Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Palladium-Catalyzed Direct C-H Thiolation of 2-Pyridyl Sulfoxide with Disulfides

Mamta Yadav, Bibek Sarma, Ram Singh Jat and M. Bhanuchandra*[a]

[a]*Department of Chemistry, School of Chemical Sciences and Pharmacy, Central University of Rajasthan, Bandarsindri, Rajasthan-305 817 (India).*

E-mail: mallibhanuchandra@curaj.ac.in

Table of contents	
Instrumentation and Chemicals	S2
Experimental Procedures and Characterization Data	S2-S16
X-ray Crystal Structures	S17
References	S18
^{1}H and ^{13}C NMR Spectra	S19-S61

Instrumentation and Chemicals: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on a Bruker Avance 500 MHz NMR spectrometer. Chemical shifts (δ) are reported in parts per million, relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C in $CDCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in (Hz), and integration. Data for ^{13}C NMR was reported in terms of chemical shift (ppm). High-resolution mass spectra (HRMS) were obtained by using a TOF analyzer in ESI mode. X-ray data were taken at 273K with a Bruker APEX-II CCD single crystal diffractometer by using graphite monochromated Mo-Kα radiation (0.71073 Å). Data integration was done using SAINT.[1] Intensities for absorption were corrected using SADABS.[2] TLC analysis were performed on commercial Aluminum TLC plate, silica gel coated with fluorescent indicator F254. Silica gel (Merk 100-200 mesh and 230-400 mesh) was used for column chromatography. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Thiophenol, 2-bromopridine, ceric ammonium nitrate (CAN) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from Sigma-Aldrich or TCI India. Dichloromethane (DCM) was distilled over CaH_2 and stored under nitrogen. All the reactions were performed in an oven-dried glass reaction tube (capacity 15 mL) procured from the Sigma-Aldrich India (catalogue No. Z181099).

Experimental Procedures and Characterization Data:

General procedure for the synthesis of 2-(arylsulfinyl)pyridines[4]

Preparation of **1a** is representative. Benzenethiol (500 mg, 4.5 mmol), 2-bromopyridine (711 mg, 4.5 mmol, 1 equiv), K_2CO_3 (1.25 mg, 9 mmol, 2 equiv), and DMSO (5 mL) were taken in an oven-dried round bottom flask. The resulting solution was stirred at 110 ^{o}C for 20 h. The reaction mixture was quenched with water and extracted with DCM (3 x 20 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (Hexane/EtOAc = 9/1) to provide 2-(phenylthio)pyridine. The 2-(phenylthio)pyridine (500 mg, 2.7 mmol) was transferred to another 100 mL flask containing CH_2Cl_2 (10 mL). The reaction flask was cooled to 0 ^{o}C. The subsequent oxidation was done by the slow addition of *m*-CPBA (465 mg, 2.7 mmol, 1 equiv) and the reaction mixture was stirred for 3-4 h at 0 ^{o}C to room

temperature. Then, saturated aqueous solution of $NaHCO_3$ was added and stirred for 30 minutes. Extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified by using column chromatography on silica gel to provide corresponding product 2-(phenylsulfinyl)pyridine (**1a**) as a white solid; yield: 470 mg (85%).

General procedure for the synthesis of 1,2-diphenyldisulfane[6]

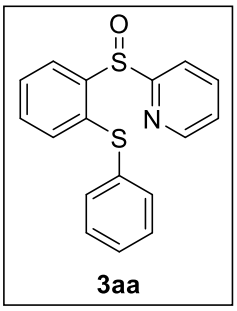
Procedure for **2a** is representative. DDQ (500 mg, 2.25 mmol) was added to an ice-cooled solution of benzenethiol (500 mg, 4.5 mmol) in dichloromethane (10.0 mL). The reaction mixture stirred for 20 min at 0 ^oC and monitored by TLC analysis. The reaction mixture was concentrated under reduced pressure and directly purified by chromatography column on silica gel to provide corresponding product 1,2-diphenyldisulfane (**2a**) as a white solid; yield: 450 mg (46 %).

General procedure for 2-pyridyl sulfoxide directed Pd-catalyzed *o*-C-H thiolation of arenes:

Preparation of **3aa** is representative. An oven-dried glass reaction tubes (capacity 15 mL) procured from the Sigma-Aldrich India (catalogue No. Z181099) was charged with aryl 2-pyridyl sulfoxide (**1a**, 102 mg, 0.5 mmol), phenyl disulfide (**2a,** 220 mg, 1.0 mmol, 2 equiv), Cerium (IV) ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ (320 mg, 0.6 mmol, 1.2 equiv), and $Pd(OAc)_2$ (11 mg, 0.05 mmol, 10 mol %) and then DCM (2.5 mL) was added under atmospheric air. The reaction tube was closed with a screw cap. Later on, the reaction mixture was stirred at 120 °C for 24 h before it was allowed to reach room temperature. The reaction mixture was quenched with water and extracted with DCM (3 x 10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (Hexane/EtOAc = 4/1) to provide 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) as a yellow solid; yield: 100 mg (64%).

Compounds **1a**,[4] **1b**,[4] **1c**,[5a] **1d**,[4] **1e**,[5] **1f**,[5b] **1g**,[4] **2a**,[6,7] **2b**,[6-9] **2c**,[10] **2d**,[8] **2e**,[6,7,9] **2f**,[11] **2g**,[12] **2h**,[6-8] **2i**,[6] **2j**,[8-9] **5**,[13] **6**,[14] **7**,[15] and **1a-*d***[17] are previously reported and showed the identical spectra according to the literature.

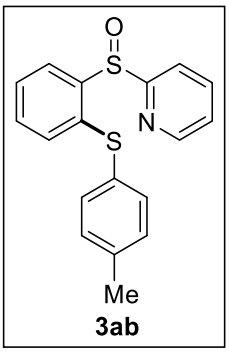
2-((2-(phenylthio)phenyl)sulfinyl)pyridine (3aa)



3aa

Light yellow solid. yield 100 mg (64%). mp 66-67 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.57 (d, *J* = 4.0 Hz, 1H), 7.99 (t, *J* = 8.5 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 12.0 Hz, 1H), 7.29–7.25 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 165.1, 149.9, 145.9, 137.8, 135.4, 135.0, 133.6, 131.5, 130.6, 129.2, 128.6, 127.2, 125.6, 124.6, 120.4 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{14}NOS_2^+$: 312.0511; found: 312.0512.

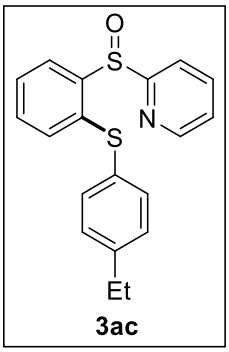
2-((2-(*p*-tolylthio)phenyl)sulfinyl)pyridine (3ab)



3ab

Brown liquid; yield 44 mg (27%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.58 (d, *J* = 3.5 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.33–7.26 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 165.4, 150.0, 145.0, 137.9, 137.8, 136.6, 132.6, 131.9, 131.5, 131.3, 130.1, 128.0, 125.5, 124.6, 120.4, 29.7 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NOS_2^+$: 326.0668; found: 326.0671.

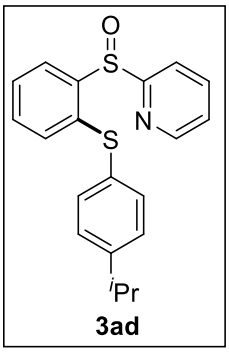
2-((2-((4-ethylphenyl)thio)phenyl)sulfinyl)pyridine (3ac)



3ac

Yellow liquid; yield 50 mg (41%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.57 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.93 (dd, J = 7.5, 1.5 Hz, 1H), 7.83 (td, J = 7.5, 1.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.33–7.25 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 2.63 (q, J = 8.0 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 165.3, 149.9, 145.0, 144.1, 137.8, 136.4, 132.7, 131.7, 131.5, 128.9, 128.1, 125.5, 124.6, 120.4, 28.4, 15.3 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{19}H_{18}NOS_2^+$: 340.0824; found: 340.0823.

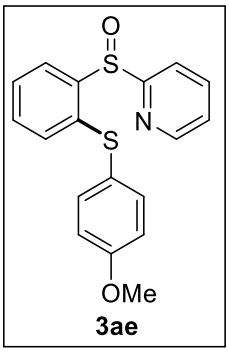
2-((2-((4-isopropylphenyl)thio)phenyl)sulfinyl)pyridine (3ad)



3ad

Yellow liquid; yield 94 mg (53%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.57 (d, J = 4.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.93 (dd, J = 8.0, 1.5 Hz, 1H), 7.82 (td, J = 7.5, 1.5 Hz, 1H), 7.41 (t, J = 7.0 Hz, 1H), 7.33 (td, J = 7.5, 1.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 2.92–2.84 (m, 1H), 1.34 (d, J = 6.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 165.3, 149.9, 148.6, 145.2, 137.8, 136.1, 132.9, 131.6, 131.49, 131.48, 128.1, 127.5, 125.5, 124.6, 120.4, 33.7, 23.8 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{20}H_{20}NOS_2^+$: 354.0981; found: 354.0982.

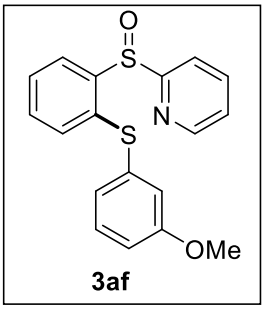
2-((2-((4-methoxyphenyl)thio)phenyl)sulfinyl)pyridine (3ae)



3ae

Brown solid; yield 52 mg (30%); mp 101-102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.60 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.91–7.84 (m, 2H), 7.37–7.27 (m, 5H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.3, 159.9, 150.0, 138.2, 137.9, 134.9, 131.5, 131.1, 127.4, 125.4, 124.7, 124.4, 120.2, 115.1 (2C), 55.4 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S_2^+$: 342.0617; found: 342.0621.

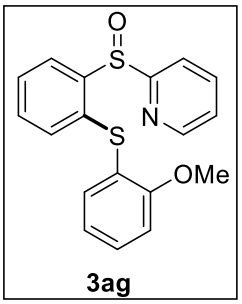
2-((2-((3-methoxyphenyl)thio)phenyl)sulfinyl)pyridine (3af)



3af

Brown liquid; yield 76 mg (44%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.59–8.53 (m, 1H), 8.02–7.93 (m, 2H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (td, *J* = 7.6, 1.6 Hz, 1H), 7.41–7.33 (m, 2H), 7.30–7.24 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.83–6.76 (m, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 160.1(2C), 150.1 (2C), 137.9, 136.8, 134.7, 134.0, 131.7, 130.1, 128.9, 125.7, 124.8, 122.8, 120.5, 115.7, 113.2, 55.4 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S_2^+$: 342.0617; found: 342.0618.

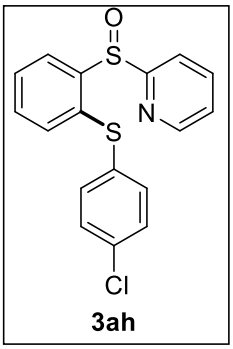
2-((2-((2-methoxyphenyl)thio)phenyl)sulfinyl)pyridine (3ag)



3ag

Yellow liquid; yield 38 mg (22%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.53 (d, J = 4.5 Hz, 1H), 7.97 (td, J = 7.5, 1.5 Hz, 2H), 7.76 (td, J = 7.5, 1.5 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.36–7.30 (m, 2H), 7.25–7.20 (m, 2H), 6.94 (dd, J = 8.0, 1.5 Hz, 1H), 6.86 (dd, J = 8.5, 1.0 Hz, 1H), 6.80 (td, J = 7.5, 1.0 Hz, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 165.1, 157.3, 150.0, 146.4, 137.7, 134.1, 134.0, 131.50, 131.46, 128.7, 125.5, 124.6, 123.8, 121.2, 120.6, 111.0, 55.9 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S_2^+$: 342.0617; found: 342.0618.

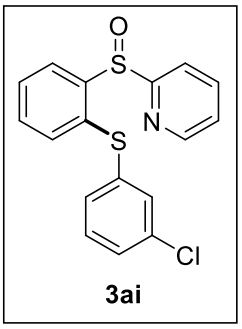
2-((2-((4-chlorophenyl)thio)phenyl)sulfinyl)pyridine (3ah)



3ah

Yellow liquid; yield 92 mg (52%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.54 (d, J = 4.8 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.83 (td, J = 7.6, 1.6 Hz, 1H), 7.47 (t, J = 7.6, 1H), 7.38 (td, J = 7.5, 1.6 Hz, 1H), 7.35–7.26 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.1, 149.9, 146.2, 137.9, 134.4, 134.2, 133.9, 133.3, 131.8, 131.6, 129.4, 129.0, 125.7, 124.7, 120.3 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{13}ClNOS_2^+$: 346.0122; found: 346.0121.

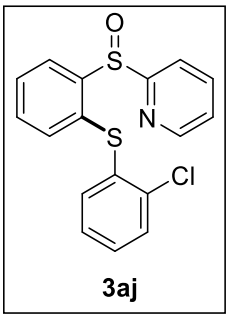
2-((2-((3-chlorophenyl)thio)phenyl)sulfinyl)pyridine (3ai)



3ai

Yellow liquid; yield 112 mg (64%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.52 (d, J = 5.2 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.80 (td, J = 7.6, 1.6 Hz, 1H), 7.53 (td, J = 7.6, 1.6 Hz, 1H), 7.45–7.39 (m, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.18–7.16 (m, 2H), 7.07–7.03 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.0, 149.9, 147.0, 138.1, 137.9, 135.0, 134.9, 132.9, 131.9, 130.1, 129.6, 129.1, 127.5, 127.0, 125.9, 124.8, 120.5 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{13}ClNOS_2^+$: 346.0122; found: 346.0123.

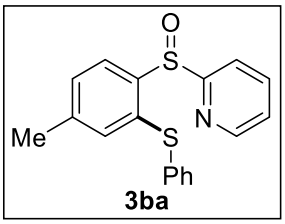
2-((2-((2-chlorophenyl)thio)phenyl)sulfinyl)pyridine (3aj)



3aj

Yellow liquid; yield 52 mg (30%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.51 (d, J = 4.0 Hz, 1H), 8.06 (dd, J = 8.0, 1.2 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.75 (td, J = 8.0, 1.6 Hz, 1H), 7.57 (td, J = 7.6, 1.2 Hz, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (dd, J = 8.0, 1.2 Hz, 2H), 7.25–7.20 (m, 1H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.03 (td, J = 7.6, 1.2 Hz, 1H), 6.79 (dd, J = 8.0, 1.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 164.6, 150.1, 147.3, 137.6, 135.4, 135.1, 133.5, 132.1, 131.8, 130.5, 129.8, 129.7, 127.8, 127.2, 126.1, 124.7, 121.0 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{13}ClNOS_2^+$: 346.0122; found: 346.0123.

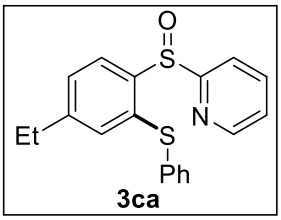
2-((4-methyl-2-(phenylthio)phenyl)sulfinyl)pyridine (3ba)



3ba

Yellow liquid; yield 42 mg (26%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.53 (d, J = 4.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.77 (dd, J = 8.0, 1.6 Hz, 2H), 7.30–7.18 (m, 7H), 7.15 (s, 1H), 2.27 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.2, 149.9, 142.9, 142.4, 137.8, 135.6, 134.4, 134.2, 130.2, 129.9, 129.1, 127.0, 125.7, 124.6, 120.4, 21.2 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NOS_2^+$: 326.0668; found: 326.0667.

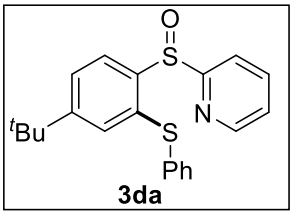
2-((4-ethyl-2-(phenylthio)phenyl)sulfinyl)pyridine (3ca)



3ca

Yellow liquid; yield 86 mg (51%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.52 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.77 (td, J = 8.0, 1.6 Hz, 1H), 7.30–7.15 (m, 8H), 2.58 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.3, 149.9, 148.5, 143.2, 137.8, 135.8, 134.2, 133.5, 130.1, 129.1, 128.8, 126.9, 125.8, 124.6, 120.4, 28.5, 15.0 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{19}H_{18}NOS_2^+$: 340.0824; found: 340.0829.

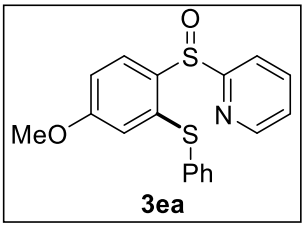
2-((4-(*tert*-butyl)-2-(phenylthio)phenyl)sulfinyl)pyridine (3da)



3da

Brown liquid; yield 74 mg (40%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.54 (d, J = 4.0 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.79 (td, J = 7.6, 1.6 Hz, 1H), 7.48 (dd, J = 8.4, 2.0 Hz, 1H), 7.36 (d, J = 1.6 Hz, 1H), 7.27–7.21 (m, 4H), 7.21–7.14 (m, 2H), 1.21 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.1, 155.3, 149.9, 143.1, 137.7, 135.9, 133.6, 131.5, 129.7, 129.1, 126.8, 126.3, 125.6, 124.6, 120.5, 35.0, 30.9 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{21}H_{22}NOS_2^+$: 368.1137; found: 368.1138.

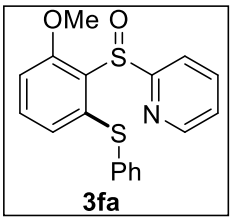
2-((4-methoxy-2-(phenylthio)phenyl)sulfinyl)pyridine (3ea)



3ea

Brown liquid; yield 52 mg (30%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.57 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 6.0 Hz, 1H), 7.83 (td, J = 7.6, 1.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.36–7.24 (m, 6H), 6.92 (dd, J = 6.8, 2.0 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 162.1, 159.4, 149.9, 137.8, 137.5, 136.5, 134.7, 131.3, 129.3, 127.7, 127.6, 124.5, 120.2, 117.8, 114.6, 55.5 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S_2^+$: 342.0617; found: 342.0618.

2-((2-methoxy-6-(phenylthio)phenyl)sulfinyl)pyridine (3fa)

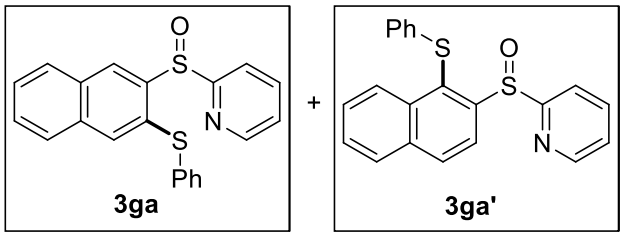


3fa

Yellow liquid; yield 28 mg (16%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.51 (d, J = 4.8 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.90 (td, J = 8.0, 2.0 Hz, 1H), 7.46 (dd, J = 7.6, 2.0 Hz, 2H), 7.40–7.32 (m, 3H), 7.30–7.23 (m, 2H), 6.68 (t, J = 8.0 Hz, 2H), 3.60 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 164.8, 159.3, 149.1, 143.2, 136.6, 133.7, 133.50, 133.48, 130.2, 129.4, 128.3, 123.5, 122.9, 121.6, 110.3, 56.0 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S_2^+$: 342.0617; found: 342.0618.

2-((3-(phenylthio)naphthalen-2-yl)sulfinyl)pyridine (3ga) +

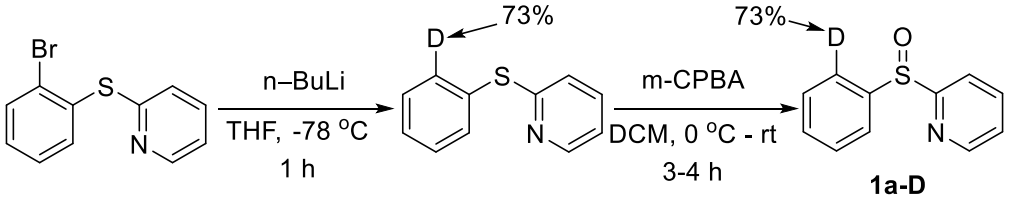
2-((1-(phenylthio)naphthalen-2-yl)sulfinyl)pyridine (3ga')



Yellow solid; yield 76 mg (molar ration of **3ga:3ga**' = 1:0.4, calculated by ^{13}C NMR; 42%); mp 130-131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.59 (s, 1H), 8.51 (d, *J* = 3.2 Hz, 1H), 8.45 (d, *J* = 4.0 Hz, 1H), 8.39 (d, *J* = 6.8 Hz, 1H), 8.12 (s, 2H), 8.02–.96 (m, 2H), 7.94–7.88 (m, 3H), 7.76–7.71 (m, 3H), 7.58–7.48 (m, 5H), 7.24–7.17 (m, 5H), 7.13–7.10 (m, 4H), 7.06 (d, *J* = 5.6 Hz, 1H), 6.92 (d, *J* = 6.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ = 165.1, 164.7, 150.0, 148.6, 143.5, 137.7, 136.5, 136.2, 135.3, 135.2, 134.7, 134.3, 132.7, 131.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 127.6, 127.5, 126.8, 126.7, 126.6, 126.5, 125.6, 124.8, 124.6, 121.3, 120.8, 120.7 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{21}H_{16}NOS_2^+$: 362.0668; found: 362.0671.

Mechanistic study experiments:

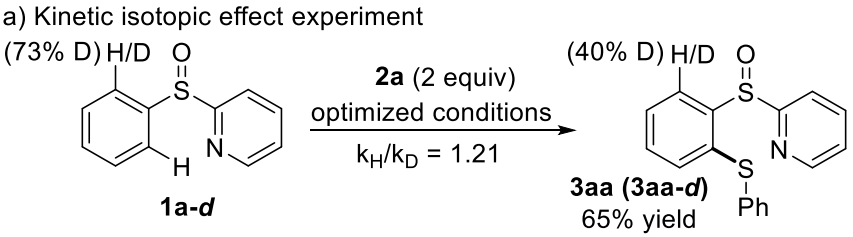
Synthesis of 2-((phenyl-2-d)sulfinyl)pyridine (1a-*d*)[17]



To a solution of 2-[(2-bromophenyl)thio]pyridine (900 mg, 3.37 mmol) in dry THF (10 mL), cooled to −78 °C and under nitrogen atmosphere, was added dropwise a 1.6 M solution of n-BuLi in hexanes (430 mg, 6.74 mmol, 2 equiv). The reaction mixture was stirred at −78 °C for 1 h then quenched with D_2O (7 mL). The reaction was allowed to reach room temperature and stirred for an extra 20 min. The reaction mixture was then diluted with H_2O (10 mL) and extracted with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was purified by column chromatography (n-hexane−EtOAc 4:1) gave the deuterated product as a colorless oil; yield: 500 mg (79%). This product was oxidized in

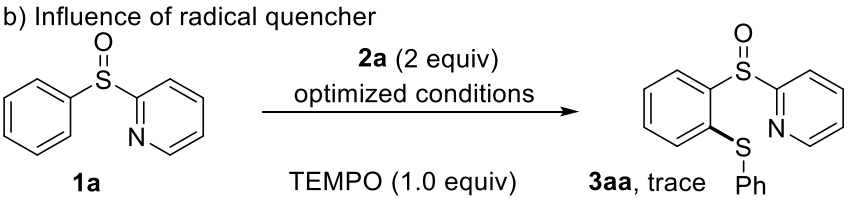
the presence of *m*-chloroperbenzoic acid (1 equiv) to give 2-((phenyl-2-d)sulfinyl)pyridine **(1a-*d*)** as a white solid; yield: 292 mg (55%).

Kinetic Isotope Effect (KIE) Experiment:



The thiolation reaction was performed according to the general procedure, in a oven-dried glass reaction tube, 2-((phenyl-2-d)sulfinyl)pyridine (**1a-d**) (50 mg, 0.25 mmol), phenyl disulfide (**2a,** 110 mg, 0.5 mmol, 2 equiv), Cerium (IV) ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] (160 mg, 0.3 mmol, 1.2 equiv), and $Pd(OAc)_2$ (6 mg, 0.03 mmol, 10 mol %) were dissolved in DCM (2.5 mL). The reaction mixture was stirred at 120 °C for 24 h before it was allowed to reach room temperature. The reaction mixture was quenched with water and extracted with DCM (3 x 10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (Hexane/EtOAc = 4/1) to provide 2-((2-(phenylthio)phenyl)sulfinyl)pyridine [**3aa** (**3aa-d**)] as a yellow solid; yield: 60 mg (76%). ^{1}H NMR (see at NMR spectra section) analysis of the isolated mixture of **3aa** and (**3aa-*d***) showed an average of 40% deuterium content at 8.01-7.97 ppm, indicating an intramolecular kinetic isotopic effect (k_H/k_D) of 1.21.

Reaction with TEMPO:

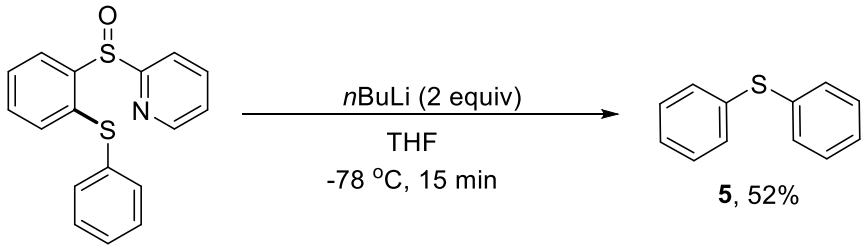


Deuterium Scrambling Experiment:

The thiolation reaction was performed according to the general procedure, in an oven-dried glass reaction tubes was charged with aryl 2-pyridyl sulfoxide (1a, 50 mg, 0.25 mmol), Cerium (IV) ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] (160 mg, 0.37 mmol, 1.2 equiv), and

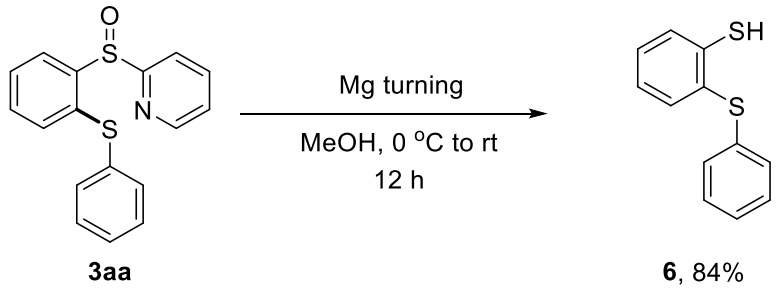
$Pd(OAc)_2$ (6 mg, 0.02 mmol, 10 mol %), DCM (2.5 mL) and then D_2O (0.02 mL, 1.25 mmol, 5 equiv) was added under atmospheric air. The reaction tube was closed with a screw cap. Later, the reaction mixture was stirred at 120 °C for 24 h before it was allowed to reach room temperature. The reaction mixture was quenched with water and extracted with DCM (3 x 5 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The ^1H NMR analysis of the reaction mixture indicated that no incorporation in **1a**.

