Organic Syntheses

Late-stage C-H Functionalization with 2,3,7,8–Tetrafluorothianthrene: Preparation of a Tetrafluorothianthrenium-salt

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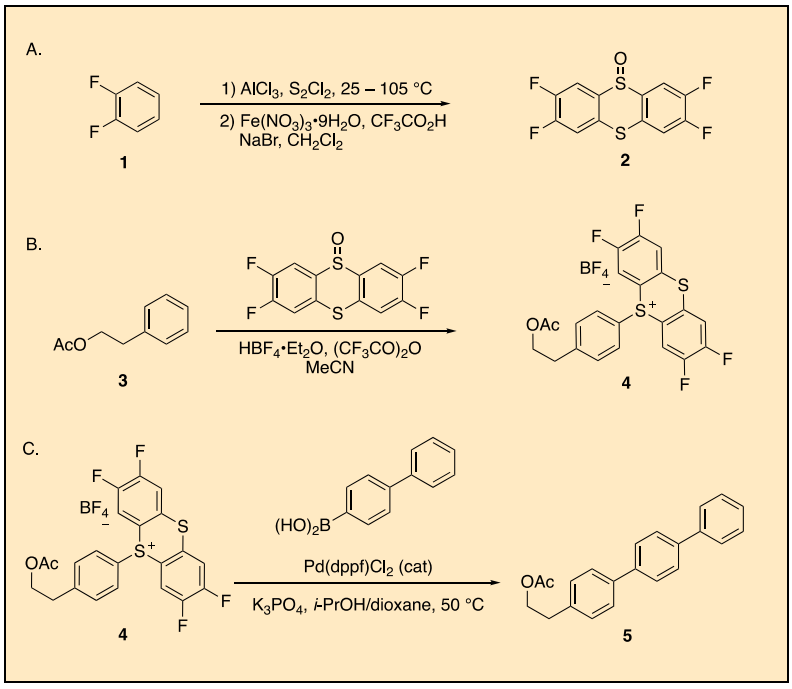
Checked by Maurus Mathis, Jorge A. González, and Cristina Nevado



Procedure (Note 1)

A. 2,3,7,8-Tetrafluorothianthrene-S-oxide (2). In air, a three-necked 1000-mL round-bottomed flask (29/32) is charged with an egg-shaped Teflon coated magnetic stir bar (50 × 17 mm) and aluminium chloride (3.33 g, 25.0 mmol, 0.10 equiv) (Note 2). The central neck of the flask is fitted with a reflux condenser with the outlet passing through a round-bottomed flask (250 mL, 29/32) before entering a Drechsel bottle containing an aqueous sodium hydroxide solution (Note 3). Through a side neck, 1,2-difluorobenzene (0.250 L, 285 g, 2.50 mol, 10.0 equiv) (Note 4) is added to the 1000-mL round-bottomed flask. The flask is fitted with an adapter for the nitrogen inlet on the left neck (Note 5) and a 50 mL dropping funnel on the right neck. Disulfur dichloride (20.0 mL, 33.8 g, 0.250 mol, 1.00 equiv) (Note 6) is added to the addition funnel (Figure 1A), and then added drop-wise at room temperature (Note 7) over a period of 10 min to the stirred reaction mixture (Note 8). Upon addition of the disulfur dichloride, the solution becomes black (Figure 1B) and evolves HCl gas. After complete addition of the disulfur dichloride, the reaction mixture is heated at a gentle reflux (105 °C, bath temp)) using a silicon oil bath (Note 9) for 1 h. The oil bath is then replaced by an ice water bath, and MeOH (200 mL) is added to the reaction mixture via the addition funnel (Note 10). The dark color quickly dissipates from the reaction mixture, resulting in a light yellow suspension with a colorless solid (2,3,7,8-tetrafluorothianthrene) (Figure 1C).

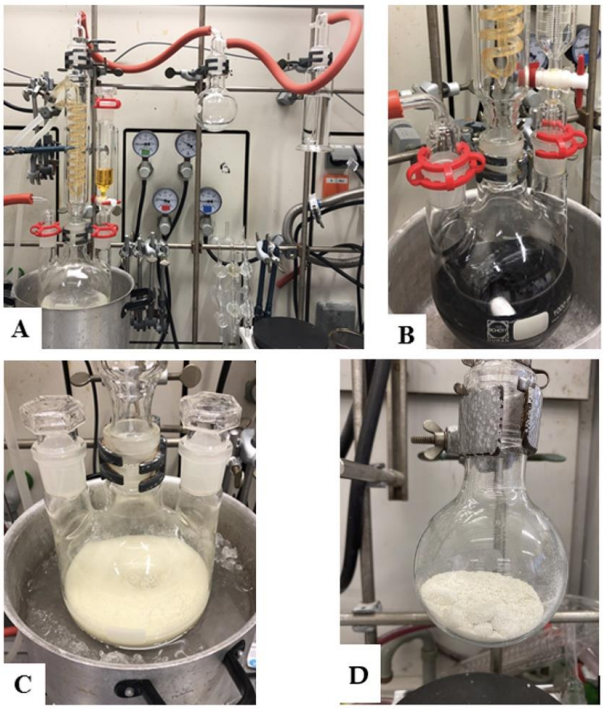


Figure 1. A) Reaction set-up, B) the reaction mixture after disulfur dichloride addition, C) reaction mixture after the methanol quench, and D) crude 2,3,7,8-tetrafluorothianthrene (photos A, B, and C were provided by the submitters; photo D was provided by the checkers)

The slurry is stirred for 30 min in the ice water bath, and the solid material is subsequently filtered by vacuum filtration (Note 11). The filter cake is washed with chilled methanol (2 × 50 mL) (Notes 10 and 12), and the resulting off-white solid is transferred into a 500-mL one-necked, round-bottomed flask (29/32) and dried under vacuum (Note 13) for 18 h at room temperature. The resulting 23.82 g off-white solid (Figure 1D) contained 74.3% of 2,3,7,8-tetrafluorothianthrene by weight (Note 14), which is used without any further purification in the subsequent reaction (Notes 15 and 16).

In air, the 500-mL one-necked, round-bottomed flask (29/32) containing 23.82 g of crude 2,3,7,8-tetrafluorothianthrene (wt% = 74.3%; Note 14) is charged with an egg-shaped Teflon-coated magnetic stir bar (27 × 10 mm), DCM (175 mL, c = 0.35 M), $Fe(NO_3)_3 \cdot 9H_2O$ (42.2 g, 105 mmol, 1.7 equiv),

NaBr (443 mg, 4.21 mmol, 0.07 equiv), and TFA (6.60 mL, 9.83 g, 86.2 mmol, 1.4 equiv) (Note 17). After addition, the flask is sealed with a rubber septum (Note 18). The resulting light brown suspension (Figure 2B) is stirred at room temperature for 20 h (Note 19). After this time, deionized water (150 mL) is added (Figure 2C).

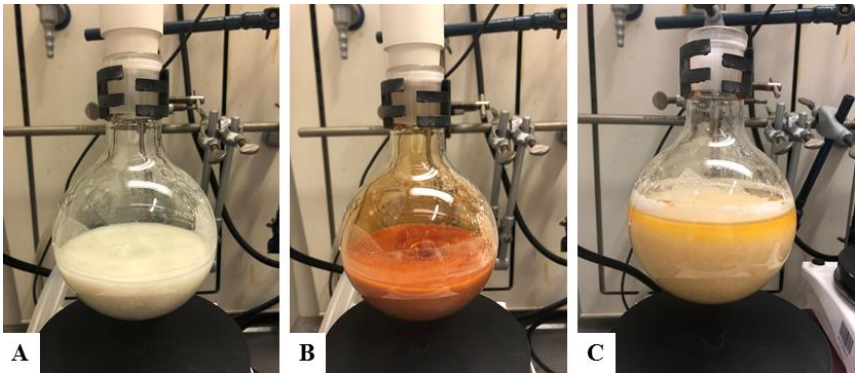


Figure 2. The reaction mixture (A) before addition of TFA, (B) after addition of TFA, and (C) after addition of water (photos provided by submitters)

The suspension is filtered by vacuum filtration (Note 11), the filtrate is poured into a 500-mL separating funnel, and the layers are separated. The aqueous layer is extracted with DCM (2 × 150 mL). The filter cake is added to the combined organic layers, and the suspension is concentrated under reduced pressure (525 to 20 mmHg, 40 °C) (Note 20). MeCN (50 mL) (Note 21) is added to the residue, and the resulting suspension is filtered by vacuum filtration (Note 11). The solid is washed with MeCN (3 × 25 mL) (Note 12) (Figure 3A), which removes the majority of the red color. The solid is transferred into a 1000-mL one-necked, round-bottomed flask. Toluene (600 mL) (Note 22) is added, the flask is equipped with a reflux condenser, and the mixture is heated to reflux (110 °C) using a silicone oil bath. After 10 min at this temperature, heating and stirring is turned off and the mixture is left in the oil bath for 5 min. Subsequently, the mixture is decanted into a 1000-mL Erlenmeyer flask in order to remove the red-brown solid. Then the toluene solution is allowed to cool down to room temperature for 3 h. The obtained crystals (Figure 3B) are collected by vacuum filtration (Notes 11 and 23), washed with Et_2O (2 × 50 mL) (Notes 12 and 24) (Figure 3C), and

transferred into a 500-mL one-necked, round-bottomed flask. The filtrate is concentrated via rotary evaporator (50 mmHg, 40 °C), and acetone (600 mL) is added to the resultant solid (Note 25). The mixture is heated at 60 °C using a silicone oil bath for 5 min. After this time the mixture is allowed to stand for 5 min. Subsequently, the mixture is decanted into a 1000-mL one-necked, round-bottomed flask (29/32). The solution is concentrated via rotary evaporator (400 mmHg, 40 °C). The product is transferred into a 250-mL one-necked, round-bottomed flask (29/32) and recrystallized from toluene (80 mL, 110 °C) using a silicone oil bath. After cooling to room temperature for 1 h the colorless crystals are collected by vacuum filtration (Note 11), washed with Et_2O (2 × 25 mL) (Note 12) (Figure 3D)and combined with the first batch of crystals in the 500-mL one-necked, round-bottomed flask (29/32). The combined batches are recrystallized again from toluene (240 mL, 110 °C) using a silicone oil bath. After cooling to room temperature for 2 h, the off-white crystals are collected by vacuum filtration (Note 11), washed with Et_2O (2 × 50 mL) (Note 12) and ground into a fine powder using a porcelain mortar. The resulting off-white powder is transferred into a 100-mL one-necked, round-bottomed flask and is dried under vacuum for 18 h at room temperature to afford 11.33 g of *2,3,7,8-tetrafluorothianthrene-S-oxide (2)* with a purity of 98.3% (15 % yield over two steps) (Figure 3E) (Notes 26 and 27).

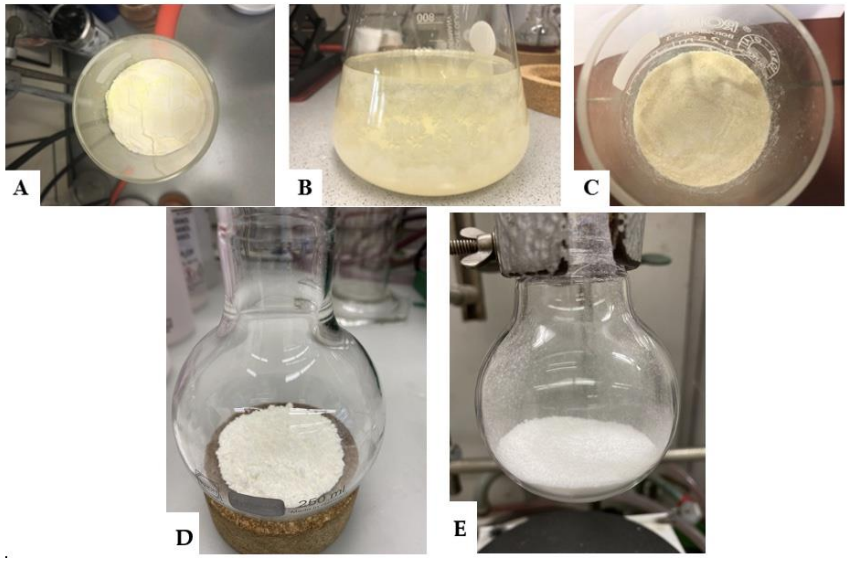


Figure 3. A) Appearance of the crude product, B) the crystals during recrystallization, C) the product after filtration, D) second batch crystals, and E) final recrystallized product (photos A, B, and C were provided by the submitters; photos D and E were provided by the checkers)

B. 2-*Phenethyl acetate-derived tetrafluorothianthrenium salt (**4**).* In air, a 250 mL one-necked, round-bottomed flask (29/32), equipped with a Teflon-coated magnetic stir bar (40 × 7 mm) is charged with 2-phenethyl acetate (6.98 mL, 7.19 g, 43.8 mmol, 1.00 equiv), acetonitrile (170 mL, c = 0.25 M) and TFAA (18.3 mL, 27.6 g, 131 mmol, 3.00 equiv) (Note 28). The reaction mixture is cooled to 0 to 5 °C with an ice water bath. *2,3,7,8-Tetrafluorothianthrene-S-oxide (**2**)* (13.32 g, 43.8 mmol, 1.00 equiv) (Note 26) is added, followed by the addition of tetrafluoroboric acid diethyl ether complex (8.9 mL, 10.6 g, 65.4 mmol, 1.49 equiv) (Note 29), resulting in a dark purple suspension (Figure 4B). The mixture is stirred at 0 to 5 °C for 1 h, after which the ice water bath is removed, and the reaction mixture is stirred for additional 23 h at room temperature (Note 30).

