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Supporting Information for the Paper

Transition Metal-Free Controlled Synthesis of Bis[(Trifluoromethyl)Sulfonyl]Ethyl-Decorated Heterocycles

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General Methods

NMR spectra were recorded at 25 ºC on a Bruker Avance AVIII-700 with cryoprobe, Bruker AMX-500, Bruker Avance III Nanobay 400 MHz, or Bruker Avance-300 spectrometers. NMR spectra were recorded in $CDCl_3$, CD_3CN, CD_3COCD_3, or DMSO-d_6 solutions, except otherwise stated. Data are reported as follows: chemical shifts, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), and coupling constants (*J*, in Hz). Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm) or CD_3CN (^{1}H, 1.94 ppm; ^{13}C, 118.2 ppm). Chemical shifts in ^{19}F NMR are given in ppm relative to (trifluoromethyl)benzene (–63.7 ppm). Chemical shifts in ^{23}Na are given in ppm relative to NaCl in D_2O (^{23}Na, 0.00 ppm). High resolution mass spectra were measured on a Waters Xevo G2-XS Tof mass spectrometer using electrospray ionization-time of flight (ESI-TOF) or were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. UV and Fluorescence spectra were recorded on a JASCO V-680 spectrometer and a Hitachi F-7100 spectrometer, respectively. Microwave irradiation was carried

out in a Monowave 300 from Anton Paar GmbH. The reaction temperatures during microwave heating were measured with an internal infrared sensor. Column chromatography was carried out using silica gel 60, 0.04-0.06 mm, for flash chromatography (230-400 mesh ASTM) provided by Scharlau.

Experimental Section

General Procedure for the Preparation of Bis(triflyl)ethyl-Sydnones 3a–e-Na (Scheme 2). 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1** (0.5 mmol) was added at room temperature to a solution of the appropriate sydnone **2** (0.5 mmol) in acetonitrile (for sydnones **2a–2e**) or toluene (for sydnones **2f–2i**) (5 mL). The reaction was stirred at room temperature for 30 min (from sydnones **2a**–**2e**) or at reflux temperature for 1h (from sydnones **2f**–**2i**) at room temperature until disappearance of the starting material (TLC), and then the mixture was concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **3-Na** follow.

4-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-3-phenyl-3*H*-1,2,3-oxadiazol-1-ium-5-olate 3a-Na. From 50 mg (0.31 mmol) of sydnone **2a** and 120 mg (0.09 mmol) of 2-fluoropyridinium salt **1**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **3a-Na** (132 mg, 94% yield) as a yellow solid. Mp 245–247 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 7.72–7.55 (m, 5H), 3.56 (s, 2H); ^{13}C NMR (75 MHz, CD_3CN): δ = 169.0, 135.0, 132.9, 130.7 (2C), 126.6 (2C), 122.1 (q, J_{C-F} = 322.5 Hz, 2C), 109.7, 61.7, 22.6; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.60 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN,): δ = –7.39 (s, 1Na); IR ($CHCl_3$): ν = 2935, 1731, 1205 cm^{-1}; HRMS (ES): calcd for $C_{12}H_8F_6N_2NaO_6S_2$ [M+Na]$^{+}$: 476.9620; found: 476.9629.

4-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-3-(*p*-tolyl)-3*H*-1,2,3-oxadiazol-1-ium-5-olate 3b-Na. From 84 mg (0.28 mmol) of 4-iodosydnone **2g** and 109mg (0.28 mmol) of 2-fluoropyridinium salt **1**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **3b-Na** (116 mg, 87% yield) as a yellow solid. Mp 141–143 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 7.44 (m, 4H), 3.55 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN): δ = 168.9, 143.6, 132.1, 131.1 (2C), 126.3 (2C), 122.1 (q, J_{C-F} = 322.5 Hz, 2C), 109.4, 61.8, 22.7, 21.4; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.87 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN): δ = –7.67 (s, 1Na); IR ($CHCl_3$): ν = 2934, 1732, 1207 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{10}F_6N_2NaO_6S_2$ [*M*+Na]$^{+}$: 490.9777; found: 490.9792.

4-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-3-(4-methoxyphenyl)-3*H*-1,2,3-oxadiazol-1-ium-5-olate 3c-Na. From 17 mg (0.09 mmol) of sydnone **2c** and 35 mg (0.09 mmol) of 2-fluoropyridinium salt **1**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **3c-Na** (27 mg, 97% yield) as a yellow solid. Mp 125–127 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 7.49 (AA'XX', 2H), 7.12 (AAXX', 2H), 3.87 (s, 3H), 3.55 (s, 2H); ^{13}C NMR (75 MHz, CD_3CN): δ = 169.2, 163.1, 128.0 (2C), 127.5, 122.1 (q, J_{C-F} = 329.6 Hz, 2C), 115.7 (2C), 109.8, 61.6, 56.6, 22.5; ^{19}F NMR (282 MHz, CD_3CN, 25 ºC): δ = –80.91 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN): δ = –7.65 (s, 1Na); IR ($CHCl_3$): ν = 2932, 1729, 1205 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{10}F_6N_2NaO_7S_2$ [*M*+Na]$^{+}$: 506.9726; found: 506.9750.

4-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-3-methyl-3*H*-1,2,3-oxadiazol-1-ium-5-olate 3e-Na. From 50 mg (0.50 mmol) of sydnone **2e** and 194 mg (0.50 mmol) of 2-fluoropyridinium salt **1**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **3e-Na** (190 mg, 97% yield) as a colorless solid. Mp 72–74 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 4.06 (s, 3H), 3.59 (s, 2H); ^{13}C NMR (75 MHz, CD_3CN): δ = 170.2, 122.0 (q, J_{C-F} = 324.8 Hz, 2CF_3), 108.8, 62.2, 38.8, 21.5; ^{19}F NMR (282 MHz, CD_3CN): δ = –81.30 (s, 6F); IR

($CHCl_3$): ν = 2938, 1735, 1208 cm^{-1}; HRMS (ES): calcd for $C_7H_6F_6N_2NaO_6S_2$ $[M+Na]^+$: 414.9464; found: 414.9478.

General Procedure for the Preparation of Compounds 5b–e and 7 (Scheme 3). 2-Fluoropyridinium salt **1** (0.2 mmol) was added at room temperature to a solution of the appropriate heterocycles **4** and **6a** (0.2 mmol) in DCE (for compounds **4a–d**) or CH_3CN (for compounds **4e** and **6a**) (5.0 mL). The reaction was stirred at room temperature until disappearance of the starting heterocycles (TLC), and then the mixture was concentrated under reduced pressure. The purification details are described for each compound. Spectroscopic and analytical data for compounds **5** and **7** follow.

1-(3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-1*H*-indol-1-yl)ethan-1-one 5b. From 31.5 mg (0.198 mmol) of *N*-acetylindole **4b** and 77.2 mg (0.198 mmol) of 2-fluoropyridinium salt, compound **5b** (87.0 mg, 0.193 mmol, 97% yield) was obtained as a colorless solid after washing the crude material with hexane (4.0 mL x 3). Mp 120–121 °C (from $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (brd, J = 8.2 Hz, 1H), 7.55–7.51 (m, 2H), 7.48–7.41 (m, 1H), 7.37 (td, J = 7.7, 1.0 Hz,1H), 5.09 (t, J = 5.8 Hz, 1H), 3.96 (d, J = 5.8 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 135.7, 128.1, 126.3, 126.2, 124.3, 119.2 (q, J_{CF} = 330 Hz), 117.5, 117.2, 112.8, 78.2, 23.9, 21.3; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –73.2 (s, 6F); IR (ATR): ν = 2907, 2891, 1697, 1454, 1384, 1203, 1099, 758, 698, 660, 639, 587, 552, 509, 481 cm^{-1}; MS (ESI-TOF) *m*/*z* 450 $[M–H]^–$; HRMS (ES): calcd for $C_{14}H_{10}F_6NO_5S_2$ $[M–H]^–$, 449.9905; found, 449.9897.

***tert*-Butyl 3-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1*H*-indole-1-carboxylate 5c**. From 42.6 mg (0.196 mmol) of *N*-(*tert*-butyloxy)carbonylindole **4c** and 78.0 mg (0.200 mmol) of 2-fluoropyridinium salt **1**, compound **5c** (91.0 mg, 0.179 mmol, 91% yield) was obtained as a brown oil after flash chromatography on silica gel of the crude material (hexane/ethyl acetate = 5:1 as

eluent), followed by acidification with 10% hydrochloric acid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (brd, J = 8.3 Hz, 1H,), 7.66 (s, 1H,), 7.53 (brd, J = 7.9 Hz,1H), 7.37-7.43 (m, 1H), 7.36–7.29(m, 1H), 5.10 (t, J = 5.8 Hz, 1H,), 3.95 (d, J = 5.8 Hz, 2H,), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 135.4, 128.2, 126.6, 125.3, 123.3, 119.2 (q, J_{CF} = 330 Hz), 117.6, 115.8, 111.2, 84.5, 78.4, 28.1, 21.3; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –73.4 (s, 6F); IR (ATR): ν = 2980, 2930, 1720, 1455, 1395, 1370, 1220, 1155, 1105, 745, 620 cm^{-1}; MS (ESI-TOF) m/z 508 $[M–H]^–$; HRMS calcd for $C_{17}H_{16}F_6NO_6S_2$ $[M–H]^–$, 508.0323; found, 508.0320.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1*H*-indole 5d. From 54.2 mg (0.200 mmol) of *N*-tosylindole **4d** and 78.8 mg (0.202 mmol) of 2-fluoropyridinium salt **1**, compound **5d** (107.5 mg, 0.191 mmol, 96% yield) was obtained as colorless crystals after washing the crude material with a 5% solution of $CHCl_3$ in hexane. Mp 159–160 °C (from $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H,) 7.66 (s, 1H), 7.49 (d, J = 7.8 Hz 1H), 7.43–7.37 (m, 1H,), 7.35-7.29 (m, 1H), 7.23 (d, J = 8.2 Hz, 2H), 5.00 (t, J = 5.8 Hz 1H), 3.92 (d, J = 5.8 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 135.0, 134.8, 129.9, 128.4, 127.1, 126.9, 125.6, 124.0, 119.1 (q, J_{CF} = 330 Hz), 118.1, 114.2, 112.8, 78.2, 21.6, 21.3; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –73.5 (s, 6F); IR (ATR): ν = 2919, 1451, 1388, 1377, 1363, 1218, 1202, 1170, 1117, 1097, 973, 748, 666, 643, 570, 502 cm^{-1}; MS (ESI-TOF) m/z 562 $[M–H]^–$; HRMS calcd for $C_{19}H_{14}F_6NO_6S_3$ $[M–H]^–$, 561.9887; found, 561.9891.

3-(2,2-Bis((trifluoromethyl)sulfonylethyl)-1-phenylethynyl-1,5,6,7-tetrahydroindol-4-one 5e. From 30 mg (0.12 mmol) of 1-phenylethynyl-1,5,6,7-tetrahydroindol-4-one **4e** and 47 mg (0.12 mmol) of 2-fluoropyridinium salt **1**, compound **5e** was obtained as a yellowish solid after washing the crude material with dicloromethane/hexane. Mp 149–151 °C (from $CHCl_3$); ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 7.55 (m, 2H), 7.38 (m, 3H), 6.41 (s, 1H), 3.75 (s, 2H), 2.86 (t, J = 6.1 Hz, 2H), 2.34 (m, 2H), 2.11 (m, 2H). ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 193.2, 146.6, 139.1, 132.2, 129.4, 129.3, 122.7, 122.5 (q, J_{CF} = 328.2 Hz), 121.8, 105.4, 78.9, 74.5, 63.3, 38.4, 26.3, 24.0, 22.5;

^{19}F NMR (282 Hz, CD_3COCD_3): δ = –79.9 (s, 6F); IR (CH_3COCH_3): ν = 2250, 1651, 1335, 1038, 1162 cm^{-1}; HRMS calcd for $C_{20}H_{16}F_6NO_5S_2^+$ $[M+H]^+$, 528.0369; found, 528.0382.

2-(2,4-Diphenyloxazol-3-ium-5-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 7. From 43.3 mg (0.196 mmol) of 2,4-diphenyloxazole **6a** and 78.4 mg (0.201 mmol) of 2-fluoropyridinium salt **1**, compound **7** (99.3 mg, 0.193 mmol, 99% yield) was obtained as colorless crystals after washing the resulting solid with a 5% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 206–207 °C (from $CHCl_3$/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.98 (d, J = 7.3 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.60–7.50 (m, 3H), 7.55–7.51 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.7, 147.1, 134.9, 132.2, 130.6, 129.4, 128.8, 127.6, 127.4, 127.1, 125.7, 121.3 (q, J_{CF} = 329 Hz), 61.7, 25.2; ^{19}F NMR (376 Hz, DMSO-d_6): δ = –81.4 (s, 6F); IR (ATR): ν = 3170, 1657, 1606, 1577, 1340, 1318, 1176, 1090, 851, 629, 576, 509 cm^{-1}; MS (ESI-TOF) m/z 536 $[M+Na]^+$; HRMS calcd for $C_{19}H_{13}F_6NNaO_5S_2$ $[M+Na]^+$, 536.0037; found, 536.0038. Anal. Calcd for $C_{19}H_{13}F_6NO_5S_2$: C, 44.45; H, 2.55; N, 2.73. Found: C, 44.40; H, 2.80; N, 2.93.

General Procedure for the Preparation of Compounds 8, 11 and 12 (Scheme 3). 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1** (0.20 mmol) was added at room temperature to a solution of the appropriate heterocycle **6b**, **9**, **10** (0.20 or 0.40 mmol) in CH_3CN (2.0 mL). The reaction was stirred for 5 min at room temperature, and then the mixture was concentrated under reduced pressure. The purification details are described for each compound. Spectroscopic and analytical data for compounds **8**, **11** and **12** follow.

2-(Oxazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 8. From 26.5 μL (0.403 mmol) of oxazole **5b** and 77.0 mg (0.198 mmol) of 2-fluoropyridinium salt **1**, compound **8** (70.5 mg, 0.195 mmol, 99% yield) was obtained as colorless crystals after evaporation of the reaction

mixture. The structure was confirmed by comparision of reproted NMR spectroscopic data.[1] ^{1}H NMR (400 MHz, CD_3CN) δ = 9.47 (1H, s), 8.25 (1H, s), 7.93 (1H, s), 5.25 (2H, brs); ^{13}C NMR (100 MHz, CD_3CN) δ = 154.5, 145.3, 122.3, 121.6 (q, J_{CF} = 325 Hz), 66.4, 51.1; ^{19}F NMR (376 Hz, CD_3CN) δ = –81.3 (s, 6F).

2-(Thiazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 11. From 16.9 mg (0.199 mmol) of thiazole **9** and 77.1 mg of 2-fluoropyridinium salt **1** (0.198 mmol), compound **11** (67.8 mg, 91% yield) was obtained as colorless crystals after washing the resulting solid with $CHCl_3$ (1.0 mL x 2). Due to the low stability in solution phase, we could not detect suitable peaks in the MS spectra. Mp. 138–140 °C (from $CHCl_3$/hexane); ^{1}H NMR (400 MHz, CD_3CN): δ = 9.72–9.67 (1H, m), 8.33 (1H, dd, J = 3.7, 1.1), 8.01 (1H, dd, J = 3.4, 2.7), 5.40 (2H, s); ^{13}C NMR (100 MHz, CD_3CN): δ = 158.4, 137.6, 127.0, 121.6 (q, J_{CF} = 325 Hz), 68.0, 56.2; ^{19}F NMR (376 Hz, CD_3CN): δ = –81.4 (s, 6F); IR (ATR): ν = 3119, 1557, 1342, 1321, 1174, 1140, 1109, 1057, 860, 728, 692, 637, 597, 565, 508 cm^{-1}; Anal. Calcd for $C_7H_5F_6NO_4S_3$: C, 22.28; H, 1.34; N, 3.71. Found: C, 22.13; H, 1.61; N, 3.84.

2-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 12. From 16.8 mg (0.205 mmol) of 1-methylimidazole **10** and 77.4 mg (0.199 mmol) of 2-fluoropyridinium salt **1**, compound **12** (73.2 mg, 0.196 mmol, 98% yield) was obtained as colorless crystals after evaporation of the reaction mixture. The structure was confirmed by comparision to reported NMR spectroscopic data.[1] ^{1}H NMR (400 MHz, CD_3CN) δ = 8.51 (1H, s), 7.48 (1H, t, J = 1.8 Hz), 7.27 (1H, t, J = 1.8 Hz), 5.04 (2H, brs), 3.80 (3H, s); ^{13}C NMR (100 MHz, CD_3CN) δ = 136.4, 124.2, 122.8, 121.7 (q, J_{CF} = 326 Hz), 64.6, 50.1, 36.7; ^{19}F NMR (376 Hz, CD_3CN) δ = –81.4 (s, 6F).

[1] H. Yanai, Y. Takahashi, H. Fukaya, Y. Dobashi, T. Matsumoto, *Chem. Commun.* **2013**, *49*, 10091.

General Procedure for the Preparation of Compounds 14a–d (Scheme 4). 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1** (0.20 mmol) was added at room temperature to a solution of the oxygen-containing heterocycle **6** (0.20 mmol) in CH_3CN (2.0 mL) (for compounds **13a–c**) or DCE (4.0 mL) (for compound **13d**). The reaction was stirred at room temperature (for compounds **13a** and **13c**), 50 ºC (for compound **13d**) or 80 ºC (for compound **13b**) until disappearance of the starting material (TLC), and then the mixture was concentrated under reduced pressure. The purification details are described for each compound. Spectroscopic and analytical data for compounds **14a–d** follow.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-4-hydroxyfuran-2(5*H*)-one 14a. From 20.2 mg (0.202 mmol) of tetronic acid **13a** and 77.7 mg (0.200 mmol) of 2-fluoropyridinium salt **1**, compound **14a** (74.2 mg, 0.189 mmol, 95% yield) was obtained as colorless crystals after washing the resulting solid with a 4% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 106–107 °C (from CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, CD_3CN): δ = 9.67 (brs, 1H), 6.20 (brs,1H), 4.66 (s, 2H), 3.37 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 176.0, 175.0, 120.0 (q, J_{CF} = 329 Hz), 93.2, 74.3, 68.0, 19.9; ^{19}F NMR (376 Hz, CD_3CN): δ = –74.4 (s, 6F); IR (ATR): ν = 3059, 1717, 1656, 1627, 1391, 1235, 1202, 1114, 1097, 597, 497 cm^{-1}; MS (ESI-TOF) *m*/*z* 391 $[M–H]^–$; HRMS calcd for $C_8H_5F_6O_7S_2$ $[M–H]^–$, 390.9381; found, 390.9378. Anal. Calcd for $C_8H_6F_6O_7S_2$: C, 24.56; H, 1.39. Found: C, 24.63; H, 1.67.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-4-methoxyfuran-2(5*H*)-one 14b. From 23.2 mg (0.203 mmol) of methyl tetronate **13b** and 79.4 mg (0.204 mmol) of 2-fluoropyridinium salt **1**, a mixture of compound **14b** (61.7 mg, 0.152 mmol, 75% yield) and 3-substituted isomer in a ratio of 7.4 : 1 was obtained as a colorless oil after purification by bulb-to-bulb distillation (180–200 °C at 5 mmHg) using a Kugelrohr oven. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.16 (t, *J* = 6.7 Hz, 1H), 4.79 (s, 2H), 4.03 (s. 3H), 3.40 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 173.1,

119.1 (q, J_{CF} = 330 Hz), 94.4, 72.3, 65.6, 58.3, 19.4; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –74.0 (s, 6F); IR (film): ν = 2940, 1750, 1675, 1470, 1390, 1345, 1215, 1105, 1025, 700, 640 cm^{-1}; MS (ESI-TOF) *m*/*z* 405 [M–H]$^-$; HRMS calcd for $C_9H_7F_6O_7S_2$ [M–H]$^-$, 404.9537; found, 404.9536. Anal. Calcd for $C_9H_8F_6O_7S_2$: C, 26.11; H, 1.98. Found: C, 26.45; H, 2.22.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-4-hydroxy-2*H*-chromen-2-one 14c. From 31.6 mg (0.195 mmol) of 4-hydroxy-2*H*-chromen-2-one **13c** and 86.1 mg (0.221 mmol) of 2-fluoropyridinium salt **1**, compound **14c** (87.9 mg, 0.193 mmol, 99% yield) was obtained as colorless crystals after washing the resulting solid with a 5% solution of Et_2O in hexane (1.0 mL x 3). Mp 287–289 °C (from $CHCl_3$); ^{1}H NMR (400 MHz, CD_3CN): δ = 9.12 (brs, 1H), 7.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.67–7.62 (m, 1H), 7.42-7.37(m, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 6.30 (br, 1H), 3.72 (s, 2H, s); ^{13}C NMR (100 MHz, CD_3CN): δ = 163.8, 163.3, 153.5, 134.0, 125,4, 124.2, 120.1 (q, J_{CF} = 329 Hz), 117.6, 116.1, 97.9, 74.9, 23.0; ^{19}F NMR (376 Hz, CD_3CN): δ = –74.5 (s, 6F); IR (ATR): ν = 2958, 2924, 1681, 1655, 1626, 1379, 1213, 1193, 1101, 1084, 644, 586, 477 cm^{-1}; MS (ESI-TOF) *m*/*z* 453 [M–H]$^-$; HRMS calcd for $C_{13}H_7F_6O_7S_2$ [M–H]$^-$, 452.9537; found, 452.9534. Anal. Calcd for $C_{13}H_8F_6O_7S_2$: C, 34.37; H, 1.77. Found: C, 34.51; H, 2.01.

2-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)benzofuran (14d). From 47.2 mg (0.400 mmol) of benzo[2,3]furan and 79.1 mg (0.203 mmol) of 2-fluoropyridinium salt **1**, compound **14c** (64.4 mg, 0.157 mmol, 77% yield) was obtained as yellowish oil after bulb-to-bulb distillation (140-160 °C at 5 mmHg) using a Kugelrohr oven. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (1H, m), 7.46 (1H, dd, *J* = 8.2, 0.8), 7.32 (1H, td, *J* = 9.6, 1.3), 7.29–7.23 (1H, m), 6.76 (1H, s), 5.43 (1H, t, *J* = 5.8 Hz), 4.00 (2H, d, *J* = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 147.4, 127.8, 125.1, 123.5, 121.4, 119.2 (q, J_{CF} = 330 Hz), 111.1, 107.4, 75.4, 24.9; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –73.8 (s, 6F); IR (ATR) ν = 2941, 1609, 1456, 1377, 1207, 1101, 948, 819, 748, 684, 632, 580, 516, 492,

464, 423 cm^{-1}; MS (ESI-TOF) *m*/*z* 409 $[M–H]^–$; HRMS calcd for $C_{12}H_7F_6O_5S_2$ $[M–H]^–$, 408.9639; found, 408.9641.

General Procedure for the Preparation of Compounds 16a–e (Scheme 5). 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1** (0.20 mmol) was added at room temperature to a solution of pyrazole **15** (0.20 mmol) in CH_3CN (2.0 mL). The reaction was stirred at room temperature (for compounds **15a**) or 90 ºC (in a sealed tube, for compound **16b–e**) until disappearance of the starting pyrazole (TLC), and then the mixture was concentrated under reduced pressure. The purification details are described for each compound. Spectroscopic and analytical data for compounds **14a–d** follow.

2-(3-Methyl-1-phenyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 16a. From 30.9 mg (0.195 mmol) of 3-methyl-1-phenyl-1*H*-pyrazole **15a** and 79.0 mg (0.203 mmol) of 2-fluoropyridinium salt **1**, compound **16a** (76.2 mg, 97% yield) was obtained as colorless crystals after washing the crude material with a 5% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 185–187 °C (from $CHCl_3$); ^1H NMR (400 MHz, CD_3CN): δ = 8.26 (s, 1H), 7.66–7.55 (m, 5H), 3.60 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 147.1, 135.6, 135.3, 131.3, 131.1, 125.3, 123.8, 122.2 (q, J_{CF} = 327 Hz), 64.8, 22.4, 9.8; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.8 (s, 6F); IR (ATR): ν = 3202, 3096, 1558, 1498, 1343, 1320, 1195, 1178, 1159, 1123, 1037, 873, 767, 616, 587, 567, 505 cm^{-1}; MS (ESI-TOF) *m*/*z* 473 $[M+Na]^+$; HRMS calcd for $C_{14}H_{12}F_6N_2NaO_4S_2$ $[M+Na]^+$, 473.0040; found, 473.0039. Anal. Calcd for $C_{14}H_{12}F_6N_2O_4S_2$: C, 37.34; H, 2.69; N, 6.22. Found: C, 37.34; H, 2.77; N, 6.37.

2-(1-Phenyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 16b. From 28.7 mg (0.199 mmol) of 1-phenylpyrazole **15b** and 76.4 mg (0.196 mmol) of 2-fluoropyridinium salt **1**, compound **16b** (85.2 mg, 98% yield) was obtained as colorless crystals (from $CHCl_3$/hexane)

after washing the crude material with a 5% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 146–148 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.09 (s, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.54 (s, 1H), 7.42-7.49 (m, 2H), 7.25 (t, J = 7.3 Hz, 1H), 3.48 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.3, 140.2, 129.9, 126.1, 125.8, 124.9, 121.5 (q, J_{CF} = 330 Hz), 118.2, 64.8, 22.9; ^{19}F NMR (376 Hz, DMSO-d_6): δ = –81.3 (s, 6F); IR (ATR): ν = 3143, 1597, 1494, 1392, 1339, 1171, 1111, 1036, 759, 599, 580, 506 cm^{-1}; MS (ESI-TOF) m/z 459 $[M+Na]^+$; HRMS calcd for $C_{13}H_{10}F_6N_2NaO_4S_2$ $[M+Na]^+$, 458.9884; found, 458.9878.

2-(1-Methyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 16c. From 16.7 mg (0.203 mmol) of 1-methylpyrazole **15c** and 77.8 mg (0.200 mmol) of 2-fluoropyridinium salt **1**, compound **16c** (73.3 mg, 0.196 mmol, 98% yield) was obtained as colorless crystals after evaporation of the reaction mixture. Mp. 206–207 °C (from $CHCl_3$/hexane); ^{1}H NMR (400 MHz, CD_3CN): δ = 7.94 (s, 2H), 3.99 (s, 3H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 136.9, 133.8, 126.6, 122.2 (q, J_{CF} = 328 Hz), 64.9, 38.9, 23.3; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.8 (s, 6F); IR (ATR): ν = 3138, 1445, 1342, 1314, 1189, 1169, 1113, 1036, 836, 595, 583, 563, 507 cm^{-1}; MS (ESI-TOF) m/z 375 $[M+H]^+$; HRMS calcd for $C_8H_9F_6N_2O_4S_2$ $[M+H]^+$, 374.9908; found, 374.9902. Anal. Calcd for $C_8H_8F_6N_2O_4S_2$: C, 25.67; H, 2.15; N, 7.48. Found: C, 25.51; H, 2.33; N, 7.58.

2-(1-Benzyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 16d. From 32.2 mg (0.204 mmol) of 1-benzylpyrazole **15d** and 77.7 mg (0.200 mmol) of 2-fluoropyridinium salt **1**, compound **16d** (87.2 mg, 0.194 mmol, 97% yield) was obtained as colorless crystals after washing the crude material with Et_2O (0.5 mL x 4). Mp. 69–70 °C (from CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, CD_3CN): δ = 8.07 (s, 1H), 7.98 (s, 1H), 7.47–7.41 (m, 3H), 7.33–7.27 (m, 2H), 5.50 (s, 2H), 3.58 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 136.4, 134.8, 133.4, 130.3, 130.1, 129.1, 127.0, 122.2 (q, J_{CF} = 327 Hz), 65.0, 55.9, 23.3; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.8 (s, 6F); IR

(ATR): ν = 3518, 3138, 3059, 2970, 1334, 1310, 1166, 1130, 1036, 873, 842, 734, 699, 588, 565, 507 cm^{-1}; MS (ESI-TOF) *m*/*z* 473 $[M+Na]^+$; HRMS calcd for $C_{14}H_{12}F_6N_2NaO_4S_2$ $[M+Na]^+$, 473.0040; found, 473.0034. Anal. Calcd for $C_{14}H_{12}F_6N_2O_4S_2$: C, 37.34; H, 2.69; N, 6.22. Found: C, 37.31; H, 2.96; N, 6.24.

2-(1-Isopropyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 16e. From 22.4 mg (0.203 mmol) of 1-isopropylpyrazole **15e** and 78.4 mg (0.201 mmol) of 2-fluoropyridinium salt **1**, compound **16e** (79.4 mg, 0.197 mmol, 97% yield) was obtained as colorless crystals after washing the crude material with Et_2O (0.5 mL x 4). Mp. 173–174 °C (from CH_2Cl_2/hexane); ^1H NMR (400 MHz, CD_3CN): δ = 8.02 (s, 1H), 7.98 (s, 1H), 4.76 (sept, *J* = 6.7 Hz, 1H), 3.58 (s, 2H), 1.53 (s, 2H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 134.0, 133.7, 126.5, 122.2 (q, J_{CF} = 327 Hz), 65.1, 56.8, 21.8; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.9 (s, 6F); IR (ATR): ν = 3201, 3147, 1331, 1309, 1183, 1168, 1117, 1039, 883, 837, 726, 652, 596, 583, 565, 509 cm^{-1}; MS (ESI-TOF) *m*/*z* 425 $[M+Na]^+$; HRMS calcd for $C_{10}H_{12}F_6N_2NaO_4S_2$ $[M+Na]^+$, 425.0040; found, 425.0037. Anal. Calcd for $C_{10}H_{12}F_6N_2O_4S_2$: C, 29.85; H, 3.01; N, 6.96. Found: C, 29.74; H, 3.31; N, 7.07.

2-(1-Phenyl-1*H*-pyrazol-2-ium-2-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 17. To a solution of 1-phenylpyrazole **15e** (28.6 mg, 0.198 mmol) in CH_3CN (2.0 mL), 2-fluoropyridinium salt **1** (76.4 mg, 0.196 mmol) was added. After being stirred for 5 min at room temperature, the reaction mixture was concentrated under reduced pressure. Thus obtained solid materials were washed with Et_2O (0.5 mL x 4) to give the product **17** in 89% yield (75.9 mg, 0.174 mmol) as colorless crystals. This compound formed an equilibrium mixture with $Tf_2C{=}CH_2$/1-phenylpyrazole in several solvents including DMSO-d_6. Finally, the structure was confirmed by an X-ray crystallographic analysis. Mp. 120–121 °C (from $CHCl_3$/hexane); ^1H NMR (400 MHz, DMSO-d_6): δ = 8.51 (d, *J* = 2.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.54–7.44 (m, 2H),

7.31 (t, J = 7.4 Hz, 1H), 6.57–6.53 (m, 1H), 4.15 (s, 1H), 4.08 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.2, 140.0, 129.8, 127.9, 126.4, 121.1 (q, J_{CF} = 328 Hz), 118.6, 108.1, 66.3, 58.4; ^{19}F NMR (376 Hz, DMSO-d_6): δ = –81.7 (s, 6F); IR (ATR): ν = 3138, 1501, 1445, 1379, 1351, 1173, 1135, 1100, 1062, 857, 768, 695, 597, 566, 509 cm^{-1}; MS (ESI-TOF) m/z 437 $[M+H]^+$; HRMS calcd for $C_{13}H_{11}F_6N_2O_4S_2$ $[M+H]^+$, 437.0064; found, 437.0056. Anal. Calcd for $C_{13}H_{10}F_6N_2O_4S_2$: C, 35.78; H, 2.31; N, 6.42. Found: C, 35.61; H, 2.54; N, 6.58.

Conversion of Bis(triflyl)ethyl-Pyrazole 16b to the Corresponding Na$^+$ Salt 16b-Na. To a solution of NaOMe (5.57 mg, 0.103 mmol) in MeOH (2.0 mL), 43.0 mg (98.5 μmol) of bis(triflyl)ethyl-pyrazole **16b** was added. After being stirred at room temperature for 10 min, the reaction mixture was evaporated and solidified by addition of $CHCl_3$ (1 mL). The resulting solid material was washed with $CHCl_3$ (0.5 mL x 2) and dried under reduced pressure to give sodium 2-(1-phenyl-1*H*-pyrazol-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide **16b-Na** (40.6 mg, 88.6 μmol, 90% yield). Mp. >250 °C (from MeOH/$CHCl_3$); ^{1}H NMR (400 MHz, CD_3CN): δ = 7.93 (s, 1H), 7.69 (d, J = 7.8 Hz, 2H), 7.58 (s, 1H), 7.48–7.40 (m, 2H), 7.26 (t, J = 7.5 Hz, 1H), 3.56 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 142.0, 141.1, 130.3, 126.7, 126.5, 126.0, 122.4 (q, J_{CF} = 328 Hz), 119.2, 65.6, 23.5; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.6 (s, 6F); IR (ATR): ν = 1600, 1501, 1403, 1343, 1313, 1198, 1174, 1114, 1091, 1040, 1009, 875, 755, 721, 610, 599, 576, 504 cm^{-1}; MS (ESI-TOF) m/z 435 $[M]^-$; HRMS calcd for $C_{13}H_9F_6N_2O_4S_2$ $[M]^-$, 434.9908; found, 434.9915.

General Procedure for the Preparation of Bis(triflyl)ethyl-Pyrazoles 18a–d-Na (Scheme 6). A stirred solution of the corresponding bis(triflyl)ethyl-sydnone **3-Na** (0.1 mmol) and dimethyl acetylenedicarboxylate (3.7 mmol) in toluene (0.8 mL) was heated at reflux temperature until disappearance of the starting material (TLC, 1 h). The reaction was allowed to cool to room

temperature, concentrated under vacuum, and purified by flash column chromatography eluting with hexanes/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compound **8-Na** follow.

Dimethyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-phenyl-1*H*-pyrazole-3,4-dicarboxylate 18a-Na. From 16 mg (0.04 mmol) of Tf-sydnone **3a-Na**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **18a-Na** (17 mg, 89% yield) as a colorless solid. Mp 141–142 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 7.51–7.42 (m, 5H), 3.96 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN): δ = 164.8, 163.9, 146.1, 143.4, 139.9, 130.2, 130.0 (2C), 127.8 (2C), 122.5 (q, J_{C-F} = 328.0 Hz, 2C), 116.3, 63.8, 52.9, 52.5, 24.0; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.6 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN): δ = –7.64 (s, 1Na); IR ($CHCl_3$): ν = 1579, 1455, 1207 cm^{-1}; HRMS (ES): calcd for $C_{17}H_{14}F_6N_2NaO_8S_2$ [*M*+Na]$^{+}$: 574.9988; found: 575.0000.

Dimethyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-(*p*-tolyl)-1*H*-pyrazole-3,4-dicarboxylate 18b-Na. From 20 mg (0.04 mmol) of Tf-sydnone **3b-Na**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **18b-Na** (23 mg, 96% yield) as a colorless solid. Mp 218–219 ºC; ^{1}H NMR (500 MHz, CD_3CN): δ = 7.30 (s, 4H), 3.91 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): δ = 164.9, 164.0, 146.0, 143.3, 140.4, 137.4, 130.5 (2C), 127.6 (2C), 122.2 (q, J_{C-F} = 328.2 Hz, 2C), 116.2, 63.9, 52.9, 52.5, 24.2, 21.3; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.6 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN): δ = –7.67 (s, 1Na); IR ($CHCl_3$): ν = 1577, 1456, 1205 cm^{-1}; HRMS (ES): calcd for $C_{18}H_{16}F_6N_2NaO_8S_2$ [*M*+Na]$^{+}$: 589.0145; found: 589.0139.

Dimethyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-dicarboxylate 18c-Na. From 20 mg (0.07 mmol) of Tf-sydnone **3c-Na**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **18c-Na**

(22 mg, 58% yield) as a colorless solid. Mp 168–169 ºC; ^{1}H NMR (500 MHz, CD_3CN): δ = 7.34 (AA'XX', 2H), 7.00 (AAXX', 2H), 3.90 (s, 2H), 3.84 (s, 6H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): δ = 164.9, 164.0, 161.2, 146.2, 143.2, 132.9, 129.2 (2C), 122.2 (q, J_{C-F} = 328.0 Hz, 2C), 116.0, 115.0 (2C), 63.9, 56.3, 52.9, 52.4, 24.1; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.6 (s, 6F); ^{23}Na NMR (132 MHz, CD_3CN): δ = –7.65 (s, 1Na); IR ($CHCl_3$): ν = 1581, 1458, 1206 cm^{-1}; HRMS (ES): calcd for $C_{18}H_{16}F_6N_2NaO_9S_2$ [M+Na]$^+$: 605.0094; found: 605.0064.

Dimethyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-(4-nitrophenyl)-1*H*-pyrazole-3,4-dicarboxylate 18d-Na. From 120 mg (0.24 mmol) of crude Tf-sydnone **3d-Na**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **18d-Na** (112 mg, 78% yield) as a colorless solid. Mp 127–128 ºC; ^{1}H NMR (300 MHz, CD_3CN): δ = 8.33 (AA'XX', 2H), 7.70 (AAXX', 2H), 4.03 (s, 2H), 3.87 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN): δ = 164.6, 163.7, 149.1, 147.0, 144.7, 144.3, 129.0 (2C), 125.5 (2C), 122.1 (q, J_{C-F} = 327.9 Hz, 2C), 116.9, 63.8, 53.2, 52.7, 23.9; ^{19}F NMR (282 MHz, CD_3CN): δ = –80.6 (s, 6F); IR ($CHCl_3$): ν = 15774, 1454, 1203 cm^{-1}; HRMS (ES): calcd for $C_{17}H_{13}F_6N_3NaO_{10}S_2$ [M+Na]$^+$: 619.9839; found: 619.9846.

General Procedure for the Preparation of Bis(triflyl)ethyl-pyrazoles 19a–c-Na/20a–c-Na. A stirred solution of the corresponding bis(triflyl)ethyl-sydnone **3-Na** (0.04 mmol) and methyl propiolate (1.8 mmol) in toluene (0.4 mL) was heated at 140 ºC under microwave irradiation until disappearance of the starting material (TLC, 1 h). The reaction was allowed to cool to room temperature, concentrated under vacuum, and purified by flash column chromatography eluting with hexanes/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compound **9-Na** follow.

Methyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-phenyl-1*H*-pyrazole-3/4-carboxylates 19a-Na/20a-Na. From 16 mg (0.04 mmol) of Tf-sydnone **3a-Na**, and after flash chromatography of

the residue using hexanes/ethyl acetate (1:1) as eluent gave compounds **19a-Na/20a-Na** (19 mg, 85%; a ratio of regioisomers = 58:42) as a colorless solid. Mp 128–130 ºC; ^{1}H NMR (700 MHz, CD_3CN): δ= 7.86 (s, 1H, M), 7.55–7.42 (m, 10H, M + m), 6.87 (s, 1H, m), 4.13 (s, 2H, M), 3.86 (s, 3H, m), 3.78 (s, 3H, M), 3.64 (s, 2H, m); ^{13}C NMR (175 MHz, CD_3CN): δ = 165.1 (CO, M), 164.0 (CO, m), 148.2 (C_5, m), 145.9 (C_5, M), 143.9 (C_3, m), 141.7 (C_3, M), 140.6 (C_{Ar}, M), 140.1 (C_{Ar}, m), 130.2 (2CH_{Ar}, m), 129.8 (CH_{Ar}, M), 129.7 (2CH_{Ar}, M), 129.6 (2CH_{Ar}, m), 127.7 (2CH_{Ar}, M), 126.8 (CH_{Ar}, m), 121.4 (q, 2C, $J_{C–F}$ = 327.8 Hz, 2CF_3, m), 121.2 (q, 2C, $J_{C–F}$ = 328.6 Hz, 2CF_3, M), 114.9 (C_4, M), 109.9 (C_4, m), 64.3 (C-Tf_2, M), 64.1 (C-Tf_2, m), 52.4 (CH_3, m), 51.6 (CH_3, M), 26.2 (2CH_2, M + m); ^{19}F NMR (282 MHz, CD_3CN): δ = –80.4 (s, 6F, M + m); IR ($CHCl_3$): ν = 1588, 1460, 1209 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{12}F_6N_2NaO_6S_2$ [*M*+Na]$^+$: 516.9933; found: 516.9920.

Methyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-(*p*-tolyl)-1*H*-pyrazole-3/4-carboxylates 19b-Na/20b-Na. From 14 mg (0.03 mmol) of Tf-sydnone **3b-Na**, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compounds **19b-Na/20b-Na** (11 mg, 70%; a ratio of regioisomers = 56:44) as a colorless solid. Mp 153–155 ºC; ^{1}H NMR (700 MHz, CD_3CN): δ = 7.84 (s, 1H, M), 7.35–7.27 (m, 8H, M + m), 6.85 (s, 1H, m), 4.11 (s, 2H, M), 3.85 (s, 3H, m), 3.78 (s, 3H, M), 3.61 (s, 2H, m), 2.42 (s, 3H, m), 2.40 (s, 3H, M); ^{13}C NMR (175 MHz, CD_3CN): δ = 165.0 (M), 163.9 (m), 148.0 (m), 145.7 (M), 143.6 (m), 141.5 (M), 139.9 (M), 139.6 (m), 138.0 (m), 137.6 (M), 130.6 (2C, M), 130.2 (2C, m), 127.5 (2C, M), 126.5 (2C, m), 121.4 (q, 2C, $J_{C–F}$ = 327.4 Hz, m), 121.2 (q, 2C, $J_{C–F}$ = 328.3 Hz, M), 114.7 (M), 109.6 (m), 64.1 (m), 64.0 (M), 52.3 (m), 51.5 (M), 26.1 (2C, M + m), 21.1 (2C, M + m); ^{19}F NMR (282 MHz, CD_3CN): δ = –80.4 (s, 6F, M + m); IR ($CHCl_3$): ν = 1589, 1461, 1207 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{14}F_6N_2NaO_6S_2$ [*M*+Na]$^+$: 531.0090; found: 531.0115.

Methyl 5-(2,2-bis((trifluoromethyl)sulfonyl)ethyl)-1-(4-methoxyphenyl)-1*H*-pyrazole-3/4-carboxylates 19c-Na/20c-Na. From 10 mg (0.03 mmol) of Tf-sydnone **3c-Na**, and after flash

chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compounds **19c-Na/20c-Na** (9 mg, 55%; a ratio of regioisomers = 50:50) as a colorless solid. Mp 138–140 ºC; ^{1}H NMR (700 MHz, CD_3CN): δ = 7.82 (s, 1H, M), 7.36–7.31 (m, 4H, m), 7.05–6.96 (m, 4H, M), 6.82 (s, 1H, m), 4.05 (s, 2H, M), 3.85 (s, 3H, m), 3.84 (s, 3H, M), 3.83 (s, 3H, M), 3.77 (s, 3H, m), 3.59 (s, 2H, m); ^{13}C NMR (175 MHz, CD_3CN): δ = 165.0 (M), 163.9 (m), 160.7 (2C, M + m), 148.0 (m), 145.9 (M), 143.6 (m), 141.4 (M), 133.6 (M), 133.1 (m), 129.1 (2C, M), 128.1 (2C, m), 122.3 (q, 2C, J_{C-F} = 327.0 Hz, m), 122.2 (q, 2C, J_{C-F} = 328.8 Hz, M), 115.2 (2C, M), 114.8 (2C, m), 114.7 (M), 109.5 (m), 64.3 (M), 64.2 (m), 56.3 (M), 56.2 (m), 52.2 (m), 51.5 (M), 26.1 (2C, M + m); ^{19}F NMR (282 MHz, CD_3CN): δ = –80.4 (s, 6F, M + m); IR ($CHCl_3$): ν = 1586, 1457, 1203 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{14}F_6N_2NaO_7S_2$ [*M*+Na]$^{+}$: 547.0039; found: 547.0049.

General Procedure for the Preparation of Compounds 22a–d and 14e (Scheme 7). 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1** (0.20 mmol) was added at room temperature to a solution of heterocycles **21a–d** and **13e** (0.20 mmol) in CH_3CN (2.0 mL). The reaction was stirred at room temperature until disappearance of the starting heterocycles (TLC), and then the mixture was concentrated under reduced pressure. The purification details are described for each compound. Spectroscopic and analytical data for compounds **22a–d** and **14e** follow.

2-(5-Hydroxy-2,3-dimethyl-1-phenyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 22a. From 36.7 mg (0.195 mmol) of Phenazone **21a** and 77.1 mg (0.198 mmol) of 2-fluoropyridinium salt **1**, compound **22a** (92.4 mg, 99% yield) was obtained as colorless crystals after washing the crude material with a 3% solution of $CHCl_3$ in hexane (1.0 mL x 3). Mp 81−83 °C (from $CHCl_3$/hexane); ^{1}H NMR (400 MHz, CD_3CN): δ = 10.65 (br, 1H), 7.74–7.64 (m, 3H), 7.47-7.42 (m, 2H), 3.58 (s, 2H), 3.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR

(100 MHz, CD_3CN): δ = 155.3, 148.3, 132.9, 131.3, 130.7, 129.5, 121.9 (q, J_{CF} = 327 Hz), 104.3, 64.3, 34.2, 21.1, 10.6; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.9 (s, 6F); IR (ATR): ν = 3034, 1572, 1503, 1339, 1170, 1118, 1065, 1004, 692, 611, 599, 580, 561, 504 cm^{-1}; MS (ESI-TOF) *m*/*z* 503 $[M+Na]^+$; HRMS calcd for $C_{15}H_{14}F_6N_2NaO_5S_2$ $[M+Na]^+$, 503.0146; found, 503.0145. Anal. Calcd for $C_{15}H_{14}F_6N_2O_5S_2$: C, 37.50; H, 2.94; N, 5.83. Found: C, 37.28; H, 2.96; N, 5.89.

2-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 22b. From 35.0 mg (0.201 mmol) of Edaravone **21b** and 79.0 mg (0.203 mmol) of 2-fluoropyridinium salt **1**, compound **22b** (93.6 mg, 0.201 mmol, 99.9% yield) was obtained as colorless crystals after washing the the crude material with hexane (2.0 mL x 5). Mp 147–148 °C (from $CHCl_3$); ^1H NMR (400 MHz, CD_3CN): δ = 7.65–7.53 (m, 5H), 3.56 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 154.6, 147.1, 133.1, 131.0, 130.7, 125.1, 122.9 (q, J_{CF} = 327 Hz), 105.2, 64.0, 20.8, 10.3; ^{19}F NMR (376 Hz, CD_3CN): δ = –80.9 (s, 6F); IR (ATR): ν = 3242, 3079, 1564, 1501, 1335, 1305, 1180, 1013, 881, 604, 587 cm^{-1}; MS (ESI-TOF) *m*/*z* 489 $[M+Na]^+$; HRMS calcd for $C_{14}H_{12}F_6N_2NaO_5S_2$ $[M+Na]^+$, 488.9990; found, 488.9987. Anal. Calcd for $C_{14}H_{12}F_6N_2O_5S_2$: C, 36.06; H, 2.59; N, 6.01. Found: C, 35.90; H, 2.74; N, 6.07.

2-(1-(4-Chlorophenyl)-5-hydroxy-3-methyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 22c. From 41.4 mg (0.198 mmol) of 2-(4-chlorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one **21c** and 78.9 mg (0.203 mmol) of 2-fluoropyridinium salt **1**, compound **22c** (94.2 mg, 0.188 mmol, 95% yield) was obtained as colorless crystals after washing the crude material with 10% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 175–177 °C (from $CHCl_3$); ^1H NMR (400 MHz, CD_3CN): δ = 7.64–7.60 (m, 2H), 7.58-7.53 (m, 2H), 3.55 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 155.0, 147.6, 136.5, 131.6, 130.9, 126.7, 121.9 (q, J_{CF} = 326 Hz), 105.6, 64.0, 20.8, 10.4; ^{19}F NMR (376 Hz, CD_3CN): δ = –

80.9 (s, 6F); IR (ATR): ν = 3245, 3088, 1497, 1337, 1304, 1183, 1173, 1069, 1010, 880, 830, 604, 586, 566, 504 cm^{-1}; MS (ESI-TOF) *m*/*z* 523 $[M+Na]^+$; HRMS calcd for $C_{14}H_{11}ClF_6N_2NaO_5S_2$ $[M+Na]^+$, 522.9600; found, 522.9603. Anal. Calcd for $C_{14}H_{11}ClF_6N_2O_5S_2$: C, 33.58; H, 2.21; N, 5.59. Found: C, 33.62; H, 2.34; N, 5.79.

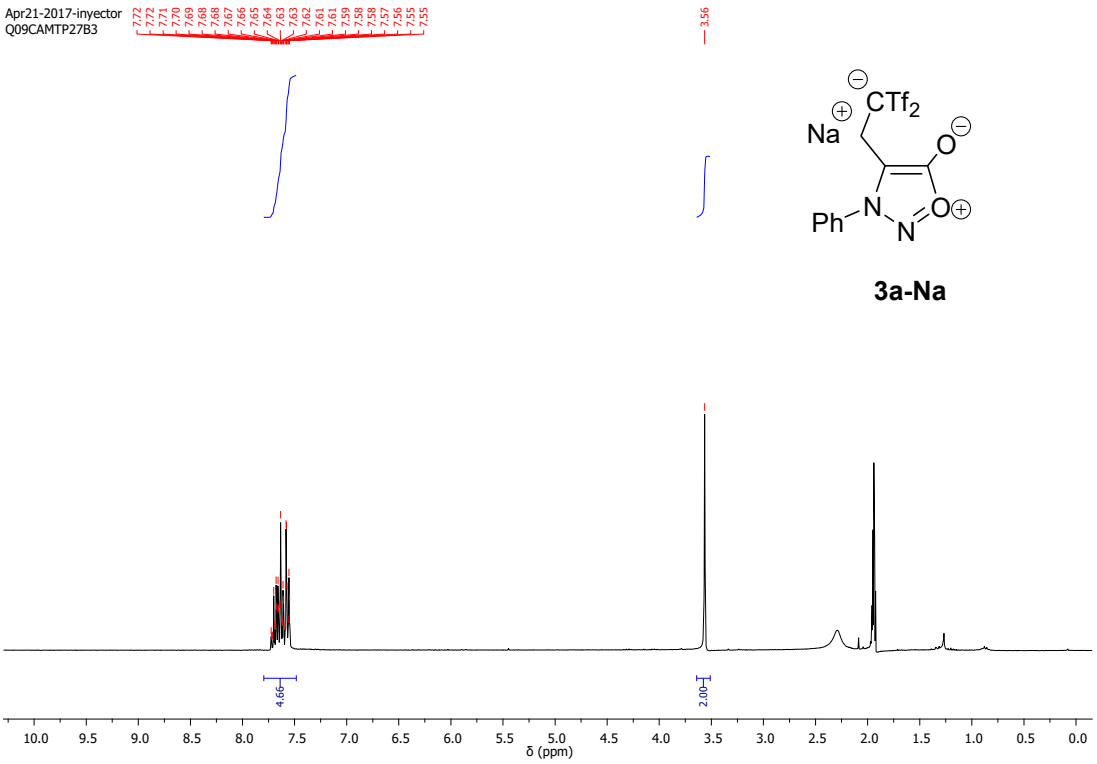
2-(5-Hydroxy-1,3-dimethyl-1*H*-pyrazol-2-ium-4-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide 22d. From 21.9 mg (0.195 mmol) of 2,5-dimethyl-2,4-dihydro-3*H*-pyrazol-3-one **21d** and 77.6 mg (0.199 mmol) of 2-fluoropyridinium salt **1**, compound **22d** (77.1 mg, 0.191 mmol, 98% yield) was obtained as colorless crystals after washing the crude material with a 5% solution of $CHCl_3$ in hexane (1.0 mL x 2). Mp 168–169 °C (from $CHCl_3$); ^1H NMR (400 MHz, CD_3CN): δ = 3.64 (s, 3H); 3.46 (br, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 154.8, 144.7, 121.9 (q, J_{CF} = 326 Hz), 104.8, 64.3, 33.1, 20.7, 10.0; ^{19}F NMR (376 Hz, CD_3CN): δ = –81.0 (s, 6F); IR (ATR): ν = 3238, 3156, 1619, 1577, 1487, 1341, 1324, 1299, 1180, 1031, 926, 820, 595, 567, 505 cm^{-1}; MS (ESI-TOF) *m*/*z* 427 $[M+Na]^+$; HRMS calcd for $C_9H_{10}F_6N_2NaO_5S_2$ $[M+Na]^+$, 426.9833; found, 426.9830. Anal. Calcd for $C_9H_{10}F_6N_2O_5S_2$: C, 26.74; H, 2.49; N, 6.93. Found: C, 26.97; H, 2.54; N, 7.13.

3-(2,2-Bis((trifluoromethyl)sulfonyl)ethyl)-7-(dimethylamino)-4-methyl-2*H*-chromen-2-one 14e. From 39.9 mg (0.196 mmol) of 7-dimethylamino-4-methylcoumarin **13e** and 84.3 mg (0.217 mmol) of 2-fluoropyridinium salt **1**, compound **14e** (92.6 mg, 0.187 mmol, 95% yield) was obtained as yellow crystals after washing the crude material with hexane (1.0 mL x 5). Mp. 137–139 °C (from $CHCl_3$/hexane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 6.35 (t, *J* = 6.9 Hz, 1H), 3.70 (d, *J* = 6.9 Hz, 2H), 3.08 (s, 6H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 154.4, 152.8, 126.3, 119.2 (q, J_{CF} = 330 Hz), 109.6, 109.5, 109.4, 73.9, 40.2, 25.4, 15.3; ^{19}F NMR (376 Hz, $CDCl_3$): δ = –74.2 (s, 6F); IR (ATR): ν = 2939, 2845, 1697, 1686, 1619, 1604, 1530, 1387, 1373, 1220, 1190, 1104,

798, 688, 639, 582, 497 cm^{-1}; MS (ESI-TOF) *m*/*z* 494 $[M–H]^–$; HRMS calcd for $C_{16}H_{14}F_6NO_6S_2$ $[M–H]^–$, 494.0167; found, 494.0172.

