Supporting Information

Nickel-Catalyzed Cross-Coupling of Chromene Acetals and Boronic Acids

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I. General Information

General Procedures. Unless otherwise noted, reactions were performed with rigorous exclusion of air or moisture. Ar-flushed stainless steel cannulae or gas-tight syringes were used to transfer air- and moisture-sensitive reagents. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Reactions were monitored by LCMS. Organic solutions were concentrated under reduced pressure using a rotary evaporator (30 °C, <50 torr). Automated column chromatography was performed using pre-packed silica gel cartridges on a Biotage SP4 (40-53 μm, 60 Å).

Materials. Commercial reagents were used as received with the following exceptions. 4-CF_3-phenylboronic acid, 4-MeO-phenyl boronic acid and phenyl boronic acid were recrystallized from water and stored on the benchtop. 1,4-dioxane (inhibitor free, ACS reagent grade >99%), and toluene (ACS reagent grade, >99%) were freshly distilled from Na under an atmosphere of dry N_2 prior to use. Anhydrous 2-methyl-2-butanol (*t*-AmOH, 1 L Sure/Seal™ bottle) was purchased from Aldrich and sparged with N_2 for 30 min under sonication prior to use.

$Ni(cod)_2$ was purchased from Strem and stored at −40 °C in a N_2 filled glovebox. Triphenylphosphine was purchased from Strem and stored in a N_2 filled glovebox.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). ^{19}F spectra were recorded on a Varian Inova 300 (282 MHz) spectrometer; chemical shifts are reported in parts per millions and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 and are reported in terms of frequency of absorption (cm^{-1}). LCMS was performed on an Agilent 1260 series instrument with a multimode detector (APCI/ESI). Prep HPLC was performed on an Agilent Prep-star with single wavelength UV detector.

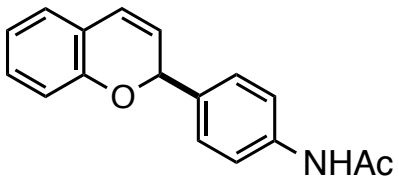
II. Procedure for preparation of 2-aryl and 2-heteroaryl-2*H*-1-benzopyrans

General procedure:

A 2-dram vial equipped with a PTFE-coated stir-bar and PTFE-tape-lined screw-thread was brought into a N_2 filled glovebox, charged with $Ni(cod)_2$ (13.6 mg, 0.05 mmol, 10 mol%) and PPh_3 (13 mg, 0.05 mmol, 10 mol%; or 30 mol%). 1,4-dioxane (1 mL) was added via micropipette and the resulting orange suspension stirred until complete dissolution (15 min, dark blood red solution was formed). The vial was tightly sealed with a PTFE-lined screw-cap and the vial further sealed with electrical tape. It was removed from the glovebox and placed on an N_2 line.

A 50 mL pear-shaped Schlenk flask equipped with a PTFE-coated stir-bar was charged with 2-ethoxy-2*H*-chromene (88 mg, 0.50 mmol, or appropriate amount of substituted chromene acetal) and the appropriate arylboronic acid (1.00 mmol, 2 equiv.). The flask was sealed with a rubber septum and subjected to 3-4 evac/purge cycles (~45 sec per cycle). The flask was then charged with 1,4-dioxane (23 mL, freshly distilled from Na) and *t*-AmOH (2 mL, degassed by sparging with N_2 in a sonicator bath for 15-30 min) to give a homogenous solution (0.02M with respect to chromene acetal) (Some boronic acids did not completely dissolve. Reactivity/reproducibility was not affected.). The catalyst solution was then added via syringe and the resulting orange/yellow solution stirred at the appropriate temperature (r.t., 40 °C, or 100 °C) until complete conversion of 2-ethoxy-2*H*-chromene or stagnation was observed by LCMS.

After this time, the reaction mixture was concentrated and the crude subjected to flash chromatography.



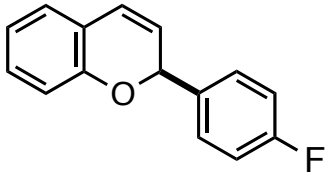
Prepared according to the general procedure (r.t., 10 mol% PPh_3, complete conversion by LCMS after 2 h), the title compound was isolated as a yellow gum (Run 1: 117 mg, 88%; Run 2: 117 mg 88%).

IR (neat, cm^{-1}): 3300, 3048, 1664, 1514.

^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 5.87 (s, 1H), 5.77 (dd, *J* = 9.8, 3.4 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.53, 153.07, 138.06, 136.63, 129.59, 128.06, 126.71, 124.76, 124.23, 121.43, 121.33, 120.07, 116.14, 76.72, 24.75.

HRMS: (ESI-TOF) calculated for $C_{17}H_{16}NO_2$ ($[M+H]^+$): 266.1176, found: 266.1189.



Prepared according to the general procedure (r.t., 10 mol% PPh_3, complete conversion by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 104 mg, 92%; Run 2: 105 mg 93%).

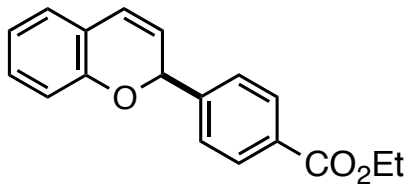
IR (neat, cm^{-1}): 3044, 1603, 1508, 1221.

^1H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.12 (td, *J* = 7.9, 1.5 Hz, 1H), 7.05 (t, *J* = 8.7 Hz, 2H), 7.02 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.56 (dd, *J* = 9.8, 1.6 Hz, 1H), 5.90 (dd, *J* = 2.8, 1.9 Hz, 1H), 5.78 (dd, *J* = 9.8, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.84 (d, *J* = 246.9 Hz), 152.99, 136.65 (d, *J* = 3.2 Hz), 129.71, 129.11 (d, *J* = 8.3 Hz), 126.77, 124.64, 124.42, 121.45, 121.34, 116.16, 115.68 (d, *J* = 21.5 Hz), 76.50.

^{19}F NMR (282 MHz, $CDCl_3$): δ −114.11.

HRMS: (ESI-TOF) calculated for $C_{15}H_{12}FO$ ($[M+H]^+$): 227.0867, found: 227.0872.



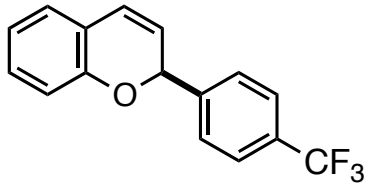
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 131 mg, 93%; Run 2: 135 mg, 96%).

IR (neat, cm^{-1}): 3044, 2903, 1712, 1290.

^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 9.8 Hz, 1H), 5.97 (s, 1H), 5.80 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.44, 153.07, 145.74, 130.47, 130.08, 129.80, 126.86, 126.82, 124.52, 124.29, 121.59, 121.33, 116.14, 76.58, 61.15, 14.47.

HRMS: (ESI-TOF) calculated for $C_{18}H_{17}O_3$ ($[M+H]^+$): 281.1172, found: 281.1169.



Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 1 h), the title compound was isolated as a white solid (Run 1: 122 mg, 88%; Run 2: 123 mg, 89%).

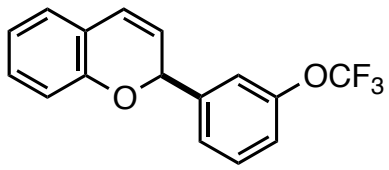
IR (neat, cm^{-1}): 3051, 1485, 1310, 1067.

^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 9.8 Hz, 1H), 5.97 (s, 1H), 5.79 (dd, *J* = 9.8, 3.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.92, 144.79, 130.50 (q, *J* = 32.4 Hz), 129.87, 127.27, 126.91, 125.77 (q, *J* = 3.7 Hz), 124.68, 124.15 (q, *J* = 272.2 Hz), 124.05, 121.67, 121.24, 116.14, 76.33.

^{19}F NMR (282 MHz, $CDCl_3$): δ -63.01.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}F_3O$ ($[M+H]^+$): 277.0835, found: 277.0849.



Prepared according to the general procedure (r.t., 10 mol% PPh_3, reaction stagnates by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 122 mg, 86%; Run 2: 132 mg, 89%).

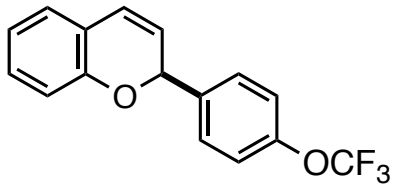
IR (neat, cm^{-1}): 3045, 1485, 1253, 1150.

^1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.38 (m, 2H), 7.31 (s, 1H), 7.17 (d, *J* = 4.5 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.89 (td, *J* = 7.4, 0.8 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.57 (d, *J* = 9.8 Hz, 1H), 5.93 (s, 1H), 5.79 (dd, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.91, 149.54 (q, *J* = 1.6 Hz), 143.25, 130.19, 129.82, 126.87, 125.36, 124.71, 124.11, 121.63, 121.26, 120.76, 120.54 (q, *J* = 257.4 Hz), 119.70, 116.16, 76.24.

^{19}F NMR (282 MHz, $CDCl_3$): δ −58.17.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}F_3O_2$ ($[M+H]^+$): 293.0784, found: 293.0787.



Prepared according to the general procedure (r.t., 10 mol% PPh_3, reaction stagnates by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 115 mg, 79%, Run 2: 103 mg, 70%).

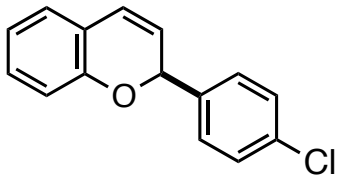
IR (neat, cm^{-1}): 3045, 1485, 1253, 1150.

^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.08 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 9.8 Hz, 1H), 5.92 (m, 1H), 5.78 (dd, *J* = 9.8, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.93, 149.21 (q, *J* = 2.0 Hz), 139.55, 129.79, 128.68, 126.84, 124.55, 124.34, 123.60, 121.57, 121.29, 120.46 (q, *J* = 275.8 Hz), 117.47, 116.15, 76.32.

^{19}F NMR (282 MHz, $CDCl_3$): δ −58.25.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}F_3O_2$ ($[M+H]^+$): 293.0784, found: 293.0792.



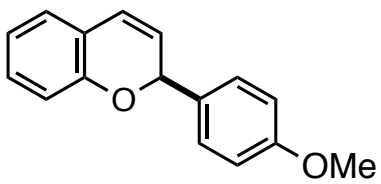
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, reaction stagnates by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 81 mg, 66%, Run 2: 83 mg, 68%).

IR (neat, cm^{-1}): 3045, 1603, 1484, 1226.

^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.12 (td, *J* = 7.8, 1.6 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.88 (td, *J* = 7.4, 0.8 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.55 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.89 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.77 (dd, *J* = 9.8, 3.5 Hz, 1H).

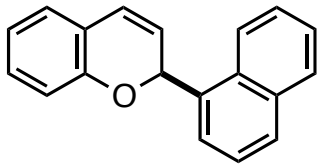
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.99, 139.36, 134.33, 129.76, 128.96, 128.58, 126.81, 124.52, 124.38, 121.51, 121.33, 116.17, 76.40.

HRMS: (ESI-TOF) calculated for $C_{15}H_{12}ClO$ ($[M+H]^+$): 243.0571, found: 243.0557.



Prepared according to the general procedure (r.t., 10 mol% PPh_3, complete conversion by LCMS after 4 h), the title compound was isolated as a colorless oil (Run #1: 101 mg, 86%, Run #2: 101 mg 86%). Spectroscopic data was in complete agreement with previously published results. (Conducting this reaction in the absence of $Ni(cod)_2/PPh_3$ resulted in no reaction.)

Ref: Moquist, P. N.; Kodama, T.; Schaus, S. E. *Angew. Chem., Int. Ed. Engl.* **2010,** *49,* 7096.



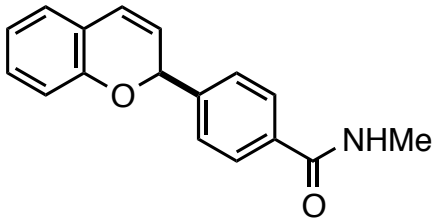
Prepared according to the general procedure (r.t., 10 mol% PPh_3, complete conversion by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 125 mg, 97%; Run 2: 125 mg, 97%).

IR (neat, cm^{-1}): 3044, 1605, 1484, 1224.

^1H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.54 (dt, *J* = 14.8, 7.1 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 9.9 Hz, 1H), 6.62 (s, 1H), 5.92 (d, *J* = 9.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.65, 135.56, 134.29, 131.07, 129.60, 129.30, 128.96, 126.84, 126.51, 125.99, 125.91, 125.44, 125.02, 124.95, 124.18, 121.77, 121.49, 116.31, 74.97.

HRMS: (ESI-TOF) calculated for $C_{19}H_{15}O$ ($[M+H]^+$): 259.1117, found: 259.1120.



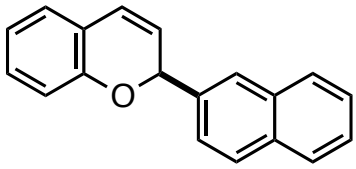
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 1 h), the title compound was isolated as a pale yellow oil (Run 1: 131 mg, 97%, Run 2: 122 mg, 93%).

IR (neat, cm^{-1}): 3317, 3058, 1660, 1548.

^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.12 (td, *J* = 7.8, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.88 (td, *J* = 7.4, 0.9 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.55 (dd, *J* = 9.8, 1.7 Hz, 1H), 6.11 (s, 1H), 5.97 – 5.93 (m, 1H), 5.79 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.01 (d, *J* = 4.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 167.93, 153.02, 144.21, 134.62, 129.77, 127.34, 127.19, 126.85, 124.50, 124.34, 121.57, 121.33, 116.13, 76.54, 27.02.

HRMS: (ESI-TOF) calculated for $C_{17}H_{16}NO_2$ ($[M+H]^+$): 266.1176, found: 266.1183.



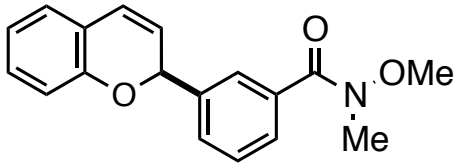
Prepared according to the general procedure (r.t., 10 mol% PPh_3, complete conversion by LCMS after 4 h), the title compound was isolated as a colorless oil (Run 1: 117 mg, 90%, Run 2: 116 mg, 89%).

IR (neat, cm^{-1}): 3054, 1602, 1484, 1226.

^1H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.80 (m, 4H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 9.8 Hz, 1H), 6.09 (s, 1H), 5.88 (dd, *J* = 9.8, 3.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.30, 138.18, 133.43, 133.33, 129.68, 128.76, 128.33, 127.83, 126.79, 126.38, 126.20, 125.09, 124.84, 124.39, 121.48, 121.38, 116.17, 77.40. One peak is obscured due to overlap.

HRMS: (ESI-TOF) calculated for $C_{19}H_{15}O$ ($[M+H]^+$): 259.1117, found: 259.1125.



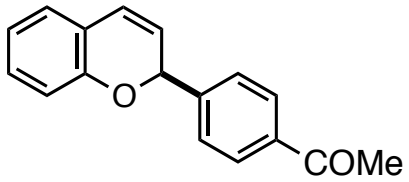
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, reaction stagnates by LCMS after 2 h), the title compound was isolated as a pale yellow oil (Run 1: 83 mg, 54%, Run 2: 75 mg, 51%).

IR (neat, cm^{-1}): 3280, 3044, 2934, 1636.

^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.11 (td, *J* = 7.8, 1.5 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 9.8, 1.6 Hz, 1H), 5.95 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.81 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.48 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 169.77, 161.95, 153.03, 140.72, 134.50, 129.67, 129.38, 128.58, 128.29, 126.94, 126.80, 124.52, 124.46, 121.46, 121.43, 116.17, 76.72, 61.18.

HRMS: (ESI-TOF) calculated for $C_{18}H_{18}NO_3$ ($[M+H]^+$): 296.1281, found: 296.1285.



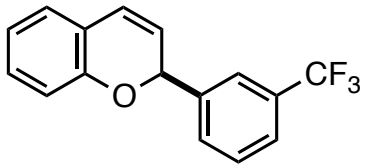
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 1 h), the title compound was isolated as a white solid (Run 1: 124 mg, 99%, Run 2: 120 mg, 96%).

IR (neat, cm^{-1}): 3043, 1679, 1605, 1484.

^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 9.8 Hz, 1H), 5.97 (s, 1H), 5.80 (dd, *J* = 9.8, 3.4 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.86, 153.04, 146.04, 137.03, 129.83, 128.90, 127.05, 126.90, 124.59, 124.15, 121.63, 121.30, 116.14, 76.50, 26.84.

HRMS: (ESI-TOF) calculated for $C_{17}H_{12}F_3O$ ($[M+H]^+$): 251.1067, found: 251.1071.



Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 1.5 h), the title compound was isolated as a colorless oil (Run 1: 134 mg, 97%; Run 2: 126 mg, 91%).

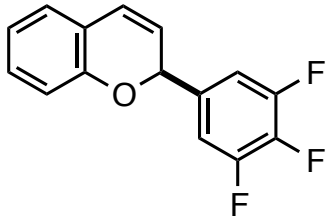
IR (neat, cm^{-1}): 3046, 1606, 1484, 1327.

^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.14 (td, *J* = 8.0, 1.4 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.58 (dd, *J* = 9.8, 1.1 Hz, 1H), 5.97 (s, 1H), 5.80 (dd, *J* = 9.8, 3.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.80, 141.81, 130.96 (q, *J* = 32.5 Hz), 130.39, 129.76, 129.21, 126.80, 125.17 (q, *J* = 3.7 Hz), 124.77, 124.14 (q, *J* = 272.0 Hz), 123.94, 123.82 (q, *J* = 3.8 Hz) 121.57, 121.14, 116.05, 76.32.

^{19}F NMR (282 MHz, $CDCl_3$): δ -63.01.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}F_3O$ ($[M+H]^+$): 277.0835, found: 277.0837.



Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 1.5 h), the title compound was isolated as a white solid (Run 1: 122 mg, 93%; Run 2: 124 mg, 95%).

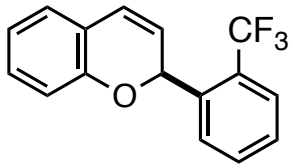
IR (neat, cm^{-1}): 3046, 1620, 1525, 1200.

^1H NMR (500 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 9.8 Hz, 1H), 5.82 (s, 1H), 5.75 (dd, *J* = 9.8, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.46, 151.35 (ddd, *J* = 250.8, 10.1, 3.7 Hz), 139.64 (dt, *J* = 252.1, 15.4 Hz), 137.03 (dd, *J* = 10.6, 6.2 Hz), 130.01, 126.99, 125.23, 123.09, 121.87, 121.04, 116.21, 111.26 (dd, *J* = 16.6, 5.1 Hz), 75.23.

^{19}F NMR (282 MHz, $CDCl_3$): δ -133.82 – -133.97 (m), -161.08 (tt, *J* = 20.5, 6.4 Hz).

HRMS: (ESI-TOF) calculated for $C_{15}H_9F_3O$ ($[M+H]^+$): 263.0678, found: 263.0679.



Prepared according to the general procedure (100 °C, 30 mol% PPh_3, >90% conversion (estimated) by LCMS after 30 min), the title compound was isolated as a colorless oil (Run 1: 98 mg, 71%; Run 2: 98 mg, 71%).

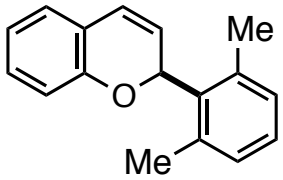
IR (neat, cm^{-1}): 3045, 1606, 1485, 1310.

^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.53 (dd, *J* = 9.9, 1.3 Hz, 1H), 6.39 (s, 1H), 5.69 (dd, *J* = 9.9, 2.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.15, 139.95, 132.45, 129.72, 129.33, 128.26, 126.81 (q, *J* = 30.5 Hz), 126.74, 125.69 (q, *J* = 5.7 Hz), 124.63, 124.19 (q, *J* = 274.0 Hz), 123.81, 121.44, 120.75, 115.84, 73.19.

^{19}F NMR (282 MHz, $CDCl_3$): δ -58.49.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}F_3O$ ([M+H]$^+$): 277.0835, found: 277.0854.



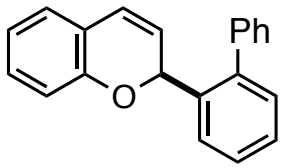
Prepared according to the general procedure (100 °C, 30 mol% PPh_3, complete conversion by LCMS after 30 min), the title compound was isolated as a colorless oil (Run 1: 94 mg, 79%; Run 2: 102 mg, 87% (product inseparable from PPh_3, yield is approximated based on NMR purity).

IR (neat, cm^{-1}): 3023, 2925, 1603, 1483.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 – 7.01 (m, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.94 – 6.91 (m, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.41 – 6.36 (m, 2H), 5.58 – 5.54 (m, 1H), 2.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.30, 137.60, 136.20, 129.58, 129.44, 128.37, 126.84, 125.20, 124.85, 121.57, 121.32, 115.89, 74.48, 20.93.

HRMS: (ESI-TOF) calculated for $C_{17}H_{17}O$ ([M+H]$^+$): 237.1274, found: 237.1275.



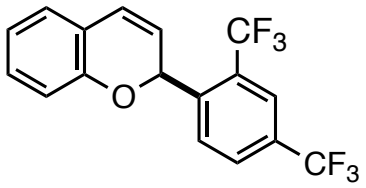
Prepared according to the general procedure (100 °C, 30 mol% PPh_3, >90% conversion (estimated) by LCMS after 30 min), the title compound was isolated as a colorless oil (Run #1: 101 mg, 71%, Run #2: 120 mg, 85%) (product inseparable from PPh_3, yield is approximated based on NMR purity).

IR (neat, cm^{-1}): 3055, 1603, 1482, 1225.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.70 (m, 1H), 7.48 – 7.30 (m, 8H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 9.9 Hz, 1H), 6.00 (s, 1H), 5.65 (dd, *J* = 9.9, 2.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.30, 141.36, 140.52, 138.02, 130.39, 129.65, 129.59, 128.60, 128.41, 128.36, 128.09, 127.44, 126.64, 125.45, 124.06, 121.37, 121.23, 116.08, 74.17.

HRMS: (ESI-TOF) calculated for $C_{21}H_{17}O$ ([M+H]$^+$): 285.1274, found: 285.1273.



Prepared according to the general procedure (100 °C, 30 mol% PPh_3, complete conversion by LCMS after 30 min), the title compound was isolated as a colorless oil (Run #1: 144 mg, 84%, Run #2: 146 mg, 86%).

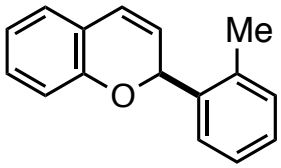
IR (neat, cm^{-1}): 3060, 1486, 1273, 1083.

^1H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.95 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.17 (td, *J* = 7.9, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.54 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.39 (s, 1H), 5.63 (dd, *J* = 9.8, 2.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.91, 144.04, 130.82 (q, *J* = 33.4 Hz), 130.33, 130.14, 129.42 (q, *J* = 3.2 Hz), 127.63 (q, *J* = 31.9 Hz), 127.05, 124.56, 123.72, 123.50 (q, *J* = 274.5 Hz), 123.36 (q, *J* = 272.8 Hz), 123.26 – 122.98 (m), 121.93, 120.61, 115.98, 72.95.

^{19}F NMR (282 MHz, $CDCl_3$): δ -58.86, -63.20.

HRMS: (ESI-TOF) calculated for $C_{17}H_{11}F_6O$ ($[M+H]^+$): 345.0709, found: 345.0715.



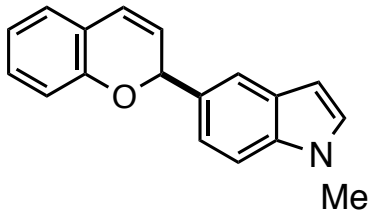
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 3 h), the title compound was isolated as a colorless oil (Run #1: 104 mg, 94%, Run #2: 106 mg, 96%).

IR (neat, cm^{-1}): 3024, 2955, 1604, 1483.

^1H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.0 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 9.8, 1.9 Hz, 1H), 6.17 – 6.13 (m, 1H), 5.75 (dd, *J* = 9.8, 3.1 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.59, 138.40, 136.06, 130.97, 129.54, 128.46, 127.84, 126.72, 126.34, 124.68, 124.61, 121.54, 121.29, 116.06, 74.80, 19.38.

HRMS: (ESI-TOF) calculated for $C_{16}H_{14}O$ ($[M+H]^+$): 223.1117, found: 223.1122.



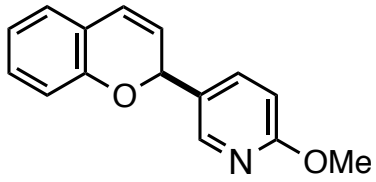
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, reaction stagnates by LCMS after 4.5 h), the title compound was isolated as a beige solid (Run #1: 68 mg, 52%, Run #2: 88 mg, 68%).

IR (neat, cm^{-1}): 3015, 2900, 1601, 1484.

^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.34 (dd, *J* = 19.7, 8.5 Hz, 2H), 7.11 – 7.00 (m, 3H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 9.9 Hz, 1H), 6.47 (d, *J* = 2.9 Hz, 1H), 6.03 (s, 1H), 5.86 (dd, *J* = 9.8, 3.3 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.37, 136.83, 131.79, 129.58, 129.44, 128.50, 126.59, 125.72, 123.78, 121.57, 121.39, 121.01, 120.20, 116.19, 109.62, 101.43, 78.22, 33.09.

HRMS: (ESI-TOF) calculated for $C_{18}H_{16}NO$ ($[M+H]^+$): 262.1226, found: 262.1234.



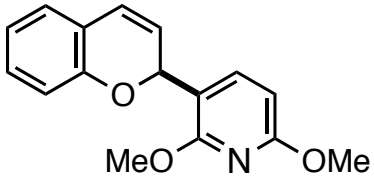
Prepared according to the general procedure (100 °C, 30 mol% PPh_3, complete conversion by LCMS after 1h), the title compound was isolated as a colorless oil (Run #1: 80 mg, 67%, Run #2: 82 mg, 69%).

IR (neat, cm^{-1}): 3044, 1603, 1484, 1224.

^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.10 (td, *J* = 7.8, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.59 (dd, *J* = 9.8, 1.4 Hz, 1H), 5.87 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.77 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 164.46, 152.82, 146.06, 138.18, 129.77, 128.96, 126.80, 124.91, 123.98, 121.52, 121.42, 116.30, 111.26, 74.64, 53.68.

HRMS: (ESI-TOF) calculated for $C_{15}H_{14}NO_2$ ($[M+H]^+$): 240.1019, found: 240.1026.



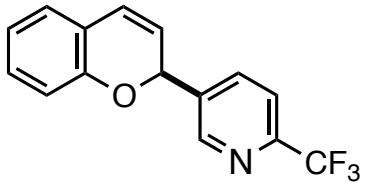
Prepared according to the general procedure (100 °C, 30 mol% PPh_3, the reaction stagnates by LCMS after 1.5 h), the title compound was isolated as a colorless oil (Run #1: 67 mg, 50%, Run #2 71 mg, 53%). (After column chromatography, the title compound was further purified by prep. HPLC 50:50 MeCN:H_2O to 100:0 MeCN:H_2O to remove protodeborylated material.)

IR (neat, cm^{-1}): 2946, 1586, 1479, 1202.

^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.1 Hz, 1H), 7.09 (td, *J* = 8.1, 1.3 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 9.8 Hz, 1H), 6.25 (d, *J* = 8.1 Hz, 1H), 6.18 (s, 1H), 5.74 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.97, 159.45, 153.29, 139.93, 129.47, 126.64, 124.40, 124.04, 121.46, 121.20, 116.21, 113.92, 100.87, 70.86, 53.78, 53.66.

HRMS: (ESI-TOF) calculated for $C_{16}H_{16}NO_3$ ($[M+H]^+$): 270.1125, found: 270.1132.



Prepared according to the general procedure (100 °C, 30 mol% PPh_3, complete conversion by LCMS after 1h), the title compound was isolated as a colorless oil (Run #1: 113 mg, 81%, Run #2: 114 mg, 82%).

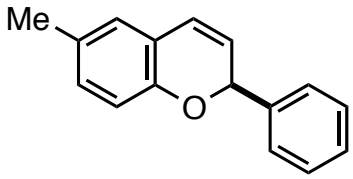
IR (neat, cm^{-1}): 3056, 1606, 1485, 1334.

^1H NMR (500 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.15 (td, *J* = 7.9, 1.2 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 9.8 Hz, 1H), 6.03 (s, 1H), 5.82 (dd, *J* = 9.8, 3.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.41, 148.81, 148.07 (q, *J* = 34.8 Hz), 139.42, 136.06, 130.18, 127.09, 125.63, 122.71, 122.07, 121.54 (q, *J* = 274.1 Hz), 121.12, 120.59 (q, *J* = 2.6 Hz), 116.31, 73.97.

^{19}F NMR (282 MHz, $CDCl_3$): δ -68.32.

HRMS: (ESI-TOF) calculated for $C_{15}H_{11}F_3NO$ ($[M+H]^+$): 278.0787, found: 278.0793.



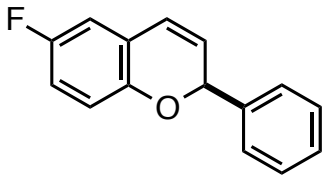
Prepared according to the general procedure (r.t., 10 mol% PPh_3, >65% conversion (estimated) by LCMS after 1h). The reaction was allowed to stir overnight before workup (at 24h the reaction shows >99% conv. by LCMS)), the title compound was isolated as a colorless oil (Run #1: 101 mg, 91%, Run #2: 103 mg, 93%).

IR (neat, cm^{-1}): 3029, 2918, 1488, 1210.

^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.30 (m, 3H), 6.92 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.83 (s, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.50 (dd, *J* = 9.8, 1.3 Hz, 1H), 5.88 (s, 1H), 5.80 (dd, *J* = 9.8, 3.4 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.03, 140.98, 130.51, 130.00, 128.78, 128.45, 127.19, 127.16, 125.09, 124.25, 121.23, 115.83, 77.18, 20.69.

HRMS: (ESI-TOF) calculated for $C_{16}H_{15}O$ ($[M+H]^+$): 223.1117, found: 223.1109.



Prepared according to the general procedure (r.t., 10 mol% PPh_3, >99% conversion by LCMS after 24h), the title compound was isolated as a colorless oil (Run #1: 101 mg, 90%, Run #2: 107 mg, 95%).

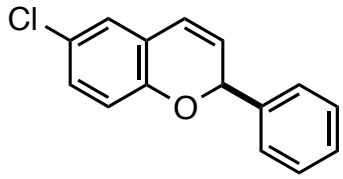
IR (neat, cm^{-1}): 3056, 2908, 1441, 1203.

^1H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.32 (m, 3H), 6.80 (td, *J* = 8.5, 3.0 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.50 (dd, *J* = 10.8, 3.0 Hz, 1H), 5.92 – 5.84 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.45 (d, *J* = 238.3 Hz), 149.04 (d, *J* = 2.2 Hz), 140.36, 128.84, 128.67, 127.20, 126.46, 123.65, 122.40 (d, *J* = 8.3 Hz), 116.97 (d, *J* = 8.0 Hz), 115.56 (d, *J* = 23.2 Hz), 112.87 (d, *J* = 23.8 Hz), 77.24.