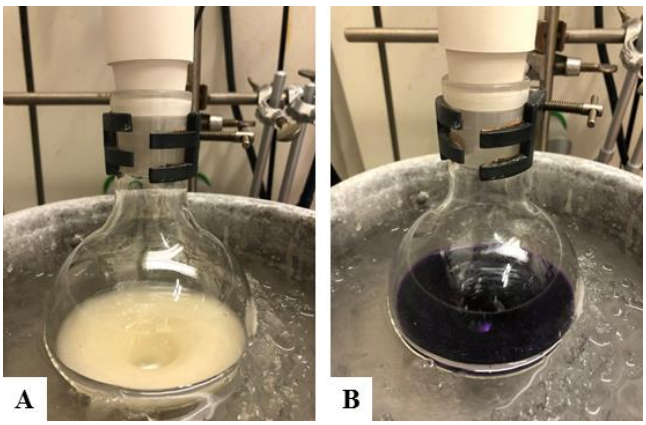


Figure 4. A) Reaction mixture before addition of tetrafluoroboric acid diethyl ether complex (A) and (B) after addition of tetrafluoroboric acid diethyl ether complex (photos provided by submitters)

After this time, the reaction mixture is concentrated on rotary evaporator (170 to 15 mmHg, 40 °C). *i*-PrOH (70 mL) (Note 31) is added in 10 mL portions during which the purple color disappears and a colorless solid precipitates (Figure 5A). The suspension is cooled to 0 to 5°C with an ice water bath, stirred at this temperature for 10 min, and then filtered (Note 11). The filter cake is washed with *i*-PrOH (15 mL) and with isohexane (100 mL) (Notes 12 and 32). The crude product is purified by flash chromatography on silica gel (Note 33), and the fractions containing the product are collected and concentrated via rotary evaporator (525 to 15 mmHg, 40 °C). The resulting colorless solid is ground into a fine powder using a porcelain mortar, transferred into a 100-mL one-necked, round-bottomed flask (29/32), and dried under vacuum at room temperature for 18 h to afford 17.9 g (76% yield) of 2-*phenethyl acetate-derived tetrafluorothianthrenium salt (**4**)* with a purity of 99.9% (Notes 34 and 35) (Figure 5B).

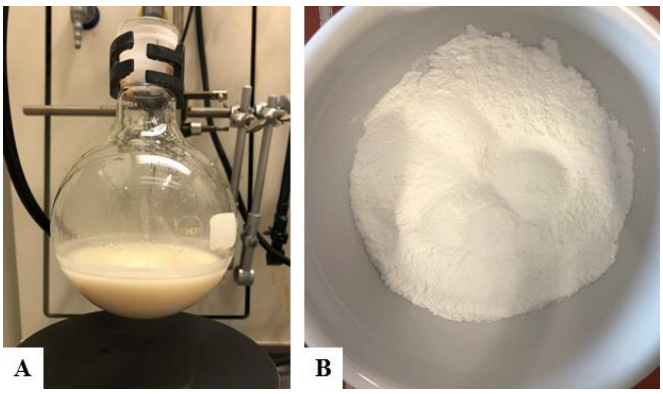


Figure 5. A) Appearance of the reaction mixture after the isopropanol quench, B) purified product (photos provided by submitters)

*C. [4-(4-Phenylphenyl)phenyl] ethyl acetate (**5**).* A 500 mL two-necked, round-bottomed flask (29/32 and 14/23), equipped with a glass stopper on the small neck (14/23), a reflux condenser on the large neck (29/32) with a nitrogen inlet on top and a Teflon-coated magnetic stir bar (30 × 7 mm), is evacuated and flame-dried. After cooling down to room temperature again, the flask is filled with nitrogen. Under nitrogen (Note 36), the flask is charged via the small neck (14/23) with *2-phenethyl acetate derived tetrafluorothianthrenium salt (**4**)* (17.94 g, 33.3 mmol, 1.00 equiv), 4-biphenylboronic acid (7.26 g, 36.7 mmol, 1.10 equiv), Pd(dppf)Cl_2 (490 mg, 0.530 mmol, 2.00 mol%), K_3PO_4 (21.23 g, 100 mmol, 3.00 equiv), iPrOH (183 mL), and 1,4-dioxane (183 mL) (Notes 23 and 37) (Figure 6A). The flask is sealed with a glass stopper, and the reaction mixture is left stirring for 10 min under a nitrogen atmosphere at room temperature. After this time, the reaction mixture is heated to 50 °C using a silicone oil bath. During heating the suspension's color changes to bright orange (Figure 6B). The reaction mixture is stirred at 50 °C for 5 h (Note 38) under nitrogen atmosphere. After this time, the reaction mixture is cooled to room temperature. The solvent is removed via rotary evaporation (150 to 22 mmHg, 40 °C). Ethyl acetate (200 mL) (Note 39) is added, the mixture is stirred (300 rpm), and deionized water (200 mL) is added. The mixture is transferred into a 1 L separating funnel and additional ethyl acetate (100 mL) and deionized water (100 mL) are added. The layers are separated, and the aqueous layer is extracted with ethyl acetate (2 × 300 mL). The organic layers

are combined, dried over 70 g of Na_2SO_4, filtered, and concentrated in vacuo (135 to 75 mmHg, 40 °C). The crude product is purified by flash chromatography on silica gel (Note 40). The fractions containing the product are collected and concentrated via rotary evaporator (525 to 15 mmHg, 40 °C). The off-white solid is transferred into a 250 mL one-necked, round-bottomed flask and recrystallized with 80 mL of ethyl acetate (77 °C) using a silicone oil bath as the heat source. The mixture is allowed to cool to room temperature for 1 hour and is subsequently filtered (Note 41) and washed with Et_2O (2 × 15 mL). The colorless crystals are grounded into a fine powder using a porcelain mortar, and the colorless powder is transferred into a 100-mL one-necked, round-bottomed flask. The powder is dried under vacuum at room temperature for 18 h to afford 8.16 g (77%) of *[4-(4-phenylphenyl)phenyl] ethyl acetate (**5**)* with a purity of 99.9 % (Notes 42 and 43) (Figure 6C).

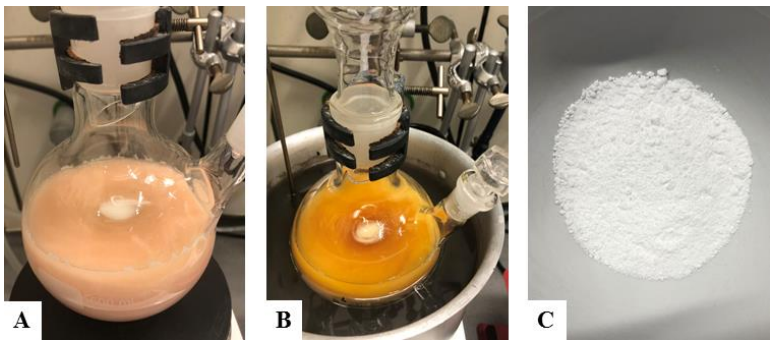


Figure 6. A) Reaction mixture at room temperature, B) after being heated to 50 °C, C) purified product (photos provided by submitters)

Notes

1. Prior to performing each reaction, a thorough hazard analysis and risk assessment should be carried out with regard to each chemical substance and experimental operation on the scale planned and in the context of the laboratory where the procedures will be carried out. Guidelines for carrying out risk assessments and for analyzing the hazards associated with chemicals can be found in references such as Chapter 4 of "Prudent

Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). See also "Identifying and Evaluating Hazards in Research Laboratories" (American Chemical Society, 2015) which is available via the associated website "Hazard Assessment in Research Laboratories" at https://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety/hazard-assessment.html. In the case of this procedure, the risk assessment should include (but not necessarily be limited to) an evaluation of the potential hazards associated with aluminium chloride, sodium hydroxide, 1,2-difluorobenzene, disulfur dichloride, methanol, 2,3,7,8-tetrafluorothianthrene, dichloromethane, Iron(III) nitrate nonahydrate, sodium bromide, trifluoroacetic acid, acetonitrile, toluene, diethyl ether, acetone, 2,3,7,8-tetrafluorothianthrene-S-oxide, 2-Phenylethyl acetate, trifluoroacetic anhydride, tetrafluoroboric acid diethyl ether complex, isopropyl alcohol, isohexane, 2-phenylethyl acetate derived tetrafluorothianthrenium salt, 4-biphenylboronic acid, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), tripotassium phosphate, 1,4-dioxane, ethyl acetate, [4-(4-phenylphenyl)-phenyl] ethyl acetate; as well as the proper procedures for quenching gaseous HCl which is evolving during a reaction.

2. Aluminium chloride (anhydrous, granular, 99%) was obtained from Alfa Aesar and used as received.
3. Sodium hydroxide (NaOH) (99%) was purchased from VWR chemicals and used as received. The Drechsel bottle was filled with aqueous NaOH solution (175 mL, 12.5 M). This HCl quenching setup using NaOH produces large amounts of heat and should be carried out with a glass container/flask rather than a plastic drying tube.
4. 1,2-Difluorobenzene (98%) was purchased from Fluorochem and used as received. The quantity of 1,2-difluorobenzene used in the reaction was consistent with its use as a solvent. When less 1,2-difluorobenzene was used, larger quantities of side-products resulted, which could not be removed by crystallization.
5. Nitrogen was used to purge HCl from the reaction flask and prevent backflow of the aqueous sodium hydroxide solution. Alternatively, argon can be used.
6. Disulfur dichloride (98%) was purchased from Sigma-Aldrich and used as received.

7. Room temperature throughout this manuscript refers to a temperature between 23 °C and 25 °C.
8. The stir plate was purchased from Heidolph Instruments GmbH & Co. KG. It has an input power of 230–240 V (50–60 Hz, 825 W), and the stirring range is from 100 rpm to 1400 rpm. Unless otherwise indicated, 500 rpm was used for stirring.
9. The silicone oil for the oil bath was purchased from abcr GmbH & Co. KG. The boiling point is over 205 °C. The oil in the oil bath should be level with the level of the reaction mixture in the reaction flask while heating. Unless otherwise indicated, the reported temperatures throughout this context refer to temperatures of oil in oil baths which were detected by the stirring plates' external temperature detectors. Approximately 15 min were necessary to increase temperature from 25 to 105 °C.
10. Methanol (MeOH, ≥ 99.8%) was purchased from Sigma-Aldrich and used as received. In order to precool the methanol, the required amount was placed in a 500 mL Erlenmeyer flask and cooled in an ice-water bath to 2–5 °C for 10 min. The addition was performed in 50 mL portions via the addition funnel.
11. Büchner funnel VitraPOR® with Por. 4 and a capacity of 125 mL was used.
12. To rinse the impurities out of the flask, manual stirring with a stainless spatula was applied to thoroughly mix the rinse solvent with the solid. When the filtration was complete, the filter cake was pressed with the top of a glass stopper to remove as much liquid as possible.
13. The vacuum pump was supplied by Vacuubrand GmbH & Co. KG. Vacuum refers to pressure lower than 0.075 mmHg.
14. Quantitative ^{19}F NMR (471 MHz, $CDCl_3$) was performed using 4,4'-difluorobenzophenone (≥ 99% purity, Sigma Aldrich) as an internal standard. The NMR sample was prepared by dissolving 4,4'-difluorobenzophenone (14.3 mg) and 2,3,7,8-tetrafluorothianthrene (10.3 mg) in $CDCl_3$ (0.5 mL) in a 5 mm NMR tube. The sample was subsequently analyzed by ^{19}F NMR spectroscopy with the following parameters: no. of scans: 32, D1: 20 s, rotation frequency: 15 Hz, spectral width: 49.7924 ppm, transmitter frequency offset: –121.3 ppm). Integration of the fluorine signals showed a 1:0.81 ratio, corresponding to 74.3 wt% of 2,3,7,8-tetrafluorothianthrene.

15. The off-white solid has the following characteristics: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (t, J = 8.5 Hz, 4H). ^{19}F NMR (471 MHz, 298 K, $CDCl_3$) δ: –136.86 (t, J = 8.6 Hz).
16. Purification of 2,3,7,8-tetrafluorothianthrene: A column (1 cm diameter) with a glass frit was charged with copper powder (2.9 g, 4.56 mmol) (powder, 99.999%, trace metal basis, Sigma Aldrich) The column was purged with argon, then, with the stopcock closed, 7 mL of concentrated HCl (37-38%, JT-Baker) was added to the copper powder, put under argon atmosphere, and gently agitated to liberate gas bubbles. After 5 min the stopcock was opened, and a positive pressure of argon was applied so that the concentrated HCl was eluted at a rate of about two drops·s^{-1} (total elution time about 2 min). The copper bed was washed twice with 10 mL of Milli-Q water by applying a positive pressure of argon (2 drops/s, about 2 min elution time for each wash). Nitrogen was allowed to flow through the column-bed for 5 min to remove as much water as possible. Then the copper was washed twice with 10 mL of anhydrous acetone using a positive pressure of argon (99.8%, ExtraDry, AcroSeal™, purchased from Fisher Scientific; about 2 min elution time for each wash). Again, argon was allowed to flow through the bed for 5 min to remove as much acetone as possible. Argon pressure was released, and the stopcock was closed. Then a solution of 320 mg of contaminated TFT in 10 mL of DCM was added to the column and allowed to sit with the stop cock closed for 10 min (all under argon atmosphere). At this point, the sample was allowed to elute into a 50 mL round-bottomed flask (approx. 10 min). The resulting column bed of black solid was washed with 10 mL of DCM using a positive pressure of argon and collected in the same 50 mL round-bottomed flask as the first DCM elution (about 2 min elution time). The combined DCM elutions were concentrated via rotary evaporator, and the colorless solid was dried under high vacuum at room temperature for 5 h yielding 225 mg of TFT with a purity of 98% (determined by quantitative ^{19}F-NMR). Purified 2,3,7,8-tetrafluorothianthrene (colorless solid) has the following characteristics: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (t, J = 8.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 117.8 (dd, J = 13.8, 6.7 Hz), 131.5 (t, J = 5.0 Hz), 150.2 (dd, J = 254.3, 15.2 Hz). ^{19}F NMR (471 MHz, 298 K, $CDCl_3$) δ: –136.86 (t, J = 8.6 Hz). IR (neat): 3096, 3073, 3039, 2194, 2159, 2130, 2037, 2007, 1995, 1972, 1730, 1589, 1562, 1466, 1373, 1277, 1221, 1193, 1089, 969, 874, 852, 791, 679, 617, 587, 463, 440, 424 cm^{-1}. EI-HRMS (m/z) calcd. for

$C_{12}H_4S_2F_4$ $[M]^+$ 287.96850 found 287.96848. mp = 199.7 °C. The compound is bench stable.

