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For

Site-selective Nucleophilic Substitution Reactions of Pentafluoropyridine with Hydroxybenzaldehydes: Synthesis of Triarylmethanes Comprising Perfluoropyridine moieties

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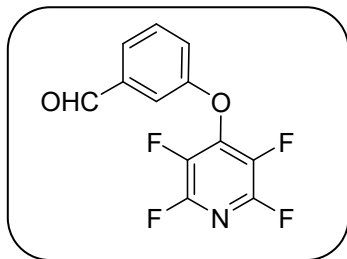
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1. General information

All chemicals and solvents, unless otherwise stated, were obtained from commercial sources and were used as received. The reaction mixtures were stirred magnetically in oil bath under optimized conditions. The progress of the reactions was monitored by TLC analysis using polyester sheets pre-coated with silica gel-60 and fluorescent indicator (F-252), commercially available from Merck company. Melting points were determined using a Stuart SMP2 apparatus and are uncorrected. FT-IR spectra were recorded as KBr pellets using a Nicolet-Impact 400D spectrophotometer. ¹H-, ¹³C-, and ¹⁹F-NMR spectra were acquired on a Varian UNITYInova 500 MHz spectrometer using CDCl₃ and DMSO-d₆ as solvent. The chemical shifts of ¹H and ¹³C spectra were recorded relative to the solvent. The chemical shifts for ¹⁹F are reported in ppm relative to CFCl₃ as the external standard. In all cases, C-F *J*-values could not be unambiguously assigned, thus they are reported either as single signals or as ranges in ¹³C NMR spectroscopic data.

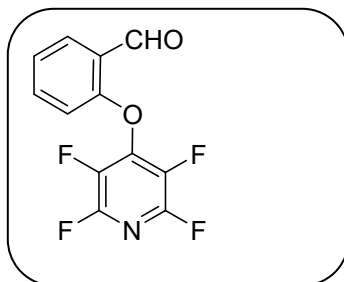
2. Spectral data of 4-((perfluoropyridinyl)oxy)benzaldehyde derivatives 3a-c

3-((perfluoropyridin-4-yl)oxy)benzaldehyde 3a



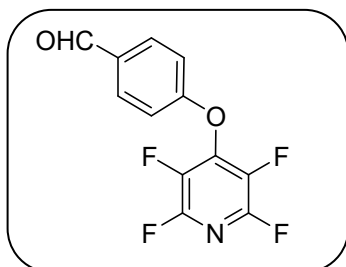
White solid. Yield 99%. MP 162-163 °C; IR (KBr) $\tilde{\nu}$ 2830, 2669, 2560, 1707, 1642, 1585 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.01 (s, 1H), 7.75 (d, 1H, $J = 7.6$ Hz), 7.61 (t, 1H, $J = 8.0$ Hz), 7.51 (s, 1H), 7.39 (dd, 1H, $J_1 = 8.2$, $J_2 = 2.7$ Hz) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 190.57, 156.30, 144.98-145.55 (m), 142.72-143.66 (m), 138.26, 137.06-137.36 (m), 134.97-135.26 (m), 130.92, 127.22, 122.73, 115.62 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -87.83_ -87.69 (m, 2F, F2,6-py), -153.95_ -153.81 (m, 2F, F3,5-py).

2-((perfluoropyridin-4-yl)oxy)benzaldehyde 3b



White solid. Yield 95%. MP 100-101 °C. IR (KBr) $\tilde{\nu}$ 3089, 3066, 3042, 2873, 2775, 2613, 1694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 10.48 (s, 1H), 7.97 (dd, 1H, $J_1 = 7.7$, $J_2 = 1.6$ Hz), 7.59-7.63 (m, 1H), 7.37 (t, 1H, $J = 7.5$ Hz), 6.96 (d, 1H, $J = 8.2$ Hz) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 187.57, 156.94, 144.99-145.23 (m), 143.67-143.76(m), 143.07-143.30 (m), 137.07-137.16 (m), 136.79-136.92 (m), 135.77, 134.96-135.07 (m), 130.25, 126.08, 125.68, 116.47 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -87.92_ -87.79 (m, 2F, F2,6-py), -154.57_ -154.43 (m, 2F, F3,5-py) ppm.

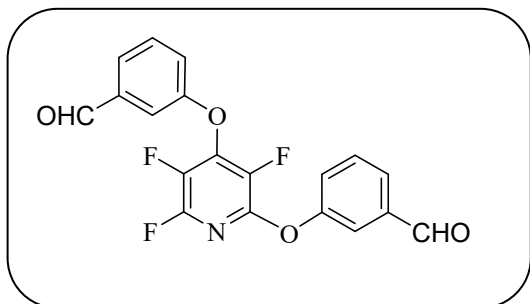
4-((perfluoropyridin-4-yl)oxy)benzaldehyde 3c



White solid. Yield 96%. MP 156-157°C. IR (KBr) $\tilde{\nu}$ 3072, 1688, 1642, 1598, 1476 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.00 (s, 1H), 7.95 (d, 2H, $J = 8.8$ Hz), 7.19 (d, 2H, $J = 8.7$ Hz) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 191.84, 159.95, 144.82-145.05 (m), 142.90-143.03 (m), 137.65-137.96 (m), 135.60-135.89 (m), 133.56, 132.34, 117.24 ppm. ^{19}F NMR (470 MHz, CDCl_3): δ -87.42_-87.28 (m, 2F, F2,6-py), -153.41_-153.27 (m, 2F, F3,5-py).

3. Spectral data of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde 4a

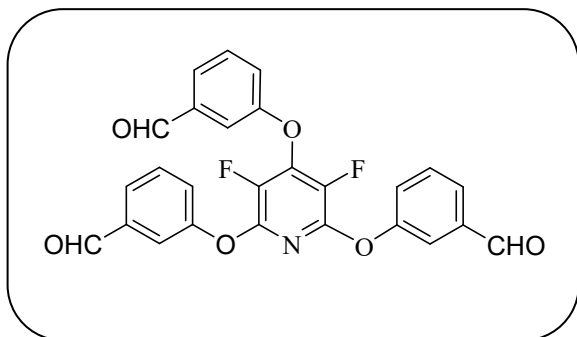
3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde 4a



White solid. MP 104-105 °C. IR (KBr) $\tilde{\nu}$ 3059, 2924, 2848, 2823, 2740, 1698 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.02 (s, 1H), 10.01 (s, 1H), 7.78 (d, 1H, $J = 7.6$ Hz), 7.73 (d, 1H, $J = 7.6$ Hz), 7.67-7.69 (m, 1H), 7.61 (td, 2H, $J_1 = 7.9$, $J_2 = 3.1$ Hz), 7.54 (s, 1H), 7.45- 7.4 9 (m, 1 H), 7.42 (dd, 1H, $J_1 = 8.2$, $J_2 = 2.5$ Hz) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 190.97, 190.83, 156.60, 153.27, 145.36-145.75 (m), 143.58-144.29 (m), 142.60-142.85 (m), 139.12-139.22 (m), 138.20, 138.07, 137.00-137.08 (m), 130.85, 130.48, 127.25, 126.95, 122.73, 120.99, 115.45 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.17 (dd, $J_1 = 26.7$ Hz, $J_2 = 21.9$ Hz, 1F), -152.06 (d, $J = 26.7$ Hz, 1F), -157.81 (d, $J = 21.7$ Hz, 1F) ppm.

Spectral data of 3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde 4b

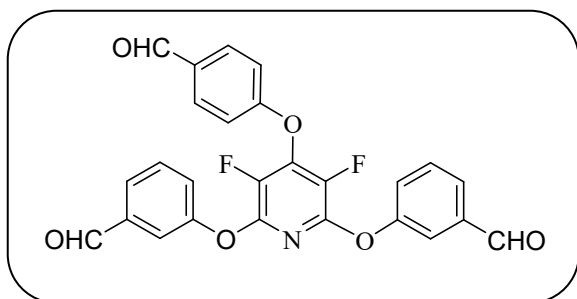
3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde 4b



White oil. Yield 60%. IR (KBr) $\tilde{\nu}$ 2924, 2853, 2733, 1700, 1629, 1585, 1456 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.03 (s, 1H), 9.87 (s, 2H), 7.72 (dt, 1H, $J_1 = 7.5$ Hz, $J_2 = 1.1$ Hz), 7.59-7.62 (m, 3H), 7.57 (s, 1H), 7.51-7.52 (m, 1H), 7.45 (dd, 2H, $J_1 = 8.1$, $J_2 = 2.1$ Hz), 7.41 (t, 2H, $J = 7.8$), 7.29-7.31 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 190.91, 190.86, 156.91, 153.40, 144.11-144.22 (m), 141.91-142.05 (m), 138.20, 137.66, 137.54, 135.41-135.54 (m), 130.75, 130.01, 126.93, 126.65, 122.73, 121.09, 115.31 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -155.96 (s, 2F, F3,5-py) ppm.

4. Spectral data of 3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde 4c

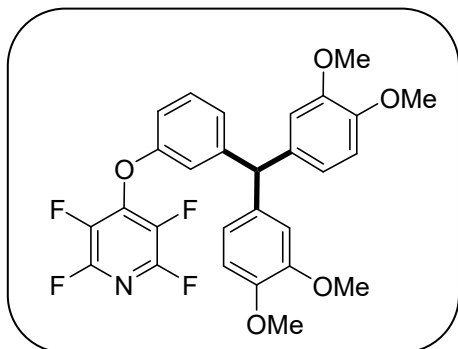
3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde 4c



Yellow oil. Yield 53%. IR (KBr) $\tilde{\nu}$ 3023, 2924, 2850, 2734, 1700, 1629, 1588, 1482 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 9.98 (s, 1H), 9.86 (s, 2H), 7.94 (d, 2H, $J = 8.6$ Hz), 7.60 (d, 2H, $J = 7.5$ Hz), 7.50 (s, 2H), 7.40 (t, 2H, $J = 7.8$ Hz), 7.28-7.30 (m, 2H), 7.24 (d, 2H, $J = 8.5$ Hz) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 190.89, 190.32, 160.44, 153.39, 144.11-144.22 (m), 137.66, 137.51, 135.43, 132.90, 131.98, 130.05, 126.90, 126.84, 120.86, 116.55 ppm; ^{19}F NMR (470 MHz, CDCl_3) δ -155.55 (s, 2F, F3,5-py) ppm.

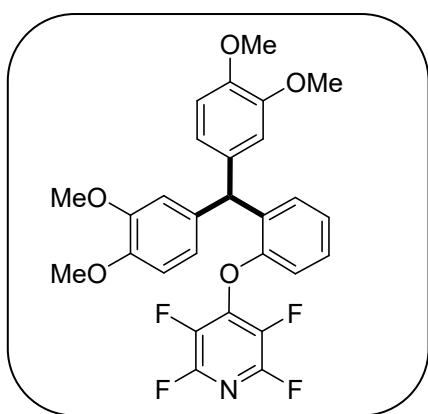
5. Spectral data of synthesized TRAMs containing tetrafluoropyridine subunits 9 a-p

4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9a



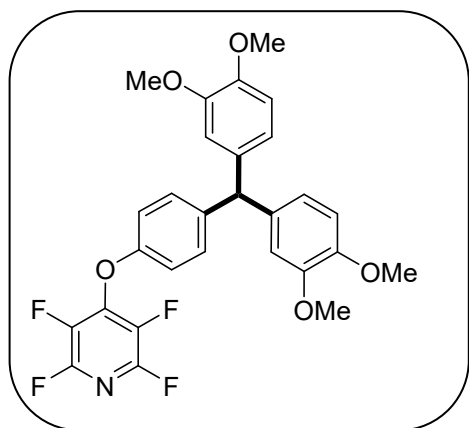
Yellow oil. Yield 93%. IR (KBr) $\tilde{\nu}$ 3015, 2936, 2836, 1642, 1606, 1504 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.27 (t, 1H, $J = 7.9$ Hz), 6.99 (d, 1H, $J = 8.3$ Hz), 6.88 (dd, 1H, $J_1 = 8.3$, $J_2 = 2.5$ Hz), 6.84 (bs, 1H), 6.78 (d, 2H, $J = 8.3$ Hz), 6.63 (d, 2H, $J = 2.0$ Hz), 6.58 (dd, 2H, $J_1 = 8.3$, $J_2 = 2.1$ Hz), 5.45 (s, 1H, Ar_3CH), 3.84 (s, 6H, OMe), 3.75 (s, 6H, OMe) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 155.75, 148.95, 147.76, 147.22, 144.94–145.21 (m), 144.38–144.61 (m), 143.00–143.27 (m), 136.72–136.97 (m), 135.80, 134.67–134.96 (m), 129.68, 126.32, 121.37, 117.93, 114.52, 112.72, 111.06, 55.80, 55.74, 55.53 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.06–-88.92 (m, 2F, F2,6-py), -154.70–-154.57 (m, 2F, F3,5-py) ppm.

4-(2-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9b



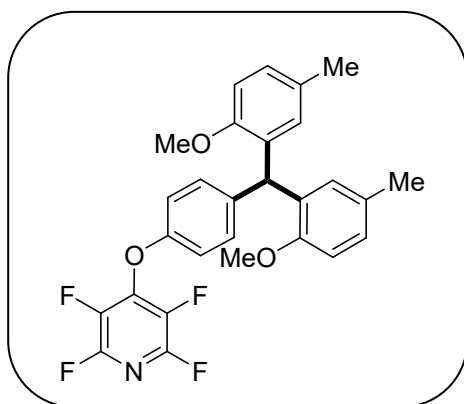
White solid. Yield 79%. MP 120-121°C. IR (KBr) $\tilde{\nu}$ 3001, 2938, 2838, 1643, 1591, 1504, 1412 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.22-7.26 (m, 1H), 7.16 (t, 1H, $J = 7.6$ Hz), 7.02 (d, 1H, $J = 7.7$ Hz), 6.94 (d, 1H, $J = 8.1$ Hz), 6.75 (d, 2H, $J = 8.3$ Hz), 6.65 (d, 2H, $J = 1.8$ Hz), 6.59 (dd, 2H, $J_1 = 8.2$, $J_2 = 1.9$ Hz), 5.79 (s, 1H, Ar_3CH), 3.83 (s, 6H, OMe), 3.74 (s, 6H, OMe) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 153.26, 148.88, 147.75, 144.71-145.09 (m), 142.92-143.14 (m), 135.93-136.22 (m), 134.96, 133.85-134.15 (m), 131.08, 127.90, 125.57, 121.41, 120.90, 117.21, 112.79, 111.12, 77.31, 77.05, 76.80, 55.88, 55.79, 49.55 ppm. ^{19}F NMR (470 MHz, CDCl_3): δ -89.77_-89.63 (m, 2F, F2,6-py), -155.59_-155.46 (m, 2F, F3,5-py).

4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9c



Yellow oil. Yield 91%. IR (KBr) $\tilde{\nu}$ 3016, 2935, 2836, 1642, 1600, 1501, 1416 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.12 (d, 2H, $J = 8.8$ Hz), 6.98 (d, 2H, $J = 8.5$ Hz), 6.79 (d, 2H, $J = 8.3$ Hz), 6.64 (d, 2H, $J = 1.6$ Hz), 6.58–6.60 (m, 2H), 5.44 (s, 1H, Ar_3CH), 3.85 (s, 6H, OMe), 3.76 (s, 6H, OMe) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 154.24, 148.96, 147.74, 144.98–145.24 (m), 144.54–144.67 (m), 143.03–143.19 (m), 141.56, 136.97–137.31 (m), 136.28, 134.84–135.22 (m), 130.75, 121.36, 116.54, 112.83, 111.14, 55.85, 55.80, 55.13 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.94–-88.80 (m, 2F, F2,6-py), -154.63–-154.50 (m, 2F, F3,5-py) ppm.

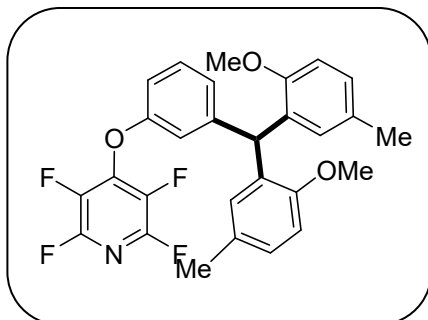
4-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9d



White solid Yield 87%. MP 118 °C. IR (KBr) $\tilde{\nu}$ 2995, 2917, 2836, 1642, 1605, 1500, 1477 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.14 (d, 2H, $J = 8.8$ Hz), 7.04–7.09 (m, 2H), 7.00 (d, 2H, $J = 8.6$ Hz), 6.83 (d, 2H, $J = 8.2$ Hz), 6.68 (bs, 2H), 6.22 (s, 1H, Ar_3CH), 3.71 (s, 6H, OMe), 2.27 (s, 6H, Me) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 155.31, 153.93, 145.07–145.34 (m), 144.87–145.00 (m), 143.14–143.40 (m), 141.66, 137.03–137.34 (m), 134.94–135.25 (m), 132.05, 130.75, 130.66, 129.36, 127.81, 116.33,

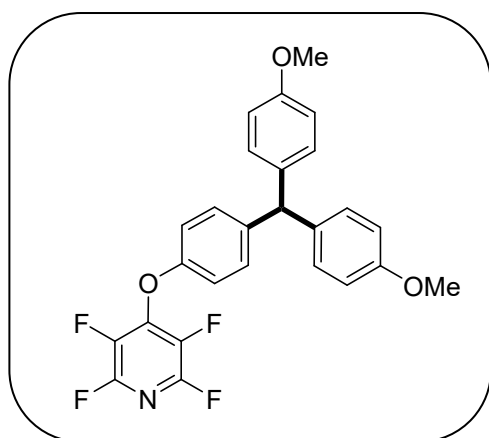
111.12, 55.88, 42.78, 20.72 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.19–89.05 (m, 2F, F2,6-py), -154.71–154.58 (m, 2F, F3,5-py) ppm.

4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9e



White solid. Yield 92%. MP 118-119 °C. IR (KBr) $\tilde{\nu}$ 3029, 2999, 2835, 1642, 1585, 1500, 1468 cm^{-1} . ^1H NMR (500 MHz, DMSO-d_6) δ 7.29 (t, 1H, $J = 8.0$ Hz), 7.09 (dd, 1H, $J_1 = 8.1$, $J_2 = 2.5$ Hz), 6.99 (dd, 2H, $J_1 = 8.3$, $J_2 = 1.9$ Hz), 6.78–6.89 (m, 4H), 6.50 (d, 2H, $J = 1.9$ Hz), 6.03 (s, 1H, Ar_3CH), 3.59 (s, 6H, OMe), 2.11 (s, 6H, Me) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.87, 155.17, 146.98, 144.73–145.04 (m, C2,6-Py), 144.19–144.49 (m, C3,5-Py), 143.142.71–143.13 (m, C4-Py), 131.37, 130.26, 130.04, 128.94, 128.34, 126.19, 117.80, 114.64, 111.67, 56.03, 42.97, 20.75 ppm. ^{19}F NMR (470 MHz, CDCl_3): δ (ppm) -91.08 (m, 2F, F2,6-py), -155.43 (m, 2F, F3,5-py) ppm.

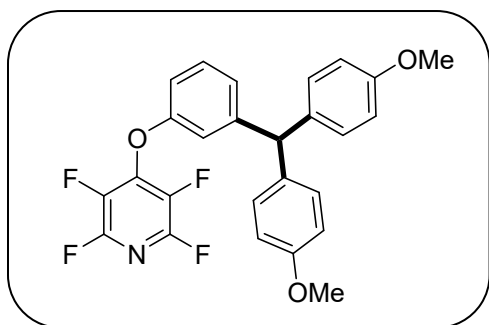
4-(4-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9f



White solid. Yield 77%. MP 95-96 °C. IR (KBr) $\tilde{\nu}$ 3004, 2875, 1641, 1502, 1247 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.12 (d, 2H, $J = 8.8$ Hz), 7.02 (d, 4H, $J = 8.8$ Hz), 6.98 (d, 2H, $J = 8.7$ Hz), 6.85 (d, 4H, J

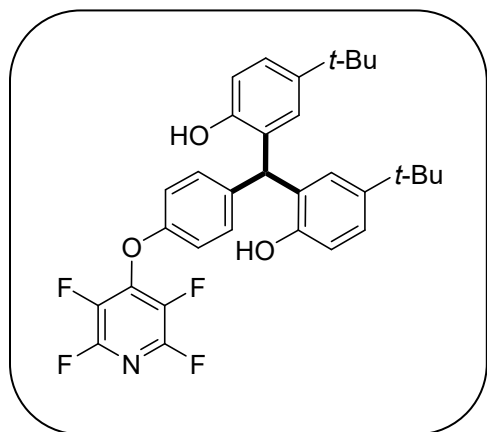
= 8.8 Hz), 5.47 (s, 1H, Ar₃CH), 3.80 (s, 6H, OMe) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 158.18, 154.18, 145.12–145.26 (m), 144.57–144.62 (m), 143.33, 143.06–143.22 (m), 141.79, 135.97, 130.74, 130.16, 116.48, 113.81, 55.22, 54.47 ppm. ¹⁹F NMR (470 MHz, CDCl₃) δ -88.85–-88.72 (m, 2F, F2,6-py), -154.43–-154.30 (m, 2F, F3,5-py) ppm.

4-(3-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9g



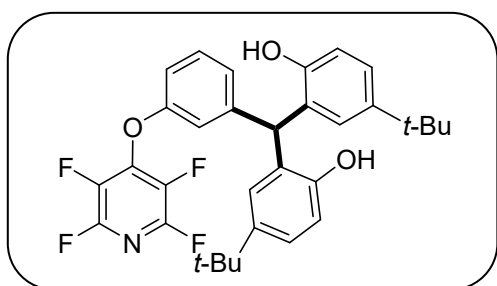
Yellow oil. Yield 83%. IR (KBr) $\tilde{\nu}$ 3004, 2955, 2837, 1641, 1610, 1505 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, 1H, *J* = 8.0 Hz), 6.98–7.05 (m, 4H), 6.83–6.91 (m, 7H), 5.48 (s, 1H, Ar₃CH), 3.80 (s, 6H, OMe) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 158.26, 155.75, 147.50, 145.00–145.26 (m), 144.37–144.59 (m), 143.16–143.22 (m), 135.52, 130.19, 129.66, 126.25, 117.88, 114.30, 113.82, 55.21, 54.89 ppm. ¹⁹F NMR (470 MHz, CDCl₃) δ -88.97–-88.84 (m, 2F, F2,6-Py), -154.41–-154.28 (m, 2F, F3,5-Py) ppm.

2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) 9h



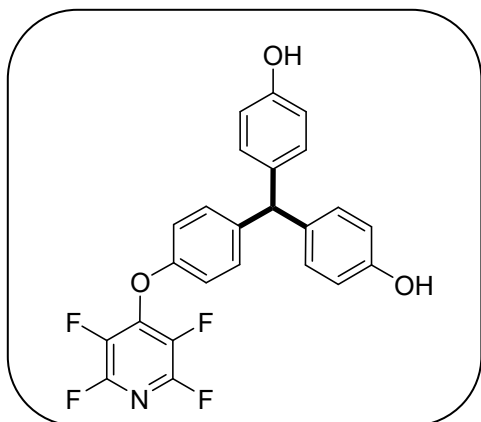
Yellow oil. Yield 76%. IR (KBr) $\tilde{\nu}$ 3405, 2962, 2907, 1640, 1603 cm^{-1} , 1499; ^1H NMR (500 MHz, CDCl_3) δ 7.19 (d, 2H, $J = 8.7$ Hz), 7.16 (dd, 2H, $J_1 = 8.6$, $J_2 = 2.6$ Hz), 7.02 (d, 2H, $J = 8.5$ Hz), 6.97 (d, 2H, $J = 2.3$ Hz), 6.75 (d, 2H, $J = 8.4$ Hz), 6.00 (s, 1H, Ar_3CH), 5.55 (s, 2H), 1.20 (s, 18H, Me) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 154.35, 150.89, 145.04-145.30 (m), 144.54-144.79 (m), 143.92, 143.09-143.24 (m), 139.31, 136.87-137.02 (m), 134.78-135.12 (m), 130.72, 128.15, 127.22, 124.79, 116.70, 115.66, 43.62, 34.11, 31.3 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.94--88.80 (m, 2F, F2,6-py), -154.64--154.51 (m, 2F, F3,5-py) ppm.

2,2'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) 9i



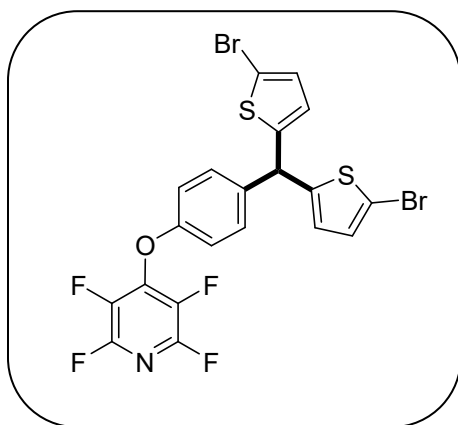
Yellow oil. Yield 81%. IR (KBr) $\tilde{\nu}$ 3387, 2962, 2907, 1640, 1608, 1501 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, 1H, $J = 8.0$ Hz), 7.14 (dd, 2H, $J_1 = 8.4$, $J_2 = 2.4$ Hz), 7.06 (d, 1H, $J = 7.8$ Hz), 6.97 (d, 1H, $J = 2.3$ Hz), 6.95 (d, 2H, $J = 2.3$ Hz), 6.86 (s, 1H), 6.75 (d, 2H, $J = 8.4$ Hz), 6.01 (s, 1H, Ar_3CH), 2.18 (s, 2H, OH), 1.18 (s, 18H, Me) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 155.92, 152.86, 150.92, 145.20, 143.90, 143.01-143.24 (m), 136.86-137.15 (m), 134.77-135.01 (m), 129.74, 127.82, 127.12, 126.25, 124.81, 117.61, 115.63, 114.93, 43.89, 34.05, 31.29 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.92--88.79 (m, 2F, F2,6-Py), -154.63--154.50 (m, 2F, F3,5-Py) ppm.

4,4'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)diphenol 9j



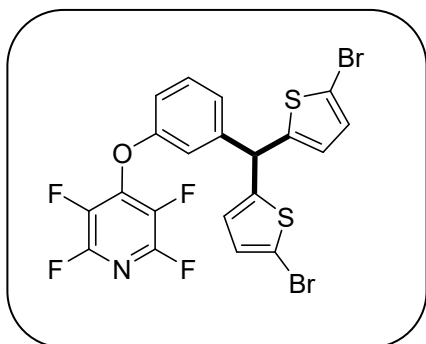
Yellow oil. Yield 72%. IR (KBr) $\tilde{\nu}$ 3427, 2252, 2125, 1648, 1500 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6) δ 9.21 (s, 2H, OH), 7.14 (d, 2H, $J = 8.5$ Hz), 7.08 (d, 2H, $J = 8.5$ Hz), 6.85 (d, 4H, $J = 8.2$ Hz), 6.66 (d, 4H, $J = 8.0$ Hz), 5.35 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 155.81, 153.96-153.98 (m), 142.22-142.28 (m), 134.66, 130.68, 130.03, 116.43, 115.37, 54.30 ppm. ^{19}F NMR (470 MHz, DMSO- d_6) δ -90.59 (m, 2F, F2,6-Py), -155.01 (m, 2F, F3,5-Py) ppm.

4-(4-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9k



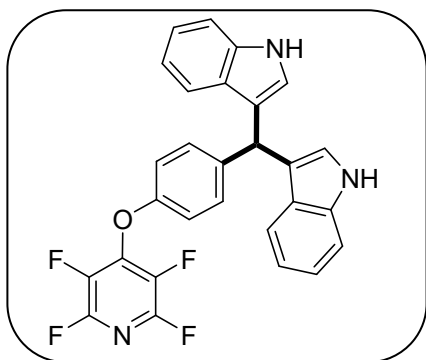
Black solid. Yield 92%. MP 102 $^{\circ}\text{C}$. IR (KBr) $\tilde{\nu}$ 2924, 1641, 1601, 1500, 1481, 1438, 1204 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, 2H, $J = 8.9$ Hz), 7.04 (d, 2H, $J = 8.7$ Hz), 6.91 (d, 2H, $J = 3.8$ Hz), 6.58 (d, 2H, $J = 3.8$ Hz), 5.68 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 155.05, 147.58, 144.99-145.28 (m), 144.14-144.29 (m), 143.07-143.25 (m), 139.02, 137.26-137.39 (m), 137.04-137.15 (m), 129.90, 129.56, 126.67, 116.91, 111.91, 47.11 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.40--88.26 (m, 2F, F2,6-Py), -154.12--153.99 (m, 2F, F3,5-Py) ppm.

4-(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9l



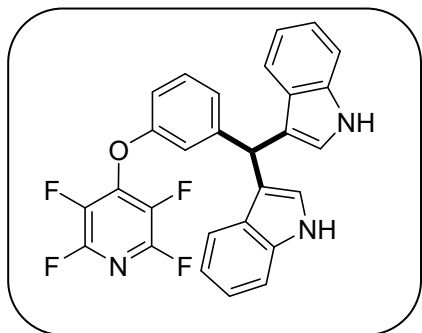
Black oil. Yield 93%. IR (KBr) $\tilde{\nu}$ 2252, 2125, 1644, 1501, 1485 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6) δ 7.42 (t, 1H, $J = 7.7$ Hz), 7.26 (bs, 1H), 7.18-7.22 (m, 2H), 7.07 (d, 2H, $J = 2.2$ Hz), 6.71 (d, 2H, $J = 3.3$ Hz), 6.04 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 156.04, 148.00, 145.01, 143.70-143.97 (m), 142.92-143.13 (m), 137.33-137.70 (m), 135.34-135.64 (m), 131.03, 130.59, 127.62, 125.11, 116.90, 115.94, 111.14, 46.48, 40.39, 40.22 ppm. ^{19}F NMR (470 MHz, DMSO- d_6) δ -85.93--85.80 (m, 2F, F2,6-py), -150.09--149.96 (m, 2F, F3,5-py) ppm.

3,3'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) 9m



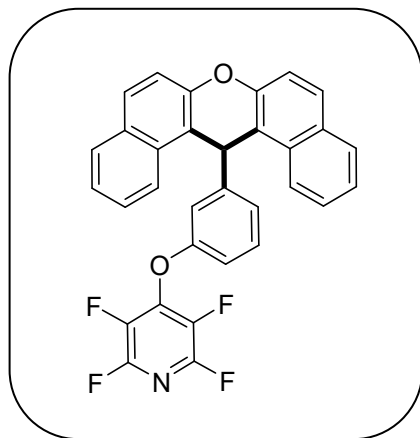
Yellow oil. Yield 89%. IR (KBr) $\tilde{\nu}$ 3413, 3056, 2925, 1641, 1601, 1499, 1479 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 2H), 7.32-7.41 (m, 6H), 7.20 (t, 2H, $J = 7.4$ Hz), 7.04 (t, 2H, $J = 7.7$ Hz), 6.98 (d, 2H, $J = 8.5$ Hz), 6.64 (d, 2H, $J = 1.4$ Hz), 5.91 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 154.17-154.21 (m), 141.18-141.25 (m), 136.61-136.79 (m), 131.95, 130.18, 129.48-129.53 (m), 126.88-126.94 (m), 123.55, 122.10, 119.80, 119.38, 119.32, 116.60, 111.10, 39.50 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.00--88.87 (m, 2F, F2,6-py), -154.59--154.46 (m, 2F, F3,5-py) ppm.

3,3'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) 9n



Yellow oil. Yield 92%. IR (KBr) $\tilde{\nu}$ 3427, 2251, 2125, 1645, 1583, 1501, 1485 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6) δ 10.84(s, 2H), 7.21-7.37(m, 7H), 7.09 (dd, 1H, $J_1 = 8.2$, $J_2 = 2.9$ Hz), 7.00-7.07(m, 2H), 6.81-6.90 (m, 4H), 5.87(s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 155.94, 148.27, 137.03, 135.55-135.61 (m), 129.98-130.14 (m), 126.98, 125.60, 124.01, 121.40, 119.41, 118.66, 117.90, 117.04, 114.39, 111.93 ppm. ^{19}F NMR (470 MHz, DMSO- d_6): δ -90.90 (m, 2F, F2,6-py), -155.22 (m, 2F, F3,5-py) ppm.

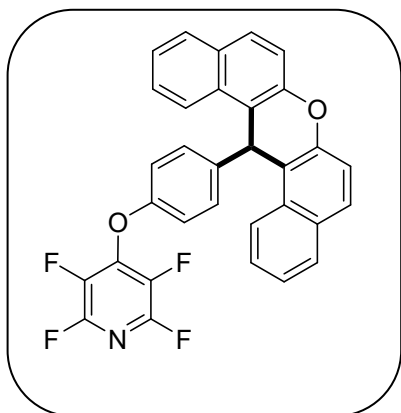
4-(3-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine 9o



Yellow oil. Yield 84%. IR (KBr) $\tilde{\nu}$ 2252, 2125, 1656, 1026 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6) δ 8.60 (d, 2H, $J = 8.6$ Hz), 7.91 (d, 4H, $J = 8.5$ Hz), 7.52-7.60 (m, 5H), 7.46 (t, 2H, $J = 7.5$ Hz), 7.08-7.11 (m, 2H), 6.86-6.90 (m, 1H), 6.66 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 155.64, 148.46, 148.31, 144.87-145.15 (m), 143.70-143.90 (m), 142.96-143.21 (m), 137.67-137.94 (m), 135.60-135.89

(m), 131.28, 131.10, 130.90, 129.69, 129.06, 127.27, 125.05, 124.75, 123.67, 118.07, 117.22, 116.08, 114.52, 36.78 ppm. ^{19}F NMR (470 MHz, DMSO- d_6) δ – 90.62 (m, 2F, F2,6-py), – 154.48 (m, 2F, F3,5-py) ppm.

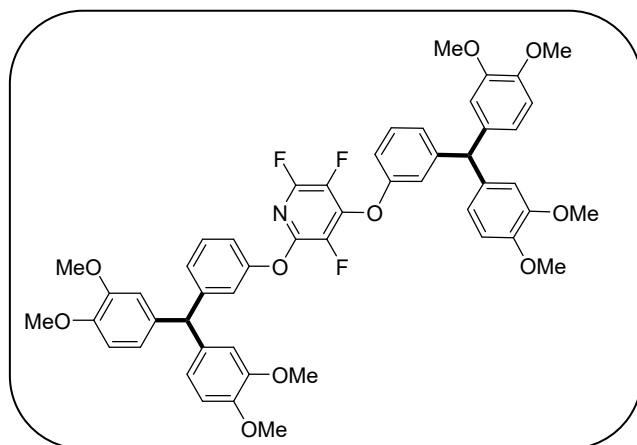
4-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine 9p



White oil. Yield 90%. IR (KBr) $\tilde{\nu}$ 1640, 1498, 1218, 1169 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, 2H, $J = 8.5$ Hz), 7.86 (d, 2H, $J = 8.1$ Hz), 7.82 (d, 2H, $J = 8.9$ Hz), 7.60 (t, 2H, $J = 8.4$ Hz), 7.60 (dd, 4H, $J_1 = 8.9$ Hz, $J_2 = 3.0$ Hz), 7.44 (t, 2H, $J = 7.4$ Hz), 6.81 (d, 2H, $J = 8.8$ Hz), 6.52 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 154.60-154.70 (m), 152.68, 138.03-138.08 (m), 133.60-133.66 (m), 130.04, 129.84, 129.79, 129.00, 127.40, 125.60-125.77 (m), 123.47, 122.36, 119.70, 118.35, 117.41, 41.87 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ –88.74_ –88.61 (m, 2F, F2,6-py), –153.96_ –153.83 (m, 2F, F3,5-py).

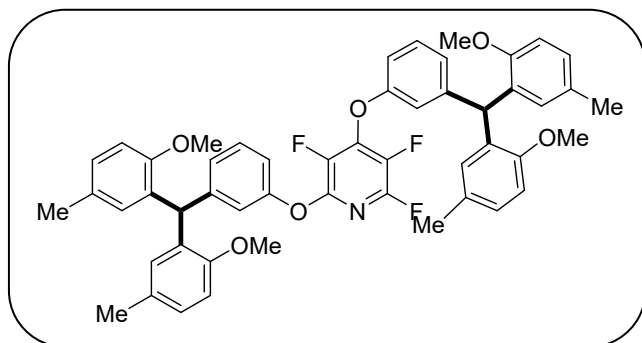
6. Spectral data of synthesized bis- and tris-TRAMs containing perfluoropyridine subunits 10 a-g

2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine 10a



85%, White solid, mp 82-85 °C, IR (KBr): ν_{max} 3017, 2935, 2835, 1606, 1583, 1512 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27–7.34 (m, 2H), 6.95–7.03 (m, 3H), 6.88 (bs, 2H), 6.80 (d, $J = 8.2$ Hz, 4H), 6.59–6.68 (m, 9H), 5.47(s, 1H, Ar_3CH), 5.46(s, 1H, Ar_3CH), 3.87 (s, 6H, OMe), 3.86 (s, 6H, OMe), 3.78 (s, 6H, OMe), 3.77 (s, 6H, OMe) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 156.13, 152.63, 148.93, 147.68–147.78 (m), 146.94–146.96 (m), 146.53, 136.14, 136.02, 135.95, 134.60–134.76 (m), 133.44, 133.05, 129.55, 129.38, 126.54, 125.80, 121.93, 121.41, 118.66, 117.93, 114.22, 112.82, 111.08, 55.87, 55.83, 55.60 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.78 (dd, $J_1 = 25.9$ Hz, $J_2 = 22.8$ Hz, 1F), -153.25 (d, $J = 26.3$ Hz, 1F), -159.47 (d, $J = 22.3$ Hz, 1F) ppm.

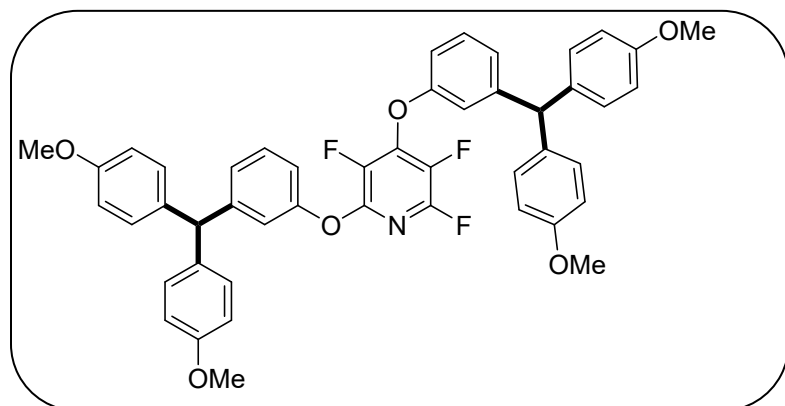
2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine 10b



White oil. Yield 89%. IR (KBr) $\tilde{\nu}$ 3006, 2925, 2835, 1637, 1607, 1583 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.29 (t, 2H, $J = 7.9$ Hz), 7.24 (t, 1H, $J = 7.9$ Hz), 6.95–7.04 (m, 8H), 6.87–6.91 (m, 2H), 6.75–6.82 (m, 7H), 6.65 (d, 1H, $J = 1.9$ Hz), 6.59 (d, 1H, $J = 2.0$ Hz), 6.17 (s, 1H, Ar_3CH), 6.13 (s, 1H, Ar_3CH), 3.67–3.69 (m, 12H), 2.19–2.22 (m, 12H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 156.00, 155.26, 155.21, 152.46–152.65 (m), 147.68, 147.03, 146.59, 145.45–145.57(m), 145.36–145.42 (m), 144.69–144.90 (m), 143.21–143.62 (m), 131.83, 131.57, 130.74, 130.63, 129.30, 129.09, 128.93, 127.79, 127.71, 126.51, 125.74, 121.80, 117.89, 117.62, 113.84, 110.97, 110.87, 55.93, 55.83, 43.18, 20.72 ppm. ^{19}F NMR (470

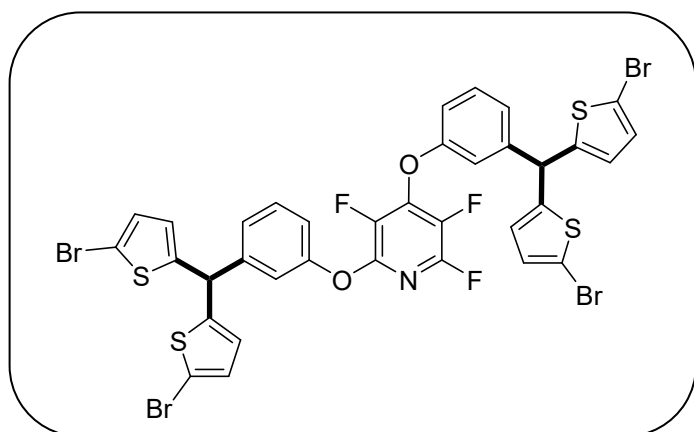
MHz, CDCl₃) δ -89.94 (dd, $J_1 = 26.1$ Hz, $J_2 = 22.7$ Hz, 1F), -153.32 (d, $J = 28.0$ Hz, 1F), -159.81 (d, $J = 22.4$ Hz, 1F) ppm.

2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine 10c



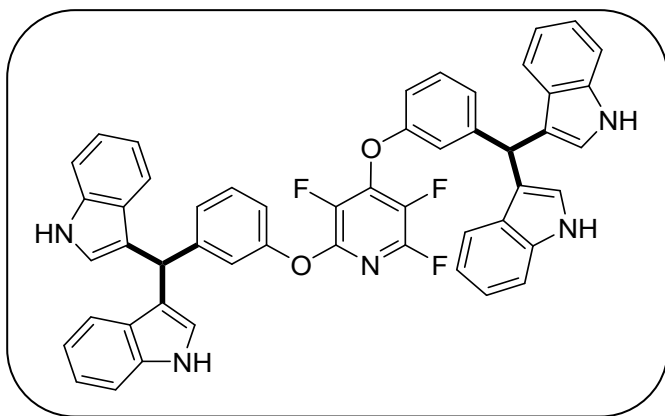
Yellow oil. Yield 81%. IR (KBr) $\tilde{\nu}$ 3005, 2954, 2932, 2836, 1637, 1609 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (t, 1H, $J = 7.9$ Hz), 7.25–7.29 (m, 1H), 7.01–7.09 (m, 12H), 6.83–6.88 (m, 10H), 5.49 (s, 1H, Ar₃CH), 5.47 (s, 1H, Ar₃CH), 3.78–3.81 (m, 12H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 158.21, 158.15, 156.12, 156.06, 152.74, 147.24, 145.42-145.59 (m), 144.66-144.70 (m), 144.45-144.57 (m), 143.50-143.61 (m), 143.13-143.27 (m), 135.88, 135.68, 130.28, 130.22, 129.52, 129.32, 126.38, 125.69, 121.84, 120.36, 118.37, 117.79, 113.99, 113.80, 113.78, 55.21, 54.95, 54.91 ppm. ¹⁹F NMR (470 MHz, CDCl₃) δ -89.59 (dd, 1F, $J_1 = 26.1$ Hz, $J_2 = 22.6$ Hz), -152.85 (d, 1F, $J = 22.3$ Hz), -159.13 (d, $J = 26.3$ Hz, 1F) ppm.

2,4-Bis(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-3,5,6-trifluoropyridine 10d



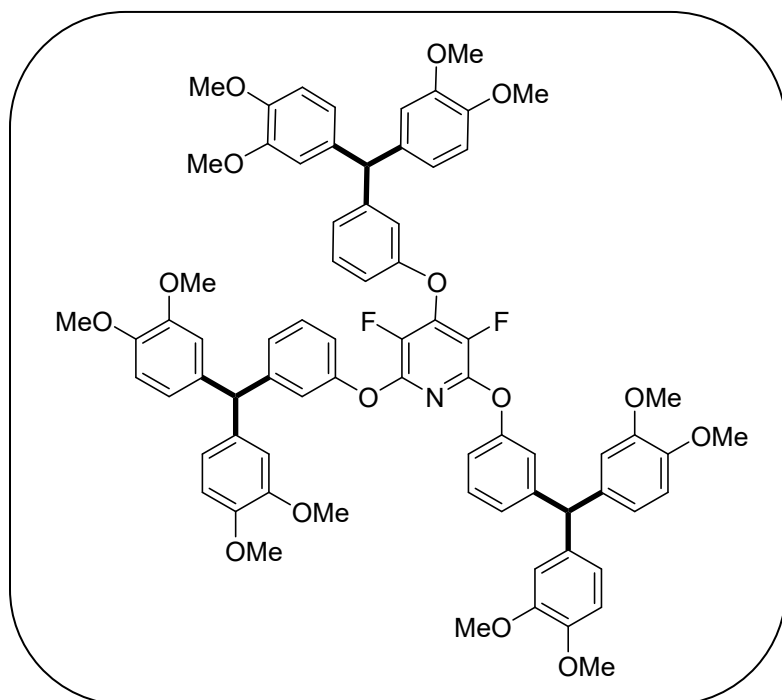
Black oil. Yield 91%. IR (KBr) $\tilde{\nu}$ 2924, 1637, 1605, 1584, 1462, 1442 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.43 (m, 2H), 7.17 (d, 1H, $J = 7.6$ Hz), 7.08-7.14 (m, 3H), 7.04 (bs, 2H), 6.98 (dd, 2H, $J_1 = 8.2$, $J_2 = 2.0$ Hz), 6.91 (d, 2H, $J = 3.7$ Hz), 6.61 (dd, 4H, $J_1 = 14.4$, $J_2 = 3.6$ Hz), 5.69 (s, 1H, Ar_3CH), 5.68 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 156.25, 152.85, 147.43, 147.19, 144.32, 143.81, 143.56, 142.91-143.20 (m), 138.85-138.90 (m), 136.78-136.82 (m), 135.11-135.37 (m), 133.27, 130.23, 129.96, 129.57, 129.55, 126.79, 125.34, 124.63, 120.92, 119.97, 116.85, 115.51, 111.99, 111.89, 47.56 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.00 (dd, $J_1 = 26.1$ Hz, $J_2 = 22.5$ Hz, 1F), -152.36 (d, $J = 26.5$ Hz, 1F), -158.55 (d, $J = 22.1$ Hz, 1F) ppm.

