# Supplementary Information

## Catalyst- and solvent-free $C_{sp2}$–H functionalization of 4-hydroxycoumarins *via* C-3 dehydrogenative aza-coupling under ball-milling[#]

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[#]This paper is dedicated to Professor Vinod K. Singh on the occasion of his 62nd birthday

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**1 General experimental.** All chemicals (analytical grade) were purchased from reputed companies and used without further purification. $^{1}$H, $^{13}$C, DEPT-135 and $^{19}$F NMR spectra were collected at 400 MHz 100 MHz and 376 MHz, respectively, on a Bruker DRX spectrometer using DMSO-$d_6$ and $CDCl_3$ as 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 acquired on a Microtek Q-Tof Micro YA 263 Waters spectrometer. X-ray single crystallographic data were collected on X′Calibur CCD area-detector diffractometer. The melting points were recorded on a Chemiline CL-725 melting point apparatus and are uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 $F_{254}$ (Merck) plates. A PM 100, Retsch GmbH, Germany, ball-milling apparatus was used for all reactions.

**2 General procedure for the synthesis of substituted (*E*)-3-(2-arylhydrazono)chroman-2,4-diones (4)**

A mixture of 4-hydroxycoumarins (**1**; 3.0 mmol), aromatic primary amines (**2**; 3.0 mmol) and *tert*-butyl nitrite (**3**; 3.0 mmol; d: 0.867g/mL; Purity: 90%) was subjected to ball-milling at 500 rpm using a 25 mL stainless steel jar with seven balls (10 mm in diameter) of the same material for 4-6 min. The ball-milling operation was performed using inverted rotation direction, with an interval of 1 min and taking a break of 10 sec. The progress of the reaction was monitored by TLC. On completion of the reaction, the crude product was added with 10 mL of aqueous ethanol (1 : 1 *v*/*v*), shaken well to dissolve out unreacted reactants and other intermediates/impurities, and then filtered off the undissolved solid mass to obtain pure products **4** (**4a** – **4u**) upon drying in the open-air. All the structures of the synthesized compounds were confirmed by spectroscopic studies, including $^{1}$H-NMR, $^{13}$C-NMR, DEPT-135, $^{19}$F-NMR (for fluorine atom-containing molecules such as **4i**, **4j**, **4k**, **4o**, **4p**, and **4u**), and HRMS. Further structural confirmation for a representative entry, (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**), based on single X-ray crystallographic studies, was also supplemented.

**3 Gram-scale synthesis of compound 4c**

A mixture of 4-hydroxycoumarin (**1a**; 5.0 mmol; 0,810 g), *p*-toluidine (**2c**; 5.0 mmol; 0.535 g) and *tert*-butyl nitrite (**3**; 5.0 mmol; 0.575 g) was ball-milled in a 25 mL stainless steel jar with seven balls (10 mm in diameter) of the same material at 500 rpm for 6 min in a similar fashion as described earlier. On completion of the reaction (as monitored by TLC), the crude product was added with 15 mL of aqueous ethanol (1 : 1 *v*/*v*), shaken well, filtered-off and dried to have the desired product, *(E)*-3-(2-(*p*-tolyl)hydrazono)chroman-2,4-dione (**4c**) in pure form with 94% of yield (1.313 g).

**4 The physical and spectral data of all the synthesized compounds 4 (4a – 4u) are given below:**

*(E)-3-(2-phenylhydrazono)chroman-2,4-dione (**4a**).* Reddish yellow amorphous solid; yield: 88% (702 mg; 3.0 mmol scale); mp = 165-166 °C. $^{1}$H NMR (400 MHz, DMSO-$d_6$): δ =15.66 (br s, 1H, -N*H*), 7.93 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.41-7.69 (m, 3H, Ar-H), 7.49 (t, 2H, *J* = 7.6 Hz, Ar-H), 7.36-7.30 (m, 3H, Ar-H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$): δ = 177.57 (oxo *C*O), 158.24 (lactone *C*O), 154.00 (*C*), 140.87 (*C*), 136.38 (*C*H), 129.90 (2C, *C*H), 127.87 (*C*H), 126.37 (*C*H), 124.63 (*C*H), 122.50 (*C*), 120.16 (*C*), 117.86 (2C, *C*H), 117.31 (*C*H) ppm. HRMS: *m/z* 289.0584 $[M + Na]^+$ calcd for $C_{15}H_{10}N_2O_3Na$, found: *m/z* 289.0597.

*(E)-3-(2-(4-bromophenyl)hydrazono)chroman-2,4-dione* (***4b***). Bright yellow amorphous solid; yield: 85% (880 mg; 3.0 mmol scale); mp = 245-247 °C. $^{1}$H NMR (400 MHz, DMSO-$d_6$): δ = 15.47 (br s, 1H, -N*H*), 7.99 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.79-7.75 (m, 1H, Ar-H), 7.71 (br s, 4H, Ar-H), 7.41-7.35 (m, 2H, Ar-H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 178.89 (oxo *C*O), 159.02 (lactone *C*O), 154.64 (*C*), 139.74 (*C*), 136.66 (*C*H), 133.18 (2C, *C*H), 127.04 (*C*H), 124.90 (*C*H), 122.79 (C), 122.09, (C), 121.69 (C), 119.55 (2C, *C*H), 117.85 (*C*H) ppm. HRMS:

*m/z* 344.9875 $[M + H]^+$ calcd for $C_{15}H_9BrN_2O_3H$, found: *m/z* 344.9856; *m/z* 346.9875 $[M +2 + H]^+$ calcd for $C_{15}H_9BrN_2O_3H$, found: *m/z* 346.9834.

*(E)-3-(2-(p-tolyl)hydrazono)chroman-2,4-dione (**4c**).* Yellow amorphous solid; yield: 88% (702 mg; 3.0 mmol scale); mp = 165-166 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 15.79 (br s, 1H, -N*H*), 7.98-7.96 (m, 1H, Ar-H), 7.77-7.73 (m, 1H, Ar-H), 7.62 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.39-7.31 (m, 4H, Ar-H), 2.33 (s, 3H, Ar-C$H_3$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$): δ = 177.43 (oxo *C*O), 158.34 (lactone *C*O), 153.98 (*C*), 138.62 (*C*), 137.94 (*C*), 136.27 (*C*H), 130.40 (2C, *C*H), 126.33 (*C*H), 124.63 (*C*H), 122.07 (*C*), 120.21 (*C*), 117.88 (2C, *C*H), 117.30 (*C*H), 20.75 (Ar-*C*H$_3$) ppm. HRMS: *m/z* 281.0926 $[M + H]^+$ calcd for $C_{16}H_{12}N_2O_3H$, found: *m/z* 281.0928

*(E)-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4d**).* Brick red amorphous solid; yield: 94% (835 mg; 3.0 mmol scale); mp = 183-184 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 16.02 (br s, 1H, -N*H*), 7.99 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.77-7.71 (m, 3H, Ar-H), 7.40-7.34 (m, 2H, Ar-H), 7.10 (d, 2H, *J* = 8.8 Hz, Ar-H), 3.81 (s, 3H, Ar-OC$H_3$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$): δ = 176.98 (oxo *C*O), 159.28 (*C*), 158.36 (lactone *C*O), 153.86 (*C*), 135.98 (*C*H), 134.23 (*C*), 126.15 (*C*H), 124.50 (*C*H), 121.50 (*C*), 120.16 (*C*), 119.64 (2C, *C*H), 117.20 (*C*H), 115.18 (2C, *C*H), 55.58 (Ar-O*C*H$_3$) ppm. HRMS: *m/z* 319.0695 $[M + Na]^+$ calcd for $C_{16}H_{12}N_2O_4Na$, found: *m/z* 319.0696.

*(E)-3-(2-(3-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4e**).* Mahogany red amorphous solid; yield: 81% (758 mg; 3.0 mmol scale); mp = 191-192 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 15.51 (br s, 1H, -N*H*), 7.99 (d, 1H, *J* = 4.4 Hz, Ar-H), 7.78-7.75 (m, 1H, Ar-H), 7.62 (br s, 1H, Ar-H), 7.51-7.49 (m, 1H, Ar-H), 7.46-7.36 (m, 1H, Ar-H), 7.21 (d, 1H, *J* = 4.4 Hz, Ar-H), 2.53 (s, 3H, Ar-H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$): δ = 177.63 (oxo *C*O), 158.31 (lactone *C*O), 154.02 (*C*), 141.65 (*C*), 140.62 (*C*), 140.57 (*C*H), 136.44 (*C*), 136.40 (*C*H), 130.25 (*C*H), 126.44 (*C*H), 124.68 (*C*H), 120.25 (*C*), 117.34 (*C*H), 114.53 (*C*H), 114.04 (*C*H), 14.45 (Ar-*C*H$_3$)ppm. HRMS: *m/z* 313.0647 $[M + H]^+$ calcd for $C_{16}H_{12}N_2O_3SH$, found: *m/z* 313.0648

*(E)-3-(2-(4-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4f**).* Crimson red amorphous solid; yield: 84% (786 mg; 3.0 mmol scale); mp = 202-205 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 15.79 (br s, 1H, -N*H*), 7.98 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.77-7.73 (m, 1H, Ar-H), 7.69 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.39-7.34 (m, 4H, Ar-H), 2.51 (s, 3H, Ar-SC$H_3$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$): δ = 177.32 (oxo *C*O), 158.28 (lactone *C*O), 153.95 (*C*), 138.66 (*C*), 138.01 (*C*), 136.21 (*C*H), 126.75 (2C, *C*H), 126.28 (*C*H), 124.59 (*C*H), 122.13 (*C*), 120.21 (*C*), 118.48 (2C, *C*H), 117.27 (*C*H), 14.59 (Ar-S*C*H$_3$) ppm. HRMS: *m/z* 313.0647 $[M + H]^+$ calcd for $C_{16}H_{12}N_2O_3SH$, found: *m/z* 313.0648.

*(E)-3-(2-(2-nitrophenyl)hydrazono)chroman-2,4-dione (**4g**).* Yellow amorphous solid; yield: 95% (883 mg; 3.0 mmol scale); mp = 275-276 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 16.76 (br s, 1H, -N*H*), 8.48 (d, 1H, *J* = 8.4 Hz, Ar-H), 8.35-8.33 (m, 1H, Ar-H), 8.23-8.19 (m, 1H, Ar-H), 7.83-7.79 (m, 1H, Ar-H), 7.74-7.69 (m, 1H, Ar-H),7.46-7.40 (m, 1H, Ar-H), 7.38-7.34 (m, 1H, Ar-H), 7.31 (d, 1H, *J* = 8.4 Hz, Ar-H) ppm. $^{13}$C NMR spectrum was not recorded due to poor solubility of the compound in deuterated solvents. HRMS: *m/z* 334.0440 $[M + Na]^+$ calcd for $C_{15}H_9N_3O_5Na$, found: *m/z* 334.0441.

*(E)-3-(2-(4-nitrophenyl)hydrazono)chroman-2,4-dione (**4h**).* Medallion yellow amorphous solid; yield: 93% (868 mg; 3.0 mmol scale); mp = 270-272 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 15.17 (br s, 1H, -N*H*), 8.36 (d, 1H, *J* = 8.8 Hz, Ar-H), 8.00 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.94 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.81-7.77 (m, 1H, Ar-H), 7.42-7.36 (m, 2H, Ar-H) ppm. $^{13}$C NMR spectrum was not recorded due to poor solubility of the compound in deuterated solvents. HRMS: *m/z* 312.0620 $[M + H]^+$ calcd for $C_{15}H_9N_3O_5H$, found: *m/z* 312.0621.

*(E)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**).* Golden yellow amorphous solid; yield: 87% (914 mg; 3.0 mmol scale); mp = 235-236 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 15.49 (br s, 1H, -

N*H*), 8.01 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.88 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.80-7.76 (m, 1H, Ar-H), 7.54 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.42-7.36 (m, 2H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 178.92 (oxo *C*O), 158.95 (lactone *C*O), 154.66 (*C*), 148.67 (*C*), 139.13 (*C*), 136.73 (*C*H), 127.05 (*C*H), 124.92 (*C*H), 122.90 (*C*), 122.61 (2C, *C*H), 121.77 (C), 120.24 (O*C*$F_3$), 119.43 (2C, *C*H), 117.85 (*C*H) ppm. $^{19}F$ NMR (376 MHz, DMSO-$d_6$): δ = −56.93 ppm. HRMS: *m/z* 351.0593 $[M + H]^+$ calcd for $C_{16}H_9F_3N_2O_4H$, found: *m/z* 351.0592.

*(E)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)*. Yellow amorphous solid; yield: 84% (922 mg; 3.0 mmol scale); mp = 201-202 °C. $^{1}H$ NMR (400 MHz, DMSO-$d_6$): δ = 15.33 (br s, 1H, -N*H*), 7.99 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.88-7.82 (m, 4H, Ar-H), 7.79-7.75 (m, 1H, Ar-H), 7.41-7.35 (m, 2H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-$d_6$): δ = 177.89 (oxo *C*O), 158.03 (lactone *C*O), 154.10 (*C*), 143.66 (*C*), 137.82 (2C, *C*H), 136.70 (*C*H), 129.53 (S*C*$F_3$, $J^{1}_{CF}$ = 306 Hz), 126.56 (*C*H), 124.74 (*C*H), 123.87 (*C*), 120.77, 120.27 (*C*), 118.83 (2C, *C*H), 117.38 (*C*H) ppm. $^{19}F$ NMR (376 MHz, DMSO-$d_6$): = −42.25 ppm. HRMS: *m/z* 367.0364 $[M + H]^+$ calcd for $C_{16}H_9F_3N_2O_3SH$, found: *m/z* 367.0365.

*(E)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)*. Bumble bee yellow amorphous solid; yield: 91% (1097 mg; 3.0 mmol scale); mp = 215-217 °C. $^{1}H$ NMR (400 MHz, DMSO-$d_6$): δ = 15.09 (br s, 1H, -N*H*), 8.39 (br s, 2H, Ar-H), 7.98-7.95 (m, 2H, Ar-H), 7.79-7.75 (m,1H, Ar-H), 7.39-7.34 (m, 2H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-$d_6$): δ = 177.85 (oxo *C*O), 157.87 (lactone *C*O), 154.17 (*C*), 143.44 (*C*), 136.92 (*C*H), 131.56 (2*C*, $J^{2}_{CF}$ = 33 Hz), 126.59 (*C*H), 124.79 (*C*H), 123.03 (2 × *C*$F_3$, $J^{1}_{CF}$ = 271 Hz), 120.24 (*C*), 119.42 (*C*H), 118.95 (*C*), 117.95 (*C*H), 117.44 (2C, *C*H) ppm. $^{19}F$ NMR (376 MHz, DMSO-$d_6$): δ = −61.67 ppm. HRMS: *m/z* 403.0517 $[M + H]^+$ calcd for $C_{17}H_8F_6N_2O_3H$, found: *m/z* 403.0518.

*(E)-3-(2-(2,5-dichlorophenyl)hydrazineylidene)chromane-2,4-dione (**4l**)*. Medallion yellow amorphous solid; yield: 88% (884 mg; 3.0 mmol scale); mp = 246-248 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ = 16.25 (br s, 1H, -N*H*), 8.13-8.10 (m, 2H, Ar-H), 7.69 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.41-7.39 (m,1H,Ar-H), 7.36-7.29 (m, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 178.90 (oxo *C*O), 158.56 (lactone *C*O), 154.69 (*C*), 138.54 (*C*), 137.08 (*C*H), 135.03 (*C*), 130.98 (*C*H), 128.43 (*C*H), 127.37 (*C*H), 125.08 (*C*H), 124.35 (*C*), 121.78 (*C*), 120.21 (*C*), 118.27 (*C*H), 117.90 (*C*H) ppm. HRMS: *m/z* 334.9990 $[M + H]^+$calcd for $C_{15}H_8Cl_2N_2O_3H$, found: *m/z* 334.9991.

*(E)-6-methyl-3-(2-(p-tolyl)hydrazono)chroman-2,4-dione (**4m**)*. Golden yellow amorphous solid; yield: 82% (723 mg; 3.0mmol scale); mp = 226-228 °C. $^{1}H$ NMR (400 MHz, DMSO-$d_6$): δ = 15.81 (br s, 1H, -N*H*), 7.76 (m, 1H, Ar-H), 7.63 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.57 (d,1H, *J* = 8.4 Hz, Ar-H), 7.34 (d, 2H, *J* = 8.0 Hz,Ar-H), 7.25 (d, 1H, *J* = 8.4 Hz, Ar-H), 2.38 (s, 3H, Ar-C*H*$_3$),2.34 (s, 3H, Ar-C*H*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ= 178.55 (oxo *C*O), 159.62 (lactone *C*O), 152.67 (*C*), 139.19 (*C*), 138.42 (*C*), 137.23 (*C*H), 134.53 (*C*), 130.60 (2C, *C*H), 126.35 (*C*H), 122.06 (*C*), 120.05 (*C*), 118.20 (2C, *C*H), 117.49 (*C*H), 21.40 (Ar-*C*H$_3$), 20.85 (Ar-*C*H$_3$) ppm. HRMS: *m/z* 317.0902 $[M + Na]^+$ calcd for $C_{17}H_{14}N_2O_3Na$, found: *m/z* 317.0903.

*(E)-3-(2-(4-methoxyphenyl)hydrazono)-6-methylchroman-2,4-dione (**4n**)*. Berry red amorphous solid; yield: 83% (772 mg; 3.0 mmol scale); mp = 218-224 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ = 16.71 (br s, 1H, -N*H*), 7.83 (br s, 1H, Ar-H), 7.63 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.44-7.42 (m, 1H, Ar-H), 7.16 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.98 (d, 2H, *J* = 9.2 Hz, Ar-H), 3.85 (s, 3H, Ar-O*C*H$_3$), 2.41 (s, 3H, Ar-C*H*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 178.28 (oxo *C*O), 160.27 (2C), 152.61 (*C*), 137.01 (*C*H), 134.46 (*C*), 134.21 (*C*), 126.23 (*C*H), 121.74 (*C*), 120.08 (*C*), 119.92 (2C, *C*H), 117.44 (*C*H), 115.30 (2C, *C*H), 55.81 (Ar-O*C*H$_3$), 20.85 (Ar-*C*H$_3$) ppm. HRMS: *m/z* 311.1032 $[M + H]^+$ calcd for $C_{17}H_{14}N_2O_4H$, found: *m/z* 311.1033.

*(E)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4o**)*. Lemon yellow amorphous solid; yield: 81% (923 mg; 3.0 mmol scale); mp = 239-241 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ = 16.17

(br s, 1H, -N*H*), 7.84 (br s, 1H, Ar-H), 7.77-7.69 (m, 4H, Ar-H), 7.49 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.18 (d, 1H, *J* = 8.4 Hz, Ar-H), 2.43 (s, 3H, Ar-C$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 179.27 (oxo *C*O), 158.87 (lactone *C*O), 152.87 (*C*H), 142.79 (*C*), 138.06 (*C*H), 138.01 (2C, *C*H), 134.93 (S*C*$F_3$), 130.98 (*C*), 126.69 (*C*H), 123.73 (*C*), 123.52 (*C*), 119.86 (*C*), 118.71 (2C, *C*H), 117.69 (*C*H), 20.85 (Ar-*C*$H_3$) ppm. $^{19}F$ NMR (376 MHz, $CDCl_3$): δ = – 42.64 ppm. HRMS: *m/z* 381.0521$[M + H]^+$ calcd for $C_{17}H_{11}F_3N_2O_3SH$, found: *m/z* 381.0522.

*(E)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4p**).* Lemon yellow amorphous solid; yield: 80% (874 mg; 3.0mmol scale); mp = 265-266 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 16.34 (br s, 1H, -N*H*), 7.85 (br s, 1H, Ar-H), 7.71 (d, 2H, *J* = 9.2 Hz,Ar-H), 7.49-7.47 (m, 1H, Ar-H), 7.33 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.19 (d, 1H, *J* = 8.4 Hz, Ar-H), 2.43 (s, 3H, Ar-C$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 179.09 (oxo *C*O), 159.18 (lactone *C*O), 152.84 (*C*), 148.62 (*C*), 139.21 (*C*), 137.82 (*C*H), 137.00 (*C*), 134.83 (*C*), 127.39 (O*C*$F_3$), 126.58 (*C*H), 123.01 (*C*), 122.61 (2C, *C*H), 119.39 (2C, *C*H), 117.66 (*C*H), 20.86 (Ar-*C*$H_3$) ppm. $^{19}F$ NMR (376 MHz, $CDCl_3$): δ = – 57.97 ppm. HRMS: *m/z* 365.0749 $[M + H]^+$ calcd for $C_{17}H_{11}F_3N_2O_4H$, found: *m/z* 365.0748.

*(E)-7-methyl-3-(2-(p-tolyl)hydrazono)chroman-2,4-dione (**4q**).* Golden yellow amorphous solid; yield: 85% (750 mg; 3.0 mmol scale); mp = 234-238 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 16.46 (br s, 1H, -N*H*), 7.94 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.55 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.26 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.11 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.06 (br s, 1H, Ar-H), 2.45 (s, 3H, Ar-C$H_3$), 2.39 (s, 3H, Ar-C$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 178.37 (oxo *C*O), 159.60 (lactone *C*O), 154.61 (*C*), 148.13 (*C*), 139.04 (2C, *C*), 138.51 (*C*), 130.58 (2C, *C*H), 126.66 (*C*H), 125.99 (*C*H), 121.99 (*C*), 118.13 (2C, *C*H), 117.74 (*C*H), 22.19 (Ar-*C*$H_3$), 21.38 (Ar-*C*$H_3$) ppm. HRMS: *m/z* 295.1083$[M + H]^+$ calcd for $C_{17}H_{14}N_2O_3H$, found: *m/z* 295.1082.

*(E)-7-methoxy-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4r**).* Blush red amorphous solid; yield: 86% (841 mg; 3.0 mmol scale); mp = 230-231 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 16.63 (br s, 1H, -N*H*), 7.96 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.59 (d, 2H, *J* = 9.2 Hz, Ar-H), 6.97 (d, 2H, *J* = 9.2 Hz, Ar-H), 6.84 (dd, 1H, *J* = 8.8 and 2.4 Hz, Ar-H), 6.71 (d, 1H, *J* = 2.4 Hz, Ar-H), 3.89 (s, 3H, Ar-OC$H_3$), 3.85 (s, 3H, Ar-OC$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.63 (oxo *C*O), 166.16 (lactone *C*O), 160.01 (*C*), 159.78 (*C*), 156.43 (*C*), 134.34 (*C*), 128.25 (*C*H), 121.26 (*C*), 119.66 (2C, *C*H), 115.25 (2C, *C*H), 113.86 (*C*), 112.96 (*C*H), 101.05 (*C*H), 56.09 (Ar-O*C*$H_3$), 55.80 (Ar-O*C*$H_3$) ppm. HRMS: *m/z* 327.0981 $[M + H]^+$ calcd for $C_{17}H_{14}N_2O_5H$, found: *m/z* 327.0982.

*(E)-6-chloro-3-(2-(p-tolyl)hydrazono)chroman-2,4-dione (**4s**).* Fire yellow amorphous solid; yield: 82% (775 mg; 3.0 mmol scale); mp = 242-243 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 16.47 (br s, 1H, -N*H*), 8.02 (d, 1H, *J* = 2.8 Hz, Ar-H), 7.59-7.57 (m, 3H, Ar-H), 7.29 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.24 (d, 1H, *J* = 8.4 Hz, Ar-H), 2.41 (s, 3H, Ar-C$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.13 (oxo *C*O), 158.93 (lactone *C*O), 152.92 (*C*), 139.82 (*C*), 139.35 (*C*), 138.25 (*C*), 135.98 (*C*H), 130.71 (2C, *C*H), 127.04 (*C*), 126.19 (*C*H), 121.49 (*C*), 119.37 (*C*H), 118.46 (2C, *C*H), 21.45 (Ar-*C*$H_3$) ppm. HRMS: *m/z* 315.0536 $[M + H]^+$ calcd for $C_{16}H_{11}ClN_2O_3$, found: *m/z* 315.0537.

*(E)-6-chloro-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4t**).* Medallion yellow amorphous solid; yield: 78% (775 mg; 3.0 mmol scale); mp = 241-242 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 16.71 (br s, 1H, -N*H*), 8.02 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.66 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.59-7.56 (m, 1H, Ar-H), 7.24 (d, 1H, *J* = 9.2 Hz, Ar-H), 7.00 (d, 2H, *J* = 8.8 Hz, Ar-H), 3.87 (s, 3H, Ar-OC$H_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 176.83 (oxo *C*O), 160.69 (*C*), 159.17 (lactone *C*O), 152.84 (*C*), 135.77 (*C*H), 134.00 (*C*), 130.36 (*C*), 126.08 (*C*H), 121.52 (*C*), 121.31 (*C*), 120.23 (2C, *C*H), 119.32 (*C*H), 115.42 (2C, *C*H), 55.87 (Ar-O*C*$H_3$) ppm. HRMS: *m/z* 331.0486 $[M + H]^+$ calcd for $C_{16}H_{11}ClN_2O_4$, found: *m/z* 331.0487.

*(E)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)-6-chlorochroman-2,4-dione* ***(4u)***. Pineapple yellow amorphous solid; yield: 81% (1062 mg; 3.0mmol scale); mp = 201-203 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 16.14 (br s, 1H, -N*H*), 8.09 (br s, 2H, Ar-H), 8.04 (d, 1H, *J* = 2.8 Hz, Ar-H), 7.83 (br s, 1H, Ar-H), 7.67-7.64 (m, 1H, Ar-H), 7.28 (d, 1H, *J* = 8.0 Hz, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 178.33 (oxo *C*O), 157.68 (lactone *C*O), 153.17 (*C*), 141.97 (*C*), 137.28 (*C*H), 134.83 (2*C*, $J^{2}_{CF}$ = 35 Hz), 130.98 (*C*), 126.65 (*C*H), 123.67 (C), 122,72 (2 × *C*$F_3$, $J^{1}_{CF}$ = 277 Hz), 121.28 (*C*H, $J^{3}_{CF}$ = 3 Hz), 120.98 (*C*), 119.68 (2C, *C*H), 117.90 (*C*H) ppm. HRMS: *m/z* 437.0128 $[M + H]^+$ calcd for $C_{17}H_7ClF_6N_2O_3H$, found: *m/z* 437.0127.

**5 Scanned copies of $^{1}H$ NMR, $^{13}C$ NMR, DEPT-135, $^{19}F$ NMR and HRMS spectra for all compounds of functionalized (*E*)-3-(2-arylhydrazono)chroman-2,4-dione 4 (4a – 4u) (Figure S1 – S85)**

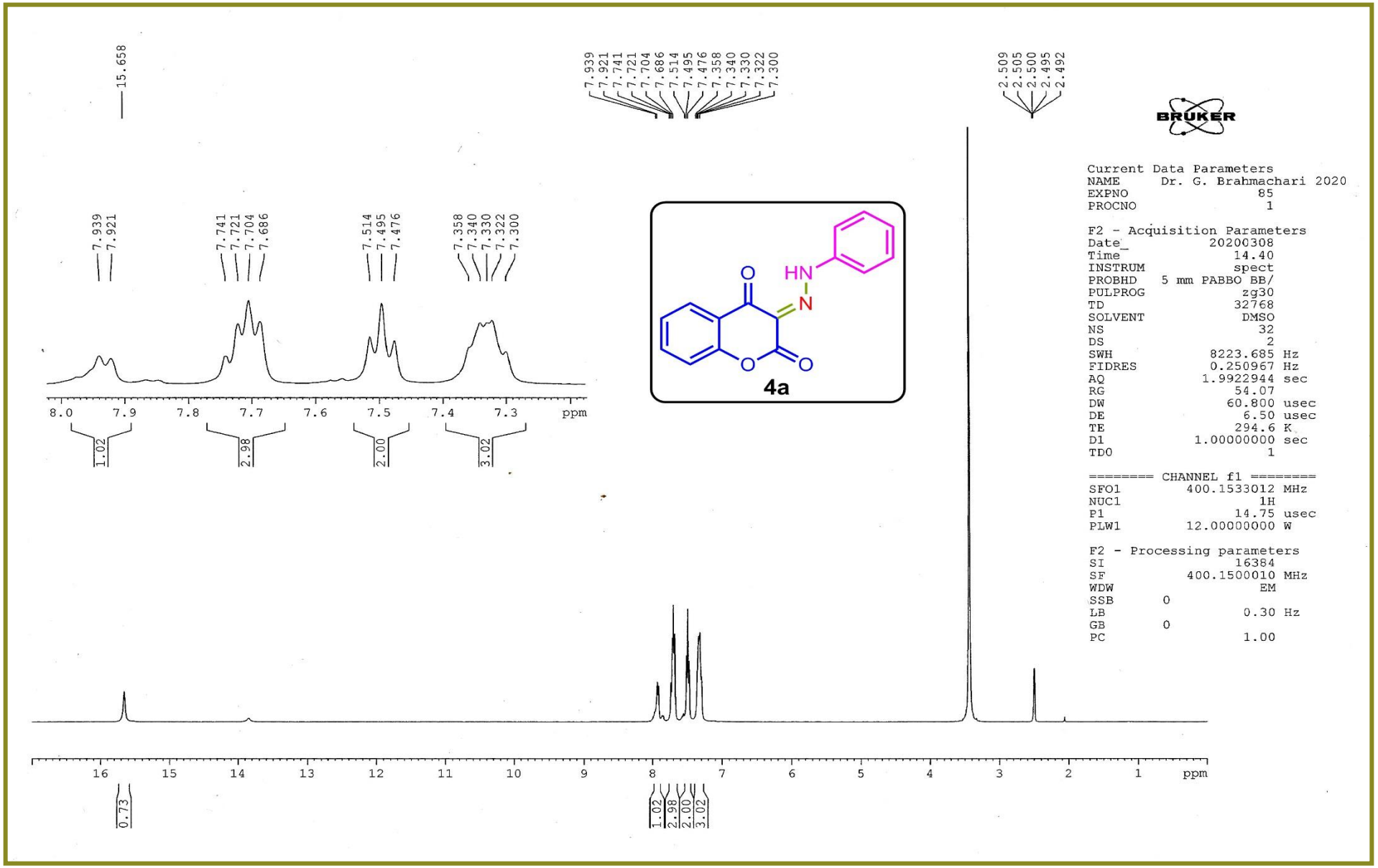



Figure S1. $^{1}H$-NMR spectrum of (*E*)-3-(2-phenylhydrazono)chroman-2,4-dione (**4a**)

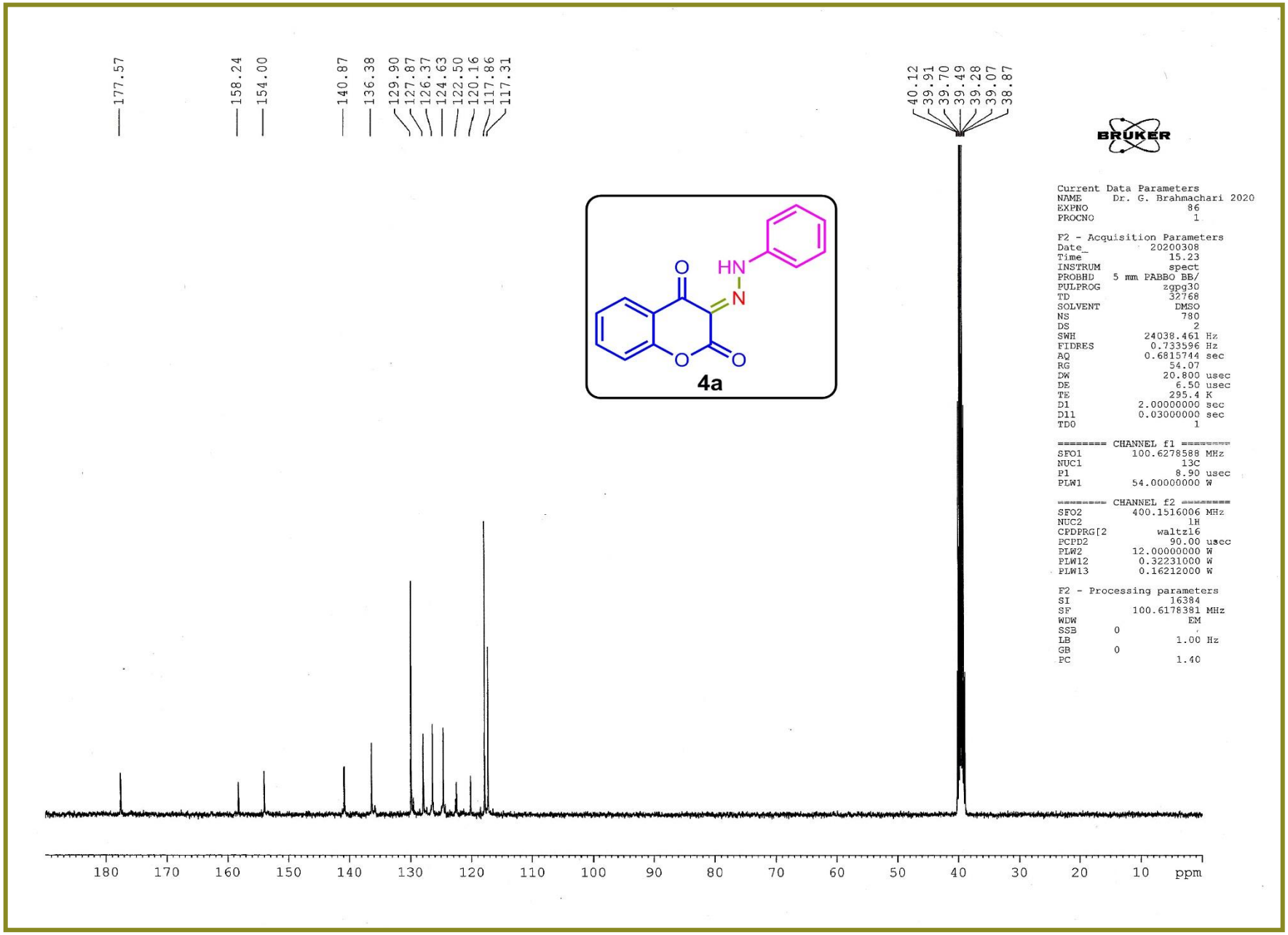



Figure S2. $^{13}$C-NMR spectrum of (*E*)-3-(2-phenylhydrazono)chroman-2,4-dione (**4a**)

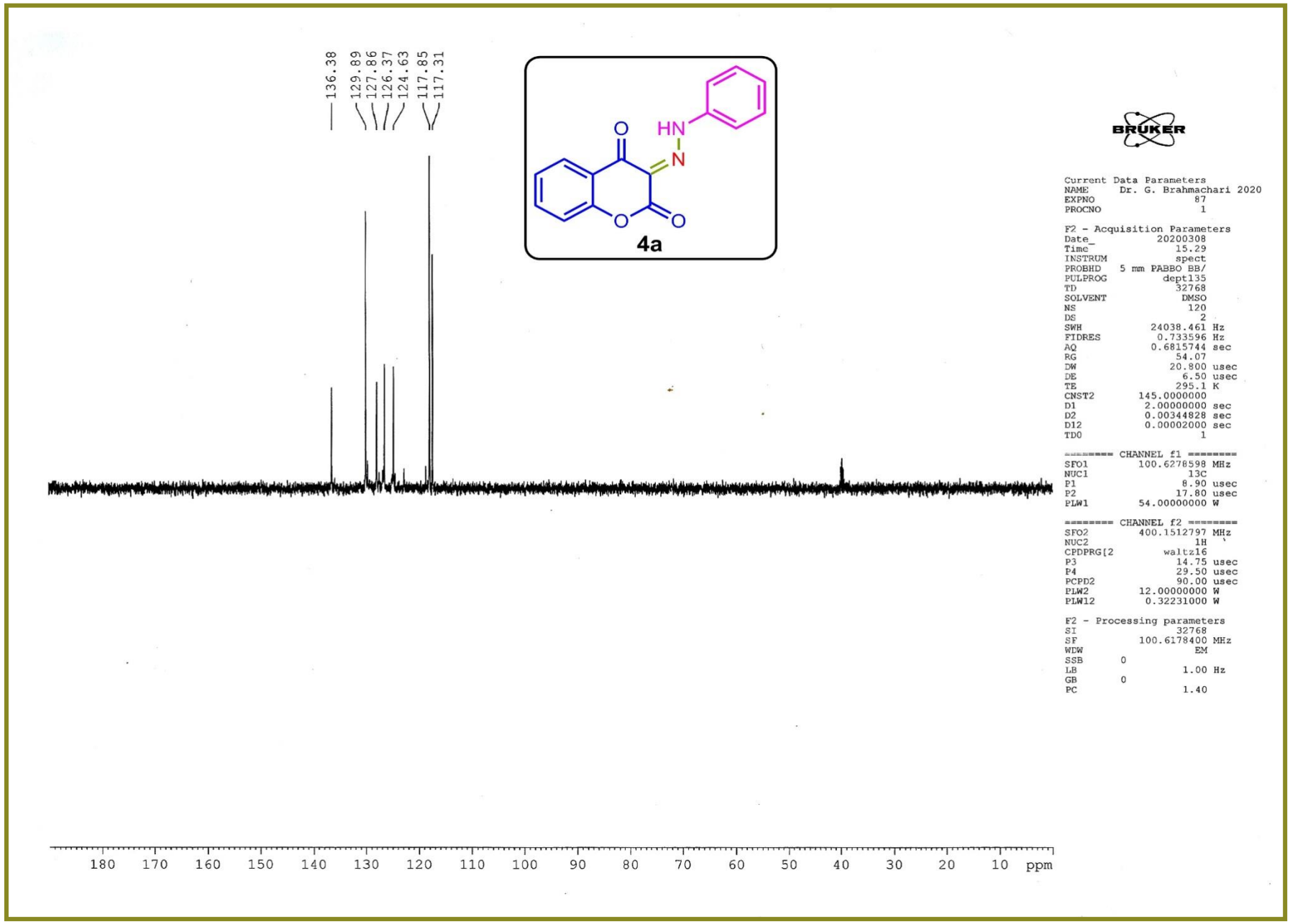



Figure S3. DEPT-135 NMR spectrum of (*E*)-3-(2-phenylhydrazono)chroman-2,4-dione (**4a**)

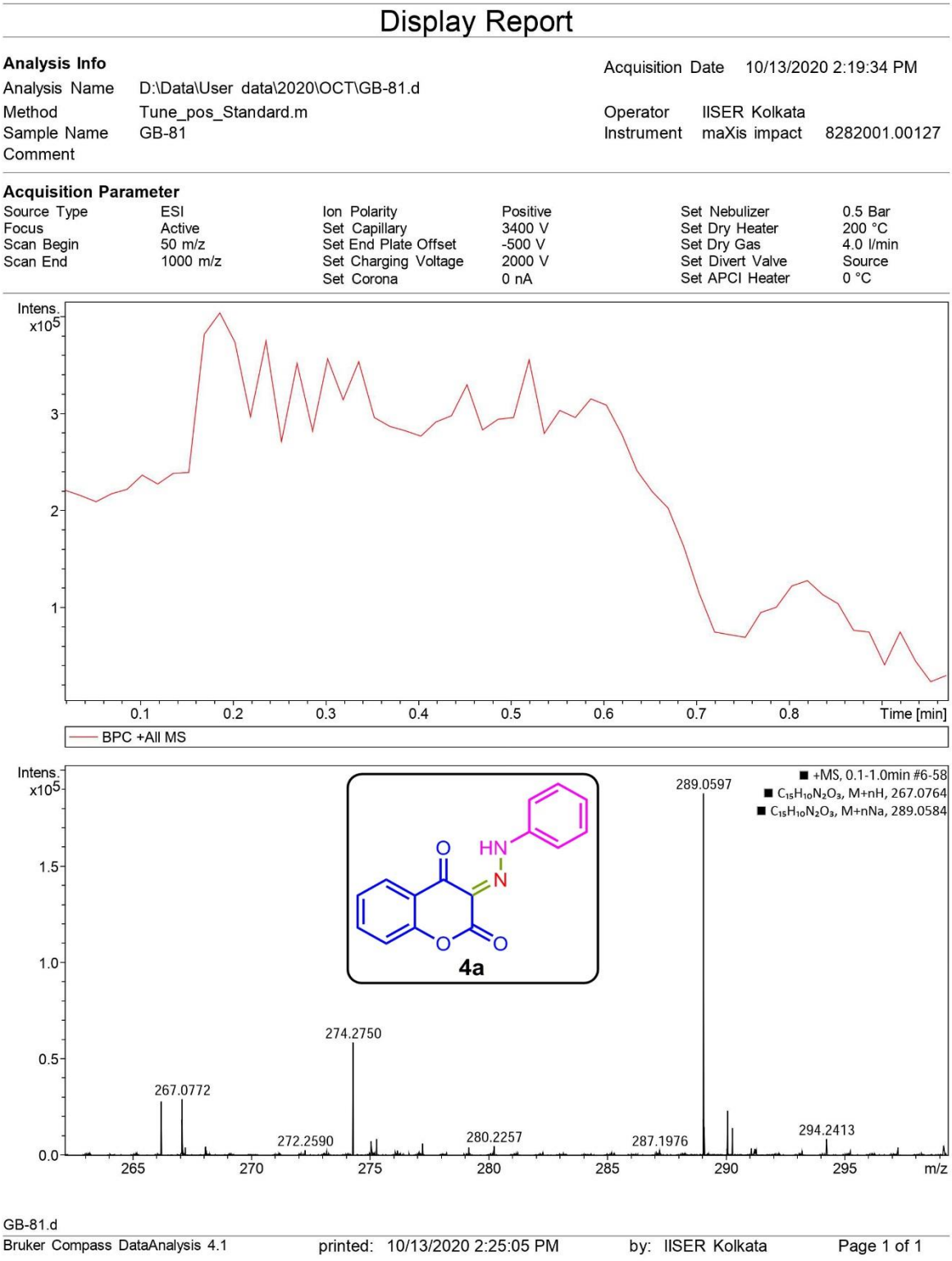



Figure S4. Mass spectra of (*E*)-3-(2-phenylhydrazono)chroman-2,4-dione (**4a**)

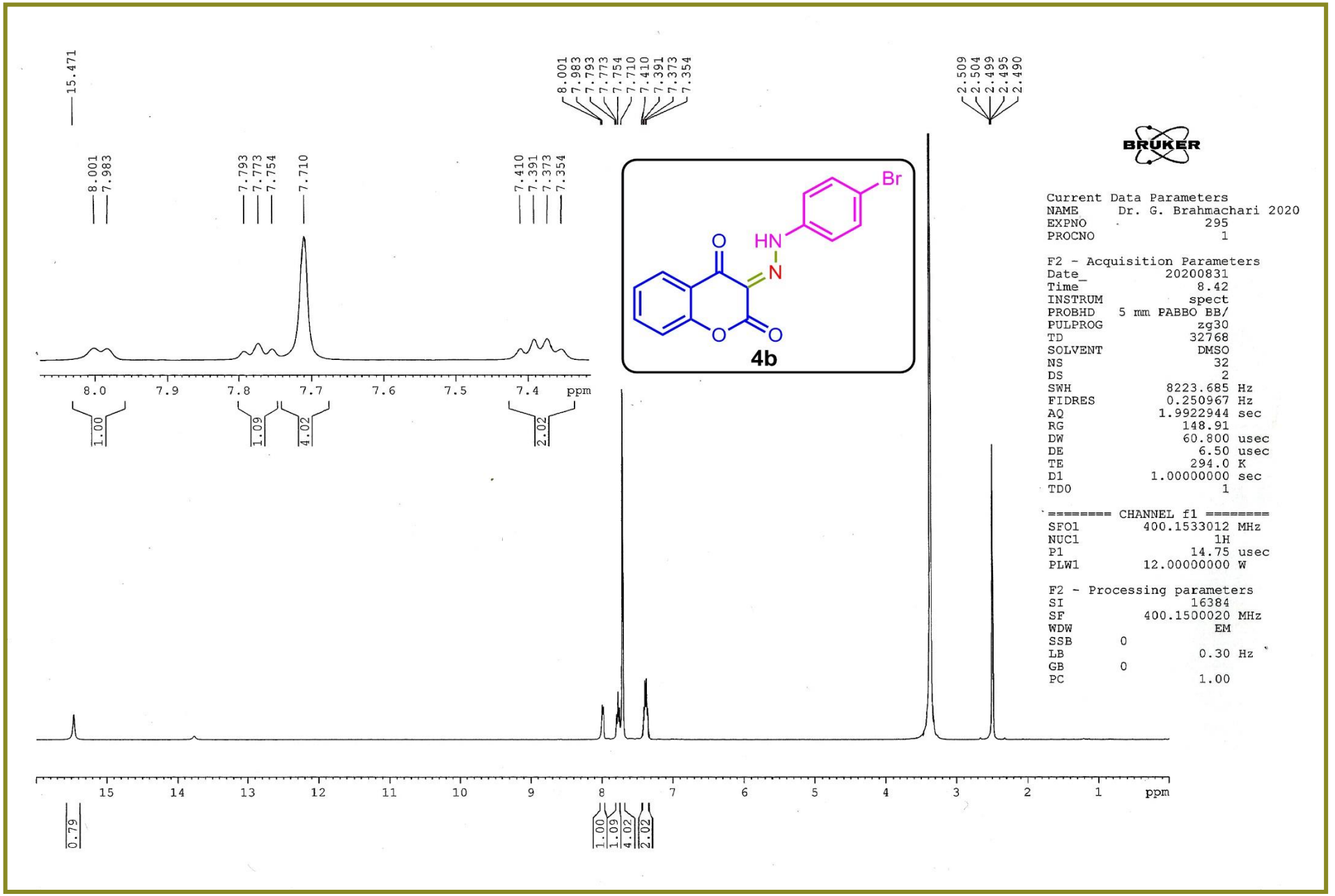



Figure S5. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-bromophenyl)hydrazono)chroman-2,4-dione (**4b**)