17. Dichloromethane (DCM) (≥99%) was purchased from Sigma-Aldrich. $Fe(NO_3)_3 \cdot 9H_2O$ (98+%, metal basis) was purchased from Alfa Aesar. Sodium bromide (99.5%) was purchased from Riedel-de Haen. TFA (99%) was purchased from abcr GmbH & Co. They were all used as received.
18. The rubber septum was equipped with a short needle to prevent over-pressure. The reaction was performed under air.
19. The progress of the reaction was followed by TLC analysis on silica gel (POLYGRAM® SIL G/UV with 0.20mm silica gel 60 with fluorescent indicator, purchased from Macherey-Nagel) with EtOAc-isohexane 1:10 (v/v) as eluent and visualized with $KMnO_4$-stain. The tetrafluorothianthrene starting material has R_f= 0.65 and the tetrafluorothianthrene-*S*-oxide product has R_f= 0.23.

Figure 7. TLC of starting material (SM) versus reaction spot of the end of reaction (P), a central co-spot (Co) and a spot for the product (R). (photo provided by submitters)

20. A BUCHI Vacuum Controller V-850 in combination with evaporator R-210 was used for rotary evaporation. Water was used in the heating bath. Unless otherwise indicated, the pressure and temperature were read from the controller.
21. Acetonitrile (MeCN) (≥ 99.9%) was purchased from Sigma-Aldrich and used as received.
22. Toluene (tech. grade) was purchased from OQEMA GmbH and used as received.

23. The filtrate was collected in a 1000-mL one-necked, round-bottomed flask.
24. Diethyl ether (Et_2O) (for analysis EMSURE® ACS, ISO, Reag. Ph Eur) was purchased from Sigma-Aldrich and dried over sodium-potassium alloy before use.
25. Acetone (tech. grade) was purchased from OQEMA GmbH and used as received.
26. The off-white solid has the following characteristics: ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.49 (dd, *J* = 9.0, 6.5 Hz, 2H), 7.73 (dd, *J* = 8.8, 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) d: 114.4 (dd, *J* = 21.3, 1.6 Hz), 118.9 (d, *J* = 20.4 Hz), 124.3 (dd, *J* = 7.2, 4.1 Hz), 138.4 (t, *J* = 3.7 Hz), 150.1 (dd, *J* = 24.4, 13.3 Hz), 152.7 (dd, *J* = 24.7, 13.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) d: –132.82 (ddd, *J* = 20.2, 9.0, 7.3 Hz), –133.66 (ddd, *J* = 20.2, 8.8, 6.5 Hz). IR (neat): 3092, 3036, 1596, 1573, 1461, 1382, 1270, 1213, 1191, 1100, 1064, 955 cm^{-1}. EI-HRMS (*m/z*) calcd. for $C_{12}H_4O_1S_2F_4$ $[M]^+$ 303.9634, found 303.9634. mp = 254.8 °C. The compound is bench stable.
    Quantitative ^{19}F NMR (471 MHz, $CDCl_3$) was performed using 4,4′-difluorobenzophenone (≥ 99% purity, Sigma Aldrich) as an internal standard. The NMR sample was prepared by dissolving 4,4′-difluorobenzophenone (7.4 mg) and 2,3,7,8-tetrafluorothianthrene-S-oxide (7.4 mg) in $CDCl_3$ (0.5 mL) in a 5 mm NMR tube. The sample was subsequently analyzed by ^{19}F NMR spectroscopy with the following parameters: no. of scans: 32, D1: 20 s, rotation frequency: 15 Hz, spectral width: 49.7923 ppm, transmitter frequency offset: –119.0 ppm). Integration of the fluorine signals showed a 1:0.705 ratio, corresponding to 97.6 wt% of 2,3,7,8-tetrafluorothianthrene-*S*-oxide.
27. The reaction (Step A) was also checked on half-scale and provided 5.94 g (15%) of the same product with purity of 97%.
28. 2-Phenylethyl acetate (98%) and TFAA (99+%) were purchased from Alfa Aesar and used as received.
29. Tetrafluoroboric acid diethyl ether complex (51.0 – 57.0 wt% HBF_4) was purchased from Sigma Aldrich and used as received.
30. The progress of the reaction was followed by TLC analysis on silica gel (POLYGRAM® SIL G/UV with 0.20mm silica gel 60 with fluorescent indicator, purchased from Macherey-Nagel) with DCM as eluent and visualized by 254 nm UV-light. The tetrafluorothianthrene-*S*-oxide starting material has R_f = 0.55 and 2-phenylethyl acetate has R_f = 0.65.

Figure 8. TLC of starting material tetrafluorothianthrene-*S*-oxide (SM TFTO, left) and starting material 2-phenylethyl acetate (SM, right) versus reaction spot of the end of reaction (P). A central co-spot (Co) for both is also shown (photo provided by submitters)

31. Isopropyl alcohol (iPrOH) (tech. grade) was purchased from OQEMA GmbH and used as received.
32. Isohexane (tech. grade) was purchased from OQEMA GmbH and distilled before use.
33. Flash column chromatography: A column (length: 26 cm, diameter: 8 cm, with a 1000 mL reservoir) was charged with 300 g SiO_2 (Geduran® Si 60 with pore size 40-63 µm from Merck KGaA) and 750 mL DCM. In order to dry load the crude 2-phenethyl acetate-derived tetrafluoro-thianthrenium salt, it was dissolved in 300 mL DCM at 40 °C using a water bath and 60 g of SiO_2 was added. The solvent was removed under reduced pressure (525 mmHg to 15 mmHg, 40 °C), and the dry residue was transferred on the column inside a fume hood. Sand (200 g) was added on top of the silica column bed. The product was eluted with 600 mL DCM. At that point, fraction collection was initiated, and elution was continued with 500 mL DCM/*i*-PrOH 100:1 (v/v), 8 L DCM/ *i*-PrOH 50:1 (v/v) and 2 L DCM/ *i*-PrOH 10:1. Fractions were collected in 50 mL test tubes. TLC analysis of the product was done with DCM/ *i*-PrOH 10:1 (v/v) as eluent and visualized with 254 nm UV light. Product could be found in fractions 41 to 219.
34. The colorless solid has the following characteristics: ^{1}H NMR (400 MHz, CD_3CN) δ: 1.91 (s, 3H), 2.96 (t, *J* = 6.5 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 7.11 – 7.17 (m, 2H), 7.38 – 7.42 (m, 2H), 7.95 (dd, *J* = 9.9, 7.0 Hz, 2H), 8.38 (dd, *J* = 9.1, 7.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ: 21.0, 35.1,

64.5, 115.4 (dd, J = 7.1, 3.6 Hz), 121.2 (d, J = 21.9 Hz), 121.2, 125.5 (dd, J = 22.0, 2.6 Hz), 129.3, 132.2, 135.2 (dd, J = 8.0, 3.9 Hz), 146.3, 151.6 (dd, J = 255.4, 13.3 Hz), 154.8 (dd, J = 261.9, 13.2 Hz), 171.4. ^{19}F NMR (471 MHz, CD_3CN) δ: –125.42 (ddd, J = 20.2, 10.0, 7.1 Hz), –133.80 (ddd, J = 20.1, 9.1, 7.0 Hz), –151.70 (br, ^{10}B), –151.75 (br, ^{11}B). IR (neat): 3093, 3048, 1726, 1574, 1481, 1380,1284, 1267, 1236, 1199, 1055, 1026, 1008, 965, 904 cm^{-1}. ESI-HRMS: (m/z) calcd. for $C_{22}H_{15}O_2S_2F_4$ $[M]^+$ 451.0444, found 451.0444. mp = 207.0 °C. The compound is bench-stable.

Quantitative ^{19}F NMR (471 MHz, CD_3CN) was performed using 4,4′-difluorobenzophenone (≥ 99% purity, Sigma Aldrich) as an internal standard. The NMR sample was prepared by dissolving 4,4′-difluorobenzophenone (10.8 mg) and 2-phenethyl acetate derived tetrafluorothianthrenium salt (10.8 mg) in CD_3CN (0.5 mL) in a 5 mm NMR tube. The sample was subsequently analyzed by ^{19}F NMR spectroscopy with the following parameters: no. of scans: 32, D1: 20 s, rotation frequency: 15 Hz, spectral width: 49.7924 ppm, transmitter frequency offset: -121.3 ppm). Integration of the fluorine signals showed a 1:0.405 ratio, corresponding to 99.9 wt% of 2-phenethyl acetate derived tetrafluorothianthrenium salt.

35. The reaction (Step B) was also checked on half-scale and provided 6.75 g (64%) of the same product.
36. Alternatively, the reaction can be carried out under argon atmosphere.
37. 4-Biphenylboronic acid (95%) was purchased from Oxchem, Pd(dppf)Cl_2 (98%) was purchased from fluorochem, K_3PO_4 (97%) was purchased from Alfa Aesar, and 1,4-dioxane (≥ 99.5%) was purchased from Fisher Scientific. They were used as received.
38. The progress of the reaction was followed by TLC analysis on silica gel (POLYGRAM® SIL G/UV with 0.20mm silica gel 60 with fluorescent indicator, purchased from Macherey-Nagel) with DCM-iPrOH 10:1 (v/v) as eluent and visualized by 254 nm UV-light. The 2-phenethyl acetate derived tetrafluorothianthrenium salt starting material has R_f = 0.47, and the Suzuki coupling product [4-(4-phenylphenyl)phenyl] ethyl acetate has R_f = 0.80.

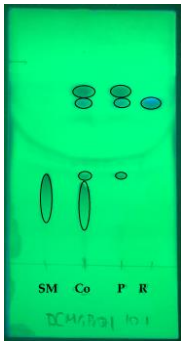


Figure 9. TLC of starting material (SM) versus reaction spot of the end of reaction (P). A central co-spot (Co) and a spot for the clean product (R) is also shown (photo provided by submitters)

39. Ethyl acetate (98-100%) was purchased from OQEMA GmbH and distilled before use.
40. Flash column chromatography: A column (length: 26 cm, diameter: 8 cm, with a 1000 mL reservoir) was charged with 300 g SiO_2 (Geduran® Si 60 with pore size 40-63 µm from Merck KGaA) and 800 mL Hex/DCM 8:1 (v/v). In order to dry load the crude [4-(4-phenylphenyl)phenyl] ethyl acetate was dissolved in 250 mL DCM at 40 °C using a water bath and 50 g of SiO_2 was added. The solvent was removed under reduced pressure (525 mmHg to 15 mmHg, 40 °C), and the dry residue was transferred on the column. Sand (200 g) was added on top of the column bed. The crude product is eluted with 1 L of a hexanes/DCM mixture (4:1 v/v) and 3.2 L (hexanes /DCM = 3:1 v/v). At that point, fraction collection is begun, and elution is continued with 4 L DCM/hexanes 1:1 (v/v) and 4 L DCM. Fractions were collected in 50 mL test tubes. TLC analysis of the product was done with DCM/*i*-PrOH 10:1 (v/v) as eluent and visualized with 254 nm UV light. Product could be found in fractions 44 to 120.
41. Büchner funnel VitraPOR® with Por. 4 and a capacity of 75 mL was used.
42. The off-white solid has the following characteristics: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08 (s, 3H), 3.00 (t, J = 7.1 Hz, 2H), 4.35 (t, J = 7.0 Hz, 2H), 7.31 – 7.35 (m, 2H), 7.35 – 7.41 (m, 1H), 7.47 (dd, J = 8.4, 6.9 Hz, 2H), 7.58 – 7.62 (m, 2H), 7.63 – 7.67 (m, 2H), 7.68 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 21.1, 34.9, 65.0, 127.2, 127.2, 127.5, 127.6, 127.6, 128.9, 129.5, 137.1, 139.1, 139.9, 140.2, 140.8, 171.2. IR (neat): 3032, 2955, 2894, 1732, 1484, 1400, 1383,

1366, 1233, 1030, 1001, 980, 829, 819, 691 cm^{-1}. ESI-HRMS (*m/z*) calcd. for $C_{22}H_{20}O_2Na_1$ $[M + Na]^+$ 339.1356, found 339.1357. mp = 168.1 °C. The compound is bench stable.

Quantitative ^1H NMR (500 MHz, $CDCl_3$) was performed using benzyl benzoate (certified reference material, TraceCERT®, Sigma Aldrich) as an internal standard. The NMR sample was prepared by dissolving benzyl benzoate (10.1 mg) and [4-(4-phenylphenyl)phenyl] ethyl acetate (9.80 mg) in $CDCl_3$ (0.5 mL) in a 5 mm NMR tube. Integration of the proton signals showed a 1:0.65 ratio, corresponding to 99.9 wt% of [4-(4-phenylphenyl)phenyl] ethyl acetate.