3,3',3'',3'''-((((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl))tetrakis(1H-indole) 10e



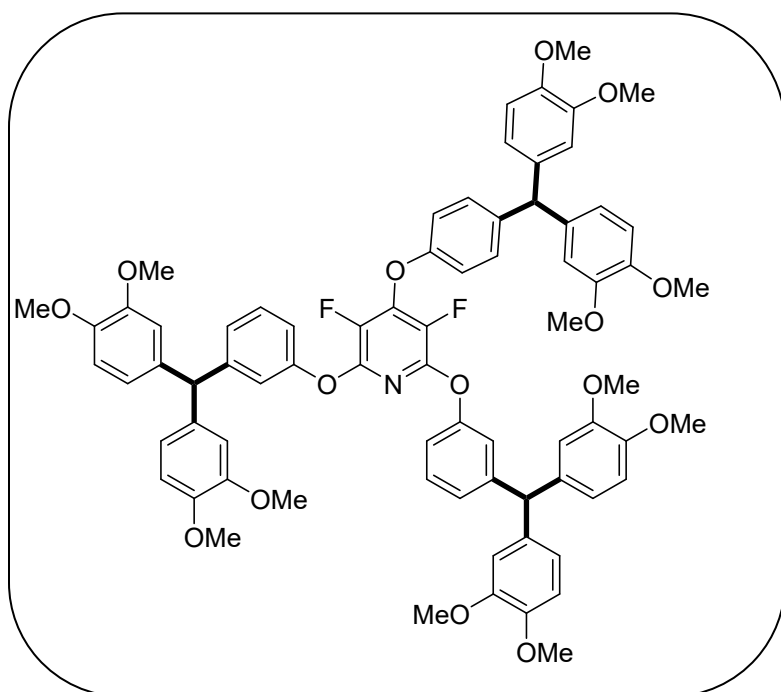
Yellow solid, Yield 90%. MP 180-181 $^{\circ}\text{C}$. IR (KBr) $\tilde{\nu}$ 3410, 3053, 1607, 1582, 1458, 1415 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.80-7.88 (m, 3H), 7.40 (d, 2H, $J = 7.9$ Hz), 7.27-7.36 (m, 8H), 7.23-7.26 (m, 2H), 7.14-7.18 (m, 5H), 7.05 (t, 1H, $J = 2.0$ Hz), 6.98-7.03 (m, 6H), 6.91 (dd, 1H, $J_1 = 8.0$ Hz, $J_2 = 2.6$ Hz), 6.67 (d, 2H, $J = 2.3$ Hz), 6.56 (d, 2H, $J = 2.3$ Hz), 5.89 (s, 1H, Ar_3CH), 5.87 (s, 1H, Ar_3CH) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 156.16, 152.92-152.96 (m), 152.58-152.59 (m), 147.36-147.39 (m), 146.52-146.62 (m), 146.13-146.19 (m), 136.65-136.66 (m), 129.55, 129.39, 126.95, 126.87, 125.77, 125.15, 123.72, 123.57, 122.02, 121.99, 121.91, 121.08, 121.03, 119.81, 119.73, 119.32, 119.08, 118.90, 118.35, 116.84, 114.70, 114.52, 114.46, 114.44, 111.06, 40.06, 39.99 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.75 (dd, $J_1 = 26.2$ Hz, $J_2 = 22.6$ Hz, 1F), -152.40 (d, $J = 26.3$ Hz, 1F), -159.49 (d, $J = 22.5$ Hz, 1F) ppm.

2,4,6-Tris(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine 10f



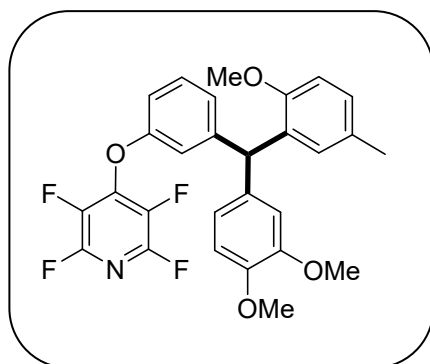
White oil. Yield 53%. IR (KBr) $\tilde{\nu}$ 2930, 1582, 1512, 1440 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.13 (t, 2H, $J = 7.9$ Hz), 6.77-6.93 (m, 10H), 6.78 (d, 2H, $J = 8.3$ Hz), 6.73 (d, 4H, $J = 8.4$ Hz), 6.64 (d, 2H, $J = 2.0$ Hz), 6.59-6.61 (m, 6H), 6.53 (dd, 4H, $J_1 = 8.3$ Hz, $J_2 = 2.0$ Hz) 5.44 (s, 1H, Ar_3CH), 5.36 (s, 2H, Ar_3CH), 3.84 (s, 6H, OMe), 3.83 (s, 12H, OMe), 3.75 (s, 6H, OMe), 3.71 (s, 12H, OMe) ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -155.27 (s, 2F, F3,5-py) ppm.

2,6-Bis(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine 10g



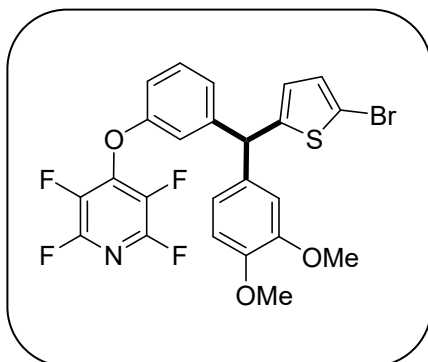
Yellow oil. Yield 48%. IR (KBr) $\tilde{\nu}$ 3016, 2932, 2835, 1588, 1512 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.14 (t, 2H, $J = 7.9$ Hz), 7.08 (d, 2H, $J = 8.7$ Hz), 6.97 (d, 2H, $J = 8.7$ Hz), 6.87-6.89 (m, 4H), 6.83 (d, 2H, $J = 1.8$ Hz), 6.79 (d, 2H, $J = 8.3$ Hz), 6.73 (d, 4H, $J = 8.3$), 6.64 (d, 2H, $J = 1.9$ Hz), 6.61 (d, 4H, $J = 1.9$ Hz), 6.59 (dd, 2H, $J_1 = 7.4$ Hz, $J_2 = 2.1$ Hz), 6.54 (dd, 4H, $J_1 = 8.2$, $J_2 = 2.0$ Hz), 5.42 (s, 1H, Ar_3CH), 5.36 (s, 2H, Ar_3CH), 3.86 (s, 6H, OMe), 3.83 (s, 12H, OMe), 3.76 (s, 6H, OMe), 3.71 (s, 12H, OMe) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 154.85, 153.68-153.81 (m), 148.88, 147.65, 146.24, 145.37-145.58 (m), 136.51-136.54 (m), 136.17-136.23 (m), 130.54, 128.87, 125.50, 121.40, 120.84, 117.72, 116.11, 112.77-112.85 (m), 110.95-111.07 (m), 55.83, 55.62 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -155.23 (s, 2F, F3,5-py) ppm.

(R)-4-(3-((3,4-dimethoxyphenyl)(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 11a



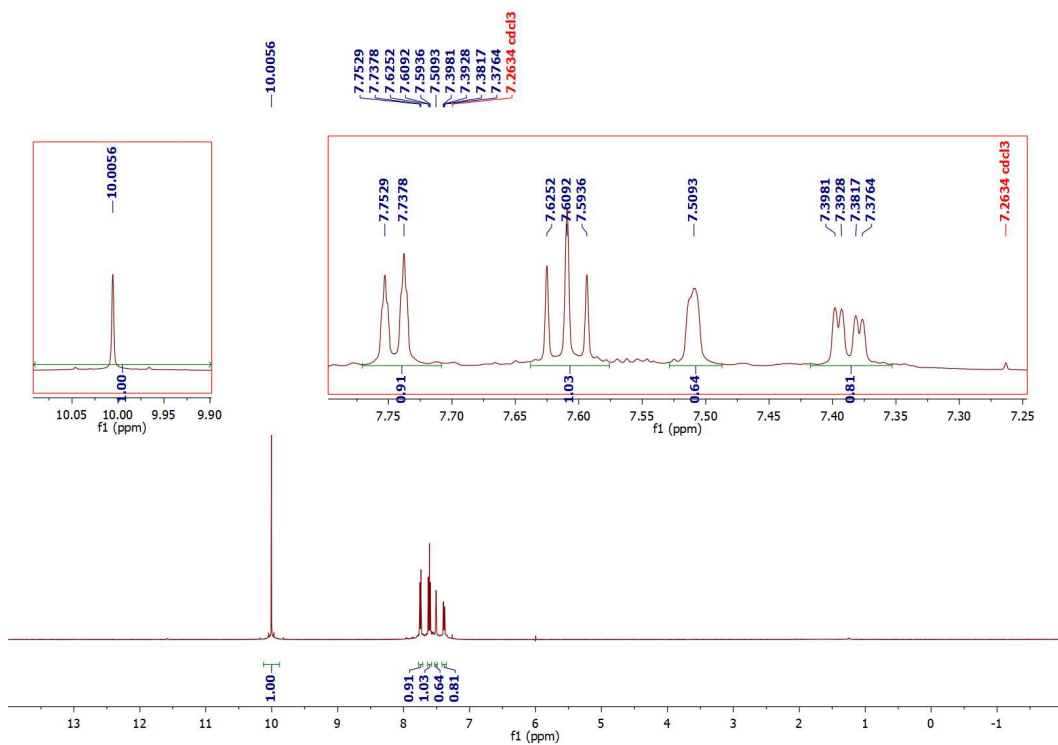
Yellow oil. Yield 29%. IR (KBr) $\tilde{\nu}$ 2928, 2837, 2254, 1641, 1608, 1500 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.26-7.29 (m, 1H), 7.02 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.8$ Hz), 6.97 (d, 1H, $J = 7.7$ Hz), 6.89 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 2.4$ Hz), 6.76-6.80 (m, 3H), 6.64 (d, 1H, $J = 1.9$ Hz), 6.62 (d, 1H, $J = 1.7$ Hz), 6.56 (dd, 1H, $J_1 = 8.3$ Hz, $J_2 = 1.9$ Hz), 5.81 (s, 1H, Ar_3CH), 3.86 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.68 (s, 3H, OMe), 2.20 (s, 3H, Me) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 155.66, 154.97, 148.81, 147.54, 147.21, 144.94-145.28 (m), 144.60-144.75 (m), 142.95-143.33 (m), 136.73-137.05 (m), 135.55, 134.67-134.96 (m), 131.67, 130.60, 129.53, 129.43, 128.12, 126.31, 121.44, 117.83, 114.33, 112.98, 110.93, 110.88, 110.74, 55.81, 55.77, 55.64, 49.09, 20.61 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -89.14--89.00 (m, 2F, F2,6-py), -154.71--154.58 (m, 2F, F3,5-py) ppm.

(R)-4-(3-((5-bromothiophen-2-yl)(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine
11b

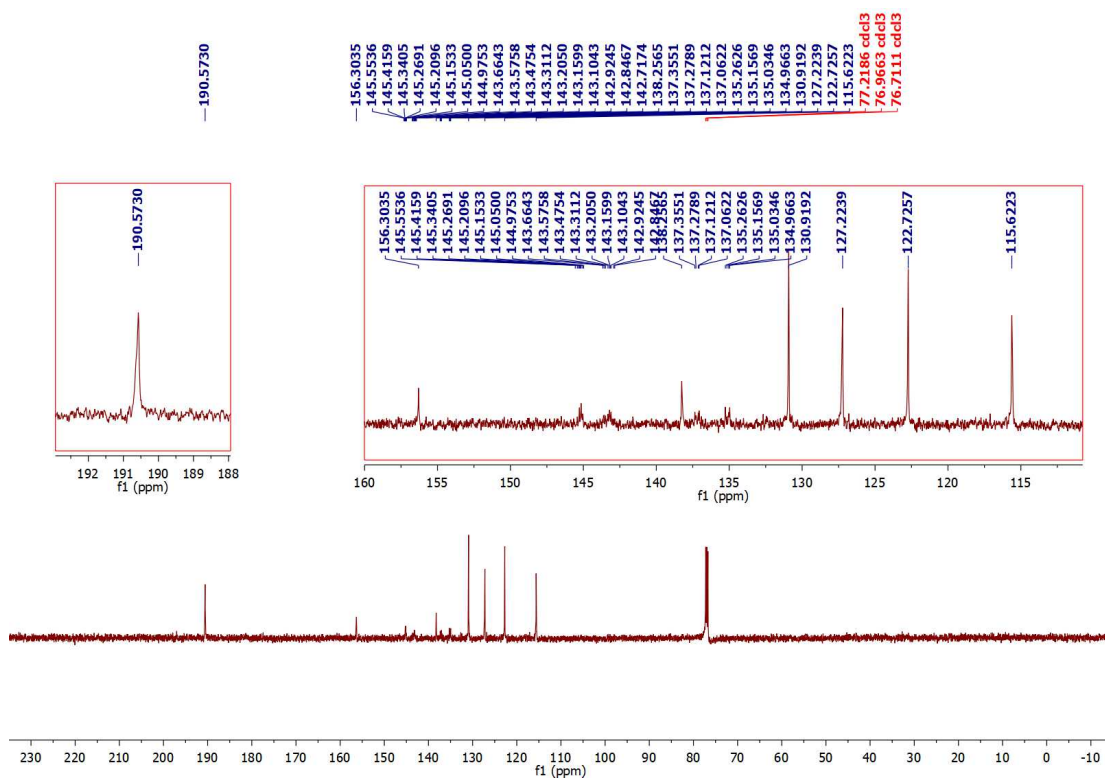


Yellow oil. Yield 33%. IR (KBr) $\tilde{\nu}$ 2931, 2837, 1642, 1608, 1586, 1502 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, 1H, $J = 7.9$ Hz), 7.07 (d, 1H, $J = 7.3$ Hz), 6.89-6.94 (m, 4H), 6.82 (d, 1H, $J = 7.9$ Hz), 6.69-6.71 (m, 1H), 6.45 (d, 1H, $J = 3.7$ Hz), 5.54 (s, 1H, Ar_3CH), 3.87 (s, 3H, OMe), 3.80 (s, 3H, OMe) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 155.82, 149.16, 148.78, 148.38, 145.82, 145.02-145.24 (m), 144.24-144.53 (m), 143.09-143.31 (m), 136.82-137.13 (m), 134.64, 129.96, 129.47, 126.76, 125.64, 120.88, 120.84, 117.41, 115.07, 112.15, 111.24, 55.88, 55.81, 51.56 ppm. ^{19}F NMR (470 MHz, CDCl_3) δ -88.69--88.56 (m, 2F, F2,6-py), -154.40--154.26 (m, 2F, F3,5-py) ppm.

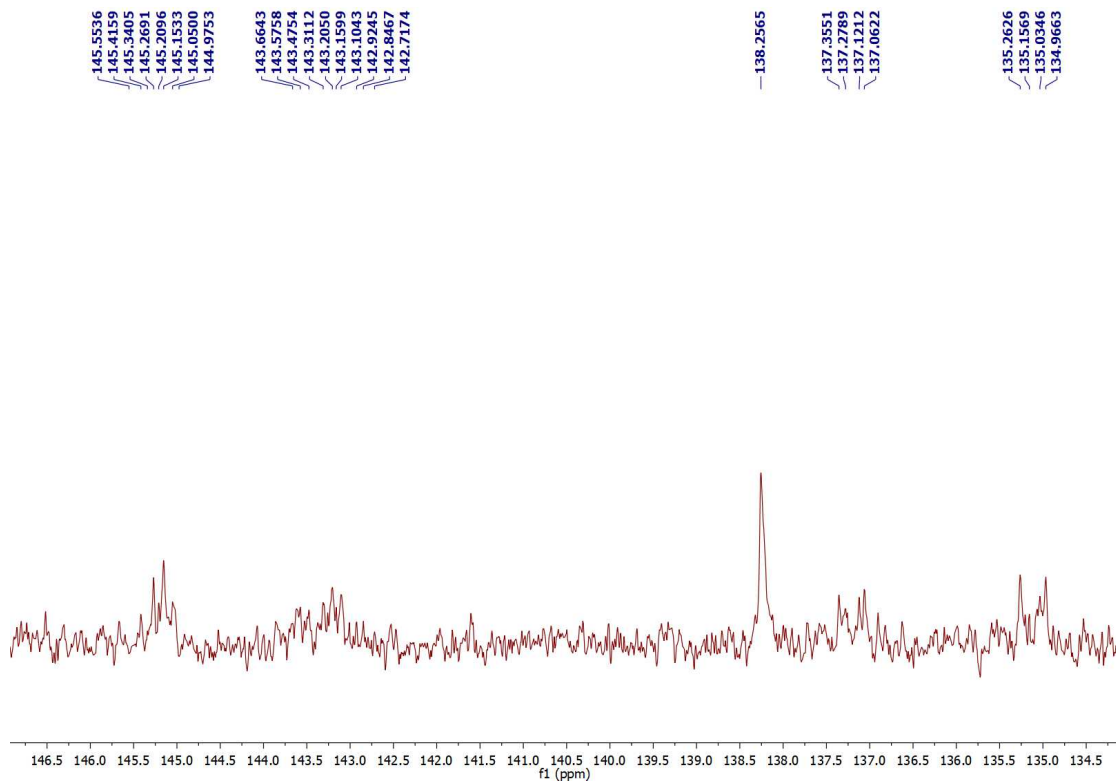
7. NMR spectra of 4-((perfluoropyridinyl)oxy)benzaldehyde derivatives 3a-c



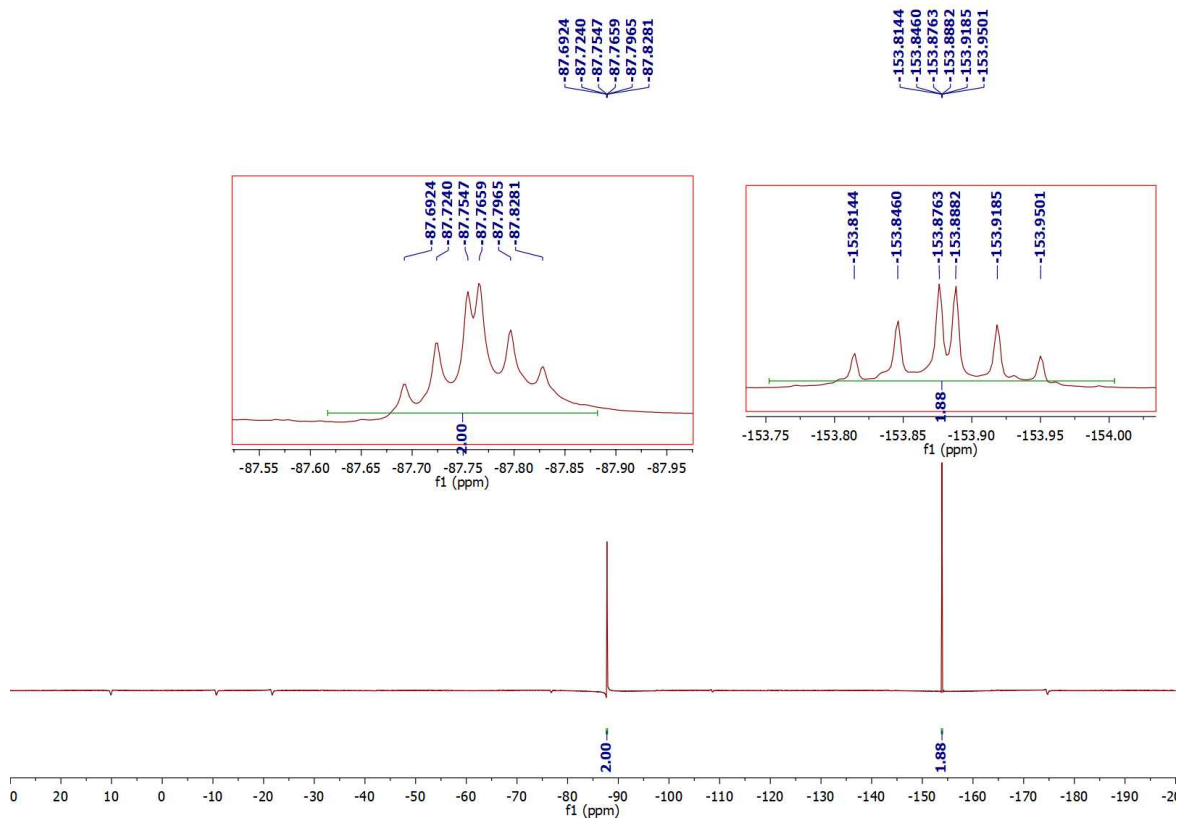
¹H NMR spectrum of 3-((perfluoropyridin-4-yl)oxy)benzaldehyde **3a**



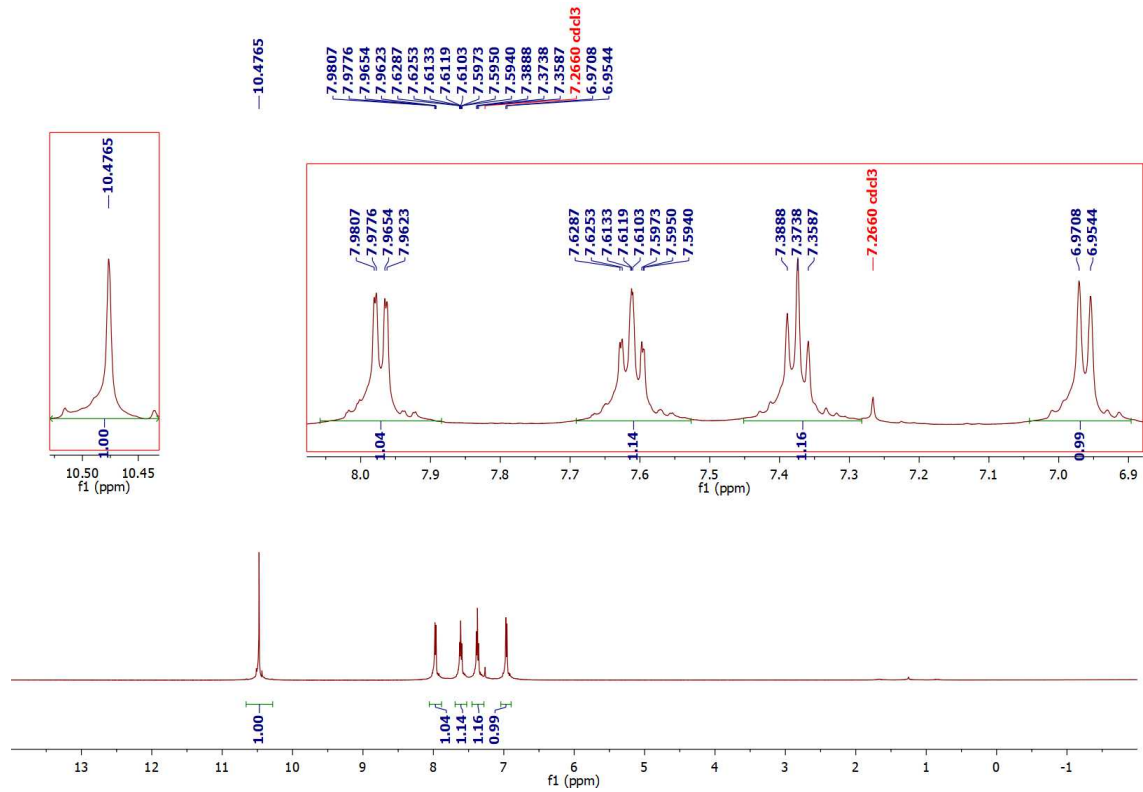
¹³C NMR spectrum of 3-((perfluoropyridin-4-yl)oxy)benzaldehyde **3a**



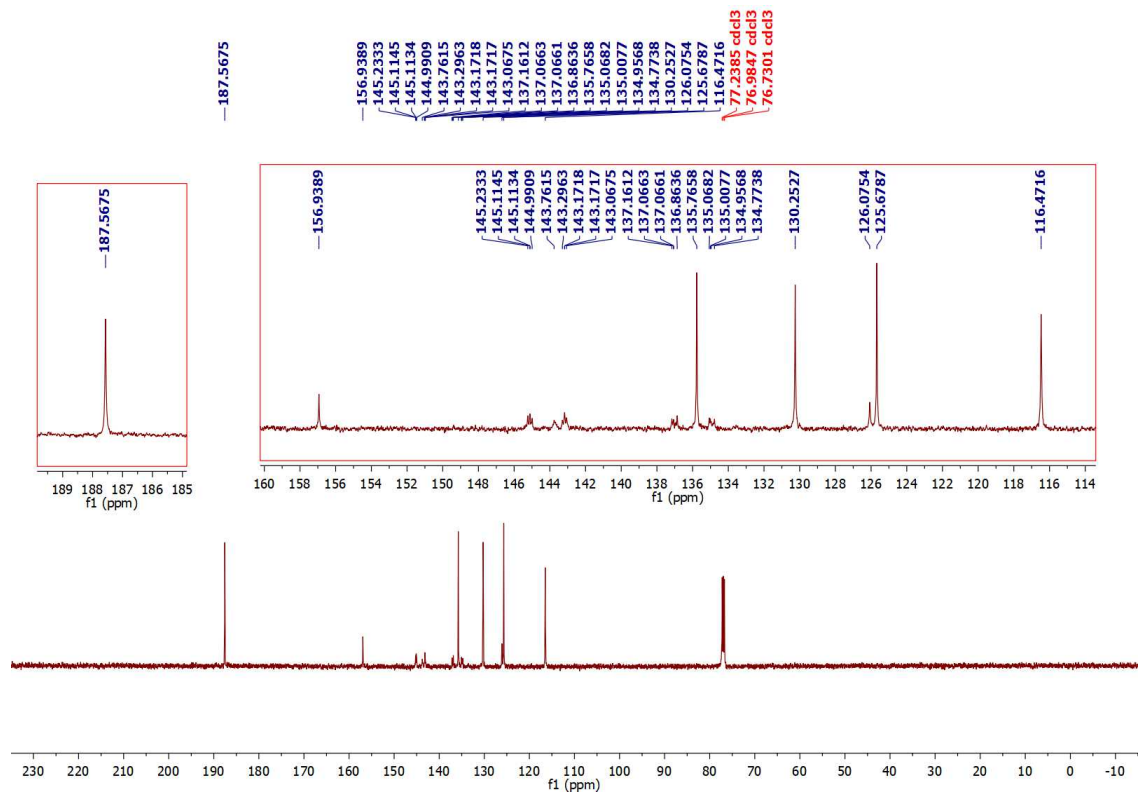
Expanded ^{13}C NMR spectrum of 3-((perfluoropyridin-4-yl)oxy)benzaldehyde **3a**



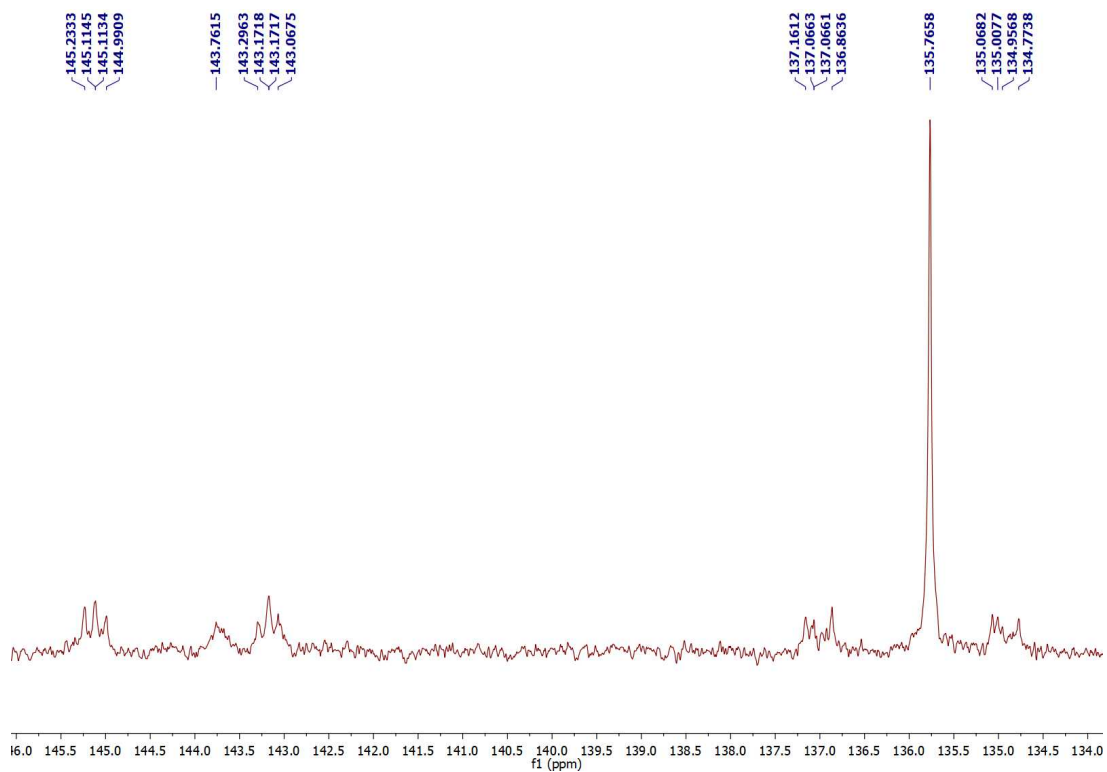
^{19}F NMR spectrum of 3-((perfluoropyridin-4-yl)oxy)benzaldehyde **3a**



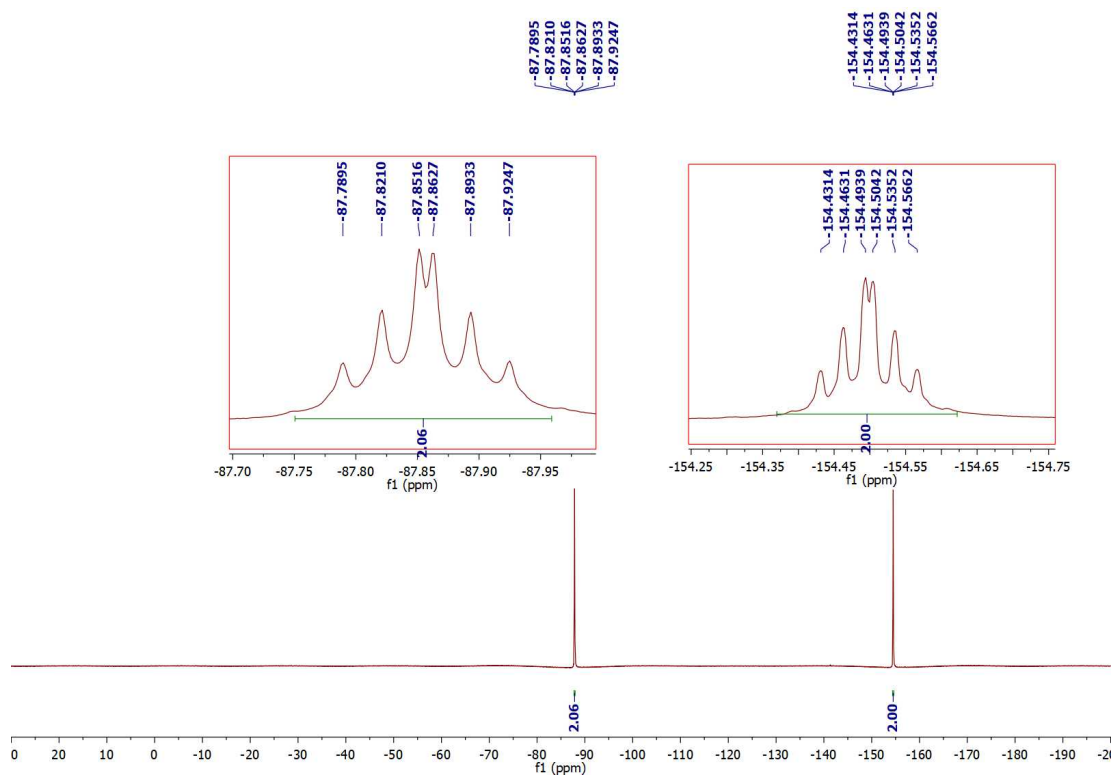
¹H NMR spectrum of 2-((perfluoropyridin-4-yl)oxy)benzaldehyde **3b**



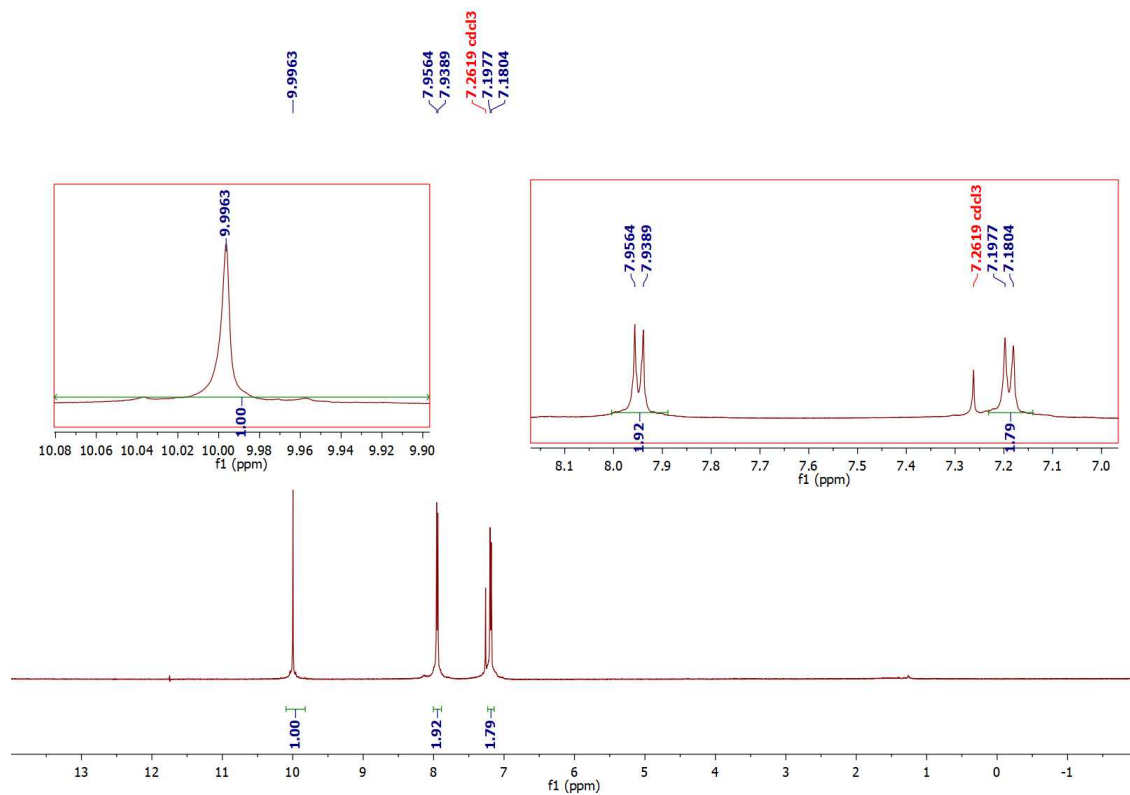
¹³C NMR spectrum of 2-((perfluoropyridin-4-yl)oxy)benzaldehyde **3b**



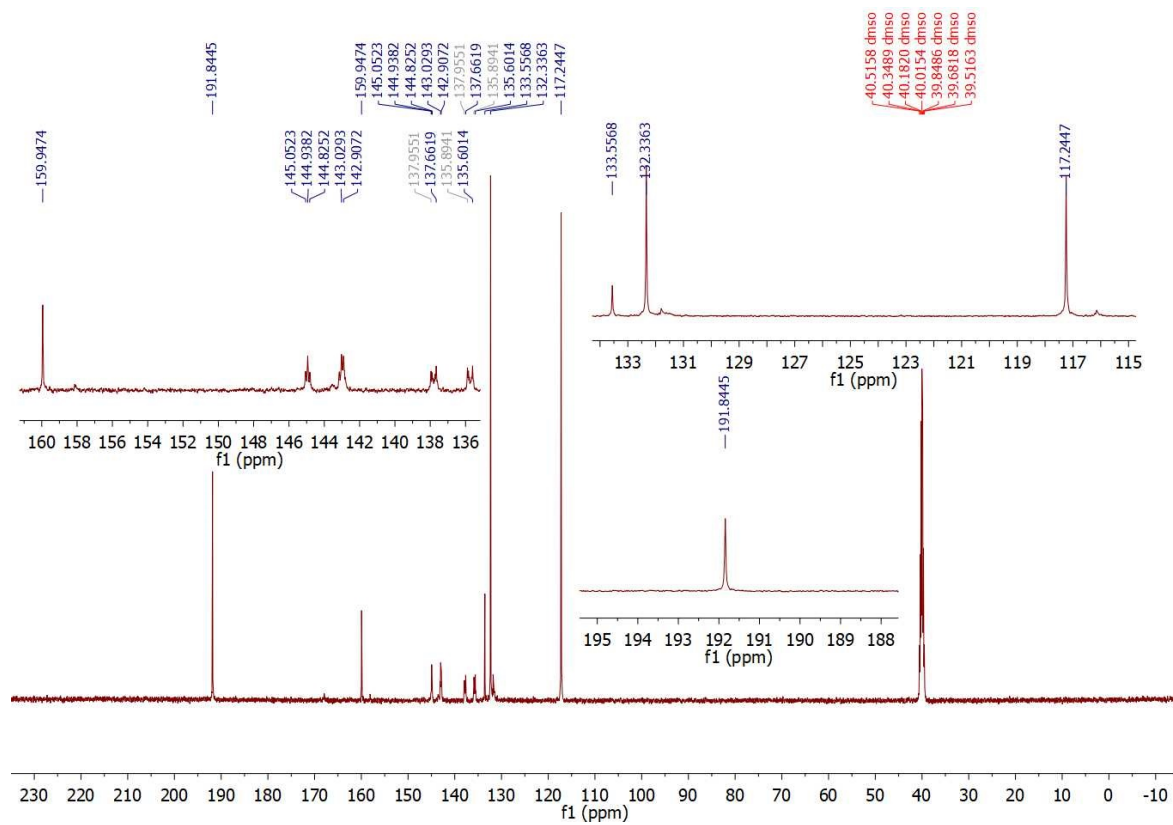
Expanded ^{13}C NMR spectrum of 2-((perfluoropyridin-4-yl)oxy)benzaldehyde **3b**



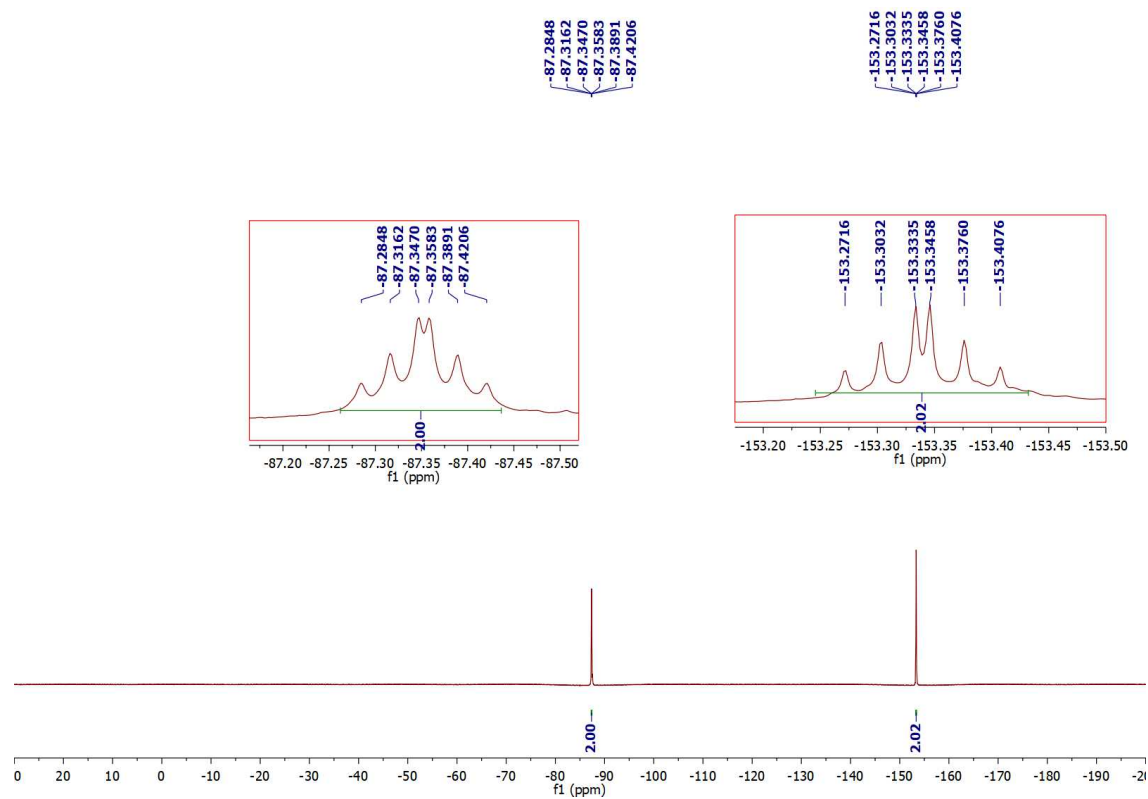
^{19}F NMR spectrum of 2-((perfluoropyridin-4-yl)oxy)benzaldehyde **3b**



¹H NMR spectrum of 4-((perfluoropyridin-4-yl)oxy)benzaldehyde **3c**

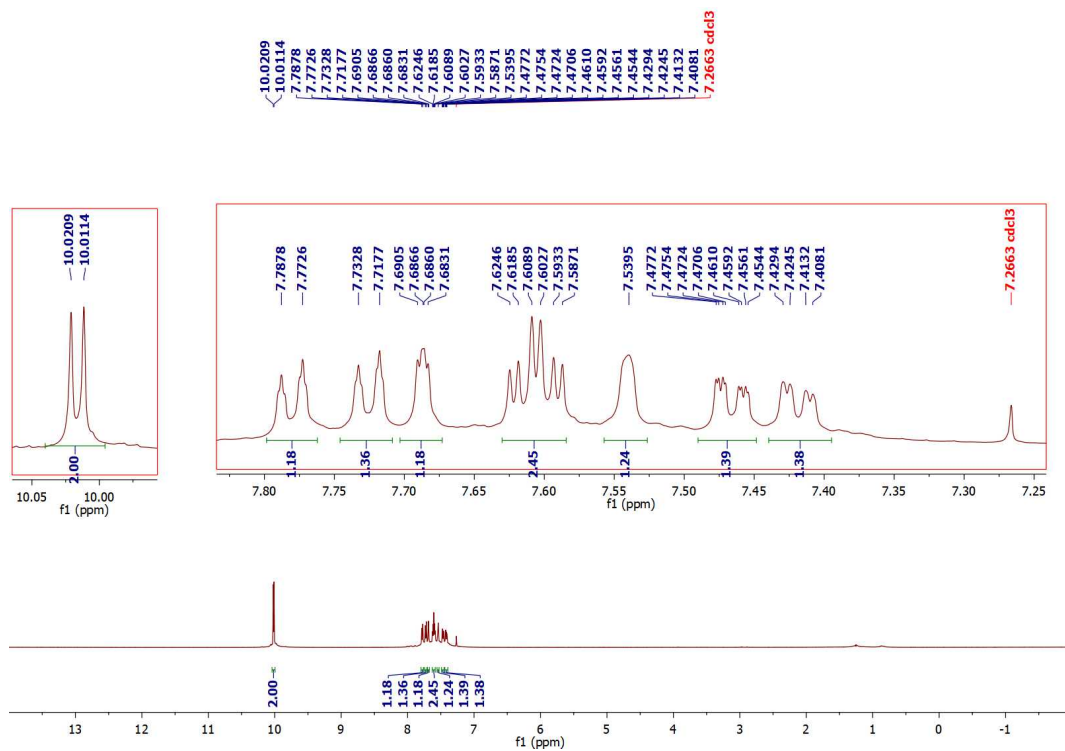


¹³C NMR spectrum of 4-((perfluoropyridin-4-yl)oxy)benzaldehyde **3c**

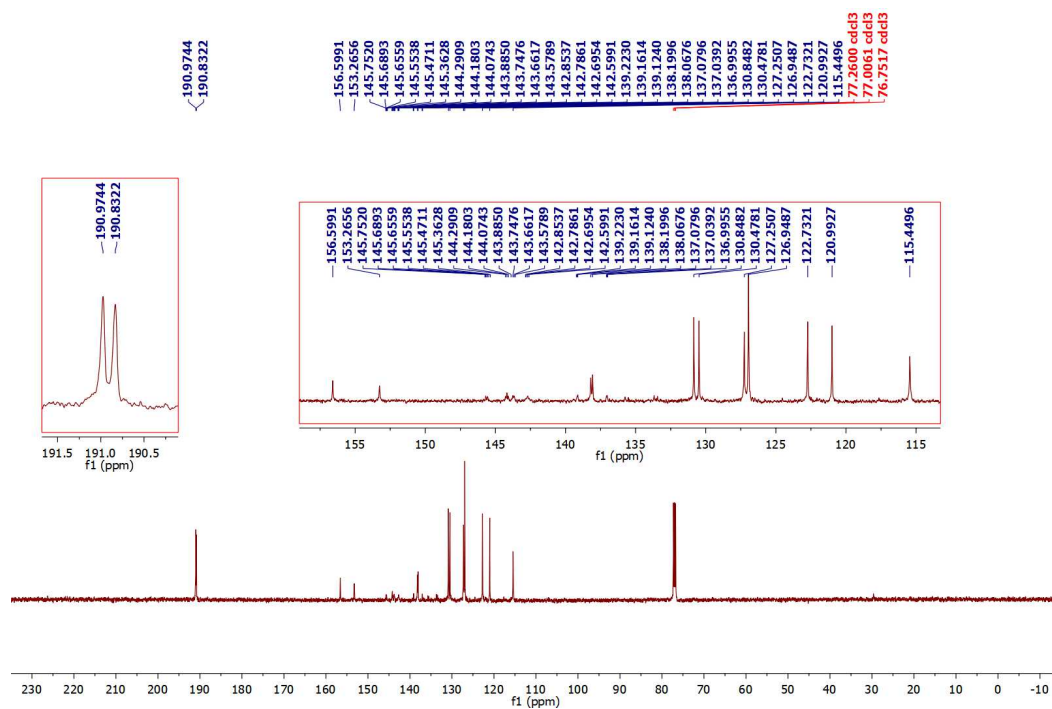


^{19}F NMR spectrum of 4-((perfluoropyridin-4-yl)oxy)benzaldehyde **3c**

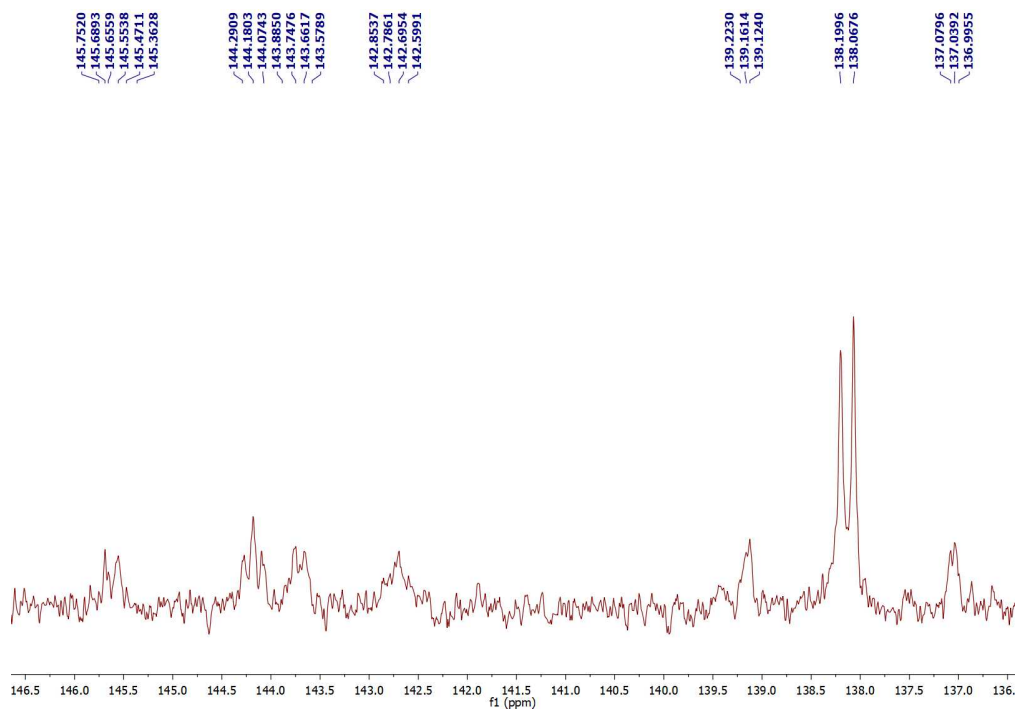
8. NMR spectra of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde **4a**



