Photochemical and electrochemical regioselective *cross*-dehydrogenative C(sp^2)-H sulfenylation and selenylation of substituted benzo[*a*]phenazin-5-ols

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EXPERIMENTAL SECTION

1. General.

All chemicals (analytical grade) other than benzo[*a*]phenazin-5-ols were purchased from reputed companies and used without further purification. Benzo[*a*]phenazin-5-ols (**1a**-**1e**) used in this present study were prepared out of the reaction between 2-hydroxynaphthoquinone and o-phenylenediamines as per the previously reported procedure.[1] ^{1}H-, ^{13}C-, ^{77}Se-NMR spectra were collected at 400, 100 and 76 MHz, respectively, on a Bruker DRX spectrometer using $CDCl_3$ and DMSO-d_6 containing 1-2 drops of saturated NaOH solution in D_2O, as the solvents. Chemical shifts were reported in δ (ppm), relative to the internal standard, TMS. The signals observed are described as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants are reported as *J* value in Hz. Mass spectrometry was obtained using a Bruker maXis Impact (Q-TOF), Agilent (Q-TOF), and Microtek Q-TOF Micro YA 263 Waters high-resolution mass spectrometer. X-ray single crystallographic data were collected on X′Calibur CCD area-detector diffractometer. UV spectra were recorded on a SHIMADZU UV-3101PC spectrophotometer. Melting point was recorded on a Chemiline CL-725 melting point apparatus and is uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 F254 (Merck) plates. Philips 9 W Standard B22 white LED Bulbs (Manufacturer: PHILIPS; Model and other details: LED Lamp B22d Crystal White, 9 W, F6500, Lumen 825 lm (91.7 lm/W), 0.060 A, 220-240 Vac, 50 Hz) were used as the light source. For accessing direct sunlight, all reactions were carried out on an open roof-top (Chemistry Building). A ‘Metravi RPS-3005 DC Regulated Power Supply’ and Graphite, Pt, Ag, Zn, and Cu plate-electrodes were used to perform the electrochemical cell reactions.

2. Pictorial views of the experimental Set-ups

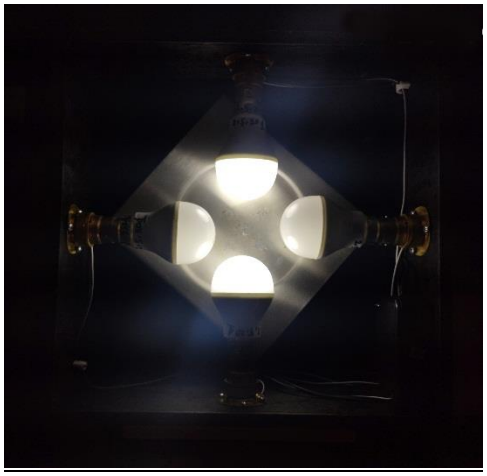


Figure S1a

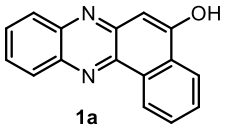
Figure S1b

Figure S1c

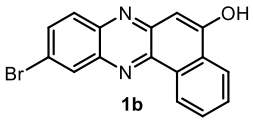
Figure S1d

Figure S1: (a) A pictorial view (from the top end) at the time of lightening of two white LED (2 × 9 W) positioned face to face; (b) Pictorial view at the time of running the experiment; (c) Pictorial view of the reaction set-up in open sunlight on the roof-top (Dept. of Chemistry, Visva-Bharati), (d) 'Metravi RPS-3005 DC Regulated Power Supply' and Platinum || Graphite plate-electrodes were used to perform the electrochemical cell reactions.

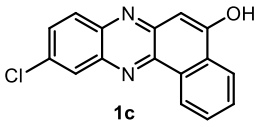
3. ***The spectral data of all the synthesized benzo[a]phenazin derivatives* 1 (1a – 1e) *are given below:***



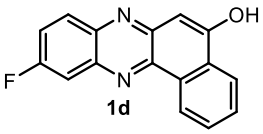
Benzo[*a*]phenazin-5-ol (1a).[1a] Orange amorphous solid; yield: 89% (220 mg, 1 mmol scale); mp =296 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.16-9.13 (m, 1H, Ar-H), 8.43-8.41 (m, 1H, Ar-H), 8.10 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.90 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.84-7.77 (m, 2H, Ar-H), 7.71-7.68 (m, 1H, Ar-H), 7.60-7.56 (m, 1H, Ar-H), 6.77 (s, 1H, *H*C=C(OH)-)) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ =166.39, 148.19, 143.11, 139.72, 137.85, 133.66, 131.46, 129.54, 129.17 (2C), 127.90, 126.92, 125.39, 124.53, 124.19, 101.51 ppm.



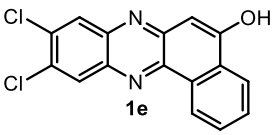
10-Bromobenzo[*a*]phenazin-5-ol (1b). Yellow crystalline solid; yield: 94% (308 mg, 1 mmol scale); mp = 274-276°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.61 (br s, 1H, Ar-*OH*), 9.16 (m, 1H, Ar-H), 8.41-8.28 (m, 2H, Ar-H), 8.15-8.03 (m, 1H, Ar-H), 7.95-7.88 (m, 3H, Ar-H), 7.14 (s, 1H, *H*C=C(OH)-)) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ = 157.45, 145.56, 141.21, 139.88, 133.15, 131.45, 131.07, 130.95, 130.64, 130.43, 129.96, 128.87, 124.94, 122.97, 121.11, 103.31 ppm.



10-Chlorobenzo[*a*]phenazin-5-ol (1c).[1c] Greenish yellow crystalline solid; yield: 87% (244 mg, 1 mmol scale); mp = 280-282 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.61 (br s, 1H, Ar-*OH*), 9.18-9.17 (m, 1H, Ar-H), 8.30-8.22 (m, 2H, Ar-H), 8.15-8.11 (m, 1H, Ar-H), 7.92-7.78 (m, 3H, Ar-H), 7.14 (s, 1H, *H*C=C(OH)-)) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ = 157.38, 145.48, 141.03, 139.49, 132.57, 131.05, 130.76, 130.70, 130.61, 130.41, 129.91, 128.84, 127.62, 124.94, 122.95, 103.29 ppm.



10-Fluorobenzo[*a*]phenazin-5-ol (1d). Yellow amorphous solid; yield: 92% (243 mg, 1 mmol scale); mp = 283-286°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.57 (br s, 1H, Ar-*OH*), 9.23-9.21 (m, 1H, Ar-H), 8.32-8.30 (m, 1H, Ar-H), 8.23-8.19 (m, 1H, Ar-H), 8.02-7.98 (m, 1H, Ar-H), 7.94-7.88 (m, 2H, Ar-H), 7.86-7.80 (m, 1H, Ar-H), 7.18 (s, 1H, *H*C=C(OH)-)) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ = 159.62 (J_{CF} = 554 Hz), 159.92, 144.86, 139.95, 139.76, 130.69, 130.57, 130.41, 128.96, 128.81, 124.97, 124.70, 122.95, 120.96 (J_{CF} = 26 Hz), 111.98 (J_{CF} = 21 Hz), 103.30 ppm.



9,10-dichlorobenzo[*a*]phenazin-5-ol (1e).[1a] Orange amorphous solid; yield: 95% (299 mg, 1 mmol scale); mp = 295-297°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.06-9.04 (m, 1H, Ar-H), 8.35-8.33 (m, 1H, Ar-H), 8.27 (s, 1H, Ar-H), 8.06 (s, 1H, Ar-H), 7.84-7.77 (m, 2H, Ar-H), 6.57 (s, 1H, *H*C=C(OH)-)) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ = 168.51, 167.60, 153.03, 149.12, 142.46, 140.97, 136.29, 131.07, 130.01, 129.52 (2C), 128.11, 127.05, 124.99, 124.16, 101.29 ppm.

4. Scanned copies of ^{1}H NMR and ^{13}C NMR spectra for all the synthesized benzo[*a*]phenazin derivatives 1 (1a – 1e) (Figure S1 – S10)

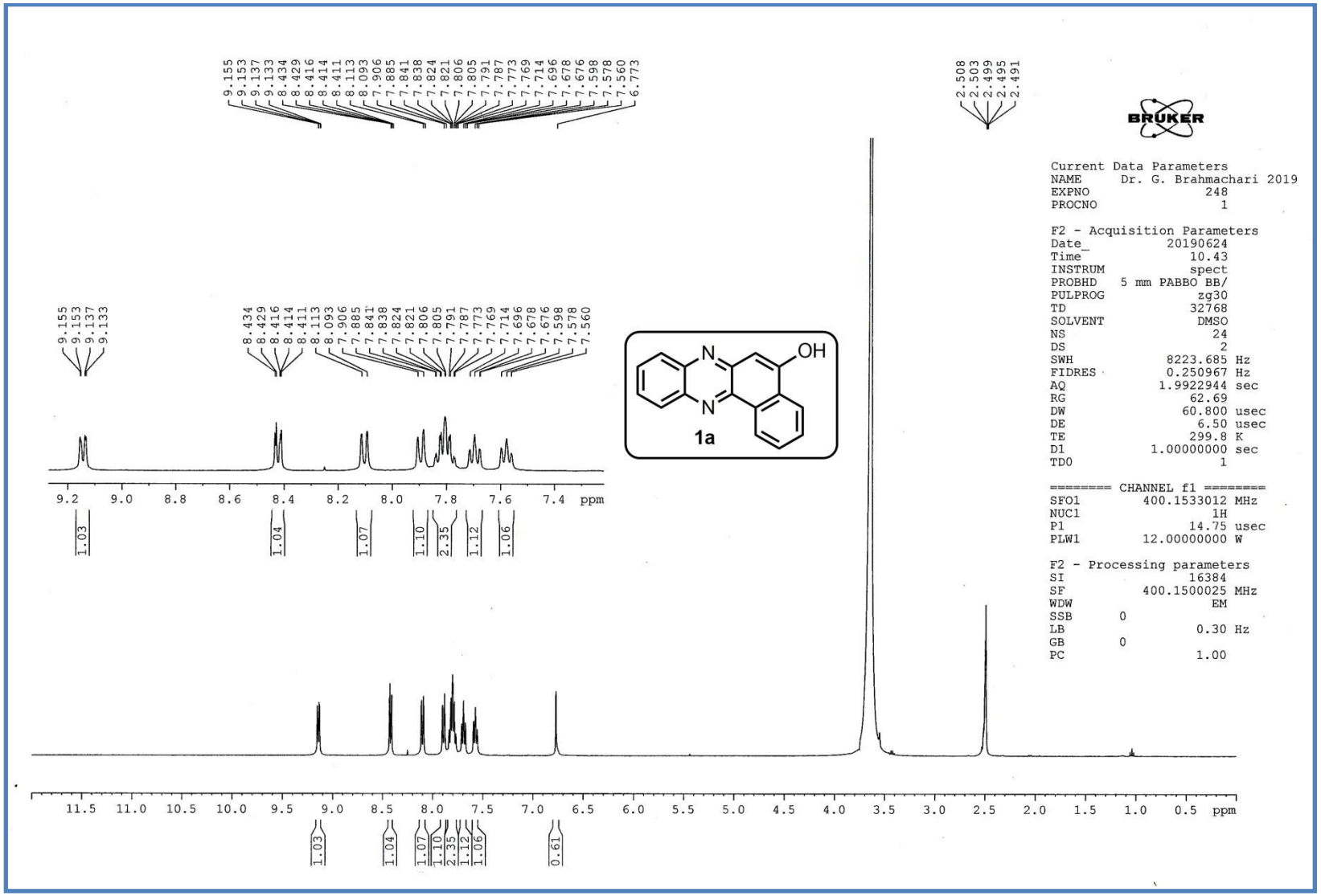


Figure S1. ^{1}H-NMR spectrum of benzo[*a*]phenazin-5-ol **(1a)**

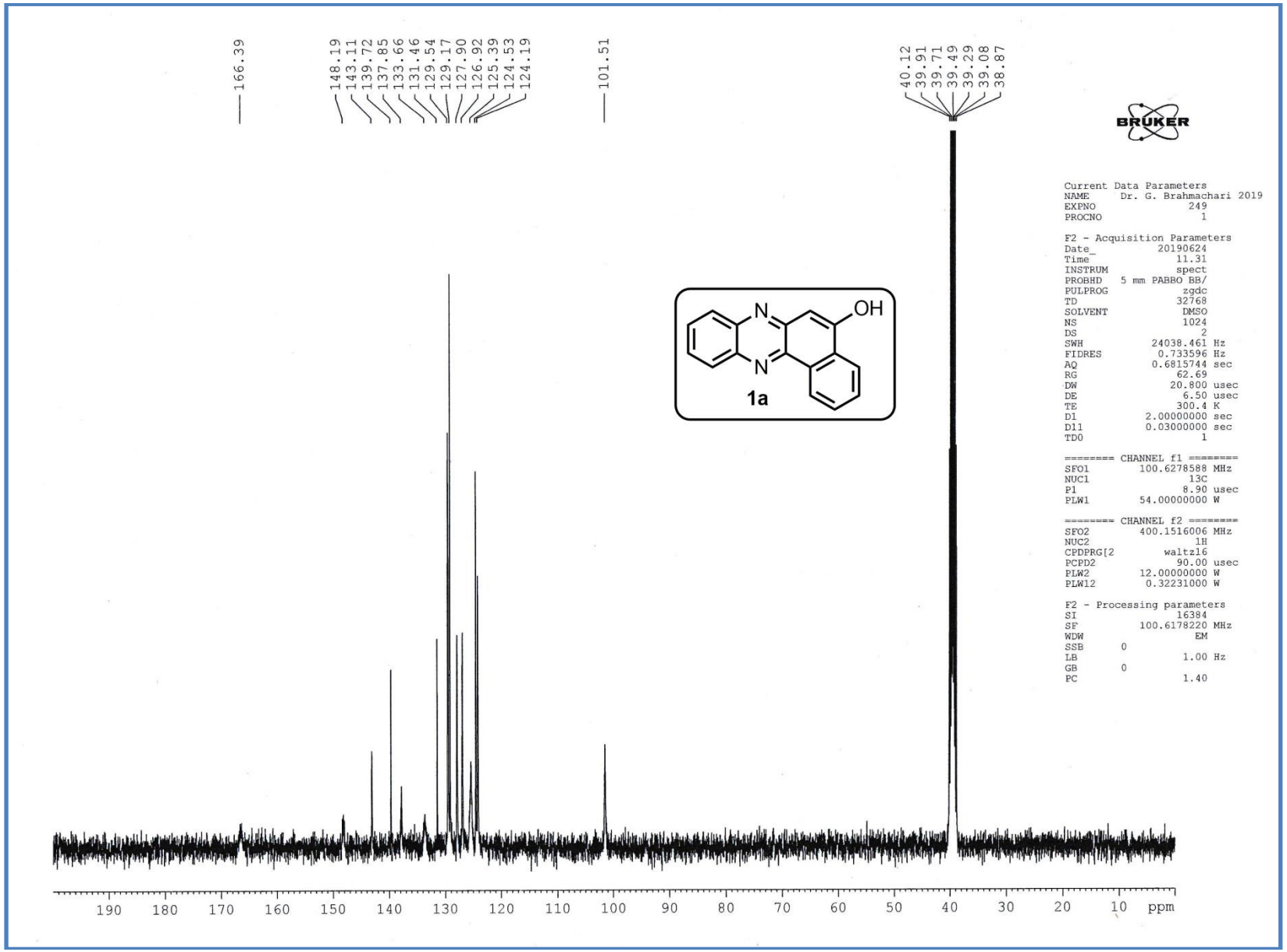


Figure S2. ^{13}C-NMR spectrum of benzo[*a*]phenazin-5-ol **(1a)**

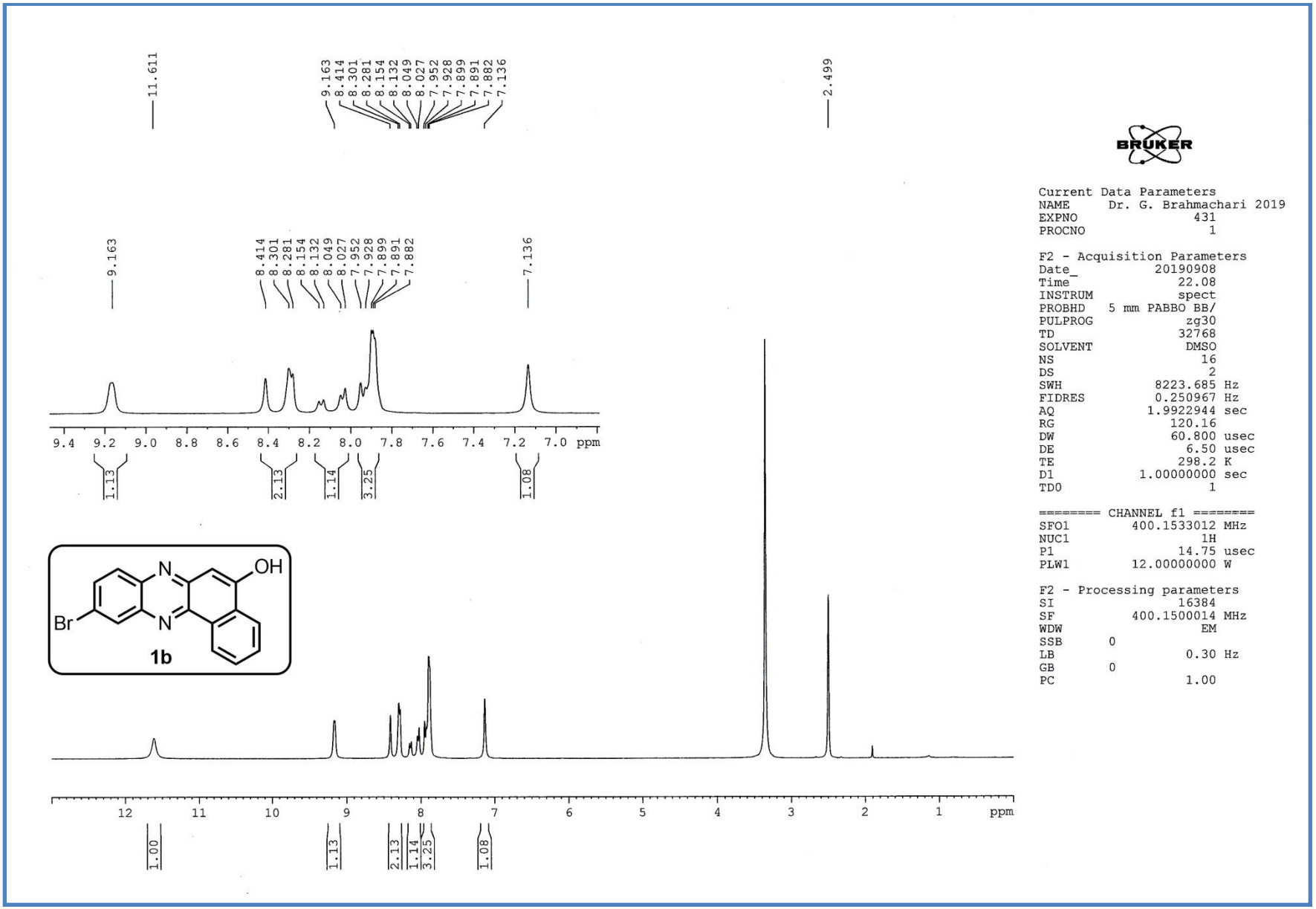


Figure S3. ^{1}H-NMR spectrum of 10-bromobenzo[*a*]phenazin-5-ol **(1b)**

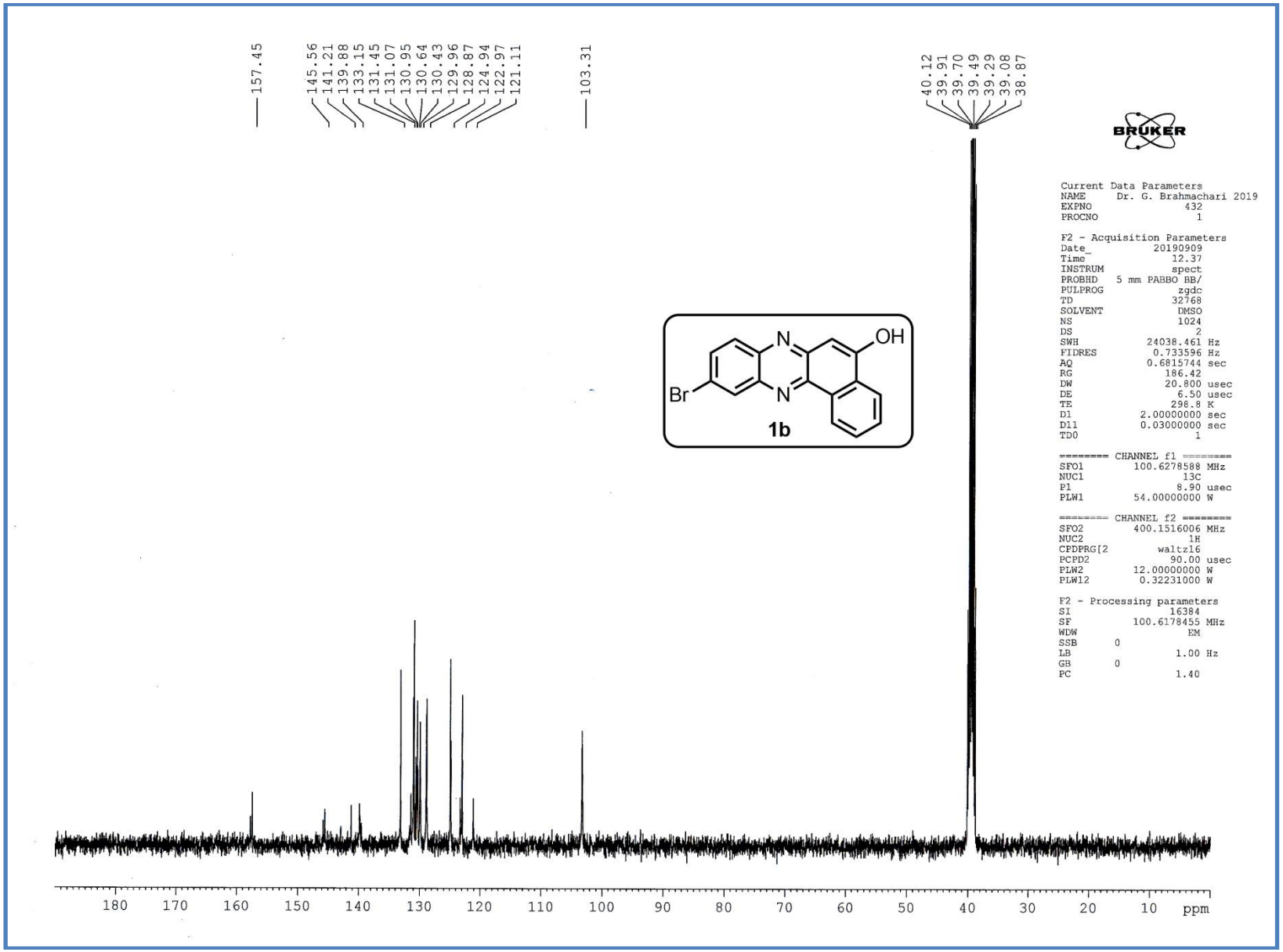


Figure S4. ^{13}C-NMR spectrum of 10-bromobenzo[*a*]phenazin-5-ol **(1b)**

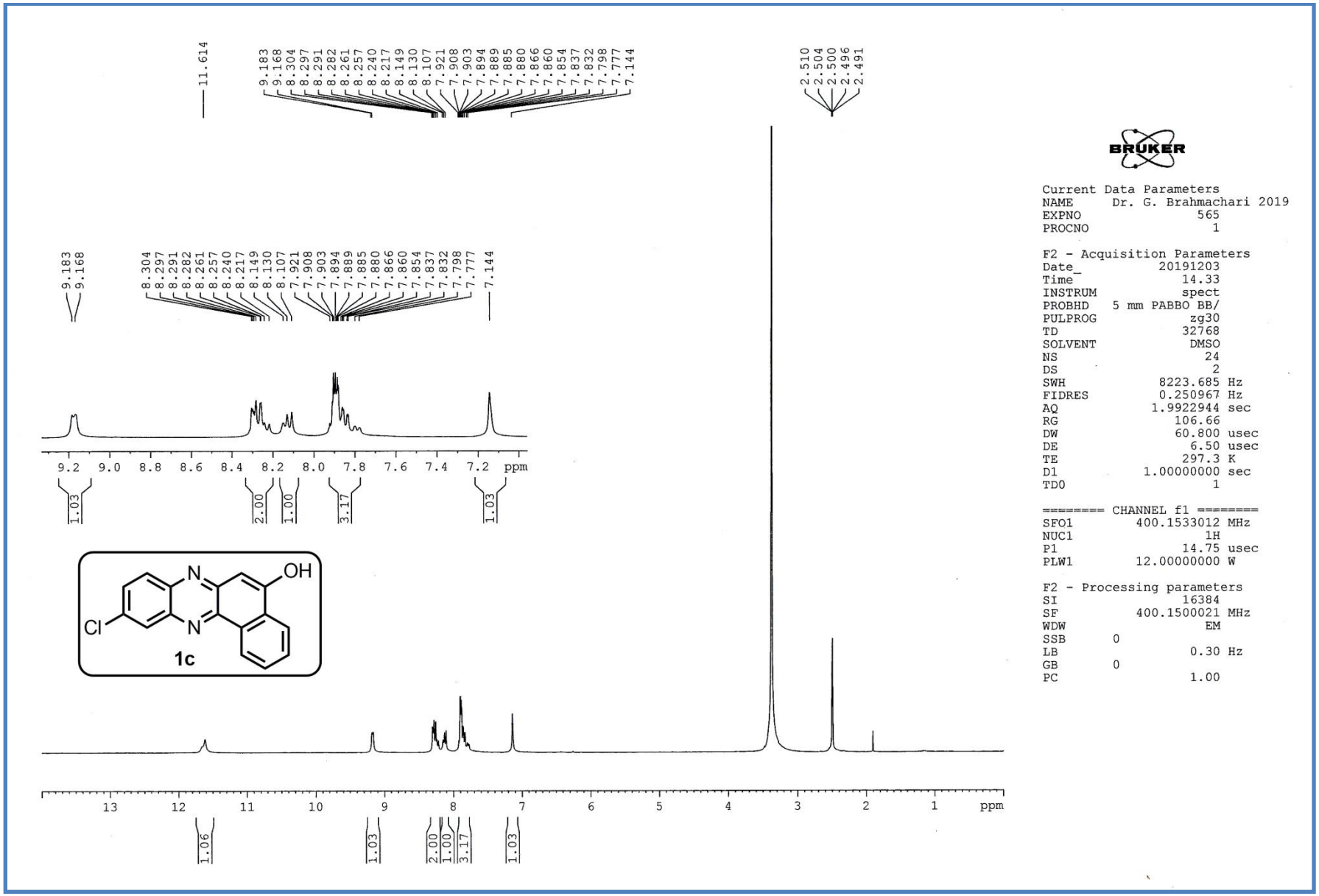


Figure S95. ^{1}H-NMR spectrum of 10-chlorobenzo[*a*]phenazin-5-ol **(1c)**

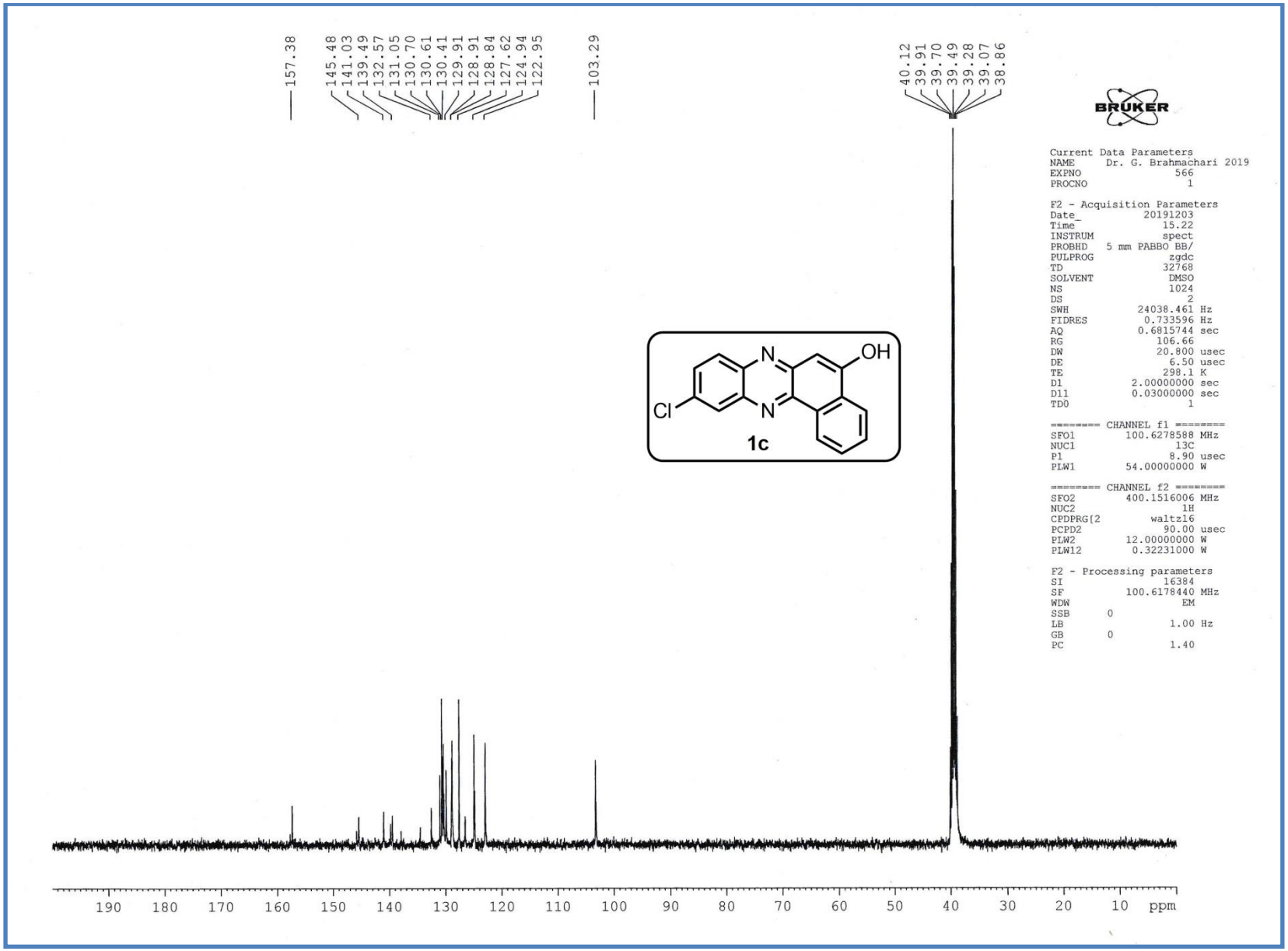


Figure S6. ^{13}C-NMR spectrum of 10-chlorobenzo[*a*]phenazin-5-ol **(1c)**

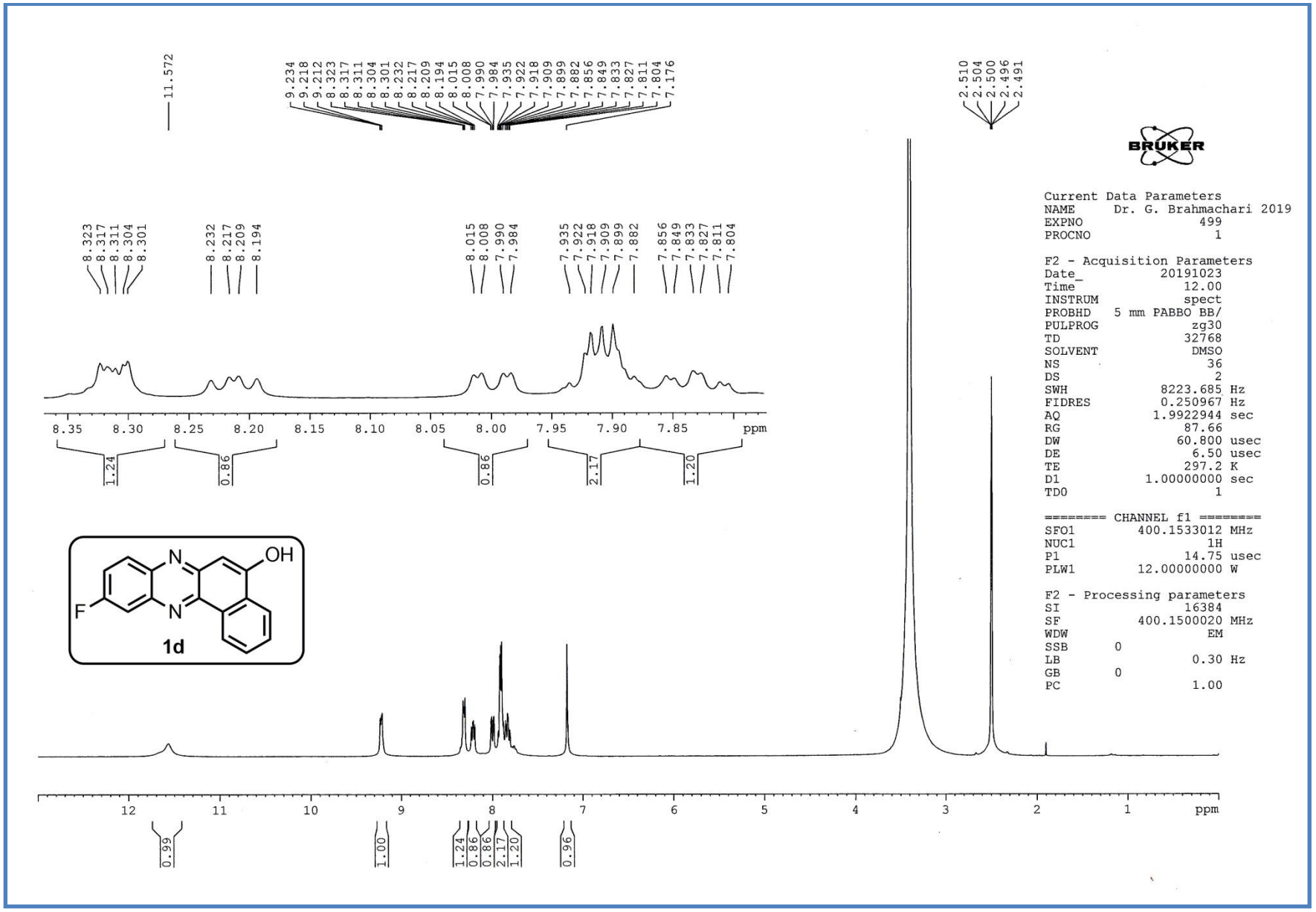


Figure S7. ^{1}H-NMR spectrum of 10-fluorobenzo[*a*]phenazin-5-ol **(1d)**

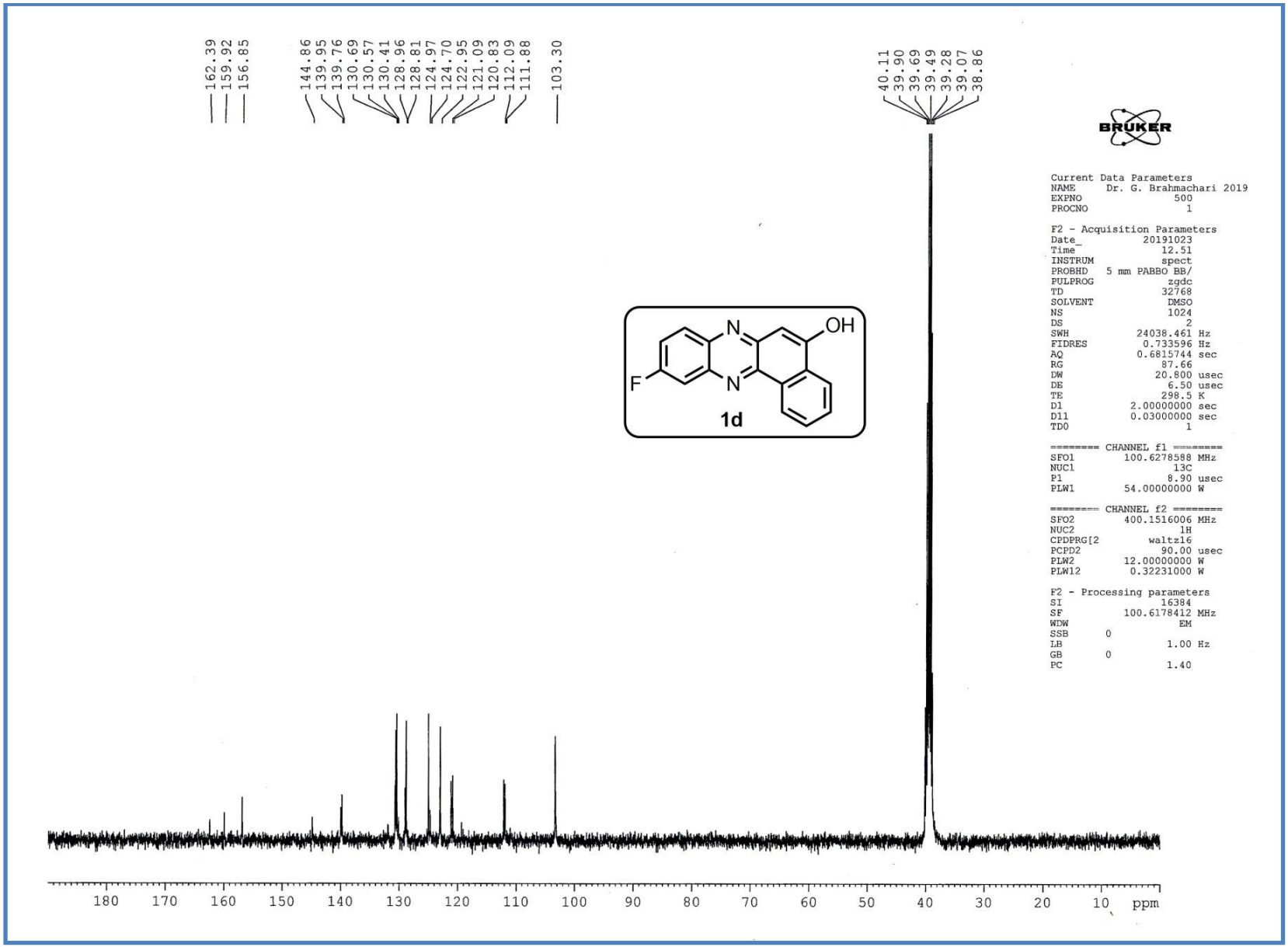


Figure S8. ^{13}C-NMR spectrum of 10-fluorobenzo[*a*]phenazin-5-ol **(1d)**

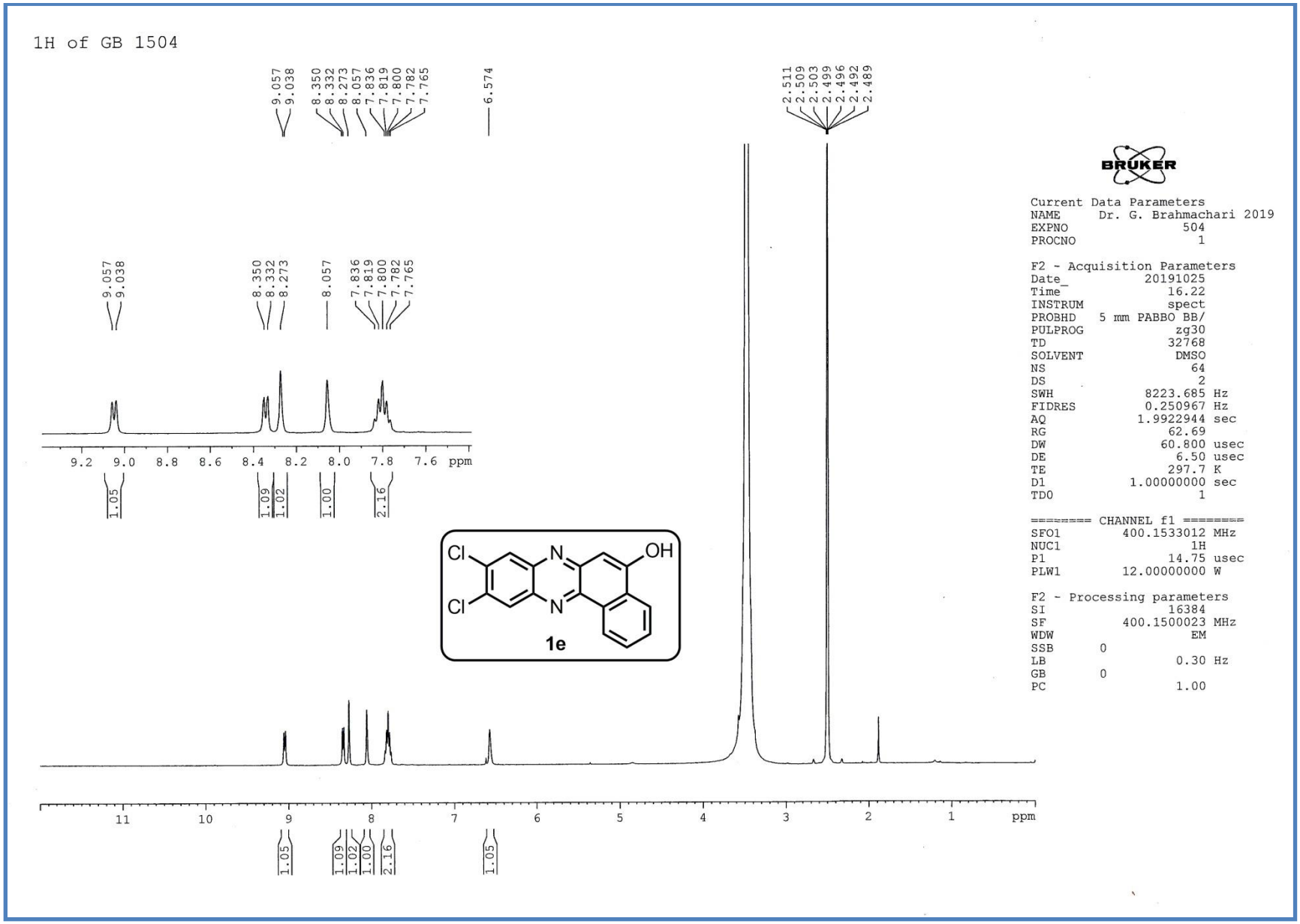


Figure S9. [1]H-NMR spectrum of 9,10-dichlorobenzo[*a*]phenazin-5-ol **(1e)**

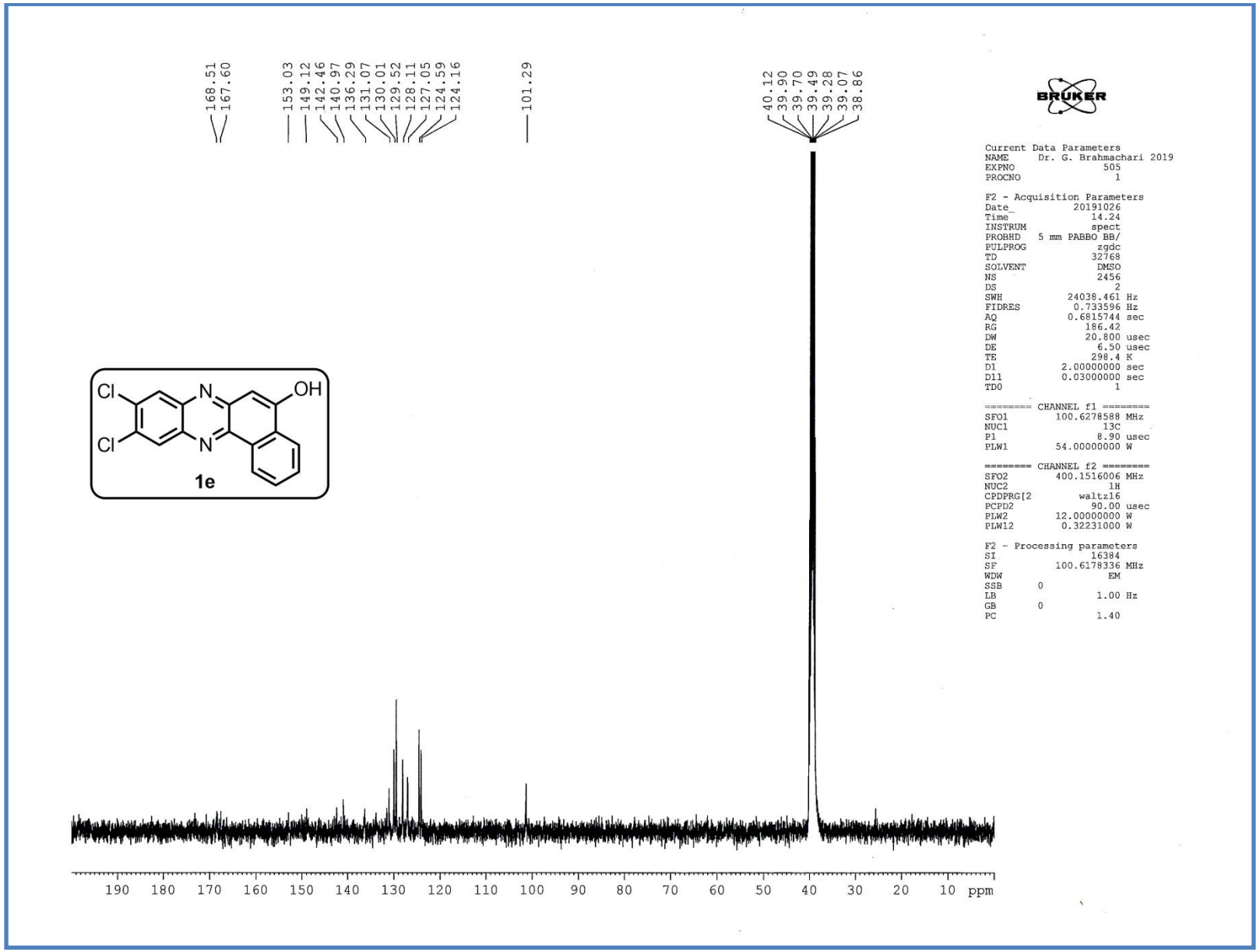


Figure S10. ^{13}C-NMR spectrum of 9,10-dichlorobenzo[*a*]phenazin-5-ol **(1e)**

5. Scanned copies of ^{1}H NMR, ^{13}C NMR, DEPT-135, ^{77}Se NMR, 2D-NMR (for representative compound 3e, along with showing the corresponding homo- and hetero-nuclear interactions in Table S1) and HRMS spectra for all the synthesized benzo[*a*]phenazin-5-ols 3 (3a–3q) and 3′ (3′a–3′e) (Figure S11 – S100)

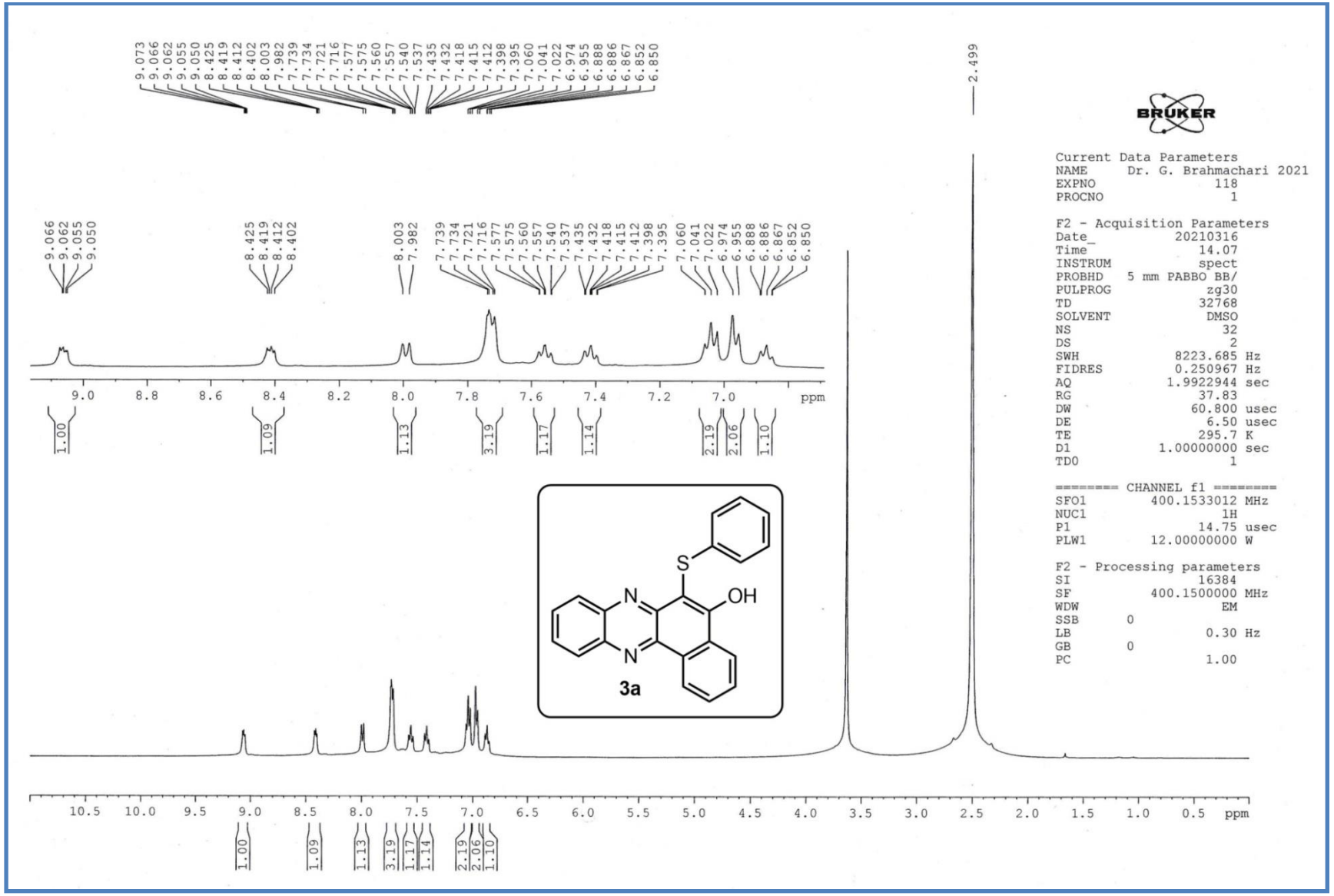


Figure S11.^{1}H-NMR spectrum of 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**) [**0.1 mmol scale**]

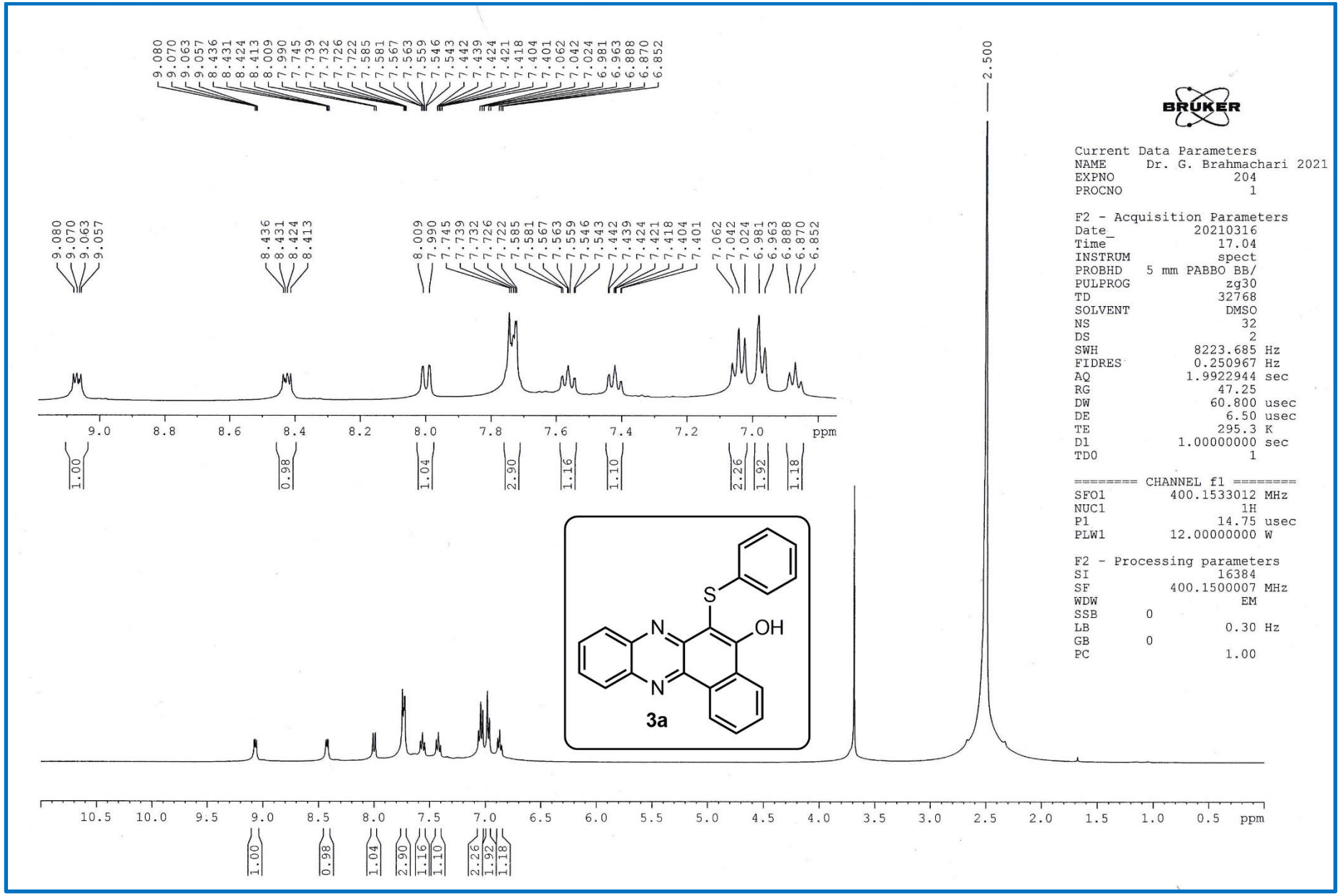


Figure S12. ^{1}H-NMR spectrum of 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**) [**1.0 mmol scale**]

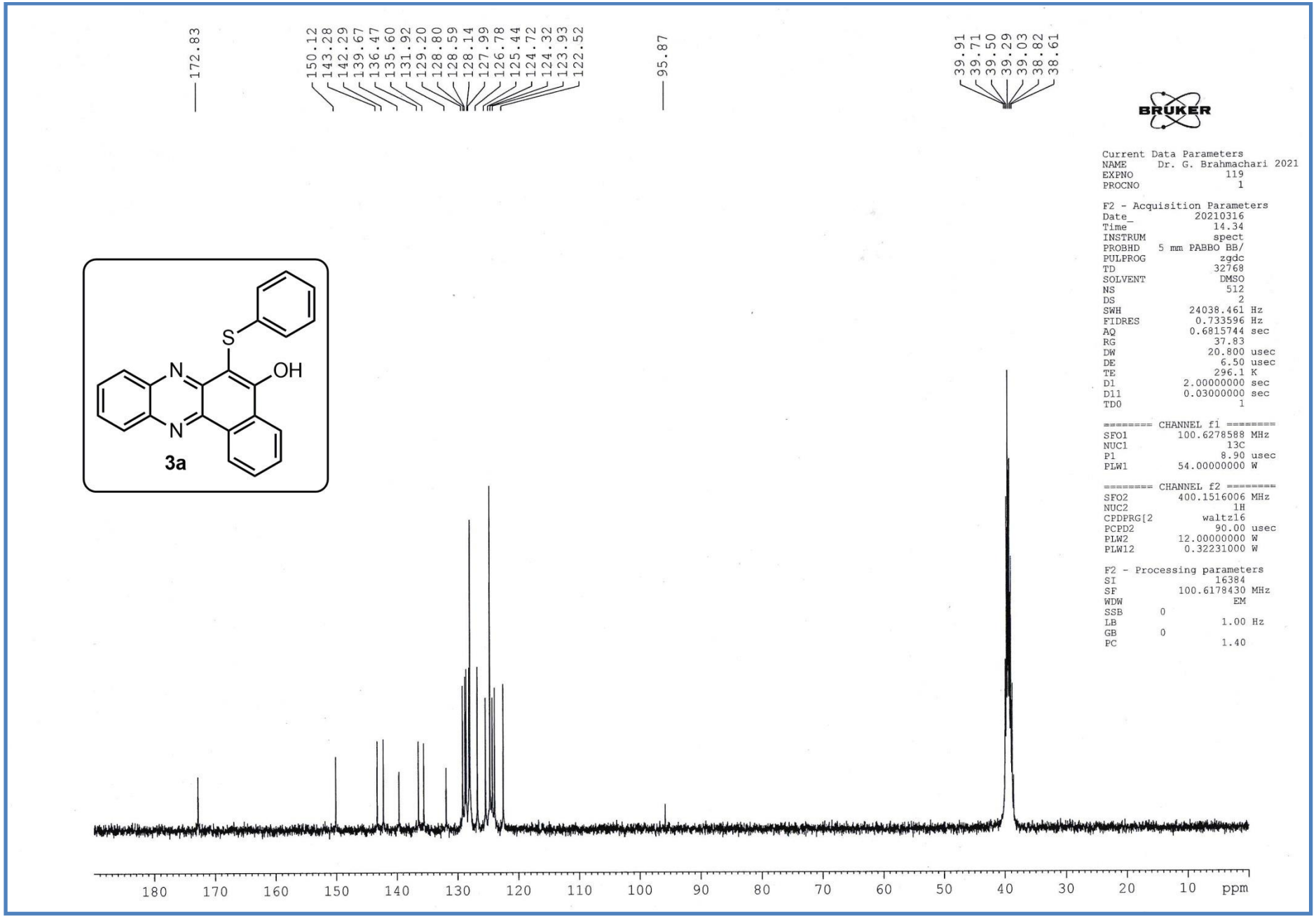


Figure S13.[13]C-NMR spectrum of 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**)

