

Supporting Information

Germylation of Arenes via Pd(I) Dimer enabled Sulfonium Salt Functionalization

Ayman Selmani, Avetik G. Gevorgian and Franziska Schoenebeck*

Institute of Organic Chemistry, RWTH Aachen University Landoltweg 1, 52074 Aachen (Germany)

E-mail: franziska.schoenebeck@rwth-aachen.de

Contents

1. General Experimental Details	3
2. General Procedures	5
2.1 Thianthrenation of Arenes	5
2.2 Pd(I)-catalyzed Germylation of Tetrafluorothianthrenium Salt	5
3. Reaction development	27
3.1 Catalyst Screening	27
3.2 Solvent Screening	28
3.3 Germane Source Screening.....	29
4. NMR spectra	30
5. References	82

1. General Experimental Details

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in dried glassware under an argon atmosphere and were performed either in an argon-filled glovebox or by using standard *Schlenk* techniques unless otherwise stated. All reagents and starting materials were commercially available and used as received. Anhydrous dichloromethane and acetonitrile were dried using an Innovative Technology PS-MD-5 solvent purification system. Solvents used in work up and purification were distilled prior to use. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 aluminium plates with unmodified silica and visualized either under UV light or stained with potassium permanganate. Flash column chromatography was performed with Merck silica gel 60 (35 – 70 mesh).

All ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance Neo 600 or Varian VNMRs 400 spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced either to residual solvent peak (CDCl_3 , CD_2Cl_2 , CD_3CN , $(\text{CD}_3)_2\text{CO}$, $(\text{CD}_3)_2\text{SO}$ for ^1H and ^{13}C) or by the instrument internally after locking and shimming to the deuterated solvent (for ^{19}F). Coupling constants (J) are given in Hertz (Hz).

Gas chromatography coupled with mass spectrometry (GC-MS) was performed on an Agilent Technologies 5975 series MSD mass spectrometer under electrospray ionization (EI) mode coupled with an Agilent Technologies 7820A gas chromatograph employing an Agilent HP-5MS column (30 m \times 0.250 μm \times 0.250 μm) or an Agilent CP-Sil8-CB column (30 m \times 0.25 μm \times 1.00 μm).

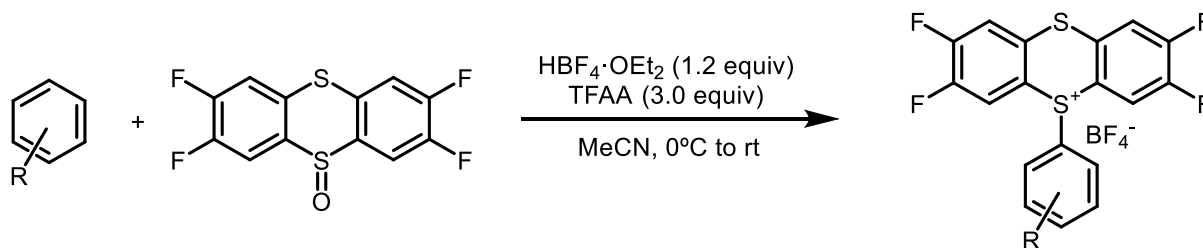
High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL (ESI), Finnigan MAT95 (EI, 70 eV) or Bruker Maxis II LC-MS-System (APCI). Low-resolution masses of known compounds were extracted from their GC-MS chromatograms. IR spectra were recorded on a Spectrum 100 spectrometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR).

Compounds 2,3,7,8-tetrafluorothianthrene¹ (TFT), 2,3,7,8-tetrafluorothianthrene-*S*-oxide¹ (TFTO), and [Pd(μ -I)P^{*t*}Bu₃]₂² were prepared according to the corresponding literature.

2. General Procedures

2.1 Thianthrenation of Arenes

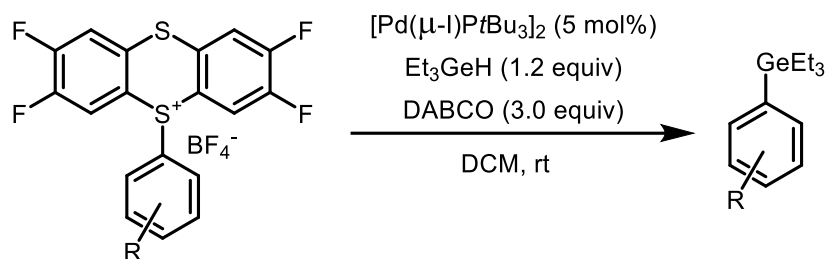
General Procedure (GP-1)



Under an ambient atmosphere, a 20 mL glass vial equipped with a magnetic stir bar was charged with arene (1.50 mmol, 1.0 equiv) and TFTO (457.0 mg, 1.50 mmol, 1.0 equiv) and anhydrous MeCN (1.5 mL, $c = 1.0$ M). After cooling to 0°C, $\text{HBF}_4 \cdot \text{OEt}_2$ (0.25 mL, 1.80 mmol, 1.2 equiv) was added in one portion to the reaction mixture. Subsequently, trifluoroacetic anhydride (0.63 mL, 4.50 mmol, 3.0 equiv) was added in one portion. The mixture was stirred at 0 °C for 1 hour, then at room temperature overnight. The solution was diluted with DCM and poured onto a mixture of DCM and saturated aqueous NaHCO_3 solution. The layers were separated, and the aqueous phase was extracted twice with DCM. Then, the combined organic layer was washed three times with aqueous NaBF_4 solution (10% w/w), then dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel.

2.2 Pd(I)-catalyzed Germylation of Tetrafluorothianthrenium Salt

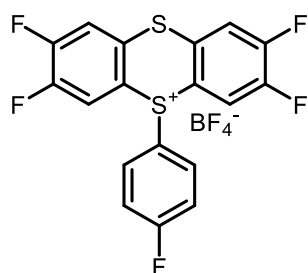
General Procedure (GP-2)



In an argon-filled glovebox, a 20 mL glass vial equipped with a magnetic stir bar was charged with the tetrafluorothianthrenium salt (0.300 mmol, 1.0 equiv), $[\text{Pd}(\mu\text{-I})\text{P}^t\text{Bu}_3]_2$

(13.0 mg, 15.0 μ mol, 5 mol%), DABCO (101.0 mg, 0.900 mmol, 3.0 equiv) and anhydrous DCM (3 mL, $c = 0.1$ M). Et_3GeH (58.0 μ L, 0.360 mmol, 1.2 equiv) was added, and the sealed vial was taken out from the glovebox and allowed to stir overnight at room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel.

Fluorobenzene derived tetrafluorothianthrenium salt (**S₁**)

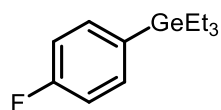


Prepared according to GP-1 from fluorobenzene (0.14 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (356.0 mg, 0.760 mmol, 51%).

$R_f = 0.42$ (DCM/MeOH 9:1). $^1\text{H NMR}$ (600 MHz, CD_3CN): $\delta/\text{ppm} = 8.40$ (dd, $J = 9.1, 7.2$ Hz, 2H), 7.96 (dd, $J = 9.9, 7.0=2$ Hz, 2H), 7.28

(d, $J = 6.4$ Hz, 4H). $^{13}\text{C NMR}$ (151 MHz, CD_3CN): $\delta/\text{ppm} = 166.4$ (d, $J = 255.0$ Hz), 154.9 (dd, $J = 261.8, 12.9$ Hz, 2C), 151.6 (dd, $J = 255.3, 13.7$ Hz, 2C), 135.3 (dd, $J = 8.8, 3.6$ Hz, 2C), 132.3 (d, $J = 9.7$ Hz, 2C), 125.5 (dd, $J = 22.3, 2.1$ Hz, 2C), 121.3 (d, $J = 22.3$ Hz, 2C), 118.9 (d, $J = 23.9$ Hz, 2C), 118.8 (d, $J = 2.9$ Hz), 115.3 (dd, $J = 6.9, 3.8$ Hz, 2C). $^{19}\text{F NMR}$ (564 MHz, CD_3CN): $\delta/\text{ppm} = -105.9, -125.2, -133.7, -151.4, -151.5$. **IR** (neat): 3105, 3047, 2661, 2570, 2323, 2204, 2162, 2080, 1989, 1904, 1578, 1479, 1404, 1381, 1282, 1234, 1199, 1167, 1040, 967, 897, 878, 834, 794, 693, 662 cm^{-1} . **HRMS** (ESI): m/z $[\text{M-BF}_4]^+$ calcd for $\text{C}_{18}\text{H}_8\text{F}_5\text{S}_2$: 382.9984; found: 382.9984.

Triethyl(4-fluorophenyl)germane (**1**)



Prepared according to GP-2 from **S₁** (141.0 mg, 0.300 mmol, 1.0 equiv).

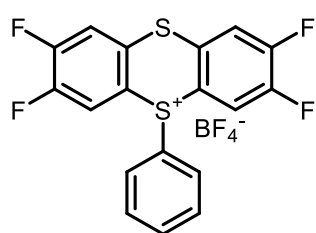
The title product was obtained after purification by column chromatography (pentane) as a colorless oil (55.0 mg, 0.220 mmol, 72%).

Scale-up reaction: In an argon-filled glovebox, a 20 mL glass vial equipped with a magnetic stir bar was charged with **S₁** (564.0 mg, 1.20 mmol, 1.0 equiv), $[\text{Pd}(\mu\text{-I})\text{P}^t\text{Bu}_3]_2$ (52.0 mg, 60.0 μ mol, 5 mol%), DABCO (404.0 mg, 3.60 mmol, 3.0 equiv) and anhydrous DCM (12 mL, $c = 0.1$ M). Et_3GeH (232.0 μ L, 1.44 mmol, 1.2 equiv) was added, and the sealed vial was taken out from the glovebox and allowed to stir overnight at room temperature.

The solvent was removed under reduced pressure, and the title product was obtained after purification by column chromatography (pentane) as a colorless oil (218.0 mg, 0.850 mmol, 72%).

R_f = 0.81 (Pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ/ppm = 7.45 – 7.35 (m, 2H), 7.23 – 7.01 (m, 2H), 1.09 – 1.02 (m, 9H), 1.01 – 0.94 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ/ppm = 163.4 (d, J = 246.4 Hz), 135.7 (d, J = 6.9 Hz), 135.1 (d, J = 4.1 Hz), 115.1 (d, J = 19.4 Hz), 9.0 (3C), 4.5 (3C). $^{19}\text{F NMR}$ (564 MHz, CDCl_3): δ/ppm = -113.8. **MS** (70 eV, EI): m/z (%): 229 (22), 228 (11), 227 (100) $[\text{M-Et}]^+$, 226 (30), 225 (75), 223 (58), 201 (13), 199 (63), 198 (18), 197 (47), 195 (36), 173 (18), 171 (89), 170 (25), 169 (88), 168 (11), 167 (67), 165 (15), 93 (23), 91 (16), 89 (13), 77 (10). These data are in agreement with those reported previously in the literature.³

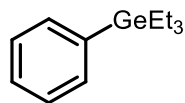
Benzene derived tetrafluorothianthrenium salt (**S₂**)



Prepared according to GP-1 from benzene (0.13 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (468.0 mg, 1.03 mmol, 69%).

R_f = 0.59 (DCM/MeOH 9:1). $^1\text{H NMR}$ (600 MHz, CD_3CN): δ/ppm = 8.52 – 8.38 (m, 2H), 7.95 (dd, J = 9.9, 7.1 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 8.1 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H). $^{13}\text{C NMR}$ (151 MHz, CD_3CN): δ/ppm = 154.9 (dd, J = 261.8, 13.2 Hz, 2C), 151.6 (dd, J = 255.6, 13.6 Hz, 2C), 135.4 (dd, J = 8.7, 3.9 Hz, 2C), 134.4, 131.4 (2C), 129.3 (2C), 125.7 (dd, J = 22.2, 2.6 Hz, 2C), 123.7, 121.2 (d, J = 21.9 Hz, 2C), 115.3 (dd, J = 7.3, 3.5 Hz, 2C). $^{19}\text{F NMR}$ (564 MHz, CD_3CN): δ/ppm = -125.4, -133.8, -151.3, -151.4. **HRMS** (ESI): m/z $[\text{M-BF}_4]^+$ calcd for $\text{C}_{18}\text{H}_9\text{F}_4\text{S}_2$: 365.0076; found: 365.0076. These data are in agreement with those reported previously in the literature.⁴

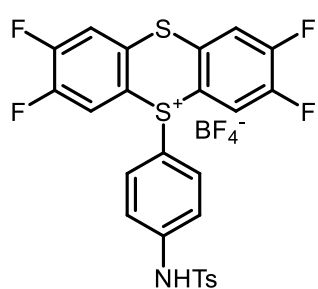
Triethyl(phenyl)germane (**2**)



Prepared according to GP-2 from **S₂** (136.0 mg, 0.300 mmol, 1.0 equiv). The yield was determined by quantitative $^1\text{H NMR}$ using mesitylene as an internal standard (69%) and the title product was obtained as a colorless oil.

$R_f = 0.76$ (Pentane). **$^1\text{H NMR}$** (600 MHz, CDCl_3): $\delta/\text{ppm} = 7.47 - 7.42$ (m, 2H), 7.37 – 7.30 (m, 3H), 1.12 – 1.04 (m, 9H), 1.05 – 0.98 (m, 6H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3): $\delta/\text{ppm} = 140.1, 134.2$ (2C), 128.3, 128.0 (2C), 9.1(3C), 4.4 (3C). **MS** (70eV, EI): m/z (%): 211 (22), 210 (11), 209 (100) $[\text{M-Et}]^+$, 208 (30), 207 (75), 205 (57), 183 (13), 181 (63), 180 (19), 179 (47), 177 (36), 155 (17), 153 (85), 152 (24), 151 (93), 149 (71), 147 (22), 99 (10). These data are in agreement with those reported previously in the literature.⁵

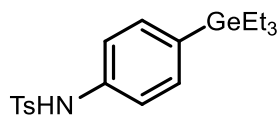
4-Methyl-*N*-phenylbenzenesulfonamide derived tetrafluorothianthrenium salt (**S₃**)



Prepared according to GP-1 from 4-methyl-*N*-phenylbenzenesulfonamide (370.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a yellow solid (428.0 mg, 0.690 mmol, 46%).

$R_f = 0.35$ (DCM/MeOH 9:1). **$^1\text{H NMR}$** (600 MHz, CD_3CN): $\delta/\text{ppm} = 8.71$ (br s, 1H), 8.33 (dd, $J = 9.0, 2.0$ Hz, 2H), 7.92 (dd, $J = 10.0, 2.0$ Hz, 2H), 7.69 – 7.66 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.19 (m, 2H), 7.11 – 7.08 (m, 2H), 2.36 (s, 3H). **$^{13}\text{C NMR}$** (151 MHz, CD_3CN): $\delta/\text{ppm} = 155.3$ (dd, $J = 261.7, 13.2$ Hz, 2C), 152.1 (dd, $J = 255.6, 13.4$ Hz, 2C), 146.6, 144.2, 137.4, 135.6 (dd, $J = 8.5, 4.0$ Hz, 2C), 131.6 (2C), 131.5 (2C), 128.7, 125.8 (dd, $J = 22.1, 2.4$ Hz, 2C), 121.7 (d, $J = 21.9$ Hz, 2C), 121.3 (2C), 117.2 (2C), 116.1 (dd, $J = 7.2, 3.4$ Hz, 2C), 22.2. **$^{19}\text{F NMR}$** (564 MHz, CD_3CN): $\delta/\text{ppm} = -125.5, -133.8, -151.0, -151.1$. **HRMS** (ESI): m/z $[\text{M-BF}_4]^+$ calcd for $\text{C}_{25}\text{H}_{16}\text{NO}_2\text{F}_4\text{S}_3$: 534.0274; found: 534.0275. These data are in agreement with those reported previously in the literature.⁶

4-Methyl-*N*-(4-(triethylgermyl)phenyl)benzenesulfonamide (**3**)

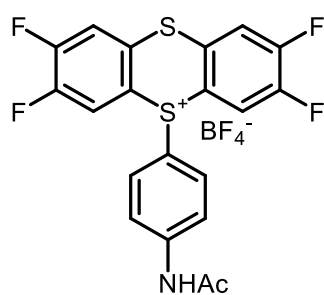


Prepared according to GP-2 from **S₃** (186.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 8.5:1.5) as a yellow oil (74.0 mg, 0.180 mmol, 61%).

$R_f = 0.59$ (Pentane/EtOAc 8:2). **$^1\text{H NMR}$** (600 MHz, CDCl_3): $\delta/\text{ppm} = 7.68$ (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 7.8$ Hz, 2H), 6.81 (s, 1H), 2.38 (s, 3H), 1.07 – 0.97 (m, 9H), 0.98 – 0.86 (m, 6H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3): $\delta/\text{ppm} = 144.0$,

136.7, 136.6, 136.6, 135.0 (2C), 129.8 (2C), 127.5 (2C), 120.8 (2C), 21.7, 9.0 (3C), 4.3 (3C). **IR** (neat): 3237, 3022, 2951, 2912, 2873, 2320, 2162, 2030, 1907, 1805, 1654, 1594, 1496, 1452, 1385, 1327, 1295, 1265, 1233, 1186, 1150, 1090, 1018, 920, 816, 756, 666 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₉H₂₈⁷⁴GeNO₂S: 408.1053; found: 408.1046.

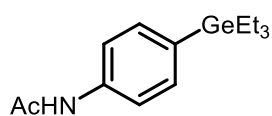
***N*-phenylacetamide derived tetrafluorothianthrenium salt (**S₄**)**



Prepared according to GP-1 from *N*-phenylacetamide (270.3 mg, 2.00 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a pale yellow solid (406.8 mg, 0.800 mmol, 40%).

R_f = 0.11 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, (CD₃)₂CO): δ /ppm = 9.62 (br s, 1H), 8.78 (dd, J = 9.3, 7.2 Hz, 2H), 8.25 (dd, J = 10.0, 7.0 Hz, 2H), 7.84 (d, J = 9.1 Hz, 2H), 7.42 (d, J = 9.1 Hz, 2H), 2.09 (s, 3H). **¹³C NMR** (151 MHz, (CD₃)₂CO): δ /ppm = 170.0, 154.6 (dd, J = 261.0, 13.3 Hz, 2C), 151.4 (dd, J = 255.2, 13.5 Hz, 2C), 145.2, 135.0 (dd, J = 8.6, 3.9 Hz, 2C), 130.6 (2C), 125.5 (dd, J = 22.2, 1.6 Hz, 2C), 121.1 (2C), 121.0 (d, J = 22.0 Hz, 2C), 116.5 (dd, J = 7.1, 3.5 Hz, 2C), 115.4, 24.4. **¹⁹F NMR** (564 MHz, (CD₃)₂CO): δ /ppm = -126.3, -134.4, -151.1, -151.2. **IR** (neat): 3344, 3102, 3043, 3012, 2160, 1693, 1579, 1526, 1479, 1398, 1380, 1314, 1286, 1255, 1194, 1057, 966, 894, 843, 797, 735, 696, 661 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₀H₁₂NOF₄S₂: 422.0291; found: 422.0288.

***N*-(4-(triethylgermyl)phenyl)acetamide (**4**)**



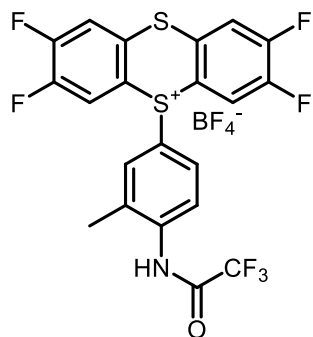
Prepared according to GP-2 from **S₄** (152.8 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (Pentane to Pentane/EtOAc 2:1) as a brown oil (26.7 mg, 0.091 mmol, 30%).

R_f = 0.33 (Pentane/EtOAc 1:1). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.46 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 7.16 (br s, 1H), 2.17 (s, 3H), 1.08 – 1.02 (m, 9H), 1.00 – 0.93 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 168.4, 138.0, 135.6, 134.8 (2C), 119.5 (2C), 24.8, 9.1 (3C), 4.4 (3C). **IR** (neat): 3300, 3177, 3100, 3029, 2950, 2871, 2329, 2097, 1901, 1667,

1589, 1524, 1459, 1428, 1385, 1319, 1289, 1255, 1185, 1089, 1014, 965, 816, 699 cm^{-1} .

HRMS (APCI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{24}^{74}\text{GeNNaO}$: 318.0884; found: 318.0882.

2-Methylaniline derived tetrafluorothianthrenium salt (**S₅**)

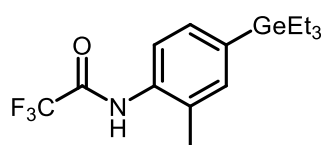


Prepared according to GP-1 from 2-methylaniline (0.16 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a light purple solid (614.0 mg, 1.06 mmol, 71%).

R_f = 0.47 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD_2Cl_2): δ /ppm = 8.96 (br s, 1H), 8.47 (dd, J = 8.7, 6.6 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.17 (d, J = 2.6 Hz, 1H), 7.02 (dd, J = 8.9, 2.6 Hz, 1H), 2.21 (s, 3H).

¹³C NMR (151 MHz, CD_2Cl_2): δ /ppm = 155.9 (q, J = 38.4 Hz), 154.4 (dd, J = 265.5, 13.2 Hz, 2C), 151.3 (dd, J = 259.4, 13.3 Hz, 2C), 139.0, 135.6, 134.6 (dd, J = 8.2, 3.9 Hz, 2C), 130.6, 126.9, 126.1, 125.2 (dd, J = 21.7, 1.5 Hz, 2C), 120.4 (d, J = 21.2 Hz, 2C), 119.7, 116.0 (q, J = 288.3 Hz), 114.8 (dd, J = 6.5, 3.3 Hz, 2C), 17.9. **¹⁹F NMR** (564 MHz, CD_2Cl_2): δ /ppm = -122.3, -130.4, -148.9, -149.0. **IR** (neat): 3296, 3050, 2925, 2570, 2325, 2161, 1999, 1927, 1727, 1576, 1537, 1479, 1382, 1337, 1285, 1257, 1049, 965, 882, 797, 765, 727, 706, 664 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}-\text{BF}_4]^+$ calcd for $\text{C}_{21}\text{H}_{11}\text{NOF}_7\text{S}_2$: 490.01648; found: 490.01611.

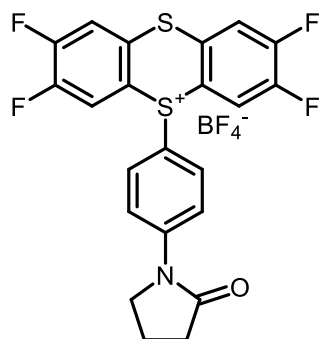
2,2,2-Trifluoro-*N*-(2-methyl-4-(triethylgermyl)phenyl)acetamide (**5**)



Prepared according to GP-2 from **S₅** (173.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (69.0 mg, 0.190 mmol, 64%).

R_f = 0.47 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl_3): δ /ppm = 7.75 (d, J = 7.9 Hz, 1H), 7.71 (br s, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.29 (s, 1H), 2.30 (s, 3H), 1.09 – 1.02 (m, 9H), 1.02 – 0.95 (m, 6H). **¹³C NMR** (151 MHz, CDCl_3): δ /ppm = 155.1 (q, J = 36.9 Hz), 139.4, 136.6, 133.0, 132.9, 129.0, 122.5, 116.1 (q, J = 288.9 Hz), 17.6, 9.1 (3C), 4.4 (3C). **¹⁹F NMR** (564 MHz, CDCl_3): δ /ppm = -75.7. **IR** (neat): 3278, 2953, 2873, 2325, 2113, 1904, 1713, 1582, 1531, 1492, 1459, 1378, 1333, 1249, 1161, 1015, 966, 912, 815, 763, 703 cm^{-1} . **HRMS** (APCI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{23}^{74}\text{GeNOF}_3$: 364.09435; found: 364.09420.

1-Phenylpyrrolidin-2-one derived tetrafluorothianthrenium salt (**S₆**)

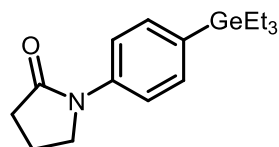


Prepared according to GP-1 from 1-phenylpyrrolidin-2-one (242.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (752.0 mg, 1.41 mmol, 94%).

R_f = 0.41 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 8.55 – 8.38 (m, 2H), 7.81 (d, J = 9.1 Hz, 2H), 7.69 (dd, J = 8.8, 6.5 Hz, 2H), 7.26 (d, J = 9.1 Hz, 2H), 3.80 (t, J = 7.1 Hz, 2H), 2.58 (t,

J = 8.1 Hz, 2H), 2.15 (p, J = 7.7 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 175.5, 153.9 (dd, J = 265.6, 13.0 Hz, 2C), 150.8 (dd, J = 259.9, 13.2 Hz, 2C), 144.3, 133.8 (dd, J = 8.0, 3.8 Hz, 2C), 129.3 (2C), 124.6 (d, J = 21.7 Hz, 2C), 121.0 (2C), 119.9 (d, J = 21.2 Hz, 2C), 115.2, 115.0 (dd, J = 6.3, 3.2 Hz, 2C), 48.4, 32.8, 17.7. **¹⁹F NMR** (564 MHz, CDCl₃): δ /ppm = -122.2, -130.1, -149.0, -149.1. **IR** (neat): 3388, 3108, 3047, 2970, 2892, 2571, 2324, 2161, 2025, 1914, 1759, 1697, 1579, 1479, 1418, 1382, 1285, 1194, 1153, 1051, 966, 887, 832, 796, 693 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₂H₁₄NOF₄S₂: 448.0447; found: 448.0442.

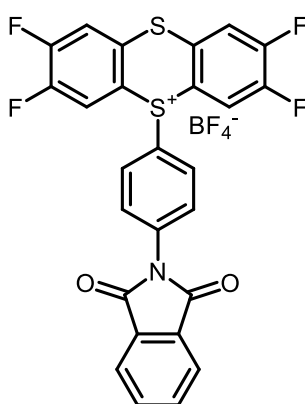
1-(4-(Triethylgermyl)phenyl)pyrrolidin-2-one (**6**)



Prepared according to GP-2 from **S₆** (161.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 7:3) as an orange oil (73.0 mg, 0.230 mmol, 76%).

R_f = 0.18 (Pentane/EtOAc 8:2). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.63 – 7.52 (m, 2H), 7.48 – 7.40 (m, 2H), 3.87 (t, J = 7.0 Hz, 2H), 2.61 (t, J = 8.1 Hz, 2H), 2.16 (p, J = 7.4 Hz, 2H), 1.08 – 1.02 (m, 9H), 1.01 – 0.93 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 174.3, 139.5, 135.7, 134.6 (2C), 119.5 (2C), 48.8, 32.9, 18.2, 9.0 (3C), 4.3 (3C). **IR** (neat): 3855, 3372, 3025, 2950, 2871, 2732, 2330, 2239, 2163, 2027, 1907, 1691, 1591, 1497, 1462, 1406, 1385, 1306, 1225, 1110, 1011, 964, 908, 874, 837, 812, 737, 692 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₆H₂₆⁷⁴GeNO: 322.1226; found: 322.1224.

***N*-Phenylphthalimide derived tetrafluorothianthrenium salt (**S₇**)**

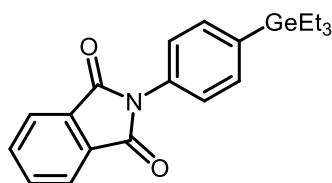


Prepared according to GP-1 from *N*-phenylphthalimide (335.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (601.0 mg, 1.00 mmol, 67%).

R_f = 0.65 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ /ppm = 8.46 (dd, J = 9.0, 7.1 Hz, 2H), 7.99 (dd, J = 9.9, 7.0 Hz, 2H), 7.93 (dd, J = 5.5, 3.1 Hz, 2H), 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.42 – 7.34 (m, 2H). **¹³C NMR** (151 MHz,

CD₃CN): δ /ppm = 167.5 (2C), 154.90 (dd, J = 262.1, 13.0 Hz, 2C), 151.59 (dd, J = 255.8, 13.6 Hz, 2C), 137.8, 136.0 (2C), 135.39 (dd, J = 8.6, 3.7 Hz, 2C), 132.5 (2C), 130.0 (2C), 129.0 (2C), 125.68 (dd, J = 22.3, 2.3 Hz, 2C), 124.6 (2C), 122.1, 121.31 (d, J = 21.9 Hz, 2C), 114.99 (dd, J = 7.2, 3.5 Hz, 2C). **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -125.1, -133.6, -151.4, -151.4. **IR** (neat): 3539, 3107, 3053, 2564, 2323, 2160, 2078, 2000, 1908, 1783, 1713, 1578, 1477, 1409, 1354, 1283, 1226, 1195, 1052, 962, 881, 828, 795, 714, 663 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₆H₁₂NO₂F₄S₂: 510.0240; found: 510.0234.

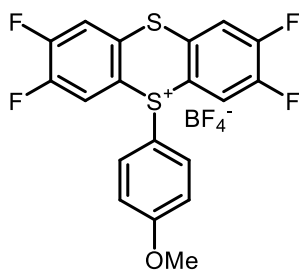
2-(4-(Triethylgermyl)phenyl)isoindoline-1,3-dione (7**)**



Prepared according to GP-2 from **S₇** (179.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (Pentane/EtOAc 10:0 to 9:1) as an orange oil (81.0 mg, 0.210 mmol, 71%).

R_f = 0.18 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.99 – 7.93 (m, 2H), 7.82 – 7.76 (m, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 1.11 – 1.06 (m, 9H), 1.04 – 0.99 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 167.5, 140.6, 134.8 (2C), 134.5 (2C), 132.0, 131.7, 125.8 (2C), 123.9 (2C), 9.1 (3C), 4.4 (3C). **IR** (neat): 3476, 3067, 3027, 2947, 2868, 2322, 2161, 1899, 1781, 1707, 1592, 1501, 1461, 1423, 1374, 1282, 1220, 1220, 1177, 1113, 1072, 1014, 960, 882, 849, 812, 787, 759, 706 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₂₀H₂₄⁷⁴GeNO₂: 384.1019; found: 384.1015.

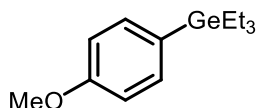
Anisole derived tetrafluorothianthrenium salt (**S₈**)



Prepared according to GP-1 from anisole (0.16 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (493.0 mg, 1.04 mmol, 69%).

R_f = 0.65 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₂Cl₂): δ /ppm = 8.37 (dd, J = 8.4, 7.0 Hz, 2H), 7.73 (dd, J = 9.1, 6.7 Hz, 2H), 7.31 (d, J = 9.2 Hz, 2H), 7.04 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H). **¹³C NMR** (151 MHz, CD₃CN): δ /ppm = 165.0, 154.6 (dd, J = 261.7, 13.0 Hz, 2C), 151.6 (dd, J = 255.4, 13.7 Hz, 2C), 134.6 (dd, J = 8.4, 3.6 Hz, 2C), 131.8 (2C), 124.8 (dd, J = 22.1, 1.9 Hz, 2C), 121.1 (d, J = 21.8 Hz, 2C), 117.3 (2C), 116.2 (dd, J = 6.9, 3.5 Hz, 2C), 112.4, 56.9. **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -126.0, -133.8, -151.6, -151.7. **IR** (neat): 3101, 3051, 2954, 2850, 2569, 2323, 2200, 2160, 2036, 1990, 1745, 1576, 1479, 1411, 1381, 1283, 1261, 1185, 1025, 963, 890, 833, 794, 698, 666 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₁₉H₁₁OF₄S₂: 395.0182; found: 395.0183.

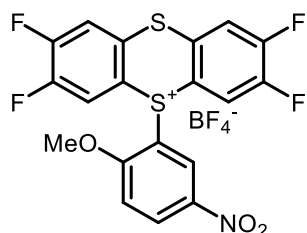
Triethyl(4-methoxyphenyl)germane (**8**)



Prepared according to GP-2 from **S₈** (145.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as a colorless oil (46.0 mg, 0.170 mmol, 58%).

R_f = 0.69 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.36 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 3.81 (s, 3H), 1.09 – 1.02 (m, 9H), 1.00 – 0.90 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 160.0, 135.3 (2C), 130.5, 113.9 (2C), 55.2, 9.1 (3C), 4.5 (3C). **MS** (70eV, EI): m/z (%): 241 (22), 240 (13), 239 (100) [M-Et]⁺, 238 (31), 237 (74), 235 (58), 213 (11), 211 (51), 210 (15), 209 (39), 207 (29), 185 (15), 183 (74), 182 (21), 181 (69), 179 (52), 177 (10), 151 (10), 149 (10), 135 (5), 121 (4), 105 (14), 103 (12). These data are in agreement with those reported previously in the literature.⁷

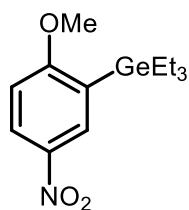
4-Nitroanisole derived tetrafluorothianthrenium salt (**S₉**)



Prepared according to GP-1 from 4-nitroanisole (0.19 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (405.0 mg, 0.77 mmol, 51%).

$R_f = 0.53$ (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ /ppm = 8.48 (dd, $J = 9.2, 2.6$ Hz, 1H), 8.39 (dd, $J = 9.2, 7.2$ Hz, 2H), 8.00 (dd, $J = 9.9, 7.0$ Hz, 2H), 7.52 (d, $J = 2.6$ Hz, 1H), 7.42 (d, $J = 9.2$ Hz, 1H), 4.12 (s, 3H). **¹³C NMR** (151 MHz, CD₃CN): δ /ppm = 163.2, 154.7 (dd, $J = 262.3, 13.2$ Hz, 2C), 151.6 (dd, $J = 255.6, 13.4$ Hz, 2C), 142.3, 136.0 (dd, $J = 8.6, 3.8$ Hz, 2C), 132.6, 126.0, 125.7 (dd, $J = 22.5, 2.6$ Hz, 2C), 121.0 (d, $J = 21.8$ Hz, 2C), 115.6, 112.8 (dd, $J = 7.4, 3.5$ Hz, 2C), 109.8, 59.3. **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -124.9, -133.6, -150.9, -150.9. **IR** (neat): 3110, 3056, 2952, 2857, 2563, 2323, 2158, 2085, 1768, 1680, 1576, 1531, 1478, 1378, 1351, 1280, 1195, 1043, 963, 898, 837, 794, 742, 697, 658 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₁₉H₁₀NO₃F₄S₂: 440.0033; found: 440.0042.

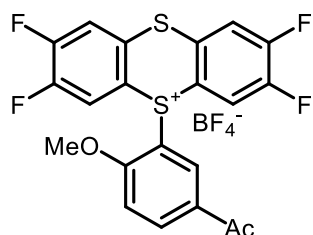
Triethyl(2-methoxy-5-nitrophenyl)germane (**9**)



Prepared according to GP-2 from **S₉** (158.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as a yellow oil (55.0 mg, 0.180 mmol, 59%).

$R_f = 0.50$ (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 8.21 (dd, $J = 9.0, 2.8$ Hz, 1H), 8.17 (d, $J = 2.8$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 1H), 3.89 (s, 3H), 1.40 – 0.88 (m, 15H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 168.4, 141.8, 131.1, 130.0, 126.8, 109.0, 56.0, 9.1 (3C), 4.7 (3C). **IR** (neat): 3867, 3097, 2950, 2872, 2732, 2454, 2328, 2112, 1998, 1889, 1818, 1597, 1574, 1510, 1465, 1393, 1335, 1254, 1179, 1142, 1119, 1057, 1018, 969, 911, 878, 822, 792, 753, 704 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₃H₂₂⁷⁴GeNO₃: 314.0812; found: 314.0812.

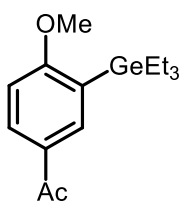
4-Acetylanisole derived tetrafluorothianthrenium salt (**S₁₀**)



Prepared according to GP-1 from 4-acetylanisole (300.4 mg, 2.00 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a pale brown solid (299.1 mg, 0.480 mmol, 32%).

$R_f = 0.29$ (DCM/MeOH 9:1). $^1\text{H NMR}$ (600 MHz, CD_3CN): $\delta/\text{ppm} = 8.31$ (dd, $J = 9.2, 7.2$ Hz, 2H), 8.25 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.97 (dd, $J = 9.9, 7.1$ Hz, 2H), 7.33 (d, $J = 8.7$ Hz, 1H), 7.25 (d, $J = 2.0$ Hz, 1H), 4.06 (s, 3H), 2.43 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CD_3CN): $\delta/\text{ppm} = 195.7, 161.9, 154.7$ (dd, $J = 262.1, 13.3$ Hz, 2C), 151.6 (dd, $J = 255.5, 13.6$ Hz, 2C), $137.6, 135.8$ (dd, $J = 8.6, 3.8$ Hz, 2C), $131.7, 130.2, 125.5$ (dd, $J = 22.0, 2.4$ Hz, 2C), 120.9 (d, $J = 21.8$ Hz, 2C), $115.1, 113.3$ (dd, $J = 7.3, 3.5$ Hz, 2C), $109.2, 58.7, 26.7$. $^{19}\text{F NMR}$ (564 MHz, CD_3CN): $\delta/\text{ppm} = -125.3, -133.8, -151.7, -151.7$. **IR** (neat): 3101, 3043, 2160, 1674, 1575, 1478, 1379, 1276, 1198, 1052, 965, 896, 832, 796, 729, 698, 662 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}-\text{BF}_4]^+$ calcd for $\text{C}_{21}\text{H}_{13}\text{O}_2\text{F}_4\text{S}_2$: 437.0288; found: 437.0301.

1-(4-Methoxy-3-(triethylgermyl)phenyl)ethan-1-one (**10**)

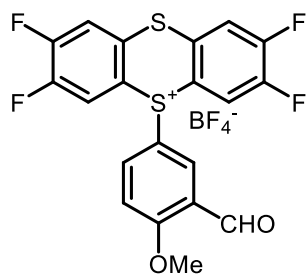


Prepared according to GP-2 from **S₁₀** (157.3 mg, 0.300 mmol, 1.0 equiv).

The title product was obtained after purification by column chromatography (Pentane to Pentane/EtOAc 12:1) as a brown oil (37.2 mg, 0.120 mmol, 40%).

$R_f = 0.26$ (Pentane/EtOAc 12:1). $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta/\text{ppm} = 7.96 - 7.93$ (m, 2H), 6.84 (d, $J = 8.5$ Hz, 1H), 3.85 (s, 3H), 2.56 (s, 3H), 1.03 (br s, 15H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): $\delta/\text{ppm} = 197.4, 167.5, 136.2, 131.6, 130.3, 128.3, 108.9, 55.5, 26.5, 9.2$ (3C), 4.8 (3C). **IR** (neat): 2948, 2871, 2325, 2084, 1898, 1676, 1580, 1461, 1379, 1352, 1300, 1244, 1178, 1153, 1065, 1020, 961, 924, 817, 703 cm^{-1} . **HRMS** (APCI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{25}^{74}\text{GeO}_2$: 311.1066; found: 311.1066.

2-Methoxybenzaldehyde derived tetrafluorothianthrenium salt (**S₁₁**)

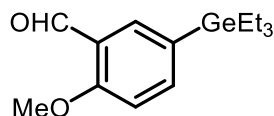


Prepared according to GP-1 from 2-methoxybenzaldehyde (204.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (473.0 mg, 0.930 mmol, 62%).

R_f = 0.47 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ /ppm = 10.26 (s, 1H), 8.39 (dd, J = 9.2, 7.2 Hz, 2H), 7.97 (dd,

J = 10.0, 7.1 Hz, 2H), 7.60 (d, J = 2.9 Hz, 1H), 7.47 (dd, J = 9.2, 2.9 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 3.98 (s, 3H). **¹³C NMR** (151 MHz, CD₃CN): δ /ppm = 188.3, 166.0, 154.8 (dd, J = 262.0, 13.2 Hz, 2C), 151.6 (dd, J = 255.6, 13.7 Hz, 2C), 136.6, 135.0 (dd, J = 8.6, 3.9 Hz, 2C), 130.0, 127.0, 125.3 (dd, J = 21.9, 2.3 Hz, 2C), 121.2 (d, J = 21.9 Hz, 2C), 116.3, 115.8 (dd, J = 7.2, 3.5 Hz, 2C), 114.2, 57.9. **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -76.0, -125.3, -133.5, -151.5, -151.6. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₀H₁₁O₂F₄S₂: 423.0131; found: 423.0131. These data are in agreement with those reported previously in the literature.⁶

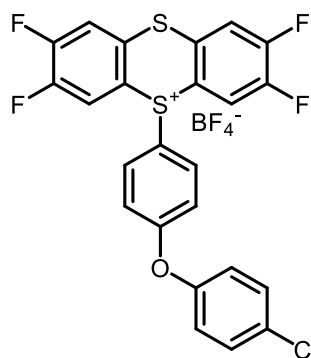
2-Methoxy-5-(triethylgermyl)benzaldehyde (**11**)



Prepared according to GP-2 from **S₁₁** (153.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (53.0 mg, 0.180 mmol, 60%).

R_f = 0.46 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 10.49 (s, 1H), 7.87 (d, J = 1.7 Hz, 1H), 7.60 (dd, J = 8.2, 1.7 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 1.10 – 1.00 (m, 9H), 1.01 – 0.94 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 190.4, 162.3, 141.8, 134.2, 131.1, 124.6, 111.5, 55.7, 9.0 (3C), 4.4 (3C). **IR** (neat): 3867, 3346, 2950, 2870, 2752, 2329, 2077, 2000, 1912, 1737, 1682, 1587, 1487, 1460, 1382, 1249, 1186, 1132, 1086, 1019, 967, 891, 814, 756, 700 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₄H₂₃⁷⁴GeO₂: 297.0910; found: 297.0910.

4-Phenoxybenzonitrile derived tetrafluorothianthrenium salt (**S₁₂**)

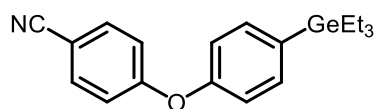


Prepared according to GP-1 from 4-phenoxybenzonitrile (293.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (700.0 mg, 1.23 mmol, 82%).

R_f = 0.56 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₂Cl₂): δ /ppm = 8.51 (dd, J = 8.5, 6.8 Hz, 2H), 7.76 (dd, J = 9.0, 6.6 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.33 – 7.27 (m, 2H), 7.21 – 7.09 (m, 4H).

¹³C NMR (151 MHz, CD₂Cl₂): δ /ppm = 161.0, 158.8, 154.4 (dd, J = 265.5, 13.0 Hz, 2C), 151.3 (dd, J = 259.7, 13.2 Hz, 2C), 135.0 (2C), 134.3 (dd, J = 7.8, 3.9 Hz, 2C), 131.2 (2C), 125.0 (dd, J = 22.1, 1.9 Hz, 2C), 121.2 (2C), 120.6 (2C), 120.3 (d, J = 21.3 Hz, 2C), 118.5, 116.6, 115.1 (dd, J = 6.7, 3.5 Hz, 2C), 109.1. **¹⁹F NMR** (564 MHz, CD₂Cl₂): δ /ppm = -122.3, -130.2, -149.3, -149.4. **IR** (neat): 3626, 3099, 3048, 2570, 2326, 2228, 2160, 2092, 1908, 1764, 1576, 1478, 1409, 1381, 1285, 1245, 1199, 1172, 1046, 966, 870, 834, 796, 733, 696, 664 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₅H₁₂ONF₄S₂: 482.0291; found: 482.0287.

4-(4-(Triethylgermyl)phenoxy)benzonitrile (**12**)

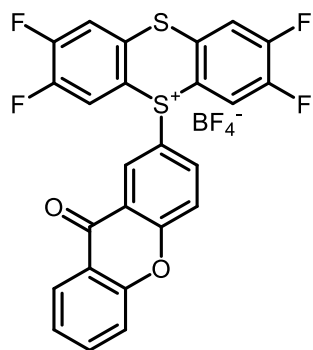


Prepared according to GP-2 from **S₁₂** (171.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5)

as a yellow oil (71.0 mg, 0.200 mmol, 67%).

R_f = 0.61 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.60 (d, J = 8.6 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H), 7.03 (dd, J = 11.7, 8.6 Hz, 2H), 1.10 – 1.05 (m, 9H), 1.03 – 0.98 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 161.8, 155.2, 136.6, 135.9 (2C), 134.3 (2C), 119.9 (2C), 119.0, 118.2 (2C), 105.9, 9.1 (3C), 4.4 (3C). **IR** (neat): 3418, 3023, 2951, 2907, 2871, 2336, 2227, 2085, 1904, 1782, 1604, 1581, 1493, 1425, 1384, 1243, 1168, 1085, 1014, 966, 869, 833, 699 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₉H₂₄⁷⁴GeNO: 356.1070; found: 356.1068.

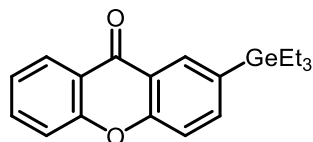
Xanthone derived tetrafluorothianthrenium salt (**S**₁₃)



Prepared according to GP-1 from xanthone (294.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (489.0 mg, 1.29 mmol, 86%).

R_f = 0.60 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, (CD₃)₂SO): δ /ppm = 8.93 (dd, J = 9.7, 7.3 Hz, 2H), 8.44 (dd, J = 10.2, 7.3 Hz, 2H), 8.20 (d, J = 2.7 Hz, 1H), 8.16 (dd, J = 8.0, 1.7 Hz, 1H), 7.93 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.73–7.69 (m, 2H), 7.54 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H). **¹³C NMR** (151 MHz, (CD₃)₂SO): δ /ppm = 174.7, 157.5, 155.4, 152.7 (dd, J = 260.2, 13.0 Hz, 2C), 149.3 (dd, J = 253.3, 13.4 Hz, 2C), 136.5, 134.3, 133.3 (dd, J = 8.7, 3.4 Hz, 2C), 127.8, 126.1, 125.4 (dd, J = 22.2, 1.9 Hz, 2C), 125.3, 122.0, 121.0, 120.8, 119.9 (d, J = 21.8 Hz, 2C), 119.7, 118.4, 115.8 (dd, J = 7.5, 3.0 Hz, 2C). **¹⁹F NMR** (564 MHz, (CD₃)₂SO): δ /ppm = -125.4, -133.9, -148.2, -148.3. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₅H₁₁O₂F₄S₂: 483.0131; found: 483.0136. These data are in agreement with those reported previously in the literature.⁴

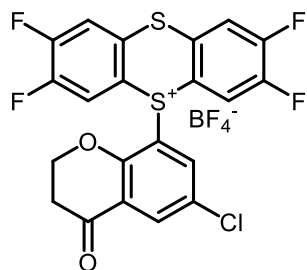
2-(Triethylgermyl)-9H-xanthen-9-one (**13**)



Prepared according to GP-2 from **S**₁₃ (171.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (67.0 mg, 0.190 mmol, 63%).

R_f = 0.39 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 8.40 (d, J = 1.6 Hz, 1H), 8.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.78 (dd, J = 8.3, 1.6 Hz, 1H), 7.71 (ddd, J = 8.3, 7.1, 1.6 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.43 – 7.35 (m, 1H), 1.11 – 1.03 (m, 15H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 177.4, 156.5, 156.2, 140.2, 135.5, 134.7, 132.3, 126.8, 123.8, 122.2, 121.3, 118.0, 117.3, 8.9 (3C), 4.3 (3C). **IR** (neat): 3889, 3316, 2951, 2871, 2733, 2327, 2078, 1825, 1659, 1595, 1460, 1405, 1305, 1275, 1219, 1173, 1142, 1107, 1073, 1016, 957, 879, 821, 758, 701 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₉H₂₃⁷⁴GeO₂: 357.0910; found: 357.0908.

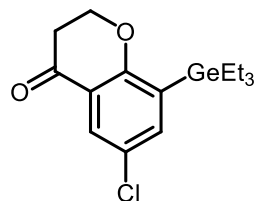
6-Chlorochroman-4-one derived tetrafluorothianthrenium salt (**S₁₄**)



Prepared according to GP-1 from 6-chlorochroman-4-one (274.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a yellow solid (524.0 mg, 0.950 mmol, 63%).