^{19}F NMR (282 MHz, $CDCl_3$): δ -123.66.

HRMS: (ESI-TOF) calculated for $C_{15}H_{12}FO$ ($[M+H]^+$): 227.0867, found: 227.0873.



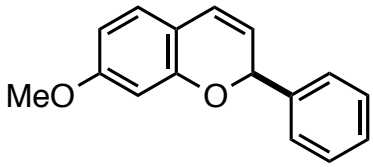
Prepared according to the general procedure (r.t., 10 mol% PPh_3, >80% conversion by LCMS (estimated) after 24h), the title compound was isolated as a colorless oil (Run #1: 94 mg, 78%, Run #2: 99 mg, 82%).

IR (neat, cm^{-1}): 3046, 1473, 1193, 1025.

^1H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 6.9 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.05 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.49 (d, *J* = 9.8 Hz, 1H), 5.91 (s, 1H), 5.86 (dd, *J* = 9.8, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.70, 140.28, 129.14, 128.88, 128.74, 127.19, 126.26, 126.17, 125.93, 123.25, 122.71, 117.44. One peak is obscured due to overlap.

HRMS: (ESI-TOF) calculated for $C_{15}H_{12}ClO$ ($[M+H]^+$): 243.0571, found: 243.0566.



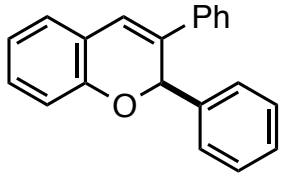
Prepared according to the general procedure (r.t., 10 mol% PPh_3, ~90% conversion by LCMS (estimated) after 16h), the title compound was isolated as a yellow oil (Run #1: 90 mg, 75%, Run #2: 90 mg, 75%).

IR (neat, cm^{-1}): 3030, 1611, 1503, 1270.

^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.30 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.50 (dd, *J* = 9.7, 1.1 Hz, 1H), 6.43 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.39 (s, 1H), 5.89 (s, 1H), 5.67 (dd, *J* = 9.8, 3.3 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.97, 154.46, 141.00, 128.80, 128.51, 127.40, 127.20, 123.77, 121.99, 114.74, 107.14, 101.89, 77.44, 55.46.

HRMS: (ESI-TOF) calculated for $C_{16}H_{15}O_2$ ($[M+H]^+$): 239.1067, found: 239.1064.



Prepared according to the general procedure (100 °C, 30 mol% PPh_3, reaction stagnates by LCMS after 3h), the title compound was isolated as a colorless oil (48 mg, 34%). (After column

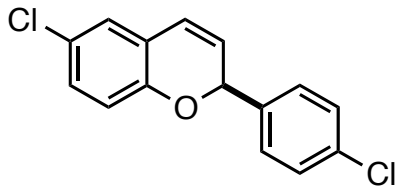
chromatography, the title compound was further purified by prep. HPLC 50:50 MeCN:H_2O to 100:0 MeCN:H_2O to remove unidentified impurities.) Note: Reactions conducted below 100 °C failed to provide significant amounts of product by LCMS. Reaction was conducted a single time.

IR (neat, cm^{-1}): 3058, 1596, 1454, 1208.

^1H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.44 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.22 – 7.15 (m, 2H), 7.12 (td, *J* = 7.7, 1.2 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.51, 138.57, 137.30, 133.13, 129.55, 128.82, 128.73, 128.71, 128.15, 128.04, 127.03, 125.55, 123.00, 121.57, 121.13, 116.59, 77.80.

HRMS: (ESI-TOF) calculated for $C_{21}H_{17}O$ ($[M+H]^+$): 285.1274, found: 285.1271.



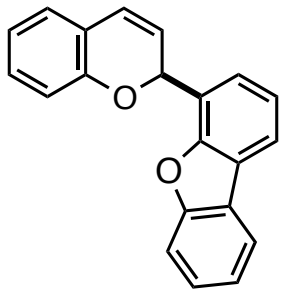
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 2h), the title compound was isolated as a yellow oil (Run #1: 111 mg, 80%, Run #2: 117 mg, 85%).

IR (neat, cm^{-1}): 3050, 2827, 1477, 1197.

^1H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 4H), 7.09 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 5.91 (s, 1H), 5.86 (dd, *J* = 9.8, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.42, 138.68, 134.58, 129.30, 129.04, 128.61, 126.35, 126.15, 125.58, 123.64, 122.59, 117.48, 76.52.

HRMS: (ESI-TOF) calculated for $C_{15}H_{11}Cl_2O$ ($[M-H]^+$): 275.0030, found: 275.0029.



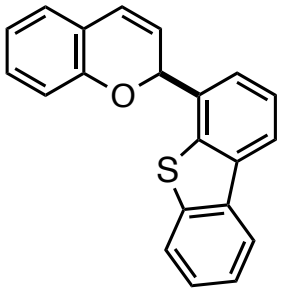
Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 2h), the title compound was isolated as a white solid (Run #1: 131 mg, 88%, Run #2: 135 mg, 90%).

IR (neat, cm^{-1}): 3040, 2903, 1603, 1453.

^1H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 24.1, 7.6 Hz, 2H), 7.63 (t, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.65 (d, *J* = 9.9 Hz, 1H), 6.03 (dd, *J* = 9.8, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.28, 153.34, 153.00, 129.64, 127.41, 126.83, 125.52, 124.84, 124.65, 124.41, 124.25, 123.93, 123.11, 123.00, 121.47, 121.45, 120.85, 120.70, 116.20, 112.00, 71.90.

HRMS: (ESI-TOF) calculated for $C_{21}H_{15}O_2$ ($[M+H]^+$): 299.1067, found: 299.1073.



Prepared according to the general procedure (40 °C, 10 mol% PPh_3, complete conversion by LCMS after 30 min), the title compound was isolated as a colorless solid (Run #1: 138 mg, 88%, Run #2: 142 mg, 90%).

IR (neat, cm^{-1}): 3057, 2873, 1604, 1483.

^1H NMR (500 MHz, $CDCl_3$): δ 8.22 – 8.10 (m, 2H), 7.93 – 7.81 (m, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.14 (td, *J* = 8.1, 1.1 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 9.8, 1.7 Hz, 1H), 6.33 – 6.24 (m, 1H), 5.90 (dd, *J* = 9.8, 3.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.39, 139.87, 137.87, 136.73, 135.43, 134.94, 129.73, 127.02, 126.92, 125.52, 124.82, 124.53, 123.39, 122.84, 121.79, 121.77, 121.69, 121.50, 116.22, 76.76. One peak is obscured due to overlap.

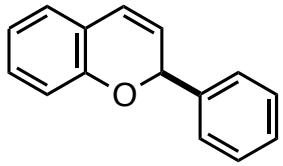
HRMS: (ESI-TOF) calculated for $C_{21}H_{15}OS$ ($[M+H]^+$): 315.0838, found: 315.0833.

III. Procedure for gram scale synthesis of 2-phenyl-2*H*-1-benzopyran

A 25-mL RBF equipped with a PTFE-coated stir-bar was brought into a N_2 filled glovebox, charged with $Ni(cod)_2$ (137 mg, 0.50 mmol, 5 mol%) and PPh_3 (131 mg, 0.50 mmol). 1,4-dioxane (6 mL) was added via micropipette and the resulting orange suspension stirred until mostly homogenous (15 min, dark blood red solution was formed). The flask was tightly sealed with a rubber septum and further sealed with electrical tape. It was removed from the glovebox and placed on an N_2 line.

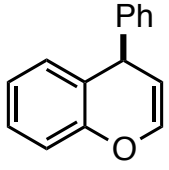
2-ethoxy-2*H*-chromene (10 mmol, 1.76 g) was transferred to a N_2-flushed 100 mL pear-shaped Schlenk flask and degassed (15 min, N_2 sparge, with stirring). $PhB(OH)_2$ (20 mmol, 2.43 g) was quickly added and the flask subjected to three evac/purge cycles with N_2. The mixture was dissolved (46 ml 1,4-dioxane, 4 ml *t*-AmOH, 0.2M with respect to 2-ethoxy-2*H*-chromene) and stirred for 30 secs. The blood red catalyst mixture was added via syringe (catalyst flask was rinsed with an additional 2 mL of 1,4-dioxane to ensure complete transfer) and the resulting mixture placed into a preheated oil bath (40 °C). After 14 h the reaction appears to stagnate (no further conversion of SM is observed by LCMS). The reaction mixture is directly concentrated and subjected to column chromatography (100 g silica, 0->20% CH_2Cl_2/hexanes) to give a mixed fraction containing 4-phenyl-4*H*-1-benzopyran (1,4 adduct) and 2-phenyl-2*H*-1-benzopyran (1,2 adduct) (250 mg, 3:1 ratio by ^{1}H NMR) followed by a clean fraction containing the desired product (1,2 adduct) (1.47 g, >20:1 rr) (overall yield of 1.72 g, 8:1 rr, 85%).
*Note that the rr resulting from this scaled-up reaction is lower than that with the 0.5 mmol reactions as a result of the more concentrated reactions conditions (0.2M rather than 0.02M).

1,2-adduct:



Matches previously recorded information. Labrosse, J. R.; Lhoste, P.; Sinou, D. *Synthetic Communications,* **2002,** *32,* 3667.

1,4-adduct:

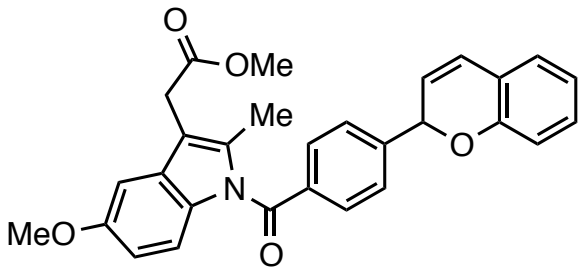


Matches previously recoded information. Hall, S. S.; Farahat, S. E. *J. Heterocyclic Chem.* **1987,** *24,* 1205.

IV. Procedure for the late stage addition of aryl boronic acids to chromene acetals

A 2-dram vial equipped with a PTFE-coated stir-bar and PTFE-tape-lined screw-thread was brought into a N_2 filled glovebox, charged with $Ni(cod)_2$ (2.75 mg, 0.01 mmol, 10 mol%) and PPh_3 (7.8 mg, 0.05 mmol, 10 mol% or 30 mol%). 1,4-dioxane (200 μL) was added via micropipette and the resulting orange suspension stirred until complete dissolution (15 min, dark blood red solution was formed). This solution was then added via micropipette to a solution (previously prepared in a 20 mL screw cap test tube) of the corresponding boronic acid (0.20 mmol, 2 equiv) and 2-ethoxy-2*H*-chromene (17 mg, 0.10 mmol) in dioxane/*t*-AmOH (10:1, 5 mL total, 0.02M with respect to 2-ethoxy-2*H*-chromene). The tube was then sealed with a teflon lined screw cap, and further wrapped with electrical tape. The tube was then removed from the glovebox and immediately placed into a preheated oil bath (100 °C) and aged until LCMS indicated the reaction has stalled or reached complete conversion.

After this time, the reaction mixture was concentrated and the crude subjected to flash chromatography.



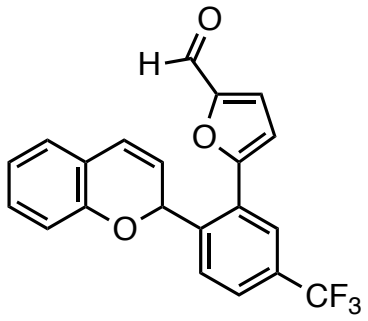
Prepared according to the general procedure (the reaction is observed to stall after 3 h by LCMS), the title compound was isolated as a pale yellow oil (12 mg, 26%). (After column chromatography, the title compound was further purified by prep. HPLC 50:50 MeCN:H_2O to 100:0 MeCN:H_2O to remove protodeborylated material.)

IR (neat, cm^{-1}): 2994, 1736, 1681, 1478.

^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.15 (td, *J* = 7.9, 1.5 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.57 (dd, *J* = 9.8, 1.3 Hz, 1H), 6.01 (s, 1H), 5.82 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.48, 169.08, 155.95, 152.89, 145.80, 136.07, 135.33, 130.91, 130.59, 130.18, 129.77, 127.07, 126.83, 124.59, 124.05, 121.61, 121.19, 116.04, 115.12, 112.28, 111.57, 101.13, 76.38, 55.75, 52.23, 30.21, 13.46.

HRMS: (ESI-TOF) calculated for $C_{29}H_{25}NO_5$ ($[M+H]^+$): 468.1805, found: 468.1801.



Prepared according to the general procedure (after 30 min, the reaction appears complete by LCMS), the title compound was isolated as a thick yellow oil (21 mg, 56%).

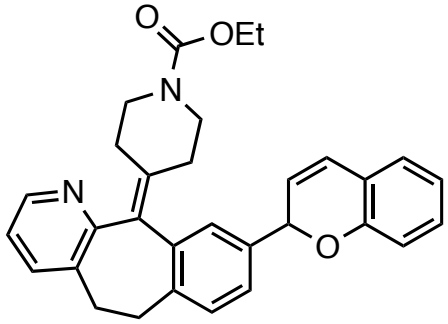
IR (neat, cm^{-1}): 3060, 2833, 1675, 1485.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (s, 1H), 8.03 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 3.7 Hz, 1H), 7.14 (td, *J* = 7.9, 1.5 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.65 (dd, *J* = 9.8, 1.5 Hz, 1H), 6.33 – 6.26 (m, 1H), 5.75 (dd, *J* = 9.8, 3.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.80, 156.10, 153.04, 152.59, 141.36, 131.11 (q, *J* = 33.0 Hz), 130.02, 129.75, 128.77, 127.03, 126.56121 .13, 116.12, 113.18, 73.27.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.79.

HRMS: (ESI-TOF) calculated for $C_{21}H_{13}F_3O_3$ ($[M+H]^+$): 371.0890, found: 371.0899.



Prepared according to the general procedure (after 10 min, the reaction appears complete by LCMS), the title compound was isolated as a white foam (38 mg, 79%).

IR (neat, cm^{-1}): 3045, 2907,1691, 1205.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 4.3 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.30 - 7.23 (m, 3H), 7.22 - 7.17 (m, 1H), 7.13 - 7.06 (m, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.86 (s, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.81 (s, 2H), 3.46 - 3.29 (m, 2H), 3.15 - 3.05 (m, 2H), 2.89 - 2.79 (m, 2H), 2.47 (s, 1H), 2.37 (s, 2H), 2.32

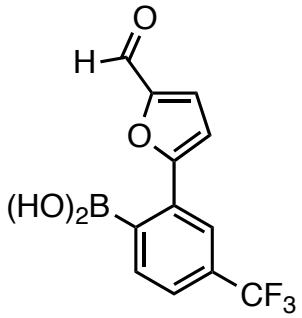
(s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 161.86, 155.54, 153.15, 146.64, 139.97, 137.48, 137.43, 137.03, 134.98, 133.65, 129.78, 129.66, 129.51, 127.93, 127.87, 126.66, 124.94, 124.87, 124.80, 124.75, 124.06, 122.21, 121.25, 121.22, 115.96, 61.35, 44.91, 31.94, 31.69, 31.63, 14.74.

HRMS: (ESI-TOF) calculated for $C_{31}H_{31}N_2O_3$ ($[M+H]^+$): 479.2329, found: 479.2341.

V. Procedure for preparation of complex aryl boronic acids

Procedures adapted from: Molander, G. A.; Trice, S. L. J.; Dreher, S. D. *J. Am. Chem. Soc.* 2010, *132,* 17701.



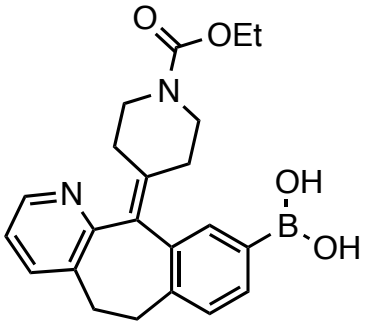
A 100 mL pear-shaped schlenk flask fitted with a magnetic stirbar was sequentially charged with 5-(2-Chloro-5-trifluoromethylphenyl)furfural (1.37 g, 5.00 mmol), 2-amino-biphenyl Pd-XPhos precatalyst (78.5 mg, 0.10 mmol, 2 mol%), XPhos (95.0 mg, 0.20 mmol, 4 mol%), $B_2(OH)_2$ (672 mg, 7.50 mmol, 1.5 eq), KOAc (1.47 g, 15.0 mmol, 3.0 eq), NaO*t*Bu (9.0 mg, 0.10 mmol, 2 mol%) and the vessel sealed with rubber septum. The vessel was subject to 3 evac/purge cycles with N_2 and then charged with 50 mL of EtOH (previously degassed with sonication under a N_2 sparge, 20 mins). The resulting mixture was placed into a pre heated oil bath (80 °C) and aged with vigorous stirring. After 2.5 h LCMS analysis indicates the complete consumption of starting material ($[M\text{-}F]^-$= 256, negative ionization mode, APCI/ESI) with formation of product ($[M\text{-}H+HCO_2H]^-$=329, negative ionization mode, APCI/ESI) and production of two unidentified major side products ($[M]^-$ =331, and $[M]^-$=568). The reaction mixture is cooled to r.t. and filtered through a short pad of celite. The resulting mixture is taken up in 100 mL 1N HCl/EtOAc (1:1 v/v) and stirred for 5 min. The layers are separated, and the organic phase washed with brine. Combined aqueous phases were extracted (1x50 mL, EtOAc) and the resulting organic layers combined and dried (Na_2SO_4). After concentration under reduced pressure, the resulting orange foam is taken up in a minimal amount of MeCN and applied to a slurry packed column of C18 silica (50:50 MeCN:H_2O) and eluted (50:50 MeCN:H_2O) to give 4 bright yellow fractions (~50 mL each). The first two fractions are combined and concentrated slowly under reduced pressure. Once the MeCN is removed a yellow slurry results with small amount of orange oil (failure to remove this impurity prevents successful execution of the next step). The orange oil is decanted and the yellow slurry concentrated to give an amorphous soild that is contaminated with unidentified impurities (LCMS). The resulting solid is suspended in 2 mL of MTBE:hexanes (1:1 v/v) and stirred for 5 minutes. The bright yellow/orange suspension is allowed to settle and the solvent decanted. The process is repeated and the resulting fine yellow powder is washed once with hexanes and dried under high vacuum to give the desired product (350 mg, ~25% yield).

IR (neat, cm^{-1}): 3298, 1661, 1332, 1089.

^1H NMR (300 MHz, DMSO): δ 9.64 (s, 1H), 8.47 (s, 2H), 8.07 (s, 1H), 7.75 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.70 (s, 1H), 7.67 (d, *J* = 3.8 Hz, 1H), 7.24 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO): δ 178.12, 158.37, 152.20, 141.53, 133.58, 131.68, 129.43 (q, *J* = 32.1 Hz), 124.87, 124.22 (q, *J* = 272.2 Hz), 122.34, 110.53. (C-B carbon not observed).

HRMS: (ESI-TOF) calculated for $C_{12}H_9BF_3O_4$ ([M+H]$^+$): 285.0541, found: 285.0544.



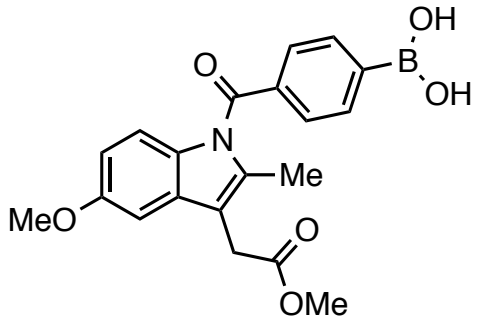
A 50 mL pear-shaped schlenk flask fitted with a magnetic stirbar was sequentially charged with loratadine (382 mg, 1.00 mmol), 2-amino-biphenyl Pd-XPhos precatalyst (19.6 mg, 0.025 mmol, 2.5 mol%), XPhos (23.8 mg, 0.50 mmol, 5 mol%), $B_2(OH)_2$ (268 mg, 3.00 mmol, 3.0 eq), KOAc (294 mg, 3.0 mmol, 3.0 eq), NaO*t*Bu (2.5 mg, 0.025 mmol, 2.5 mol%) and the vessel sealed with rubber septum. The vessel was subject to 3 evac/purge cycles with N_2 and then charged with 20 mL of EtOH (previously degassed with sonication under a N_2 sparge, 20 mins). The resulting mixture was placed into a pre heated oil bath (80 °C) and aged with vigorous stirring. After 3 h LCMS analysis indicates the complete consumption of starting material (observed [M+1] in positive mode APCI/ESI) with formation of product (observed [M+1] in positive mode APCI/ESI). The reaction mixture is cooled to r.t. and filtered through a short pad of celite. The resulting mixture is taken up in 50 mL 1N HCl/EtOAc (1:1 v/v) and stirred for 30 min. The layers are separated, and the aqueous phase washed (2x25 mL, EtOAc) and the combined organics discarded. The pH of the aqueous phase is adjusted (ph>11, addition of 10N NaOH) and the resulting slurry extracted (3x50 mL EtOAc). The combined organics were washed with brine, dried (Na_2SO_4), and concentrated to give a yellow solid (~85LCAP). The solid was dissolved in a minimal amount of CH_2Cl_2 and hexanes were slowly added with stirring until a fine white powder was observed. The powder was collected via vacuum filtration and washed with hexanes. The resulting white powder was dried for 3h under high vacuum to give the desired product as a mixture of boroxine and boronic acid (>95LCAP, 250 mg, 63%).

IR (neat, cm^{-1}): 3406, 2978, 1678, 1340.

^{1}H NMR (300 MHz, DMSO): δ 8.33 (d, *J* = 3.6 Hz, 1H), 8.00 (s, 2H), 7.65 – 7.52 (m, 3H), 7.19 (dd, *J* = 7.4, 4.8 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.67 – 3.56 (m, 2H), 3.36 – 3.27 (m, 2H), 3.17 (broad s, 2H), 2.88 – 2.73 (m, 2H), 2.35 – 2.25 (m, 2H), 2.25 – 2.10 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO): δ 157.72, 154.98, 146.68, 140.98, 137.86, 136.83, 135.97, 135.79, 135.25, 134.03, 131.96, 128.53, 122.77, 61.17, 44.97, 44.88, 31.81, 31.41, 30.78, 30.69, 15.11. (C-B carbon not observed).

HRMS: (ESI-TOF) calculated for $C_{22}H_{25}BN_2O_4$ ([M+H]$^+$): 393.1980, found: 393.1989.



A 50 mL pear-shaped schlenk flask fitted with a magnetic stirbar was sequentially charged with indomethacin methyl ester (1 g, 2.92 mmol), 2-amino-biphenyl Pd-XPhos precatalyst (22 mg, 0.020 mmol, 1.0 mol%), XPhos (27 mg, 0.050 mmol, 2 mol%), $B_2(OH)_2$ (392 mg, 4.38 mmol, 1.5 eq), KOAc (859 mg, 8.76 mmol, 3.0 eq), NaO*t*Bu (2.8 mg, 0.020 mmol, 1.0 mol%) and the vessel sealed with rubber septum. The vessel was subject to 3 evac/purge cycles with N_2 and then charged with 29 mL of EtOH (previously degassed with sonication under a N_2 sparge, 20 mins). The resulting mixture was placed into a pre heated oil bath (80 °C) with vigorous stirring and aged for 3 h. After this time, LCMS analysis indicates the complete consumption of starting material (observed [M+1] in positive mode APCI/ESI) with formation of product (observed [M+1] in positive mode APCI/ESI). The reaction proceeds from yellow to green during this time period. The reaction mixture is cooled to r.t. and filtered through a short pad of celite. The resulting crude mixture is taken up in 200 mL 1N HCl/EtOAc (1:1 v/v) and stirred for 30 min. The layers are separated, and the aqueous phase extracted (1x50 mL, EtOAc). The combined organics were then washed with brine, and dried (Na_2SO_4). Concentration under reduced pressure gives a yellow foam, observed to contain both the desired material (Boronic acid) and an impurity resulting from dimerization of the aryl chloride (LCMS, obs. [M+1] in positive mode APCI/ESI). The solid was dissolved in ~50 mL of CH_2Cl_2 and hexanes were slowly added with stirring until a fine white powder was observed. The powder was collected via vacuum filtration and washed several times with hexanes. The resulting white powder was dried for 3h under high vacuum to give the desired product as a mixture of boroxine and boronic acid (>95LCAP, 354 mg, 32%).

IR (neat, cm^{-1}): 3412, 2954, 1736, 1662.

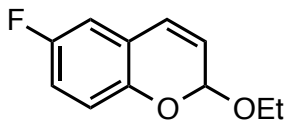
^{1}H NMR (500 MHz, DMSO): δ 8.40 (s, 2H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.78 (s, 2H), 3.75 (s, 3H), 3.62 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (126 MHz, DMSO): δ 171.12, 169.13, 155.45, 136.55, 135.49, 134.35, 130.44, 130.21, 127.99, 114.53, 112.48, 111.27, 101.44, 55.35, 51.82, 29.06, 13.14. (C-B carbon not observed).

HRMS: (ESI-TOF) calculated for $C_{20}H_{21}BNO_6$ ($[M+H]^+$): 382.1456, found: 3821453.

VI. Preparation of Acetals

Chromene acetals were prepared from their corresponding coumarins in direct analogy to previously reported methods: Moquist, P. N.; Kodama, T.; Schaus, S. E. *Angew. Chem., Int. Ed. Engl.* 2010, *49,* 7096.

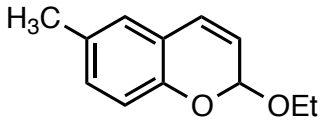


^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (dd, *J* = 6.7, 1.9 Hz, 2H), 6.85 (dt, *J* = 8.3, 1.8 Hz, 1H), 6.67 (d, *J* = 9.7 Hz, 1H), 5.93 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.66 (d, *J* = 3.8 Hz, 1H), 3.93 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.66 (dq, *J* = 9.7, 7.1 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.36, 156.46, 147.27 (d, *J* = 2.0 Hz), 125.91, 121.61 (d, *J* = 8.5 Hz), 117.55 (d, *J* = 8.1 Hz), 115.72 (d, *J* = 23.5 Hz), 113.01 (d, *J* = 23.7 Hz), 94.81, 63.82, 15.30.

^{19}F NMR (282 MHz, $CDCl_3$): δ -123.19.

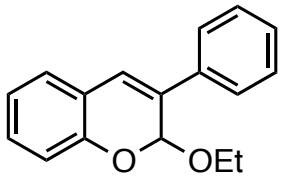
LRMS (APCI/ESI): calculated for C_9H_6FO ([M-OEt]$^+$): 149, found: 149.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, *J* = 7.7 Hz, 1H), 6.94 (s, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 9.6 Hz, 1H), 5.85 (dd, *J* = 9.6, 3.7 Hz, 1H), 5.66 (d, *J* = 3.7 Hz, 1H), 3.93 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.65 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.28 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.35, 130.80, 130.02, 127.54, 126.76, 120.63, 120.10, 116.39, 94.94, 63.56, 20.75, 15.43.

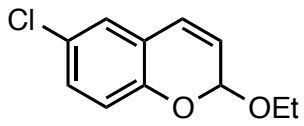
LRMS (APCI/ESI): calculated for $C_{10}H_9O$ ([M-OEt]$^+$): 145, found: 145.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.07 – 6.97 (m, 3H), 5.99 (s, 1H), 4.09 – 3.98 (m, 1H), 3.87 – 3.77 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 150.26, 136.78, 130.67, 129.27, 128.78, 127.96, 127.52, 125.57, 121.88, 121.79, 121.66, 116.48, 96.99, 63.77, 15.40.

LRMS (APCI/ESI): calculated for C_9H_6FO ([M-OEt]$^+$): 207, found: 207.

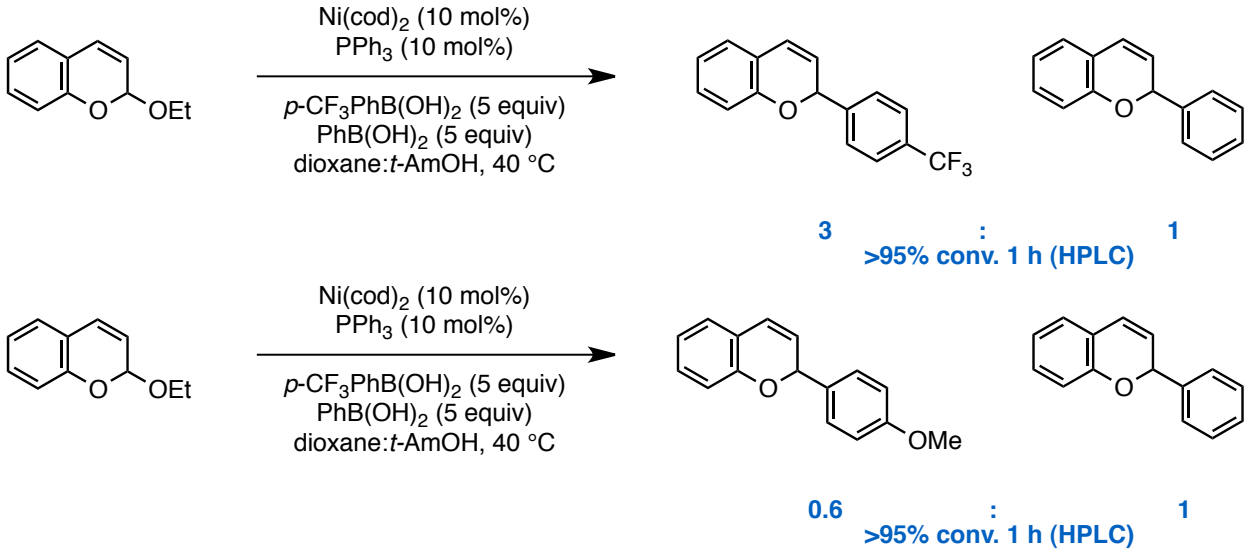


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.66 (d, *J* = 9.7 Hz, 1H), 5.91 (dd, *J* = 9.7, 3.7 Hz, 1H), 5.68 (d, *J* = 3.7 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.71 – 3.61 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): 150.05, 129.12, 126.67, 126.33, 125.73, 122.16, 121.30, 118.07, 95.01, 63.95, 15.38.

LRMS (APCI/ESI): calculated for C_9H_6ClO ([M-OEt]$^+$): 165, found: 165.