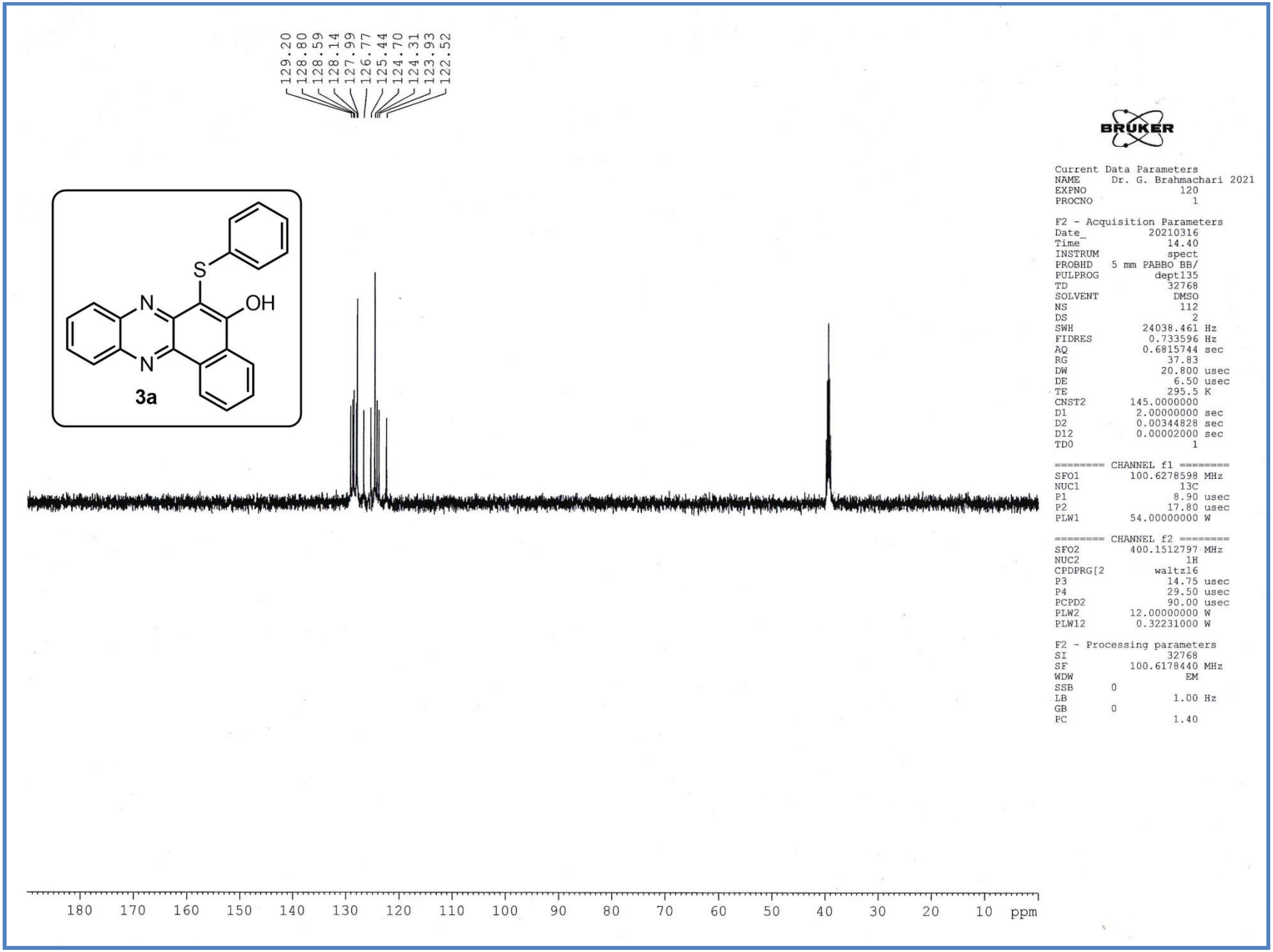


Figure S14. DEPT-135 NMR spectrum of 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**)

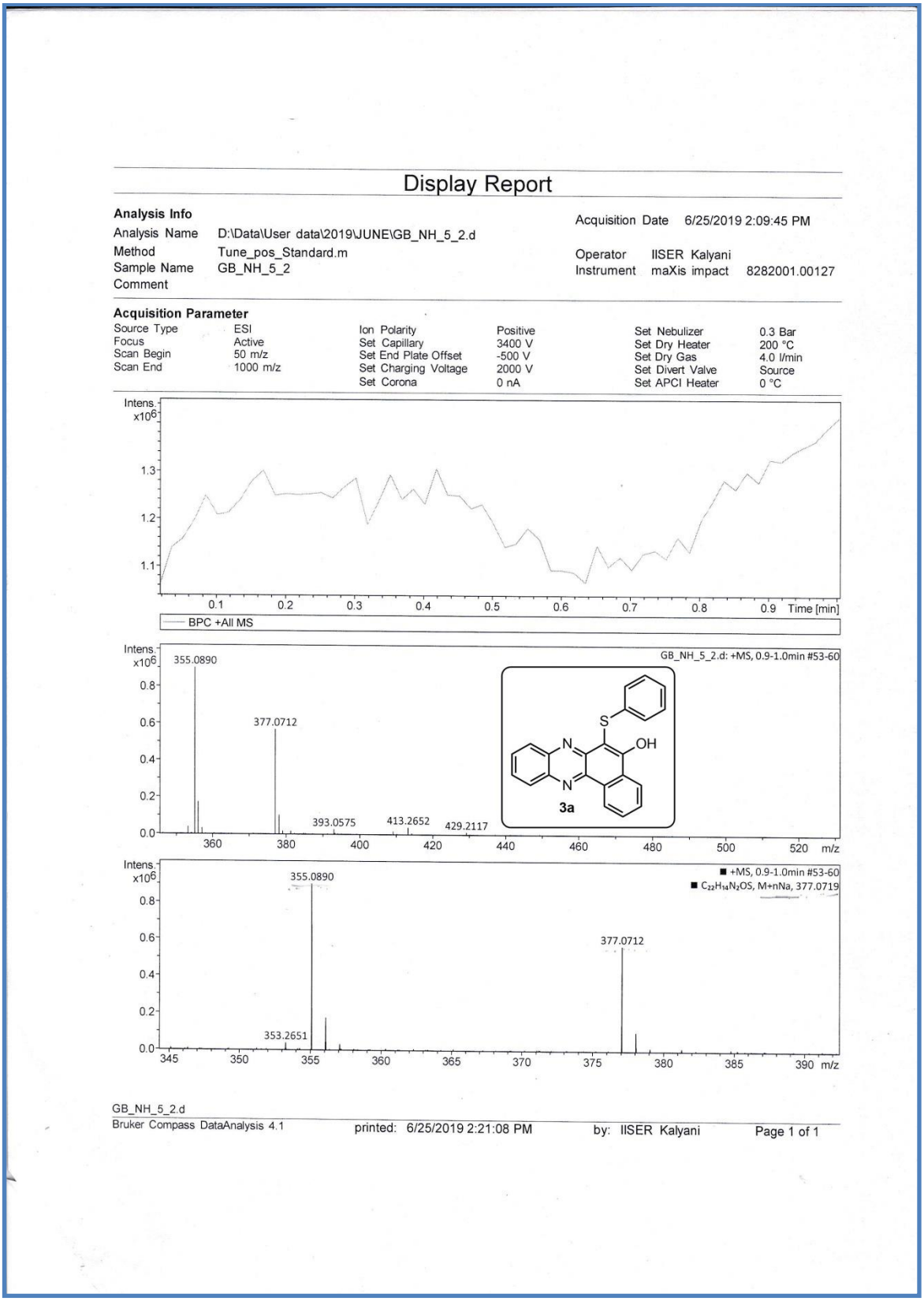


Figure S15. High-resolution Mass spectra of 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**)

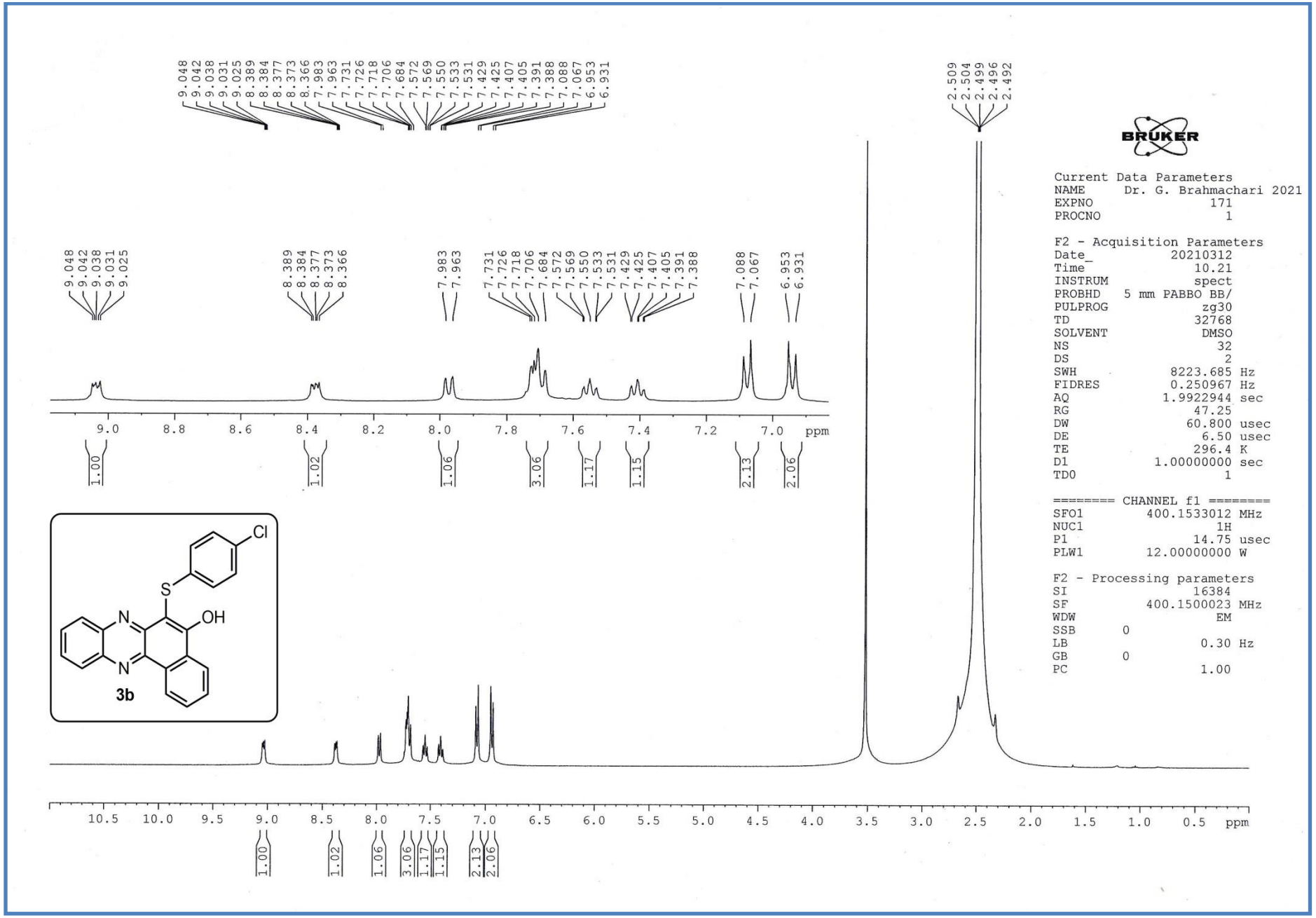


Figure S16. ^{1}H-NMR spectrum of 6-((4-chlorophenyl)thio)benzo[*a*]phenazin-5-ol (**3b**)

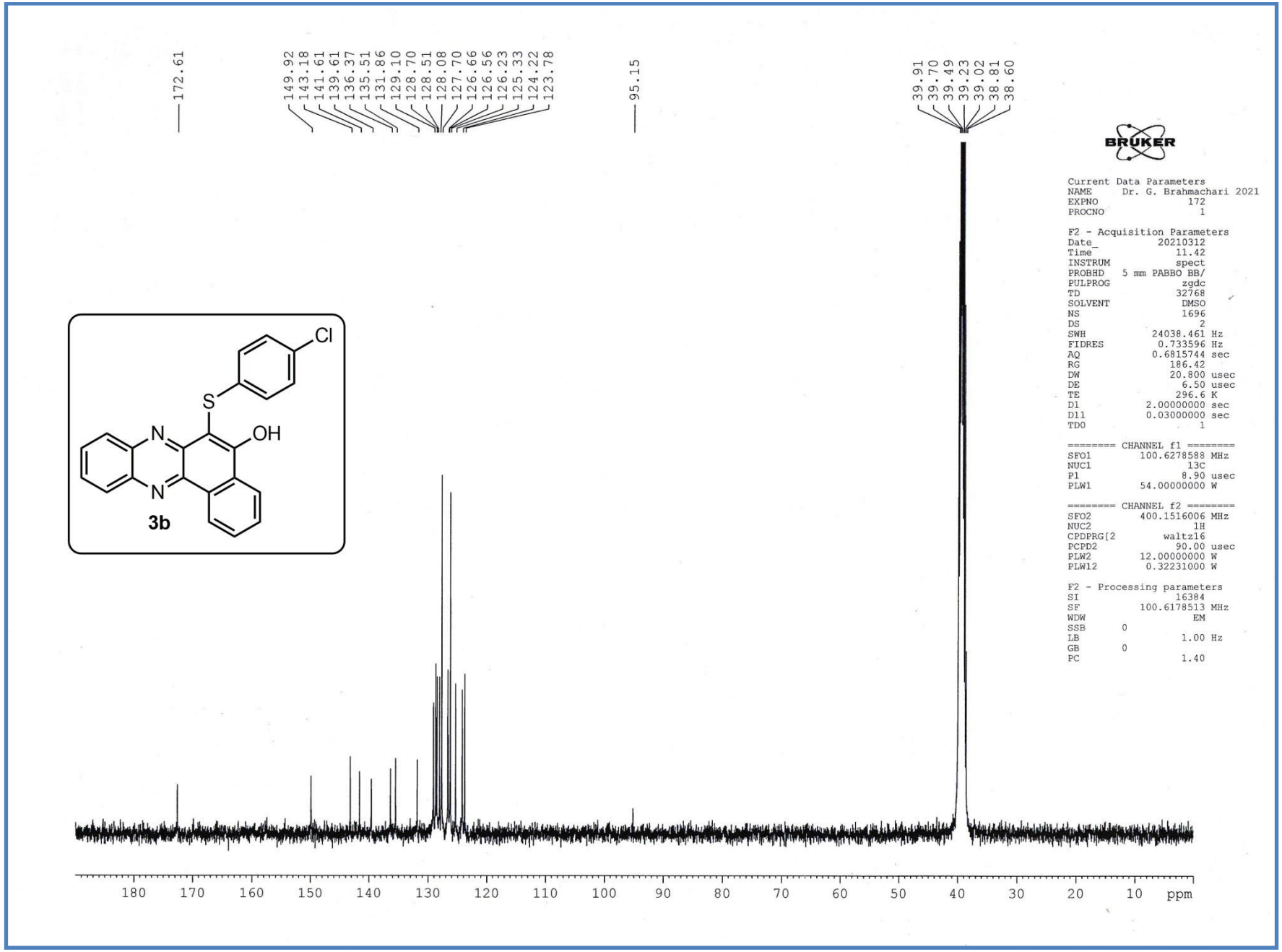


Figure S17. ^{13}C-NMR spectrum of 6-((4-chlorophenyl)thio)benzo[*a*]phenazin-5-ol (**3b**)

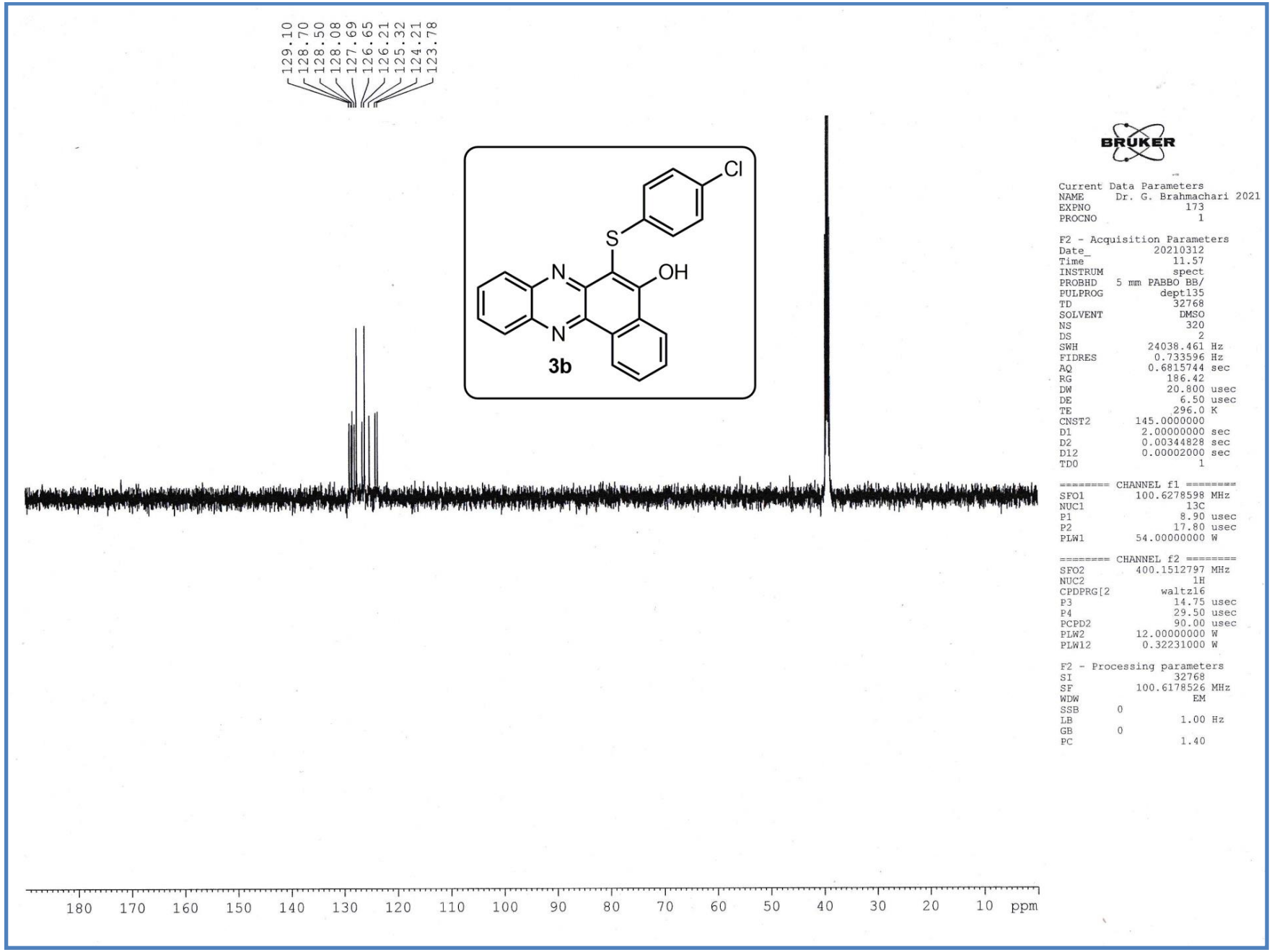


Figure S17. DEPT-135 NMR spectrum of 6-((4-chlorophenyl)thio)benzo[*a*]phenazin-5-ol (**3b**)

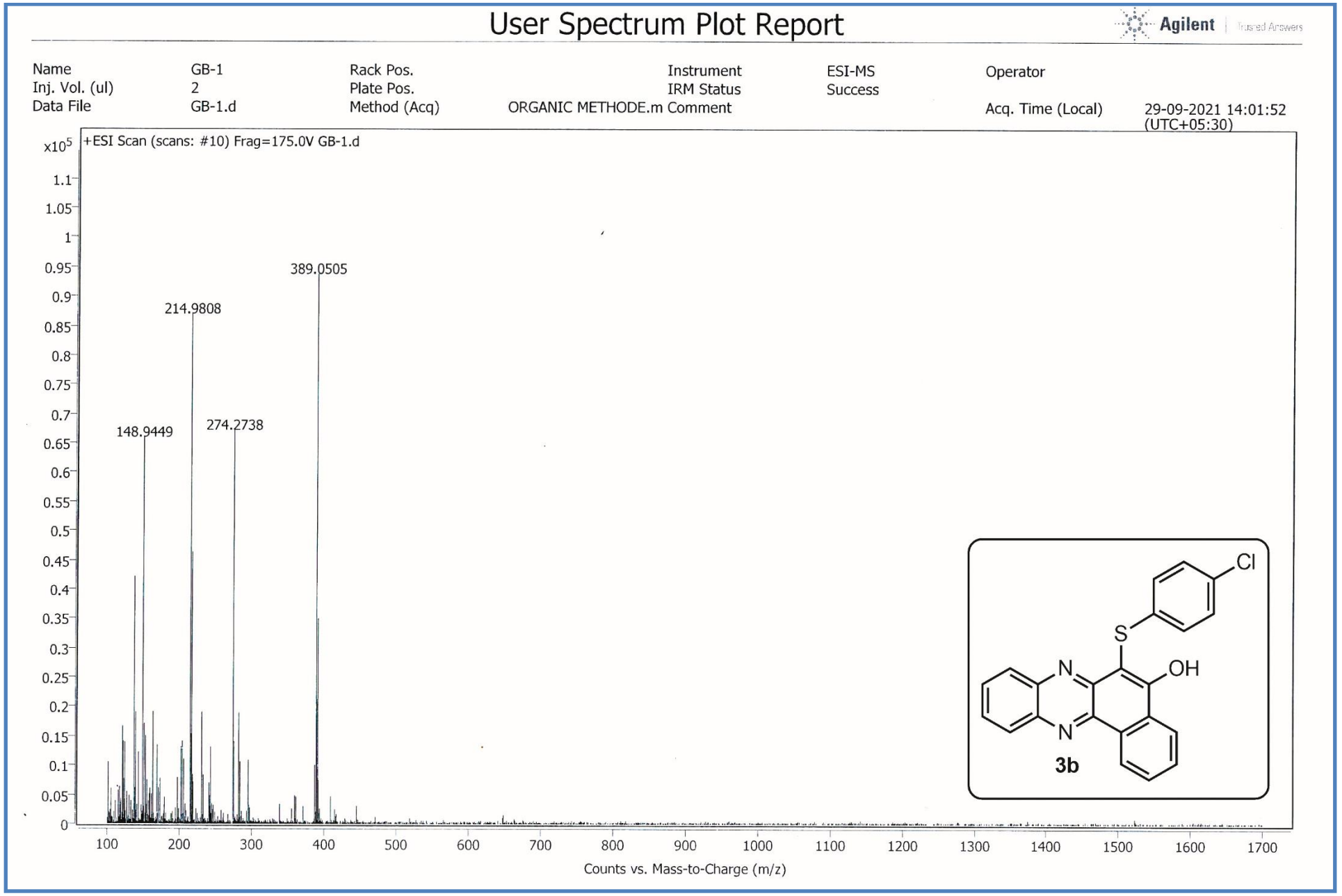


Figure S18. High-resolution Mass spectra of 6-((4-chlorophenyl)thio)benzo[*a*]phenazin-5-ol (**3b**)

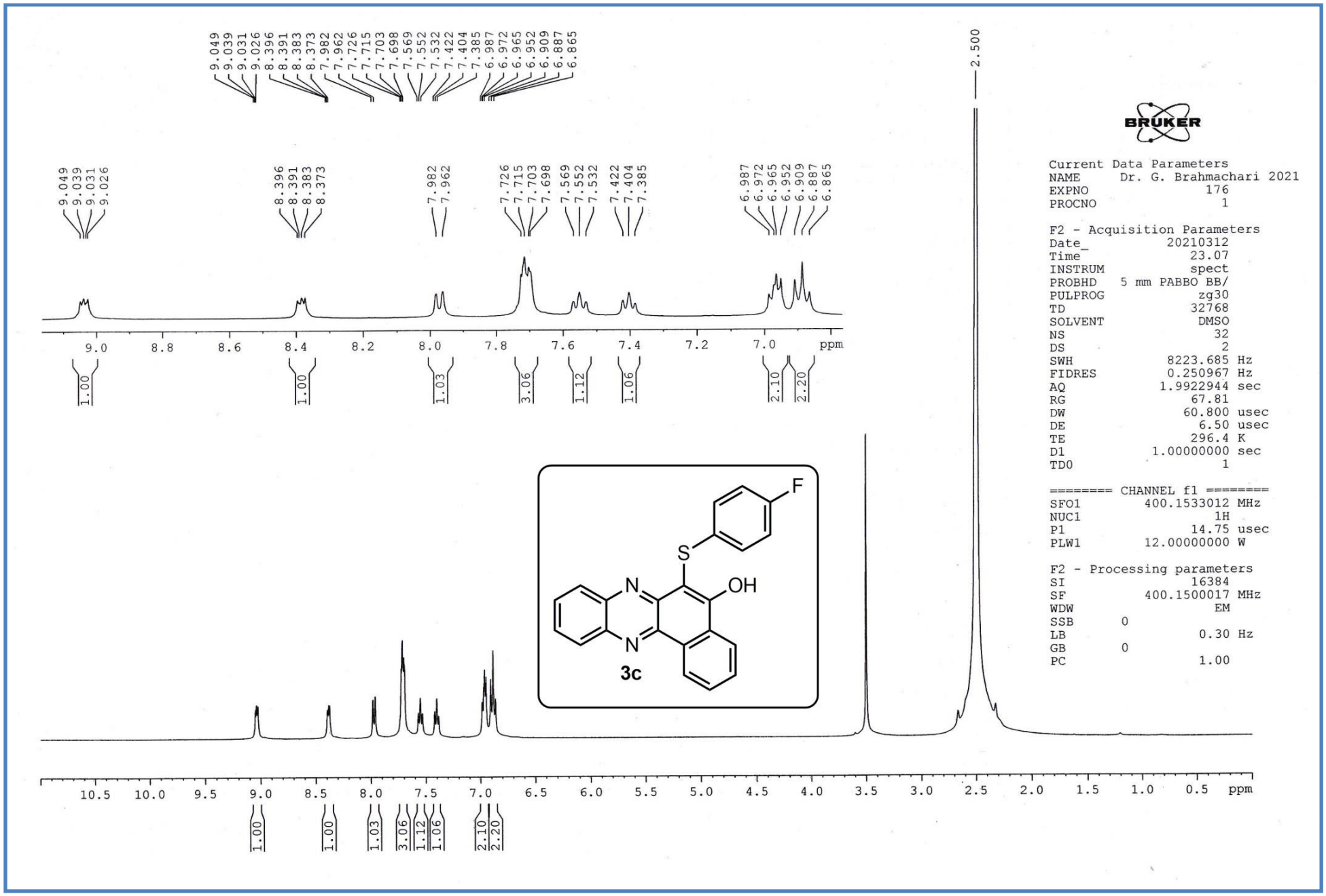


Figure S19.[1]H-NMR spectrum of 6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3c**)

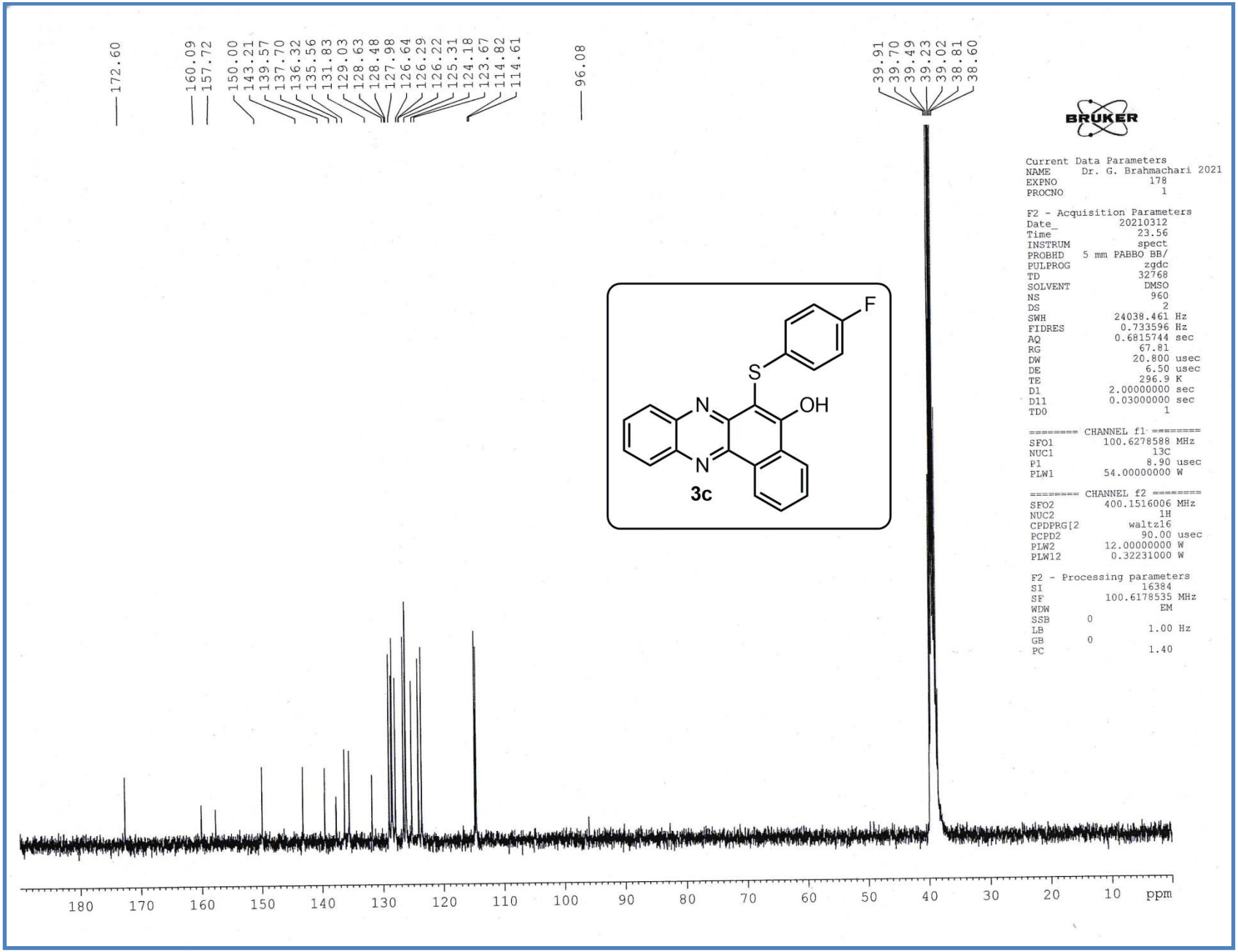


Figure S20.[13]C-NMR spectrum of 6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3c**)

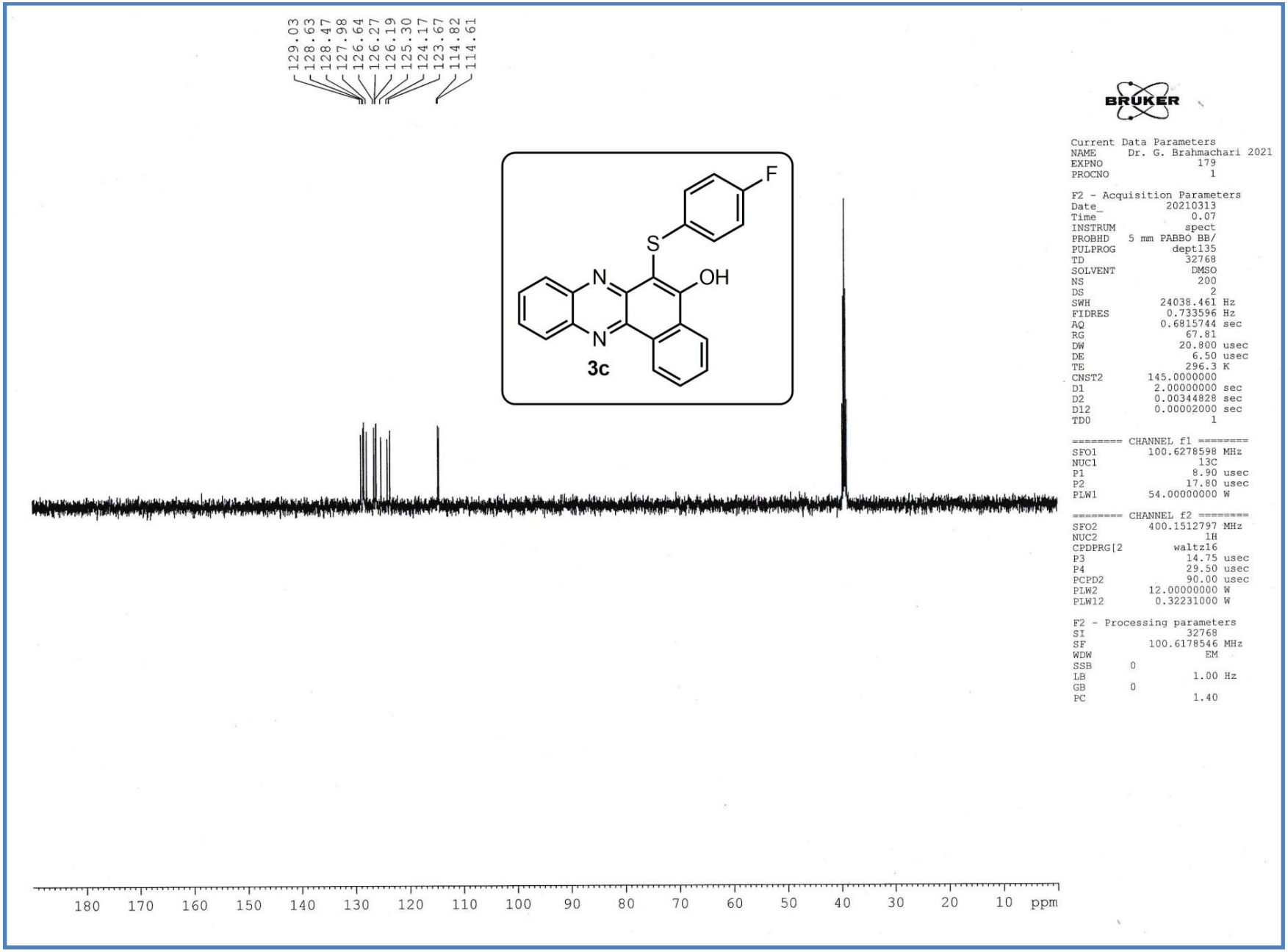


Figure S21. DEPT-135 NMR spectrum of 6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3c**)

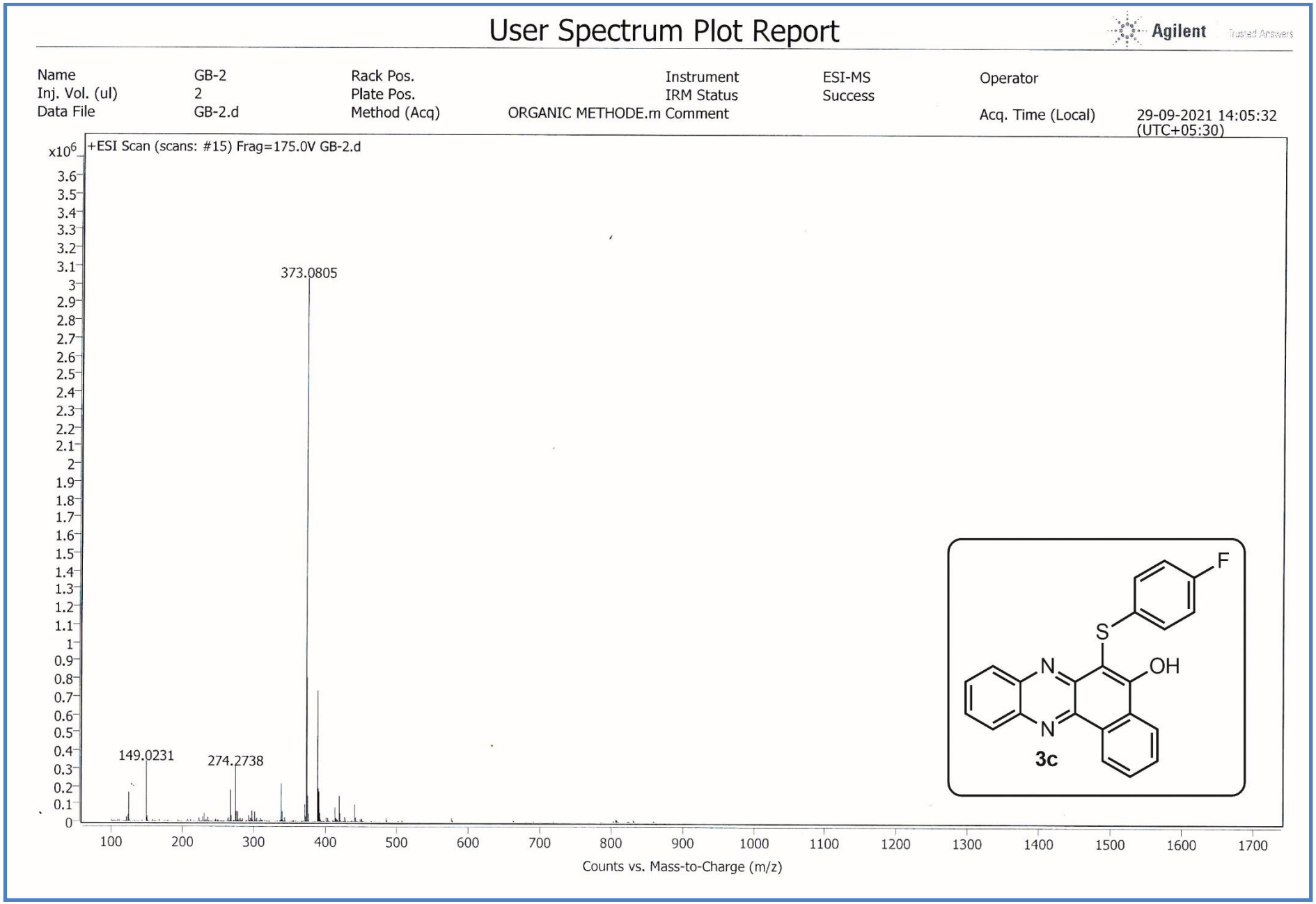


Figure S22. High-resolution Mass spectra of 6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3c**)

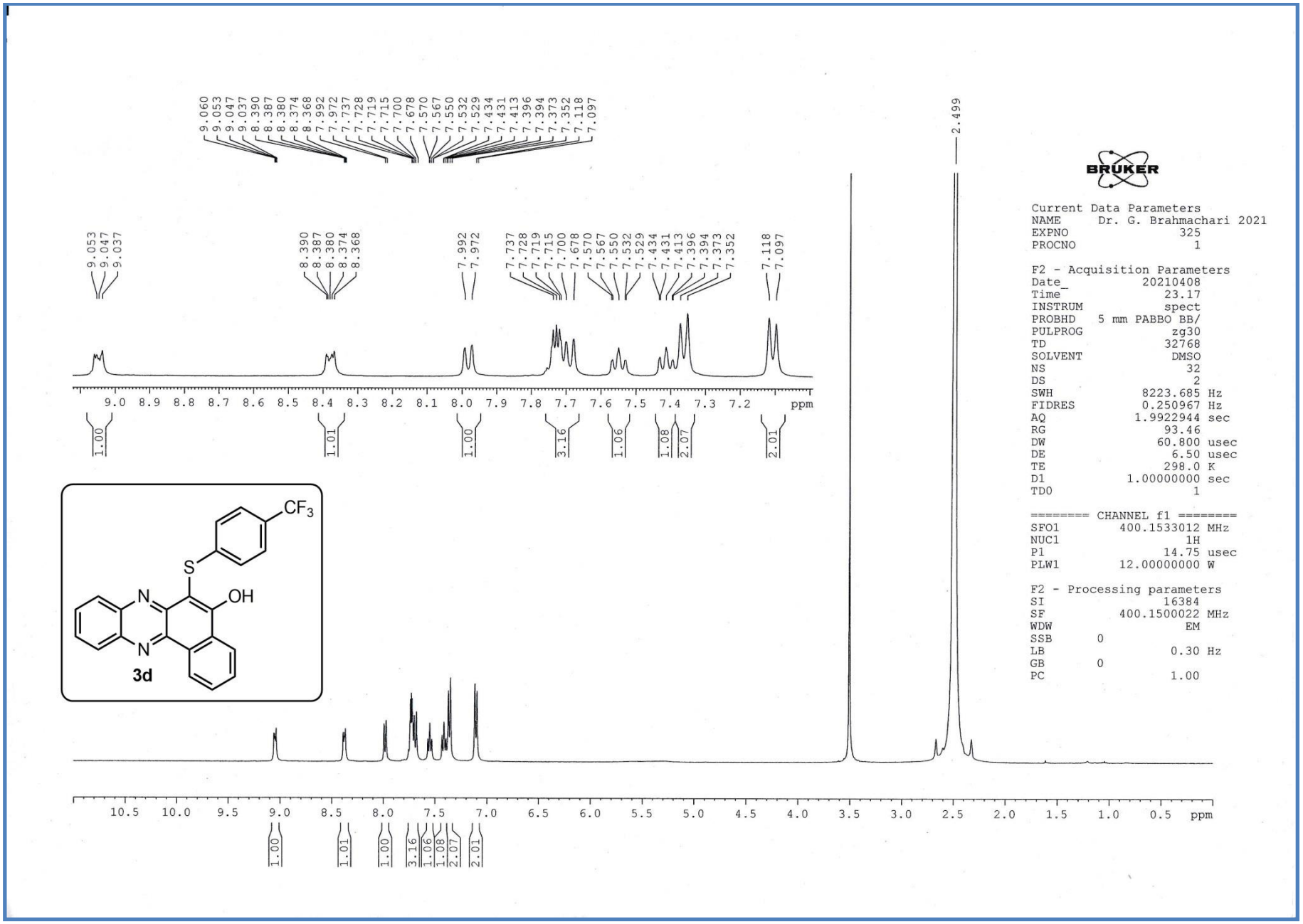


Figure S23. ^{1}H-NMR spectrum of 6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3d**)

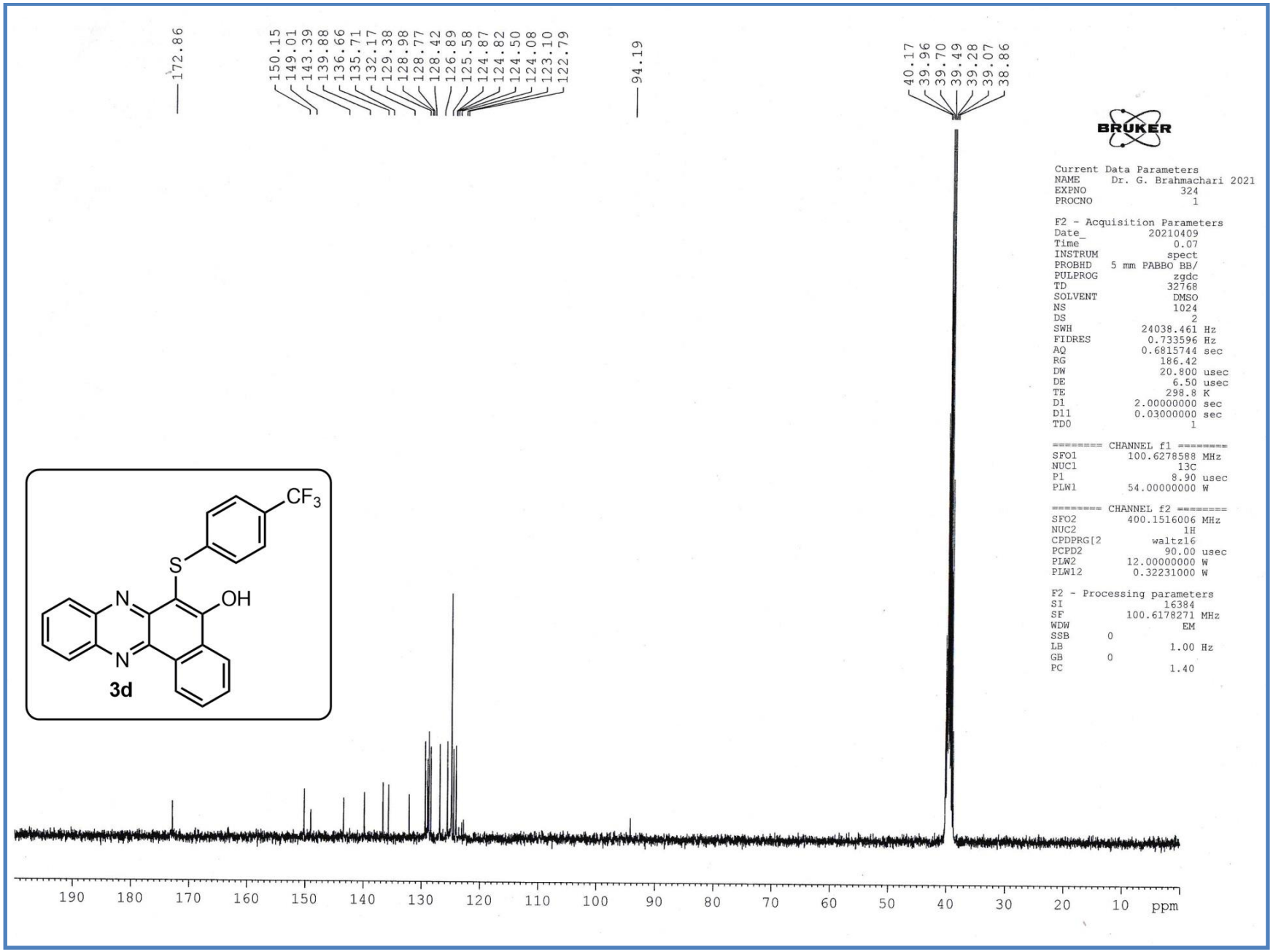


Figure S24.[13]C-NMR spectrum of 6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3d**)

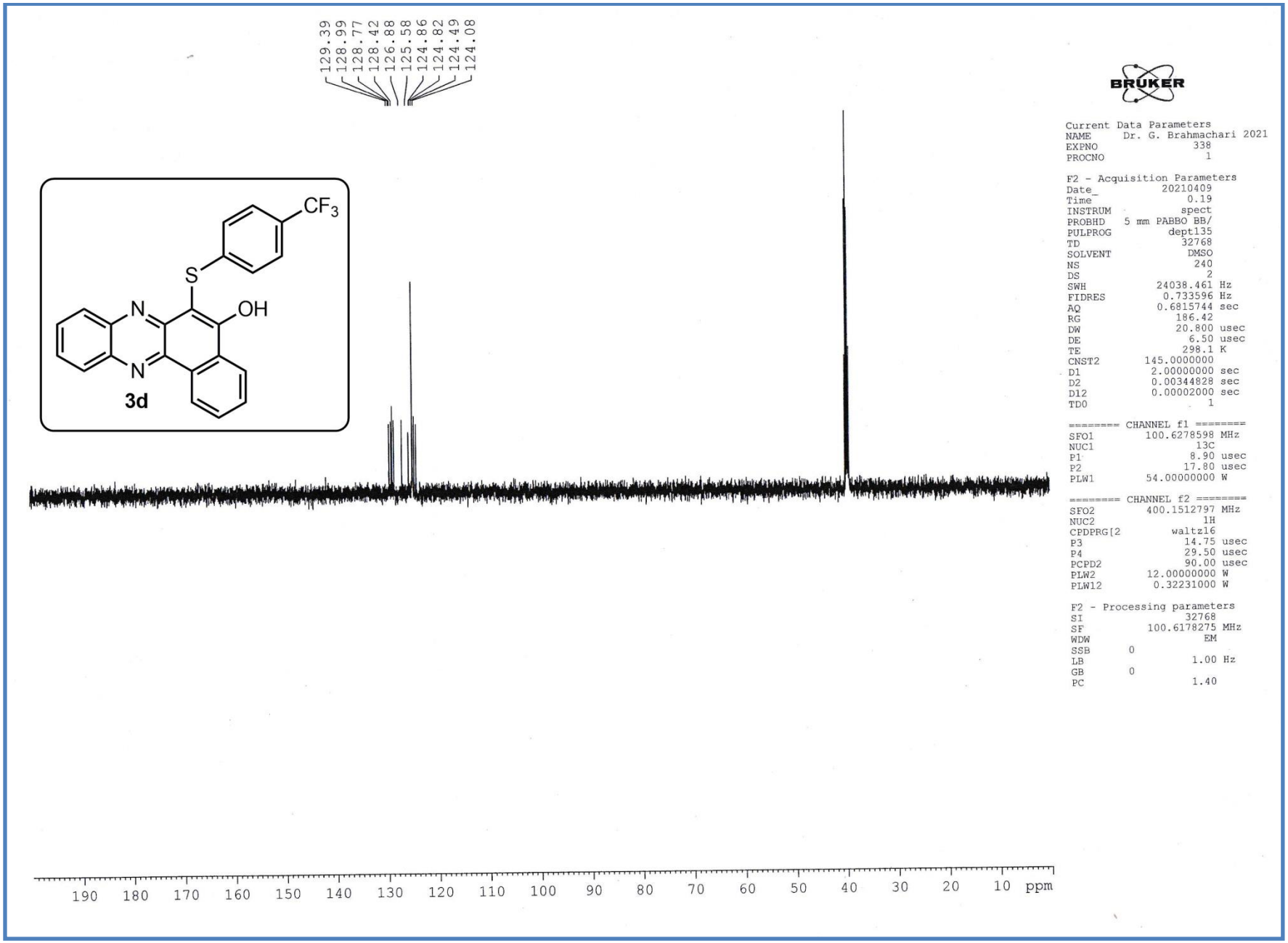


Figure S25. DEPT-135 NMR spectrum of 6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3d**)

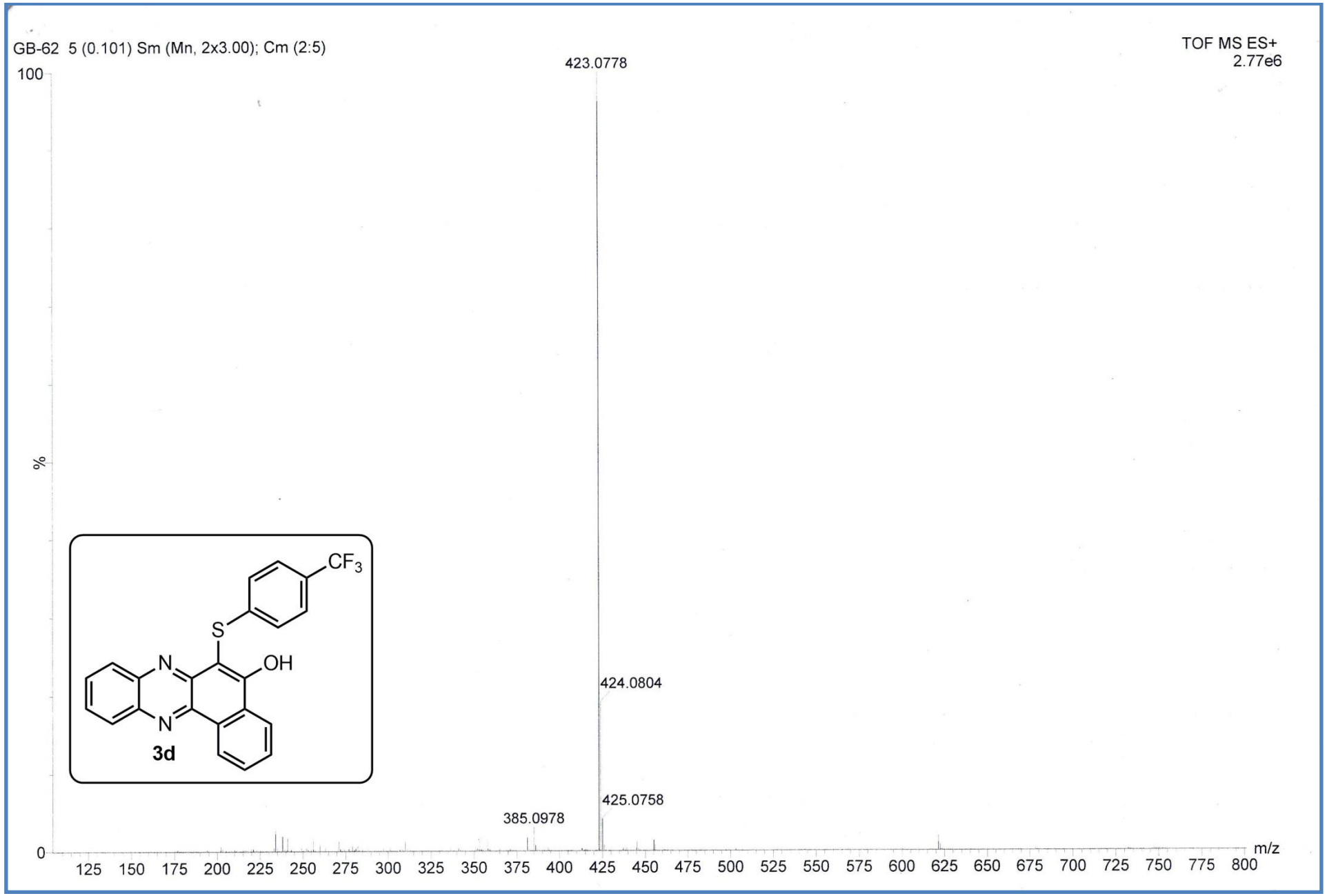


Figure S26. High-resolution Mass spectra of 6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3d**)