R_f = 0.44 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₂Cl₂): δ /ppm = 8.52 (dd, J = 8.7, 6.8 Hz, 2H), 8.13 – 8.01 (m, 1H), 7.78 (dd, J = 9.1, 6.7 Hz, 2H), 6.79 (d, J = 2.5 Hz, 1H), 4.86 (t, J = 6.5 Hz, 2H), 2.90 (t, J = 6.5 Hz, 2H). **¹³C NMR** (151 MHz, CD₂Cl₂): δ /ppm = 187.6, 158.9, 154.4 (dd, J = 266.0, 13.0 Hz, 2C), 151.3 (dd, J = 259.5, 13.3 Hz, 2C), 135.2 (dd, J = 7.5, 3.8 Hz, 2C), 133.5, 133.4, 128.2, 125.7 (dd, J = 22.2, 1.9 Hz, 2C), 124.9, 120.3 (d, J = 21.6 Hz, 2C), 112.8 (dd, J = 7.3, 3.6 Hz, 2C), 110.6, 70.3, 37.5. **¹⁹F NMR** (564 MHz, CD₂Cl₂): δ /ppm = -121.6, -129.7, -150.1, -150.2. **IR** (neat): 3624, 3049, 2563, 2326, 2162, 2076, 2031, 1897, 1703, 1577, 1477, 1444, 1379, 1274, 1198, 1047, 965, 878, 796, 754, 708, 662 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₁H₁₀O₂ClF₄S₂: 468.9741; found: 468.9742.

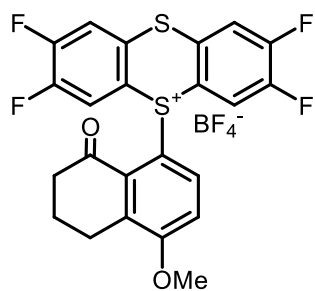
6-Chloro-8-(triethylgermyl)chroman-4-one (**14**)



Prepared according to GP-2 from **S₁₄** (167.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (63.0 mg, 0.190 mmol, 62%).

R_f = 0.32 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.82 (d, J = 2.7 Hz, 1H), 7.39 (d, J = 2.7 Hz, 1H), 4.49 (t, J = 6.5 Hz, 2H), 2.79 (t, J = 6.5 Hz, 2H), 1.04 (br s, 15H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 191.6, 164.1, 141.3, 132.1, 127.4, 126.8, 121.4, 67.0, 37.6, 9.1 (3C), 4.8 (3C). **IR** (neat): 3866, 3378, 3067, 2951, 2872, 2733, 2329, 2081, 1989, 1907, 1797, 1693, 1641, 1579, 1464, 1427, 1361, 1266, 1191, 1100, 1061, 1024, 971, 931, 889, 854, 815, 786, 759, 704 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₅H₂₂O₂⁷⁴GeCl: 343.0520; found: 343.0513.

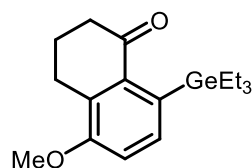
5-Methoxy-1-tetralone derived tetrafluorothianthrenium salt (**S₁₅**)



Prepared according to GP-1 from 5-methoxy-1-tetralone (264.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a beige solid (501.0 mg, 0.920 mmol, 61%).

R_f = 0.54 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ /ppm = 8.39 (dd, J = 9.7, 7.4 Hz, 2H), 7.90 (dd, J = 9.9, 7.1 Hz, 2H), 7.09 (d, J = 9.1 Hz, 1H), 6.93 (d, J = 9.1 Hz, 1H), 3.91 (s, 3H), 2.89 (t, J = 6.1 Hz, 2H), 2.72 (dd, J = 7.4, 6.1 Hz, 2H), 2.07 (p, J = 6.1 Hz, 2H). **¹³C NMR** (151 MHz, CD₃CN): δ /ppm = 200.0, 162.7, 153.9 (dd, J = 260.8, 13.2 Hz, 2C), 151.3 (dd, J = 254.1, 13.5 Hz, 2C), 140.8, 137.0 (dd, J = 8.4, 3.9 Hz, 2C), 132.5, 131.7, 125.9 (dd, J = 22.1, 1.9 Hz, 2C), 121.0 (d, J = 21.5 Hz, 2C), 117.5 (dd, J = 6.9, 3.5 Hz, 2C), 114.9, 109.4, 57.6, 38.3, 23.8, 21.7. **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -127.2, -134.8, -151.8, -151.9. **IR** (neat): 3136, 3100, 3051, 2954, 2896, 2562, 2324, 2158, 2014, 1907, 1672, 1577, 1476, 1380, 1340, 1277, 1230, 1194, 1027, 966, 929, 875, 833, 795, 663 cm⁻¹. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₃H₁₅O₂F₄S₂: 463.0444; found: 463.0441.

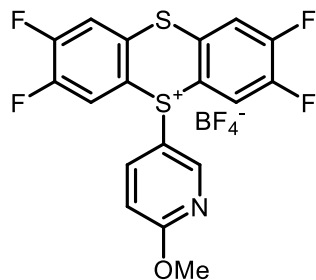
5-Methoxy-8-(triethylgermyl)-3,4-dihydronaphthalen-1(2H)-one (**15**)



Prepared according to GP-2 from **S₁₅** (165.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (51.0 mg, 0.150 mmol, 51%).

R_f = 0.79 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.43 (d, J = 8.1 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 3.86 (s, 3H), 2.92 (t, J = 6.2 Hz, 2H), 2.64 (t, J = 6.2 Hz, 2H), 2.10 (p, J = 6.2 Hz, 2H), 1.06 – 0.95 (m, 15H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 199.6, 157.3, 138.2, 134.7, 134.6, 131.8, 113.3, 55.7, 39.5, 23.6, 22.6, 9.6 (3C), 5.9 (3C). **IR** (neat): 3869, 3355, 3067, 2945, 2869, 2729, 2543, 2330, 2178, 2076, 1989, 1875, 1734, 1683, 1572, 1500, 1463, 1395, 1324, 1274, 1250, 1176, 1127, 1053, 1031, 968, 927, 874, 815, 708, 672 cm⁻¹. **HRMS** (APCI): m/z [M+H]⁺ calcd for C₁₇H₂₂⁷⁴GeO₂: 337.1217; found: 337.1220.

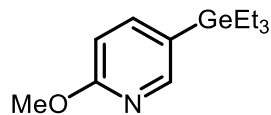
2-Methoxypyridine derived tetrafluorothianthrenium salt (**S₁₆**)



Prepared according to GP-1 from 2-methoxypyridine (0.16 mL, 1.50 mmol, 1.0 equiv) with slight modifications: TMSOTf (0.54 mL, 3.00 mmol, 2.0 equiv) was used instead of HBF₄·Et₂O. The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a pale yellow solid (352.0 mg, 1.10 mmol, 73%).

R_f = 0.53 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ/ppm = 8.35 (dd, *J* = 9.1, 7.2 Hz, 2H), 8.06 (dd, *J* = 2.9, 0.5 Hz, 1H), 7.97 (dd, *J* = 9.9, 7.1 Hz, 2H), 7.54 (dd, *J* = 9.2, 2.9 Hz, 1H), 6.91 (dd, *J* = 9.2, 0.6 Hz, 1H), 3.93 (s, 3H). **¹³C NMR** (151 MHz, CD₃CN): δ/ppm = 168.1, 154.8 (dd, *J* = 261.6, 13.1 Hz, 2C), 151.7 (dd, *J* = 155.6 Hz, 13.7 Hz, 2C), 149.5, 139.6, 134.9 (dd, *J* = 8.8, 4.0 Hz, 2C), 125.0 (dd, *J* = 22.3, 2.4 Hz, 2C), 121.3 (d, *J* = 21.9 Hz, 2C), 115.5 (dd, *J* = 7.2 Hz, 3.6 Hz, 2C), 114.2, 112.1, 55.5. **¹⁹F NMR** (564 MHz, CD₃CN): δ/ppm = -125.6, -133.6, -151.1, -151.1. **HRMS** (ESI): *m/z* [M-BF₄]⁺ calcd for C₁₈H₁₀NOF₄S₂: 396.0134; found: 396.0134. These data are in agreement with those reported previously in the literature.¹

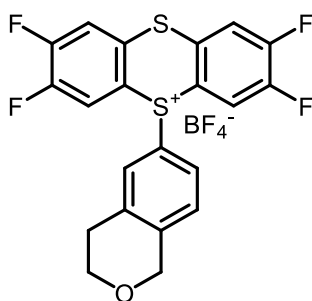
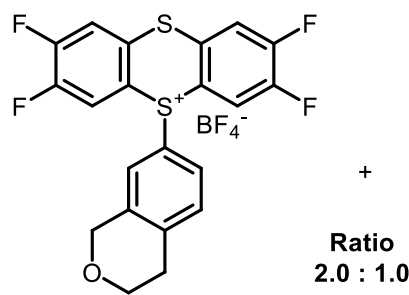
2-Methoxy-5-(triethylgermyl)pyridine (**16**)



Prepared according to GP-2 from **S₁₆** (145.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as an orange oil (57.0 mg, 0.210 mmol, 71%).

R_f = 0.75 (Pentane/EtOAc 9.5:0.5). **¹H NMR** (600 MHz, CDCl₃): δ/ppm = 8.15 (d, *J* = 1.9 Hz, 1H), 7.59 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 3.94 (s, 3H), 1.09 – 1.02 (m, 9H), 1.00 – 0.95 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ/ppm = 164.6, 151.6, 144.1, 125.6, 111.1, 53.3, 9.0 (3C), 4.4 (3C). **IR** (neat): 2950, 2873, 2734, 2327, 2191, 2107, 1918, 1661, 1580, 1482, 1430, 1351, 1281, 1176, 1127, 1098, 1020, 968, 825, 752, 700 cm⁻¹. **HRMS** (APCI): *m/z* [M+H]⁺ calcd for C₁₂H₂₂⁷⁴GeNO: 270.0913; found: 270.0914.

Isochromane derived tetrafluorothianthrenium salt (**S₁₇**)

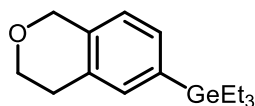
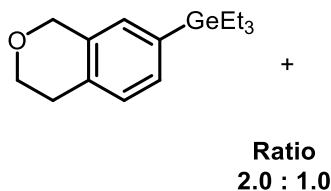


Prepared according to GP-1 from isochromane (189.0 mg, 1.50 mmol, 1.0 equiv). A mixture of both regioisomers was obtained after purification by column chromatography (DCM/MeOH

95:5) as a white solid (512.0 mg, 1.01 mmol, 67%).

R_f = 0.51 (DCM/MeOH 9:1). $^1\text{H NMR}$ (600 MHz, CD_3CN): **Major isomer:** δ/ppm = 8.42 – 8.33 (m, 2H), 7.99 – 7.92 (m, 2H), 7.28 (d, J = 8.4 Hz, 1H), 7.00 (dd, J = 8.4, 2.4 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 4.59 (s, 2H), 3.87 (t, J = 5.8 Hz, 2H), 2.84 (t, J = 5.8 Hz, 3H). **Minor isomer:** 8.44 – 8.36 (m, 2H), 8.00 – 7.88 (m, 2H), 7.16 (d, J = 8.5 Hz, 1H), 6.98 – 6.96 (m, 2H), 4.70 (s, 2H), 3.85 (t, J = 5.9 Hz, 2H), 2.75 (t, J = 5.8 Hz, 2H). $^{13}\text{C NMR}$ (151 MHz, CD_3CN): **Major isomer:** δ/ppm = 154.4 (dd, J = 261.7, 13.2 Hz, 2C), 151.2 (dd, J = 255.6, 13.4 Hz, 2C), 140.9, 139.1, 134.8 (dd, J = 8.6, 3.8 Hz, 2C), 131.8, 126.4, 125.2, 125.1 (dd, J = 21.9, 2.1 Hz, 2C), 120.8 (d, J = 21.8 Hz, 2C), 120.0, 115.0 (dd, J = 7.0, 3.4 Hz, 2C), 67.4, 64.8, 28.3. **Minor isomer:** δ/ppm = 154.4 (dd, J = 261.7, 13.2 Hz, 2C), 151.2 (dd, J = 255.6, 13.4 Hz, 2C), 142.2, 137.8, 134.8 (dd, J = 8.6, 3.8 Hz, 2C), 129.1, 127.5, 126.0, 125.1 (dd, J = 21.9, 2.1 Hz, 2C), 120.8 (d, J = 21.8 Hz, 2C), 120.5, 115.0 (dd, J = 7.0, 3.4 Hz, 2C), 67.4, 64.8, 28.3. $^{19}\text{F NMR}$ (564 MHz, CD_3CN): δ/ppm = -125.5, -133.9, -151.2. **IR** (neat): 3095, 3049, 2850, 2566, 2330, 2159, 2079, 2031, 1968, 1781, 1576, 1480, 1422, 1381, 1338, 1285, 1232, 1198, 1144, 1050, 965, 890, 797, 746, 696 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}-\text{BF}_4]^+$ calcd for $\text{C}_{21}\text{H}_{13}\text{OF}_4\text{S}_2$: 421.0339; found: 421.0336.

Triethyl(isochroman-6-yl)germane (**17**)

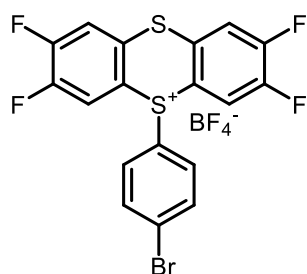


Prepared according to GP-2 from **S₁₇** (152.0 mg, 0.300 mmol, 1.0 equiv). A mixture of both regioisomers was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as a yellow

oil (56.0 mg, 0.190 mmol, 64%).

R_f = 0.62 (Pentane/EtOAc 9.5:0.5). **^1H NMR** (600 MHz, CDCl_3): **Major isomer:** δ/ppm = 7.24 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.04 (s, 1H), 4.80 (s, 2H), 4.01 – 3.97 (m, 2H), 2.89 – 2.84 (m, 2H), 1.10 – 1.04 (m, 9H), 1.02 – 0.95 (m, 6H). **Minor isomer:** δ/ppm = 7.24 (d, J = 7.5 Hz, 1H), 7.18 (s, 1H), 6.97 (d, J = 7.5 Hz, 1H), 4.78 (s, 2H), 4.01 – 3.97 (m, 2H), 2.89 – 2.84 (m, 2H), 1.10 – 1.04 (m, 9H), 1.02 – 0.95 (m, 6H). **^{13}C NMR** (151 MHz, CDCl_3): δ/ppm = **Major isomer:** 137.3, 134.7, 134.6, 132.1, 130.1, 128.6, 68.3, 65.6, 28.5, 9.1 (3C), 4.4 (3C). **Minor isomer:** δ/ppm = 137.8, 135.1, 133.4, 132.8, 131.7, 124.0, 68.1, 65.7, 28.6, 9.1 (3C), 4.4 (3C). **IR** (neat): 3882, 3421, 2950, 2870, 2734, 2327, 2089, 1789, 1597, 1566, 1458, 1426, 1375, 1332, 1273, 1230, 1204, 1106, 1013, 946, 880, 843, 748, 701 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{25}^{74}\text{GeO}$: 295.1112; found: 295.1115.

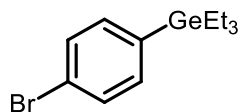
Bromobenzene derived tetrafluorothianthrenium salt (**S₁₈**)



Prepared according to GP-1 from bromobenzene (0.15 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (458.0 mg, 1.01 mmol, 67%).

R_f = 0.59 (DCM/MeOH 9:1). **^1H NMR** (600 MHz, CD_2Cl_2): δ/ppm = 8.58 (dd, J = 8.4, 7.1 Hz, 2H), 7.77 (dd, J = 9.1, 6.7 Hz, 2H), 7.67 (d, J = 9.1 Hz, 2H), 7.08 (d, J = 9.1 Hz, 2H). **^{13}C NMR** (151 MHz, CD_2Cl_2): δ/ppm = 154.5 (dd, J = 266.1, 13.1 Hz, 2C), 151.4 (dd, J = 260.5, 13.4 Hz, 2C), 134.5 (2C), 134.4 (dd, J = 8.0, 4.2 Hz, 2C), 129.7 (2C), 129.4, 125.5 (dd, J = 21.8, 2.6 Hz, 2C), 122.0, 120.3 (d, J = 21.3 Hz, 2C), 114.7 (dd, J = 6.8, 3.6 Hz, 2C). **^{19}F NMR** (564 MHz, CD_2Cl_2): δ/ppm = -121.7, -129.6, -149.3, -149.4. **HRMS** (ESI): m/z $[\text{M}-\text{BF}_4]^+$ calcd for $\text{C}_{18}\text{H}_8^{79}\text{BrF}_4\text{S}_2$: 442.9181; found: 442.9184. These data are in agreement with those reported previously in the literature.⁴

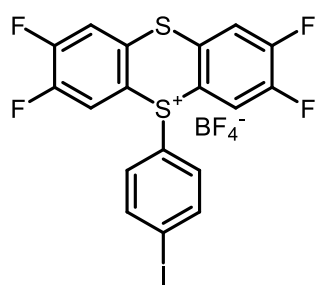
(4-Bromophenyl)triethylgermane (**18**)



Prepared according to GP-2 from **S₁₈** (159.0 mg, 0.300 mmol, 1.0 equiv). The yield was determined by quantitative ^1H NMR using mesitylene as an internal standard (60%) and the title product was obtained as a colorless oil.

$R_f = 0.85$ (Pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta/\text{ppm} = 7.49 - 7.45$ (m, 2H), 7.33 – 7.28 (m, 2H), 1.10 – 1.02 (m, 9H), 1.01 – 0.94 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): $\delta/\text{ppm} = 139.3, 138.8, 135.7$ (2C), 133.6, 131.1 (2C), 123.0, 9.0 (3C), 4.3 (3C). **MS** (70 eV, EI): m/z (%): 291 (12), 289 (69), 288 (24), 287 (100) $[\text{M-Et}]^+$, 286 (22), 285 (76), 283 (34), 261 (40), 260 (12), 259 (58), 258 (12), 257 (44), 255 (20), 233 (51), 232 (15), 231 (83), 230 (17), 229 (74), 227 (39), 155 (15), 153 (23), 151 (22), 149 (13). These data are in agreement with those reported previously in the literature.³

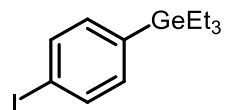
Iodobenzene derived tetrafluorothianthrenium salt (**S₁₉**)



Prepared according to GP-1 from iodobenzene (0.17 mL, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (541.0 mg, 0.950 mmol, 63%).

$R_f = 0.38$ (DCM/MeOH 9:1). $^1\text{H NMR}$ (600 MHz, CD_2Cl_2): $\delta/\text{ppm} = 8.57$ (dd, $J = 8.4, 7.0$ Hz, 2H), 7.87 (d, $J = 9.0$ Hz, 2H), 7.76 (dd, $J = 9.1, 6.7$ Hz, 2H), 6.90 (d, $J = 9.0$ Hz, 2H). $^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2): $\delta/\text{ppm} = 154.6$ (dd, $J = 266.3, 13.2$ Hz, 2C), 151.4 (dd, $J = 260.6, 13.4$ Hz, 2C), 140.5 (2C), 134.5 (dd, $J = 8.0, 4.1$ Hz, 2C), 129.4 (2C), 125.5 (dd, $J = 21.8, 2.7$ Hz, 2C), 122.8, 120.3 (d, $J = 21.4$ Hz, 2C), 114.6 (dd, $J = 6.8, 3.7$ Hz, 2C), 101.6. $^{19}\text{F NMR}$ (564 MHz, CD_2Cl_2): $\delta/\text{ppm} = -121.6, -129.6, -149.4, -149.5$. **HRMS** (ESI): m/z $[\text{M-BF}_4]^+$ calcd for $\text{C}_{18}\text{H}_8\text{IF}_4\text{S}_2$: 490.9043; found: 490.9042. These data are in agreement with those reported previously in the literature.⁴

Triethyl(4-iodophenyl)germane (**19**)

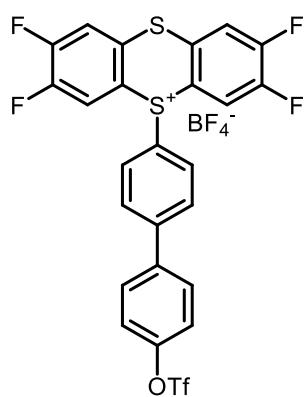


Prepared according to GP-2 from **S₁₉** (173.0 mg, 0.300 mmol, 1.0 equiv). The yield was determined by quantitative $^1\text{H NMR}$ using mesitylene as an internal standard (58%) and the title product was obtained as a colorless oil.

$R_f = 0.86$ (Pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta/\text{ppm} = 7.70 - 7.65$ (m, 2H), 7.20 – 7.14 (m, 2H), 1.08 – 1.02 (m, 9H), 1.01 – 0.94 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): $\delta/\text{ppm} = 139.5, 137.0$ (2C), 135.9 (2C), 95.0, 9.0 (3C), 4.3 (3C). **MS** (70eV, EI): m/z (%): 337 (22), 336 (12), 335 (100), 334 (31), 333 (75), 331 (57), 309 (12), 307 (55), 306 (16), 305 (42), 303

(32), 281 (14), 279 (68), 278 (19), 277 (65), 275 (49), 273 (10), 201 (15), 199 (11), 152 (12), 151 (11), 150 (15), 149 (10), 148 (11). These data are in agreement with those reported previously in the literature.³

[1,1'-Biphenyl]-4-yl trifluoromethanesulfonate derived tetrafluorothianthrenium salt (S₂₀)

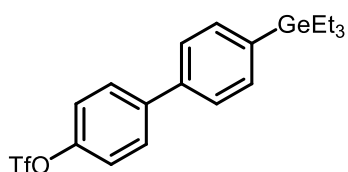


Prepared according to GP-1 from [1,1'-biphenyl]-4-yl trifluoromethanesulfonate (453.0 mg, 1.50 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (DCM/MeOH 95:5) as a white solid (608.0 mg, 0.900 mmol, 60%).

R_f = 0.62 (DCM/MeOH 9:1). **¹H NMR** (600 MHz, CD₃CN): δ /ppm = 8.46 (dd, J = 9.1 Hz, 7.2 Hz, 2H), 7.98 (dd, J = 9.9 Hz, 7.0 Hz, 2H), 7.79 – 7.74 (m, 4H), 7.48 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.9 Hz, 2H).

¹³C NMR (151 MHz, CD₃CN): δ /ppm = 154.9 (dd, J = 262.0, 13.1 Hz, 2C), 151.6 (dd, J = 255.8, 13.5 Hz, 2C), 151.0, 145.0, 139.5, 135.3 (dd, J = 8.3, 3.7 Hz, 2C), 130.6 (2C), 130.1 (2C), 129.9 (2C), 125.7 (dd, J = 22.7, 1.9 Hz, 2C), 123.1 (2C), 122.9, 121.2 (d, J = 21.9 Hz, 2C), 120.8, 115.2 (dd, J = 7.1, 3.5 Hz, 2C). **¹⁹F NMR** (564 MHz, CD₃CN): δ /ppm = -74.7, -126.1, -134.5, -152.1, -152.2. **HRMS** (ESI): m/z [M-BF₄]⁺ calcd for C₂₅H₁₂O₃F₇S₃: 588.9831; found: 588.9829. These data are in agreement with those reported previously in the literature.¹

4'-(Triethylgermyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (20)



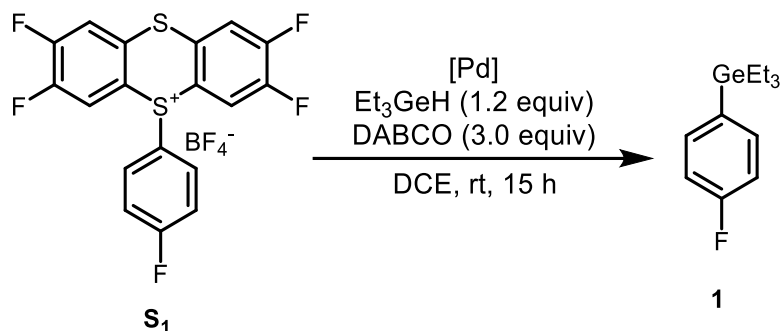
Prepared according to GP-2 from S₂₀ (203.0 mg, 0.300 mmol, 1.0 equiv). The title product was obtained after purification by column chromatography (pentane/EtOAc 10:0 to 9.5:0.5) as a colorless oil (99.0 mg, 0.220 mmol, 72%).

R_f = 0.14 (Pentane). **¹H NMR** (600 MHz, CDCl₃): δ /ppm = 7.65 (d, J = 8.4 Hz, 2H), 7.57 – 7.51 (m, 4H), 7.34 (d, J = 8.4 Hz, 2H), 1.12 – 1.06 (m, 9H), 1.05 – 1.00 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃): δ /ppm = 149.1, 141.9, 140.2, 139.1, 134.8 (2C), 129.0 (2C), 126.7 (2C), 121.8 (2C), 119.0 (q, J = 320.9 Hz), 9.1 (3C), 4.4 (3C). **¹⁹F NMR** (564 MHz, CDCl₃): δ /ppm = -72.8. **IR** (neat): 3883, 3018, 2952, 2873, 2328, 2078, 1997, 1905, 1767, 1595, 1486, 1423,

1247, 1210, 1138, 1012, 966, 885, 812, 704 cm^{-1} . **HRMS** (APCI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{F}_3^{74}\text{GeO}_3\text{S}$: 463.0605; found: 465.0598.

3. Reaction development

3.1 Catalyst Screening



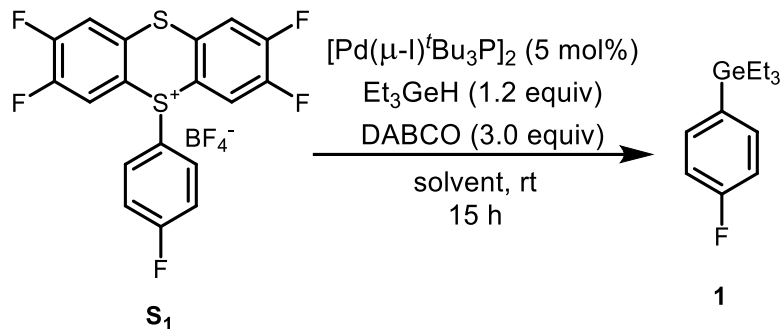
In an argon-filled glovebox, a glass vial equipped with a magnetic stir bar was charged in the following order with the tetrafluorothianthrenium salt **S**₁ (14.1 mg, 0.030 mmol, 1.0 equiv), Pd-source [Pd] (3 μmol, 10 mol% Pd) (followed by addition of ligand for entries 1 and 2) i.e. [(1) Pd₂(dba)₃ (1.4 mg, 5 mol%)/Xantphos (1.7 mg, 10 mol%); (2) Pd(OAc)₂ (0.7 mg, 10 mol%)/Ph₃P (1.3 mg, 17 mol%); (3) Pd(Ph₃P)₂Cl₂ (2.1 mg, 10 mol%); (4) Pd(dppf)Cl₂ (2.1 mg, 10 mol%); (5) [Pd(P^{*t*}Bu₃)]₂ (0.8 mg, 5 mol%); (6) [Pd(μ-I)^{*t*}Bu₃P)]₂ (1.3 mg, 5 mol%)], DABCO (10.1 mg, 0.090 mmol, 3.0 equiv) and anhydrous DCE (0.3 mL, c = 0.1 M). Et₃GeH (5.8 μL, 0.036 mmol, 1.2 equiv) was added, and the sealed vial was taken out from the glovebox and allowed to stir overnight at room temperature. For entries 1 and 2, no-premixing of Pd-catalyst and ligand was performed. 1,4-Difluorobenzene (0.3 M in CH₃CN, 100 μL, 0.030 mmol, 1.0 equiv) was added as internal standard and the reaction mixture was transferred into NMR tube to determine a yield of **1** by ¹⁹F NMR quantification. Results are shown in Table S1.

Table S1. Screening of catalytic systems

Entry	[Pd]	Yield of 1 , %
1	Pd ₂ (dba) ₃ (5 mol%)/Xantphos (10 mol%) ^a	22
2	Pd(OAc) ₂ (10 mol%)/Ph ₃ P (17 mol%) ^b	No product
3	Pd(Ph ₃ P) ₂ Cl ₂ (10 mol%)	No product
4	Pd(dppf)Cl ₂ (10 mol%)	14
5	[Pd(P ^{<i>t</i>} Bu ₃)] ₂ (5 mol%)	No product
6	[Pd(μ-I)^{<i>t</i>}Bu₃P)]₂ (5 mol%)	75

^a1.7 mg (3 μmol) of Xantphos; ^b1.3 mg (5.1 μmol) of Ph₃P; ^c1.1 mg (6 μmol) of CuI

3.2 Solvent Screening

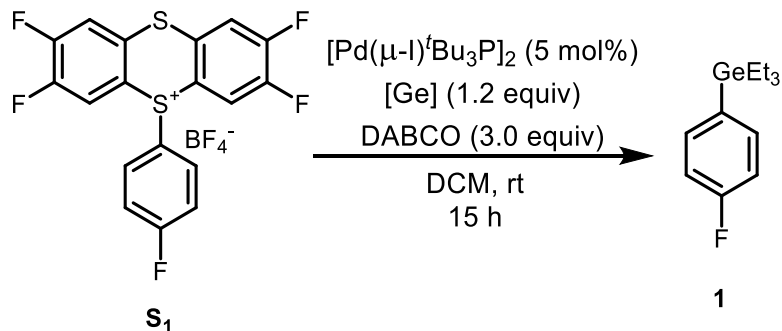


In an argon-filled glovebox, a glass vial equipped with a magnetic stir bar was charged with the tetrafluorothianthrenium salt **S**₁ (14.1 mg, 0.030 mmol, 1.0 equiv), [Pd(μ-I)^tBu₃P]₂ (1.3 mg, 1.5 μmol, 5 mol%), DABCO (10.1 mg, 0.090 mmol, 3.0 equiv) and anhydrous solvent (0.3 mL, c = 0.1 M). Et₃GeH (5.8 μL, 0.036 mmol, 1.2 equiv) was added, and the sealed vial was taken out from the glovebox and allowed to stir overnight at room temperature. 1,4-Difluorobenzene (0.3 M in CH₃CN, 100 μL, 0.030 mmol, 1.0 equiv) was added as internal standard and the reaction mixture was transferred into NMR tube to determine a yield of **1** by ¹⁹F NMR quantification. Results are shown in Table S2.

Table S2. Screening of solvents

Entry	Solvent	Yield of 1 , %
1	1,2-Dichloroethane	75
2	Dioxane	42
3	THF	No product
4	1,2-Dimethoxyethane	53
5	EtOAc	68
6	Et ₂ O	27
7	Cyclohexane	9
8	MeOH	68
9	PhCl	12
10	DCM	82
11	NMP	32

3.3 Germane Source Screening



In an argon-filled glovebox, a glass vial equipped with a magnetic stir bar was charged with the tetrafluorothianthrenium salt **S**₁ (14.1 mg, 0.030 mmol, 1.0 equiv), [Pd(μ-I)^tBu₃P]₂ (1.3 mg, 1.5 μmol, 5 mol%), DABCO (10.1 mg, 0.090 mmol, 3.0 equiv) and anhydrous DCM (0.3 mL, c = 0.1 M). Germane source [Ge] (0.036 mmol, 1.2 equiv) was added, and the sealed vial was taken out from the glovebox and allowed to stir overnight at room temperature. 1,4-Difluorobenzene (0.3 M in CH₃CN, 100 μL, 0.030 mmol, 1.0 equiv) was added as internal standard and the reaction mixture was transferred into NMR tube to determine a yield of **1** by ¹⁹F NMR quantification. Results are shown Table S3.

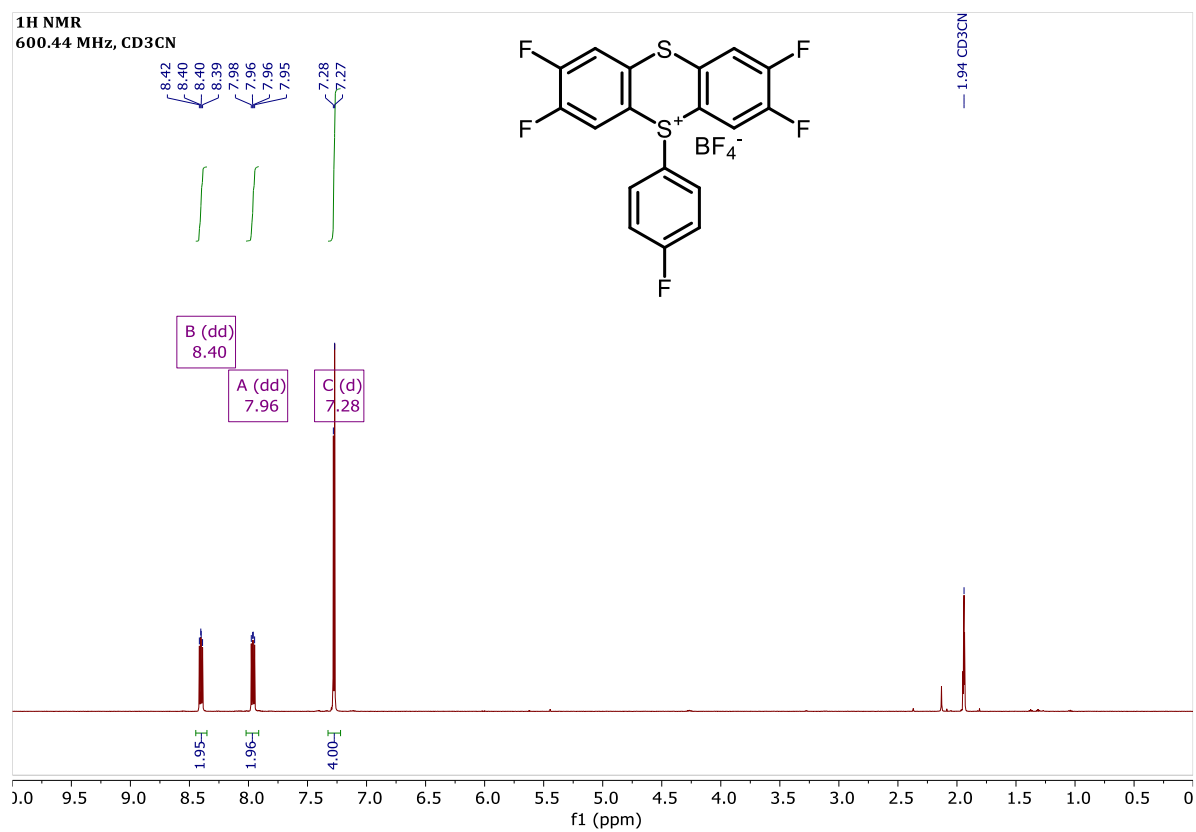
Table S3. Germane Source Screening

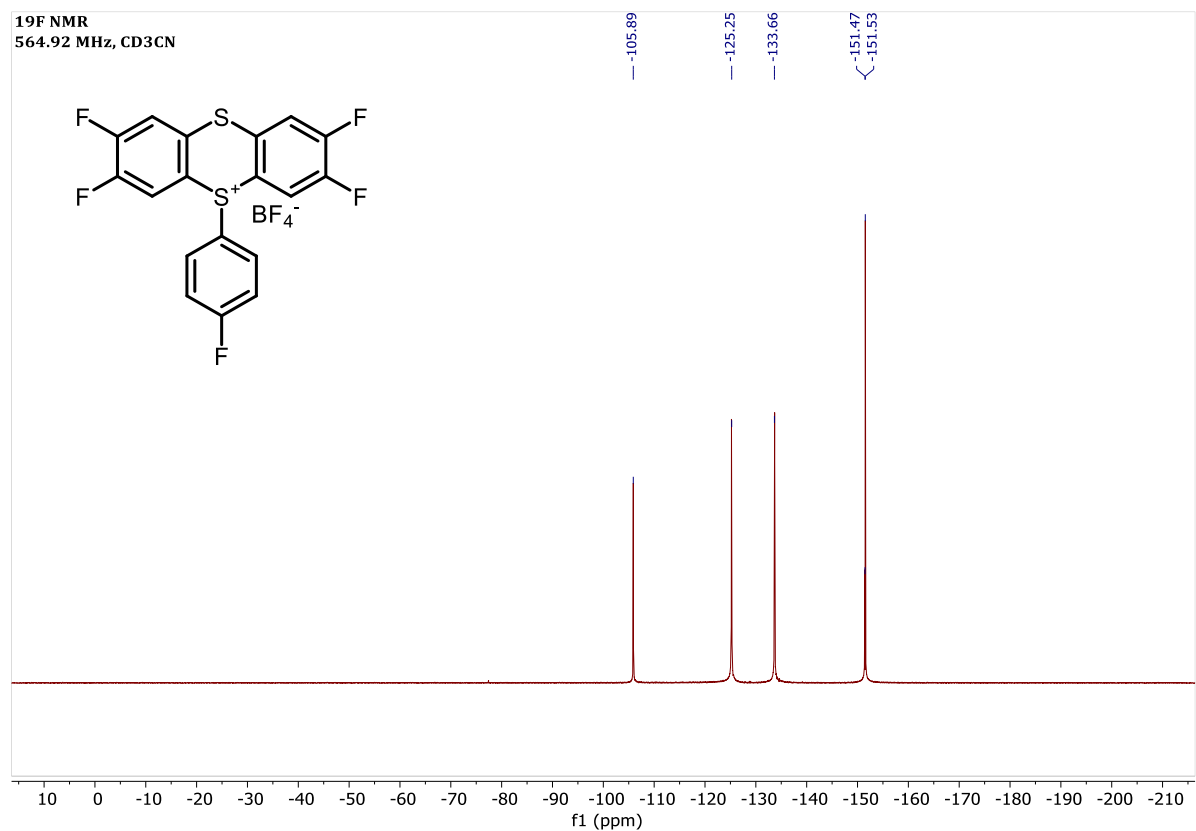
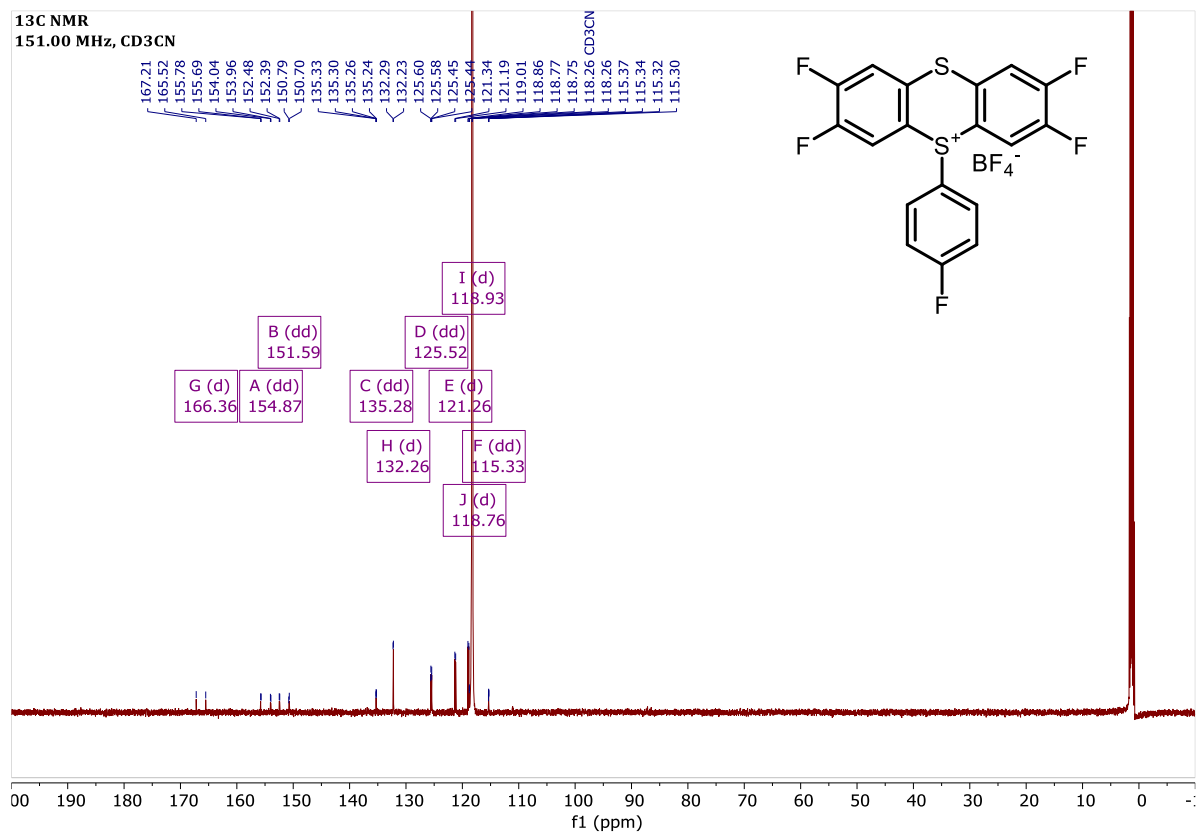
Entry	[Ge]	Yield of 1 , %
1 ^a	Ge ₂ Et ₆	No product
2 ^b	Ge ₂ Me ₆	No product
3 ^c	Et ₃ GeCl	No product
4 ^d	PhMe ₂ Si-GeEt ₃	No product

^a11.5 mg of Ge₂Et₆ were used; ^b8.5 mg of Ge₂Me₆ were used; ^c7.0 mg of Et₃GeCl; ^d10.6 mg of PhMe₂Si-GeEt₃ were used

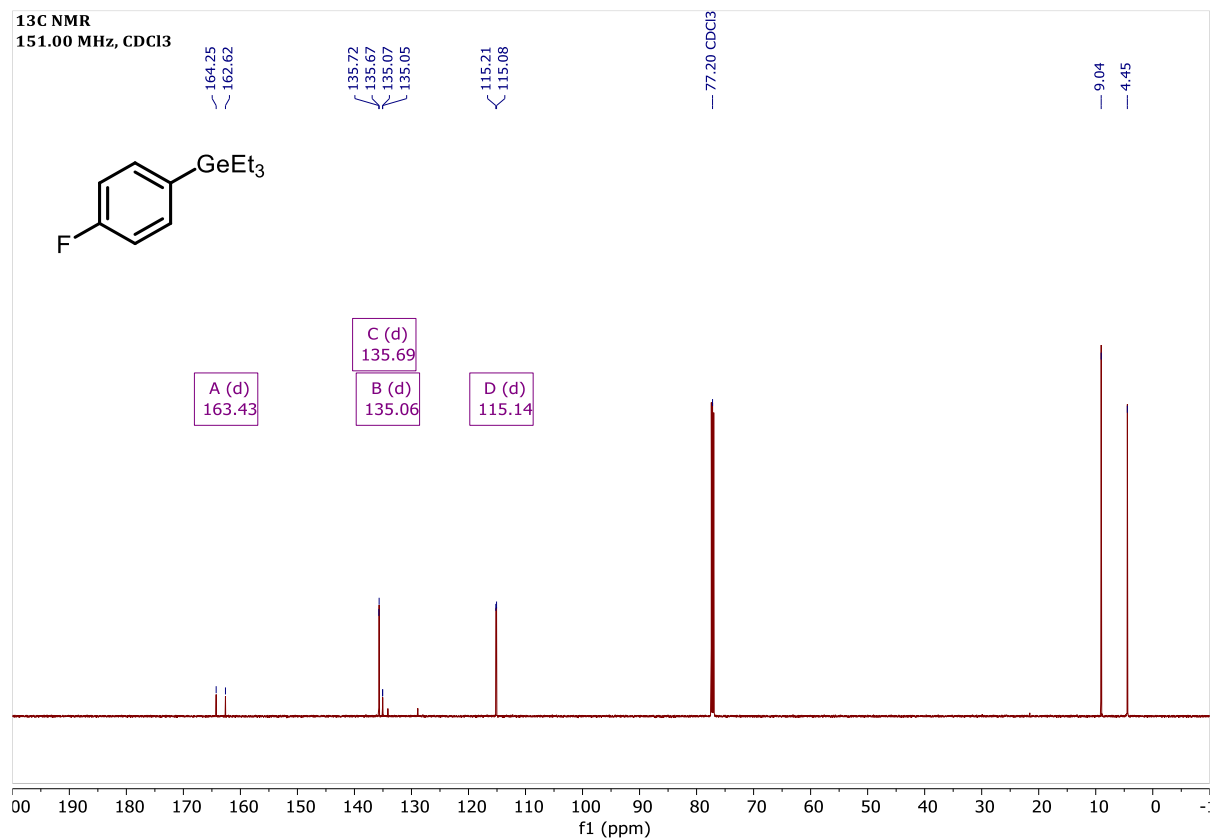
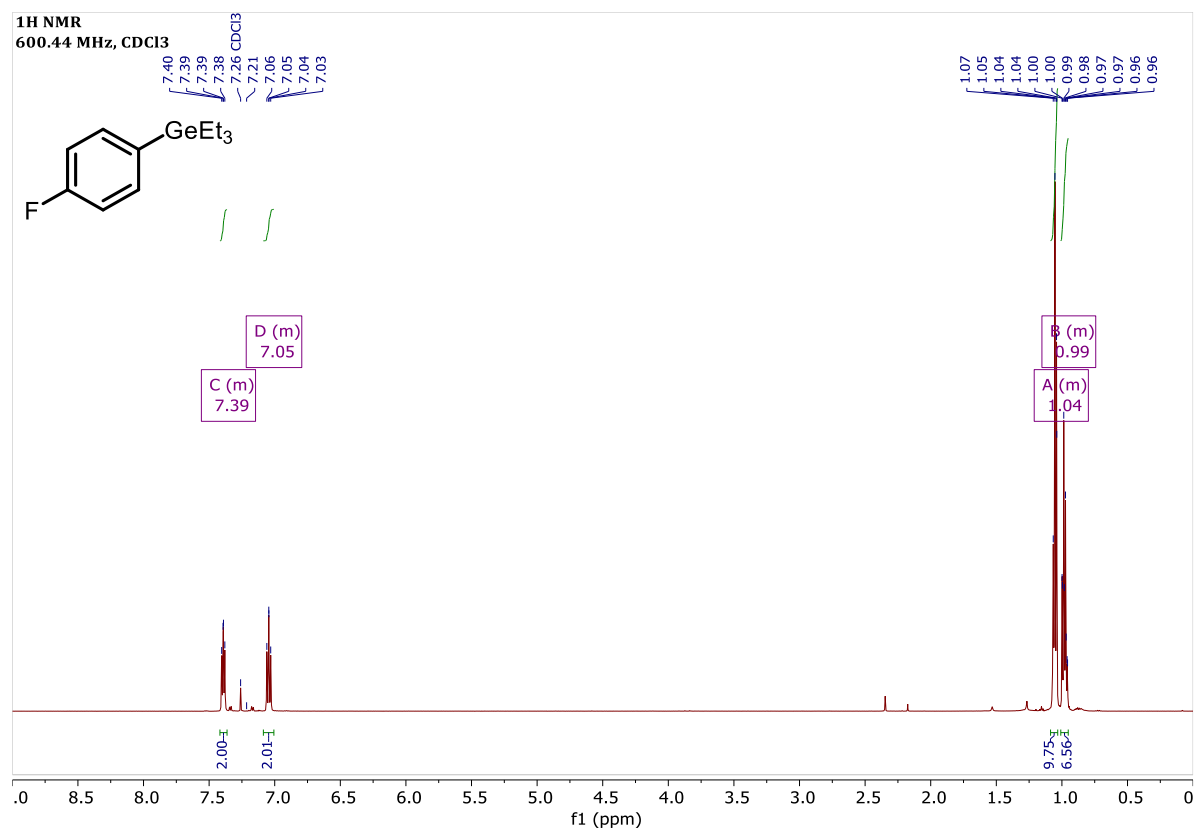
4. NMR spectra

Fluorobenzene derived tetrafluorothianthrenium salt (S_1)