Diphenylsulfane (5)[5]



To a solution of 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) (100 mg, 0.32 mmol) in dry THF (3.5 mL), cooled at –78 ºC under nitrogen atmosphere, was added a 1.6 M solution of BuLi in hexane (0.4 mL, 0.64 mmol). The reaction mixture was stirred at –78 ºC for 15 min before a saturated aqueous solution of NH_4Cl was added. The two phases were separated and the aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (hexane) to give diphenylsulfane **(5)** as colourless oil; yield: 30 mg (52%).

2-(phenylthio)benzenethiol (6) [5]

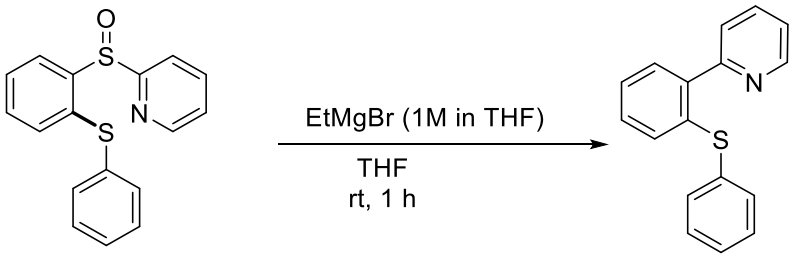


A suspension of the 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) (156 mg, 0.5 mmol) and Mg (243 mg, 10 mmol) in MeOH (5 mL) was stirred at 0 ºC for 2 h, and then at room temperature until consumption of the starting material (monitored by TLC monitoring). The

mixture was diluted with EtOAc (10 mL) and filtered through Celite. The filtrate was successively washed with aqueous saturated solution of $NaHCO_3$ (10 mL) and brine (10 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography to give the 2-(phenylthio)benzenethiol **(6)**.

White solid; yield 92 mg (84%); mp 120-121 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.49 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.33–7.27 (m, 2H), 7.26–7.20 (m, 4H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 140.4, 135.8, 135.0, 131.6, 129.34, 129.29, 129.2, 127.0, 126.6, 126.5 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{12}H_{11}S_2^+$: 219.0297; found: 219.0298.

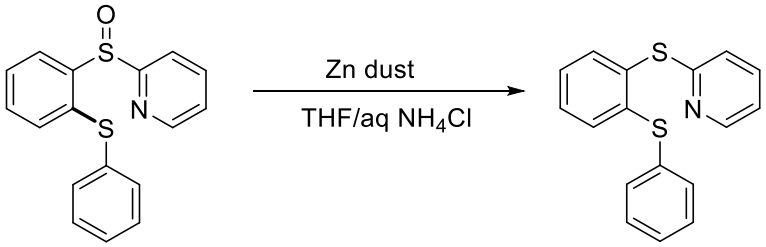
2-(2-(phenylthio)phenyl)pyridine (7)[16]



3aa **7**, 73%

To a solution of the 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) (100 mg, 0.32 mmol) in THF (10 mL) was added EtMgBr (47 mg, 1.1 equiv) drop wise. The reaction mixture was stirred for 1 h before cautiously adding sat. aq. NH_4Cl (10 mL) and extracting with EtOAc (3 x 20 mL). The combined organic layers were dried ($MgSO_4$) before concentrating under reduced pressure. The residue was purified by column chromatography (hexane:EtOAc 9:1) to give 2-(2-(phenylthio)phenyl)pyridine (**7)** as yellow liquid; yield: 62 mg (73%).

2-((2-(phenylthio)phenyl)thio)pyridine (8)[5]

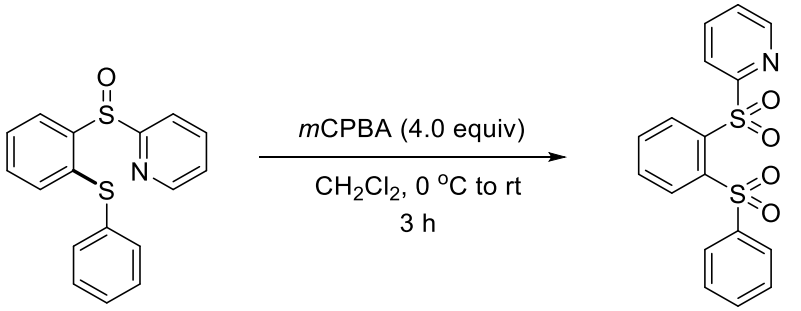


3aa **8**, 89%

A suspension of 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) (50 mg, 0.16 mmol) and Zn dust (775 mg, 74 equiv, 11.84 mmol) in a 1:1 mixture of THF/sat. aq NH_4Cl (5 mL) was stirred at room temperature for 12 h. The mixture was diluted with EtOAc (5 mL) and filtered through a pad of Celite. The filtrate was washed with sat. aq solution of NaCl, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (hexane:EtOAc 9:1) to give 2-((2-(phenylthio)phenyl)thio)pyridine (**8)**.

Yellow solid; yield 42 mg (89%); mp 77-78 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.45 (d, *J* = 4.5 Hz, 1H), 7.60 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44–7.42 (m, 2H), 7.38–7.33 (m, 3H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (td, *J* = 7.5, 1.5 Hz, 1H), 7.04–7.00 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 160.1, 149.7, 144.3, 136.7, 136.6, 133.8, 133.3, 130.0, 129.6, 129.5, 129.3, 128.3, 126.6, 121.4, 120.1 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{14}NS_2^+$: 296.0562; found: 296.0561.

2-((2-(phenylsulfonyl)phenyl)sulfonyl)pyridine (9)[4]



3aa **9**, 96%

To a solution of 2-((2-(phenylthio)phenyl)sulfinyl)pyridine (**3aa**) (35 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) at 0 ºC, was added *m*CPBA (77% wt, 80 mg, 0.44 mmol). The reaction mixture was stirred for 3 h, during which time the temperature was slowly allowed to raise from 0 ºC to room temperature. Then, saturated aqueous solution of $NaHCO_3$ was added and stirred for 30 minutes. Extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (hexane:EtOAc 7:3) to give the 2-((2 (phenylsulfonyl)phenyl)sulfonyl)pyridine (**9)**.

Colourless solid; yield 38 mg (96%); mp 194-195 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.67 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.53 (d, *J* = 4.5 Hz, 1H), 8.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.32 (d, *J* =

8.0 Hz, 1H), 8.01–7.98 (m, 3H), 7.90–7.85 (m, 2H), 7.60–7.57 (m, 1H), 7.53–7.46 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 159.6, 149.3, 141.4, 140.7, 137.61, 137.59, 134.5, 134.2, 133.7, 133.4, 132.9, 128.8, 128.2, 126.8, 121.9 ppm. HRMS (ESI-TOF) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{14}NO_4S_2^+$: 360.0359; found: 360.0358.

X-ray Crystallographic Analysis

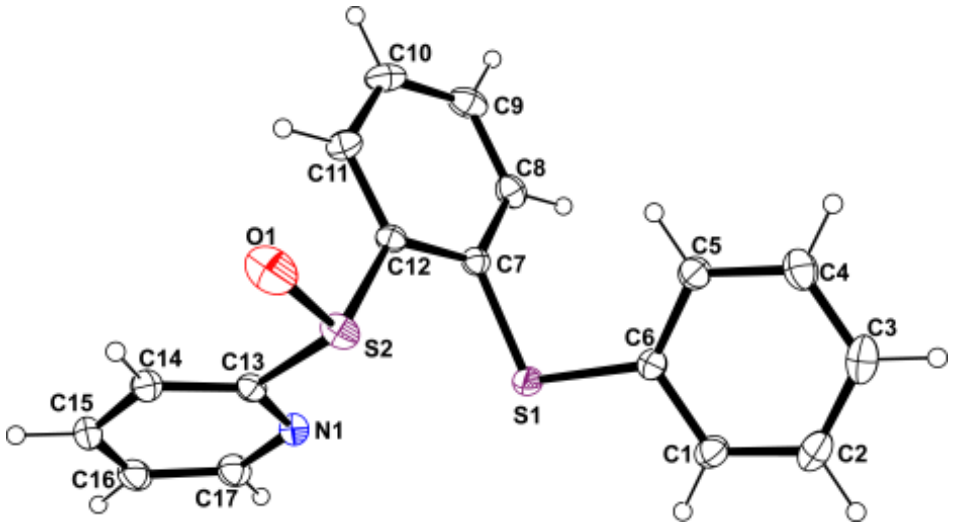


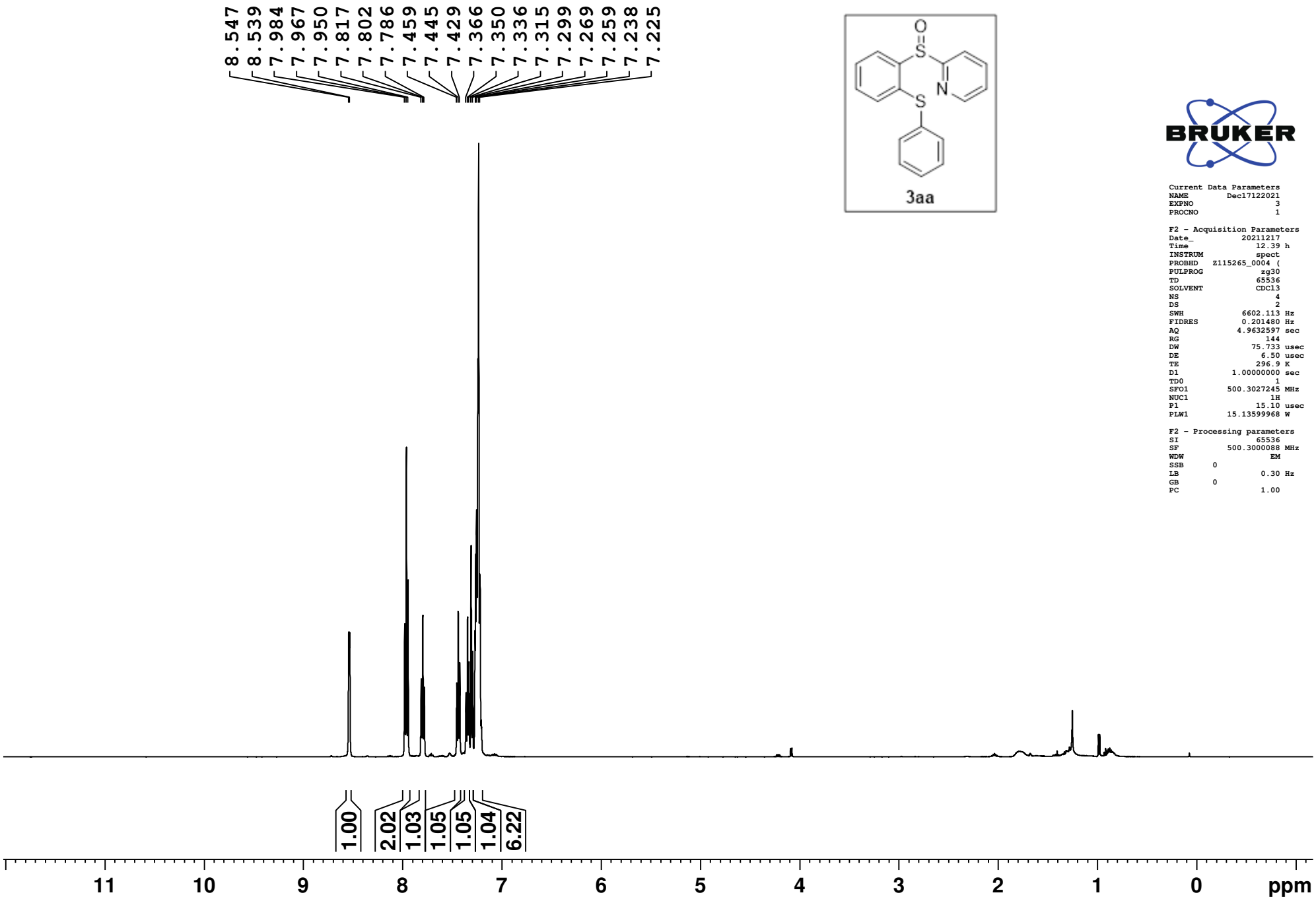
Figure S1. Molecular structure of compound **3aa** thermal ellipsoids is set at 30% probability and hydrogen atoms omitted for clarity.

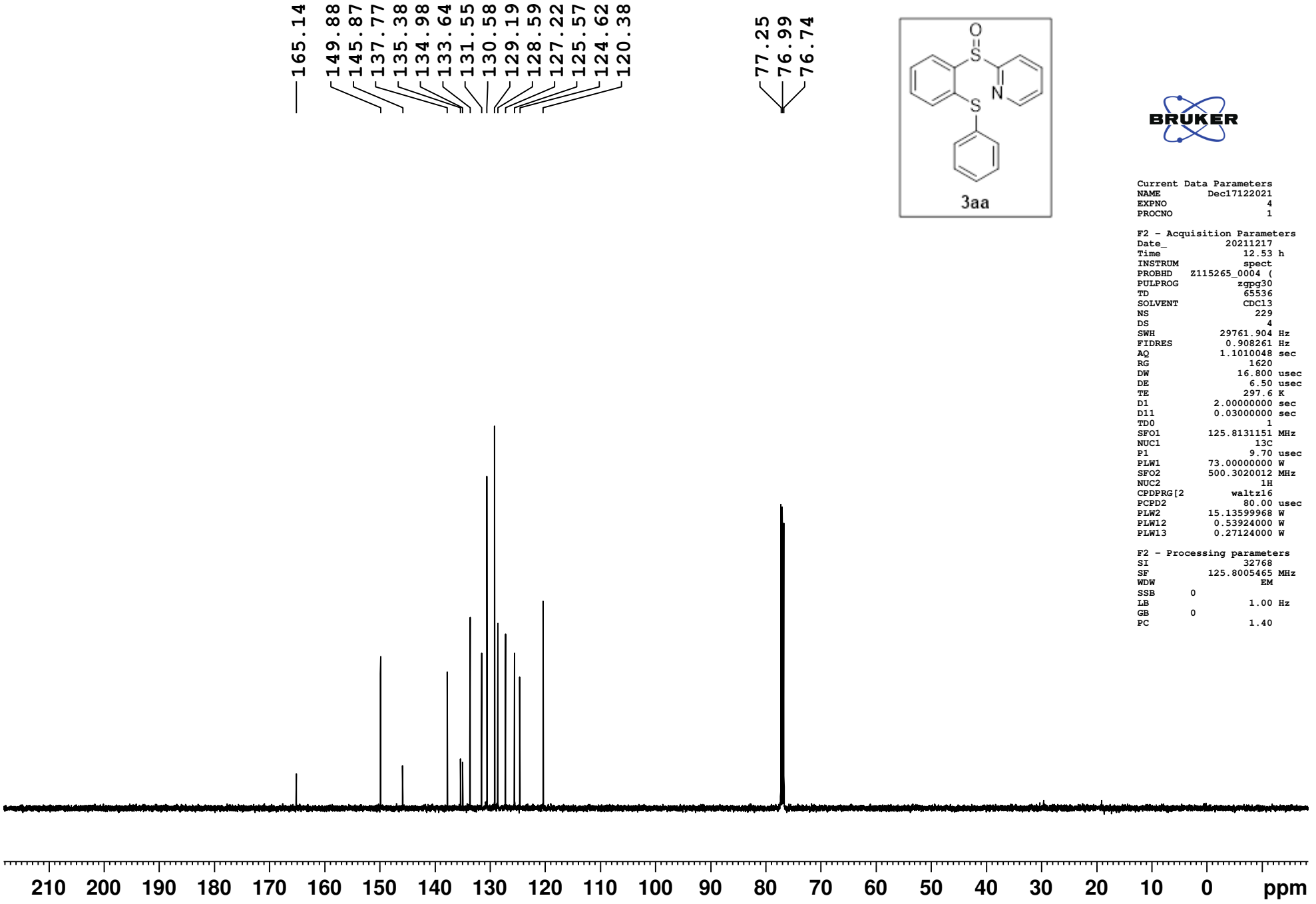
Table S1. Crystal data and structure refinements for **3aa**.

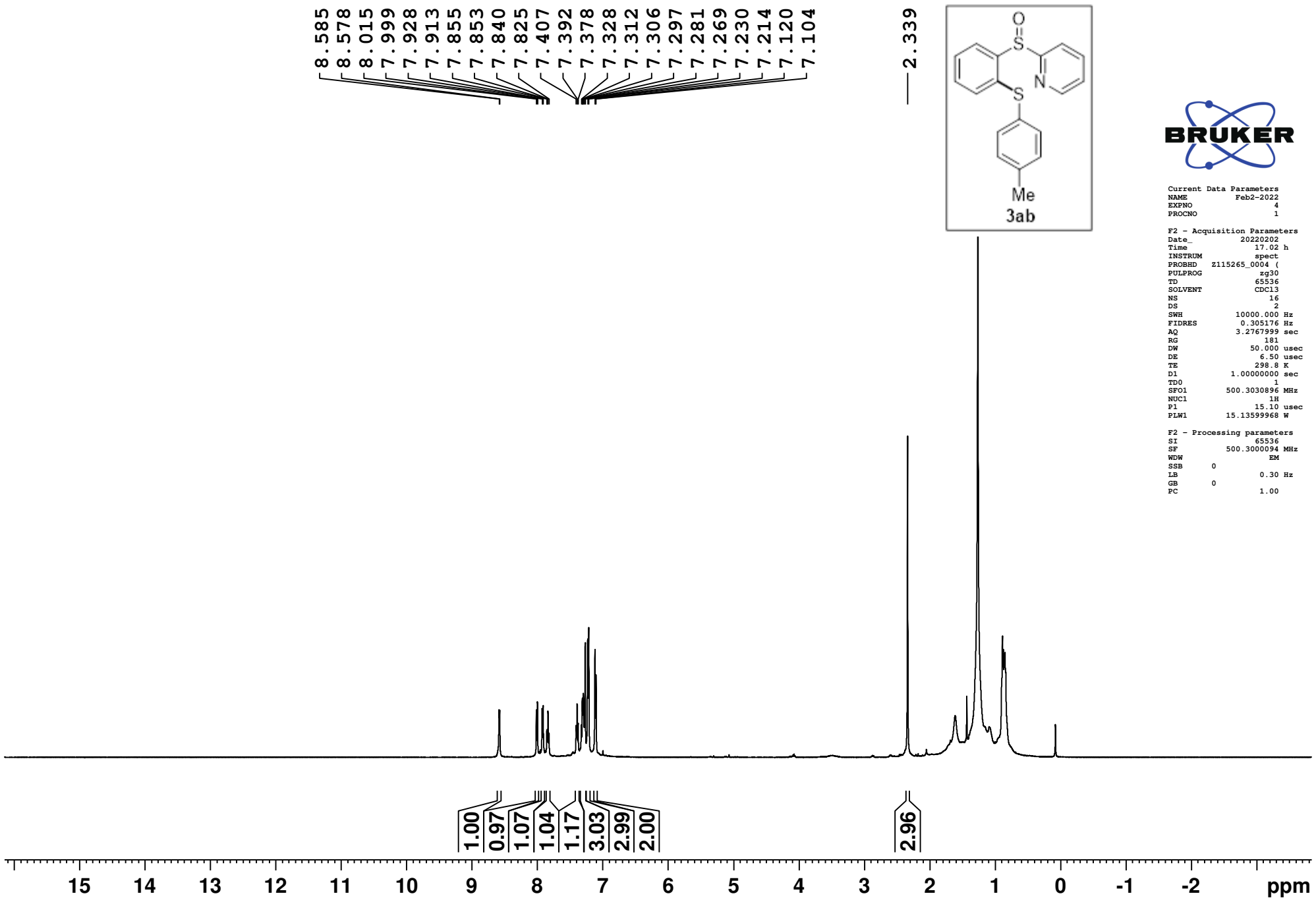
Compound	**3aa**
Formula	$C_{17}H_{13}NOS_2$
Fw	311.41
Crystal System	Monoclinic
Space Group	*P*21/*n*
a	13.973(2) Å
b	7.1655(9) Å
c	14.941(2) Å
α	90°
β	96.041(5)°
γ	90°
Volume	1487.7(4) Å3
Z	4
Density (calcd.)	1.390 Mg/m^3
Completeness	0.998
GOF (all data)	1.080
R_1 ($I>2\sigma(I)$)	0.0366
wR_2 (all data)	0.1006
CCDC No.	2166274

