

Supporting Information

Convenient Synthesis of Pentafluoroethyl Thioethers via Catalytic Sandmeyer
Reaction with a Stable Fluoroalkylthiolation Reagent

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General Methods

The reactions were performed in oven-dried glassware containing a Teflon-coated stirrer bar and septum under a nitrogen atmosphere. Acetonitrile were dried by refluxing over CaH_2 and subsequent fractionally distillation. All reactions were monitored by GC and the yields were determined by ^{19}F NMR using trifluoroethanol as internal standard. GC analyses were carried out using a HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and Grace Reveleris packed flash columns (12 g). NMR spectra were obtained on a Bruker AMX 400 system using chloroform- d_1 , acetonitrile- d_3 or methanol- d_4 as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 101 MHz and 375 MHz, respectively. Mass spectral data were acquired on a Varian Saturn 2100 T.

All commercially available starting materials were used without further purification. $\text{Me}_4\text{NSC}_2\text{F}_5$ was commercially available by CF Plus Chemicals s. r. o.

Synthesis of Starting Materials

Synthesis of arene diazonium tetrafluoroborates

In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol) and *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3×10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 minutes and was then directly used without further purification.

Synthesis of pentafluoroethyl thioethers from arenediazonium salts

Standard procedure: An oven-dried 20 mL crimp-cap vessel with stirrer bar was charged with Cu (6.4 mg, 0.10 mmol), Me₄NSC₂F₅ (338 mg, 1.50 mmol) and MeCN (2 mL). Then, the arenediazonium salt (1.00 mmol) in MeCN (2 mL) was added dropwise and the reaction mixture was stirred for 15 h at room temperature. The resulting mixture was diluted with diethyl ether (20 mL). The organic solution was washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over MgSO₄, filtered and concentrated (700 mbar, 40 °C). The residue was purified by flash chromatography (SiO₂, cyclohexane / ethyl acetate gradient), yielding the aryl pentafluoroethyl thioethers. The yields of particularly volatile compounds were determined by ¹⁹F NMR, and their identity by mass spectroscopy.

Synthesis of 1-methoxy-4-[(pentafluoroethyl)thio]benzene (2a). Compound **2a** was prepared following the standard procedure, starting from 4-methoxybenzenediazonium tetrafluoroborate (222 mg, 1.00 mmol). After purification, **2a** was isolated as colorless oil (253 mg, 0.98 mmol, 98%). ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, ³J = 8.8 Hz, 2H), 6.94 (d, ³J = 8.8 Hz, 2H), 3.85 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, J = 4.1 Hz, 3F), -92.8 ppm (q, J = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 162.0, 139.0 (2C), 115.0 (2C), 113.1 (t, ³J(C,F) = 2.7 Hz), 120.0 (qt, ¹J(C,F) = 287.0 Hz, ²J(C,F) = 40.3 Hz), 118.8 (tq, ¹J(C,F) = 286.1 Hz, ²J(C,F) = 37.0 Hz), 55.4 ppm; IR (neat): ν = 2934, 2842, 1593, 1495, 1293, 1252, 1205, 1102, 1087, 1030, 956, 828, 749 cm⁻¹; MS (Ion trap, EI, 70 eV): m/z (%) = 258 [*M*⁺] (73), 139 (100), 123 (11), 96 (14); HRMS (EI-TOF) calcd. for C₉H₇F₅OS: 258.0138; found: 258.0143.

Synthesis of 1-methyl-3-[(pentafluoroethyl)thio]benzene (2b). Compound **2b** was prepared following the standard procedure, starting from 3-methylbenzenediazonium tetrafluoroborate (206 mg, 1.00 mmol). After purification, **2b** was isolated as colorless oil (225 mg, 0.93 mmol, 93%). ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.47 (m, 2H), 7.33-7.32 (m, 2H), 2.41 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, J = 4.1 Hz, 3F), -91.0 ppm (q, J = 3.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 139.5, 137.7, 134.2, 131.8, 129.2, 122.4 (t, ³J(C,F) = 2.7 Hz), 120.2 (qt, ¹J(C,F) = 288.4 Hz, ²J(C,F) = 40.0 Hz), 118.8 (tq, ¹J(C,F) = 286.8 Hz, ²J(C,F) = 36.8 Hz), 21.1 ppm; IR (neat): ν = 3053, 2929, 1595, 1477, 1330, 1203, 1095, 957, 780, 750, 691 cm⁻¹; MS

(Ion trap, EI, 70 eV): m/z (%) = 242 [M^+] (100), 173 (12), 123 (67), 91 (14); HRMS (EI-TOF) calcd. for $C_9H_7F_5S$: 242.0189; found: 242.0183.

Synthesis of 4-[(pentafluoroethyl)thio]-1,1'-biphenyl [CAS No.: 933673-37-1] (2c). Compound **2c** was prepared following the standard procedure, starting from [1,1-biphenyl]-4-diazonium tetrafluoroborate (268 mg, 1.00 mmol). After purification, **2c** was isolated as colorless solid (289 mg, 0.95 mmol, 95%). m.p.: 60-61°C; 1H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.78 (m, 2H), 7.70-7.66 (m, 4H), 7.56-7.45 ppm (m, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = -82.4 (t, J = 3.8 Hz, 3F), -91.7 ppm (s, 2F); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.1, 139.6, 137.6, 129.0 (2C), 128.2 (2C), 128.1 (2C), 127.2 (2C), 121.4, 120.5 (qt, $^1J(C,F)$ = 288.4 Hz, $^2J(C,F)$ = 39.9 Hz), 118.9 ppm (tq, $^1J(C,F)$ = 287.0 Hz, $^2J(C,F)$ = 37.1 Hz); IR (neat): ν = 3033, 1478, 1333, 1200, 1100, 960, 836, 760, 688 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 304 [M^+] (100), 190 (19), 188 (59), 185 (85), 152 (44); HRMS (EI-TOF) calcd. for $C_{14}H_9F_5S$: 304.0345; found: 304.0368.

Synthesis of 1-phenoxy-4-[(pentafluoroethyl)thio]benzene (2d). Compound **2d** was prepared following the standard procedure, starting from 4-phenoxybenzenediazonium tetrafluoroborate (284 mg, 1.00 mmol). After purification, **2d** was isolated as colorless oil (311 mg, 0.97 mmol, 97%). 1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 3J = 8.8 Hz, 2H), 7.42 (t, 3J = 8.0 Hz, 2H), 7.22 (t, 3J = 7.5 Hz, 1H), 7.09 (d, 3J = 8.5 Hz, 2H), 7.01 ppm (d, 3J = 8.8 Hz, 2H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = -82.4 (t, J = 3.8 Hz, 3F), -92.5 ppm (q, J = 4.1 Hz, 2F); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.6, 155.5, 139.0 (2C), 130.1 (2C), 124.6, 120.1 (2C), 120.0 (tq, $^1J(C,F)$ = 286.1 Hz, $^2J(C,F)$ = 36.3 Hz), 118.5 (2C), 118.7 (qt, $^1J(C,F)$ = 288.8 Hz, $^2J(C,F)$ = 40.4 Hz), 115.5 ppm (t, $^3J(C,F)$ = 3.2 Hz); IR (neat): ν = 3043, 1582, 1485, 1331, 1242, 1200, 1085, 957, 869, 833, 749, 691 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 320 [M^+] (94), 201 (100), 129 (16), 77 (23); HRMS (EI-TOF) calcd. for $C_{14}H_9F_5OS$: 320.0294; found: 320.0279.

Synthesis of 1-bromo-4-[(pentafluoroethyl)thio]benzene [CAS No.: 782491-17-2] (2e). Compound **2e** was prepared following the standard procedure, starting from 4-bromobenzenediazonium tetrafluoroborate (271 mg, 1.00 mmol). After purification, **2e** was isolated as colorless oil (239 mg, 0.78 mmol, 78%). 1H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.51 ppm (m, 4H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = -82.7 (t,

$J = 4.1$ Hz, 3F), -92.0 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 138.6$ (2C), 132.8 (2C), 126.4 , 121.9 (t, $^3J(\text{C},\text{F}) = 2.7$ Hz), 120.0 (qt, $^1J(\text{C},\text{F}) = 288.8$ Hz, $^2J(\text{C},\text{F}) = 40.9$ Hz), 118.7 ppm (tq, $^1J(\text{C},\text{F}) = 286.6$ Hz, $^2J(\text{C},\text{F}) = 36.8$ Hz); IR (neat): $\nu = 3023, 1569, 1475, 1388, 1331, 1204, 1103, 1012, 954, 817, 749, 731\text{ cm}^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = $305 [M^+]$ (100), 189 (72), 171 (11), 108 (52); HRMS (EI-TOF) calcd. for $\text{C}_8\text{H}_4\text{F}_5\text{S}^{79}\text{Br}$: 305.9137; found: 305.9154.

Synthesis of 1-fluoro-4-[(pentafluoroethyl)thio]-benzene [CAS No.: 75220-65-4]

(2f).^[1] Compound **2f** was prepared following the standard procedure, starting from 4-fluorodiazonium tetrafluoroborate (105 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard ($36.0\text{ }\mu\text{L}$, 0.50 mmol) was added to the reaction mixture and the pentafluoroethylthiolated product **2f** was formed in 61% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, CDCl_3): $\delta = -85.7$ (t, $J = 3.6$ Hz, 3F), -92.1 ppm (q, $J = 4.1$ Hz, 2F); MS (Ion trap, EI, 70 eV): m/z (%) = $245.9 [M^+]$ (100), 177.0 (9), 127.0 (92), 83.0 (44), 75.0 (9), 68.9 (23), 57.0 (15).

Synthesis of 1-chloro-4-[(pentafluoroethyl)thio]-benzene [CAS No.: 782491-17-2]

(2g). Compound **2g** was prepared following the standard procedure, starting from 4-chlorobenzenediazonium tetrafluoroborate (226 mg, 1.00 mmol). After purification, **2g** was isolated as colorless oil (181 mg, 0.69 mmol, 69%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.59$ (d, $^3J = 8.5$ Hz, 2H), 7.41 ppm (d, $^3J = 8.8$ Hz, 2H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.5$ (t, $J = 3.8$ Hz, 3F), -92.0 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 138.4$ (2C), 138.0 , 129.8 (2C), 121.2 (t, $^3J(\text{C},\text{F}) = 3.2$ Hz), 120.2 (qt, $^1J(\text{C},\text{F}) = 288.8$ Hz, $^2J(\text{C},\text{F}) = 40.3$ Hz), 119.1 ppm (tq, $^1J(\text{C},\text{F}) = 287.0$ Hz, $^2J(\text{C},\text{F}) = 36.3$ Hz); IR (neat): $\nu = 3045, 2925, 2855, 1575, 1478, 1331, 1204, 1088, 957, 822, 749\text{ cm}^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = $261 [M^+]$ (100), 145 (31), 143 (82), 108 (32); HRMS (EI-TOF) calcd. for $\text{C}_8\text{H}_4\text{F}_5^{35}\text{ClS}$: 261.9642; found: 261.9633.

Synthesis of 4-[(pentafluoroethyl)thio]acetophenone [CAS No.: 1328939-62-3]

(2h). Compound **2h** was prepared following the standard procedure, starting from 4-acetylbenzenediazonium tetrafluoroborate (234 mg, 1.00 mmol). After purification, **2h** was isolated as colorless oil (264 mg, 0.98 mmol, 98%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.99$ (d, $^3J = 7.0$ Hz, 2H), 7.76 (d, $^3J = 7.0$ Hz, 2H), 2.64 ppm (s, 3H); ^{19}F NMR

(375 MHz, CDCl_3): $\delta = -82.5$ (t, $J = 4.1$ Hz, 3F), -91.2 ppm (q, $J = 3.8$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 197.0$, 138.7, 136.9 (2C), 128.9 (2C), 128.4 (t, $^3J(\text{C},\text{F}) = 2.7$ Hz), 120.3 (qt, $^1J(\text{C},\text{F}) = 289.7$ Hz, $^2J(\text{C},\text{F}) = 40.8$ Hz), 118.6 (tq, $^1J(\text{C},\text{F}) = 286.5$ Hz, $^2J(\text{C},\text{F}) = 36.4$ Hz), 26.7 ppm; IR (neat): $\nu = 3015$, 2971, 1690, 1365, 1207, 1104, 954, 827, 750 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 270 [M^+] (39), 255 (100), 136 (9); HRMS (EI-TOF) calcd. for $\text{C}_{10}\text{H}_7\text{F}_5\text{OS}$: 270.0138; found: 270.0132.

Synthesis of 4-[(pentafluoroethyl)thio]benzophenone (2i). Compound **2i** was prepared following the standard procedure, starting from 4-benzoylbenzenediazonium tetrafluoroborate (296 mg, 1.00 mmol). After purification, **2i** was isolated as colorless solid (309 mg, 0.99 mmol, 99%). m.p.: 56-57°C; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.88$ -7.77 (m, 6H), 7.64 (t, $^3J = 7.5$ Hz, 1H), 7.52 ppm (t, $^3J = 7.5$ Hz, 2H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.4$ (t, $J = 3.8$ Hz, 3F), -91.1 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 195.6$, 139.7, 136.7, 136.7, 133.0, 130.6, 130.1, 128.5, 127.4 (t, $^3J(\text{C},\text{F}) = 2.7$ Hz), 120.0 (qt, $^1J(\text{C},\text{F}) = 289.7$ Hz, $^2J(\text{C},\text{F}) = 41.0$ Hz), 118.6 ppm (tq, $^1J(\text{C},\text{F}) = 286.6$ Hz, $^2J(\text{C},\text{F}) = 36.8$ Hz); IR (neat): $\nu = 2929$, 1650, 1592, 1448, 1304, 1199, 1103, 961, 850, 791, 730, 694 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 332 [M^+] (100), 254 (28), 108 (6); HRMS (EI-TOF) calcd. for $\text{C}_{15}\text{H}_9\text{F}_5\text{OS}$: 332.0296; found: 332.0288.

Synthesis of methyl-4-[(pentafluoroethyl)thio]benzoate (2j). Compound **2j** was prepared following the standard procedure, starting from 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (250 mg, 1.00 mmol). After purification, **2j** was isolated as colorless oil (269 mg, 0.94 mmol, 94%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.08$ (d, $^3J = 8.2$ Hz, 2H), 7.73 (d, $^3J = 8.0$ Hz, 2H), 3.95 ppm (s, 3H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.5$ (t, $J = 3.8$ Hz, 3F), -91.2 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 168.0$, 136.7 (2C), 132.5, 130.3 (2C), 128.2 (t, $^3J(\text{C},\text{F}) = 2.7$ Hz), 120.0 (qt, $^1J(\text{C},\text{F}) = 289.7$ Hz, $^2J(\text{C},\text{F}) = 40.9$ Hz), 118.6 (tq, $^1J(\text{C},\text{F}) = 286.6$ Hz, $^2J(\text{C},\text{F}) = 36.3$ Hz), 52.5 ppm; IR (neat): $\nu = 2925$, 1713, 1438, 1282, 1214, 1106, 961, 764 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 286 [M^+] (56), 154 (100), 135 (17), 108 (15); HRMS (EI-TOF) calcd. for $\text{C}_{10}\text{H}_7\text{F}_5\text{O}_2\text{S}$: 286.0087; found: 286.0105.

Synthesis of *N,N*-dimethyl-4-[(pentafluoroethyl)thio]benzenamine (2k).

Compound **2k** was prepared following the standard procedure, starting from 4-(dimethylamino)benzenediazonium tetrafluoroborate (235 mg, 1.00 mmol). After purification, **2k** was isolated as colorless oil (247 mg, 0.91 mmol, 91%). ¹H NMR (400 MHz, CDCl₃): δ = 7.52-7.50 (m, 2H), 6.72-6.69 (m, 2H), 3.04 ppm (s, 6H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.4 (t, *J* = 4.1 Hz, 3F), -93.5 ppm (q, *J* = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 151.1, 138.6 (2C), 120.3 (qt, ¹*J*(C,F) = 287.9 Hz, ²*J*(C,F) = 39.9 Hz), 120.0 (tq, ¹*J*(C,F) = 286.1 Hz, ²*J*(C,F) = 37.2 Hz), 112.2 (2C), 106.3 (t, ³*J*(C,F) = 2.7 Hz), 39.9 (2C) ppm; IR (neat): ν = 2896, 1593, 1509, 1446, 1365, 1329, 1193, 1086, 955, 810, 749 cm⁻¹; MS (Ion trap, EI, 70 eV): *m/z* (%) = 271 [*M*⁺] (19), 257 (38), 152 (49), 138 (100), 109 (26), 104 (20), 82 (29), 62 (40); HRMS (EI-TOF) calcd. for C₁₀H₁₀F₅NS: 271.0454; found: 271.0450.

Synthesis of *N*-[4-[(pentafluoroethyl)thio]phenyl]acetamide (2l).

Compound **2l** was prepared following the standard procedure, starting from 4-(acetylamino)benzenediazonium tetrafluoroborate (249 mg, 1.00 mmol). After purification, **2l** was isolated as slightly yellow solid (234 mg, 0.82 mmol, 82%). m.p.: 137-138°C; ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (s, 4H), 2.21 ppm (s, 3H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.4 (t, *J* = 4.1 Hz, 3F), -92.3 ppm (q, *J* = 4.1 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 172.1, 143.4, 139.3 (2C), 121.6 (2C), 121.5 (qt, ¹*J*(C,F) = 286.8 Hz, ²*J*(C,F) = 40.1 Hz), 120.4 (tq, ¹*J*(C,F) = 285.9 Hz, ²*J*(C,F) = 37.1 Hz), 117.3 (t, ³*J*(C,F) = 2.9 Hz), 24.1 ppm; IR (neat): ν = 3456, 3018, 2975, 1738, 1368, 1229, 1217 cm⁻¹; MS (Ion trap, EI, 70 eV): *m/z* (%) = 285 [*M*⁺] (40), 243 (35), 124 (100); HRMS (EI-TOF) calcd. for C₁₀H₈NF₅OS: 285.0247; found: 285.0254.

Synthesis of 4-[(pentafluoroethyl)thio]nitrobenzene (2m).

Compound **2m** was prepared following the standard procedure, starting from 4-nitrobenzenediazonium tetrafluoroborate (237 mg, 1.00 mmol). After purification, **2m** was isolated as slightly yellow oil (262 mg, 0.96 mmol, 96%). ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (d, ³*J* = 8.8 Hz, 2H), 7.86 ppm (d, ³*J* = 8.8 Hz, 2H); ¹⁹F NMR (375 MHz, CDCl₃): δ = -82.5 (t, *J* = 3.8 Hz, 3F), -90.8 ppm (q, *J* = 3.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃): δ = 149.4, 137.5 (2C), 130.8 (t, ³*J*(C,F) = 2.7 Hz), 124.2 (2C), 120.0 (qt, ¹*J*(C,F) = 290.5 Hz, ²*J*(C,F) = 41.1 Hz), 118.4 ppm (tq, ¹*J*(C,F) = 286.5 Hz,

$^2J(\text{C},\text{F}) = 36.0 \text{ Hz}$; IR (neat): $\nu = 3459, 3003, 2971, 1602, 1524, 1347, 1207, 1103, 956, 851, 750, 729, 685 \text{ cm}^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = 272 [M^+] (56), 243 (98), 206 (12), 124 (100), 108 (30), 96 (12), 80 (21); HRMS (EI-TOF) calcd. for $\text{C}_8\text{H}_4\text{NF}_5\text{O}_2\text{S}$: 272.9883; found: 272.9897.

Synthesis of 4-[(pentafluoroethyl)thio]benzonitrile (2n). Compound **2n** was prepared following the standard procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate (217 mg, 1.00 mmol). After purification, **2n** was isolated as colorless solid (208 mg, 0.82 mmol, 82%). m.p.: 45-46°C; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.79$ (d, $^3J = 8.3 \text{ Hz}$, 2H), 7.73 ppm (d, $^3J = 8.8 \text{ Hz}$, 2H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.5$ (t, $J = 3.4 \text{ Hz}$, 3F), -91.0 ppm (q, $J = 3.8 \text{ Hz}$, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 137.2$ (2C), 132.8 (2C), 128.9 (t, $^3J(\text{C},\text{F}) = 2.7 \text{ Hz}$), 120.0 (qt, $^1J(\text{C},\text{F}) = 290.6 \text{ Hz}$, $^2J(\text{C},\text{F}) = 40.9 \text{ Hz}$), 118.4 (tq, $^1J(\text{C},\text{F}) = 287.0 \text{ Hz}$, $^2J(\text{C},\text{F}) = 36.3 \text{ Hz}$), 117.5, 115.0 ppm; IR (neat): $\nu = 3073, 3039, 2232, 1487, 1318, 1202, 1092, 959, 851, 830, 749 \text{ cm}^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = 253 [M^+] (100), 184 (69), 134 (94), 102 (13), 90 (16); HRMS (EI-TOF) calcd. for $\text{C}_9\text{H}_4\text{NF}_5\text{S}$: 252.9985; found: 252.9991.

Synthesis of 3-[(pentafluoroethyl)thio]quinoline (2o). Compound **2o** was prepared following the standard procedure, starting from quinoline-3-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, **2o** was isolated as colorless solid (249 mg, 0.89 mmol, 89%). m.p.: 35-36°C; ^1H NMR (400 MHz, CDCl_3): $\delta = 9.00$ (s, 1H), 8.49 (s, 1H), 8.14 (d, $^3J = 8.5 \text{ Hz}$, 1H), 7.84-7.79 (m, 2H), 8.19 ppm (t, $^3J = 7.5 \text{ Hz}$, 1H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.5$ (t, $J = 4.1 \text{ Hz}$, 3F), -91.4 ppm (q, $J = 4.1 \text{ Hz}$, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 154.9, 148.4, 145.5, 131.7, 129.5, 128.0, 127.7, 119.6, 120.3$ (qt, $^1J(\text{C},\text{F}) = 289.6 \text{ Hz}$, $^2J(\text{C},\text{F}) = 40.6 \text{ Hz}$), 118.6 (tq, $^1J(\text{C},\text{F}) = 286.1 \text{ Hz}$, $^2J(\text{C},\text{F}) = 36.3 \text{ Hz}$), 116.7 ppm (t, $^3J(\text{C},\text{F}) = 2.9 \text{ Hz}$); IR (neat): $\nu = 3031, 1972, 1617, 1565, 1489, 1321, 1199, 1090, 948, 786, 748 \text{ cm}^{-1}$; MS (Ion trap, EI, 70 eV): m/z (%) = 279 [M^+] (87), 160 (100), 116 (14), 89 (31); HRMS (EI-TOF) calcd. for $\text{C}_{11}\text{H}_6\text{NF}_5\text{S}$: 279.0141; found: 279.0145.

Synthesis of 6-[(pentafluoroethyl)thio]quinoline (2p). Compound **2p** was prepared following the standard procedure, starting from quinoline-6-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, **2p** was isolated as colorless oil (229 mg, 0.82 mmol, 82%). ^1H NMR (400 MHz, CDCl_3): $\delta = 9.01$ (dd, $^3J = 4.3$,

1.8 Hz, 1H), 8.19 (d, $^3J = 8.8$ Hz, 2H), 8.14 (d, $^3J = 8.8$ Hz, 1H), 7.89 (dd, $^3J = 8.8$, 1.8 Hz, 1H), 7.48 ppm (dd, $^3J = 8.5$, 4.3 Hz, 1H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.4$ (t, $J = 3.8$ Hz, 3F), -91.5 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 152.4$, 148.7, 137.7, 136.2, 136.1, 130.8, 128.3, 122.1, 121.1 (t, $^3J(\text{C},\text{F}) = 2.9$ Hz), 120.2 (qt, $^1J(\text{C},\text{F}) = 289.0$ Hz, $^2J(\text{C},\text{F}) = 40.6$ Hz), 118.6 ppm (tq, $^1J(\text{C},\text{F}) = 286.8$ Hz, $^2J(\text{C},\text{F}) = 36.7$ Hz); IR (neat): $\nu = 3037$, 1591, 1488, 1331, 1202, 1095, 959, 835, 794, 749, 660 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 279 [M^+] (88), 160 (100), 116 (23); HRMS (EI-TOF) calcd. for $\text{C}_{11}\text{H}_6\text{NF}_5\text{S}$: 279.0141; found: 279.0130.

Synthesis of 8-[(pentafluoroethyl)thio]quinoline (2q). Compound **2q** was prepared following the standard procedure, starting from quinoline-8-diazonium tetrafluoroborate (243 mg, 1.00 mmol). After purification, **2q** was isolated as colorless oil (198 mg, 0.71 mmol, 71%). ^1H NMR (400 MHz, CDCl_3): $\delta = 9.07$ (dd, $^3J = 4.3$, 1.8 Hz, 1H), 8.21 (dd, $^3J = 8.3$, 1.5 Hz, 1H), 8.15 (d, $^3J = 7.3$ Hz, 1H), 7.94 (dd, $^3J = 8.0$, 1.3 Hz, 1H), 7.58 (t, $^3J = 7.8$ Hz, 1H), 7.50 ppm (dd, $^3J = 8.3$, 4.3 Hz, 1H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.6$ (t, $J = 4.1$ Hz, 3F), -91.0 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 151.2$, 147.9, 137.5, 136.5, 130.9, 130.0, 126.4, 124.3, 122.0, 120.3 (qt, $^1J(\text{C},\text{F}) = 290.3$ Hz, $^2J(\text{C},\text{F}) = 40.6$ Hz), 118.7 ppm (tq, $^1J(\text{C},\text{F}) = 286.6$ Hz, $^2J(\text{C},\text{F}) = 36.8$ Hz); IR (neat): $\nu = 3065$, 1596, 1493, 1328, 1204, 1093, 950, 826, 787, 750, 660 cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 279 [M^+] (80), 160 (100), 116 (15); HRMS (EI-TOF) calcd. for $\text{C}_{11}\text{H}_6\text{NF}_5\text{S}$: 279.0141; found: 279.0134.

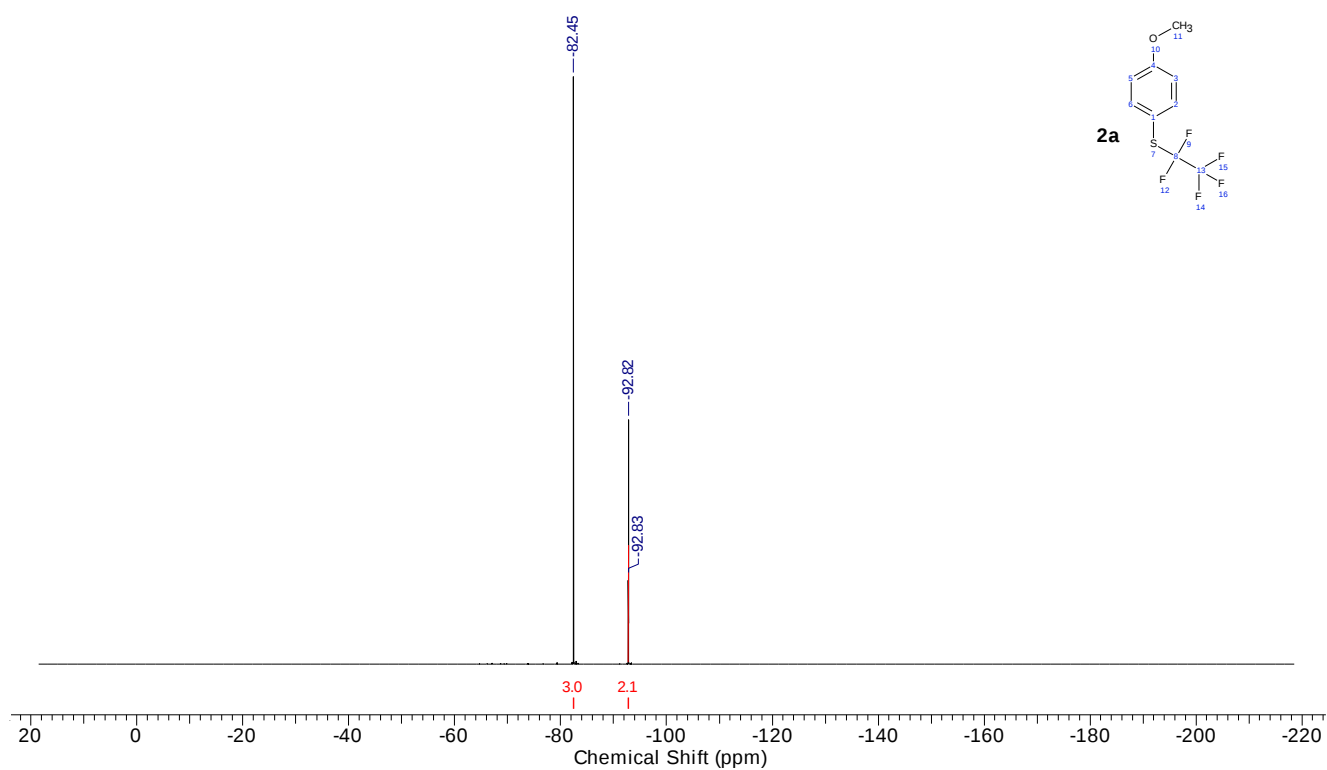
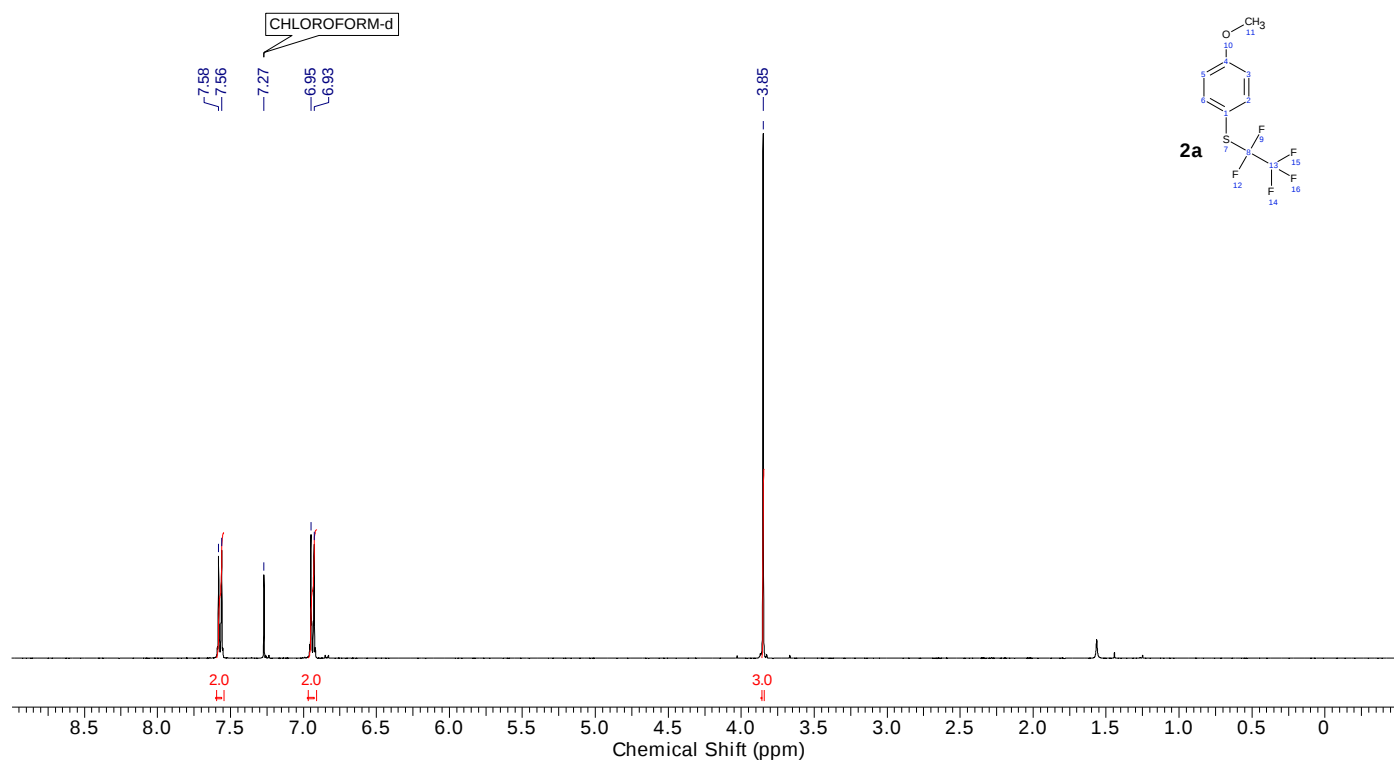
Synthesis of 9-ethyl-3-[(pentafluoroethyl)thio]-9H-carbazole (2r). Compound **2r** was prepared following the standard procedure, starting from 9-ethyl-9H-carbazol-3-diazonium tetrafluoroborate (309 mg, 1.00 mmol). After purification, **2r** was isolated as colorless solid (249 mg, 0.72 mmol, 72%). m.p.: 64-65°C; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.40$ (s, 1H), 8.14 (d, $^3J = 7.8$ Hz, 1H), 7.73 (dd, $^3J = 8.5$, 1.8 Hz, 1H), 7.55 (dt, $^3J = 7.7$, 1.1 Hz, 1H), 7.44 (t, $^3J = 8.8$ Hz, 2H), 7.32 (t, $^3J = 7.8$ Hz, 1H), 4.38 (q, $^3J = 7.3$ Hz, 2H), 1.47 ppm (t, $^3J = 7.3$ Hz, 3H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.2$ (t, $J = 4.1$ Hz, 3F), -92.7 ppm (q, $J = 3.6$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 141.1$, 140.3, 134.3, 130.2, 126.6, 123.9, 122.2, 120.7, 120.2 (qt, $^1J(\text{C},\text{F}) = 287.9$ Hz, $^2J(\text{C},\text{F}) = 40.0$ Hz), 119.8, 118.8 (tq, $^1J(\text{C},\text{F}) = 287.0$ Hz,