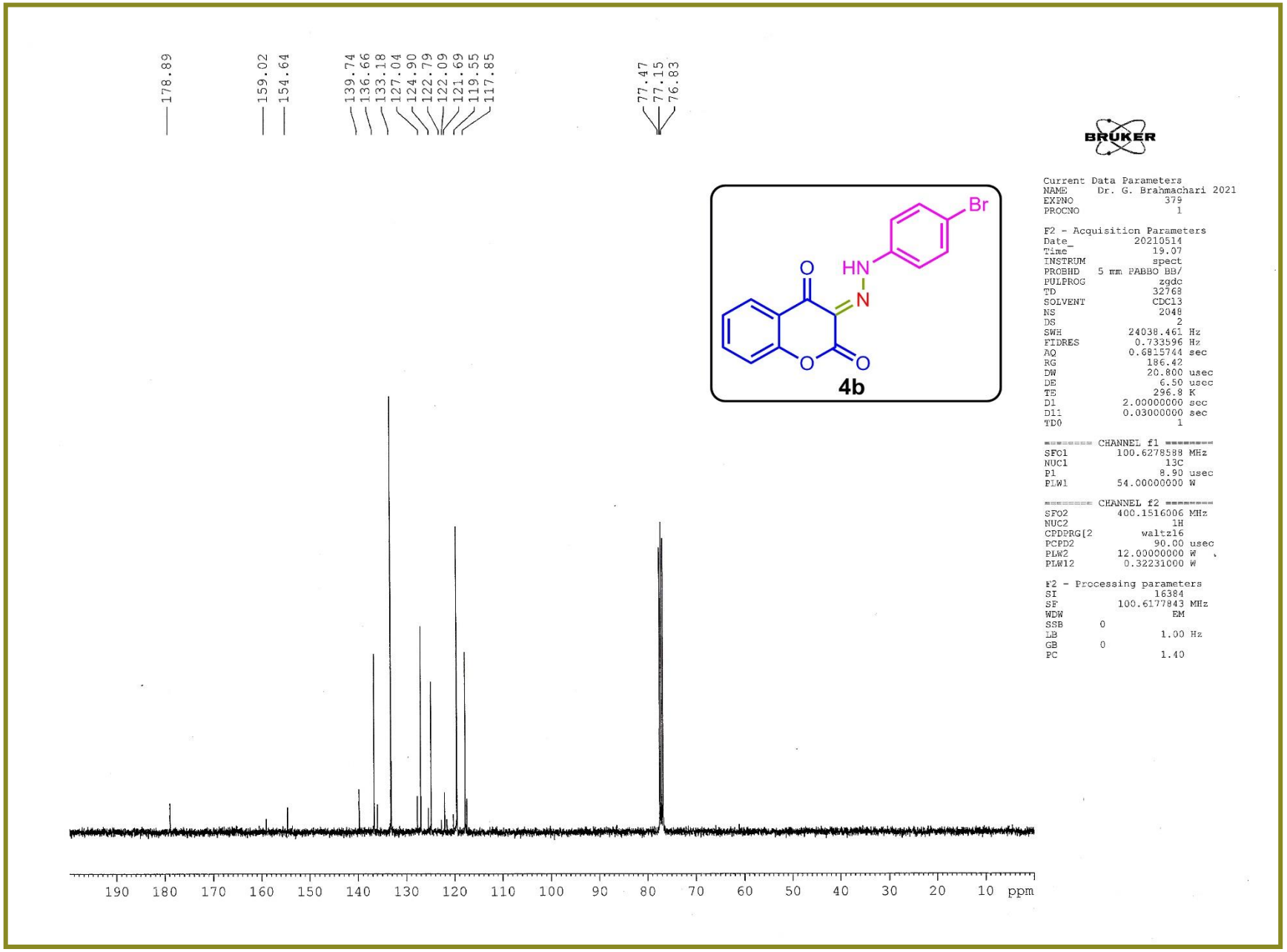



Figure S6. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-bromophenyl)hydrazono)chroman-2,4-dione (**4b**)

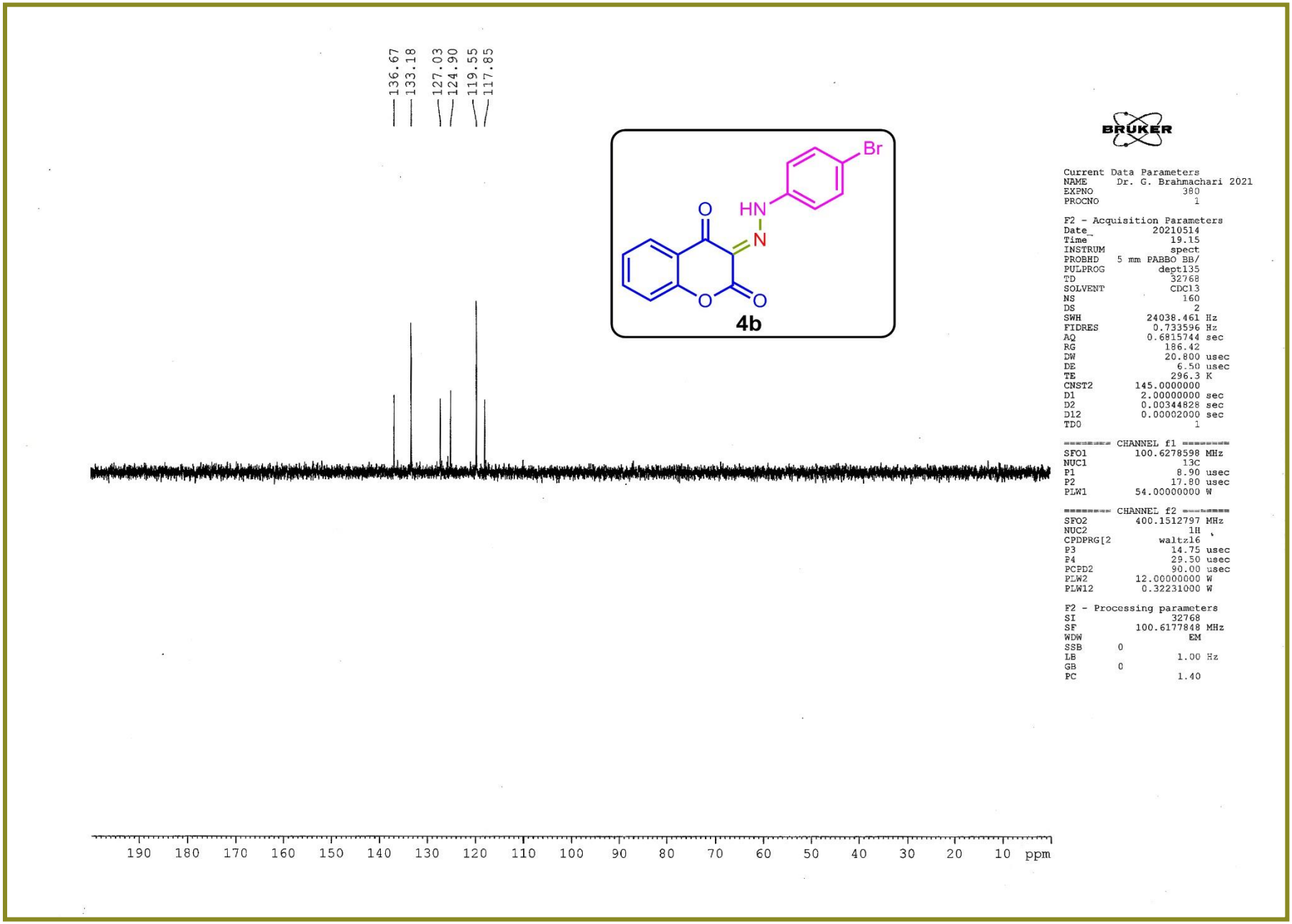



Figure S7. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-bromophenyl)hydrazono)chroman-2,4-dione (**4b**)

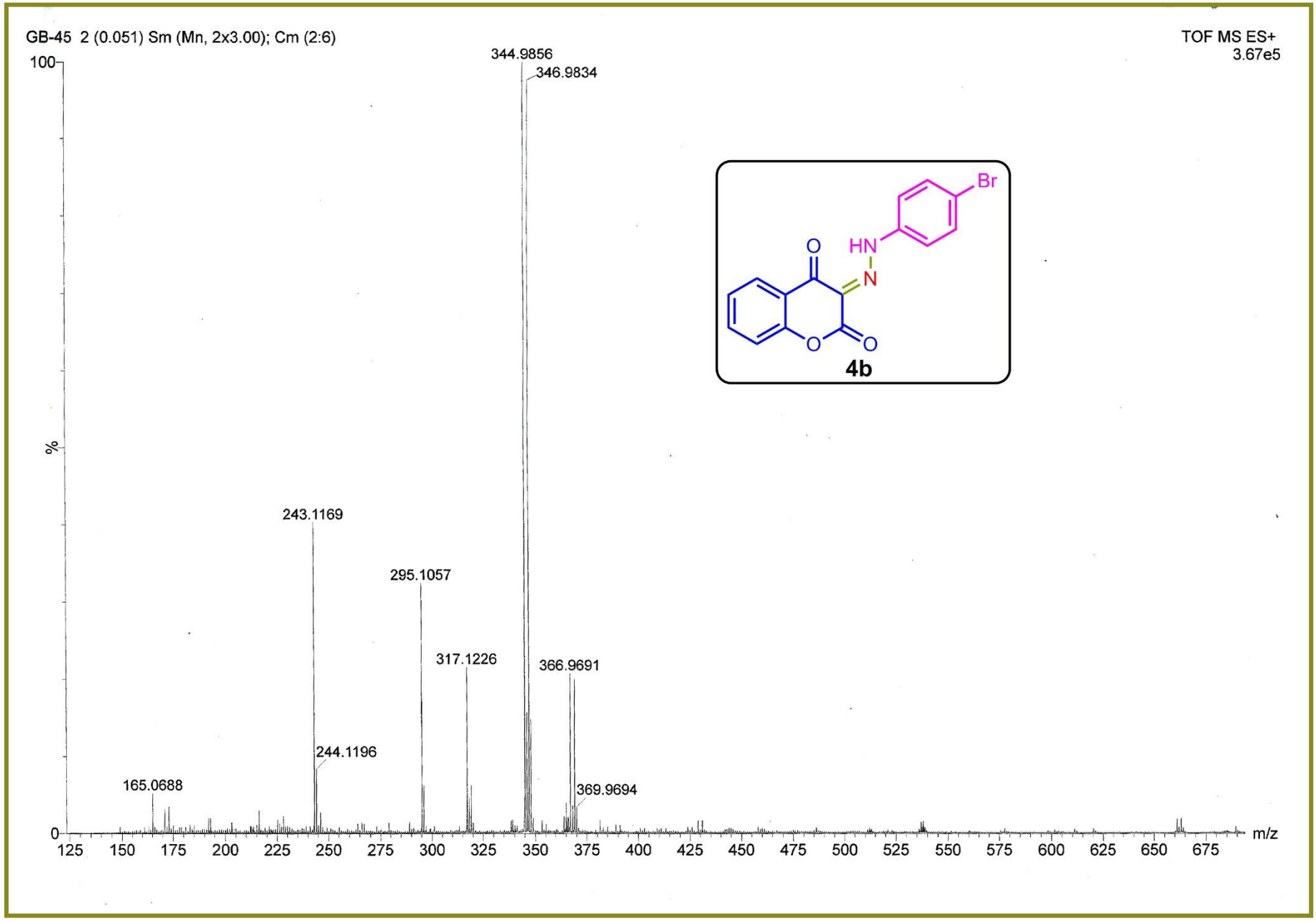



Figure S8. Mass spectra of (*E*)-3-(2-(4-bromophenyl)hydrazono)chroman-2,4-dione (**4b**)

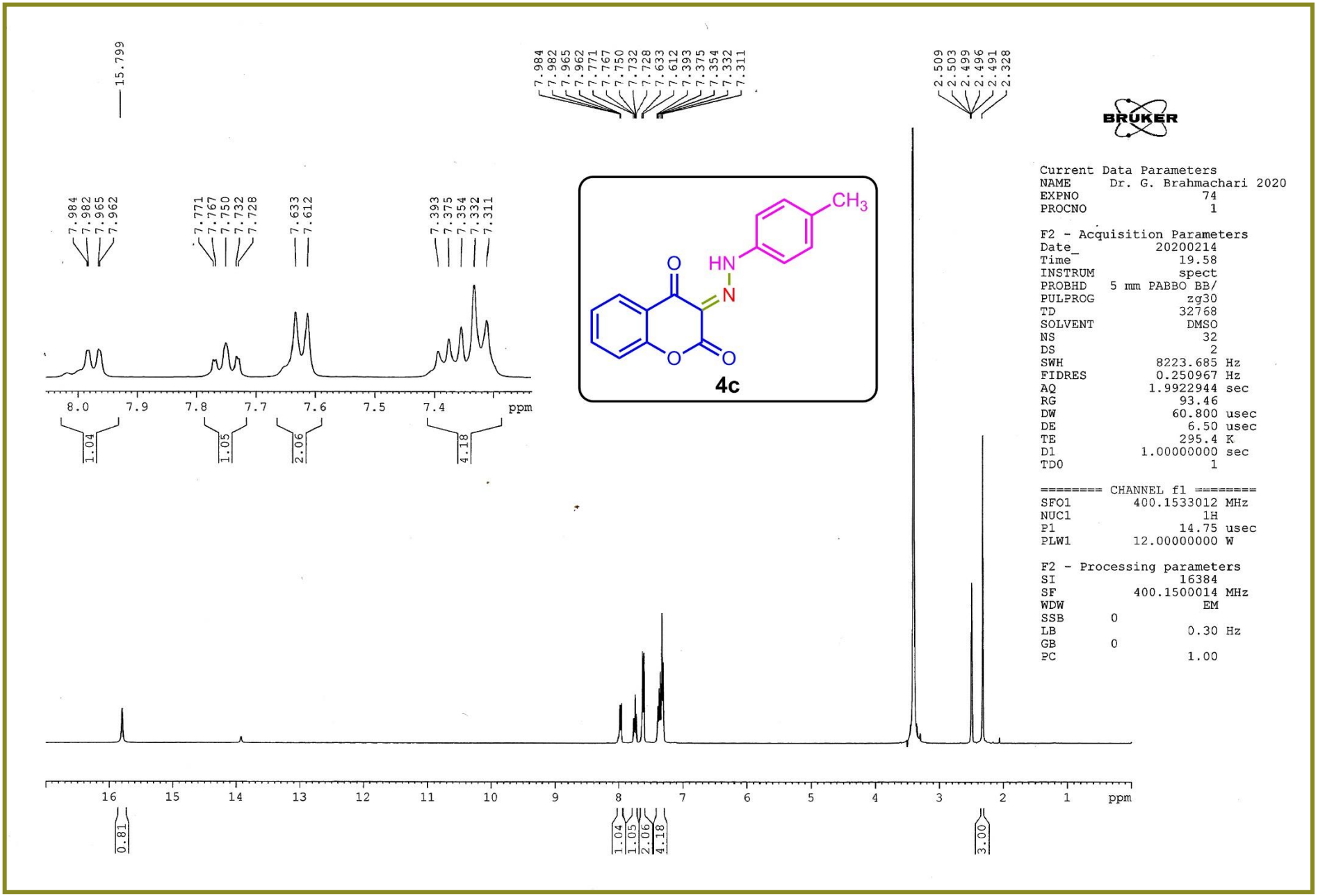



Figure S9. $^{1}$H-NMR spectrum of (*E*)-3-(2-(*p*-tolyl)hydrazono)chroman-2,4-dione (**4c**)

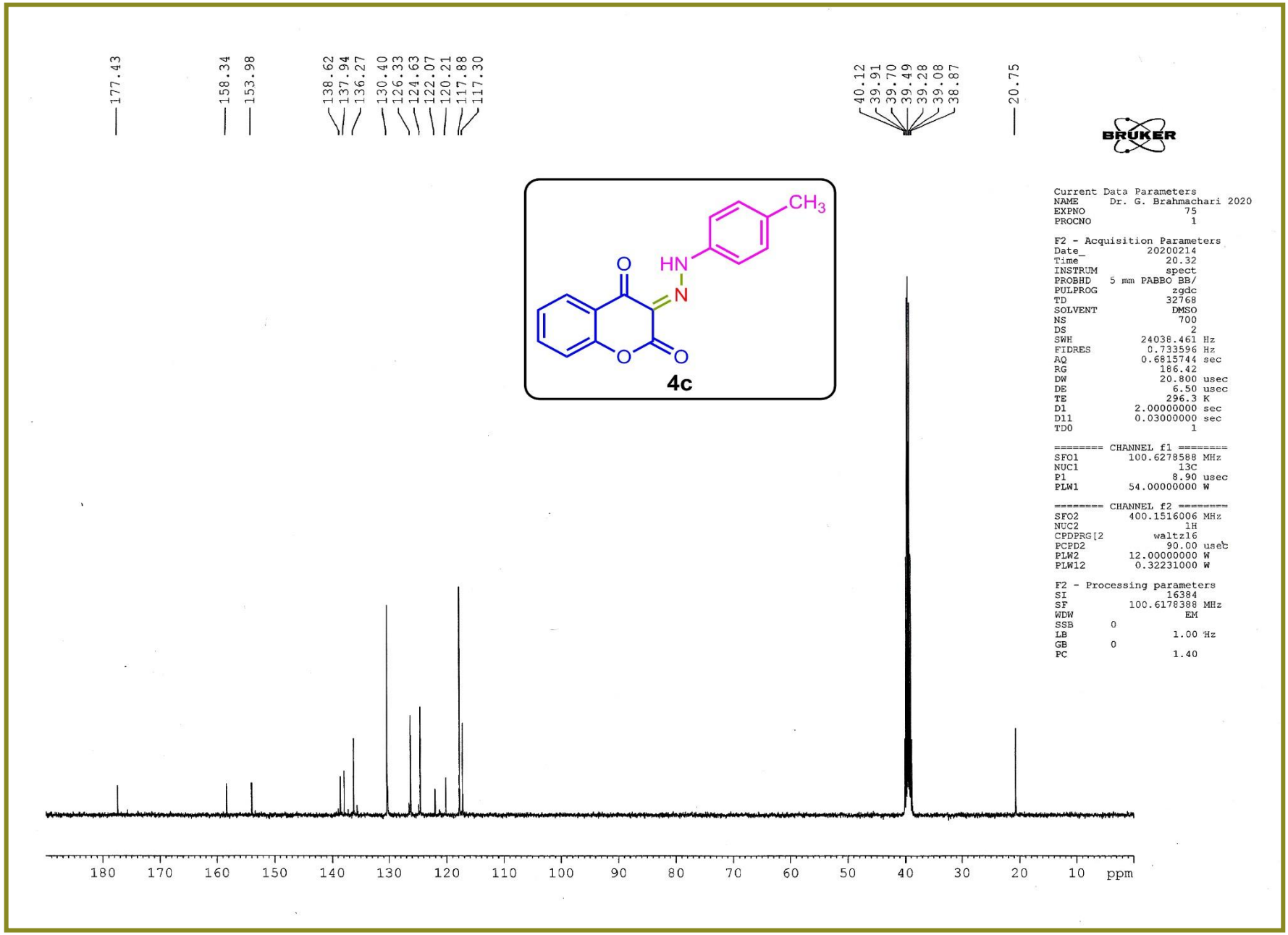



Figure S10. $^{13}$C-NMR spectrum of (*E*)-3-(2-(*p*-tolyl)hydrazono)chroman-2,4-dione (**4c**)

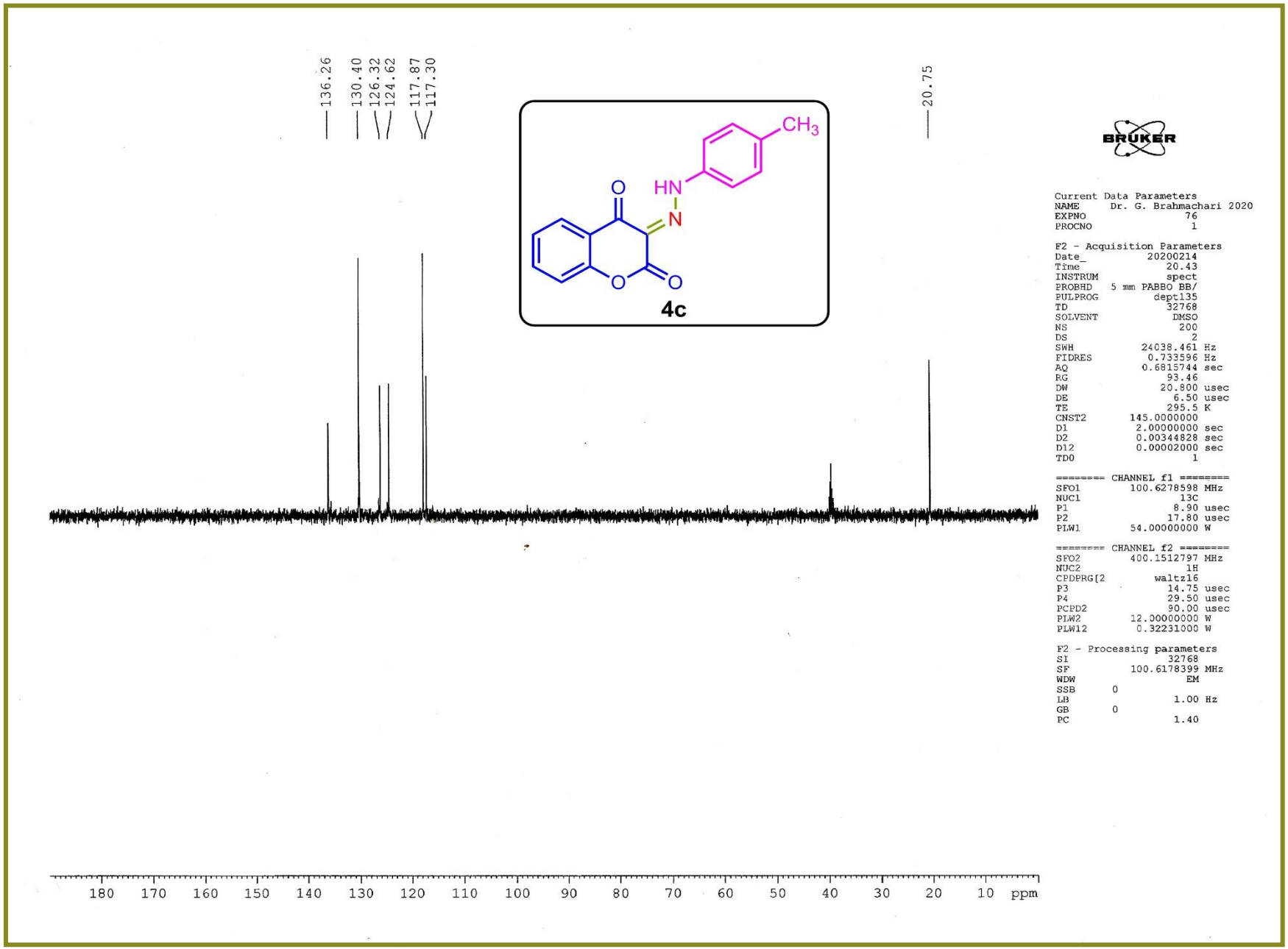



Figure S11. DEPT-135 NMR spectrum of (*E*)-3-(2-(*p*-tolyl)hydrazono)chroman-2,4-dione (**4c**)

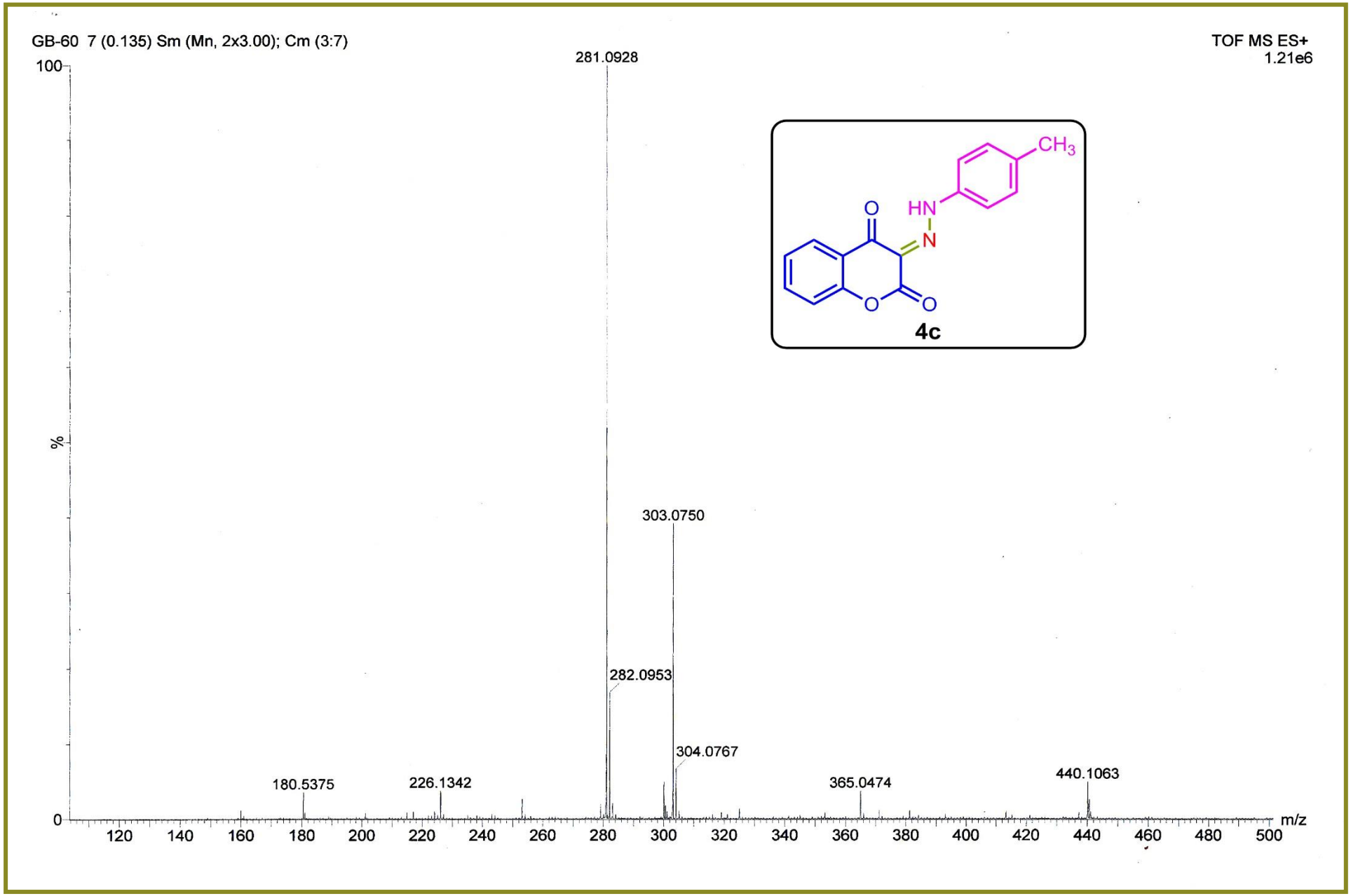



Figure S12. Mass spectra of (*E*)-3-(2-(*p*-tolyl)hydrazono)chroman-2,4-dione (**4c**)

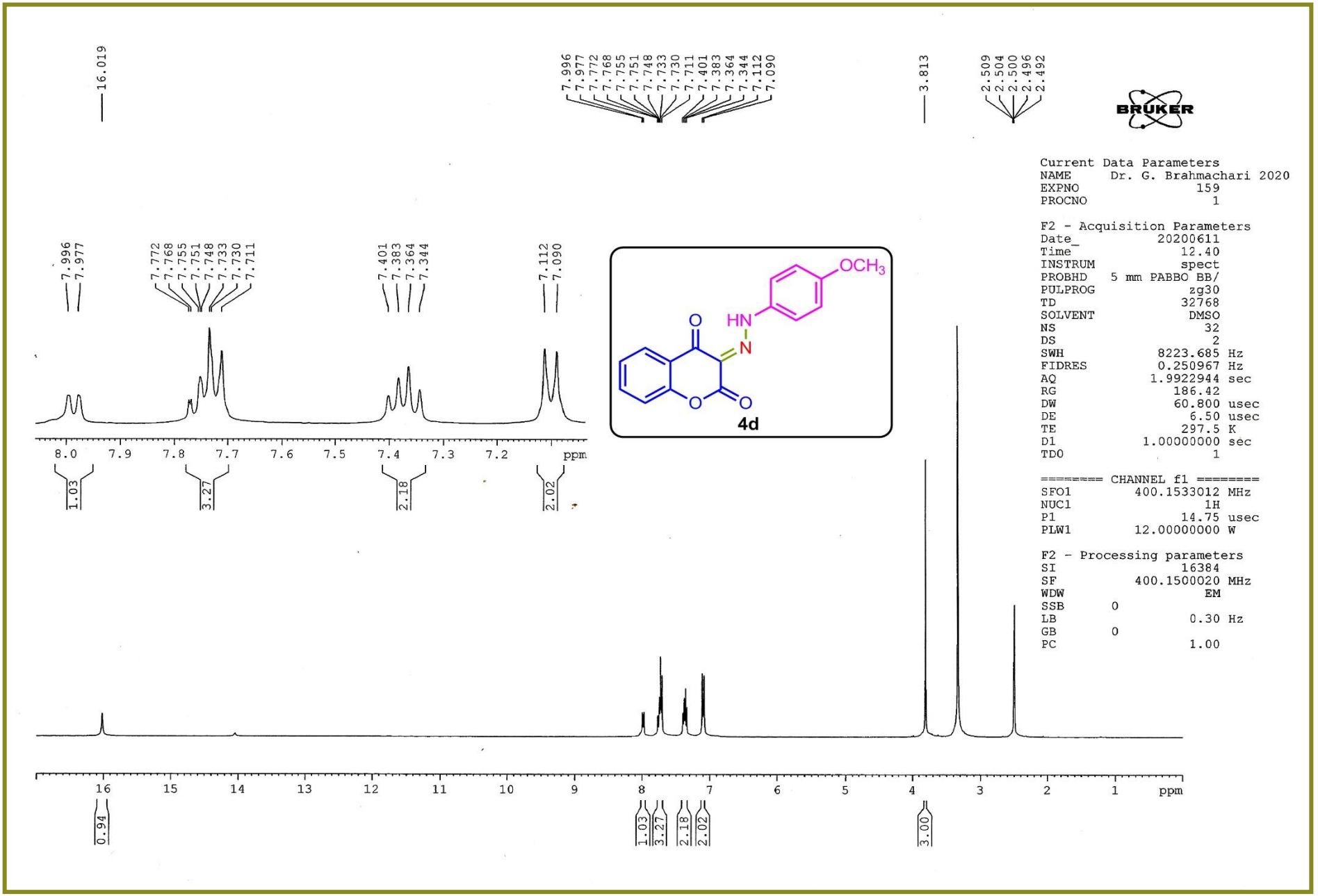



Figure S13. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4d**)

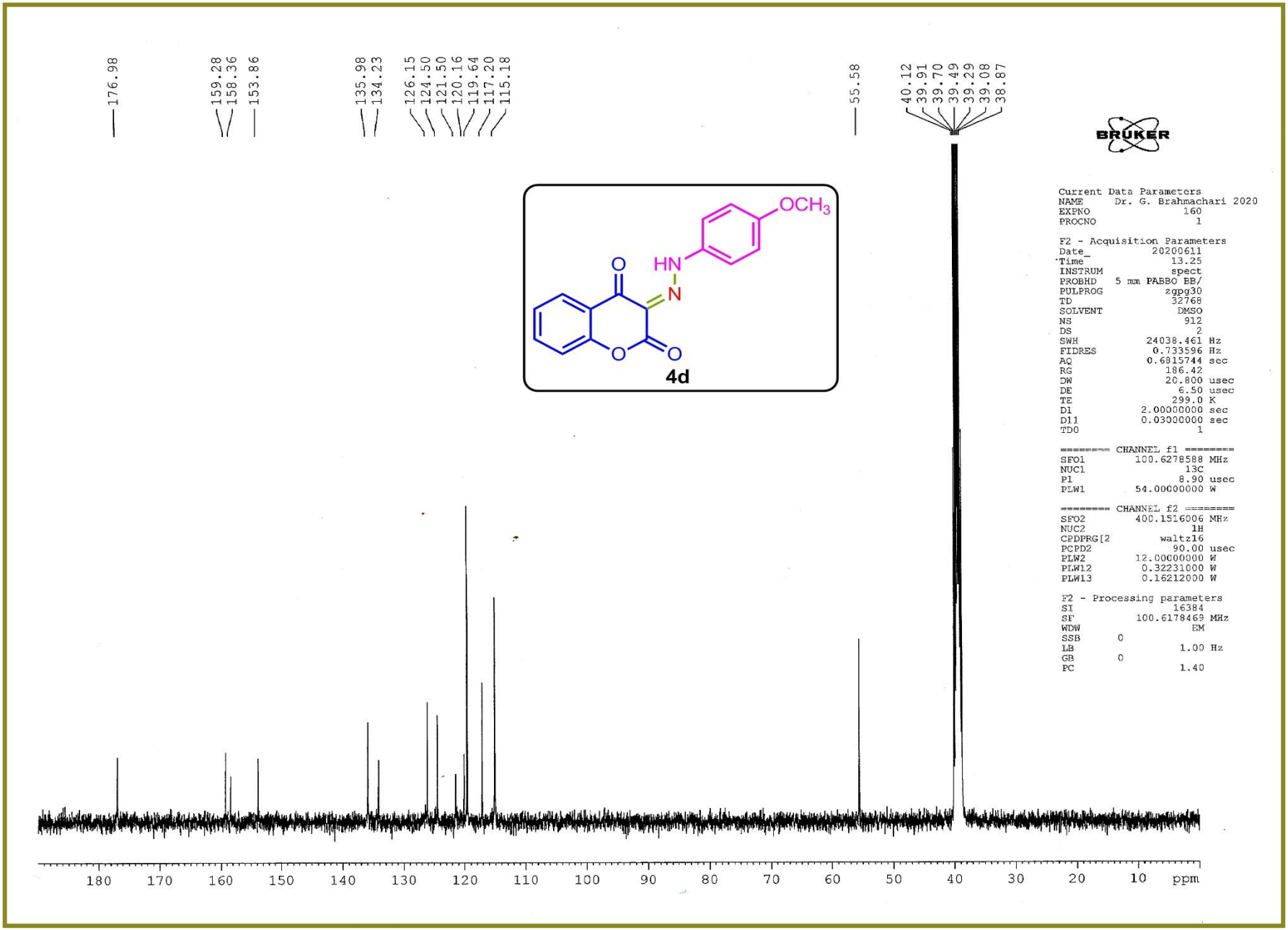



Figure S14. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4d**)

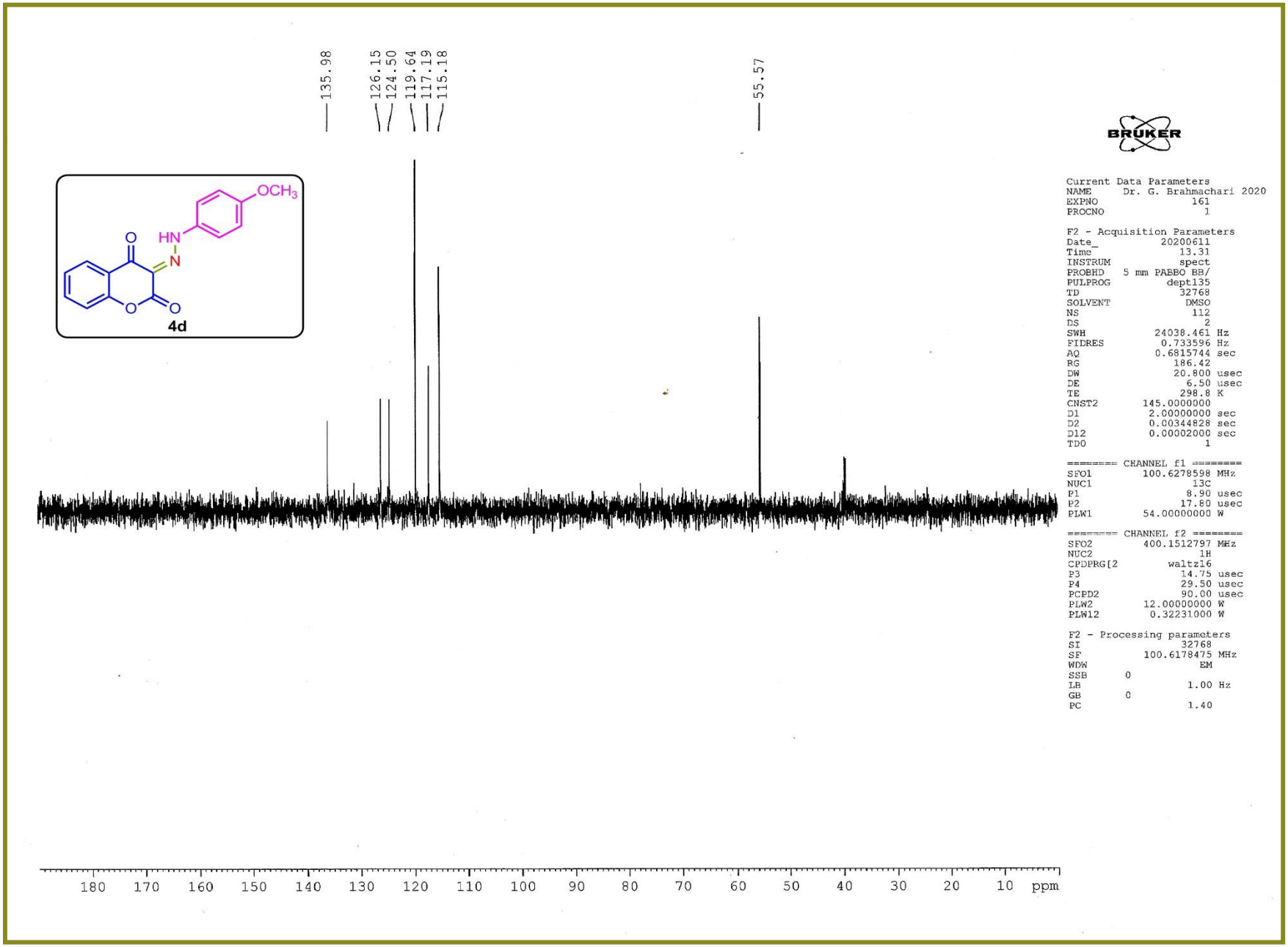



Figure S15. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4d**)

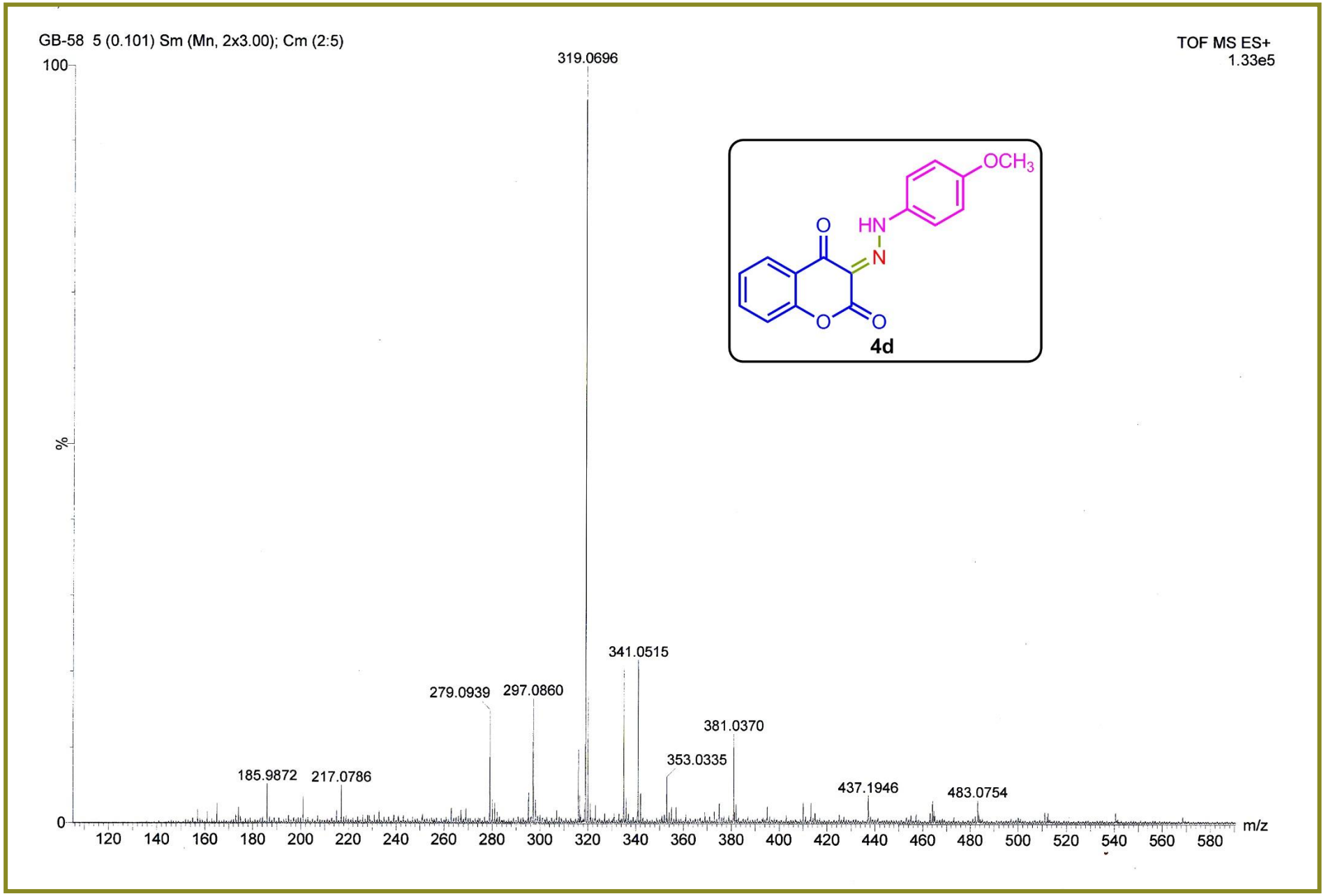



Figure S16. Mass spectra of (*E*)-3-(2-(4-methoxyphenyl)hydrazono)chroman-2,4-dione (**4d**)