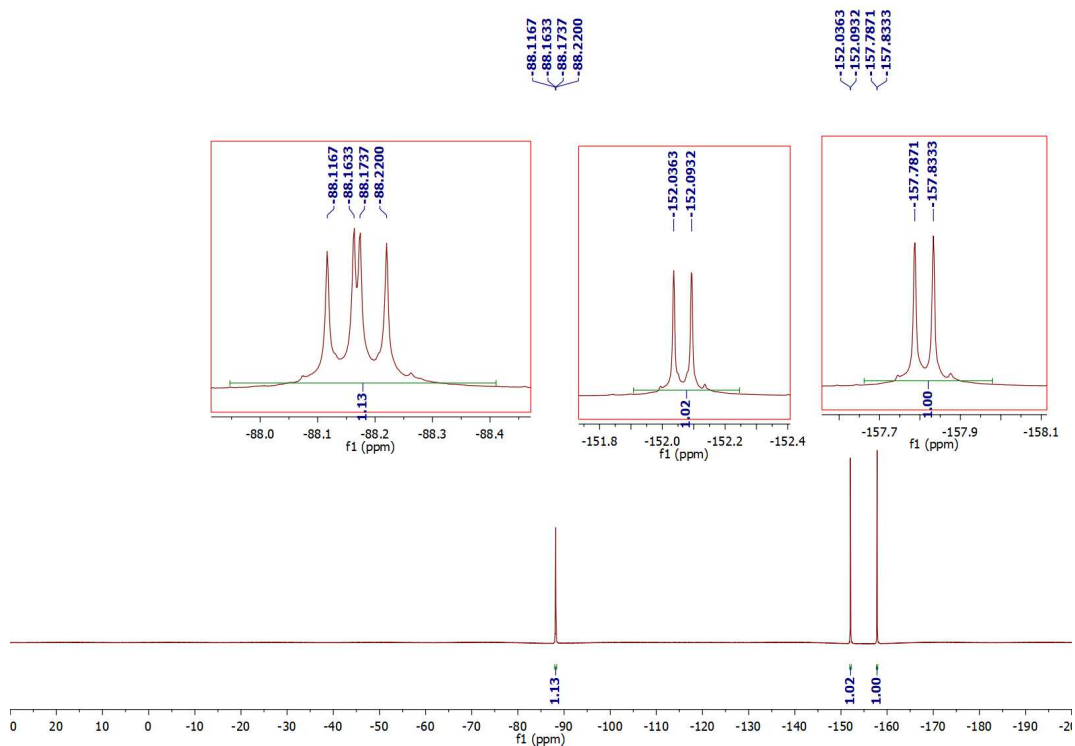
¹H NMR spectrum of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde **4a**



¹³C NMR spectrum of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde **4a**

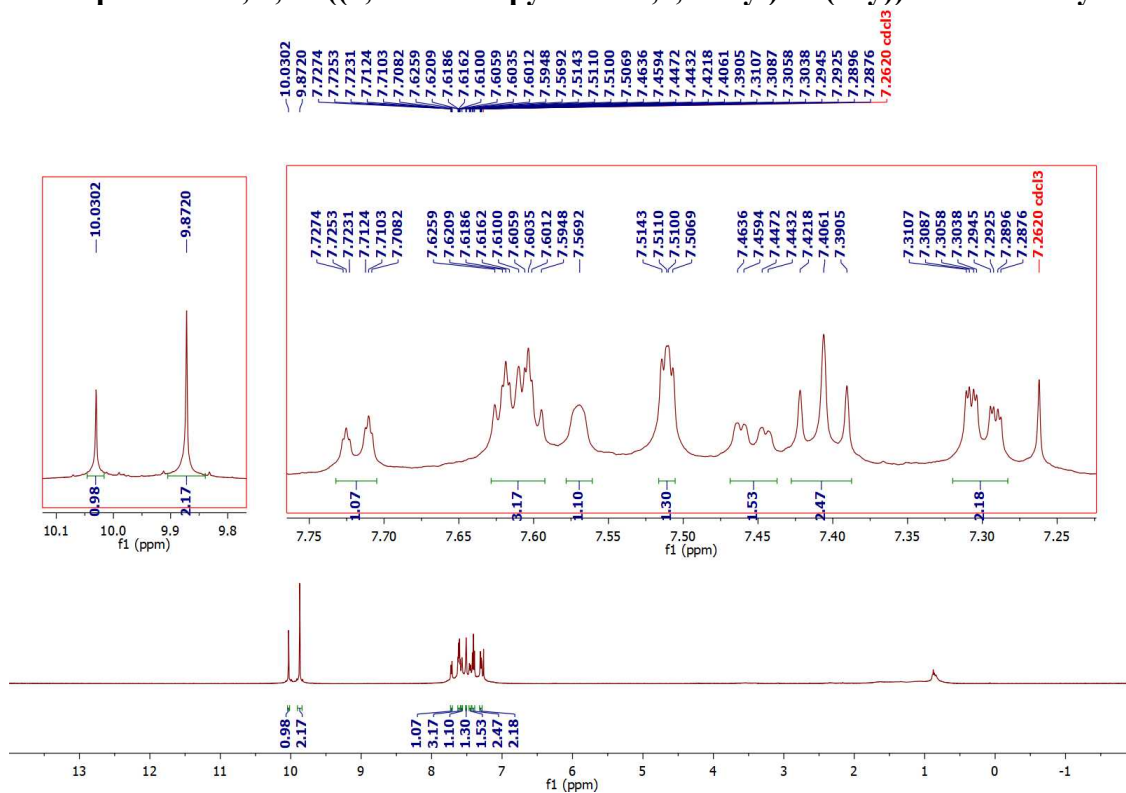


Expanded ^{13}C NMR spectrum of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde **4a**

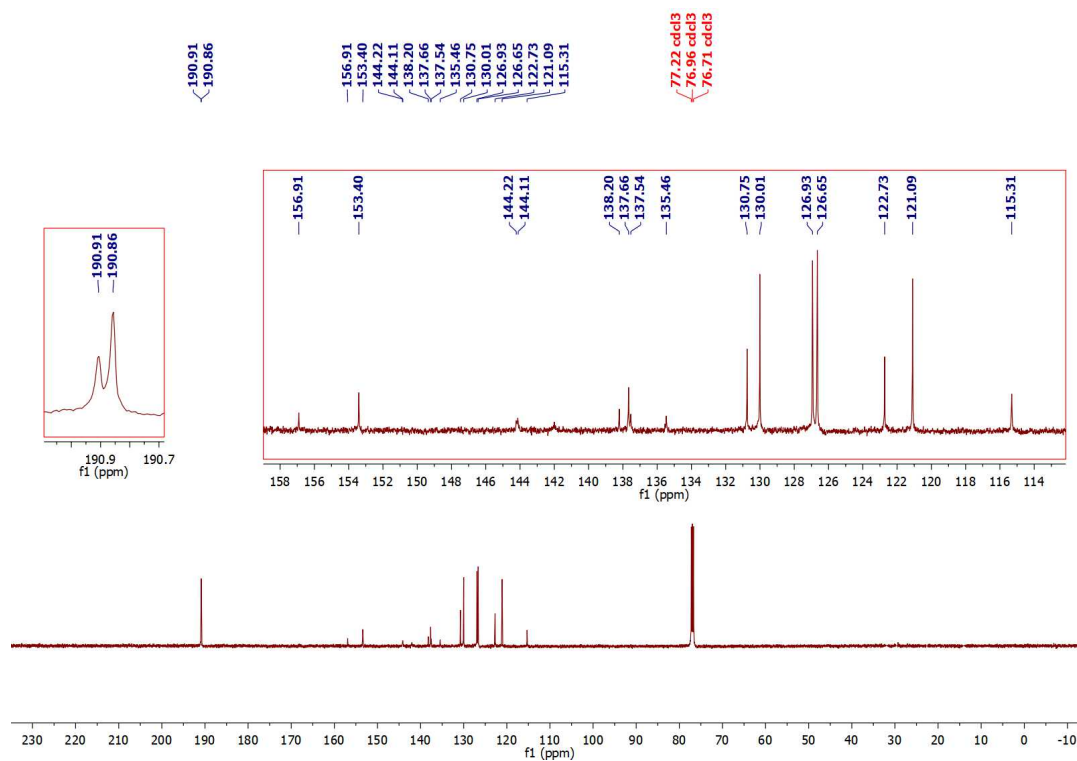


^{19}F NMR spectrum of 3,3'-((3,5,6-trifluoropyridine-2,4-diyl)bis(oxy))dibenzaldehyde **4a**

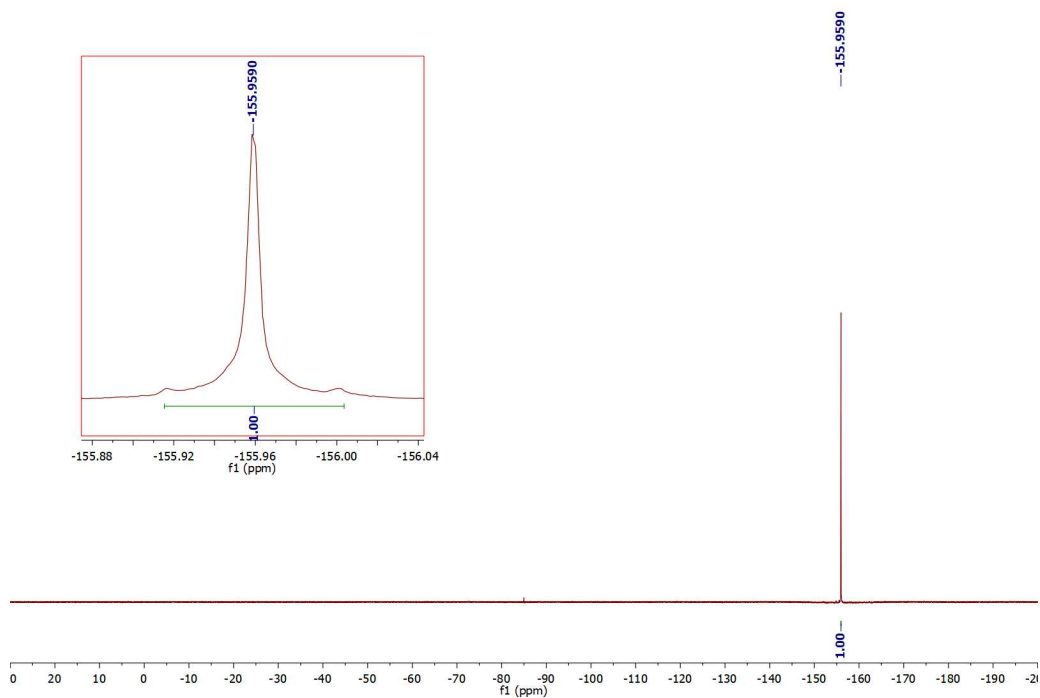
9. NMR spectra of 3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde **4b**



¹H NMR spectrum of 3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde **4b**

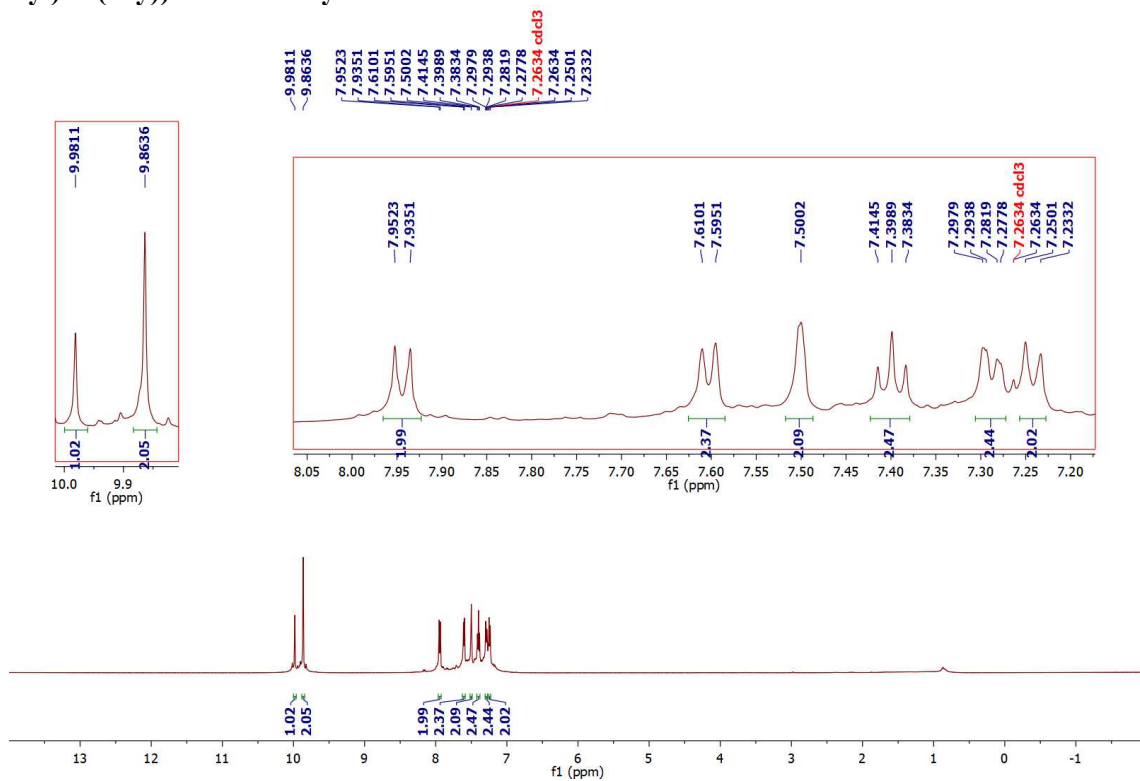


¹³C NMR spectrum of 3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde **4b**

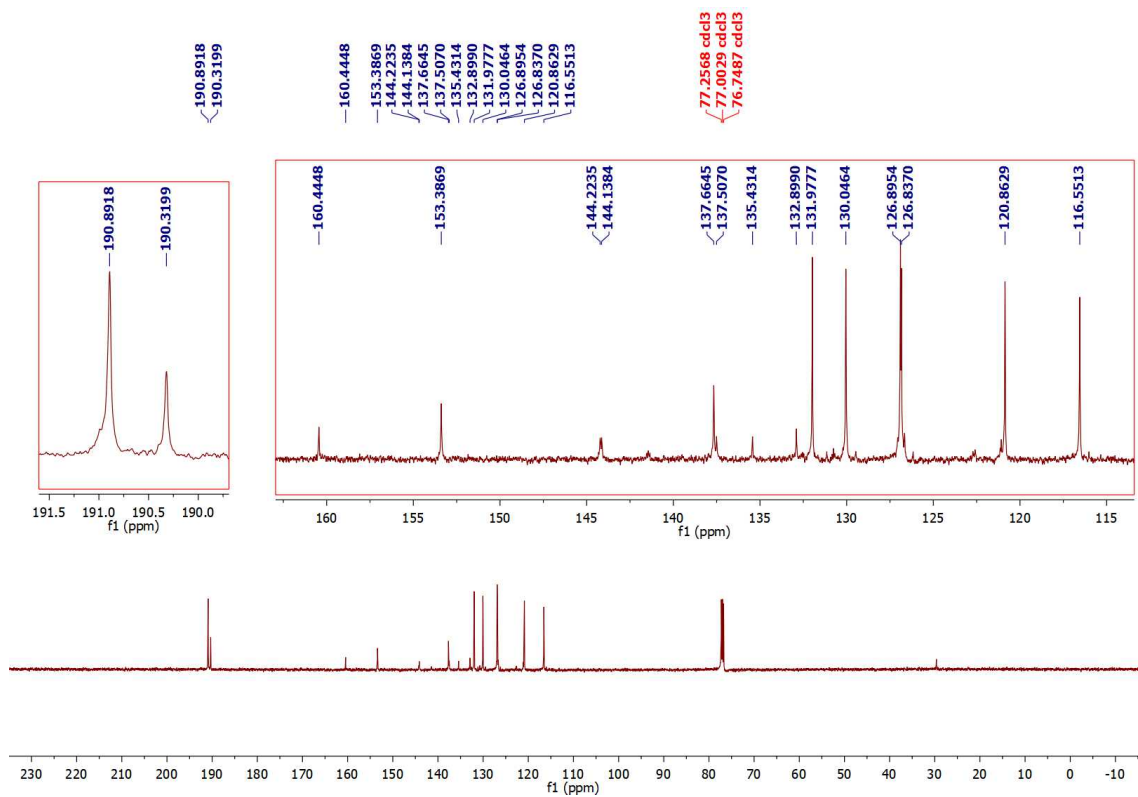


¹⁹F NMR spectrum of 3,3',3''-((3,5-difluoropyridine-2,4,6-triyl)tris(oxy))tribenzaldehyde **4b**

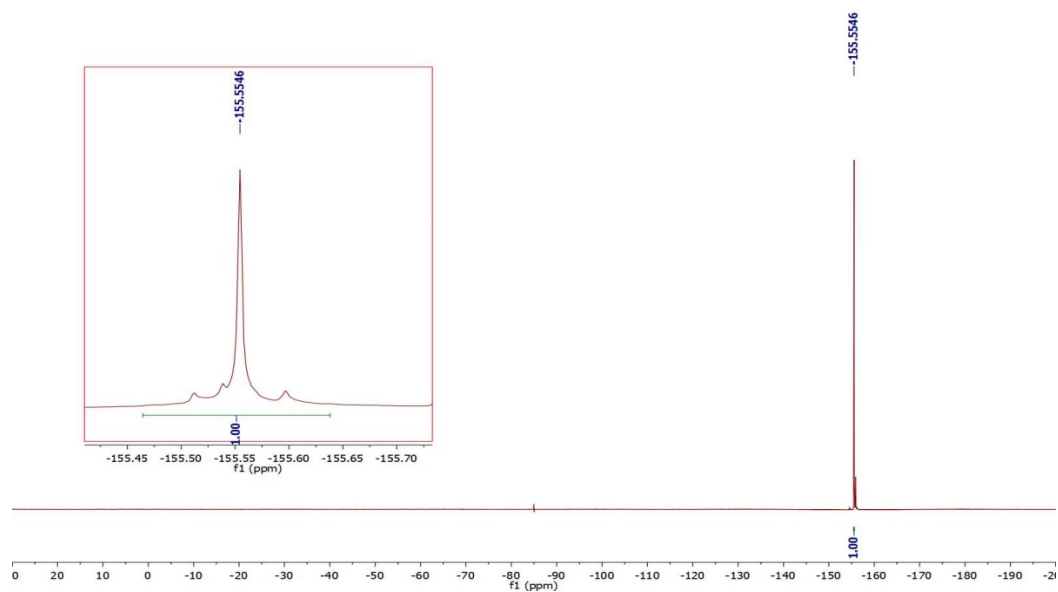
10. NMR spectra of 3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde **4c**



¹H NMR spectrum of 3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde **4c**

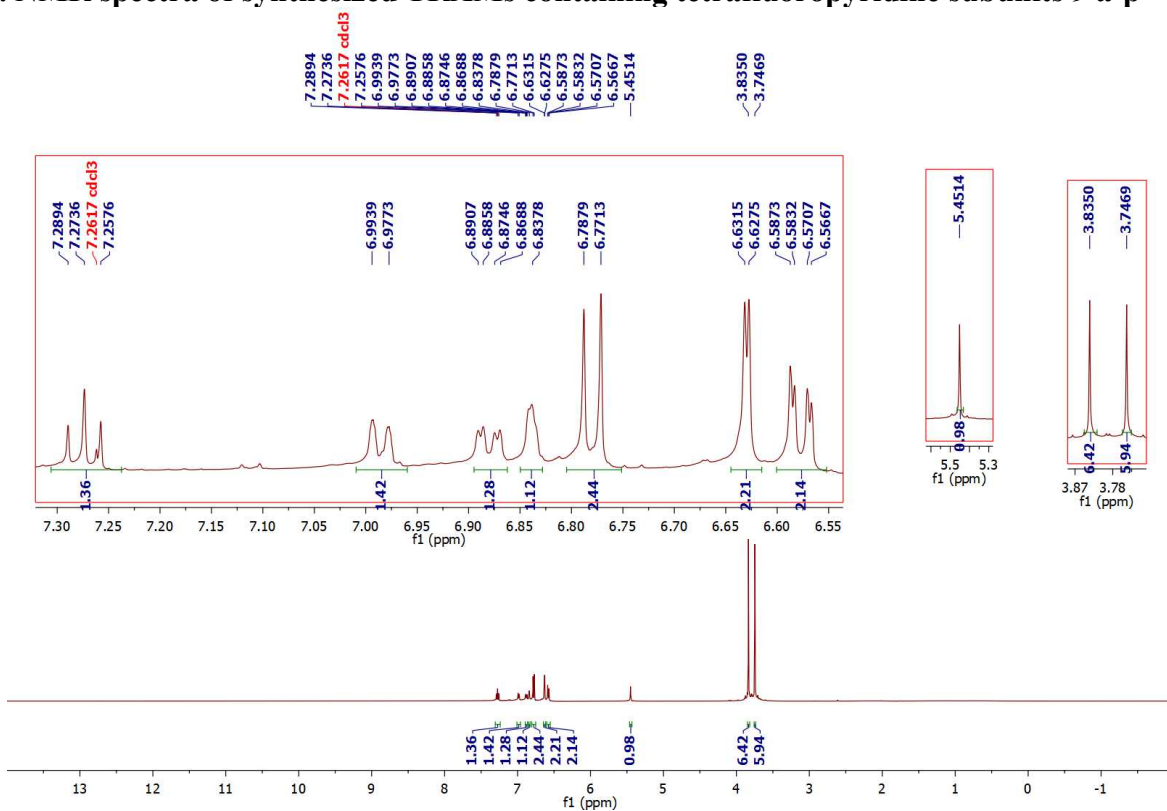


^{13}C NMR spectrum of 3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde **4c**

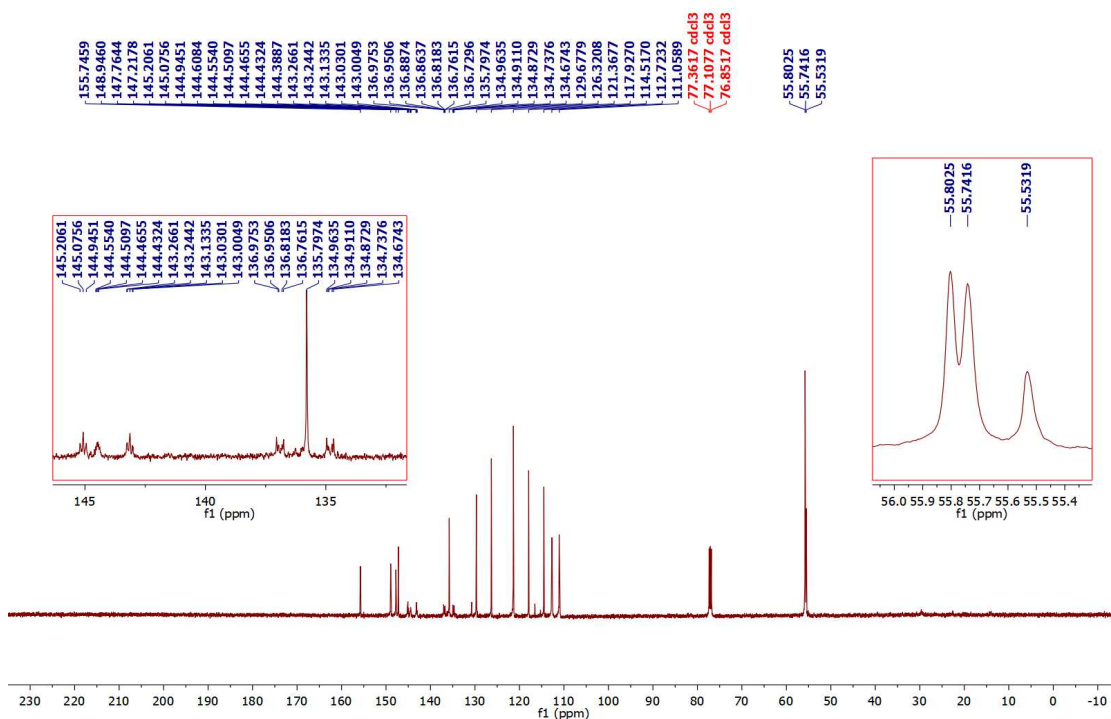


^{19}F NMR spectrum of 3,3'-((3,5-difluoro-4-(4-formylphenoxy)pyridine-2,6-diyl)bis(oxy))dibenzaldehyde **4c**

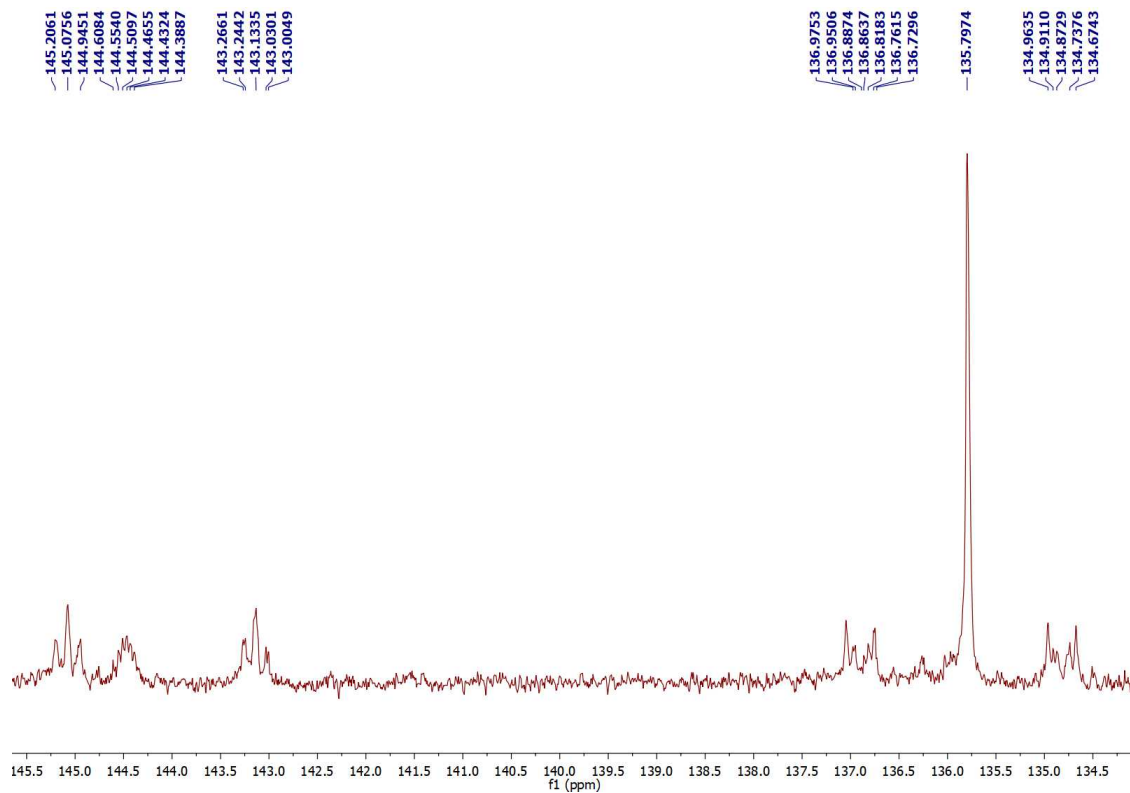
11. NMR spectra of synthesized TRAMs containing tetrafluoropyridine subunits 9 a-p



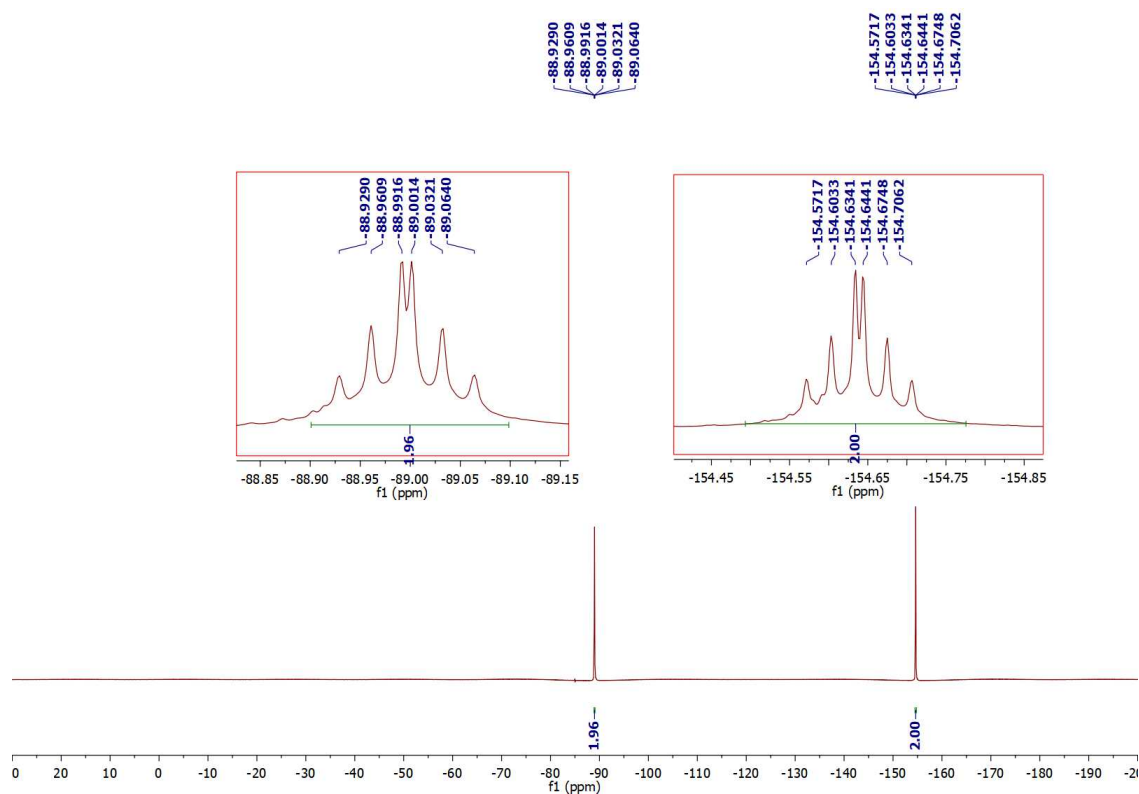
¹H NMR spectrum of 4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9a



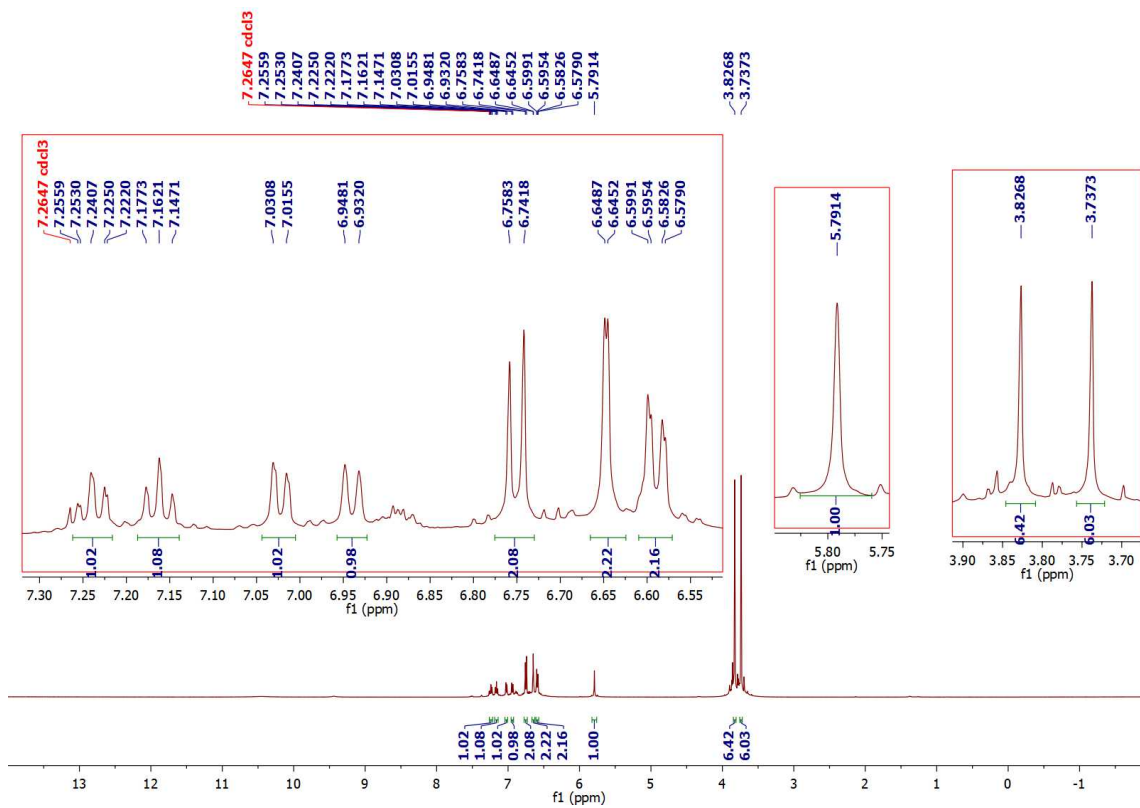
¹³C NMR spectrum of 4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine 9a



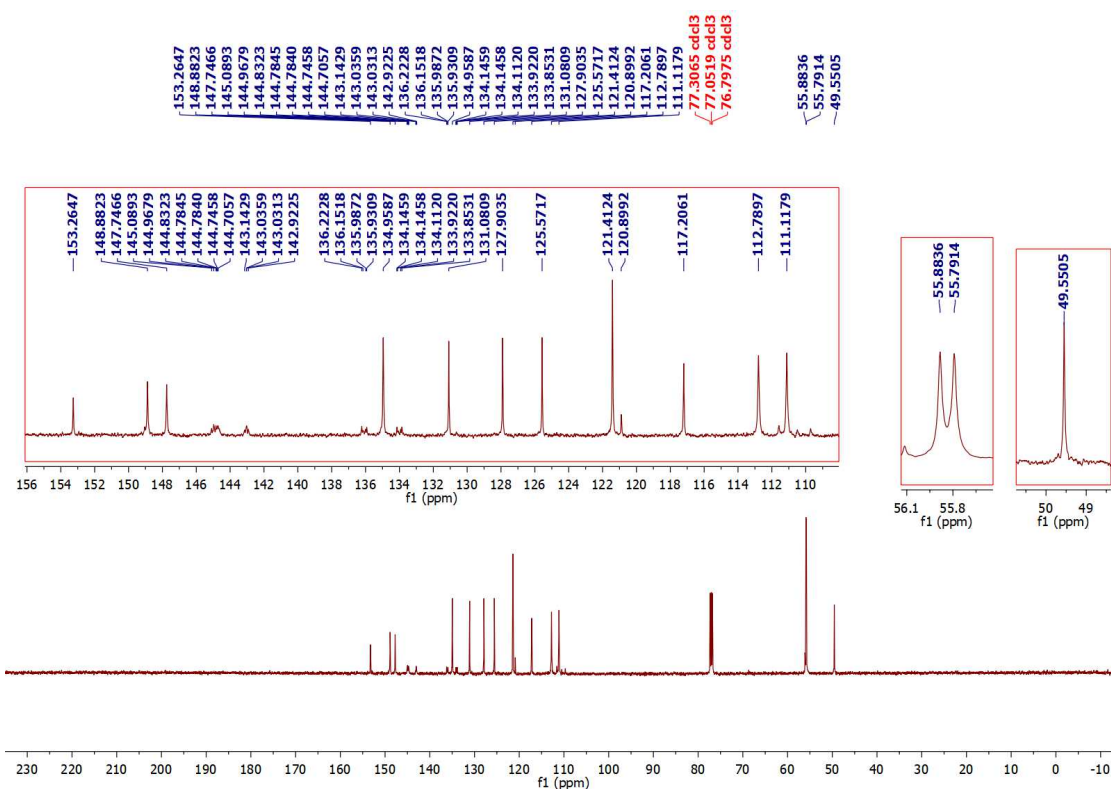
Expanded ^{13}C NMR spectrum of 4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9a**



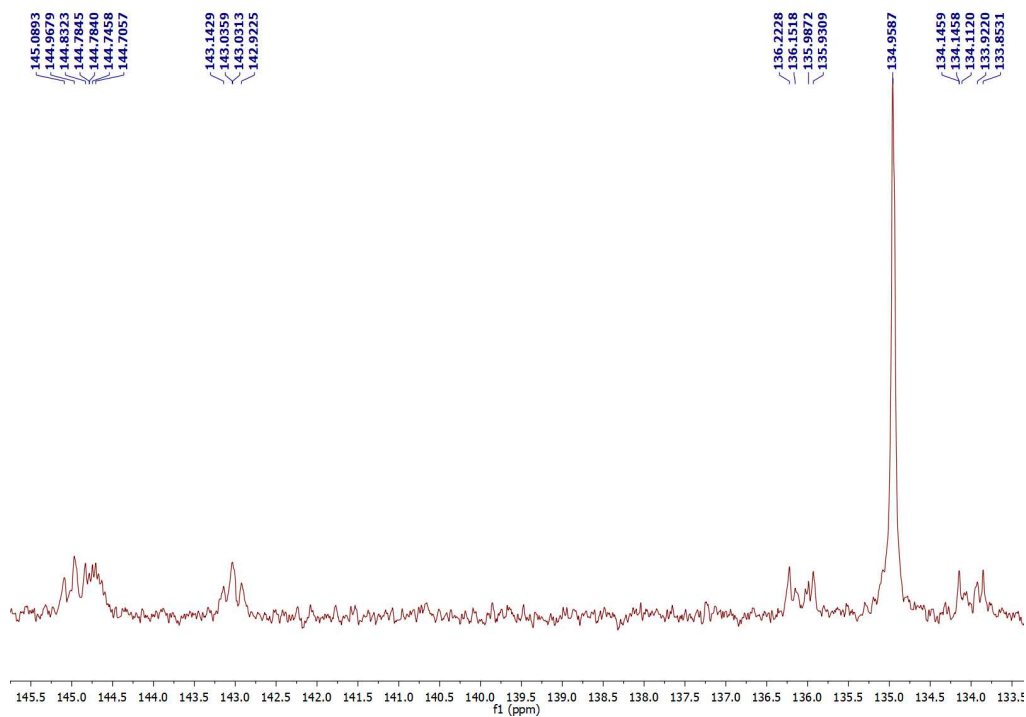
^{19}F NMR spectrum of 4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9a**



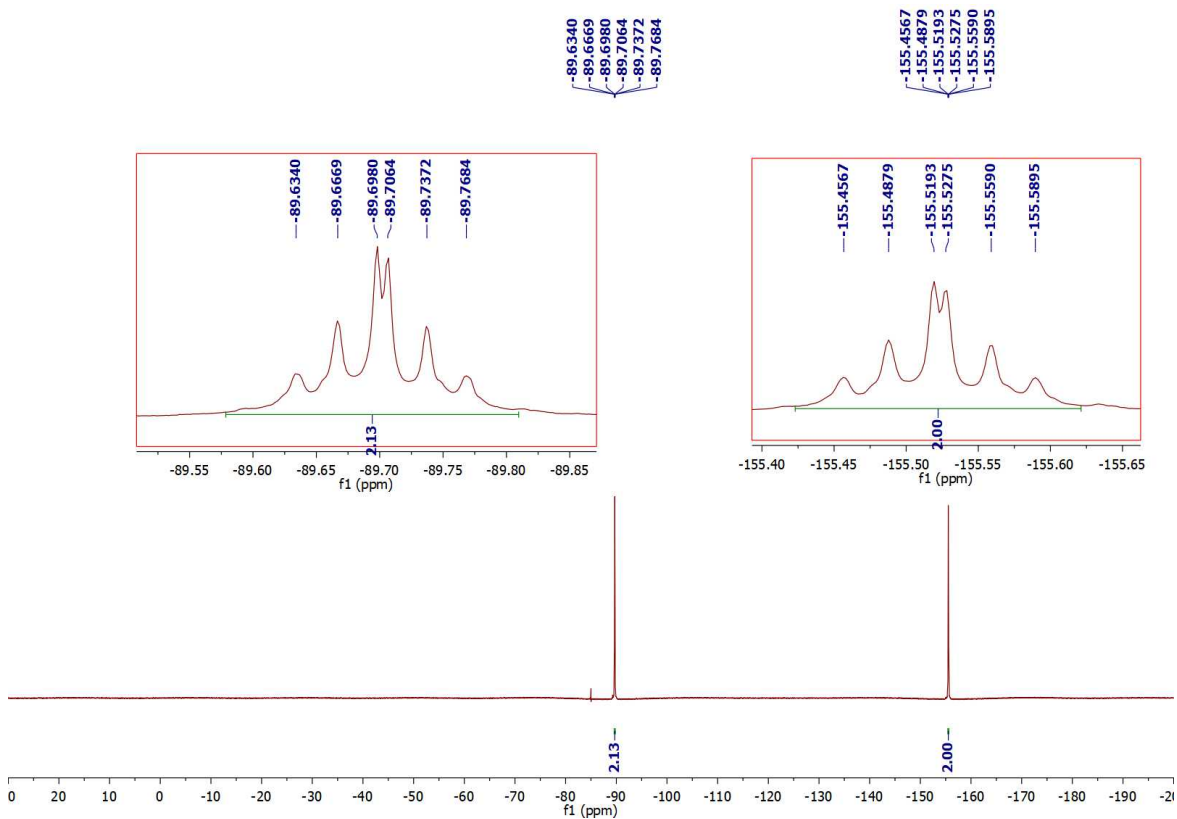
¹H NMR spectrum of 4-(2-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9b**



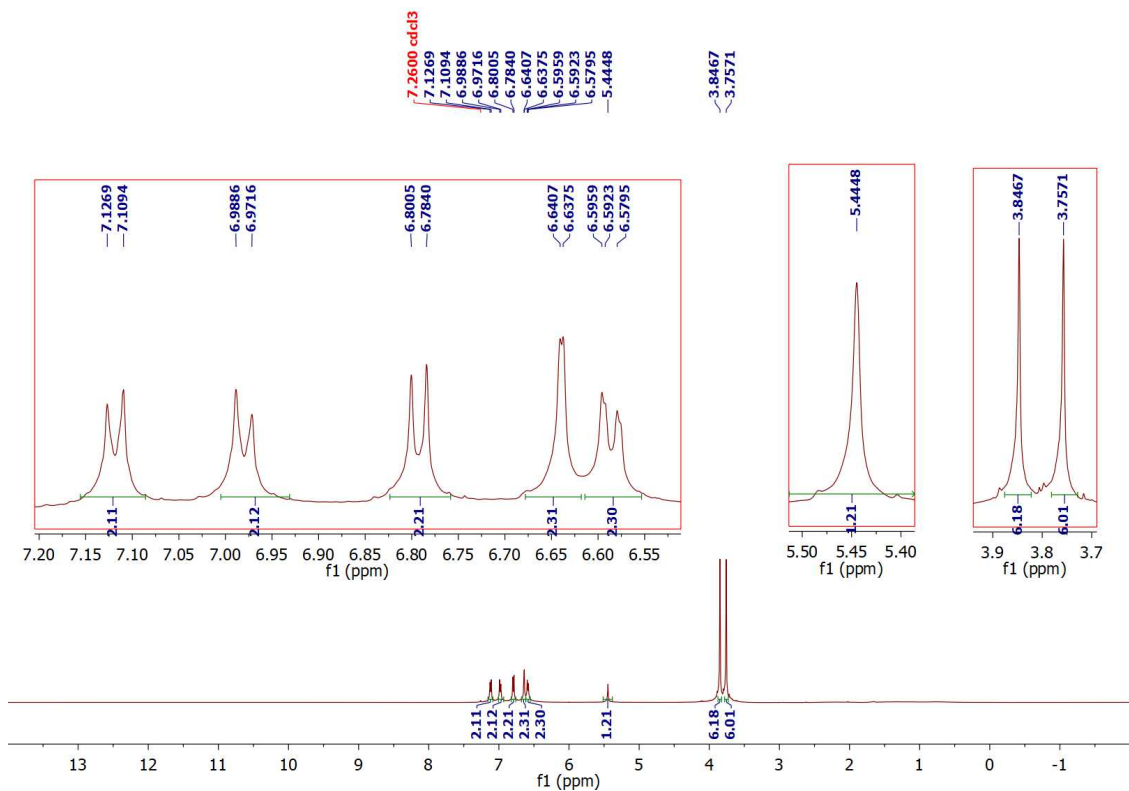
¹³C NMR spectrum of 4-(2-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9b**