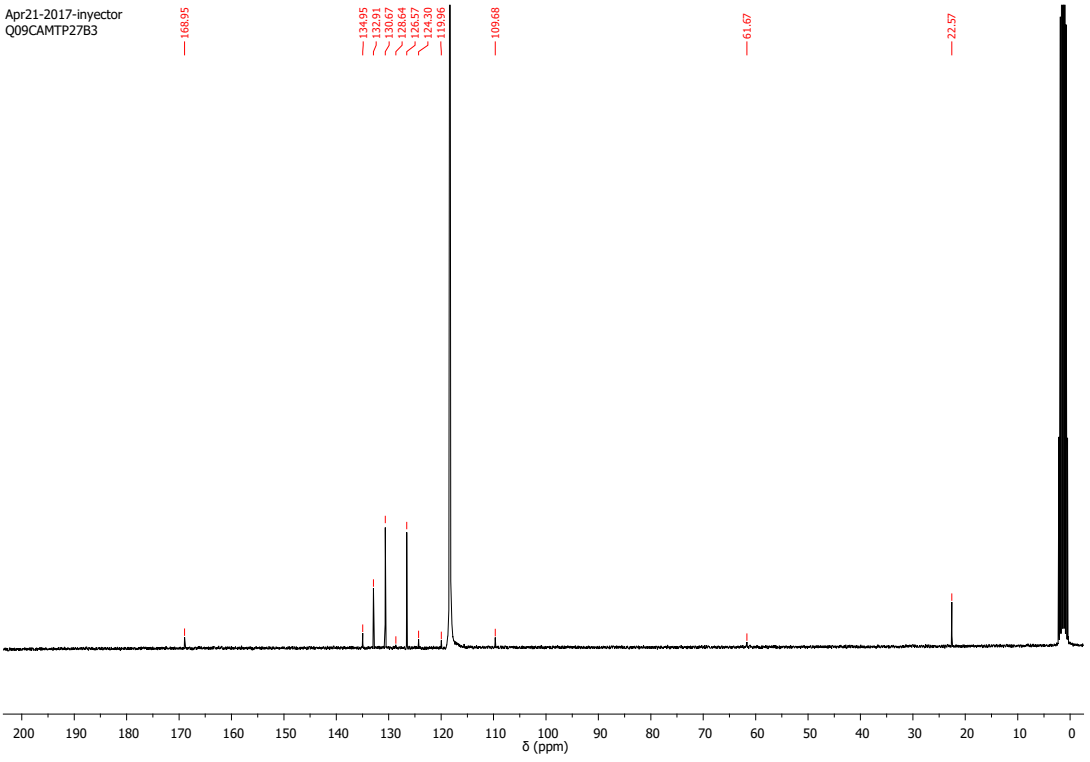
^{1}H, ^{13}C, ^{19}F and ^{23}Na NMR Spectra

^{1}H NMR (300 MHz, CD_3CN, 25 °C)

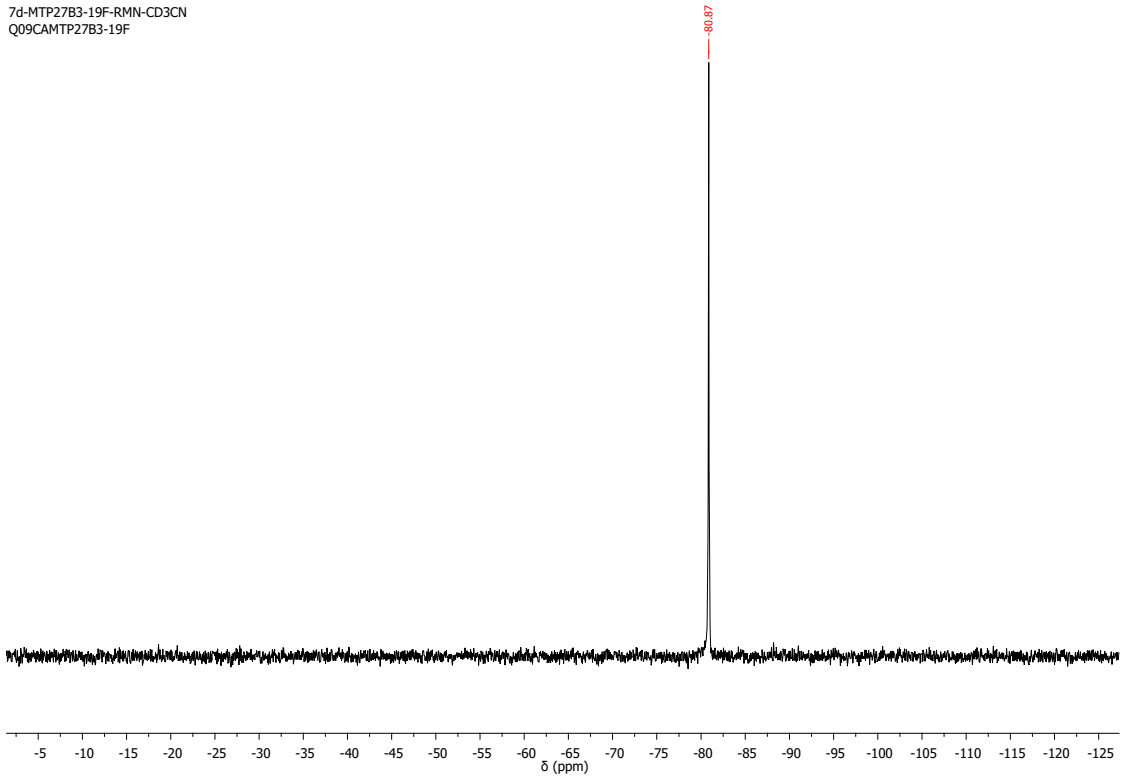


3a-Na

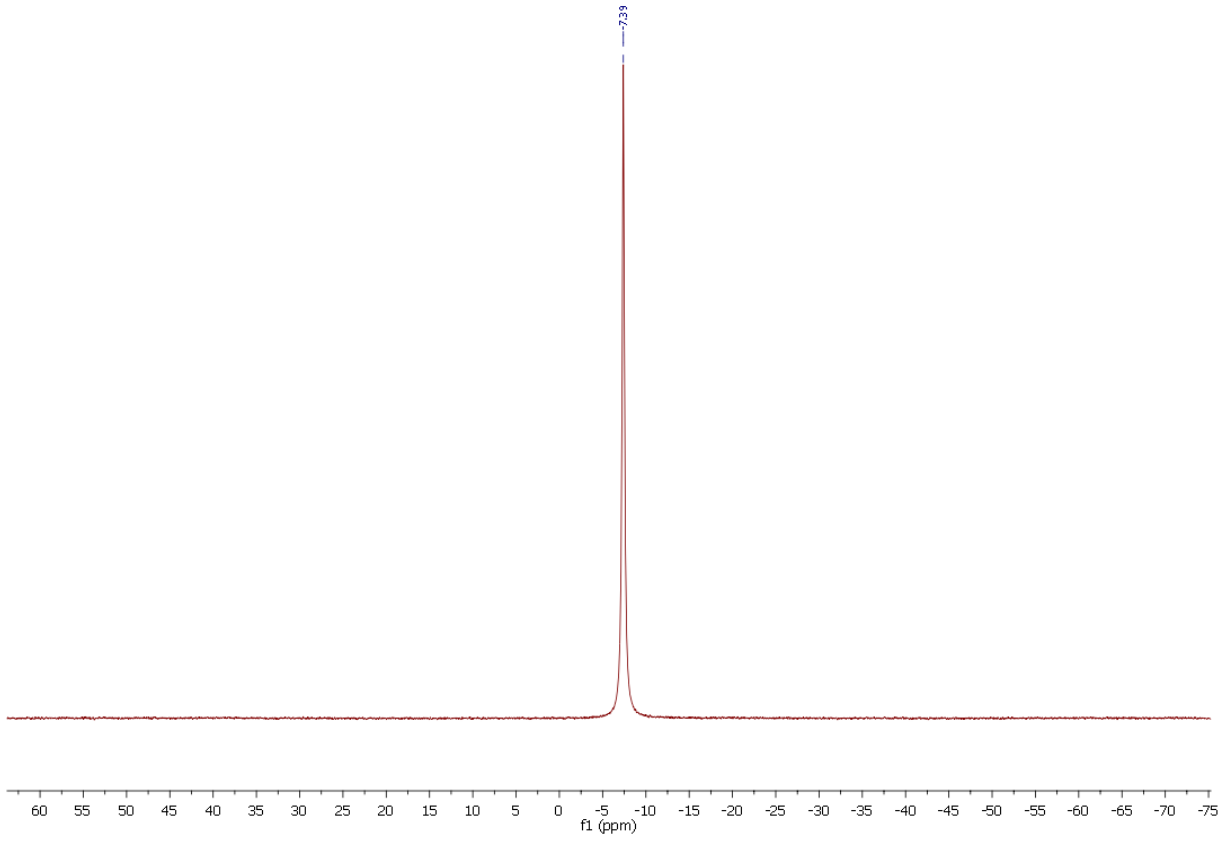
^{13}C NMR (75 MHz, CD_3CN, 25 °C)



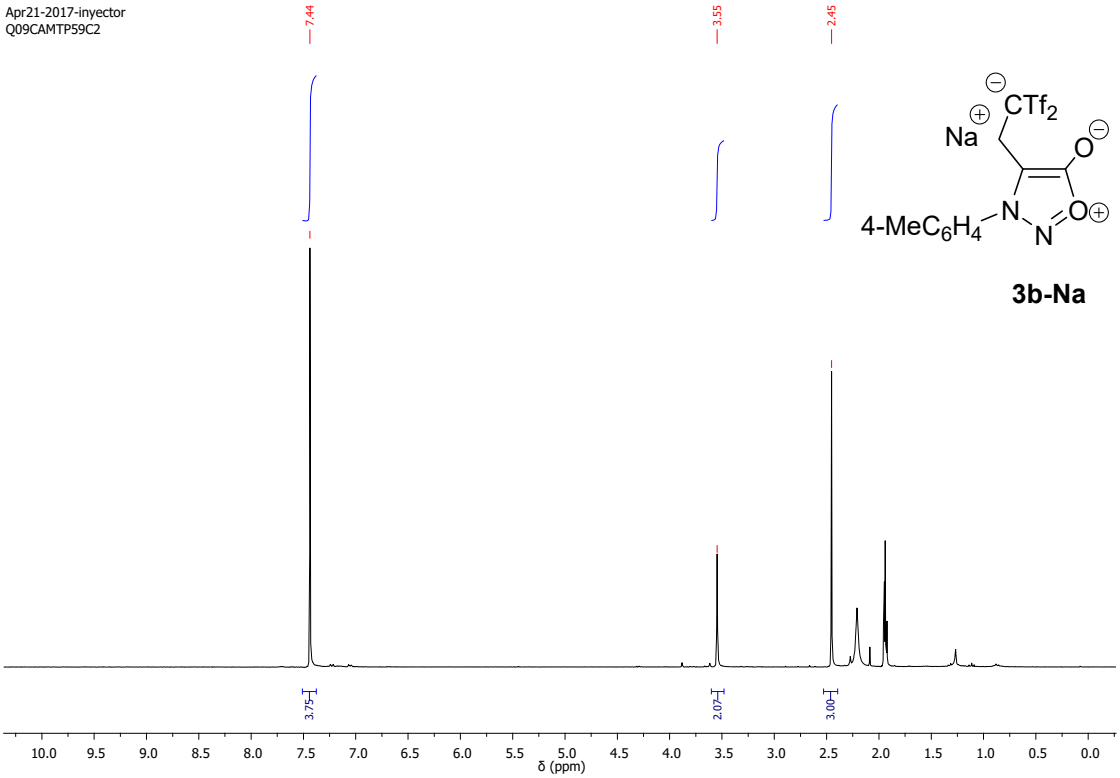
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



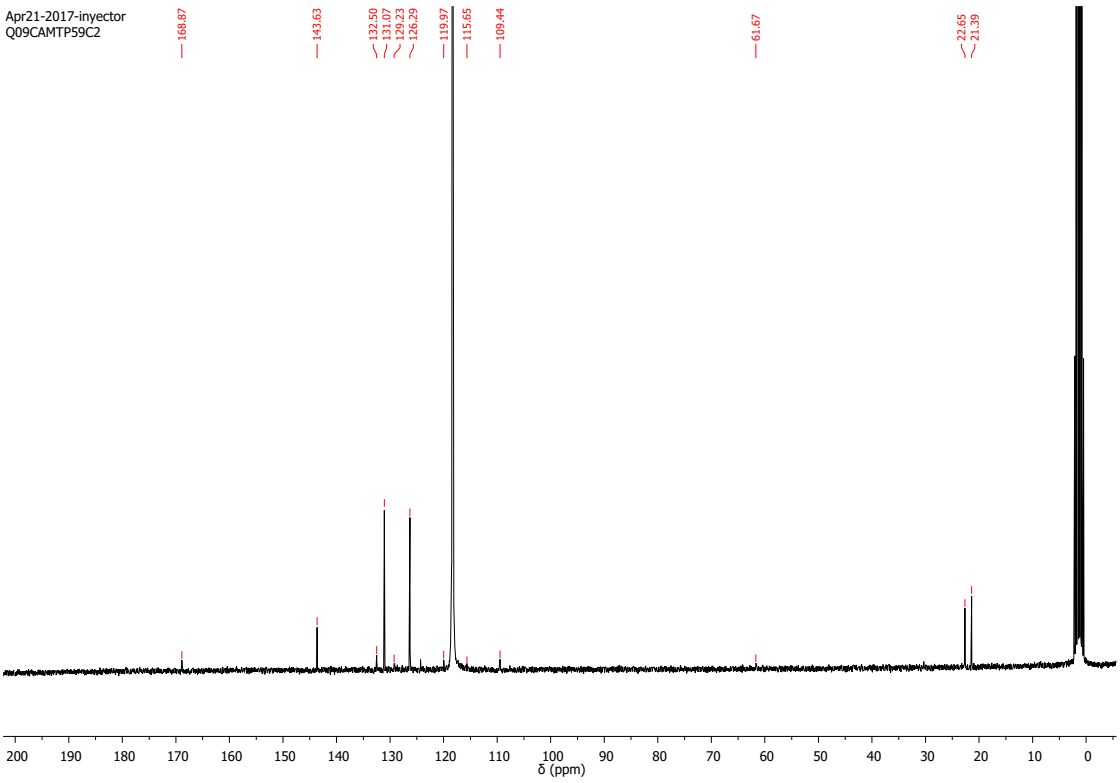
^{23}Na NMR (132 MHz, CD_3CN, 25 °C)



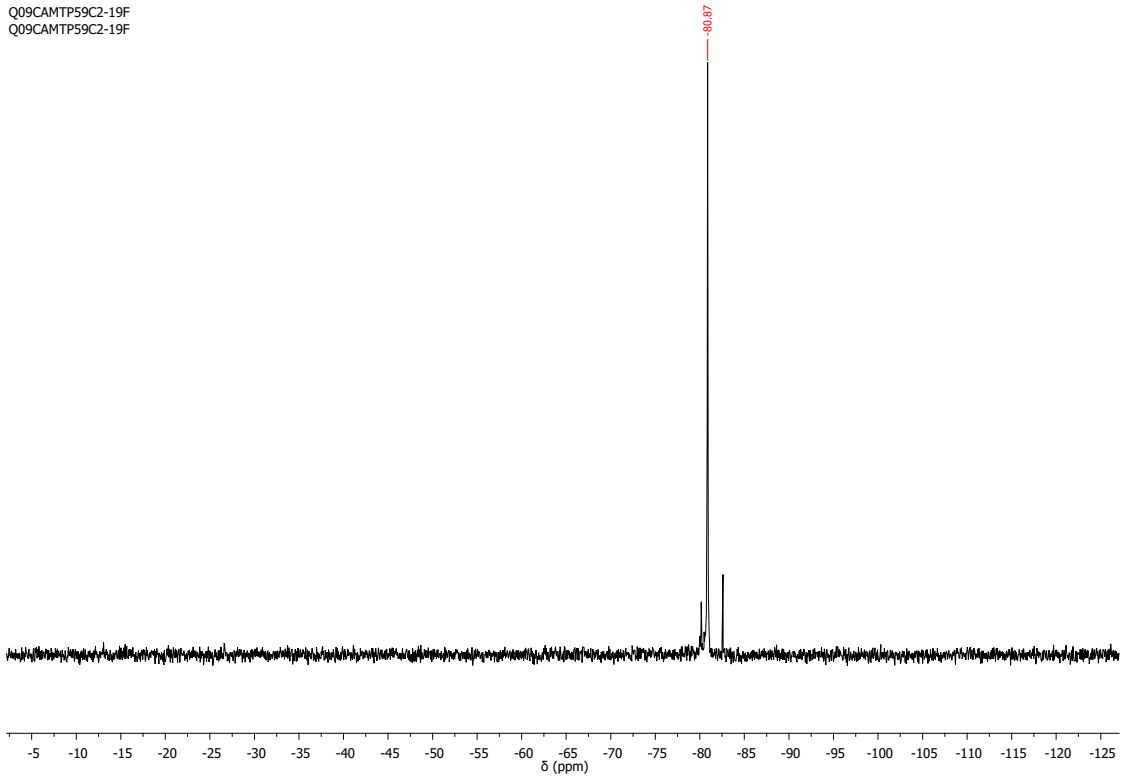
^{1}H-NMR (300 MHz, CD_3CN, 25 ºC)



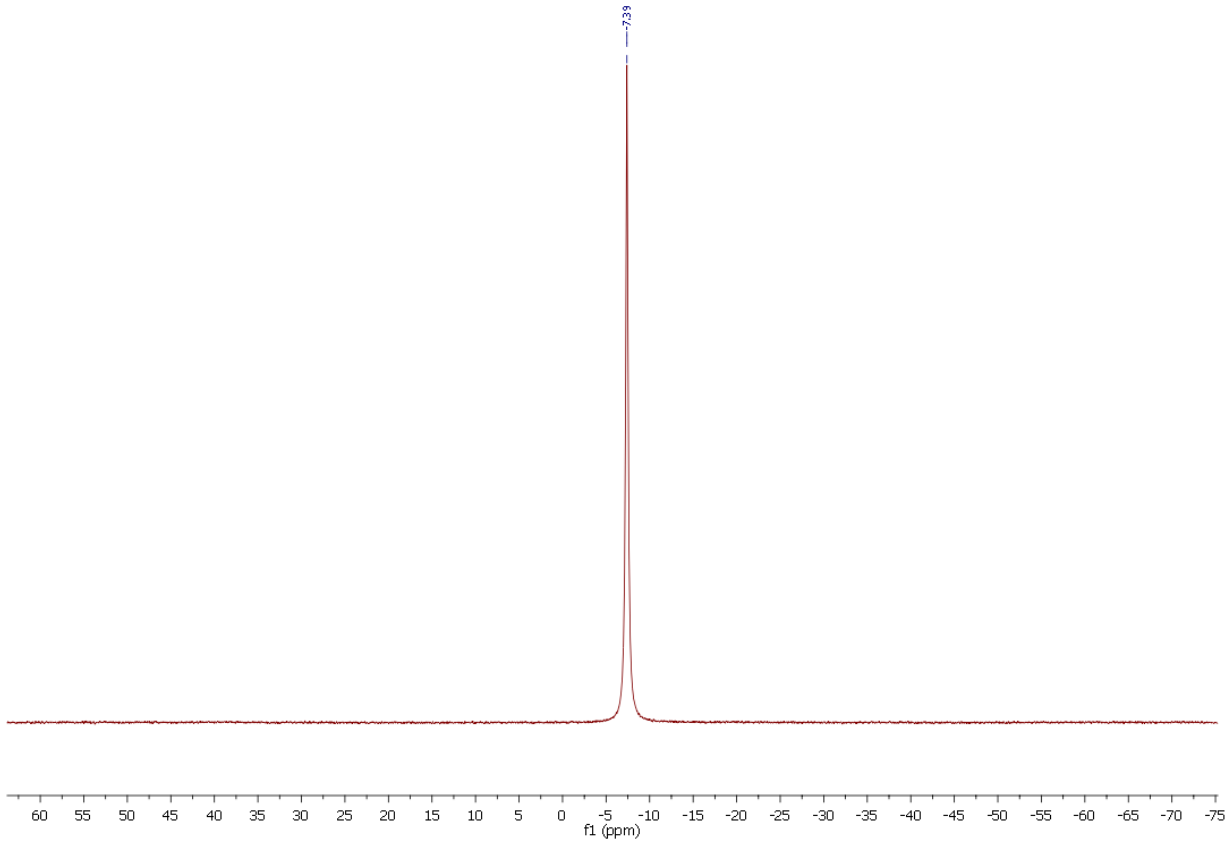
^{13}C NMR (75 MHz, CD_3CN, 25 ºC)



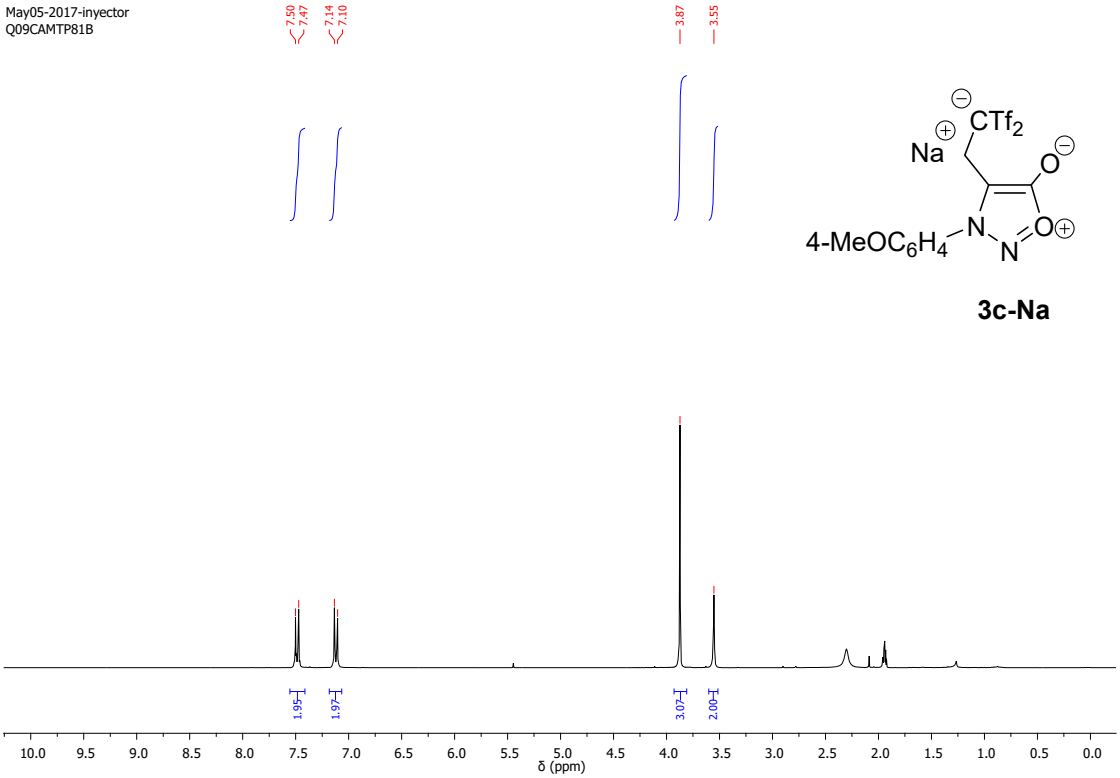
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



^{23}Na NMR (132 MHz, CD_3CN, 25 °C)

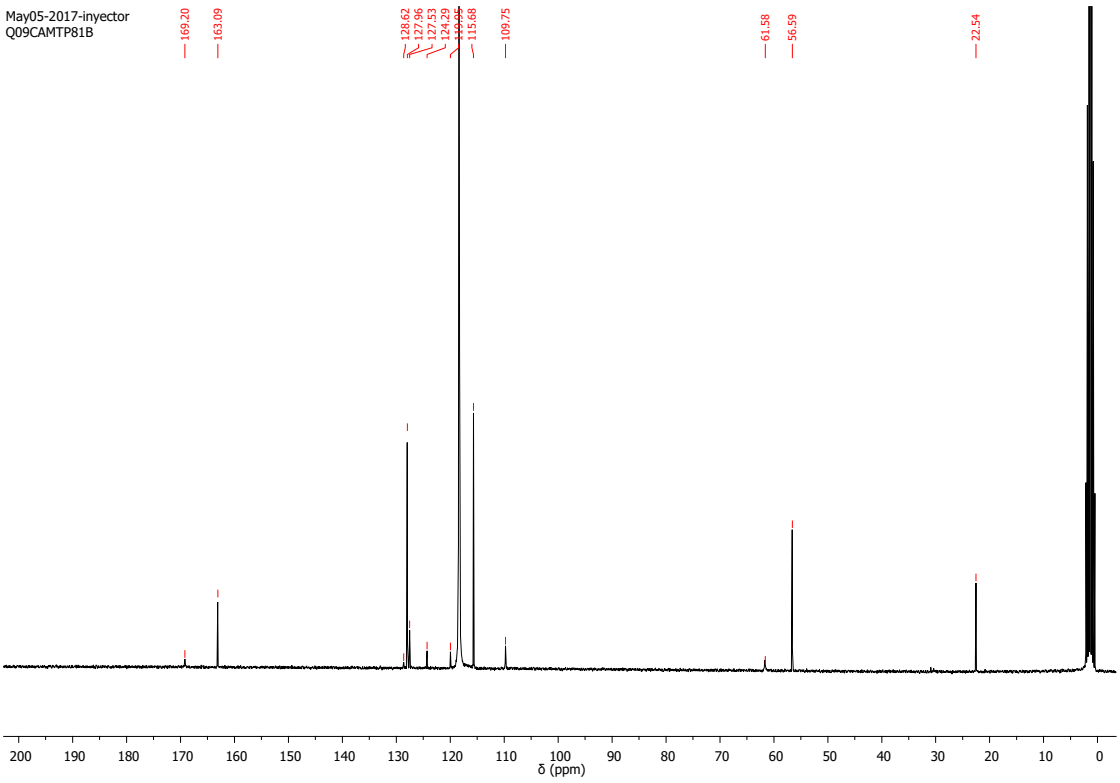


^{1}H-NMR (300 MHz, CD_3CN, 25 ºC)

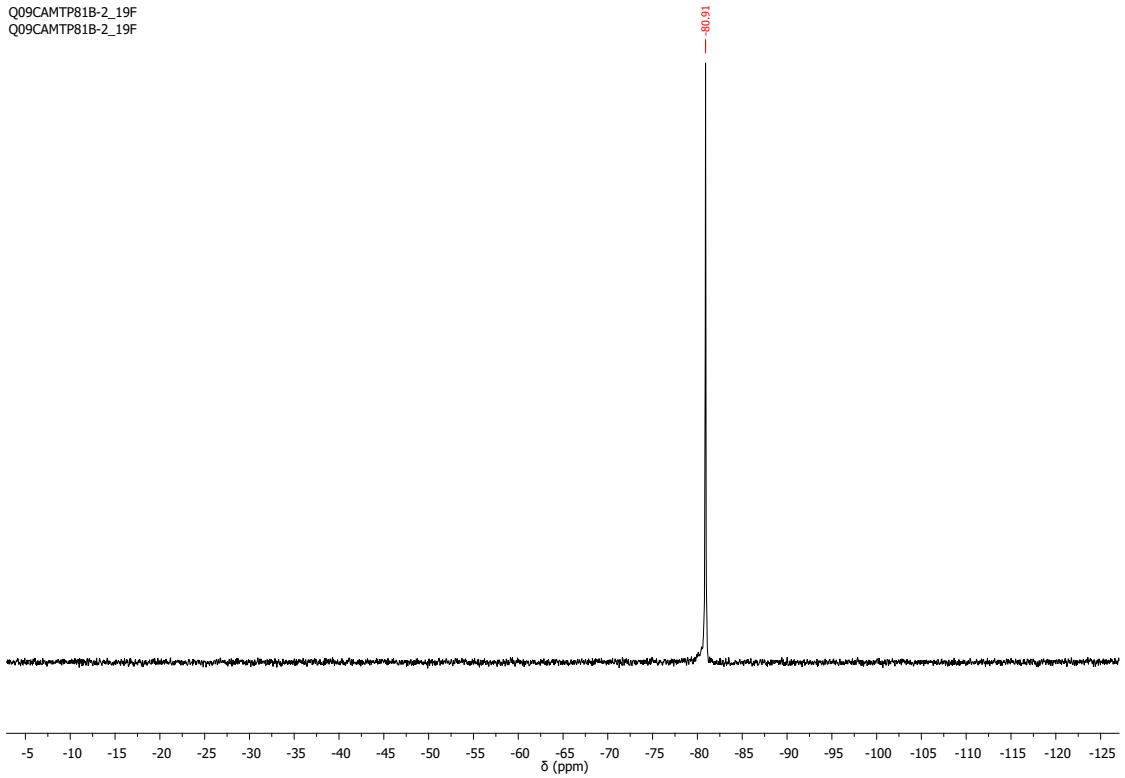


3c-Na

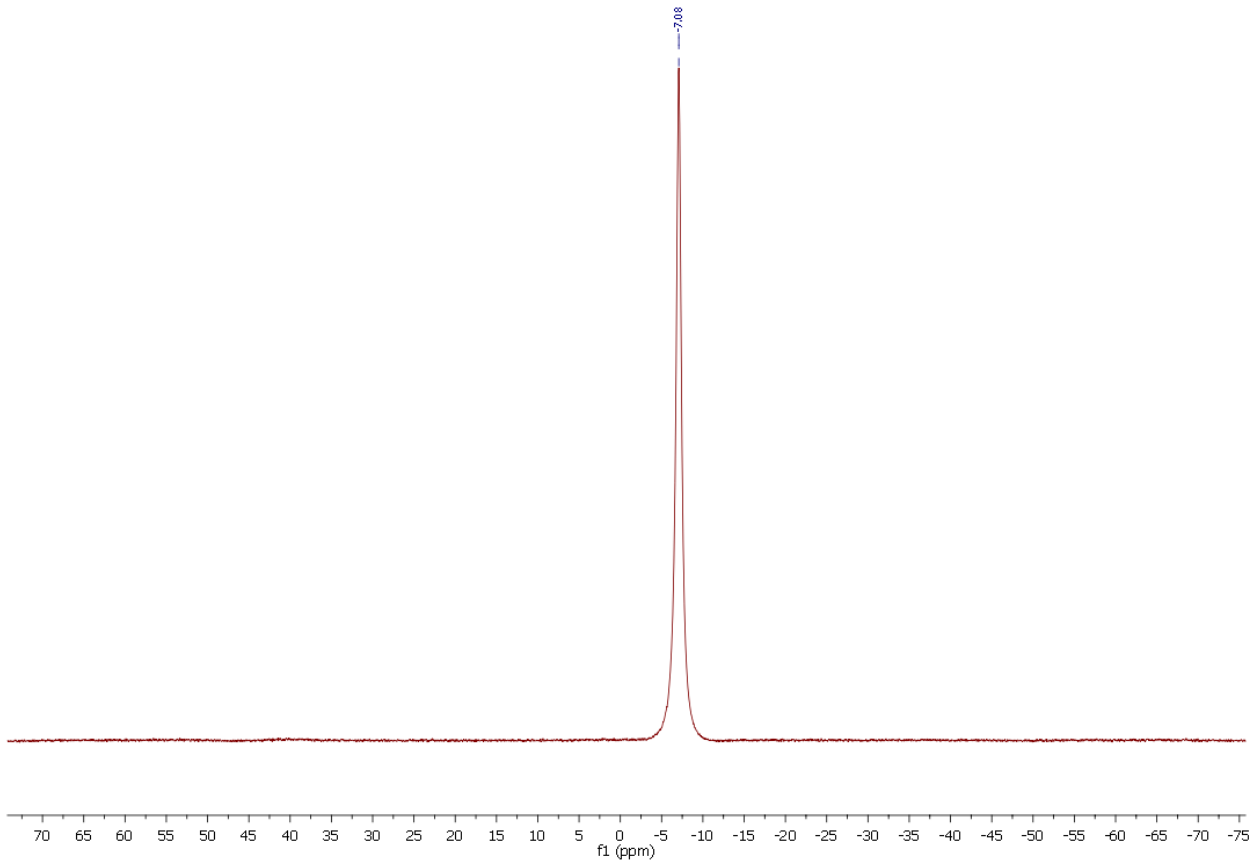
^{13}C NMR (75 MHz, CD_3CN, 25 ºC)



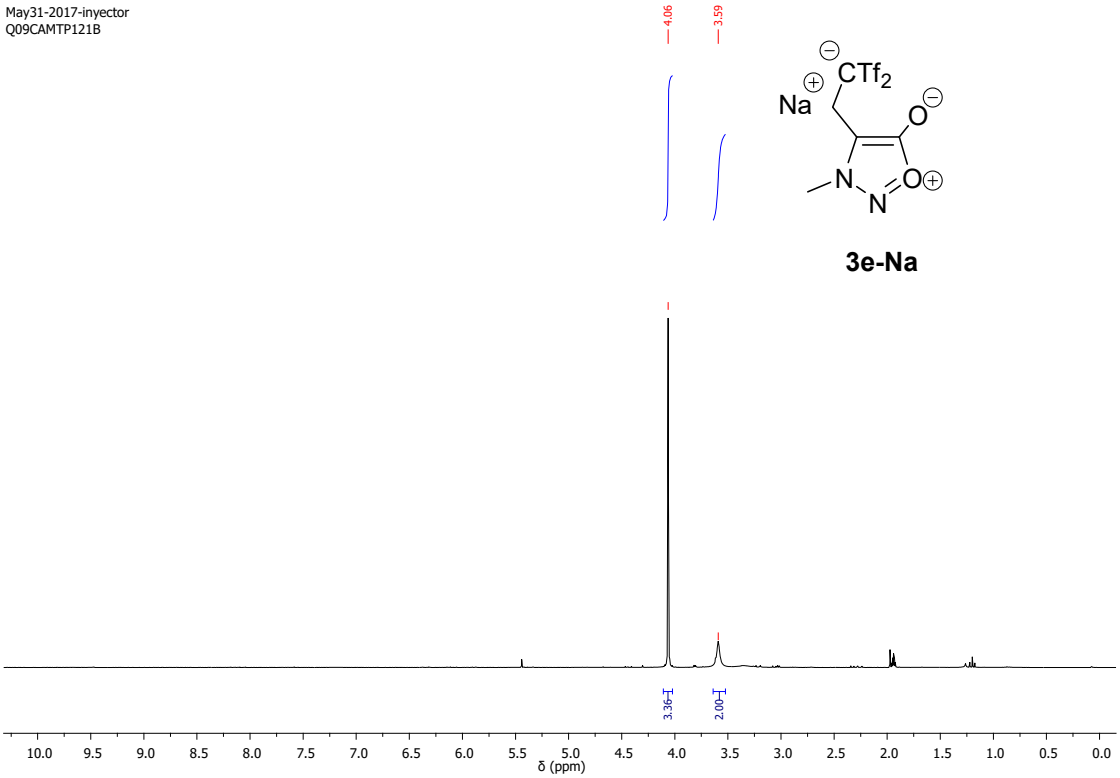
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



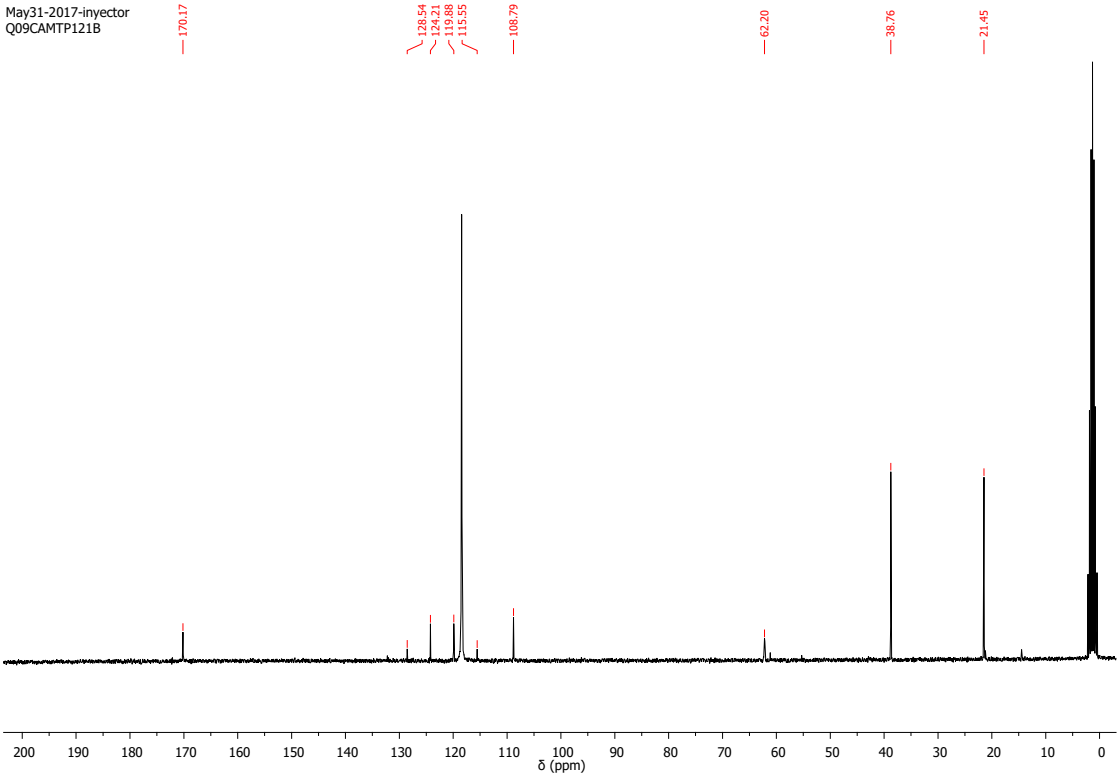
^{23}Na NMR (132 MHz, CD_3CN, 25 °C)



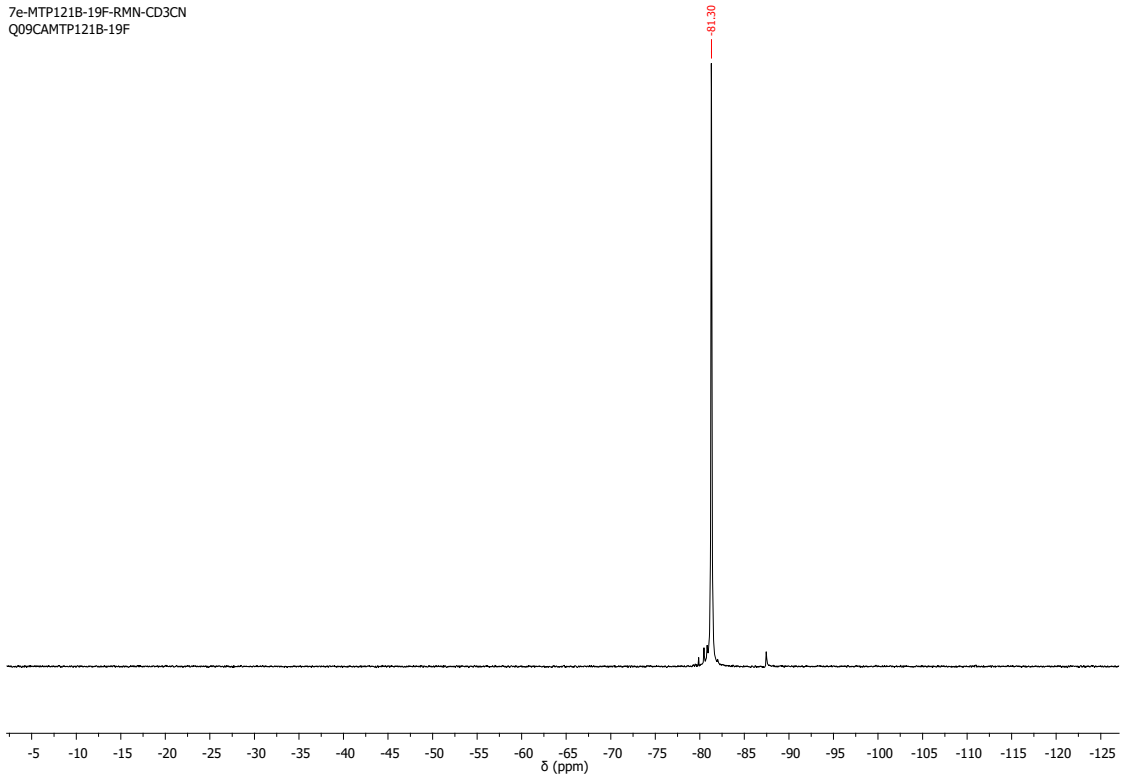
^{1}H-NMR (300 MHz, CD_3CN, 25 ºC)



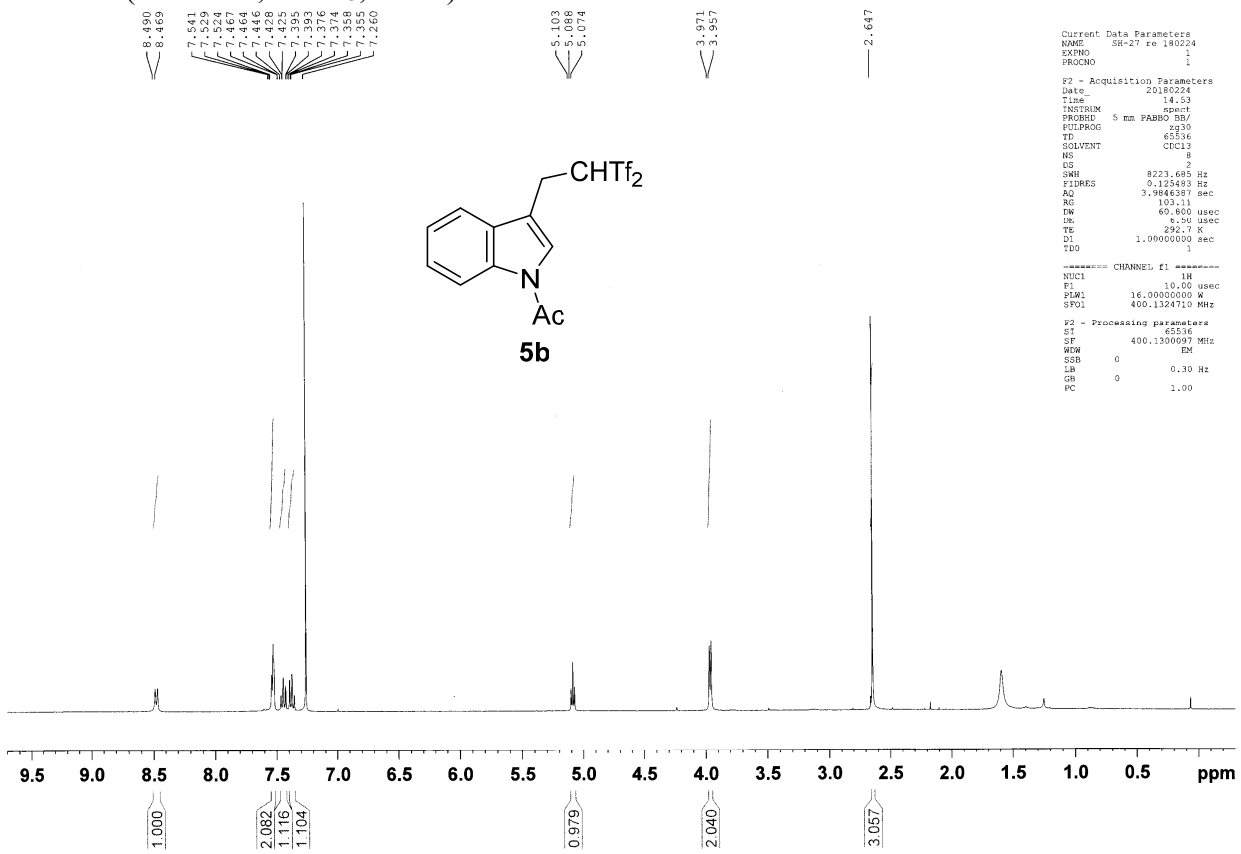
^{13}C NMR (75 MHz, CD_3CN, 25 ºC)



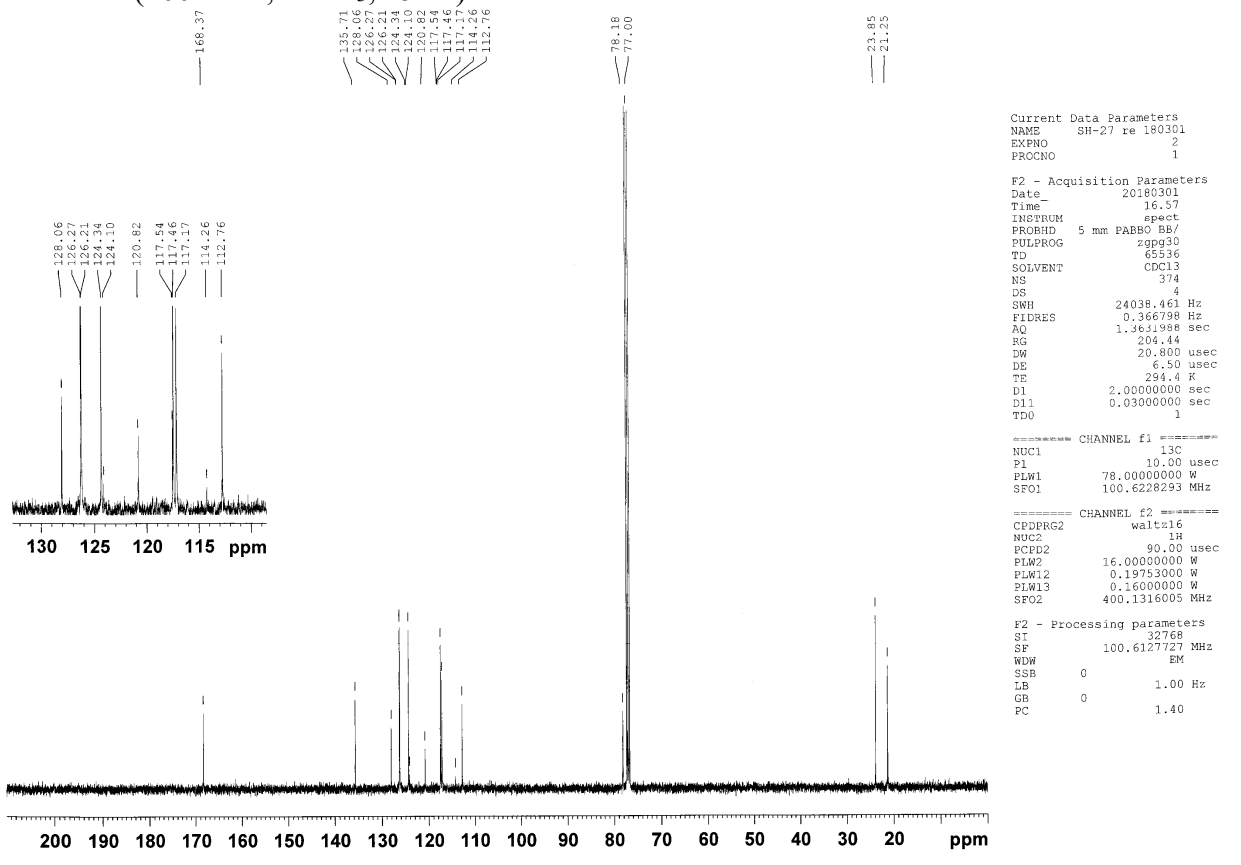
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



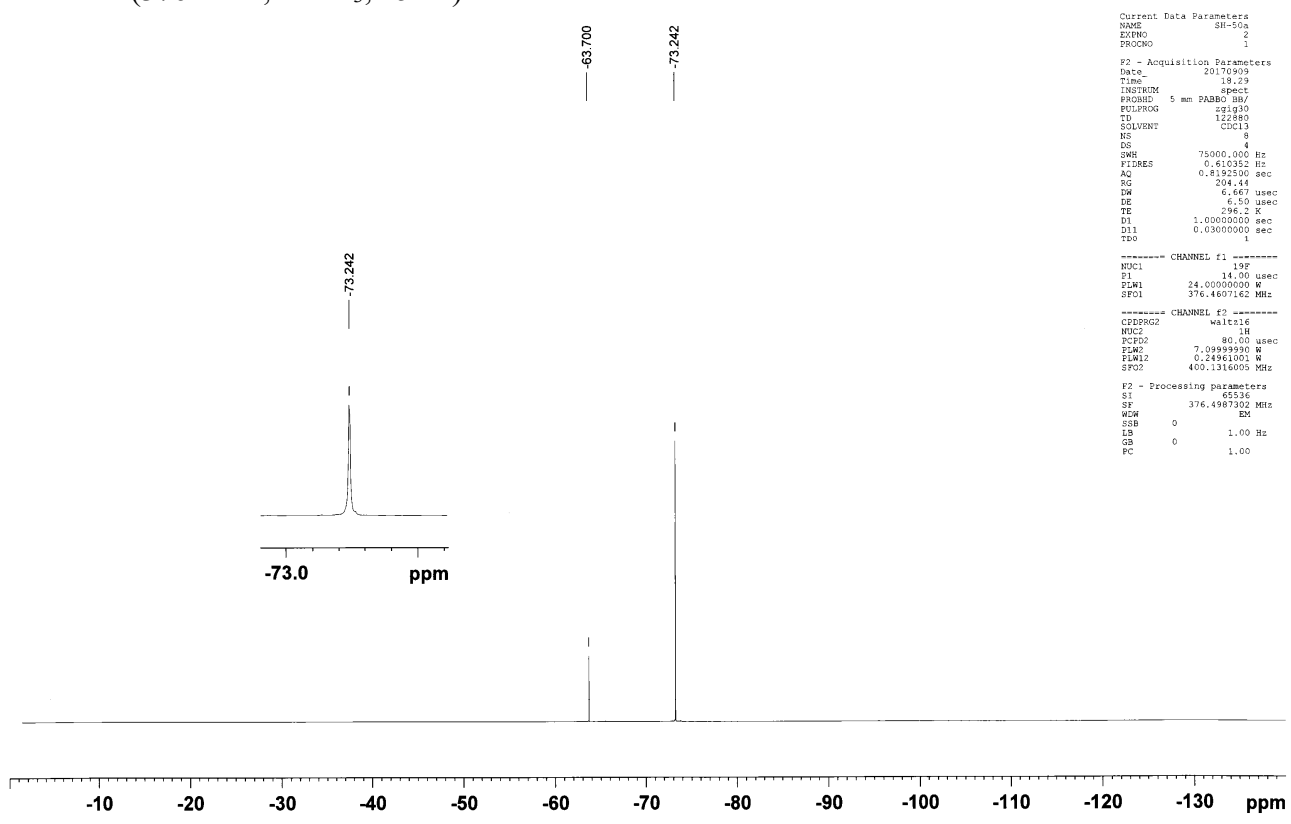
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC)



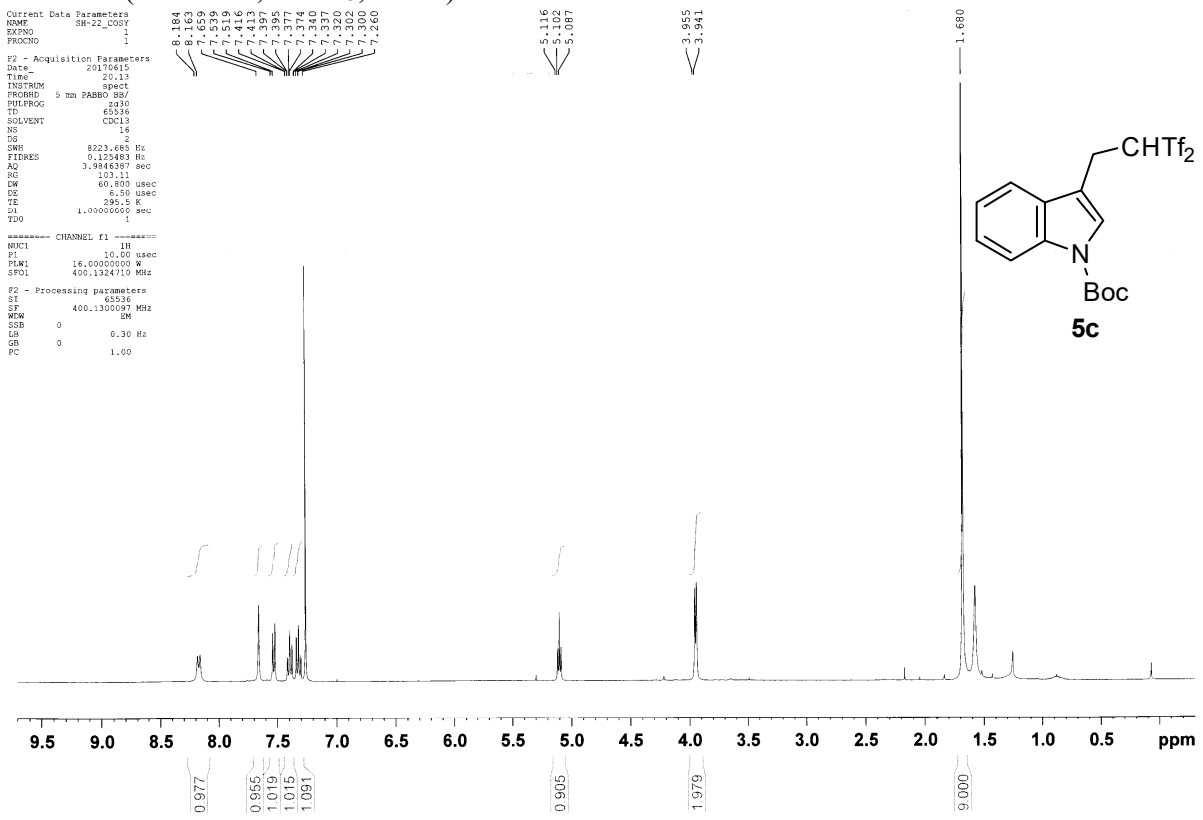
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



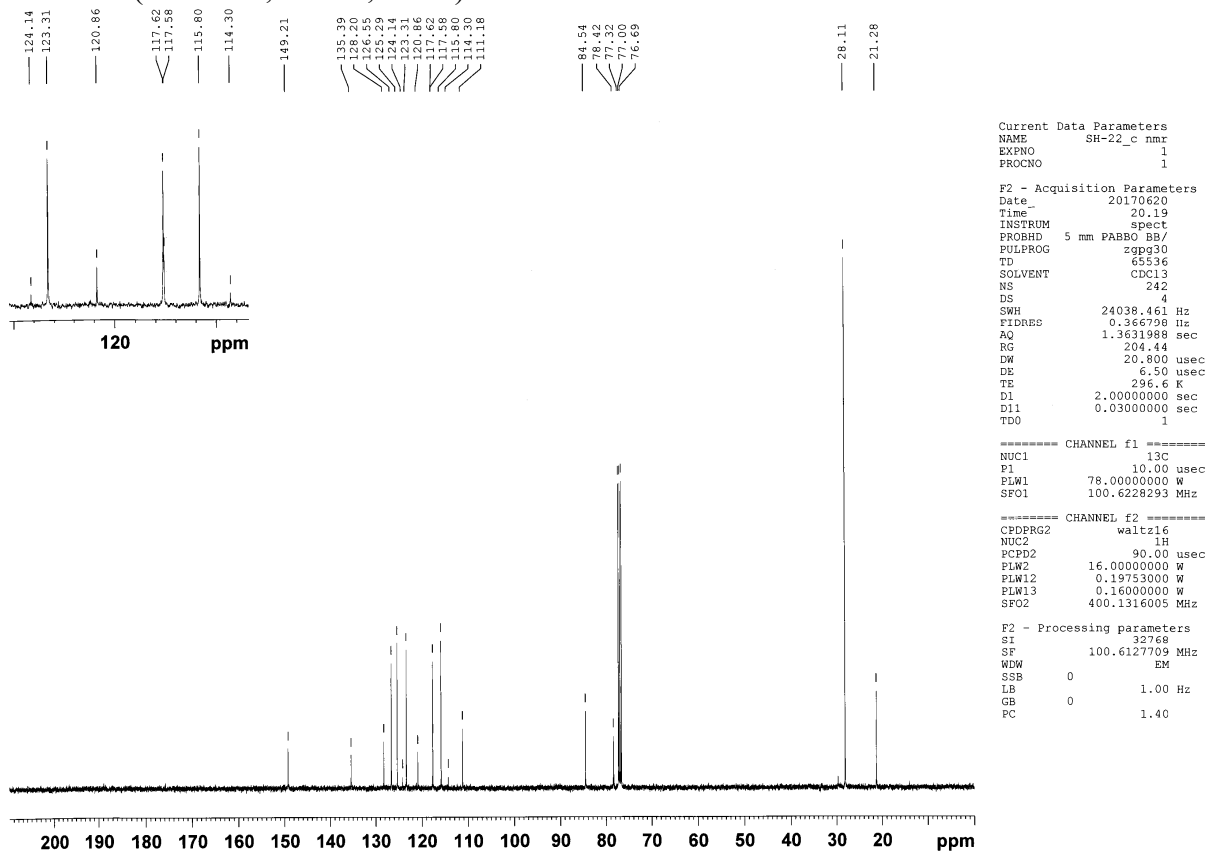
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)



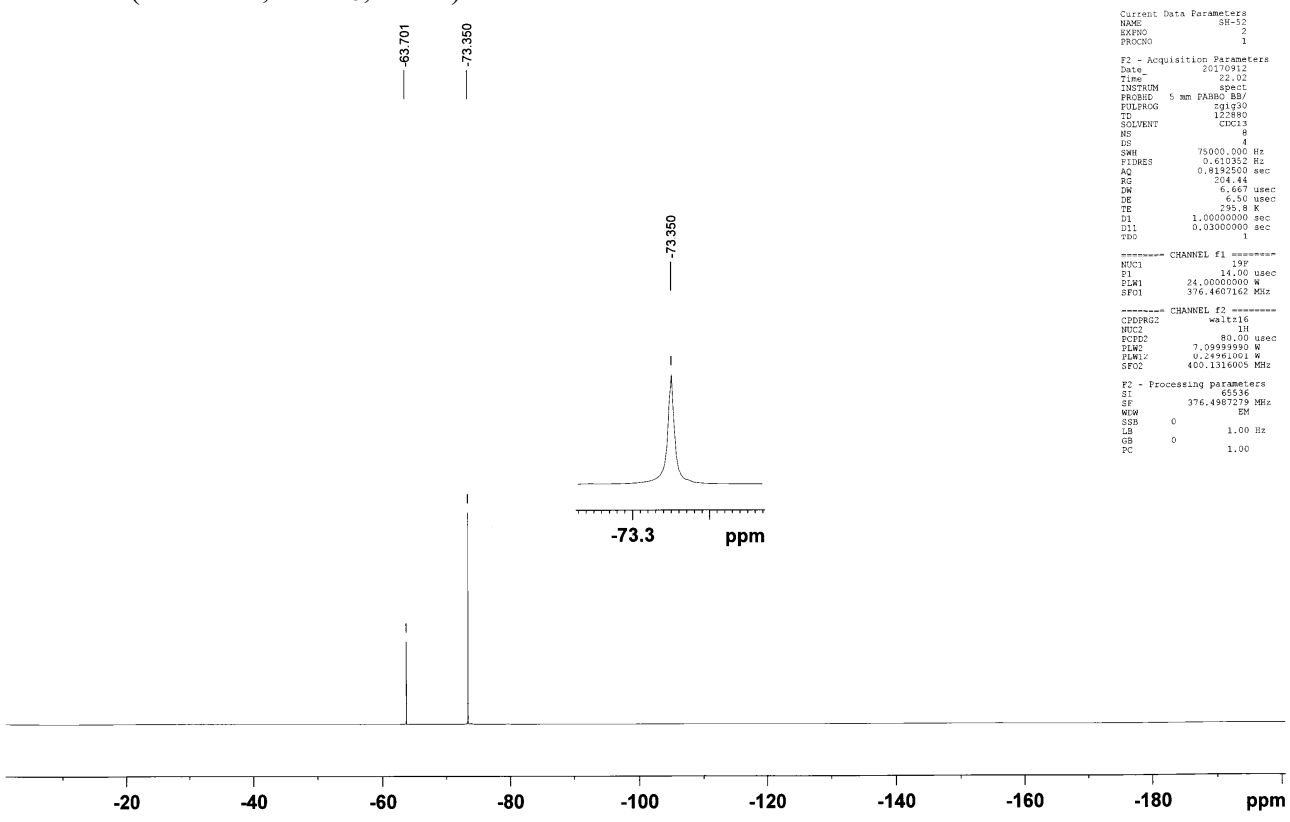
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC)



