Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Lewis Adduct Formation of Hydrogen Cyanide and Nitriles with Arsenic and Antimony Pentafluoride

Thomas Saal, Karl O. Christe and Ralf Haiges*

*E-mail: haiges@usc.edu

Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California Los Angeles, CA 90089-1661 (USA)

Experimental Details

General

Materials and Apparatus

All reactions were carried out in either Teflon-FEP ampules or NMR tubes that were closed by stainless steel valves. Volatile materials were handled in grease-less Pyrex glass or in stainless steel/Teflon-FEP vacuum line.[1] Reaction vessels and the stainless steel vacuum line were passivated with ClF_3 prior to use. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. Sulfur dioxide (Matheson Tri-Gas) was dried by storage over CaH_2. AsF_5 was prepared from AsF_3 and F_2.[2-4] SbF_5 (Ozark Mahoning) was triple distilled before use. HCN was prepared by reacting stearic acid with KCN at 120 °C. Malononitrile (Sigma-Aldrich) was purified by recrystallization from hot ethanol. Butyronitrile, cyclopropanecarbonitrile, trimethylacetonitrile and benzonitrile (all Sigma-Aldrich) were used as received. The NMR spectra were recorded 298 K unless otherwise stated on Bruker AMX-500 or Varian Mercury 400 or VNMRS-500 spectrometers. Spectra were externally referenced to neat tetramethylsilane for ^{1}H and ^{13}C NMR spectra, to neat nitromethane for ^{14}N NMR spectra and to 80% $CFCl_3$ in chloroform-d for ^{19}F NMR spectra. Raman spectra were recorded directly in the Teflon reactors in the range 4000–80 cm^{-1} on a Vertex 70/RAM II spectrophotometer, using a Nd-YAG laser at 1064 nm.

Crystal Structure Determination

The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube or Cu Kα radiation (multi-layeroptics monochromator) from a IμS microsource. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The frames were integrated using the SAINT algorithm to give the hkl files corrected for Lp/decay.[5] The absorption correction was performed using the SADABS program.[6] The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[7-11] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the Mercury CSD program.[12] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. 1855712-1855722.

Preparation of $RCN{\bullet}AsF_5$ (R = H, CH_2CN, C_3H_7, c-C_3H_5, $C(CH_3)_3$, C_6H_5)

Anhydrous SO_2 (2.0 mL) and AsF_5 (1.65 mmol, 1.1 eq.) were condensed into a Teflon-FEP ampule containing a frozen sample of hydrogen cyanide or the corresponding nitrile (1.5 mmol, 1.0 eq.) at -196 ˚C. The mixture was allowed to warm to -64 ˚C, kept at this temperature for 10 min and sporadically agitated. The volatile compounds were removed *in vacuo* at -64 ˚C, leaving behind a colorless solid. Single crystals were grown from SO_2 solution by slow evaporation of the solvent *in vacuo* at -64 to -45 °C.

$HCN{\bullet}AsF_5$ (293 mg; weight expected for 1.50 mmol: 295 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 7.13 (s, 1H, ***H***$CN{\bullet}AsF_5$). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 100.39 (s, H***C***$N{\bullet}AsF_5$)
^{14}N NMR (SO_2, unlocked, 25˚C) δ = -186.7 (s, Δ½= 86 Hz, HC***N***$\bullet AsF_5$).^{19}F NMR (SO_2, unlocked, 25˚C) δ = -39.5 (s, Δ½= 4150 Hz, $HCN{\bullet}As\boldsymbol{F_5}$). Raman (-90 °C, 350 mW): $\tilde{\nu}$(rel. Intensity) = 3199.7 (0.3), 2191.6 (10.0), 2162.7 (0.2), 1145.8 (0.3), 806.4 (0.3), 707.8 (7.8), 674.0 (2.1), 610.6 (1.4), 414.0 (0.7), 389.5 (1.9), 363.6 (0.6), 342.6 (0.4), 294.2 (0.8), 270.6 (2.4), 175.2 (1.4), 141.0 (1.8) cm^{-1}.

$NCCH_2CN{\bullet}AsF_5$ (356 mg; weight expected for 1.50 mmol: 354 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 5.64 (s, 2H, C***H*****$_2$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 104.99 (s, ***C***N), 10.85 (s, ***C***H_2).^{14}N NMR (SO_2, unlocked, 25˚C) δ = -151.7 (s, Δ½= 303 Hz, C***N***). ^{14}N NMR (SO_2, unlocked, -55˚C) δ = -121.4 (s, Δ½= 668 Hz, C***N***): -187.4 (s, Δ½= 433 Hz, C***N***$\bullet AsF_5$); ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -45.1 (s, Δ½= 1403 Hz, As***F*****$_5$**). Raman (-90 °C, 350 mW): $\tilde{\nu}$(rel. Intensity) = 2967.4 (2.6), 2918.9 (6.9), 2366.3 (7.5), 2291.2 (2.5), 2282.0 (2.8), 1379.0 (4.6), 1308.5 (1.4), 1206.0 (3.3), 1146.0 (0.4), 990.7 (0.4), 910.3 (1.4), 904.3 (1.2), 716.5 (8.0), 681.3 (10.0), 608.9 (2.3), 422.0 (1.7), 417.7 (1.5), 386.3 (2.2), 363.6 (1.0), 354.7 (3.9), 328.0 (1.1), 312.1 (1.3), 266.4 (1.6), 245.6 (1.0), 140.9 (4.5), 118.2 (2.6), 96.8 (1.3) cm^{-1}.

$C_3H_7CN{\bullet}AsF_5$ (350 mg; weight expected for 1.50 mmol: 359 mg).

^{1}H NMR (SO_2, unlocked, 25˚C) δ = 4.28 (t, J = 7.1 Hz, 2H, C***H*****$_2$**CN), 3.25 (h, zzJ = 7.3 Hz, 2H, C***H*****$_2$**CH3), 2.43 (t, J = 7.4 Hz, 3H, C***H*****$_3$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 113.64 (s, ***C***N), 19.38 (s, ***C***H2CN), 18.85 (***C***H2), 13.88 (***C***H3). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -195.0 ppm (s, Δ½= 74 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -37.6 (s, 4F, Δ½= 255 Hz, As***F*****$_4$**F), -80.0 (s, 1F, Δ½= 410 Hz, AsF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3000.6 (2.1), 2972.9 (2.9), 2964.4 (4.0), 2945.0 (2.6), 2931.5 (4.8), 2916.2 (1.0), 2886.7 (2.0), 2765.5 (0.7), 2331.2 (6.6), 2466.2 (1.2), 1454.1 (2.0), 1412.2 (1.7), 1346.3 (0.6), 1323.3 (2.4), 1258.4 (0.9), 1230.4 (0.8), 1107.7 (0.7), 1082.3 (0.6), 1046.2 (1.7), 934.6 (0.7), 873.1 (0.7), 841.1 (2.5), 718.7 (5.4), 693.8 (0.5), 670.1 (10.0), 599.8 (1.9), 574.6 (1.0), 434.7 (0.9), 400.5 (1.0), 363.8 (0.7), 342.4 (0.7), 326.5 (1.0), 250.3 (0.9), 153.8 (1.2), 114.6 (2.3), 83.9 (2.2) cm^{-1}.

***c*-C$_3$H$_5$CN•AsF$_5$** (354 mg; weight expected for 1.50 mmol: 356 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 3.16 – 3.25 (m, 1H, C***H***), 2.92 – 2.86 (m, 2H, C***H***H), 2.84 – 2.78 (m, 2H, CH***H***). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 115.41 (s, ***C***N), 11.75 (s, ***C***H), -4.30 (***C***HH). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -206.3 ppm (s, Δ½= 80 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -37.8 (s, 4F, Δ½= 260 Hz, As***F*****$_4$**F), -78.7 (s, 1F, Δ½= 400 Hz, AsF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3117.9 (0.6), 3082.4 (0.7), 3065.6 (0.3), 3036.8 (1.7), 2318.1 (10.0), 2286.8 (1.2), 1608.5 (0.3), 1459.0 (2.6), 1436.1 (0.9), 1342.7 (3.9), 1192.4 (4.5), 1149.0 (0.1), 1134.7 (0.4), 1064.0 (1.5), 952.8 (2.6), 851.5 (2.6), 820.8 (0.5), 814.7 (1.8), 773.9 (1.1), 707.3 (7.7), 663.0 (3.6), 602.4 (0.9), 558.2 (1.4), 395.8 (0.5), 360.0 (1.8), 259.9 (0.9), 241.5 (0.2), 162.5 (0.8), 85.8 (0.2) cm^{-1}.

(CH$_3$)$_3$CCN•AsF$_5$ (367 mg; weight expected for 1.50 mmol: 380 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 2.88 (m, 9H, (C***H*****$_3$)$_3$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 117.28 (s, ***C***N), 30.44 (s, ***C***(CH$_3$)$_3$), 27.27 (***C***H$_3$). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -196.8 ppm (s, Δ½= 87 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -37.6 (s, 4F, Δ½= 225 Hz, As***F*****$_4$**F), -80.2 (s, 1F, Δ½= 410 Hz, AsF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3010.7 (3.1), 3000.2 (2.8), 2970.1 (1.8), 2946.0 (3.9), 2928.5 (1.7), 2912.7 (1.3), 2880.3 (1.1), 2795.5 (0.5), 2729.0 (0.7), 2403.0 (0.2), 2317.6 (10.0), 1484.8 (0.4), 1467.3 (5.1), 1449.5 (1.1), 1402.0 (0.6), 1206.9 (2.7), 1148.0 (0.2), 1038.7 (1.6), 940.9 (2.5), 865.6 (1.7), 708.4 (9.0), 666.0 (9.0), 607.4 (1.5), 589.8 (0.7), 435.2 (0.4), 382.5 (2.4), 369.6 (0.8), 362.7 (0.7), 352.6 (0.8), 266.7 (2.0), 192.7 (1.6), 157.5 (2.0) cm^{-1}.

C$_6$H$_5$CN•AsF$_5$ (406 mg; weight expected for 1.50 mmol: 409 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 9.18 (d, J = 8.2 Hz, 2H), 9.07 (t, J = 7.5 Hz, 1H), 8.82 (t, J = 7.8 Hz, 2H). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 139.40 (s, ***C***H), 136.09 (s, 2x***C***H), 131.32 (s 2x***C***H), 110.29 (s, ***C***N), 104.37 (s, ***C***CN). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -185.4 ppm (s, Δ½= 120 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -37.0 (s, 4F, Δ½= 250 Hz, As***F*****$_4$**F), -80.0 (s, 1F, Δ½= 410 Hz, AsF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3092.9 (1.1), 3081.3 (0.8), 2969.3 (0.1), 2597.4 (0.2), 2413.3 (0.3), 2391.5 (0.3), 2307.6 (10.0), 1597.1 (7.0), 1577.3 (0.4), 1488.3 (0.4), 1453.3 (0.3), 1329.3 (0.3), 1207.9 (3.4), 1186.5 (1.8), 1171.8 (0.7), 1128.0 (0.2), 1030.0 (0.7), 1010.0 (0.4), 1000.6 (6.1), 990.1 (0.3), 968.4 (0.3), 782.3 (0.8), 722.3 (1.0), 711.3 (2.3), 671.0 (2.8), 626.9 (1.1), 603.1 (0.5), 564.9 (0.8), 522.1 (0.4), 410.7 (0.4), 382.5 (1.0), 358.0 (1.0), 340.7 (0.4), 294.4 (0.7), 263.8 (0.6), 182.3 (0.6), 147.6 (2.8), 111.9 (4.3), 74.8 (3.9) cm^{-1}.

Preparation of RCN•SbF$_5$ (R = H, CH$_2$CN, C$_3$H$_7$, c-C$_3$H$_5$, C(CH$_3$)$_3$, C$_6$H$_5$)

Anhydrous SO_2 (2.0 mL) and was condensed into a Teflon-FEP ampule containing a frozen sample of SbF_5 (1.5 mmol, 1.0 eq.) at -196 ˚C. The mixture was allowed to warm to -64 ˚C forming a clear solution. A stochiometric amount of hydrogen cyanide was condensed into the ampule at -196 ˚C. In case of the nitrile adducts, the SbF_5/SO_2 mixture to -64 ˚C was transferred under a stream of dry nitrogen into a second into a second Teflon-FEP ampule containing a sample of the corresponding nitrile (1.50 mmol) at -78˚C. The mixture was allowed to warm to -64 ˚C, kept at this temperature for 10 min and sporadically agitated. The volatile compounds were removed *in vacuo* at -64 ˚C, leaving behind a colorless solid. Single crystals were grown from SO_2 solution by slow evaporation of the solvent *in vacuo* at -64 to -45 °C.

HCN•SbF$_5$ (370 mg; weight expected for 1.50 mmol: 366 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 7.33 (m, 1H, ***H***C). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 106.88 (s, ***C***N). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -194.6 (s, Δ½= 104 Hz, C***N***•Sb). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -100.6 (s, 4F, Δ½= 1190 Hz, Sb***F*****$_4$**F), -133.2 (s, 1F, Δ½= 1150 Hz, SbF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3151.3 (0.2), 2176.7 (10.0), 2148.4 (0.3), 1145.5 (0.3), 686.1 (0.5), 663.2 (9.5), 639.3 (2.6), 600.6 (1.3), 381.4 (0.8), 327.5 (0.7), 294.4 (2.0), 288.9 (1.3), 278.3 (0.7), 260.1 (0.6), 220.6 (1.4), 207.0 (1.5, 154.1 (1.1) cm^{-1}.

NCCH$_2$CN•SbF$_5$ (428 mg; weight expected for 1.50 mmol: 424 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 5.59 (s, 2H, C***H*****$_2$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 110.38 (s, ***C***N), 106.75 (s, ***C***N•SbF$_5$), 11.23 (s, ***C***H$_2$). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -123.1 (s, Δ½= 443 Hz, C***N***): -192.3 (s, Δ½= 270Hz, C***N***•SbF$_5$). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -100.1 (s, 4F, Δ½= 564 Hz, Sb***F*****$_4$**F), -133.5 (s, 1F, Δ½= 503 Hz, SbF$_4$***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 2960.8

(1.9), 2951.3 (0.9), 2919.2 (4.3), 2908.9 (2.1), 2366.9 (2.6), 2357.6 (6.5), 2290.8 (2.0), 1373.8 (3.2), 1360.9 (1.3), 1325.7 (1.1), 1313.3 (1.0), 1204.2 (1.7), 1151.1 (5.9), 909.7 (1.3), 903.2 (0.8), 701.9 (0.9), 679.6 (2.6), 666.7 (10.0), 654.5 (2.9), 648.2 (4.5), 605.2 (1.9), 600.7 (2.3), 528.3 (1.1), 387.0 (2.2), 353.7 (1.9), 290.4 (3.0), 280.5 (2.3), 263.7 (1.7), 247.6 (1.6), 228.5 (1.3), 197.6 (2.0), 139.2 (2.9), 114.2 (2.7), 92.2 (2.3) cm^{-1}.

$C_3H_7CN•SbF_5$ (429 mg; weight expected for 1.50 mmol: 429 mg).
^1H NMR (SO_2, unlocked, 25˚C) δ = 4.12 (t, J = 7.1+ Hz, 2H, C***H*****$_2$**CN), 3.05(h, J = 7.3 Hz, 2H, C***H*****$_2$**CH3), 2.21 (t, J = 7.4 Hz, 3H, C***H*****$_3$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 121.51 (s, ***C***N), 19.55 (s, ***C***H2CN), 18.68 (***C***H2), 13.64 (***C***H3), ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -202.5 (s, Δ½= 94 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -101.1 (s, 4F, Δ½= 780 Hz, Sb***F*****$_4$**F), -130.4 (s, 1F, Δ½= 800 Hz, SbF_4***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 2944.6 (2.8),2928.6 (4.9), 2885.1 (2.3), 2764.7 (0.8), 2317.2 (8.9), 1465.1 (1.9), 1454.6 (2.6), 1411.1 (2.4), 1321.1 (2.8), 1255.9 (1.6), 1105.7 (1.5), 1080.7 (1.4), 1044.7 (2.1), 933.9 (1.3), 871.6 (1.5), 841.9 (2.8), 686.3 (3.7), 672.0 (6.4), 652.3 (2.2), 640.4 (10.0), 576.3 (3.0), 407.5 (2.1), 199.6 (2.3), 145.7 (2.2), 108.9 (3.4) cm^{-1}.

c-$C_3H_5CN•SbF_5$ (415 mg; weight expected for 1.50 mmol: 426 mg).
^1H NMR (SO_2, unlocked, 25˚C) δ = 3.12 – 3.01 (m, 1H, C***H***), 2.80 – 2.72 (m, 2H, C***H***H), 2.72 – 2.64 (m, 2H, CH***H***). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 123.56 (s, ***C***N), 12.80 (s, ***C***H), -3.87 (***C***HH). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -213.8ppm (s, Δ½= 75 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -101.0 (s, 4F, Δ½= 757 Hz, Sb***F*****$_4$**F), -128.8 (s, 1F, Δ½= 890 Hz, SbF_4***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3120.1 (0.9), 3063.1 (0.6), 3035.9 (2.4), 2306.7 (10.0), 2281.3 (3.3), 1457.7 (3.0), 1435.5 (1.1), 1359.7 (0.4), 1342.4 (4.3), 1190.1 (7.3), 1056.9 (2.3), 951.2 (4.2), 844.5 (1.8), 822.7 (1.5), 811.3 (2.9), 768.9 (2.2), 683.1 (1.0), 664.1 (9.2), 652.7 (1.4), 639.1 (4.8), 559.0 (2.5), 278.9 (0.5), 229.9 (0.5), 207.7 (1.4), 153.8 (1.0), 115.2 (0.5), 241.5 (0.2), 162.5 (0.7), 85.8 (0.2) cm^{-1}.

$(CH_3)_3CCN•SbF_5$ (438 mg; weight expected for 1.50 mmol: 450 mg).
^1H NMR (SO_2, unlocked, 25˚C) δ = 2.81 (m, 9H, (C***H*****$_3$**$)_3$). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 125.08 (s, ***C***N), 30.70 (s, ***C***$(CH_3)_3$), 27.15 (***C***H_3). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -204.0 ppm (s, Δ½= 118 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -100.9 (s, 4F, Δ½= 620 Hz, Sb***F*****$_4$**F), -130.2 (s, 1F, Δ½= 740 Hz, SbF_4***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3011.0 (4.1), 3000.6 (3.1), 2969.0 (2.1), 2944.9 (4.8), 2928.1 (1.7), 2912.8 (1.7), 2879.2 (1.3), 2792.6 (0.6), 2727.9 (0.8), 2401.1 (0.5), 2305.8 (9.6), 1483.7 (1.0), 1466.7 (5.1), 1449.2 (2.0), 1400.9 (1.2), 1232.6 (0.9), 1205.1 (3.2), 1147.5 (0.9), 1037.8 (2.0), 940.9 (2.9), 864.3 (2.3), 718.5 (2.2), 697.7 (1.8), 689.9 (1.8), 678.5 (1.6), 663.5 (10.0), 649.4 (2.2), 637.9 (6.1), 600.1 (1.6), 590.6 (1.4), 436.6 (1.3), 365.0 (1.7), 295.9 (2.2), 285.9 (2.8), 278.0 (2.0), 265.2 (1.5), 231.6 (1.5), 207.5 (4.1), 192.1 (2.2), 143.7 (1.6) cm^{-1}.

$C_6H_5CN•SbF_5$ (481 mg; weight expected for 1.50 mmol: 480 mg).
^1H NMR (SO_2, unlocked, 25˚C) δ = 9.37 (d, J = 7.4 Hz, 2H), 9.24 (t, J = 7.4 Hz, 1H), 8.97 (t, J = 8.1 Hz, 2H). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 140.19 (s, ***C***H), 136.77 (s, 2x***C***H), 131.55 (s 2x***C***H), 117.92 (s, ***C***N), 103.90 (s, ***C***CN). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -192.6 ppm (s, Δ½= 145 Hz, C***N***). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -100.8 (s, 4F, Δ½= 490 Hz, Sb***F*****$_4$**F), -130.3 (s, 1F, Δ½= 580 Hz, SbF_4***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 3092.4 (1.3), 2281.8 (9.6), 2263.6 (1.1), 1620.8 (0.5), 1592.9 (10.0), 1564.4 (0.7), 1519.3 (0.3), 1485.9 (0.5), 1452.9 (0.4), 1328.2 (0.6), 1303.4 (0.8), 1282.6 (1.1), 1209.5 (3.4), 1182.4 (2.4), 1149.0 (0.3), 1125.8 (0.4), 1024.7 (1.8), 1010.0 (0.5), 1000.0 (7.0), 989.2 (0.4), 958.5 (0.3), 834.0 (0.3), 779.0 (1.1), 673.8 (2.4), 641.3 (3.7), 626.9 (1.3), 612.0 (0.3), 591.5 (0.6), 565.4 (0.9), 525.3 (0.7), 2416.4 (0.2), 2390.9 (0.3), 271.3 (0.9), 201.7 (1.0), 138.9 (4.4), 289.7 (1.4) cm^{-1}.

Preparation of $AsF_5•NCCH_2CN•AsF_5$

Anhydrous SO_2 (3.0 mL) and AsF_5 (3.3 mmol, 2.2 eq.) were condensed into a Teflon-FEP ampule containing a frozen sample of malononitrile (1.5 mmol, 1.0 eq.) at -196 ˚C. The mixture was allowed to warm to -64 ˚C, kept at this temperature for 10 min and sporadically agitated. The volatile compounds were removed *in vacuo* at -64 ˚C, leaving behind a colorless solid. Single crystals were grown from SO_2 solution by slow evaporation of the solvent *in vacuo* at -64 to -45 °C.

$AsF_5•NCCH_2CN•AsF_5$ (602 mg; weight expected for 1.50 mmol: 608 mg).
^1H NMR (SO_2, unlocked, 25˚C) δ = 5.95 (s, 2H, C***H*****$_2$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 100.83 (s, ***C***N), 11.76 (s, ***C***H_2). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -175.8 (s, Δ½= 414 Hz, C***N***•AsF_5). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -45.3 (s, Δ½= 487 Hz, As***F*****$_5$**). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 2963.9 (0.9), 2926.5 (3.0), 2376.9 (4.1), 2369.0 (2.2), 1370.9 (1.3), 1331.9 (1.2), 1327.7 (1.6), 1311.9 (0.3), 1213.6 (0.4), 1154.4 (10.0), 1147.2 (0.7), 914.5 (0.4), 724.1 (3.6), 719.7 (1.8), 692.2 (4.9), 682.5 (2.1), 618.2 (0.5), 606.9 (1.5), 524.5 (0.8), 421.1 (0.8), 388.6 (1.1), 355.8 (0.4), 317.3 (1.2), 309.2 (0.6), 270.1 (0.9), 222.0 (0.5), 101.3 (1.4), 81.2 (1.8) cm^{-1}.

Preparation of SbF_5•$NCCH_2CN$•SbF_5

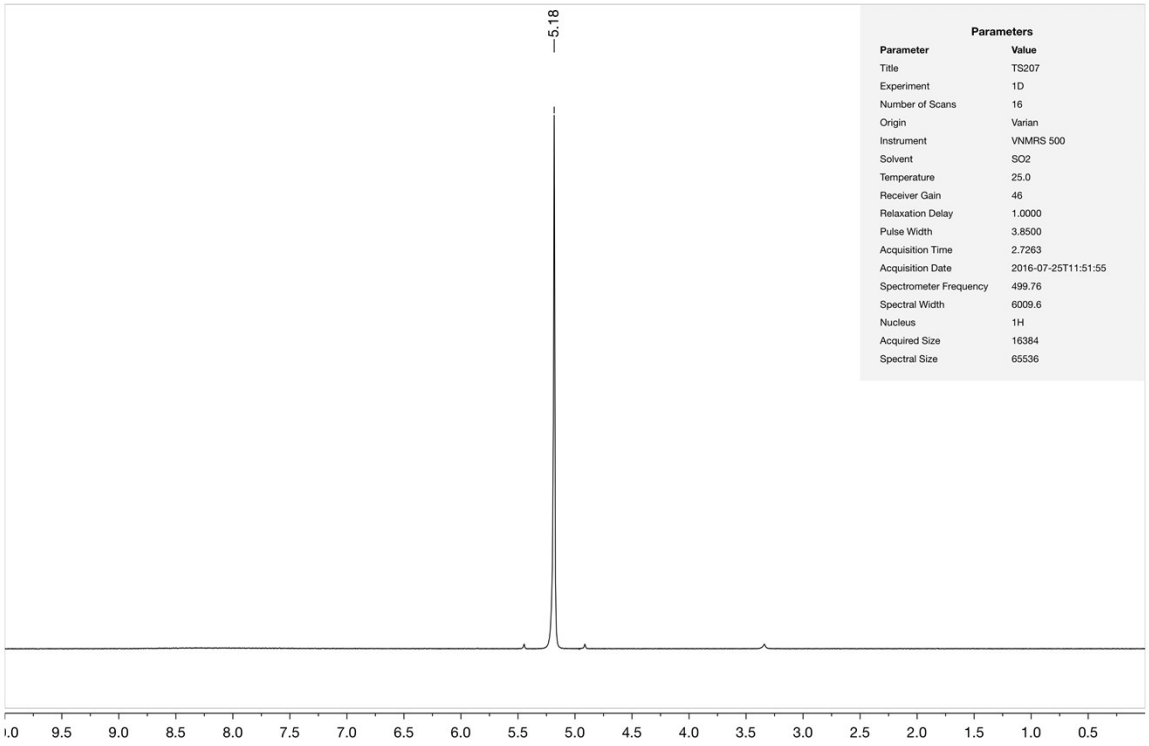
Anhydrous SO_2 (2.0 mL) and was condensed into a Teflon-FEP ampule containing a frozen sample of SbF_5 (3 mmol, 2.0 eq.) at -196 ˚C. The mixture was allowed to warm to -64 ˚C forming a clear solution. The cold mixture was transferred under a stream of dry nitrogen into a second into a second Teflon-FEP ampule containing a sample of the corresponding nitrile (1.50 mmol, 1.0 eq.) at -78˚C. The mixture was allowed to warm to -64 ˚C, kept at this temperature for 10 min and sporadically agitated. The volatile compounds were removed *in vacuo* at -64 ˚C, leaving behind a colorless solid.

SbF_5•$NCCH_2CN$•SbF_5 (756 mg; weight expected for 1.50 mmol: 749 mg).
^{1}H NMR (SO_2, unlocked, 25˚C) δ = 6.36 (s, 2H, C***H*****$_2$**). ^{13}C NMR (SO_2, unlocked, 25˚C) δ = 106.25 (s, ***C***N), 13.23 (s, ***C***H_2). ^{14}N NMR (SO_2, unlocked, 25˚C) δ = -186.1 (s, Δ½= 325 Hz, C***N***•SbF_5). ^{19}F NMR (SO_2, unlocked, 25˚C) δ = -99.5 (s, 4F, Δ½= 538 Hz, Sb***F*****$_4$**F), -134.7 (s, 1F, Δ½= 420 Hz, SbF_4***F***). Raman (-90 °C, 350 mW): $\tilde{\upsilon}$(rel. Intensity) = 2951.3 (1.1), 2909.0 (2.8), 2367.3 (3.4), 2354.8 (2.1), 2329.8 (0.3), 1382.6 (1.0), 1361.0 (1.3), 1325.8 (1.5), 1316.7 (2.2), 1151.1 (10.0), 1107.6 (0.5), 1085.8 (0.7), 909.1 (0.3), 701.8 (0.9), 679.7 (3.6), 668.1 (7.4), 663.5 (4.6), 654.7 (4.1), 645.2 (3.2), 619.8 (1.0), 605.5 (1.6), 578.8 (0.8), 540.7 (0.9), 528.4 (1.5), 406.1 (1.8), 387.1 (1.7), 295.8 (3.4), 263.3 (1.5), 230.7 (2.1), 199.6 (1.6), 135.5 (1.8), 92.1 (2.9) cm^{-1}.

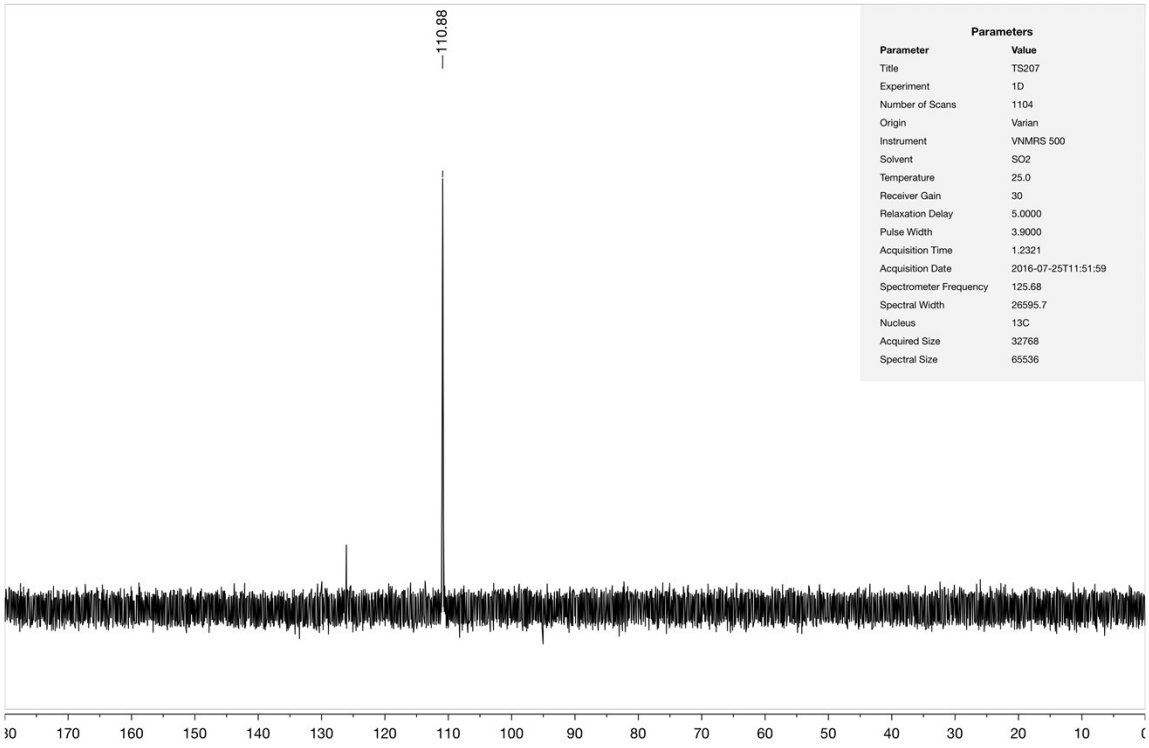
NMR Spectra

HCN

^{1}H - HCN



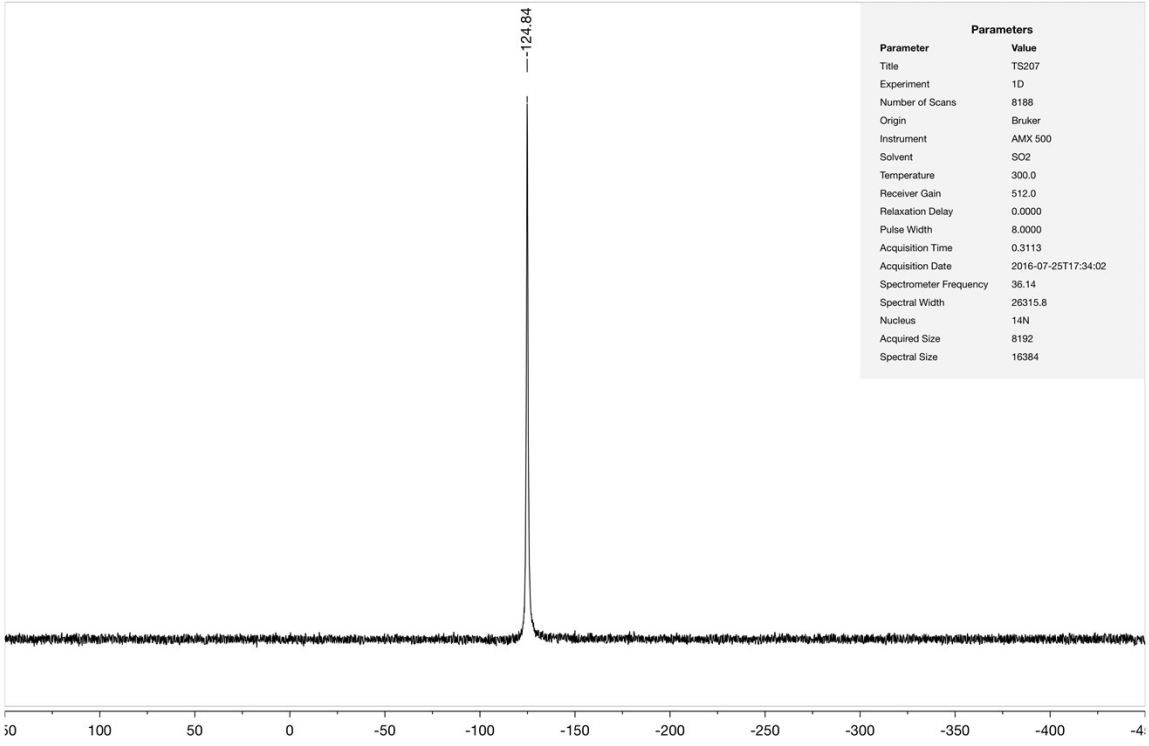
^{13}C - HCN



Parameters

Parameter	Value
Title	TS207
Experiment	1D
Number of Scans	1104
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	3.9000
Acquisition Time	1.2321
Acquisition Date	2016-07-25T11:51:59
Spectrometer Frequency	125.68
Spectral Width	26595.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - HCN

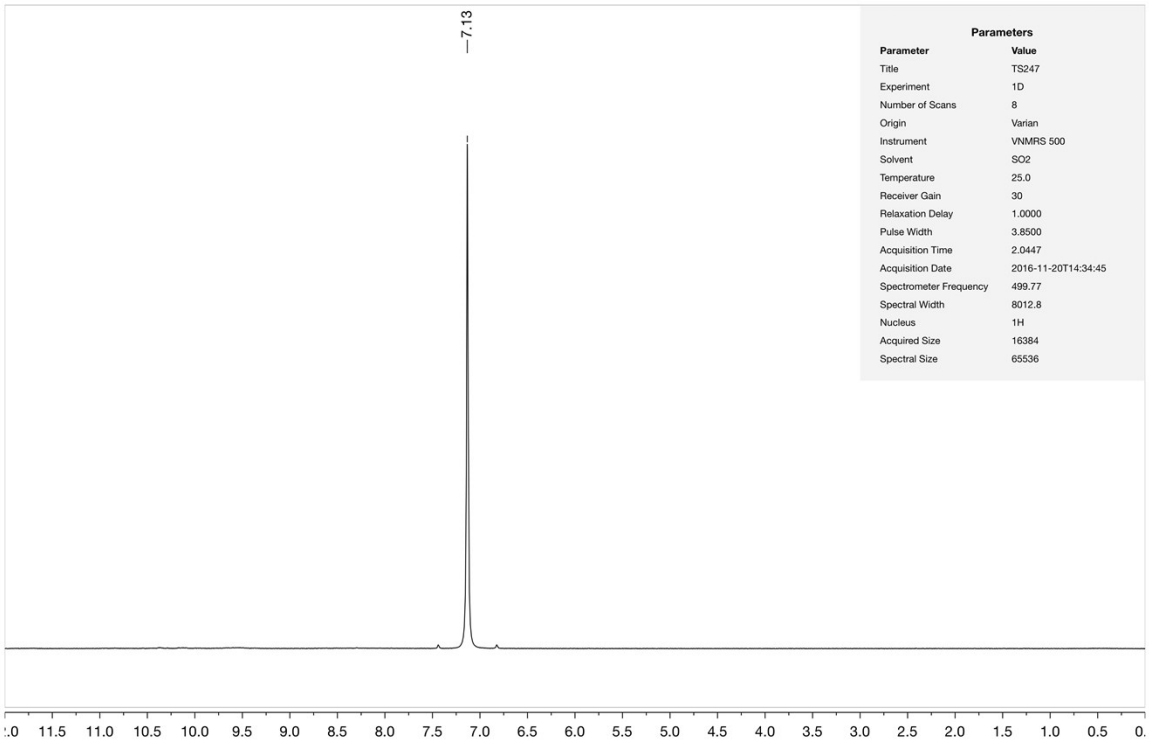


Parameters

Parameter	Value
Title	TS207
Experiment	1D
Number of Scans	8188
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-07-25T17:34:02
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

$HCN•AsF_5$

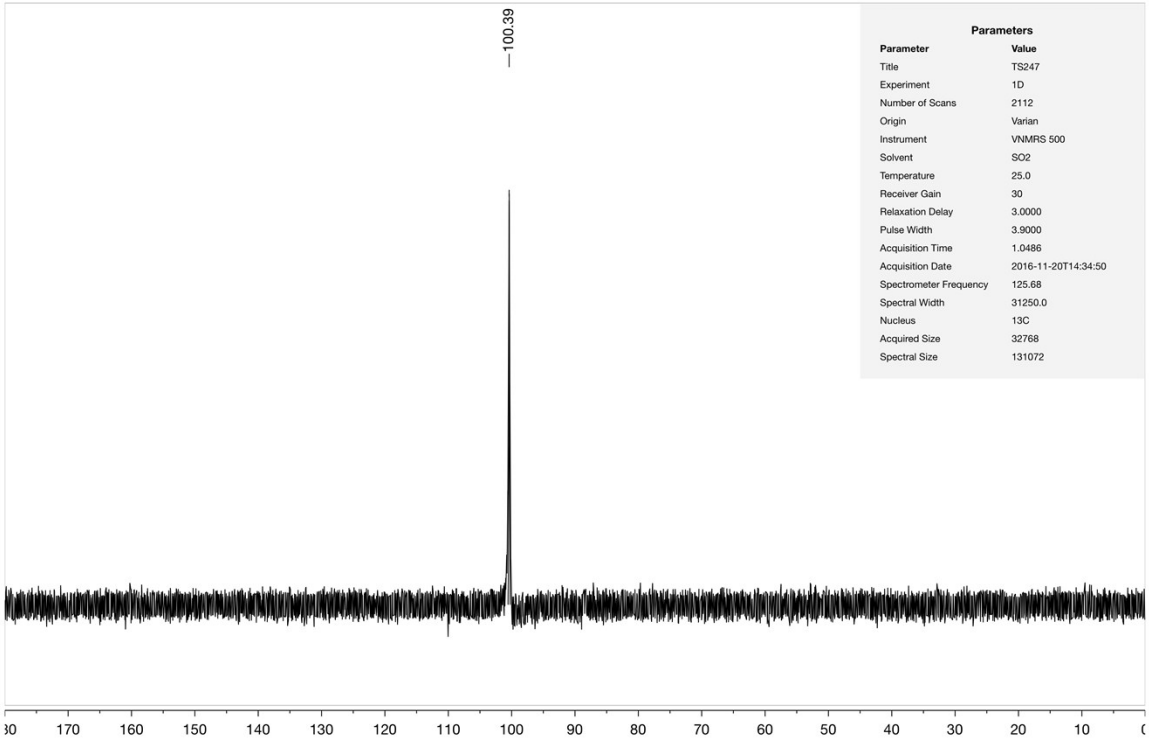
^1H - $HCN•AsF_5$



Parameters

Parameter	Value
Title	TS247
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.0447
Acquisition Date	2016-11-20T14:34:45
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

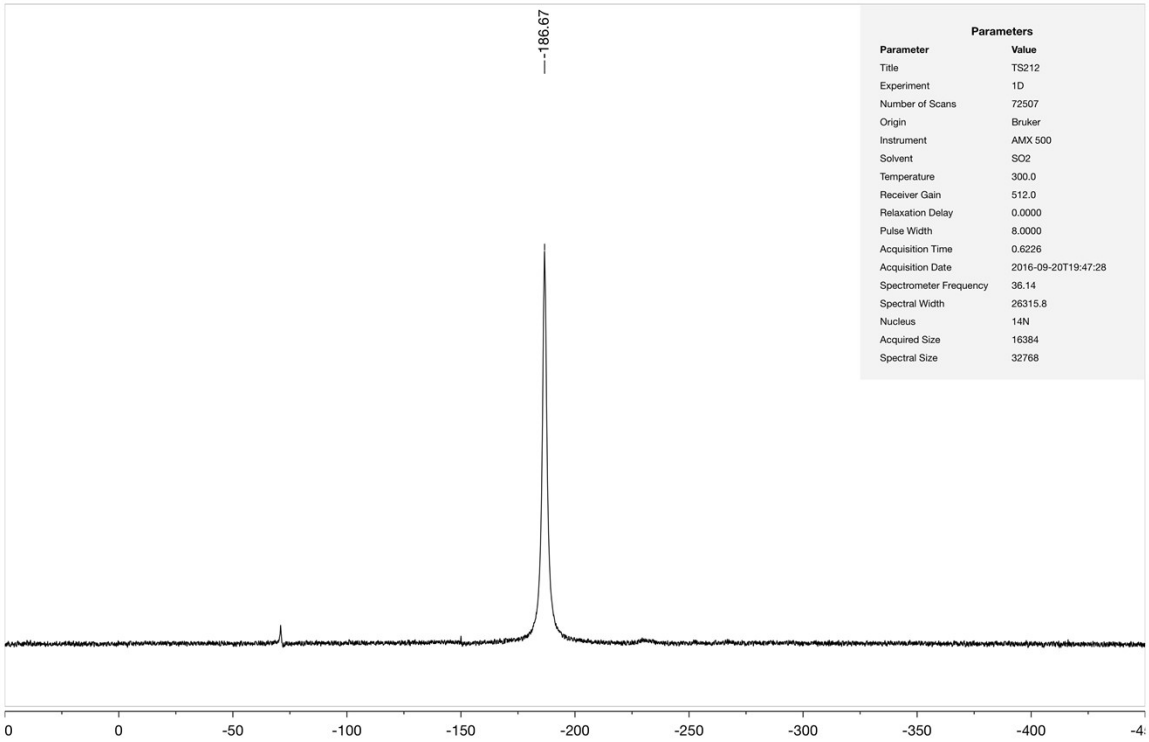
^{13}C - $HCN•AsF_5$



Parameters

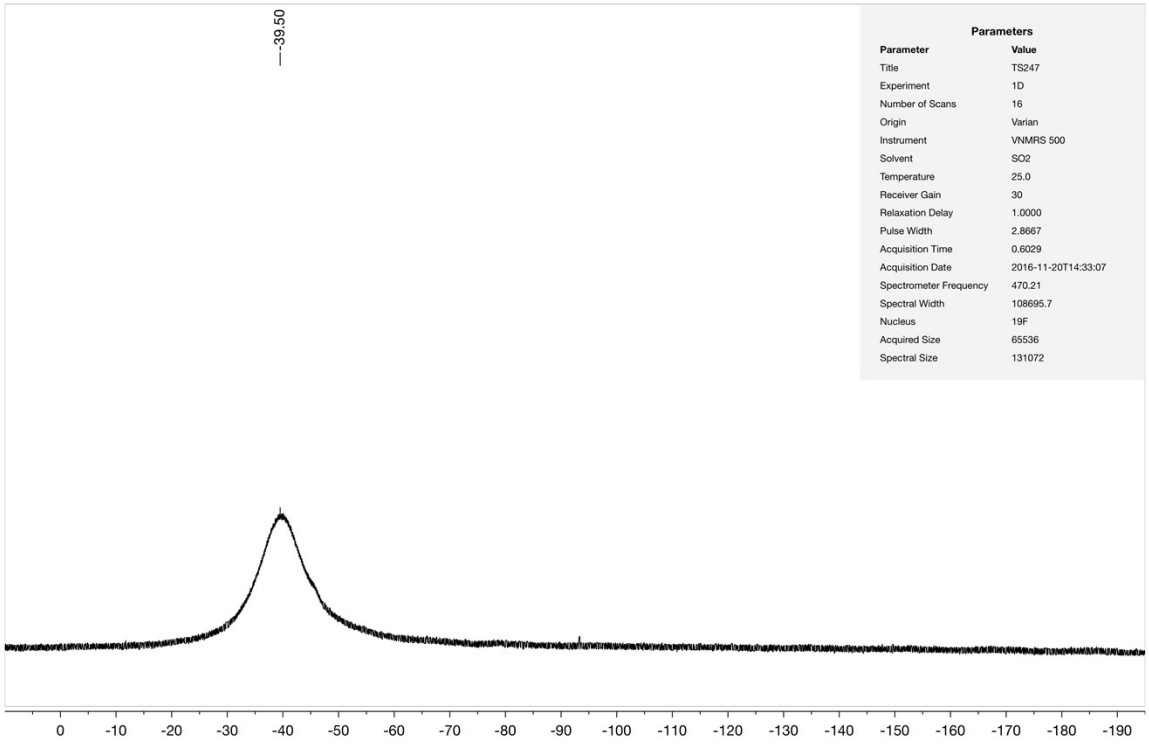
Parameter	Value
Title	TS247
Experiment	1D
Number of Scans	2112
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	3.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-20T14:34:50
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	131072

^{14}N - $HCN{\cdot}AsF_5$



Parameters	
Parameter	**Value**
Title	TS212
Experiment	1D
Number of Scans	72507
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2016-09-20T19:47:28
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

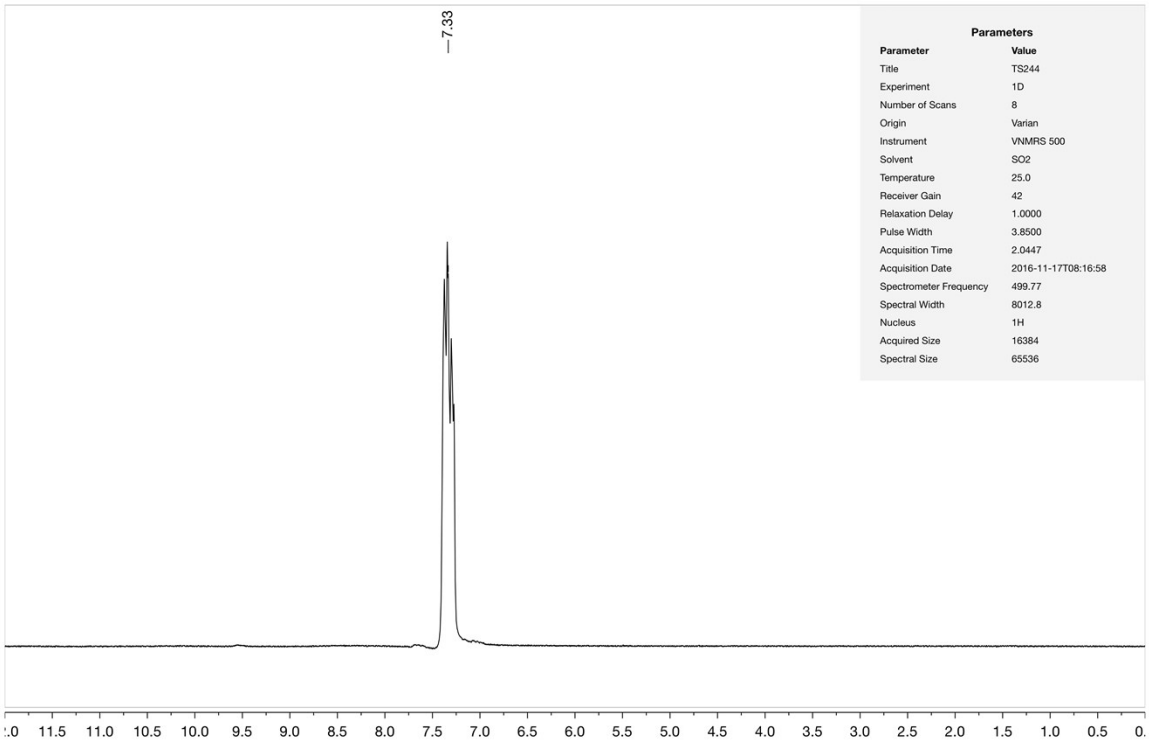
^{19}F - $HCN{\cdot}AsF_5$



Parameters	
Parameter	**Value**
Title	TS247
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.8667
Acquisition Time	0.6029
Acquisition Date	2016-11-20T14:33:07
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

HCN•SbF_5

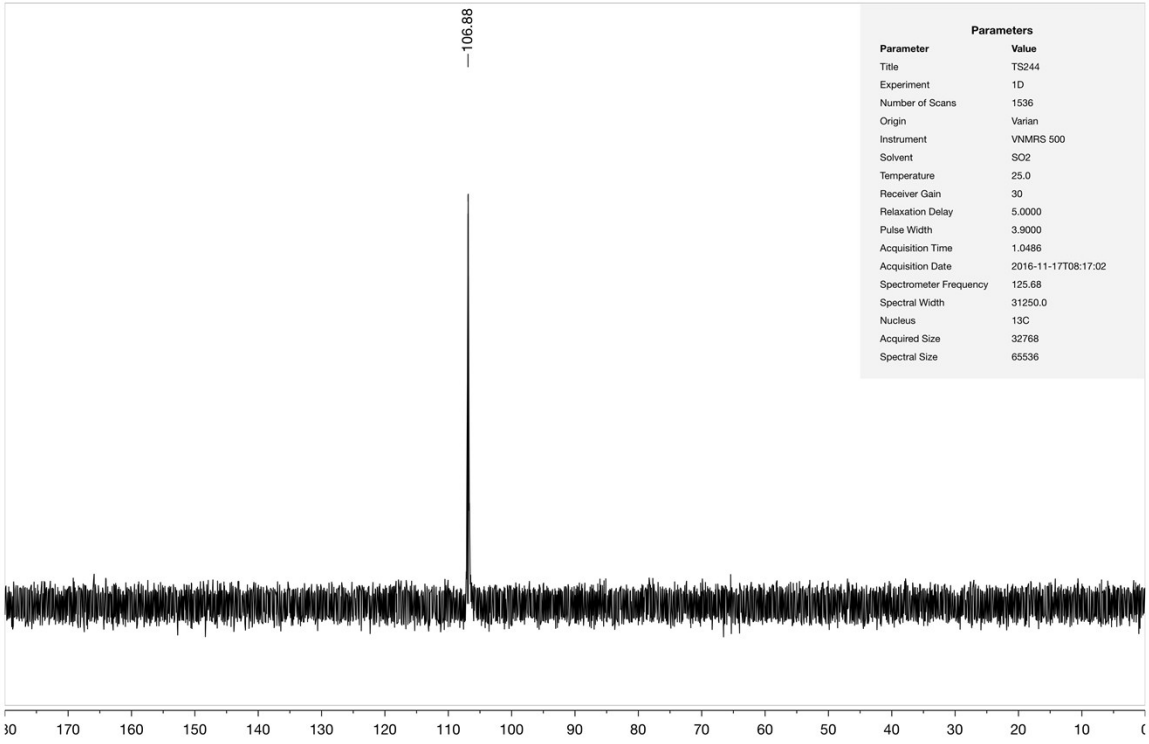
^1H - HCN•SbF_5



Parameters

Parameter	Value
Title	TS244
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.0447
Acquisition Date	2016-11-17T08:16:58
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