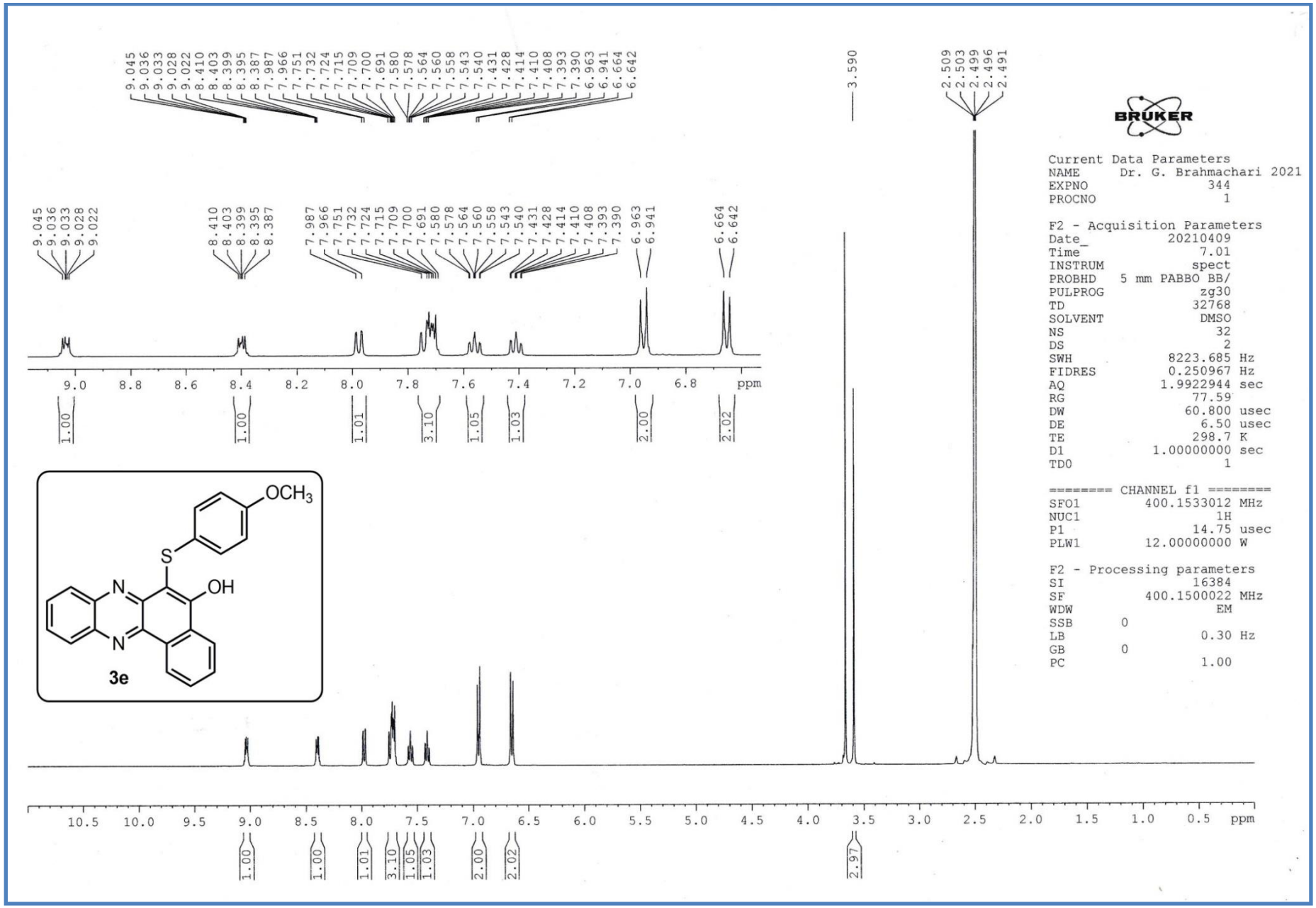


Figure S27. ^{1}H-NMR spectrum of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

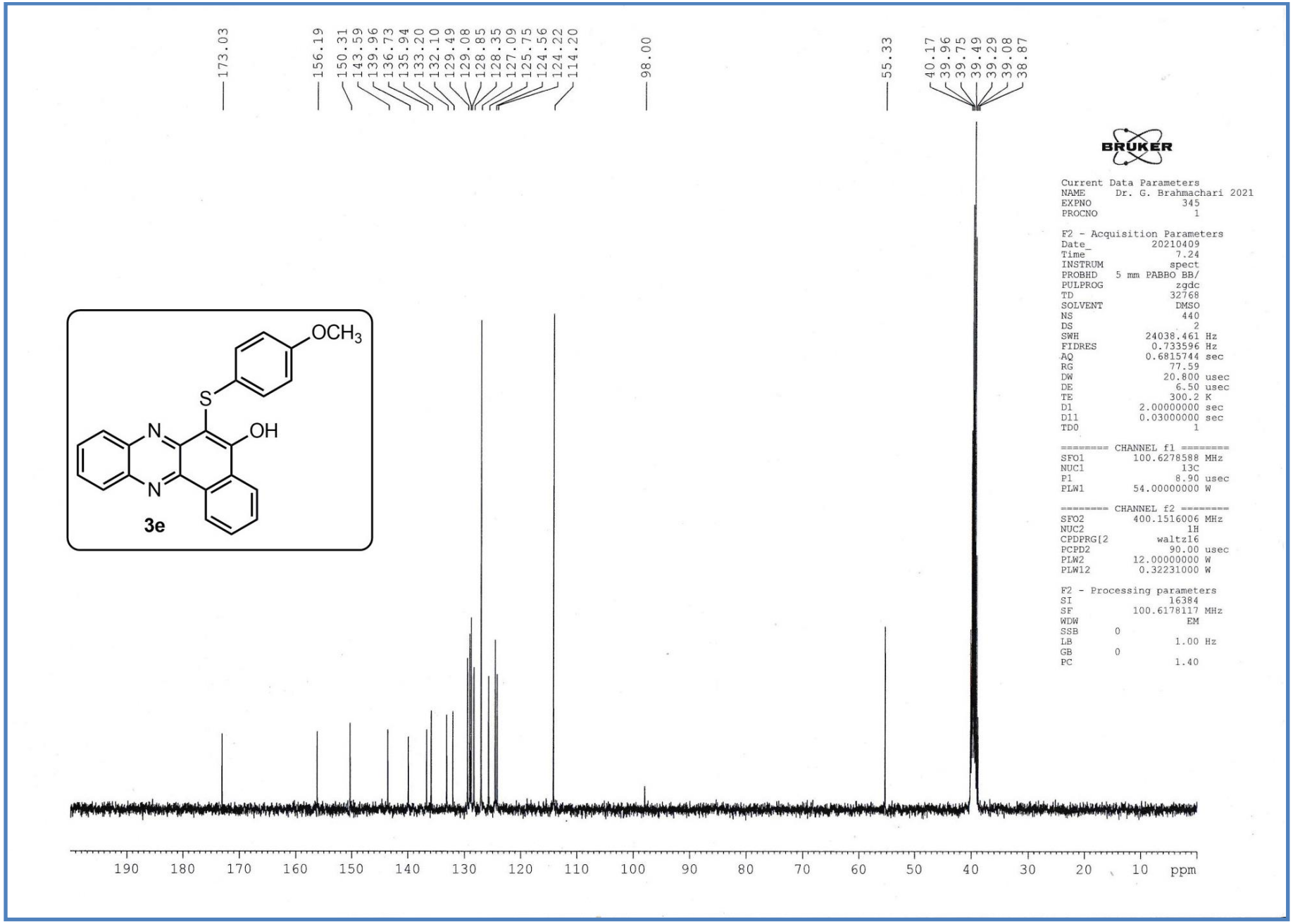


Figure S28. ^{13}C-NMR spectrum of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-o l (**3e**)

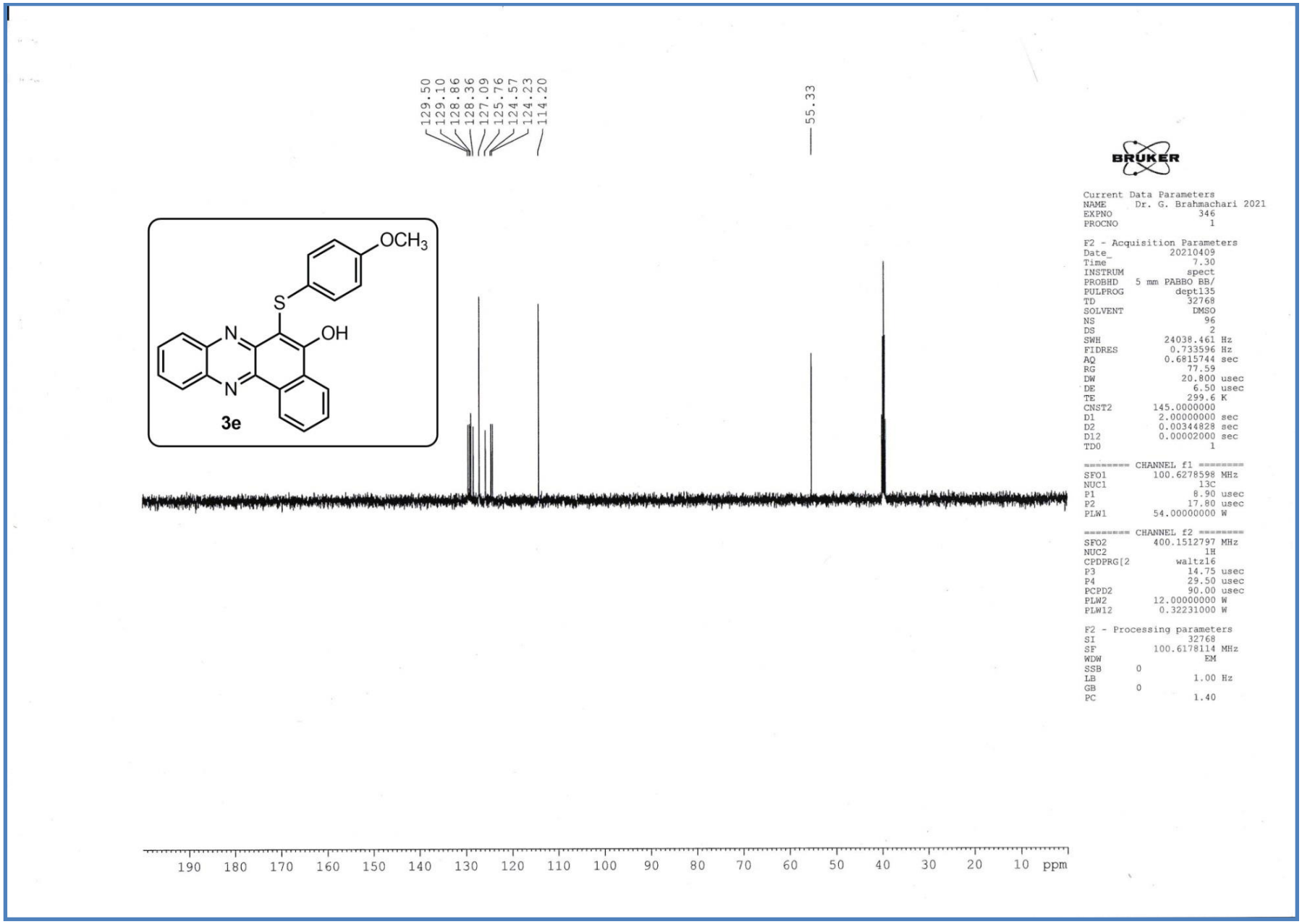


Figure S29. DEPT-135 NMR spectrum of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

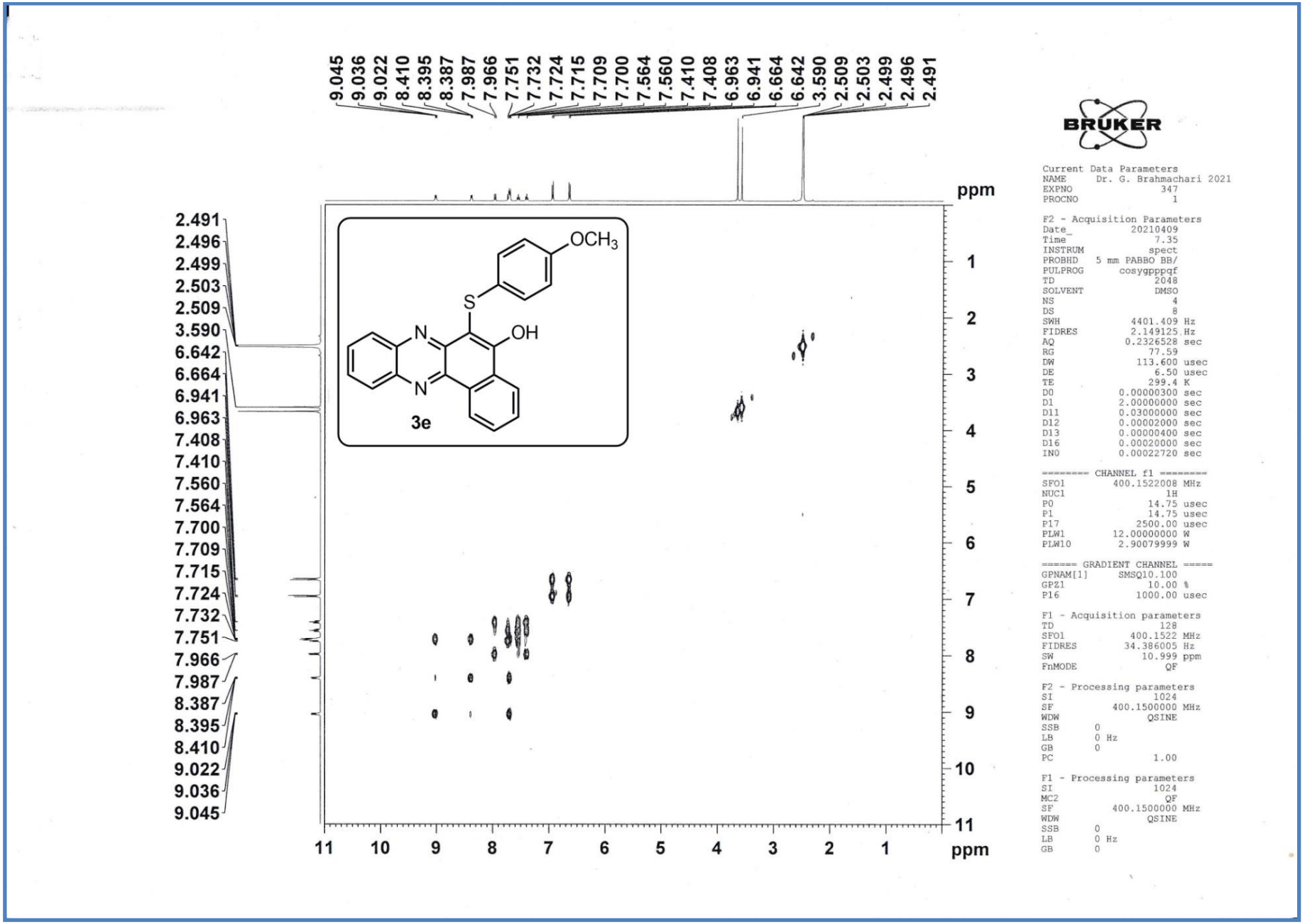


Figure S30. $^{1}H-^{1}H$ COSY45 spectra of6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

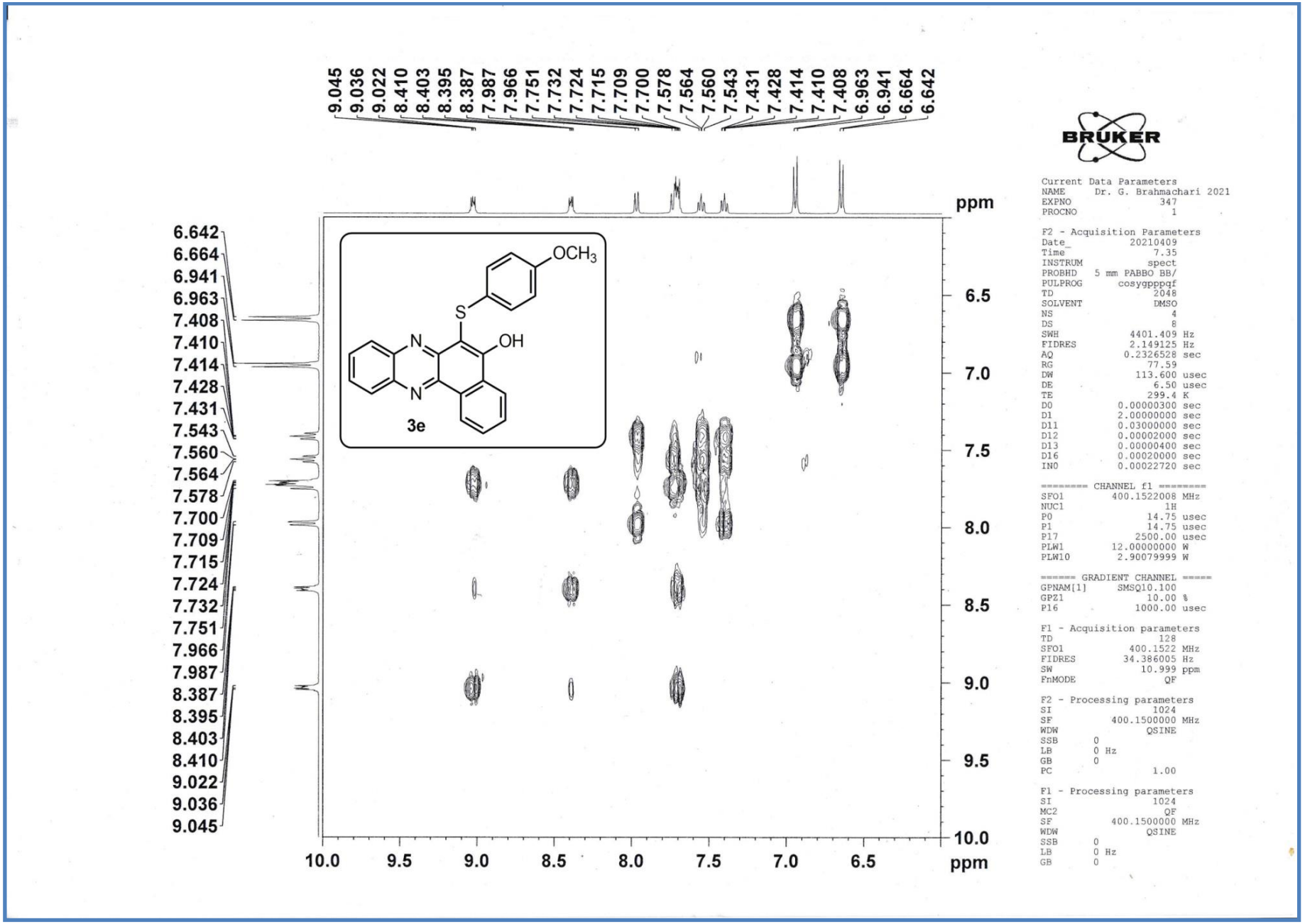


Figure S30a. $^{1}H–^{1}H$ COSY45 spectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**) [extended form]

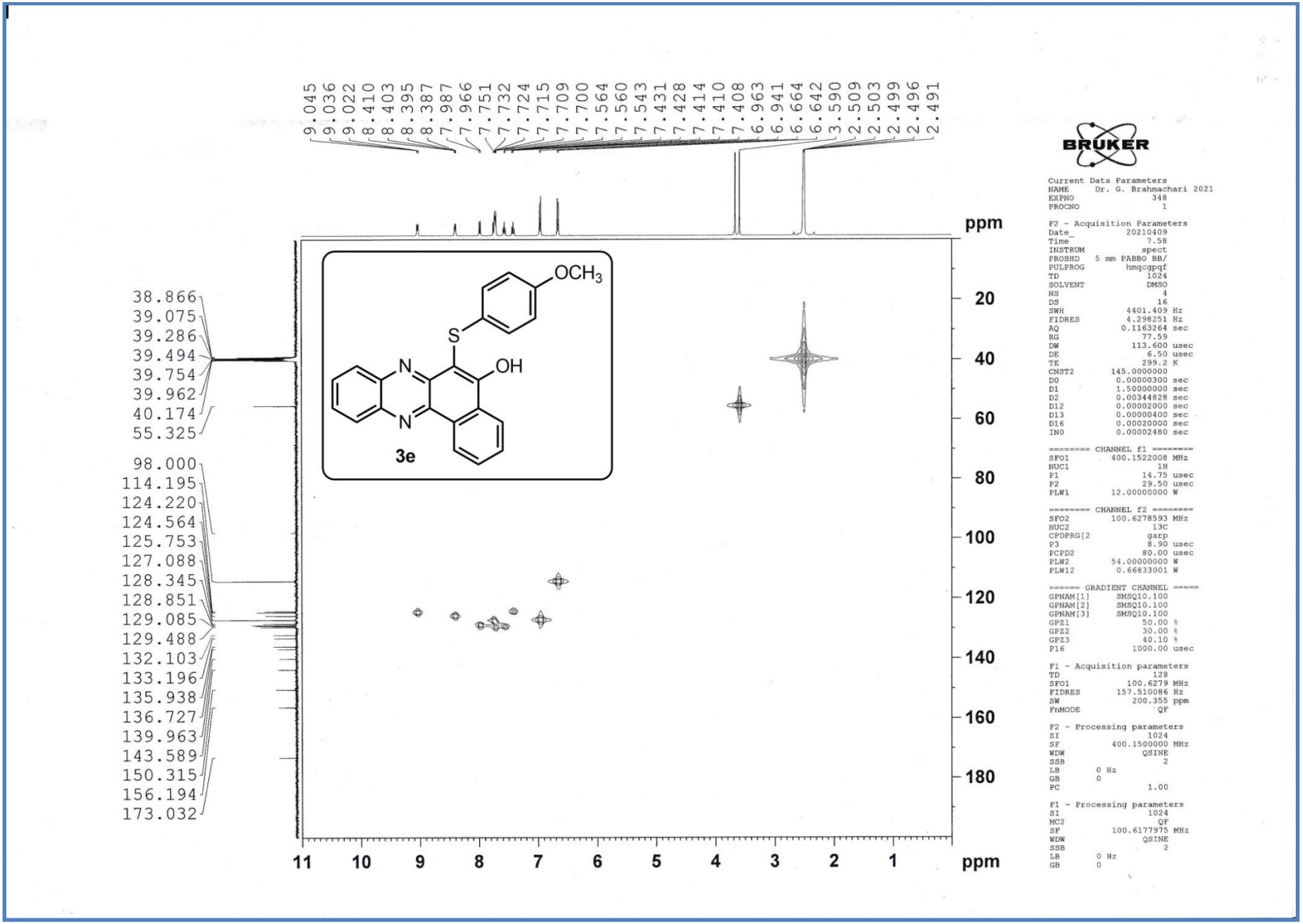


Figure S31. $^{1}H-^{13}C$ HMQC spectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

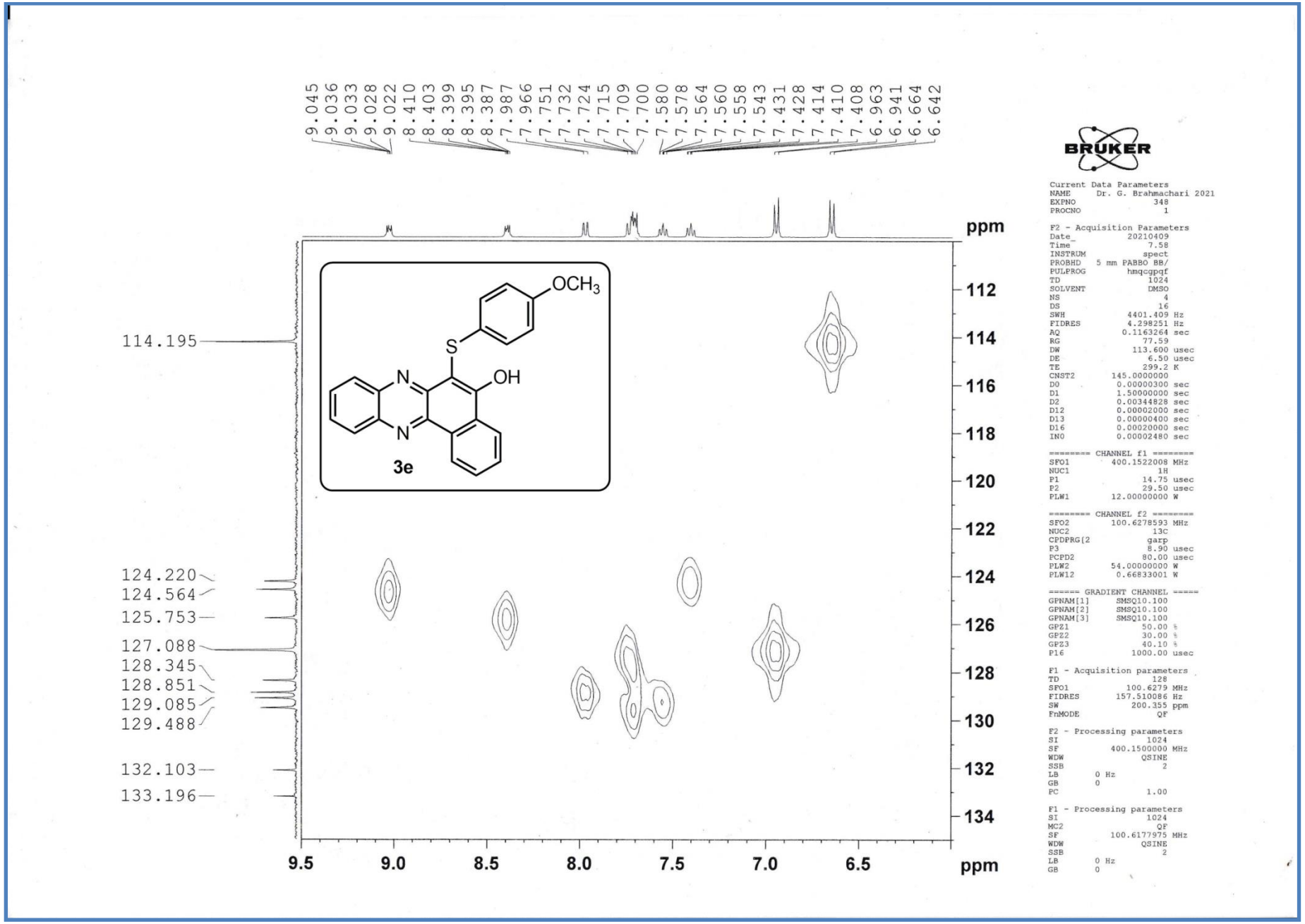


Figure S31a. $^{1}H-^{13}C$ HMQC spectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**) [extended form]

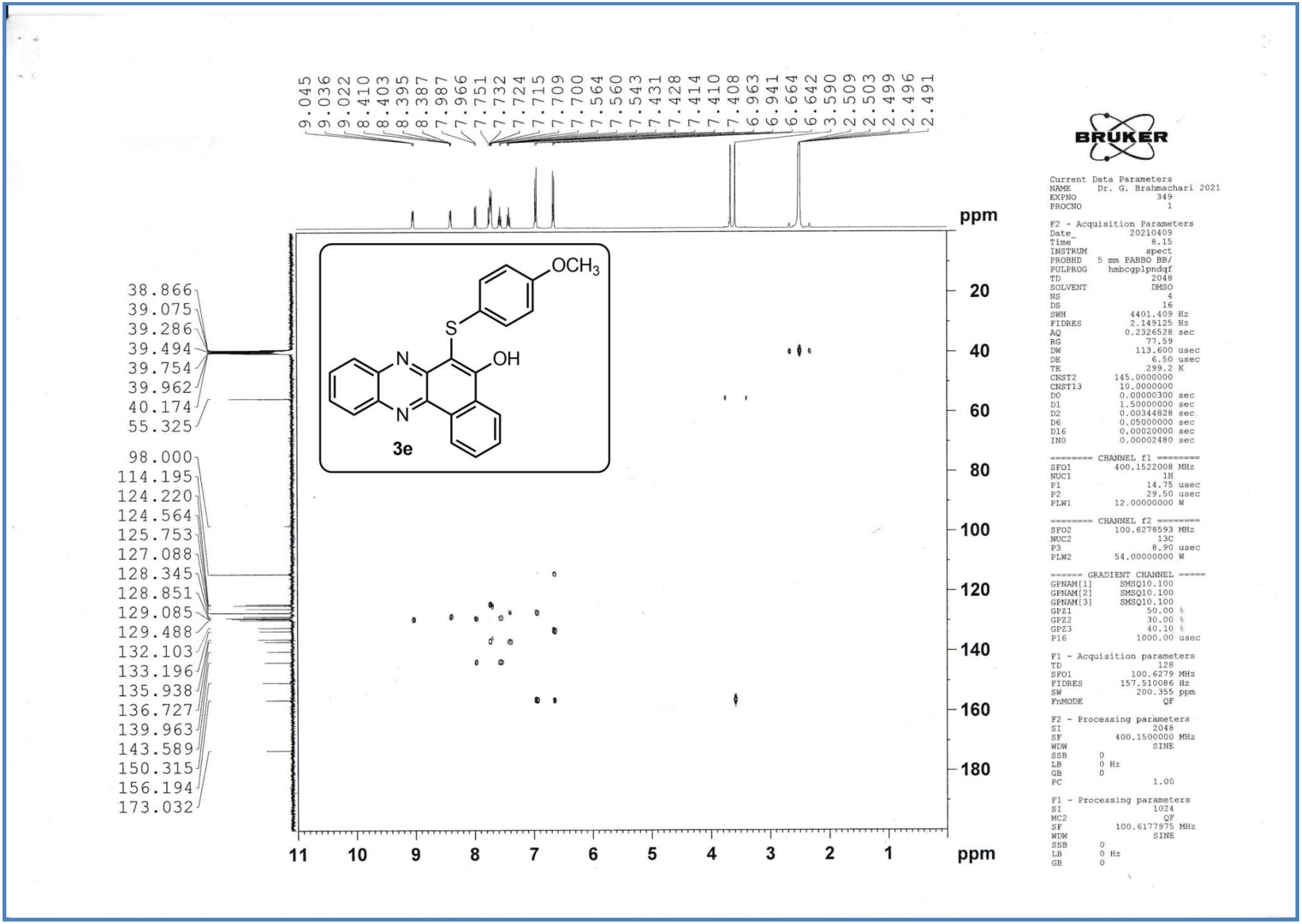


Figure S32.$^{1}H-^{13}C$ HMBCspectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

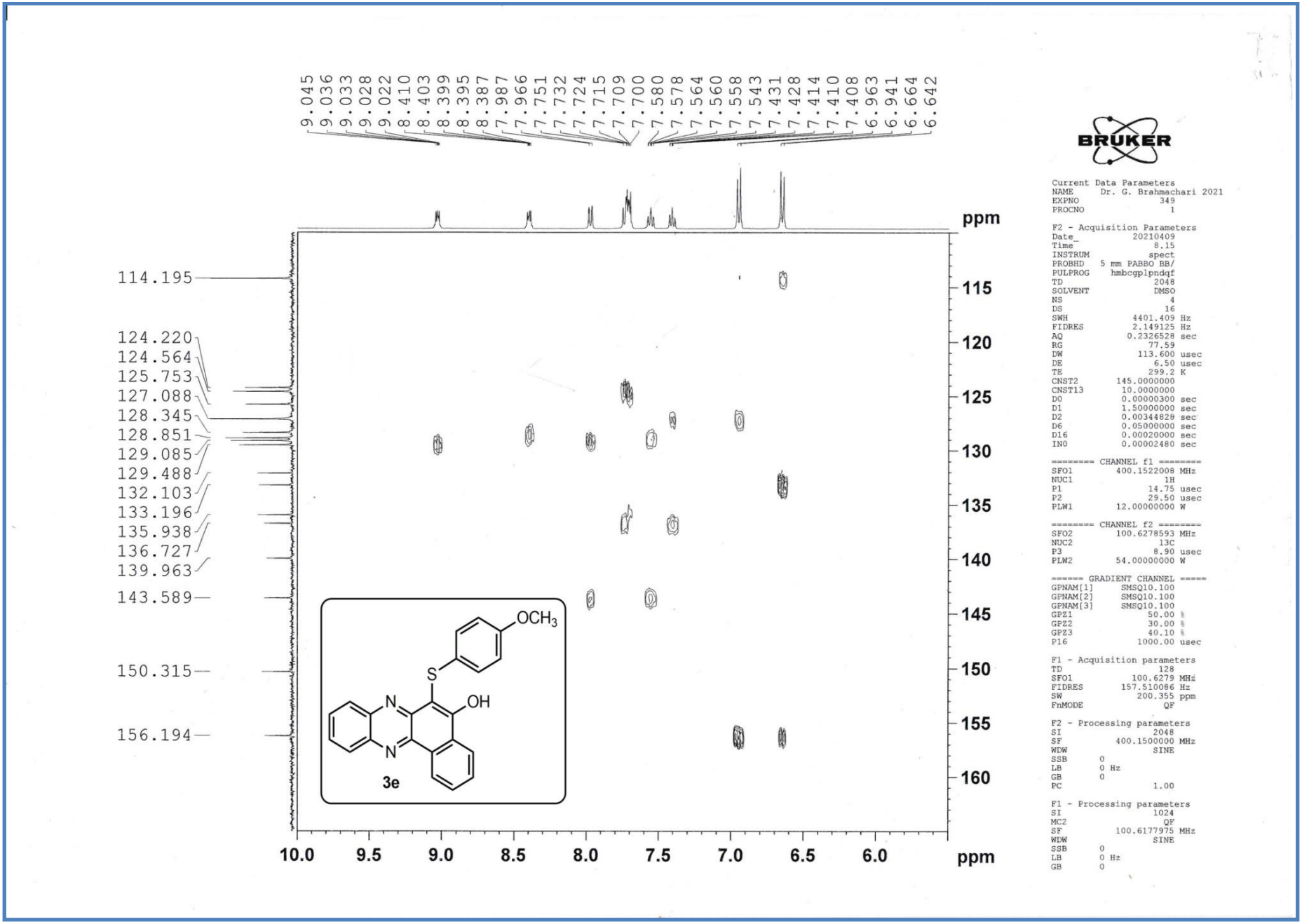
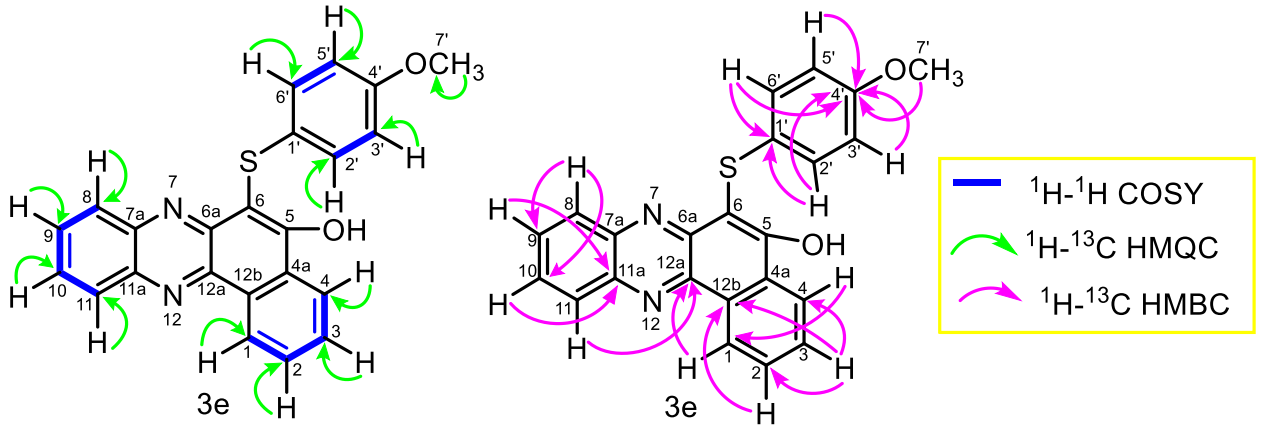


Figure S32a.$^{1}H-^{13}C$ HMBCspectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

Table S1. 2D-NMR properties of representative compound 3e showing the corresponding homo- and hetero-nuclear interactions



Carbon	^{1}H (ppm/δ)	^{13}C (ppm/δ)	DEPT-135	^{1}H-^{1}H COSY-45	^{1}H-^{13}C HMQC	^{1}H-^{13}C HMBC
C-1	7.98 (d, 1H, J = 8.4 Hz, Ar-H)	129.09	CH	H-1 (δ 7.98) *vs* H-2 (δ 7.43-7.39)	δ 7.98 (H-1) *vs* δ 129.09 (C-1)	δ 7.98 (H-1) *vs* δ 143.59 (C-12a)
C-2	7.43-7.39 (m, 1H, Ar-H)	124.22	CH	H-2 (δ 7.43-7.39) *vs* H-1 (δ 7.98) & H-3 (δ 7.75-7.69)	δ 7.43-7.39 (H-2) *vs* δ 124.22 (C-2)	δ 7.43-7.39 (H-2) *vs* δ 135.94 (C-12b)
C-3	7.75-7.69 (m, 1H, Ar-H)	128.34	CH	H-3 (δ 7.75-7.69) *vs* H-2 (δ 7.43-7.39) & H-4 (δ 9.05-9.02)	δ 7.75 (H-3) *vs* δ 128.34 (C-3)	δ 7.75 (H-3) *vs* δ 124.22 (C-2), δ 124.56(C-4), δ 135.94 (C-12b)
C-4	9.05-9.02 (m, 1H, Ar-H)	124.56	CH	H-4 (δ 9.05-9.02) *vs* H-3 (δ 7.75-7.69)	δ 9.05-9.02 (H-4) *vs* δ 124.56 (C-4)	δ 9.05-9.02 (H-4) *vs* δ 129.09 (C-1)
C-4a	–	132.10	C	–	–	–
C-5	–	173.03	C	–	–	–
C-6	–	98.00	C	–	–	–
C-6a	–	150.31	C	–	–	–
C-7a	–	139.96	C	–	–	–
C-8	8.41-8.39 (m, 1H, Ar-H)	125.75	CH	H-8 (δ 8.41-8.39) *vs* H-9 (δ 7.75-7.69)	δ 8.41-8.39 (H-8) *vs* δ 125.75 (C-8)	δ 8.41-8.39 (H-8) *vs* δ 128.85 (C-9/ C-10)
C-9	7.75-7.69 (m, 1H, Ar-H)	128.85	CH	H-9 (δ 7.75-7.69) *vs*H-8 (δ 8.41-8.39)	δ 7.75-7.69 (H-9) *vs* δ 128.85 (C-9)	δ 7.75-7.69 (H-9) *vs* δ 136.73 (C-11a)

C-10	7.75-7.69 (m, 1H, Ar-H)	128.85	CH	H-10 (δ 7.75-7.69) *vs*H-11 (δ 7.58-7.54)	δ 7.75-7.69 (H-10) *vs* δ 128.85 (C-10)	δ 7.75-7.69 (H-10) *vs* δ 136.73 (C-11a)
C-11	7.58-7.54 (m, 1H, Ar-H)	129.49	CH	H-11 (δ 7.58-7.54) *vs* H-10 (δ 7.75-7.69)	δ 7.58-7.54 (H-11) *vs* δ 128.85 (C-11)	δ 7.58-7.54 (H-11) *vs* δ 129.49 (C-12a)
C-11a	–	136.73	C	–	–	–
C-12a	–	143.59	C	–	–	–
C-12b	–	135.94	C	–	–	–
C-1'	–	133.20	C	–	–	–
C-2' &C-6'	6.95 (d, 2H, *J* = 8.8 Hz,Ar-H)	127.09	CH	H-2'/ H-6' (δ 6.95) *vs* H-3'/ H-5' (δ 6.65)	δ 6.95 (H-2'/H-6') *vs* δ 127.09 (C-2'/C-6')	δ 6.95 (H-2'/H-6') *vs* δ 156.19 (C-4'), 133.20 (C-1')
C-3' &C-5'	6.65 (d, 2H, *J* = 8.8 Hz,Ar-H)	114.20	CH	H-3'/ H-5' (δ 6.65) *vs* H-2'/ H-6' (δ 6.95)	δ 6.65 (H-3'/H5') *vs* δ 114.20 (C-3'/C-5')	δ 6.65 (H-3'/H-5') *vs* δ 156.19 (C-4'),
C-4'	–	156.19	C	–	–	–
C-7'	3.75 (s, 3H, Ar-OCH_3)	55.33	OCH_3	–	δ 3.59 (Ar-OCH_3) *vs* δ 55.33 (Ar-OCH_3)	δ 3.59 (Ar-OCH_3) *vs* δ 156.19 (C-4')

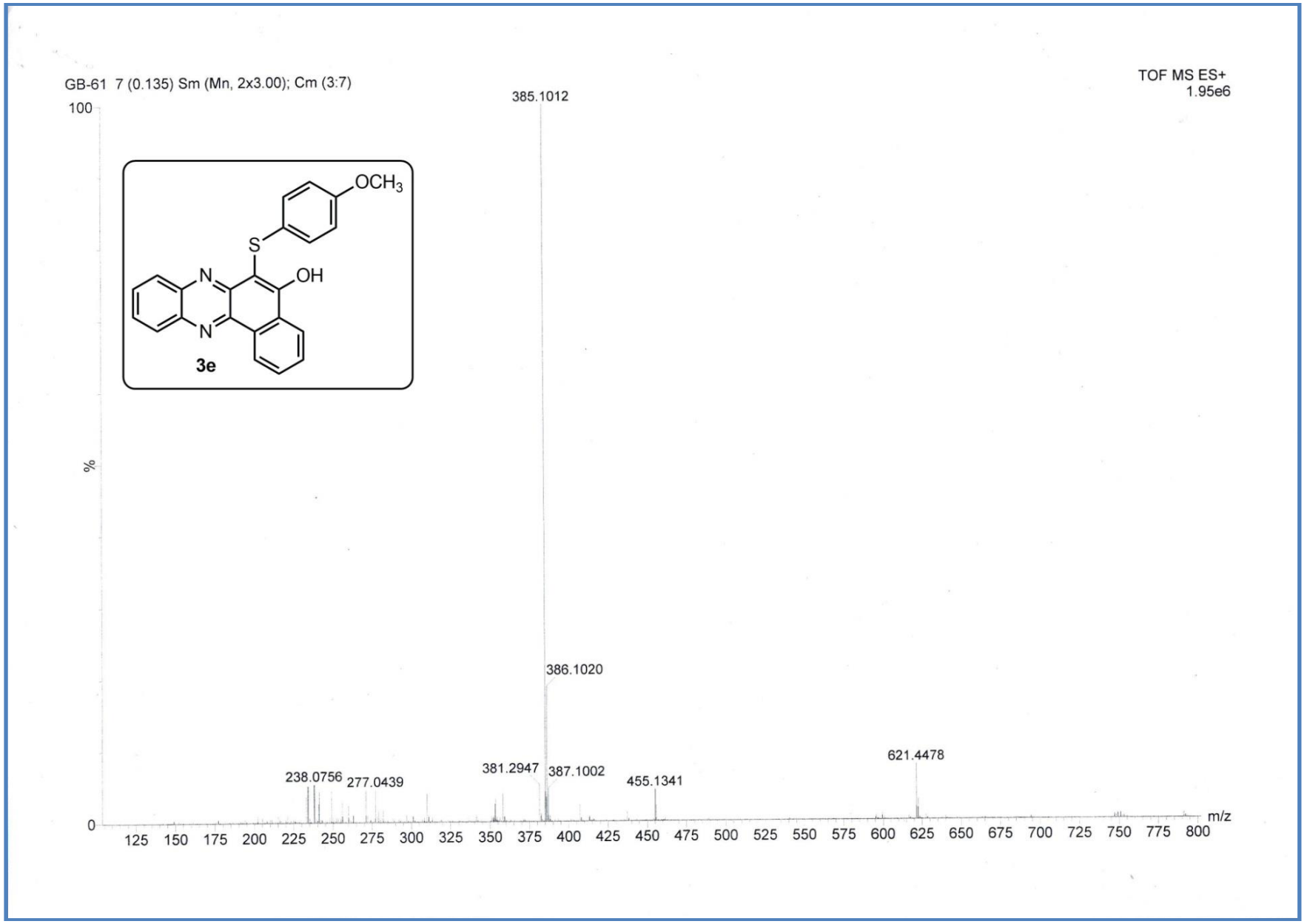


Figure S33. High-resolution Mass spectra of 6-((4-methoxyphenyl)thio)benzo[*a*]phenazin-5-ol (**3e**)

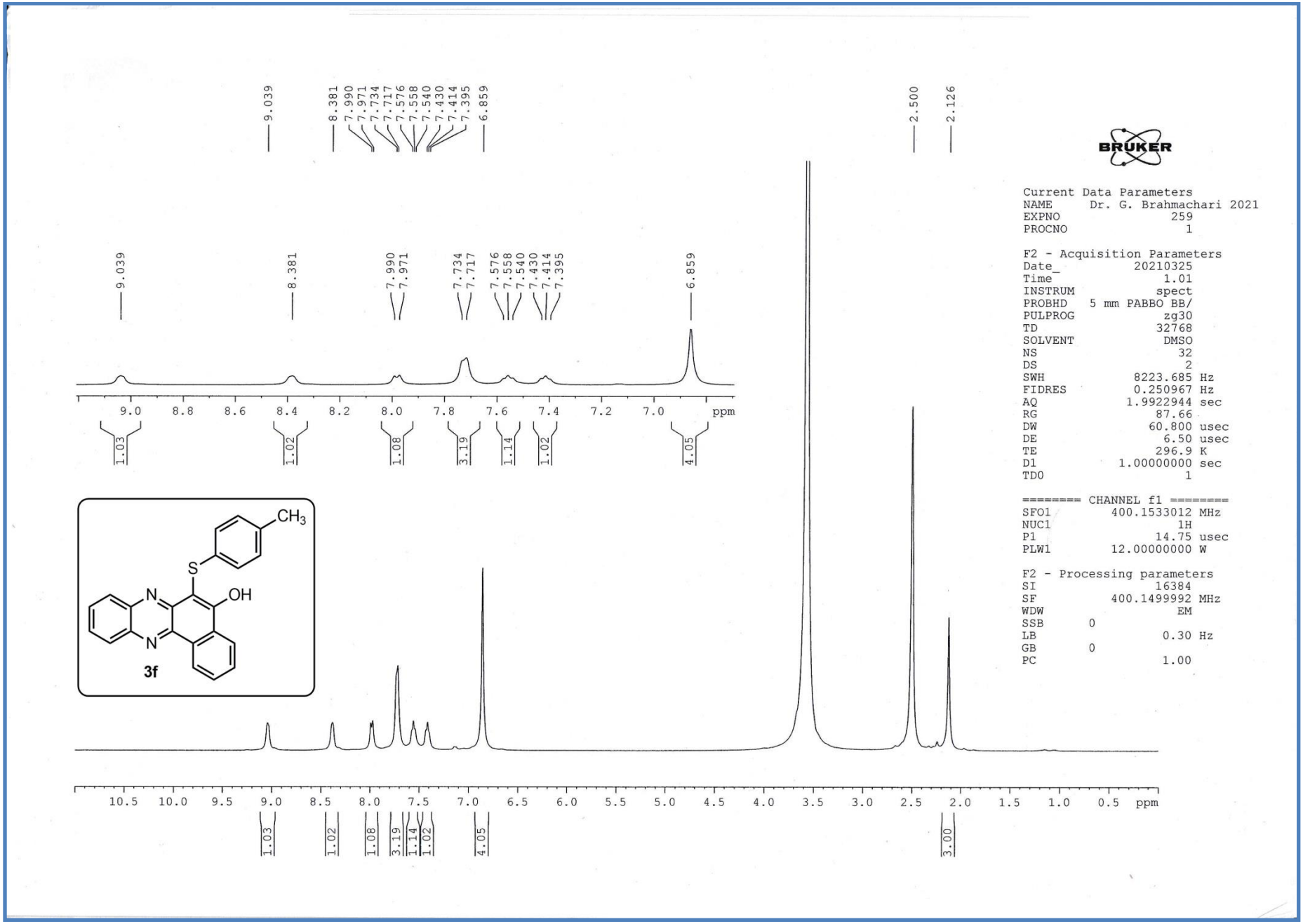


Figure S34.[1]H-NMR spectrum of 6-(*p*-tolylthio)benzo[*a*]phenazin-5-ol (**3f**)

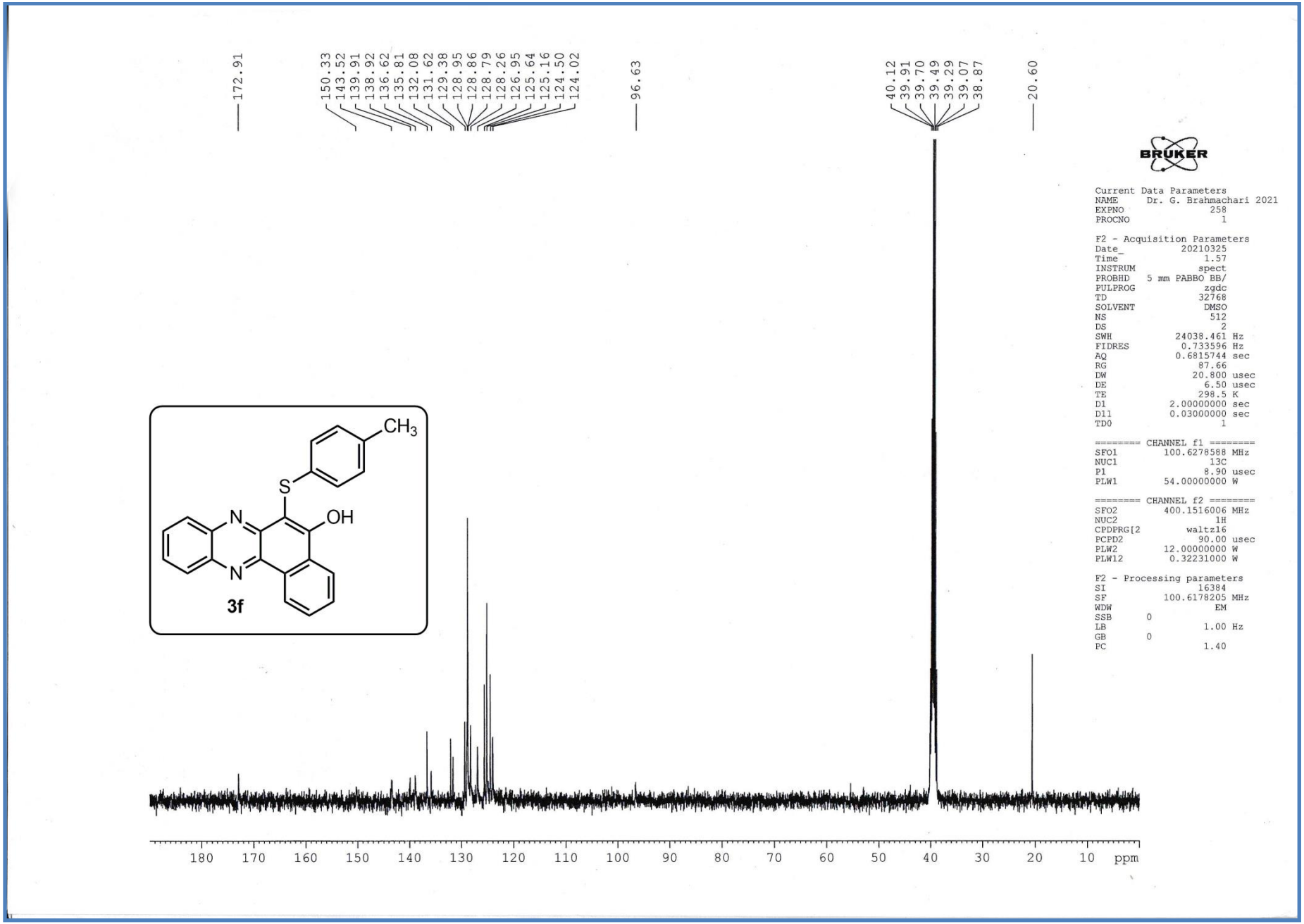


Figure S35.[13]C-NMR spectrum of 6-(*p*-tolylthio)benzo[*a*]phenazin-5-ol (**3f**)

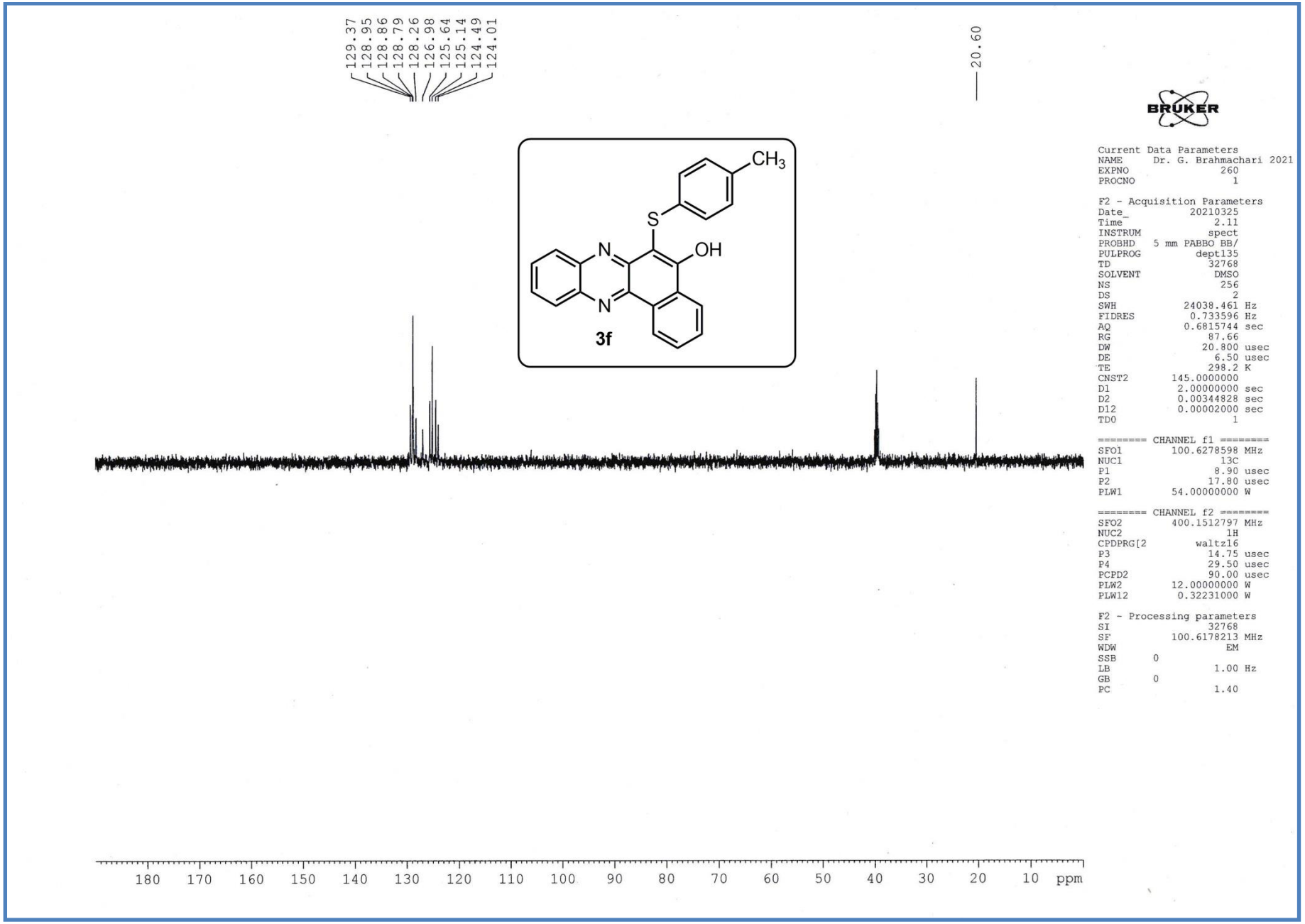


Figure S36. DEPT-135 NMR spectrum of 6-(*p*-tolylthio)benzo[*a*]phenazin-5-ol (**3f**)

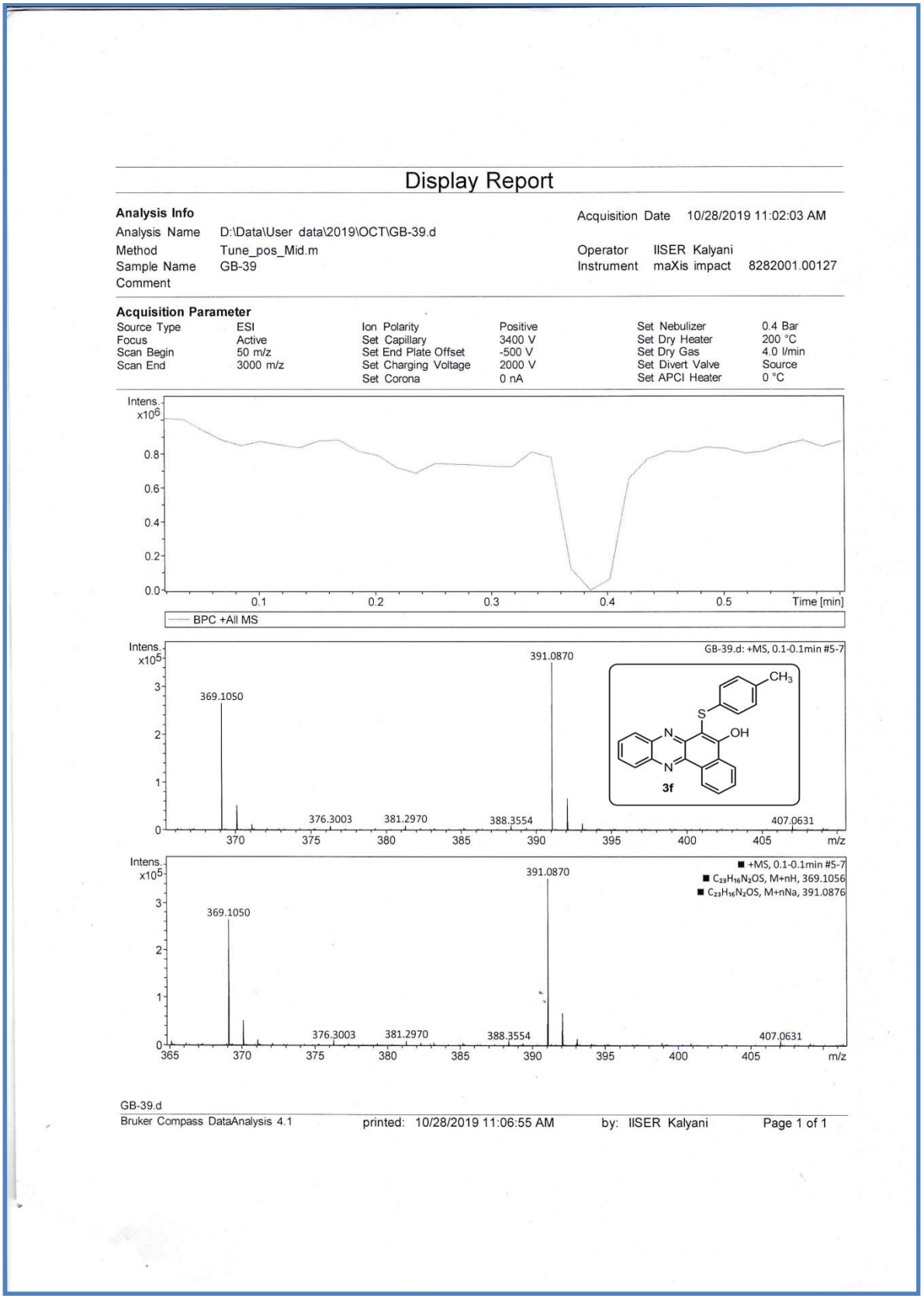


Figure S37. High-resolution Mass spectra of 6-(*p*-tolylthio)benzo[*a*]phenazin-5-ol (**3f**)