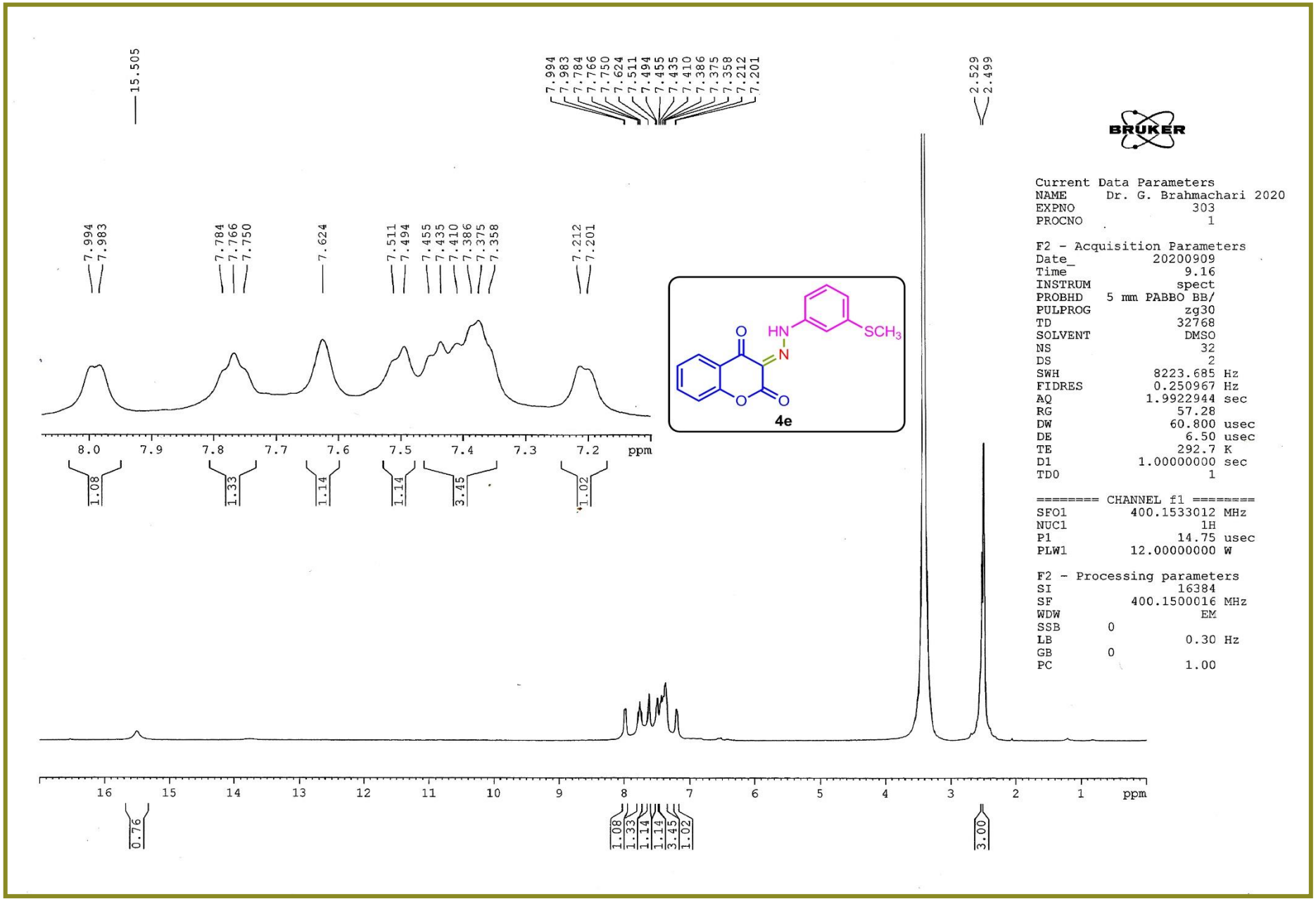



Figure S17. $^{1}$H-NMR spectrum of (*E*)-3-(2-(3-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4e**)

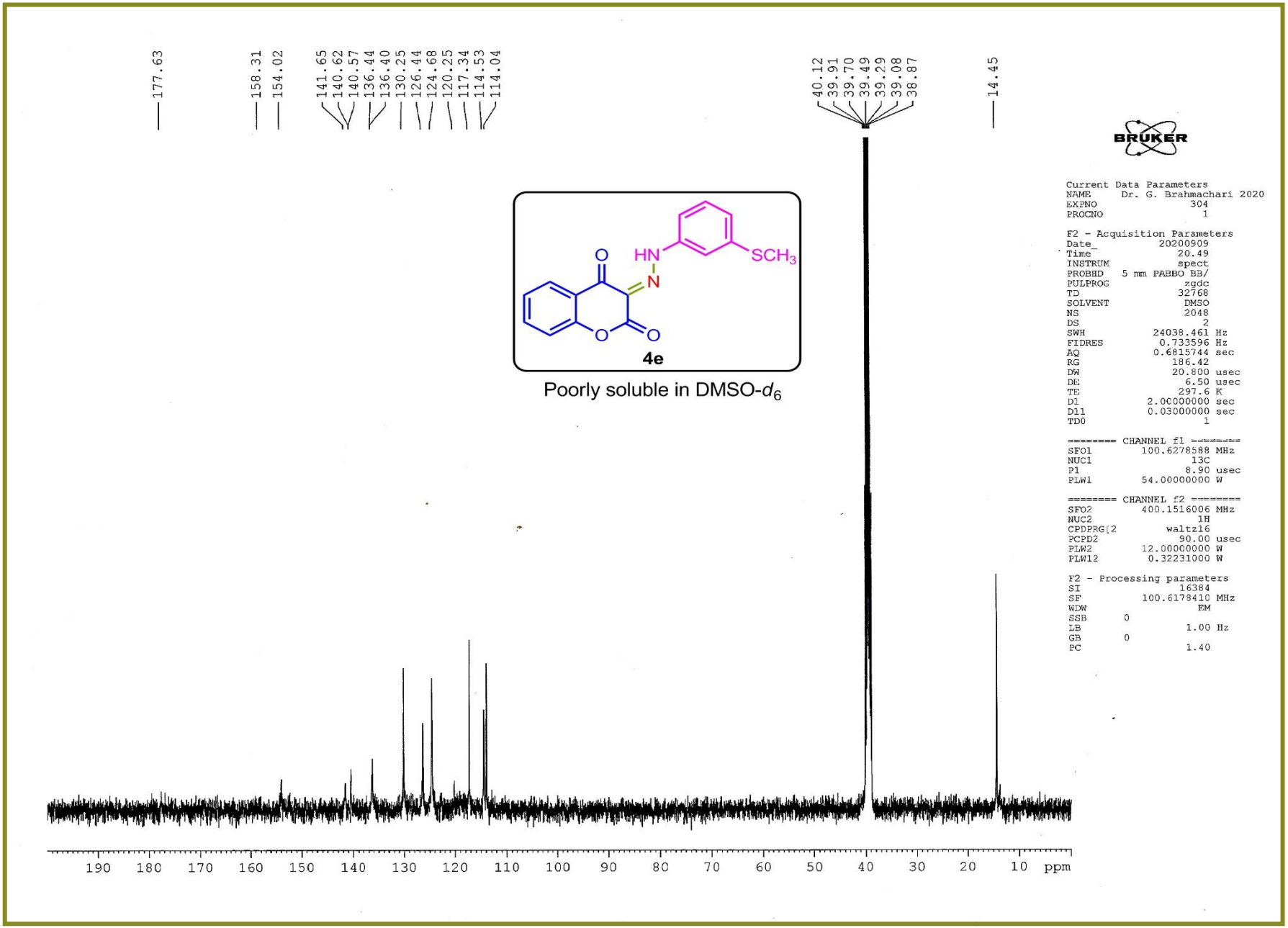



Figure S18. $^{13}$C-NMR spectrum of (*E*)-3-(2-(3-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4e**)

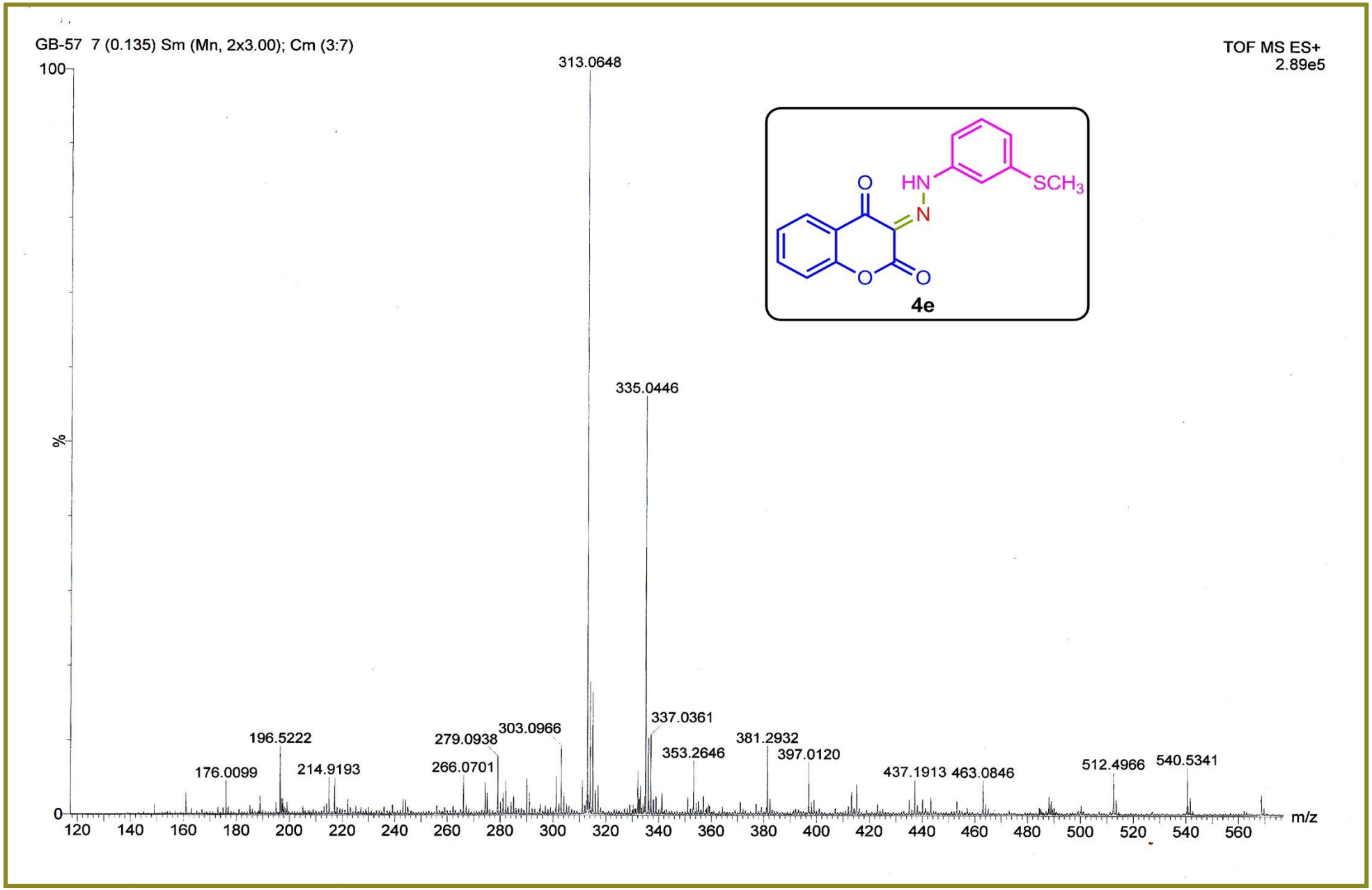



Figure S19. Mass spectra of (*E*)-3-(2-(3-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4e**)

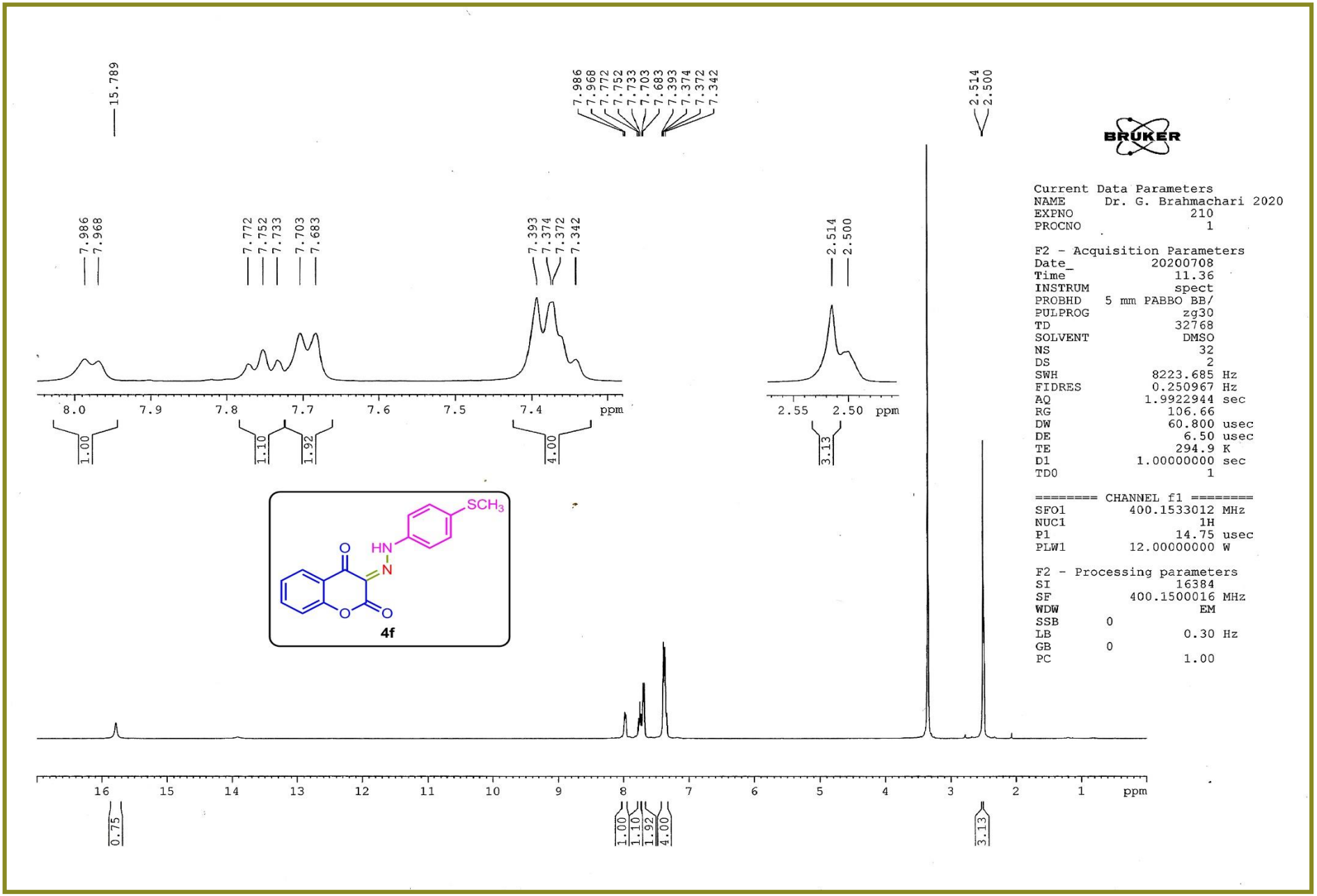



Figure S20. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4f**)

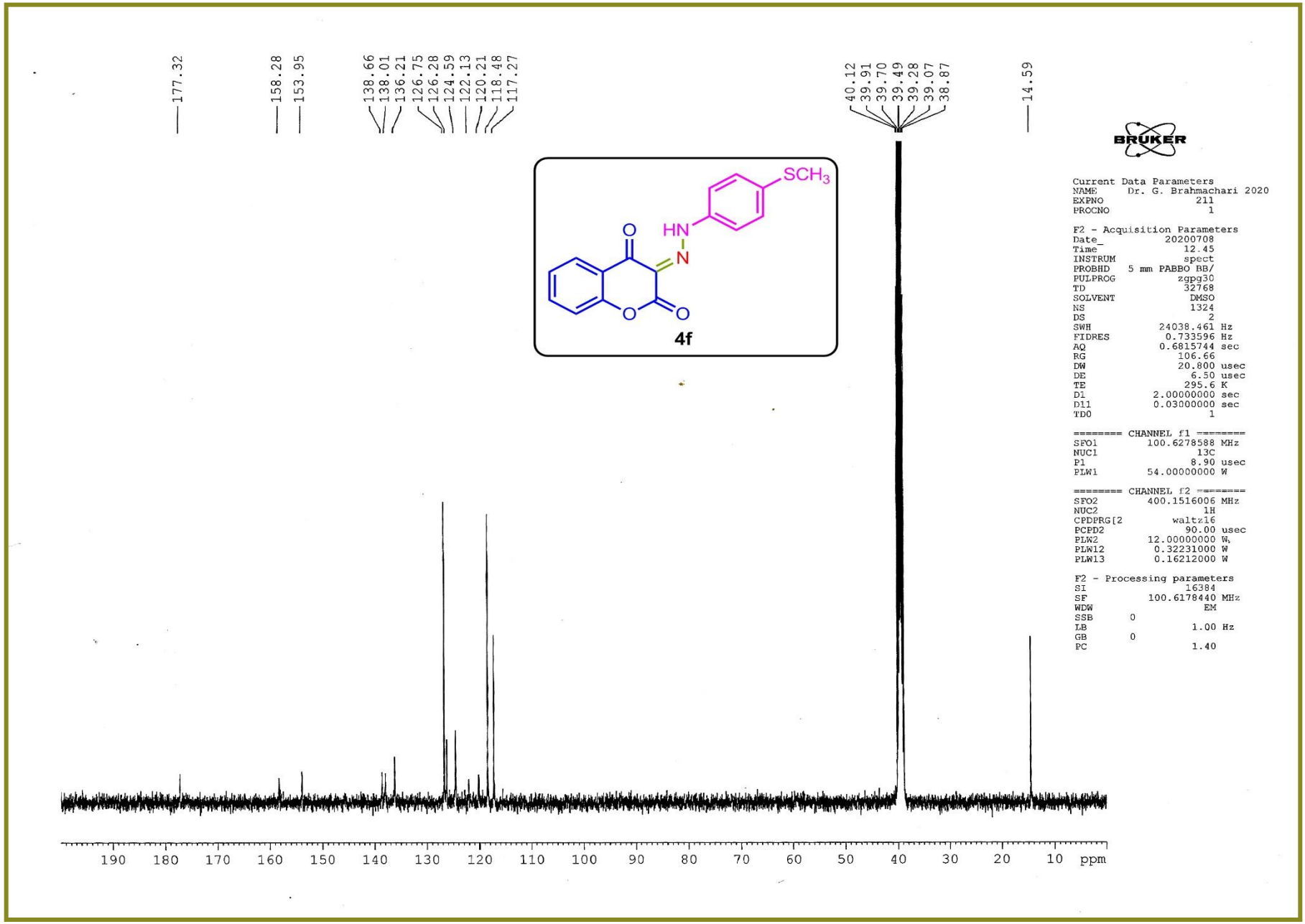



Figure S21. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4f**)

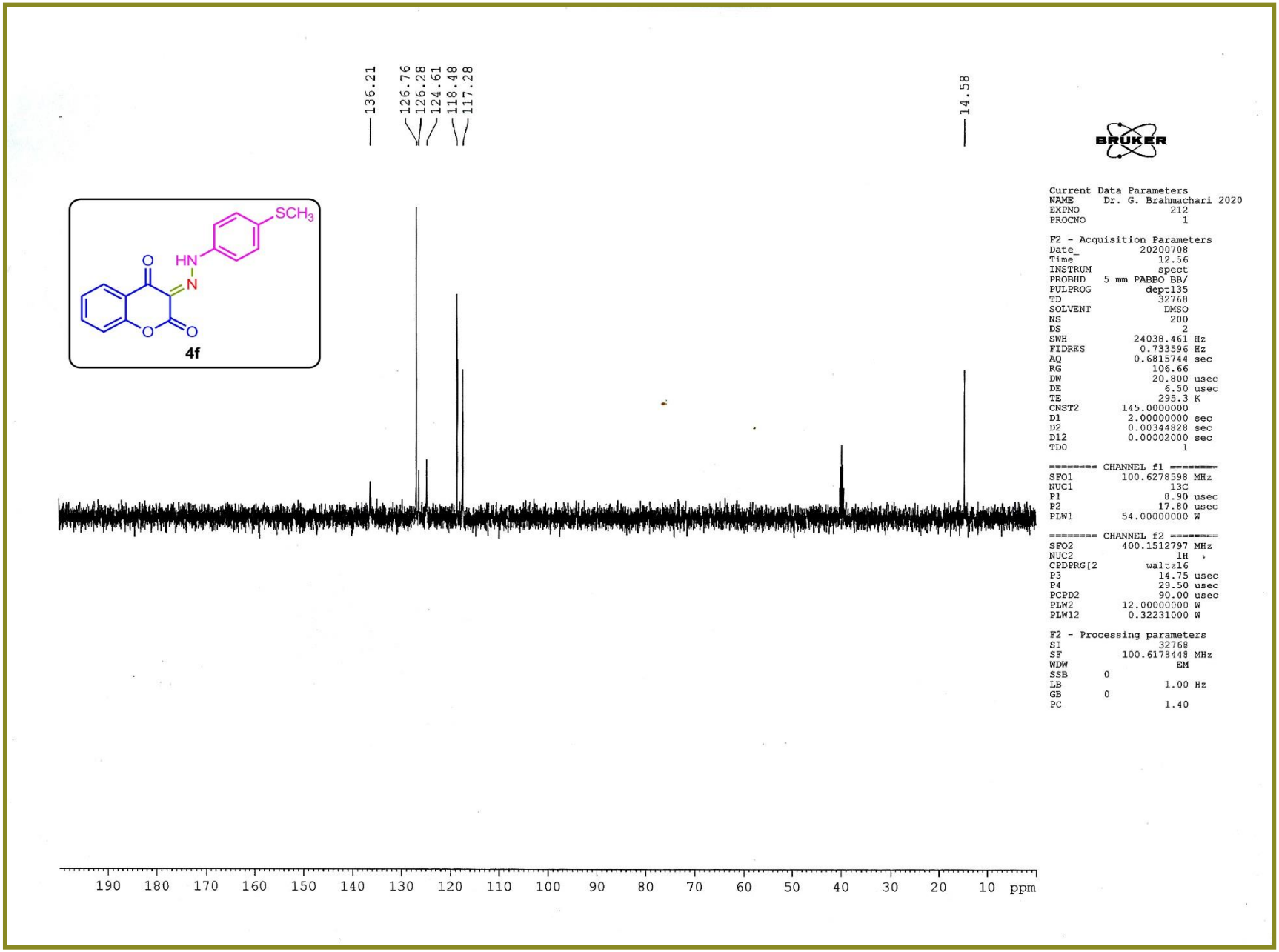



Figure S22. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4f**)

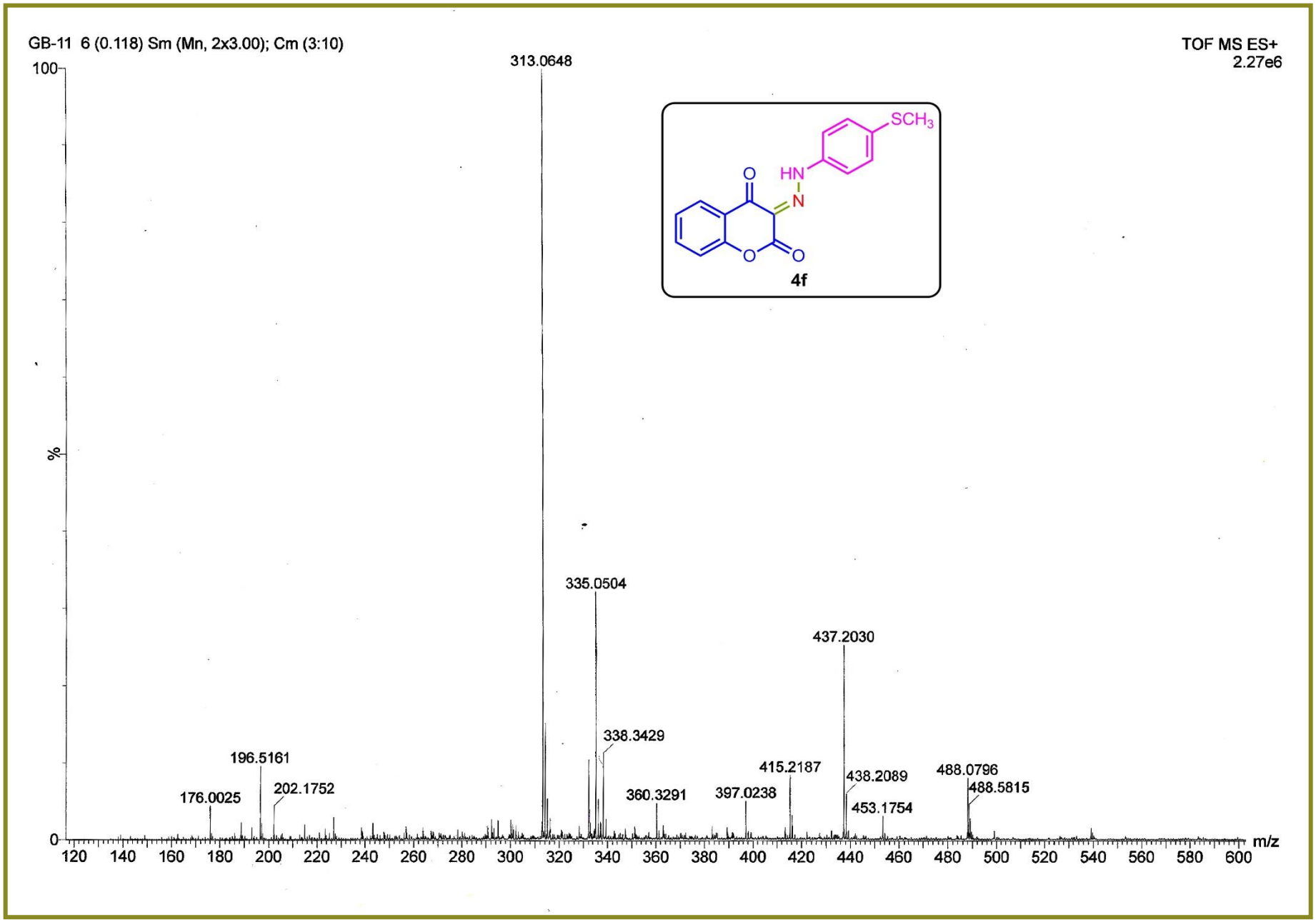



Figure S23. Mass spectra of (*E*)-3-(2-(4-(methylthio)phenyl)hydrazono)chroman-2,4-dione (**4f**)

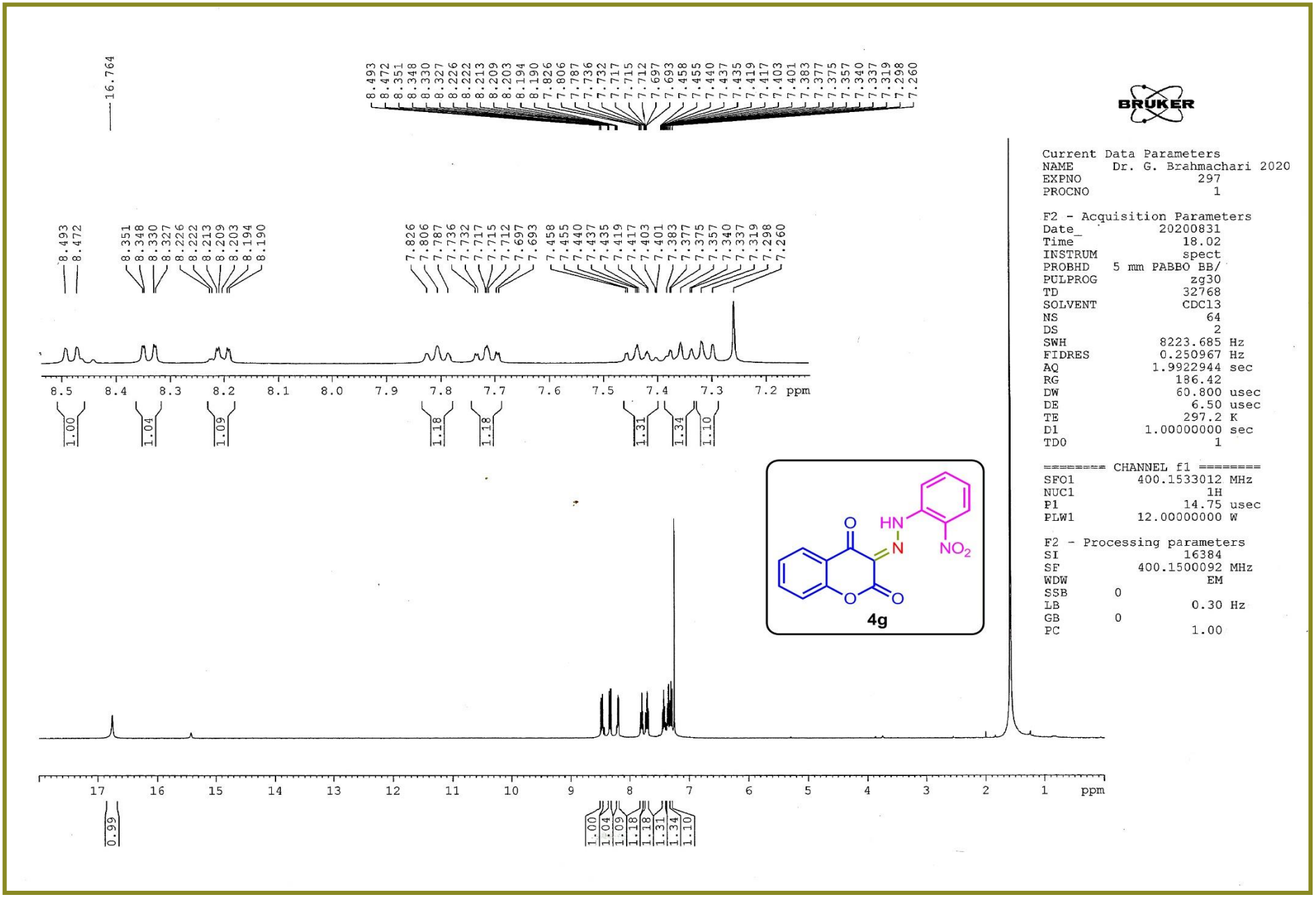



Figure S24. $^{1}$H-NMR spectrum of (*E*)-3-(2-(2-nitrophenyl)hydrazono)chroman-2,4-dione (**4g**)

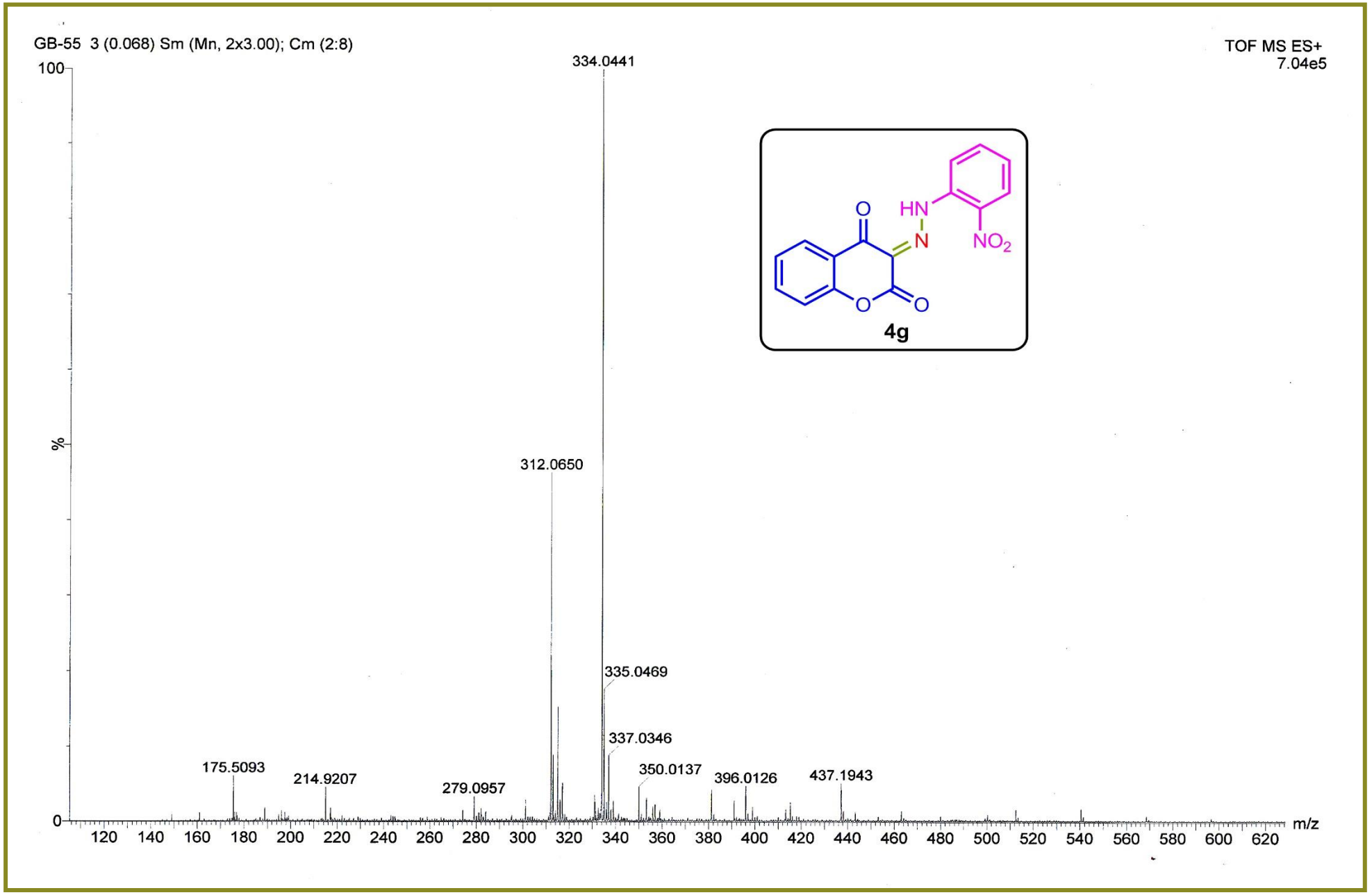



Figure S25. Mass spectra of (*E*)-3-(2-(2-nitrophenyl)hydrazono)chroman-2,4-dione (**4g**)

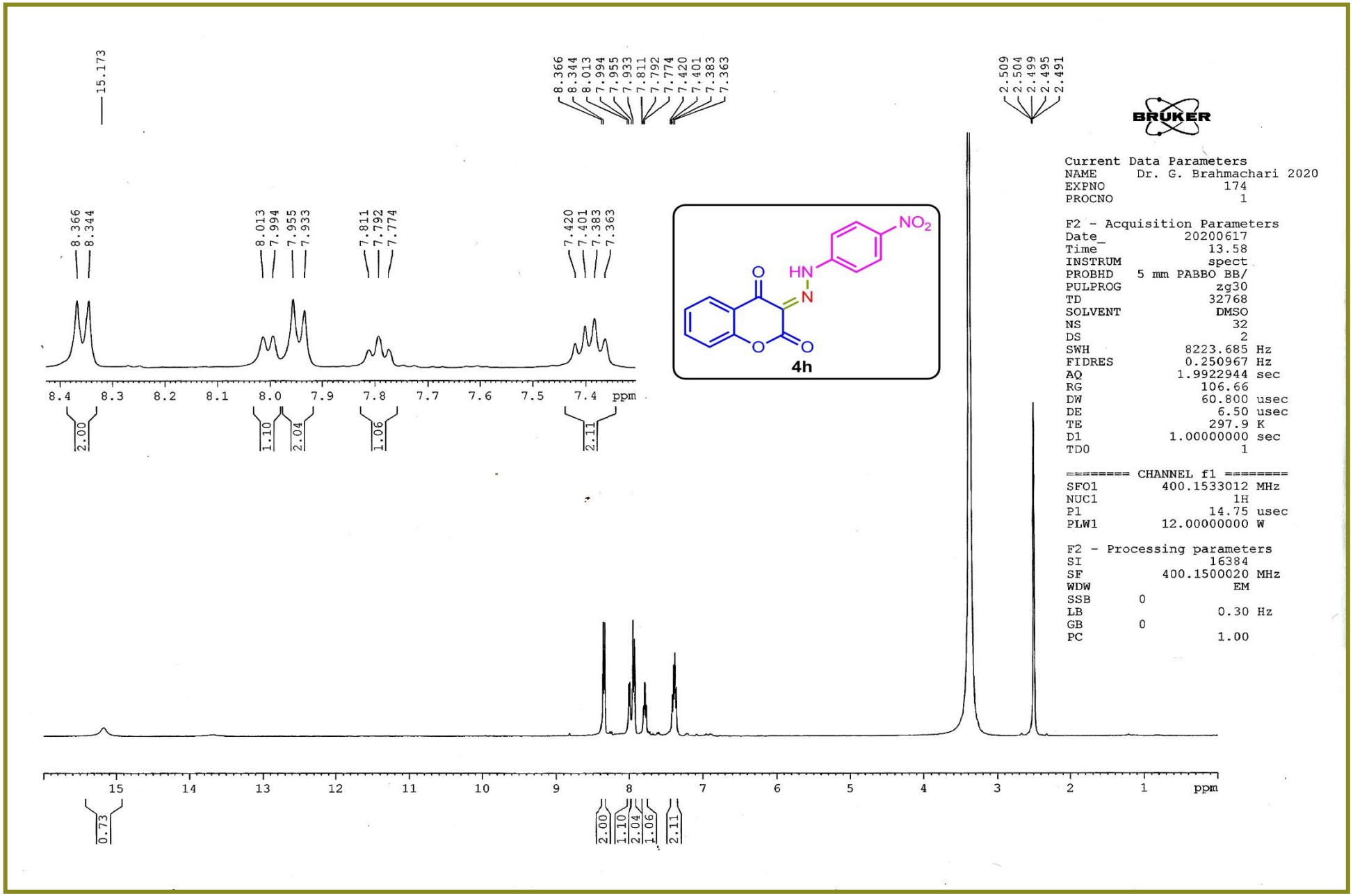



Figure S26. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-nitrophenyl)hydrazono)chroman-2,4-dione (**4h**)

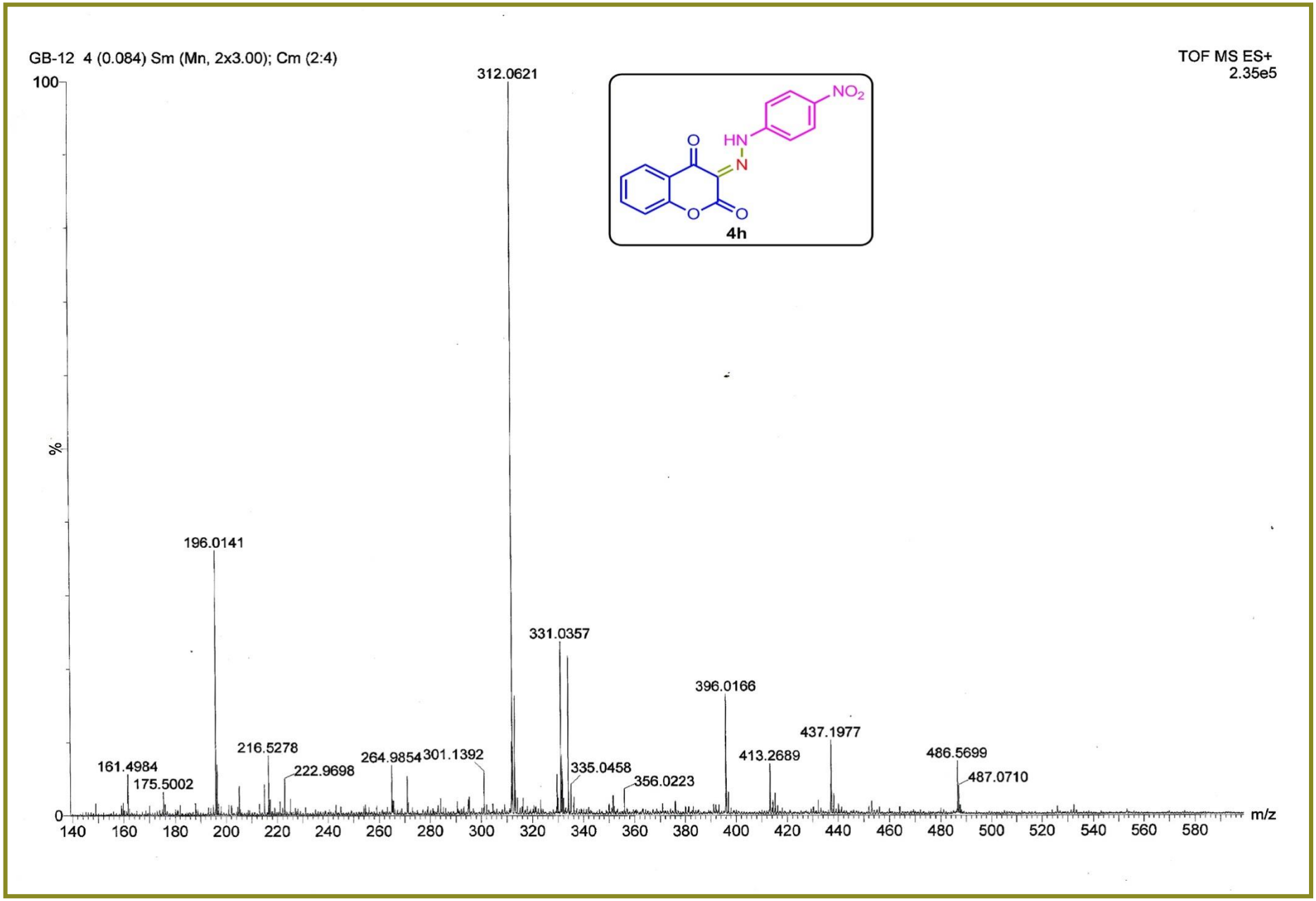



Figure S27. Mass spectra of (*E*)-3-(2-(4-nitrophenyl)hydrazono)chroman-2,4-dione (**4h**)