VII. Competition study

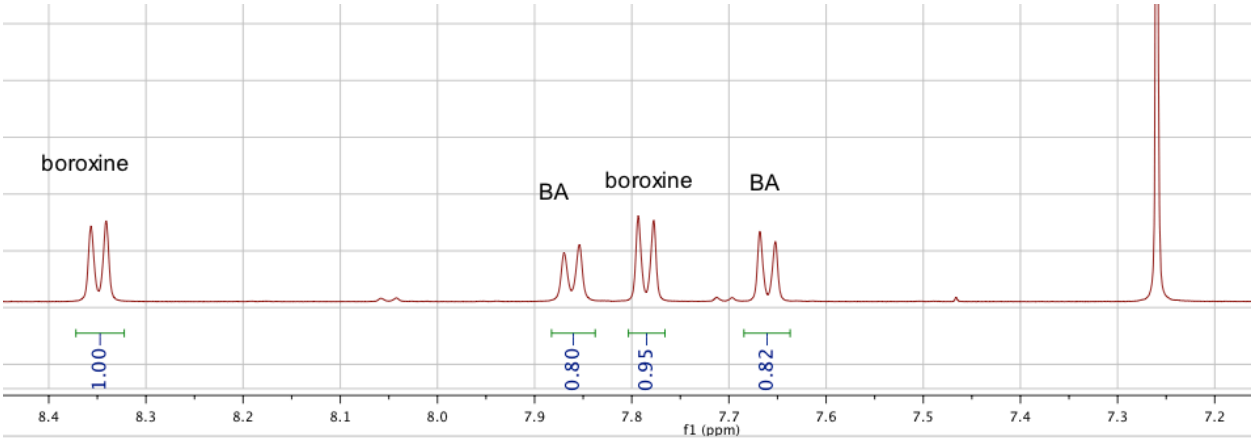


The competition reactions were run in a fashion identical to the general procedure for the arylation of chromene acetals with the follow exceptions:

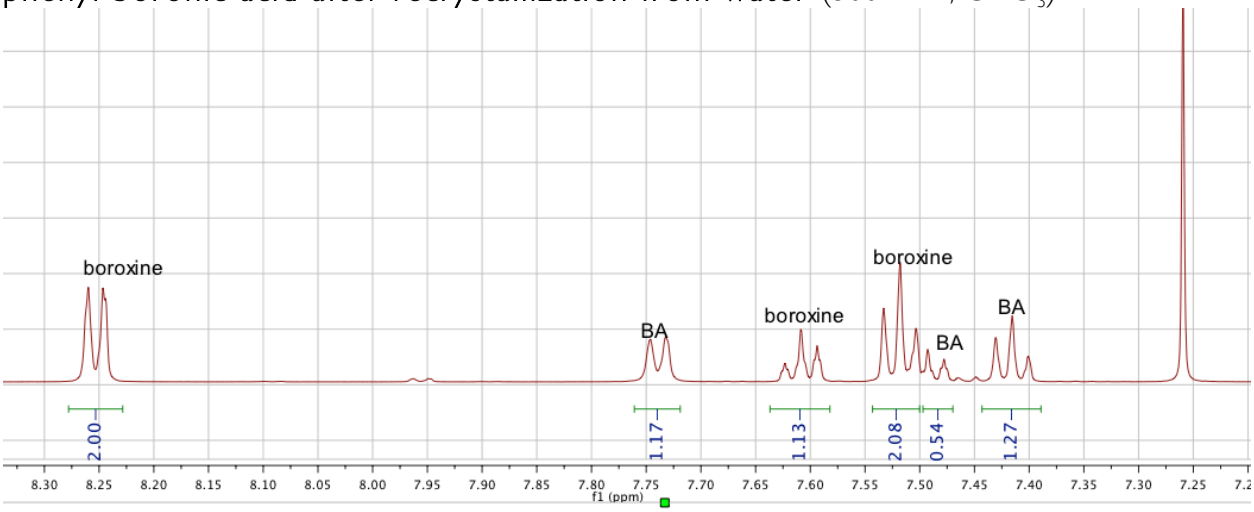
Boronic acids employed in the study were recrystallized from water prior to use ensure reproducible results from batch to batch. In line with previous knowledge, we have observed that commercial samples frequently contain varying amounts of boroxine and boronic acid.

The initial ratios of nucleophile were determined by removing a small aliquot from the reaction mixture prior to the addition of the catalyst solution. The aliquot was concentrated and then analyzed by ^{1}H NMR. The reaction progress was monitored by LCMS, and was determined to be complete when 2-ethoxy-2*H*-chromene could no longer be detected (<2LCAP). The reaction mixture was then concentrated under reduced pressure to the crude reaction mixture. This was then suspended in $CDCl_3$ and filtered through a 0.2 μm syringe filter and further diluted with $CDCl_3$. Analysis by ^{1}H NMR allowed the direct determination of the product ratios. Spectra of recrystallized boronic acids, initial ratios of boronic acids and product distributions are included below:

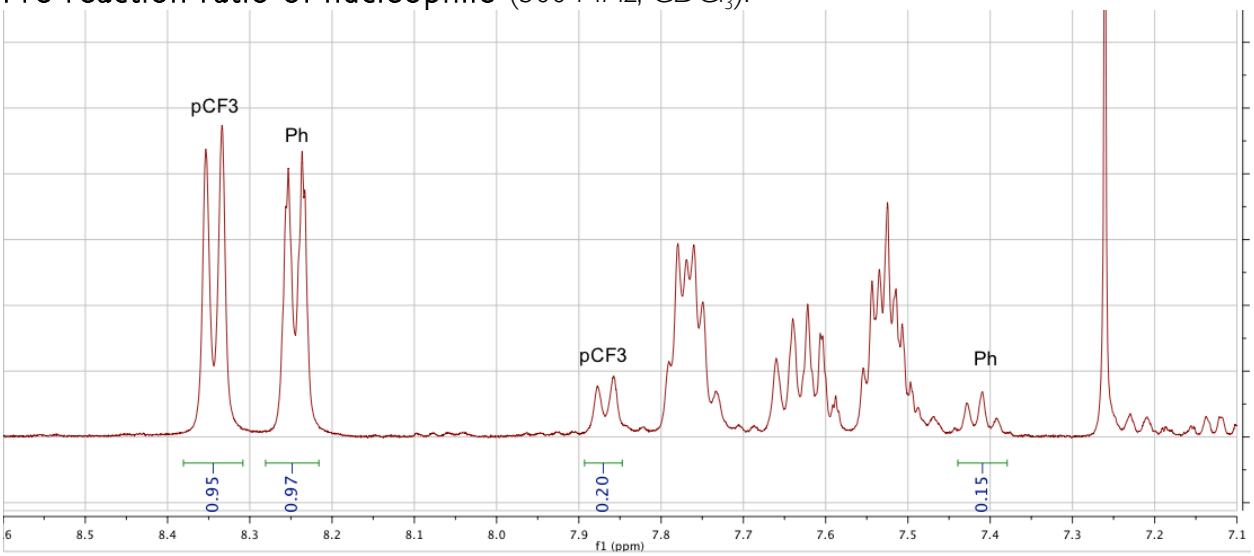
4-trifluoromethylphenyl boronic acid after recrystallization from water (500 MHz, $CDCl_3$):



phenyl boronic acid after recrystallization from water (500 MHz, $CDCl_3$):

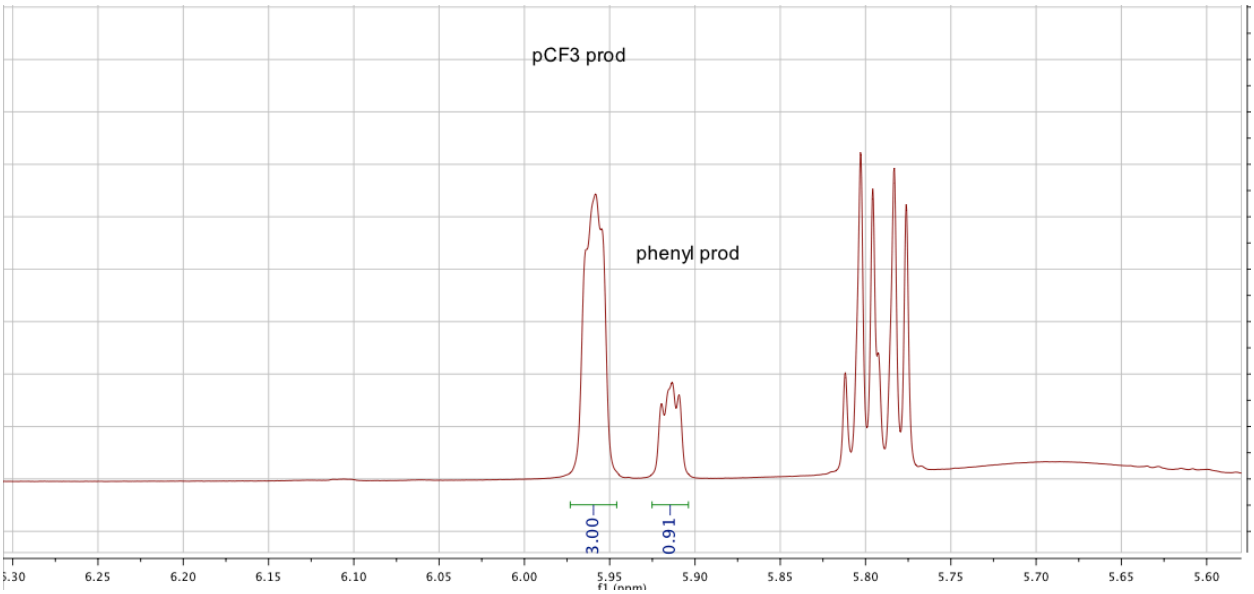


Pre-reaction ratio of nucleophile (500 MHz, $CDCl_3$):



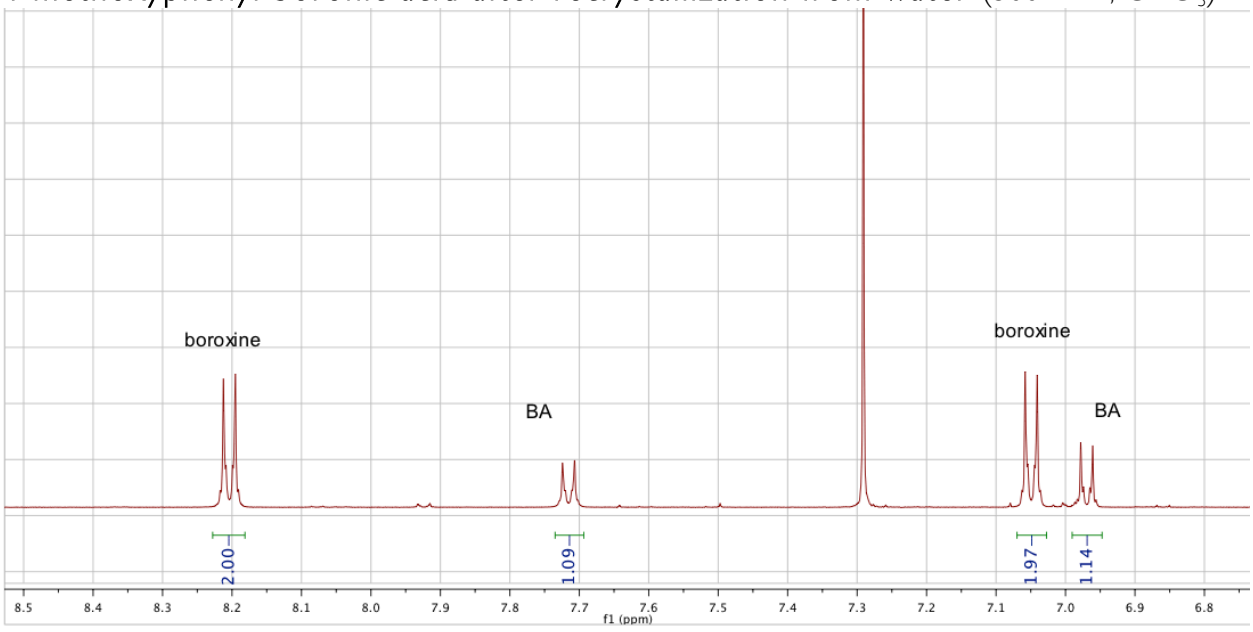
Ratio pCF_3 boroxine to Ph boroxine ~ 1:1
Ratio pCF_3 boronic acid to Ph boronic acid ~ 0.20:0.15

Post reaction Product ratio:

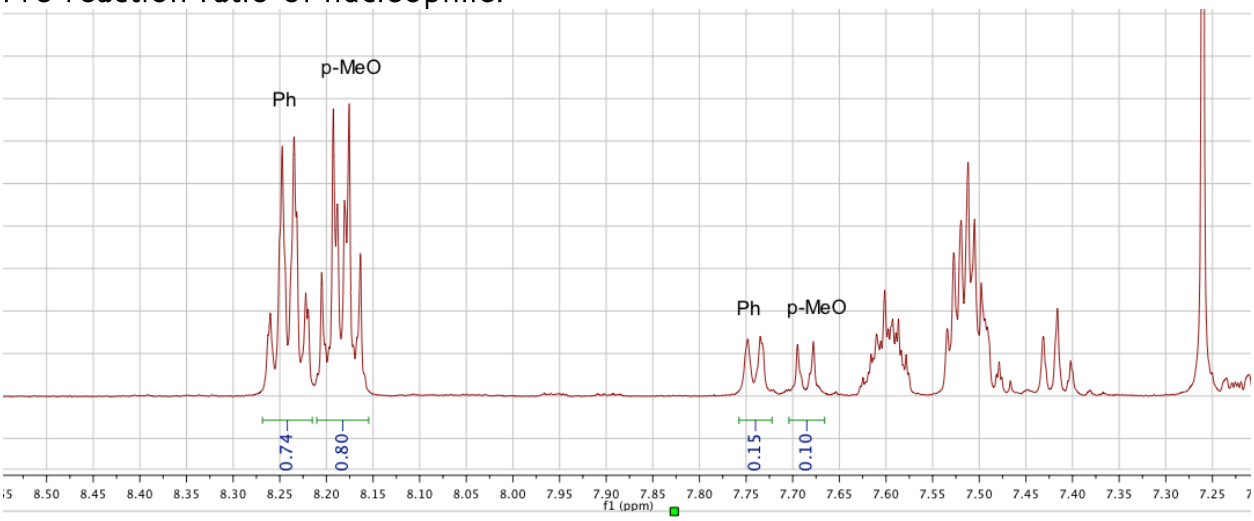


Ratio ~ 3.0:0.91 (p-CF_3 product:phenyl product)

4-methoxyphenyl boronic acid after recrystallization from water (500 MHz, $CDCl_3$):

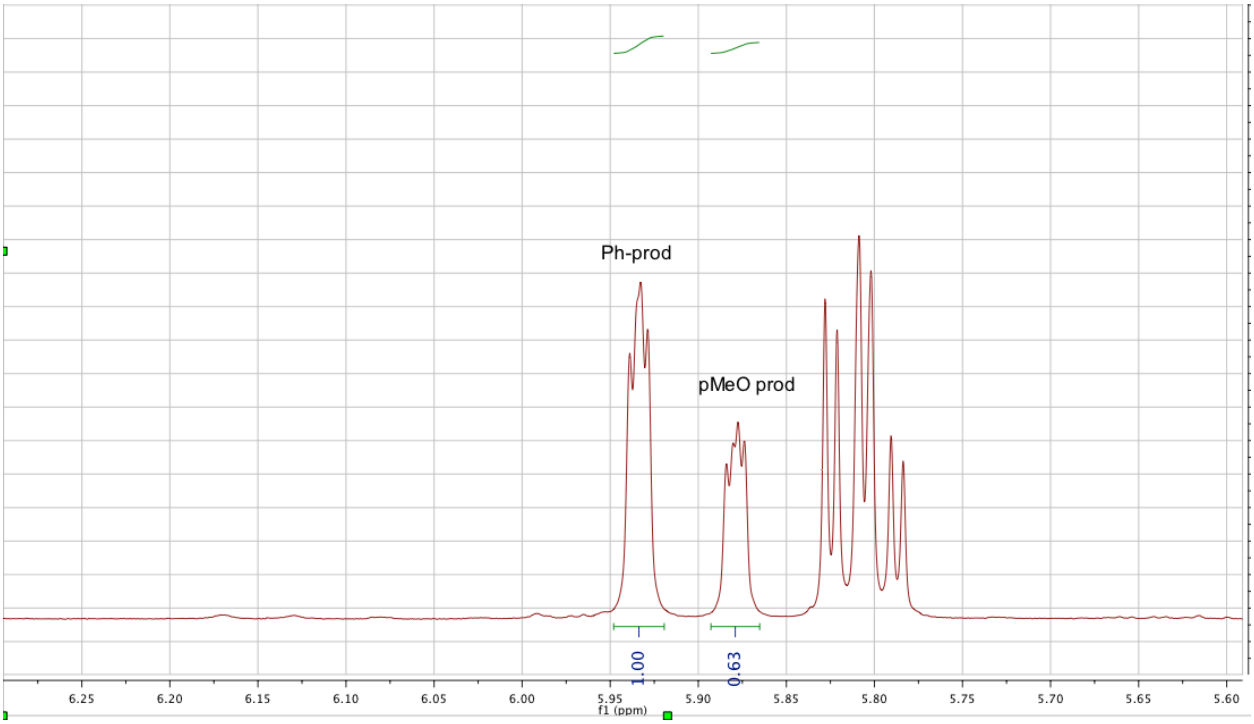


Pre-reaction ratio of nucleophile:



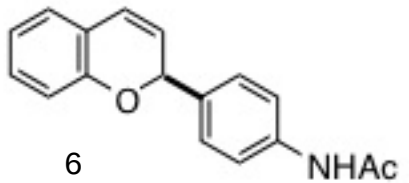
Ratio pMeO boroxine to Ph boroxine ~ 0.80:0.74
Ratio pMeO boronic acid to Ph boronic acid ~ 0.10:0.15

Post reaction Product ratio:



Ratio ~ 1.0:0.63 (p-CF_3 product:phenyl product)

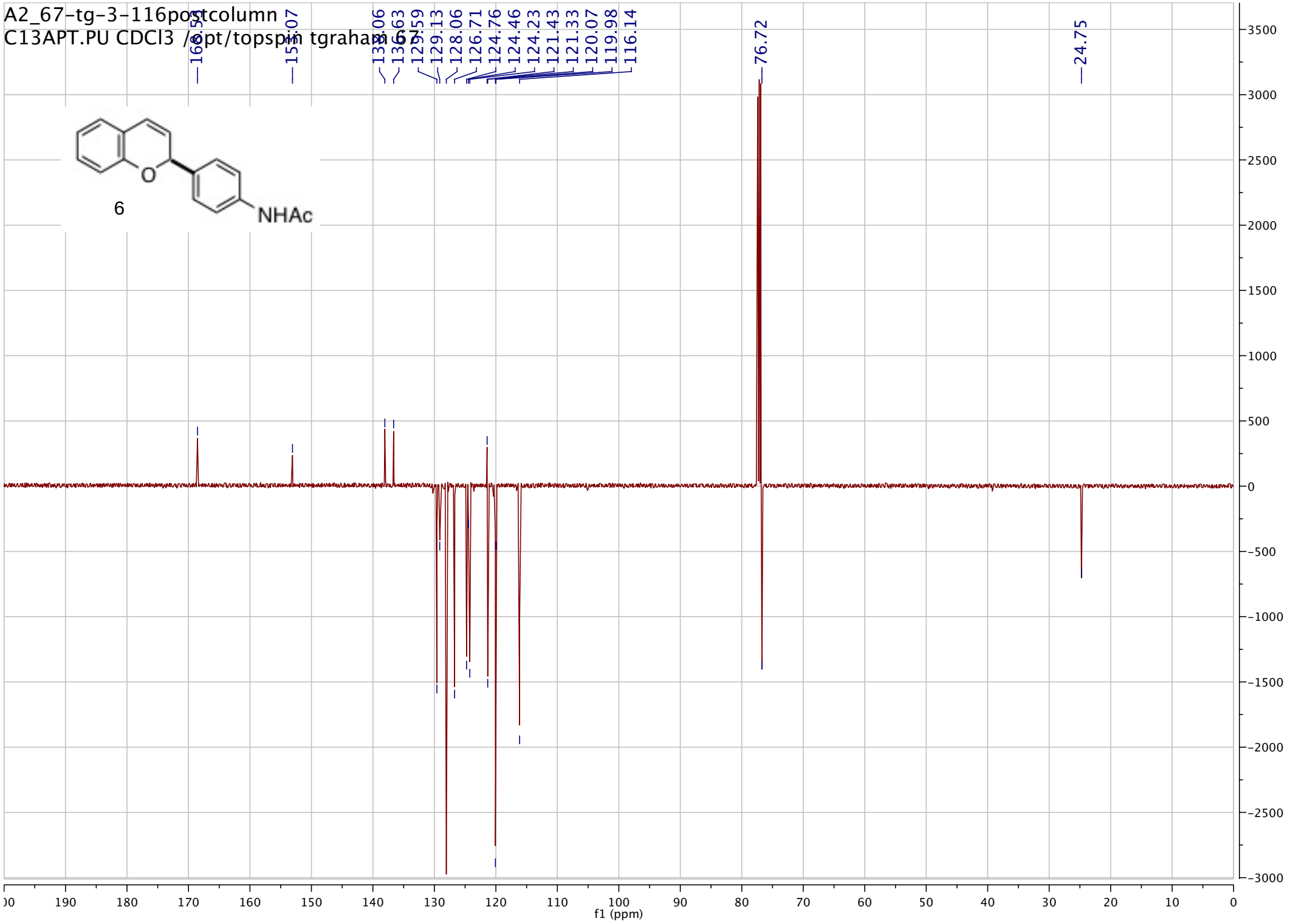
A2_67-tg-3-116postcolumn
PROTON.PU CDCl3 /opt/topspin tgraham 67



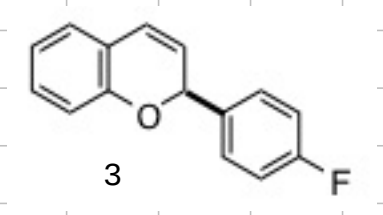
6

2.26 2.62 0.52 1.18 0.97 0.97 0.94 0.95 0.93 0.97 3.47

f1 (ppm)

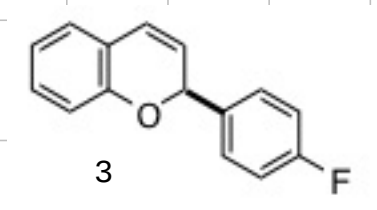

A2_67-tg-3-116postcolumn
C13APT.PU CDCl3 /opt/topspin tgraham 67
166.58
151.07
139.06
136.63
129.59
129.13
128.06
126.71
124.76
124.46
124.23
121.43
121.33
120.07
119.98
116.14
76.72
24.75
O
6
NHAc
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

A2_95-tg-3-108postcolumn
PROTON.PU CDCl3 /opt/topspin tgraham 95



3

A2_95-tg-3-108postcolumn
C13APT.PU CDCl3 /opt/topspin tgraham 95



3

152.99
129.71
126.77
124.64
124.42
121.45
121.34
116.16
76.50

C (d)
162.84

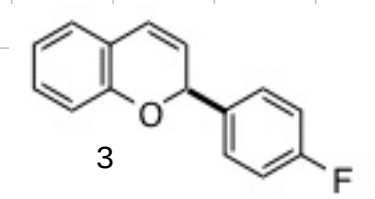
A (d)
136.65

B (d)
129.11

D (d)
115.68

f1 (ppm)

tg-3-108f19postcolumn
F19 OBSERVE
STANDARD PARAMETERS

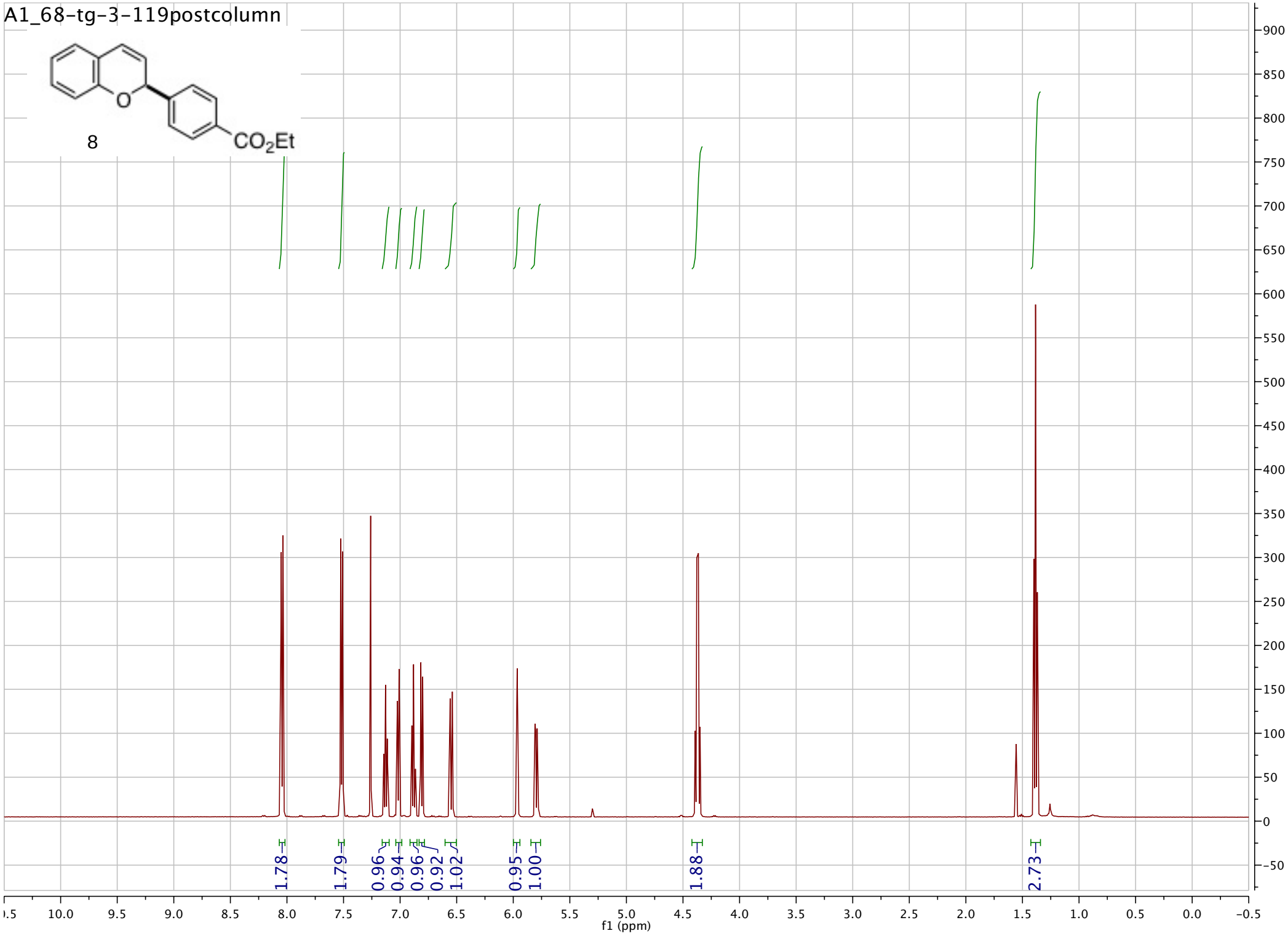


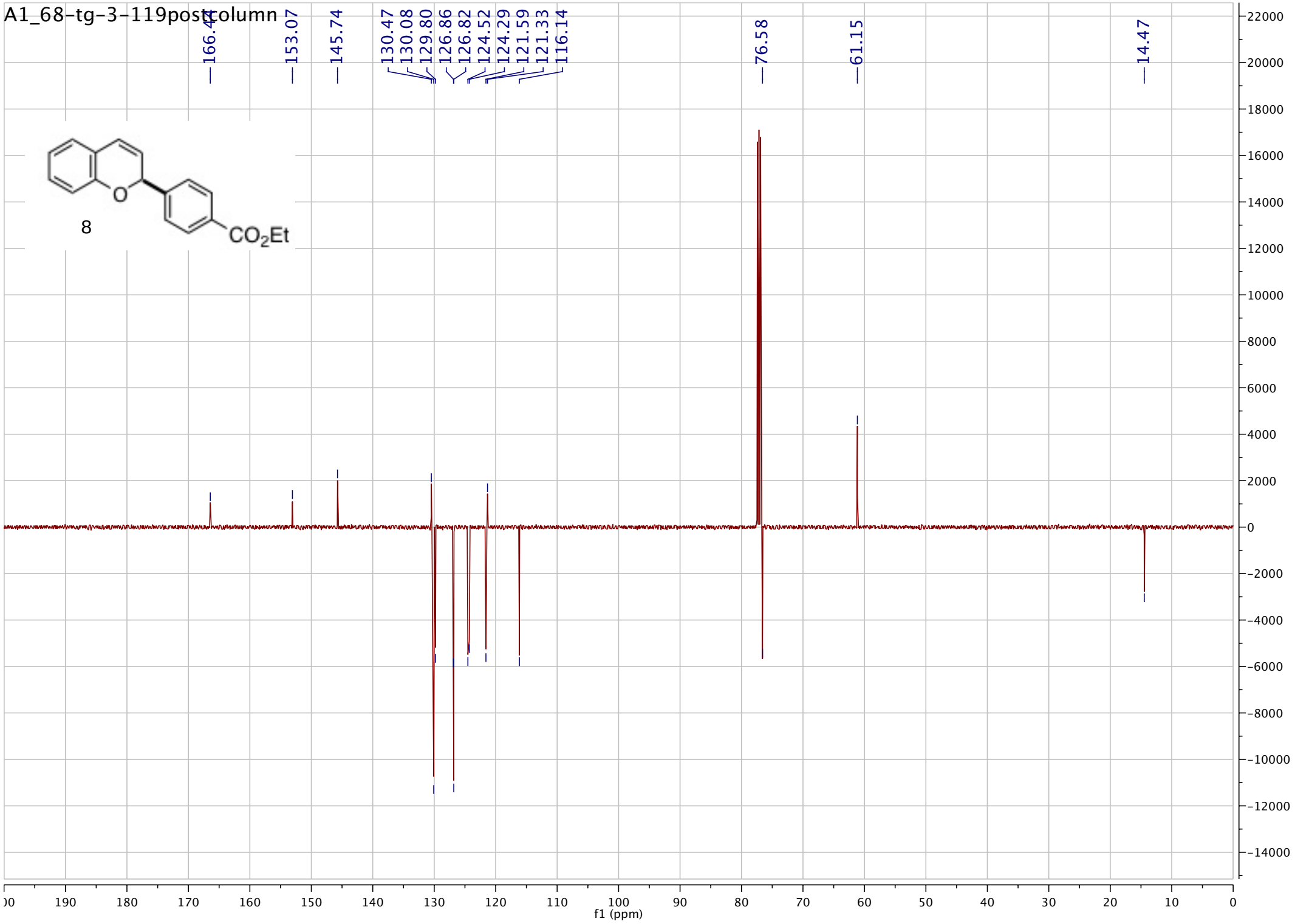
3

A (s)
-114.11

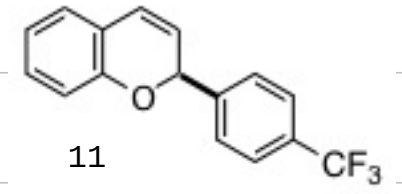
3500
3000
2500
2000
1500
1000
500
0

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

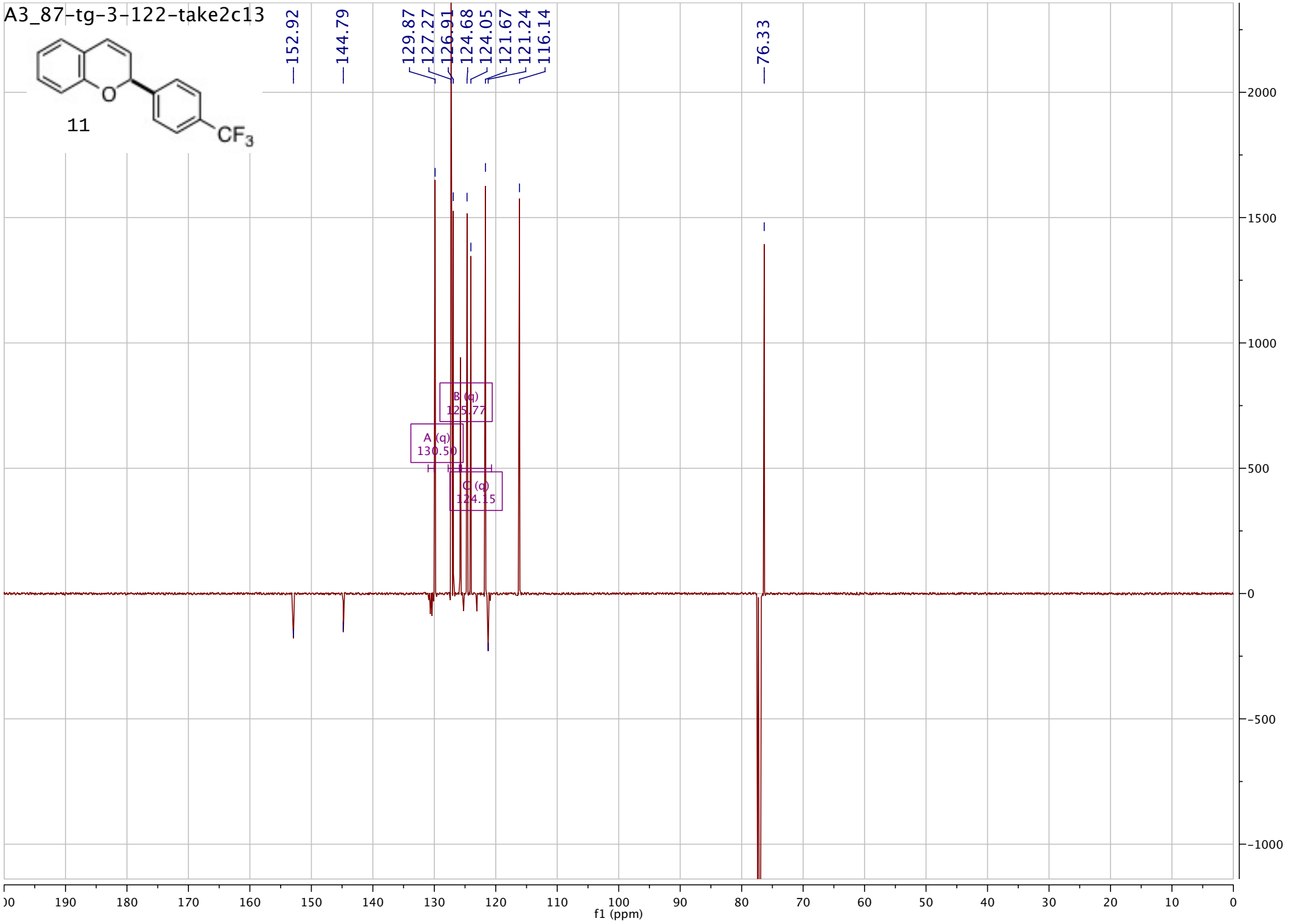

A1_68-tg-3-119postcolumn
O
8
CO2Et
1.78
1.79
0.96
0.94
0.96
0.92
1.02
0.95
1.00
1.88
2.73
f1 (ppm)