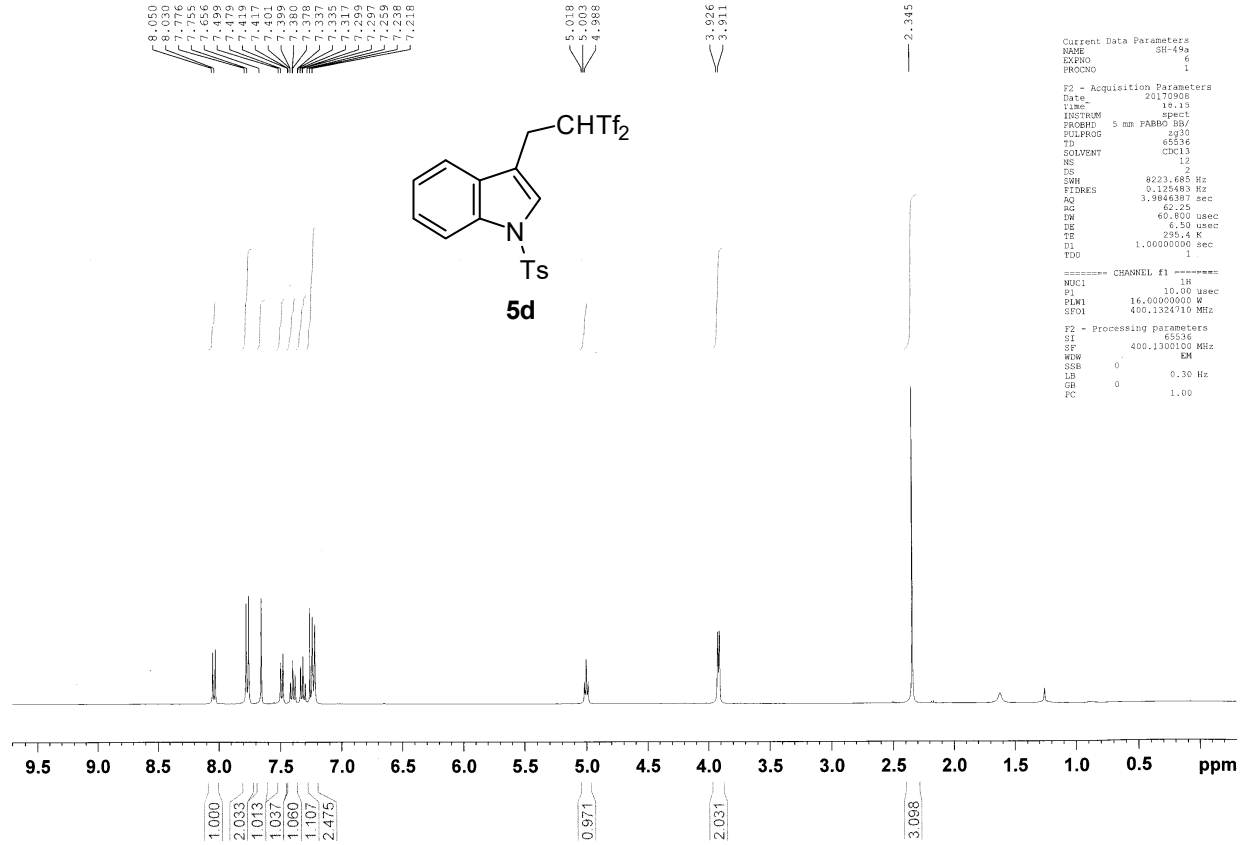
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



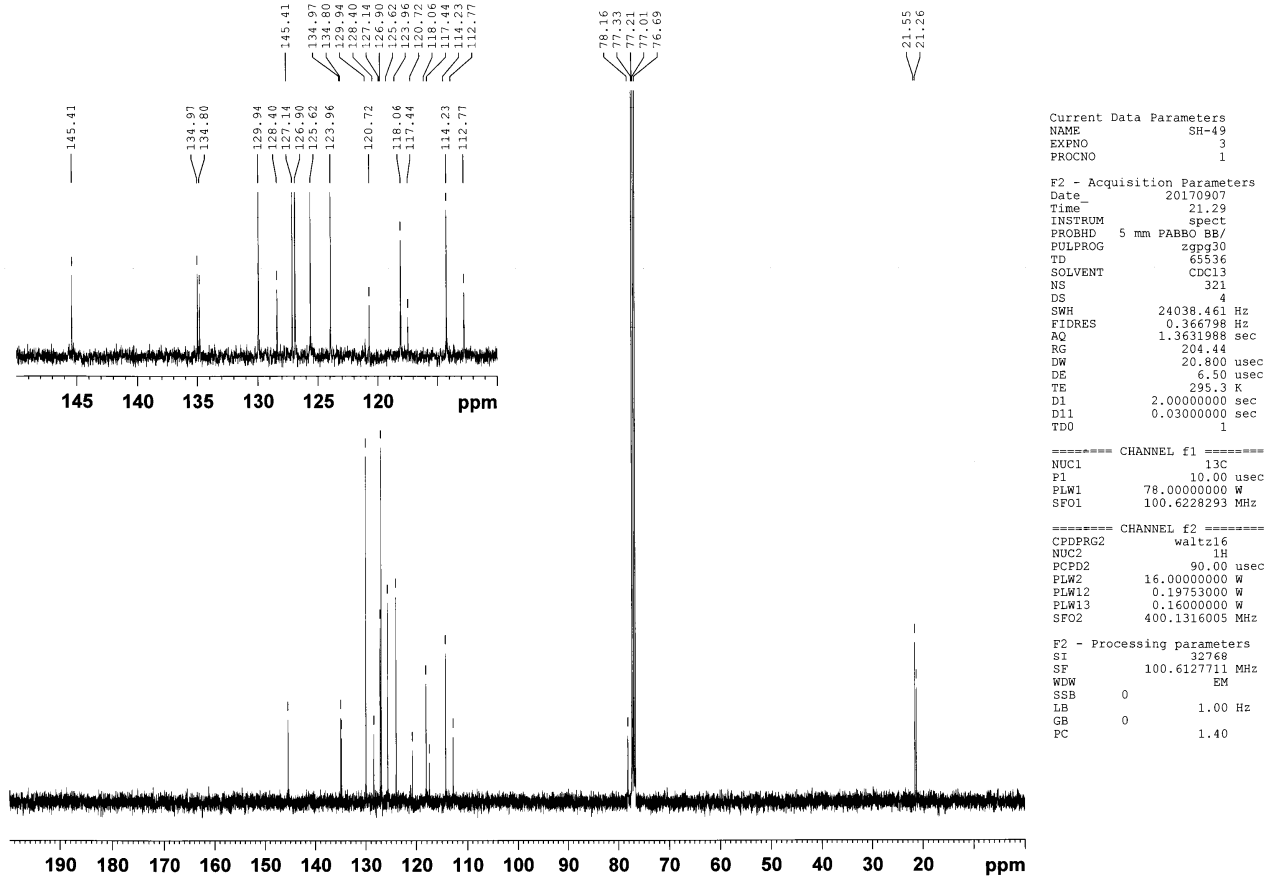
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)



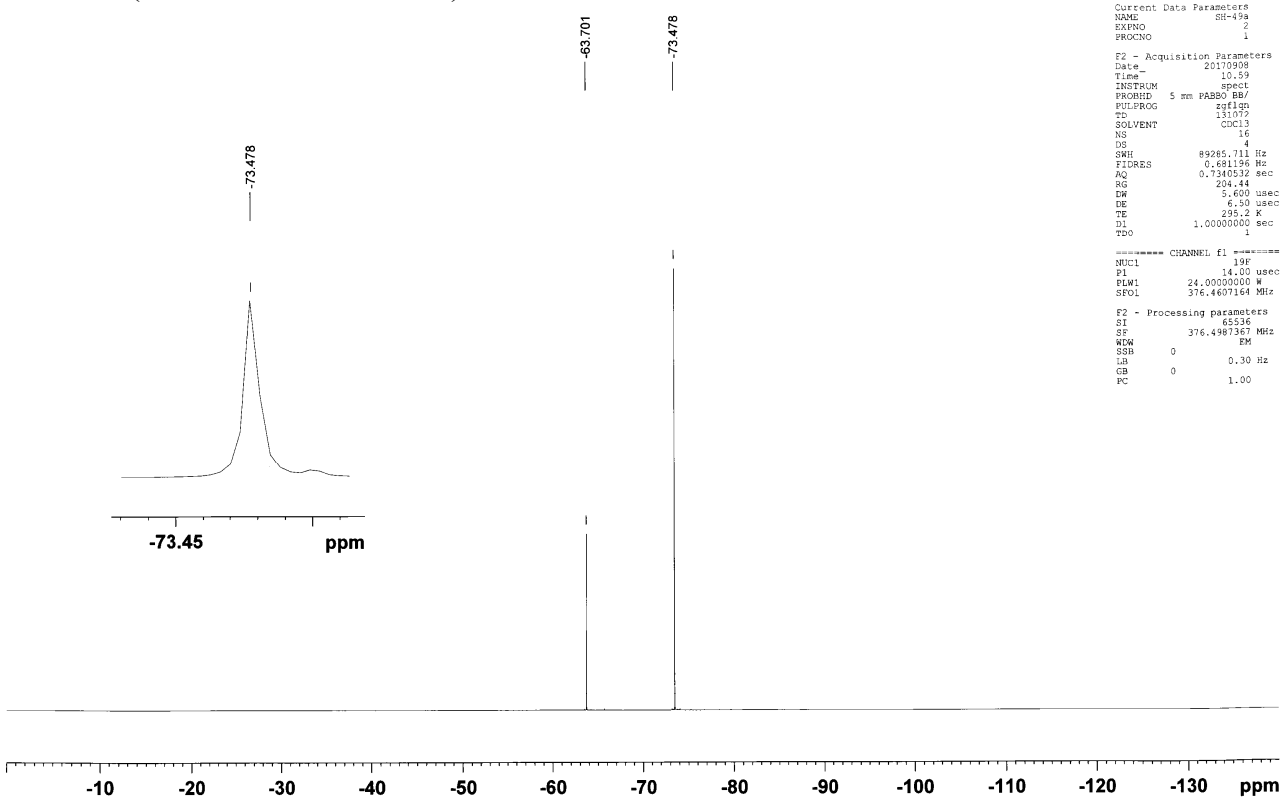
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC)



^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)

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Current Data Parameters
NAME                  SH-49a
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170908
Time                  10.59
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgflqn
TD                  131072
SOLVENT               CDCl3
NS                       16
DS                        4
SWH               89285.711 Hz
FIDRES             0.681196 Hz
AQ                0.7340532 sec
RG                    204.44
DW                  5.600 usec
DE                  6.50 usec
TE                  295.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     19F
P1                  14.00 usec
PLW1           24.00000000 W
SFO1           376.4607164 MHz

F2 - Processing parameters
SI                       65536
SF             376.4987367 MHz
WDW                        EM
SSB          0
LB                    0.30 Hz
GB           0
PC                        1.00
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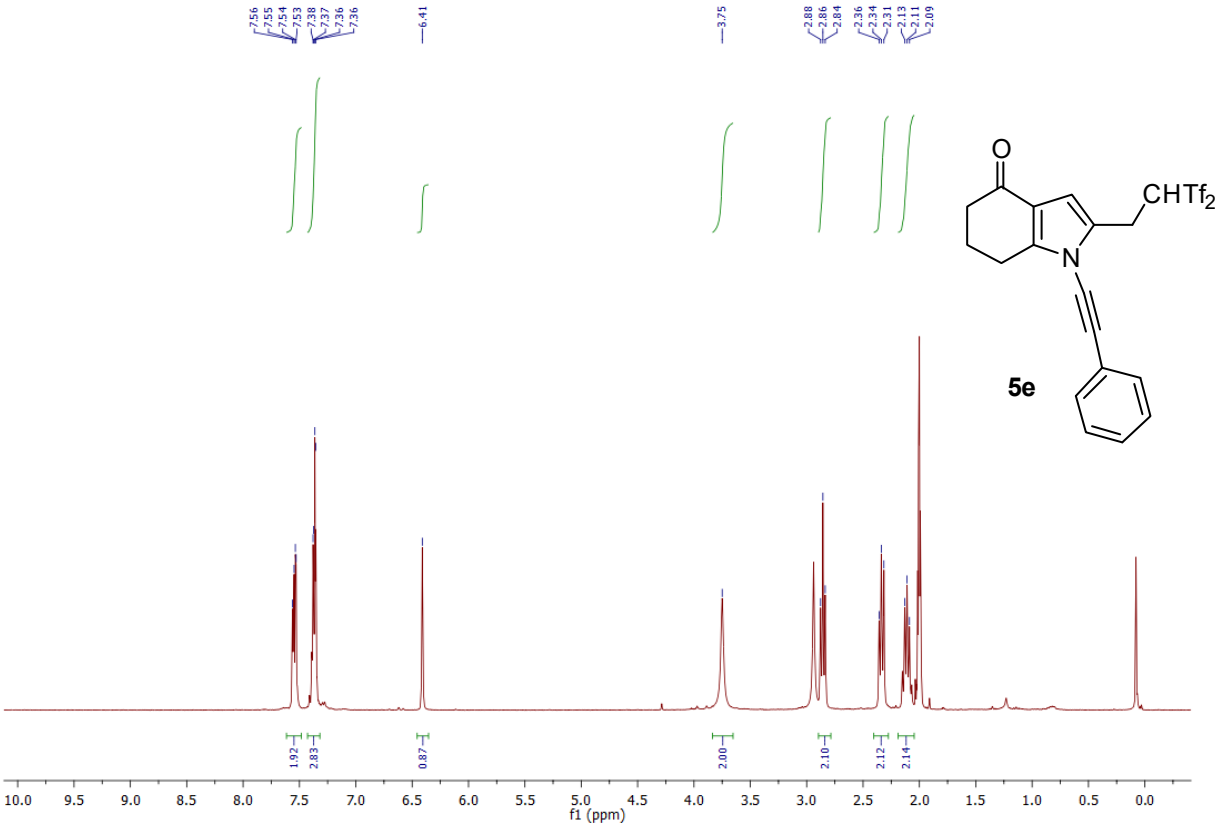
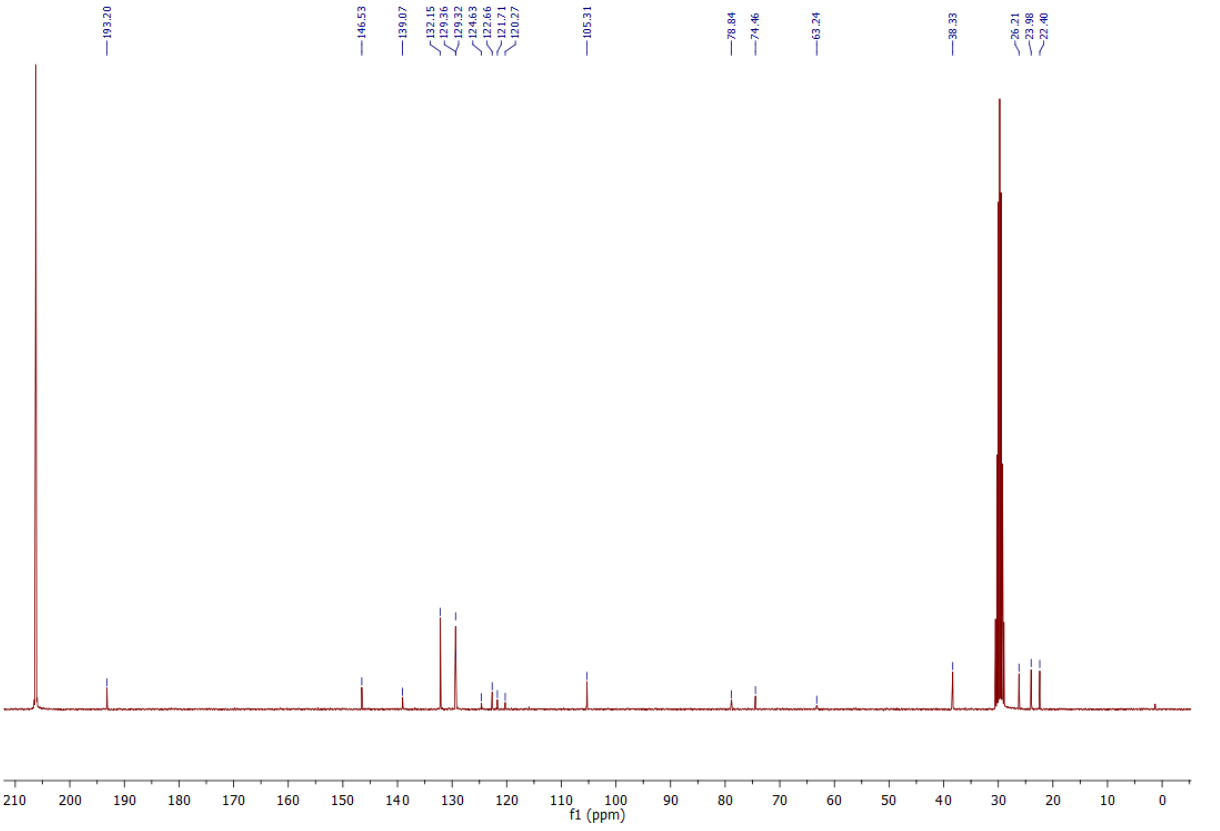
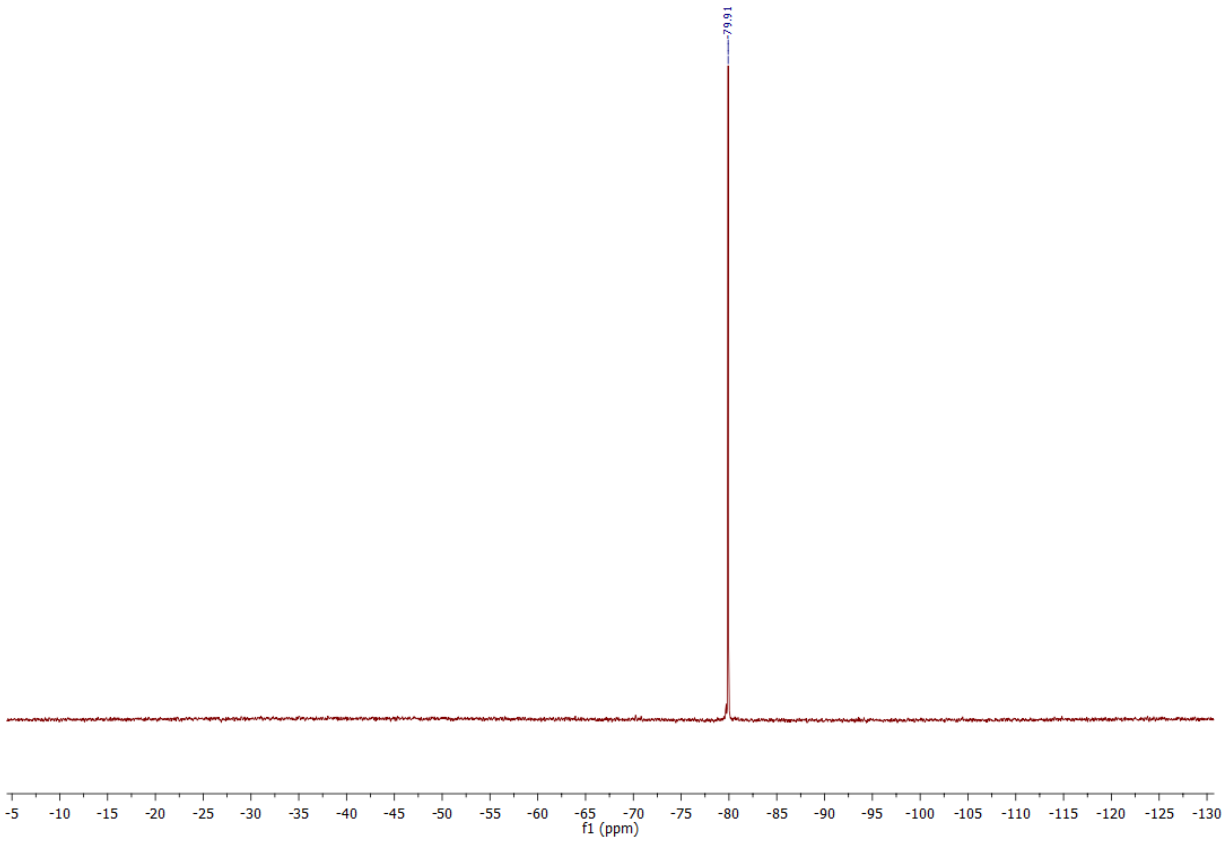
^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C)



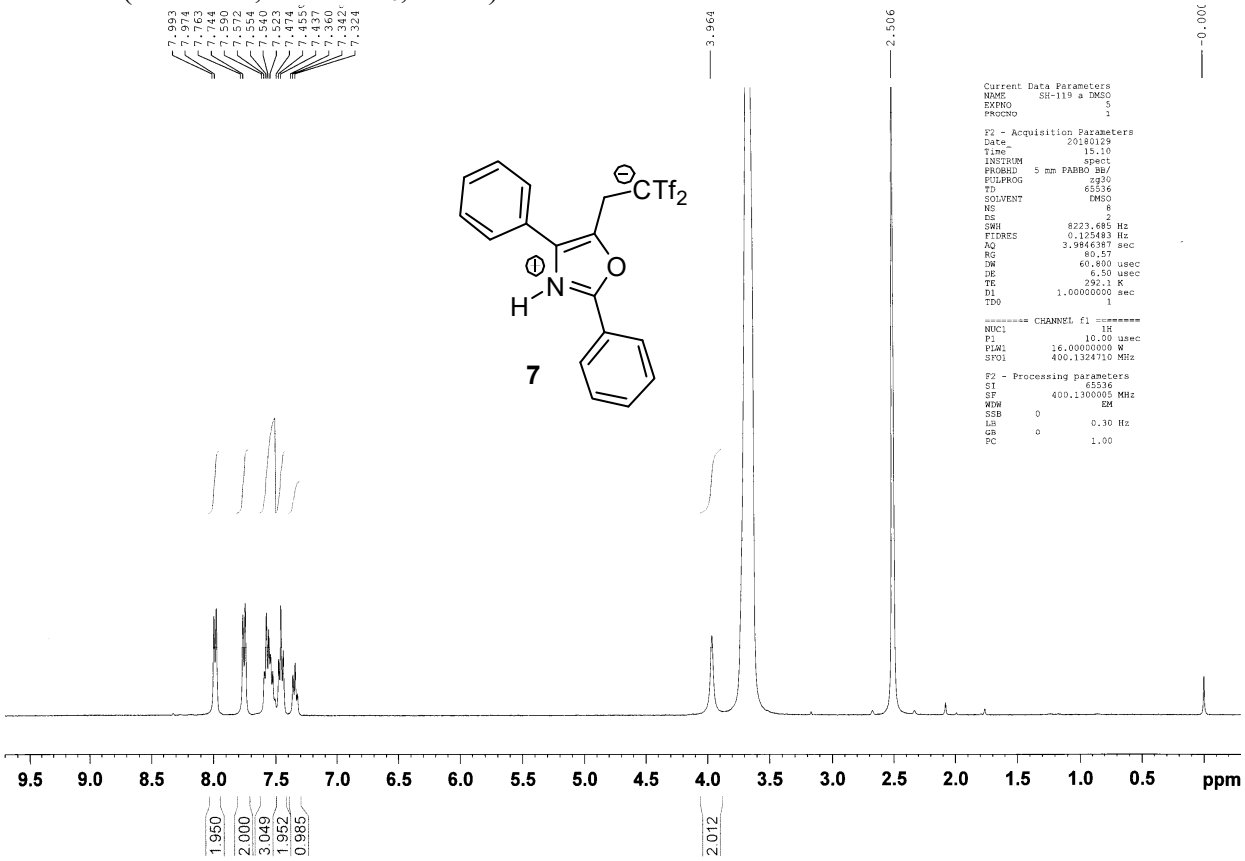
^{13}C NMR (75 MHz, CD_3COCD_3, 25 °C)



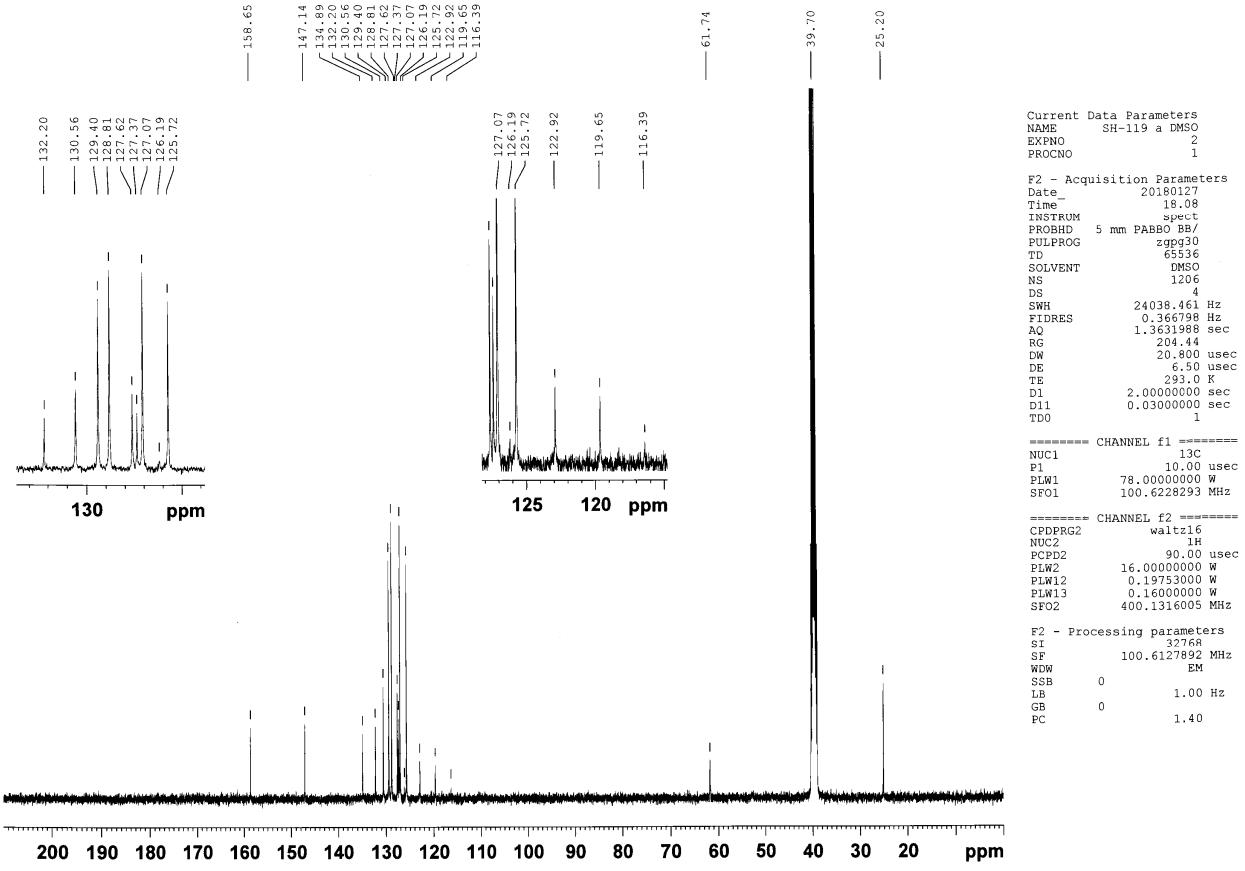
^{19}F NMR (132 MHz, CD_3COCD_3, 25 °C)



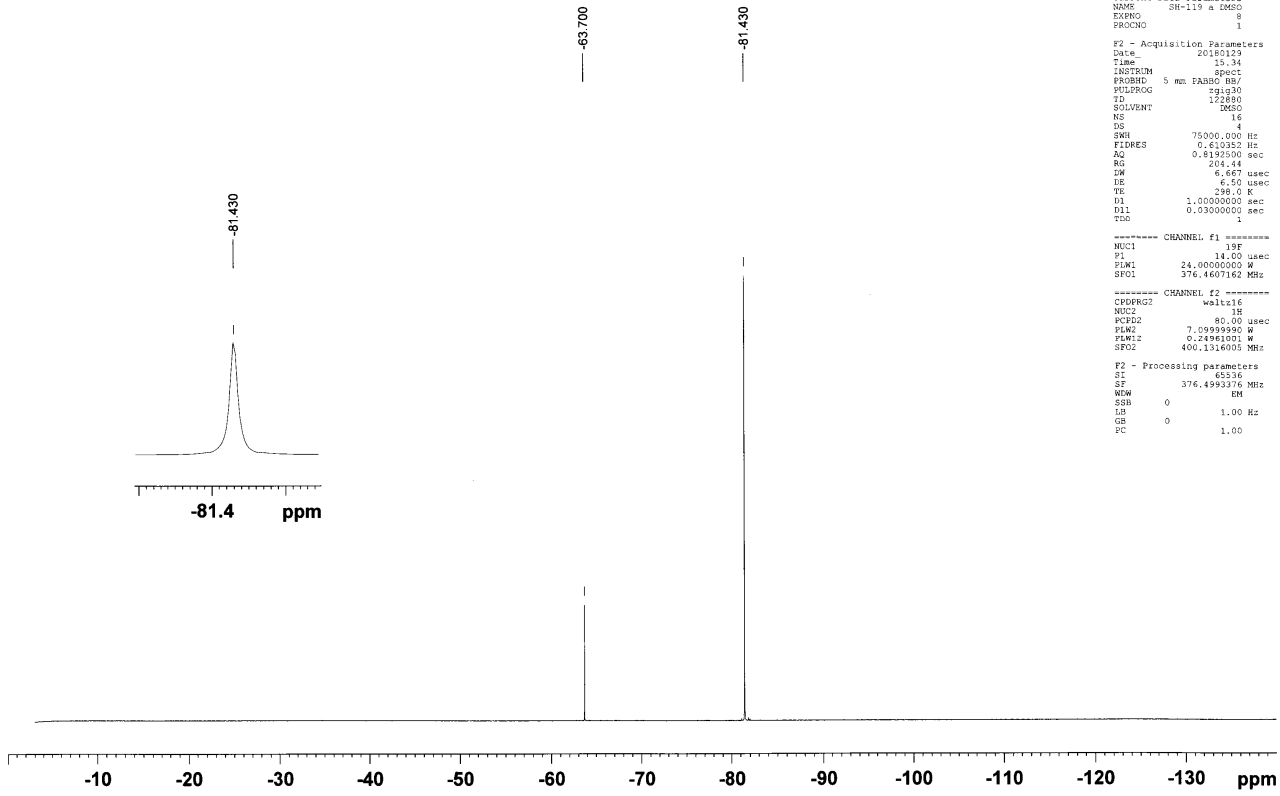
^{1}H NMR (400 MHz, DMSO-d_6, 25 °C)



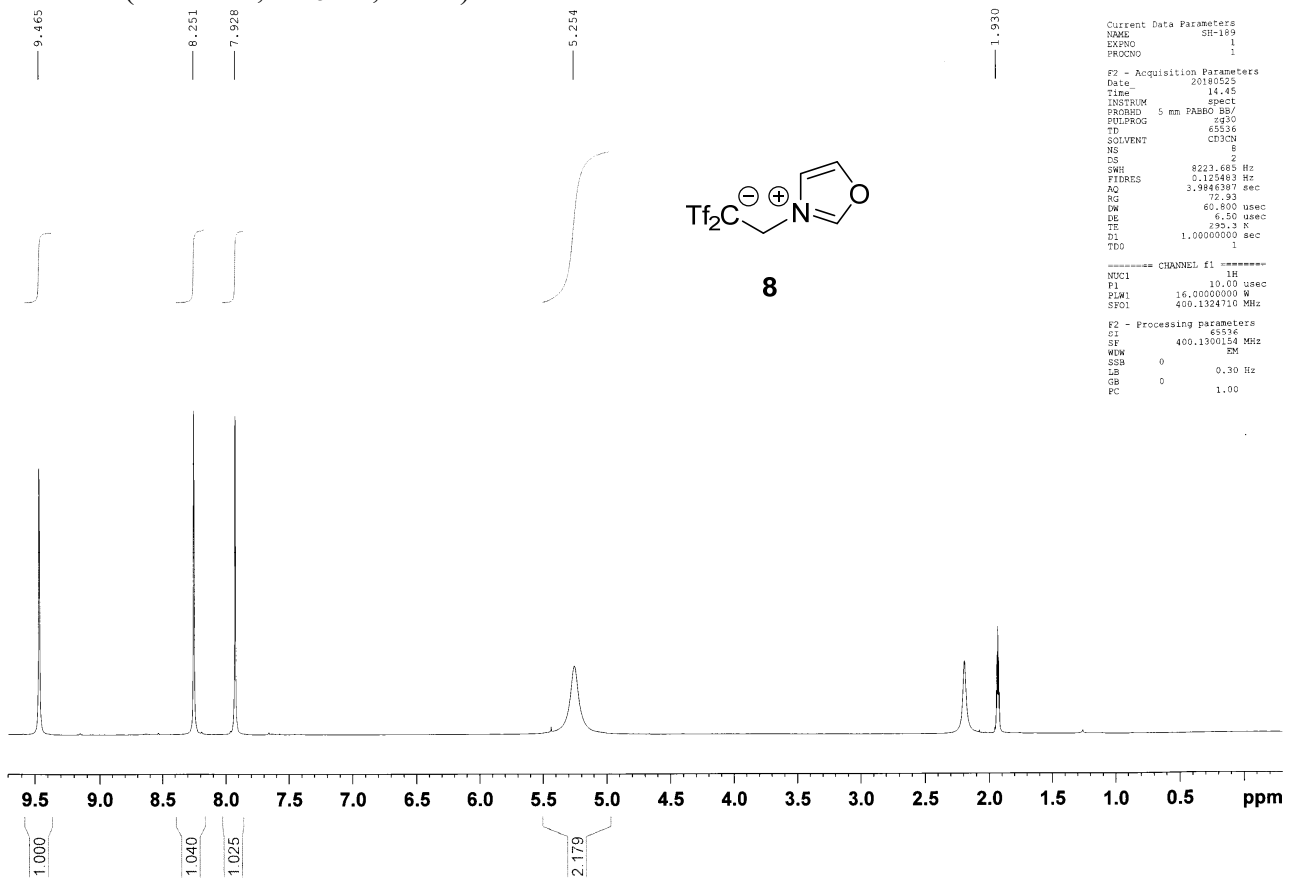
^{13}C NMR (100 MHz, DMSO-d_6, 25 °C)



^{19}F NMR (376 MHz, DMSO-d_6, 25 °C)

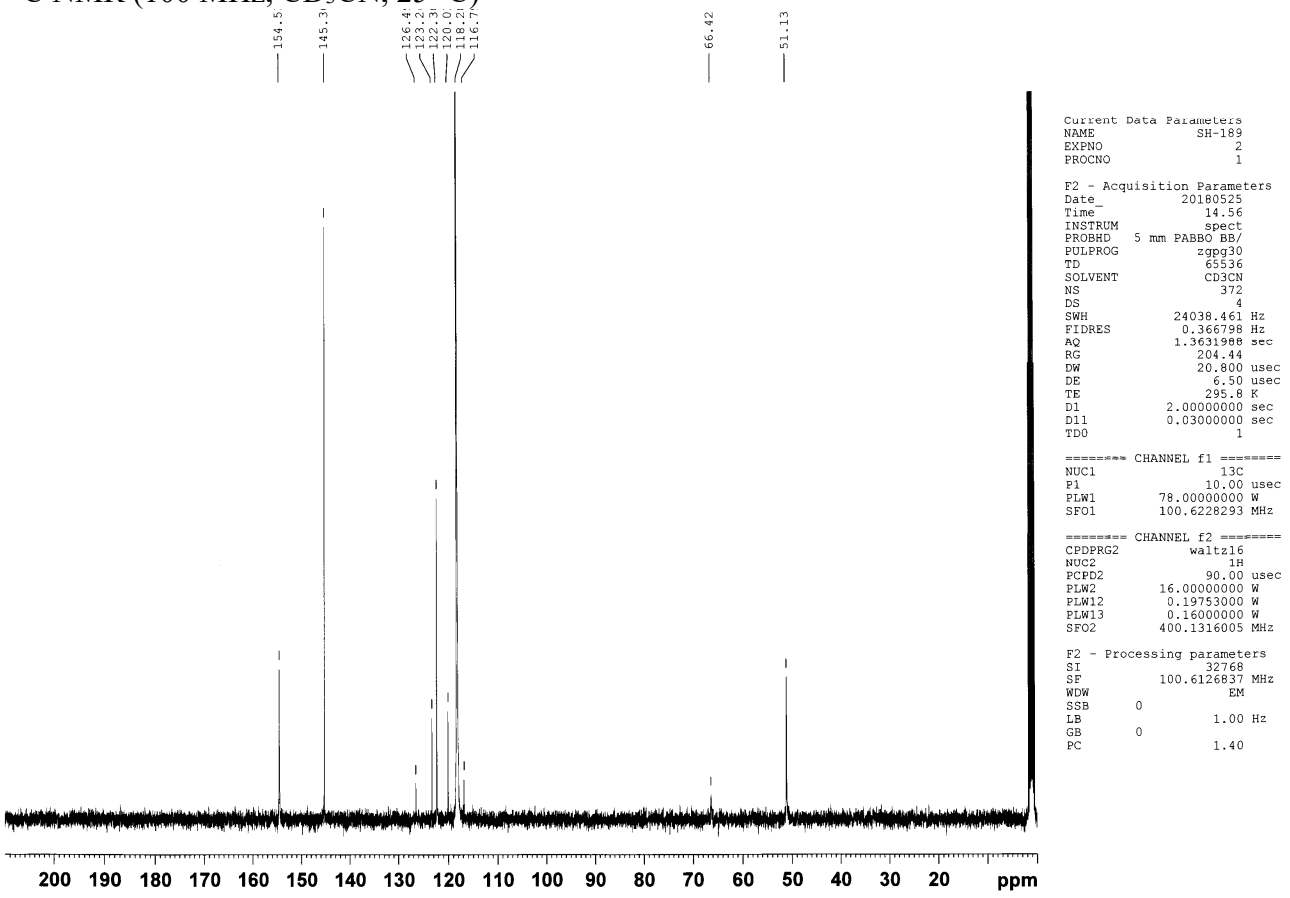


^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)

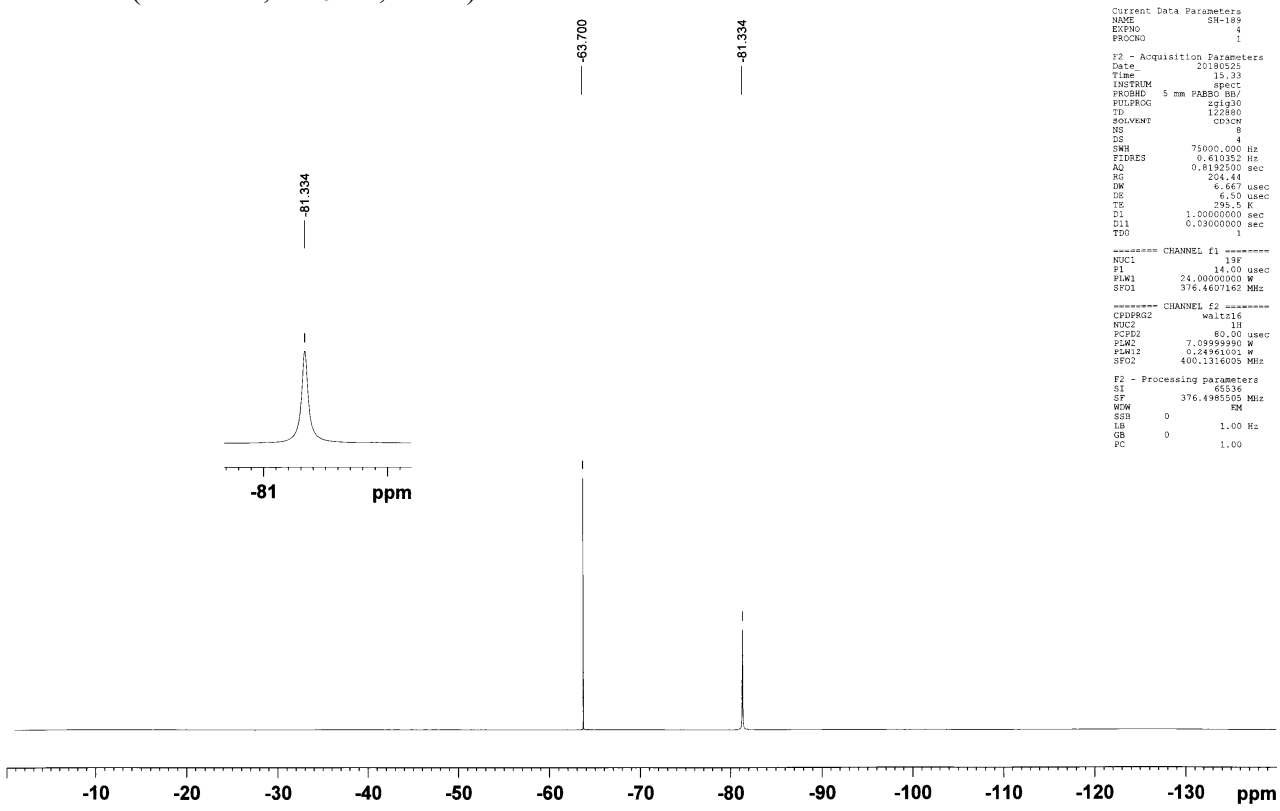


8

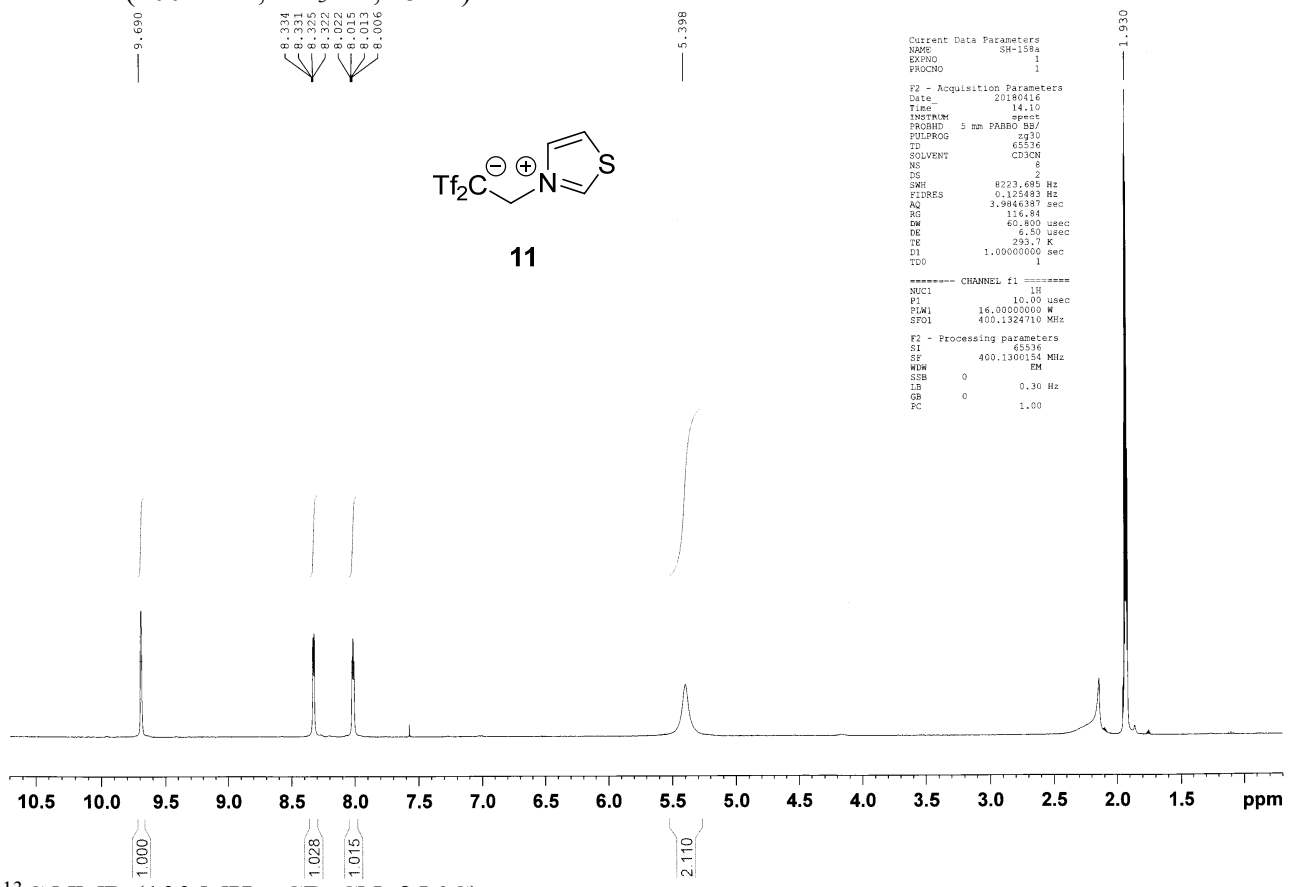
^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



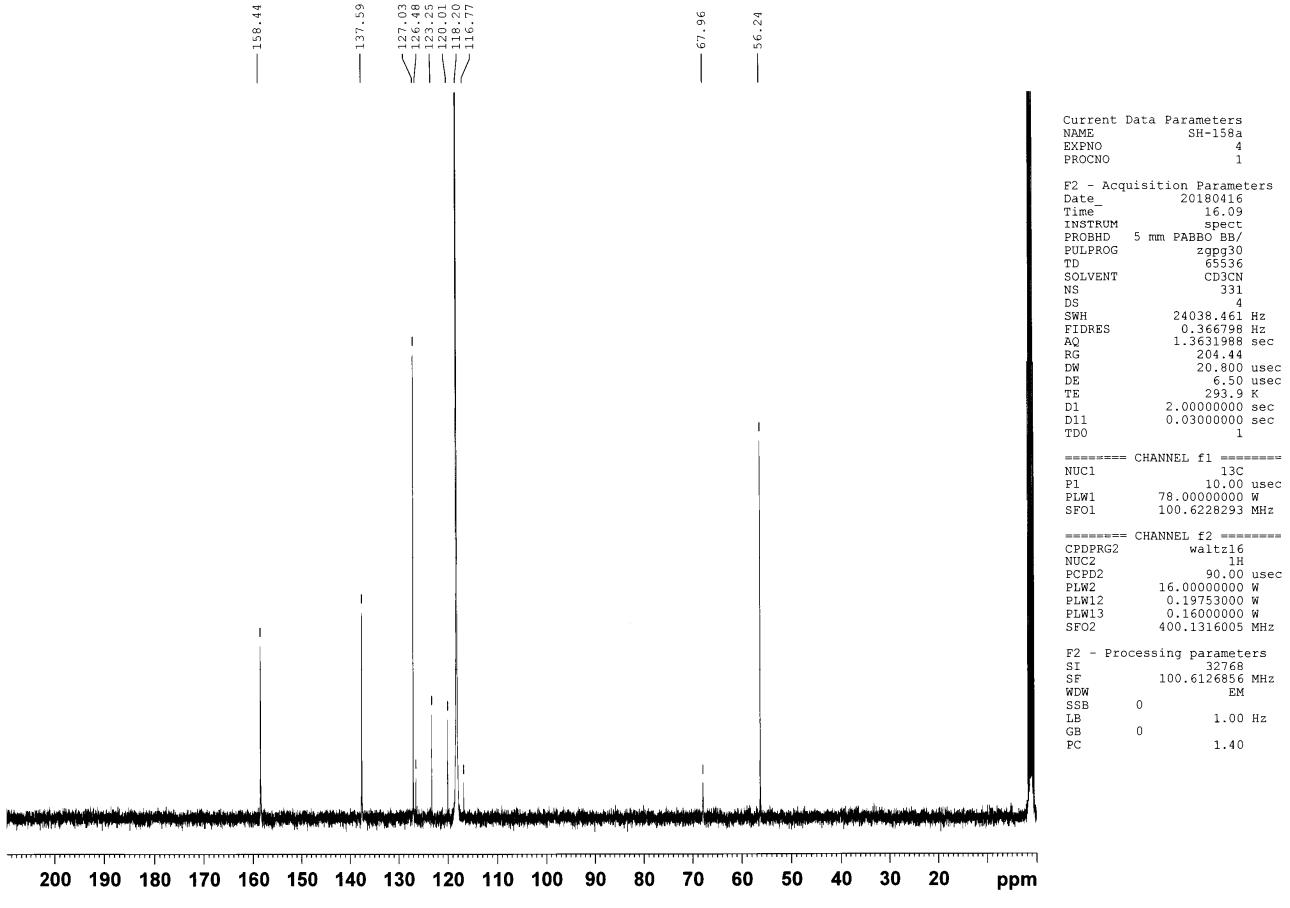
^{19}F NMR (376 MHz, CD_3CN, 25 °C)



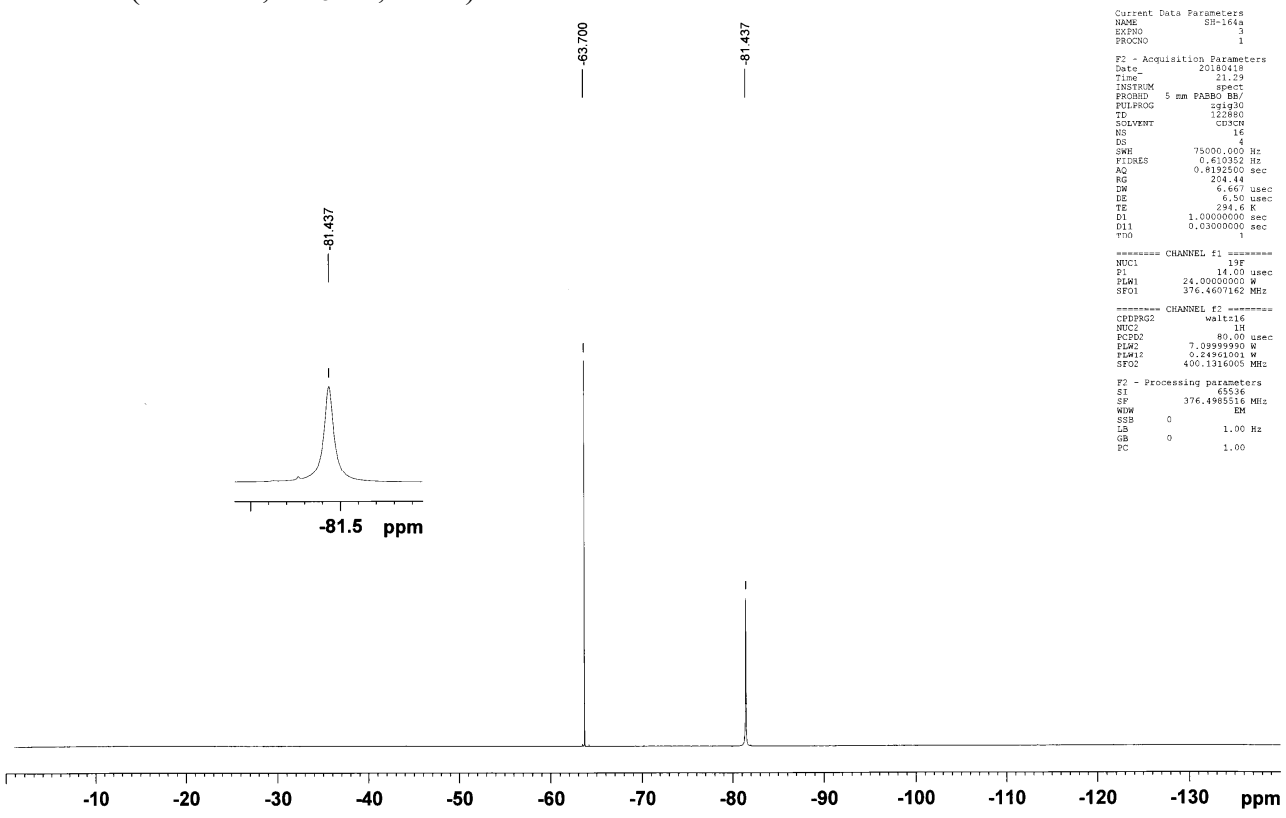
^{1}H NMR (400 MHz, CD_3CN, 25 ºC)



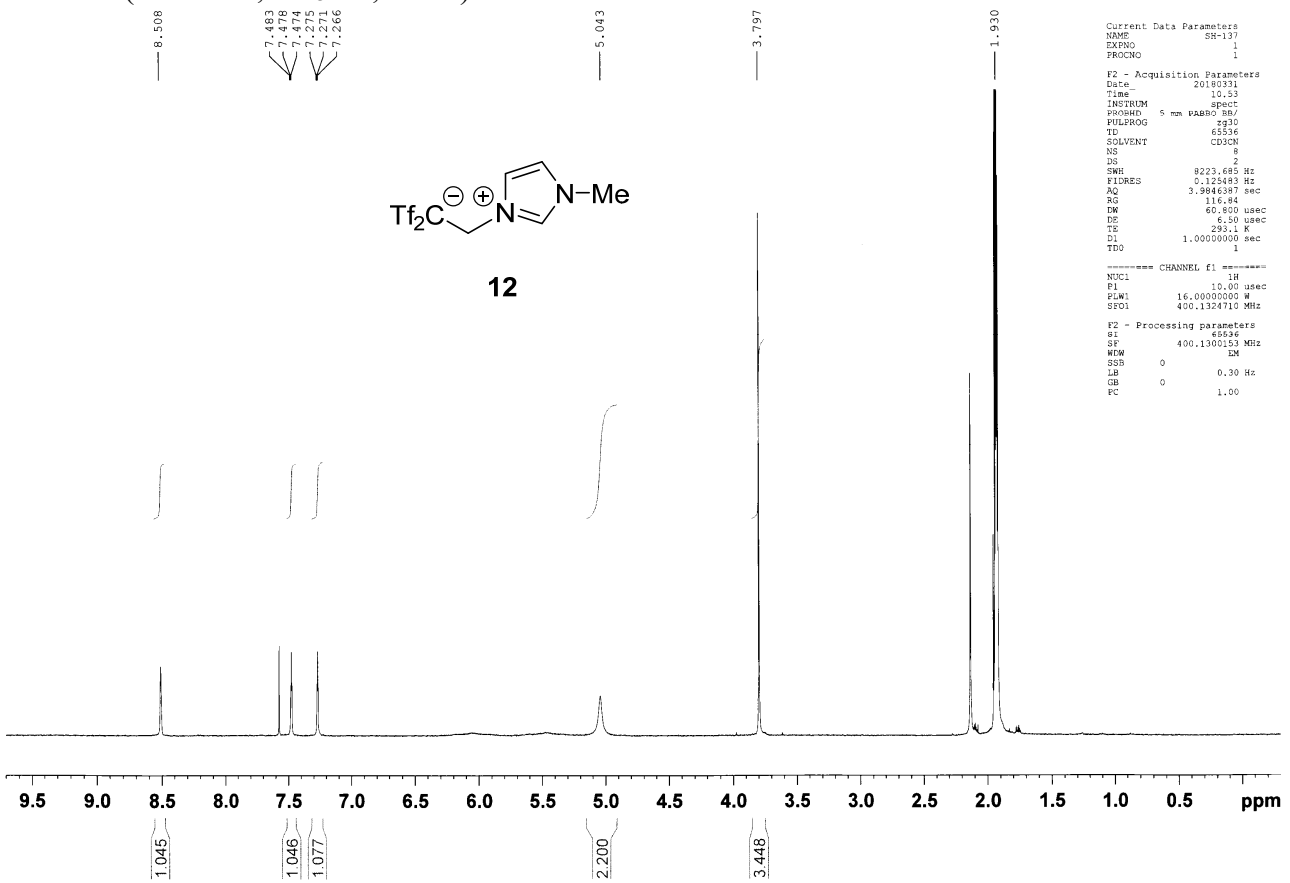
^{13}C NMR (100 MHz, CD_3CN, 25 ºC)