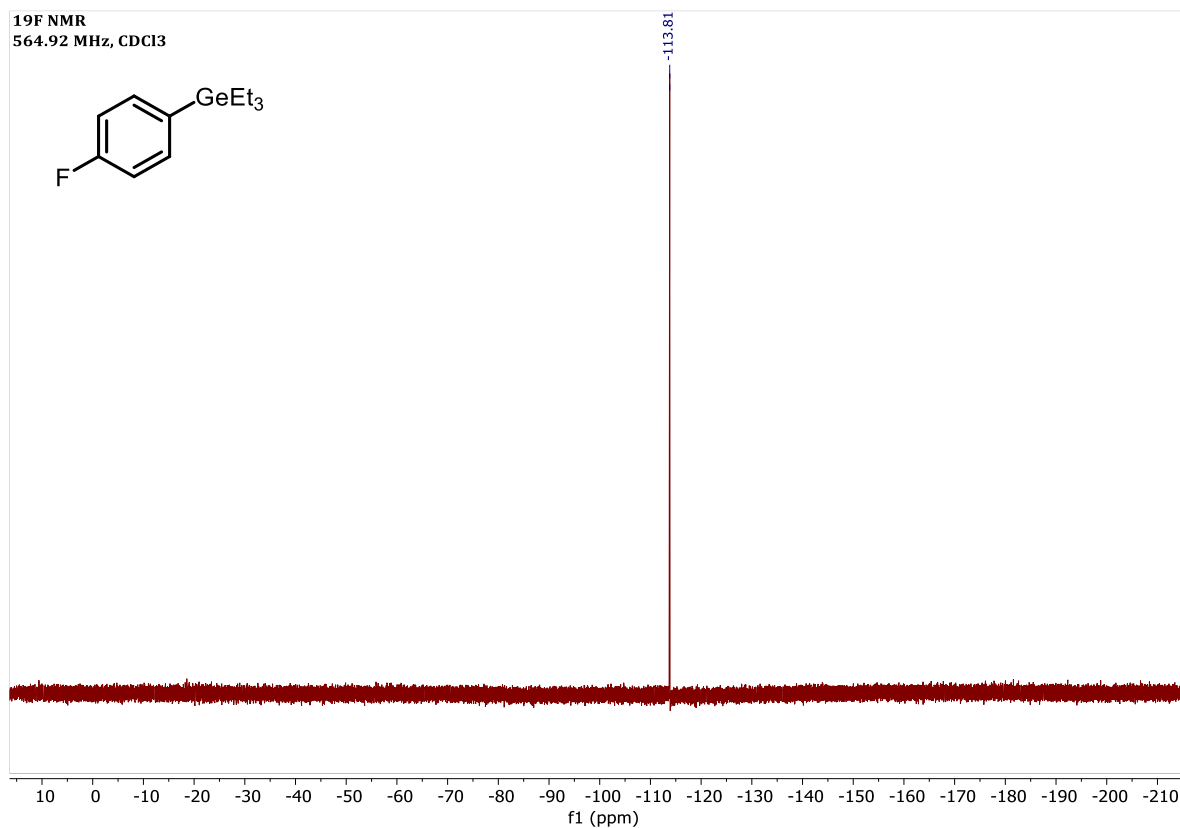




Triethyl(4-fluorophenyl)germane (1)

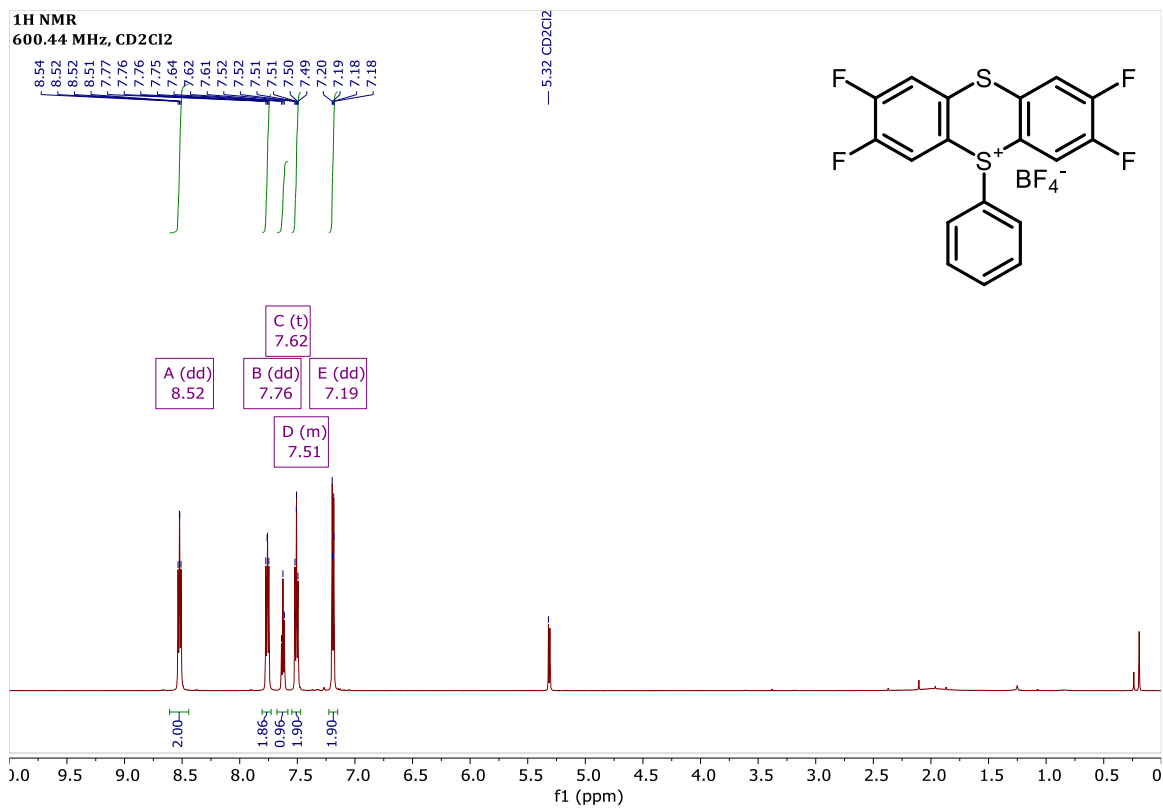


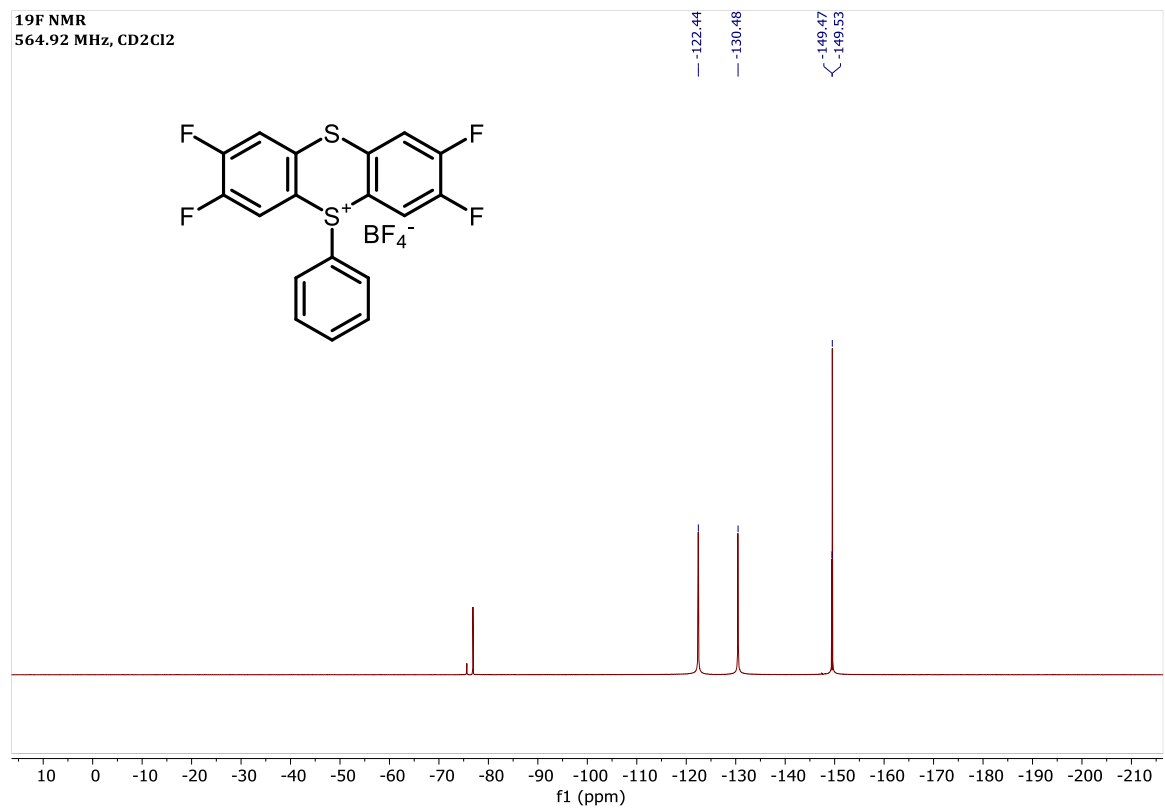
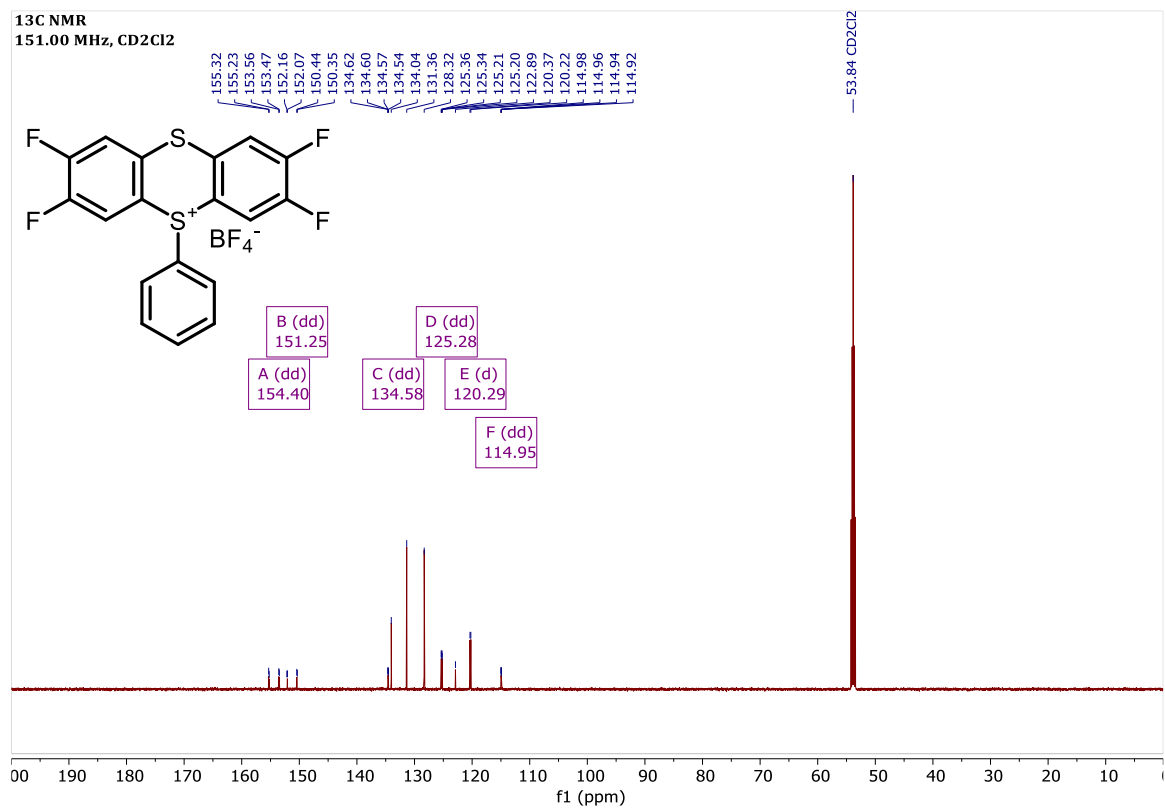
¹⁹F NMR
564.92 MHz, CDCl₃



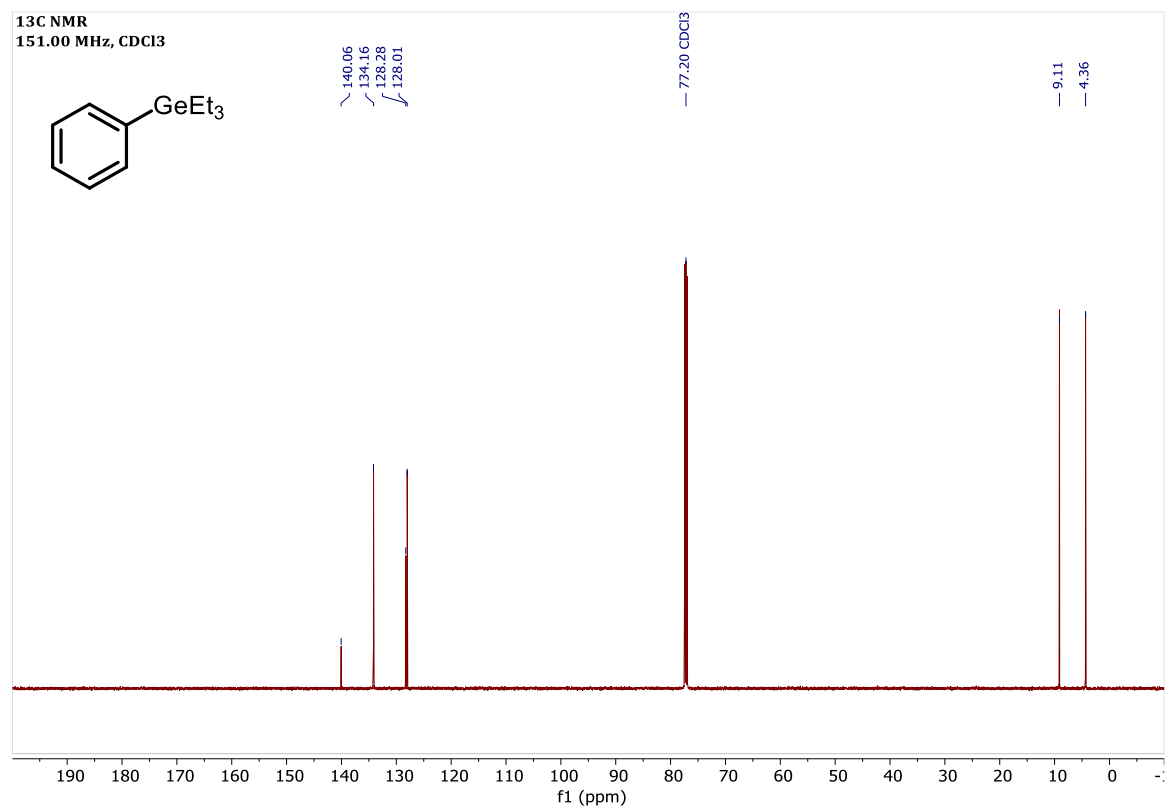
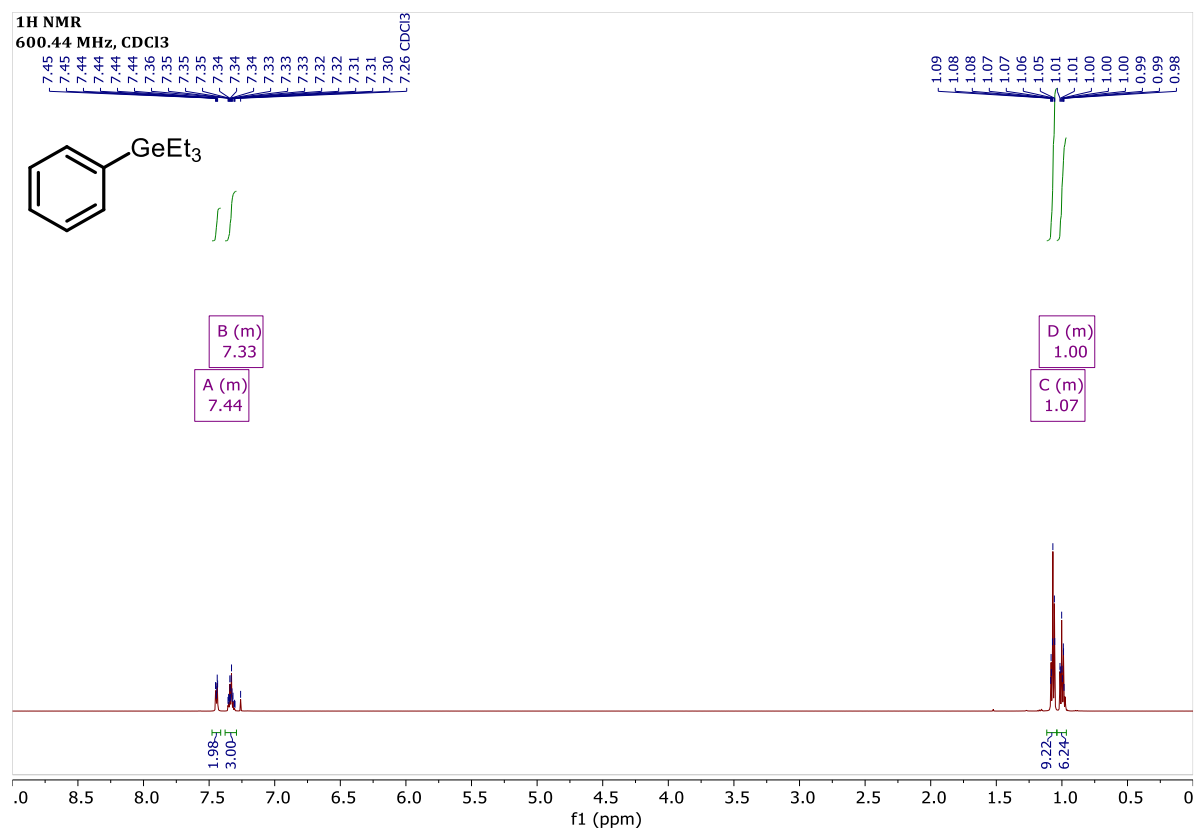
Benzene derived tetrafluorothianthrenium salt (S₂)

¹H NMR
600.44 MHz, CD₂Cl₂

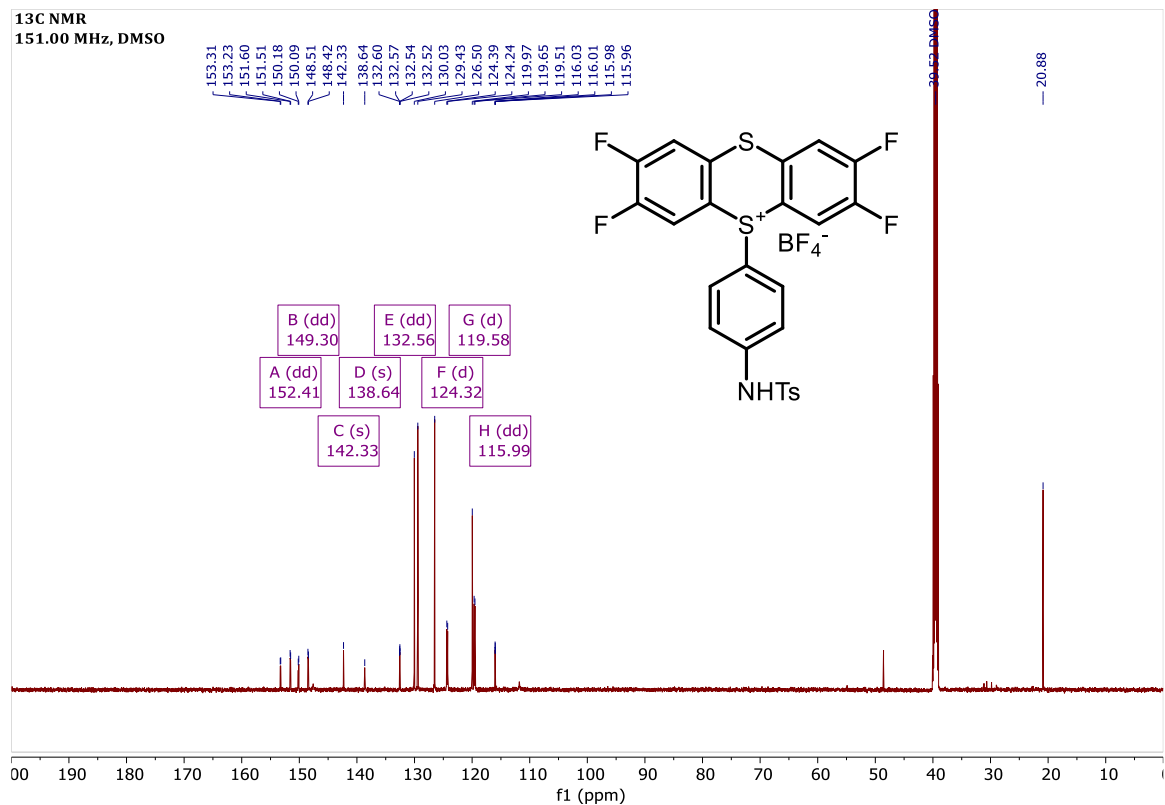
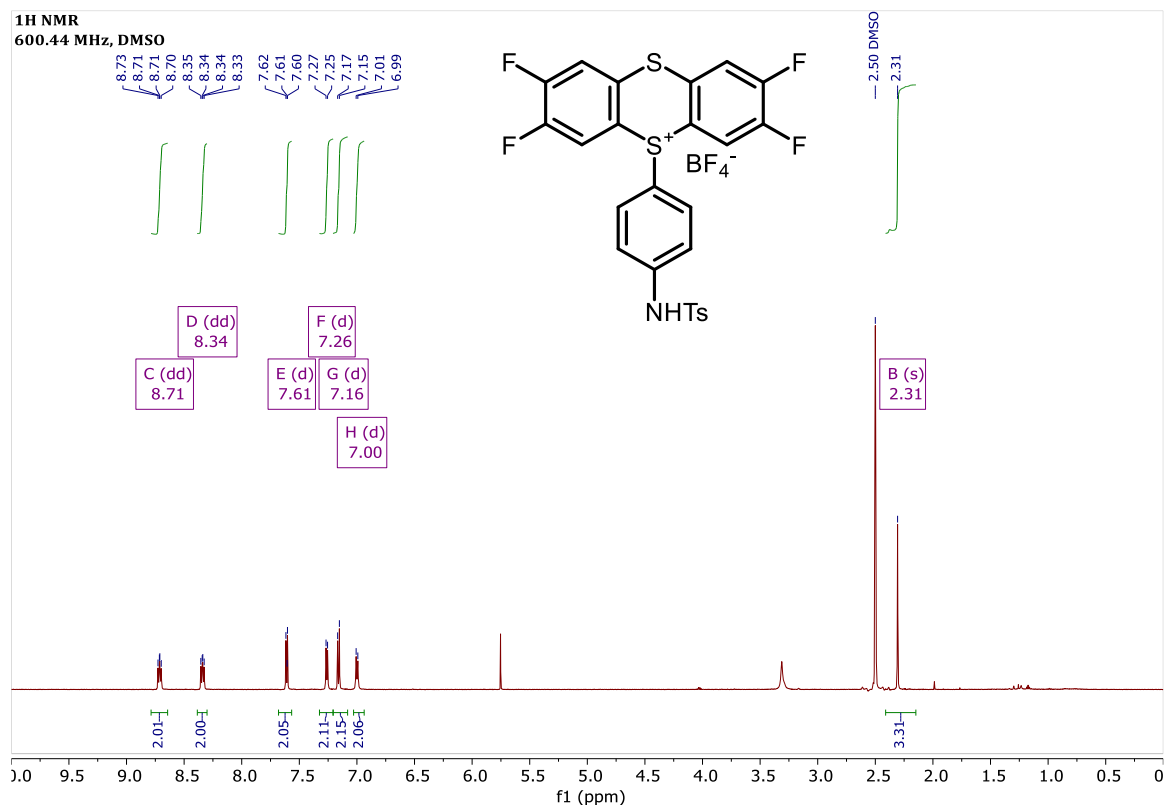




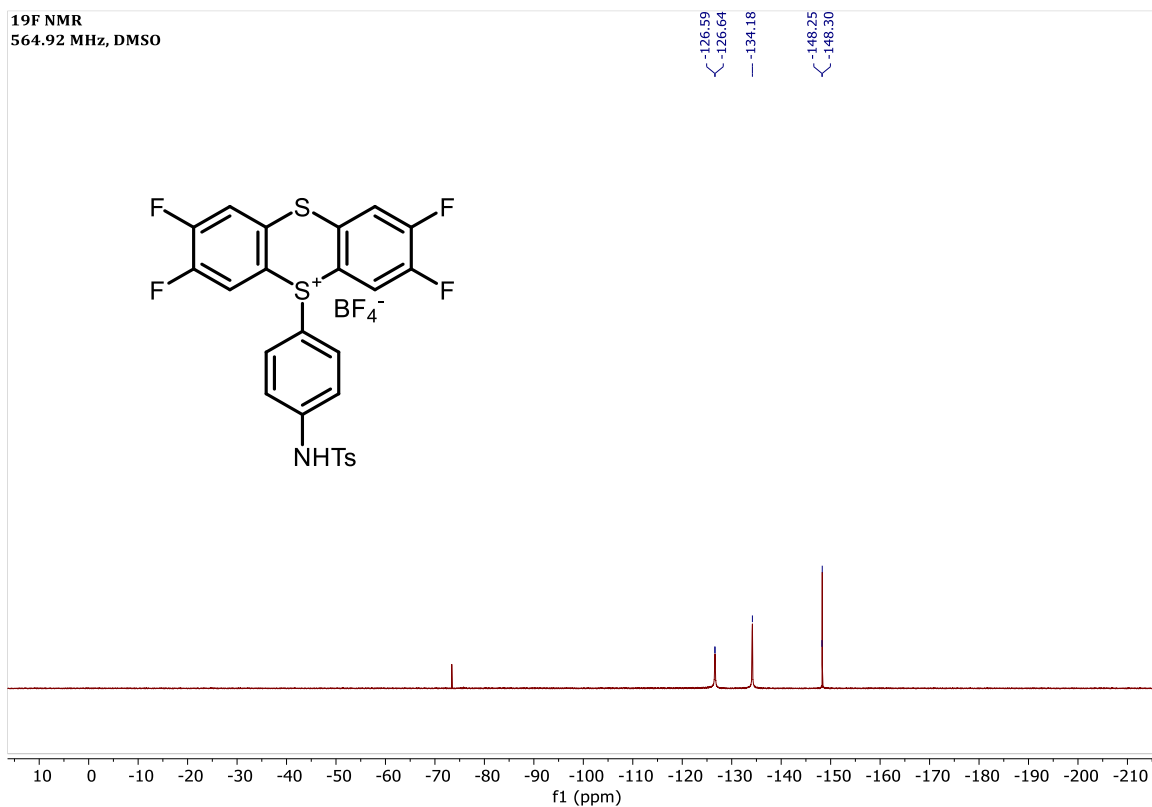
Triethyl(phenyl)germane (2)



4-Methyl-*N*-phenylbenzenesulfonamide derived tetrafluorothianthrenium salt (S₃)

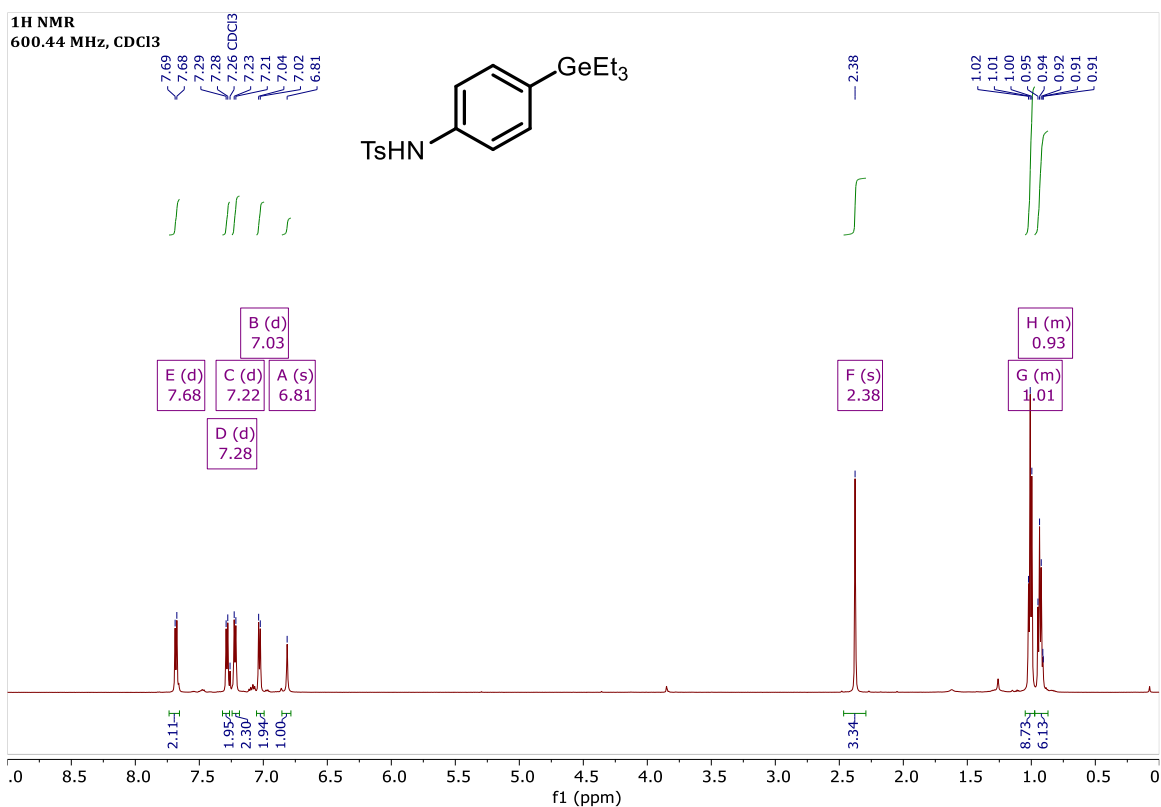


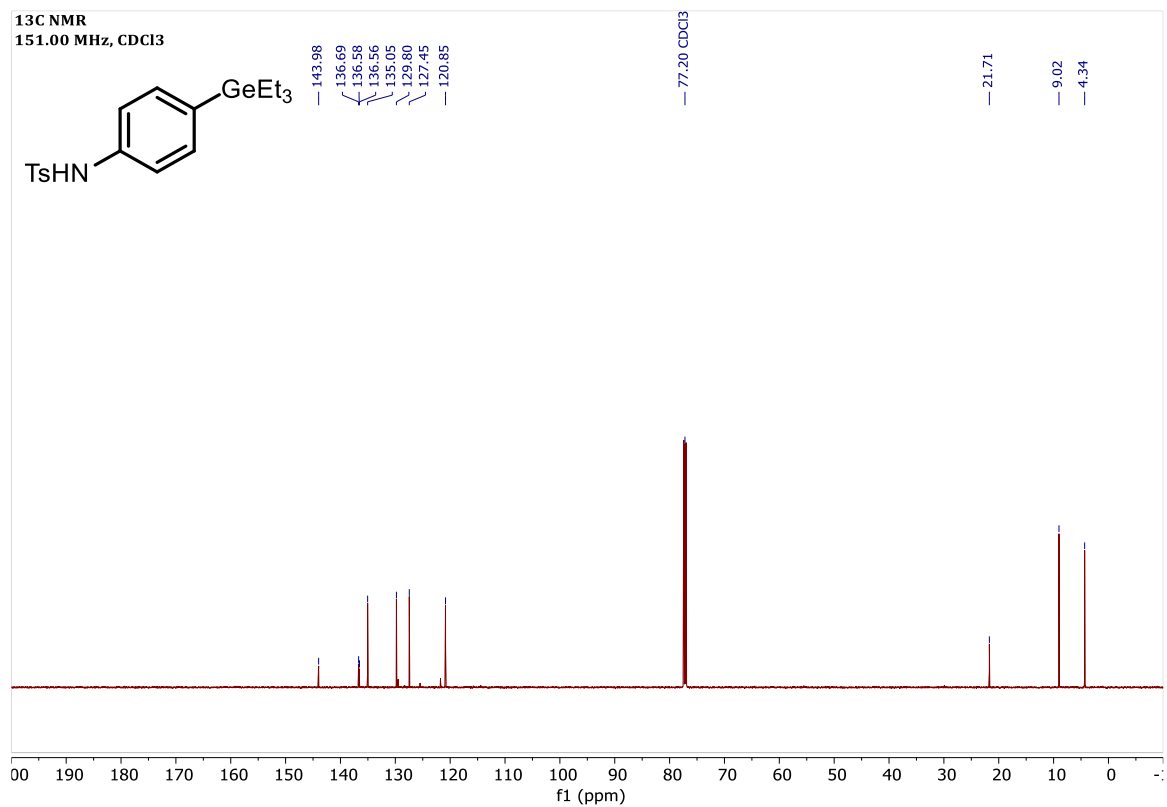
¹⁹F NMR
564.92 MHz, DMSO



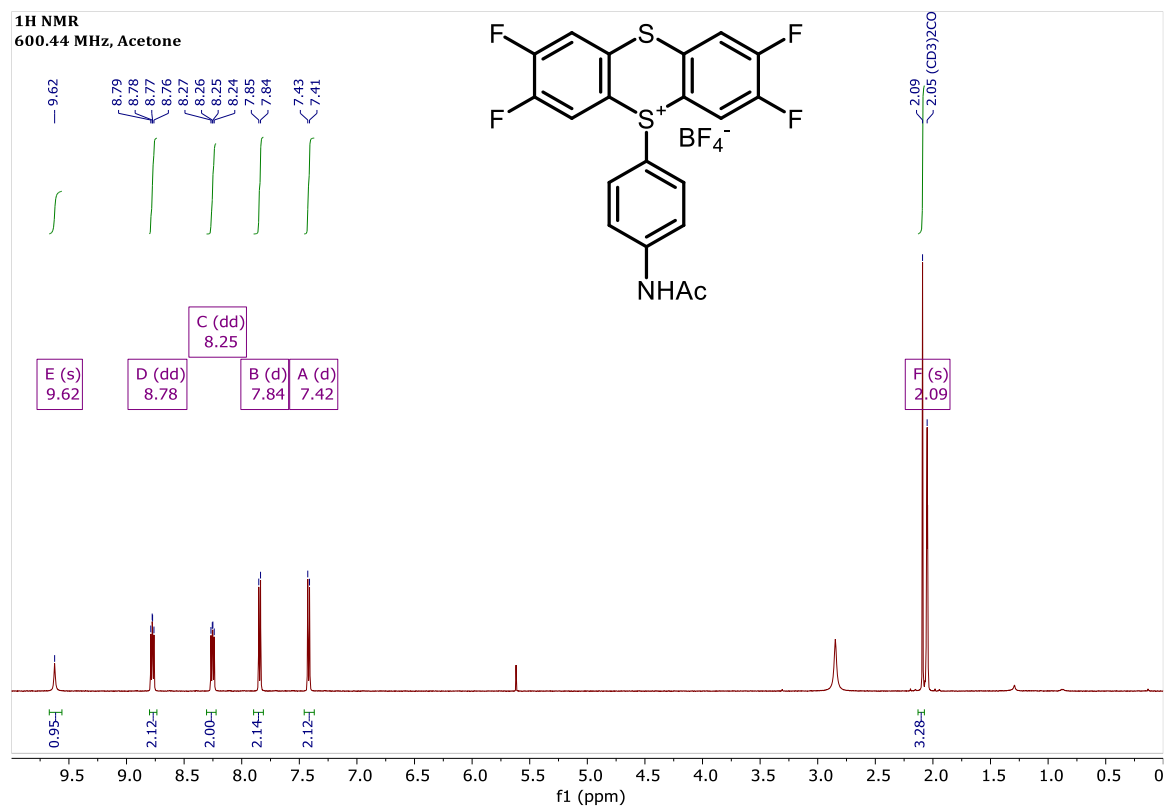
4-Methyl-N-(4-(triethylgermyl)phenyl)benzenesulfonamide (3)

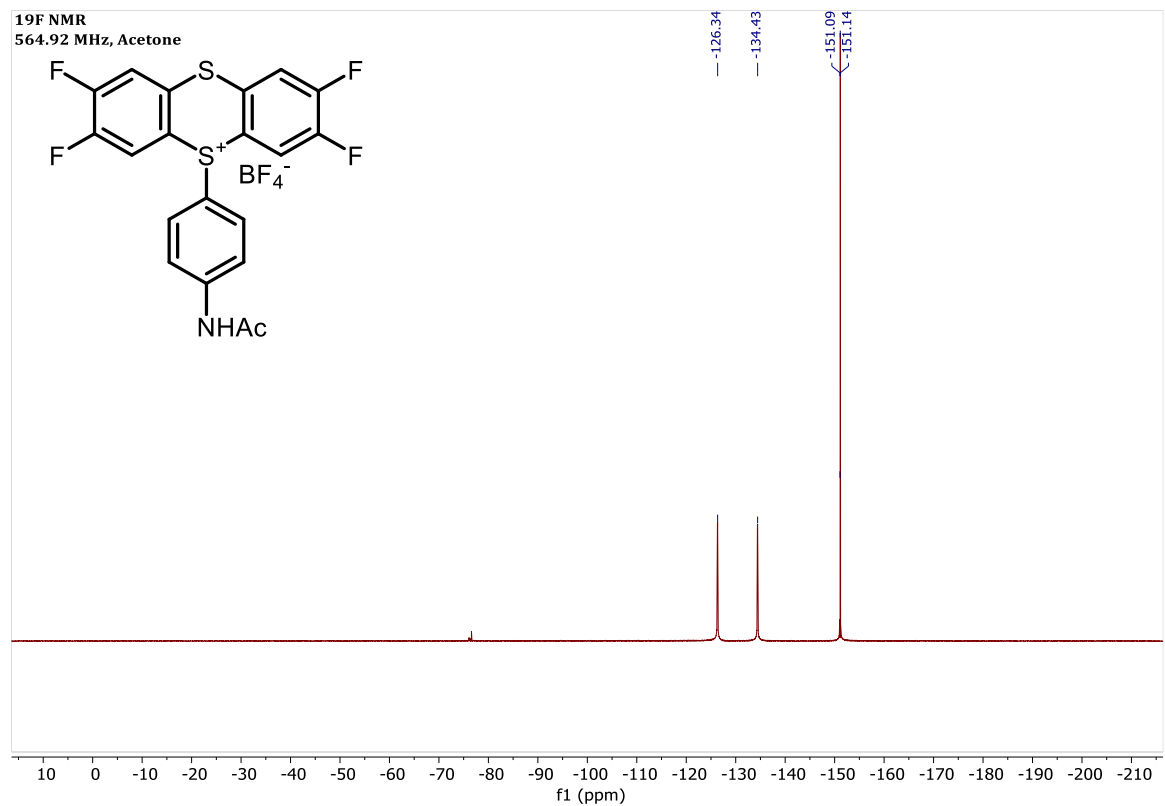
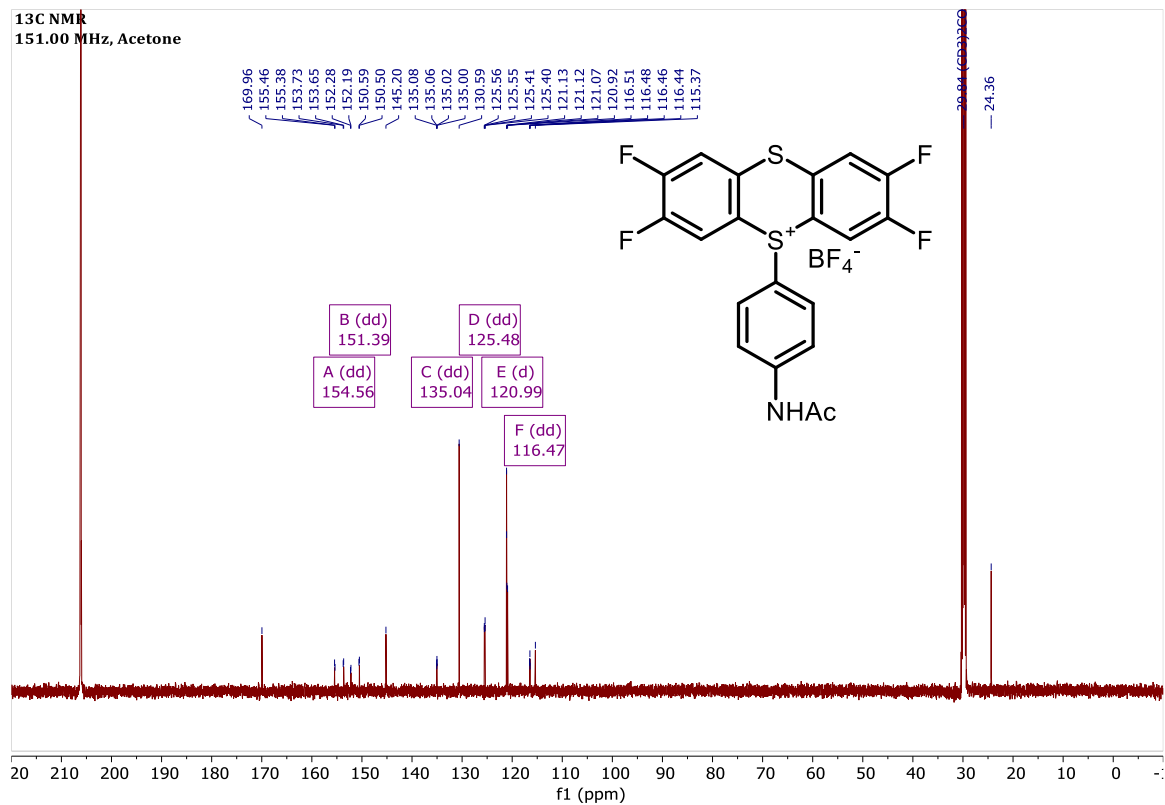
¹H NMR
600.44 MHz, CDCl₃



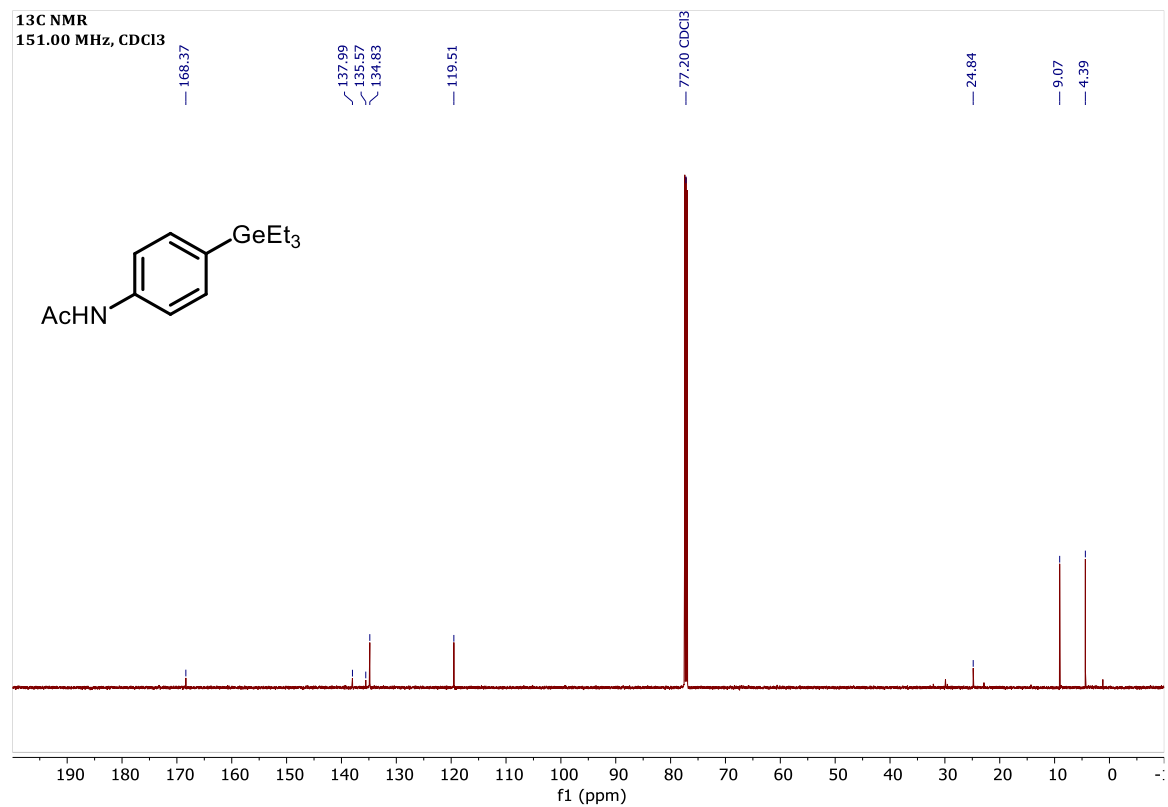
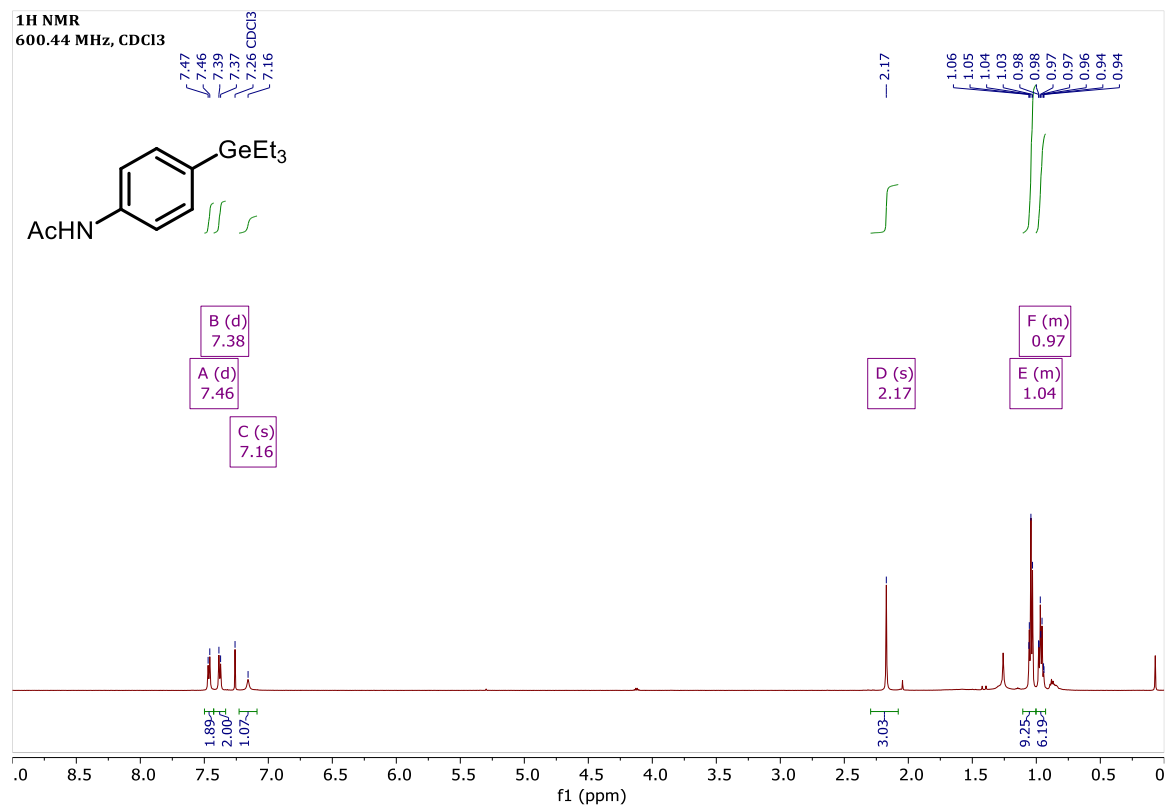


N-phenylacetamide derived tetrafluorothianthrenium salt (S₄)