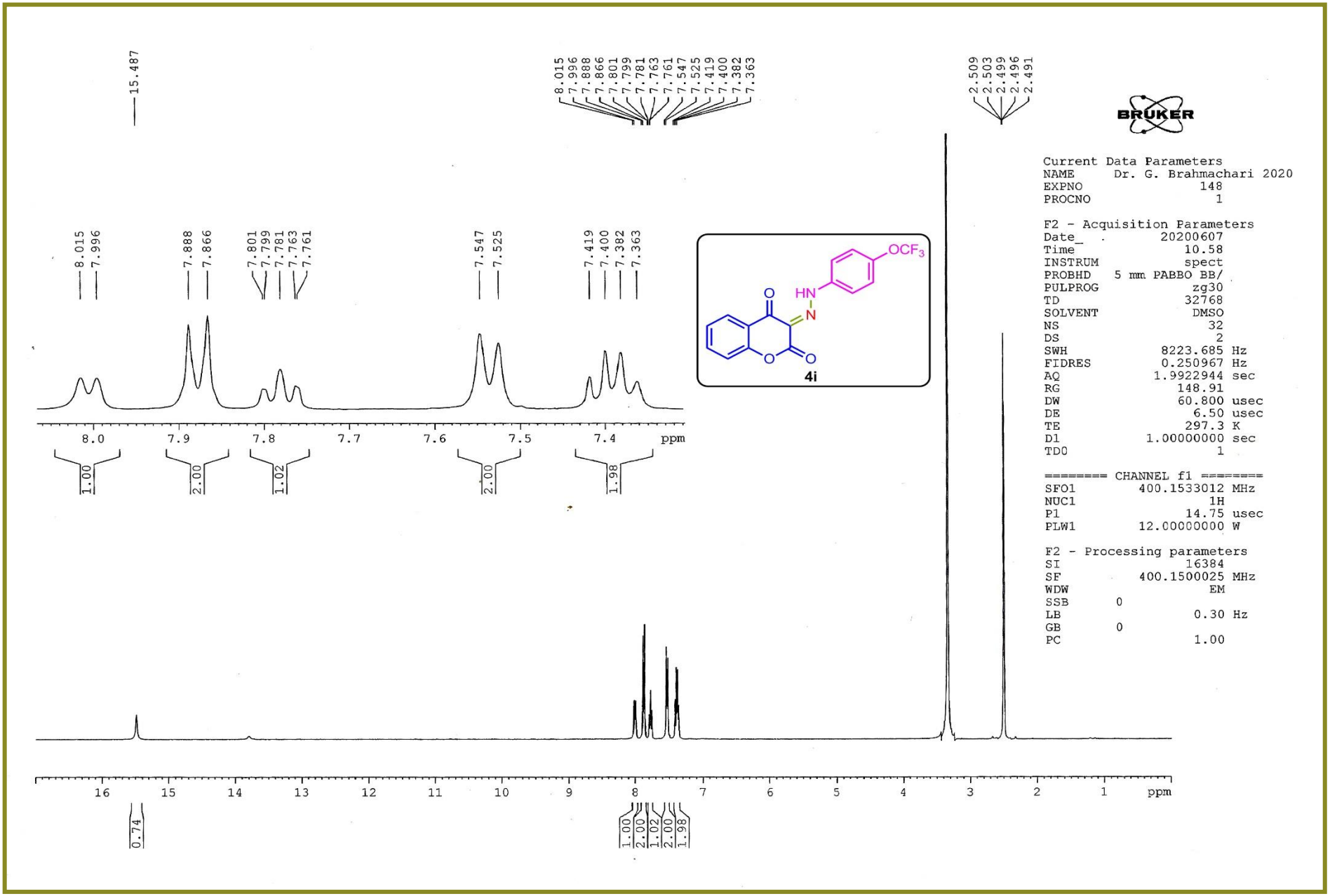



Figure S28. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**)

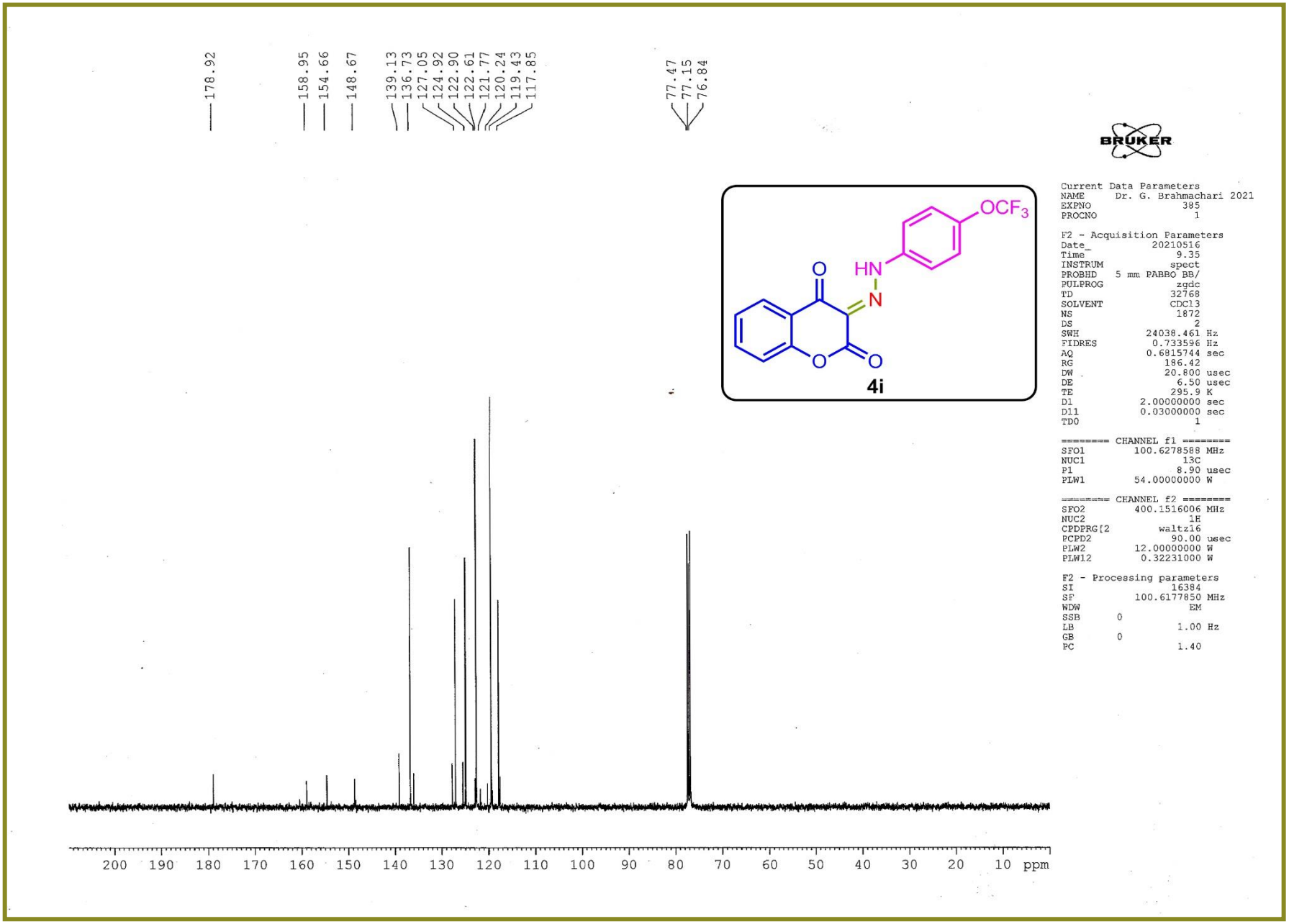



Figure S29. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**)

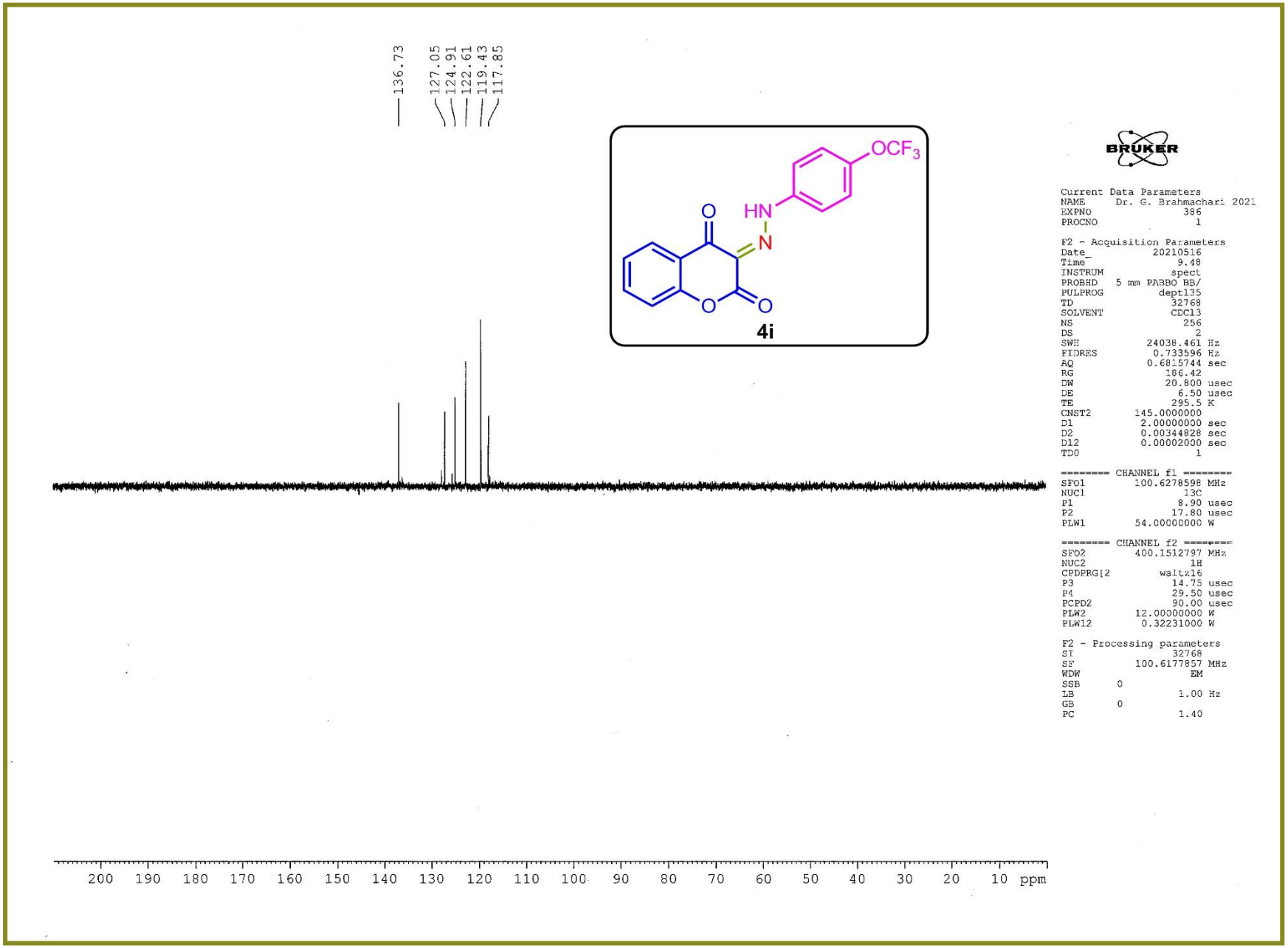



Figure S30. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**)

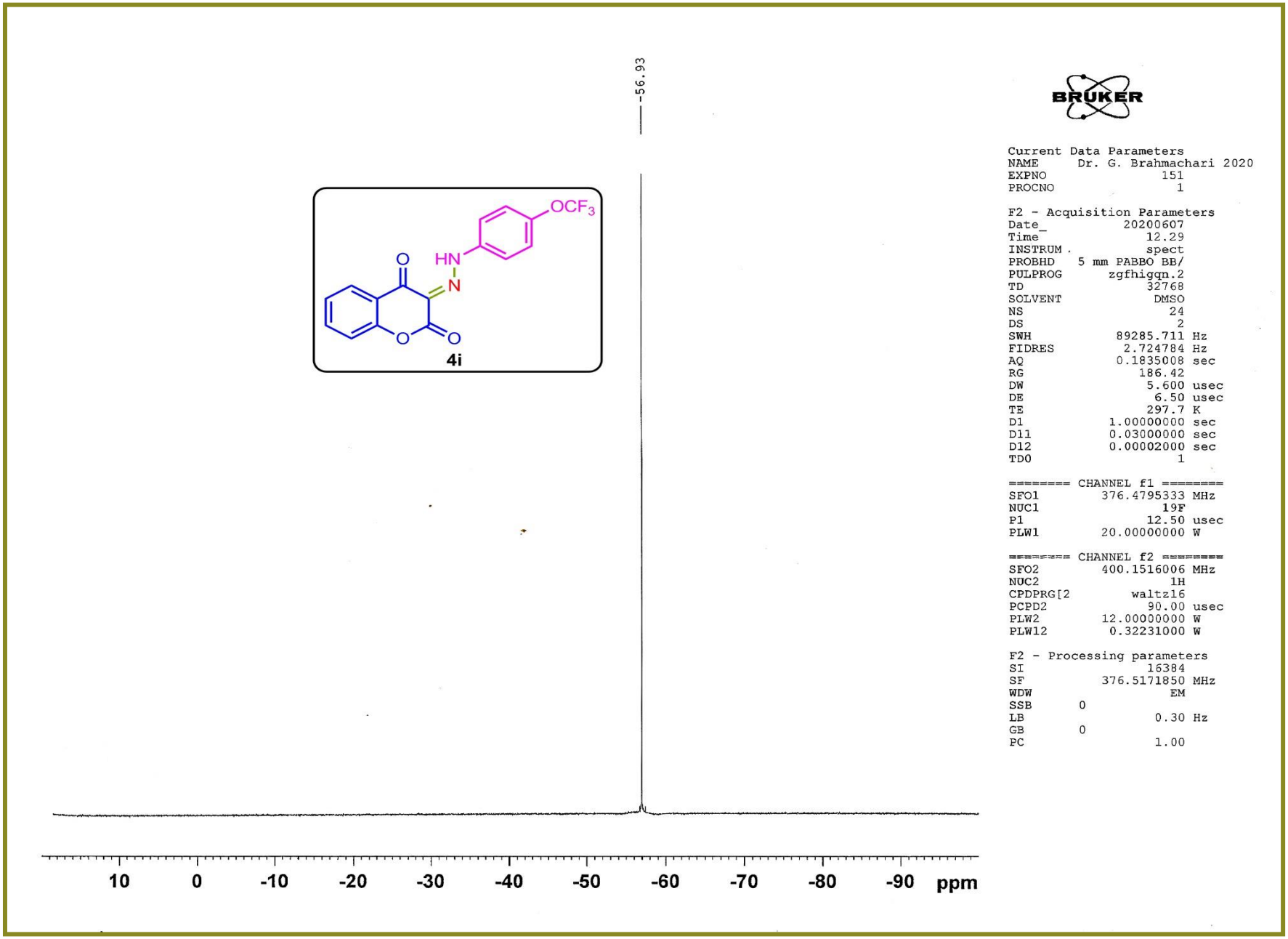



Figure S31. $^{19}$F NMR spectrum of (*E*)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**)

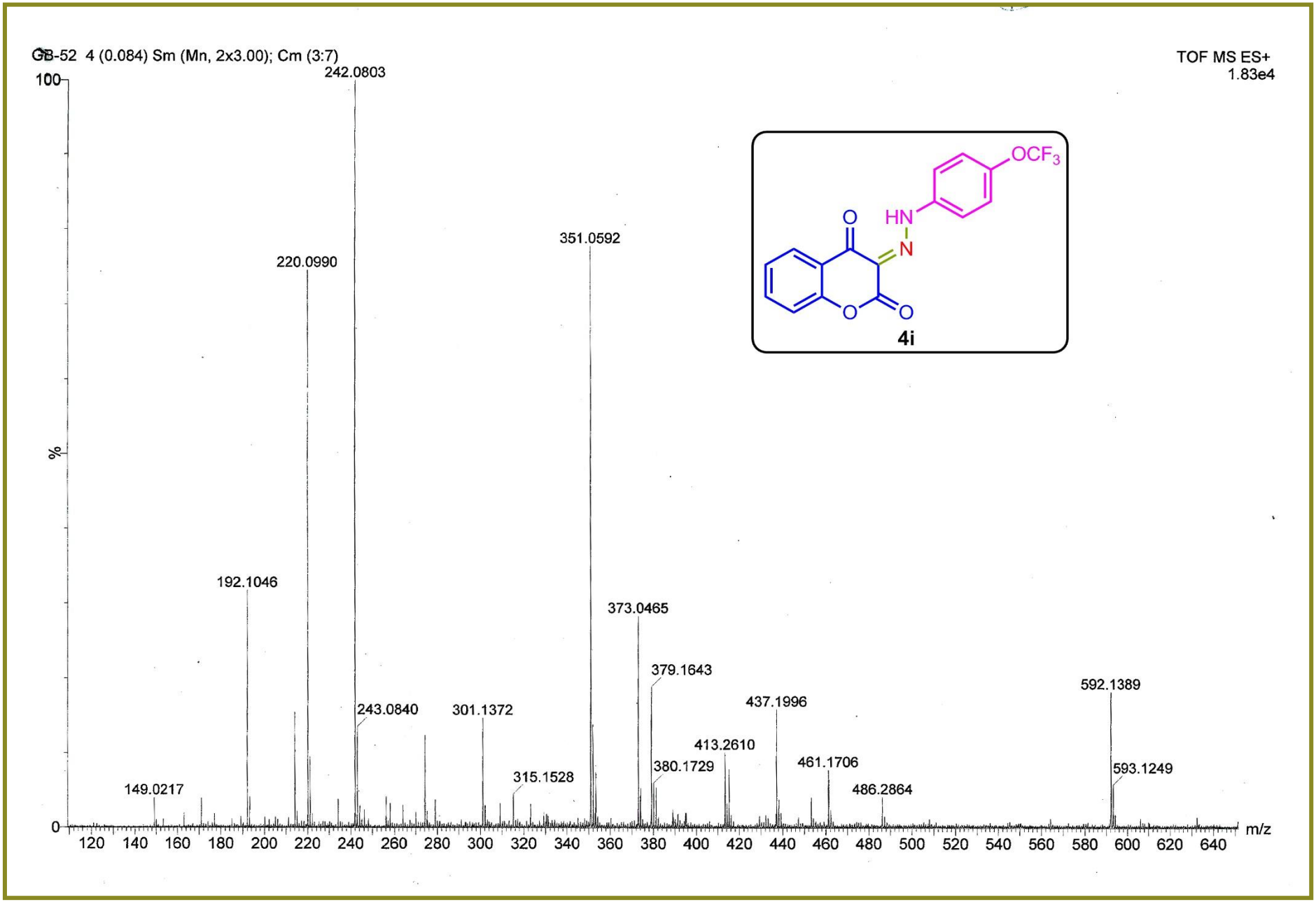



Figure S32. Mass spectra of (*E*)-3-(2-(4-(trifluoromethoxy)phenyl)hydrazono)chroman-2,4-dione (**4i**)

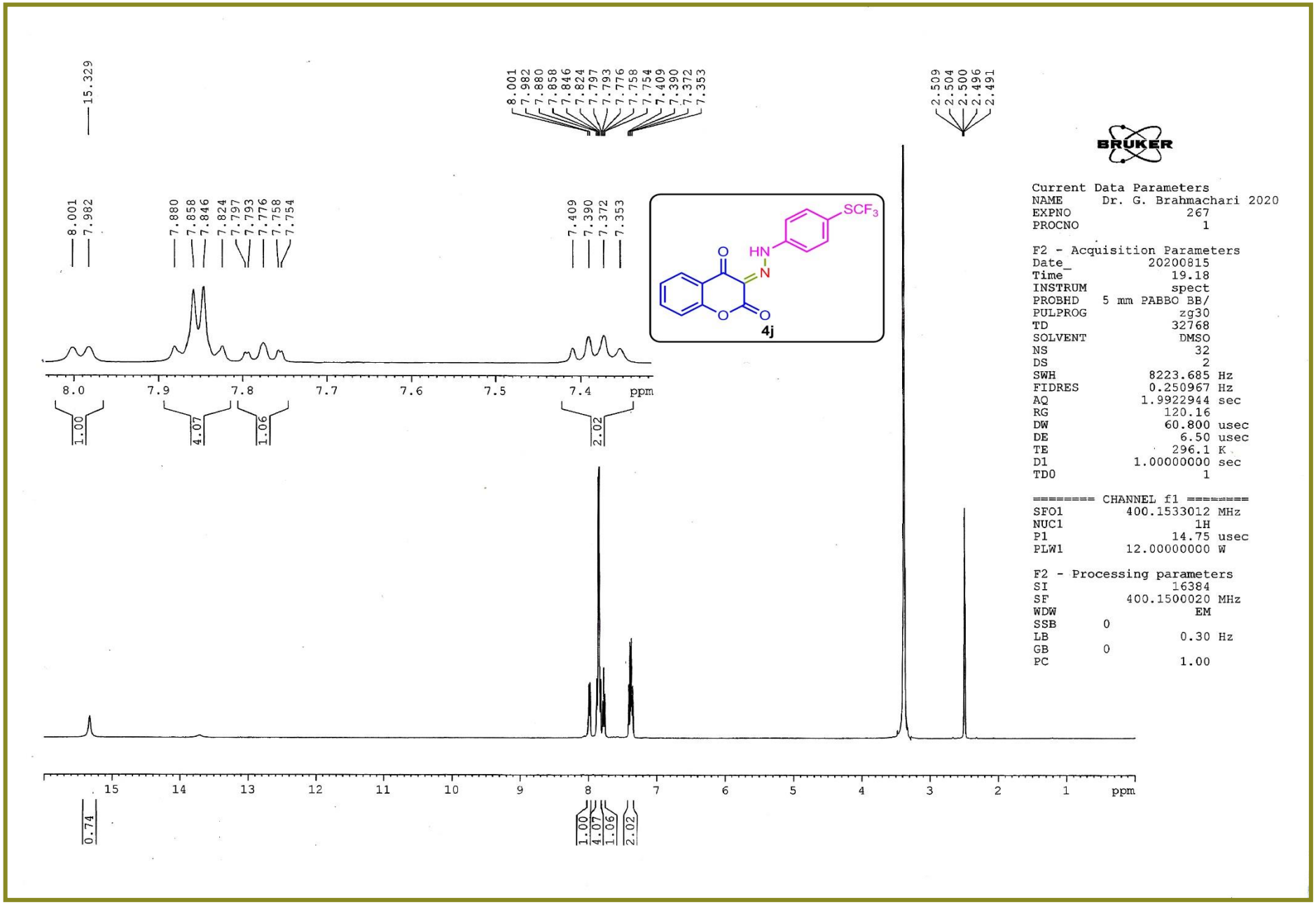



Figure S33. $^{1}$H-NMR spectrum of (*E*)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)

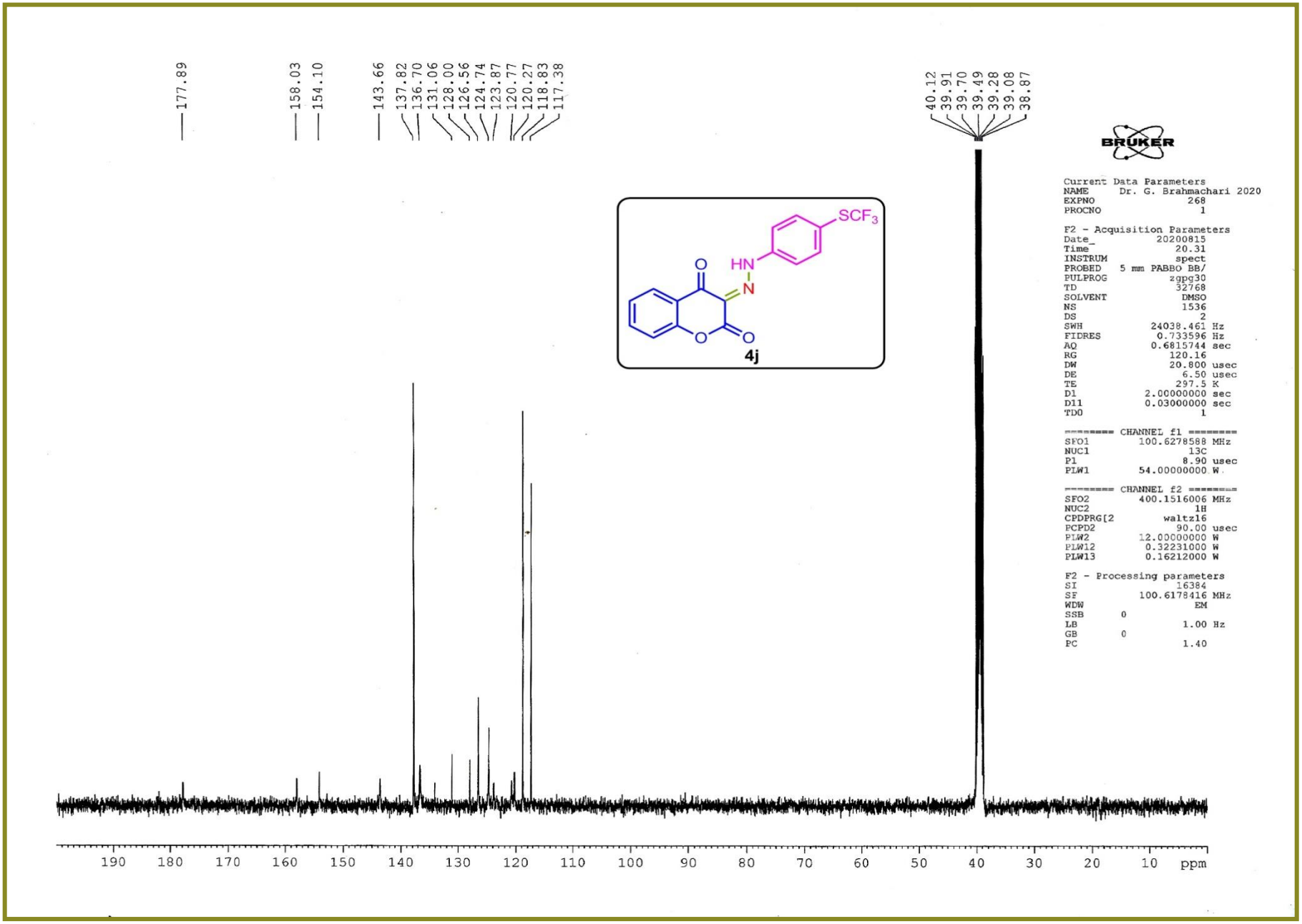



Figure S34. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)

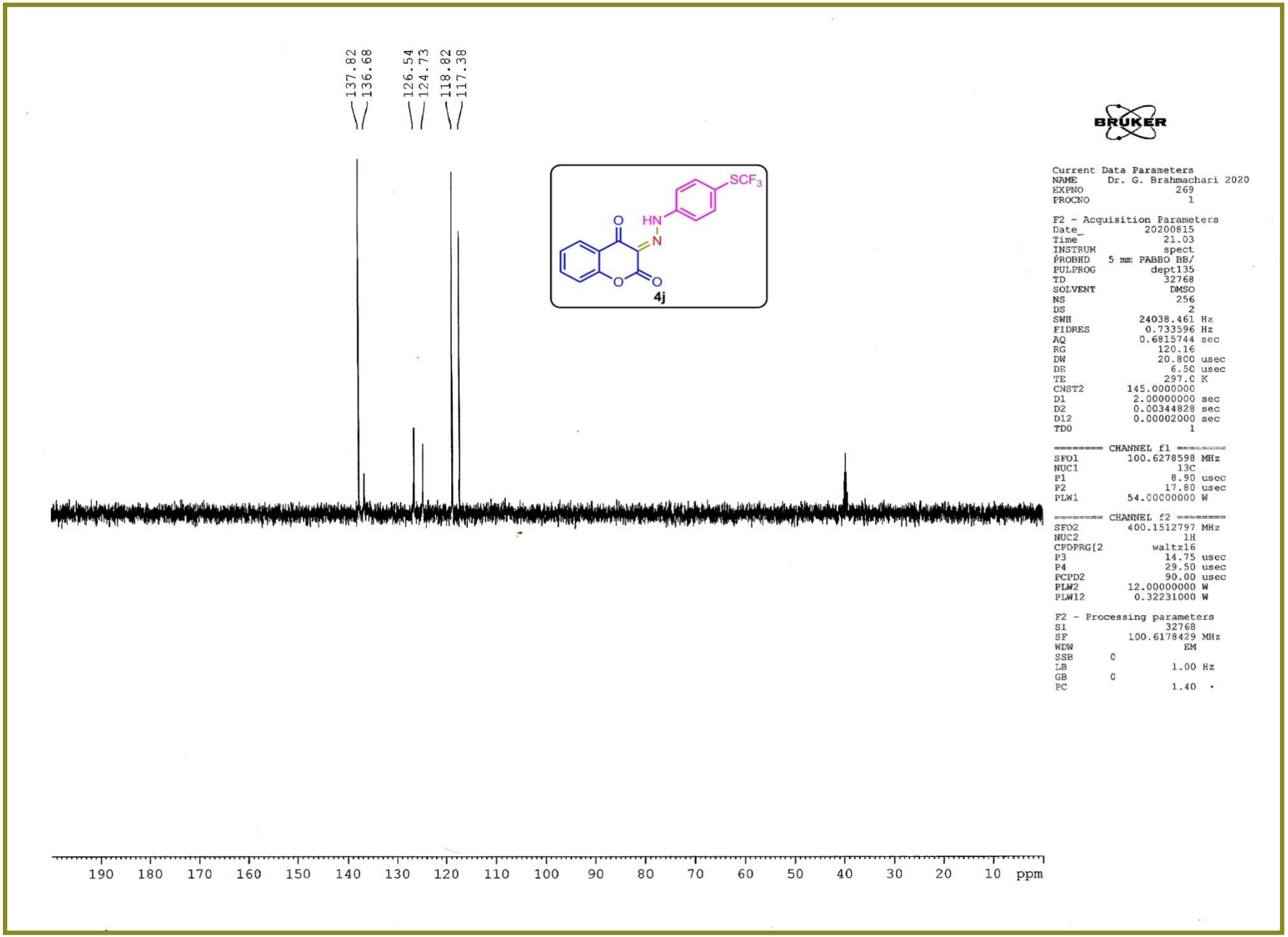
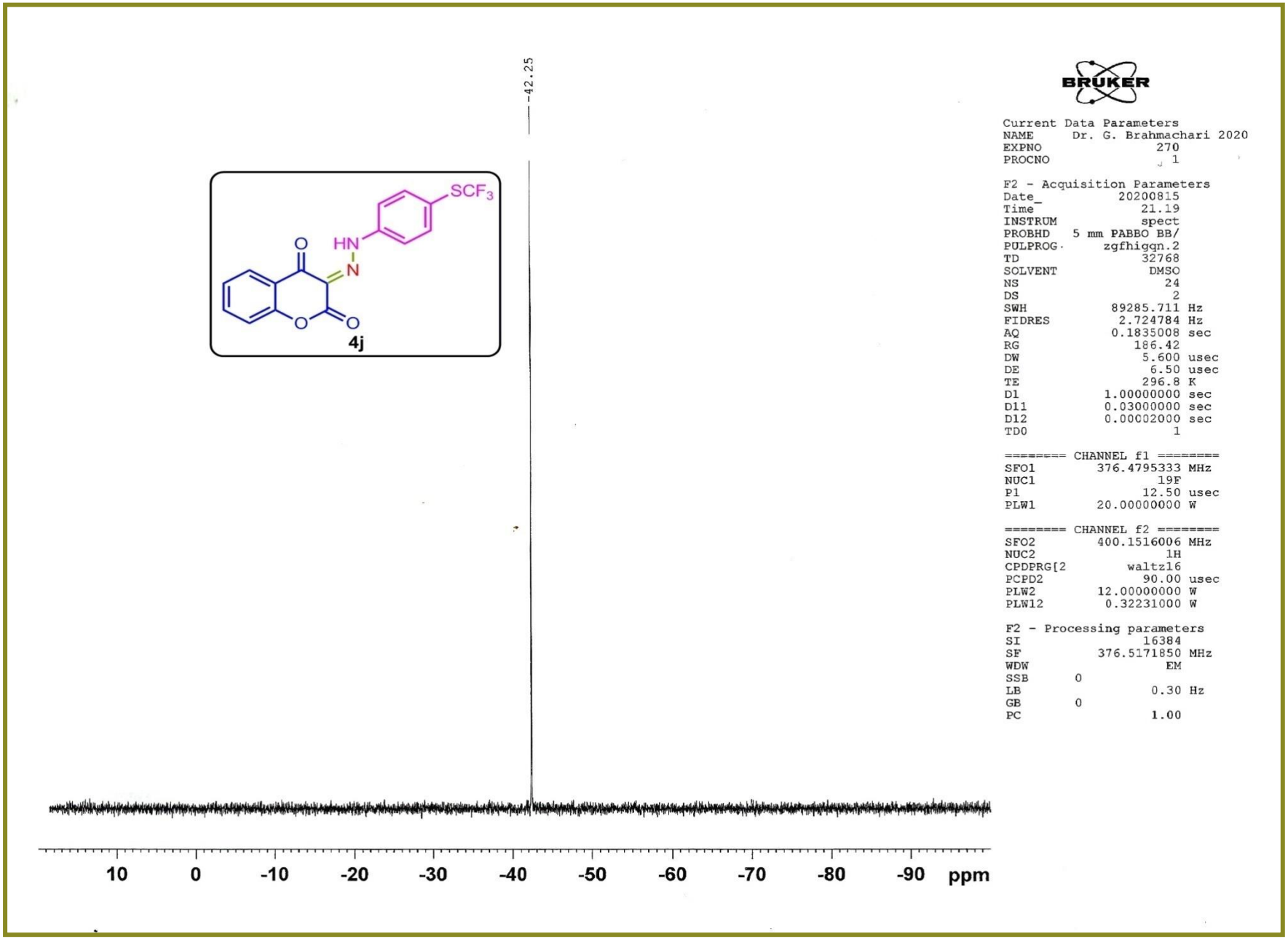



Figure S35. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)




BRUKER

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NAME Dr. G. Brahmachari 2020
EXPNO 270
PROCNO 1

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Time 21.19
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FIDRES 2.724784 Hz
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LB 0.30 Hz
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PC 1.00

Figure S36. $^{19}$F NMR spectrum of (*E*)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)

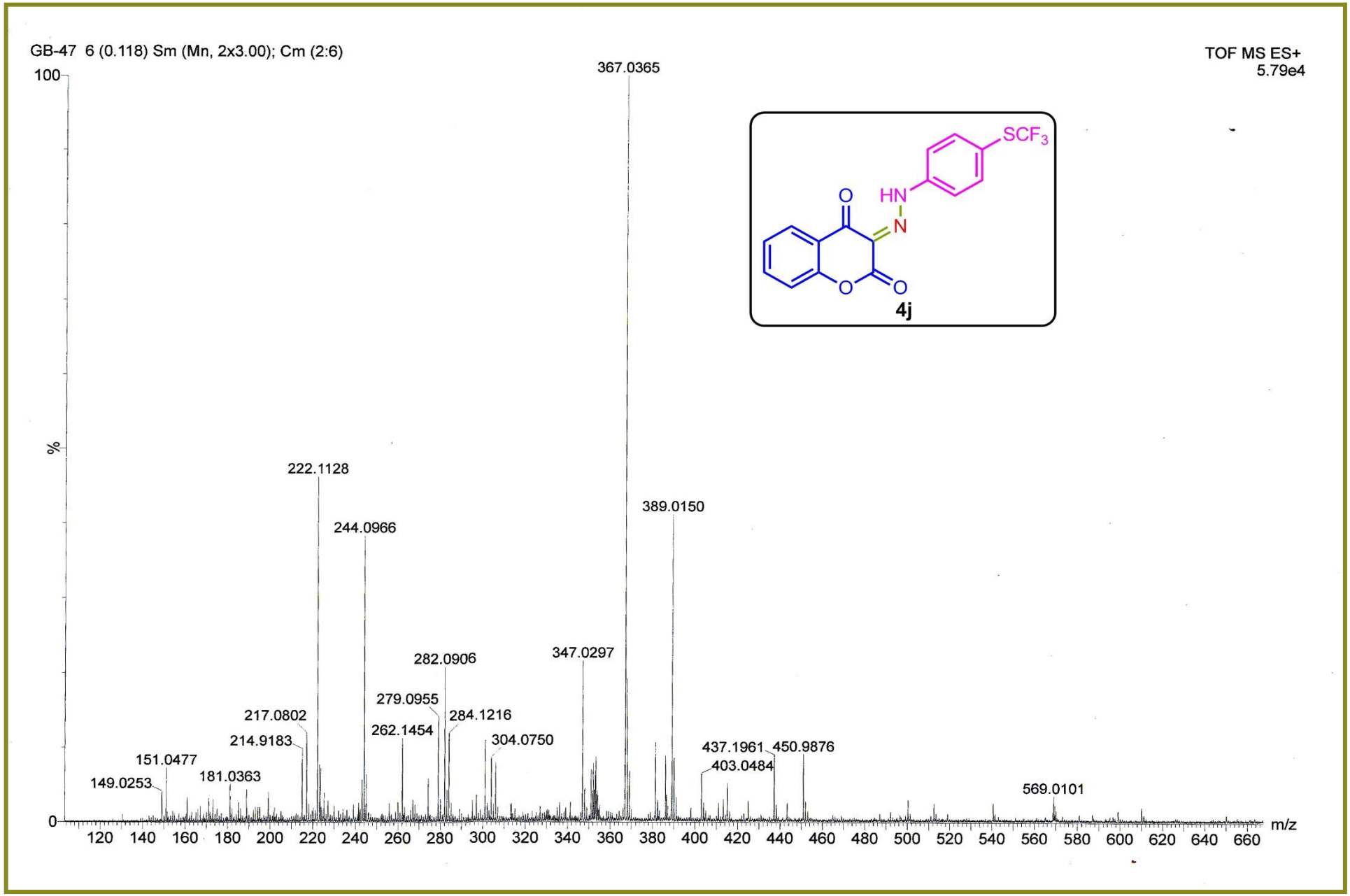


Figure S37. Mass spectra of (*E*)-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazono)chroman-2,4-dione (**4j**)

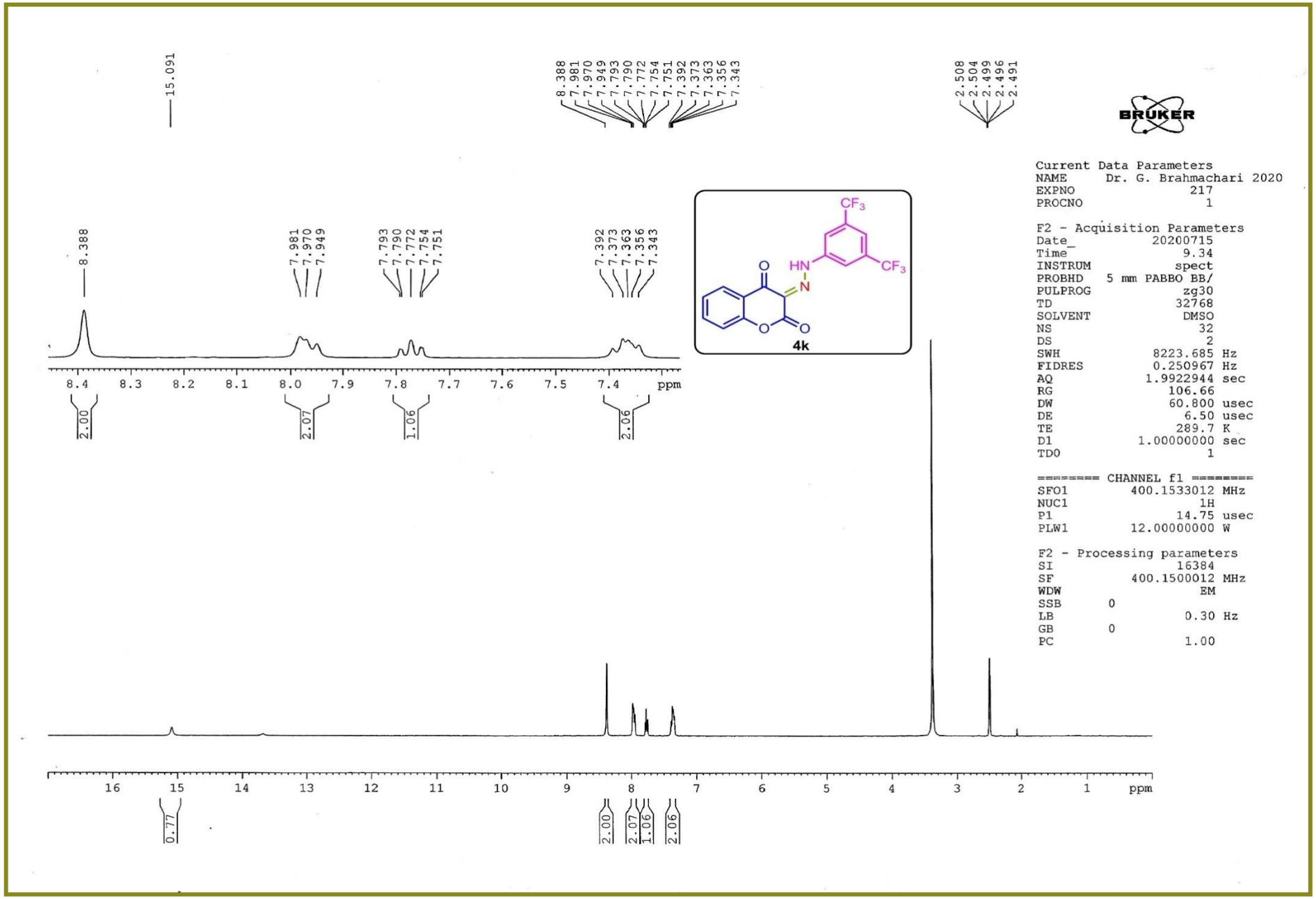


Figure S38. $^{1}$H-NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)

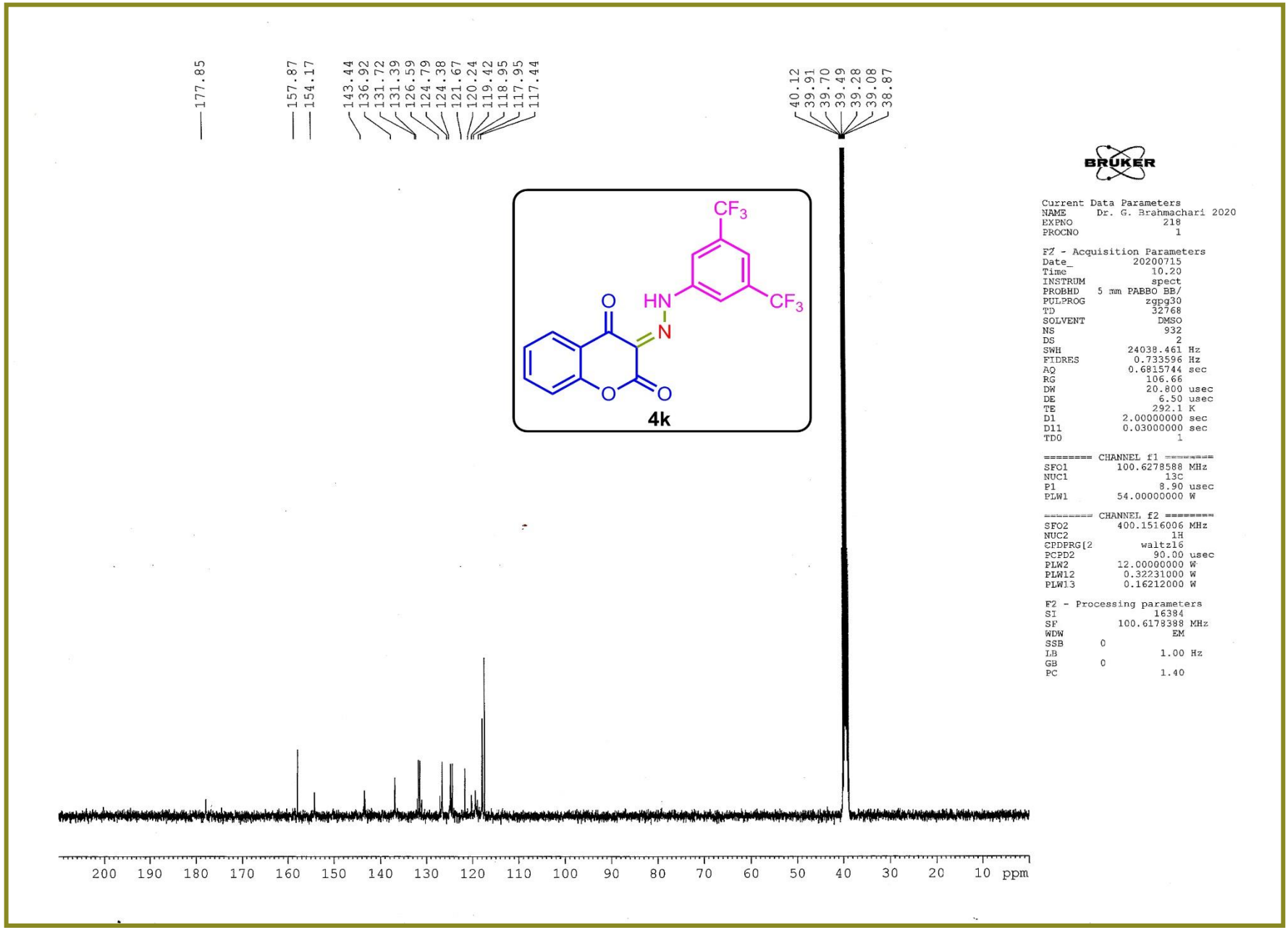


Figure S39. $^{13}$C-NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)