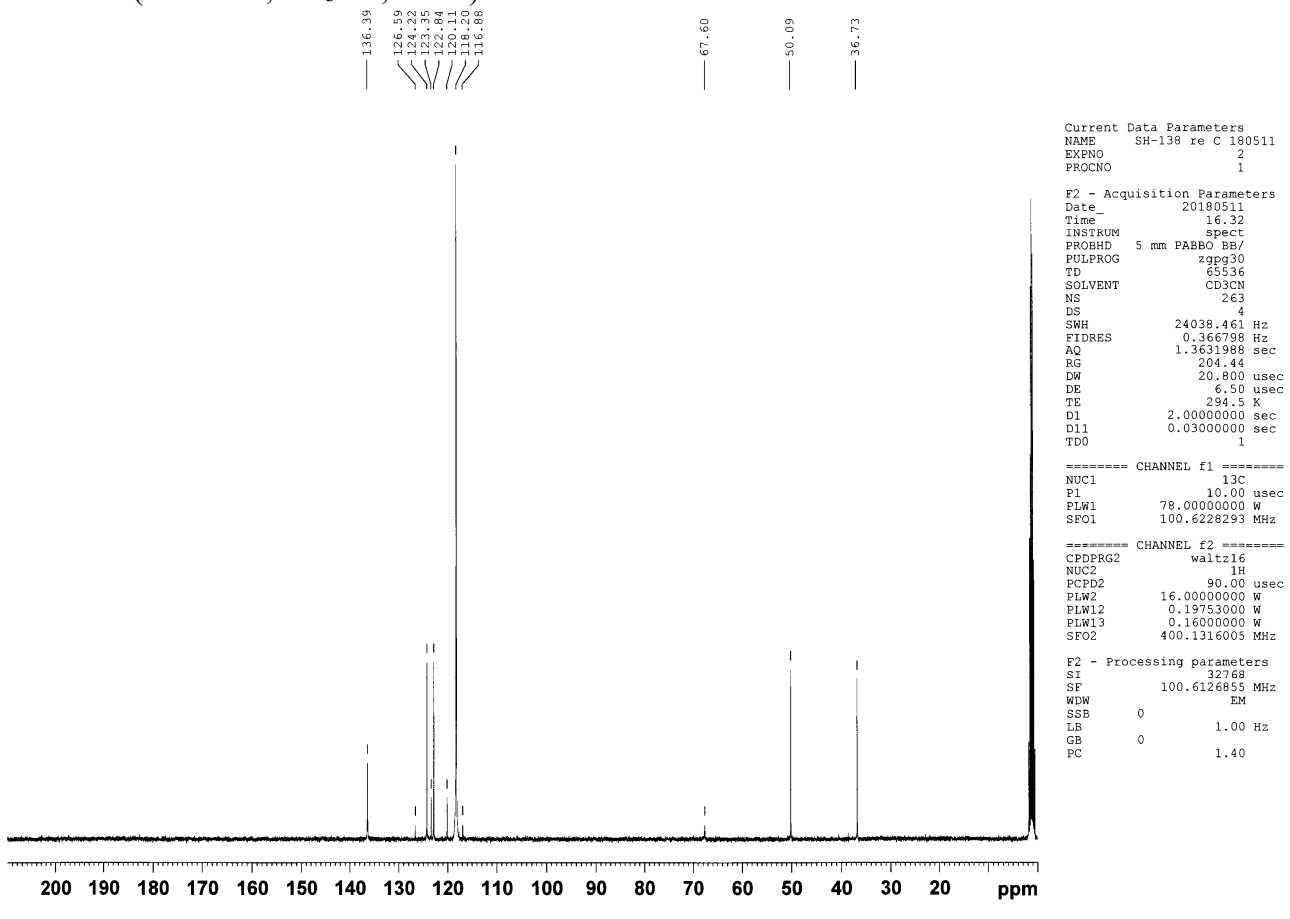
^{19}F NMR (376 MHz, CD_3CN, 25 °C)



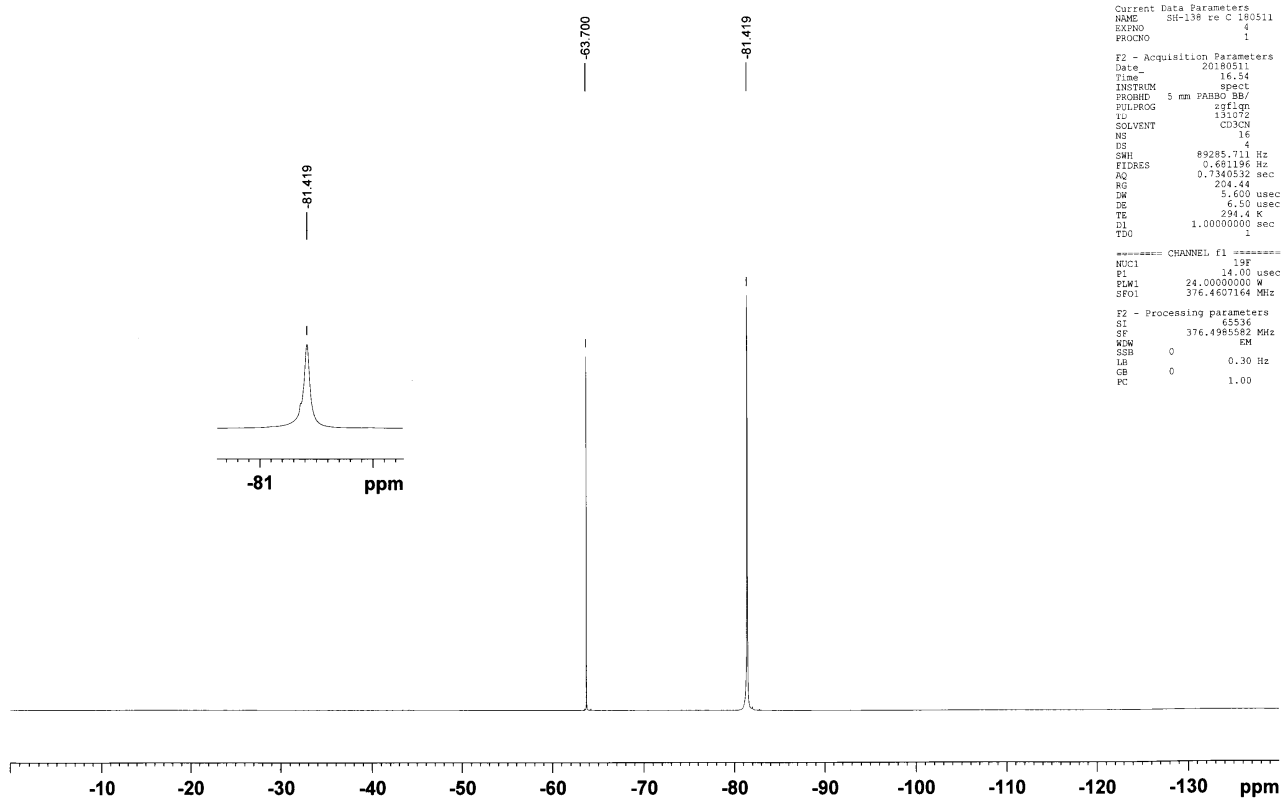
^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)



^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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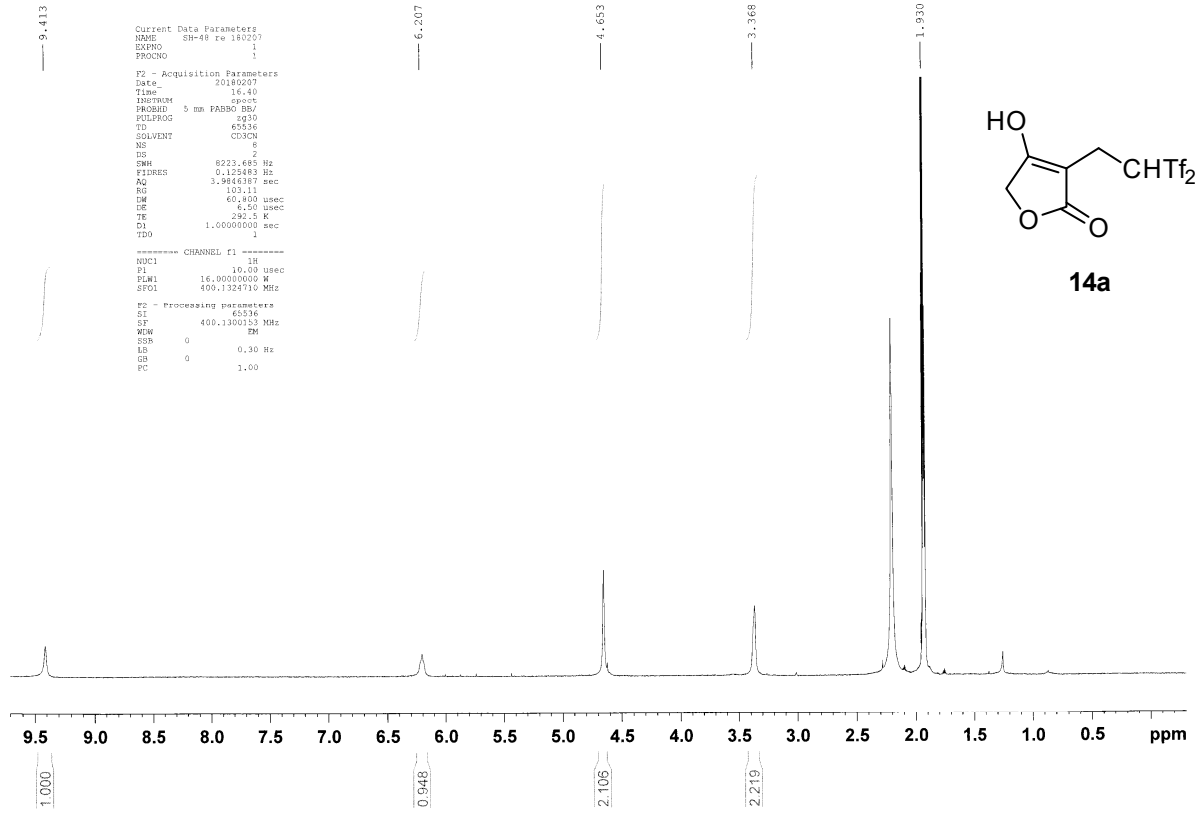
Current Data Parameters
NAME      SH-138 re C 180511
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180511
Time               16.54
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT            CD3CN
NS                 16
DS                 4
SWH                89285.711 Hz
FIDRES             0.681196 Hz
AQ                 0.7340532 sec
RG                 204.44
DW                 5.600 usec
DE                 6.50 usec
TE                 294.4 K
D1                 1.00000000 sec
TD0                1

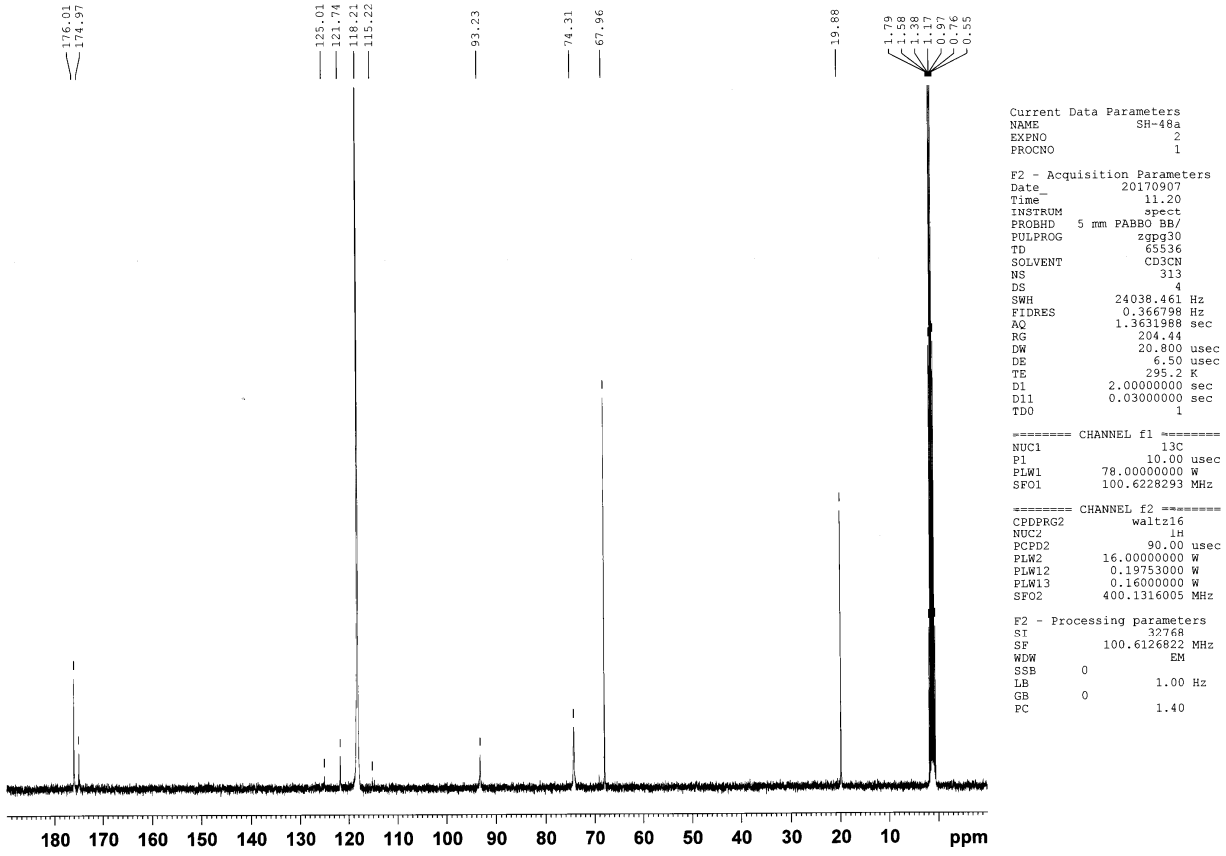
======== CHANNEL f1 ========
NUC1               19F
P1                 14.00 usec
PLW1               24.00000000 W
SFO1               376.4607164 MHz

F2 - Processing parameters
SI                 65536
SF                 376.4965582 MHz
WDW                EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)



^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)




```
Current Data Parameters
NAME                  SH-48a
EXPNO                      2
PROCNO                     1

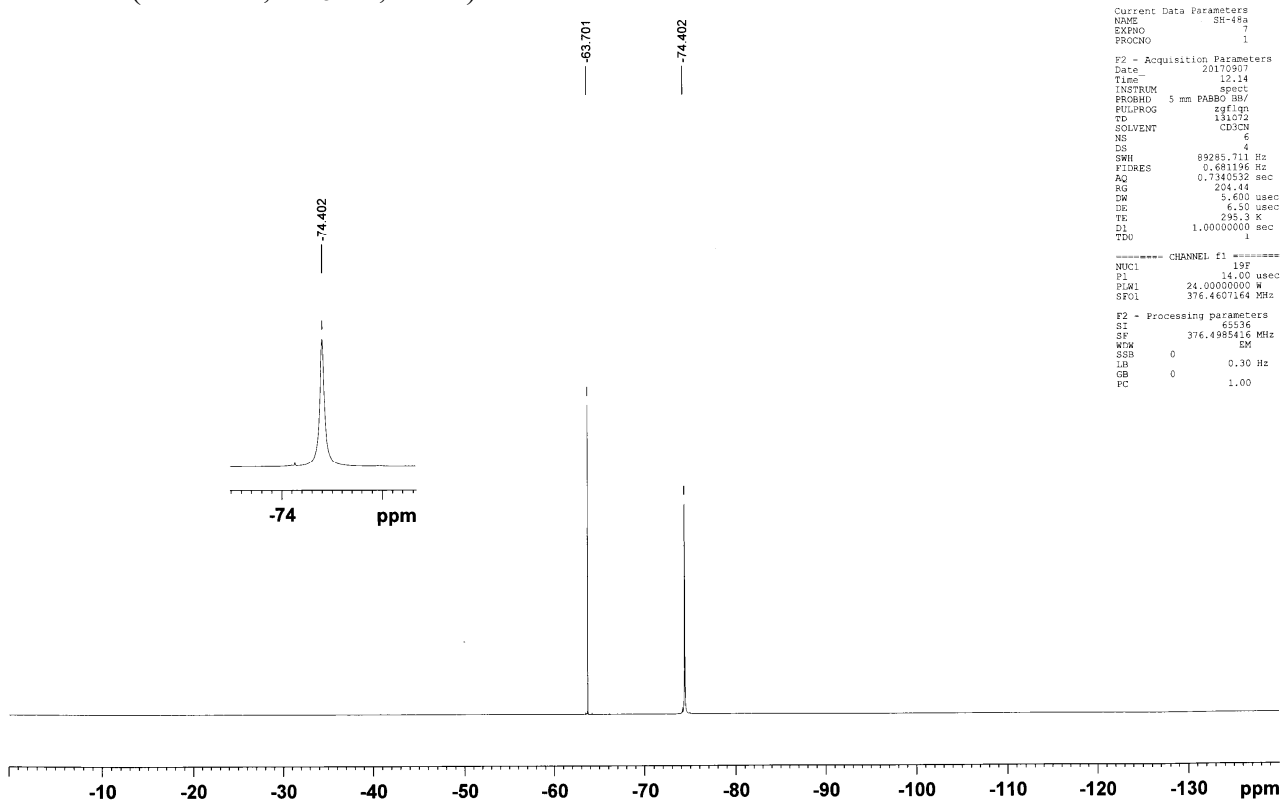
F2 - Acquisition Parameters
Date_               20170907
Time                   11.20
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                      65536
SOLVENT                 CD3CN
NS                        313
DS                          4
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631988 sec
RG                        204.44
DW                       20.800 usec
DE                        6.50 usec
TE                       295.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PLW1                78.00000000 W
SFO1               100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PLW2                16.00000000 W
PLW12                0.19753000 W
PLW13                0.16000000 W
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6126822 MHz
WDW                           EM
SSB                0
LB                         1.00 Hz
GB                 0
PC                         1.40
```

^{19}F NMR (376 MHz, CD_3CN, 25 °C)



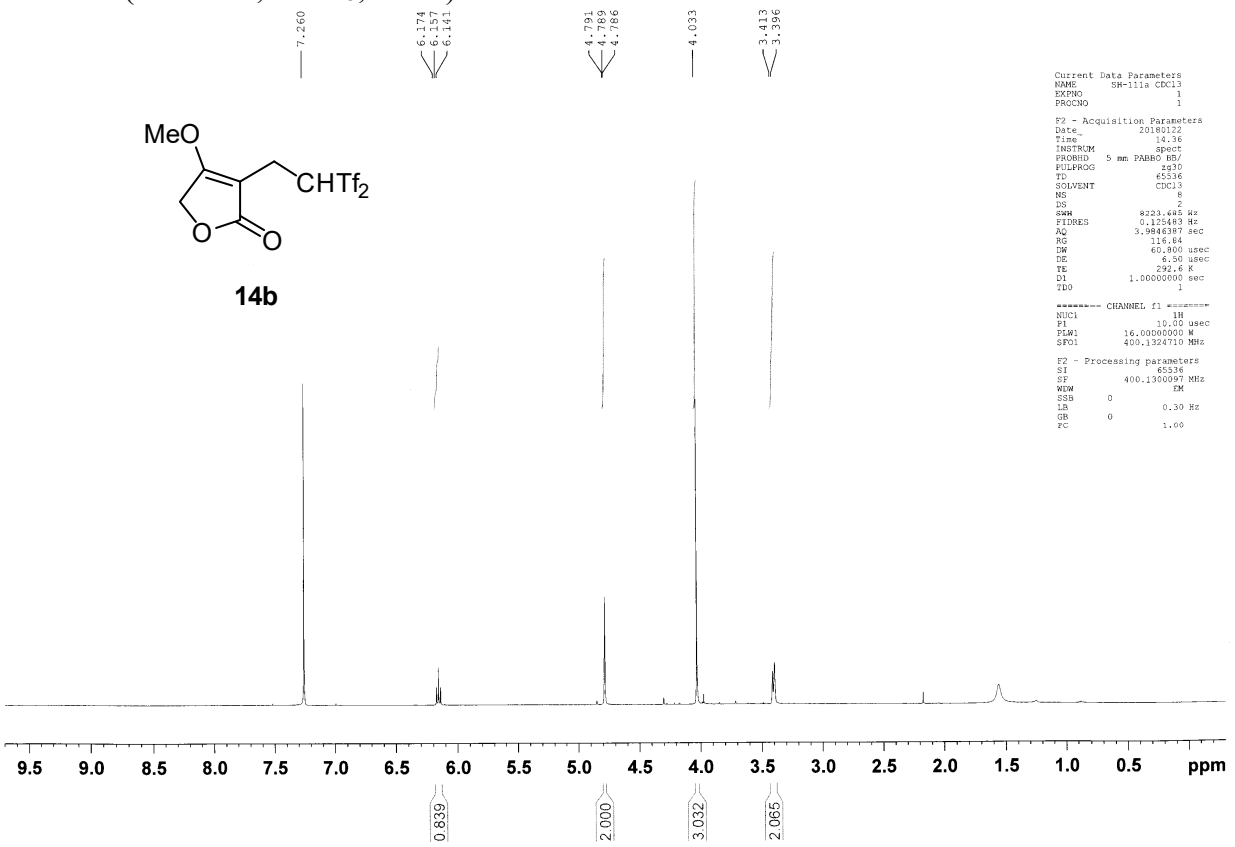

```
Current Data Parameters
NAME                  SH-48a
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170907
Time                  12.14
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgflqn
TD                  131072
SOLVENT               CD3CN
NS                         6
DS                         4
SWH               89285.711 Hz
FIDRES             0.681196 Hz
AQ                 0.7340532 sec
RG                    204.44
DW                   5.600 usec
DE                   6.50 usec
TE                   295.3 K
D1                1.00000000 sec
TD0                        1

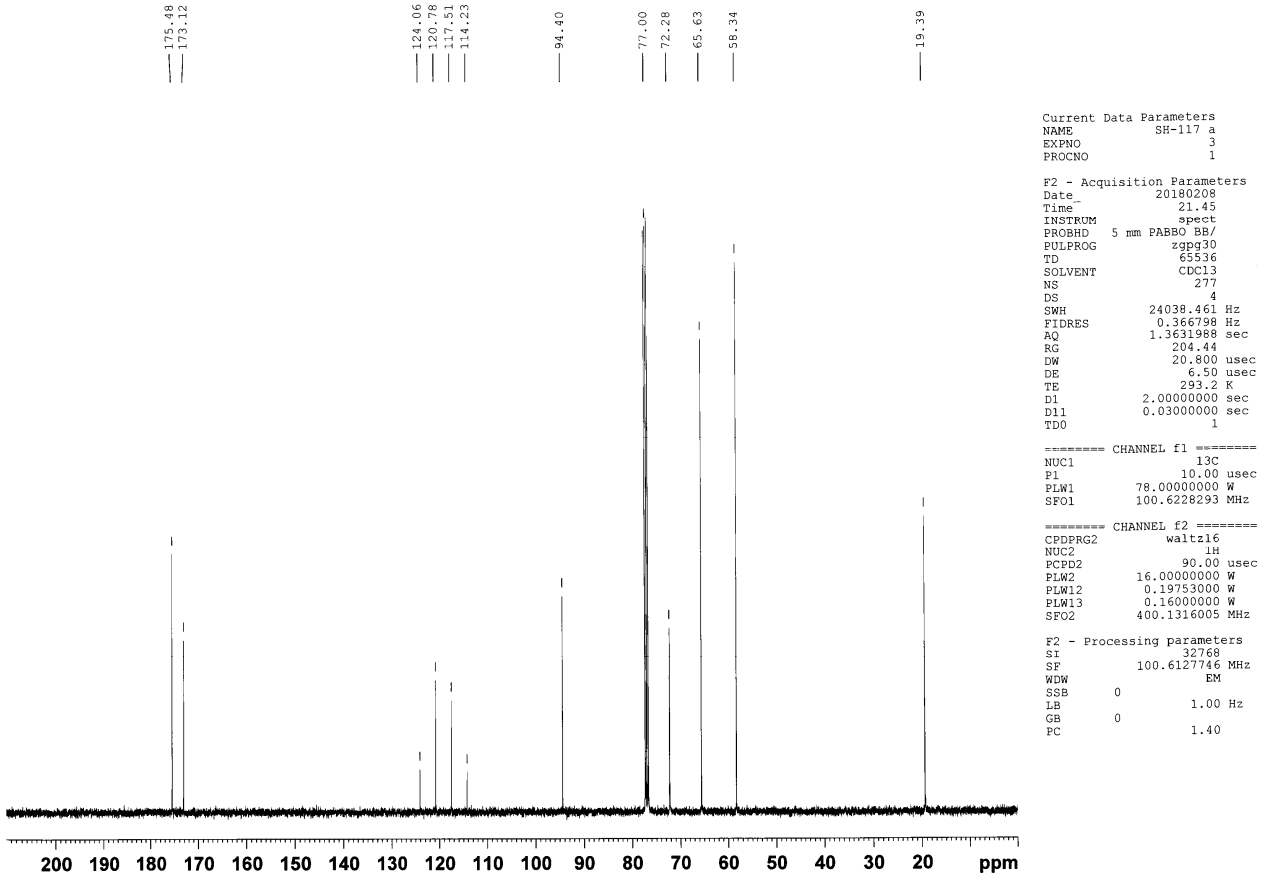
======== CHANNEL f1 ========
NUC1                     19F
P1                     14.00 usec
PLW1           24.00000000 W
SFO1           376.4607164 MHz

F2 - Processing parameters
SI                       65536
SF             376.4985416 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                       1.00
```

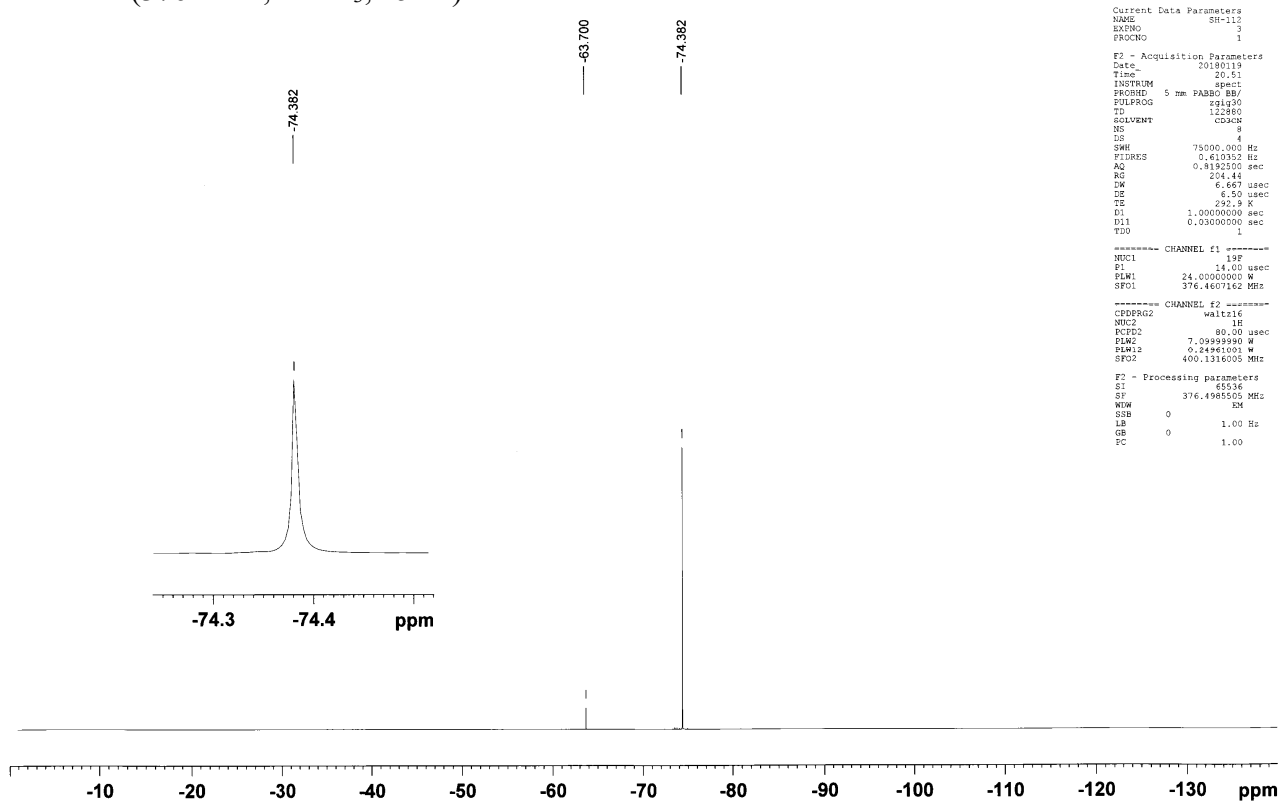
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC)



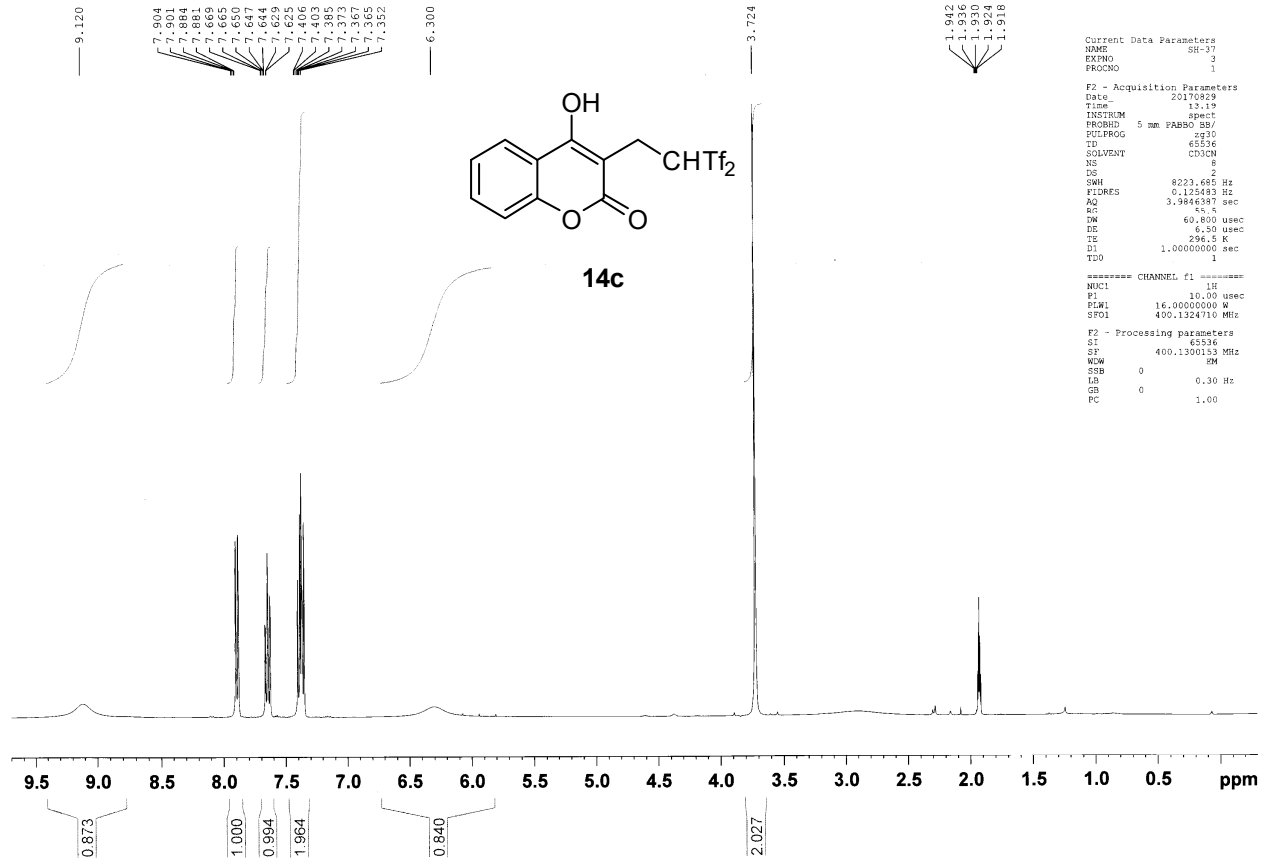
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)



^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)



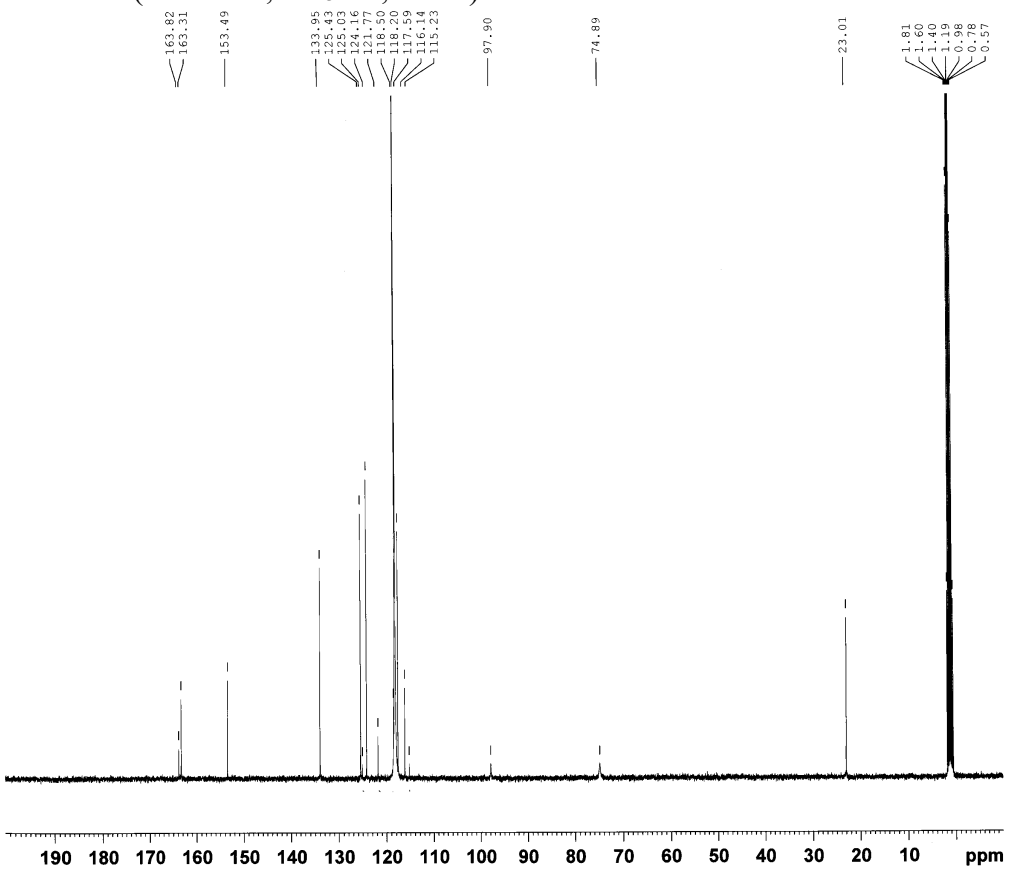
Current Data Parameters
NAME SH-37
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170829
Time 13.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300153 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



Current Data Parameters
NAME SH-37
EXPNO 4
PROCNO 1

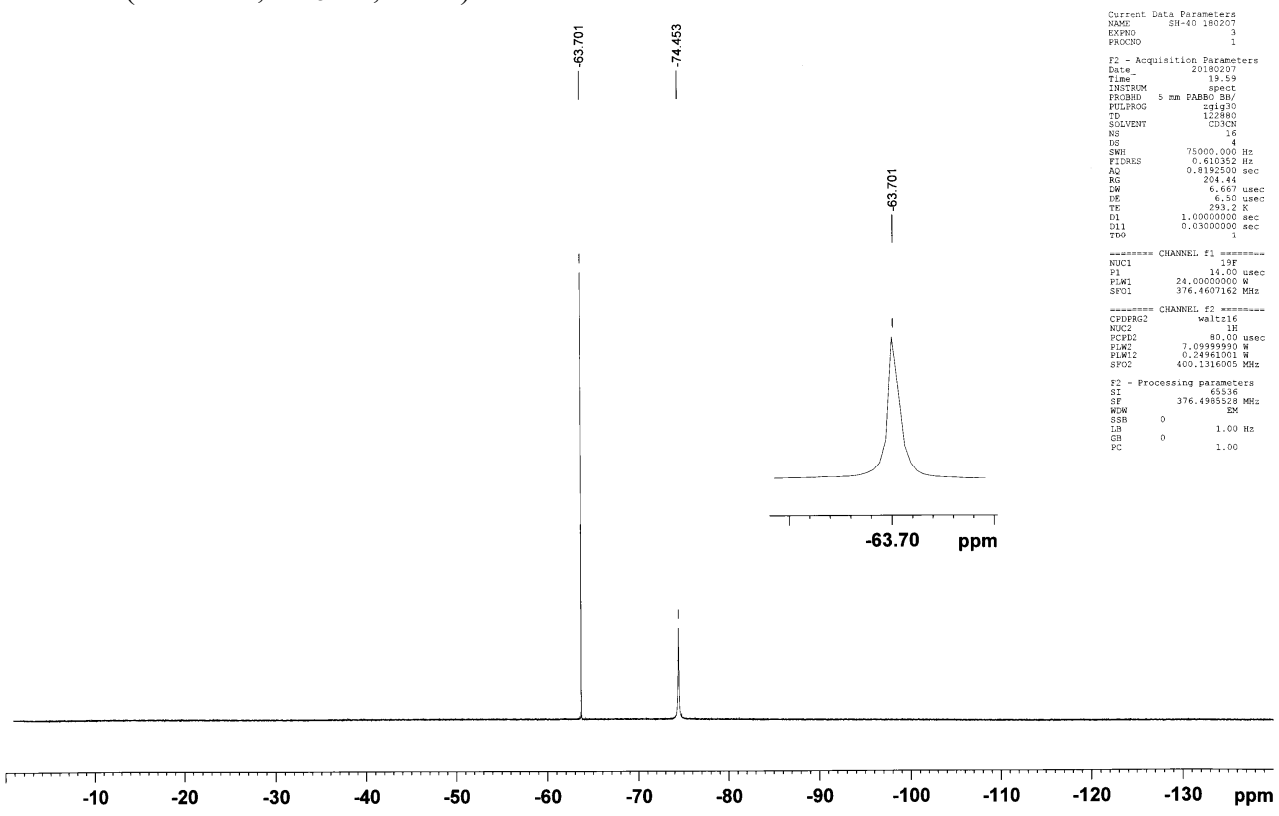
F2 - Acquisition Parameters
Date_ 20170829
Time 13.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 402
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.19753000 W
PLW13 0.16000000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126822 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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Current Data Parameters
NAME        SH-40 180207
EXPNO                  3
PROCNO                 1

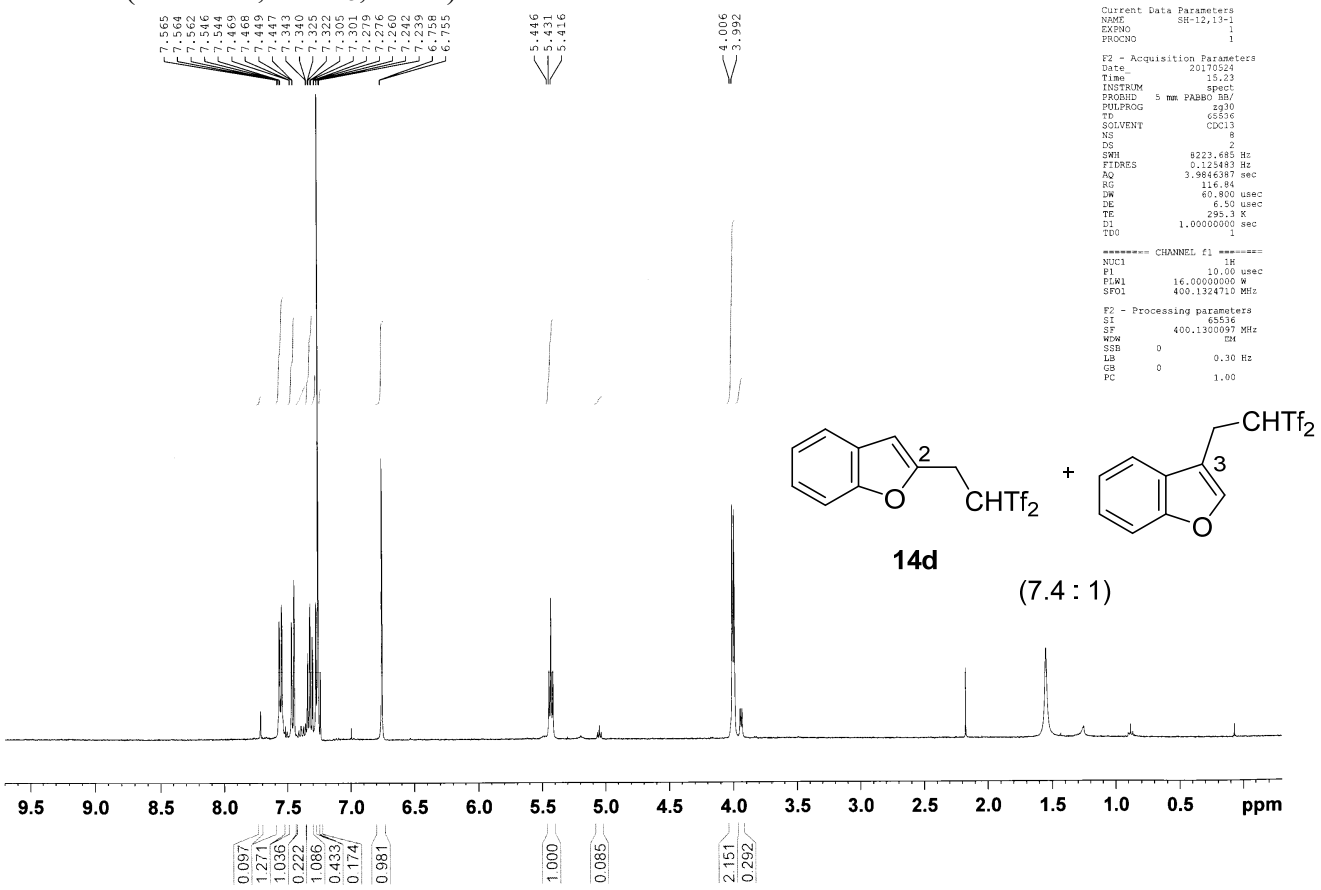
F2 - Acquisition Parameters
Date_           20180207
Time               19.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD               122880
SOLVENT           CD3CN
NS                   16
DS                    4
SWH           75000.000 Hz
FIDRES        0.610352 Hz
AQ            0.8192500 sec
RG               204.44
DW                6.667 usec
DE                6.50 usec
TE               293.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.00 usec
PLW1         24.00000000 W
SFO1         376.4607162 MHz

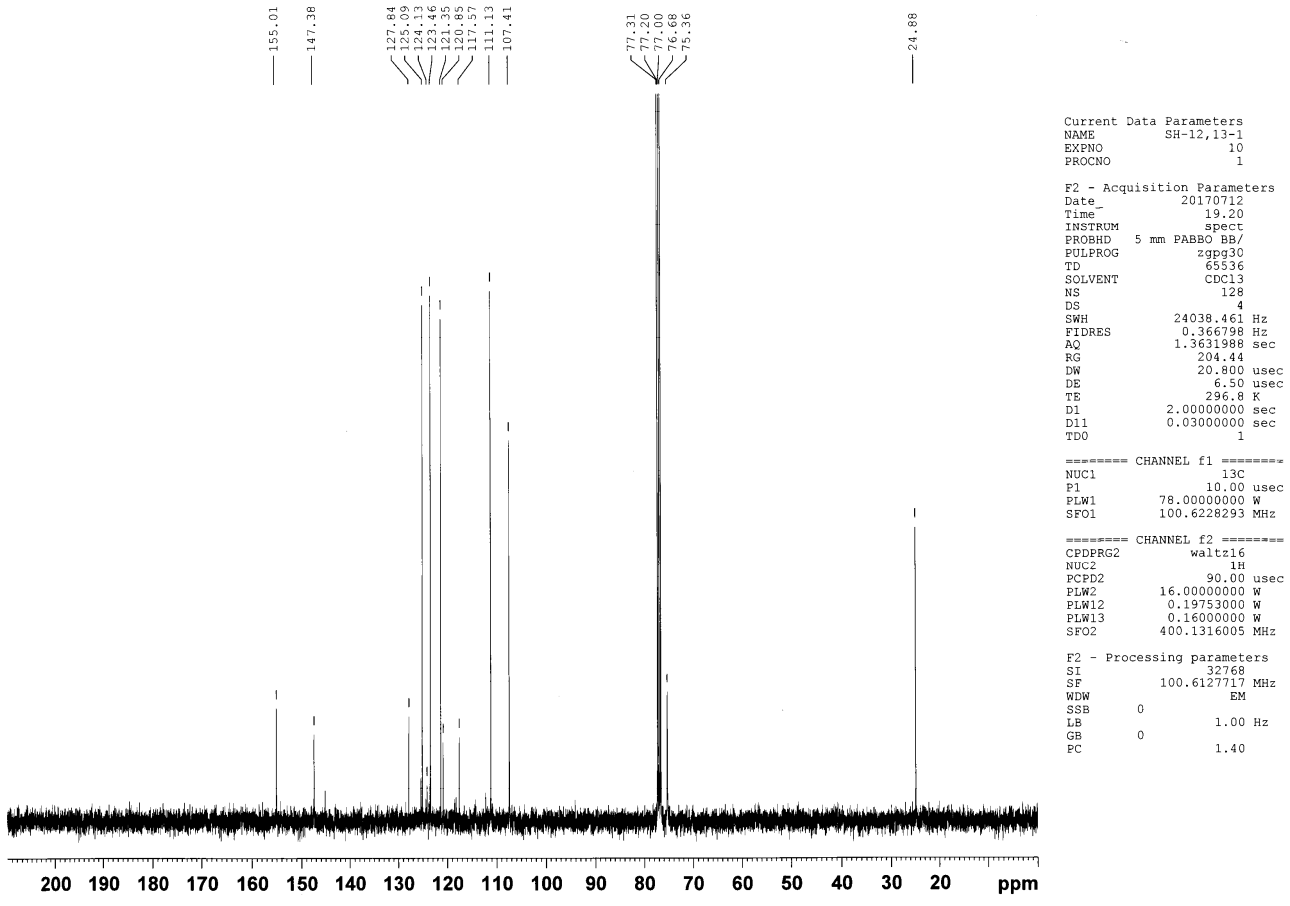
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PLW2          7.09999990 W
PLW12         0.24961001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF           376.4985528 MHz
WDW                    EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```

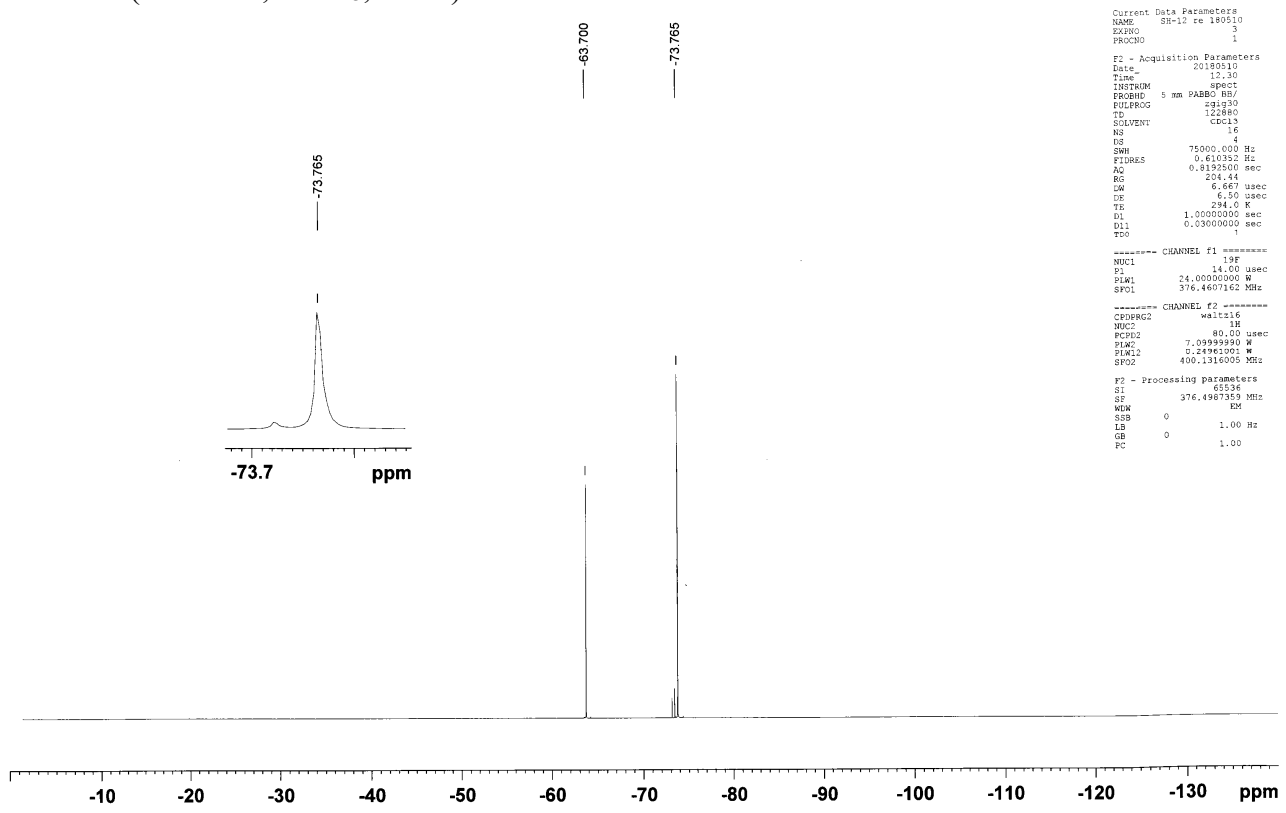
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)



^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)

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Current Data Parameters
NAME        SH-12 re 180510
EXPNO                    3
PROCNO                   1

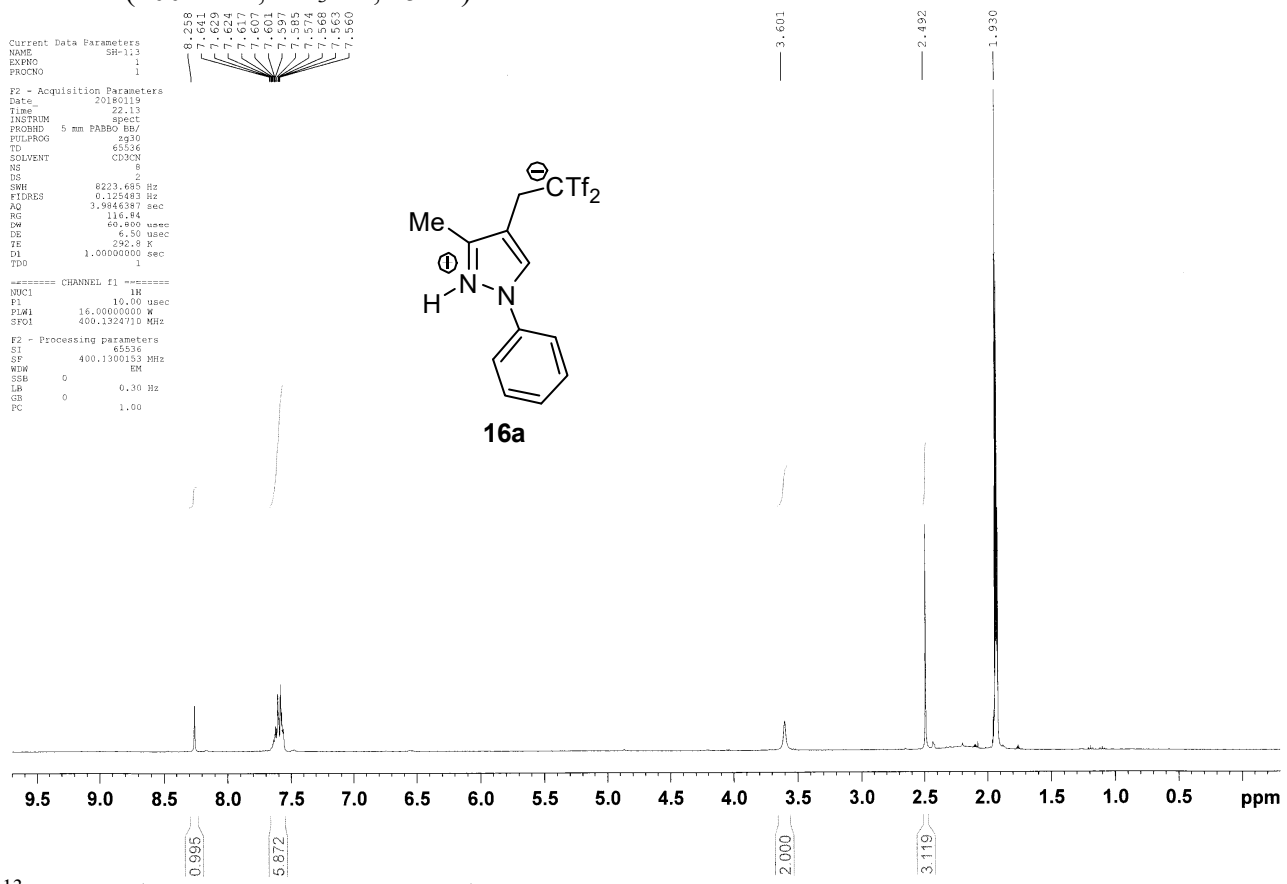
F2 - Acquisition Parameters
Date_              20180510
Time_                 12.30
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig30
TD                  122880
SOLVENT              CDCl3
NS                       16
DS                        4
SWH               75000.000 Hz
FIDRES             0.610352 Hz
AQ                 0.8192500 sec
RG                    204.44
DW                   6.667 usec
DE                    6.50 usec
TE                  294.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     19F
P1                     14.00 usec
PLW1              24.00000000 W
SFO1             376.4607162 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 80.00 usec
PLW2               7.09999990 W
PLW12              0.24961001 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                       65536
SF               376.4987359 MHz
WDW                         EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```

^{1}H NMR (400 MHz, CD_3CN, 25 °C)



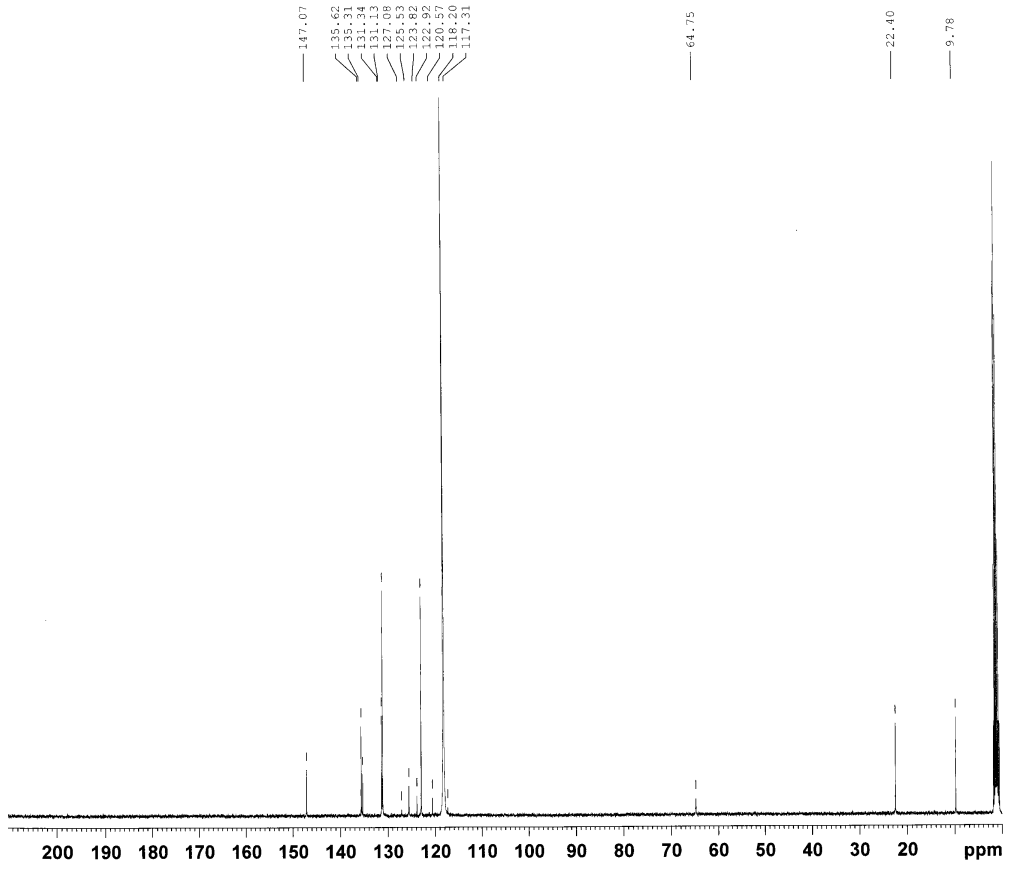
Current Data Parameters
NAME SH-1,3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180119
Time_ 22.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 116.84
DW 60.800 usec
DE 6.50 usec
TE 292.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300153 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR (100 MHz, CD_3CN, 25 °C)



