aug-cc-pVTZ were computed using TMS as reference standard (σ_0 for ^{1}H = 31.99202 and σ_0 for ^{13}C = 189.3465 at the PCM/mPW1PW91/6-31+G**//PCM/ M06-2X/aug-cc-pVTZ level of theory).



Atom	σ_c	σ_c Averaged for the CH_3	δ_u (ppm)
1C	61.31870	61.31870	128.03
2C	43.08540	43.08540	146.26
3C	75.31430	75.31430	114.03
4C	30.00060	30.00060	159.35
5C	55.61370	55.61370	133.73
6C	59.51440	59.51440	129.83

8C	33.81100	33.81100	155.54
9C	-46.84900	-46.84900	236.20
10C	162.44460	162.44460	26.90
13H	24.74470	24.74470	7.25
14H	24.09890	24.09890	7.89
15H	24.85470	24.85470	7.14
16H	23.96990	23.96990	8.02
17H	27.77660		
18H	29.12310	28.67427	4.22
19H	29.12310		

Table S5. Unscaled chemical shifts (δu) for **3a** optimized at the M06-2X/aug-cc-pVTZ were computed using TMS as reference standard (σ_0 for ^{1}H = 31.99202 and σ_0 for ^{13}C = 189.3465 at the PCM/mPW1PW91/6-31+G**//PCM/ M06-2X/aug-cc-pVTZ level of theory).



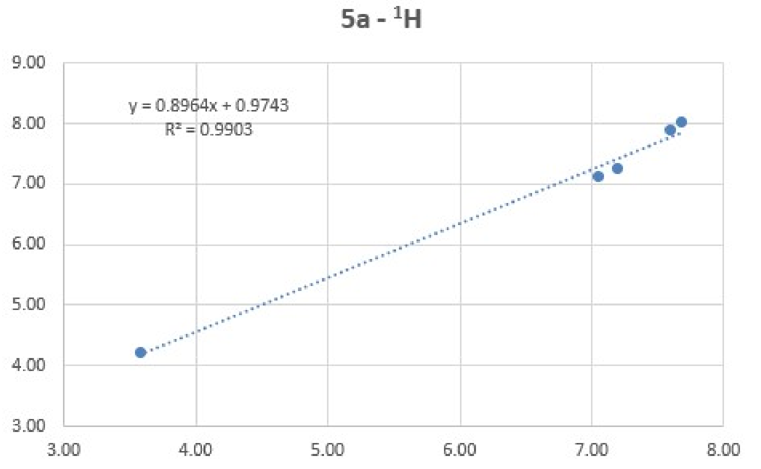
Atom	σ_c	σ_c Averaged for the CH_3	δ_u (ppm)
1C	58.91120	58.91120	130.44
2C	44.99000	44.99000	144.36
3C	73.85330	73.85330	115.49
4C	30.56230	30.56230	158.78
5C	65.80910	65.80910	123.54
6C	56.10460	56.10460	133.24
8C	-6.57310	-6.57310	195.92
9C	8.85840	8.85840	180.49
10C	157.38440	157.38440	31.96
13H	24.44430	24.44430	7.55
14H	23.94450	23.94450	8.05
15H	24.56060	24.56060	7.43
16H	23.87620	23.87620	8.12
17H	27.11160		
18H	28.83990	28.26383	4.88
19H	28.84000		

Table S6. Experimental and calculated (at the PCM/mPW1PW91/6-31+G**//PCM/ M06-2X/aug-cc-pVTZ level of theory) shifts for 1H and 13C for both **3a** and **5a**.

^{1}H Data

Experimental δ (ppm)	5a δu (ppm)	Error (5a)	3a δu (ppm)	Error (3a)
7.68	8.02	-0.34	8.115816667	-0.44

7.59	7.89	-0.30	8.047516667	-0.46
7.19	7.25	-0.06	7.547716667	-0.36
7.04	7.14	-0.10	7.431416667	-0.39
3.57	4.22	-0.65	4.880416667	-1.31
MAE 5a		-0.29	**MAE 3a**	-0.59
		^{13}C Data		
Experimental δ (ppm)	**5a δu (ppm)**	**Error (5a)**	**3a δu (ppm)**	**Error (3a)**
186.12	236.20	-50.08	195.9196	-9.80
176.83	159.35	17.48	180.4881	-3.66
151.75	155.54	-3.79	158.7842	-7.03
137.42	146.26	-8.84	144.3565	-6.94
126.83	133.73	-6.90	133.2419	-6.41
124.98	129.83	-4.85	130.4353	-5.46
119.45	128.03	-8.58	123.5374	-4.09
110.36	114.03	-3.67	115.4932	-5.13
31.25	26.90	4.35	31.9621	-0.71
MAE 5a		-7.21	**MAE 3a**	-5.47