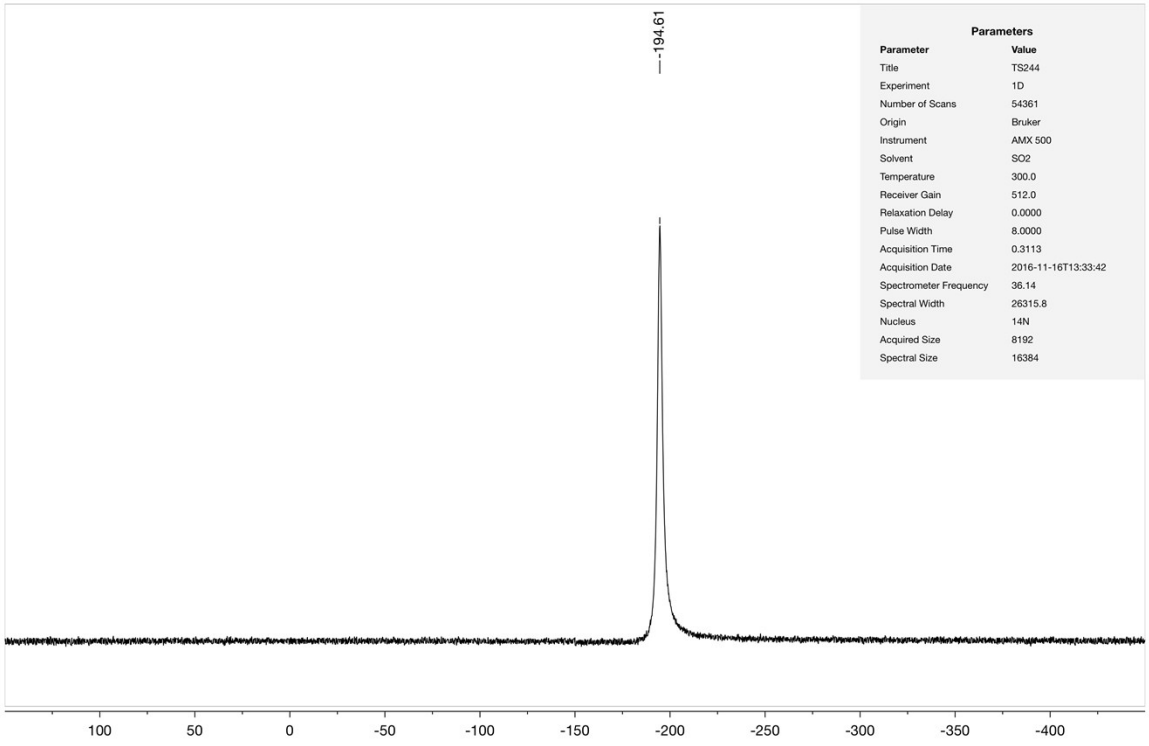
^{13}C - HCN•SbF_5



Parameters

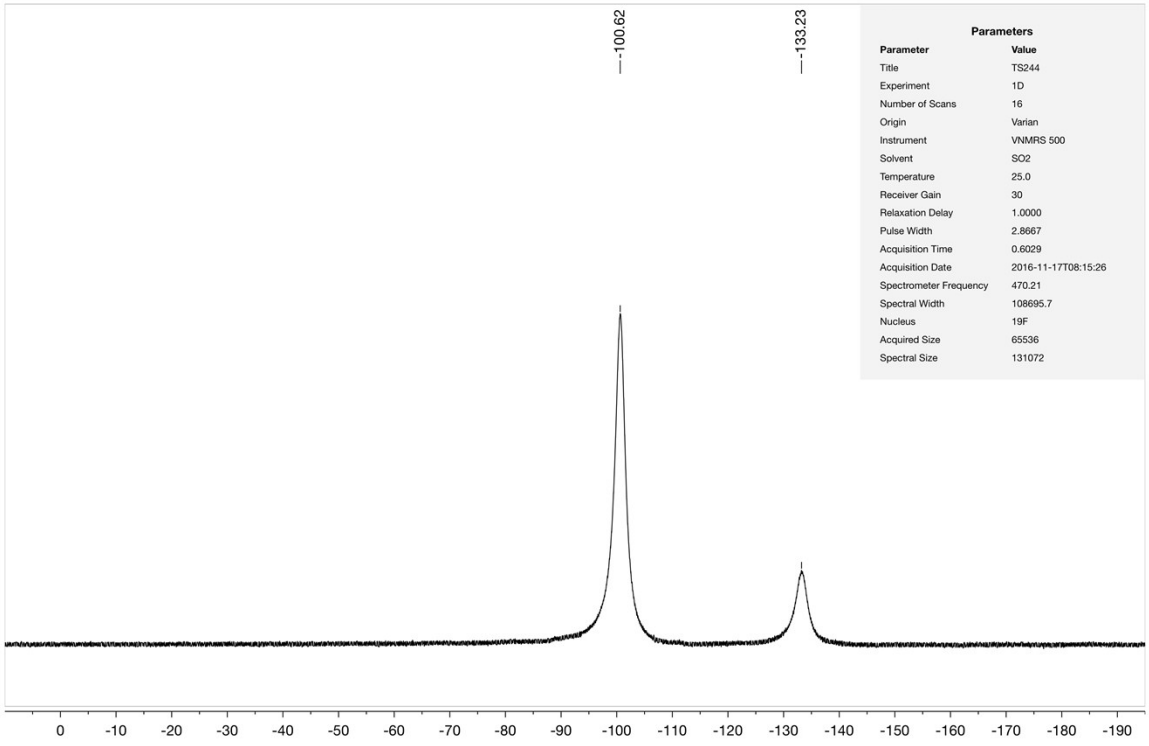
Parameter	Value
Title	TS244
Experiment	1D
Number of Scans	1536
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-17T08:17:02
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $HCN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS244
Experiment	1D
Number of Scans	54361
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-11-16T13:33:42
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

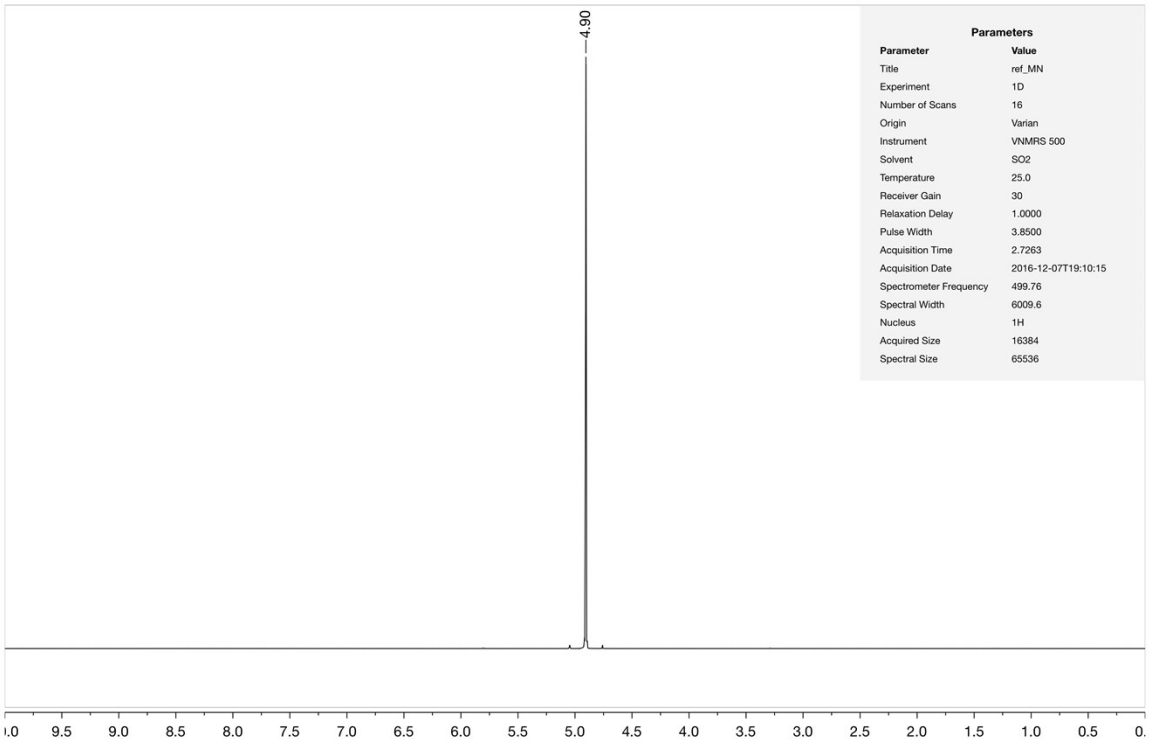
^{19}F - $HCN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS244
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.8667
Acquisition Time	0.6029
Acquisition Date	2016-11-17T08:15:26
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

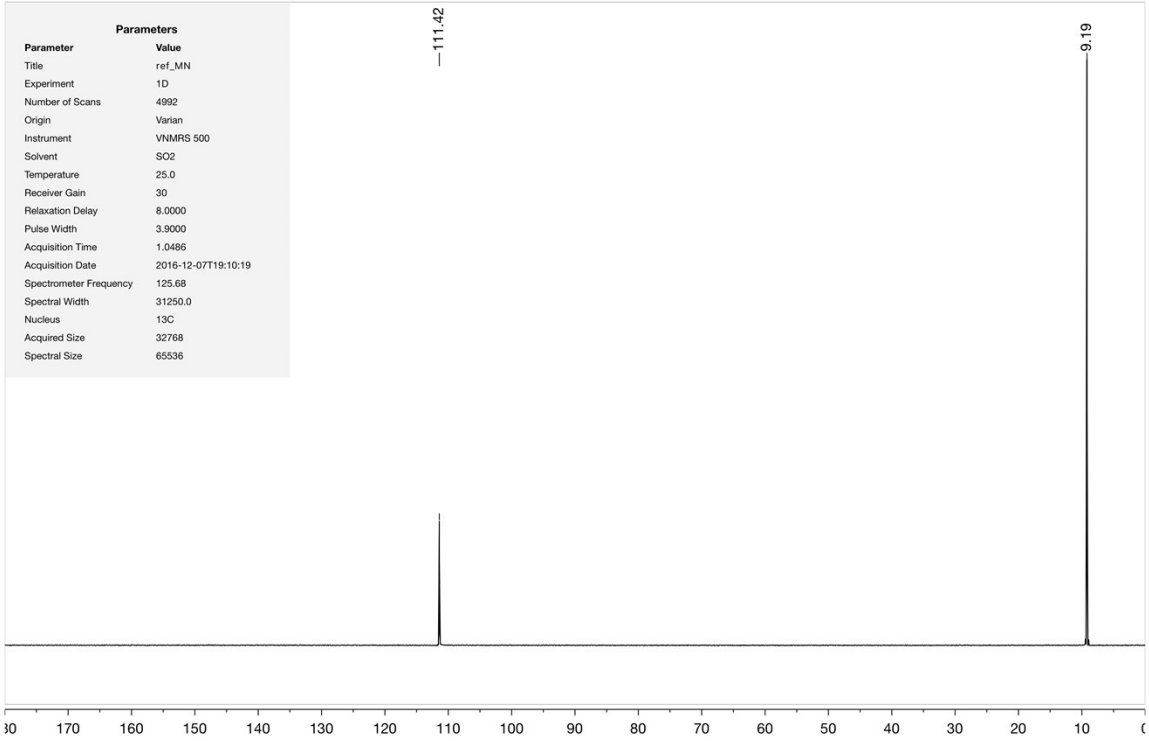
$NCCH_2CN$

^1H - $NCCH_2CN$



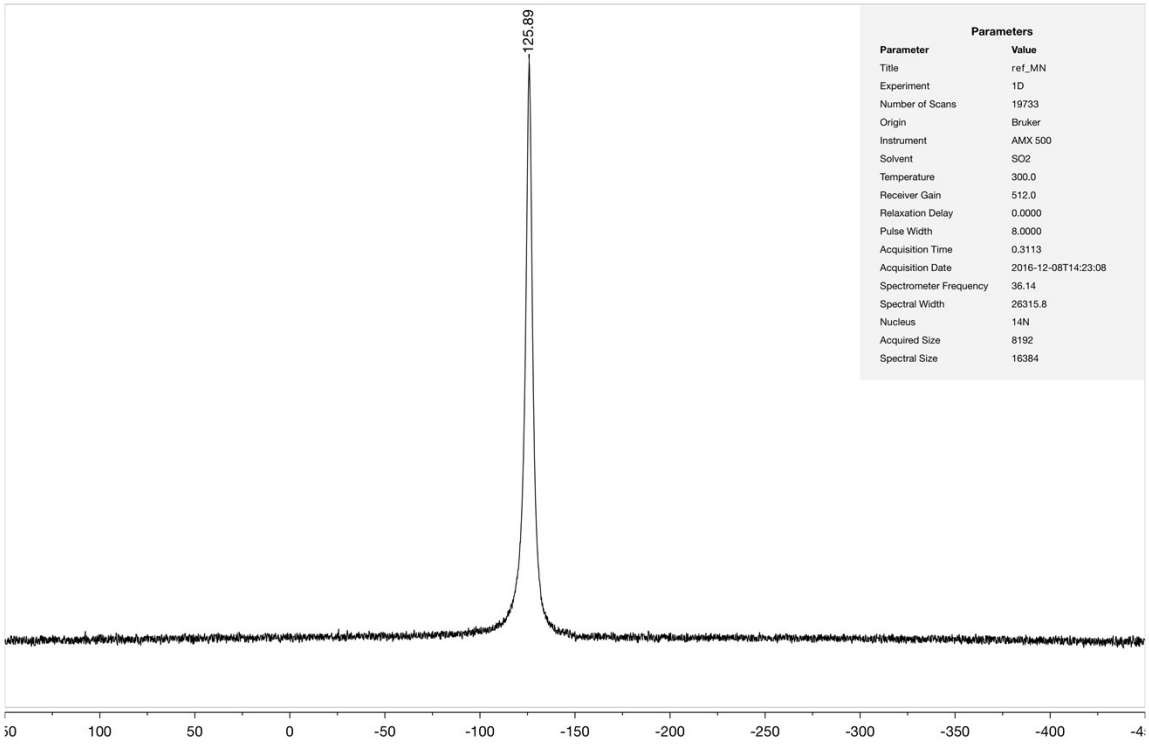
Parameters	
Parameter	**Value**
Title	ref_MN
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.7263
Acquisition Date	2016-12-07T19:10:15
Spectrometer Frequency	499.76
Spectral Width	6009.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

^{13}C - $NCCH_2CN$



Parameters	
Parameter	**Value**
Title	ref_MN
Experiment	1D
Number of Scans	4992
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	8.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-12-07T19:10:19
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $NCCH_2CN$

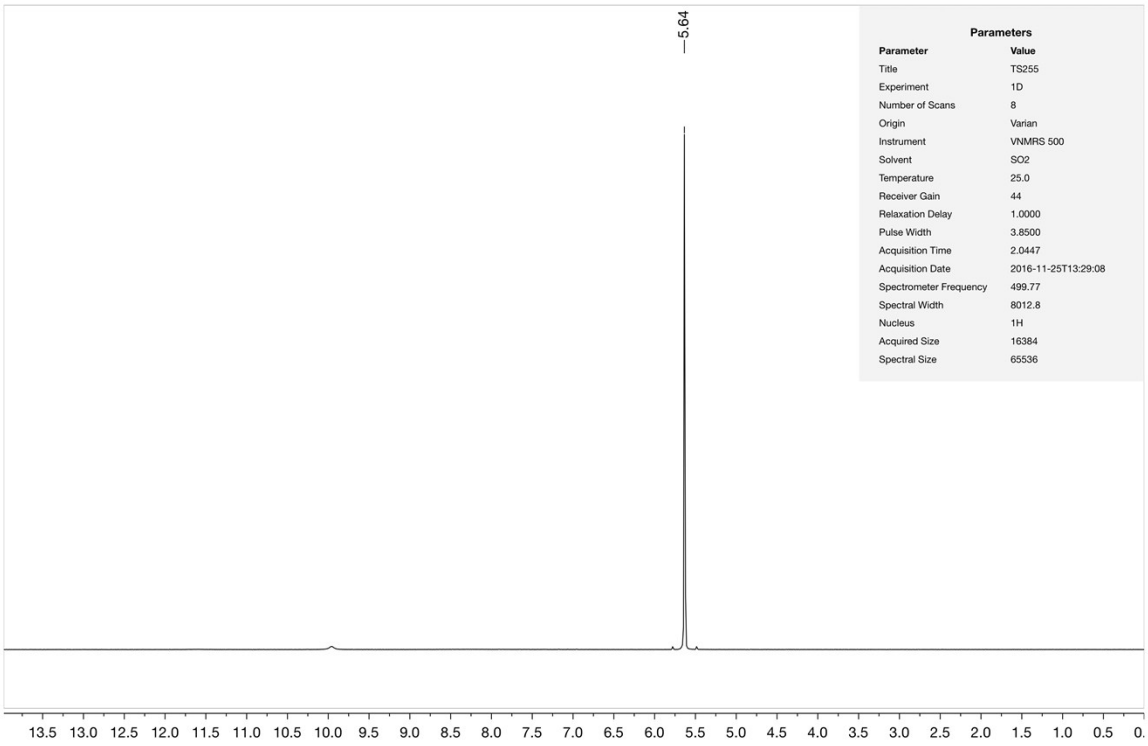


Parameters

Parameter	Value
Title	ref_MN
Experiment	1D
Number of Scans	19733
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-12-08T14:23:08
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

$NCCH_2CN{\bullet}AsF_5$

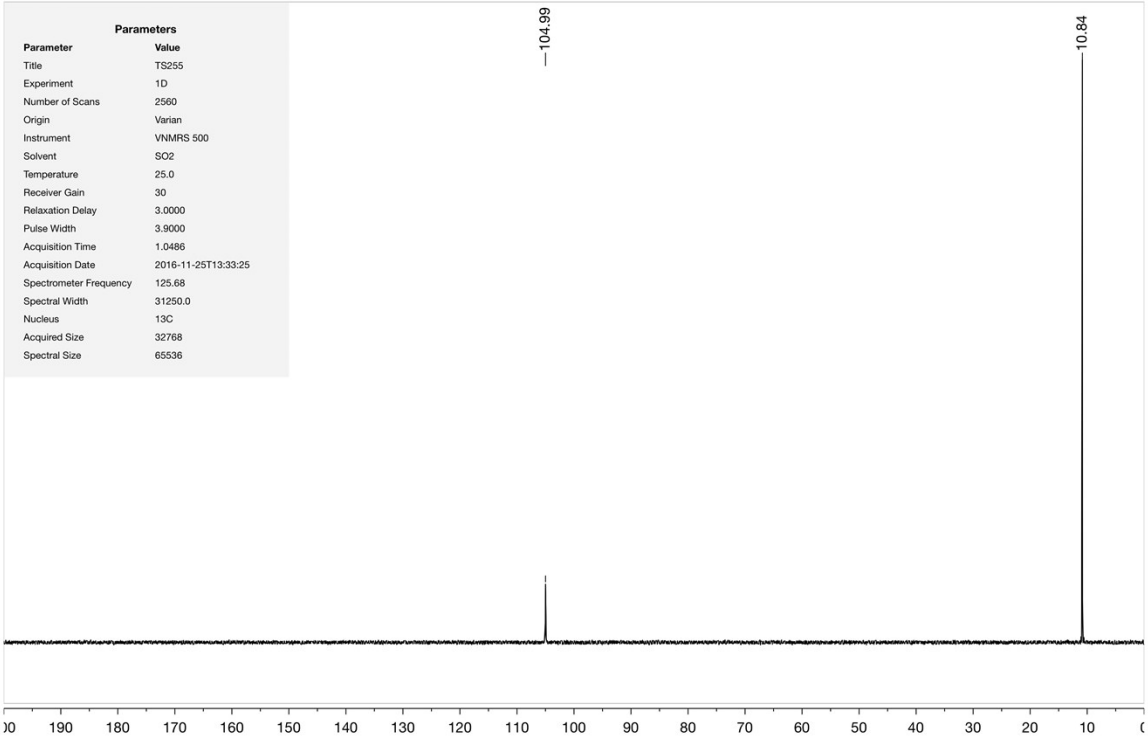
^1H - $NCCH_2CN{\bullet}AsF_5$



Parameters

Parameter	Value
Title	TS255
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.0447
Acquisition Date	2016-11-25T13:29:08
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

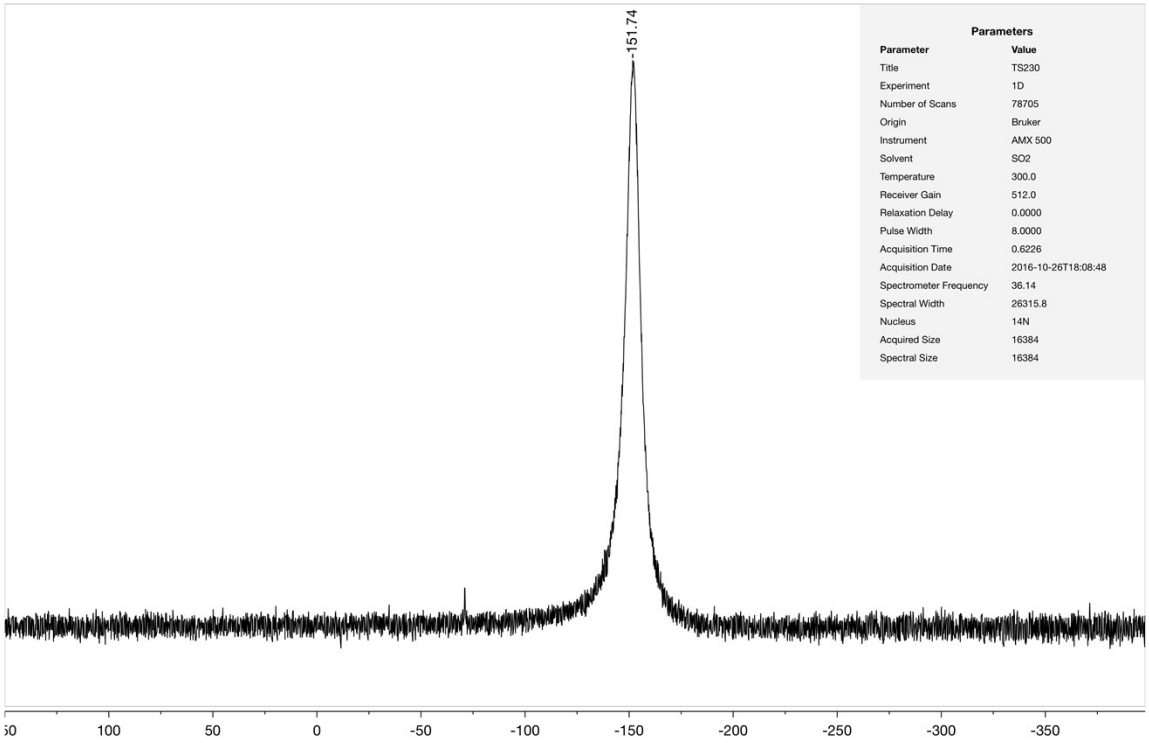
^{13}C - $NCCH_2CN{\bullet}AsF_5$



Parameters

Parameter	Value
Title	TS255
Experiment	1D
Number of Scans	2560
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	3.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-25T13:33:25
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

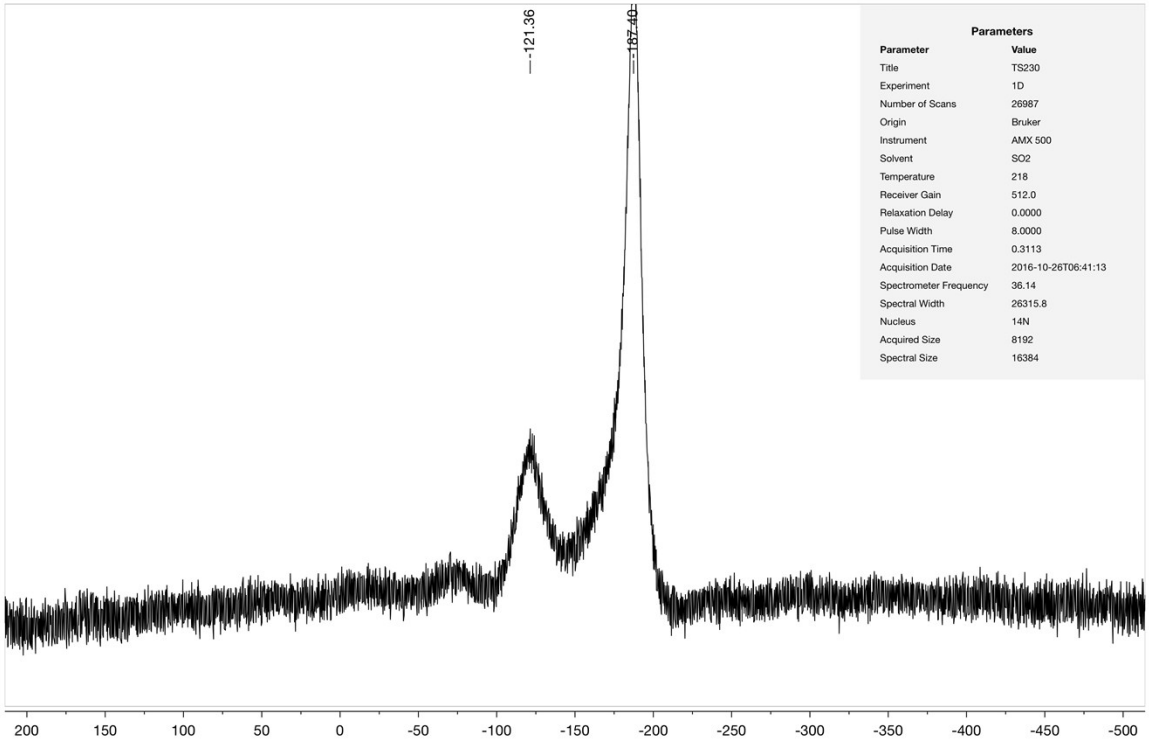
^{14}N - $NCCH_2CN{\cdot}AsF_5$ @ 25°C



Parameters

Parameter	Value
Title	TS230
Experiment	1D
Number of Scans	78705
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2016-10-26T18:08:48
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	16384

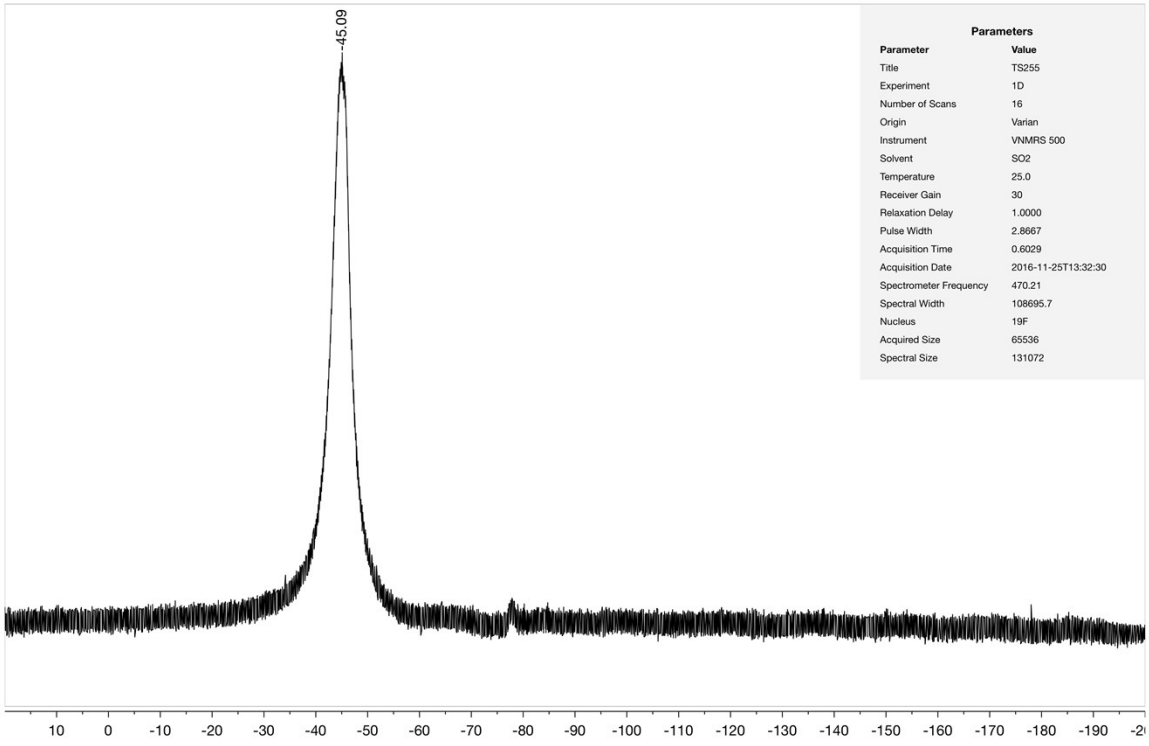
^{14}N - $NCCH_2CN{\cdot}AsF_5$ @ –55°C



Parameters

Parameter	Value
Title	TS230
Experiment	1D
Number of Scans	26987
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	218
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-10-26T06:41:13
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

^{19}F - $NCCH_2CN{\cdot}AsF_5$

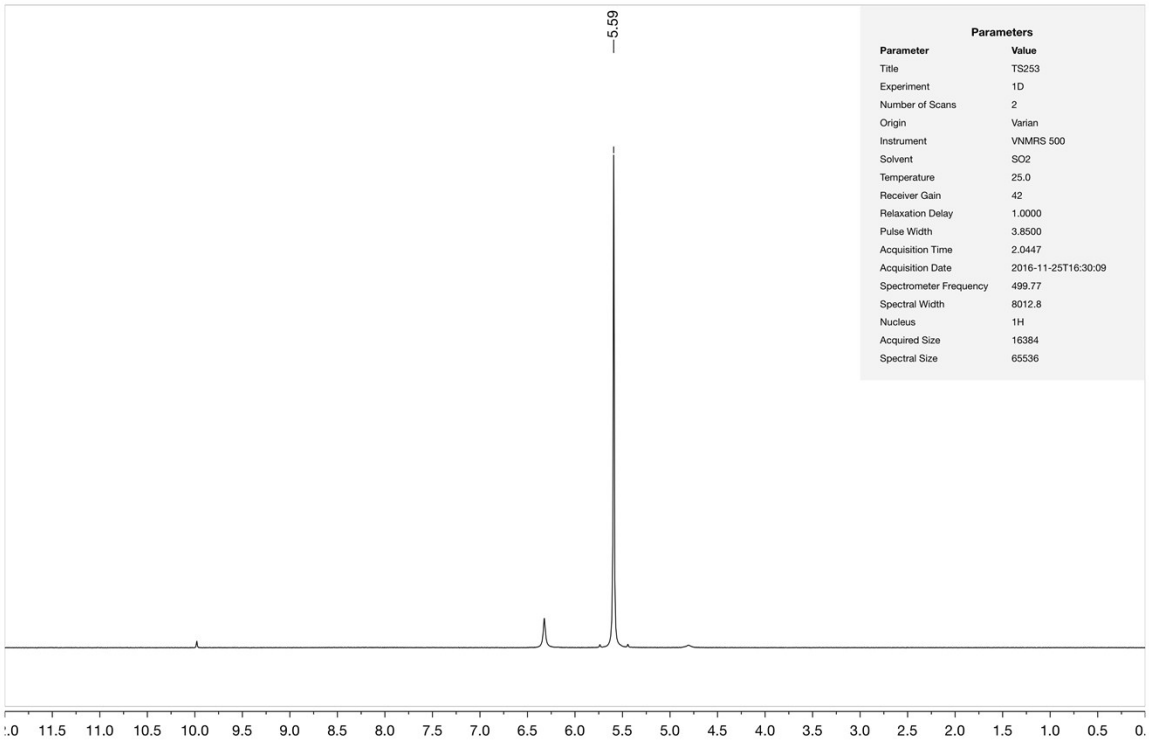


Parameters

Parameter	Value
Title	TS255
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.8667
Acquisition Time	0.6029
Acquisition Date	2016-11-25T13:32:30
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

$NCCH_2CN{\bullet}SbF_5$

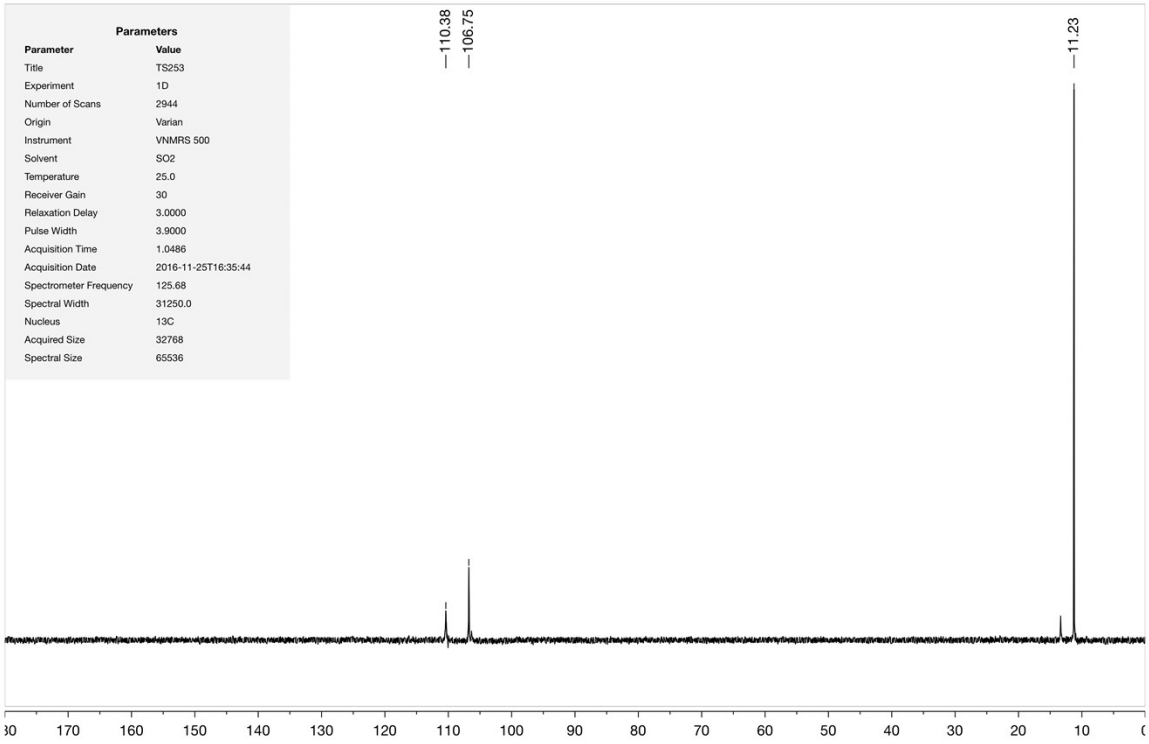
^1H - $NCCH_2CN{\bullet}SbF_5$



Parameters

Parameter	Value
Title	TS253
Experiment	1D
Number of Scans	2
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.0447
Acquisition Date	2016-11-25T16:30:09
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

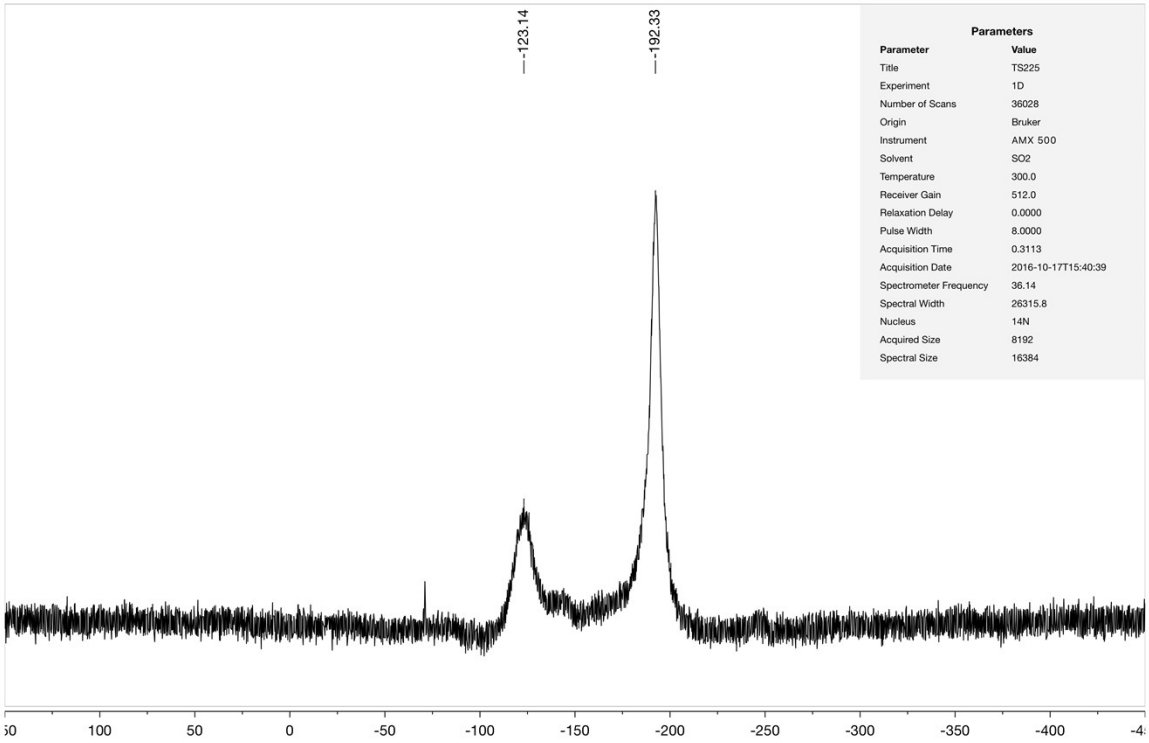
^{13}C - $NCCH_2CN{\bullet}SbF_5$



Parameters

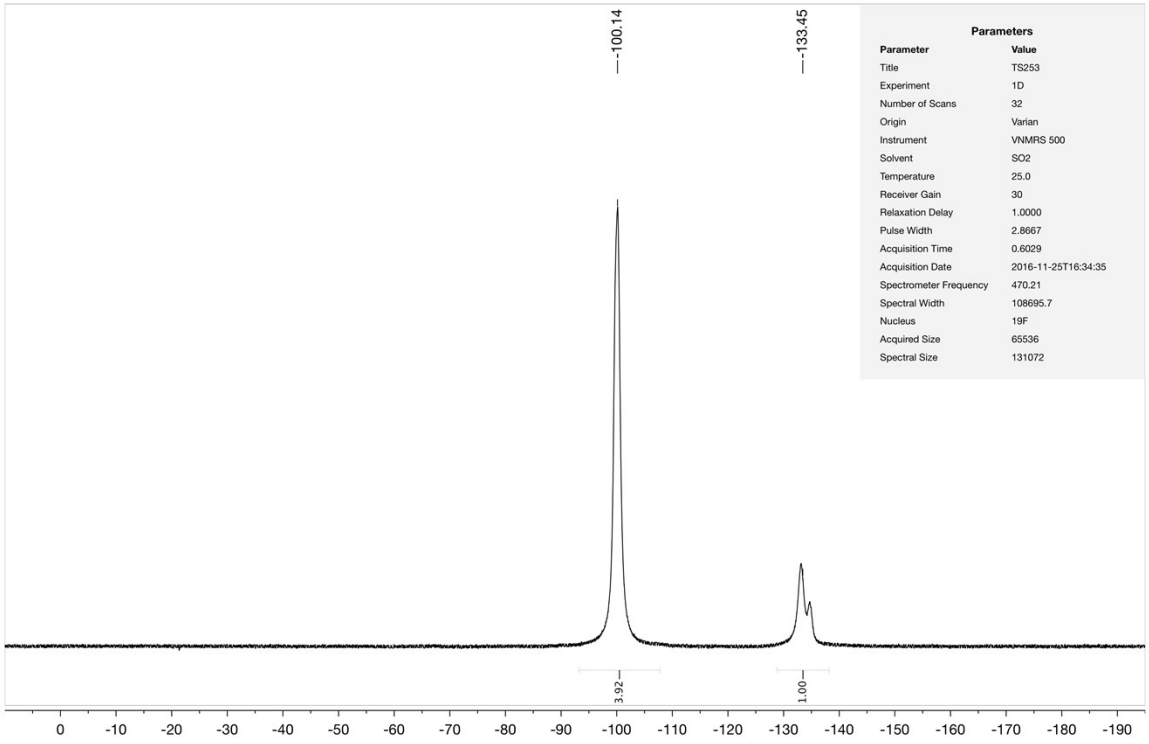
Parameter	Value
Title	TS253
Experiment	1D
Number of Scans	2944
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	3.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-25T16:35:44
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $NCCH_2CN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS225
Experiment	1D
Number of Scans	36028
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-10-17T15:40:39
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

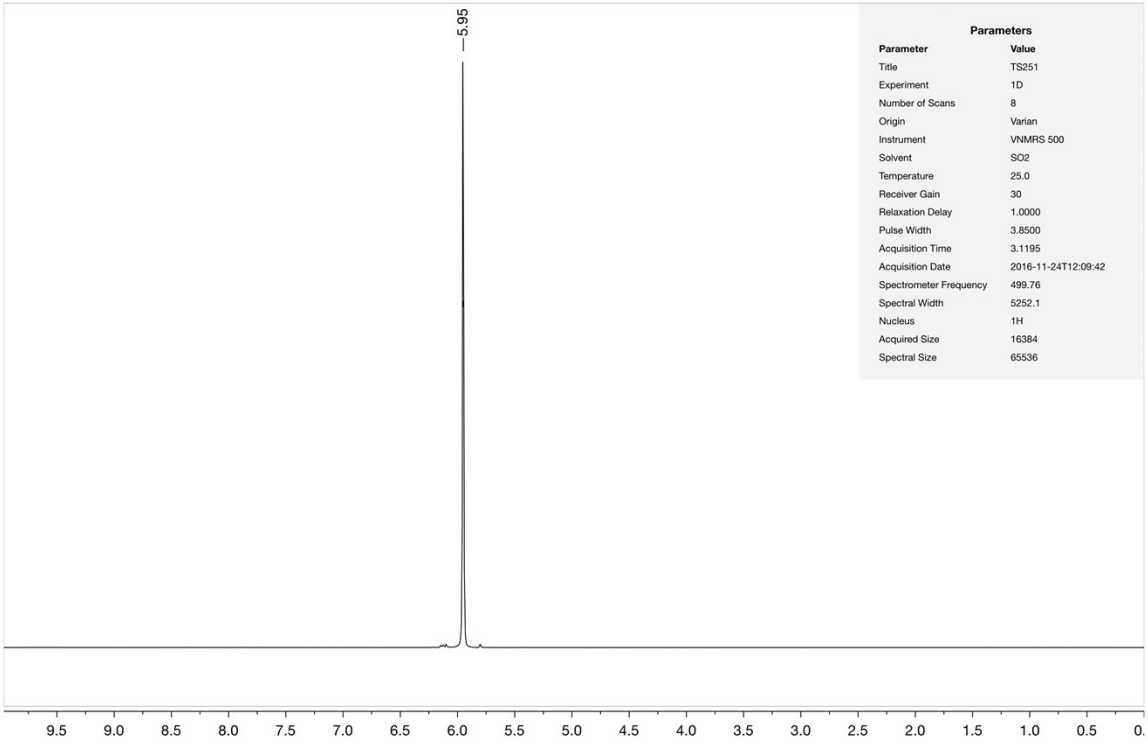
^{19}F - $NCCH_2CN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS253
Experiment	1D
Number of Scans	32
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.8667
Acquisition Time	0.6029
Acquisition Date	2016-11-25T16:34:35
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

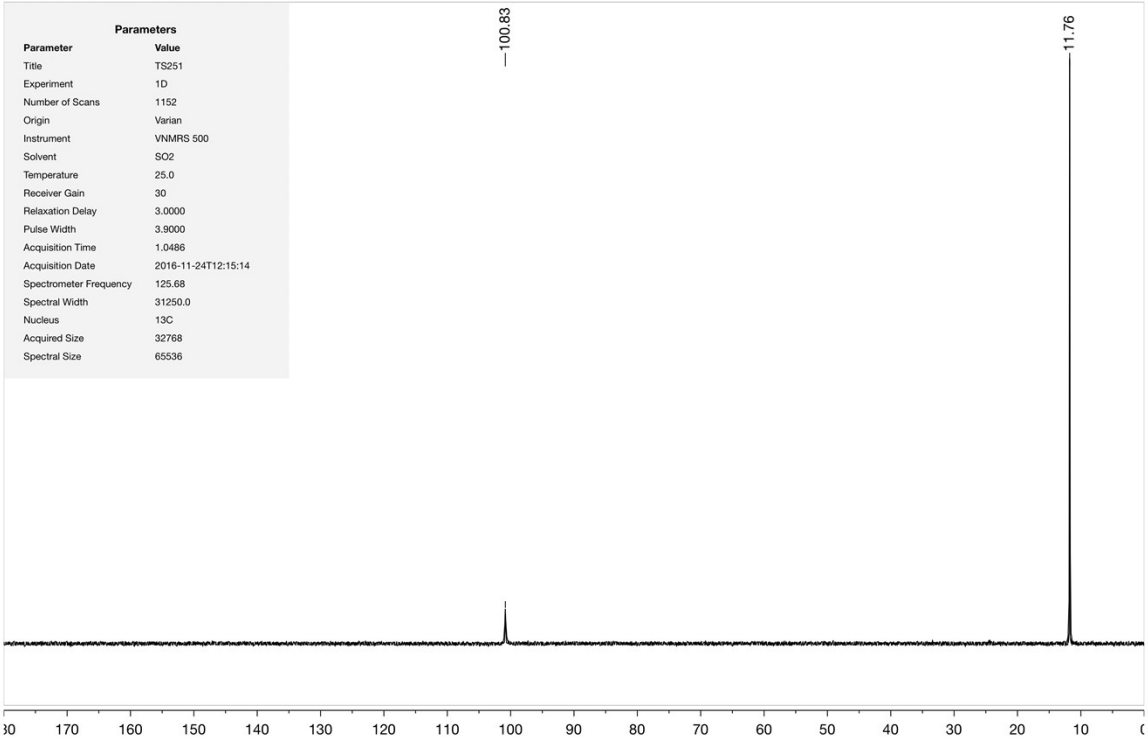
AsF_5•$NCCH_2CN$•AsF_5

^1H - AsF_5•$NCCH_2CN$•AsF_5



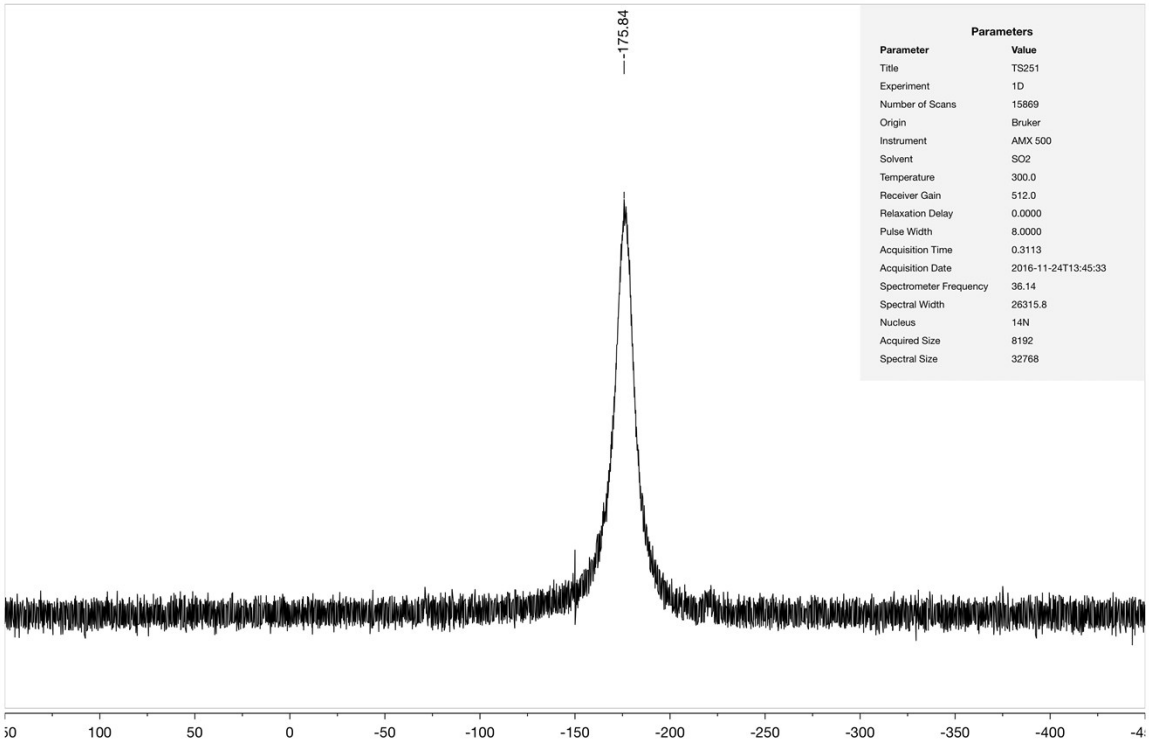
Parameters	
Parameter	**Value**
Title	TS251
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	3.1195
Acquisition Date	2016-11-24T12:09:42
Spectrometer Frequency	499.76
Spectral Width	5252.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

^{13}C - AsF_5•$NCCH_2CN$•AsF_5



Parameters	
Parameter	**Value**
Title	TS251
Experiment	1D
Number of Scans	1152
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	3.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-24T12:15:14
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

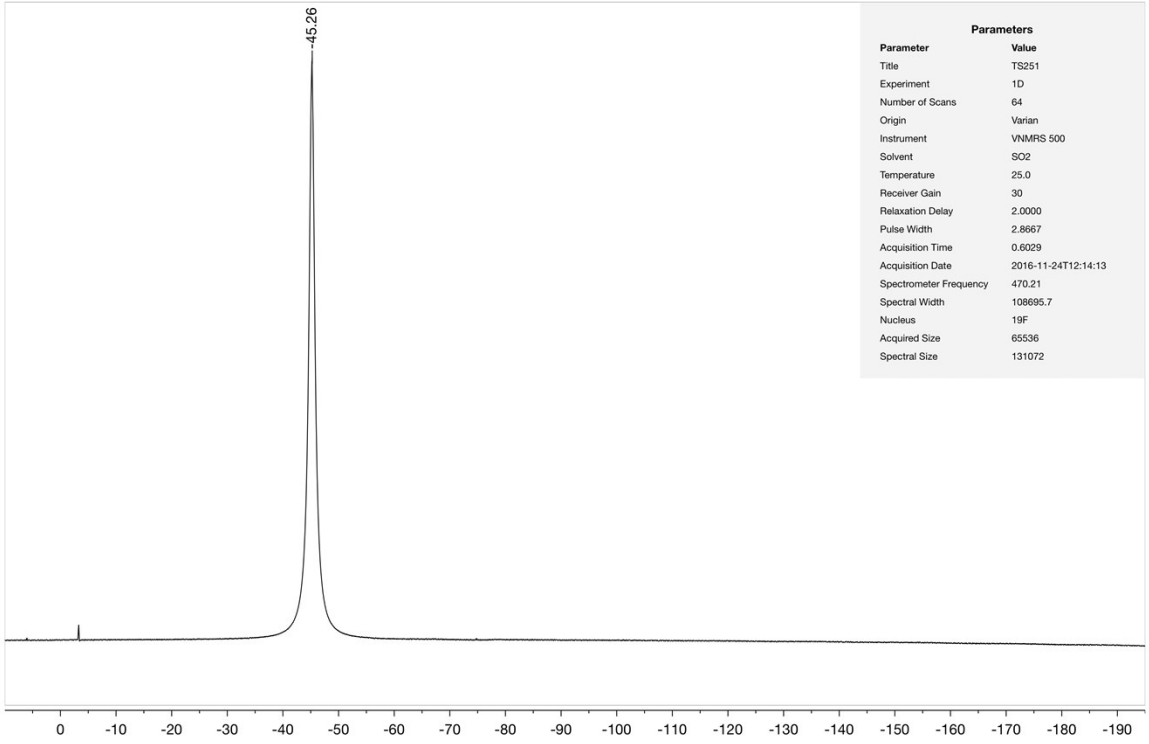
^{14}N - $AsF_5 \cdot NCCH_2CN \cdot AsF_5$