Current Data Parameters
NAME SH-106 a3
EXPNO 7
PROCNO 1

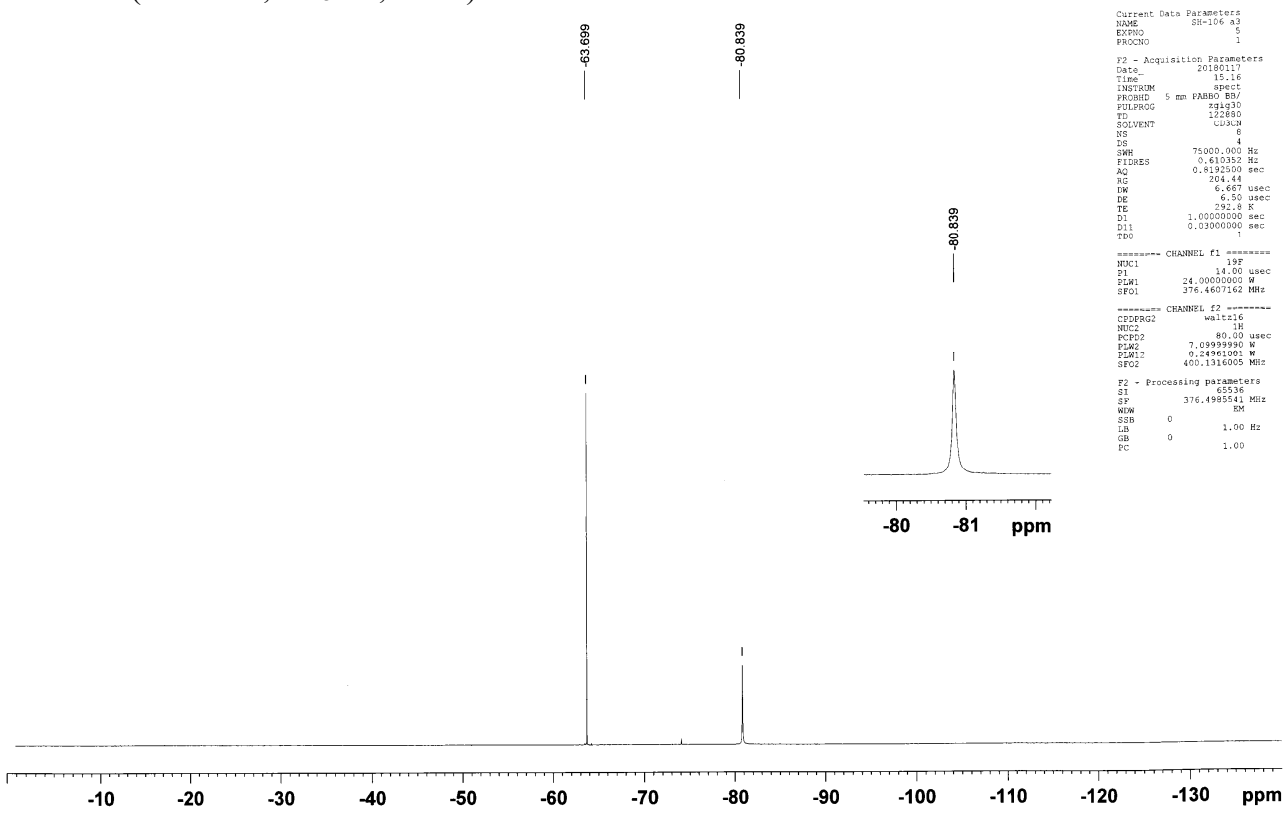
F2 - Acquisition Parameters
Date_ 20180117
Time_ 21.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 599
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

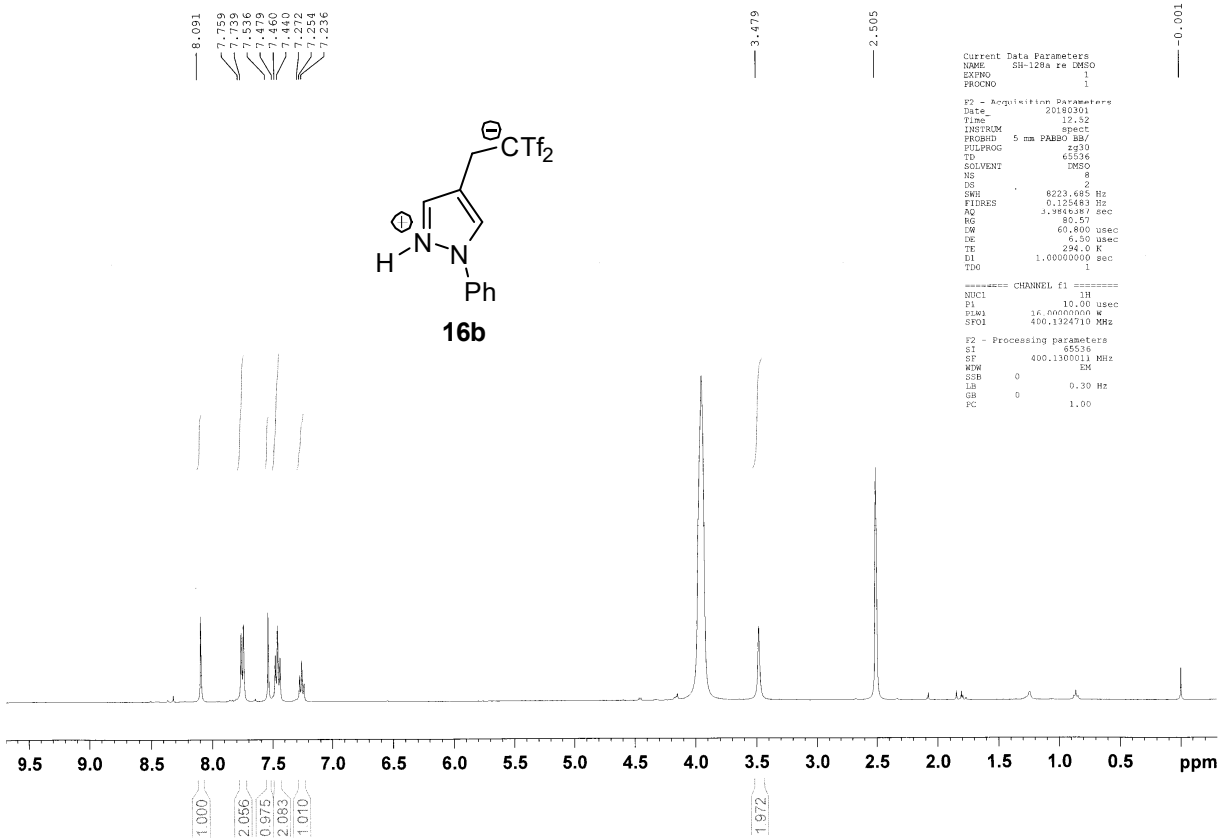
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.19753000 W
PLW13 0.16000000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126870 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

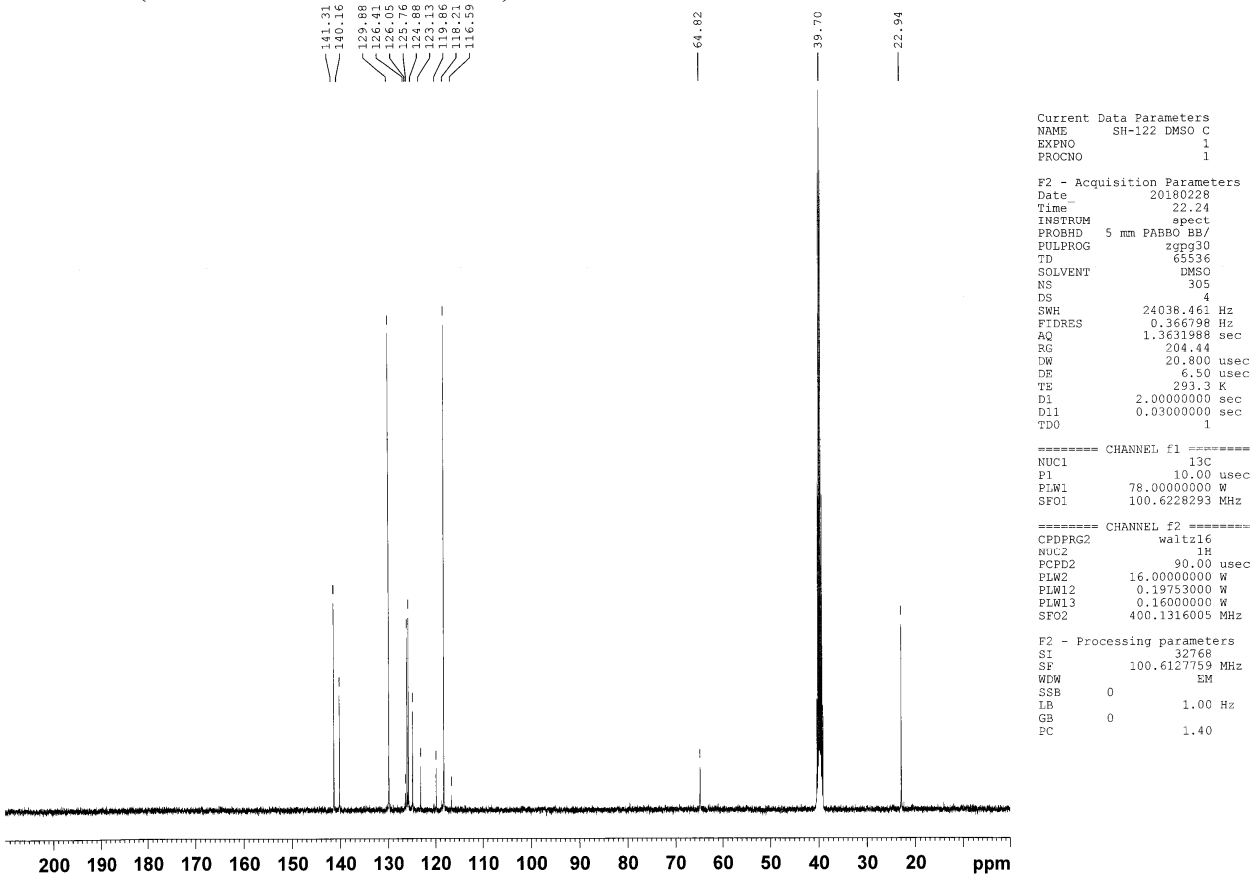
^{19}F NMR (376 MHz, CD_3CN, 25 °C)



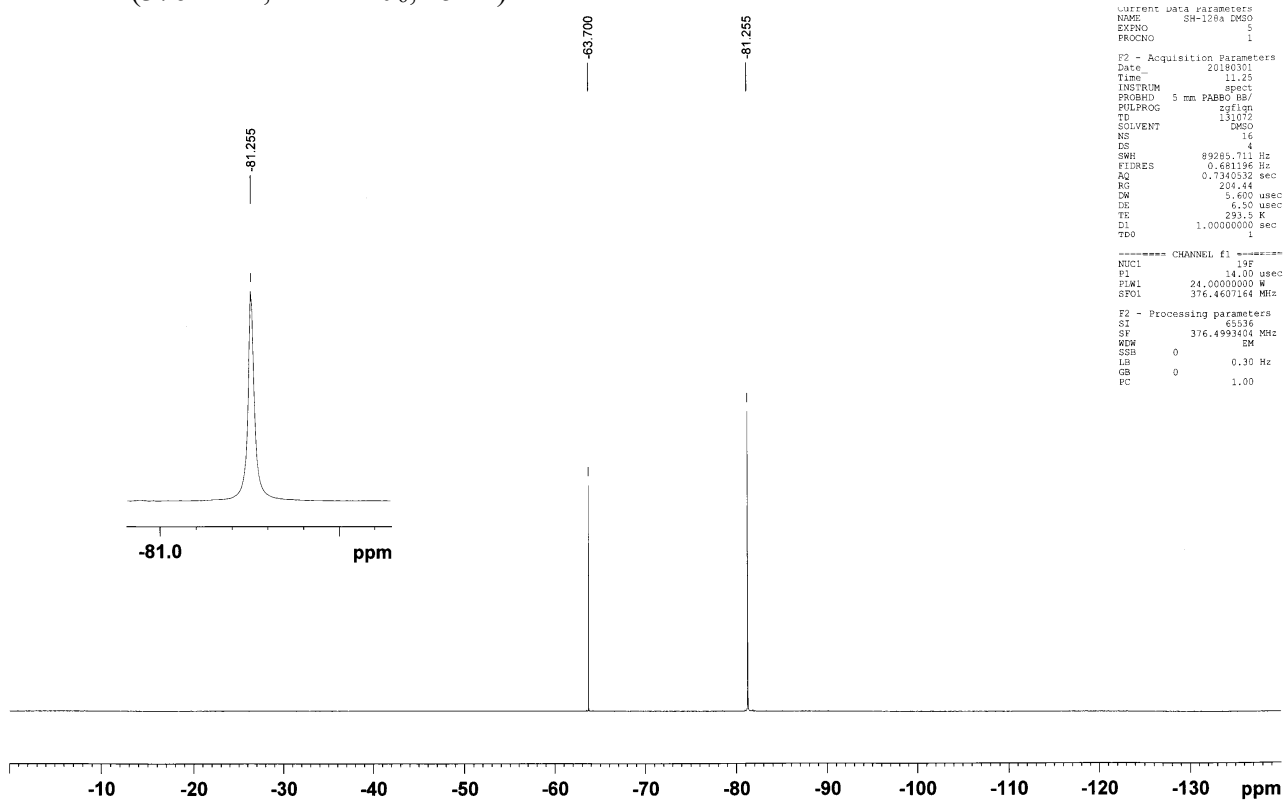
^{1}H NMR (400 MHz, DMSO-d_6, 25 °C)



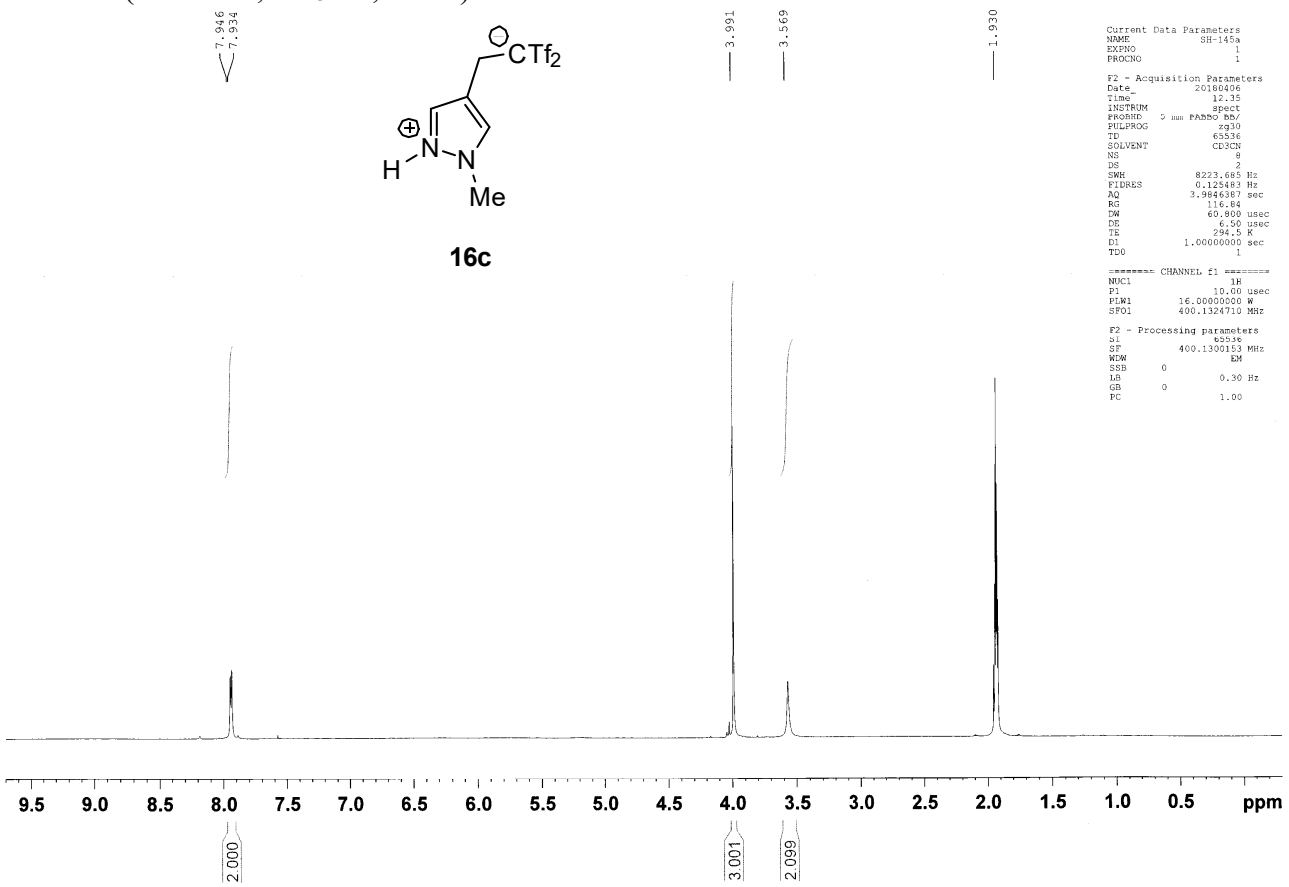
^{13}C NMR (100 MHz, DMSO-d_6, 25 °C)



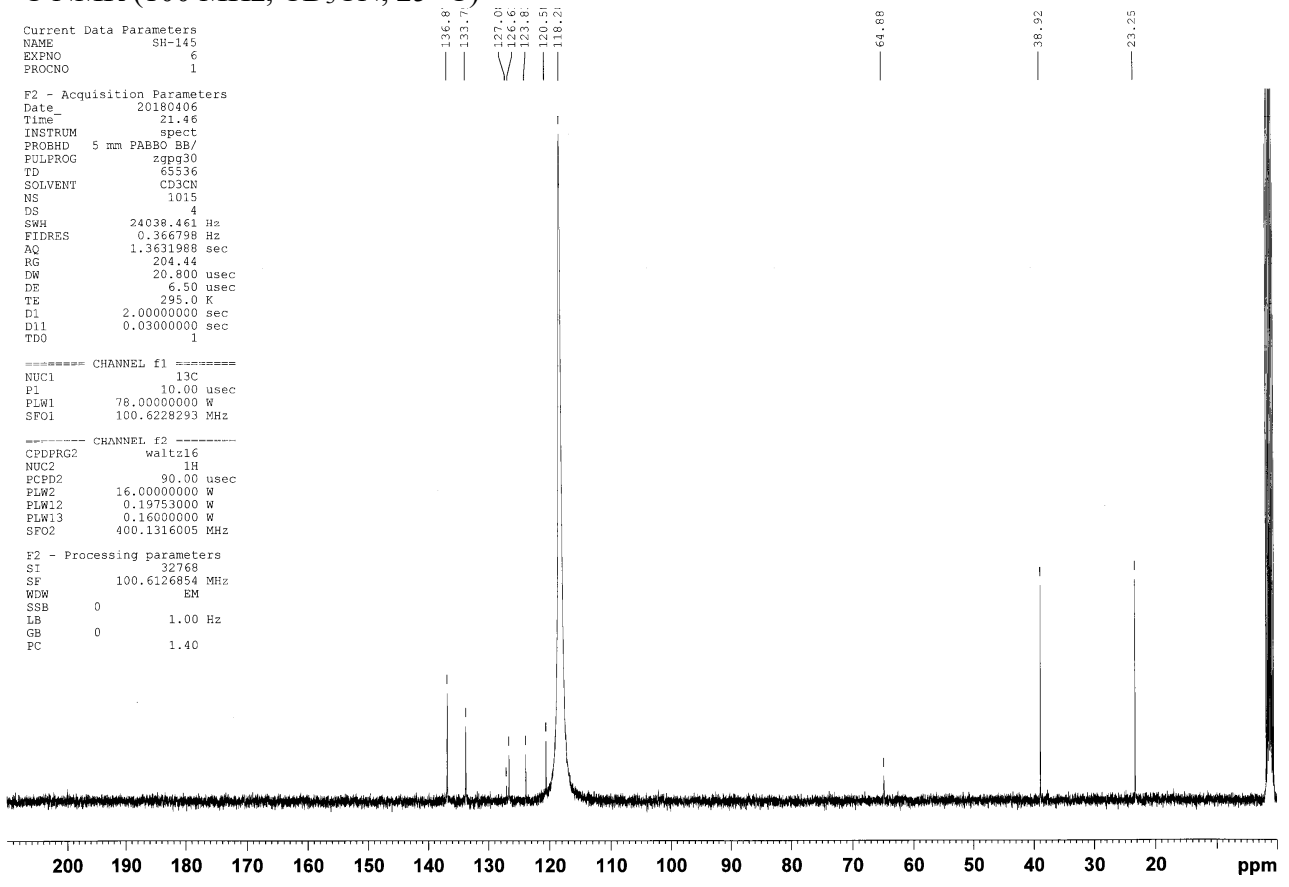
^{19}F NMR (376 MHz, DMSO-d_6, 25 °C)



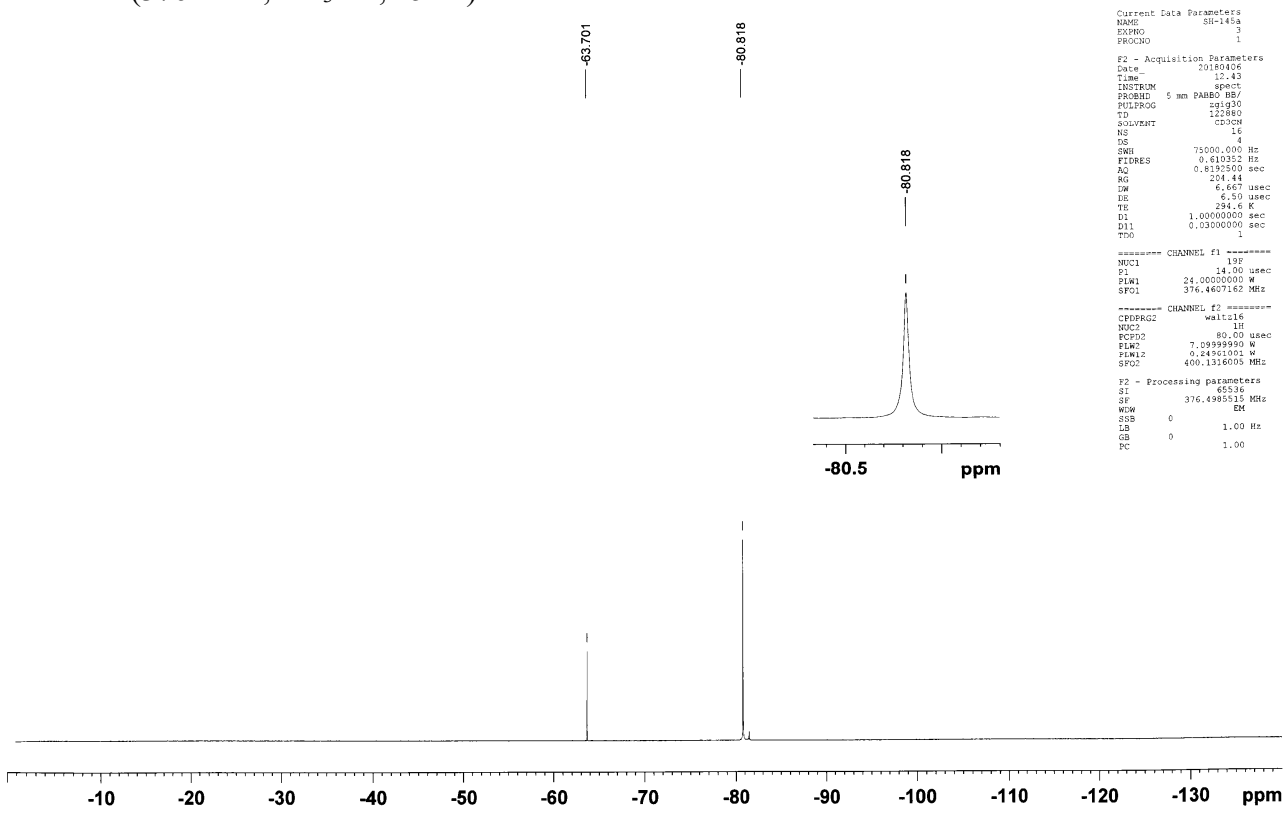
^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)



^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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PROCNO                      1

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PULPROG             zgig30
TD                     122880
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NS                         16
DS                          4
SWH                75000.000 Hz
FIDRES                 0.610352 Hz
AQ                     0.8192500 sec
RG                       204.44
DW                       6.667 usec
DE                       6.50 usec
TE                     294.6 K
D1                     1.00000000 sec
D11                    0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       19F
P1                       14.00 usec
PLW1                24.00000000 W
SFO1                376.4607162 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    80.00 usec
PLW2                 7.09999990 W
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F2 - Processing parameters
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WDW                           EM
SSB                 0
LB                       1.00 Hz
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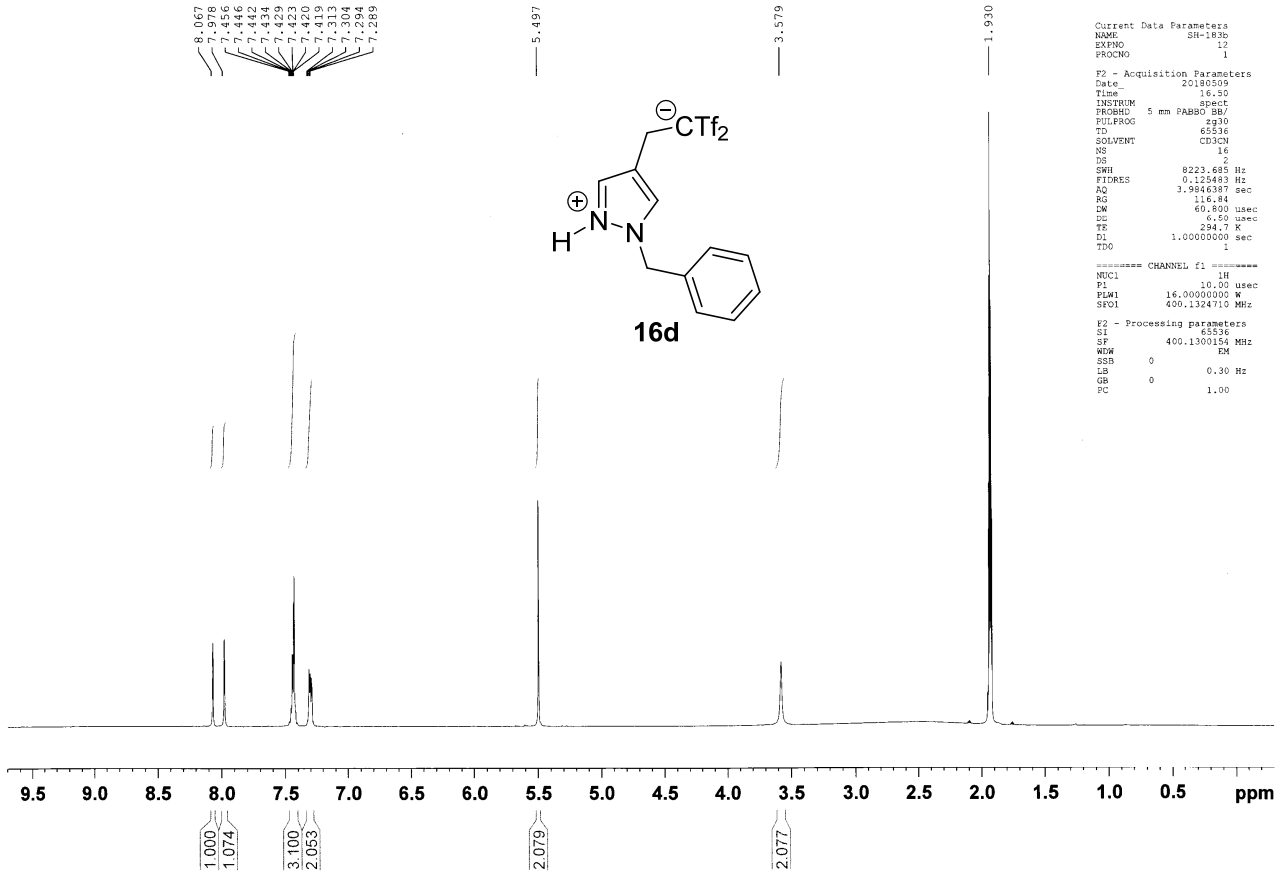
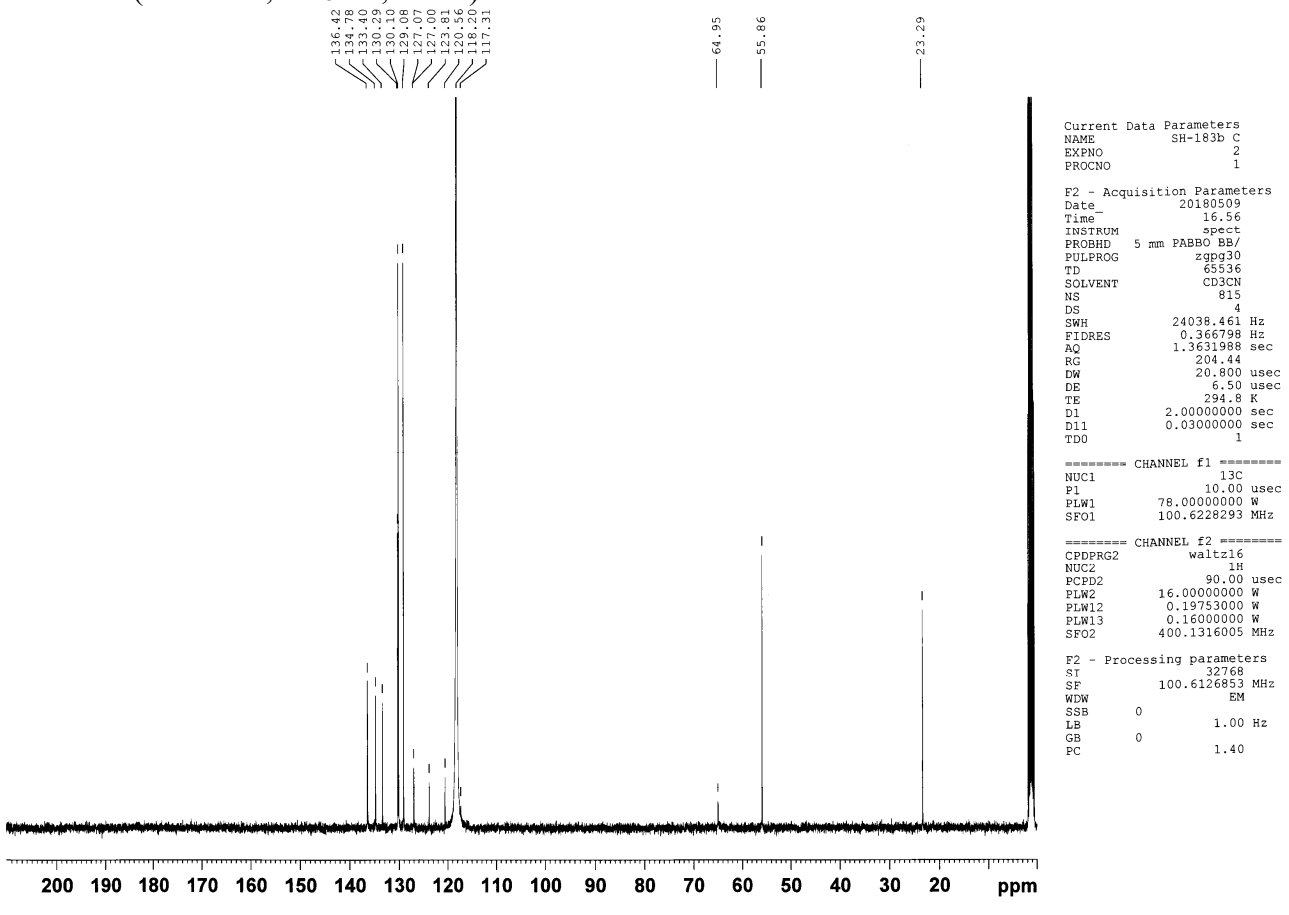
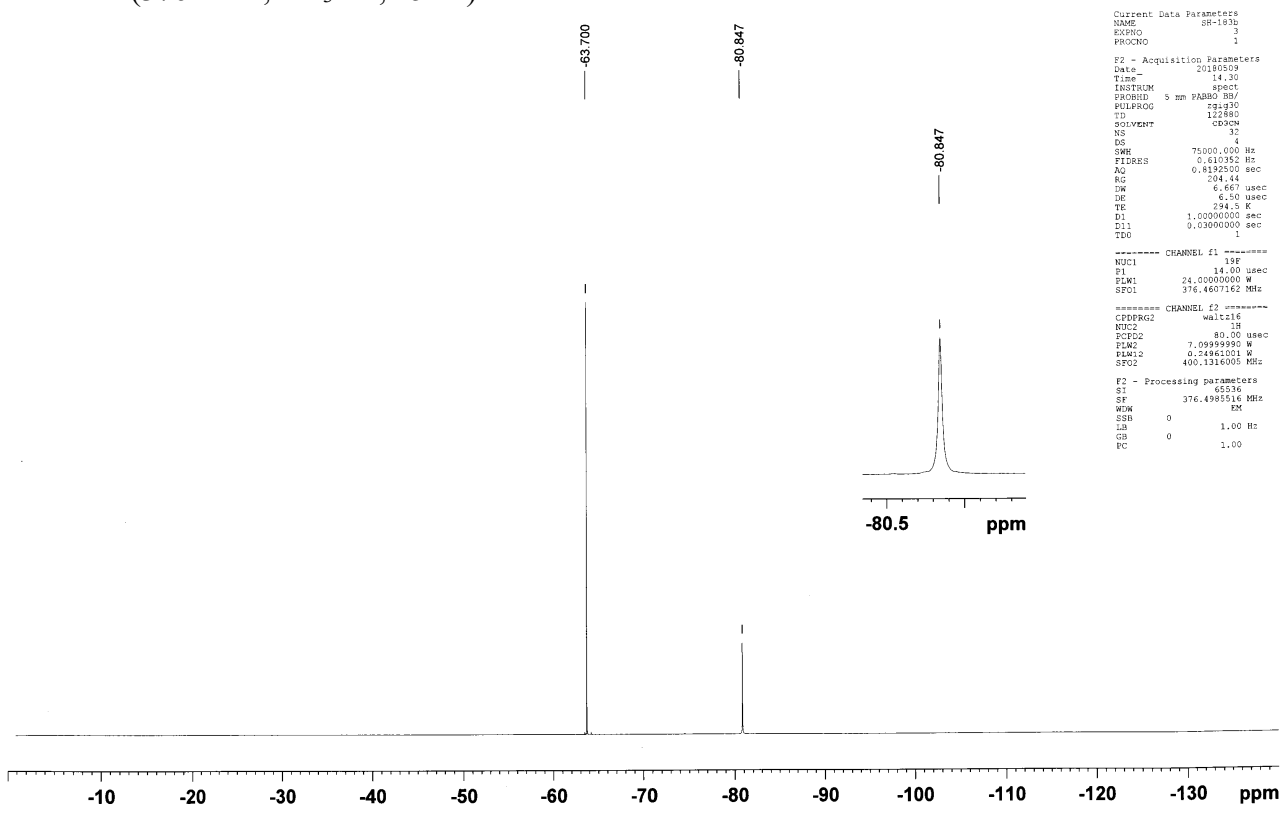
^{1}H NMR (400 MHz, CD_3CN, 25 °C)



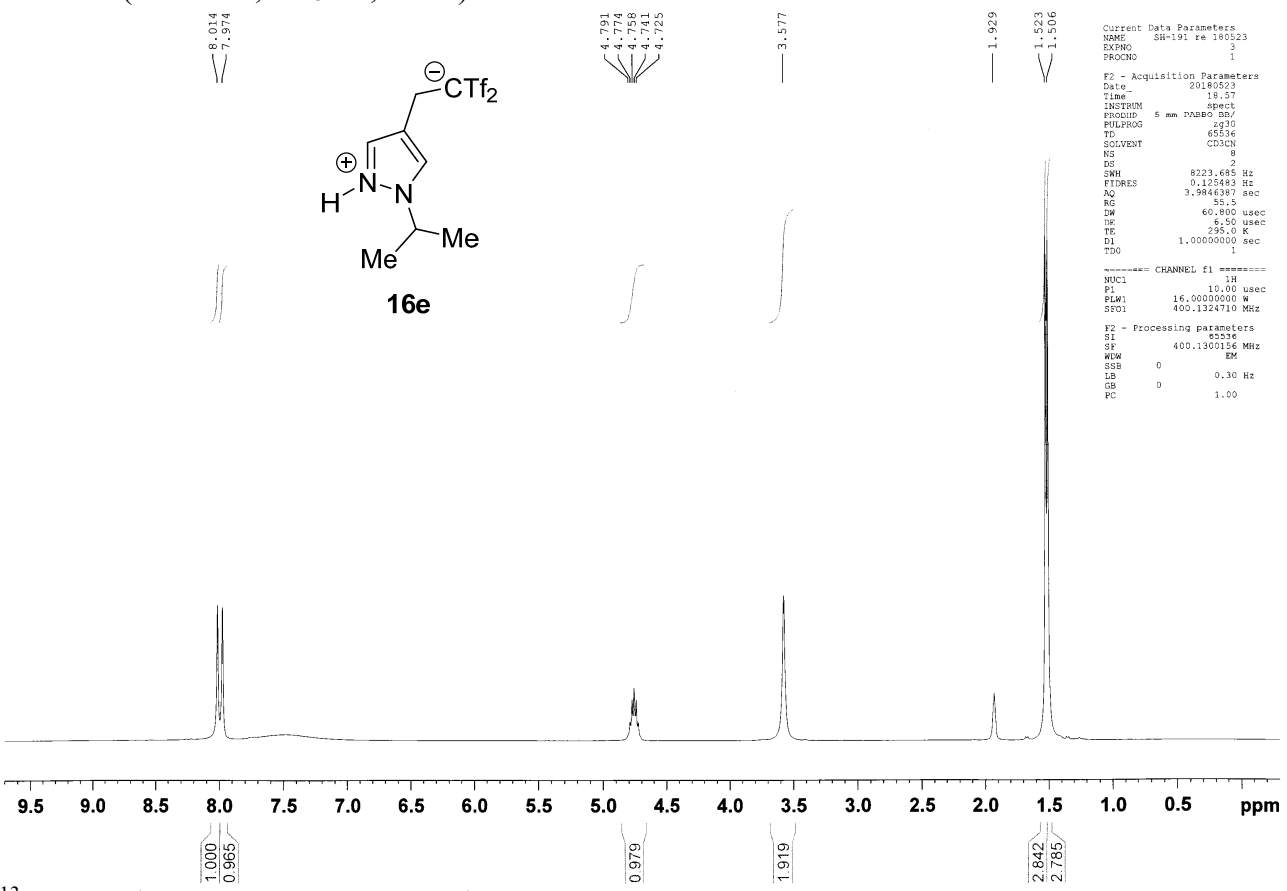
^{13}C NMR (100 MHz, CD_3CN, 25 °C)



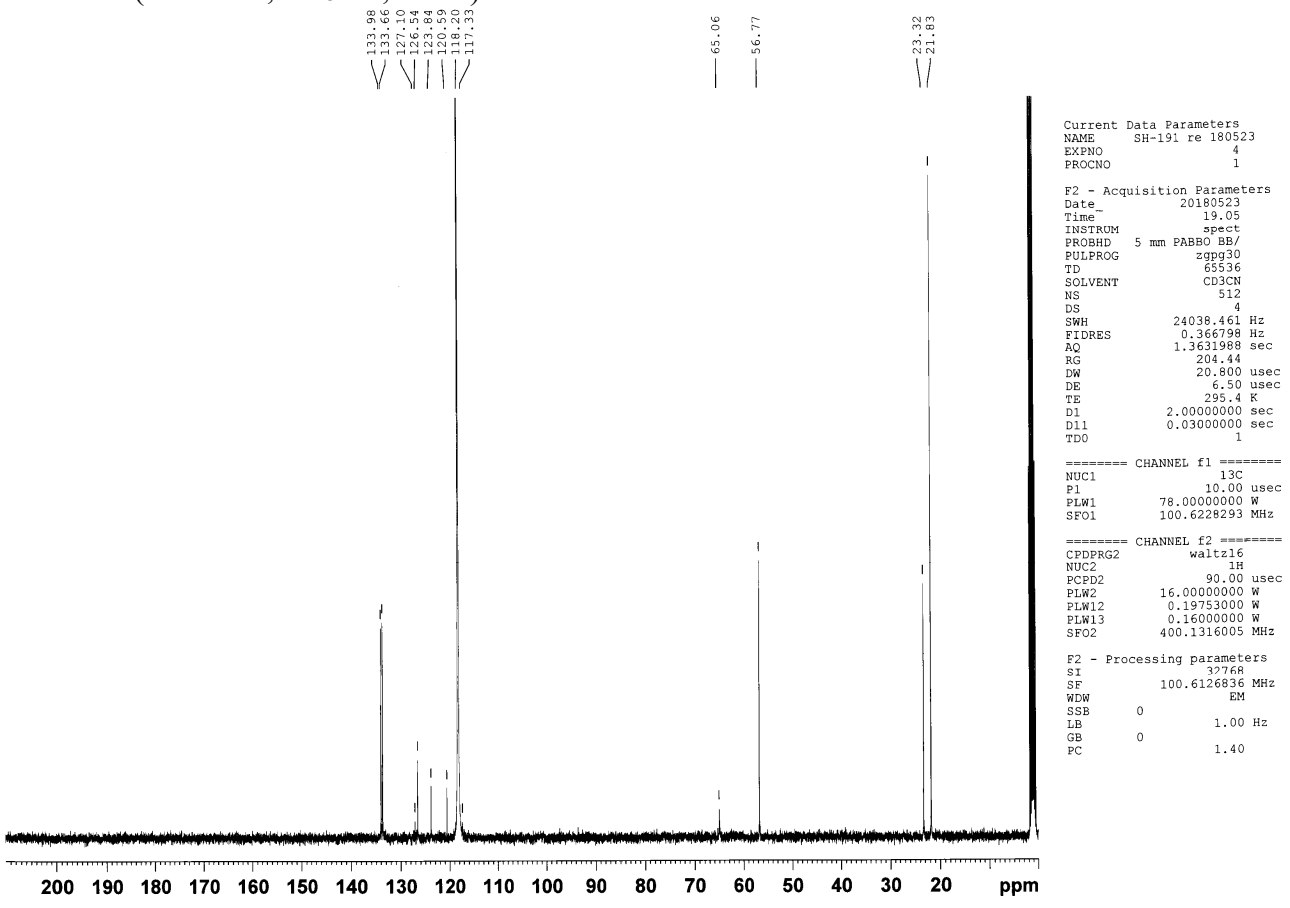
^{19}F NMR (376 MHz, CD_3CN, 25 °C)



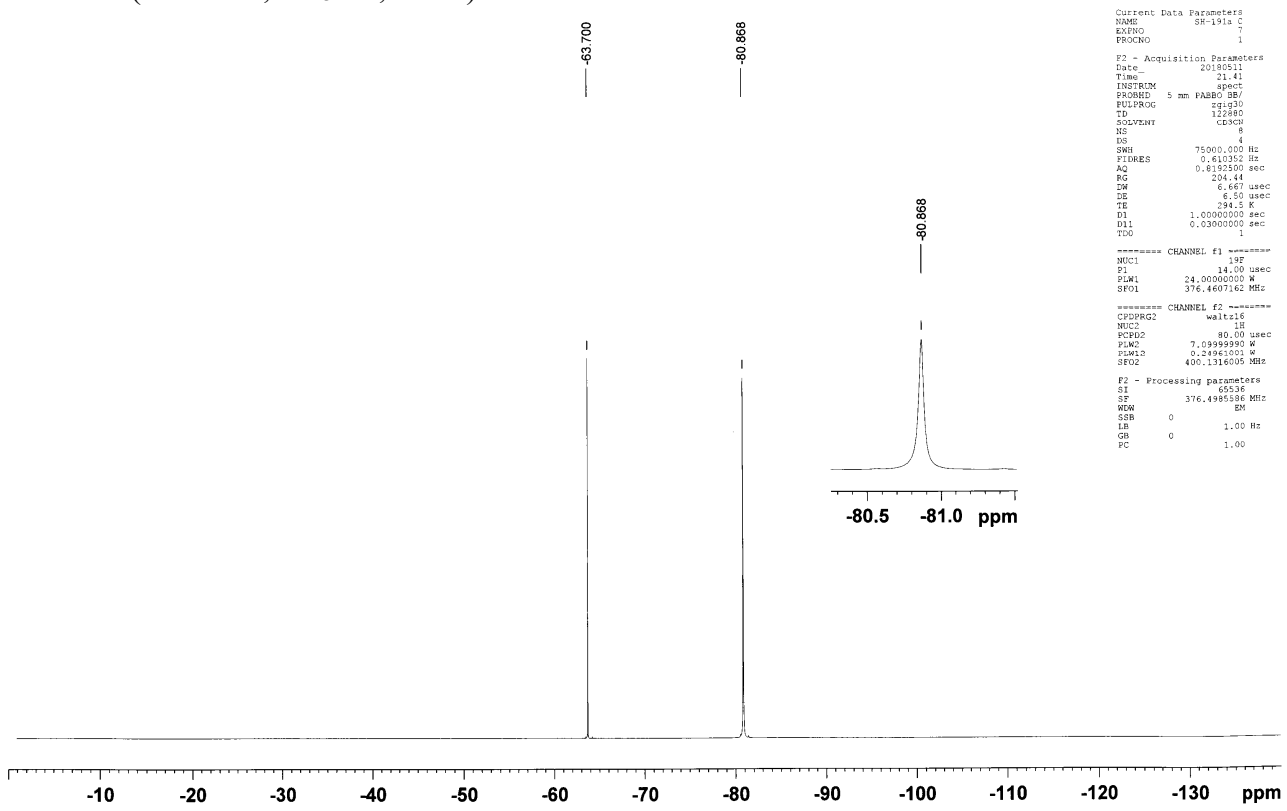
^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)



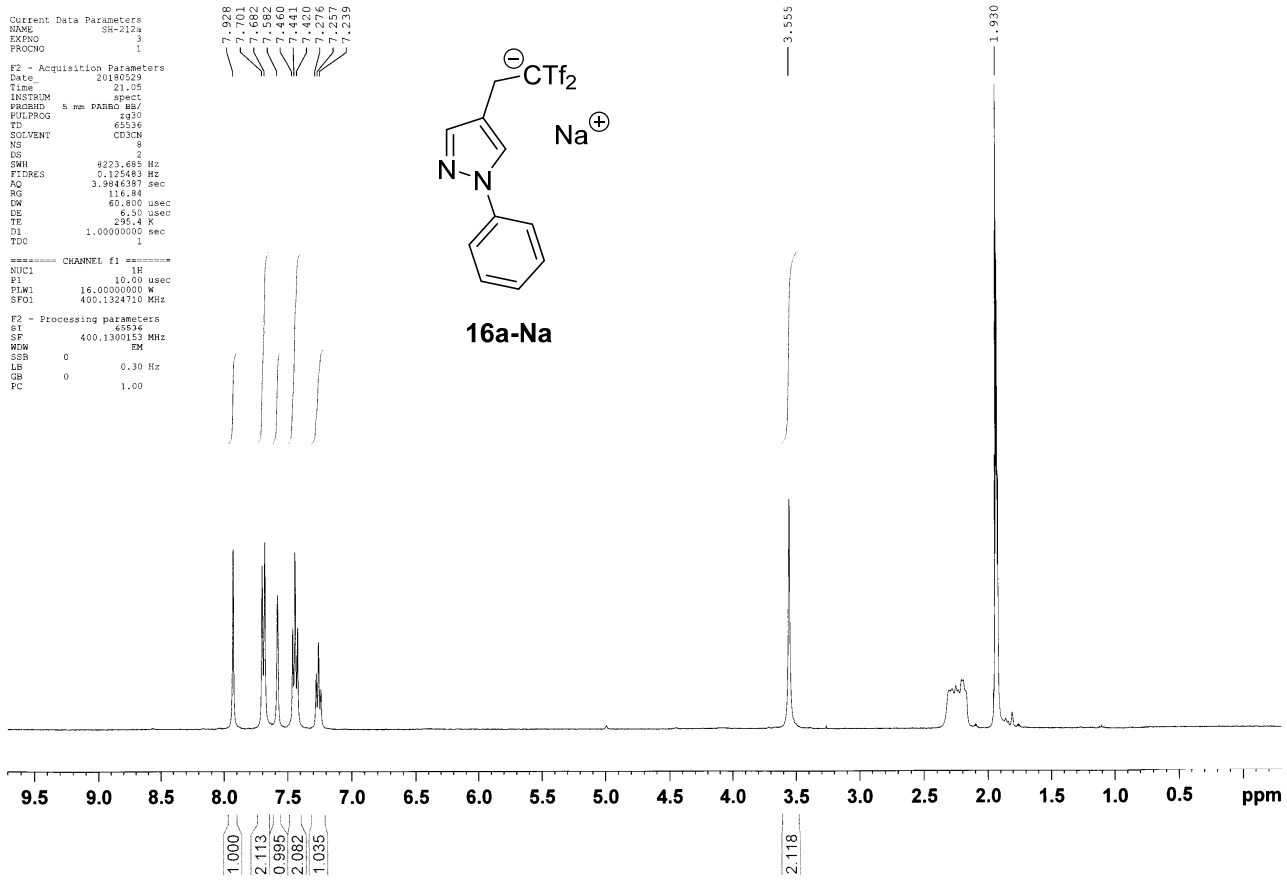
^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)



^{1}H NMR (400 MHz, CD_3CN, 25 °C)



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PROCNO 1

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PULPROG zg30
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DS 2
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FIDRES 0.125483 Hz
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RG 116.84
DW 60.800 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
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PLW1 16.00000000 W
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F2 - Processing parameters
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WDW EM
SSB 0
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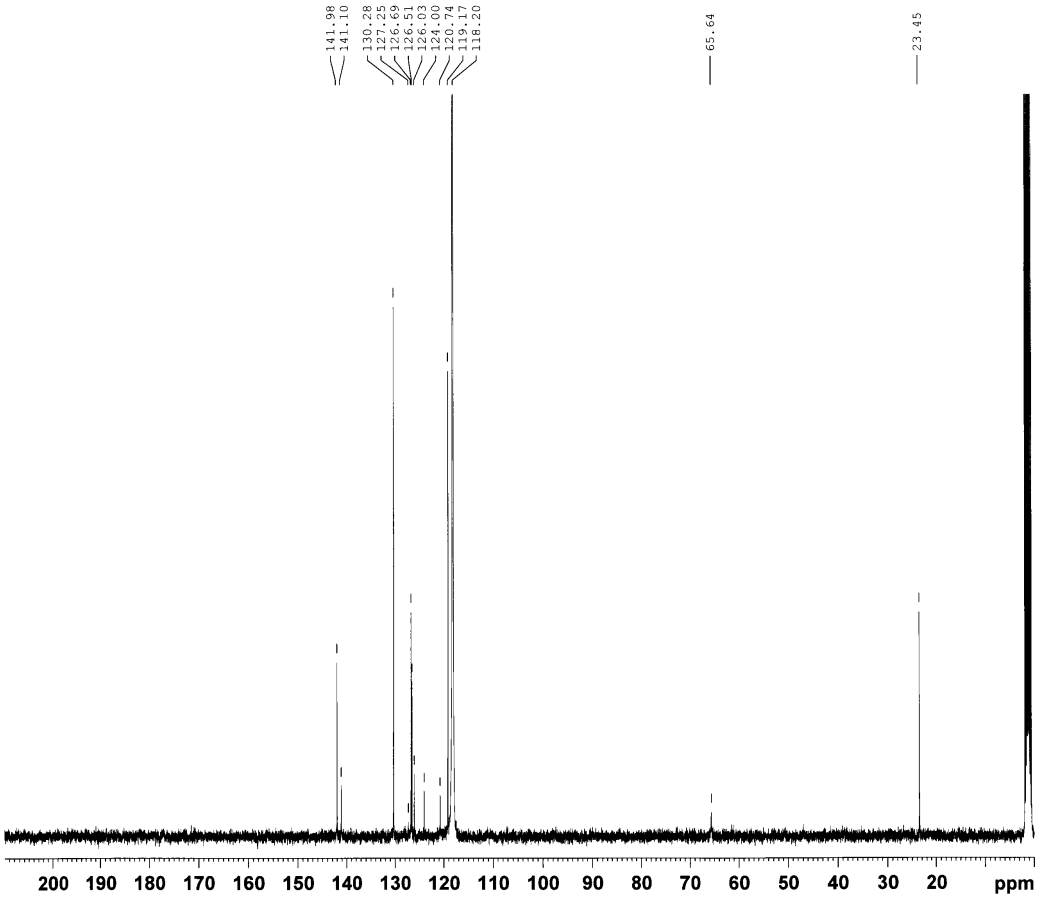
GB 0
PC 1.00

^{13}C NMR (100 MHz, CD_3CN, 25 °C)



Current Data Parameters
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PROCNO 1

