

Supporting Information

Efficient synthesis of trifluoromethyl-containing vicinal chlorohydrins and dichlorides via Mn-mediated chlorohydroxylation and dichlorination of α -(trifluoromethyl)styrenes

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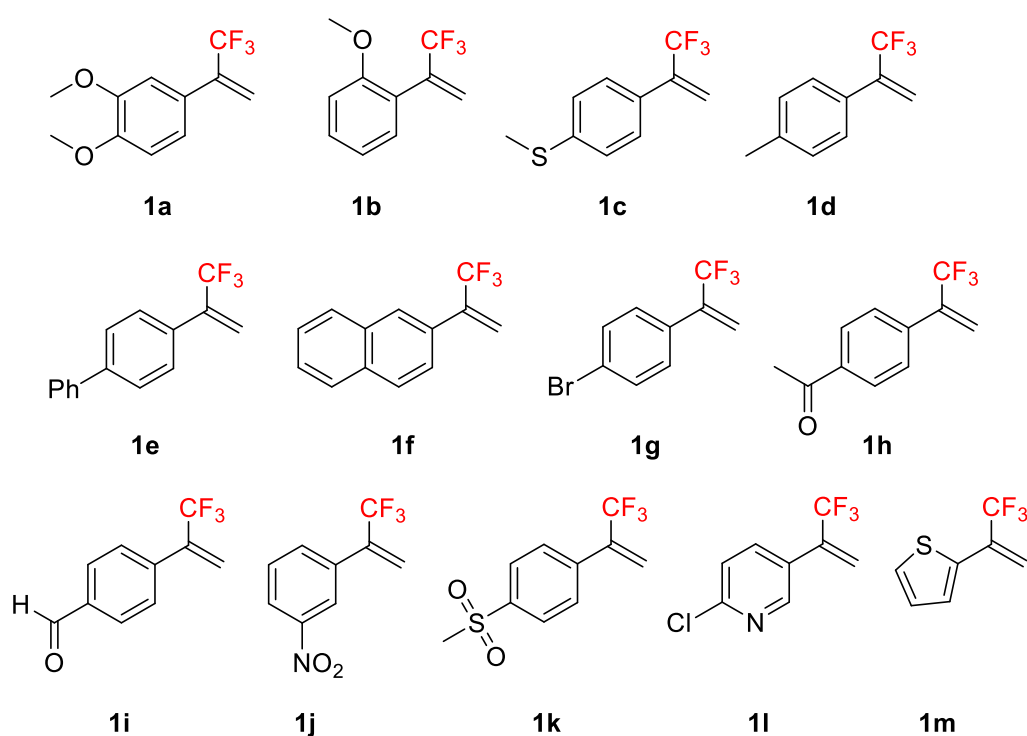
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1. General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. Melting points were measured in an open capillary using EZ-Melt automated melting point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C , respectively) using TMS as an internal standard. The ^{19}F NMR spectra were obtained on a 400 spectrometer (376 MHz). ^{13}C and ^{19}F NMR spectra were recorded with broad-band proton decoupling. CDCl_3 and $\text{DMSO}-d_6$ were used as the NMR solvents. High resolution mass spectra (HRMS) were acquired in the ESI mode using a TOF mass analyzer. The GC-MS were recorded on HP 5973 MSD with 6890 GC. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. α -(Trifluoromethyl)styrenes (1a–m) used in this reaction



The α -(trifluoromethyl)styrenes (1a–m) were prepared according to the reported procedure.^[1–5]

3. General procedure for the synthesis of the target compounds 2a–m

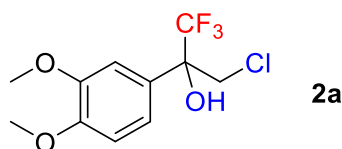
To a glass tube charged with a stirring bar were added NaCl (117.0 mg, 2.0 mmol, 2.0 equiv.), Mn_2O_3 (31.6 mg, 0.20 mmol, 20 mol%), $\text{Na}_2\text{S}_2\text{O}_8$ (476.2 mg, 2.0 mmol, 2.0 equiv.), α -(trifluoromethyl)styrenes (1a–m, 1.0 mmol), DMSO (3.0 mL) and H_2O (0.5 mL). And then the reaction mixture was stirred for 12 h at 50 °C with the condenser open to the air (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (3×10 mL) and extracted with ethyl acetate (3×10 mL). The

organic layer was separated and dried over Na₂SO₄, filtered and concentrated *in vacuo*. The resultant residue was purified by column chromatography on silica gel using *n*-hexane/ ethyl acetate (30/1~3/1) as eluent to afford the pure target compounds **2a–m**.

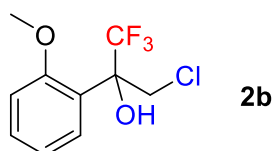
4. General procedure for the synthesis of the target compounds **3a**, **3c**, **3e**, **3f**, **3l** and **3m**

To a glass tube charged with a stirring bar were added NaCl (175.5 mg, 3.0 mmol, 3.0 equiv.), Mn₂O₃ (31.6 mg, 0.20 mmol, 20 mol%), Na₂S₂O₈ (714.3 mg, 3.0 mmol, 3.0 equiv.), α -(trifluoromethyl)styrenes (**1a**, **1c**, **1e**, **1f**, **1l** and **1m**, 1.0 mmol), DMSO (4.0 mL). And then the reaction mixture was stirred for 12 h at 80 °C with the condenser open to the air (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with saturated aqueous solution of NH₄Cl (3 $\times$ 10 mL) and extracted with ethyl acetate (3 $\times$ 10 mL). The organic layer was separated and dried over Na₂SO₄, filtered and concentrated *in vacuo*. The resultant residue was purified by column chromatography on silica gel using *n*-hexane/ ethyl acetate (30/1~3/1) as eluent to afford the pure target compounds **3a**, **3c**, **3e**, **3f**, **3l** and **3m**.

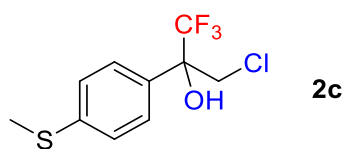
5. Analytical data of the target compounds



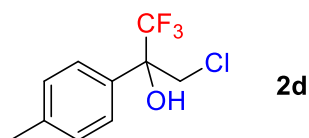
3-Chloro-2-(3,4-dimethoxyphenyl)-1,1,1-trifluoropropan-2-ol (2a). White solid, m.p. 98.7–100.2 °C, yield 60% (209.4 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.30 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 128.7 (q, ¹*J*_{CF} = 286.0 Hz), 124.1, 123.2, 121.0, 112.0, 110.5, 107.3, 76.3 (q, ²*J*_{CF} = 27.5 Hz), 56.0, 47.2; ¹⁹F NMR (367 MHz, CDCl₃) δ –76.9 (s, 3F); HRMS (ESI) *m/z*: calcd for C₁₁H₁₂ClF₃O₃Na [M+Na]⁺: 307.0325, found: 307.0336.



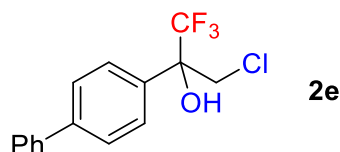
3-Chloro-1,1,1-trifluoro-2-(2-methoxyphenyl)propan-2-ol (2b). Yellow oil, yield 61% (154.9 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.37 (m, 2H), 7.10–7.01 (m, 2H), 5.91 (s, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 130.9, 129.9, 124.8 (q, ¹*J*_{CF} = 286.5 Hz), 121.6, 121.4, 112.7, 78.9 (q, ²*J*_{CF} = 27.9 Hz), 56.4, 46.3; ¹⁹F NMR (367 MHz, CDCl₃) δ –73.9 (s, 3F); HRMS (ESI) *m/z*: calcd for C₁₀H₁₀ClF₃O₂Na [M+Na]⁺: 277.0219, found: 277.0223.



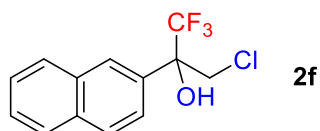
3-Chloro-1,1,1-trifluoro-2-(4-(methylthio)phenyl)propan-2-ol (2c). Yellow oil, yield 70% (189.0 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 4.15 (d, J = 12.0 Hz, 1H), 4.03 (d, J = 12.0 Hz, 1H), 3.24 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 131.1, 128.7, 127.7, 126.8, 126.1, 124.3 (q, $^1J_{\text{CF}}$ = 284.7 Hz), 76.3 (q, $^2J_{\text{CF}}$ = 28.5 Hz), 48.2, 15.9; ^{19}F NMR (367 MHz, CDCl_3) δ -78.2 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_{11}\text{ClF}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 271.0171, found: 271.0172.



3-Chloro-1,1,1-trifluoro-2-(p-tolyl)propan-2-ol (2d). Yellow oil, yield 88% (209.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 4.64–4.61 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 136.2, 129.6, 129.1, 127.3, 127.0, 125.4 (q, $^1J_{\text{CF}}$ = 276.5 Hz), 76.8 (q, $^2J_{\text{CF}}$ = 27.9 Hz), 46.2, 21.2; ^{19}F NMR (367 MHz, CDCl_3) δ -74.9 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_{11}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 239.0451, found: 239.0451.

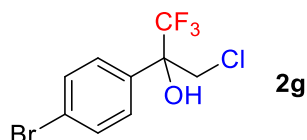


2-([1,1'-Biphenyl]-4-yl)-3-chloro-1,1,1-trifluoropropan-2-ol (2e). White solid, m.p. 128.7–130.6 °C, yield 83% (249.0 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.88–7.81 (m, 6H), 7.69–7.55 (m, 3H), 4.42 (d, J = 12.0 Hz, 1H), 4.30 (d, J = 11.6 Hz, 1H), 3.49 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 140.2, 133.6, 128.9, 127.8, 127.4, 127.2, 126.8, 124.4 (q, $^1J_{\text{CF}}$ = 286.2 Hz), 76.5 (q, $^2J_{\text{CF}}$ = 28.4 Hz), 47.7; ^{19}F NMR (367 MHz, CDCl_3) δ -76.9 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{15}\text{H}_{12}\text{ClF}_3\text{ONa}$ $[\text{M}+\text{Na}]^+$: 323.0426, found: 323.0421.

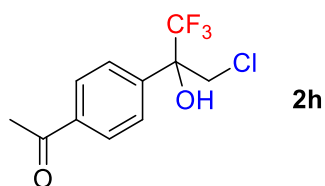


3-Chloro-1,1,1-trifluoro-2-(naphthalen-2-yl)propan-2-ol (2f). White solid, m.p. 106.9–109.6 °C, yield 67% (183.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.96–7.90 (m, 3H), 7.66 (d, J = 8.4 Hz, 1H), 7.61–7.56 (m, 2H), 4.31 (d, J = 12.0 Hz, 1H), 4.20 (d, J = 12.0 Hz, 1H), 3.40 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.4, 132.6, 129.2, 129.1, 128.8, 128.4, 127.7, 127.5, 126.9, 124.5, 123.9 (q, $^1J_{\text{CF}}$ = 281.6 Hz), 73.2 (q, $^2J_{\text{CF}}$ = 28.7 Hz), 47.2; ^{19}F NMR (367 MHz, CDCl_3) δ -74.6 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{11}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 275.0451, found:

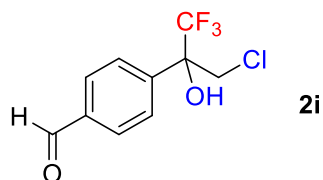
275.0454.



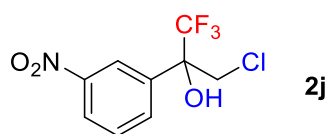
2-(4-Bromophenyl)-3-chloro-1,1,1-trifluoropropan-2-ol (2g). Yellow oil, yield 40% (120.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.62 (m, 2H), 7.52–7.48 (m, 2H), 4.25 (d, $J = 12.0$ Hz, 1H), 4.13 (d, $J = 12.0$ Hz, 1H), 3.33 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 135.5, 130.8, 129.0, 128.4, 127.5, 124.3 (q, $^1J_{\text{CF}} = 285.4$ Hz), 76.2 (q, $^2J_{\text{CF}} = 28.7$ Hz), 47.1; ^{19}F NMR (367 MHz, CDCl_3) δ -77.2 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_7\text{BrClF}_3\text{ONa}$ $[\text{M}+\text{Na}]^+$: 324.9219, found: 324.9224.



1-(4-(3-Chloro-1,1,1-trifluoro-2-hydroxypropan-2-yl)phenyl)ethan-1-one (2h). Yellow oil, yield 60% (159.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 4.18 (d, $J = 12.0$ Hz, 1H), 4.07 (d, $J = 12.8$ Hz, 1H), 3.61 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 139.7, 137.7, 129.8, 128.6, 127.3, 126.8, 124.1 (q, $^1J_{\text{CF}} = 284.9$ Hz), 76.4 (q, $^2J_{\text{CF}} = 28.7$ Hz), 47.4, 26.7; ^{19}F NMR (367 MHz, CDCl_3) δ -77.8 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{11}\text{ClF}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 267.0400, found: 267.0397.

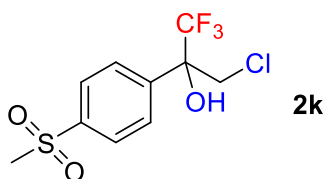


4-(3-Chloro-1,1,1-trifluoro-2-hydroxypropan-2-yl)benzaldehyde (2i). Yellow oil, yield 54% (136.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 10.10 (s, 1H), 8.00 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 4.23 (d, $J = 12.4$ Hz, 1H), 4.12 (d, $J = 12.0$ Hz, 1H), 3.53 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.7, 141.0, 136.9, 129.8, 127.2, 124.0 (q, $^1J_{\text{CF}} = 284.9$ Hz), 76.4 (q, $^2J_{\text{CF}} = 28.7$ Hz), 47.3; ^{19}F NMR (367 MHz, CDCl_3) δ -75.9 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_9\text{ClF}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 253.0243, found: 253.0243.

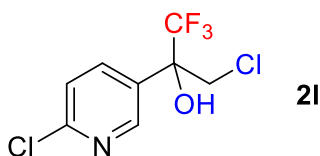


3-Chloro-1,1,1-trifluoro-2-(3-nitrophenyl)propan-2-ol (2j). Yellow oil, yield 66% (178.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.31 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 4.21 (d, J

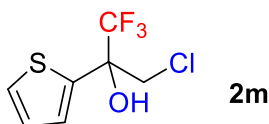
= 12.0 Hz, 1H), 4.11 (d, J = 12.4 Hz, 1H) 3.41 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 135.5, 130.8, 129.0, 128.4, 127.5, 126.4 (q, $^1J_{\text{CF}}$ = 280.0 Hz), 76.2 (q, $^2J_{\text{CF}}$ = 28.7 Hz), 47.1; ^{19}F NMR (367 MHz, CDCl_3) δ -76.3 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_8\text{ClF}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$: 270.0145, found: 270.0139.



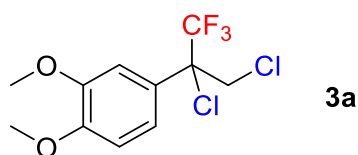
3-Chloro-1,1,1-trifluoro-2-(4-(methylsulfonyl)phenyl)propan-2-ol (2k). Yellow oil, yield 60% (181.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 4.23 (d, J = 12.0 Hz, 1H), 4.11 (d, J = 12.0 Hz, 1H), 3.55 (s, 1H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 140.8, 131.0, 127.8, 127.4, 126.5 (q, $^1J_{\text{CF}}$ = 277.0 Hz), 76.3 (q, $^2J_{\text{CF}}$ = 27.4 Hz), 47.2, 44.5; ^{19}F NMR (367 MHz, CDCl_3) δ -74.9 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_{10}\text{ClF}_3\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 324.9889, found: 324.9897.



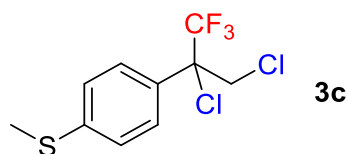
3-Chloro-2-(6-chloropyridin-3-yl)-1,1,1-trifluoropropan-2-ol (2l). Yellow oil, yield 44% (113.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, J = 1.6 Hz, 1H), 7.87 (dd, J = 10.8 Hz, 2.4 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 4.16 (d, J = 12.4 Hz, 1H), 4.06 (d, J = 12.0 Hz, 1H), 3.43 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 148.1, 137.4, 129.8, 124.3, 123.8 (q, $^1J_{\text{CF}}$ = 283.8 Hz), 75.7 (q, $^2J_{\text{CF}}$ = 29.0 Hz), 46.8; ^{19}F NMR (367 MHz, CDCl_3) δ -75.6 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_8\text{H}_7\text{Cl}_2\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 259.9857, found: 259.9863.



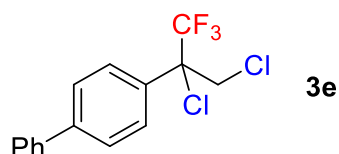
3-Chloro-1,1,1-trifluoro-2-(thiophen-2-yl)propan-2-ol (2m). Yellow oil, yield 30% (69 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 4.8 Hz, 1H), 7.16 (d, J = 4.8 Hz, 1H), 7.08–7.06 (m, 1H), 4.13 (d, J = 12.0 Hz, 1H), 4.00 (d, J = 12.0 Hz, 1H), 3.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 127.4, 127.1, 126.4, 121.8 (q, $^1J_{\text{CF}}$ = 283.0 Hz), 75.1 (q, $^2J_{\text{CF}}$ = 29.2 Hz), 48.1; ^{19}F NMR (367 MHz, CDCl_3) δ -77.2 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_7\text{H}_7\text{ClF}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 230.9858, found: 250.9851.



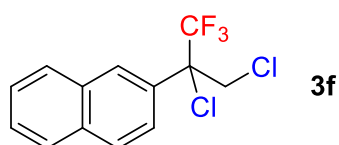
4-(2,3-Dichloro-1,1,1-trifluoropropan-2-yl)-1,2-dimethoxybenzene (3a). Yellow oil, yield 50% (150.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.18–7.15 (m, 2H), 6.90 (d, $J = 9.2$ Hz, 1H), 4.39 (d, $J = 12.8$ Hz, 1H), 4.19 (d, $J = 12.4$ Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.5, 148.1, 123.4, 123.1 (q, $^1J_{\text{CF}} = 282.0$ Hz), 120.3, 111.3, 109.9, 72.1 (q, $^2J_{\text{CF}} = 28.7$ Hz), 55.4, 55.3, 46.4; ^{19}F NMR (367 MHz, CDCl_3) δ -75.6 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}_2\text{F}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 324.9980, found: 324.9977.



(4-(2,3-Dichloro-1,1,1-trifluoropropan-2-yl)phenyl)(methyl)sulfane (3c). Yellow oil, yield 72% (206.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 4.40 (d, $J = 12.4$ Hz, 1H), 4.18 (d, $J = 12.4$ Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 128.8, 128.3, 125.8, 123.8 (q, $^1J_{\text{CF}} = 282.2$ Hz), 72.8 (d, $^2J_{\text{CF}} = 28.8$ Hz), 47.1, 15.2; ^{19}F NMR (367 MHz, CDCl_3) δ -74.3 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_9\text{Cl}_2\text{F}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 310.9646, found: 310.9641.

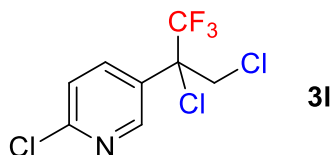


4-(2,3-Dichloro-1,1,1-trifluoropropan-2-yl)-1,1'-biphenyl (3e). White solid, m.p. 128.0–130.7 °C, yield 61% (194.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 1H), 4.47 (d, $J = 12.4$ Hz, 1H), 4.24 (d, $J = 12.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 139.8, 130.8, 129.0, 128.8, 128.0, 127.3, 127.2, 123.8 (q, $^1J_{\text{CF}} = 282.1$ Hz), 72.9 (q, $^2J_{\text{CF}} = 28.4$ Hz), 47.1; ^{19}F NMR (367 MHz, CDCl_3) δ -78.8 (s, 3F); HRMS (ESI) m/z : calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{F}_3$ $[\text{M}+\text{H}]^+$: 319.0268, found: 319.0262.

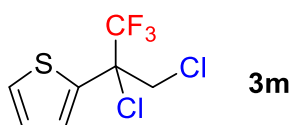


2-(2,3-Dichloro-1,1,1-trifluoropropan-2-yl)naphthalene (3f). White solid, m.p. 104.2–106.3 °C, yield 57% (165.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 7.92–7.85 (m, 3H), 7.66 (d, $J = 8.8$ Hz, 1H), 7.58–7.53 (m, 2H), 4.56 (d, $J = 12.4$ Hz, 1H), 4.29 (d, $J = 12.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.0, 133.2, 129.8, 129.7, 129.4, 129.0, 128.3, 128.1, 127.5, 125.1, 124.5 (q, $^1J_{\text{CF}} = 283.3$ Hz), 73.8 (q, $^2J_{\text{CF}} = 28.3$ Hz), 47.8; ^{19}F NMR (367

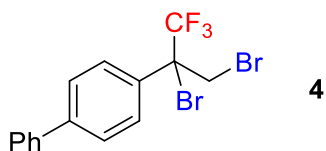
MHz, CDCl₃) δ -75.7 (s, 3F); HRMS (ESI) m/z : calcd for C₁₃H₉Cl₂F₃Na [M+Na]⁺: 314.9931, found: 314.9940.