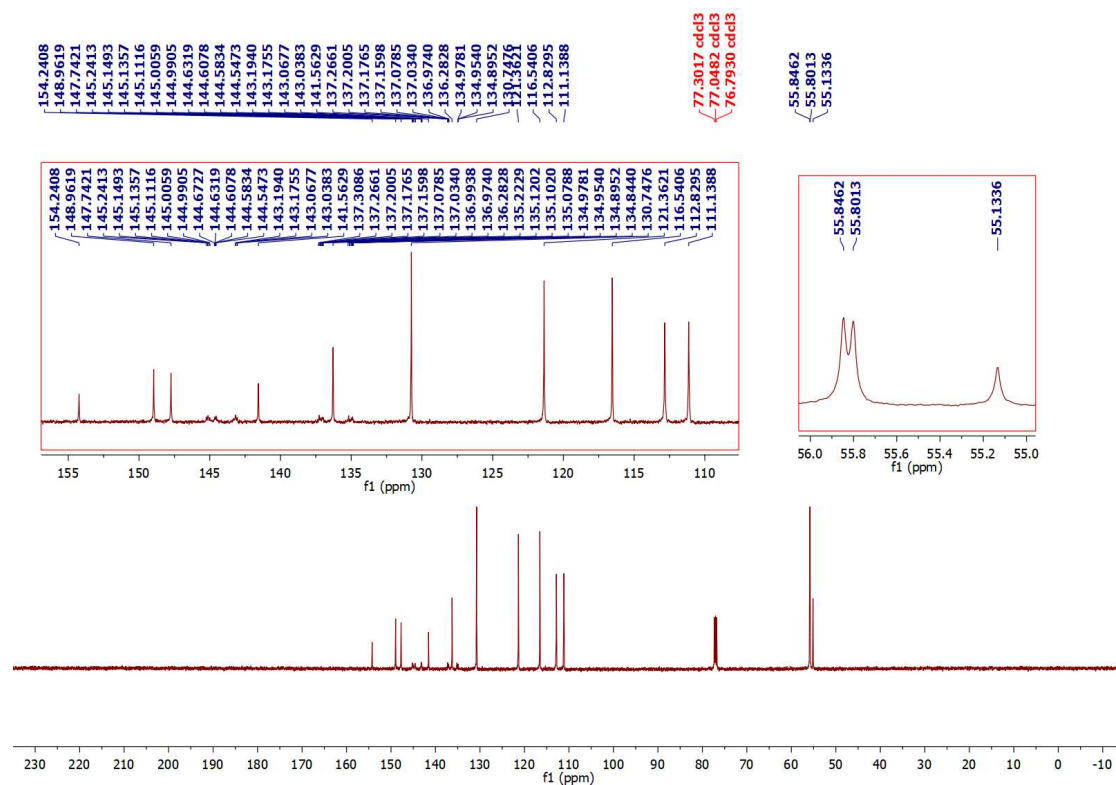
Expanded ^{13}C NMR spectrum of 4-(2-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9b**



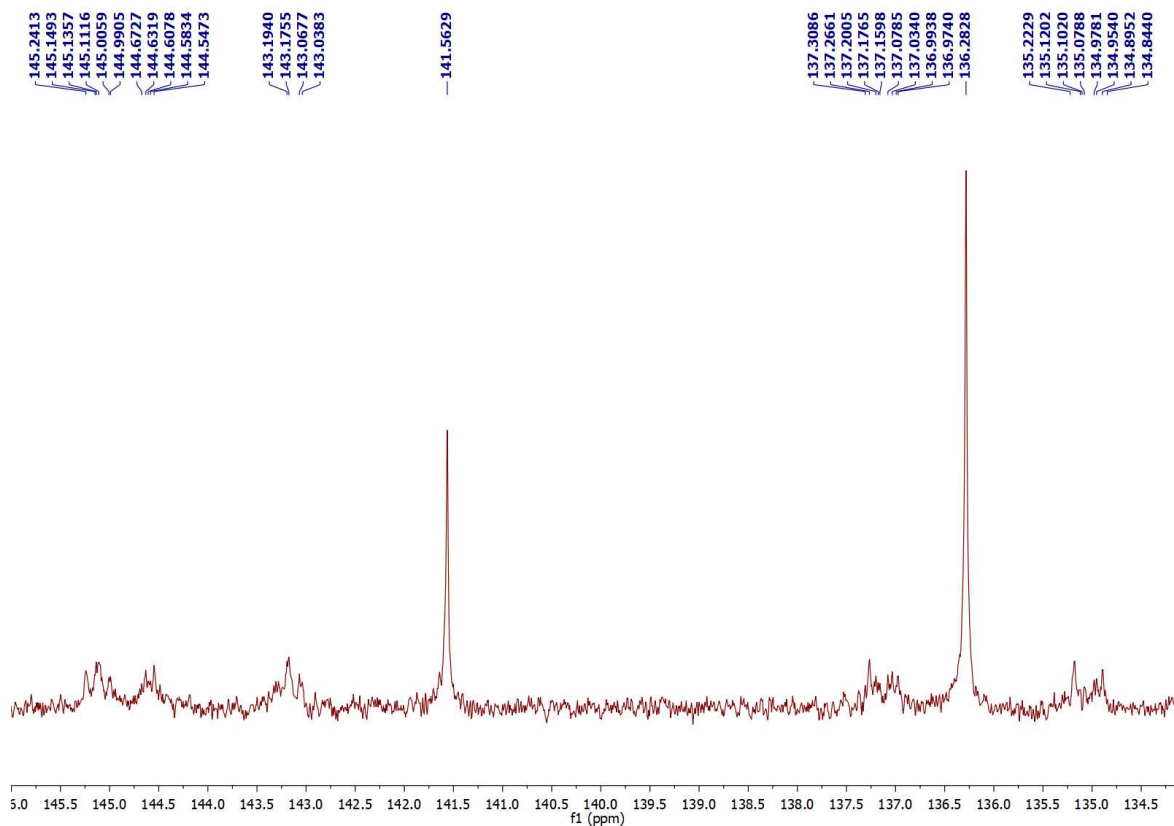
^{19}F NMR spectrum of 4-(2-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9b**



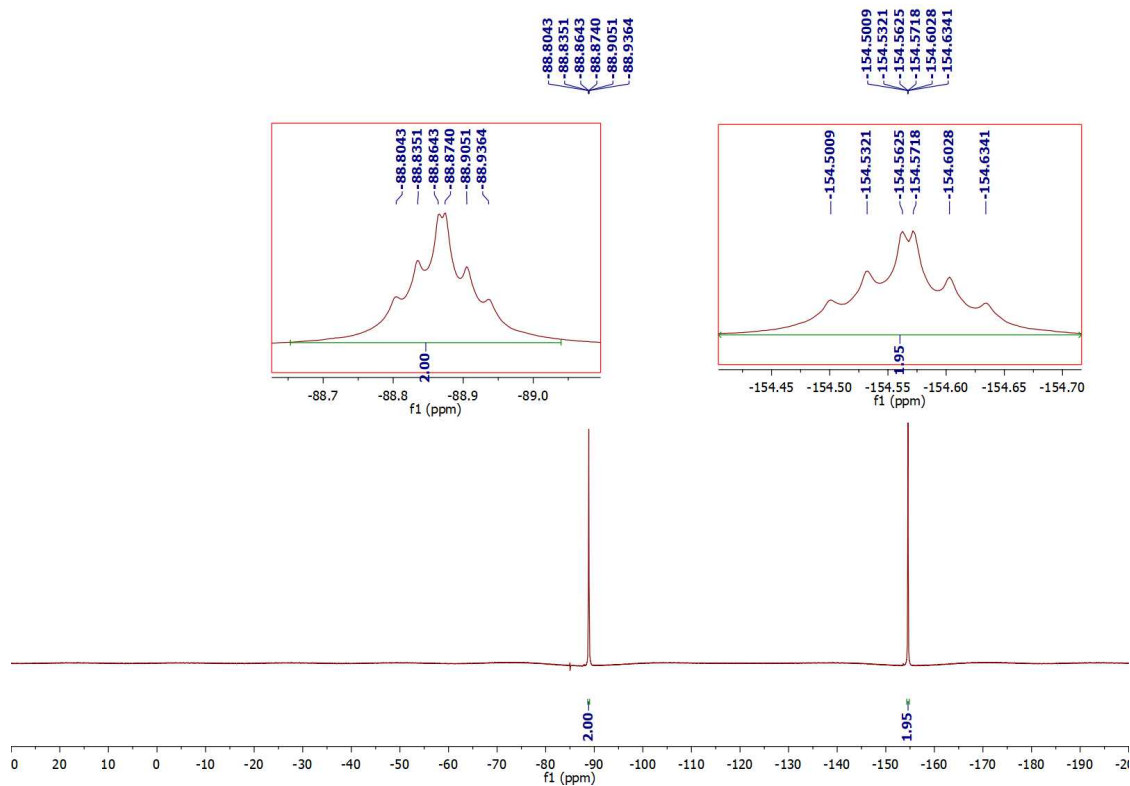
¹H NMR spectrum of 4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9c**



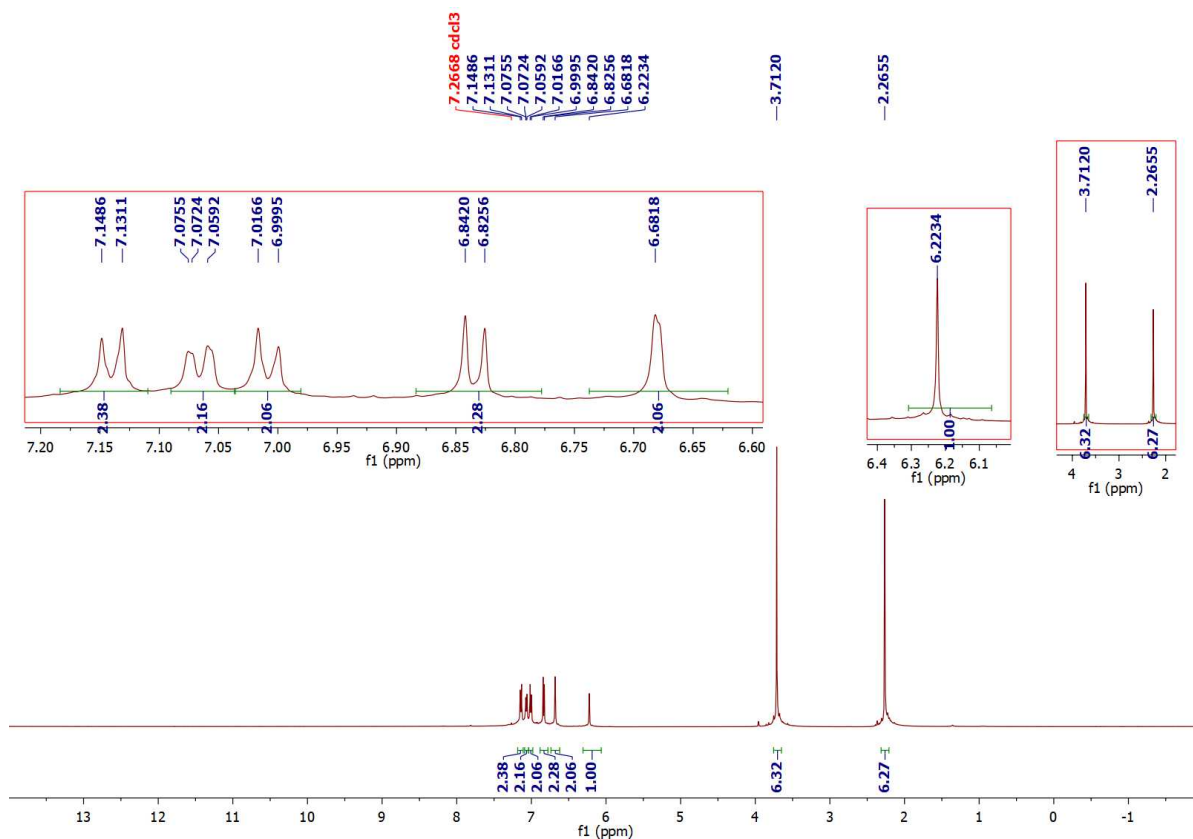
¹³C NMR spectrum of 4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9c**



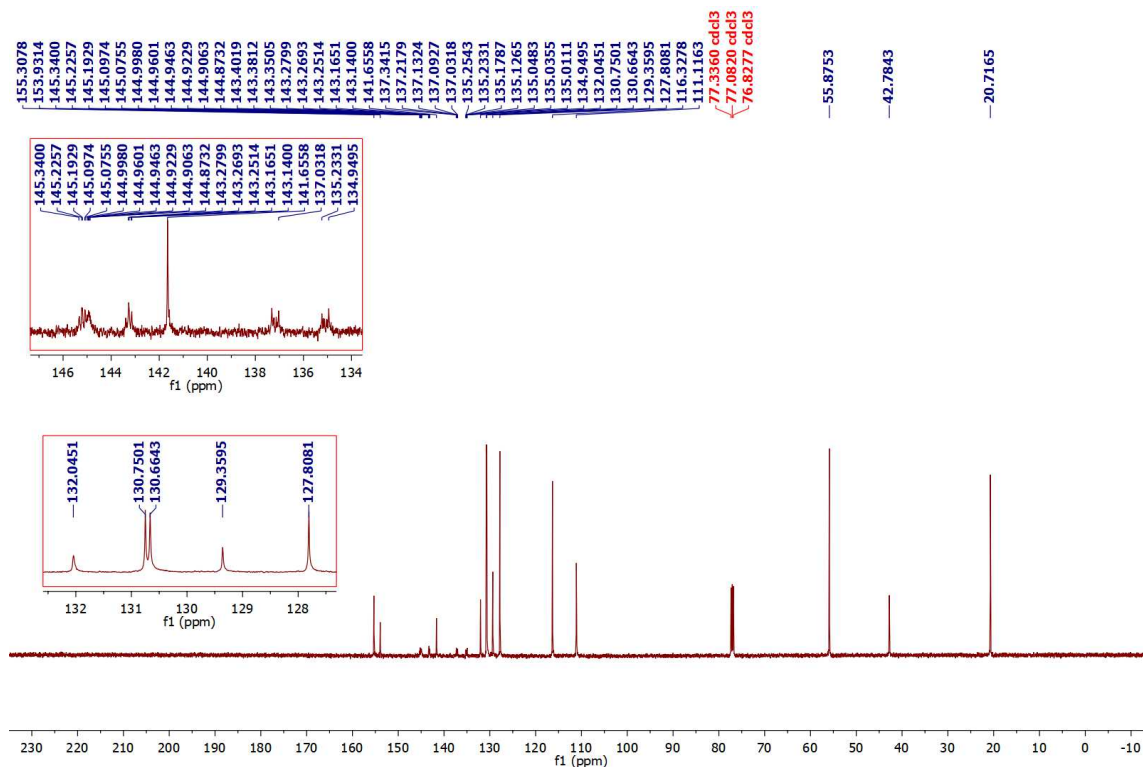
Expanded ^{13}C NMR spectrum of 4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9c**



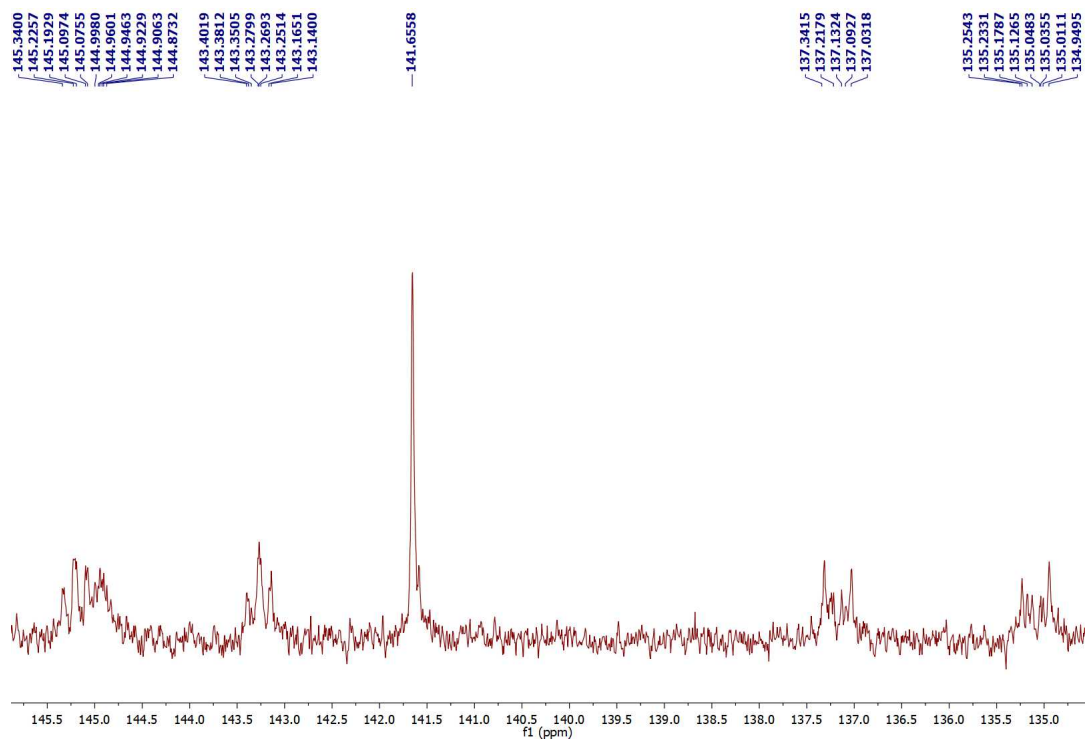
^{19}F NMR spectrum of 4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9c**



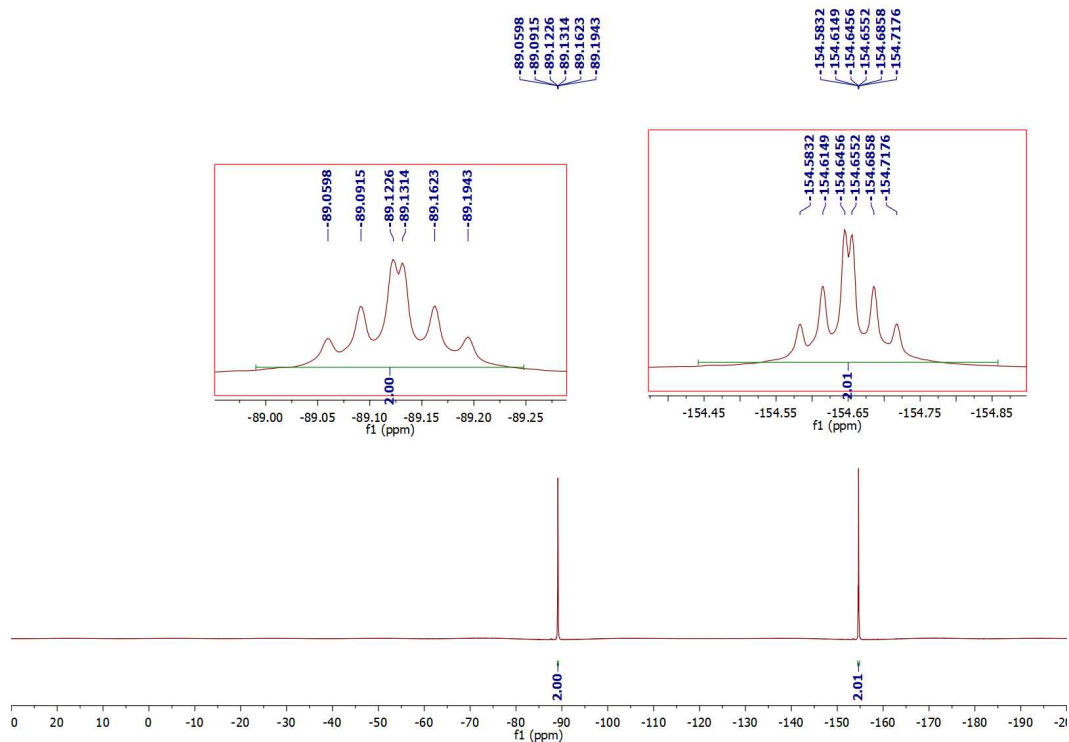
¹H NMR spectrum of 4-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9d**



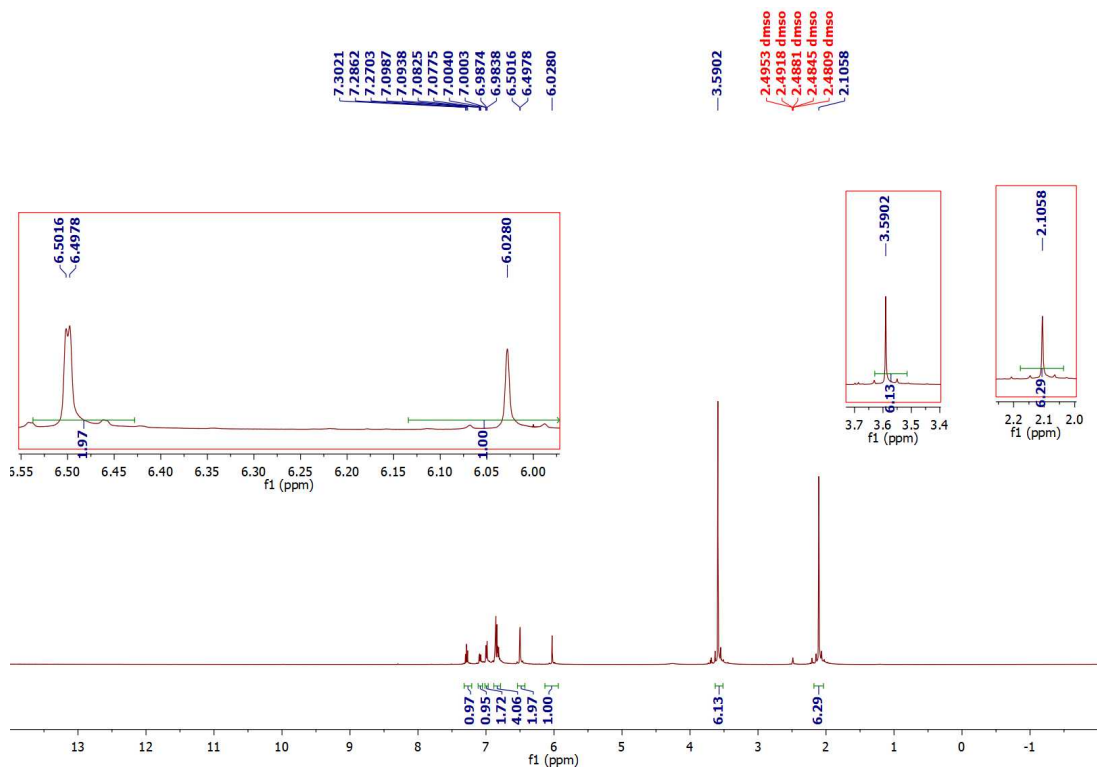
¹³C NMR spectrum of 4-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9d**



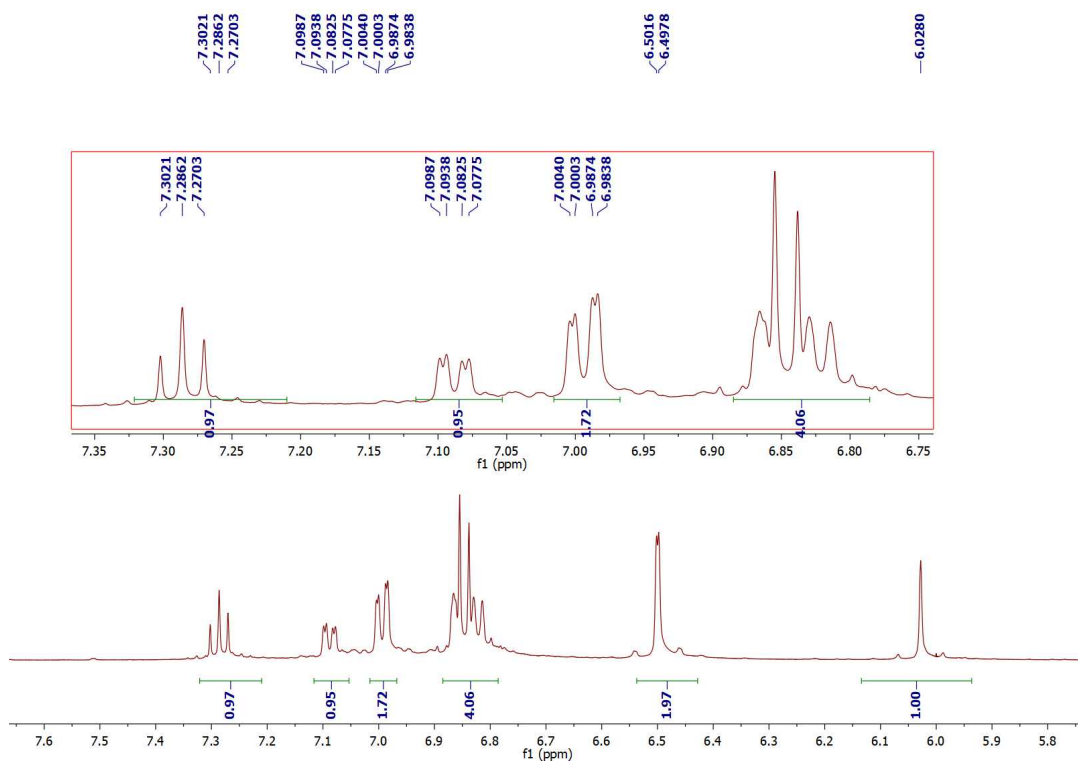
Expanded ^{13}C NMR spectrum of 4-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9d**



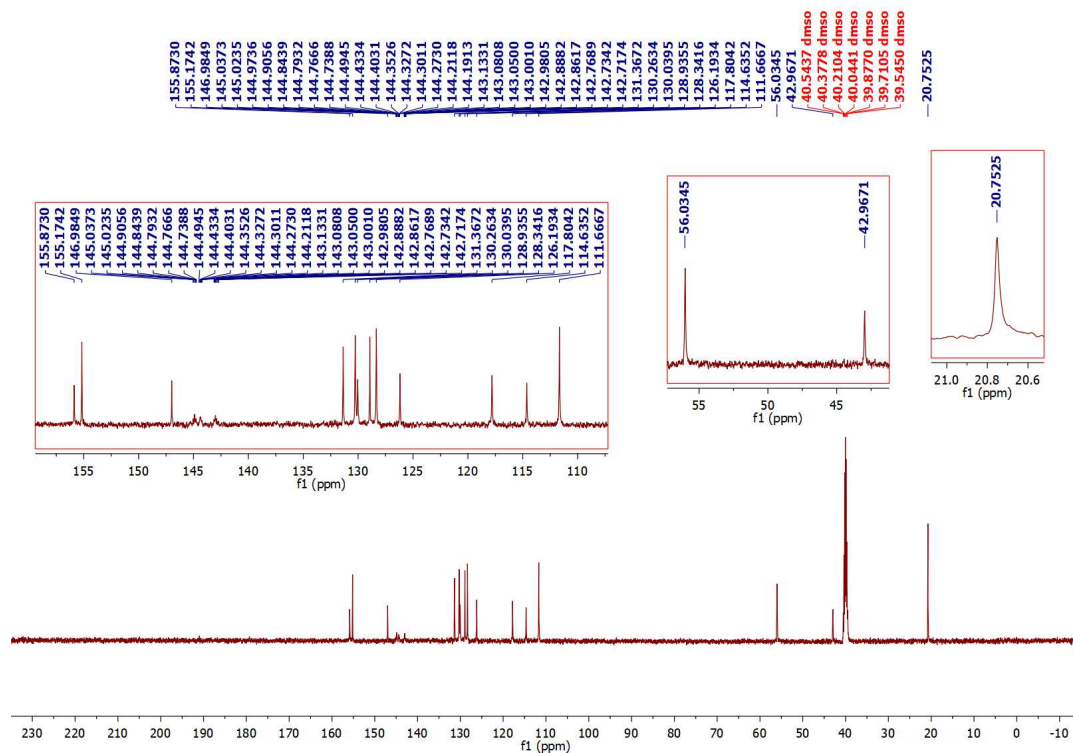
^{19}F NMR spectrum of 4-(4-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9d**



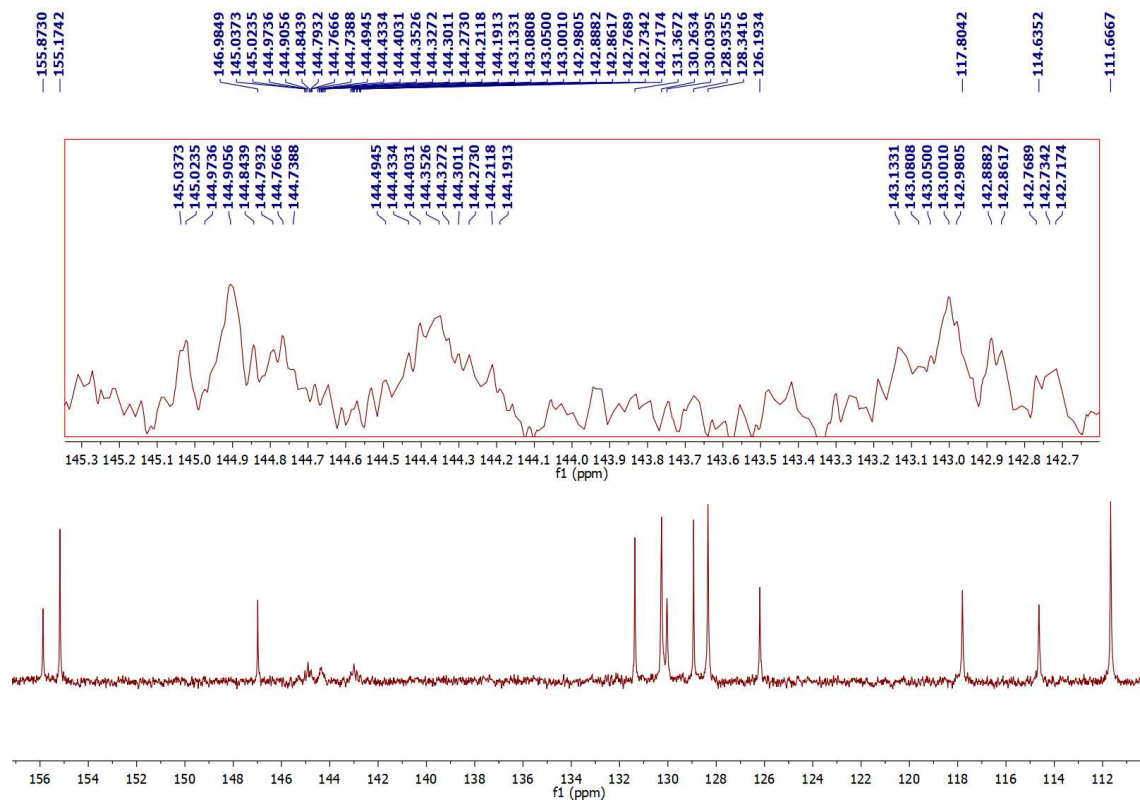
¹H NMR spectrum of 4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9e**



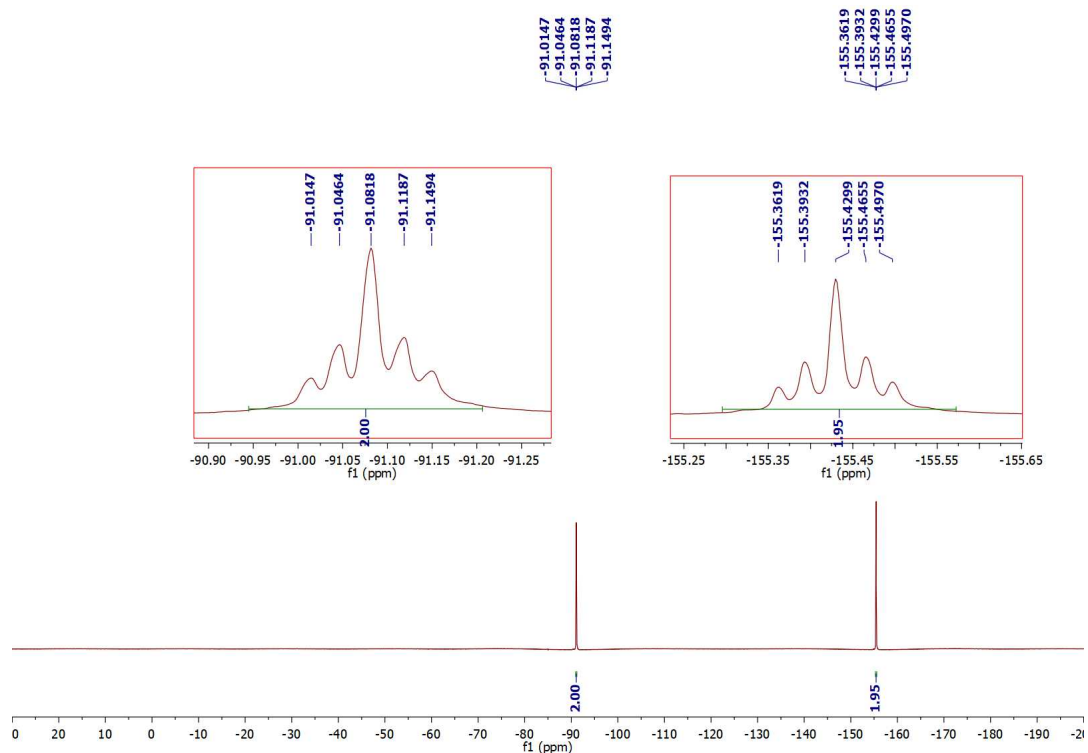
Expanded ¹H NMR spectrum of 4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9e**



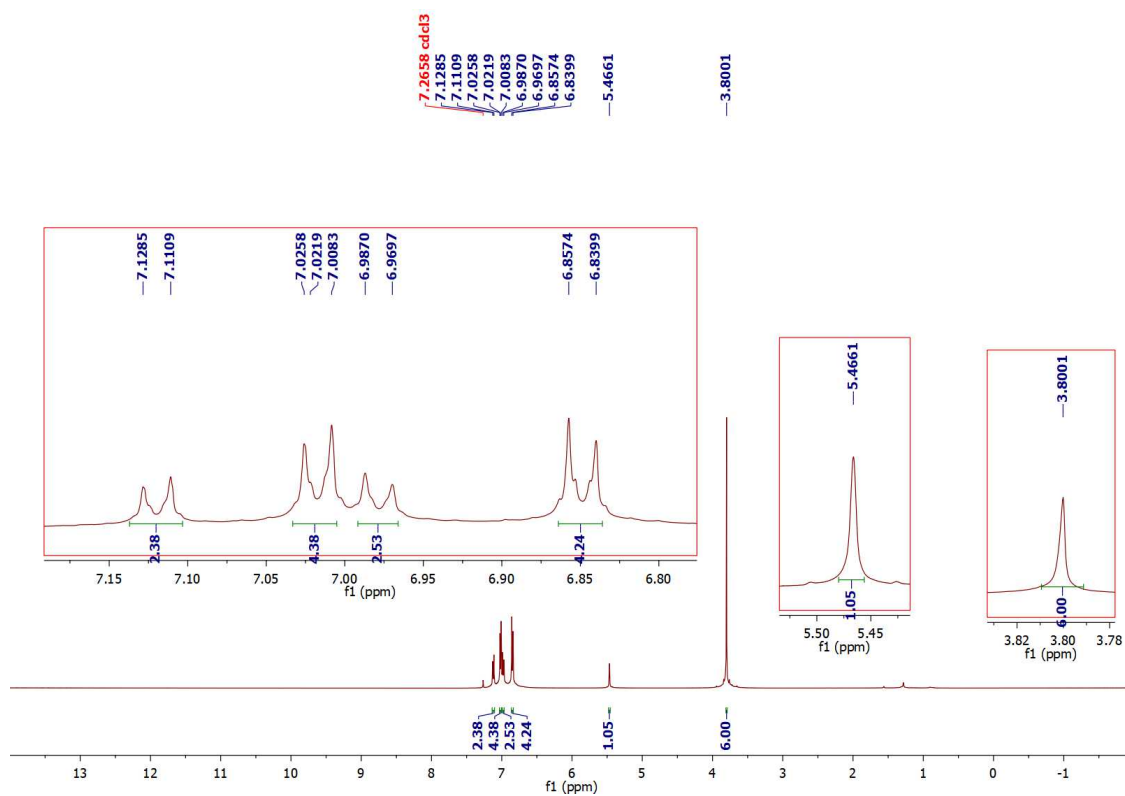
13C NMR spectrum of 4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9e**



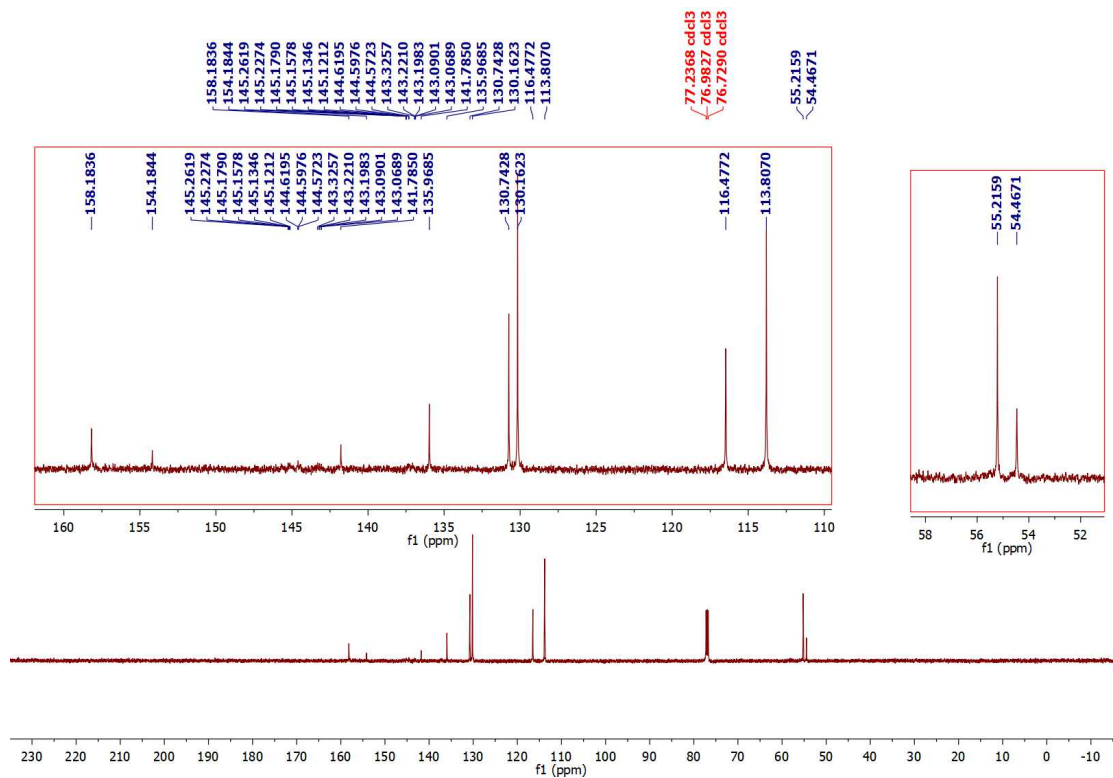
Expanded 13C NMR spectrum of 4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9e**



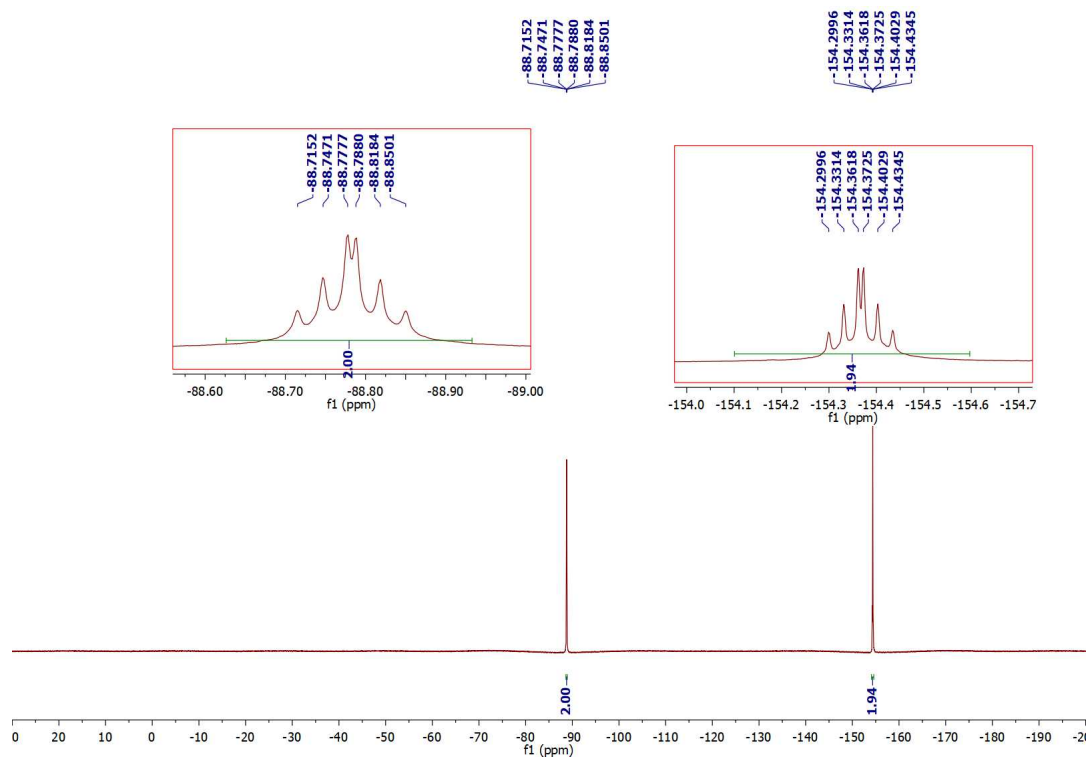
^{19}F NMR spectrum of 4-(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9e**



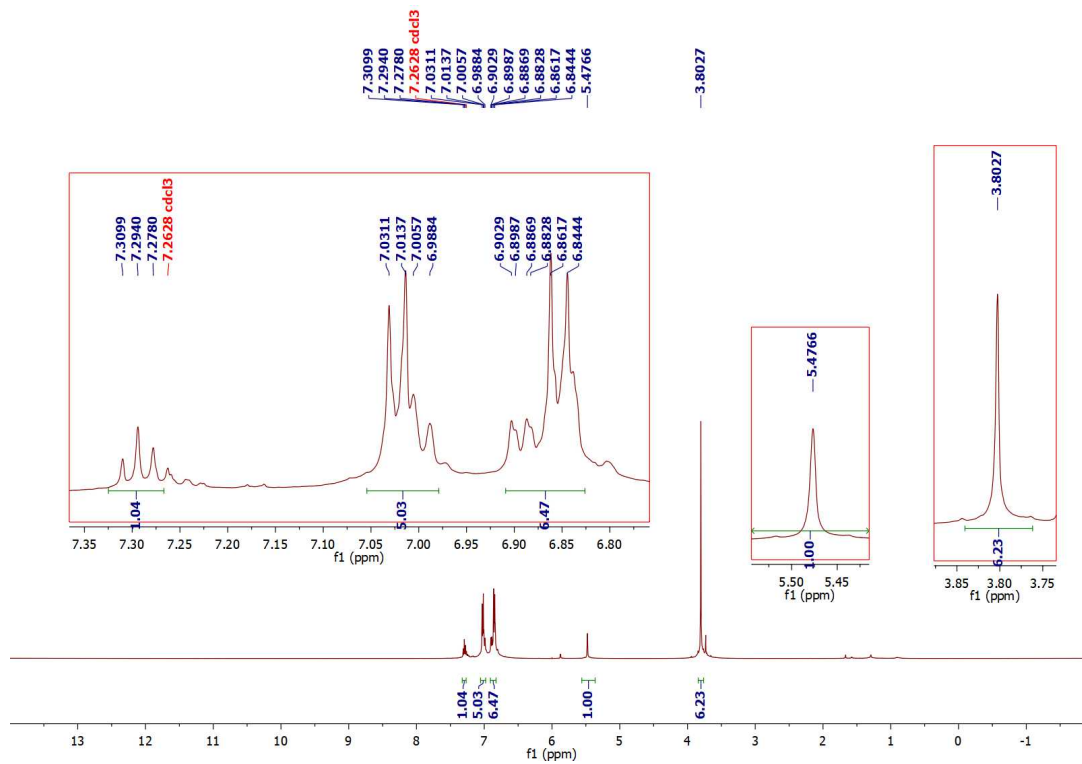
^1H NMR spectrum of 4-(4-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9f**