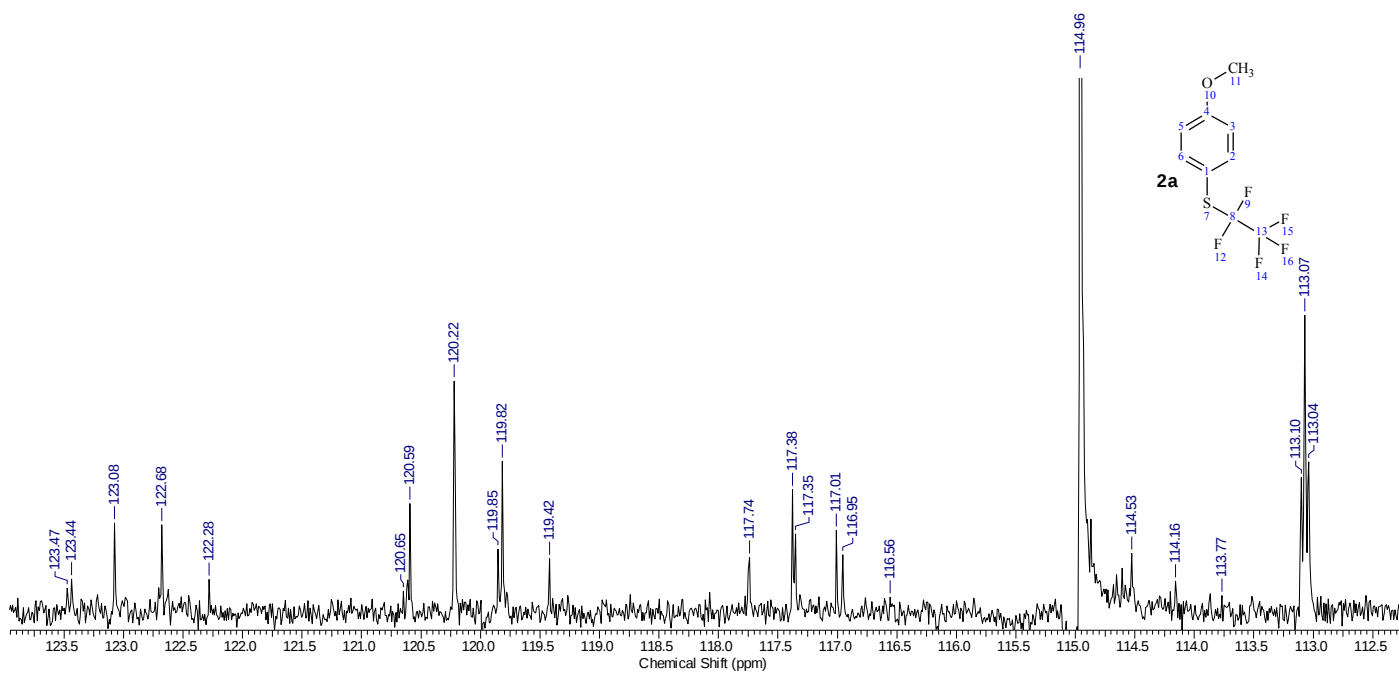
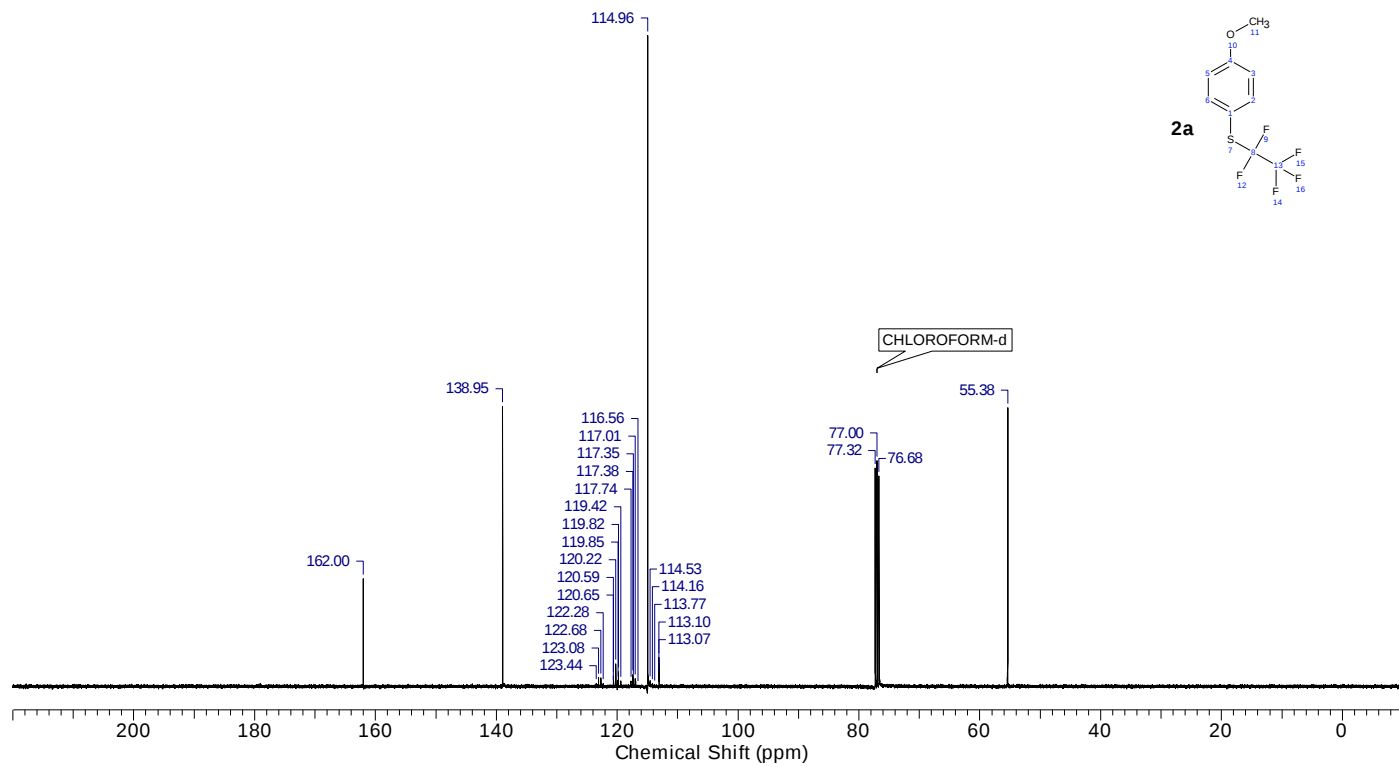
$^2J(\text{C},\text{F}) = 37.2$ Hz), 110.7 (t, $^3J(\text{C},\text{F}) = 3.1$ Hz), 109.2, 108.9, 37.7, 13.8 ppm; IR (neat): $\nu = 3055, 2975, 1588, 1474, 1330, 1200, 1074, 958, 884, 798, 742, 654$ cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 345 [M^+] (54), 330 (12), 226 (100), 211 (27), 197 (14), 167 (16); HRMS (EI-TOF) calcd. for $\text{C}_{16}\text{H}_{12}\text{NF}_5\text{S}$: 345.0611; found: 345.0616.

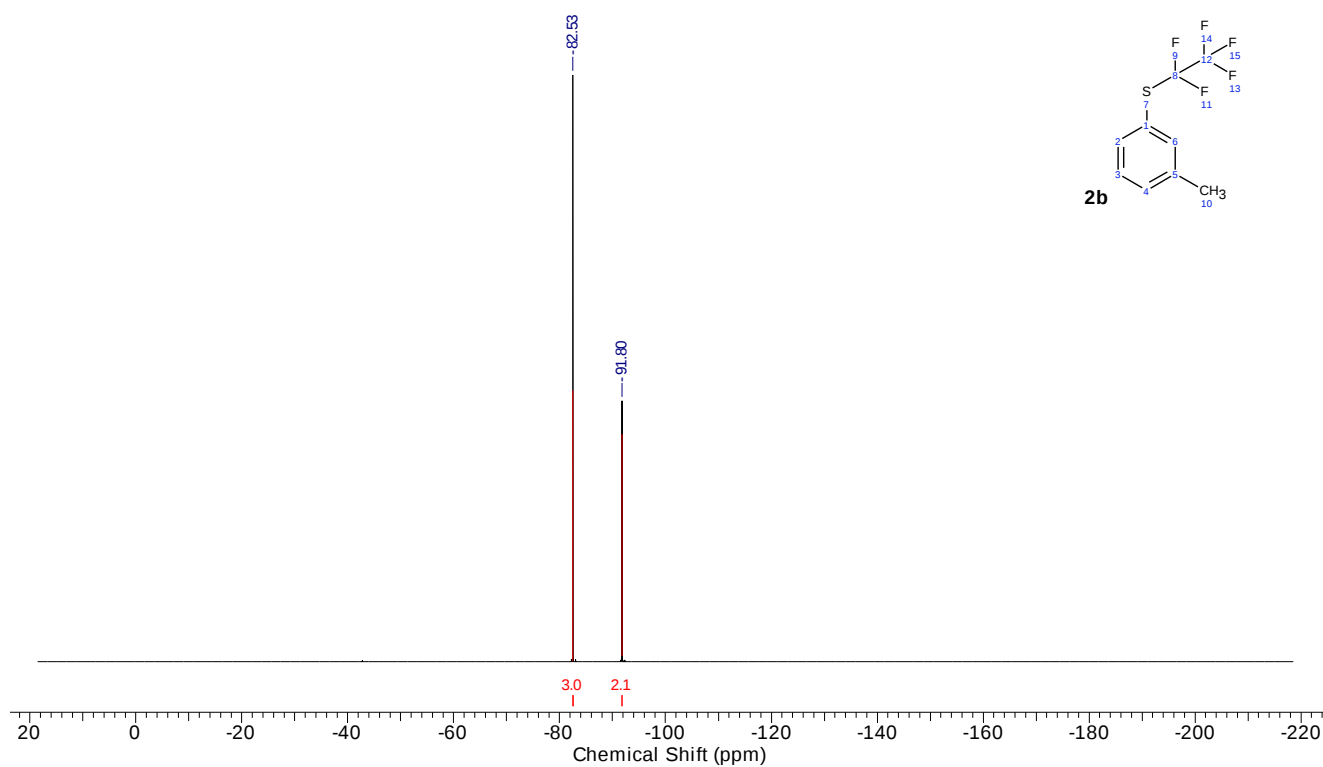
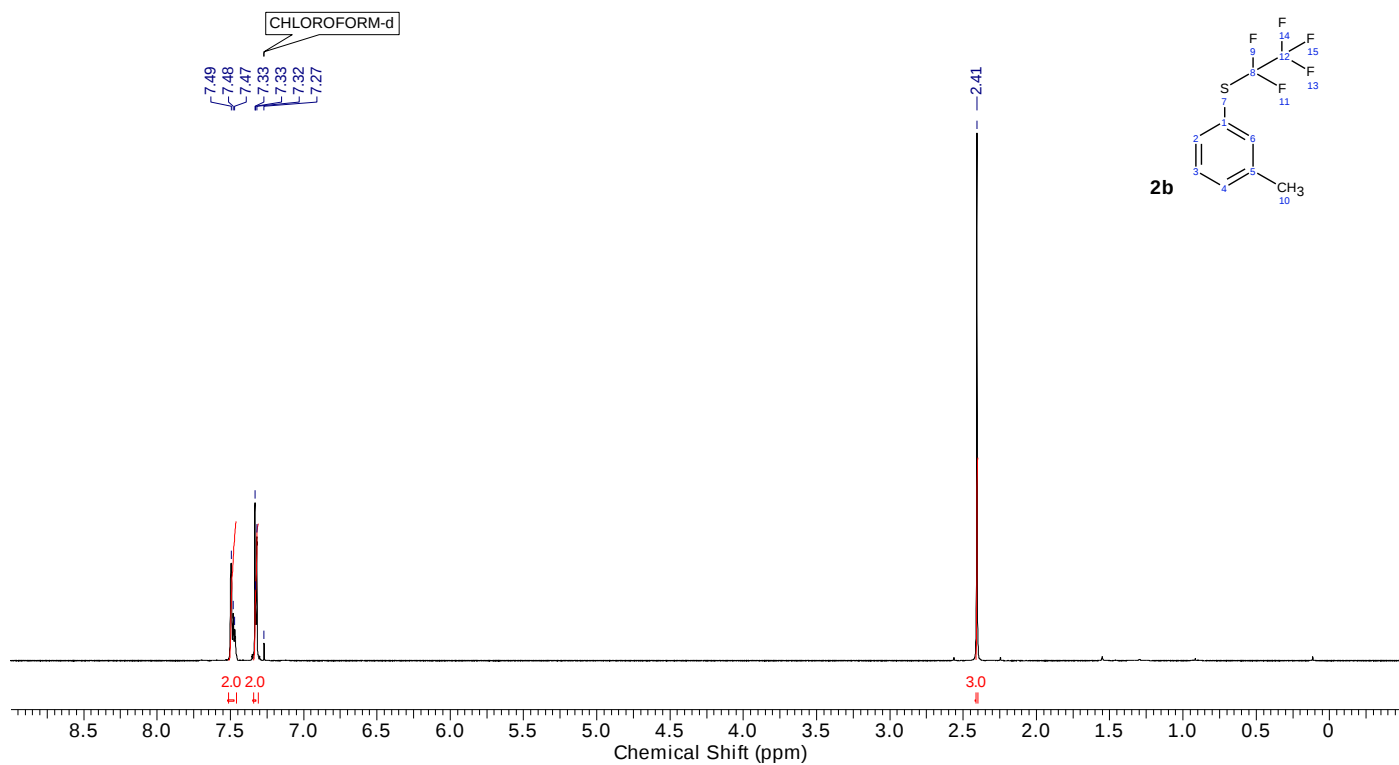
Synthesis of methyl-3-[(pentafluoroethyl)thio]thiophene-2-carboxylate (2s).

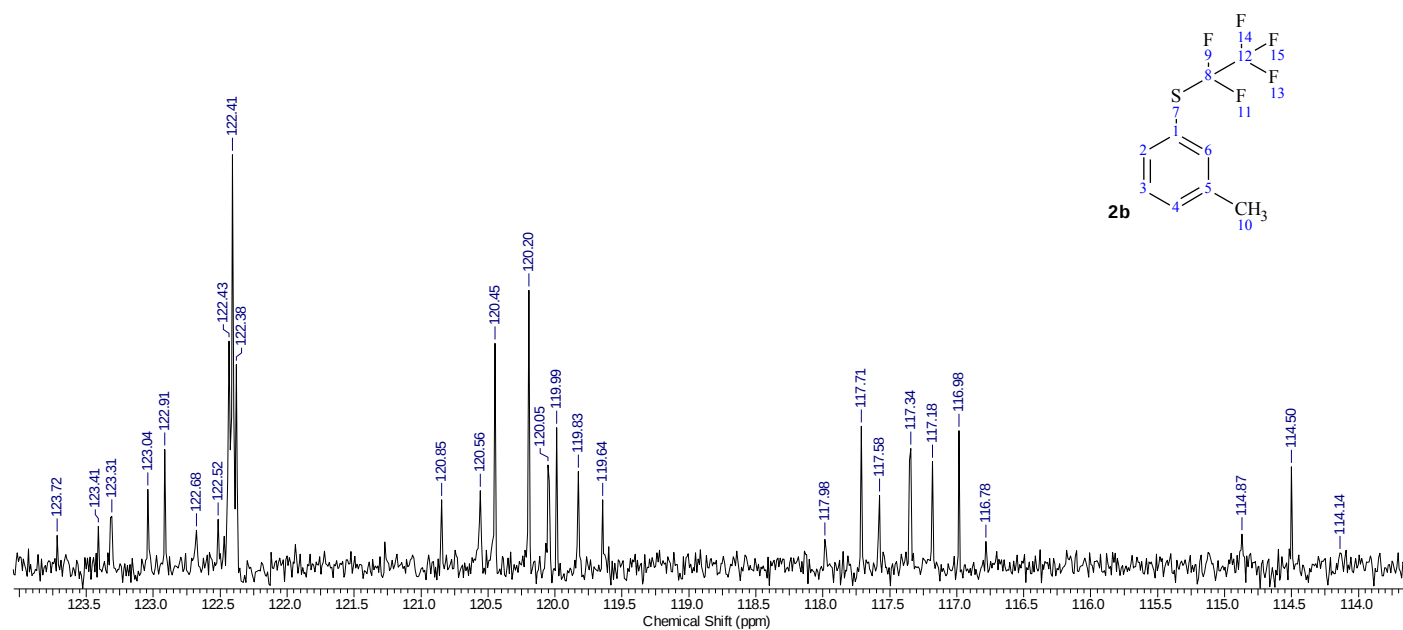
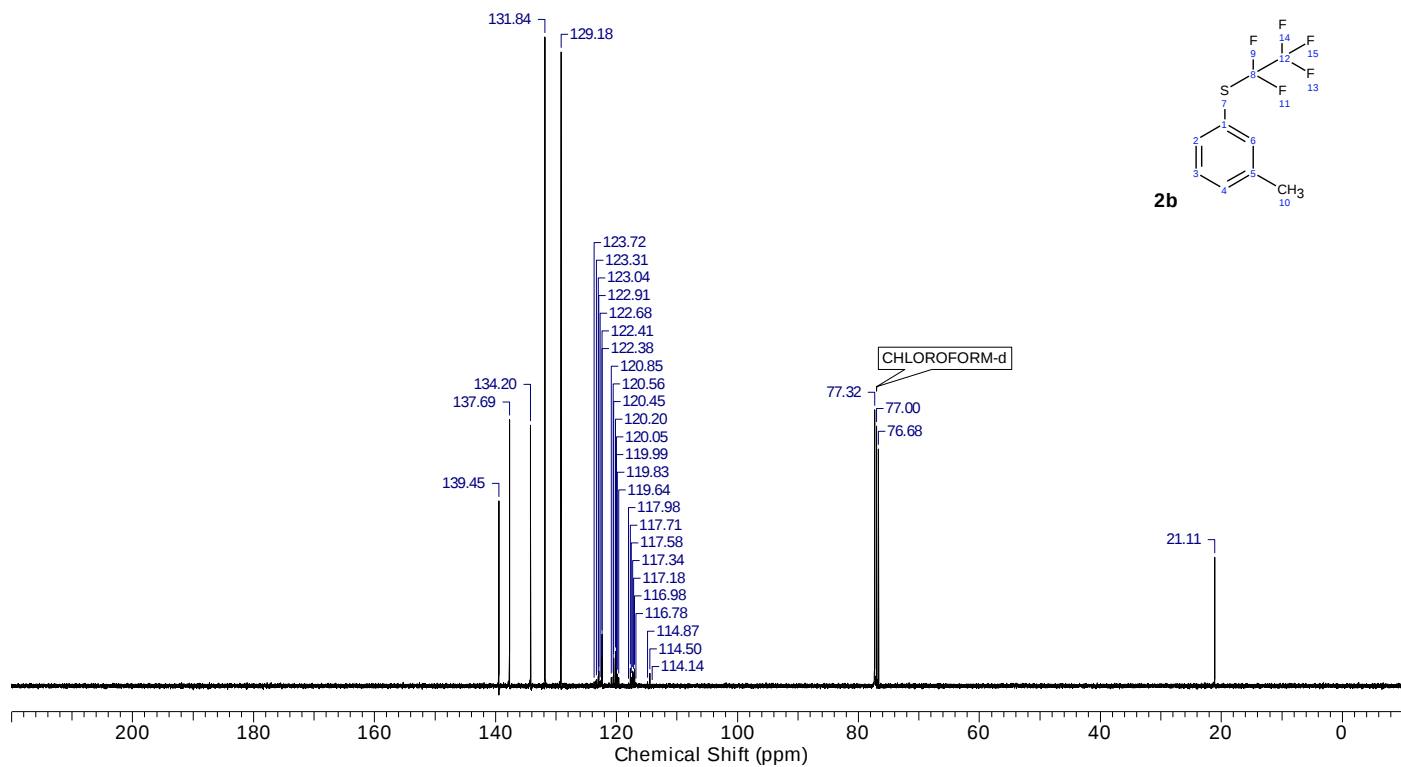
Compound **2s** was prepared following the standard procedure, starting from 2-(methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate (256 mg, 1.00 mmol). After purification, **2s** was isolated as colorless oil (286 mg, 0.98 mmol, 98%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.59$ (d, $^3J = 5.3$ Hz, 1H), 7.30 (d, $^3J = 5.3$ Hz, 1H), 3.92 ppm (s, 3H); ^{19}F NMR (375 MHz, CDCl_3): $\delta = -82.8$ (t, $J = 4.1$ Hz, 3F), -91.2 ppm (q, $J = 4.1$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 161.3, 132.6, 132.2$ (t, $^3J(\text{C},\text{F}) = 2.7$ Hz), 131.0, 126.6 (t, $^3J(\text{C},\text{F}) = 1.8$ Hz), 120.3 (qt, $^1J(\text{C},\text{F}) = 291.9$ Hz, $^2J(\text{C},\text{F}) = 41.3$ Hz), 118.1 (tq, $^1J(\text{C},\text{F}) = 287.0$ Hz, $^2J(\text{C},\text{F}) = 35.8$ Hz), 52.5 ppm; IR (neat): $\nu = 2955, 1709, 1502, 1439, 1266, 1204, 1075, 958, 893, 793, 768, 750$ cm^{-1} ; MS (Ion trap, EI, 70 eV): m/z (%) = 291 [M^+] (95), 261 (52), 172 (100), 142 (43), 114 (20); HRMS (EI-TOF) calcd. for $\text{C}_8\text{H}_5\text{F}_5\text{O}_2\text{S}_2$: 291.9651; found: 291.9675.

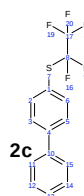
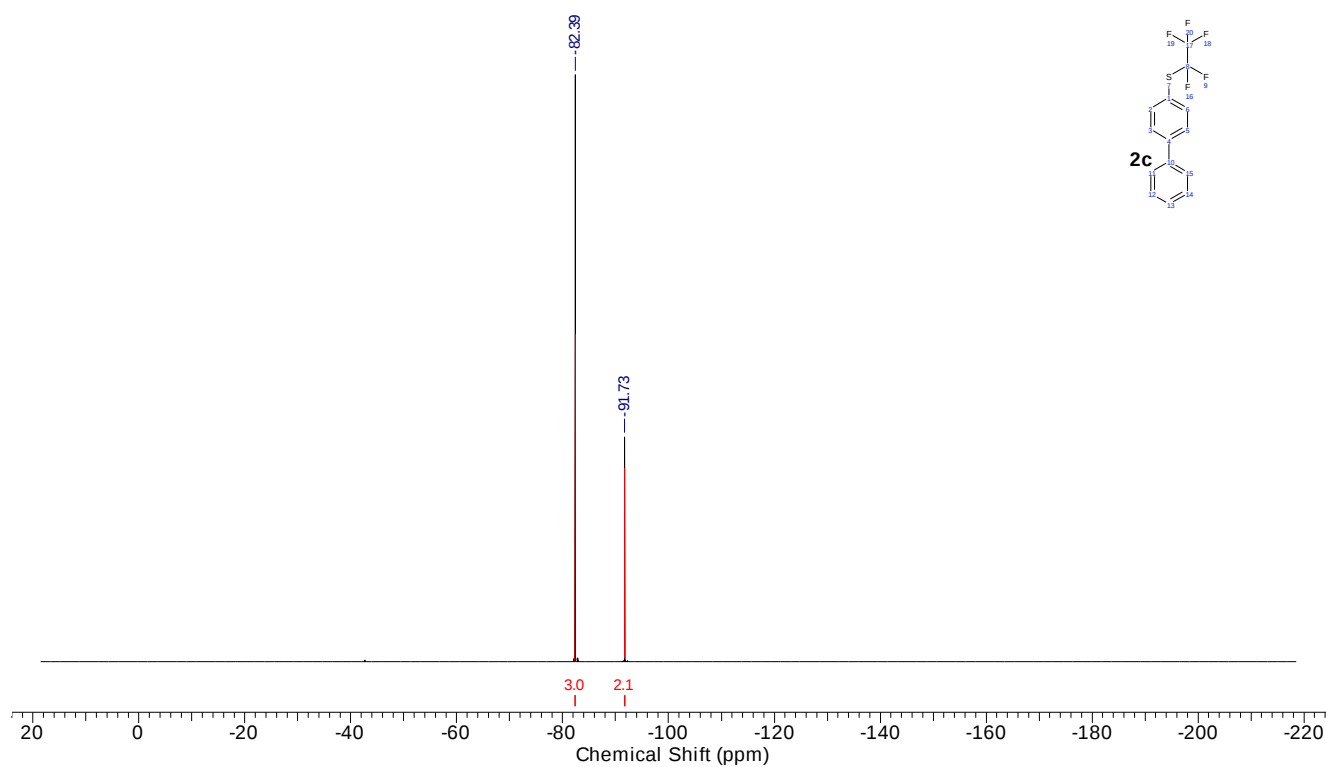
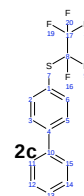
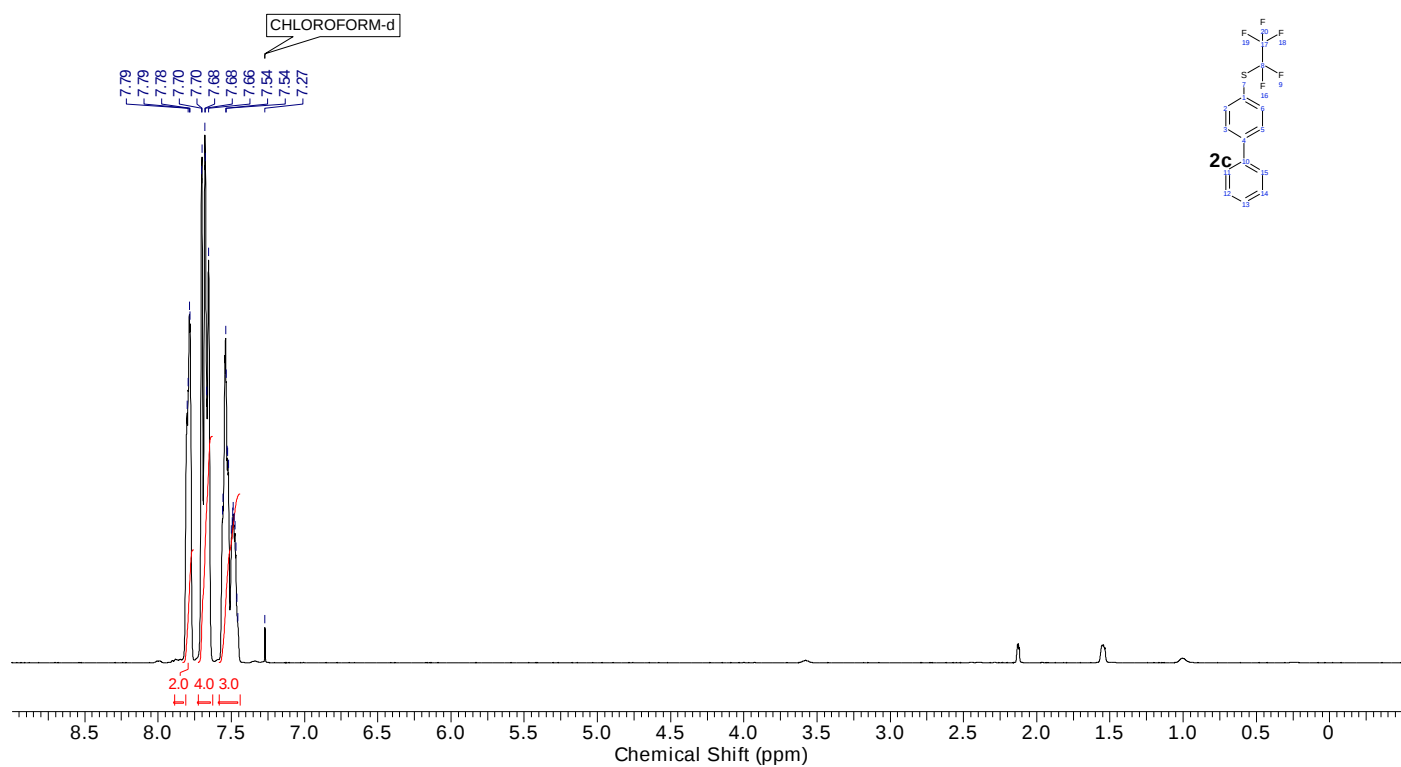
Spectroscopic data

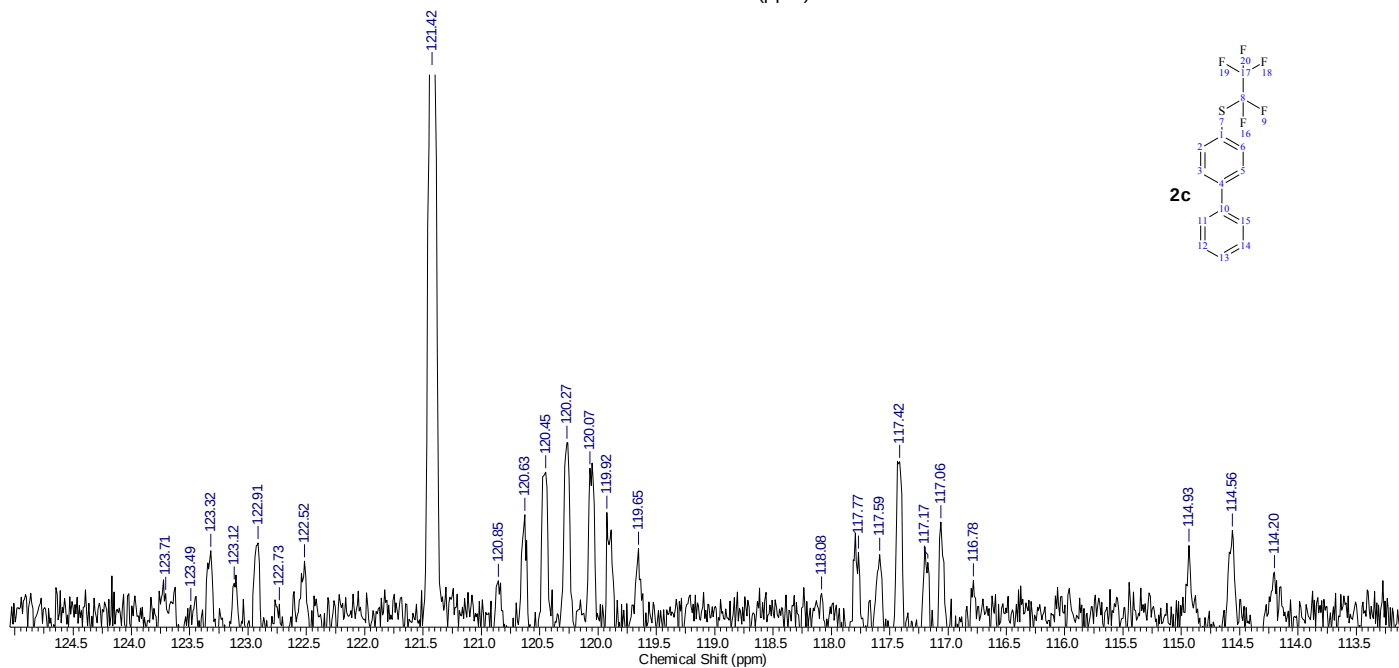
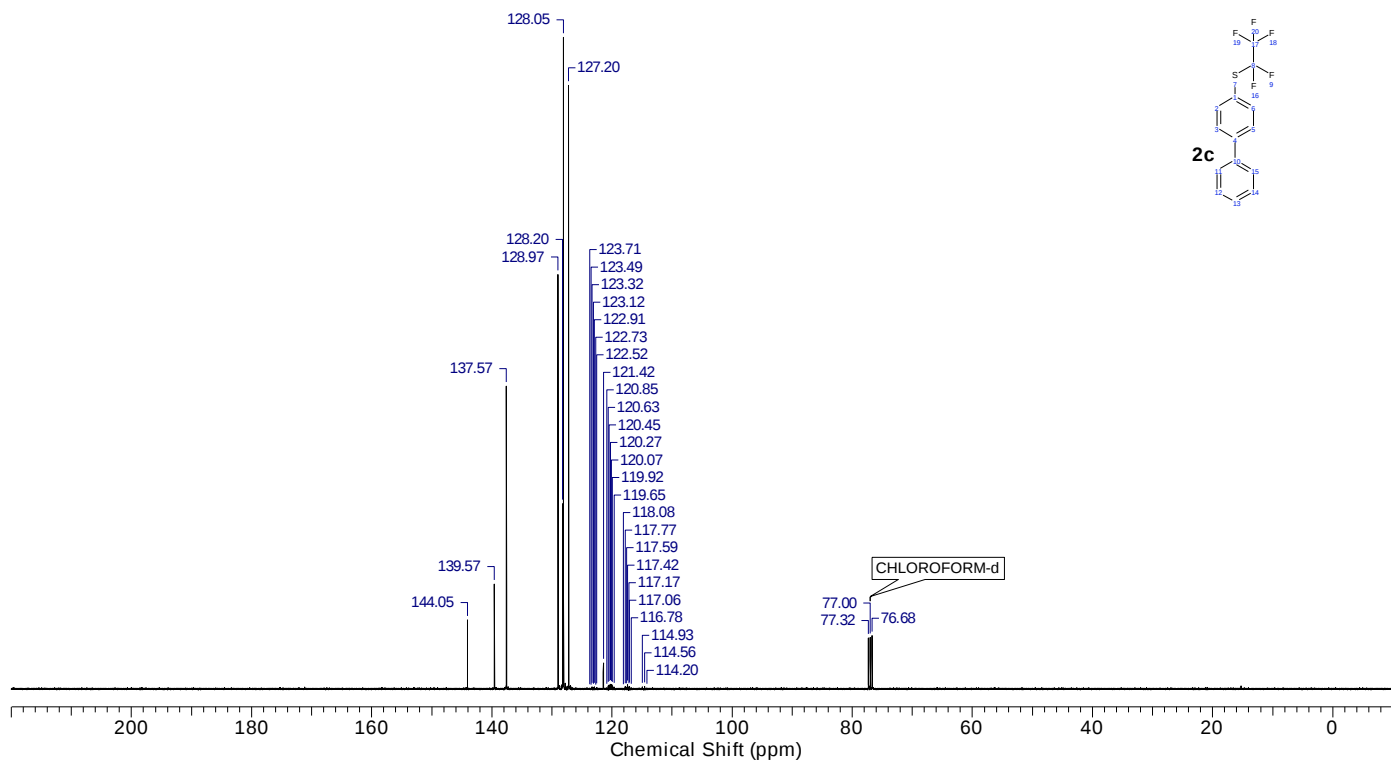


