Direct α-Arylation/Heteroarylation of 2-Trifluoroboratochromanones *via* Photoredox/Nickel Dual Catalysis

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Supporting Information

GENERAL CONSIDERATIONS:

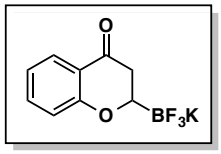
NMR Spectra (^{1}H, ^{13}C, ^{19}F) were performed at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, acetone-d_5 (δ 2.09) in acetone-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.2), DMSO-d_6 (δ 39.5), or the nitrile carbon of MeCN-d_3 (δ 118.3), respectively. Reactions were monitored by HPLC, GC/MS, ^{1}H NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32–63 μm). Flash chromatography was accomplished using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60 Å porosity, 20–40 μm). Solvents were purified by use of drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Deuterated NMR solvents were either used as purchased (DMSO-d_6) or were stored over 4Å molecular sieves. $NiCl_2$•dme, 4,4'-di-*tert*-butyl-2,2'-dipyridine, K_2HPO_4, dioxane, $MgSO_4$, CH_2Cl_2, pentane, and Et_2O were used as purchased. Aryl bromides were purchased from commercial suppliers and used without further purification. Before use, dioxane was degassed thoroughly with N_2 and stored under N_2 and molecular sieves. The photocatalyst 4CzIPN was synthesized according to Zhang's protocol.[1]

[1] Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873.

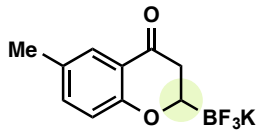
GENERAL PROCEDURE FOR BETA BORYLATION

2-(Trifluoro-λ_4-boranyl)chroman-4-one, potassium salt (IV)



A 50 mL round bottom flask was charged with chroman-4-one (585 mg, 4.0 mmol, 1.0 equiv) and brought into the glove box. $(HO)_2BB(OH)_2$ (538.2 mg, 6.0 mmol, 1.5 equiv), Cu(I)Cl (7 mg, 0.08 mmol, 0.02 equiv), CyJohnPhos (28 mg, 0.08 mmol, 0.02 equiv), and NaO*t*-Bu (115.3 mg, 1.2 mmol, 0.3 equiv) were added to the flask, which was capped in the glovebox. Under nitrogen, freshly distilled EtOH (20 mL) was added, and the mixture was stirred for 3 h at rt. Upon completion of the reaction, the EtOH was removed *in vacuo*, and the residue was dissolved in MeOH (20 mL) and cooled to 0 °C. Saturated KHF_2 (8 mL, 4.5 M) was added dropwise to the reaction, and the resulting mixture was allowed to warm to rt. After 30 min, the solution was concentrated *in vacuo* and placed on the lyophilizer overnight. A Soxhlet extraction of the solid was performed using *i*-PrOAc for 16 h, and the extract was concentrated. The resulting red solid was dissolved in acetone (~5 mL), and Et_2O was added dropwise until precipitation was induced. Additional Et_2O (20 mL) was added, and the solid was filtered to afford a light orange powder (650 mg, 64% yield). mp = 135–140 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.41 (ddd, *J* = 8.6, 6.9, 1.8 Hz, 1H), 7.00 – 6.75 (m, 2H), 3.79 – 3.47 (m, 1H), 2.72 – 2.55 (m, 1H), 2.30 (dd, *J* = 16.9, 2.4 Hz, 1H).
^{13}C NMR (126 MHz, DMSO) δ 206.5, 195.4, 164.5, 134.9, 126.1, 120.9, 118.9, 117.9, 30.7.
^{19}F NMR (471 MHz, C_6D_6) δ -143.3.
^{11}B NMR (128 MHz, DMSO) δ 3.9.
FT-IR (cm^{-1}, neat, ATR) 2848, 1674, 1604, 1463, 1308, 1149, 907, 755.
HRMS (ESI) m/z calc. for $C_9H_7O_2BF_3$ (M^-) 215.0491, found 215.0483.



6-Methyl-2-(trifluoro-l$_4$-boranyl)chroman-4-one, potassium salt

The general procedure was followed with chromone (320.2 mg, 2.0 mmol, 1.0 equiv). After 2 h at rt, the title compound was isolated (294 mg, 1.10 mmol, 55% yield).

Physical properties: light yellow solid (mp = 122–125 °C).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.44 (s, 1H), 7.23 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 3.52 (d, J = 15.6 Hz, 1H), 2.58 (t, J = 15.9 Hz, 1H), 2.28 (d, J = 16.9 Hz, 1H), 2.22 (s, 3H).

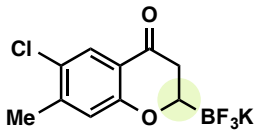
^{13}C NMR (126 MHz, DMSO) δ 195.4, 162.5, 135.9, 127.7, 125.7, 120.5, 117.8, 30.7, 20.0 (did not observe highlighted carbon).

^{19}F NMR (471 MHz, C_6D_6) δ -143.40.

^{11}B NMR (128 MHz, DMSO) δ 2.8.

FT-IR (cm^{-1}, neat, ATR) 2877, 1676, 1489, 1293, 996, 868.

HRMS (ESI) m/z calc. for $C_{12}H_{12}O_3NBF_2$ [M-F+CH_3N] 251.0929, found 251.0929.



6-Chloro-7-methyl-2-(trifluoro-l$_4$-boranyl)chroman-4-one, potassium salt

The general procedure was followed with chromone (388 mg, 2.0 mmol, 1.0 equiv). After 2 h at rt, the title compound was isolated (374 mg, 1.24 mmol, 62% yield).

Physical properties: white powdery solid (mp = 165 °C).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.54 (s, 1H), 6.92 (s, 1H), 3.57 (t, J = 16.7 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.56 (d, J = 15.7 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 193.9, 163.0, 142.8, 125.3, 123.9, 120.3, 47.3, 20.1 (did not observe highlighted carbon.)

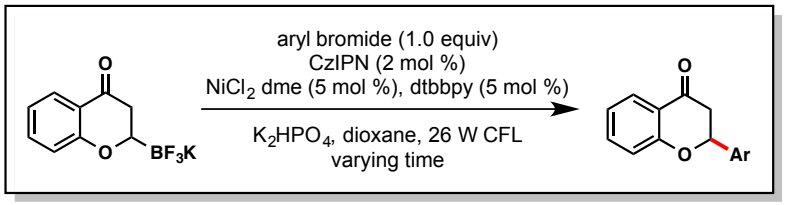
^{19}F NMR (471 MHz, C_6D_6) δ -155.36.

^{11}B NMR (128 MHz, DMSO) δ 2.6.

FT-IR (cm^{-1}, neat, ATR) 2952, 3592, 1665, 1611, 1452, 1091, 863.

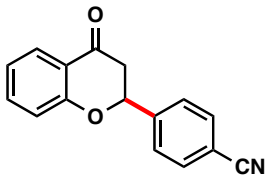
HRMS (ESI) m/z calc. for $C_{10}H_8BClF_3O_2$ [M] 263.0258, found 263.0237.

GENERAL PROCEDURE FOR PHOTOREDOX/NICKEL ARYLATION



To an 8 mL vial equipped with a stir bar was added trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), and aryl halide (0.50 mmol, 1.0 equiv). The vial was then evacuated and purged three times. Under nitrogen, degassed dioxane (4.0 mL) was added under nitrogen. The resulting solution was stirred next to a 26 W CFL for varying amounts of time. After completion, the mixture was quenched with saturated $NaHCO_3$ (10 mL) and transferred to a separatory funnel with CH_2Cl_2 (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The organic layers were combined and dry loaded with Celite. The crude mixture was purified by column chromatography.

ARYL BROMIDE SCOPE



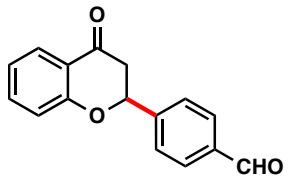
4-(4-Oxochroman-2-yl)benzonitrile (2a)

Reference: Wang, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 8670.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 4-bromobenzonitrile (91 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 36 h. The title compound was purified by column chromatography (silica gel, 4:1 hexanes/EtOAc) to afford a crystalline solid (81 mg, 65% yield). mp = 75–77 °C (lit mp = 84–86 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.05 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.97 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.53 – 7.47 (m, 1H), 7.11 – 7.00 (m, 2H), 6.21 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.63 (dd, *J* = 17.0, 10.7 Hz, 1H), 3.12 (dd, *J* = 17.1, 3.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 160.6, 148.9, 146.7, 142.2, 140.4, 136.3, 132.0, 127.1, 122.2, 121.5, 118.2, 76.2, 40.4.



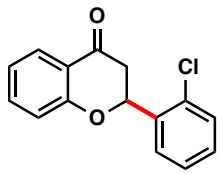
4-(4-Oxochroman-2-yl)benzaldehyde (2b)

Reference: Ahmed, N.; Konduru, N. K.; Ahmad, S.; Owais, M. *Eur. J. Med. Chem.* **2014**, *75*, 233.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 4-bromo benzaldehyde (93 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a light yellow oil (85 mg, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.02 – 7.96 (m, 3H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 8.0, 5.3 Hz, 2H), 5.62 (dd, *J* = 13.0, 3.2 Hz, 1H), 3.08 (dd, *J* = 16.8, 13.1 Hz, 1H), 3.03 – 2.95 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 191.2, 161.3, 145.4, 136.7, 136.6, 130.4, 127.3, 126.7, 122.2, 121.1, 118.3, 79.0, 44.8.



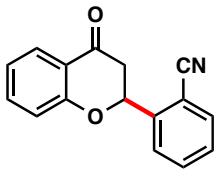
2-(2-Chlorophenyl)chroman-4-one (2c)

Reference: Jiang, H.; Zheng, X.; Yin, Z.; Xie, J. *J. Chem. Res.* **2011**, *35*, 220.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 1-bromo-2-chlorobenzene (96 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv),

$NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a yellow oil (120 mg, 93% yield).

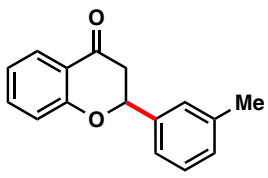
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.40 (q, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 5.88 (dd, *J* = 13.5, 2.6 Hz, 1H), 3.04 (dd, *J* = 16.7, 2.8 Hz, 1H), 2.89 (dd, *J* = 16.8, 13.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 161.7, 136.9, 136.3, 131.8, 129.9, 129.74, 127.6, 127.4, 127.3, 122.0, 121.1, 118.2, 76.7, 43.7.



2-(4-Oxochroman-2-yl)benzonitrile (2d)

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 2-bromobenzonitrile (91 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 36 h. The title compound was purified by column chromatography (silica gel, 4:1 hexanes/EtOAc) to afford a clear oil (32 mg, 35% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.53 (dt, *J* = 15.4, 7.7 Hz, 2H), 7.15 – 7.05 (m, 2H), 5.85 (dd, *J* = 13.1, 3.4 Hz, 1H), 3.16 – 2.93 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 161.2, 142.3, 136.6, 133.6, 133.5, 129.3, 127.4, 127.1, 122.4, 121.1, 118.2, 116.9, 110.9, 77.3, 44.1.
FT-IR (cm^{-1}, neat, ATR) 3072, 2223, 1688, 1605, 1463, 1225, 730.
HRMS (ES+) m/z calc. for $C_{16}H_{11}NO_2$ [M+H] 250.0868, found 250.0874.



2-(3-Tolyl)chroman-4-one (2e)

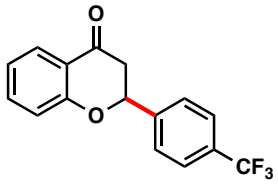
Reference: Zhao, D.; Beiring, B.; Glorius, F. *Angew. Chem. Int. Ed.* **2013**, *52*, 8454.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 1-bromo-3-methylbenzene (85 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (93 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.08 – 7.02 (m, 3H), 5.75 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.26 – 3.15 (m, 1H), 3.07 (dd, *J* = 16.8, 3.3 Hz, 1H), 2.88 (d, *J* = 16.7 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 161.8, 138.8, 138.8, 136.3, 129.7, 128.9, 127.2, 127.0, 123.4, 121.7, 121.1, 118.3, 79.9, 44.9, 21.6.

FT-IR (cm^{-1}, neat, ATR) 3070, 2924, 2925, 1691, 1608, 1577, 1472, 1463, 1378, 1304, 1224, 1149, 1114, 1066, 1035, 982, 891, 851, 764, 708, 530, 490.



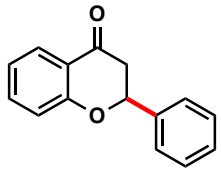
2-(4-(Trifluoromethyl)phenyl)chroman-4-one (2f)

Reference: Zhao, D.; Beiring, B.; Glorius, F. *Angew. Chem. Int. Ed.* **2013**, *52*, 8454.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 1-bromo-4-(trifluoromethyl)benzene (112 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (107 mg, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 4H), 7.11 – 7.02 (m, 2H), 5.47 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.04 (dd, *J* = 16.9, 13.2 Hz, 1H), 2.89 (dd, *J* = 16.8, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 161.3, 142.9, 136.5, 130.9 (q, *J* = 32.5 Hz), 127.3, 126.5, 126.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.0 Hz), 121.1, 118.2, 78.9, 44.8.

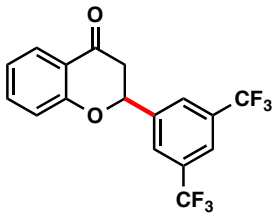


2-Phenylchroman-4-one (2g)

Reference: Zhao, D.; Beiring, B.; Glorius, F. *Angew. Chem. Int. Ed.* **2013**, *52*, 8454.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), bromobenzene (78.5 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a white solid (62 mg, 55% yield). mp = 68–70 °C (lit mp = 64–66 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.35 (m, 6H), 7.06 (dt, *J* = 7.5, 3.2 Hz, 2H), 5.49 (dd, *J* = 13.4, 2.9 Hz, 1H), 3.10 (dd, *J* = 16.9, 13.3 Hz, 1H), 2.90 (dd, *J* = 16.9, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 161.7, 138.9, 136.4, 129.0, 128.9, 127.2, 126.3, 121.8, 121.1, 118.3, 79.8, 44.9.



2-(3,5-Bis(trifluoromethyl)phenyl)chroman-4-one (2h)

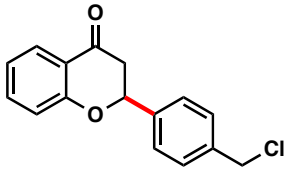
The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 3,5-bistrifluoromethyl bromobenzene (84 μL, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 4:1 hexanes/EtOAc) to afford a clear oil (120 mg, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 3H), 7.92 (s, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 2H), 5.61 (dd, *J* = 13.1, 3.3 Hz, 1H), 3.11 – 2.91 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 161.0, 141.7, 136.7, 132.7, 132.4, 132.1, 127.4, 126.3, 124.3, 122.8, 122.5, 122.2, 121.0, 118.2, 78.3, 44.9.

FT-IR (cm^{-1}, neat, ATR) 2934, 1698, 1605, 1354, 1339, 1308, 1287, 1227, 1204, 1164, 1151, 1126, 1077, 897, 882, 856, 843, 768, 705, 685.

HRMS (ES+) m/z calc. for $C_{17}H_{11}FO_2$ [M+H] 361.0623, found 361.0651.



2-(4-(Chloromethyl)phenyl)chroman-4-one (2i)

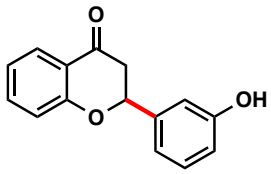
Reference: Wang, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 8670.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 4-bromo benzyl chloride (103 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (74 mg, 27% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.18 – 7.11 (m, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.65 (dq, *J* = 9.0, 6.3 Hz, 1H), 3.14 (dd, *J* = 14.1, 6.8 Hz, 1H), 3.00 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.70 – 2.65 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 161.4, 136.2, 135.4, 131.8, 131.5, 127.1, 121.6, 121.1, 121.1, 118.1, 78.0, 42.4, 40.7.

FT-IR (cm^{-1}, neat, ATR) 2076, 2930, 1692, 1606, 1464, 1305, 1227, 1119, 764.



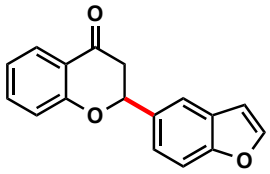
2-(3-Hydroxyphenyl)chroman-4-one (2j)

Reference: Jung, H.; Shin, S. Y.; Jung, Y.; Tran, T. A.; Lee, H. O.; Jung, K. -Y. Koh, D.; Cho, S. K.; Lim, Y. *Chem. Biol. Drug, Des.* **2015**, *86*, 496.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 3-bromophenol (86 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a white semi-solid (76 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 4H), 7.11 – 7.02 (m, 2H), 5.75 (br s, 1H), 5.47 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.04 (dd, *J* = 16.9, 13.2 Hz, 1H), 2.89 (dd, *J* = 16.8, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6, 161.7, 156.3, 140.6, 136.6, 130.3, 127.2, 125.9, 121.9, 121.0, 118.4, 118.31, 115.9, 113.3, 44.7.



2-(Benzofuran-5-yl)chroman-4-one (2k)

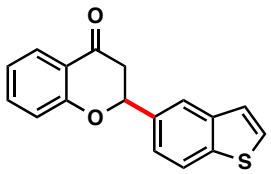
The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 5-bromo benzofuran (98 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 4:1 hexanes/EtOAc) to afford a clear oil (102 mg, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.07 (t, *J* = 6.9 Hz, 2H), 6.81 (s, 1H), 5.58 (dd, *J* = 13.5, 2.7 Hz, 1H), 3.17 (dd, *J* = 16.7, 13.6 Hz, 1H), 2.93 (dd, *J* = 16.9, 2.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 161.8, 155.1, 146.1, 136.4, 133.6, 127.95, 127.2, 122.8, 121.8, 121.1, 119.4, 118.3, 111.9, 106.9, 80.1, 45.2.

FT-IR (cm^{-1}, neat, ATR) 3076, 2896, 1688, 1606, 1578, 1572, 1472, 1464, 1449, 1377, 1305, 1265, 1224, 1149, 1128, 1114, 765.

HRMS (ES+) m/z calc. for $C_{17}H_{13}O_3$ [M+H] 265.0865, found 265.0864.



2-(Benzo[*b*]thiophen-5-yl)chroman-4-one (2l)

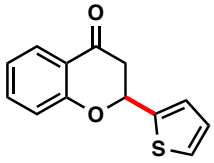
The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 2-bromo benzothiophene (103 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 36 h. The title compound was purified by column chromatography (silica gel, 4:1 hexanes/EtOAc) to afford a clear oil (80 mg, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.77 – 7.74 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.06 (dd, *J* = 14.0, 7.7 Hz, 2H), 5.84 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.25 (dd, *J* = 16.9, 10.8 Hz, 1H), 3.15 (dd, *J* = 16.8, 3.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 160.8, 142.2, 139.9, 139.1, 136.5, 136.4, 127.2, 125.1, 124.7, 124.1, 122.6, 122.1, 121.2, 118.4, 75.7, 44.1.

FT-IR (cm^{-1}, neat, ATR) 3368, 3059, 2900, 1687, 1604, 1577, 1471, 1461, 1438, 1362, 1299, 1221, 1148, 1112, 1066, 906, 891, 862, 828, 761, 747, 726, 558.

HRMS (ES+) m/z calc. for $C_{17}H_{13}O_2S$ [M+H] 281.0636, found 281.0658.



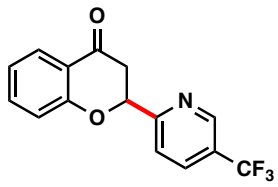
2-(Thiophen-2-yl)chroman-4-one (2m)

Reference: Kavala, V.; Lin, C.; Kuo, C. -W.; Fang, H.; Yao, C. -F. *Tetrahedron* **2012**, *68*, 1321.

The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 2-bromothiophene (81 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to

run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (105 mg, 91% yield).