43. The reaction (Step C) was also checked on half-scale and provided 2.69 g (68%) of the same product.

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of

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Discussion

The C–H functionalization of arenes using 2,3,7,8–tetrafluorothianthrene-*S*-oxide accesses a versatile synthetic lynchpin (aryl tetrafluorothianthrenium salt) in a highly selective manner. While aryl halides and aryl boronic acids are proven synthetic lynchpins, no late-stage halogenation or borylation method currently has the same selectivity and scope which tetrafluorothianthrenation demonstrates.[2] Additionally, aryl tetrafluorothianthrenium salts are competent substrates for activation by palladium and photoredox catalysis. In contrast to mononuclear leaving groups such as bromide, complex leaving groups like tetrafluorothianthrene can raise the reduction potential of the aryl substrate and still possess the ability to engage in productive bond forming reactions.[3] We have shown that from aryl thianthrenium salts, C–F,[3] C–CF_3,[4] C–N,[5] and C–O[6] bonds can be formed using photoredox catalysis. A disadvantage of tetrafluoro-thianthrenium salts is their ability to undergo a nucleophilic aromatic substitution on the thianthrene scaffold by displacement of fluoride.[5] This problem was encountered in the coupling of amines, but this issue was overcome by using the non-fluorinated aryl thianthrenium analogs. The thianthrenation procedure entails the same protocol as reported here, however, with thianthrene-*S*-oxide. Thianthrenation has a similarly broad scope and functional group tolerance, but it cannot readily functionalize electron-poor aromatic rings. In addition to arene functionalization, we have shown that the regioselective thianthrenation of unactivated olefins produces versatile alkenyl electrophiles.[8] A minor drawback of the two thianthrene derivatives is their inability to cleanly react by direct substitution with nucleophiles. Direct substitution is important for applications such as ^{18}F-labeling with [^{18}F]fluoride. By employing dibenzothiophene-*S*-oxide derivatives, a light- and transition metal-free C–H to ^{18}F sequence is feasible.[7] The obvious disadvantage of the C–H functionalization reactions to form sulfonium salts is the low atom economy. Until equivalent C–H functionalizations are developed, stoichiometric waste is the price that must be paid.

References

1. Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Muelheim an der Ruhr, Germany, E-mail: ritter@mpi-muelheim.mpg.de. ORCID: 0000-0002-6957-450X. Generous support by the Max-Planck-Society is gratefully acknowledged. The submitters acknowledge N. Haupt, D. Kampen, F. Kohler, S. Marcus and D. Margold for mass spectrometry analysis, D. Chamier Cieminski for collecting analytical data and J. Chen and Dr. F. Berger for helpful discussions.
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8. Chen, J.; Li, J.; Plutschack, M. B.; Berger, F.; Ritter, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 5616–5620.

Appendix
Chemical Abstracts Nomenclature (Registry Number)

Aluminium chloride: aluminium chloride; (7446-70-0)
1,2-Difluorobenzene: 1,2-Difluorobenzene; (367-11-3)
Disulfur dichloride: disulfur dichloride (10025-67-9)
$Fe(NO_3)_3 \cdot 9H_2O$: iron(III) nitrate nonahydrate (7782-61-8)
NaBr: sodium bromide (7647-15-6)
TFA: trifluoroacetic acid (76-05-1)
2-Phenylethyl acetate: 2-Phenylethyl acetate (103-45-7)
TFAA: trifluoroacetic anhydride (407-25-0)

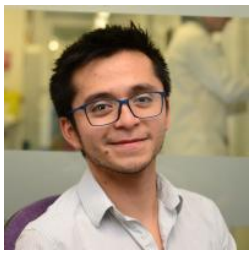
Tetrafluoroboric acid diethyl ether complex: tetrafluoroboric acid diethyl ether complex (67969-82-8)
4-Biphenylboronic acid: 4-Biphenylboronic acid (5122-94-1)
Pd(dppf)Cl_2: [1,1′-Bis-(diphenylphosphino)ferrocene]dichloropalladium(II) (72287-26-4)
K_3PO_4: potassium phosphate (7778-53-2)
1,4-Dioxane: 1,4-Dioxane (123-91-1)

Samira Speicher completed her apprenticeship as a technician in chemistry in 2017 (Max-Planck-Institut fuer Kohlenforschung, Muelheim an der Ruhr). During this time, she worked in the group of Prof. Benjamin List (homogenous catalysis) and in the group of Prof. Alois Fürstner (natural product synthesis). Since 2017, she is working in the group of Prof. Tobias Ritter on organic synthesis and radiochemistry.

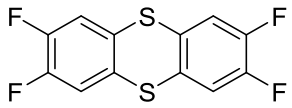
Matthew B. Plutschack received his undergraduate degree from the University of Wisconsin – Madison, and he began conducting research under Prof. Howard E. Zimmerman. In 2013, he obtained his M.S. from Florida State University under the tutelage of Prof. D. Tyler McQuade. He conducted research at the Max-Planck-Institut fuer Kolloid- und Grenzflaechenforschung, and in 2017, he earned his doctorate from the Freie Universitaet Berlin under the mentorship of Prof. Peter H. Seeberger. Since 2017 he is a Post-doc in the lab of Prof. Tobias Ritter at the Max-Planck-Institut fuer Kohlenforschung.

Tobias Ritter received his undergraduate education in Braunschweig, Bordeaux, Lausanne, and Stanford. He has performed undergraduate research with Prof. Barry M. Trost, obtained his Ph.D. with Prof. Erick M. Carreira at ETH Zurich in 2004, and was a postdoc with Prof. Robert H. Grubbs at Caltech. In 2006, Tobias was appointed as Assistant Professor in the Department of Chemistry and Chemical Biology at Harvard, promoted to Associate Professor in 2010, and to Professor of Chemistry and Chemical Biology in 2012. Since 2015 he is director at the Max-Planck-Institut fuer Kohlenforschung. In 2011, Tobias founded SciFluor LifeScience, a pharmaceutical development company.

Maurus Mathis completed his apprenticeship in synthetic chemistry in 2018 while working in the group of Prof. Cristina Nevado at the University of Zürich. He is currently doing his Bachelor's Degree in chemistry at the UZH while still working as a laboratory technician in the Nevado group.



Jorge A. González was born in Xalapa, Mexico. He completed his Undergraduate Degree in Chemistry at the National and Autonomous University of Mexico in 2011. He obtained his PhD at the University of Edinburgh in 2016. He is currently a postdoctoral associate research associate in the group of Prof. Cristina Nevado.



^{13}C-NMR for purified 2,3,7,8-tetrafluorothianthrene
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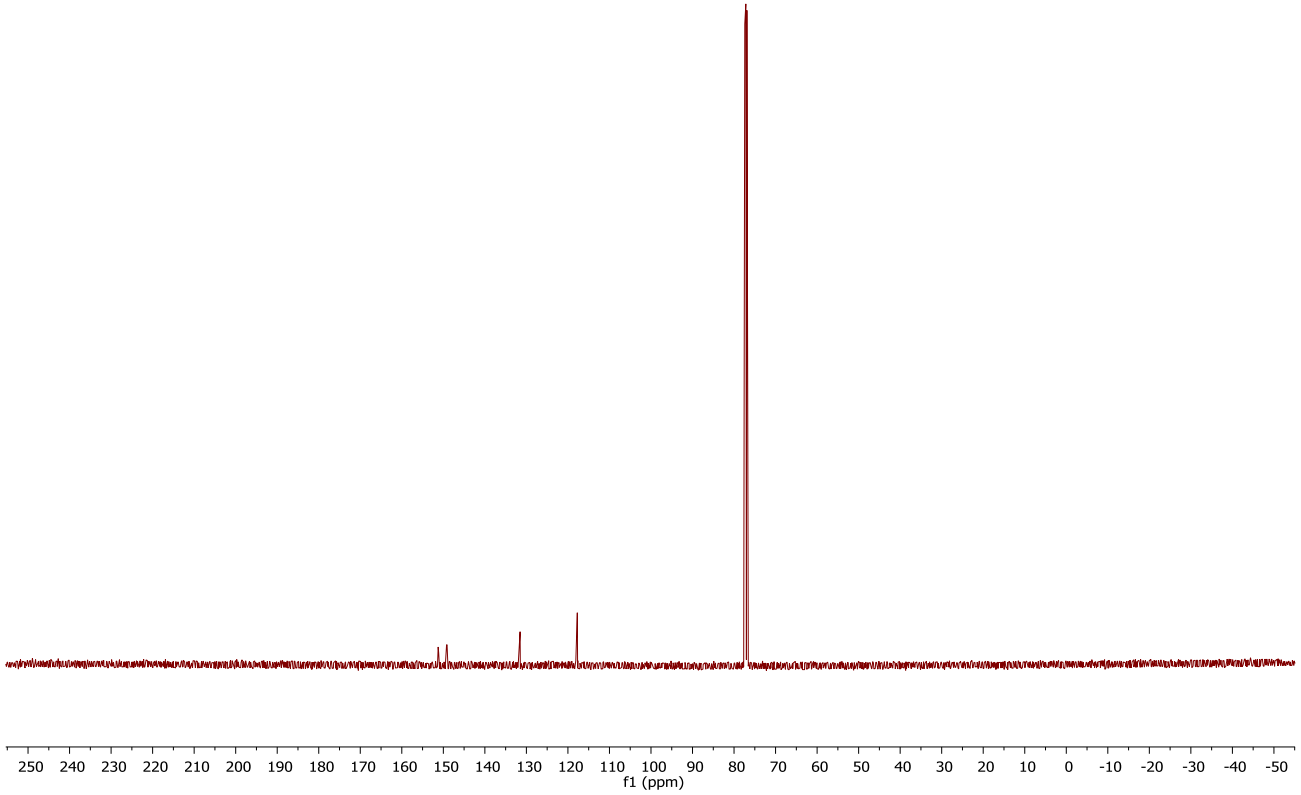