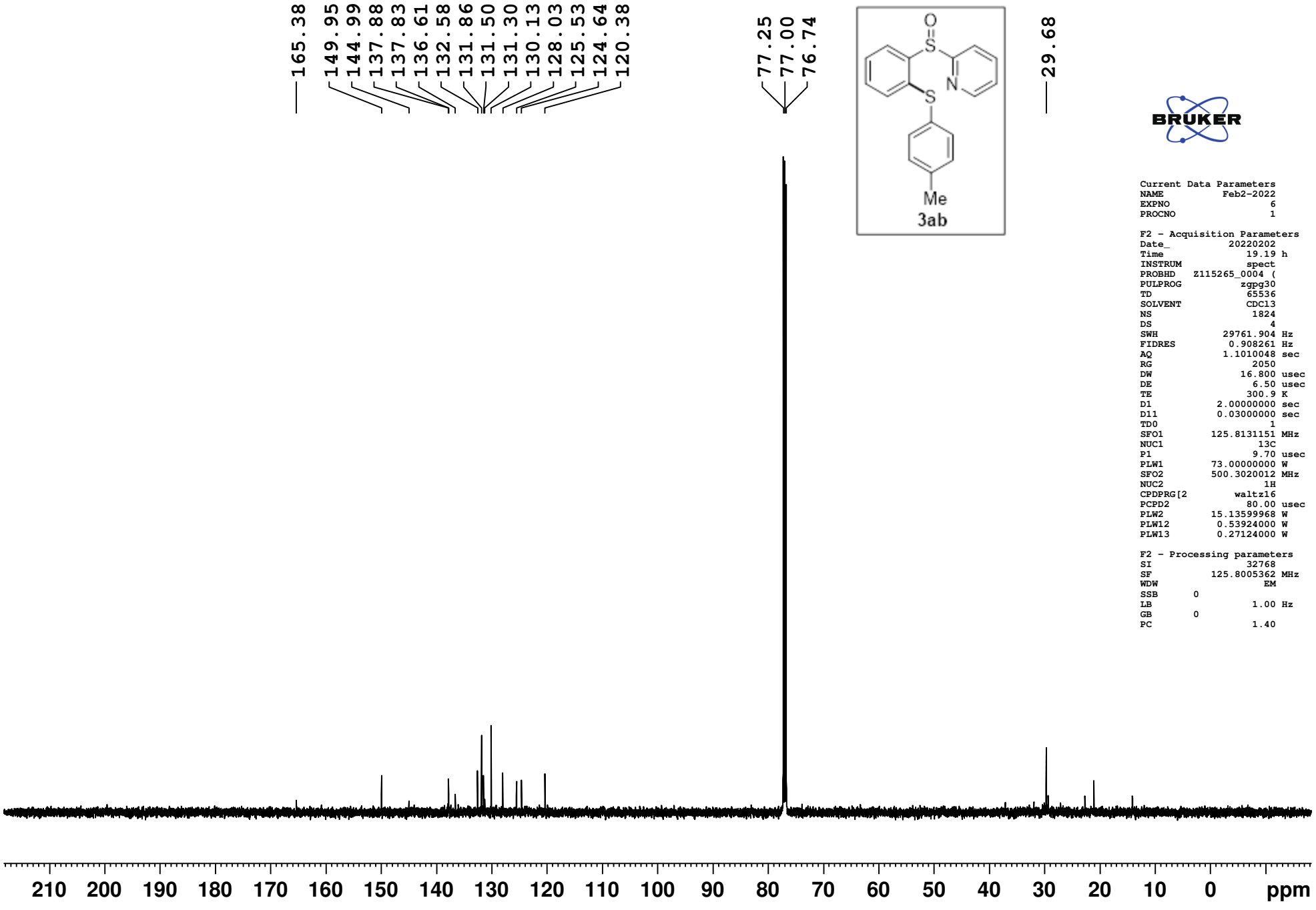
References

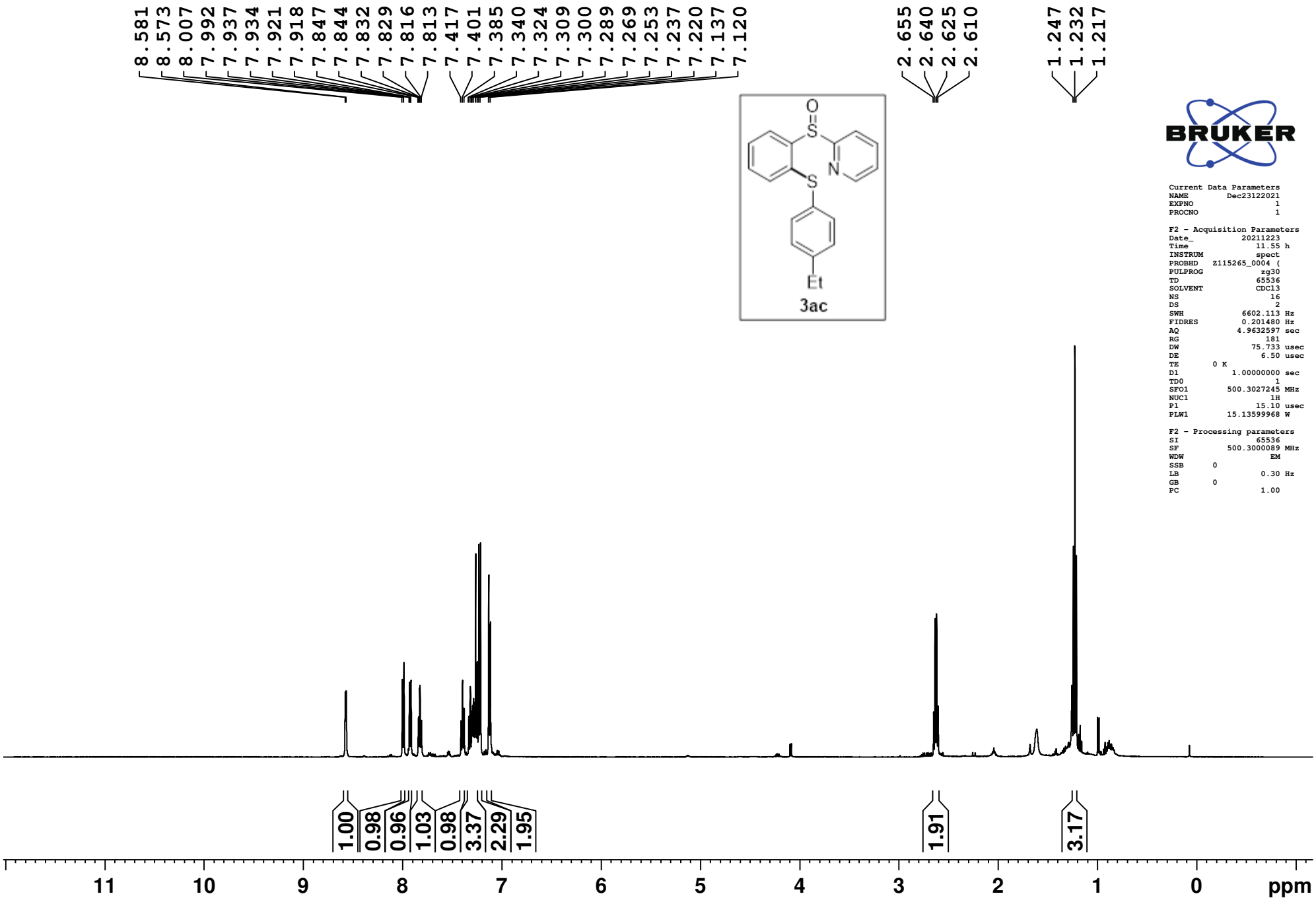
1. *SAINT-Plus, version 6.45*, Bruker AXS Inc. Madison, WI, 2003.
2. a) *SMART (version 5.625), SHELX-TL (version 6.12)*, Bruker AXS Inc. Madison, WI, 2000. b) G. M. Sheldrick, *SHELXS-97*, University of Gottingen, Germany, 1997.
3. G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingenn, Germany, 1997.
4. M. Yadav, R. S. Jat, B. Sarma and M. Bhanuchandra, *Synthesis*, 2021, **53**, 2269-2276.
5. (a) A. García-Rubia, M. Á. Fernández-Ibáñez, R. G. Arrayás, and J. C. Carretero, *Chem. Eur. J.*, 2011, **17**, 3567 – 3570, (b) H. Richter, S. Beckendorf and O. G. MancheÇo, *Advanced Synthesis & Catalysis*, 2011, **353**, 295-302.
6. J. K. Vandavasi, W.-P. Hu, C.-Y. Chen and J.-J. Wang, *Tetrahedron*, 2011, **67**, 8895-8901.
7. M. Oka, R. Kozako and H. Iida, *Synlett*, 2021, **32**, 1227-1230.
8. Y. Liu, H. Wang, C. Wang, J.-P. Wan and C. Wen, *RSC Adv.*, 2013, **3**, 21369–21372.
9. W. Ouyang, X. Cai, X. Chen, J. Wang, J. Rao, Y. Gao, Y. Huo, Q. Chen and X. Li, *Chem. Commun.*, 2021, **57**, 8075-8078.
10. L. Ji, J. Qiao, J. Liu, M. Tian, K. Lu and X. Zhao,*Tetrahedron Letters*, 2021, **75,** 153202.
11. N. Spiliopoulou and C. G. Kokotos, *Green Chem.*, 2021, **23**, 546-551
12. X. Tui, Y. Zhu, R. Dai, C. Huang, C. Wang, D. Si, X. Wang, X. Zhang, H. Wen, W. Li, and J. Liu, *Asian Journal of Organic Chemistry*, 2021, **10**, 793-798.
13. F. Takahashi, K. Nogi, and H. Yorimitsu, *Eur. J. Org. Chem*. 2020, **20**, 3009–3012.
14. M. Gennari, I. Bassanetti and L. Marchiò, *Polyhedron*, 2010, **29**, 361–371.
15. M. Chaitanya and P. Anbarasan, *Org. Lett*., 2018, **20**, 3362–3366.
16. (a) M. Sun, Z. Wang, J. Wang, P. Guo, X. Chena and Y.-M. Li, *Org. Biomol. Chem*., 2016, **14**, 10585–10588; (b) W. M. Dean, M. Šiaučiulis, T. E. Storr, W. Lewis, and R. A. Stockman, *Angew. Chem. Int. Ed*., 2016, **55**, 10013-10016.
17. J. A. Romero-Revilla, A. García-Rubia, R. G. Arrayás, M. Á. Fernández-Ibáñez and J. C. Carretero, *J. Org. Chem.*, 2011, **76**, 9525-9530.


8.547
8.539
7.984
7.967
7.950
7.817
7.802
7.786
7.459
7.445
7.429
7.366
7.350
7.336
7.315
7.299
7.269
7.259
7.238
7.225
O
S
N
S
3aa
BRUKER
Current Data Parameters
NAME Dec17122021
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211217
Time 12.39 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6602.113 Hz
FIDRES 0.201480 Hz
AQ 4.9632597 sec
RG 144
DW 75.733 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
SFO1 500.3027245 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
2.02
1.03
1.05
1.05
1.04
6.22
11
10
9
8
7
6
5
4
3
2
1
0
ppm

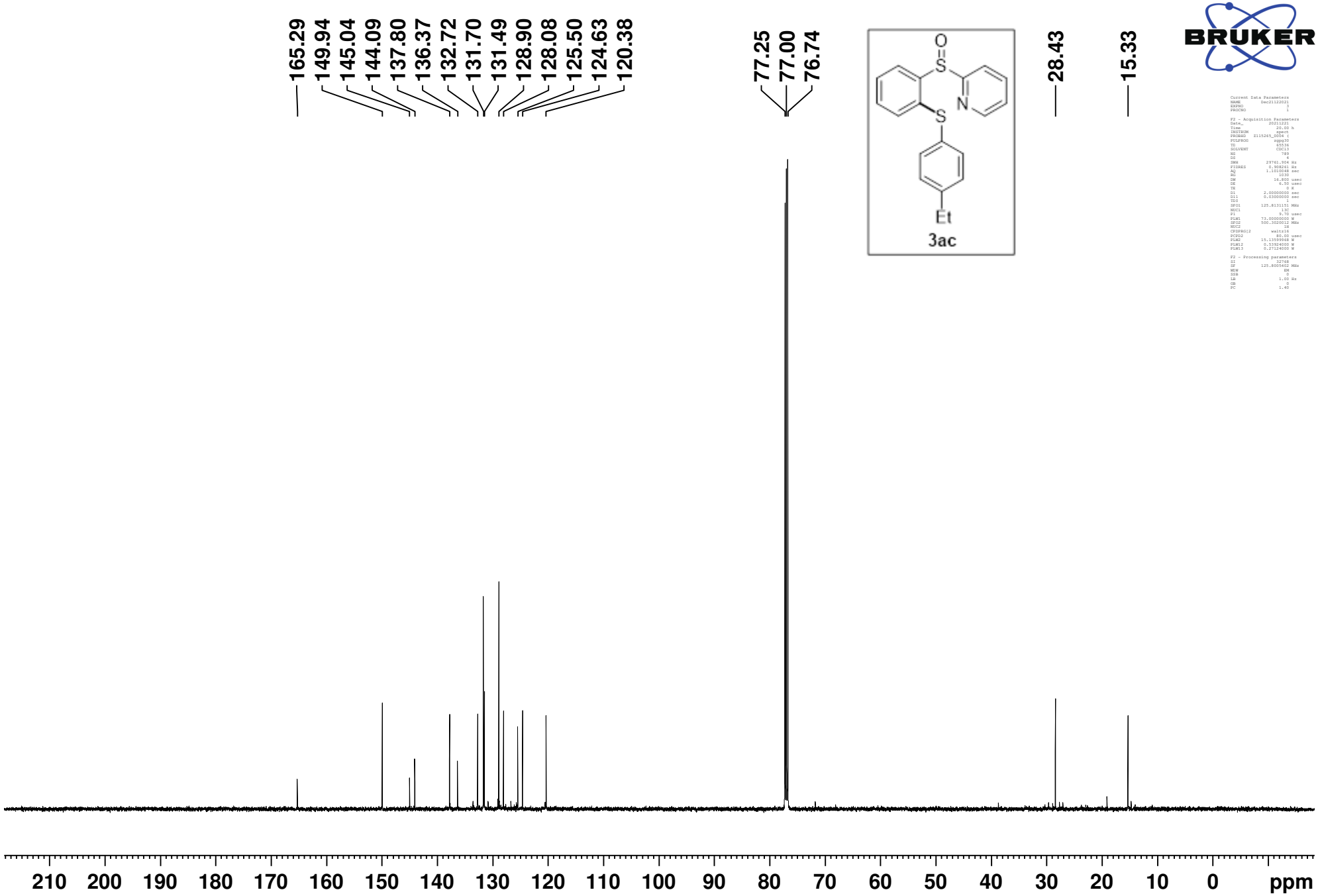

165.14
149.88
145.87
137.77
135.38
134.98
133.64
131.55
130.58
129.19
128.59
127.22
125.57
124.62
120.38
77.25
76.99
76.74
O
S
N
S
3aa
BRUKER
Current Data Parameters
NAME Dec17122021
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211217
Time 12.53 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 229
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 1620
DW 16.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005465 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

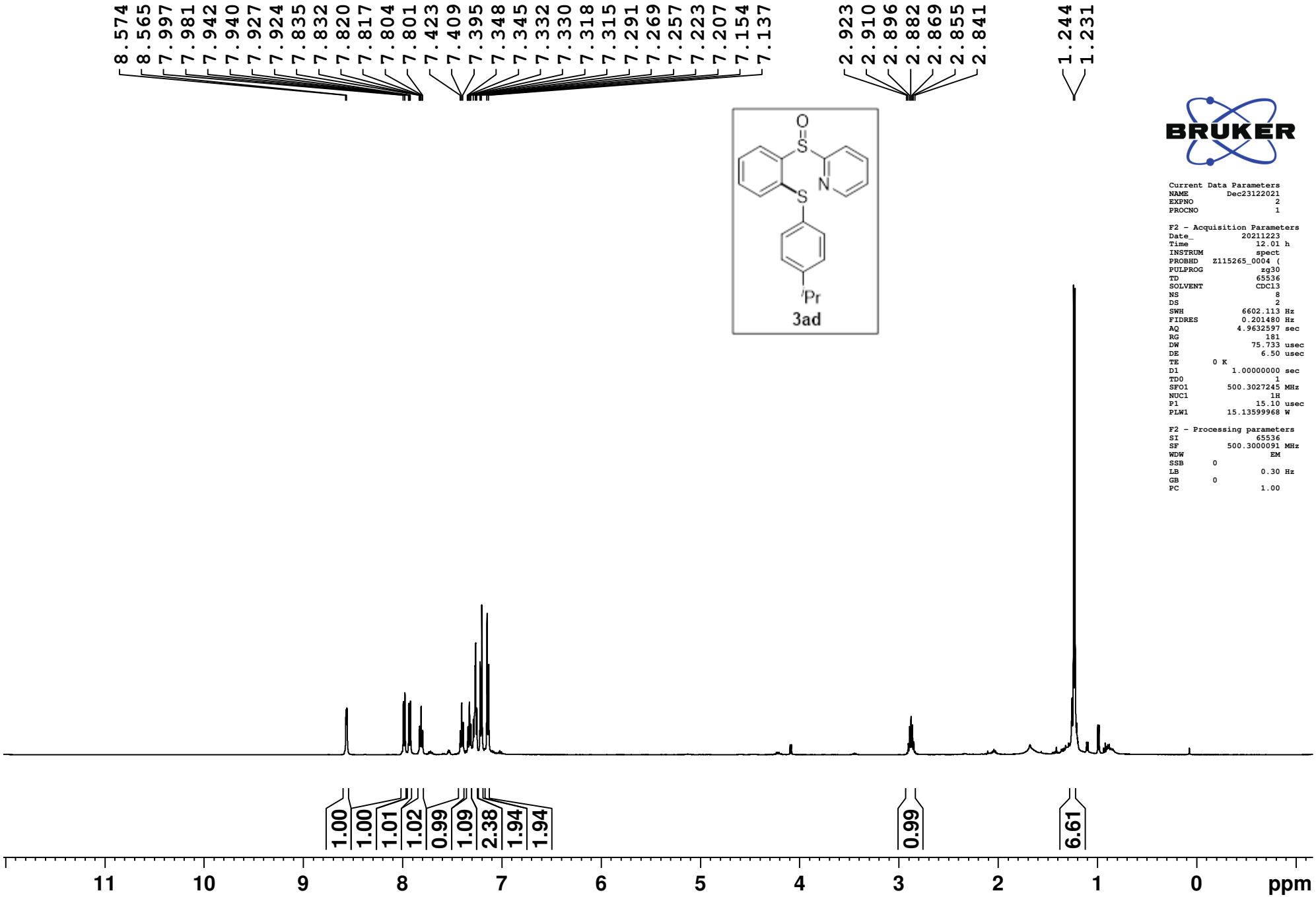

8.585
8.578
8.015
7.999
7.928
7.913
7.855
7.853
7.840
7.825
7.407
7.392
7.378
7.328
7.312
7.306
7.297
7.281
7.269
7.230
7.214
7.120
7.104
2.339
O
S
N
S
Me
3ab
BRUKER
Current Data Parameters
NAME Feb2-2022
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220202
Time 17.02 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 181
DW 50.000 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030896 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
0.97
1.07
1.04
1.17
3.03
2.99
2.00
2.96
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

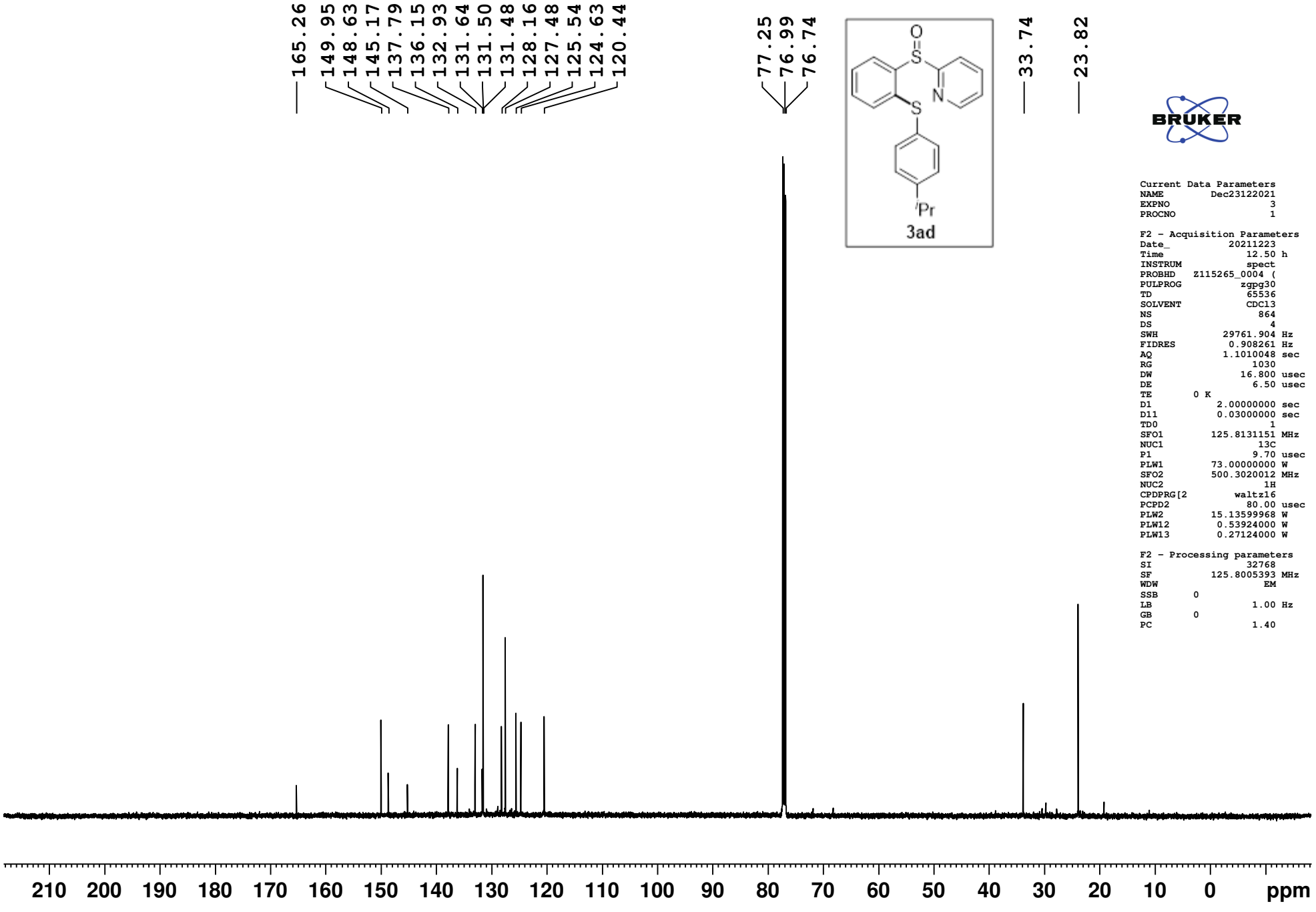

165.38
149.95
144.99
137.88
137.83
136.61
132.58
131.86
131.50
131.30
130.13
128.03
125.53
124.64
120.38
77.25
77.00
76.74
29.68
O
S
N
S
Me
3ab
BRUKER
Current Data Parameters
NAME Feb2-2022
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220202
Time 19.19 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1824
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 300.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005362 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

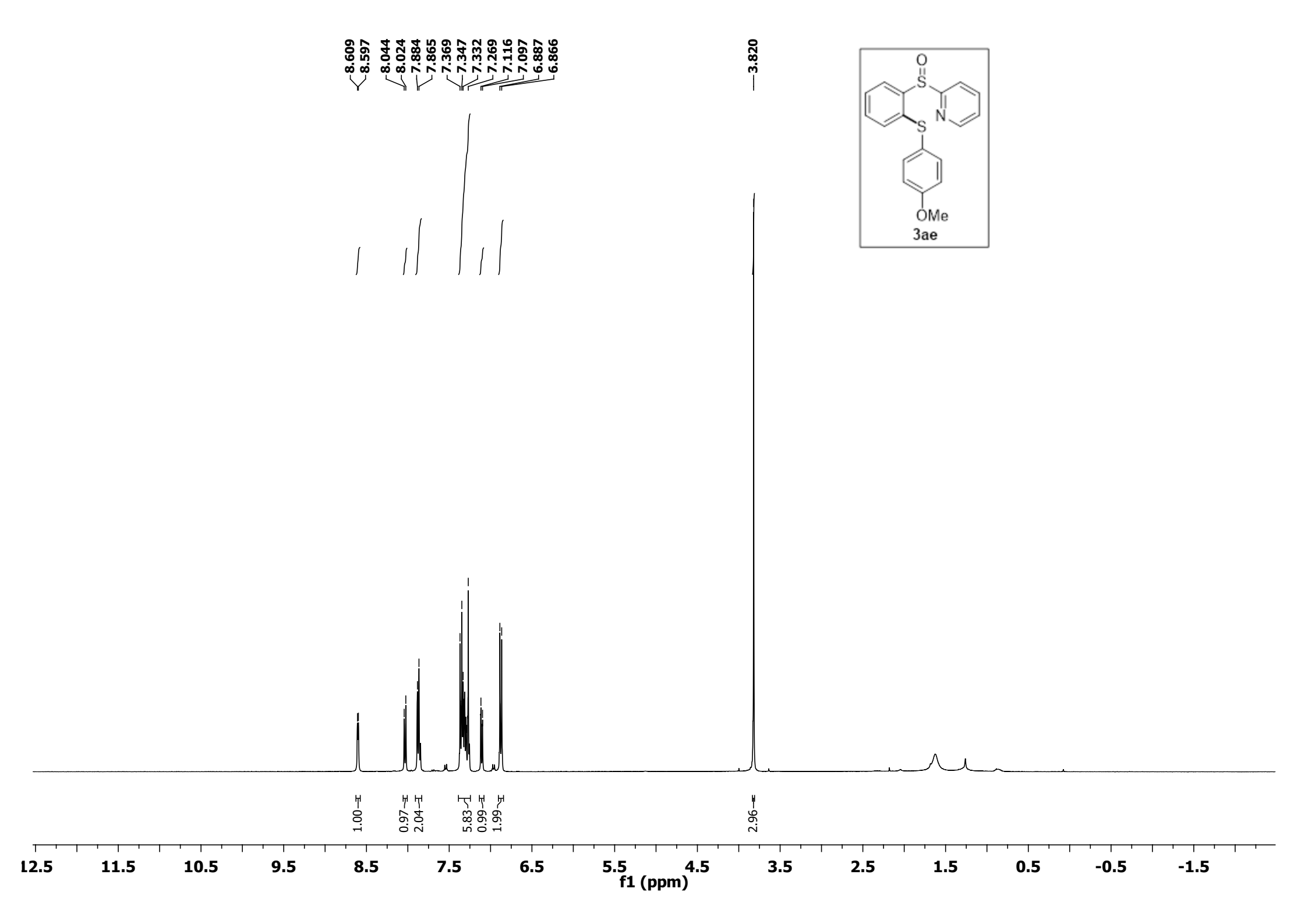

8.581
8.573
8.007
7.992
7.937
7.934
7.921
7.918
7.847
7.844
7.832
7.829
7.816
7.813
7.417
7.401
7.385
7.340
7.324
7.309
7.300
7.289
7.269
7.253
7.237
7.220
7.137
7.120
2.655
2.640
2.625
2.610
1.247
1.232
1.217
O
S
N
S
Et
3ac
BRUKER
Current Data Parameters
NAME Dec23122021
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211223
Time 11.55 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6602.113 Hz
FIDRES 0.201480 Hz
AQ 4.9632597 sec
RG 181
DW 75.733 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3027245 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
0.98
0.96
1.03
0.98
3.37
2.29
1.95
1.91
3.17
11
10
9
8
7
6
5
4
3
2
1
0
ppm