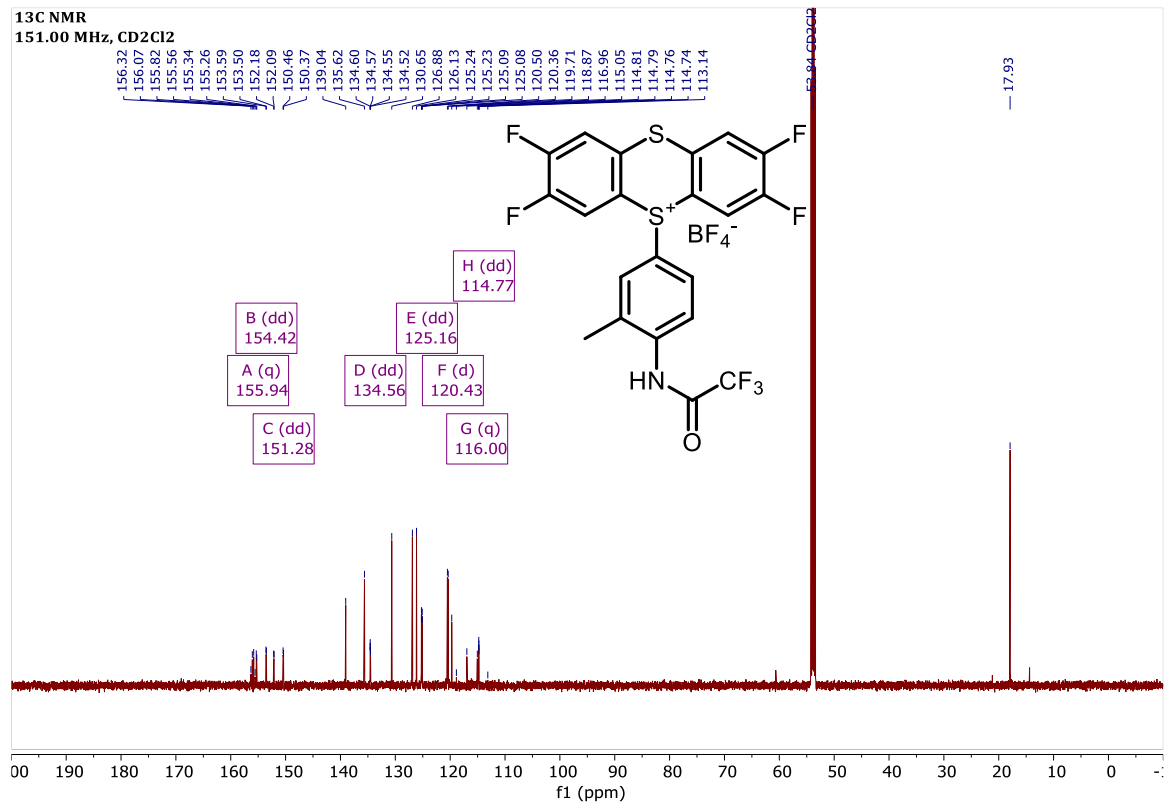
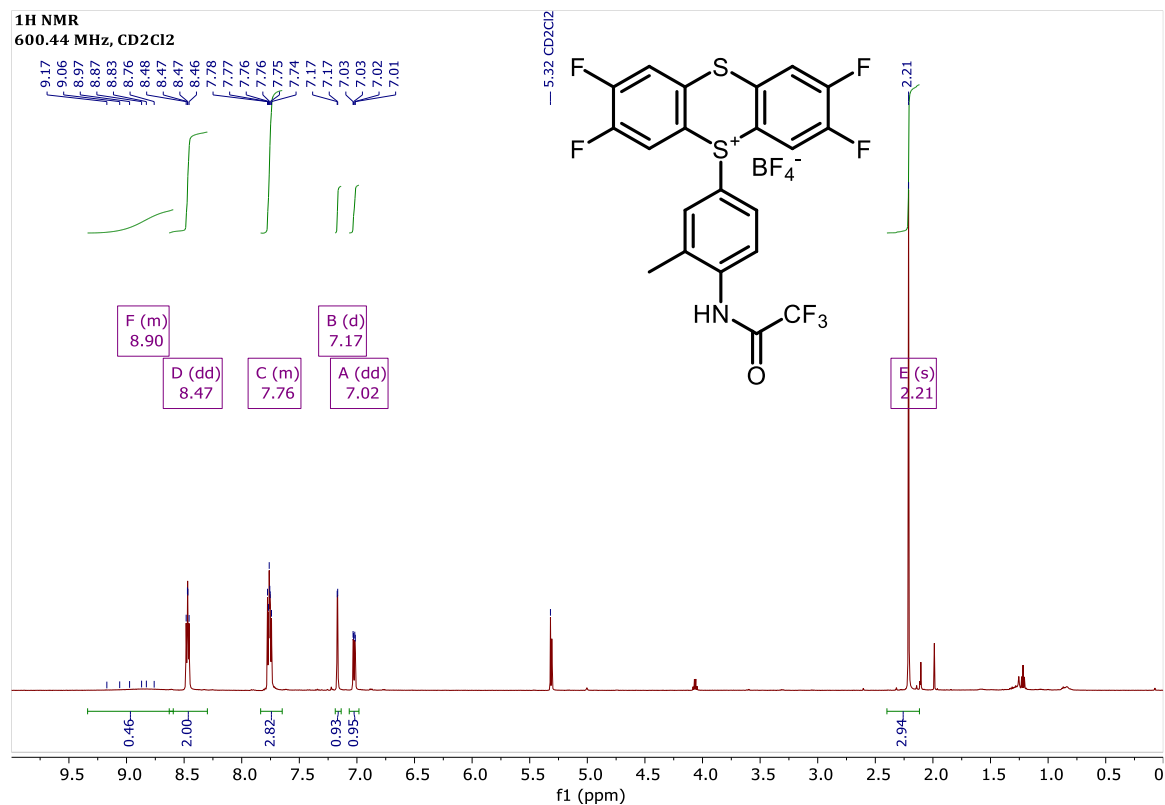




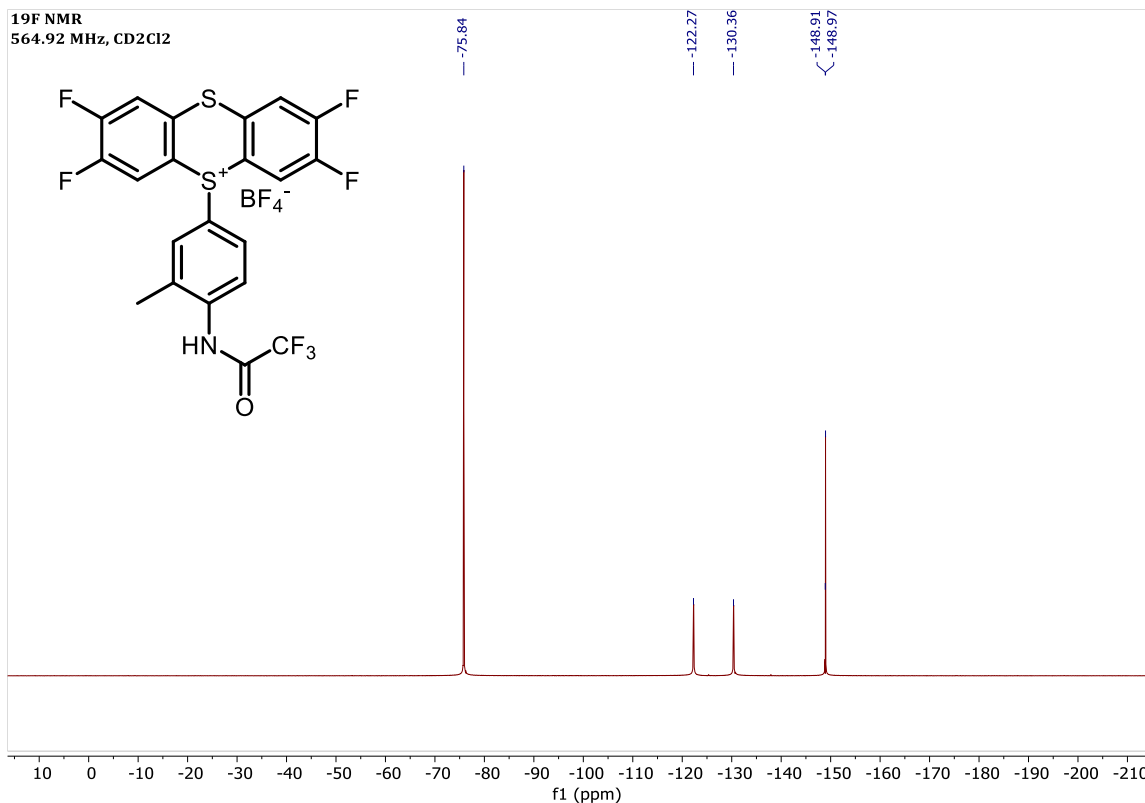
***N*-(4-(triethylgermyl)phenyl)acetamide (4)**



2-Methylaniline derived tetrafluorothianthrenium salt (S₅)

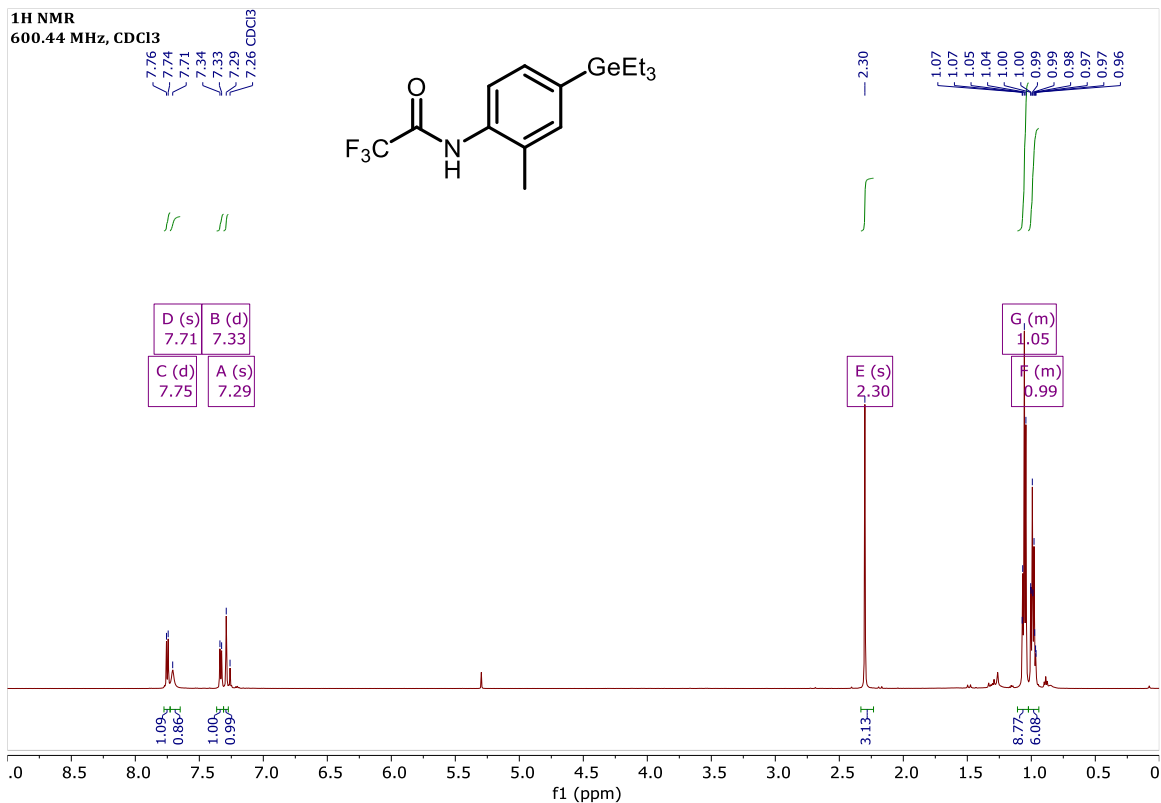


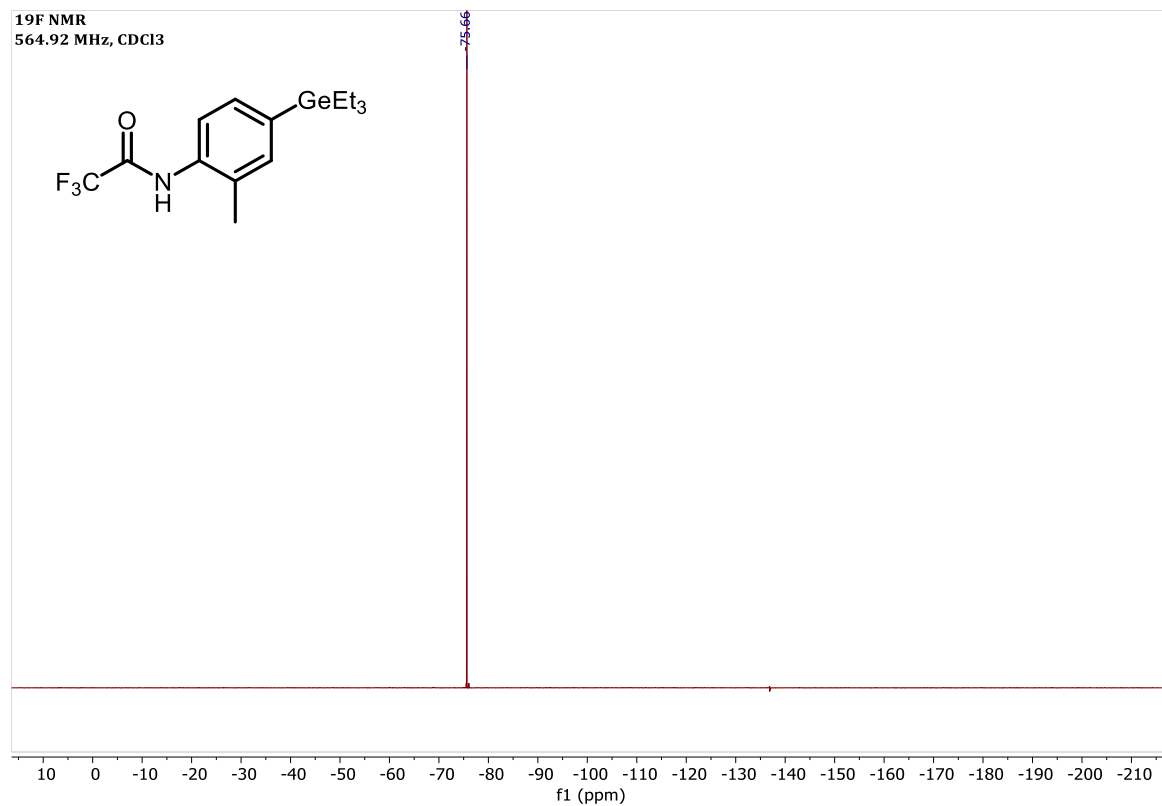
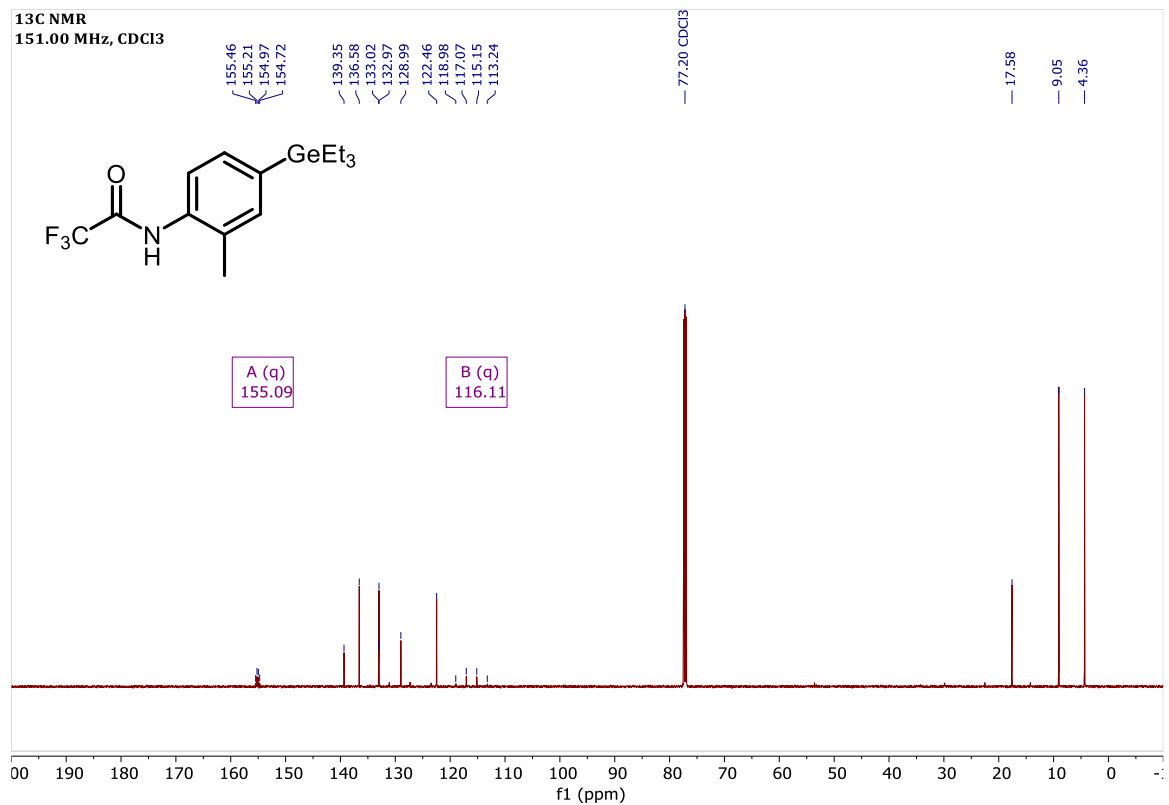
¹⁹F NMR
564.92 MHz, CD₂Cl₂



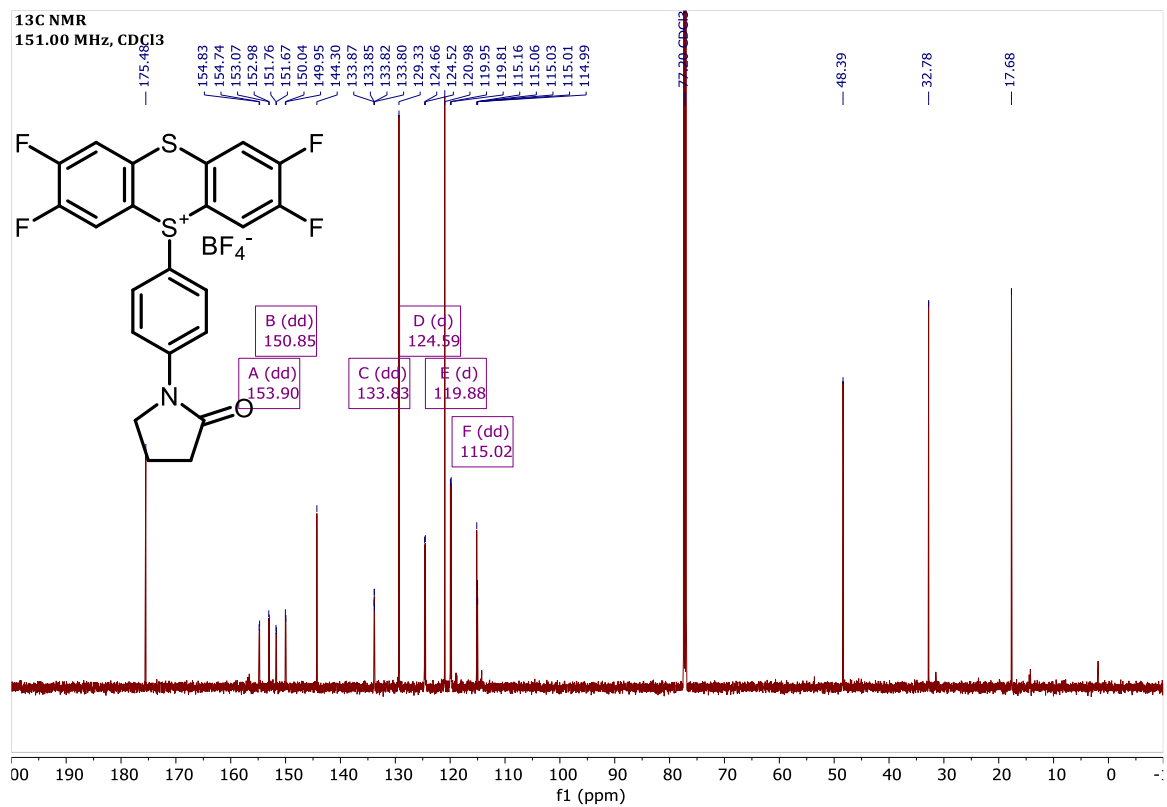
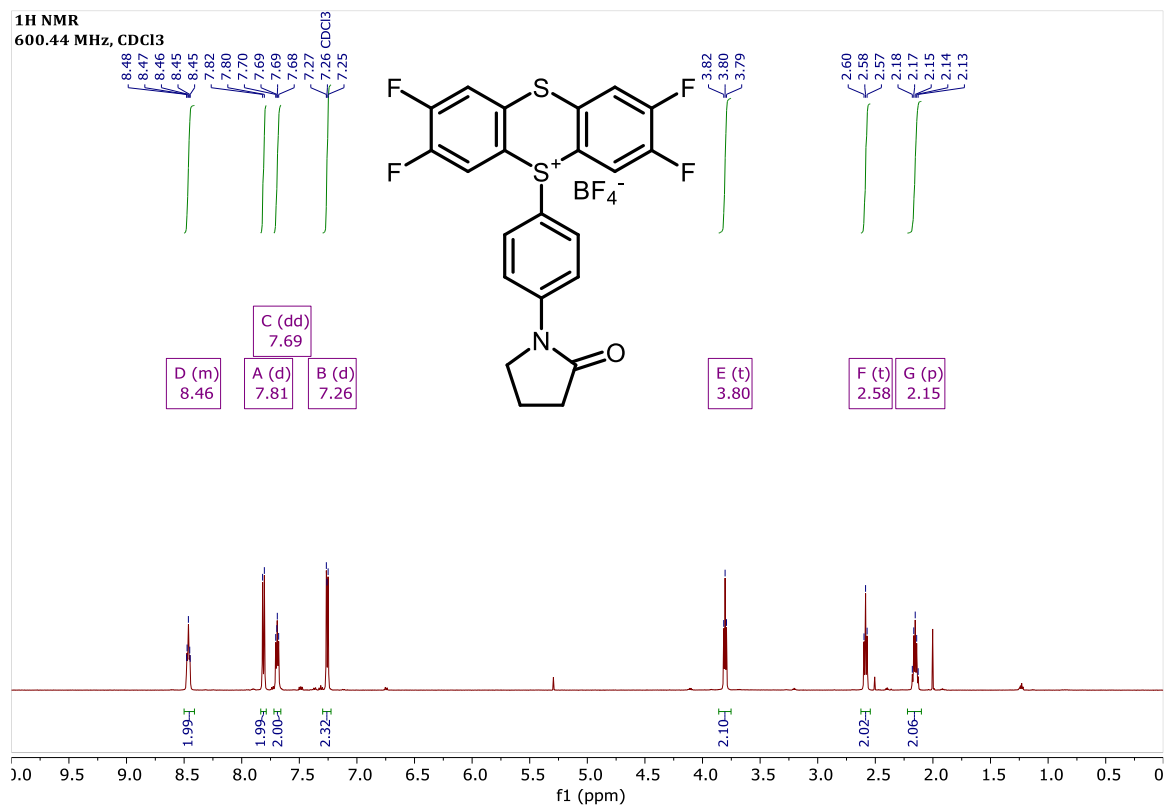
2,2,2-Trifluoro-N-(2-methyl-4-(triethylgermyl)phenyl)acetamide (5)

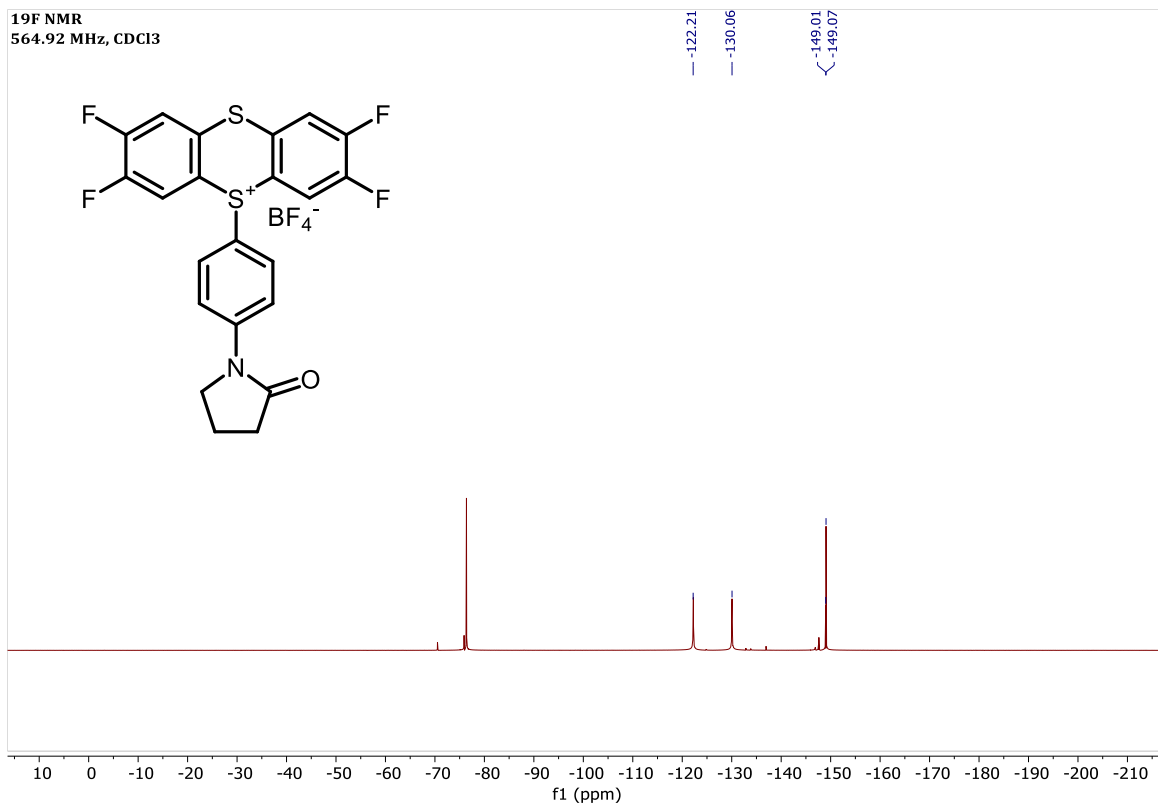
¹H NMR
600.44 MHz, CDCl₃



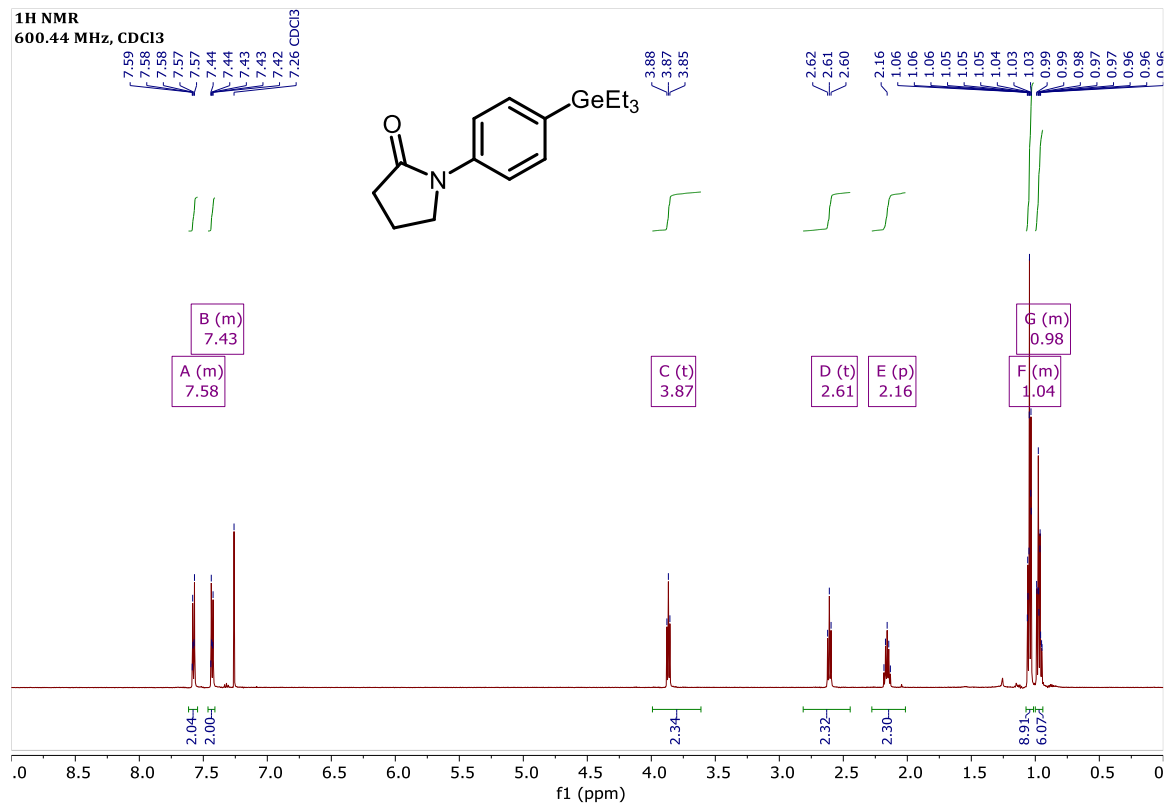


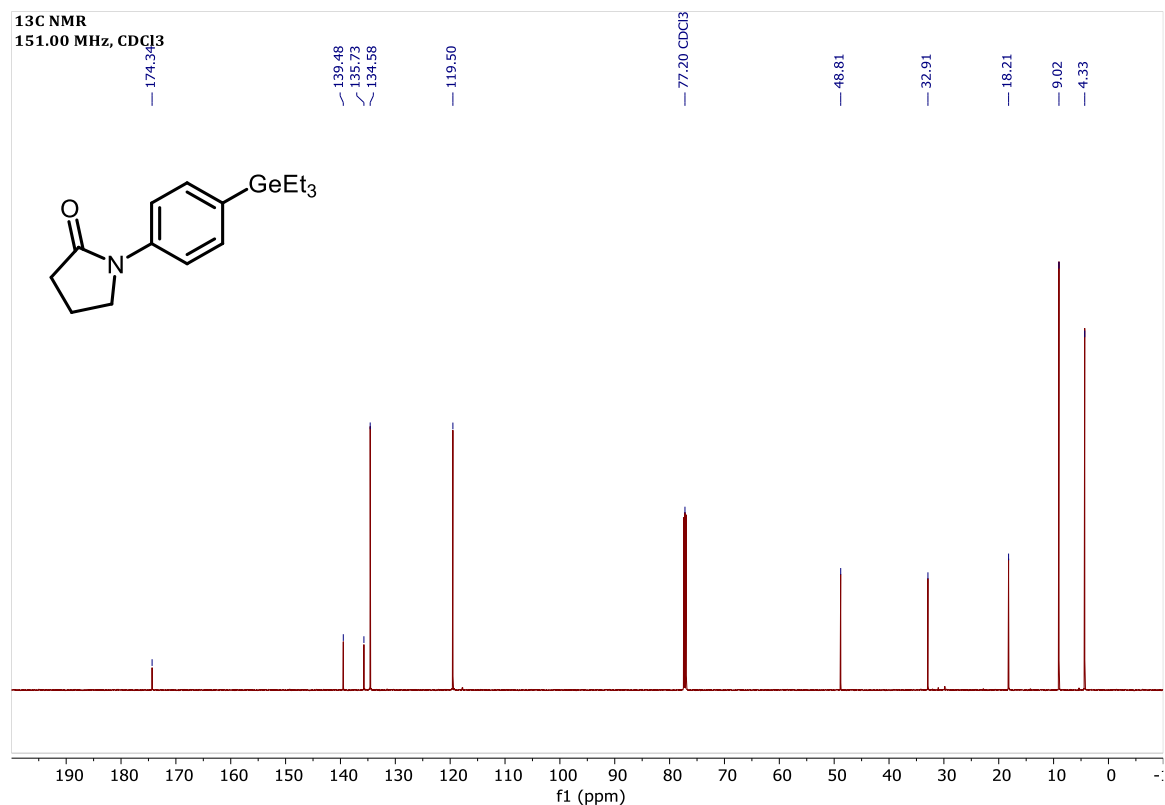
1-Phenylpyrrolidin-2-one derived tetrafluorothianthrenium salt (S₆)



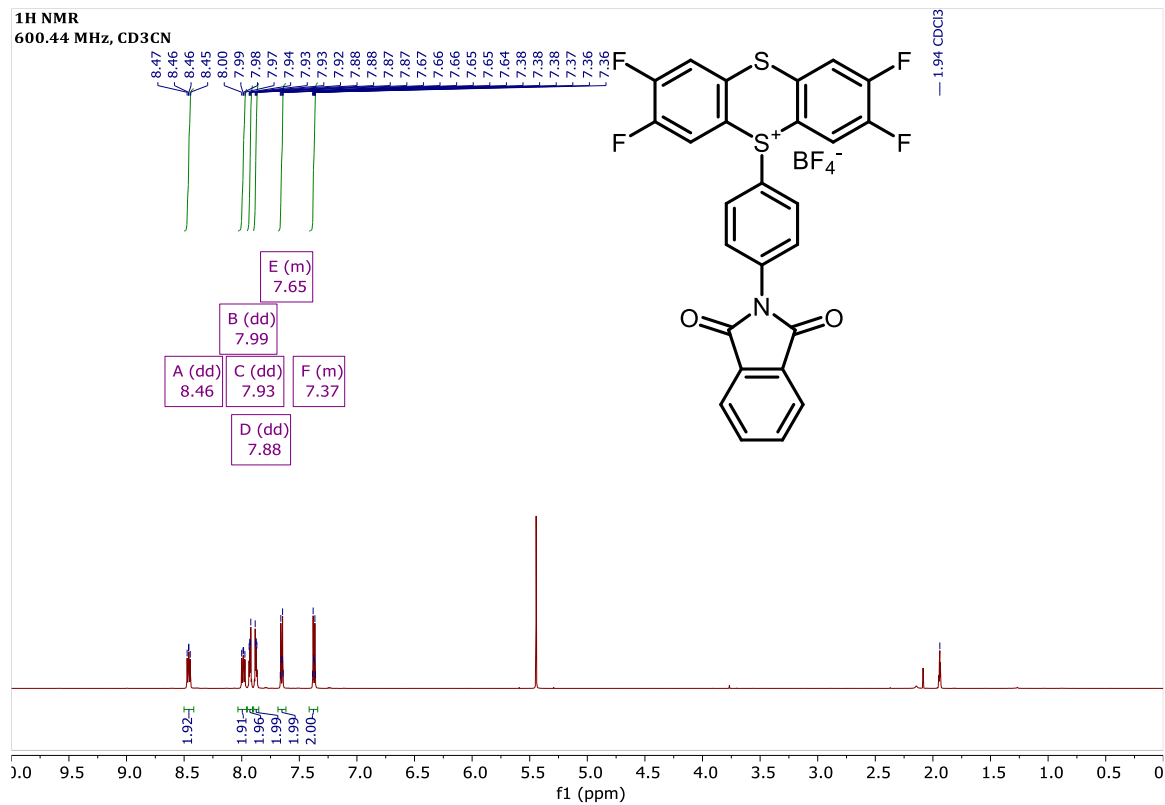


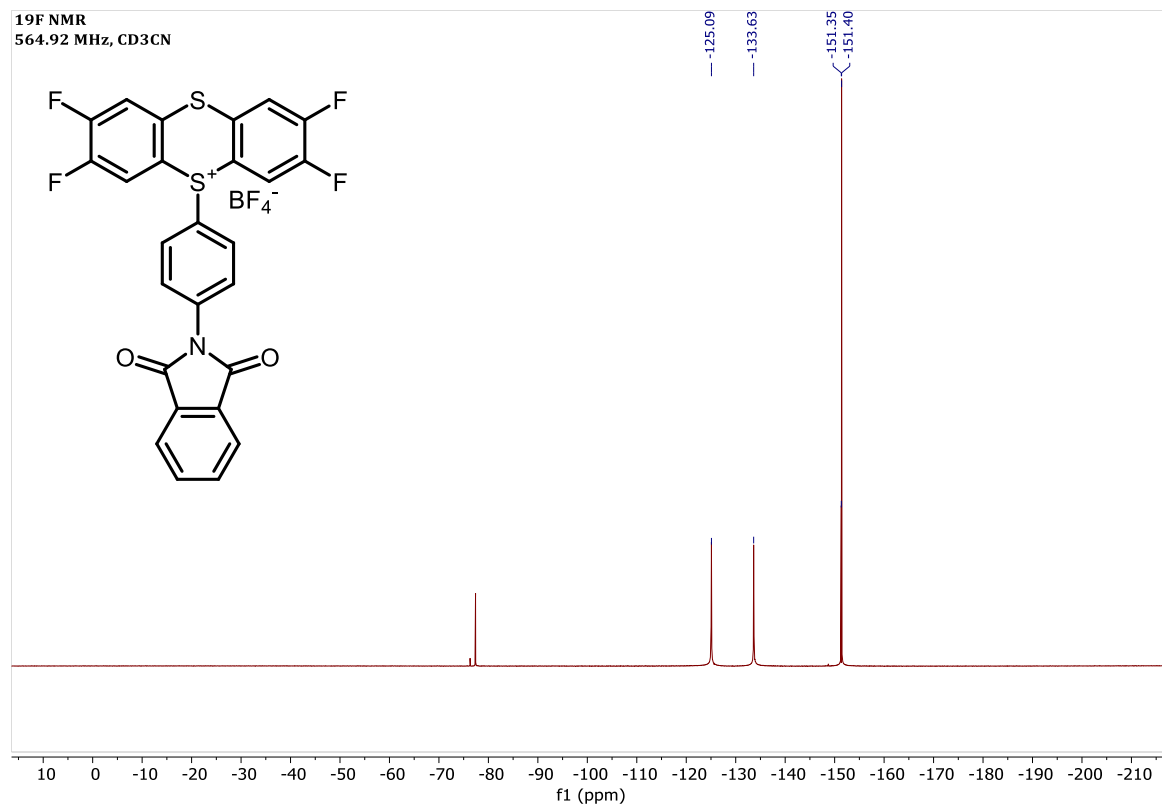
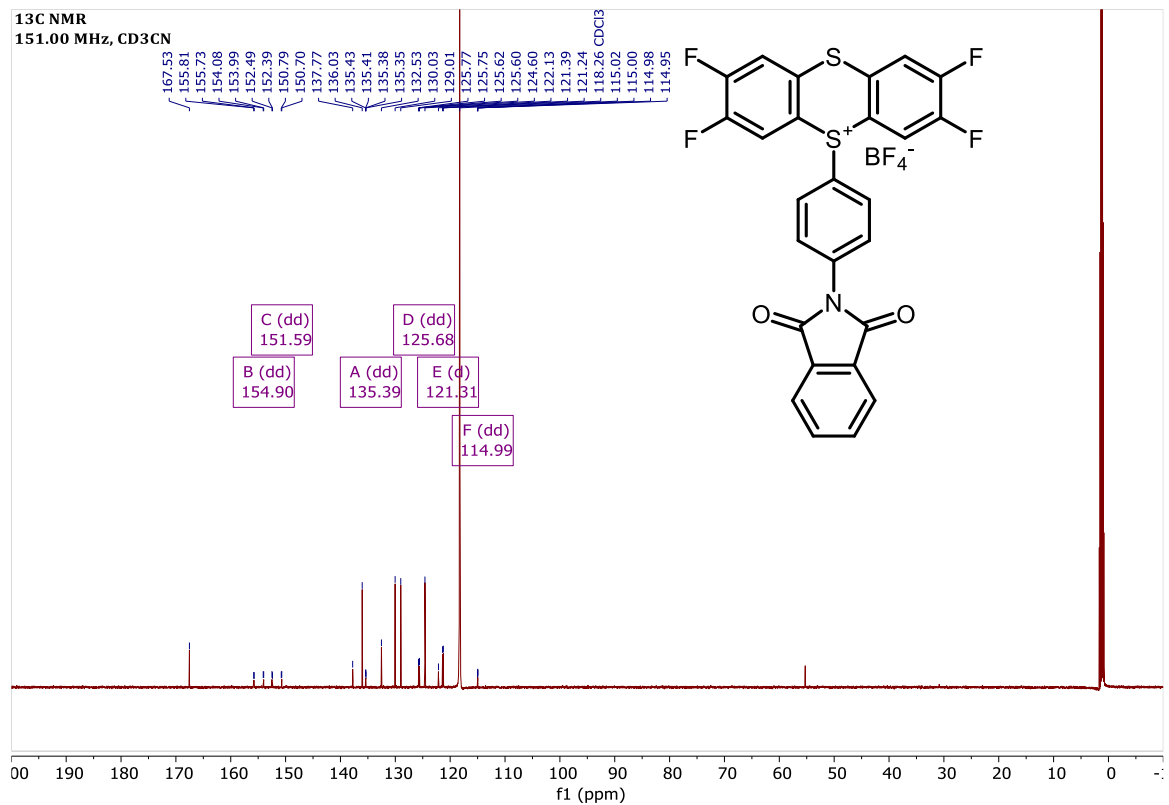
1-(4-(Triethylgermyl)phenyl)pyrrolidin-2-one (6)



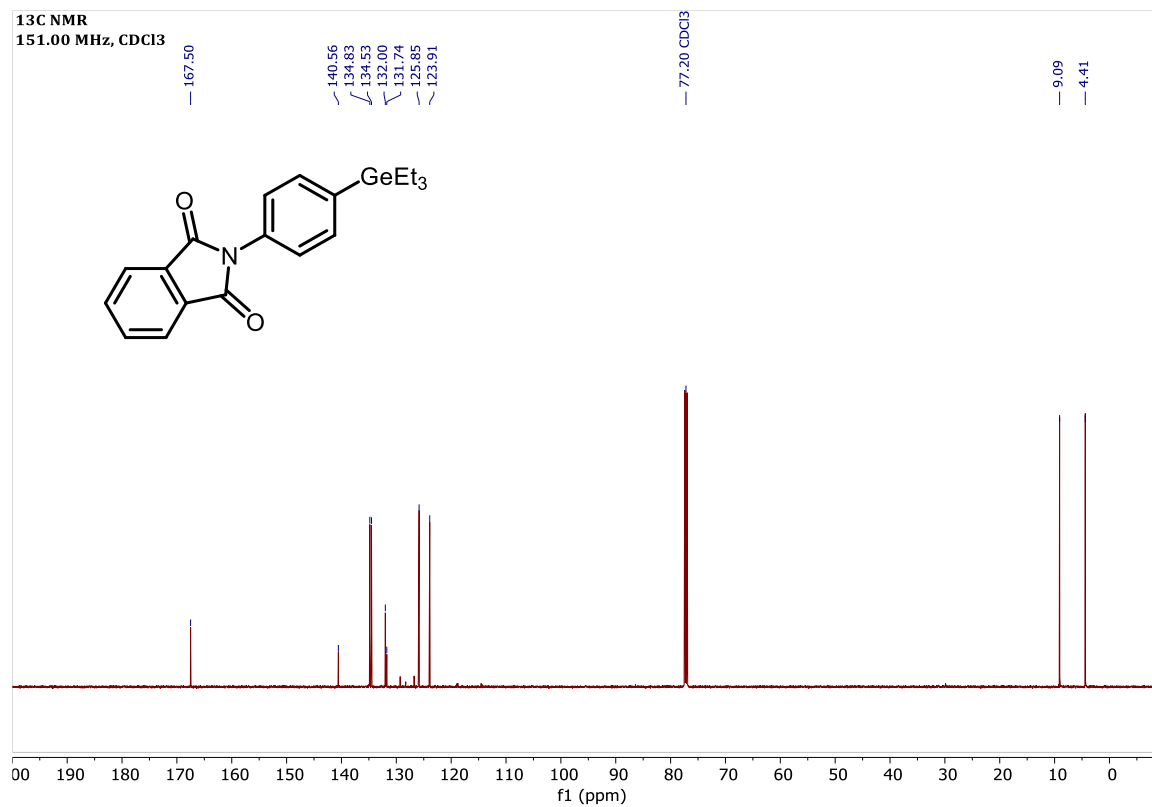
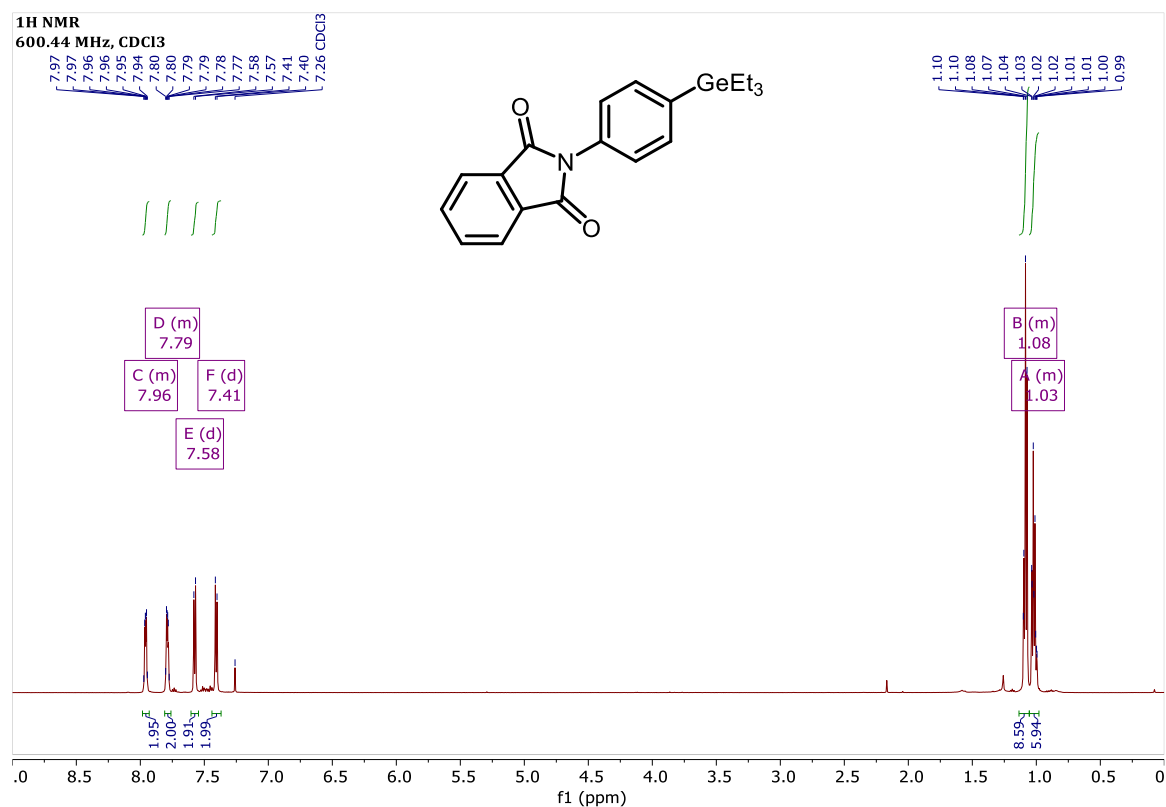


N-Phenylphthalimide derived tetrafluorothianthrenium salt (S₇)