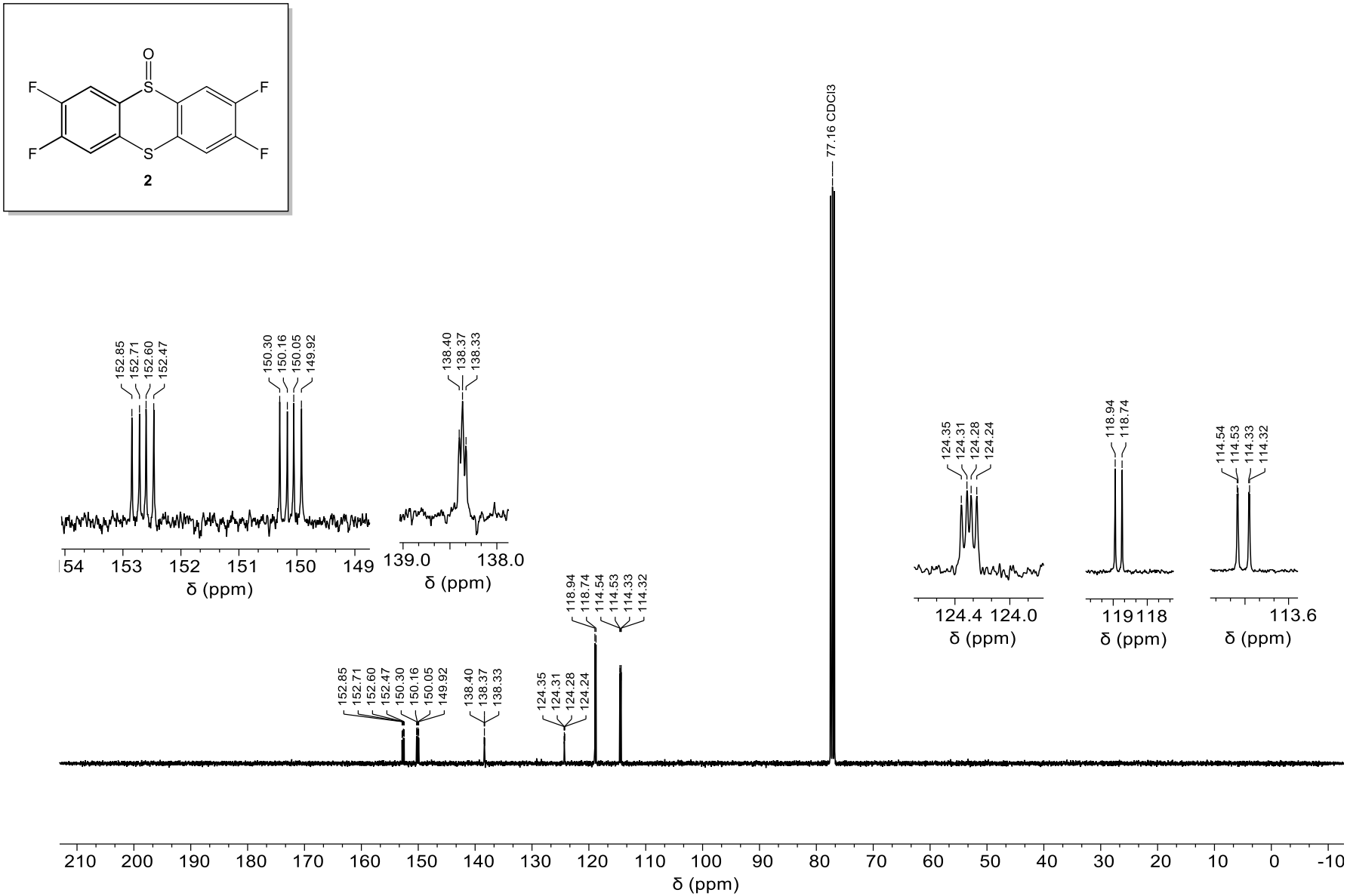
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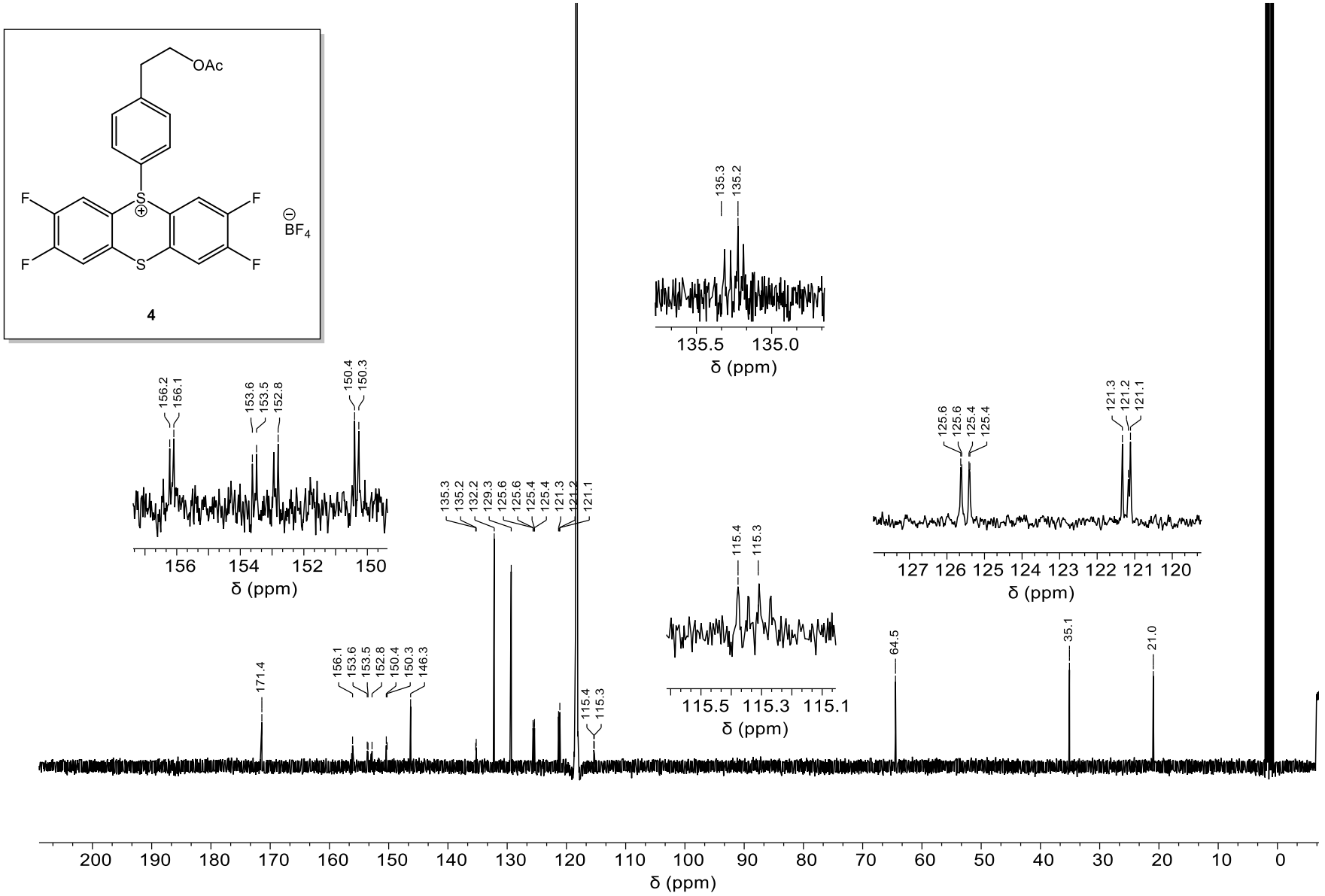
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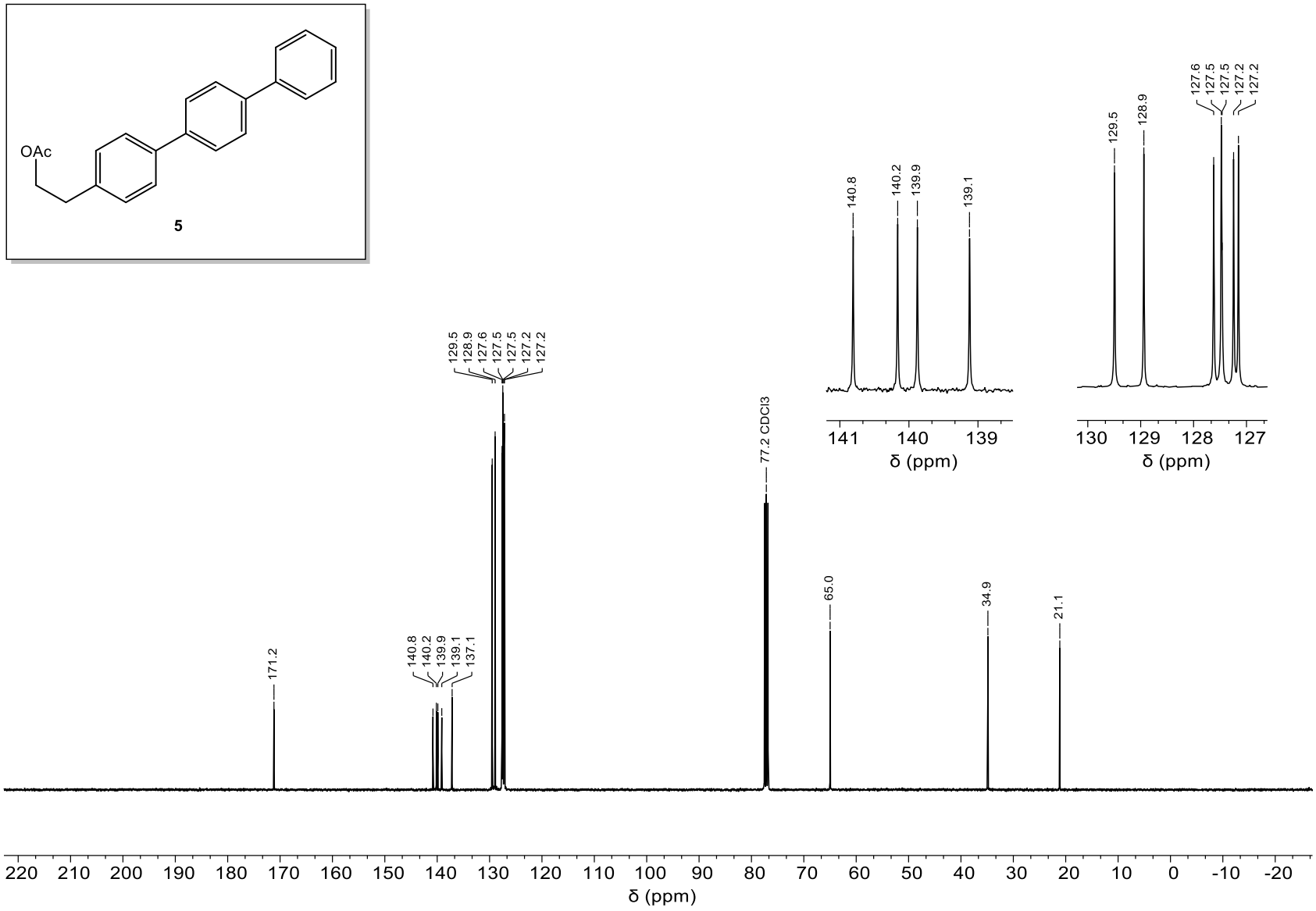
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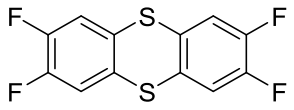
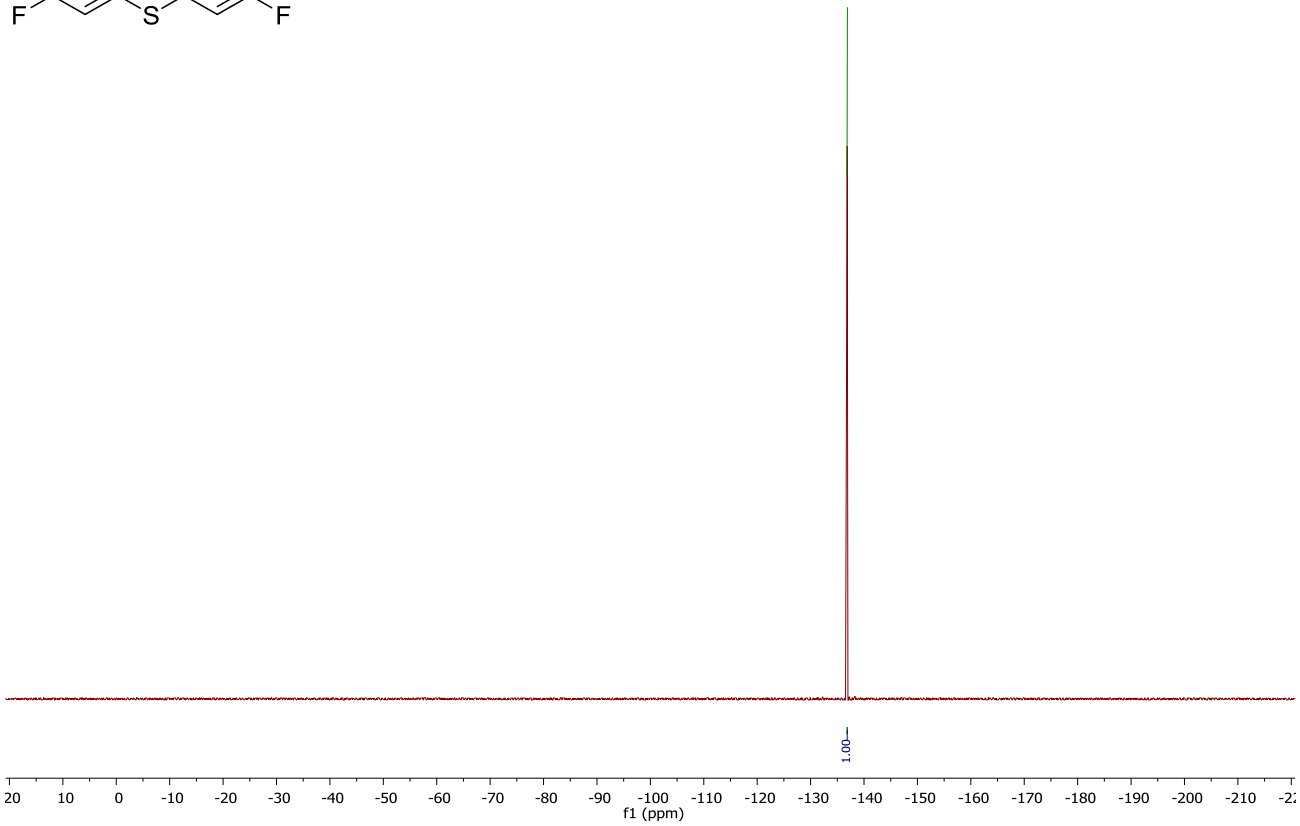
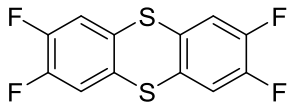


^{19}F-NMR for crude 2,3,7,8-tetrafluorothianthrene
471 MHz, 298 K, $CDCl_3$





^{19}F-NMR for purified 2,3,7,8-tetrafluorothianthrene
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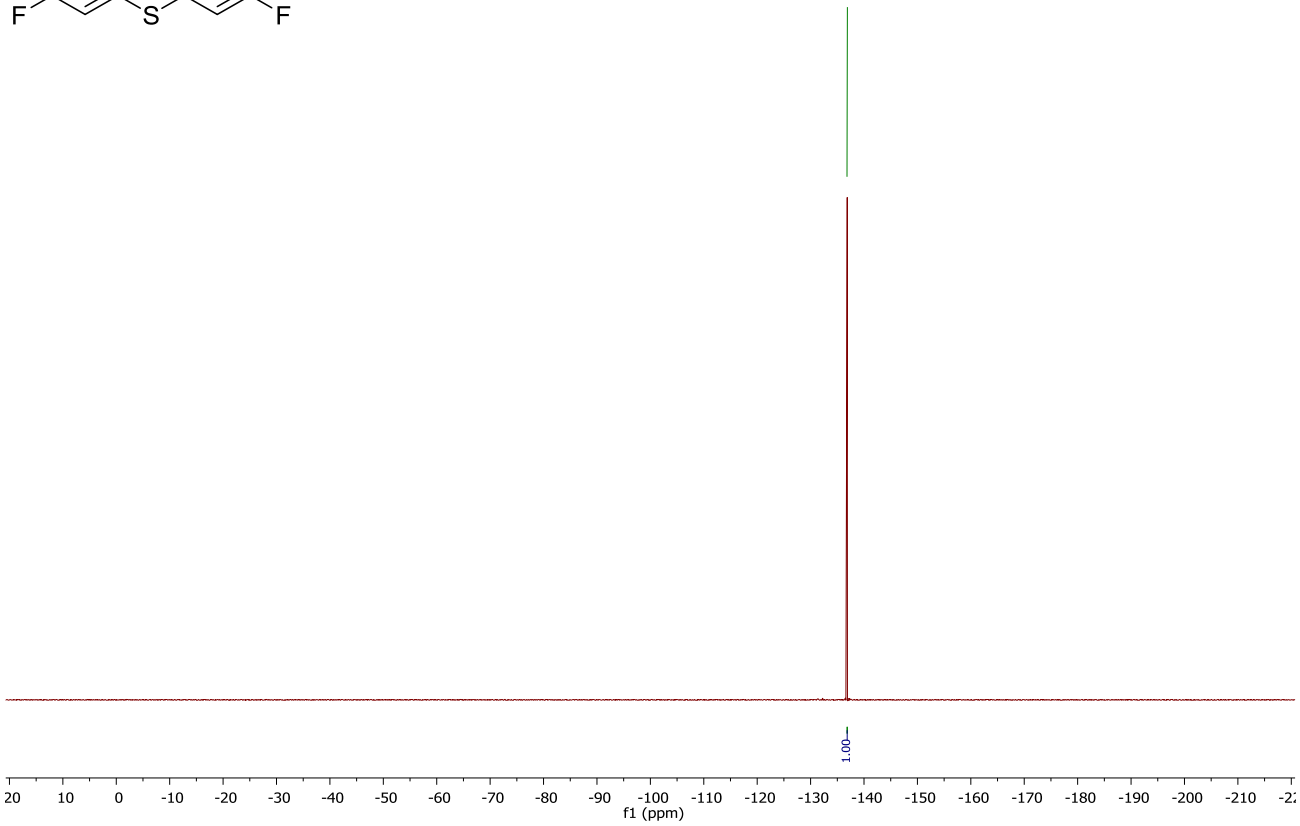