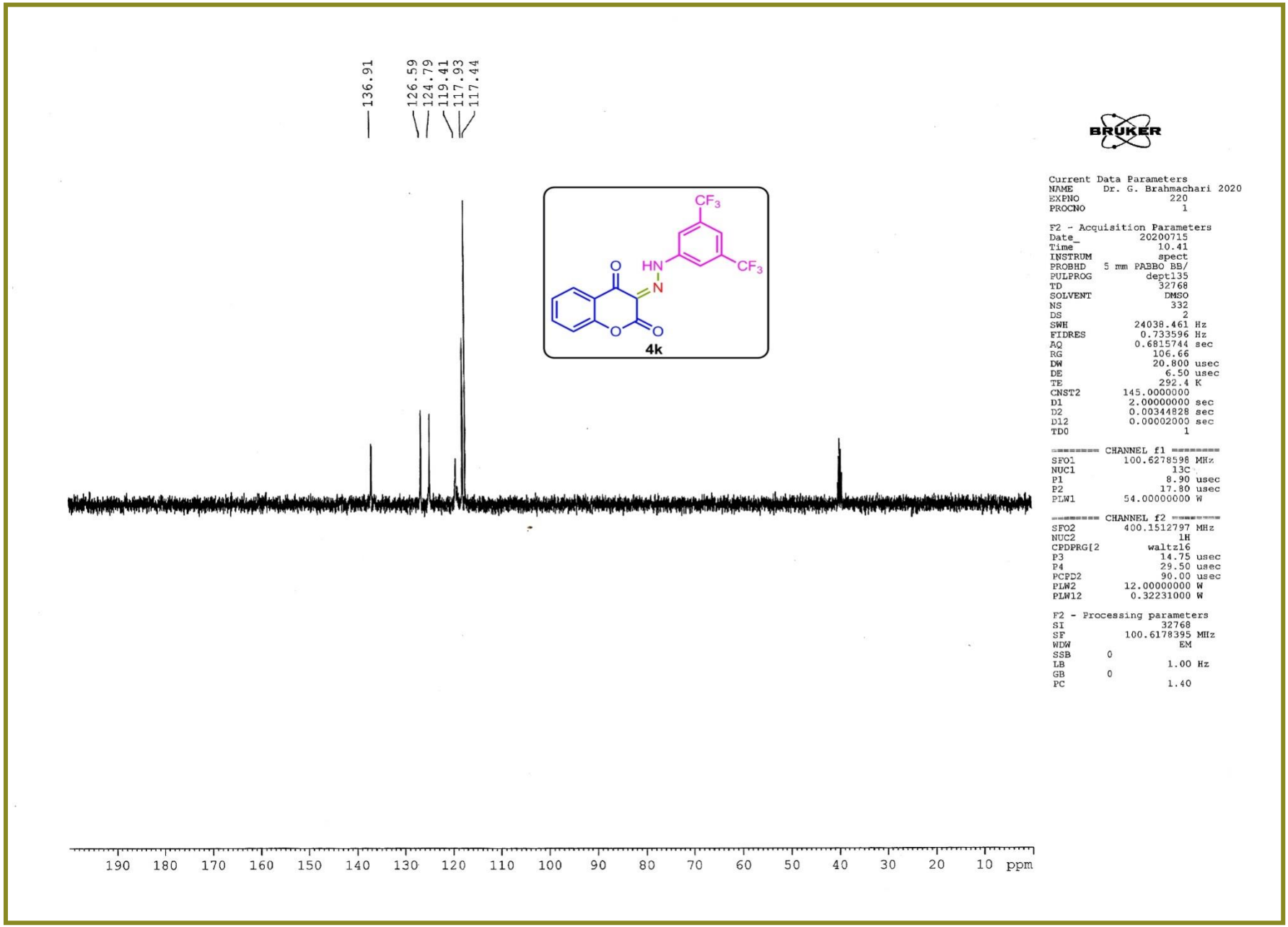


Figure S40. DEPT-135 NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)

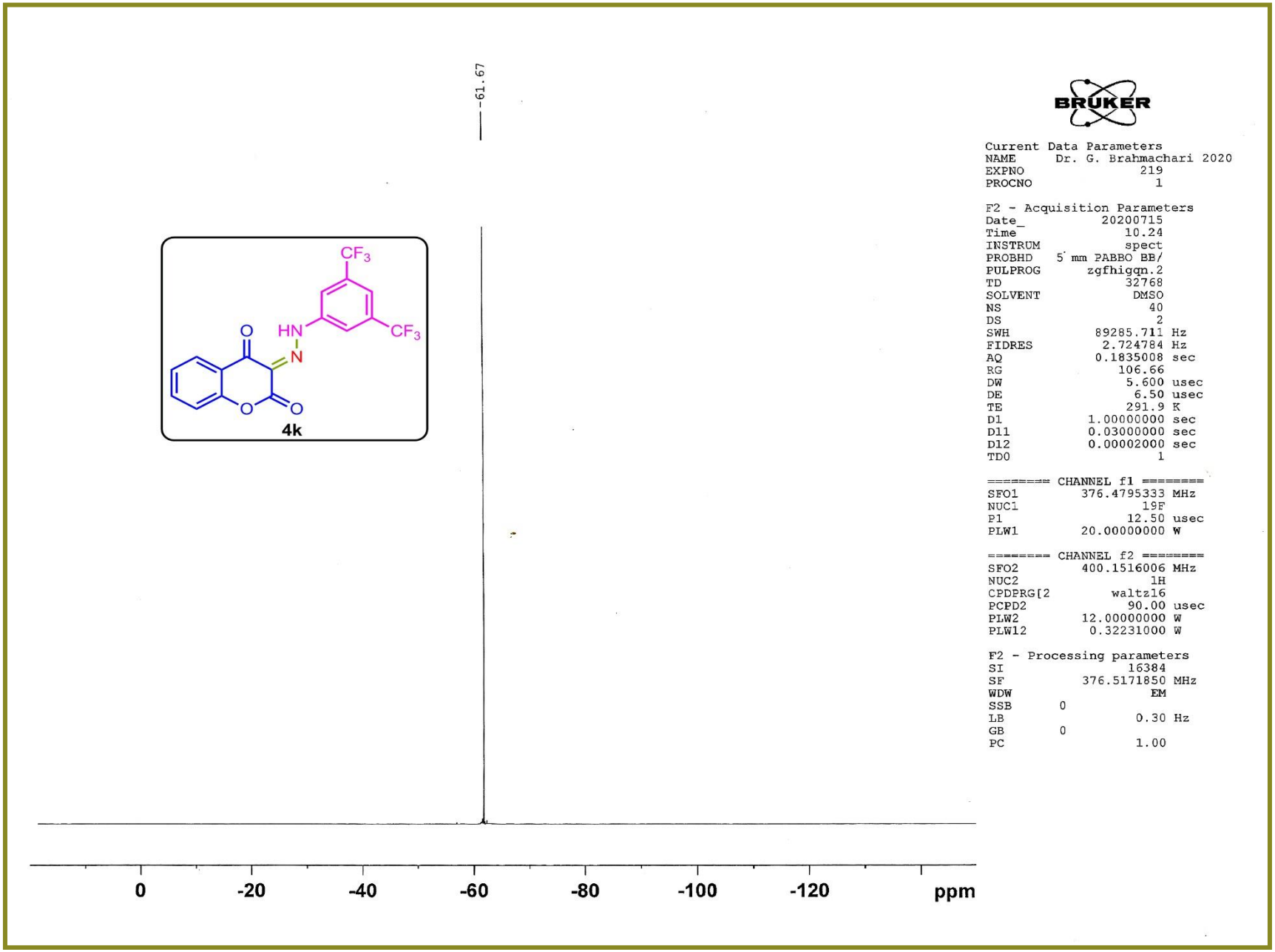


Figure S41. $^{19}$F NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)

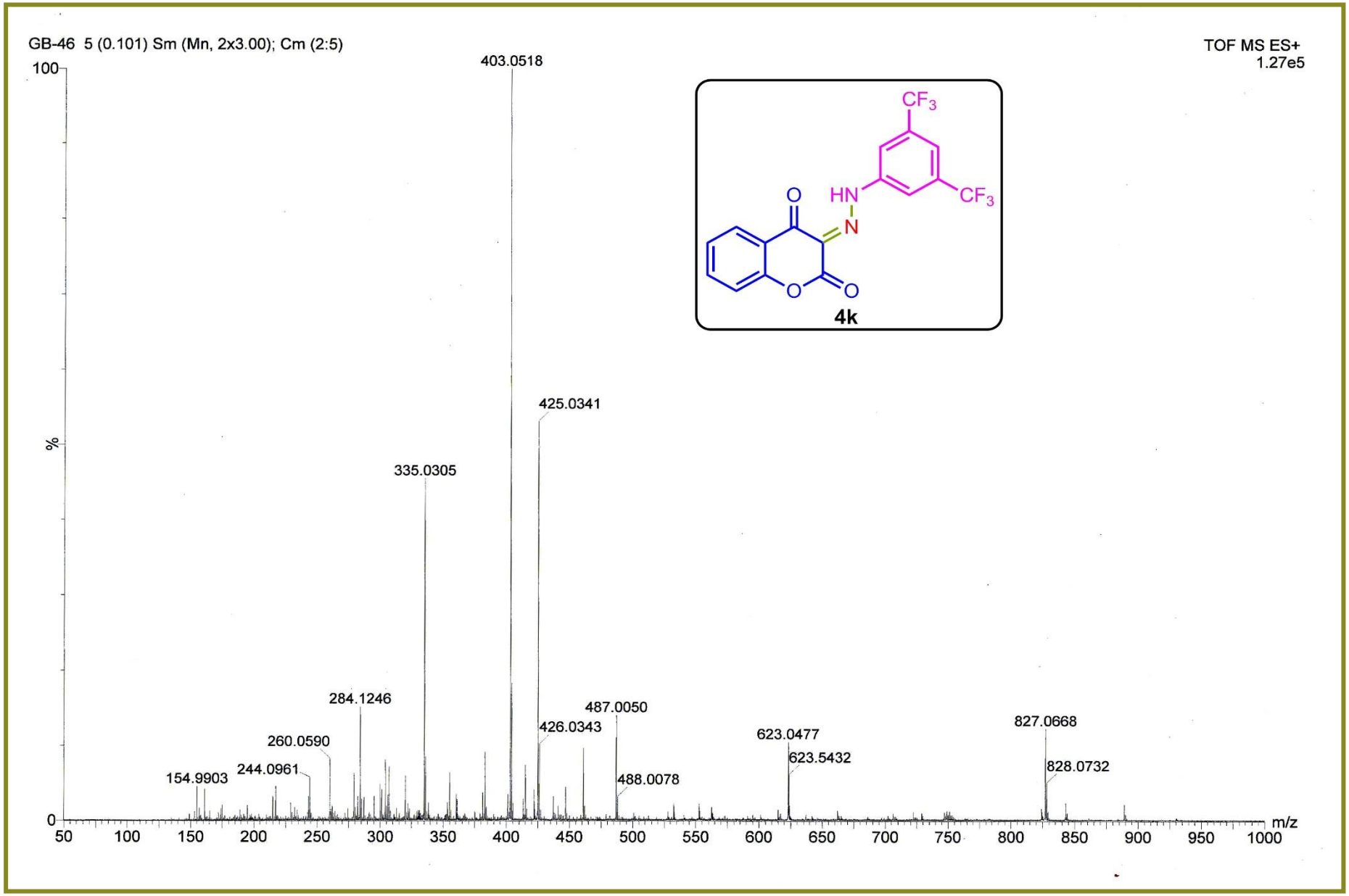


Figure S42. Mass spectra of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (**4k**)

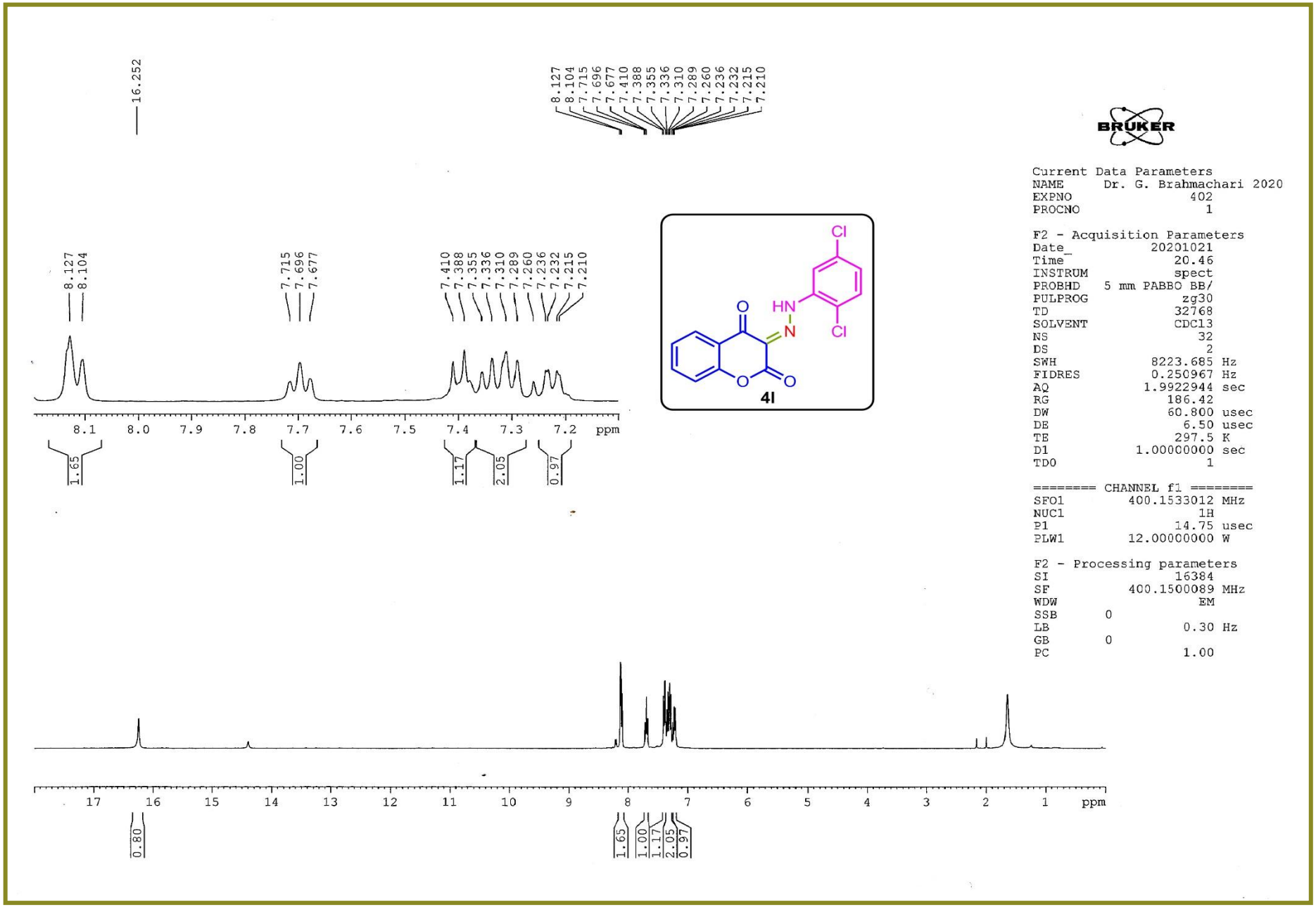


Figure S43. $^{1}$H-NMR spectrum of (*E*)-3-(2-(2,5-dichlorophenyl)hydrazono)chroman-2,4-dione (**4l**)

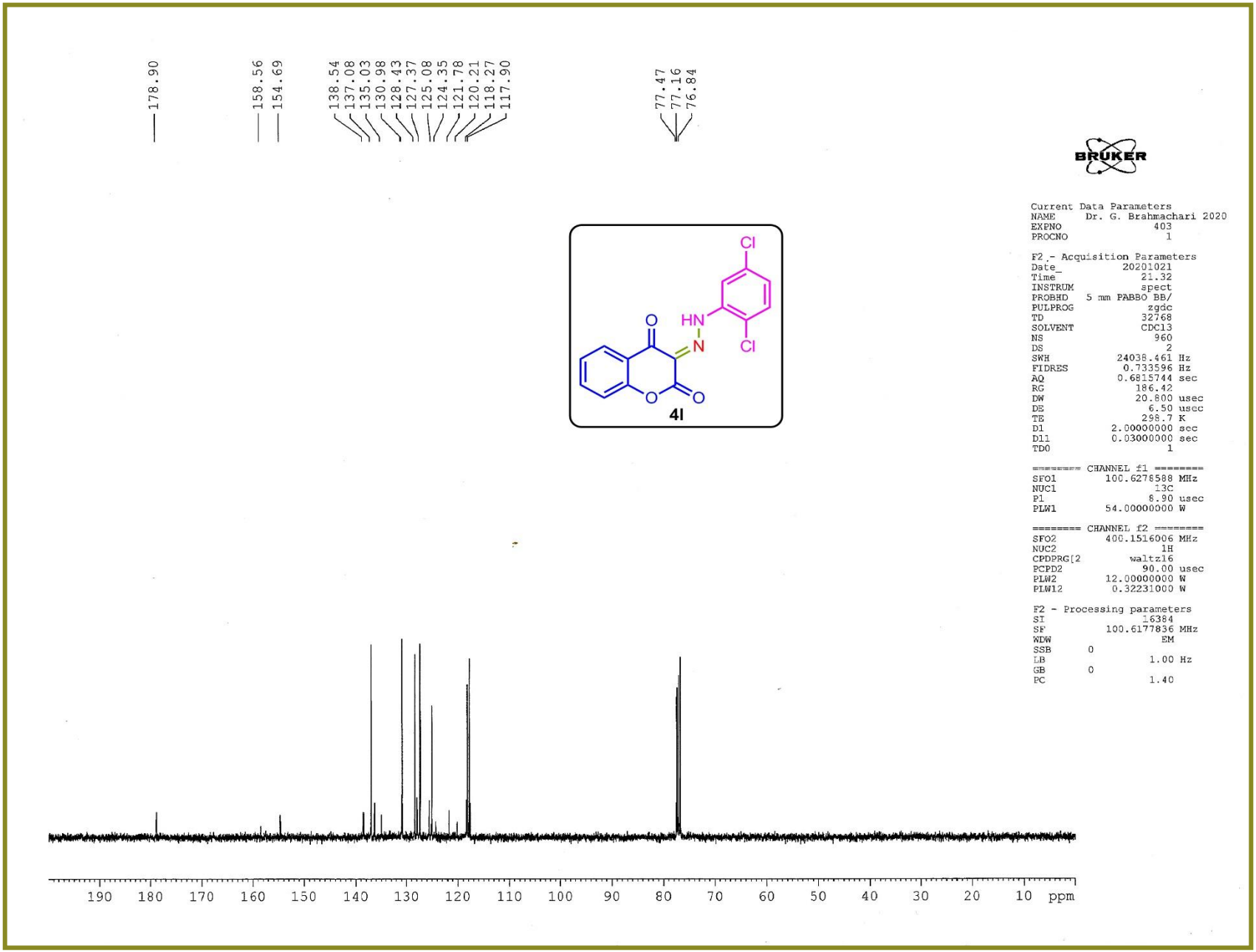


Figure S44. $^{13}$C-NMR spectrum of (*E*)-3-(2-(2,5-dichlorophenyl)hydrazono)chroman-2,4-dione (**4l**)

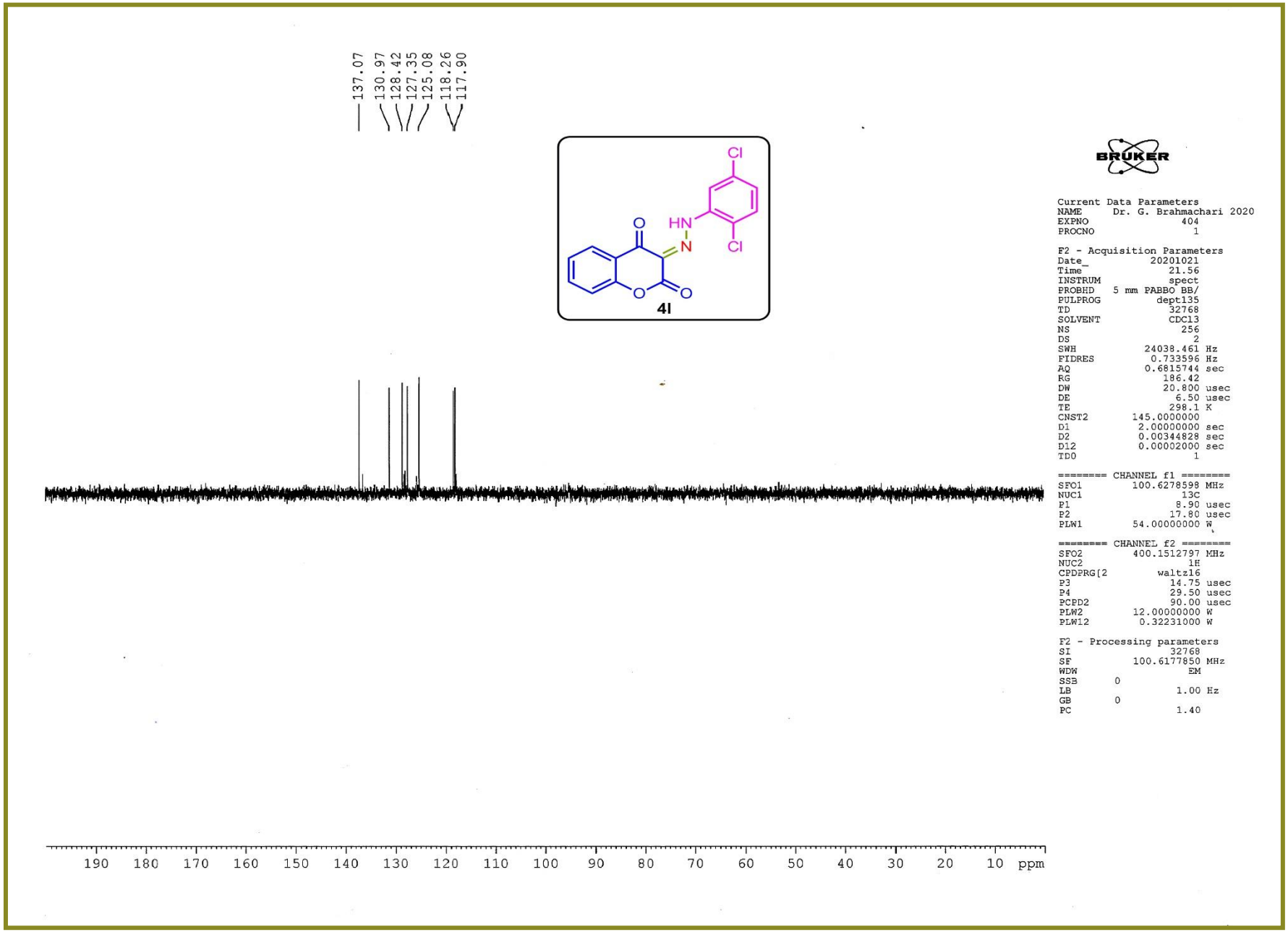


Figure S45. DEPT-135 NMR spectrum of (*E*)-3-(2-(2,5-dichlorophenyl)hydrazono)chroman-2,4-dione (**4l**)

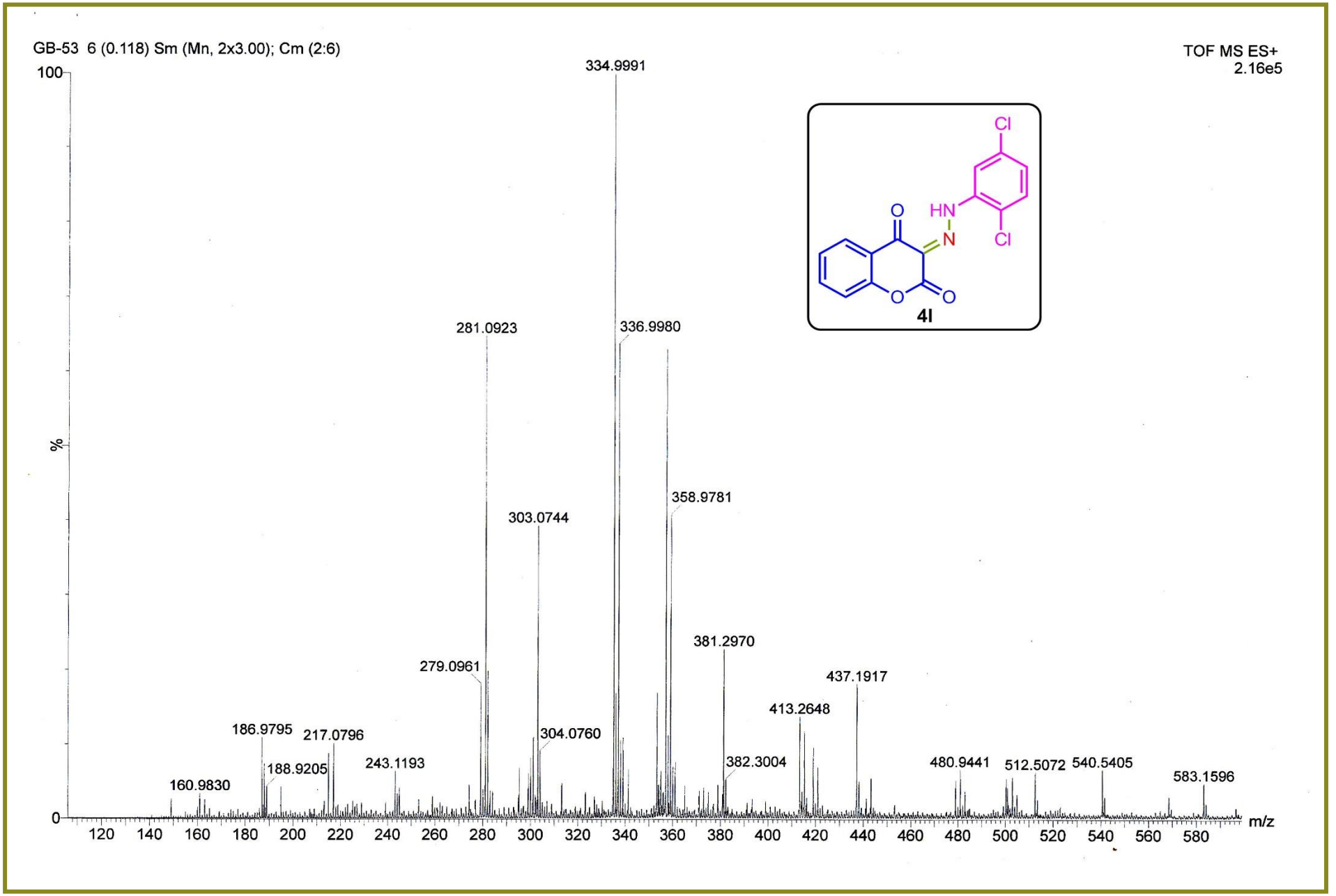


Figure S46. Mass spectra of (*E*)-3-(2-(2,5-dichlorophenyl)hydrazono)chroman-2,4-dione (**4l**)

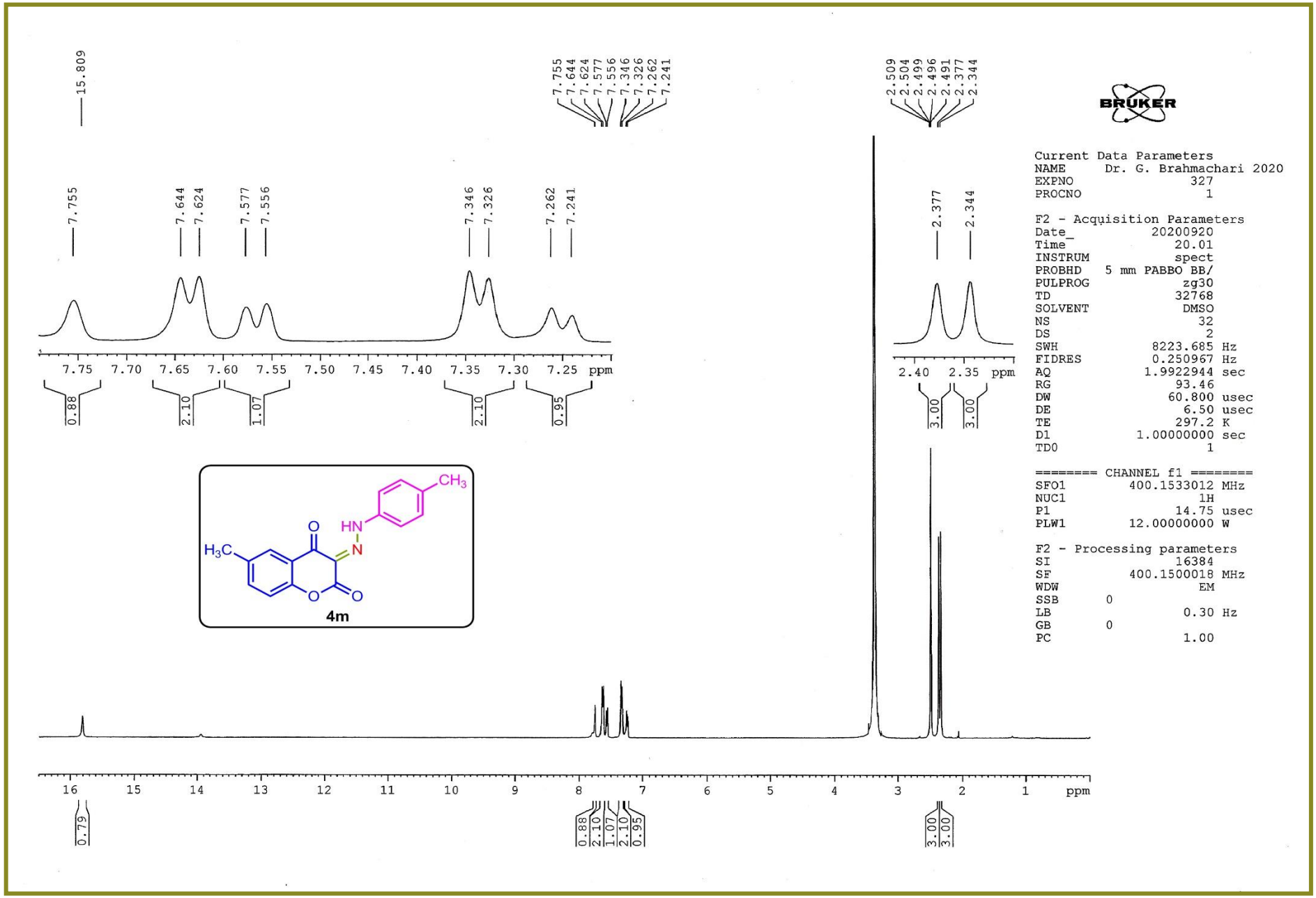


Figure S47. $^{1}$H-NMR spectrum of (*E*)-6-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4m**)

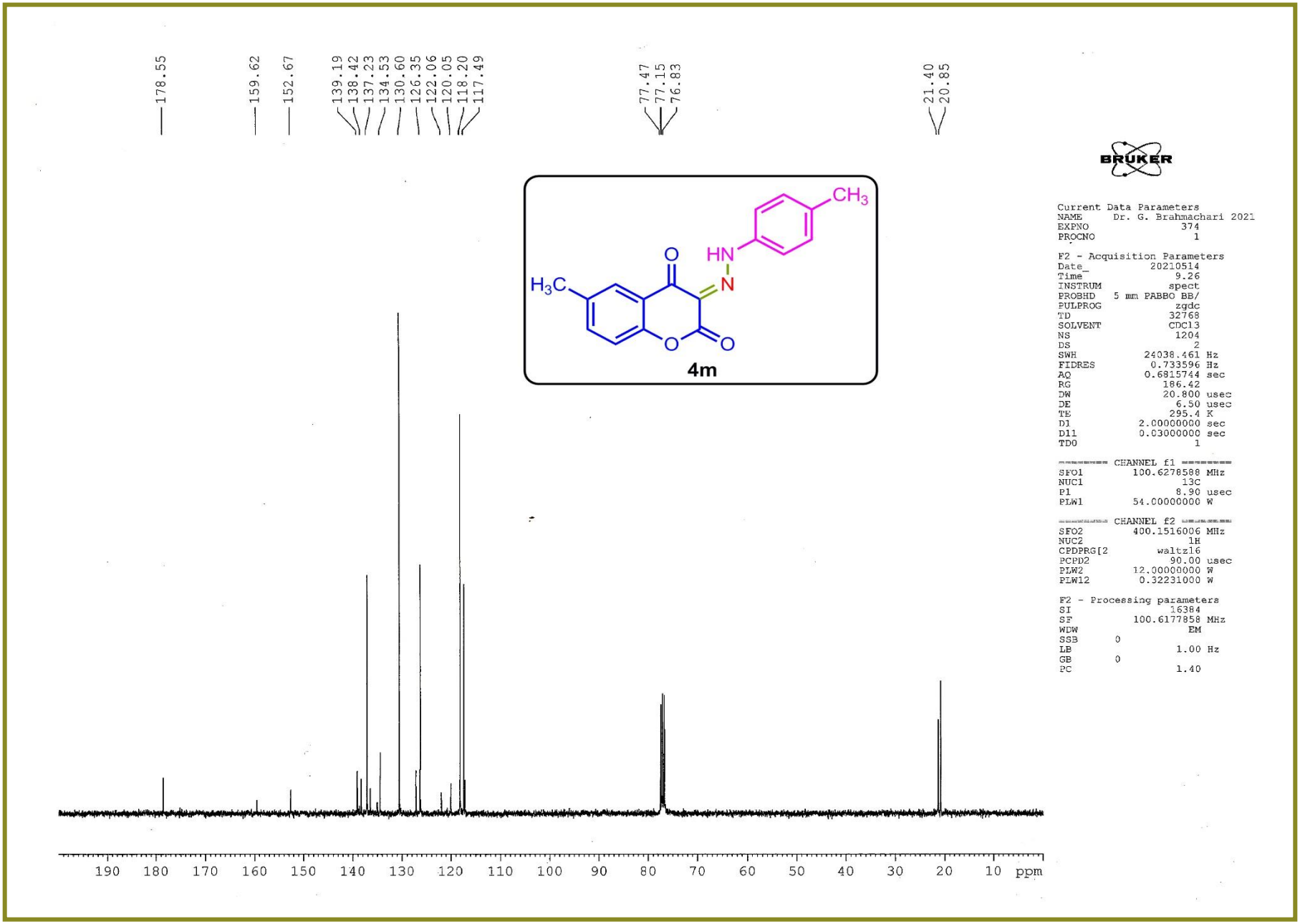


Figure S48. $^{13}$C-NMR spectrum of (*E*)-6-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4m**)

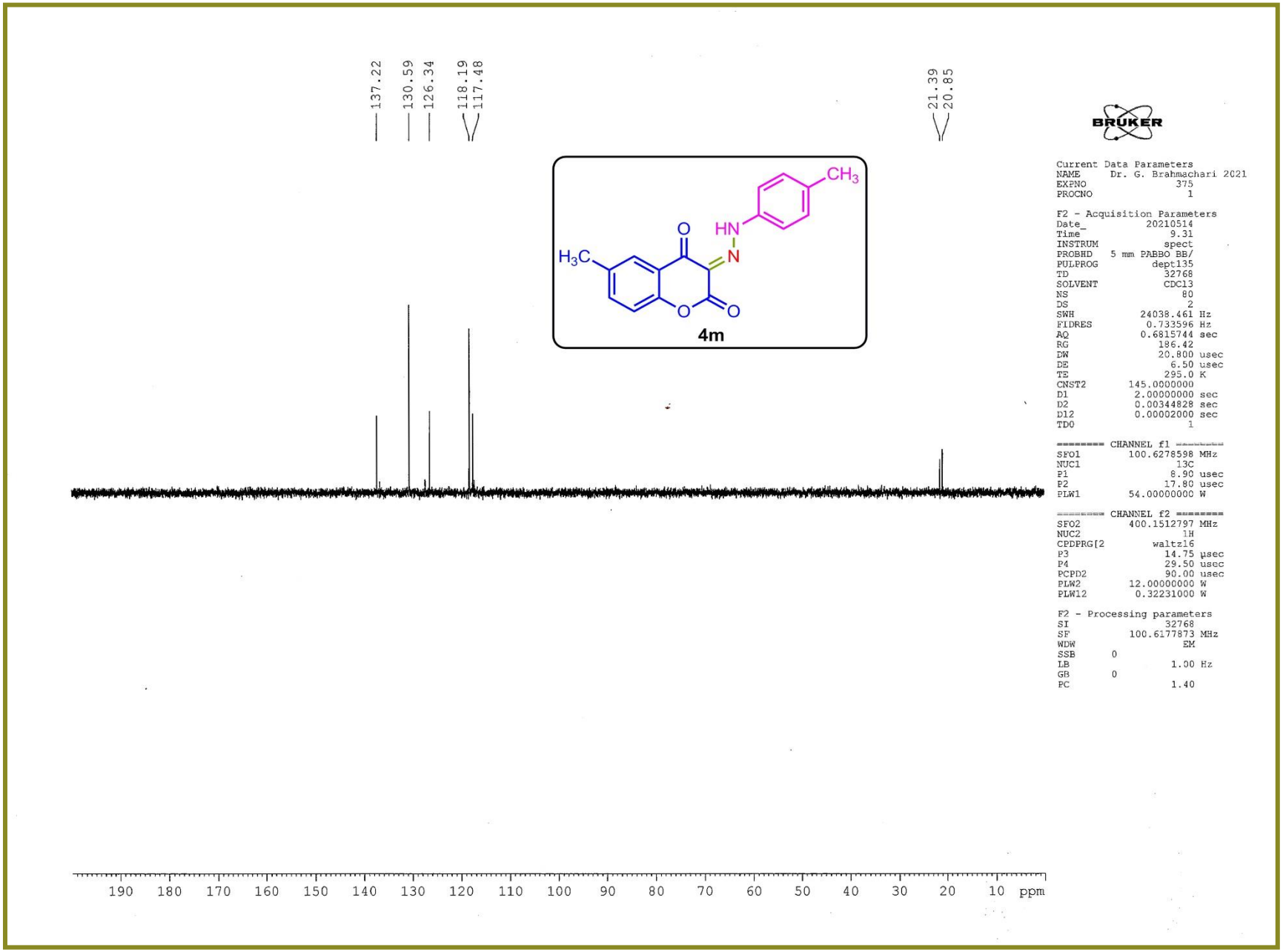


Figure S49. Dept-135 NMR spectrum of (*E*)-6-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4m**)

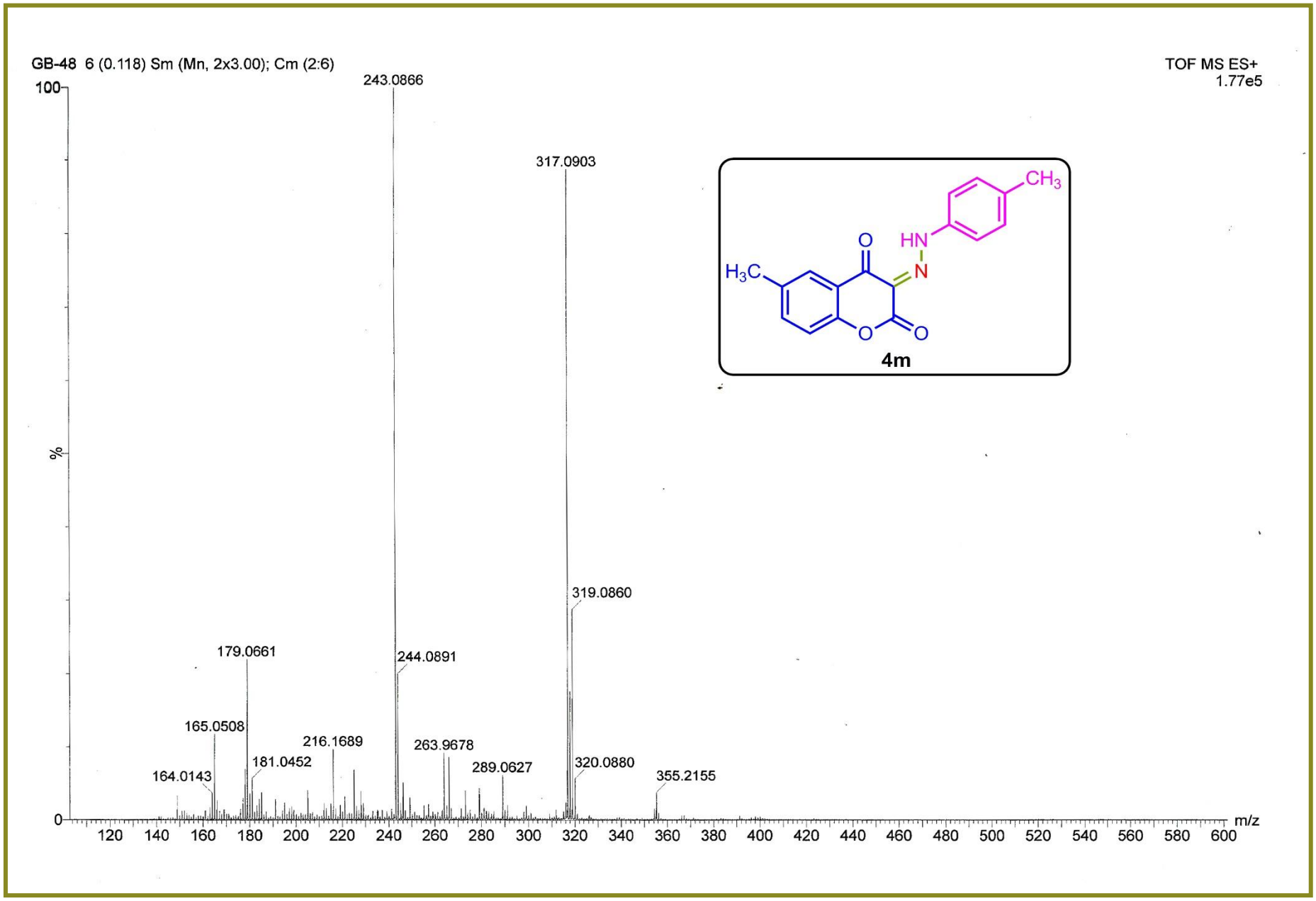


Figure S50. Mass spectra of (*E*)-6-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4m)**


Figure S51. [1]H-NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazineylidene)-6-methylchromane-2,4-dione (**4n**)