2-Chloro-5-(2,3-dichloro-1,1,1-trifluoropropan-2-yl)pyridine (3l). Yellow oil, yield 40% (110.0 mg); ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, J = 2.0 Hz, 1H), 7.88 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 4.16 (d, J = 12.0 Hz, 1H), 4.06 (d, J = 12.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 148.1, 137.4, 129.8, 124.3, 123.9 (q, ¹ J_{CF} = 279.8 Hz), 75.7 (q, ² J_{CF} = 27.9 Hz), 46.9; ¹⁹F NMR (367 MHz, CDCl₃) δ -76.2 (s, 3F); HRMS (ESI) m/z : calcd for C₈H₆Cl₃F₃N [M+H]⁺: 277.9518, found: 277.9516.



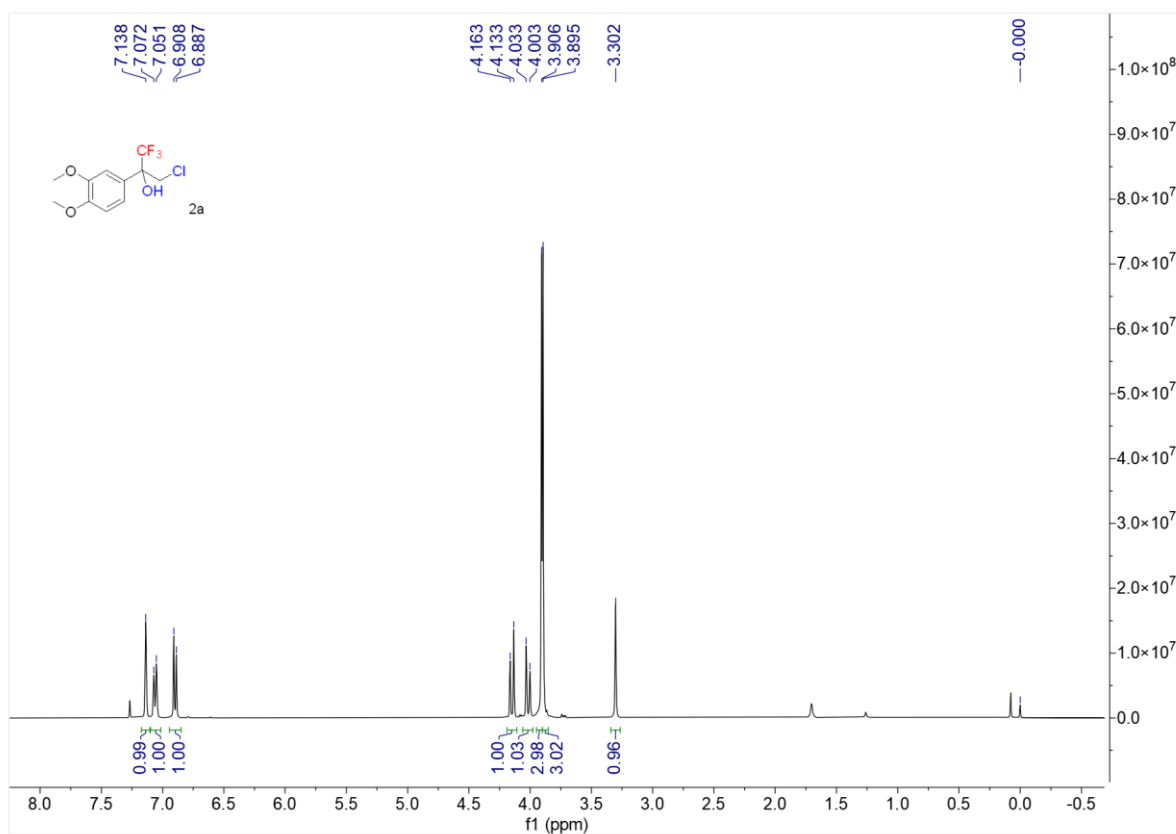
2-(2,3-Dichloro-1,1,1-trifluoropropan-2-yl)thiophene (3m). Yellow oil, yield 35% (86.5 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.30 (d, J = 4.0 Hz, 1H), 7.06 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 4.25 (d, J = 12.4 Hz, 1H), 4.18 (d, J = 12.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 129.2, 128.3, 127.3, 123.4 (q, ¹ J_{CF} = 281.8 Hz), 64.8, 48.3; ¹⁹F NMR (367 MHz, CDCl₃) δ -74.0 (s, 3F); HRMS (ESI) m/z : calcd for C₇H₆Cl₂F₃S [M+H]⁺: 248.9519, found: 248.9513.



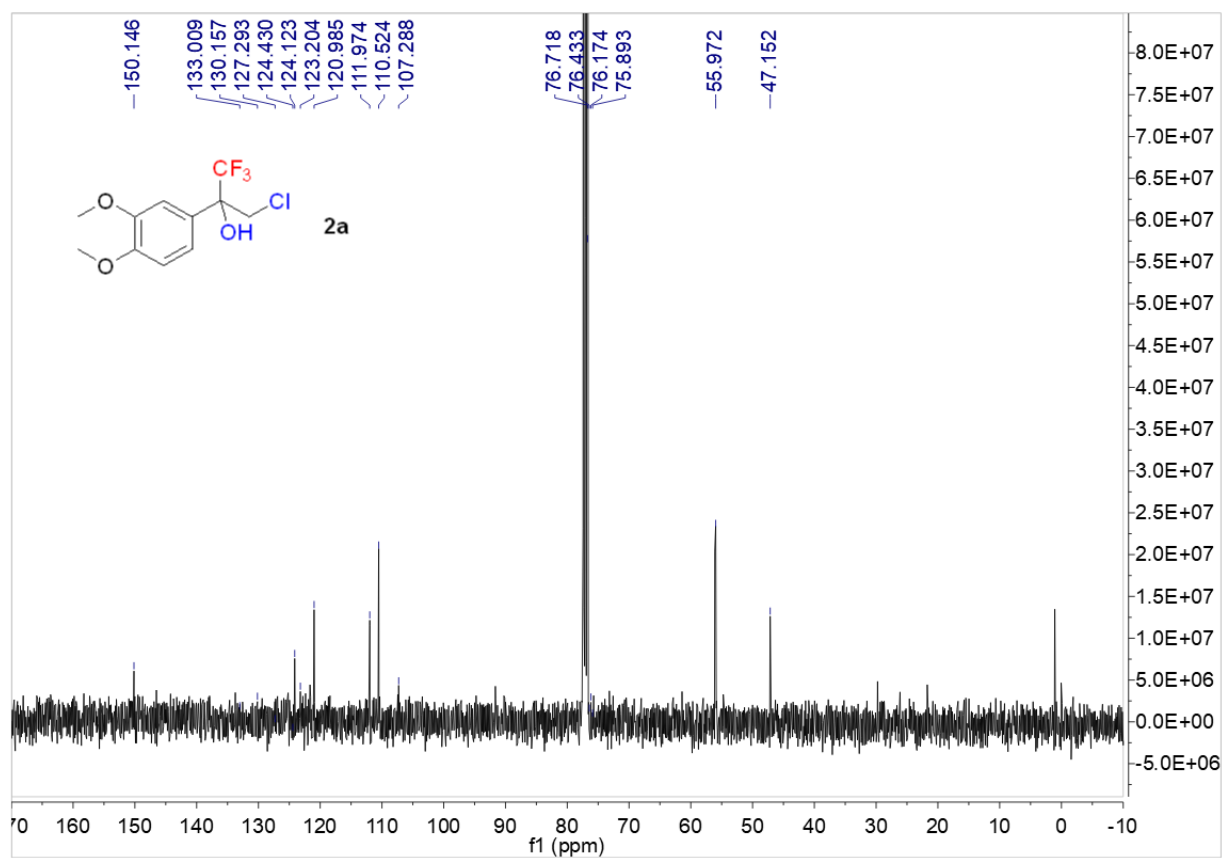
4-(2,3-Dibromo-1,1,1-trifluoropropan-2-yl)-1,1'-biphenyl (4). White solid, m.p. 99.7–102.3 °C, yield 10% (40.7 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.4 Hz, 2H), 7.65–7.60 (m, 4H), 7.48–7.44 (m, 2H), 7.40–7.37 (m, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.23 (d, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 142.6, 139.7, 132.0, 129.4, 129.0, 128.0, 127.2, 127.1, 123.7 (q, ¹ J_{CF} = 281.7 Hz), 65.5 (q, ² J_{CF} = 27.8 Hz), 34.9; ¹⁹F NMR (367 MHz, CDCl₃) δ -73.6 (s, 3F); HRMS (ESI) m/z : calcd for C₁₅H₁₂Br₂F₃ [M+H]⁺: 406.9258, found: 406.9250.

6. ^1H , ^{13}C , ^{19}F NMR and HRMS spectra of the target compounds

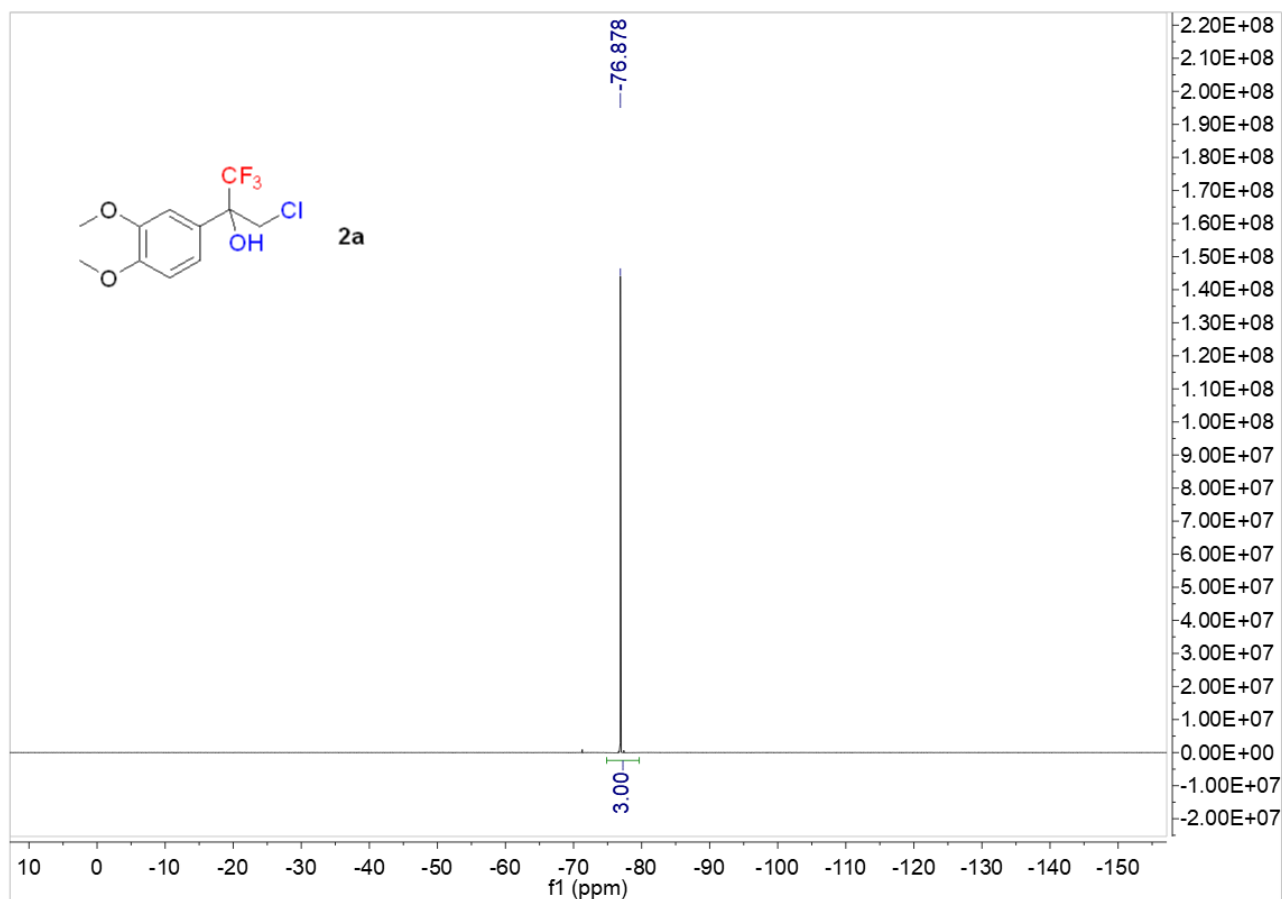
^1H NMR spectrum of **2a** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2a** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2a** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2a**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1468 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

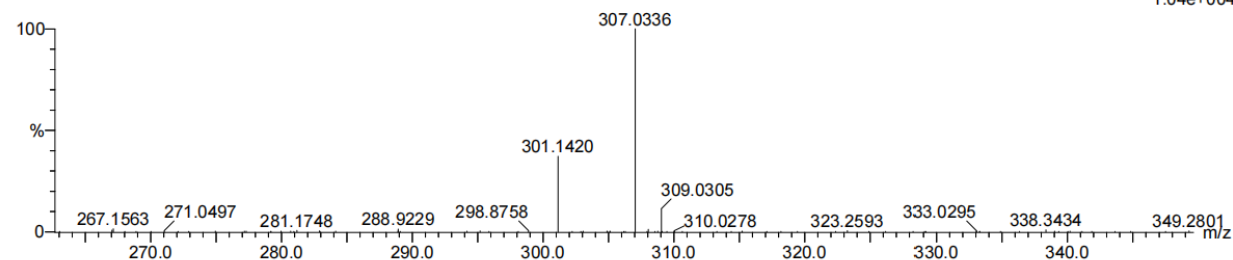
Elements Used:

C: 11-11 H: 12-12 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 Cl: 1-5

31

240308-3-16 15 (0.090)

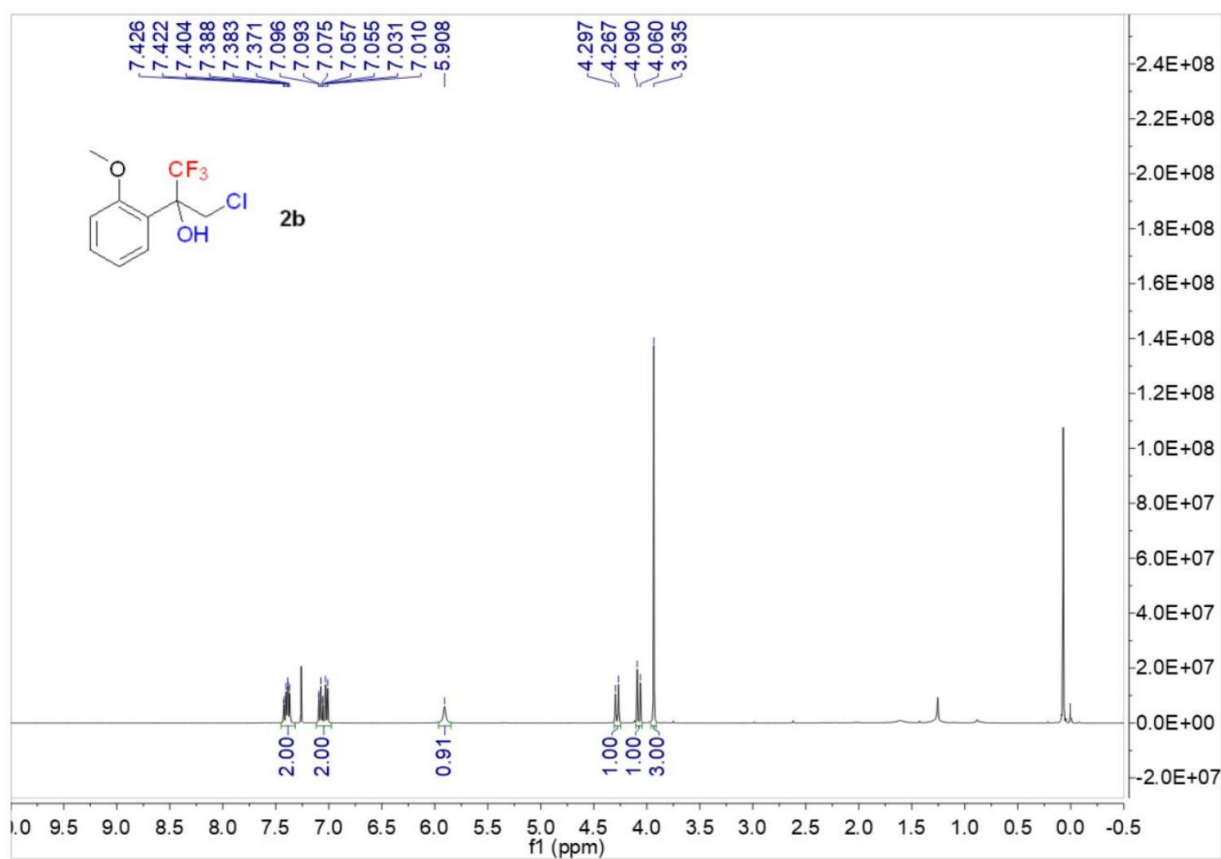
1: TOF MS ES+
1.04e+004



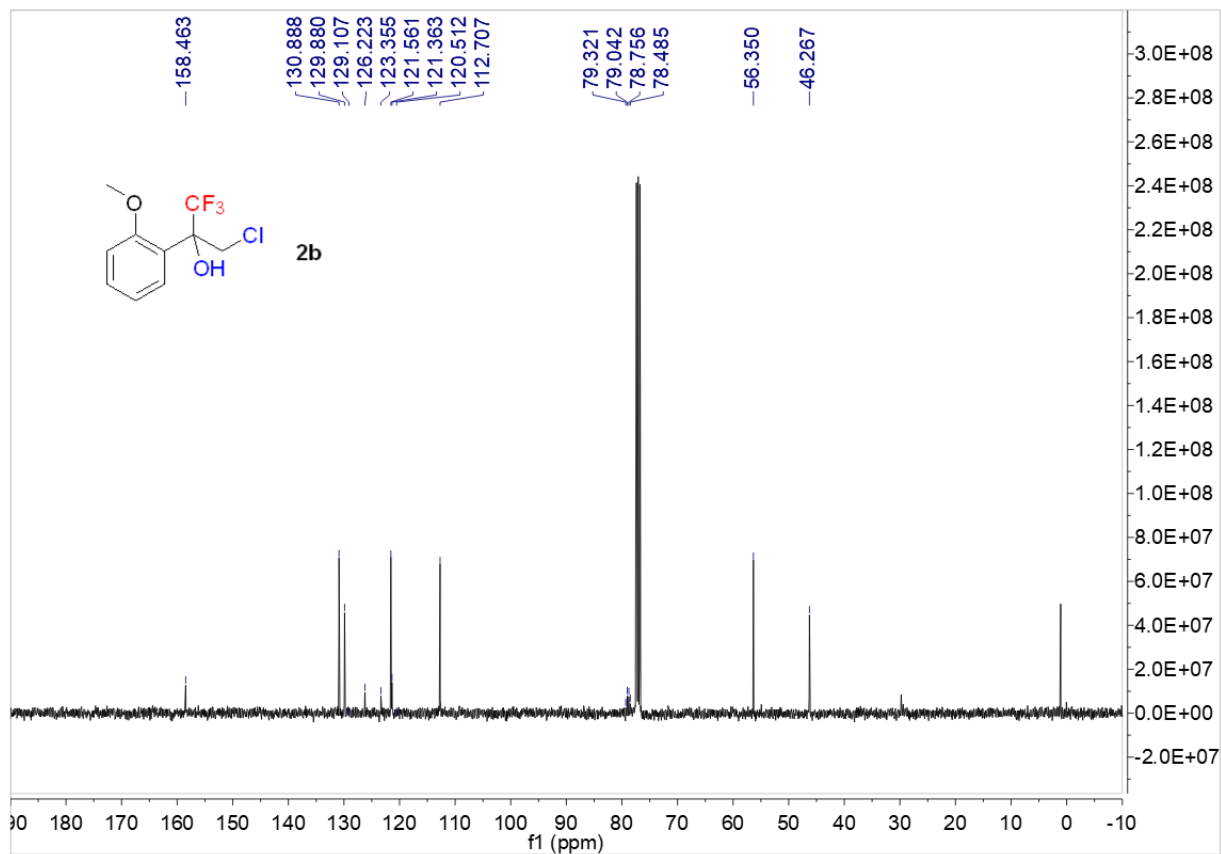
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
307.0336	307.0325	1.1	3.6	3.5	50.2	n/a	n/a	C11 H12 O3 F3 Na Cl