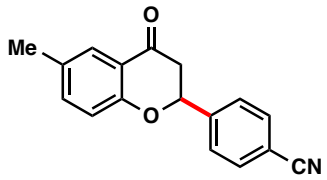
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.08 – 7.02 (m, 3H), 5.75 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.26 – 3.15 (m, 1H), 3.07 (dd, *J* = 16.8, 3.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 161.1, 141.6, 136.4, 127.2, 127.0, 126.5, 126.0, 122.0, 121.2, 118.4, 75.3, 44.5.
FT-IR (cm^{-1}, neat, ATR) 3070, 2924, 2925, 1691, 1608, 1577, 1472, 1463, 1378, 1304, 1224, 1149, 1114, 1066, 1035, 982, 891, 851, 764, 708, 530, 490.



2-(5-(Trifluoromethyl)pyridin-2-yl)chroman-4-one (2o)
The general procedure was followed with trifluoroborate (191 mg, 0.75 mmol, 1.5 equiv), 2-bromo-5-trifluoromethyl pyridine (113 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a yellow oil (120 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 12.7, 7.7 Hz, 2H), 5.68 (dd, *J* = 11.9, 3.7 Hz, 1H), 3.22 (dd, *J* = 16.9, 3.7 Hz, 1H), 3.12 (dd, *J* = 17.0, 11.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 161.8, 160.7, 147.8, 146.5 (q, *J* = 4.2 Hz), 134.5 (q, *J* = 3.4 Hz), 127.8, 126.6, 126.3, 122.3, 121.4, 120.6, 118.2, 79.4, 42.7.
FT-IR (cm^{-1}, neat, ATR) 3063, 1681, 1609, 1578, 1474, 1328, 1217, 1161, 1135, 1116, 1084, 1017, 852, 769, 759.
HRMS (ES+) m/z calc. for $C_{15}H_{11}F_3NO_2$ [M+H] 294.0742, found 294.0754.

TRIFLUOROBORATOCHROMANONE SCOPE



4-(6-Methyl-4-oxochroman-2-yl)benzonitrile (3a)

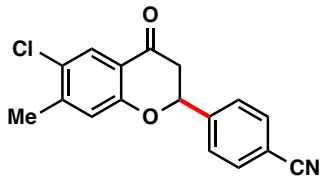
The general procedure was followed with trifluoroborate (201.0 mg, 0.75 mmol, 1.5 equiv), 4-bromobenzonitrile (91.0 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (89.5 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 3H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.5 Hz,1H), 6.98 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 12.4 Hz, 1H), 3.07 – 2.83 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 159.2, 144.2, 137.7, 132.8, 131.8, 126.9, 126.8, 120.7, 118.5, 118.0, 112.7, 78.6, 44.7, 20.6.

FT-IR (cm^{-1}, neat, ATR) 2918, 1687, 1617, 1489, 1134, 829, 596.

HRMS (ES+) m/z calc. for $C_{17}H_{14}NO_2$ [M+H] 263.0946, found 264.1016.



4-(6-chloro-7-methyl-4-oxochroman-2-yl)benzonitrile (3c)

The general procedure was followed with trifluoroborate (226.5 mg, 0.75 mmol, 1.5 equiv), 4-bromobenzonitrile (91.0 mg, 0.50 mmol, 1.0 equiv), 4CzIPN photocatalyst (7.9 mg, 0.004 mmol, 0.02 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv). Under a 26 W CFL, the reaction was allowed to run for 16 h. The title compound was purified by column chromatography (silica gel, 5:1 hexanes/EtOAc) to afford a clear oil (105.4 mg, 71% yield).

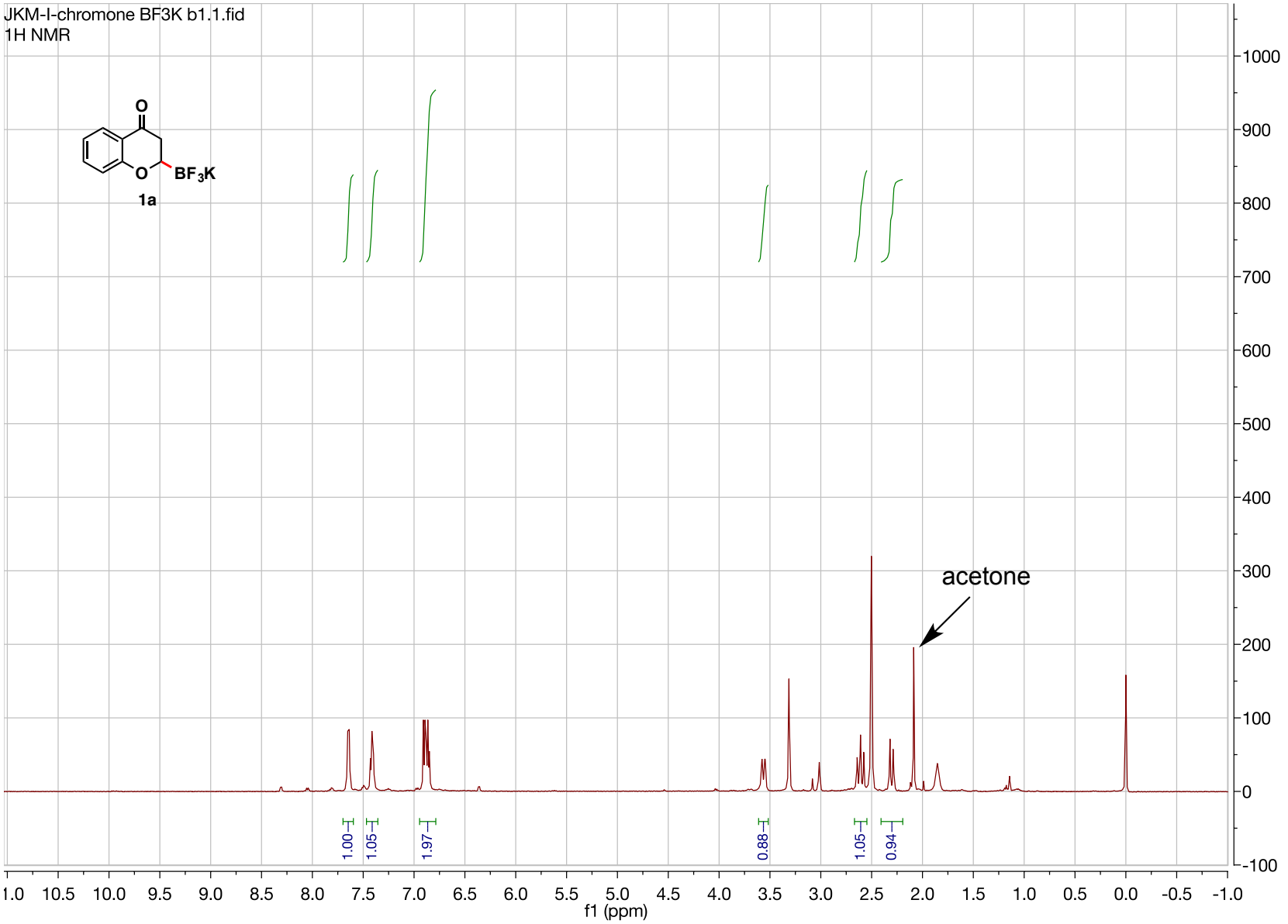
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 6.97 (s, 1H), 5.52 (d, *J* = 12.3 Hz, 1H), 3.02 – 2.84 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6, 159.3, 145.8, 143.7, 132.9, 128.5, 127.0, 126.7, 120.3, 120.0, 118.4, 112.82, 78.8, 44.3, 21.0.

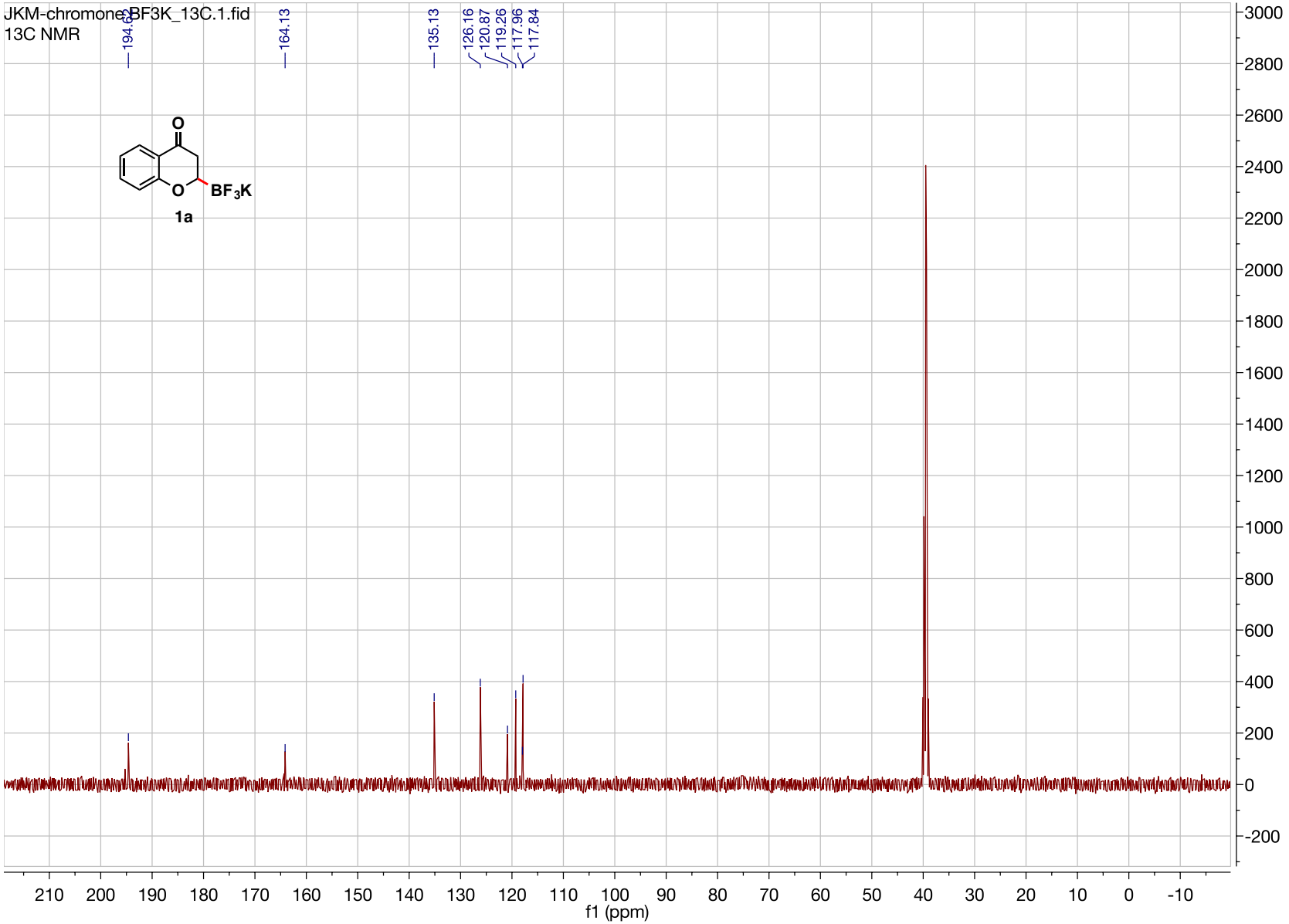
FT-IR (cm^{-1}, neat, ATR) 3066, 1690, 1613, 1407, 1236, 1154, 893, 837, 655.

HRMS: compound unstable.

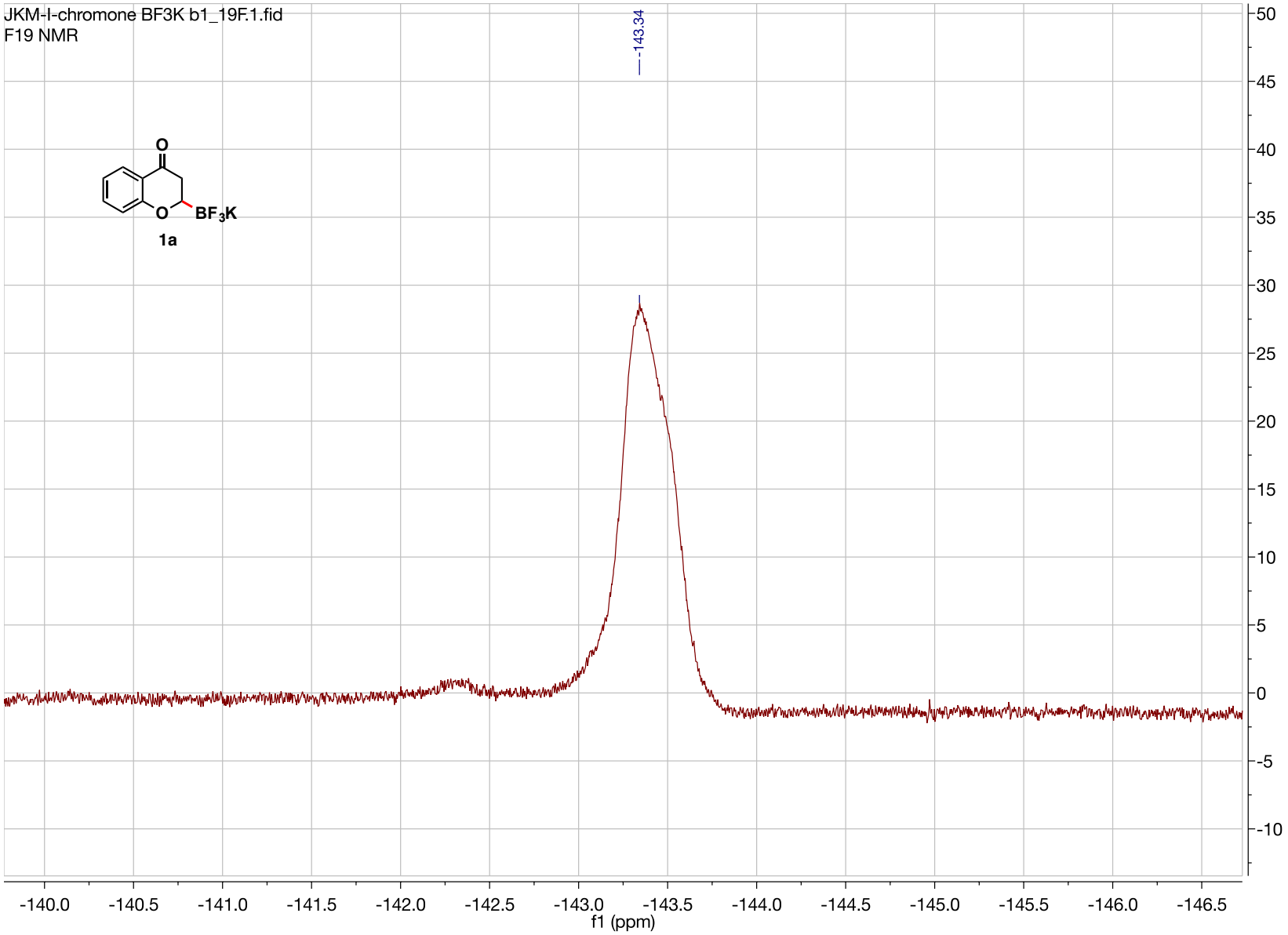
^{1}H NMR (DMSO-d^{6}, 500 MHz) spectrum of 2-(trifluoro-λ_4-boranyl)chroman-4-one, potassium salt (**1a**)



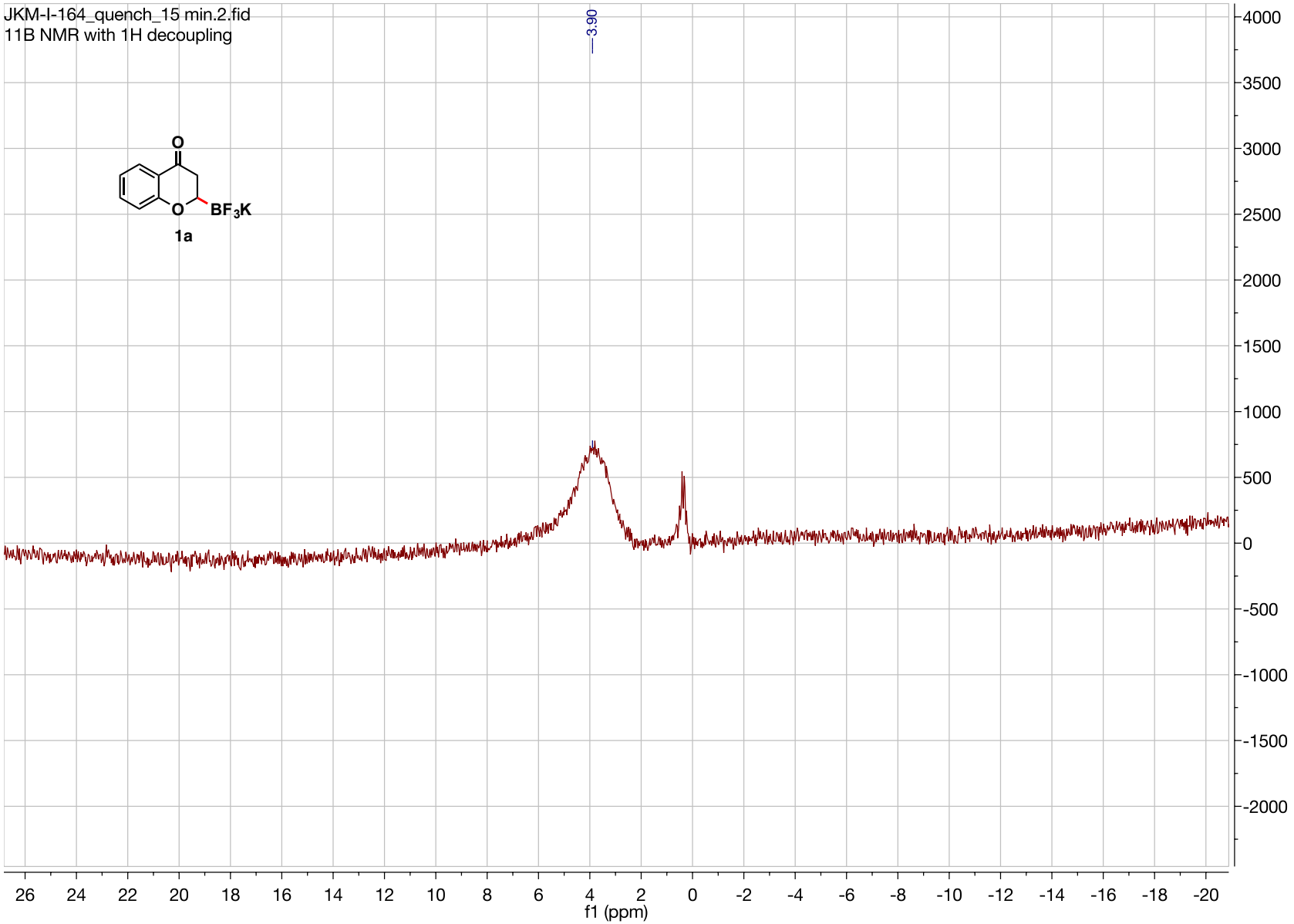
^{13}C NMR (DMSO-d^{6}, 125.8 MHz) spectrum of 2-(trifluoro-λ_4-boranyl)chroman-4-one, potassium salt (**1a**)