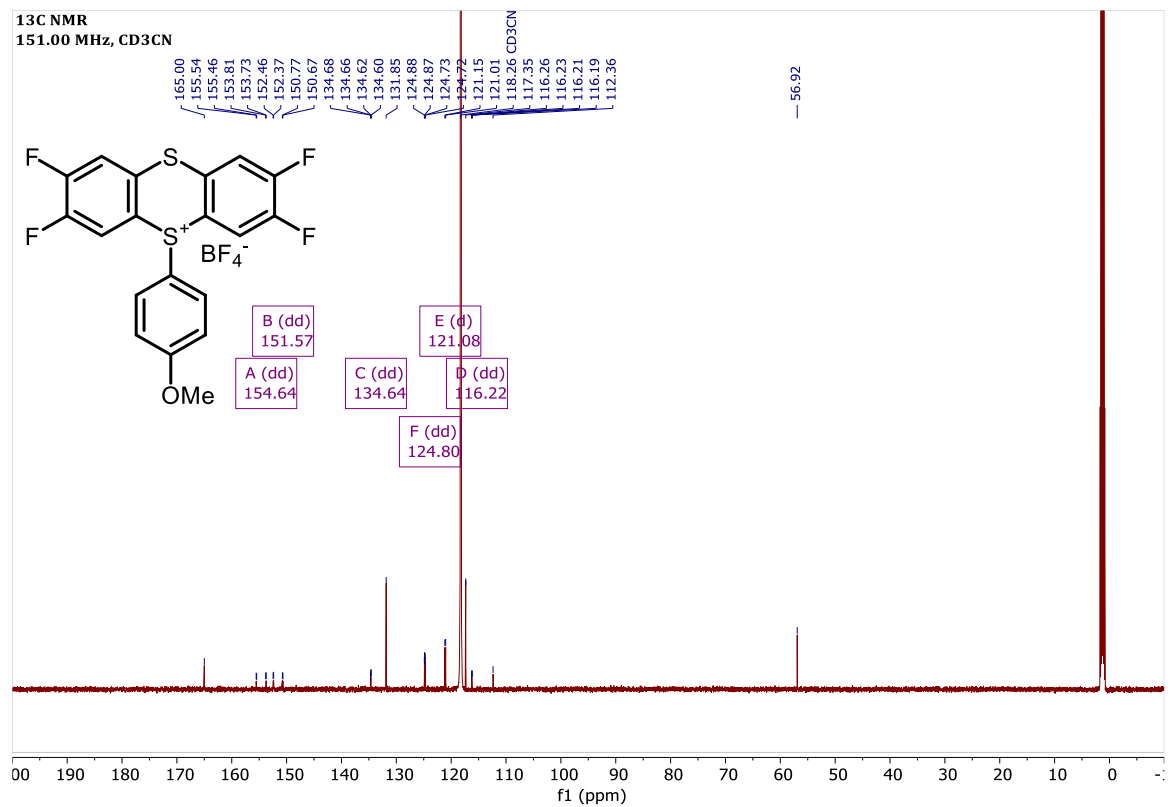
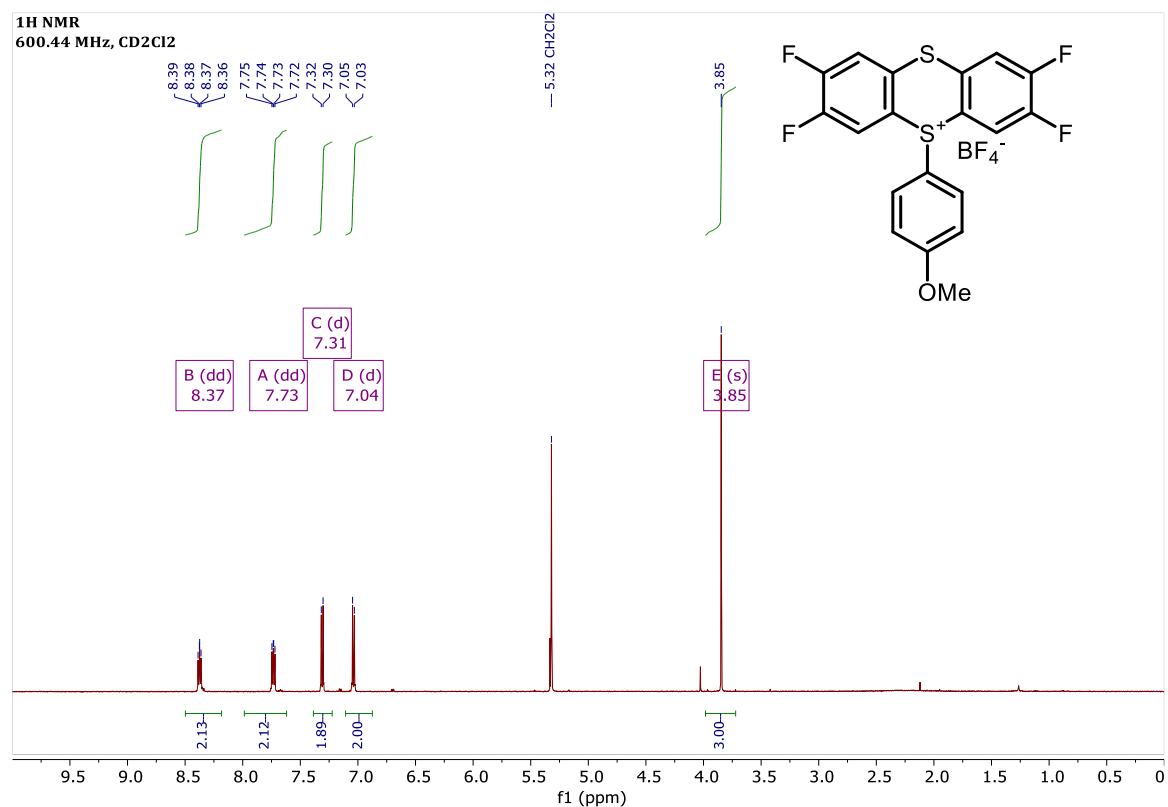


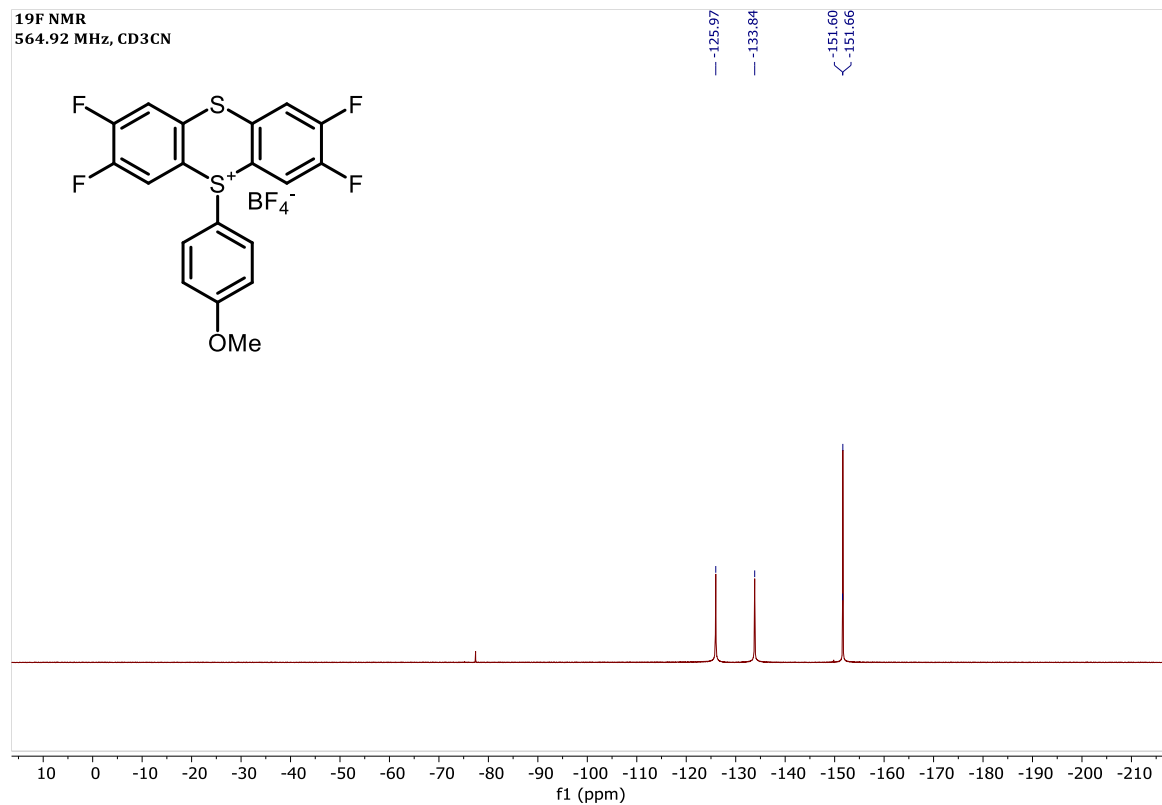


2-(4-(Triethylgermyl)phenyl)isoindoline-1,3-dione (7)

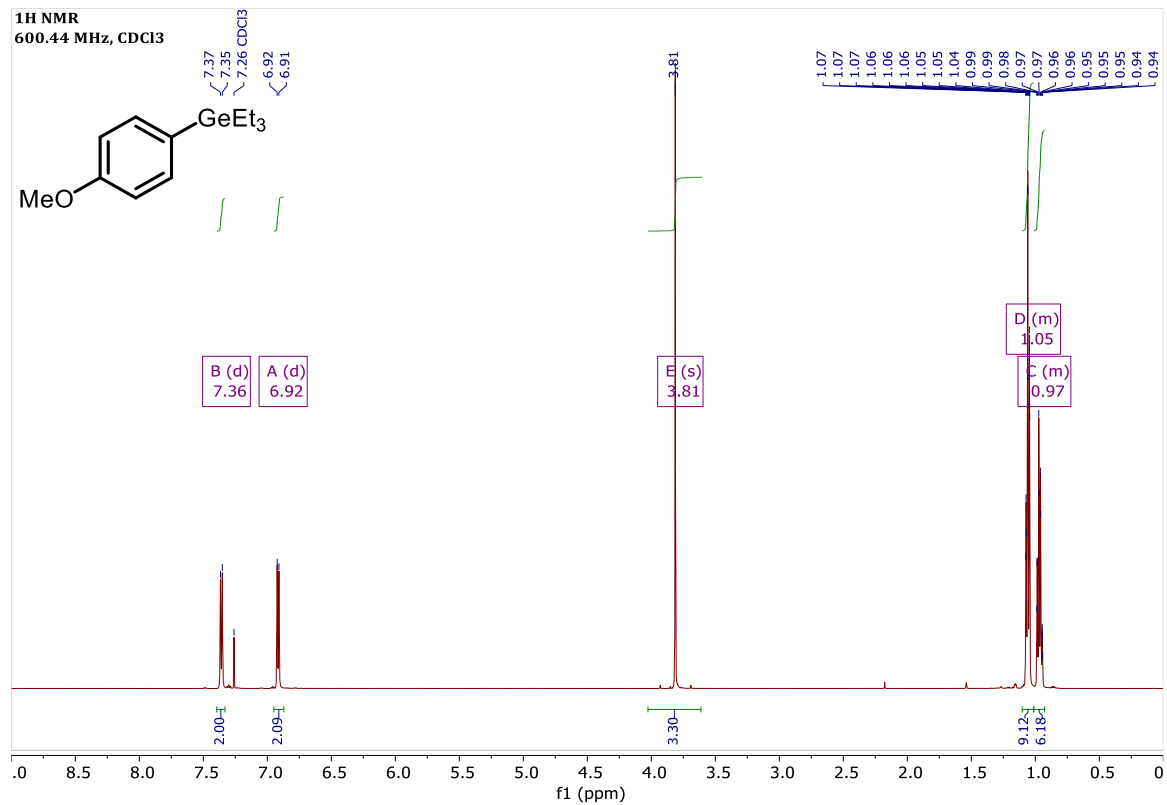


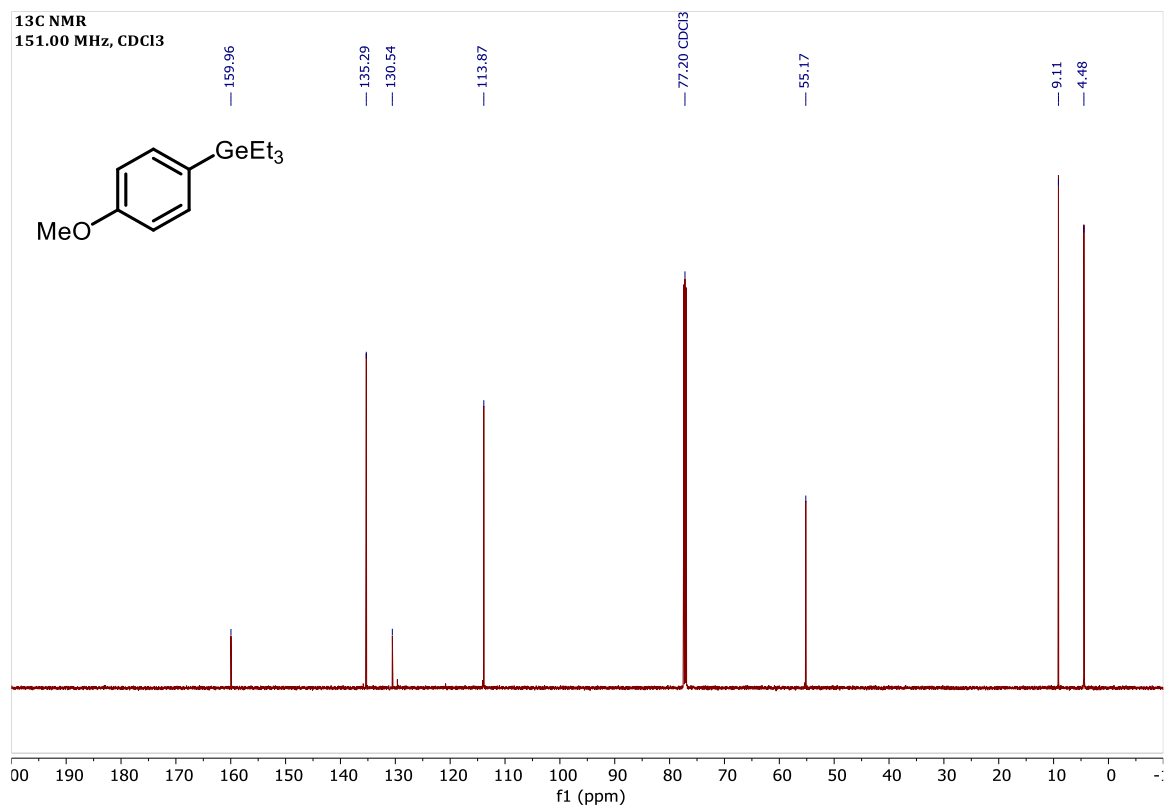
Anisole derived tetrafluorothianthrenium salt (S₈)



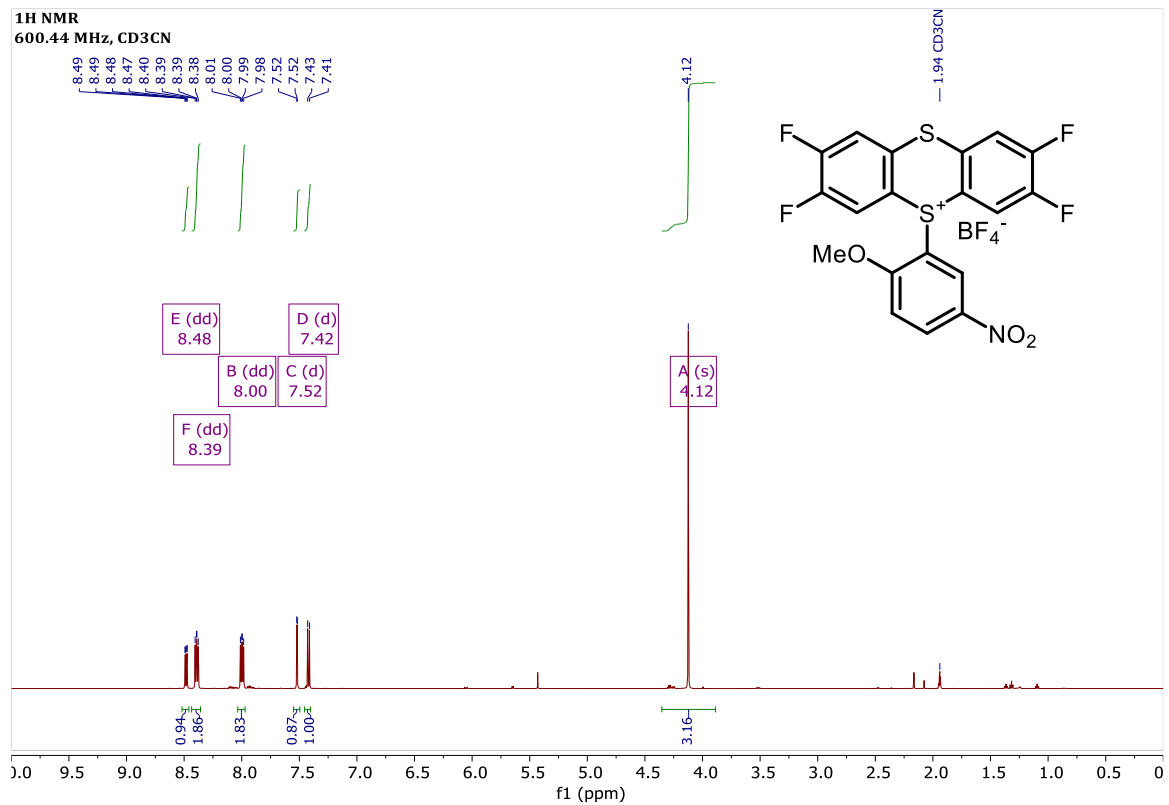


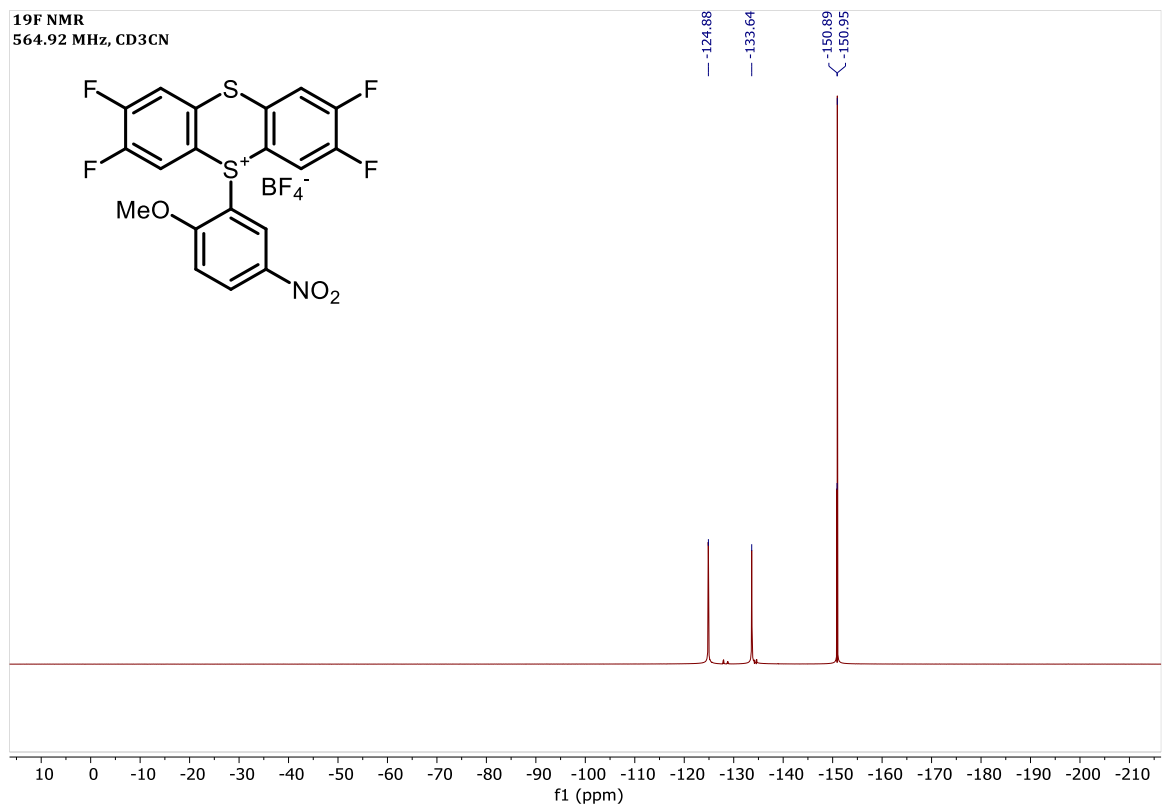
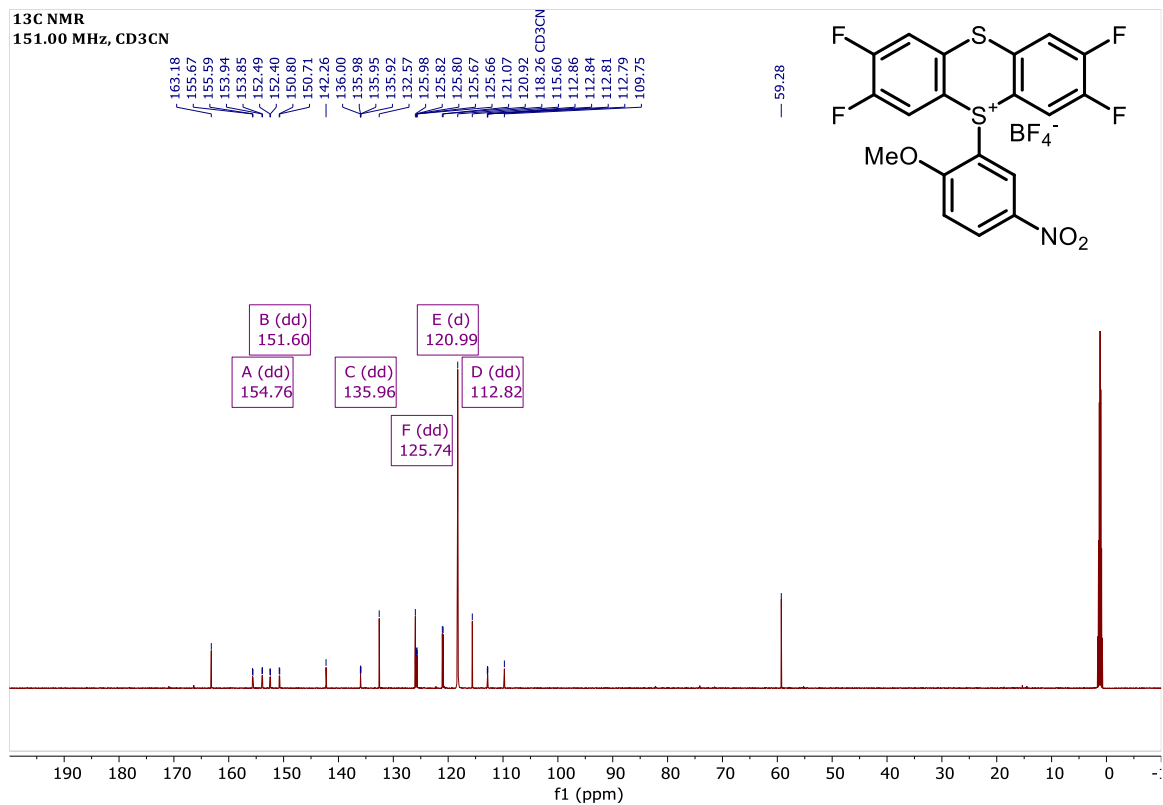
Triethyl(4-methoxyphenyl)germane (8)



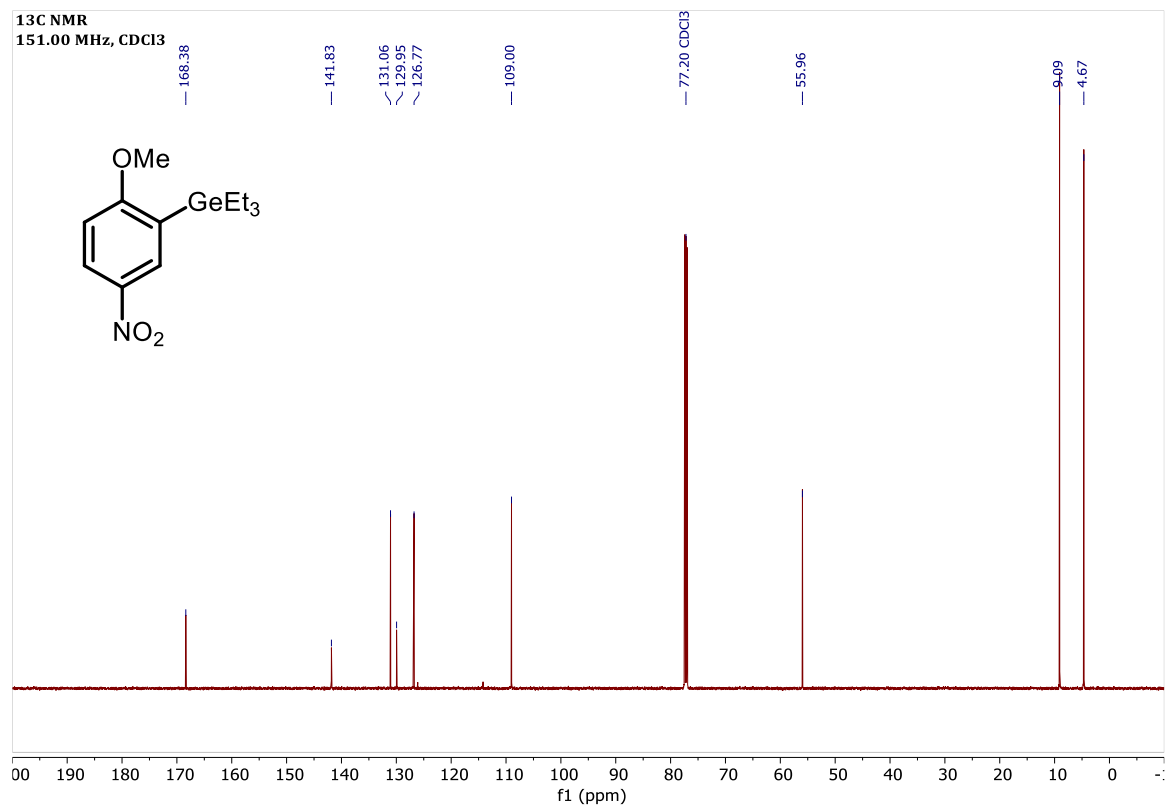
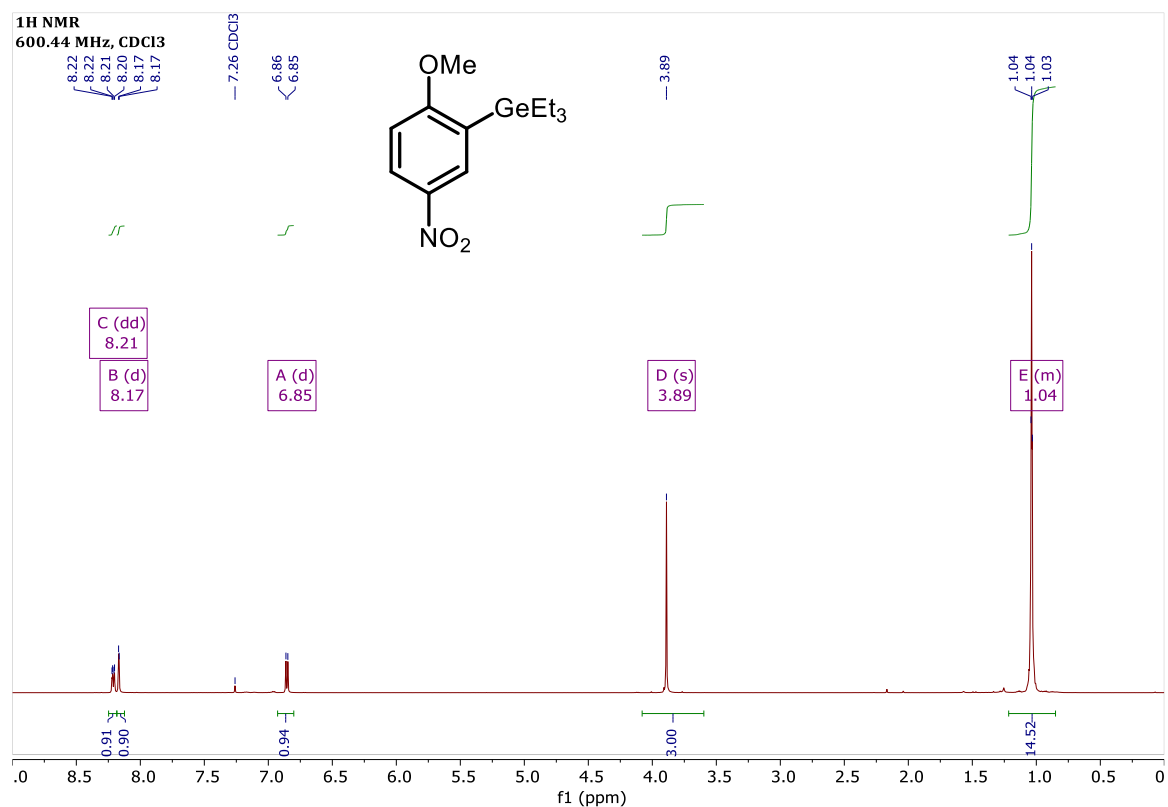


4-Nitroanisole derived tetrafluorothianthrenium salt (S₉)

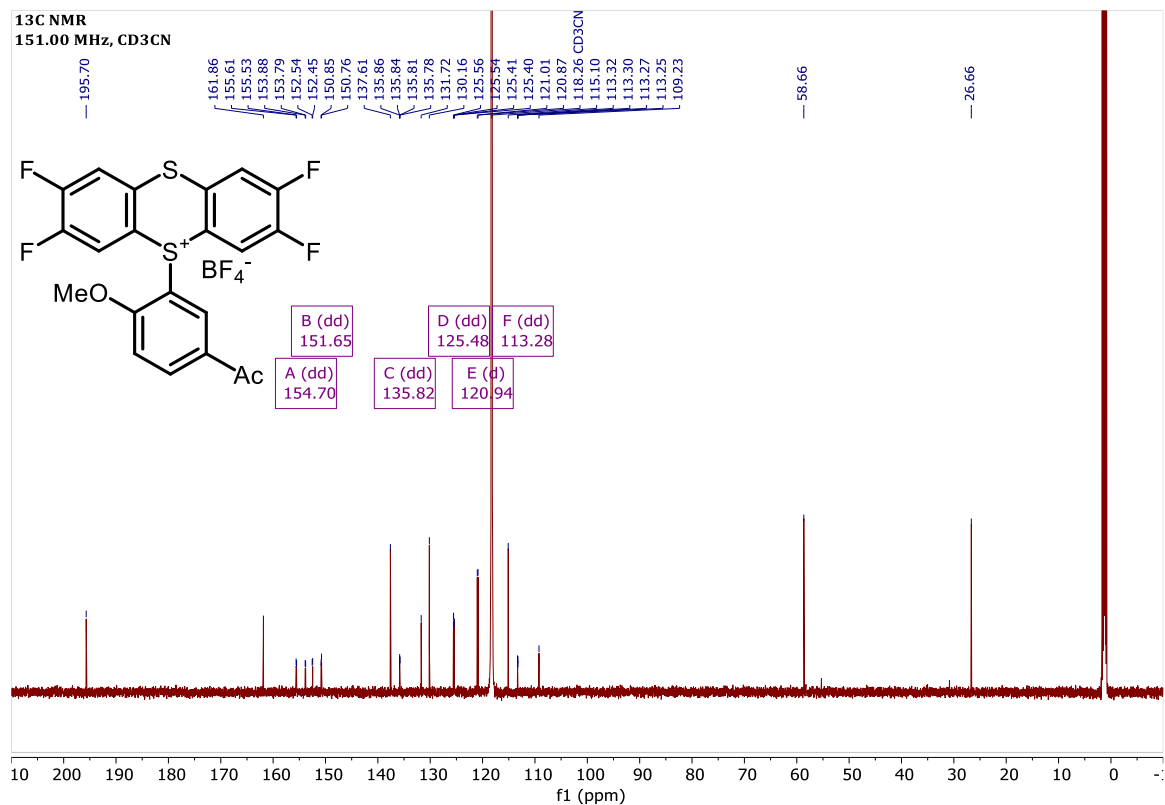
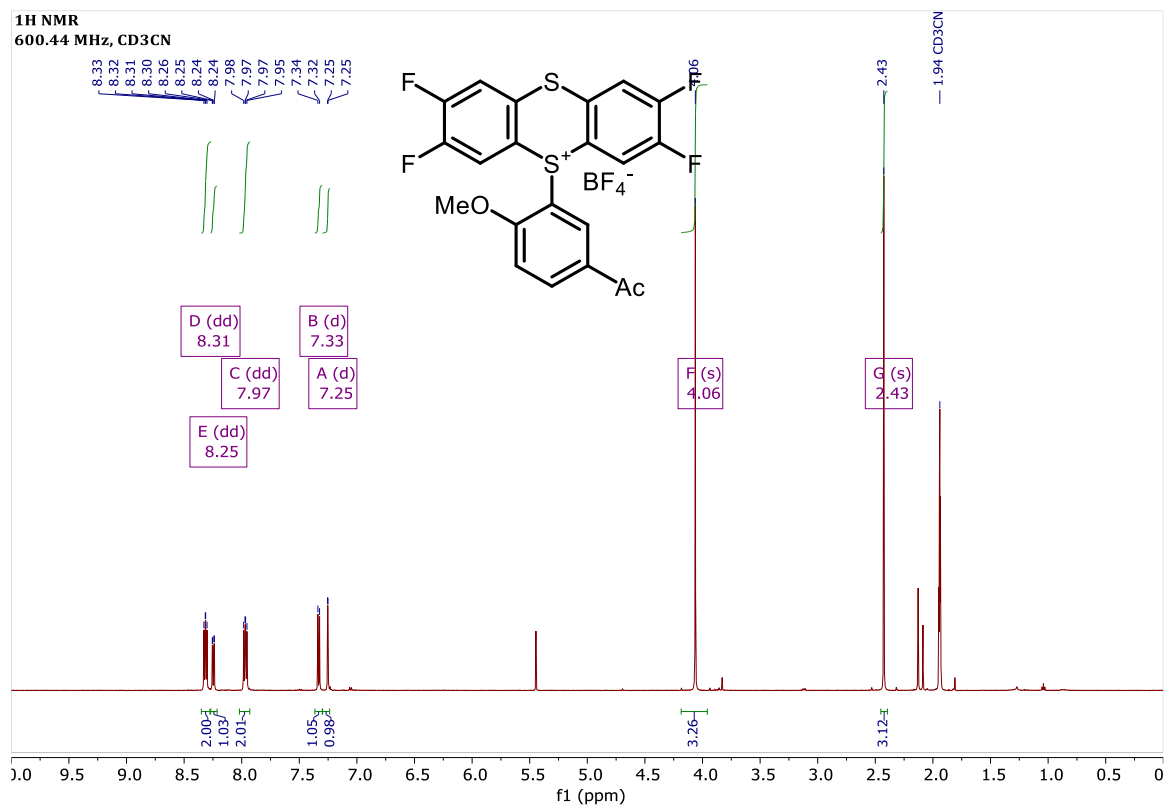


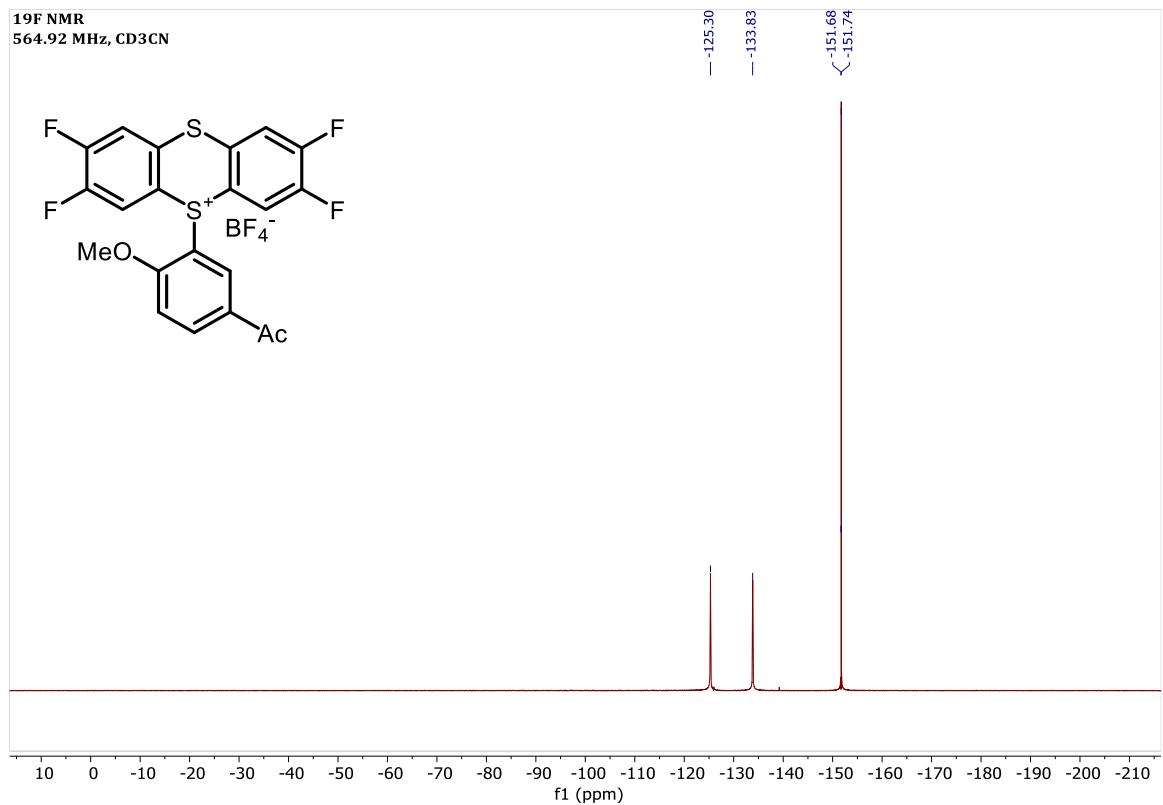


Triethyl(2-methoxy-5-nitrophenyl)germane (9)

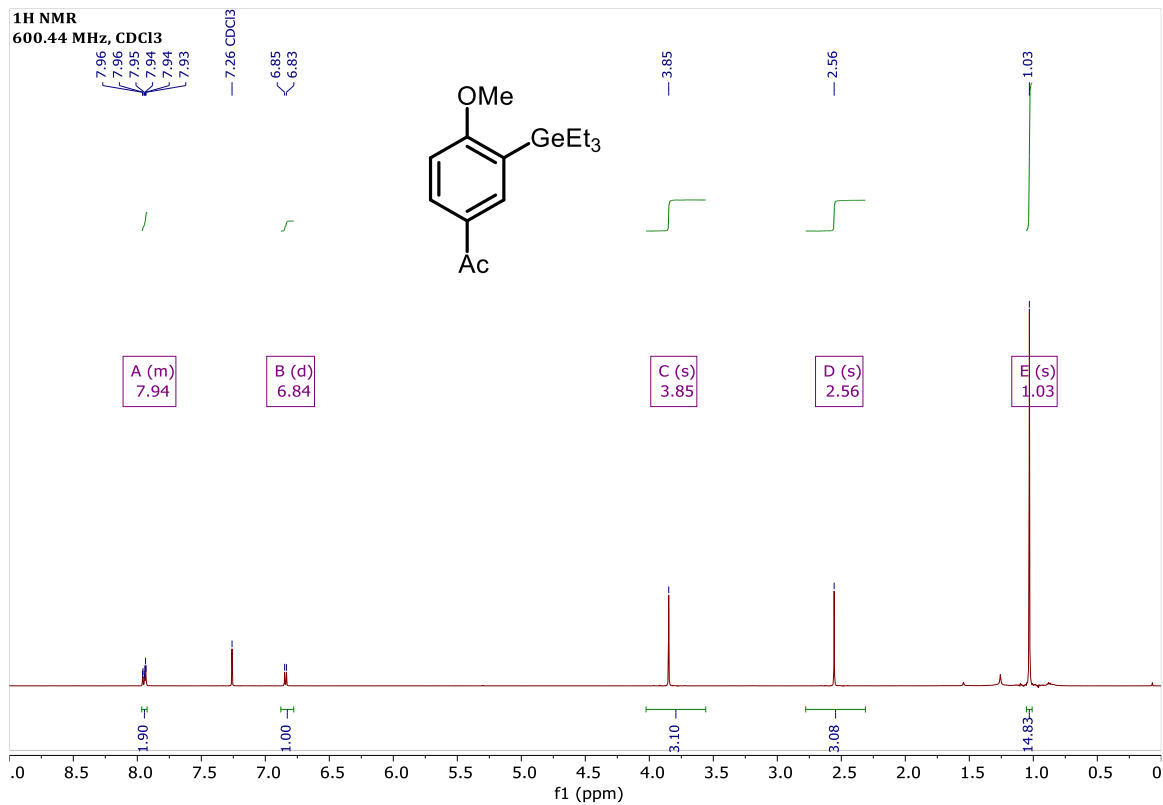


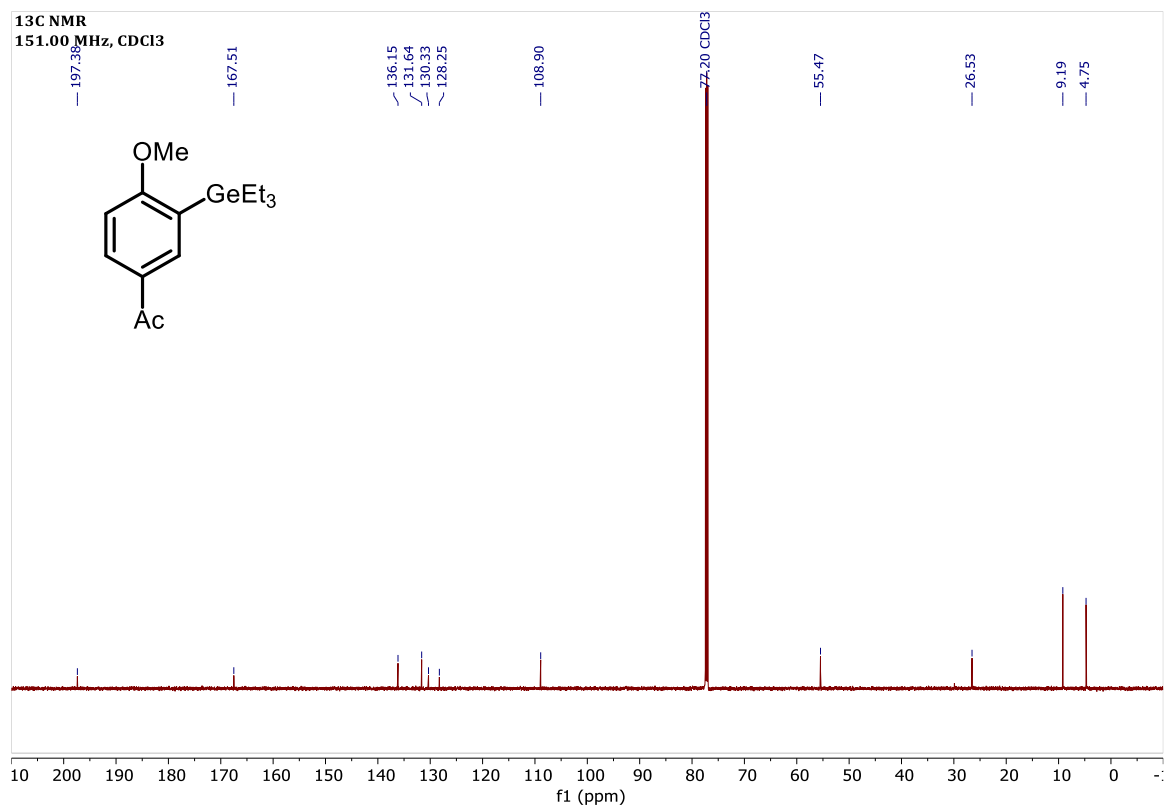
4-Acetylanisole derived tetrafluorothianthrenium salt (S₁₀)



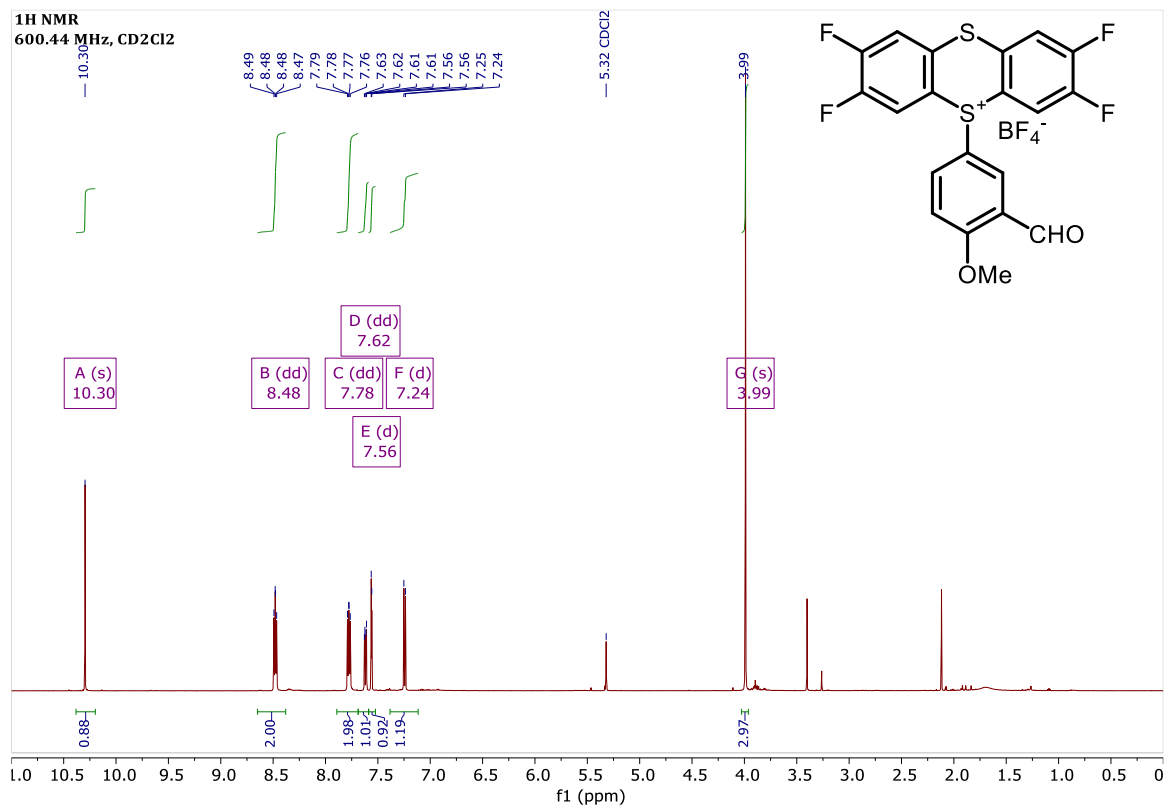


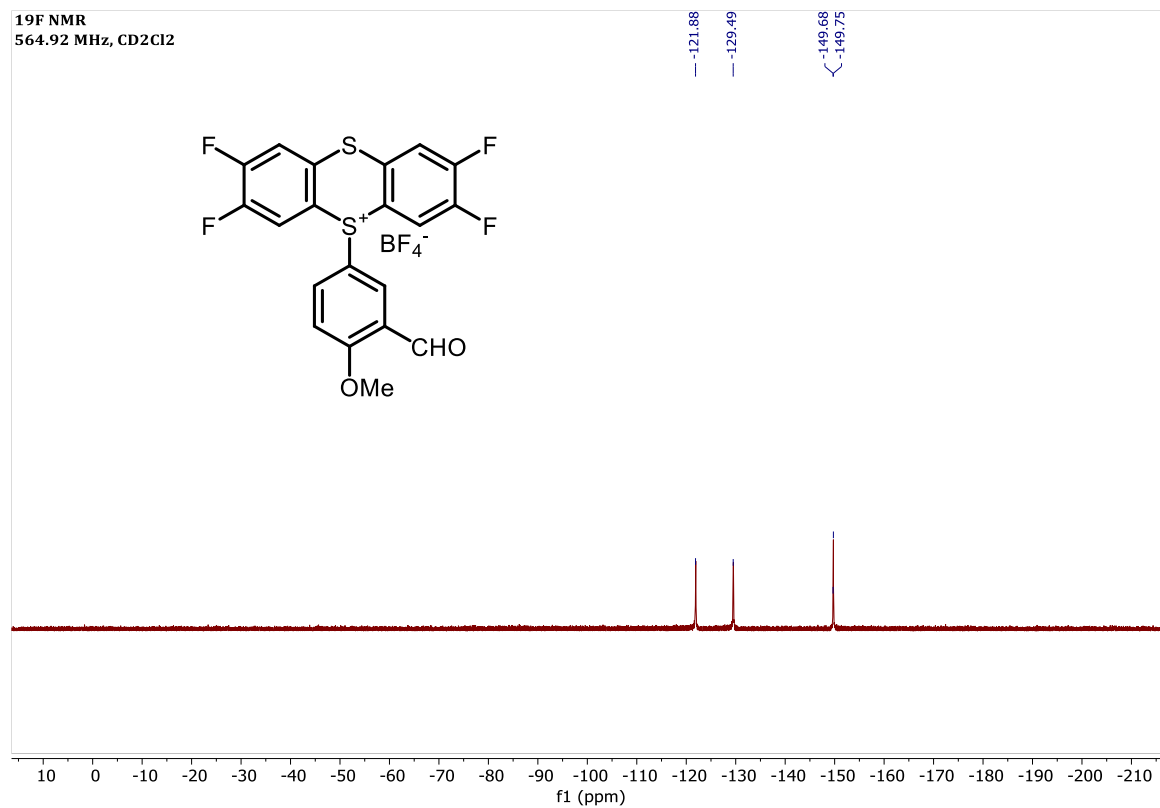
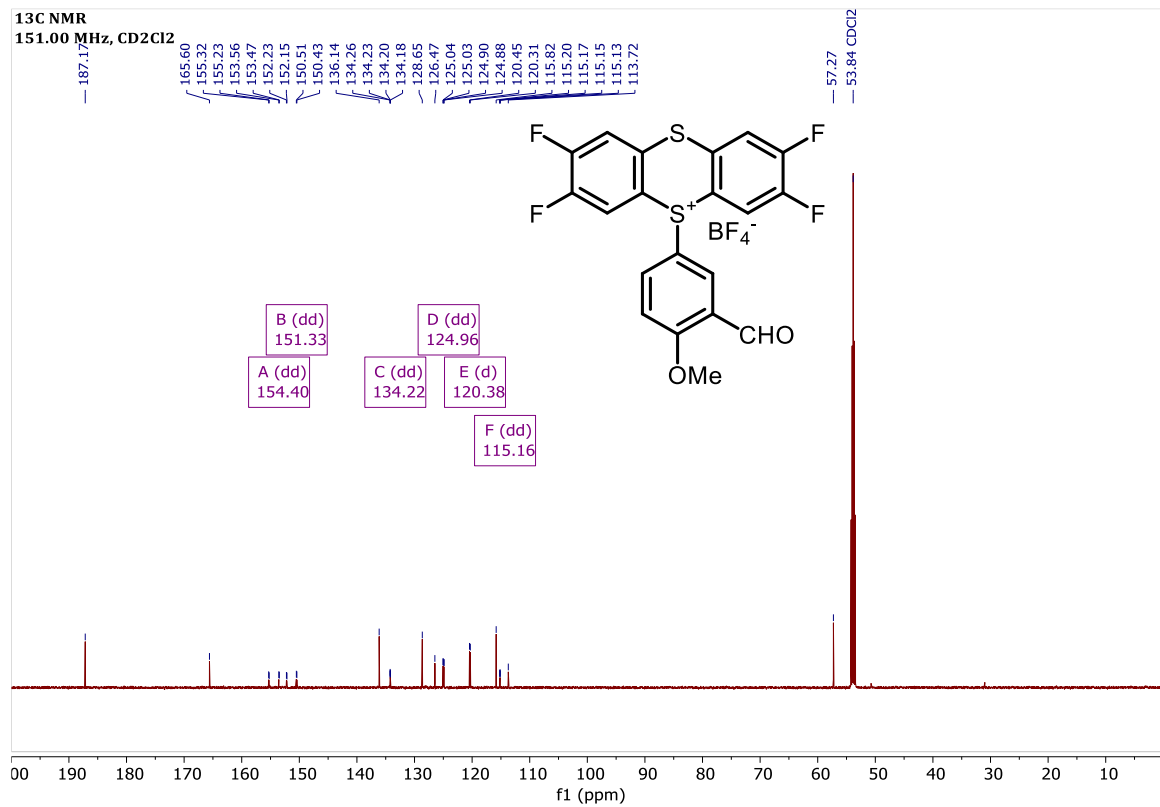
1-(4-Methoxy-3-(triethylgermyl)phenyl)ethan-1-one (10)