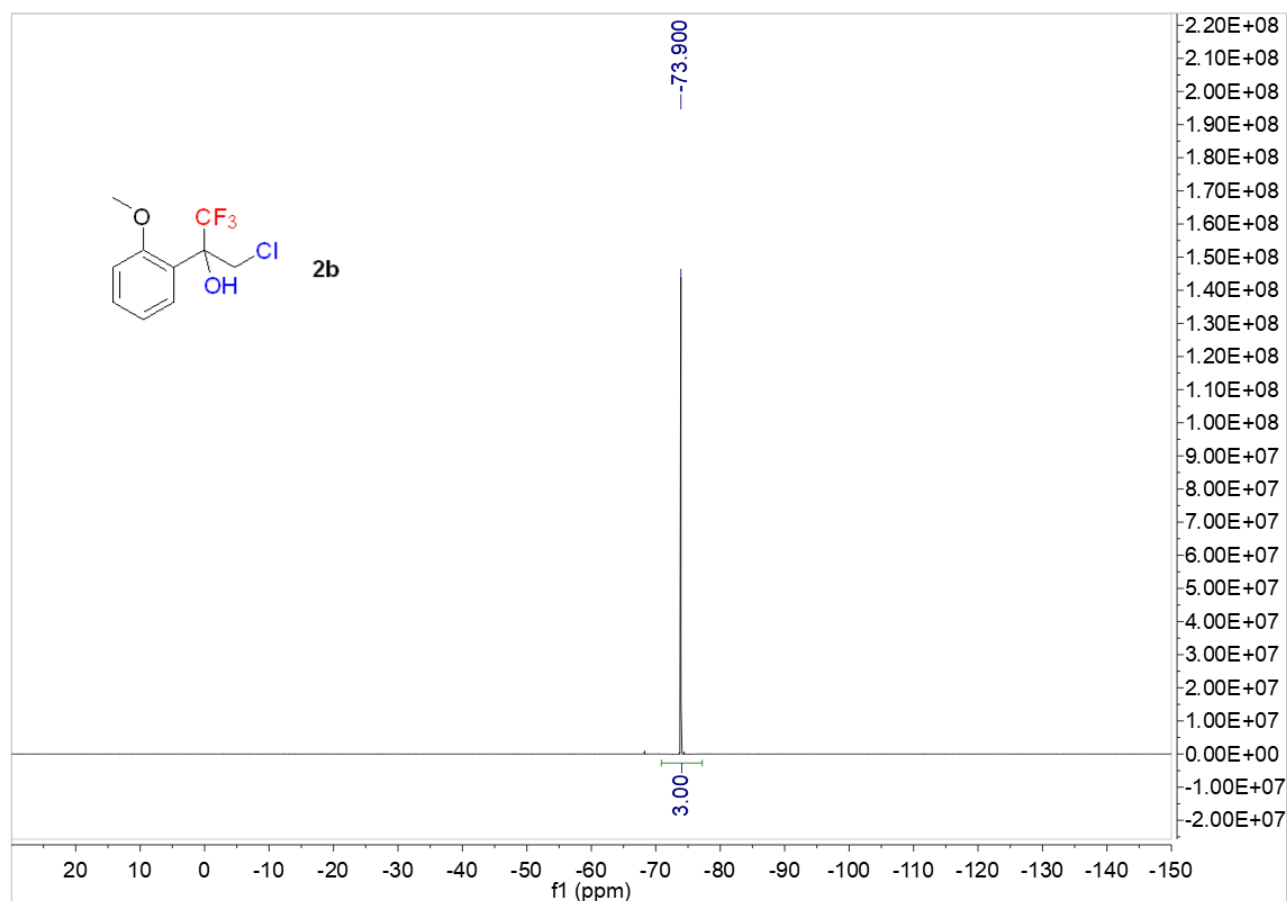
^1H NMR spectrum of **2b** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2b** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2b** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2b**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

944 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

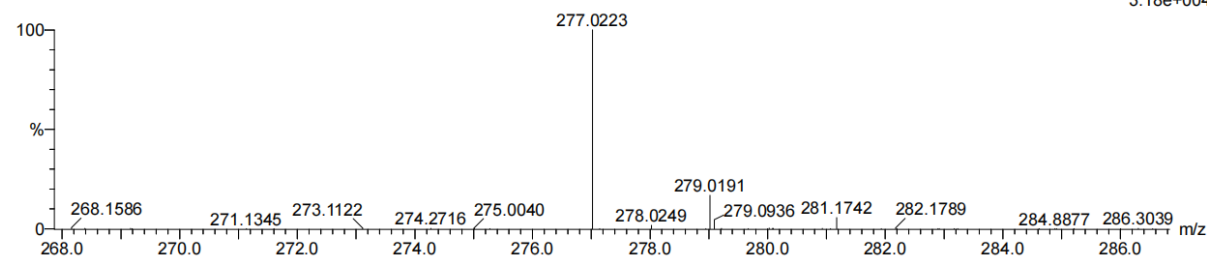
Elements Used:

C: 10-10 H: 10-10 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 Cl: 1-5

14

240308-3-14 10 (0.072)

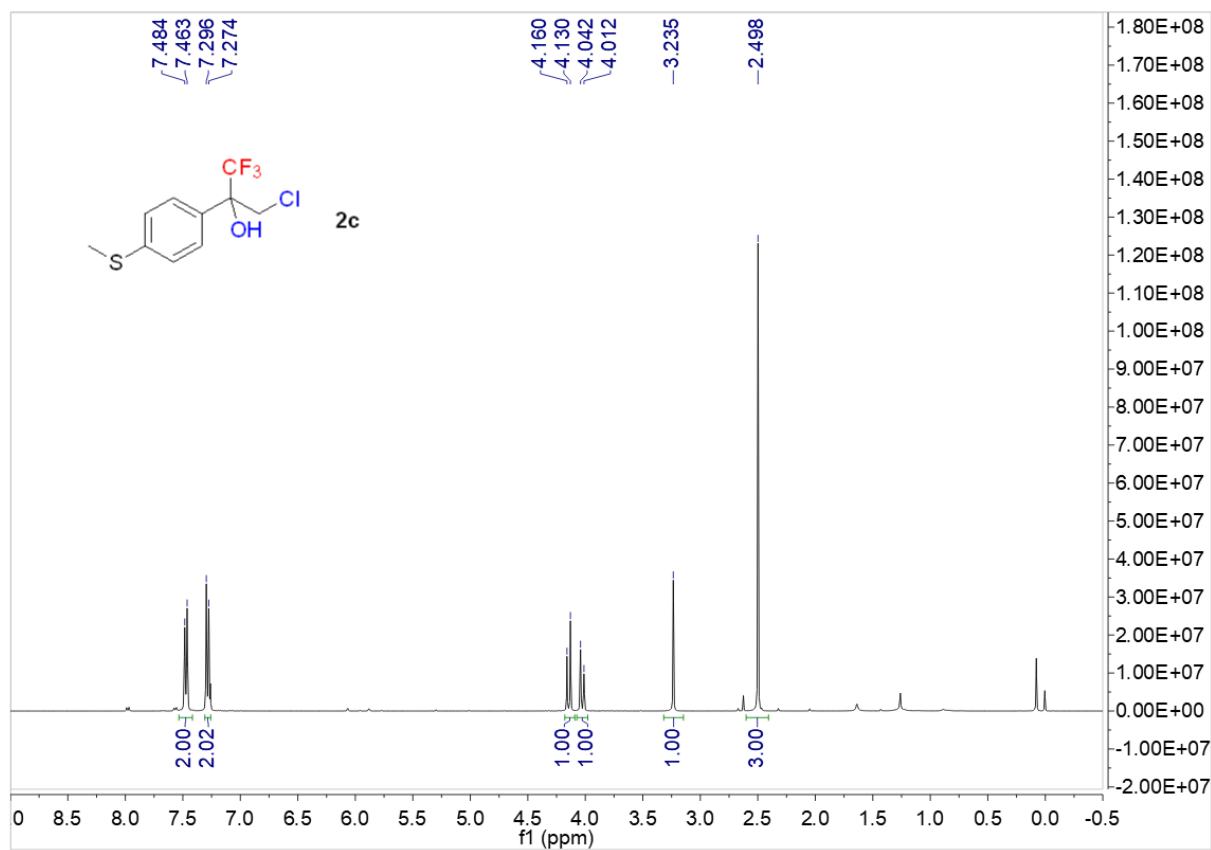
1: TOF MS ES+
3.18e+004



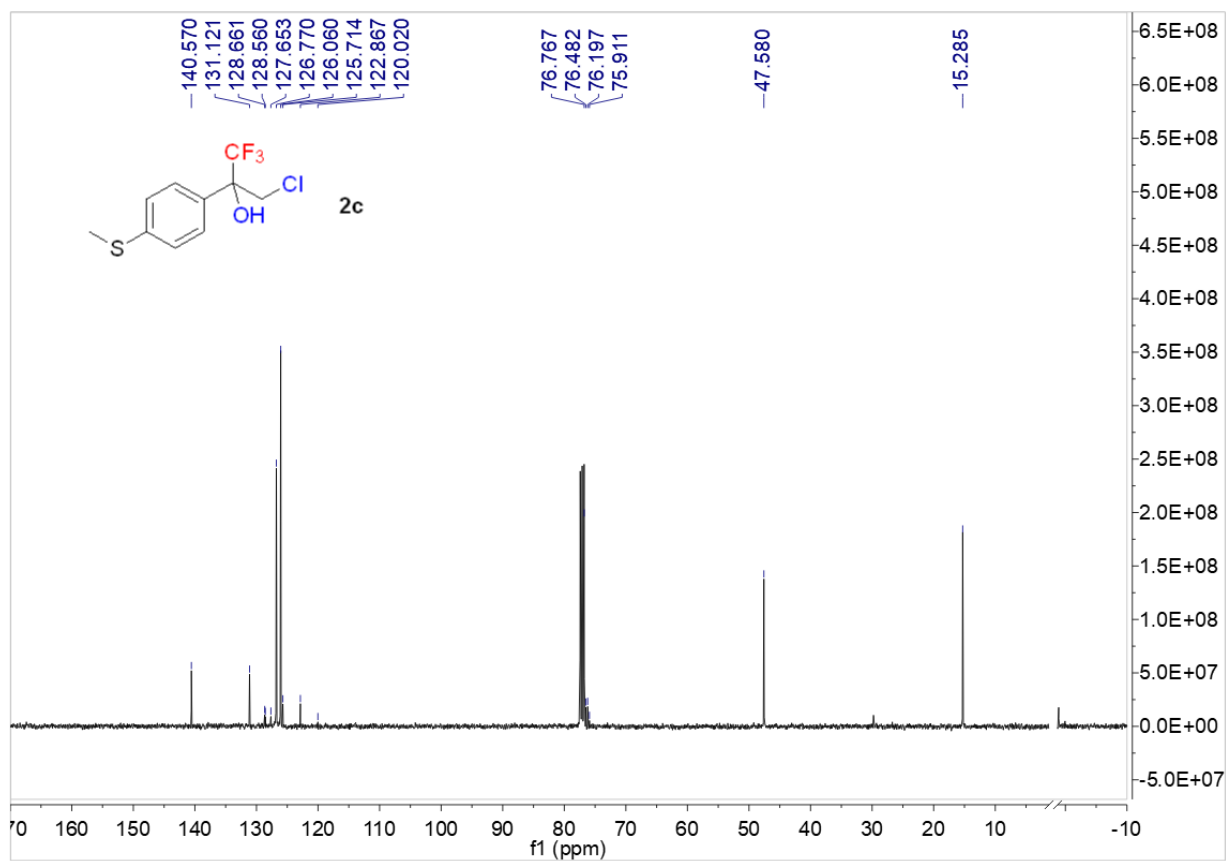
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
277.0223	277.0219	0.4	1.4	3.5	54.7	n/a	n/a	C10 H10 O2 F3 Na Cl

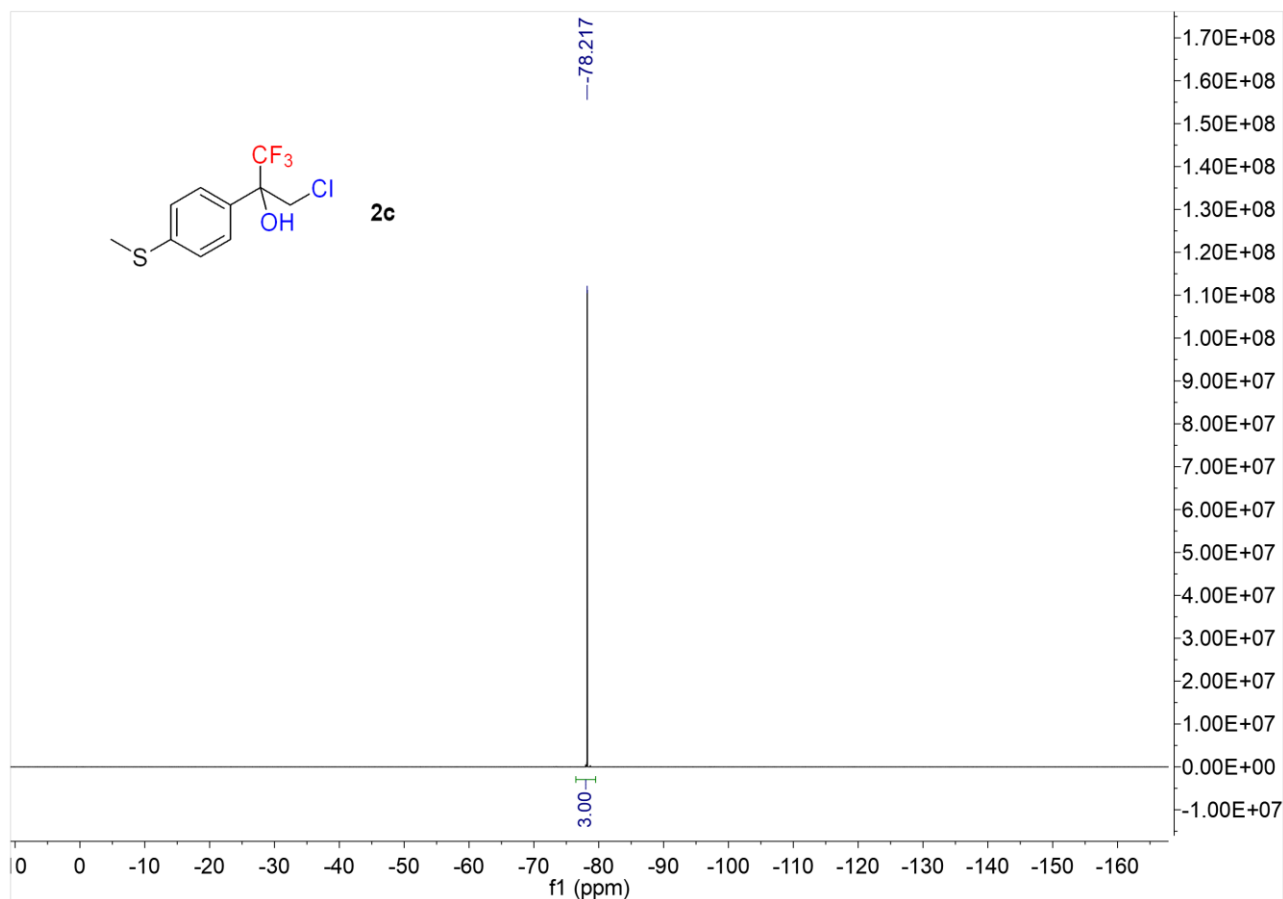
^1H NMR spectrum of **2c** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2c** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2c** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2c**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1578 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

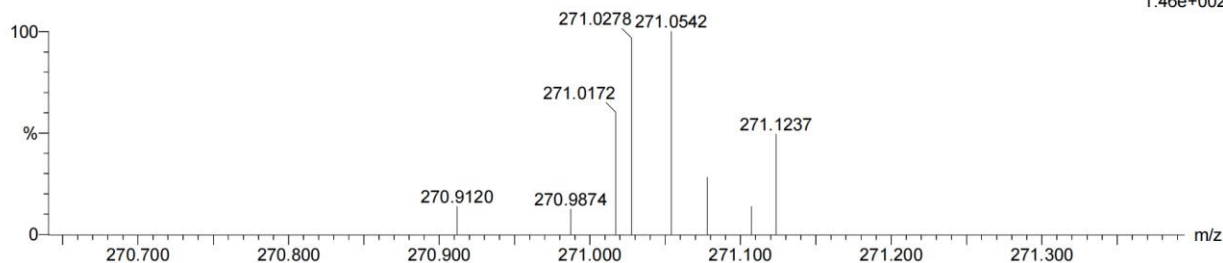
Elements Used:

C: 10-10 H: 11-11 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 S: 1-6 Cl: 1-3

6

241205-17-9 37 (0.250)

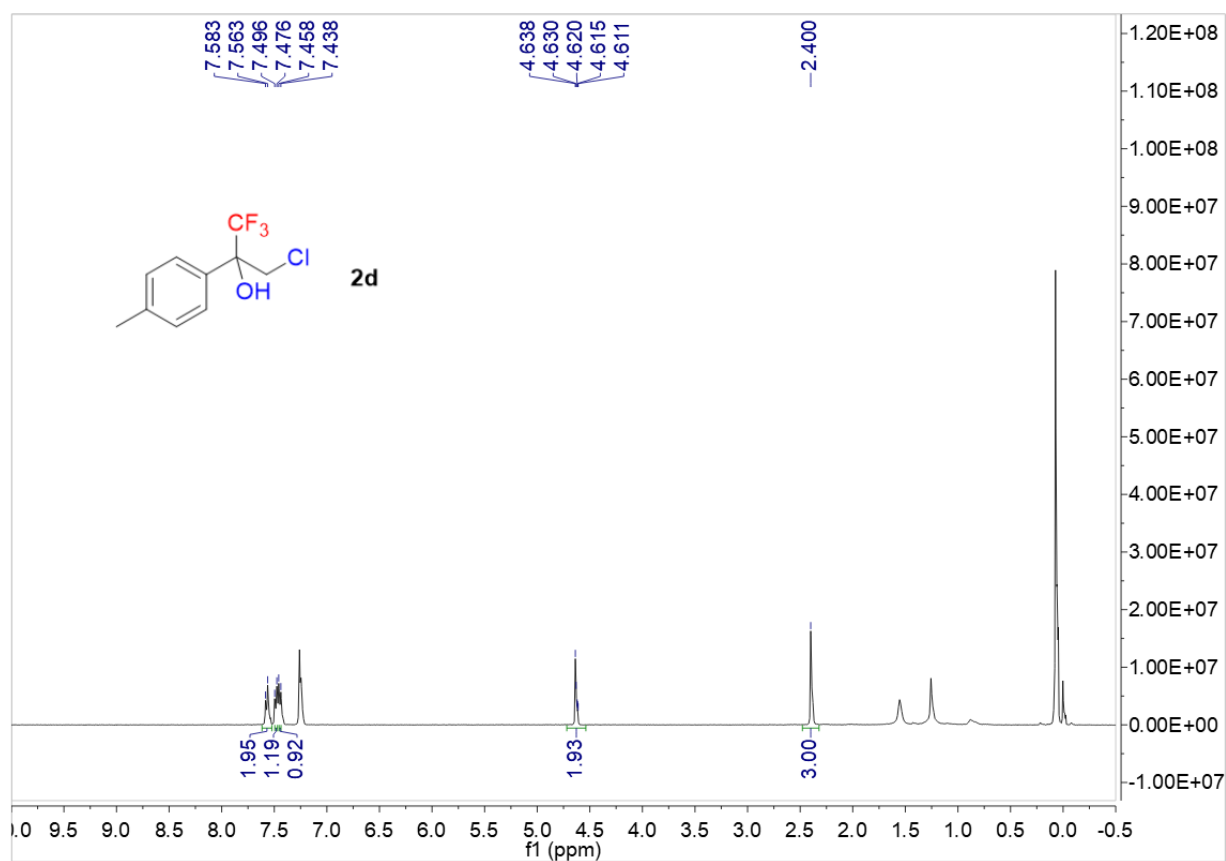
1: TOF MS ES+
1.46e+002



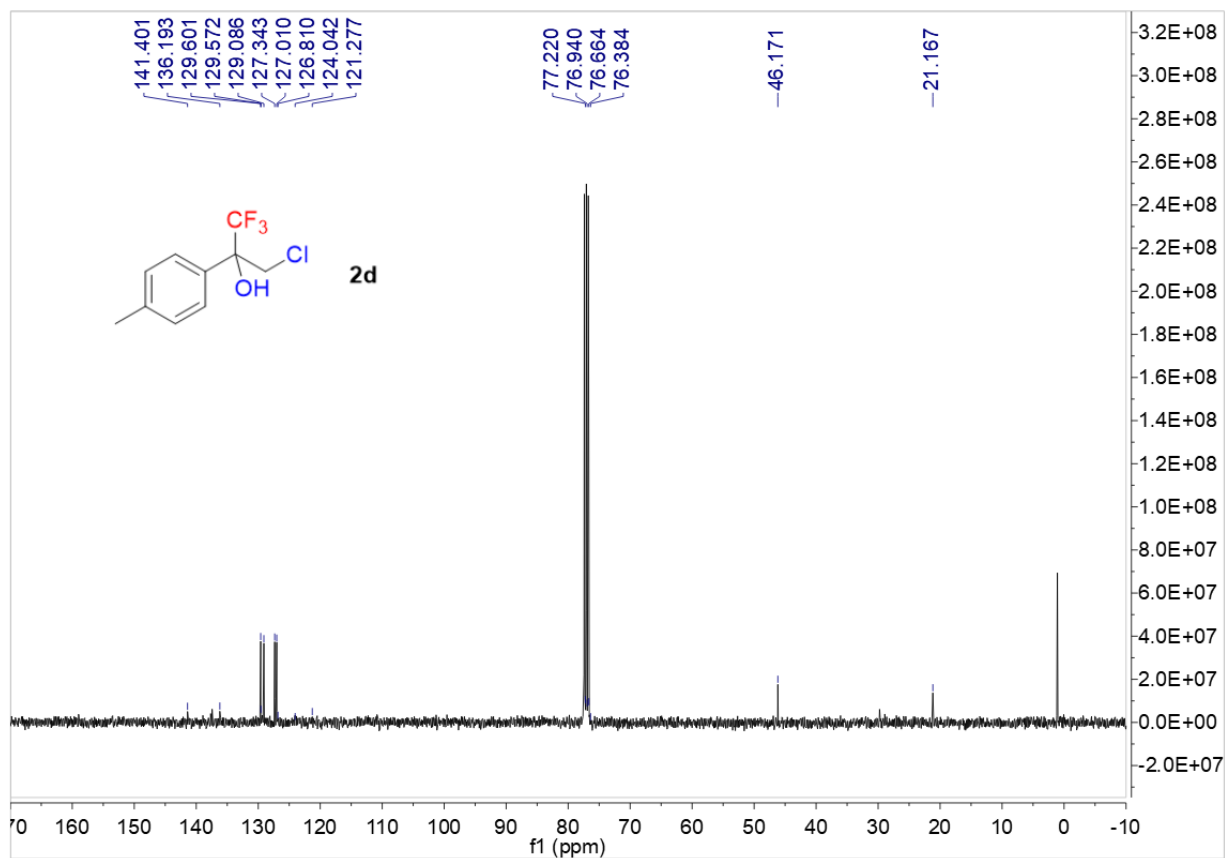
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
271.0172	271.0171	0.1	0.4	3.5	59.6	n/a	n/a	C10 H11 O F3 S Cl