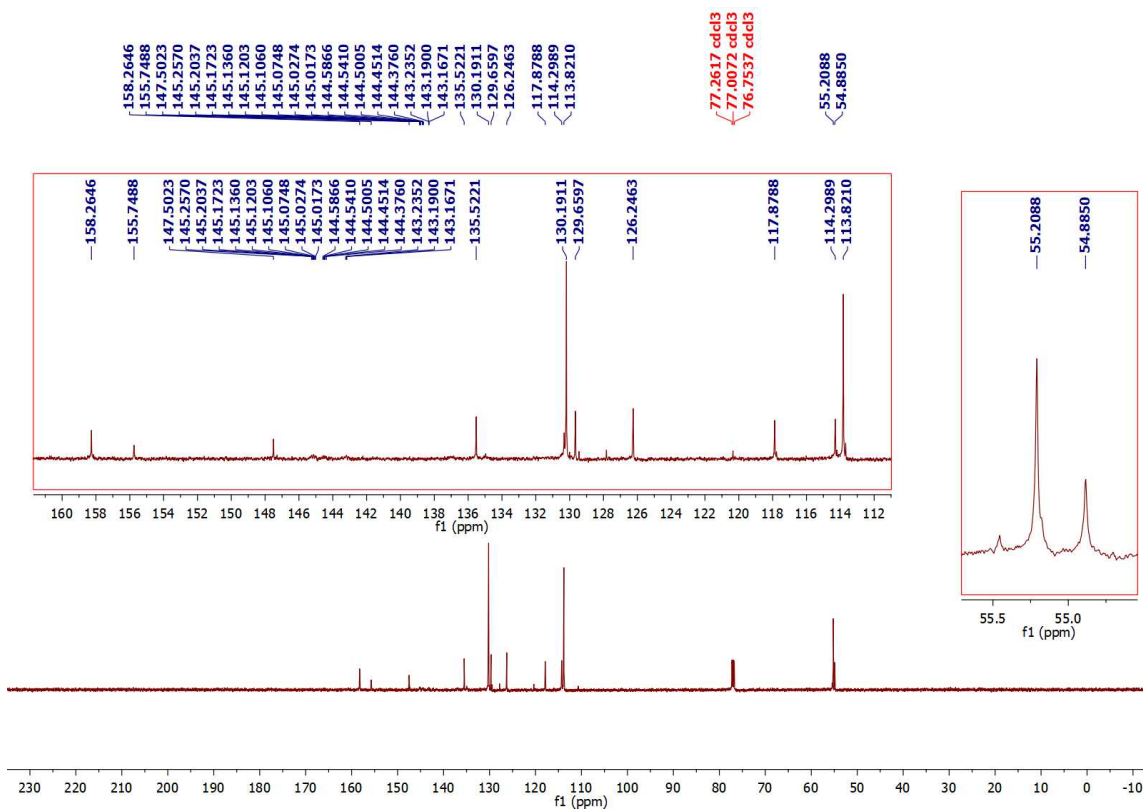
^{13}C NMR spectrum of 4-(4-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9f**



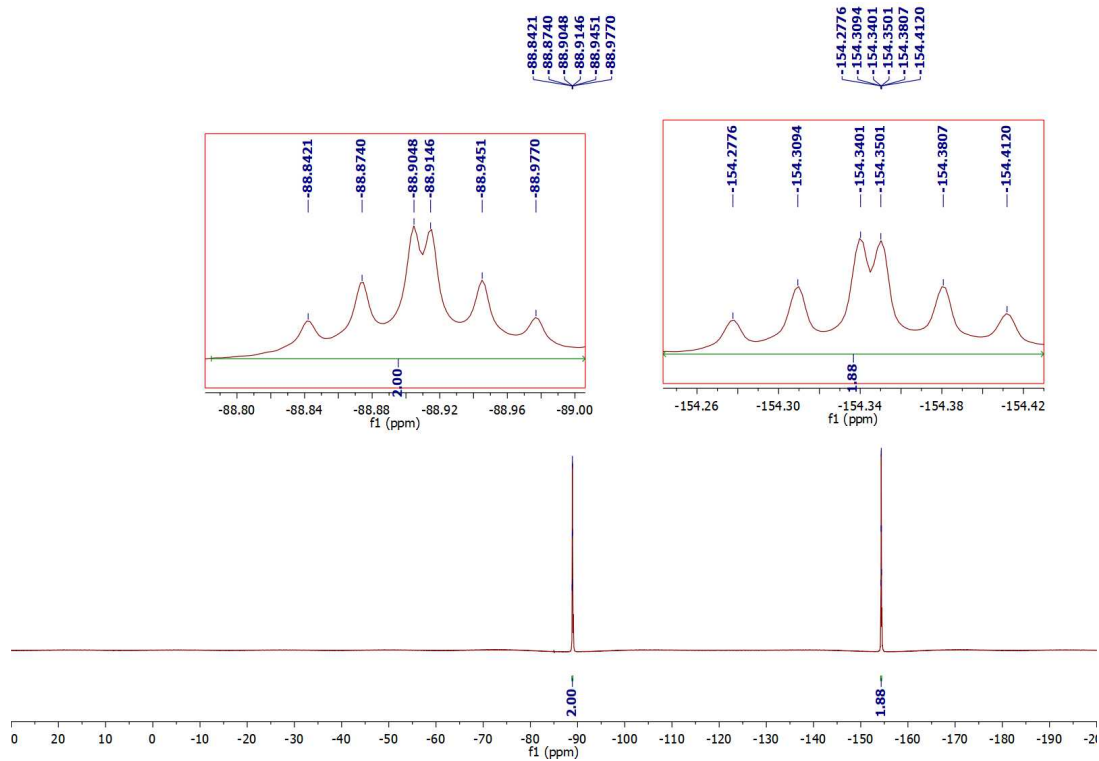
^{19}F NMR spectrum of 4-(4-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9f**



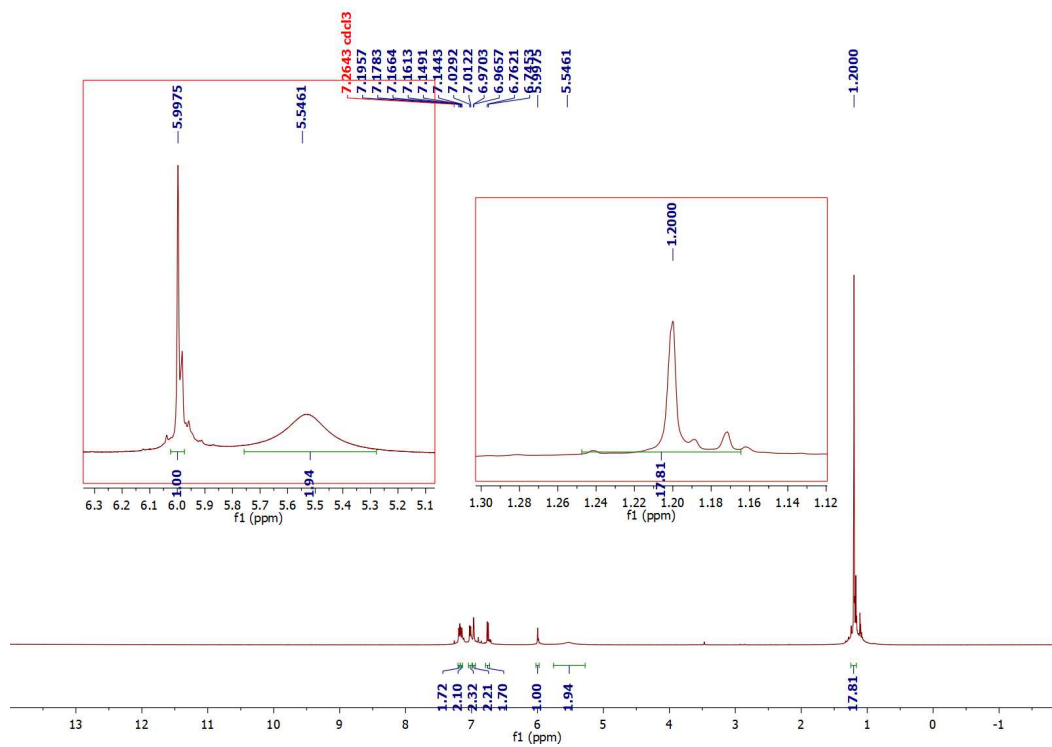
¹H NMR spectrum of 4-(3-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9g**



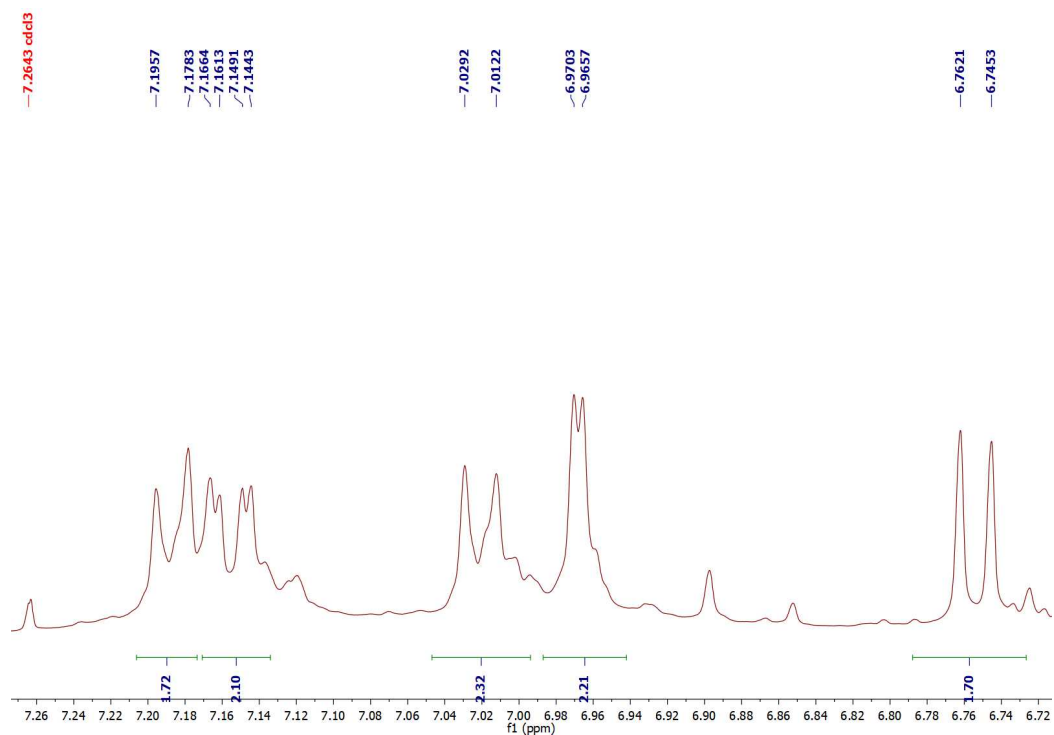
¹³C NMR spectrum of 4-(3-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9g**



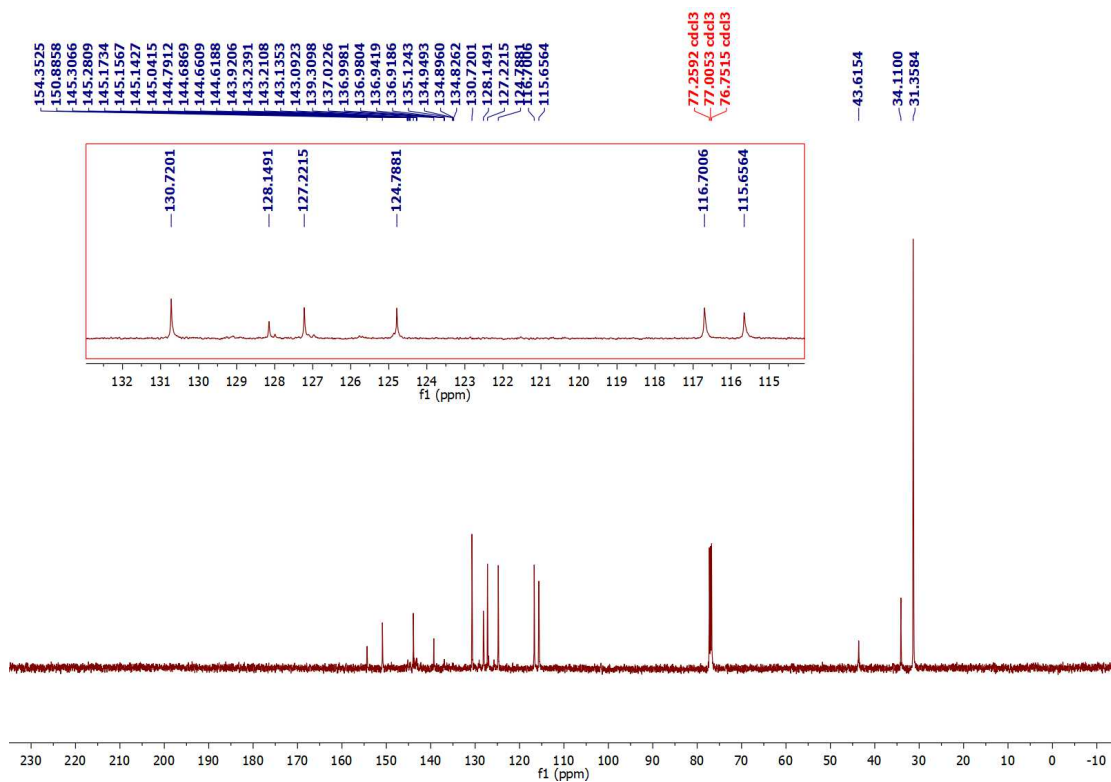
¹⁹F NMR spectrum of 4-(3-(bis(4-methoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9g**



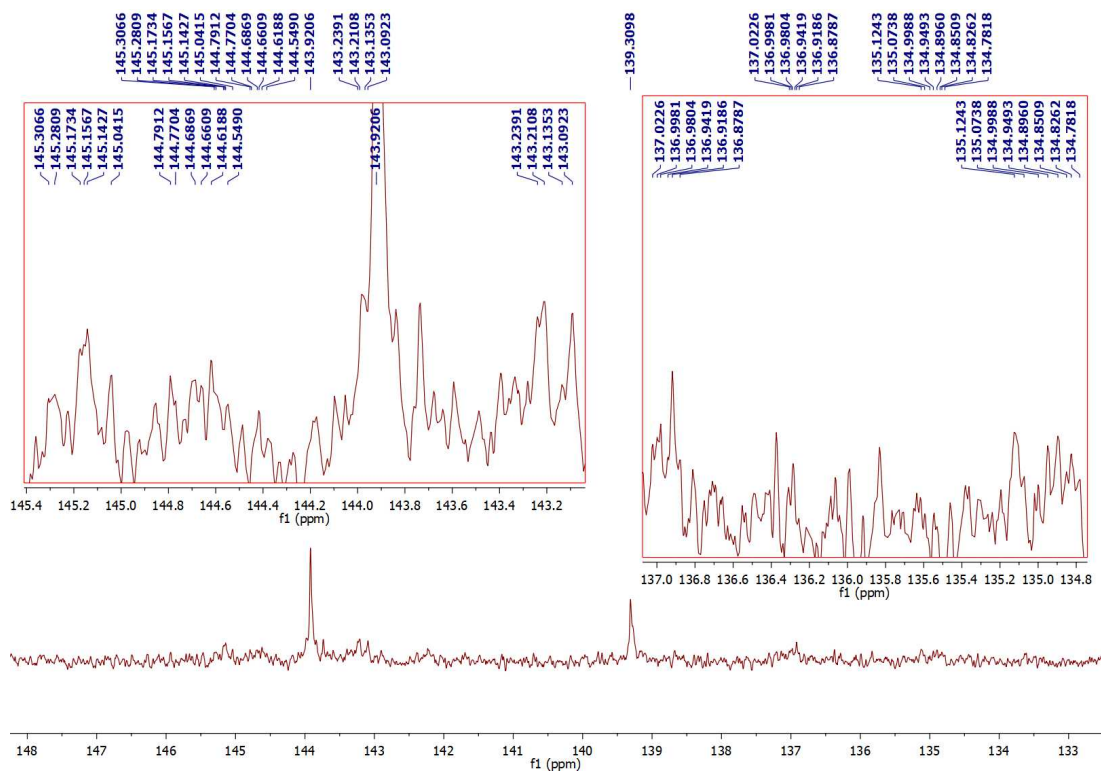
¹H NMR spectrum of 2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9h**



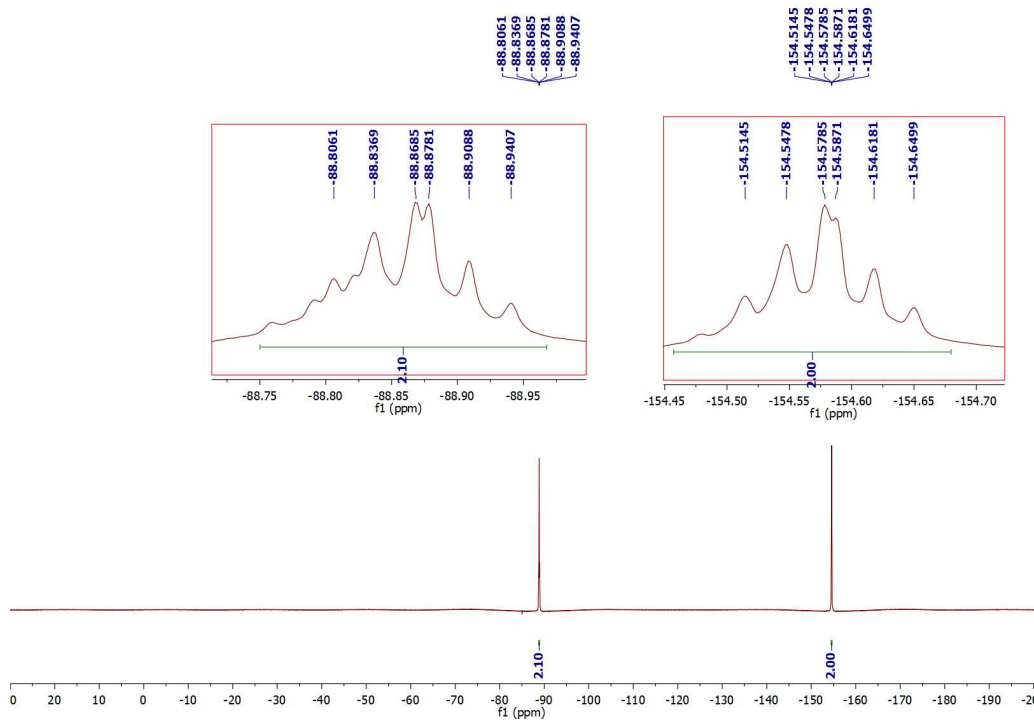
Expanded ^1H NMR spectrum of 2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9h**



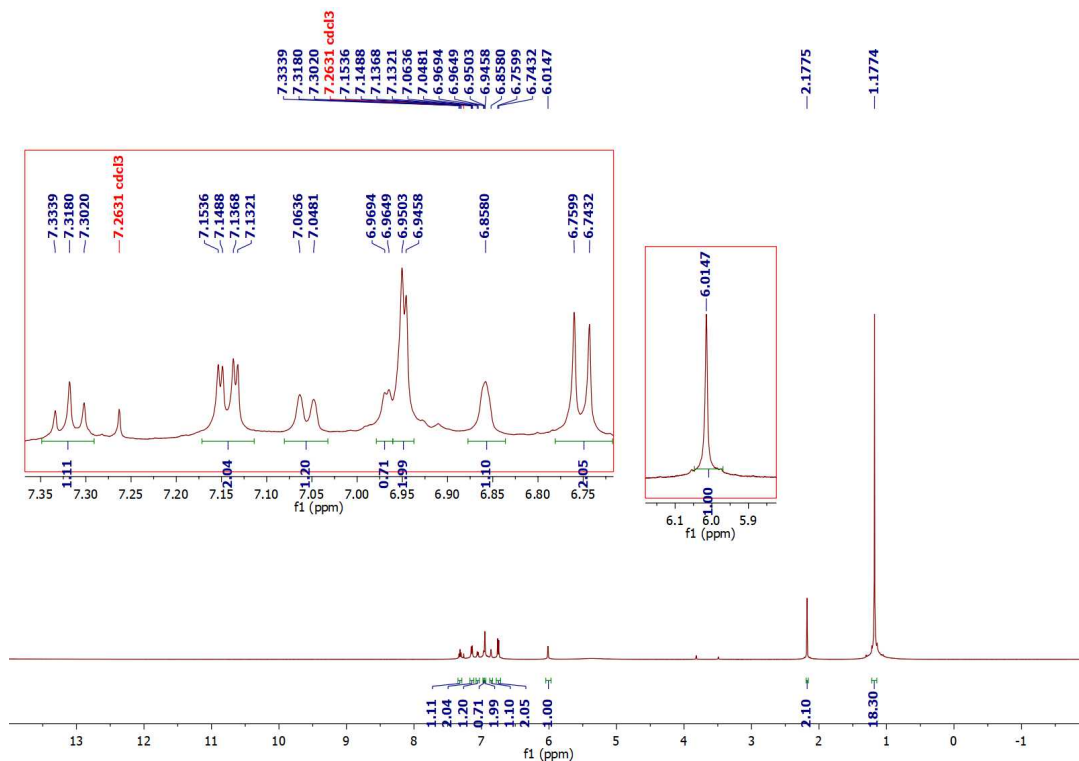
^{13}C NMR spectrum of 2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9h**



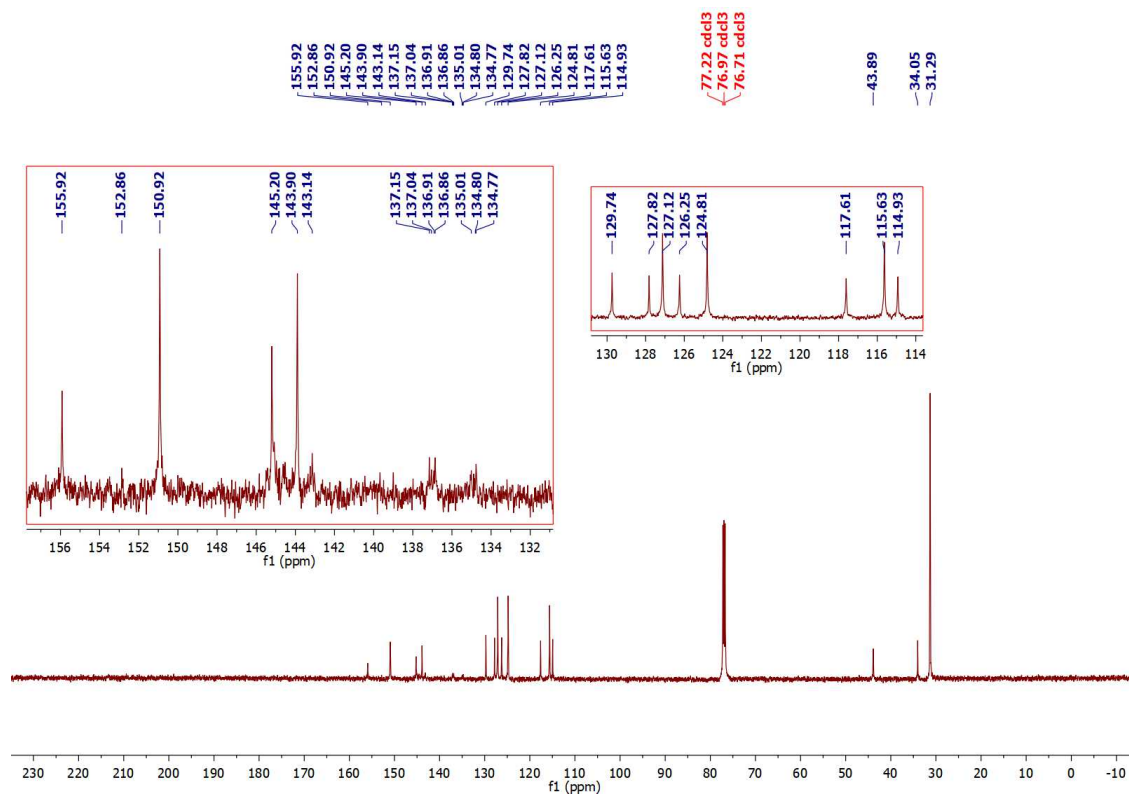
Expanded ^{13}C NMR spectrum of 2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9h**



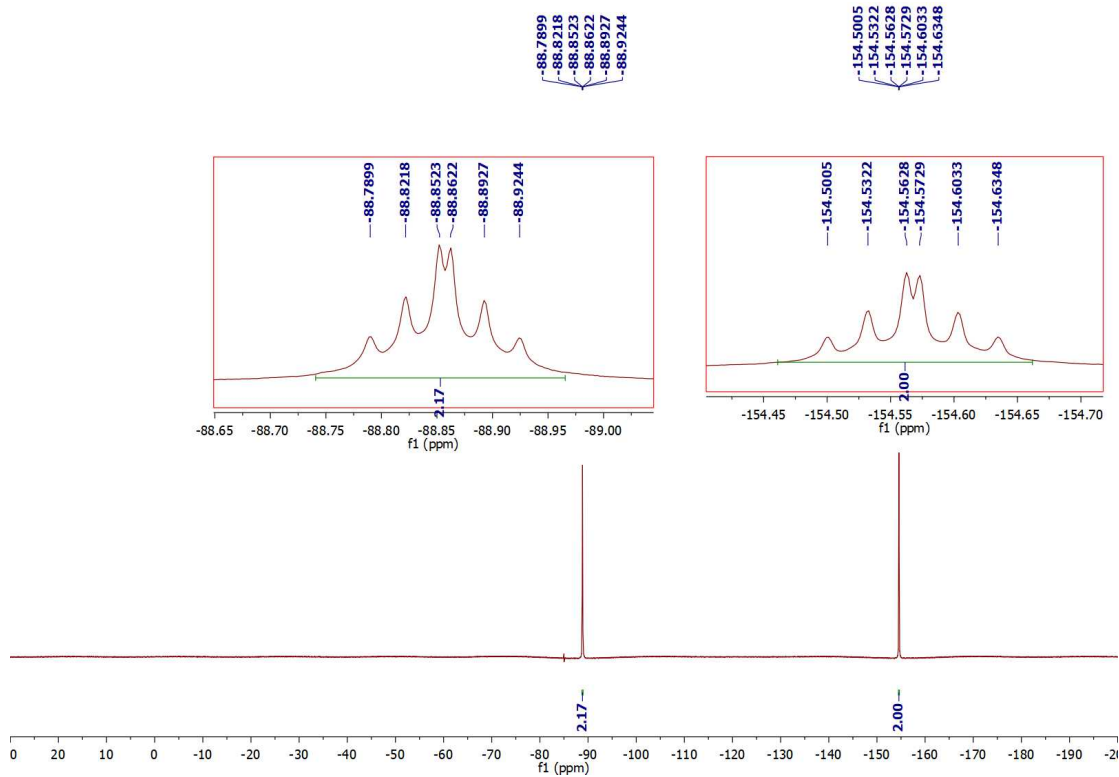
^{19}F NMR spectrum of 2,2'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9h**



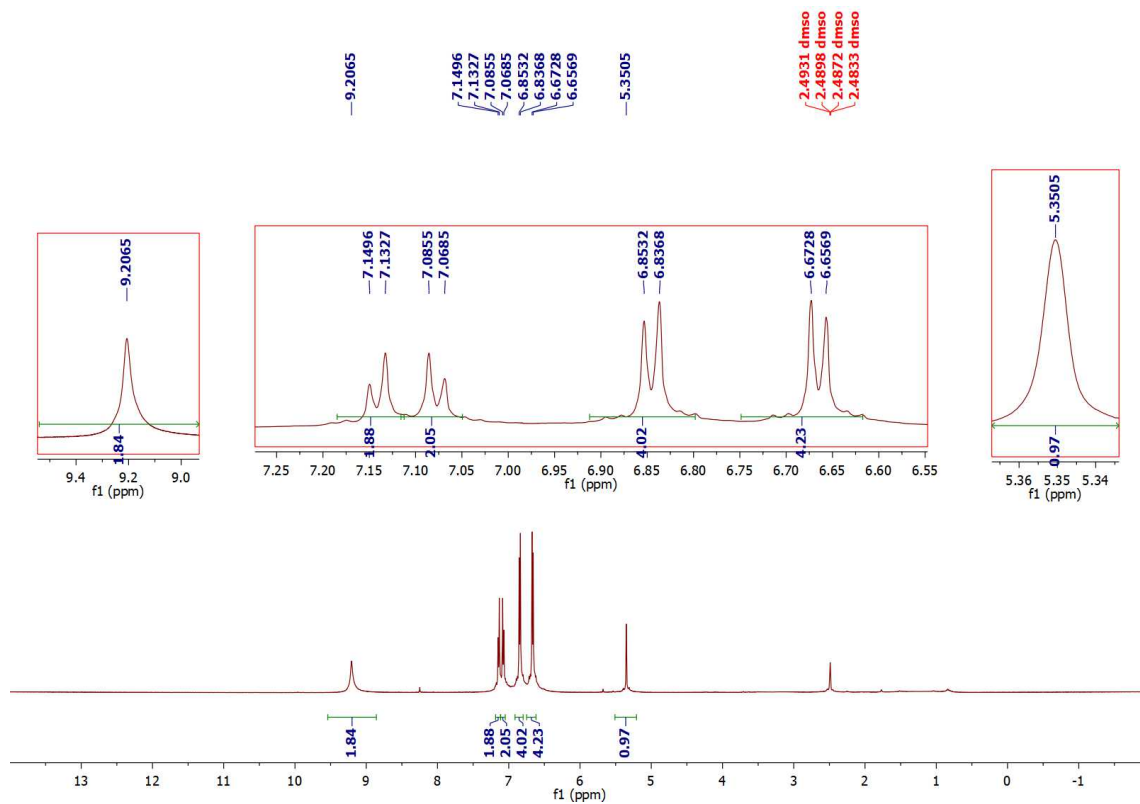
¹H NMR spectrum of 2,2'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9i**



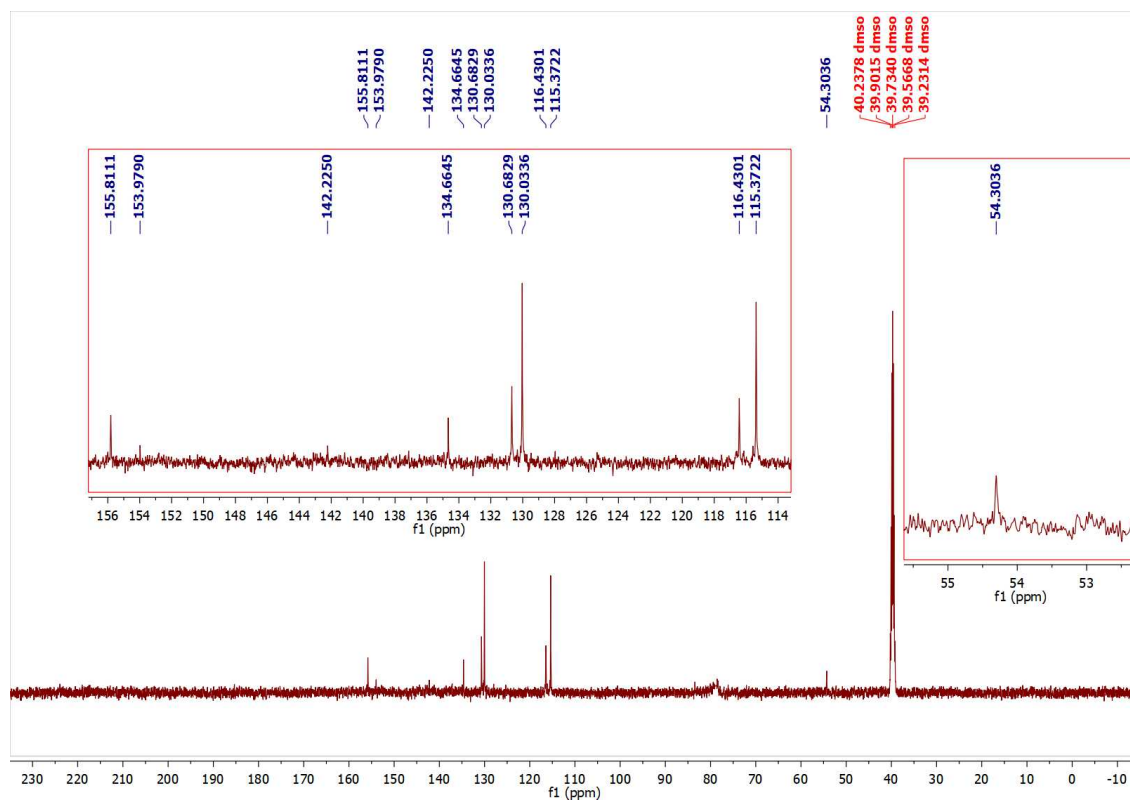
¹³C NMR spectrum of 2,2'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9i**



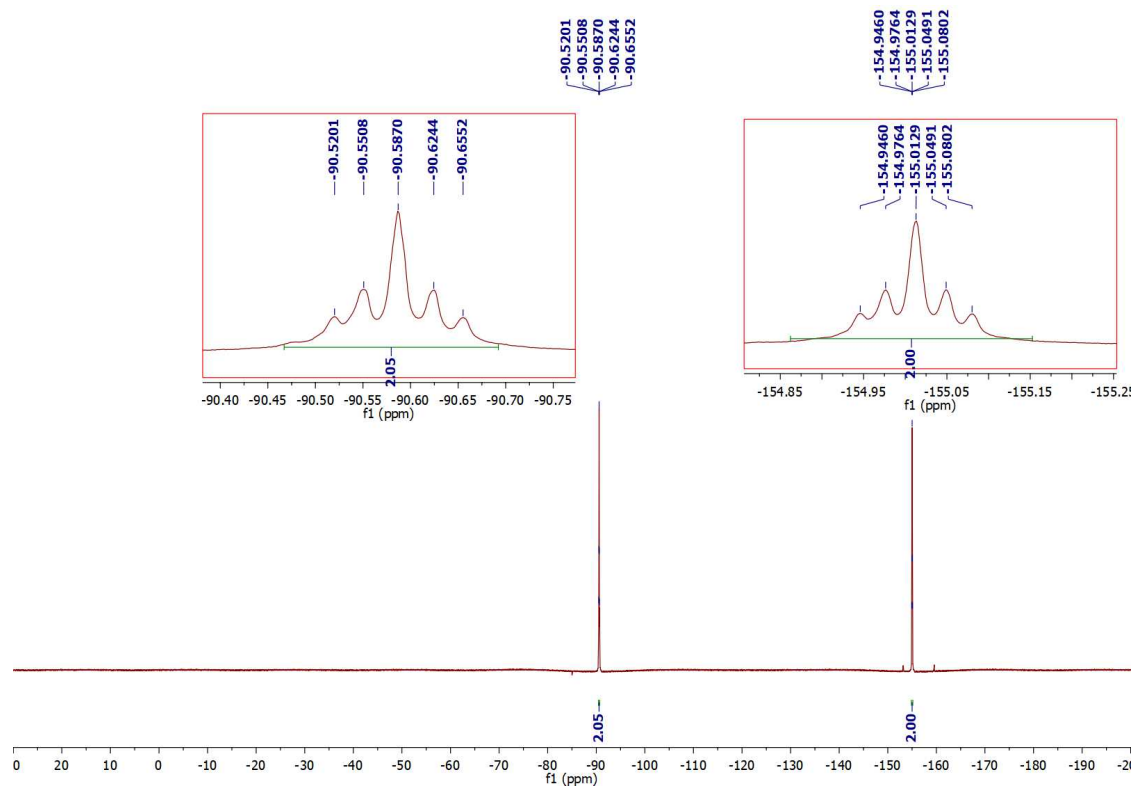
^{19}F NMR spectrum of 2,2'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(4-(tert-butyl)phenol) **9i**



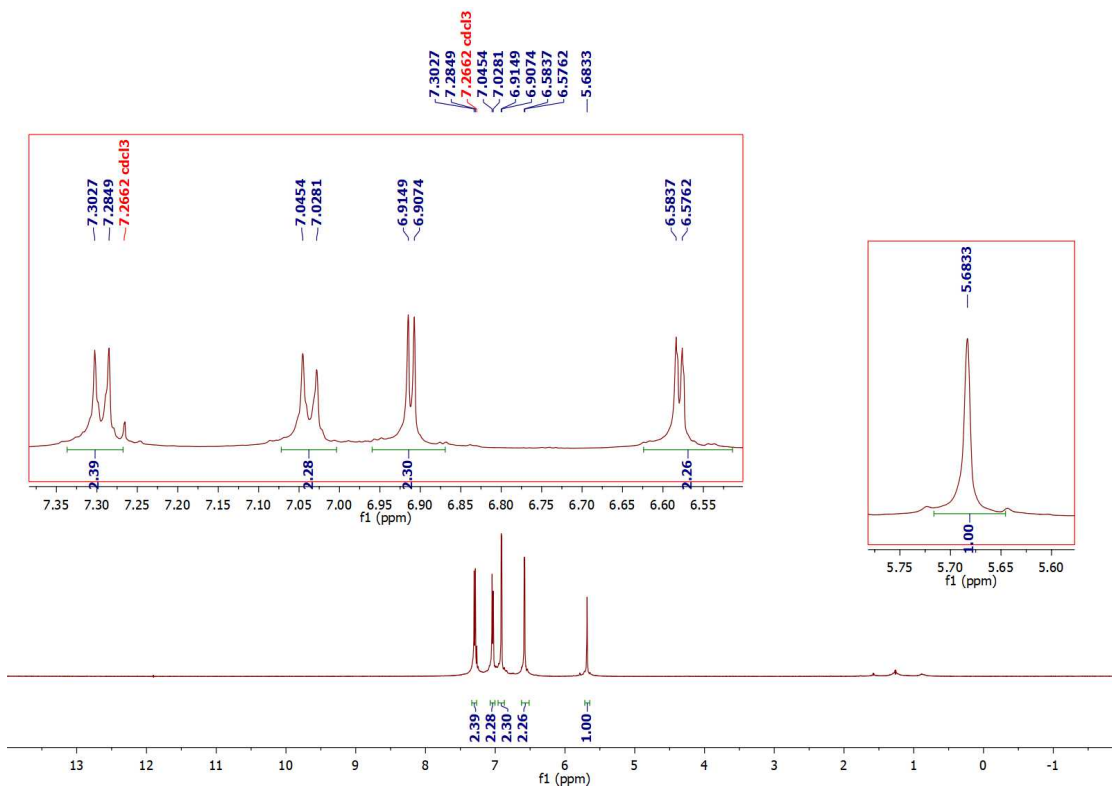
^1H NMR spectrum of 4,4'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)diphenol **9j**



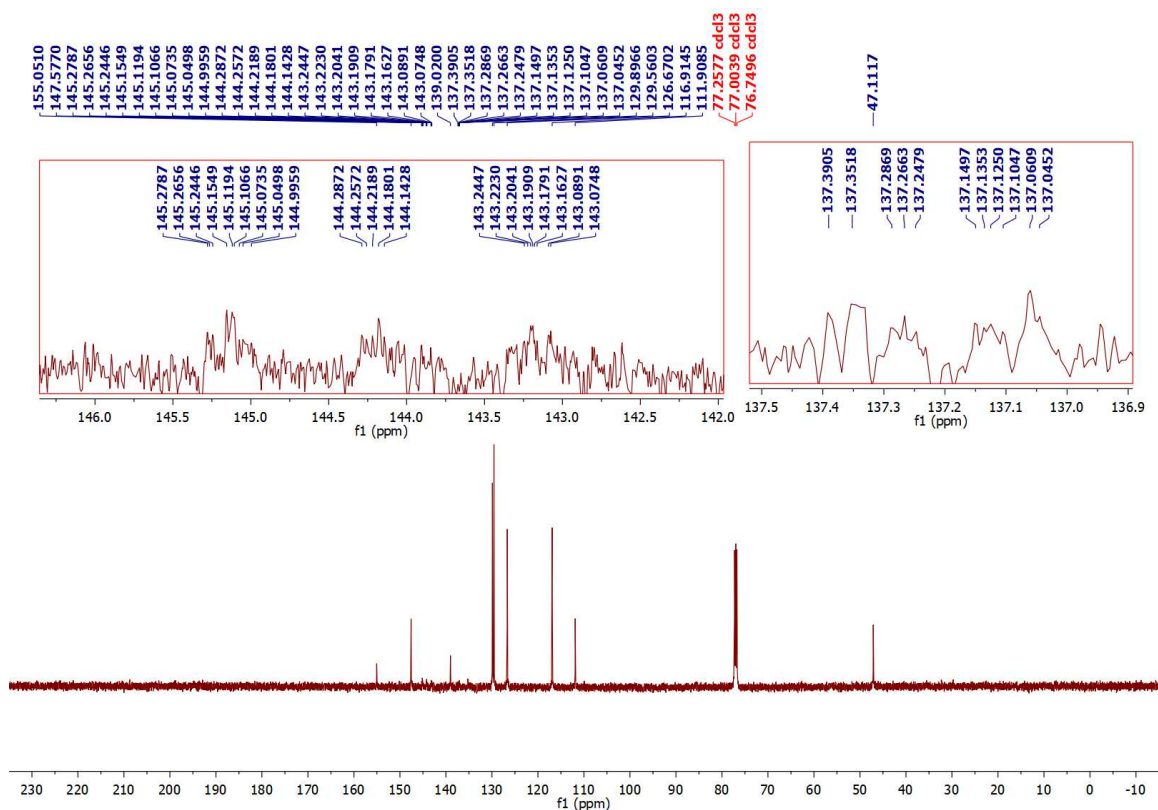
¹³C NMR spectrum of 4,4'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)diphenol **9j**



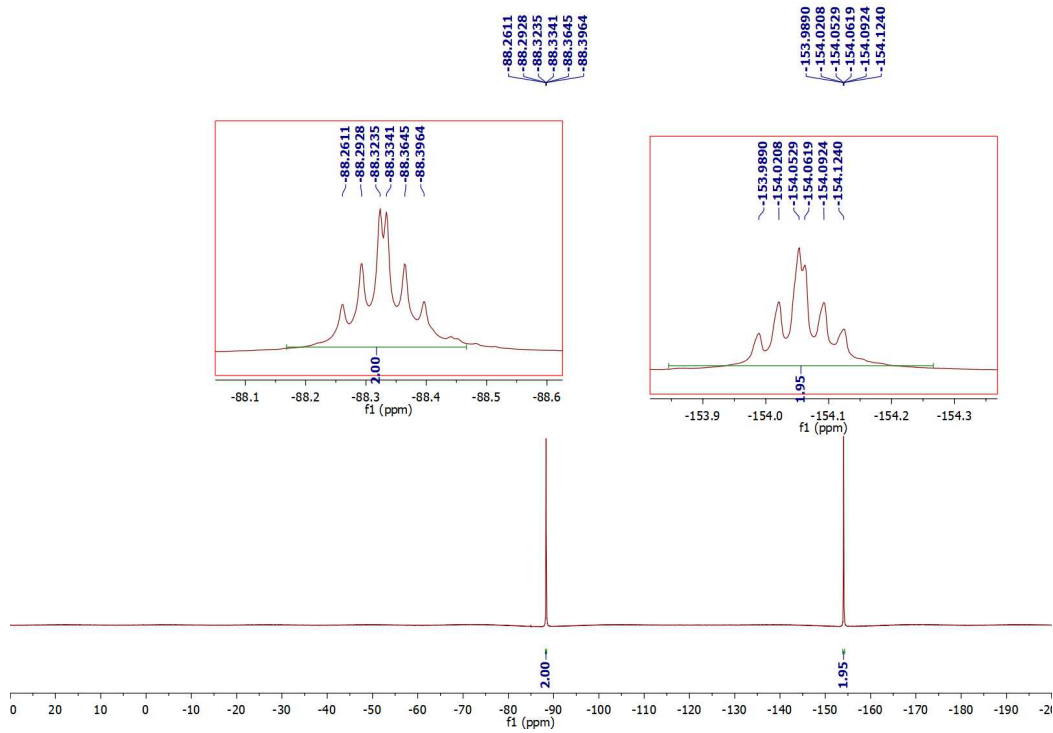
¹⁹F NMR spectrum of 4,4'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)diphenol **9j**



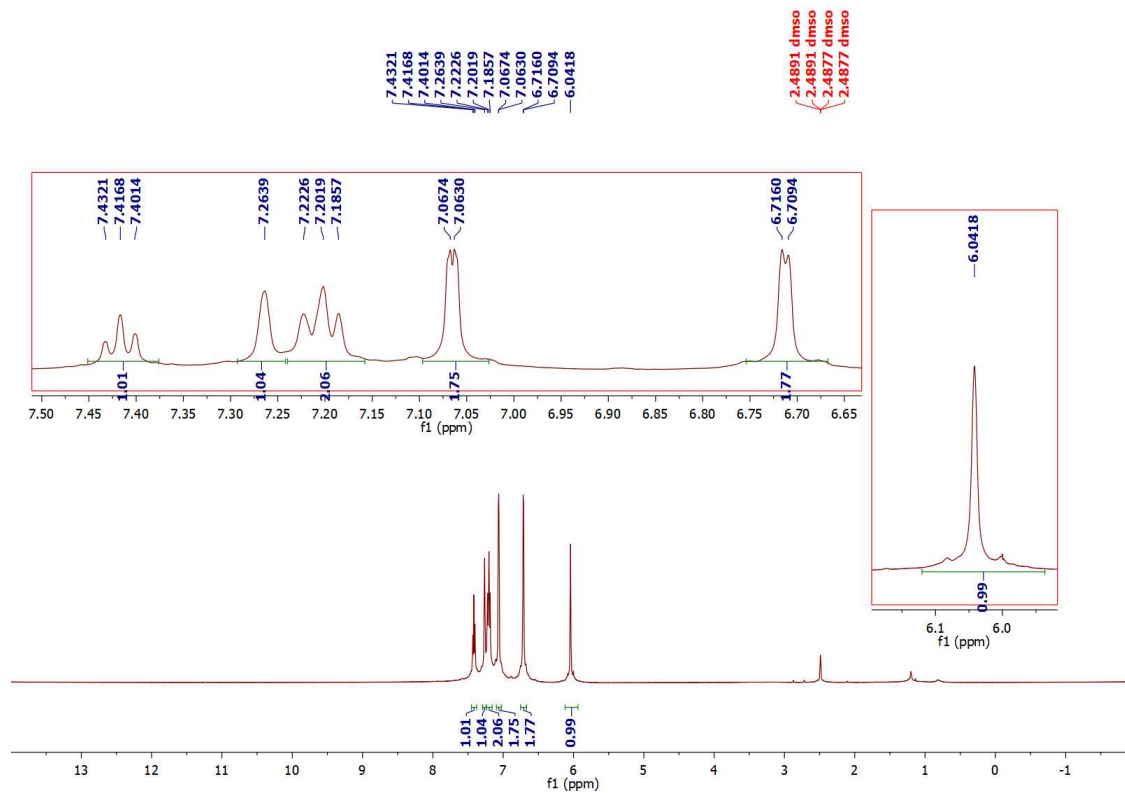
¹H NMR spectrum of 4-(4-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9k**