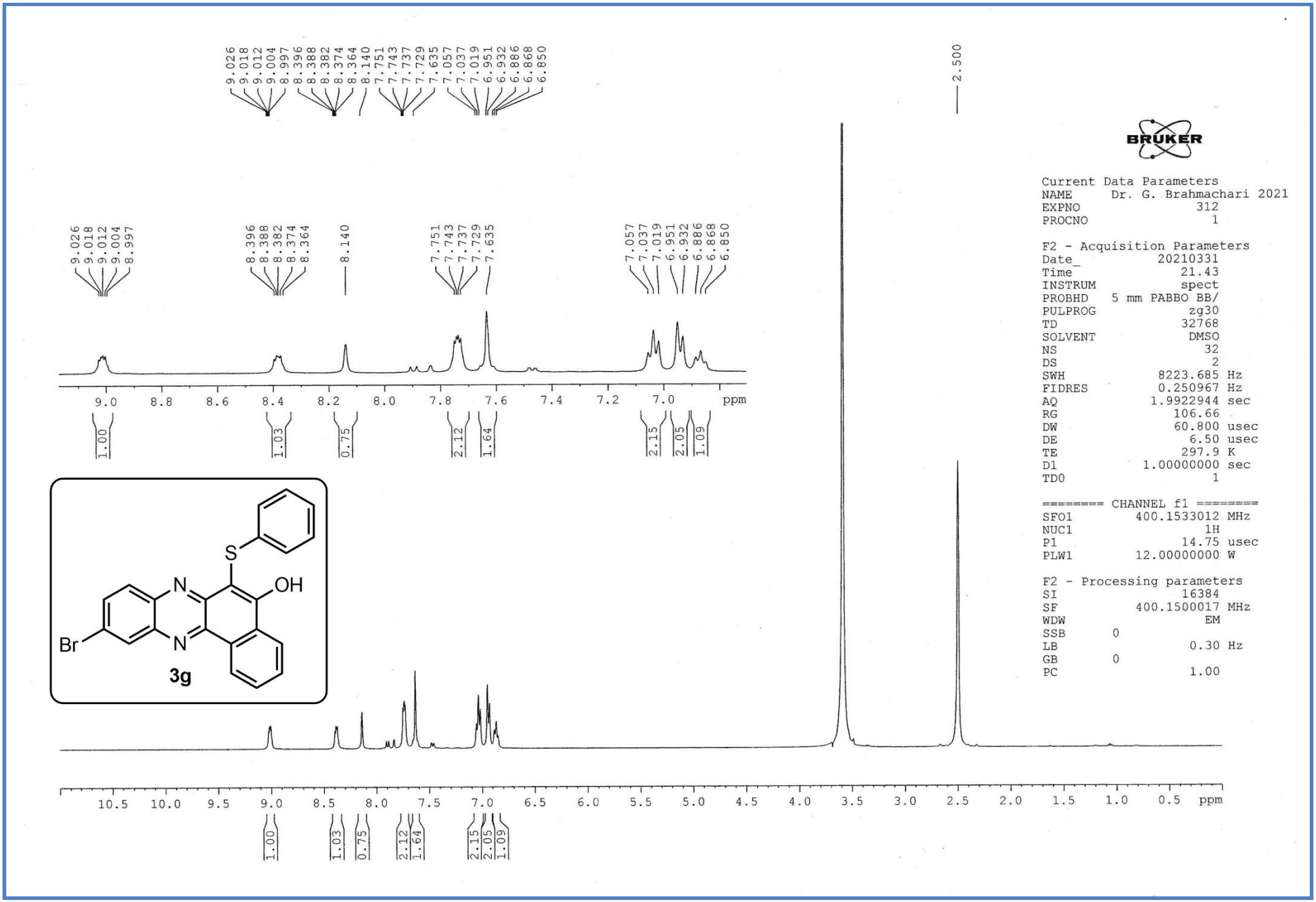


Figure S38. ^{1}H-NMR spectrum of 10-bromo-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3g**)

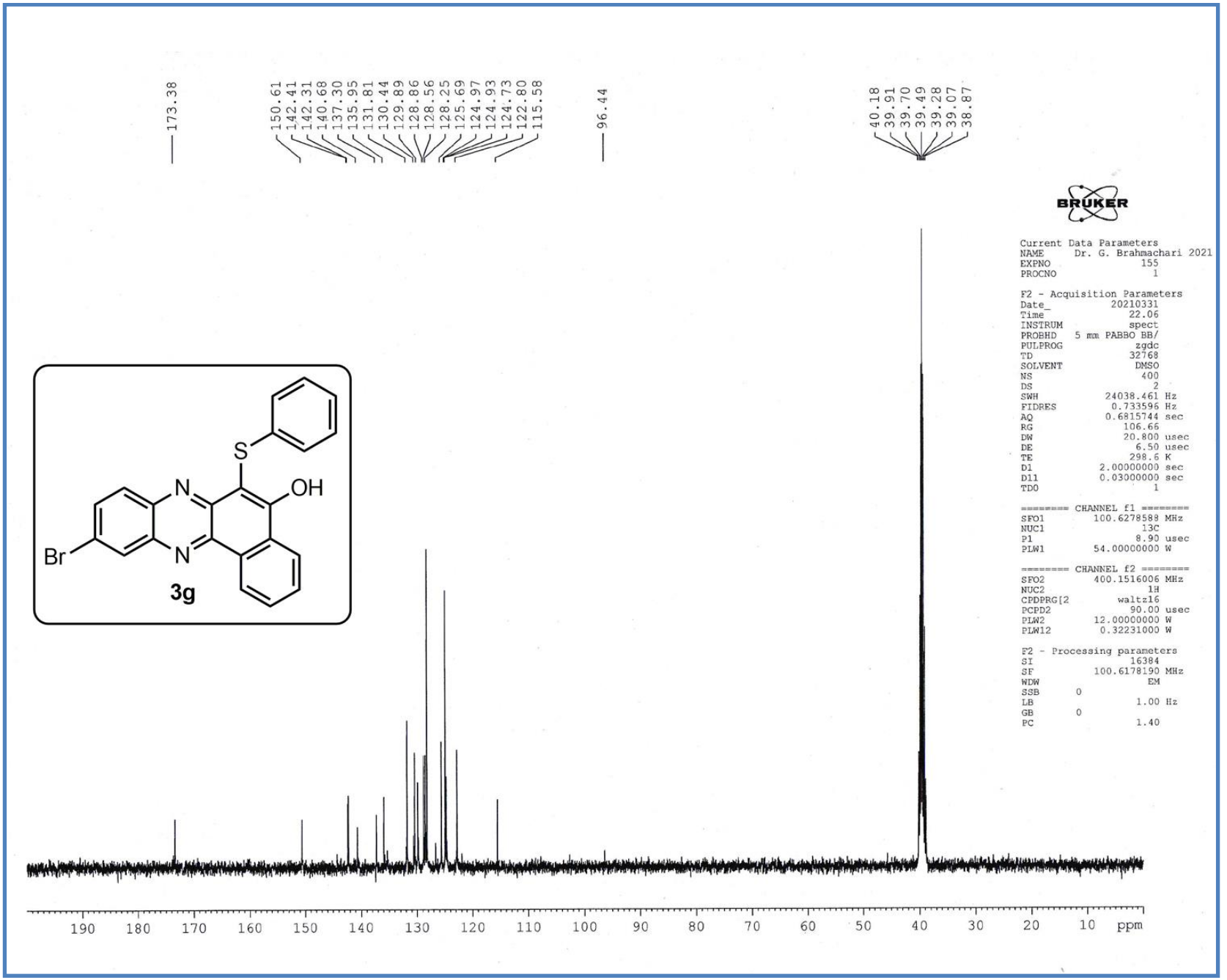


Figure S39. ^{13}C-NMR spectrum of 10-bromo-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3g**)

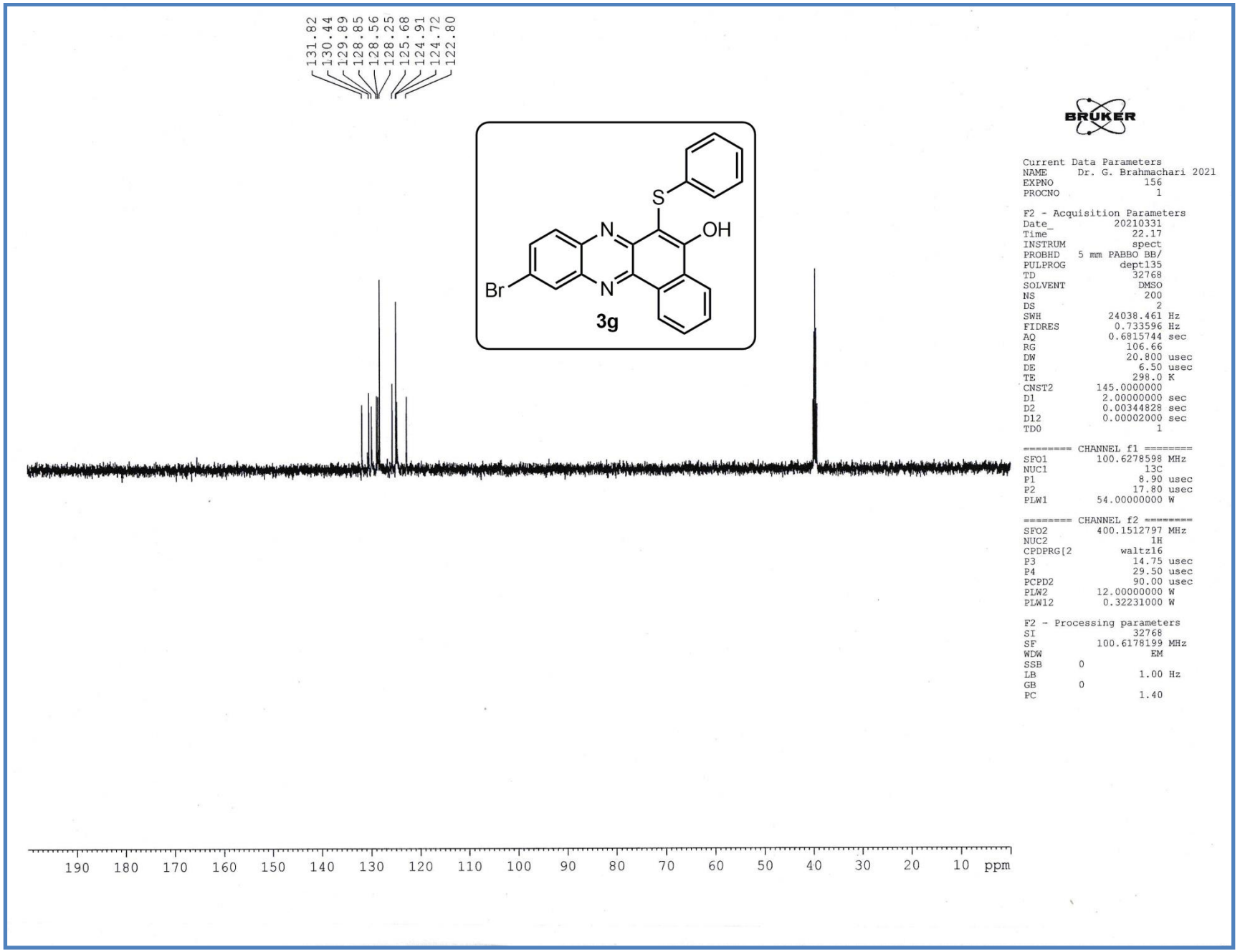


Figure S40. DEPT-135 NMR spectrum of 10-bromo-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3g**)

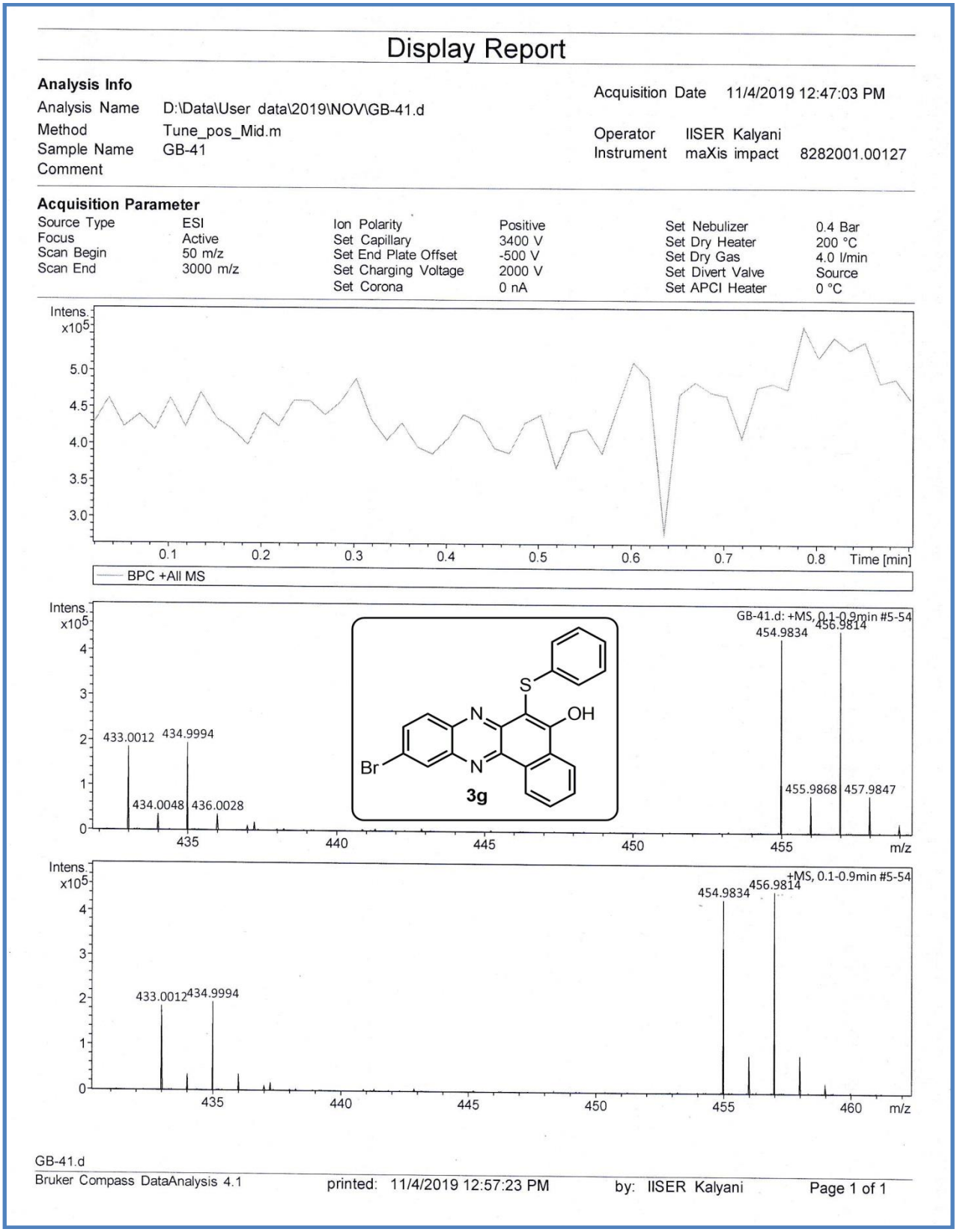


Figure S41. High-resolution Mass spectra of 10-bromo-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3g**)

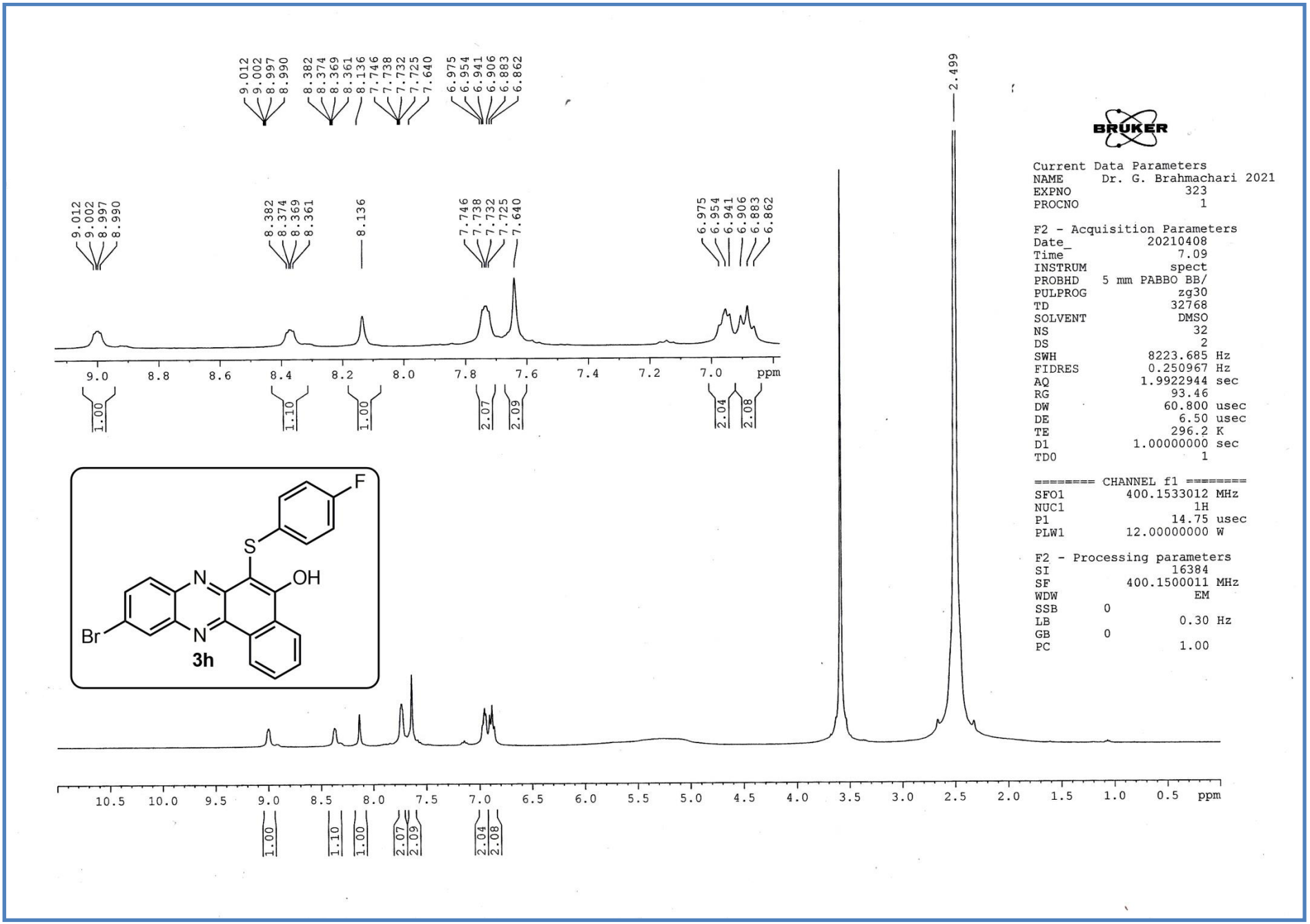


Figure S42. ^{1}H-NMR spectrum of 10-bromo-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3h**)

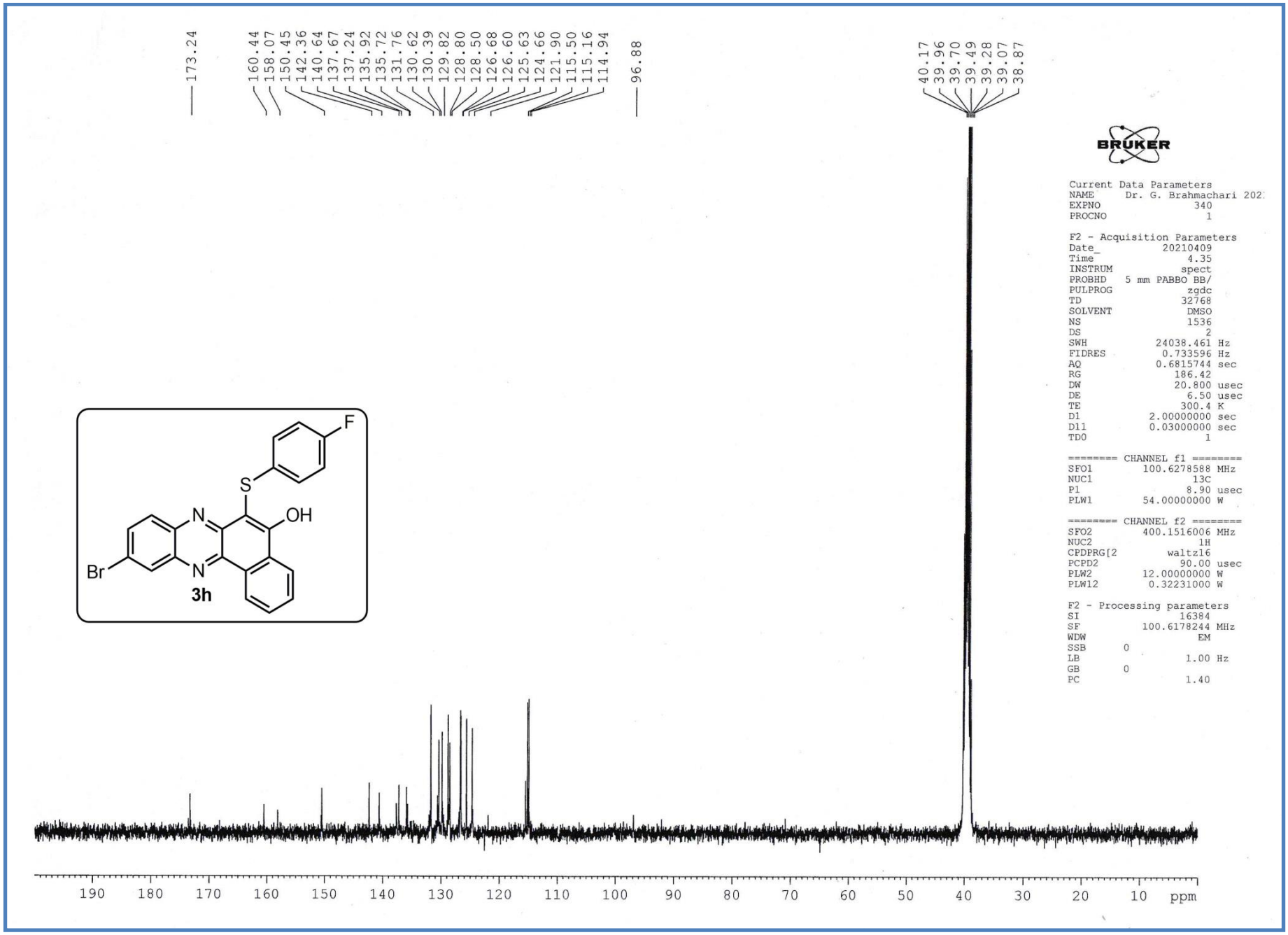


Figure S43. ^{13}C-NMR spectrum of 10-bromo-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3h**)

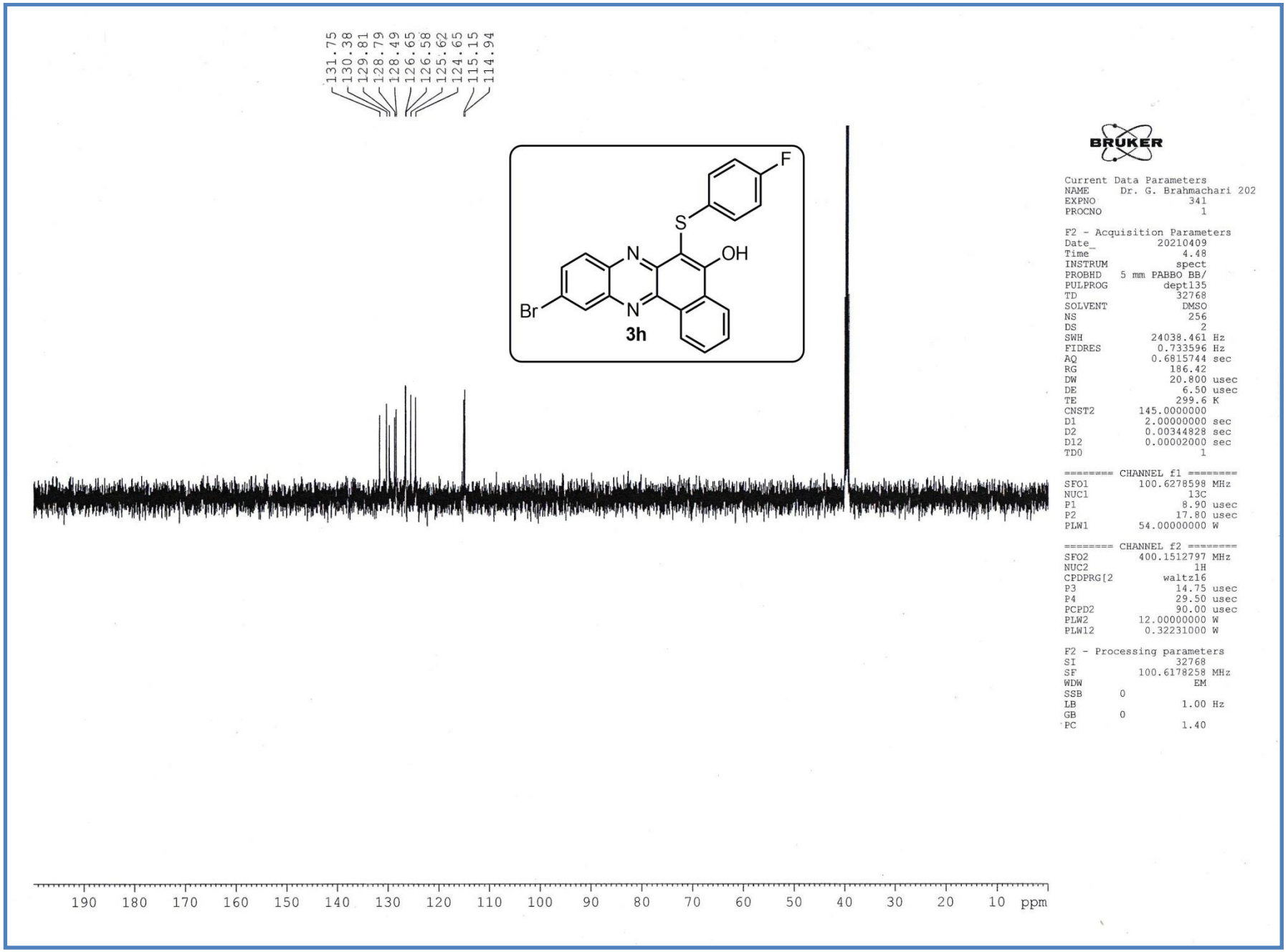


Figure S40. DEPT-135 NMR spectrum of 10-bromo-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3h**)

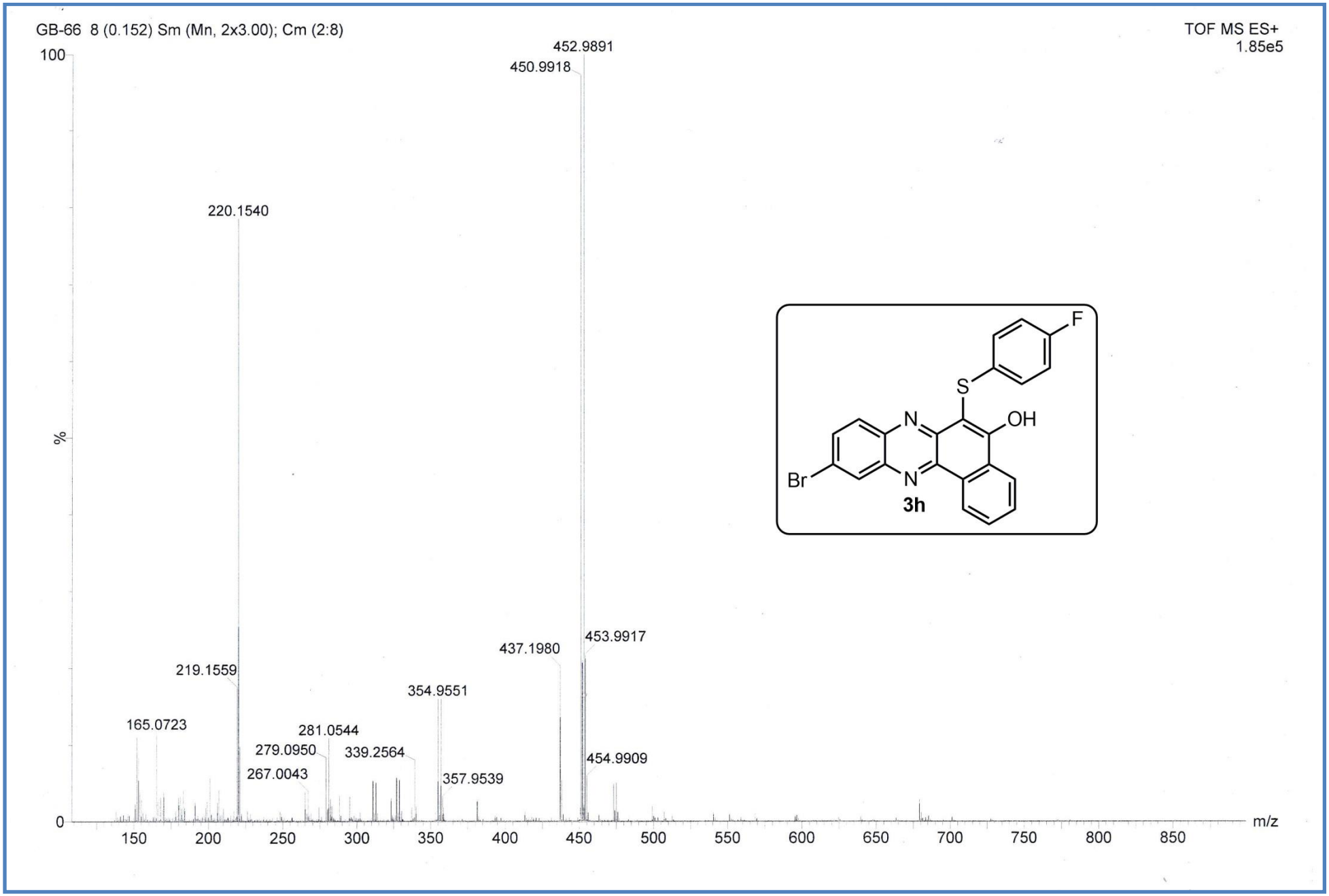


Figure S41. High-resolution Mass spectra of 10-bromo-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3h**)

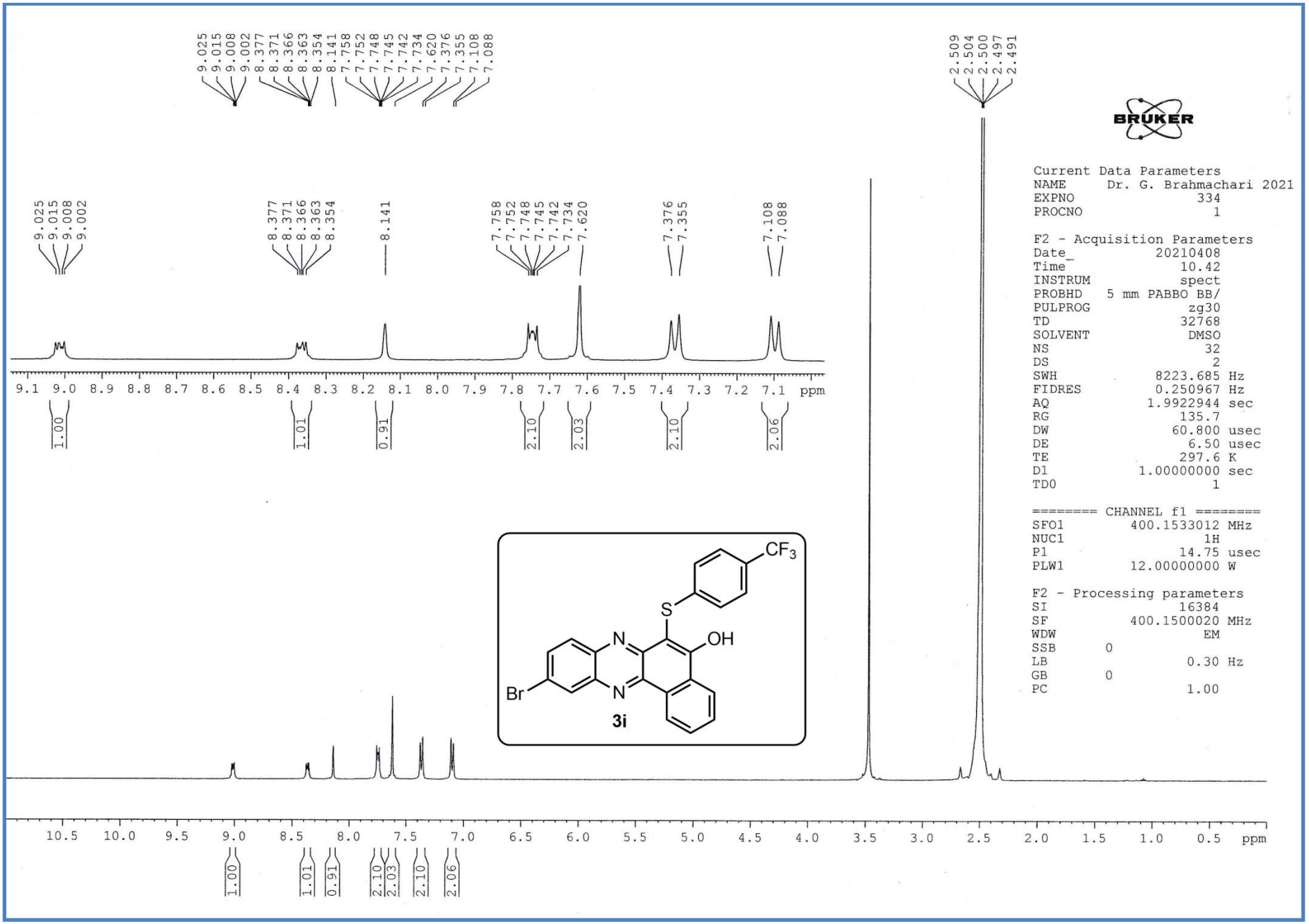


Figure S42. ^{1}H-NMR spectrum of 10-bromo-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3i**)

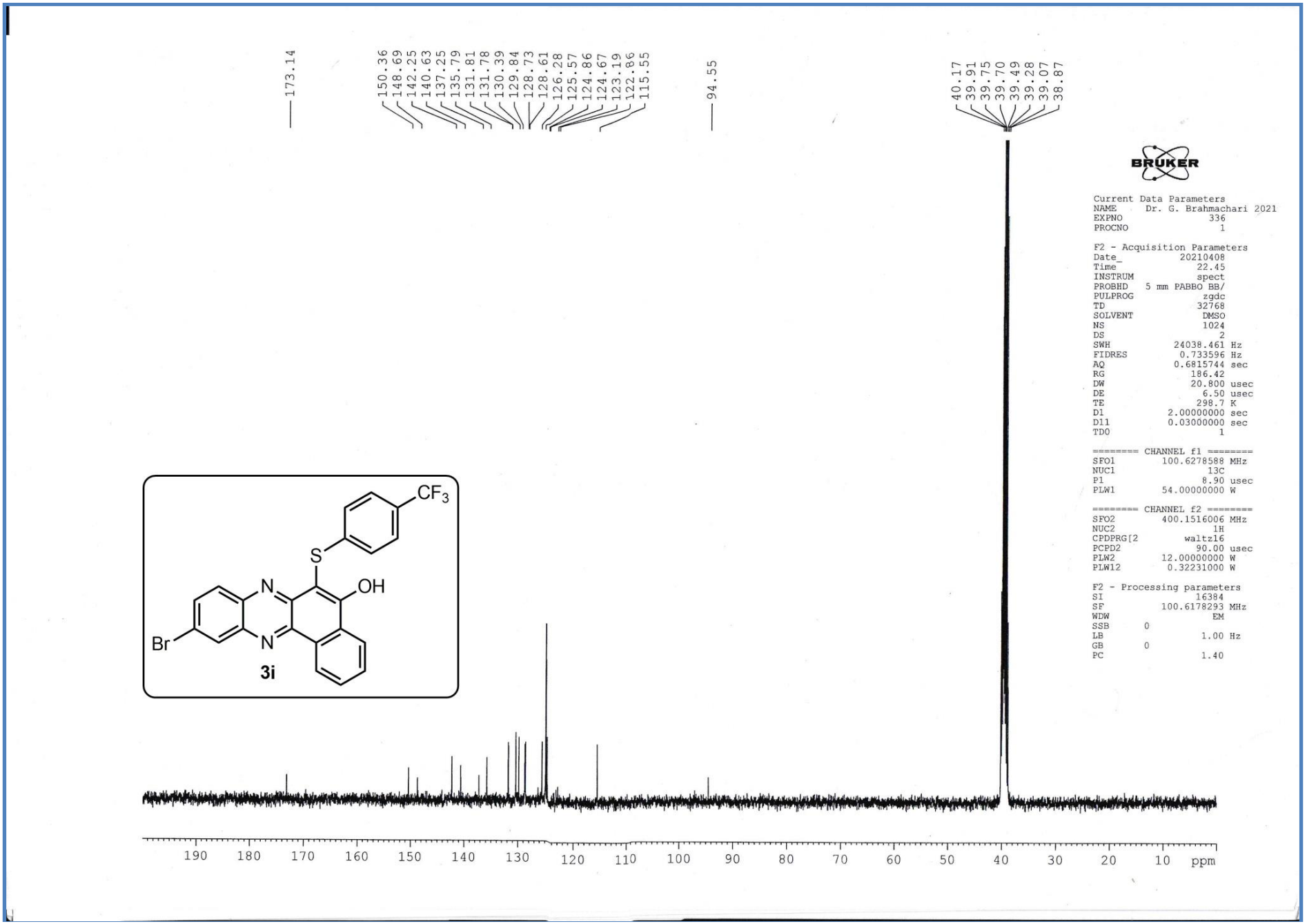


Figure S43. ^{13}C-NMR spectrum of 10-bromo-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3i**)

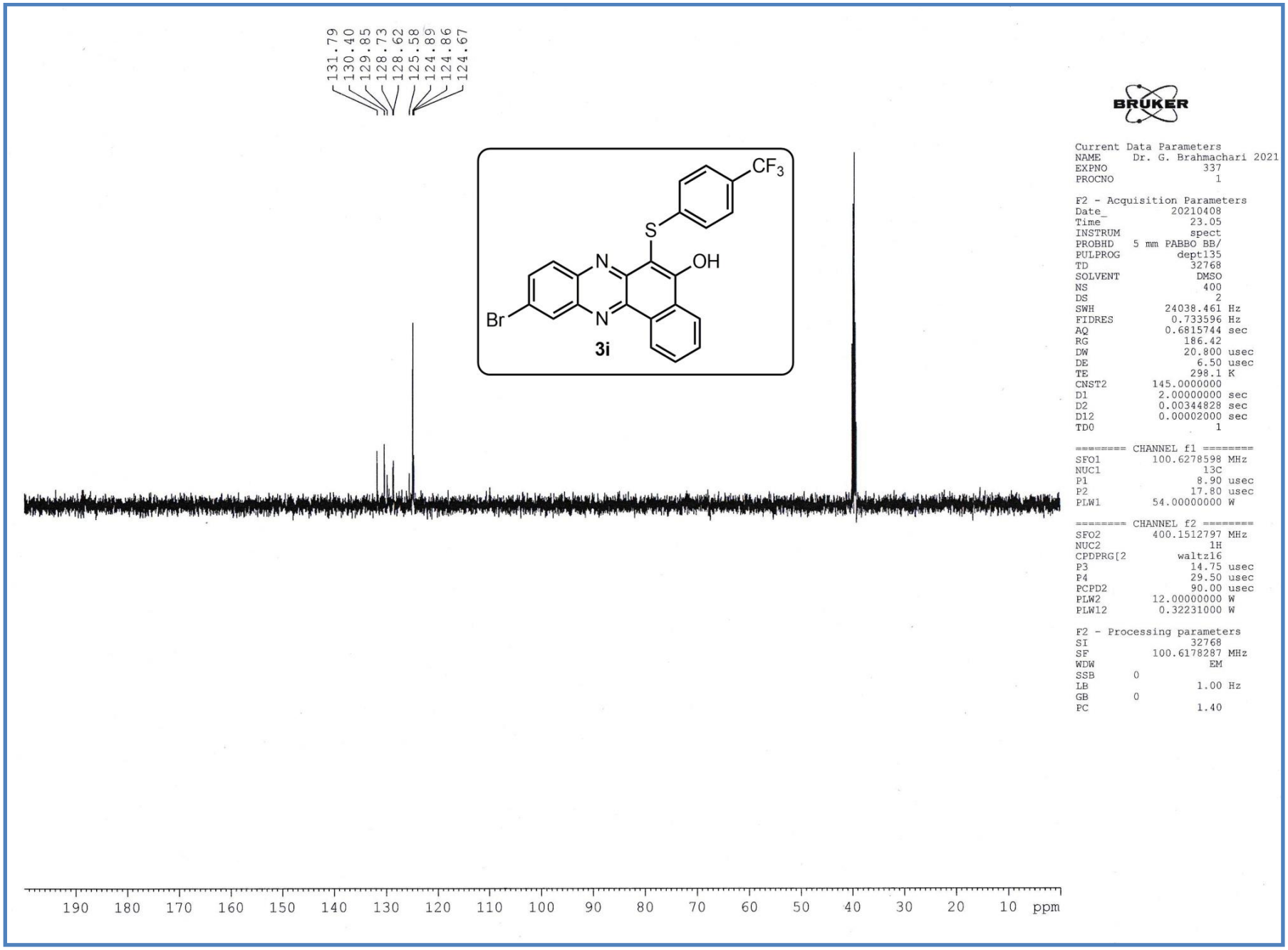


Figure S44. DEPT-135 NMR spectrum of 10-bromo-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3i**)

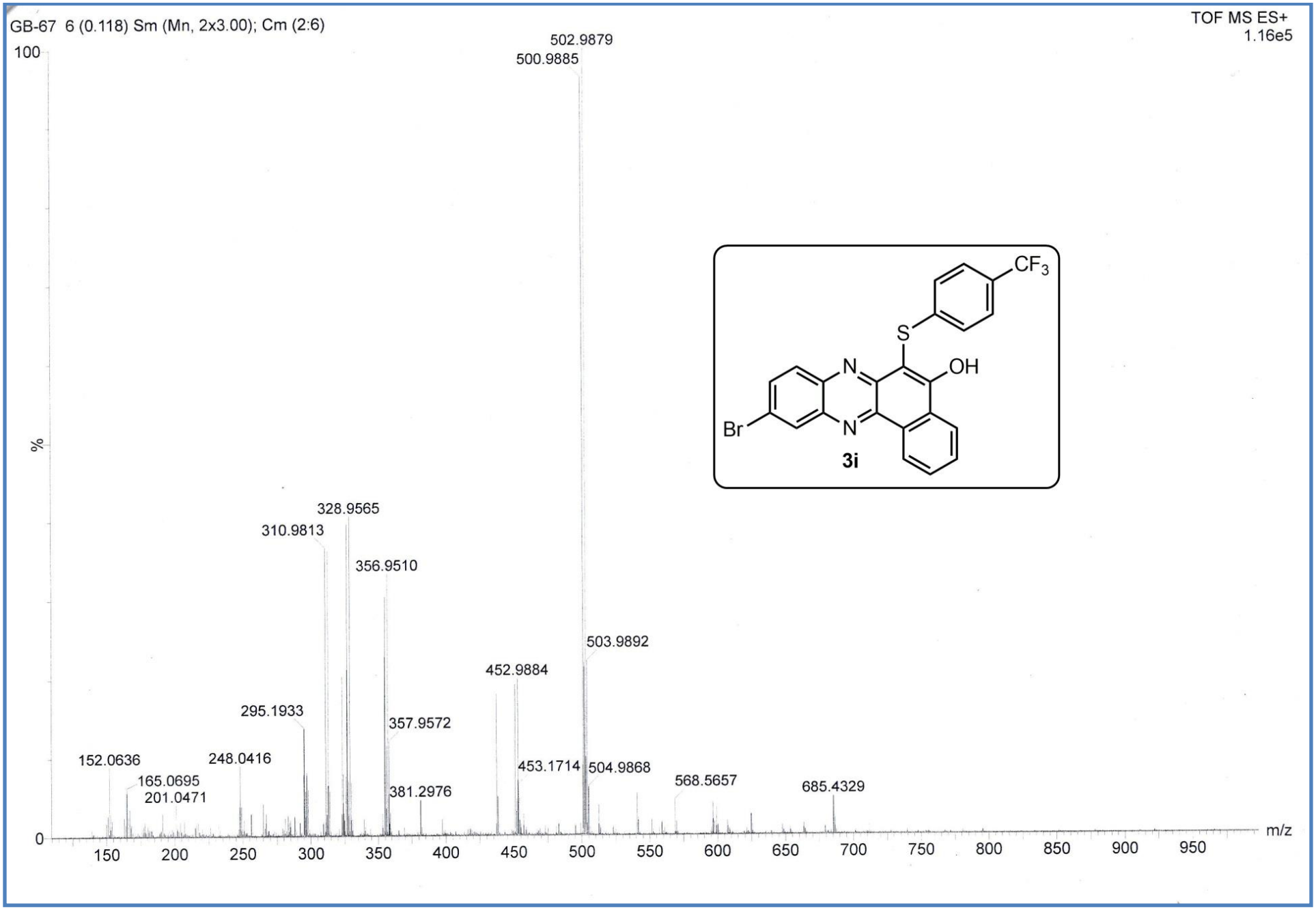


Figure S45. High-resolution Mass spectra 10-bromo-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3i**)

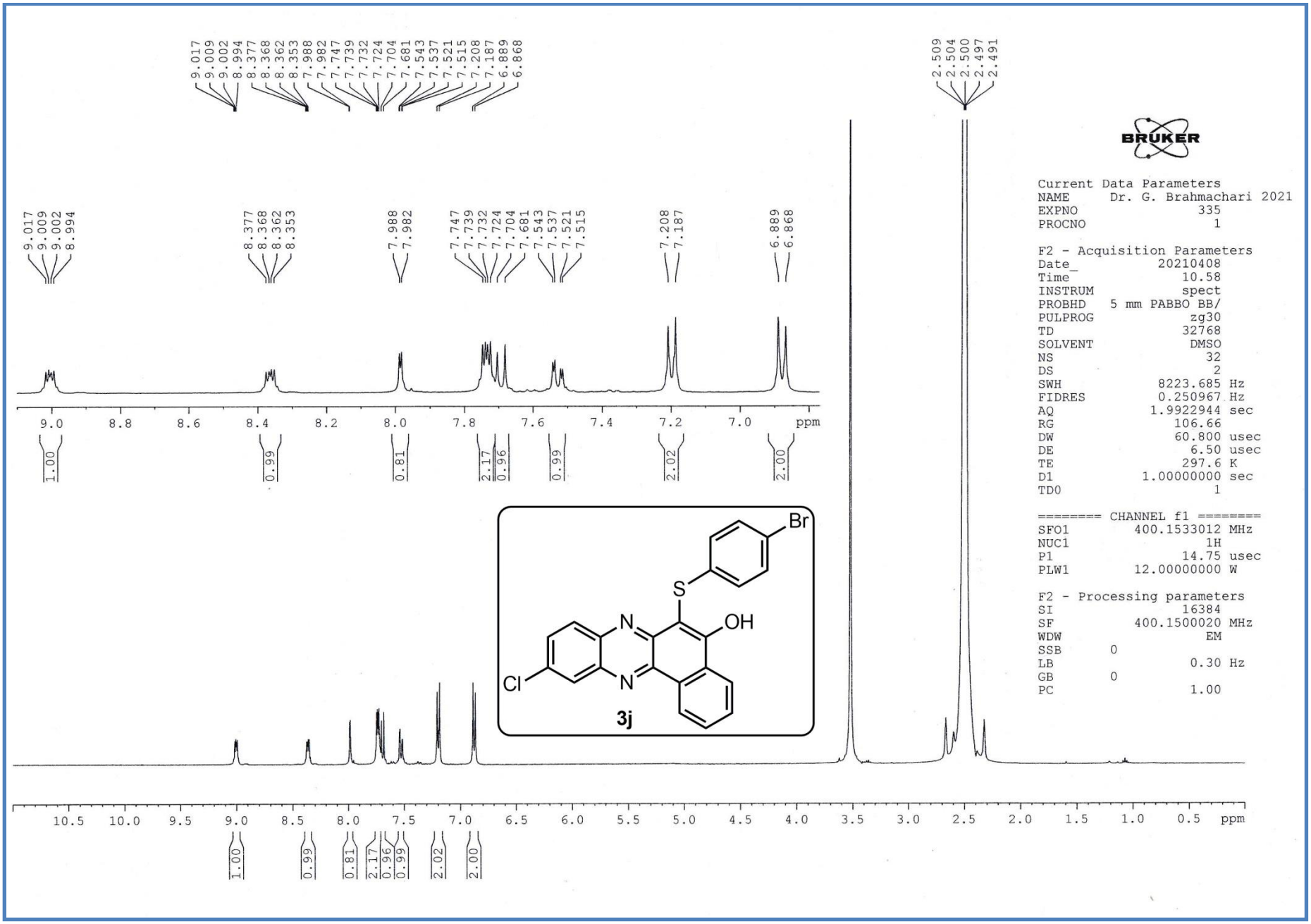


Figure S46. ^{1}H-NMR spectrum of 6-((4-bromophenyl)thio)-10-chlorobenzo[*a*]phenazin-5-ol (**3j**)

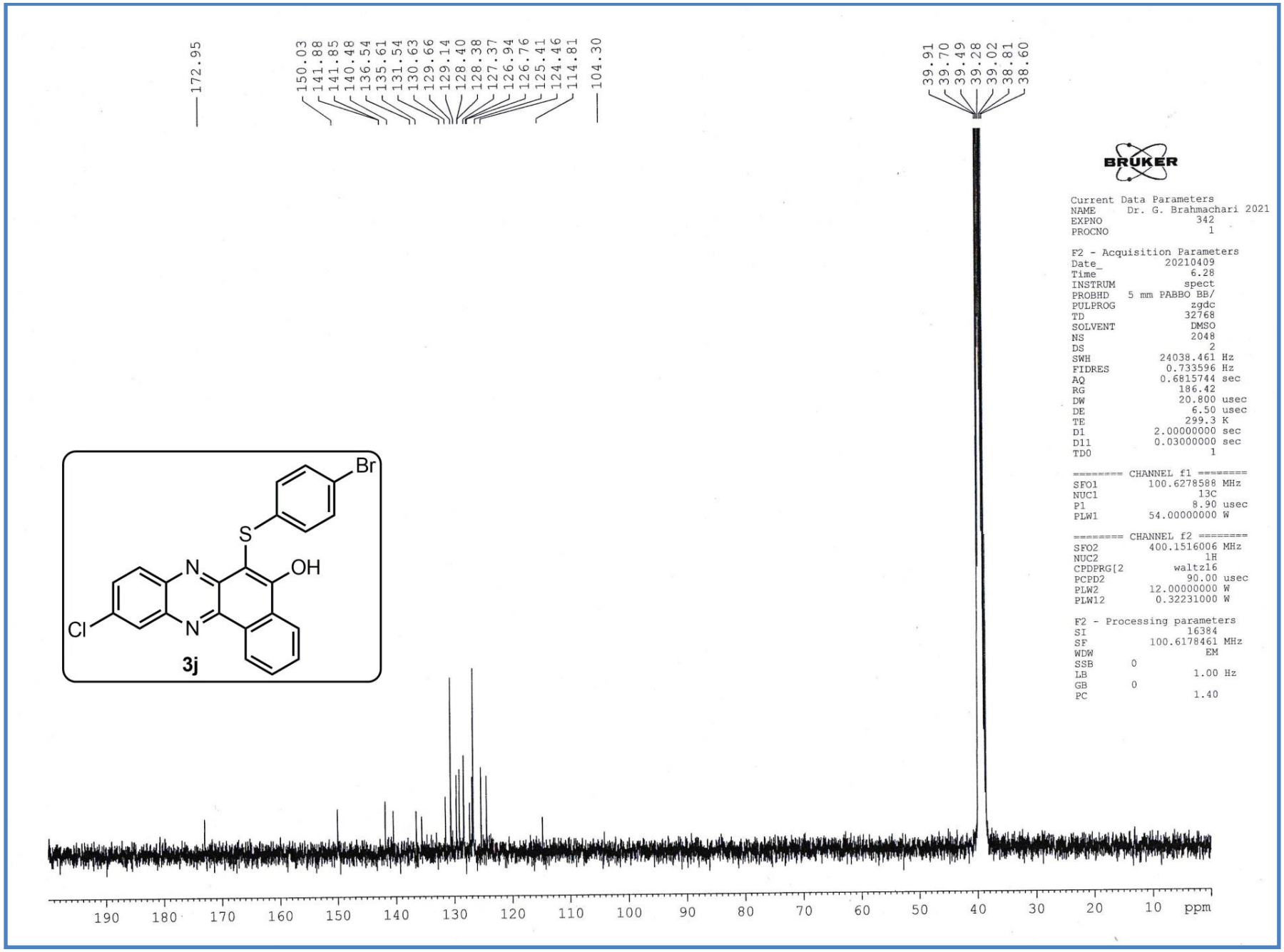


Figure S47. ^{13}C-NMR spectrum of 6-((4-bromophenyl)thio)-10-chlorobenzo[*a*]phenazin-5-ol (**3j**)