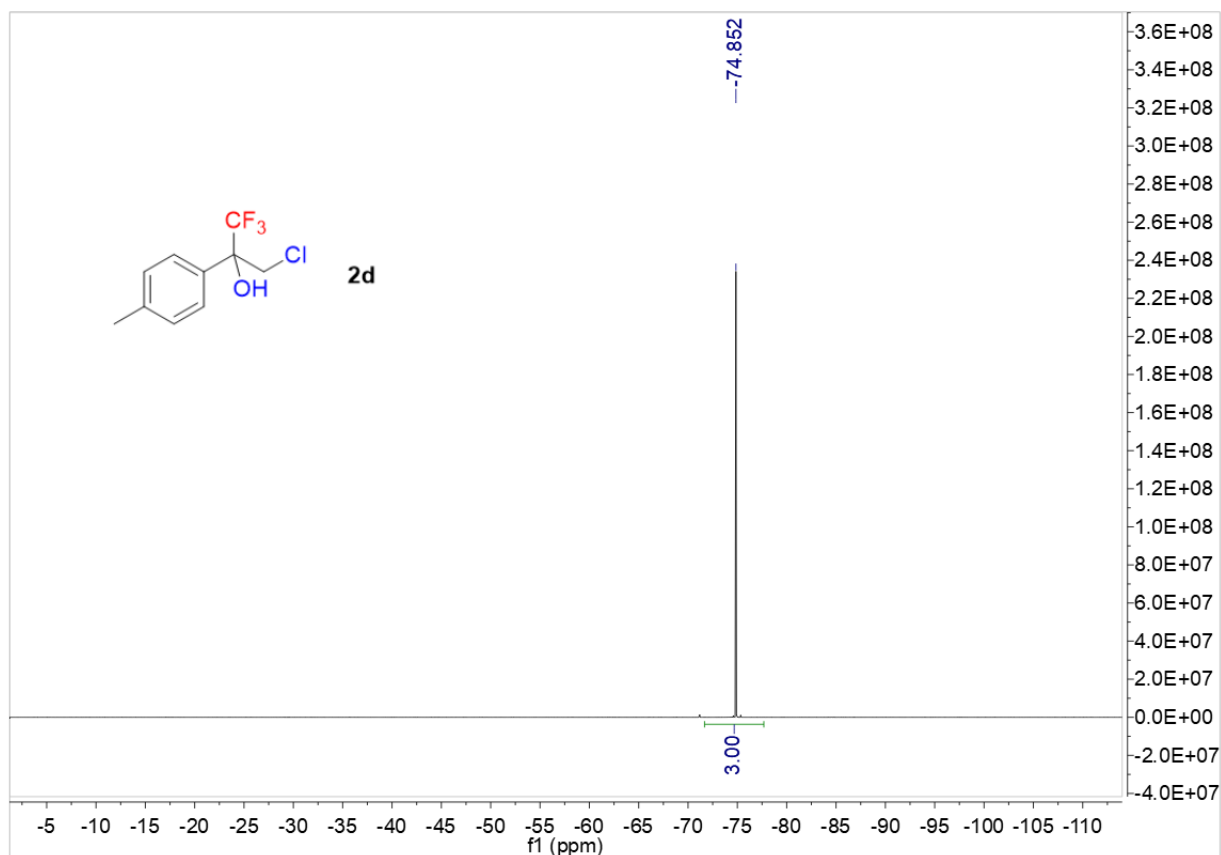
^1H NMR spectrum of **2d** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2d** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2d** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2d**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

727 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

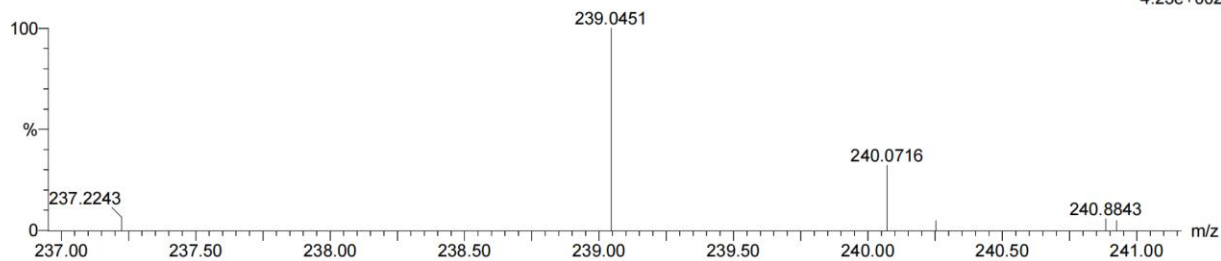
Elements Used:

C: 10-10 H: 11-11 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-6 77 (0.480)

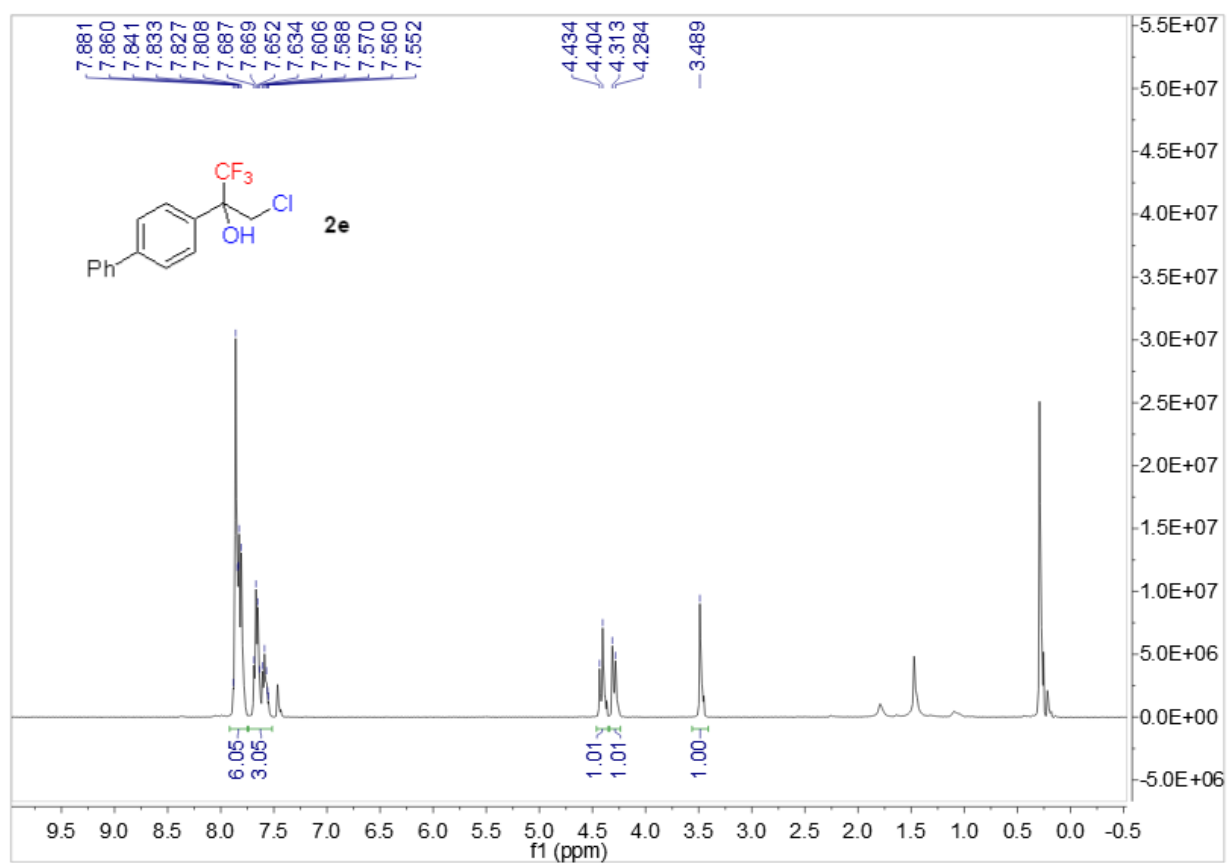
1: TOF MS ES+
4.23e+002



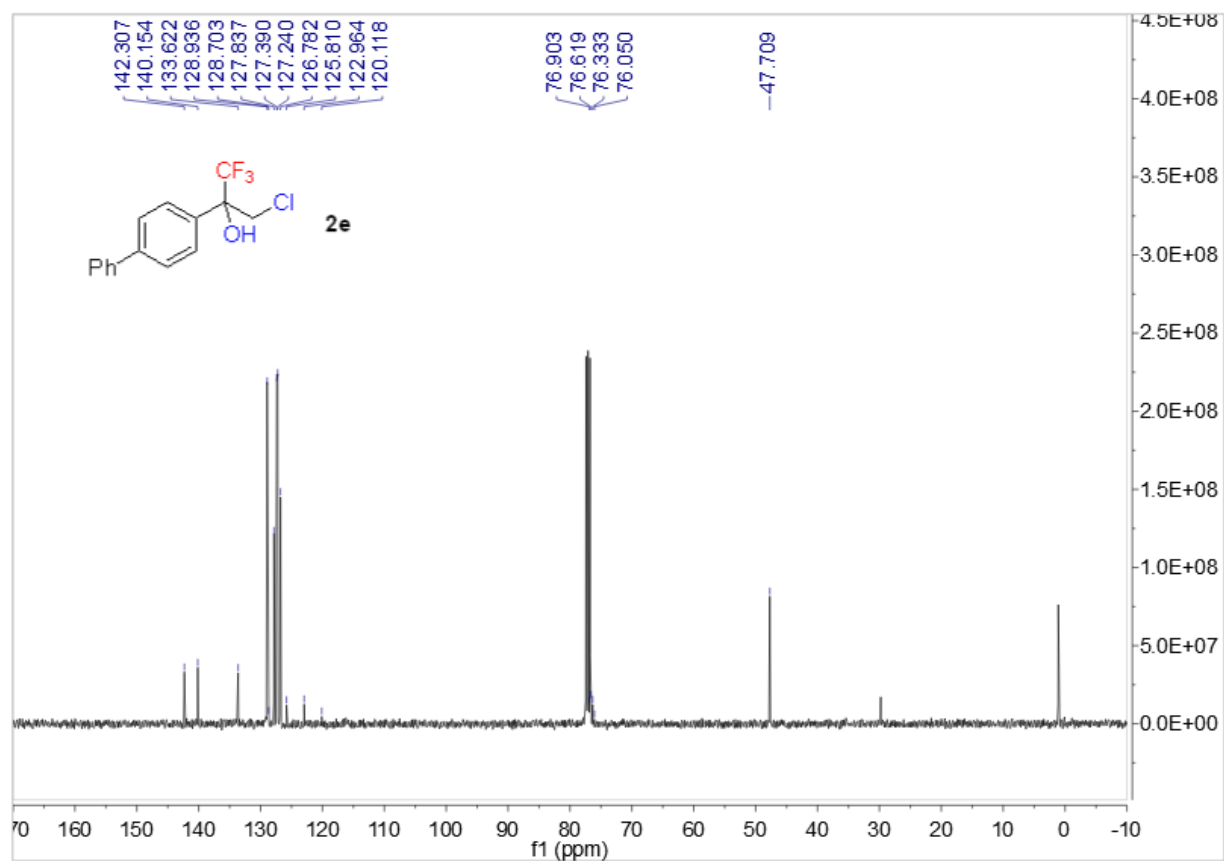
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
239.0451	239.0451	0.0	0.0	3.5	224.7	n/a	n/a	C10 H11 O F3 Cl

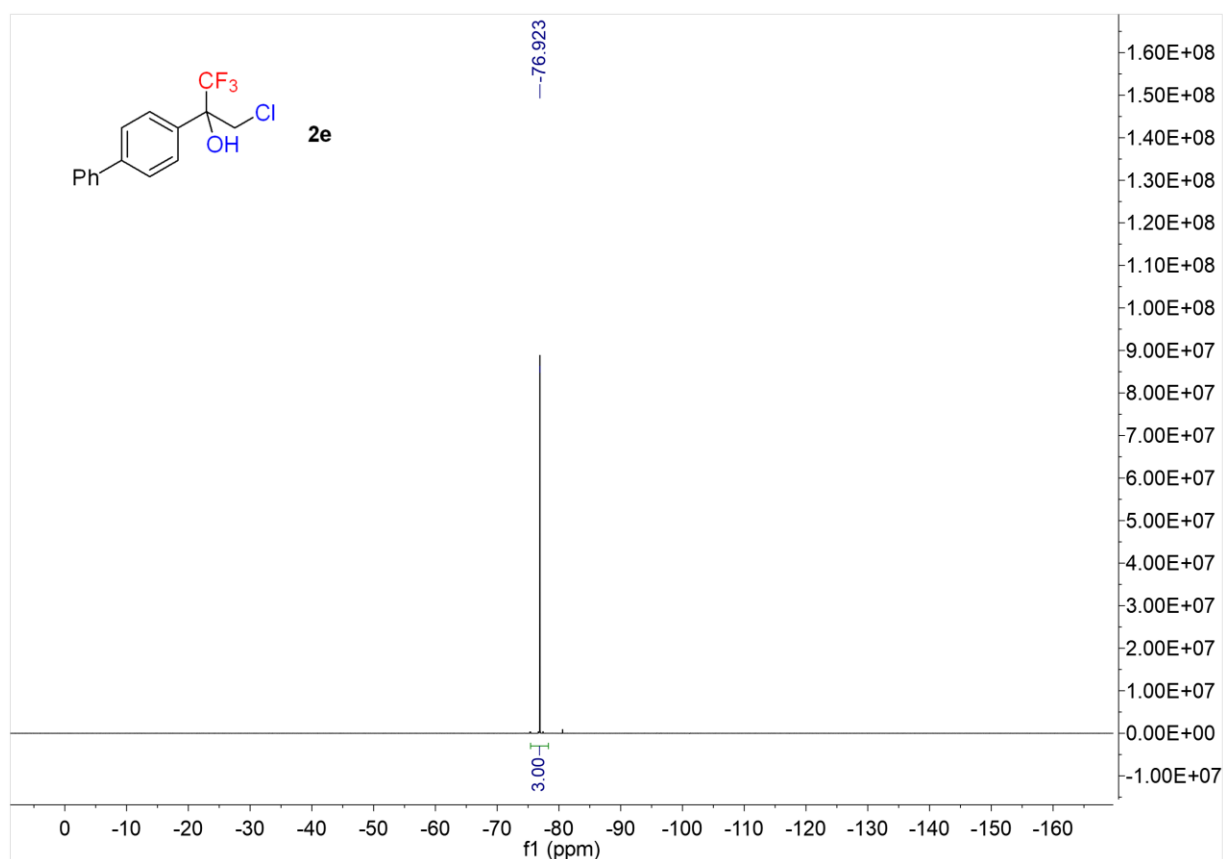
^1H NMR spectrum of **2e** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2e** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2e** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2e**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1865 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

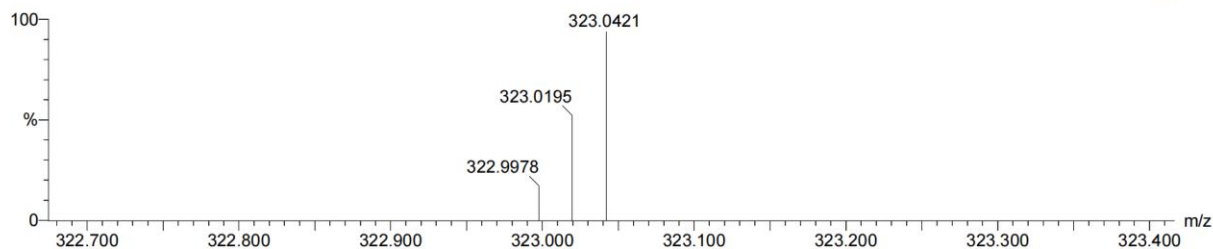
Elements Used:

C: 15-15 H: 12-12 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-5 9 (0.084)