Parameters

Parameter	Value
Title	TS251
Experiment	1D
Number of Scans	15869
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2016-11-24T13:45:33
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	32768

^{19}F - $AsF_5 \cdot NCCH_2CN \cdot AsF_5$

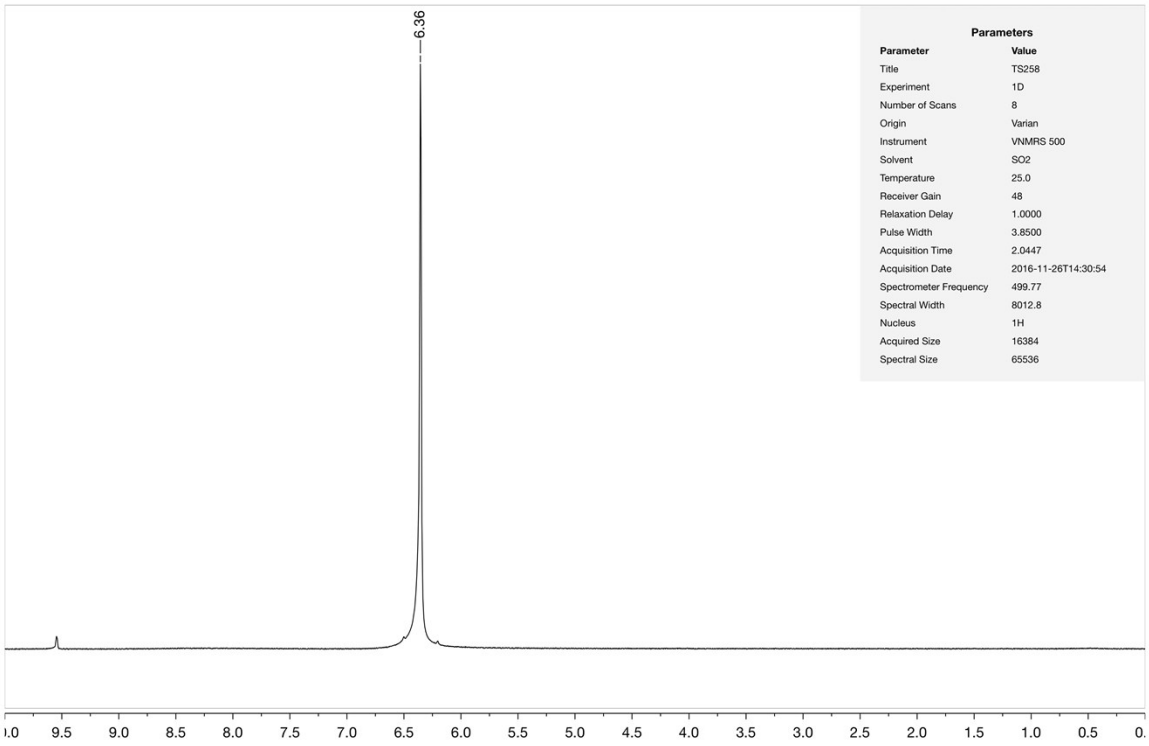


Parameters

Parameter	Value
Title	TS251
Experiment	1D
Number of Scans	64
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	2.0000
Pulse Width	2.8667
Acquisition Time	0.6029
Acquisition Date	2016-11-24T12:14:13
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

SbF_5•$NCCH_2CN$•SbF_5

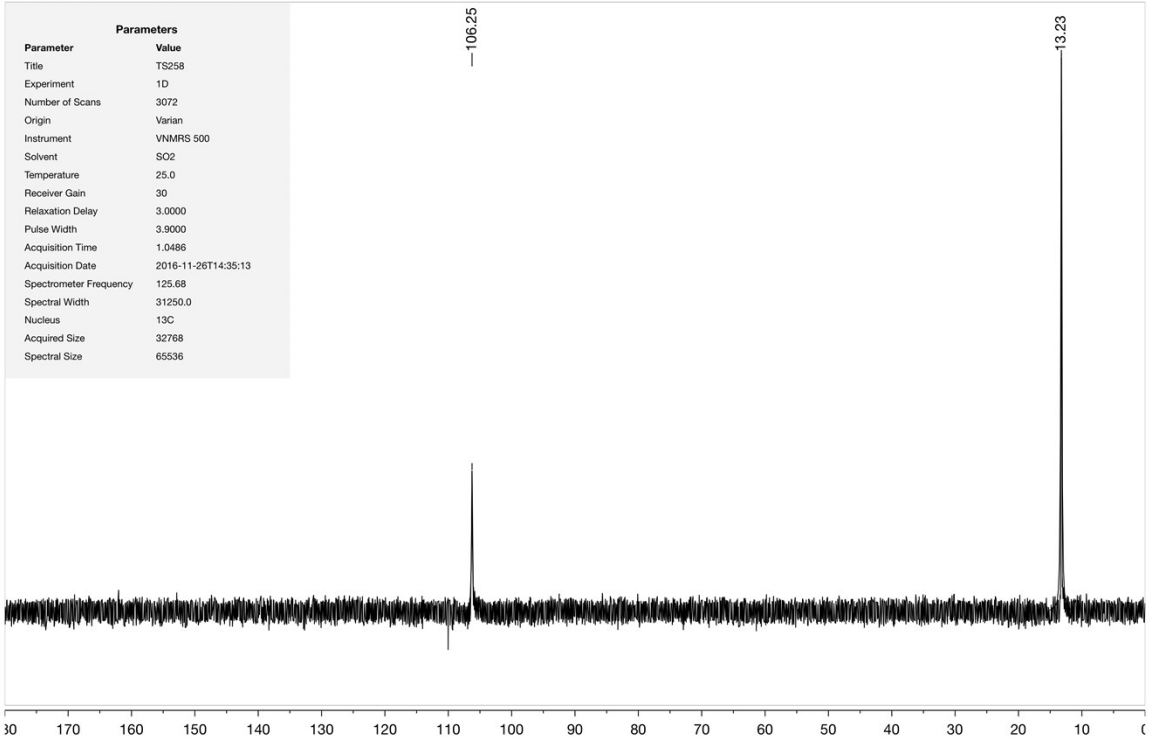
^1H - SbF_5•$NCCH_2CN$•SbF_5



Parameters

Parameter	Value
Title	TS258
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	48
Relaxation Delay	1.0000
Pulse Width	3.8500
Acquisition Time	2.0447
Acquisition Date	2016-11-26T14:30:54
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

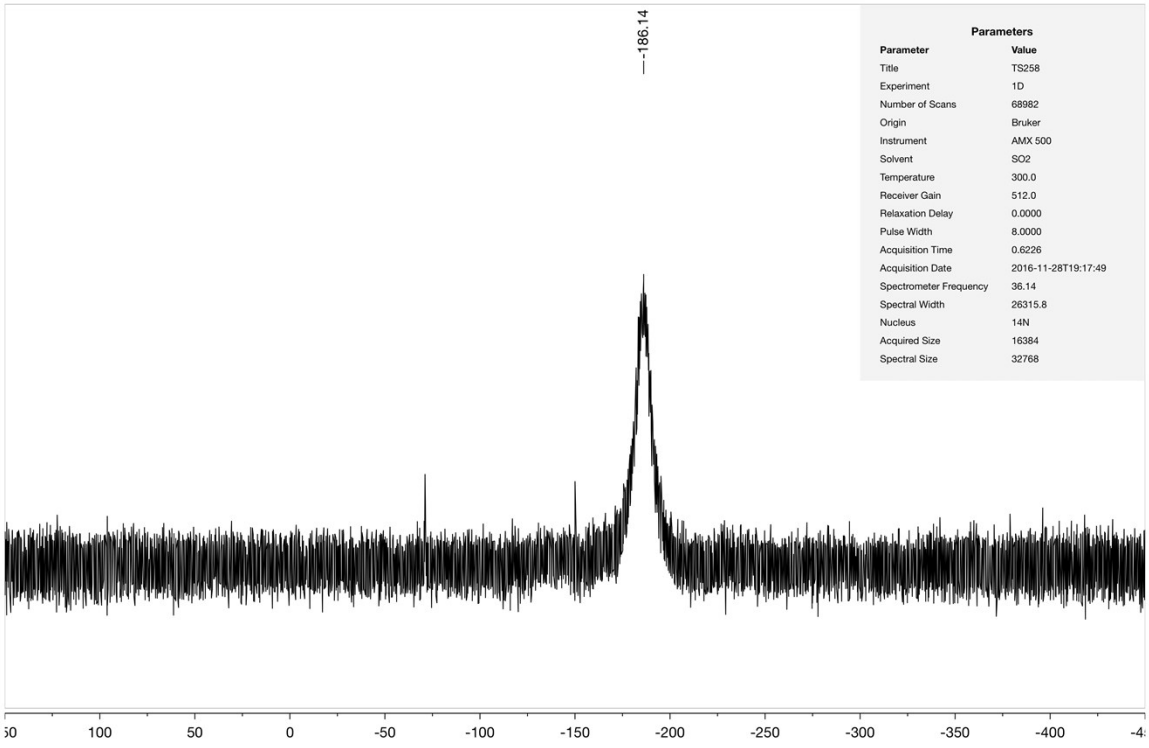
^{13}C - SbF_5•$NCCH_2CN$•SbF_5



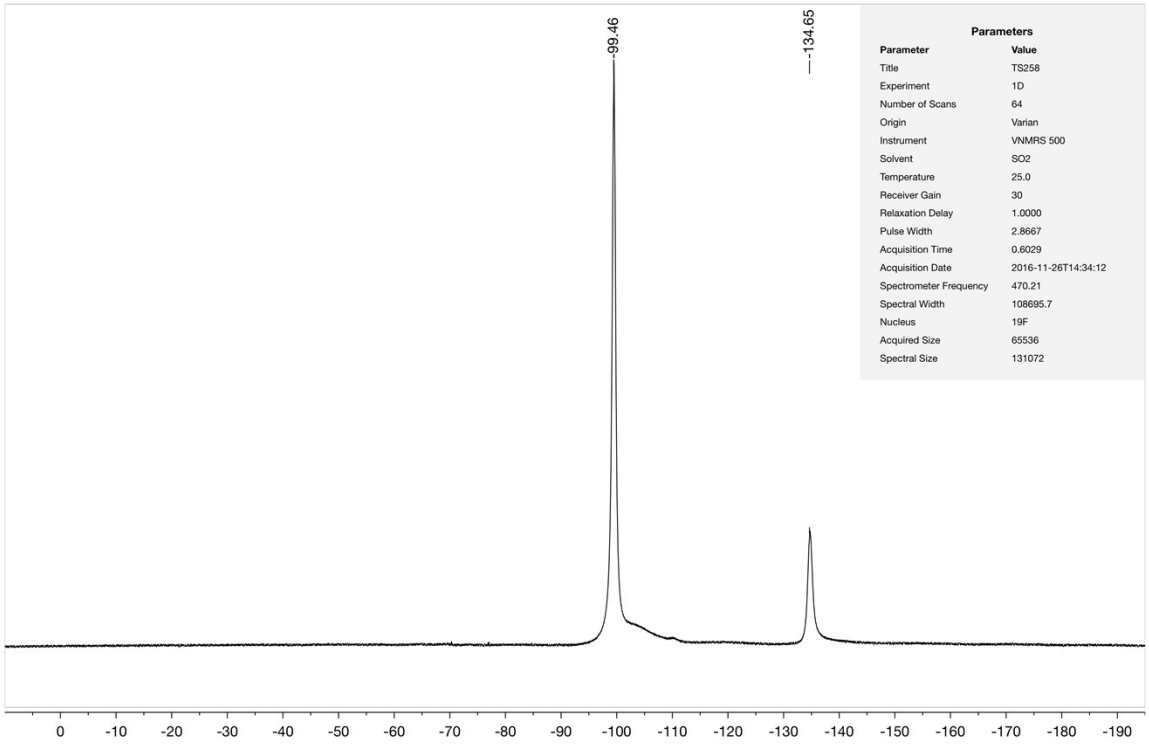
Parameters

Parameter	Value
Title	TS258
Experiment	1D
Number of Scans	3072
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	3.0000
Pulse Width	3.9000
Acquisition Time	1.0486
Acquisition Date	2016-11-26T14:35:13
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $SbF_5 \cdot NCCH_2CN \cdot SbF_5$



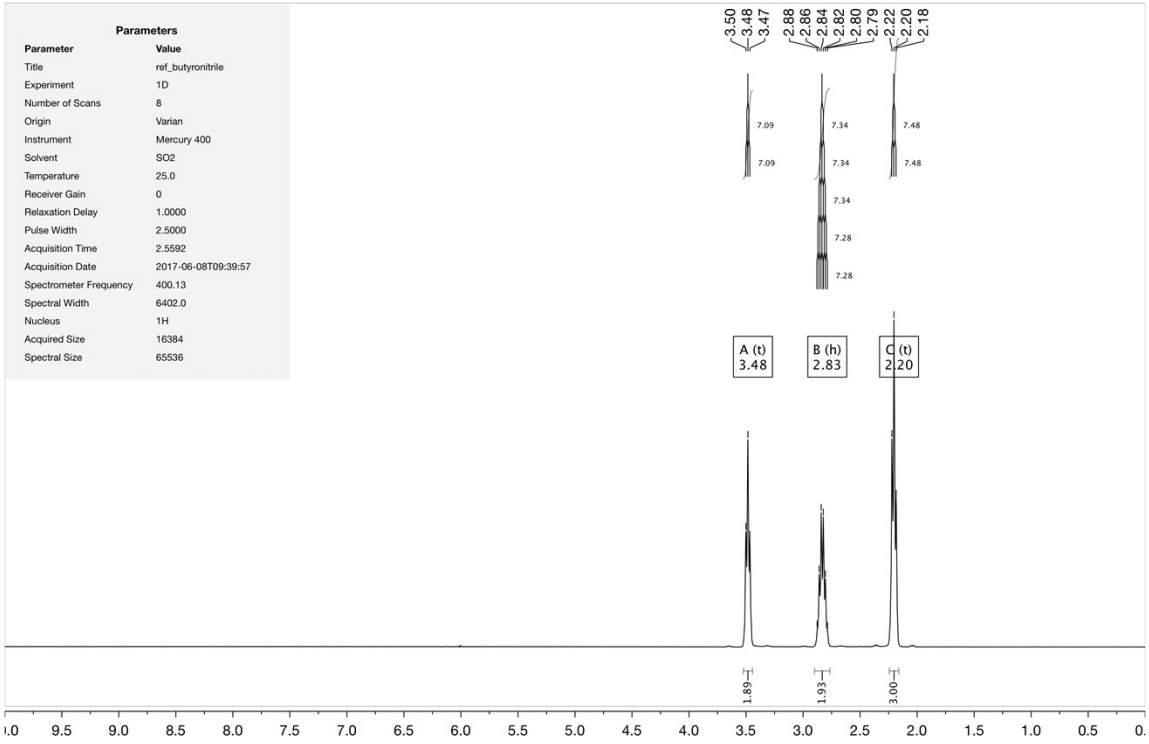
^{19}F - $SbF_5 \cdot NCCH_2CN \cdot SbF_5$



C_3H_7CN

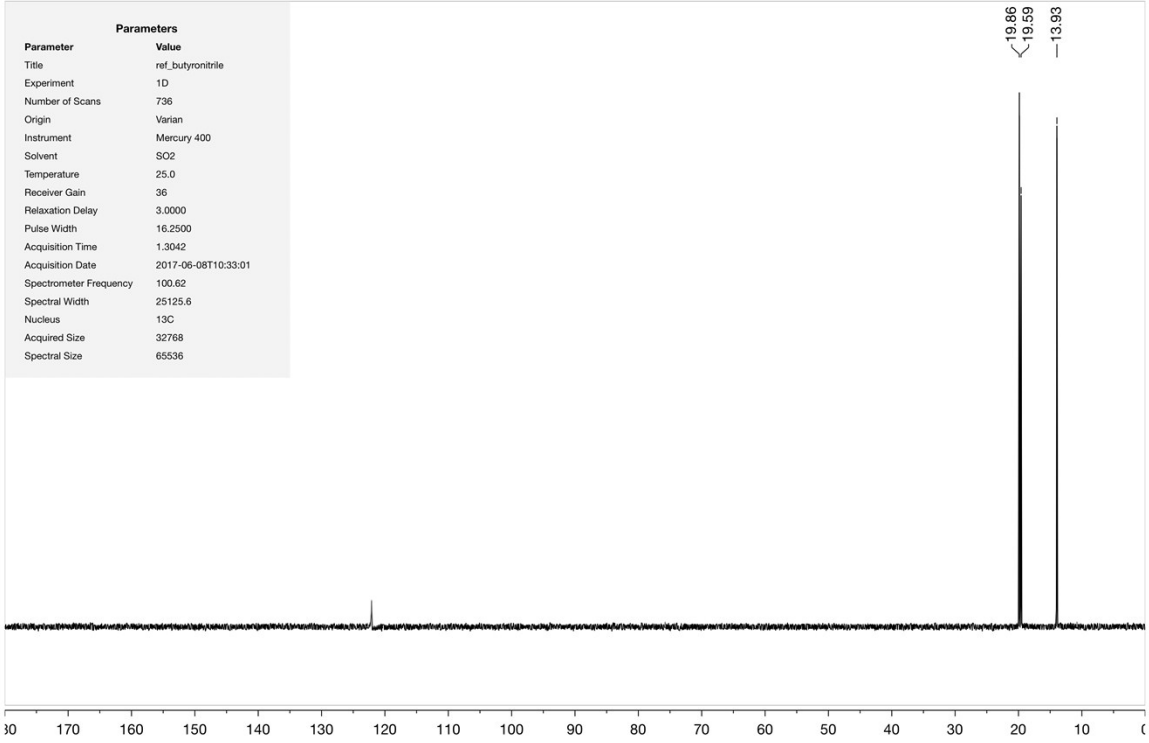
^1H - C_3H_7CN

Parameters	
Parameter	**Value**
Title	ref_butyronitrile
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	Mercury 400
Solvent	SO2
Temperature	25.0
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	2.5000
Acquisition Time	2.5592
Acquisition Date	2017-06-08T09:39:57
Spectrometer Frequency	400.13
Spectral Width	6402.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

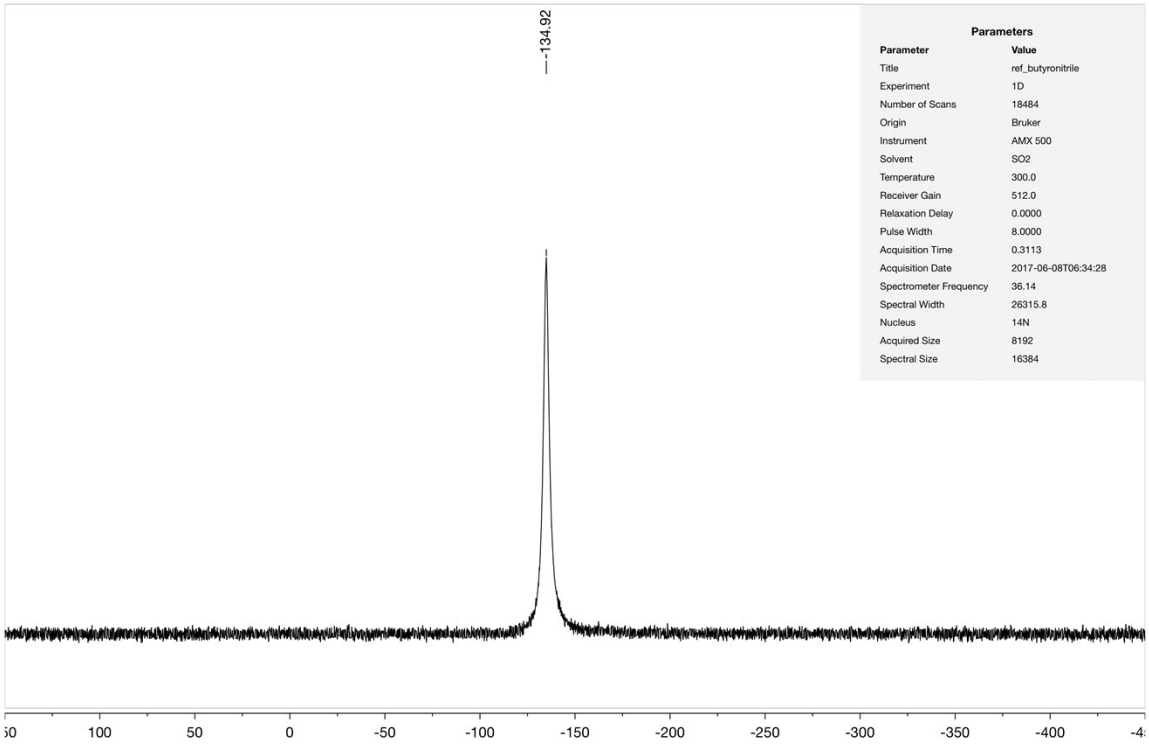


^{13}C - C_3H_7CN

Parameters	
Parameter	**Value**
Title	ref_butyronitrile
Experiment	1D
Number of Scans	736
Origin	Varian
Instrument	Mercury 400
Solvent	SO2
Temperature	25.0
Receiver Gain	36
Relaxation Delay	3.0000
Pulse Width	16.2500
Acquisition Time	1.3042
Acquisition Date	2017-06-08T10:33:01
Spectrometer Frequency	100.62
Spectral Width	25125.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



^{14}N - C_3H_7CN



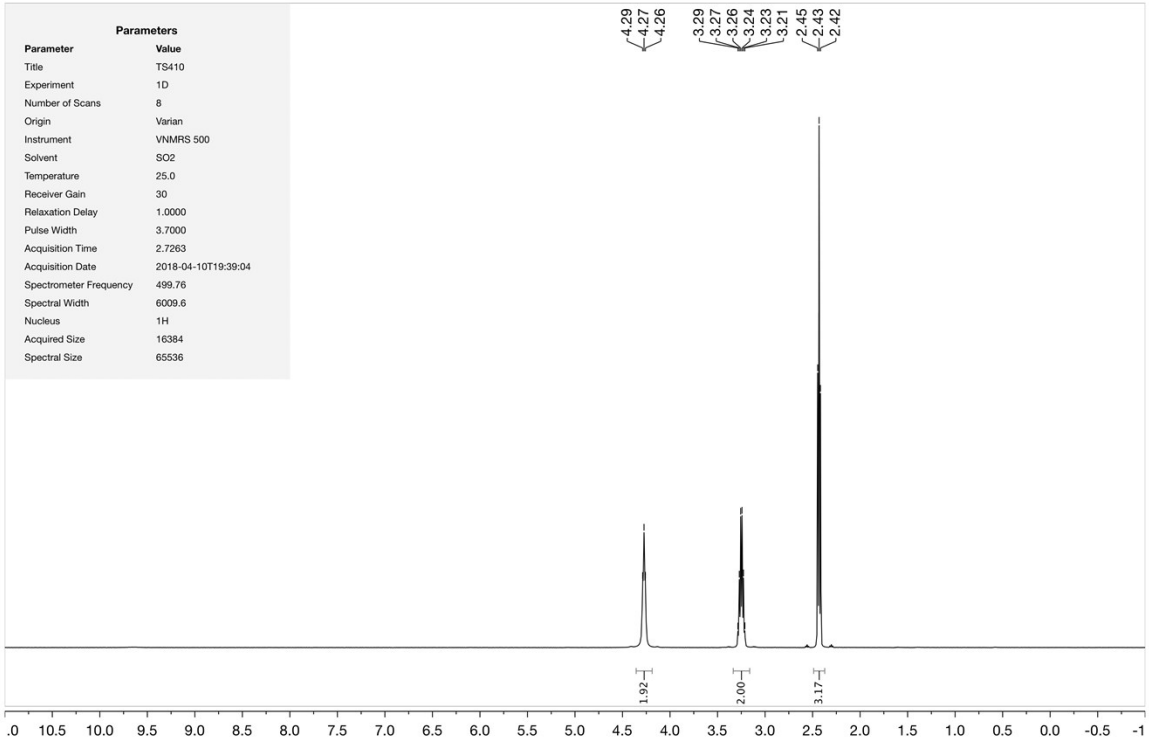
Parameters

Parameter	Value
Title	ref_butyronitrile
Experiment	1D
Number of Scans	18484
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2017-06-08T06:34:28
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

$C_3H_7CN•AsF_5$

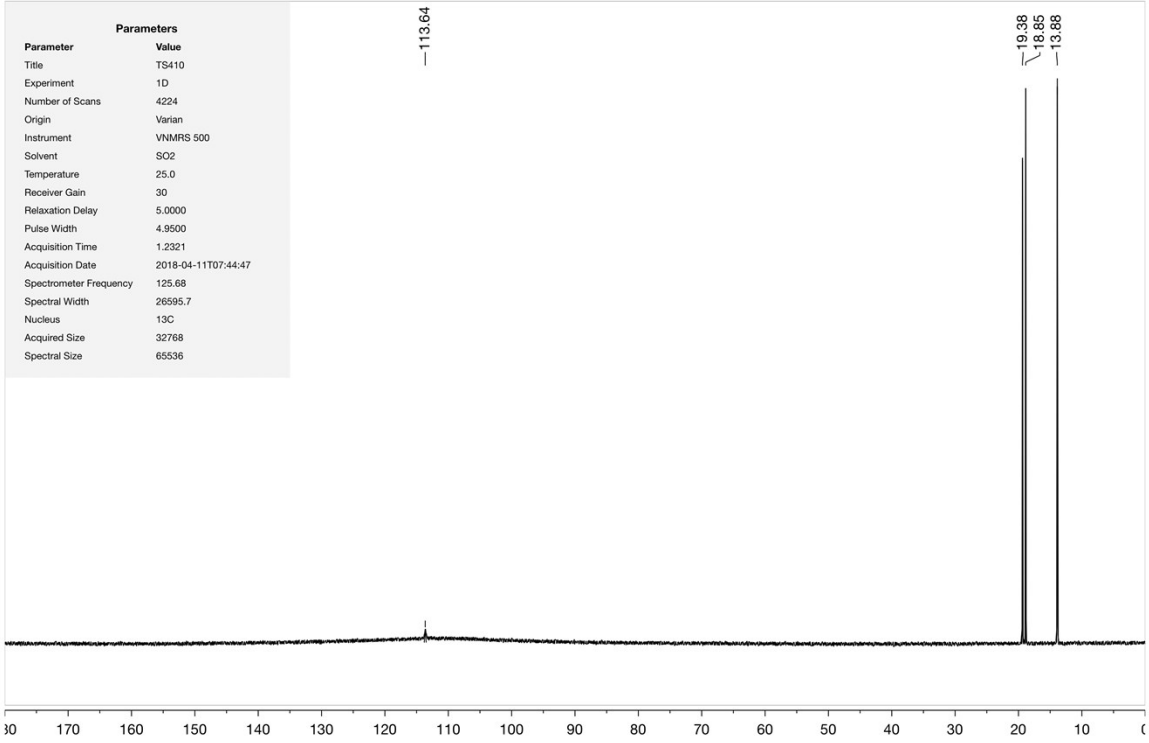
^1H - $C_3H_7CN•AsF_5$

Parameters	
Parameter	**Value**
Title	TS410
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.7263
Acquisition Date	2018-04-10T19:39:04
Spectrometer Frequency	499.76
Spectral Width	6009.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

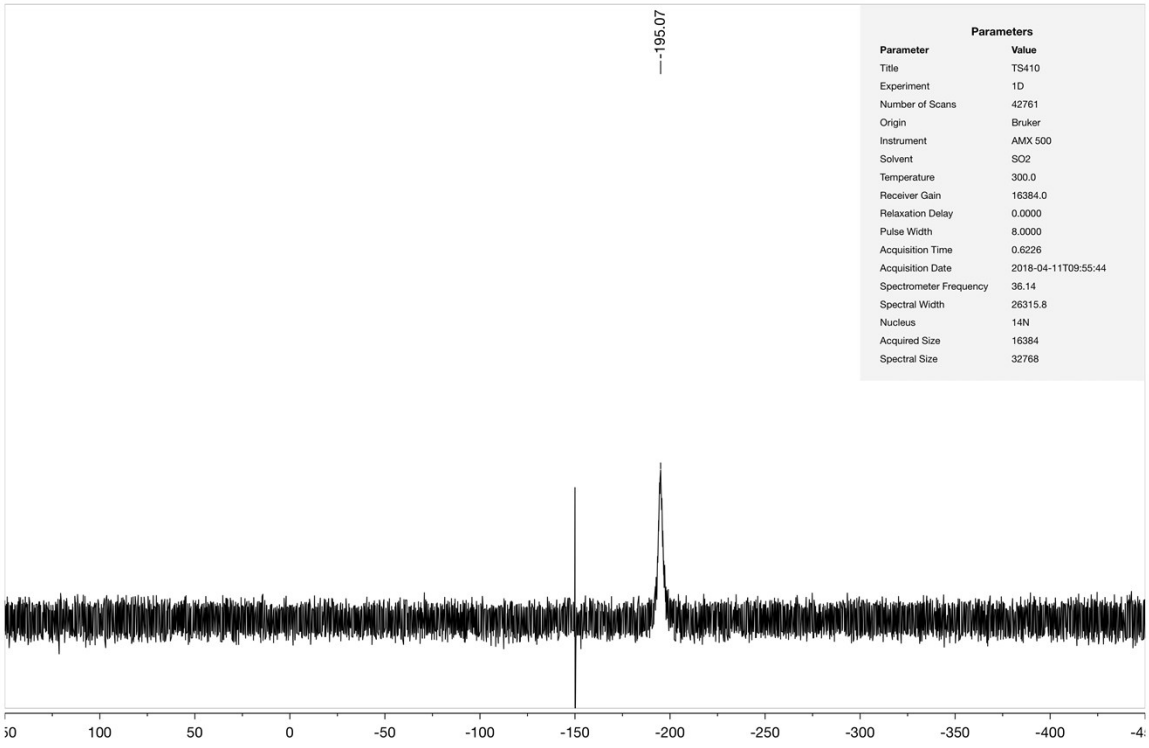


^{13}C - $C_3H_7CN•AsF_5$

Parameters	
Parameter	**Value**
Title	TS410
Experiment	1D
Number of Scans	4224
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	4.9500
Acquisition Time	1.2321
Acquisition Date	2018-04-11T07:44:47
Spectrometer Frequency	125.68
Spectral Width	26595.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



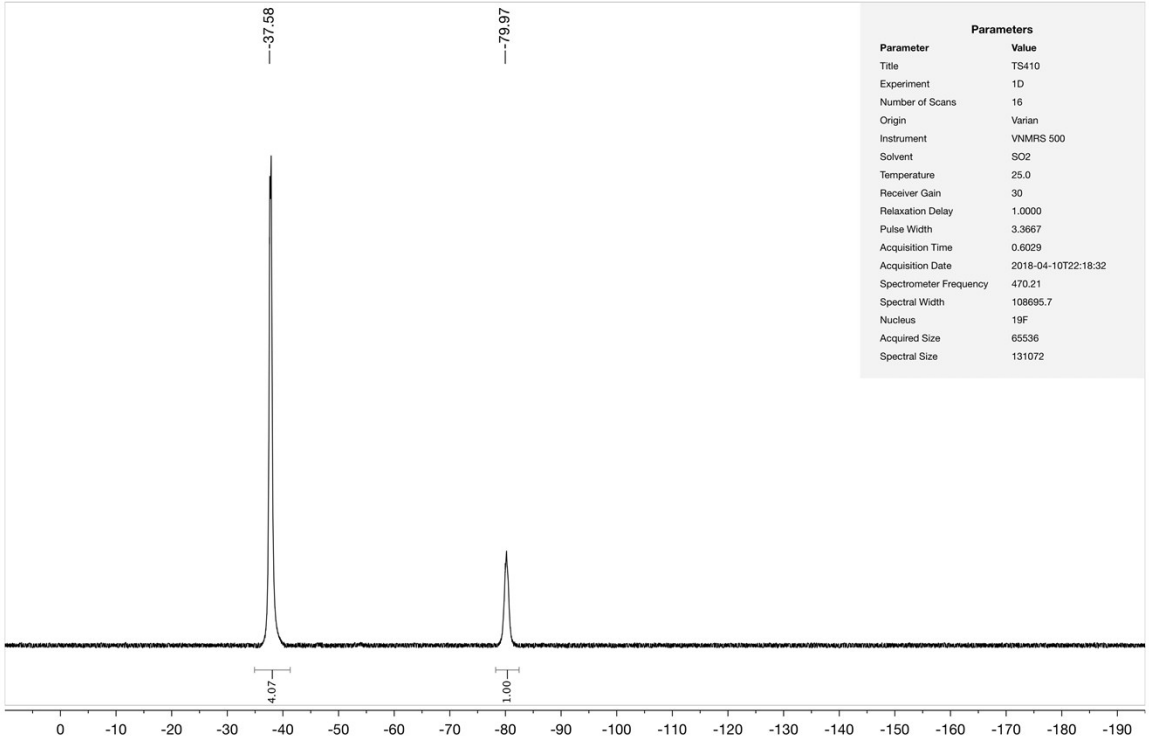
^{14}N - $C_3H_7CN{\cdot}AsF_5$



Parameters

Parameter	Value
Title	TS410
Experiment	1D
Number of Scans	42761
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	16384.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2018-04-11T09:55:44
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

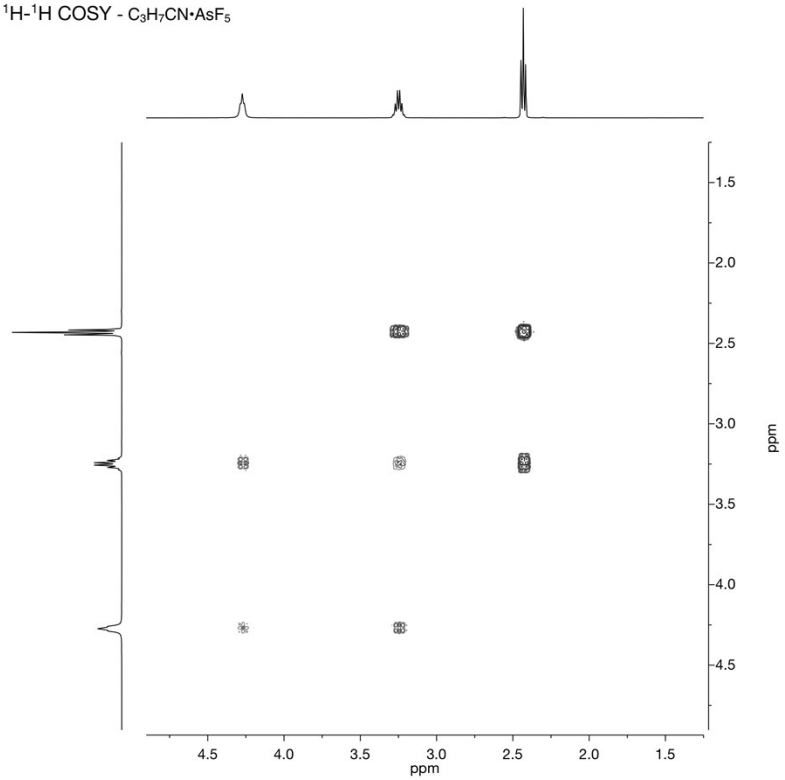
^{19}F - $C_3H_7CN{\cdot}AsF_5$



Parameters

Parameter	Value
Title	TS410
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2018-04-10T22:18:32
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

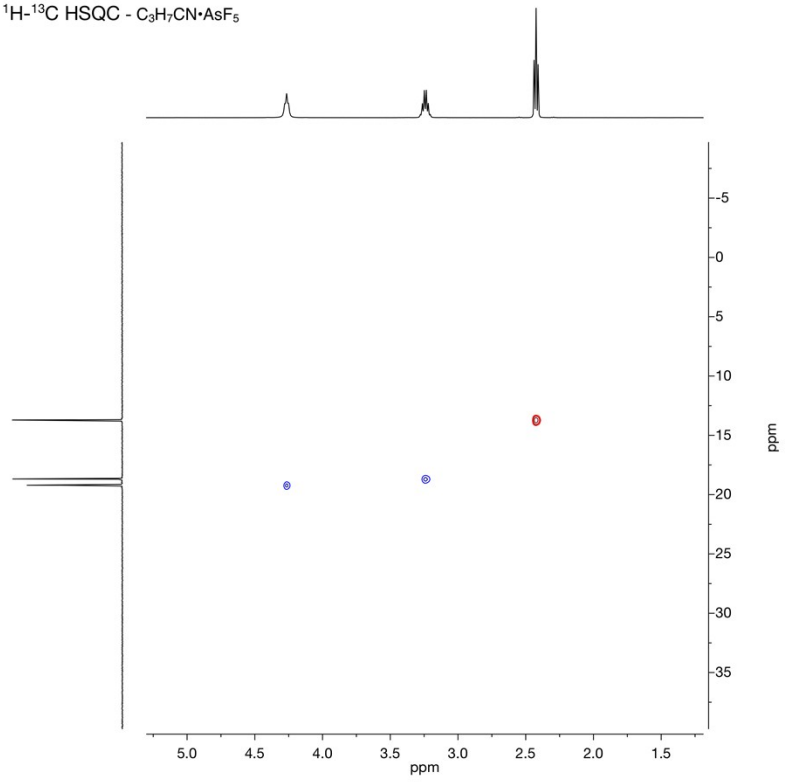
^{1}H-^{1}H COSY - $C_3H_7CN{\cdot}AsF_5$



Parameters

Parameter	Value
Title	TS410
Experiment	COSY
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Pulse Sequence	gCOSY
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	7.4000
Acquisition Time	0.1500
Acquisition Date	2018-04-10T23:02:58
Nucleus	(1H, 1H)
Spectrometer Frequency	(499.76, 499.76)
Spectral Width	(1899.7, 1899.7)
Lowest Frequency	(550.8, 550.8)
Acquired Size	(285, 256)
Spectral Size	(512, 512)

^{1}H-^{13}C HSQC - $C_3H_7CN{\cdot}AsF_5$



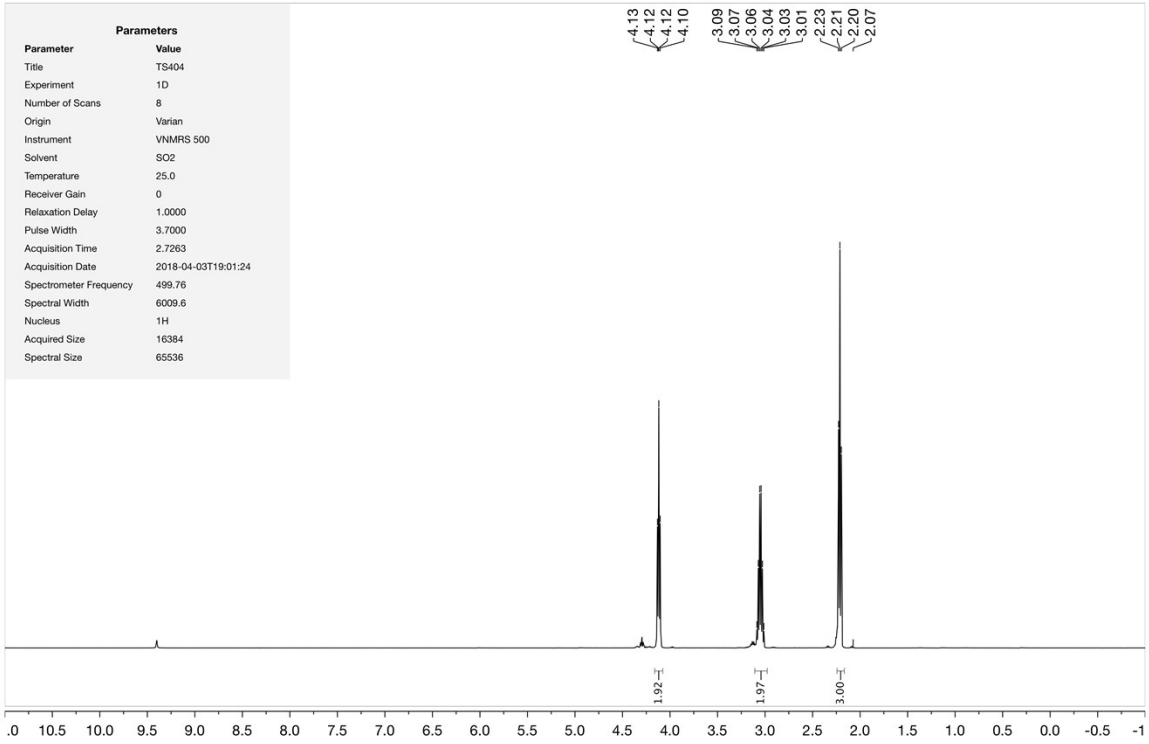
Parameters

Parameter	Value
Title	TS410
Experiment	HSQC
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Pulse Sequence	gHSQCAD
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	7.4000
Acquisition Time	0.1499
Acquisition Date	2018-04-11T00:25:43
Nucleus	(1H, 13C)
Spectrometer Frequency	(499.76, 125.68)
Spectral Width	(6009.6, 25133.5)
Lowest Frequency	(-506.0, -1256.9)
Acquired Size	(901, 256)
Spectral Size	(1024, 1024)

$C_3H_7CN•SbF_5$

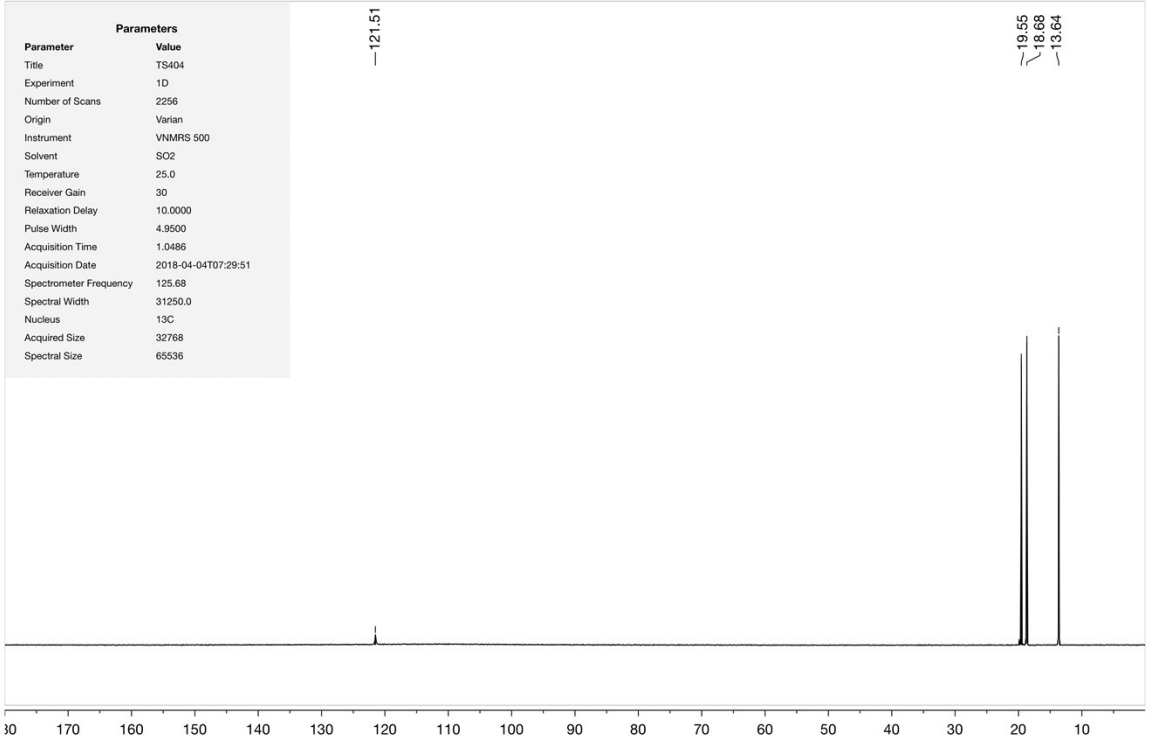
^1H - $C_3H_7CN•SbF_5$

Parameters	
Parameter	**Value**
Title	TS404
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.7263
Acquisition Date	2018-04-03T19:01:24
Spectrometer Frequency	499.76
Spectral Width	6009.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

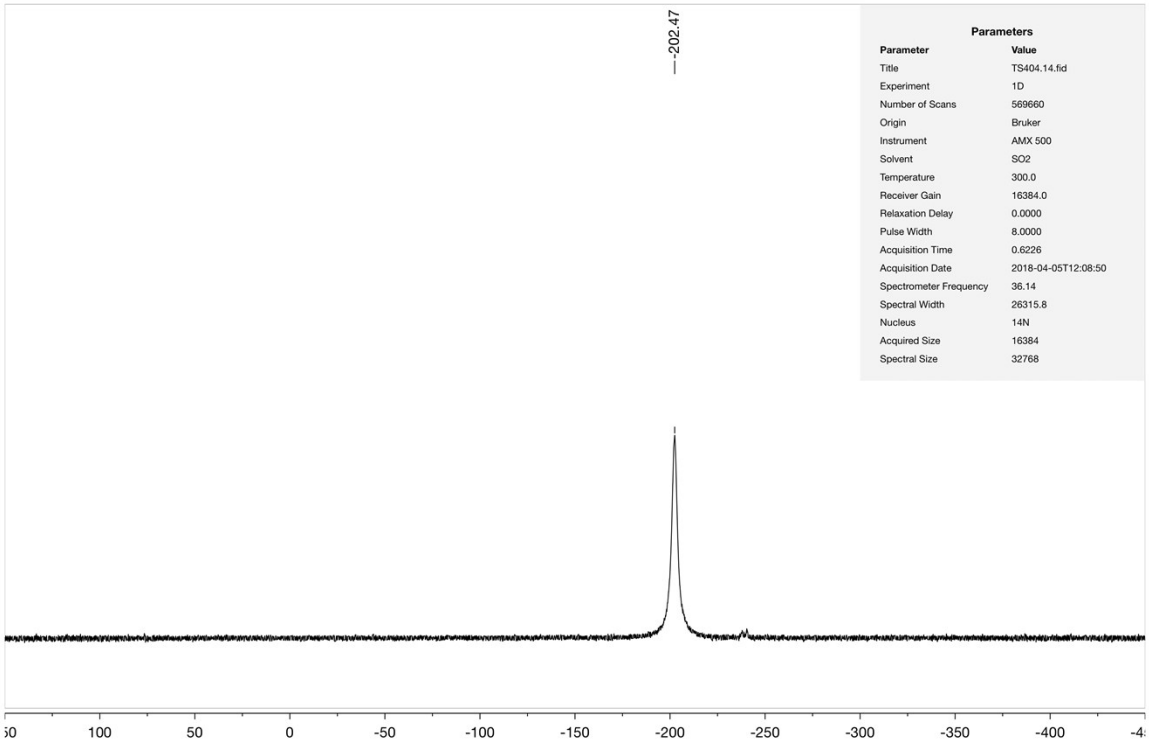


^{13}C - $C_3H_7CN•SbF_5$

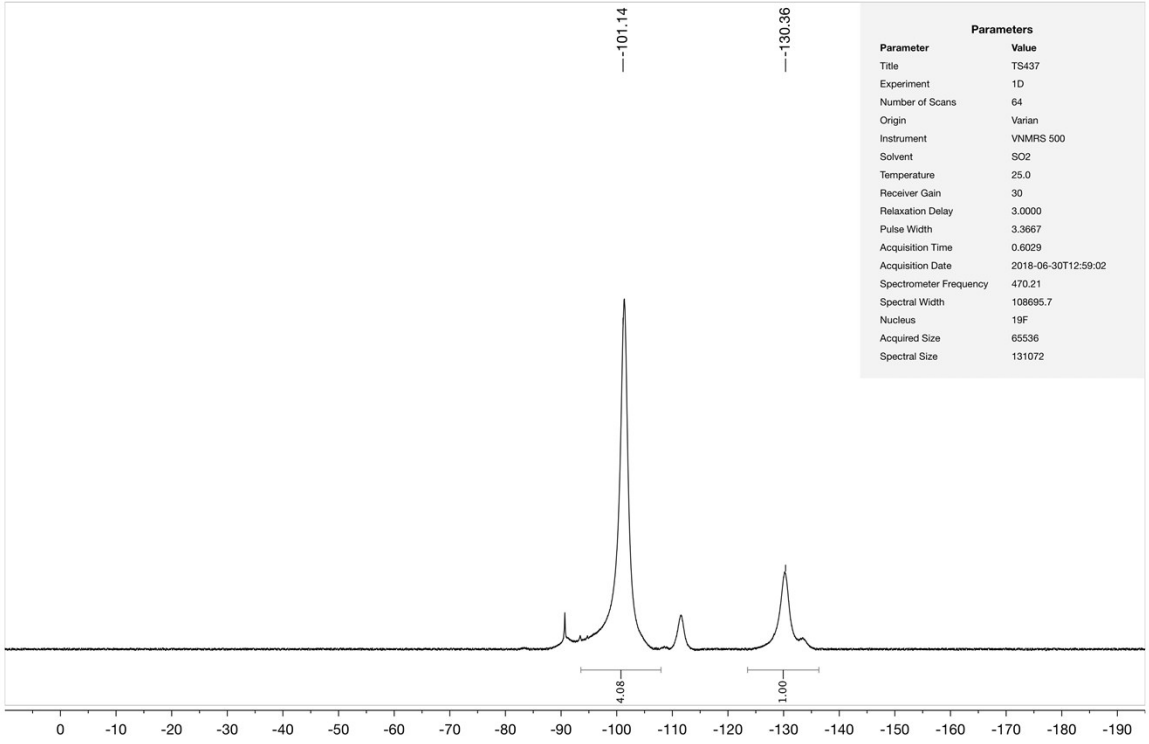
Parameters	
Parameter	**Value**
Title	TS404
Experiment	1D
Number of Scans	2256
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	10.0000
Pulse Width	4.9500
Acquisition Time	1.0486
Acquisition Date	2018-04-04T07:29:51
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