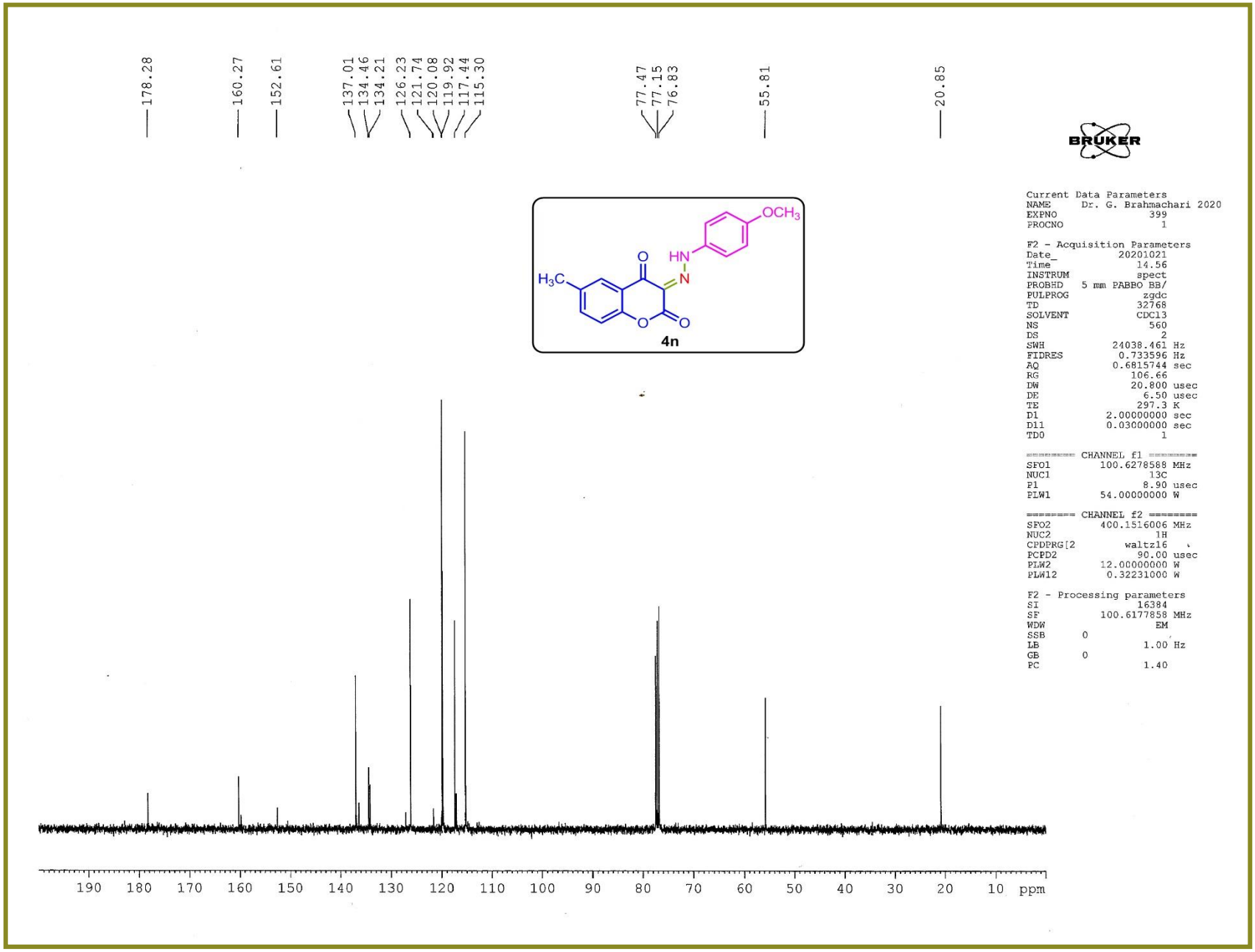


Figure S52. $^{13}$C-NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazineylidene)-6-methylchromane-2,4-dione (**4n**)

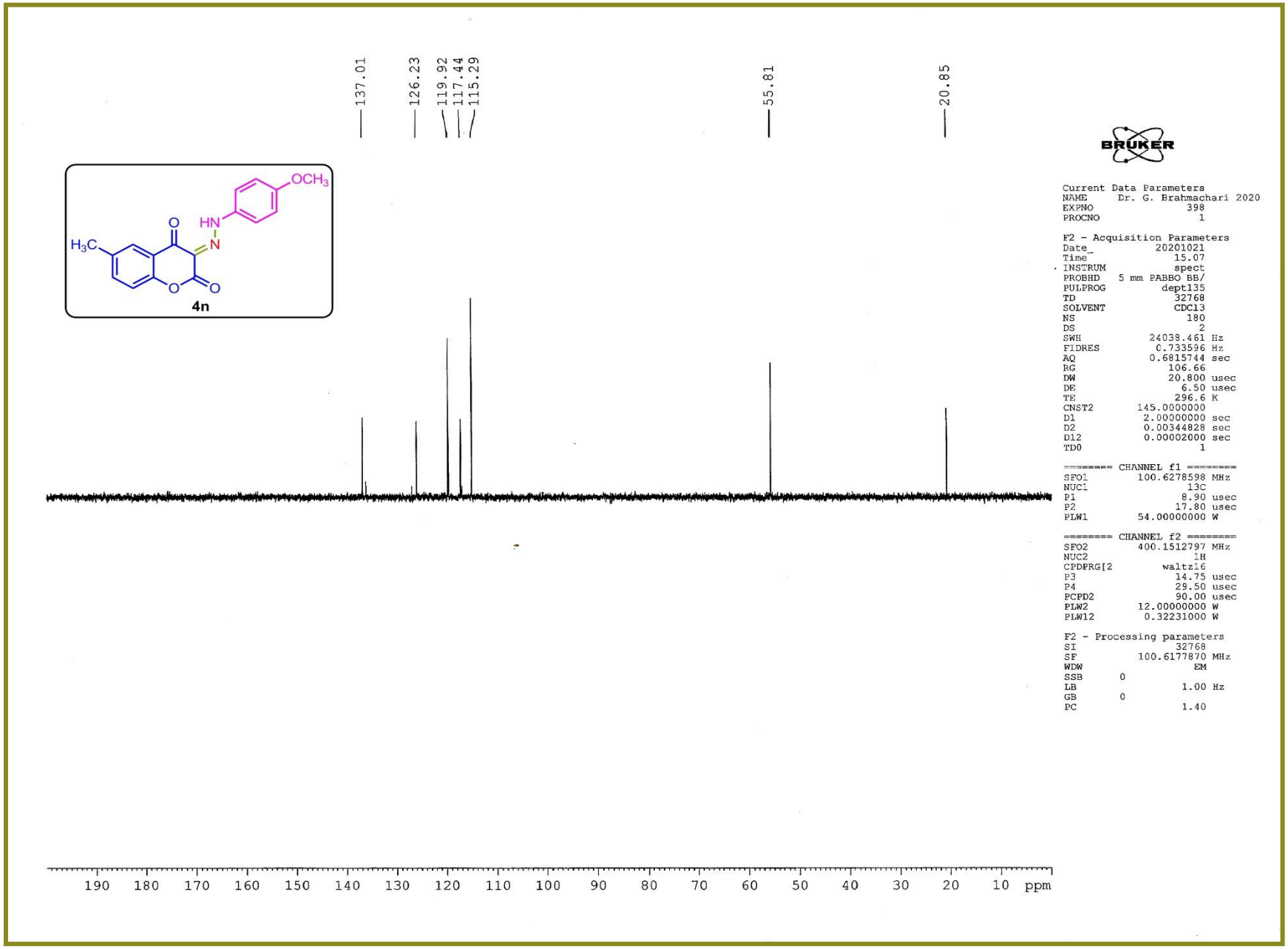


Figure S53. DEPT-135 NMR spectrum of (*E*)-3-(2-(4-methoxyphenyl)hydrazineylidene)-6-methylchromane-2,4-dione (**4n**)

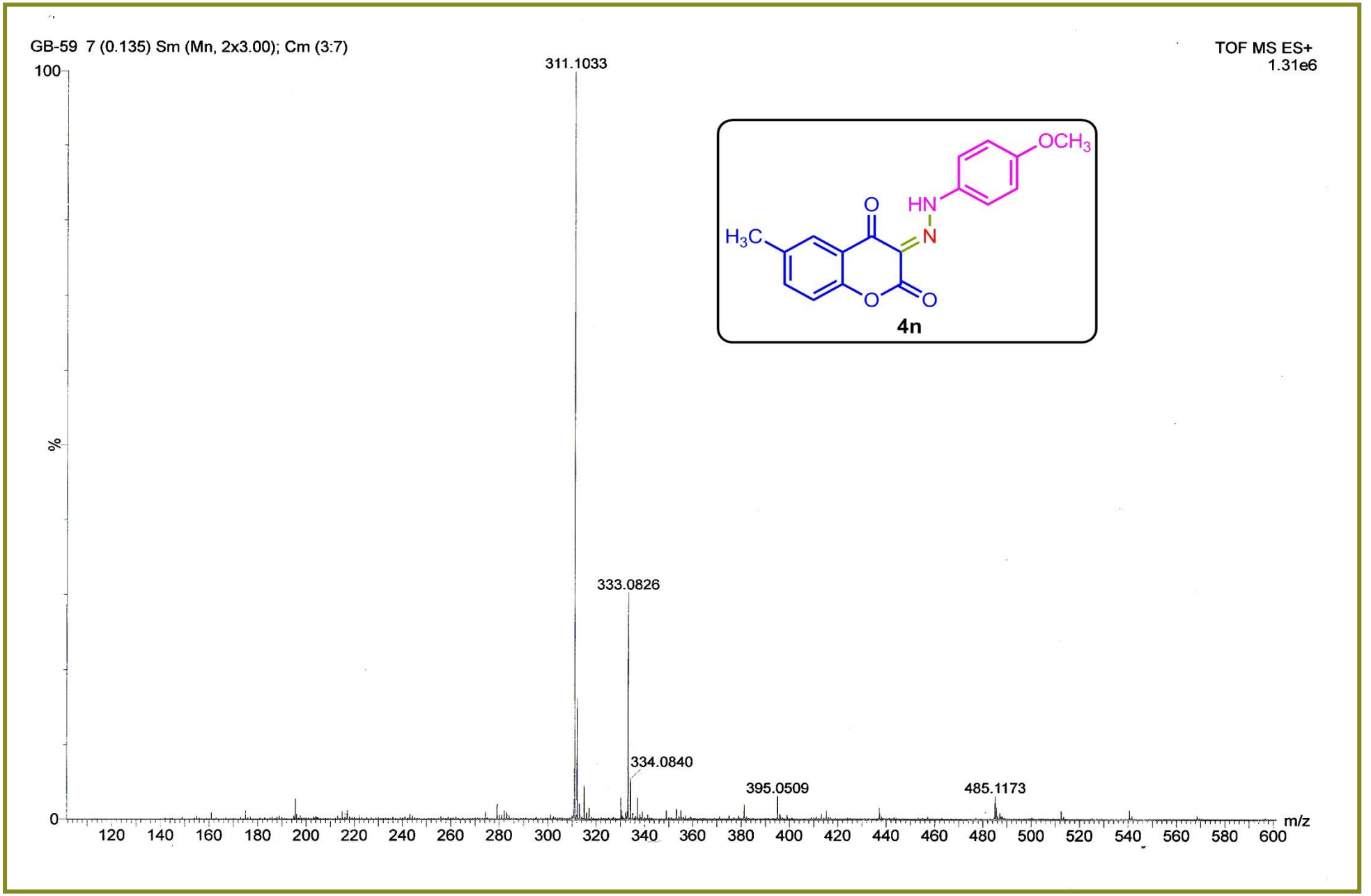


Figure S54. Mass spectra of (*E*)-3-(2-(4-methoxyphenyl)hydrazineylidene)-6-methylchromane-2,4-dione (**4n**)

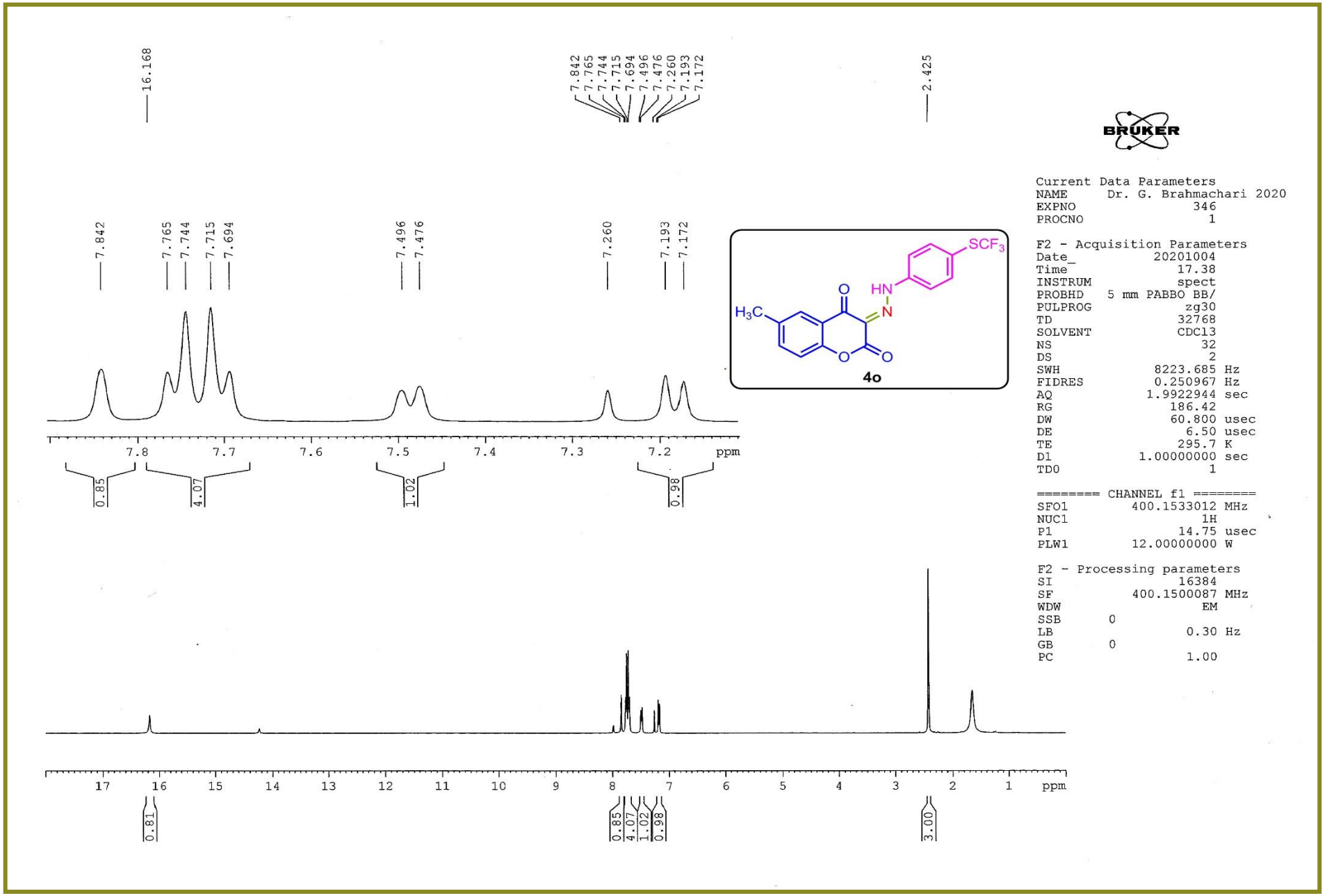


Figure S55. $^{1}$H-NMR spectrum of (*E*)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazineylidene)chromane-2,4-dione (**4o**)

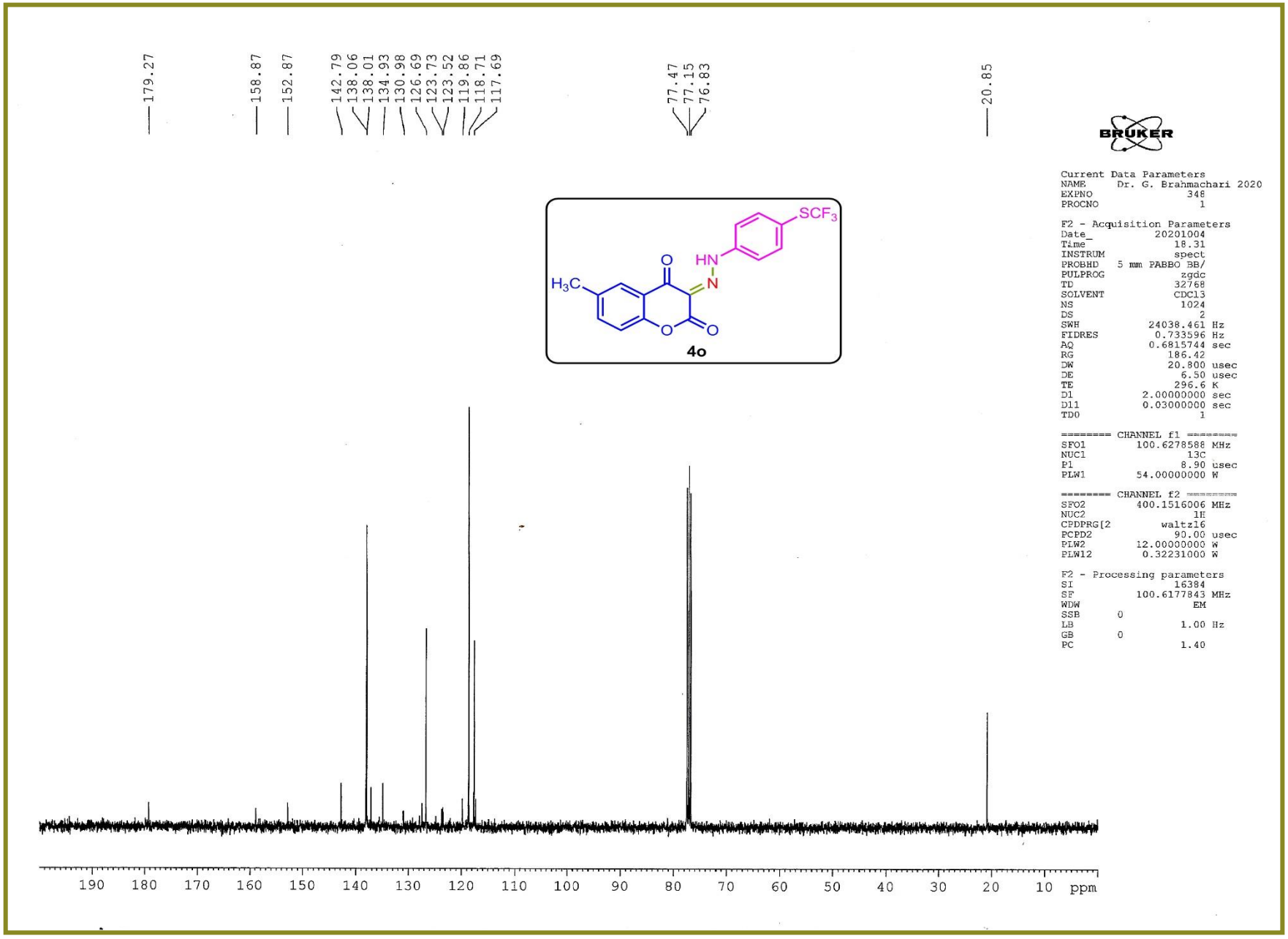


Figure S56. $^{13}$C-NMR spectrum of (*E*)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazineylidene)chromane-2,4-dione (**4o**)

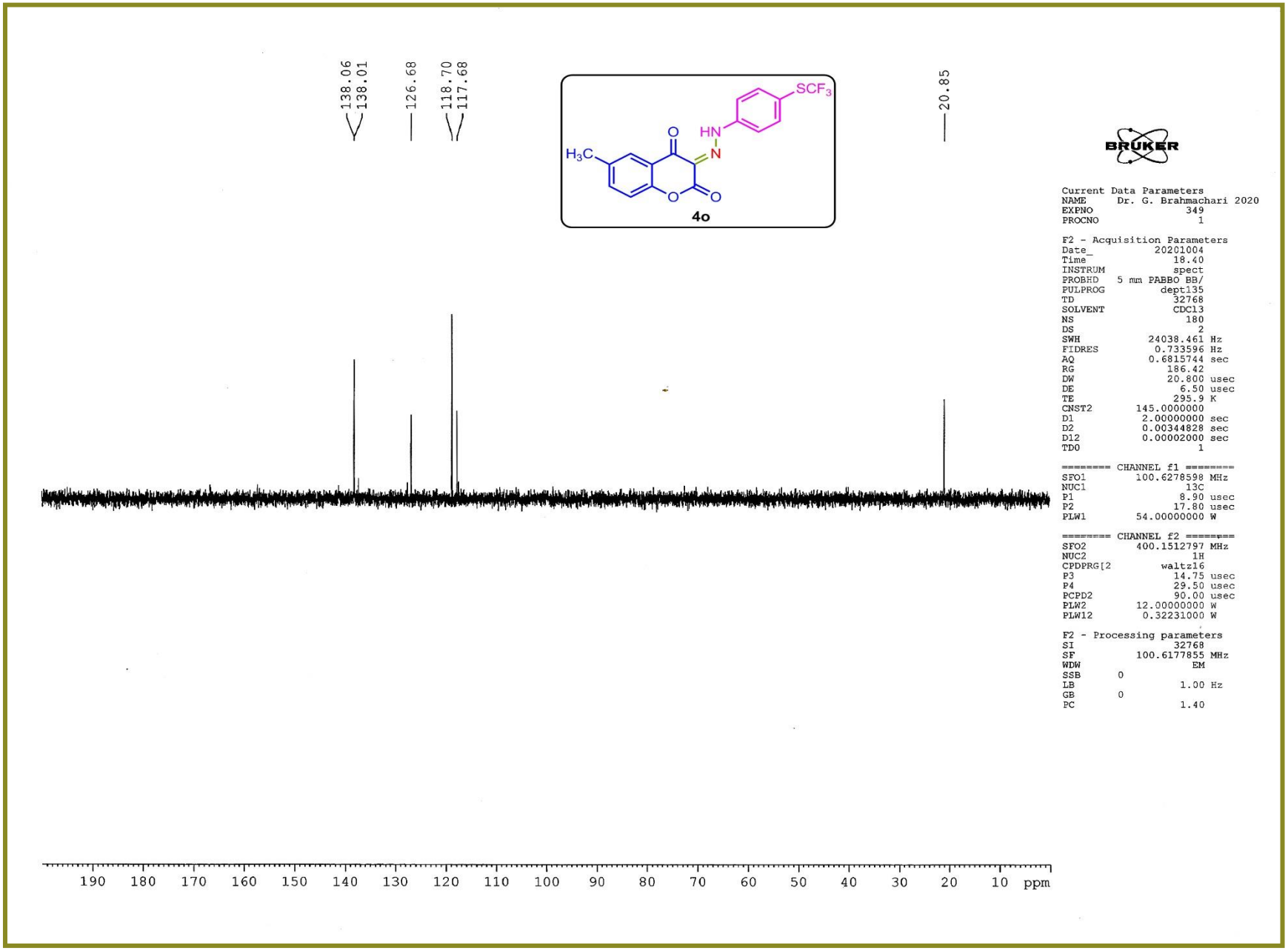


Figure S57. DEPT-135 NMR spectrum of (*E*)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazineylidene)chromane-2,4-dione (**4o**)

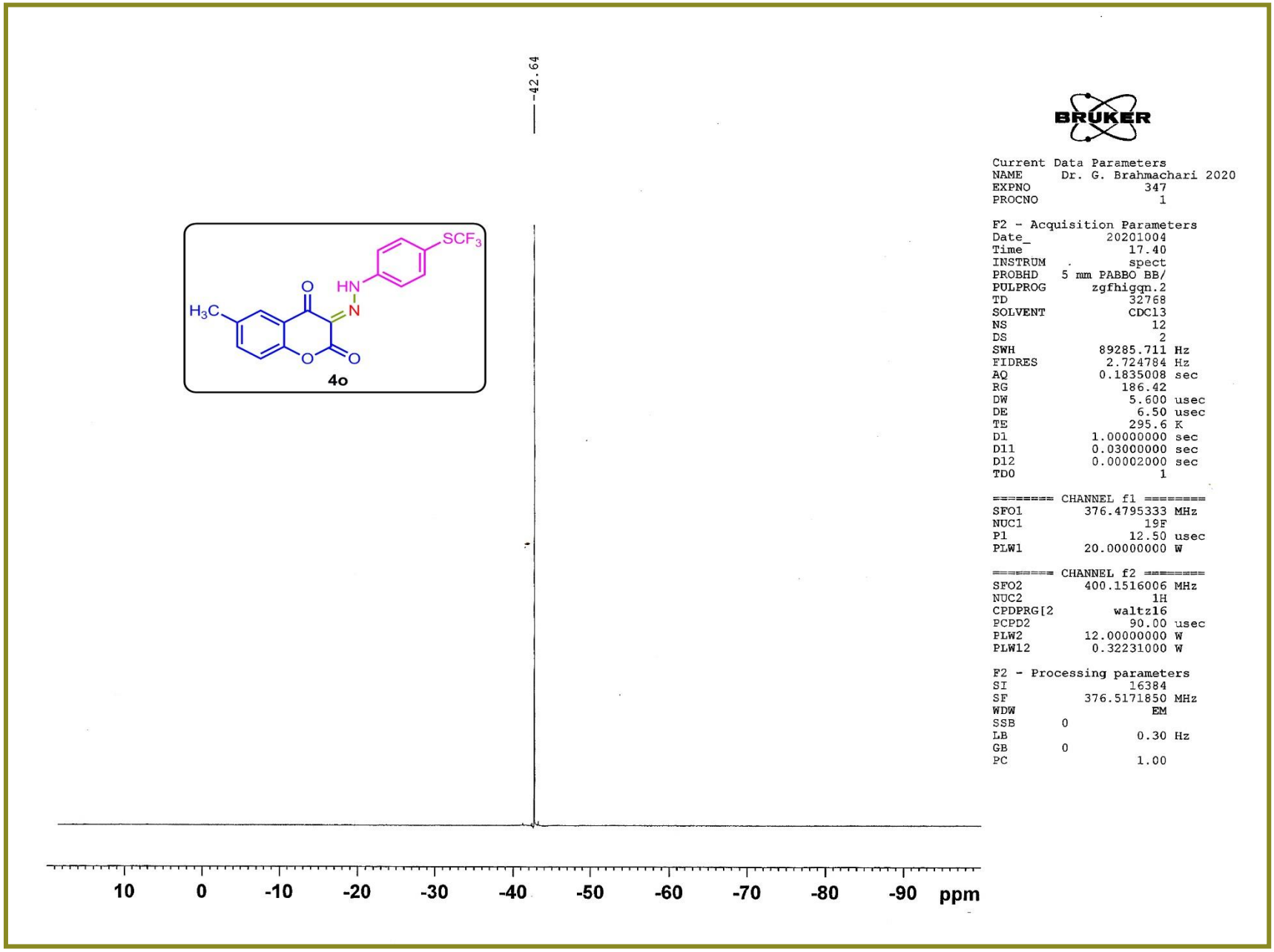


Figure S58. $^{19}$F NMR spectrum of (*E*)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazineylidene)chromane-2,4-dione (**4o**)

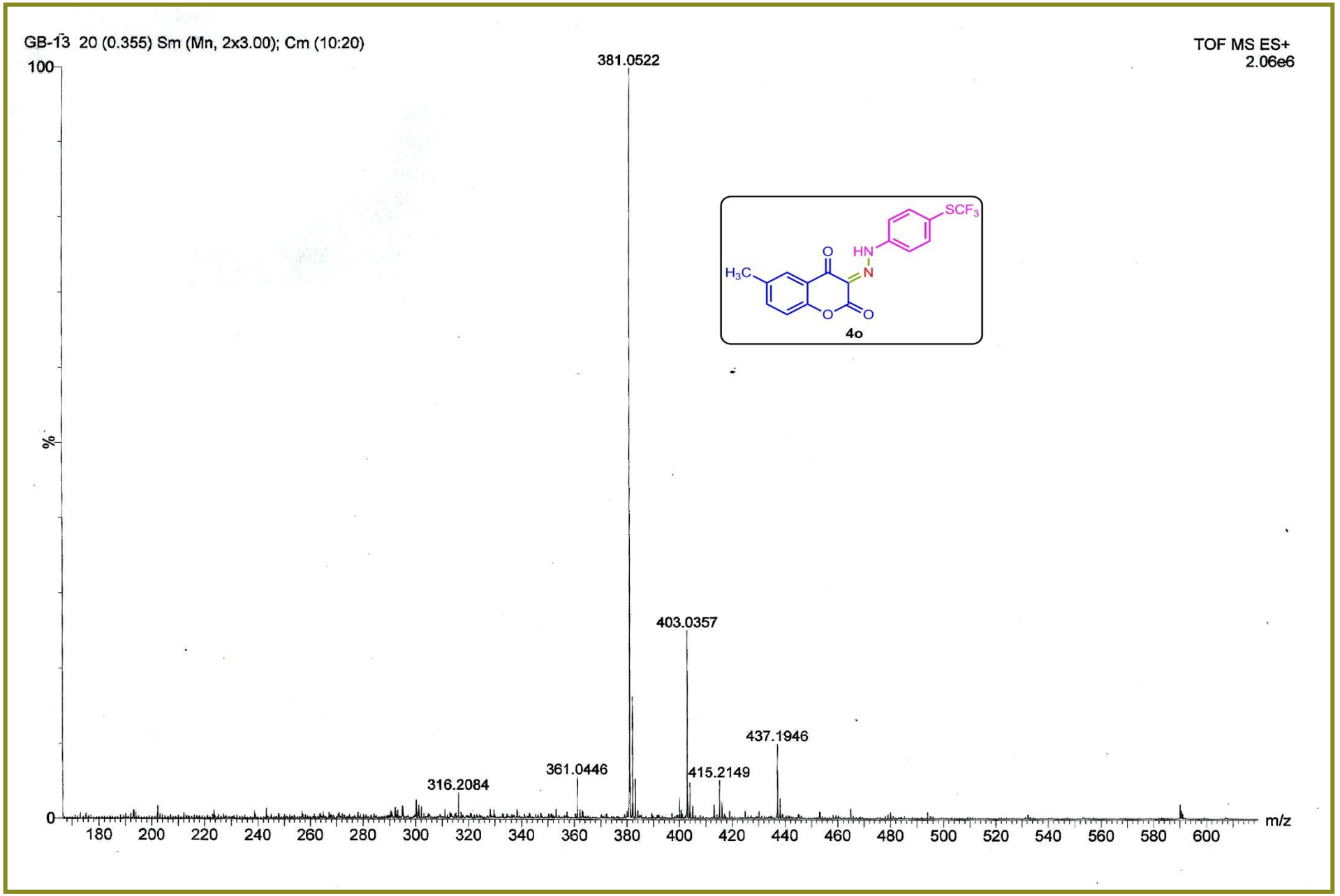


Figure S59. Mass spectra of (*E*)-6-methyl-3-(2-(4-((trifluoromethyl)thio)phenyl)hydrazineylidene)chromane-2,4-dione (**4o**)


Figure S60. $^{1}$H-NMR spectrum of (*E*)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazineylidene)chromane-2,4-dione (**4p**)

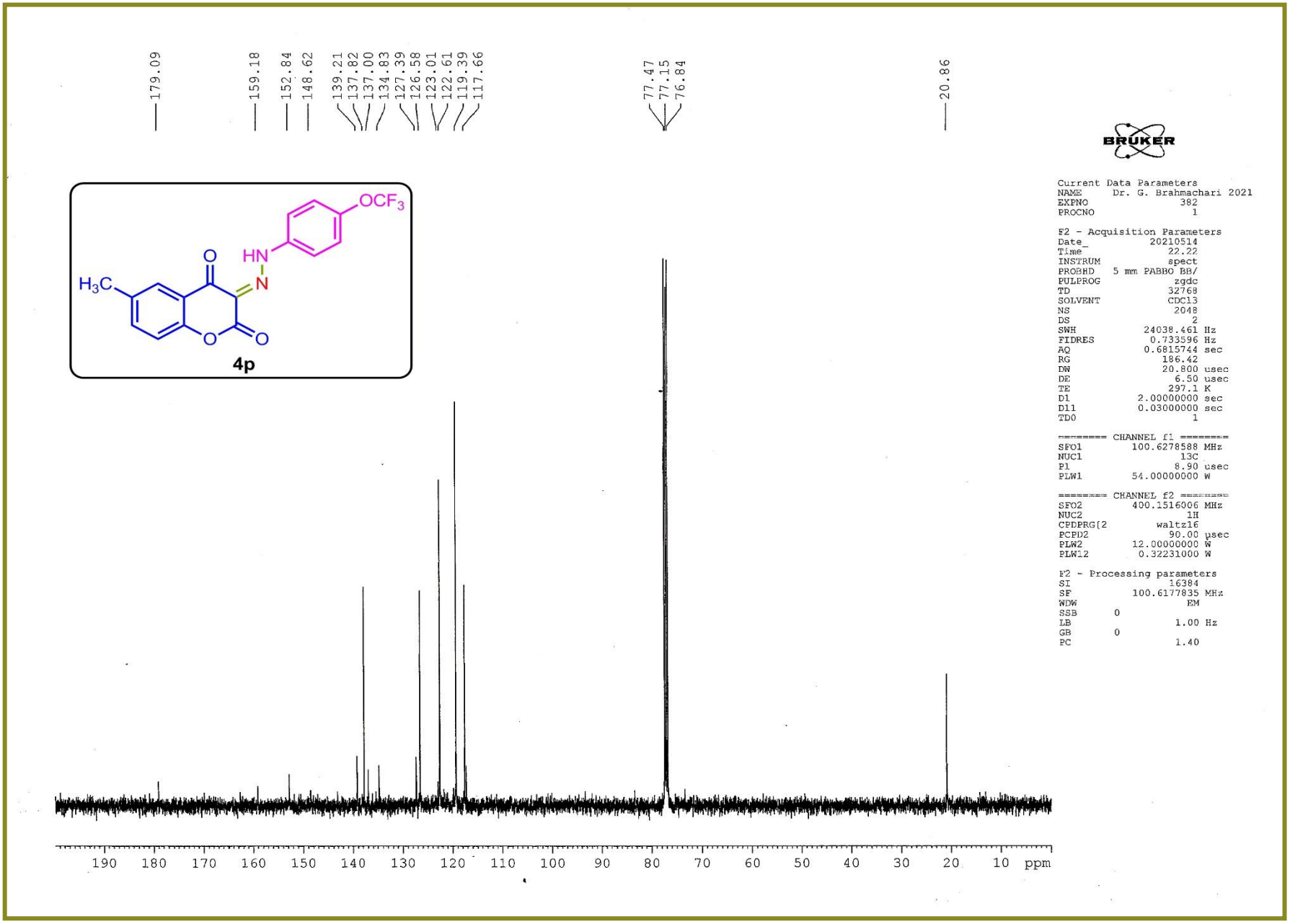


Figure S61. $^{13}$C-NMR spectrum of (*E*)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazineylidene)chromane-2,4-dione (**4p**)

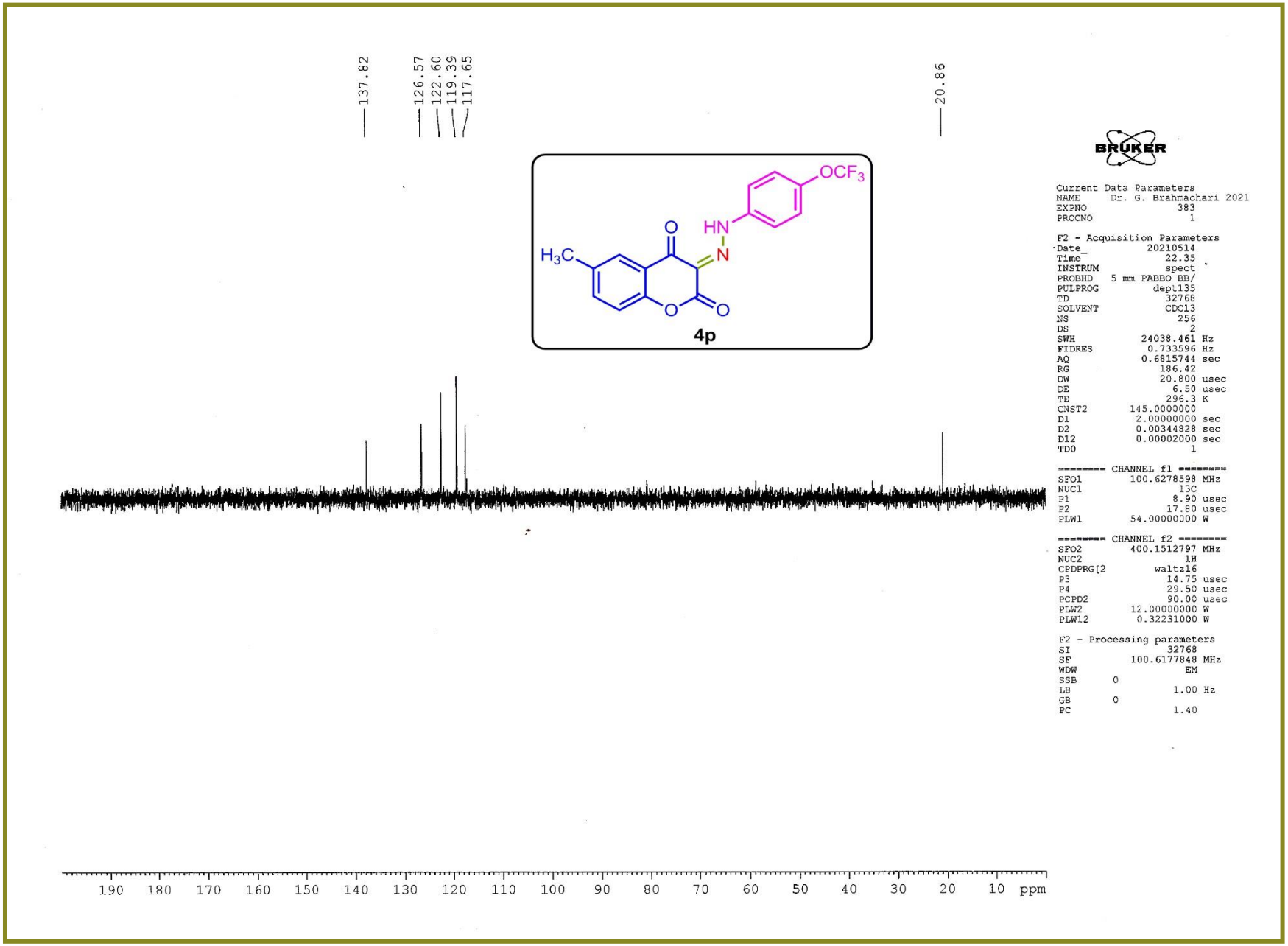


Figure S62. DEPT-135 NMR spectrum of (*E*)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazineylidene)chromane-2,4-dione (**4p**)

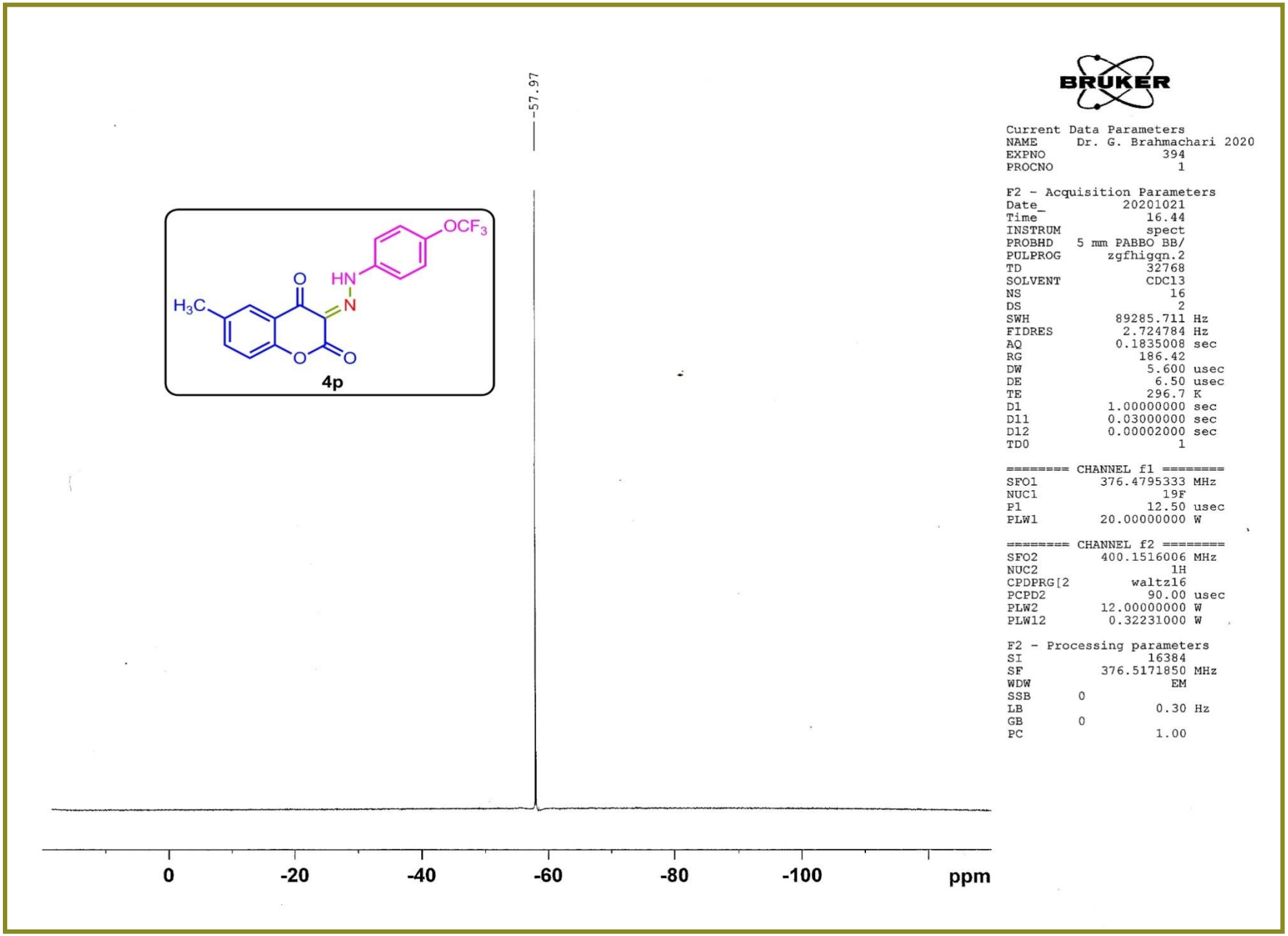


Figure S63. $^{19}$F NMR spectrum of (*E*)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazineylidene)chromane-2,4-dione (**4p**)

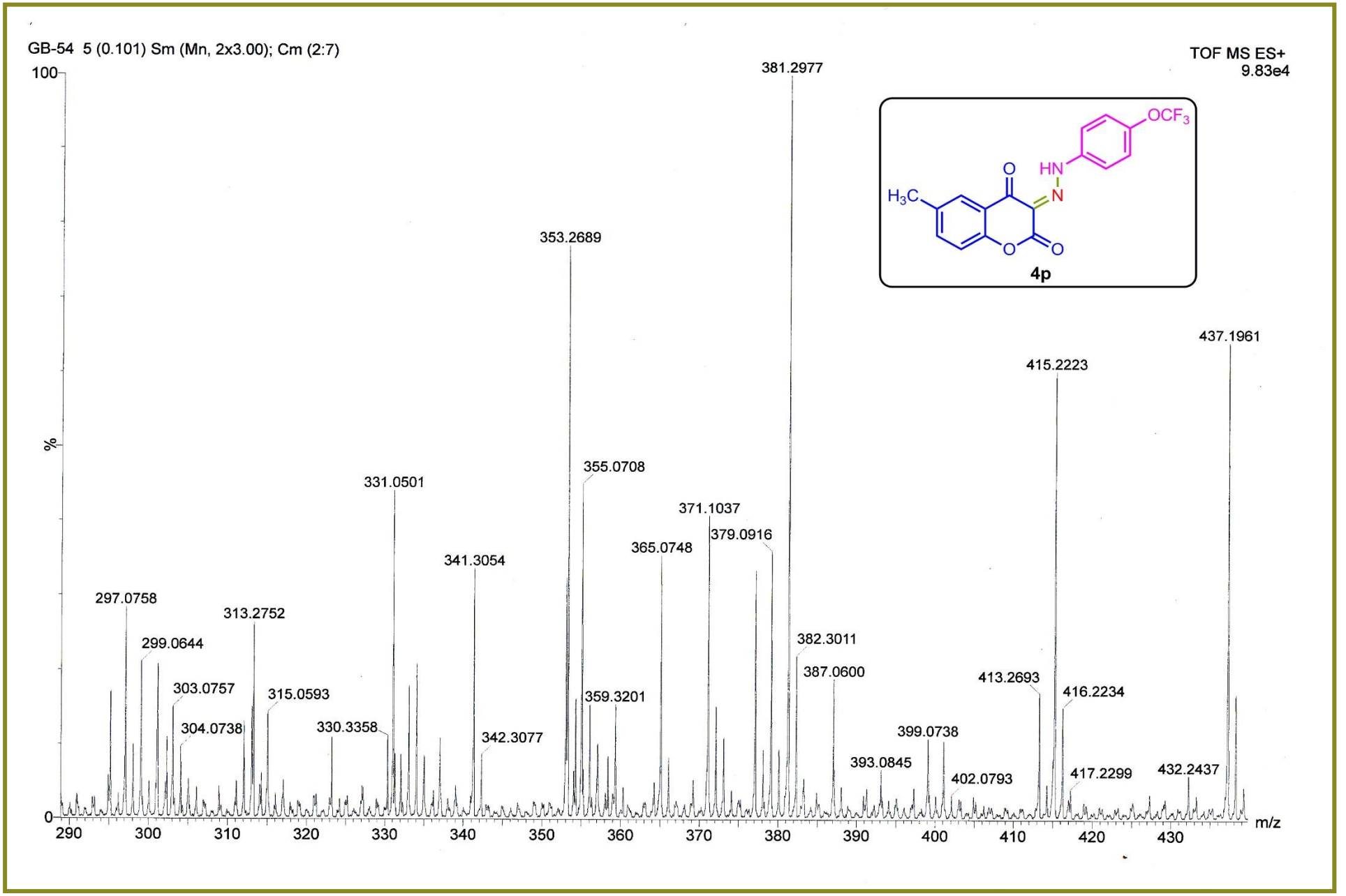


Figure S64. Mass spectra of (*E*)-6-methyl-3-(2-(4-(trifluoromethoxy)phenyl)hydrazineylidene)chromane-2,4-dione (**4p**)