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SOLVENT CD3CN
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SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
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NUC2 1H
PCPD2 90.00 usec
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PLW12 0.19753000 W
PLW13 0.16000000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
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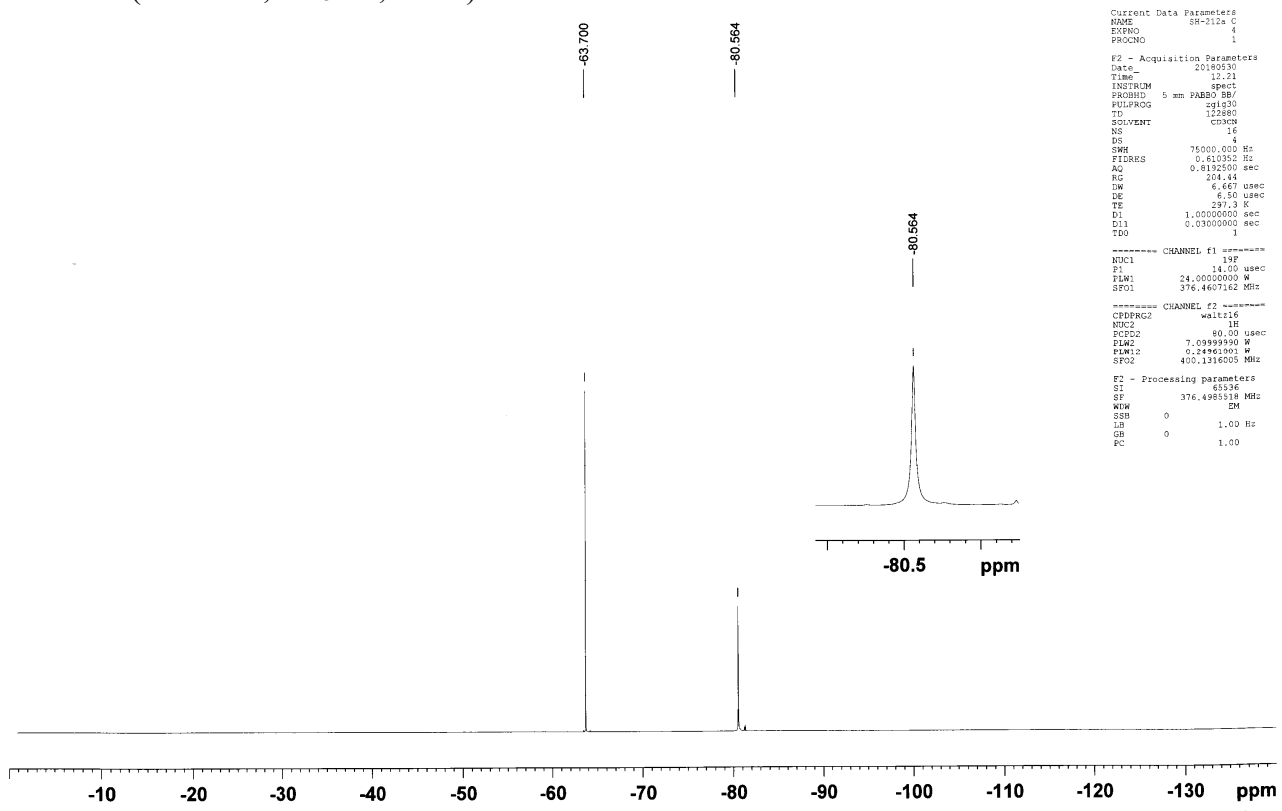
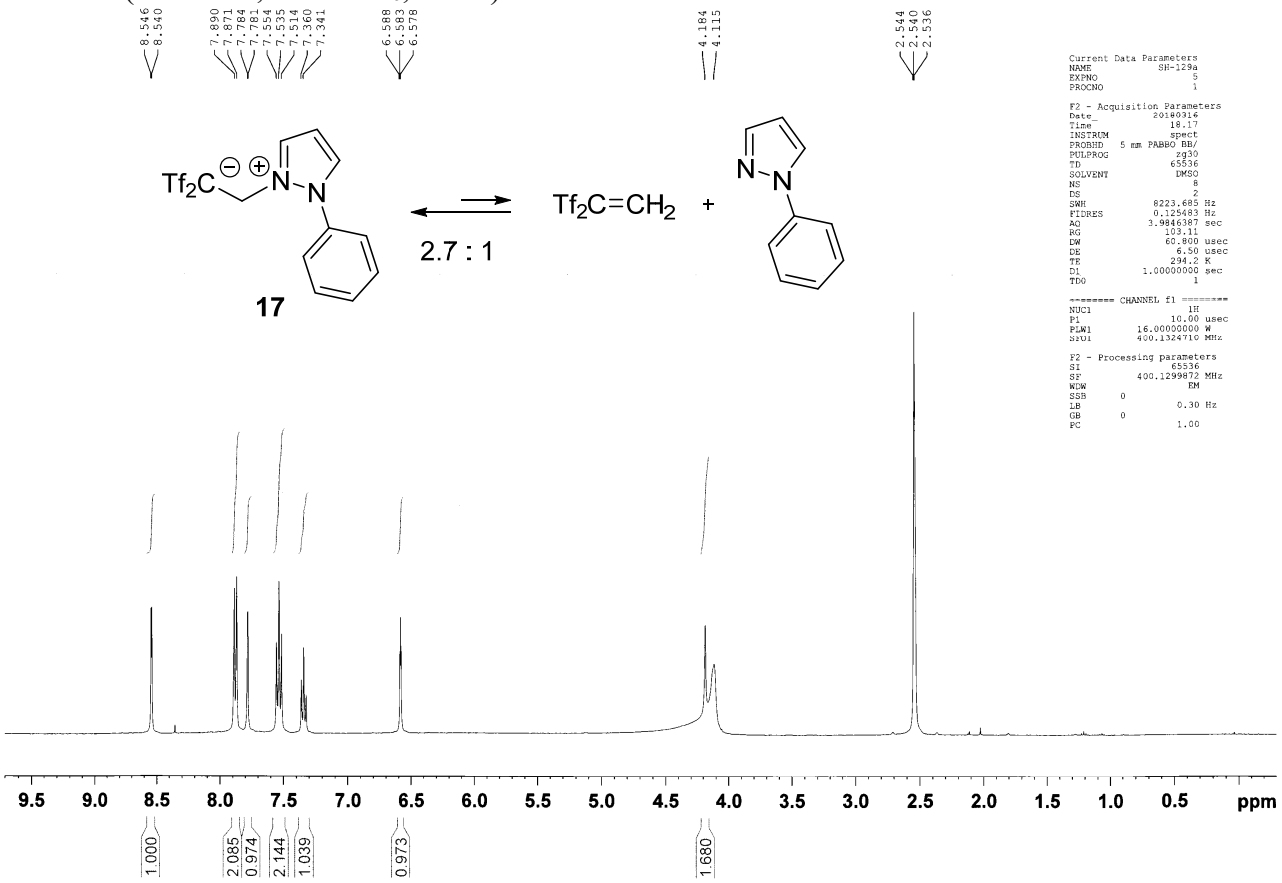
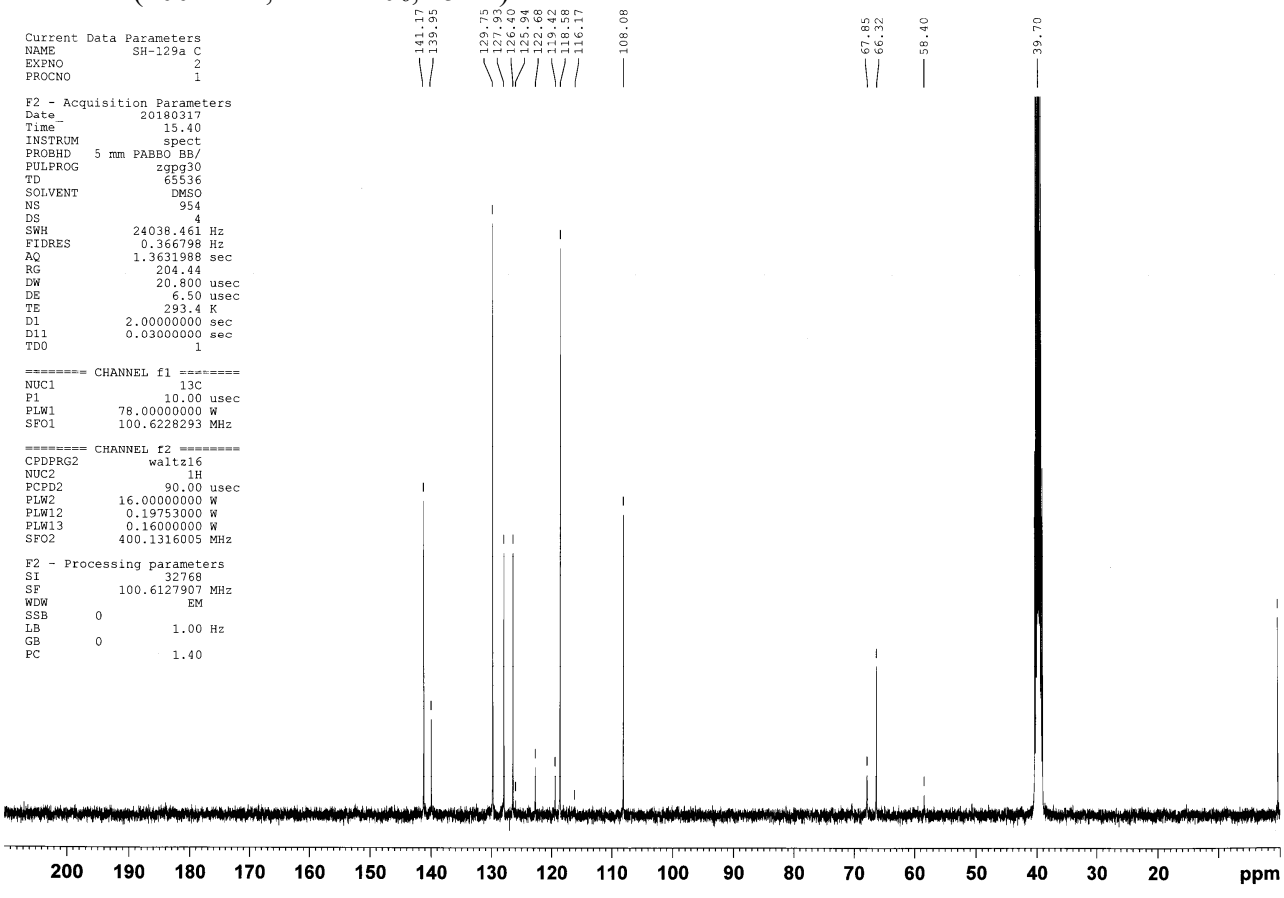
^{19}F NMR (376 MHz, CD_3CN, 25 °C)



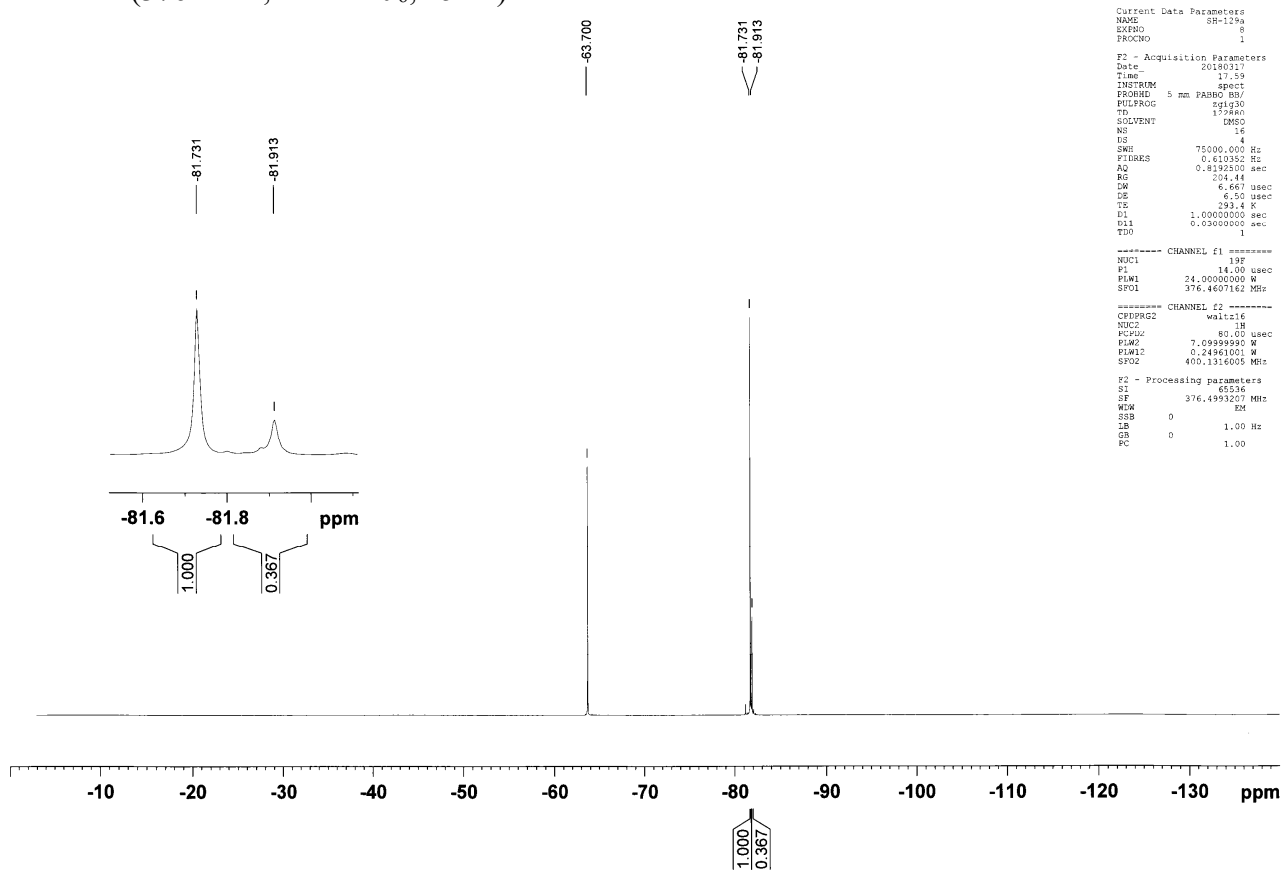
^{1}H NMR (400 MHz, DMSO-d_6, 25 °C)



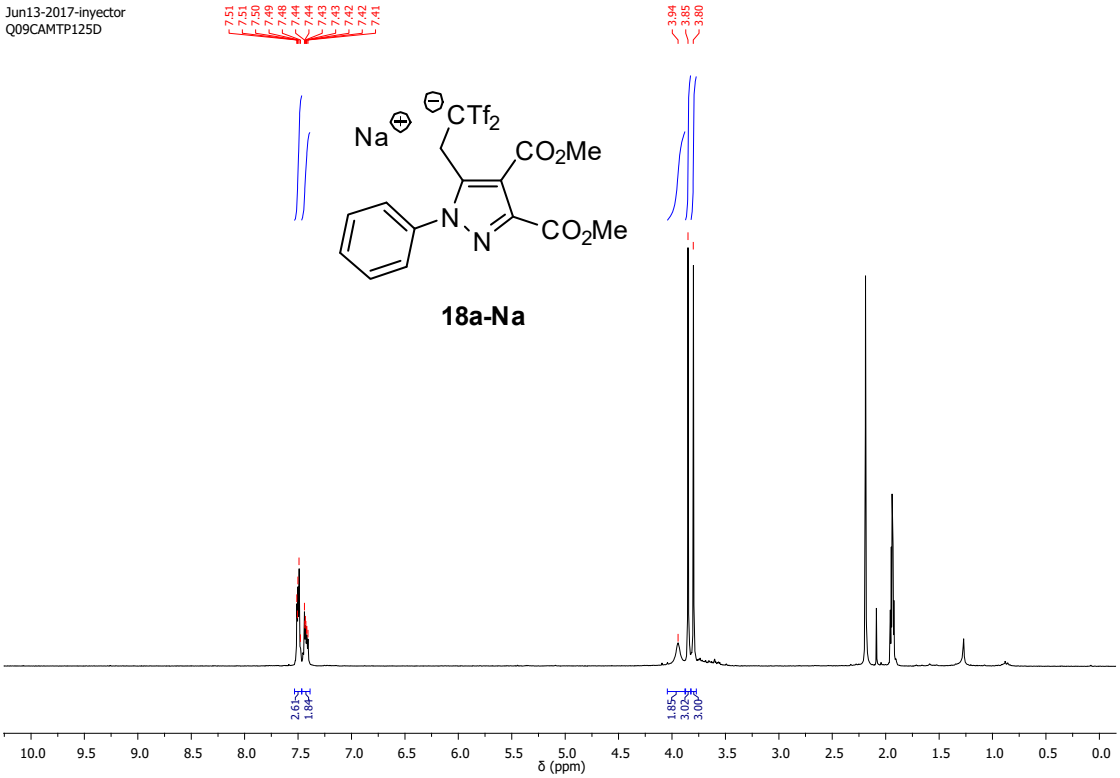
^{13}C NMR (100 MHz, DMSO-d_6, 25 °C)



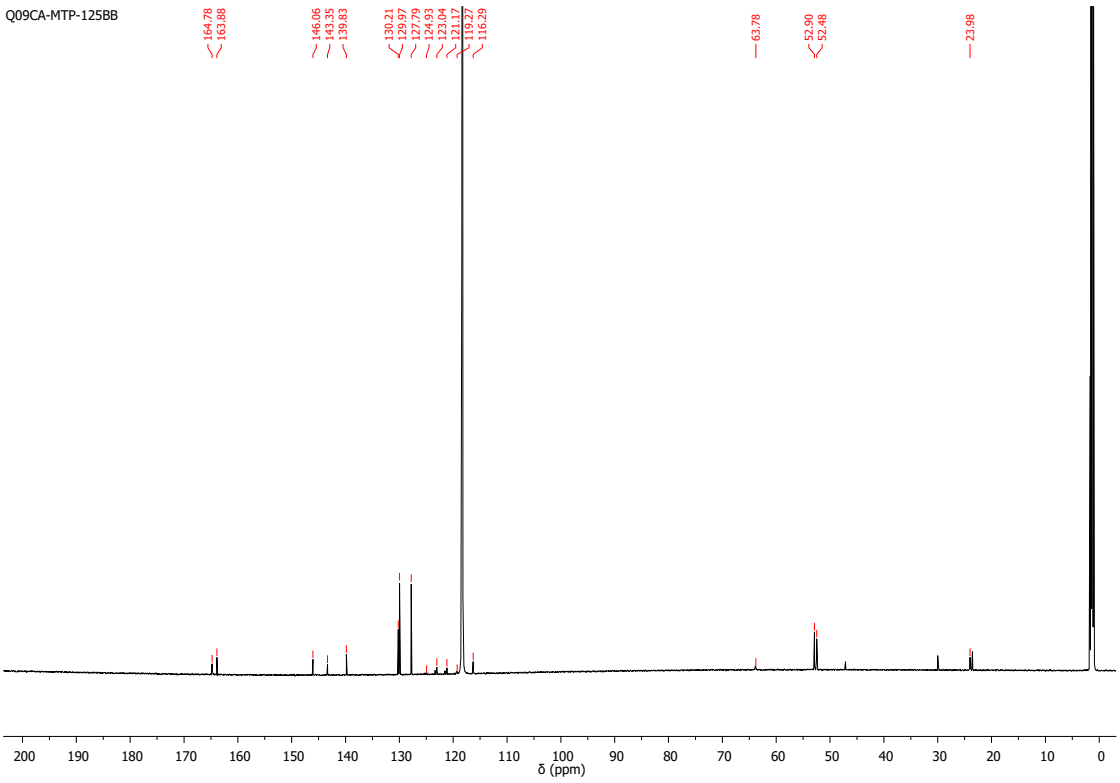
^{19}F NMR (376 MHz, DMSO-d_6, 25 °C)



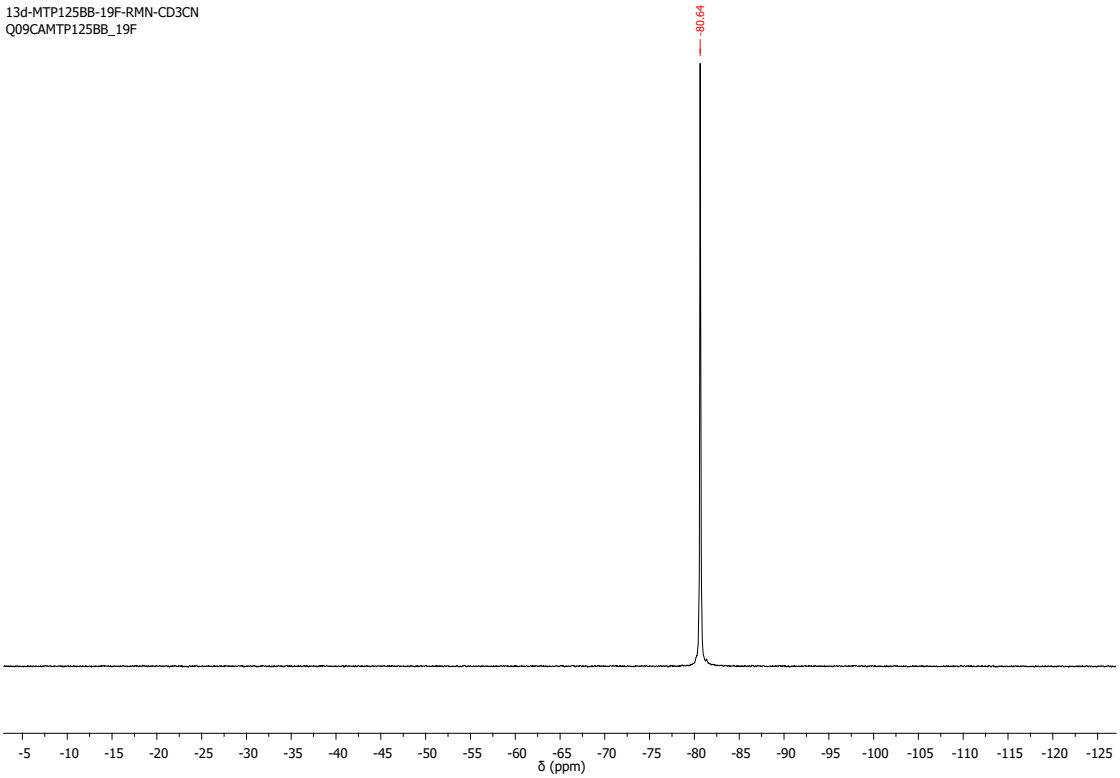
^{1}H NMR (300 MHz, CD_3CN, 25 °C)



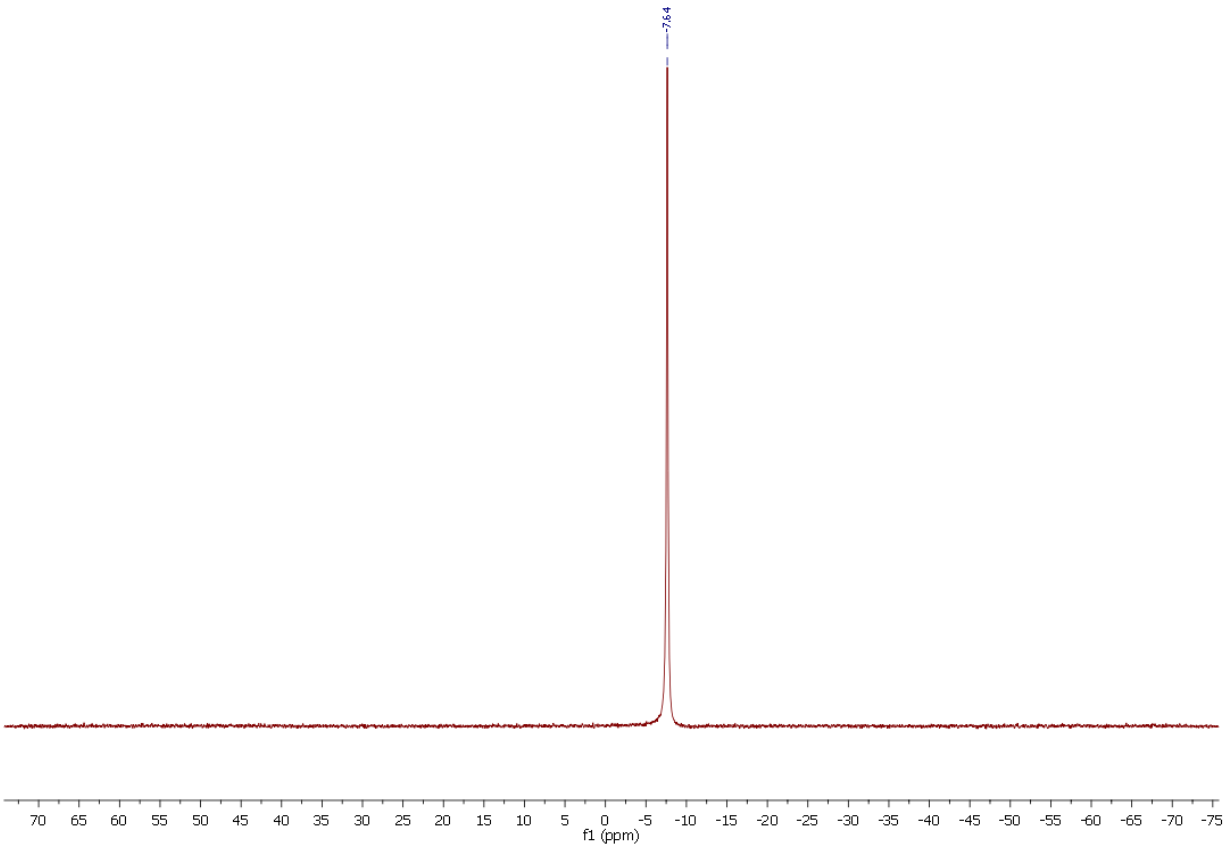
^{13}C NMR (75 MHz, CD_3CN, 25 °C)



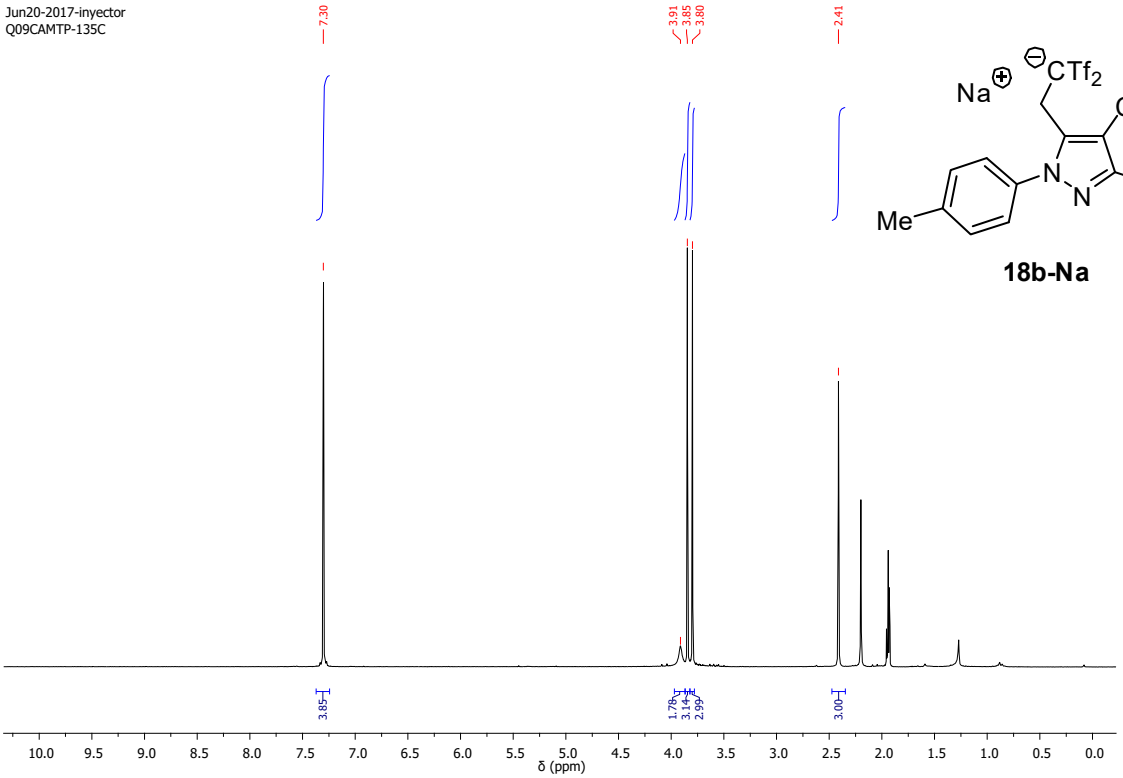
^{19}F NMR (282 MHz, CD_3CN, 25 ºC)



^{23}Na NMR (132 MHz, CD_3CN, 25 ºC)

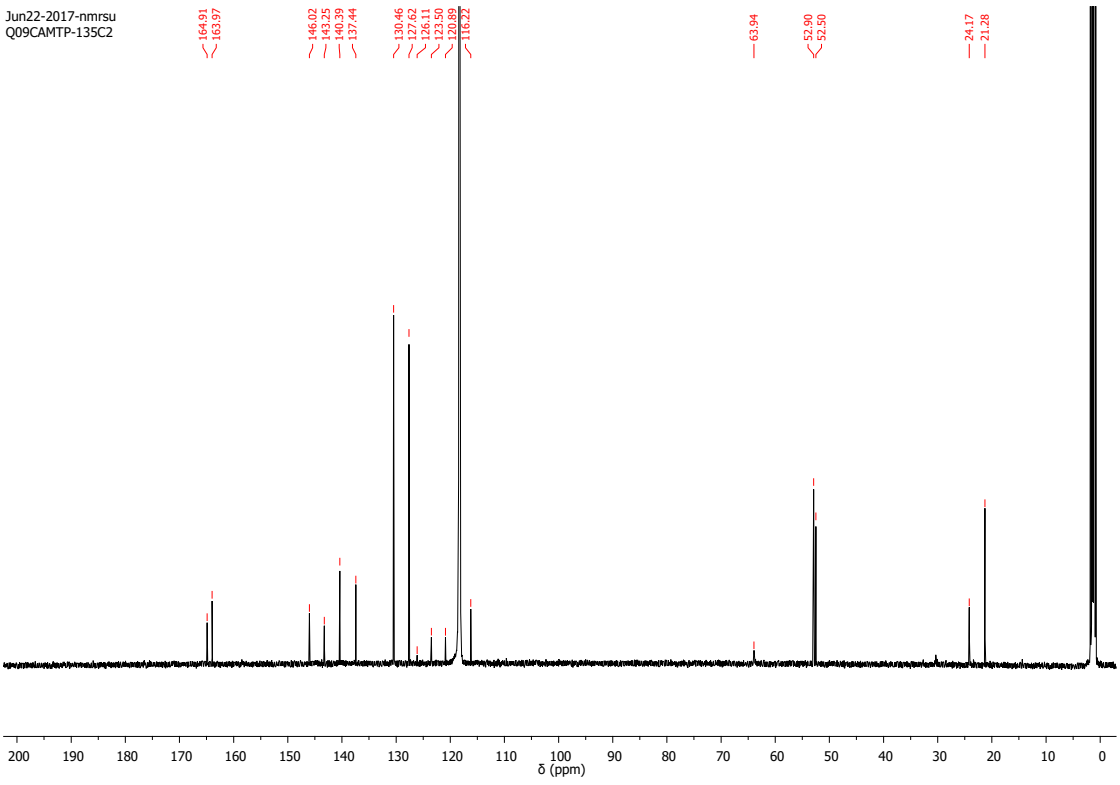


^{1}H NMR (500 MHz, CD_3CN, 25 ºC)

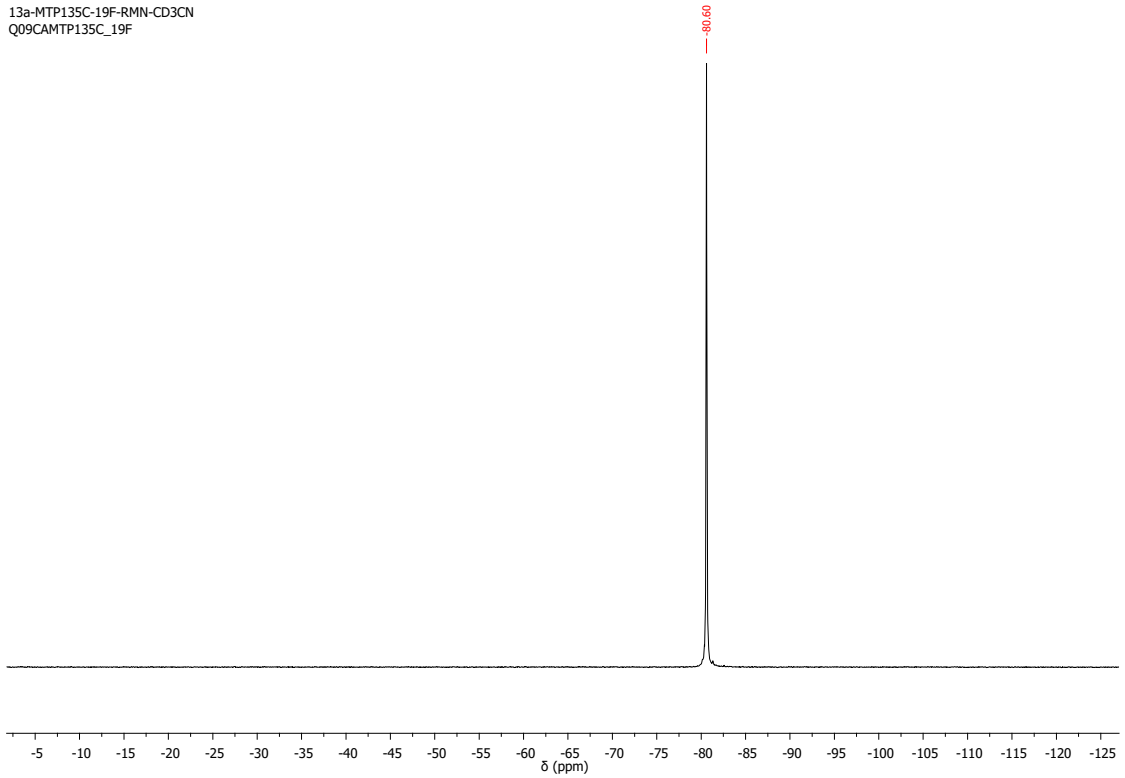


18b-Na

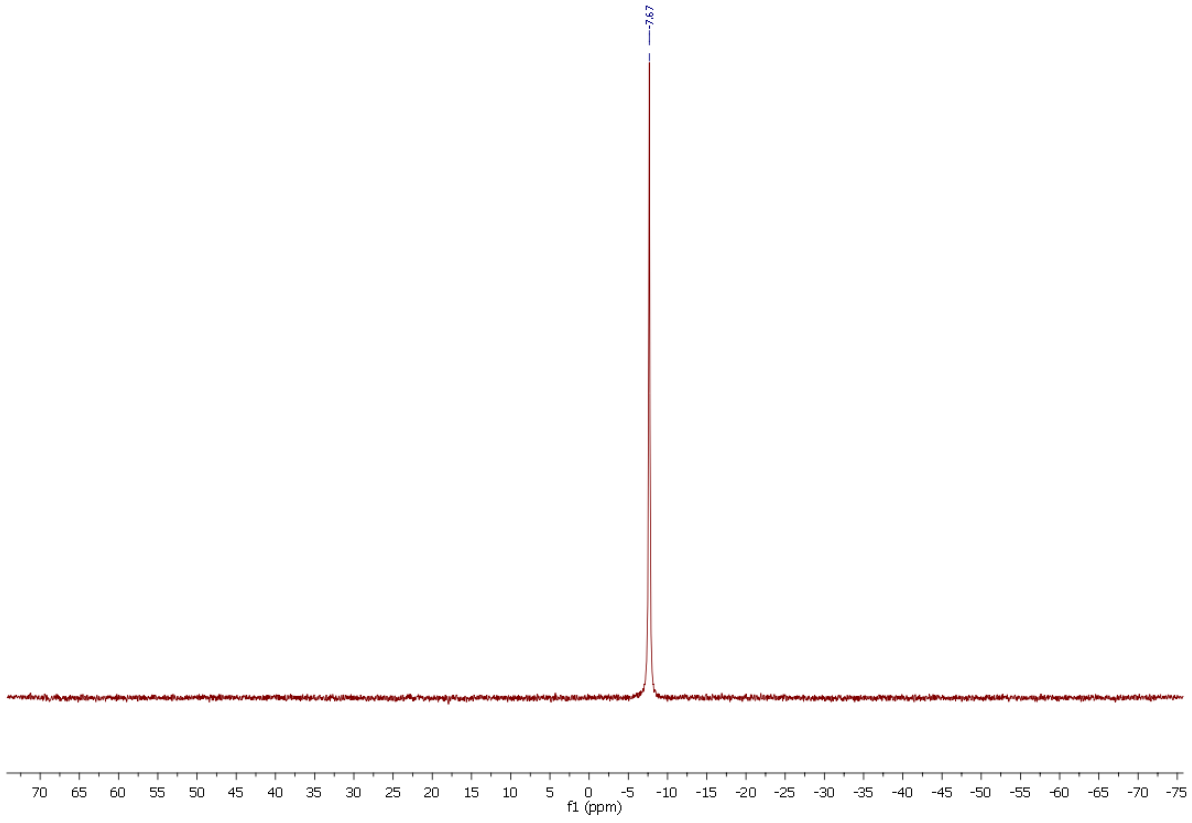
^{13}C NMR (125 MHz, CD_3CN, 25 ºC)



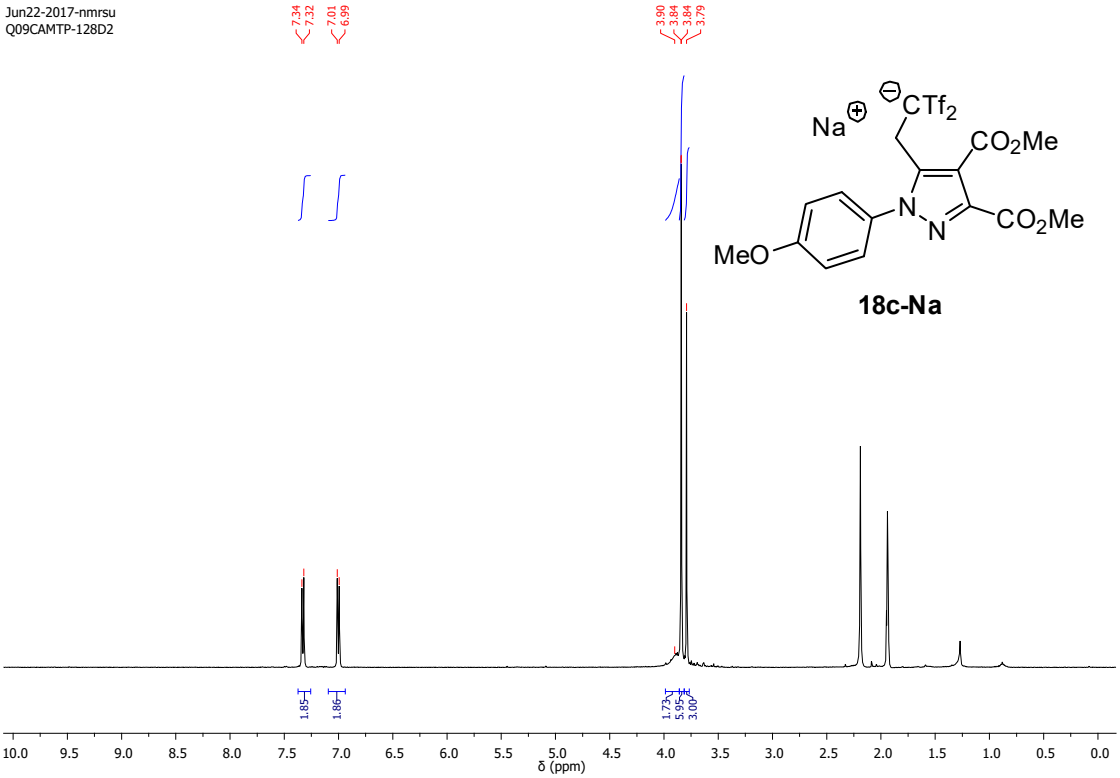
^{19}F NMR (282 MHz, CD_3CN, 25 ºC)



^{23}Na NMR (132 MHz, CD_3CN, 25 ºC)

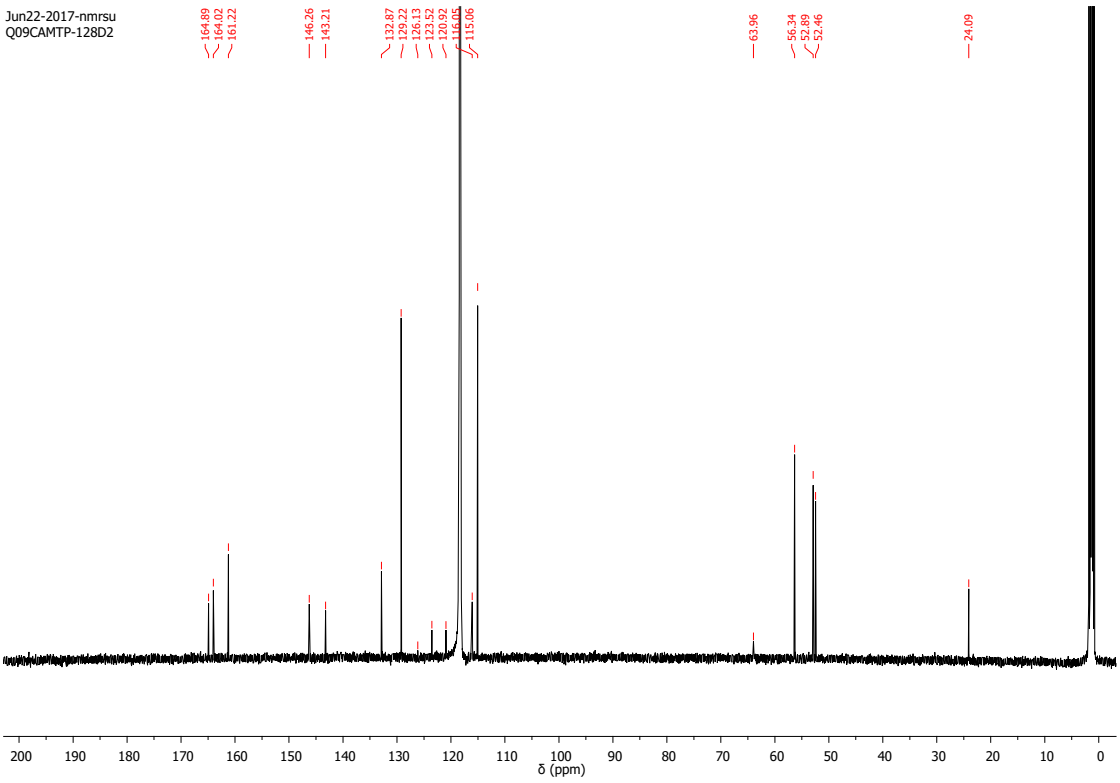


^{1}H NMR (500 MHz, CD_3CN, 25 °C)

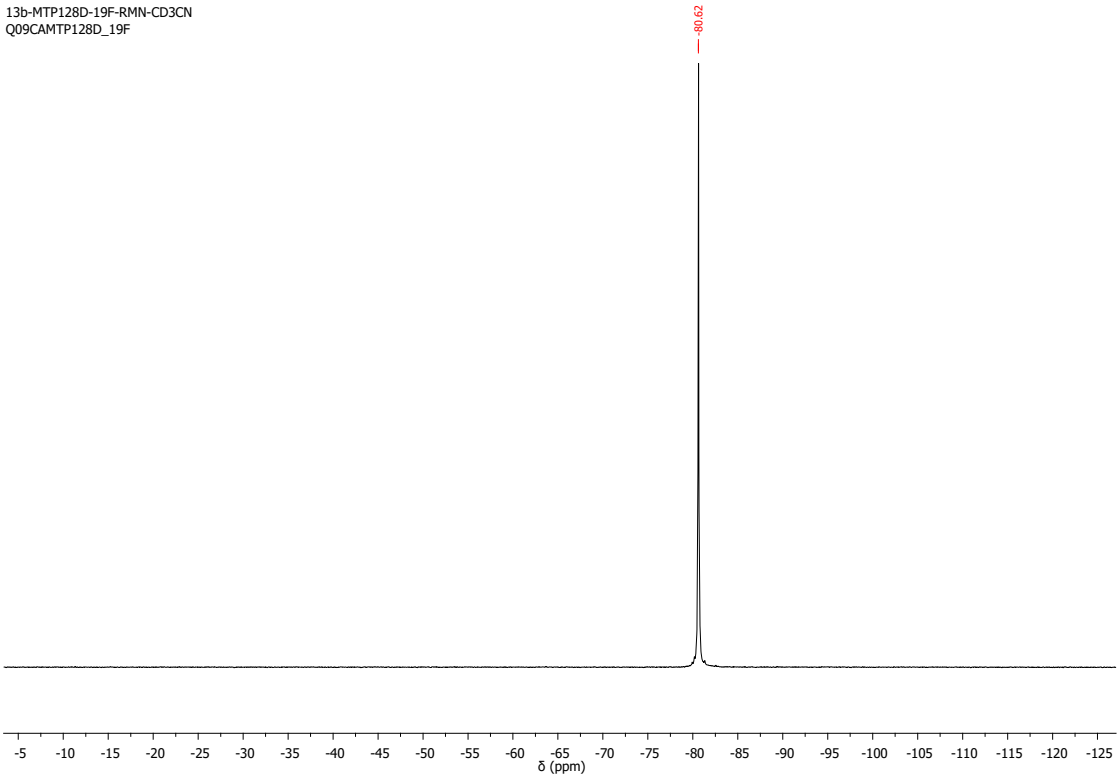


18c-Na

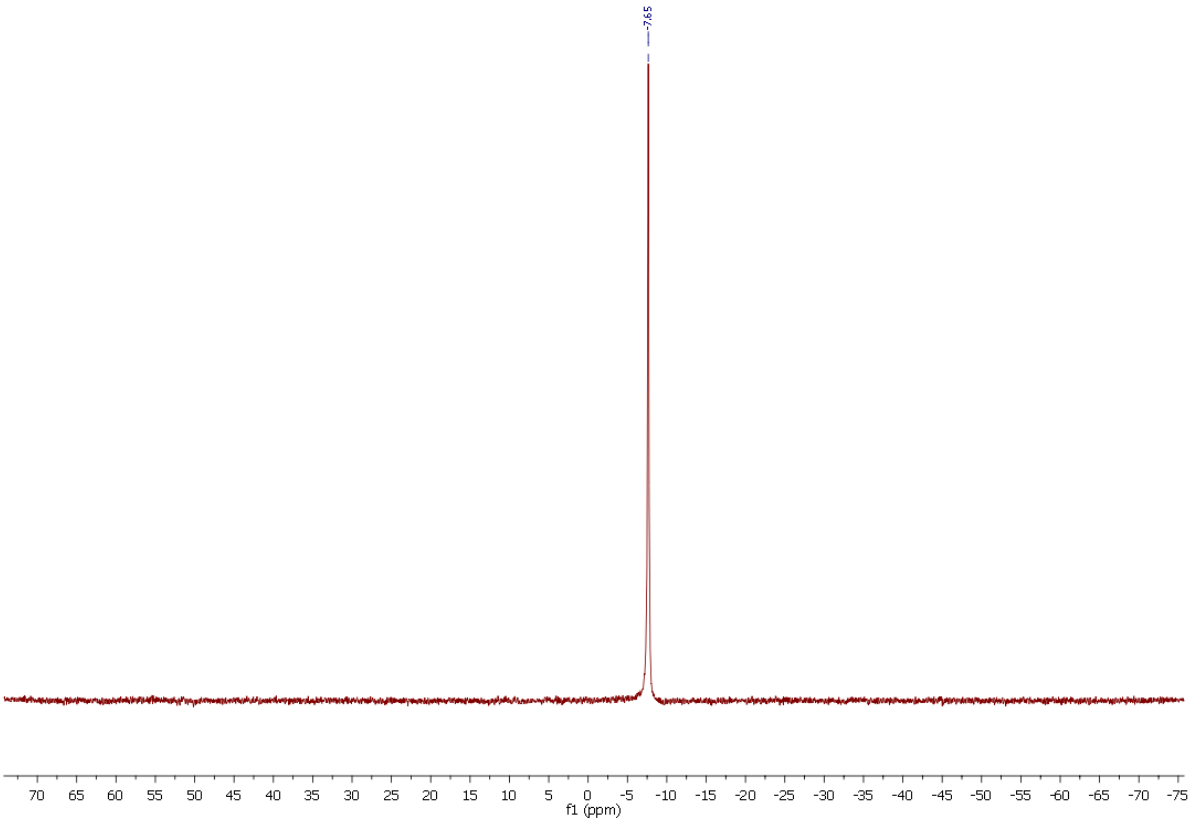
^{13}C NMR (125 MHz, CD_3CN, 25 °C)



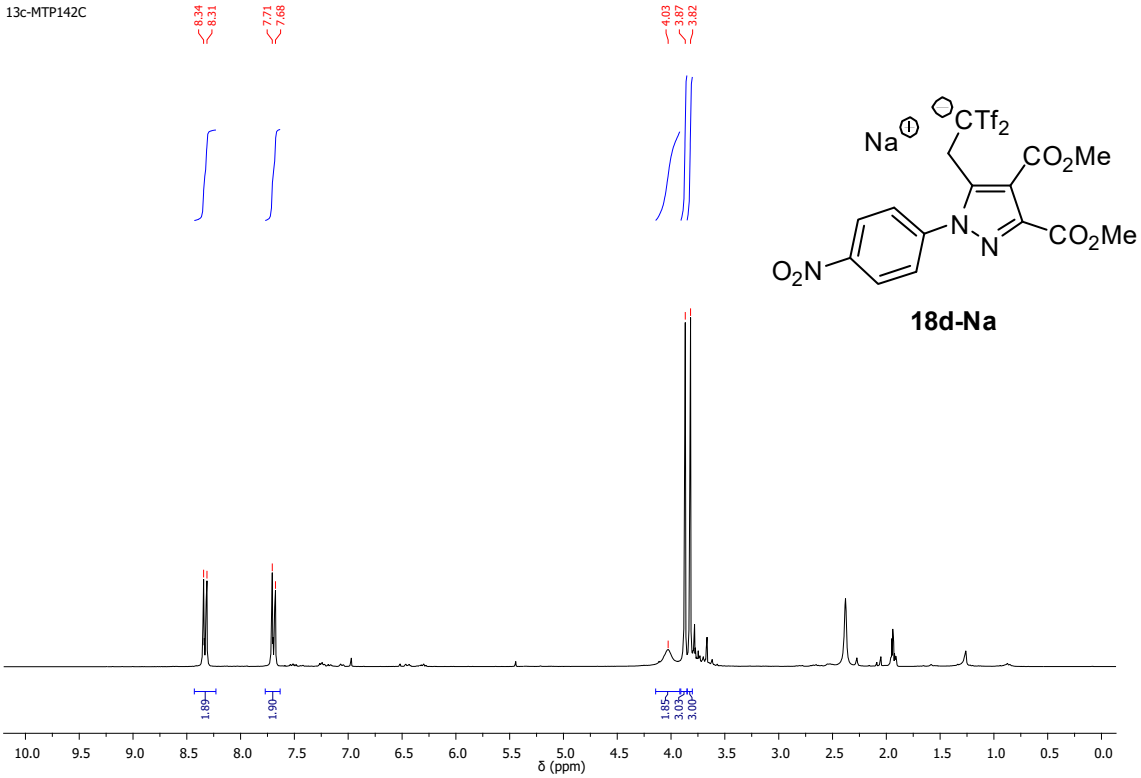
^{19}F NMR (282 MHz, CD_3CN, 25 ºC)



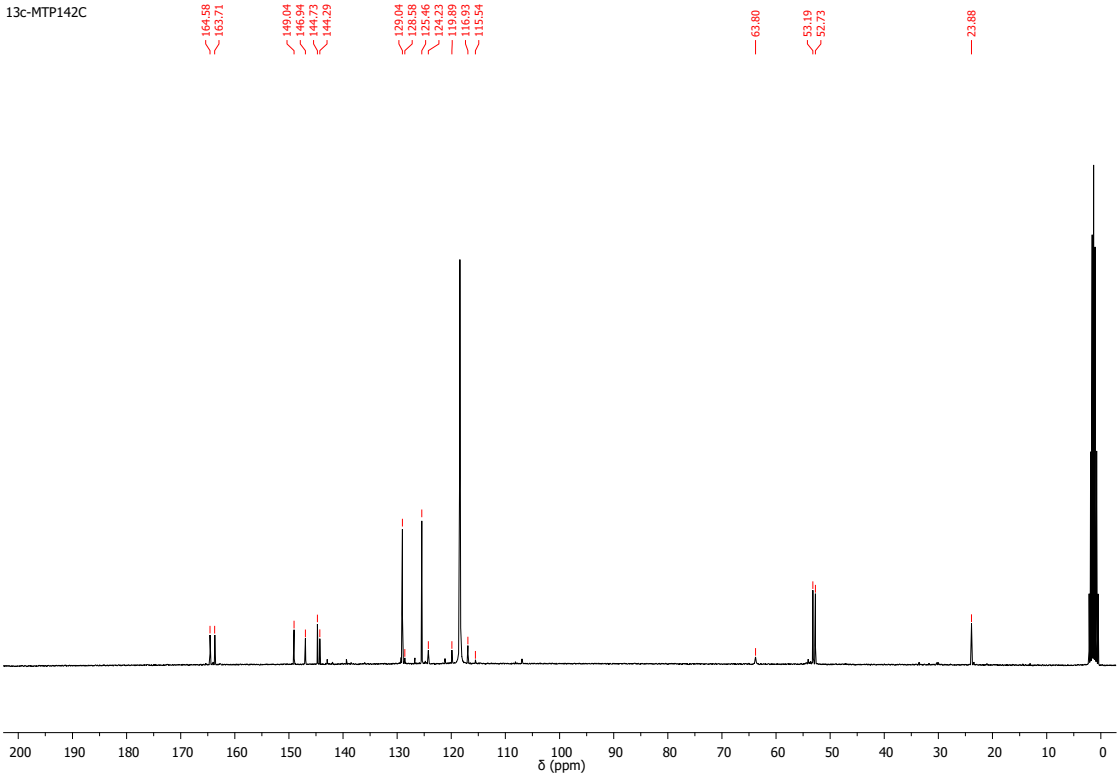
^{23}Na NMR (132 MHz, CD_3CN, 25 ºC)



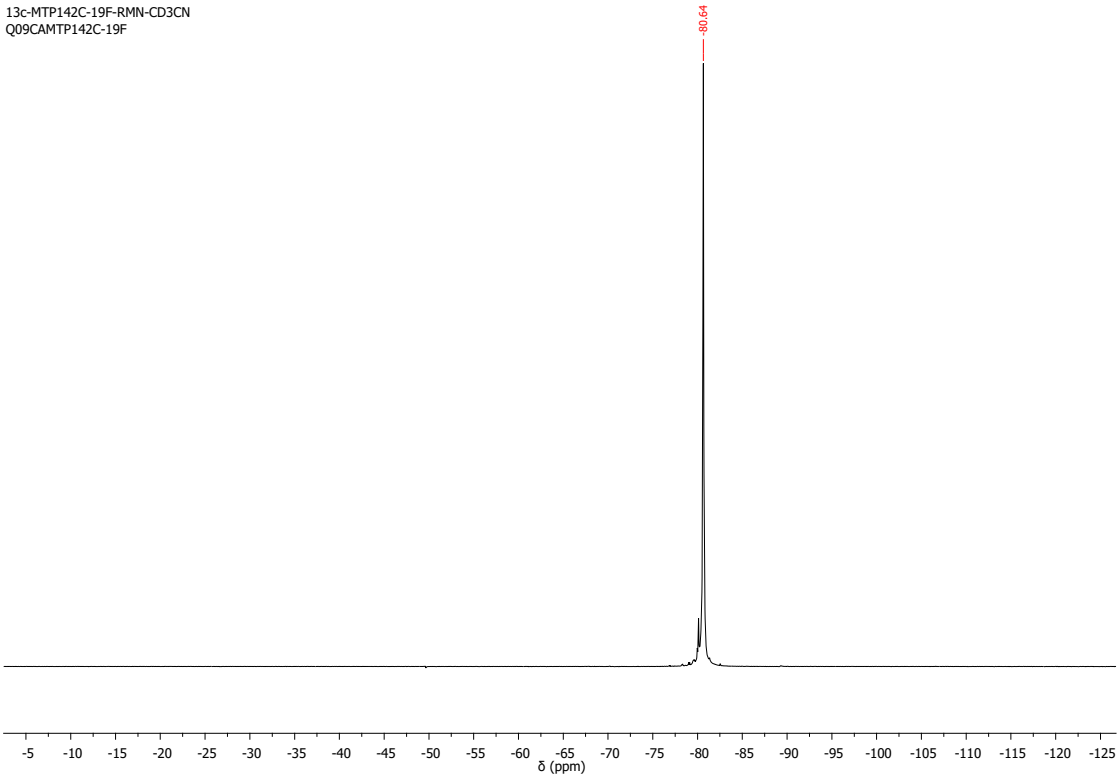
^{1}H NMR (300 MHz, CD_3CN, 25 °C)



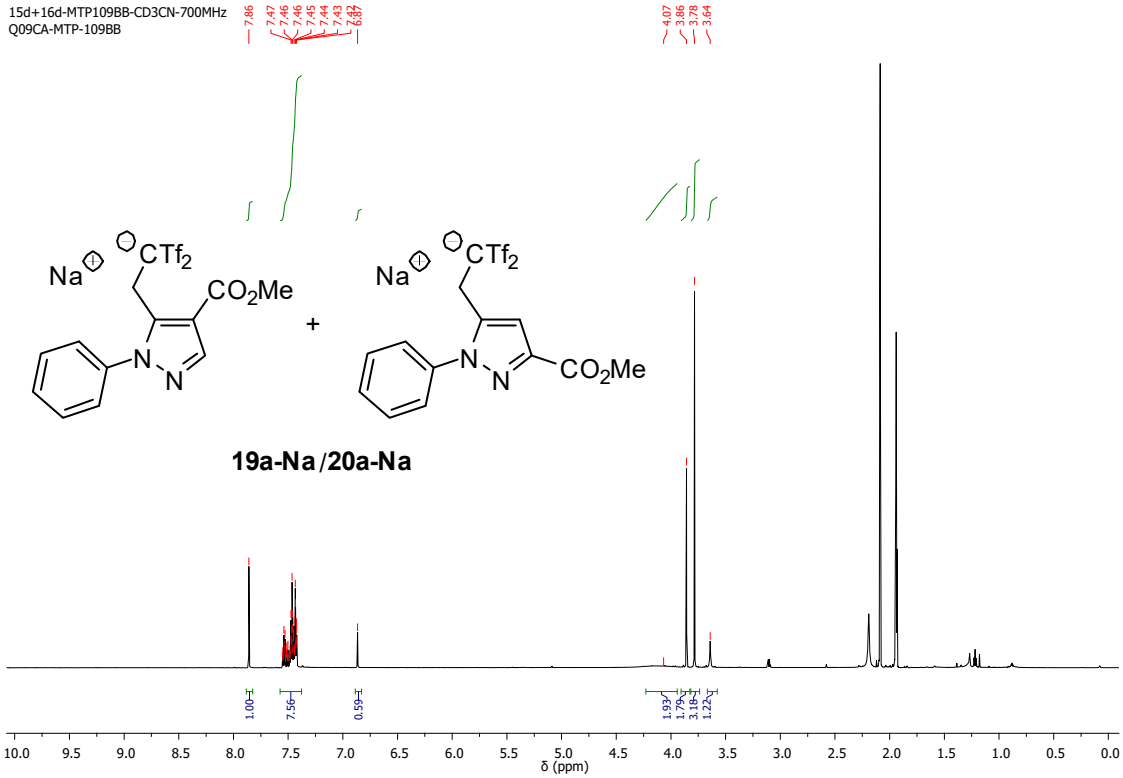
^{13}C NMR (75 MHz, CD_3CN, 25 °C)