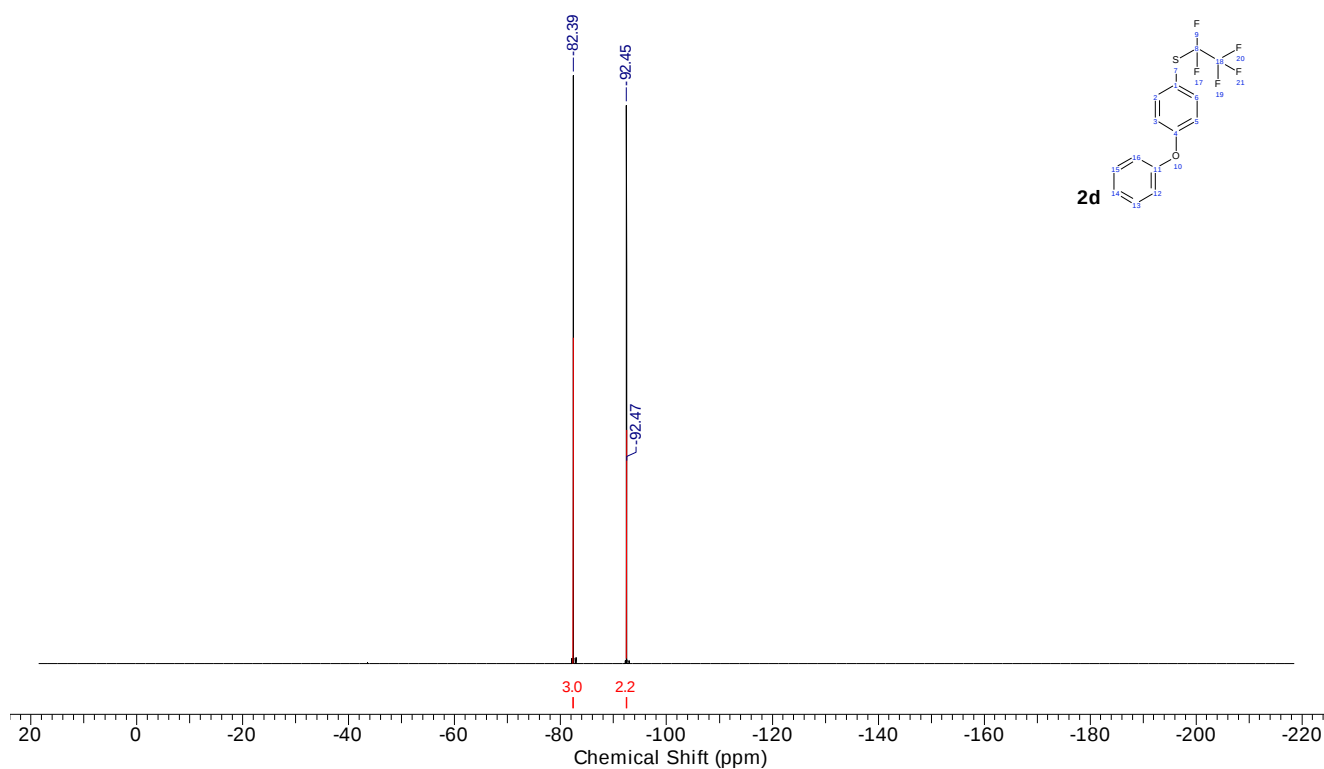
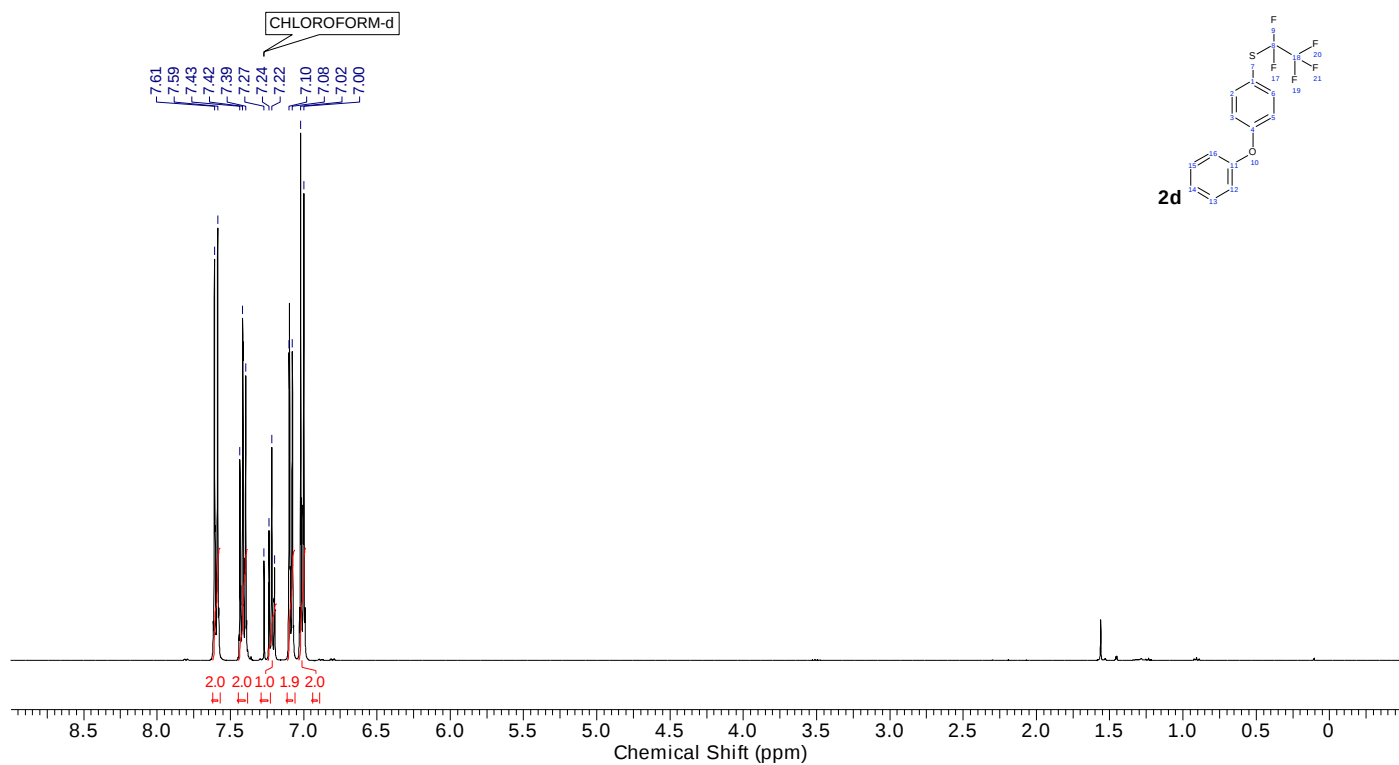


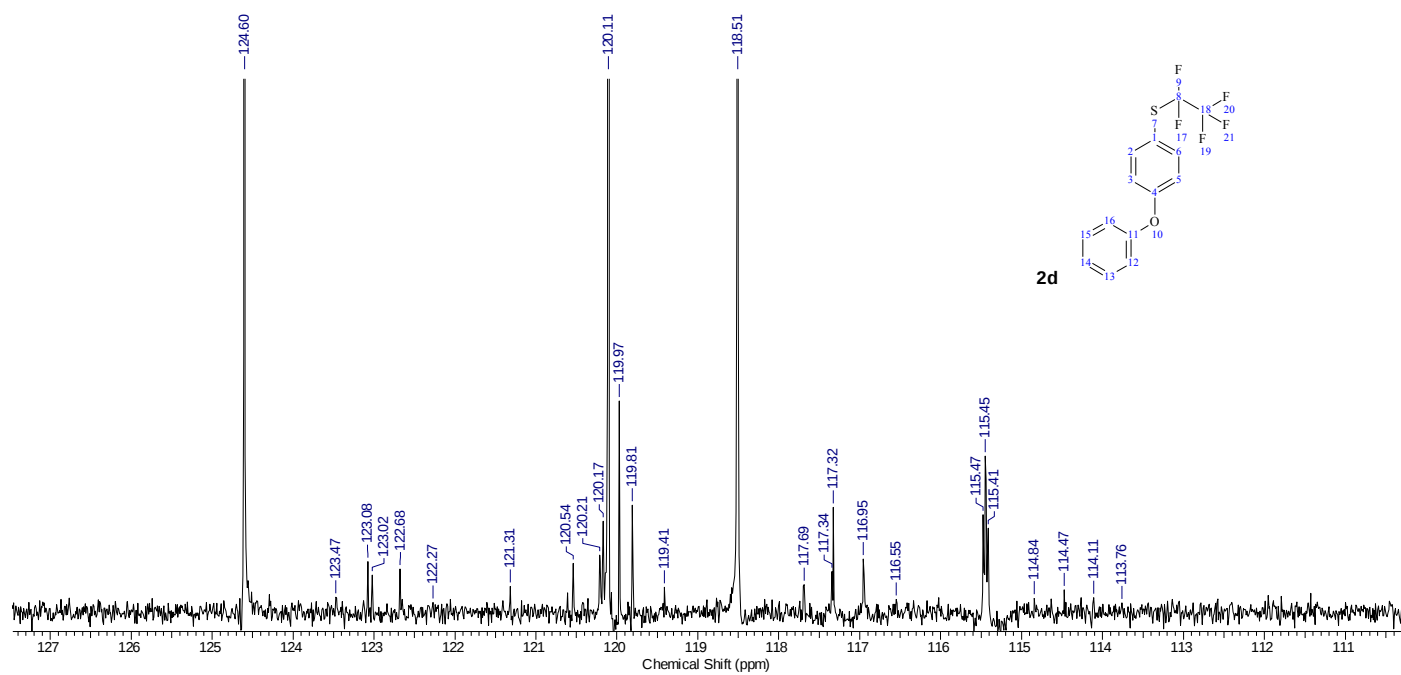
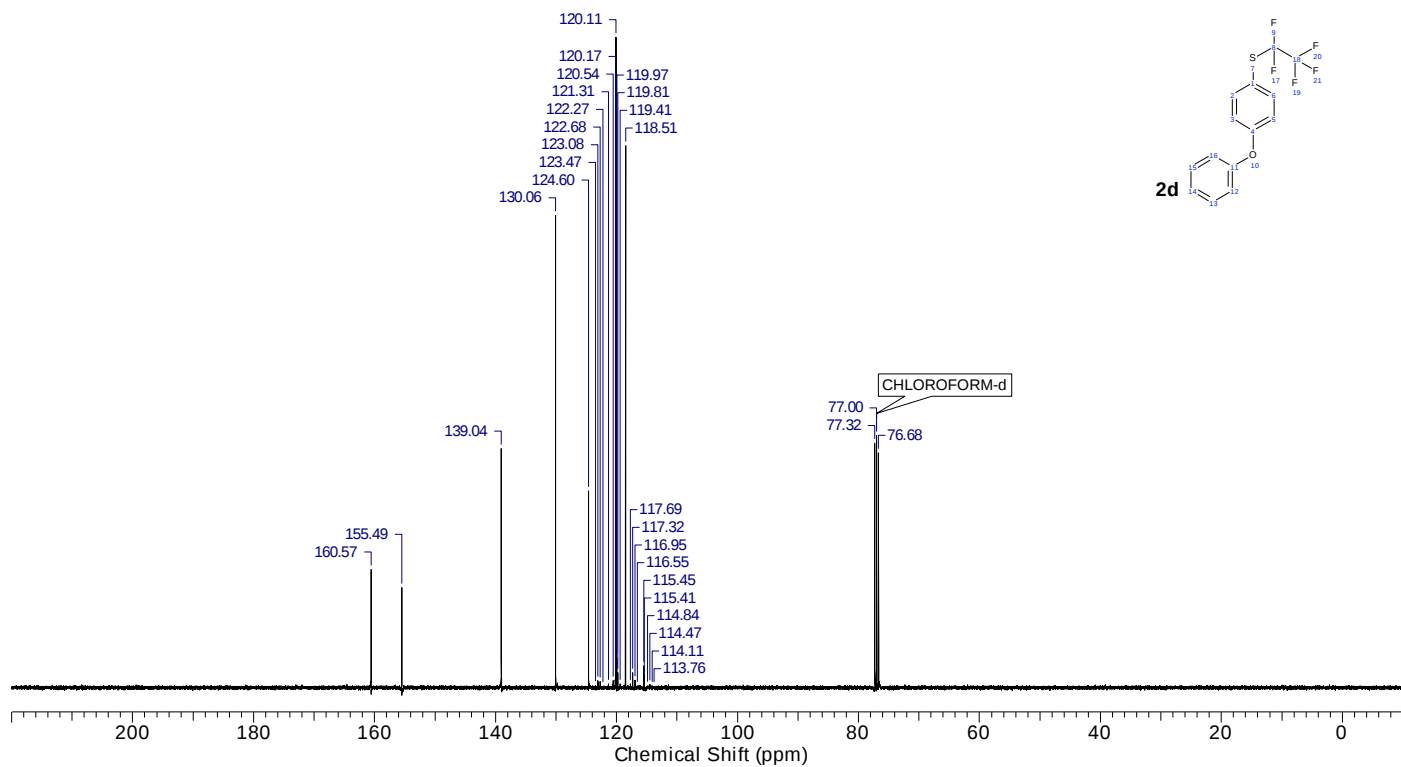


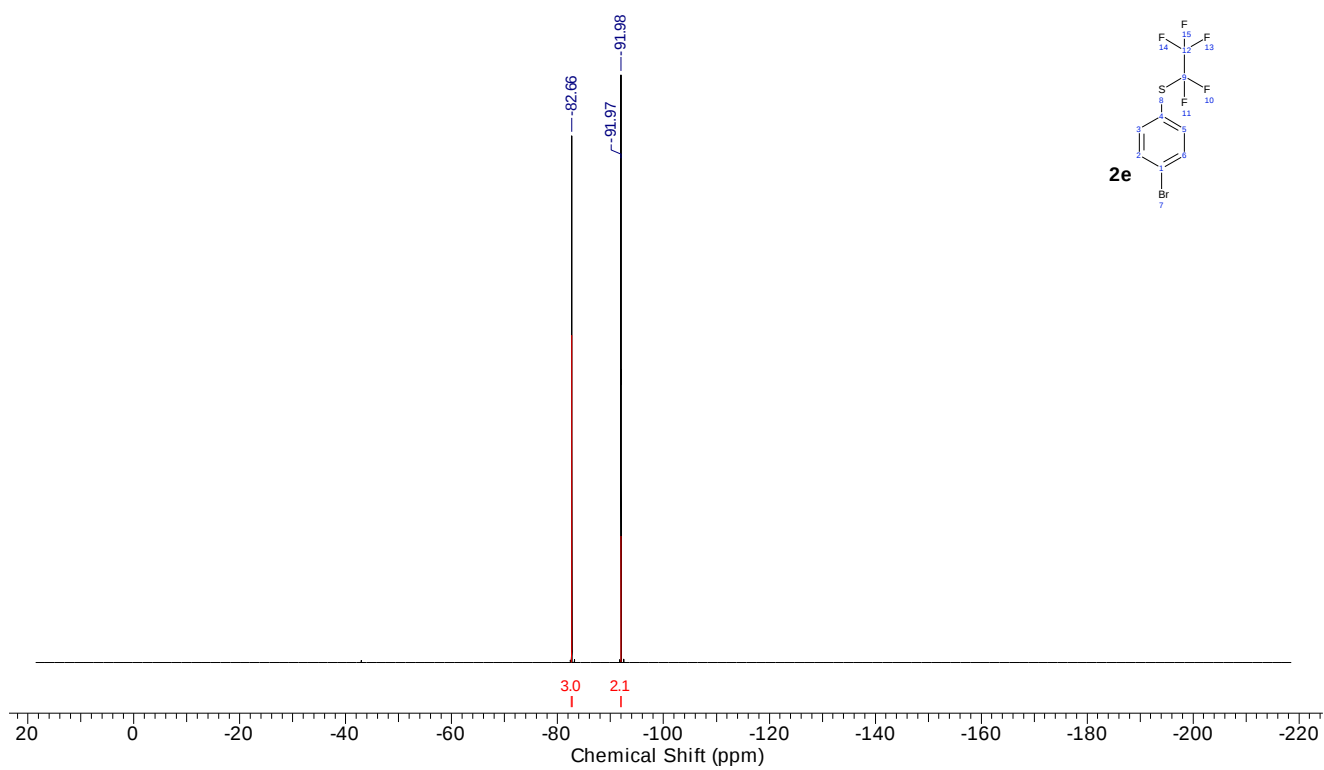
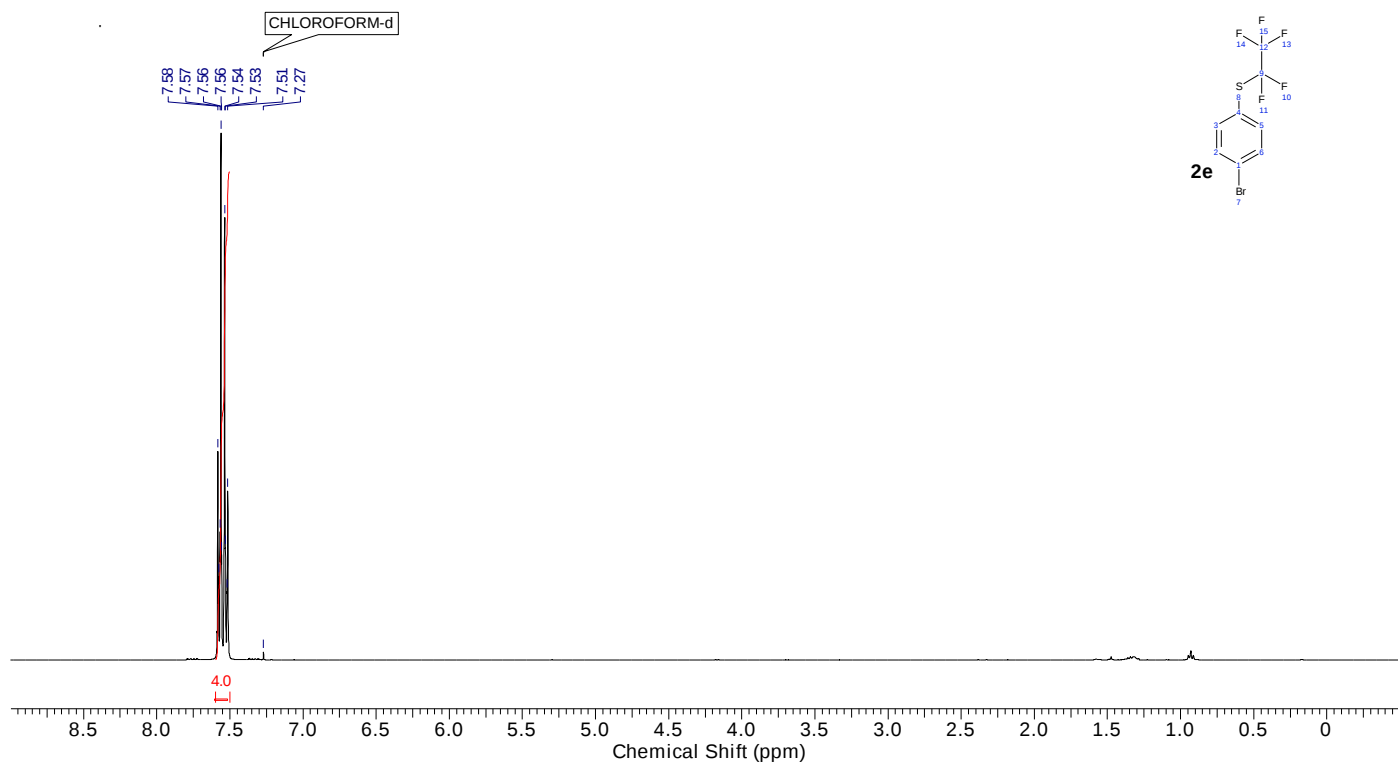


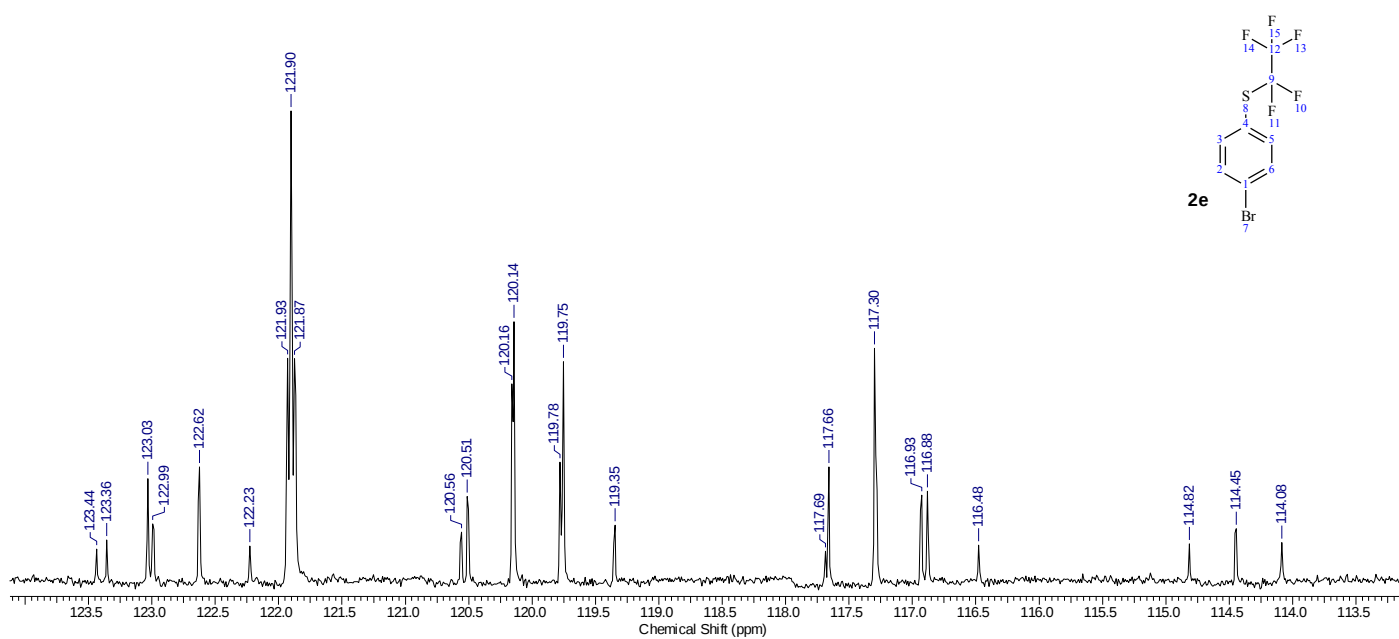
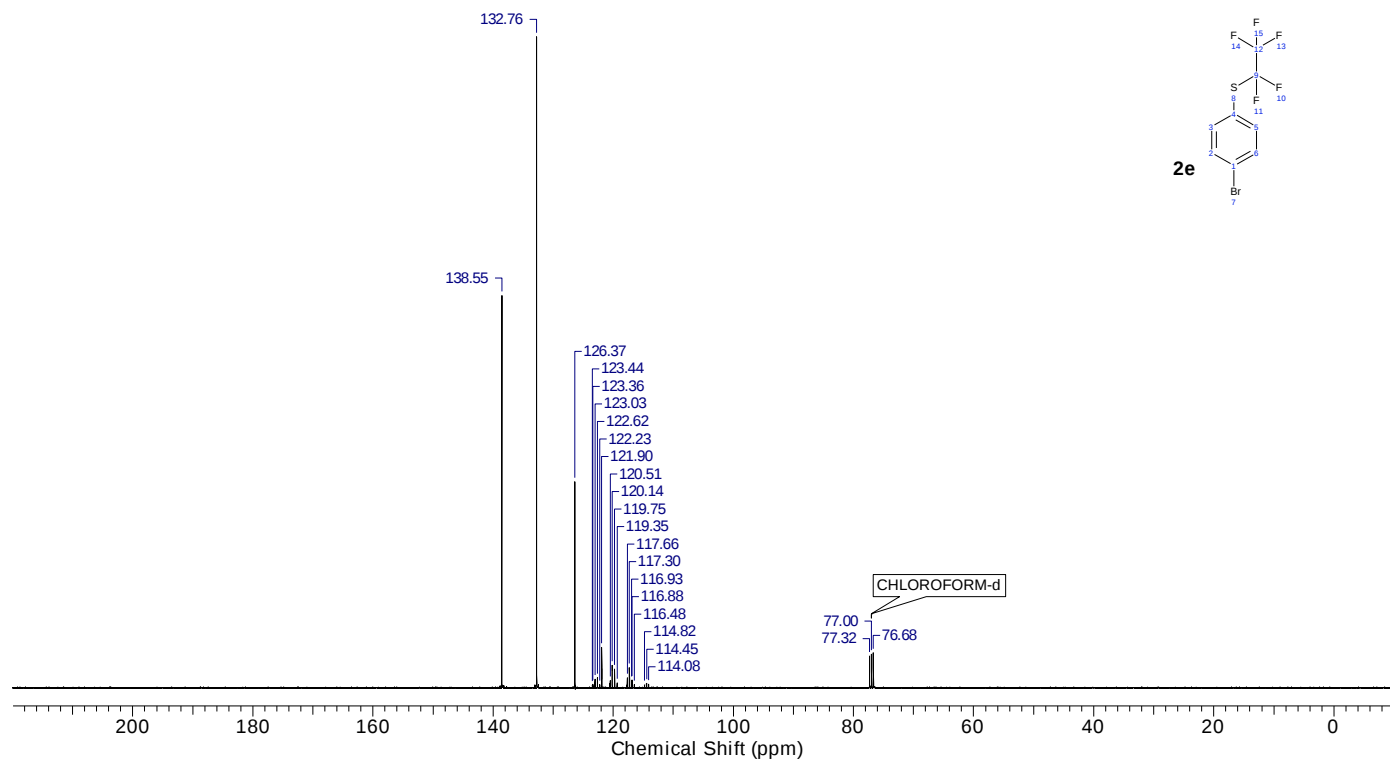


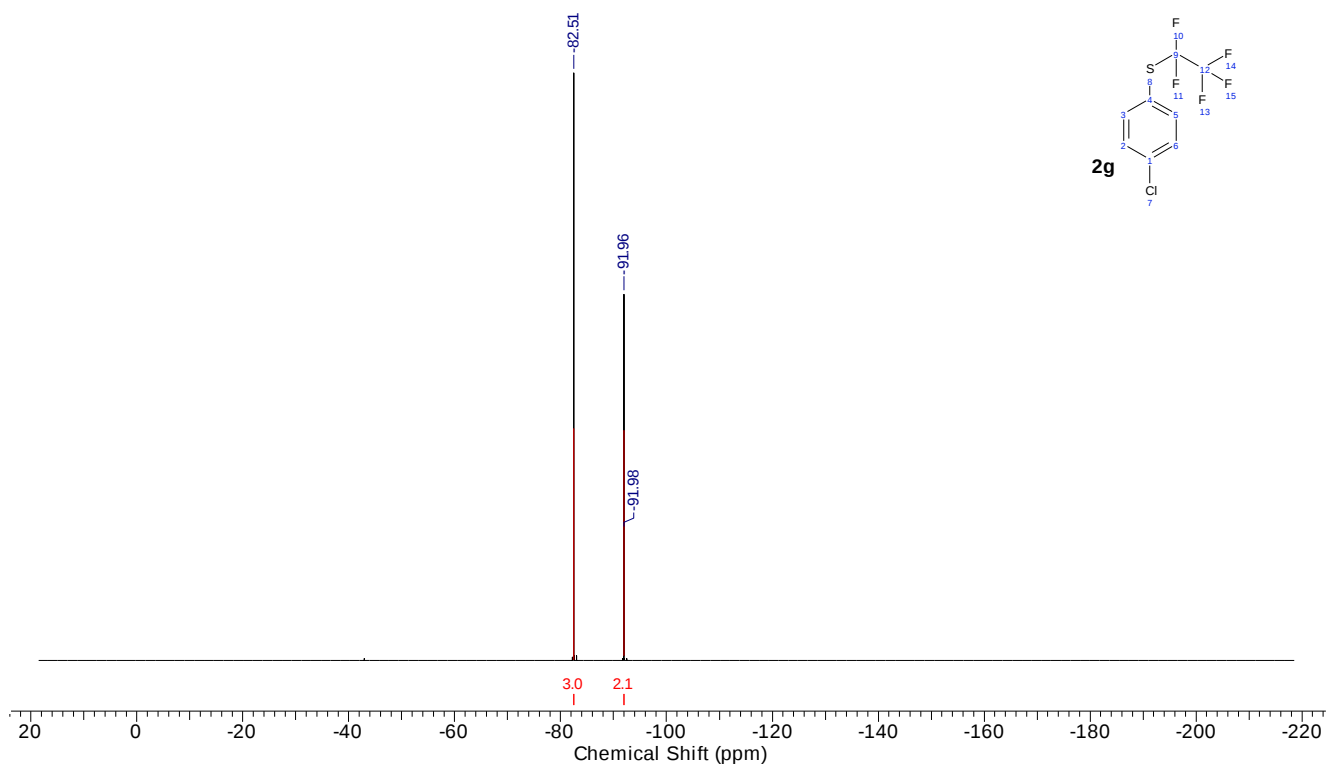
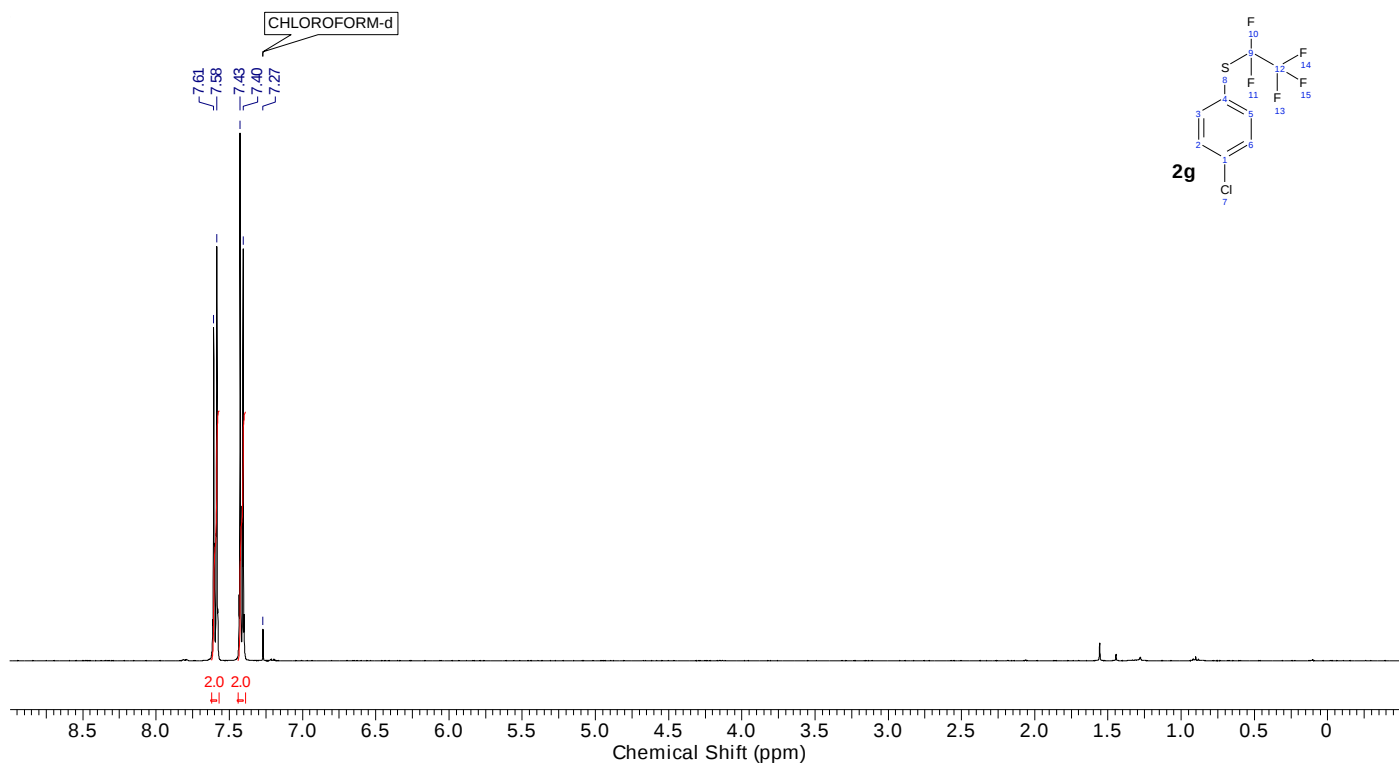