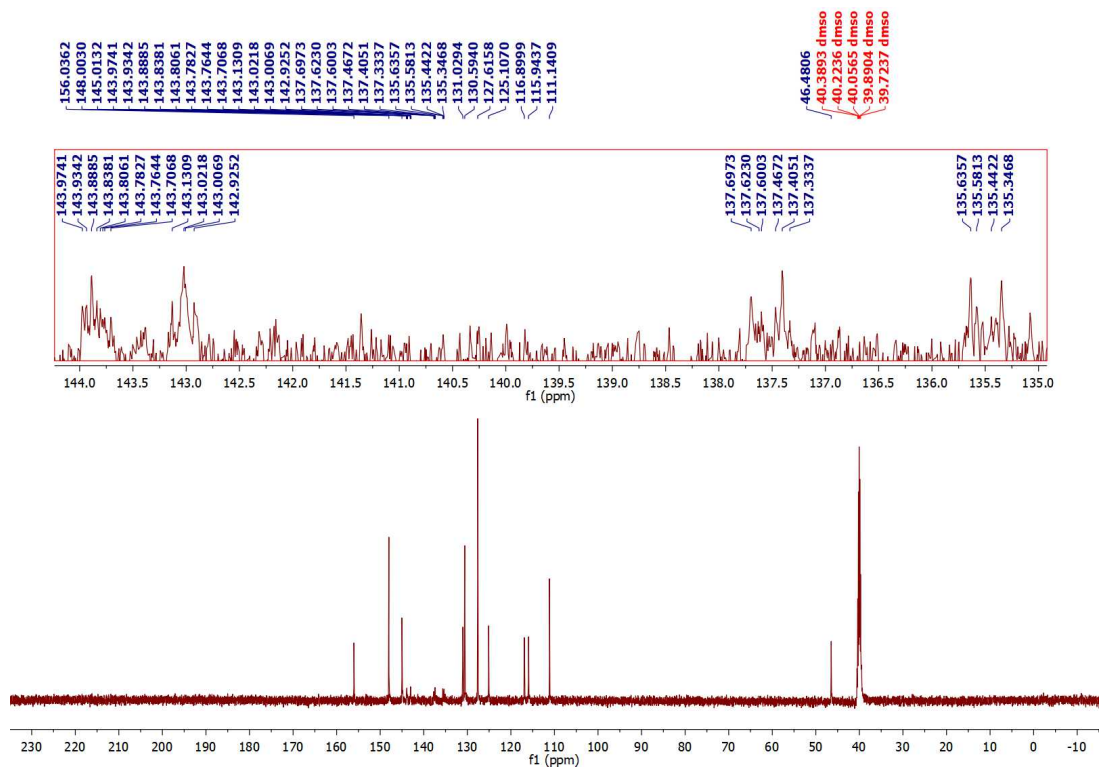
¹³C NMR spectrum of 4-(4-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9k**



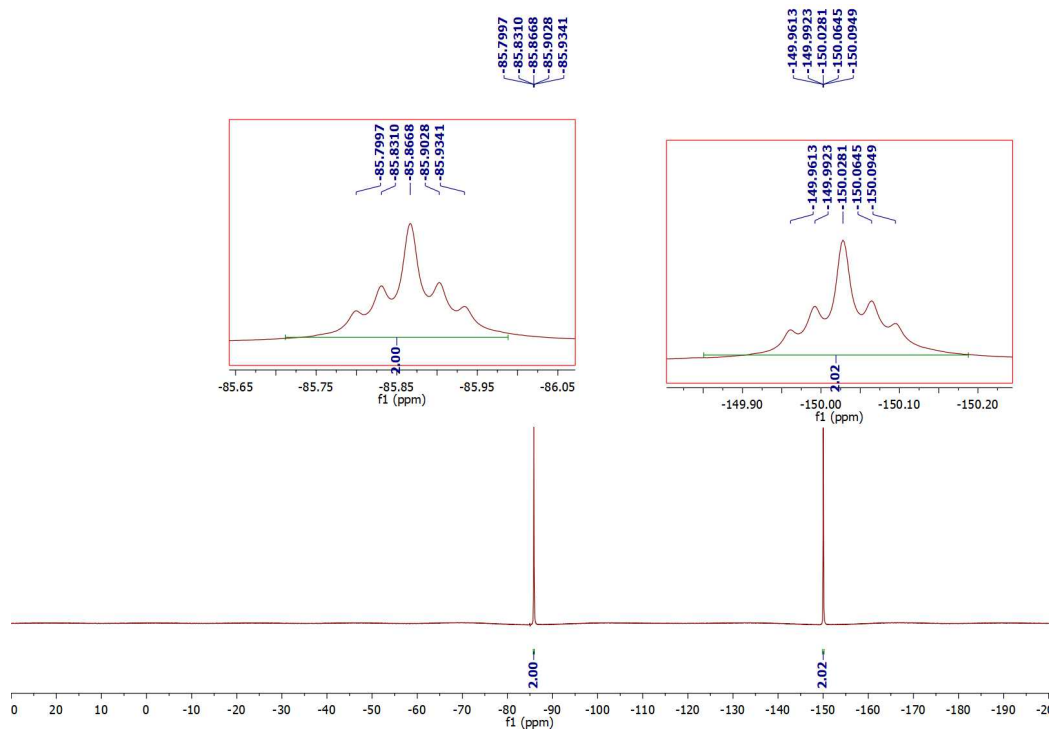
¹⁹F NMR spectrum of 4-(4-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9k**



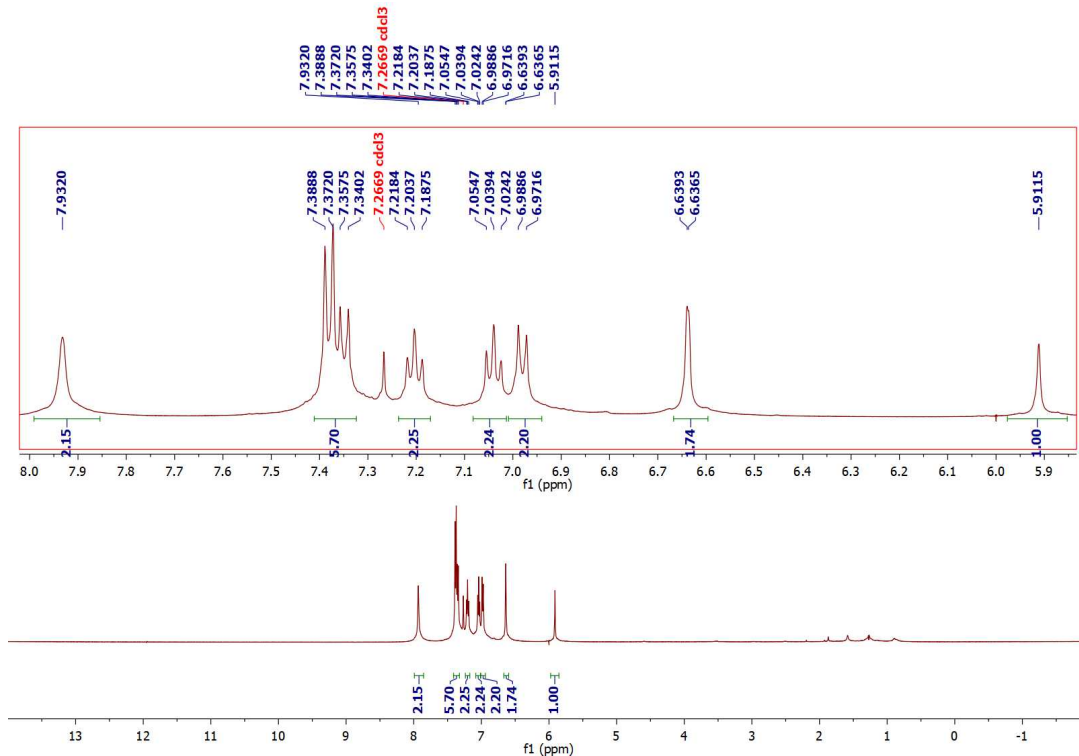
¹H NMR spectrum of 4-(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **9l**



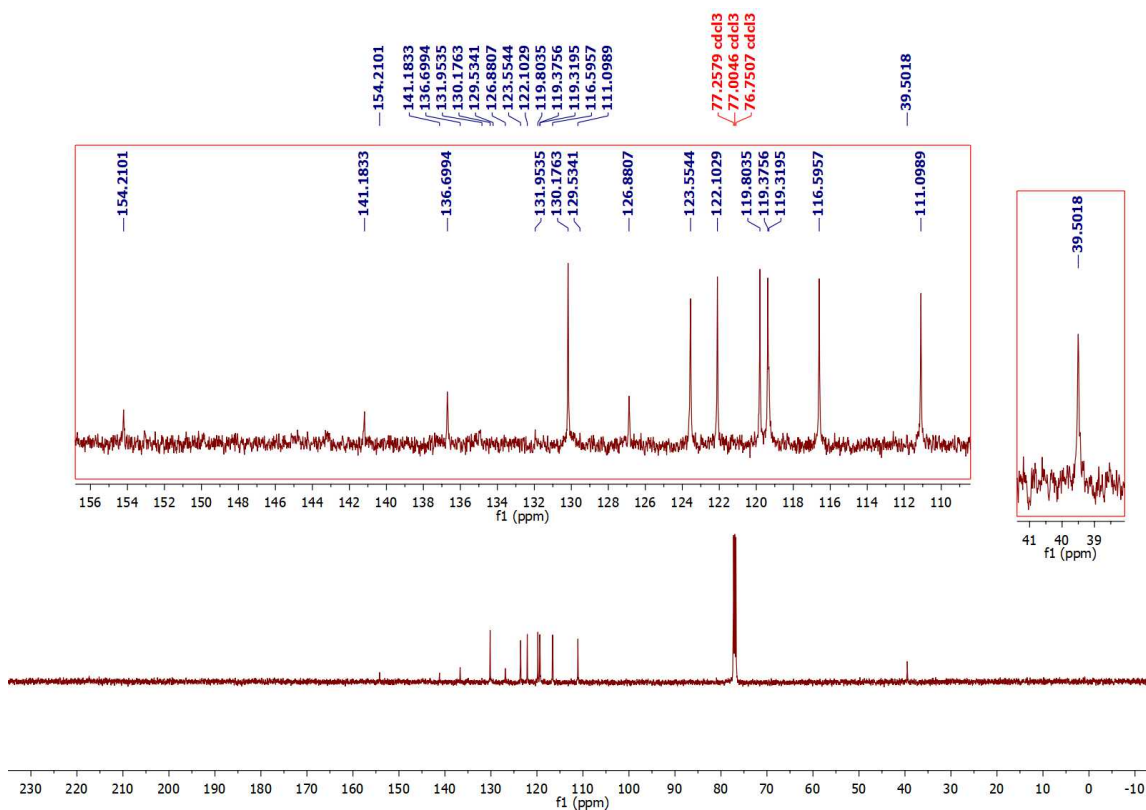
¹³C NMR spectrum of 4-(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **91**



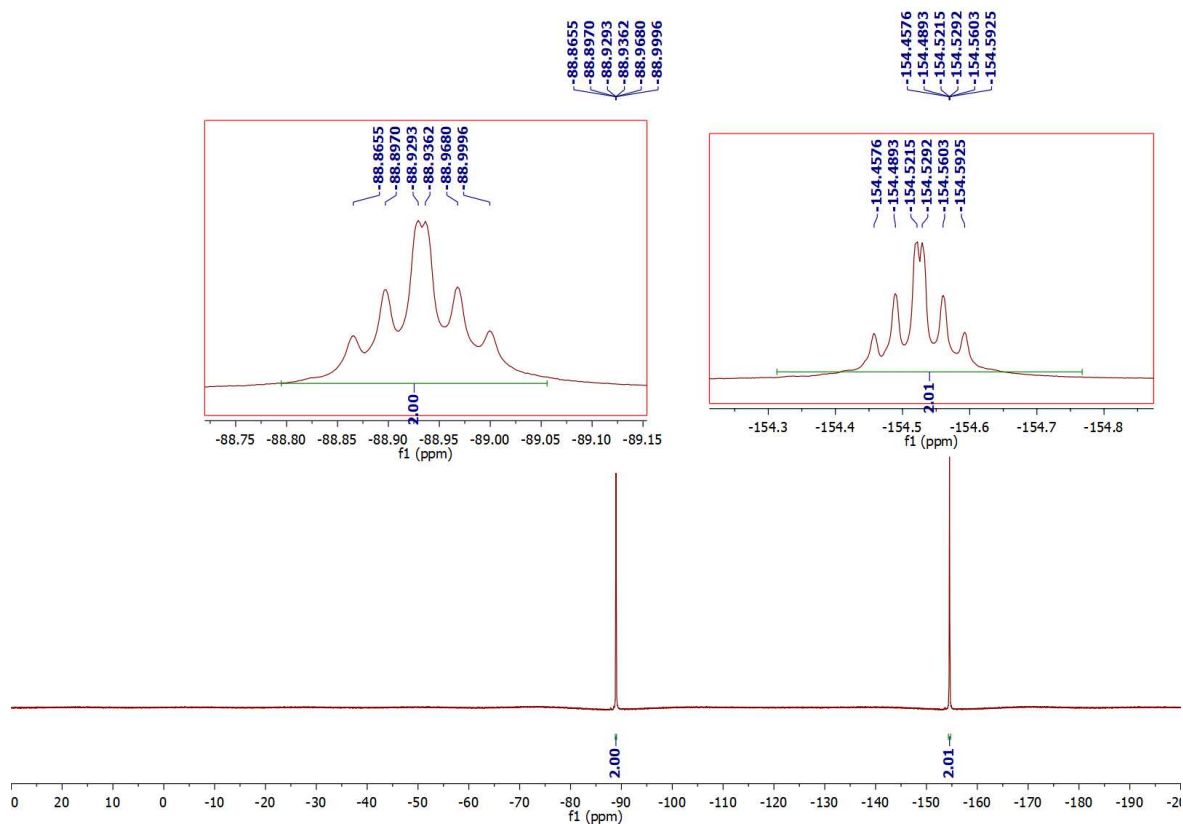
¹⁹F NMR spectrum of 4-(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **91**



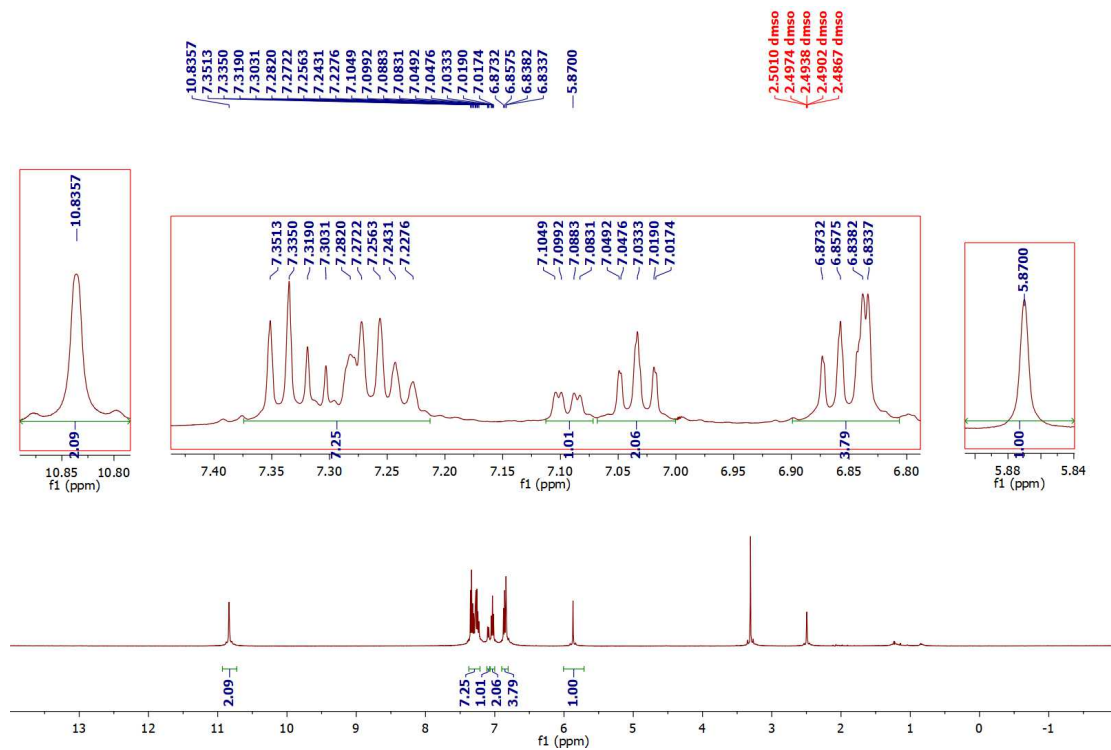
¹H NMR spectrum of 3,3'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9m**



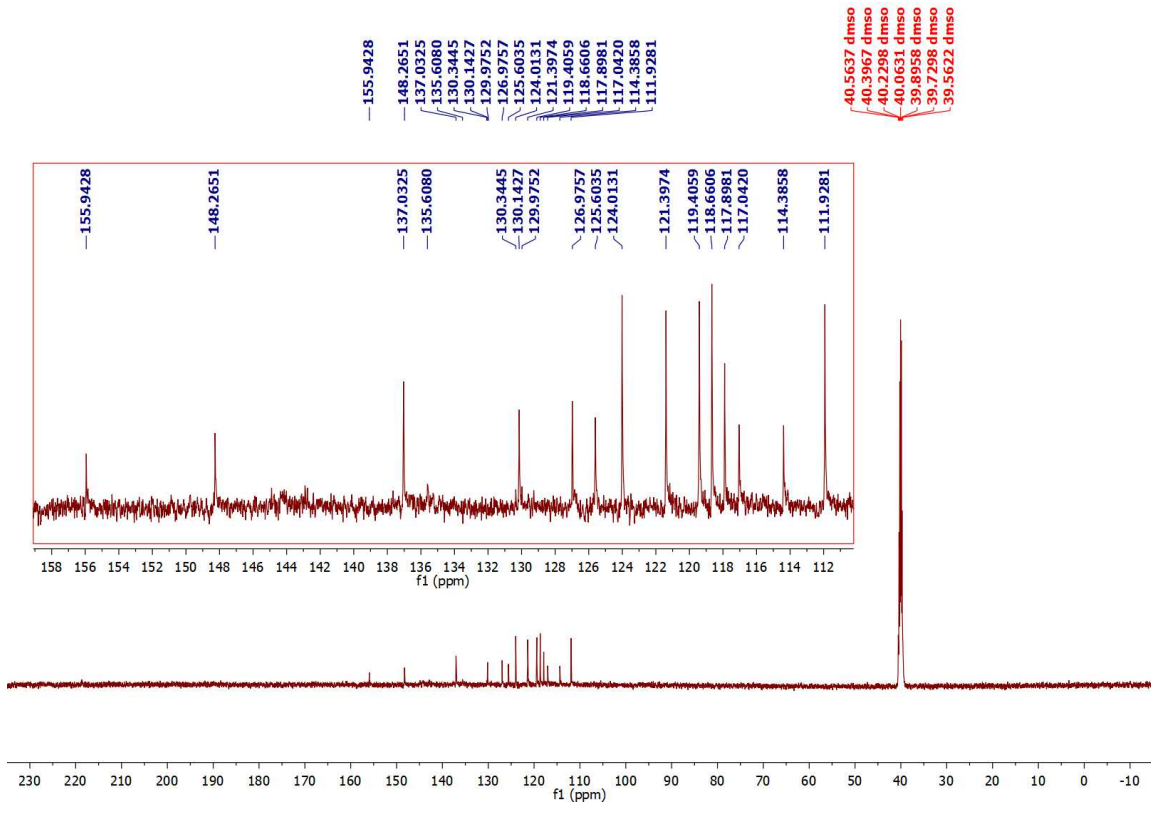
¹³C NMR spectrum of 3,3'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9m**



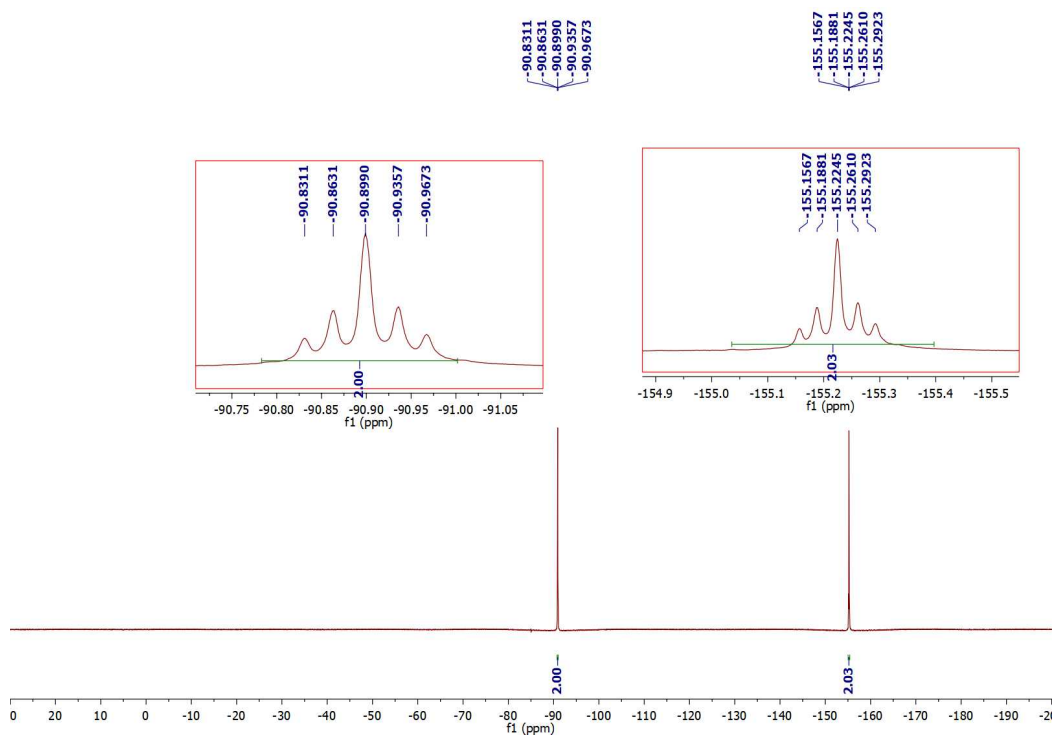
¹⁹F NMR spectrum of 3,3'-((4-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9m**



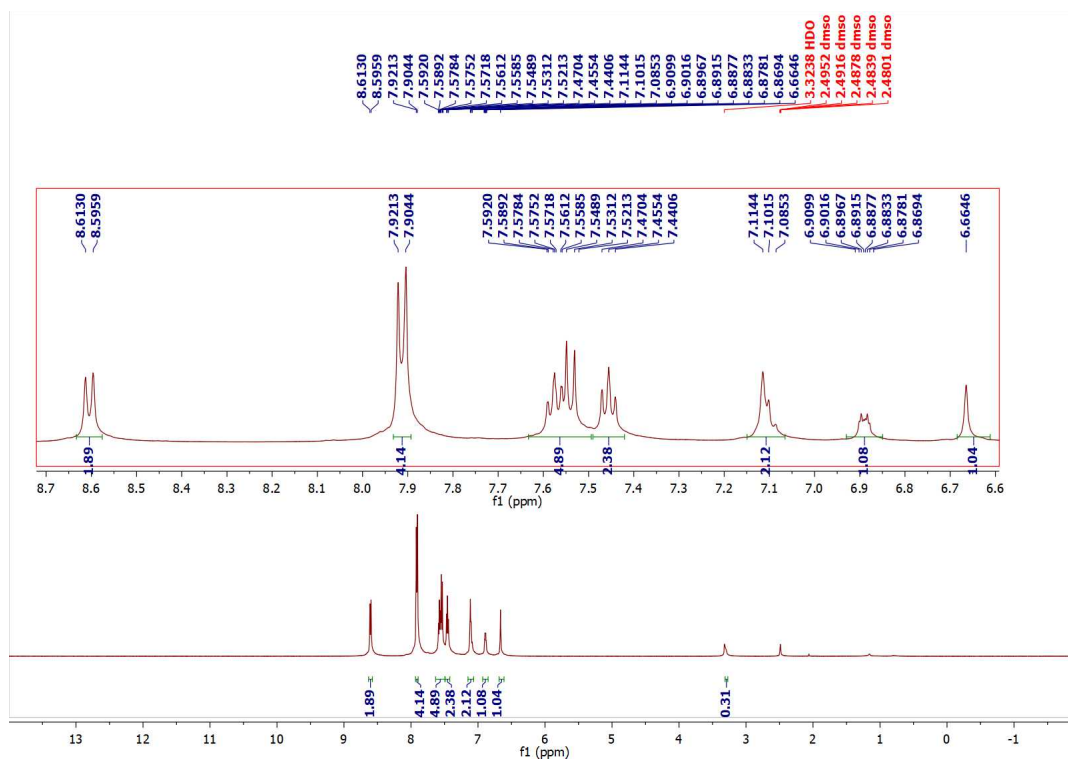
¹H NMR spectrum of 3,3'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9n**



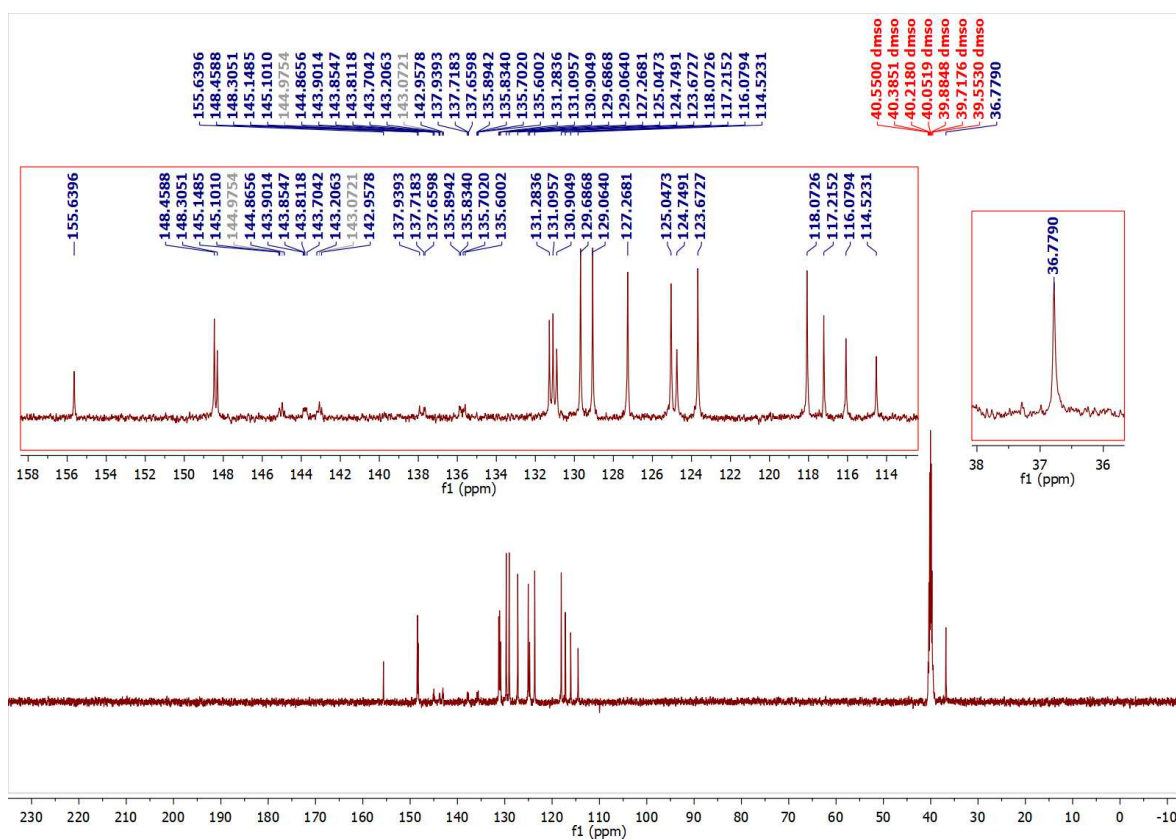
^{13}C NMR spectrum of 3,3'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9n**



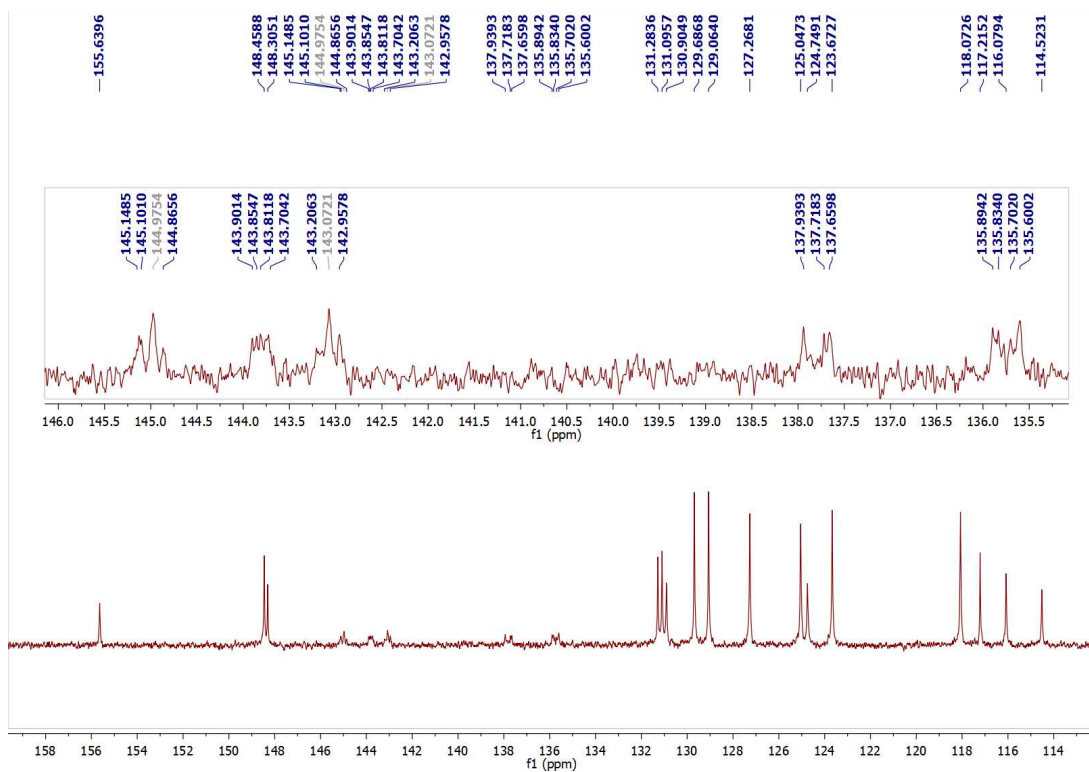
^{19}F NMR spectrum of 3,3'-((3-((perfluoropyridin-4-yl)oxy)phenyl)methylene)bis(1H-indole) **9n**



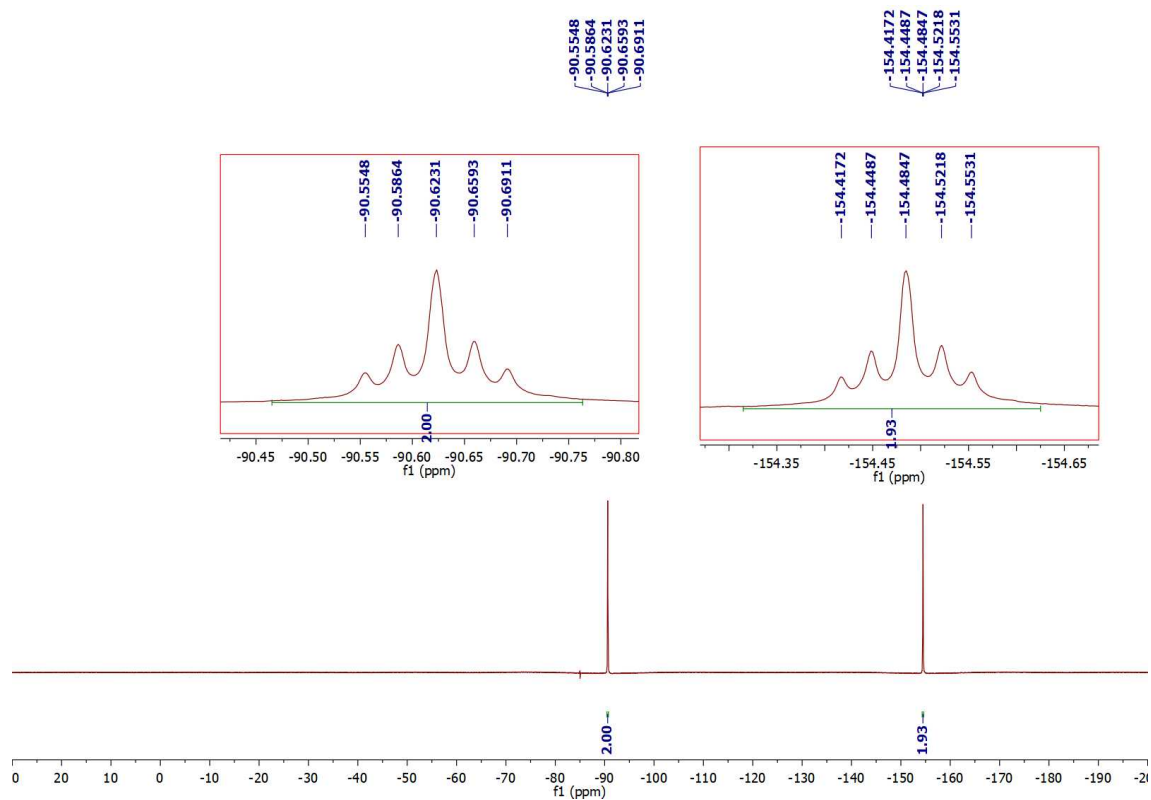
¹H NMR spectrum of 4-(3-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **9o**



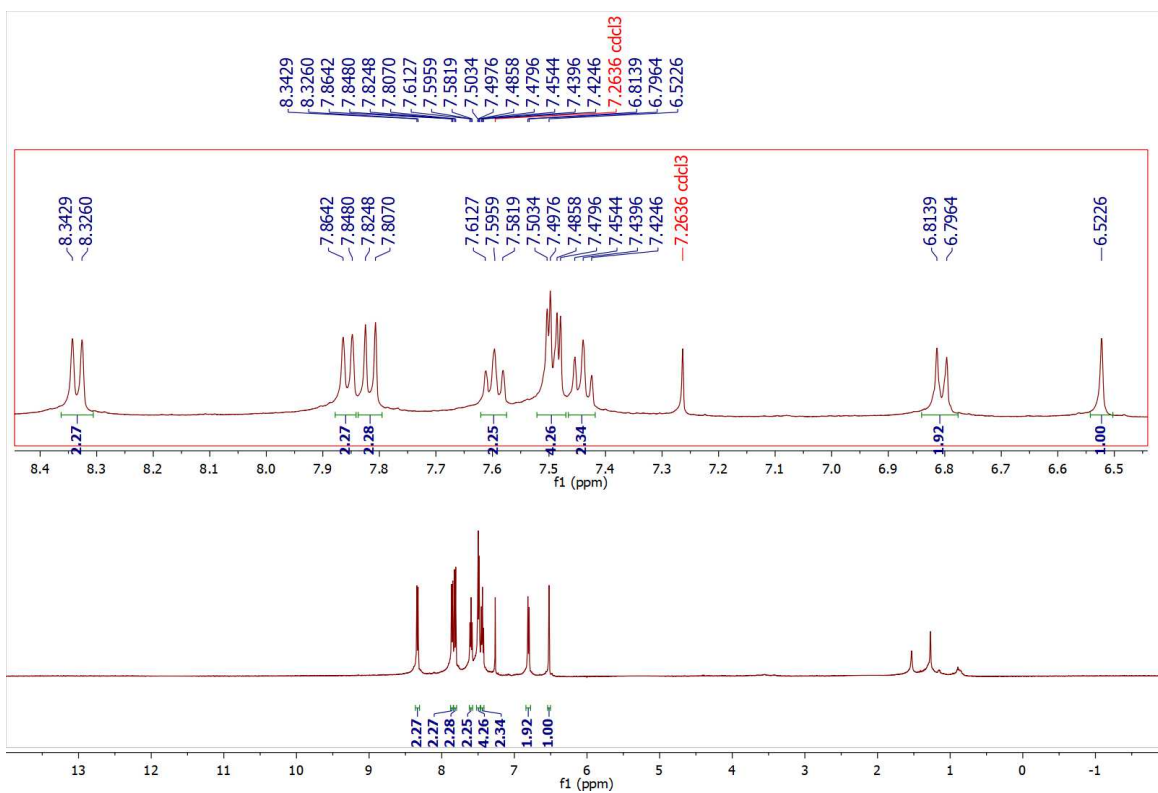
¹³C NMR spectrum of 4-(3-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **9o**



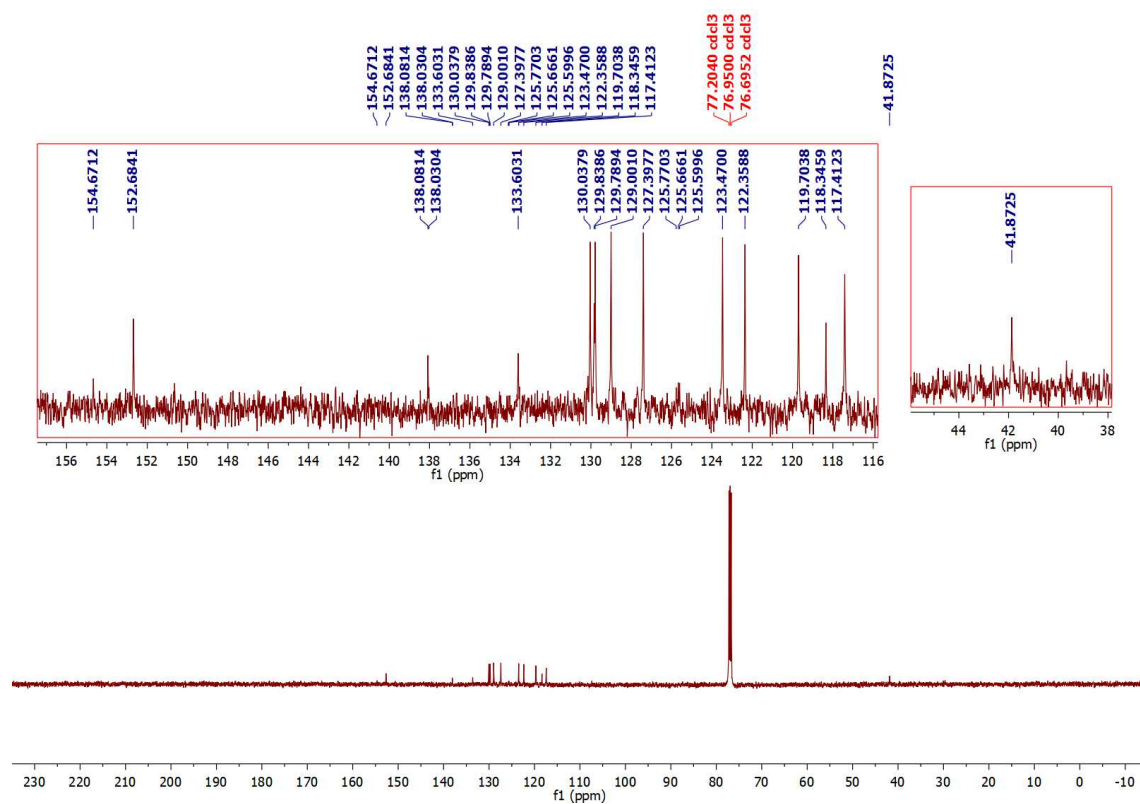
Expanded ^{13}C NMR spectrum of 4-(3-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **90**



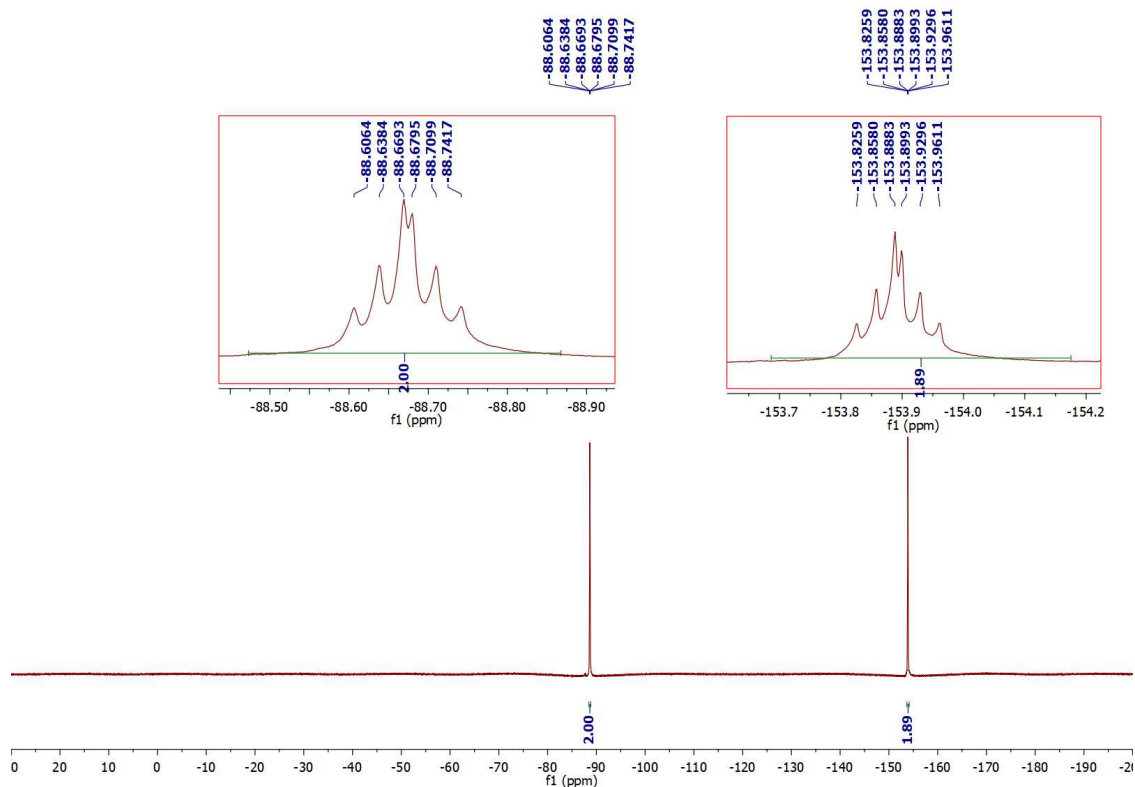
^{19}F NMR spectrum of 4-(3-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **90**



¹H NMR spectrum of 4-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **9p**

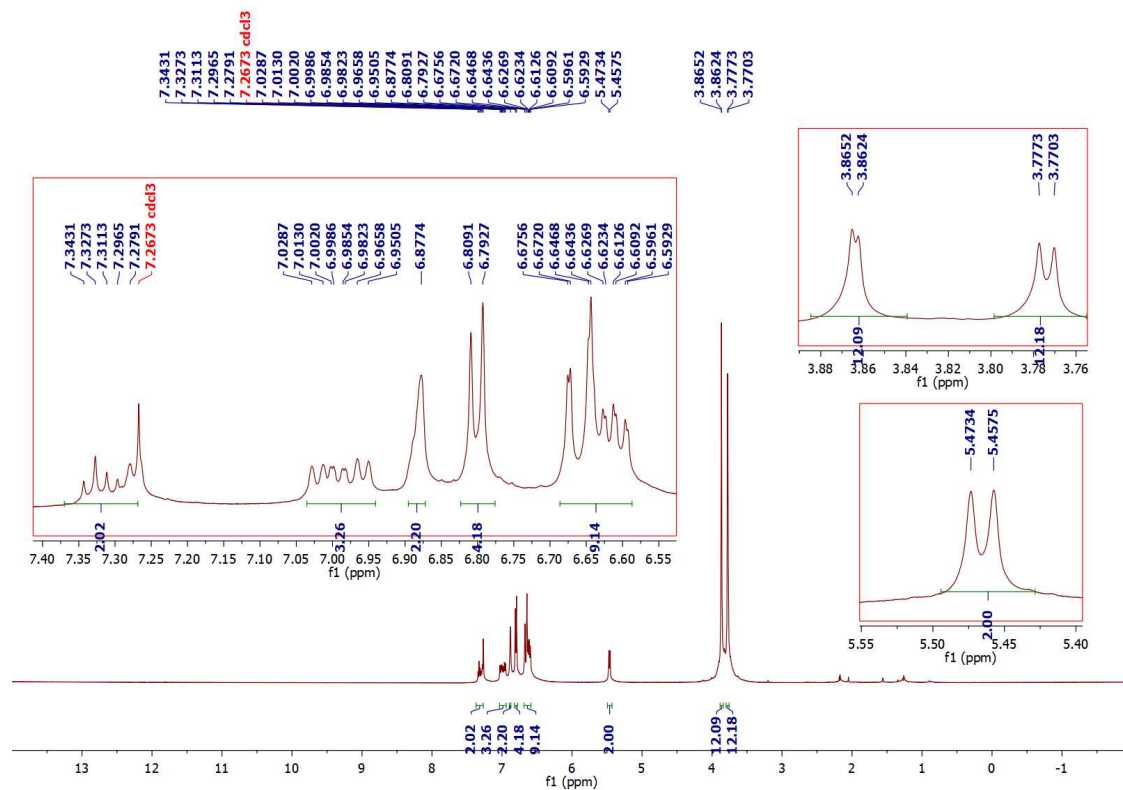


¹³C NMR spectrum of 4-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **9p**