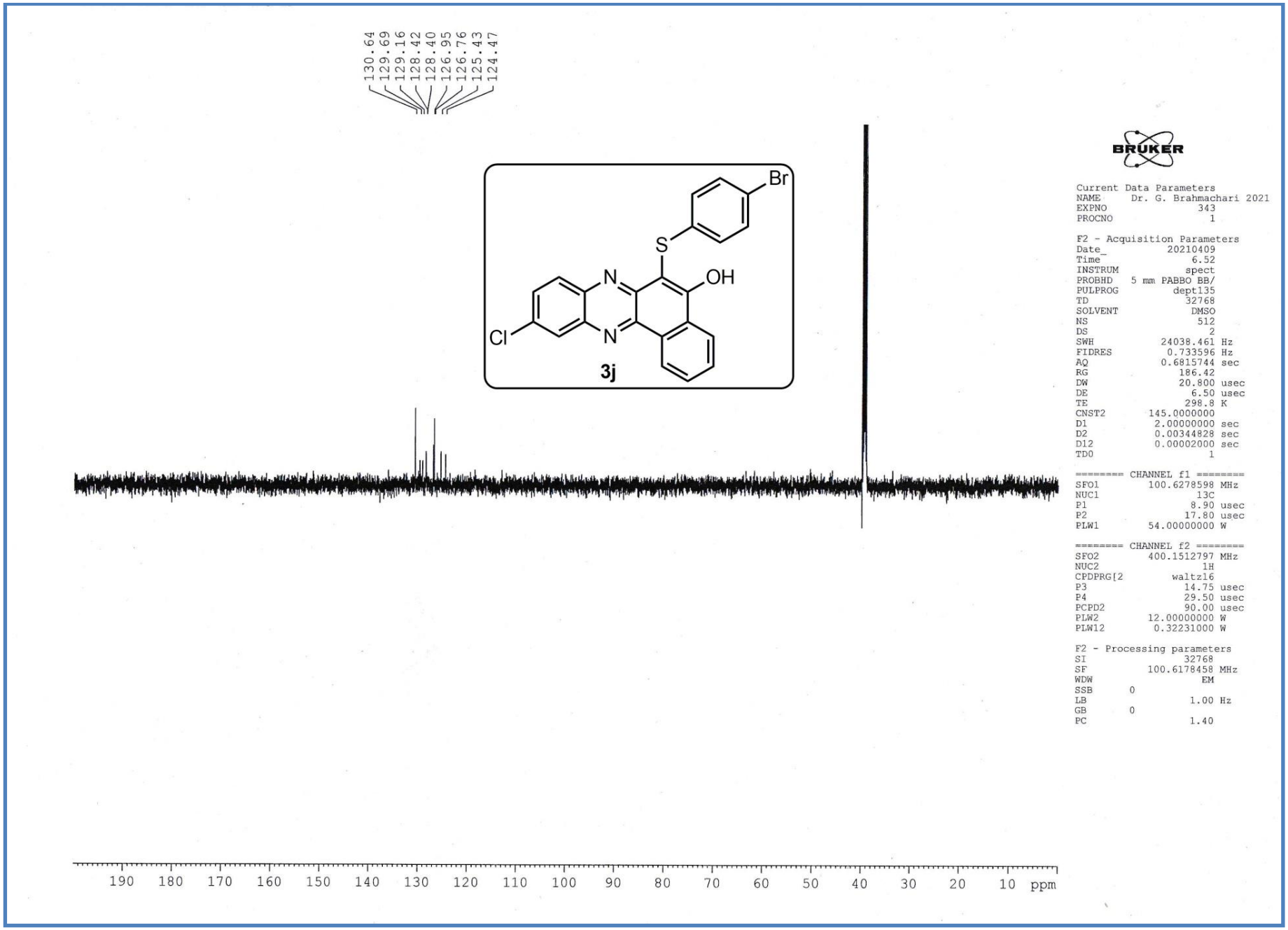


Figure S48. DEPT-135 NMR spectrum of 6-((4-bromophenyl)thio)-10-chlorobenzo[*a*]phenazin-5-ol (**3j**)

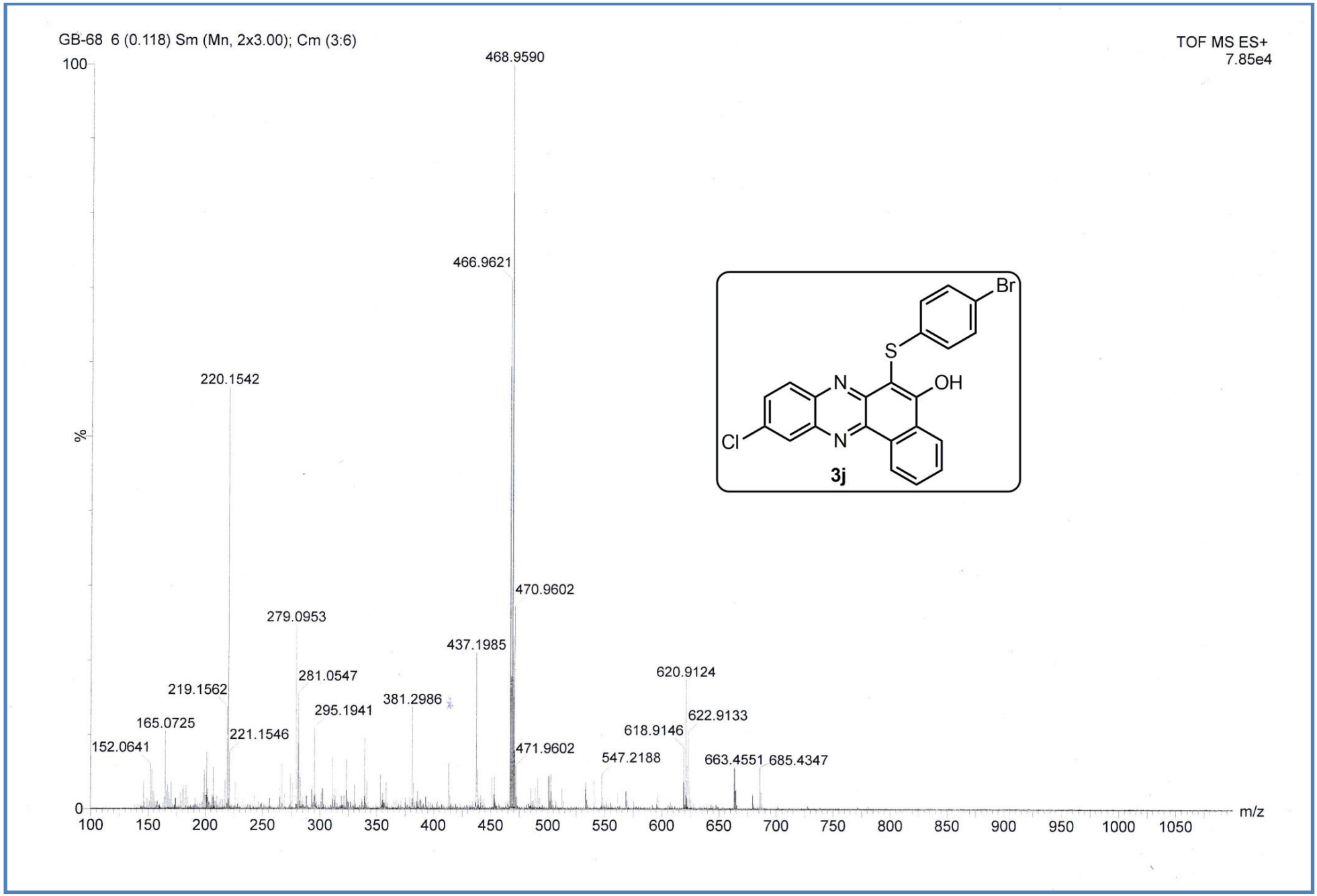


Figure S49. High-resolution Mass spectra of 6-((4-bromophenyl)thio)-10-chlorobenzo[*a*]phenazin-5-ol (**3j**)

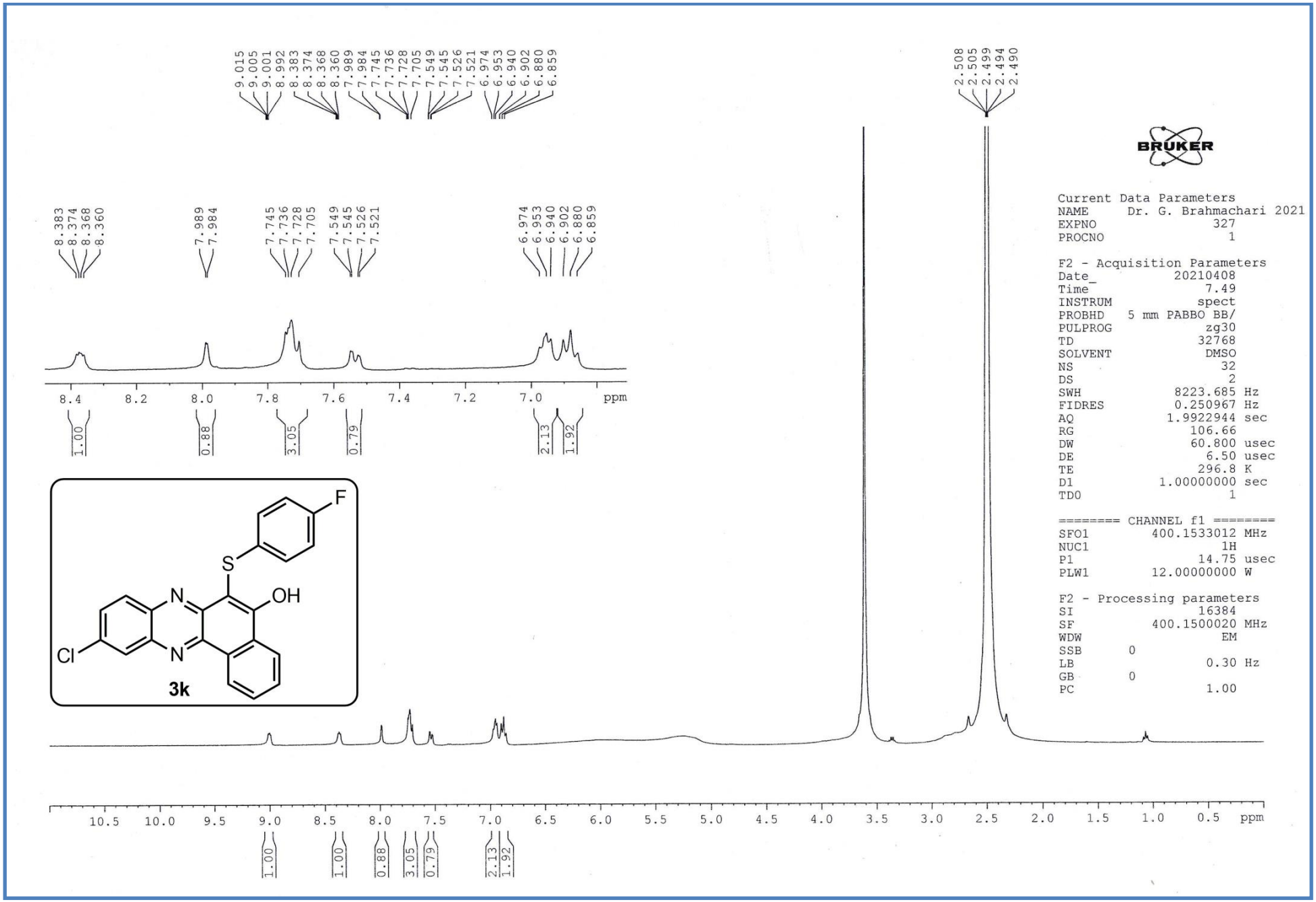


Figure S50. ^{1}H-NMR spectrumof 10-chloro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3k**)

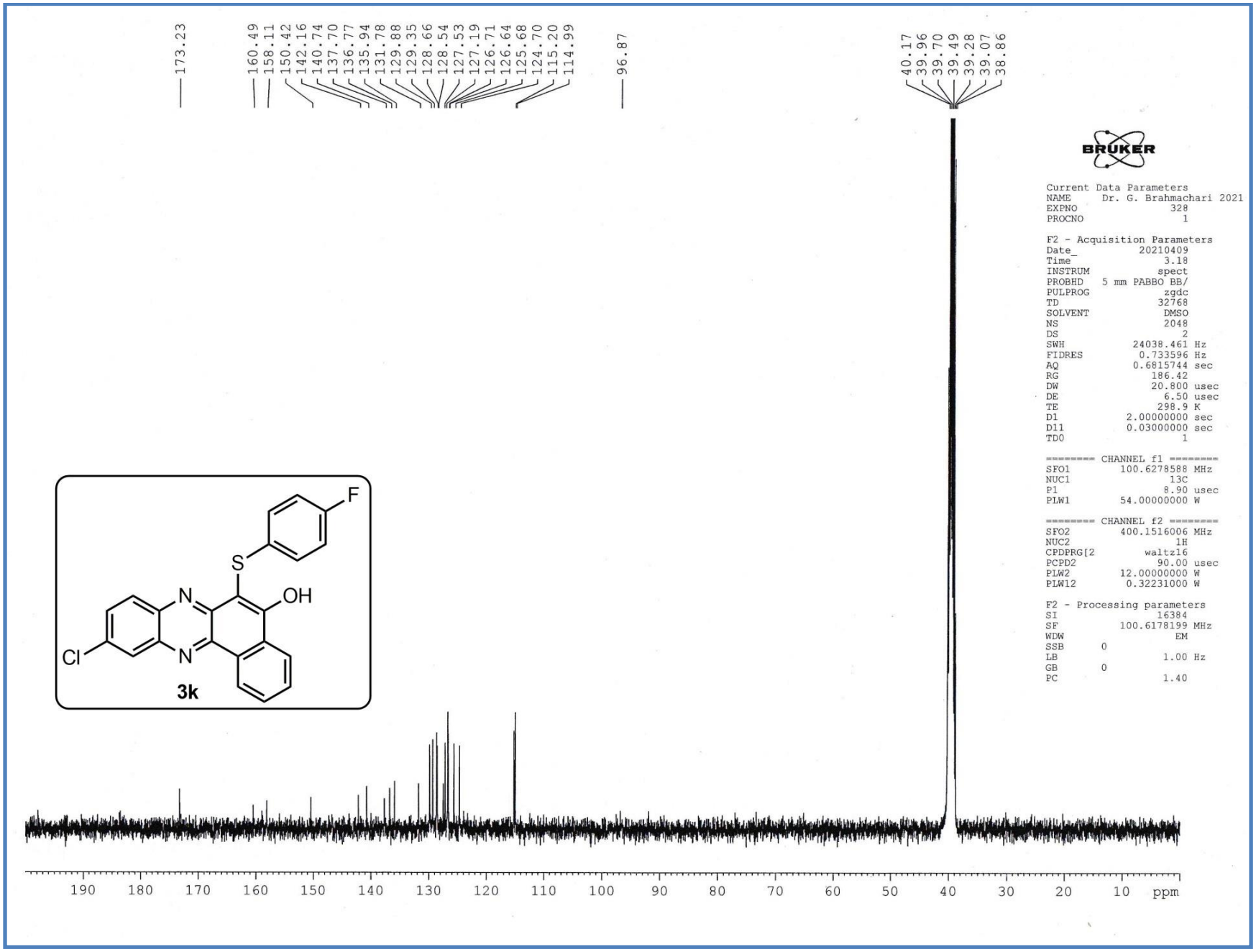


Figure S51. ^{13}C-NMR spectrum of 10-chloro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3k**)

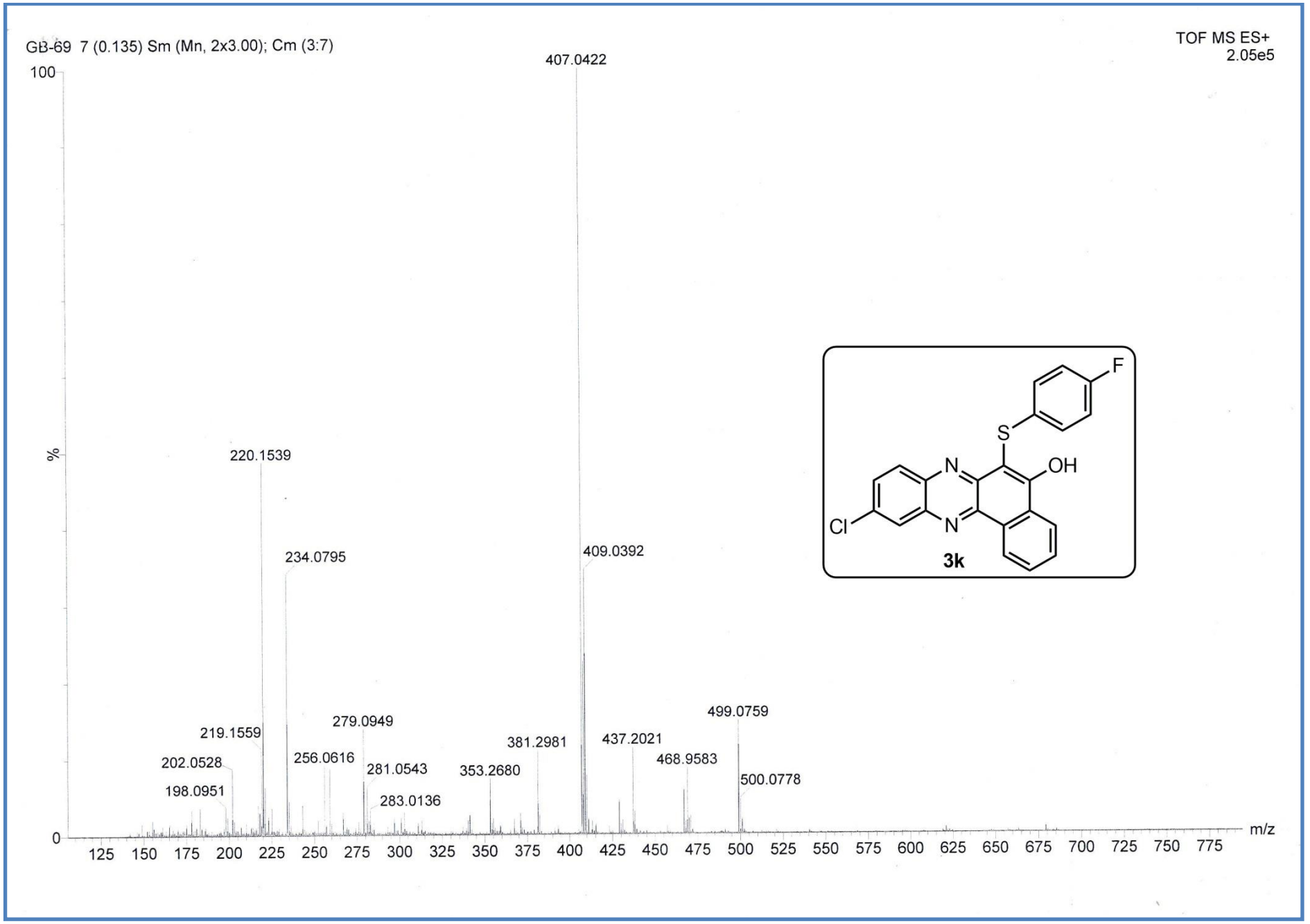


Figure S52. High-resolution Mass spectra of 10-chloro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3k**)

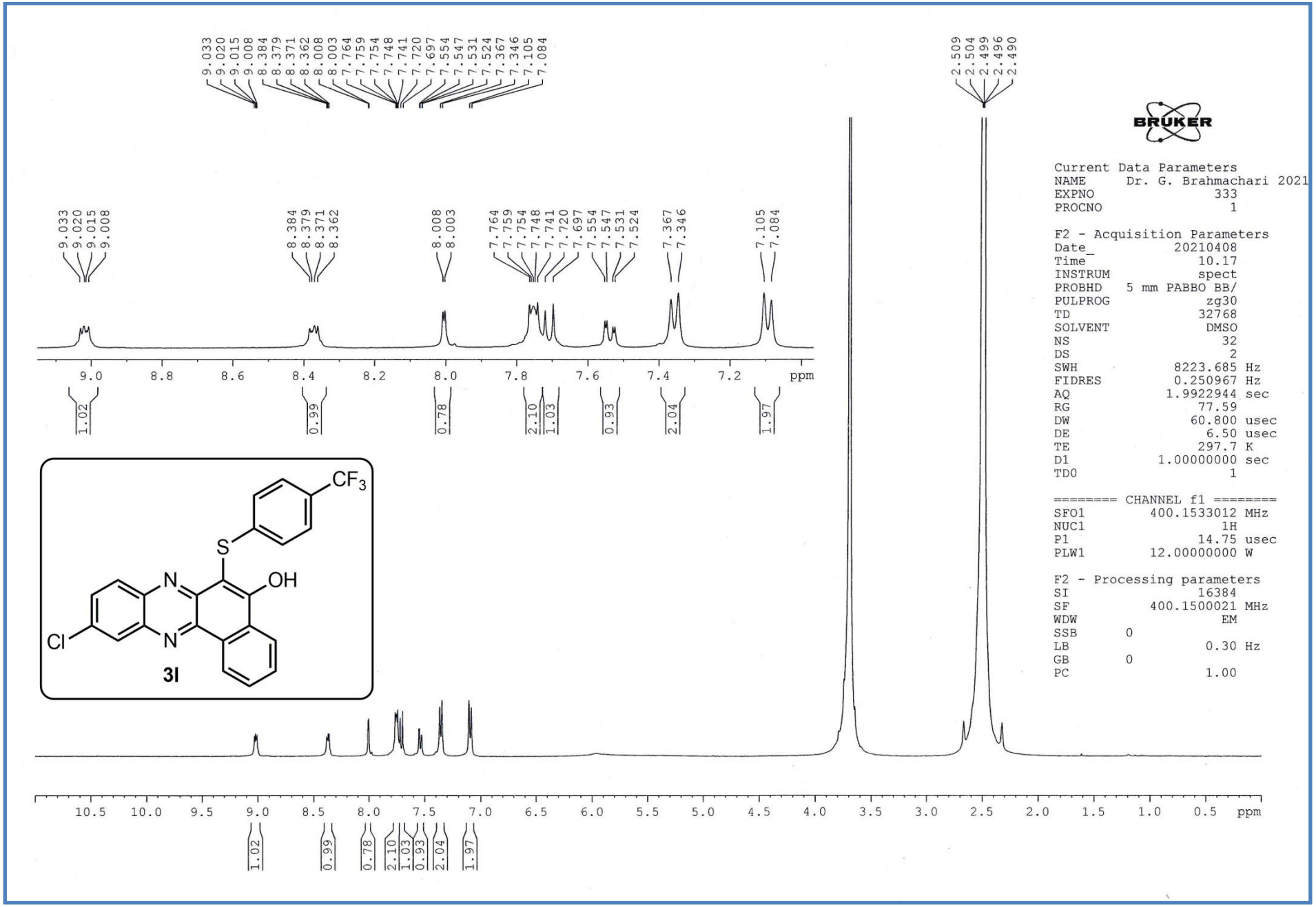


Figure S53. ^{1}H-NMR spectrum of 10-chloro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3l**)

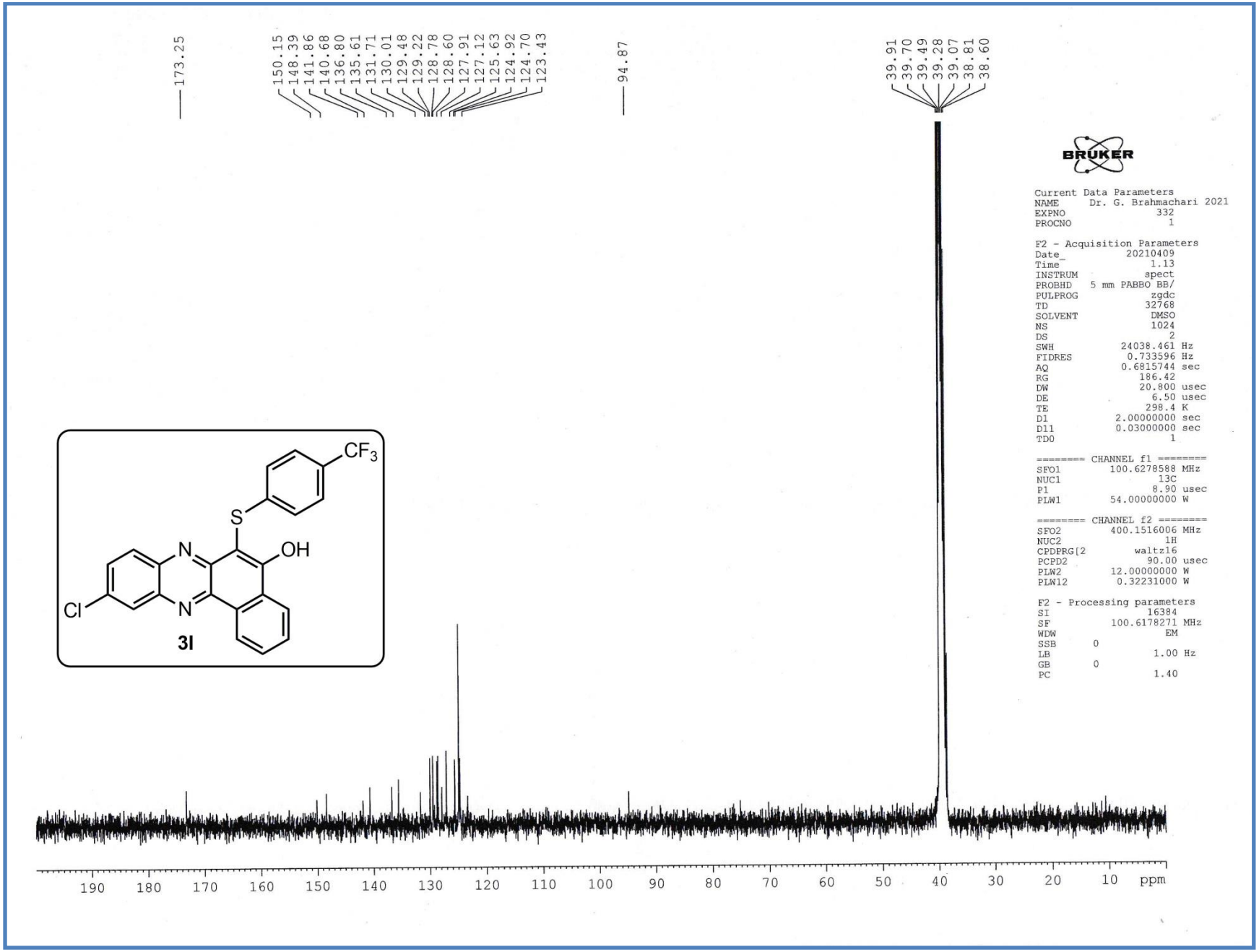


Figure S54. ^{13}C-NMR spectrum of 10-chloro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3l**)

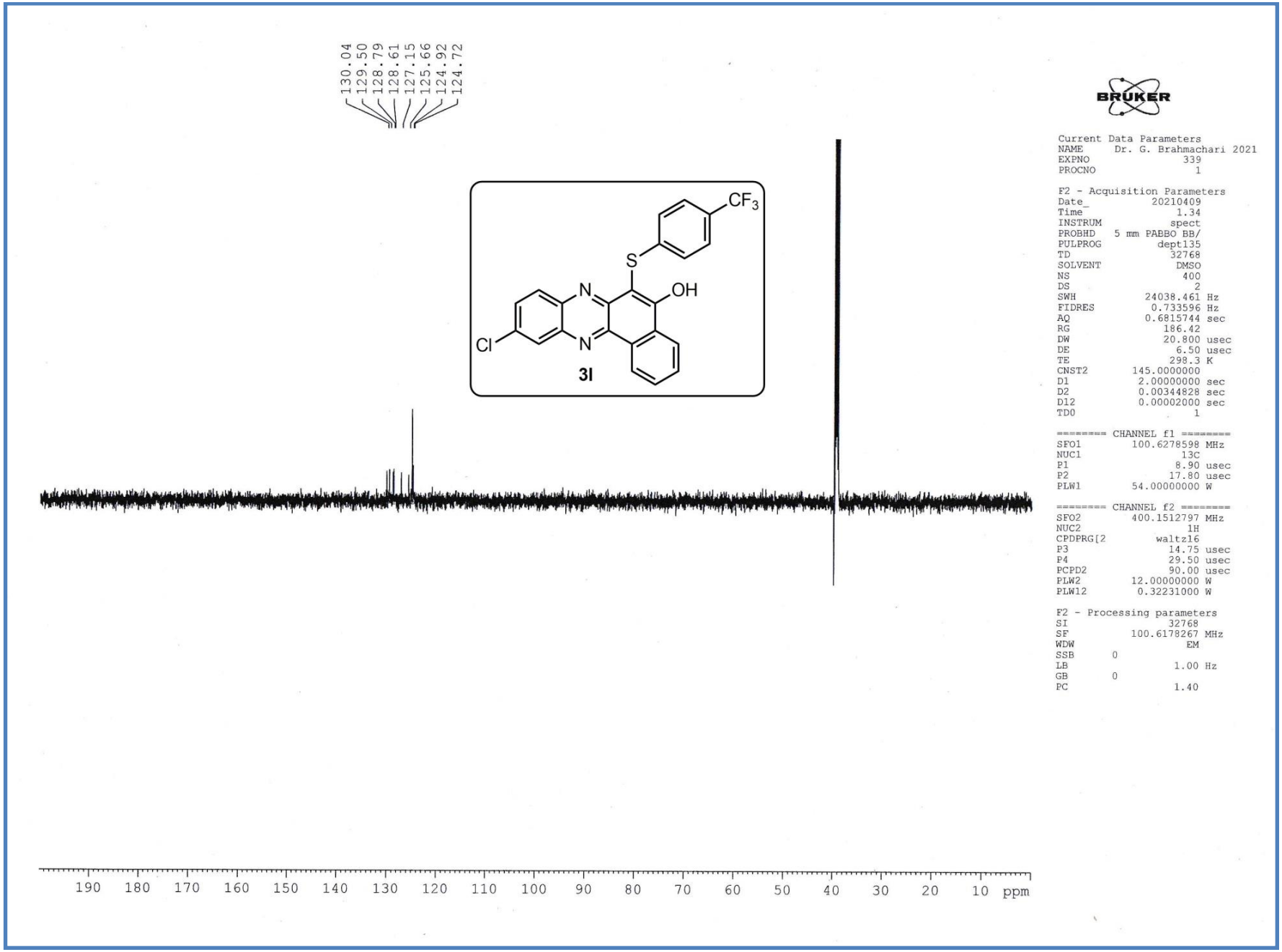


Figure S55. DEPT-135 NMR spectrum of 10-chloro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3l**)

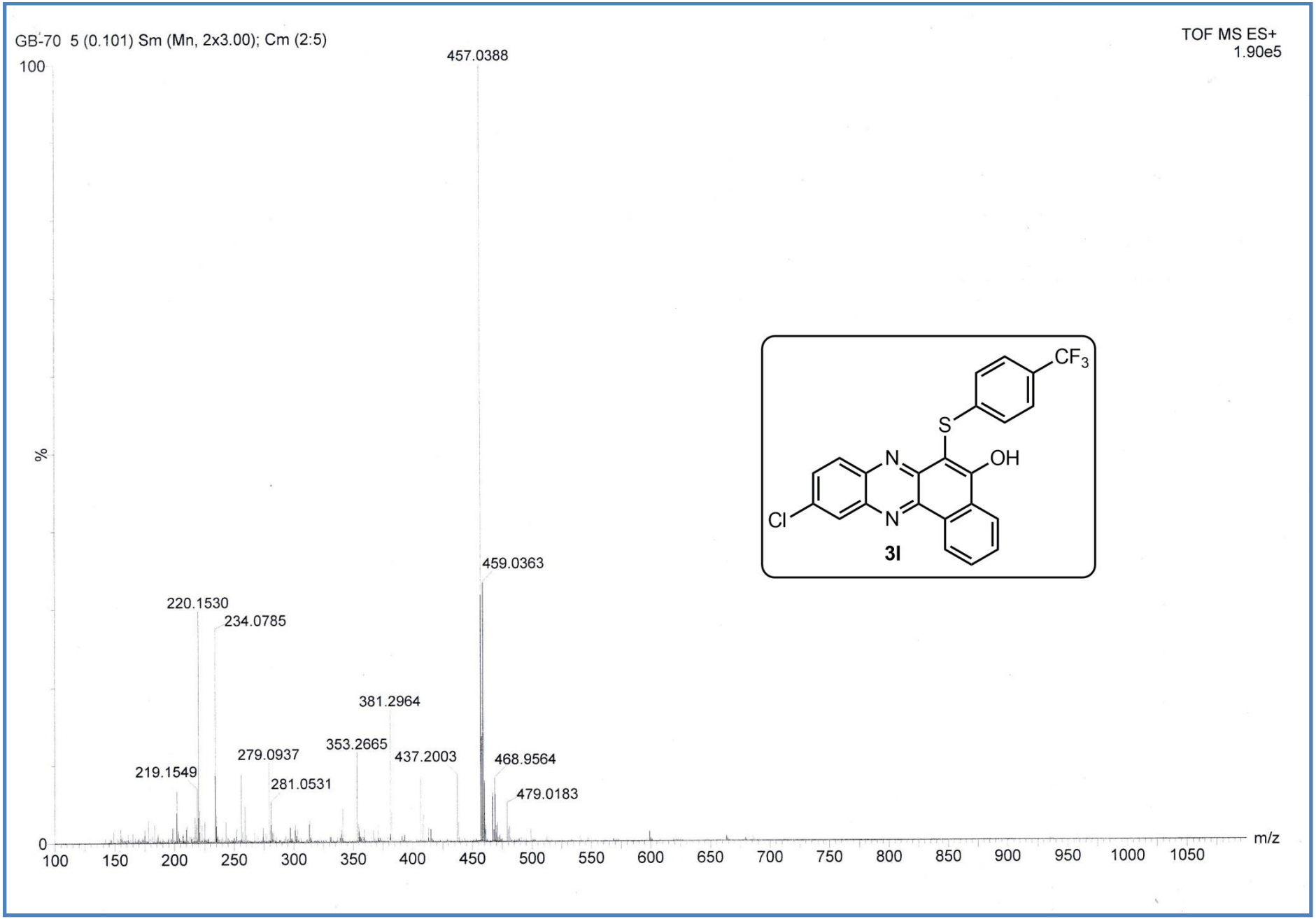


Figure S56. High-resolution Mass spectra of 10-chloro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3l**)

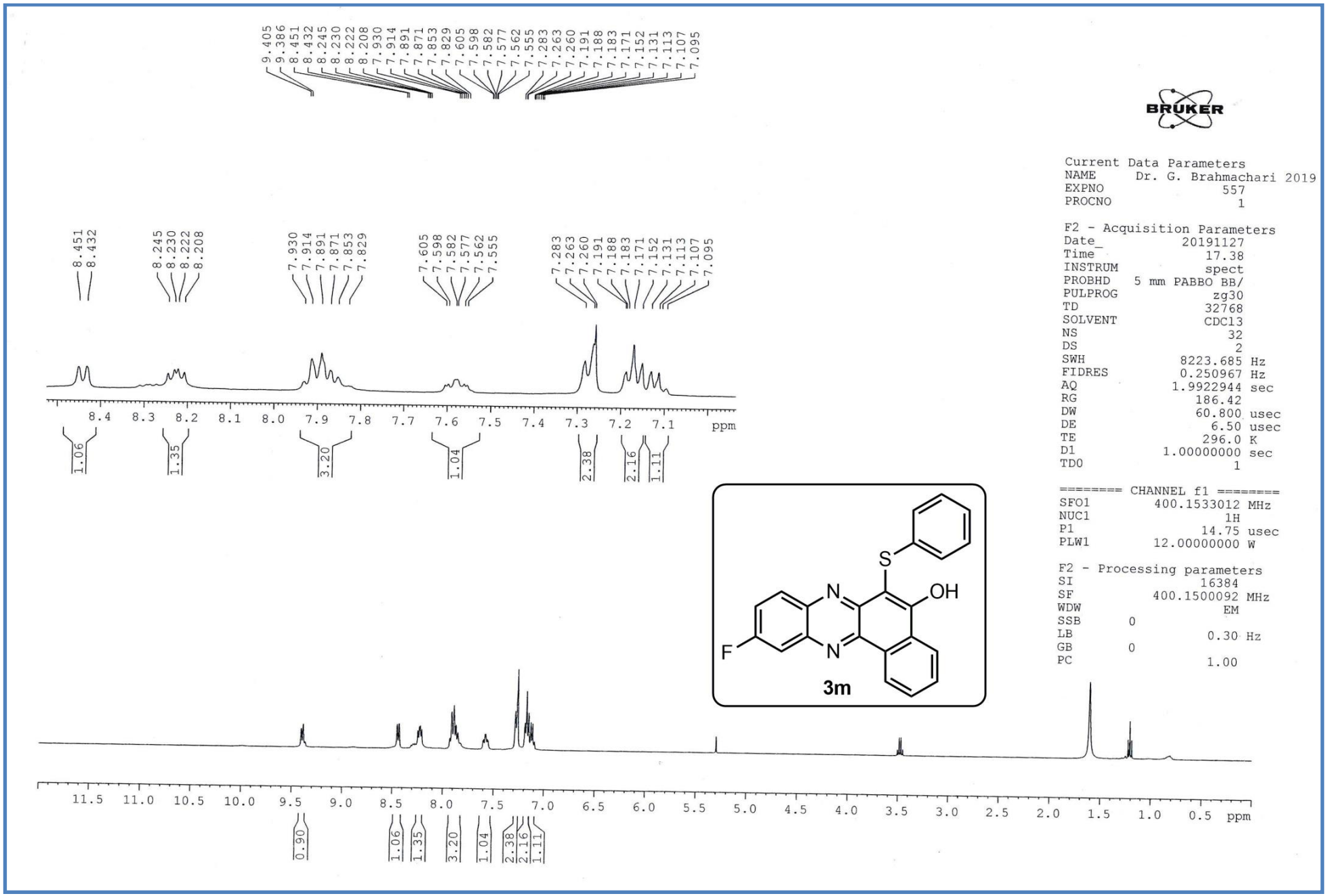


Figure S57. ^{1}H-NMR spectrum of 10-fluoro-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3m**)

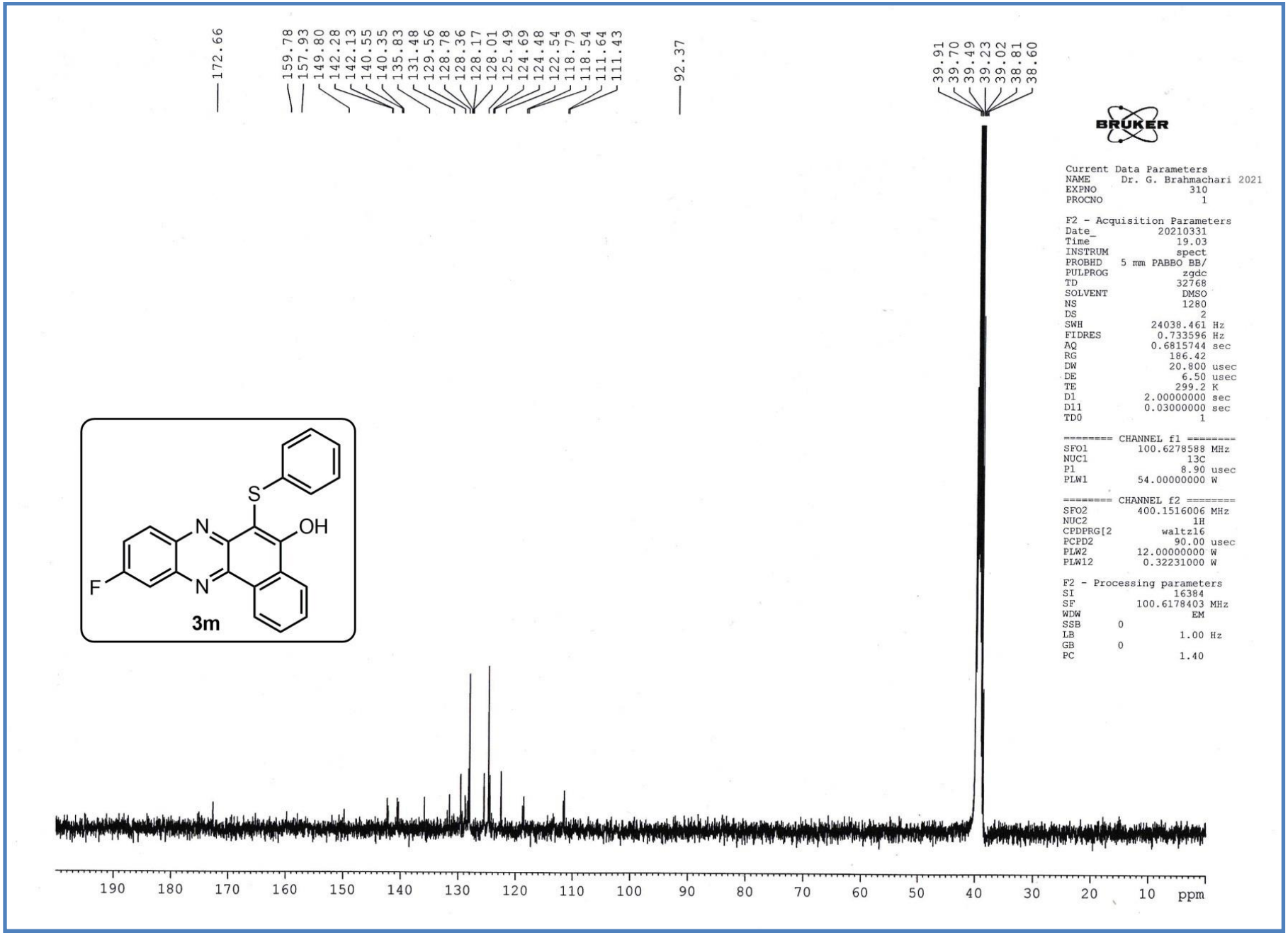


Figure S58. ^{13}C-NMR spectrum of 10-fluoro-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3m**)

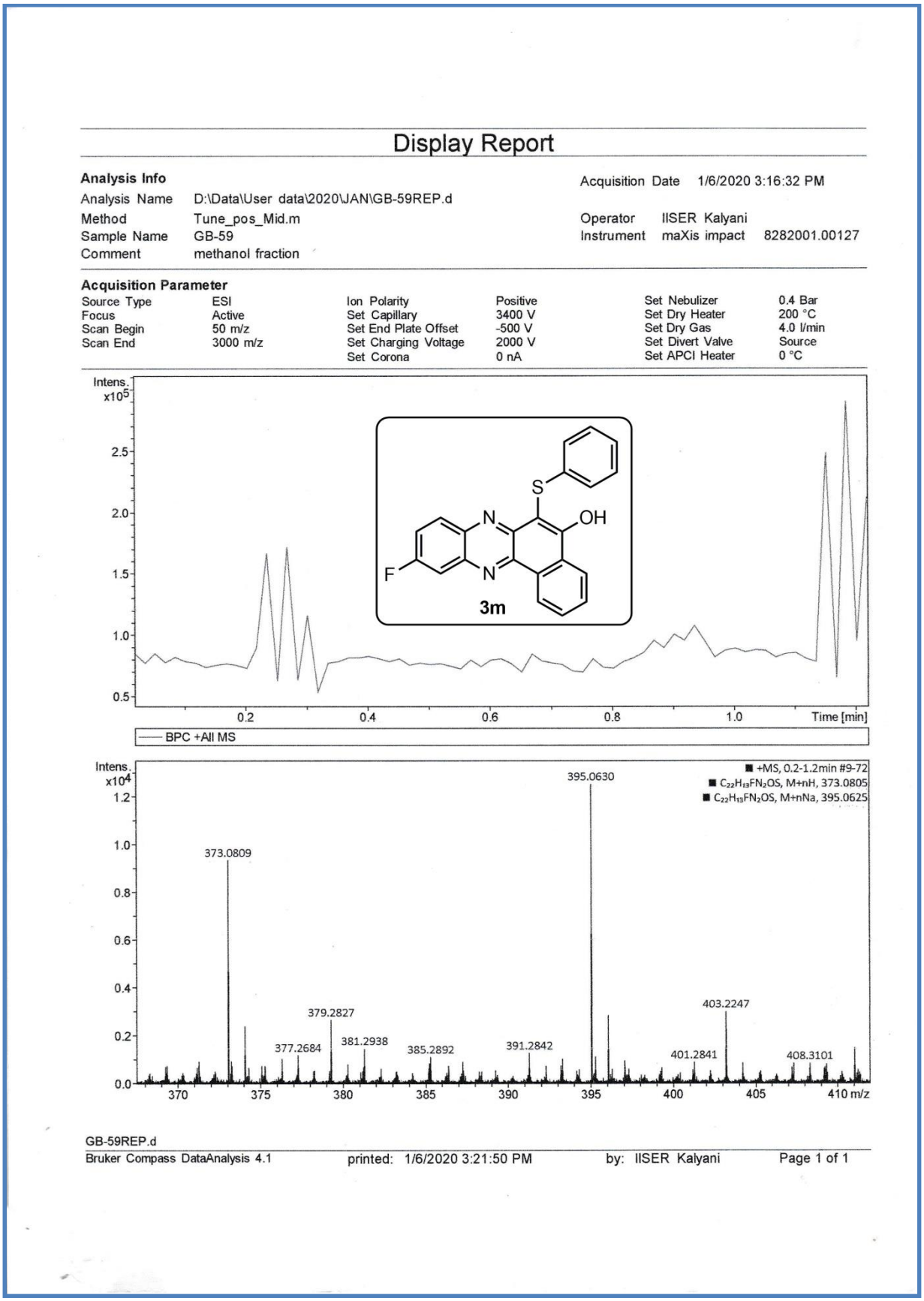


Figure S59. High-resolution Mass spectra of 10-fluoro-6-(phenylthio)benzo[*a*]phenazin-5-ol (**3m**)

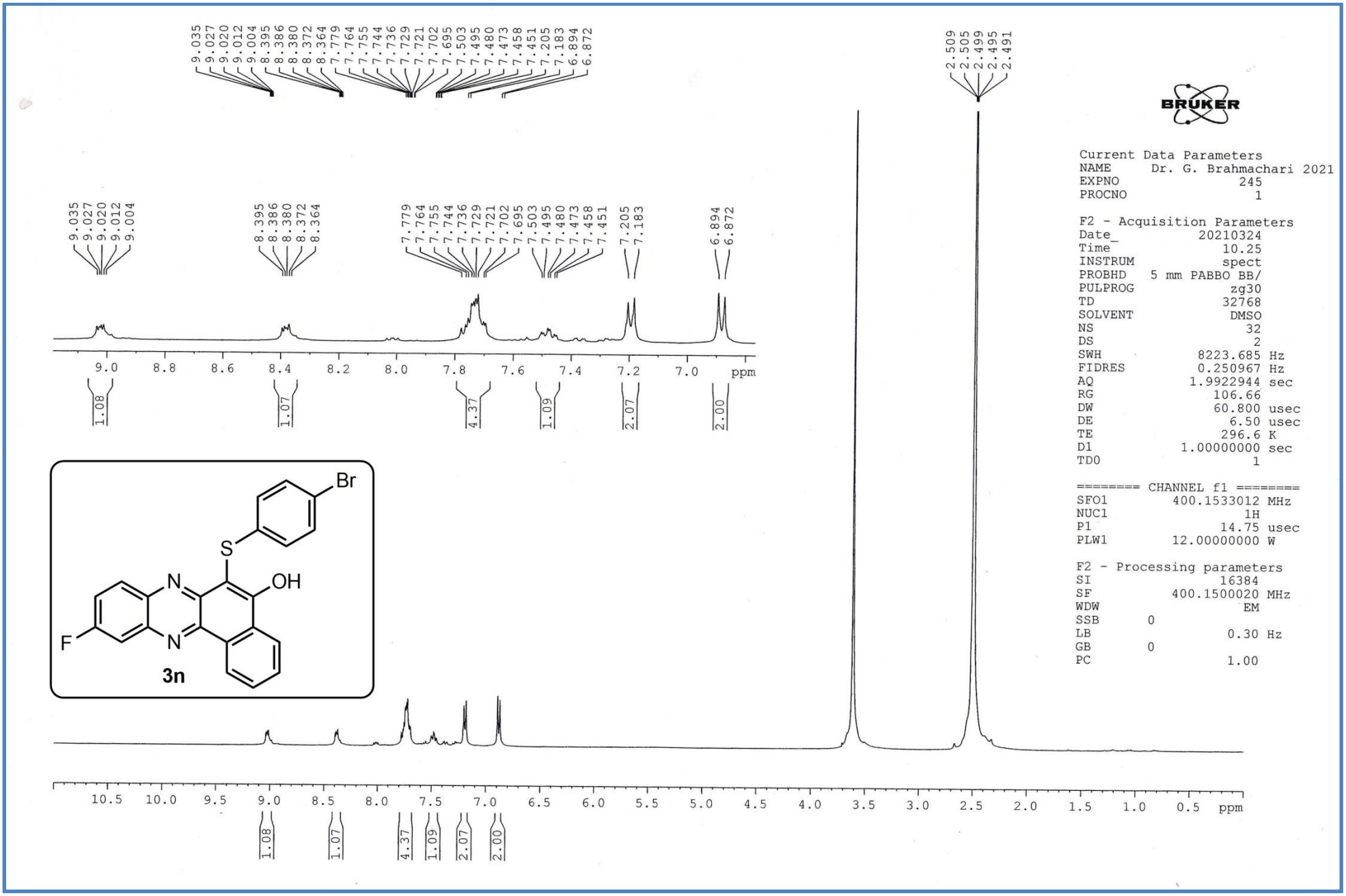


Figure S60. [1]H-NMR spectrum of 6-((4-bromophenyl)thio)-10-fluorobenzo[a]phenazin-5-ol (**3n**)

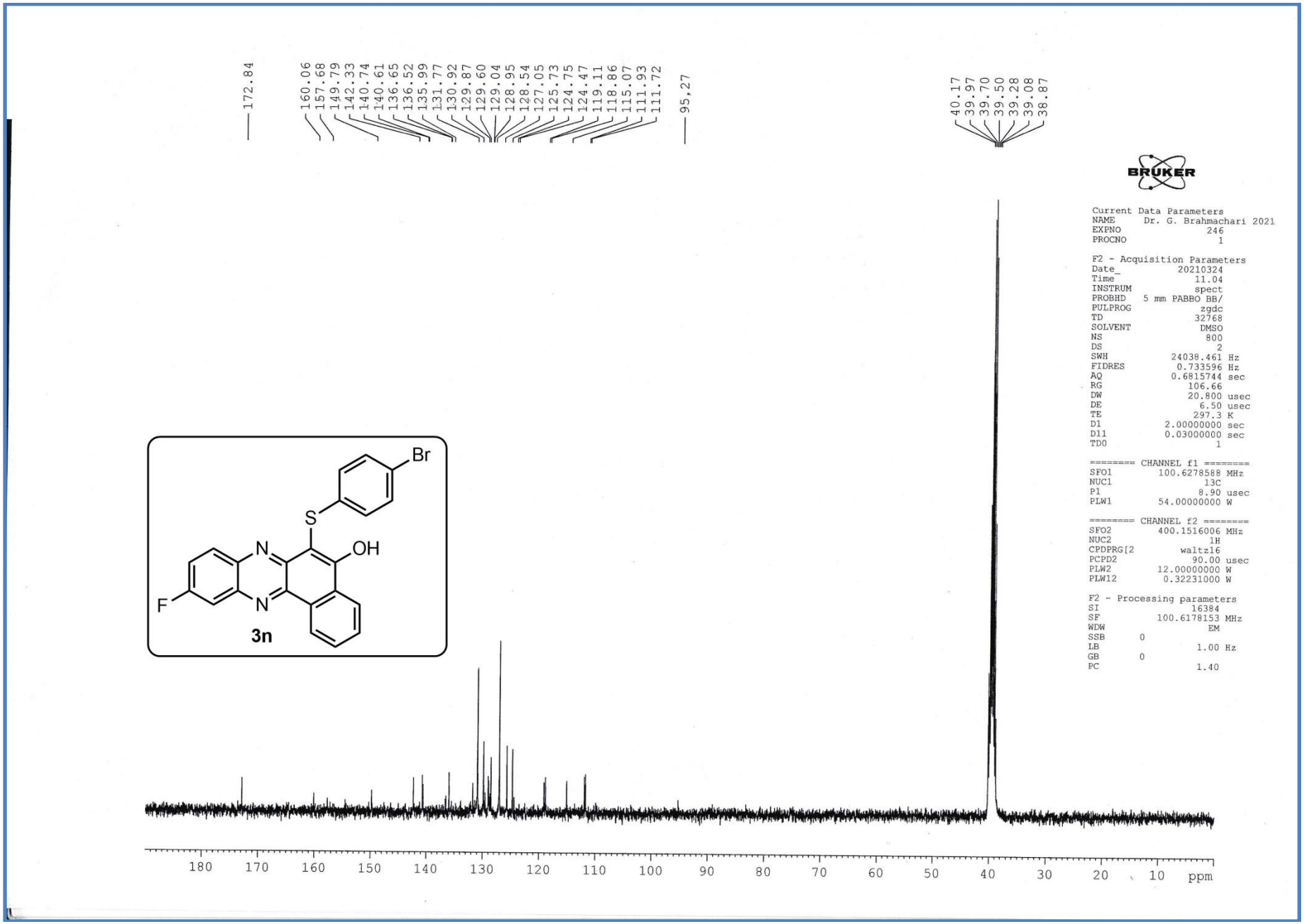


Figure S61. ^{13}C-NMR spectrum of 6-((4-bromophenyl)thio)-10-fluorobenzo[a]phenazin-5-ol (**3n**)

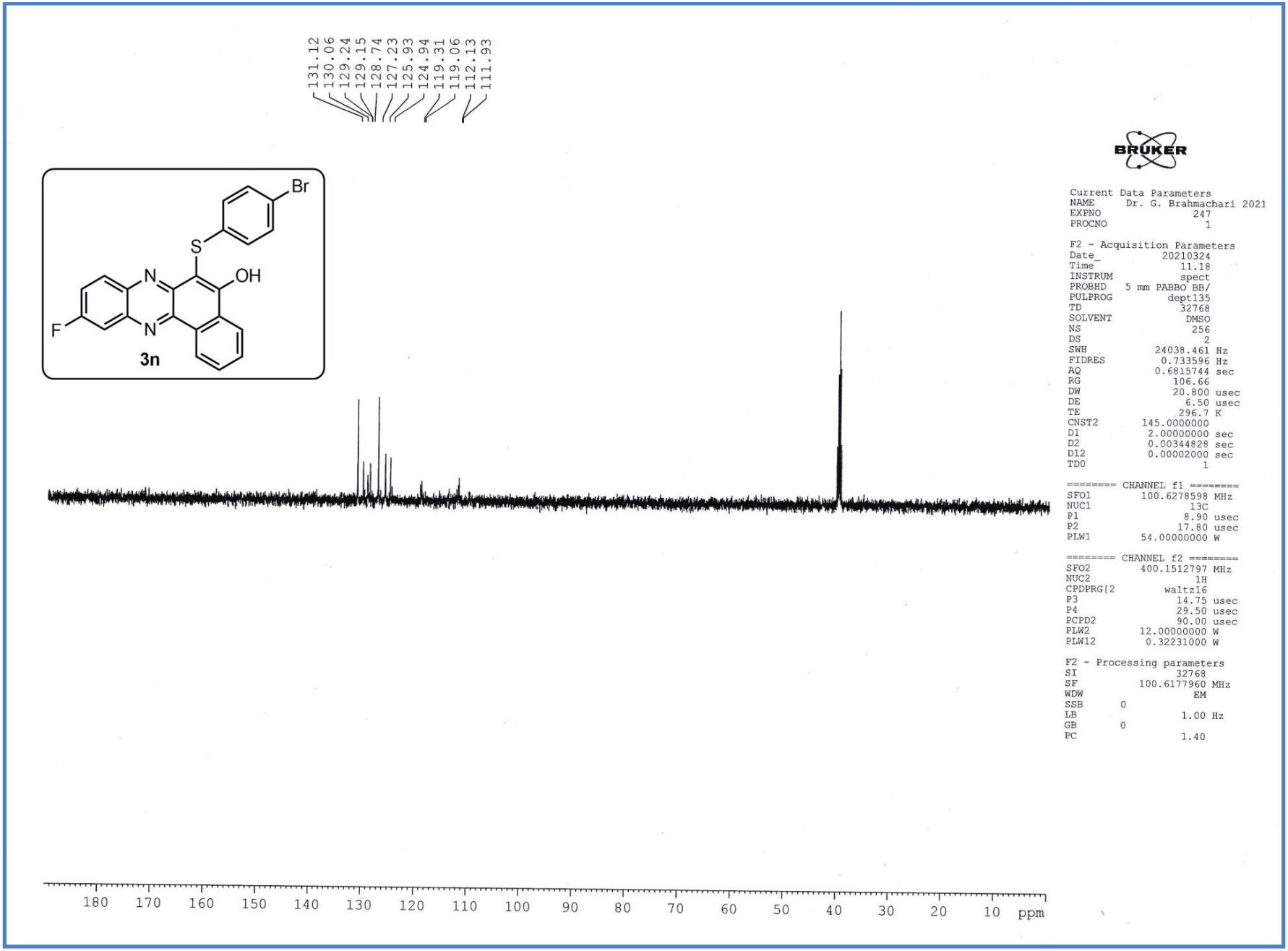


Figure S62. DEPT-135 NMR spectrum of 6-((4-bromophenyl)thio)-10-fluorobenzo[a]phenazin-5-ol (**3n**)