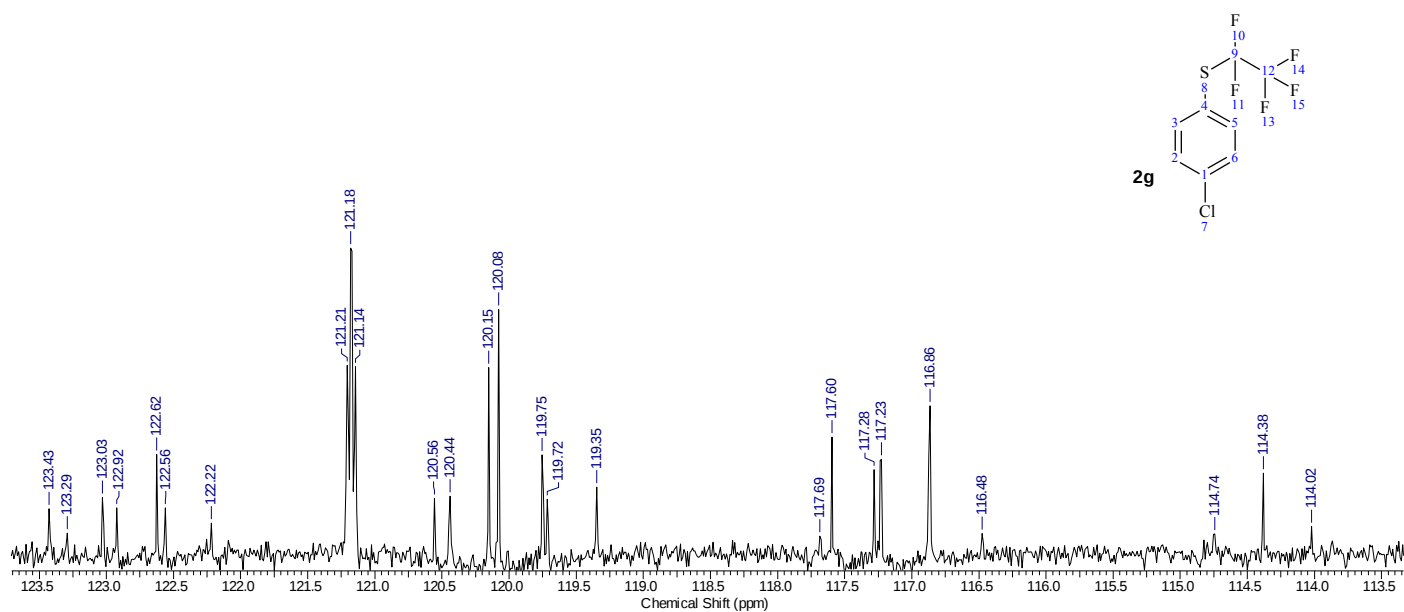
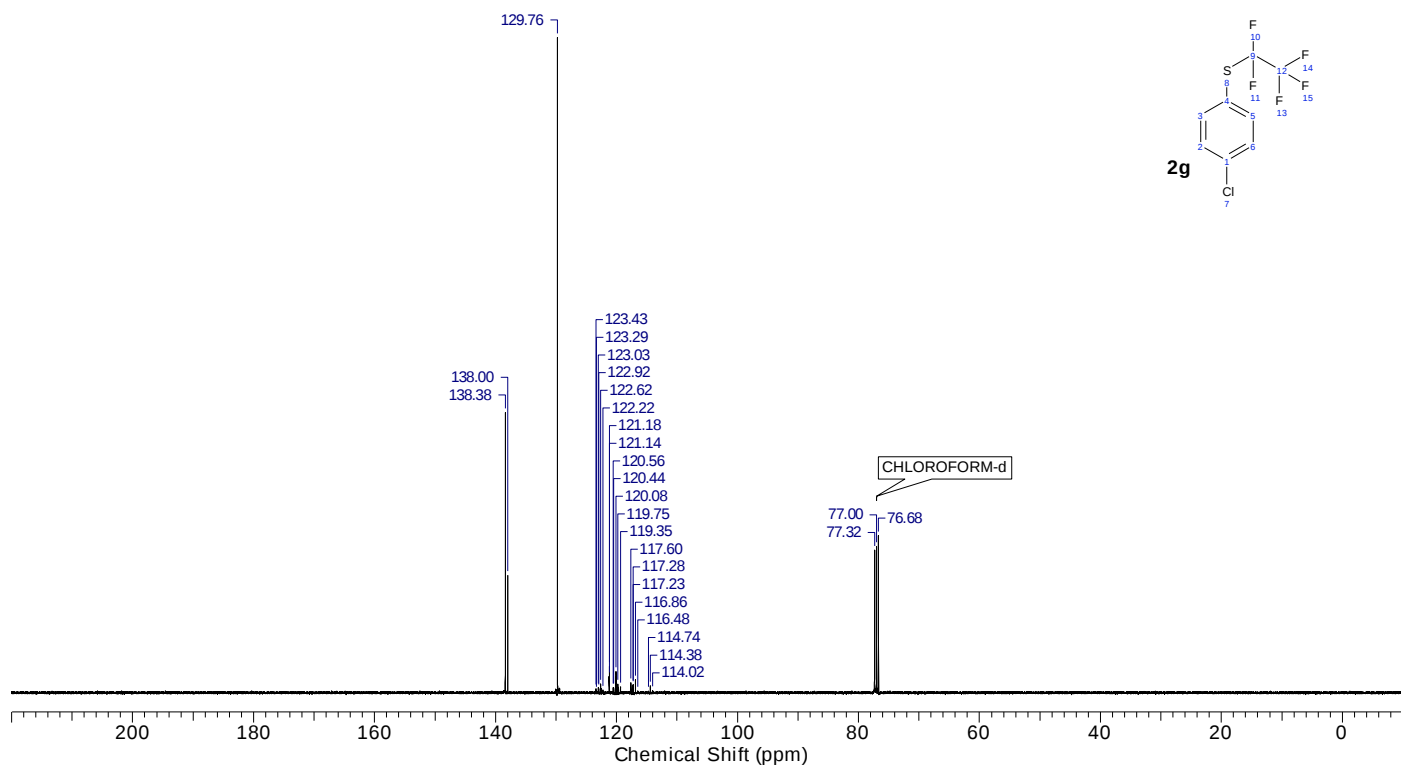


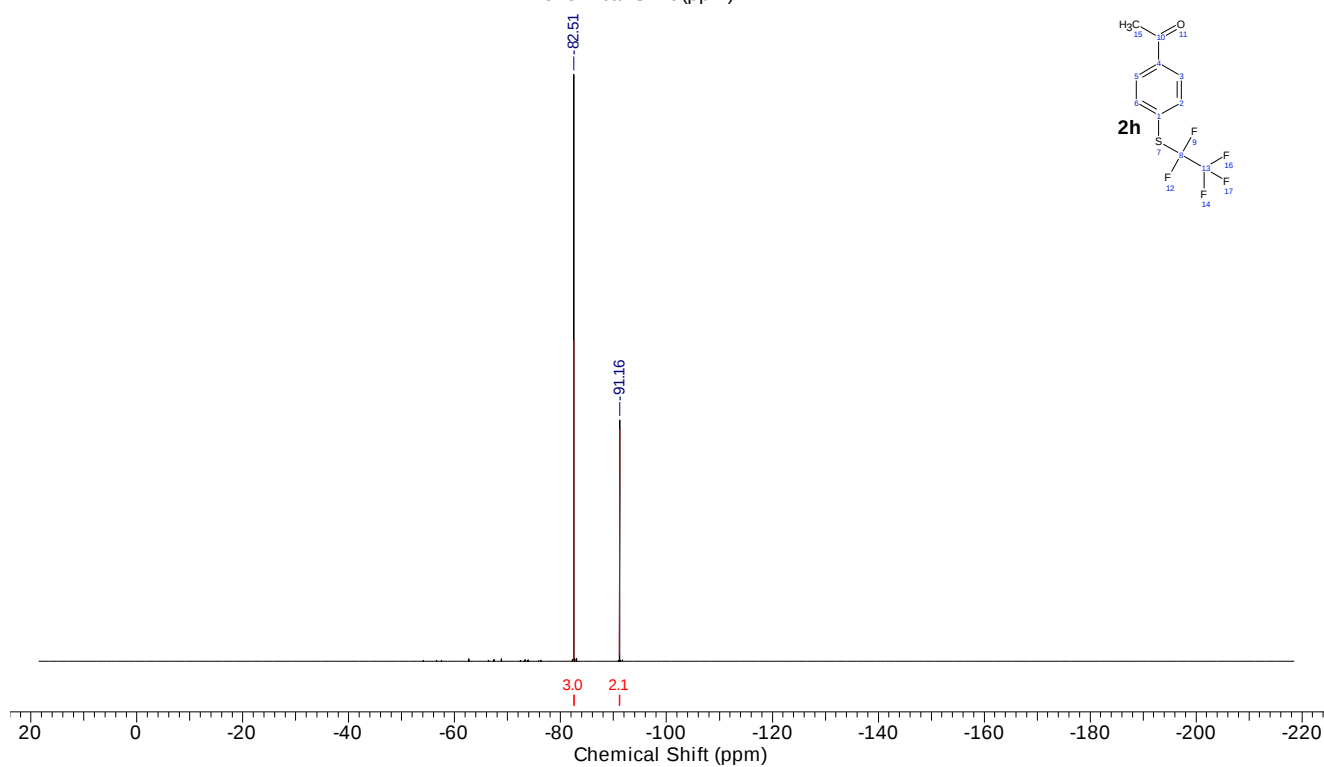
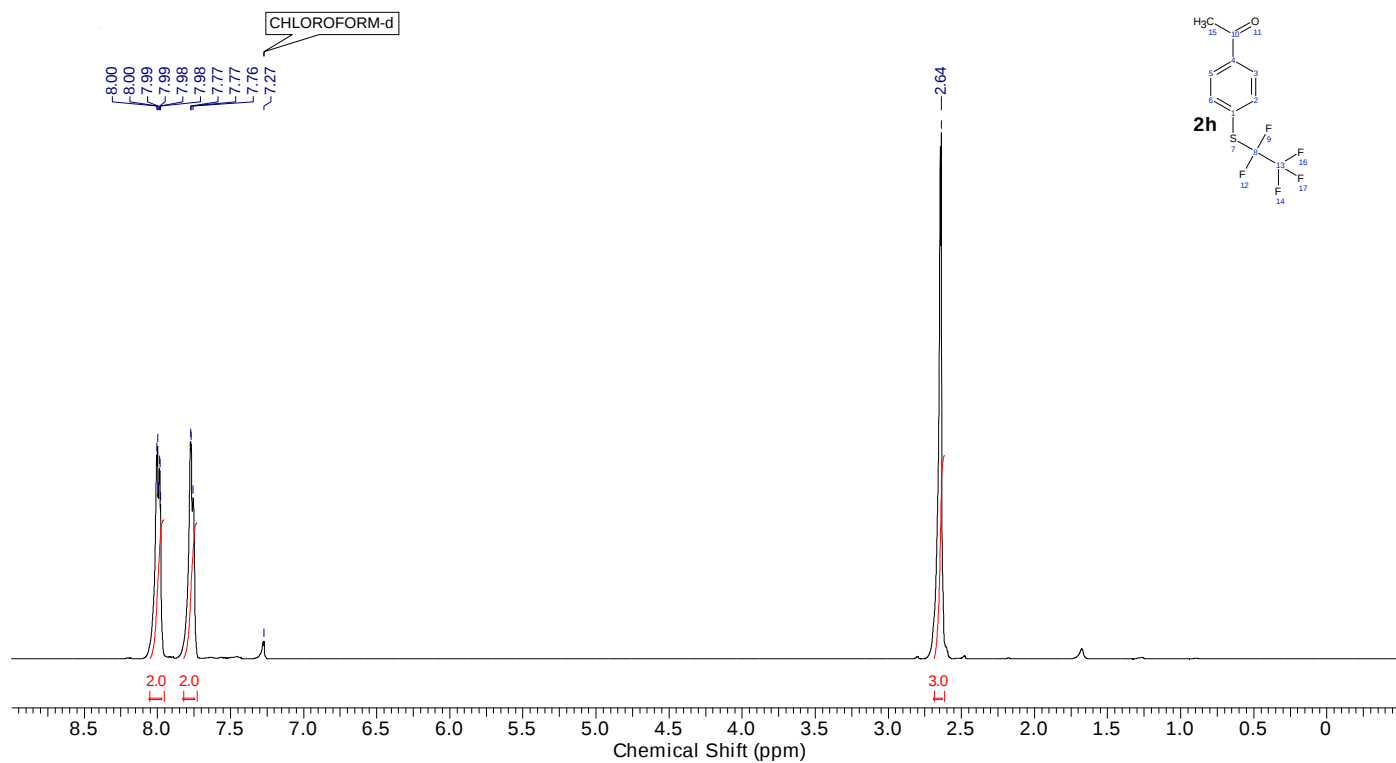


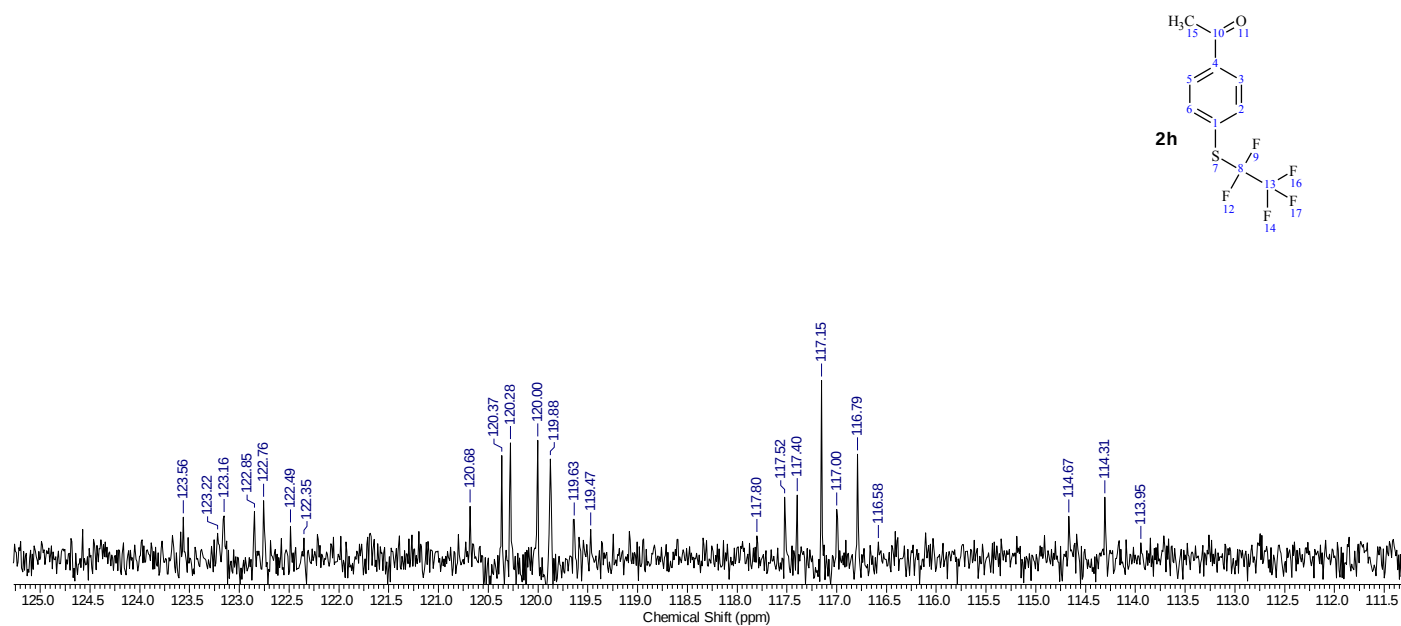
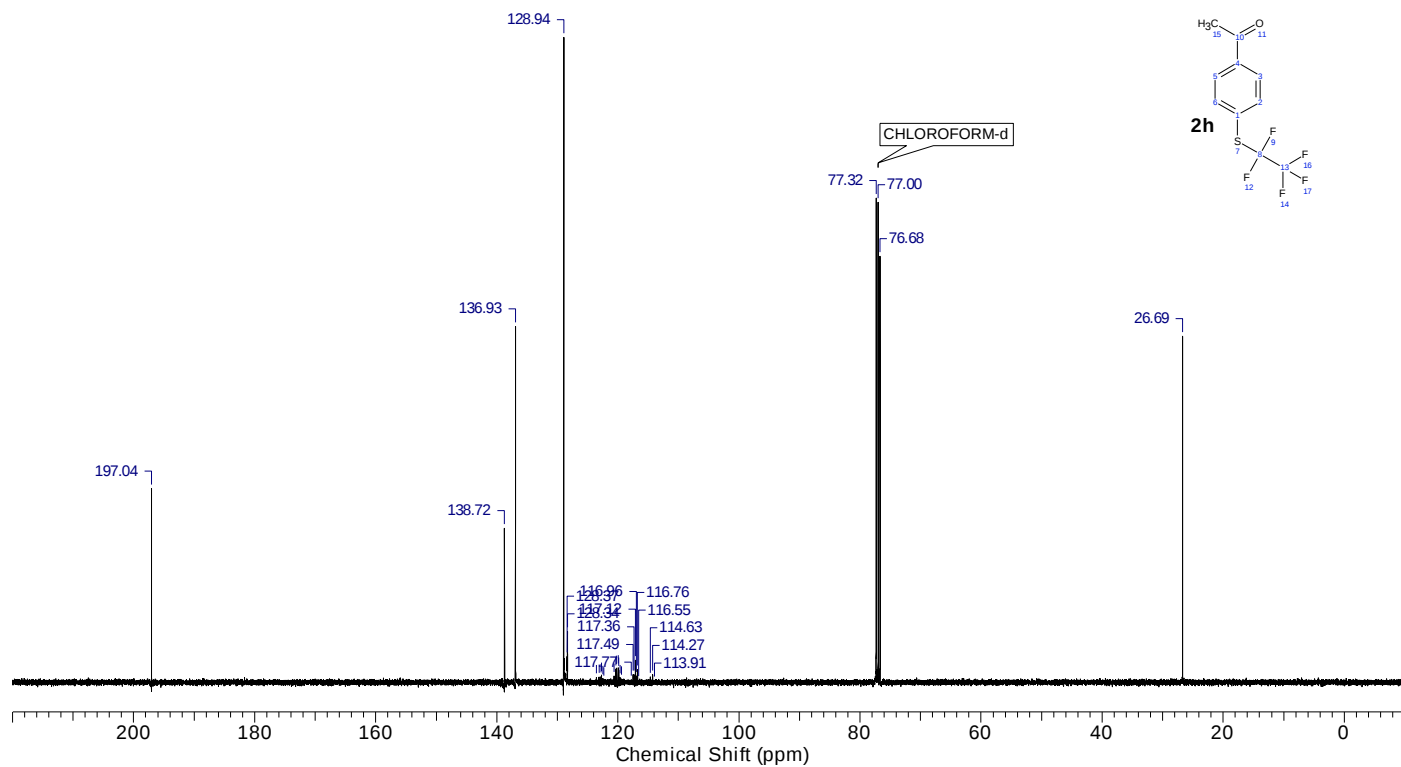


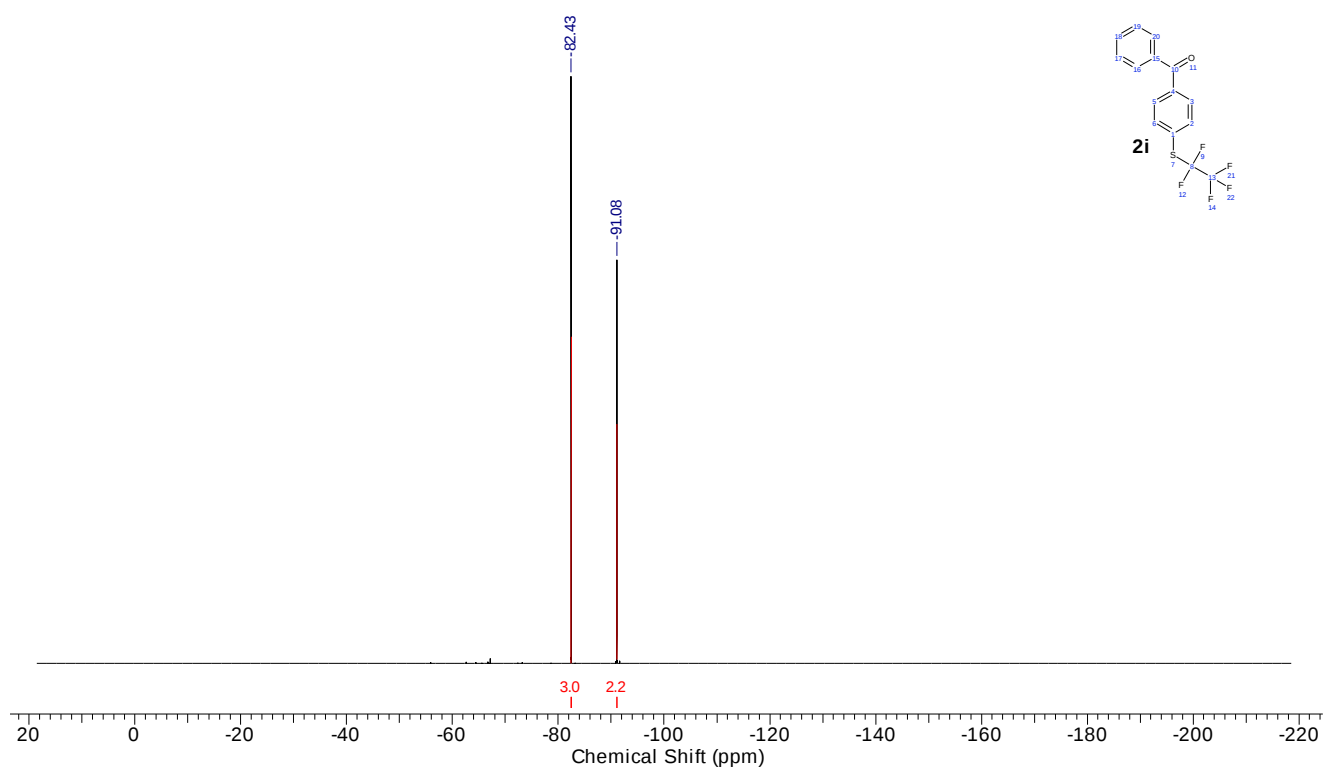
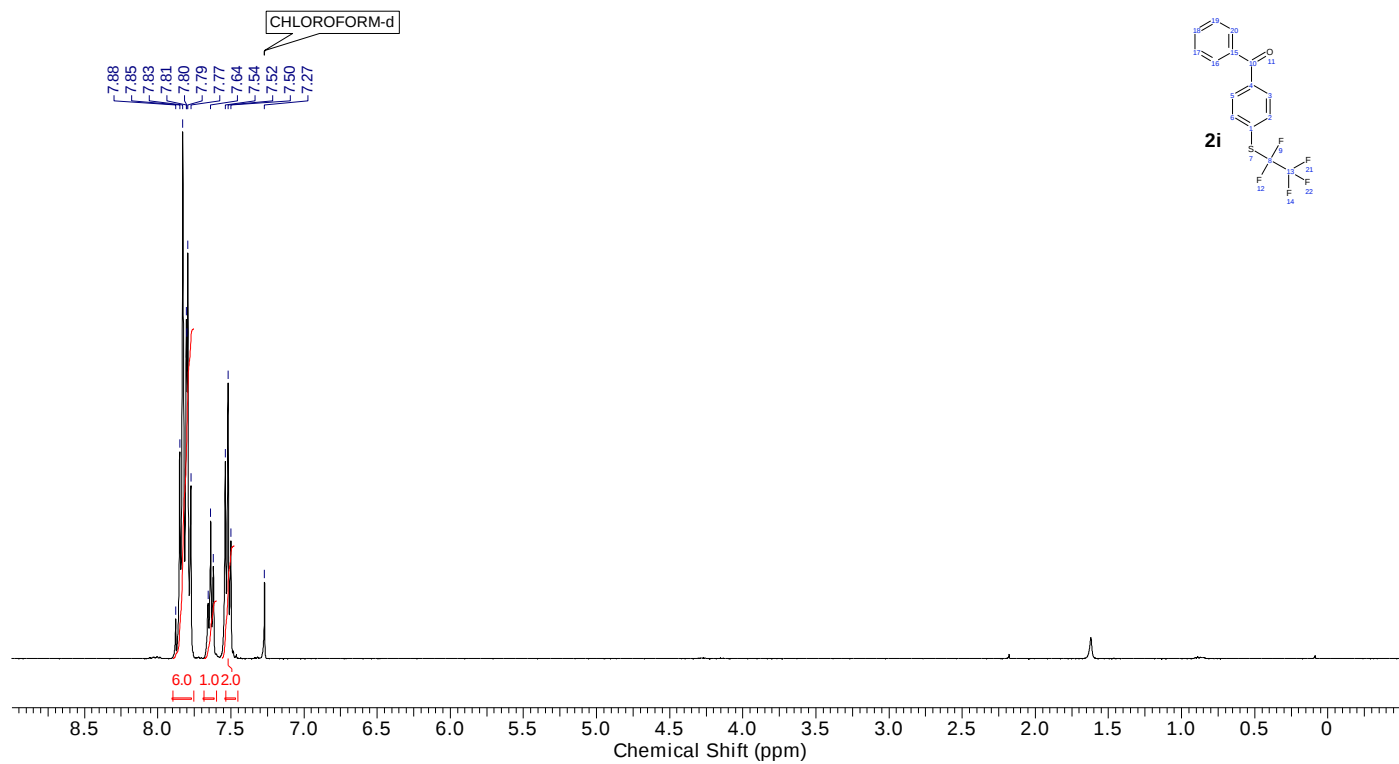


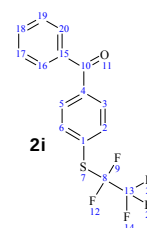
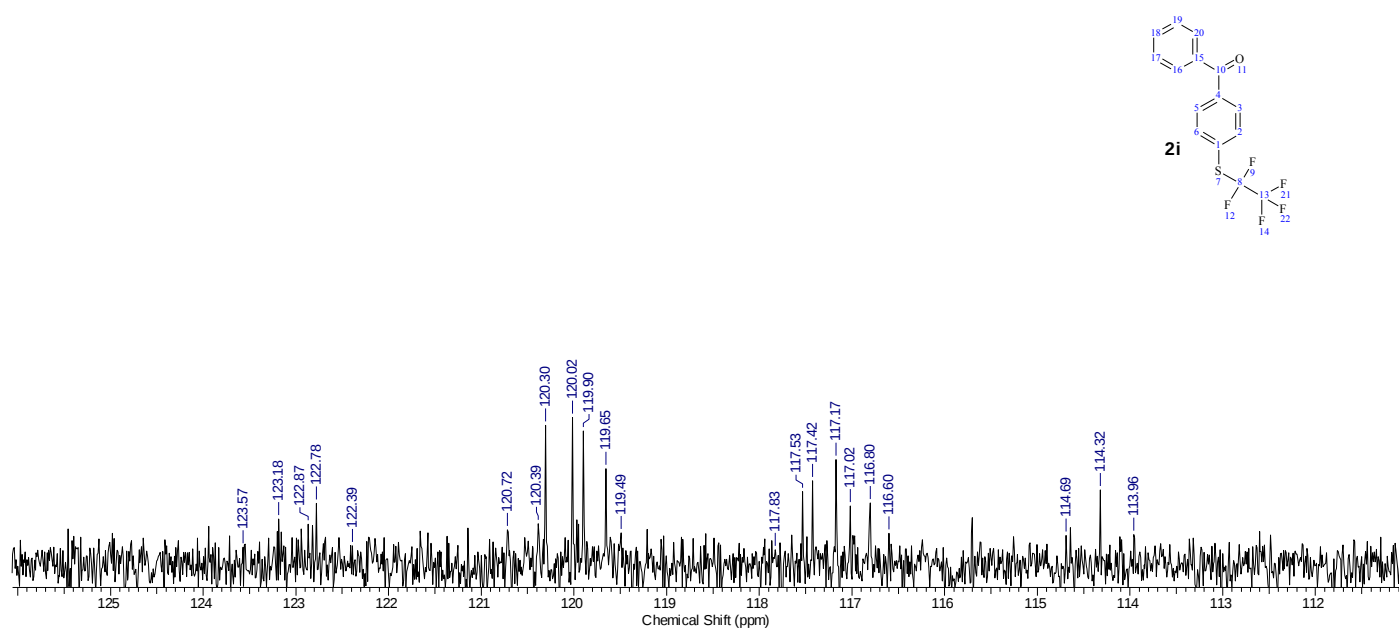
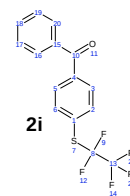
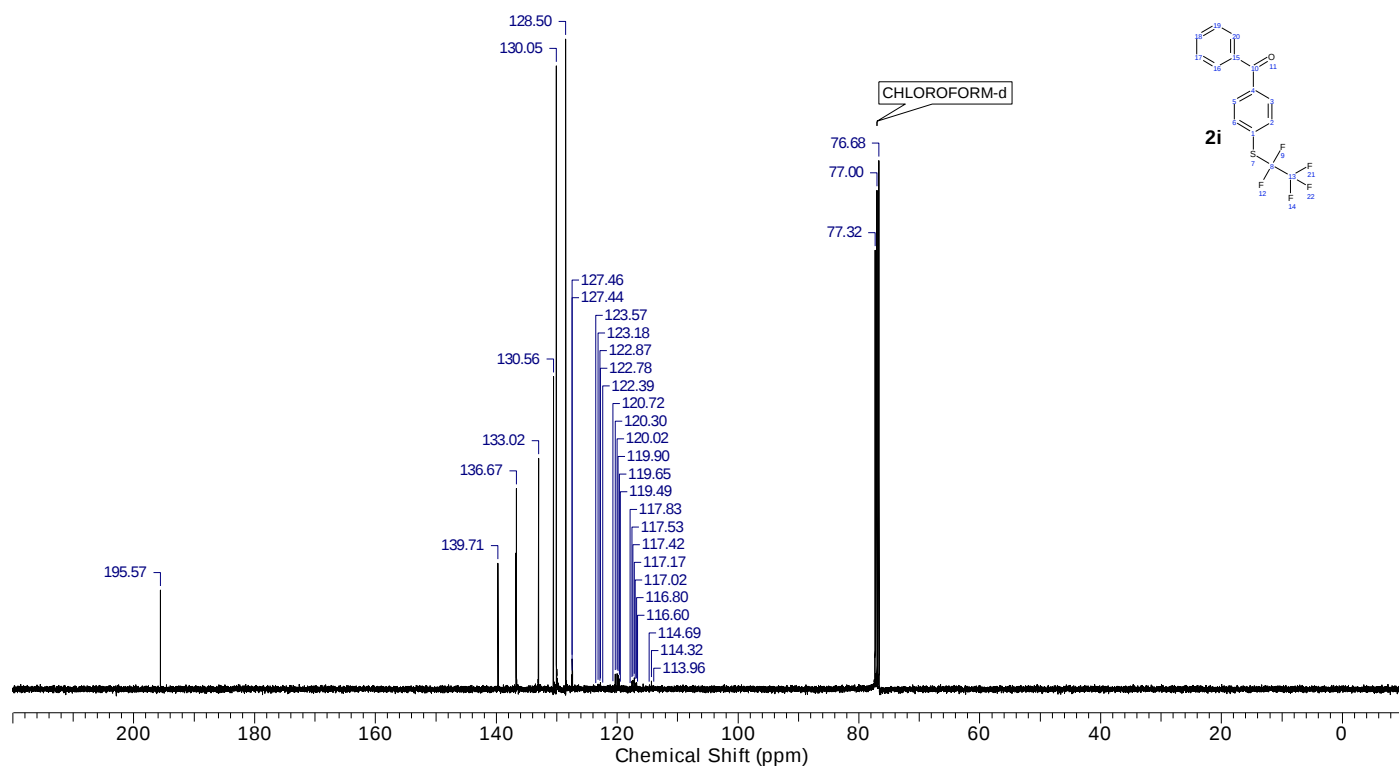