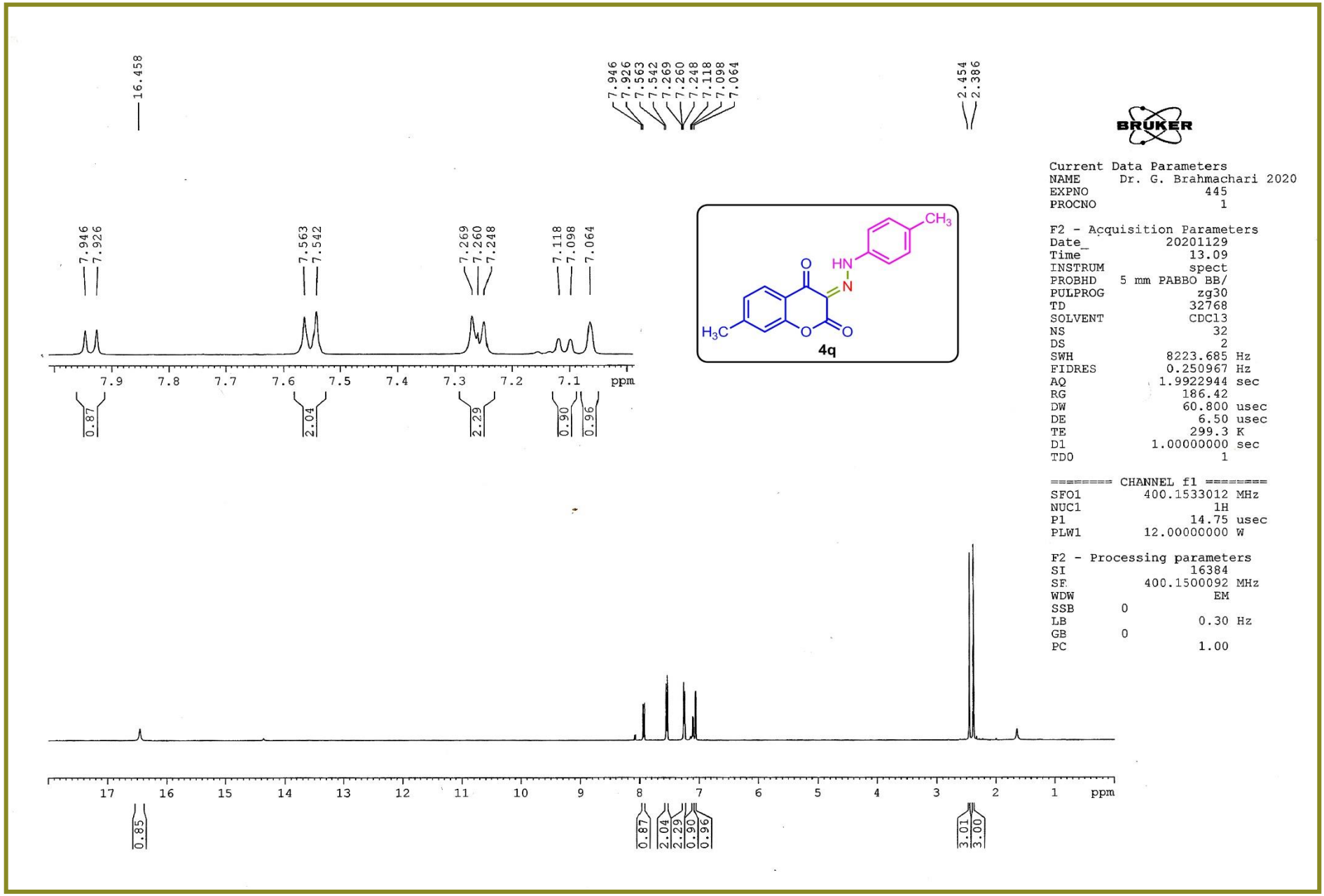


Figure S65. $^{1}$H-NMR spectrum of (*E*)-7-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4q**)

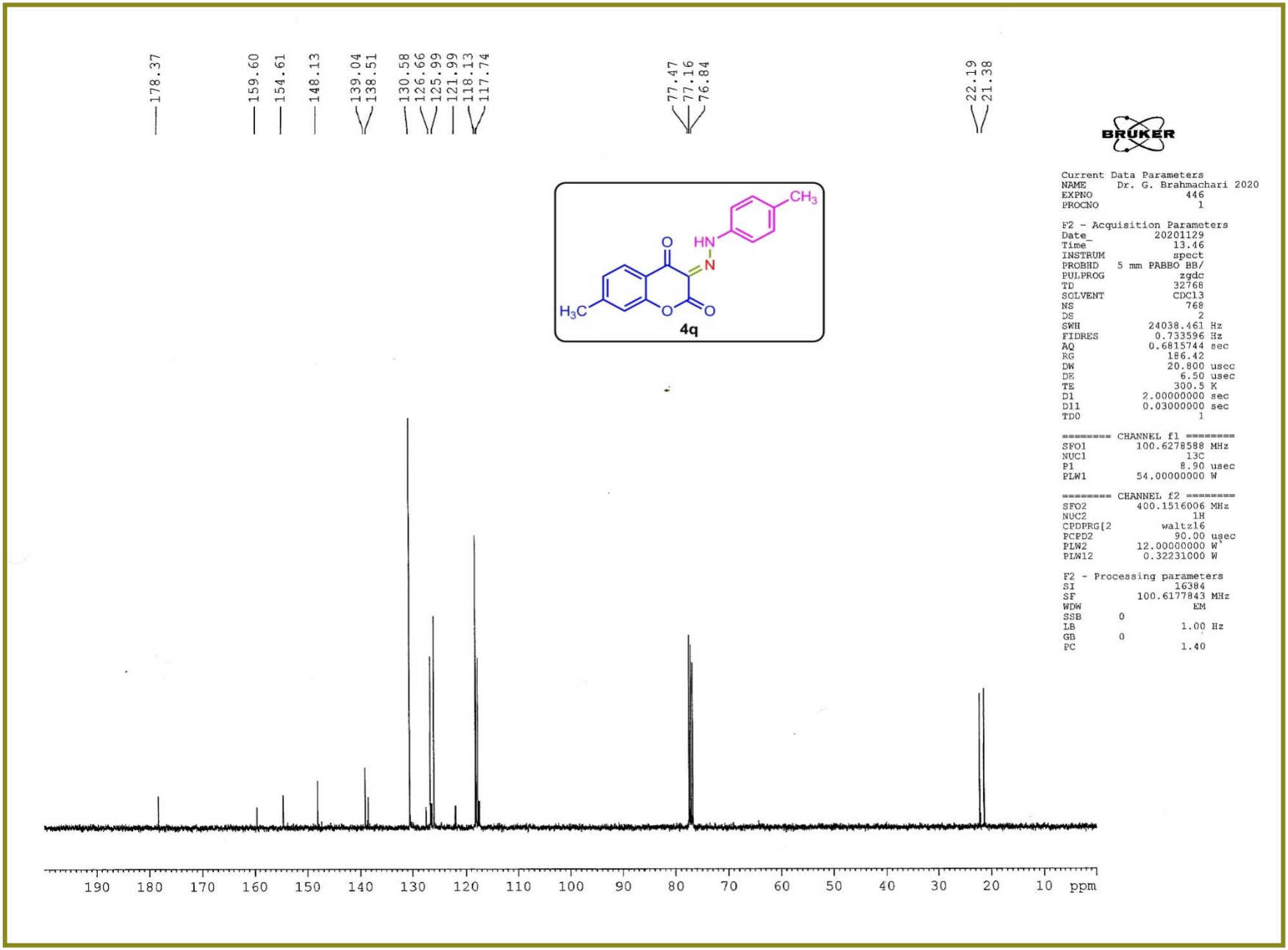


Figure S66. $^{13}$C-NMR spectrum of (*E*)-7-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4q**)

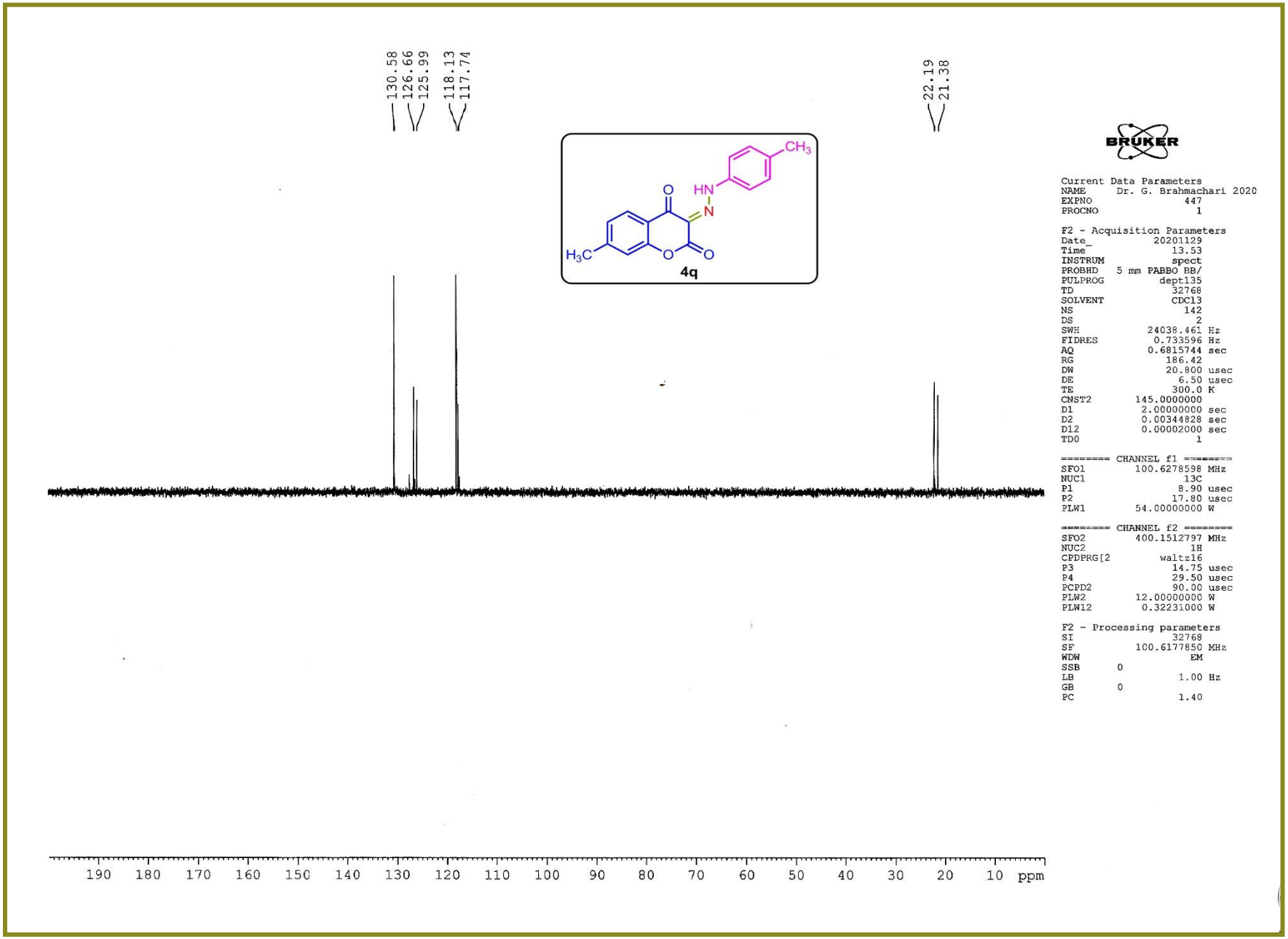


Figure S67. DEPT-135 NMR spectrum of (*E*)-7-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4q**)

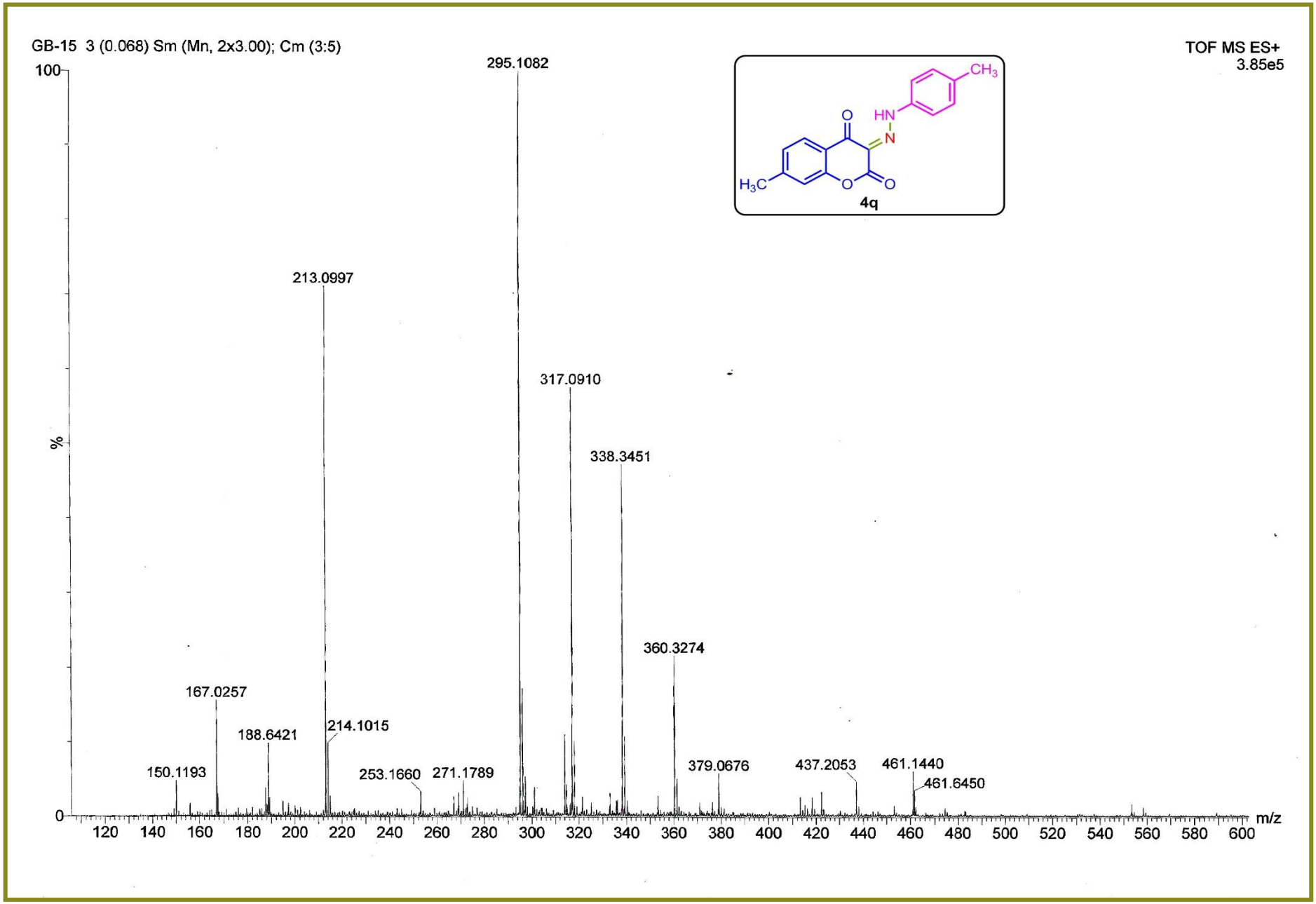


Figure S68. Mass spectra of (*E*)-7-methyl-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4q**)


Figure S69. $^{1}$H-NMR spectrum of (*E*)-7-methoxy-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4r**)

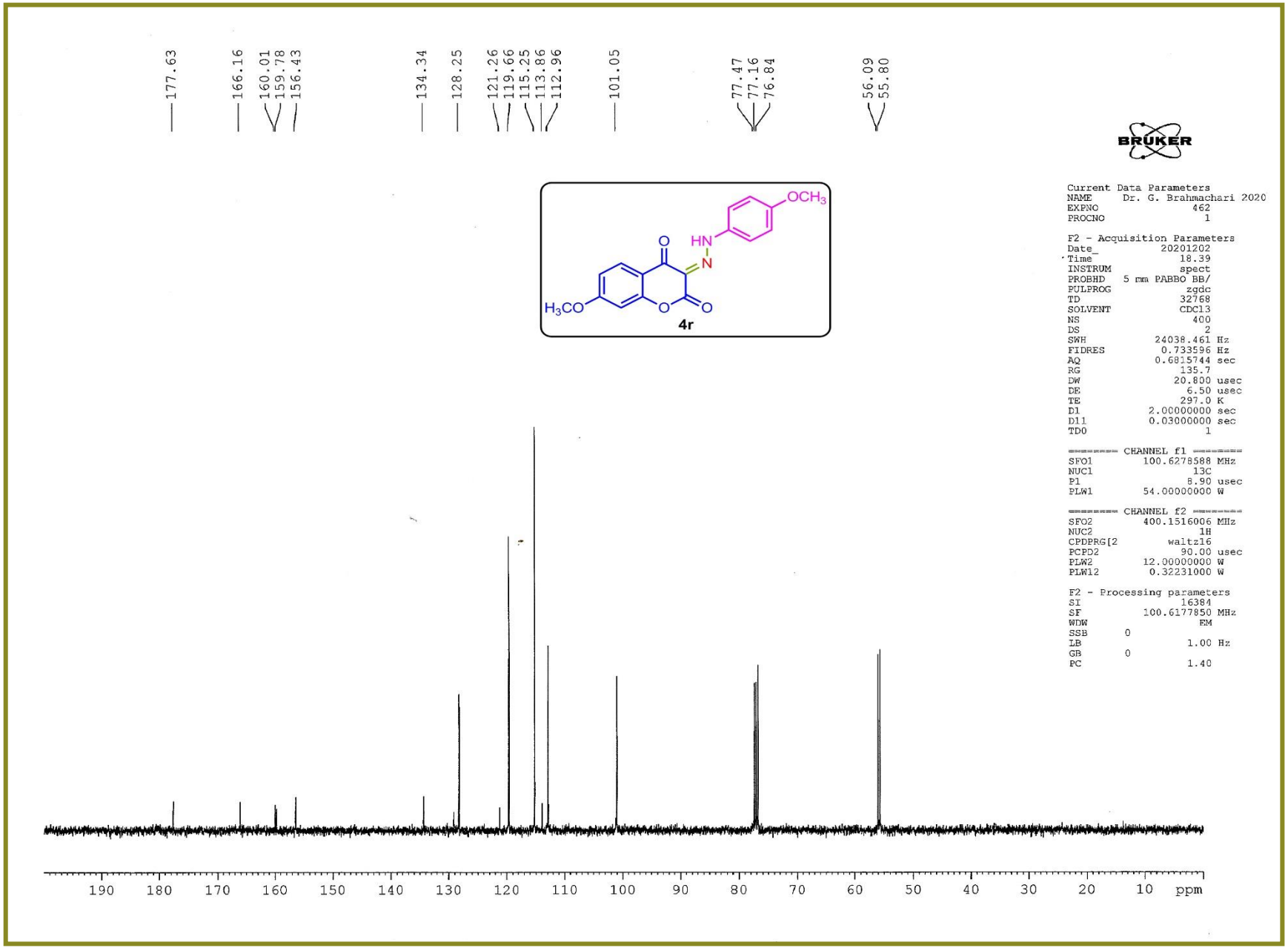


Figure S70. $^{13}$C-NMR spectrum of (*E*)-7-methoxy-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4r**)

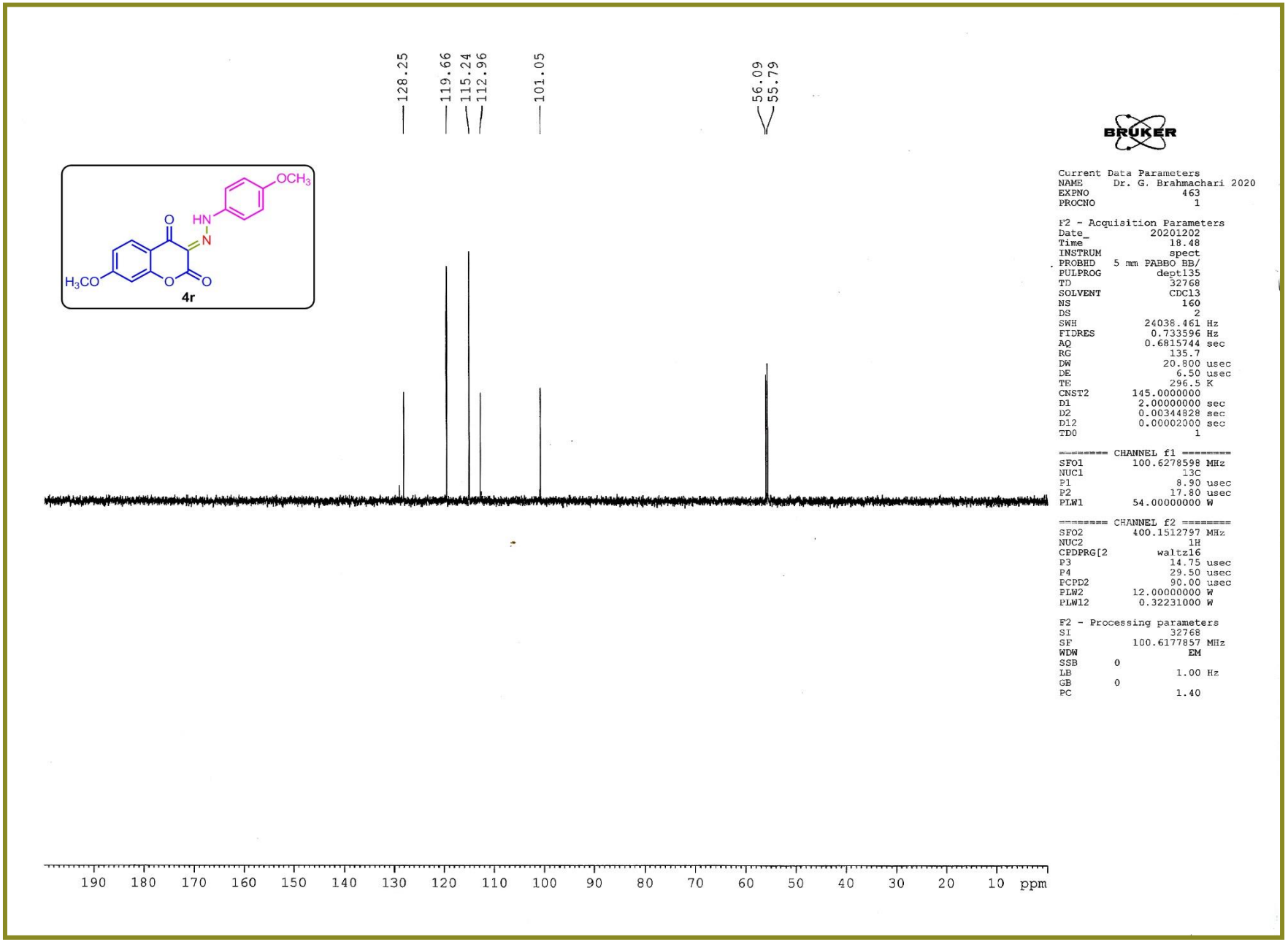


Figure S71. DEPT-135 NMR spectrum of (*E*)-7-methoxy-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4r**)

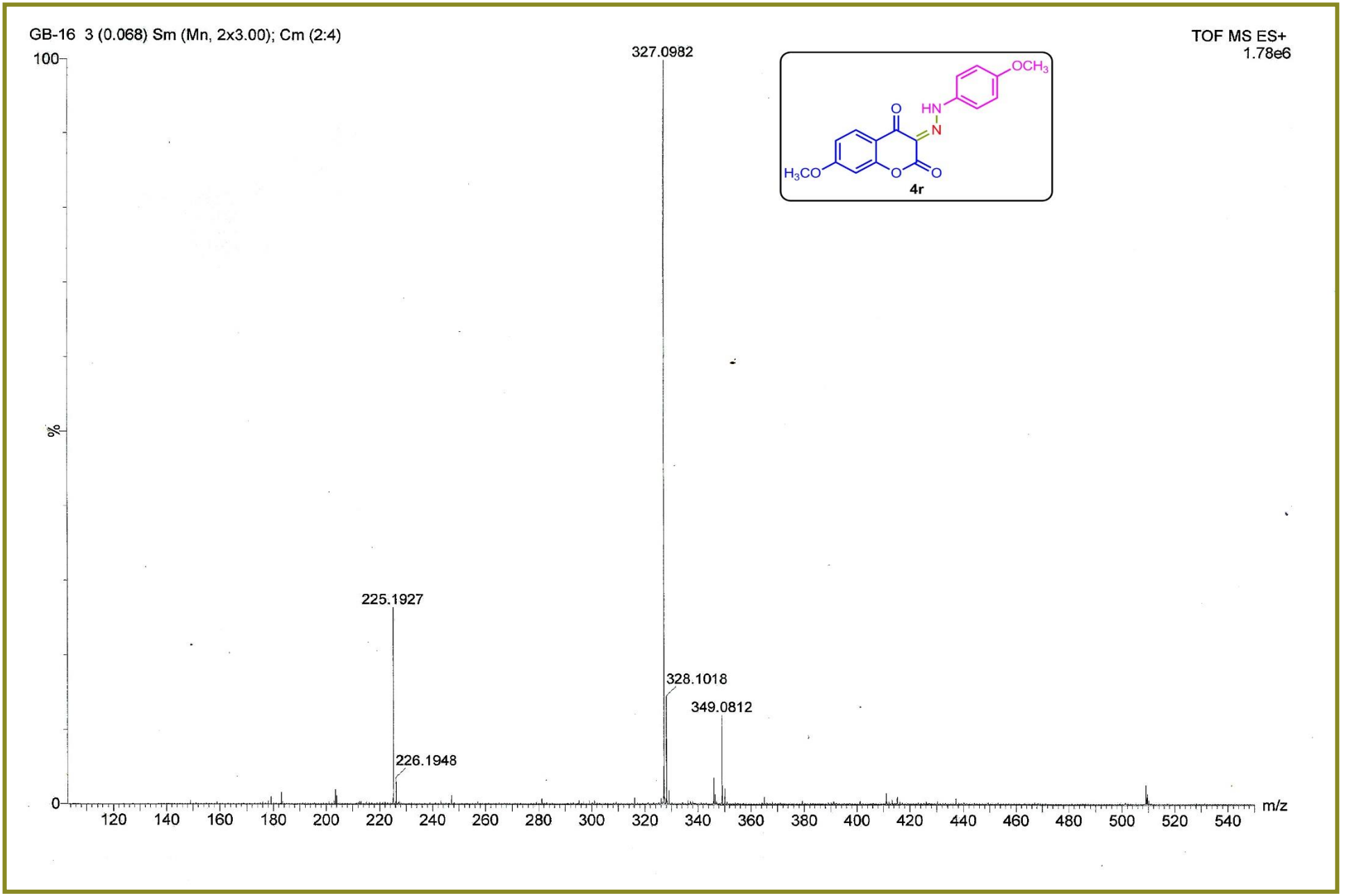


Figure S72. Mass spectra of (*E*)-7-methoxy-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4r**)

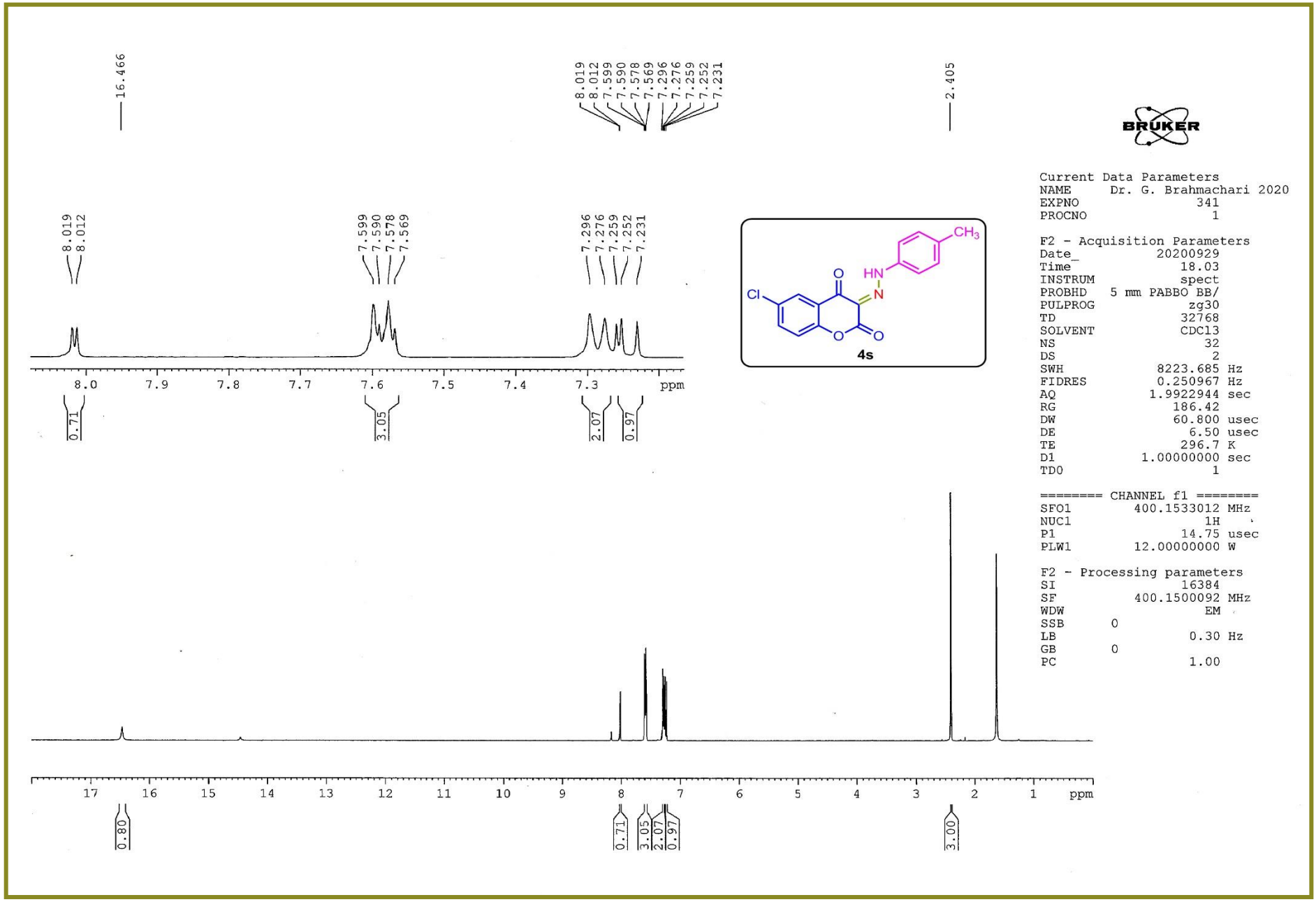


Figure S73. $^{1}$H-NMR spectrum of (*E*)-6-chloro-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4s**)

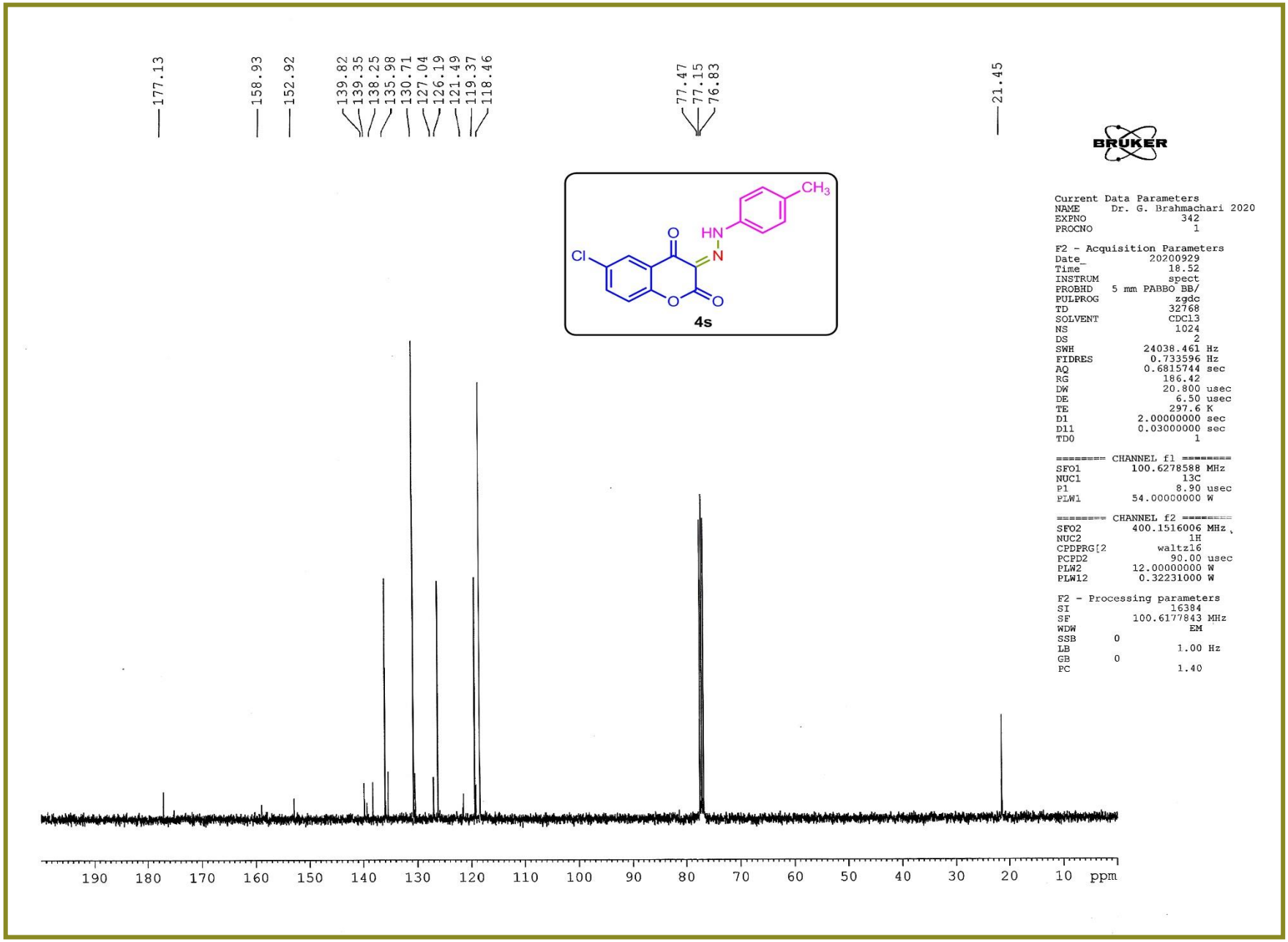


Figure S74. $^{13}$C-NMR spectrum of (*E*)-6-chloro-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4s**)

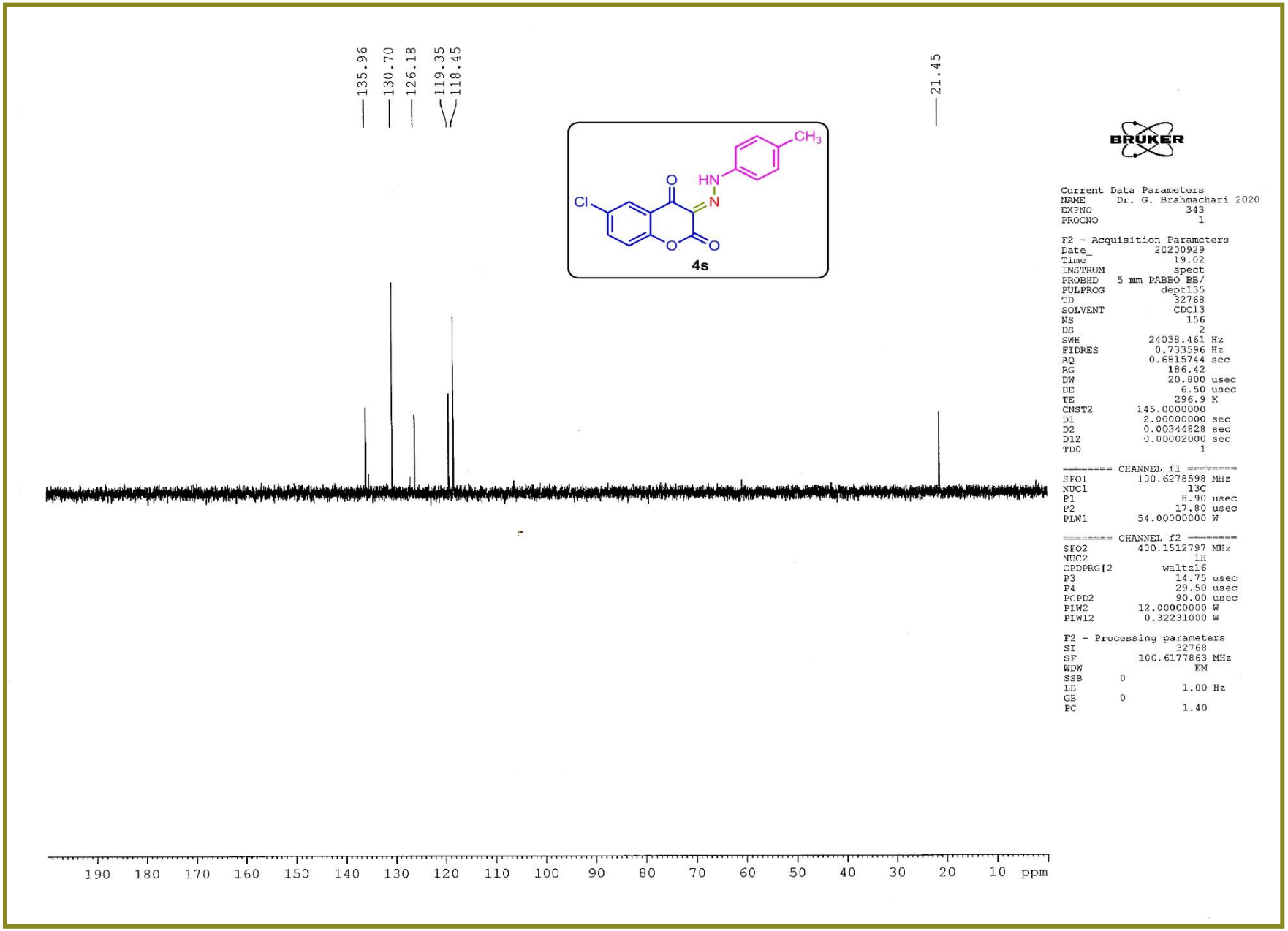


Figure S75. DEPT-135 NMR spectrum of (*E*)-6-chloro-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4s**)

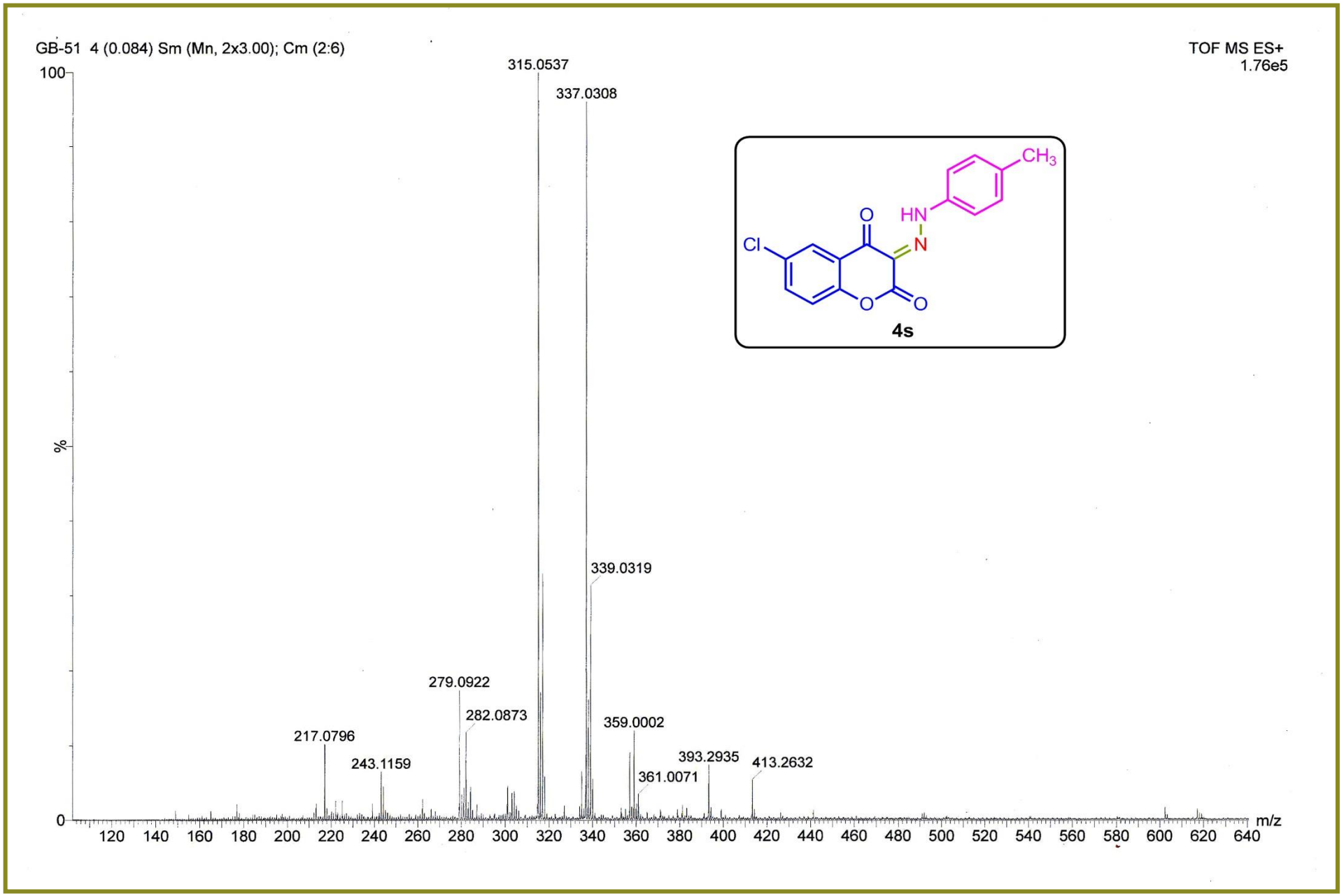


Figure S76. Mass spectra of (*E*)-6-chloro-3-(2-(*p*-tolyl)hydrazineylidene)chromane-2,4-dione (**4s**)