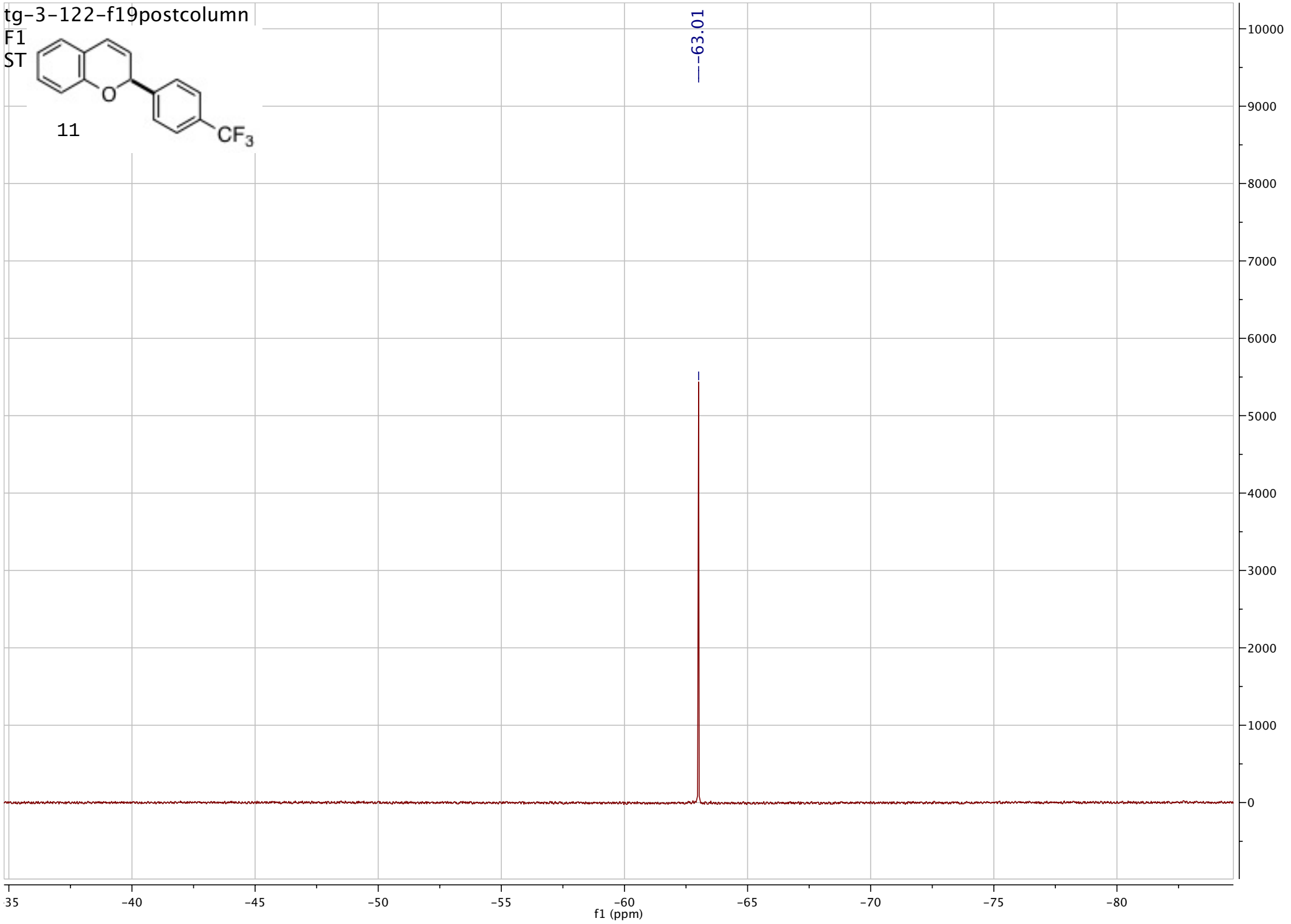

A1_68-tg-3-119postcolumn
166.47
153.07
145.74
130.47
130.08
129.80
126.86
126.82
124.52
124.29
121.59
121.33
116.14
76.58
61.15
14.47
O
8
CO2Et
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
-10000
-12000
-14000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

A1_70-tg-3-122postcolumn

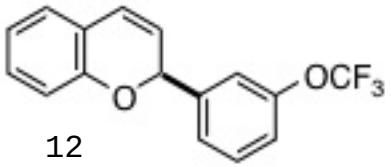


11


A3_87-tg-3-122-take2c13
11
CF3
152.92
144.79
129.87
127.27
126.91
124.68
124.05
121.67
121.24
116.14
76.33
B (q)
125.77
A (q)
130.50
C (q)
124.15
2000
1500
1000
500
0
-500
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

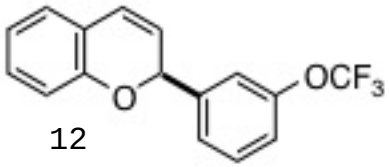

tg-3-122-f19postcolumn
F1
ST
11
O
CF3
-63.01
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
f1 (ppm)

A3_34-tg-3-102postcolumn



12

A3_34-tg-3-102postcolumn



12

152.91
143.25
130.19
129.82
126.87
125.36
124.71
124.11
121.63
121.26
120.76
119.70
116.16
76.24

A (q)
149.54

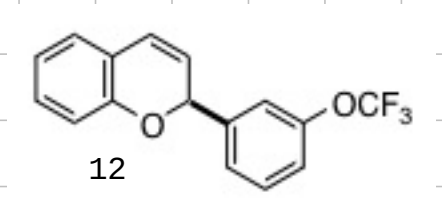
B (q)
120.54

600
500
400
300
200
100
0
-100
-200
-300
-400

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

tg-3-102postcolumnf19
F19 OBSERVE
STANDARD PARAMETERS



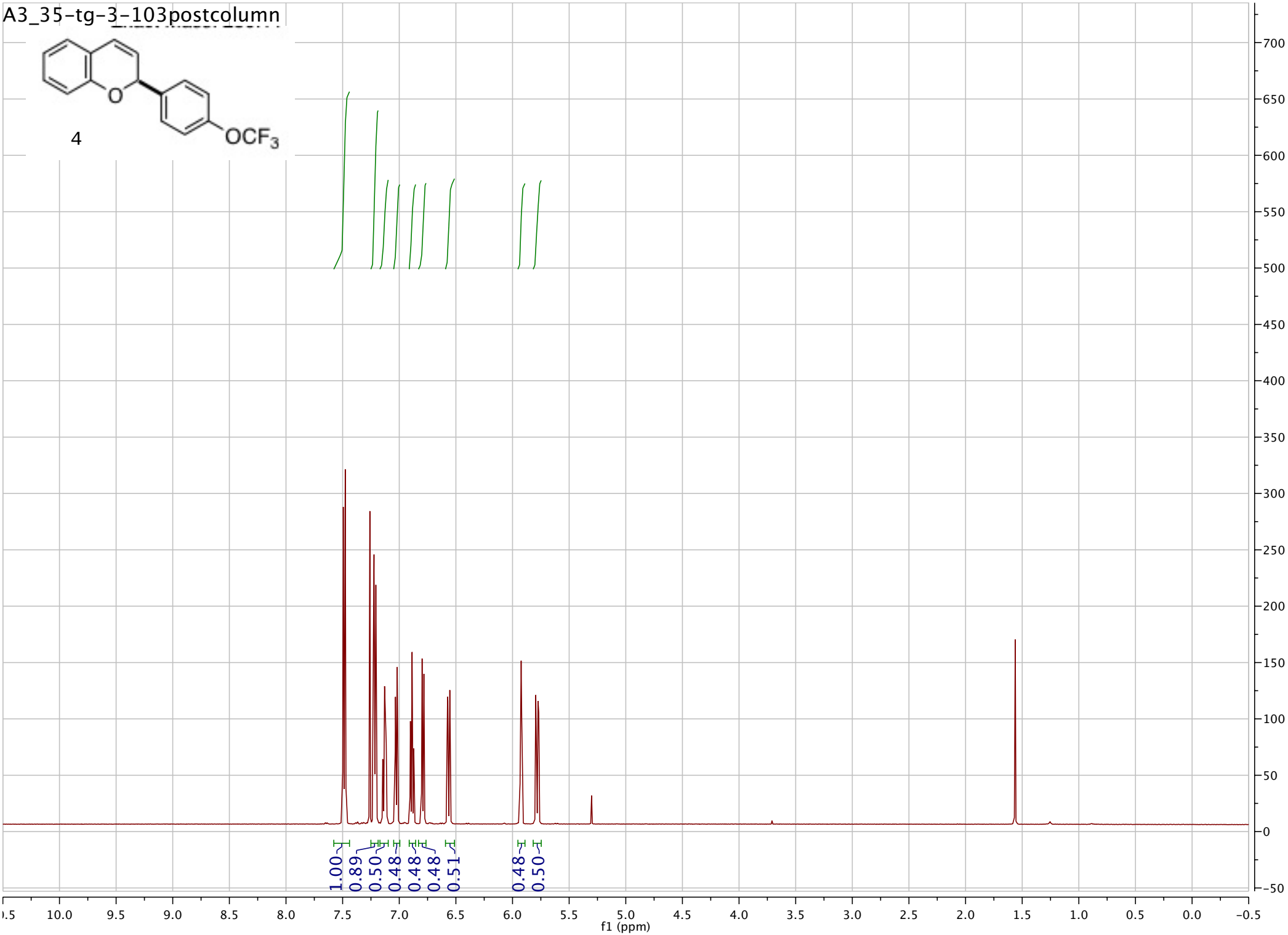
12

-58.17

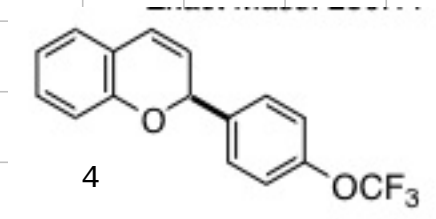
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

-44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94

f1 (ppm)


A3_35-tg-3-103postcolumn
O
4
OCF3
1.00
0.89
0.50
0.48
0.48
0.48
0.51
0.48
0.50
f1 (ppm)

A3_35-tg-3-103postcolumn



4

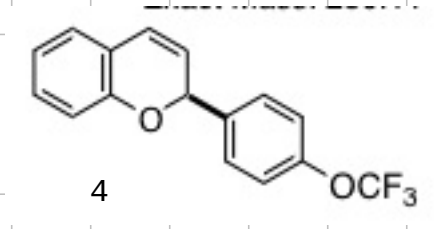
152.93
139.55
129.79
128.68
126.84
124.55
124.34
123.60
121.57
121.29
117.47
116.15
76.32

C (q)
149.21

A (q)
120.46

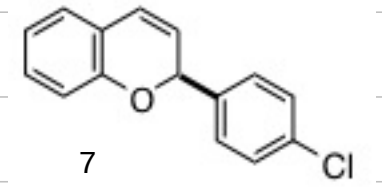
f1 (ppm)

tg-3-103postcolumnf19
F19 OBSERVE
STANDARD PARAMETERS



4

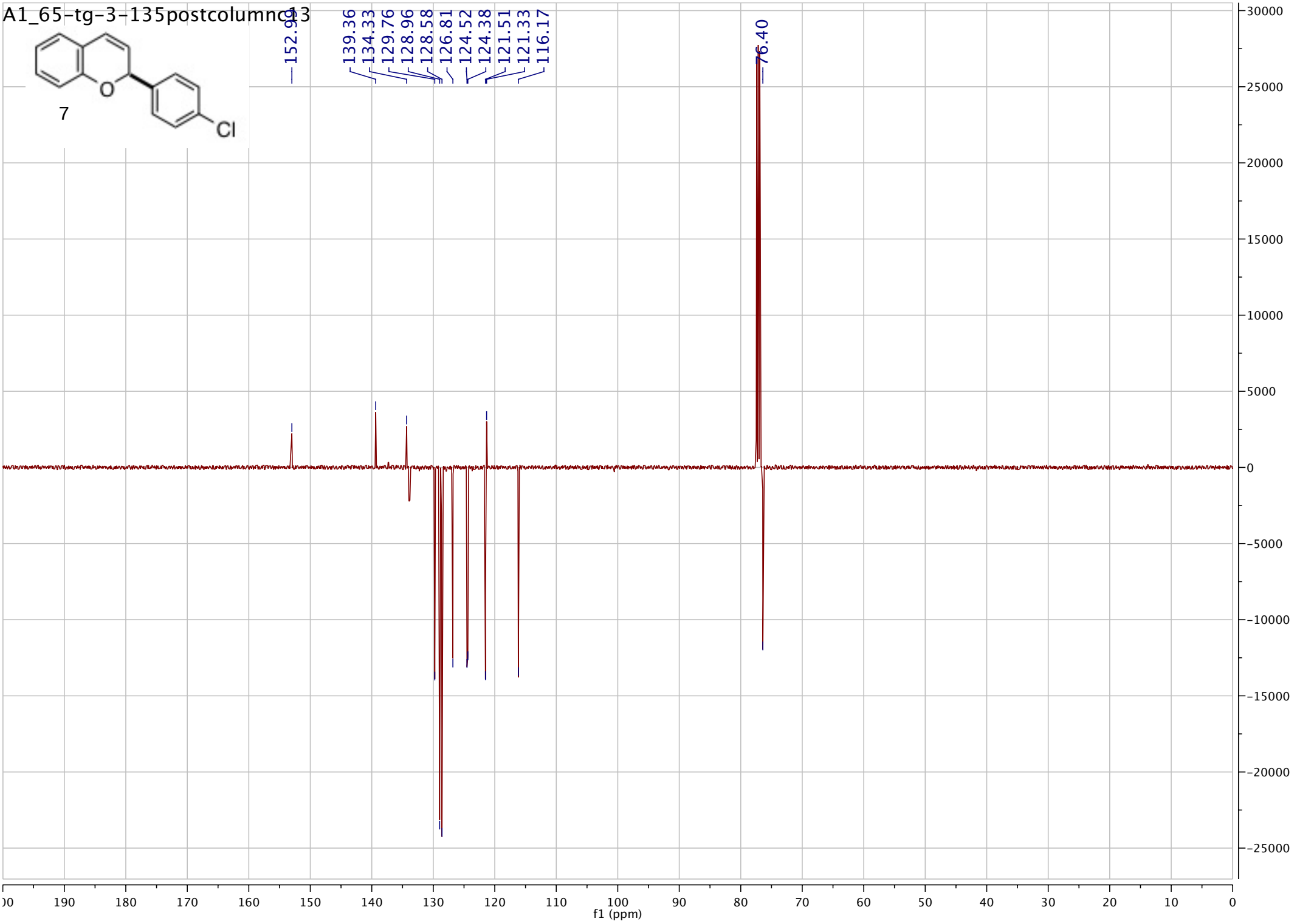
A1_65-tg-3-135postcolumn



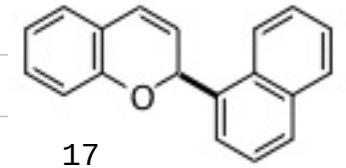
7

2.00 2.49 1.06 1.02 1.05 0.98 1.00 0.98 1.01

f1 (ppm)


A1_65-tg-3-135postcolumnc13
7
O
Cl
152.90
139.36
134.33
129.76
128.96
128.58
126.81
124.52
124.38
121.51
121.33
116.17
76.40
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

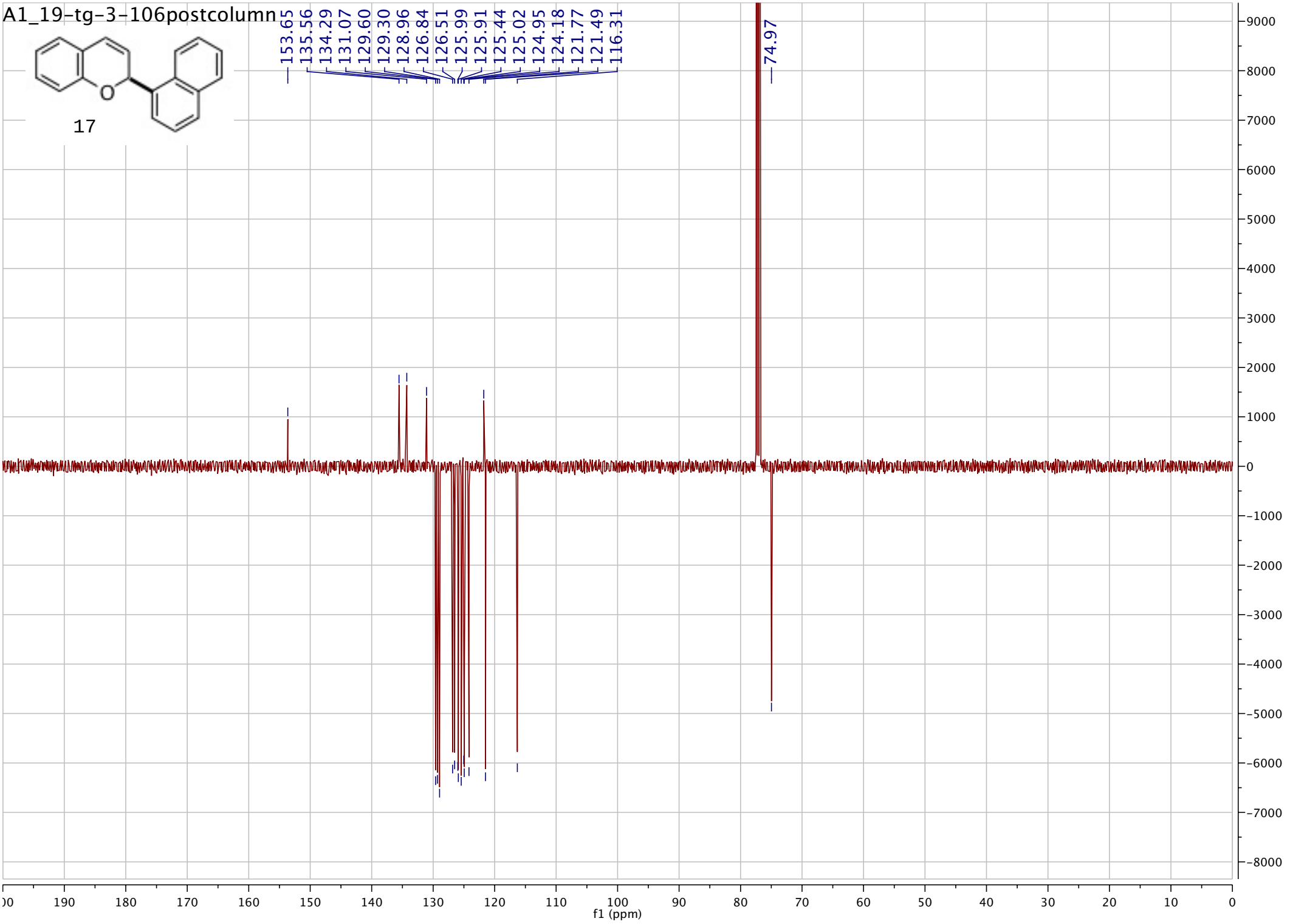
A1_19-tg-3-106postcolumn



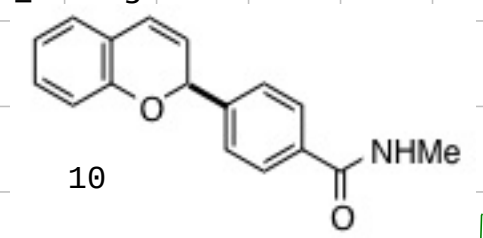
17

0.87 0.86 0.88 0.88 1.76 0.89 1.75 0.87 0.86 1.76 0.87

f1 (ppm)


A1_19-tg-3-106postcolumn
153.65
135.56
134.29
131.07
129.60
129.30
128.96
126.84
126.51
125.99
125.91
125.44
125.02
124.95
124.18
121.77
121.49
116.31
74.97
O
17
f1 (ppm)

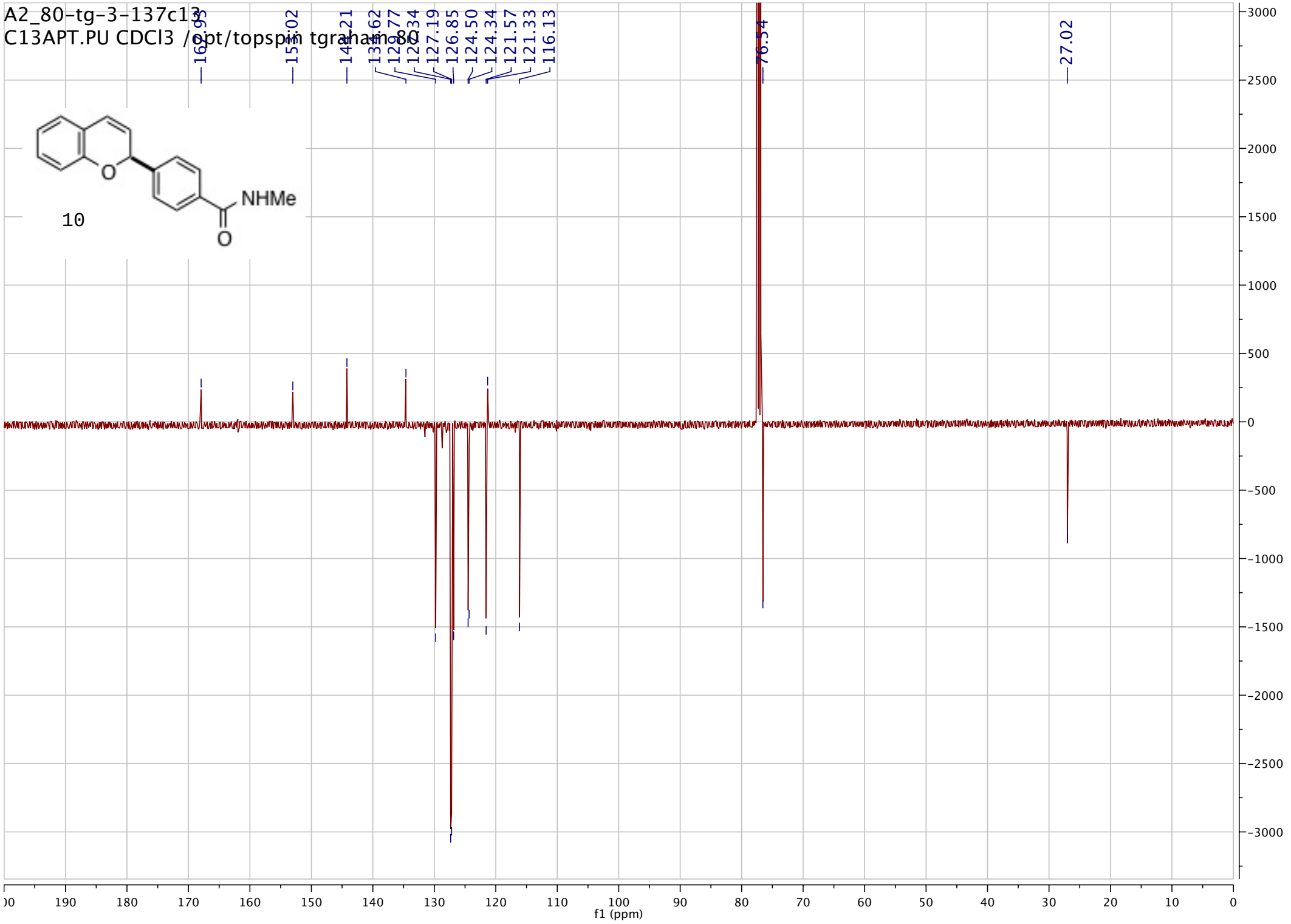
A3_109-tg-3-137



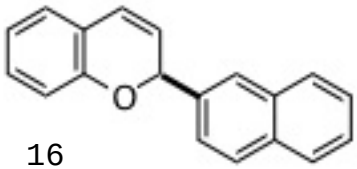
10

2.15 2.05 1.01 0.98 1.01 0.96 0.98 1.02 1.00 1.00 3.34

f1 (ppm)


A2_80-tg-3-137c13
C13APT.PU CDCl3 /opt/topspin tgraham 80
169.95
155.02
142.21
133.62
128.77
128.34
127.19
126.85
124.50
124.34
121.57
121.33
116.13
76.54
27.02
NHMe
O
O
10
f1 (ppm)

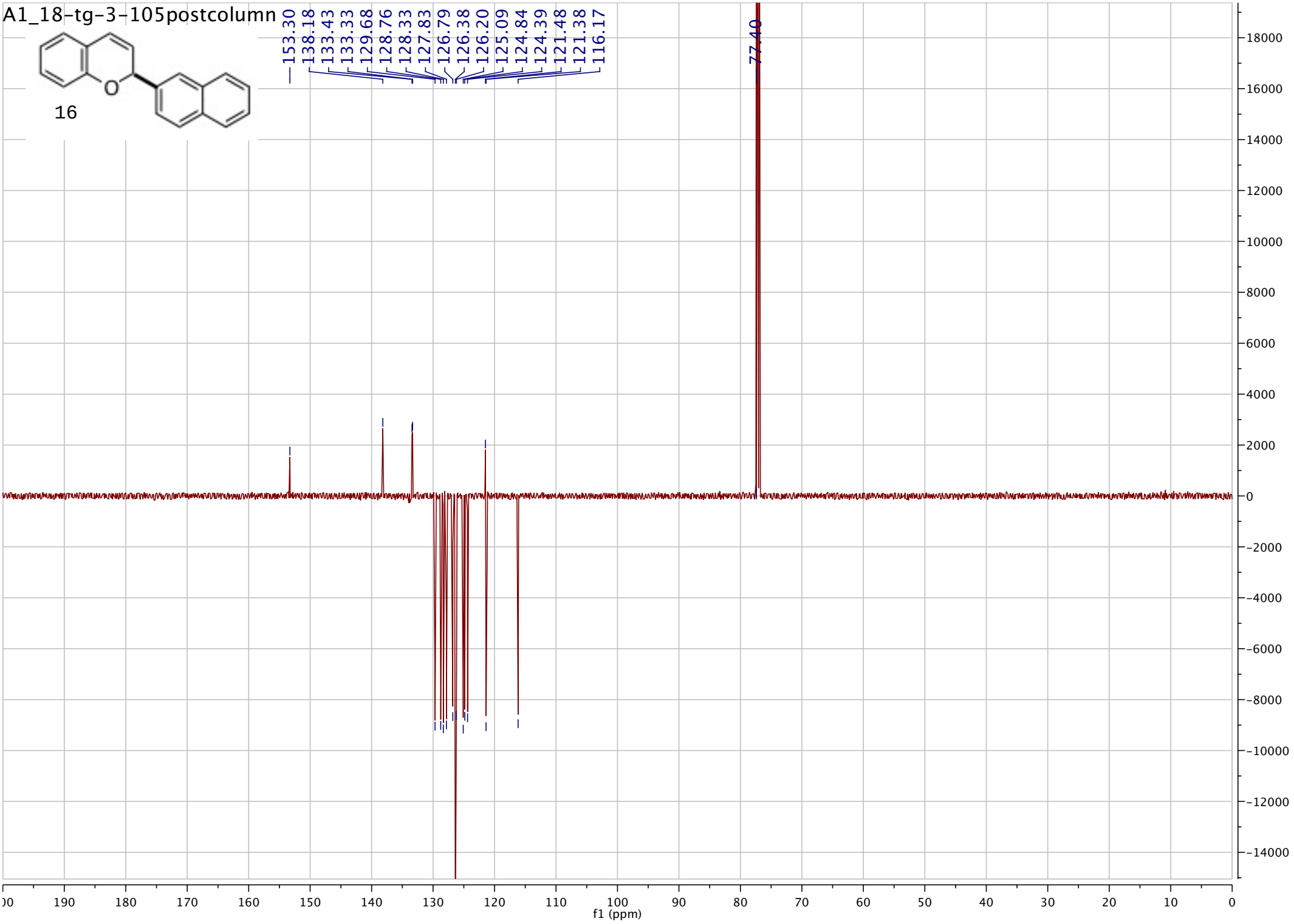
A1_18-tg-3-105postcolumn



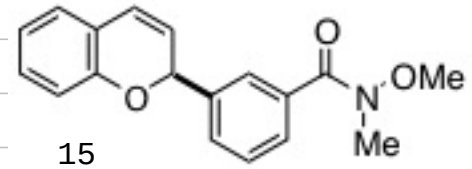
16

3.56 1.03 1.78 1.96 1.92 1.02 1.02 1.00

f1 (ppm)