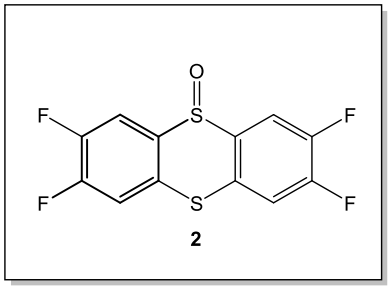
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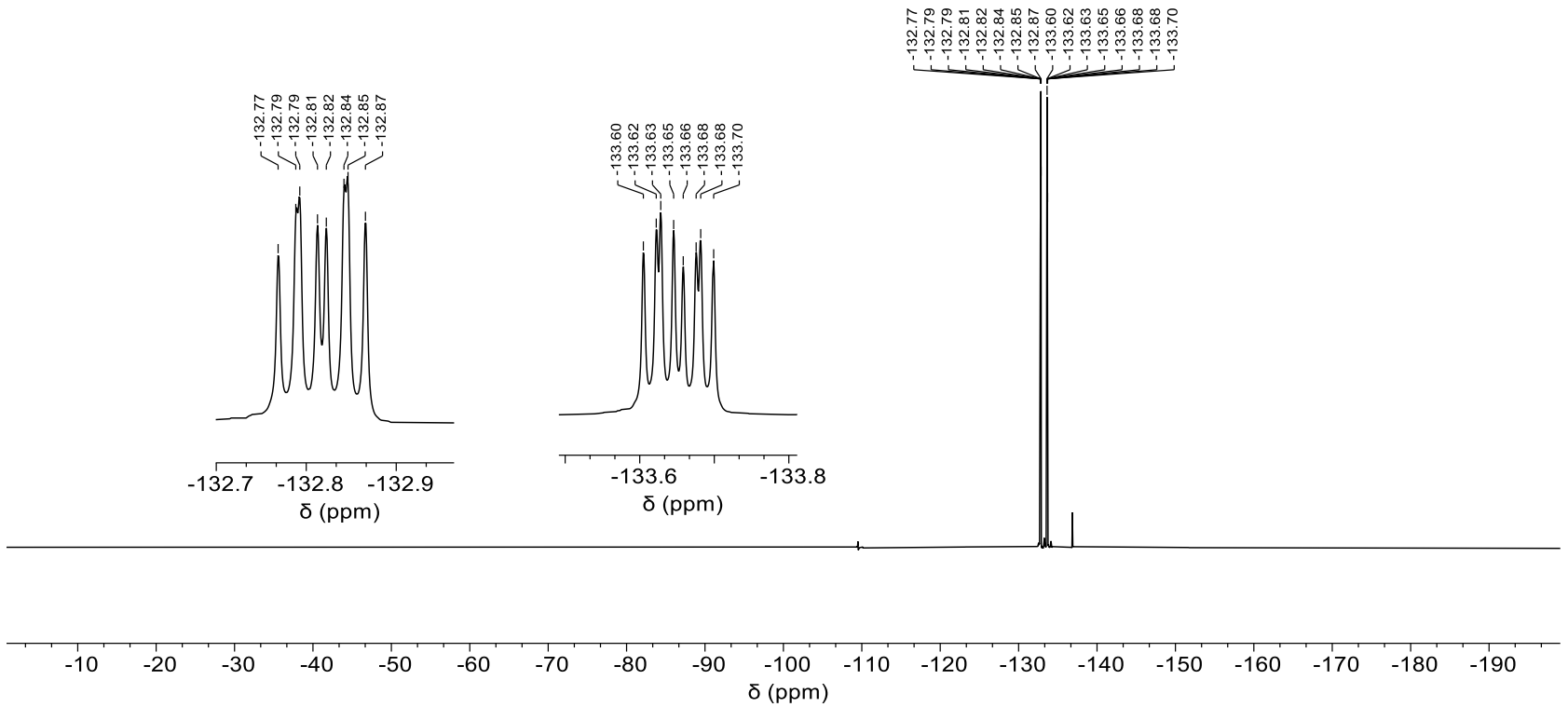
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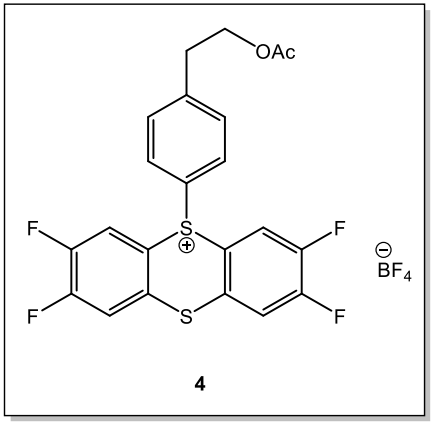
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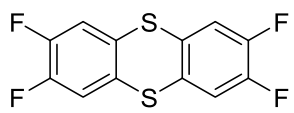
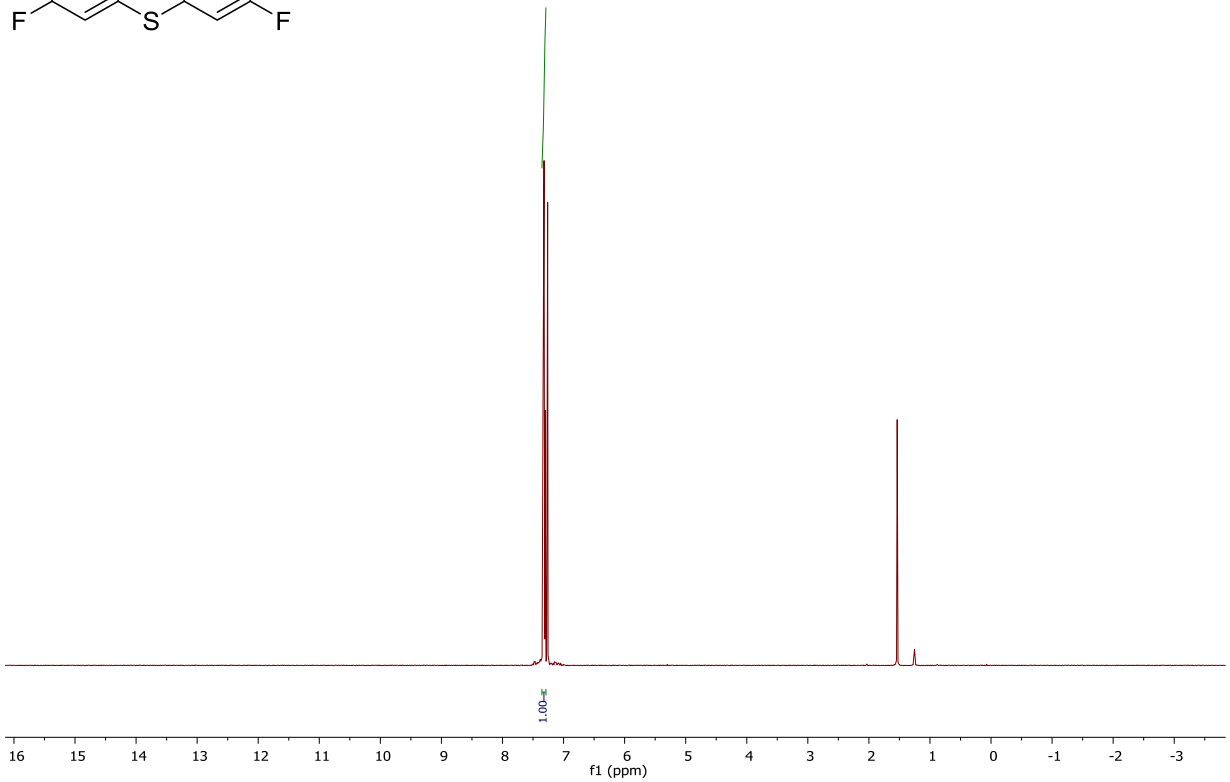
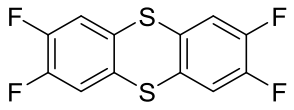
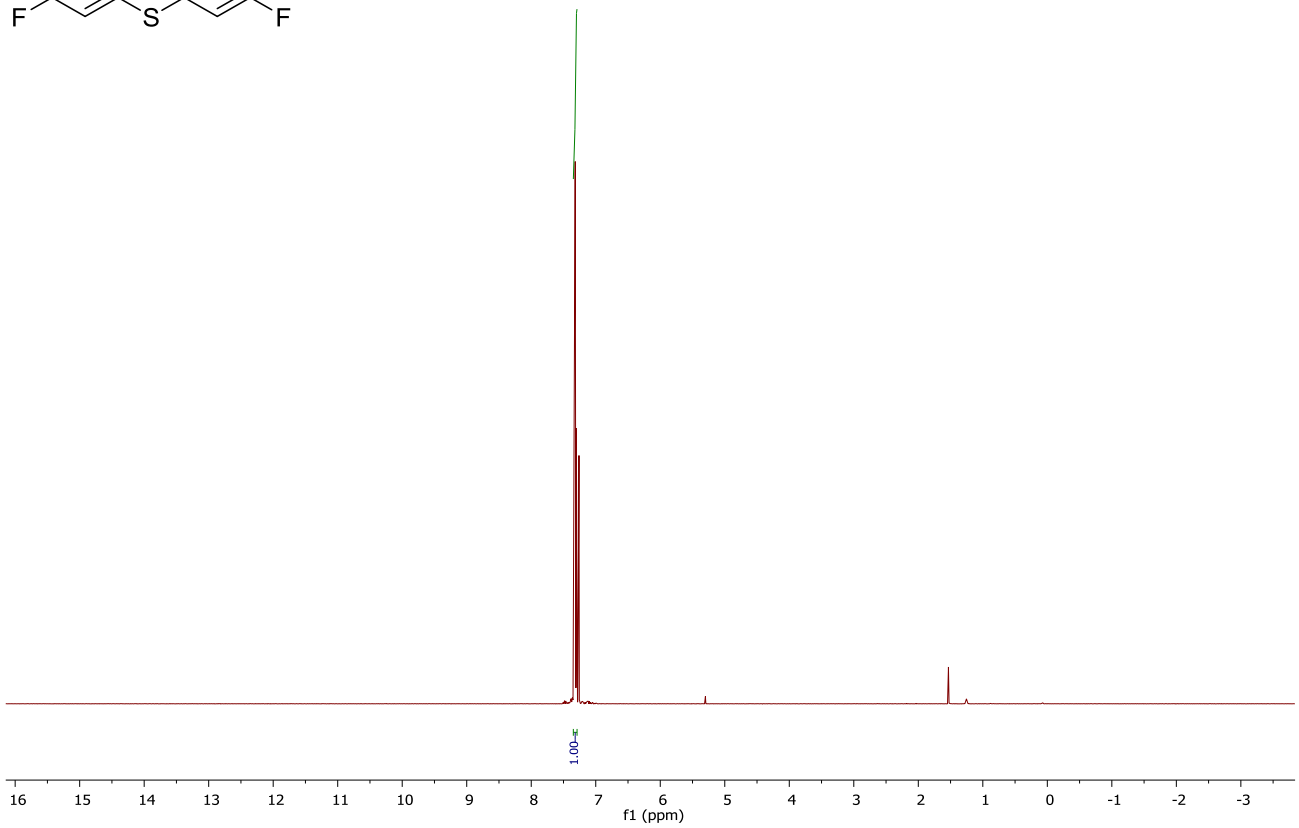


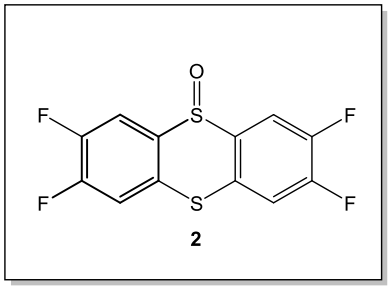
^{1}H-NMR for crude 2,3,7,8-tetrafluorothianthrene
500 MHz, 298 K, $CDCl_3$