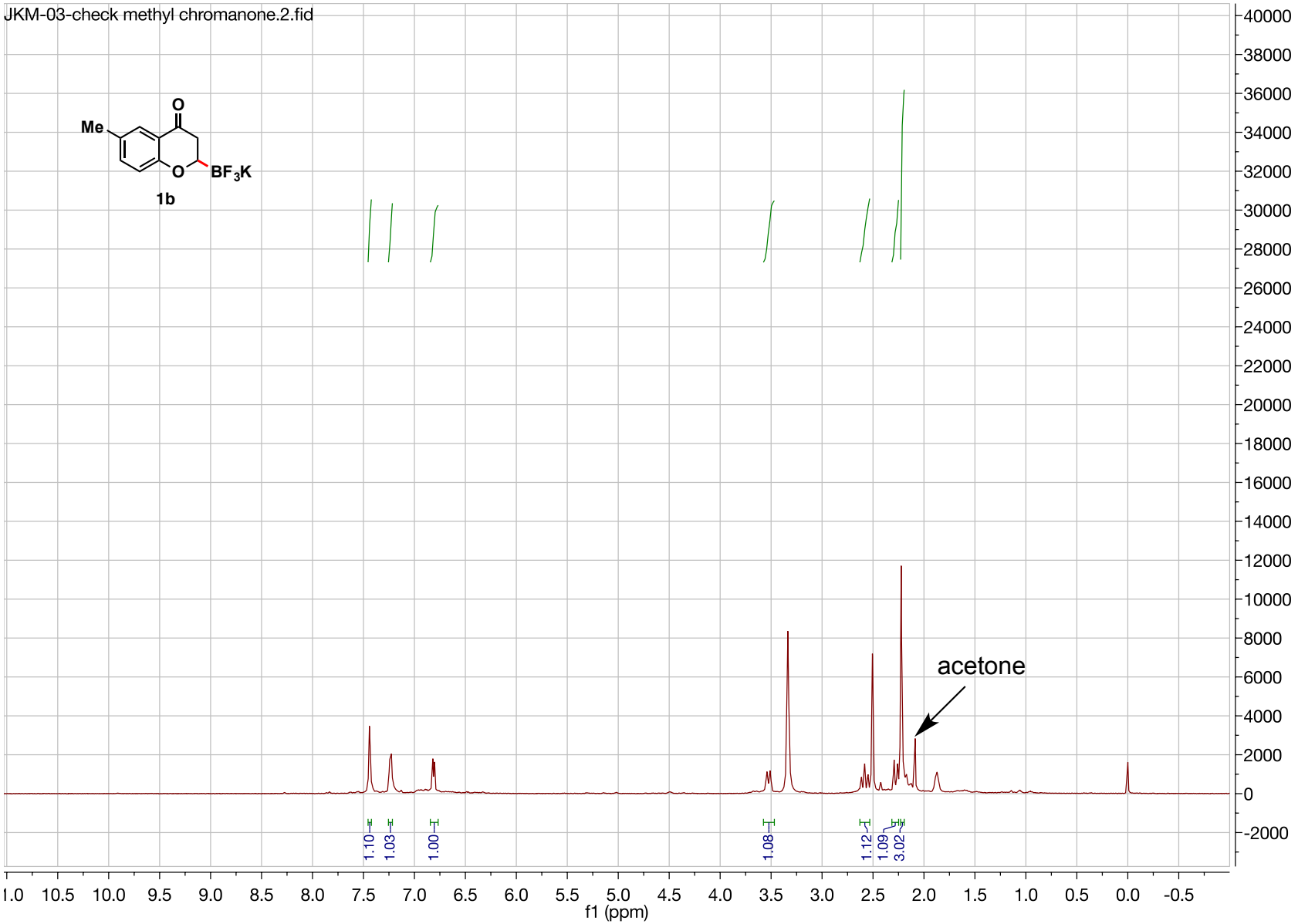
^{19}F NMR (DMSO-d^{6}, 470.8 MHz) spectrum of 2-(trifluoro-λ_4-boranyl)chroman-4-one, potassium salt (**1a**)



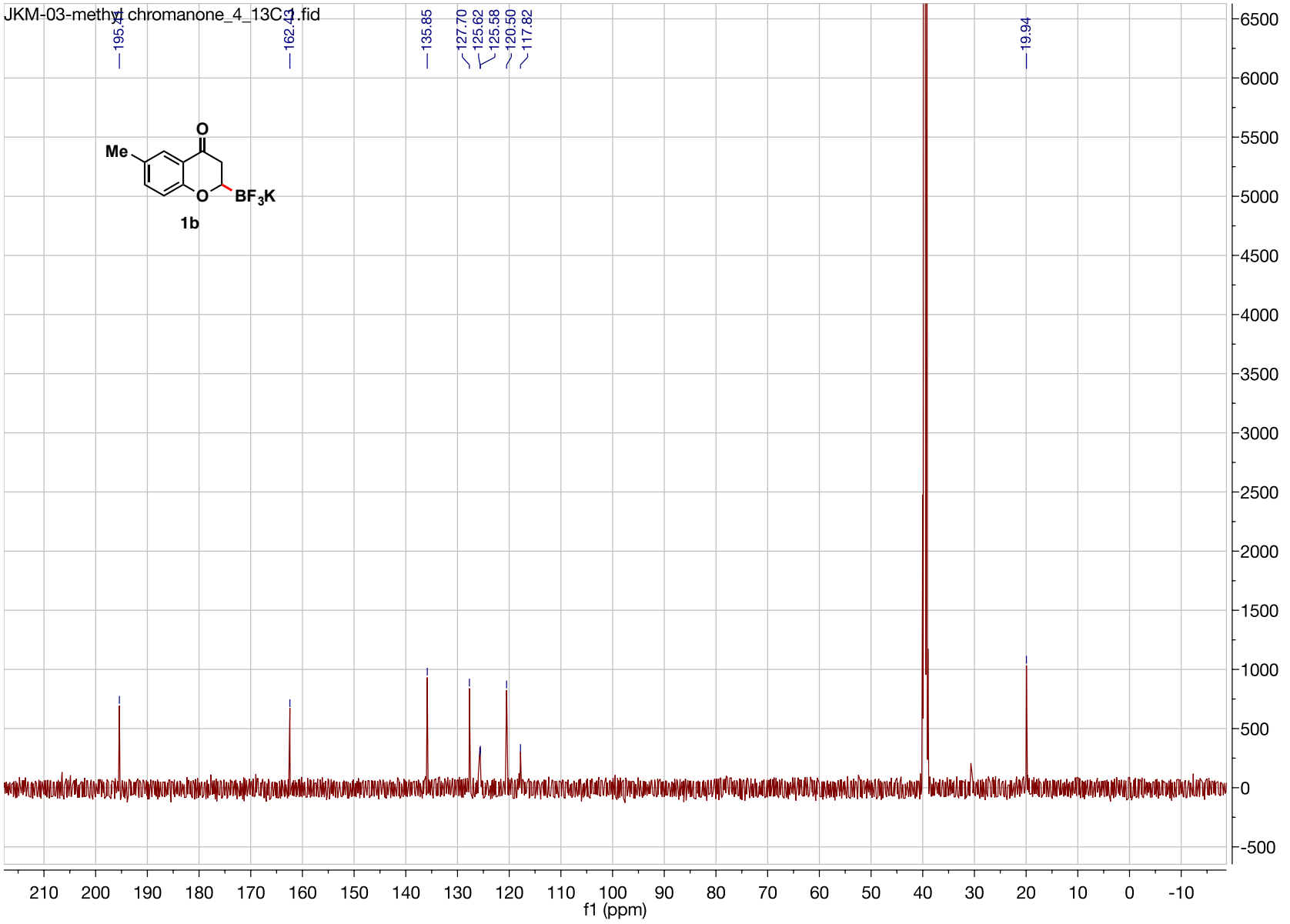
^{11}B NMR (DMSO-d^{6}, 128.4 MHz) spectrum of 2-(trifluoro-λ_4-boranyl)chroman-4-one, potassium salt (**1a**)



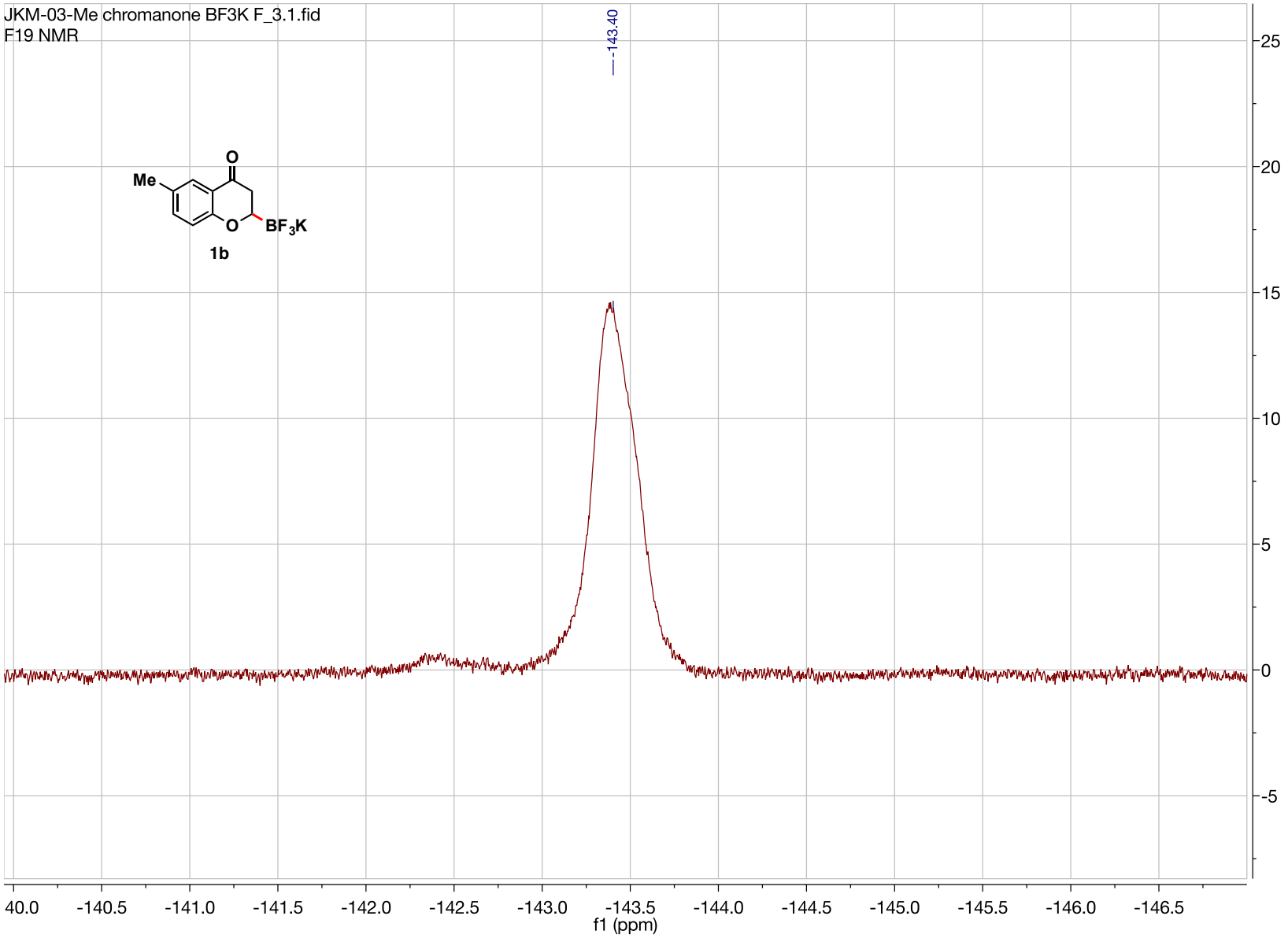
^{1}H NMR (DMSO-d^{6}, 500 MHz) spectrum of 6-methyl-2-(trifluoro-l$_{4}$-boranyl)chroman-4-one, potassium salt (**1b**)



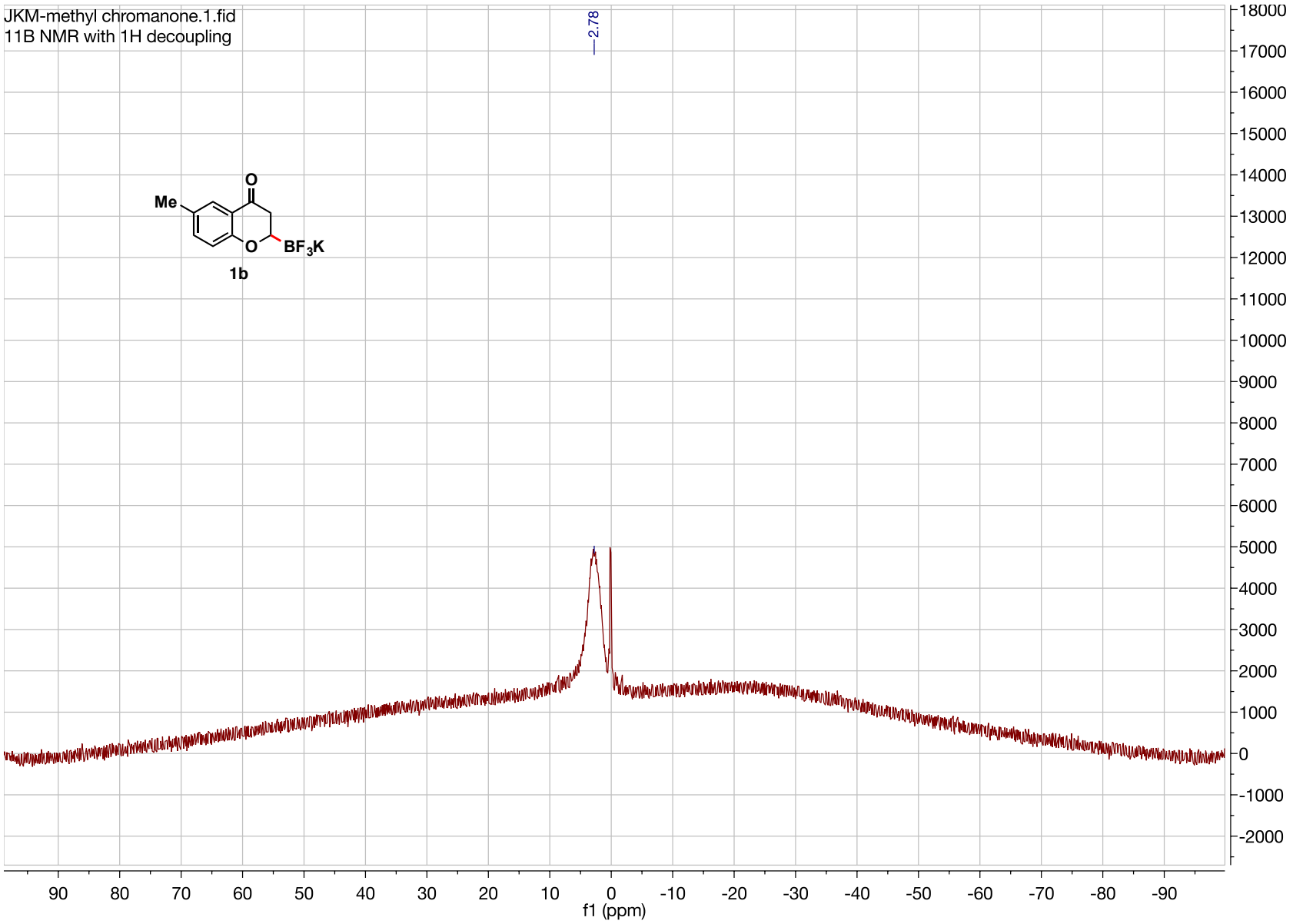
^{13}C NMR (DMSO-d^{6}, 125.8 MHz) spectrum of 6-methyl-2-(trifluoro-l$_{4}$-boranyl)chroman-4-one, potassium salt (**1b**)



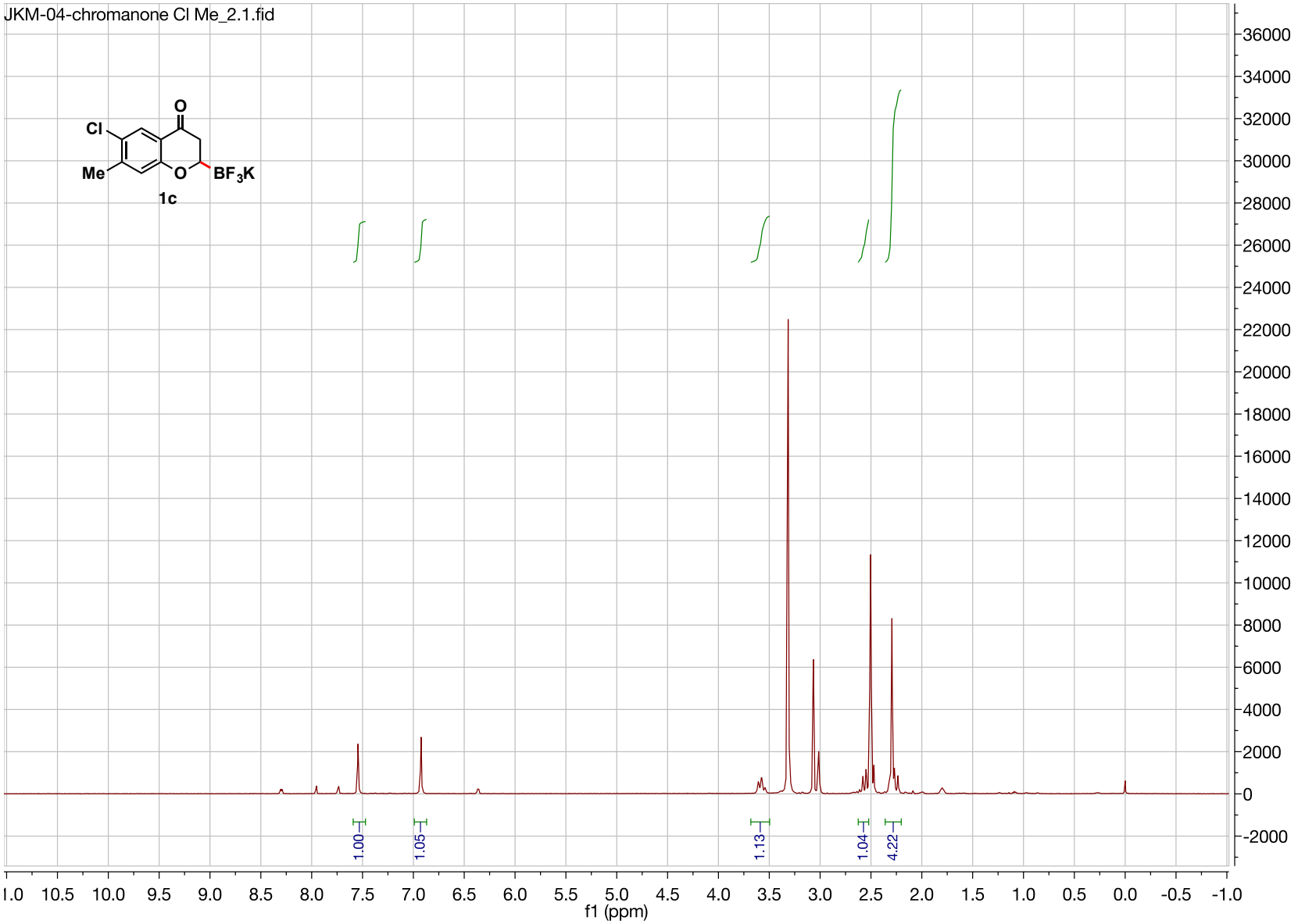
^{19}F NMR (DMSO-d^{6}, 470.8 MHz) spectrum of 6-methyl-2-(trifluoro-l$_4$-boranyl)chroman-4-one, potassium salt (**1b**)