A1_18-tg-3-105postcolumn
16
153.30
138.18
133.43
133.33
129.68
128.76
128.33
127.83
126.79
126.38
126.20
125.09
124.84
124.39
121.48
121.38
116.17
77.40
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
-10000
-12000
-14000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

A3_108-tg-3-136

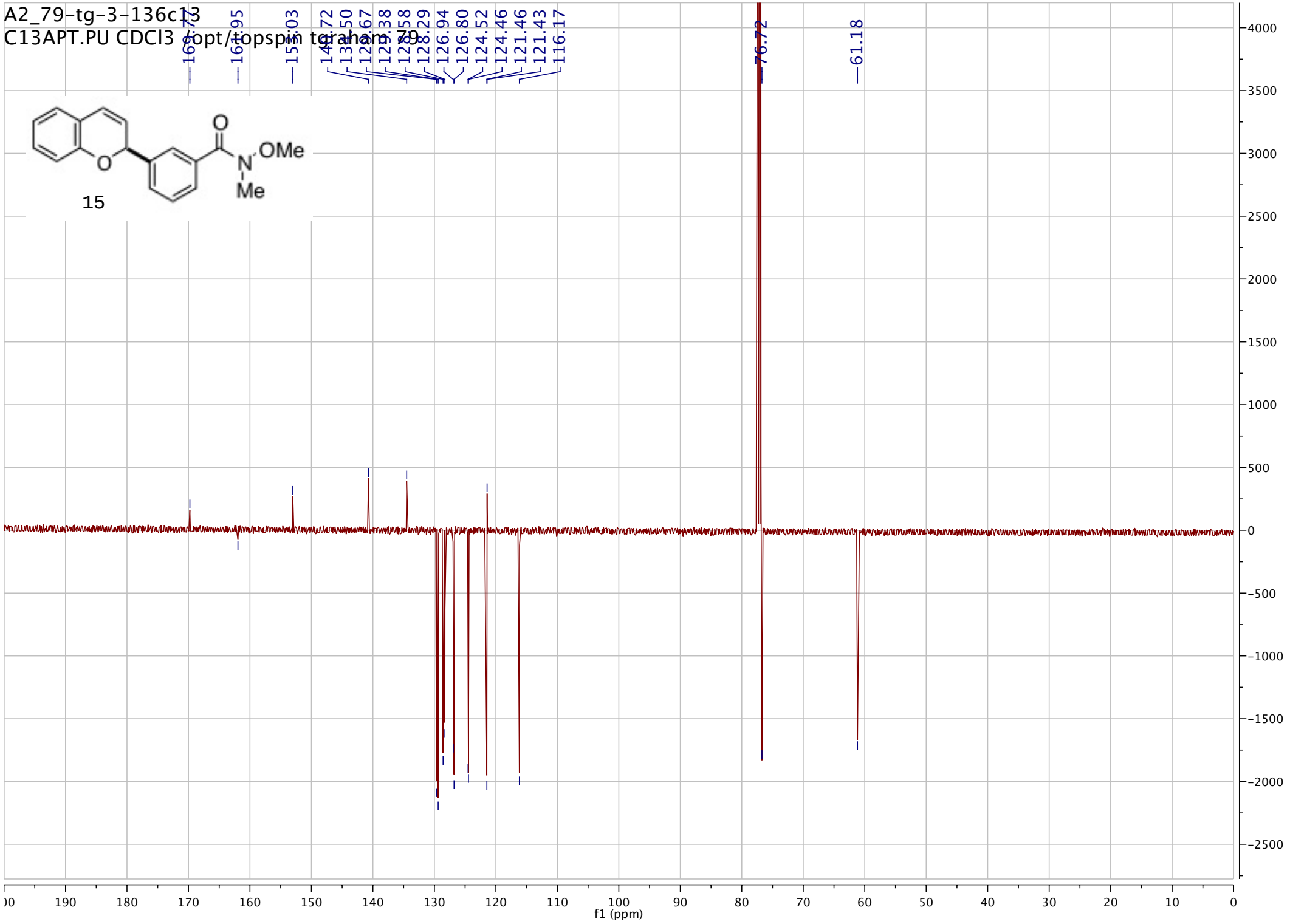


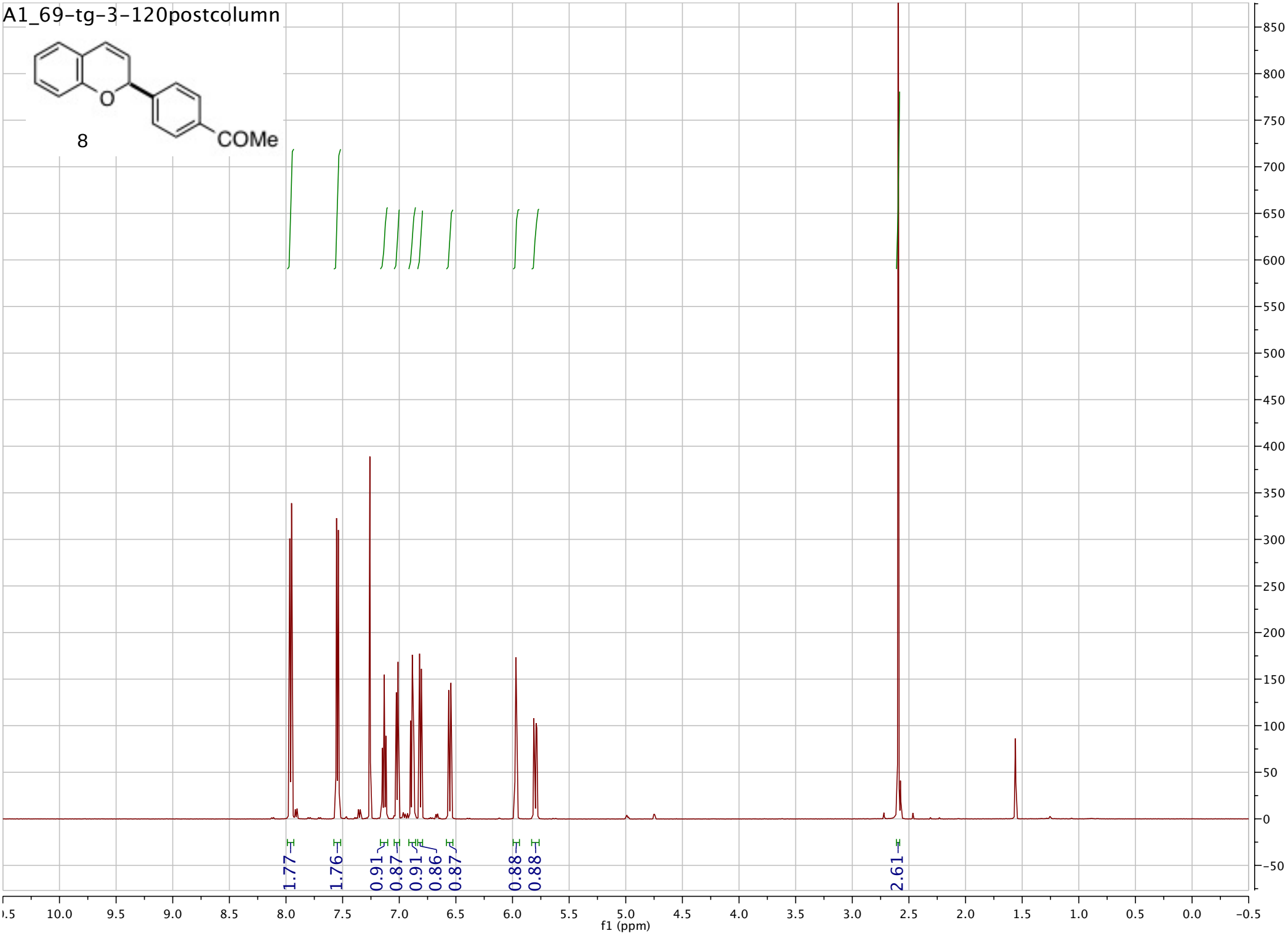
15

DCM

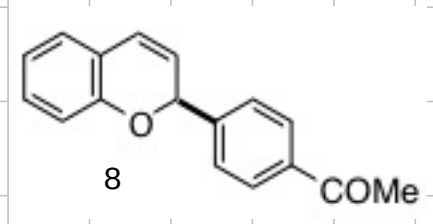
1.00 0.85 0.87 0.87 0.92 0.81 0.94 0.85 0.85 0.85 1.00 2.08 1.97

f1 (ppm)


A2_79-tg-3-136c13
C13APT.PU CDCl3 /opt/topspin tgraham 79
169.73
169.95
155.03
144.72
133.50
129.67
129.38
129.58
128.29
126.94
126.80
124.52
124.46
121.46
121.43
116.17
76.72
61.18
O
O
N
OMe
Me
15
f1 (ppm)


A1_69-tg-3-120postcolumn
O
8
COMe
1.77
1.76
0.91
0.87
0.91
0.86
0.87
0.88
0.88
2.61
f1 (ppm)

A1_69-tg-3-120postcolumn

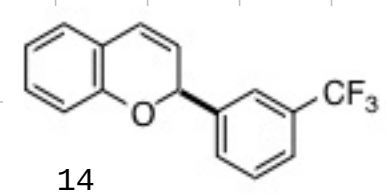


8

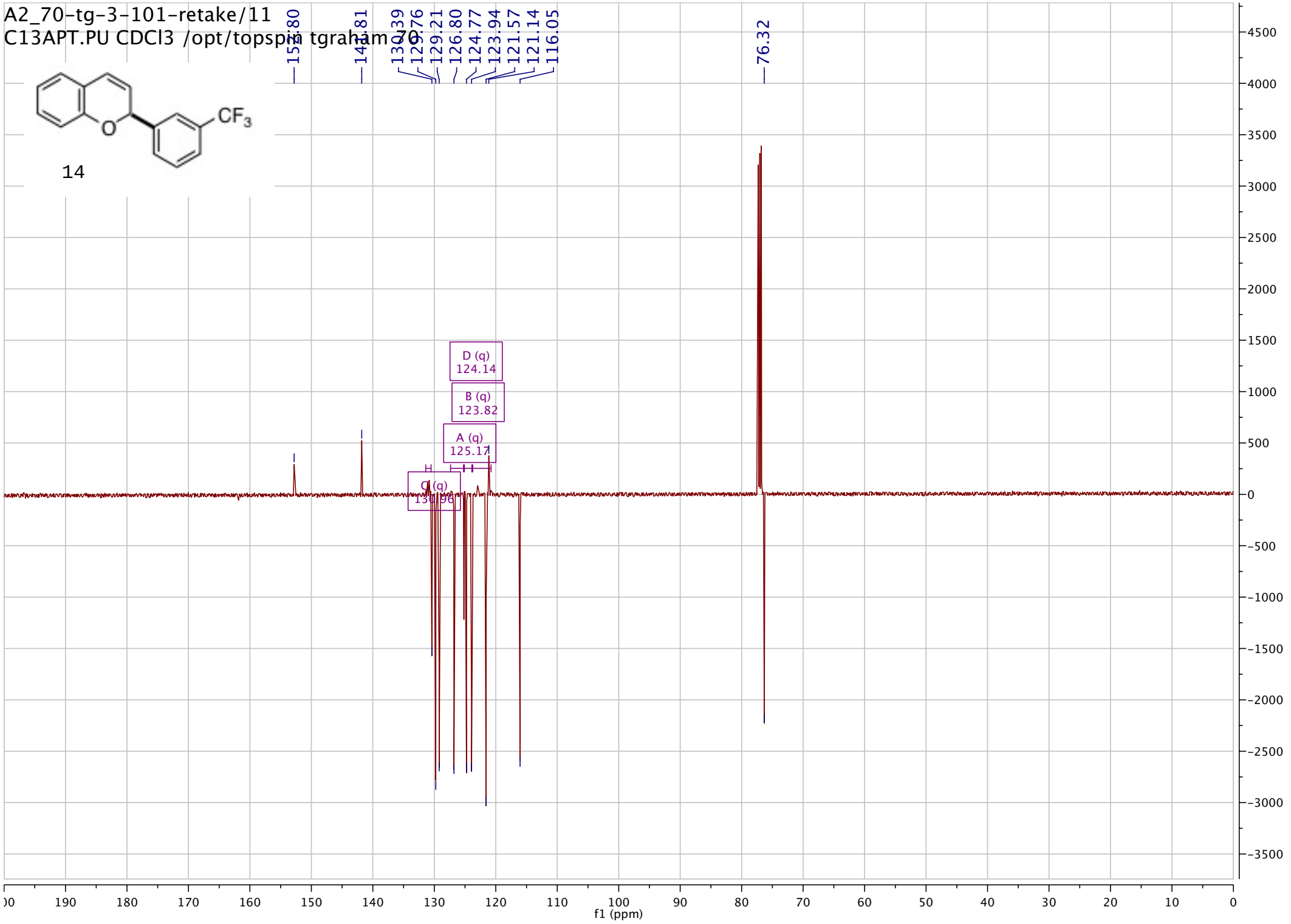
197.88
153.04
146.04
137.03
129.83
128.90
127.05
126.90
124.59
124.15
121.63
121.30
116.14
76.50
26.84

f1 (ppm)

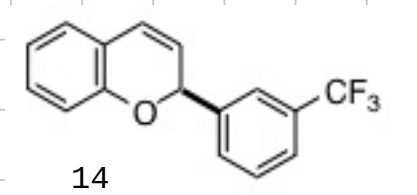
A2_70-tg-3-101-retake
PROTON.PU CDCl3 /opt/topspin tgraham 70



14


A2_70-tg-3-101-retake/11
C13APT.PU CDCl3 /opt/topspin tgraham 70
155.80
144.81
130.39
129.76
129.21
126.80
124.77
123.94
121.57
121.14
116.05
76.32
CF3
O
14
D (q)
124.14
B (q)
123.82
A (q)
125.17
C (q)
130.96
f1 (ppm)

tg-3-101postcolumnf19
F19 OBSERVE
STANDARD PARAMETERS



14

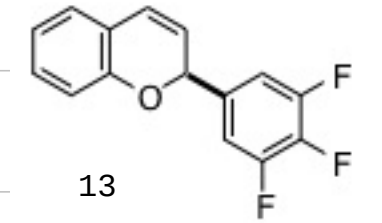
-63.01

9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

-61.9 -62.1 -62.3 -62.5 -62.7 -62.9 -63.1 -63.3 -63.5 -63.7 -63.9 -64.1 -64.3 -64.5

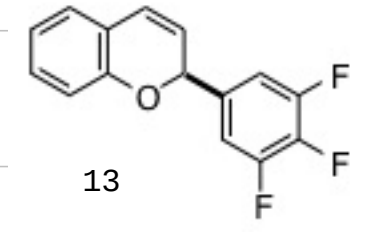
f1 (ppm)

A1_71-tg-3-123postcolumn



13

A3_88-tg-3-123-take2c13



13

130.01
126.99
125.23
123.09
121.87
121.04
116.21
75.23

E (s)
152.46

A (dt)
139.64

D (ddd)
151.35

C (dd)
137.03

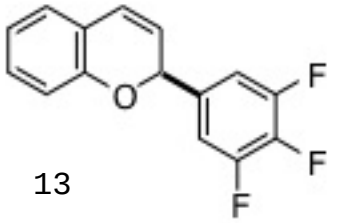
F (dd)
111.26

3500
3000
2500
2000
1500
1000
500
0
-500
-1000

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

tg-3-123-f19postcolumn
F19 OBSERVE
STANDARD PARAMETERS



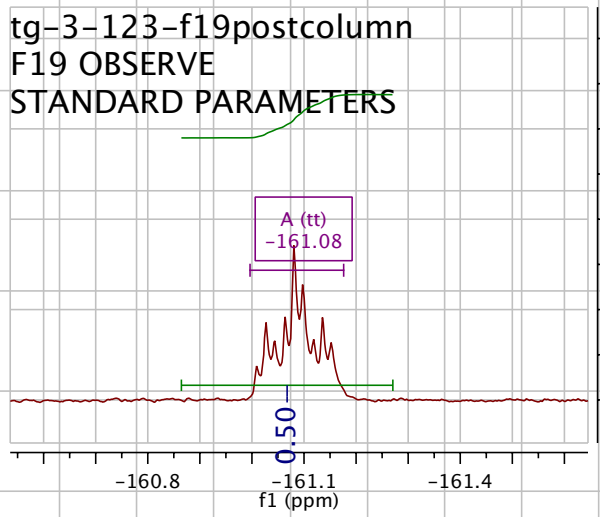
13

B (m)
-133.89
H

A (tt)
-161.08
H

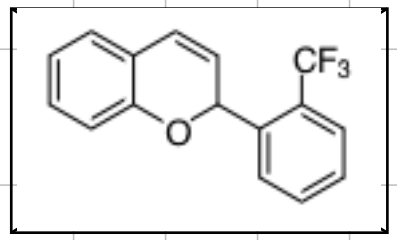
1.01

0.50



f1 (ppm)

A1_72-tg-3-100-postcolumn

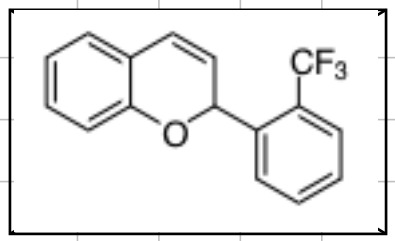


24

1.00 0.98 1.01 1.00 1.03 0.99 1.01 0.98 1.01 1.00 1.04

f1 (ppm)

A1_72-tg-3-100-postcolumn



24

153.15
139.95
132.45
129.72
129.33
128.26
126.74
124.63
123.81
121.44
120.75
115.84
73.19

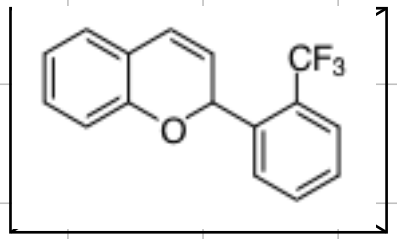
B (q)
126.81

A (q)
125.69

C (q)
124.19

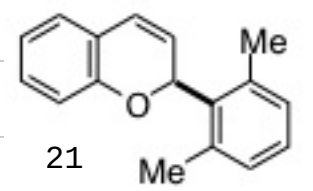
f1 (ppm)

tg-3-100postcolumnf19
F19 OBSERVE
STANDARD PARAMETERS



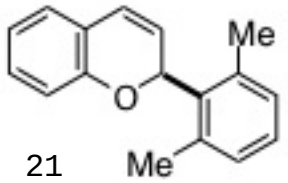
24

A2_71-tg-3-156-retake
PROTON.PU CDCl3 /opt/topspin tgraham 71



21

A2_71-tg-3-156-retake
C13APT.PU CDCl3 /opt/topspin tgraham 1



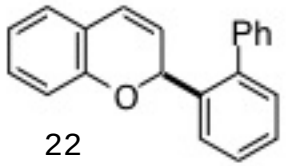
21

154.30
137.60
136.20
129.58
129.44
128.37
126.84
125.20
124.85
121.57
121.32
115.89
74.48
20.93

pph3
pph3
pph3

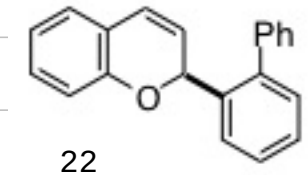
f1 (ppm)

A1_67-tg-3-118postcolumn



22

A1_67-tg-3-118postcolumn



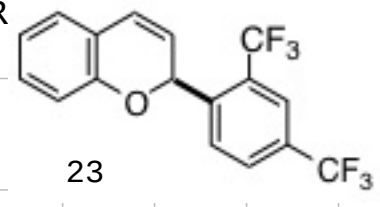
22

153.30
141.36
140.52
138.02
130.39
129.65
129.59
128.60
128.41
128.36
128.09
127.44
126.64
125.45
124.06
121.37
121.23
116.08
74.17

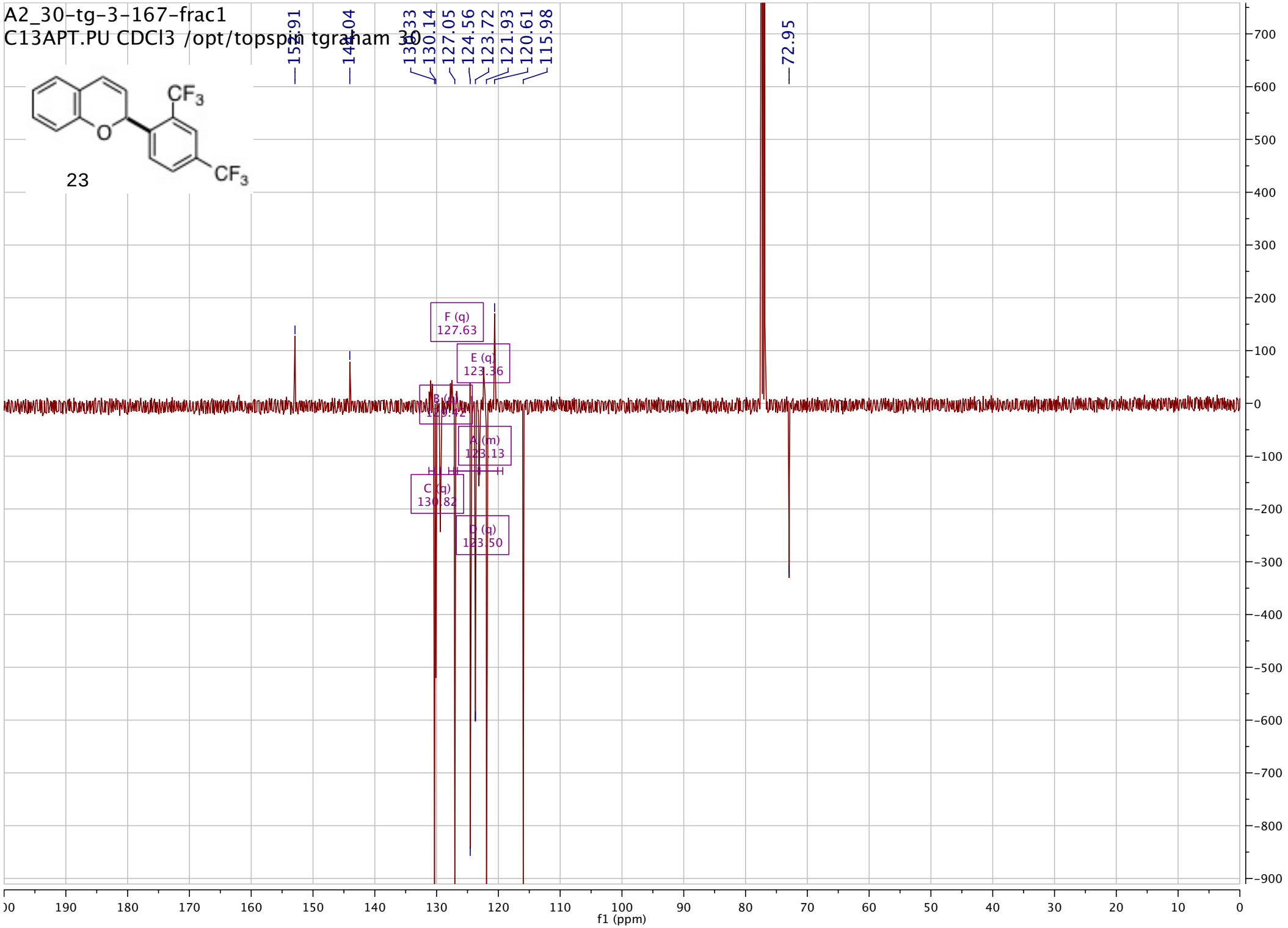
f1 (ppm)

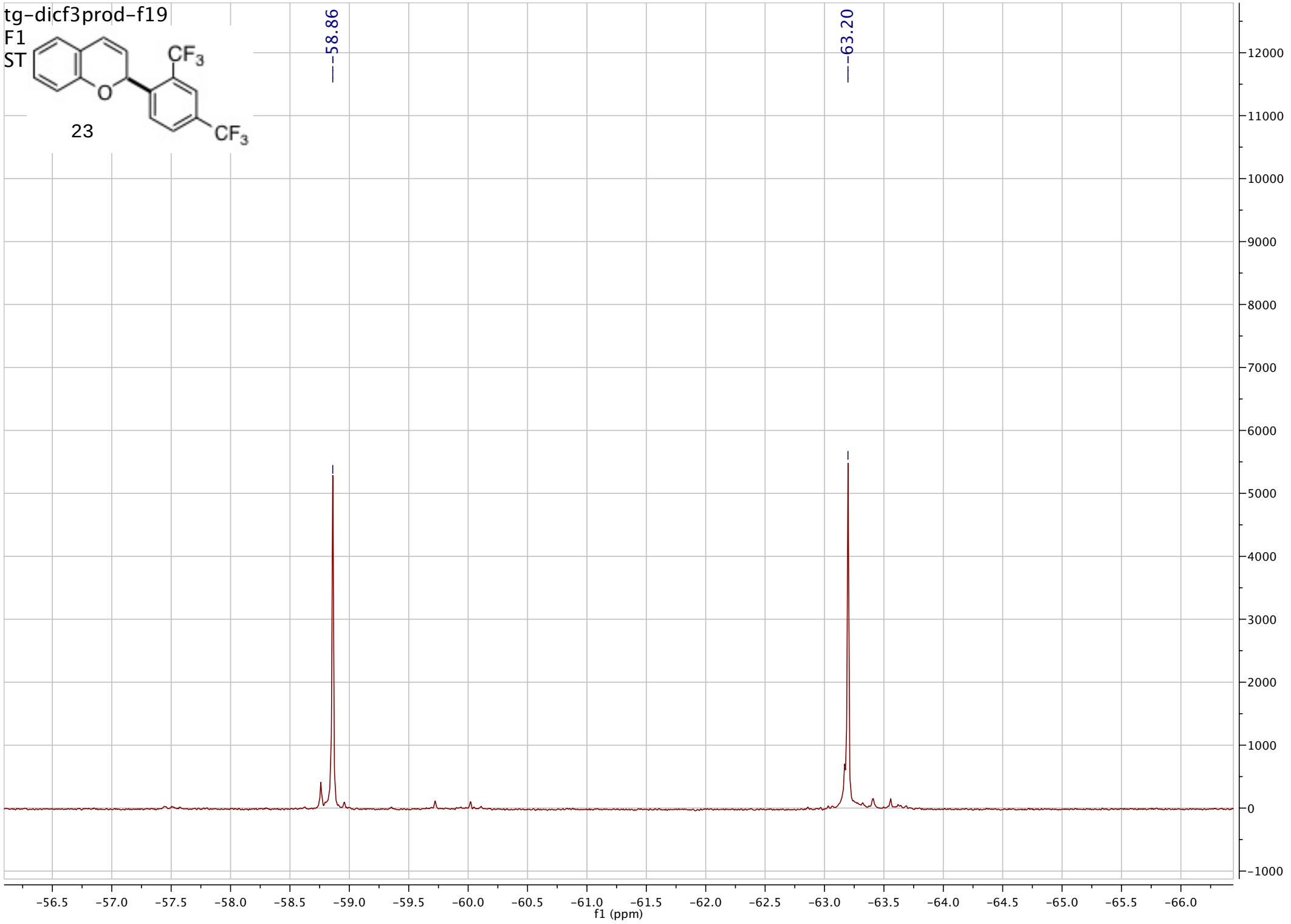
A2_30-tg-3-167-frac1

PR ...opspin tgraham 30

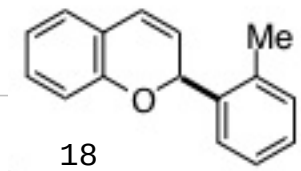


23

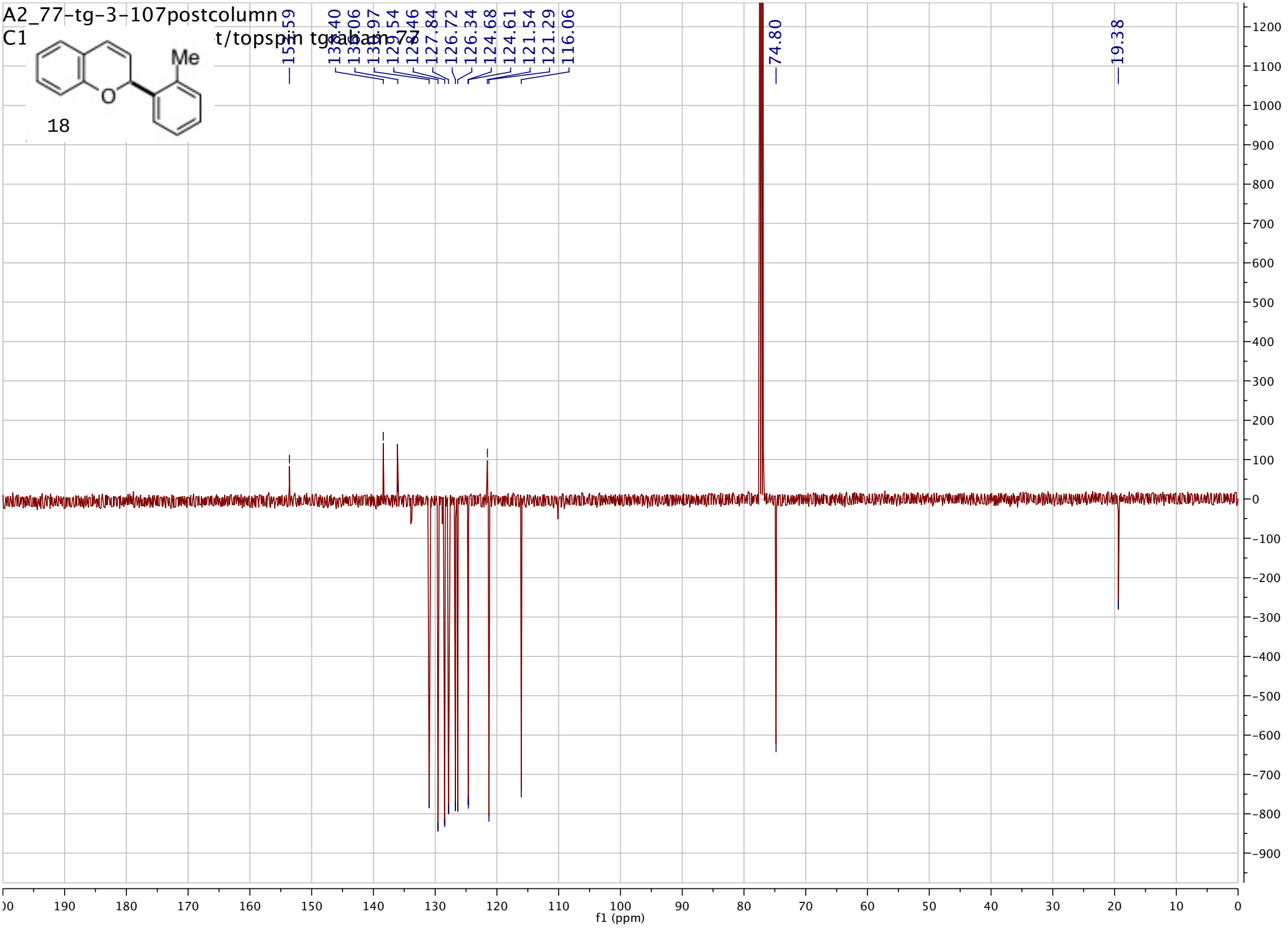

A2_30-tg-3-167-frac1
C13APT.PU CDCl3 /opt/topspin tgraham 30
CF3
O
CF3
23
155.91
144.04
133.33
130.14
127.05
124.56
123.72
121.93
120.61
115.98
72.95
F (q)
127.63
E (q)
123.36
A (m)
123.13
C (q)
130.82
D (q)
123.50
f1 (ppm)


tg-dicf3prod-f19
F1
ST
23
CF3
CF3
O
-58.86
-63.20
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
f1 (ppm)