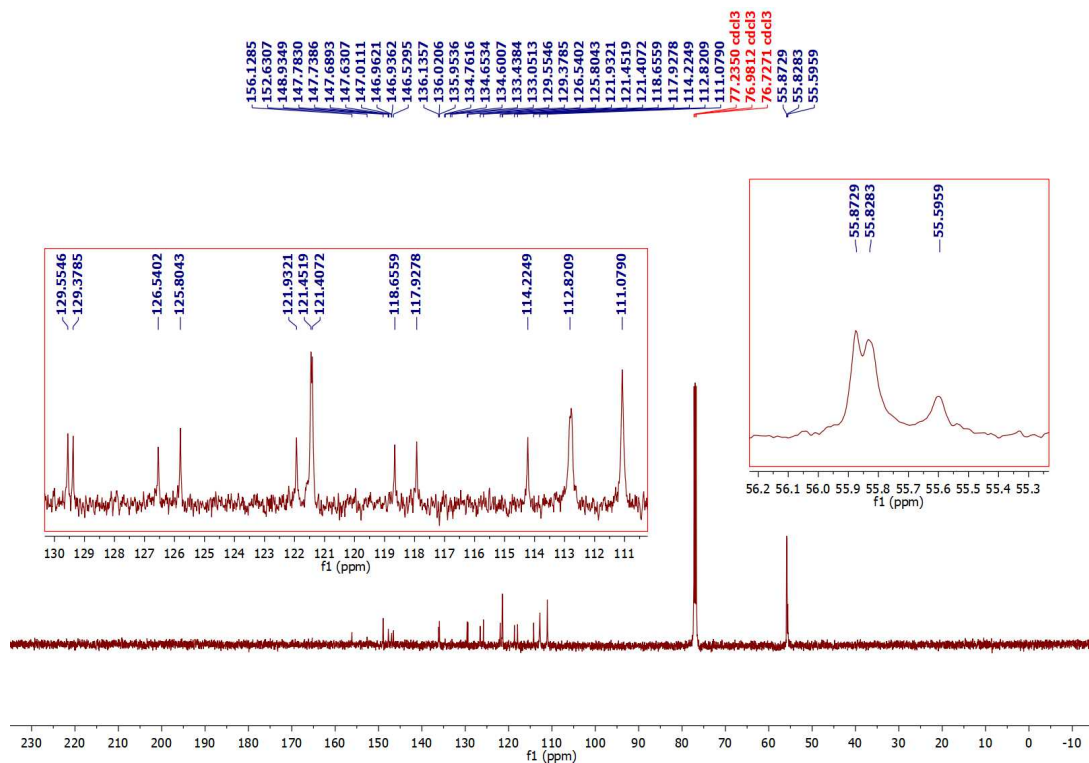


^{19}F NMR spectrum of 4-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenoxy)-2,3,5,6-tetrafluoropyridine **9p**

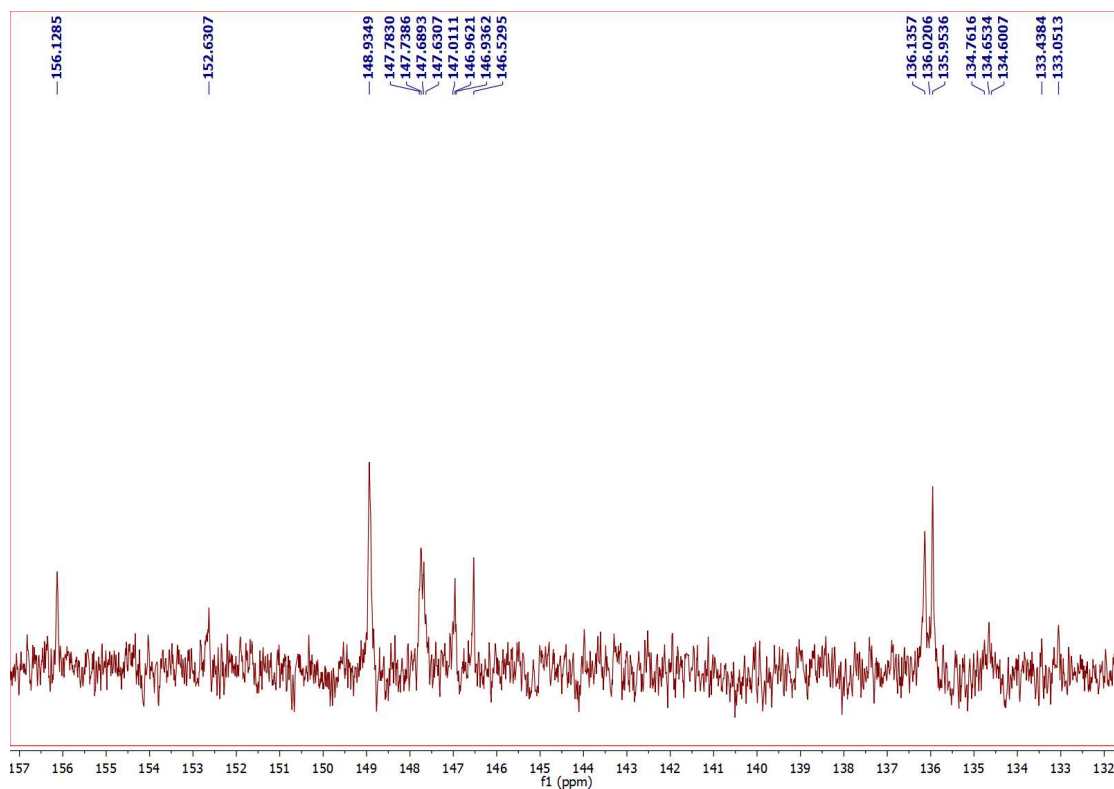
12. NMR spectra of synthesized bis- and tris-TRAMs containing perfluoropyridine subunits **10 a-g**



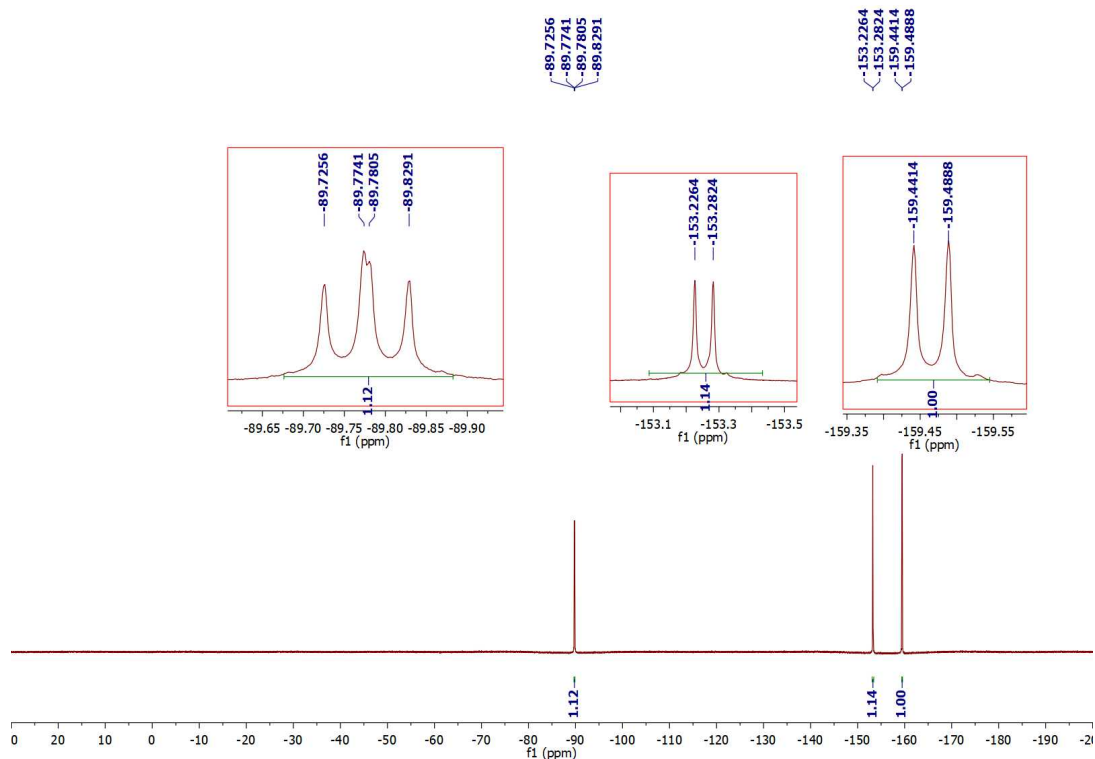
^1H NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10a**



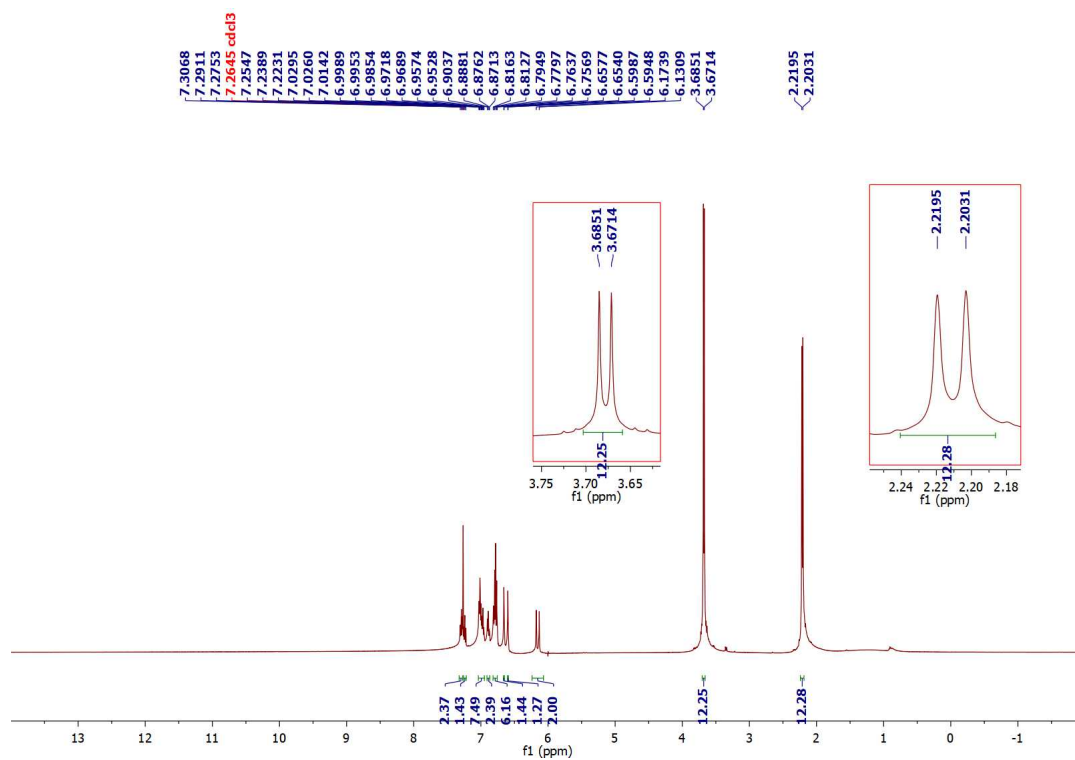
¹³C NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10a**



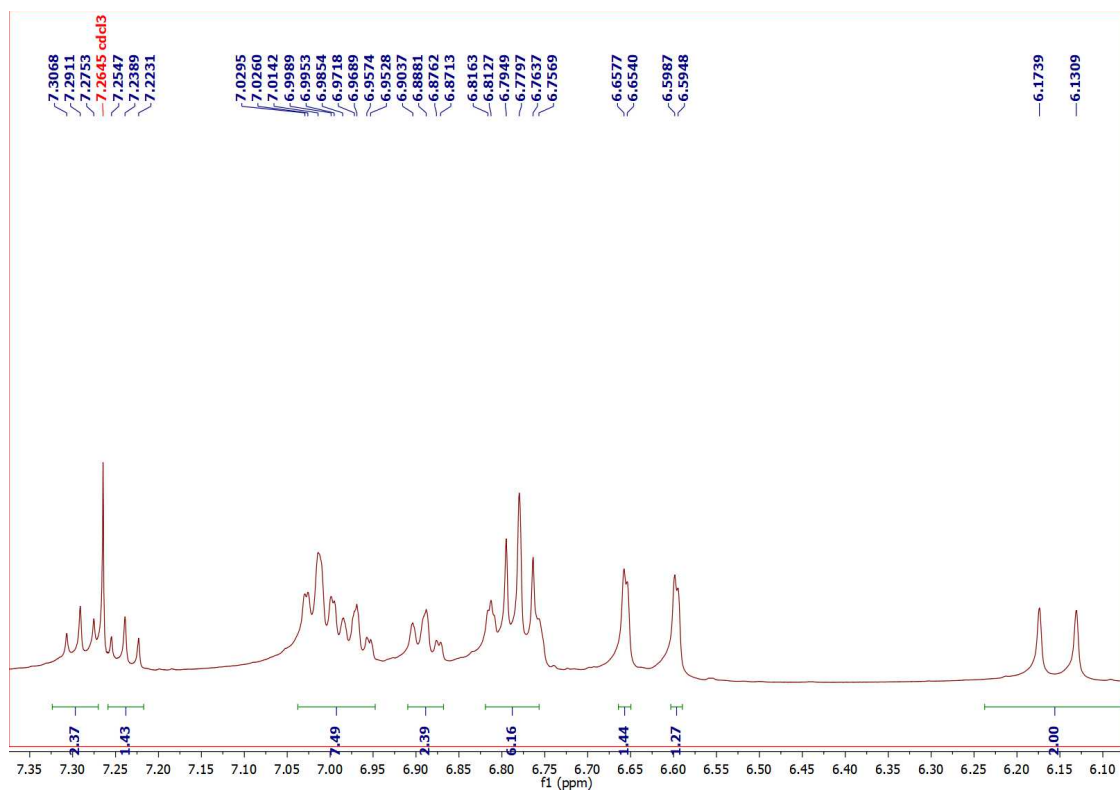
Expanded ¹³C NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10a**



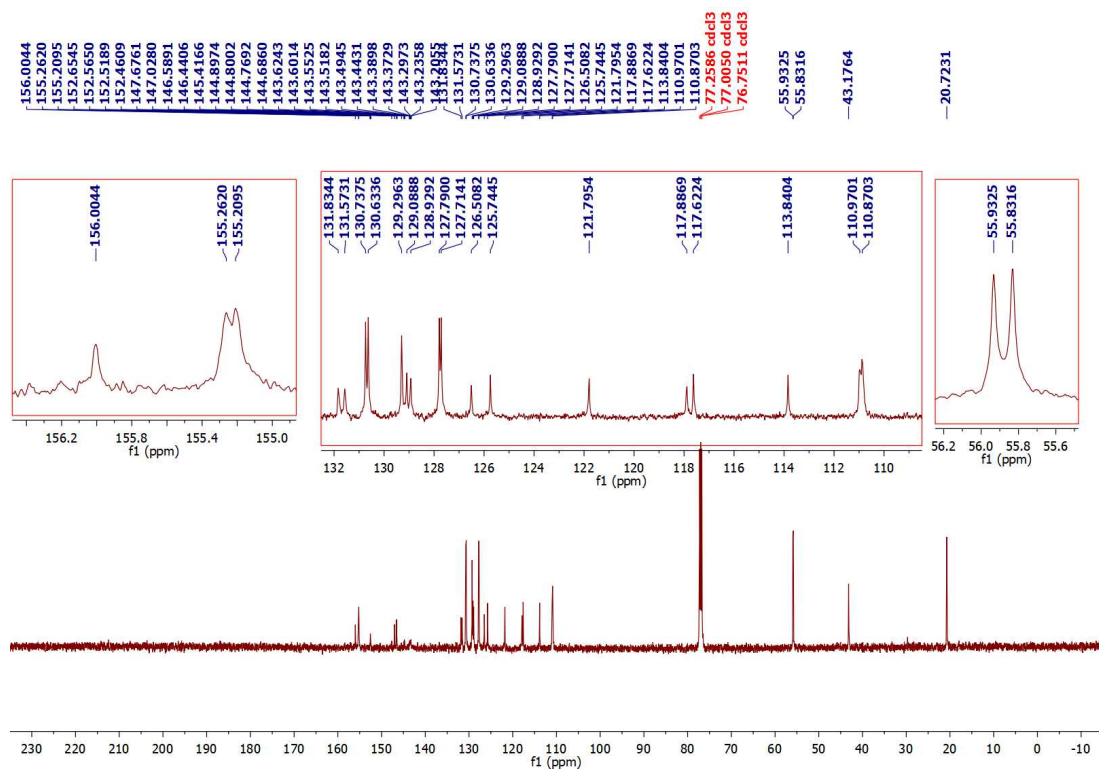
^{19}F NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10a**



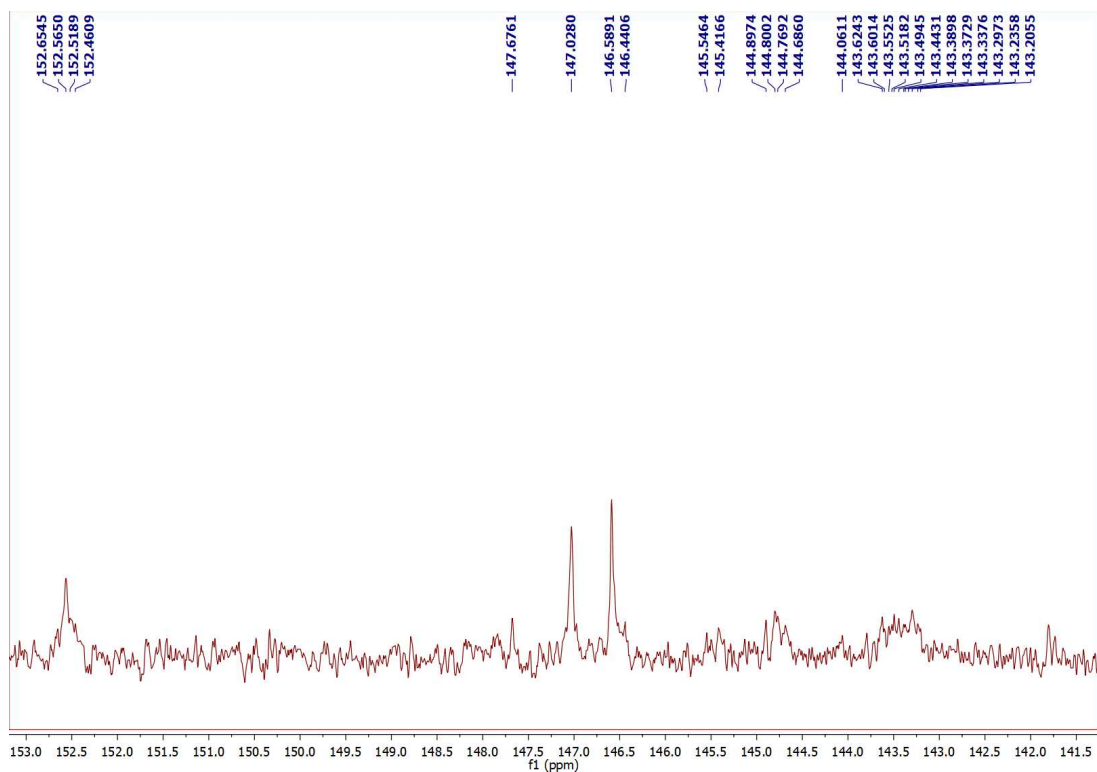
^1H NMR spectrum of 2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10b**



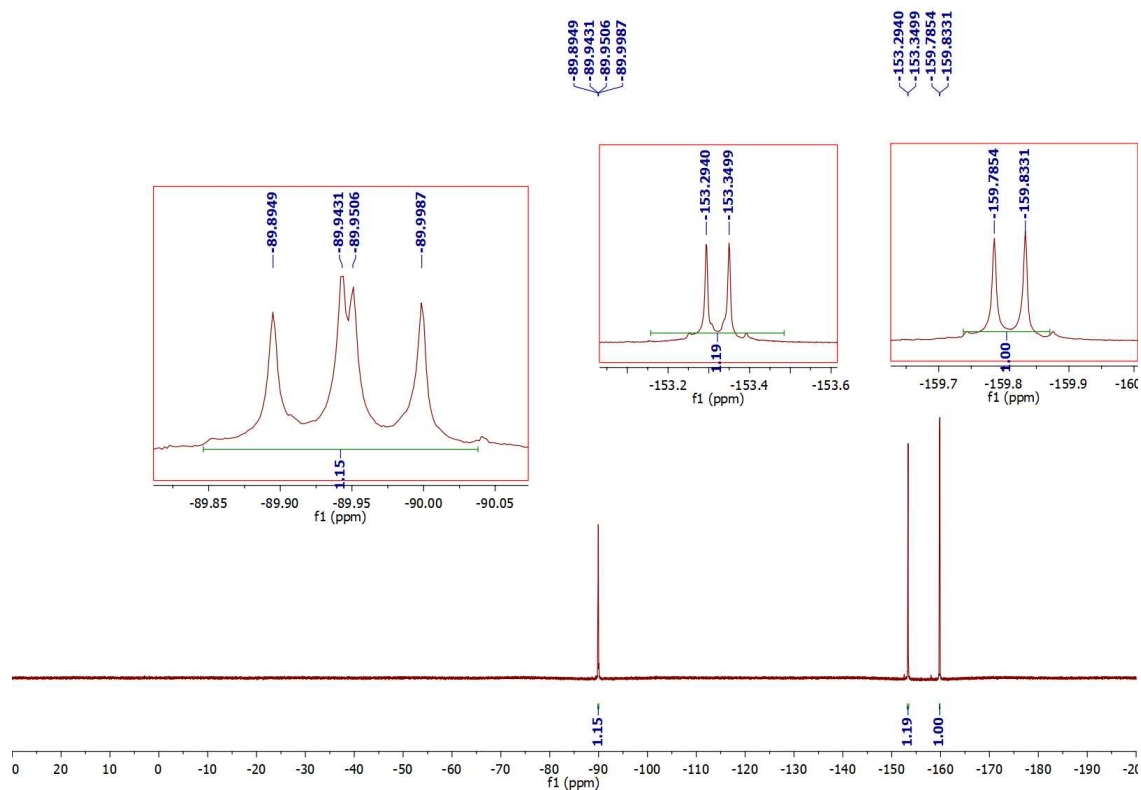
Expanded ¹H NMR spectrum of 2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10b**



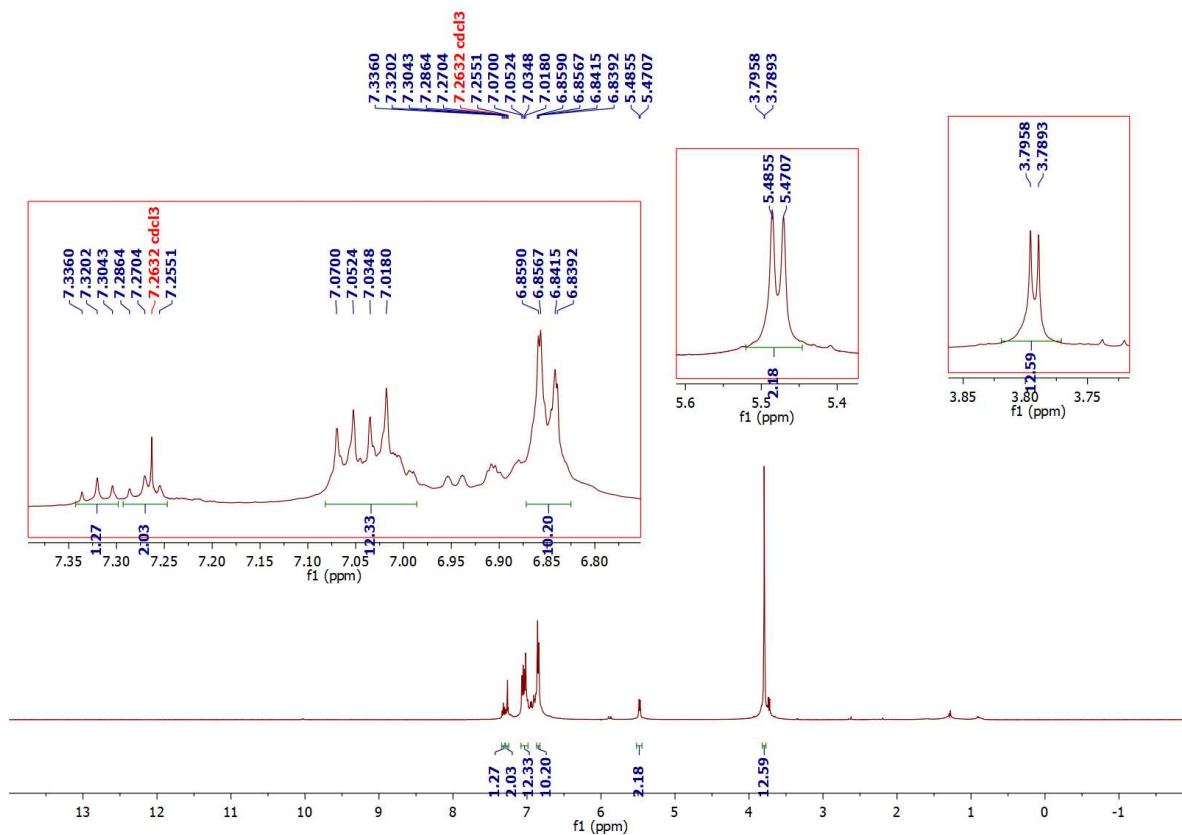
¹³C NMR spectrum of 2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10b**



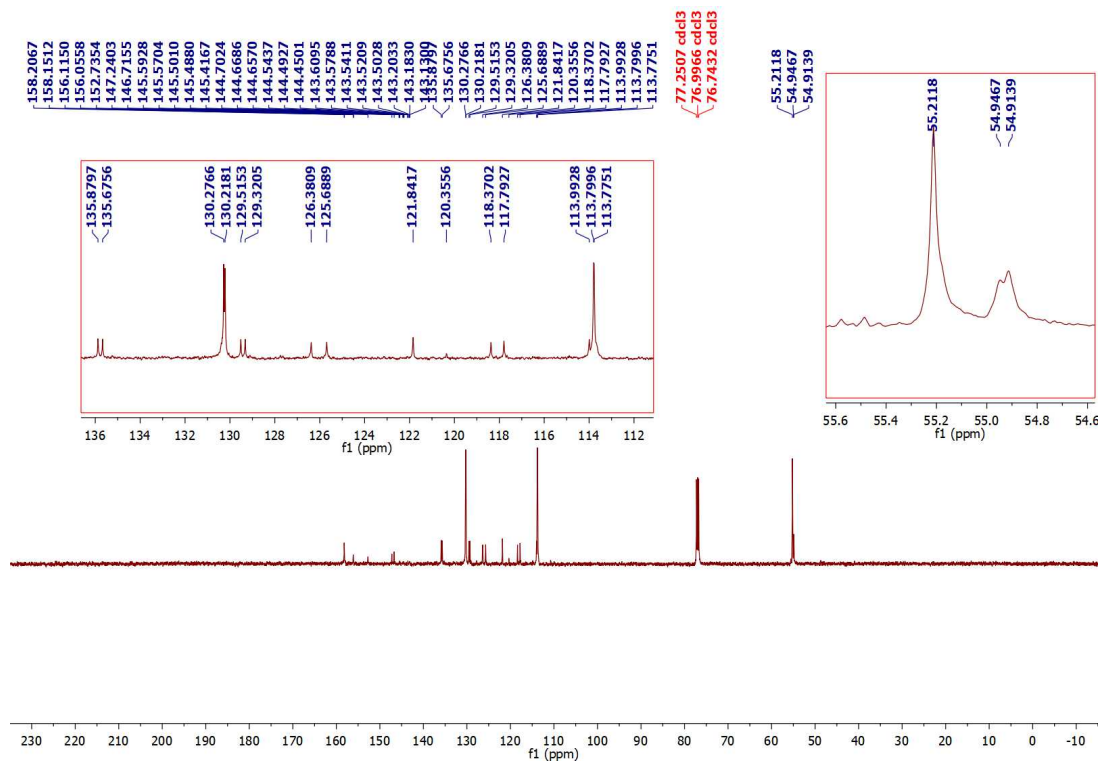
Expanded ^{13}C NMR spectrum of 2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10b**



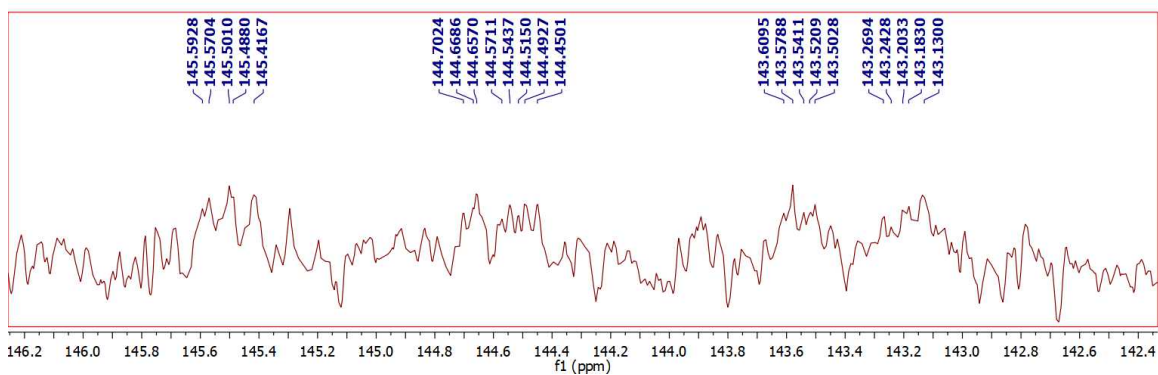
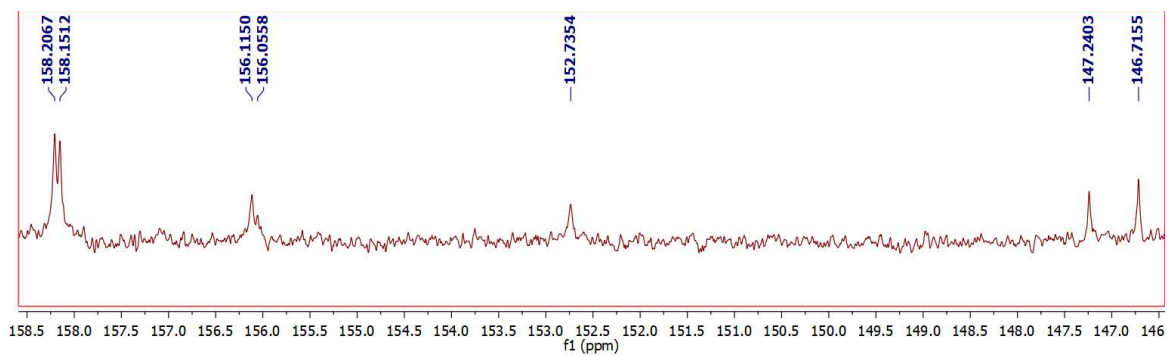
^{19}F NMR spectrum of 2,4-Bis(3-(bis(2-methoxy-5-methylphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10b**



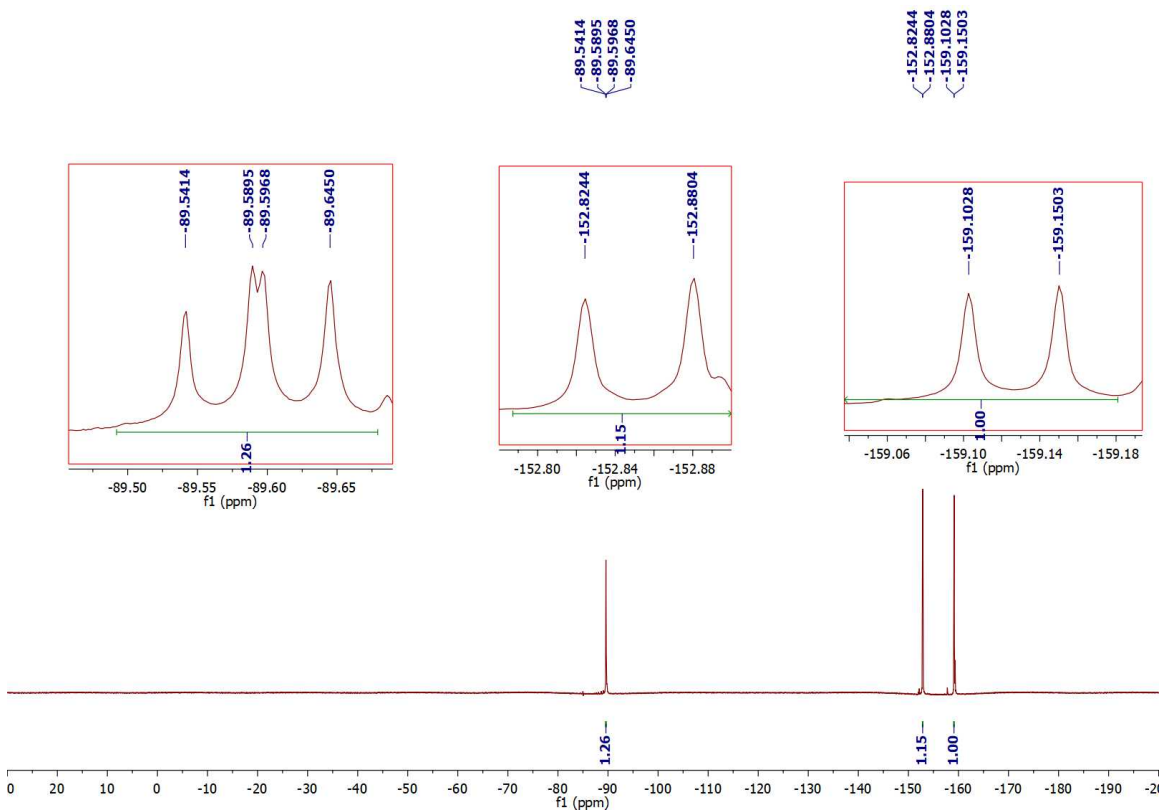
¹H NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10c**



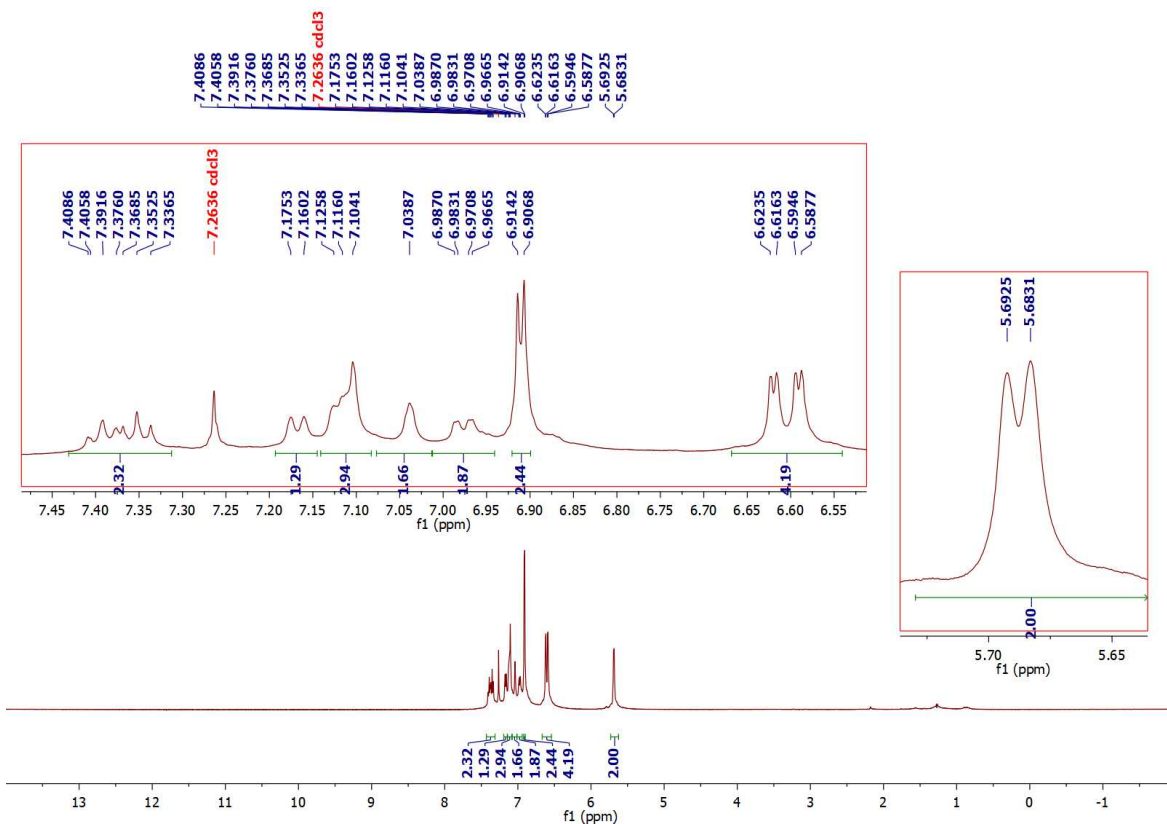
¹³C NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10c**



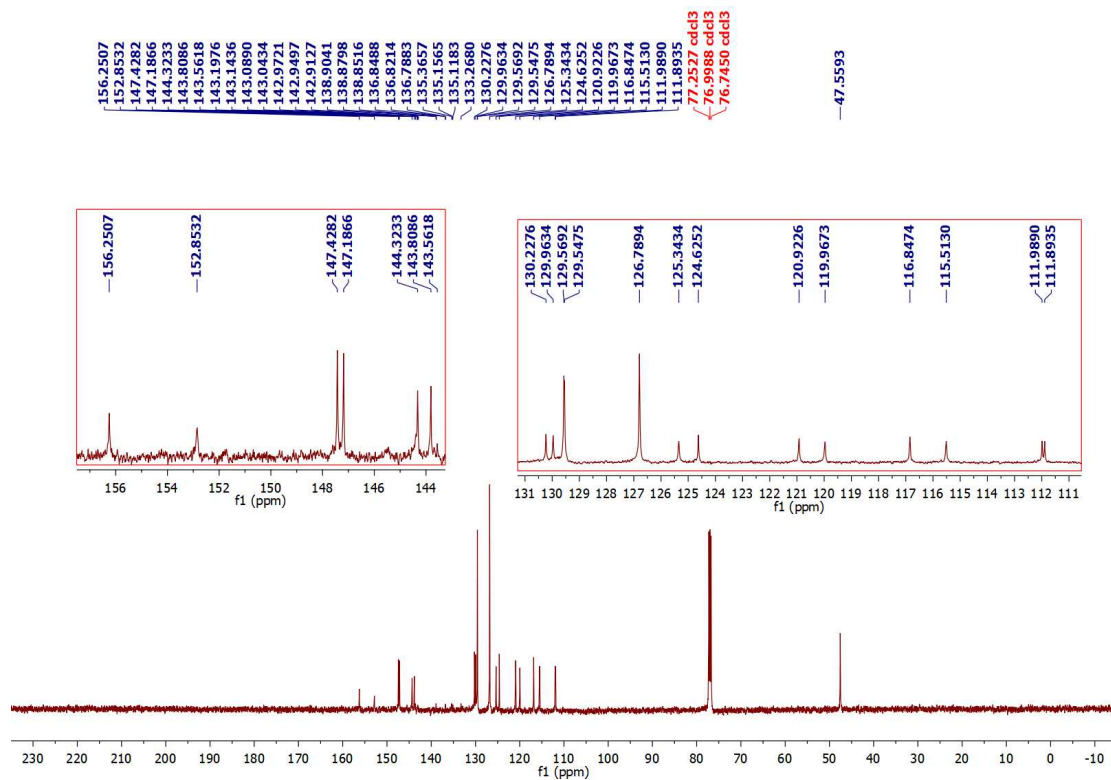
Expanded ¹³C NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10c**



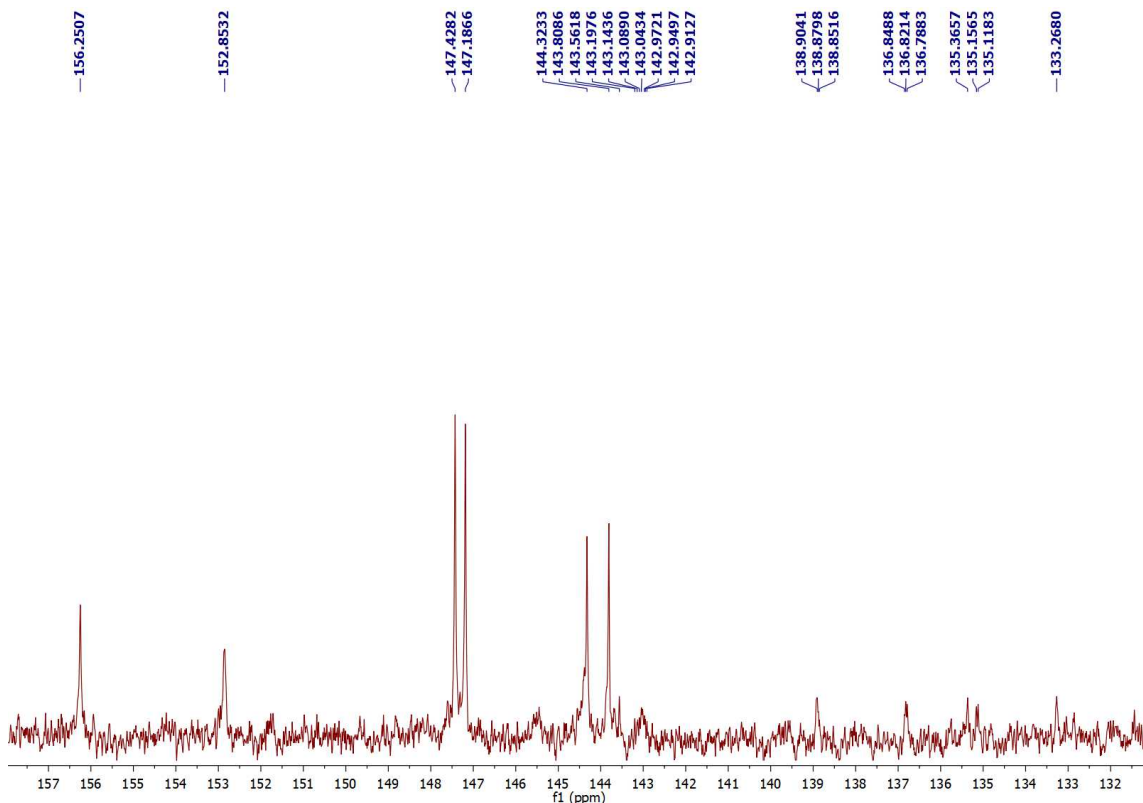
¹⁹F NMR spectrum of 2,4-Bis(3-(bis(4-methoxyphenyl)methyl)phenoxy)-3,5,6-trifluoropyridine **10c**



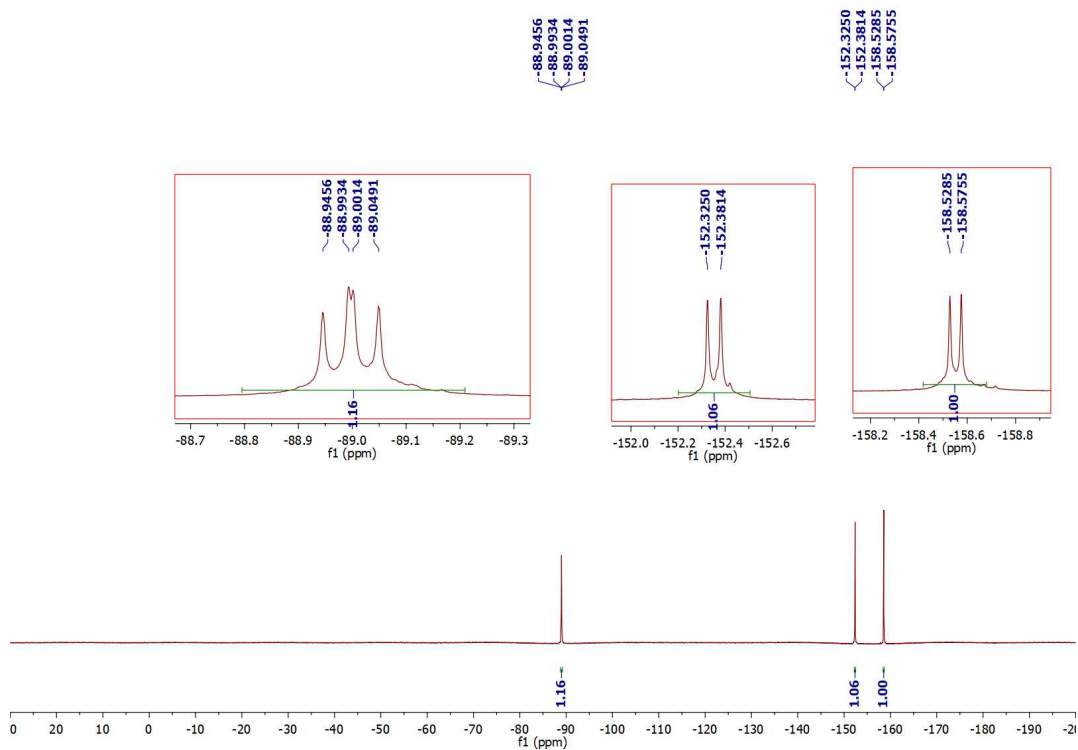
¹H NMR spectrum of 2,4-Bis(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-3,5,6-trifluoropyridine **10d**