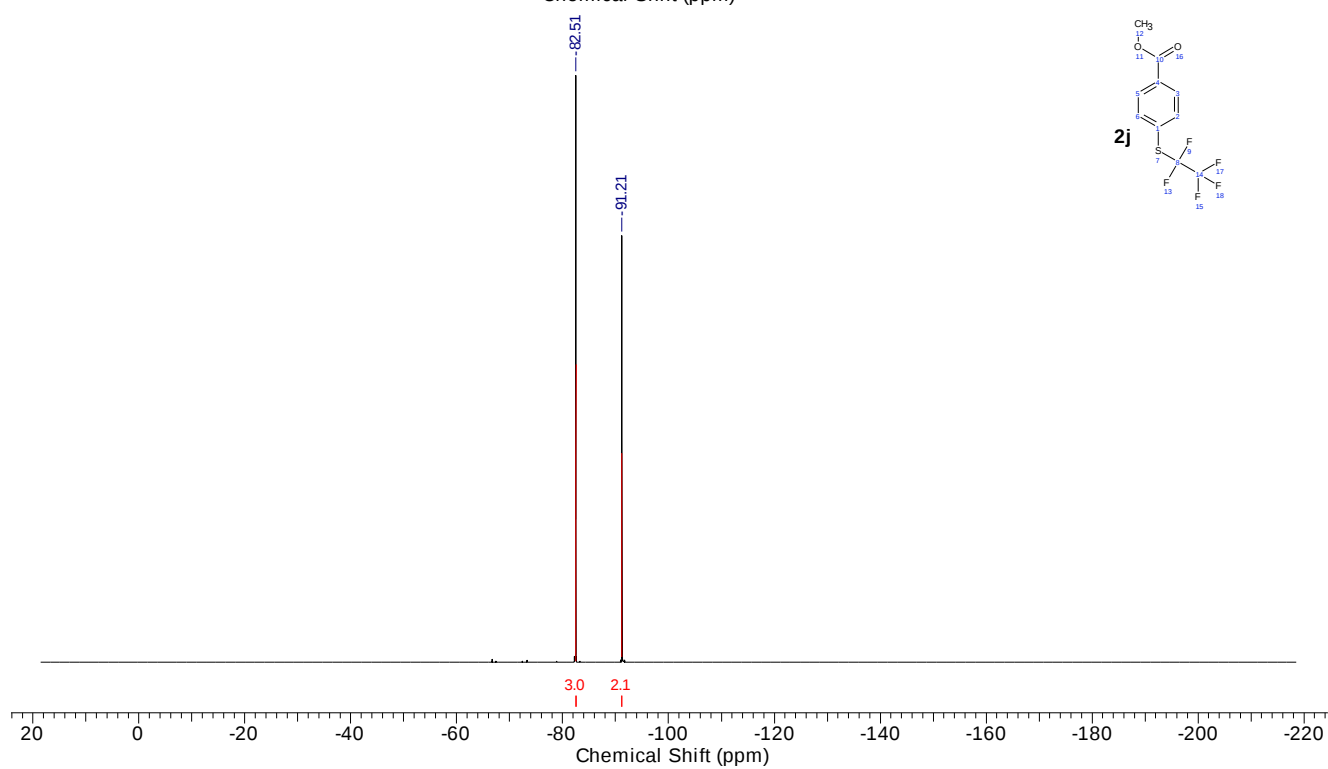
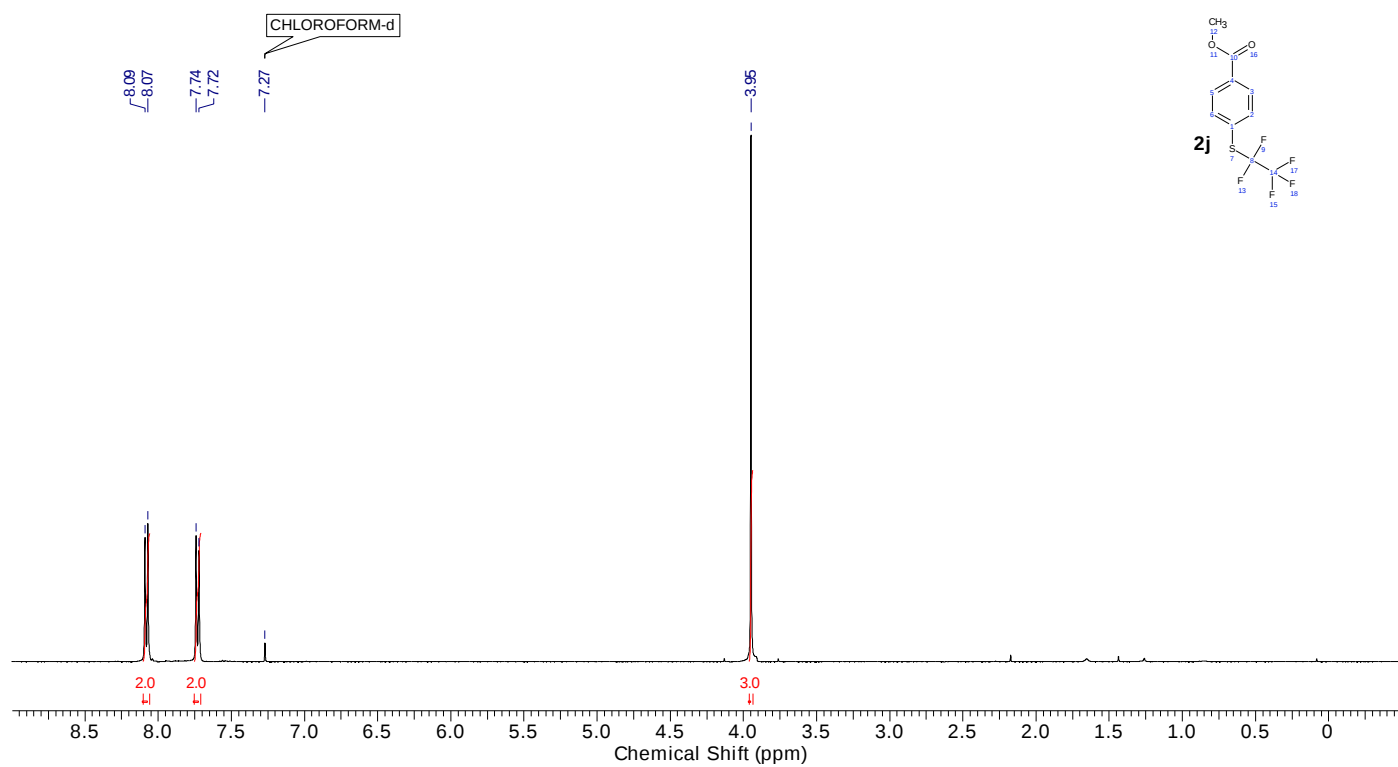


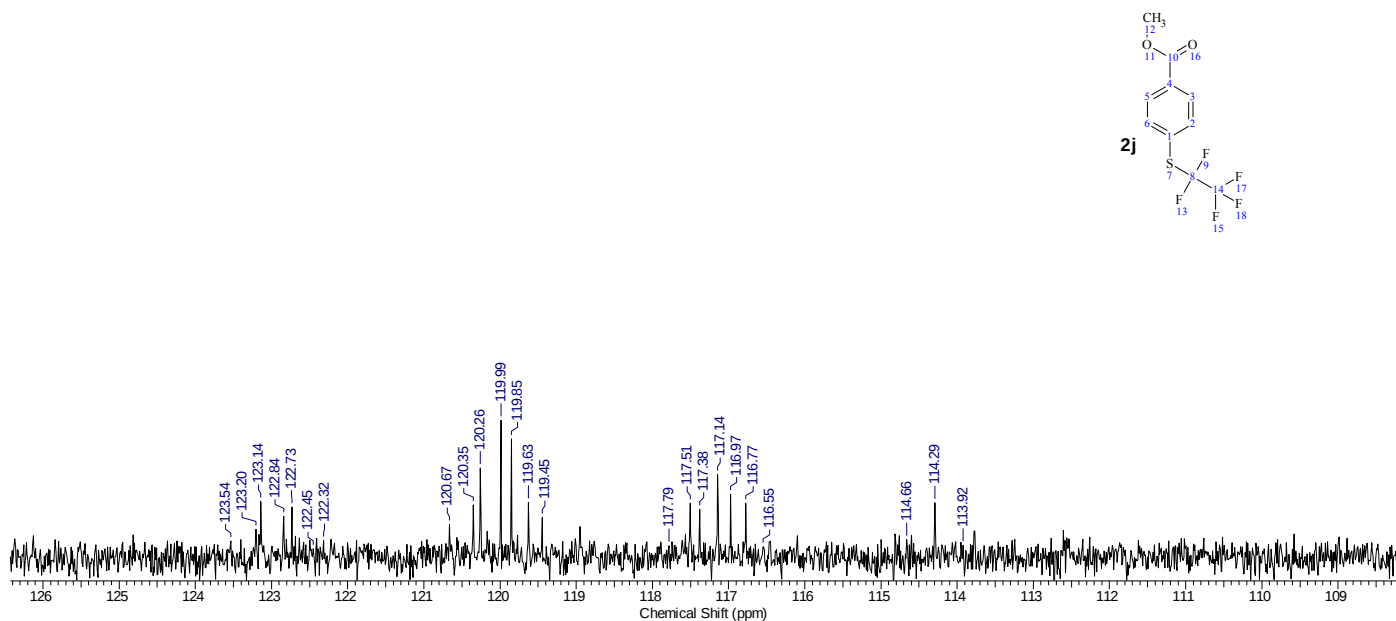
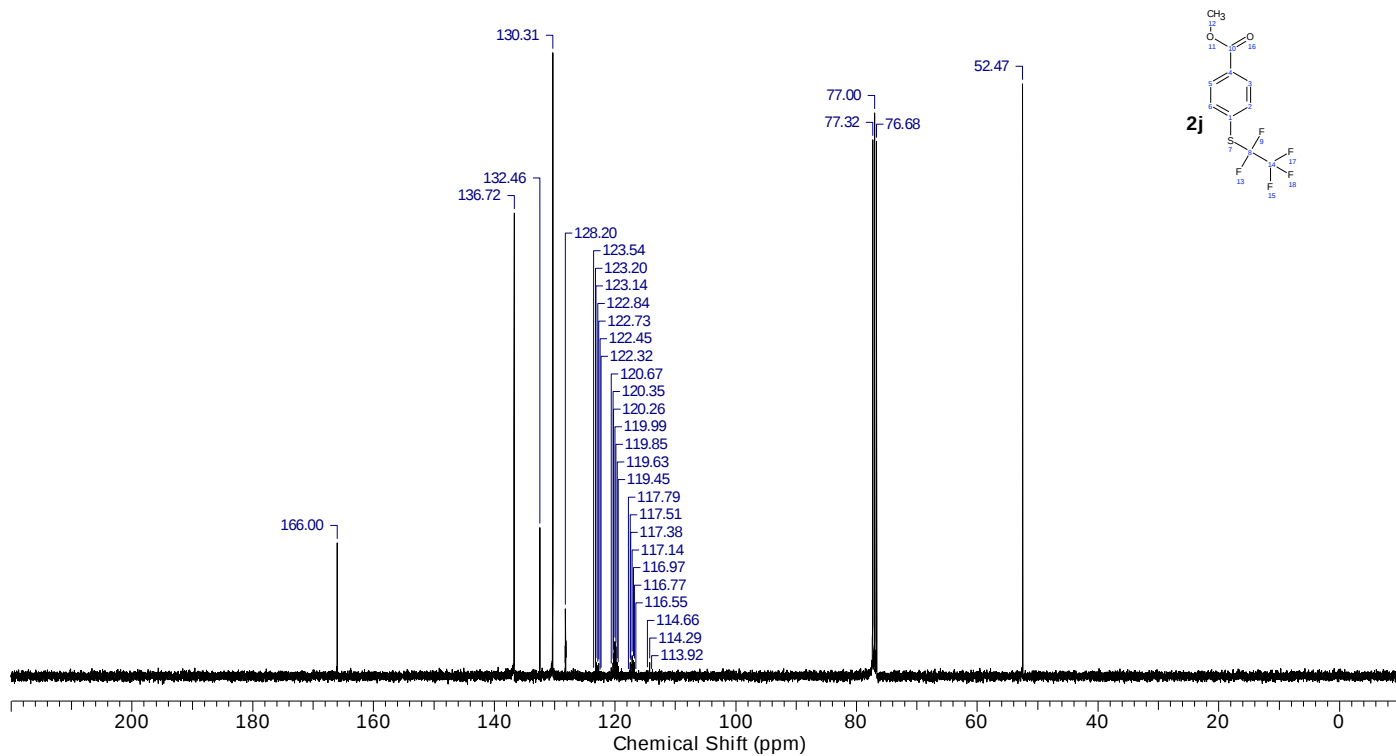


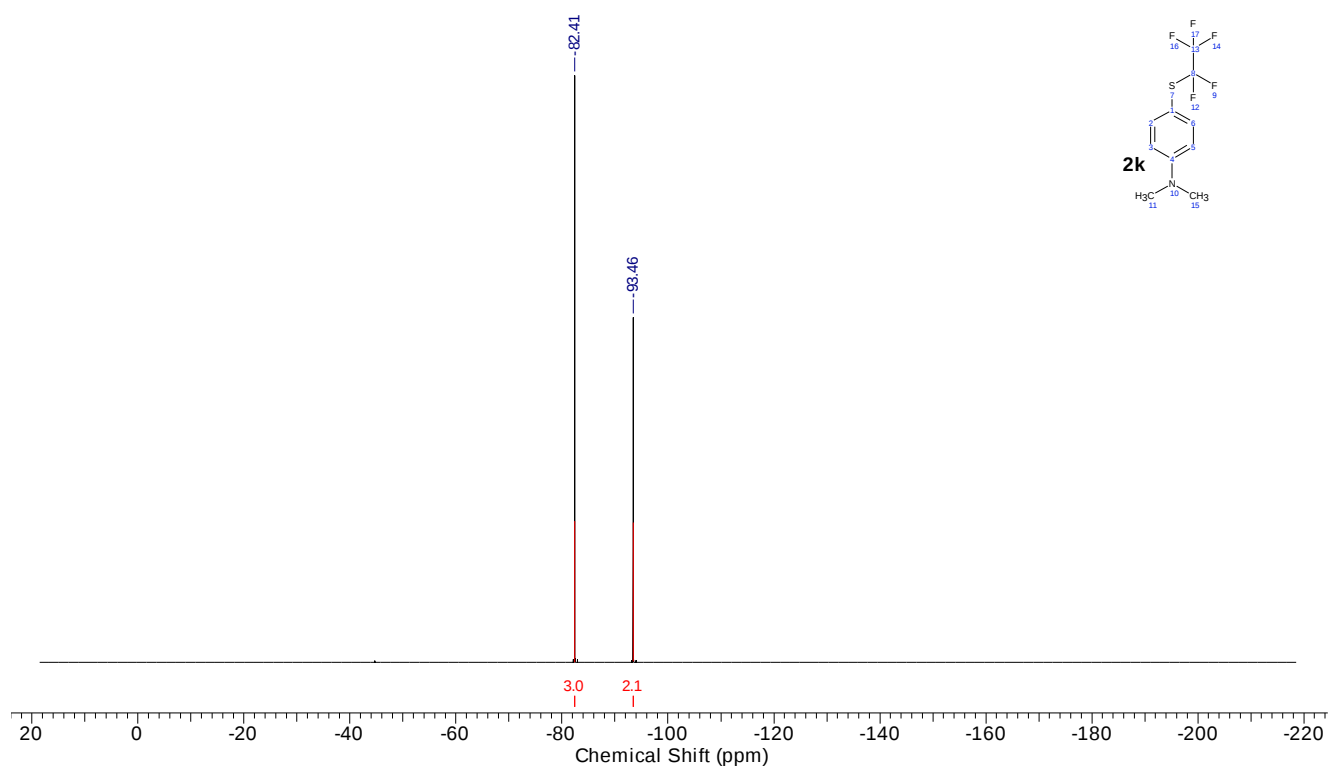
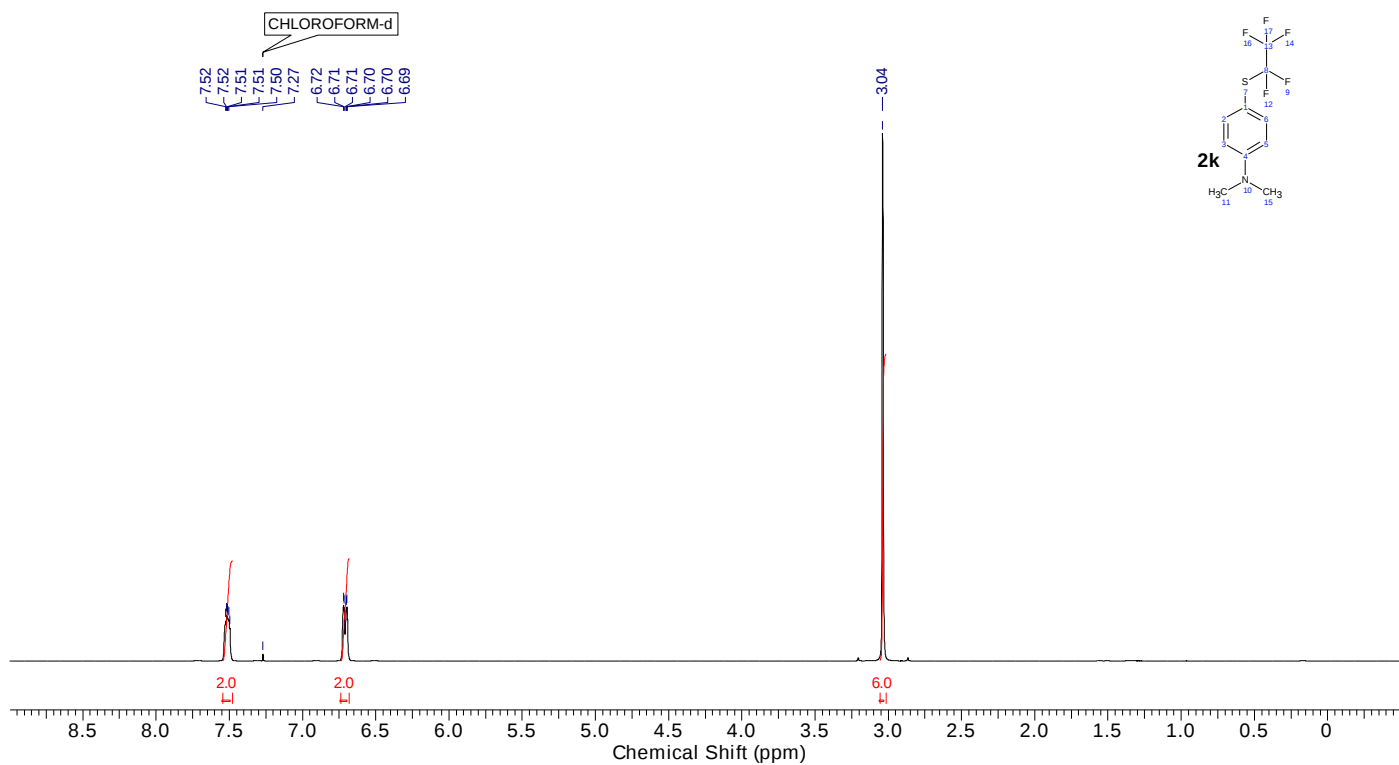


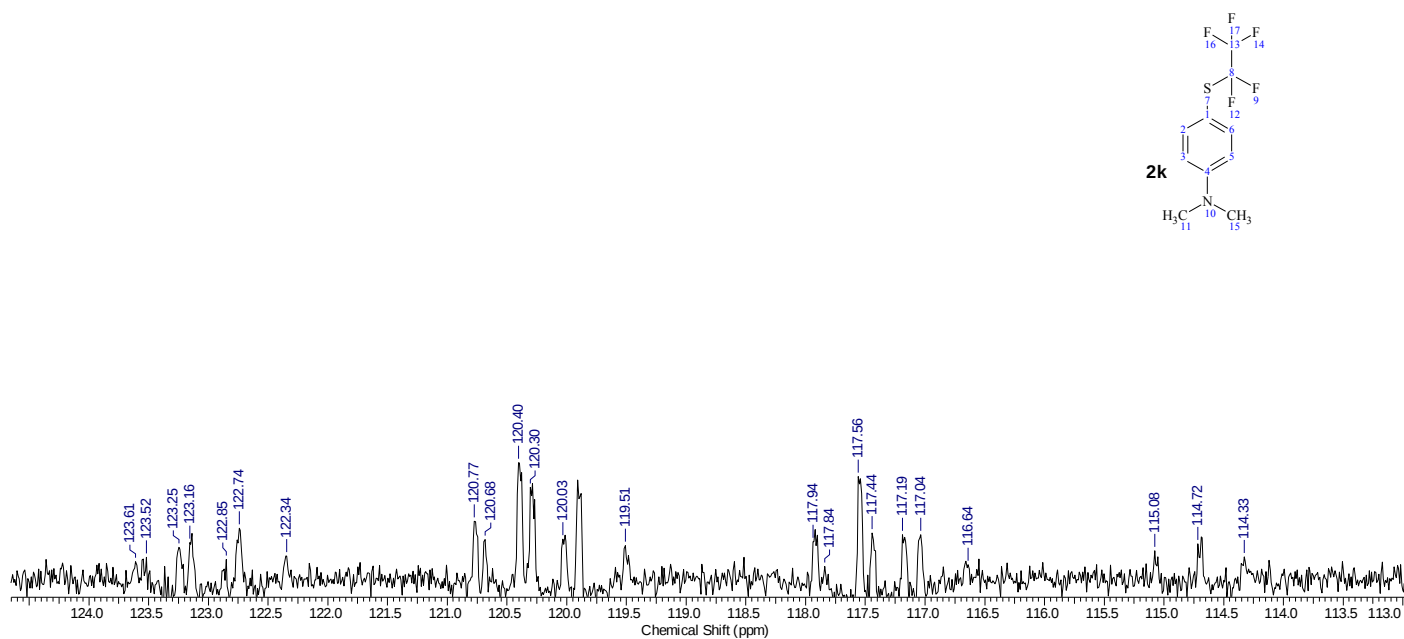
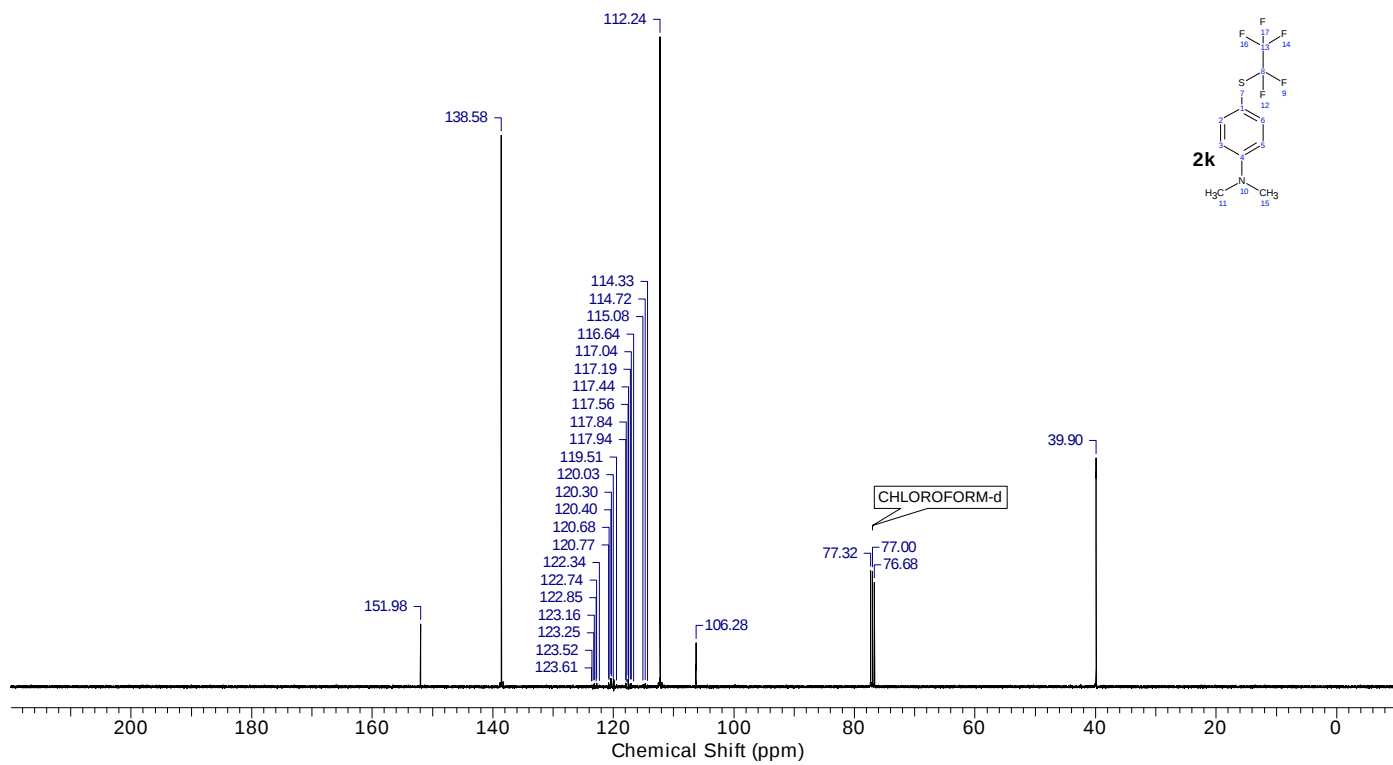


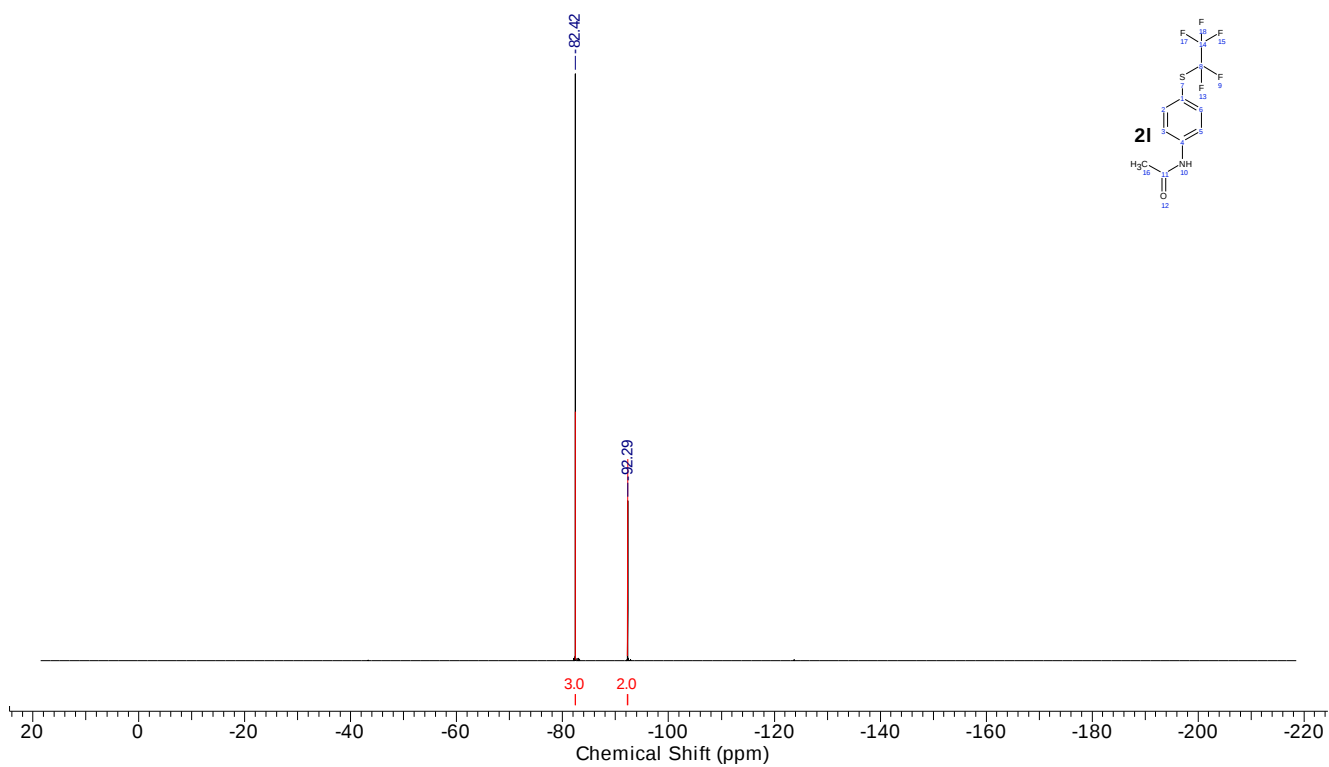
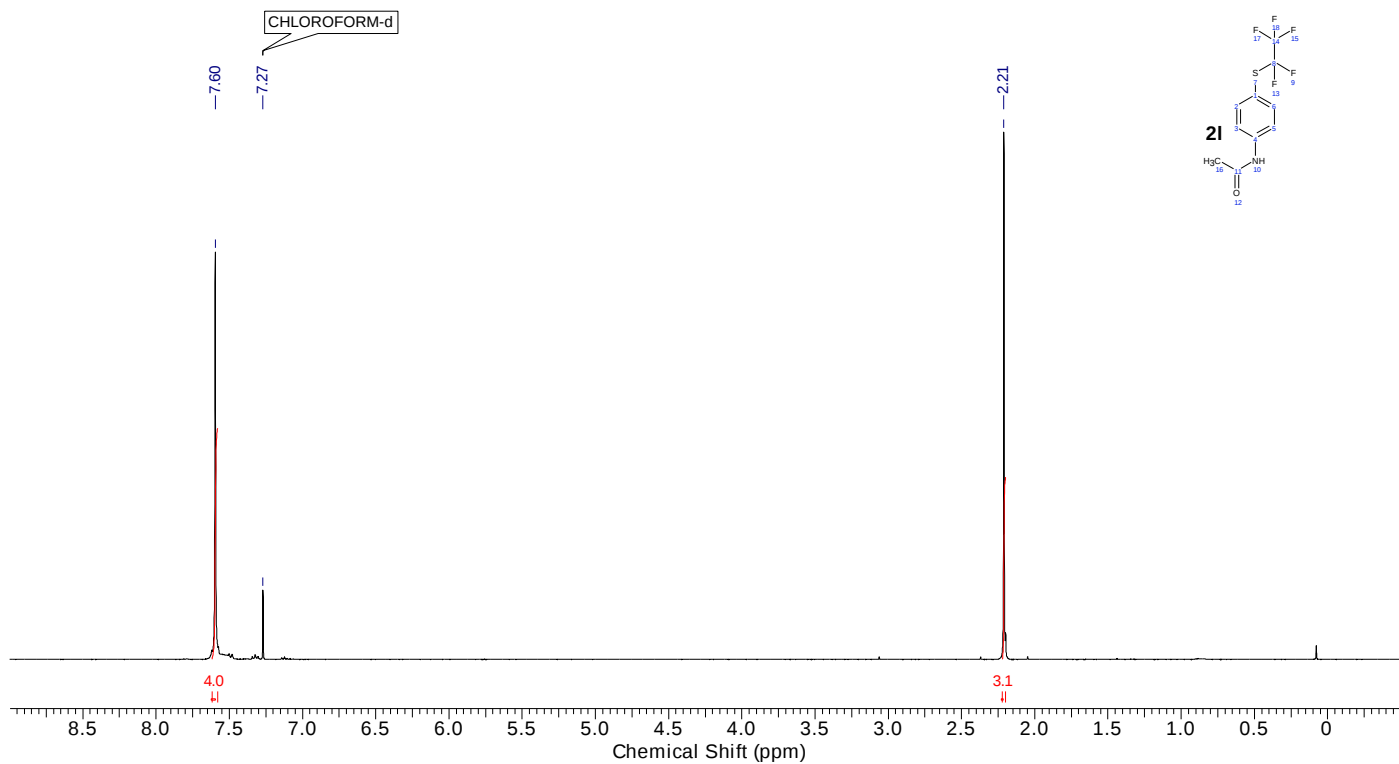