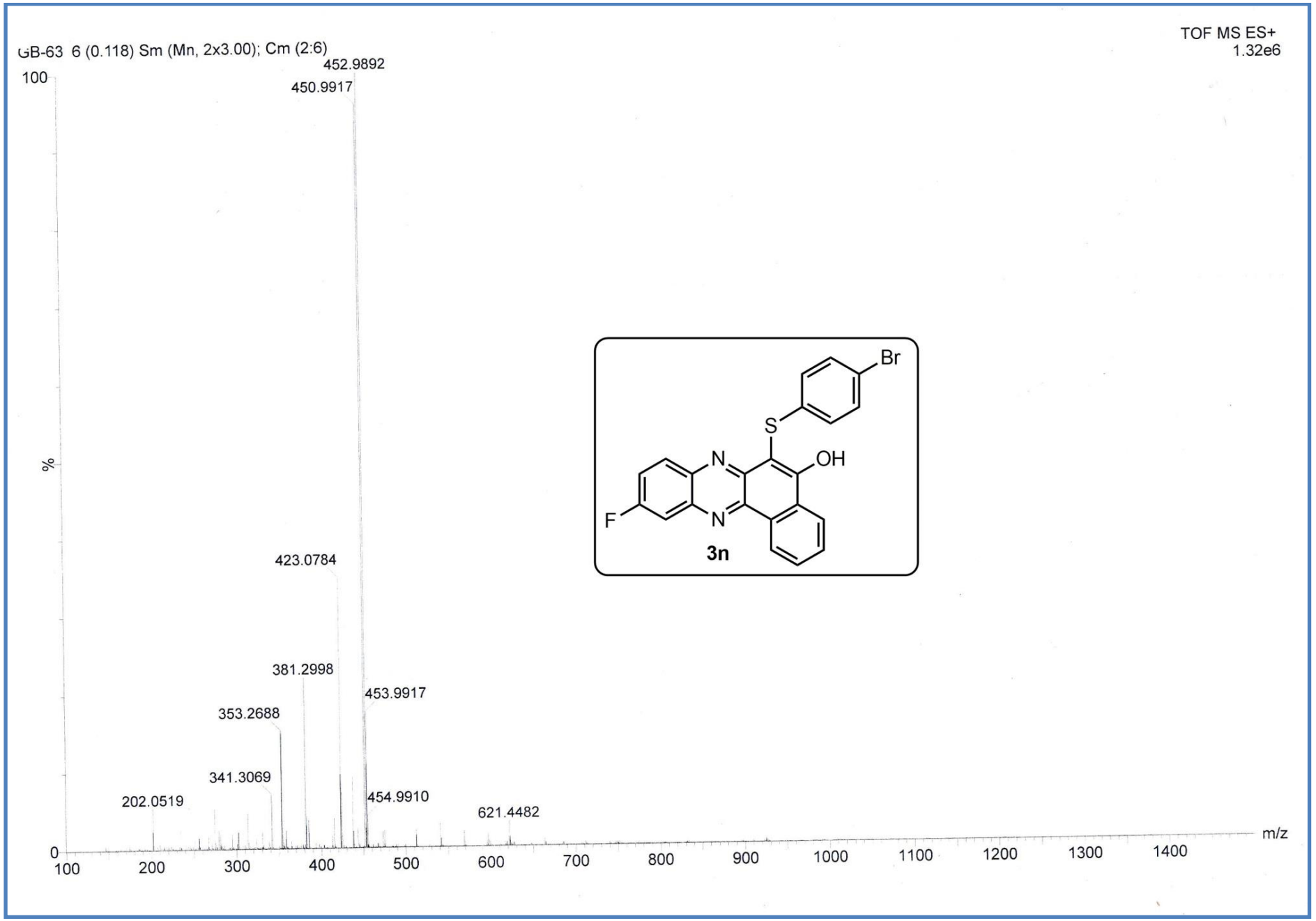


Figure S63. High-resolution Mass spectra of 6-((4-bromophenyl)thio)-10-fluorobenzo[a]phenazin-5-ol (**3n**)

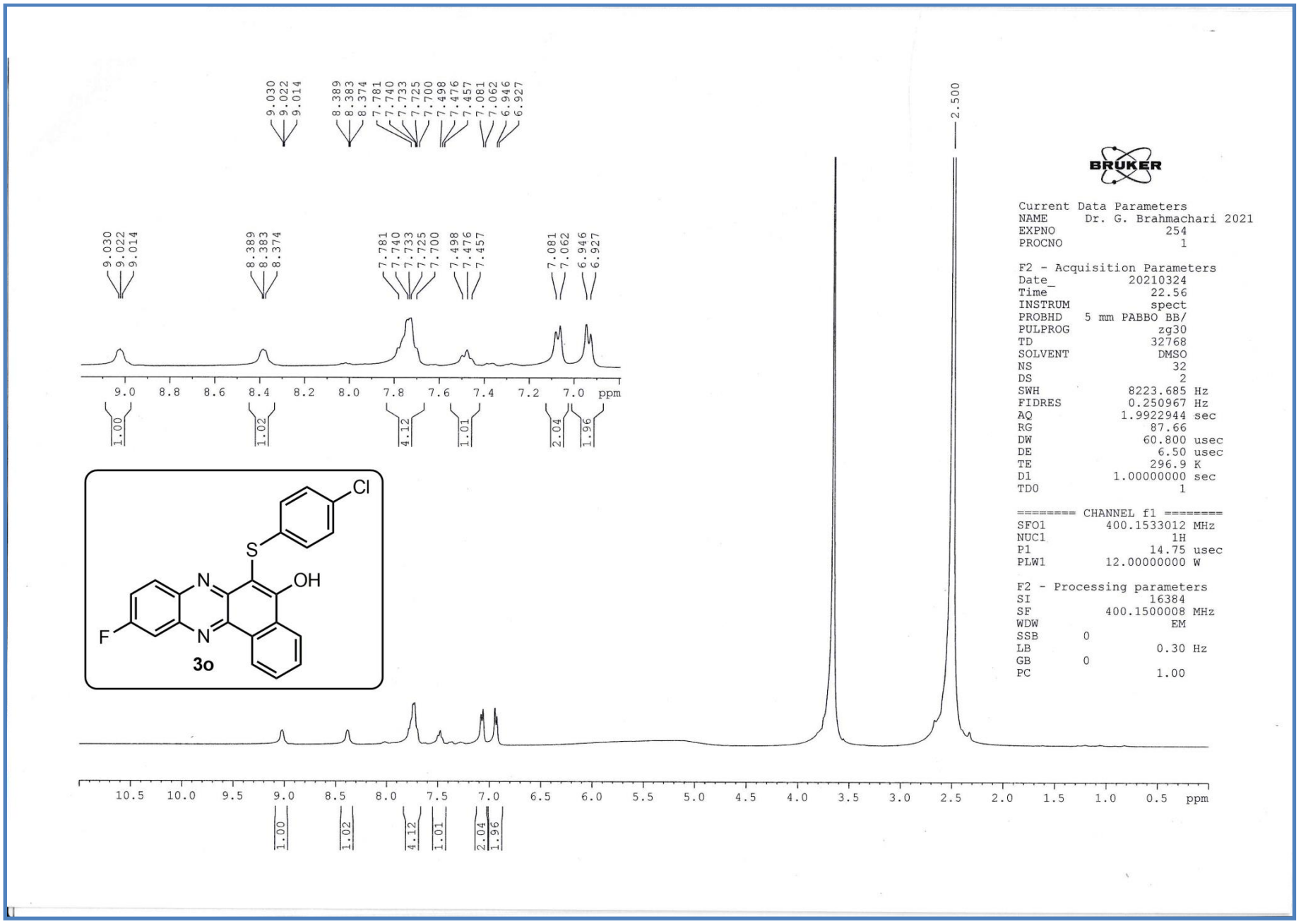


Figure S64. [1]H-NMR spectrum of 6-((4-chlorophenyl)thio)-10-fluorobenzo[*a*]phenazin-5-ol (**3o**)

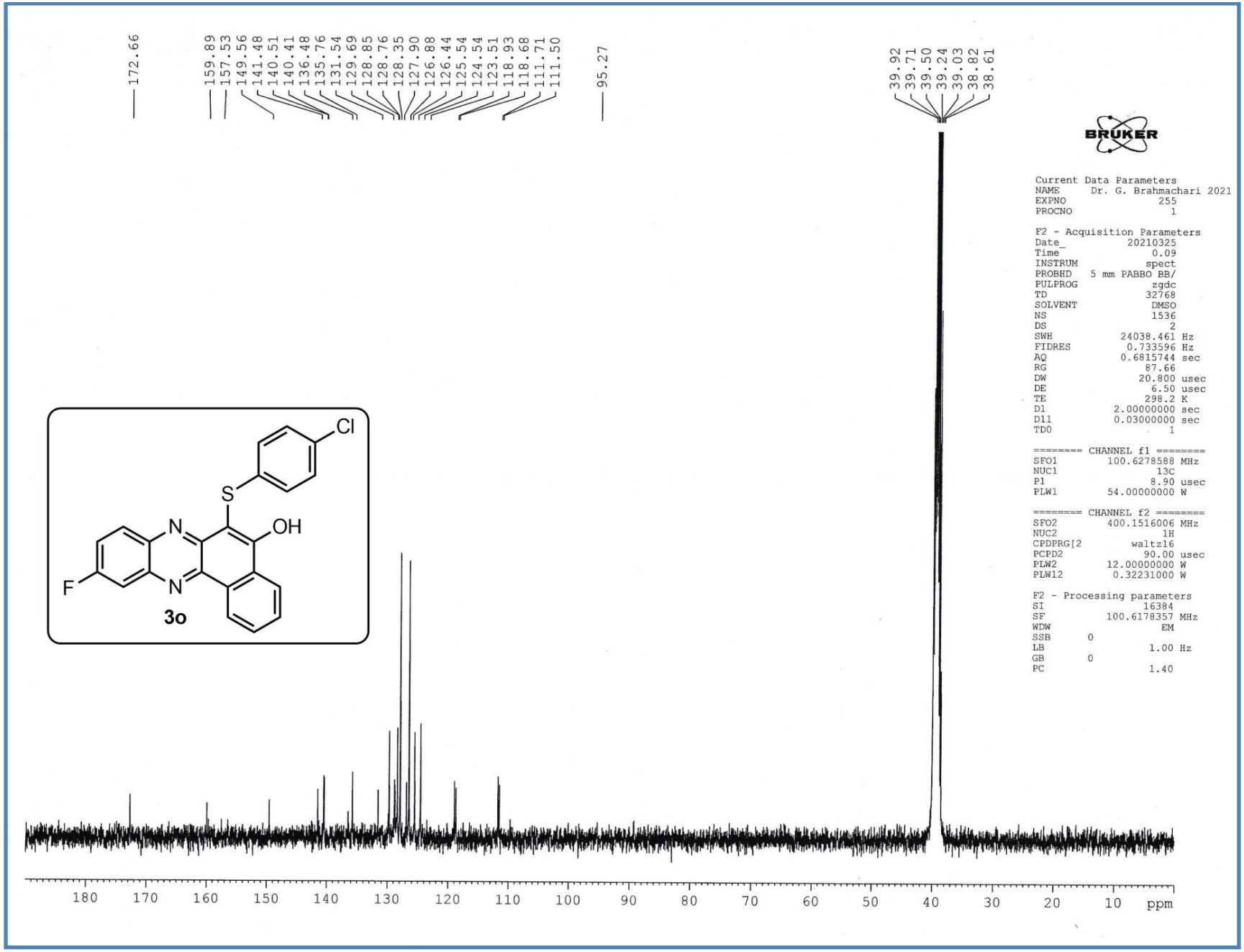


Figure S65. ^{13}C-NMR spectrum of 6-((4-chlorophenyl)thio)-10-fluorobenzo[*a*]phenazin-5-ol (**3o**)

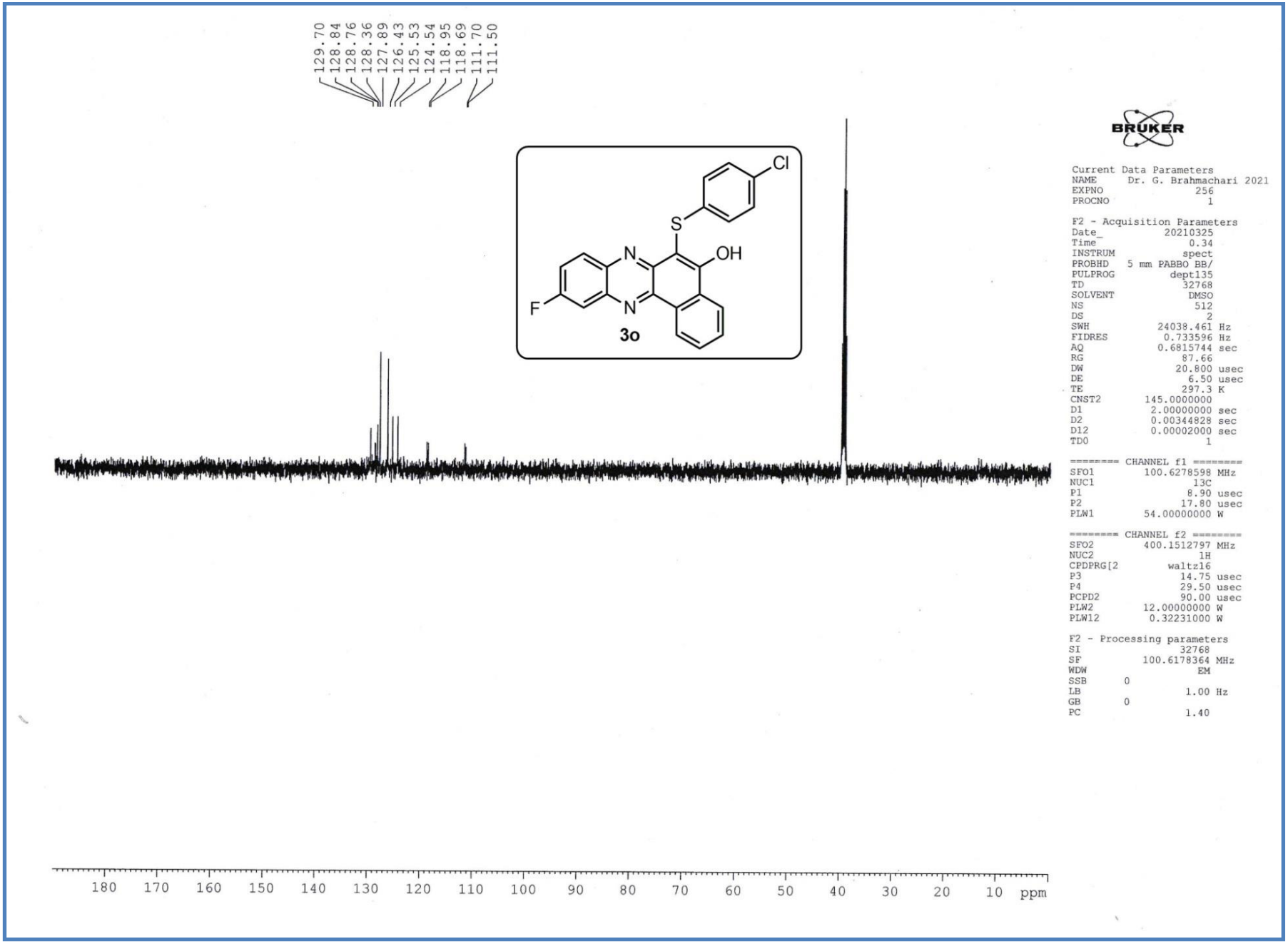


Figure S66. DEPT-135 NMR spectrum of 6-((4-chlorophenyl)thio)-10-fluorobenzo[*a*]phenazin-5-ol (**3o**)

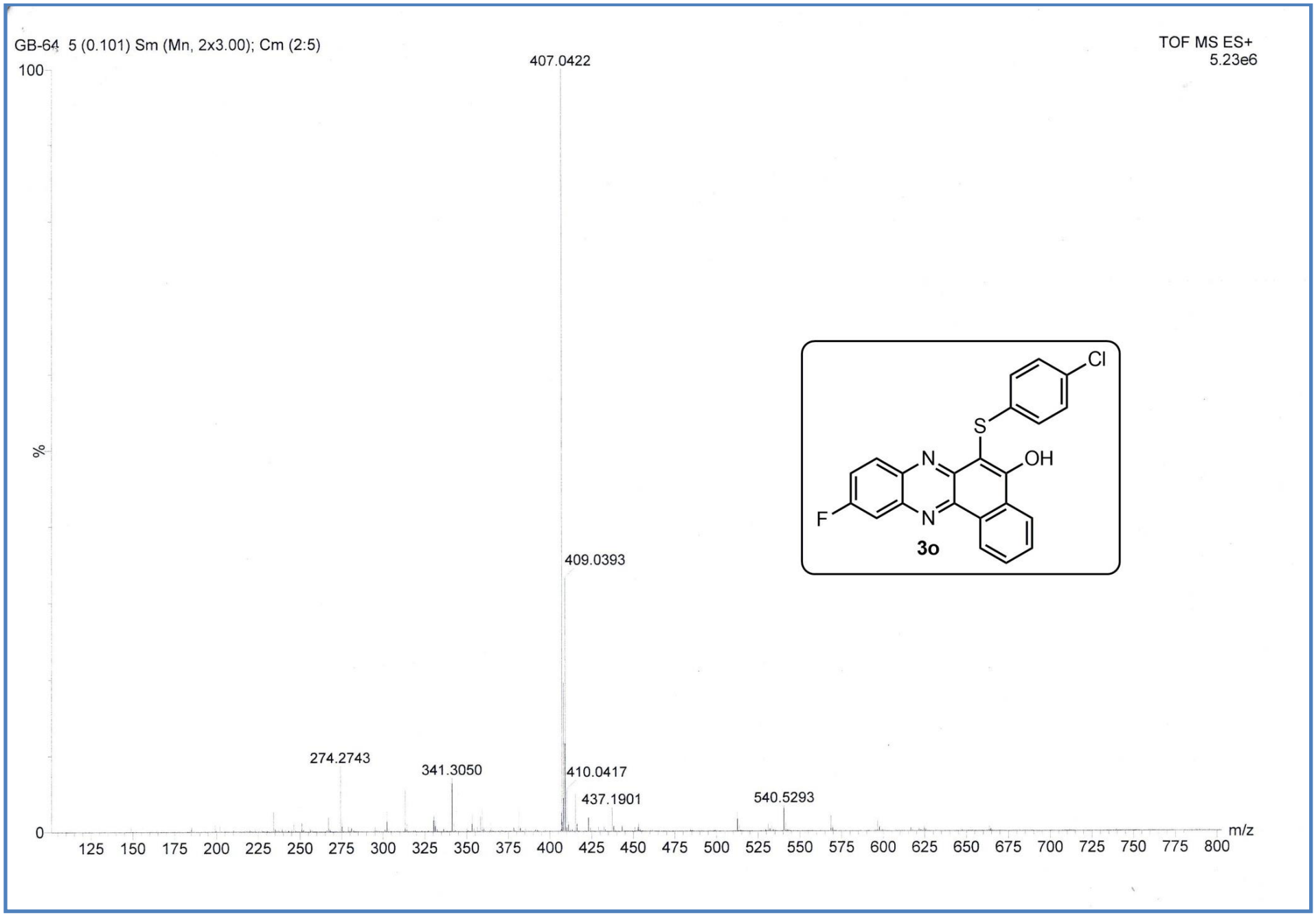


Figure S67. High-resolution Mass spectra of 6-((4-chlorophenyl)thio)-10-fluorobenzo[*a*]phenazin-5-ol (**3o**)

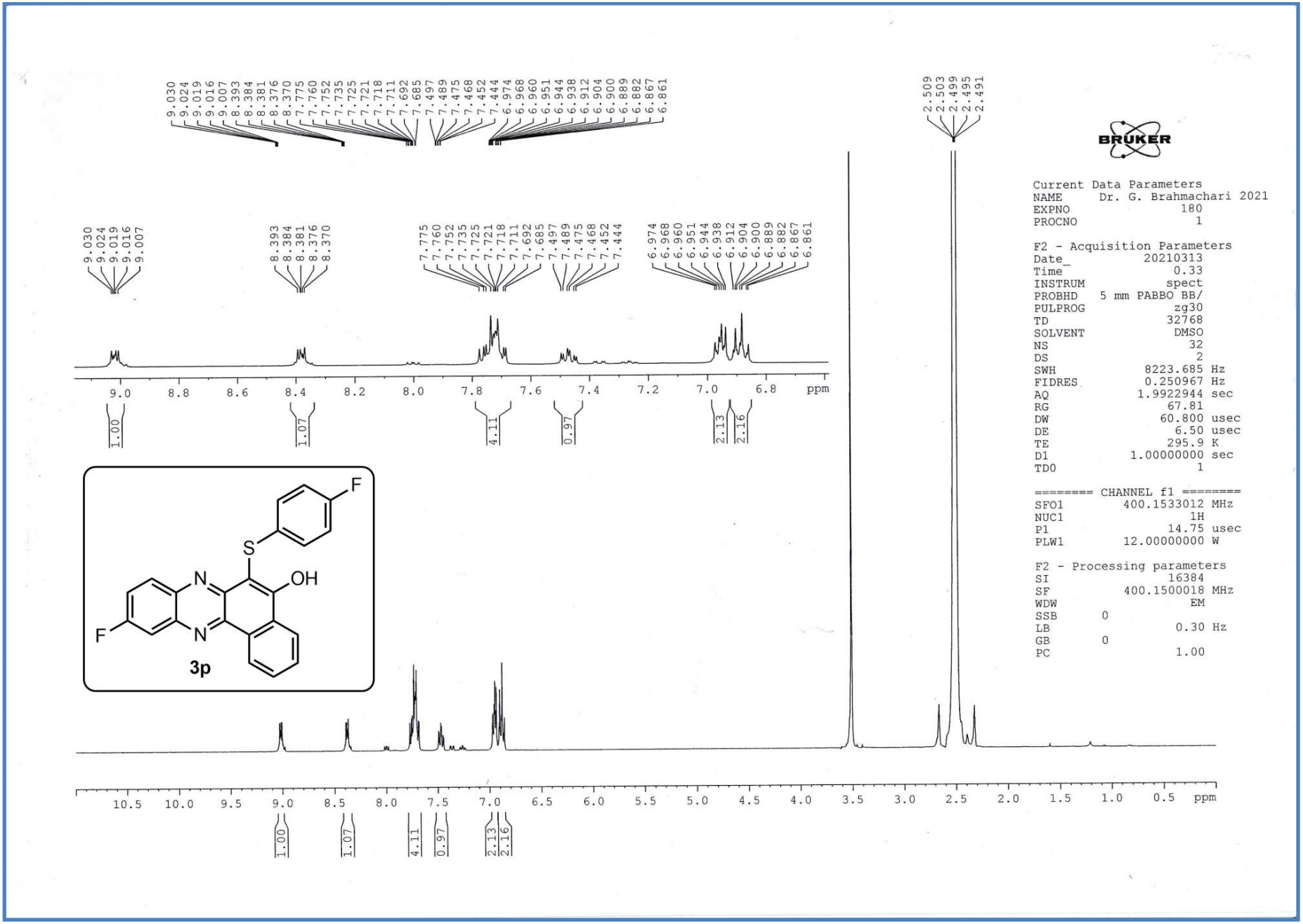


Figure S68. ^{1}H-NMR spectrum of 10-fluoro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3p**)

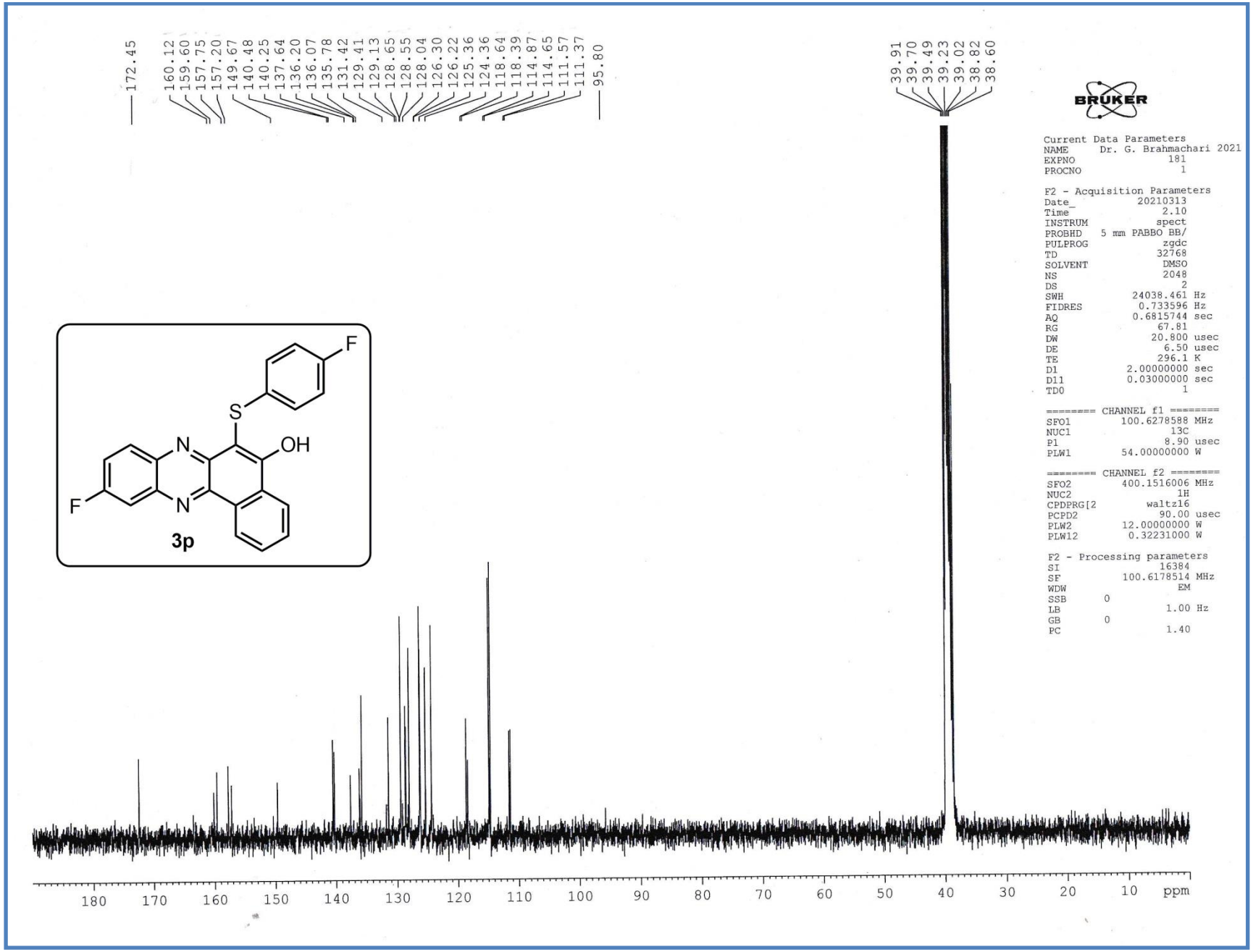


Figure S69. ^{13}C-NMR spectrum of 10-fluoro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3p**)

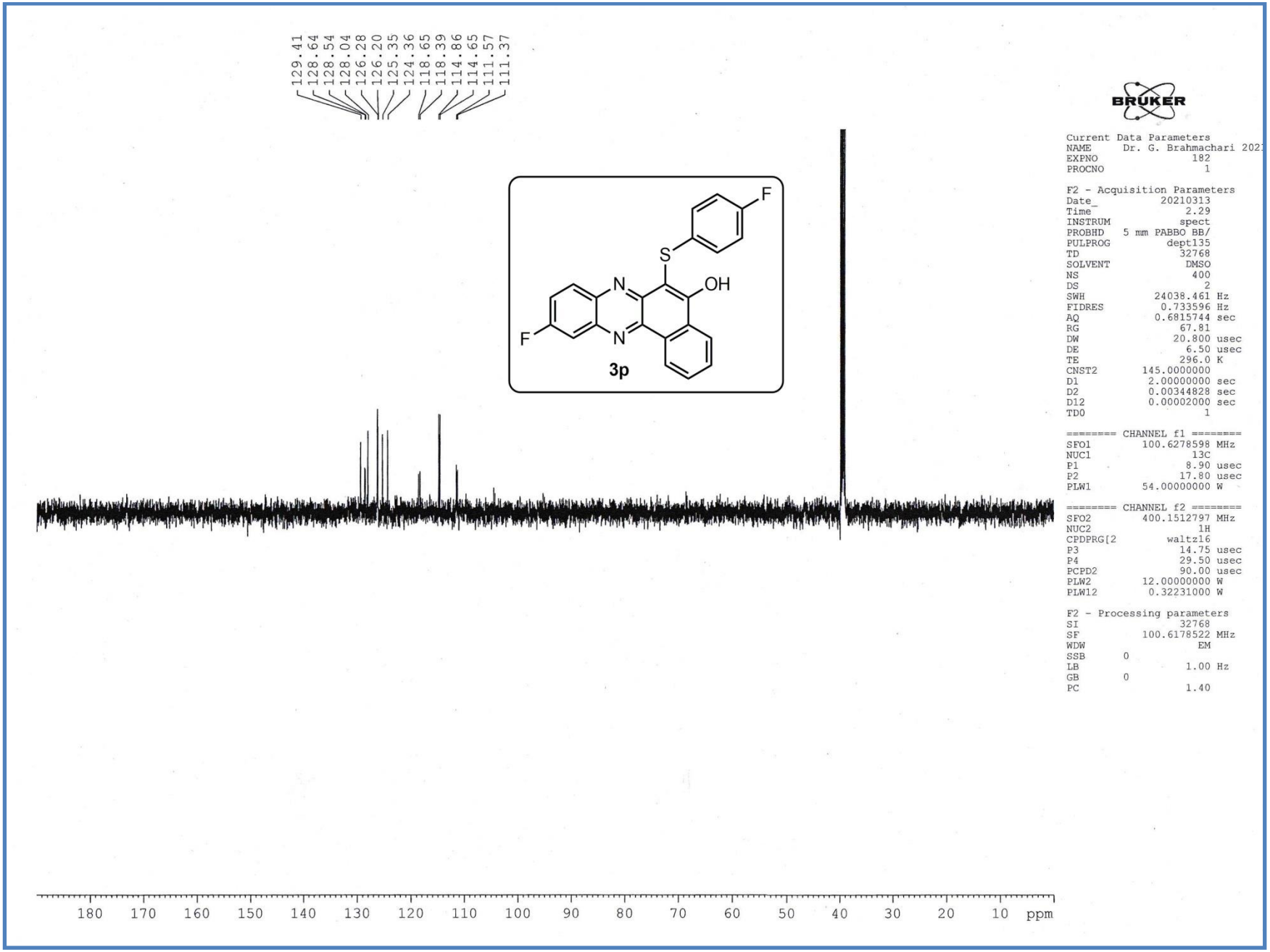


Figure S70. DEPT-135 NMR spectrum of 10-fluoro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3p**)

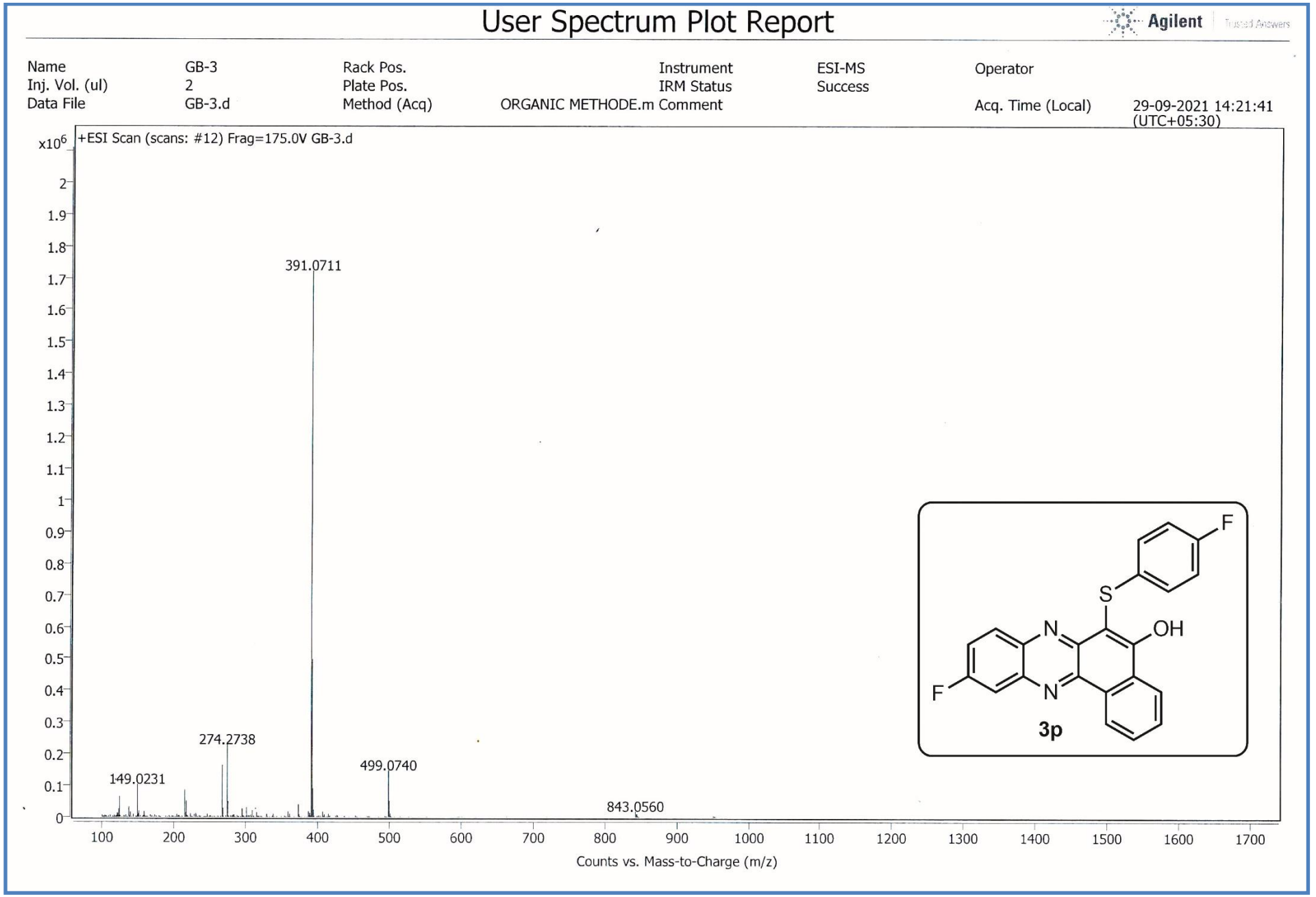


Figure S71. High-resolution Mass spectra of 10-fluoro-6-((4-fluorophenyl)thio)benzo[*a*]phenazin-5-ol (**3p**)

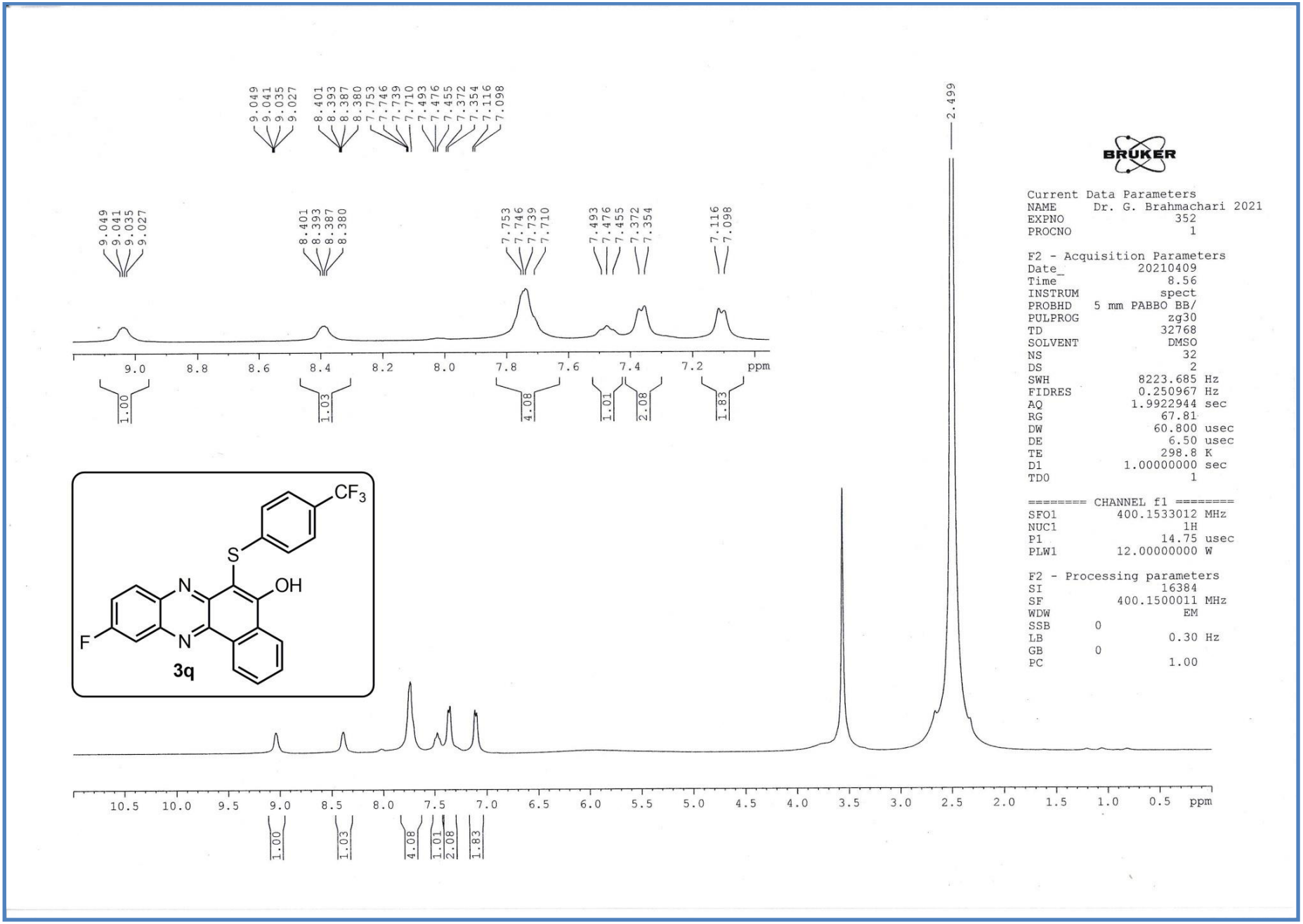


Figure S72. ^{1}H-NMR spectrum of 10-fluoro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3q**)

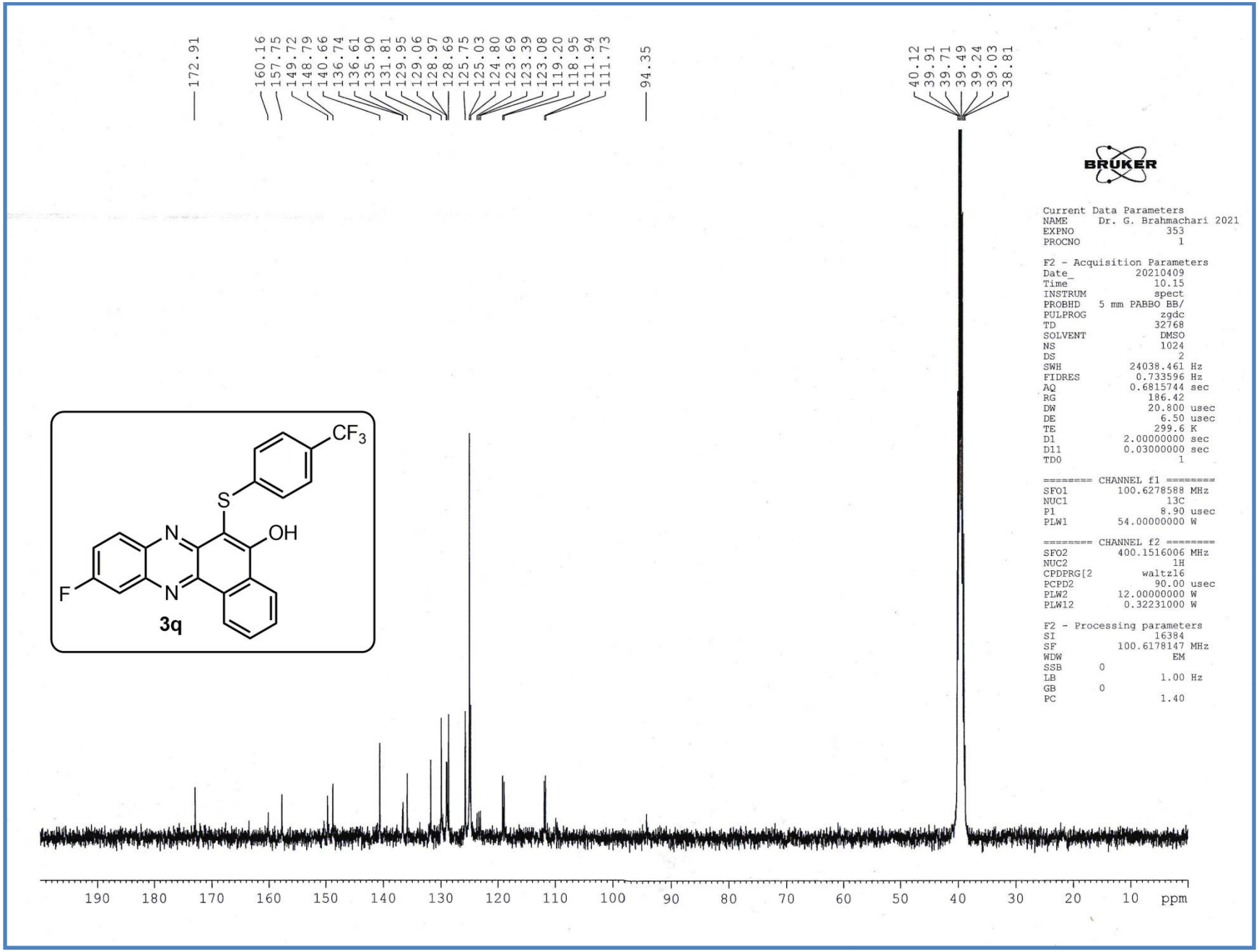


Figure S73. ^{13}C-NMR spectrum of 10-fluoro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3q**)

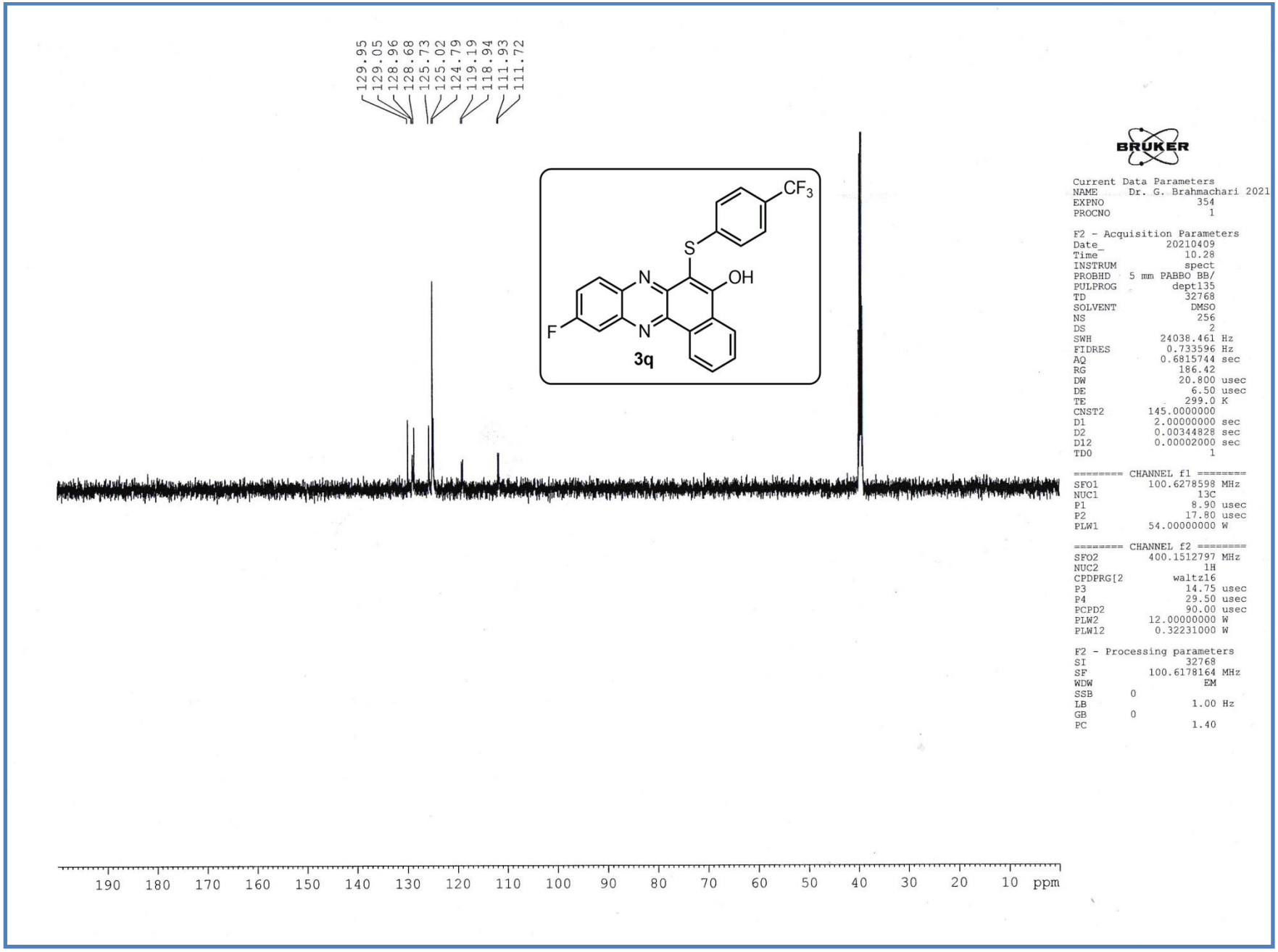


Figure S74. DEPT-135 NMR spectrum of 10-fluoro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3q**)

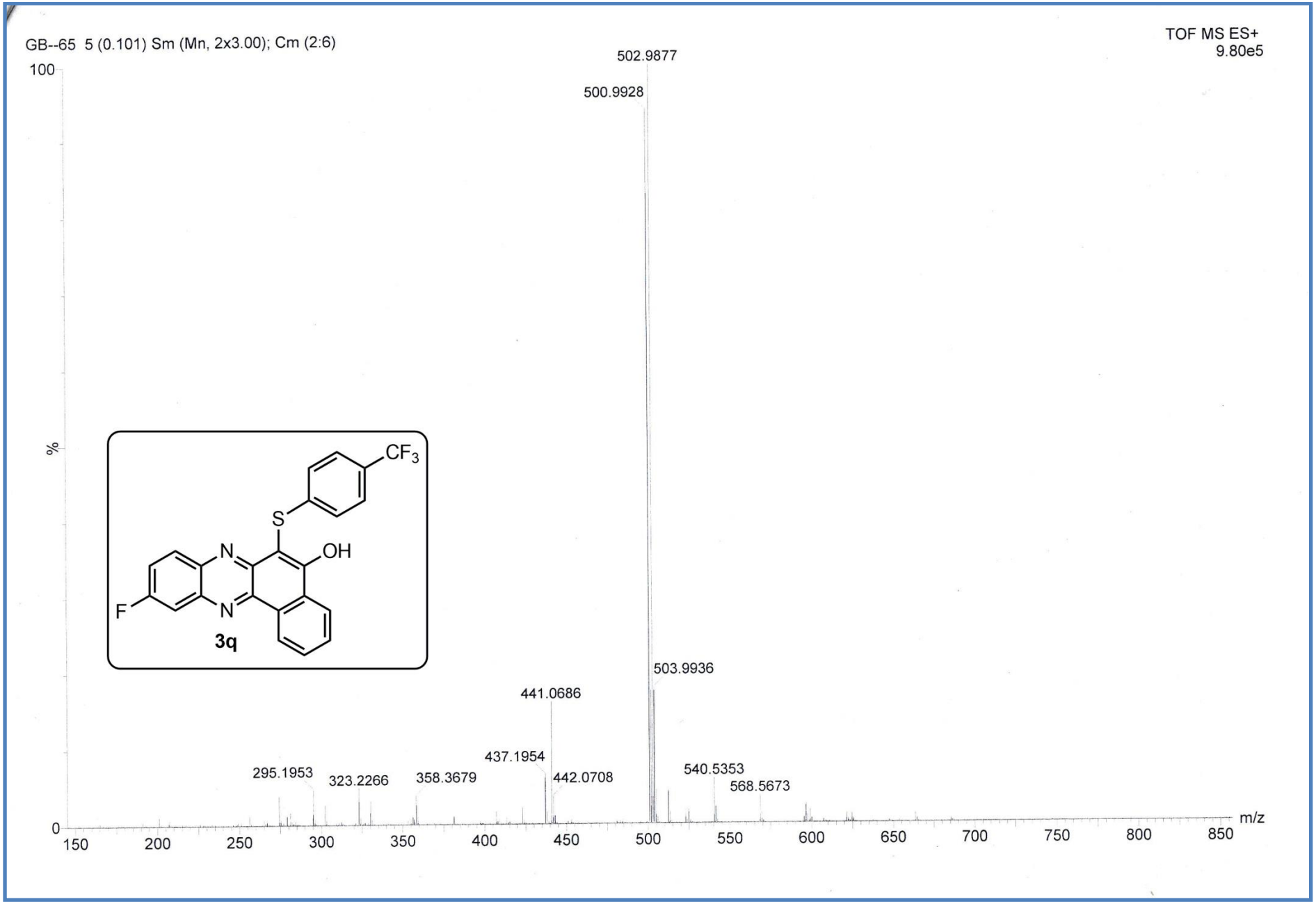


Figure S75. High-resolution Mass spectra of 10-fluoro-6-((4-(trifluoromethyl)phenyl)thio)benzo[*a*]phenazin-5-ol (**3q**)

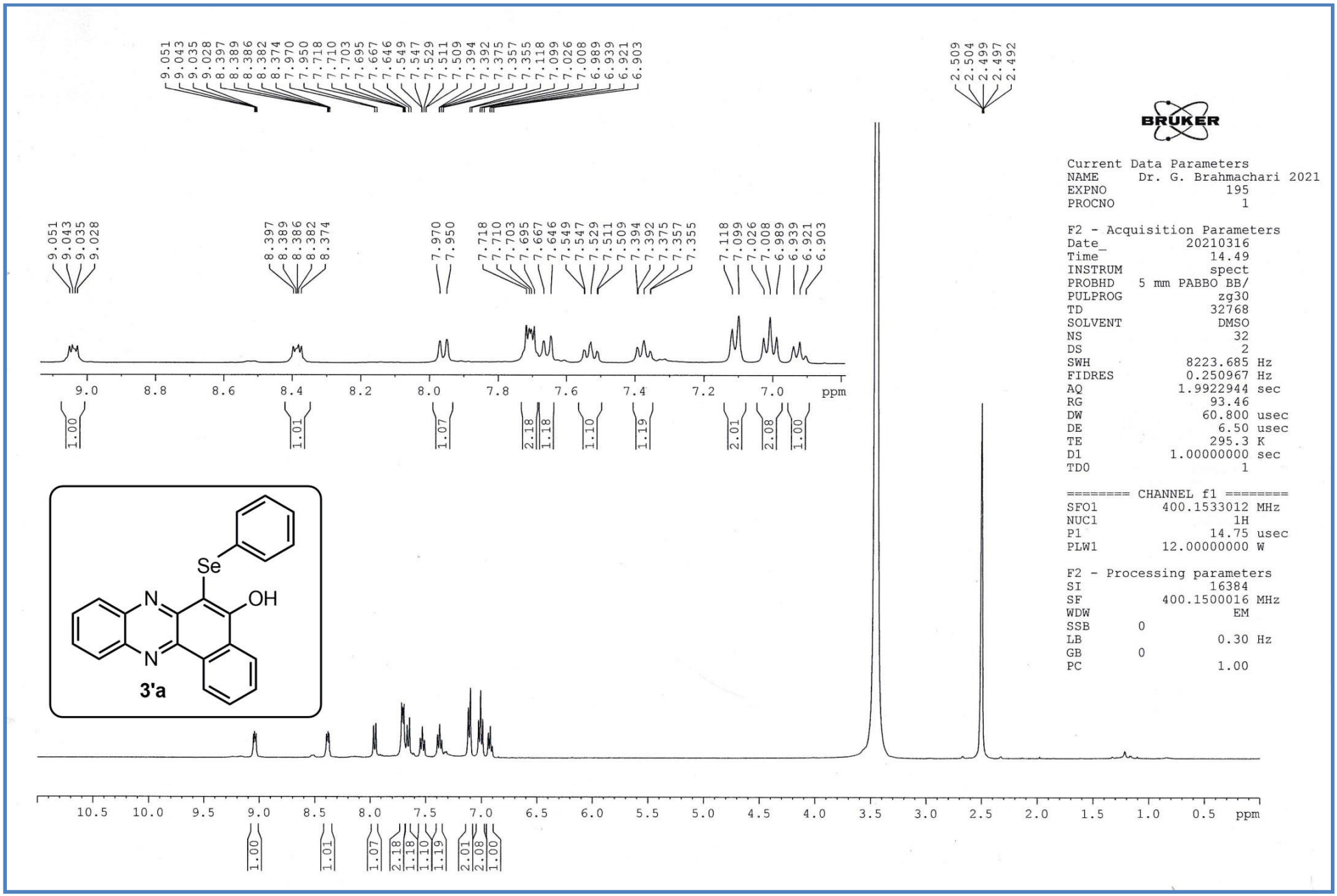


Figure S76. ^{1}H-NMR spectrum of 6-(Phenylselanyl)benzo[*a*]phenazin-5-ol (**3′a**)

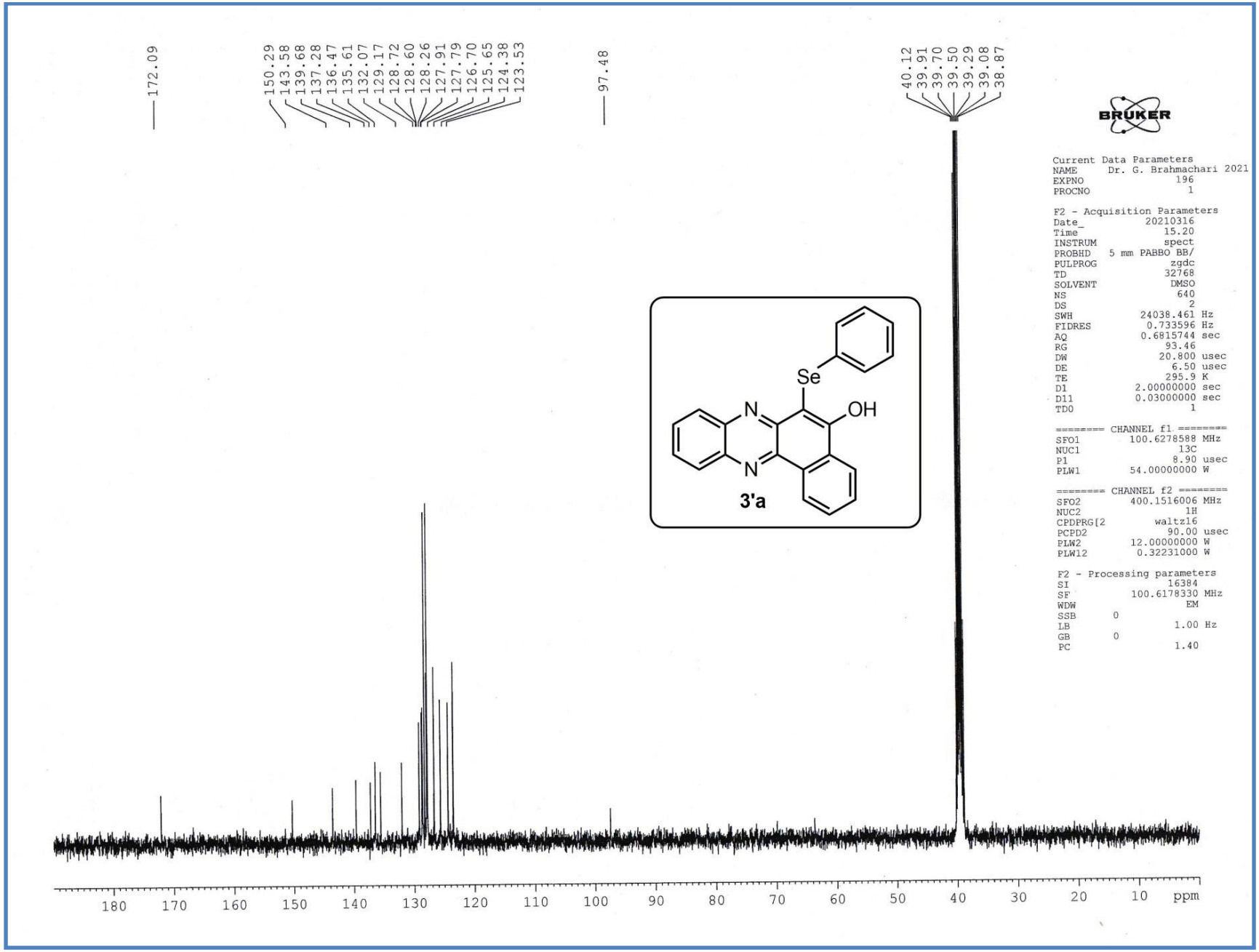


Figure S77. ^{13}C-NMR spectrum of 6-(Phenylselanyl)benzo[*a*]phenazin-5-ol (**3′a**)