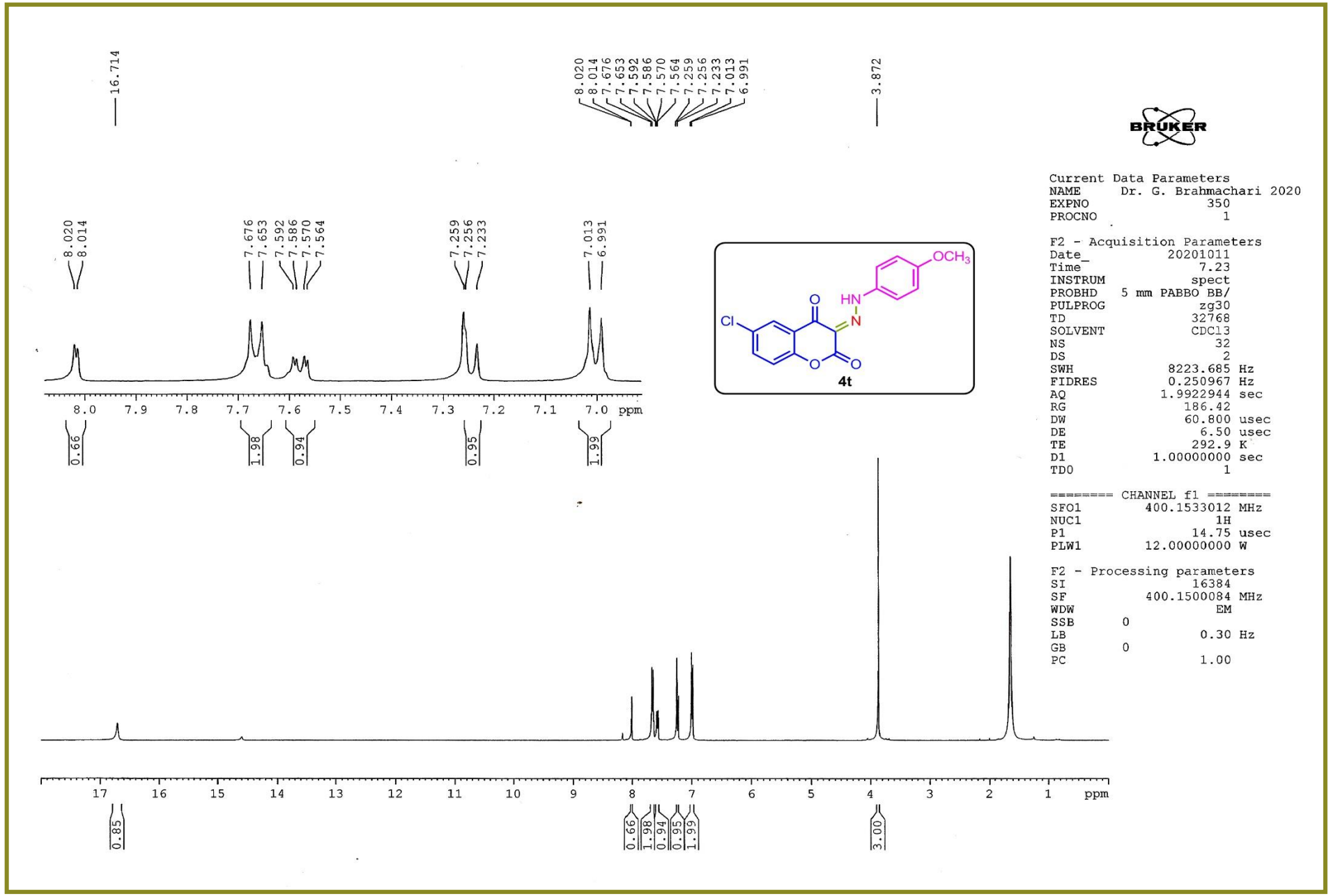


Figure S77. $^{1}$H-NMR spectrum of (*E*)-6-chloro-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4t**)

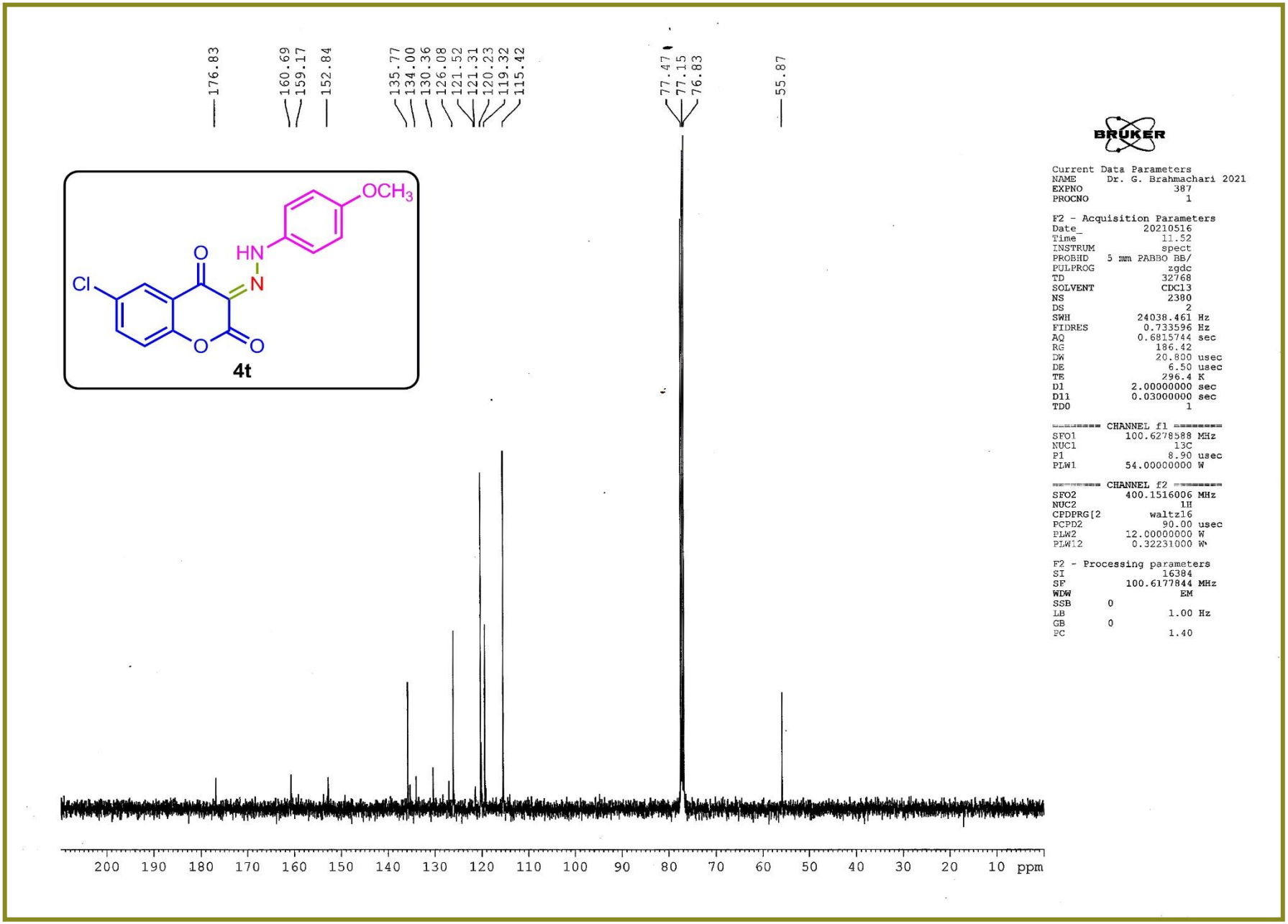


Figure S78. $^{13}$C-NMR spectrum of (*E*)-6-chloro-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4t**)

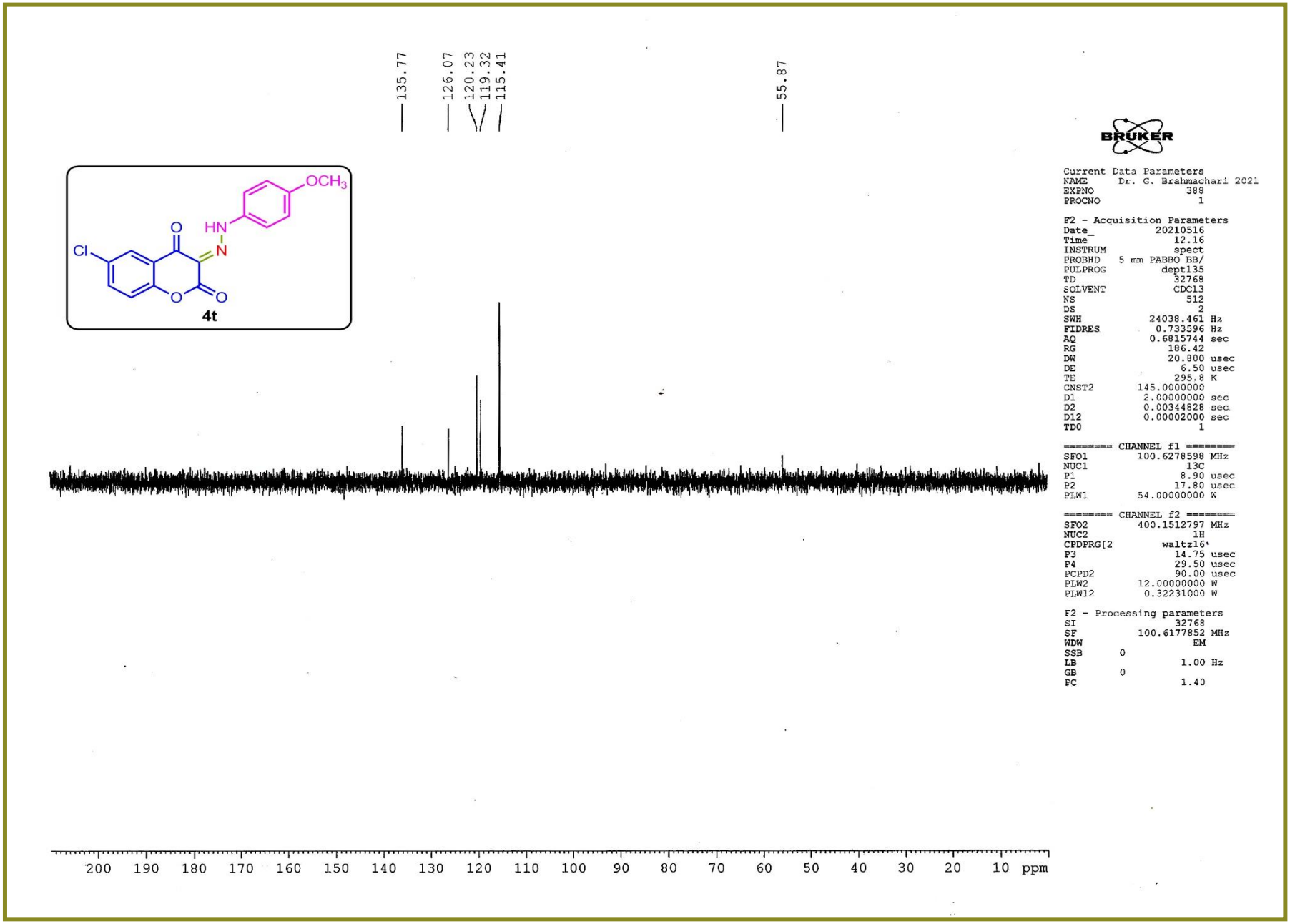


Figure S79. DEPT-135 NMR spectrum of (*E*)-6-chloro-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4t**)

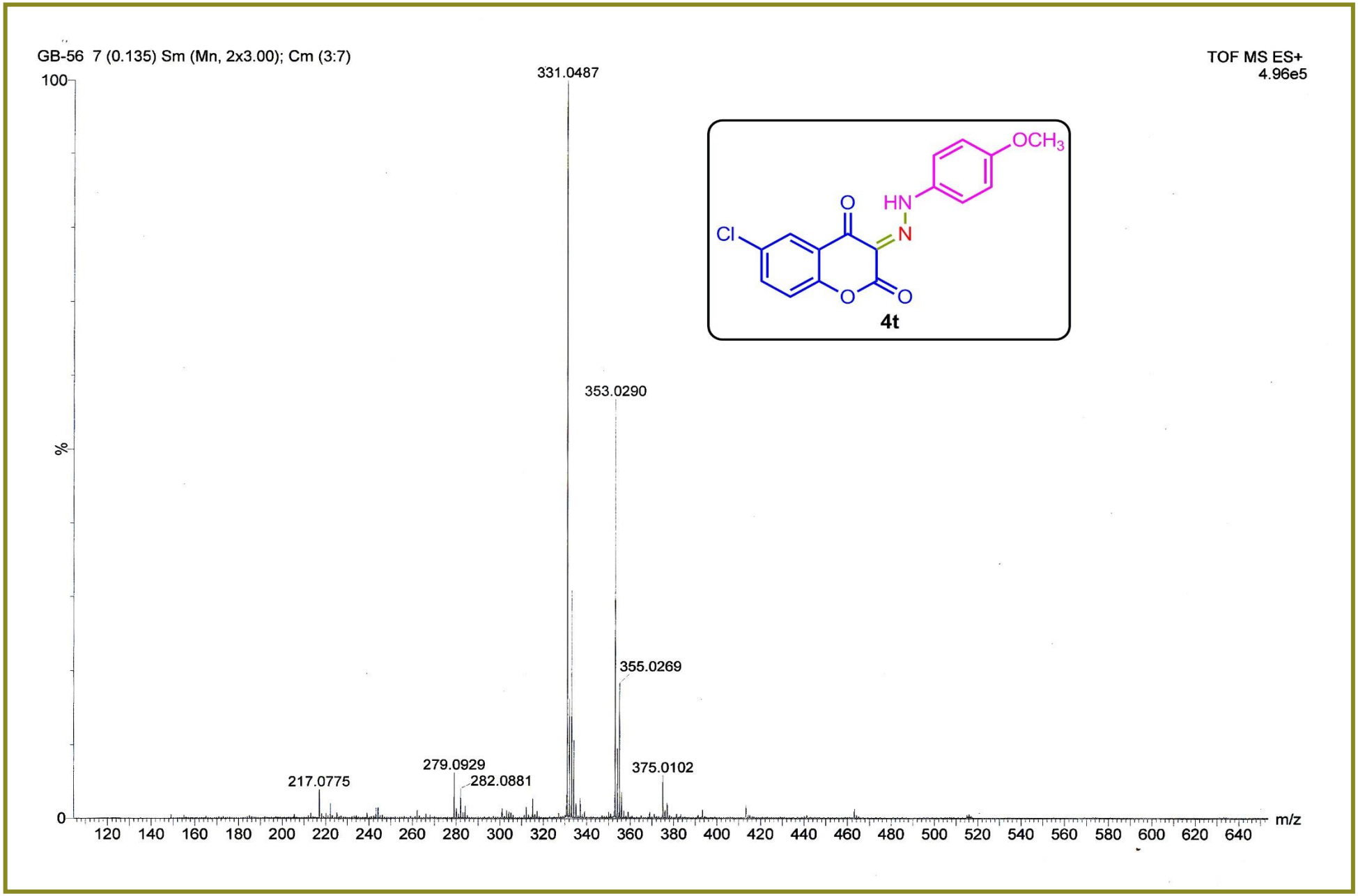


Figure S80. Mass spectra of (*E*)-6-chloro-3-(2-(4-methoxyphenyl)hydrazineylidene)chromane-2,4-dione (**4t**)

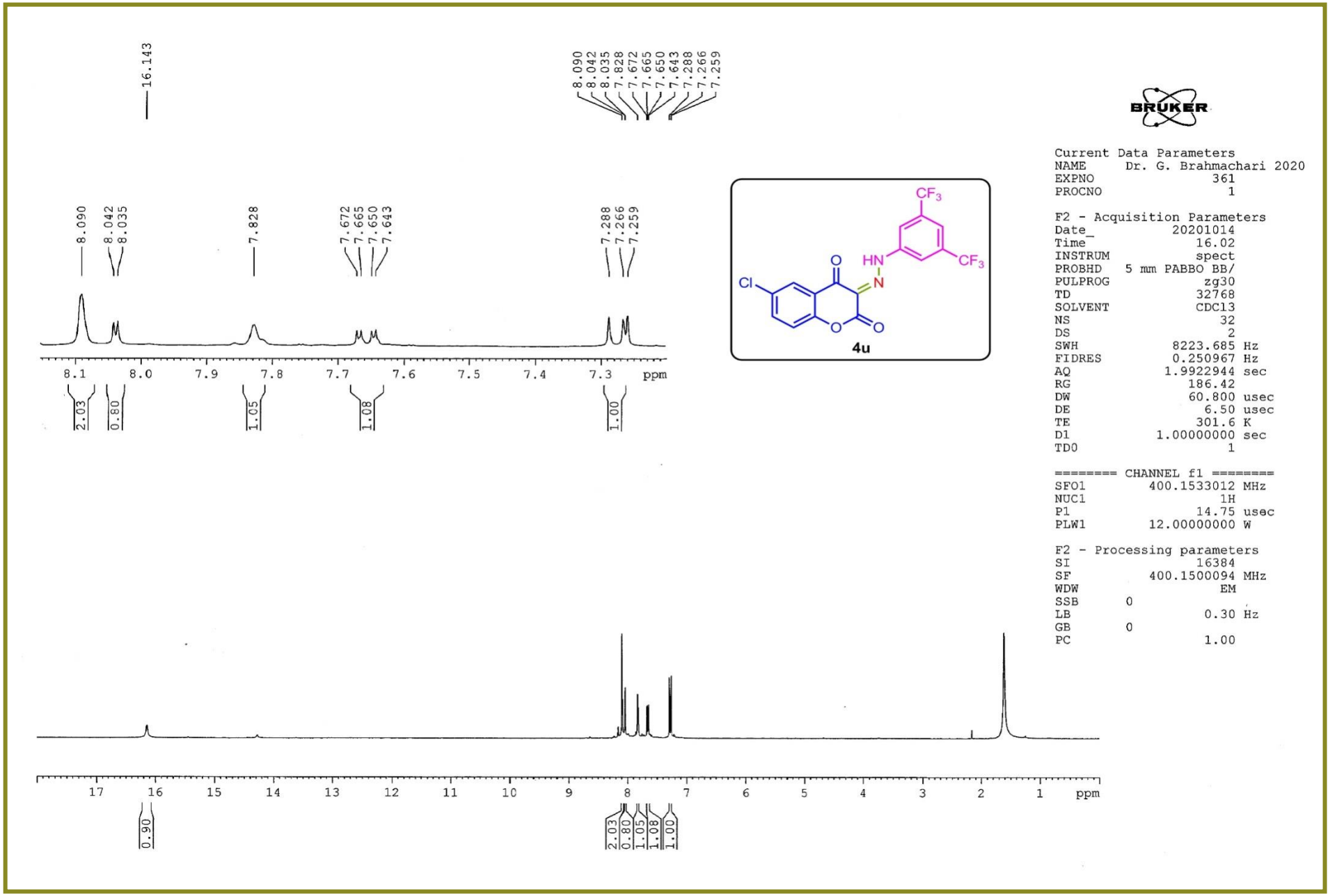


Figure S81. $^{1}$H-NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-6-chlorochromane-2,4-dione (**4u**)

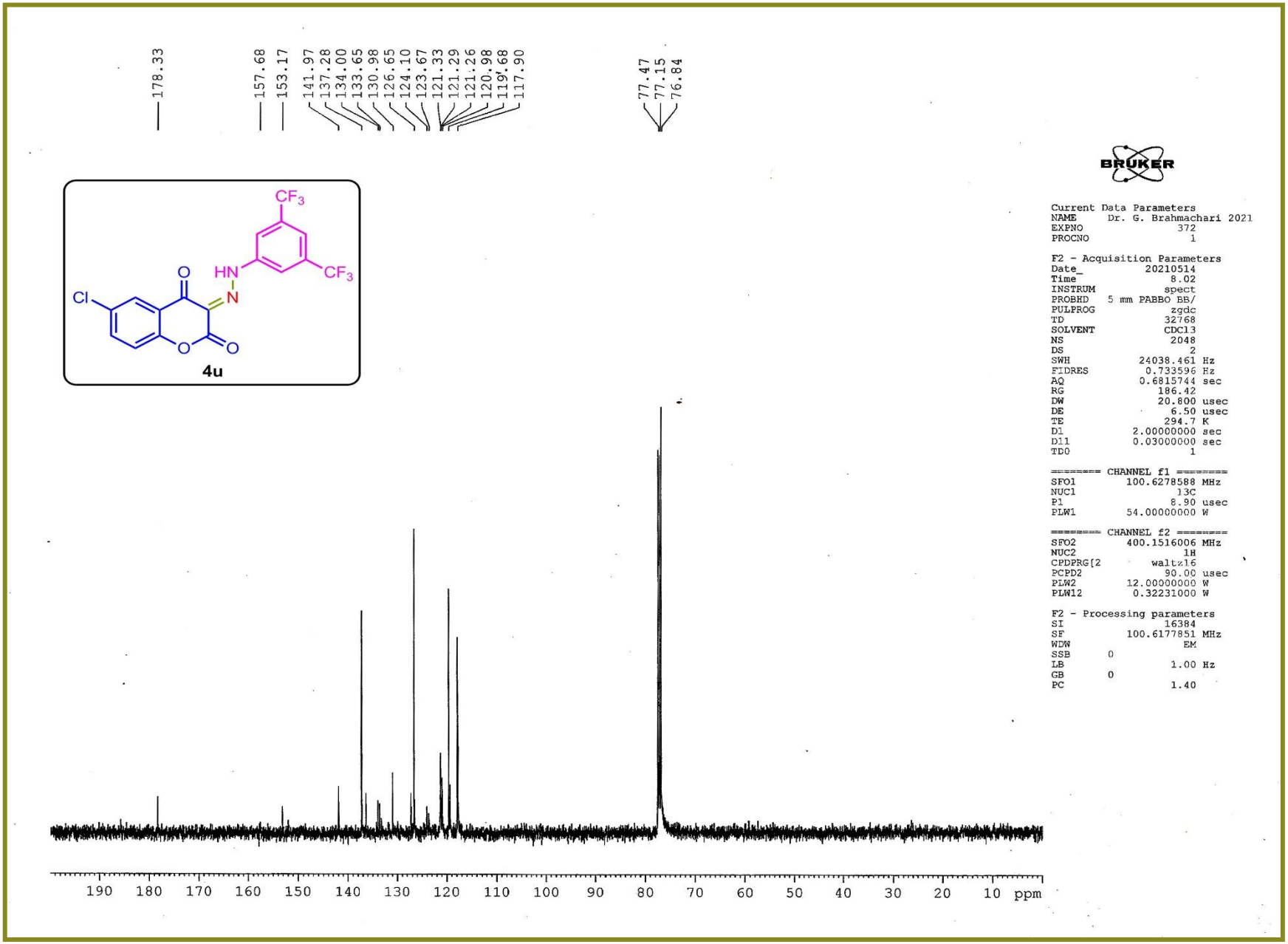


Figure S82. $^{13}$C-NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-6-chlorochromane-2,4-dione (**4u**)

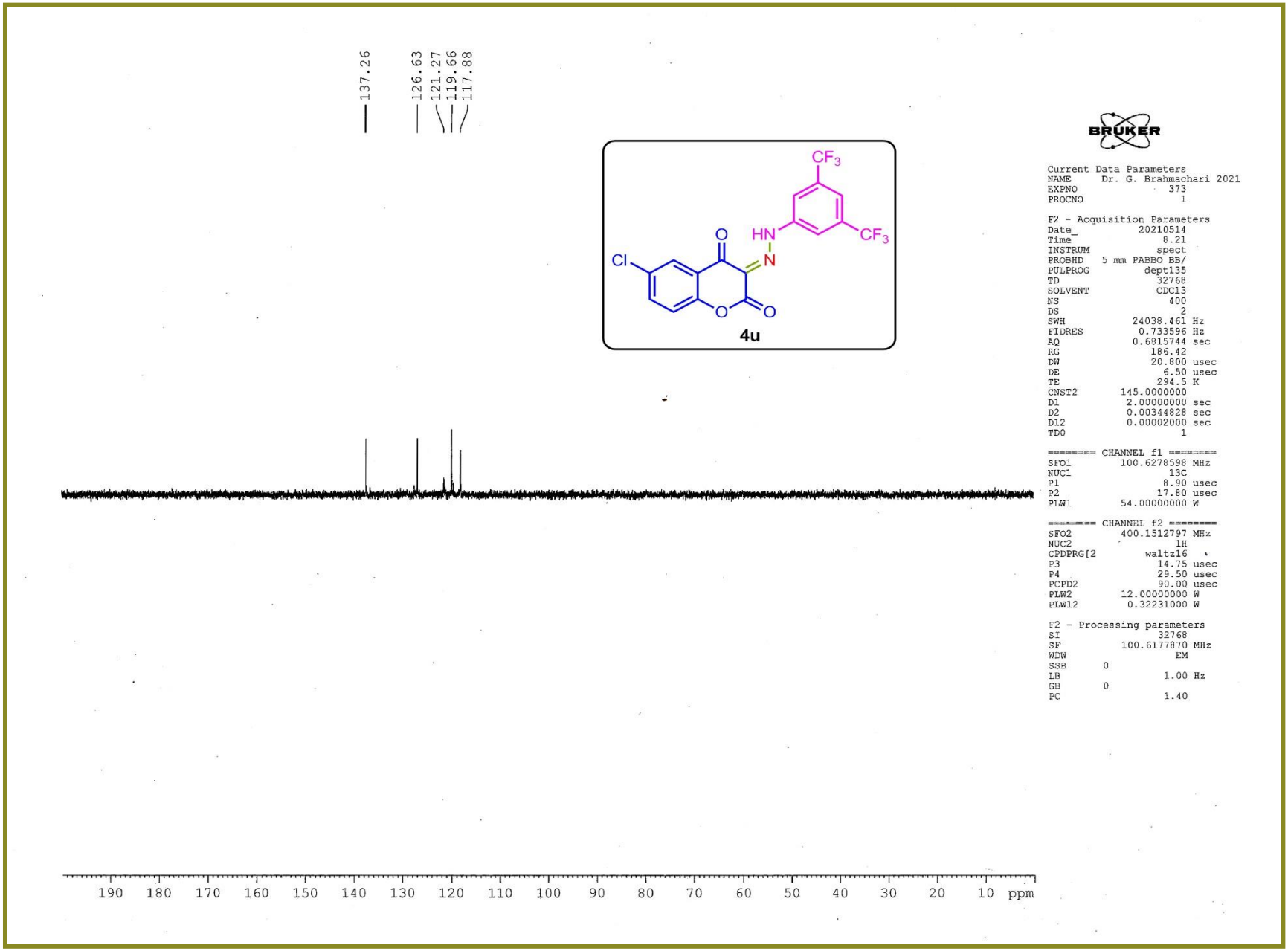


Figure S83. DEPT-135 NMR spectrum of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-6-chlorochromane-2,4-dione (**4u**)

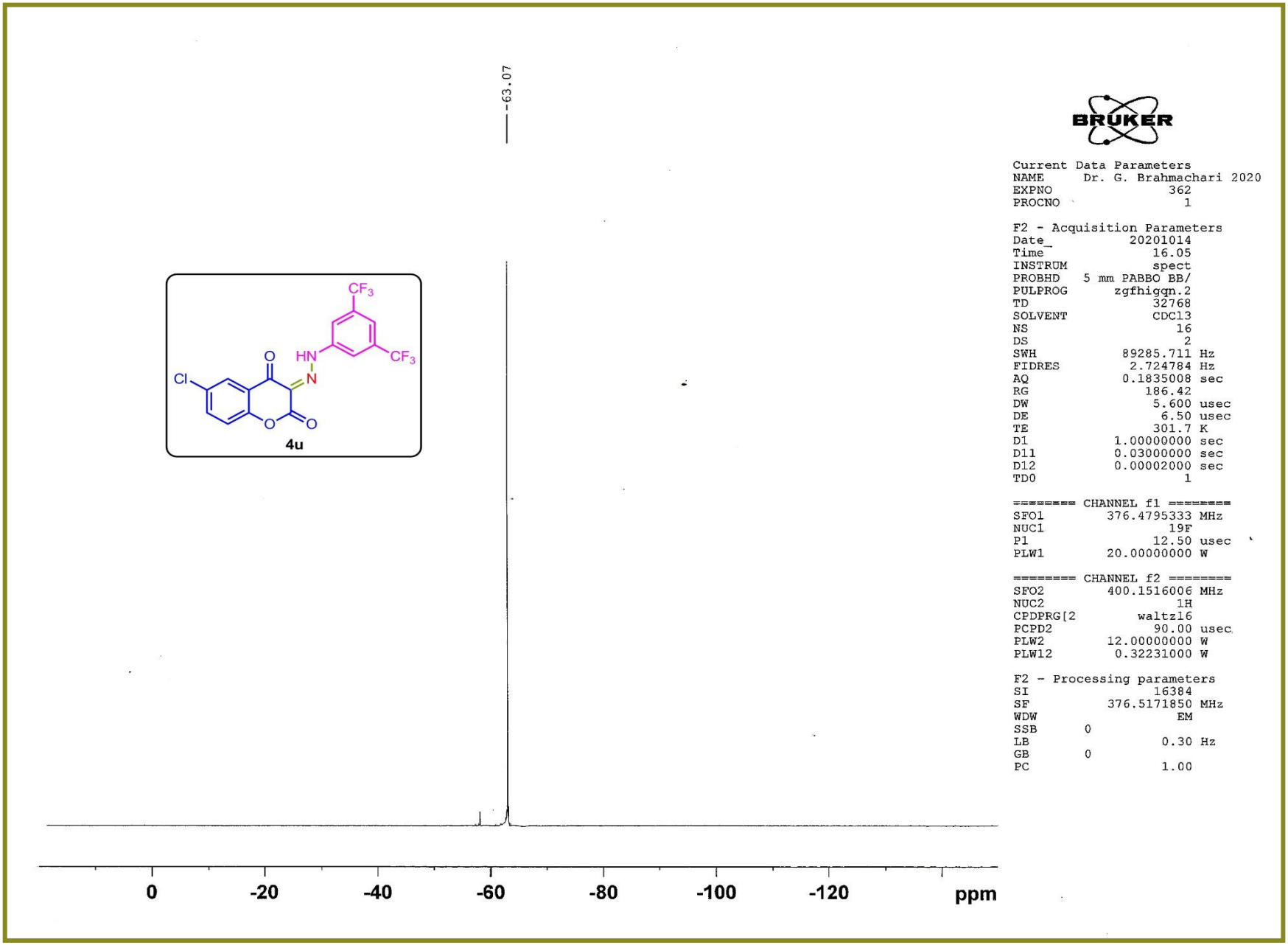


Figure S84. $^{19}$F NMR of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-6-chlorochromane-2,4-dione (**4u**)

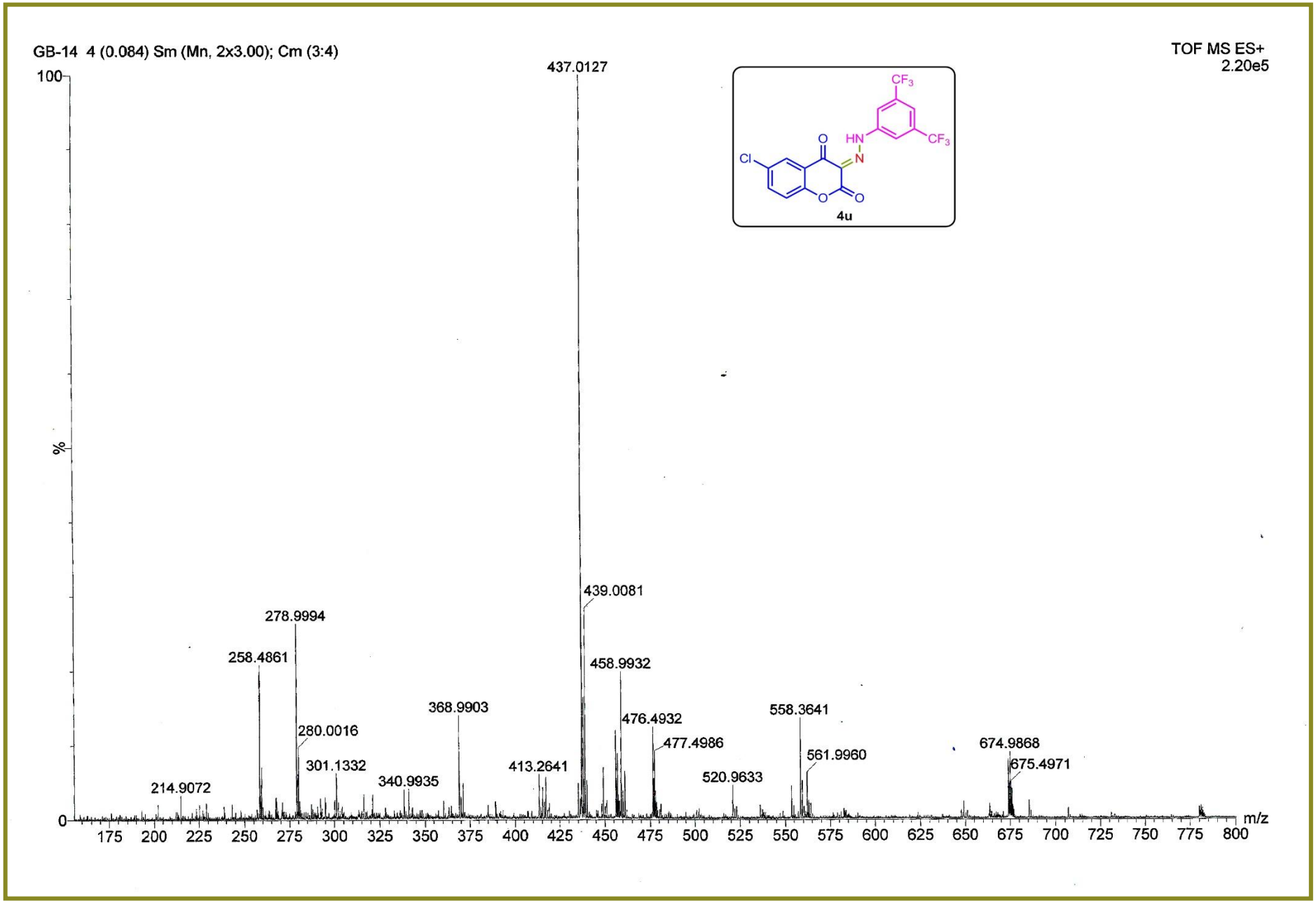


Figure S85. $^{19}F$ NMR of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-6-chlorochromane-2,4-dione (**4u**)

## 3. Single X-ray crystal structure analysis of (*E*)-3-(2-(3,5-bis(trifluoromethyl)phenyl)hydrazono)chroman-2,4-dione (4k)

*4.1 Preparation of single crystals of compound **4k***

For preparing single crystals of compound **4k**, 30 mg of the sample was dissolved in 5 mL of commercial dimethyl sulphoxide, and the solution was left for 15 days for slow evaporation at ambient conditions to yield orange block-shaped crystals.

*4.2 Single crystal X-ray diffraction studies of compound **4k**: crystal structure determination and refinement*

CCDC 2070059 (Compound **4k**) 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

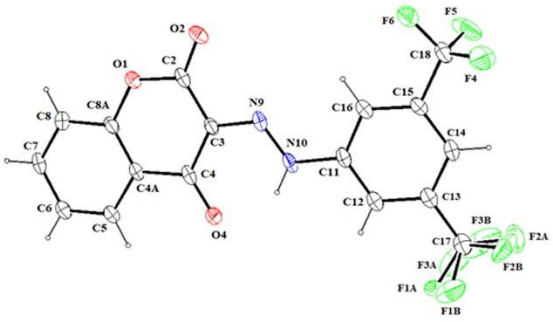


**Figure S86a**

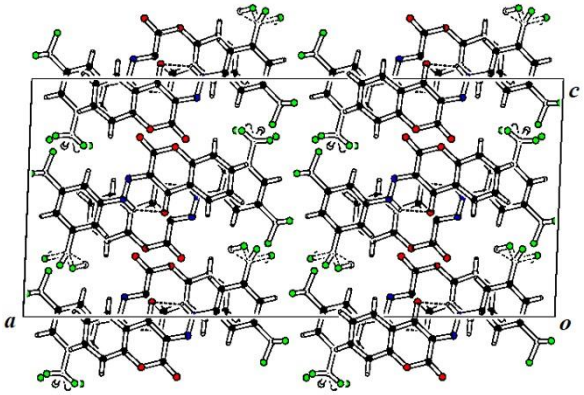


**Figure S86b**

**Figure S86a** *ORTEP* view of the molecule, showing the atom-labelling scheme
**Figure S86b.** Packing view of molecules down to b-axis [non-interacting hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 40% probability level, and H atoms are shown as small spheres of arbitrary radii.

**Table S1. Crystal data and structure refinement for (*E*)-3-(2-(3,5-bis(trifluoromethyl)-phenyl)hydrazono)chroman-2,4-dione (4k)**

| | | |
|---|---|---|
| CCDC Number | 2070059 | |
| Empirical formula | $C_{17}H_8F_6N_2O_3$ | |
| Formula weight | 402.25 | |
| Temperature | 150.01(11) K | |
| Wavelength | 0.71073Å | |
| Crystal system | Monoclinic | |
| Space group | C 2/c | |
| Unit cell dimensions | a = 31.1491(1) Å | α =90° |
| | b = 7.2268(4) Å | β =92.130(4)° |
| | c = 13.9792(7) Å | γ=90° |
| Volume | 3144.2(3) $Å^3$ | |
| Z | 8 | |

| | |
|---|---|
| Density (calculated) | 1.700 $Mg/m^3$ |
| Absorption coefficient (μ) | 0.164 $mm^{-1}$ |
| F(000) | 1616 |
| Crystal size | 0.30 × 0.20× 0.20 $mm^3$ |
| Crystal shape (colour) | Block (orange) |
| Theta range for data collection | 2.6160 to 27.5610° |
| Index ranges | -36<=h<=32, -8<=k<=3, -16<=l<=8 |
| Reflections collected | 4195 |
| Independent reflections | 2733 [R(int) = 0.1022] |
| Completeness to theta = 24.998° | 98.4 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2733 / 0 / 285 |
| Goodness-of-fit on $F^2$ | 1.174 |
| Final R indices [I>2σ(I)] | R1 = 0.1339, wR2 = 0.3394 |
| R indices (all data) | R1 = 0.1088, wR2 = 0.2891 |
| Largest diff. peak and hole | 0.543 and -0.565 $e.Å^{-3}$ |
| Scan mode | ω scan |
| θ range for entire data collection | 2.62º to 27.56º |
| Reflections observed (I > 2σ(I)) | 1788 |
| R(sigma) | 0.0876 |
| Structure determination | Direct methods |
| No. of parameters refined | 285 |
| Final residual electron density | 0.543 and -0.565 $e.Å^{-3}$ |
| Software for geometry calculation | WinGX [1] |
| Software for structure solution: | SHELXS-97 [4] |
| Software for refinement: | SHELXL-97[5] |
| Software for molecular plotting: | Ortep3 [6], PLATON[3] |
| Software for geometrical calculation | PARST [2] |

**4. Calculation of E-factors for all the synthesized compounds (4a-4u)**

The following formulae were used for calculating E-factor.[7-15] Calculated data for compounds **4a** – **4u** are presented in Table S2.

$$\text{E-factor} = \frac{\text{Total mass of wastes}}{\text{Mass of product}} = \frac{\text{Mass of raw materials - Mass of product}}{\text{Mass of product}}$$

**Respective amounts:**

*Reagents:* 4-Hydroxycoumarin: 0.486g (MW: 162.14); 6-chloro-4-hydroxy-2*H*-chromen-2-one: 0.590g (MW: 196.59); 4-hydroxy-6-methyl-2*H*-chromen-2-one: 0.529g (MW: 176.17); 4-hydroxy-7-methyl-2*H*-chromen-2-one: 0.529g (MW: 176.17); 4-hydroxy-7-methoxy-2H-chromen-2-one: 0.577g (MW: 192.17); aniline: 0.279g (MW: 93.13); *p*-toluidine: 0.321g (MW: 107.15); *p*-anisidine: 0.369g (MW:123.15); 4-(methylthio)aniline: 0.418g (MW: 139.22); 3-(methylthio)aniline: 0.418g (MW: 139.22); *p*-bromoaniline: 0.516g (MW: 172.02); 2,5-dichloroaniline 0.486g (MW: 162.01); 4-trifluoromethylaniline: 0.483g (MW: 161.12); 3,4-

bis(trifluoromethyl)aniline: 0.387g (MW: 229.12); 4-trifluoromethoxyaniline: 0.531g (MW: 177.12); (trifluoromethylthio)aniline: 0.580g (MW: 193.19); 4-nitroaniline: 0.414g (MW: 138.13); 2-nitroaniline: 0.414g (MW: 138.13); *tert*-butyl nitrite: 0.309g (MW: 103.12).

***Products*** (Molecular weight, MW): **4a**: 0.702g (MW: 266.26); **4b:** 0.880g (MW: 345.15); **4c:** 0.702g (MW: 280.28); **4d:** 0.835g (MW: 296.28); **4e:** 0.758g (MW: 312.34); **4f:** 0.786g (MW: 312.34); **4g:** 0.883g (MW: 311.25); **4h:** 0.868g (MW: 311.25); **4i:** 0.914g (MW: 350.25); **4j:** 0.922g (MW: 366,31); **4k:** 1.097g (MW: 402.25); **4l:** 0.884g (MW: 435.14); **4m:** 0.723g (MW: 294.31); **4n:** 0.772g (MW: 310.31); **4o:** 0.923g (MW: 380.34); **4p:** 0.874g (MW: 364.28); **4q:** 0.750g (MW: 294.31); **4r:** 0.841g (MW: 326.31); **4s:** 0.775g (MW: 314.73); **4t:** 0.775g (MW: 330.72); **4u:** 1.062g (MW: 436.69).

**Documentation of Calculations of Green Metric (E-factor) for One Representative Entry, *viz.* (*E*)-3-(2-phenylhydrazono)chroman-2,4-dione (4a):**

$$\text{E-factor} = \frac{\text{Mass of wastes}}{\text{Mass of product}} = \frac{\text{Mass of raw materials} - \text{Mass of product}}{\text{Mass of product}}$$

$$= \frac{(0.486\ \text{g} + 0.279\ \text{g} + 0.309\ \text{g}) - 0.702\ \text{g}}{0.702\ \text{g}} = 0.53\ \ (\text{g/g})$$

**Table S2**. Calculated E-factors for the compounds (**4a** – **4u)**

| **Sl. No** | **Product** | **E-Factor** (g/g) |
|---|---|---|
| 1 | **4a** | 0.53 |
| 2 | **4b** | 0.49 |
| 3 | **4c** | 0.59 |
| 4 | **4d** | 0.39 |
| 5 | **4e** | 0.60 |
| 6 | **4f** | 0.54 |
| 7 | **4g** | 0.37 |
| 8 | **4h** | 0.39 |
| 9 | **4i** | 0.45 |
| 10 | **4j** | 0.49 |
| 11 | **4k** | 0.35 |
| 12 | **4l** | 0.45 |
| 13 | **4m** | 0.59 |
| 14 | **4n** | 0.56 |
| 15 | **4o** | 0.54 |
| 16 | **4p** | 0.57 |
| 17 | **4q** | 0.55 |
| 18 | **4r** | 0.49 |
| 19 | **4s** | 0.57 |
| 20 | **4t** | 0.64 |
| 21 | **4u** | 0.49 |

[#]Lower is the value, greener is the process

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