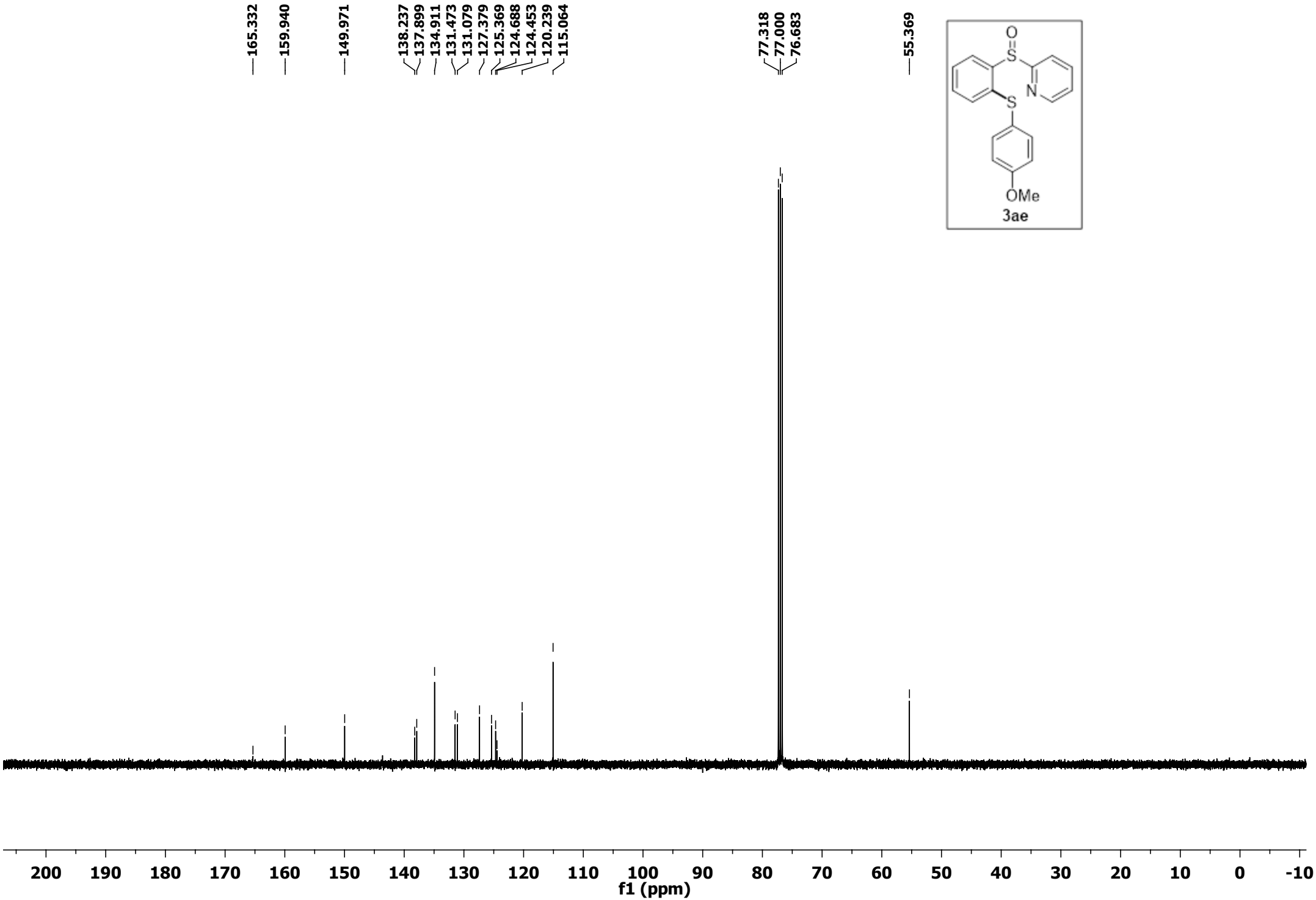
MY-3-146-III-13C

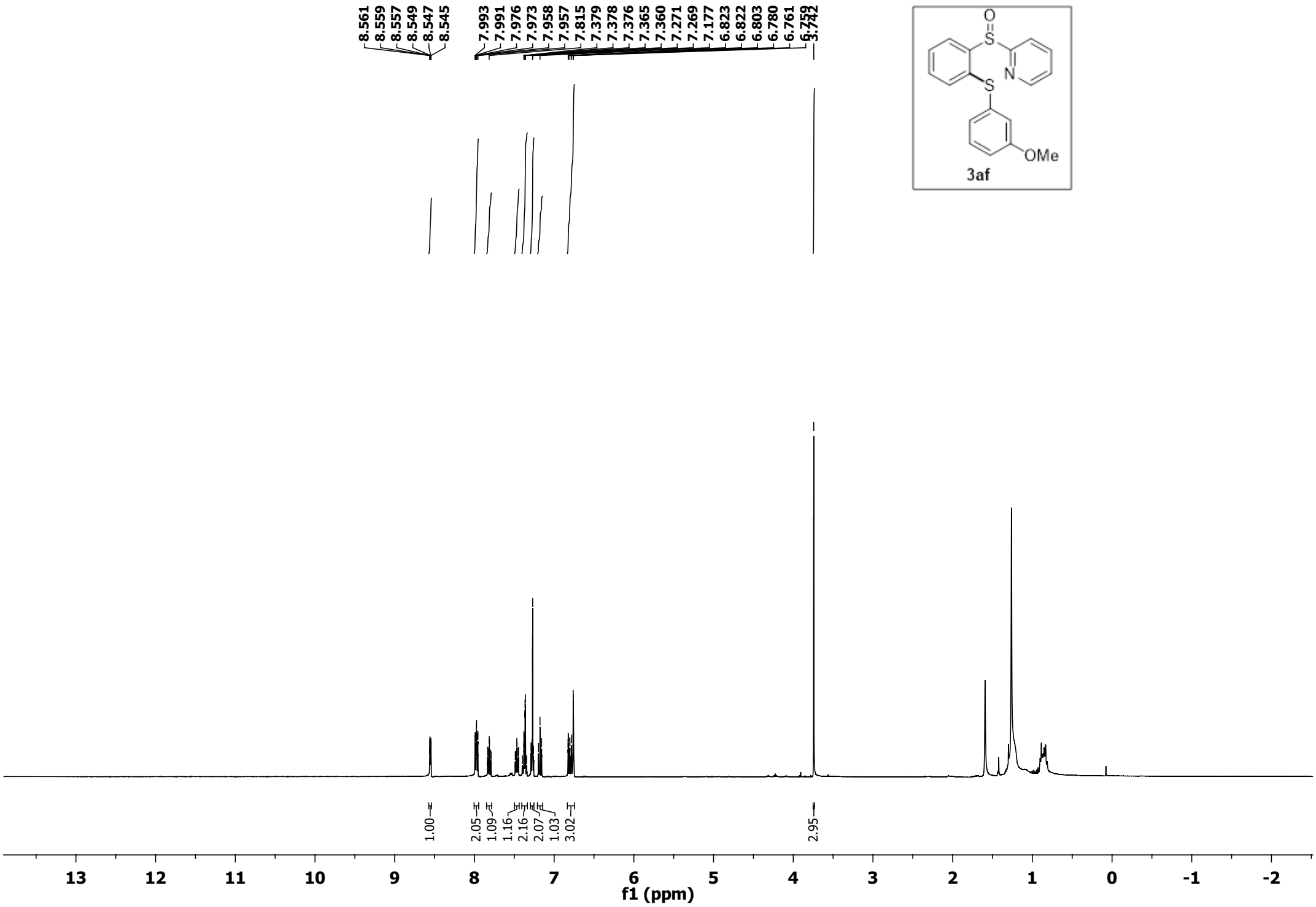


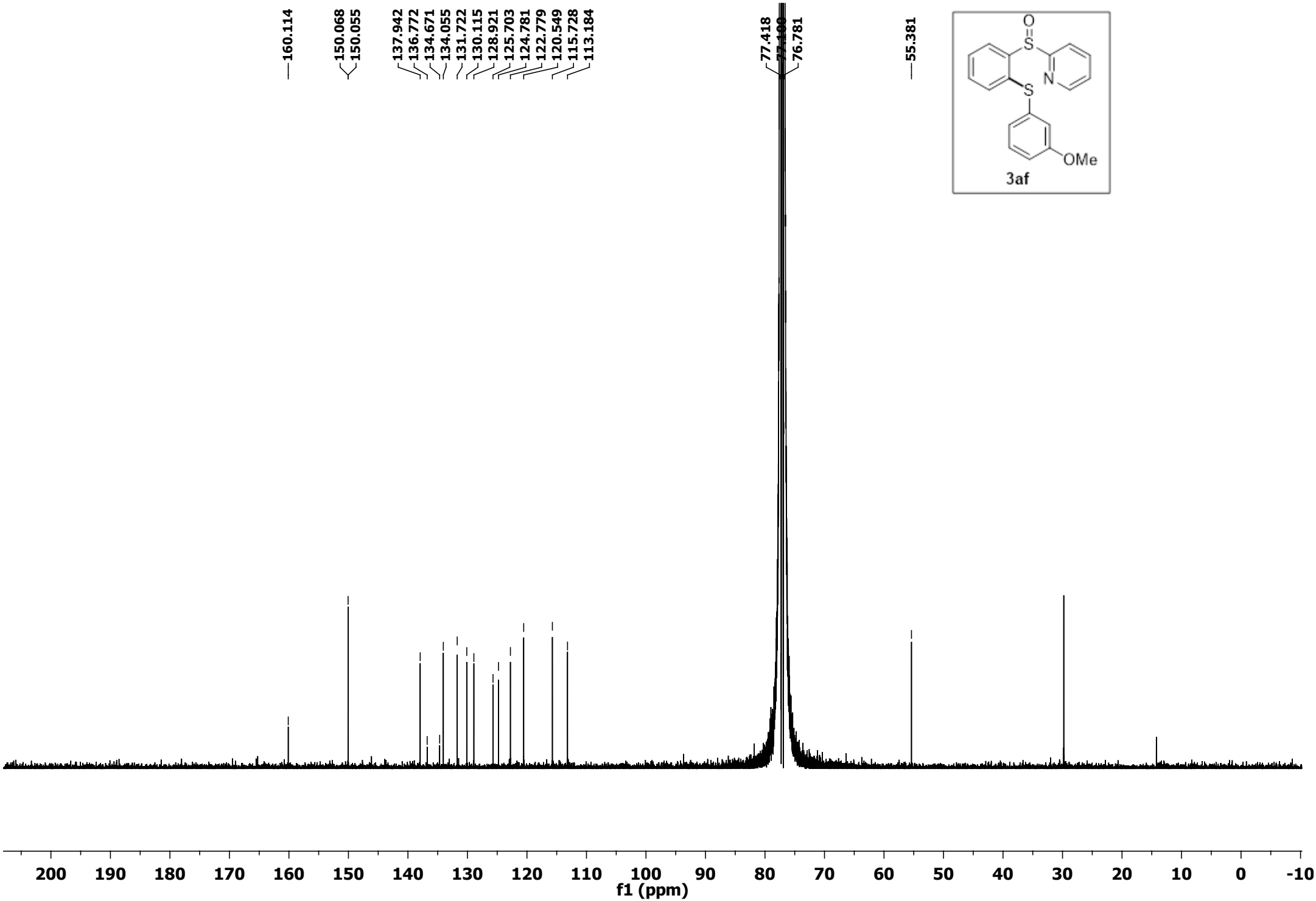

8.574
8.565
7.997
7.981
7.942
7.940
7.927
7.924
7.835
7.832
7.820
7.817
7.804
7.801
7.423
7.409
7.395
7.348
7.345
7.332
7.330
7.318
7.315
7.291
7.269
7.257
7.223
7.207
7.154
7.137
2.923
2.910
2.896
2.882
2.869
2.855
2.841
1.244
1.231
O
S
N
S
iPr
3ad
BRUKER
Current Data Parameters
NAME Dec23122021
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211223
Time 12.01 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6602.113 Hz
FIDRES 0.201480 Hz
AQ 4.9632597 sec
RG 181
DW 75.733 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3027245 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.00
1.01
1.02
0.99
1.09
2.38
1.94
1.94
0.99
6.61
11
10
9
8
7
6
5
4
3
2
1
0
ppm

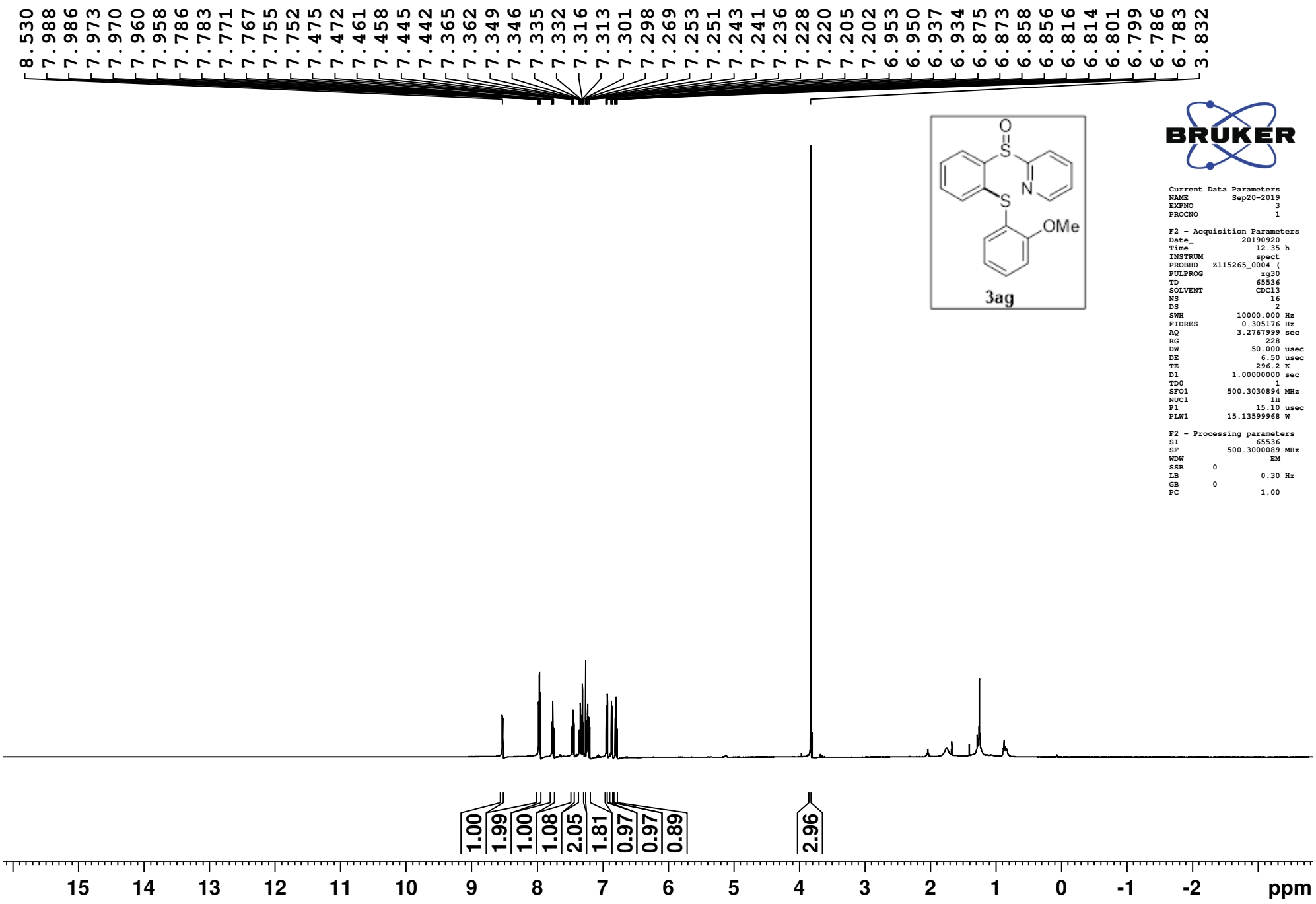

165.26
149.95
148.63
145.17
137.79
136.15
132.93
131.64
131.50
131.48
128.16
127.48
125.54
124.63
120.44
77.25
76.99
76.74
33.74
23.82
O
S
N
S
iPr
3ad
BRUKER
Current Data Parameters
NAME Dec23122021
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211223
Time 12.50 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 864
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 1030
DW 16.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.609
8.597
8.044
8.024
7.884
7.865
7.369
7.347
7.332
7.269
7.116
7.097
6.887
6.866
3.820
O
S
N
S
OMe
3ae
1.00
0.97
2.04
5.83
0.99
1.99
2.96
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


165.332
159.940
149.971
138.237
137.899
134.911
131.473
131.079
127.379
125.369
124.688
124.453
120.239
115.064
77.318
77.000
76.683
55.369
O
S
N
S
OMe
3ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

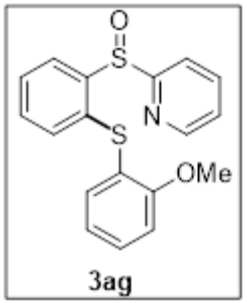

8.561
8.559
8.557
8.549
8.547
8.545
7.993
7.991
7.976
7.973
7.958
7.957
7.815
7.379
7.378
7.376
7.365
7.360
7.271
7.269
7.177
6.823
6.822
6.803
6.780
6.761
3.742
O
S
N
S
OMe
3af
1.00
2.05
1.09
1.16
2.16
2.07
1.03
3.02
2.95
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


160.114
150.068
150.055
137.942
136.772
134.671
134.055
131.722
130.115
128.921
125.703
124.781
122.779
120.549
115.728
113.184
77.418
77.100
76.781
55.381
O
S
N
S
OMe
3af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.530
7.988
7.986
7.973
7.970
7.960
7.958
7.786
7.783
7.771
7.767
7.755
7.752
7.475
7.472
7.461
7.458
7.445
7.442
7.365
7.362
7.349
7.346
7.335
7.332
7.316
7.313
7.301
7.298
7.269
7.253
7.251
7.243
7.241
7.236
7.228
7.220
7.205
7.202
6.953
6.950
6.937
6.934
6.875
6.873
6.858
6.856
6.816
6.814
6.801
6.799
6.786
6.783
3.832
O
S
N
S
OMe
3ag
BRUKER
Current Data Parameters
NAME Sep20-2019
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190920
Time 12.35 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 228
DW 50.000 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.99
1.00
1.08
2.05
1.81
0.97
0.97
0.89
2.96
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

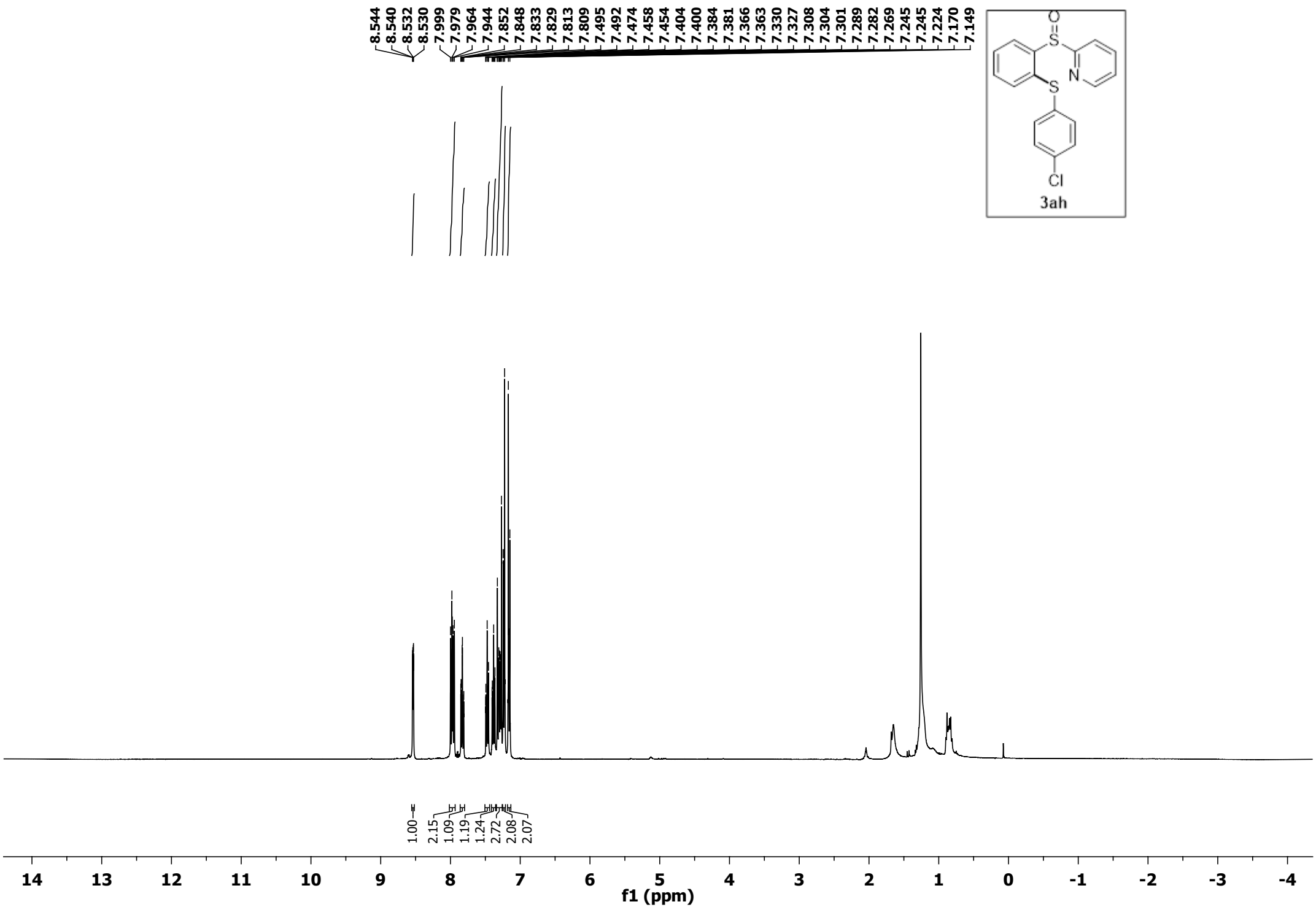
B-195

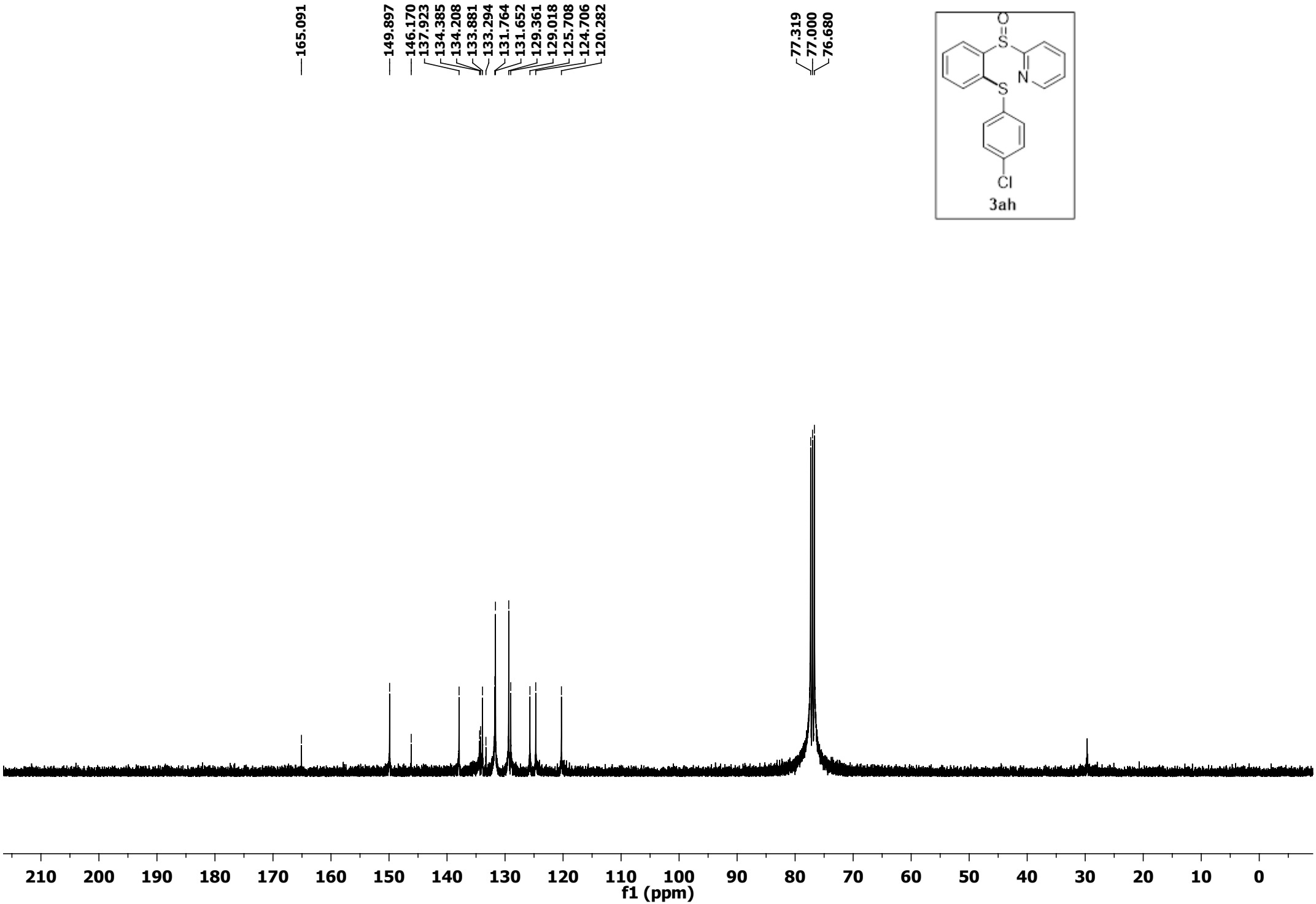
165.07
157.31
150.02
146.39
137.68
134.11
134.01
131.50
131.46
128.72
125.52
124.63
123.78
121.18
120.63
110.98
77.30
77.05
76.79
55.89