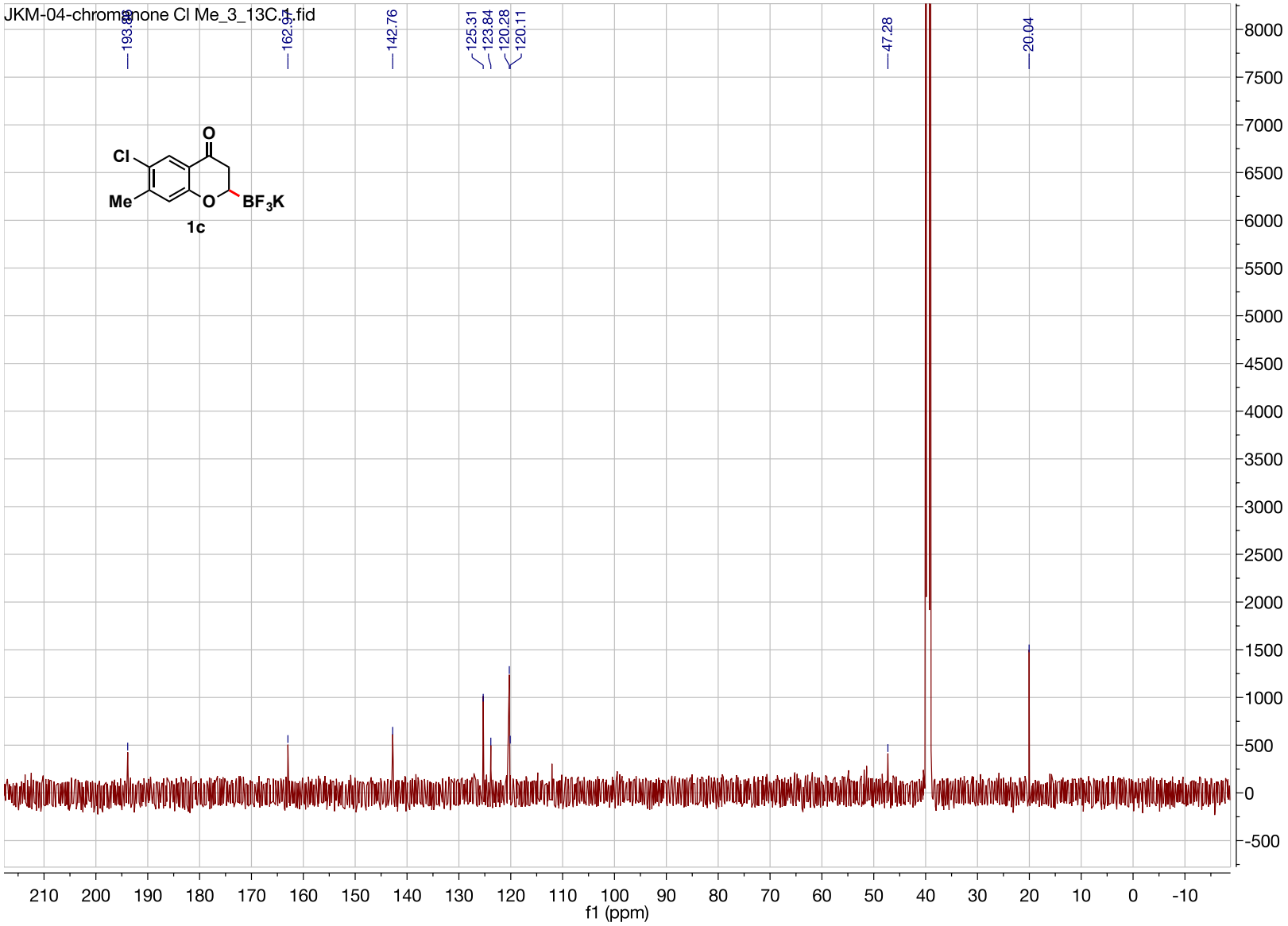
^{11}B NMR (DMSO-d^{6}, 128.4 MHz) spectrum of 6-methyl-2-(trifluoro-l$_4$-boranyl)chroman-4-one, potassium salt (**1b**)



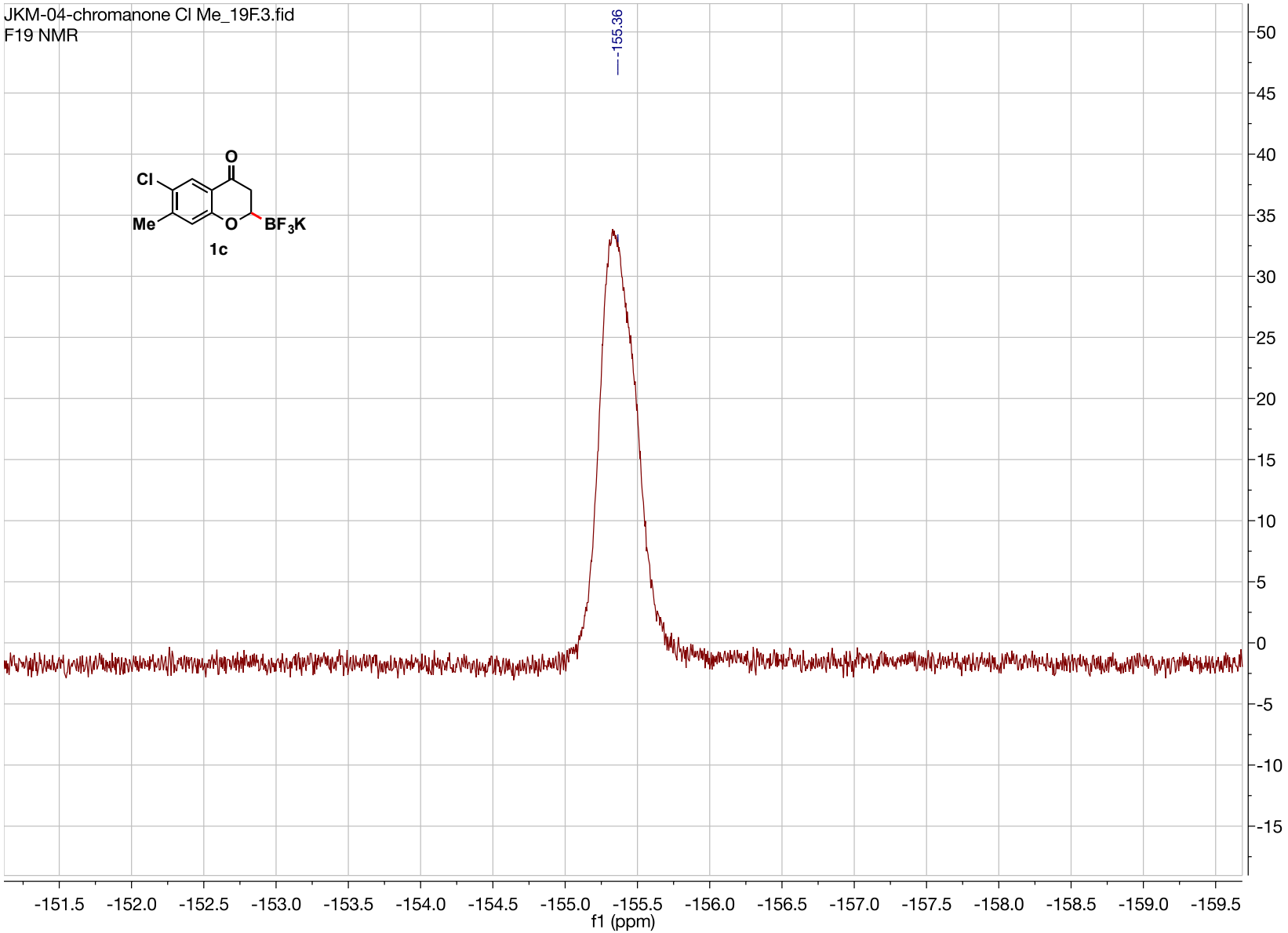
^{1}H NMR (DMSO-d^{6}, 500 MHz) spectrum of 6-chloro-7-methyl-2-(trifluoro-l$_{4}$-boranyl)chroman-4-one, potassium salt (**1c**)



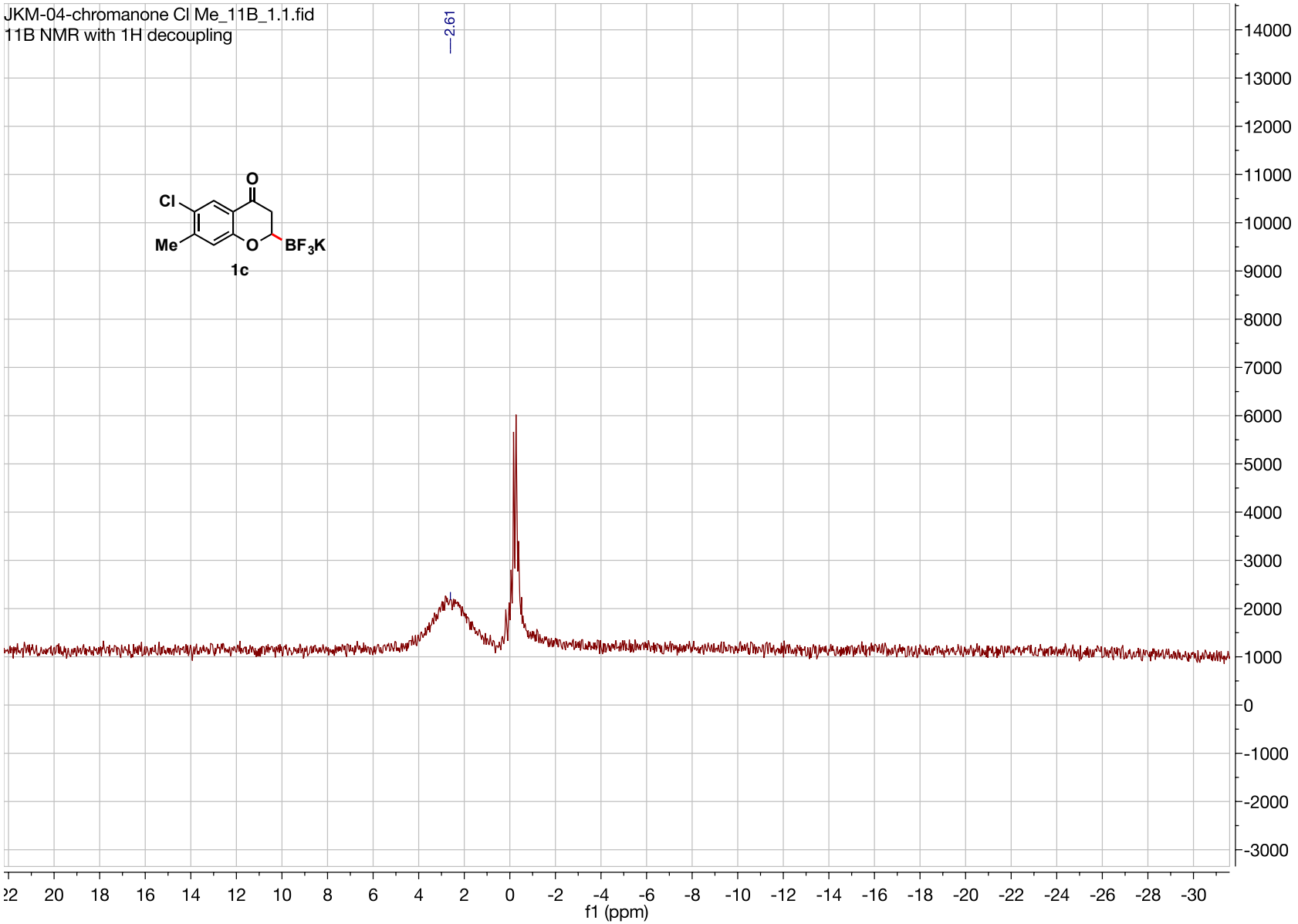
^{13}C NMR (DMSO-d^{6}, 125.8 MHz) spectrum of 6-chloro-7-methyl-2-(trifluoro-l$_{4}$-boranyl)chroman-4-one, potassium salt (**1c**)



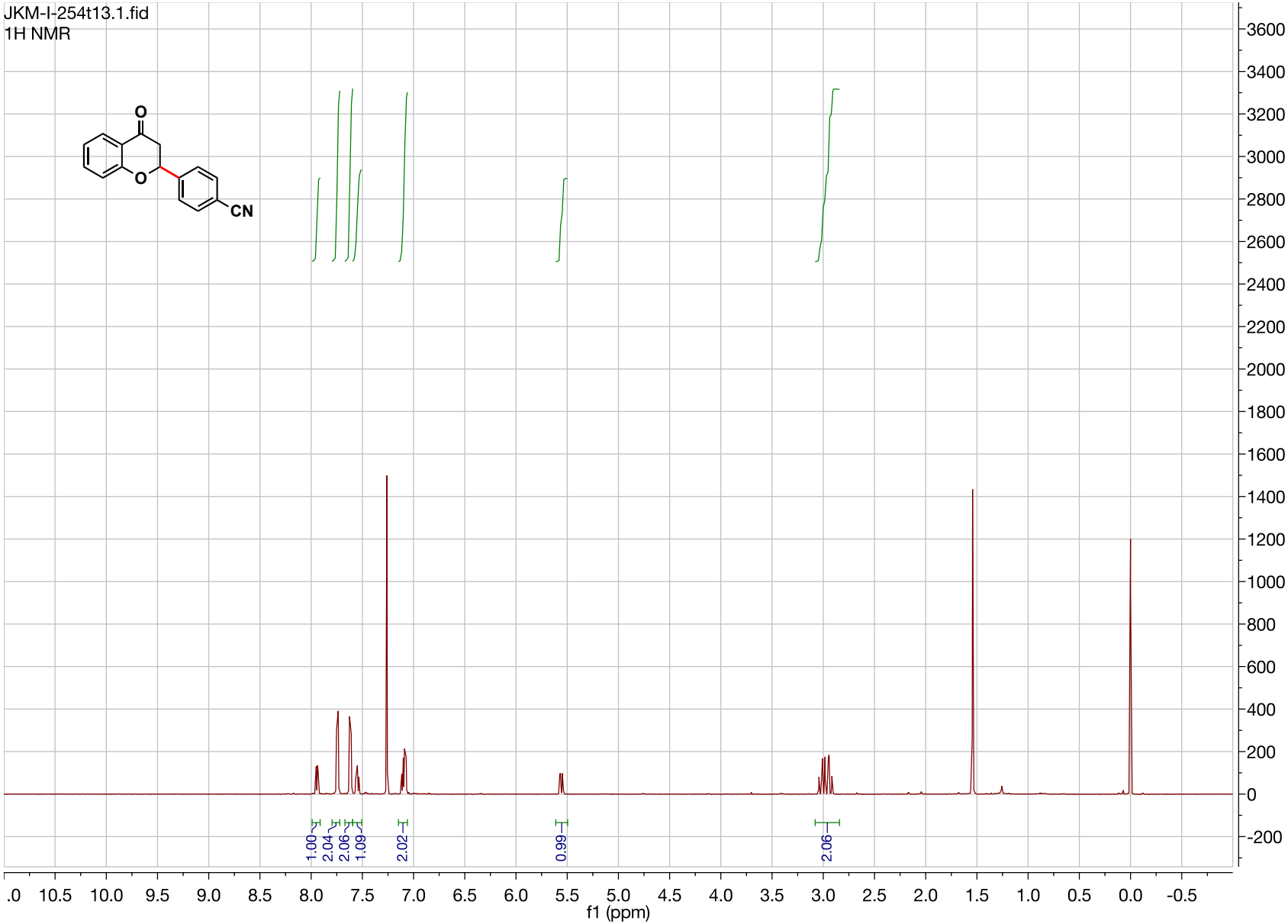
^{19}F NMR (DMSO-d^{6}, 470.8 MHz) spectrum of 6-chloro-7-methyl-2-(trifluoro-l$_4$-boranyl)chroman-4-one, potassium salt (**1c**)



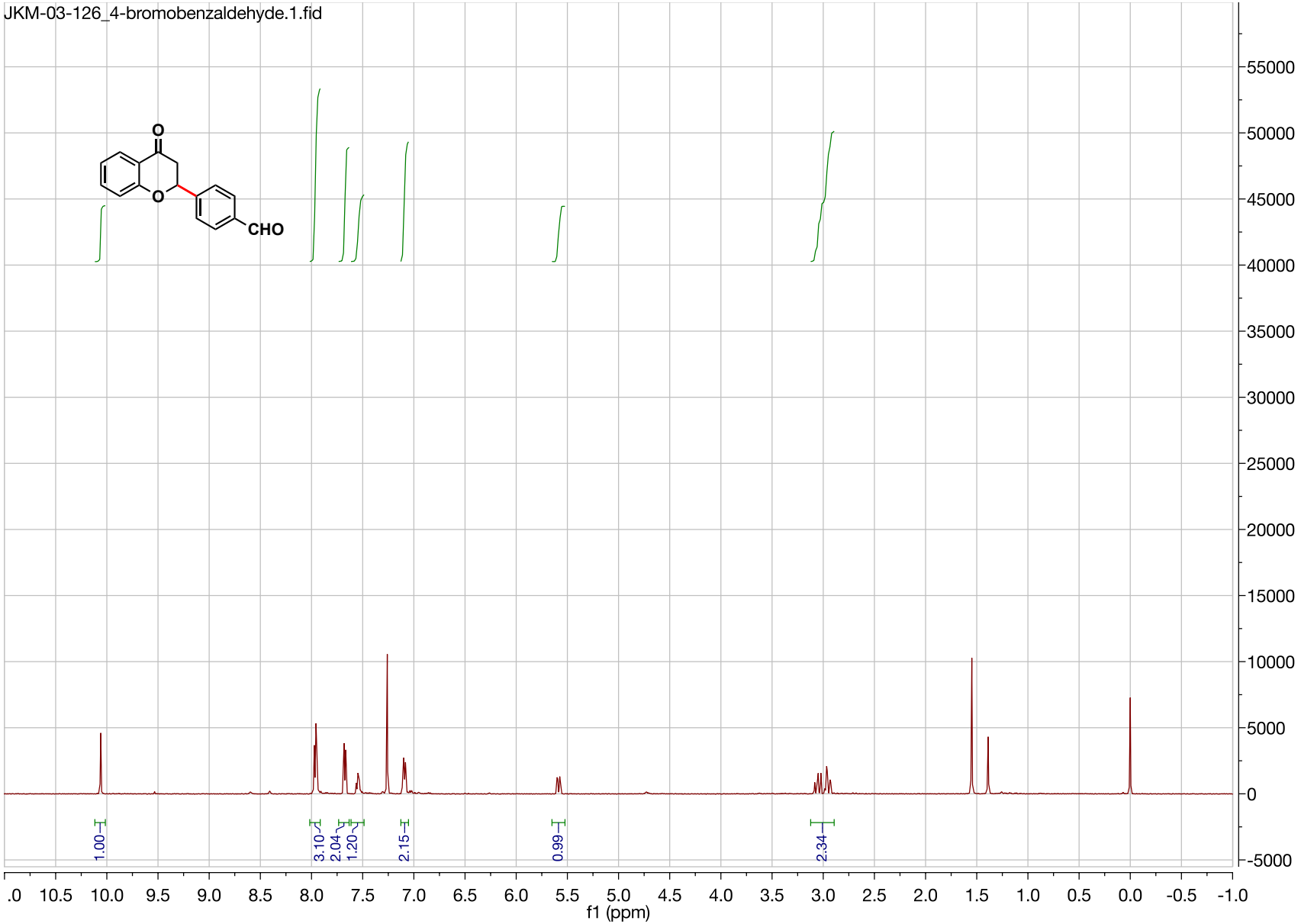
^{11}B NMR (DMSO-d^{6}, 128.4 MHz) spectrum of 6-chloro-7-methyl-2-(trifluoro-l$_{4}$-boranyl)chroman-4-one, potassium salt (**1c**)