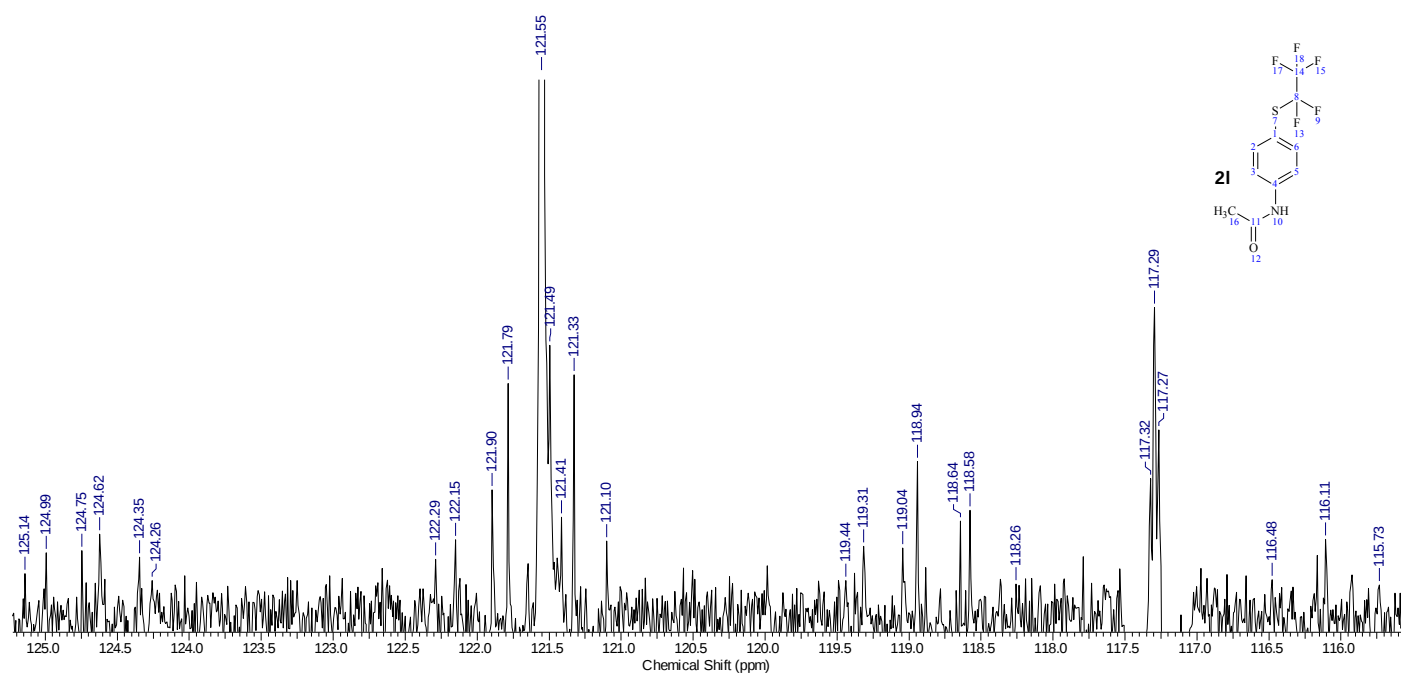
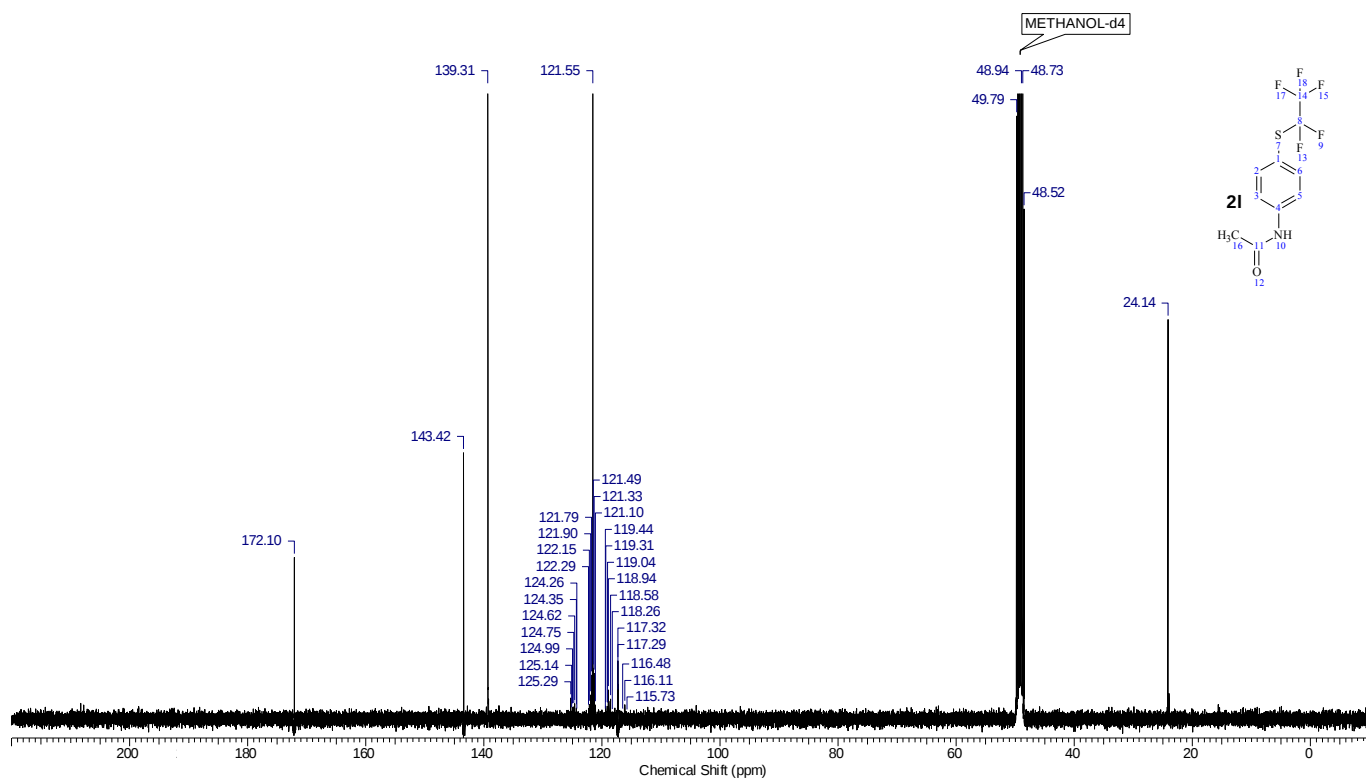


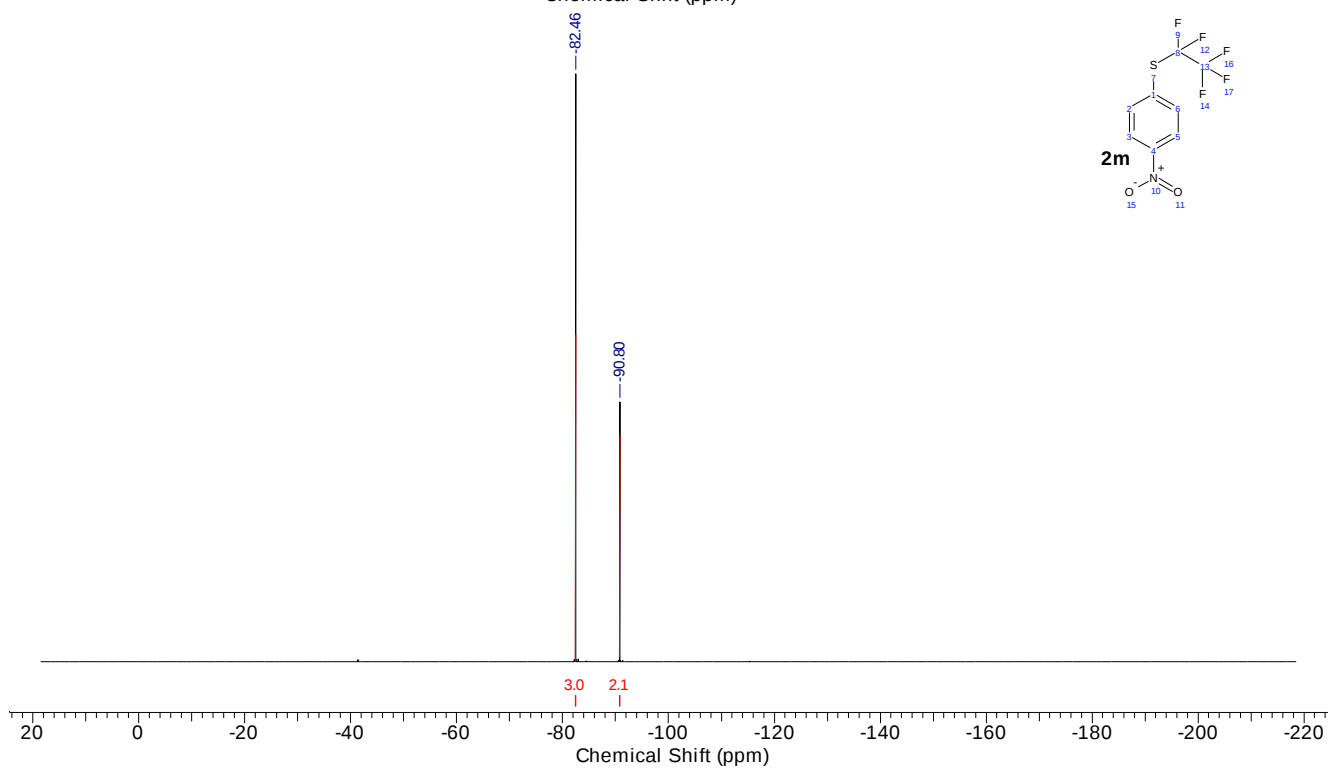
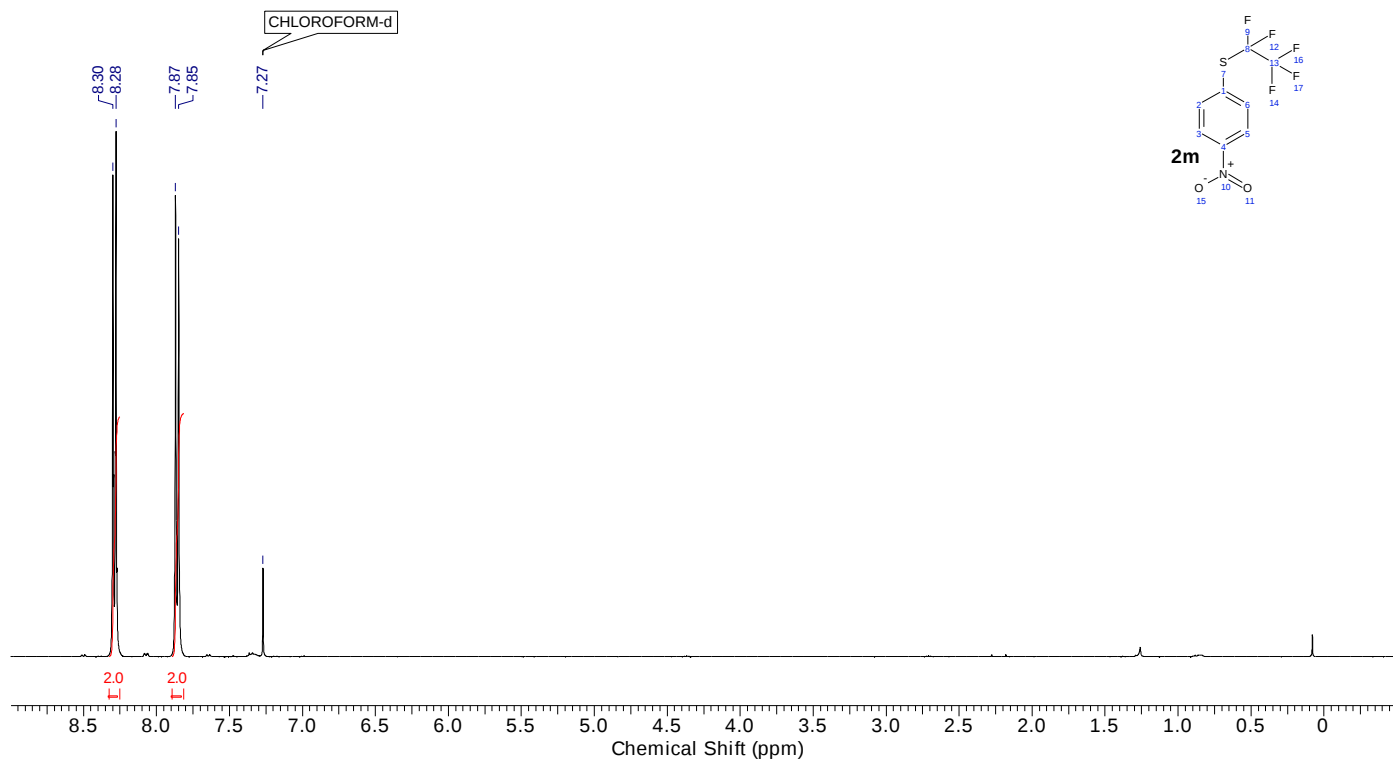


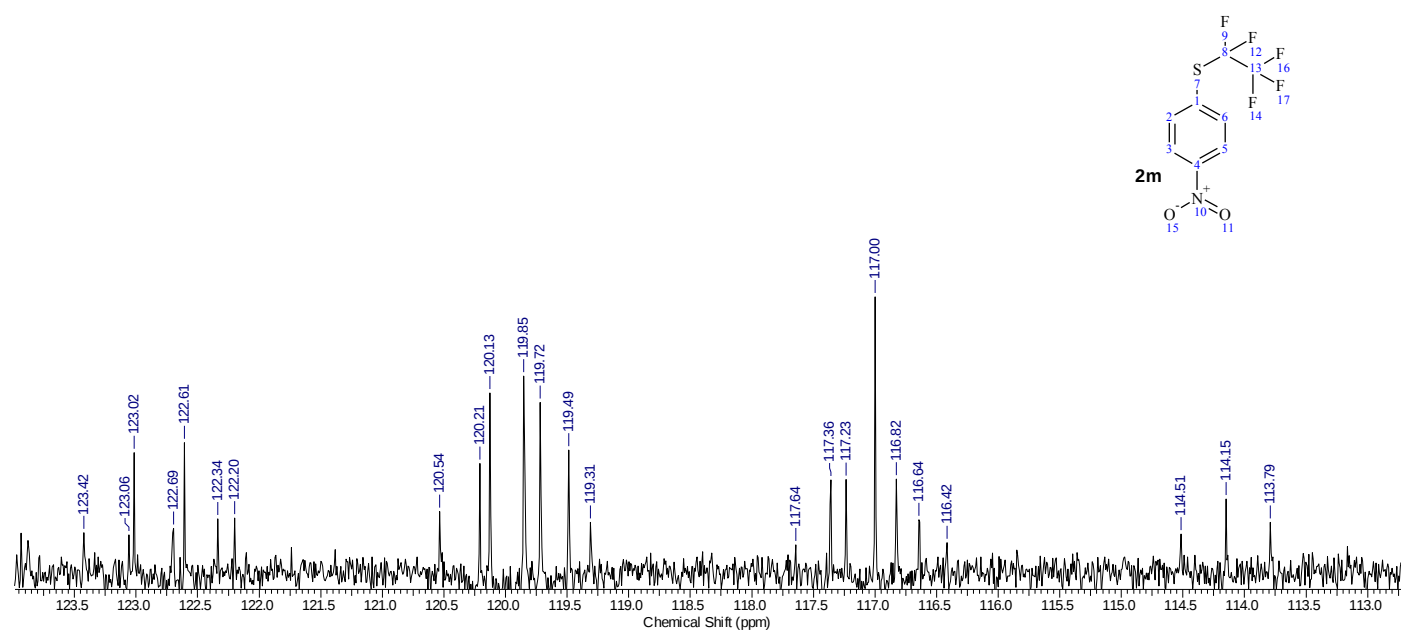
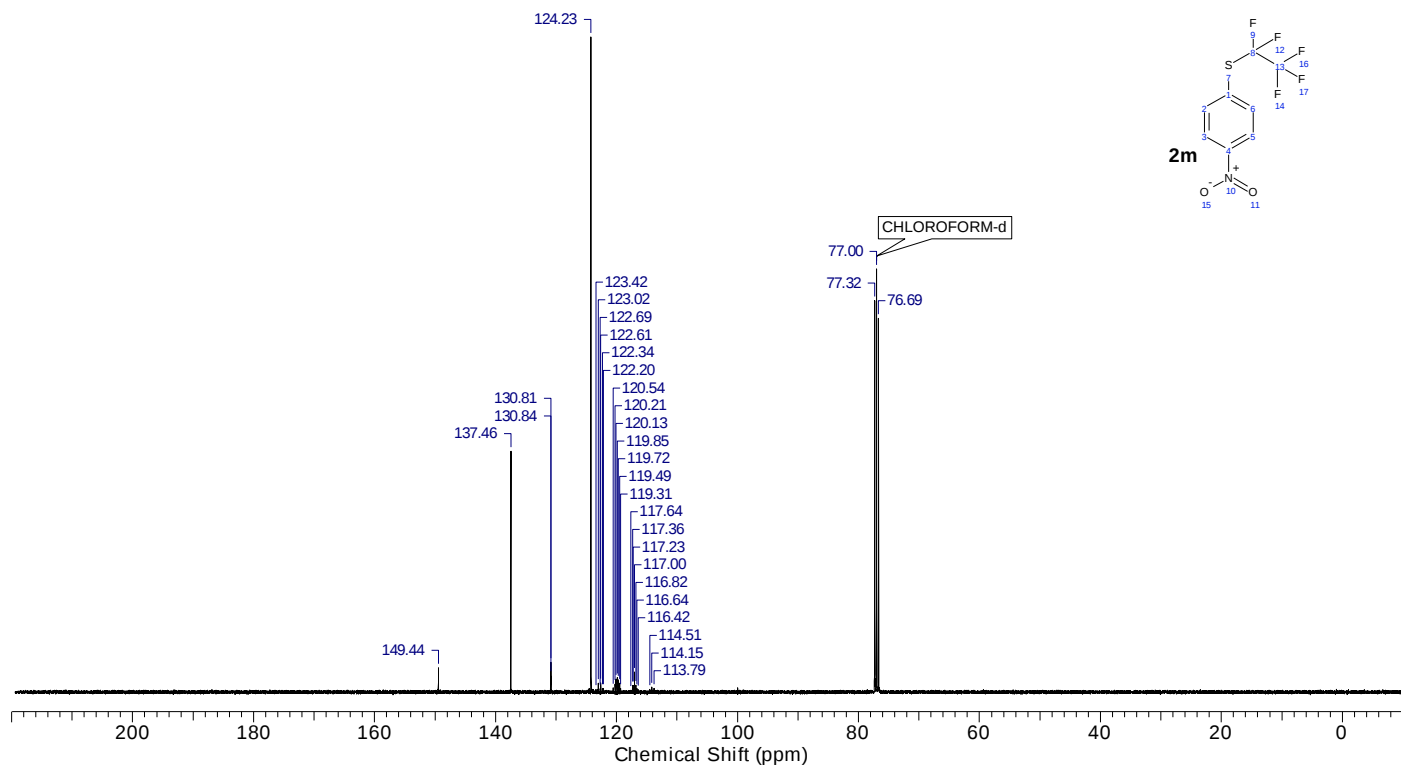


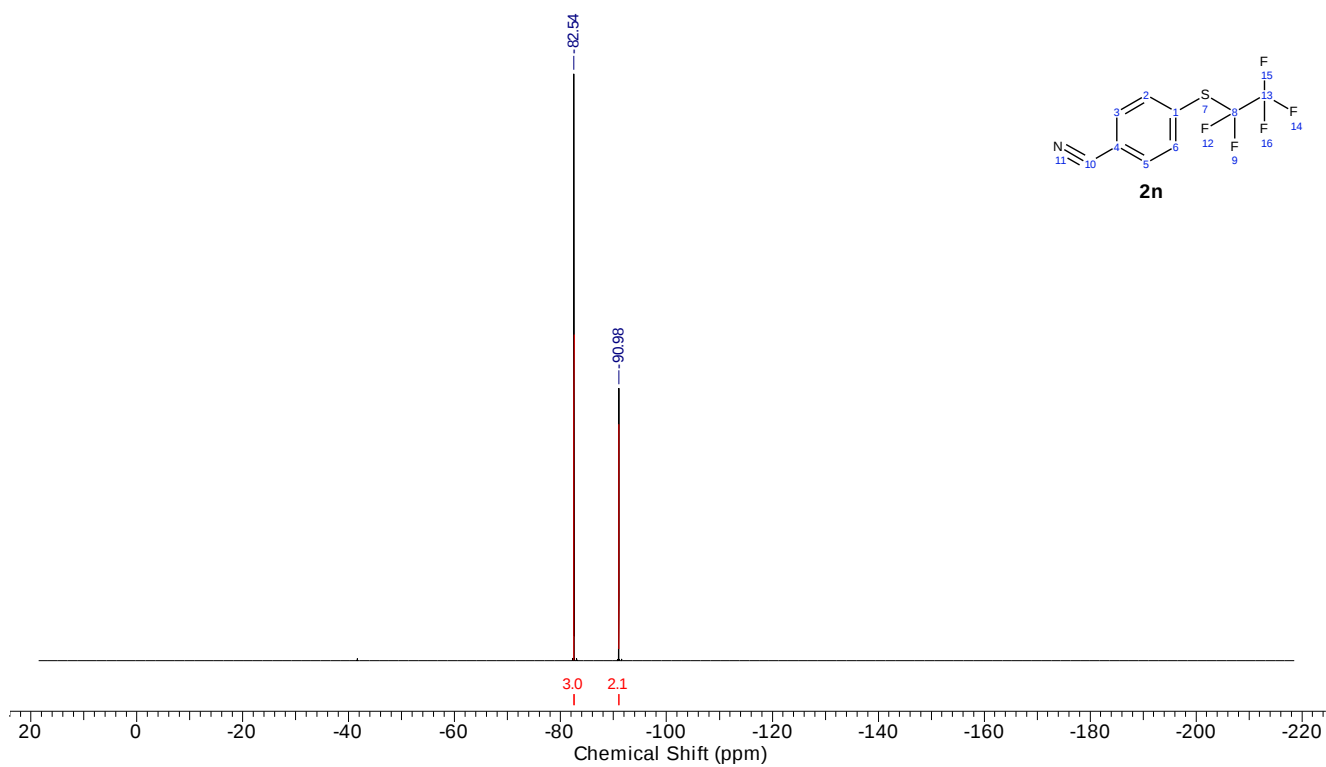
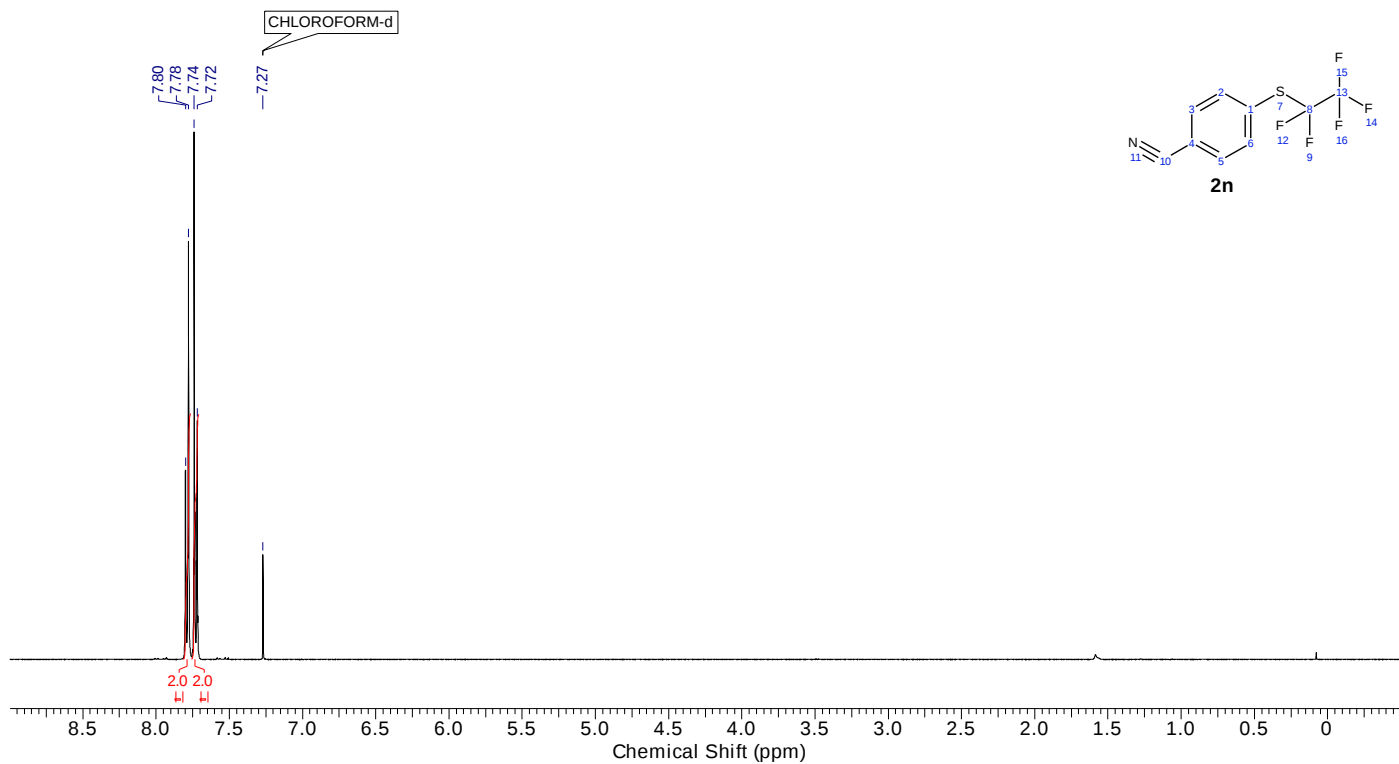


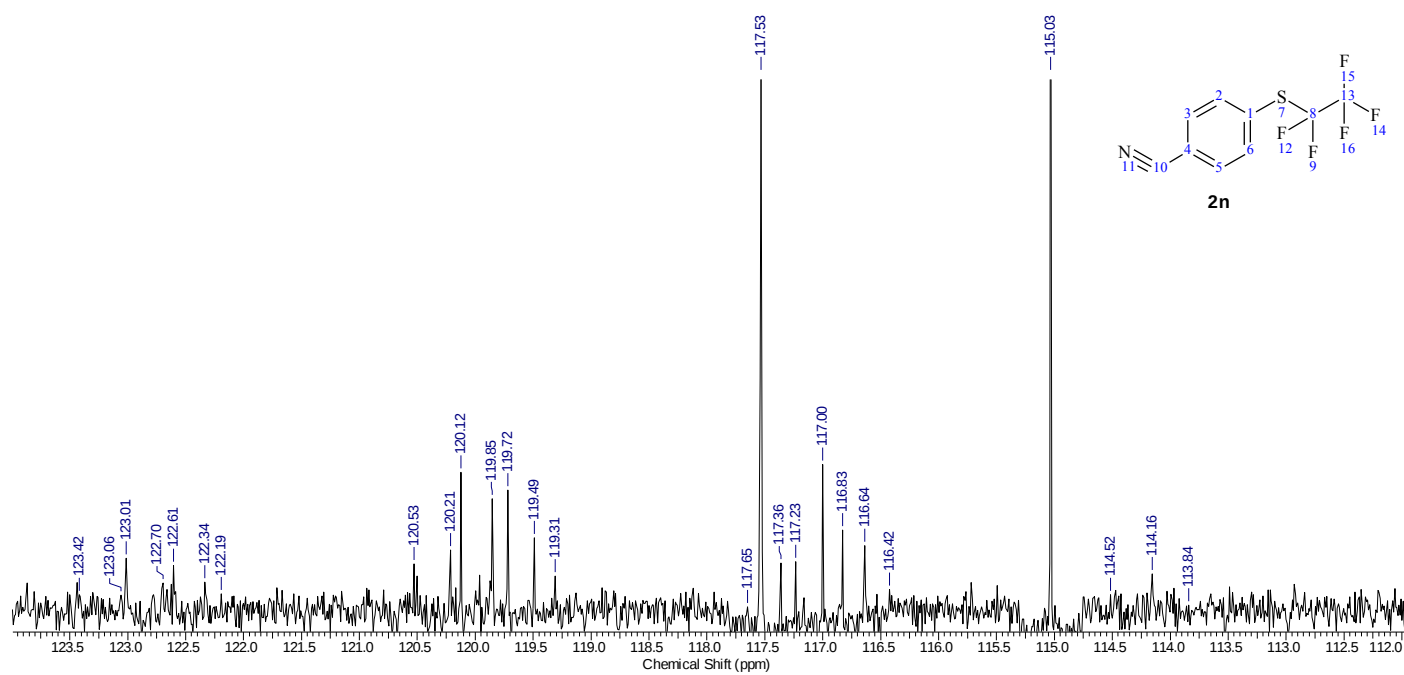
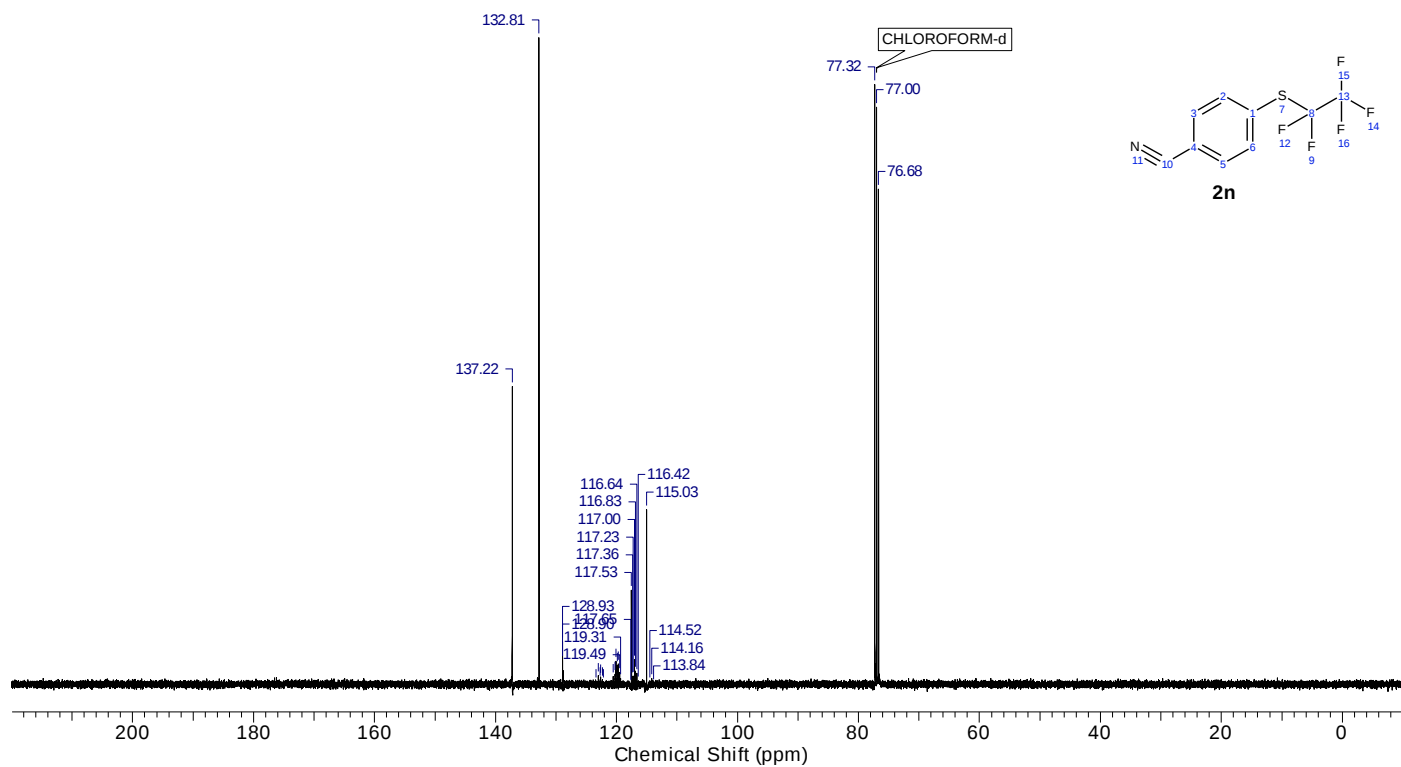