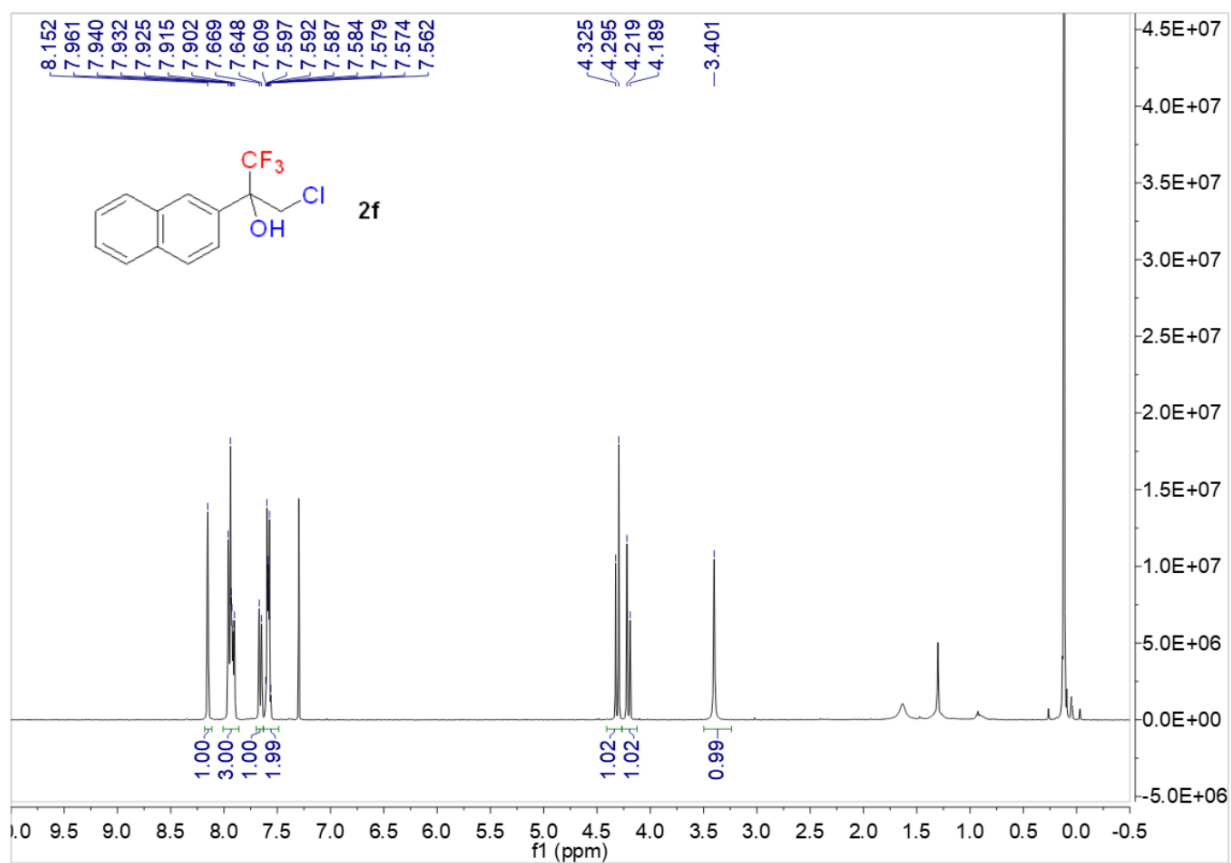
1: TOF MS ES+
1.98e+002



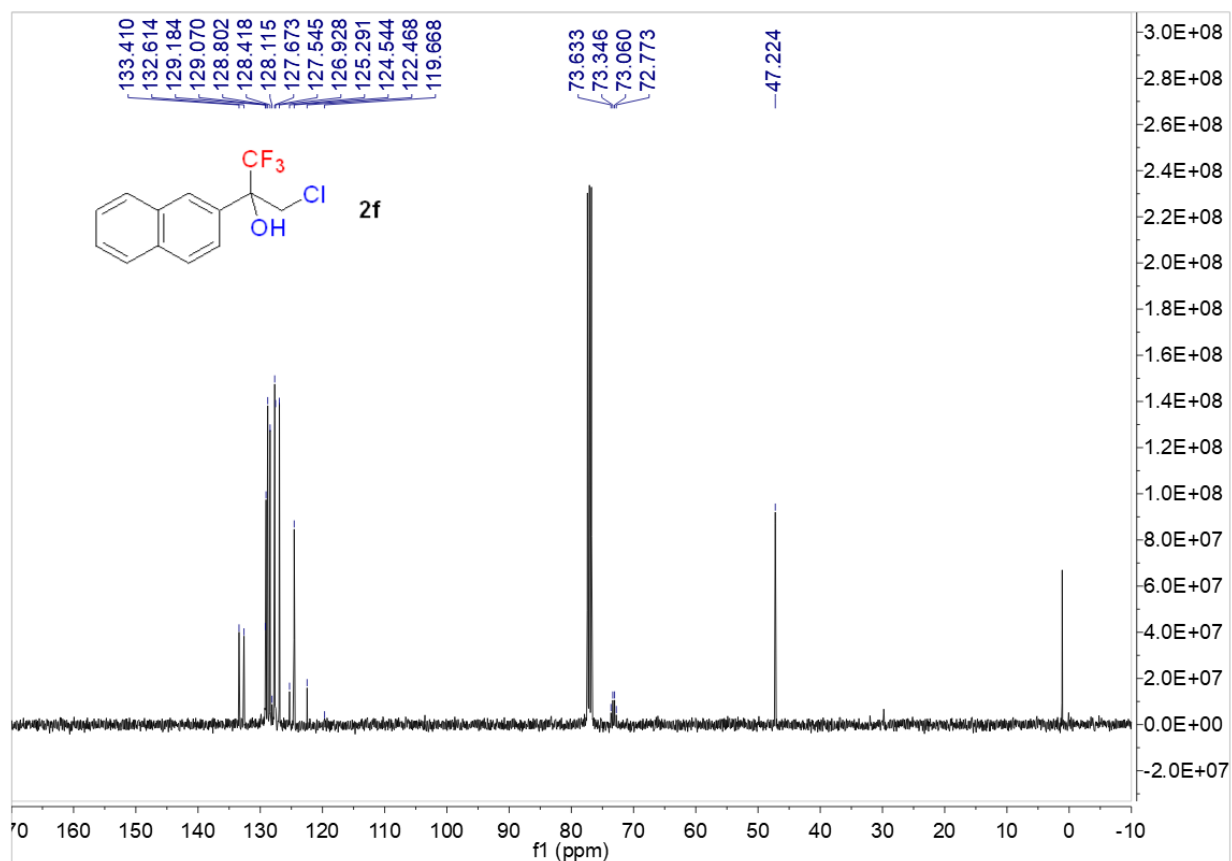
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
323.0421	323.0426	-0.5	-1.5	7.5	49.2	n/a	n/a	C ₁₅ H ₁₂ O F ₃ Na Cl

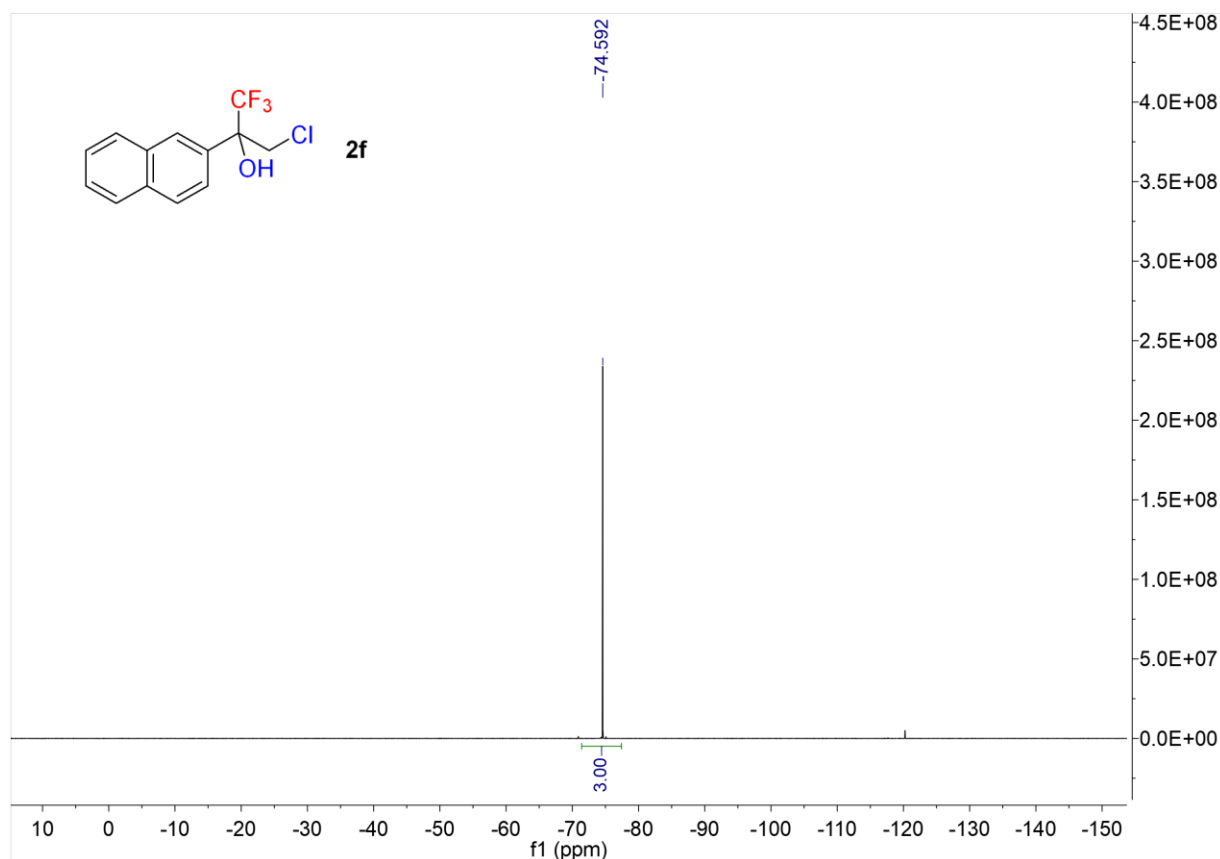
^1H NMR spectrum of **2f** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2f** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2f** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2f**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1170 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

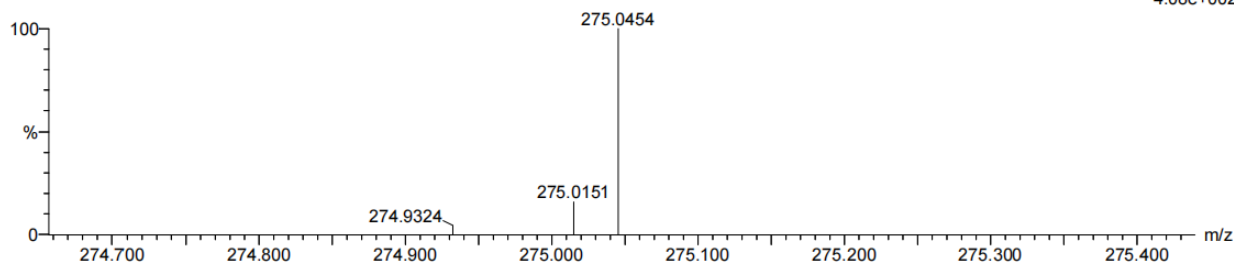
Elements Used:

C: 13-13 H: 11-11 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-10 16 (0.121)

1: TOF MS ES+
4.08e+002

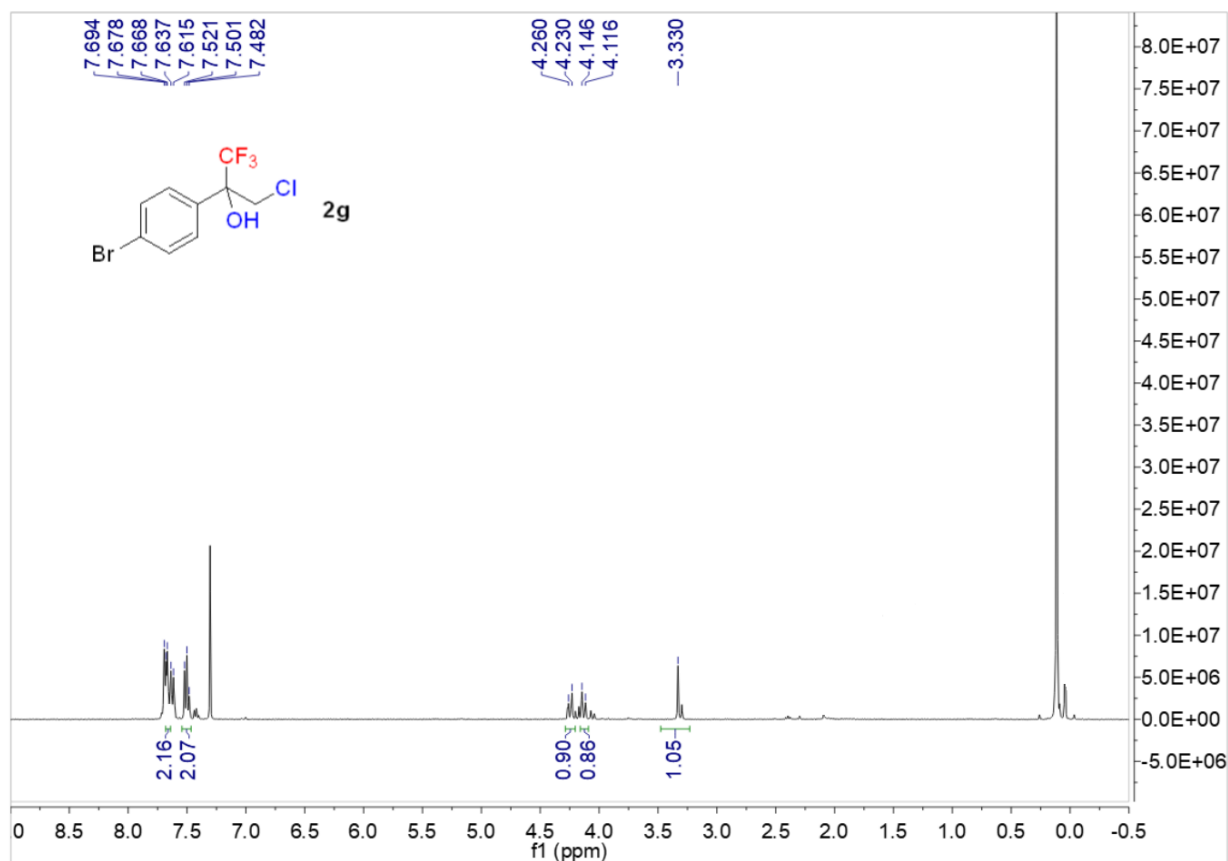


Minimum:

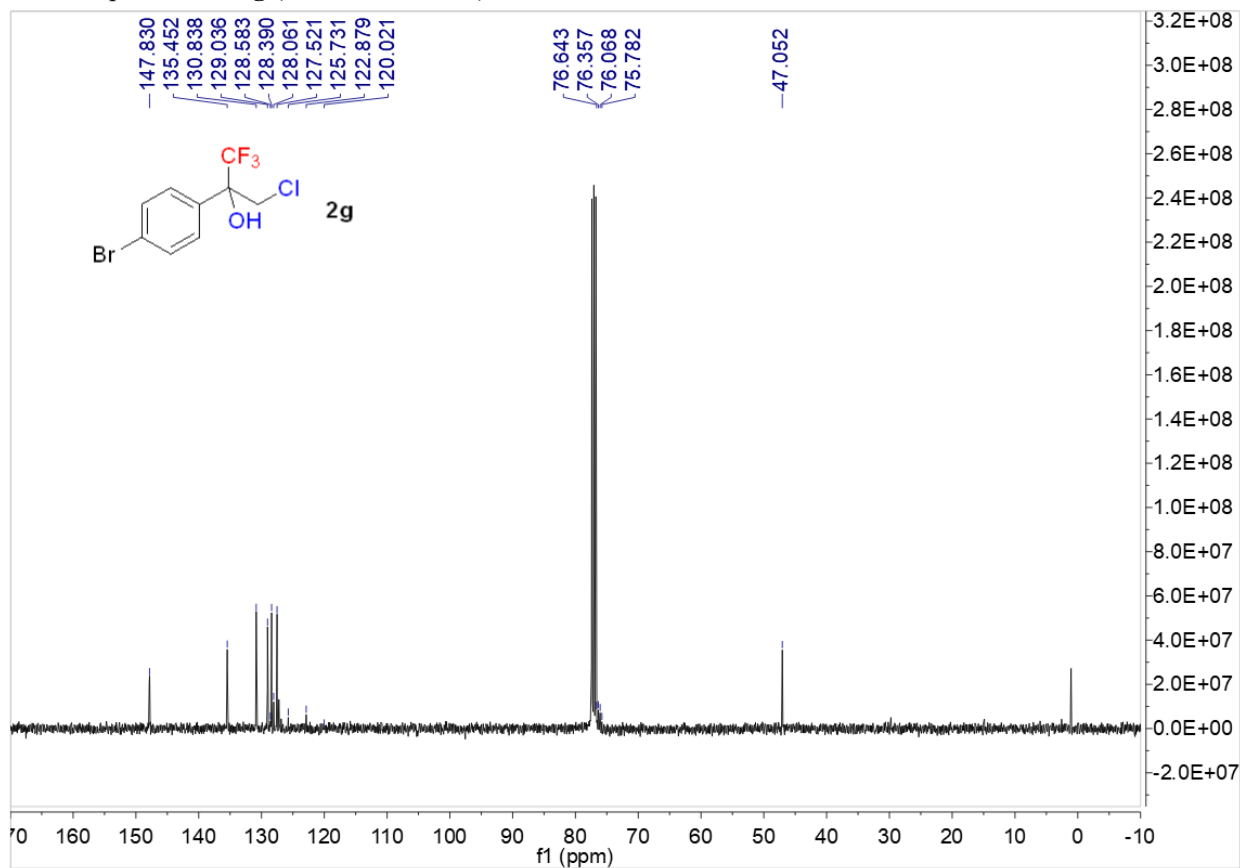
Maximum: 5.0 10.0 -1.5 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
275.0454	275.0451	0.3	1.1	6.5	77.8	n/a	n/a	C13 H11 O F3 Cl

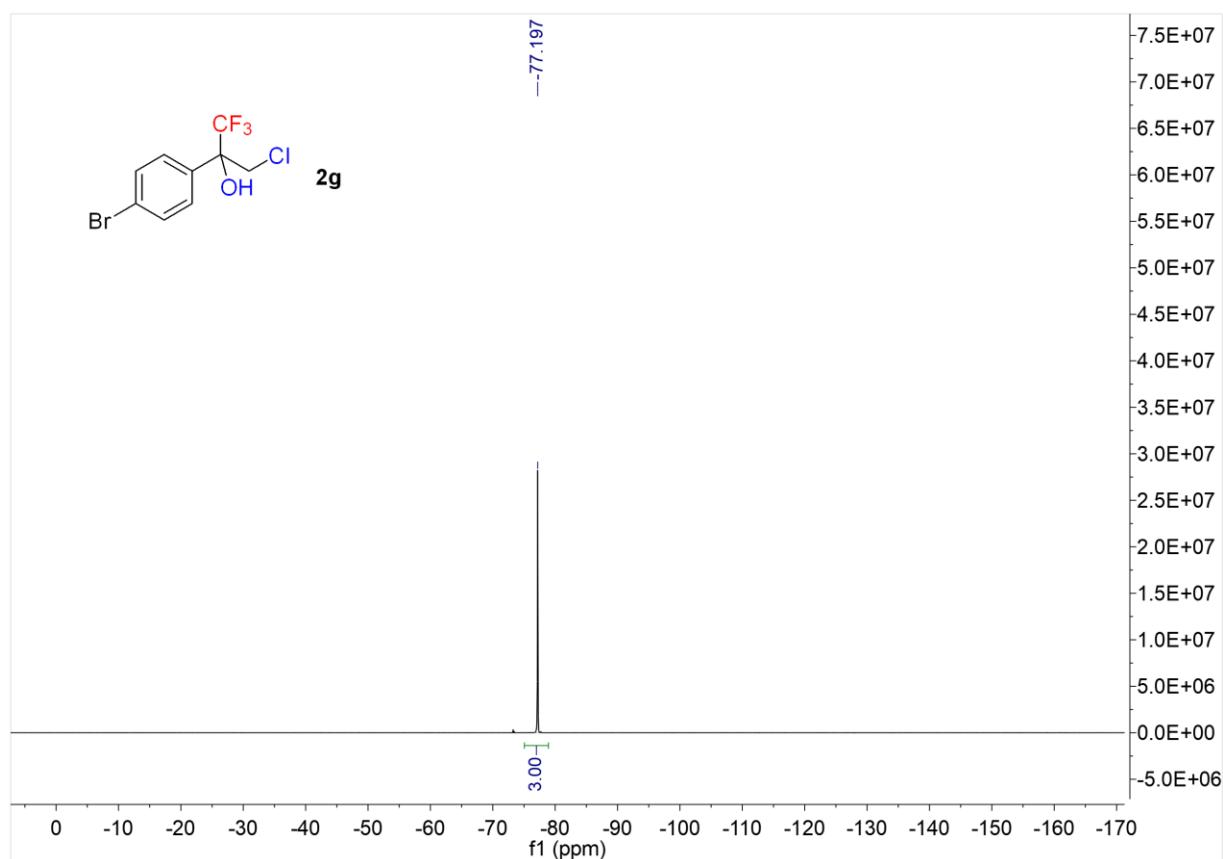
^1H NMR spectrum of **2g** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2g** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2g** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2g**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

988 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

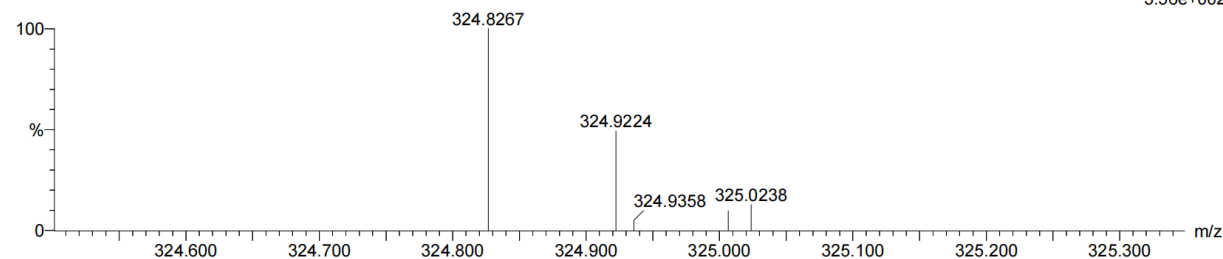
Elements Used:

C: 9-9 H: 7-7 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3 Br: 1-4

6

241205-17-2 6 (0.068)