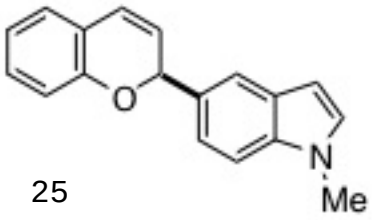
A2_86-tg-3-107-postcolfrac2
PROTON.PU CDCl3 /opt/topspin tgraham 86



18

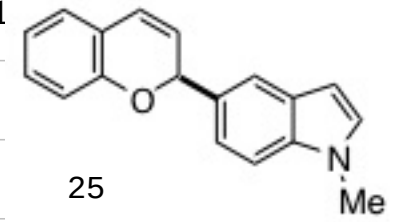

A2_77-tg-3-107postcolumn
C1
t/topspin tgadiam 77
Me
O
18
155.59
134.40
133.06
130.97
129.54
128.46
127.84
126.72
126.34
124.68
124.61
121.54
121.29
116.06
74.80
19.38
f1 (ppm)

A2_88-tg-3-131
PROTON.PU CDCl3 /opt/topspin tgraham 88



25

A2_88-tg-3-131
C1 pin tgraham 88

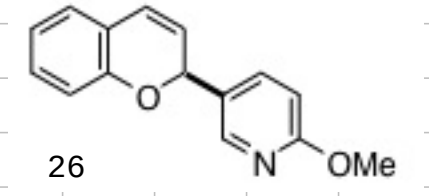


25

153.37
137.79
126.58
125.44
125.50
125.59
125.72
123.78
121.57
121.39
121.01
120.20
116.19
109.62
101.43
78.22
33.09

f1 (ppm)

A1_120-tg-3-130postcolumn

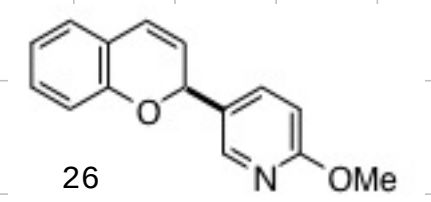


26

1.00 1.01 1.01 0.97 1.00 1.91 1.02 0.98 1.01 2.74

f1 (ppm)

A1_120-tg-3-130postcolumn



26

164.46
152.82
146.06
138.18
129.77
128.96
126.80
124.91
123.98
121.52
121.42
116.30
111.26
74.64
53.68

40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000

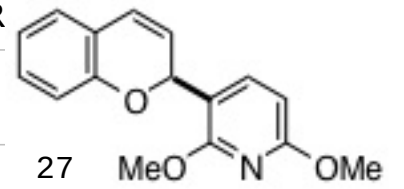
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

A2_119-tg-3-190-postHPLC

PR

spin tgraham 119

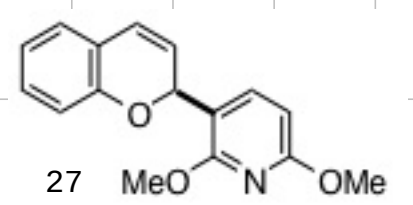


27

1.00 1.03 1.01 1.03 0.99 1.02 1.01 0.97 1.01 2.99 2.98

f1 (ppm)

A2_64-tg-3-190posthplc2
C13APT.PU CDCl3 /opt/topspin tgraham 64



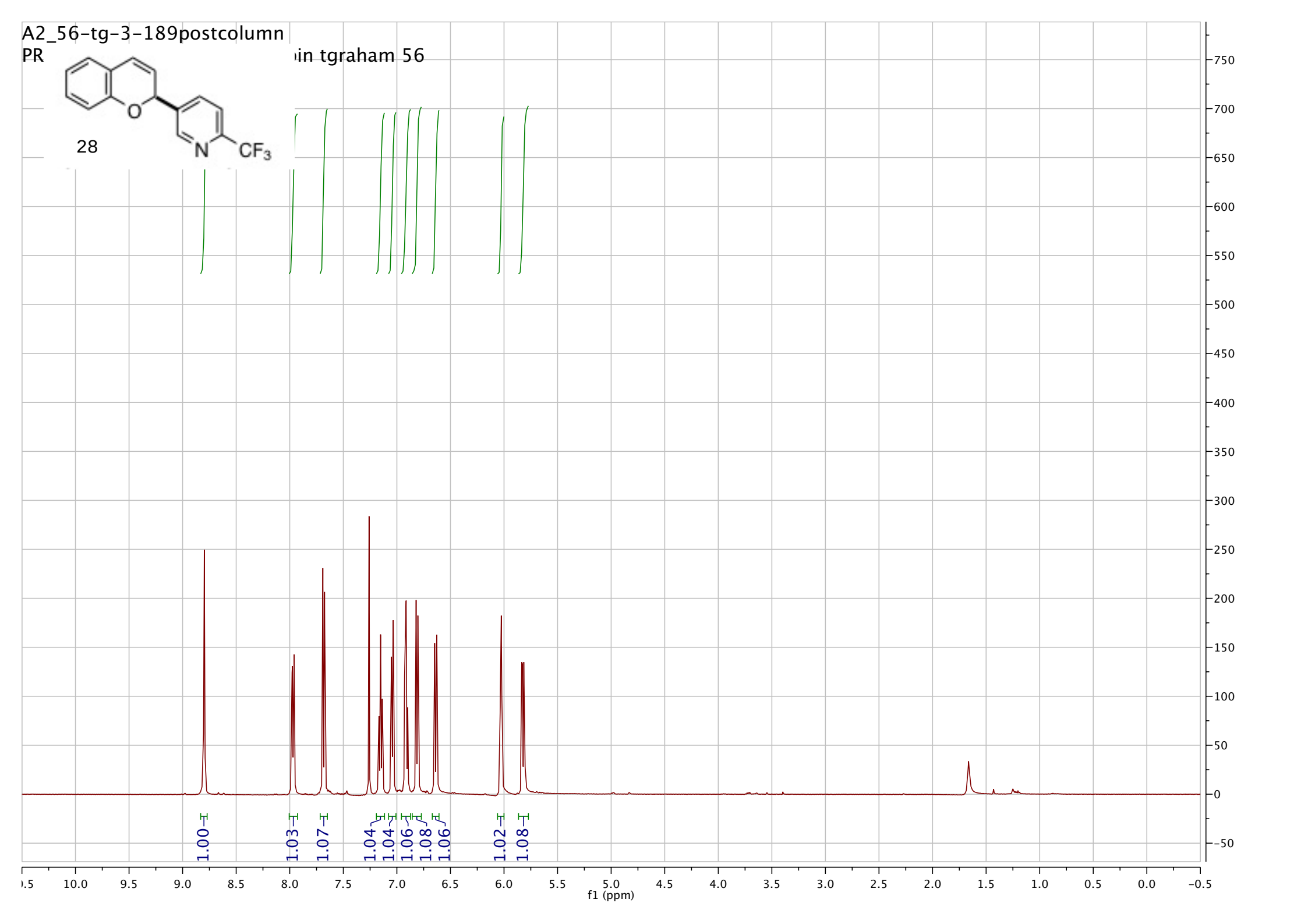
27

160.99
155.45
152.29
139.93
129.47
126.64
124.40
124.04
121.46
121.20
116.21
113.92
100.87
70.86
53.78
53.66

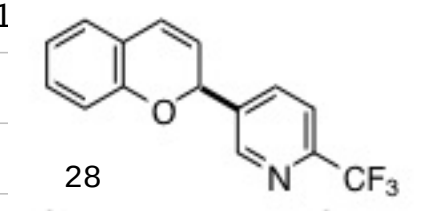
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


A2_56-tg-3-189postcolumn
PR
in tgraham 56
28
O
N
CF3
1.00
1.03
1.07
1.04
1.04
1.06
1.08
1.06
1.02
1.08
f1 (ppm)

A2_56-tg-3-189postcolumn
C1 1 tgraham 56



28

152.41
148.81
133.42
130.06
130.18
127.09
125.63
122.71
122.07
121.12
116.31
73.97

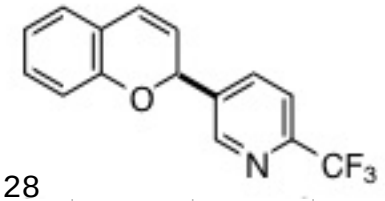
A (q)
148.07

C (q)
121.54

B (q)
120.59

f1 (ppm)

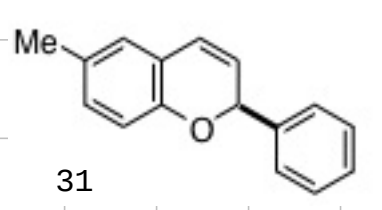
tg-3-189-postcolumnf19
F1
ST



28

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.32.

A2_96-tg-3-148postcolumn
PROTON.PU CDCl3 /opt/topspin tgraham 96



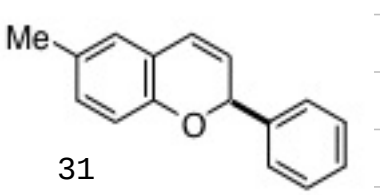
31

DCM

1.87 3.11 0.99 1.01 0.97 1.00 0.94 1.00 2.79

f1 (ppm)

A2_96-tg-3-148postcolumn
C13APT.PU CDCl3 /opt/topspin tgraham 96

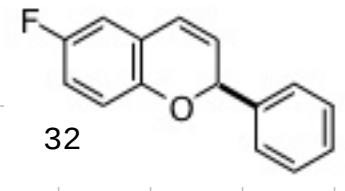


31

153.03
140.98
130.51
130.00
128.78
128.45
127.19
127.16
125.09
124.25
121.23
115.83
77.18
20.69

f1 (ppm)

A1_101-tg-3-145postcolumn

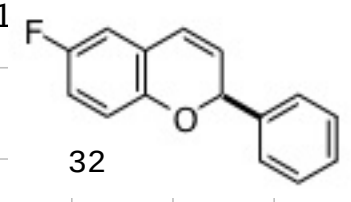


32

1.88
3.12
1.01
1.89
1.00
1.91

f1 (ppm)

A2_116-tg-3-145postcolumn
C1 opspin tgraham 116



32

140.36
128.84
128.67
127.20
126.46
123.65
77.24

B (d)
157.45

A (d)
149.04

C (d)
122.40

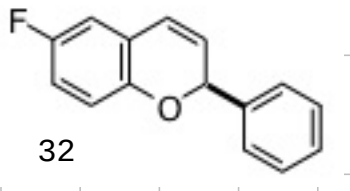
E (d)
115.56

D (d)
112.87

F (d)
115.97

f1 (ppm)

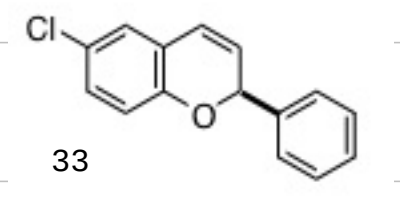
tg-3-145postcolumn-f19
F1
ST



32

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.66.

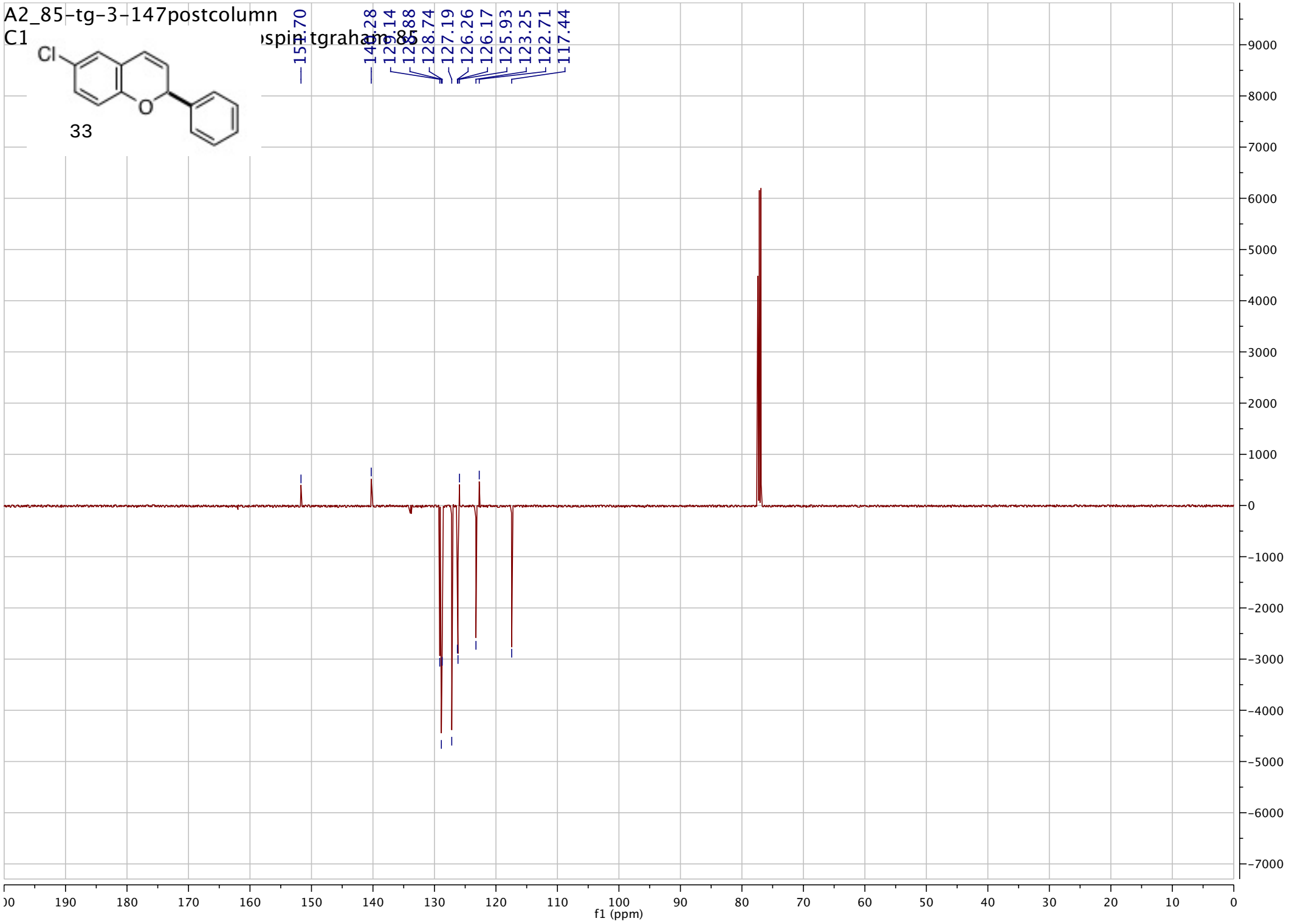
A3_87-tg-3-147postcolumn



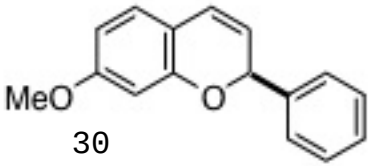
33

1.79 2.94 0.96 0.90 0.98 1.00 0.92 1.00

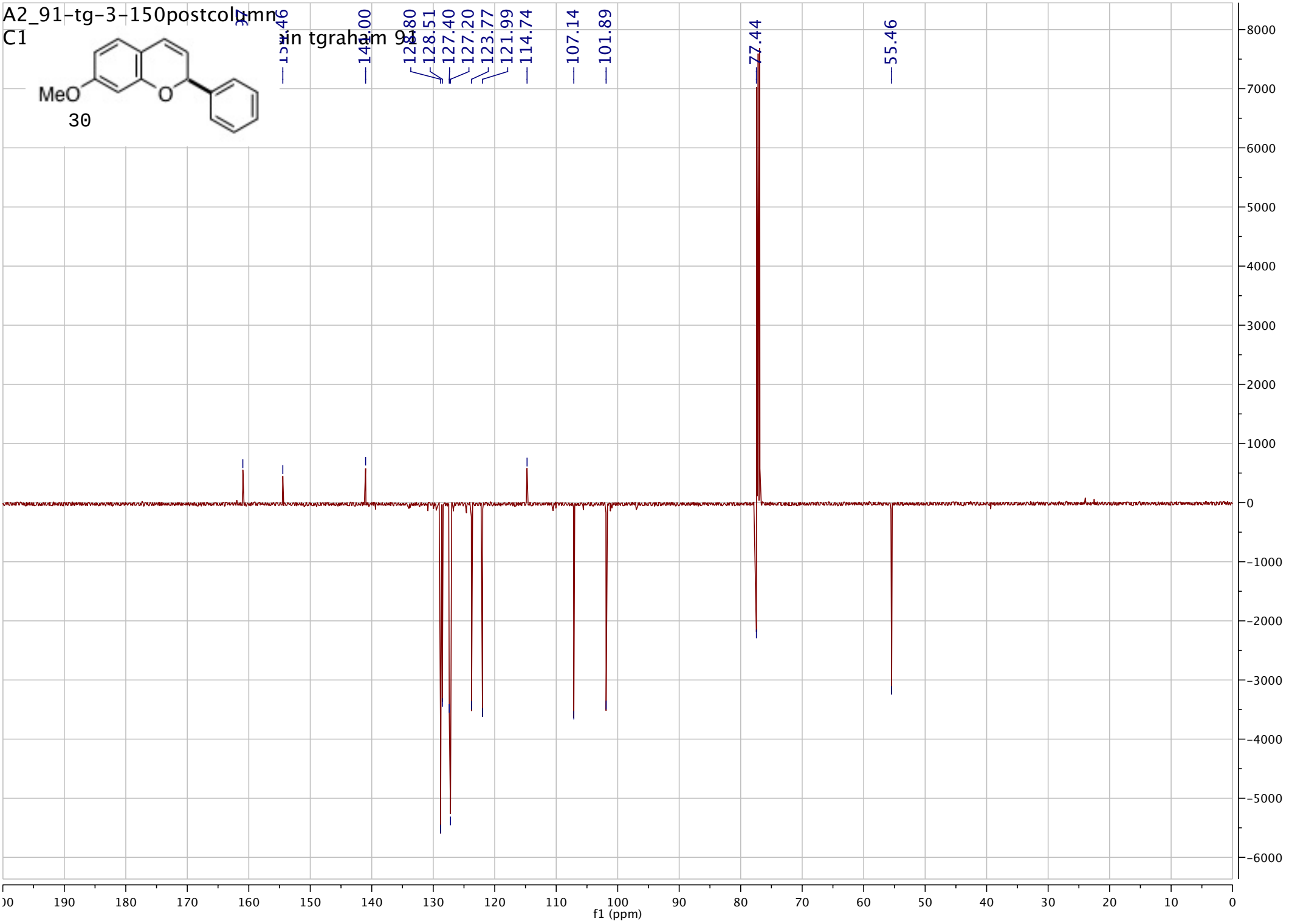
f1 (ppm)


A2_85-tg-3-147postcolumn
C1
spin itgraham 85
Cl
O
33
151.70
140.28
129.14
128.88
128.74
127.19
126.26
126.17
125.93
123.25
122.71
117.44
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

A3_20-TG-3-150-PostColumn



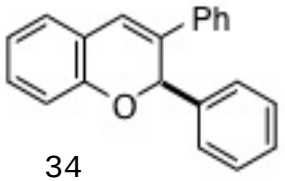
30


A2_91-tg-3-150postcolumn
C1
in tgraham 91
MeO
O
30
159.46
140.00
128.80
128.51
127.40
127.20
123.77
121.99
114.74
107.14
101.89
77.44
55.46
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

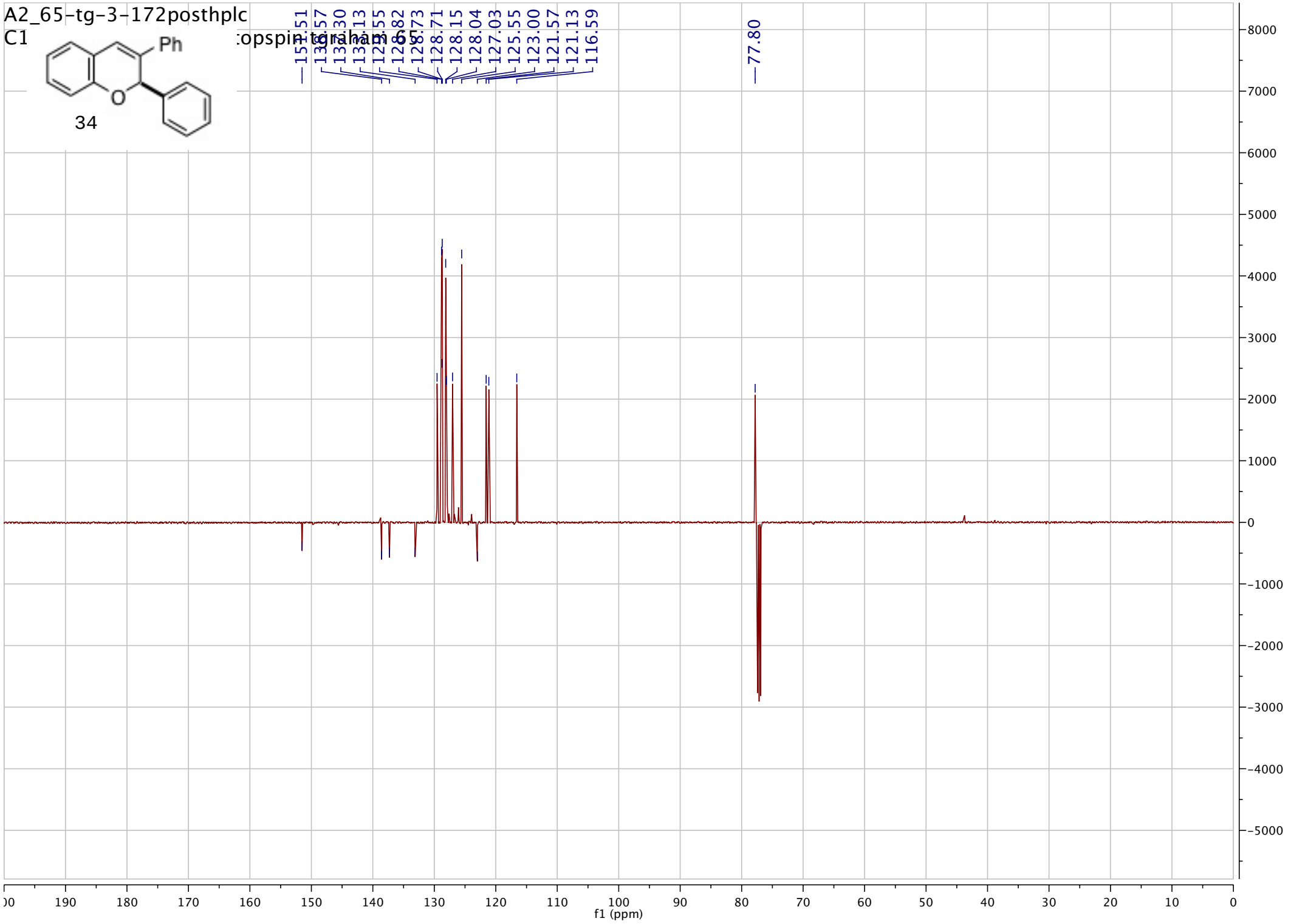
A2_65-tg-3-172posthplc

PR

topspin tgraham 65

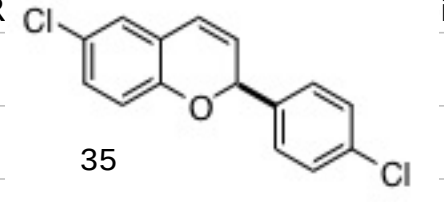


34


A2_65-tg-3-172posthplc
C1
opspin tgraham 65
Ph
O
34
151.51
137.57
133.30
133.13
125.55
125.82
128.73
128.71
128.15
128.04
127.03
125.55
123.00
121.57
121.13
116.59
77.80
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

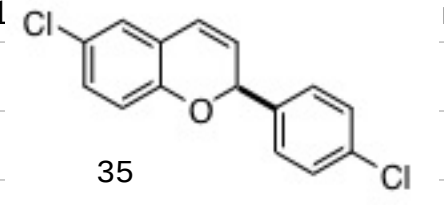
A2_87-tg-3-158frac1-postcolumn

PR in tgraham 87



35

A2_87-tg-3-158frac1-postcolumn
C1 n-tgraham-87



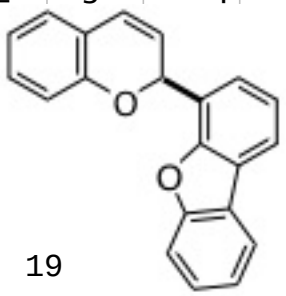
35

151.44
139.68
139.58
129.30
128.04
128.61
126.35
126.15
125.58
123.64
122.59
117.48
76.52

f1 (ppm)

A2_78-tg-3-115postcolumn

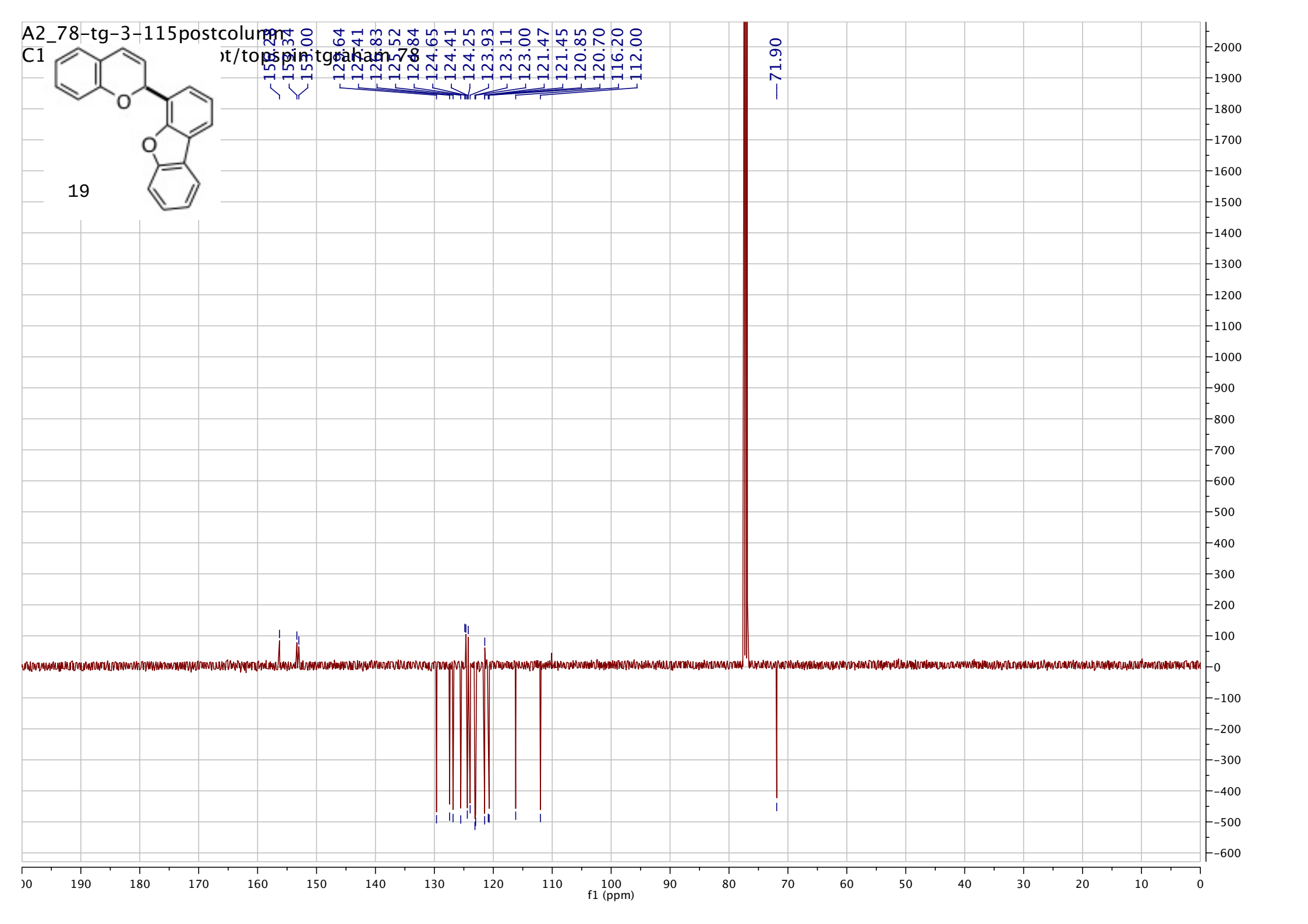
PR pt/topspin tgraham 78



19

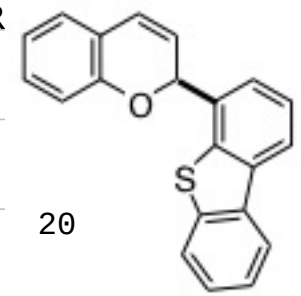
2.00 1.76 1.06 1.94 0.99 0.96 0.98 0.89 1.83 1.09

f1 (ppm)


A2_78-tg-3-115postcolumn
C1
ot/topspin-tgraham-78
19
O
O
155.29
155.34
155.00
126.64
126.41
126.83
125.52
124.84
124.65
124.41
124.25
123.93
123.11
123.00
121.47
121.45
120.85
120.70
116.20
112.00
71.90
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