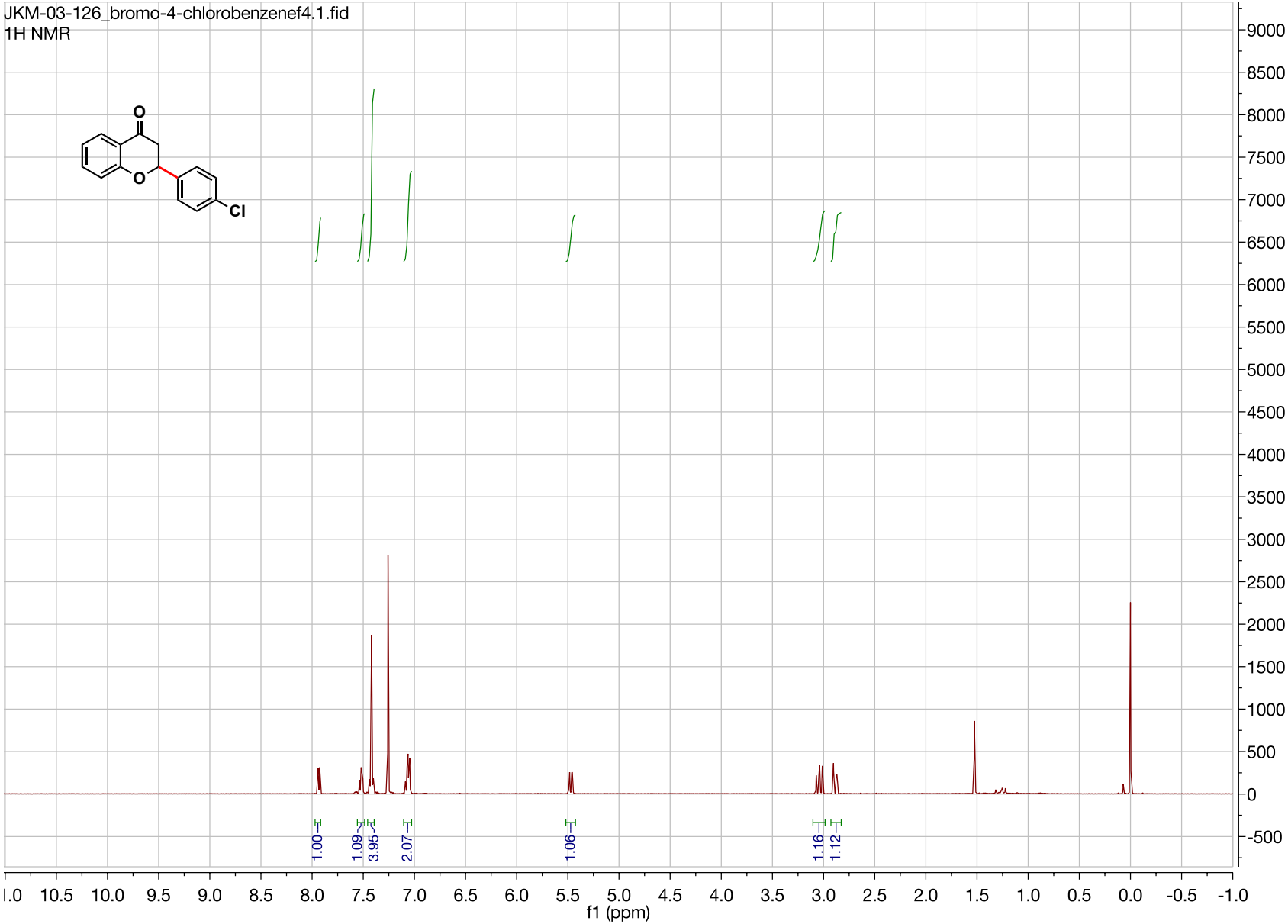
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(4-(chloromethyl)phenyl)chroman-4-one (**2a**)



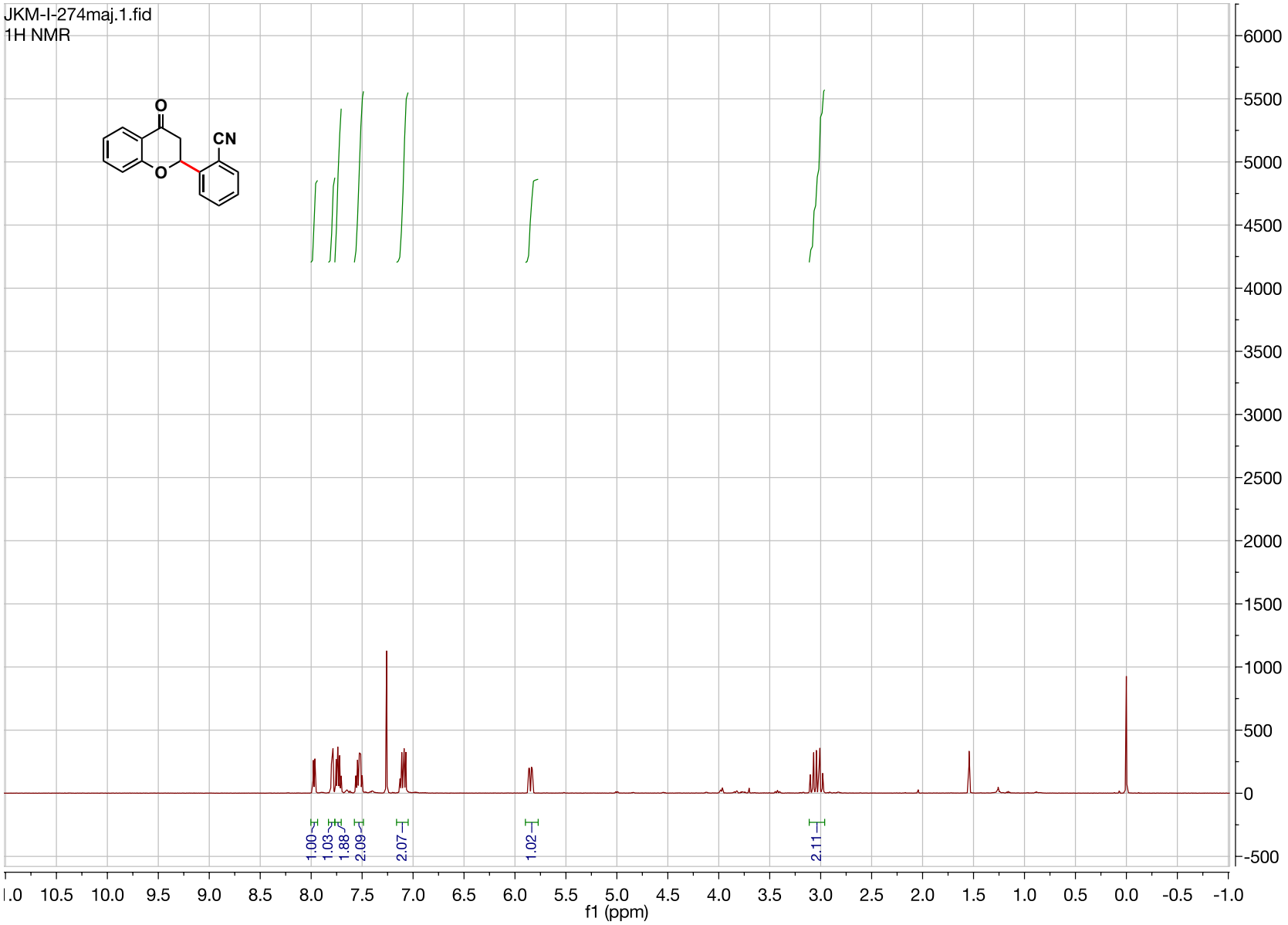
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(4-oxochroman-2-yl)benzaldehyde (**2b**)



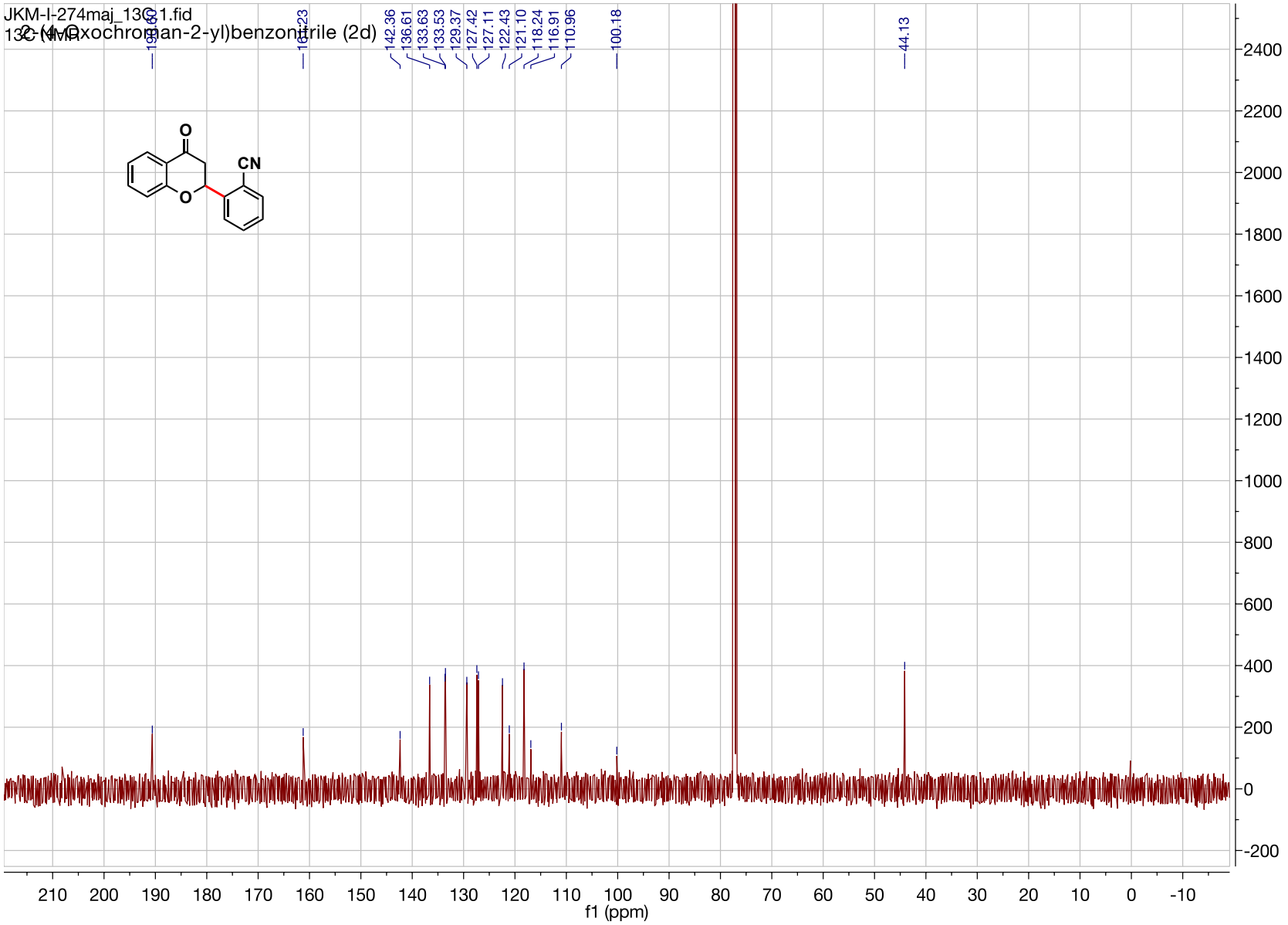
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(4-chlorophenyl)chroman-4-one (**2c**)



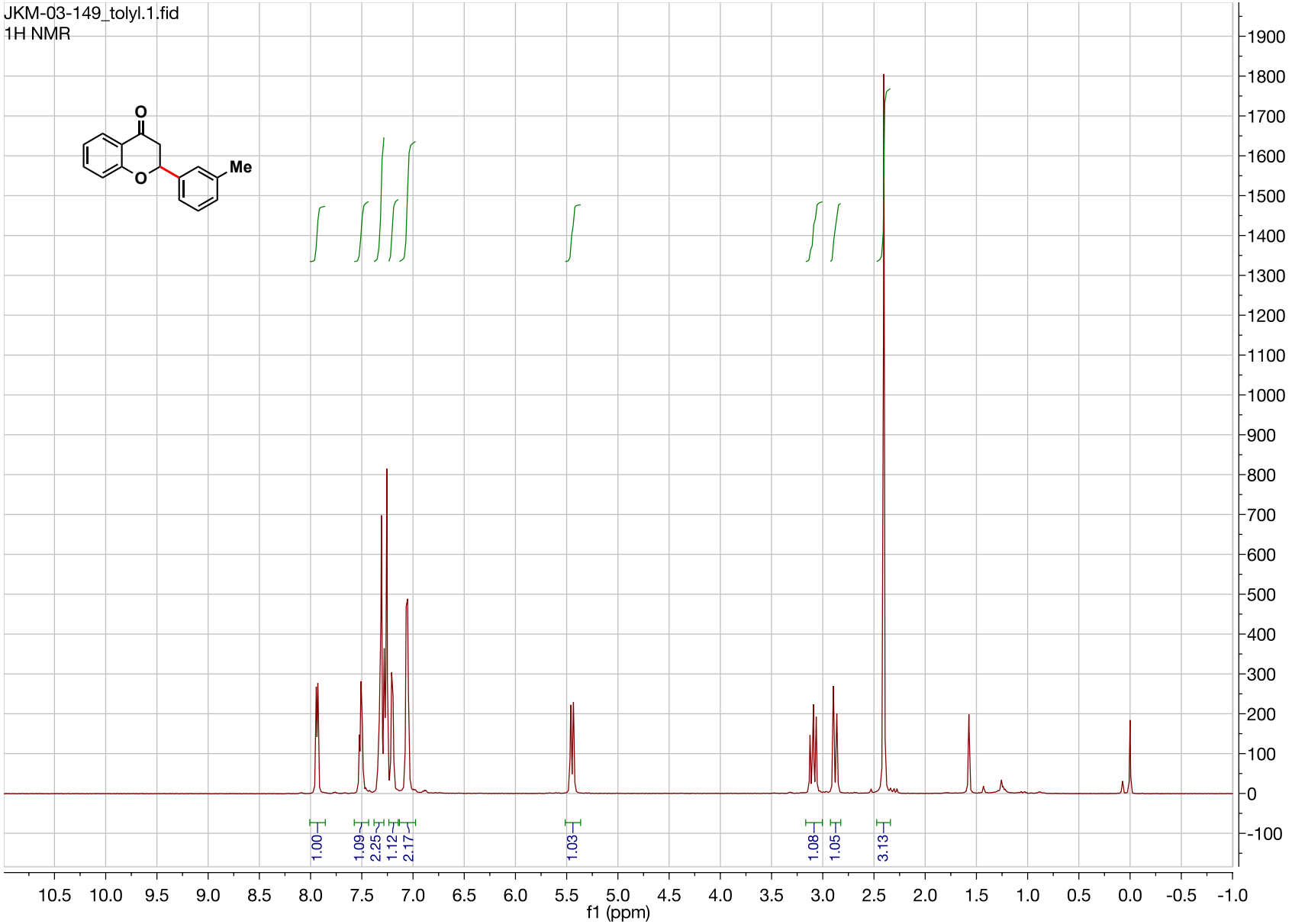
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(4-oxochroman-2-yl)benzonitrile (**2d**)



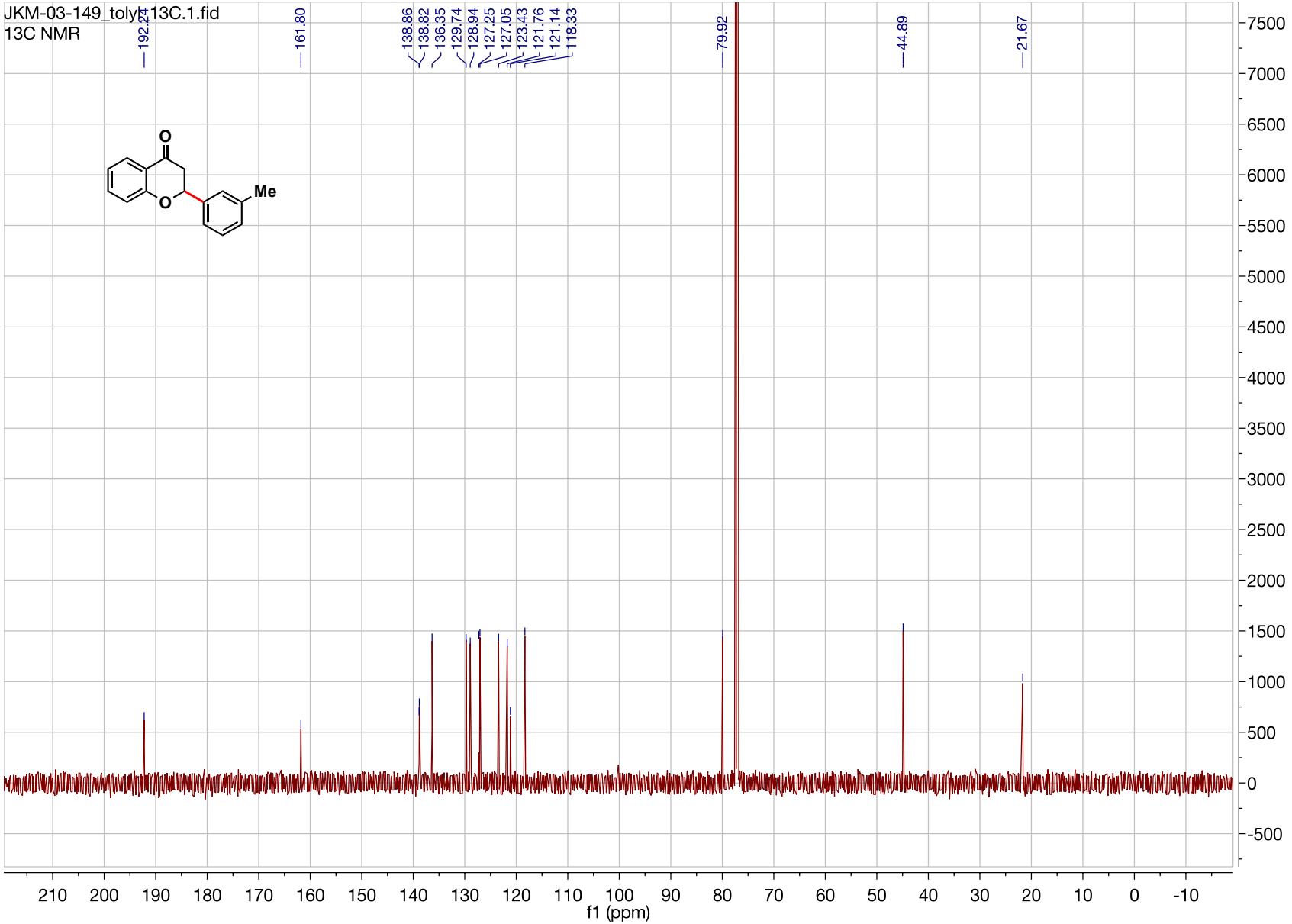
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(4-oxochroman-2-yl)benzonitrile (**2d**)