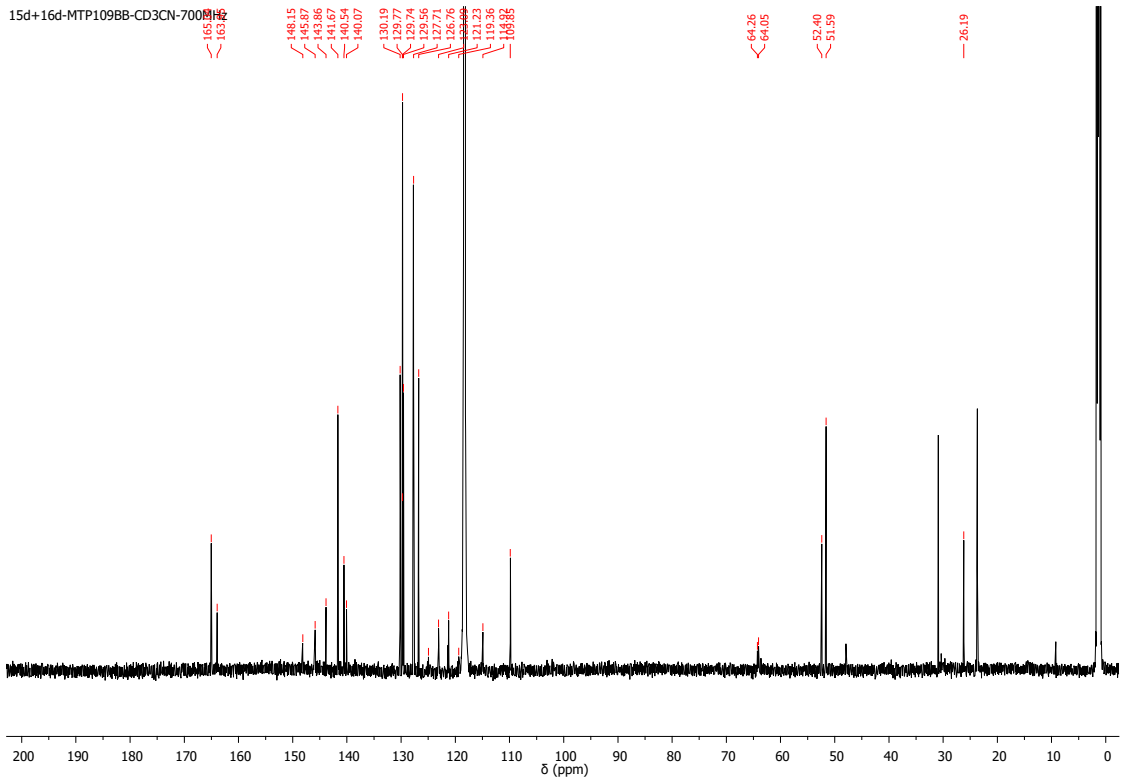
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



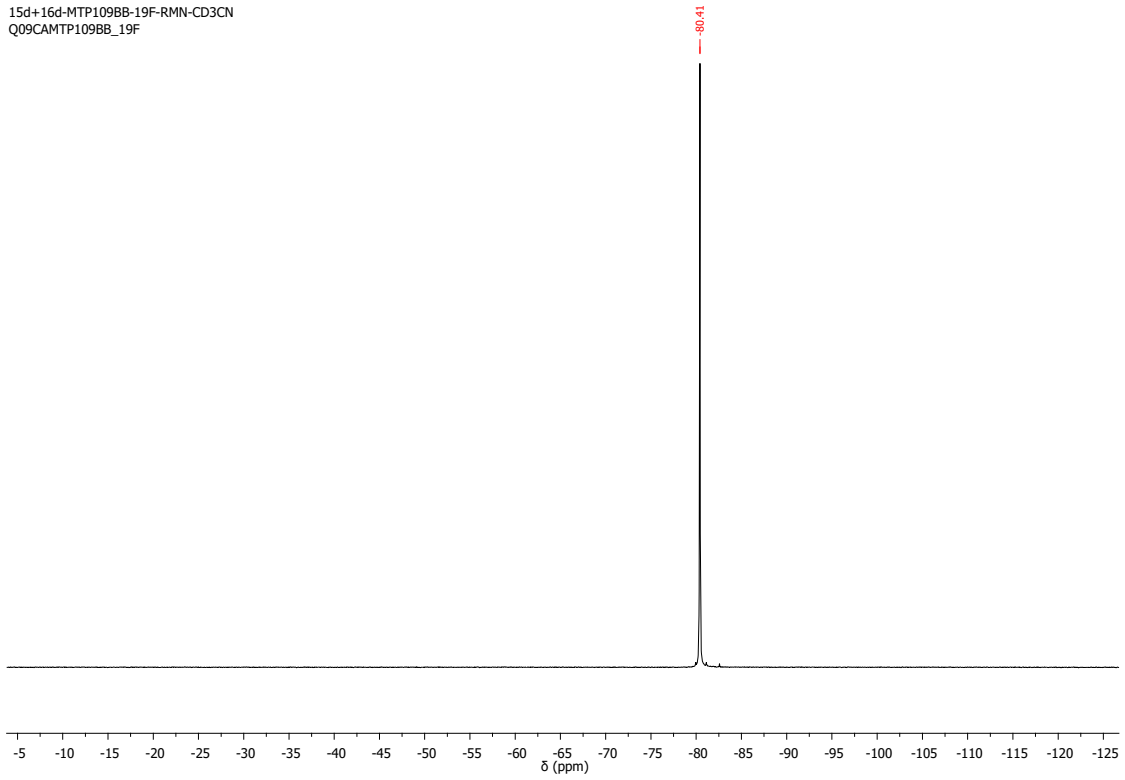
^{1}H NMR (700 MHz, CD_3CN, 25 °C)



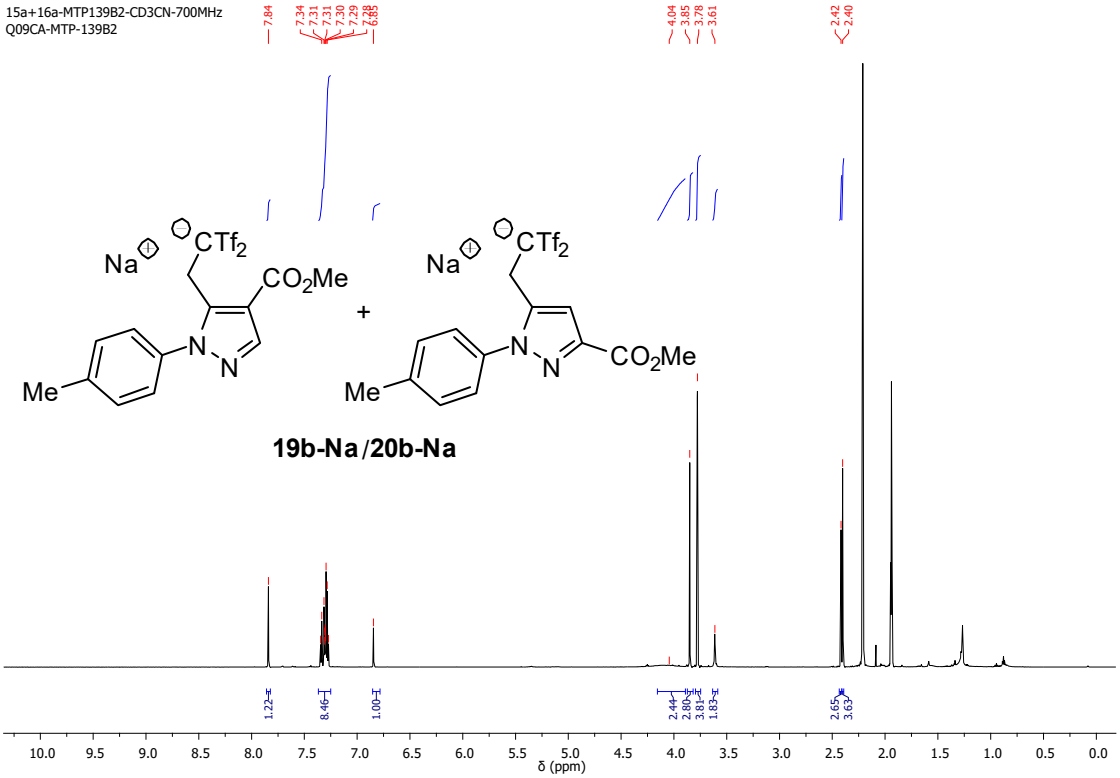
^{13}C NMR (175 MHz, CD_3CN, 25 °C)



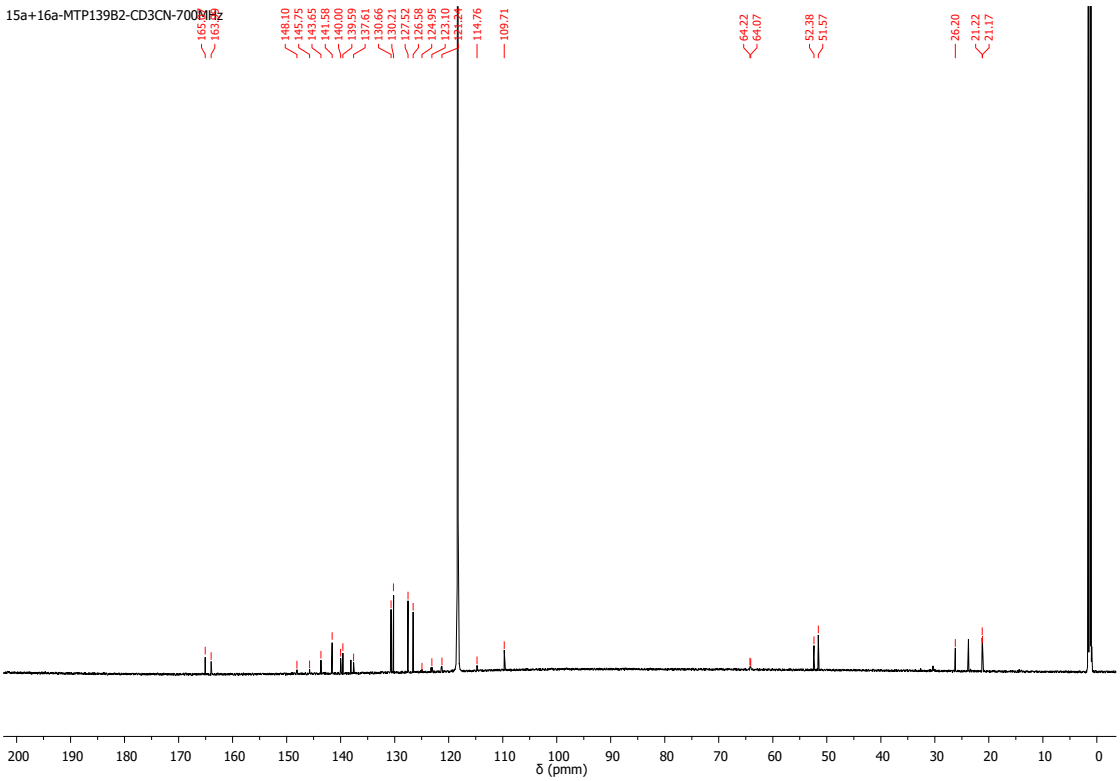
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



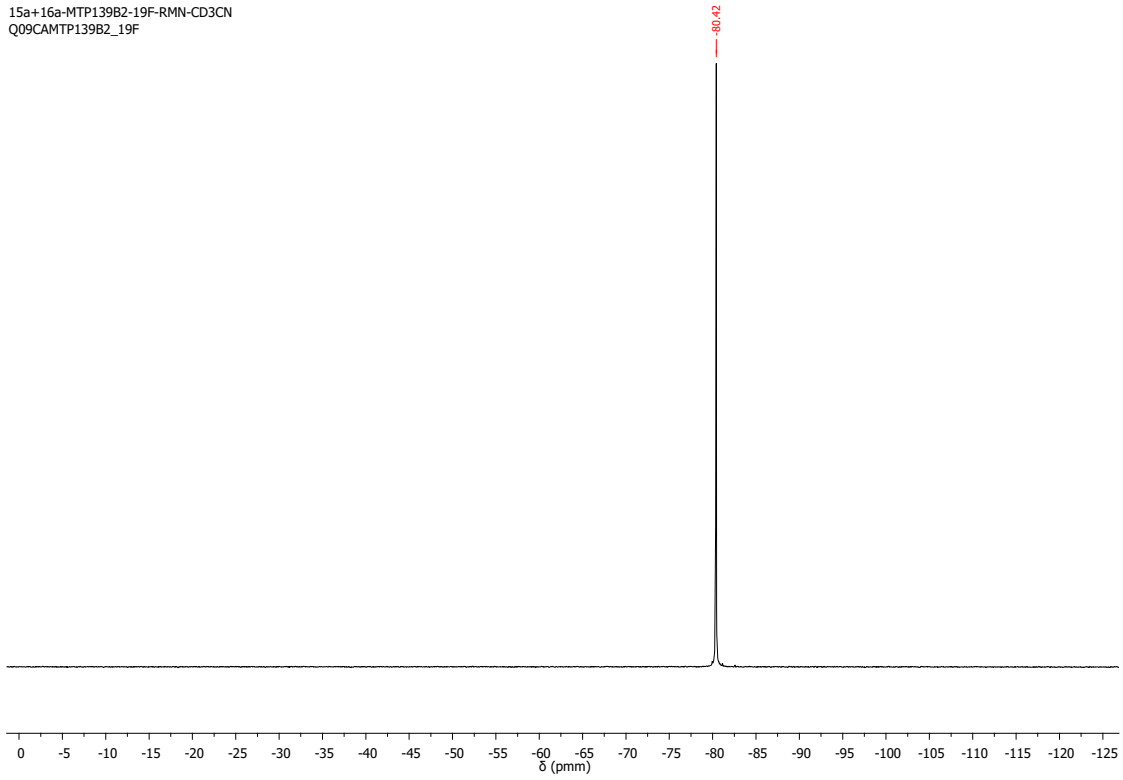
^{1}H NMR (700 MHz, CD_3CN, 25 °C)



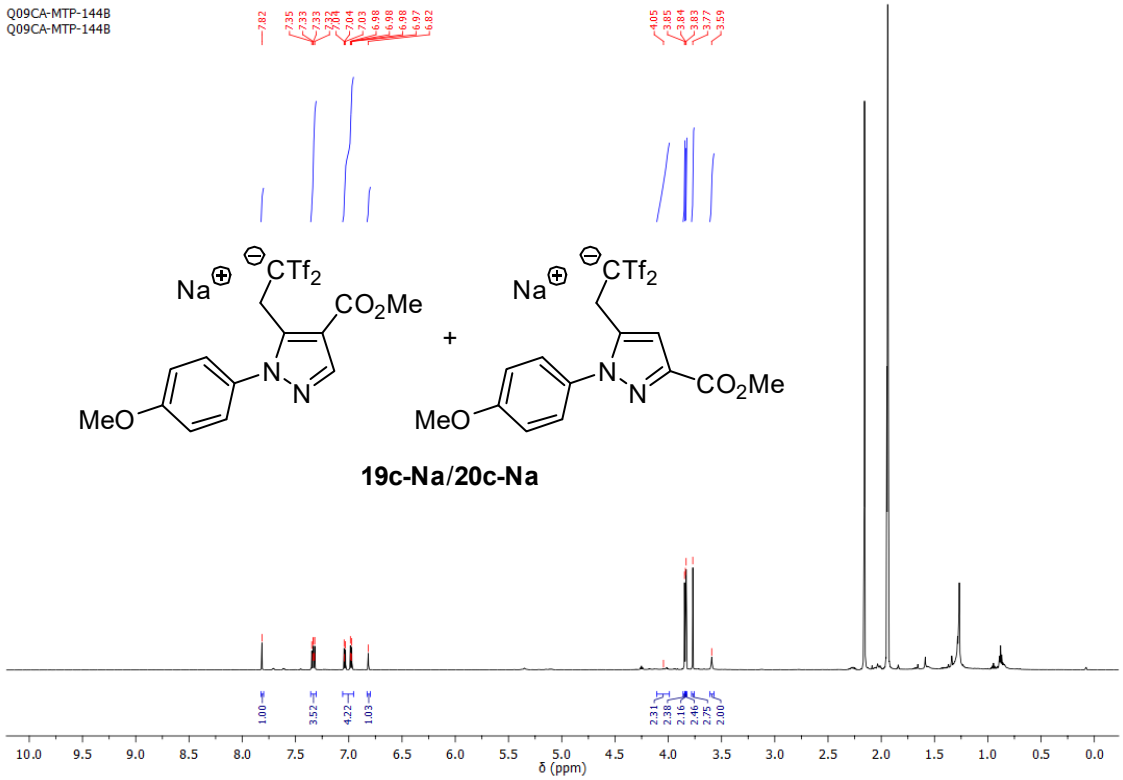
^{13}C NMR (175 MHz, CD_3CN, 25 °C)



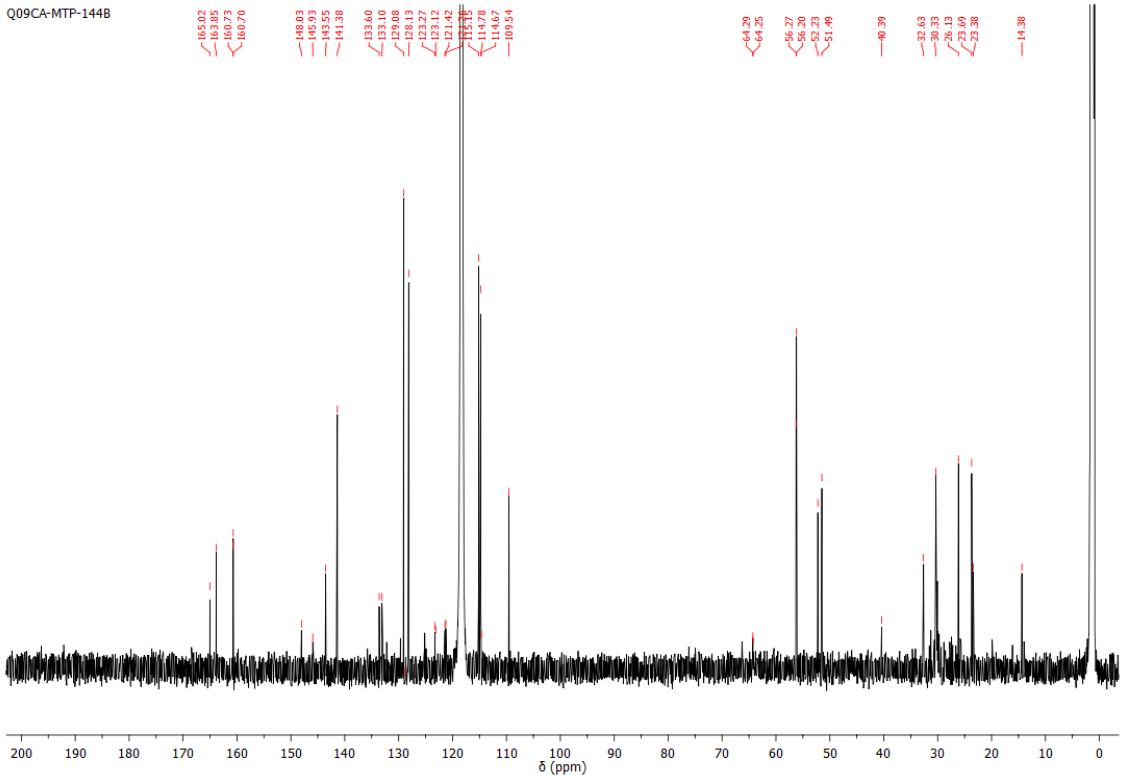
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



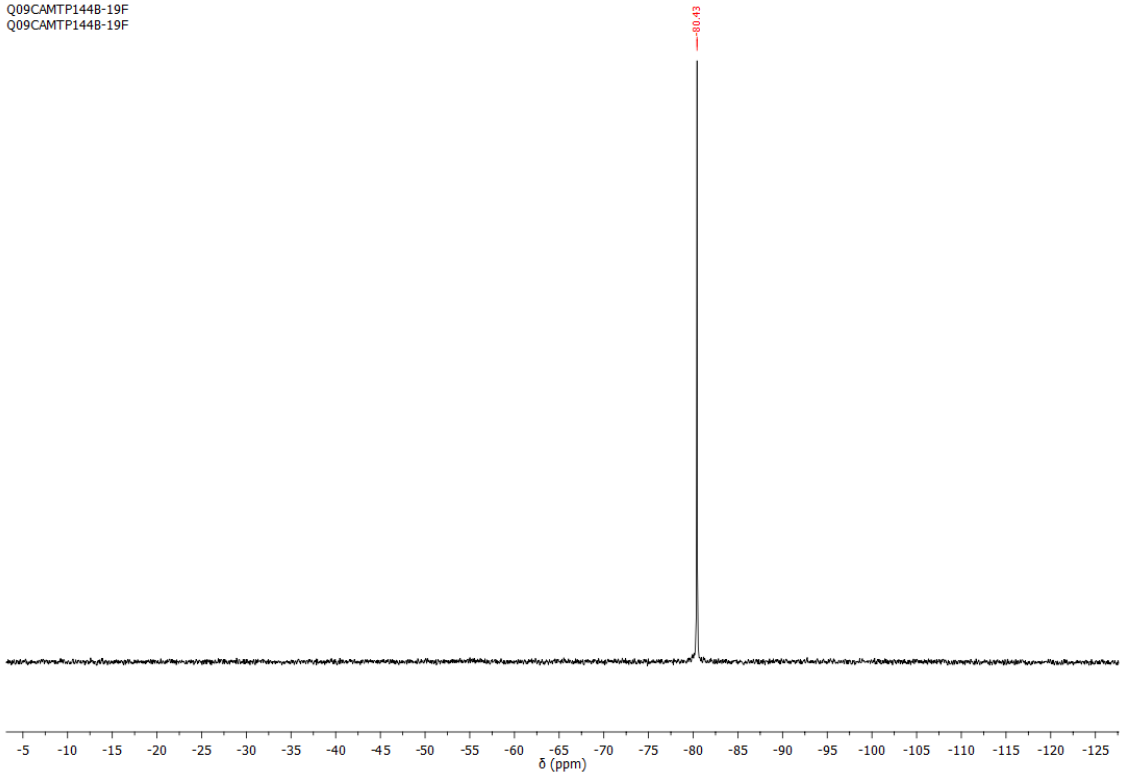
^{1}H NMR (700 MHz, CD_3CN, 25 °C)



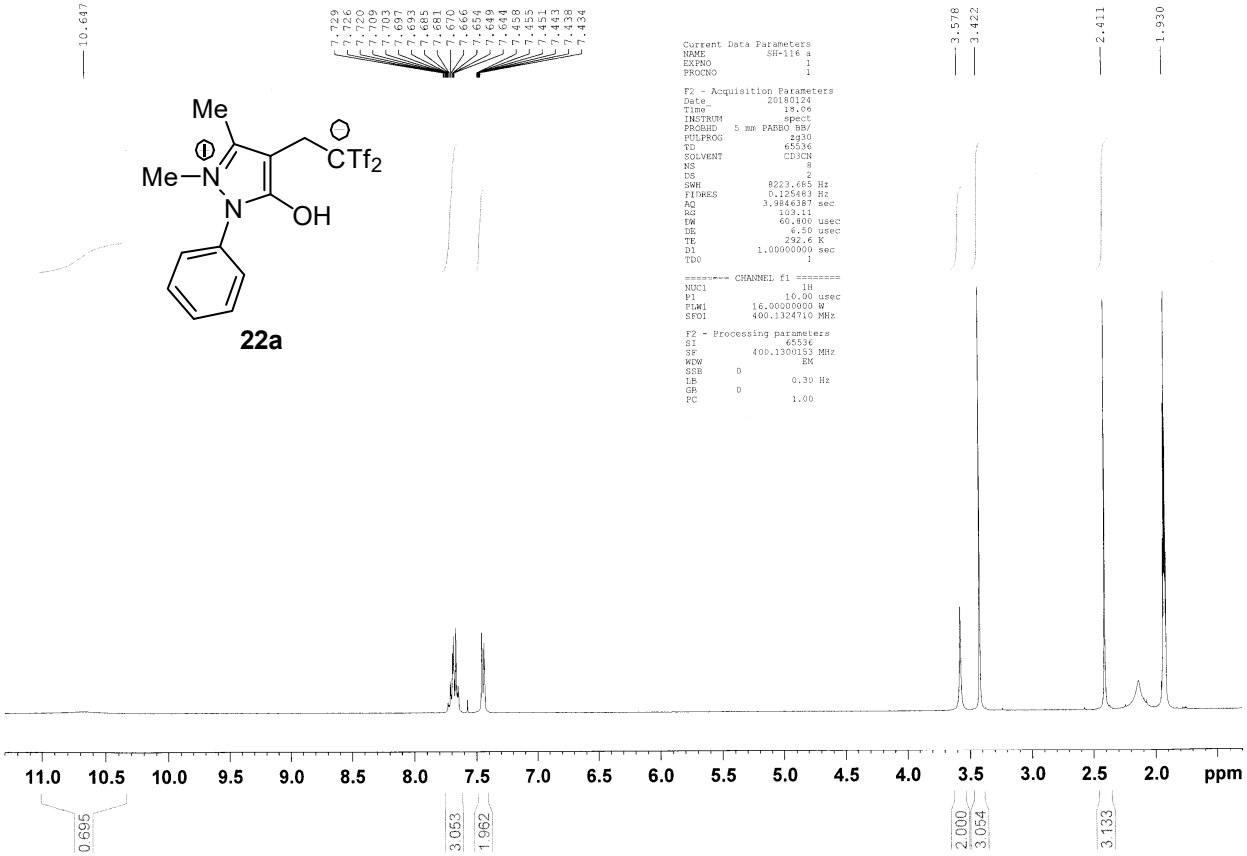
^{13}C NMR (175 MHz, CD_3CN, 25 °C)



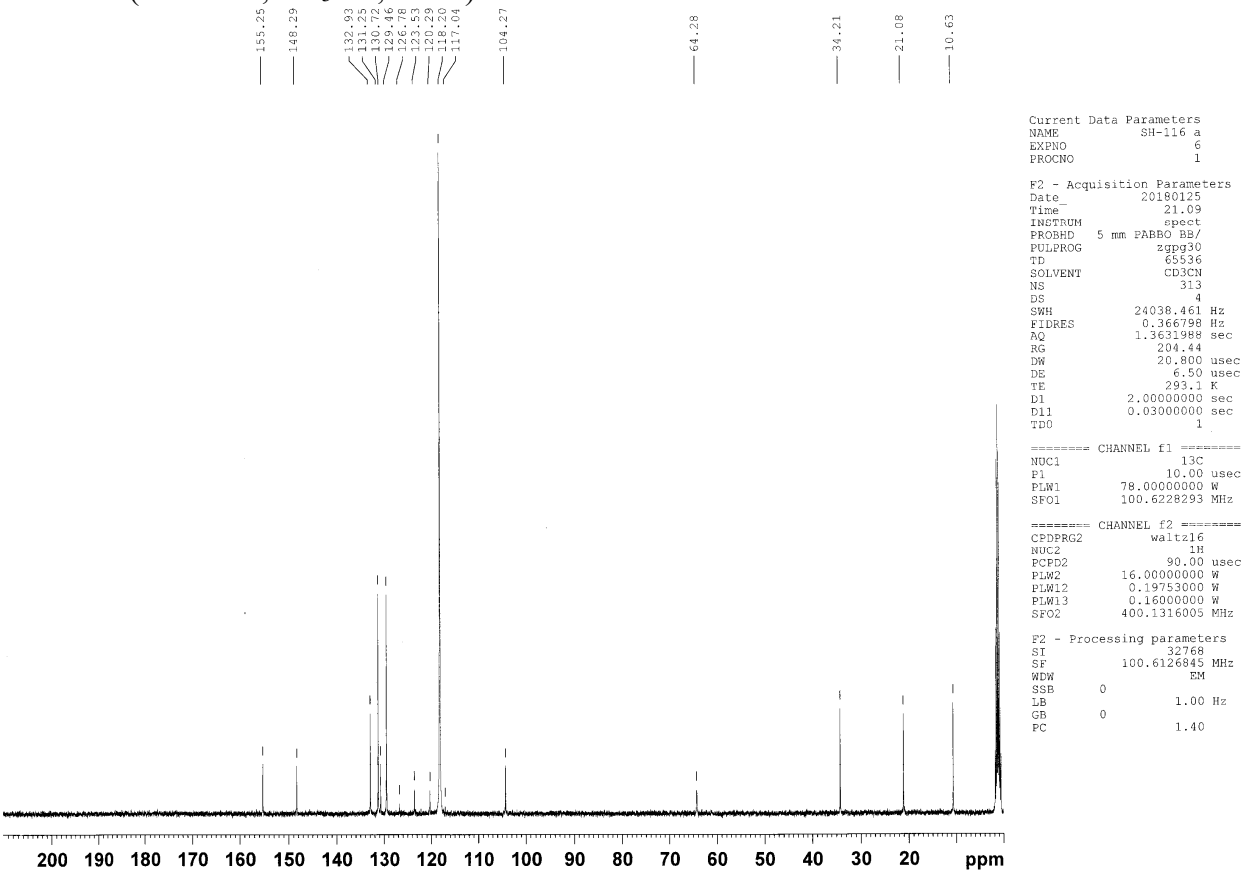
^{19}F NMR (282 MHz, CD_3CN, 25 °C)



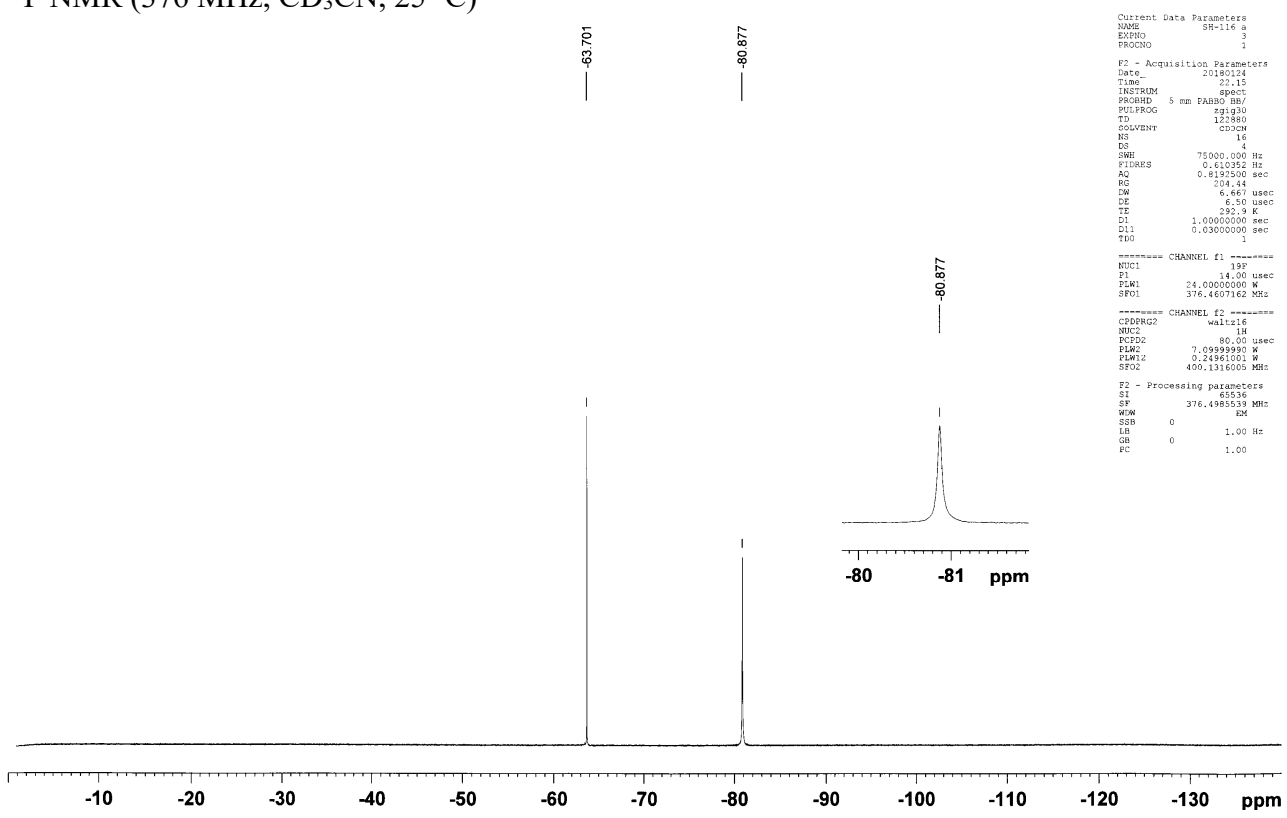
^{1}H NMR (400 MHz, CD_3CN, 25 ºC)



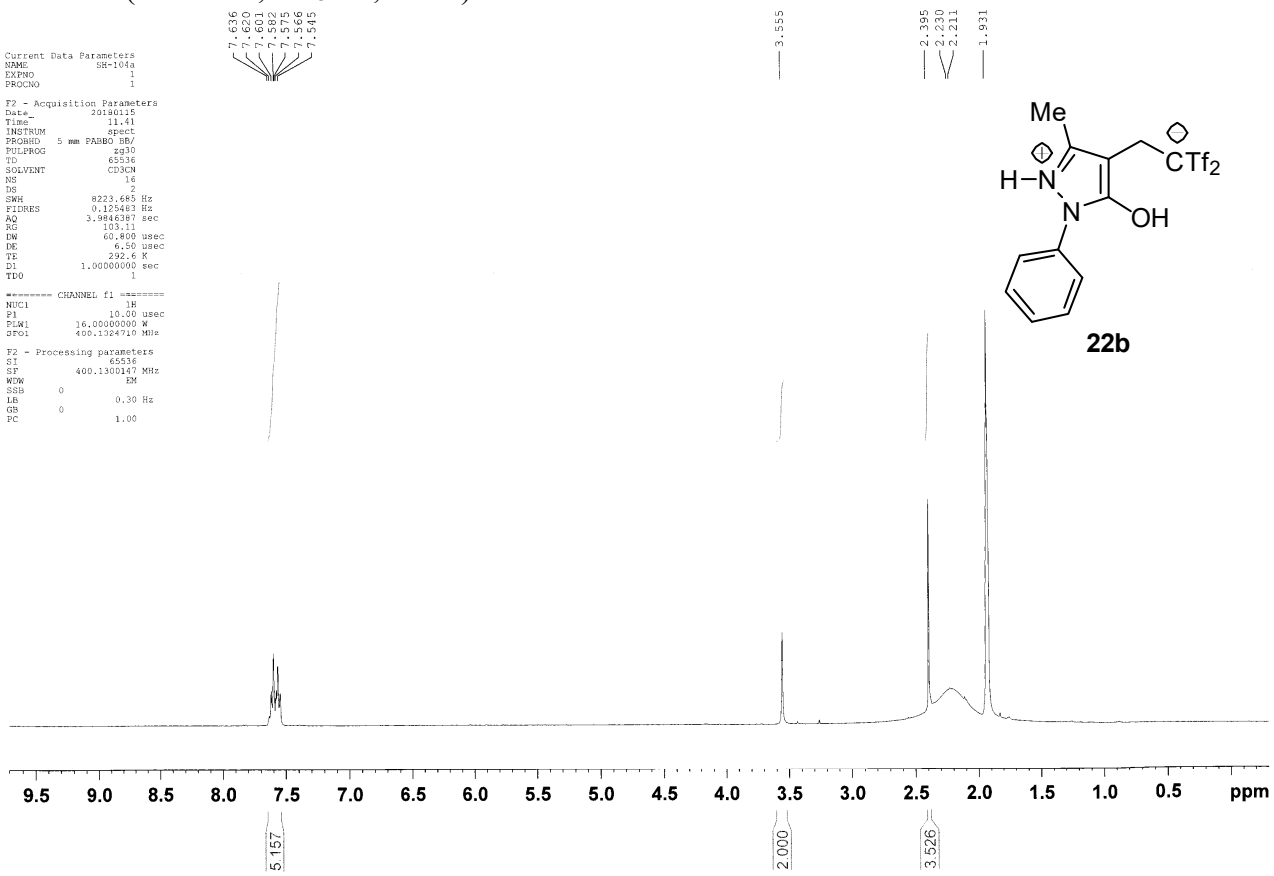
^{13}C NMR (100 MHz, CD_3CN, 25 ºC)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)



^{1}H NMR (400 MHz, CD_3CN, 25 ºC)



Current Data Parameters
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EXPNO 1
PROCNO 1

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PULPROG zg30
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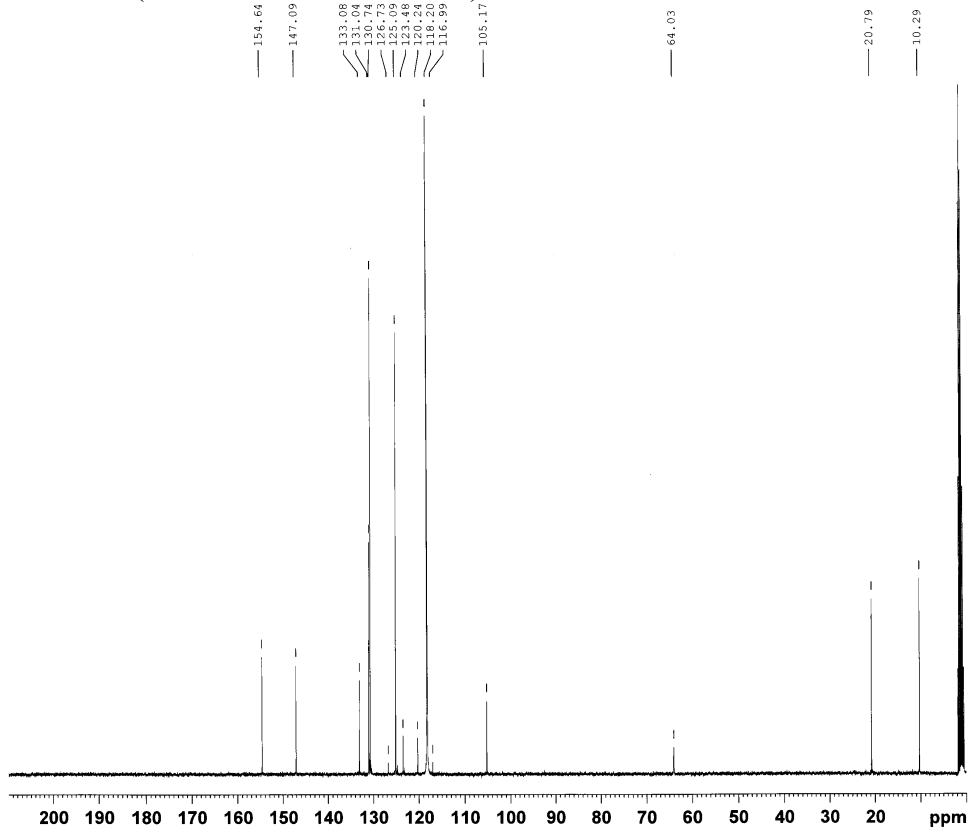
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 103.11
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR (100 MHz, CD_3CN, 25 ºC)



Current Data Parameters
NAME SH-104a
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180116
Time 12.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 276
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.19753000 W
PLW13 0.16000000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
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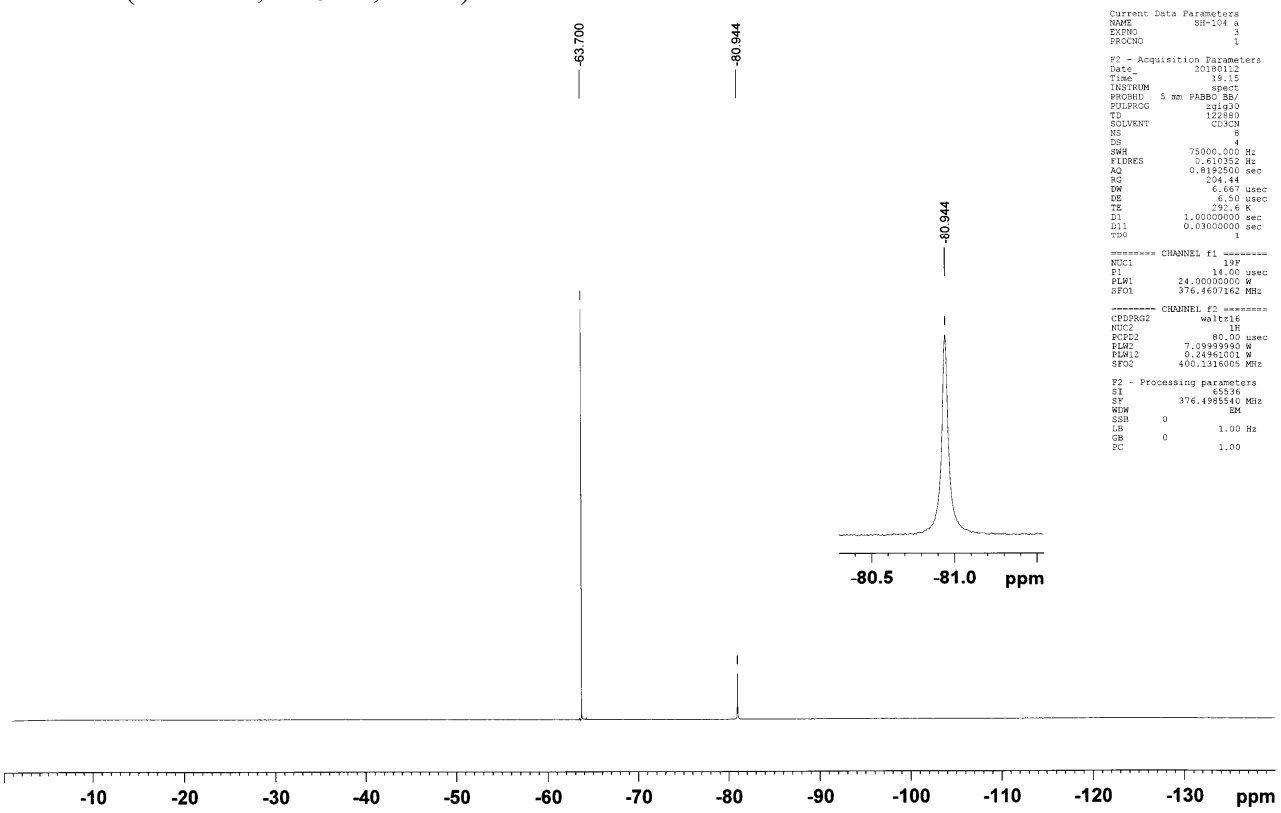
SF 100.6126890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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Current Data Parameters
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EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
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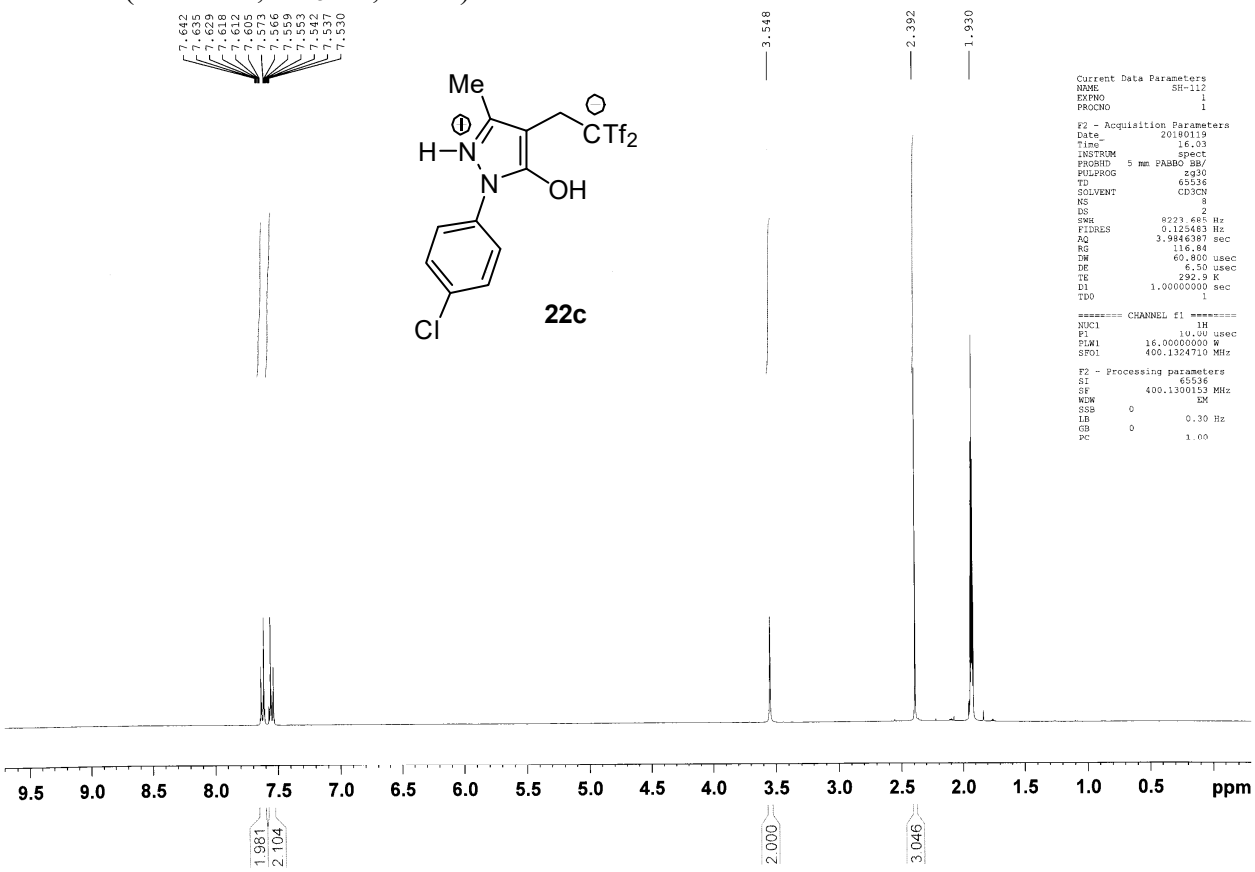
Time               19.15
INSTRUM            spect
PROBHD     5 mm PABBO BB/
PULPROG            zgig30
TD                 122880
SOLVENT            CD3CN
NS                      8
DS                      4
SWH                75000.000 Hz
FIDRES             0.610352 Hz
AQ                 0.8192500 sec
RG                    204.44
DW                    6.667 usec
DE                    6.50 usec
TE                    292.6 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       19F
P1                       14.00 usec
PLW1               24.00000000 W
SFO1               376.4607162 MHz

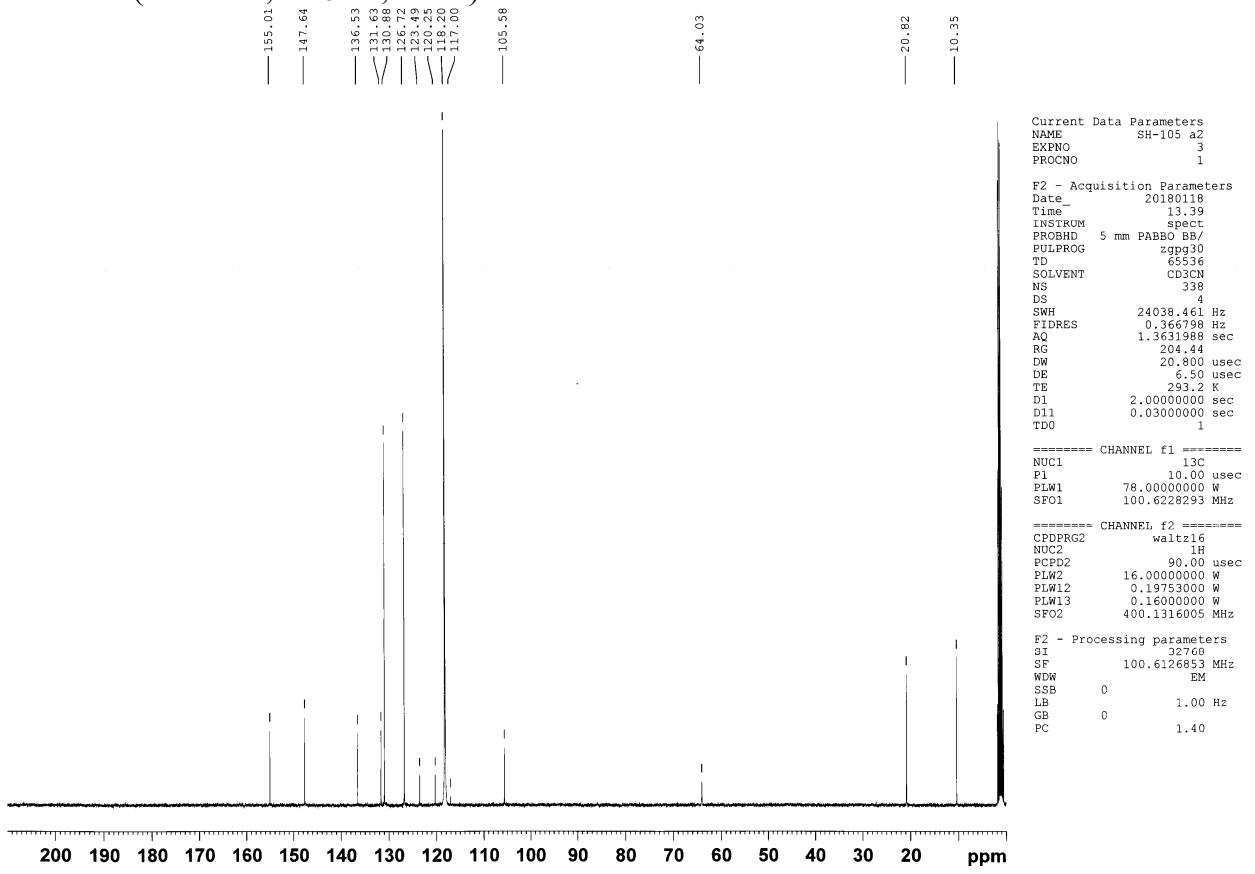
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    80.00 usec
PLW2               7.09999990 W
PLW12              0.24962001 W
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                        65536
SF                 376.4985540 MHz
WDW                          EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.00
```

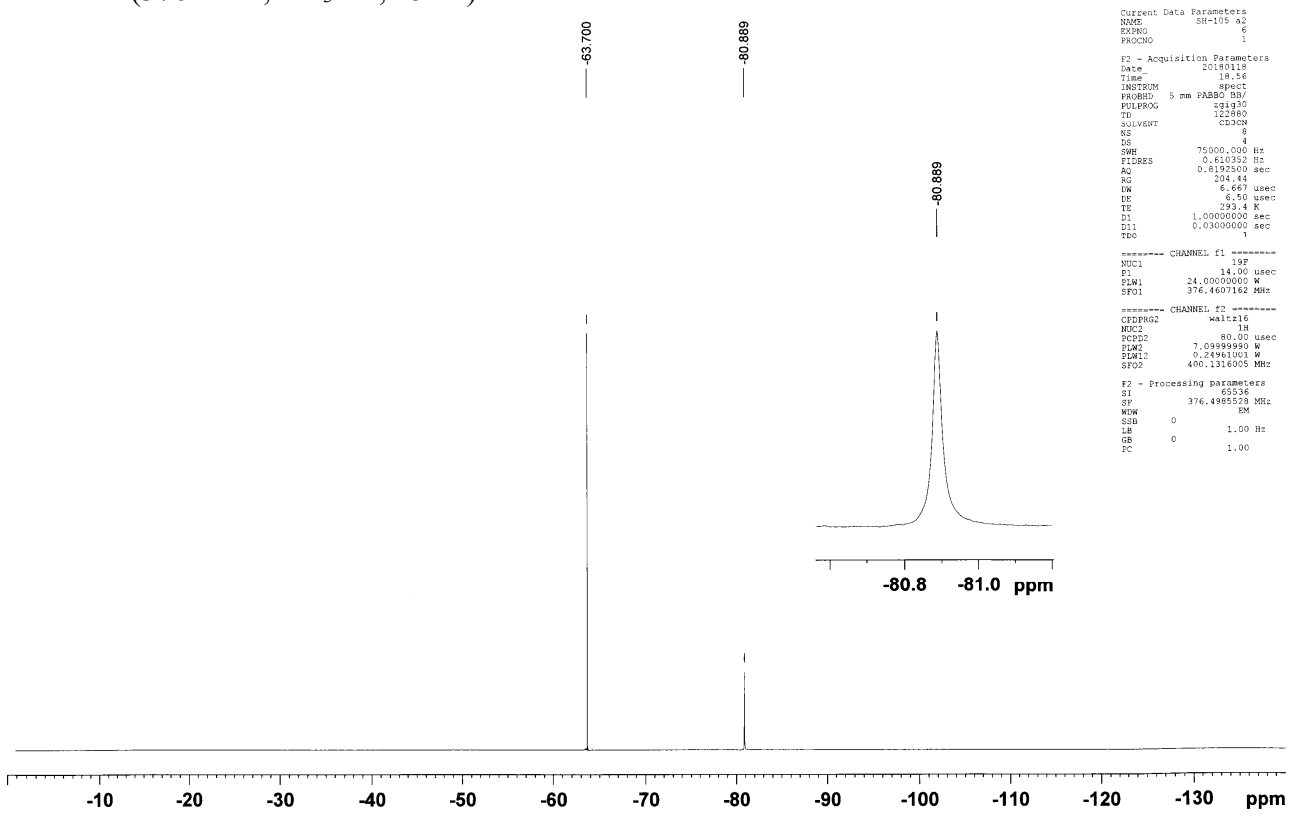
^{1}H NMR (400 MHz, CD_3CN, 25 °C)



^{13}C NMR (100 MHz, CD_3CN, 25 °C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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Current Data Parameters
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EXPNO                         6
PROCNO                        1

F2 - Acquisition Parameters
Date_               20180118
Time                   18.56
INSTRUM                 spect
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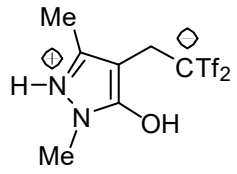
PULPROG                zgig30
TD                     122880
SOLVENT                CD3CN
NS                          8
DS                          4
SWH                75000.000 Hz
FIDRES                 0.610352 Hz
AQ                     0.8192500 sec
RG                       204.44
DW                        6.667 usec
DE                        6.50 usec
TE                       293.4 K
D1                     1.00000000 sec
D11                    0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        19F
P1                        14.00 usec
PLW1                24.00000000 W
SFO1                376.4607162 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PLW2                 7.09999990 W
PLW12                0.24961001 W
SFO2                400.1316005 MHz

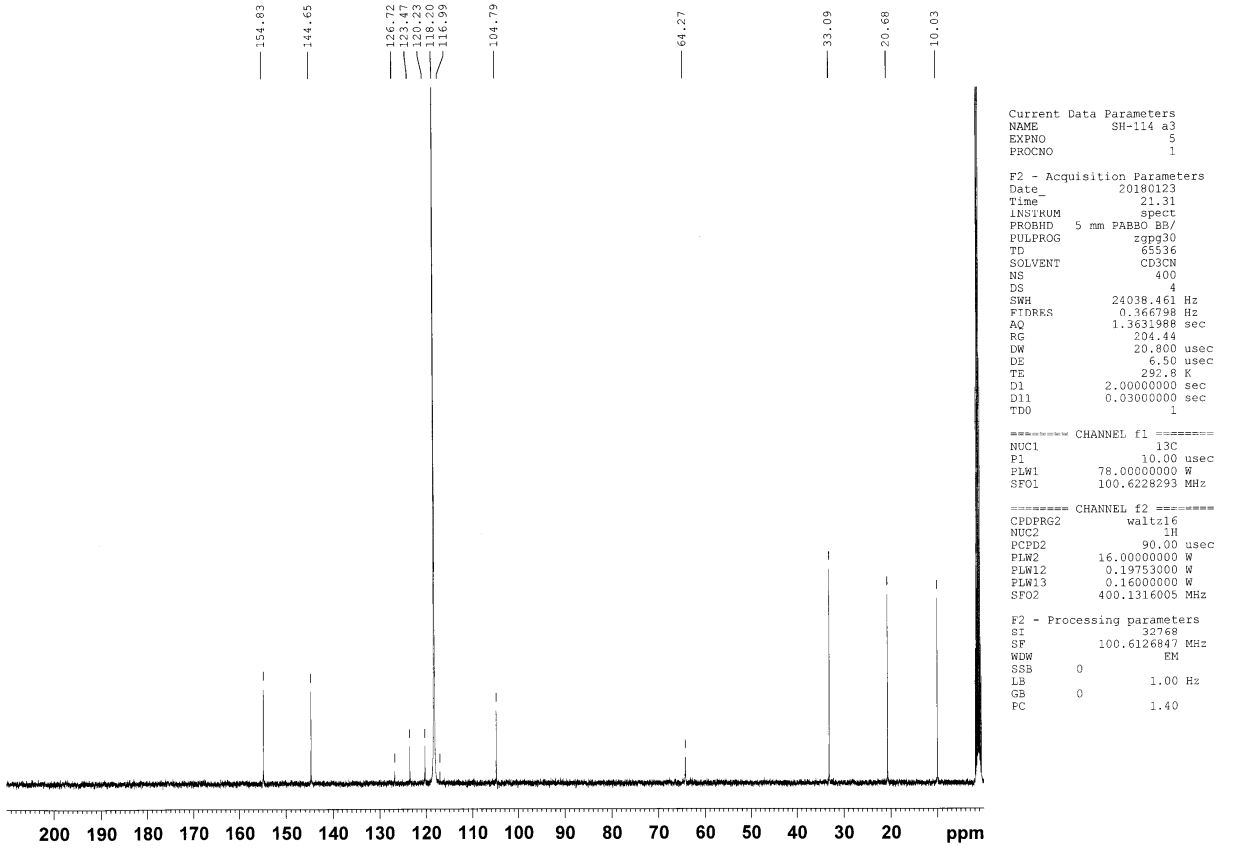
F2 - Processing parameters
SI                          65536
SF                  376.4985528 MHz
WDW                            EM
SSB                 0
LB                        1.00 Hz
GB                  0
PC                        1.00
```