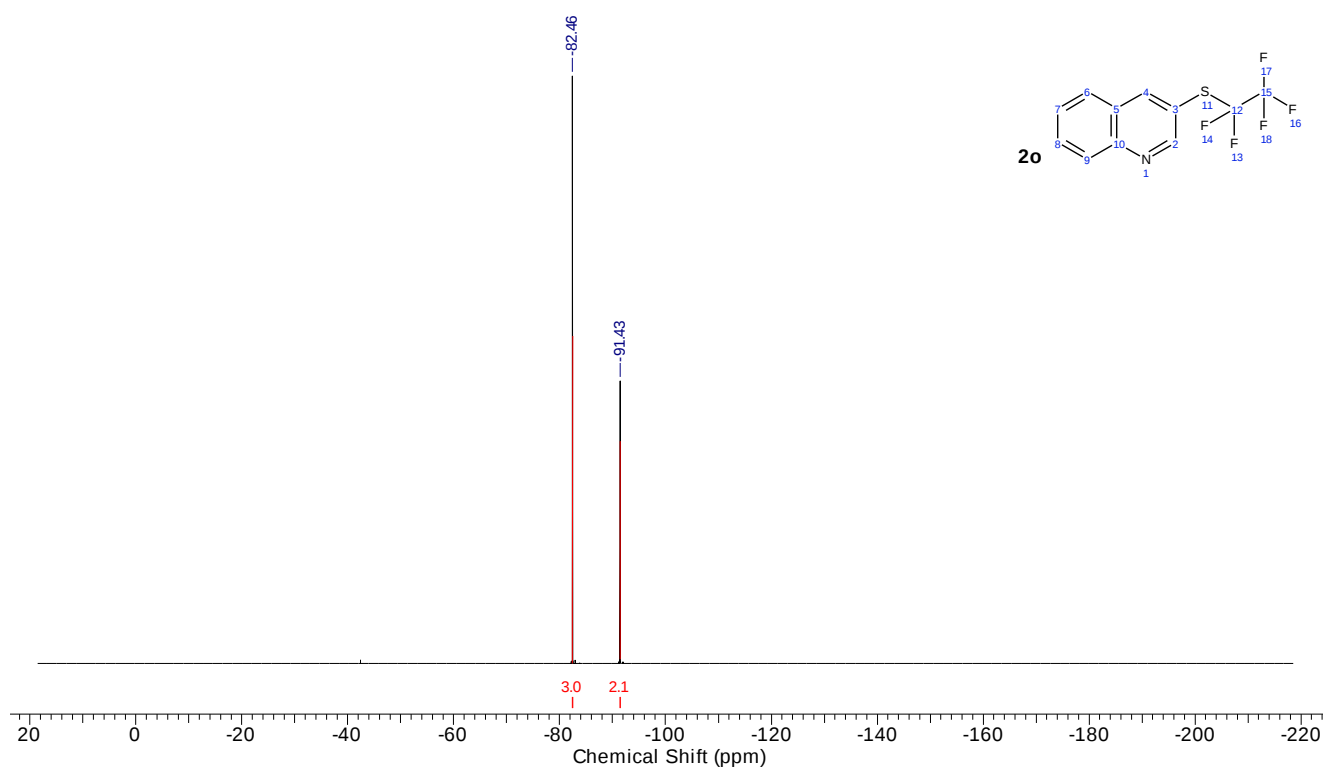
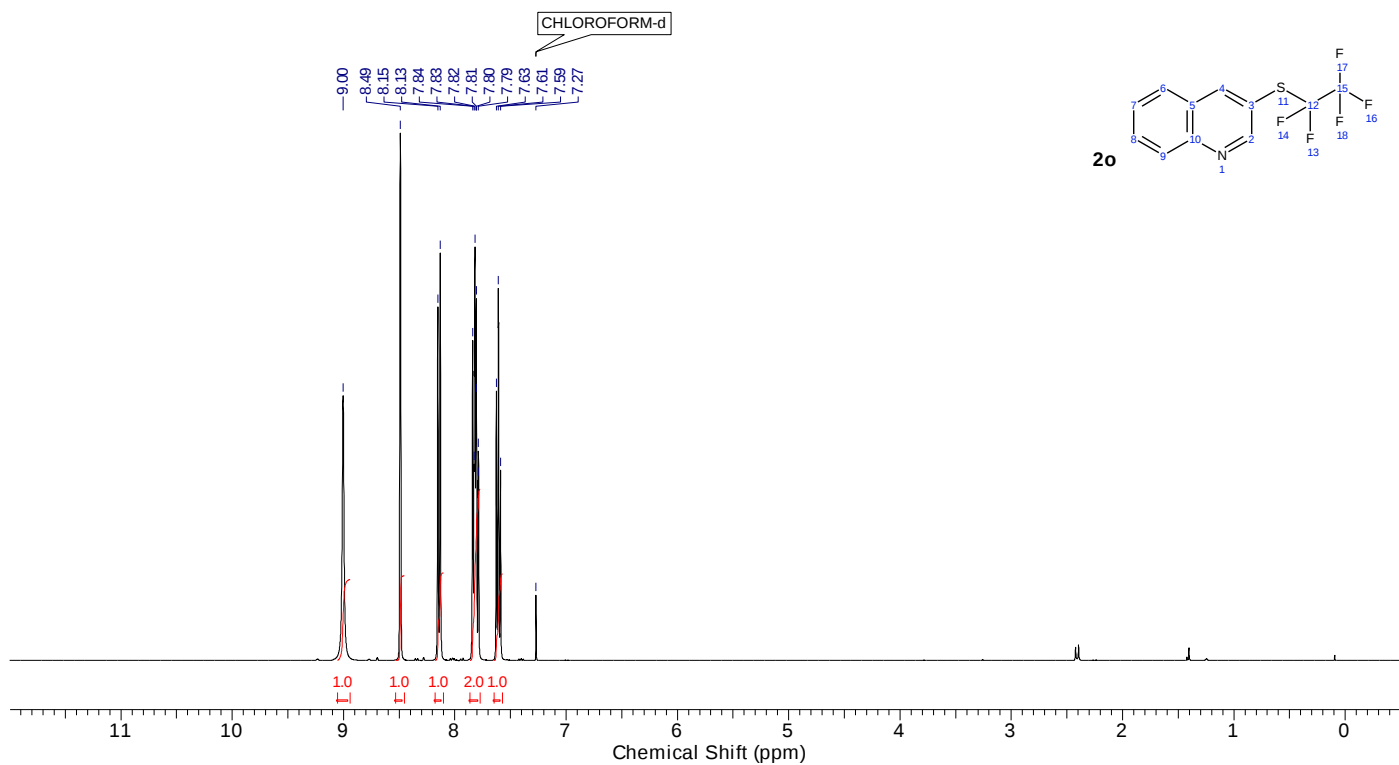


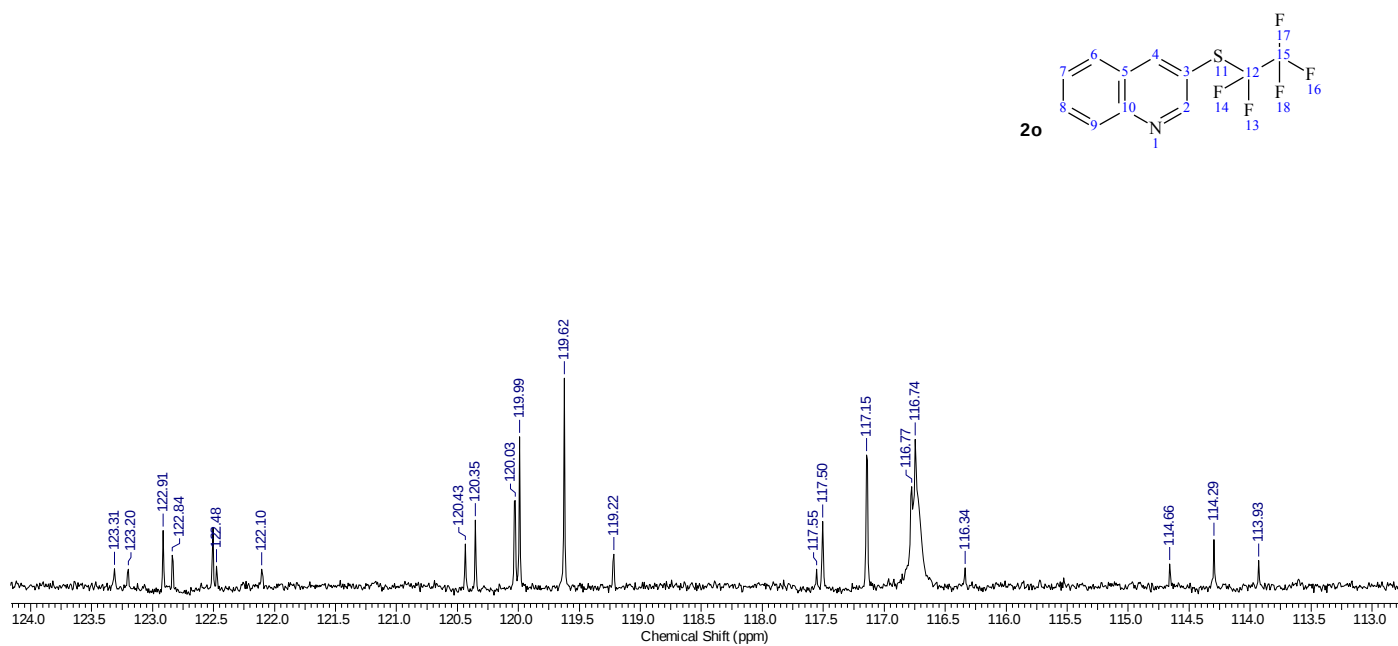
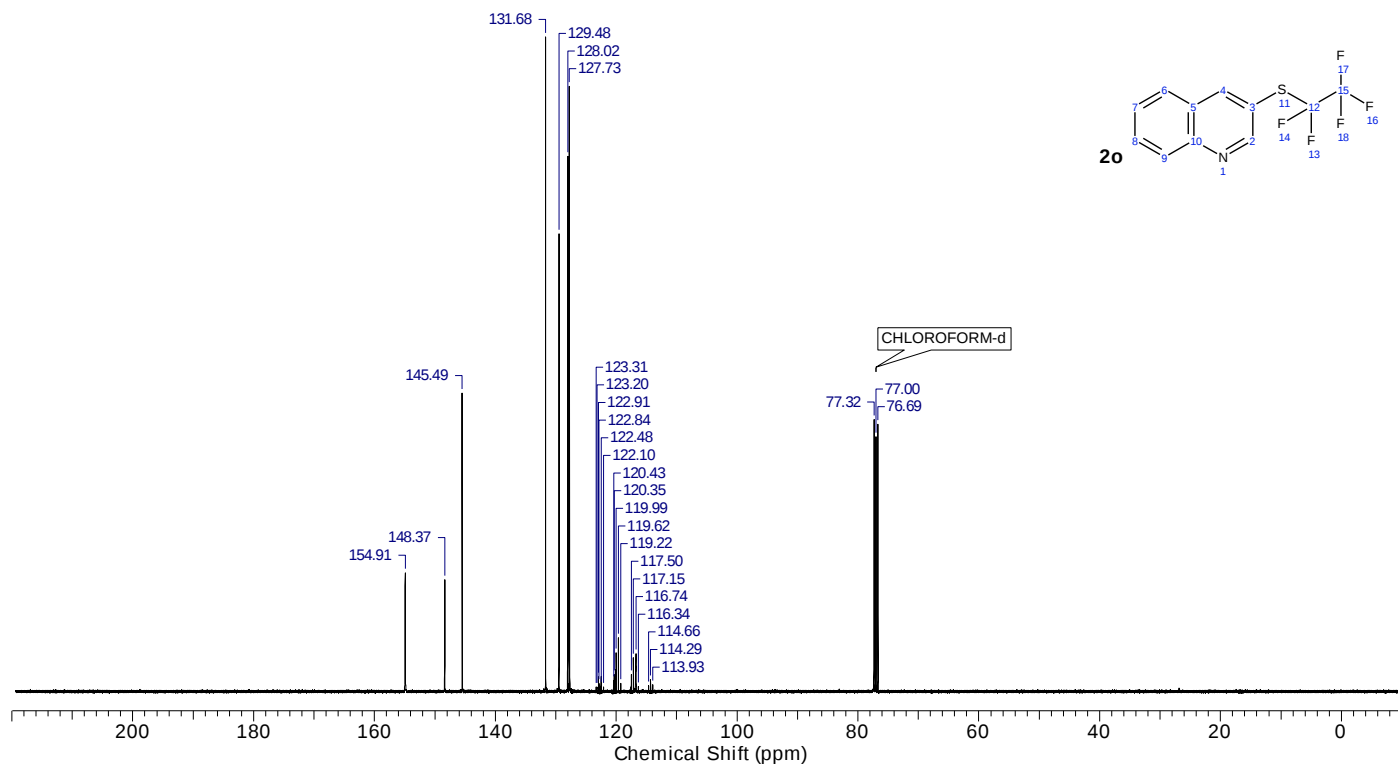


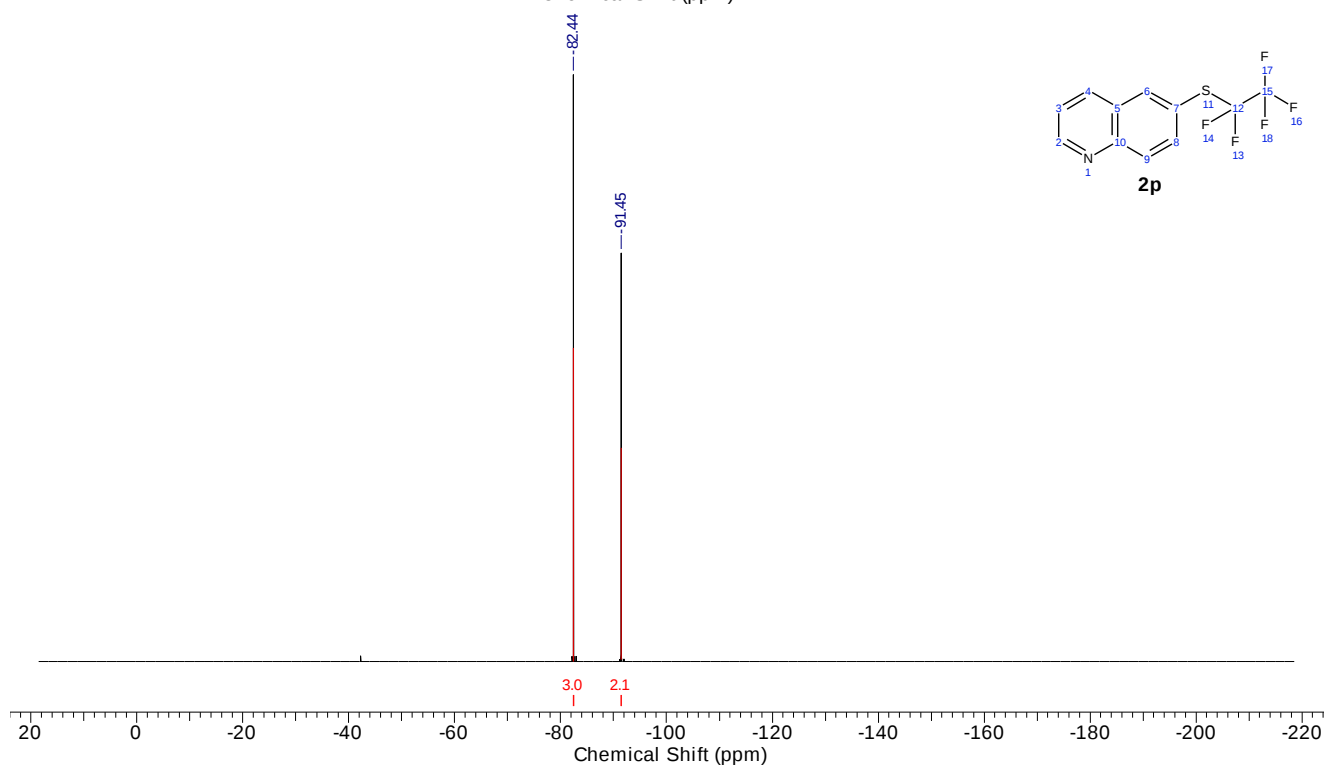
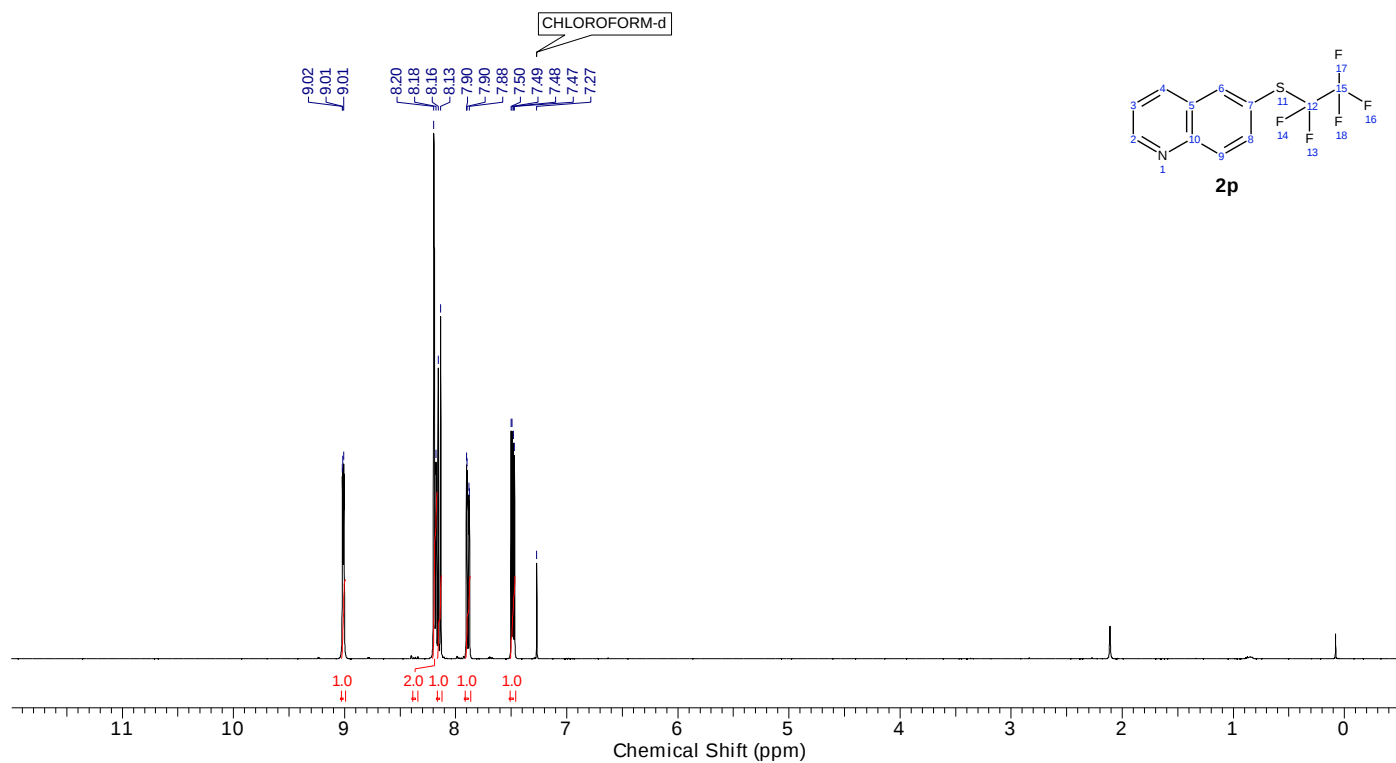


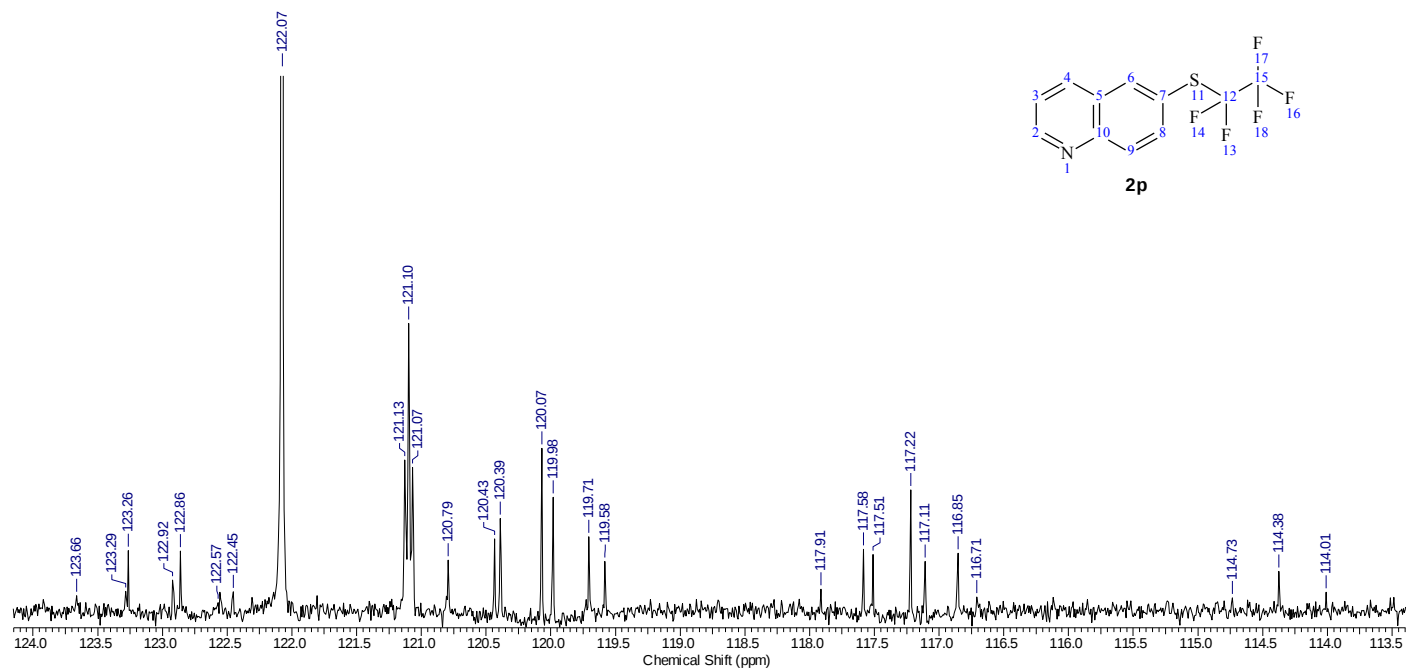
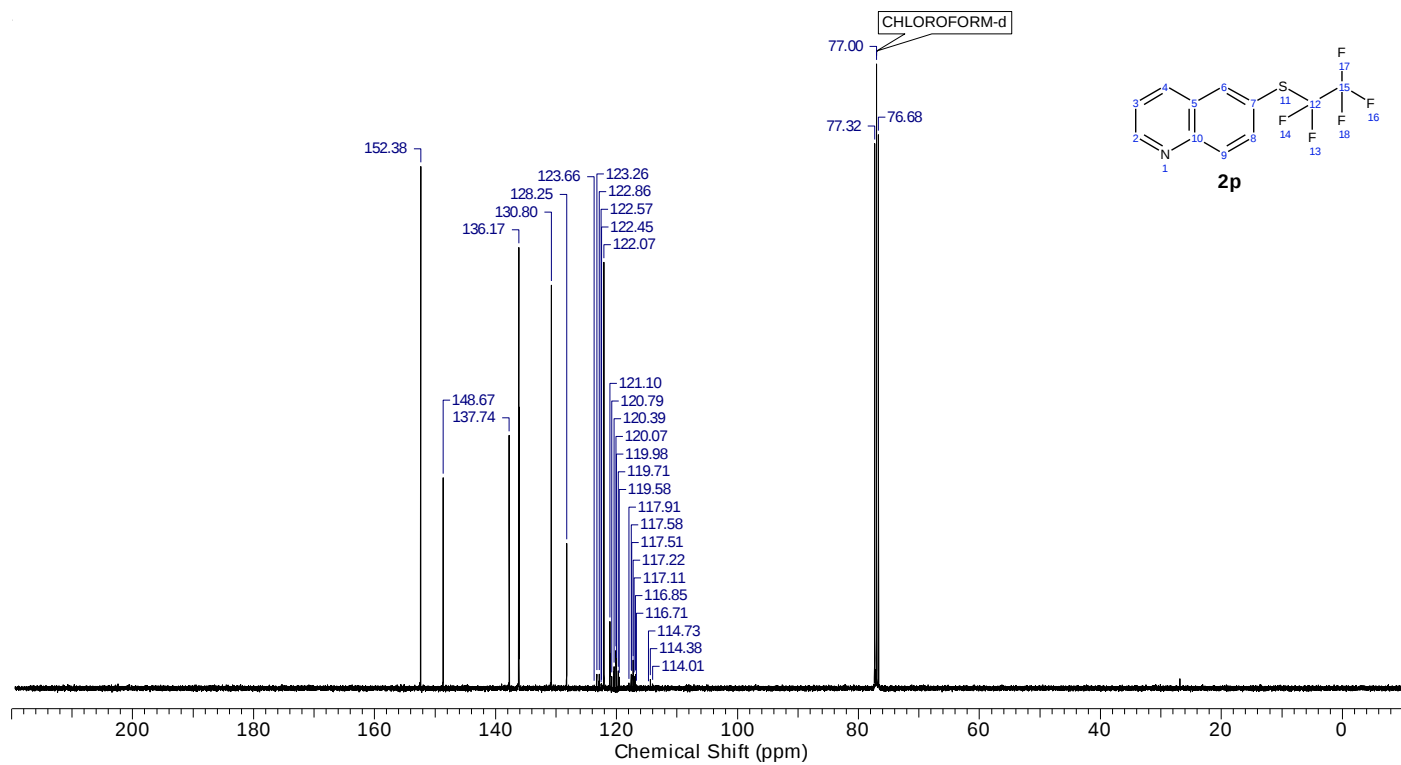


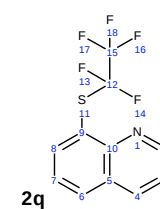
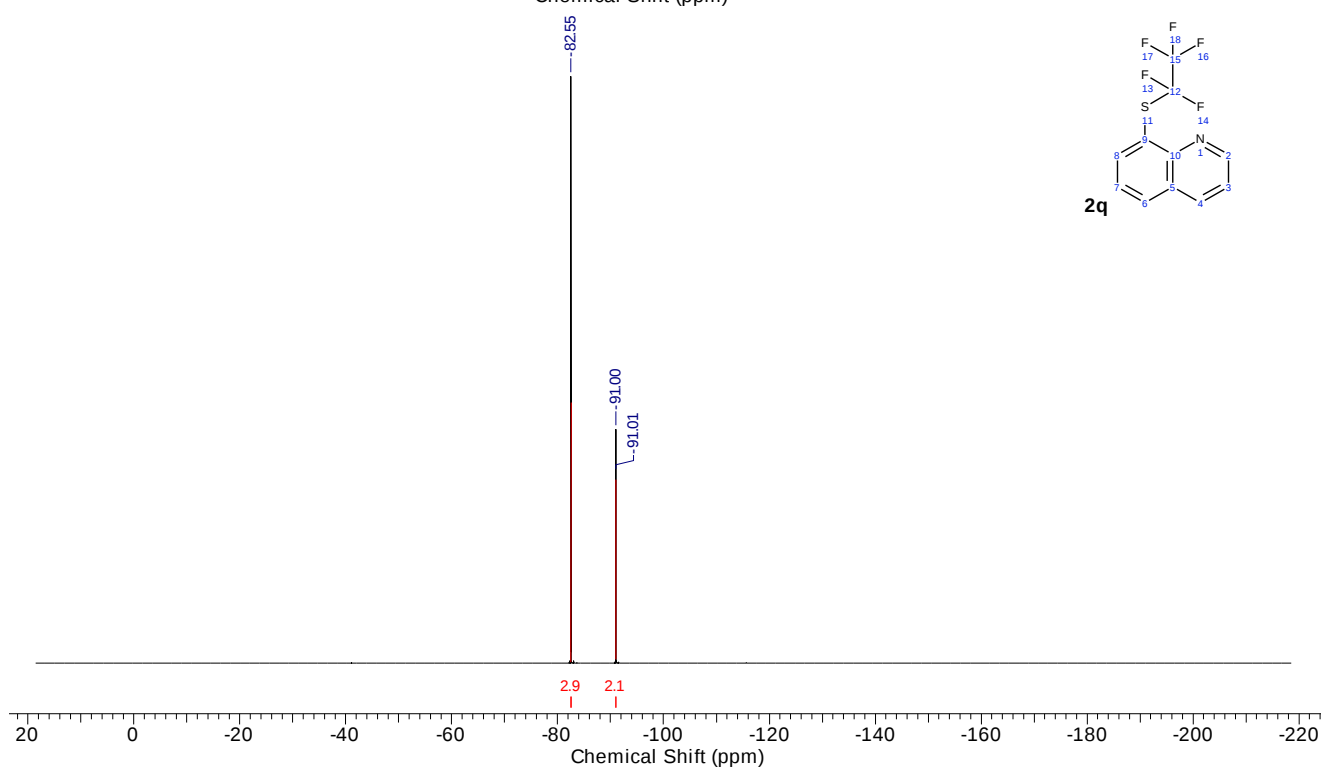
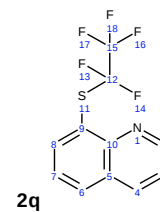
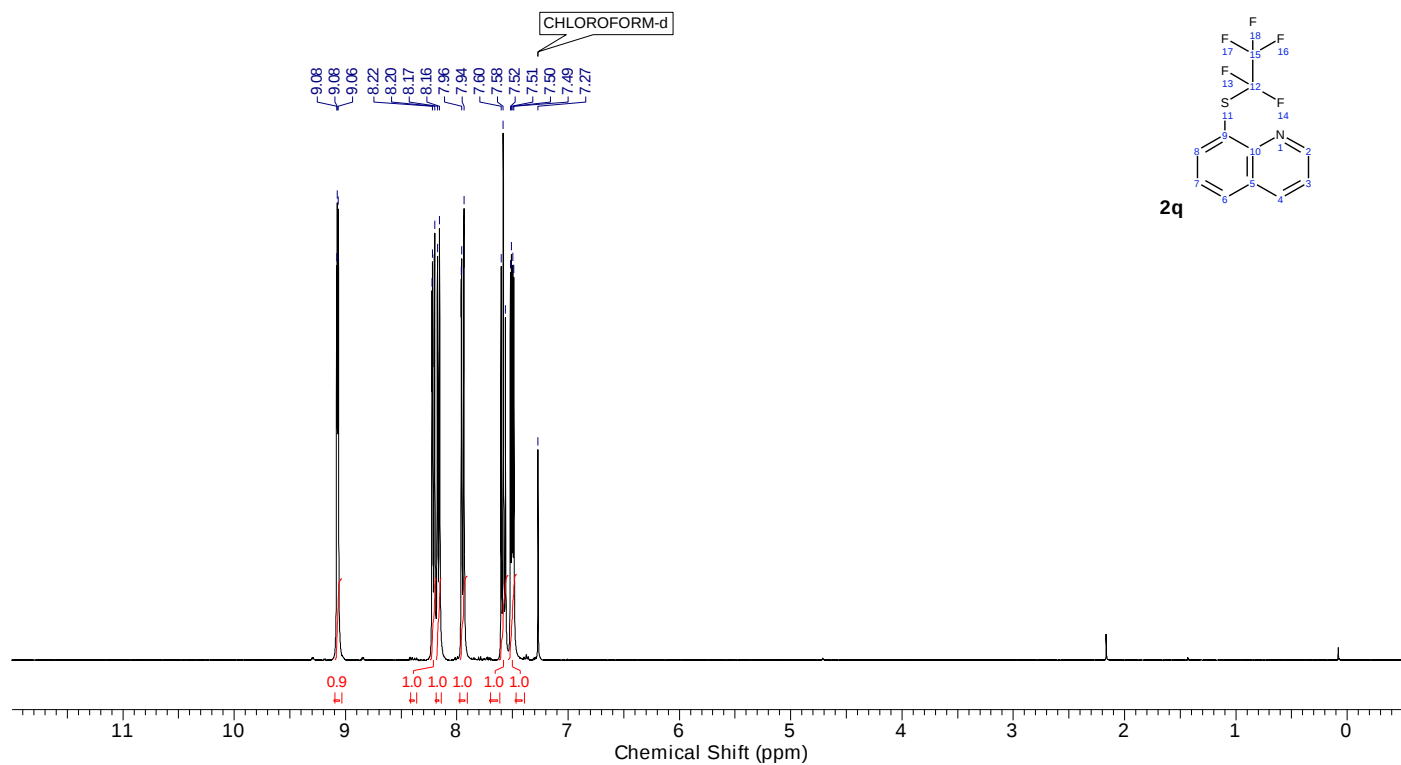