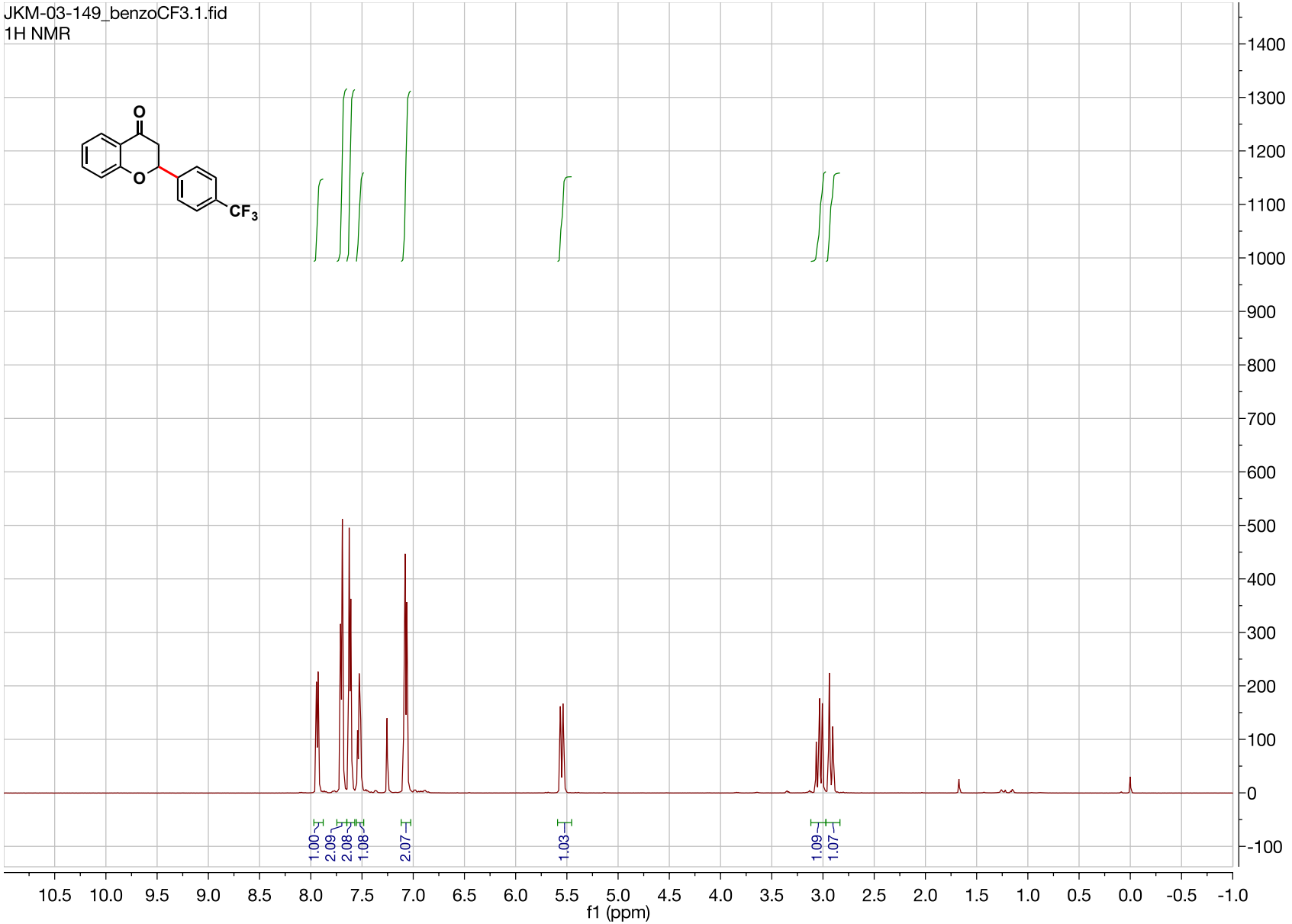
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(*m*-tolyl)chroman-4-one (**2e**)



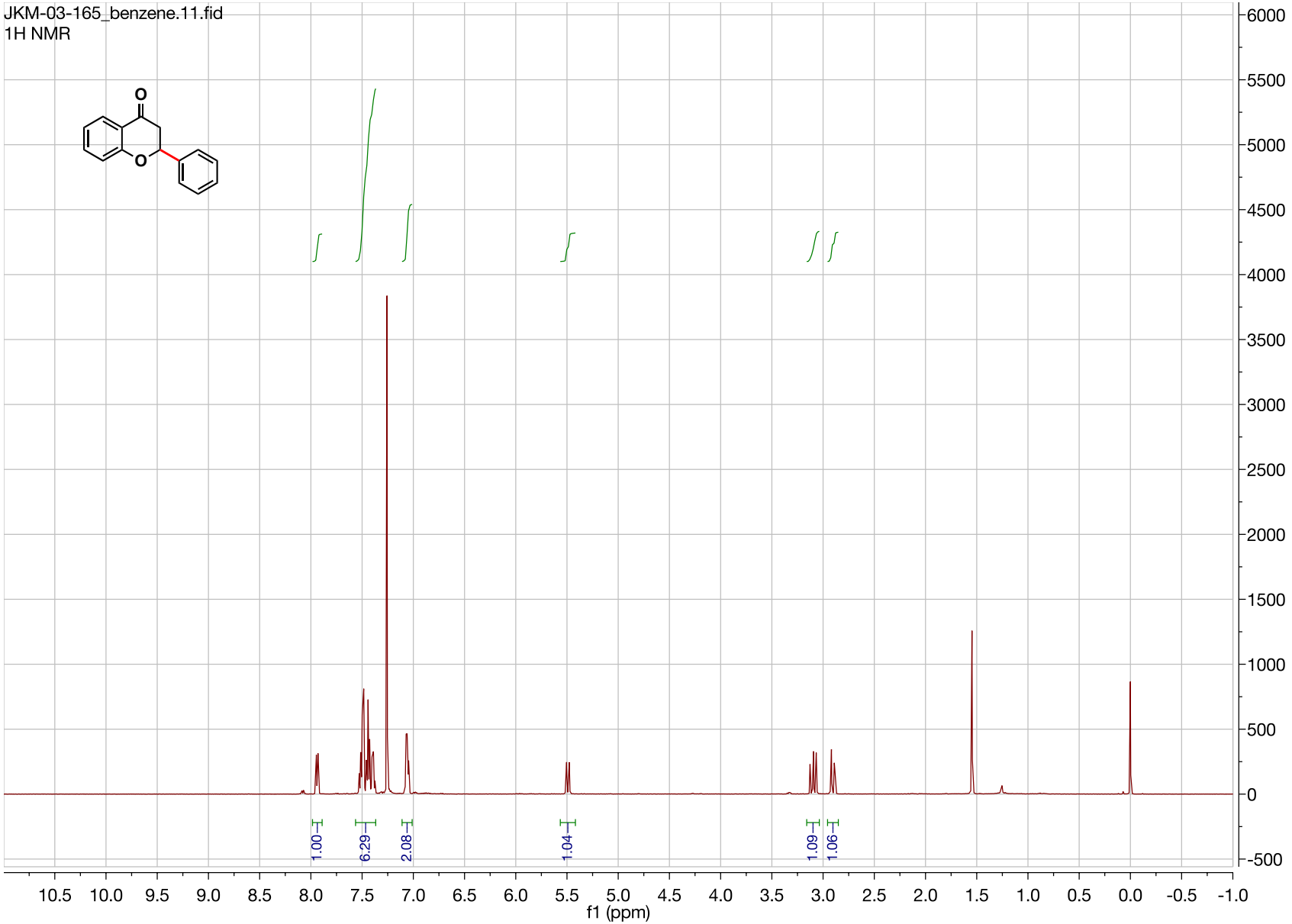
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(*m*-tolyl)chroman-4-one (**2e**)



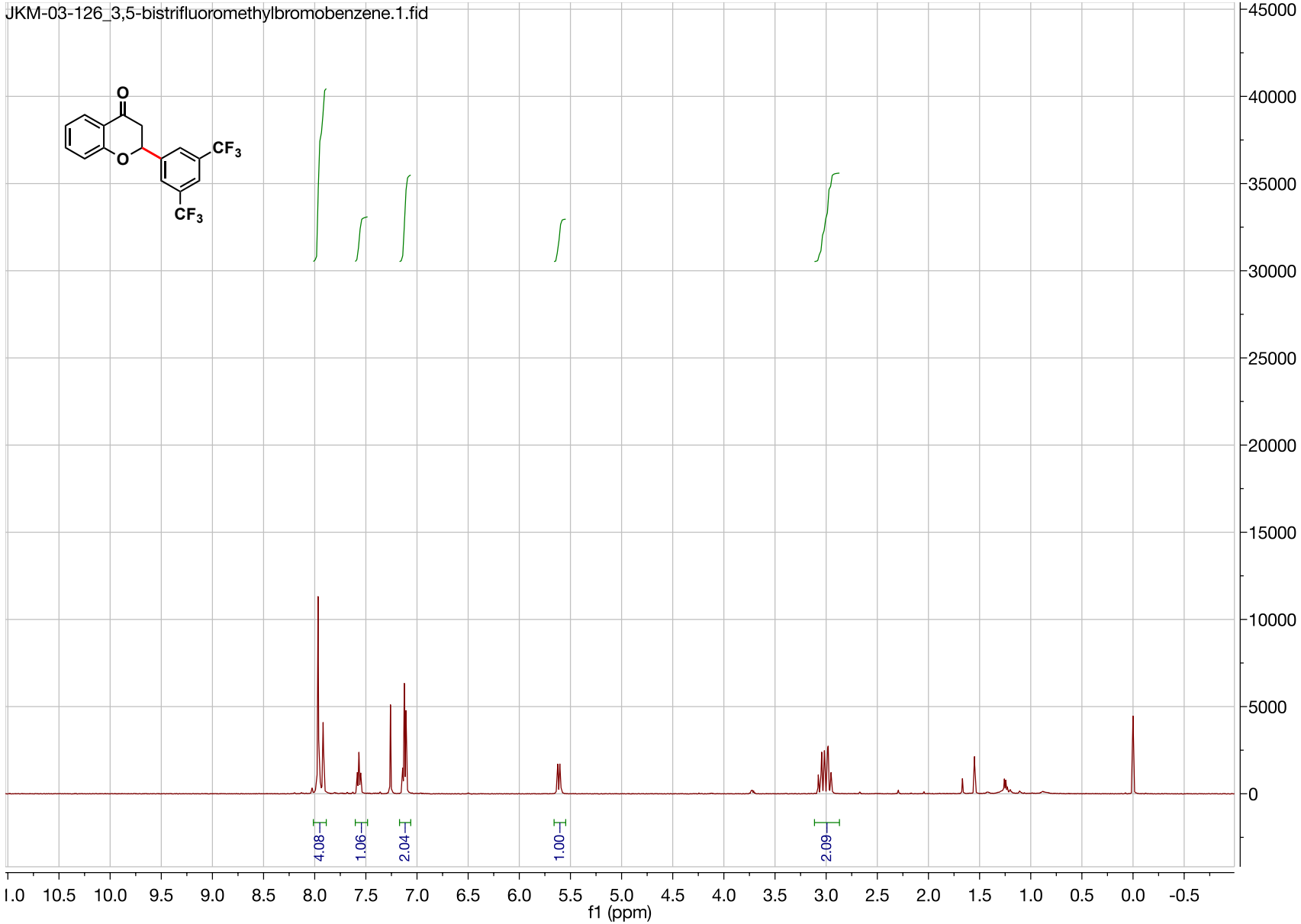
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(4-(trifluoromethyl)phenyl)chroman-4-one (**2f**)



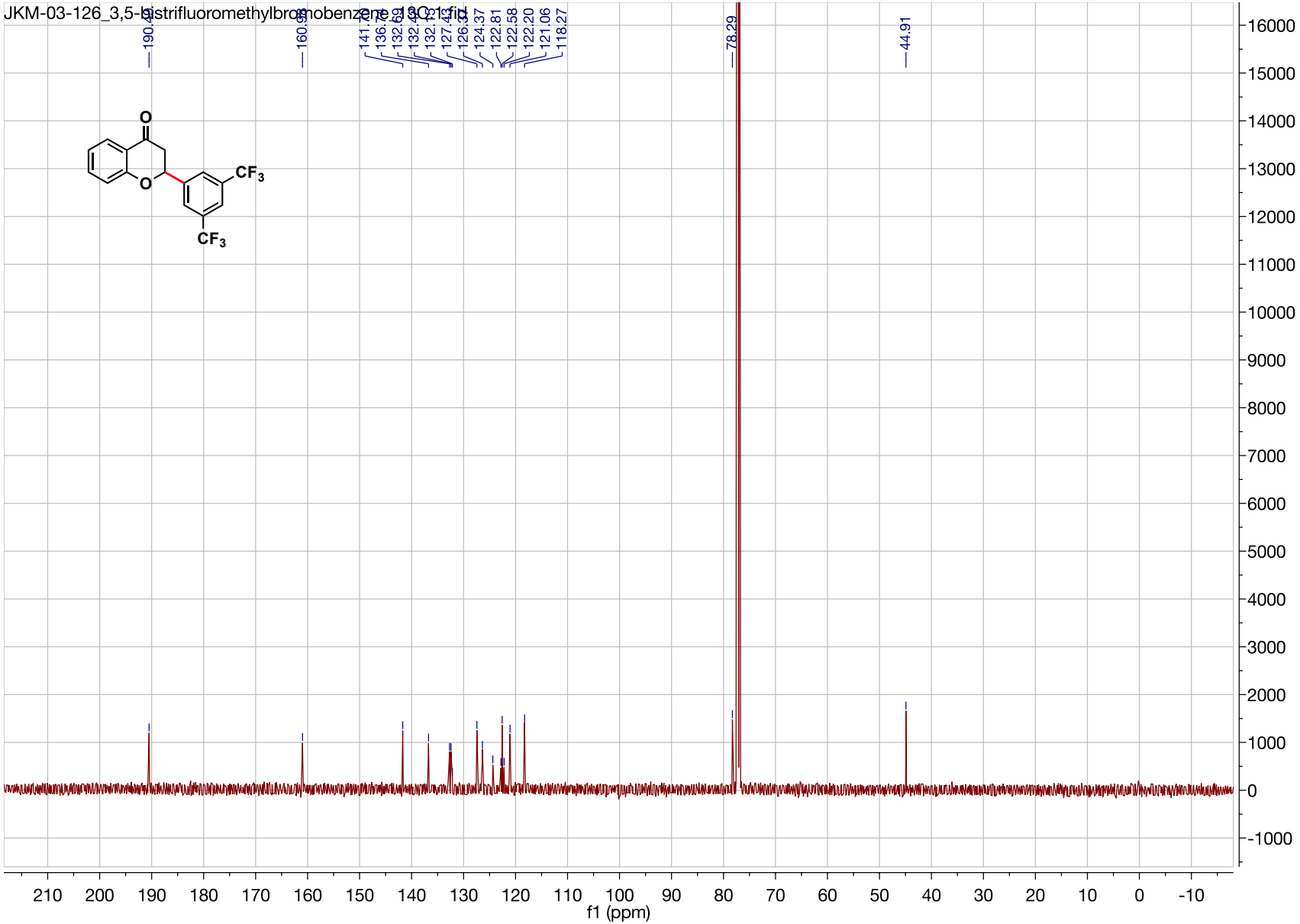
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-phenylchroman-4-one (**2g**)



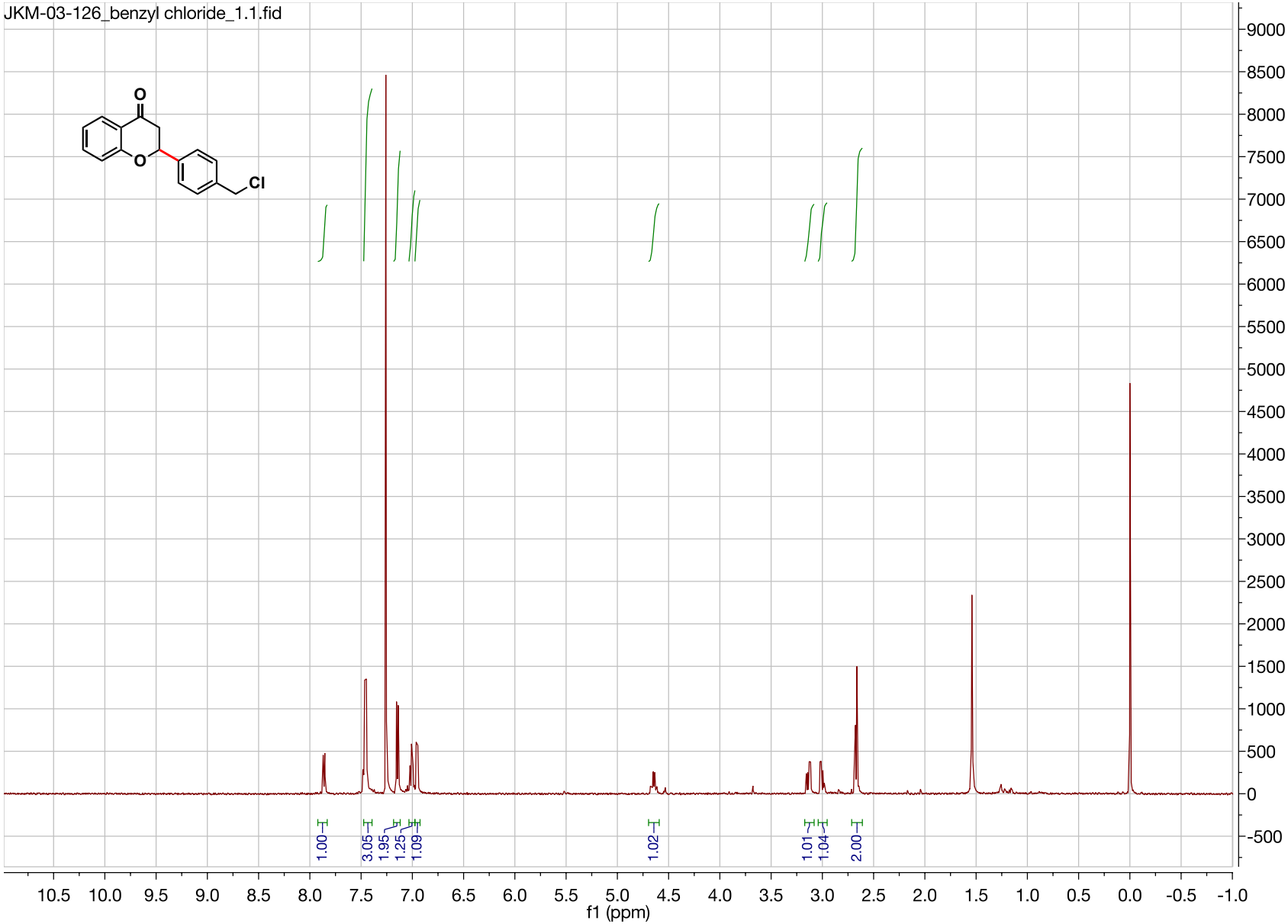
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(3,5-bis(trifluoromethyl)phenyl)chroman-4-one (**2h**)



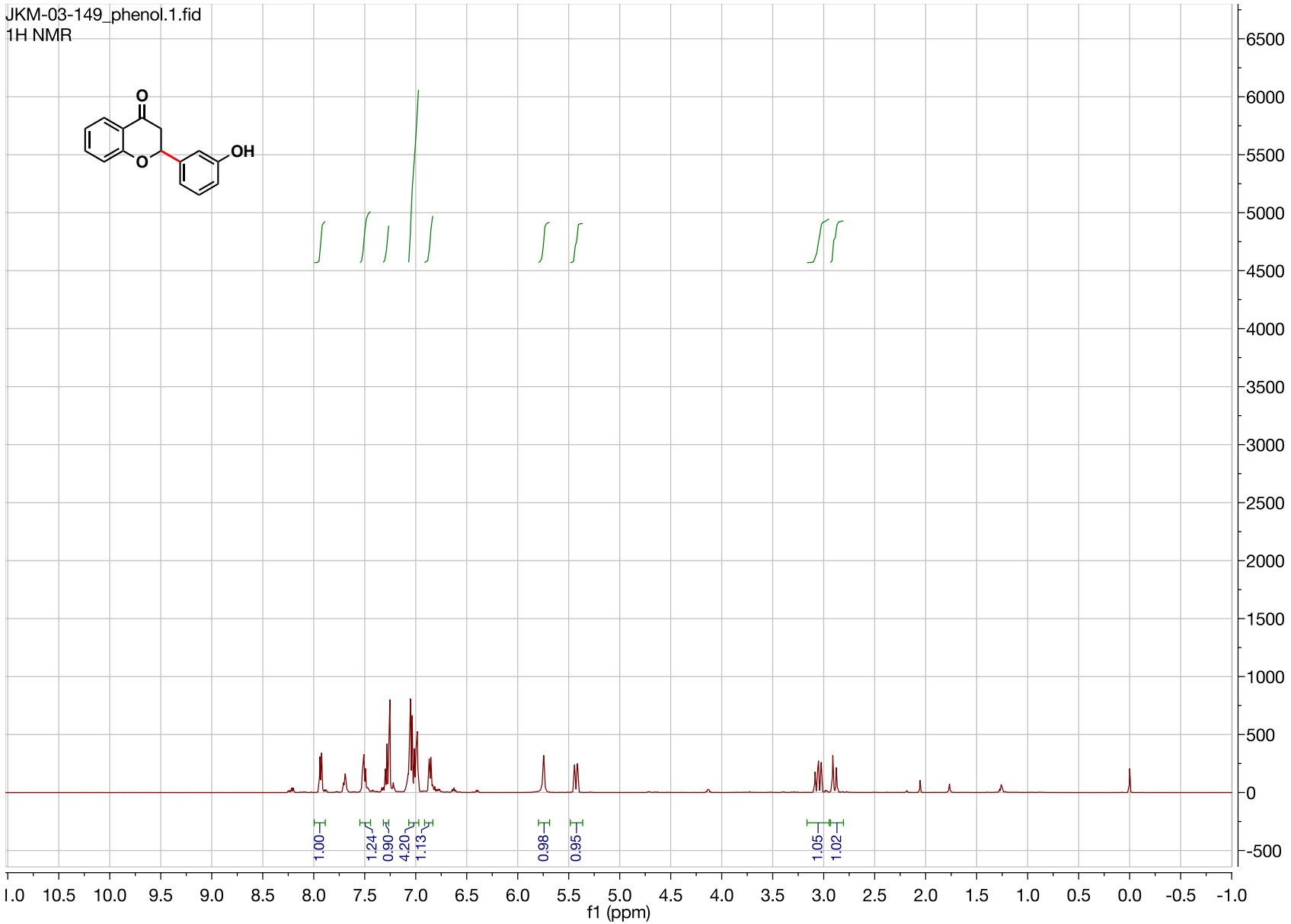
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(3,5-bis(trifluoromethyl)phenyl)chroman-4-one (**2h**)