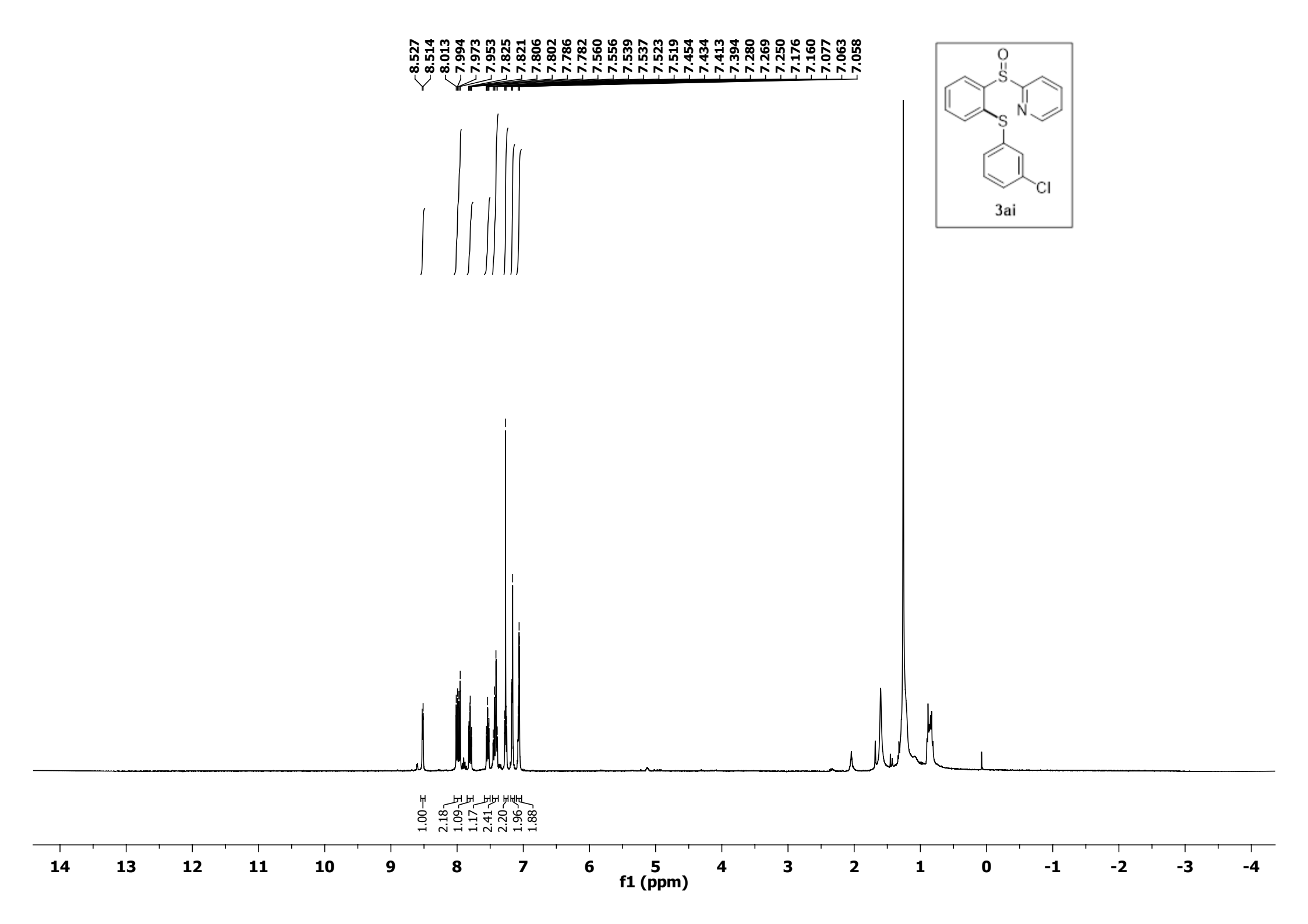


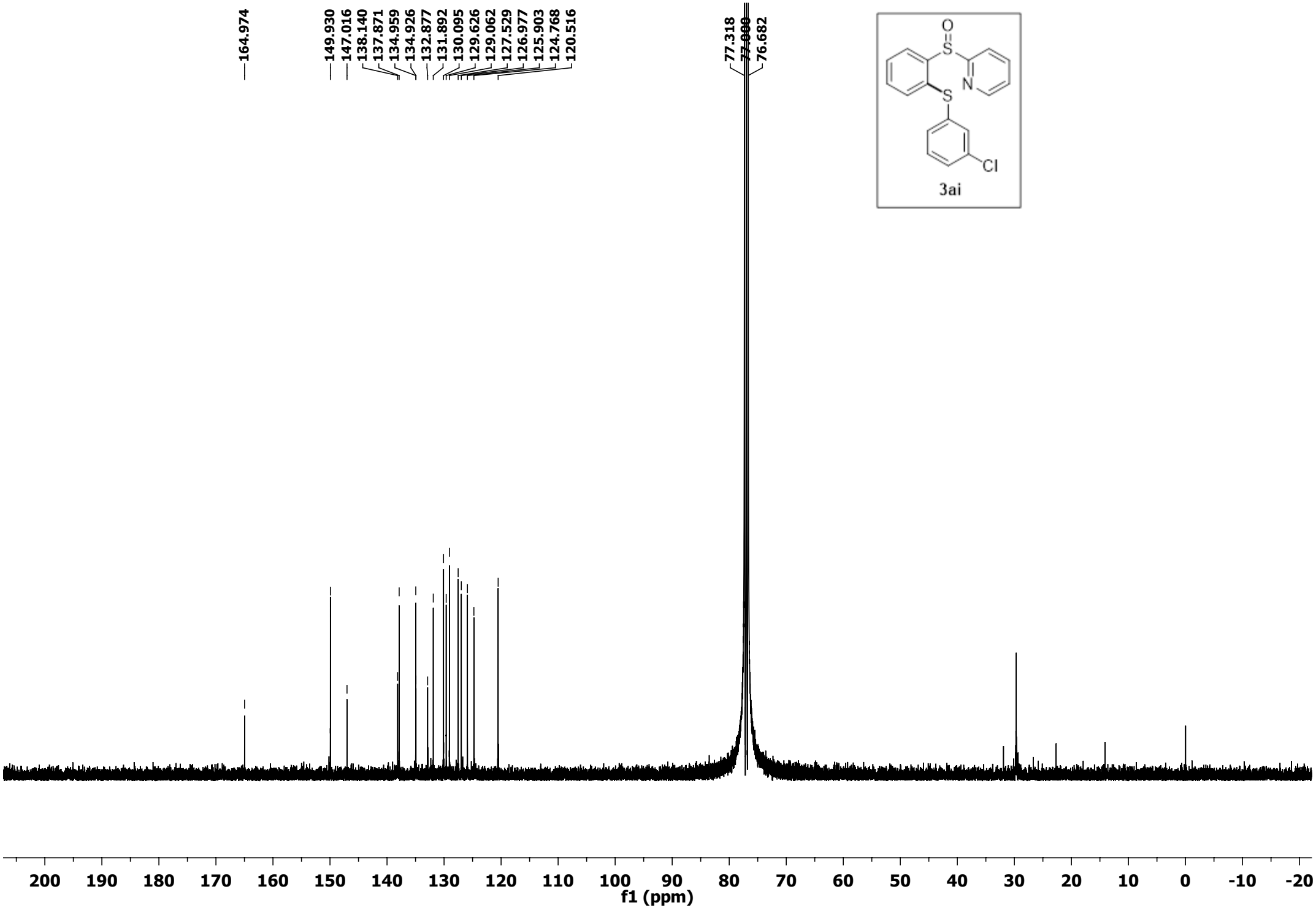
3ag

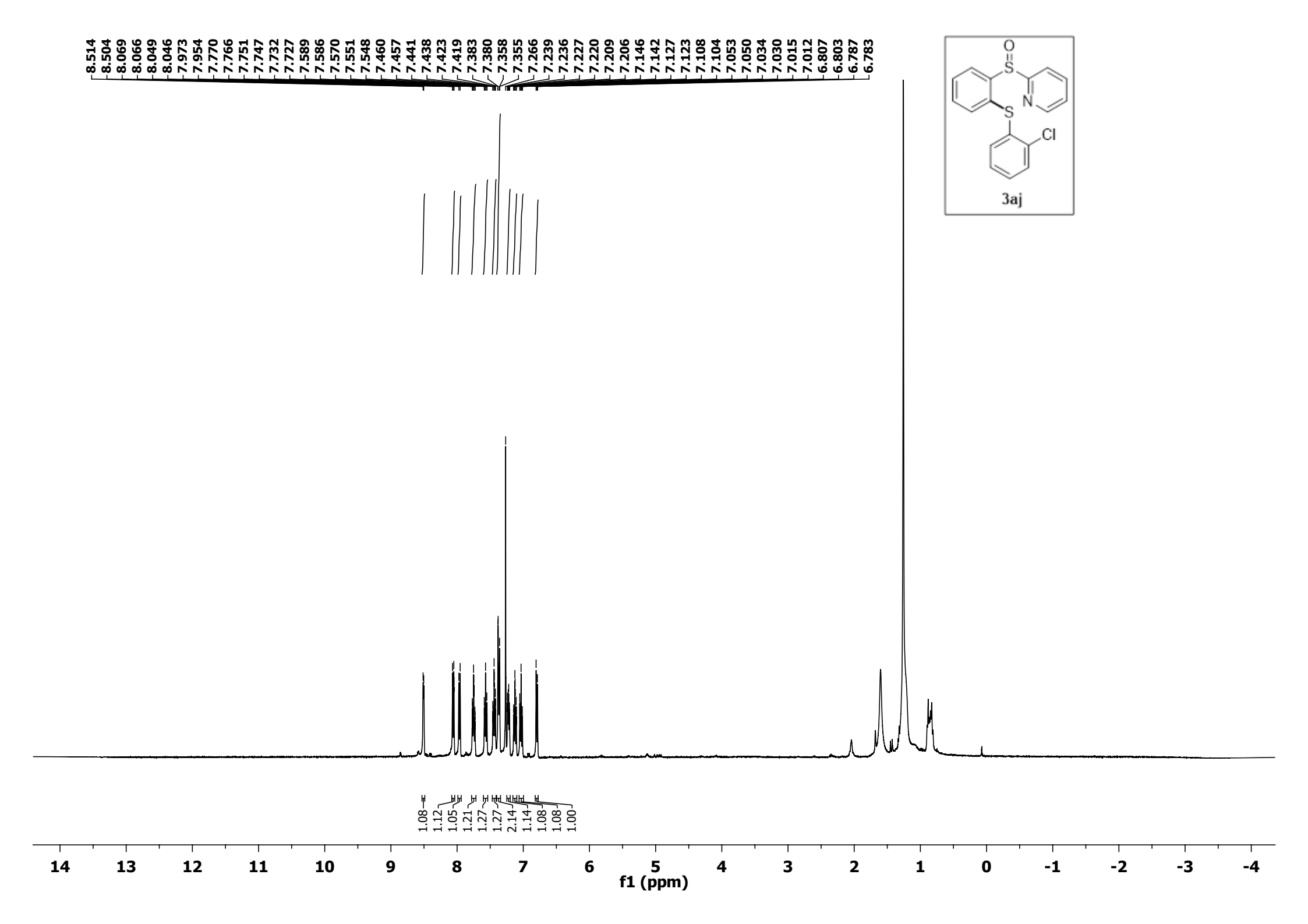
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

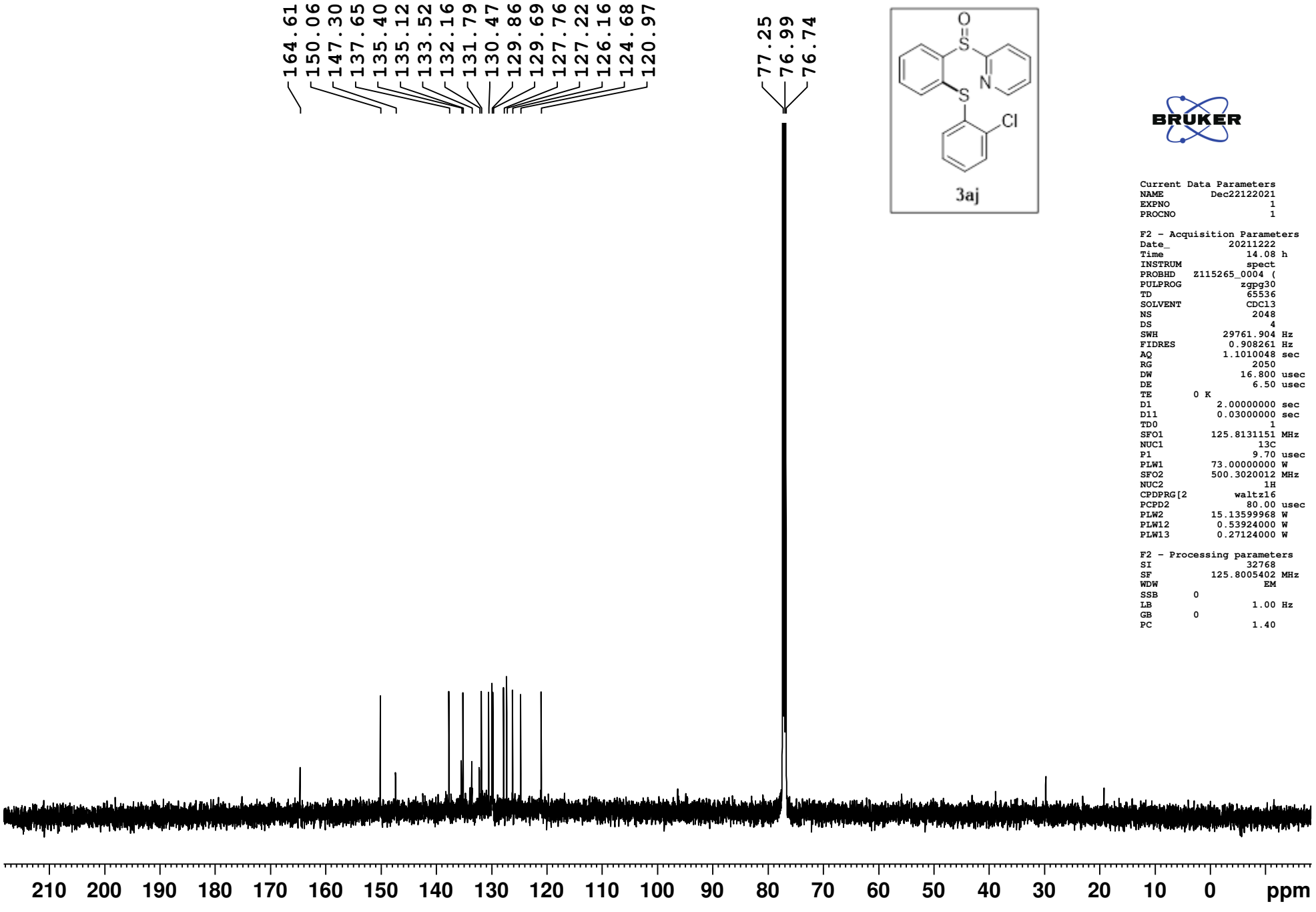

8.544
8.540
8.532
8.530
7.999
7.979
7.964
7.944
7.852
7.848
7.833
7.829
7.813
7.809
7.495
7.492
7.474
7.458
7.454
7.404
7.400
7.384
7.381
7.366
7.363
7.330
7.327
7.308
7.304
7.301
7.289
7.282
7.269
7.245
7.245
7.224
7.170
7.149
O
S
N
S
Cl
3ah
1.00
2.15
1.09
1.19
1.24
2.72
2.08
2.07
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

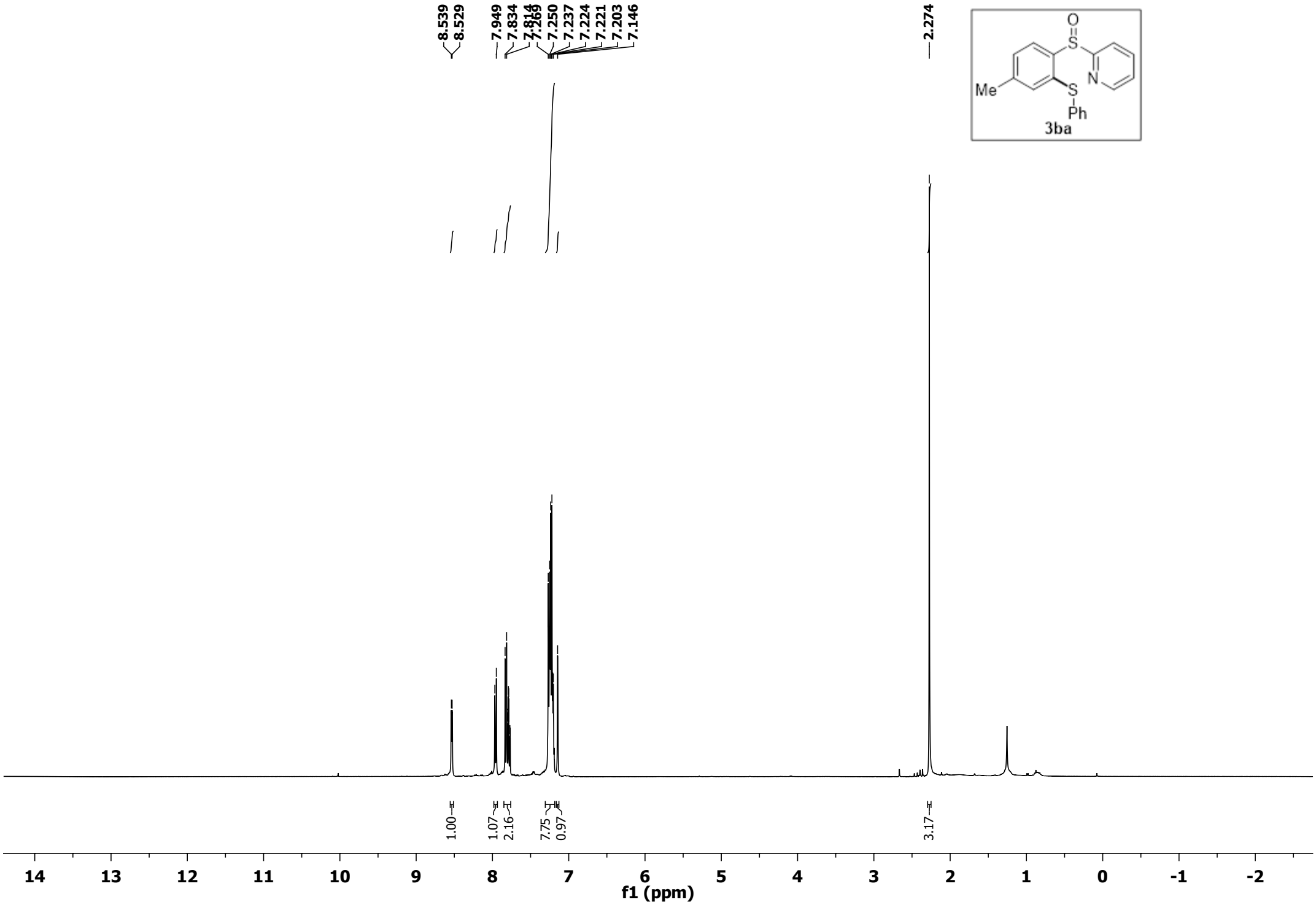

165.091
149.897
146.170
137.923
134.385
134.208
133.881
133.294
131.764
131.652
129.361
129.018
125.708
124.706
120.282
77.319
77.000
76.680
O
S
N
S
Cl
3ah
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

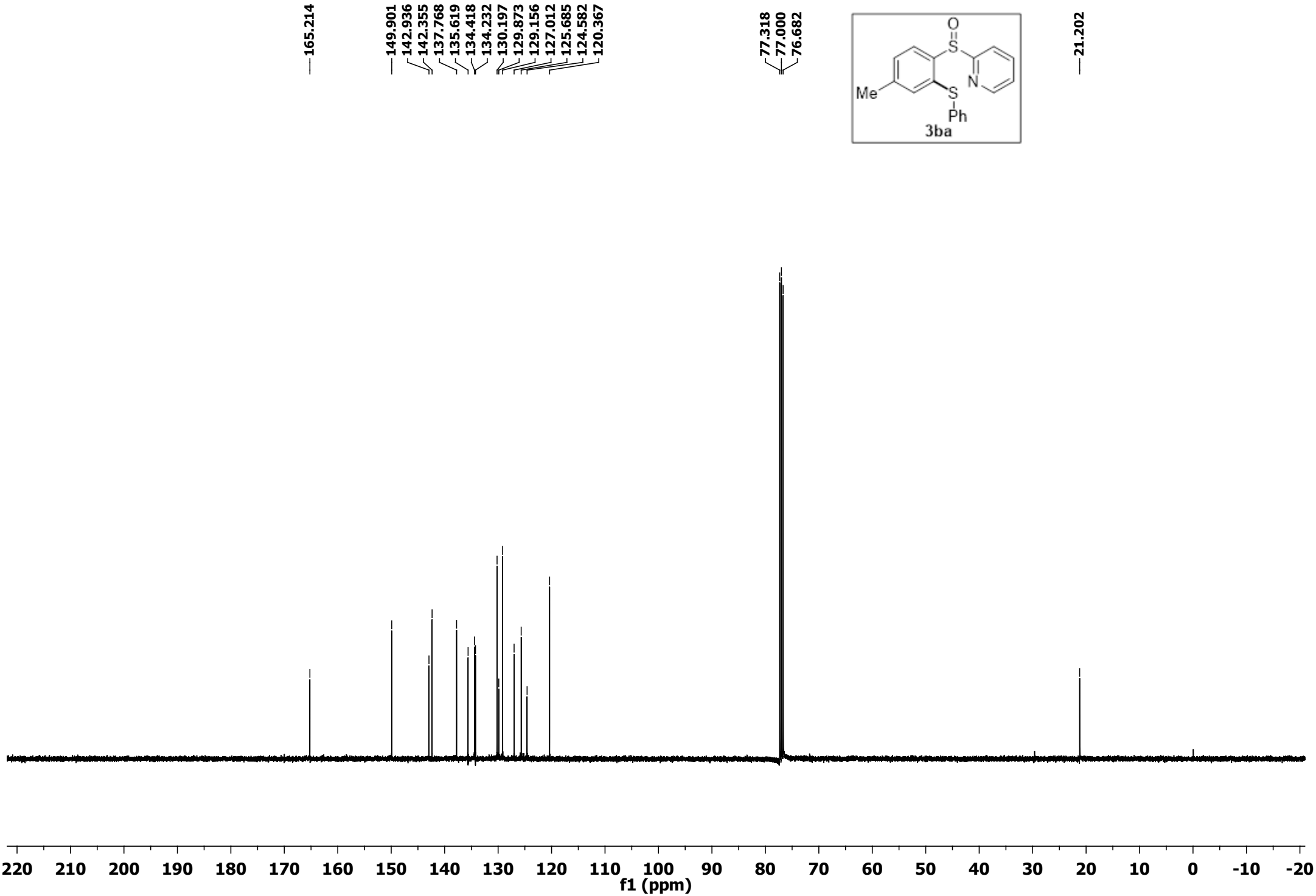

8.527
8.514
8.013
7.994
7.973
7.953
7.825
7.821
7.806
7.802
7.786
7.782
7.560
7.556
7.539
7.537
7.523
7.519
7.454
7.434
7.413
7.394
7.280
7.269
7.250
7.176
7.160
7.077
7.063
7.058
O
S
N
S
Cl
3ai
1.00
2.18
1.09
1.17
2.41
2.20
1.96
1.88
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

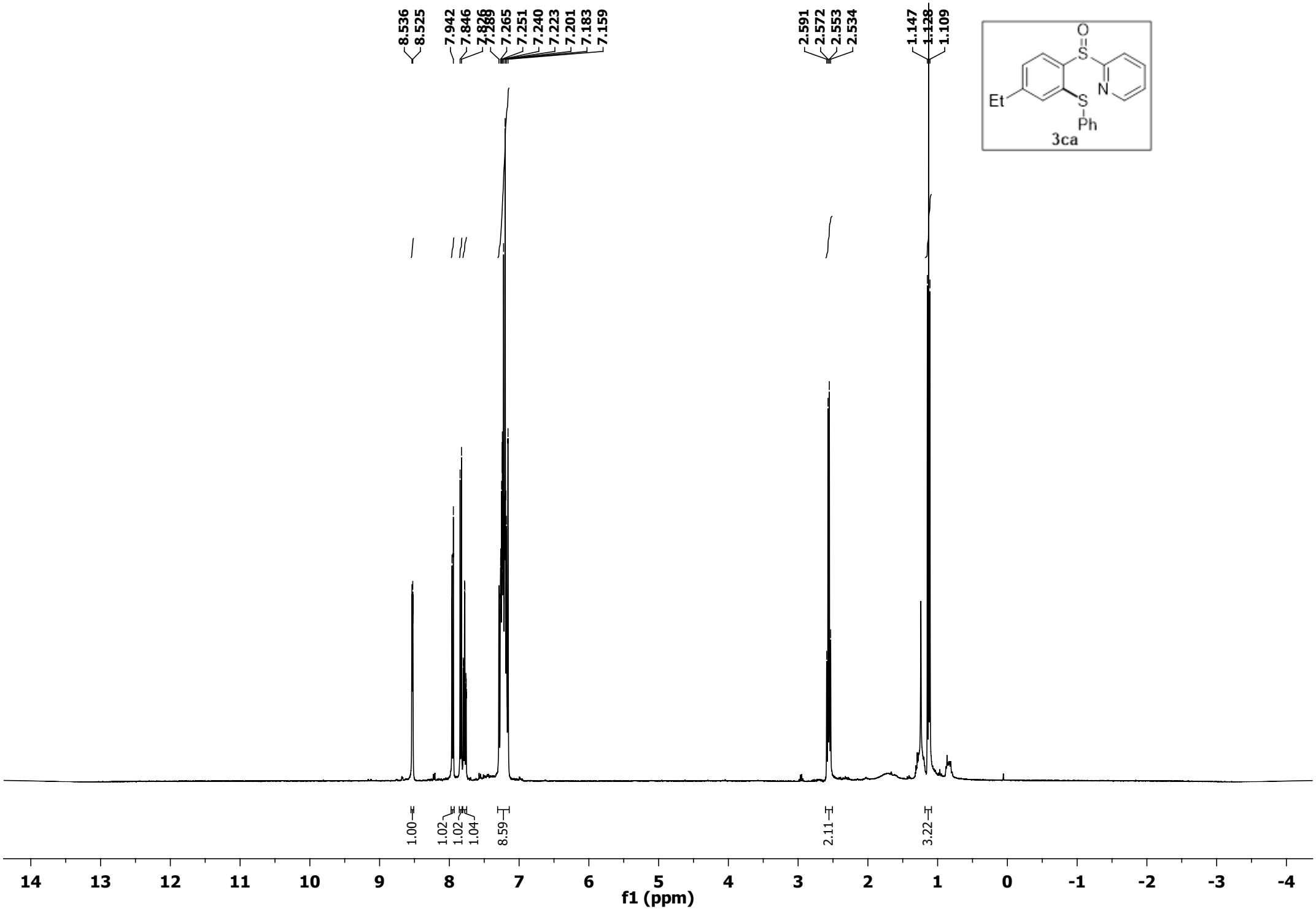

164.974
149.930
147.016
138.140
137.871
134.959
134.926
132.877
131.892
130.095
129.626
129.062
127.529
126.977
125.903
124.768
120.516
77.318
77.000
76.682
O
S
N
S
Cl
3ai
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

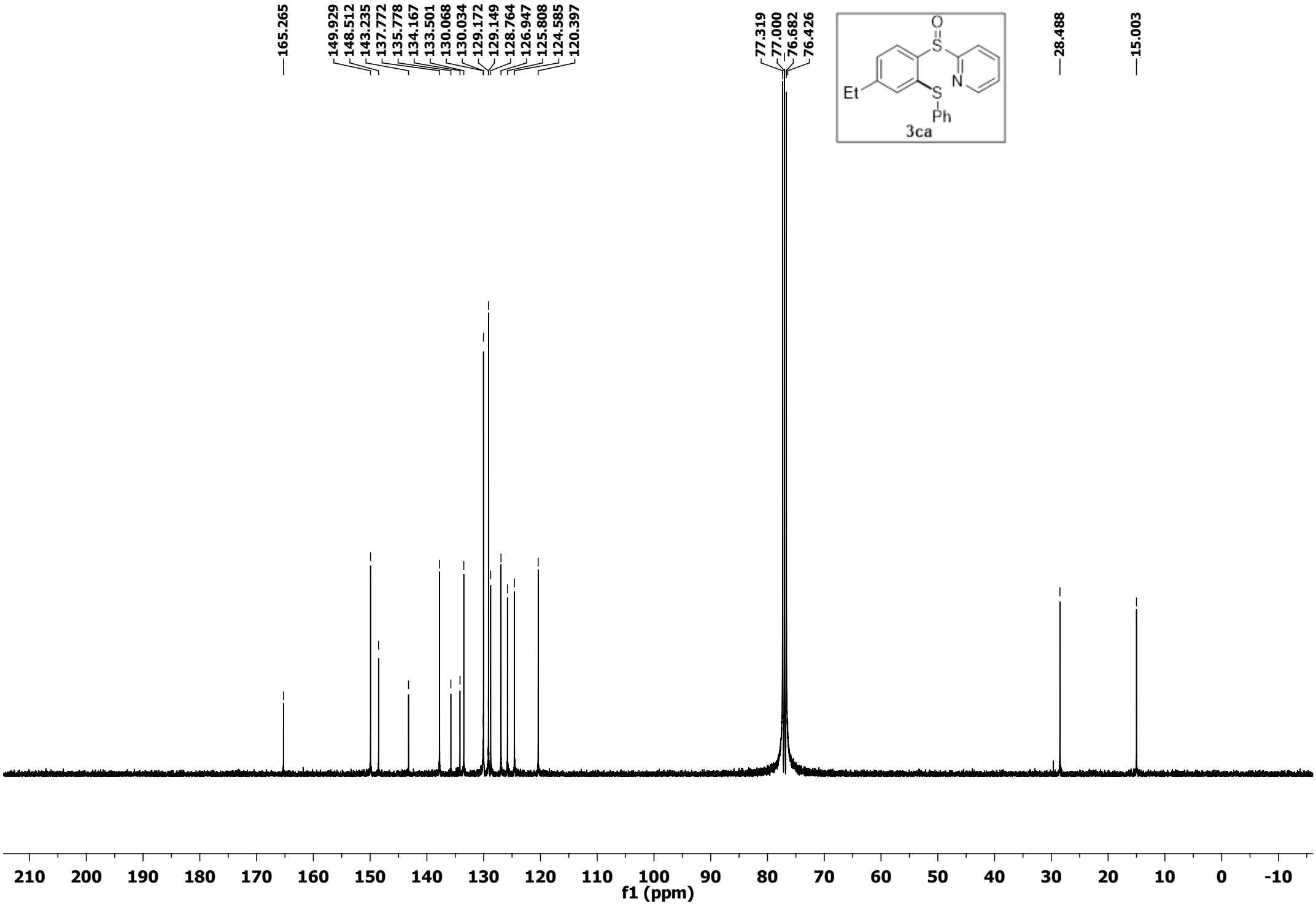

8.514
8.504
8.069
8.066
8.049
8.046
7.973
7.954
7.770
7.766
7.751
7.747
7.732
7.727
7.589
7.586
7.570
7.551
7.548
7.460
7.457
7.441
7.438
7.423
7.419
7.383
7.380
7.358
7.355
7.266
7.239
7.236
7.227
7.220
7.209
7.206
7.146
7.142
7.127
7.123
7.108
7.104
7.053
7.050
7.034
7.030
7.015
7.012
6.807
6.803
6.787
6.783
O
S
N
S
Cl
3aj
1.08
1.12
1.05
1.21
1.27
1.27
2.14
1.14
1.08
1.08
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