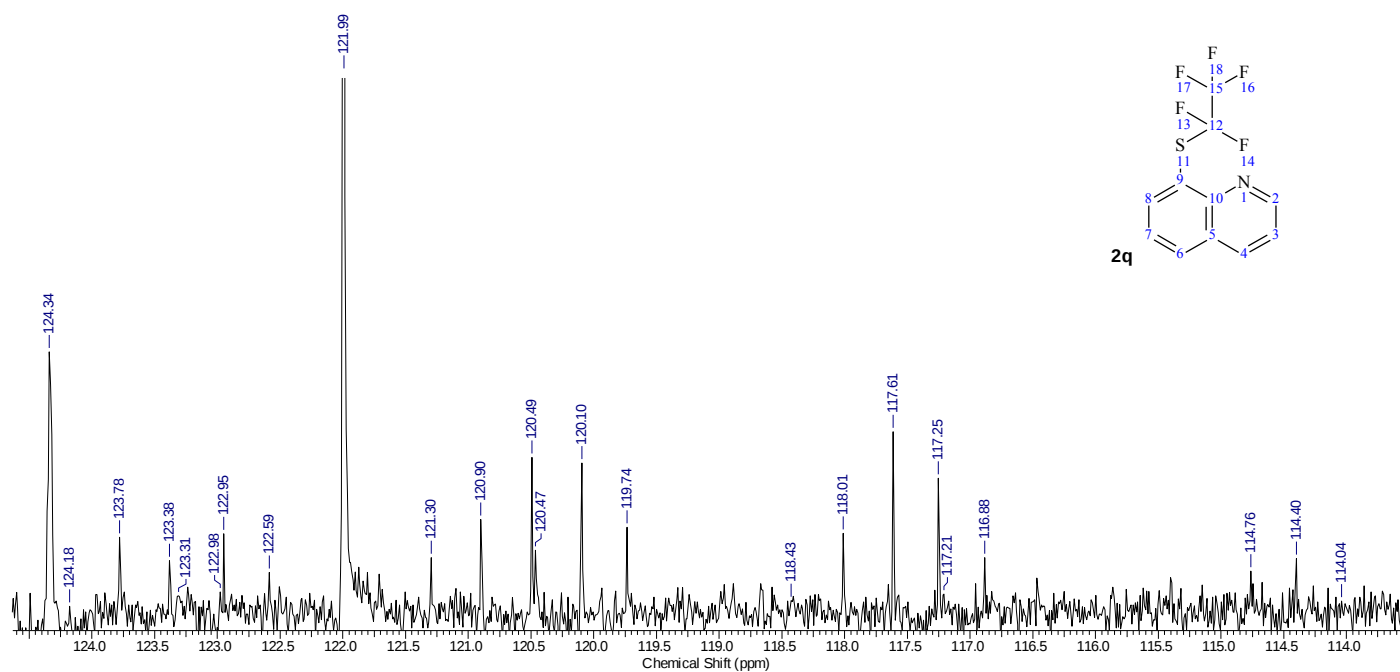
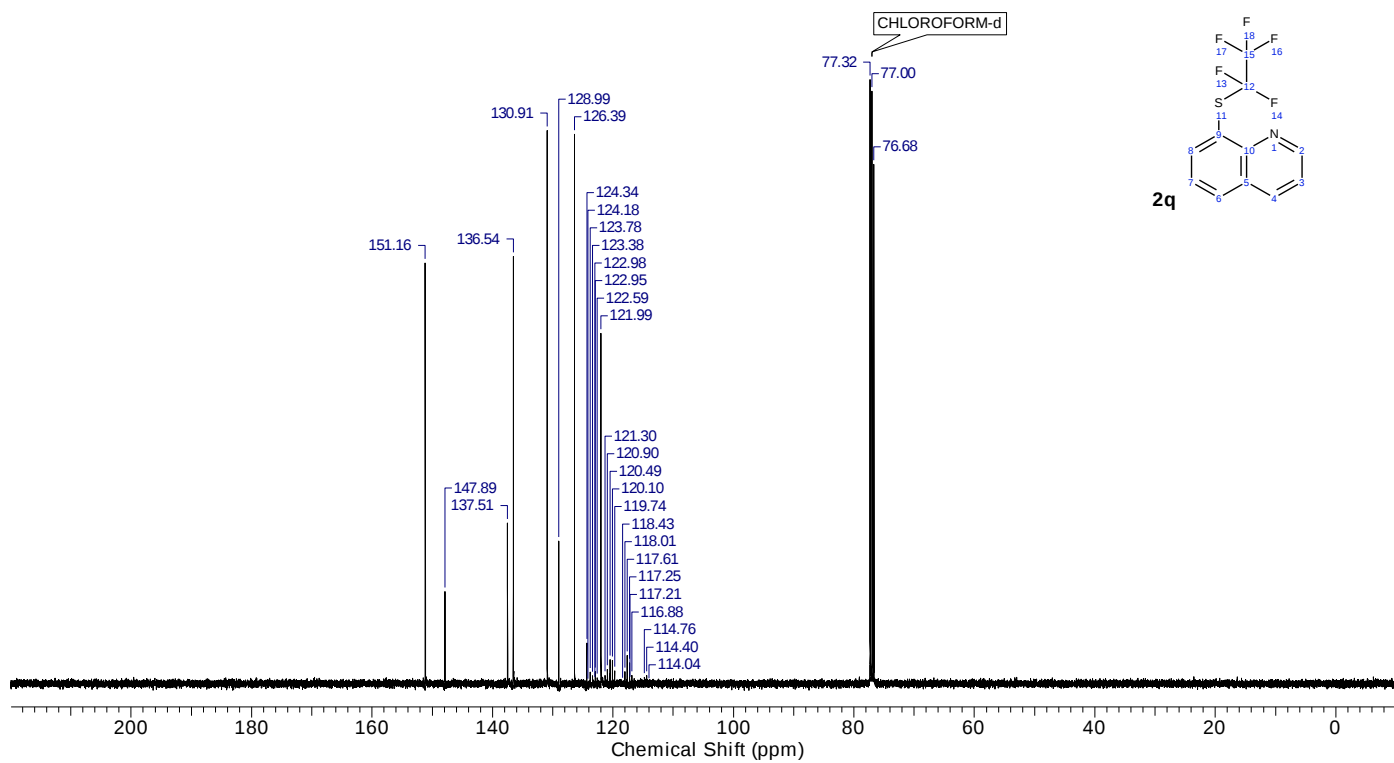


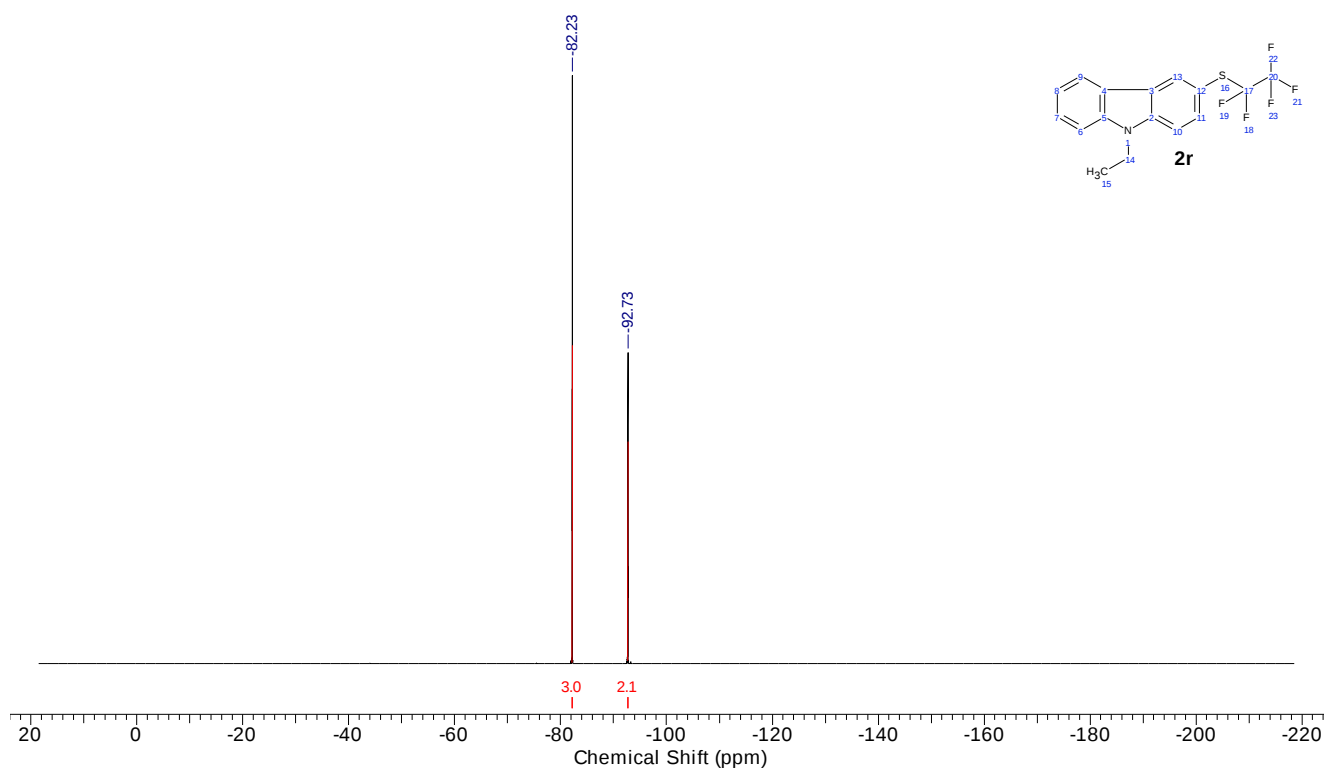
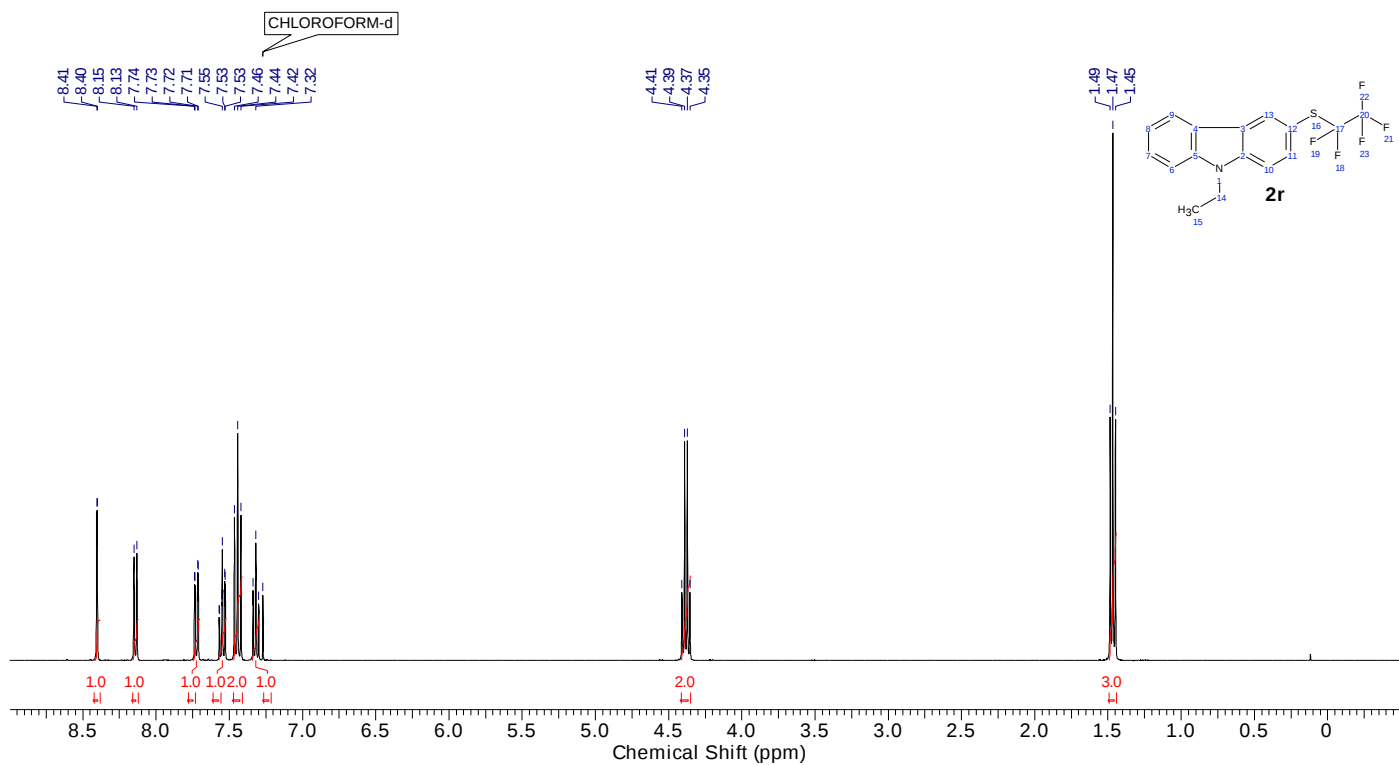


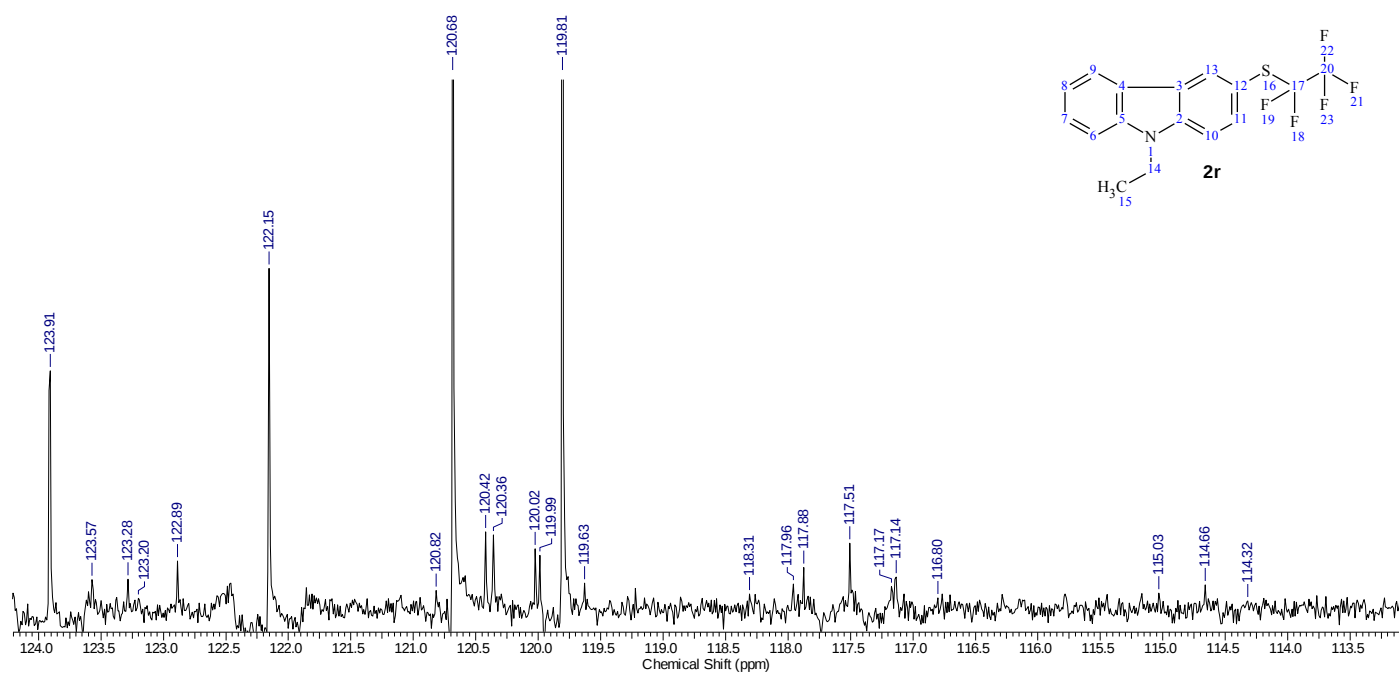
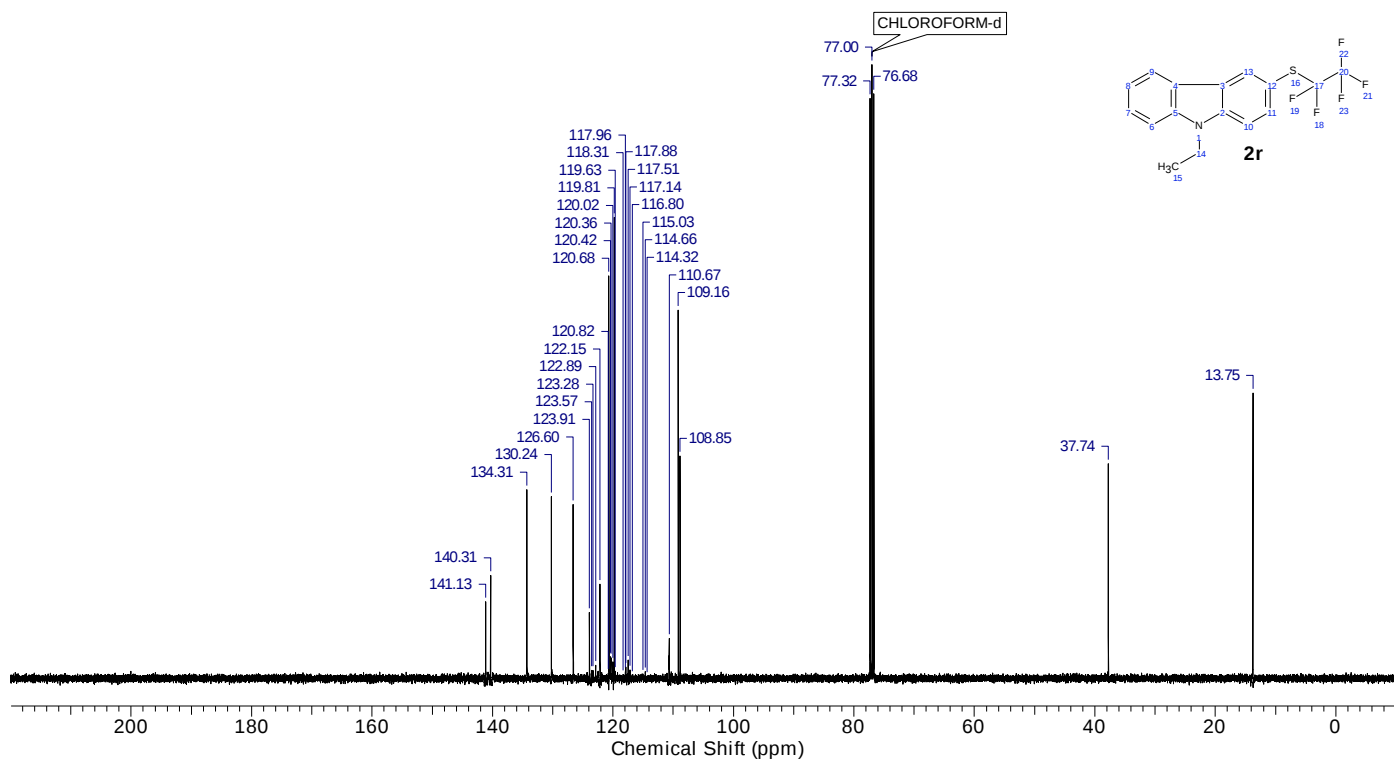


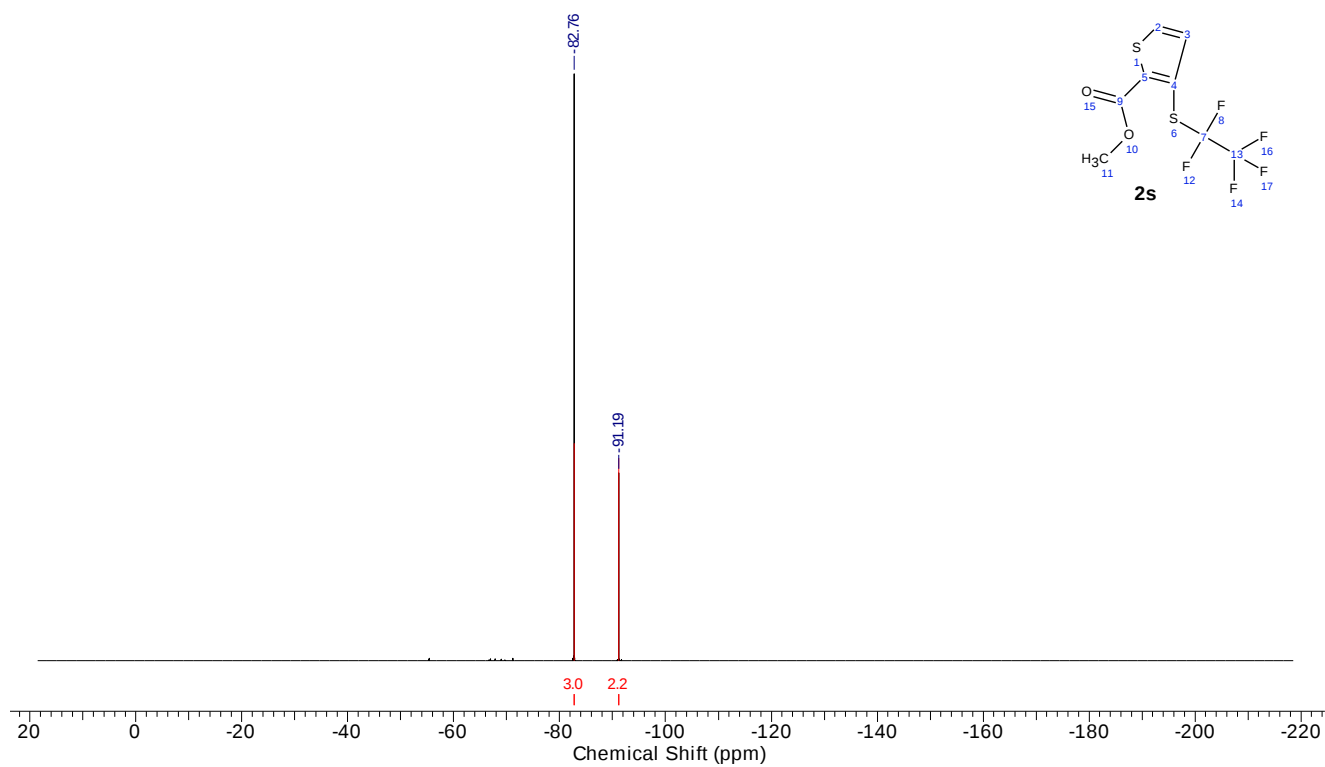
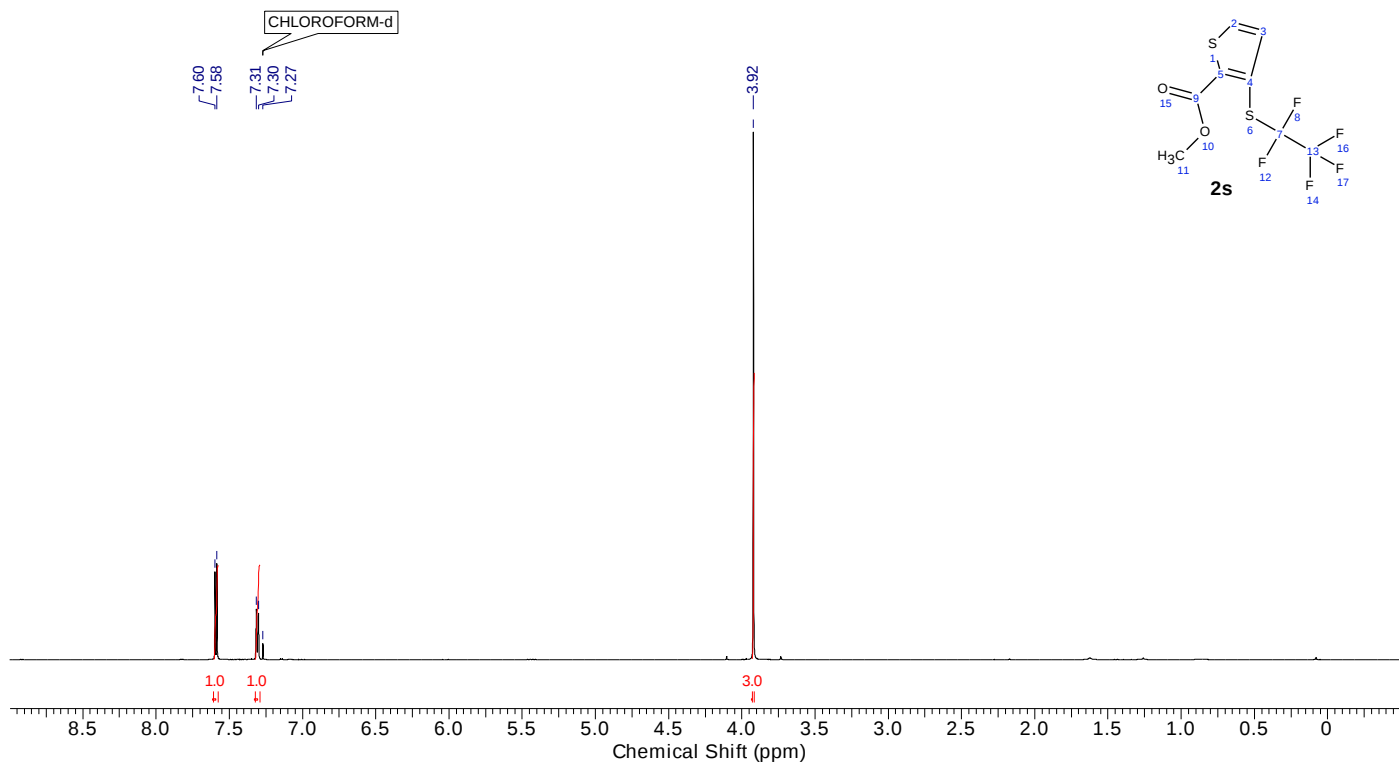


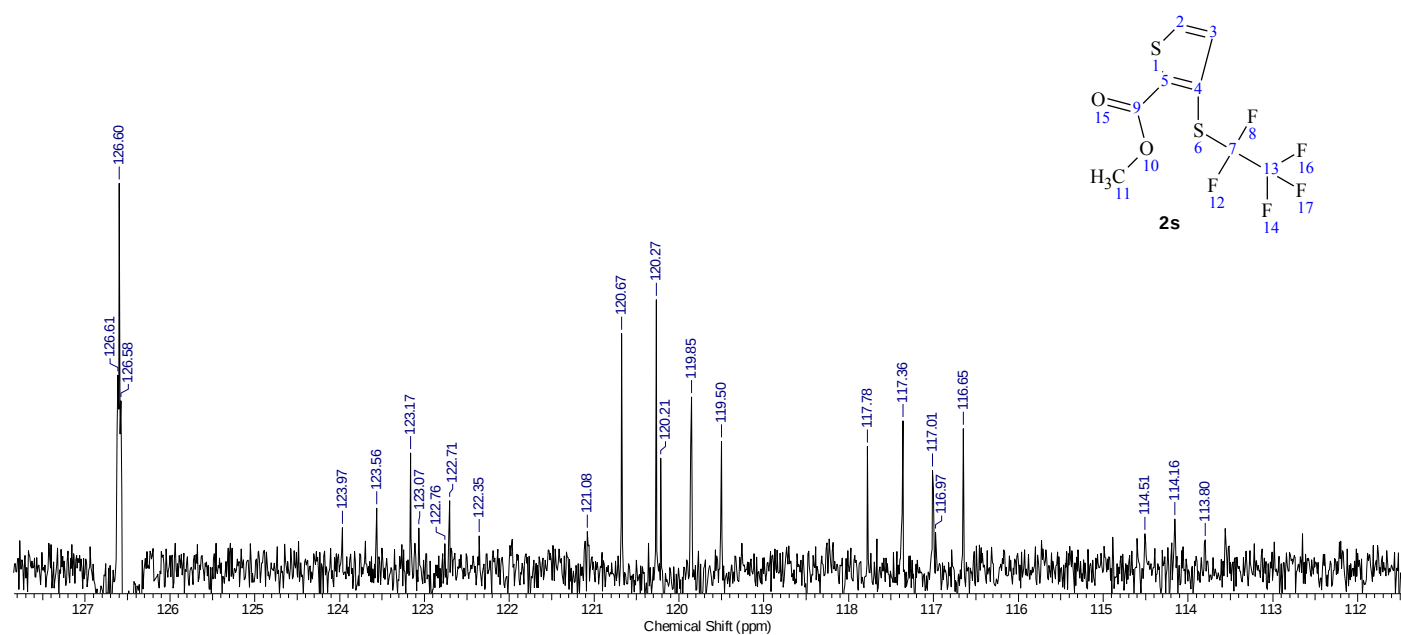
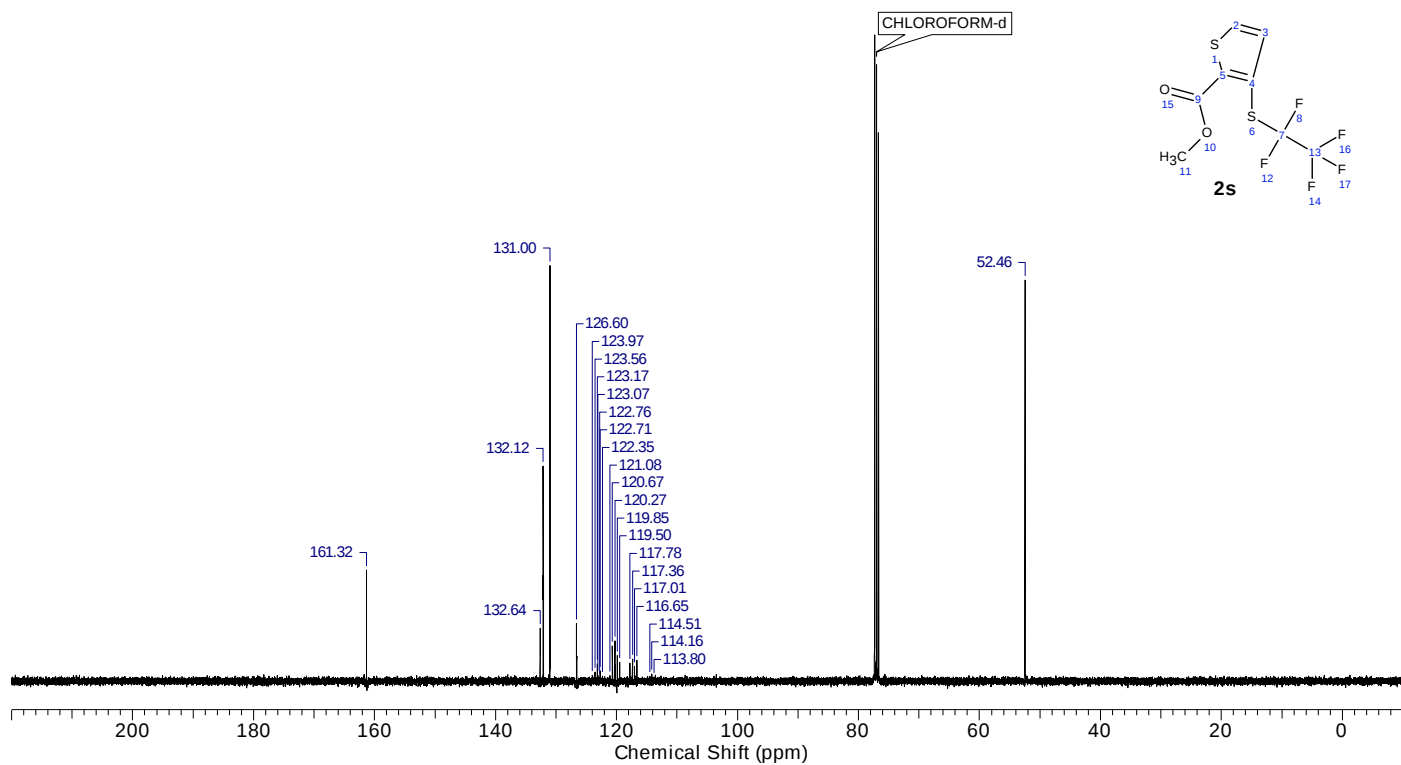












1 N. V. Kondratenko, V. I. Popov, A. A. Kolomeitsev, E. P. Saenko, V. V. Prezhdov, A. E. Lutsii, L. M. Yagupol'skii *Zhurnal Organicheskoi Khimii* **1980**, V16(6).