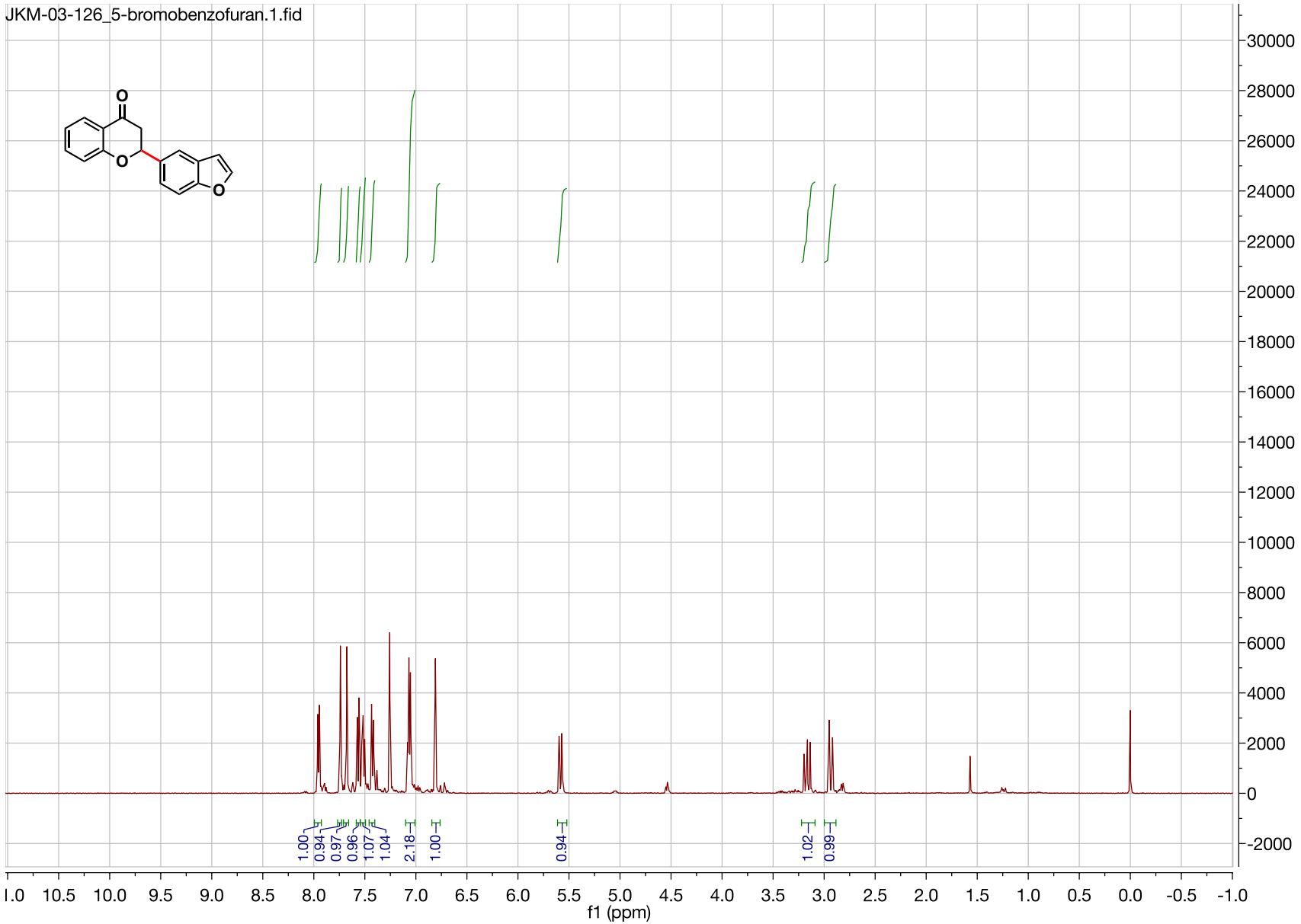
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(4-(chloromethyl)phenyl)chroman-4-one (**2i**)



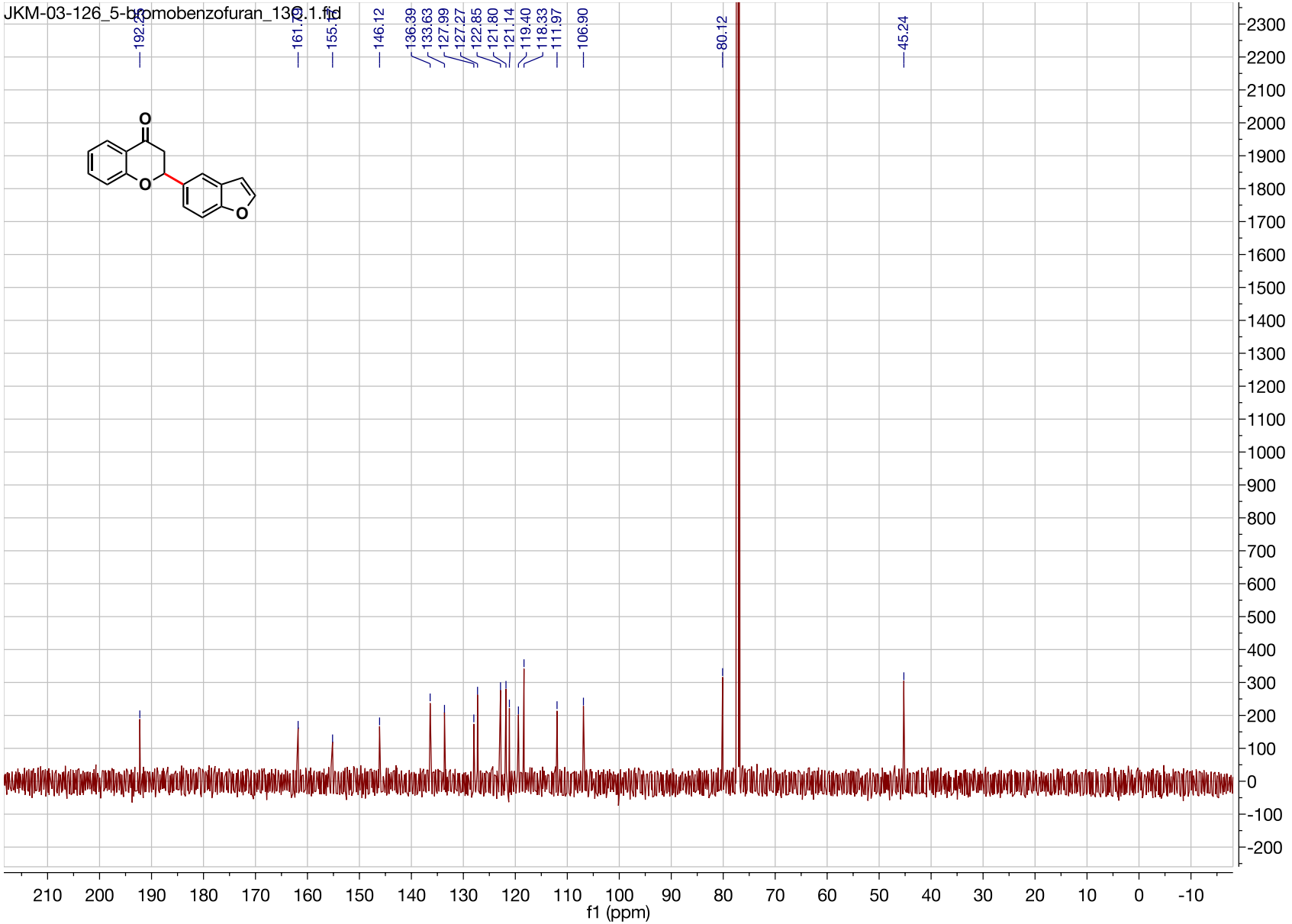
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(3-hydroxyphenyl)chroman-4-one (**2j**)



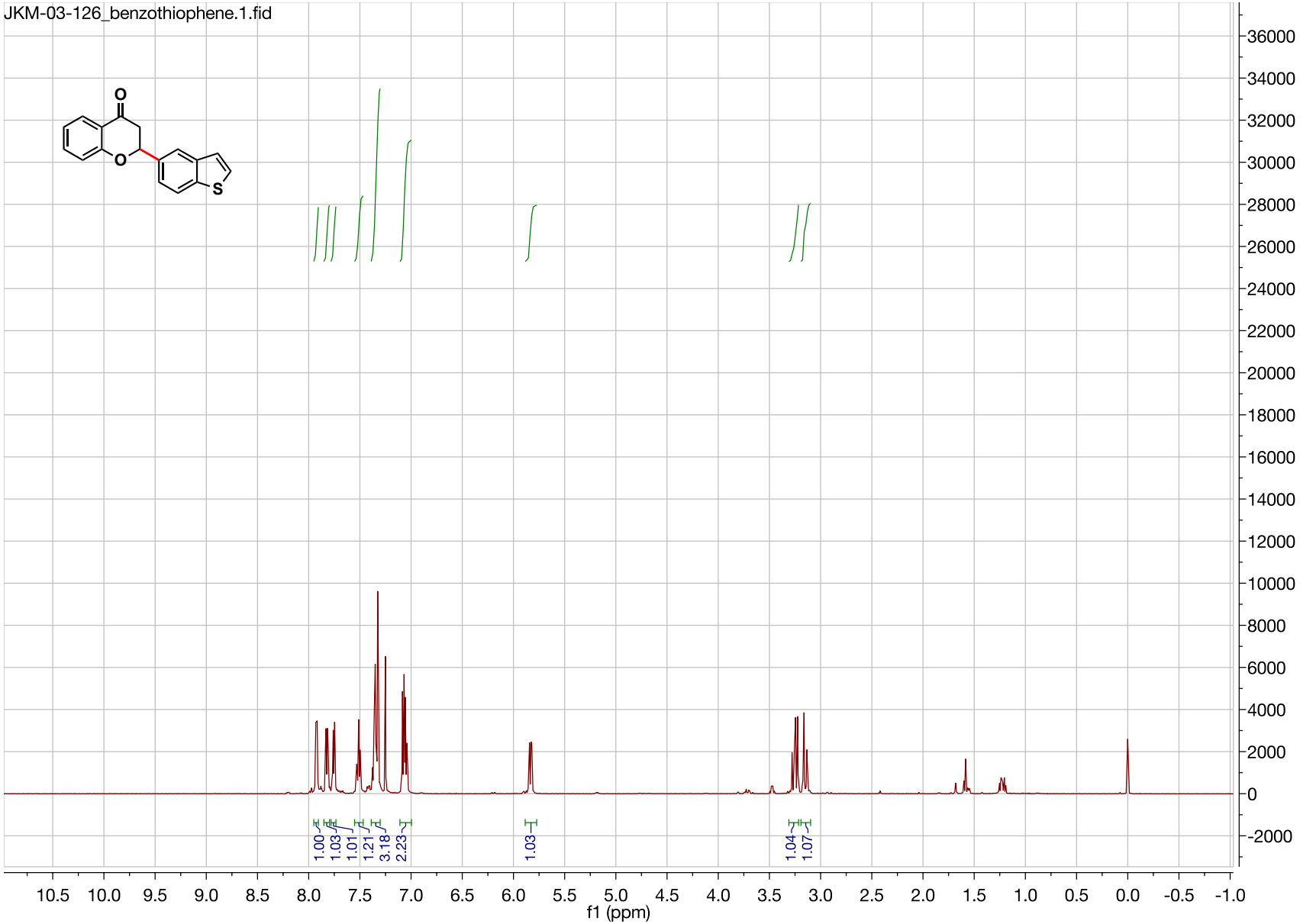
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(benzofuran-5-yl)chroman-4-one (**2k**)



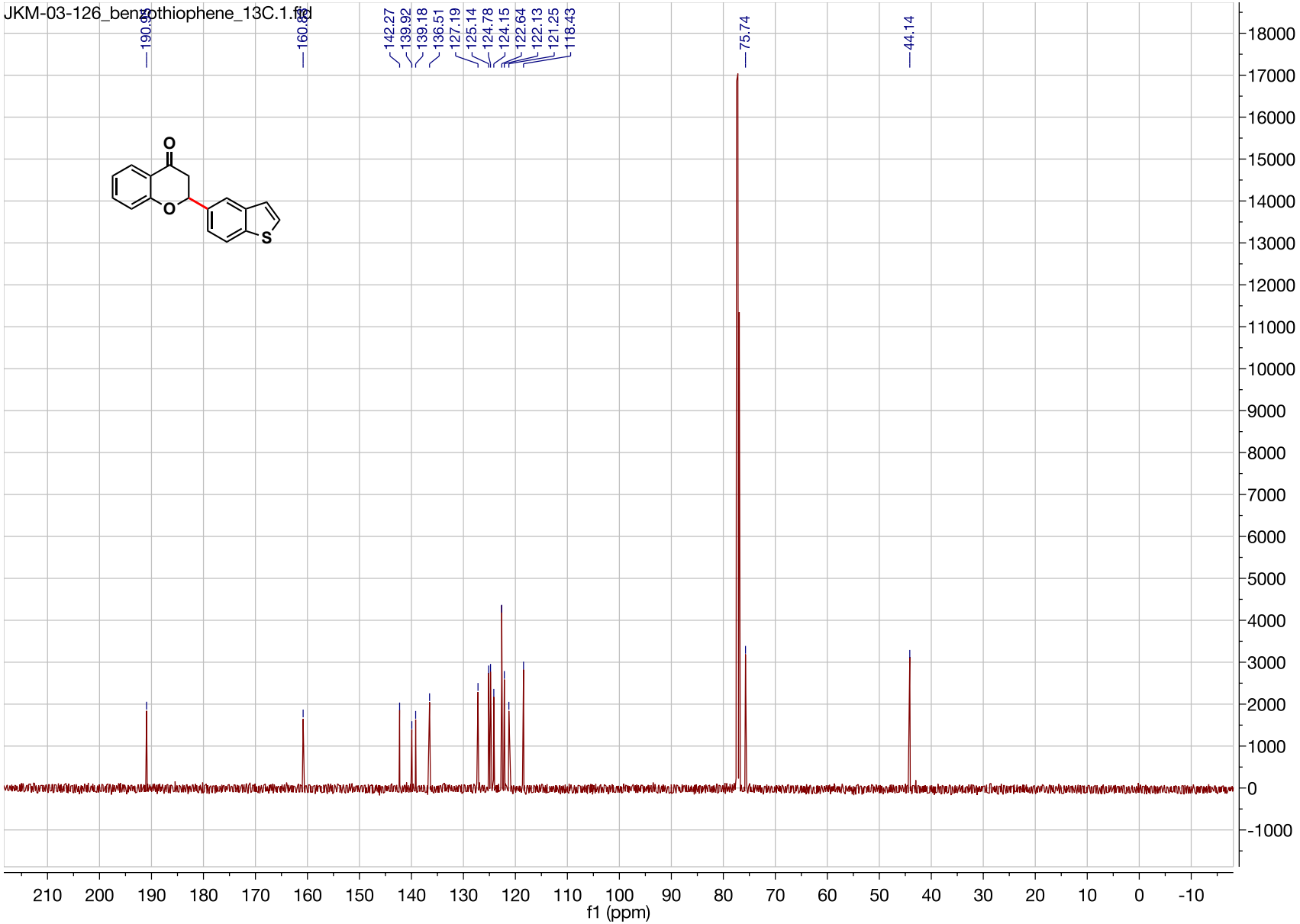
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(benzofuran-5-yl)chroman-4-one (**2k**)



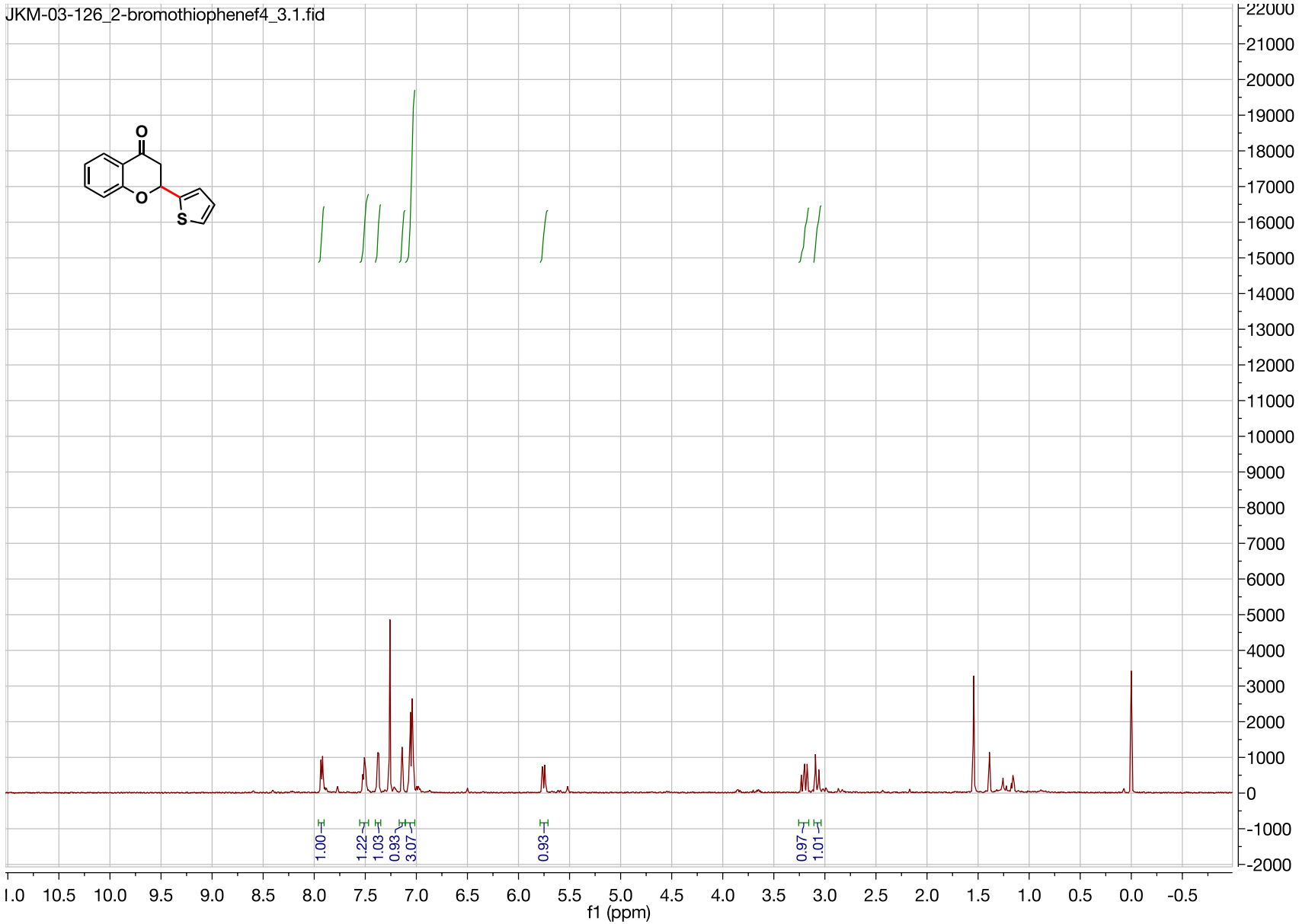
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(benzo[*b*]thiophen-5-yl)chroman-4-one (**2l**)