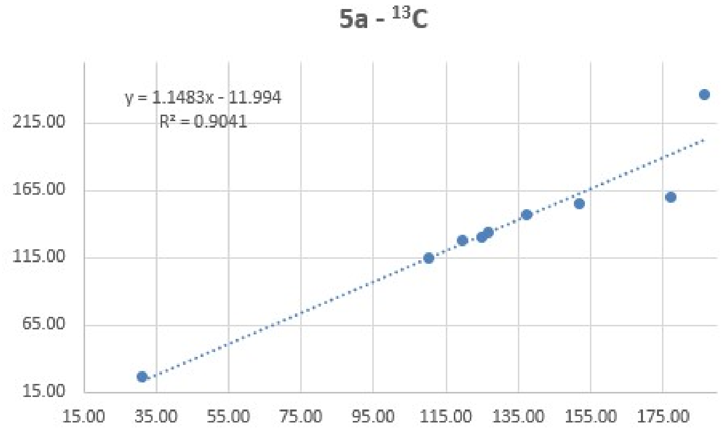


Figure S58. Plot of the calculated δ against the experimental values for **5a**. The equations and the R^2 values are shown in the graphs.

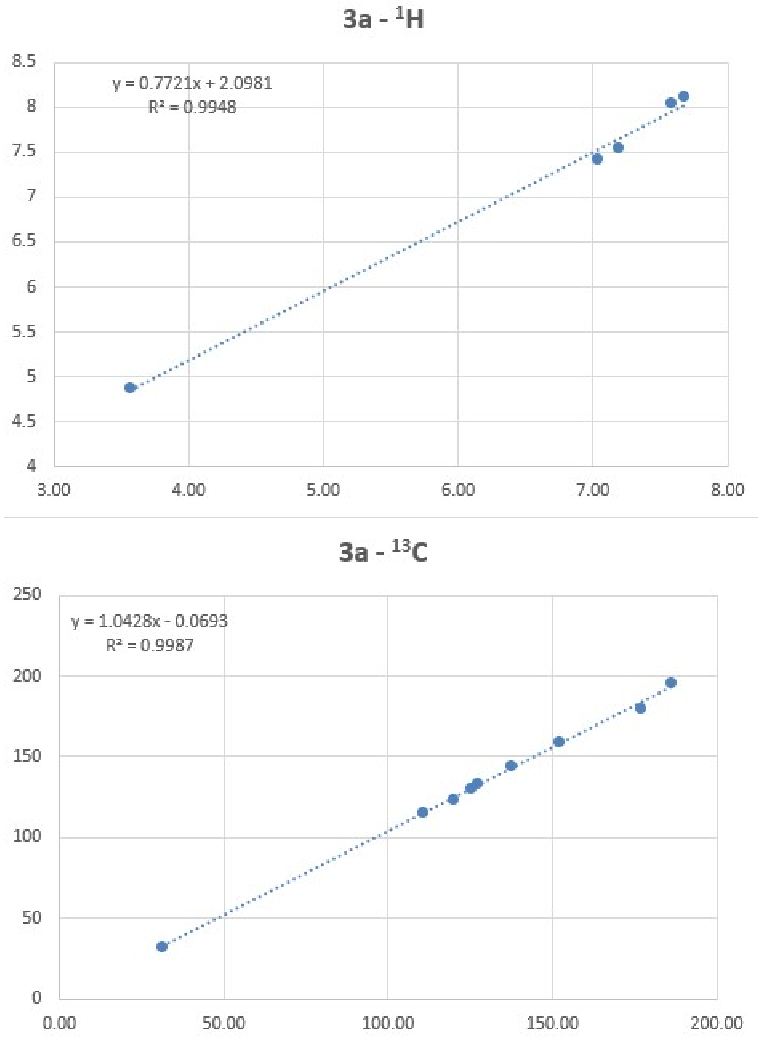


Figure S59. Plot of the calculated δ against the experimental values for **3a**. The equations and the R^2 values are shown in the graphs.

From the data above, data strongly suggests that **3a** is the correct structure for the isomer obtained, which is in accordance to the 2D-NMR data (^{1}H-^{13}C-HMBC) recorded for the compound. DP4+ results directly indicate **3a** as the correct isomer, but classical chemical shift calculation, especially for the ^{13}C unscaled shifts, already shows a better correlation of the data obtained for **3a** and a great discrepancy, especially at the shift for the thionated carbon, for **5a**.