^{14}N - $C_3H_7CN{\cdot}SbF_5$

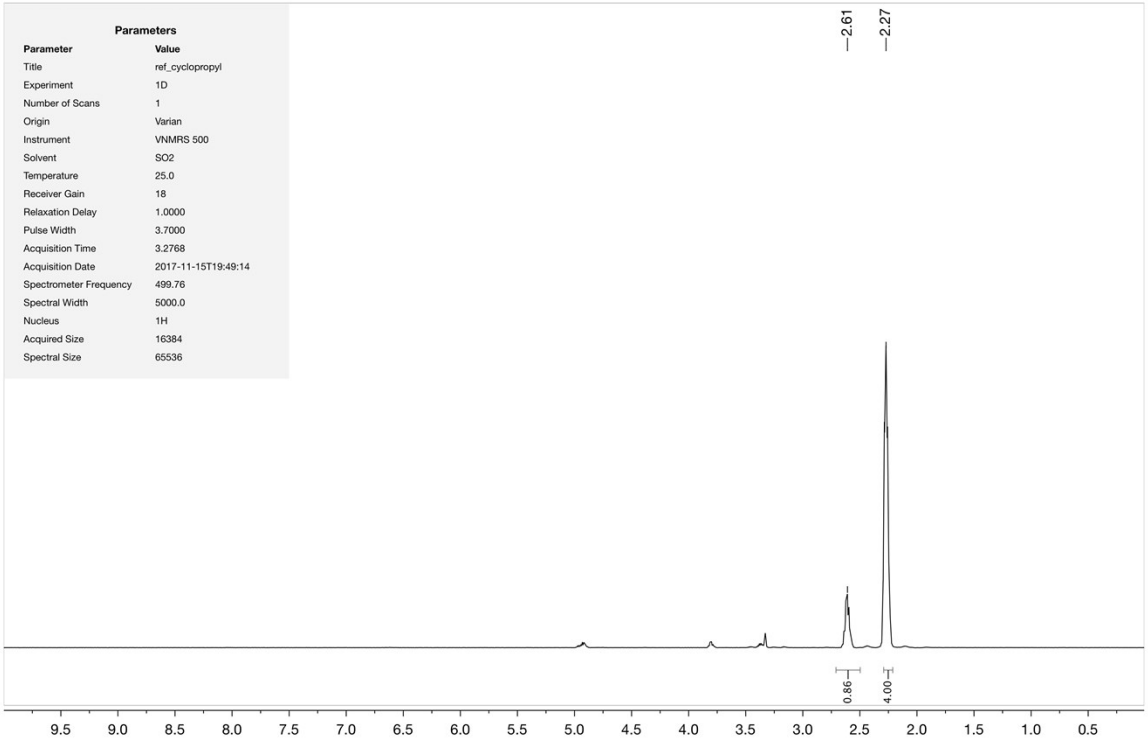


^{19}F - $C_3H_7CN{\cdot}SbF_5$



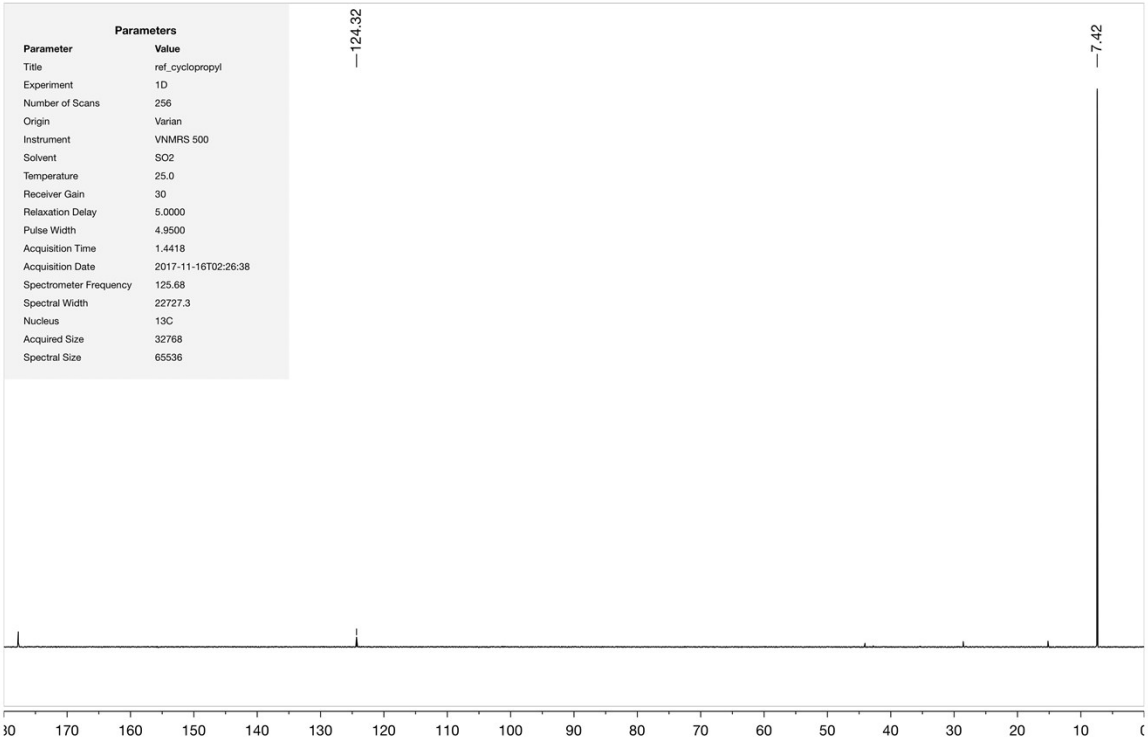
cyclo-C_3H_5CN

^1H - *c*-C_3H_5CCN



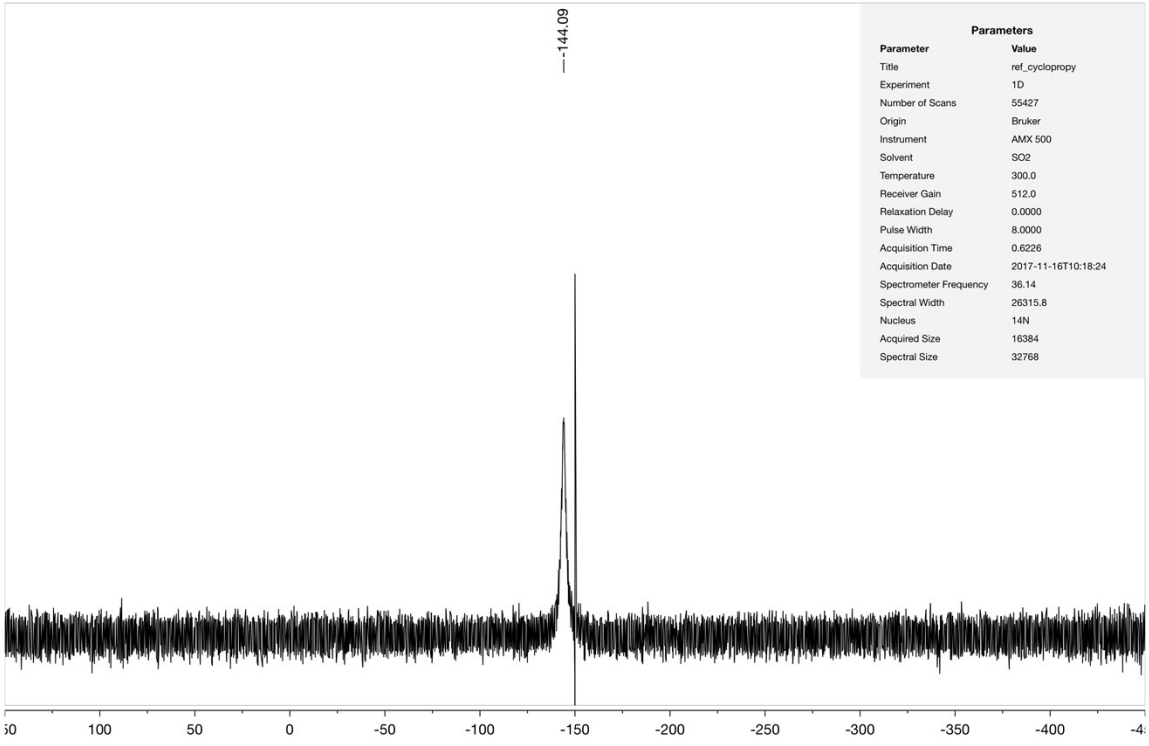
Parameters	
Parameter	**Value**
Title	ref_cyclopropyl
Experiment	1D
Number of Scans	1
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	18
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	3.2768
Acquisition Date	2017-11-15T19:49:14
Spectrometer Frequency	499.76
Spectral Width	5000.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

^{13}C - *c*-C_3H_5CCN



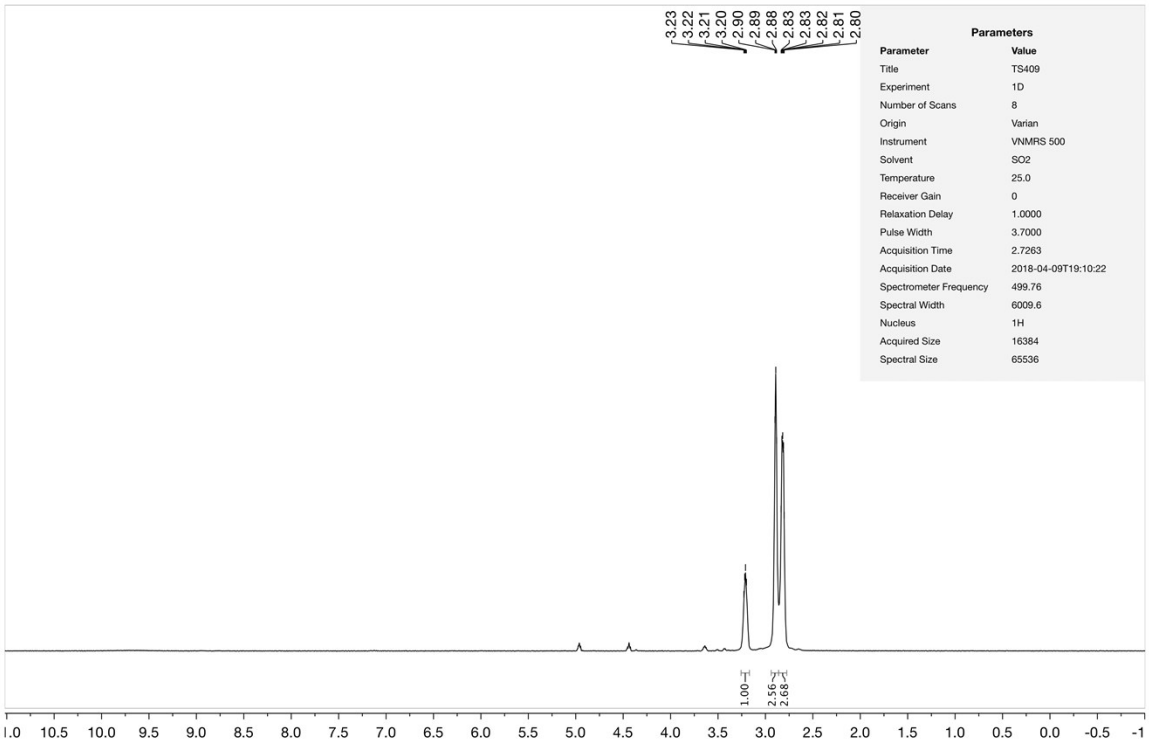
Parameters	
Parameter	**Value**
Title	ref_cyclopropyl
Experiment	1D
Number of Scans	256
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	4.9500
Acquisition Time	1.4418
Acquisition Date	2017-11-16T02:26:38
Spectrometer Frequency	125.68
Spectral Width	22727.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - *c*-C_3H_5CCN



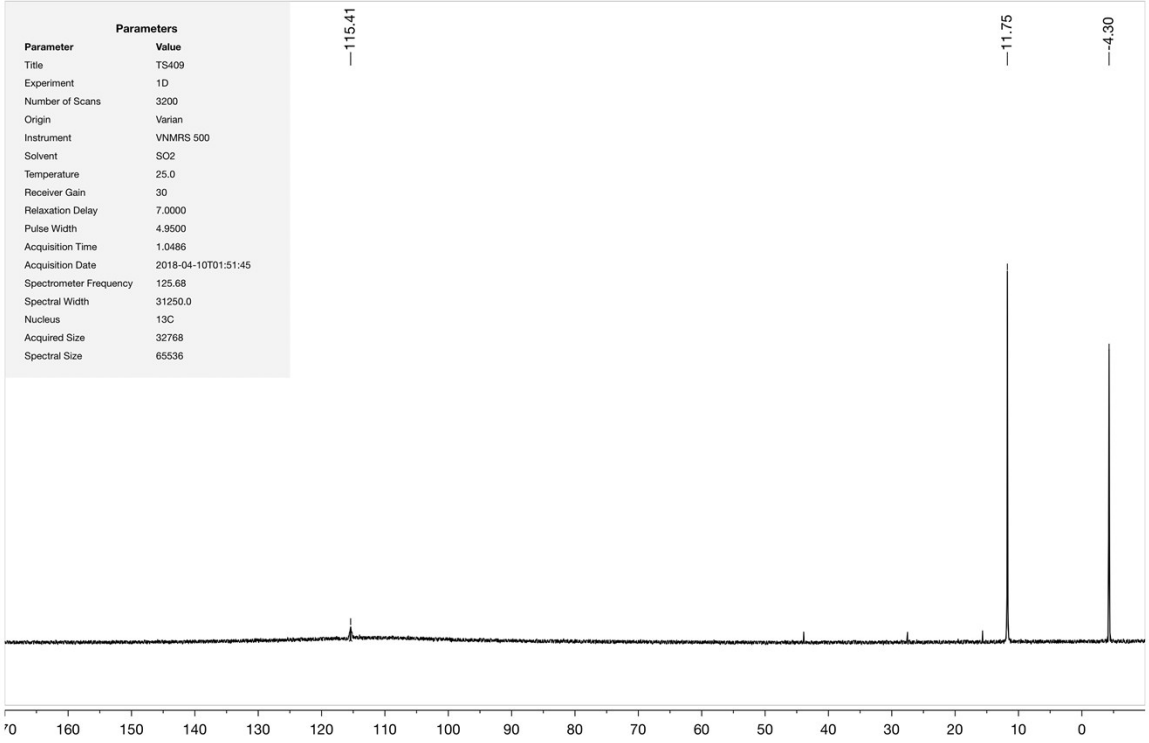
cyclo-$C_3H_5CN{\bullet}AsF_5$

^1H - *c*-$C_3H_5CN{\bullet}AsF_5$



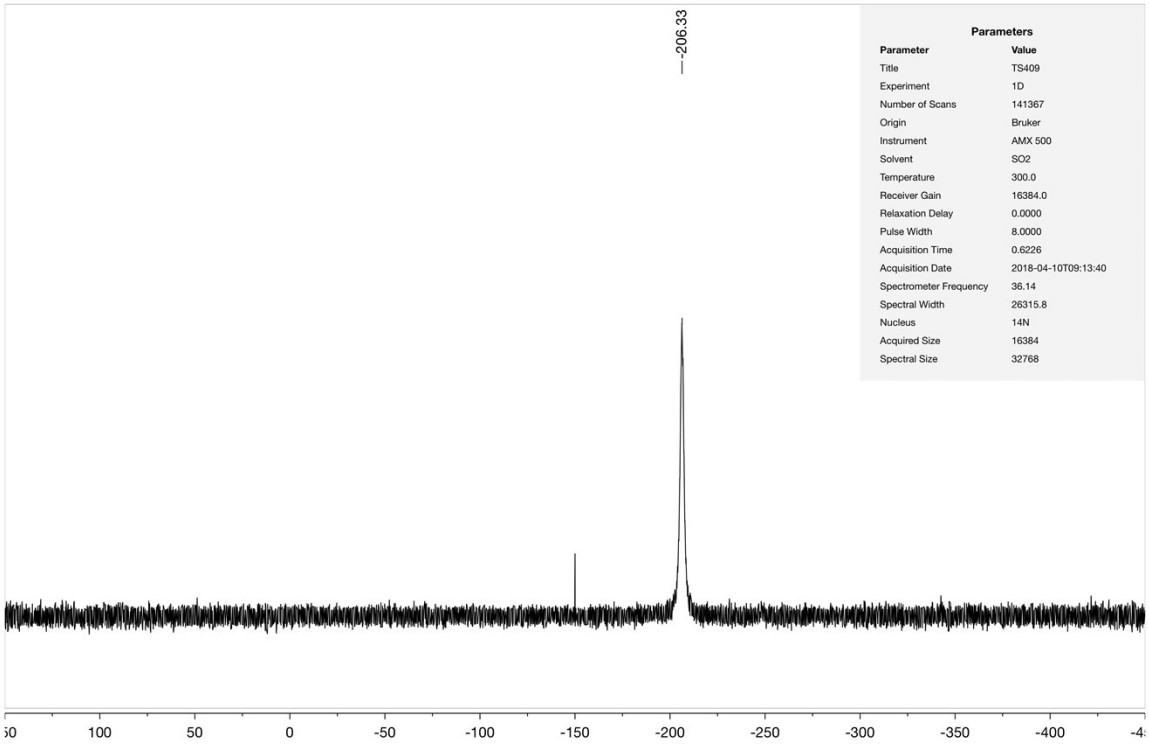
Parameters	
Parameter	**Value**
Title	TS409
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.7263
Acquisition Date	2018-04-09T19:10:22
Spectrometer Frequency	499.76
Spectral Width	6009.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

^{13}C - *c*-$C_3H_5CN{\bullet}AsF_5$

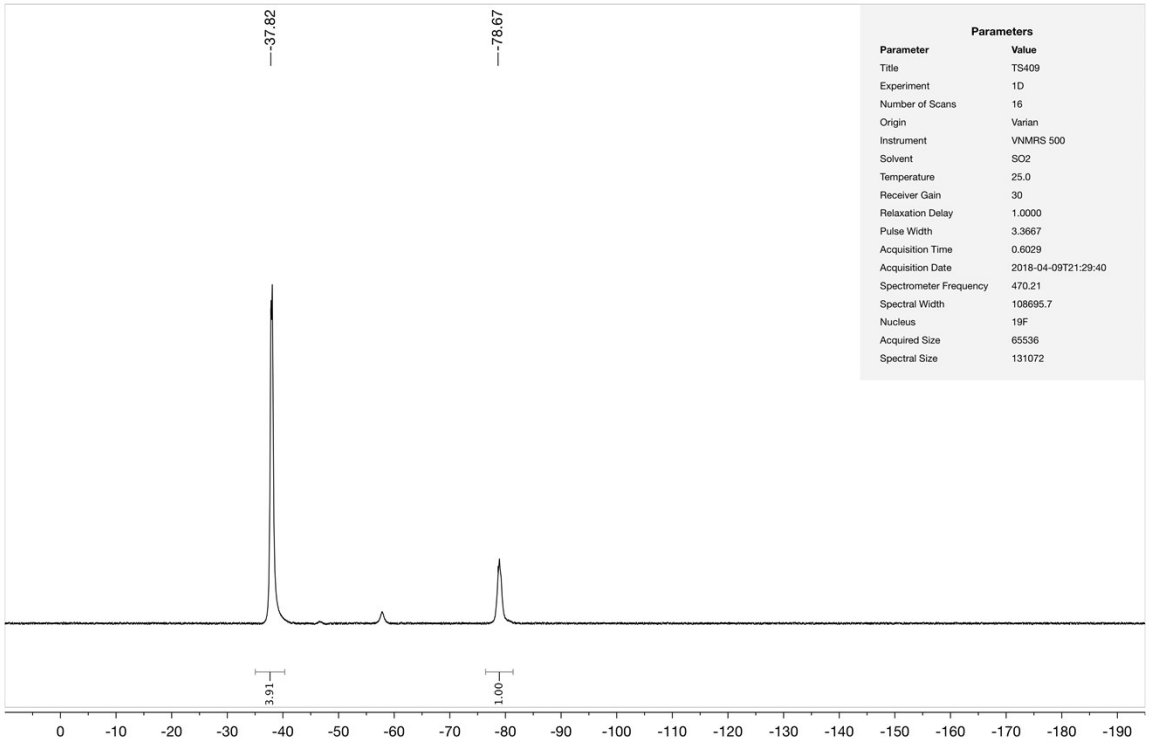


Parameters	
Parameter	**Value**
Title	TS409
Experiment	1D
Number of Scans	3200
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	7.0000
Pulse Width	4.9500
Acquisition Time	1.0486
Acquisition Date	2018-04-10T01:51:45
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - *c*-$C_3H_5CN{\cdot}AsF_5$



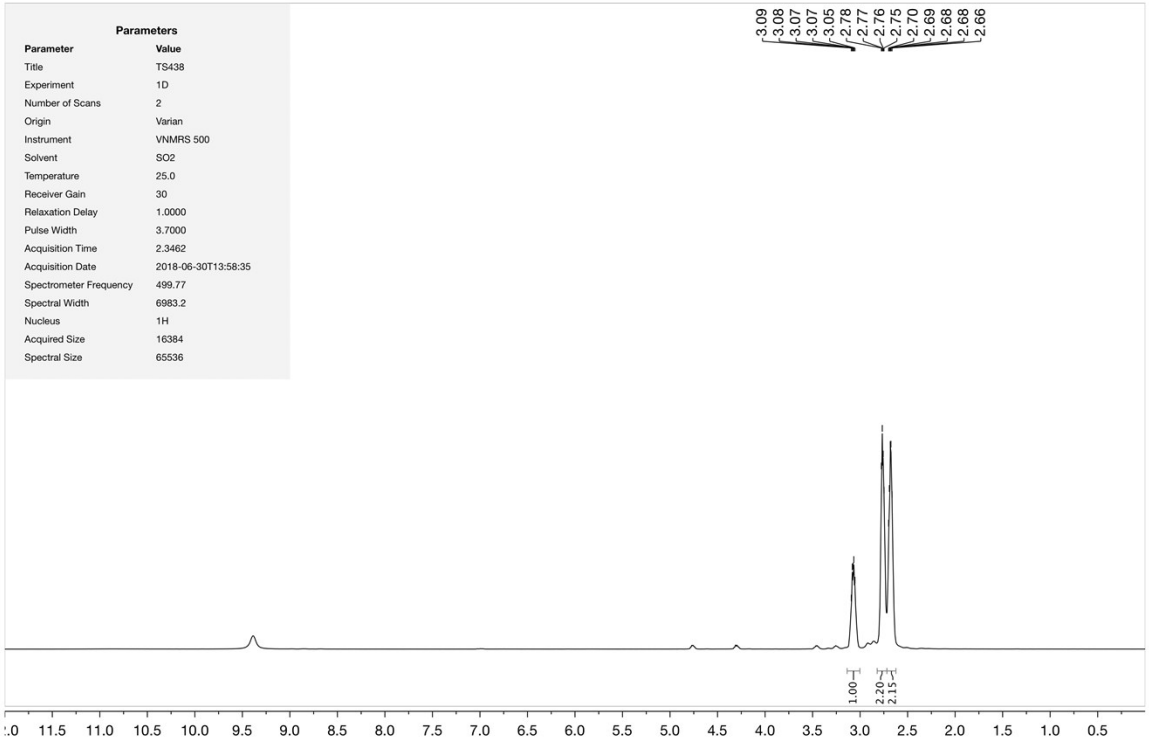
^{19}F - *c*-$C_3H_5CN{\cdot}AsF_5$



cyclo-$C_3H_5CN{\bullet}SbF_5$

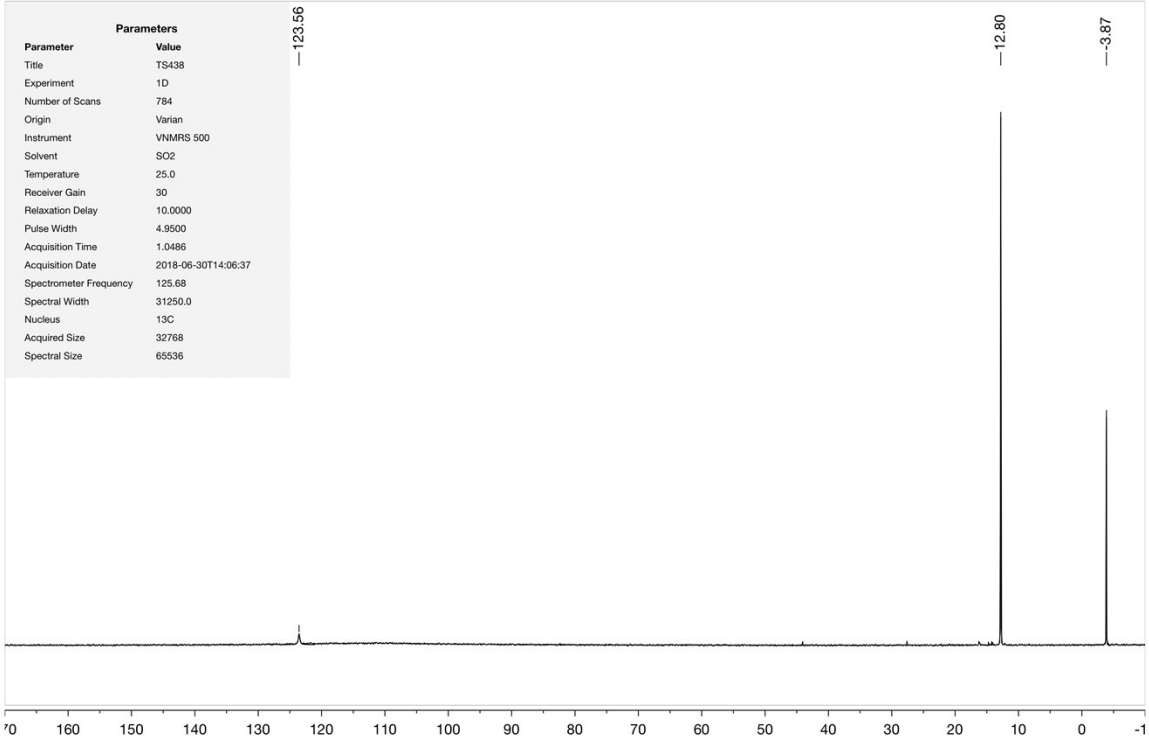
^1H - *c*-$C_3H_5CN{\bullet}SbF_5$

Parameters	
Parameter	**Value**
Title	TS438
Experiment	1D
Number of Scans	2
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.3462
Acquisition Date	2018-06-30T13:58:35
Spectrometer Frequency	499.77
Spectral Width	6983.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

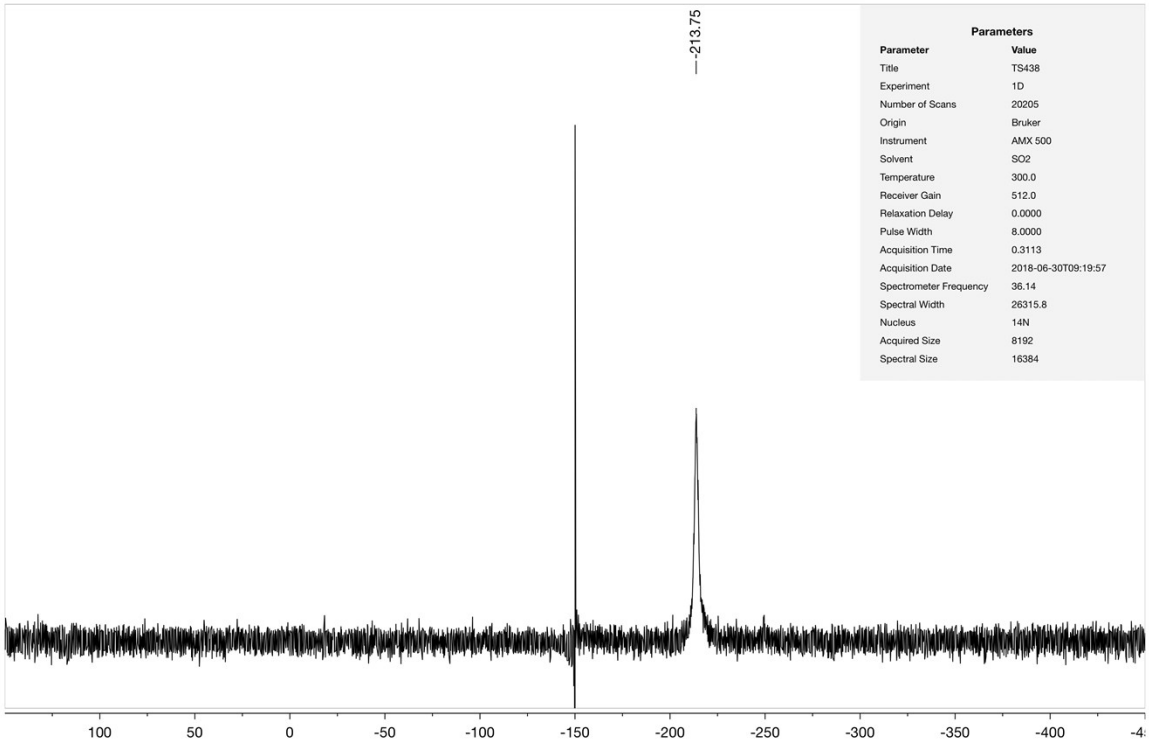


^{13}C - *c*-$C_3H_5CN{\bullet}SbF_5$

Parameters	
Parameter	**Value**
Title	TS438
Experiment	1D
Number of Scans	784
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	10.0000
Pulse Width	4.9500
Acquisition Time	1.0486
Acquisition Date	2018-06-30T14:06:37
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



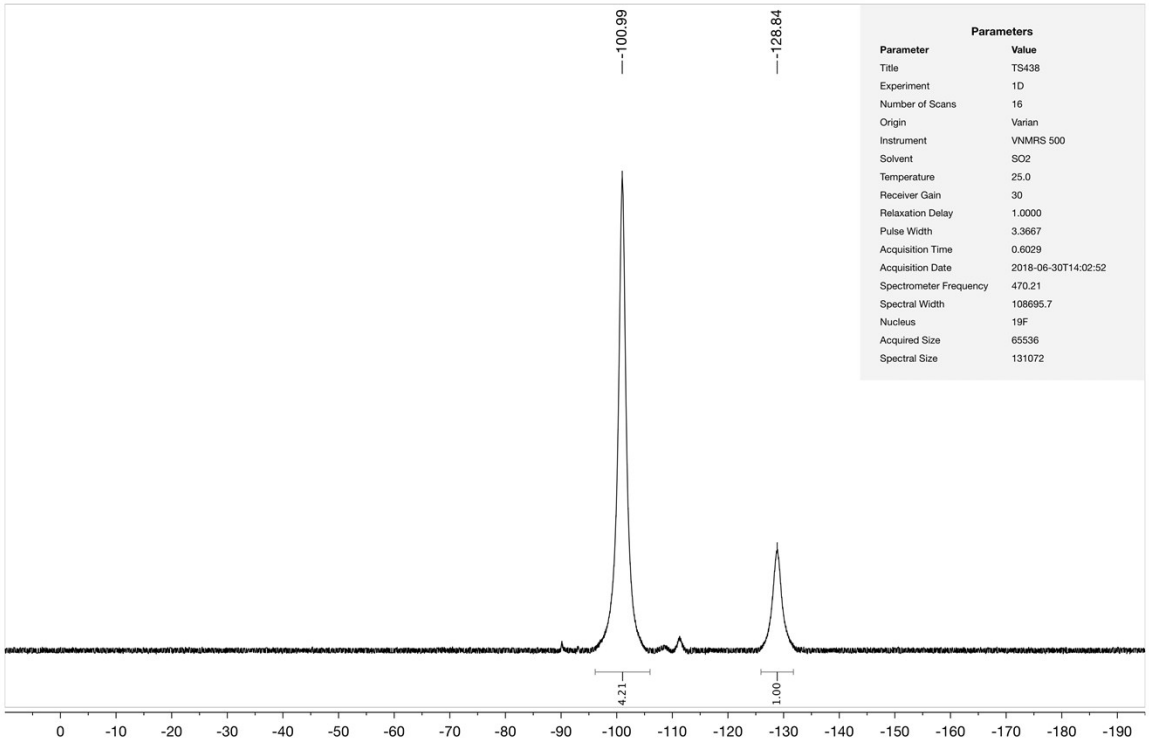
^{14}N - *c*-$C_3H_5CN{\cdot}SbF_5$



Parameters

Parameter	Value
Title	TS438
Experiment	1D
Number of Scans	20205
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2018-06-30T09:19:57
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

^{19}F - *c*-$C_3H_5CN{\cdot}SbF_5$

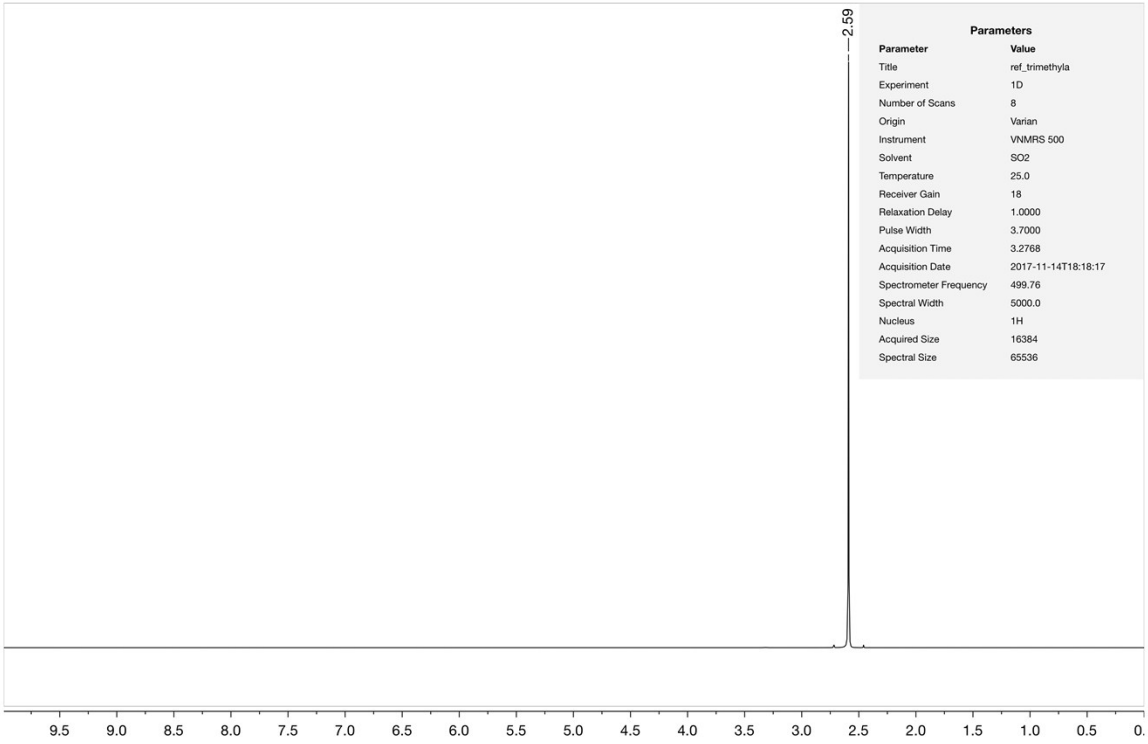


Parameters

Parameter	Value
Title	TS438
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2018-06-30T14:02:52
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

$(CH_3)_3CCN$

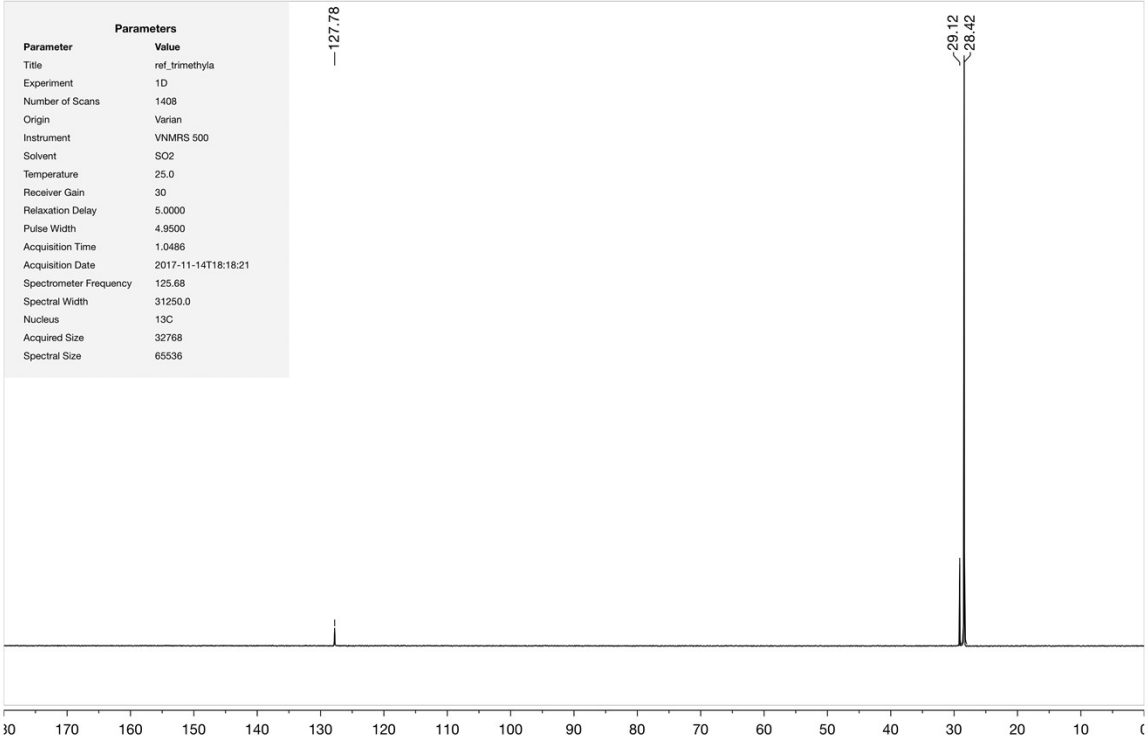
^1H - $(CH_3)_3CCN$



Parameters

Parameter	Value
Title	ref_trimethyla
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	18
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	3.2768
Acquisition Date	2017-11-14T18:18:17
Spectrometer Frequency	499.76
Spectral Width	5000.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

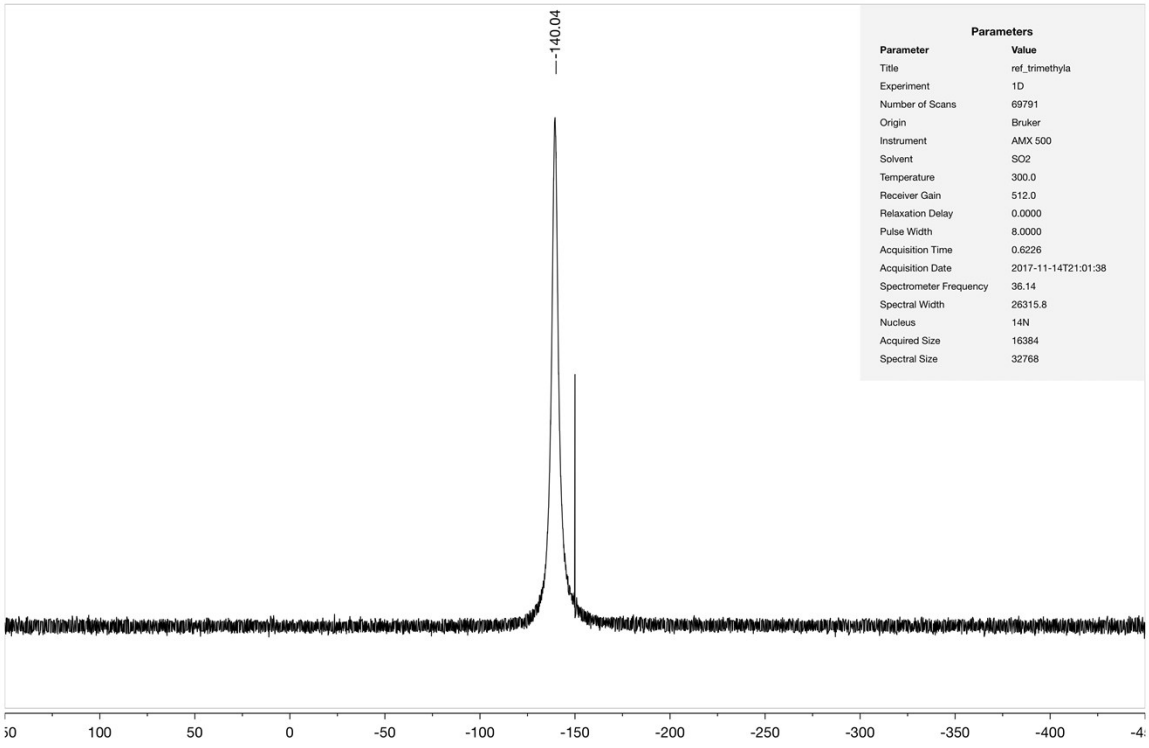
^{13}C - $(CH_3)_3CCN$



Parameters

Parameter	Value
Title	ref_trimethyla
Experiment	1D
Number of Scans	1408
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	4.9500
Acquisition Time	1.0486
Acquisition Date	2017-11-14T18:18:21
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $(CH_3)_3CCN$



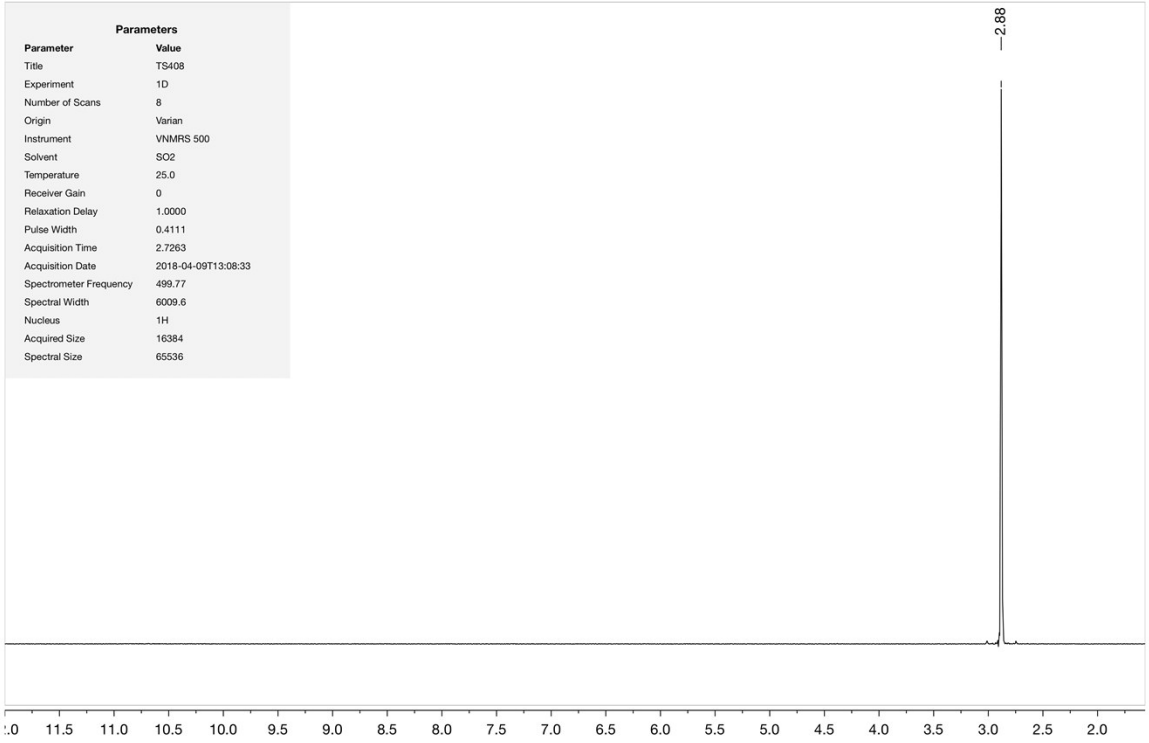
Parameters

Parameter	Value
Title	ref_trimethyla
Experiment	1D
Number of Scans	69791
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2017-11-14T21:01:38
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

$(CH_3)_3CCN•AsF_5$

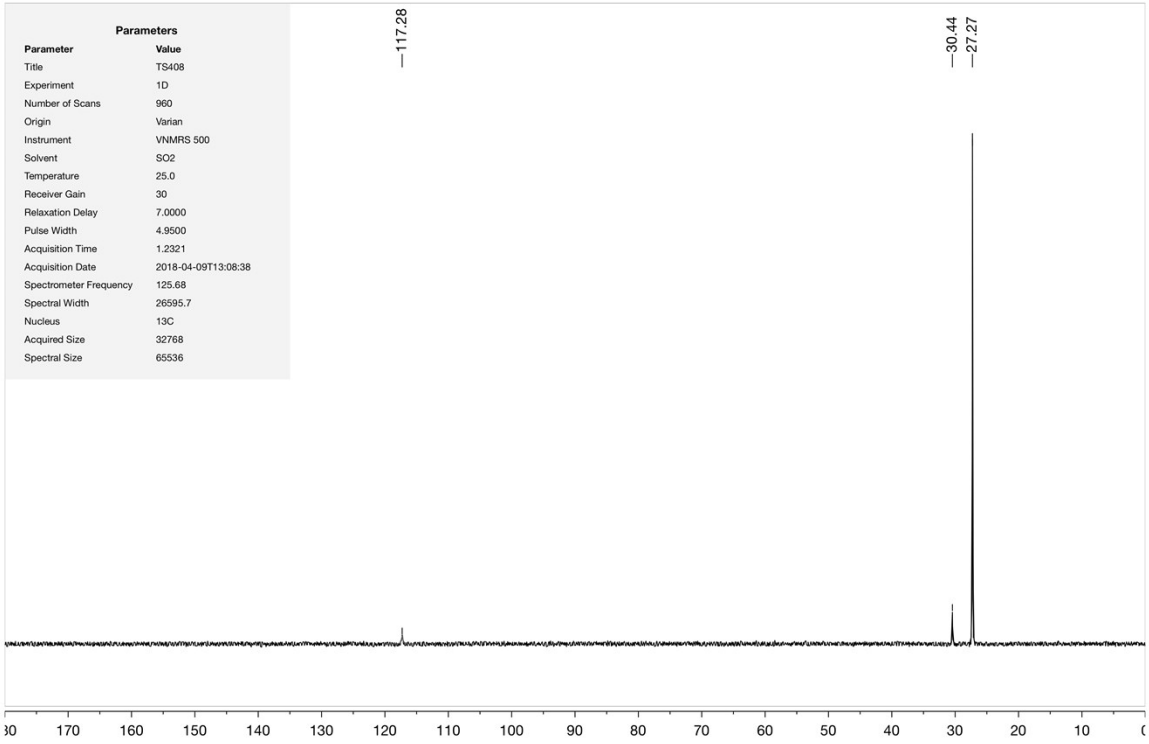
^1H - $(CH_3)_3CCN•AsF_5$

Parameters	
Parameter	**Value**
Title	TS408
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	0.4111
Acquisition Time	2.7263
Acquisition Date	2018-04-09T13:08:33
Spectrometer Frequency	499.77
Spectral Width	6009.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

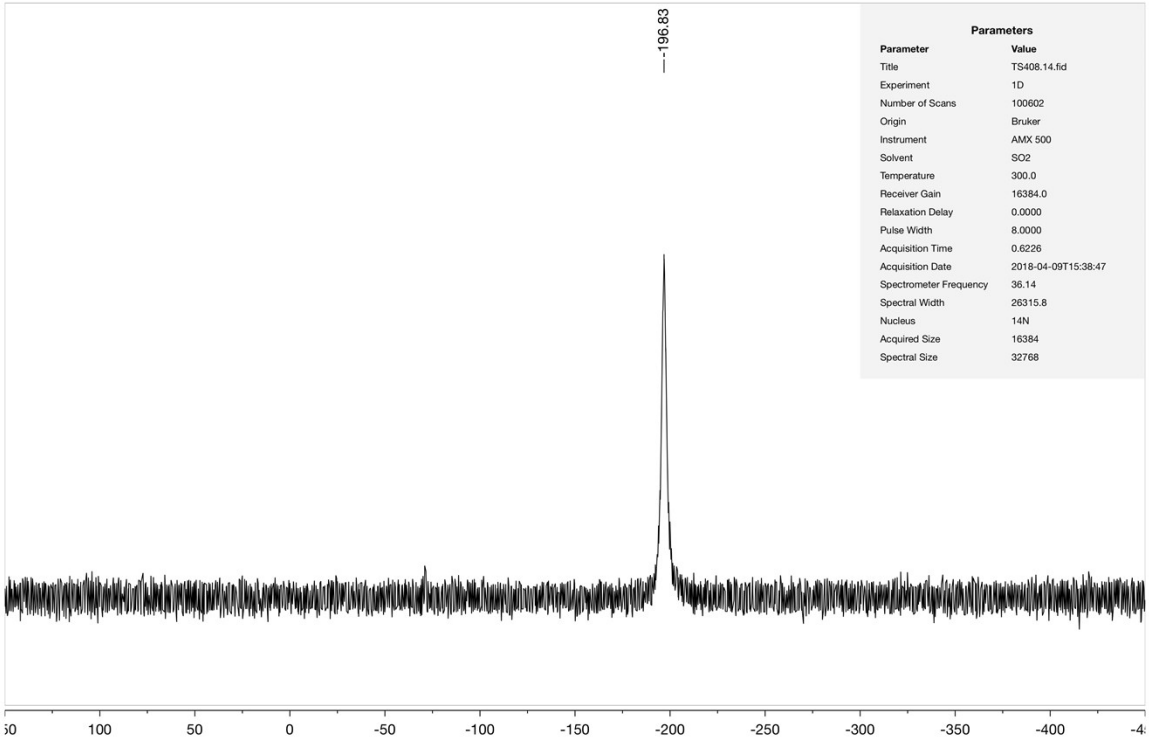


^{13}C - $(CH_3)_3CCN•AsF_5$

Parameters	
Parameter	**Value**
Title	TS408
Experiment	1D
Number of Scans	960
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	7.0000
Pulse Width	4.9500
Acquisition Time	1.2321
Acquisition Date	2018-04-09T13:08:38
Spectrometer Frequency	125.68
Spectral Width	26595.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



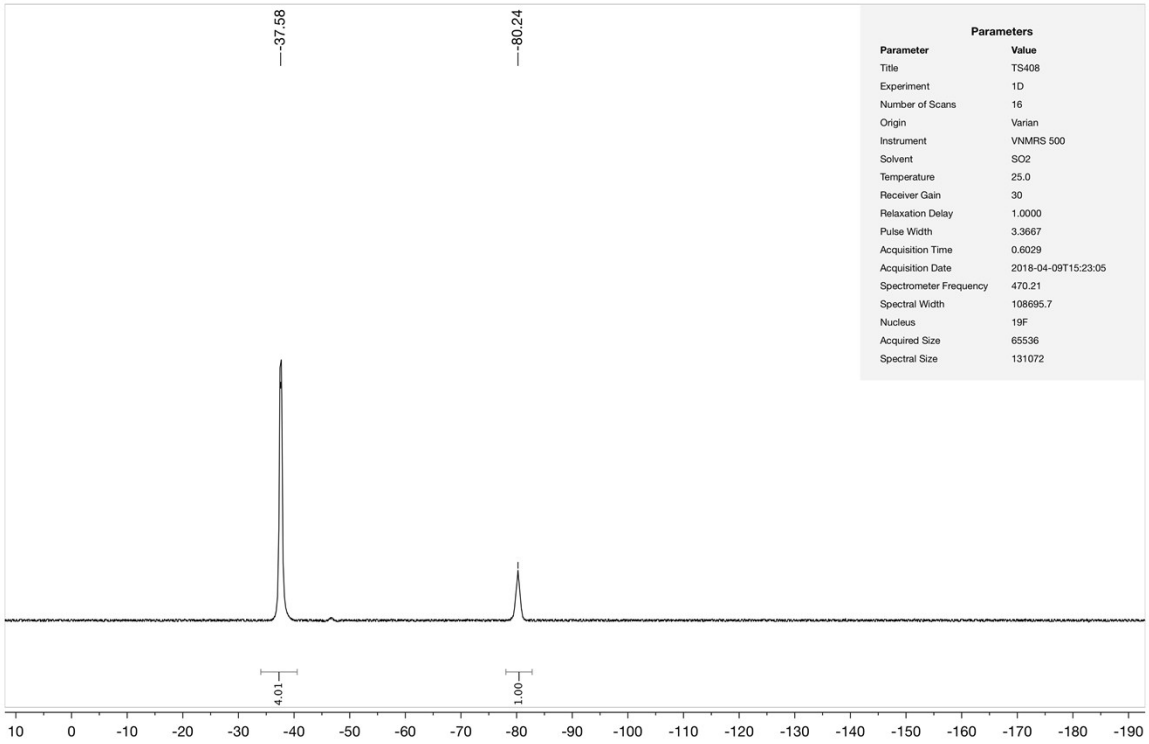
^{14}N - $(CH_3)_3CCN{\cdot}AsF_5$



Parameters

Parameter	Value
Title	TS408.14.fid
Experiment	1D
Number of Scans	100602
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	16384.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2018-04-09T15:38:47
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