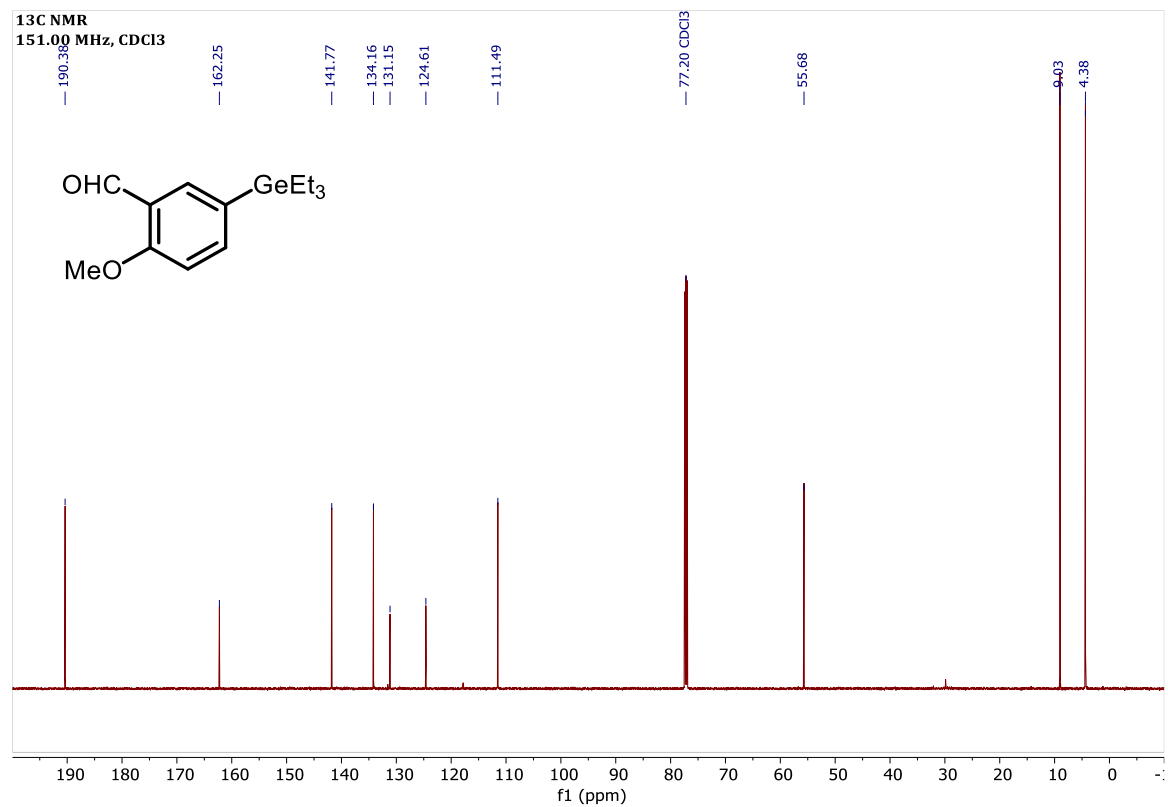
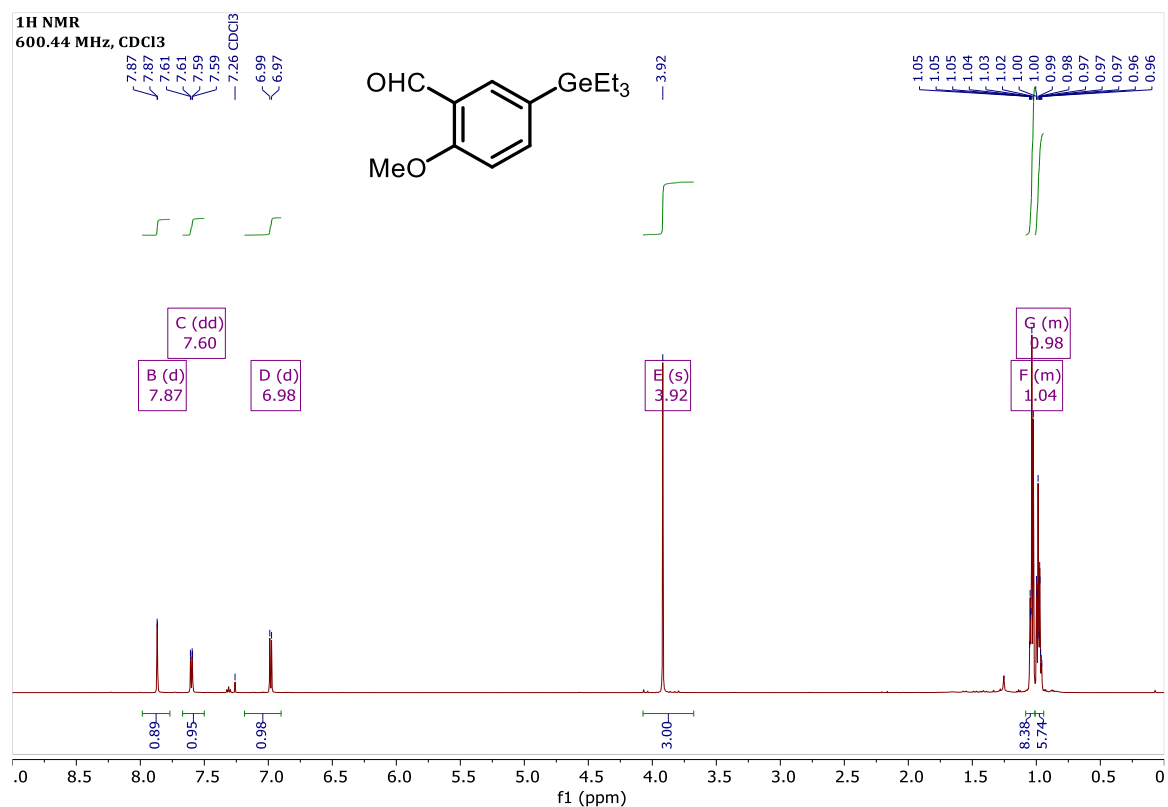


2-Methoxybenzaldehyde derived tetrafluorothianthrenium salt (S₁₁)

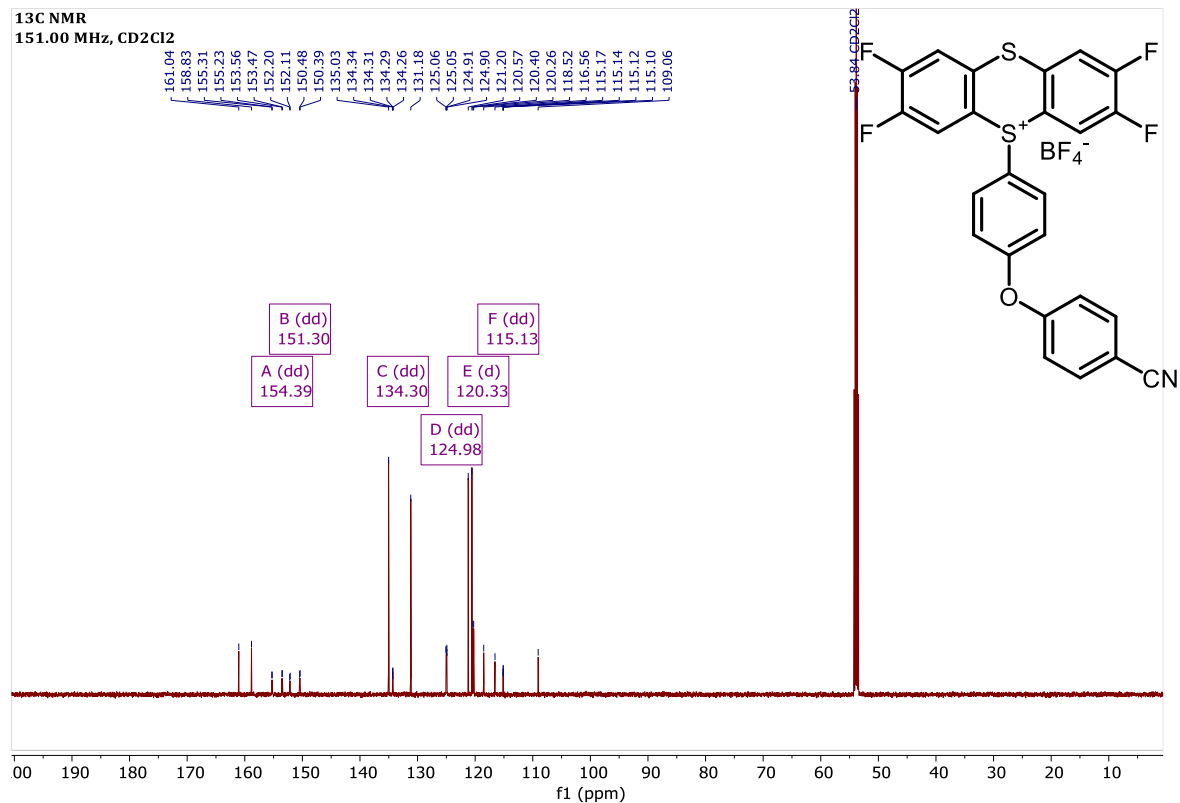
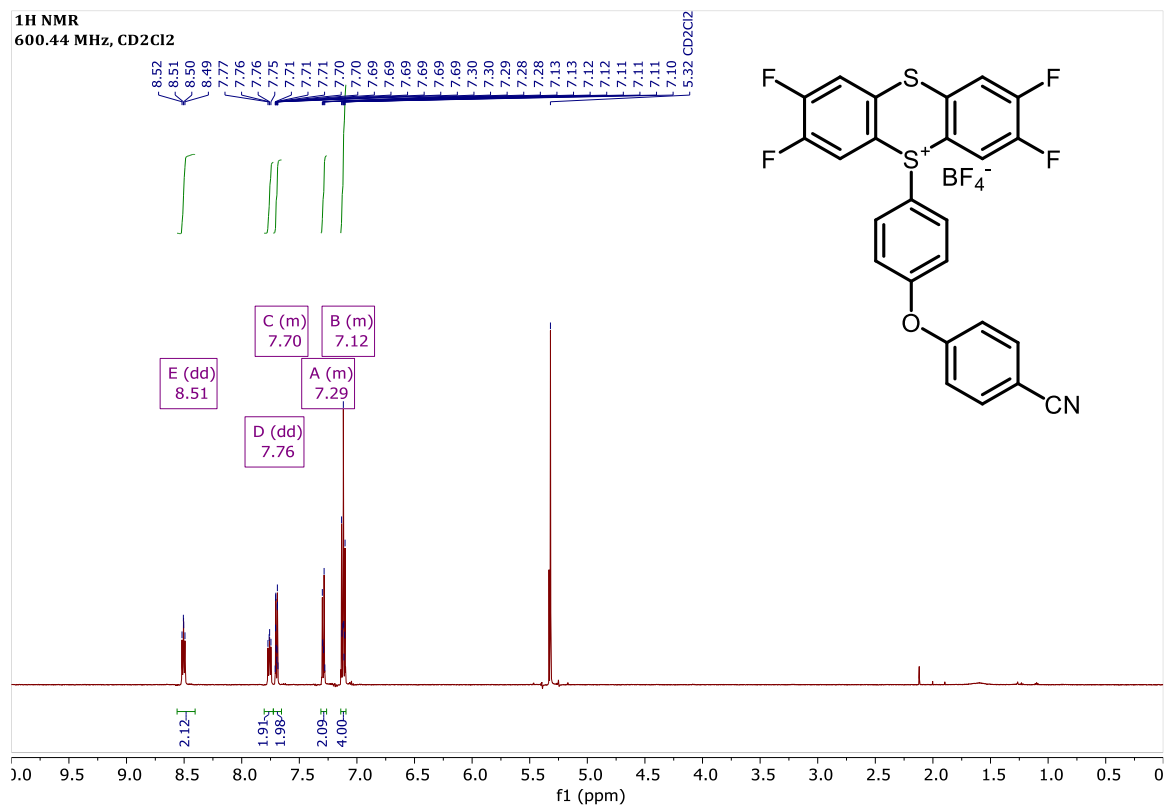


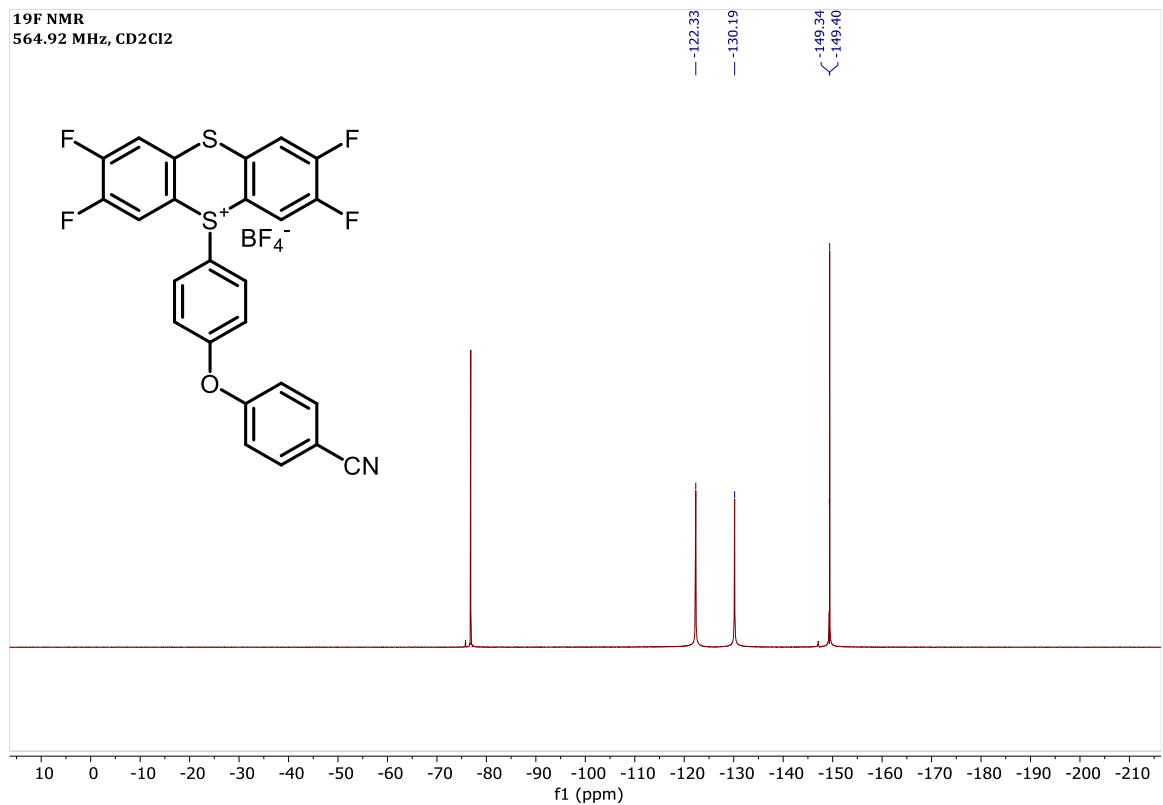


2-Methoxy-5-(triethylgermyl)benzaldehyde (11)

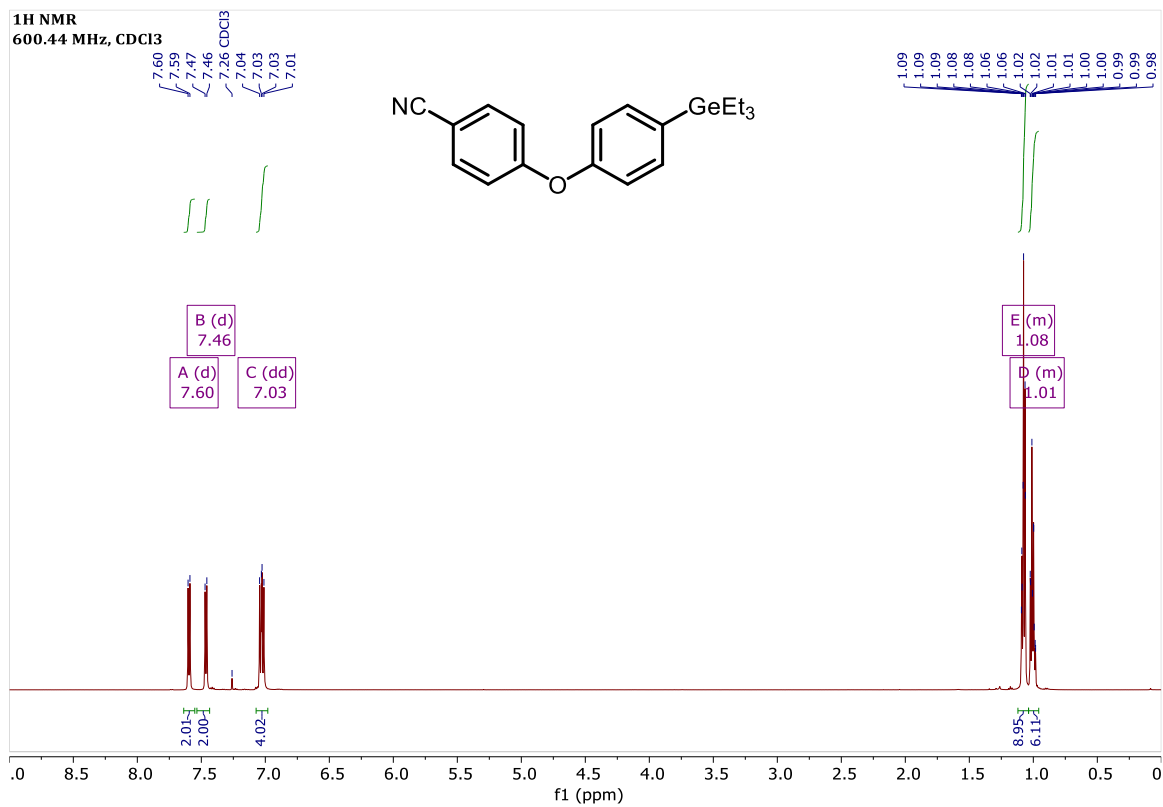


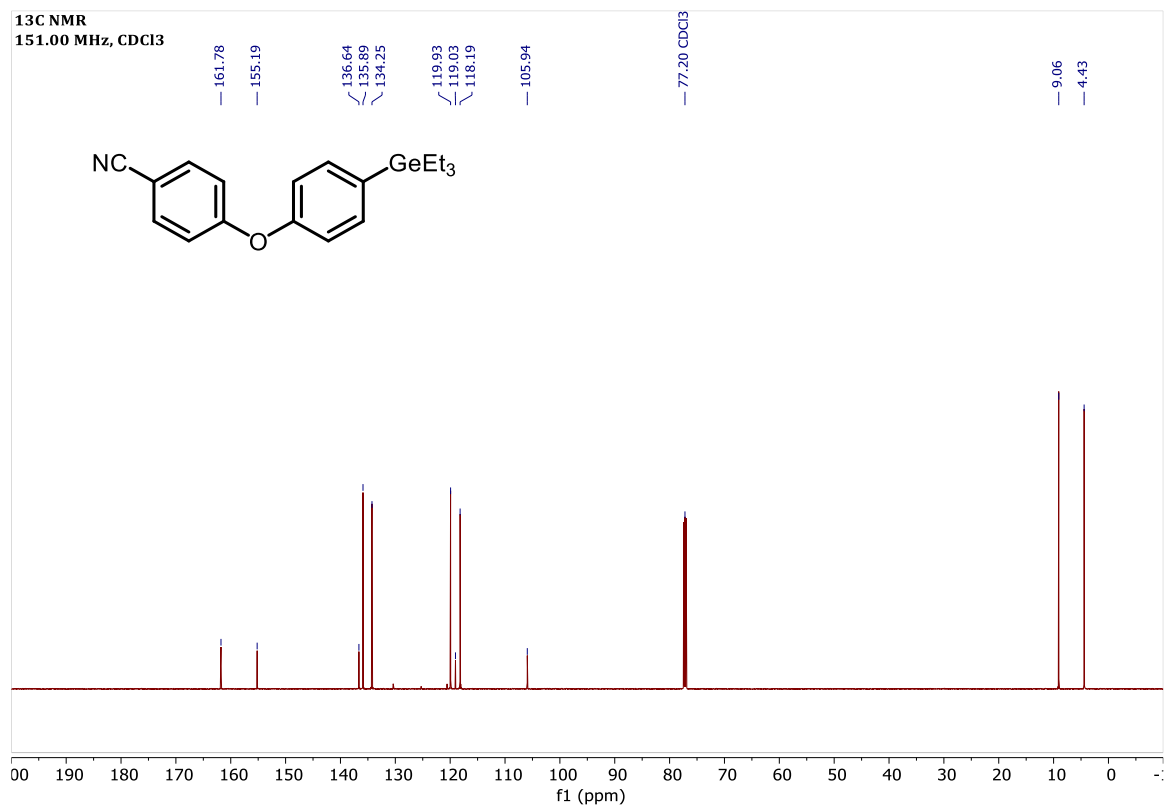
4-Phenoxybenzonitrile derived tetrafluorothianthrenium salt (S₁₂)



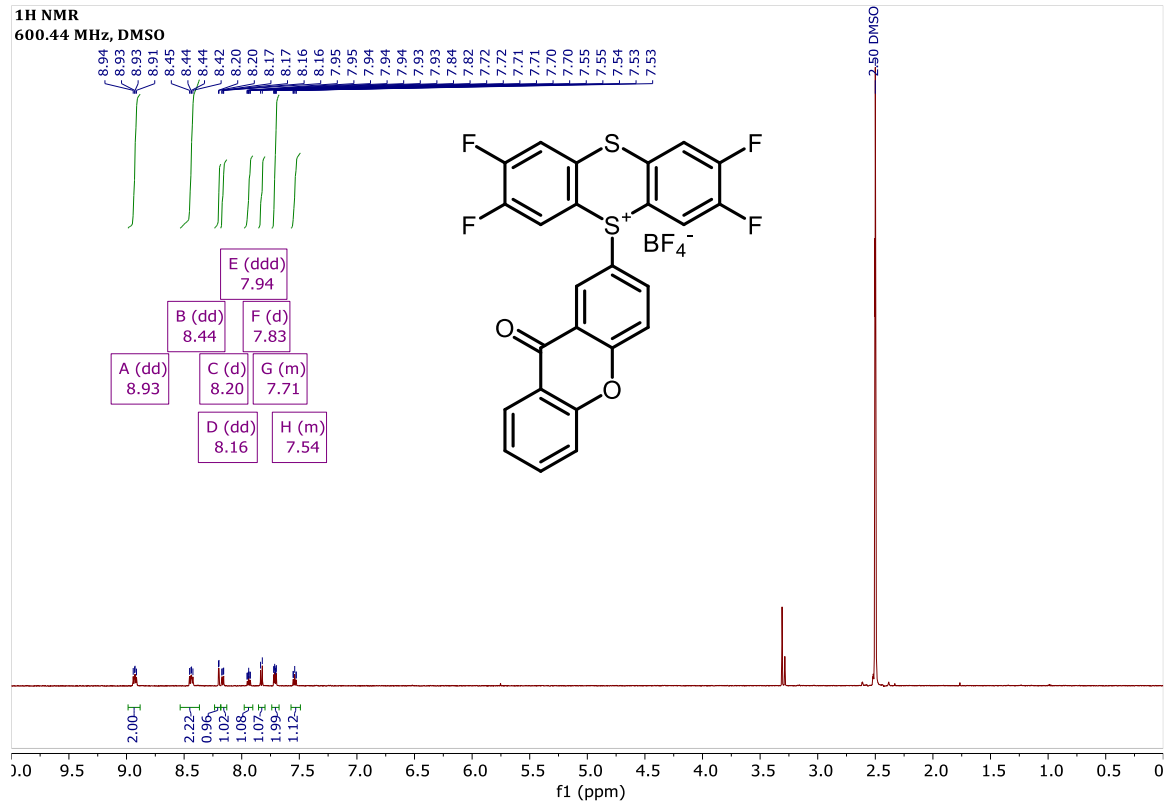


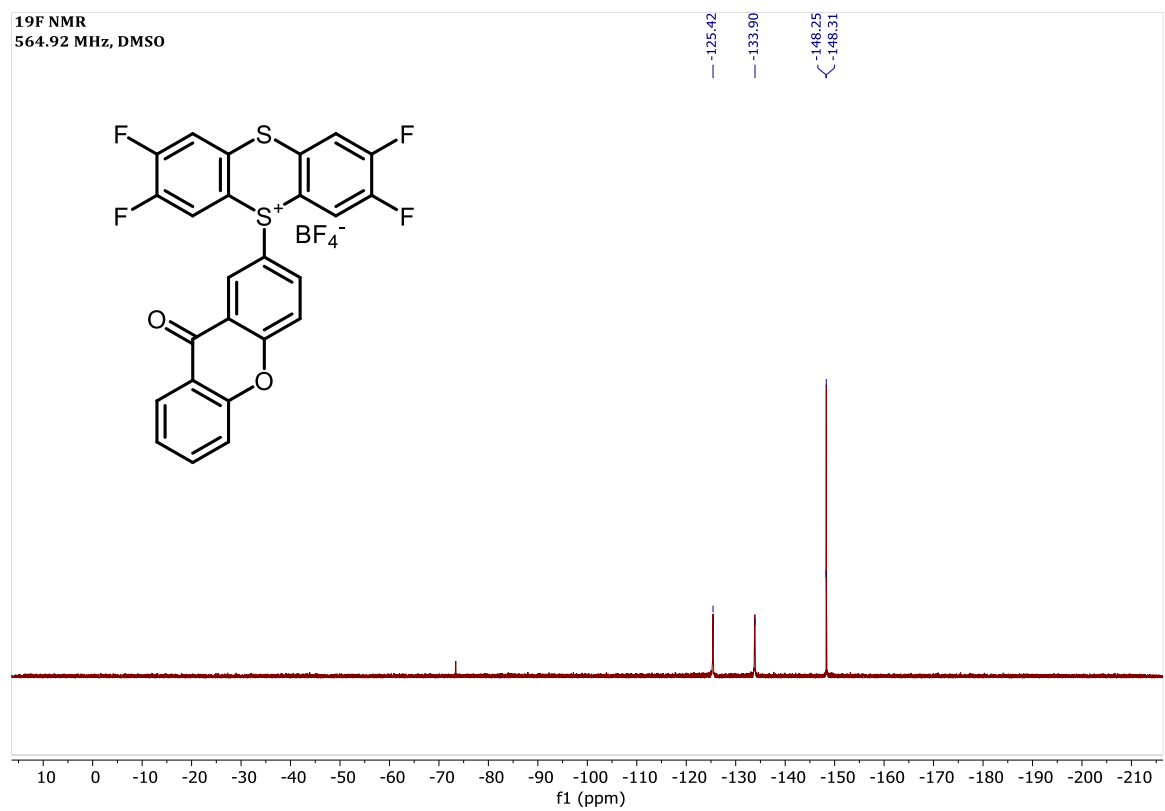
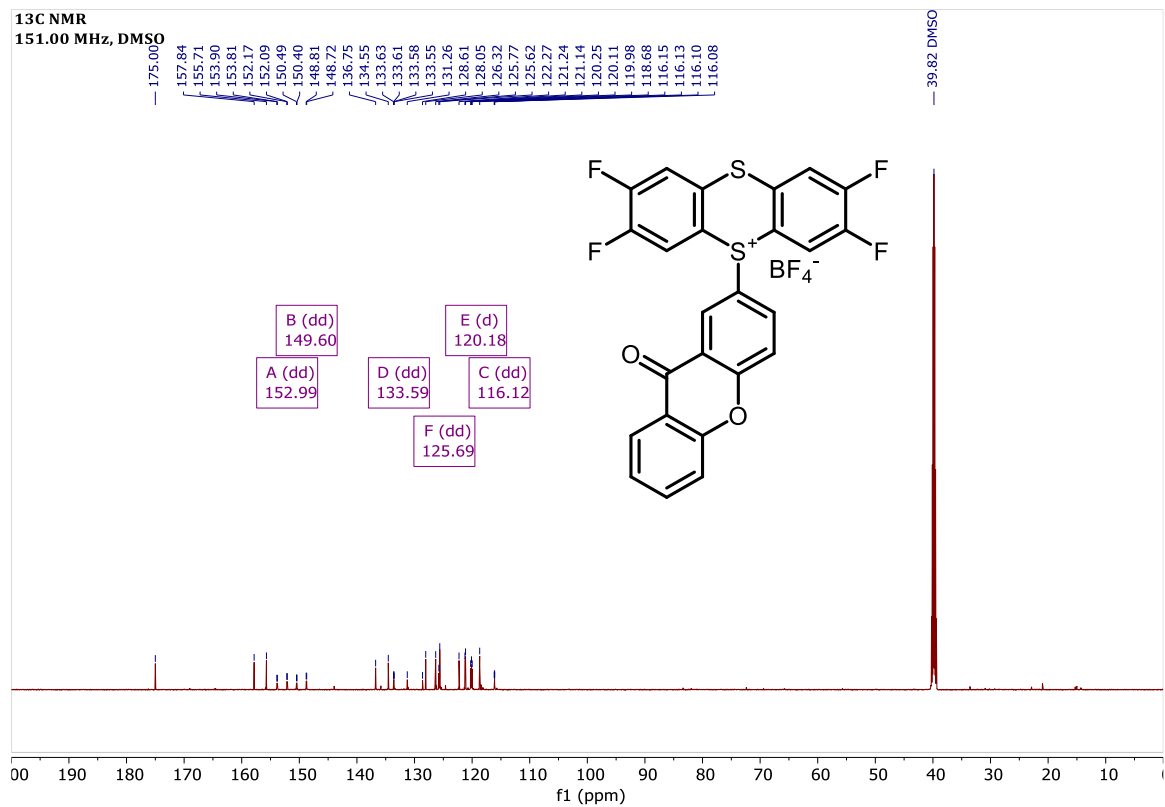
4-(4-(Triethylgermyl)phenoxy)benzonitrile (12)



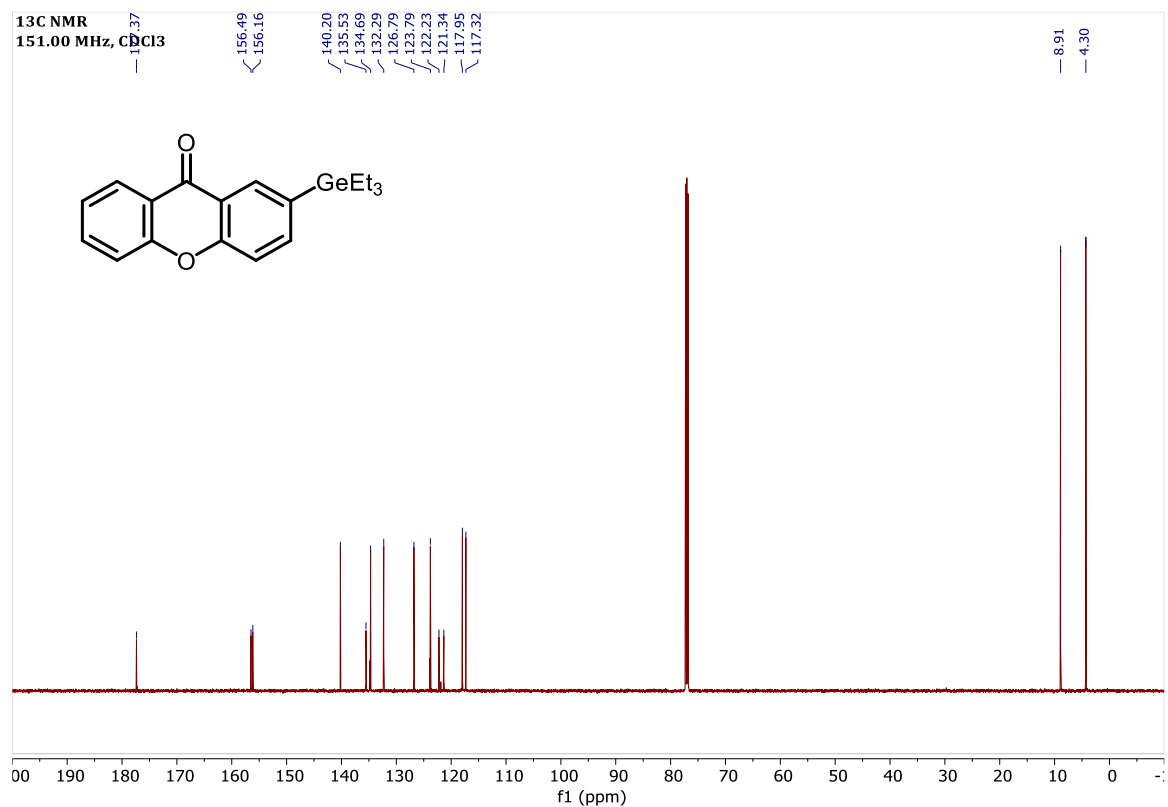
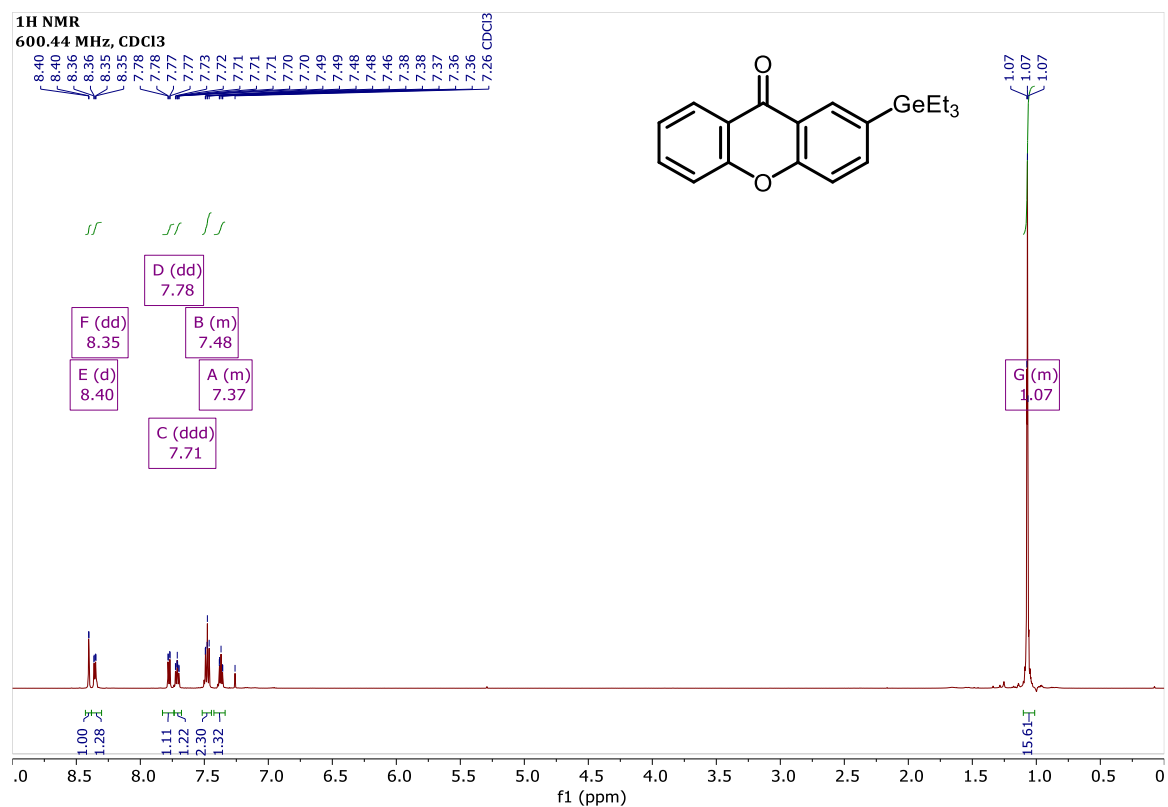


Xanthone derived tetrafluorothianthrenium salt (S₁₃)

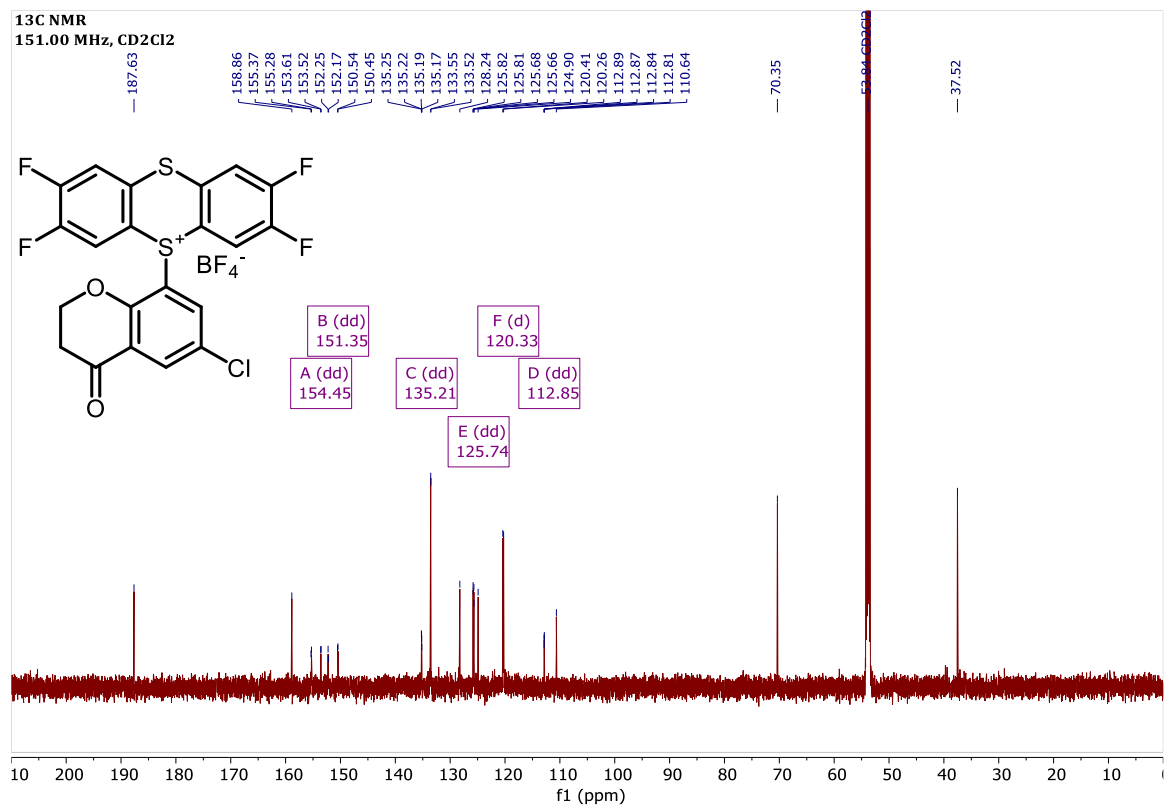
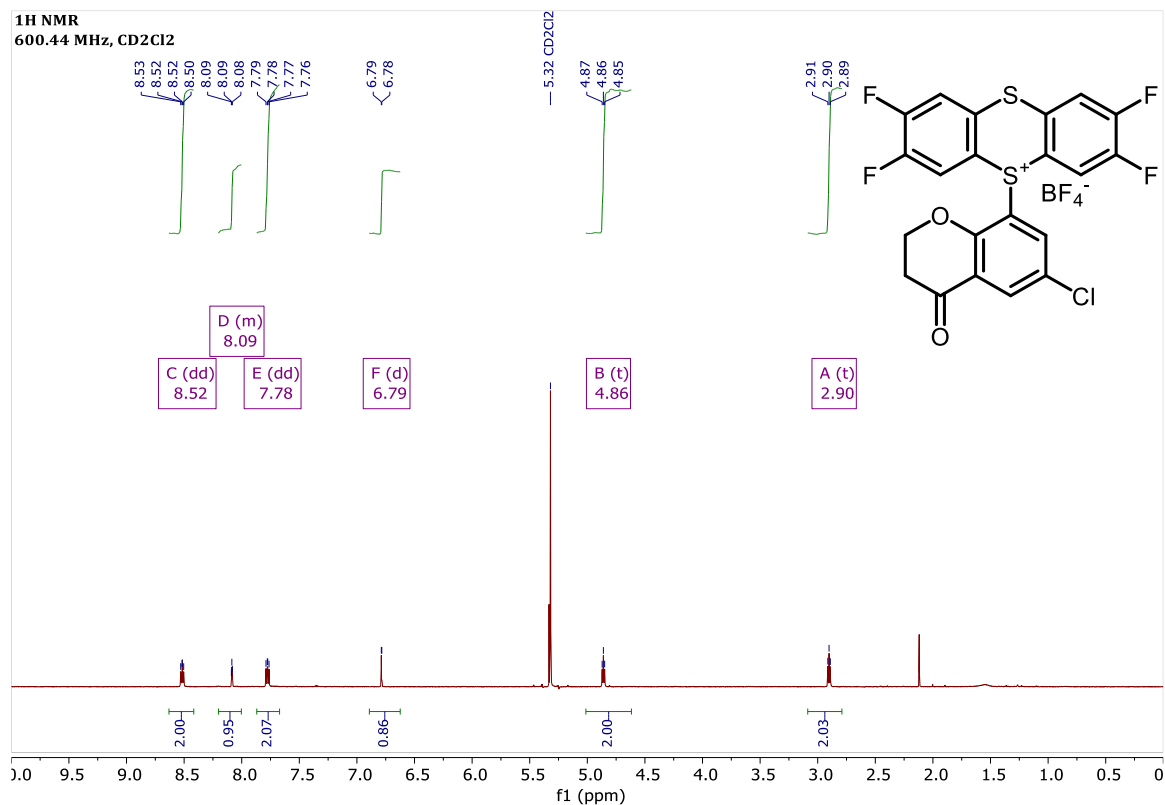


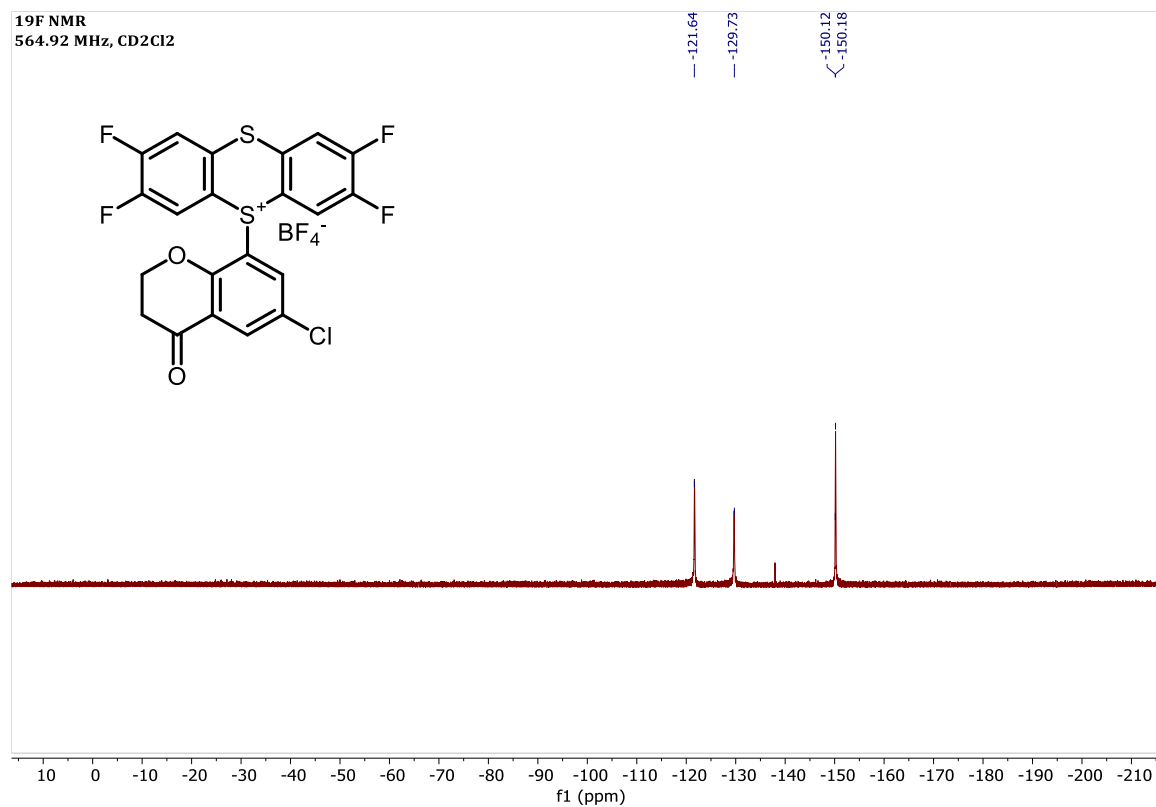


2-(Triethylgermyl)-9H-xanthen-9-one (13)