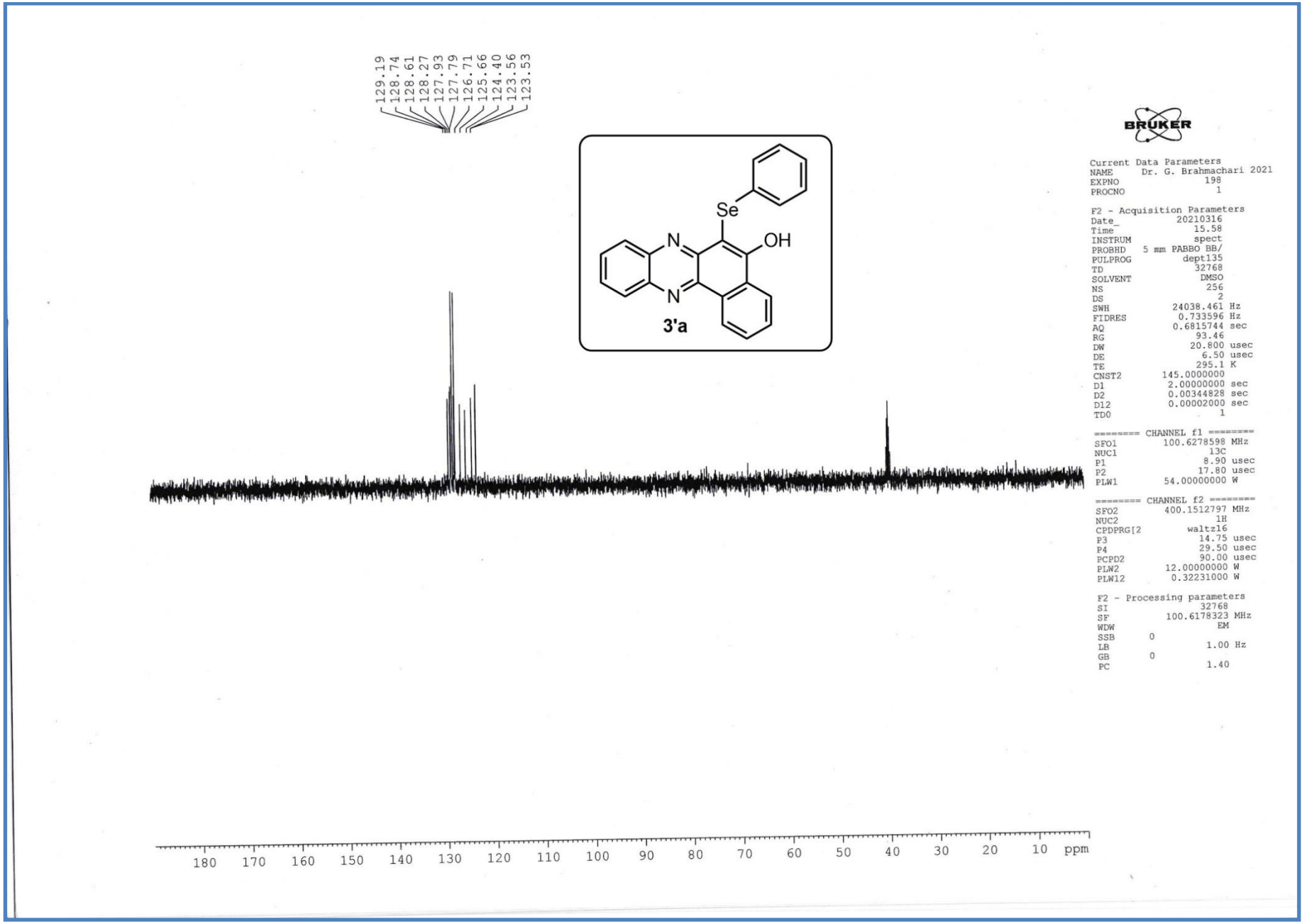


Figure S78. DEPT-135 NMR spectrum of 6-(Phenylselanyl)benzo[*a*]phenazin-5-ol (**3'a**)

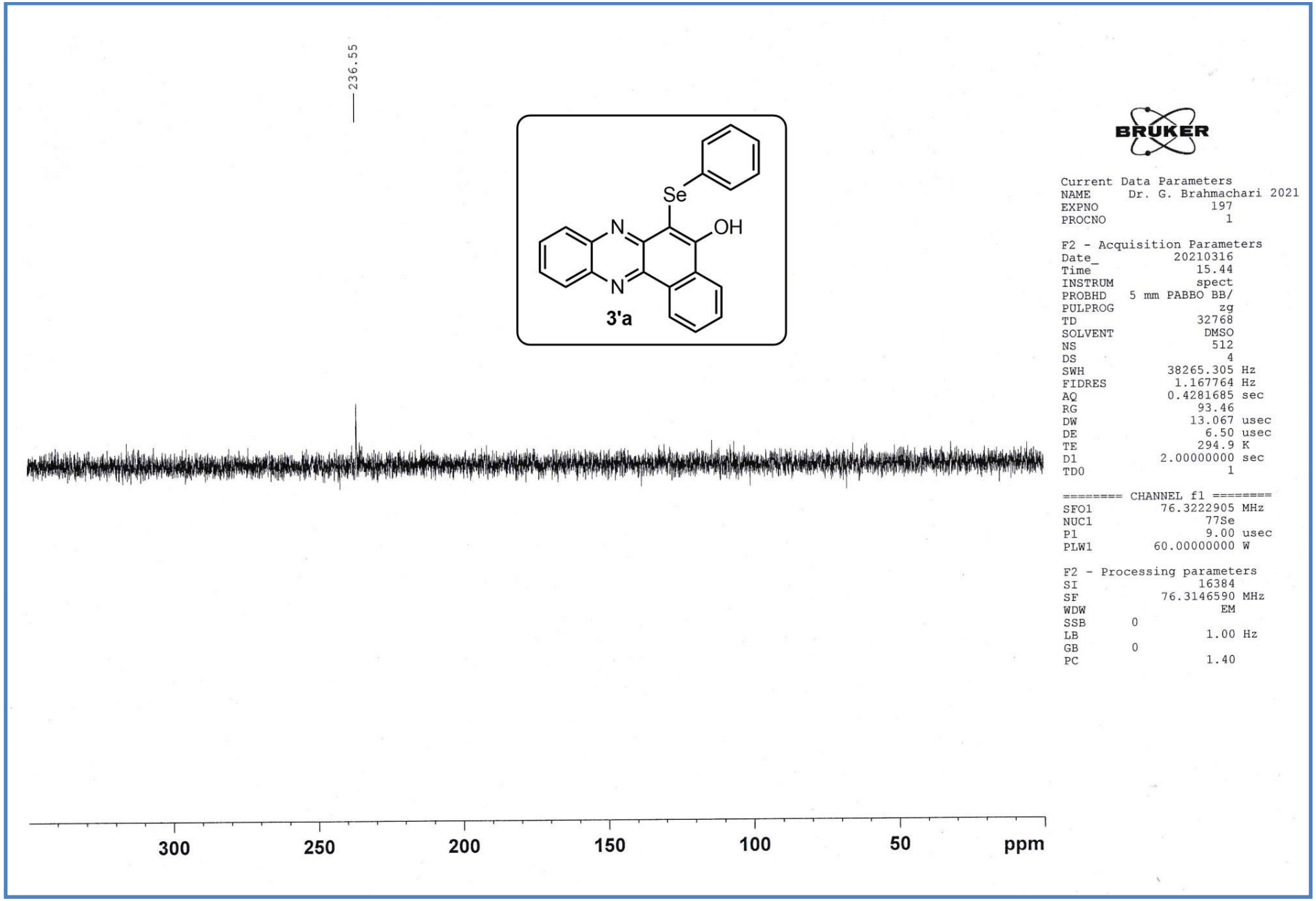


Figure S79. ^{77}Se-NMR spectrum of 6-(Phenylselanyl)benzo[*a*]phenazin-5-ol (**3′a**)

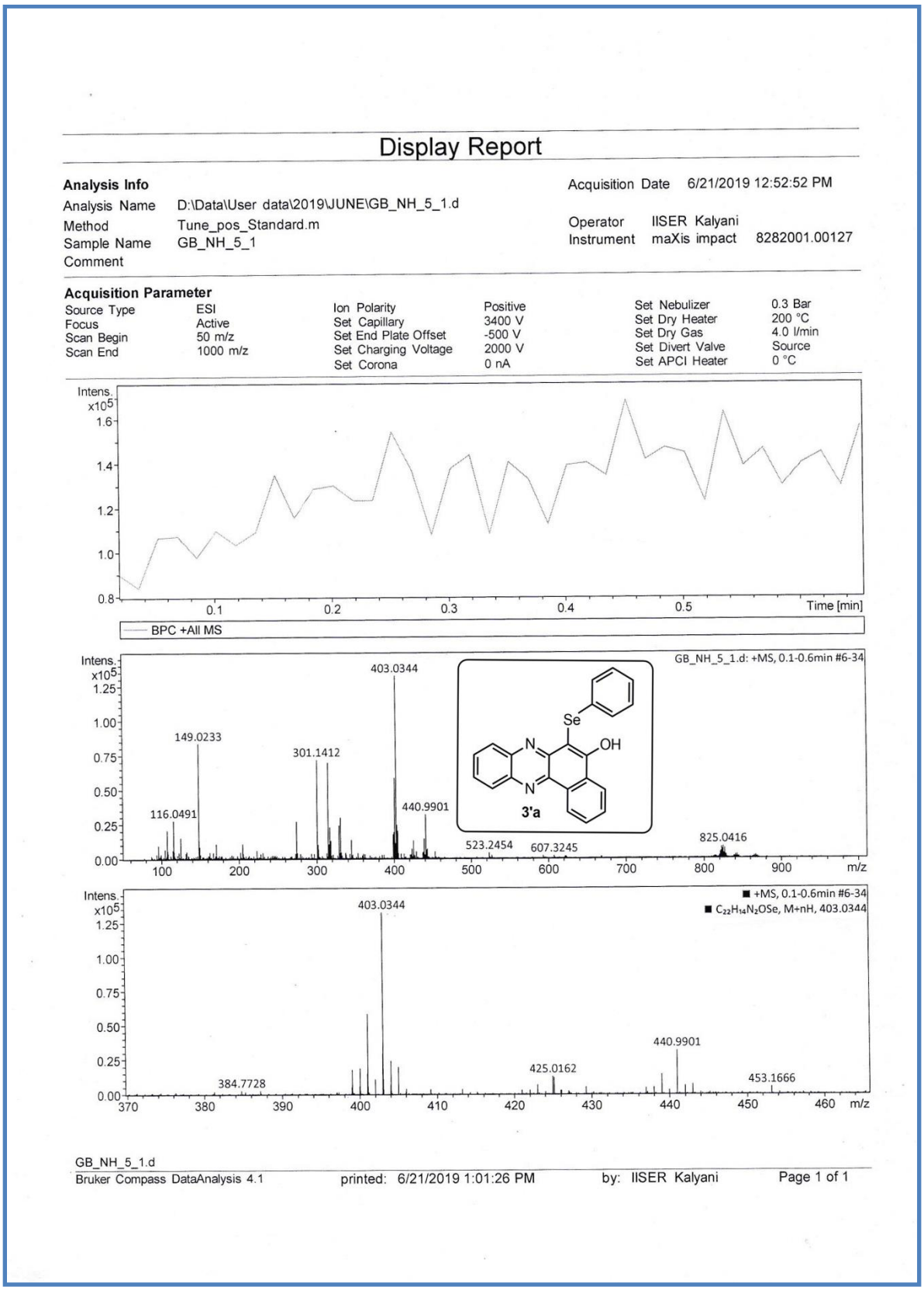


Figure S80. High-resolution Mass spectra of 6-(Phenylselanyl)benzo[*a*]phenazin-5-ol (**3′a**)

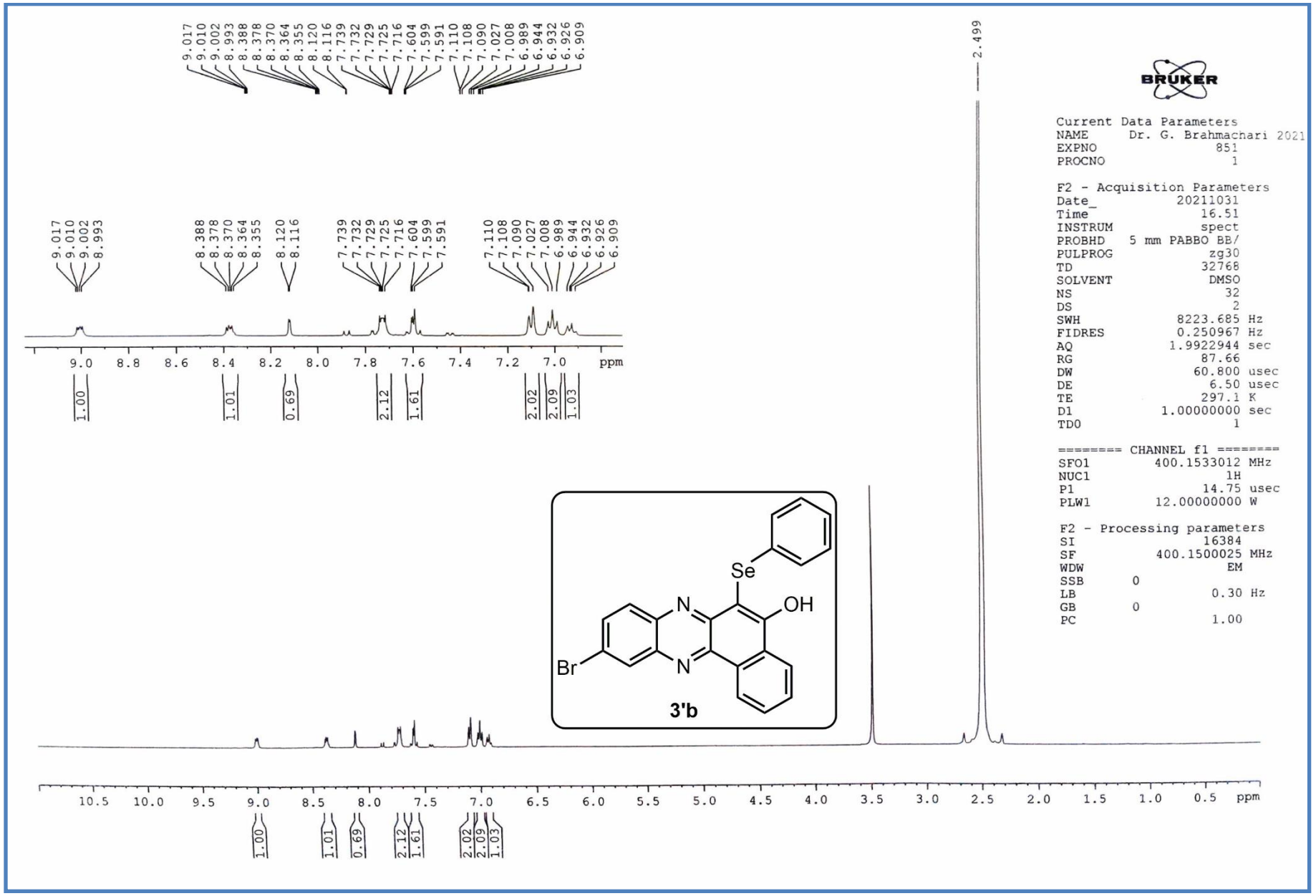


Figure S81. [1]H-NMR spectrum of 10-bromo-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′b**)

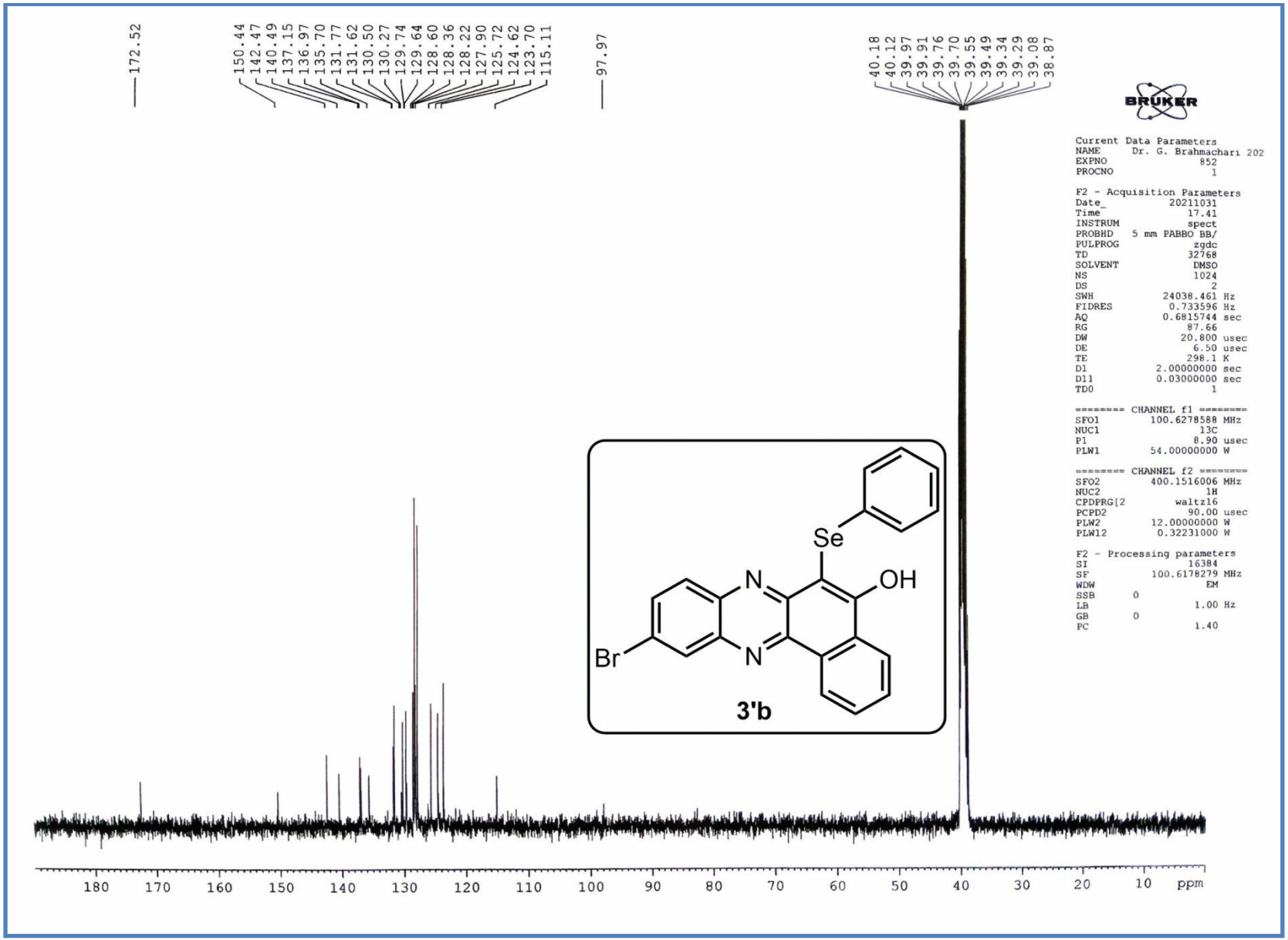


Figure S82. ^{13}C-NMR spectrum of 10-bromo-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'b**)

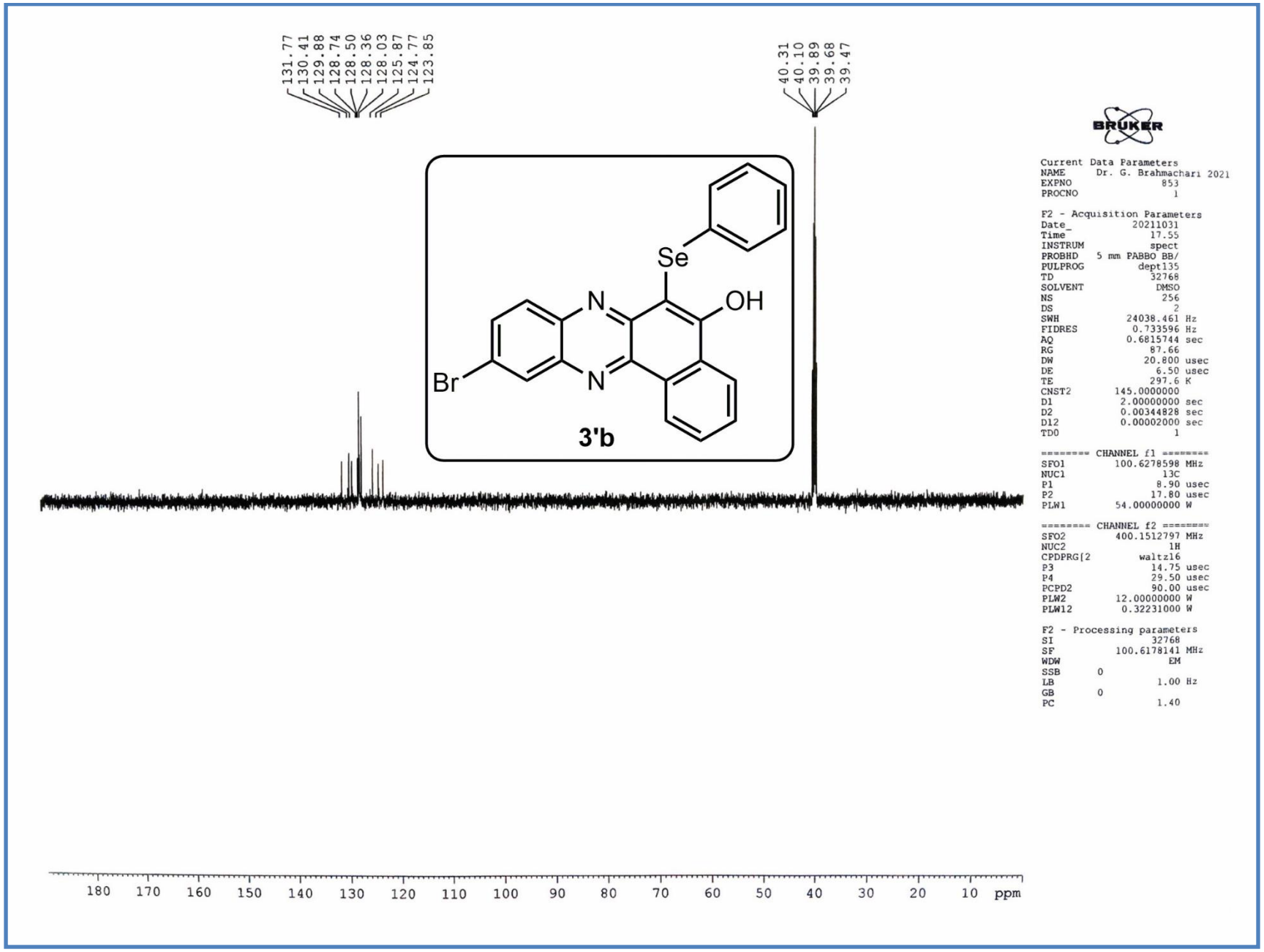


Figure S83. DEPT-135 NMR spectrum of 10-bromo-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'b**)

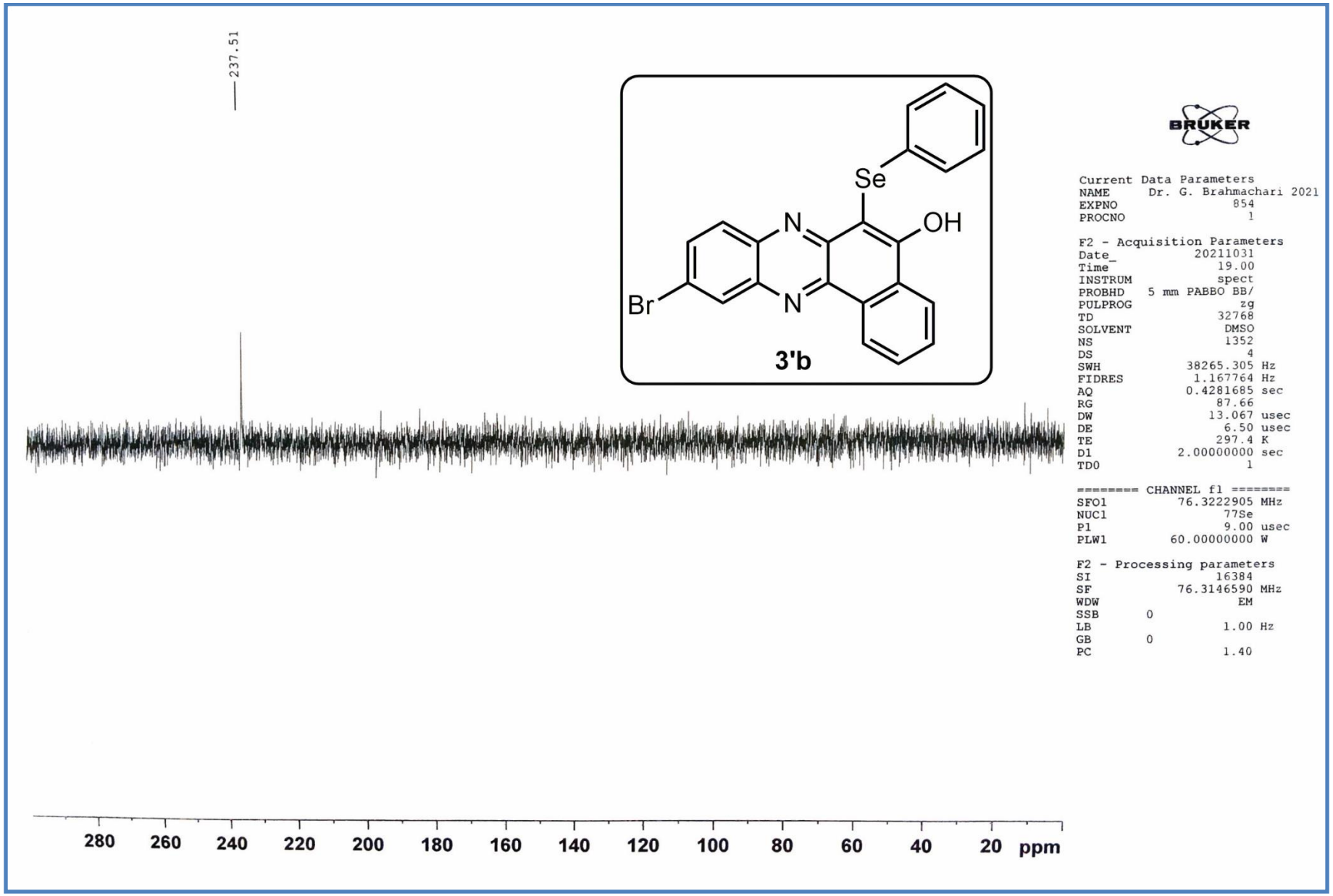


Figure S84. ^{77}Se NMR spectrum of 10-bromo-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'b**)

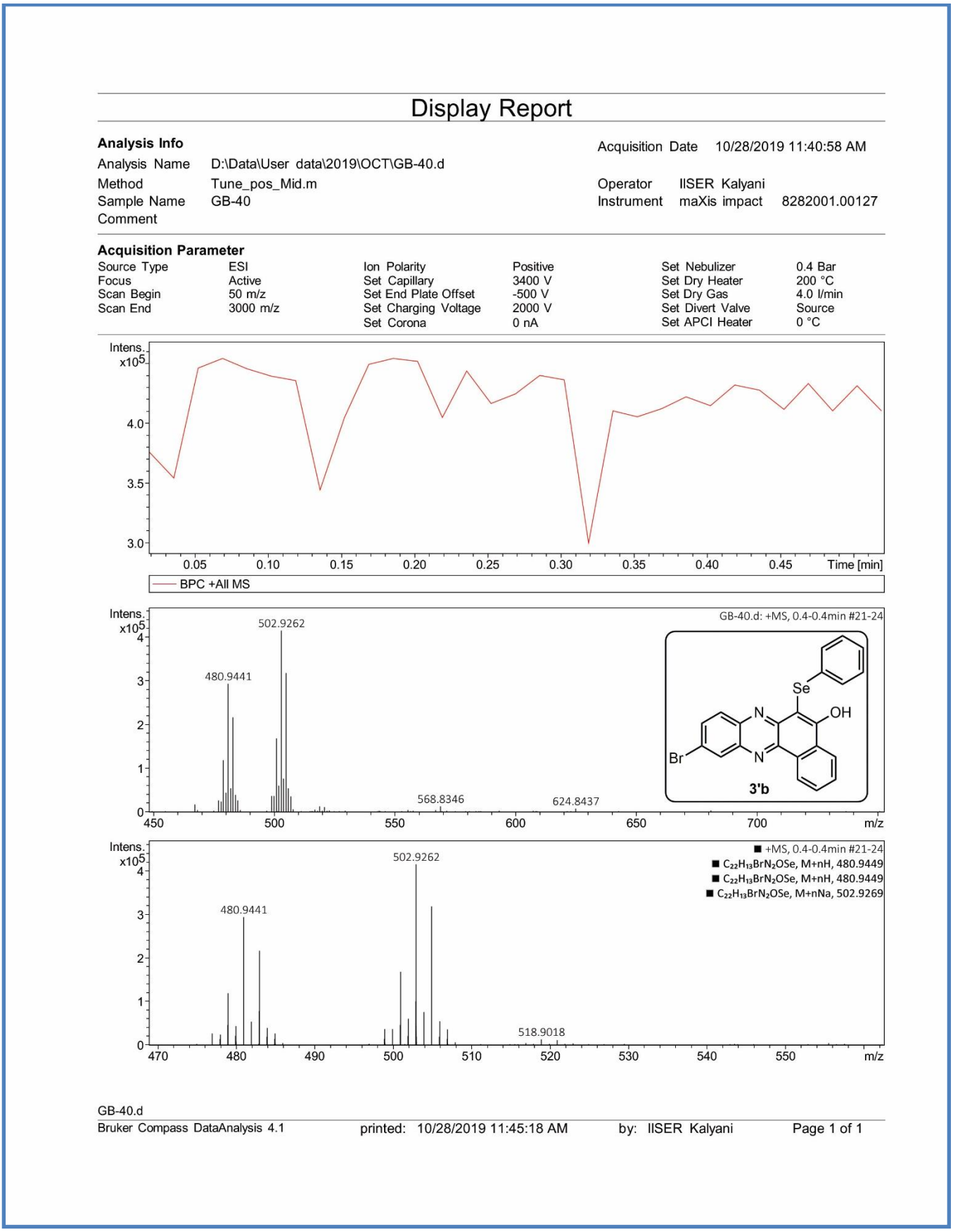


Figure S85. HRMS NMR spectrum of 10-bromo-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'b**)

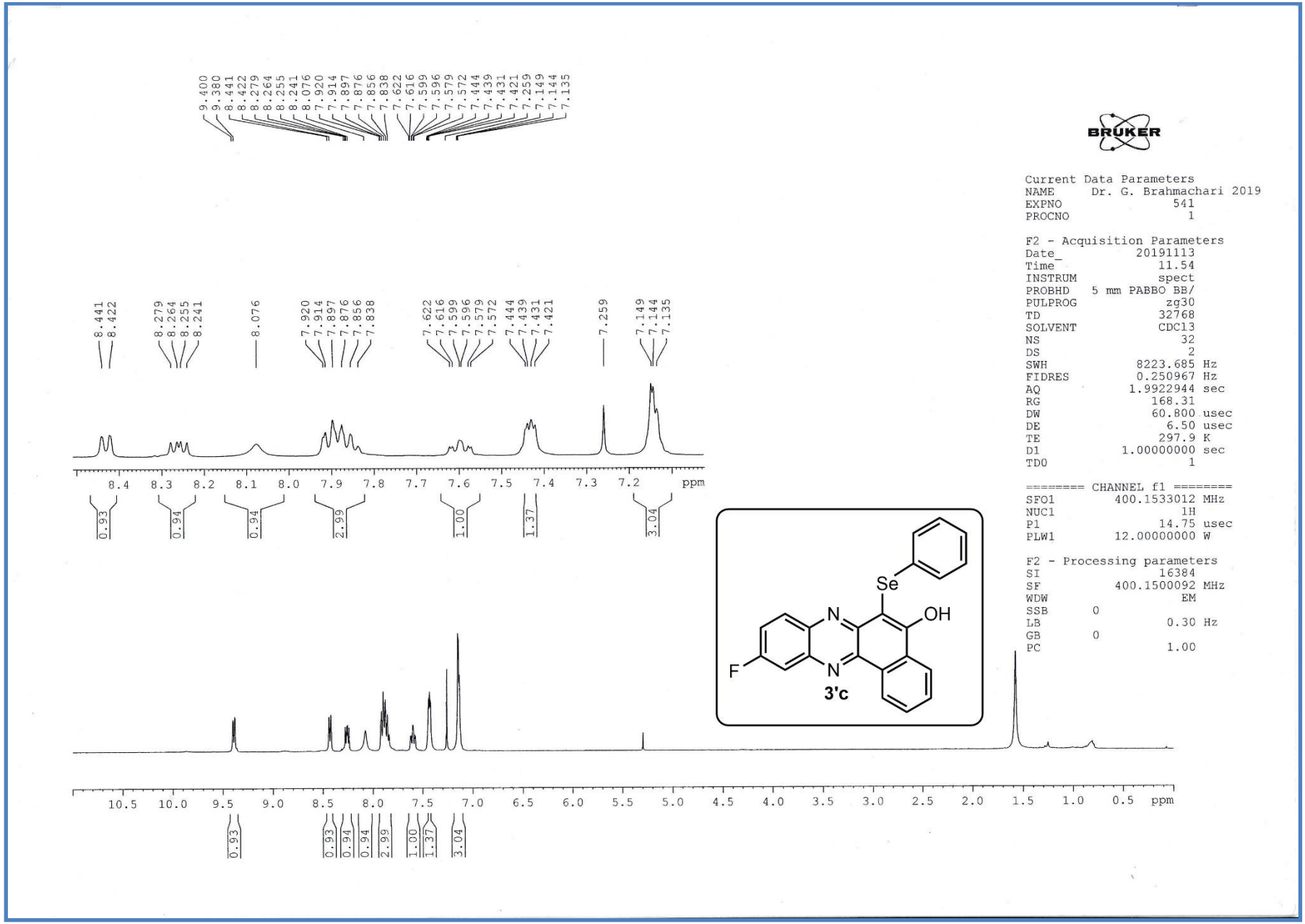


Figure S86. ^{1}H-NMR spectrum of 10-fluoro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'c**)

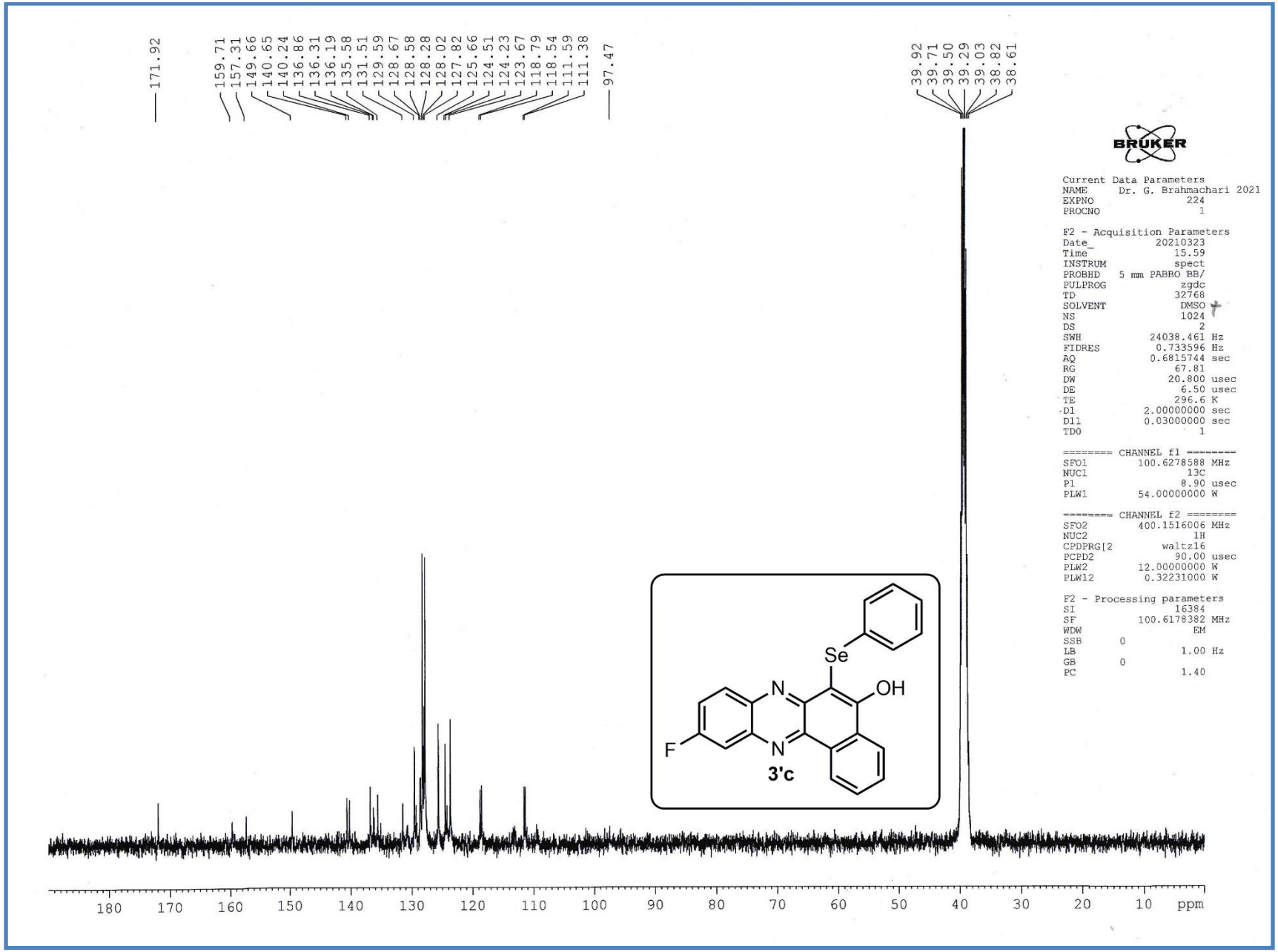


Figure S87. ^{13}C-NMR spectrum of 10-fluoro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′c**)

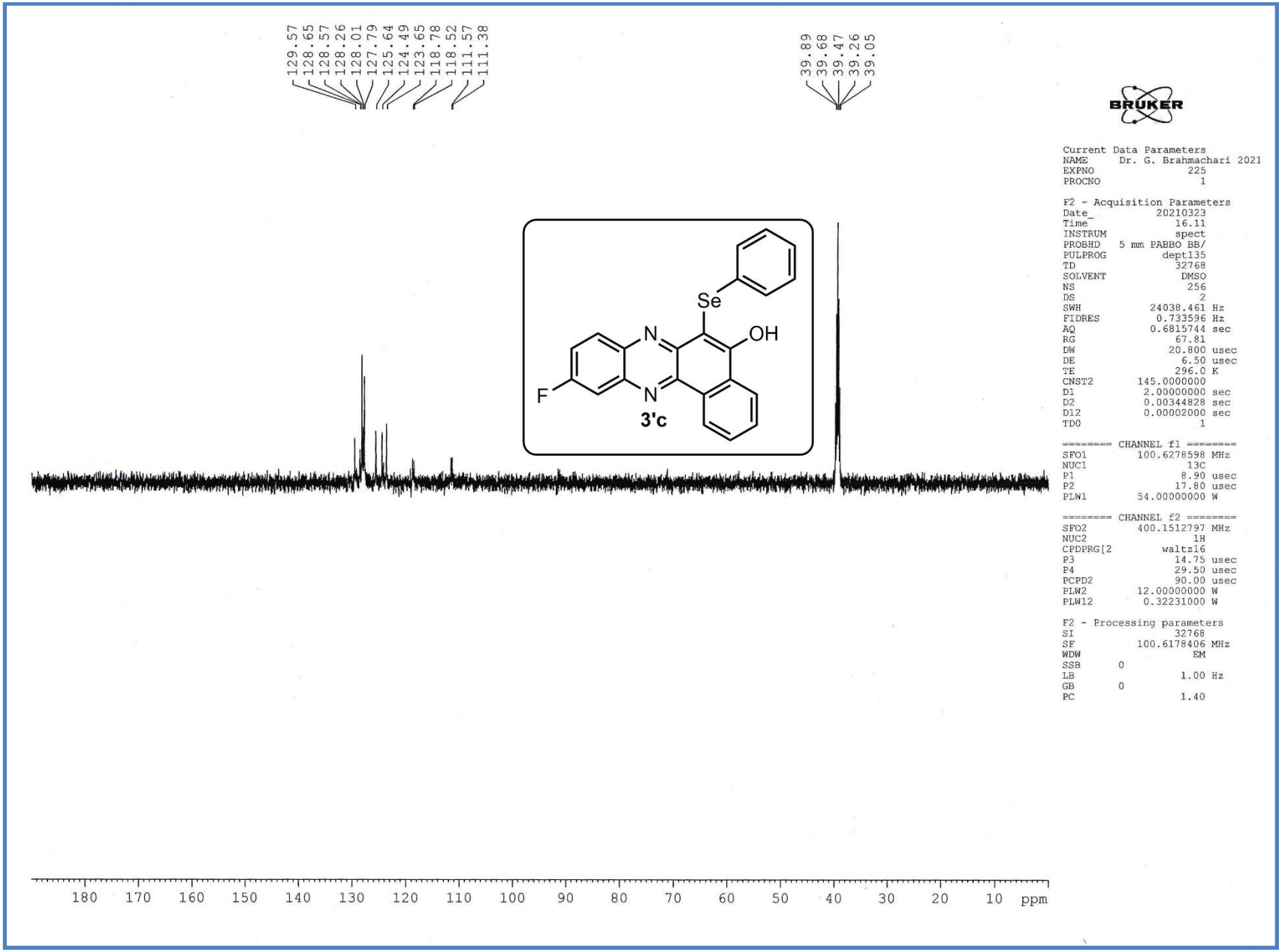


Figure S88. DEPT-135 NMR spectrum of 10-fluoro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'c**)

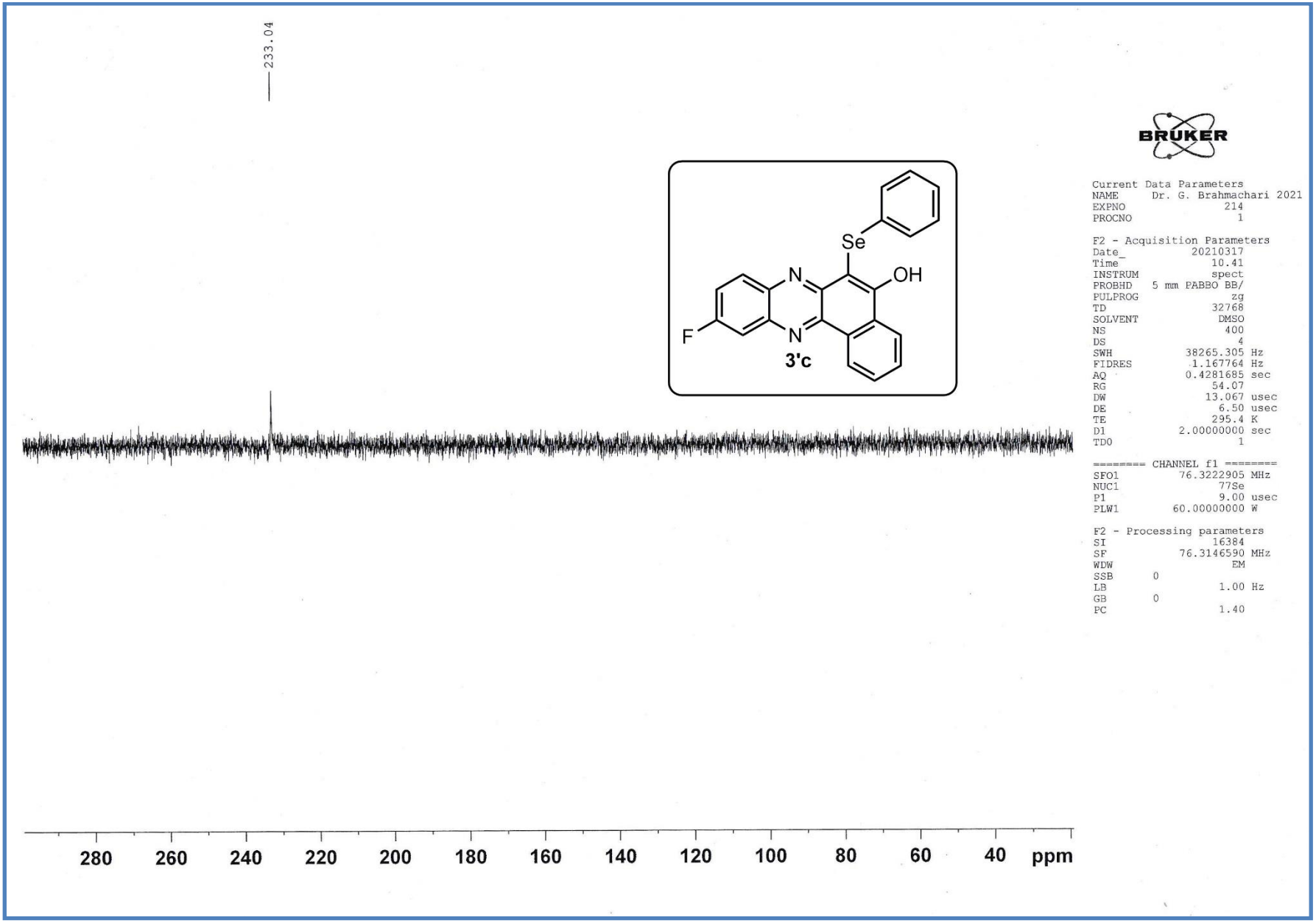


Figure S89. ^{77}Se-NMR spectrum of 10-fluoro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′c**)

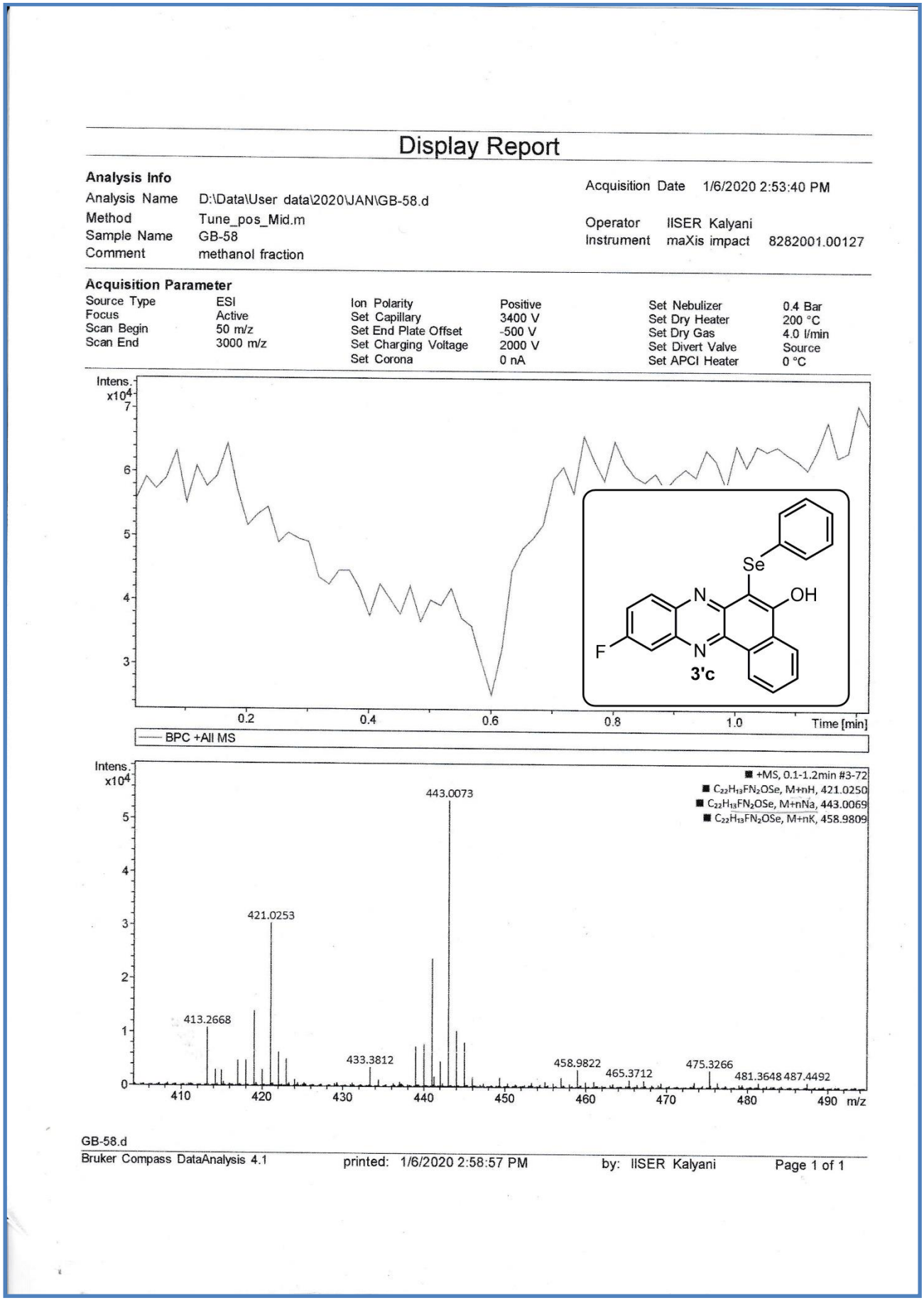


Figure S90. High-resolution Mass spectra of 10-fluoro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'c**)

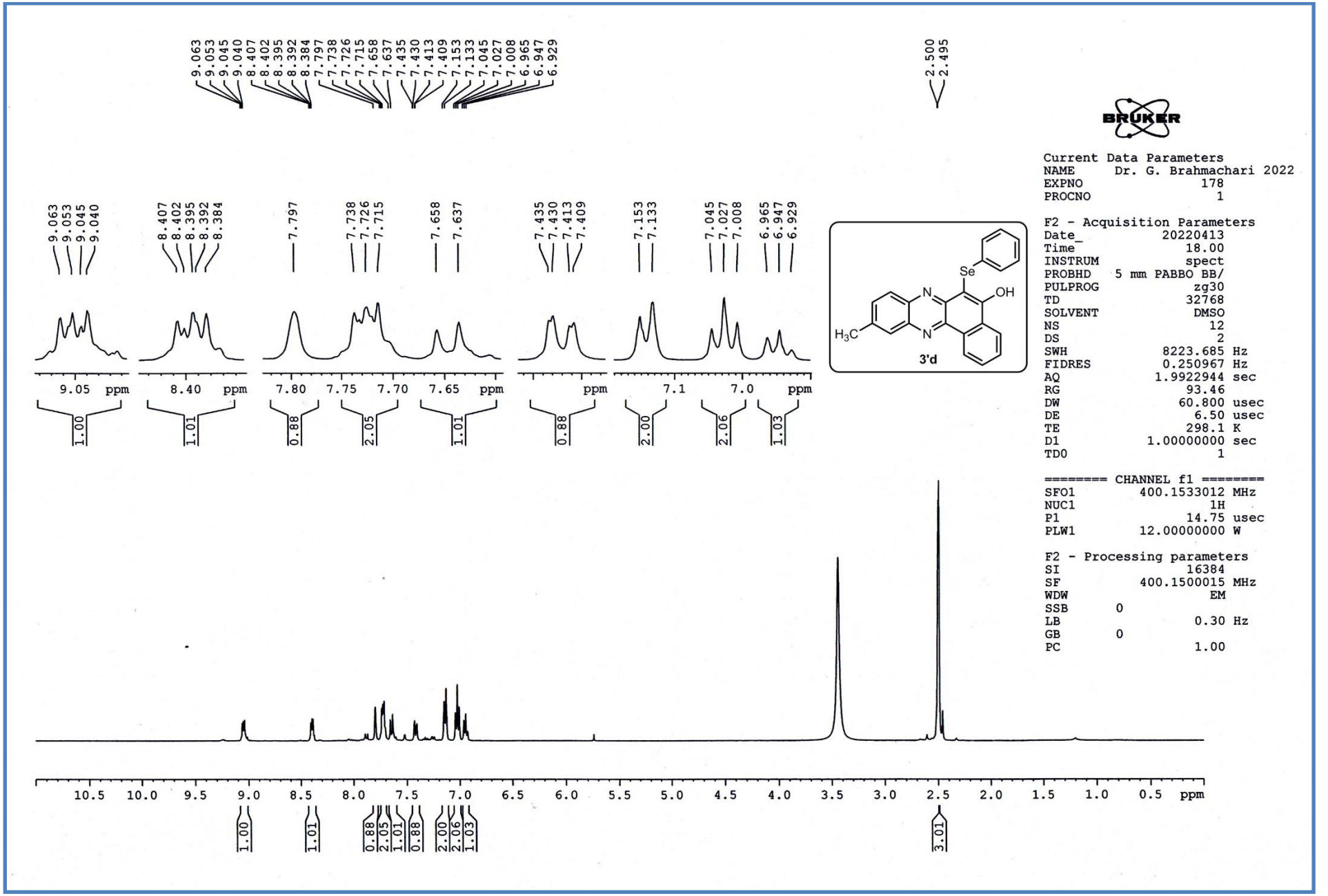


Figure S91. [1]H-NMR spectrum of 10-methyl-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′d**)

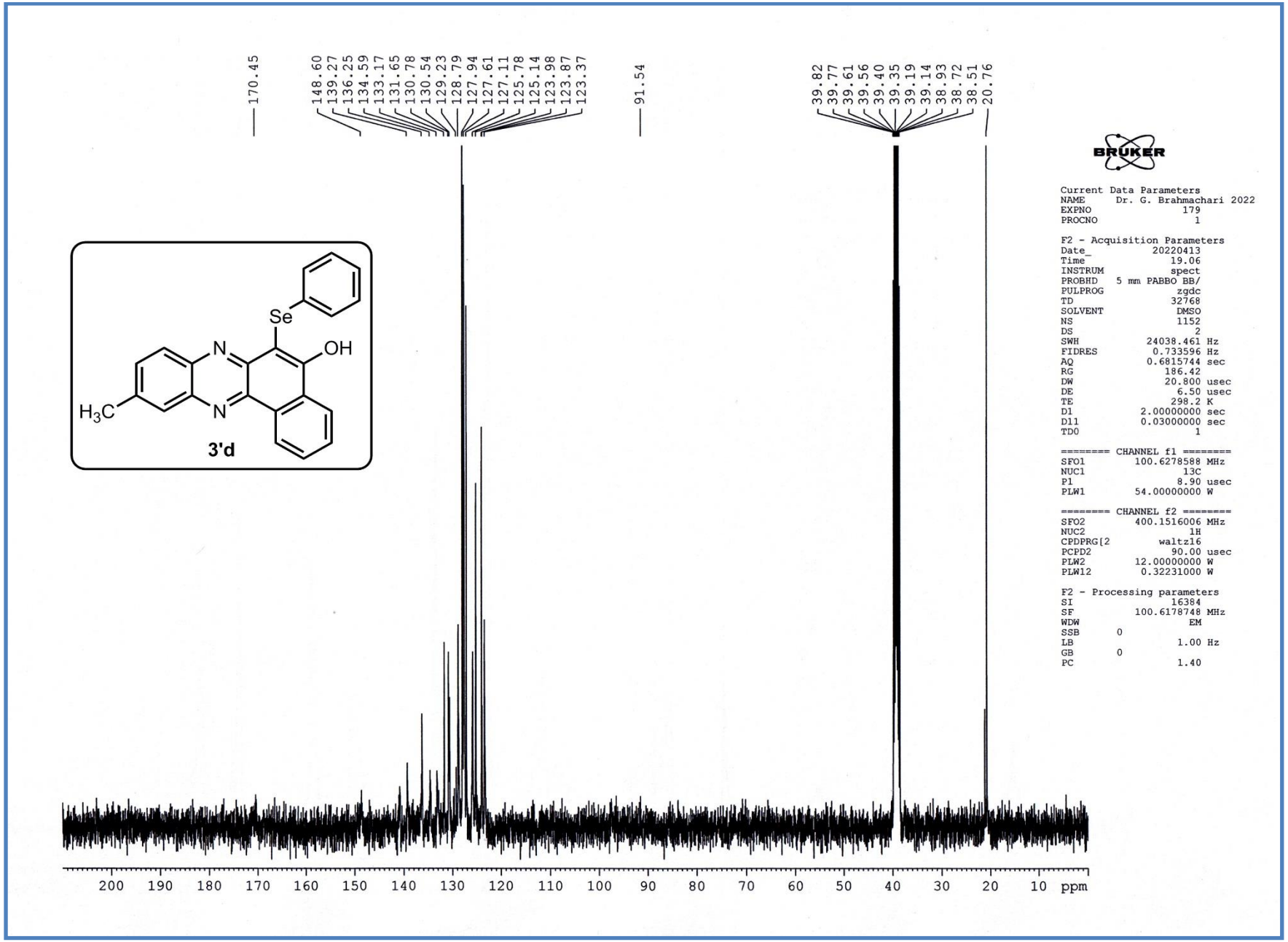


Figure S92. ^{13}C-NMR spectrum of 10-methyl-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'd**)