A2_66-tg-3-114postcolumn

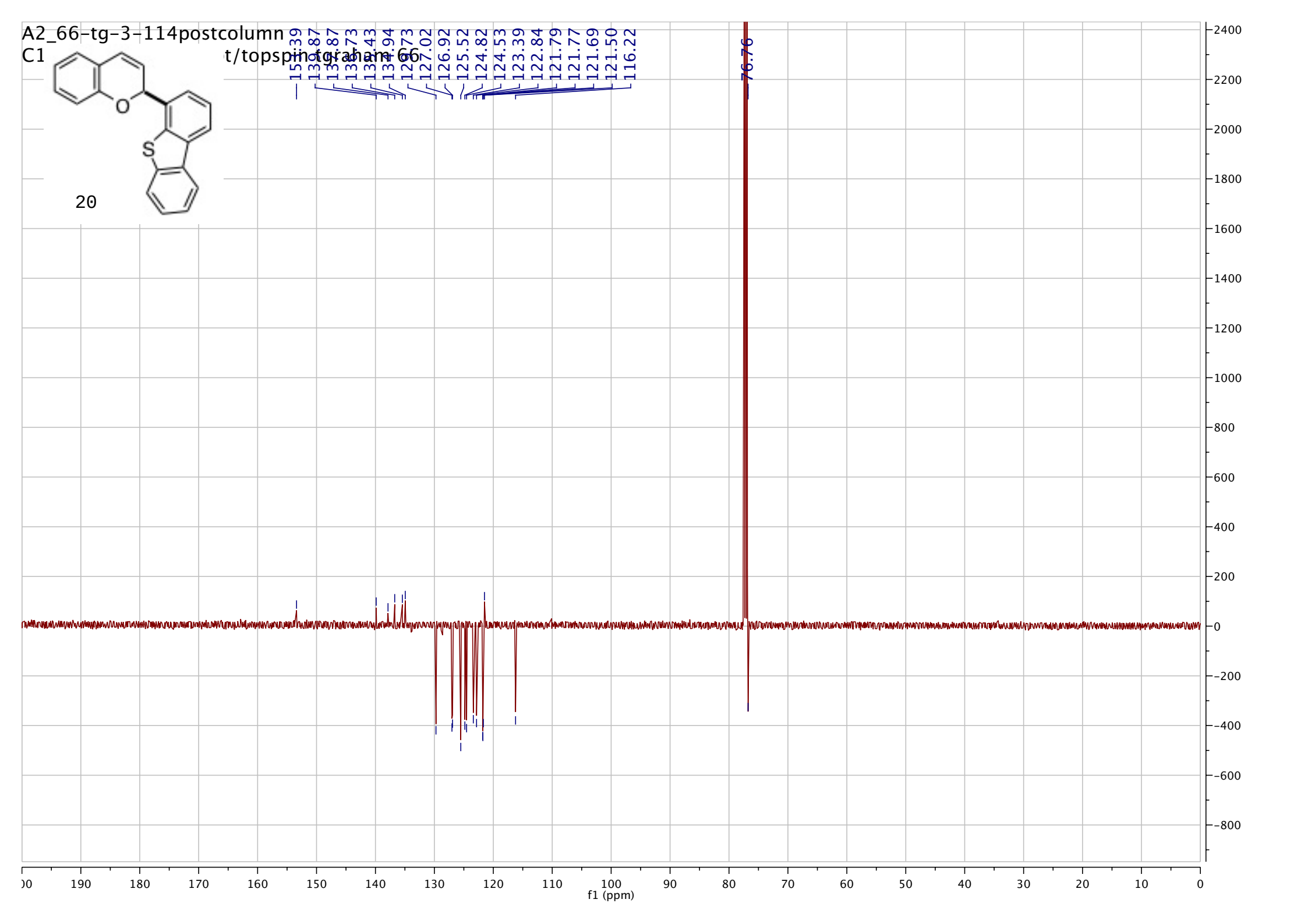
PR ot/topspin tgraham 66



20

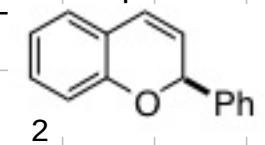
2.02 0.99 0.99 3.09 1.01 0.99 1.00 0.98 0.98 0.97 0.98

f1 (ppm)


A2_66-tg-3-114postcolumn
C1 t/topspin tgraham 66
O
S
20
155.39
139.87
139.87
139.73
139.43
139.94
127.73
127.02
126.92
125.52
124.82
124.53
123.39
122.84
121.79
121.77
121.69
121.50
116.22
76.76
f1 (ppm)

tg-3-149postcolumntake2

ST J PARAMETERS



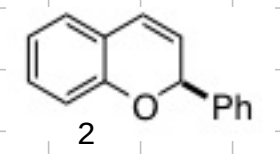
2

fraction containing 1,2 isomer

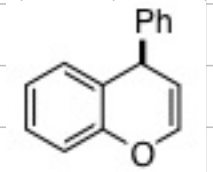
2.02 3.17 1.07 1.02 1.08 1.03 1.06 0.99 1.03

f1 (ppm)

tg-3-149topspot
STANDARD PROTON PARAMETERS



2



fraction containing 1,2 and 1,4 isomer

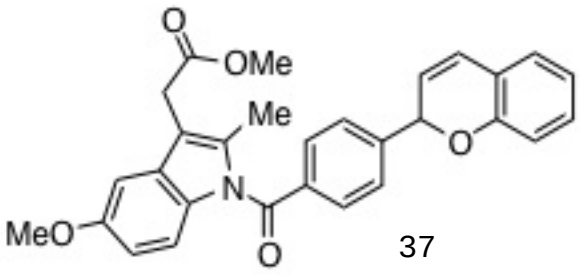
1,2 isomer

1,4 isomer

0.74 7.13 1.46 3.08 0.96 0.33 0.33 1.00 1.01

f1 (ppm)

A2_62-tg-3-211-indomethprod
PROTON.PU CDCl3 /opt/topspin tgraham 62

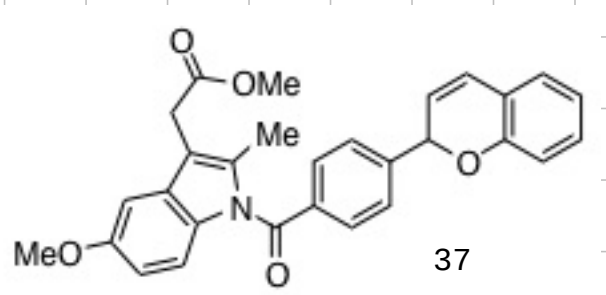


37

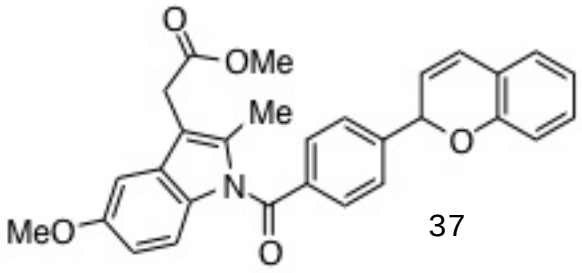
2.00 1.94 1.22 1.06 1.03 2.17 1.07 1.06 1.04 1.01 0.99 2.83 2.83 1.88 2.73

f1 (ppm)

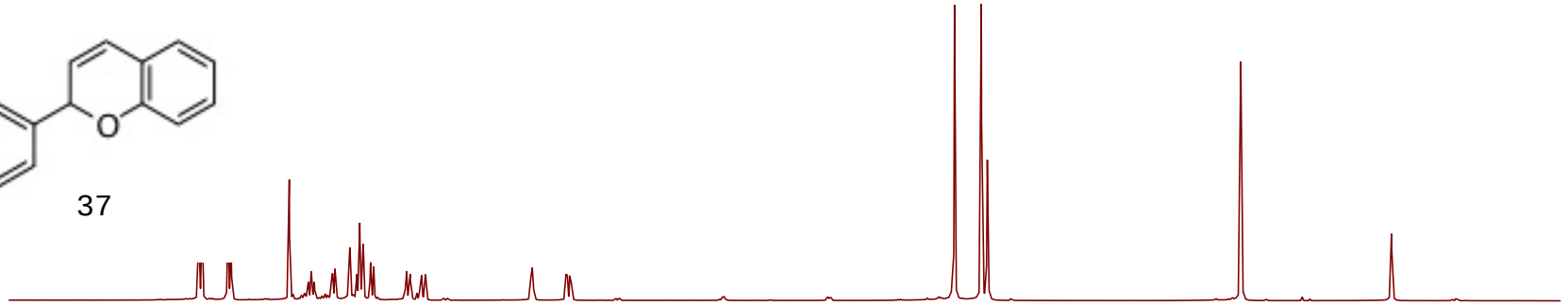
A2_62-tg-3-211-indomethprod
C13APT.PU CDCl3 /opt/topspin-tgraham.62

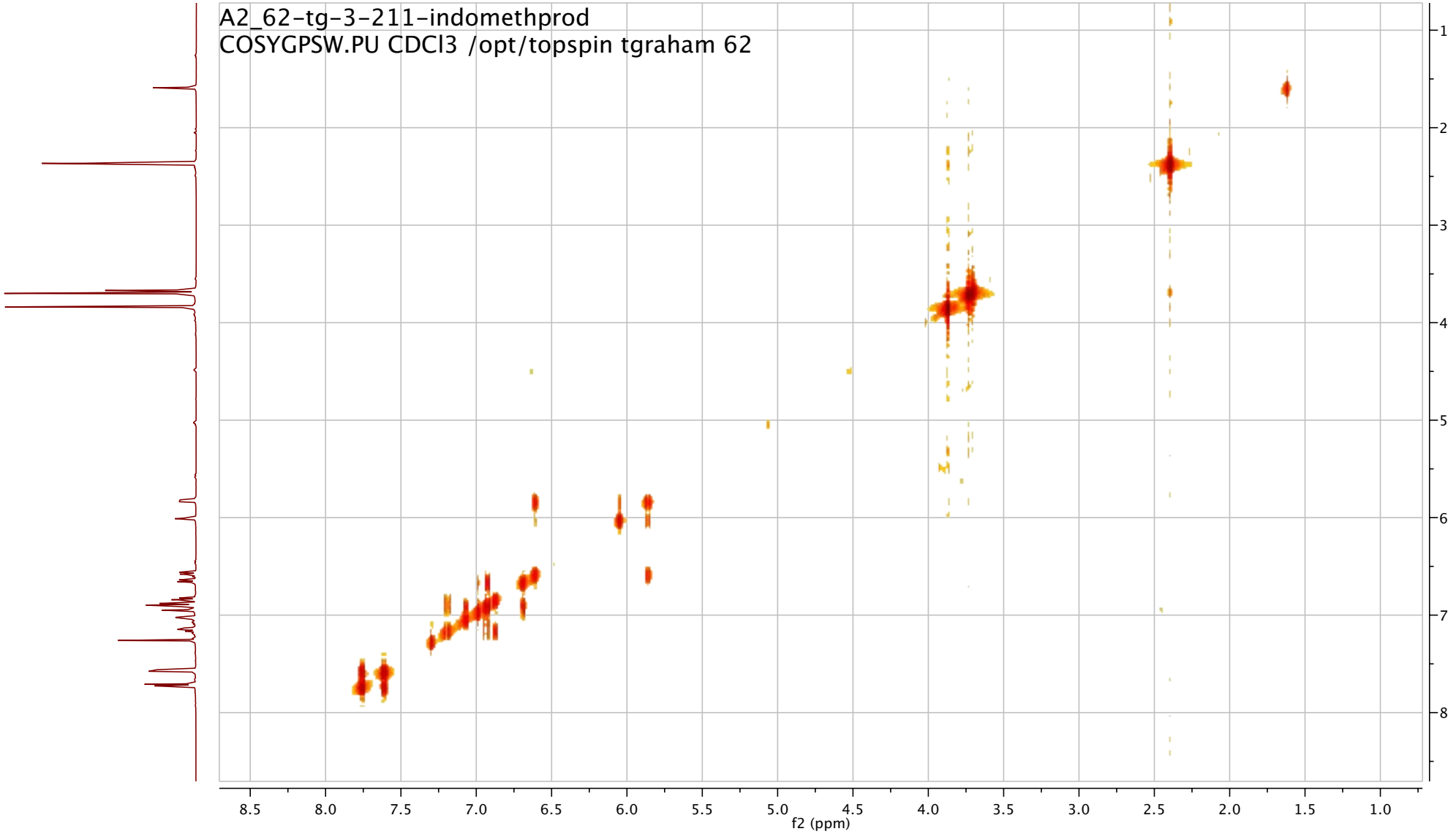


37

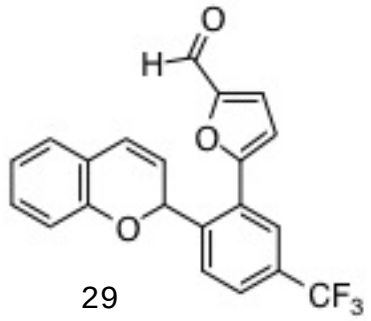

O
OMe
Me
N
O
MeO
O

37



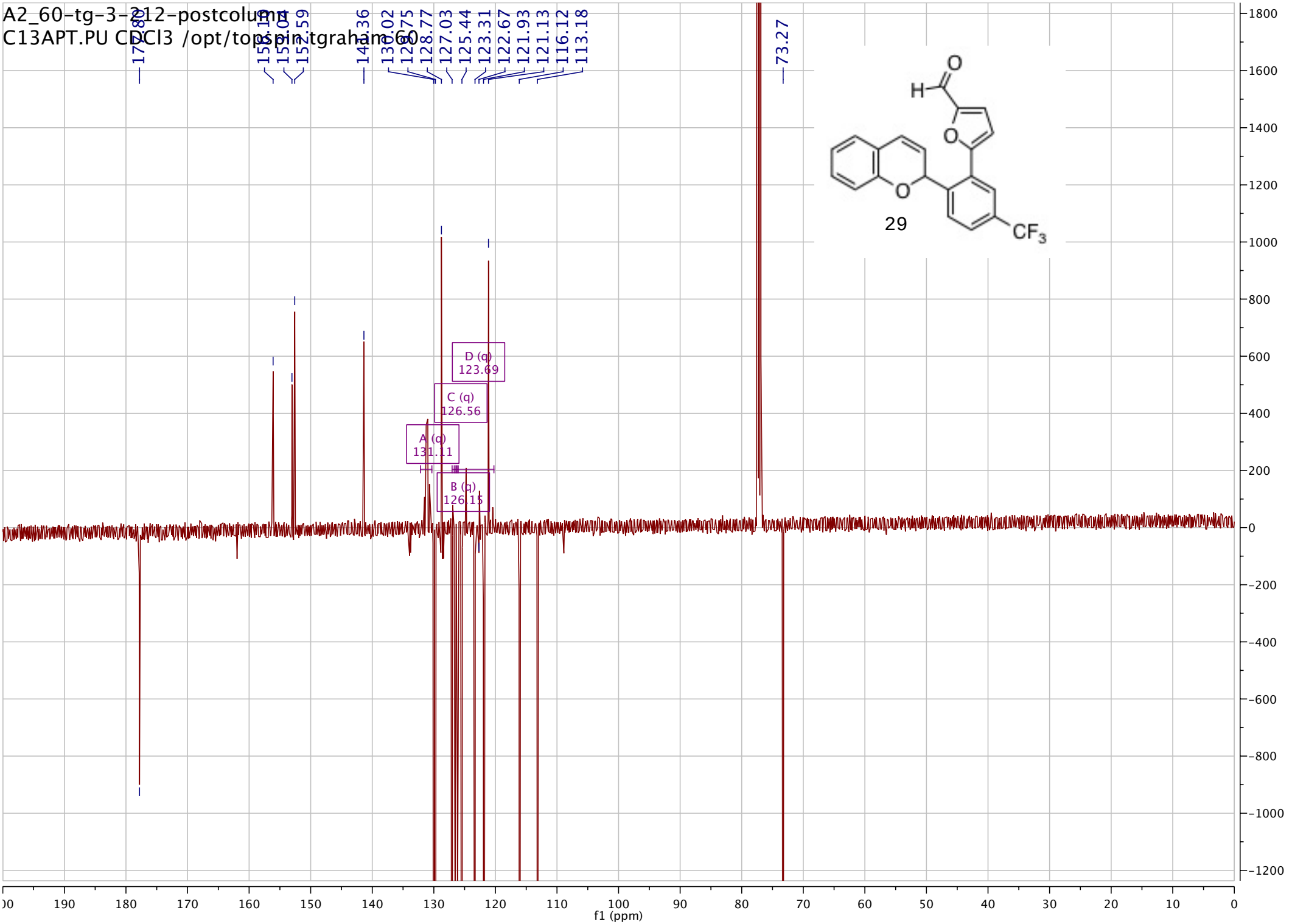

A2_62-tg-3-211-indomethprod
COSYGPSW.PU CDCl3 /opt/topspin tgraham 62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

A2_60-tg-3-212-postcolumn
PROTON.PU CDCl3 /opt/topspin tgraham 60

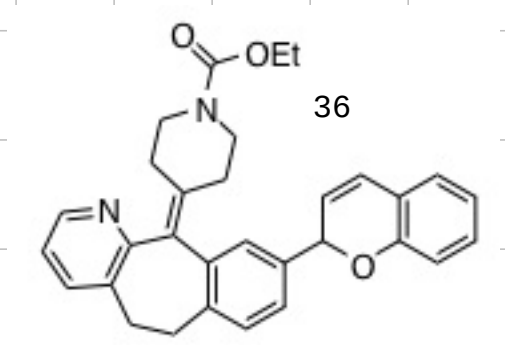


29

A2_60-tg-3-212-postcolumn
C13APT.PU CDCl3 /opt/topspin/tgraham 60

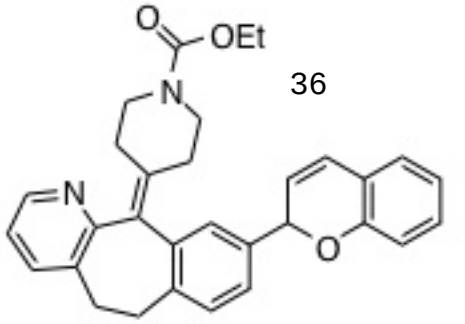


A2_22-tg-3-208-analyticalprod
PROTON.PU CDCl3 /opt/topspin tgraham 22



36

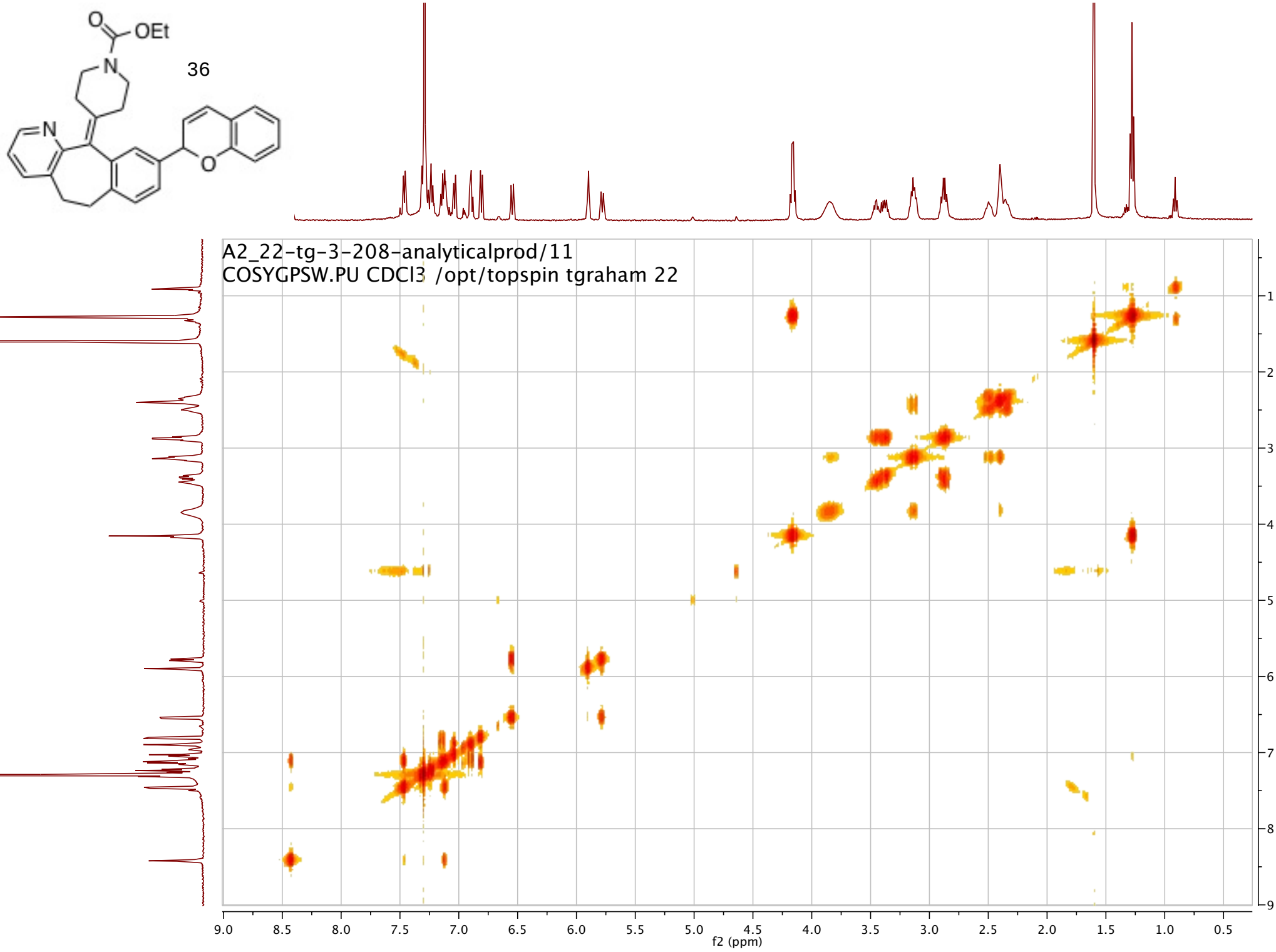
A2_22-tg-3-208-analyticalprod
C13APT.PU CDCl3 /opt/topspin tgraham 22



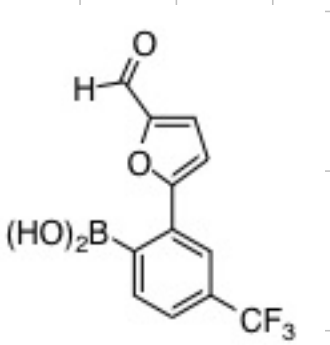
36

166.88 155.51 151.11 144.68 139.97 134.48 134.43 134.03 134.98 135.65 129.78 129.66 129.51 127.93 127.87 126.66 124.94 124.87 124.80 124.75 124.06 122.21 121.25 121.22 115.96 61.35 44.91 31.94 31.69 31.63 14.74

f1 (ppm)

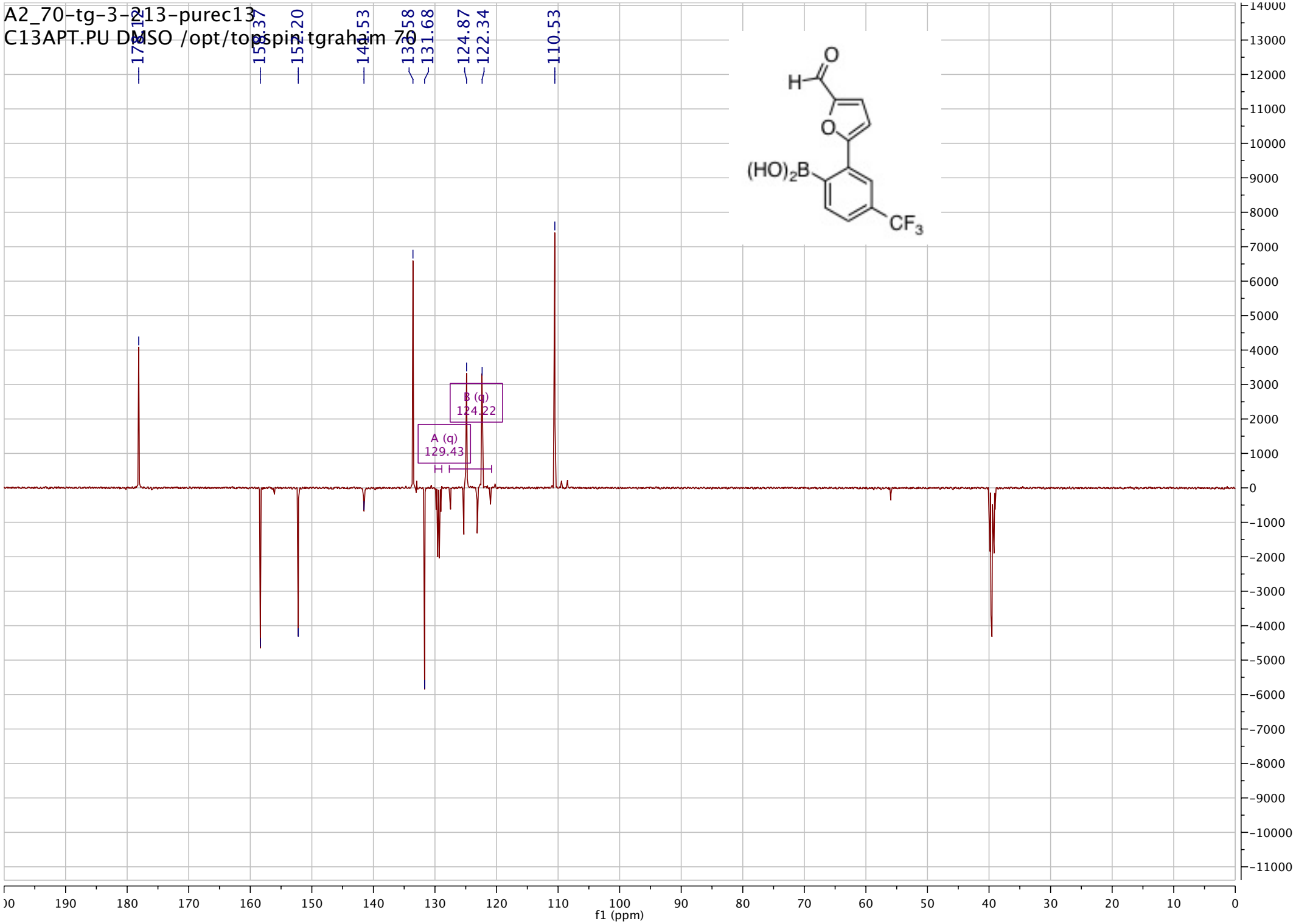

O
OEt
N
36
N
O
A2_22-tg-3-208-analyticalprod/11
COSYGPSW.PU CDCl3 /opt/topspin tgraham 22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
9
f1 (ppm)

NB3_tg-3-213-cleanprod



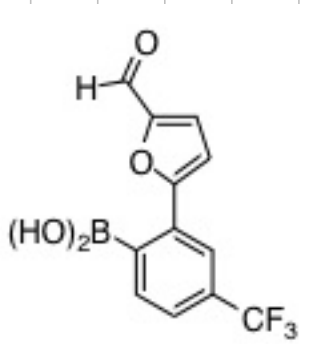
1.00 2.05 1.10 1.11 0.75 1.35 1.10

f1 (ppm)


A2_70-tg-3-213-purec13
C13APT.PU DMSO /opt/topspin tgraham 70
178.11
159.37
152.20
144.53
135.58
131.68
124.87
122.34
110.53
B (q)
124.22
A (q)
129.43
O
H
O
(HO)2B
CF3
f1 (ppm)

NB3_tg-3-213-cleanprod1

-61.35

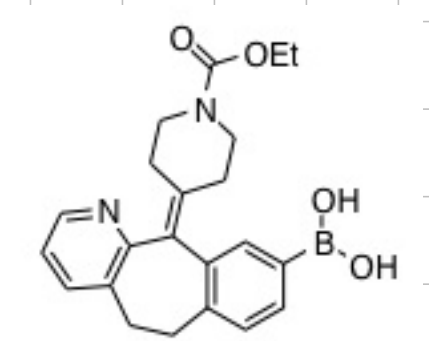


50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240

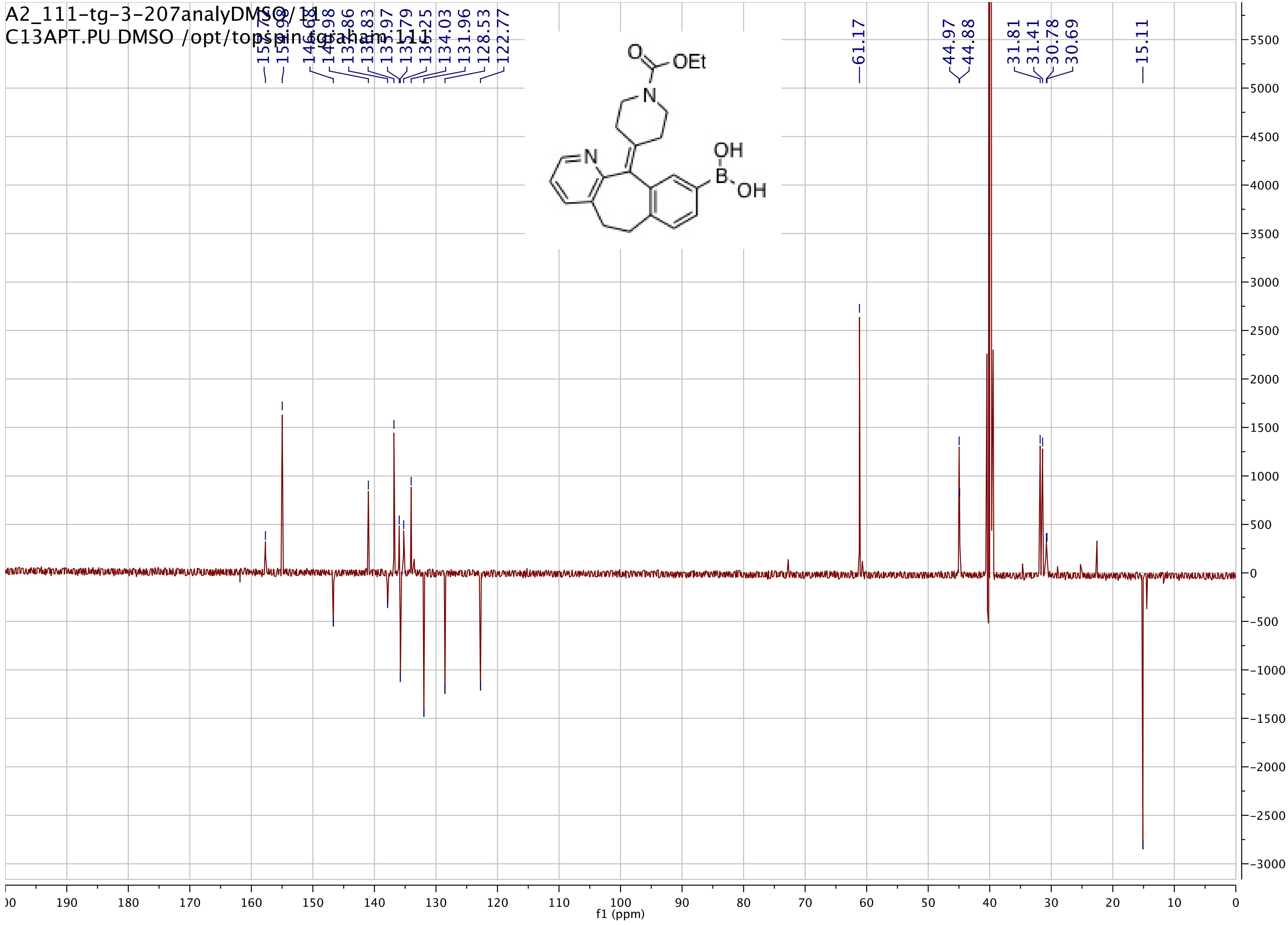
f1 (ppm)