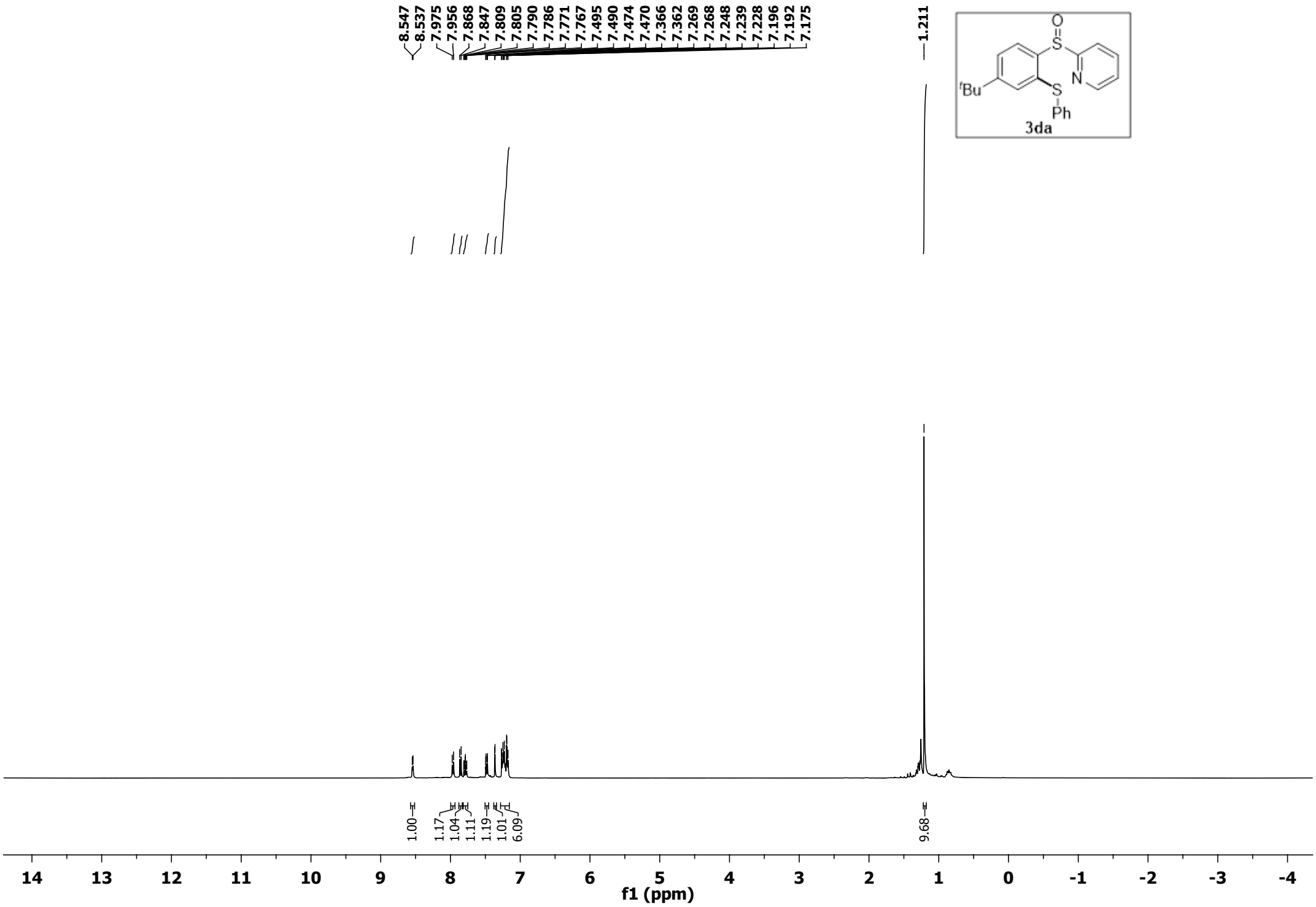

164.61
150.06
147.30
137.65
135.40
135.12
133.52
132.16
131.79
130.47
129.86
129.69
127.76
127.22
126.16
124.68
120.97
77.25
76.99
76.74
O
S
N
S
Cl
3aj
BRUKER
Current Data Parameters
NAME Dec22122021
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211222
Time 14.08 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005402 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

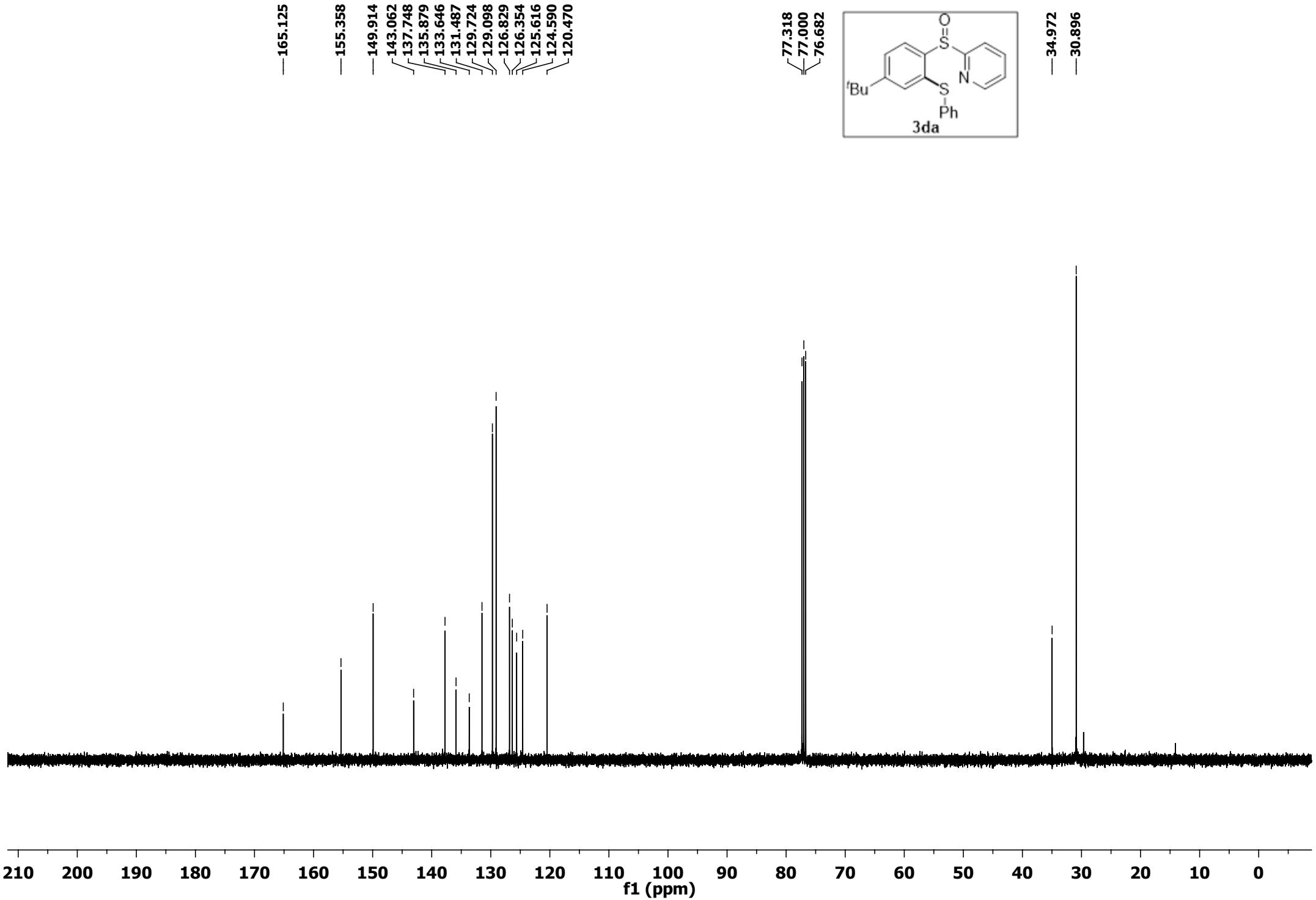

8.539
8.529
7.949
7.834
7.814
7.269
7.250
7.237
7.224
7.221
7.203
7.146
2.274
O
S
N
Me
S
Ph
3ba
1.00
1.07
2.16
7.75
0.97
3.17
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

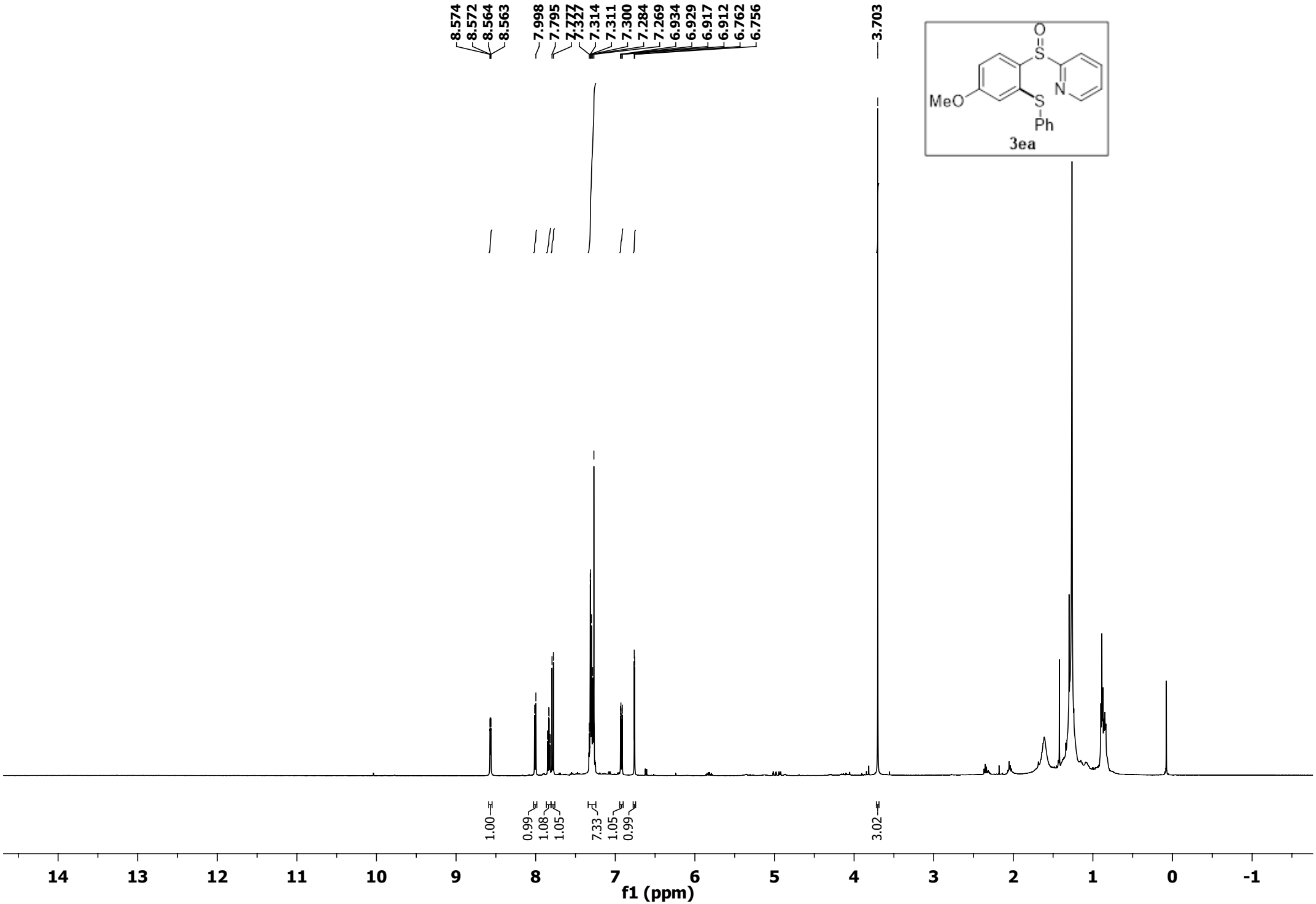

165.214
149.901
142.936
142.355
137.768
135.619
134.418
134.232
130.197
129.873
129.156
127.012
125.685
124.582
120.367
77.318
77.000
76.682
21.202
O
S
N
Me
S
Ph
3ba
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

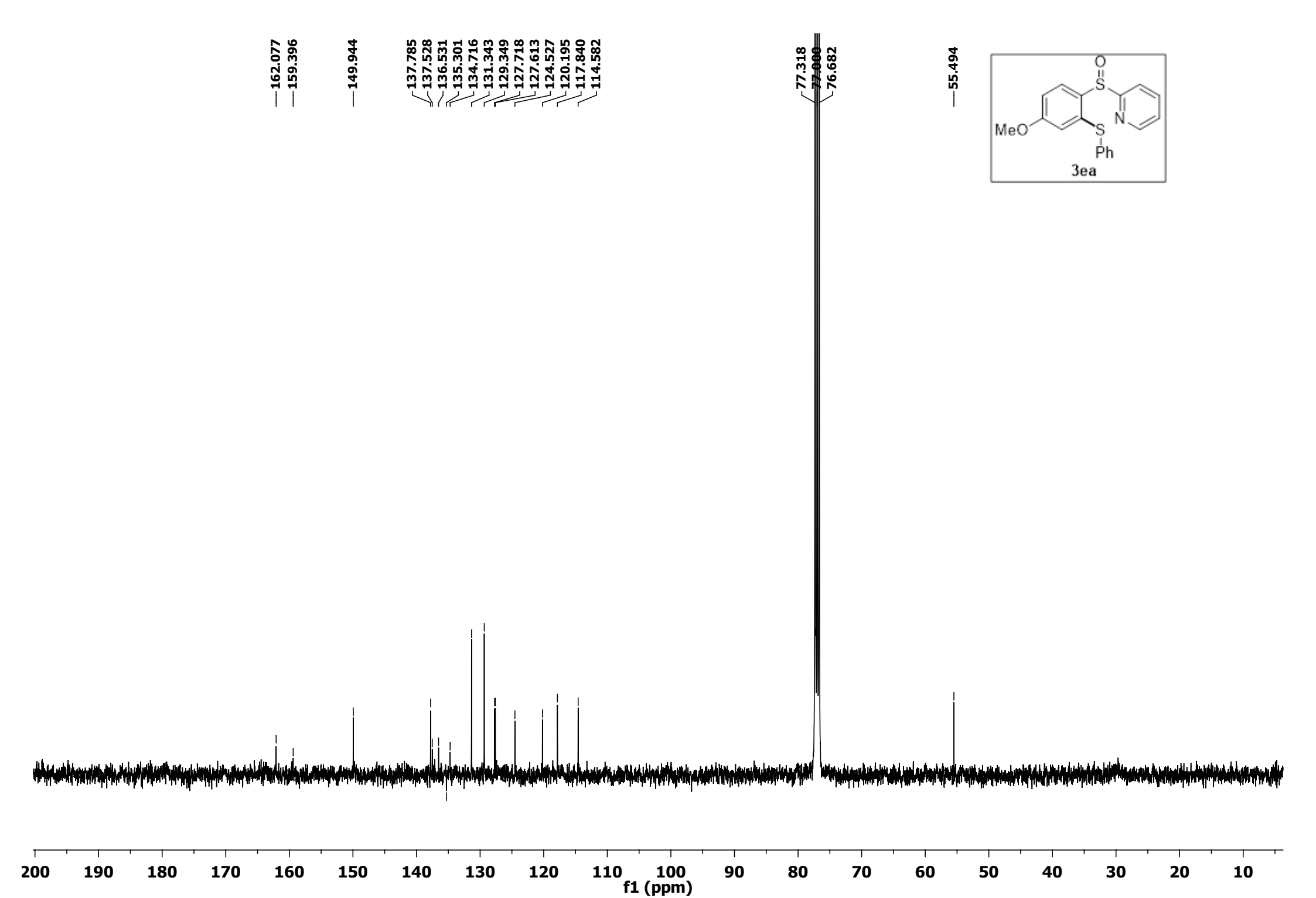

8.536
8.525
7.942
7.846
7.826
7.265
7.251
7.240
7.223
7.201
7.183
7.159
2.591
2.572
2.553
2.534
1.147
1.128
1.109
O
S
N
Et
S
Ph
3ca
1.00
1.02
1.02
1.04
8.59
2.11
3.22
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

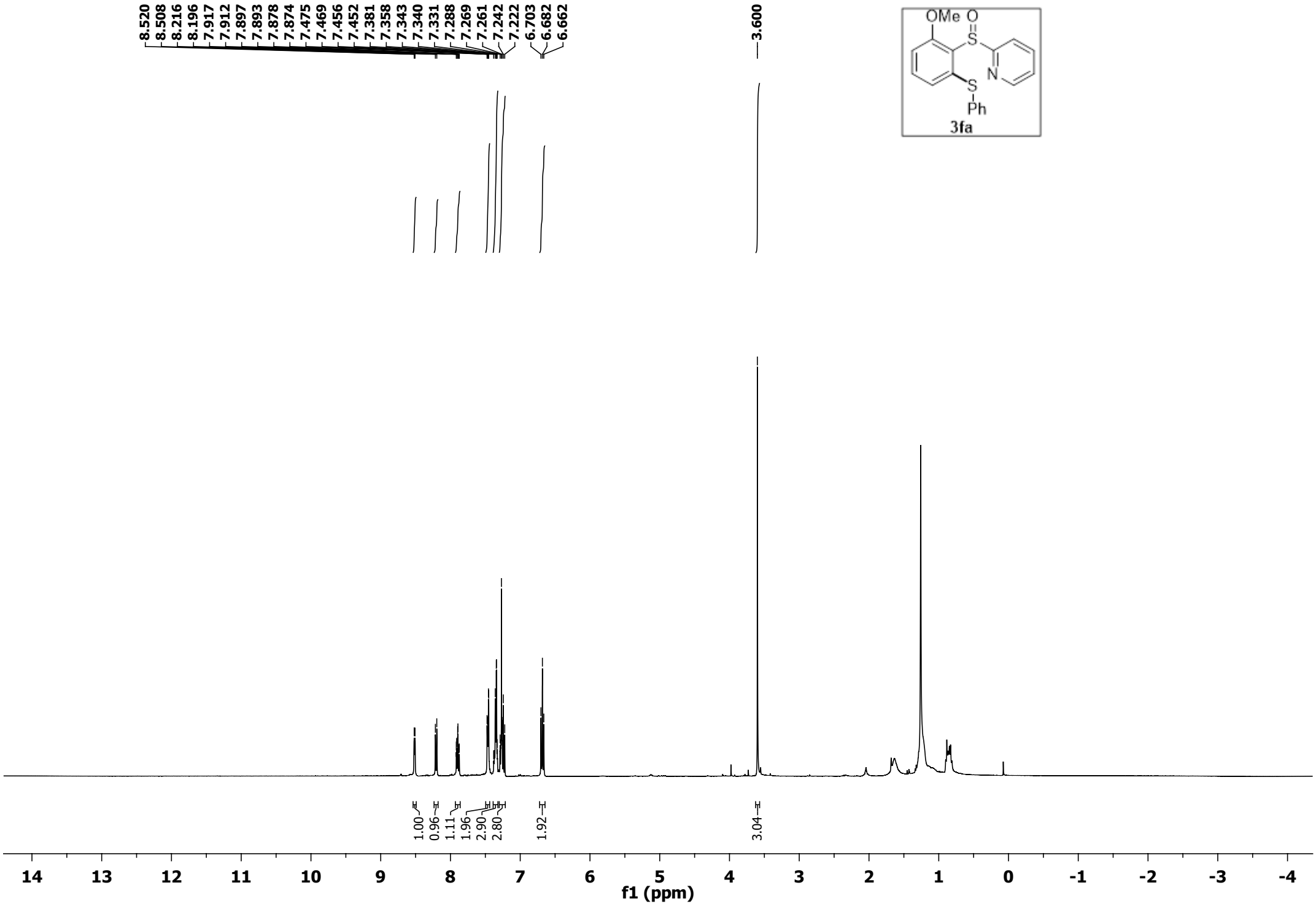

165.265
149.929
148.512
143.235
137.772
135.778
134.167
133.501
130.068
130.034
129.172
129.149
128.764
126.947
125.808
124.585
120.397
77.319
77.000
76.682
76.426
28.488
15.003
O
S
N
Et
S
Ph
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

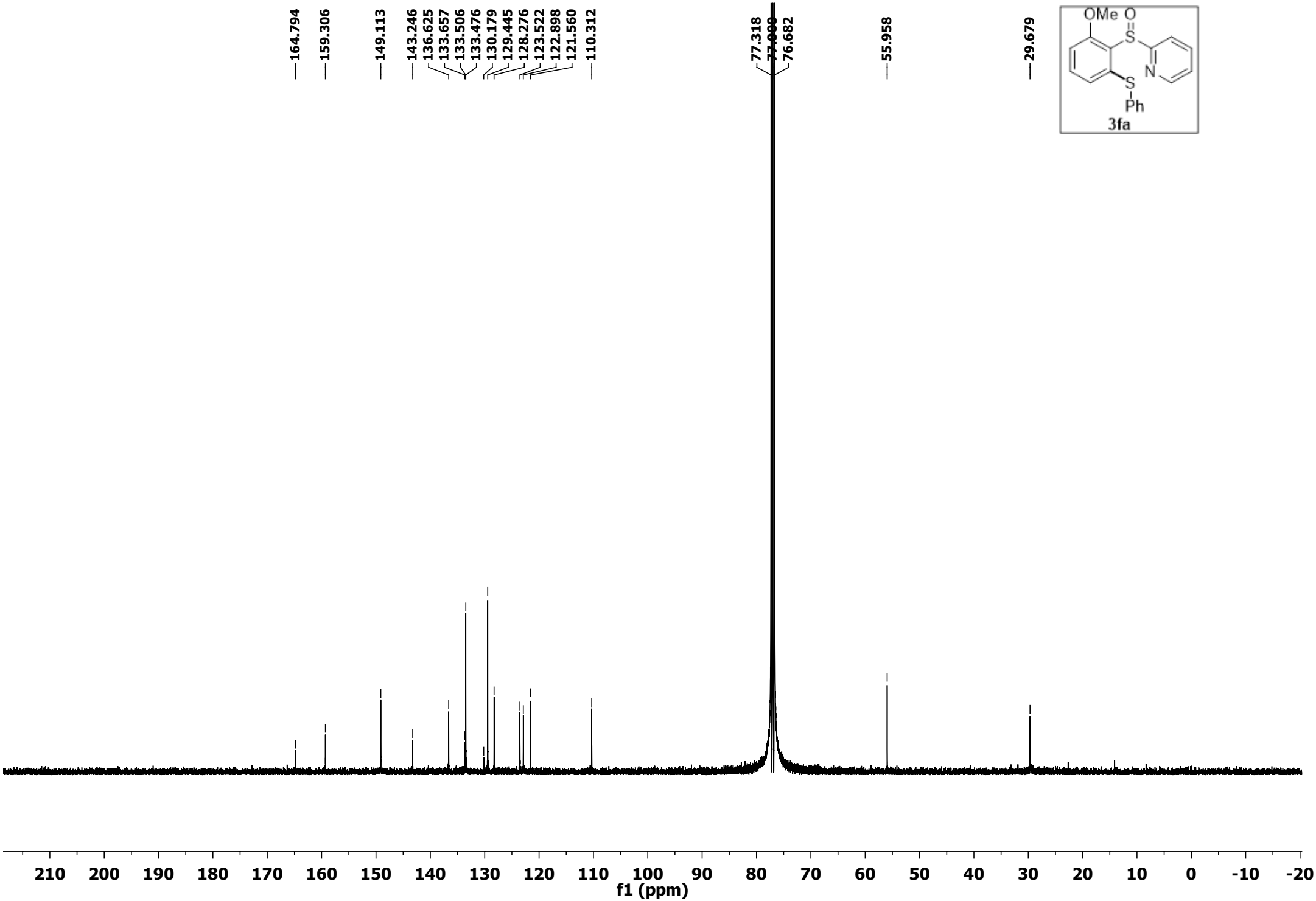

8.547
8.537
7.975
7.956
7.868
7.847
7.809
7.805
7.790
7.786
7.771
7.767
7.495
7.490
7.474
7.470
7.366
7.362
7.269
7.268
7.248
7.239
7.228
7.196
7.192
7.175
1.211
O
S
N
tBu
S
Ph
3da
1.00
1.17
1.04
1.11
1.19
1.01
6.09
9.68
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

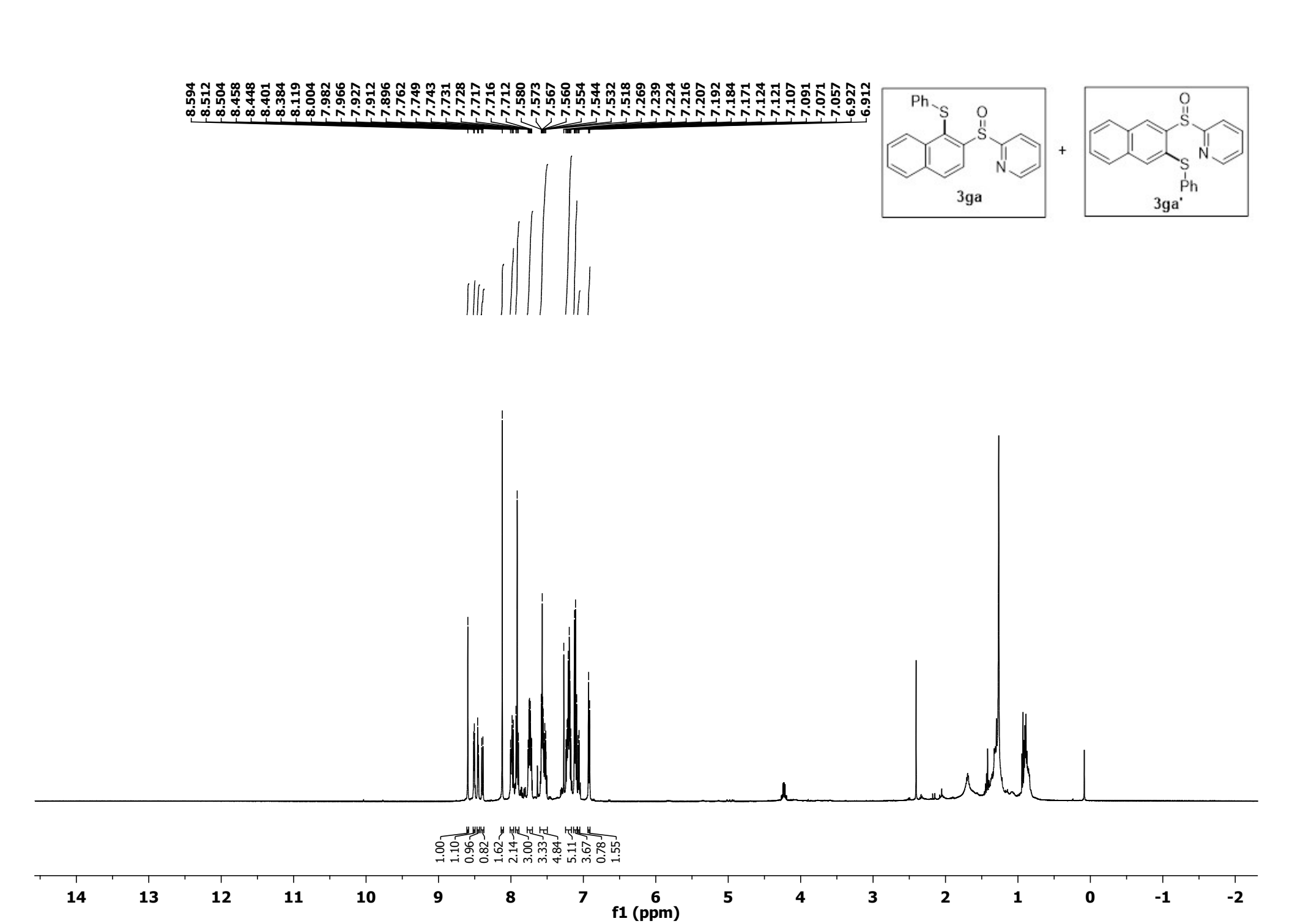

165.125
155.358
149.914
143.062
137.748
135.879
133.646
131.487
129.724
129.098
126.829
126.354
125.616
124.590
120.470
77.318
77.000
76.682
34.972
30.896
O
S
N
tBu
S
Ph
3da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