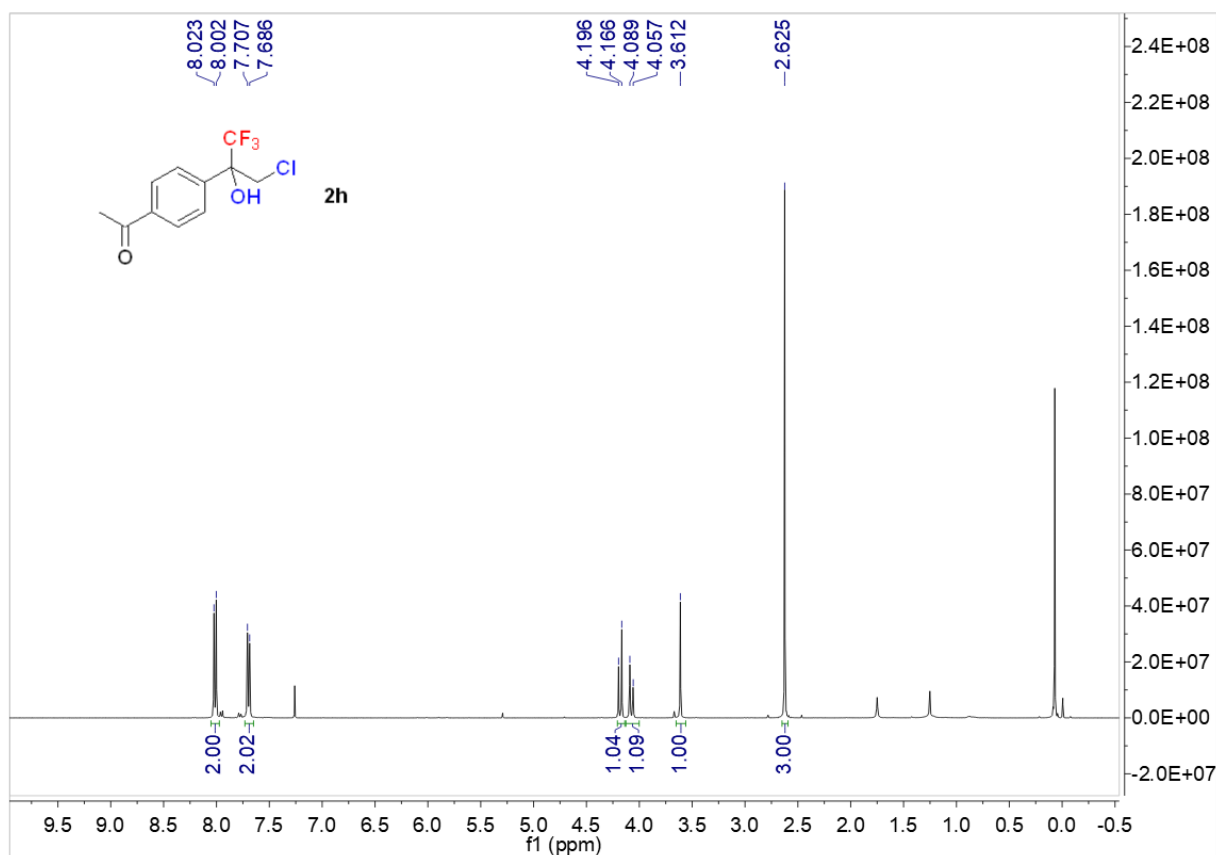
1: TOF MS ES+
3.56e+002



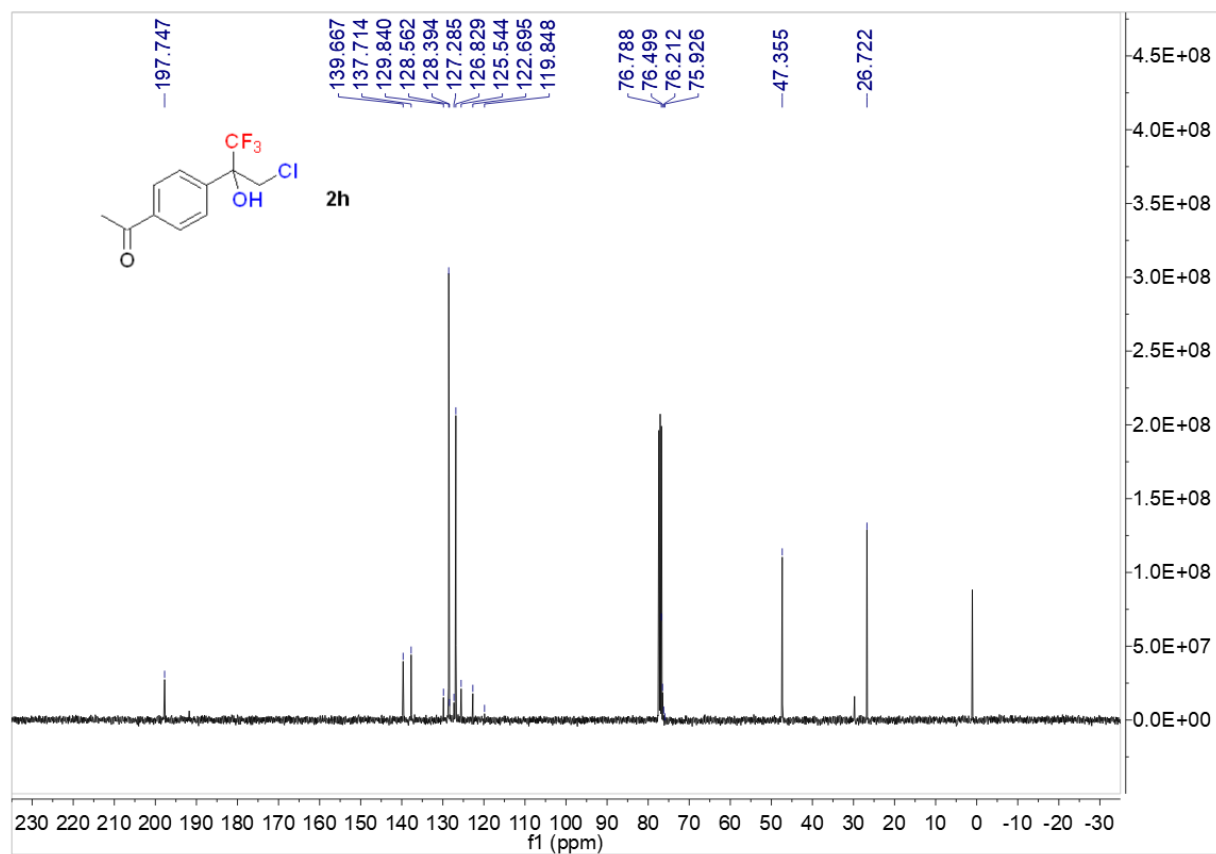
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
324.9224	324.9219	0.5	1.5	3.5	41.0	n/a	n/a	C ₉ H ₇ O ₂ F ₃ NaClBr

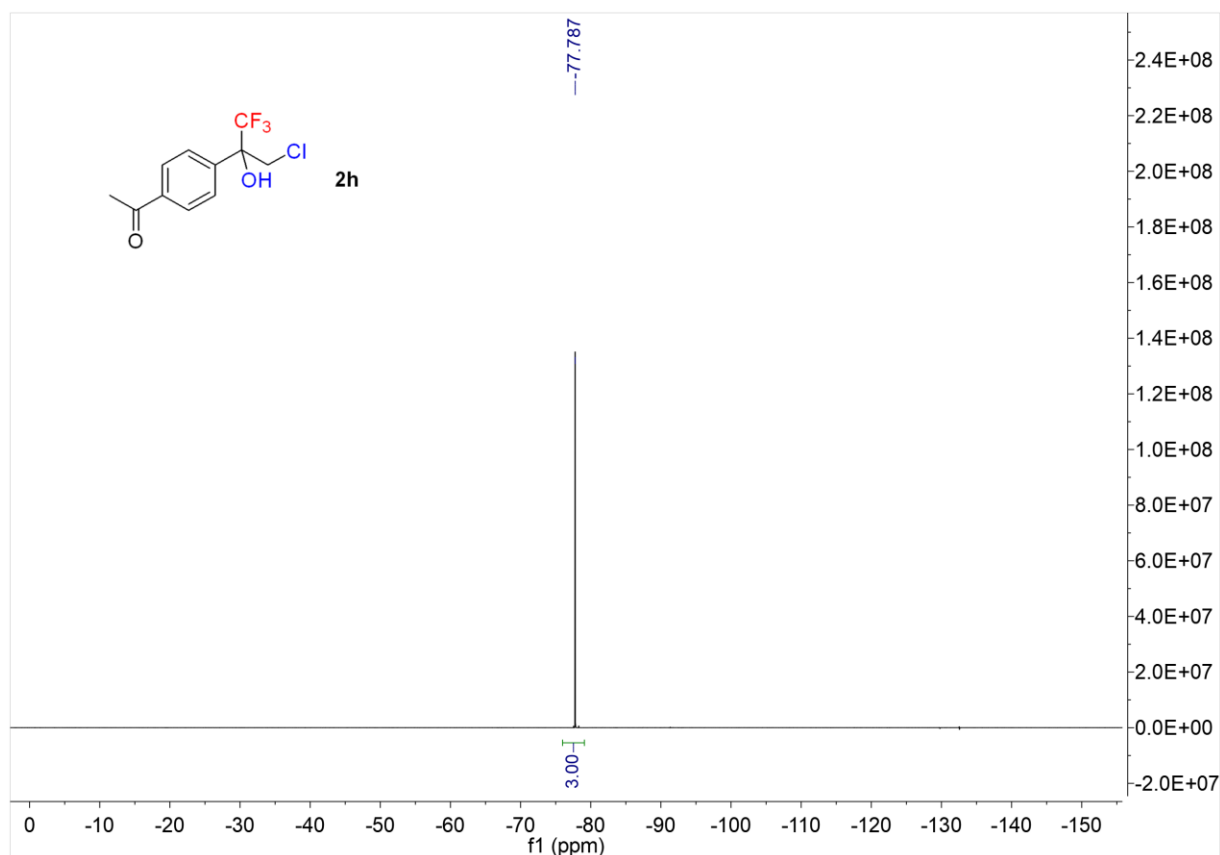
^1H NMR spectrum of **2h** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2h** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2h** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2h**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

825 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

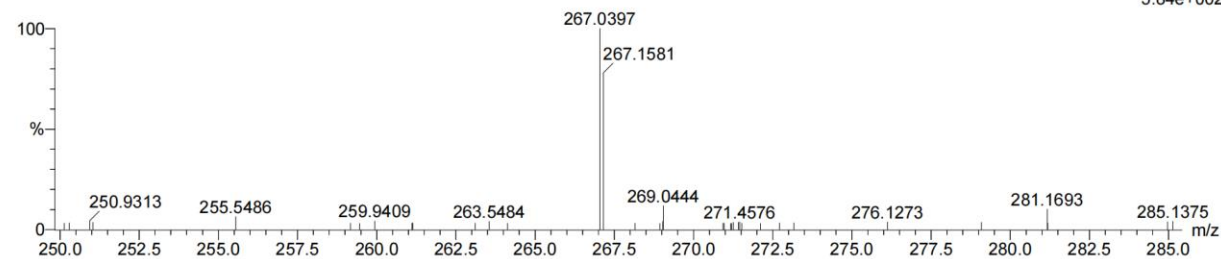
Elements Used:

C: 11-11 H: 11-11 N: 0-100 O: 0-100 Na: 0-1 Cl: 1-5 F: 3-6

14

240308-3-3 7 (0.062)

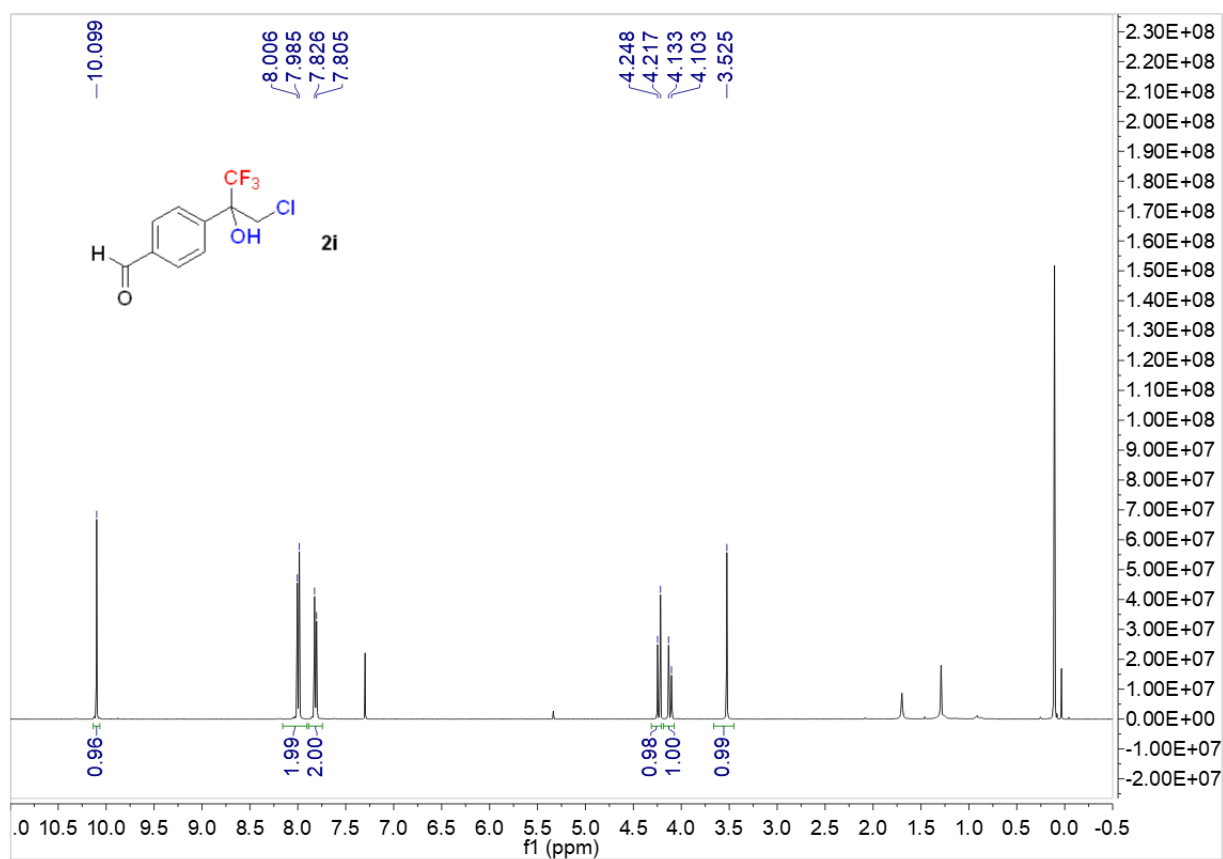
1: TOF MS ES+
5.84e+002



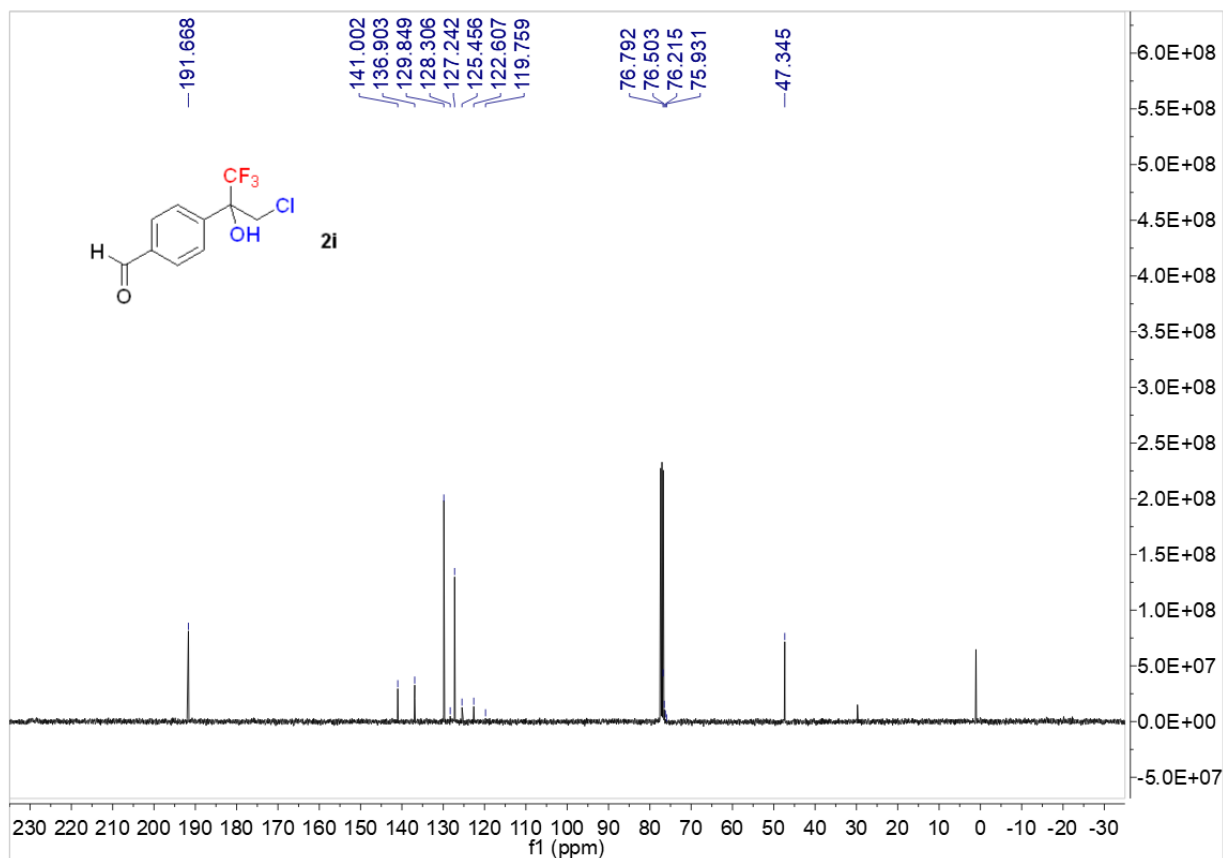
Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
267.0397	267.0400	-0.3	-1.1	4.5	53.3	n/a	n/a	C11 H11 O2 Cl F3

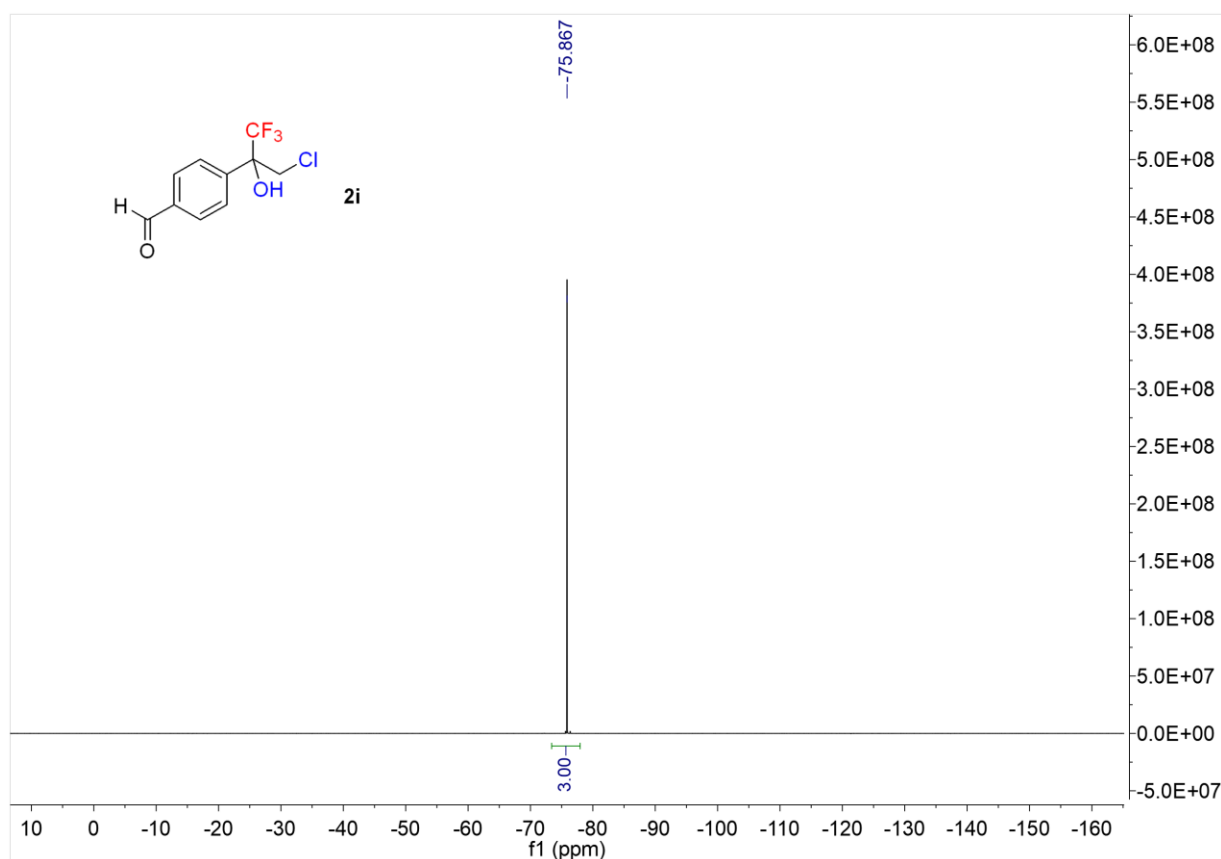
^1H NMR spectrum of **2i** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2i** (100 MHz, CDCl_3)



¹⁹F NMR spectrum of **2i** (367 MHz, CDCl₃)



HRMS (ESI) spectrum of **2i**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