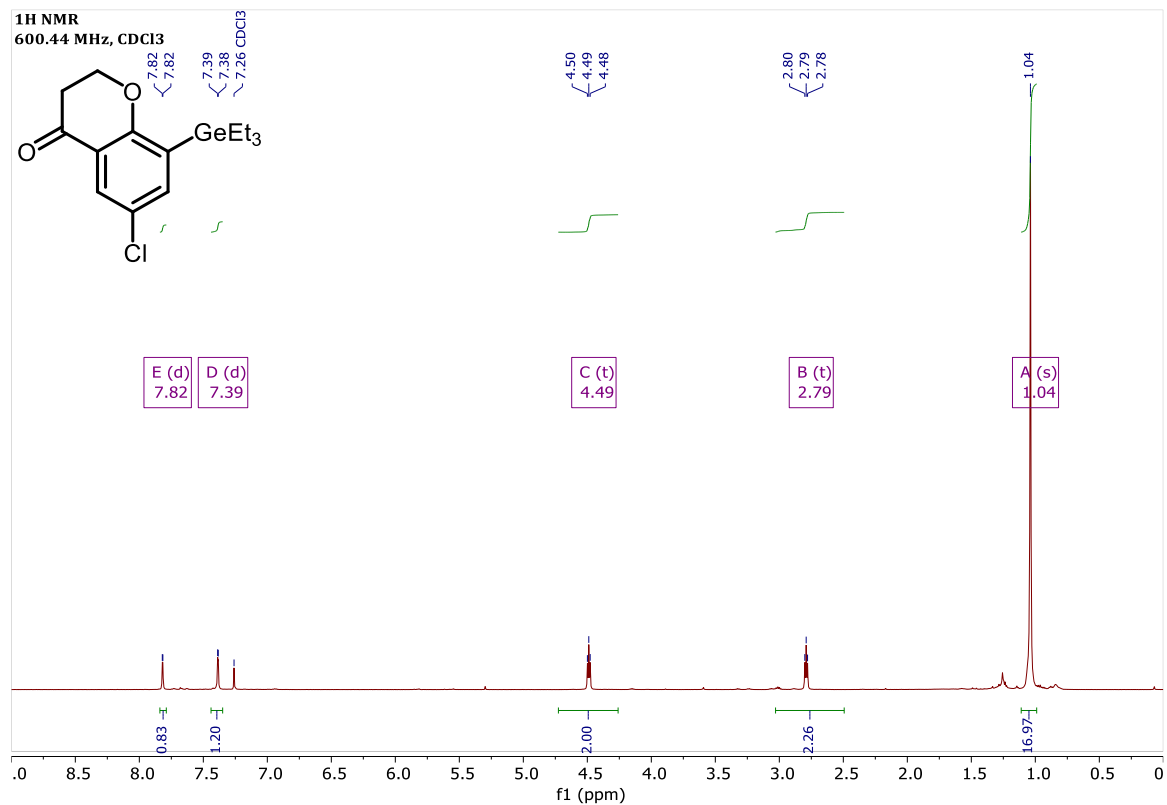


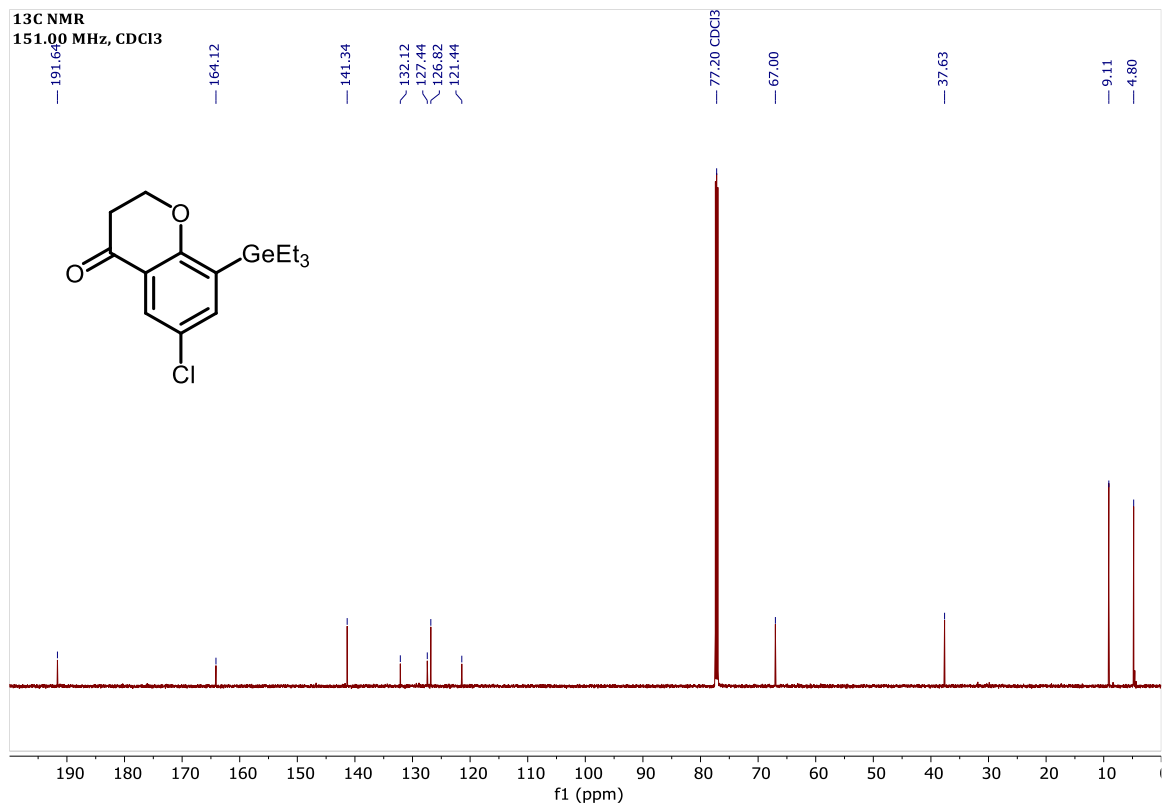
6-Chlorochroman-4-one derived tetrafluorothianthrenium salt (S₁₄)



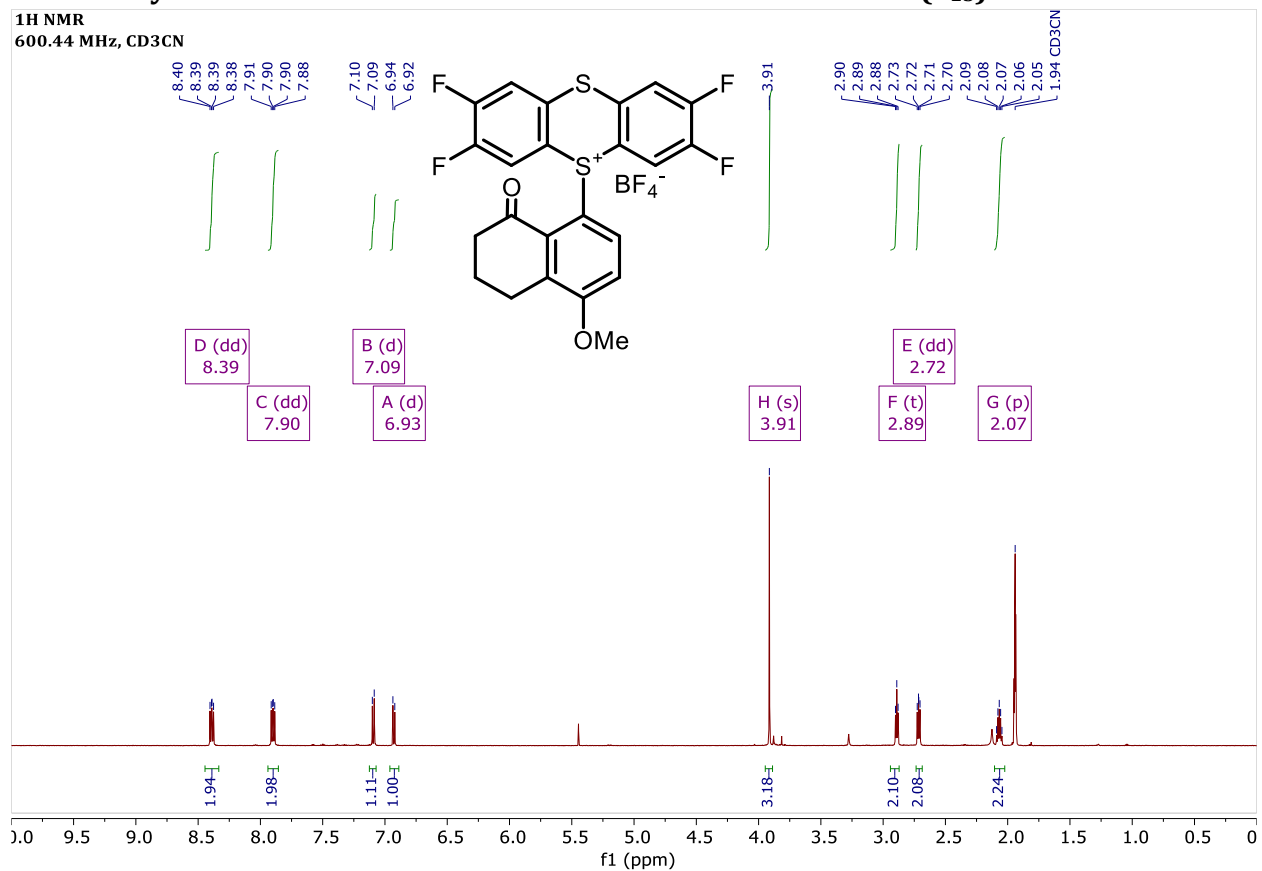


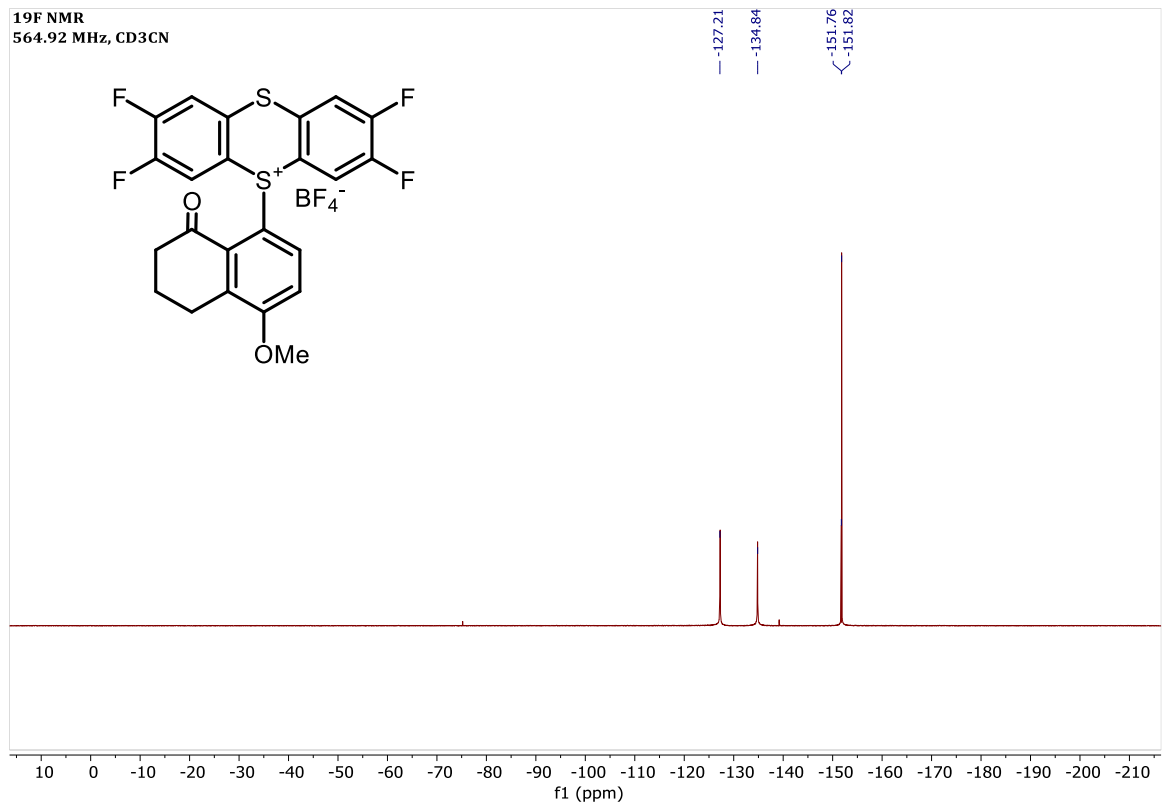
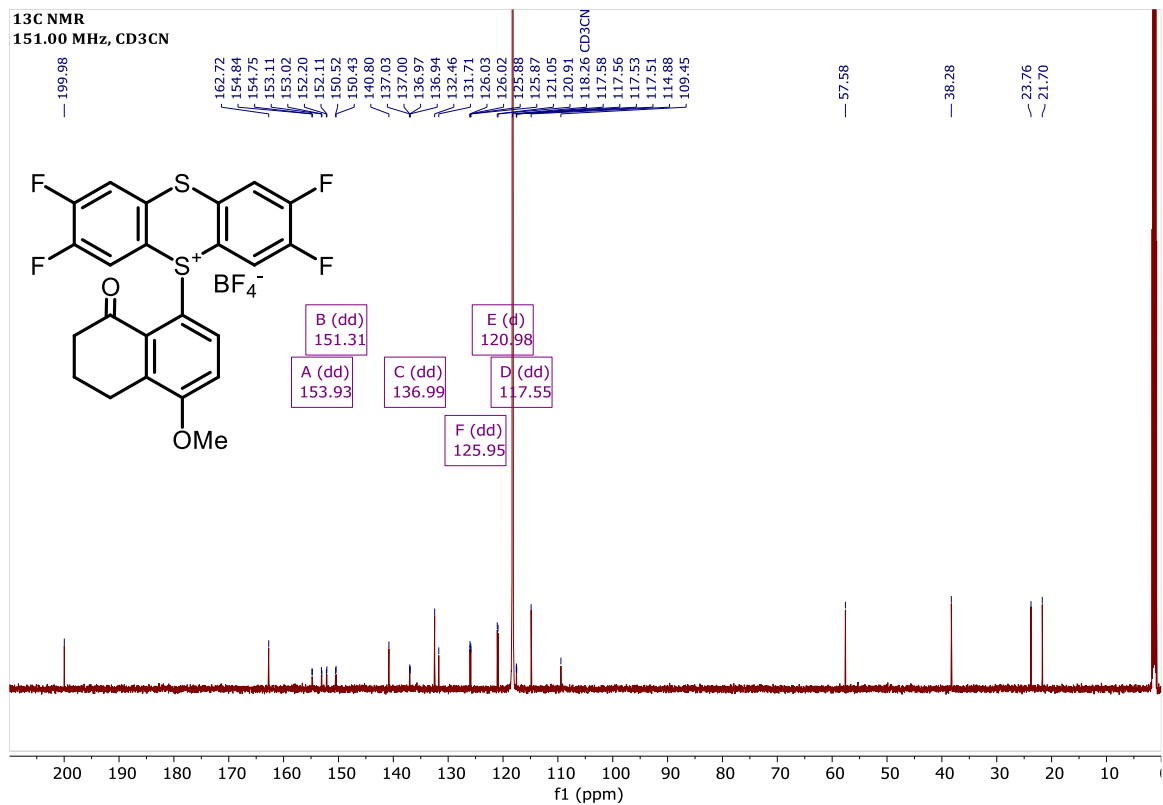
6-Chloro-8-(triethylgermyl)chroman-4-one (14)



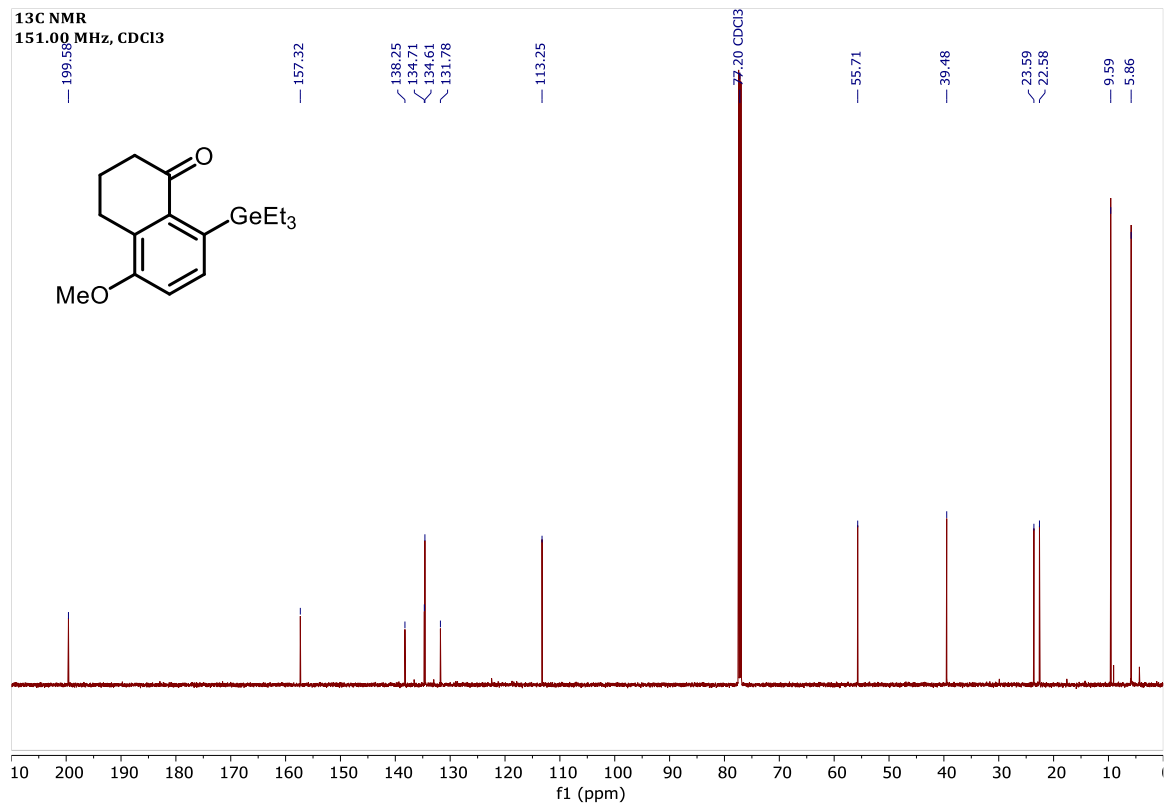
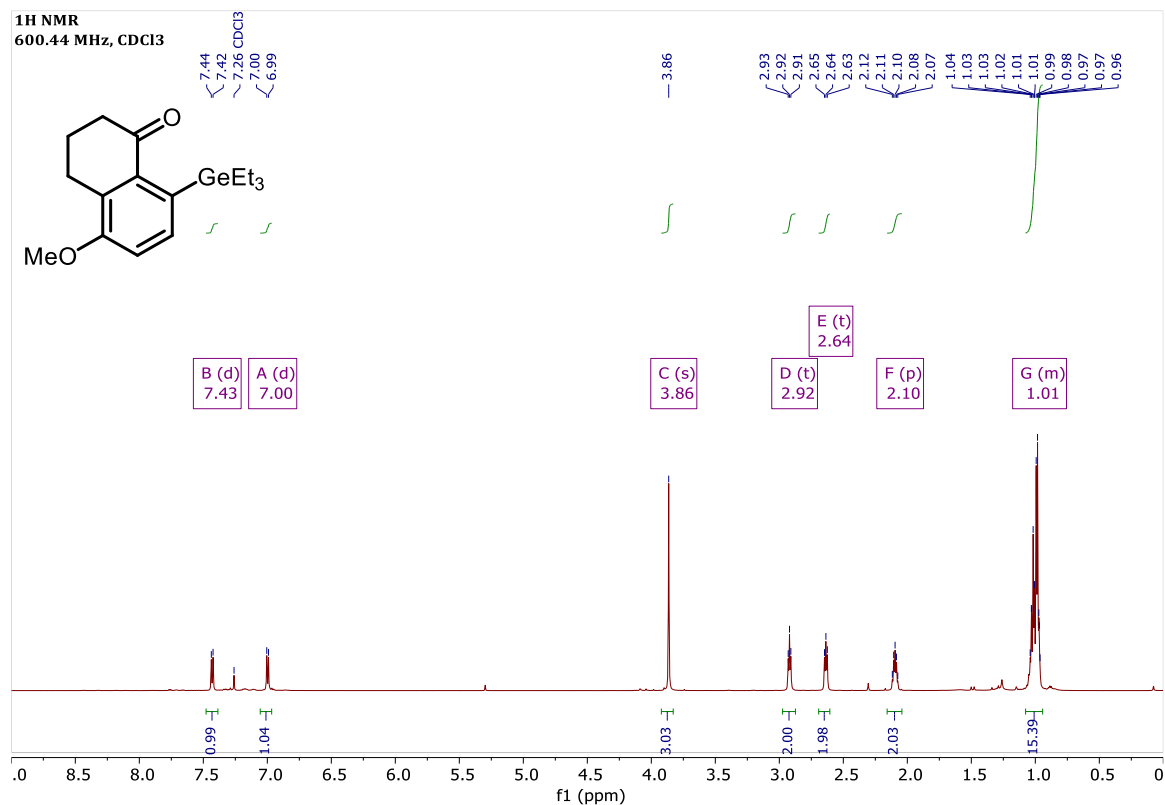


5-Methoxy-1-tetralone derived tetrafluorothianthrenium salt (S₁₅)

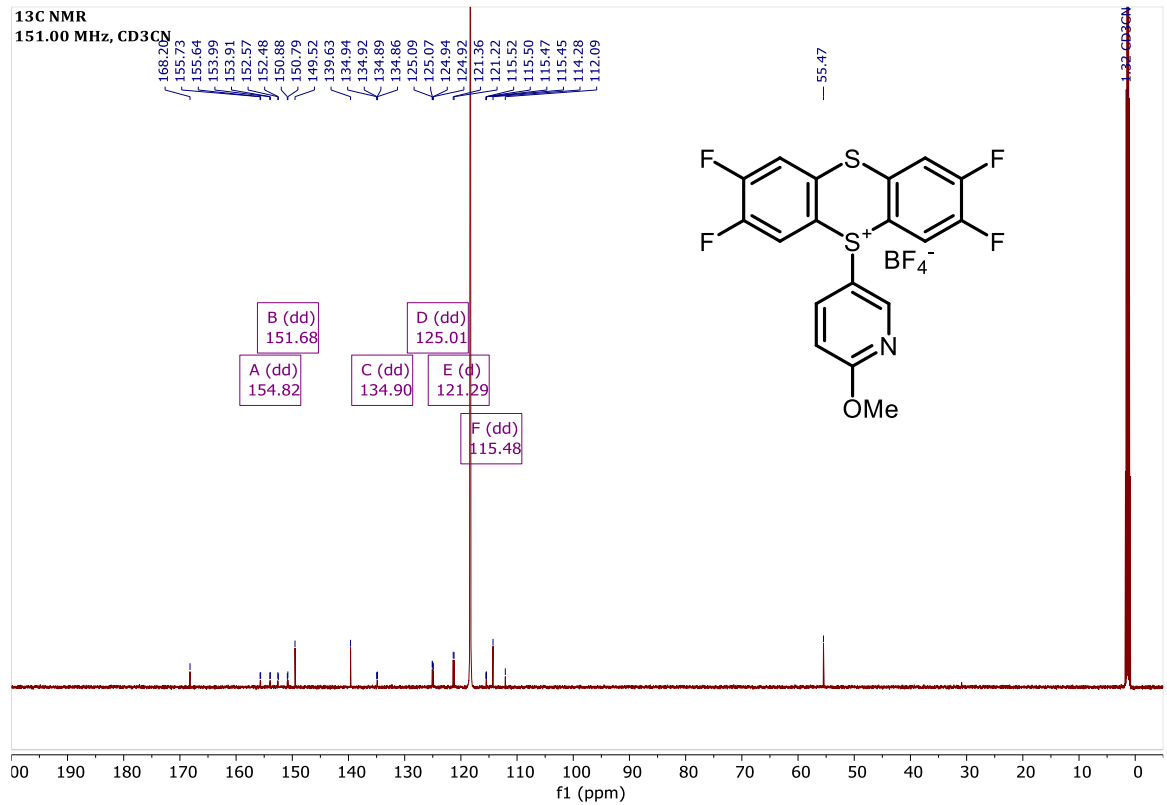
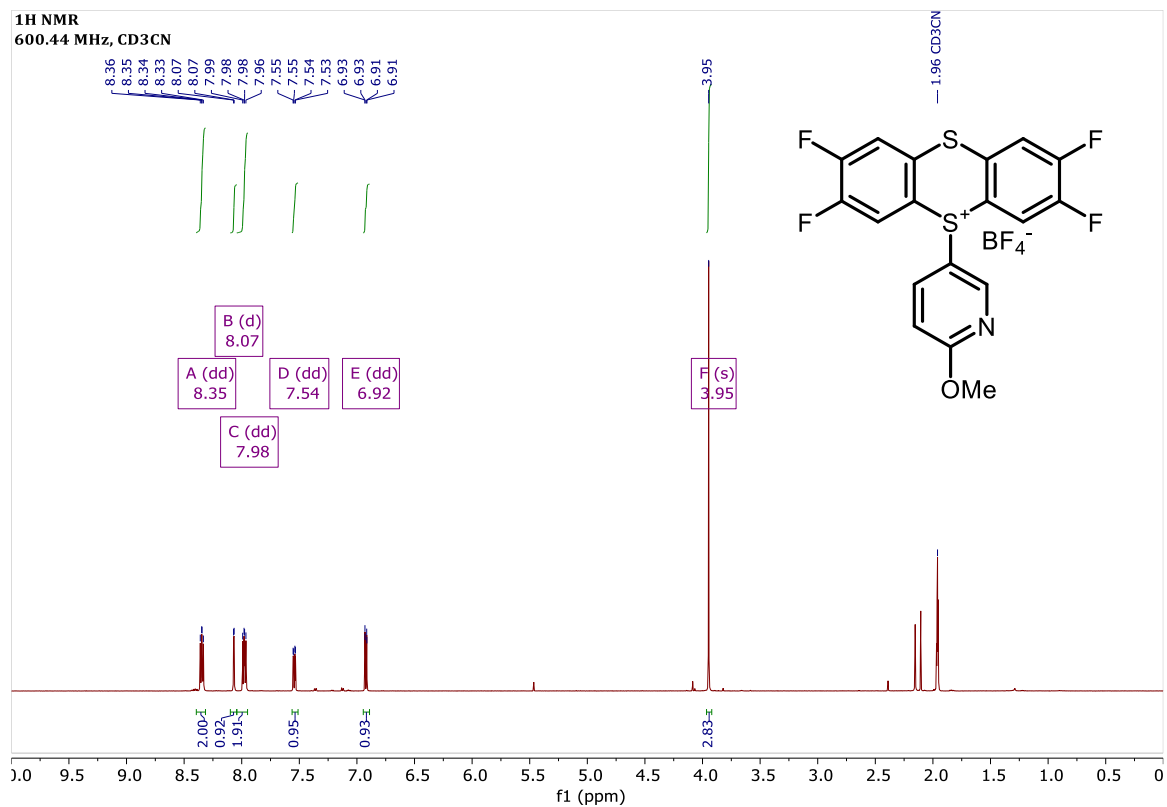




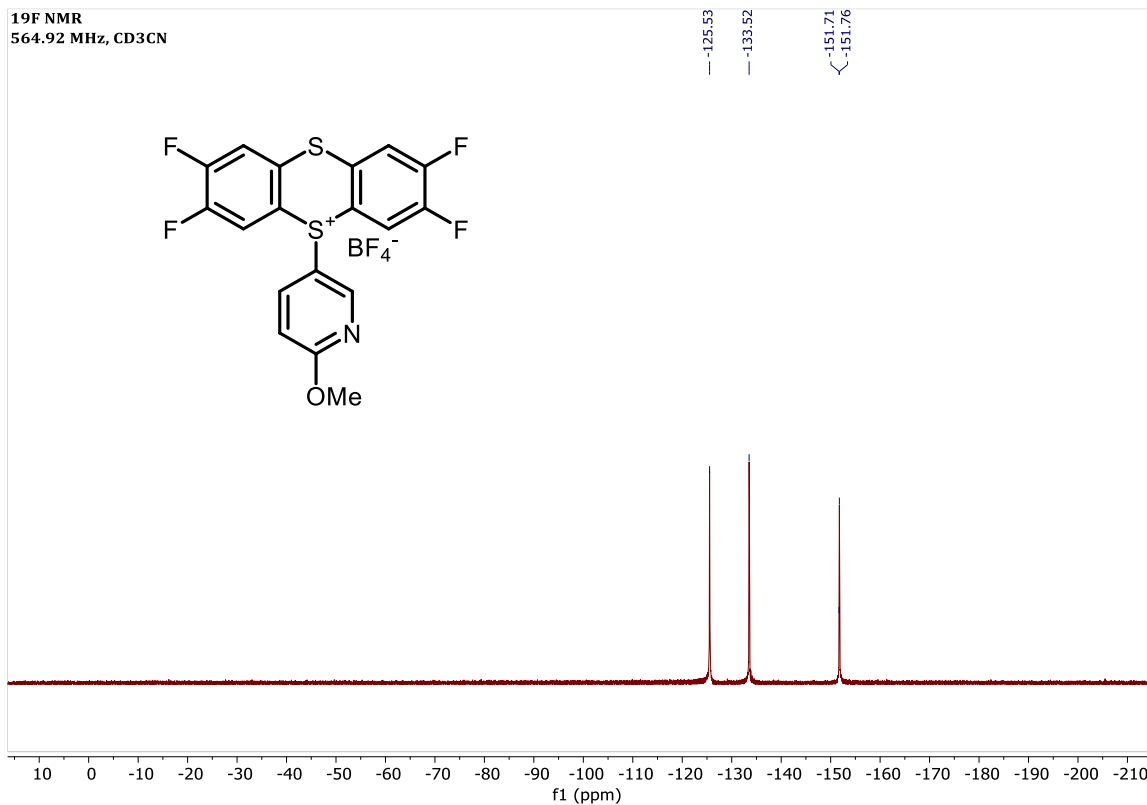
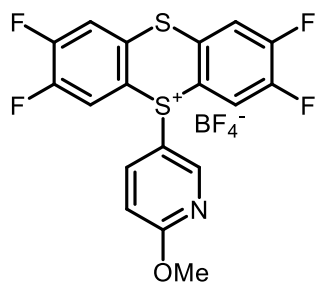
5-Methoxy-8-(triethylgermyl)-3,4-dihydronaphthalen-1(2H)-one (15)



2-Methoxypyridine derived tetrafluorothianthrenium salt (S₁₆)

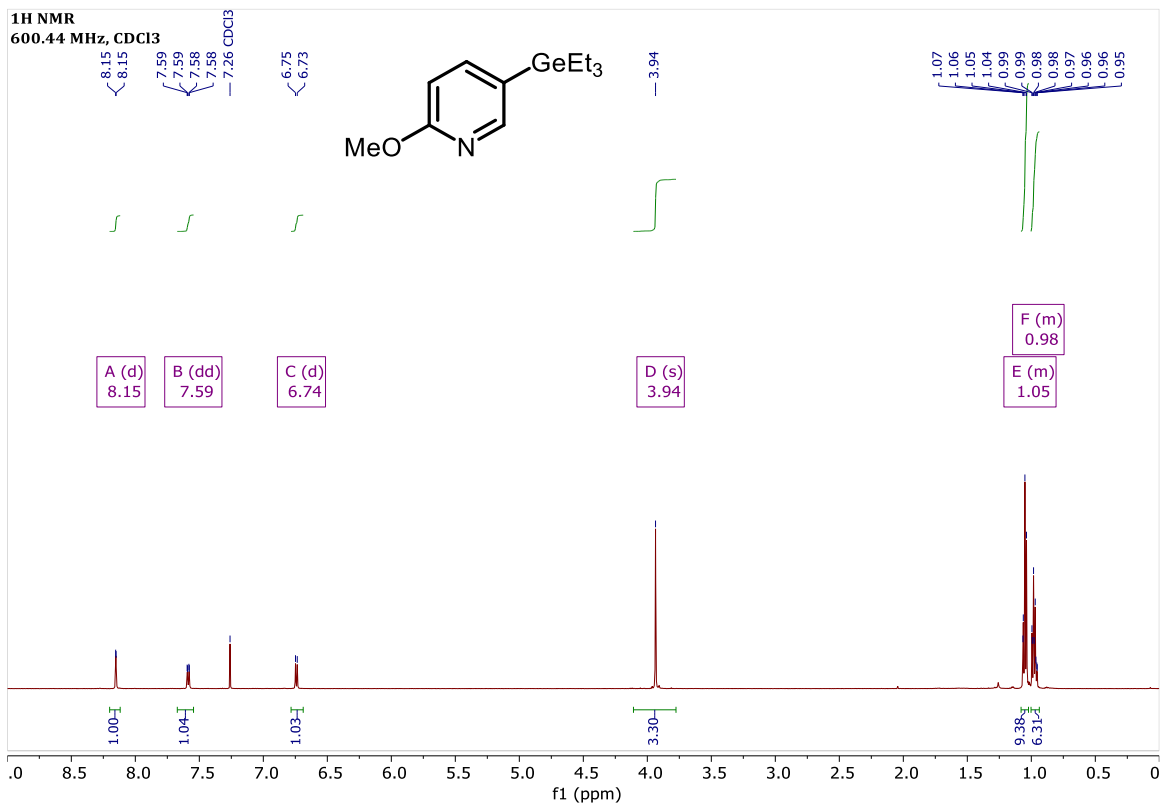
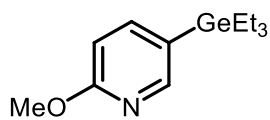


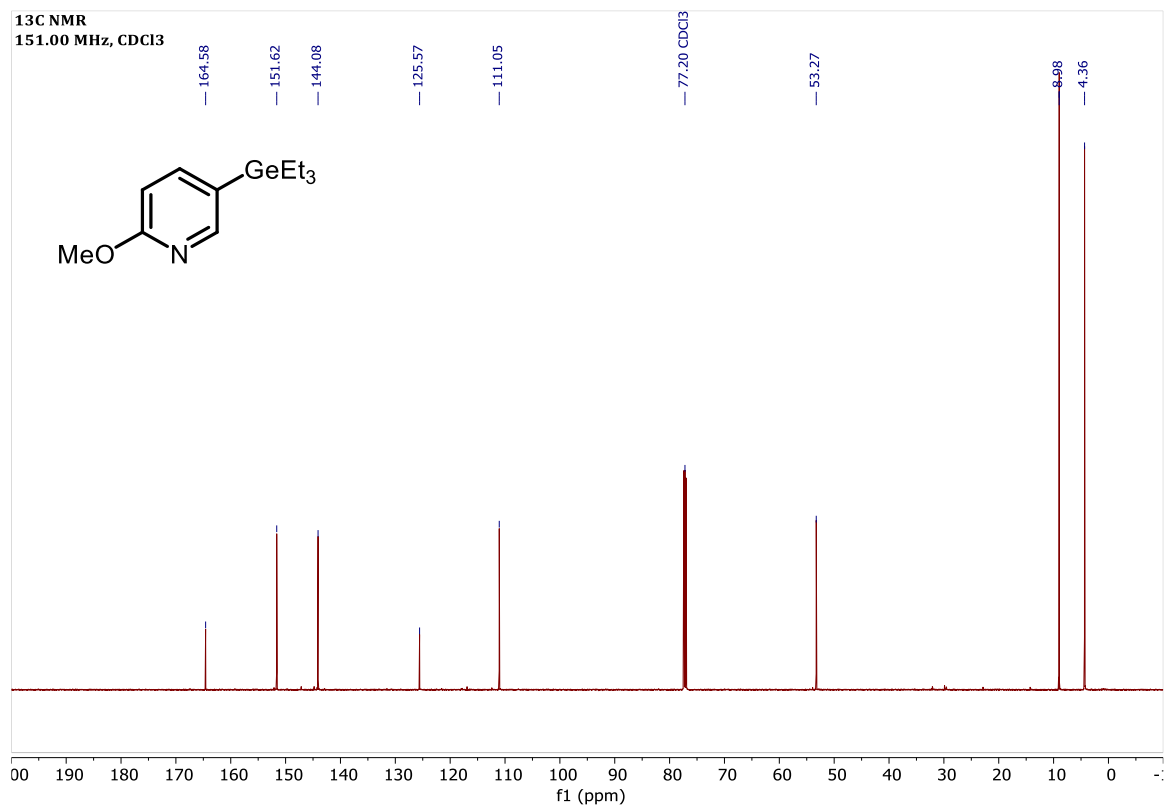
¹⁹F NMR
564.92 MHz, CD₃CN



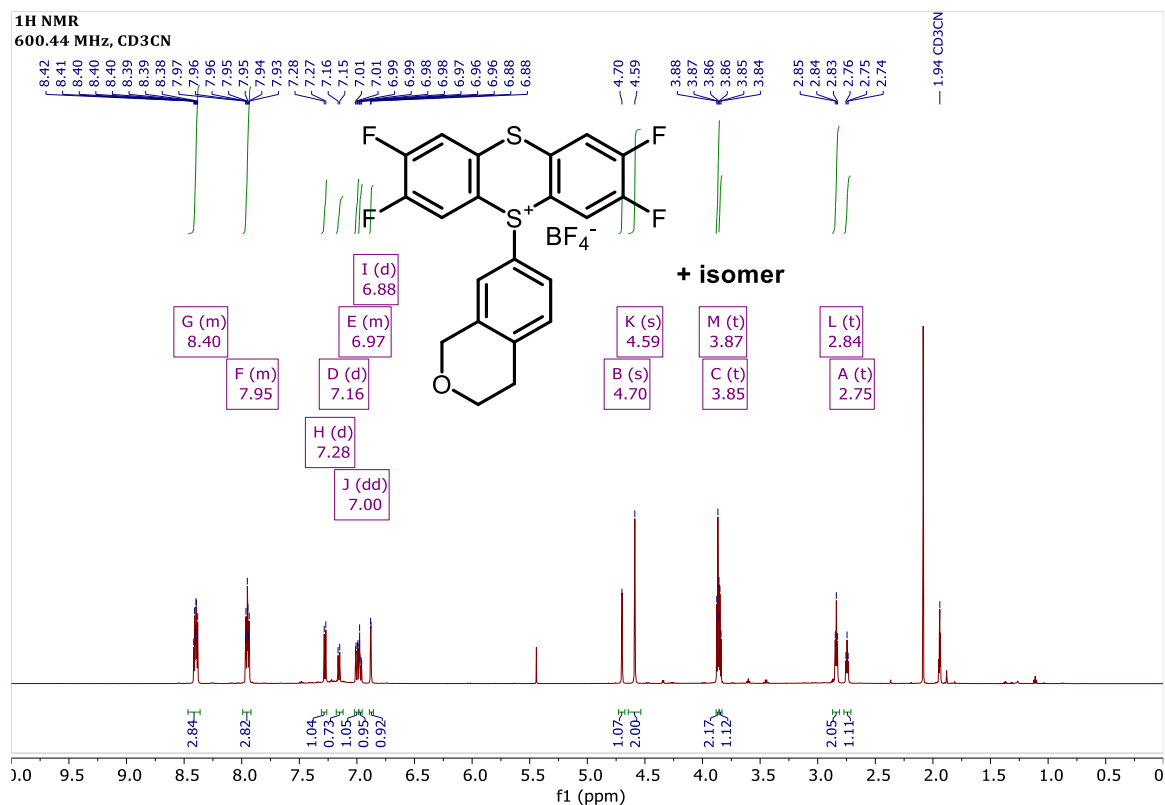
2-Methoxy-5-(triethylgermyl)pyridine (16)

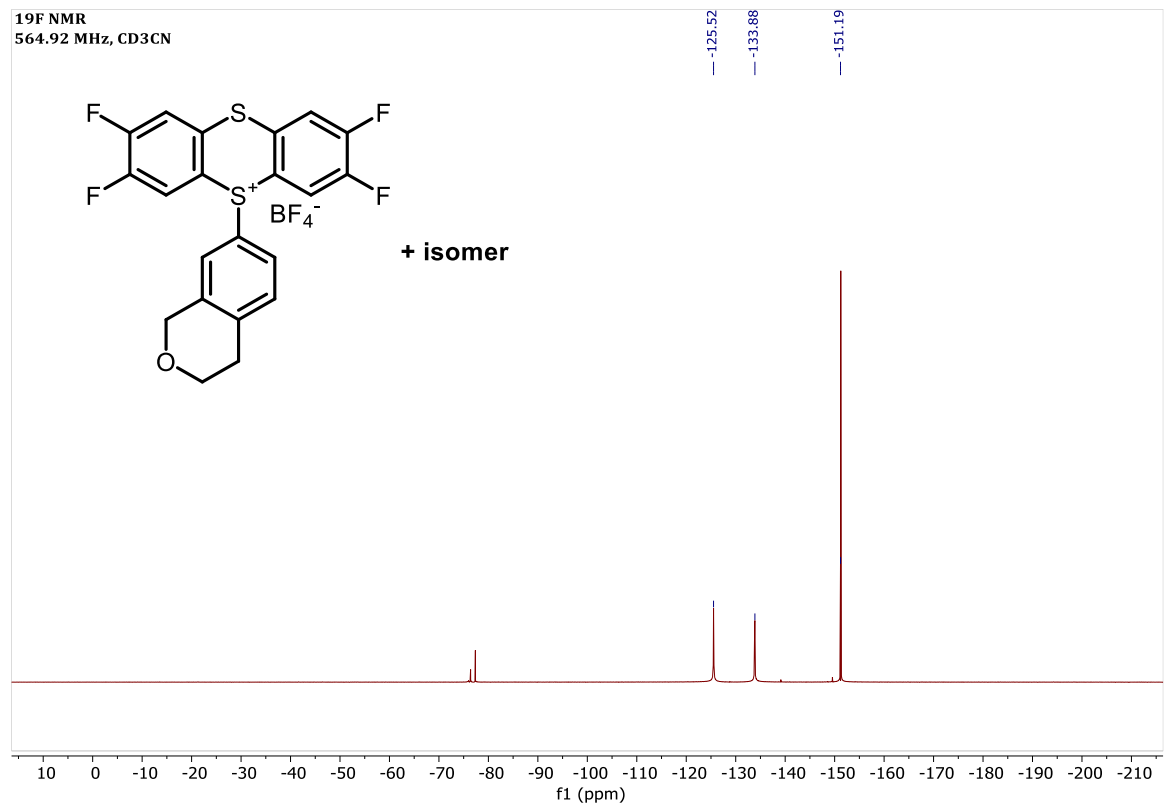
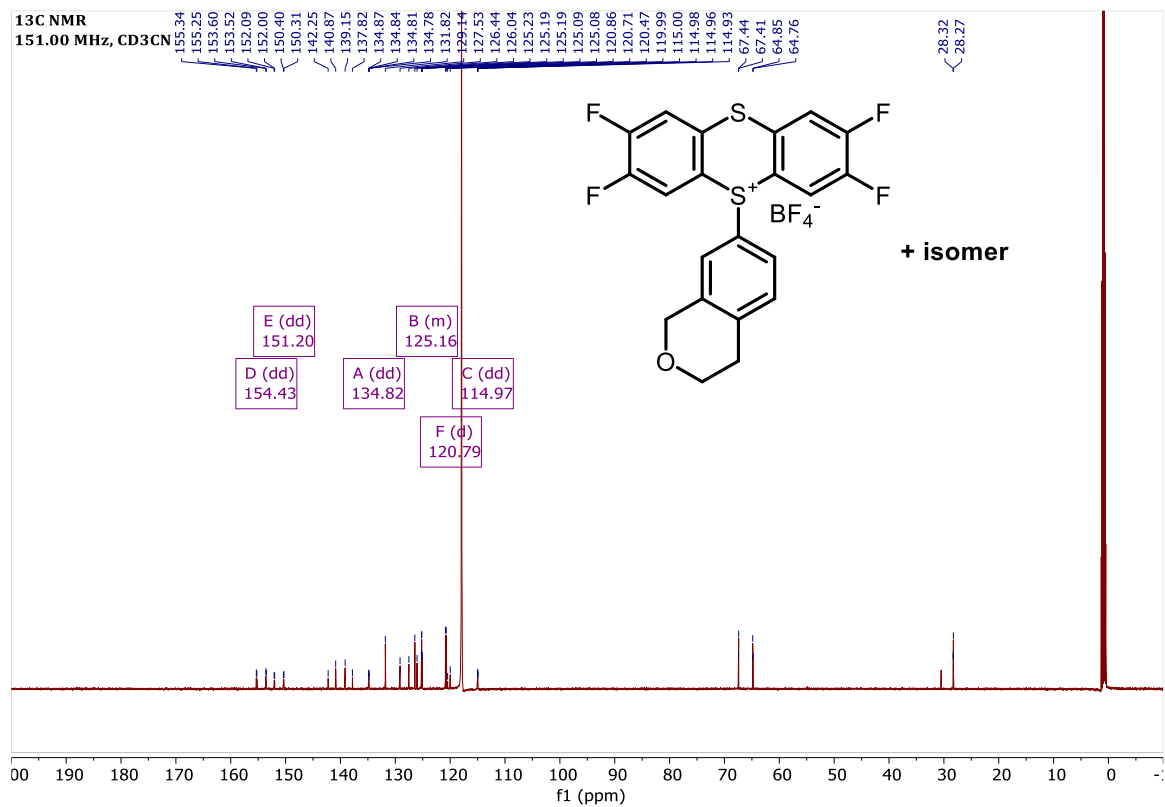
¹H NMR
600.44 MHz, CDCl₃