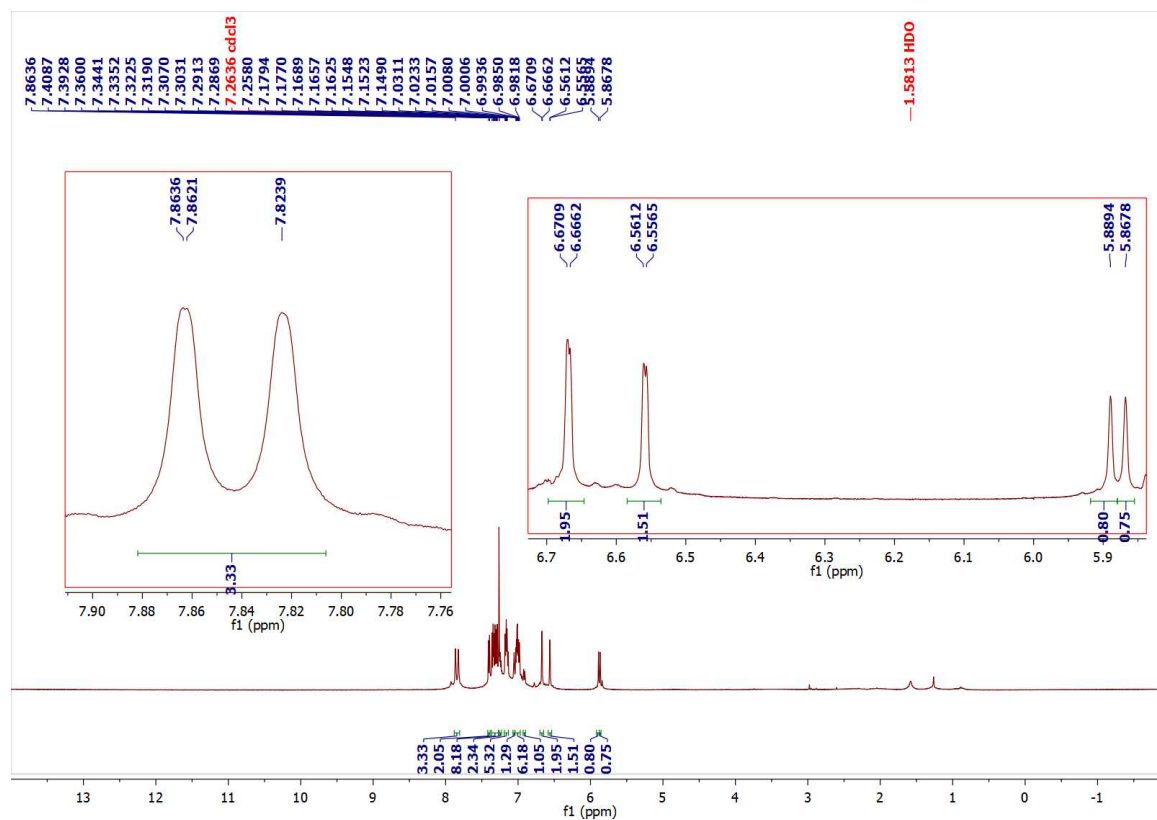
¹³C NMR spectrum of 2,4-Bis(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-3,5,6-trifluoropyridine **10d**



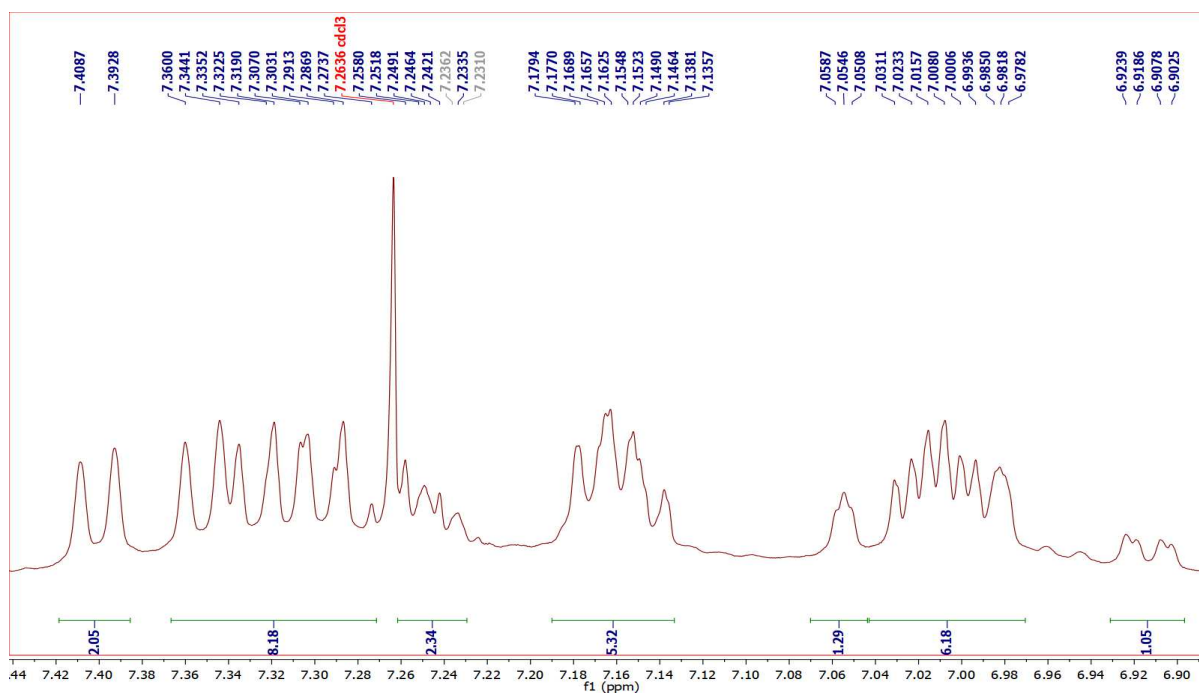
Expanded ^{13}C NMR spectrum of 2,4-Bis(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-3,5,6-trifluoropyridine **10d**



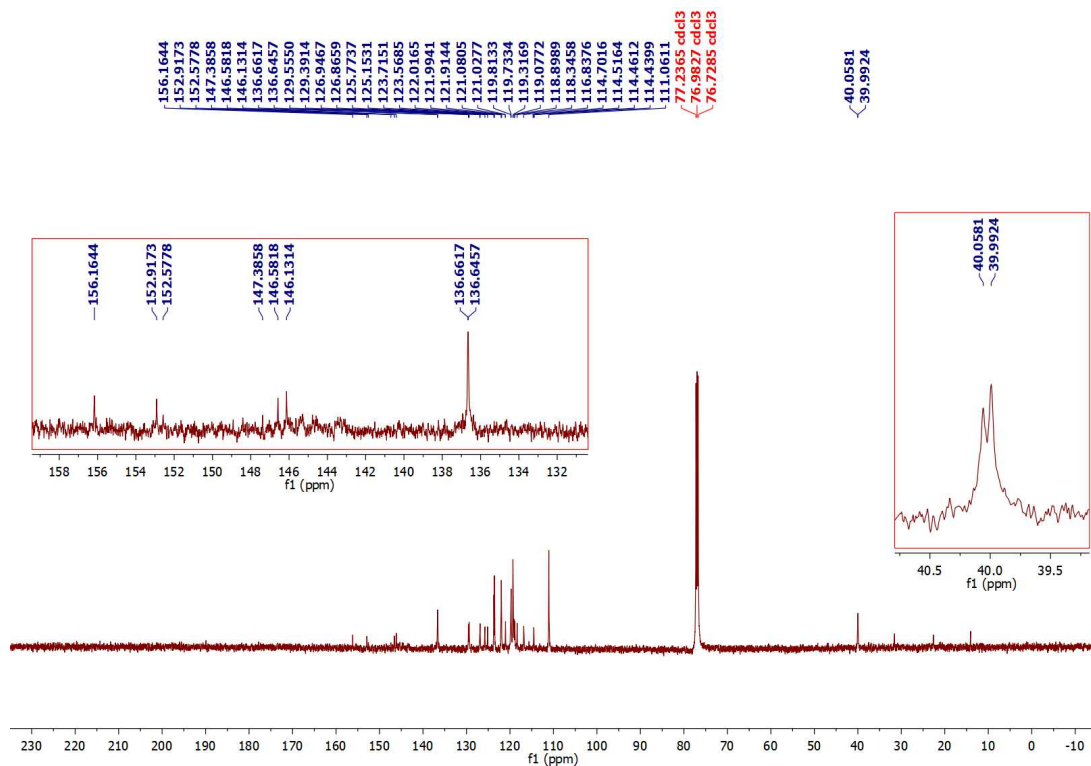
^{19}F NMR spectrum of 2,4-Bis(3-(bis(5-bromothiophen-2-yl)methyl)phenoxy)-3,5,6-trifluoropyridine **10d**



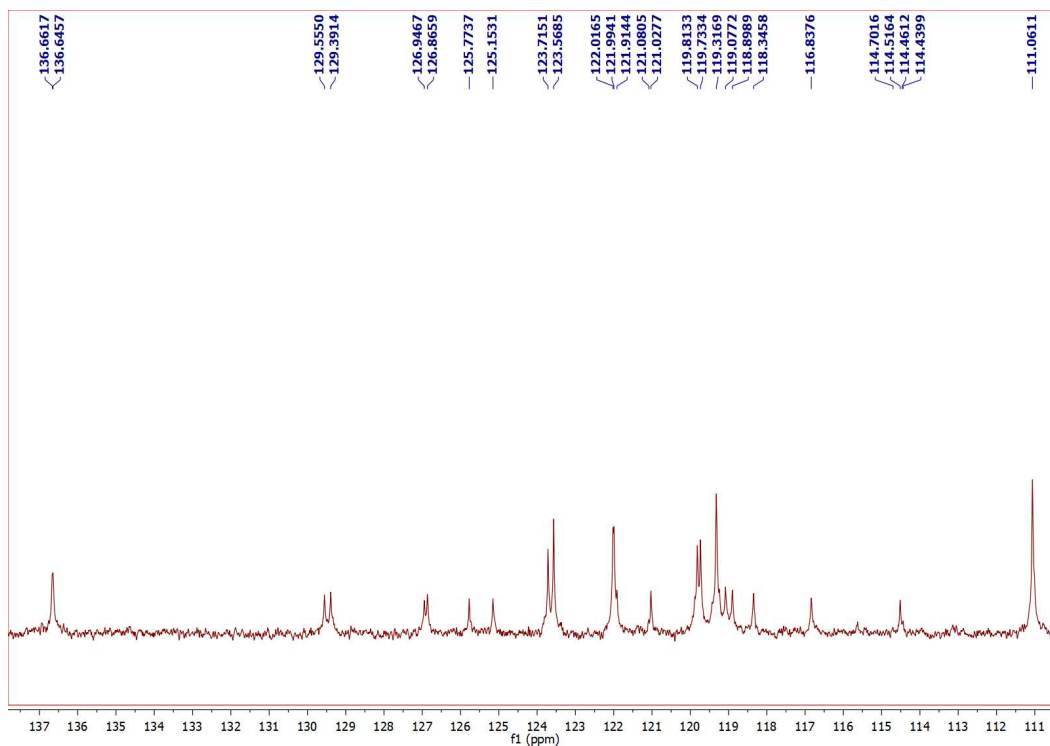
^1H NMR spectrum of 3,3',3'',3'''-((((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl))tetrakis(1H-indole) **10e**



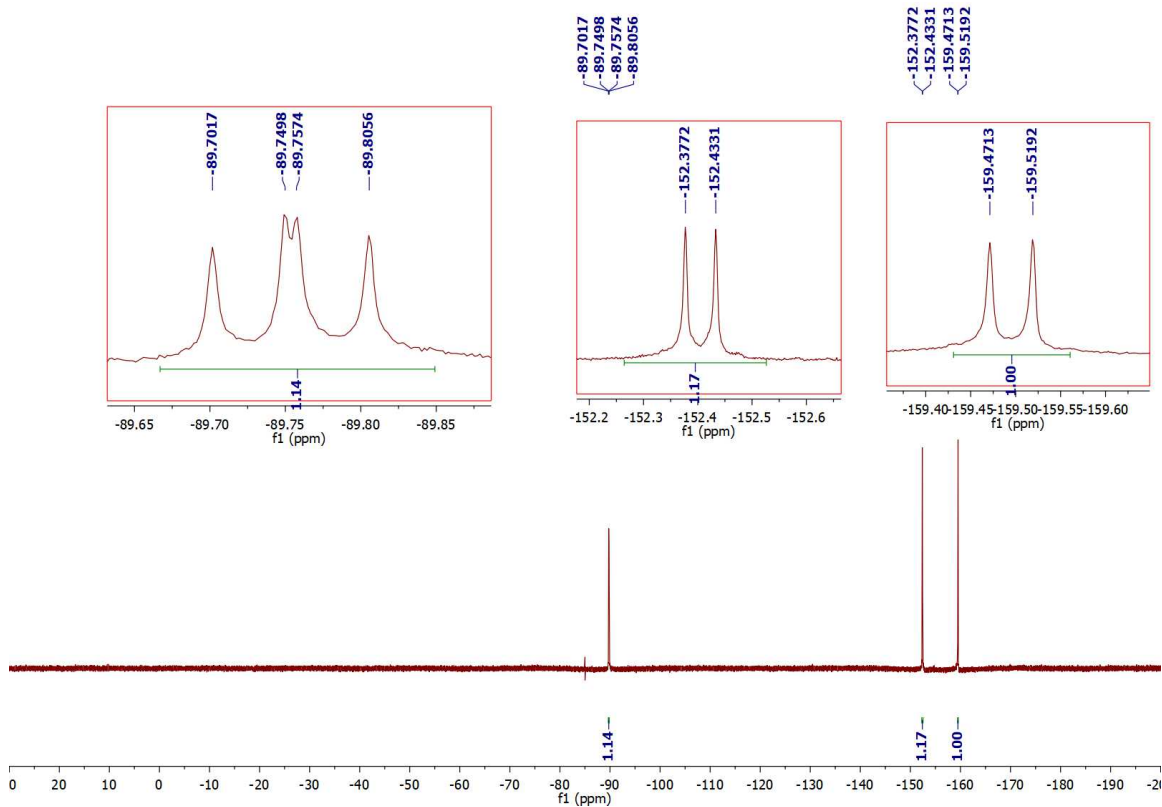
Expanded ^1H NMR spectrum of 3,3',3'',3'''-((((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl))tetrakis(1H-indole) **10e**



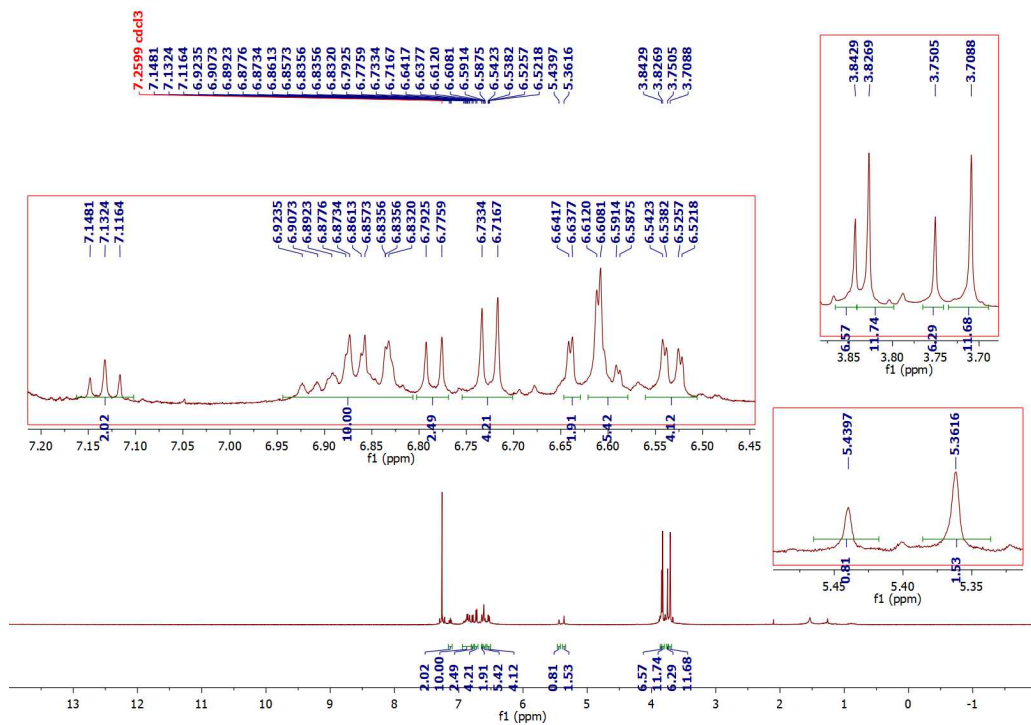
^{13}C NMR spectrum of 3,3',3'',3'''-(((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl)tetrakis(1H-indole) **10e**



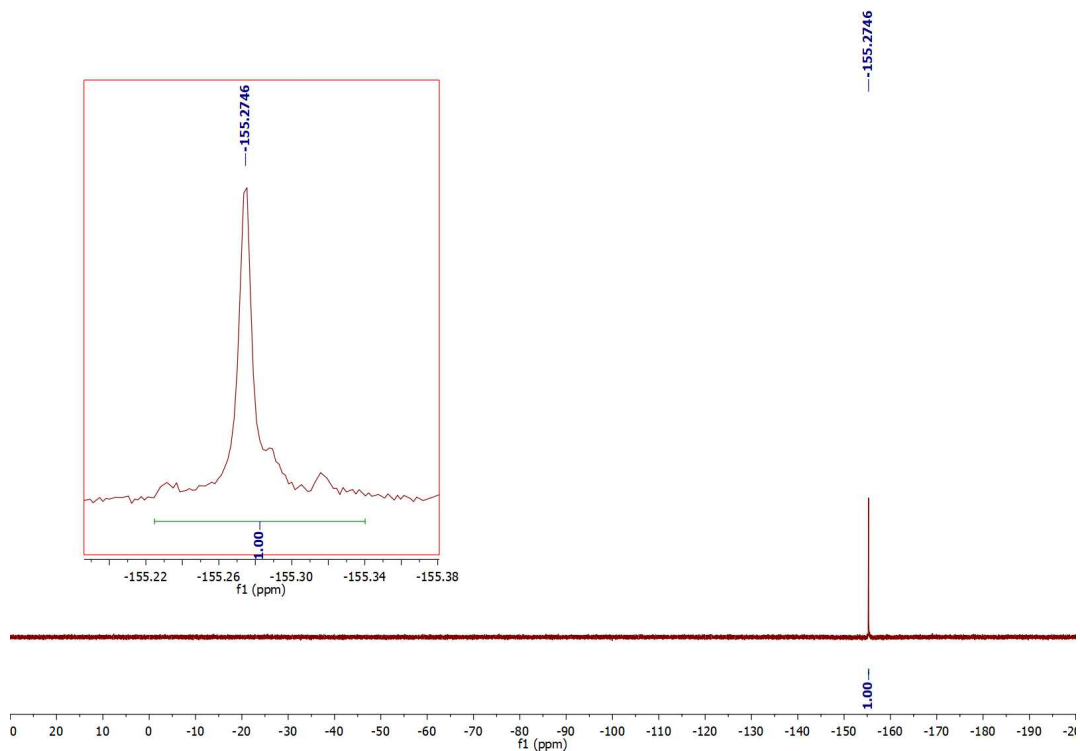
Expanded ^{13}C NMR spectrum of 3,3',3'',3'''-(((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl)tetrakis(1H-indole) **10e**



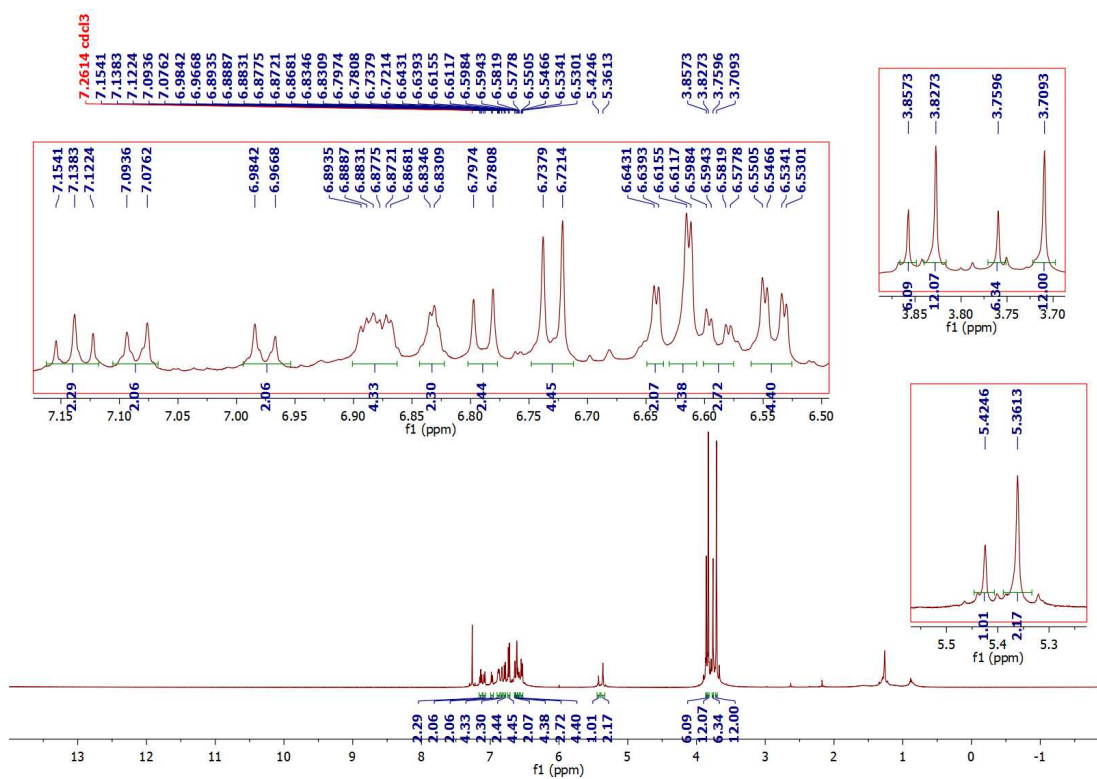
^{19}F NMR spectrum of 3,3',3'',3'''-(((3,5,6-Trifluoropyridine-2,4-diyl)bis(oxy))bis(3,1-phenylene))bis(methanetriyl))tetrakis(1H-indole) **10e**



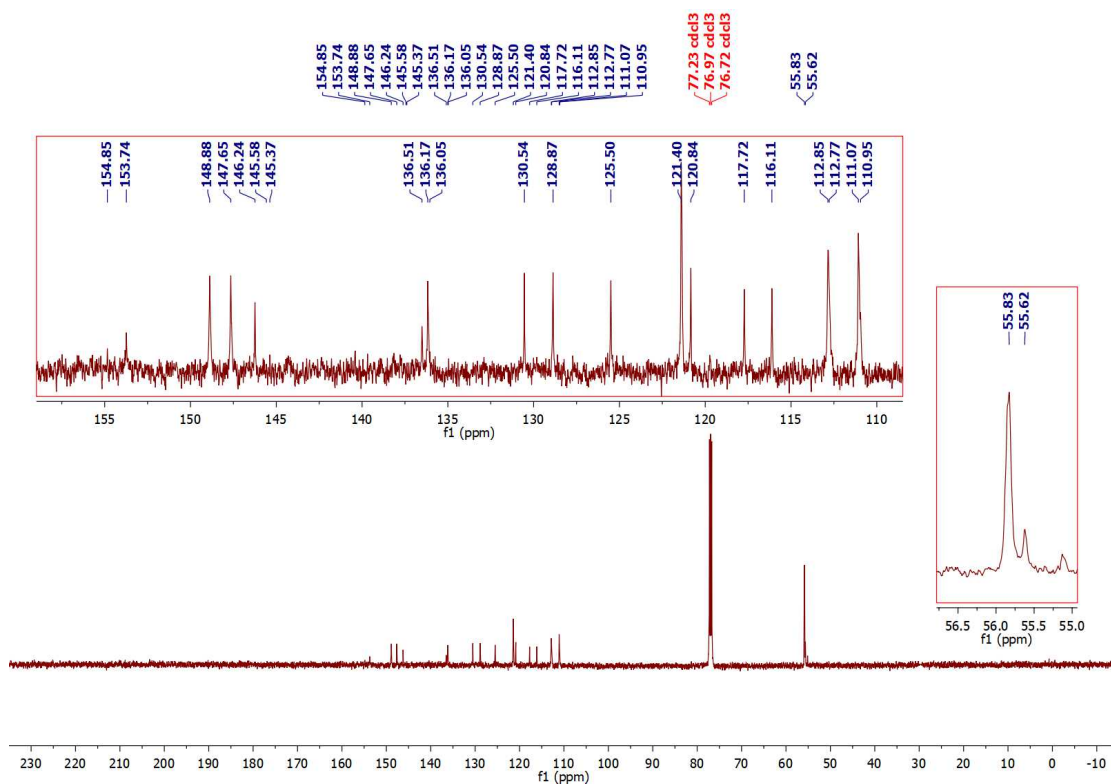
^1H NMR spectrum of 2,4,6-Tris(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine **10f**



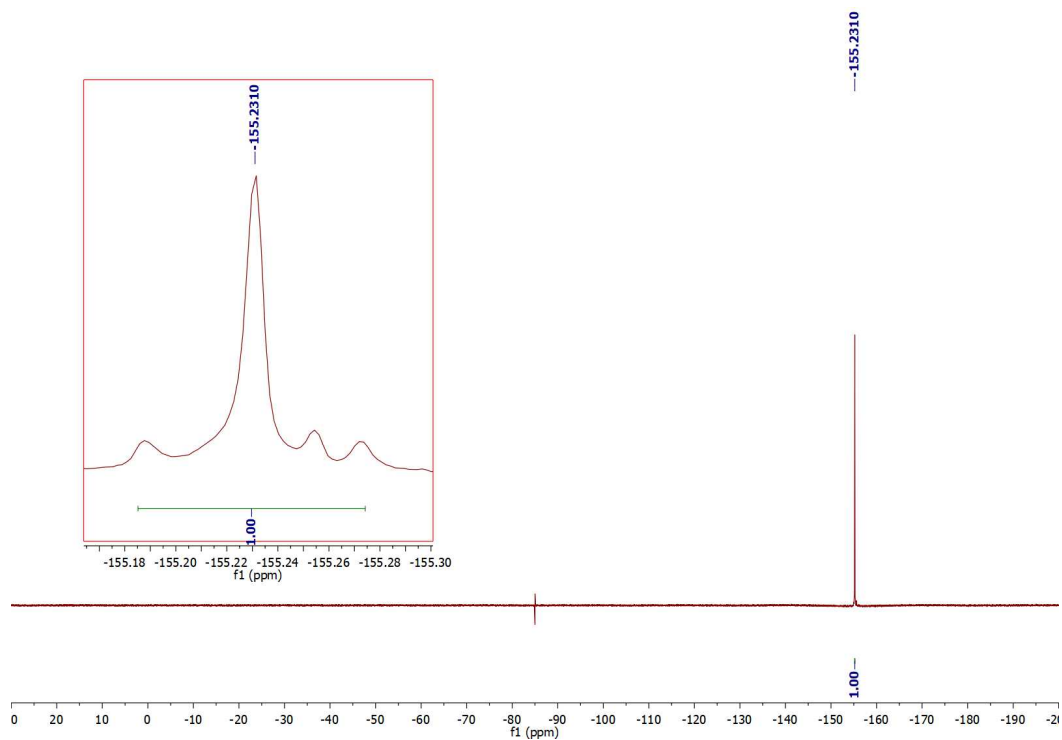
^{19}F NMR spectrum of 2,4,6-Tris(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine **10f**



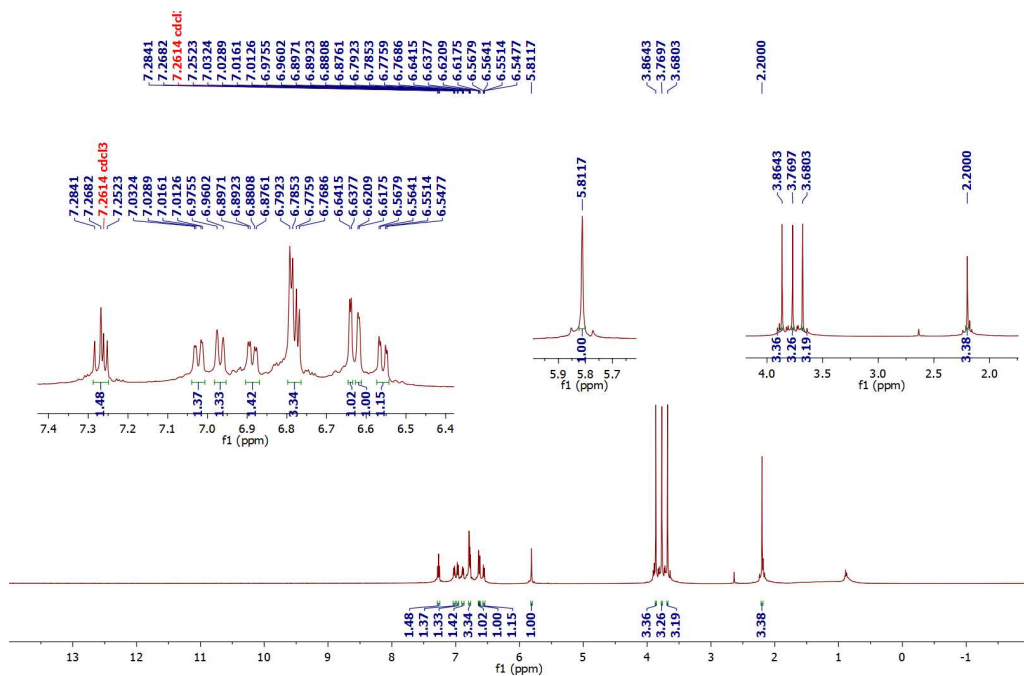
^1H NMR spectrum of 2,6-Bis(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine **10g**



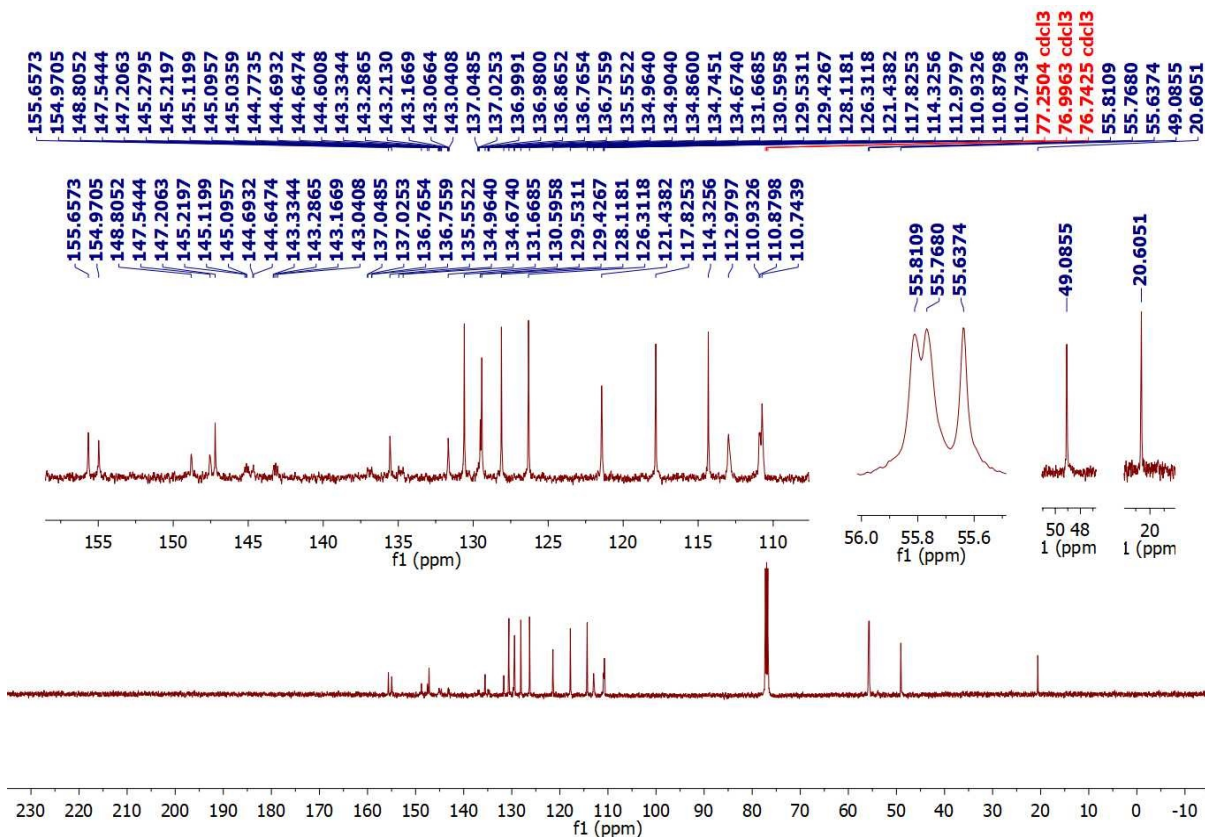
¹³C NMR spectrum of 2,6-Bis(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine **10g**



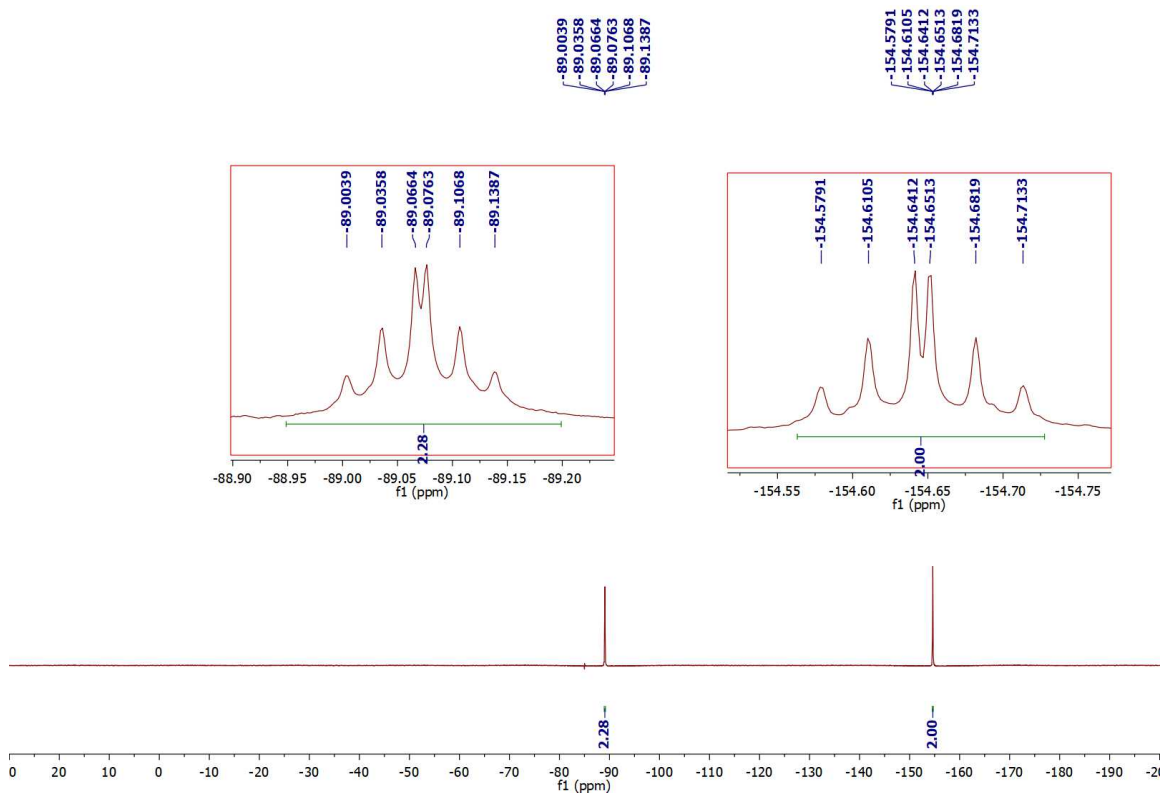
¹⁹F NMR spectrum of 2,6-Bis(3-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-4-(4-(bis(3,4-dimethoxyphenyl)methyl)phenoxy)-3,5-difluoropyridine **10g**



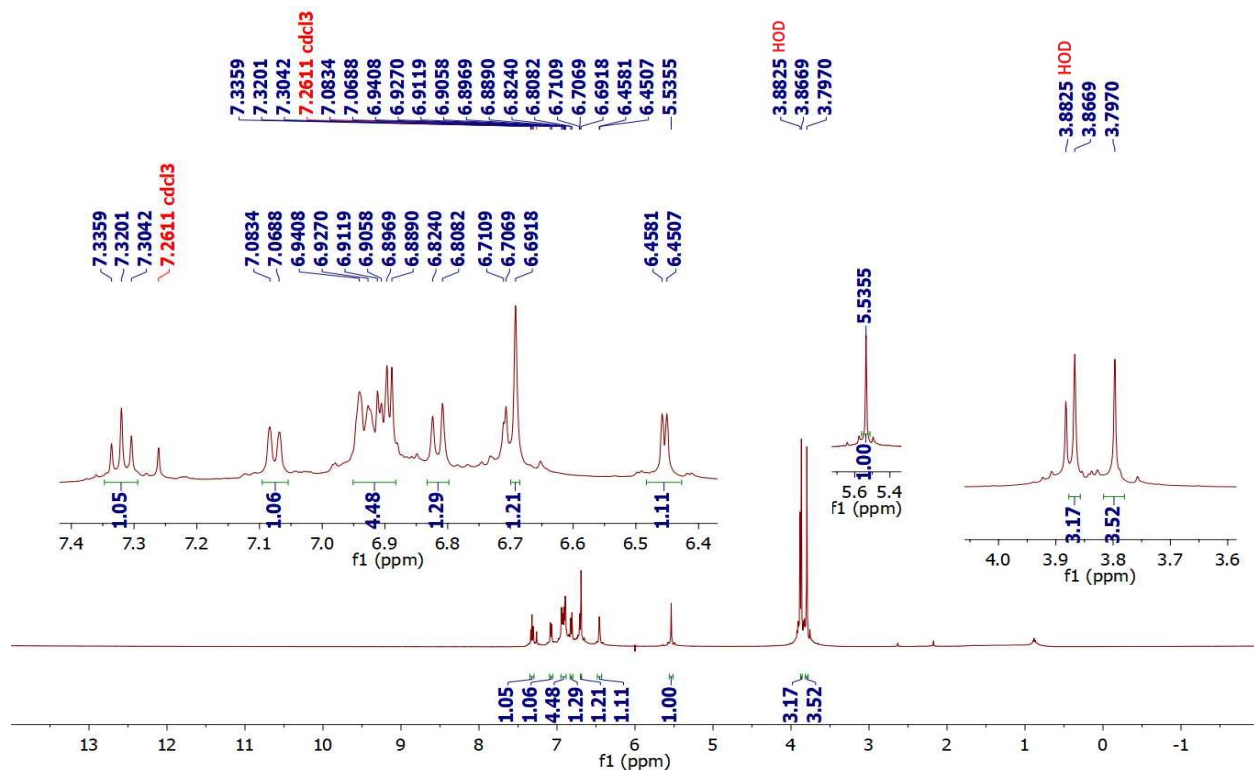
¹H NMR spectrum of (R)-4-(3-((3,4-dimethoxyphenyl)(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11a**



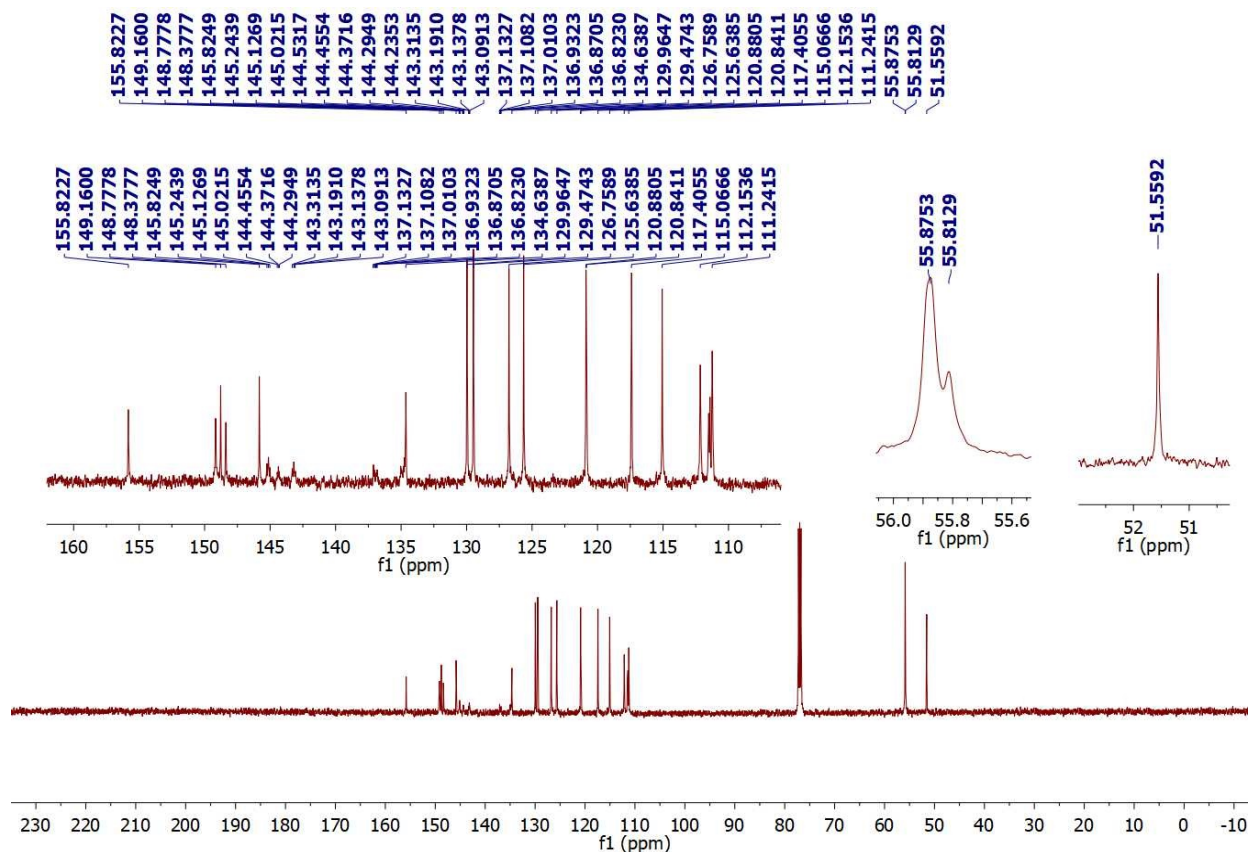
¹³C NMR spectrum of (R)-4-(3-((3,4-dimethoxyphenyl)(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11a**



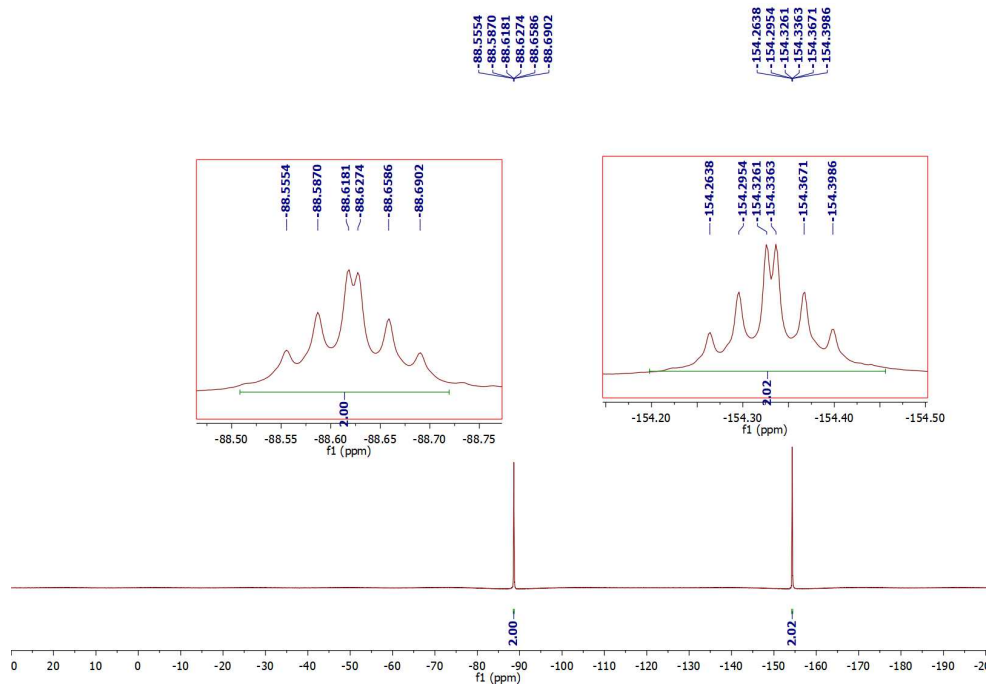
^{19}F NMR spectrum of (R)-4-(3-((3,4-dimethoxyphenyl)(2-methoxy-5-methylphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11a**



^1H NMR spectrum of (R)-4-(3-((5-bromothiophen-2-yl)(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11b**



^{13}C NMR spectrum of (R)-4-(3-((5-bromothiophen-2-yl)(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11b**



^{19}F NMR spectrum of (R)-4-(3-((5-bromothiophen-2-yl)(3,4-dimethoxyphenyl)methyl)phenoxy)-2,3,5,6-tetrafluoropyridine **11b**