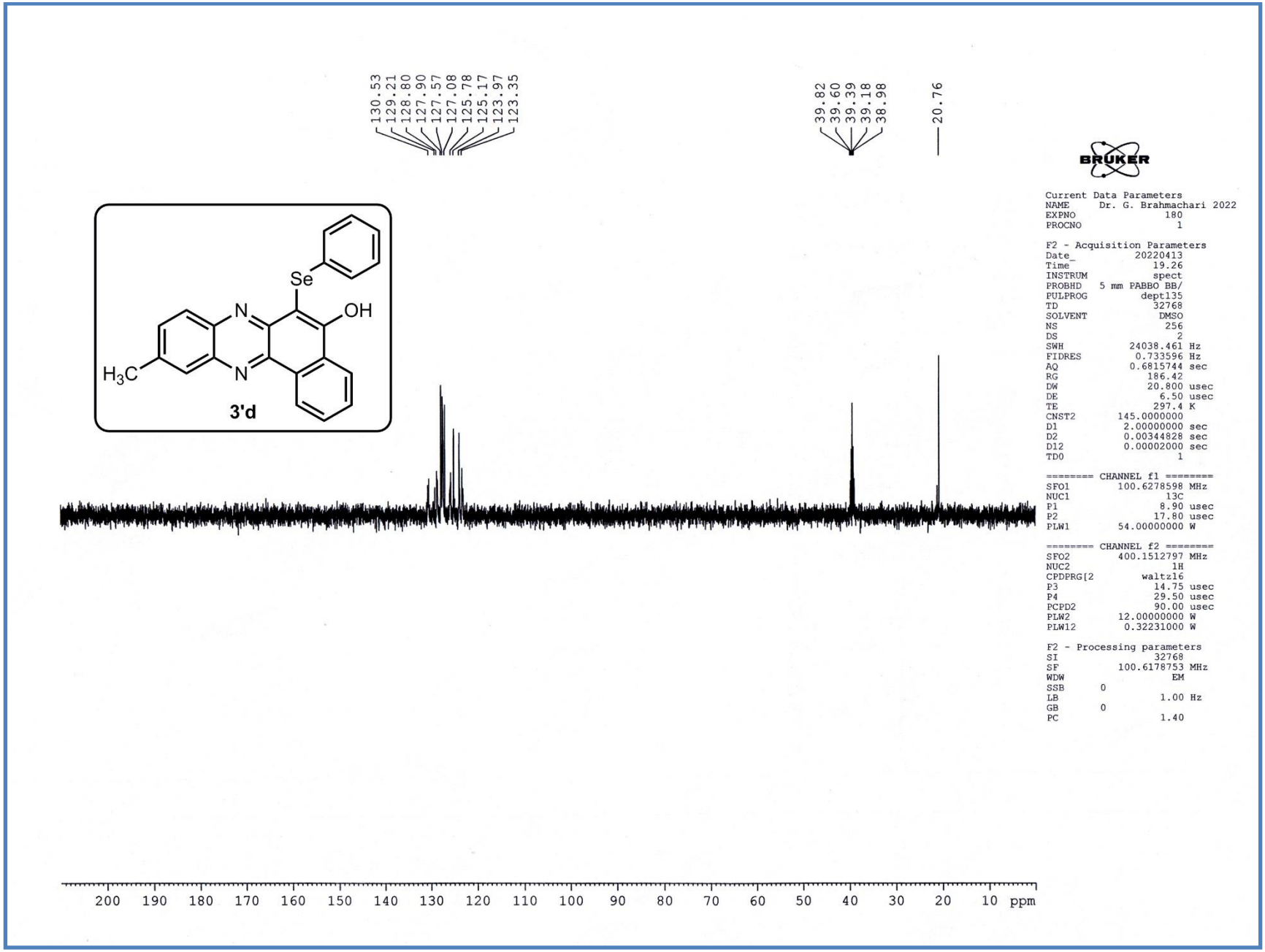


Figure S93. DEPT-135 NMR spectrum of 10-methyl-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′d**)

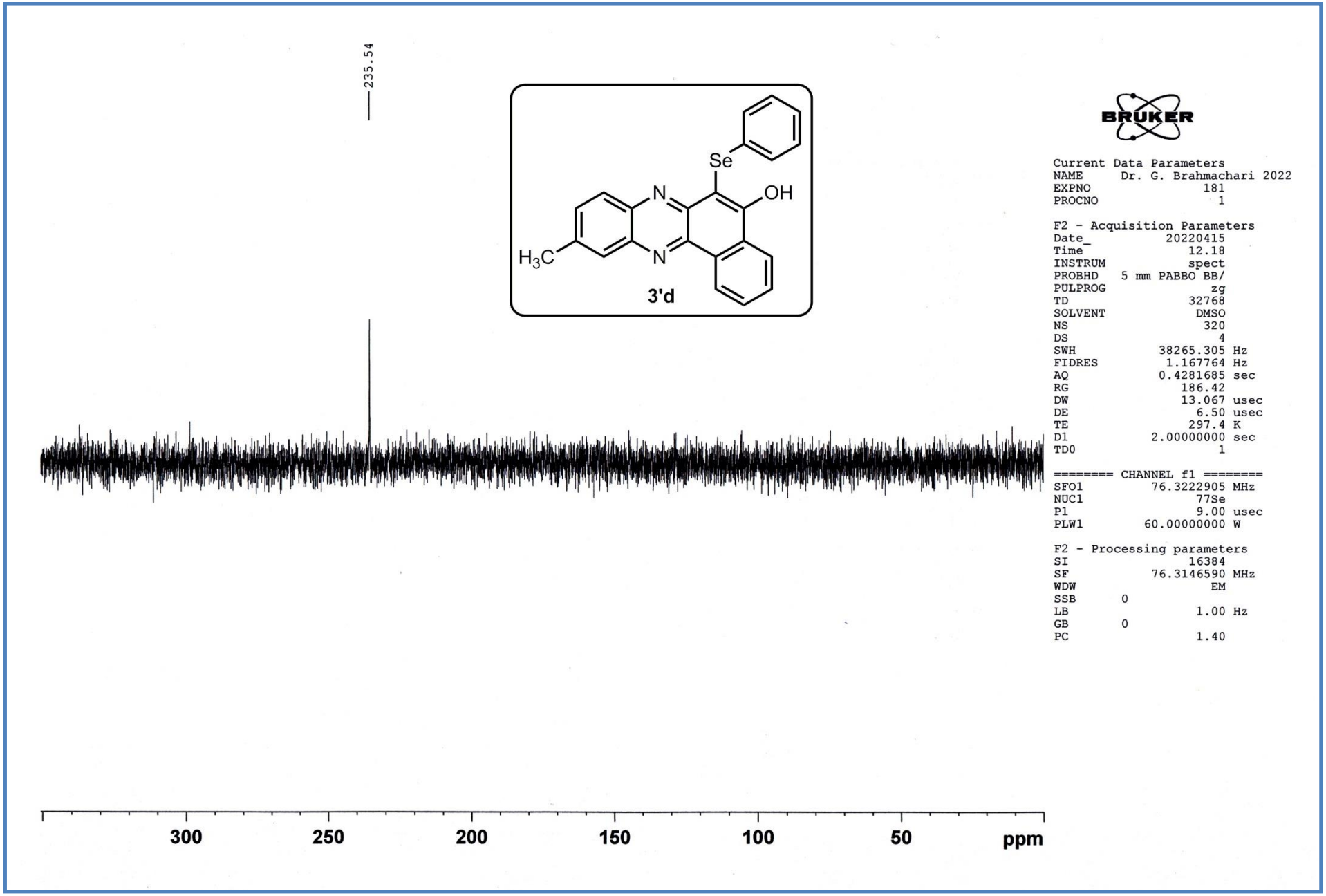


Figure S94. ^{77}Se-NMR spectrum of 10-methyl-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'd**)

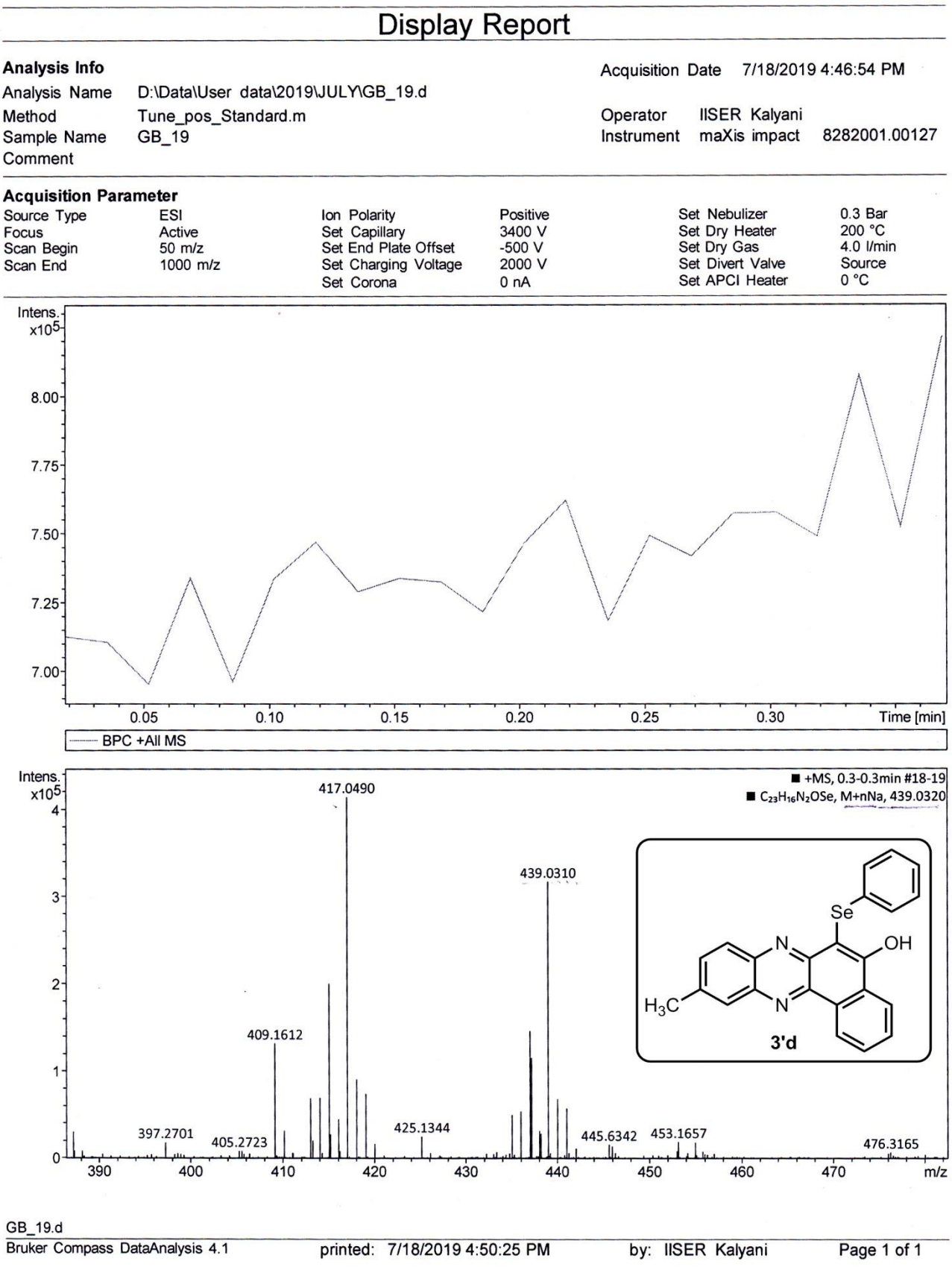


Figure S95. High-resolution Mass spectra of 10-methyl-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'd**)

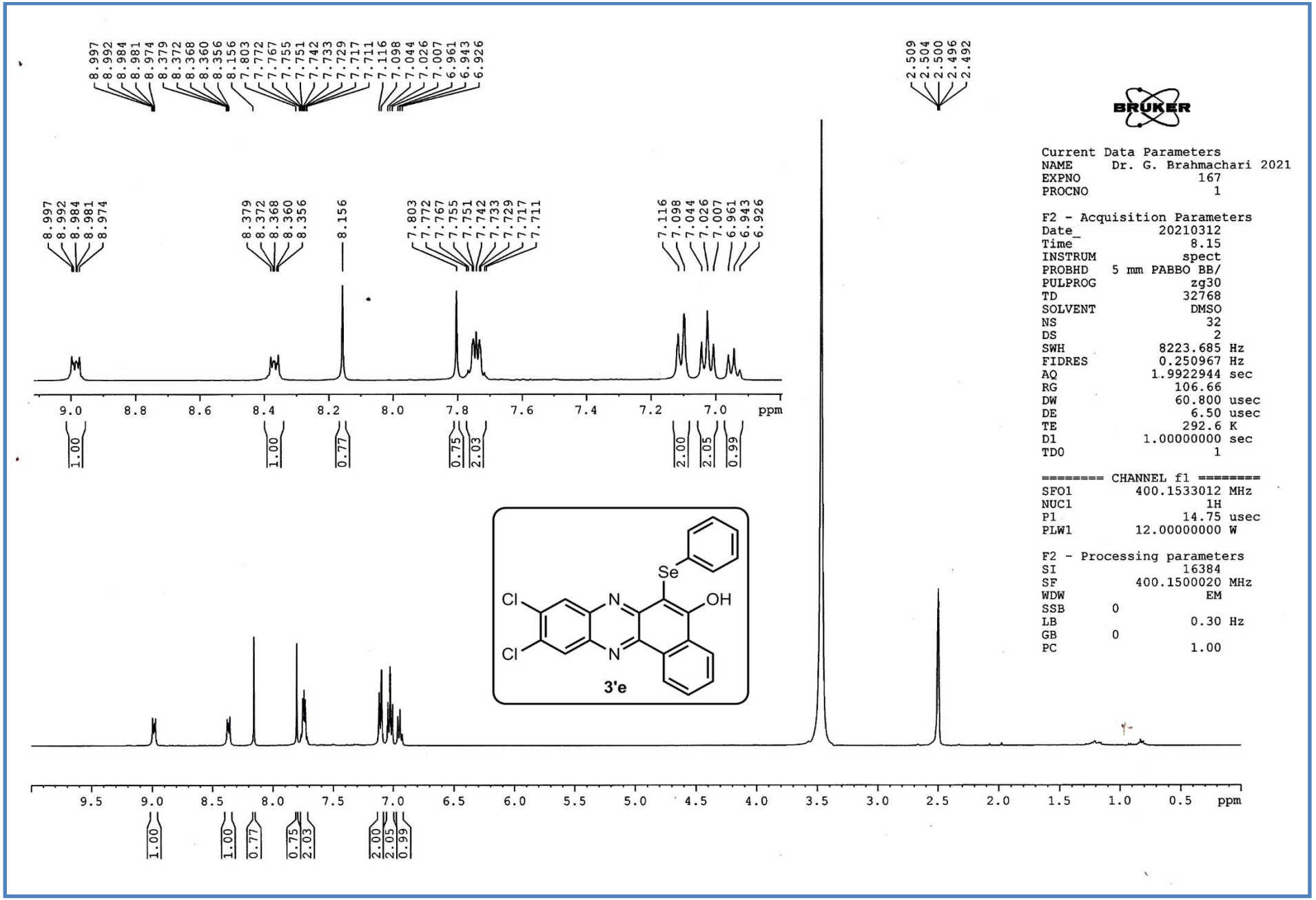


Figure S96. ^{1}H-NMR spectrum of 9,10-dichloro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′e**)

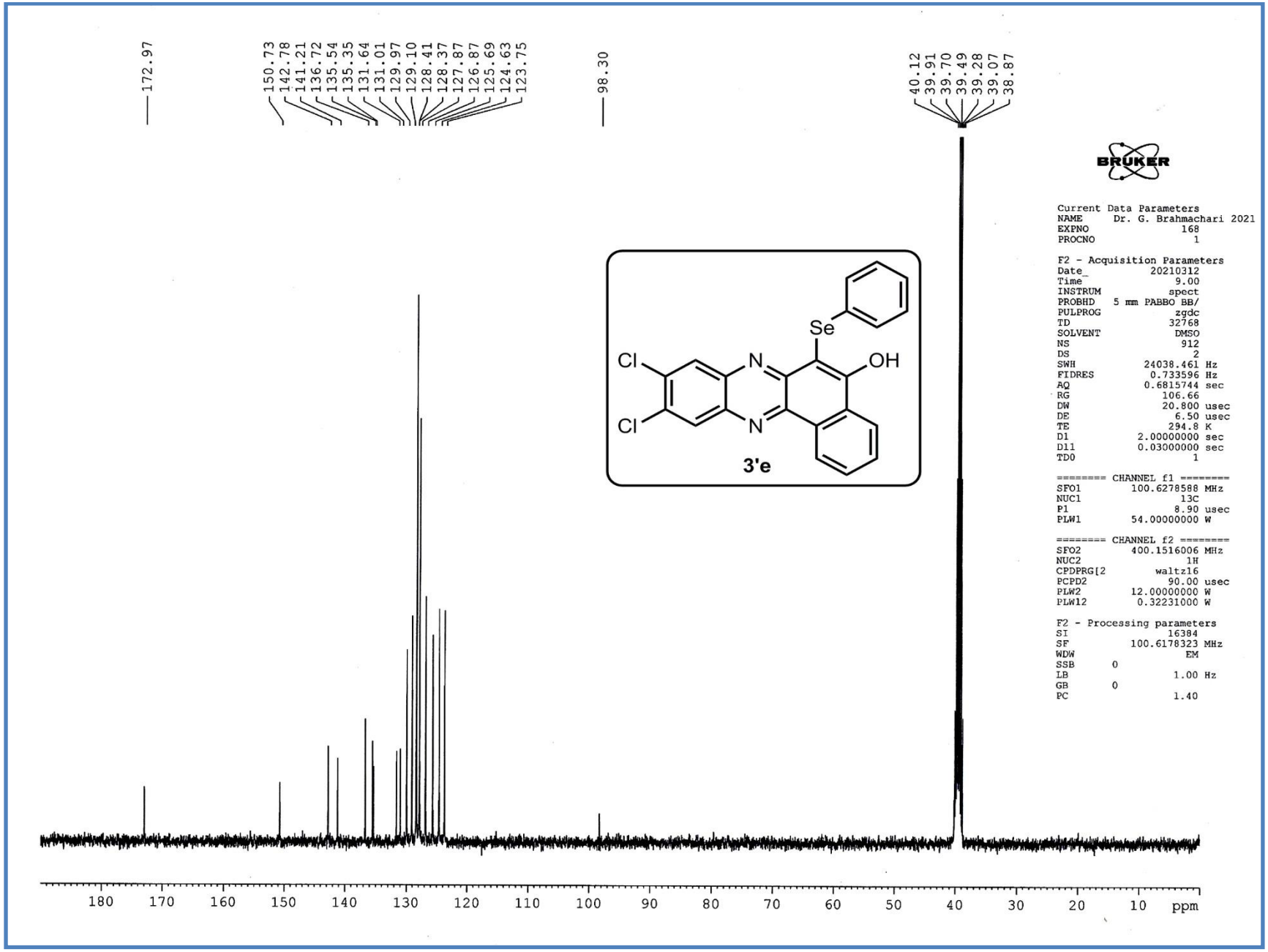


Figure S97. ^{13}C-NMR spectrum of 9,10-dichloro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'e**)

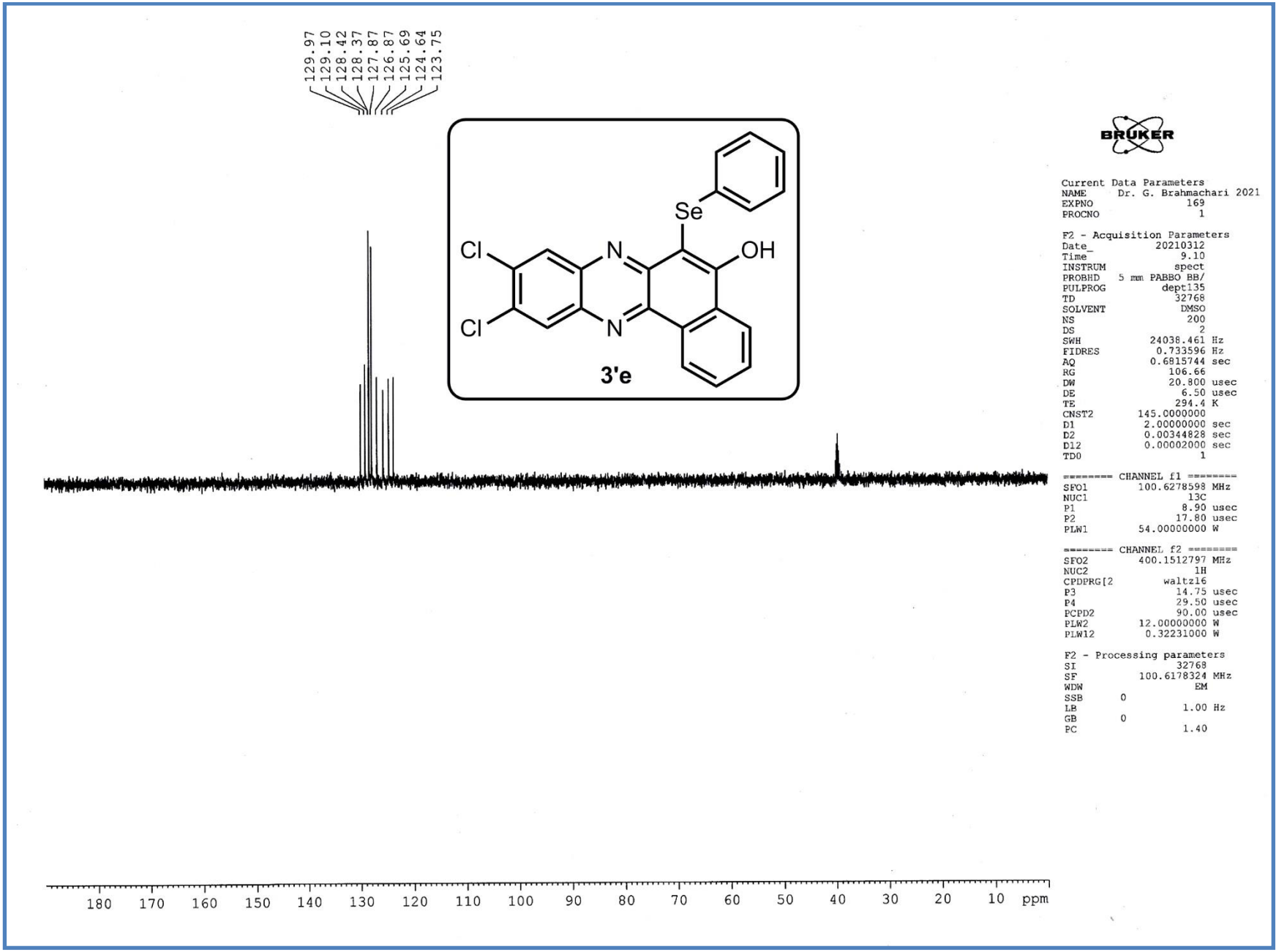


Figure S98. DEPT-135 NMR spectrum of 9,10-dichloro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′e**)

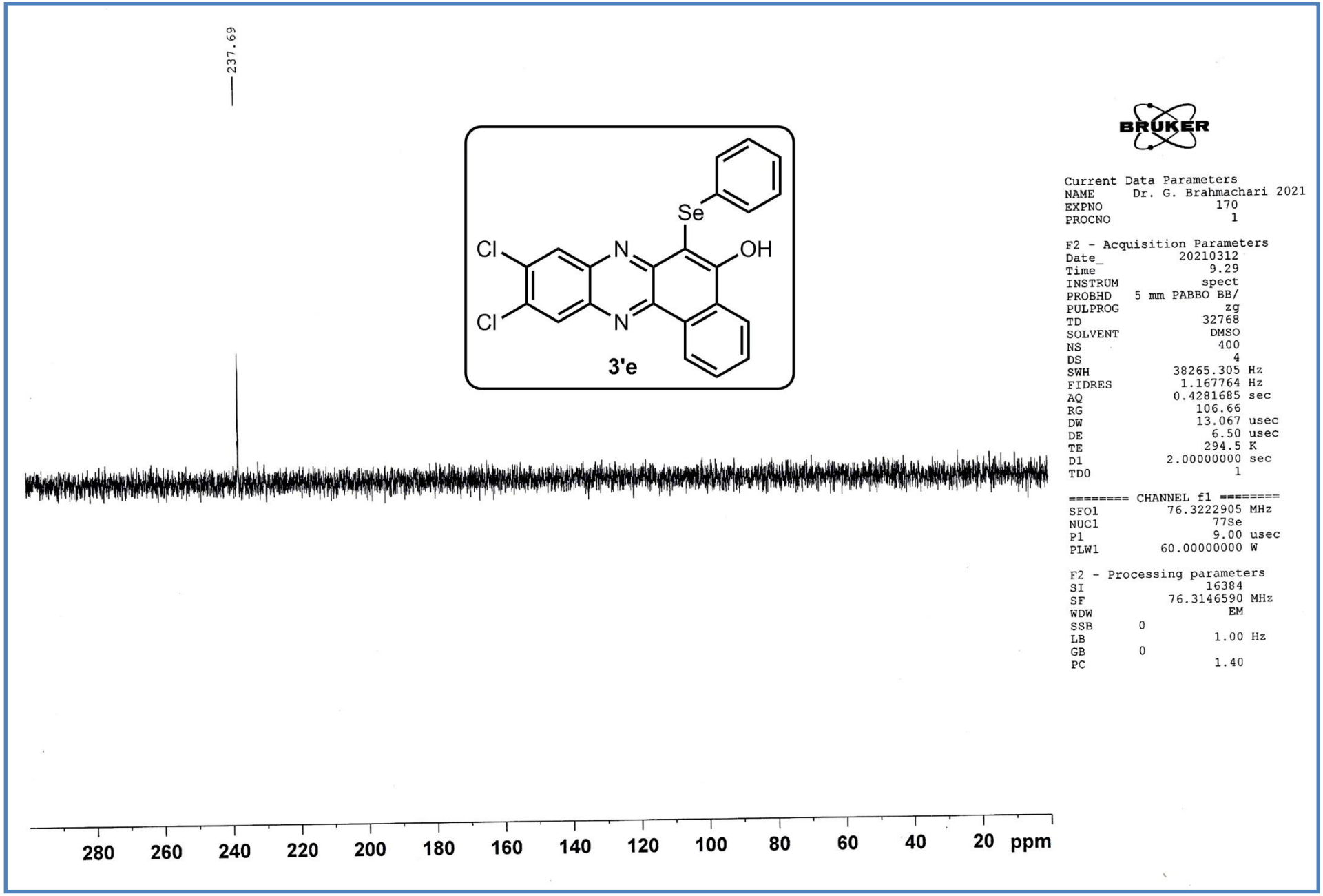


Figure S99. ^{77}Se-NMR spectrum of 9,10-dichloro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3′e**)

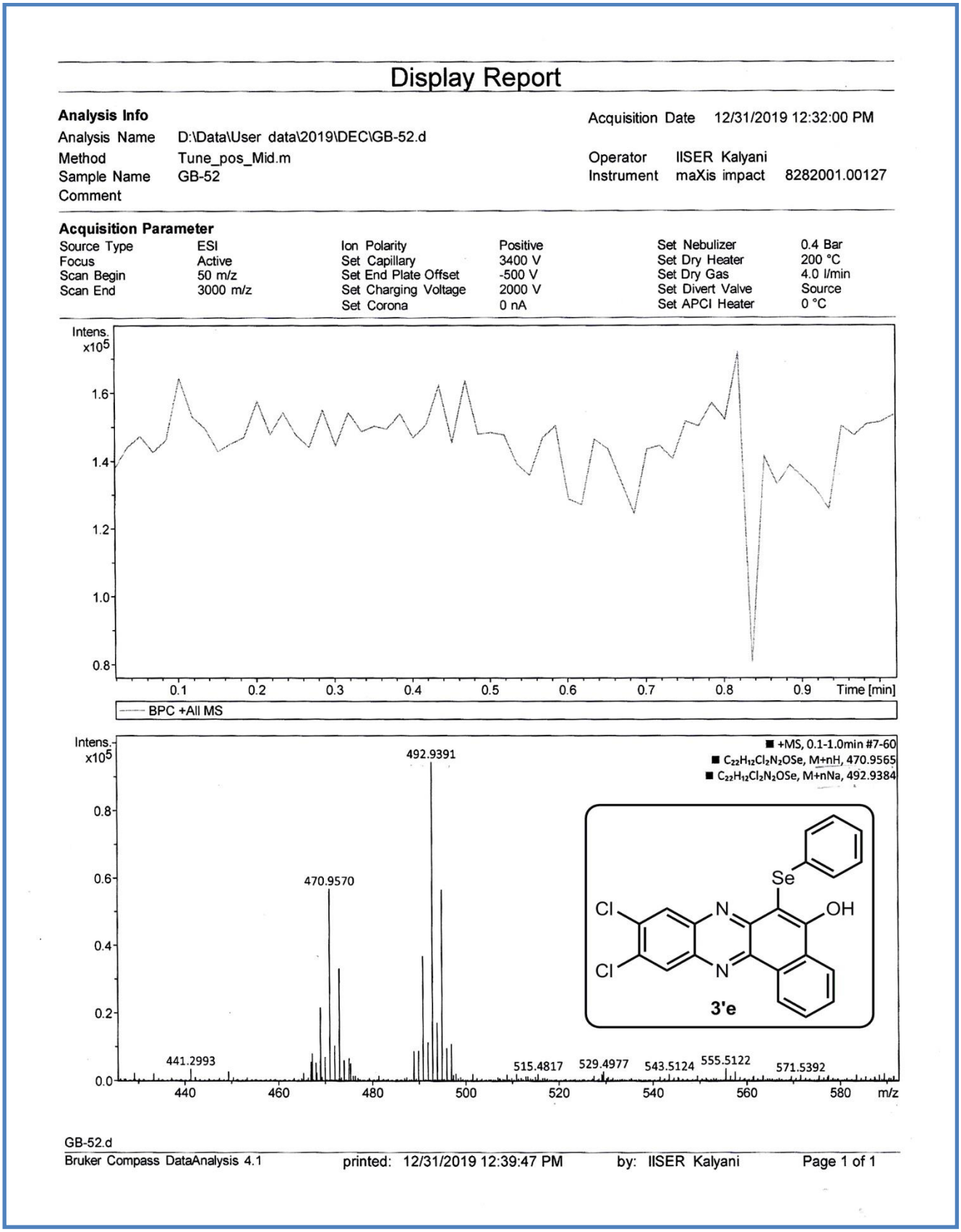


Figure S100. High-resolution Mass spectra of 9,10-dichloro-6-(phenylselanyl)benzo[*a*]phenazin-5-ol (**3'e**)

6. Scanned copies of ^{1}H NMR and ^{13}C NMR (for representative compound 7b) spectra for all the synthesized benzophenones 7 (7a–7c) and benzaldehydes 9 (9a–9b) (Figure S101 – S105)

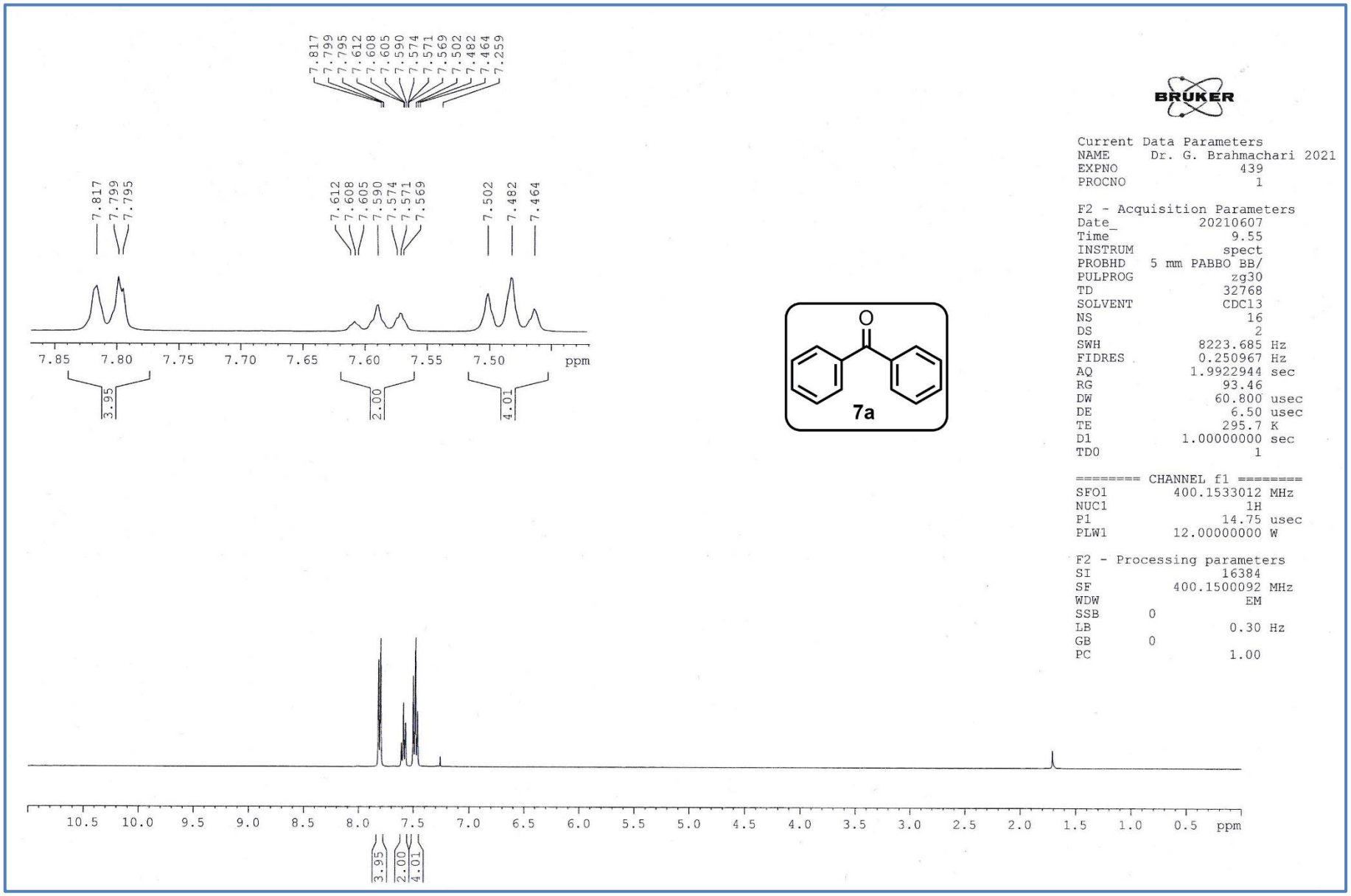


Figure S101. ^{1}H-NMR spectrum of benzophenone (**7a**)

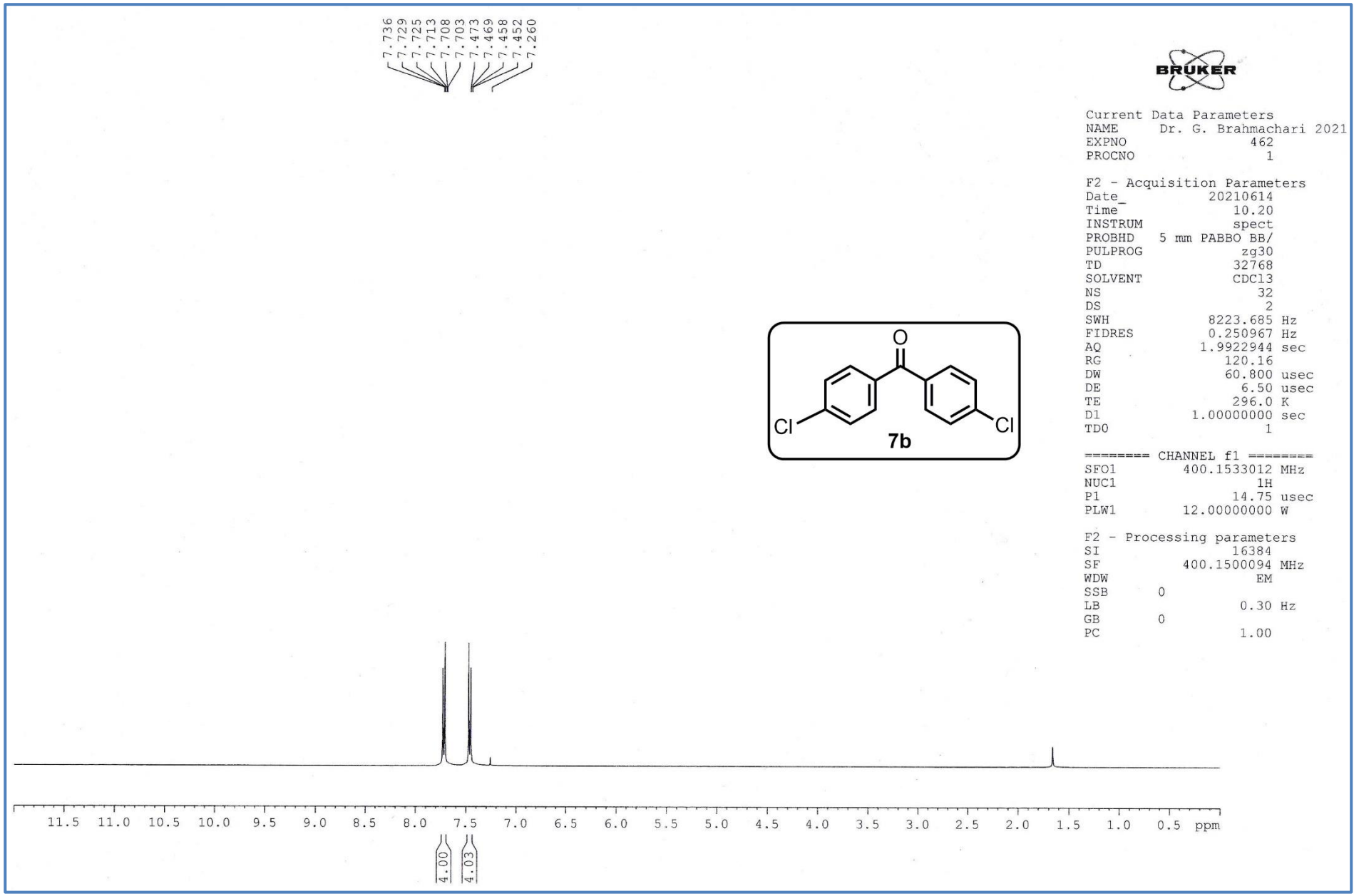


Figure S102. ^{1}H-NMR spectrum of bis(4-chlorophenyl)methanone (**7b**)

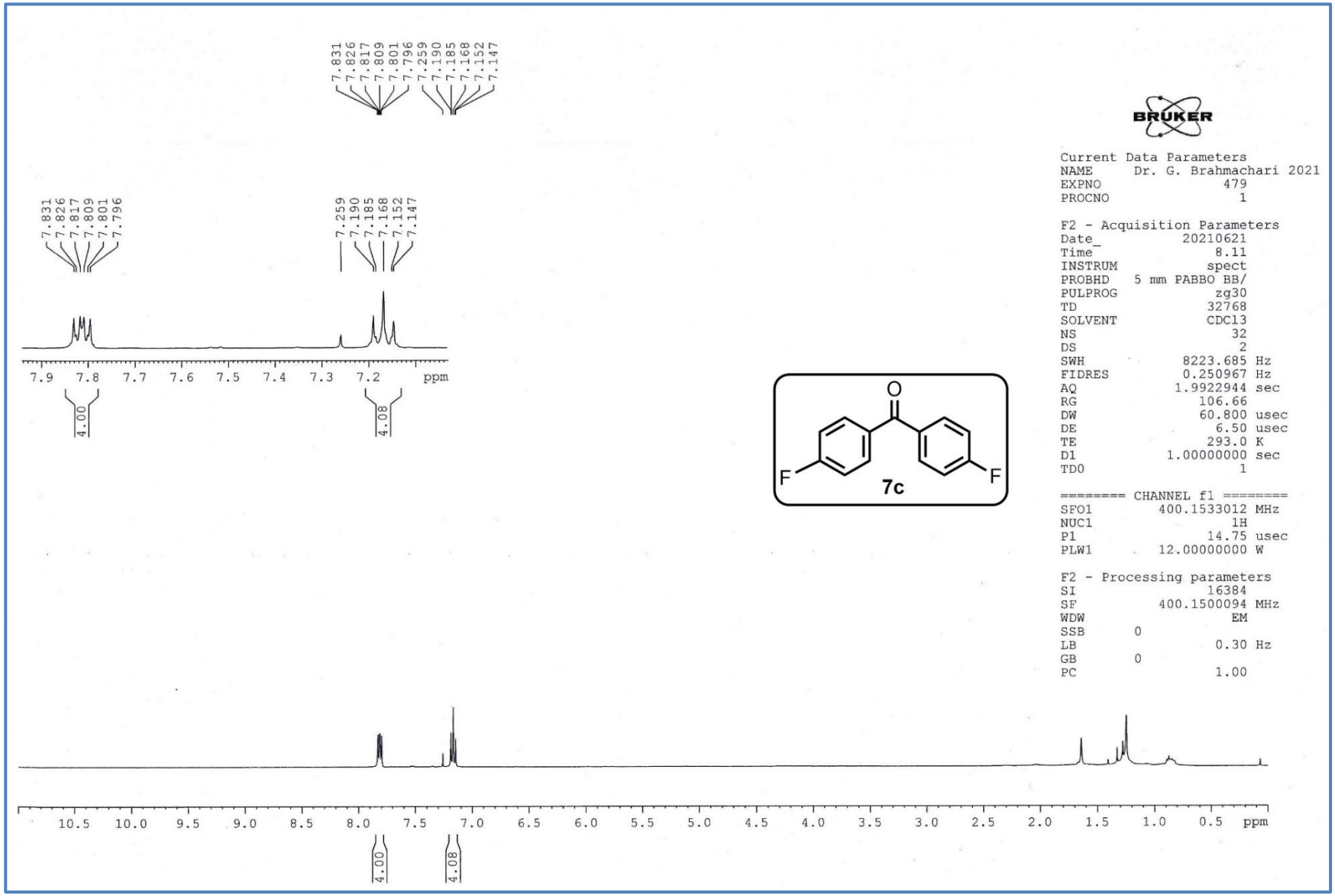


Figure S103. ^{1}H-NMR spectrum of bis(4-fluorophenyl)methanone (**7c**)

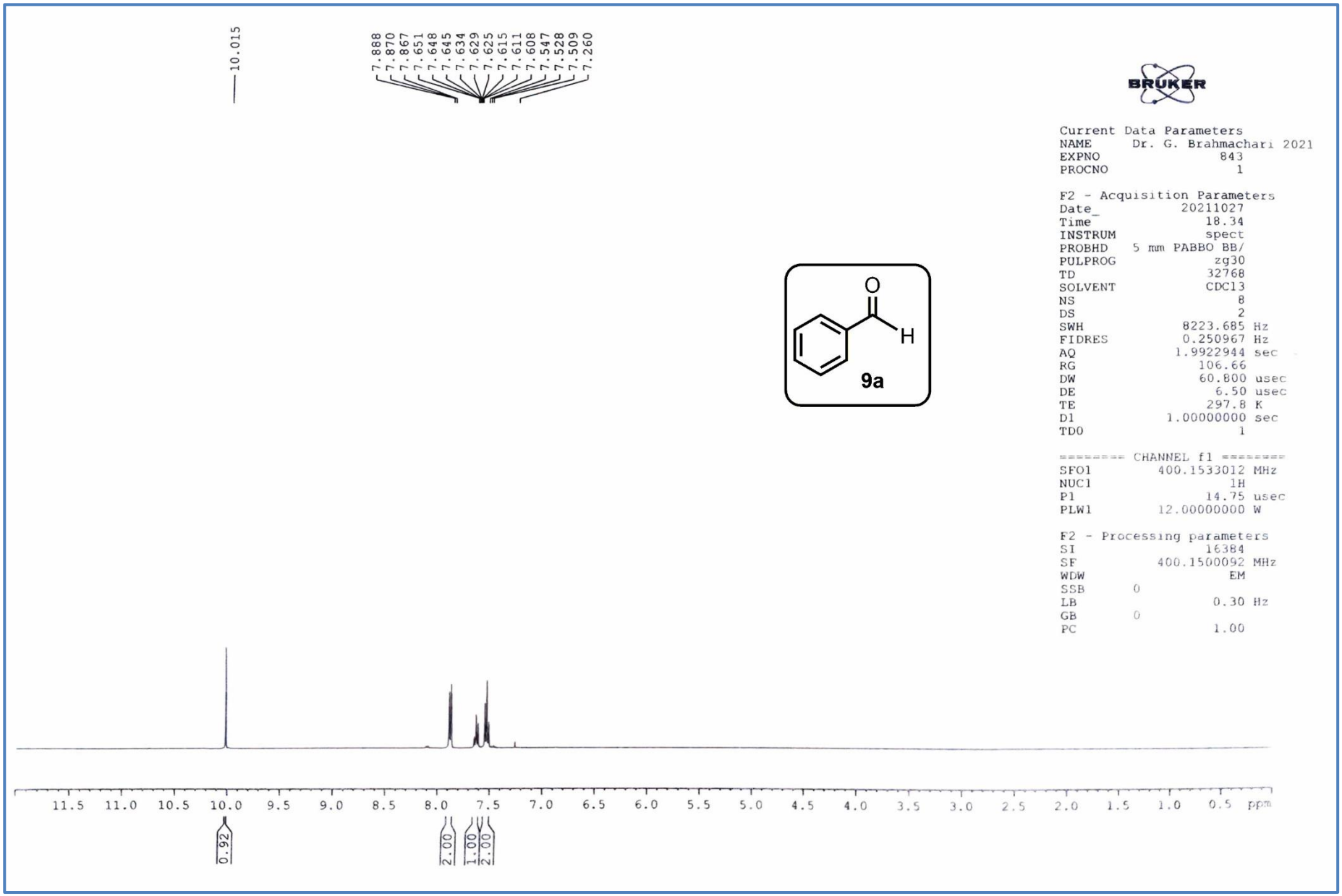


Figure S104. ^{1}H-NMR spectrum of benzaldehyde (**9a**)

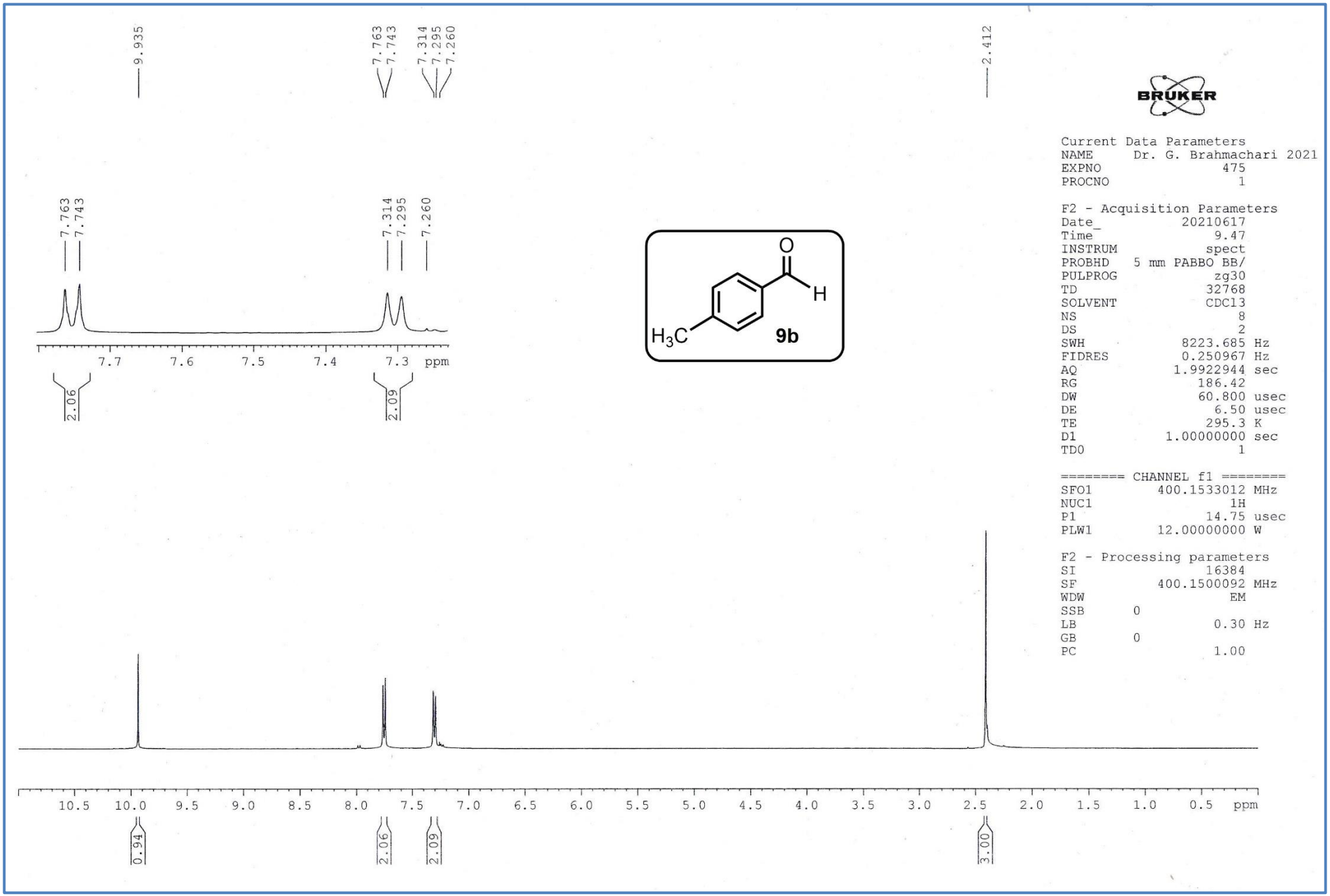


Figure S105. ^{1}H-NMR spectrum of 4-methylbenzaldehyde (**9b**)

7. Single X-ray crystal structure analysis of *6-(Phenylthio)benzo[a]phenazin-5-ol* (**3a**)

*Preparation of single crystals of compound **3a***

For preparing single crystals of compound **3a**, 30 mg of the sample was dissolved in 5 mL of DMSO, and the solution was left for 3 days for slow evaporation at ambient temperature to yield reddish block-shaped crystals.

CCDC 2116546 (Compound **3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif

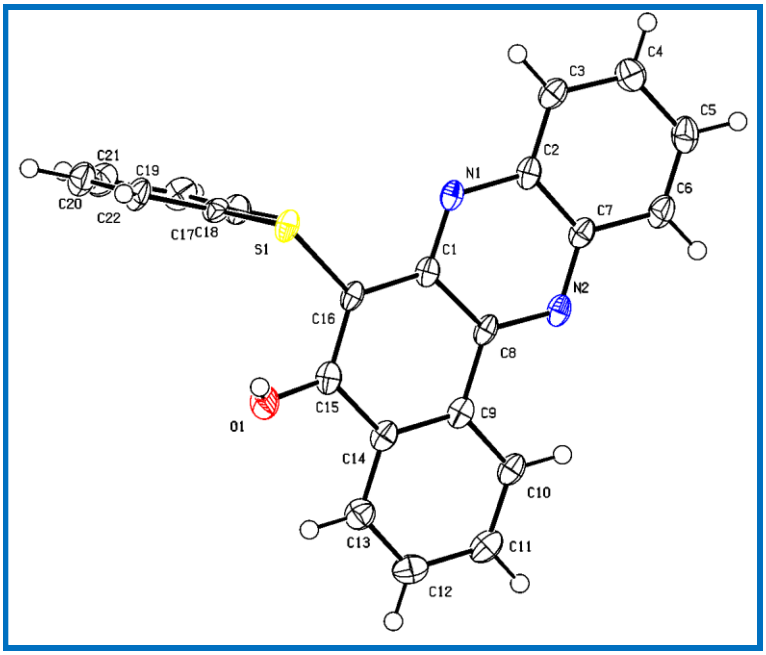
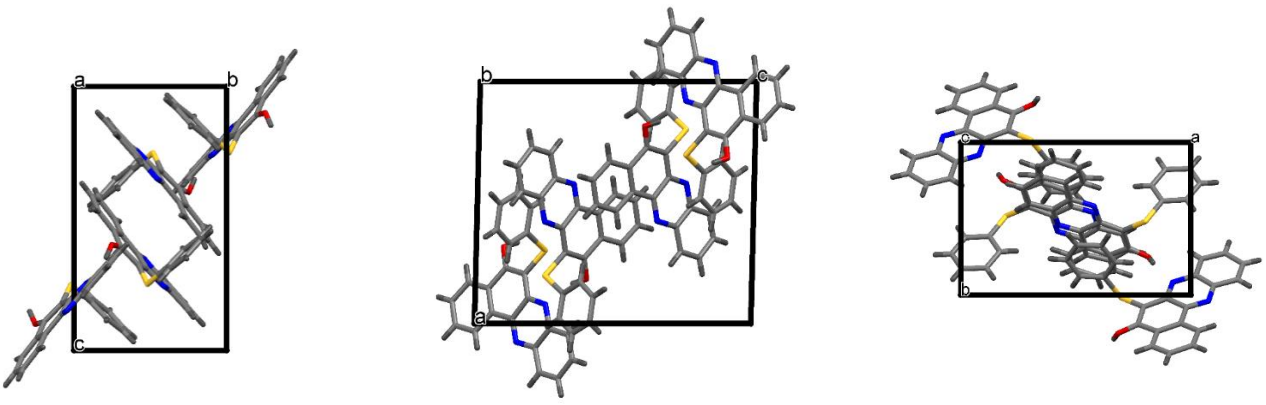


Figure S106a. *ORTEP* view of the molecule, showing the atom-labelling scheme Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



a-axis *b*-axis *c*-axis

Figure S106b. The packing arrangement of molecules viewed down the *a*-axis, *b*-axis and *c*-axis

Table S2. Crystal data and structure refinement for 6-(phenylthio)benzo[*a*]phenazin-5-ol (**3a**)

CCDC Number	**2116546**	
Empirical formula	$C_{22}H_{14}N_2OS$	
Formula weight	354.41	
Temperature	150.02 (18) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 12.9621(4) Å	α= 90°
	b = 8.5724 (3) Å	β= 91.399 (3)°
	c = 14.8322 (6) Å	γ = 90°
Volume	1647.60 (10) $Å^3$	
Z	4	
Density (calculated)	1.429 g/cm^3	
Absorption coefficient	0.210 mm^{-1}	
F(000)	736.0	
Crystal size	0.334×0.131×0.118 mm^3	
Crystal shape (colour)	Block (Red color)	
Theta range for data collection	4.12 to 56.68°	
Index ranges	-16<=h<=14, -4<=k<=11, -9<=l<=19	
Reflections collected	5264	
Independent reflections	3661 [R_{int} = 0.0528, R_{sigma} = 0.0764]	
Completeness to theta = 28.340°	86.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3561 / 0 / 236	
Goodness-of-fit on F^2	1.049	
Final R indices [I>= 2σ(I)]	R_1 = 0.0673, wR_2 = 0.1783	
R indices (all data)	R_1 = 0.0858, wR_2 = 0.2057	
Largest diff. peak and hole	0.73 and -0.76 e.$Å^{-3}$	
Scan mode	ω scan	
Reflections observed (I > 2σ(I))	5264	
Structure determination	Direct methods	
No. of parameters refined	236	
Final residual electron density	0.73 and -0.76 e.$Å^{-3}$	
Software for geometry calculation	WinGX [2]	
Software for geometrical calculation	PARST [3]	
Software for molecular plotting	PLATON [4], Ortep3 [5]	
Software for structure solution	SHELXS-97 [6]	
Software for refinement	SHELXL-97 [7]	

8. References

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