A2_111-tg-3-207analyDMSO
PROTON.PU DMSO /opt/topspin tgraham 111



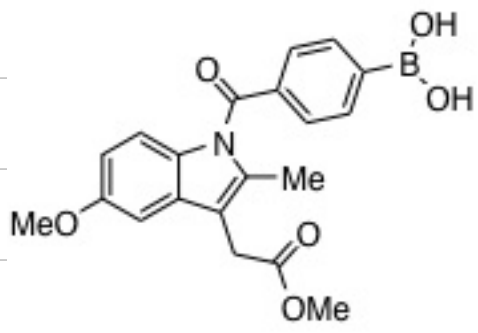
1.00 1.71 2.76 1.03 0.87 2.00 2.04 1.74 2.07 2.06 2.03 2.07 2.92

f1 (ppm)



A2_111-tg-3-207analyDMSO/11
C13APT.PU DMSO /opt/topspin tgraham 111
146.68
140.98
135.97
135.79
135.25
134.03
131.96
128.53
122.77
61.17
44.97
44.88
31.81
31.41
30.78
30.69
15.11
O
OEt
N
N
OH
B
OH
f1 (ppm)

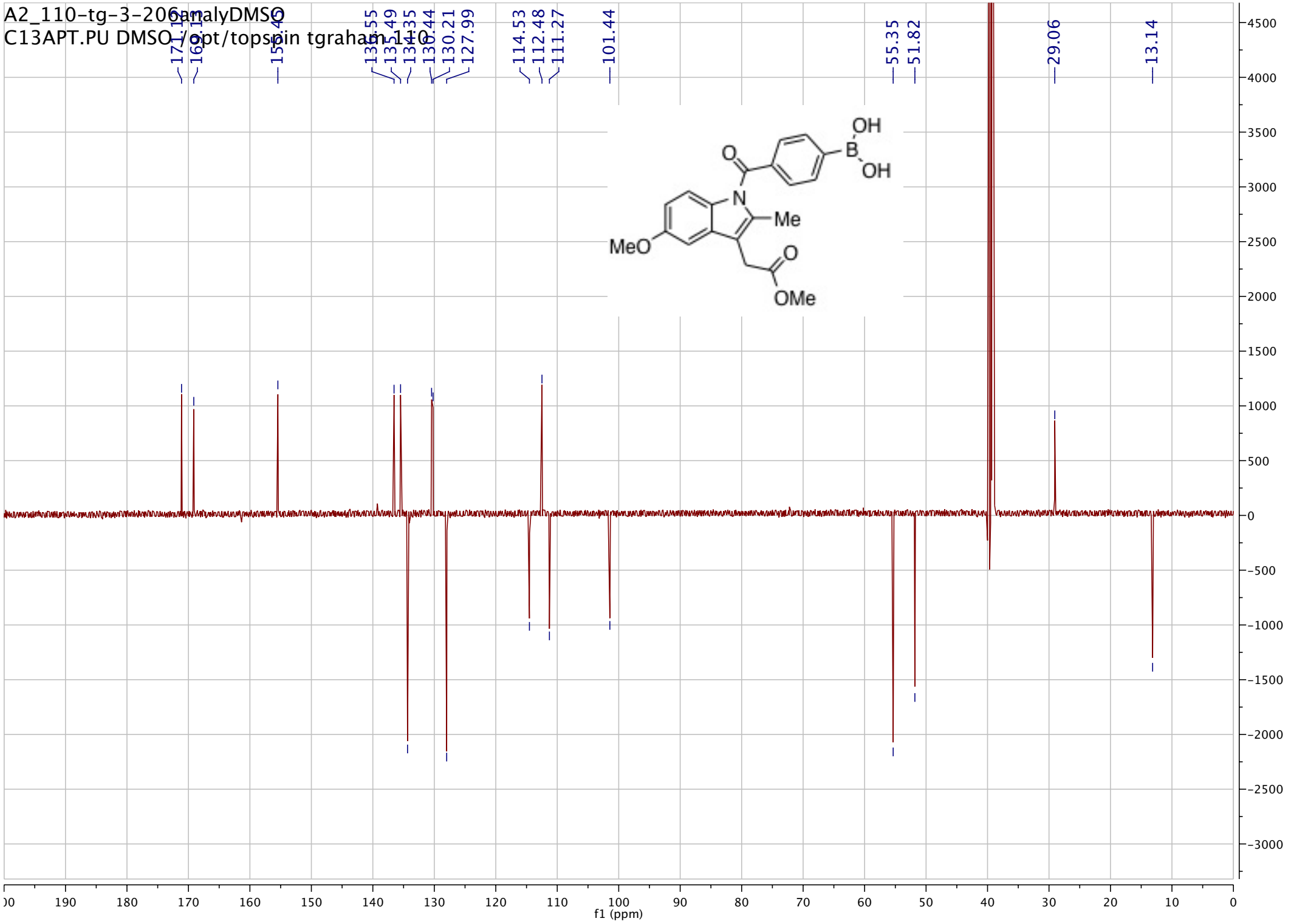
A2_110-tg-3-206analyDMSO
PROTON.PU DMSO /opt/topspin tgraham 110



E (s) 8.40
F (d) 7.94
G (d) 7.60
H (d) 7.02
I (d) 6.85
J (dd) 6.68
C (s) 3.75
B (s) 3.62
D (s) 3.78
A (s) 2.20

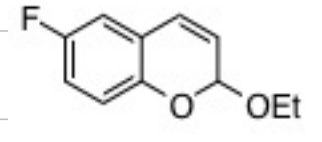
2.00 2.03 2.11 1.15 1.17 1.27 1.83 2.85 2.74 2.84

f1 (ppm)


A2_110-tg-3-206analyDMSO
C13APT.PU DMSO /opt/topspin tgraham 110
169.11
155.40
135.55
135.49
134.35
130.44
130.21
127.99
114.53
112.48
111.27
101.44
55.35
51.82
29.06
13.14
OH
B
OH
O
N
Me
MeO
O
OMe
f1 (ppm)

tg-3-140postcolumn

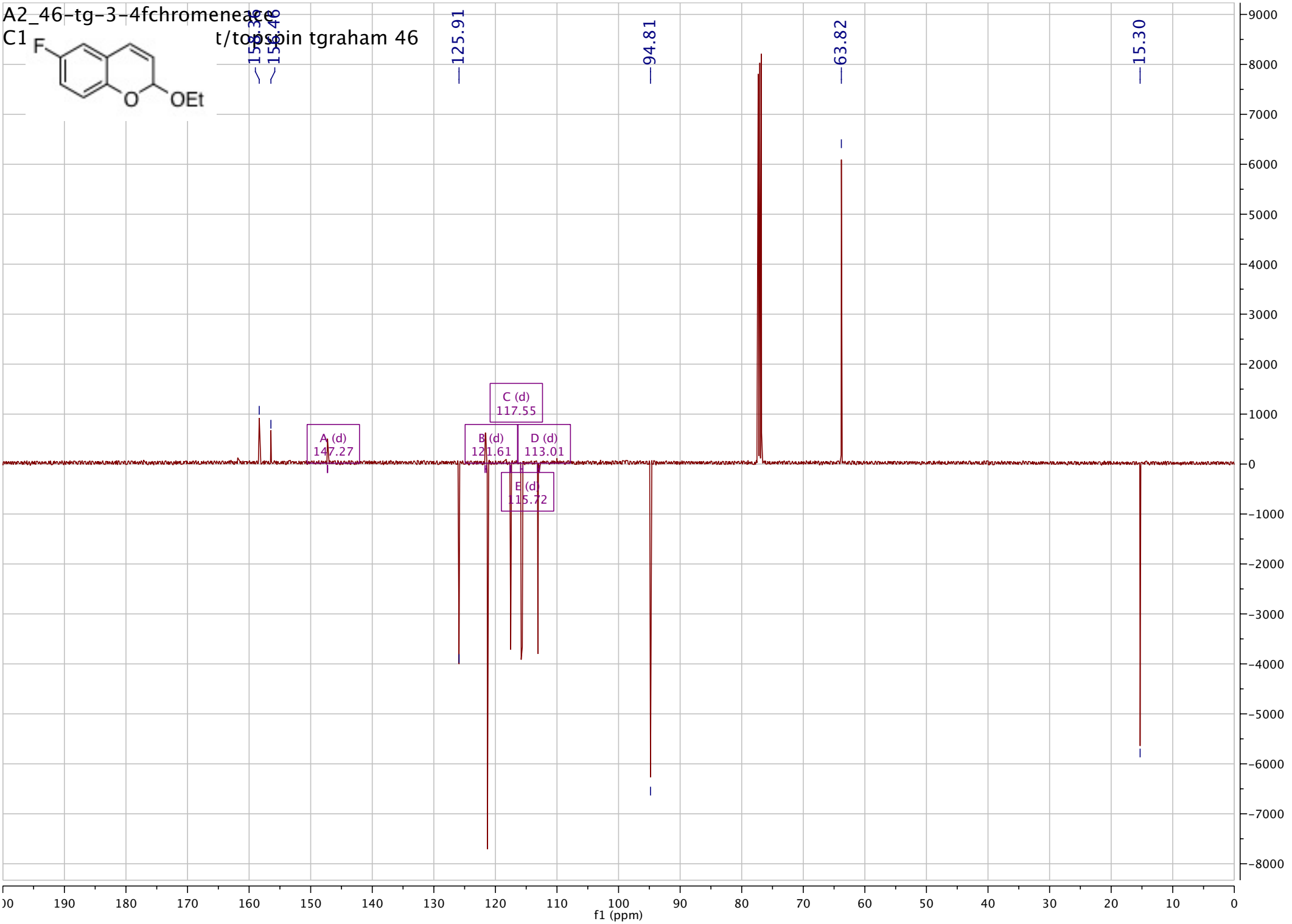
ST ARAMETERS

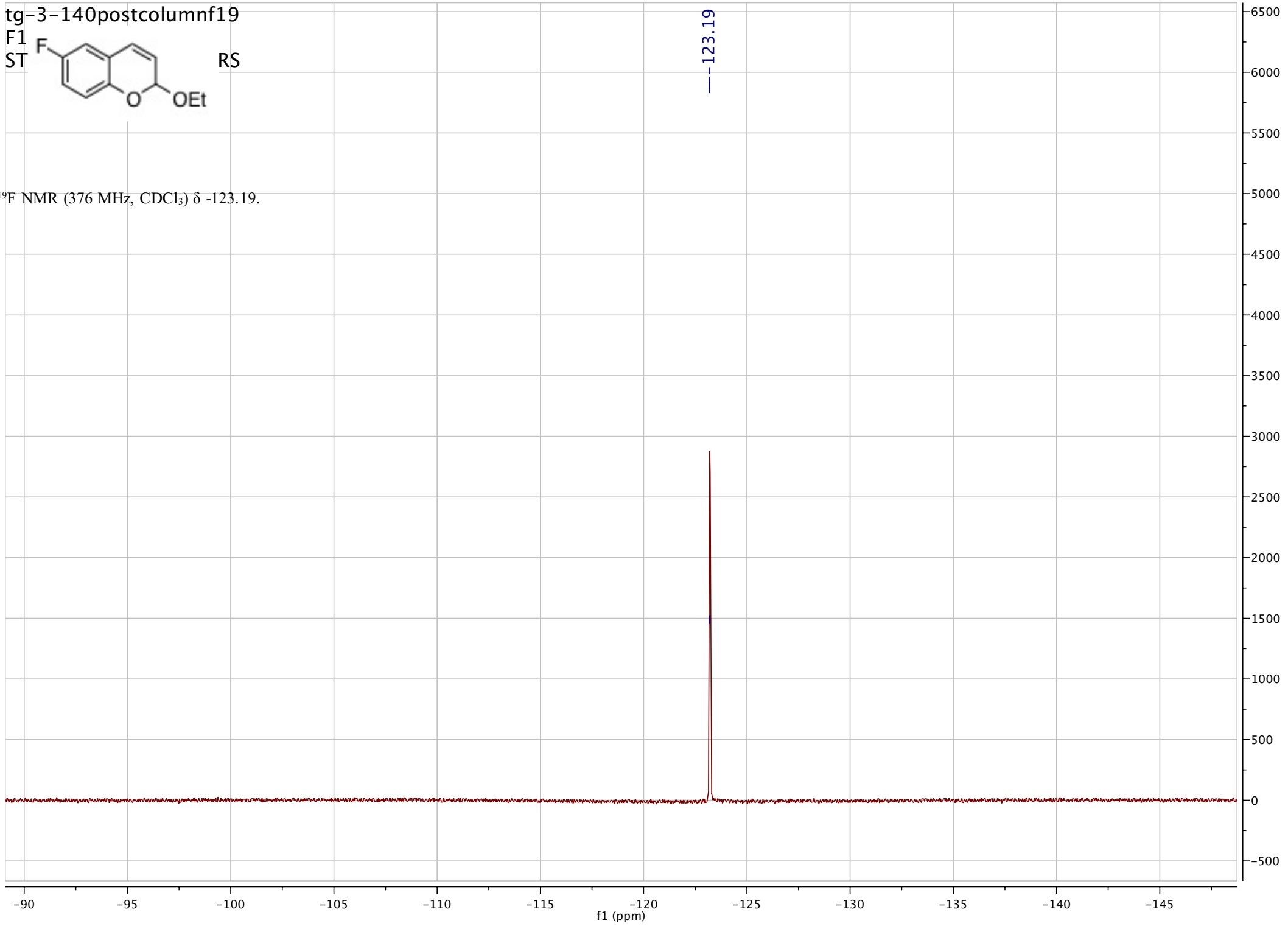


G (dt) 6.85
F (d) 6.67
H (dd) 6.91
E (dd) 5.93
D (d) 5.66
C (dq) 3.93
B (dq) 3.66
A (t) 1.20

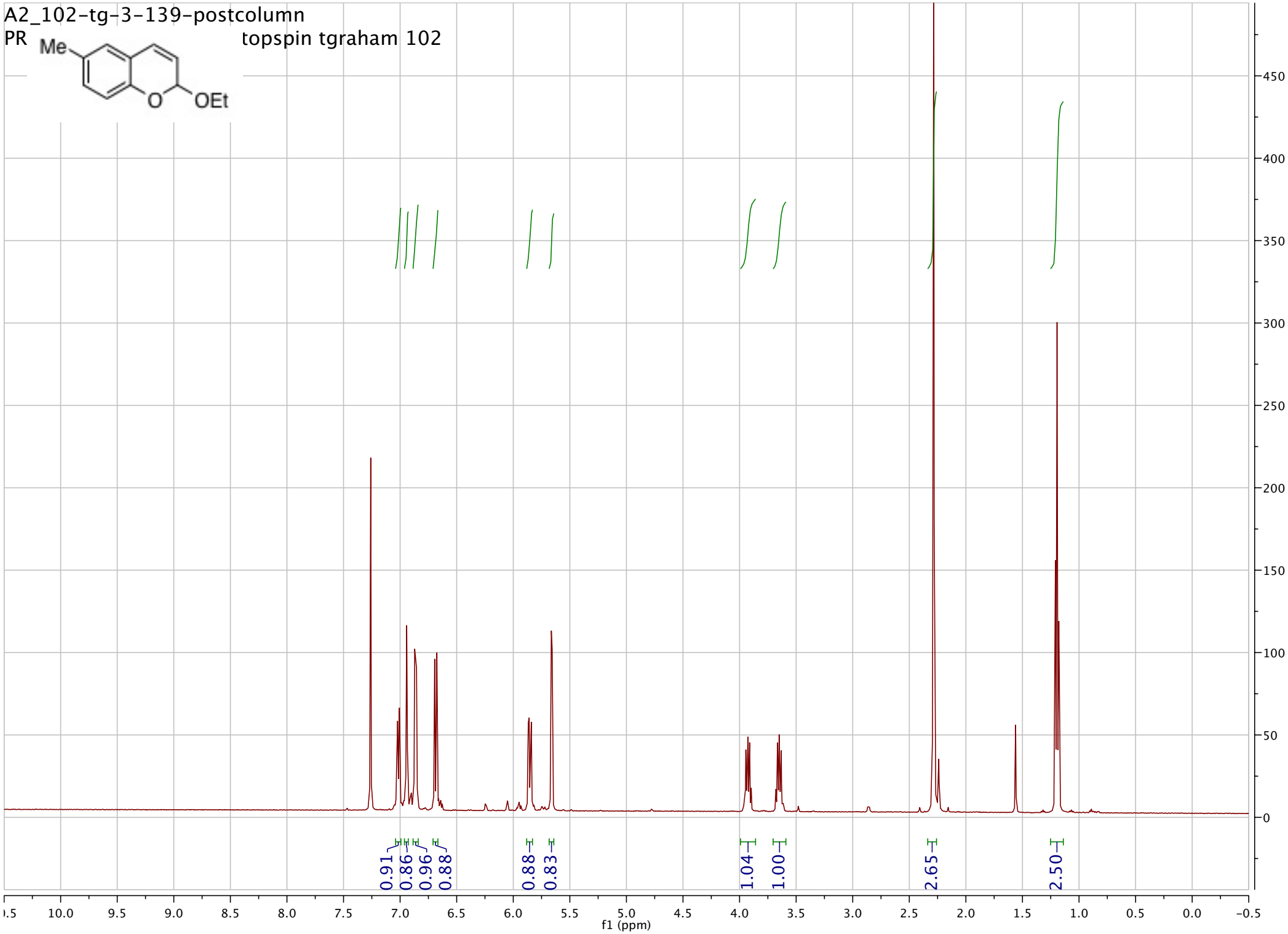
1.61 0.85 0.85 0.86 0.82 0.96 1.00 2.83

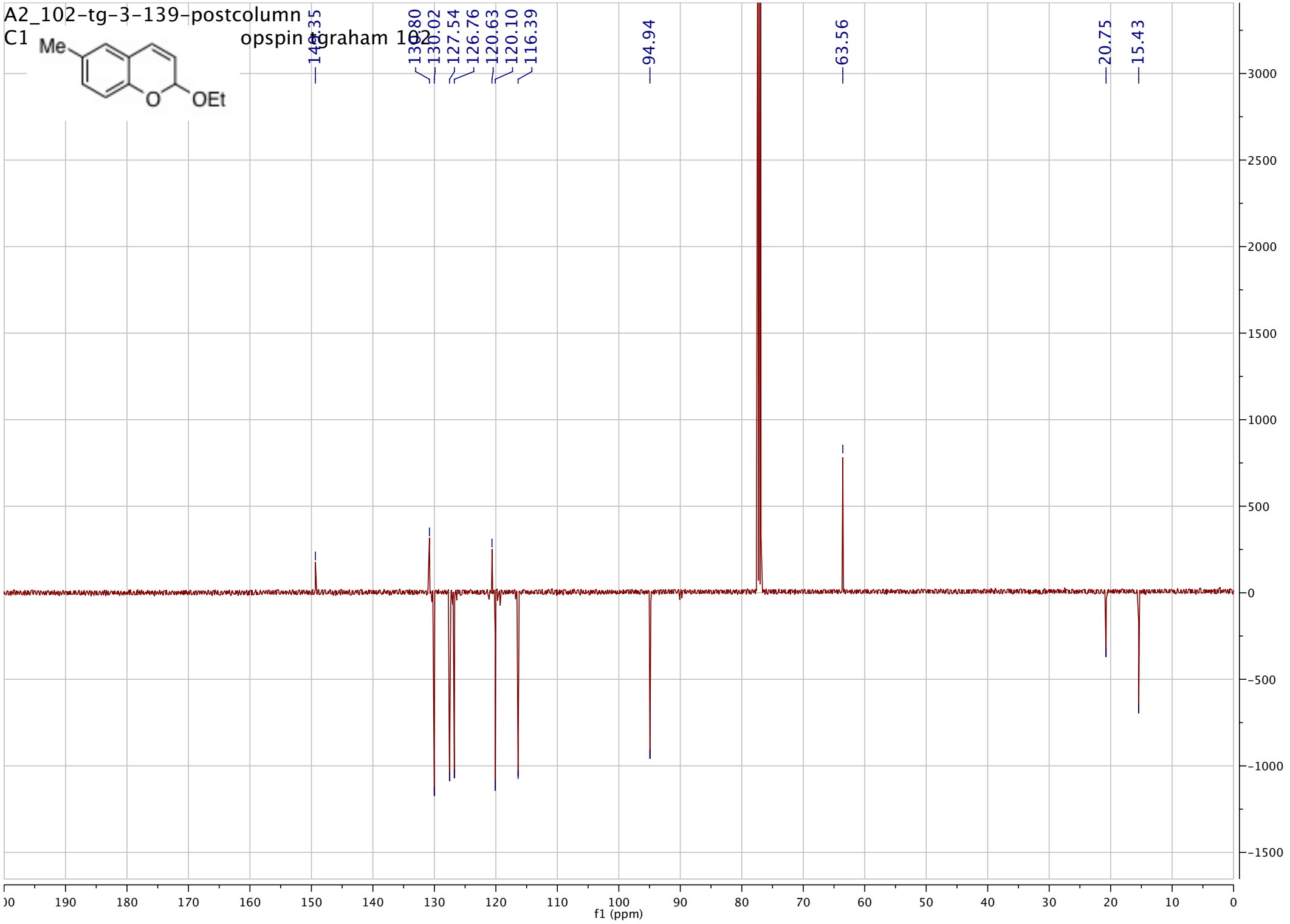
f1 (ppm)

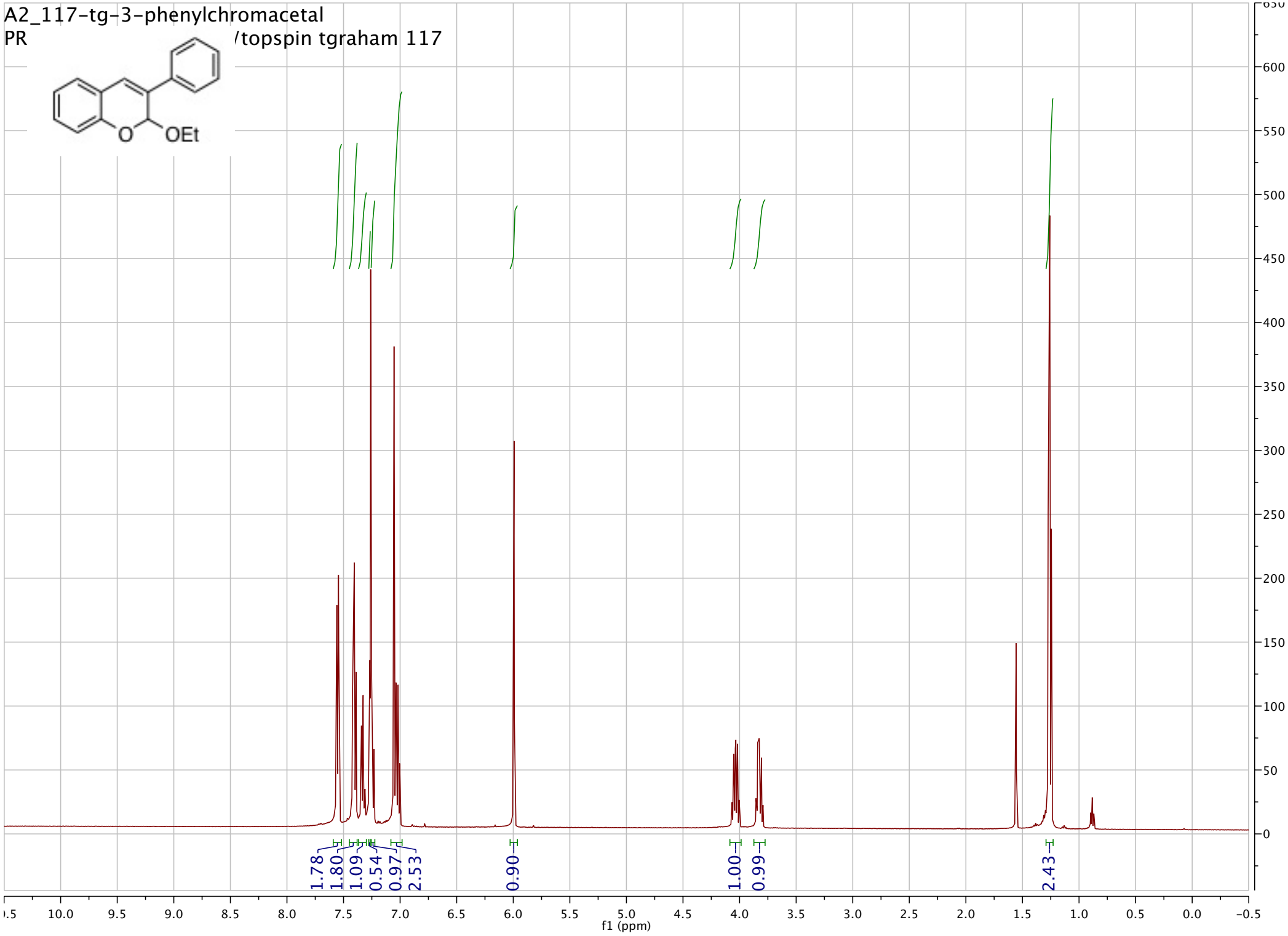

A2_46-tg-3-4fchromeneace
C1 t/topspin tgraham 46
F
O
OEt
155.30
154.48
125.91
94.81
63.82
15.30
A (d)
147.27
B (d)
121.61
C (d)
117.55
D (d)
113.01
E (d)
115.72
f1 (ppm)

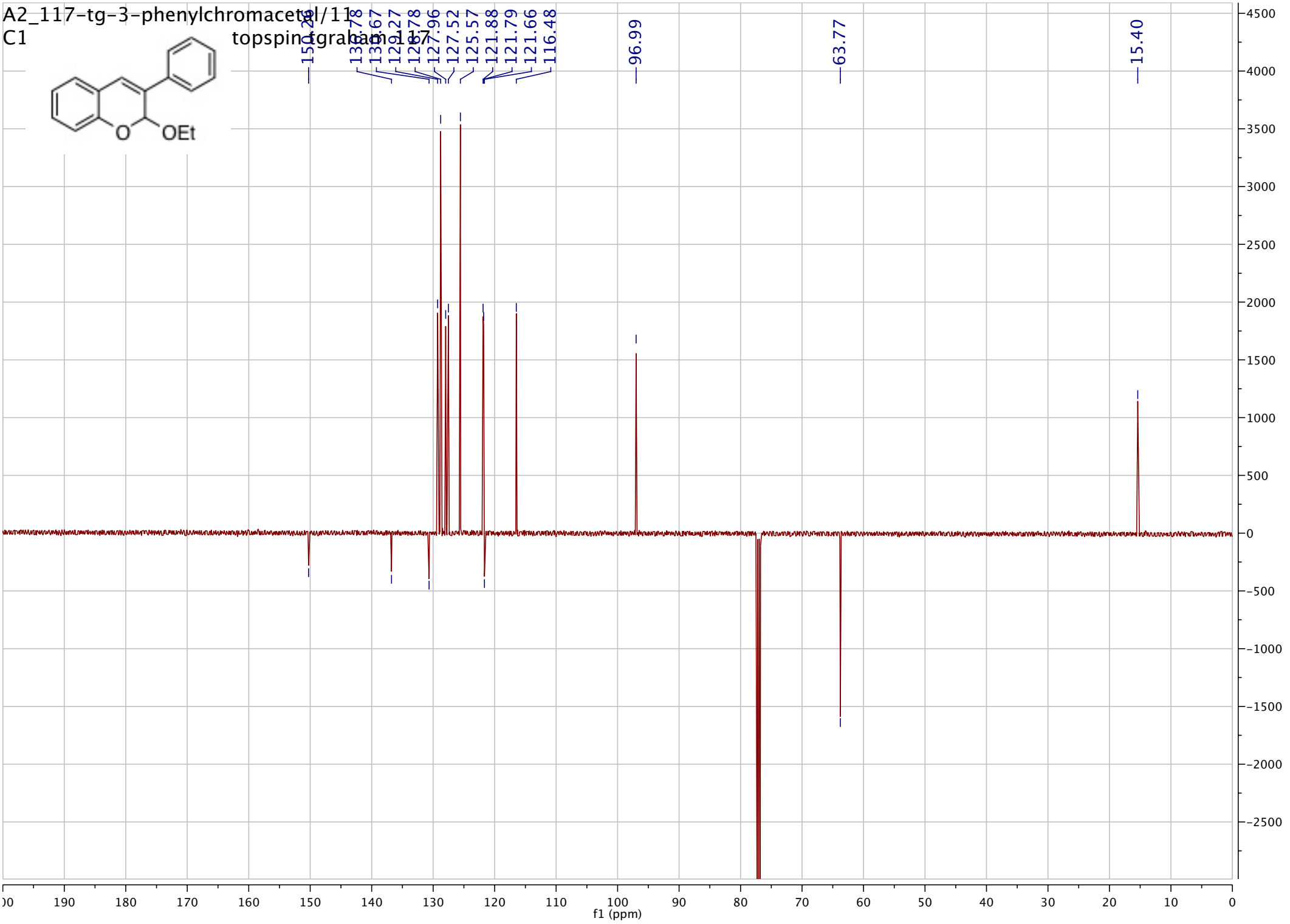


^{19}F NMR (376 MHz, $CDCl_3$) δ -123.19.

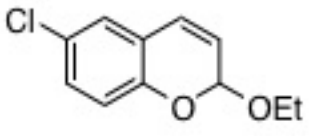

A2_102-tg-3-139-postcolumn
PR
topspin tgraham 102
Me
O
OEt
0.91
0.86
0.96
0.88
0.88
0.83
1.04
1.00
2.65
2.50
f1 (ppm)


A2_102-tg-3-139-postcolumn
C1
opspin tgraham 102
Me
O
OEt
140.35
130.80
130.02
127.54
126.76
120.63
120.10
116.39
94.94
63.56
20.75
15.43
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


A2_117-tg-3-phenylchromacetal
PR
/topspin tgraham 117
O
OEt
1.78
1.80
1.09
0.54
0.97
2.53
0.90
1.00
0.99
2.43
f1 (ppm)


A2_117-tg-3-phenylchromacetal/11
C1
topspin tgraham 117
O
OEt
151.29
133.78
130.67
129.27
128.78
127.96
127.52
125.57
121.88
121.79
121.66
116.48
96.99
63.77
15.40
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

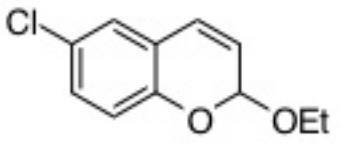
A1_36-ML-1-7



1.00 0.98 1.00 1.01 1.06 1.06 1.18 1.18 2.84

f1 (ppm)

A2_76-tg-chloroacetal
C13APT.PU CDCl3 /opt/topspin tgraham 76



150.05
129.12
126.67
126.33
125.73
122.16
121.30
118.07
95.01
63.95
15.38

4000 3500 3000 2500 2000 1500 1000 500 0 -500 -1000 -1500 -2000 -2500 -3000

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)