^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C)

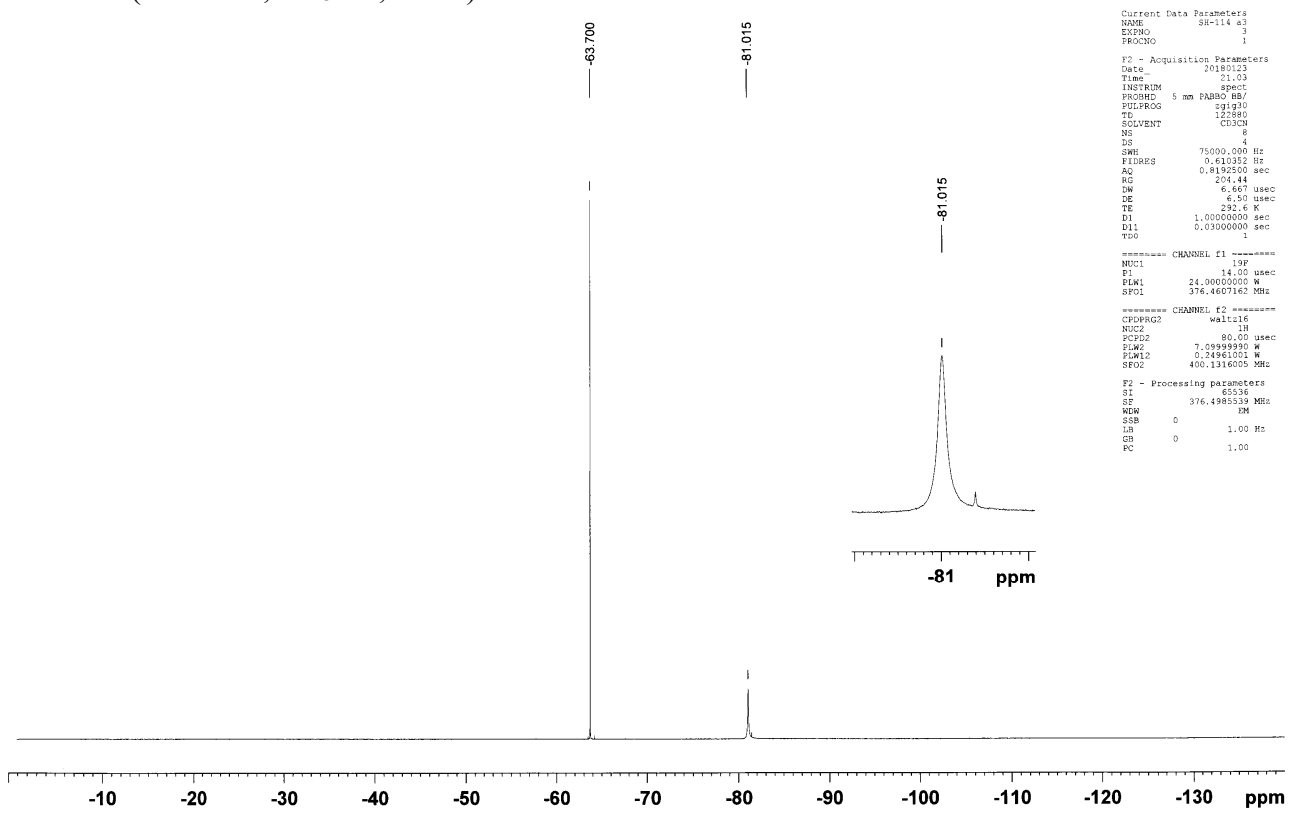


22d

^{13}C NMR (100 MHz, CD_3CN, 25 ^{o}C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)

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Current Data Parameters
NAME            SH-114 a3
EXPNO                    3
PROCNO                   1

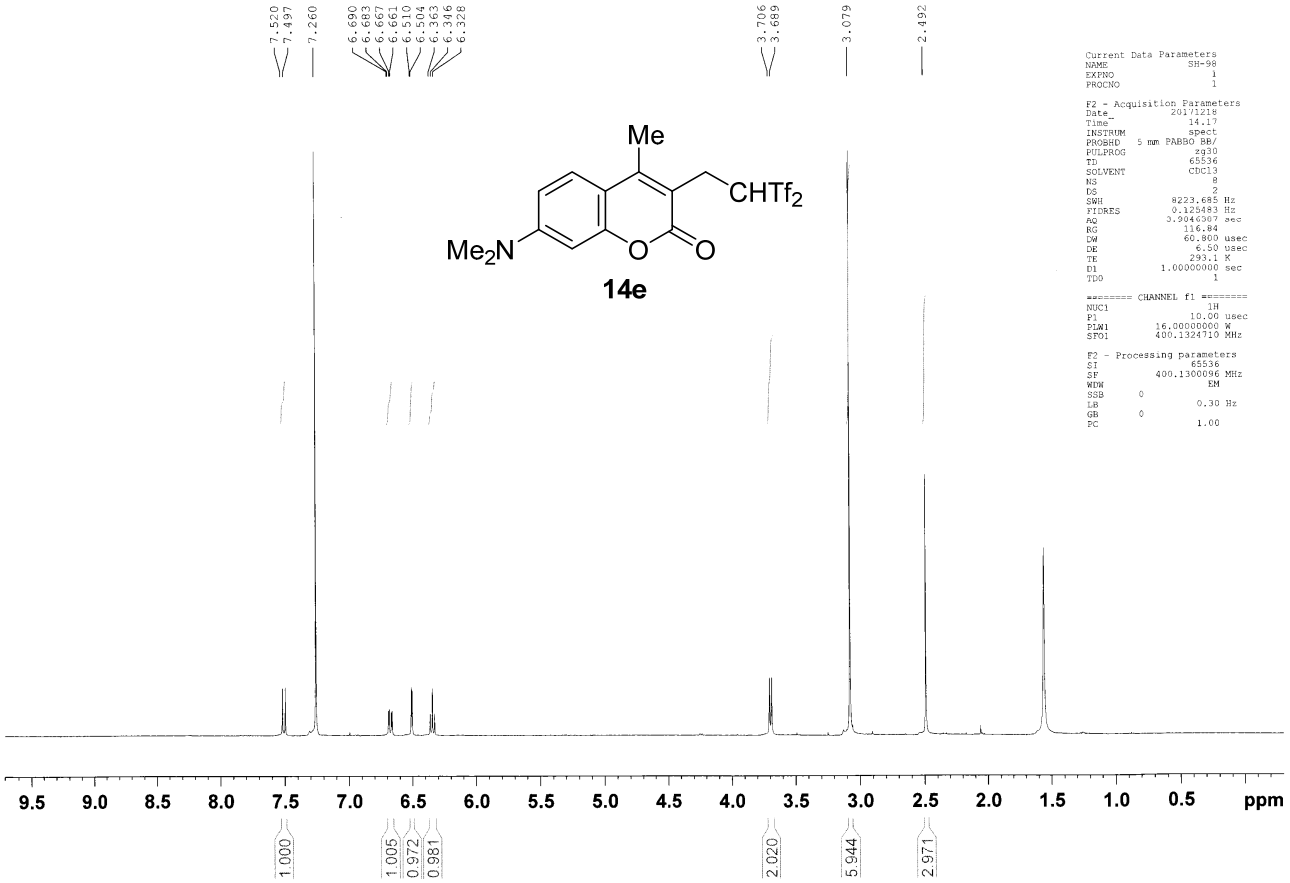
F2 - Acquisition Parameters
Date_          20180123
Time           21.03
INSTRUM        spect
PROBHD   5 mm PABBO BB/
PULPROG        zgig30
TD             122880
SOLVENT        CD3CN
NS                    8
DS                    4
SWH            75000.000 Hz
FIDRES         0.610352 Hz
AQ             0.8192500 sec
RG                204.44
DW                6.667 usec
DE                6.50 usec
TE              292.6 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                   1

========= CHANNEL f1 =========
NUC1                 19F
P1                 14.00 usec
PLW1          24.00000000 W
SFO1          376.4607162 MHz

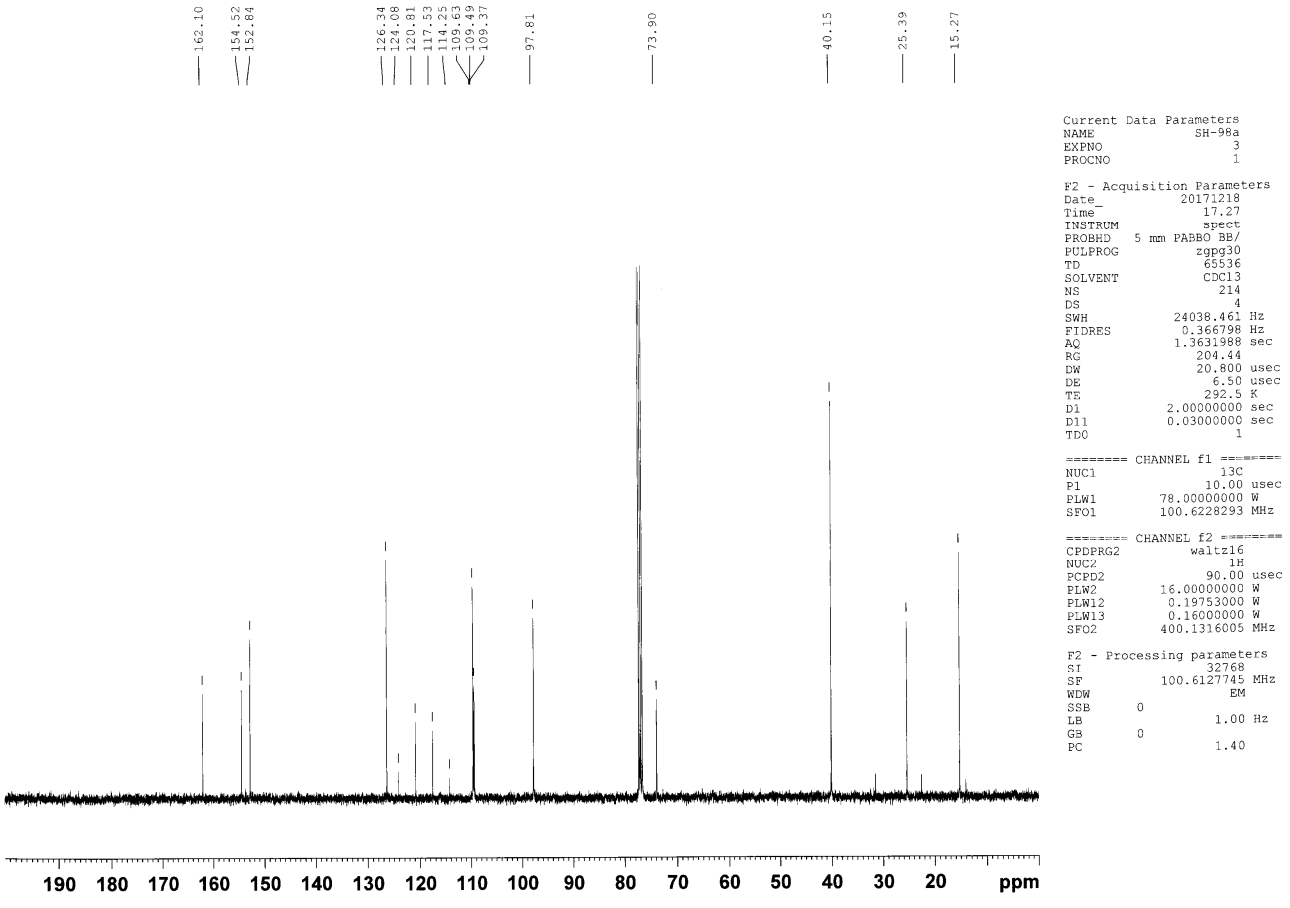
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PLW2           7.09999990 W
PLW12          0.24961001 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            376.4985539 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```

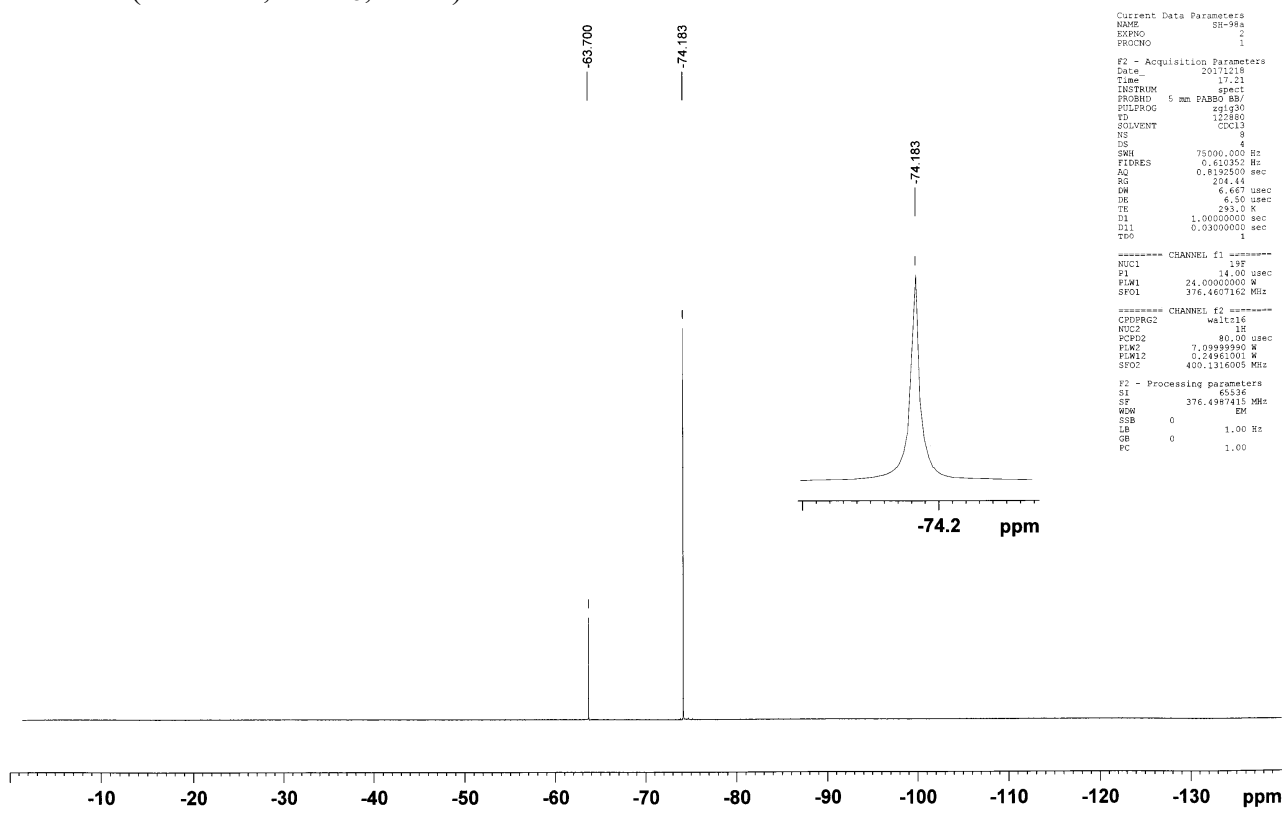
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC)



^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC)



^{19}F NMR (376 MHz, $CDCl_3$, 25 °C)

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Current Data Parameters
NAME                  SH-98a
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171218
Time                   17.21
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig30
TD                  123880
SOLVENT               CDCl3
NS                         8
DS                         4
SWH               75000.000 Hz
FIDRES            0.610352 Hz
AQ                0.81925200 sec
RG                    204.44
DW                  6.667 usec
DE                  6.50 usec
TE                  293.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                        1

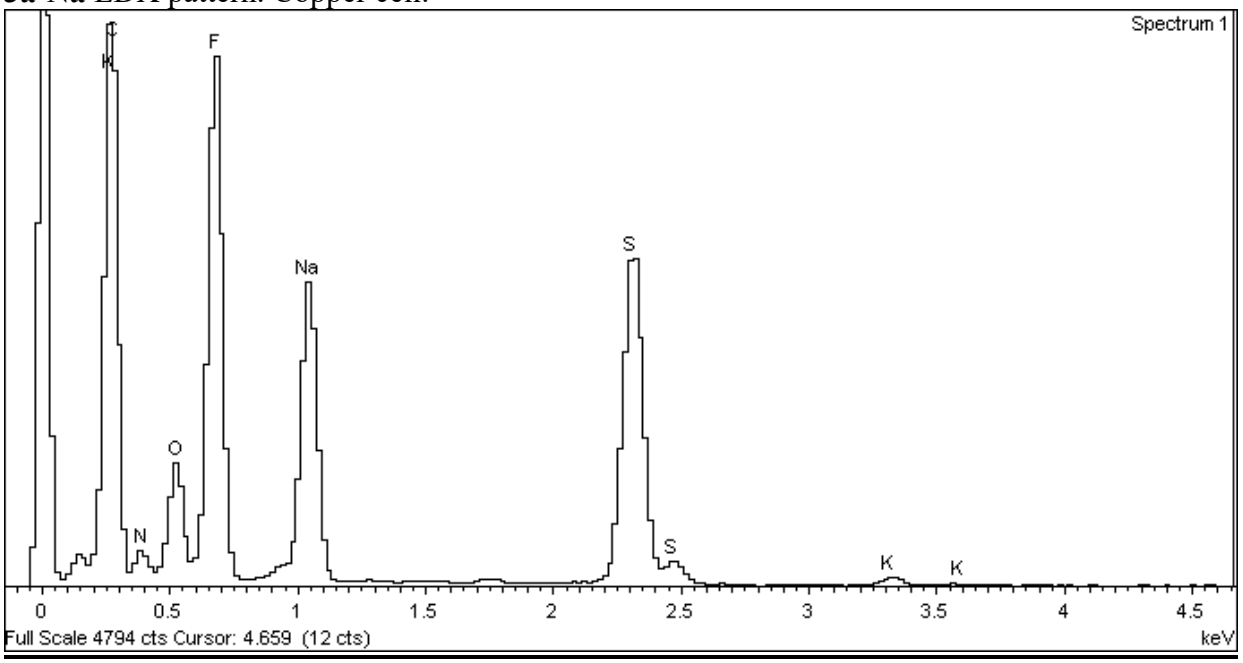
======== CHANNEL f1 ========
NUC1                      19F
P1                    14.00 usec
PLW1             24.00000000 W
SFO1            376.4607162 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PLW2              7.09999990 W
PLW12             0.24961001 W
SFO2            400.1316005 MHz

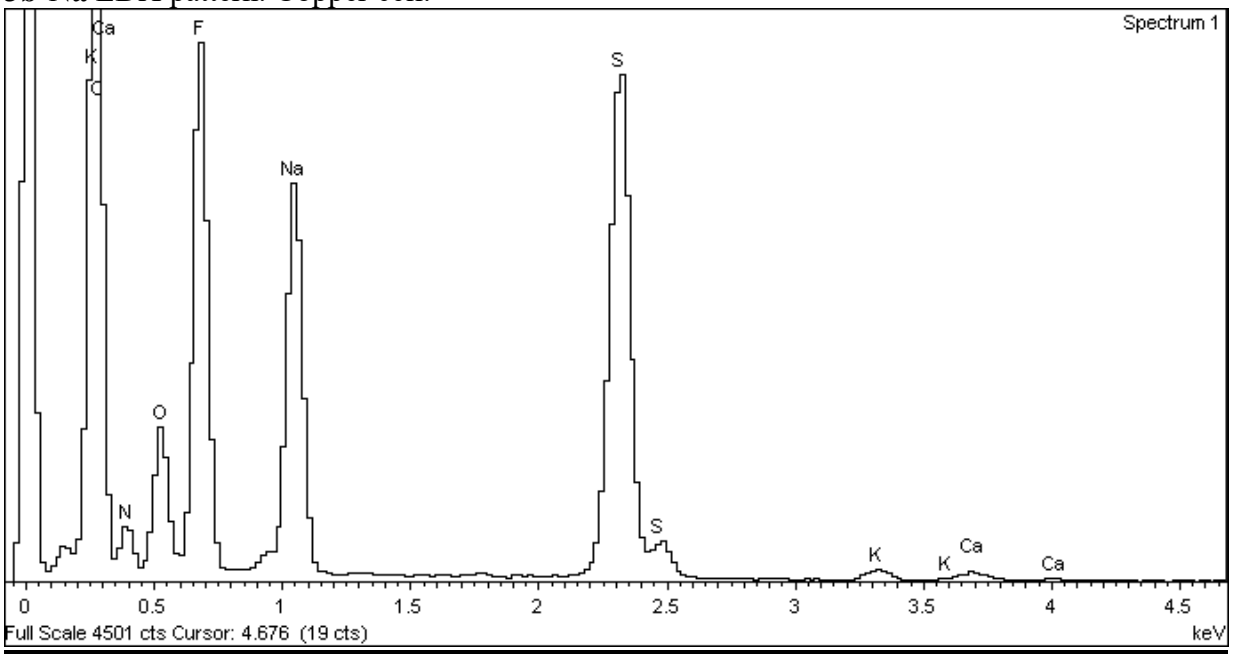
F2 - Processing parameters
SI                        65536
SF              376.4987415 MHz
WDW                          EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```

EDX Spectra

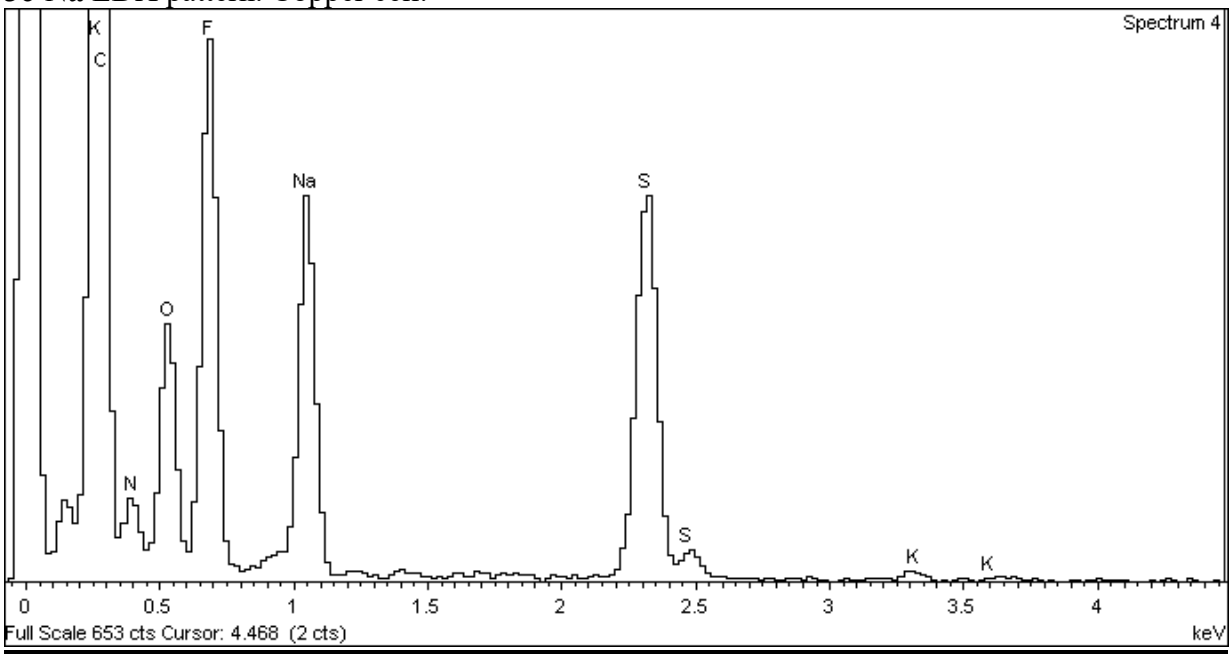
3a-Na EDX pattern. Copper cell.



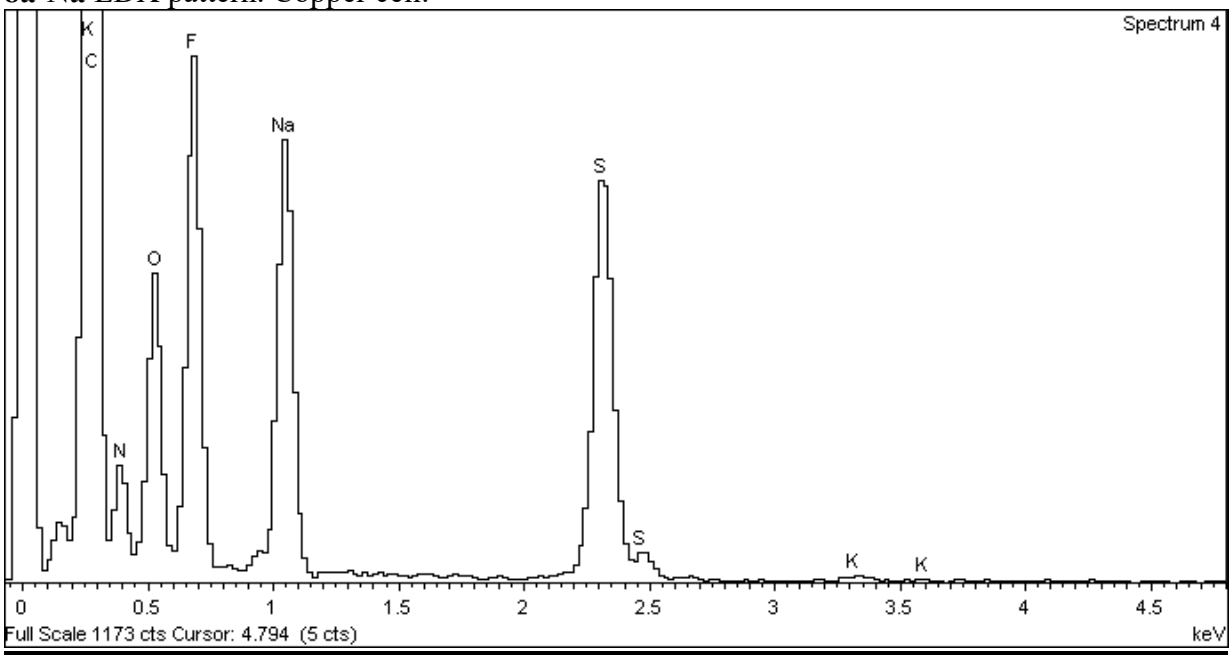
3b-Na EDX pattern. Copper cell.



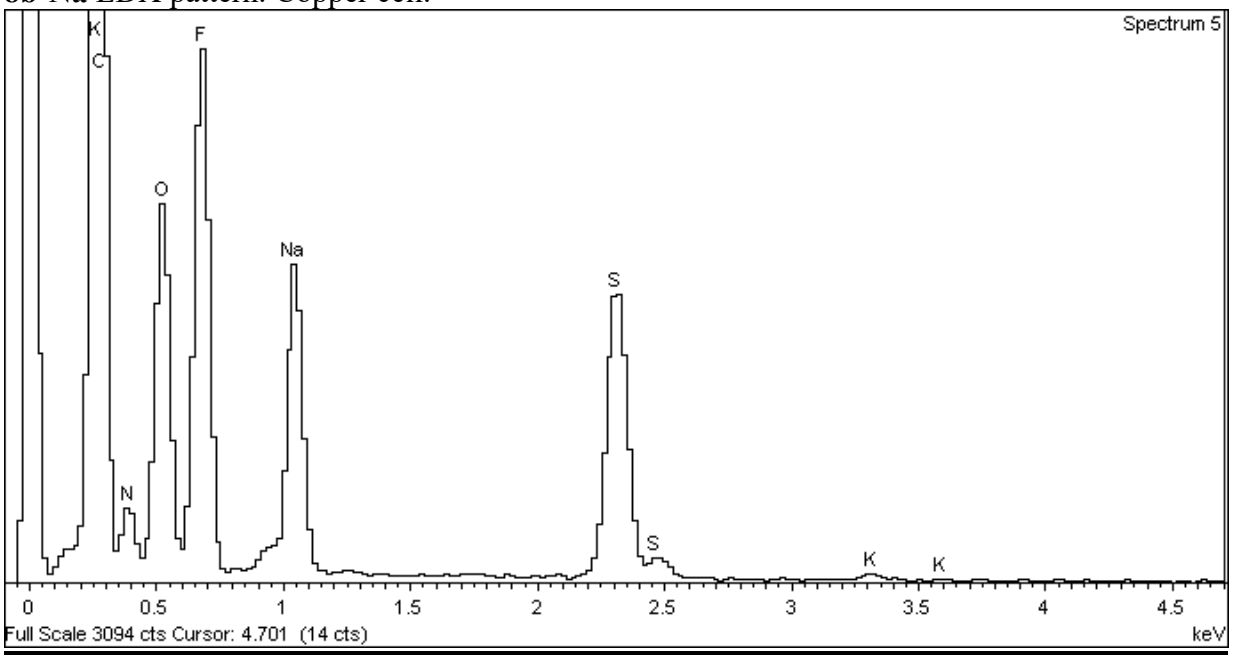
3c-Na EDX pattern. Copper cell.



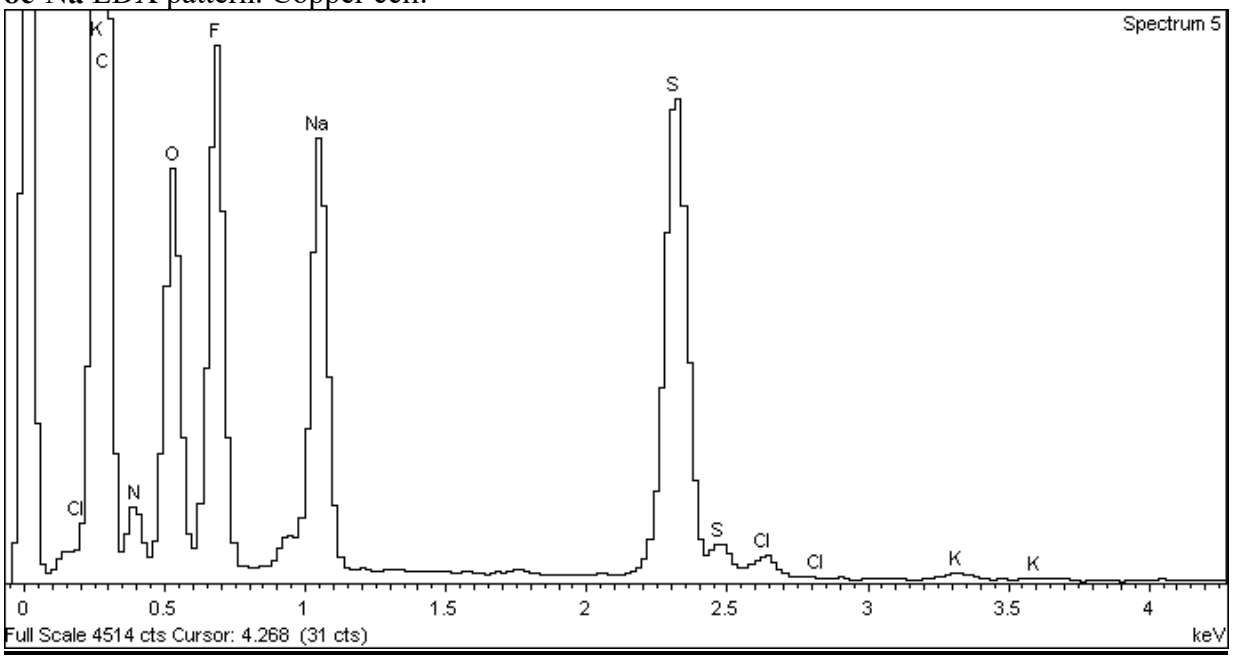
8a-Na EDX pattern. Copper cell.



8b-Na EDX pattern. Copper cell.



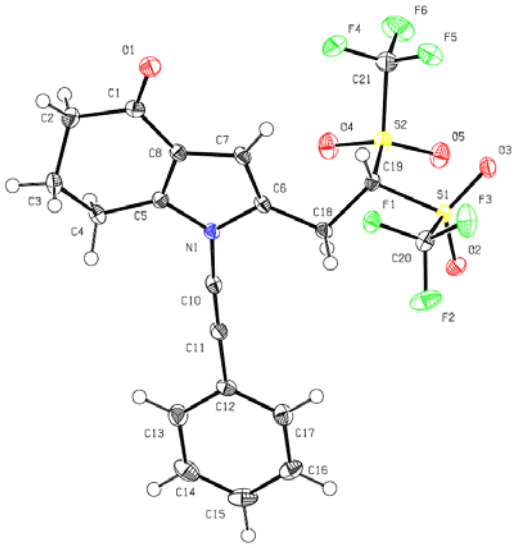
8c-Na EDX pattern. Copper cell.



X-ray Crystallographic Data

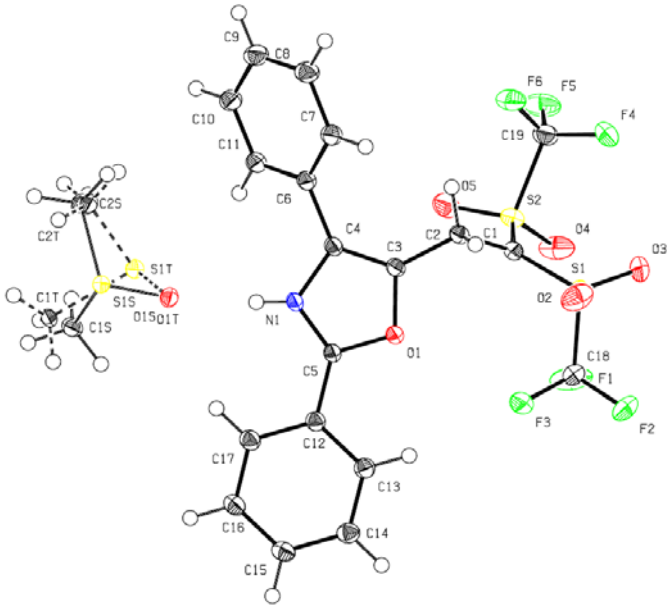
Crystallographic data by the X-ray diffraction study has been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDCs: 1833410 (**5e**), 1832228 (**7**·CH_3SOCH_3), 1832226 (**14c**), 1832225 (**16a**), 1843015 (**17**), 1832230 (**22a**), 1832227 (**22c**), and 1832229 (**22d**). These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **5e**



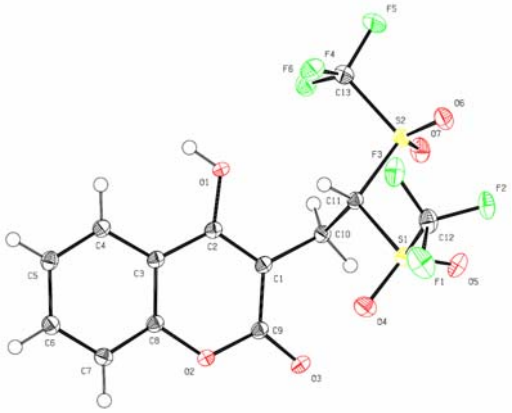
$C_{20}H_{15}F_6NO_5S_2$	$F(000) = 1072$
$M_r = 527.45$	$D_x = 1.620$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4443 reflections
$a = 12.6441$ (9) Å	$\theta = 2.3–27.9°$
$b = 11.3643$ (8) Å	$\mu = 0.33$ mm^{-1}
$c = 16.2034$ (11) Å	$T = 90$ K
$\beta = 111.751$ (1)°	Block, colurless
$V = 2162.5$ (3) Å^3	0.16 × 0.11 × 0.03 mm
$Z = 4$	
Bruker APEXII CCD area detector diffractometer	3817 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	3362 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	$R_{int} = 0.023$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
phi and ω scans	$h = -13\rightarrow15$
Absorption correction:	$k = -7\rightarrow13$
analytical Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.949$, $T_{max} = 0.990$	$l = -19\rightarrow18$
10342 measured reflections	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.079$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 1.3932P]$, where $P = (F_o^2 + 2F_c^2)/3$
3817 reflections	$(\Delta/\sigma)_{max} = 0.001$
310 parameters	$\Delta\rangle_{max} = 0.44$ e Å^{-3}
192 restraints	$\Delta\rangle_{min} = -0.32$ e Å^{-3}

Table S2. Crystal data and structure refinement for **7**·CH_3SOCH_3



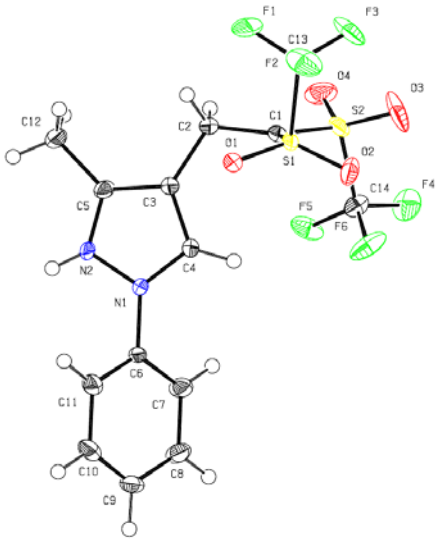
$C_{19}H_{13}F_6NO_5S_2 \cdot C_2H_6OS$	$F(000) = 1208$
$M_r = 591.55$	$D_x = 1.606$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.0371$ (9) Å	Cell parameters from 4035 reflections
$b = 14.5605$ (10) Å	$\theta = 2.2–27.0°$
$c = 14.0643$ (10) Å	$\mu = 0.39$ mm^{-1}
$\beta = 113.617$ (1)°	$T = 90$ K
$V = 2446.2$ (3) Å^3	Block, colourless
$Z = 4$	0.22 × 0.19 × 0.14 mm
Bruker D8 goniometer diffractometer	4313 independent reflections
Radiation source: rotating-anode X-ray tube,	3661 reflections with $I > 2\sigma(I)$
Bruker TXS fine-focus Turbo X-ray Source	
Bruker Helios multilayer confocal mirror monochromator	$R_{int} = 0.027$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
ω scans	$h = -15 \rightarrow 13$
Absorption correction: numerical Crystal Faces	$k = -17 \rightarrow 12$
plugin in Bruker *APEX2* software	
$T_{min} = 0.9$, $T_{max} = 0.948$	$l = -16 \rightarrow 16$
11761 measured reflections	
Refinement on F^2	548 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 3.1294P]$, where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
4313 reflections	$\Delta\rangle_{max} = 0.55$ e Å^{-3}
378 parameters	$\Delta\rangle_{min} = -0.45$ e Å^{-3}

Table S3. Crystal data and structure refinement for **14c**



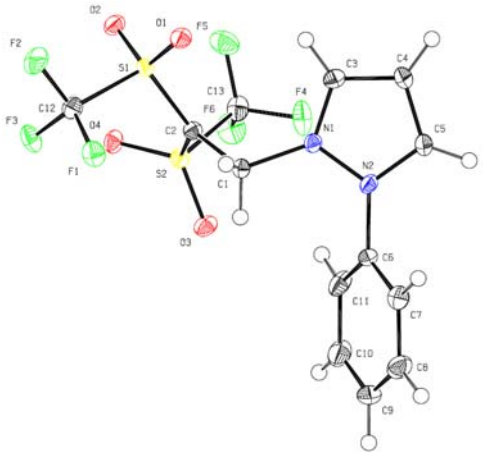
$C_{13}H_8F_6O_7S_2$	$F(000) = 912$
$M_r = 454.31$	$D_x = 1.830$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.7308$ (5) Å	Cell parameters from 3992 reflections
$b = 13.6484$ (13) Å	$\theta = 2.4$–$27.6°$
$c = 21.184$ (2) Å	$\mu = 0.43$ mm^{-1}
$\beta = 95.748$ (1)°	$T = 90$ K
$V = 1648.6$ (3) Å^3	Needle, colourless
$Z = 4$	0.28 × 0.15 × 0.07 mm
Bruker SMART APEX II CCD diffractometer	2904 independent reflections
Radiation source: rotating anode, Bruker TXS fine-focus rotating anode	2593 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror monochromator	$R_{int} = 0.020$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
phi and ω scans	$h = -6 \rightarrow 6$
Absorption correction: numerical Crystal Faces plugin in Bruker *APEX2* software	$k = -16 \rightarrow 15$
$T_{min} = 0.871$, $T_{max} = 0.969$ 7796 measured reflections	$l = -25 \rightarrow 20$
Refinement on F^2	174 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.074$	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 1.5701P]$, where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
2904 reflections	$\Delta\rangle_{max} = 0.38$ e Å^{-3}
256 parameters	$\Delta\rangle_{min} = -0.30$ e Å^{-3}

Table S4. Crystal data and structure refinement for **16a**



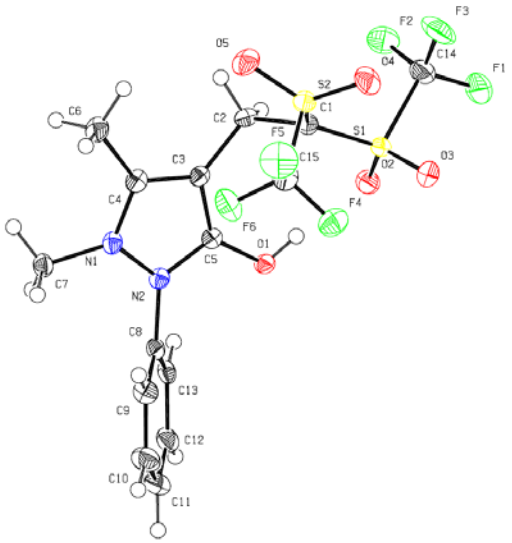
$C_{14}H_{12}F_6N_2O_4S_2$	$F(000) = 912$
$Mr = 450.38$	$D_x = 1.710$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, l = 0.71073 Å
$a = 8.4088$ (5) Å	Cell parameters from 2721 reflections
$b = 17.3980$ (11) Å	$\theta = 2.3–27.2°$
$c = 12.1982$ (8) Å	$\mu = 0.39$ mm-1
$\beta = 101.318$ (1)°	$T = 90$ K
$V = 1749.85$ (19) Å3	Block, colourless
$Z = 4$	0.50 × 0.40 × 0.25 mm
Bruker D8 goniometer diffractometer	3079 independent reflections
Radiation source: rotating-anode X-ray tube,	2618 reflections with $I > 2\sigma(I)$
Bruker TXS fine-focus Turbo X-ray Source	
Bruker Helios multilayer confocal mirror monochromator	$R_{int} = 0.026$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
ω scans	$h = -10 \rightarrow 8$
Absorption correction: numerical Crystal Faces plugin	$k = -20 \rightarrow 16$
in Bruker *APEX2* software	
$T_{min} = 0.867$, $T_{max} = 0.909$	$l = -13 \rightarrow 14$
8458 measured reflections	
Refinement on F^2	342 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.973P]$, where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.057$
3079 reflections	$\Delta\rangle_{max} = 0.40$ e Å^{-3}
258 parameters	$\Delta\rangle_{min} = -0.53$ e Å^{-3}

Table S5. Crystal data and structure refinement for **17**



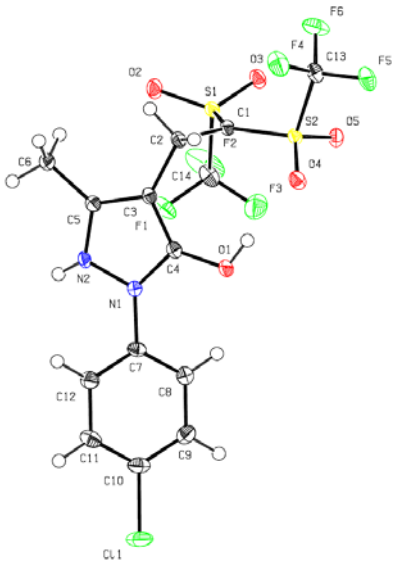
$C_{13}H_{10}F_6N_2O_4S_2$	$F(000) = 880$
$M_r = 436.35$	$D_x = 1.768$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.266$ (2) Å	Cell parameters from 1854 reflections
$b = 6.0883$ (9) Å	$\theta = 2.5–26.8°$
$c = 18.922$ (3) Å	$\mu = 0.41$ mm^{-1}
$\beta = 94.123$ (2)°	$T = 90$ K
$V = 1639.2$ (4) Å^3	Block, colourless
$Z = 4$	0.18 × 0.15 × 0.13 mm
Bruker D8 goniometer diffractometer	2900 independent reflections
Radiation source: rotating-anode X-ray tube, Bruker TXS fine-focus Turbo X-ray Source	2376 reflections with $I > 2\sigma(I)$
Bruker Helios multilayered confocal mirror monochromator	$R_{int} = 0.037$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.4°$
ω scans	$h = -16 \rightarrow 16$
Absorption correction: numerical	$k = -6 \rightarrow 7$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.892$, $T_{max} = 0.948$	$l = -19 \rightarrow 22$
7671 measured reflections	
Refinement on F^2	330 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.9851P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2900 reflections	$\Delta\rangle_{max} = 0.30$ e Å^{-3}
244 parameters	$\Delta\rangle_{min} = -0.37$ e Å^{-3}

Table S6. Crystal data and structure refinement for **22a**



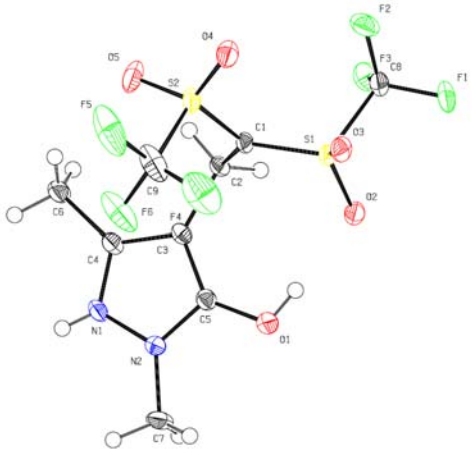
$C_{15}H_{14}F_6N_2O_5S_2$	D_x = 1.563 Mg m^{-3}
M_r = 480.40	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $Pna2_1$	Cell parameters from 9921 reflections
a = 27.2048 (18) Å	θ = 2.5–27.3°
b = 18.3507 (12) Å	μ = 0.34 mm^{-1}
c = 12.2694 (8) Å	T = 90 K
V = 6125.2 (7) Å^3	Block, colourless
Z = 12	0.34 × 0.28 × 0.23 mm
F(000) = 2928	
Bruker D8 goniometer diffractometer	10834 independent reflections
Radiation source: rotating-anode X-ray tube,	10264 reflections with $I > 2\sigma(I)$
Bruker TXS fine-focus Turbo X-ray Source	
Bruker Helios multilayer confocal mirror monochromator	R_{int} = 0.037
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.3°
ω scans	h = -32→32
Absorption correction: numerical Crystal Faces	k = -21→21
plugin in Bruker *APEX2* software	
T_{min} = 0.838, T_{max} = 0.925	l = -14→14
58829 measured reflections	
Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.026	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 1.0061P]$, where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.067	$(\Delta/\sigma)_{max}$ = 0.015
S = 1.01	$\Delta\rangle_{max}$ = 0.38 e Å^{-3}
10834 reflections	$\Delta\rangle_{min}$ = -0.24 e Å^{-3}
820 parameters	Absolute structure: Flack x determined using 4669 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
1099 restraints	Absolute structure parameter: -0.002 (15)

Table S7. Crystal data and structure refinement for **22c**



$C_{14}H_{11}ClF_6N_2O_5S_2$	$Z = 8$
$M_r = 500.82$	$F(000) = 2016$
Monoclinic, $C2/c$	$D_x = 1.669$ Mg m^{-3}
$a = 31.442$ (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.7594$ (5) Å	$\mu = 0.49$ mm^{-1}
$c = 16.3435$ (11) Å	$T = 90$ K
$\beta = 91.740$ (1)°	Block, colourless
$V = 3985.5$ (5) Å^3	0.76 × 0.20 × 0.14 mm
Bruker D8 goniometer diffractometer	3512 independent reflections
Radiation source: rotating-anode X-ray tube,	3143 reflections with $I > 2\sigma(I)$
Bruker TXS fine-focus Turbo X-ray Source	
Bruker Helios multilayer confocal mirror monochromator	$R_{int} = 0.023$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.3°$
ω scans	$h = -37 \rightarrow 37$
Absorption correction: numerical Crystal Faces plugin	$k = -5 \rightarrow 9$
in Bruker *APEX2* software	
$T_{min} = 0.886$, $T_{max} = 0.935$	$l = -19 \rightarrow 19$
9381 measured reflections	
Refinement on F^2	366 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 4.2061P]$, where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
3512 reflections	$\Delta\rangle_{max} = 0.30$ e Å^{-3}
276 parameters	$\Delta\rangle_{min} = -0.38$ e Å^{-3}

Table S8. Crystal data and structure refinement for **22d**



$C_9H_{10}F_6N_2O_5S_2$	D_x = 1.755 Mg m^{-3}
M_r = 404.31	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, *Pbca*	Cell parameters from 7817 reflections
a = 17.2641 (10) Å	θ = 2.4–27.2°
b = 14.8304 (8) Å	μ = 0.44 mm^{-1}
c = 23.9088 (14) Å	T = 90 K
V = 6121.5 (6) Å^3	Block, pale yellow
Z = 16	0.29 × 0.26 × 0.17 mm
F(000) = 3264	
Bruker D8 goniometer diffractometer	5403 independent reflections
Radiation source: rotating-anode X-ray tube,	4636 reflections with $I > 2\sigma(I)$
Bruker TXS fine-focus Turbo X-ray Source	
Bruker Helios multilayer confocal mirror monochromator	R_{int} = 0.034
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.7°
ω scans	h = -20→19
Absorption correction: numerical Crystal Faces	k = -17→15
plugin in Bruker *APEX2* software	
T_{min} = 0.869, T_{max} = 0.927	l = -28→27
28505 measured reflections	
Refinement on F^2	576 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.037	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.093	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 6.9113P]$, where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.001
5403 reflections	$\Delta\rangle_{max}$ = 0.50 e Å^{-3}
445 parameters	$\Delta\rangle_{min}$ = -0.43 e Å^{-3}

UV and Fluorescence Spectra

As initial solutions (4.0 x 10^{-4} mol L^{-1}), Tf_2CHCH_2-decorated aminocoumarin **14e** (4.95 mg, 10.0 µmol) was diluted to 25 mL with acetonitrile or 0.1 M phosphate buffers. To prepare 5.0 x 10^{-5} mol L^{-1} solutions for the UV/Vis spectroscopy, 1.25 mL of the initial solution was filled the same solvents to a volume of 10 mL. Likewise, 5.0 x 10^{-6} mol L^{-1} solutions used as fluorescence spectroscopy were prepared from 125 µL of the initial solutions. The UV, fluorescence excitation and emission spectra of aqueous solutions were obtained by measuring the samples three times. Due to low stability of **14e** in CH_3CN under UV irradiation conditions, the fluorescence spectra of **14e** in CH_3CN were obtained by measuring once. The data are shown in Figures S1-S3, respectively. The fluorescence spectra were corrected by rhodamine B (in a range from 200 nm to 600 nm).

Figure S1. UV spectra (5.0 x 10^{-5} mol L^{-1} solutions, 25 °C)

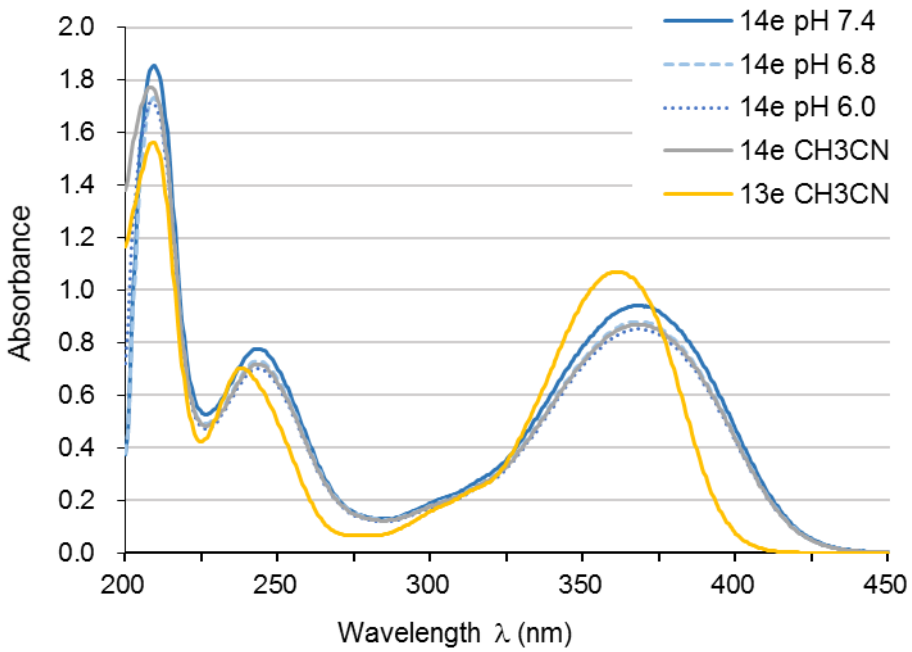


Figure S2. Fluorescence emission spectra (corrected, 5.0 x 10^{-6} mol L^{-1} solutions, 25 °C)

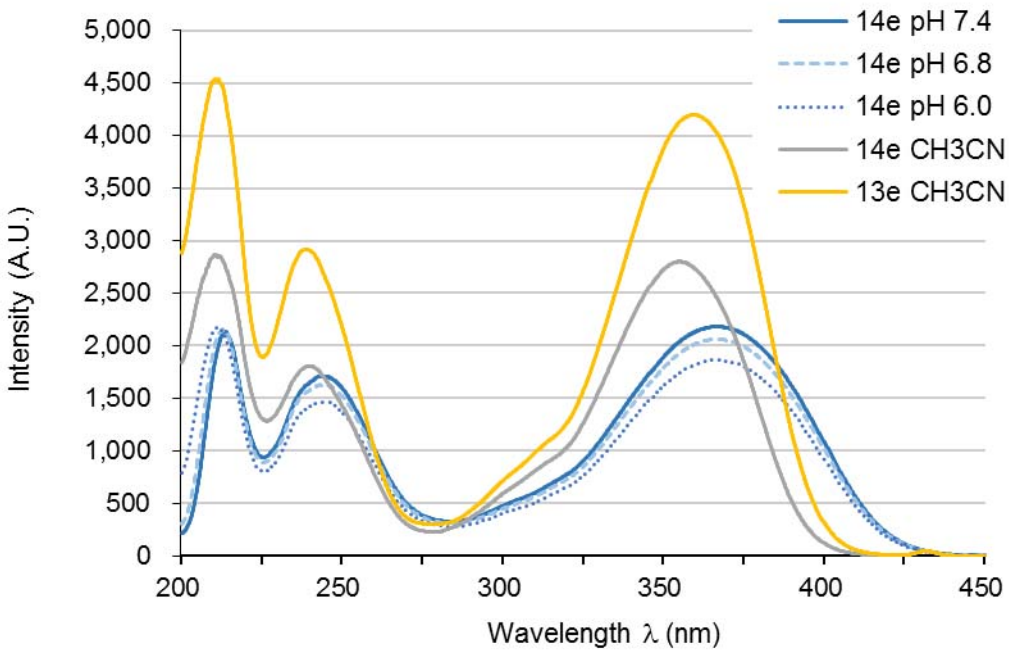


Figure S3. Fluorescence excitation spectra (corrected, 5.0 x 10^{-6} mol L^{-1} solutions, 25 °C)