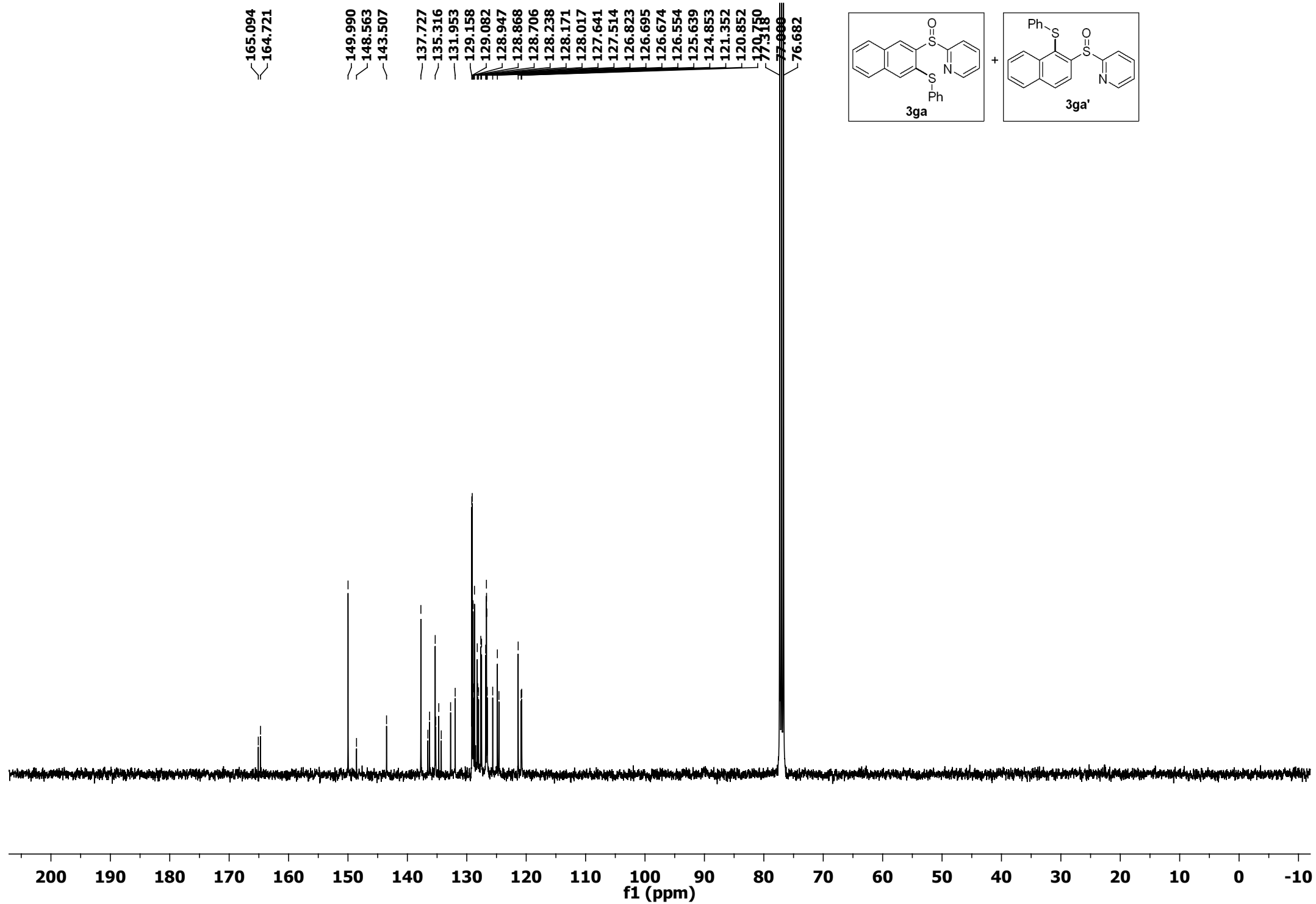

8.574
8.572
8.564
8.563
7.998
7.795
7.777
7.327
7.314
7.311
7.300
7.284
7.269
6.934
6.929
6.917
6.912
6.762
6.756
3.703
O
S
N
MeO
S
Ph
3ea
1.00
0.99
1.08
1.05
7.33
1.05
0.99
3.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

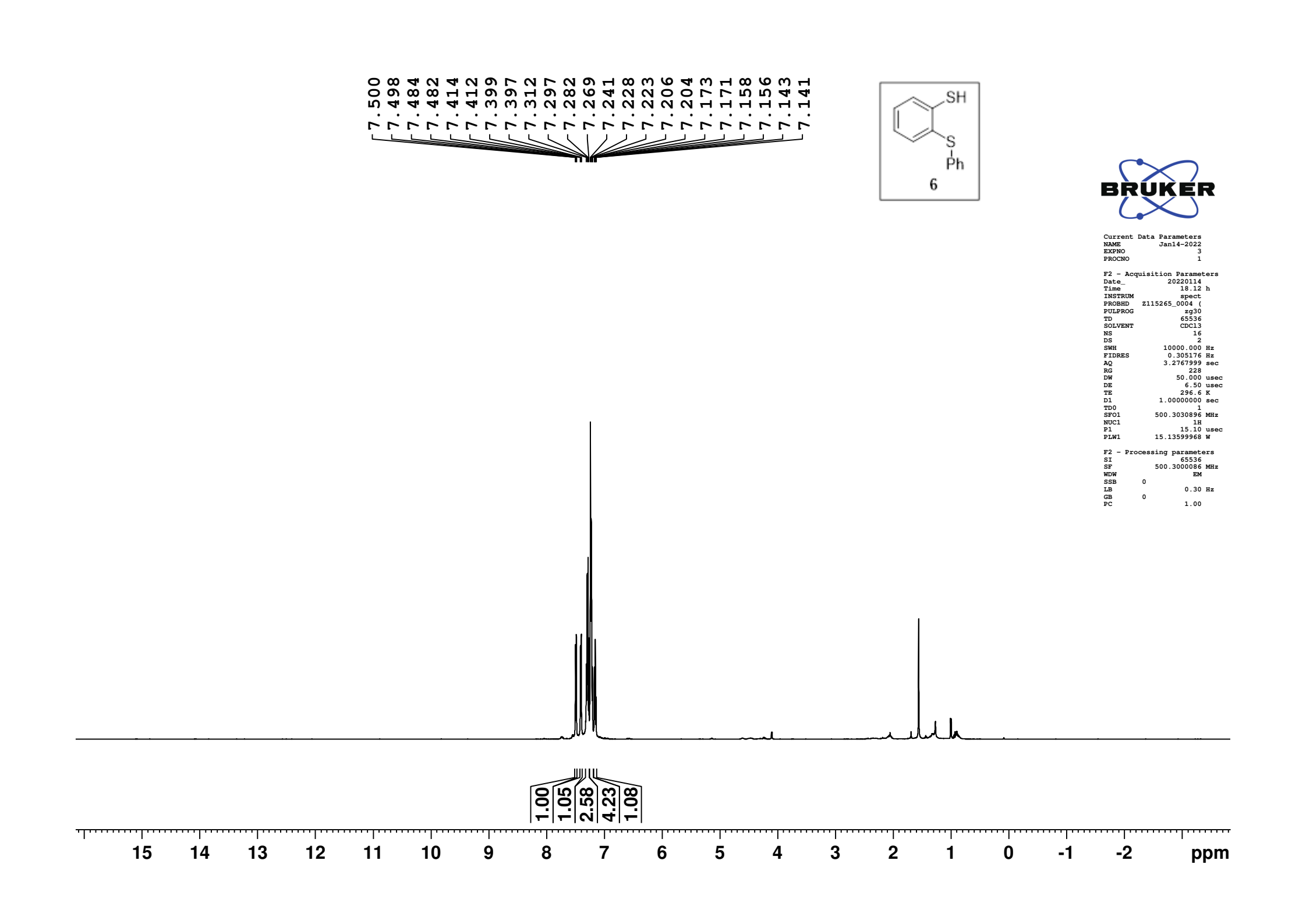

162.077
159.396
149.944
137.785
137.528
136.531
135.301
134.716
131.343
129.349
127.718
127.613
124.527
120.195
117.840
114.582
77.318
77.000
76.682
55.494
MeO
S
O
N
S
Ph
3ea
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

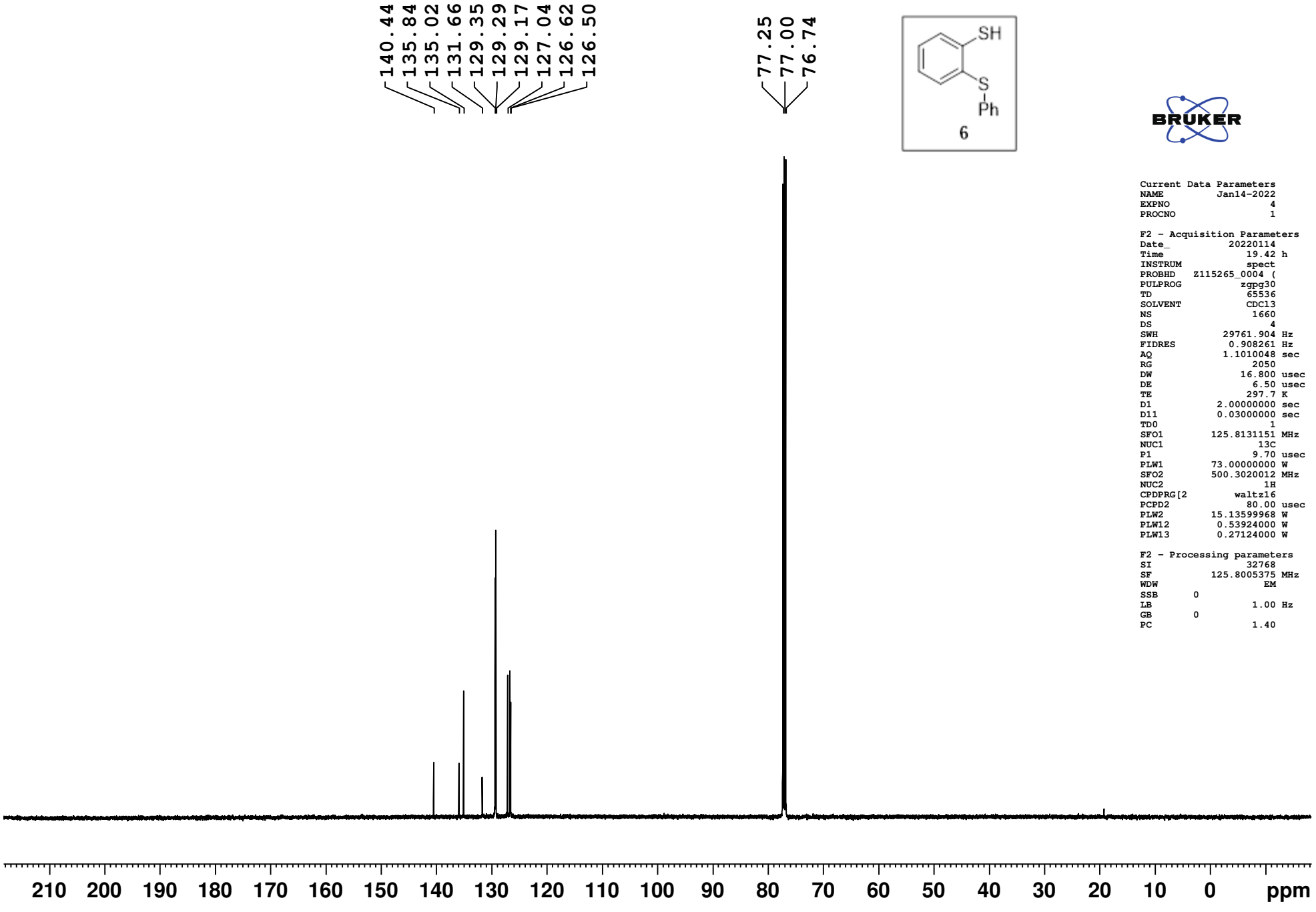

8.520
8.508
8.216
8.196
7.917
7.912
7.897
7.893
7.878
7.874
7.475
7.469
7.456
7.452
7.381
7.358
7.343
7.340
7.331
7.288
7.269
7.261
7.242
7.222
6.703
6.682
6.662
3.600
OMe
O
S
N
S
Ph
3fa
1.00
0.96
1.11
1.96
2.90
2.80
1.92
3.04
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

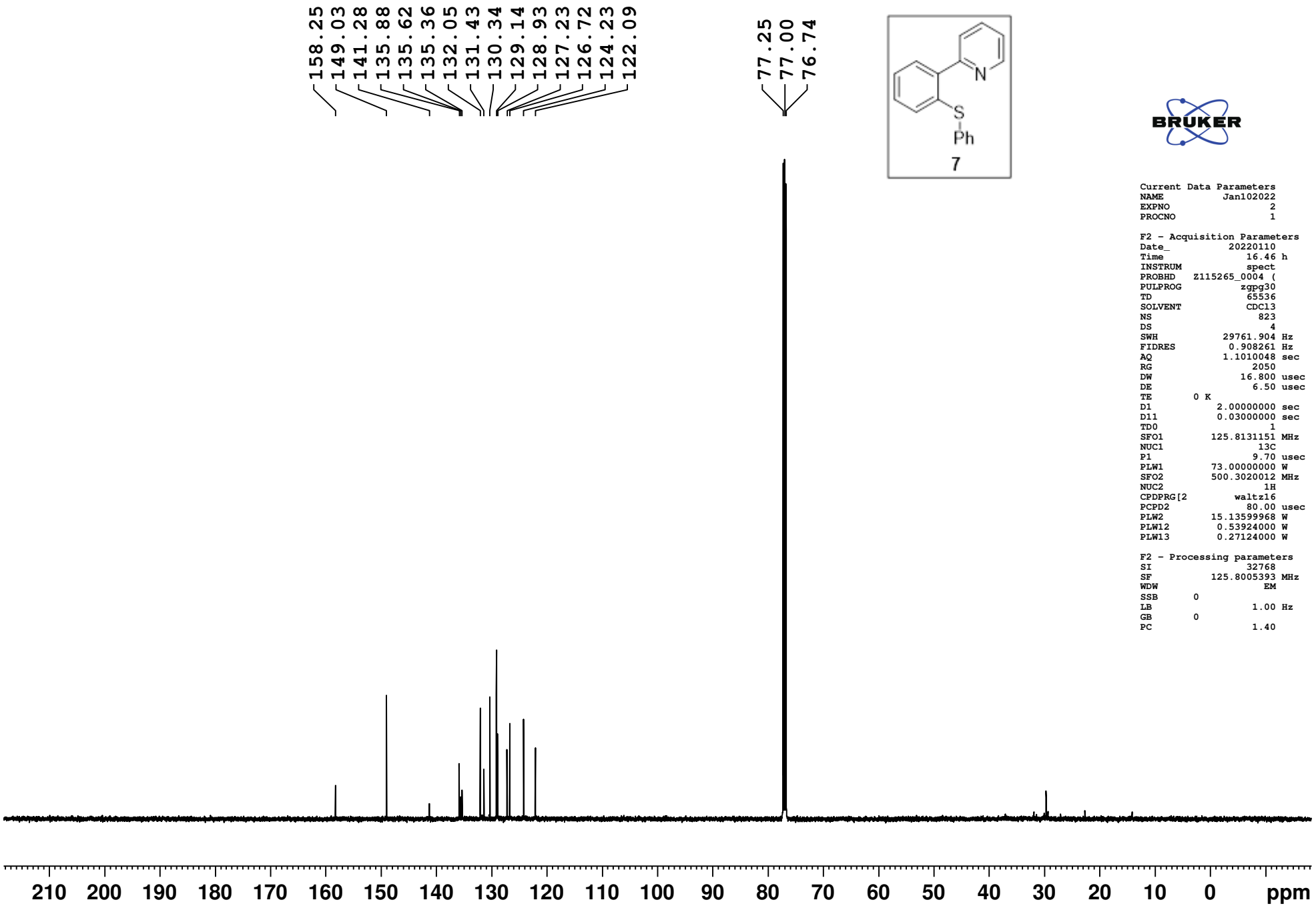

164.794
159.306
149.113
143.246
136.625
133.657
133.506
133.476
130.179
129.445
128.276
123.522
122.898
121.560
110.312
77.318
77.000
76.682
55.958
29.679
OMe
O
S
N
S
Ph
3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

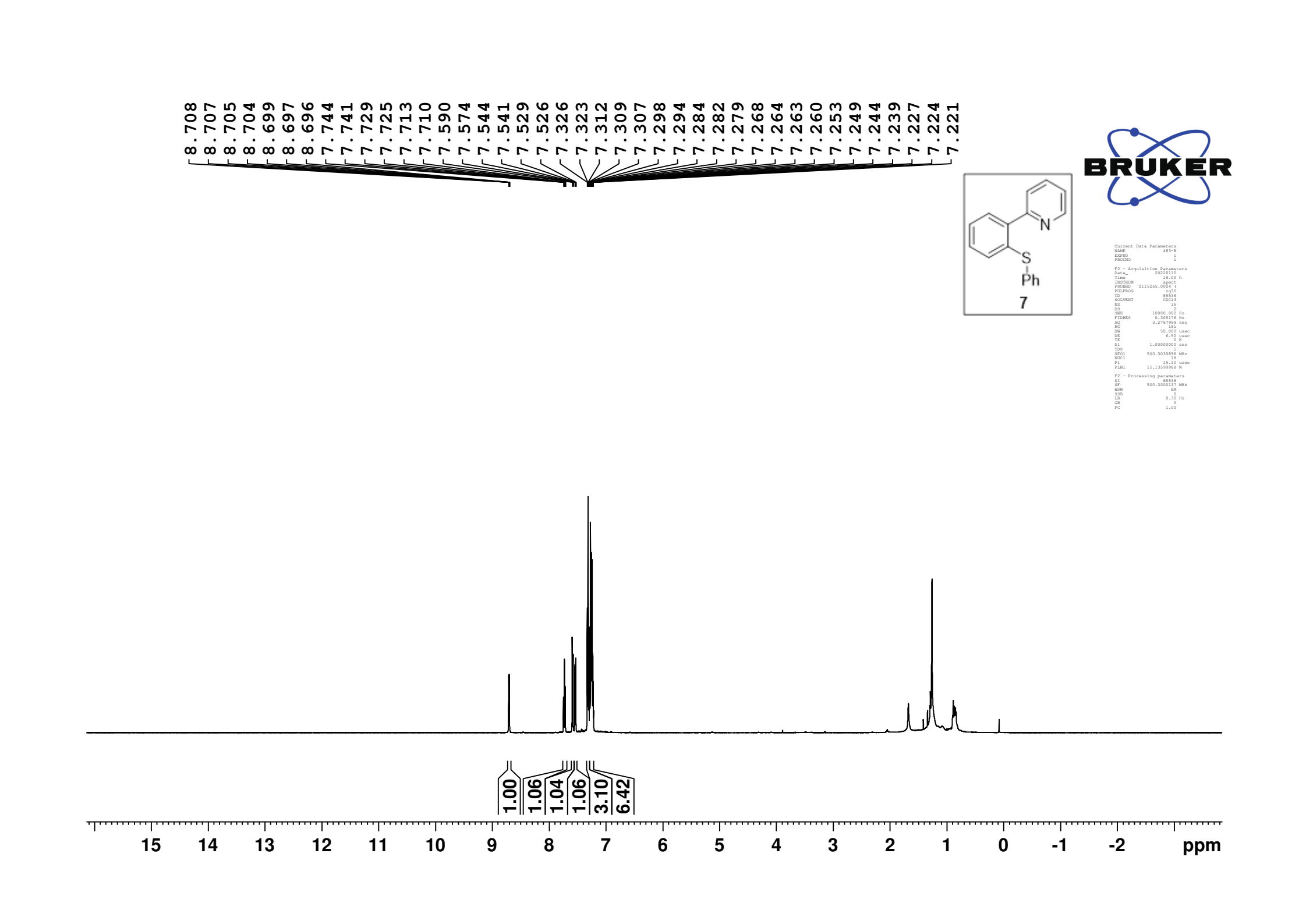

8.594
8.512
8.504
8.458
8.448
8.401
8.384
8.119
8.004
7.982
7.966
7.927
7.912
7.896
7.762
7.749
7.743
7.731
7.728
7.717
7.716
7.712
7.580
7.573
7.567
7.560
7.554
7.544
7.532
7.518
7.269
7.239
7.224
7.216
7.207
7.192
7.184
7.171
7.124
7.121
7.107
7.091
7.071
7.057
6.927
6.912
Ph
S
O
S
N
3ga
+
O
S
N
S
Ph
3ga'
1.00
1.10
0.96
0.82
1.62
2.14
3.00
3.33
4.84
5.11
3.67
0.78
1.55
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

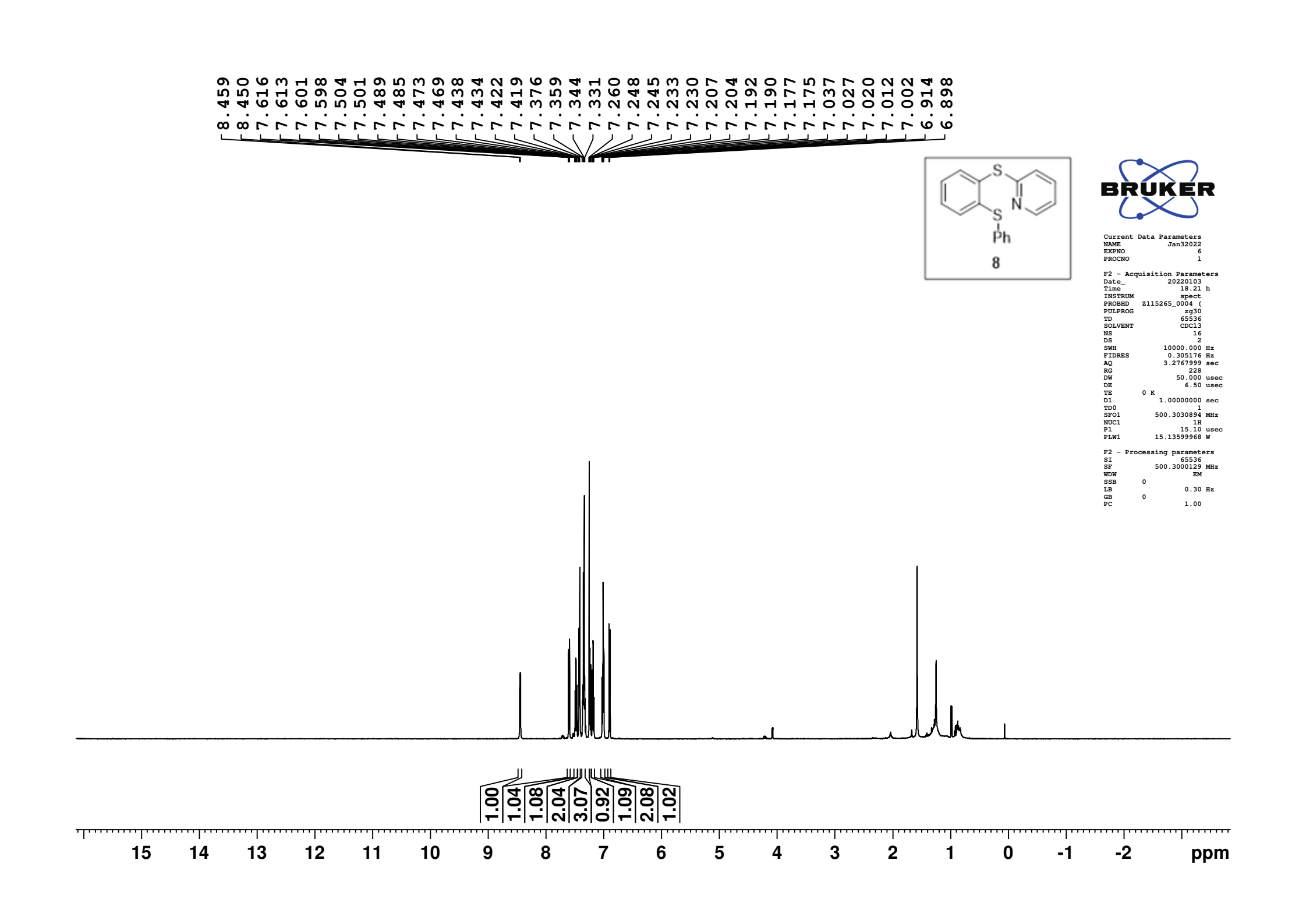

165.094
164.721
149.990
148.563
143.507
137.727
135.316
131.953
129.158
129.082
128.947
128.868
128.706
128.238
128.171
128.017
127.641
127.514
126.823
126.695
126.674
126.554
125.639
124.853
121.352
120.852
120.750
77.318
77.000
76.682
3ga
3ga'
f1 (ppm)