867 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

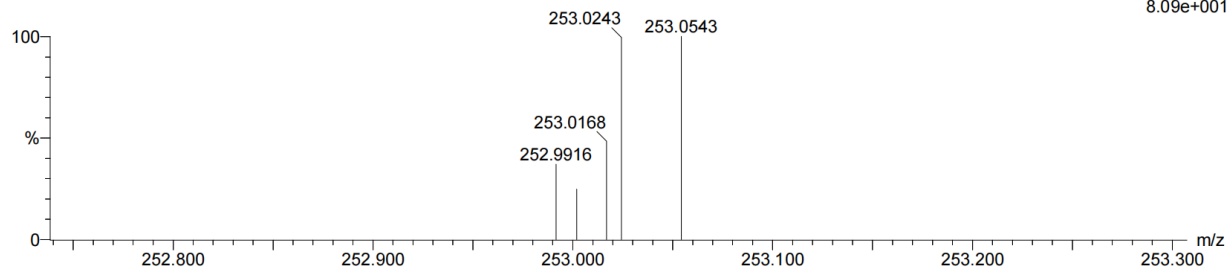
Elements Used:

C: 10-10 H: 9-9 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-1 16 (0.121)

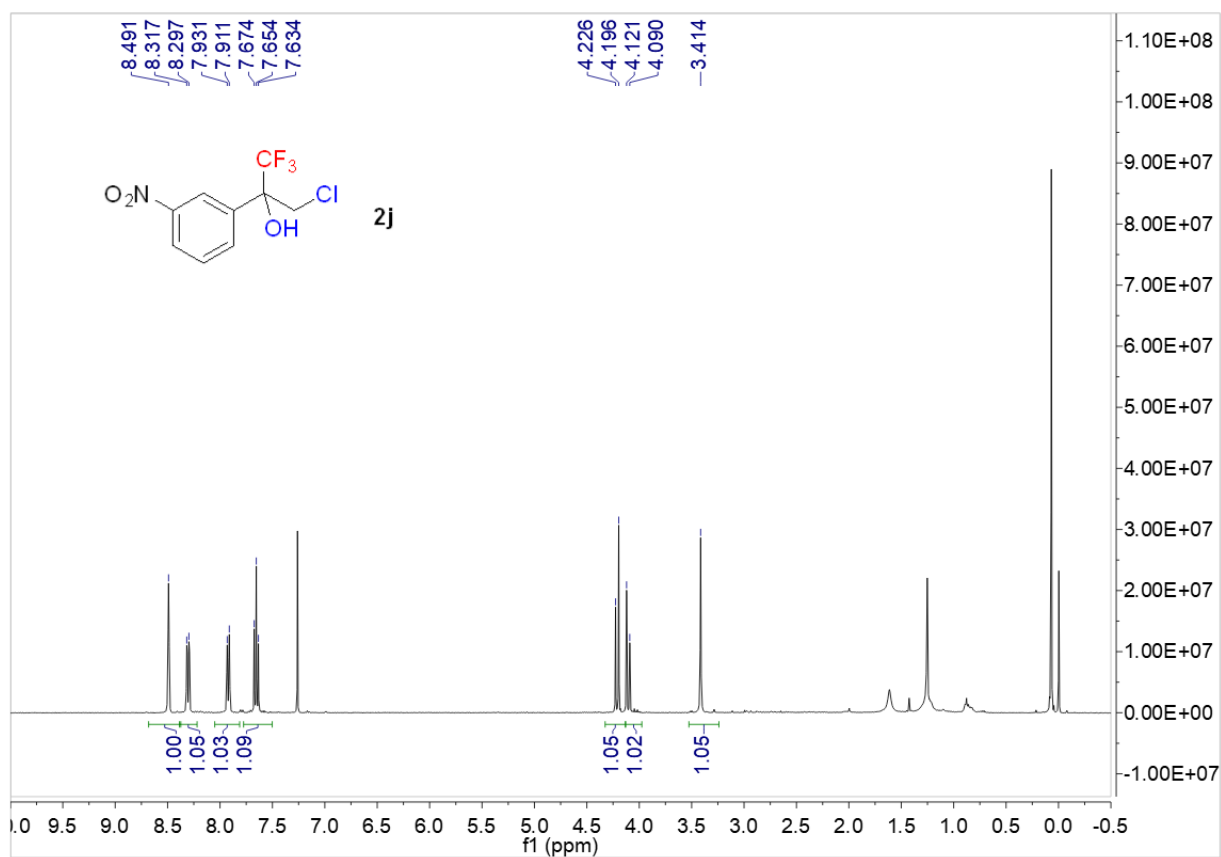
1: TOF MS ES+
8.09e+001



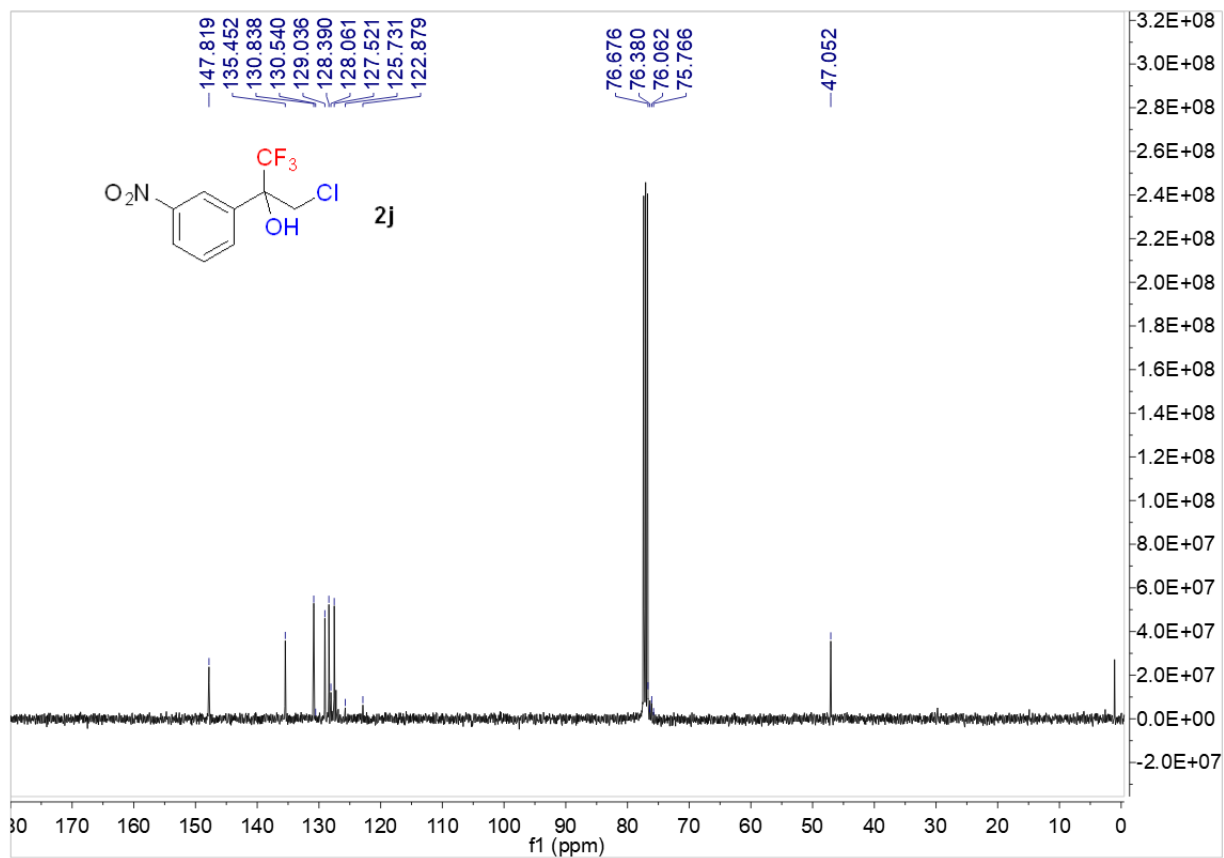
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
253.0243	253.0243	0.0	0.0	4.5	25.9	n/a	n/a	C10 H9 O2 F3 Cl

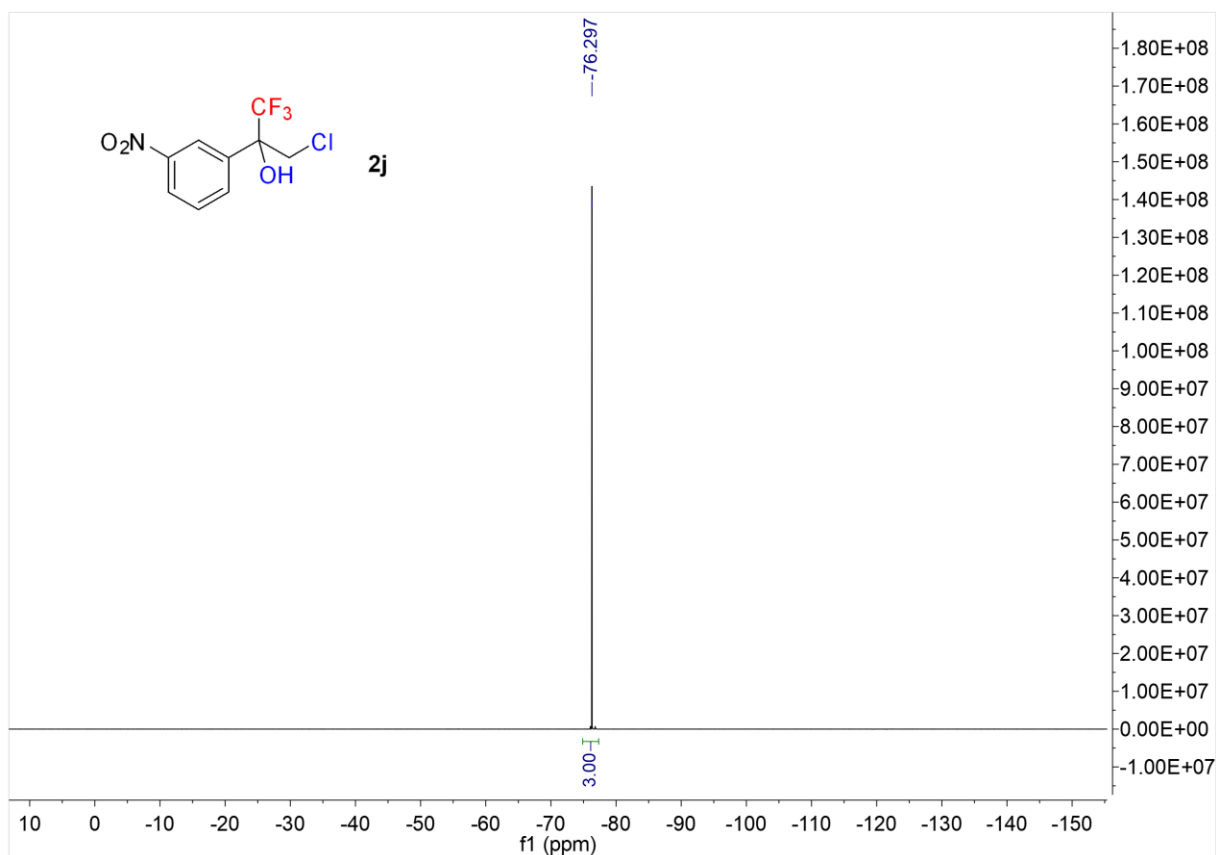
^1H NMR spectrum of **2j** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2j** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2j** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2j**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1013 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

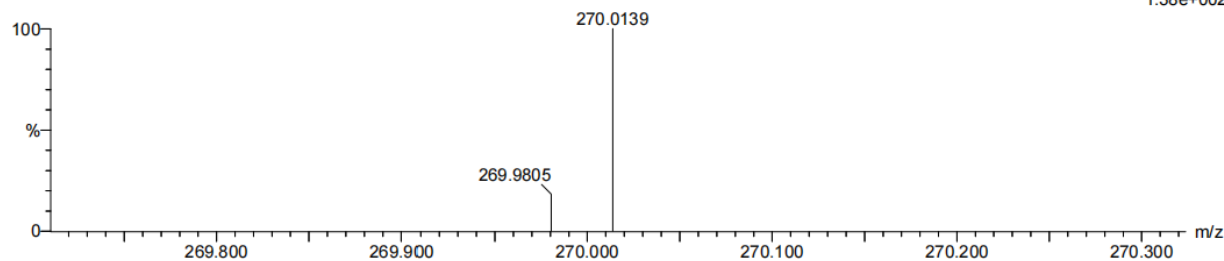
Elements Used:

C: 9-9 H: 8-8 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-8 22 (0.152)

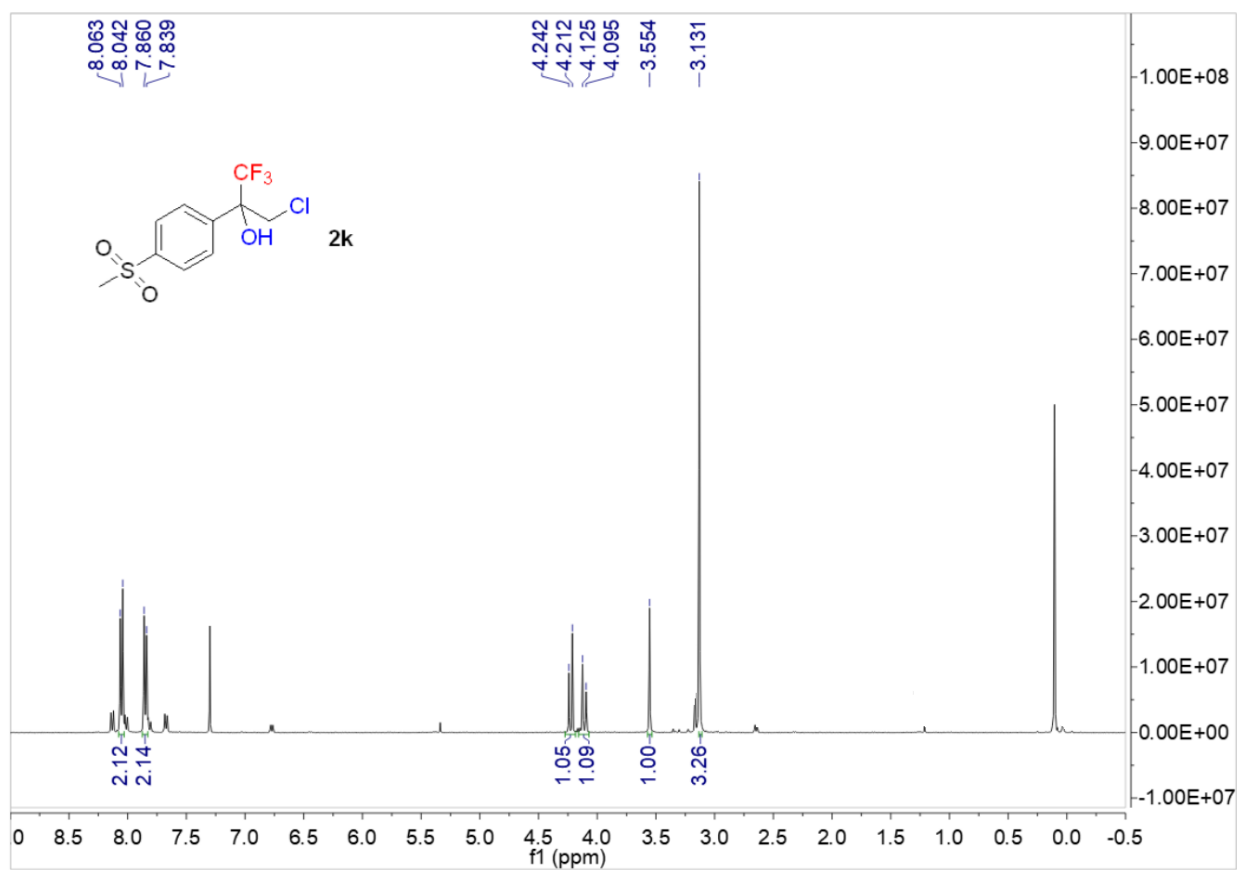
1: TOF MS ES+
1.38e+002



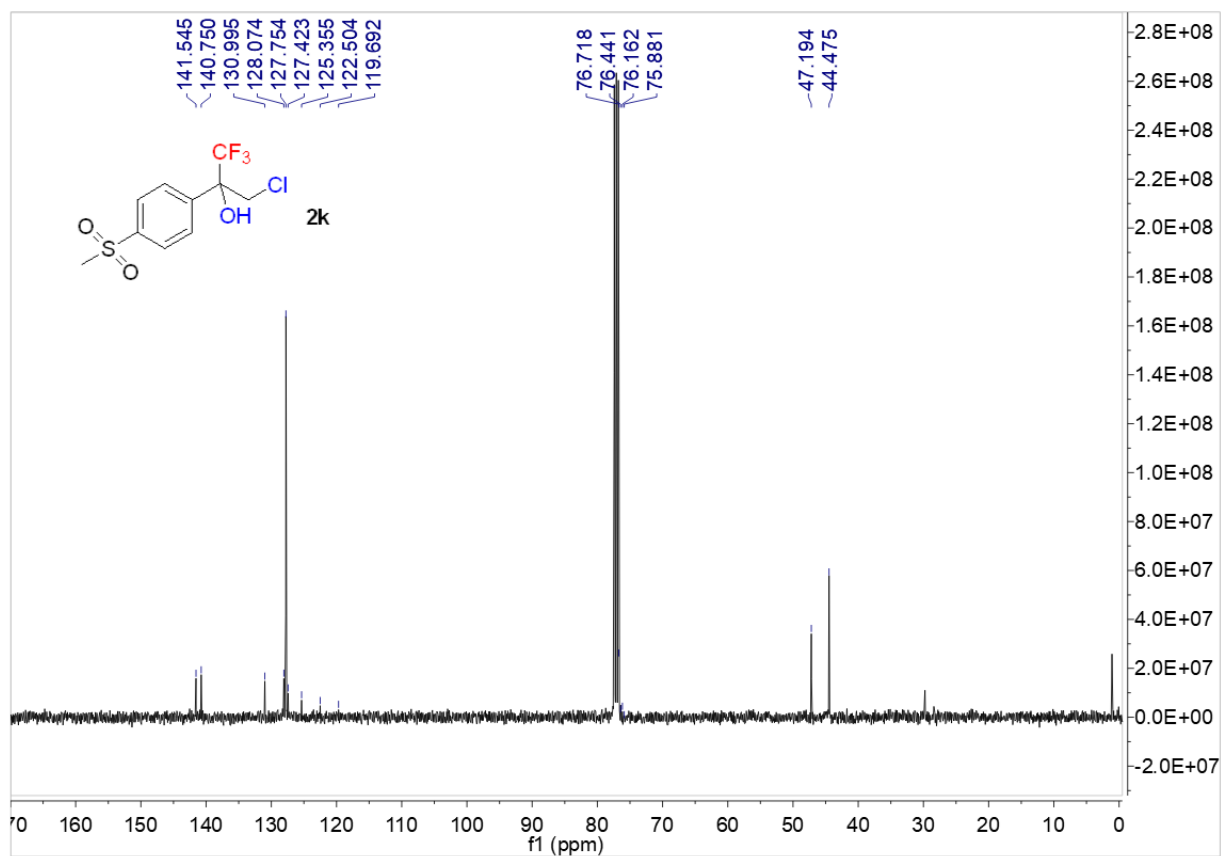
Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
270.0139	270.0145	-0.6	-2.2	4.5	33.7	n/a	n/a	C ₉ H ₈ N ₀ O ₃ F ₃ Cl ₁

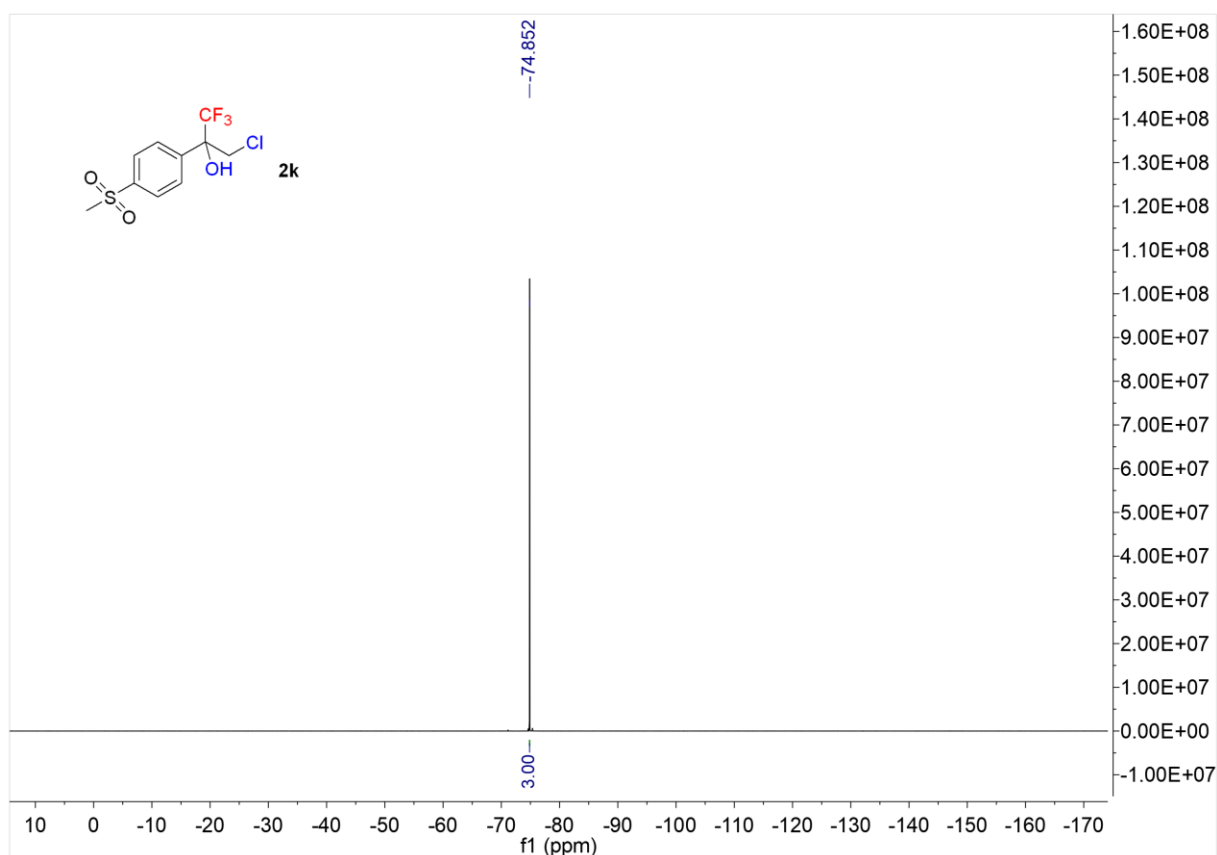
^1H NMR spectrum of **2k** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2k** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2k** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2k**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1924 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