^{19}F - $(CH_3)_3CCN{\cdot}AsF_5$



Parameters

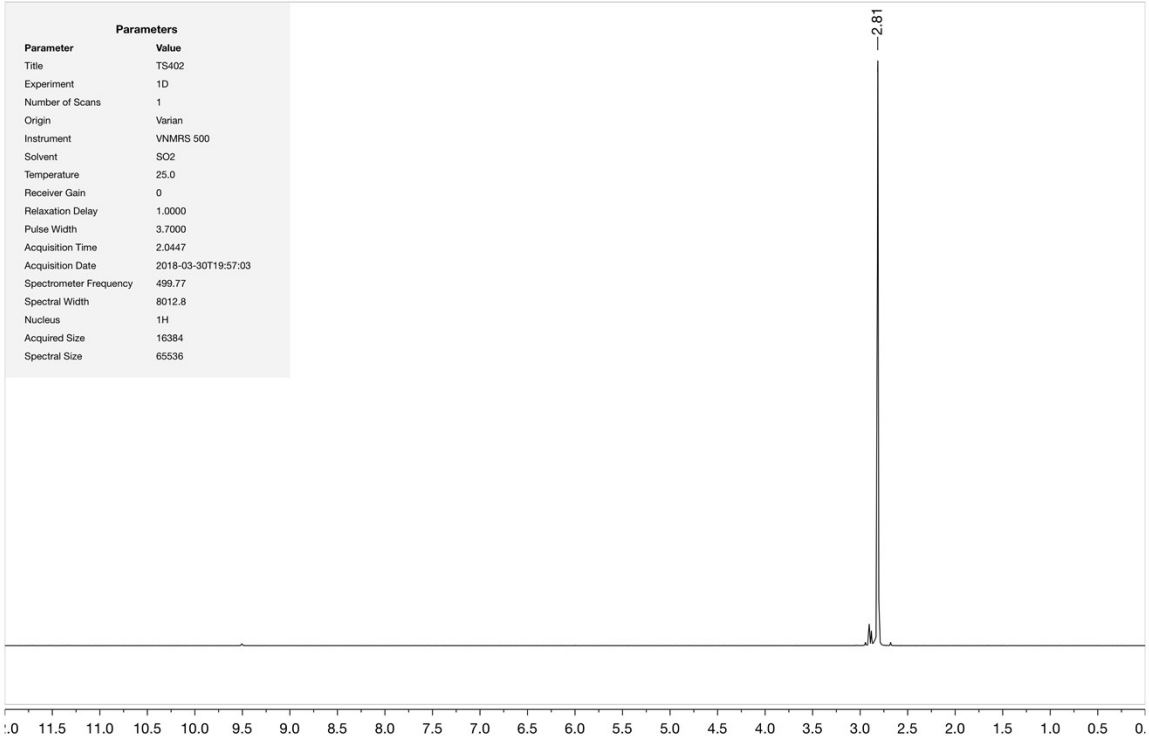
Parameter	Value
Title	TS408
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2018-04-09T15:23:05
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

$(CH_3)_3CCN•SbF_5$

^1H - $(CH_3)_3CCN•SbF_5$

Parameters

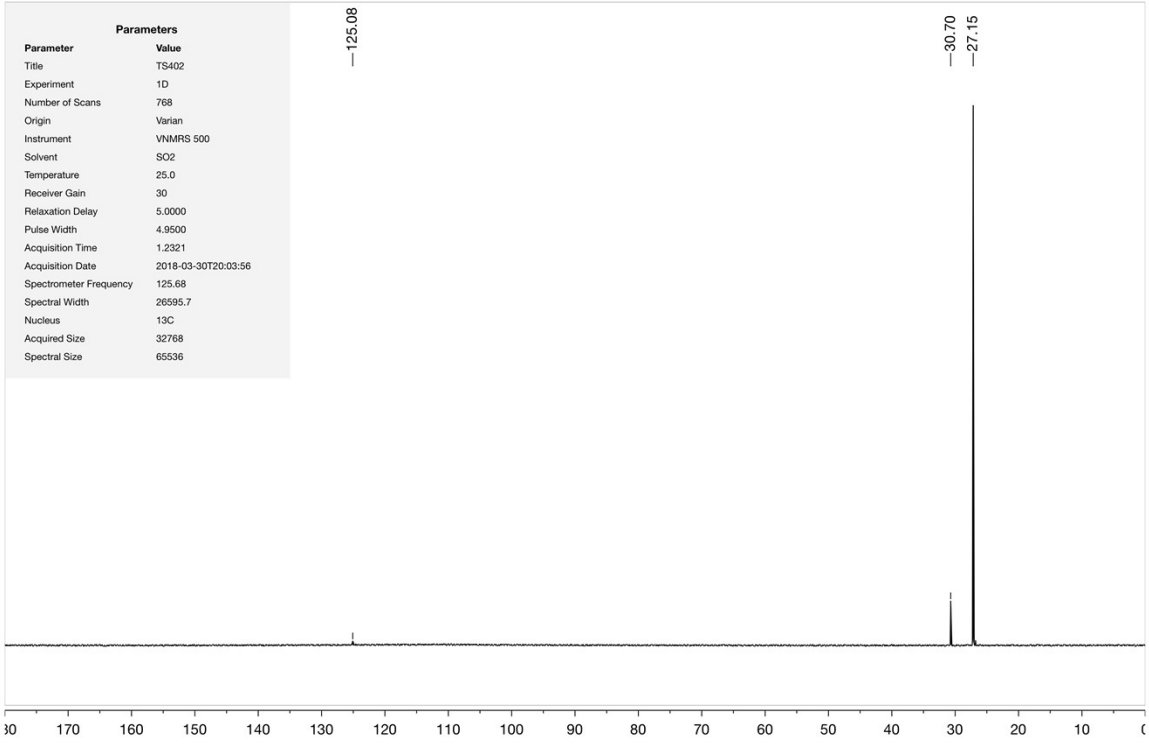
Parameter	Value
Title	TS402
Experiment	1D
Number of Scans	1
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.0447
Acquisition Date	2018-03-30T19:57:03
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536



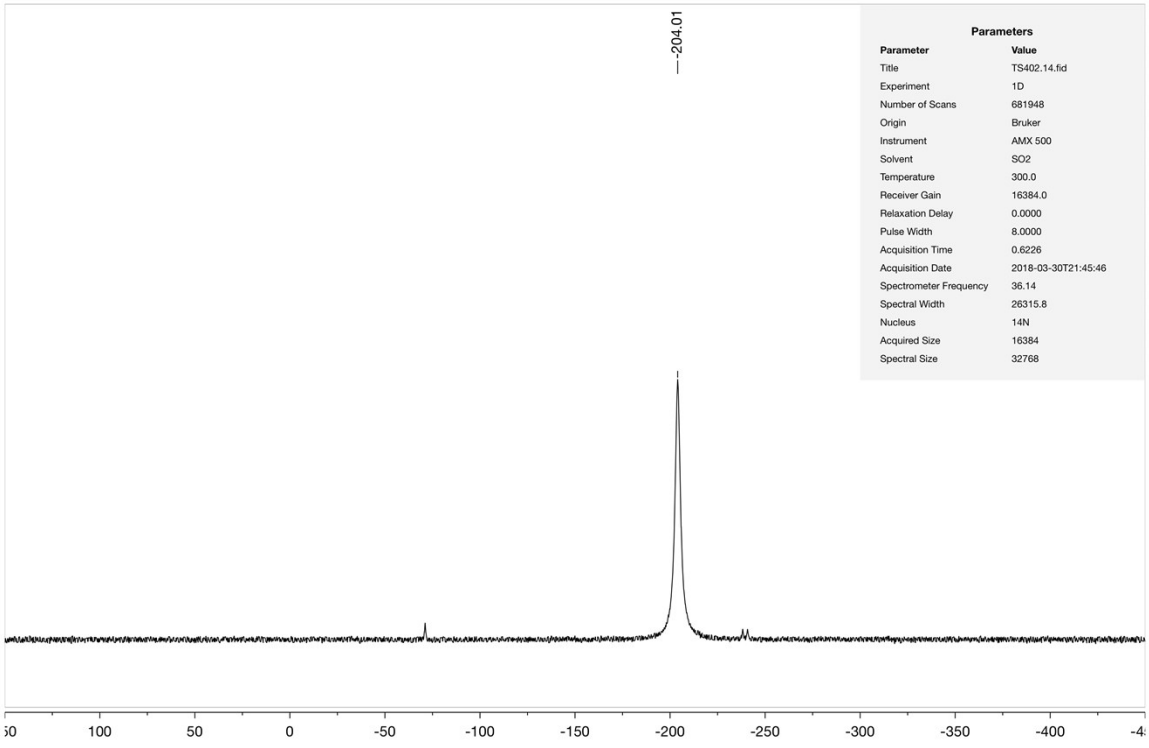
^{13}C - $(CH_3)_3CCN{\cdot}SbF_5$

Parameters

Parameter	Value
Title	TS402
Experiment	1D
Number of Scans	768
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	4.9500
Acquisition Time	1.2321
Acquisition Date	2018-03-30T20:03:56
Spectrometer Frequency	125.68
Spectral Width	26595.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

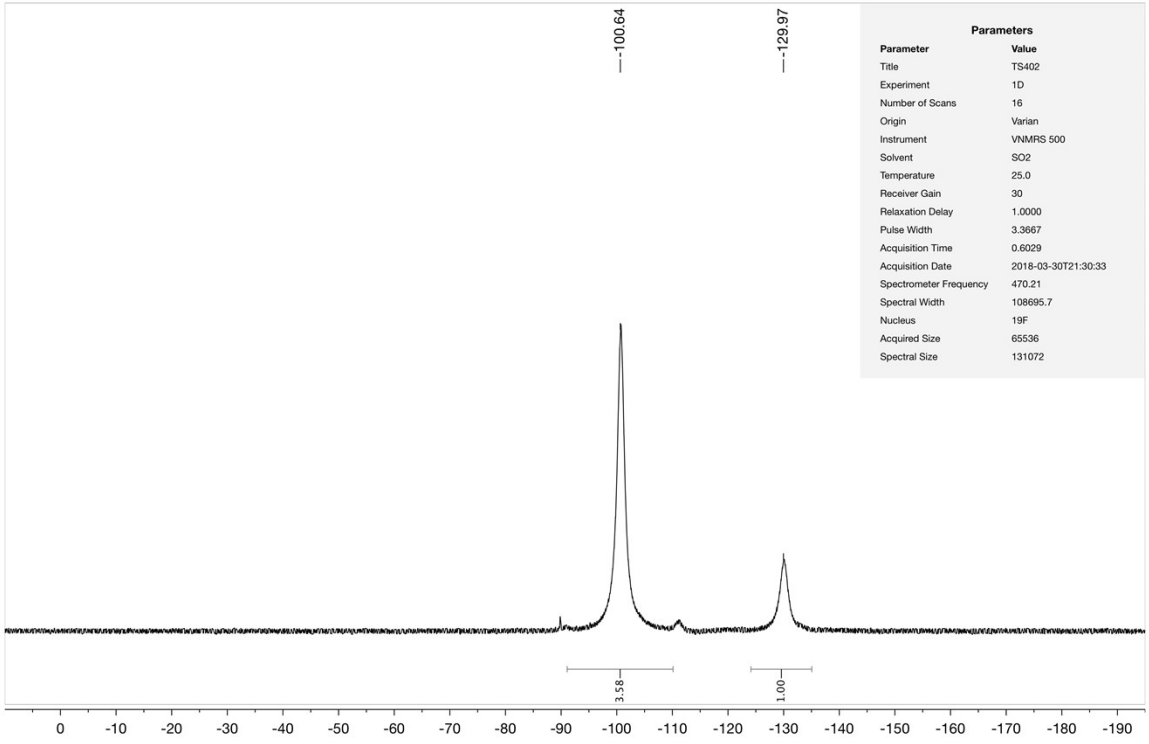


^{14}N - $(CH_3)_3CCN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS402.14.fid
Experiment	1D
Number of Scans	681948
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	16384.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2018-03-30T21:45:46
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

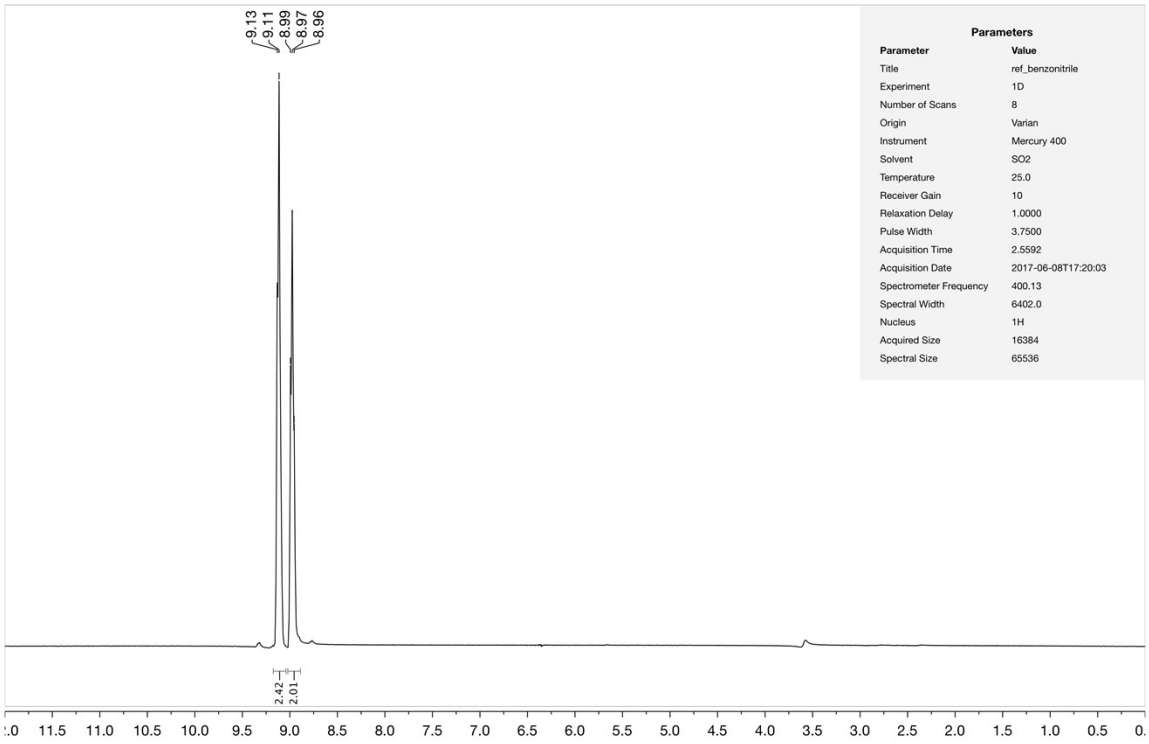
^{19}F - $(CH_3)_3CCN{\cdot}SbF_5$



Parameters	
Parameter	**Value**
Title	TS402
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2018-03-30T21:30:33
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

C_6H_5CN

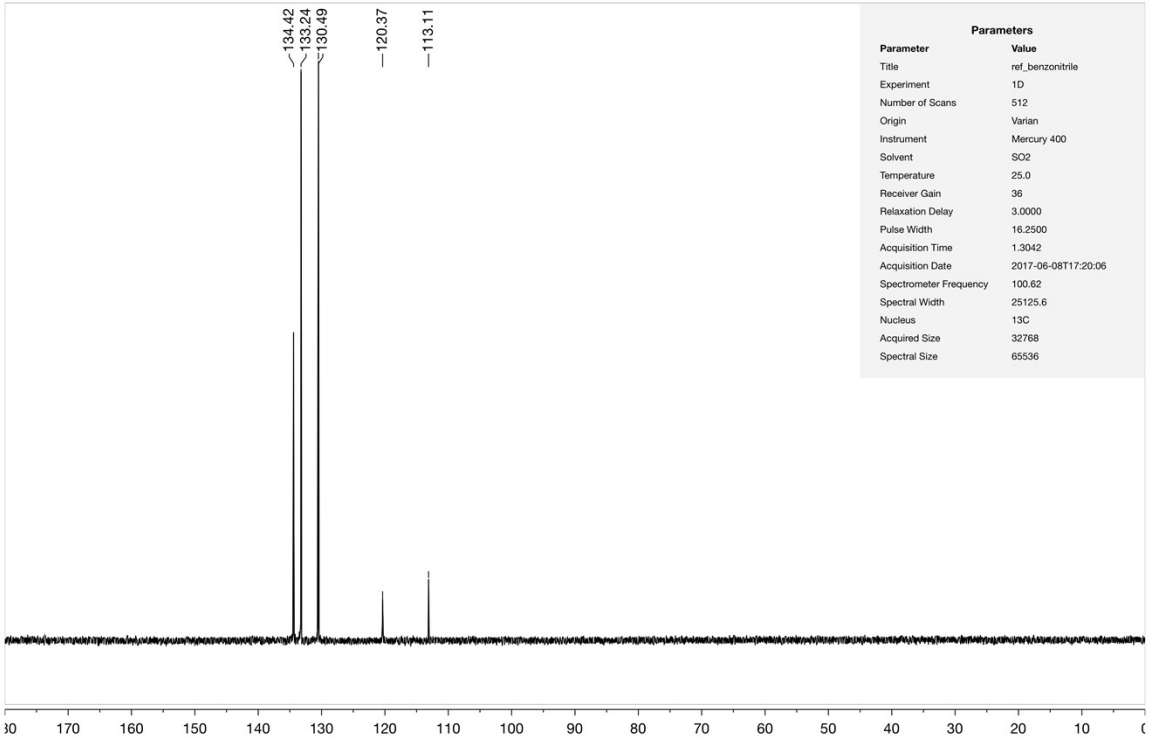
^1H - C_6H_5CN



Parameters

Parameter	Value
Title	ref_benzonitrile
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	Mercury 400
Solvent	SO2
Temperature	25.0
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	3.7500
Acquisition Time	2.5592
Acquisition Date	2017-06-08T17:20:03
Spectrometer Frequency	400.13
Spectral Width	6402.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

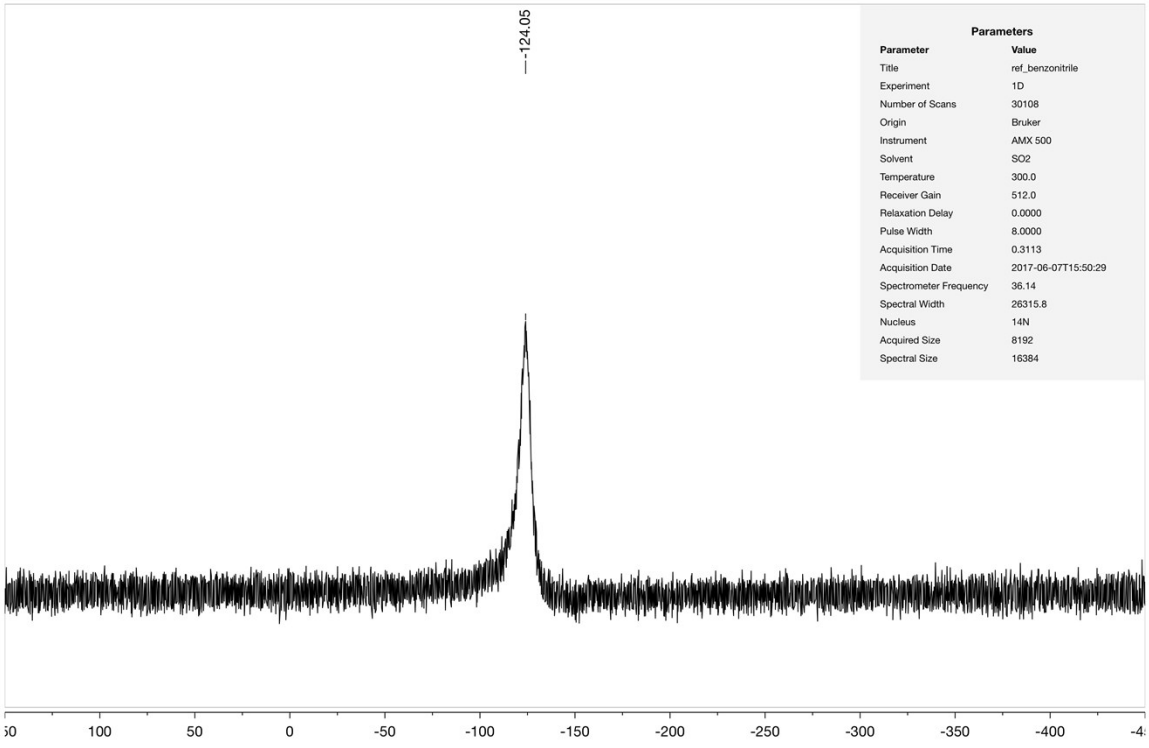
^{13}C - C_6H_5CN



Parameters

Parameter	Value
Title	ref_benzonitrile
Experiment	1D
Number of Scans	512
Origin	Varian
Instrument	Mercury 400
Solvent	SO2
Temperature	25.0
Receiver Gain	36
Relaxation Delay	3.0000
Pulse Width	16.2500
Acquisition Time	1.3042
Acquisition Date	2017-06-08T17:20:06
Spectrometer Frequency	100.62
Spectral Width	25125.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - C_6H_5CN

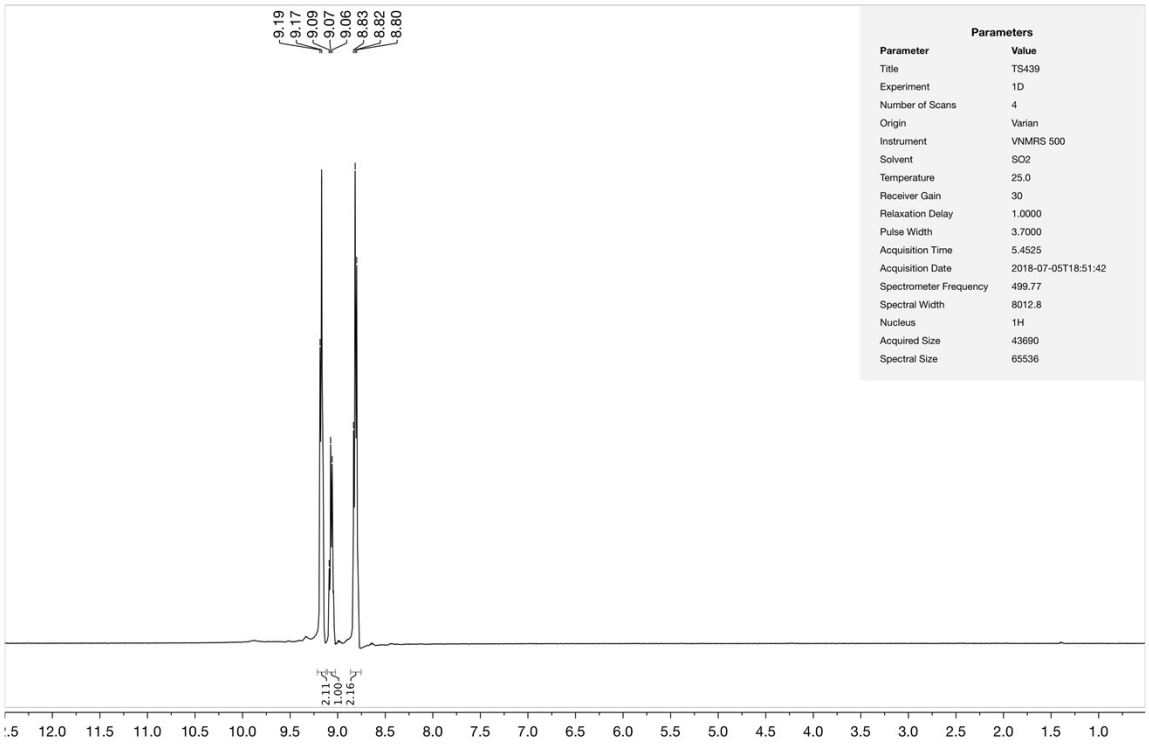


Parameters

Parameter	Value
Title	ref_benzonitrile
Experiment	1D
Number of Scans	30108
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.3113
Acquisition Date	2017-06-07T15:50:29
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	8192
Spectral Size	16384

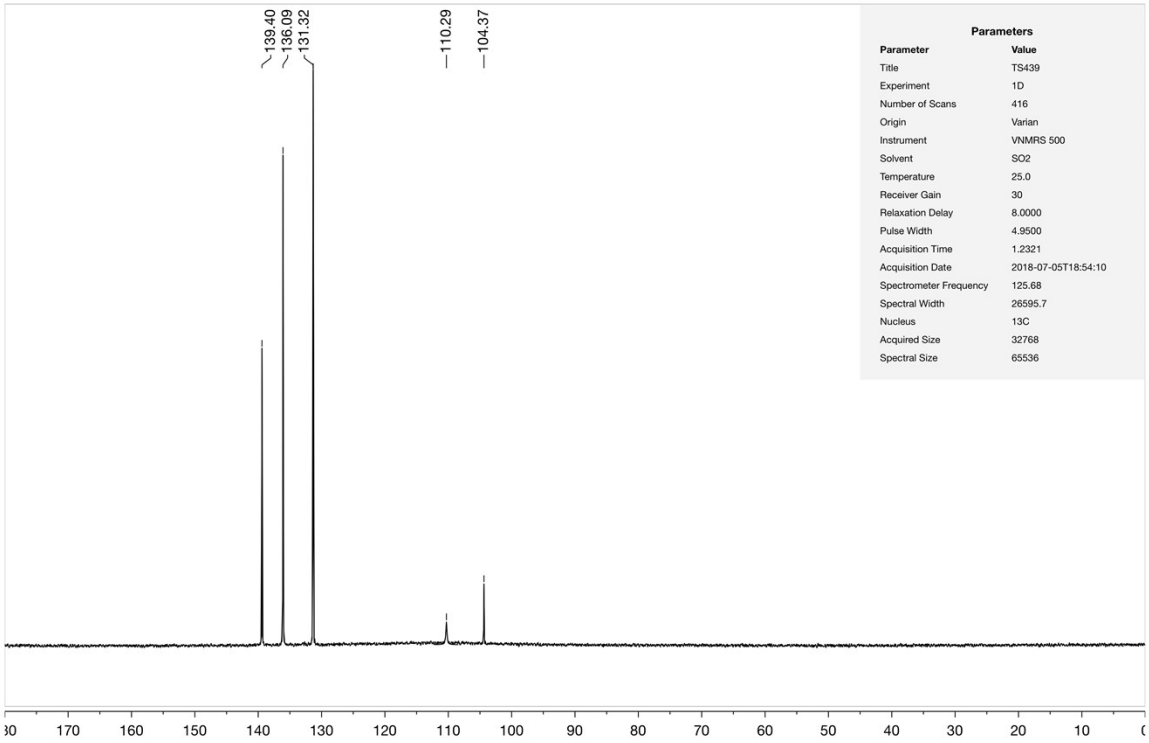
$C_6H_5CN{\bullet}AsF_5$

^1H - $C_6H_5CN{\bullet}AsF_5$



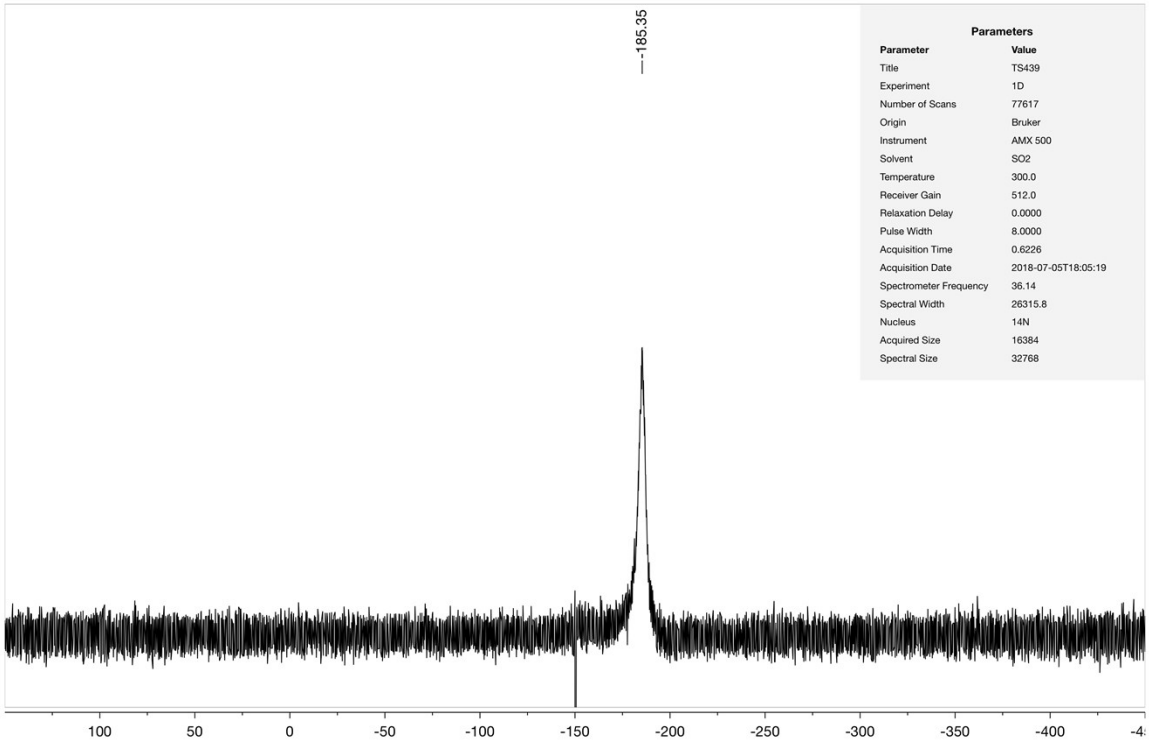
Parameters	
Parameter	**Value**
Title	TS439
Experiment	1D
Number of Scans	4
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	5.4525
Acquisition Date	2018-07-05T18:51:42
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	43690
Spectral Size	65536

^{13}C - $C_6H_5CN{\bullet}AsF_5$



Parameters	
Parameter	**Value**
Title	TS439
Experiment	1D
Number of Scans	416
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	8.0000
Pulse Width	4.9500
Acquisition Time	1.2321
Acquisition Date	2018-07-05T18:54:10
Spectrometer Frequency	125.68
Spectral Width	26595.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

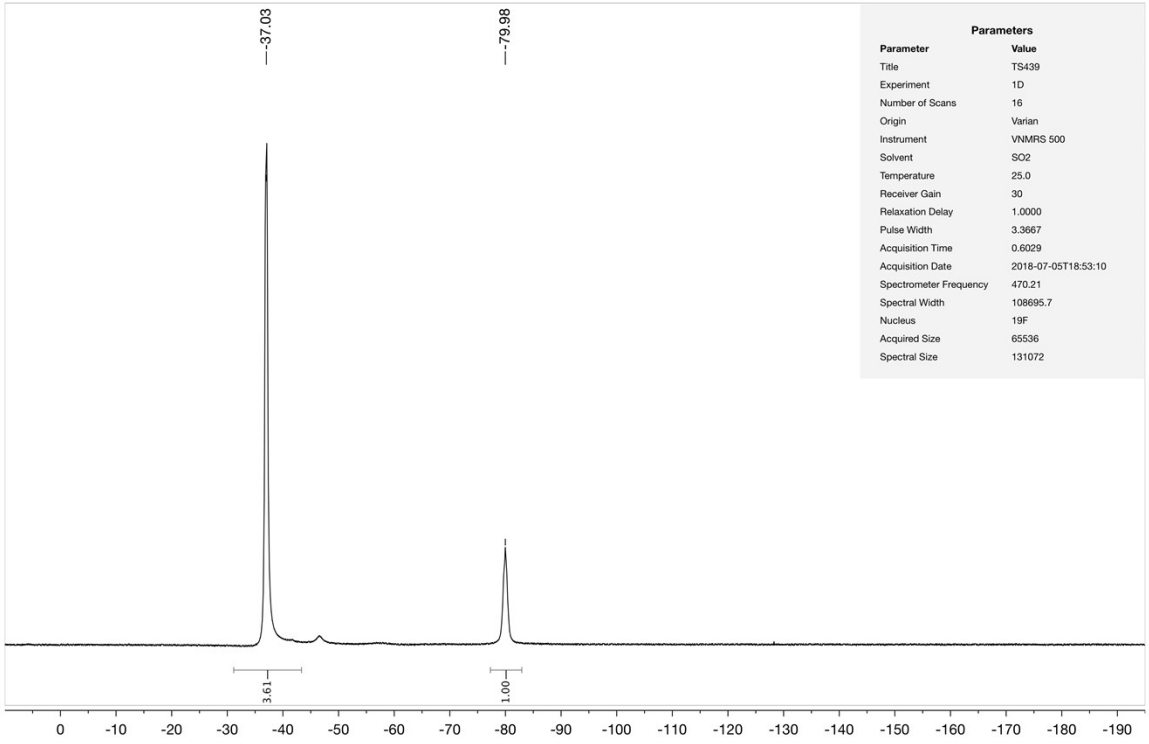
^{14}N - $C_6H_5CN{\cdot}AsF_5$



Parameters

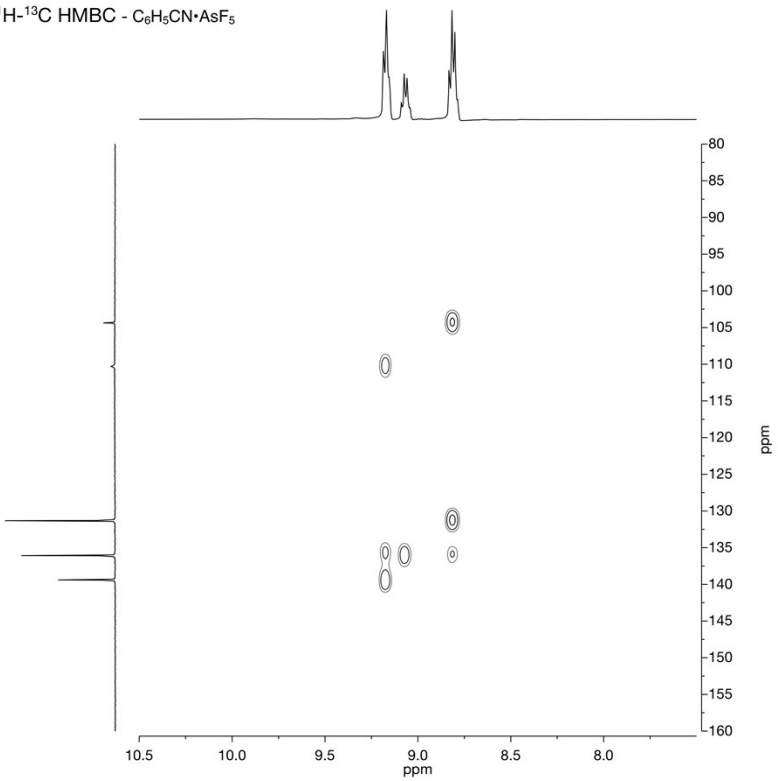
Parameter	Value
Title	TS439
Experiment	1D
Number of Scans	77617
Origin	Bruker
Instrument	AMX 500
Solvent	SO2
Temperature	300.0
Receiver Gain	512.0
Relaxation Delay	0.0000
Pulse Width	8.0000
Acquisition Time	0.6226
Acquisition Date	2018-07-05T18:05:19
Spectrometer Frequency	36.14
Spectral Width	26315.8
Nucleus	14N
Acquired Size	16384
Spectral Size	32768

^{19}F - $C_6H_5CN{\cdot}AsF_5$



Parameters

Parameter	Value
Title	TS439
Experiment	1D
Number of Scans	16
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2018-07-05T18:53:10
Spectrometer Frequency	470.21
Spectral Width	108695.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

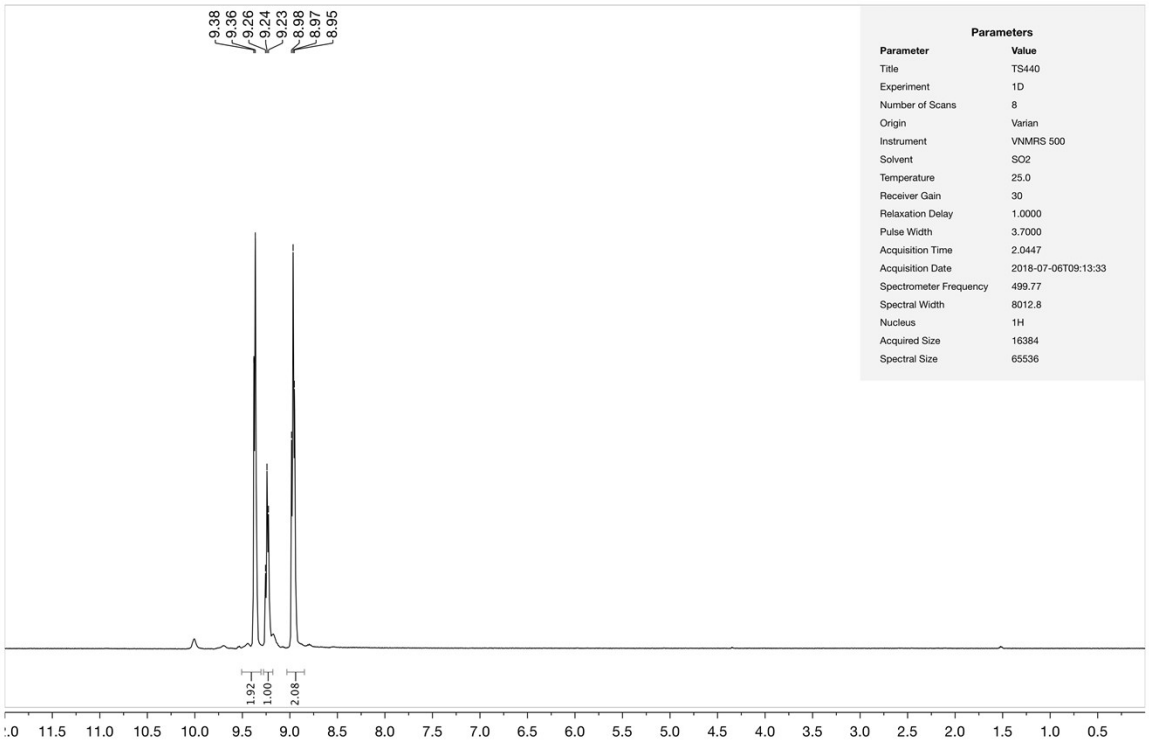


Parameters

Parameter	Value
Title	TS439
Experiment	HMBC
Number of Scans	2
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Pulse Sequence	gHMBCAD
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	7.4000
Acquisition Time	0.1500
Acquisition Date	2018-07-05T20:05:16
Nucleus	(1H, 13C)
Spectrometer Frequency	(499.77, 125.68)
Spectral Width	(8012.8, 30154.5)
Lowest Frequency	(255.3, -1579.3)
Acquired Size	(1202, 64)
Spectral Size	(2048, 512)

$C_6H_5CN•SbF_5$

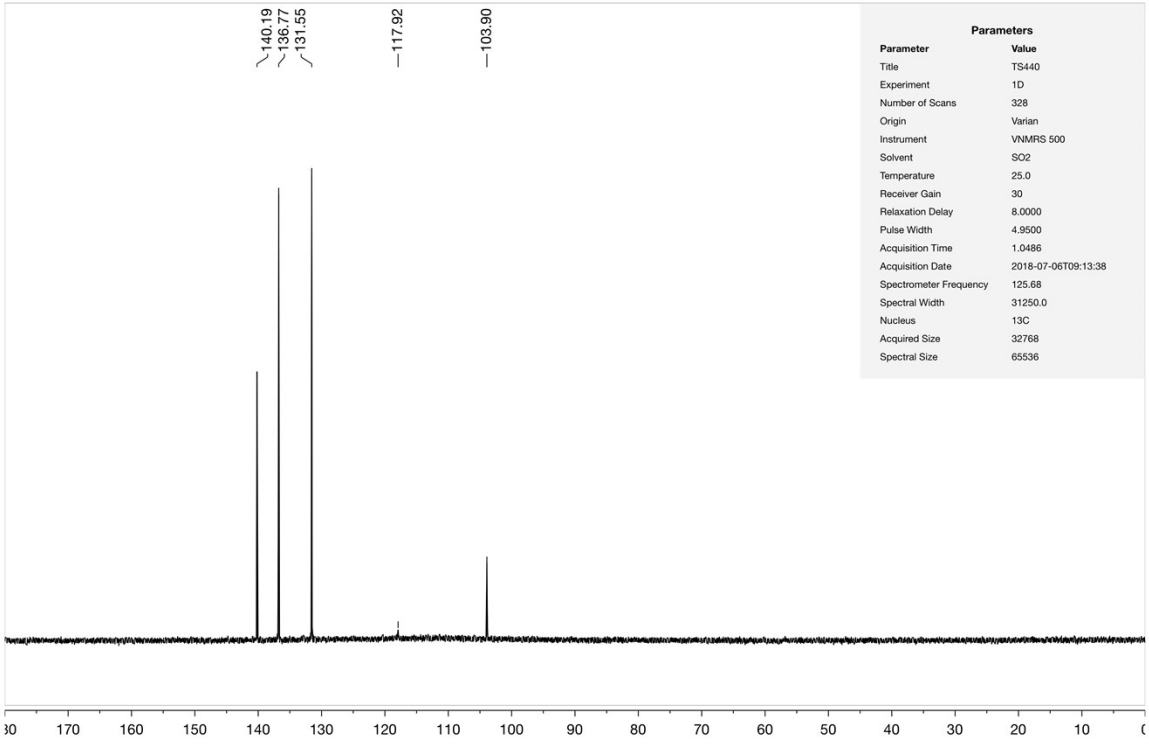
^1H - $C_6H_5CN•SbF_5$



Parameters

Parameter	Value
Title	TS440
Experiment	1D
Number of Scans	8
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.7000
Acquisition Time	2.0447
Acquisition Date	2018-07-06T09:13:33
Spectrometer Frequency	499.77
Spectral Width	8012.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

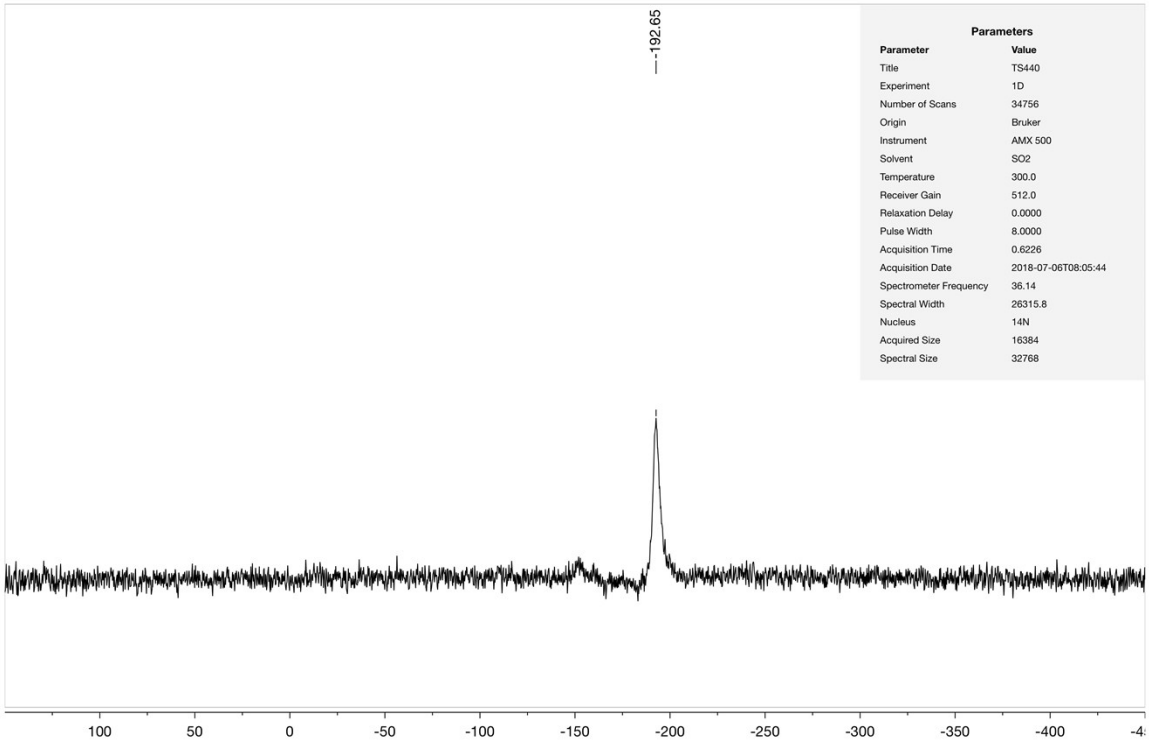
^{13}C - $C_6H_5CN•SbF_5$



Parameters

Parameter	Value
Title	TS440
Experiment	1D
Number of Scans	328
Origin	Varian
Instrument	VNMRS 500
Solvent	SO2
Temperature	25.0
Receiver Gain	30
Relaxation Delay	8.0000
Pulse Width	4.9500
Acquisition Time	1.0486
Acquisition Date	2018-07-06T09:13:38
Spectrometer Frequency	125.68
Spectral Width	31250.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{14}N - $C_6H_5CN{\cdot}SbF_5$



^{19}F - $C_6H_5CN{\cdot}SbF_5$

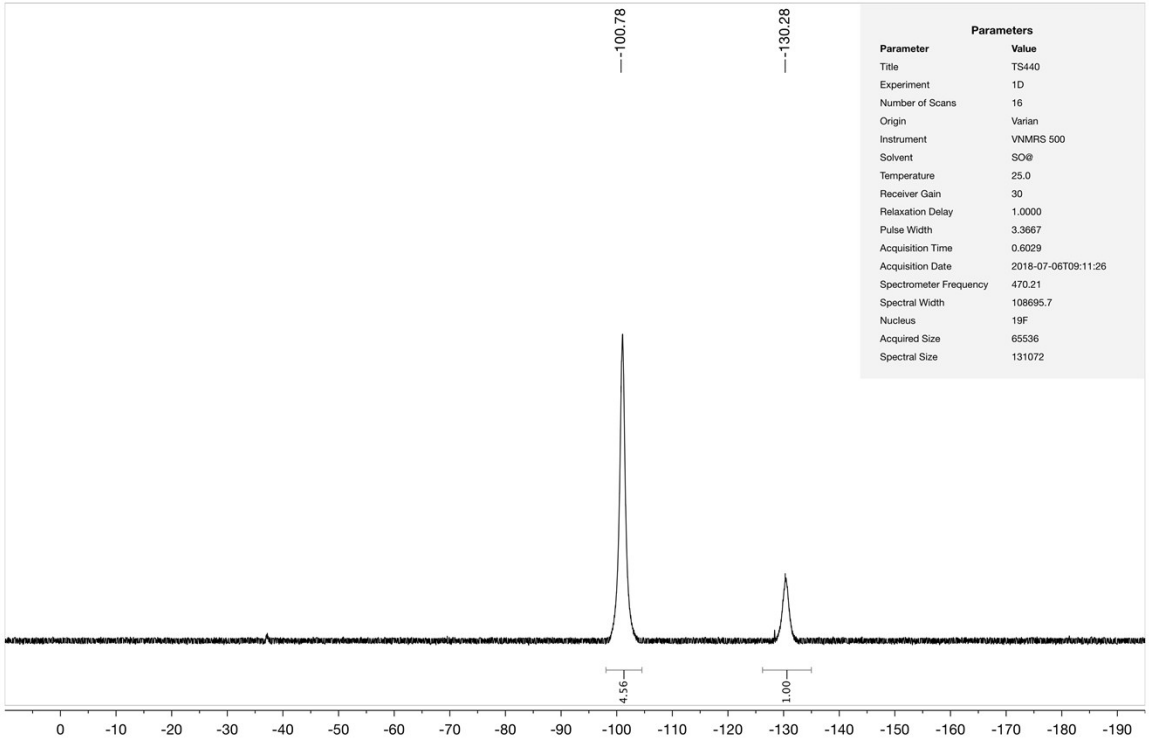


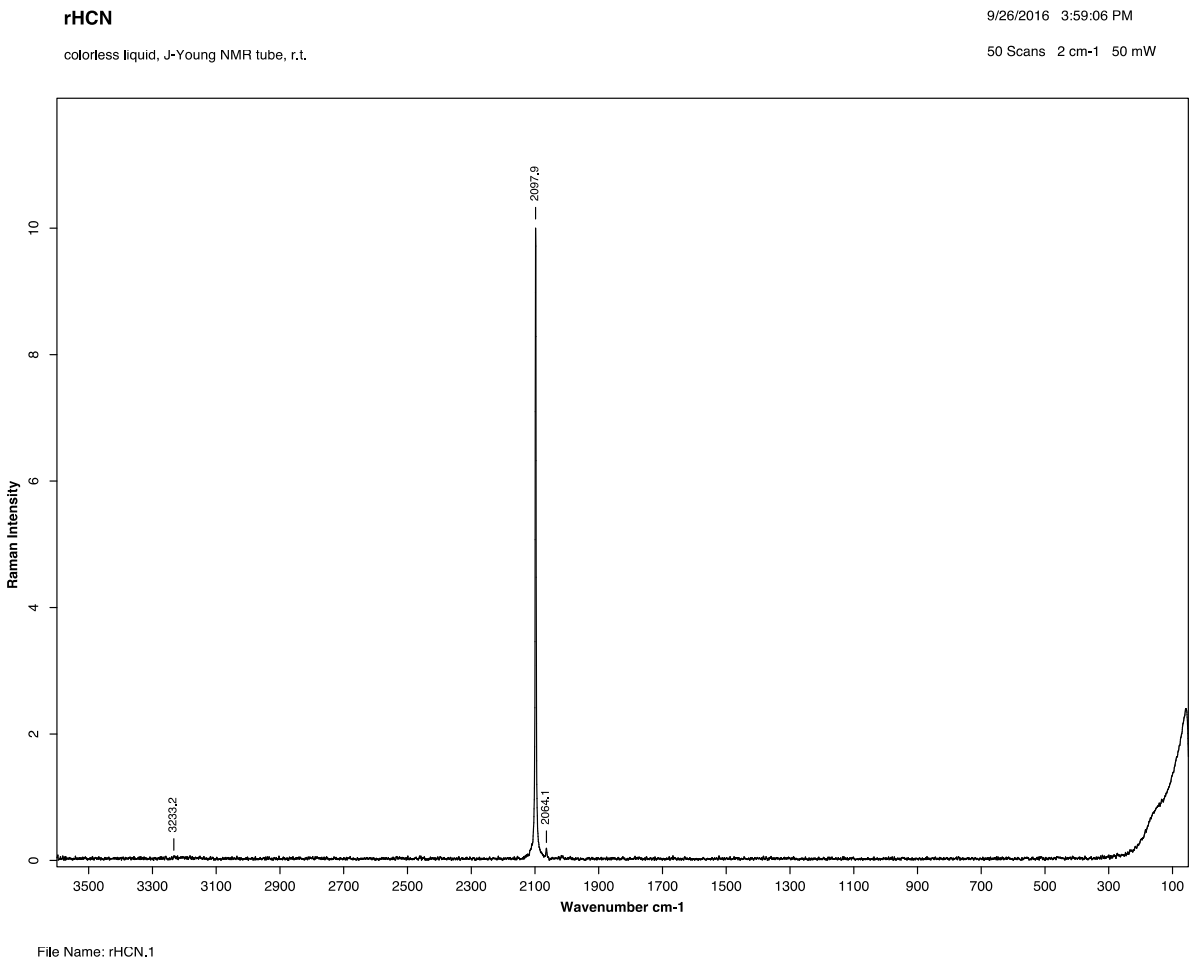
Table S1-0. Comparison of NMR chemical shifts for the Lewis adducts and the free nitriles.