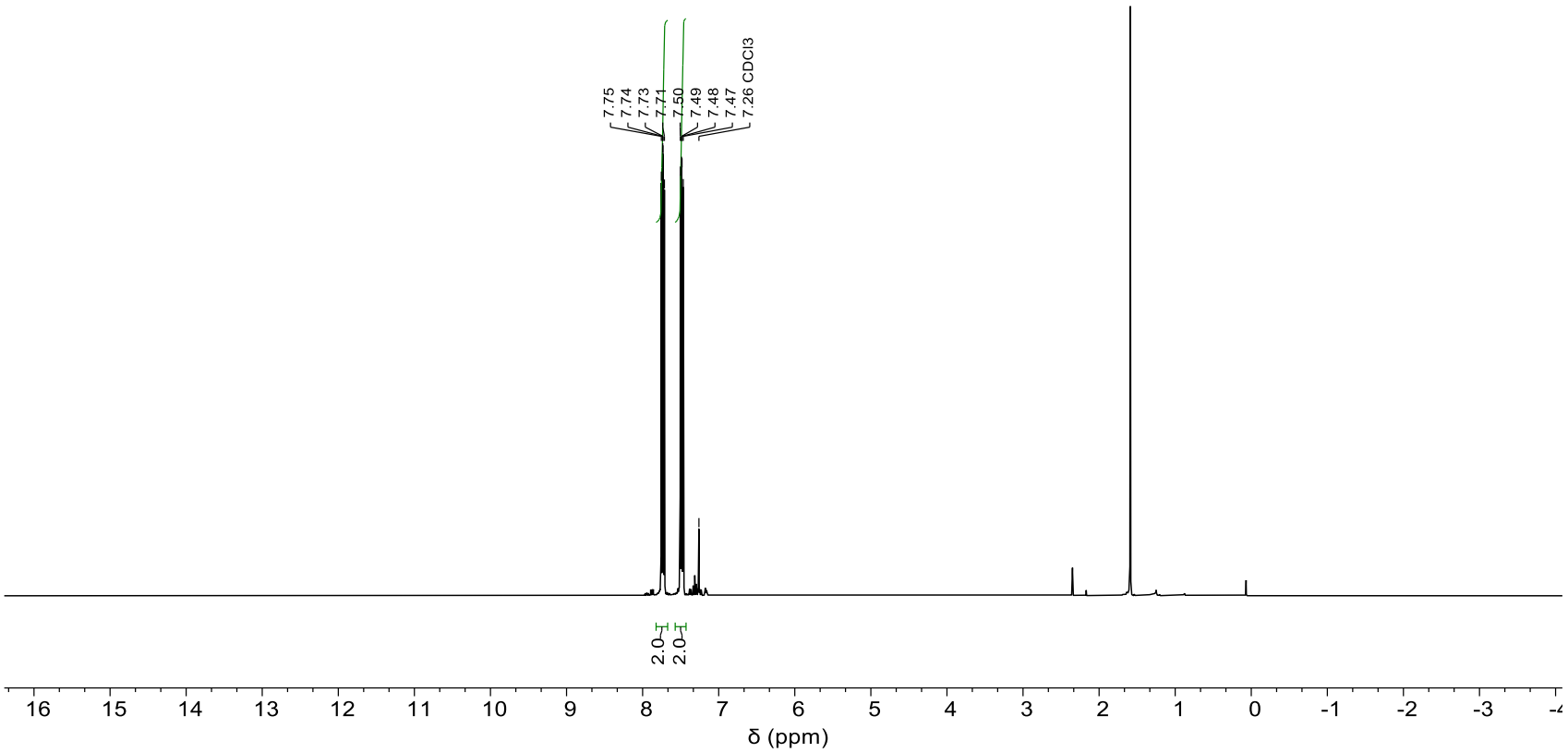


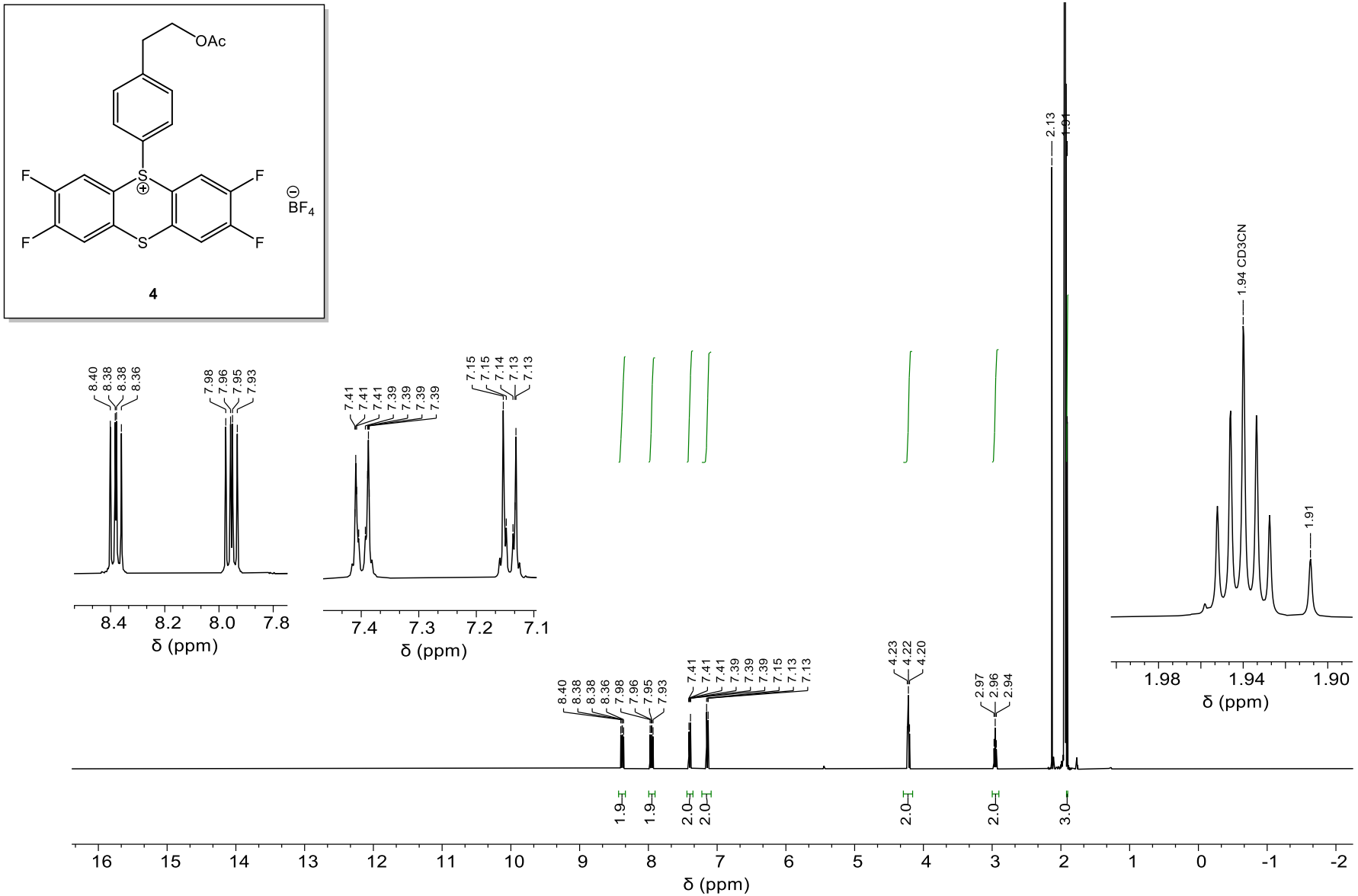
^{1}H-NMR for purified 2,3,7,8-tetrafluorothianthrene
500 MHz, 298 K, $CDCl_3$

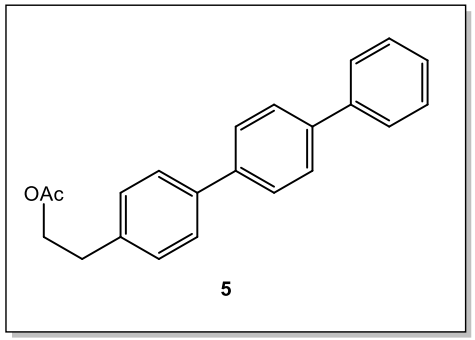


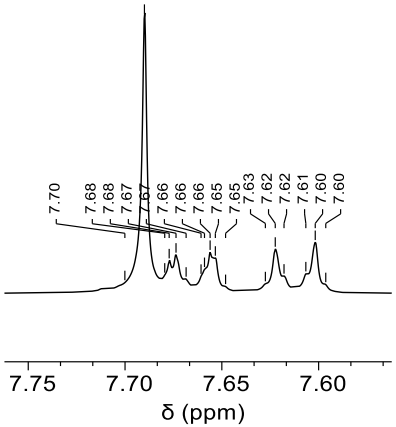

O
S
F
F
F
F
S

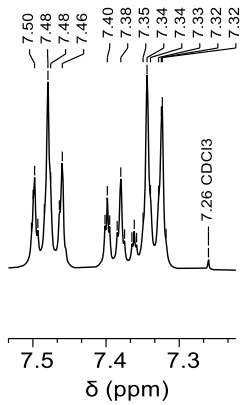
2

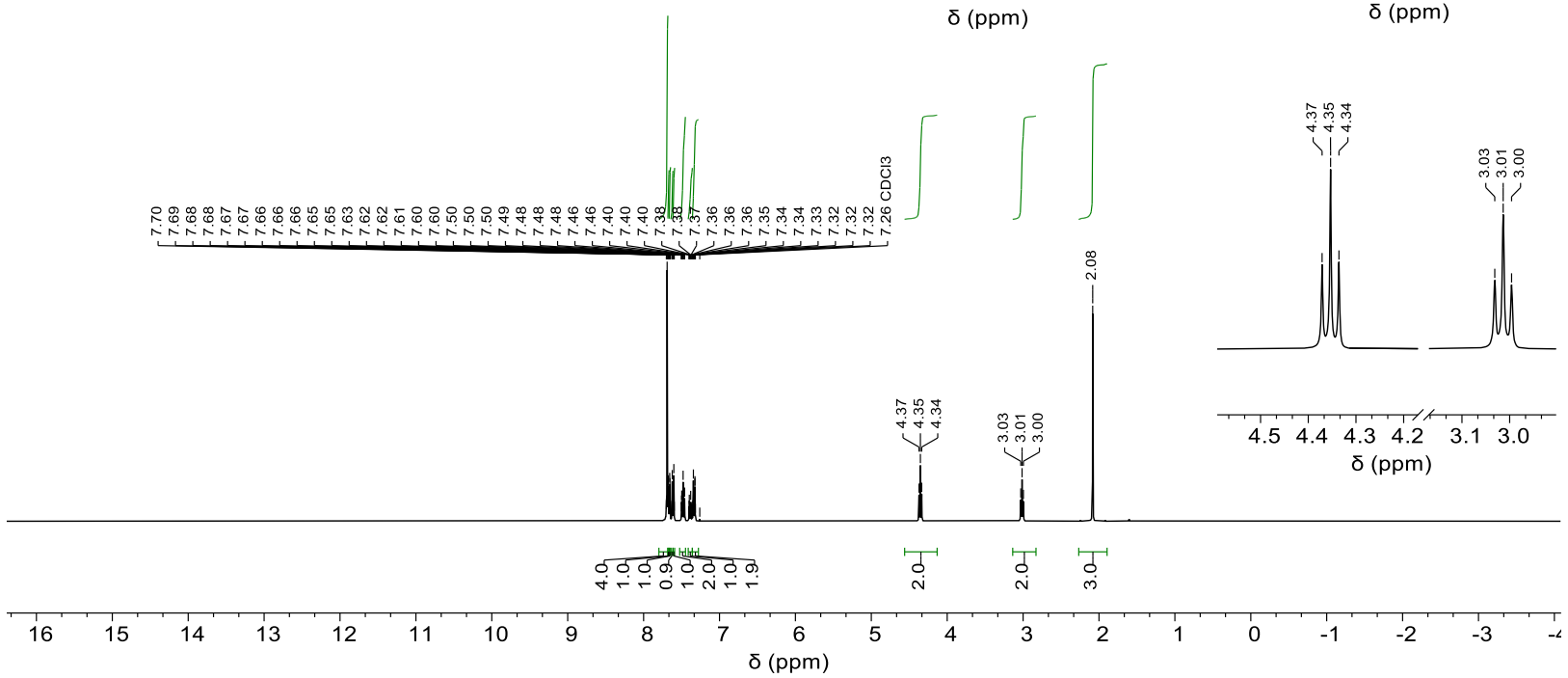

7.75
7.74
7.73
7.71
7.50
7.49
7.48
7.47
7.26 CDCl3
2.0
2.0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)


OAc
F
F
F
F
S
S
BF4
4
8.40
8.38
8.38
8.36
7.98
7.96
7.95
7.93
7.41
7.41
7.41
7.39
7.39
7.39
7.15
7.15
7.14
7.13
7.13
8.4
8.2
8.0
7.8
7.4
7.3
7.2
7.1
δ (ppm)
4.23
4.22
4.20
2.97
2.96
2.94
2.13
1.94 CD3CN
1.91
1.98
1.94
1.90
1.9
1.9
2.0
2.0
2.0
2.0
3.0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

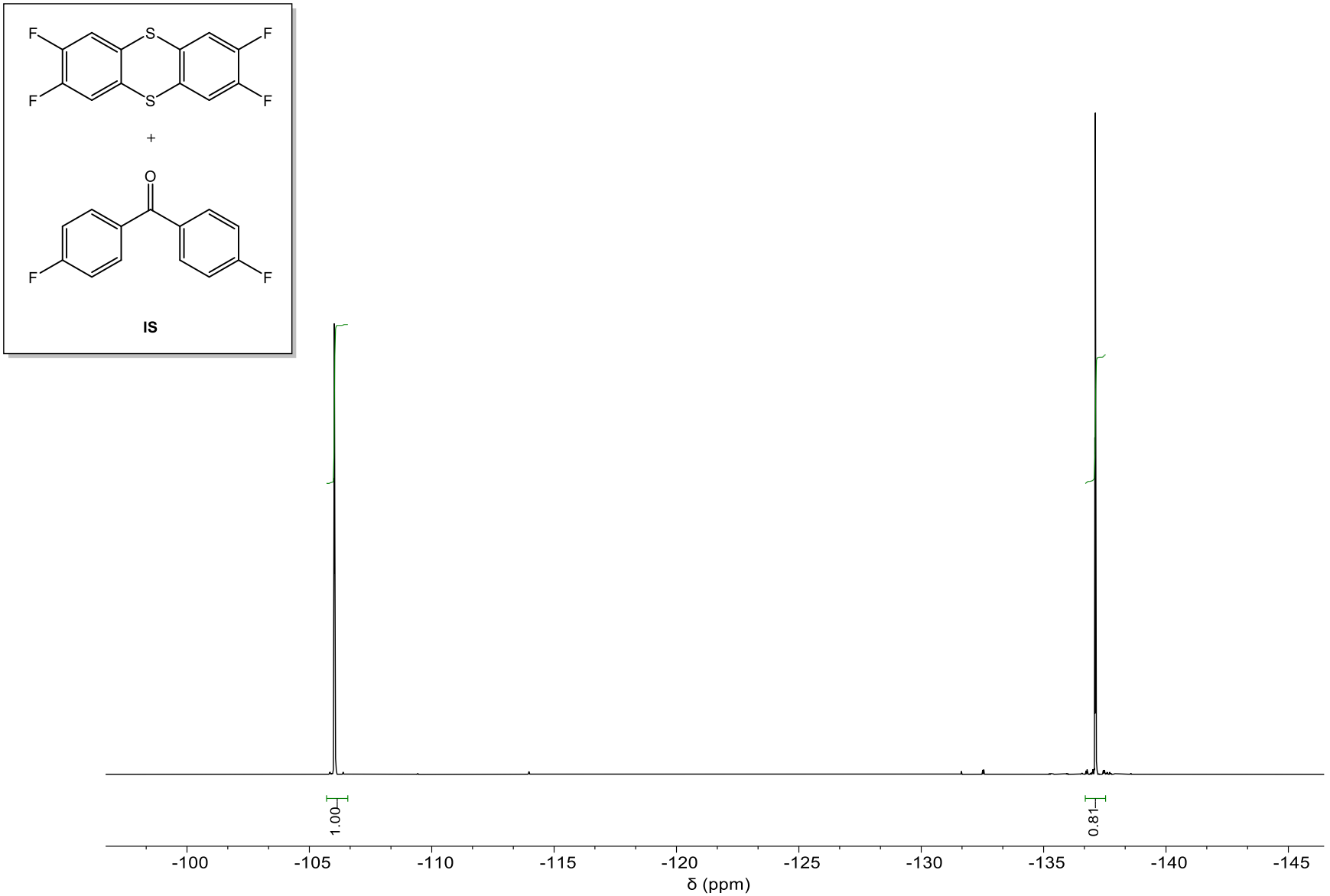

OAc
5


7.70
7.68
7.68
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.63
7.62
7.62
7.61
7.60
7.60
7.75
7.70
7.65
7.60
δ (ppm)