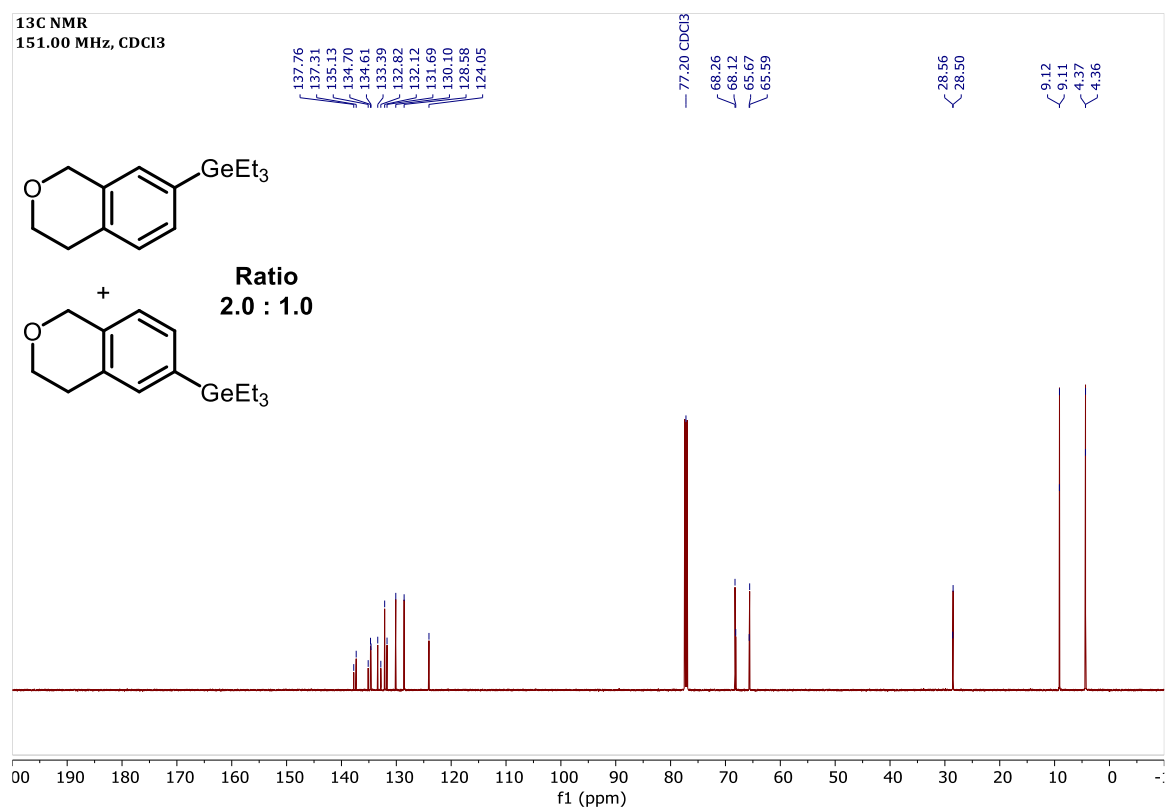
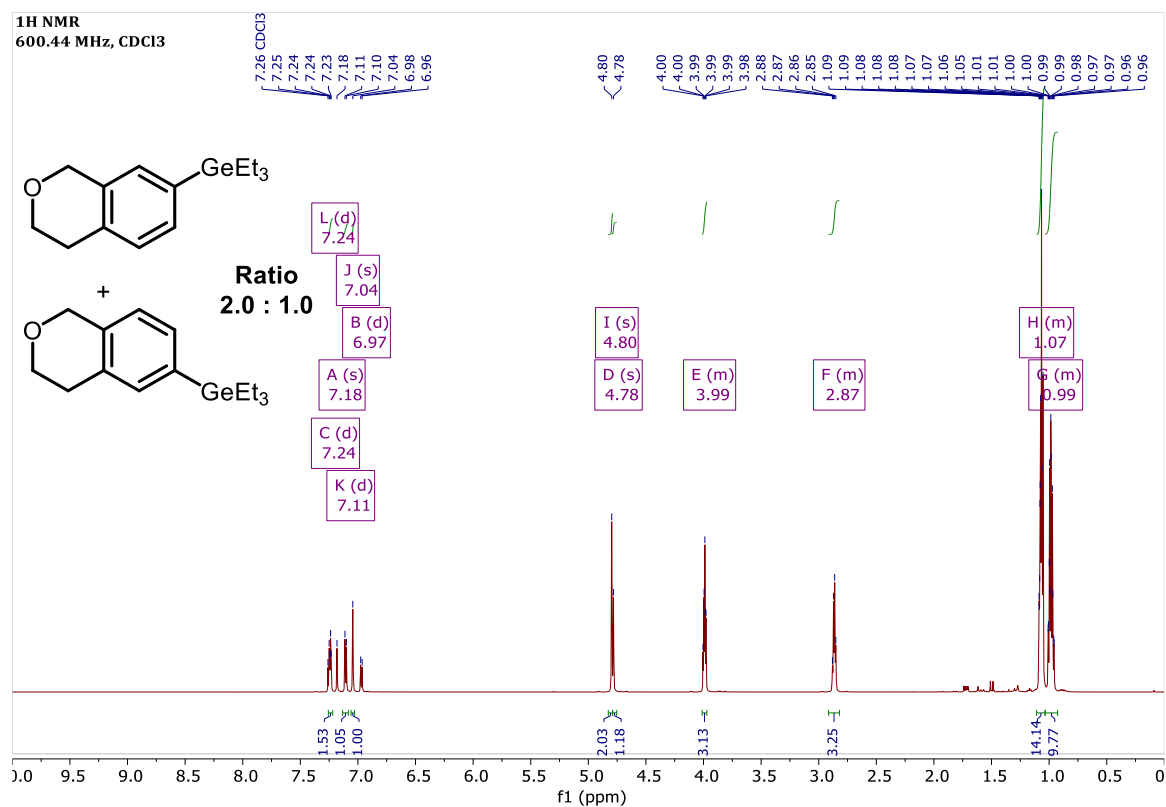


Isochromane derived tetrafluorothianthrenium salt (S₁₇)

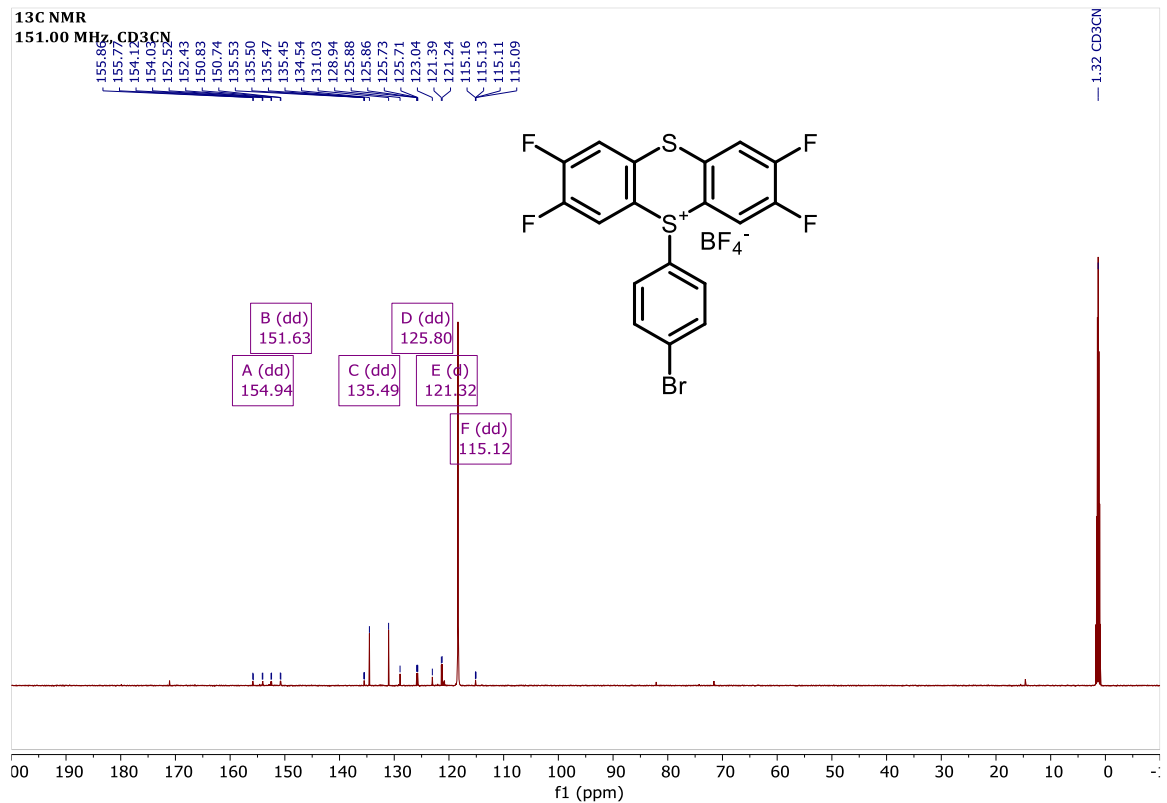
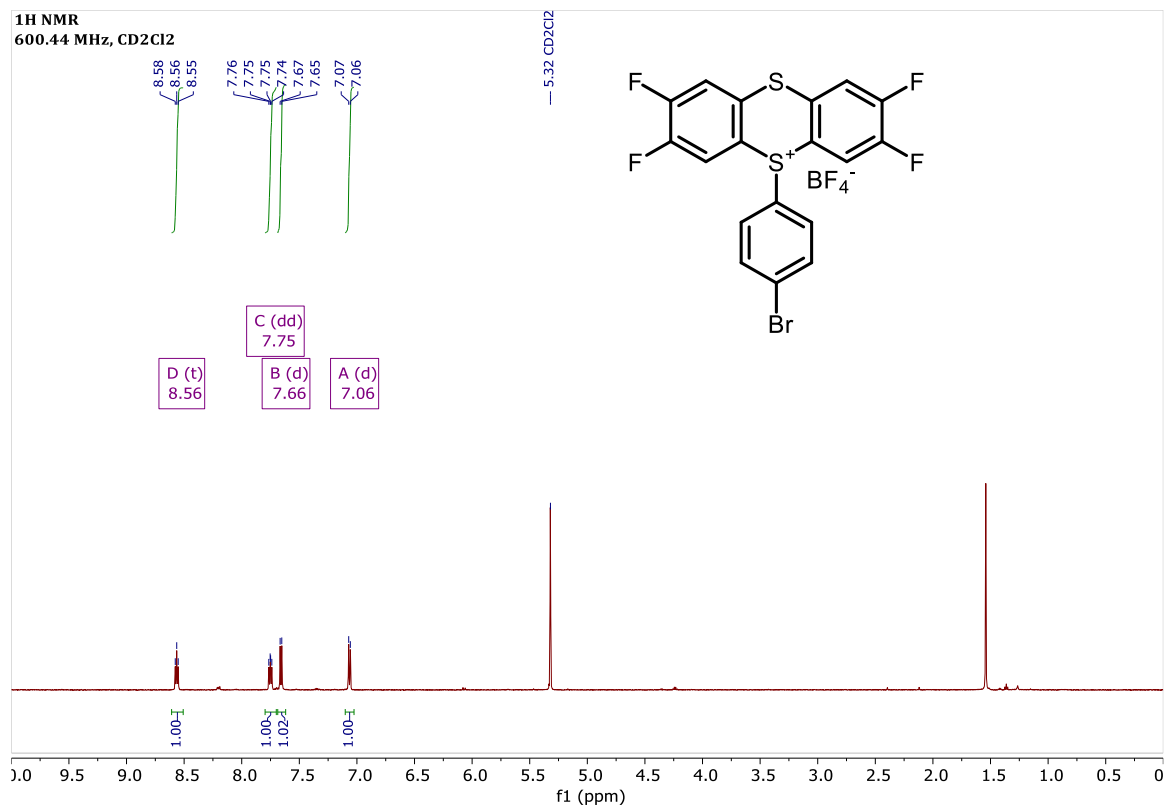


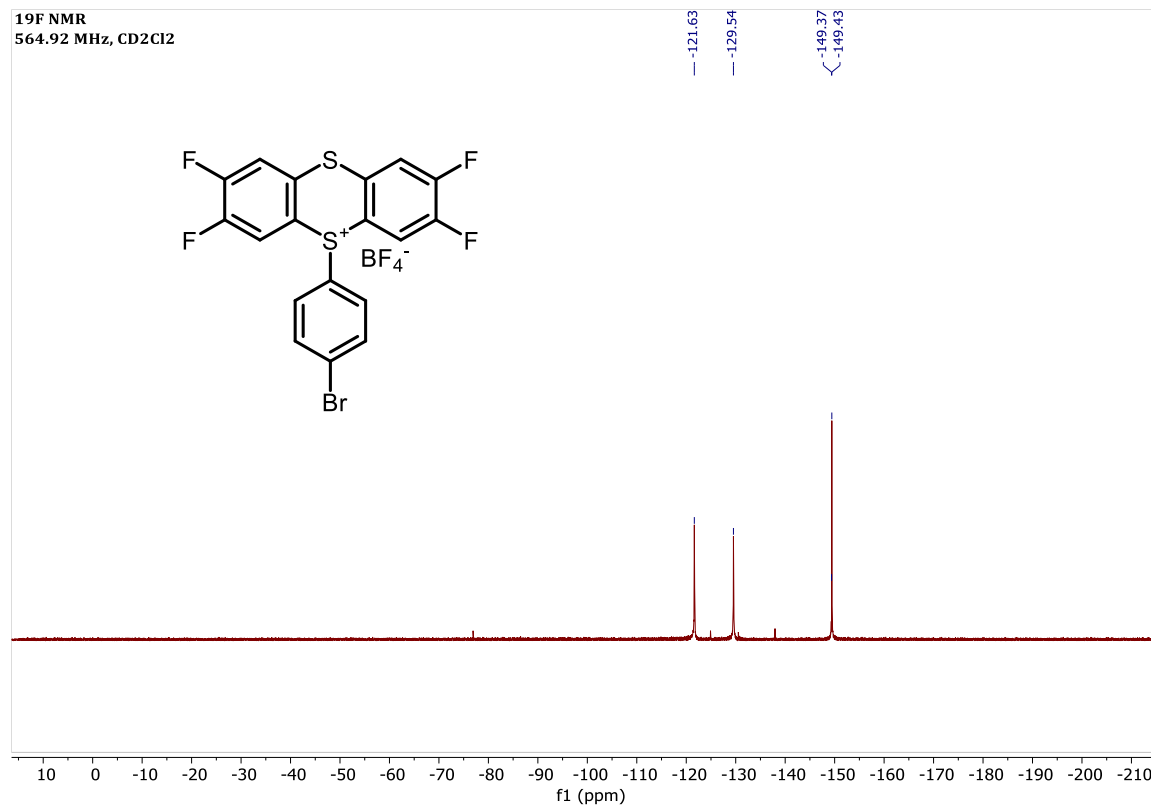


Triethyl(isochroman-6-yl)germane (17)

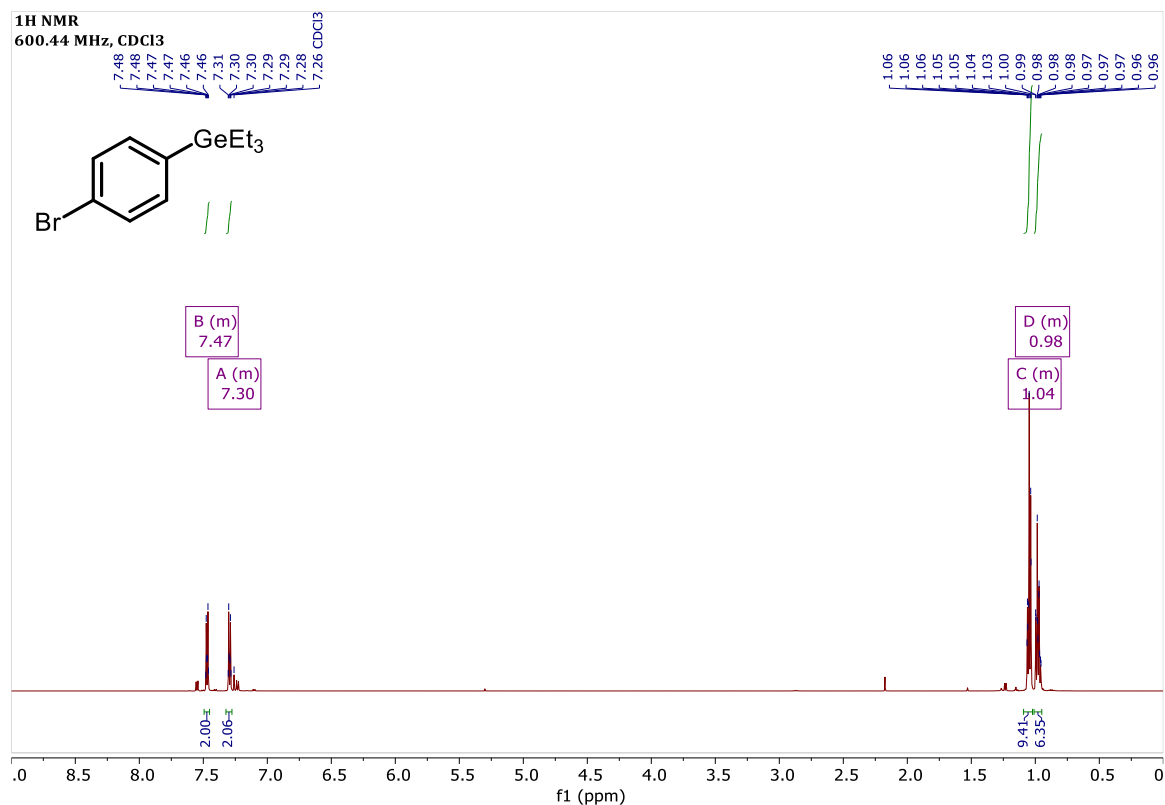


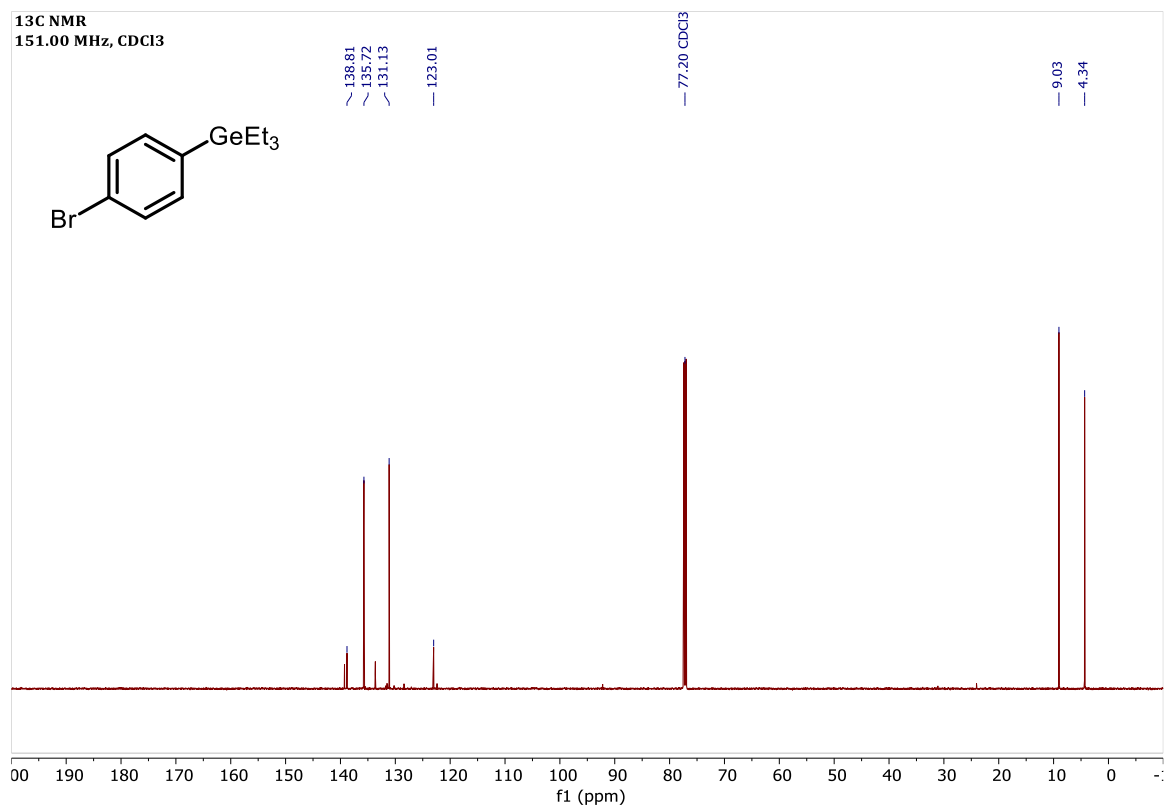
Bromobenzene derived tetrafluorothianthrenium salt (S₁₈)



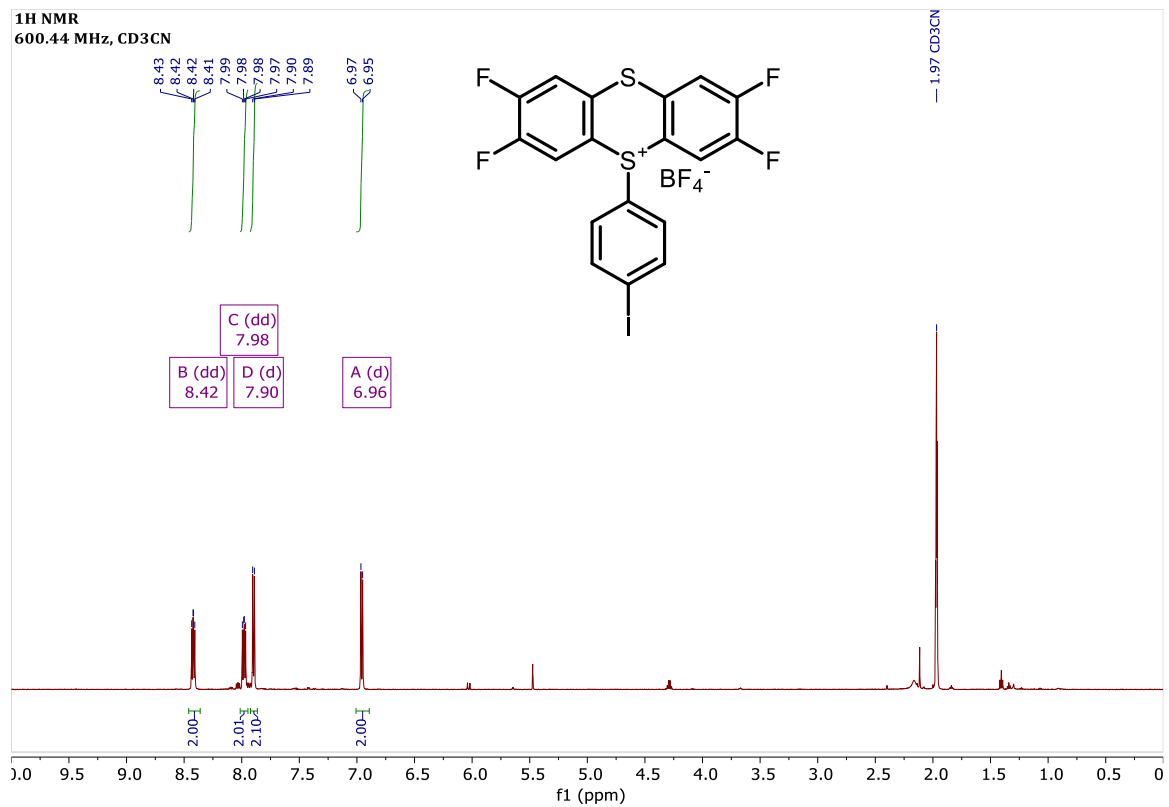


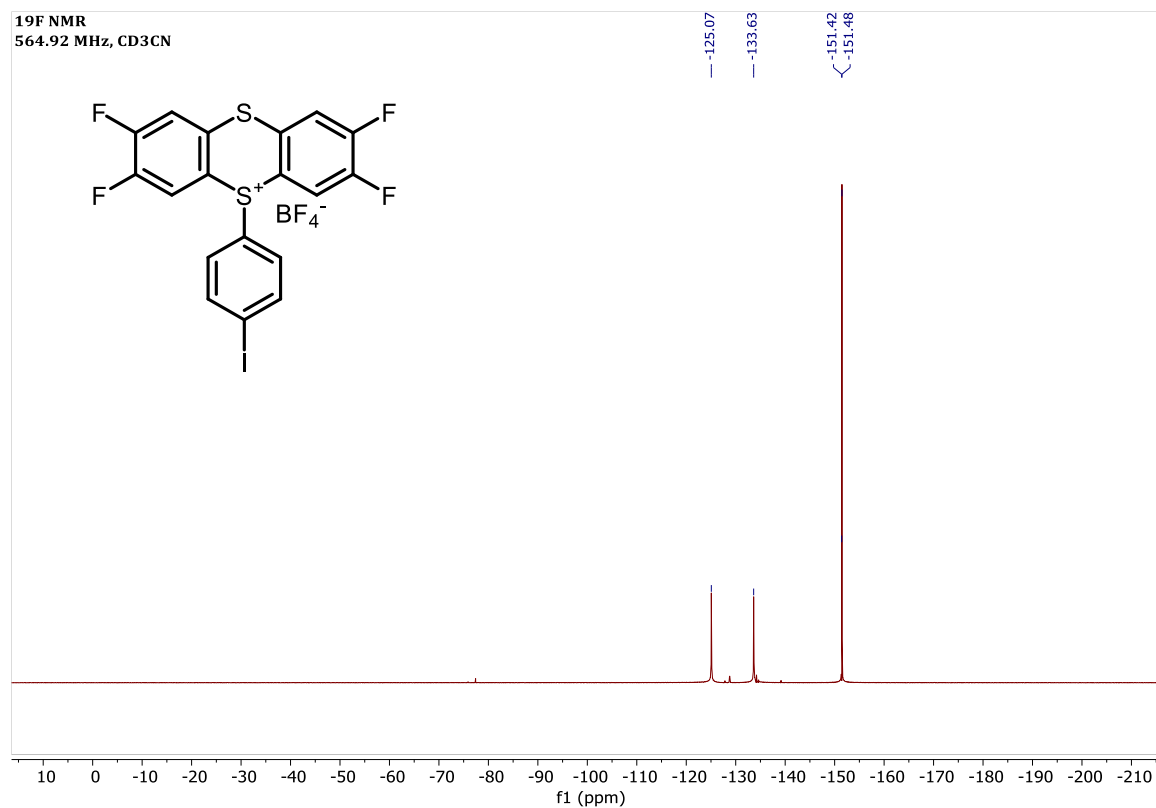
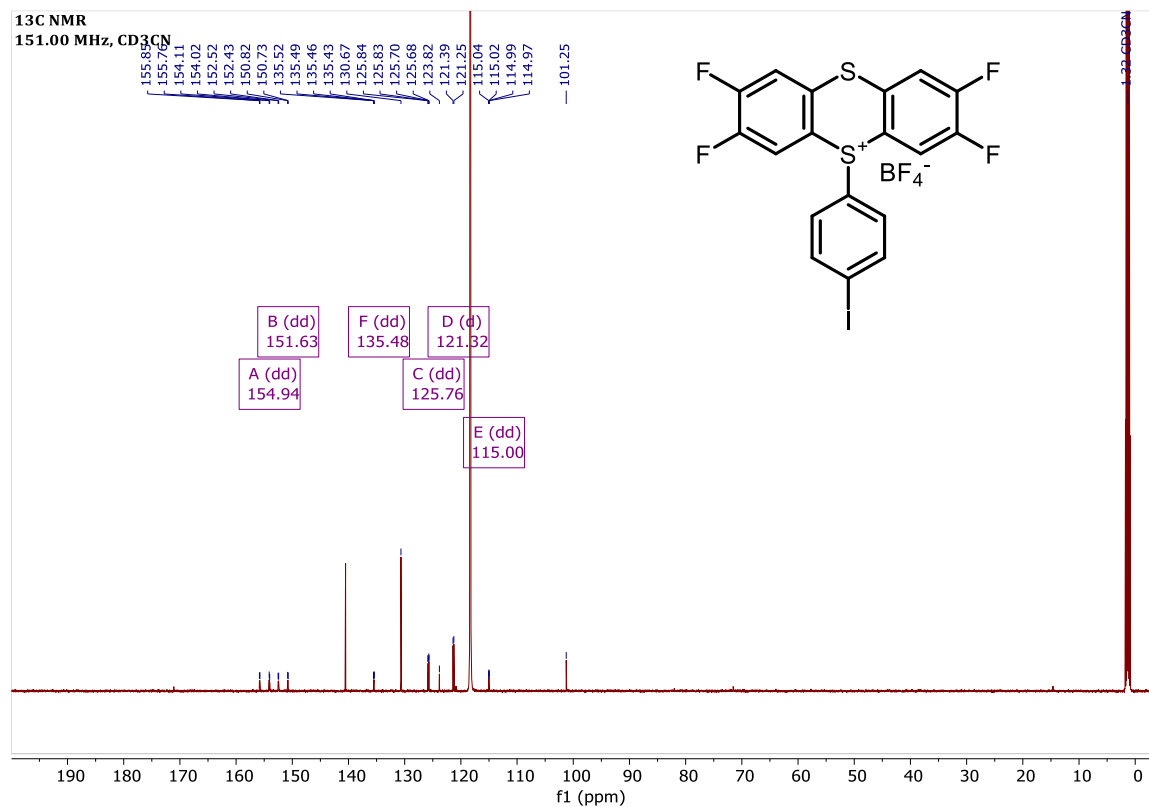
(4-Bromophenyl)triethylgermane (18)





Iodobenzene derived tetrafluorothianthrenium salt (S₁₉)





¹H NMR
600.44 MHz, CDCl₃

Chemical structure: CC[Ge](CC)(CC)c1ccc(I)cc1

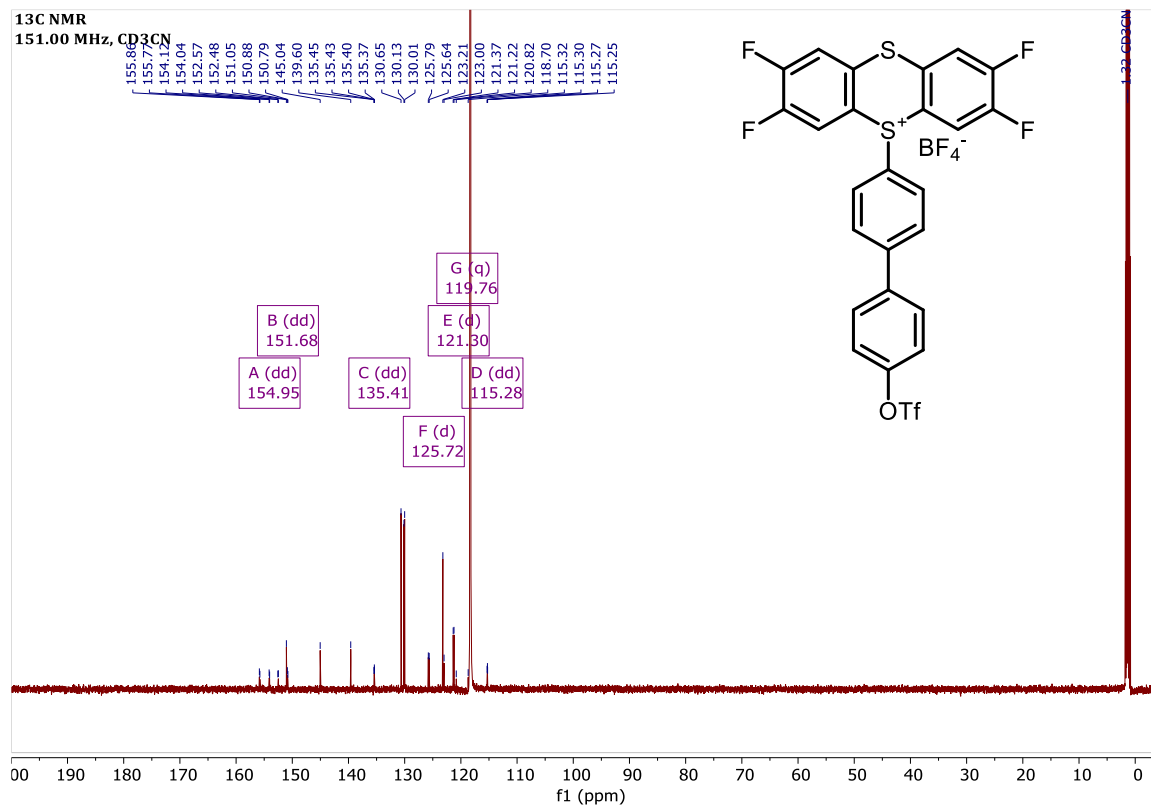
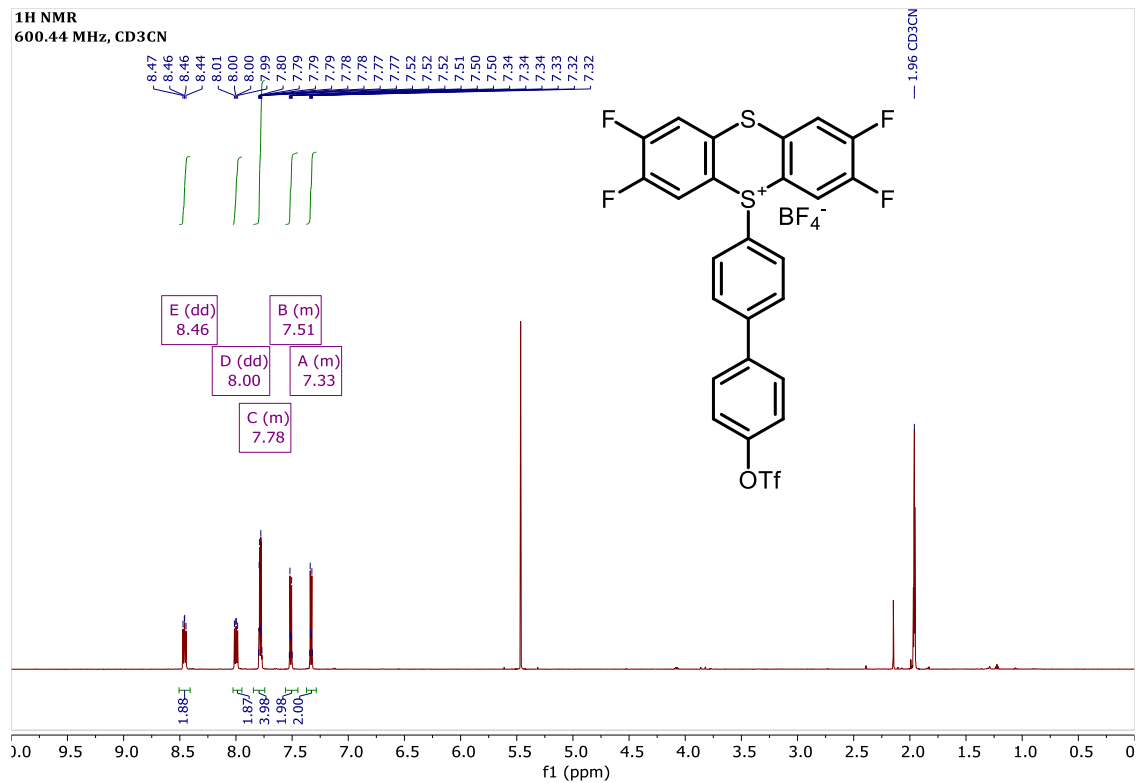
Peak list (ppm): 7.68, 7.68, 7.67, 7.66, 7.26, 7.17, 7.17, 7.16, 7.16, 7.15, 1.07, 1.07, 1.06, 1.06, 1.05, 1.05, 1.05, 1.04, 1.03, 1.03, 0.99, 0.99, 0.98, 0.98, 0.97, 0.97, 0.96, 0.95, 0.95.

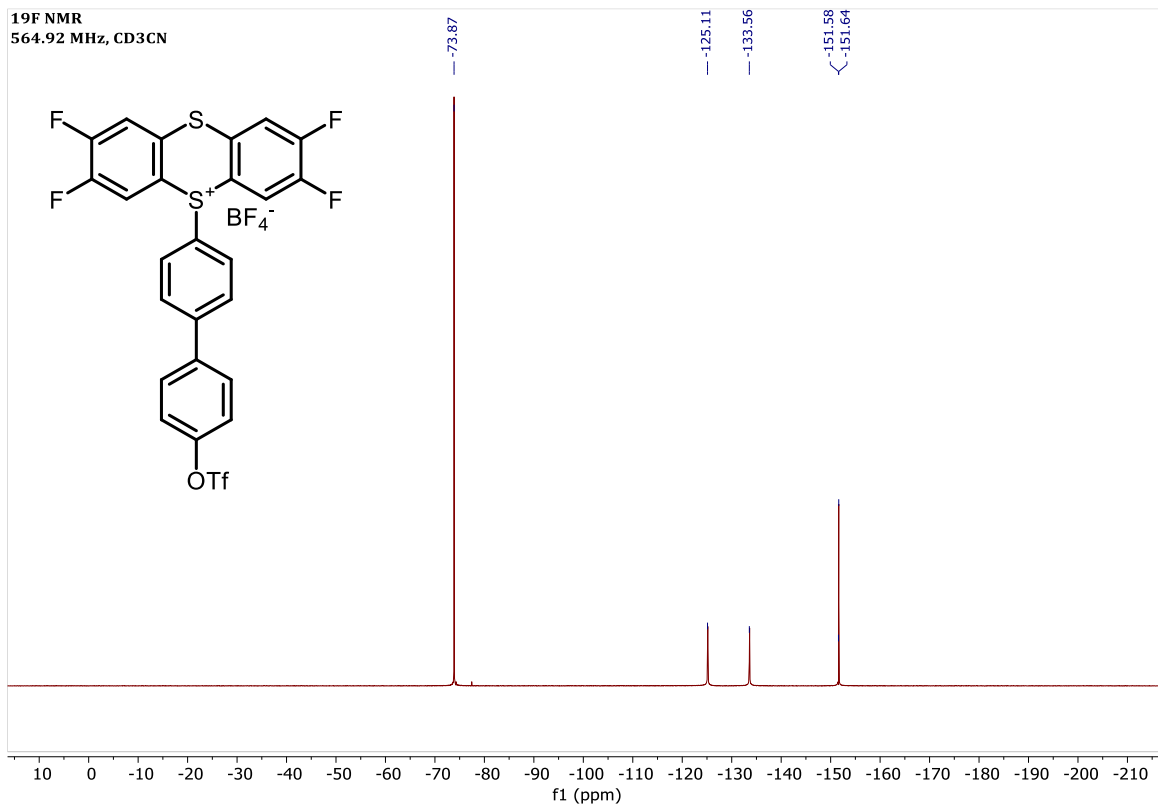
Integration values: 2.00, 2.02, 10.20, 7.10.

Integration labels: B (m) 7.67, A (m) 7.16, D (m) 1.05, C (m) 0.98.

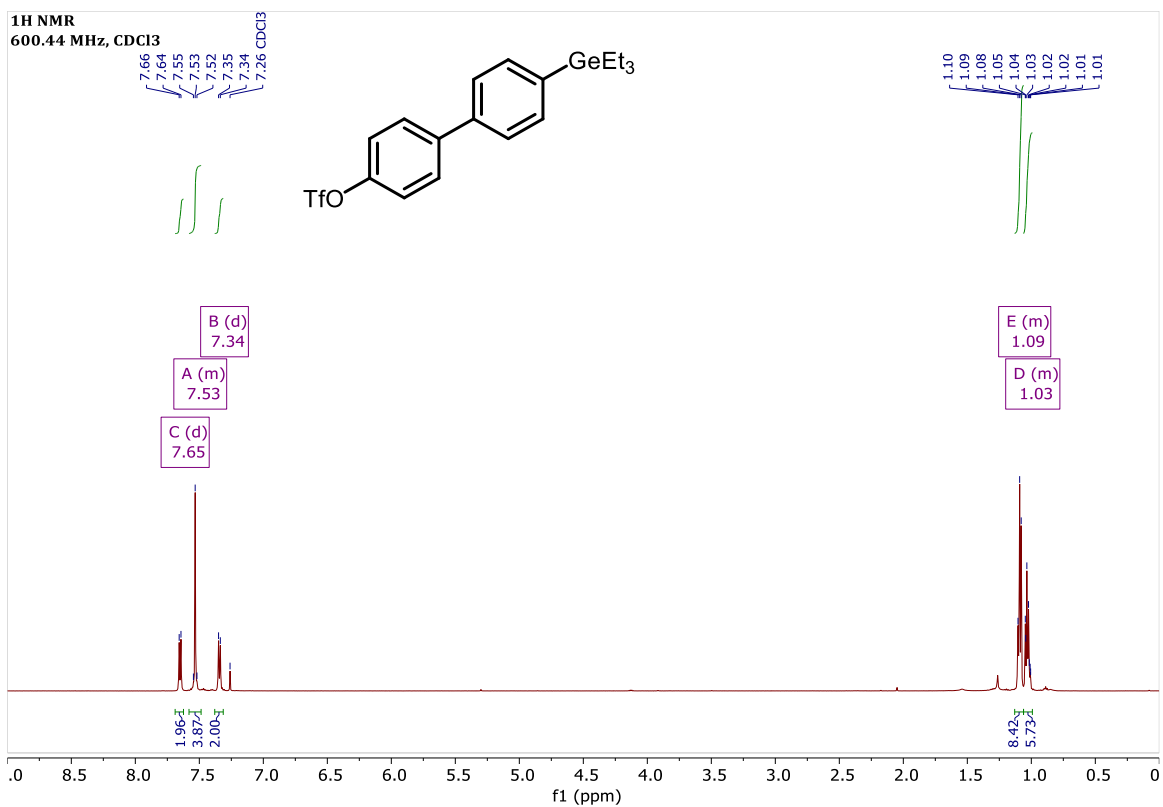


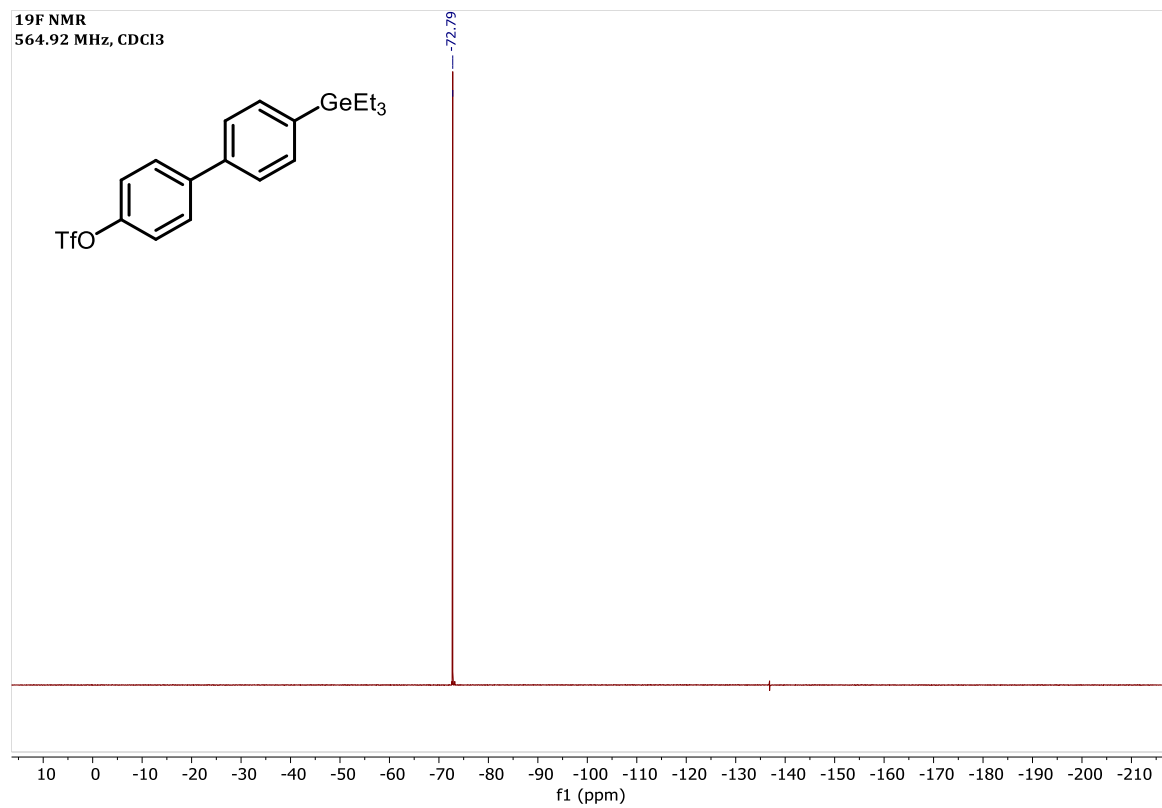
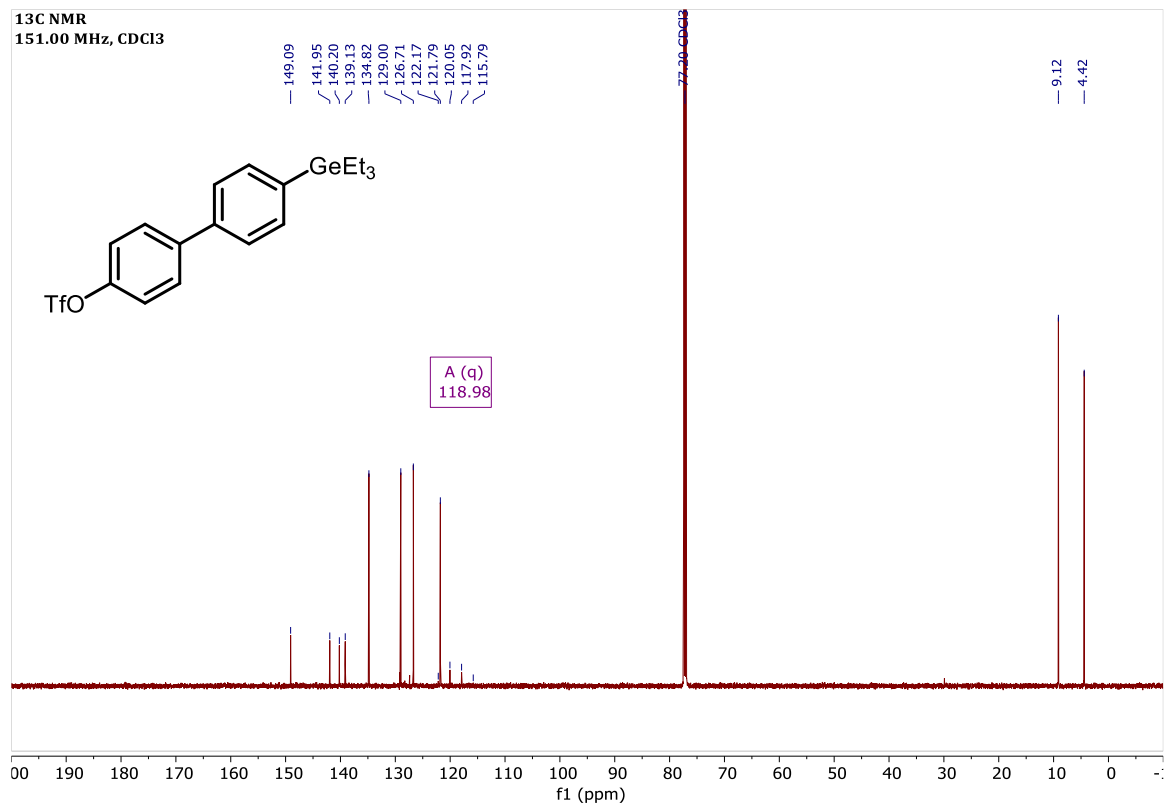
[1,1'-Biphenyl]-4-yl trifluoromethanesulfonate derived tetrafluorothianthrenium salt (S₂₀)





4'-(Triethylgermyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (20)





5. References

- (1) Berger, F.; Plutschack, M. B.; Riegger, J.; Yu, W.; Speicher, S.; Ho, M.; Frank, N.; Ritter, T. Site-Selective and Versatile Aromatic C–H Functionalization by Thianthrenation. *Nature* **2019**, 567 (7747), 223–228.
- (2) Aufiero, M.; Sperger, T.; Tsang, A. S.-K.; Schoenebeck, F. Highly Efficient C–SeCF₃ Coupling of Aryl Iodides Enabled by an Air-Stable Dinuclear Pd^I Catalyst. *Angew. Chem. Int. Ed.* **2015**, 54 (35), 10322–10326.
- (3) Fricke, C.; Dahiya, A.; Reid, W. B.; Schoenebeck, F. Gold-Catalyzed C–H Functionalization with Aryl Germanes. *ACS Catal.* **2019**, 9 (10), 9231–9236.
- (4) Li, J.; Chen, J.; Sang, R.; Ham, W.-S.; Plutschack, M. B.; Berger, F.; Chhabra, S.; Schnegg, A.; Genicot, C.; Ritter, T. Photoredox Catalysis with Aryl Sulfonium Salts Enables Site-Selective Late-Stage Fluorination. *Nat. Chem.* **2020**, 12 (1), 56–62.
- (5) Kobayashi, M.; Kobayashi, M. Photochemical Reactions of Aryltriethylgermanes and Diethyldiphenylgermane. *Bull. Chem. Soc. Jpn.* **1986**, 59 (9), 2807–2810.
- (6) Sang, R.; Korkis, S. E.; Su, W.; Ye, F.; Engl, P. S.; Berger, F.; Ritter, T. Site-Selective C–H Oxygenation via Aryl Sulfonium Salts. *Angew. Chem. Int. Ed.* **2019**, 58 (45), 16161–16166.
- (7) Fricke, C.; Sherborne, G. J.; Funes-Ardoiz, I.; Senol, E.; Guven, S.; Schoenebeck, F. Orthogonal Nanoparticle Catalysis with Organogermanes. *Angew. Chem. Int. Ed.* **2019**, 58 (49), 17788–17795.