Compound	^{13}C / ppm		^{14}N / ppm		^{19}F / ppm	
	R***C***N•MF_5	R***C***N	RC***N***•MF_5	RC***N***	M***F*****$_4$**F	MF_4***F***
HCN•AsF_5	100.39	110.88	-186.7	-124.8	-39.5	
HCN•SbF_5	106.88		-194.6		-100.6	-133.2
$NCCH_2CN$•AsF_5	104.99[a]	111.42	-187.4[b] (-121.4)[c]	-125.9	-45.1	
$NCCH_2CN$•SbF_5	110.38 (106.75)[c]		-192.3 (-123.1)[c]		-100.1	-133.5
C_3H_7CN•AsF_5	113.64	122.11	-195.07	-134.9	-37.6	-80.0
C_3H_7CN•SbF_5	121.51		-202.5		-101.1	-130.4
c-C_3H_5CN•AsF_5	115.41	124.32	-206.3	-144.1	-37.8	-78.7
c-C_3H_5CN•SbF_5	123.56		-213.8		-101.0	-128.8
$(CH_3)_3CCN$•AsF_5	117.28	127.78	196.8	-140.0	-37.6	-80.24
$(CH_3)_3CCN$•SbF_5	125.08		-204.0		-100.6	-130.0
C_6H_5CN•AsF_5	110.29	120.37	-185.4	-124.1	-37.0	80.0
C_6H_5CN•SbF_5	117.92		-192.7		-100.78	-130.3
AsF_5•$NCCH_2CN$•AsF_5	100.83	111.42	175.8	-125.9	-45.3	
SbF_5•$NCCH_2CN$•SbF_5	106.25		186.1		-99.5	-134.7

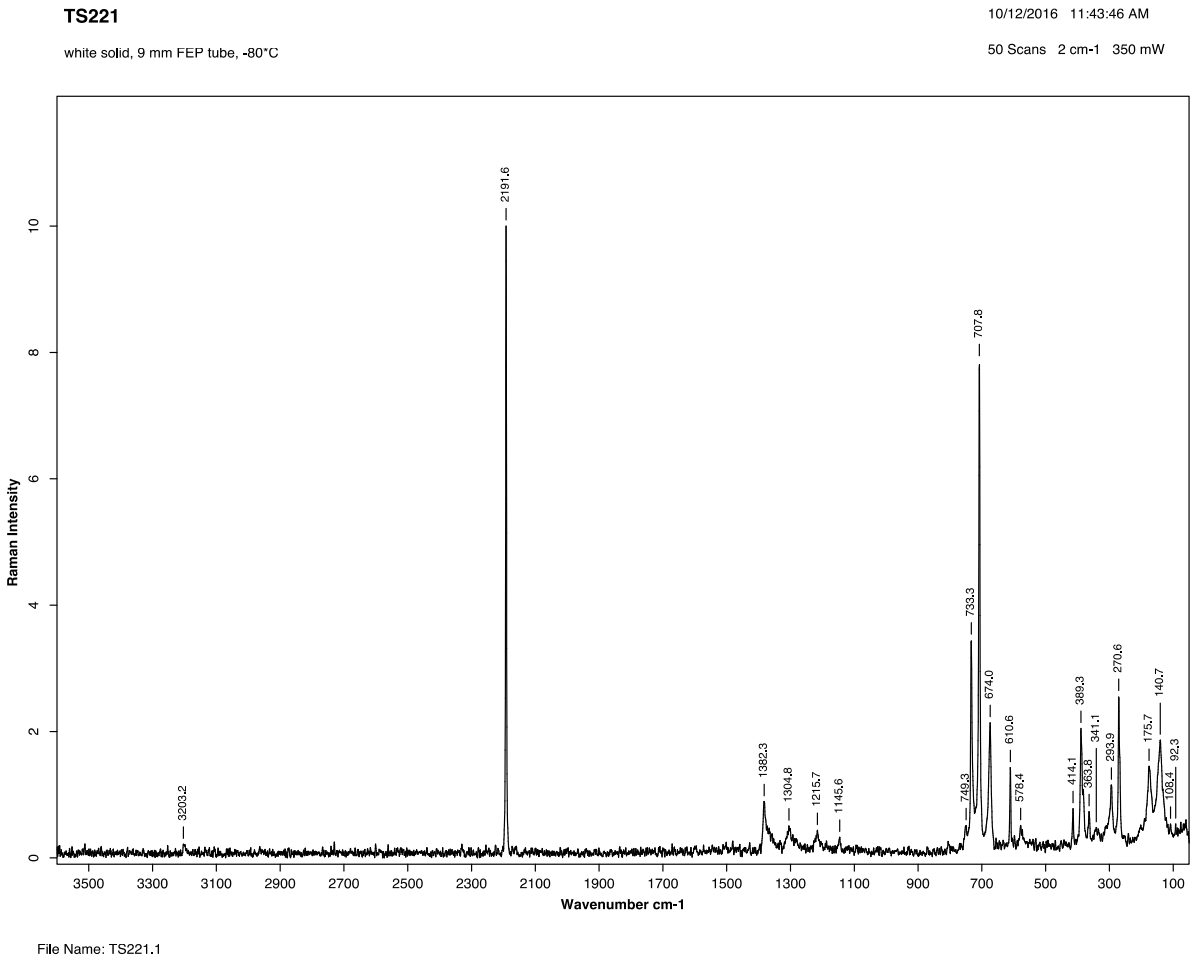
(a) recorded at 298 K, exchange of coordinated and free CN, mean chemical shift (b) recorded at 218 K to freeze exchange (c) shift of non-coordinating cyano group in parenthesis.

Raman Spectra

HCN



$HCN•AsF_5$


TS221
10/12/2016 11:43:46 AM
white solid, 9 mm FEP tube, -80°C
50 Scans 2 cm-1 350 mW
Raman Intensity
Wavenumber cm-1
3203.2
2191.6
1382.3
1304.8
1215.7
1145.6
749.3
733.3
707.8
674.0
610.6
578.4
414.1
389.3
363.8
341.1
293.9
270.6
175.7
140.7
108.4
92.3
File Name: TS221.1

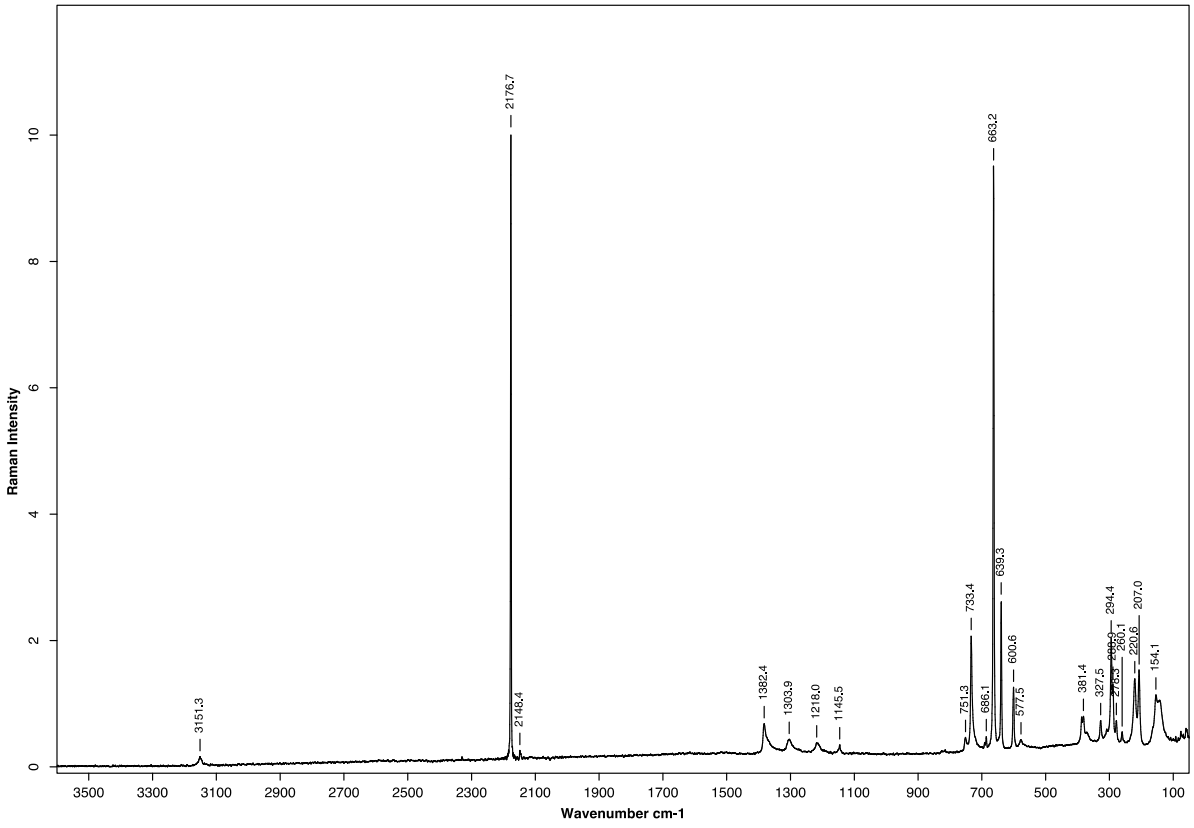
$HCN•SbF_5$

TS244

11/16/2016 10:17:51 AM

off white solid, 9 mm FEP tube, -90°C

1740 Scans 2 cm-1 350 mW



File Name: TS244.0

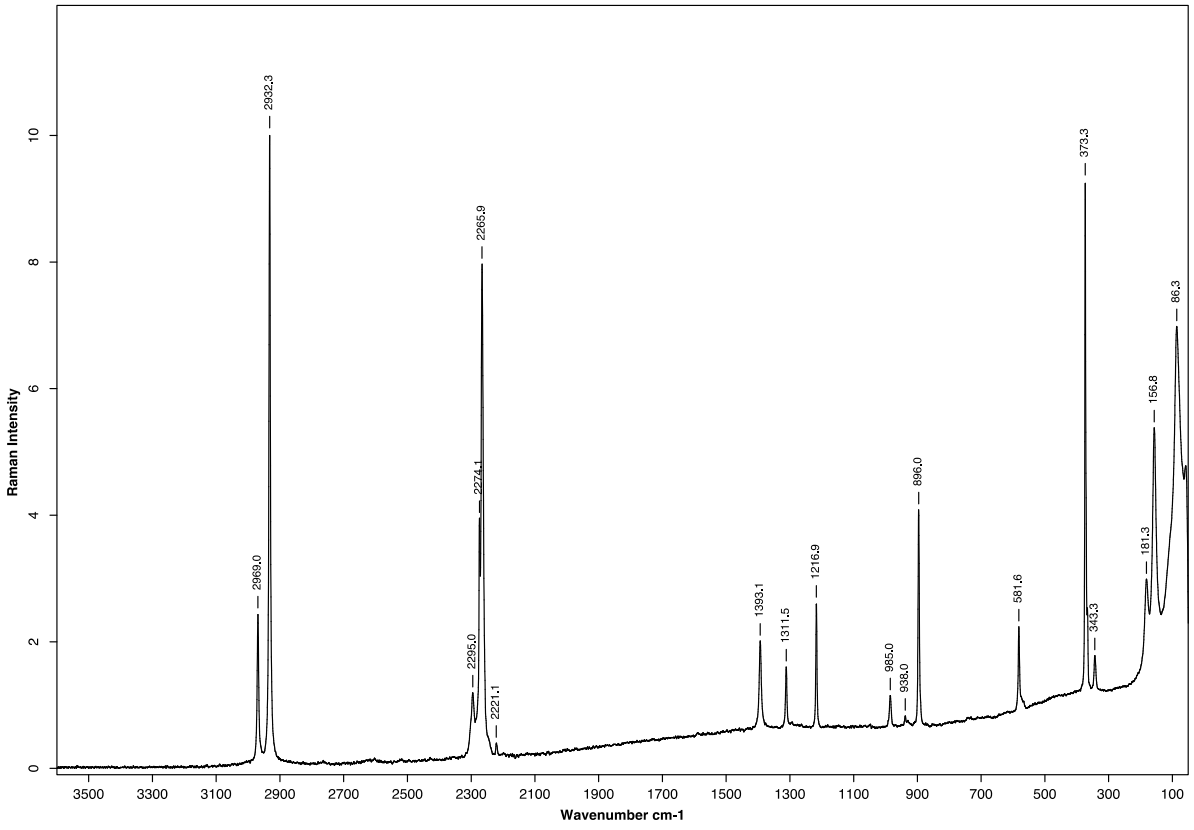
$NCCH_2CN$

ref_Malononitrile

10/7/2016 9:16:52 AM

colorless crystals, 5 mm NMR tube, r.t.

1000 Scans 2 cm-1 100 mW



File Name: ref_Malononitrile.0

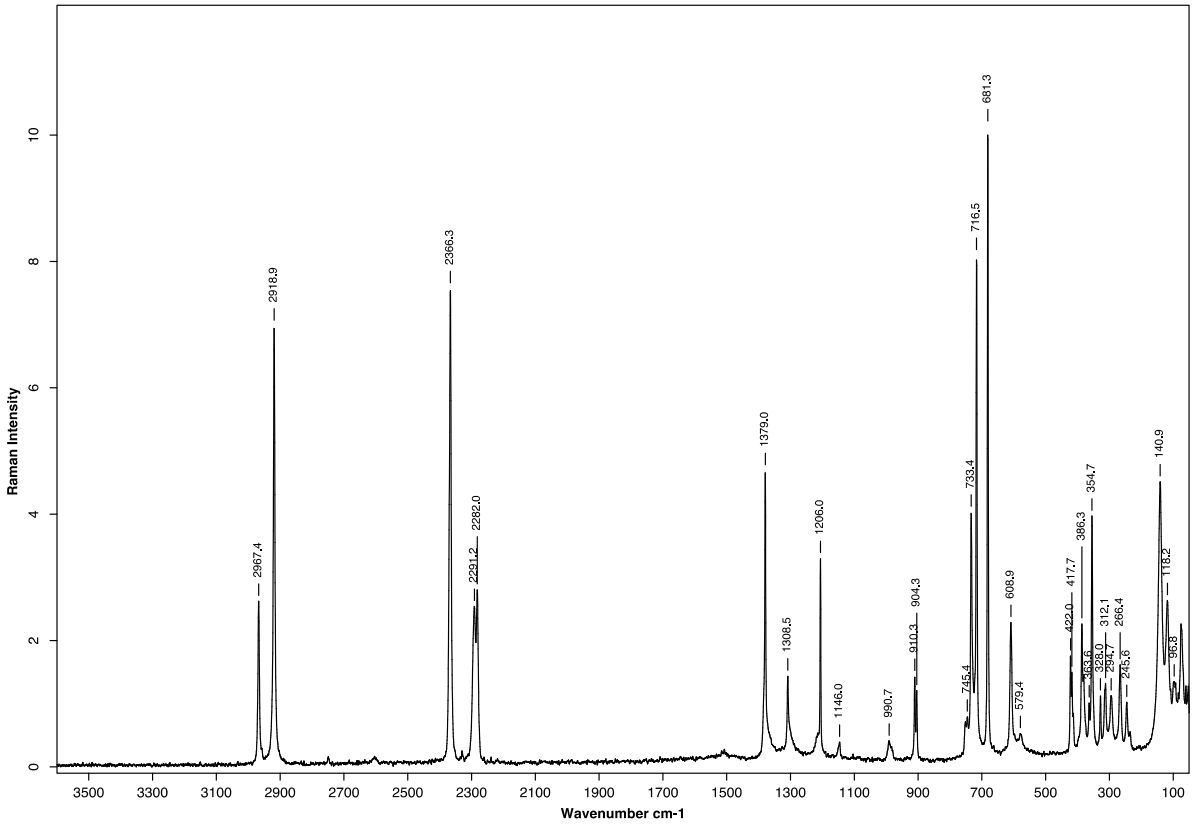
$NCCH_2CN{\bullet}AsF_5$

TS230

10/26/2016 4:45:35 AM

pale orange solid,9 mm FEP, -90°C

500 Scans 2 cm-1 350 mW



File Name: TS230.0

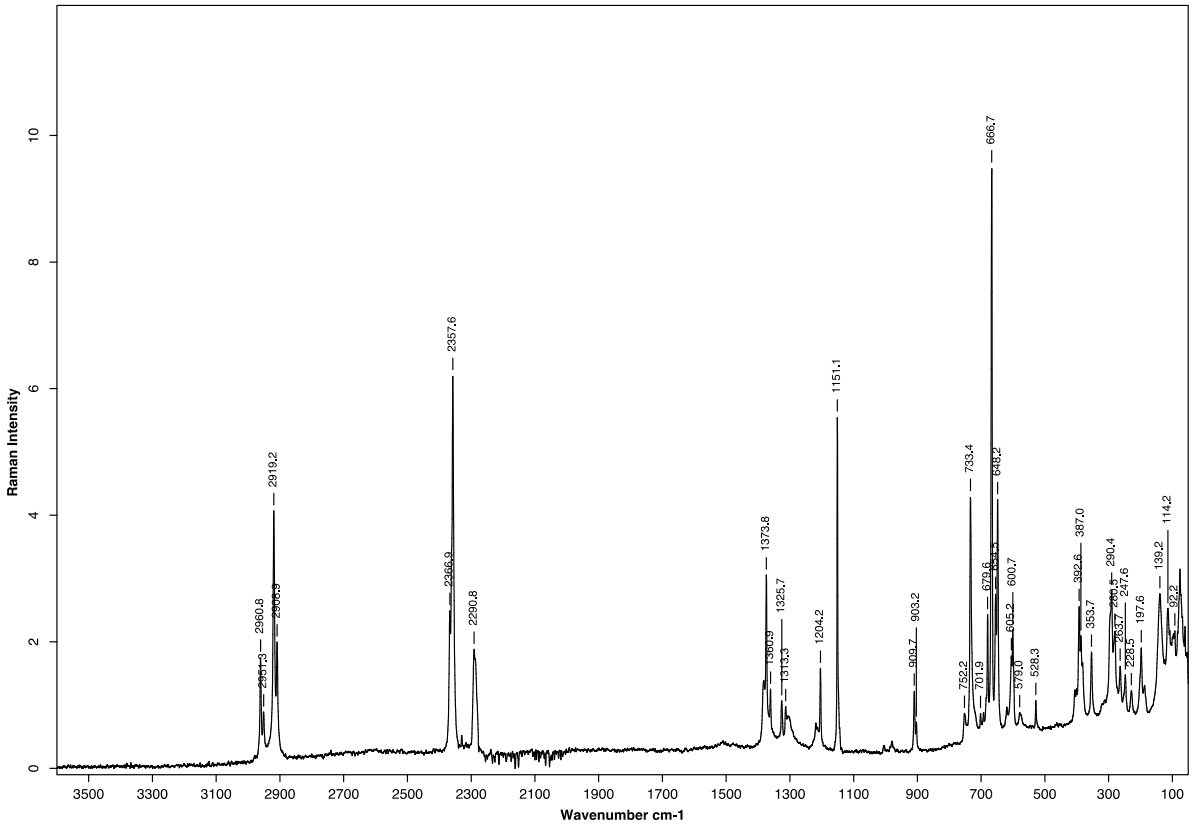
$NCCH_2CN{\bullet}SbF_5$

TS225

10/17/2016 11:36:33 AM

white solid, 9 mm FEP tube, -90°C

1501 Scans 2 cm-1 350 mW



File Name: TS225.1

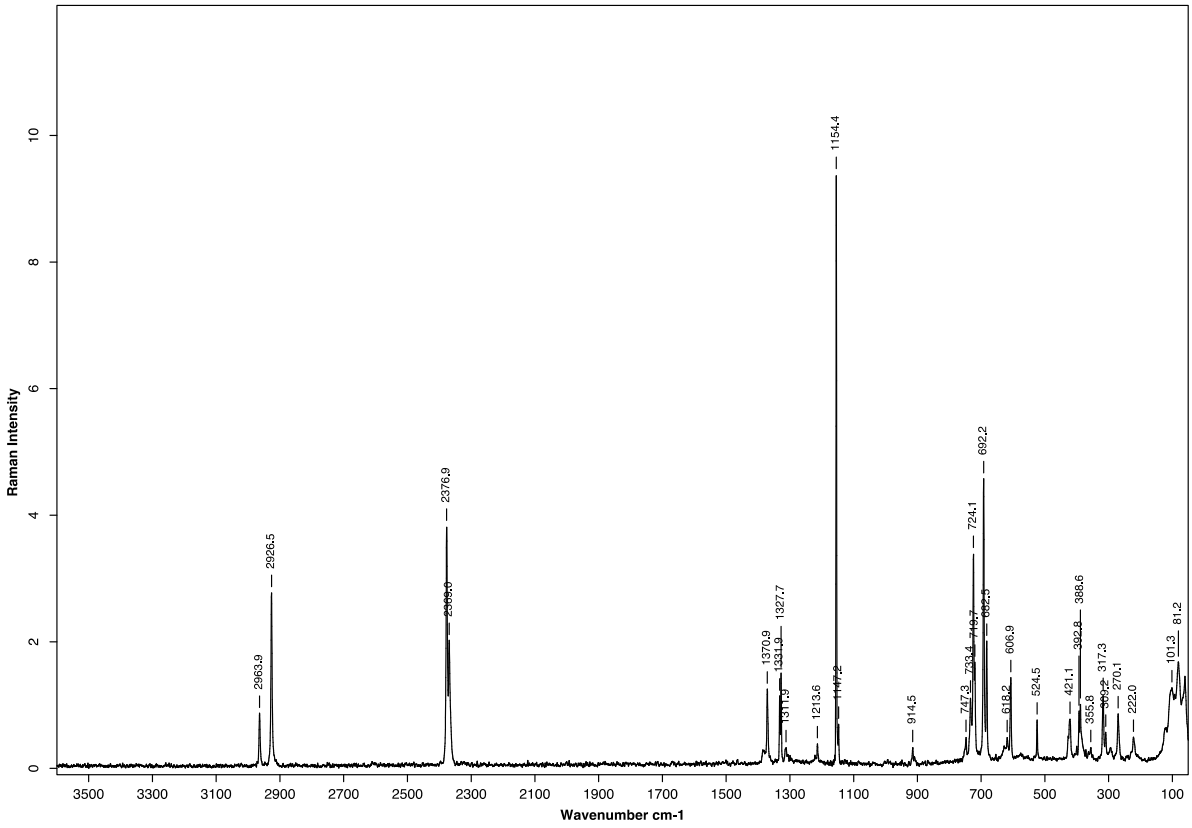
AsF_5•$NCCH_2CN$•AsF_5

TS223

10/13/2016 6:15:23 PM

white solid, 9 mm FEP tube, -90°C

25 Scans 2 cm-1 350 mW



File Name: TS223.1

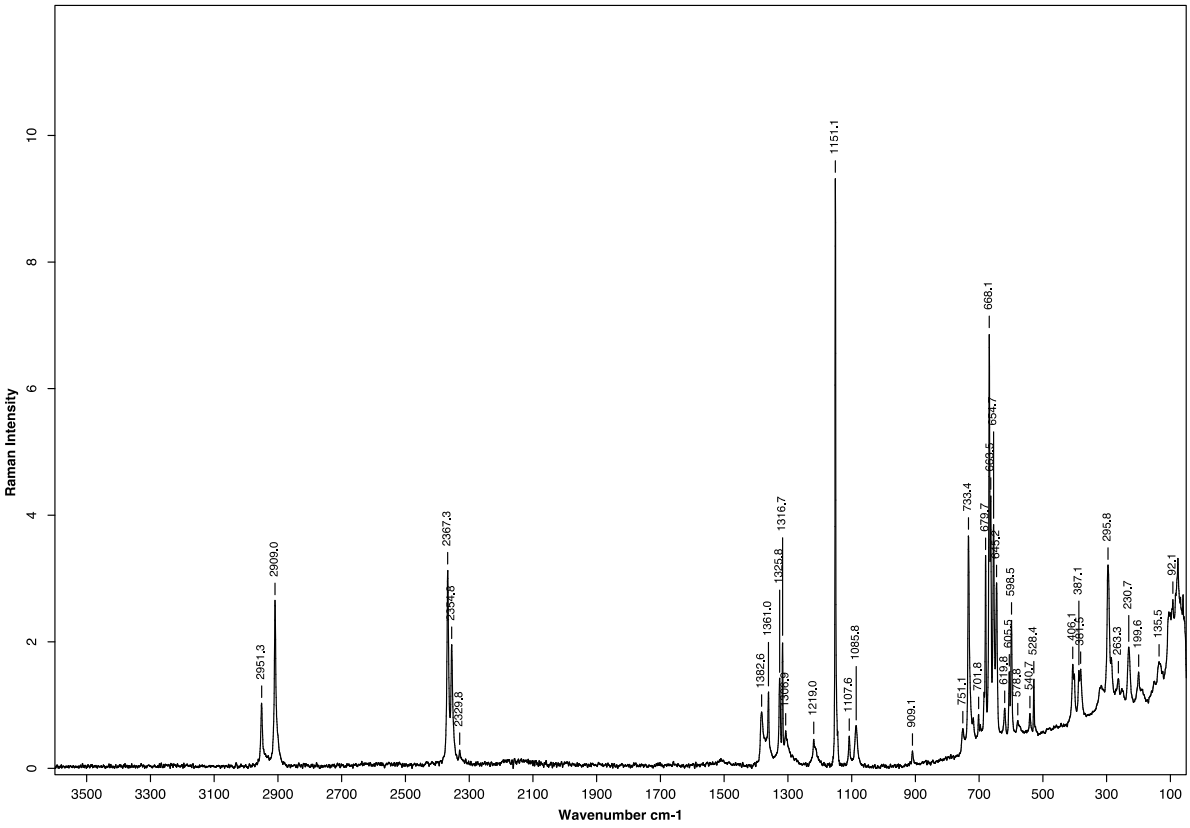
SbF_5•$NCCH_2CN$•SbF_5

TS258

11/26/2016 11:34:05 AM

colorless solid, 9mm FEP, -90°C

1502 Scans 2 cm-1 350 mW



File Name: TS258.1

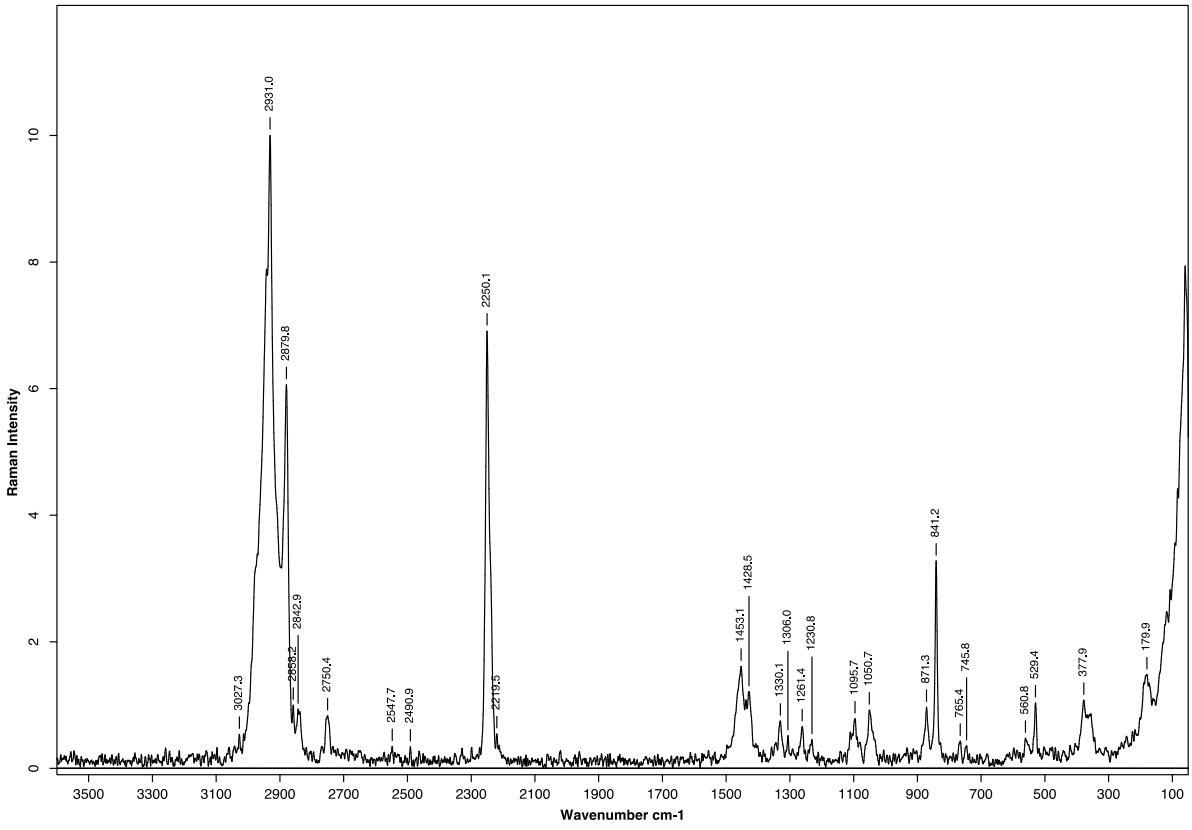
C_3H_7CN

ref_Butanenitrile

6/6/2017 3:18:33 PM

colorless liquid, 5 mm NMR tube, r.t.

2000 Scans 4 cm-1 100 mW



File Name: ref_Butanenitrile.1

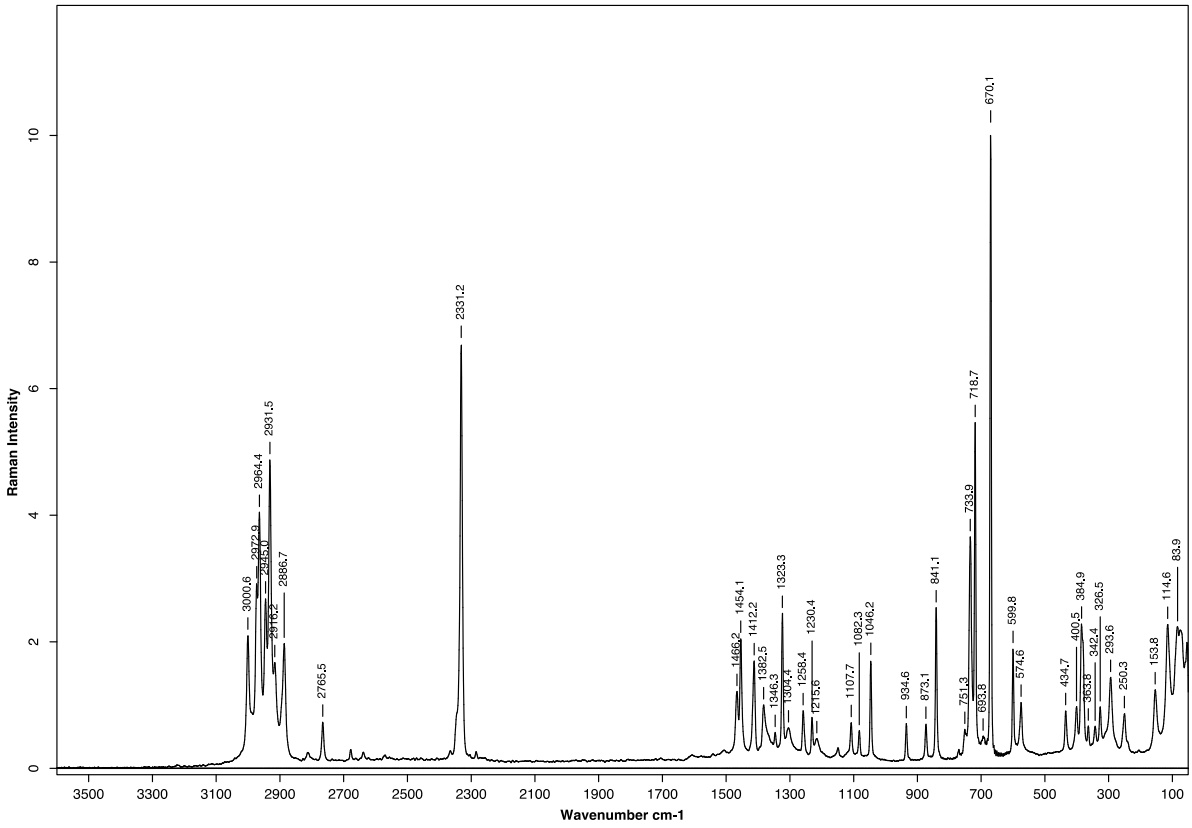
$C_3H_7CN•AsF_5$

TS410

4/6/2018 12:31:14 PM

colorless solid, 9 mm FEP, -90°C

2000 Scans 4 cm-1 350 mW



File Name: TS410.1

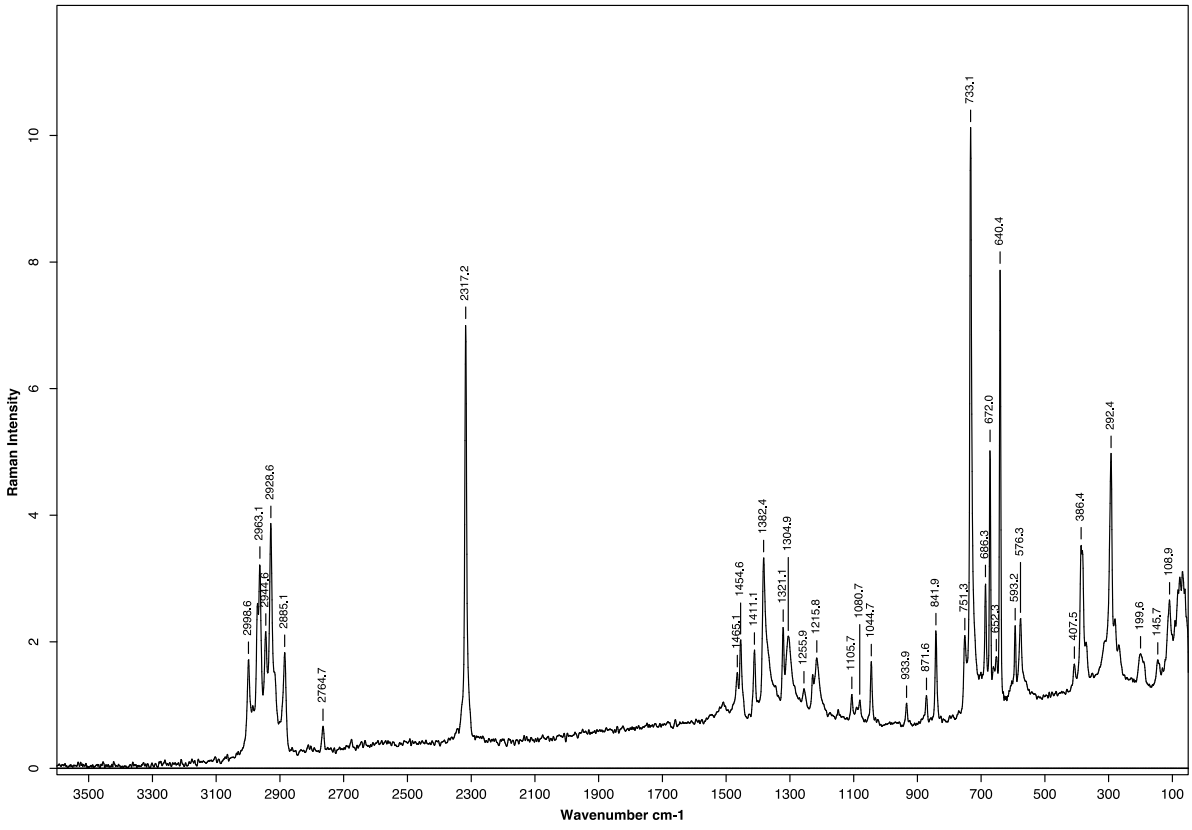
$C_3H_7CN•SbF_5$

TS404

4/3/2018 11:04:24 AM

colorless solid, 9 mm FEP, -90°C

1000 Scans 4 cm-1 350 mW



File Name: TS404.1

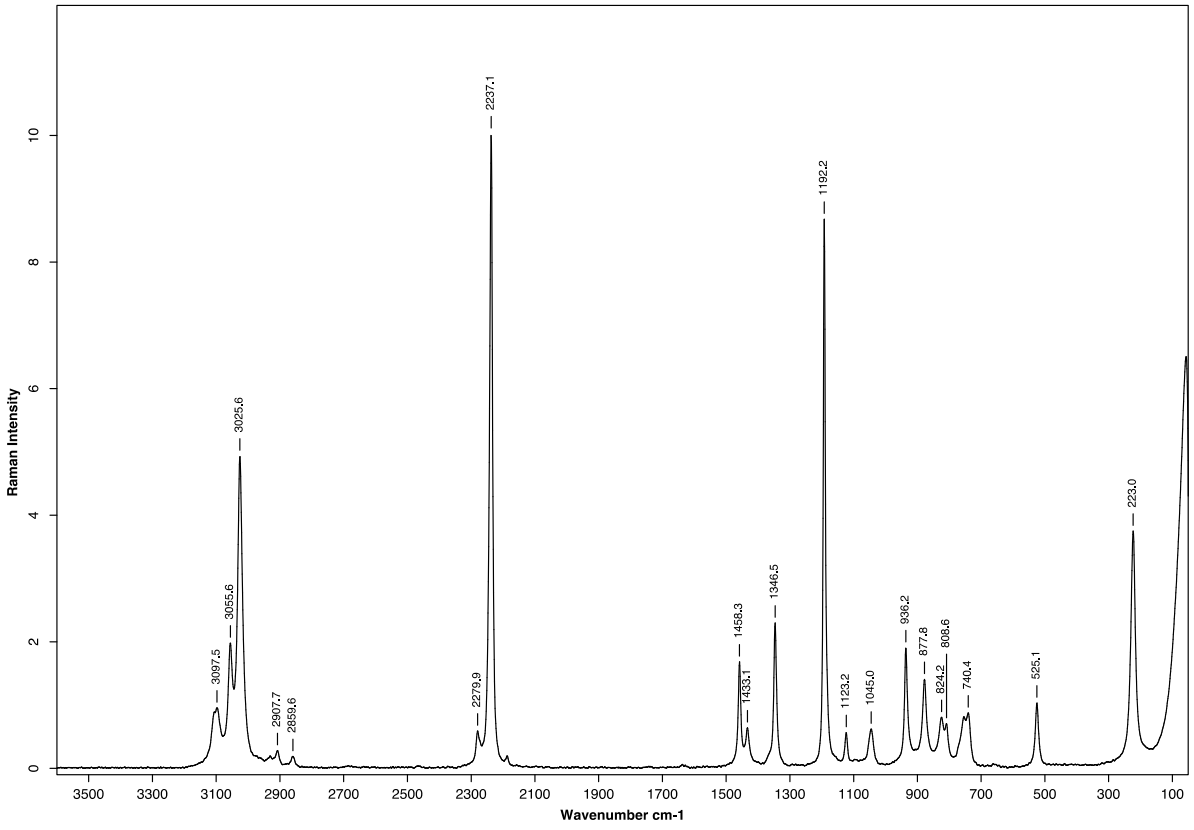
cyclo-C_3H_5CN

ref_cyclopropanecarbonitrile

11/17/2017 5:34:14 PM

colorless crystalline solid, r.t.

1000 Scans 4 cm-1 75 mW



File Name: ref_cyclopropanecarbonitrile.0

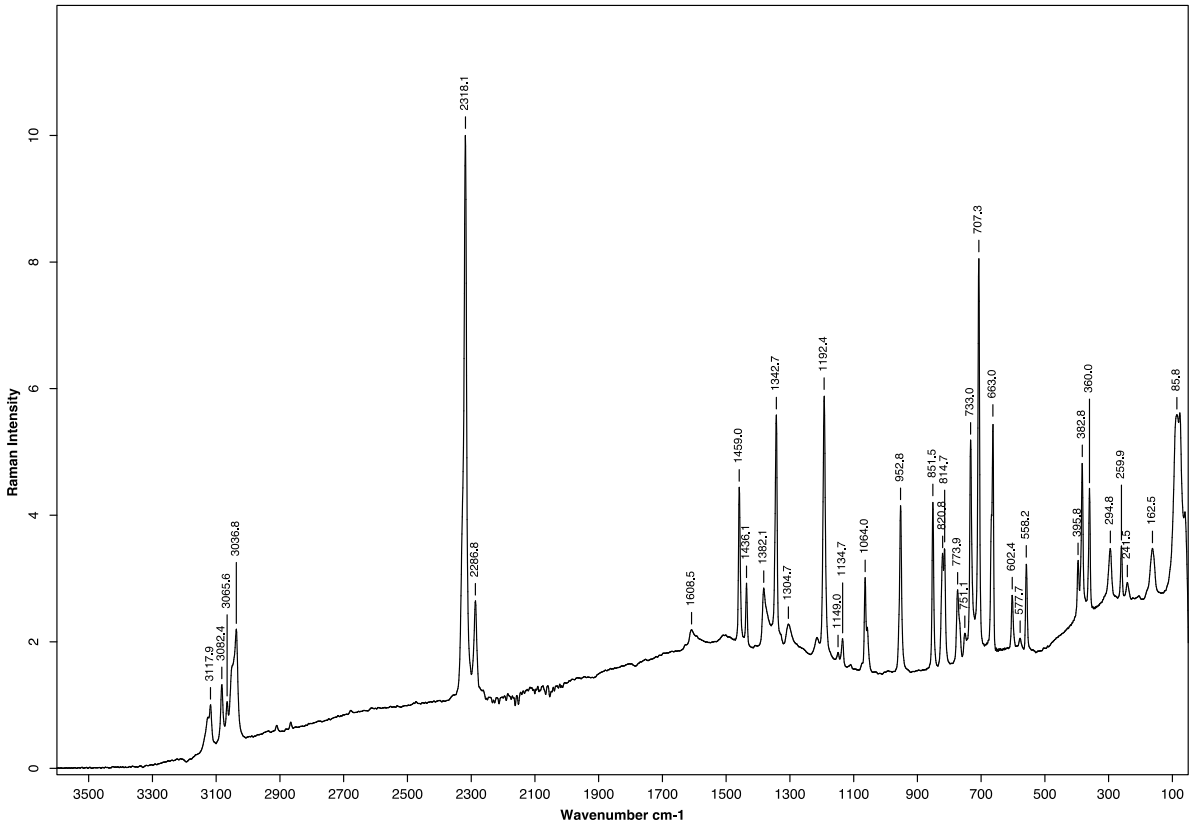
cyclo-C_3H_5CN•AsF_5

TS409

4/5/2018 12:59:53 PM

colorless solid, 9 mm FEP, -90°C

2000 Scans 4 cm-1 350 mW



File Name: TS409.1

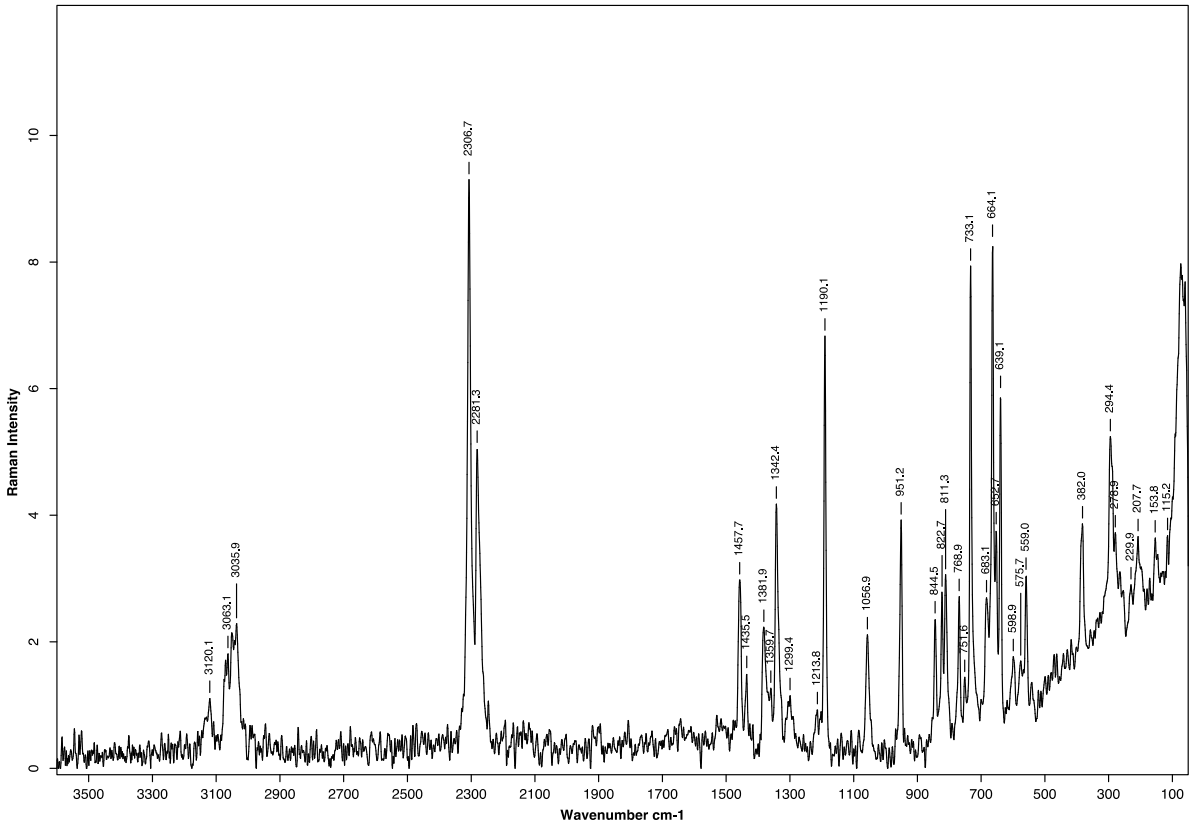
cyclo-$C_3H_5CN{\bullet}SbF_5$

TS405

4/3/2018 12:40:13 PM

pale orange solid, 9 mm FEP, -90°C

200 Scans 4 cm-1 350 mW



File Name: TS405.1

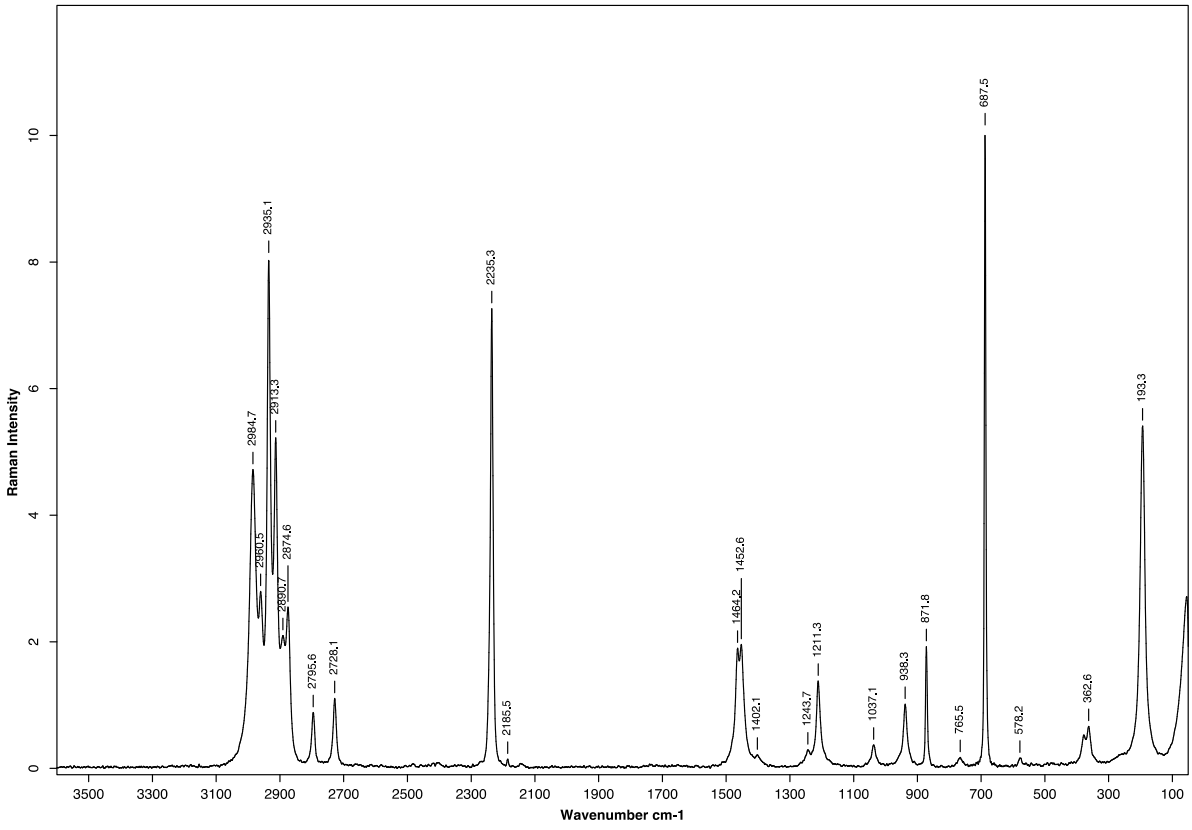
$(CH_3)_3CCN$

ref_Trimethylacetonitrile

11/18/2017 1:45:13 PM

colorless crystalline solid, r.t.