7.50
7.48
7.48
7.46
7.40
7.38
7.35
7.34
7.34
7.33
7.32
7.32
7.26 CDCl3
7.5
7.4
7.3
δ (ppm)


7.70
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.63
7.62
7.62
7.61
7.60
7.60
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.48
7.46
7.46
7.40
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26 CDCl3
4.37
4.35
4.34
3.03
3.01
3.00
2.08
4.0
1.0
1.0
0.9
1.0
2.0
1.0
1.9
2.0
2.0
3.0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

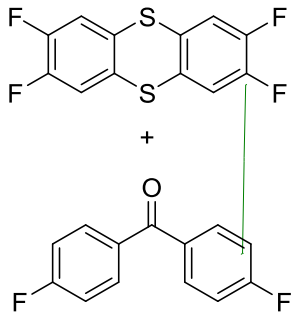
4.37
4.35
4.34
3.03
3.01
3.00
4.5
4.4
4.3
4.2
3.1
3.0
δ (ppm)


F
S
F
F
S
F
+
O
F
F
IS
1.00
0.81
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
δ (ppm)

Quant. ^{19}F NMR (471 MHz, $CDCl_3$) at 25 °C for 2,3,7,8-tetrafluorothianthrene

$$wt(\%) = \frac{mg_{IS} \text{ x } MW_{cpd} \text{ x molar ratio x } P_{IS}}{mg_{cpd} MW_{IS}}$$

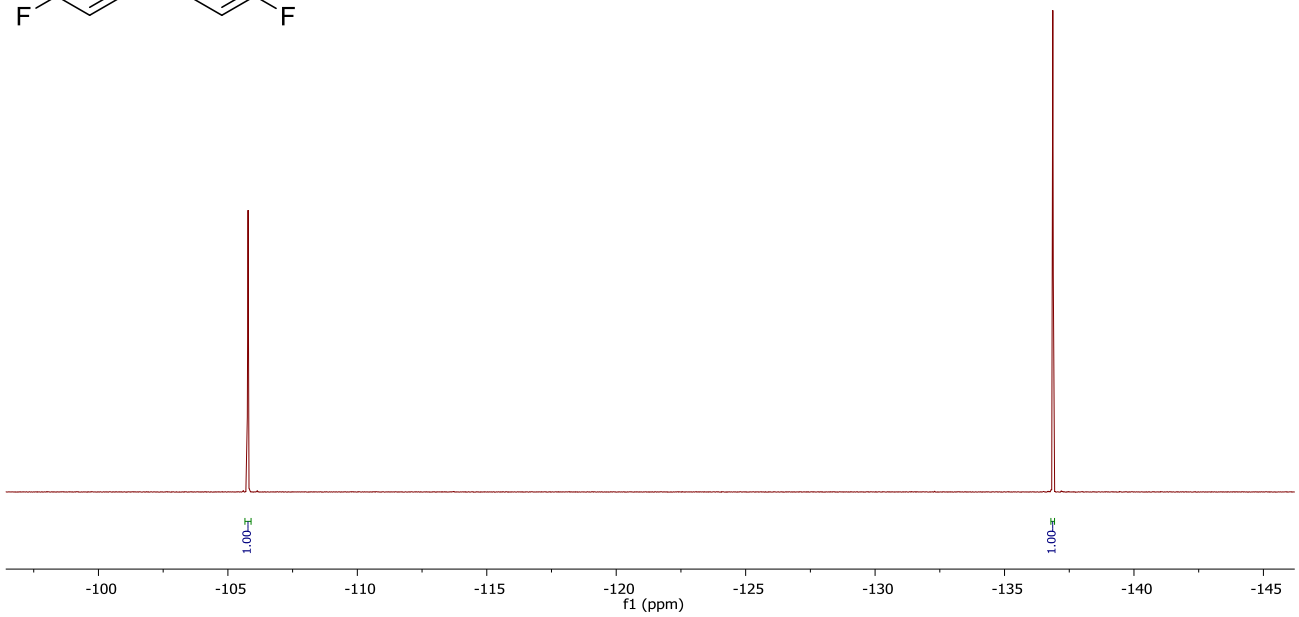
$$wt(\%) = \frac{14.3 \text{ mg } x \text{ } 288.28 \text{ gmol}^{-1} x \text{ } 0.405 \text{ } x \text{ } 1.0}{10.3 \text{ mg } x \text{ } 218.20 \text{ gmol}^{-1}} \text{ x } 100 = 74.3\%$$

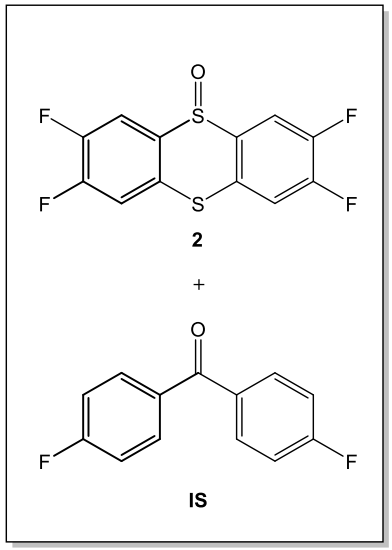


Quant. ^{19}F-NMR for purified 2,3,7,8-tetrafluorothianthrene
471 MHz, 298 K, $CDCl_3$

$$wt\% = \frac{mg_{Std}\ x\ MW_{cpd}\ x\ molar\ ratio\ x\ P_{std}}{mg_{cpd}\ x\ MW_{std}}\ x\ 100$$

$$= \frac{13.1mg\ x\ 288.28\frac{g}{mol}\ x\ 0.5\ x\ 1.00}{8.9\ mg\ x\ 218.20\frac{g}{mol}}\ x\ 100 = 97.2\ \%$$



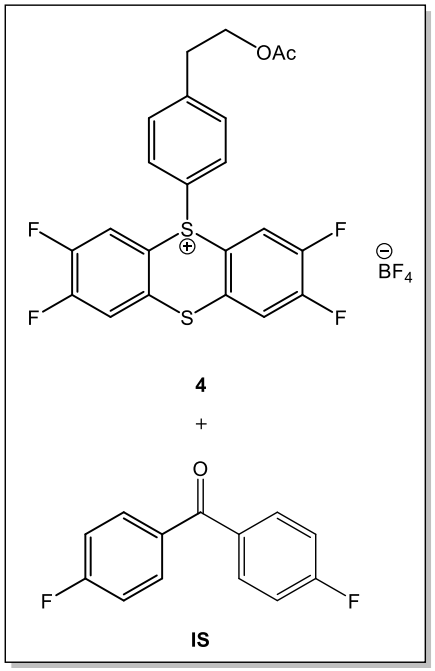

O
S
F
F
F
F
S
2
+
O
F
F
IS

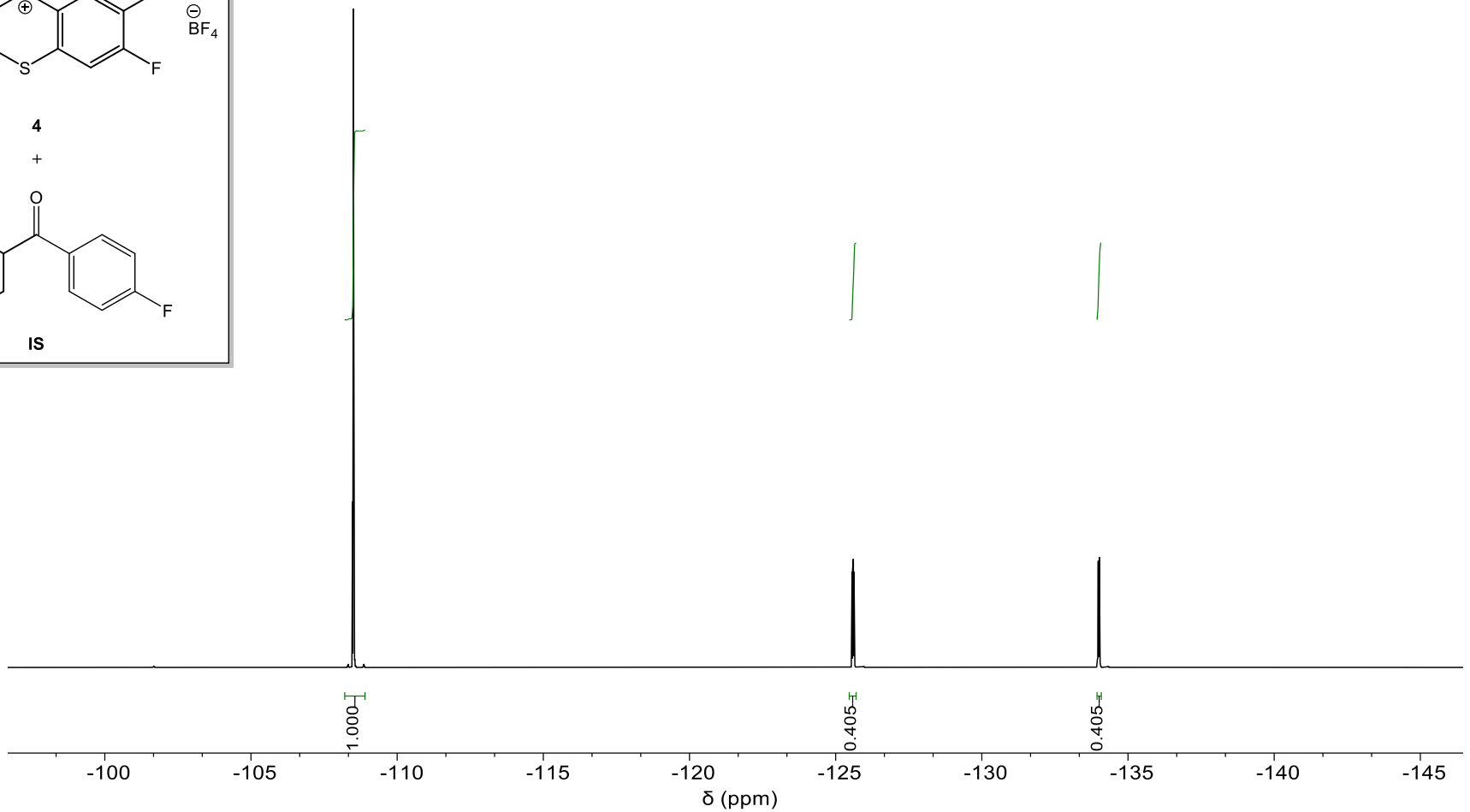
1.000
0.705
0.705
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
δ (ppm)

Quant. ^{19}F NMR (471 MHz, $CDCl_3$) at 25 °C for 2,3,7,8-tetrafluorothianthrene-S-oxide

$$wt(\%) = \frac{mg_{IS} \times MW_{cpd} \times \text{molar ratio} \times P_{IS}}{mg_{cpd} MW_{IS}}$$

$$wt(\%) = \frac{7.4\ mg\ \ x\ \ 304.28\ gmol^{-1} x\ \ 0.705\ x\ 1.0}{7.4\ mg\ \ x\ \ 218.20\ gmol^{-1}} \times 100 = 98.3\%$$

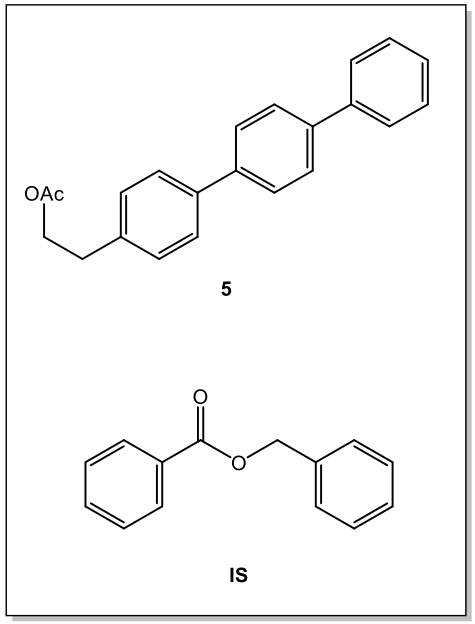

OAc
F
F
F
F
S
S
BF4
4
+
O
F
F
IS


1.000
0.405
0.405
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
δ (ppm)

Quant. ^{19}F NMR (471 MHz, CD_3CN) at 25 °C for 2-Phenethyl acetate derived tetrafluorothianthrene salt (**4**)

$$wt(\%) = \frac{mg_{IS} \times MW_{cpd} \times \text{molar ratio} \times P_{IS}}{mg_{cpd} MW_{IS}}$$

$$wt(\%) = \frac{10.8\ mg\ \ x\ \ 538.28\ gmol^{-1}\ x\ \ 0.405\ x\ 1.0}{10.8\ mg\ \ x\ \ 218.20\ gmol^{-1}} \times 100 = 99.9\%$$


OAc
5
O
O
IS

7.26 CDCl3
1.00
0.65
0.65
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)

Quant. ^{1}H NMR (400 MHz, $CDCl_3$) at 25 °C for [4-(4-phenylphenyl)phenyl] ethyl acetate

$$wt(\%) = \frac{mg_{IS} \times MW_{cpd} \times \text{molar ratio} \times P_{IS}}{mg_{cpd} MW_{IS}}$$

$$wt(\%) = \frac{10.1\ mg \times 316.40\ gmol^{-1} \times 0.65 \times 1.0}{9.80\ mg \times 212.25\ gmol^{-1}} \times 100 = 99.9\%$$