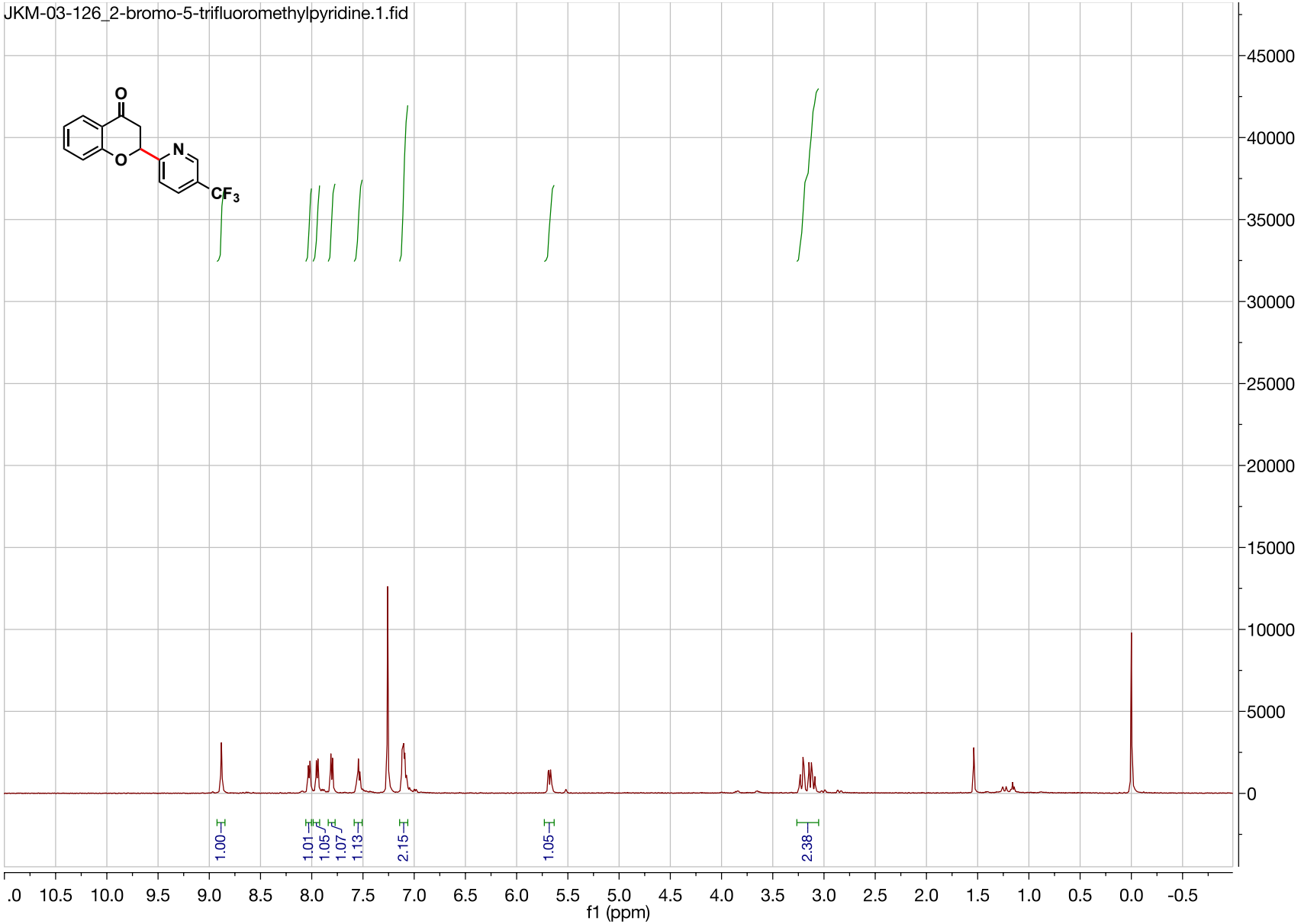
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(benzo[*b*]thiophen-5-yl)chroman-4-one (**2l**)



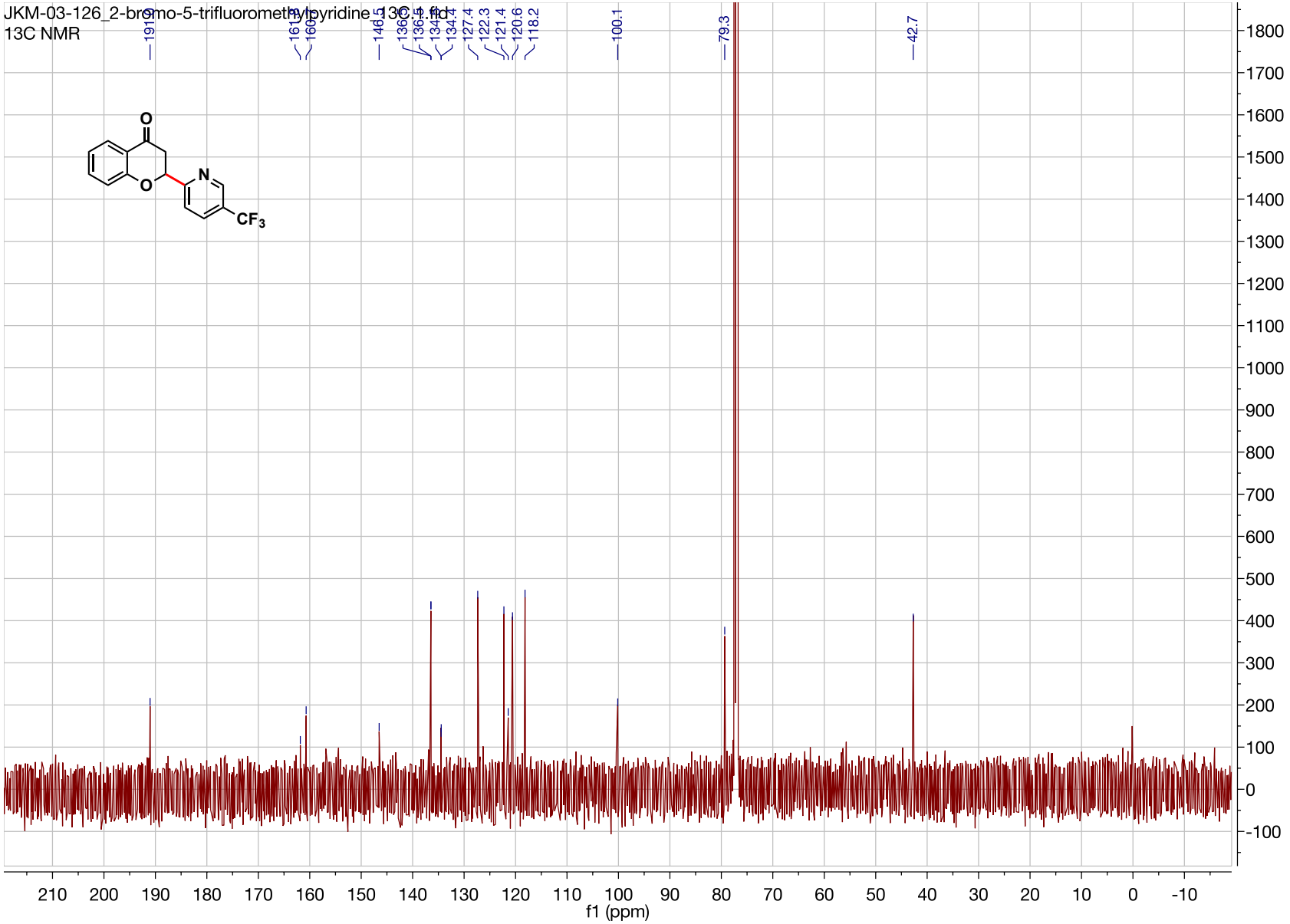
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(thiophen-2-yl)chroman-4-one (**2m**)



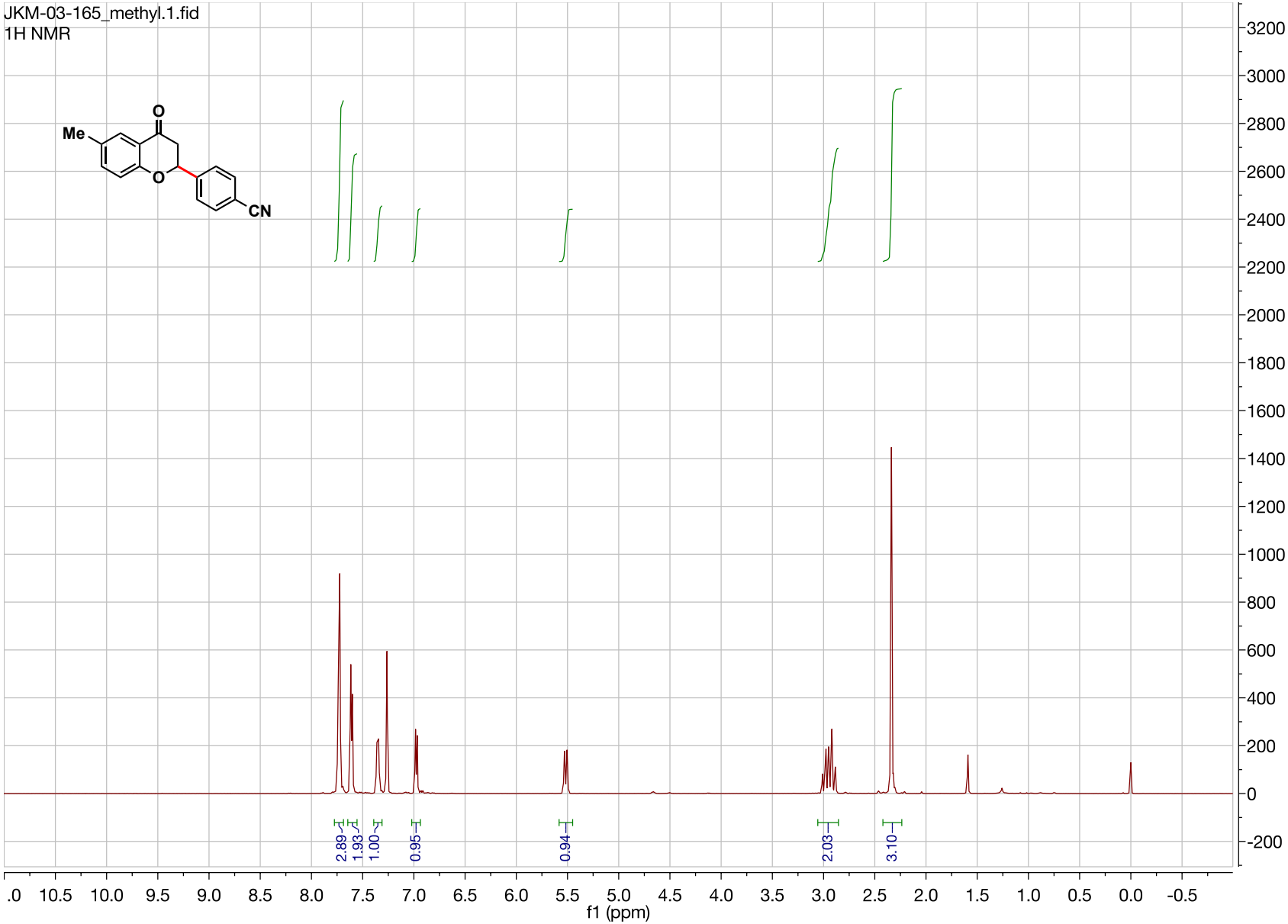
^{1}H ($CDCl_3$, 500 MHz) spectra of 2-(5-(trifluoromethyl)pyridin-2-yl)chroman-4-one (**2o**)



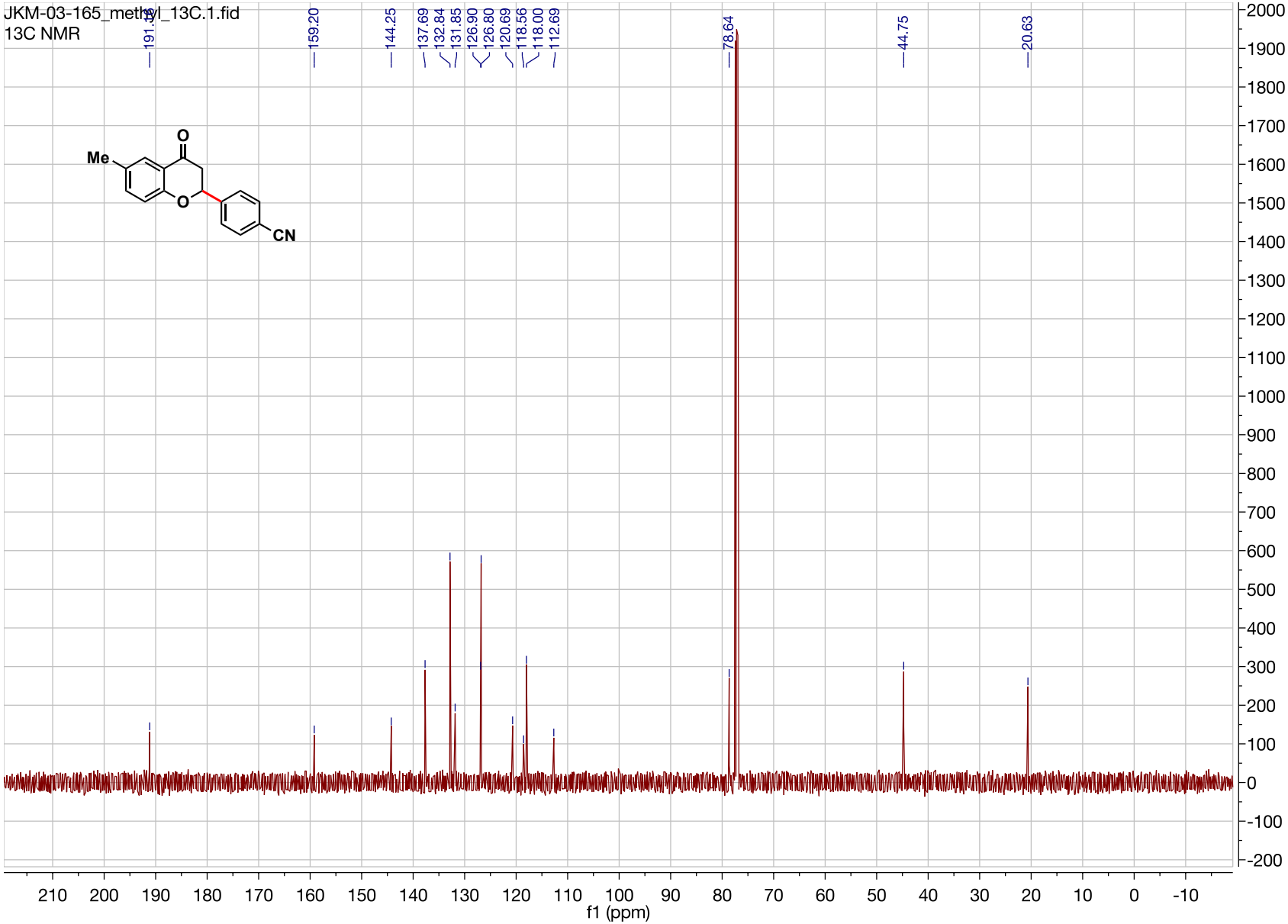
^{13}C NMR ($CDCl_3$-d^6, 125.8 MHz) spectrum of 2-(5-(trifluoromethyl)pyridin-2-yl)chroman-4-one (**2o**)



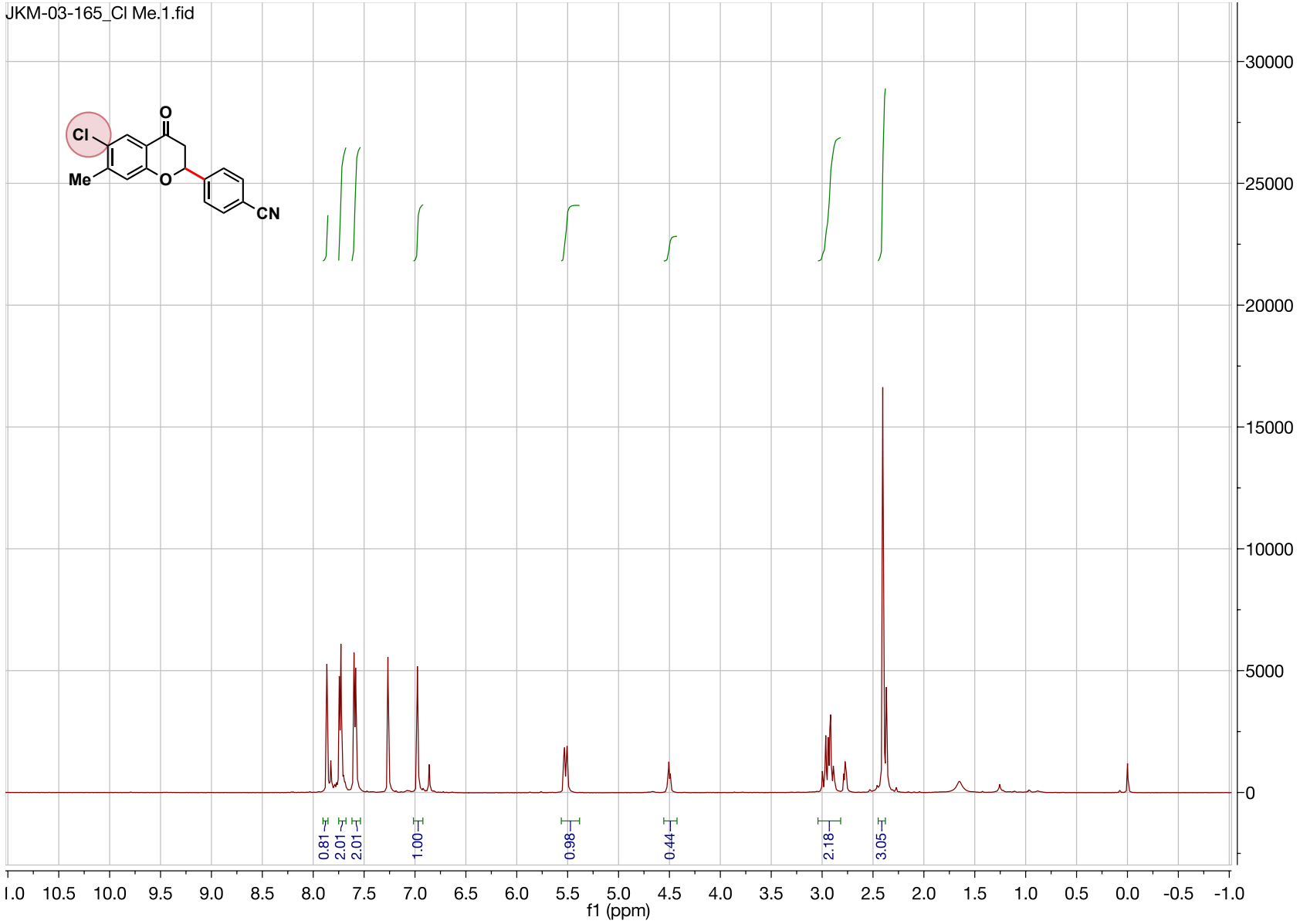
^{1}H ($CDCl_3$, 500 MHz) spectra of 4-(6-methyl-4-oxochroman-2-yl)benzonitrile (**3a**)



^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(6-methyl-4-oxochroman-2-yl)benzonitrile (**3a**)



^{1}H ($CDCl_3$, 500 MHz) spectra of 4-(6-chloro-7-methyl-4-oxochroman-2-yl)benzonitrile (**3c**)



^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(6-chloro-7-methyl-4-oxochroman-2-yl)benzonitrile (**3c**)