1000 Scans 4 cm-1 75 mW



File Name: ref_Trimethylacetonitrile.0

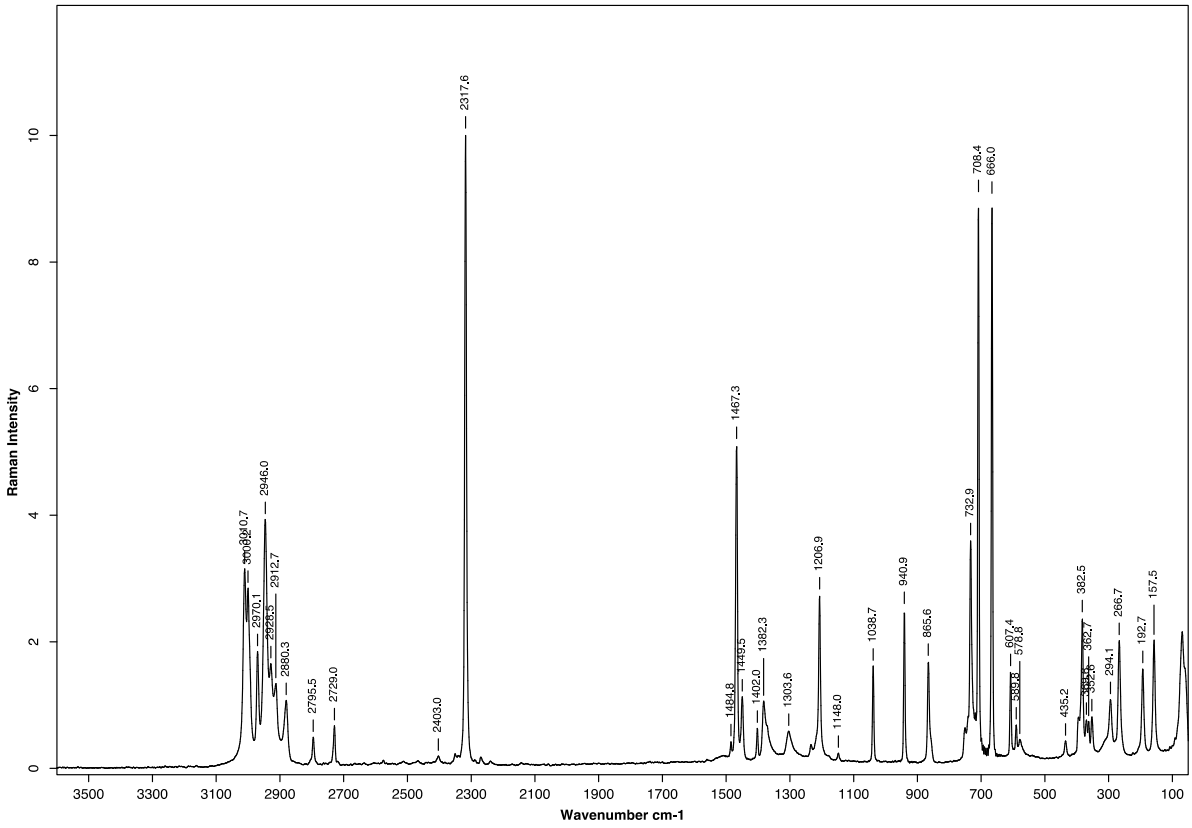
$(CH_3)_3CCN•AsF_5$

TS408

4/5/2018 11:56:40 AM

colorless solid, 9 mm FEP, -90°C

1000 Scans 4 cm-1 350 mW



File Name: TS408.1

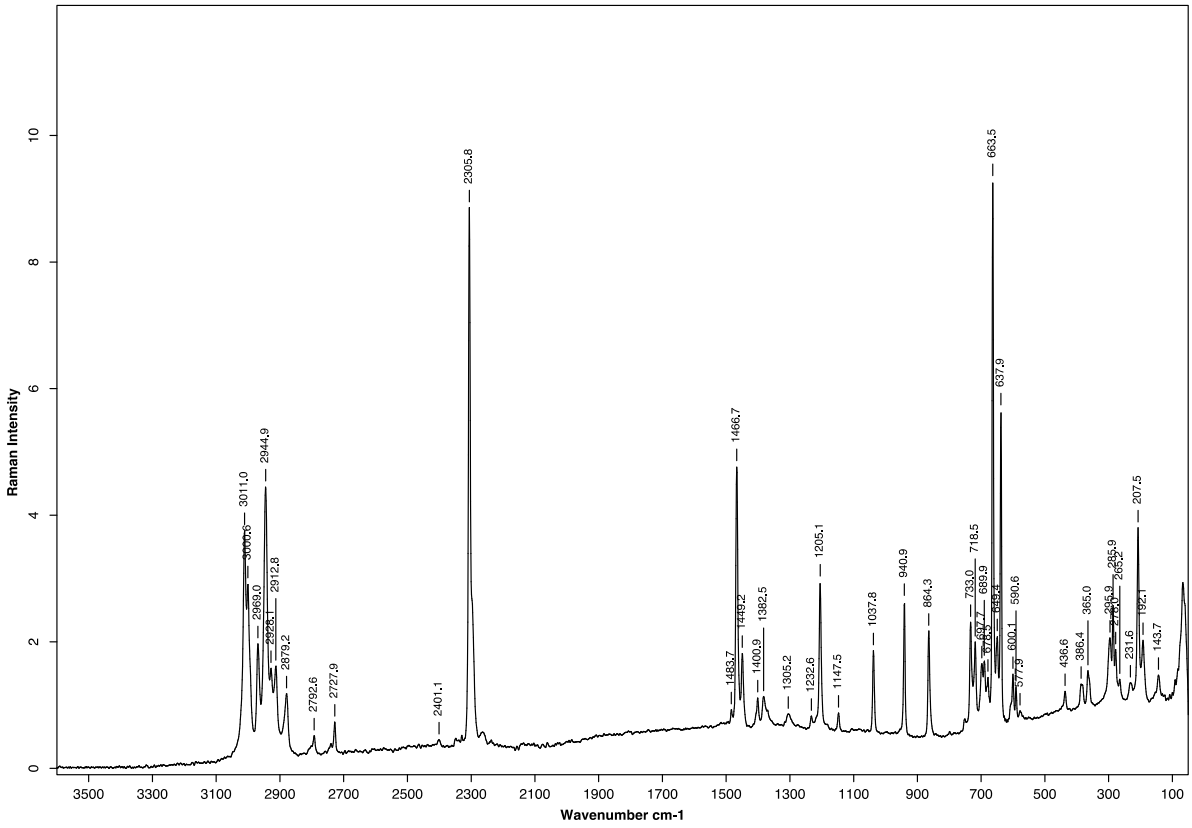
$(CH_3)_3CCN•SbF_5$

TS402

3/30/2018 3:20:31 PM

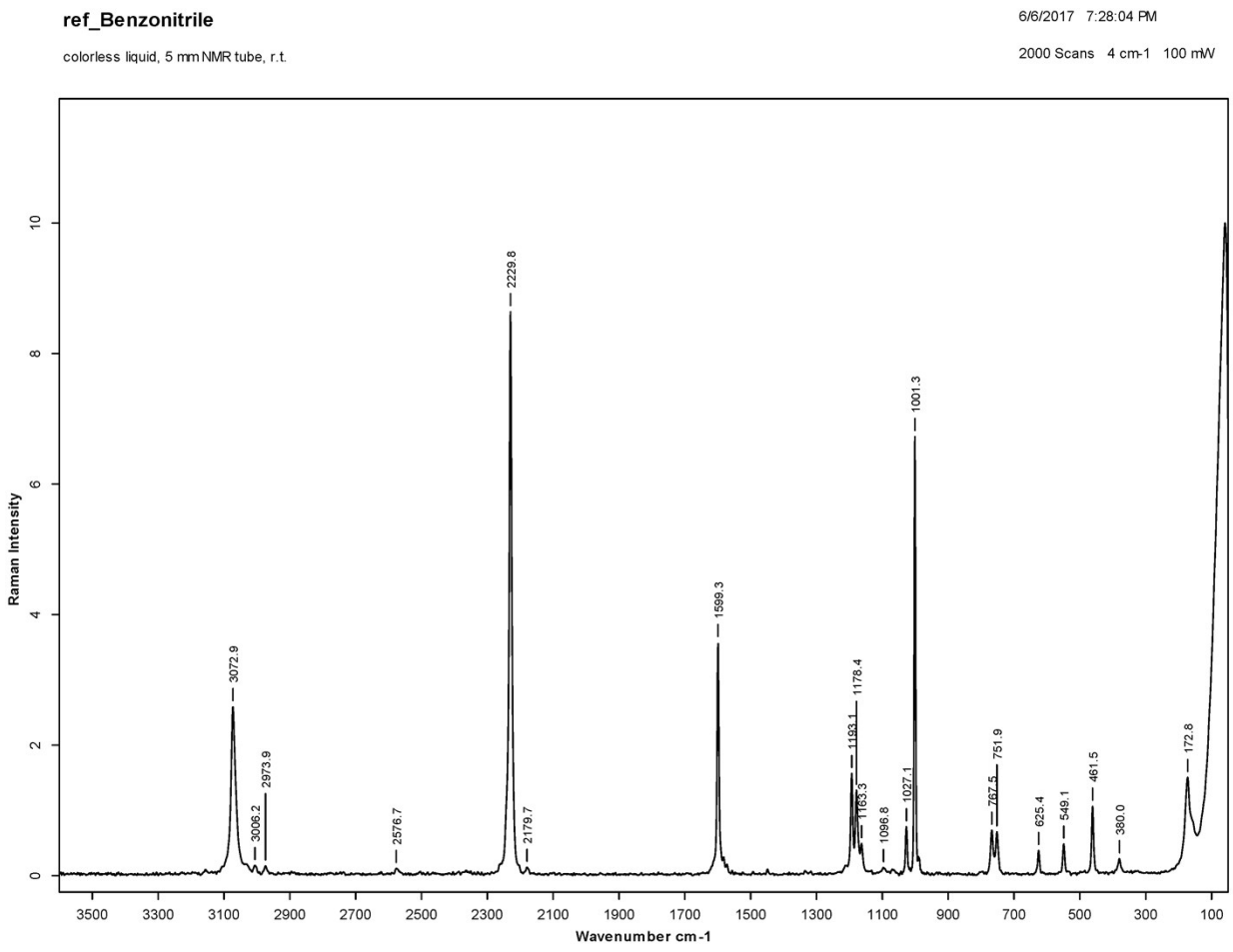
colorless solid, 9 mm FEP, -90°C

1801 Scans 4 cm-1 350 mW



File Name: TS402.0

C_6H_5CN


ref_Benzonitrile
colorless liquid, 5 mm NMR tube, r.t.
6/6/2017 7:28:04 PM
2000 Scans 4 cm-1 100 mW
Raman Intensity
Wavenumber cm-1
3072.9
2973.9
3006.2
2576.7
2229.8
2179.7
1599.3
1178.4
1183.1
1163.3
1098.8
1027.1
1001.3
767.5
751.9
625.4
549.1
461.5
380.0
172.8

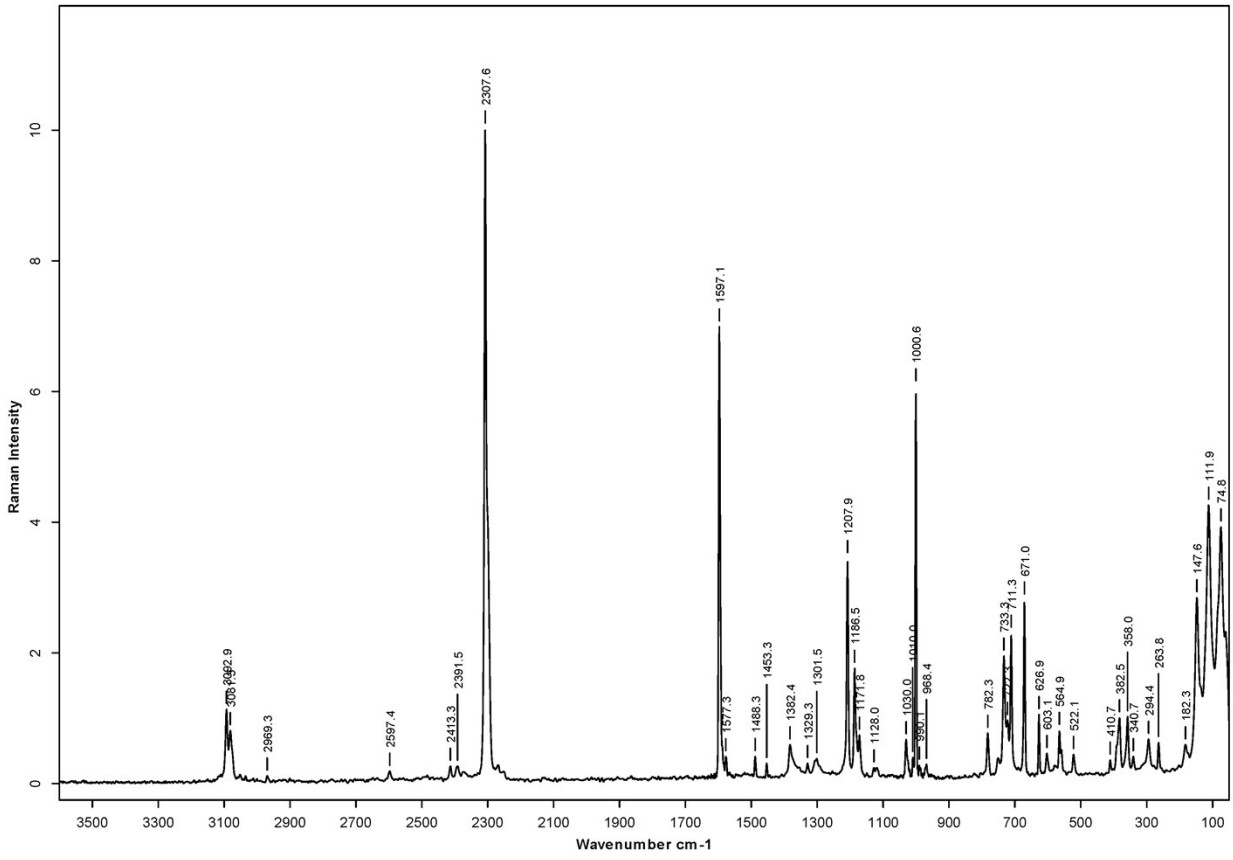
$C_6H_5CN•AsF_5$

TS439

7/10/2018 9:50:53 AM

colorless solid, 9 mm FEP tube, -90°C

500 Scans 4 cm-1 350 mW



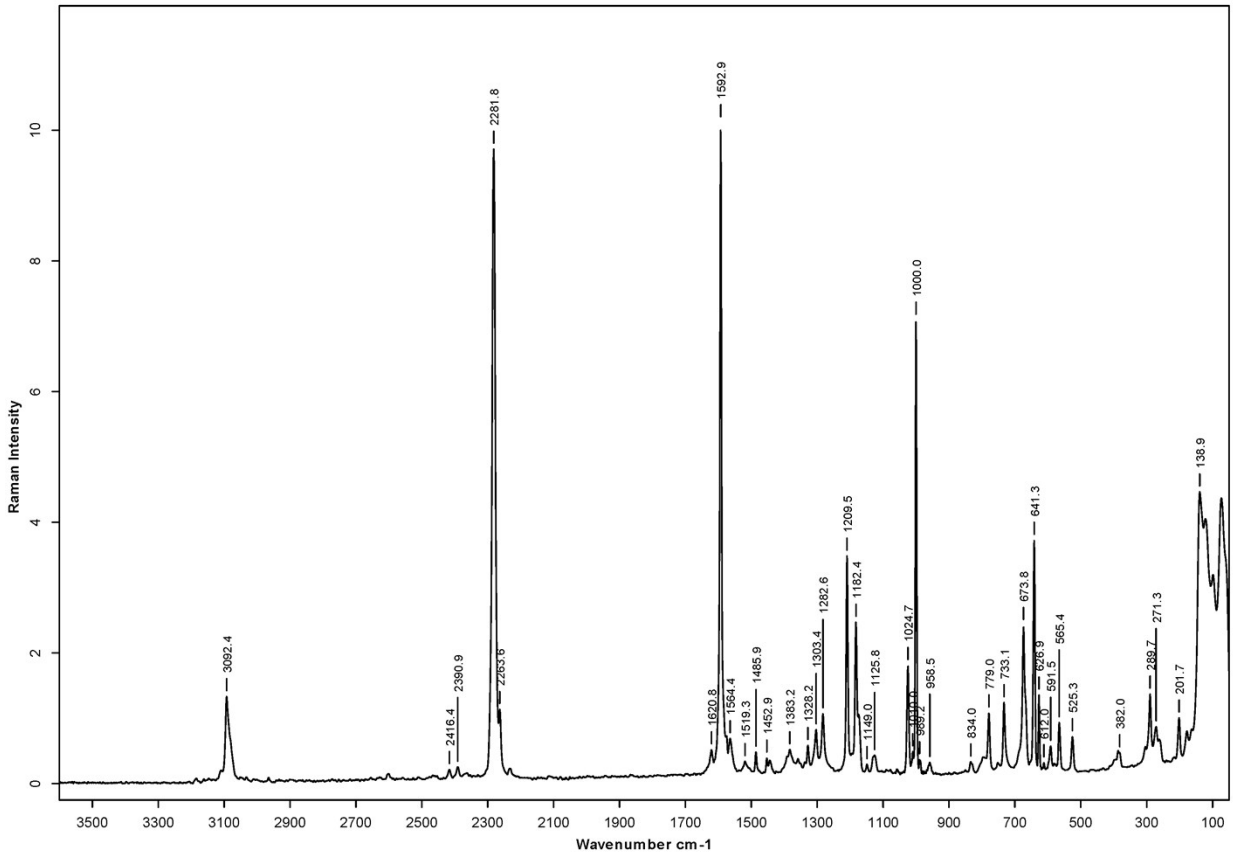
$C_6H_5CN•SbF_5$

TS440

pale yellow solid, 9 mm FEP tube, -90°C

7/10/2018 10:10:40 AM

500 Scans 4 cm-1 350 mW



FEP

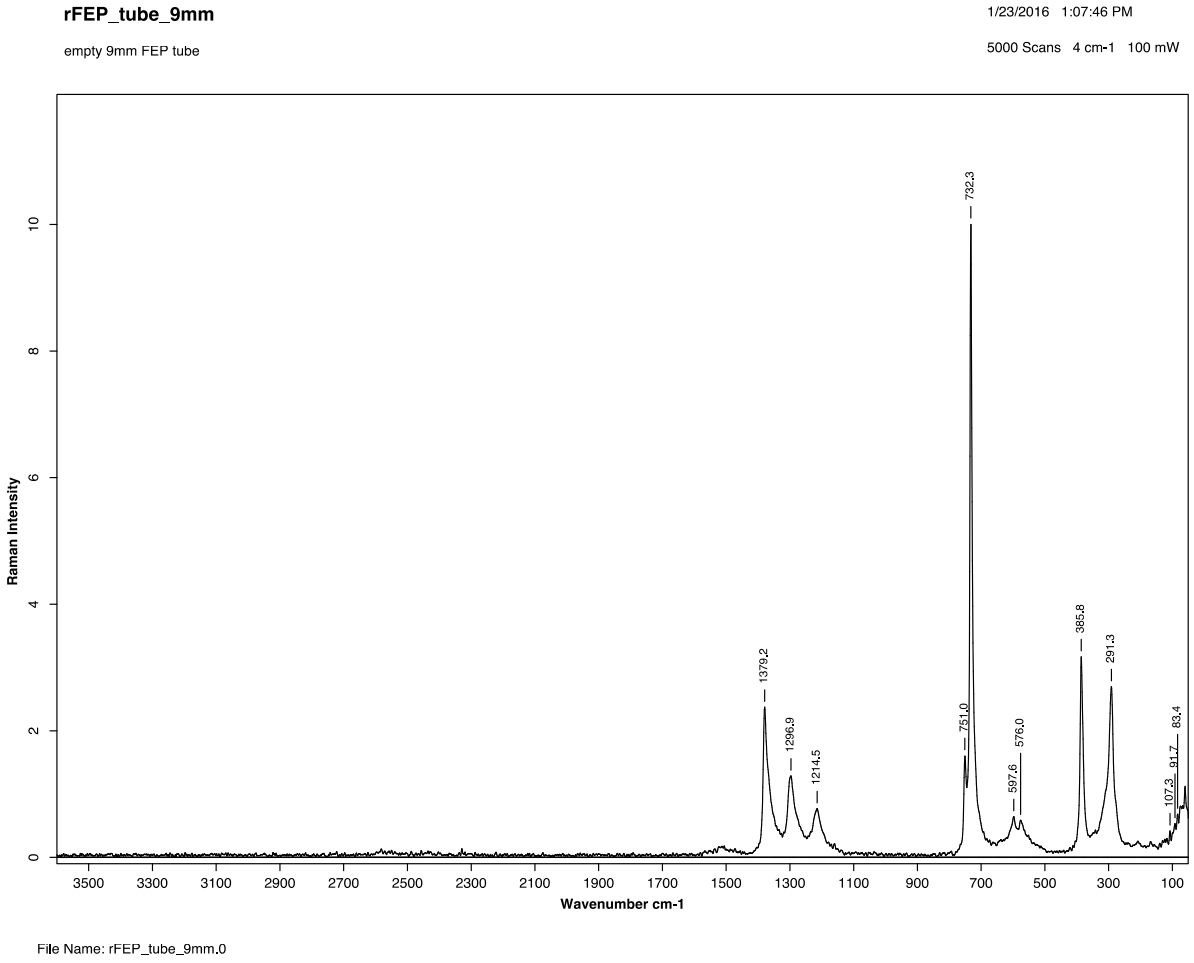


Table S2-1. Comparison of CN stretching vibration frequencies of the Lewis adducts and the free nitriles.

Compound	**ν(CN)** / cm^{-1}	
	$RCN{\bullet}MF_5$	RCN
$HCN{\bullet}AsF_5$	2191.6	2097.9
$HCN{\bullet}SbF_5$	2176.7	
$NCCH_2CN{\bullet}AsF_5$	2366.3 (2282.0)[a]	2265.9
$NCCH_2CN{\bullet}SbF_5$	2357.6 (2290.8)[a]	
$C_3H_7CN{\bullet}AsF_5$	2331.2	2250.1
$C_3H_7CN{\bullet}SbF_5$	2317.2	
c-$C_3H_5CN{\bullet}AsF_5$	2318.1	2237.1
c-$C_3H_5CN{\bullet}SbF_5$	2306.7	
$(CH_3)_3CCN{\bullet}AsF_5$	2317.6	2235.3
$(CH_3)_3CCN{\bullet}SbF_5$	2305.8	
$C_6H_5CN{\bullet}AsF_5$	2307.6	2229.8
$C_6H_5CN{\bullet}SbF_5$	2281.8	
$AsF_5{\bullet}NCCH_2CN{\bullet}AsF_5$	2376.9	2265.9
$SbF_5{\bullet}NCCH_2CN{\bullet}SbF_5$	2367.3	

(a) stretching frequency of non-coordinating cyano group in parenthesis.

Crystallographic Details

$HCN•AsF_5$

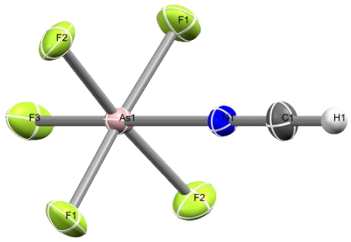


Figure S1-1. Molecular unit of $HCN•AsF_5$. View along the 100 direction.

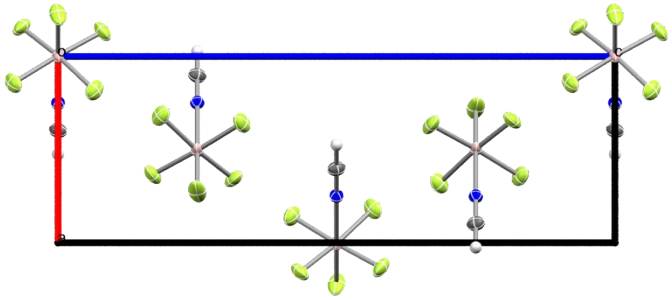


Figure S2-1. Packing of $HCN•AsF_5$. View along the 010 direction.

Table S1-1. Sample and crystal data for $HCN•AsF_5$.

Identification code	AsF5HCN	
Chemical formula	$CHAsF_5N$	
Formula weight	196.95 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.176 x 0.232 x 0.338 mm	
Crystal habit	colorless block	
Crystal system	Tetragonal	
Space group	P 21 21 2	
Unit cell dimensions	a = 5.4973(15) Å	α = 90°
	b = 5.4973(15) Å	β = 90°
	c = 16.475(5) Å	γ = 90°
Volume	497.9(3) $Å^3$	
Z	4	
Density (calculated)	2.628 g/cm^3	
Absorption coefficient	6.836 mm^{-1}	
F(000)	368	

Table S2-1. Data collection and structure refinement for HCN•AsF_5.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	3.91 to 30.57°	
Index ranges	-7<=h<=7, -7<=k<=7, -23<=l<=23	
Reflections collected	12048	
Independent reflections	762 [R(int) = 0.0400]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.3780 and 0.2060	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	762 / 1 / 41	
Goodness-of-fit on F^2	1.195	
Final R indices	673 data; I>2σ(I)	R1 = 0.0246, wR2 = 0.0552
	all data	R1 = 0.0288, wR2 = 0.0567
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0167P)^2+0.5235P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.329 and -0.472 eÅ^{-3}	
R.M.S. deviation from mean	0.089 eÅ^{-3}	

Table S3-1. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for HCN•AsF_5.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.1026(5)	0.8974(5)	0.25	0.0236(8)
As1	0.50372(5)	0.49628(5)	0.25	0.01659(13)
F1	0.3572(5)	0.3663(4)	0.33001(11)	0.0318(4)
F2	0.3184(4)	0.3431(4)	0.18455(11)	0.0309(4)
F3	0.7239(3)	0.2761(3)	0.25	0.0390(8)
N1	0.2487(4)	0.7513(4)	0.25	0.0179(6)

Table S4-1. Bond lengths (Å) for HCN•AsF_5.

C1-N1	1.136(5)	C1-H1	1.00(2)
As1-F1	1.7020(17)	As1-F1	1.7021(17)
As1-F2	1.7058(18)	As1-F2	1.7058(18)
As1-F3	1.712(2)	As1-N1	1.983(3)

Table S5-1. Bond angles (°) for HCN•AsF_5.

N1-C1-H1	180.0	F1-As1-F1	175.7(2)
F1-As1-F2	89.70(10)	F1-As1-F2	89.98(10)
F1-As1-F2	89.98(10)	F1-As1-F2	89.70(10)

F2-As1-F2	171.60(17)	F1-As1-F3	92.17(10)
F1-As1-F3	92.17(10)	F2-As1-F3	94.20(9)
F2-As1-F3	94.20(9)	F1-As1-N1	87.83(10)
F1-As1-N1	87.83(10)	F2-As1-N1	85.80(9)
F2-As1-N1	85.80(9)	F3-As1-N1	180.00(2)
C1-N1-As1	180.0(2)		

Table S6-1. Anisotropic atomic displacement parameters (Å^2) for HCN•AsF_5.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0202(11)	0.0202(11)	0.030(2)	0.0025(14)	0.0025(14)	0.0004(15)
As1	0.01828(15)	0.01828(15)	0.01320(19)	0.00090(10)	0.00090(10)	0.00657(12)
F1	0.0358(12)	0.0329(12)	0.0266(8)	0.0138(9)	0.0078(9)	0.0063(9)
F2	0.0378(14)	0.0254(11)	0.0296(9)	-0.0120(9)	-0.0076(9)	0.0044(8)
F3	0.0444(12)	0.0444(12)	0.0283(14)	0.0060(15)	0.0060(15)	0.0329(15)
N1	0.0176(9)	0.0176(9)	0.0184(15)	-0.0004(14)	-0.0004(14)	0.0011(12)

Table S7-1. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for HCN•AsF_5.

	x/a	y/b	z/c	U(eq)
H1	-0.025(3)	1.025(3)	0.2500	0.028

HCN•SbF_5

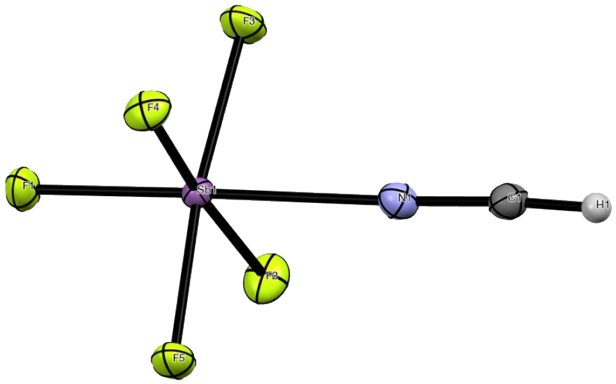


Figure S1-3. Asymmetric unit of HCN•SbF_5.

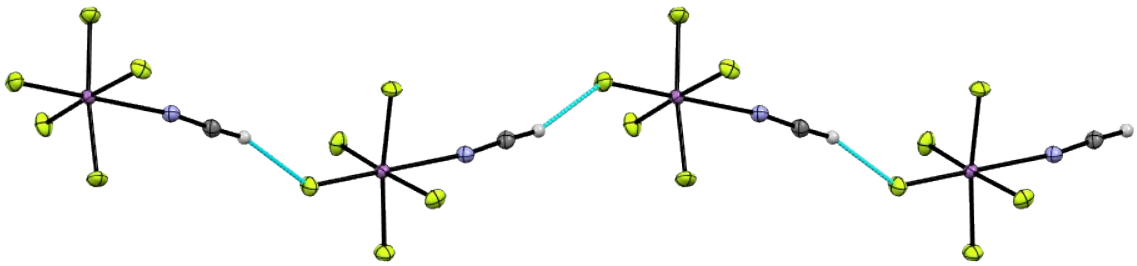


Figure S2-3. Hydrogen bonding in HCN•SbF_5. View along the 001 direction.

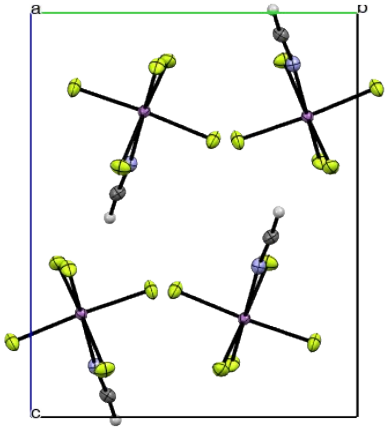


Figure S3-3. Packing of HCN•SbF_5 in the unit cell. View along the 010 direction.

Table S1-3. Sample and crystal data for $HCN•SbF_5$.

Identification code	HCNSbF5	
Chemical formula	CHF_5NSb	
Formula weight	243.78 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.052 x 0.189 x 0.217 mm	
Crystal habit	clear colorless plate	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.2721(13) Å	α = 90°
	b = 8.1472(17) Å	β = 95.375(4)°
	c = 10.157(2) Å	γ = 90°
Volume	516.74(19) $Å^3$	
Z	4	
Density (calculated)	3.134 g/cm^3	
Absorption coefficient	5.348 mm^{-1}	
F(000)	440	

Table S2-3. Data collection and structure refinement for $HCN•SbF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	3.21 to 30.43°	
Reflections collected	1543	
Coverage of independent reflections	98.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7680 and 0.3900	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1543 / 0 / 76	
Goodness-of-fit on F^2	1.109	
Final R indices	1434 data; I>2σ(I)	R1 = 0.0224, wR2 = 0.0571
	all data	R1 = 0.0251, wR2 = 0.0580
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0262P)^2+0.5137P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.655 and -1.020 $eÅ^{-3}$	
R.M.S. deviation from mean	0.179 $eÅ^{-3}$	

Table S3-3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for $HCN•SbF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x/a	y/b	z/c	U(eq)

C1	0.6421(5)	0.2651(3)	0.4458(3)	0.0155(5)
N1	0.5037(4)	0.3030(3)	0.3737(3)	0.0152(5)
F1	0.9729(3)	0.3857(2)	0.13287(18)	0.0188(4)
F2	0.0711(3)	0.2746(2)	0.38204(18)	0.0203(4)
F3	0.2530(3)	0.1326(2)	0.18482(19)	0.0196(4)
F4	0.4016(3)	0.4190(2)	0.11873(17)	0.0181(4)
F5	0.2286(3)	0.5584(2)	0.31426(18)	0.0189(4)
Sb1	0.22230(3)	0.34653(2)	0.24369(2)	0.01044(7)

Table S4-3. Bond lengths (Å) for HCN•SbF_5.

C1-N1	1.125(4)	C1-H1	0.91(4)
N1-Sb1	2.132(3)	F1-Sb1	1.8673(18)
F2-Sb1	1.8620(17)	F3-Sb1	1.8585(17)
F4-Sb1	1.8686(17)	F5-Sb1	1.8679(17)

Table S5-3. Bond angles (°) for HCN•SbF_5.

N1-C1-H1	176.(2)	C1-N1-Sb1	172.7(3)
F3-Sb1-F2	91.32(8)	F3-Sb1-F1	94.17(8)
F2-Sb1-F1	92.96(8)	F3-Sb1-F5	172.27(9)
F2-Sb1-F5	89.73(8)	F1-Sb1-F5	93.42(8)
F3-Sb1-F4	89.46(8)	F2-Sb1-F4	173.48(8)
F1-Sb1-F4	93.44(8)	F5-Sb1-F4	88.64(8)
F3-Sb1-N1	86.48(9)	F2-Sb1-N1	86.04(9)
F1-Sb1-N1	178.82(8)	F5-Sb1-N1	85.96(9)
F4-Sb1-N1	87.55(9)		

Table S6-3. Anisotropic atomic displacement parameters (Å²) for HCNSbF5.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0154(13)	0.0167(12)	0.0144(13)	-0.0027(10)	0.0010(11)	-0.0004(10)
N1	0.0155(12)	0.0133(10)	0.0169(11)	-0.0009(9)	0.0018(9)	-0.0002(9)
F1	0.0167(9)	0.0179(8)	0.0201(9)	-0.0020(7)	-0.0066(7)	0.0020(7)
F2	0.0161(9)	0.0279(9)	0.0175(8)	0.0040(7)	0.0054(7)	-0.0038(7)
F3	0.0215(10)	0.0116(7)	0.0251(10)	-0.0049(7)	-0.0007(8)	0.0011(6)
F4	0.0215(9)	0.0186(8)	0.0151(8)	0.0005(6)	0.0062(7)	-0.0035(7)
F5	0.0204(9)	0.0142(8)	0.0214(9)	-0.0056(6)	-0.0017(7)	0.0012(6)
Sb1	0.01064(11)	0.01055(11)	0.01001(11)	-0.00064(5)	0.00037(7)	-0.00031(5)

Table S7-3. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for HCN•SbF_5.

	x/a	y/b	z/c	U(eq)
H1	0.752(6)	0.241(4)	0.507(3)	0.019

$NCCH_2CN•AsF_5$

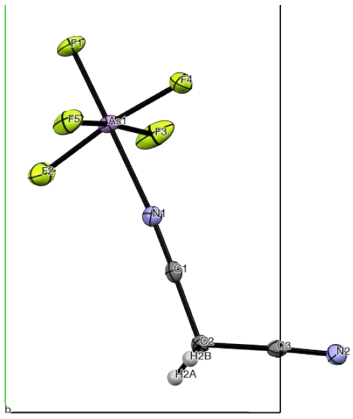


Figure S1-3. Asymmetric unit of $NCCH_2CN•AsF_5$. View along the 001 direction.

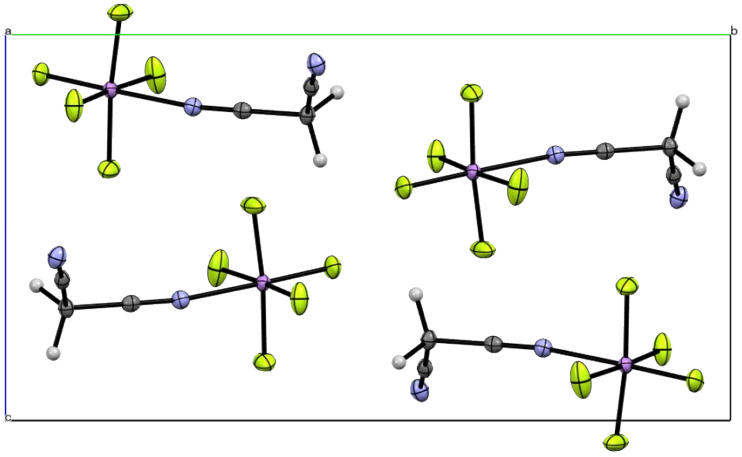


Figure S2-3. Packing of $NCCH_2CN•AsF_5$. View along the 010 direction.

Table S1-3. Sample and crystal data for $NCCH_2CN•AsF_5$

Identification code	AsF5_MN	
Chemical formula	$C_3H_2AsF_5N_2$	
Formula weight	235.99 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.181 x 0.225 x 0.268 mm	
Crystal habit	clear orange prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 5.3370(14) Å	α = 90°
	b = 15.253(4) Å	β = 104.093(4)°
	c = 8.351(2) Å	γ = 90°
Volume	659.4(3) Å3	
Z	4	
Density (calculated)	2.377 g/cm3	
Absorption coefficient	5.188 mm-1	
F(000)	448	

Table S2-3. Data collection and structure refinement for $NCCH_2CN•AsF_5$.

Diffractometer	Bruker APEX II CCD Bruker APEX DUO	
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)	
Theta range for data collection	2.67 to 30.55°	
Index ranges	-7<=h<=7, -21<=k<=21, -11<=l<=11	
Reflections collected	15118	
Independent reflections	2020 [R(int) = 0.0273]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.4540 and 0.3370	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2020 / 0 / 100	
Goodness-of-fit on F^2	1.106	
Δ/σ_{max}	0.003	
Final R indices	1813 data; I>2σ(I)	R1 = 0.0183, wR2 = 0.0414
	all data	R1 = 0.0233, wR2 = 0.0427
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0177P)^2+0.3993P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.319 and -0.503 eÅ^{-3}	
R.M.S. deviation from mean	0.070 eÅ^{-3}	

Table S3-3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $NCCH_2CN•AsF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.6133(3)	0.82689(10)	0.30272(17)	0.0133(3)
C2	0.7098(3)	0.91608(9)	0.29123(18)	0.0139(3)
C3	0.9894(3)	0.92159(9)	0.36438(17)	0.0139(3)
As1	0.37743(3)	0.64484(2)	0.35627(2)	0.01279(5)
F1	0.24072(19)	0.54919(6)	0.39684(12)	0.0222(2)
F2	0.1338(2)	0.70672(7)	0.39459(16)	0.0342(3)
F3	0.5449(2)	0.65826(7)	0.55680(12)	0.0345(3)
F4	0.63935(19)	0.59439(6)	0.31564(14)	0.0277(2)
F5	0.2295(2)	0.64279(6)	0.15168(12)	0.0265(2)
N1	0.5351(2)	0.75852(8)	0.31240(15)	0.0145(2)
N2	0.2053(2)	0.92865(9)	0.42225(16)	0.0183(2)

Table S4-3. Bond lengths (Å) for $NCCH_2CN•AsF_5$.

C1-N1	1.1334(19)	C1-C2	1.466(2)
C2-C3	1.471(2)	C2-H2A	0.99
C2-H2B	0.99	C3-N2	1.1412(19)
As1-F5	1.6989(10)	As1-F2	1.6990(11)
As1-F4	1.7007(10)	As1-F1	1.7018(10)
As1-F3	1.7078(11)	As1-N1	1.9999(13)

Table S5-3. Bond angles (°) for $NCCH_2CN•AsF_5$.

N1-C1-C2	178.82(15)	C1-C2-C3	111.28(12)
C1-C2-H2A	109.4	C3-C2-H2A	109.4
C1-C2-H2B	109.4	C3-C2-H2B	109.4
H2A-C2-H2B	108.0	N2-C3-C2	177.79(15)
F5-As1-F2	90.58(6)	F5-As1-F4	89.67(6)
F2-As1-F4	173.15(5)	F5-As1-F1	93.88(5)
F2-As1-F1	93.09(5)	F4-As1-F1	93.72(5)
F5-As1-F3	172.95(5)	F2-As1-F3	89.46(7)
F4-As1-F3	89.45(6)	F1-As1-F3	93.15(5)
F5-As1-N1	86.84(5)	F2-As1-N1	85.88(5)
F4-As1-N1	87.30(5)	F1-As1-N1	178.75(5)
F3-As1-N1	86.13(5)	C1-N1-As1	171.69(12)

Table S6-3. Anisotropic atomic displacement parameters (Å^2) for $NCCH_2CN•AsF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0112(6)	0.0165(6)	0.0125(6)	-0.0005(5)	0.0033(5)	0.0016(5)
C2	0.0131(6)	0.0122(6)	0.0172(6)	0.0007(5)	0.0055(5)	-0.0005(5)

C3	0.0169(6)	0.0105(6)	0.0163(6)	-0.0005(5)	0.0080(5)	0.0003(5)
As1	0.01498(7)	0.01103(7)	0.01234(7)	-0.00072(5)	0.00331(5)	-0.00263(5)
F1	0.0285(5)	0.0150(4)	0.0240(5)	0.0002(4)	0.0082(4)	-0.0087(4)
F2	0.0284(5)	0.0197(5)	0.0638(8)	-0.0079(5)	0.0294(5)	-0.0034(4)
F3	0.0549(7)	0.0298(6)	0.0131(4)	0.0021(4)	-0.0028(5)	-0.0214(5)
F4	0.0203(5)	0.0157(4)	0.0494(7)	0.0000(4)	0.0130(5)	0.0020(4)
F5	0.0335(5)	0.0232(5)	0.0165(4)	0.0015(4)	-0.0059(4)	-0.0092(4)
N1	0.0137(5)	0.0148(6)	0.0149(5)	0.0000(4)	0.0035(4)	-0.0002(4)
N2	0.0169(6)	0.0166(6)	0.0229(6)	-0.0028(5)	0.0076(5)	-0.0003(5)

Table S7-3. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for $NCCH_2CN•AsF_5$.

	x/a	y/b	z/c	U(eq)
H2A	0.6183	0.9571	0.3493	0.017
H2B	0.6731	0.9339	0.1738	0.017

$NCCH_2CN \bullet SbF_5$

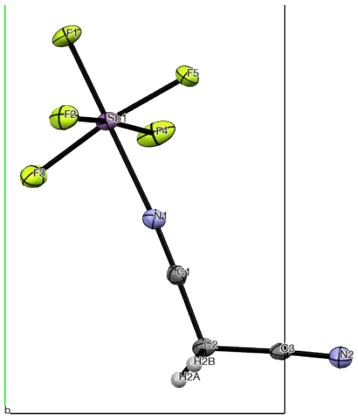


Figure S1-4. Asymmetric unit of $NCCH_2CN \bullet SbF_5$. View along the 001 direction.

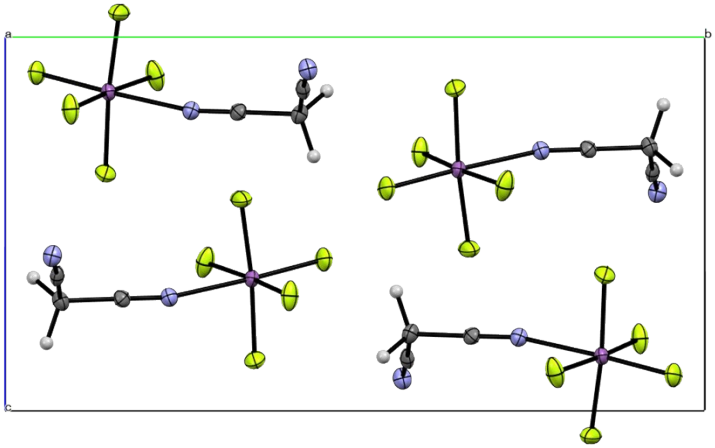


Figure S2-4. Packing of $NCCH_2CN \bullet SbF_5$. View along the 010 direction.

Table S1-4. Sample and crystal data for $NCCH_2CN•SbF_5$.

Identification code	AN26	
Chemical formula	$C_3H_2F_5N_2Sb$	
Formula weight	282.82 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.078 x 0.171 x 0.323 mm	
Crystal habit	red prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 5.3862(16) Å	α = 90°
	b = 15.562(5) Å	β = 102.140(5)°
	c = 8.490(3) Å	γ = 90°
Volume	695.7(4) $Å^3$	
Z	4	
Density (calculated)	2.700 g/cm^3	
Absorption coefficient	3.997 mm^{-1}	
F(000)	520	

Table S2-4. Data collection and structure refinement for $NCCH_2CN•SbF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.62 to 30.50°	
Index ranges	-7<=h<=7, -22<=k<=22, -12<=l<=12	
Reflections collected	15914	
Independent reflections	2112 [R(int) = 0.0647]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7460 and 0.3580	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2112 / 0 / 100	
Goodness-of-fit on F^2	1.107	
Final R indices	1691 data; I>2σ(I)	R1 = 0.0402, wR2 = 0.0942
	all data	R1 = 0.0573, wR2 = 0.1024
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0474P)^2+3.0277P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.820 and -1.064 $eÅ^{-3}$	
R.M.S. deviation from mean	0.241 $eÅ^{-3}$	

Table S3-4. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for $NCCH_2CN•SbF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.6140(10)	0.8332(3)	0.3000(6)	0.0155(9)
C2	0.7113(10)	0.9208(3)	0.2941(7)	0.0176(10)
C3	0.9853(10)	0.9255(3)	0.3608(6)	0.0162(9)
F1	0.2211(7)	0.5449(2)	0.4048(4)	0.0249(7)
F2	0.2121(7)	0.6432(2)	0.1359(4)	0.0254(7)
F3	0.1022(7)	0.7141(2)	0.3974(5)	0.0299(8)
F4	0.5400(8)	0.6629(2)	0.5667(4)	0.0327(9)
F5	0.6510(6)	0.5932(2)	0.3075(5)	0.0272(7)
N1	0.5327(8)	0.7657(3)	0.3035(5)	0.0169(8)
N2	0.1986(9)	0.9325(3)	0.4141(6)	0.0203(9)
Sb1	0.36676(6)	0.64759(2)	0.35362(4)	0.01500(11)

Table S4-4. Bond lengths (Å) for $NCCH_2CN•SbF_5$.

C1-N1	1.141(7)	C1-C2	1.465(7)
C2-C3	1.467(8)	C2-H2A	0.99
C2-H2B	0.99	C3-N2	1.148(7)
F1-Sb1	1.871(3)	F2-Sb1	1.862(3)
F3-Sb1	1.860(3)	F4-Sb1	1.868(3)
F5-Sb1	1.862(3)	N1-Sb1	2.126(4)

Table S5-4. Bond angles (°) for $NCCH_2CN•SbF_5$.

N1-C1-C2	178.4(5)	C1-C2-C3	111.7(4)
C1-C2-H2A	109.3	C3-C2-H2A	109.3
C1-C2-H2B	109.3	C3-C2-H2B	109.3
H2A-C2-H2B	107.9	N2-C3-C2	177.3(5)
C1-N1-Sb1	168.9(4)	F3-Sb1-F2	90.97(17)
F3-Sb1-F5	173.28(15)	F2-Sb1-F5	89.46(17)
F3-Sb1-F4	89.03(19)	F2-Sb1-F4	173.69(15)
F5-Sb1-F4	89.80(18)	F3-Sb1-F1	92.99(15)
F2-Sb1-F1	94.44(15)	F5-Sb1-F1	93.66(15)
F4-Sb1-F1	91.86(15)	F3-Sb1-N1	86.05(16)
F2-Sb1-N1	87.26(16)	F5-Sb1-N1	87.28(16)
F4-Sb1-N1	86.44(16)	F1-Sb1-N1	178.06(16)

Table S6-4. Anisotropic atomic displacement parameters (Å²) for $NCCH_2CN•SbF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.015(2)	0.015(2)	0.016(2)	0.0008(17)	0.0018(18)	0.0021(17)
C2	0.019(2)	0.014(2)	0.020(2)	0.0026(18)	0.0044(19)	-0.0011(18)
C3	0.020(2)	0.010(2)	0.021(2)	-0.0021(17)	0.0102(19)	0.0001(18)
F1	0.0302(18)	0.0163(15)	0.0285(17)	-0.0001(13)	0.0069(14)	-0.0091(13)
F2	0.0321(18)	0.0217(16)	0.0179(15)	-0.0021(12)	-0.0047(13)	-0.0029(14)
F3	0.0275(18)	0.0197(16)	0.048(2)	-0.0088(15)	0.0206(17)	-0.0024(14)
F4	0.054(3)	0.0246(18)	0.0145(15)	0.0009(13)	-0.0037(16)	-0.0137(16)

F5	0.0202(16)	0.0156(15)	0.047(2)	-0.0021(14)	0.0101(15)	0.0038(13)
N1	0.019(2)	0.0149(19)	0.0172(19)	0.0011(15)	0.0038(16)	0.0008(16)
N2	0.020(2)	0.017(2)	0.023(2)	-0.0016(17)	0.0047(18)	0.0000(17)
Sb1	0.01866(17)	0.01123(16)	0.01497(17)	-0.00078(12)	0.00319(11)	-0.00226(13)

Table S7-4. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for AN26.

	x/a	y/b	z/c	U(eq)
H2A	0.6213	0.9596	0.3558	0.021
H2B	0.6763	0.9409	0.1809	0.021

$C_3H_7CN•AsF_5$

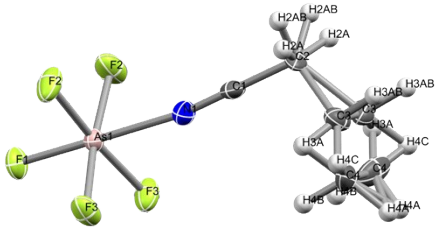


Figure S1-5. Molecular unit of $C_3H_7CN•AsF_5$.

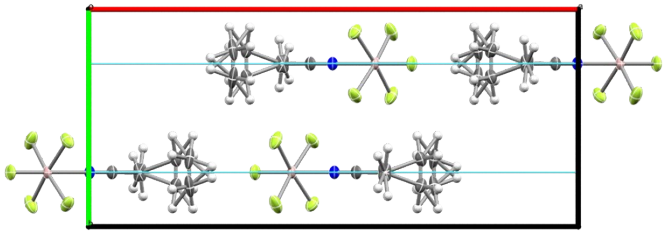


Figure S2-5. Packing of $C_3H_7CN•AsF_5$ in the unit cell. View along the 001 direction (mirror plane in cyan).

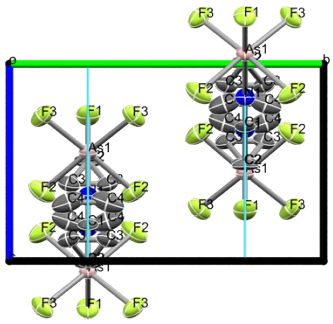


Figure S3-5. Packing of $C_3H_7CN•AsF_5$ in the unit cell. View along the 010 direction (mirror plane in cyan)..

Table S1-5. Sample and crystal data for $C_3H_7CN•AsF_5$.

Identification code	TS410	
Chemical formula	$C_4H_7AsF_5N$	
Formula weight	239.03 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.090 x 0.120 mm	
Crystal habit	clear colorless prism	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 18.521(4) Å	α = 90°
	b = 8.217(2) Å	β = 90°
	c = 5.1493(13) Å	γ = 90°
Volume	783.7(3) $Å^3$	
Z	4	
Density (calculated)	2.026 g/cm^3	
Absorption coefficient	4.363 mm^{-1}	
F(000)	464	

Table S2-5. Data collection and structure refinement for $C_3H_7CN•AsF_5$.