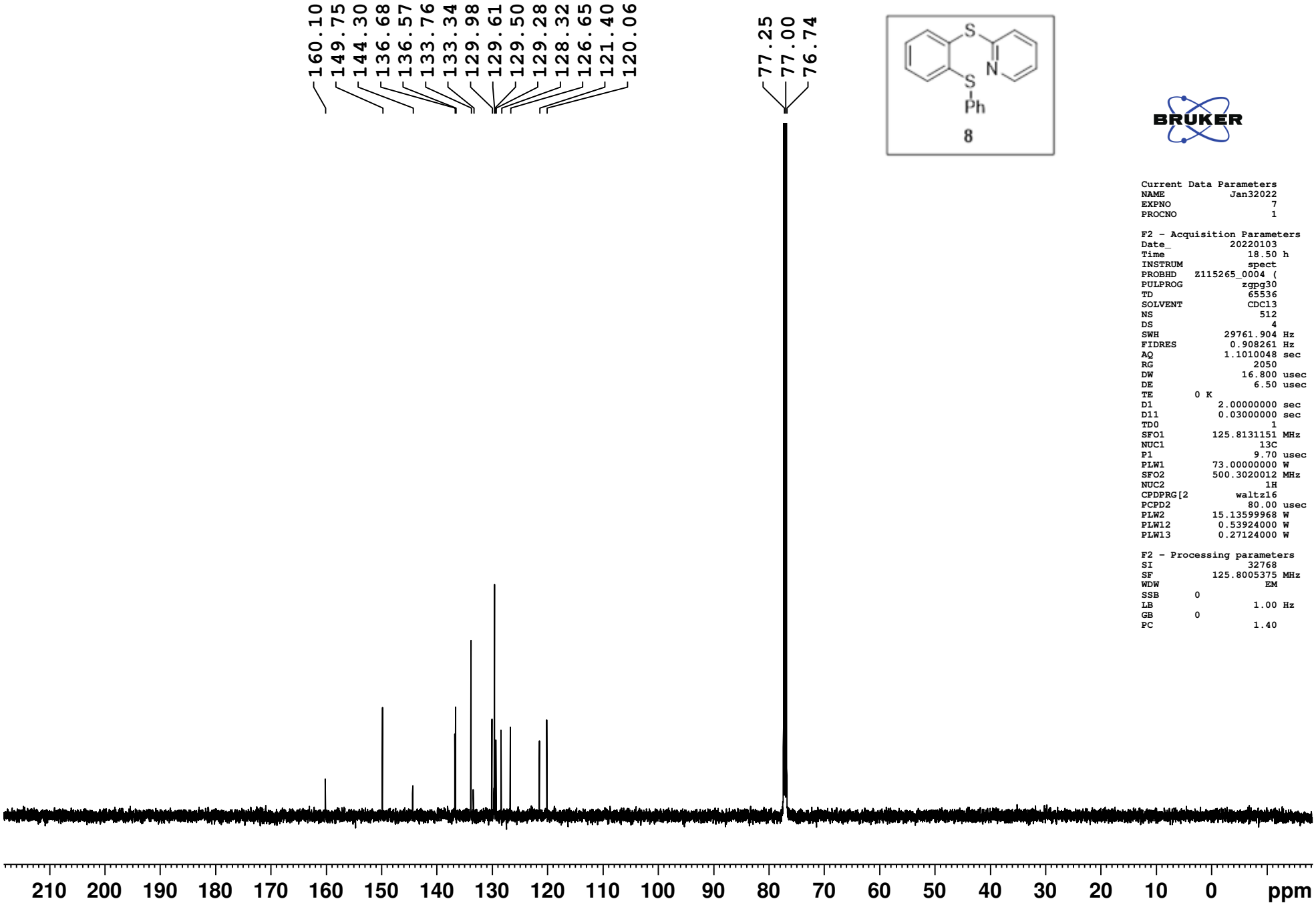

7.500
7.498
7.484
7.482
7.414
7.412
7.399
7.397
7.312
7.297
7.282
7.269
7.241
7.228
7.223
7.206
7.204
7.173
7.171
7.158
7.156
7.143
7.141
SH
S
Ph
6
BRUKER
Current Data Parameters
NAME Jan14-2022
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220114
Time 18.12 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 228
DW 50.000 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030896 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.05
2.58
4.23
1.08
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

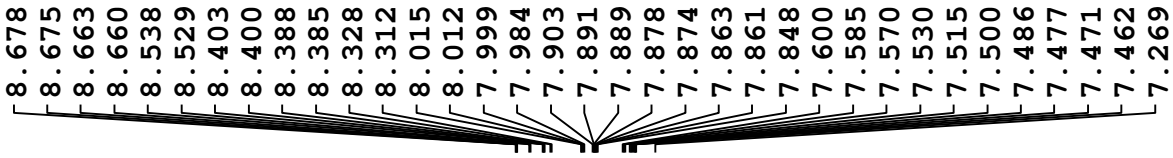

140.44
135.84
135.02
131.66
129.35
129.29
129.17
127.04
126.62
126.50
77.25
77.00
76.74
SH
S
Ph
6
BRUKER
Current Data Parameters
NAME Jan14-2022
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220114
Time 19.42 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1660
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005375 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

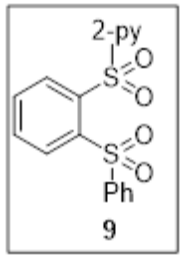

158.25
149.03
141.28
135.88
135.62
135.36
132.05
131.43
130.34
129.14
128.93
127.23
126.72
124.23
122.09
77.25
77.00
76.74
N
S
Ph
7
BRUKER
Current Data Parameters
NAME Jan102022
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220110
Time 16.46 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 823
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.708
8.707
8.705
8.704
8.699
8.697
8.696
7.744
7.741
7.729
7.725
7.713
7.710
7.590
7.574
7.544
7.541
7.529
7.526
7.326
7.323
7.312
7.309
7.307
7.298
7.294
7.284
7.282
7.279
7.268
7.264
7.263
7.260
7.253
7.249
7.244
7.239
7.227
7.224
7.221
BRUKER
N
S
Ph
7
Current Data Parameters
NAME 483-B
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220110
Time 16.00 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 181
DW 50.000 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030896 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000137 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.06
1.04
1.06
3.10
6.42
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


8.459
8.450
7.616
7.613
7.601
7.598
7.504
7.501
7.489
7.485
7.473
7.469
7.438
7.434
7.422
7.419
7.376
7.359
7.344
7.331
7.260
7.248
7.245
7.233
7.230
7.207
7.204
7.192
7.190
7.177
7.175
7.037
7.027
7.020
7.012
7.002
6.914
6.898
S
N
S
Ph
8
BRUKER
Current Data Parameters
NAME Jan32022
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220103
Time 18.21 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 228
DW 50.000 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P1 15.10 usec
PLW1 15.13599968 W
F2 - Processing parameters
SI 65536
SF 500.3000129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.04
1.08
2.04
3.07
0.92
1.09
2.08
1.02
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


160.10
149.75
144.30
136.68
136.57
133.76
133.34
129.98
129.61
129.50
129.28
128.32
126.65
121.40
120.06
77.25
77.00
76.74
S
N
S
Ph
8
BRUKER
Current Data Parameters
NAME Jan32022
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220103
Time 18.50 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005375 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

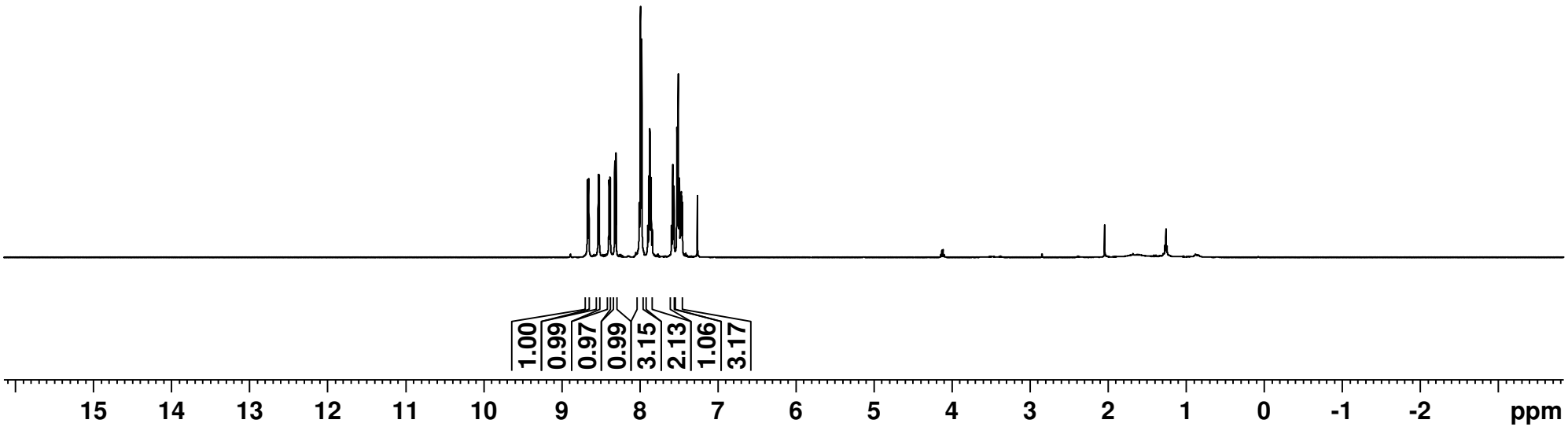


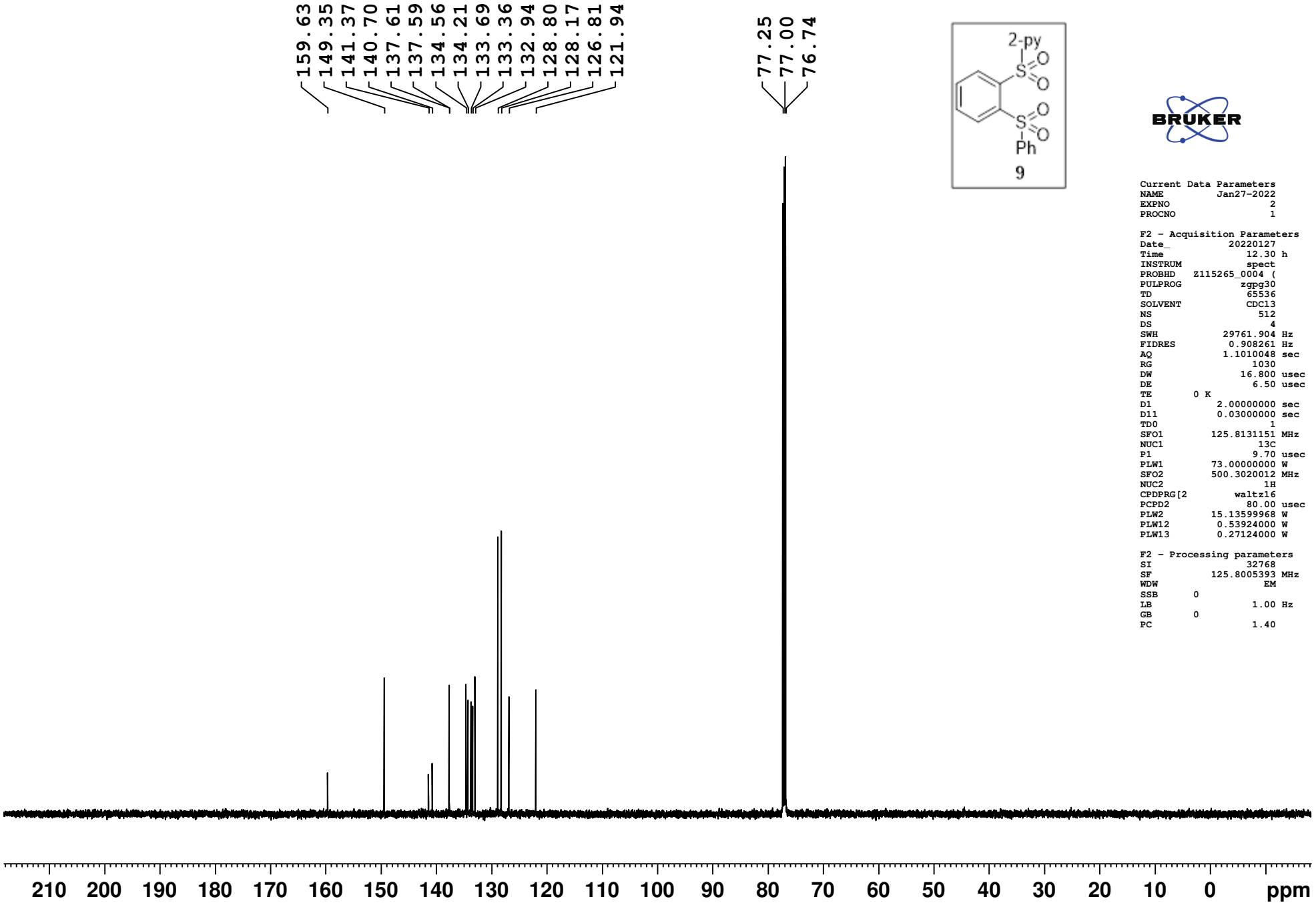


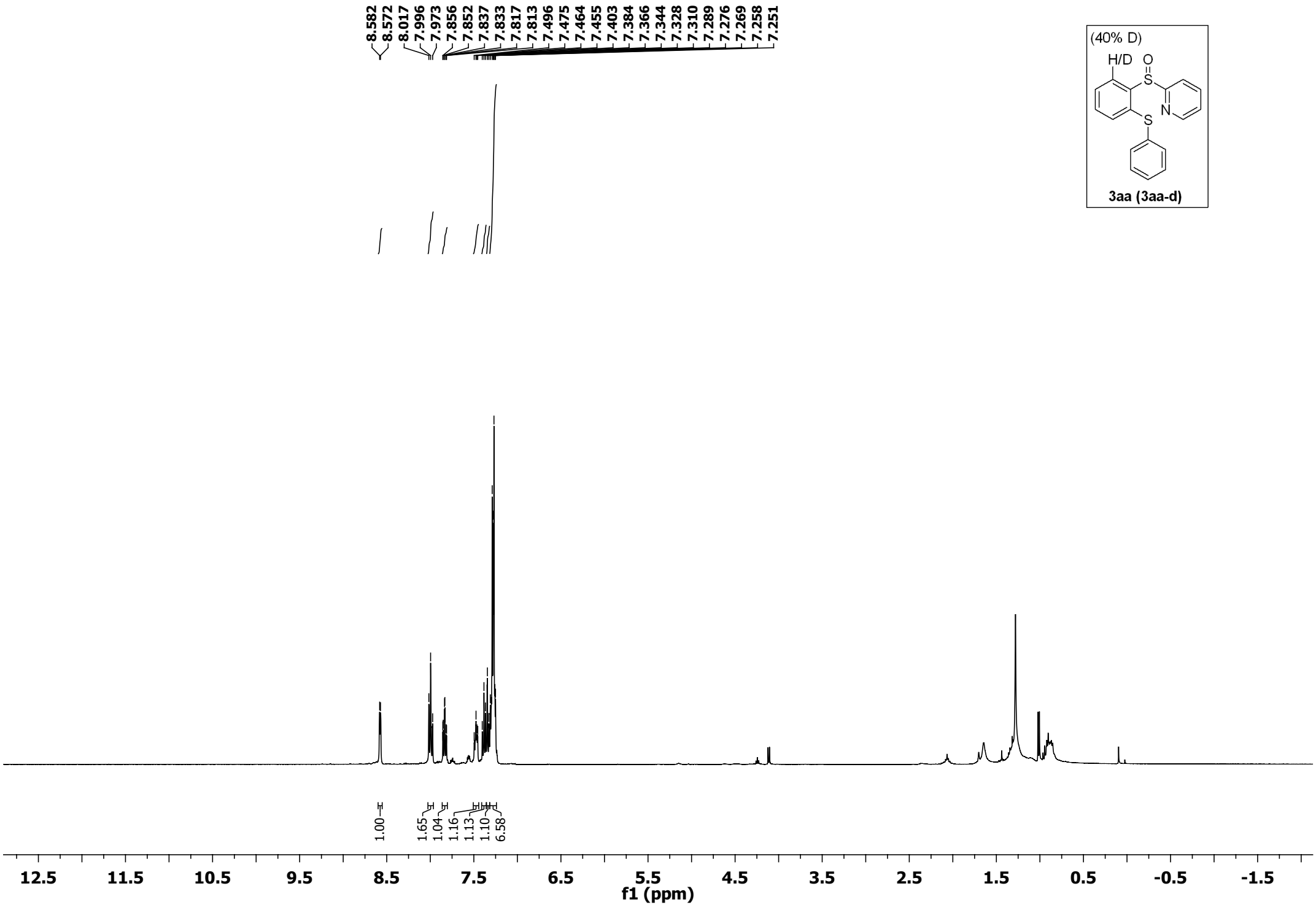

```
Current Data Parameters
NAME          Jan27-2022
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220127
Time              12.00 h
INSTRUM             spect
PROBHD   Z115265_0004 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                   256
DW                50.000 usec
DE                 6.50 usec
TE        0 K
D1          1.00000000 sec
TD0                    1
SFO1        500.3030896 MHz
NUC1                  1H
P1                15.10 usec
PLW1         15.13599968 W

F2 - Processing parameters
SI                 65536
SF          500.3000086 MHz
WDW                   EM
SSB       0
LB             0.30 Hz
GB        0
PC                 1.00
```

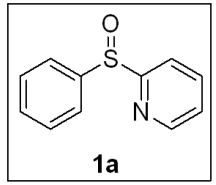



159.63
149.35
141.37
140.70
137.61
137.59
134.56
134.21
133.69
133.36
132.94
128.80
128.17
126.81
121.94
77.25
77.00
76.74
2-py
Ph
9
BRUKER
Current Data Parameters
NAME Jan27-2022
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220127
Time 12.30 h
INSTRUM spect
PROBHD Z115265_0004 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 1030
DW 16.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P1 9.70 usec
PLW1 73.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.13599968 W
PLW12 0.53924000 W
PLW13 0.27124000 W
F2 - Processing parameters
SI 32768
SF 125.8005393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.582
8.572
8.017
7.996
7.973
7.856
7.852
7.837
7.833
7.817
7.813
7.496
7.475
7.464
7.455
7.403
7.384
7.366
7.344
7.328
7.310
7.289
7.276
7.269
7.258
7.251
(40% D)
H/D
O
S
N
S
3aa (3aa-d)
1.00
1.65
1.04
1.16
1.13
1.10
6.58
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

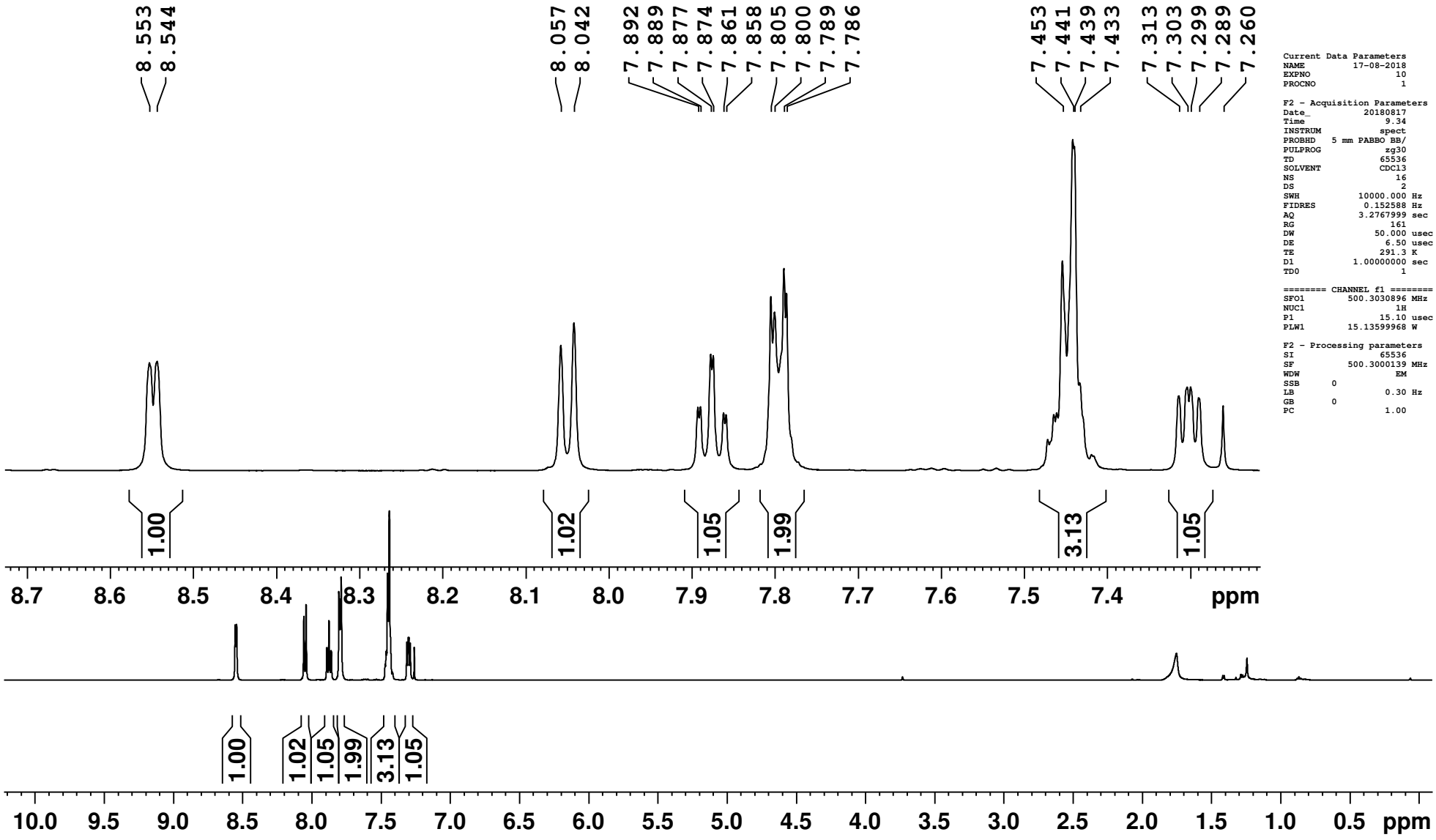
MB-MY-1-186;17-08-2018

8.553 8.544 8.057 8.042 7.892 7.889 7.877 7.874 7.861 7.858 7.805 7.800 7.789 7.786 7.453 7.441 7.439 7.433 7.313 7.303 7.299 7.289 7.260



1a

BRUKER

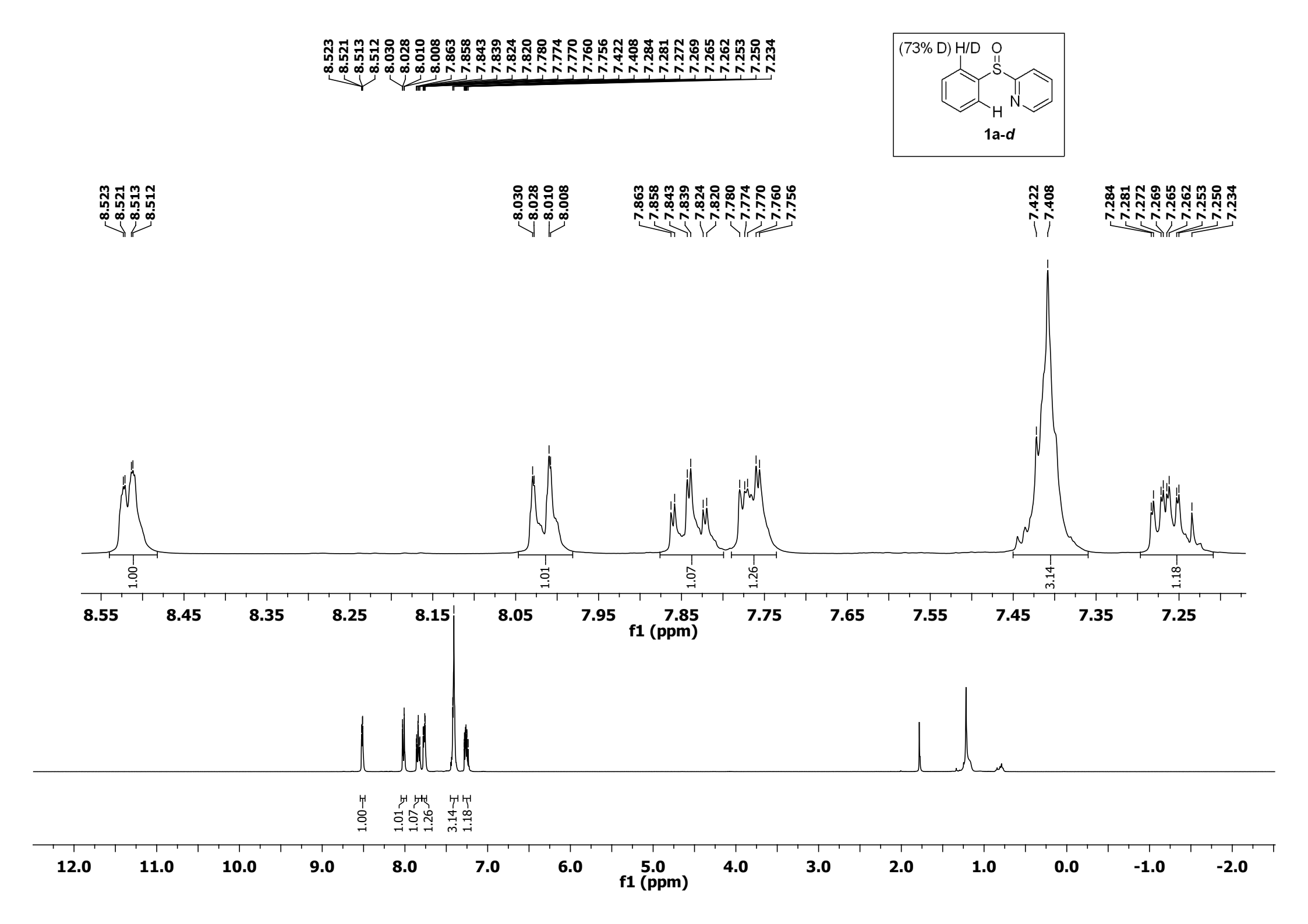



```
Current Data Parameters
NAME                  17-08-2018
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20180817
Time                        9.34
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                   10000.000 Hz
FIDRES                0.152588 Hz
AQ                    3.2767999 sec
RG                          161
DW                     50.000 usec
DE                      6.50 usec
TE                        291.3 K
D1                  1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                500.3030896 MHz
NUC1                          1H
P1                       15.10 usec
PLW1                15.13599968 W

F2 - Processing parameters
SI                            65536
SF                  500.3000139 MHz
WDW                           EM
SSB                 0
LB                            0.30 Hz
GB                  0
PC                            1.00
```


8.523
8.521
8.513
8.512
8.030
8.028
8.010
8.008
7.863
7.858
7.843
7.839
7.824
7.820
7.780
7.774
7.770
7.760
7.756
7.422
7.408
7.284
7.281
7.272
7.269
7.265
7.262
7.253
7.250
7.234
(73% D) H/D
O
S
N
H
1a-d
1.00
1.01
1.07
1.26
3.14
1.18
8.55
8.45
8.35
8.25
8.15
8.05
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)