Diffractometer	Bruker APEX II CCD Bruker APEX DUO	
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)	
Theta range for data collection	2.20 to 27.48°	
Index ranges	-24<=h<=23, -10<=k<=10, -6<=l<=6	
Reflections collected	11247	
Independent reflections	964 [R(int) = 0.1164]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7220 and 0.6230	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/4 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	964 / 54 / 71	
Goodness-of-fit on F^2	1.140	
Final R indices	729 data; I>2σ(I)	R1 = 0.0506, wR2 = 0.0704
	all data	R1 = 0.0795, wR2 = 0.0764
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0261P)^2+0.8497P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.018 and -0.710 $eÅ^{-3}$	
R.M.S. deviation from mean	0.127 $eÅ^{-3}$	

Table S3-5. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for $C_3H_7CN•AsF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.0469(3)	0.75	0.3174(11)	0.0216(13)
C2	0.1046(4)	0.751(6)	0.5083(10)	0.0291(17)
C3	0.1779(4)	0.8107(9)	0.3920(15)	0.026(2)
C4	0.2054(4)	0.6861(11)	0.2023(18)	0.042(3)
As1	0.91496(3)	0.75	0.94754(11)	0.01817(19)
F1	0.83995(18)	0.75	0.7598(7)	0.0296(8)
F2	0.88210(12)	0.6030(3)	0.1469(5)	0.0379(7)
F3	0.95645(12)	0.6043(3)	0.7639(5)	0.0323(6)
N1	0.0019(3)	0.75	0.1681(9)	0.0223(11)

Table S4-5. Bond lengths (Å) for $C_3H_7CN•AsF_5$.

C1-N1	1.134(7)	C1-C2	1.451(8)
C2-C3	1.562(15)	C2-H2A	0.99
C2-H2AB	0.99	C3-C4	1.504(10)
C3-H3A	0.99	C3-H3AB	0.99
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	As1-F1	1.693(3)
As1-F2	1.698(2)	As1-F2	1.698(2)
As1-F3	1.708(2)	As1-F3	1.708(2)
As1-N1	1.971(5)		

Table S5-5. Bond angles (°) for $C_3H_7CN•AsF_5$.

N1-C1-C2	180.(2)	C1-C2-C3	112.5(9)
C1-C2-H2A	109.1	C3-C2-H2A	109.1
C1-C2-H2AB	109.1	C3-C2-H2AB	109.1
H2A-C2-H2AB	107.8	C4-C3-C2	109.4(17)
C4-C3-H3A	109.8	C2-C3-H3A	109.8
C4-C3-H3AB	109.8	C2-C3-H3AB	109.8
H3A-C3-H3AB	108.2	C3-C4-H4A	109.5
C3-C4-H4B	109.5	H4A-C4-H4B	109.5
C3-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	F1-As1-F2	92.94(12)
F1-As1-F2	92.94(12)	F2-As1-F2	90.68(19)
F1-As1-F3	93.04(12)	F2-As1-F3	89.84(13)
F2-As1-F3	173.96(12)	F1-As1-F3	93.04(12)
F2-As1-F3	173.96(12)	F2-As1-F3	89.84(13)
F3-As1-F3	89.02(17)	F1-As1-N1	179.64(19)
F2-As1-N1	86.81(12)	F2-As1-N1	86.81(12)
F3-As1-N1	87.21(12)	F3-As1-N1	87.21(12)
C1-N1-As1	172.5(5)		

Table S6-5. Torsion angles (°) for $C_3H_7CN•AsF_5$.

C1-C2-C3-C4	-11.(4)

Table S7-5. Anisotropic atomic displacement parameters (Å^2) for $C_3H_7CN•AsF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.020(3)	0.030(3)	0.015(3)	0	0.005(2)	0
C2	0.026(4)	0.052(5)	0.010(3)	0.005(15)	-0.005(2)	-0.013(11)
C3	0.023(4)	0.036(5)	0.019(5)	0.005(3)	-0.003(3)	-0.004(3)
C4	0.015(5)	0.077(8)	0.033(5)	-0.018(4)	0.002(4)	-0.011(4)
As1	0.0132(3)	0.0241(3)	0.0172(3)	0	-0.0019(3)	0
F1	0.0180(17)	0.0391(19)	0.0316(19)	0	-0.0113(14)	0
F2	0.0265(14)	0.0510(16)	0.0362(14)	0.0199(13)	-0.0055(12)	-0.0140(13)
F3	0.0276(14)	0.0357(14)	0.0335(14)	-0.0139(12)	-0.0070(11)	0.0101(11)
N1	0.017(3)	0.028(3)	0.022(3)	0	0.000(2)	0

Table S8-5. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_3H_7CN•AsF_5$.

	x/a	y/b	z/c	U(eq)
H2A	0.1108	0.6403	0.5791	0.035
H2AB	0.0907	0.8239	0.6537	0.035
H3A	0.1710	0.9163	0.3028	0.031
H3AB	0.2135	0.8263	0.5331	0.031
H4A	0.2514	0.7232	0.1288	0.063
H4B	0.1701	0.6717	0.0625	0.063
H4C	0.2127	0.5822	0.2921	0.063

$C_3H_7CN \bullet SbF_5$

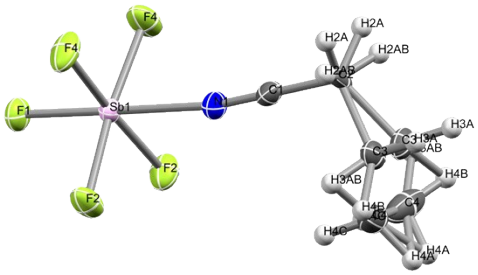


Figure S1-5. Molecular unit of $C_3H_7CN \bullet SbF_5$.

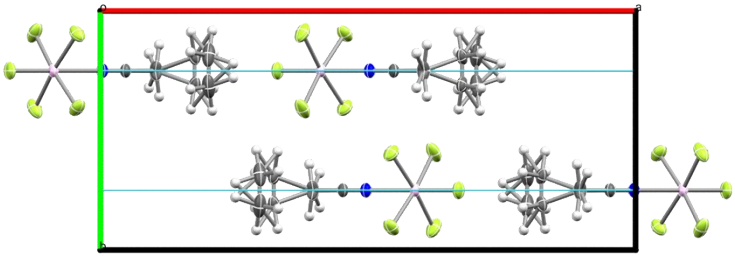


Figure S2-5. Packing of $C_3H_7CN \bullet SbF_5$ in the unit cell. View along the 001 direction (mirror plane in cyan).

Table S1-6. Sample and crystal data for $C_3H_7CN \bullet SbF_5$.

Identification code	AN30	
Chemical formula	$C_4H_7F_5NSb$	
Formula weight	285.86 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.079 x 0.093 x 0.149 mm	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 18.894(7) Å	α = 90°
	b = 8.416(3) Å	β = 90°
	c = 5.261(2) Å	γ = 90°
Volume	836.6(5) $Å^3$	
Z	4	
Density (calculated)	2.270 g/cm^3	
Absorption coefficient	3.322 mm^{-1}	
F(000)	536	

Table S2-6. Data collection and structure refinement for $C_3H_7CN•SbF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)	
Theta range for data collection	2.16 to 28.27°	
Index ranges	-25<=h<=25, -11<=k<=11, -7<=l<=7	
Reflections collected	17084	
Independent reflections	1101 [R(int) = 0.0521]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7790 and 0.6370	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2017/1 (Bruker AXS, 2017)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1101 / 54 / 71	
Goodness-of-fit on F^2	1.068	
Final R indices	949 data; I>2σ(I)	R1 = 0.0167, wR2 = 0.0335
	all data	R1 = 0.0239, wR2 = 0.0348
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0173P)^2+0.1271P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.419 and -0.594 eÅ^{-3}	
R.M.S. deviation from mean	0.081 eÅ^{-3}	

Table S3-6. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for $C_3H_7CN•SbF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Sb1	0.91202(2)	0.25	0.94928(4)	0.01793(6)
F1	0.83083(8)	0.25	0.7493(3)	0.0305(4)
F2	0.95661(6)	0.40484(15)	0.7506(2)	0.0330(3)
F4	0.87736(7)	0.09143(16)	0.1631(3)	0.0396(3)
N1	0.00349(12)	0.25	0.1796(5)	0.0235(5)
C1	0.04750(14)	0.25	0.3268(6)	0.0225(6)
C2	0.10385(16)	0.249(2)	0.5170(7)	0.0322(11)
C3	0.1759(2)	0.1918(5)	0.4006(8)	0.0261(9)
C4	0.2025(2)	0.3149(6)	0.2129(9)	0.0457(14)

Table S4-6. Bond lengths (Å) for $C_3H_7CN•SbF_5$.

Sb1-F1	1.8602(16)	Sb1-F4	1.8642(13)
Sb1-F4	1.8643(13)	Sb1-F2	1.8711(12)
Sb1-F2	1.8711(12)	Sb1-N1	2.111(2)
N1-C1	1.136(4)	C1-C2	1.461(4)
C2-C3	1.569(6)	C2-H2A	0.99
C2-H2AB	0.99	C3-C4	1.517(6)
C3-H3A	0.99	C3-H3AB	0.99

C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98		

Table S5-6. Bond angles (°) for $C_3H_7CN•SbF_5$.

F1-Sb1-F4	92.96(6)	F1-Sb1-F4	92.96(6)
F4-Sb1-F4	91.43(10)	F1-Sb1-F2	93.17(6)
F4-Sb1-F2	89.82(7)	F4-Sb1-F2	173.67(5)
F1-Sb1-F2	93.17(6)	F4-Sb1-F2	173.67(5)
F4-Sb1-F2	89.82(7)	F2-Sb1-F2	88.28(9)
F1-Sb1-N1	179.41(8)	F4-Sb1-N1	86.63(6)
F4-Sb1-N1	86.63(6)	F2-Sb1-N1	87.26(6)
F2-Sb1-N1	87.26(6)	C1-N1-Sb1	172.1(2)
N1-C1-C2	179.7(6)	C1-C2-C3	111.5(3)
C1-C2-H2A	109.3	C3-C2-H2A	109.3
C1-C2-H2AB	109.3	C3-C2-H2AB	109.3
H2A-C2-H2AB	108.0	C4-C3-C2	109.3(6)
C4-C3-H3A	109.8	C2-C3-H3A	109.8
C4-C3-H3AB	109.8	C2-C3-H3AB	109.8
H3A-C3-H3AB	108.3	C3-C4-H4A	109.5
C3-C4-H4B	109.5	H4A-C4-H4B	109.5
C3-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5		

Table S6-6. Torsion angles (°) for $C_3H_7CN•SbF_5$.

C1-C2-C3-C4	68.1.(11)

Table S7-6. Anisotropic atomic displacement parameters (Å^2) for $C_3H_7CN•SbF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb1	0.01406(9)	0.02218(10)	0.01754(10)	0	-0.00110(8)	0
F1	0.0197(8)	0.0421(10)	0.0297(10)	0	-0.0091(7)	0
F2	0.0329(7)	0.0348(7)	0.0314(7)	0.0128(6)	-0.0044(6)	-0.0110(5)
F4	0.0314(7)	0.0497(8)	0.0378(8)	0.0205(7)	-0.0058(6)	-0.0158(6)
N1	0.0182(12)	0.0291(13)	0.0232(14)	0	-0.0027(10)	0
C1	0.0171(14)	0.0266(14)	0.0239(16)	0	0.0032(12)	0
C2	0.0218(15)	0.055(3)	0.0201(19)	-0.021(7)	-0.0041(13)	0.003(7)
C3	0.0183(18)	0.034(2)	0.026(2)	-0.0059(15)	-0.0058(16)	0.0032(15)
C4	0.024(2)	0.079(4)	0.034(3)	0.019(2)	0.002(2)	0.004(2)

Table S8-6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_3H_7CN•SbF_5$.

	x/a	y/b	z/c	U(eq)
H2A	0.0904	0.1782	0.6588	0.039
H2AB	0.1097	0.3579	0.5864	0.039

H3A	0.2112	0.1767	0.5377	0.031
H3AB	0.1691	0.0888	0.3132	0.031
H4A	0.2480	0.2801	0.1422	0.069
H4B	0.2088	0.4168	0.3000	0.069
H4C	0.1681	0.3272	0.0751	0.069

cyclo-$C_3H_5CN{\bullet}AsF_5$

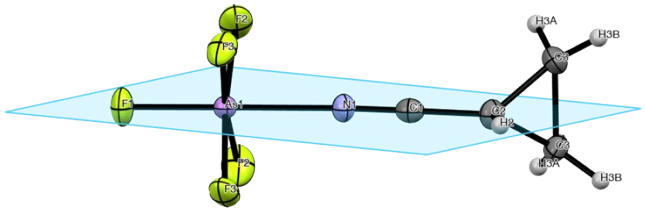


Figure S1-7. Molecular unit of cyclo-$C_3H_5CN{\bullet}AsF_5$ (mirror plane in cyan).

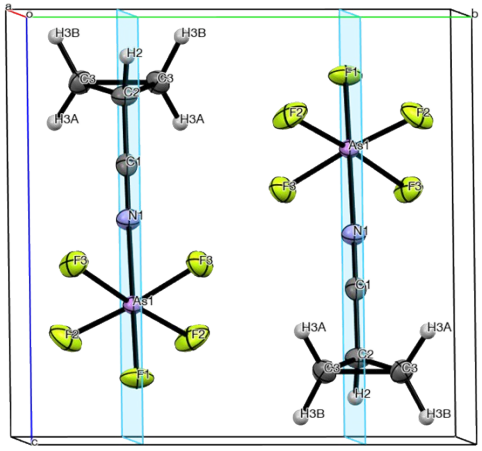


Figure S2-7. Packing of cyclo-$C_3H_5CN{\bullet}AsF_5$ in the unit cell. View along the 010 direction (mirror plane in cyan).

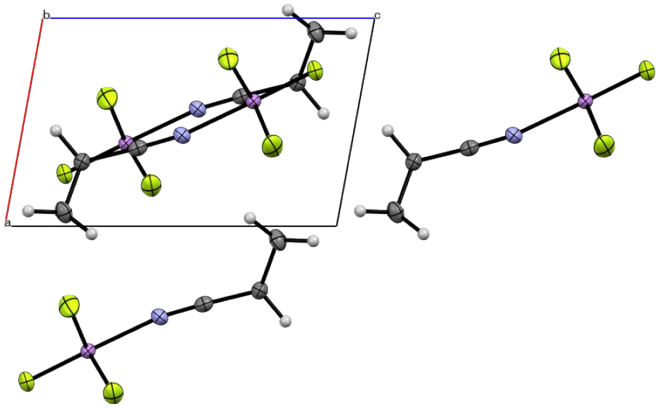


Figure S3-7. Packing of cyclo-$C_3H_5CN{\bullet}AsF_5$ in the unit cell. View along the 100 direction.

Table S1-7. Sample and crystal data for cyclo-C_3H_5CN•AsF_5.

Identification code	TS383	
Chemical formula	$C_8H_{10}As_2F_{10}N_2$	
Formula weight	474.02 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.225 x 0.328 x 0.402 mm	
Crystal habit	clear colorless prism	
Crystal system	monoclinic	
Space group	P 1 21/m 1	
Unit cell dimensions	a = 5.227(5) Å	α = 90°
	b = 8.481(7) Å	β = 100.370(12)°
	c = 8.215(7) Å	γ = 90°
Volume	358.2(5) $Å^3$	
Z	1	
Density (calculated)	2.197 g/cm^3	
Absorption coefficient	4.772 mm^{-1}	
F(000)	228	

Table S2-7. Data collection and structure refinement for cyclo-C_3H_5CN•AsF_5.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.52 to 30.65°	
Index ranges	-7<=h<=7, -12<=k<=12, -11<=l<=11	
Reflections collected	8928	
Independent reflections	1148 [R(int) = 0.0577]	
Coverage of independent reflections	97.0%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1148 / 0 / 58	
Goodness-of-fit on F^2	1.096	
Δ/σ_{max}	0.001	
Final R indices	1025 data; I>2σ(I)	R1 = 0.0249, wR2 = 0.0478
	all data	R1 = 0.0315, wR2 = 0.0490
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0136P)^2+0.1813P]$, where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.456 and -0.753 $eÅ^{-3}$	
R.M.S. deviation from mean	0.103 $eÅ^{-3}$	

Table S3-7. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for cyclo-C_3H_5CN•AsF_5.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x/a	y/b	z/c	U(eq)

C1	0.3754(4)	0.75	0.6427(3)	0.0183(5)
C2	0.3094(5)	0.75	0.8032(3)	0.0202(5)
C3	0.0663(4)	0.6629(2)	0.8303(3)	0.0236(4)
As1	0.60080(5)	0.75	0.31950(3)	0.01407(8)
F1	0.7483(3)	0.75	0.1509(2)	0.0274(4)
F2	0.3852(2)	0.60751(15)	0.23790(16)	0.0352(3)
F3	0.8041(2)	0.89142(13)	0.41862(15)	0.0290(3)
N1	0.4368(4)	0.75	0.5164(3)	0.0188(4)

Table S4-7. Bond lengths (Å) for cyclo-C_3H_5CN•AsF_5.

C1-N1	1.140(4)	C1-C2	1.422(4)
C2-C3	1.521(3)	C2-C3	1.521(3)
C2-H2	1.0	C3-C3	1.478(4)
C3-H3A	0.99	C3-H3B	0.99
As1-F1	1.702(2)	As1-F2	1.7051(15)
As1-F2	1.7051(15)	As1-F3	1.7085(14)
As1-F3	1.7085(14)	As1-N1	1.962(3)

Table S5-7. Bond angles (°) for cyclo-C_3H_5CN•AsF_5.

N1-C1-C2	177.7(3)	C1-C2-C3	118.97(19)
C1-C2-C3	118.98(19)	C3-C2-C3	58.15(18)
C1-C2-H2	116.1	C3-C2-H2	116.1
C3-C2-H2	116.1	C3-C3-C2	60.93(9)
C3-C3-H3A	117.7	C2-C3-H3A	117.7
C3-C3-H3B	117.7	C2-C3-H3B	117.7
H3A-C3-H3B	114.8	F1-As1-F2	92.53(7)
F1-As1-F2	92.53(7)	F2-As1-F2	90.26(12)
F1-As1-F3	93.09(7)	F2-As1-F3	174.36(6)
F2-As1-F3	90.01(9)	F1-As1-F3	93.09(7)
F2-As1-F3	90.01(9)	F2-As1-F3	174.36(6)
F3-As1-F3	89.17(10)	F1-As1-N1	179.00(8)
F2-As1-N1	88.18(8)	F2-As1-N1	88.18(8)
F3-As1-N1	86.19(8)	F3-As1-N1	86.19(8)
C1-N1-As1	170.6(2)		

Table S6-7. Torsion angles (°) for cyclo-C_3H_5CN•AsF_5.

C1-C2-C3-C3	-107.93(16)

Table S7-7. Anisotropic atomic displacement parameters (Å^2) for cyclo-C_3H_5CN•AsF_5.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0158(11)	0.0164(11)	0.0213(14)	0	0.0000(10)	0
C2	0.0191(11)	0.0250(13)	0.0161(13)	0	0.0018(9)	0

C3	0.0288(10)	0.0215(9)	0.0227(10)	0.0013(7)	0.0108(8)	-0.0041(7)
As1	0.01376(11)	0.01459(12)	0.01349(13)	0	0.00143(8)	0
F1	0.0244(8)	0.0428(10)	0.0165(8)	0	0.0077(6)	0
F2	0.0342(6)	0.0425(7)	0.0288(7)	-0.0158(6)	0.0056(5)	-0.0195(6)
F3	0.0327(6)	0.0292(6)	0.0258(7)	-0.0058(5)	0.0069(5)	-0.0155(5)
N1	0.0167(9)	0.0220(11)	0.0185(12)	0	0.0054(8)	0

Table S8-7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for cyclo-C_3H_5CN•AsF_5.

	x/a	y/b	z/c	U(eq)
H2	0.4586	0.7500	0.8984	0.024
H3A	-0.0383	0.6086	0.7341	0.028
H3B	0.0719	0.6086	0.9376	0.028

$(CH_3)_3CCN•AsF_5$

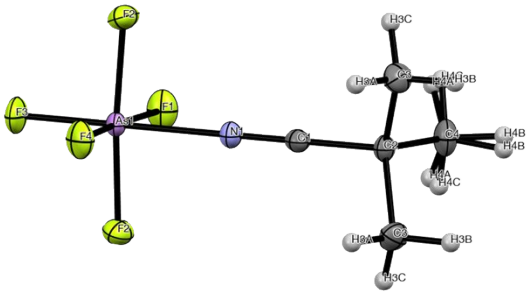


Figure S1-8. Molecular unit of $(CH_3)_3CCN•AsF_5$.

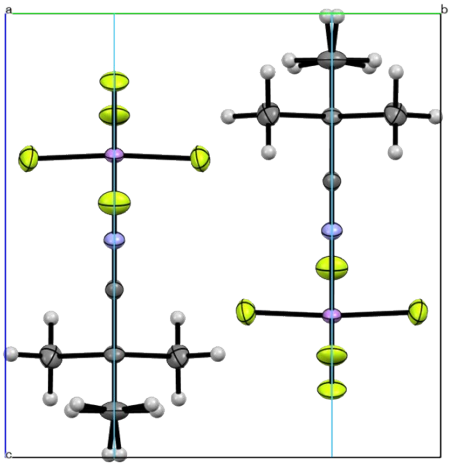


Figure S2-8. Packing of $(CH_3)_3CCN•AsF_5$ in the unit cell. View along the 010 direction (mirror plane in cyan).

Table S1-8. Sample and crystal data for $(CH_3)_3CCN•AsF_5$.

Identification code	TS408	
Chemical formula	$C_5H_9AsF_5N$	
Formula weight	253.05 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.142 x 0.163 x 0.252 mm	
Crystal habit	clear colorless prism	
Crystal system	monoclinic	
Space group	P 1 21/m 1	
Unit cell dimensions	a = 5.9896(16) Å	α = 90°
	b = 8.660(2) Å	β = 97.932(4)°
	c = 8.905(2) Å	γ = 90°
Volume	457.5(2) $Å^3$	
Z	2	
Density (calculated)	1.837 g/cm^3	
Absorption coefficient	3.742 mm^{-1}	
F(000)	248	

Table S2-8. Data collection and structure refinement for $(CH_3)_3CCN•AsF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.31 to 30.55°	
Index ranges	-8<=h<=8, -12<=k<=12, -12<=l<=12	
Reflections collected	9013	
Independent reflections	1482 [R(int) = 0.0442]	
Coverage of independent reflections	99.3%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1482 / 0 / 69	
Goodness-of-fit on F^2	1.064	
Final R indices	1366 data; I>2σ(I)	R1 = 0.0184, wR2 = 0.0444
	all data	R1 = 0.0217, wR2 = 0.0456
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0146P)^2+0.0888P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.343 and -0.334 eÅ^{-3}	
R.M.S. deviation from mean	0.068 eÅ^{-3}	

Table S3-8. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for $(CH_3)_3CCN•AsF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.7784(3)	0.25	0.6220(2)	0.0159(3)
C2	0.9290(3)	0.25	0.7673(2)	0.0158(3)
C3	0.0766(2)	0.39603(16)	0.77271(16)	0.0232(3)
C4	0.7803(3)	0.25	0.8951(2)	0.0240(4)
As1	0.45088(3)	0.25	0.31923(2)	0.01420(6)
F1	0.23578(19)	0.25	0.42687(13)	0.0281(3)
F2	0.45877(13)	0.44741(9)	0.32748(9)	0.02626(19)
F3	0.2711(2)	0.25	0.15329(13)	0.0298(3)
F4	0.6846(2)	0.25	0.22973(13)	0.0277(3)
N1	0.6598(3)	0.25	0.51047(17)	0.0173(3)

Table S4-8. Bond lengths (Å) for $(CH_3)_3CCN•AsF_5$.

C1-N1	1.139(2)	C1-C2	1.471(2)
C2-C4	1.539(2)	C2-C3	1.5398(17)
C2-C3	1.5398(17)	C3-H3A	0.98
C3-H3B	0.98	C3-H3C	0.98
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	As1-F4	1.7036(12)
As1-F3	1.7041(11)	As1-F1	1.7087(12)

As1-F2	1.7115(9)	As1-F2	1.7115(9)
As1-N1	1.9692(15)		

Table S5-8. Bond angles (°) for $CH_3)_3CCN•AsF_5$.

N1-C1-C2	179.23(18)	C1-C2-C4	107.65(14)
C1-C2-C3	107.90(10)	C4-C2-C3	111.40(10)
C1-C2-C3	107.90(10)	C4-C2-C3	111.40(10)
C3-C2-C3	110.43(15)	C2-C3-H3A	109.5
C2-C3-H3B	109.5	H3A-C3-H3B	109.5
C2-C3-H3C	109.5	H3A-C3-H3C	109.5
H3B-C3-H3C	109.5	C2-C4-H4A	109.5
C2-C4-H4B	109.5	H4A-C4-H4B	109.5
C2-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	F4-As1-F3	93.22(6)
F4-As1-F1	173.85(5)	F3-As1-F1	92.94(6)
F4-As1-F2	90.03(3)	F3-As1-F2	92.73(3)
F1-As1-F2	89.68(3)	F4-As1-F2	90.03(3)
F3-As1-F2	92.73(3)	F1-As1-F2	89.68(3)
F2-As1-F2	174.53(5)	F4-As1-N1	86.53(6)
F3-As1-N1	179.75(6)	F1-As1-N1	87.31(6)
F2-As1-N1	87.27(3)	F2-As1-N1	87.27(3)
C1-N1-As1	179.17(15)		

Table S6-8. Anisotropic atomic displacement parameters (Å²) for $CH_3)_3CCN•AsF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0182(8)	0.0128(7)	0.0173(8)	0	0.0041(6)	0
C2	0.0143(7)	0.0179(8)	0.0140(7)	0	-0.0021(6)	0
C3	0.0209(6)	0.0219(6)	0.0249(7)	-0.0008(5)	-0.0040(5)	-0.0048(5)
C4	0.0223(9)	0.0356(11)	0.0141(8)	0	0.0021(7)	0
As1	0.01636(10)	0.01489(9)	0.01055(9)	0	-0.00101(6)	0
F1	0.0187(5)	0.0422(7)	0.0240(6)	0	0.0051(5)	0
F2	0.0324(5)	0.0154(4)	0.0285(4)	0.0020(3)	-0.0048(4)	0.0026(3)
F3	0.0335(7)	0.0343(7)	0.0173(6)	0	-0.0115(5)	0
F4	0.0281(6)	0.0382(7)	0.0186(6)	0	0.0096(5)	0
N1	0.0188(7)	0.0175(7)	0.0145(7)	0	-0.0017(6)	0

Table S7-8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for $CH_3)_3CCN•AsF_5$.

	x/a	y/b	z/c	U(eq)
H3A	1.1626	0.3956	0.6867	0.035
H3B	1.1809	0.3976	0.8677	0.035
H3C	0.9802	0.4879	0.7672	0.035
H4A	0.6729	0.3358	0.8799	0.036

H4B	0.8756	0.2620	0.9931	0.024
H4C	0.6978	0.1522	0.8938	0.036

$(CH_3)_3CCN•SbF_5$

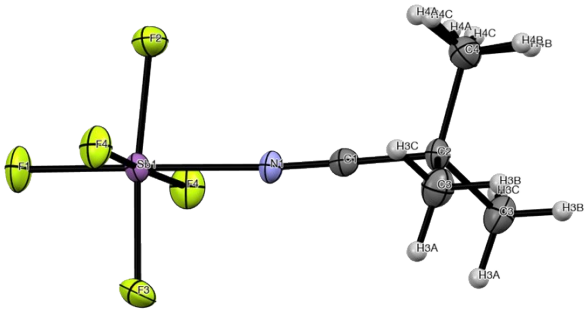


Figure S1-9. Molecular unit of $(CH_3)_3CCN•SbF_5$.

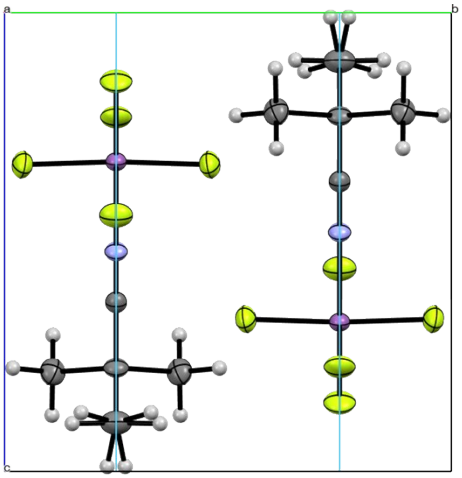


Figure S2-9. Packing of $(CH_3)_3CCN•SbF_5$ in the unit cell. View along the 010 direction (mirror plane in cyan).

Table S1-9. Sample and crystal data for $(CH_3)_3CCN•SbF_5$.

Identification code	TS377	
Chemical formula	$C_5H_9F_5NSb$	
Formula weight	299.88 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.064 x 0.079 x 0.138 mm	
Crystal habit	clear colorless prism	
Crystal system	monoclinic	
Space group	P 1 21/m 1	
Unit cell dimensions	a = 5.970(3) Å	α = 90°
	b = 8.897(5) Å	β = 97.380(8)°
	c = 9.201(5) Å	γ = 90°
Volume	484.7(4) $Å^3$	
Z	2	
Density (calculated)	2.055 g/cm^3	
Absorption coefficient	2.872 mm^{-1}	
F(000)	284	

Table S2-9. Data collection and structure refinement for $(CH_3)_3CCN•SbF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.23 to 30.44°	
Reflections collected	1532	
Independent reflections	1532 [R(int) = 0.0000]	
Coverage of independent reflections	98.3%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1532 / 0 / 70	
Goodness-of-fit on F^2	1.067	
Final R indices	1334 data; I>2σ(I)	R1 = 0.0398, wR2 = 0.0715
	all data	R1 = 0.0649, wR2 = 0.0826
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0186P)^2+2.7268P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.292 and -2.683 eÅ^{-3}	
R.M.S. deviation from mean	0.256 eÅ^{-3}	

Table S3-9. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for TS377.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.7897(12)	0.25	0.6316(7)	0.0184(13)
C2	0.9324(12)	0.25	0.7744(8)	0.0202(14)
C3	0.0797(10)	0.3919(6)	0.7836(6)	0.0273(11)
C4	0.7722(14)	0.25	0.8941(8)	0.0285(17)
F1	0.2530(9)	0.25	0.1500(5)	0.0342(11)
F2	0.2159(8)	0.25	0.4419(4)	0.0307(10)
F3	0.7060(8)	0.25	0.2279(4)	0.0294(10)
F4	0.4569(6)	0.4597(3)	0.3316(3)	0.0286(6)
N1	0.6755(10)	0.25	0.5210(6)	0.0186(12)
Sb1	0.45059(9)	0.25	0.32521(5)	0.01680(12)

Table S4-9. Bond lengths (Å) for $(CH_3)_3CCN•SbF_5$.

C1-N1	1.150(8)	C1-C2	1.471(9)
C2-C3	1.535(7)	C2-C3	1.535(7)
C2-C4	1.548(10)	C3-H3A	0.98
C3-H3B	0.98	C3-H3C	0.98
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	F1-Sb1	1.871(4)

F2-Sb1	1.871(5)	F3-Sb1	1.865(5)
F4-Sb1	1.867(3)	N1-Sb1	2.104(6)
Sb1-F4	1.867(3)		

Table S5-9. Bond angles (°) for $(CH_3)_3CCN•SbF_5$.

N1-C1-C2	179.1(7)	C1-C2-C3	108.1(4)
C1-C2-C3	108.1(4)	C3-C2-C3	110.7(6)
C1-C2-C4	107.2(6)	C3-C2-C4	111.3(4)
C3-C2-C4	111.3(4)	C2-C3-H3A	109.5
C2-C3-H3B	109.5	H3A-C3-H3B	109.5
C2-C3-H3C	109.5	H3A-C3-H3C	109.5
H3B-C3-H3C	109.5	C2-C4-H4A	109.5
C2-C4-H4B	109.5	H4A-C4-H4B	109.5
C2-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	C1-N1-Sb1	176.7(6)
F3-Sb1-F4	90.05(11)	F3-Sb1-F4	90.05(11)
F4-Sb1-F4	175.96(19)	F3-Sb1-F1	92.9(2)
F4-Sb1-F1	92.01(9)	F4-Sb1-F1	92.01(9)
F3-Sb1-F2	173.8(2)	F4-Sb1-F2	89.73(11)
F4-Sb1-F2	89.73(11)	F1-Sb1-F2	93.4(2)
F3-Sb1-N1	86.6(2)	F4-Sb1-N1	87.99(9)
F4-Sb1-N1	87.99(9)	F1-Sb1-N1	179.4(3)
F2-Sb1-N1	87.2(2)		

Table S6-9. Anisotropic atomic displacement parameters (Å²) for $(CH_3)_3CCN•SbF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.018(3)	0.018(3)	0.020(3)	0	0.004(3)	0
C2	0.018(3)	0.026(4)	0.016(3)	0	-0.003(3)	0
C3	0.024(3)	0.026(2)	0.031(2)	0.000(2)	-0.003(2)	-0.004(2)
C4	0.024(4)	0.040(5)	0.022(3)	0	0.003(3)	0
F1	0.033(3)	0.042(3)	0.023(2)	0	-0.013(2)	0
F2	0.022(2)	0.045(3)	0.026(2)	0	0.006(2)	0
F3	0.030(3)	0.040(3)	0.021(2)	0	0.0113(19)	0
F4	0.0357(15)	0.0173(12)	0.0311(14)	0.0015(12)	-0.0027(16)	0.0031(15)
N1	0.018(3)	0.021(3)	0.016(3)	0	-0.003(2)	0
Sb1	0.0186(2)	0.01707(19)	0.01429(18)	0	0.00030(18)	0

Table S7-9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for $(CH_3)_3CCN•SbF_5$.

	x/a	y/b	z/c	U(eq)
H3A	1.1734	0.3914	0.7036	0.041
H3B	1.1771	0.3937	0.8778	0.041
H3C	0.9827	0.4811	0.7753	0.041
H4A	0.6573	0.3282	0.8721	0.043

H4B	0.8595	0.2701	0.9897	0.043
H4C	0.6986	0.1517	0.8961	0.043

AsF_5•$NCCH_2CN$•AsF_5

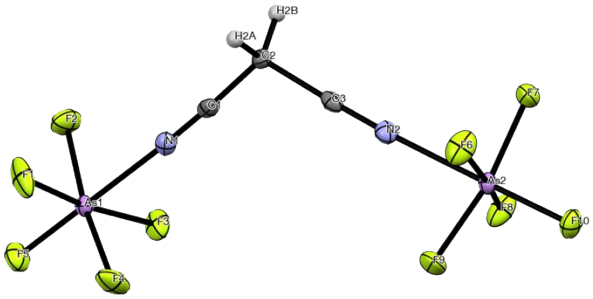


Figure S1-10. Asymmetric unit of AsF_5•$NCCH_2CN$•AsF_5.

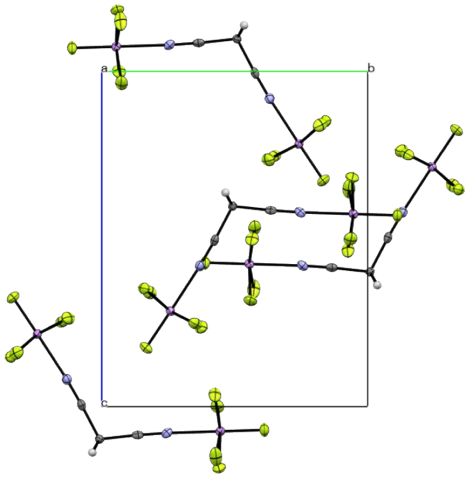


Figure S2-10. Packing of AsF_5•$NCCH_2CN$•AsF_5 in the unit cell. View along the 010 direction.

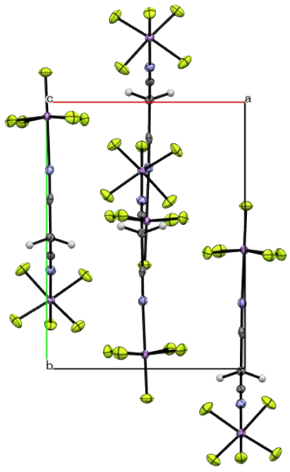


Figure S3-10. Packing of AsF_5•$NCCH_2CN$•AsF_5 in the unit cell. View along the 001 direction.

Table S1-10. Sample and crystal data for AsF_5•$NCCH_2CN$•AsF_5.

Identification code	MalononitrileAsF5	
Chemical formula	$C_3H_2As_2F_{10}N_2$	
Formula weight	405.91 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.050 x 0.180 mm	
Crystal habit	clear colorless rod	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.5930(13) Å	α = 90°
	b = 10.1881(18) Å	β = 90°
	c = 12.803(2) Å	γ = 90°
Volume	990.4(3) $Å^3$	
Z	4	
Density (calculated)	2.722 g/cm^3	
Absorption coefficient	6.878 mm^{-1}	
F(000)	760	

Table S2-10. Data collection and structure refinement for AsF_5•$NCCH_2CN$•AsF_5.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.56 to 30.47°	
Index ranges	-10<=h<=10, -14<=k<=14, -18<=l<=18	
Reflections collected	24363	
Independent reflections	3002 [R(int) = 0.0457]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7250 and 0.3710	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3002 / 0 / 154	
Goodness-of-fit on F^2	1.055	
Δ/σ_{max}	0.001	
Final R indices	2758 data; I>2σ(I)	R1 = 0.0207, wR2 = 0.0375
	all data	R1 = 0.0258, wR2 = 0.0387
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0121P)^2+0.4306P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.5(0)	
Largest diff. peak and hole	0.341 and -0.374 $eÅ^{-3}$	
R.M.S. deviation from mean	0.081 $eÅ^{-3}$	

Table S3-10. Atomic coordinates and equivalent isotropic atomic displacement param. (Å²) for AsF_5•$NCCH_2CN$•AsF_5.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
As1	0.49615(5)	0.94566(3)	0.42531(2)	0.01171(7)
As2	0.48030(4)	0.25857(3)	0.71591(2)	0.01241(7)
C1	0.4832(5)	0.6355(3)	0.4144(2)	0.0133(5)
C2	0.4807(5)	0.4917(3)	0.4019(2)	0.0123(6)
C3	0.4797(4)	0.4244(3)	0.5041(2)	0.0141(6)
F1	0.6789(3)	0.9286(2)	0.3500(2)	0.0325(6)
F2	0.3704(3)	0.9412(3)	0.31597(15)	0.0267(5)
F3	0.3103(3)	0.9348(2)	0.49952(16)	0.0232(5)
F4	0.6214(3)	0.9253(2)	0.53379(17)	0.0279(5)
F5	0.5057(3)	0.11110(16)	0.42942(14)	0.0237(4)
F6	0.6547(3)	0.1798(2)	0.65968(19)	0.0263(6)
F7	0.3415(3)	0.1589(2)	0.64771(18)	0.0234(5)
F8	0.3045(3)	0.3509(2)	0.75242(15)	0.0253(5)
F9	0.6199(3)	0.3736(2)	0.76351(17)	0.0279(5)
F10	0.4802(3)	0.16684(17)	0.82540(13)	0.0214(4)
N1	0.4852(3)	0.7455(2)	0.42028(17)	0.0149(4)
N2	0.4795(4)	0.3691(2)	0.58044(19)	0.0166(5)

Table S4-10. Bond lengths (Å) for AsF_5•$NCCH_2CN$•AsF_5.

As1-F5	1.6879(17)	As1-F2	1.695(2)
As1-F4	1.696(2)	As1-F1	1.698(2)
As1-F3	1.7049(19)	As1-N1	2.042(3)
As2-F10	1.6848(17)	As2-F9	1.694(2)
As2-F8	1.698(2)	As2-F7	1.704(2)
As2-F6	1.707(2)	As2-N2	2.068(3)
C1-N1	1.123(4)	C1-C2	1.474(4)
C2-C3	1.476(4)	C2-H2A	0.99
C2-H2B	0.99	C3-N2	1.129(4)

Table S5-10. Bond angles (°) for AsF_5•$NCCH_2CN$•AsF_5.

F5-As1-F2	94.41(11)	F5-As1-F4	94.17(11)
F2-As1-F4	171.42(13)	F5-As1-F1	94.87(12)
F2-As1-F1	89.34(12)	F4-As1-F1	89.68(12)
F5-As1-F3	94.76(12)	F2-As1-F3	89.56(11)
F4-As1-F3	89.98(12)	F1-As1-F3	170.37(13)
F5-As1-N1	179.86(11)	F2-As1-N1	85.65(11)
F4-As1-N1	85.77(10)	F1-As1-N1	85.01(11)
F3-As1-N1	85.36(10)	F10-As2-F9	94.86(10)
F10-As2-F8	94.46(10)	F9-As2-F8	90.54(12)

F10-As2-F7	95.47(11)	F9-As2-F7	169.65(11)
F8-As2-F7	89.16(11)	F10-As2-F6	95.20(11)
F9-As2-F6	89.51(12)	F8-As2-F6	170.30(10)
F7-As2-F6	89.05(10)	F10-As2-N2	179.28(9)
F9-As2-N2	85.80(11)	F8-As2-N2	85.82(10)
F7-As2-N2	83.86(11)	F6-As2-N2	84.51(11)
N1-C1-C2	177.7(3)	C1-C2-C3	111.5(2)
C1-C2-H2A	109.3	C3-C2-H2A	109.3
C1-C2-H2B	109.3	C3-C2-H2B	109.3
H2A-C2-H2B	108.0	N2-C3-C2	177.7(3)
C1-N1-As1	177.4(2)	C3-N2-As2	177.0(2)

1

Table S6-10. Anisotropic atomic displacement parameters (Å2) for AsF_5•$NCCH_2CN$•AsF_5.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As1	0.00930(13)	0.01259(12)	0.01323(12)	0.00086(11)	0.00137(15)	-0.00001(16)
As2	0.01244(13)	0.01140(13)	0.01339(13)	0.00153(11)	0.00062(13)	0.00070(14)
C1	0.0078(14)	0.0216(14)	0.0105(12)	0.0008(11)	-0.0017(13)	-0.0019(14)
C2	0.0130(15)	0.0125(12)	0.0113(12)	-0.0004(10)	0.0002(12)	0.0006(13)
C3	0.0123(14)	0.0111(12)	0.0191(14)	-0.0036(11)	0.0017(13)	0.0001(13)
F1	0.0221(11)	0.0227(12)	0.0526(15)	-0.0023(12)	0.0246(11)	-0.0041(10)
F2	0.0361(12)	0.0259(12)	0.0180(11)	0.0031(10)	-0.0094(9)	0.0022(11)
F3	0.0167(10)	0.0260(12)	0.0268(11)	-0.0020(10)	0.0118(8)	-0.0002(9)
F4	0.0286(11)	0.0224(12)	0.0325(13)	-0.0006(10)	-0.0189(10)	-0.0019(10)
F5	0.0295(10)	0.0130(8)	0.0288(10)	-0.0003(7)	0.0044(13)	-0.0001(10)
F6	0.0217(11)	0.0309(14)	0.0264(13)	0.0047(11)	0.0059(10)	0.0142(10)
F7	0.0286(12)	0.0223(12)	0.0193(11)	0.0006(10)	-0.0022(9)	-0.0107(9)
F8	0.0279(12)	0.0280(13)	0.0199(12)	0.0052(10)	0.0080(9)	0.0142(10)
F9	0.0325(13)	0.0277(13)	0.0235(12)	-0.0021(10)	-0.0040(10)	-0.0158(10)
F10	0.0231(11)	0.0223(9)	0.0190(9)	0.0084(7)	-0.0015(9)	0.0007(10)
N1	0.0116(10)	0.0171(11)	0.0159(11)	0.0038(11)	-0.0016(11)	-0.0009(14)
N2	0.0176(14)	0.0140(11)	0.0181(12)	-0.0018(10)	0.0021(13)	0.0008(11)

Table S7-10. Hydrogen atomic coordinates and isotropic atomic displacement param. (Å²) for AsF_5•$NCCH_2CN$•AsF_5.

	x/a	y/b	z/c	U(eq)
H2A	0.5857	0.4638	0.3618	0.015
H2B	0.3747	0.4658	0.3619	0.015

$C_6H_5CN•AsF_5$

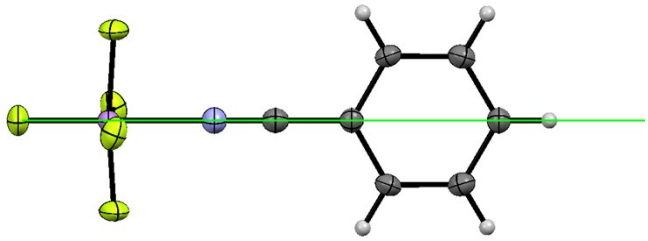


Figure S1-11. Molecular unit of $C_6H_5CN•AsF_5$. (2-fold rotation axis in green)

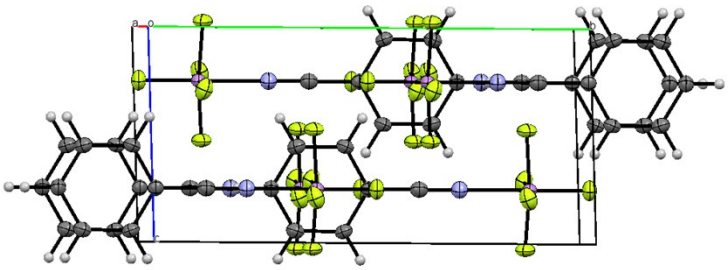


Figure S2-11. Packing of $C_6H_5CN•AsF_5$ in the unit cell. View along the 010 direction.

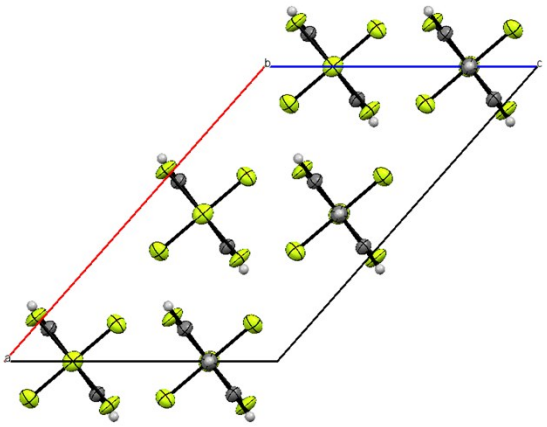


Figure S3-11. Packing of $C_6H_5CN•AsF_5$ in the unit cell. View along the 100 direction.

Table S1-11. Sample and crystal data for $C_6H_5CN•AsF_5$.

Identification code	PhCNAsF5	
Chemical formula	$C_7H_5AsF_5N$	
Formula weight	273.04 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.160 x 0.190 mm	
Crystal habit	clear colorless prism	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 11.705(5) Å	α = 90°
	b = 12.542(6) Å	β = 131.518(7)°
	c = 8.136(4) Å	γ = 90°
Volume	894.3(7) Å^3	
Z	4	
Density (calculated)	2.028 g/cm^3	
Absorption coefficient	3.838 mm^{-1}	
F(000)	528	

Table S2-11. Data collection and structure refinement for $C_6H_5CN•AsF_5$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.83 to 28.27°	
Index ranges	-15<=h<=15, -16<=k<=16, -10<=l<=10	
Reflections collected	9247	
Independent reflections	1120 [R(int) = 0.0598]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1120 / 0 / 67	
Goodness-of-fit on F^2	1.072	
Final R indices	1025 data; I>2σ(I)	R1 = 0.0341, wR2 = 0.0877
	all data	R1 = 0.0378, wR2 = 0.0914
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0641P)^2+0.2125P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.122 and -1.174 eÅ^{-3}	
R.M.S. deviation from mean	0.132 eÅ^{-3}	

Table S3-11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_6H_5CN•AsF_5$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)

C1	0.5	0.3788(3)	0.25	0.0242(7)
C2	0.5	0.4929(3)	0.25	0.0217(7)
C3	0.6129(3)	0.5478(2)	0.4477(4)	0.0223(5)
C4	0.6116(3)	0.6578(2)	0.4455(4)	0.0245(5)
C5	0.5	0.7135(3)	0.25	0.0238(7)
N1	0.5	0.2872(2)	0.25	0.0253(6)
F1	0.5	0.99316(17)	0.25	0.0315(5)
F2	0.3734(2)	0.13645(11)	0.2897(3)	0.0321(4)
F3	0.6493(2)	0.13690(12)	0.5273(3)	0.0344(4)
As1	0.5	0.12879(2)	0.25	0.02006(16)

Table S4-11. Bond lengths (Å) for $C_6H_5CN•AsF_5$.

C1-N1	1.148(4)	C1-C2	1.432(5)
C2-C3	1.410(3)	C2-C3	1.410(3)
C3-C4	1.380(4)	C3-H3	0.95
C4-C5	1.404(3)	C4-H4	0.95
C5-C4	1.404(3)	C5-H5	0.95
N1-As1	1.987(3)	F1-As1	1.701(2)
F2-As1	1.7157(19)	F3-As1	1.7108(19)
As1-F3	1.7107(19)	As1-F2	1.7157(19)

Table S5-11. Bond angles (°) for $C_6H_5CN•AsF_5$.

N1-C1-C2	180.0	C3-C2-C3	121.6(3)
C3-C2-C1	119.19(16)	C3-C2-C1	119.19(16)
C4-C3-C2	118.6(2)	C4-C3-H3	120.7
C2-C3-H3	120.7	C3-C4-C5	120.4(2)
C3-C4-H4	119.8	C5-C4-H4	119.8
C4-C5-C4	120.3(3)	C4-C5-H5	119.9
C4-C5-H5	119.9	C1-N1-As1	180.0
F1-As1-F3	93.41(5)	F1-As1-F3	93.41(5)
F3-As1-F3	173.18(10)	F1-As1-F2	93.21(5)
F3-As1-F2	90.18(10)	F3-As1-F2	89.43(10)
F1-As1-F2	93.21(5)	F3-As1-F2	89.43(10)
F3-As1-F2	90.18(10)	F2-As1-F2	173.58(10)
F1-As1-N1	180.0	F3-As1-N1	86.59(5)
F3-As1-N1	86.59(5)	F2-As1-N1	86.79(5)
F2-As1-N1	86.79(5)		

Table S6-11. Torsion angles (°) for $C_6H_5CN•AsF_5$.

C3-C2-C3-C4	0.00(15)	C1-C2-C3-C4	180.00(15)
C2-C3-C4-C5	0.0(3)	C3-C4-C5-C4	0.00(16)

Table S7-11. Anisotropic atomic displacement parameters (Å²) for $C_6H_5CN•AsF_5$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

C1	0.0253(17)	0.0254(18)	0.0219(17)	0	0.0155(15)	0
C2	0.0262(17)	0.0204(16)	0.0222(16)	0	0.0176(14)	0
C3	0.0218(11)	0.0251(11)	0.0168(11)	0.0036(9)	0.0114(9)	0.0026(9)
C4	0.0237(11)	0.0278(12)	0.0194(11)	-0.0028(10)	0.0132(10)	0.0024(10)
C5	0.0274(18)	0.0196(16)	0.0242(18)	0	0.0171(16)	0
N1	0.0262(16)	0.0218(15)	0.0248(16)	0	0.0156(14)	0
F1	0.0380(12)	0.0167(10)	0.0341(12)	0	0.0215(10)	0
F2	0.0353(9)	0.0269(8)	0.0410(11)	-0.0060(6)	0.0282(9)	-0.0056(6)
F3	0.0311(9)	0.0334(10)	0.0154(8)	0.0011(6)	0.0055(7)	-0.0031(6)
As1	0.0204(2)	0.0170(2)	0.0146(2)	0	0.00810(17)	0

Table S8-11. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_6H_5CN•AsF_5$.

	x/a	y/b	z/c	U(eq)
H3	0.6882	0.5097	0.5797	0.027
H4	0.6868	0.6960	0.5772	0.029
H5	0.5000	0.7892	0.2500	0.029

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