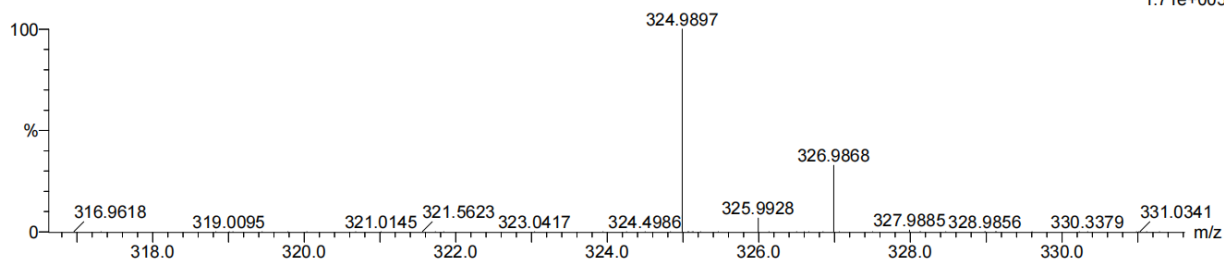
Elements Used:

C: 10-10 H: 10-10 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 S: 1-2 Cl: 1-5

31

240308-3-20 8 (0.065)

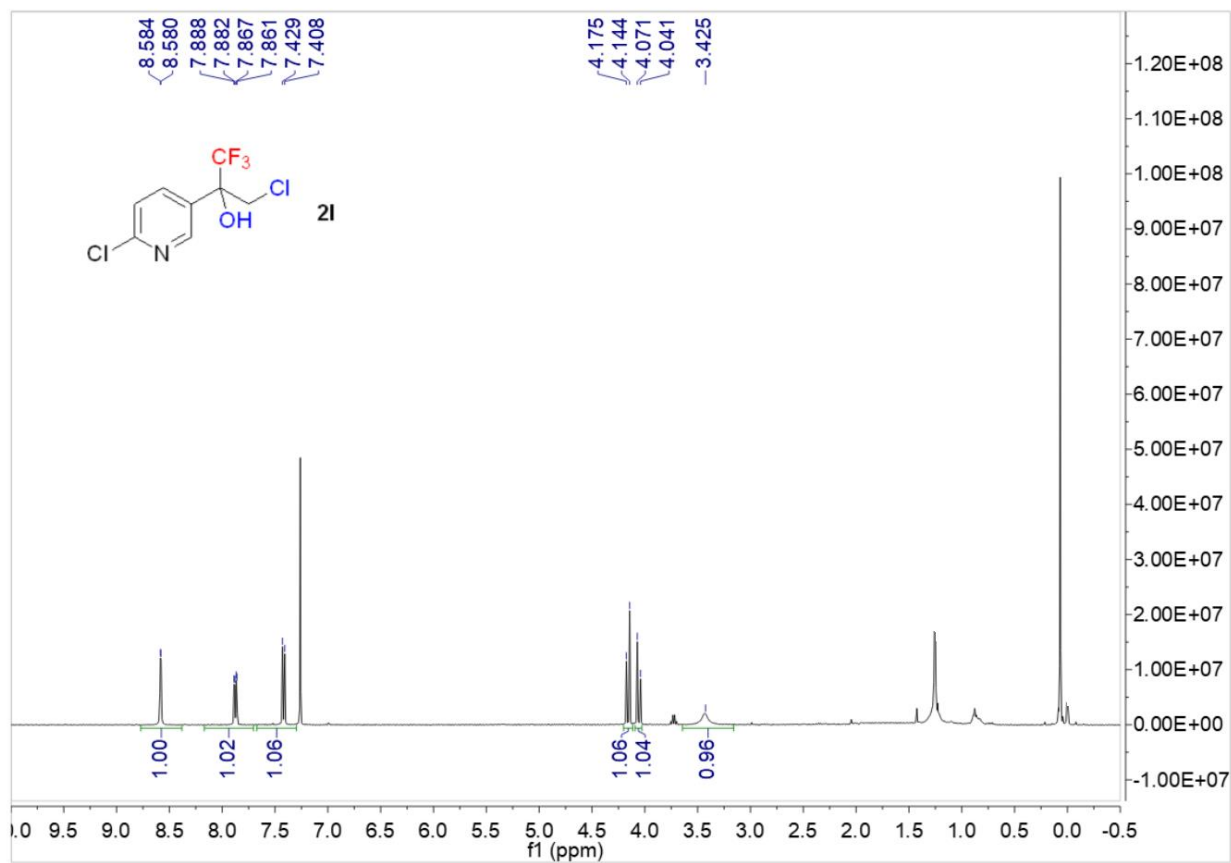
1: TOF MS ES+
1.71e+005



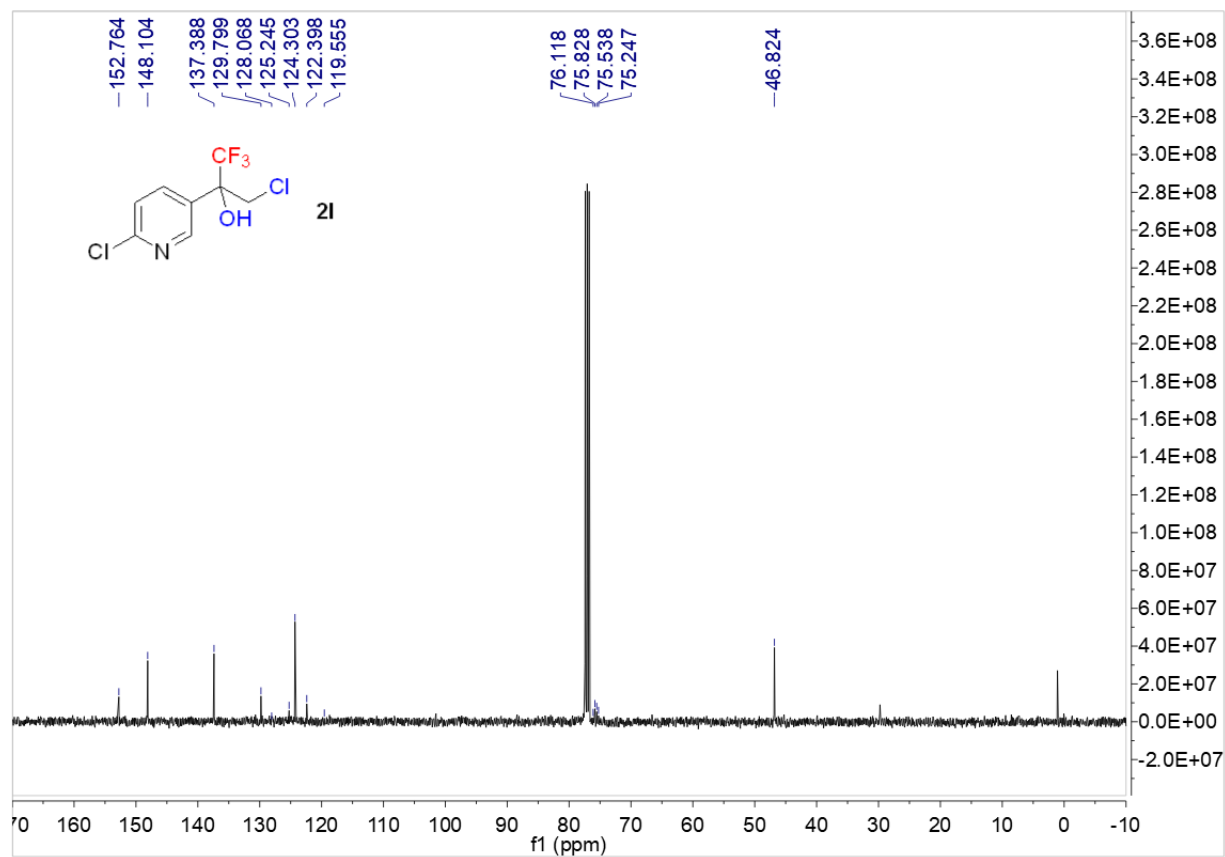
Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
324.9897	324.9889	0.8	2.5	3.5	99.3	n/a	n/a	C10 H10 O3 F3 Na S Cl

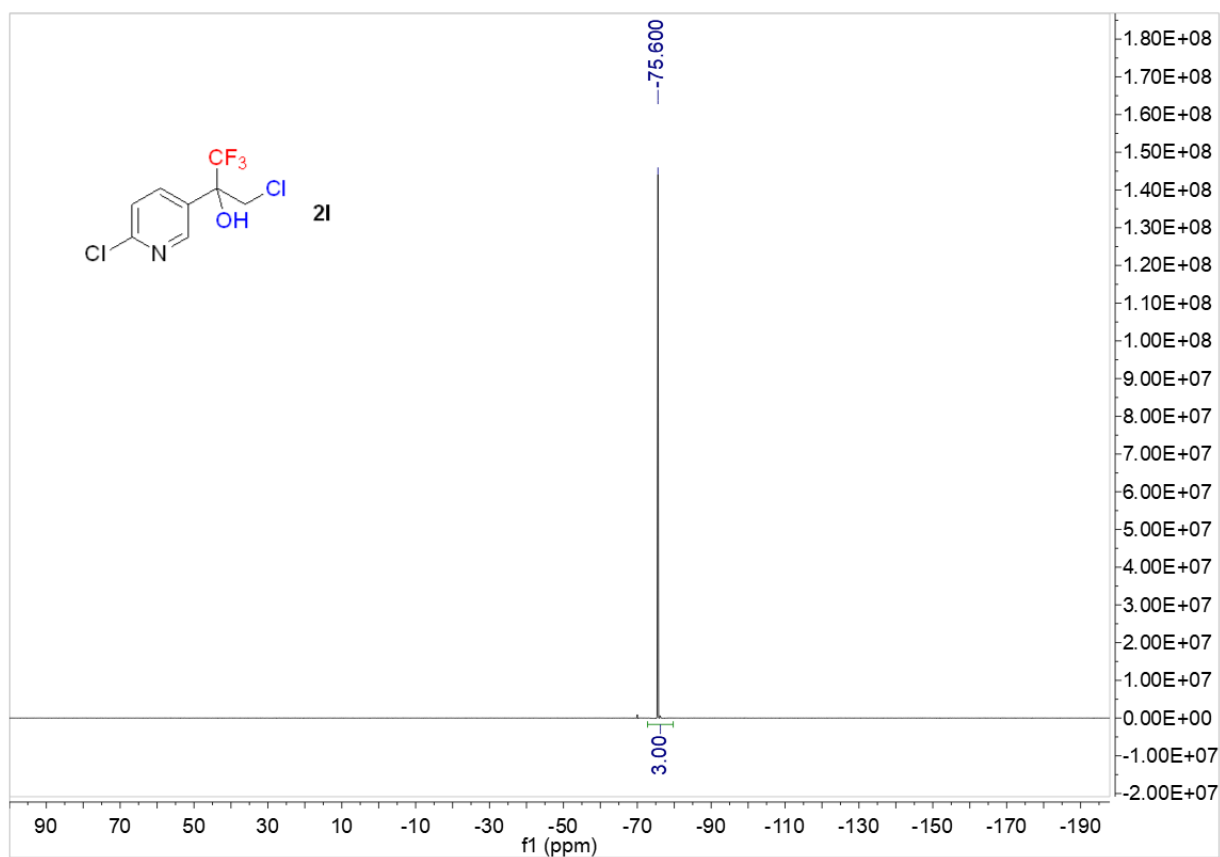
^1H NMR spectrum of **21** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **21** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **2I** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2I**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

686 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

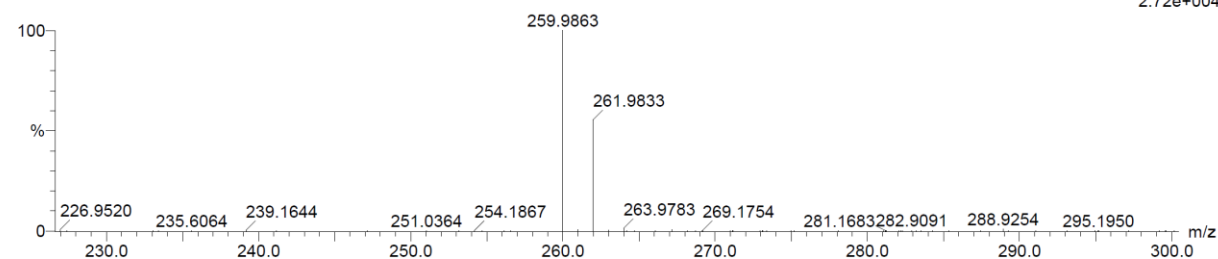
Elements Used:

C: 8-8 H: 7-7 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 Cl: 1-5

31

240308-3-19 16 (0.094)

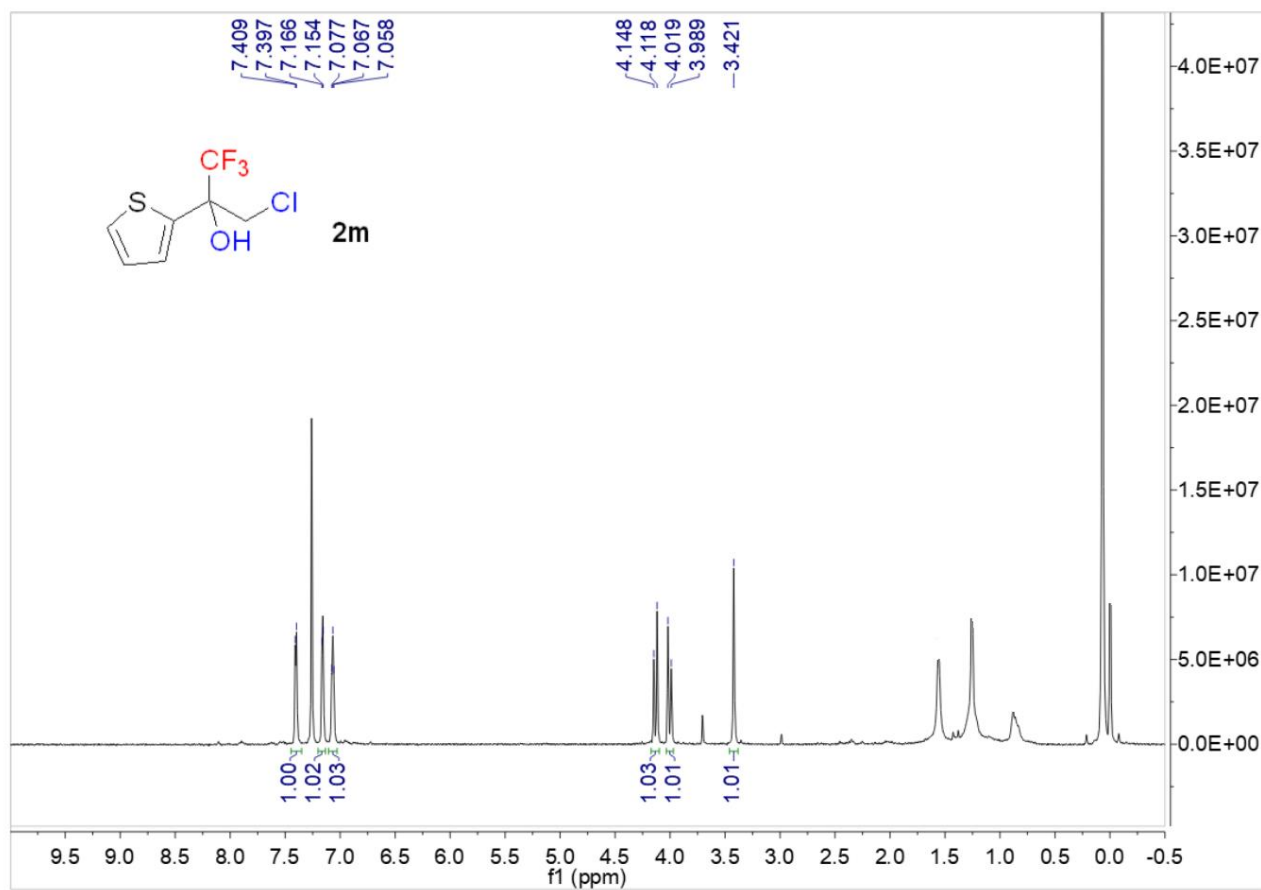
1: TOF MS ES+
2.72e+004



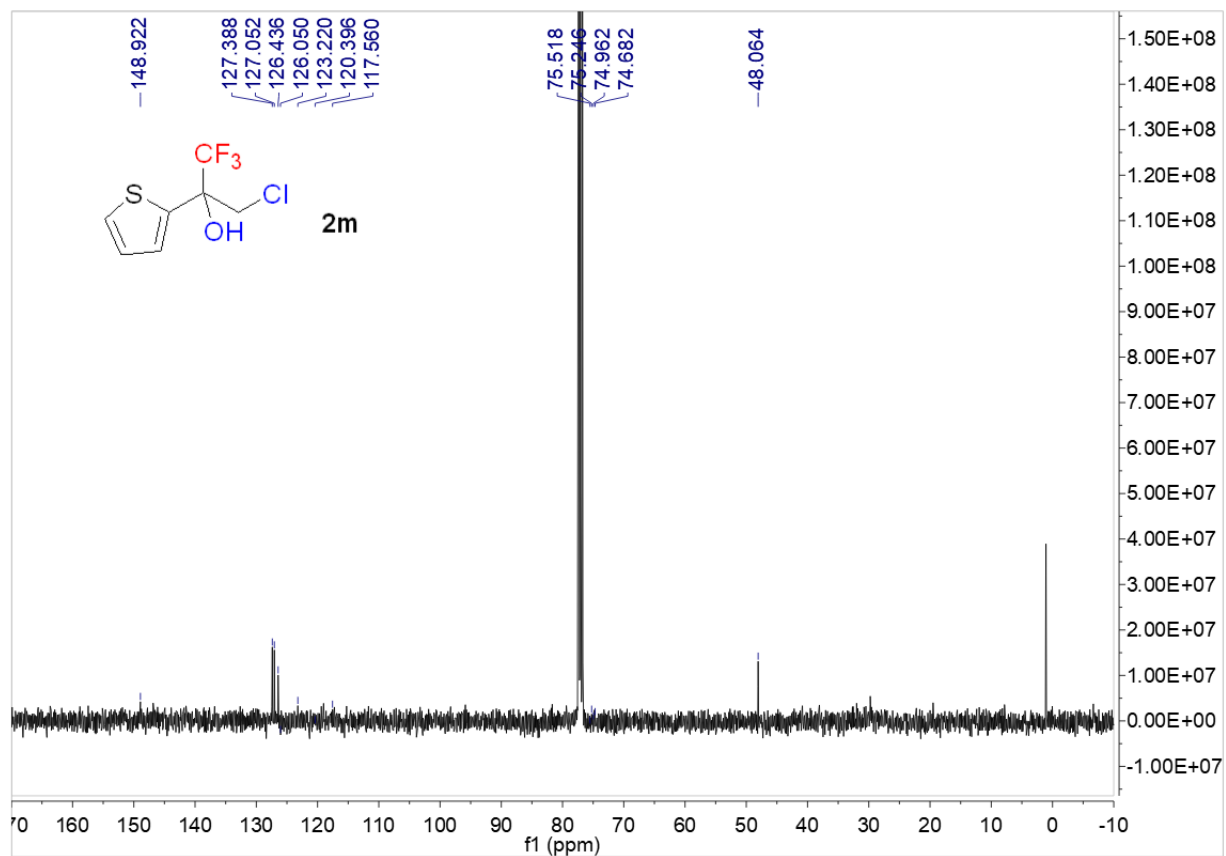
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
259.9863	259.9857	0.6	2.3	3.5	34.4	n/a	n/a	C8 H7 N 0 F3 Cl2

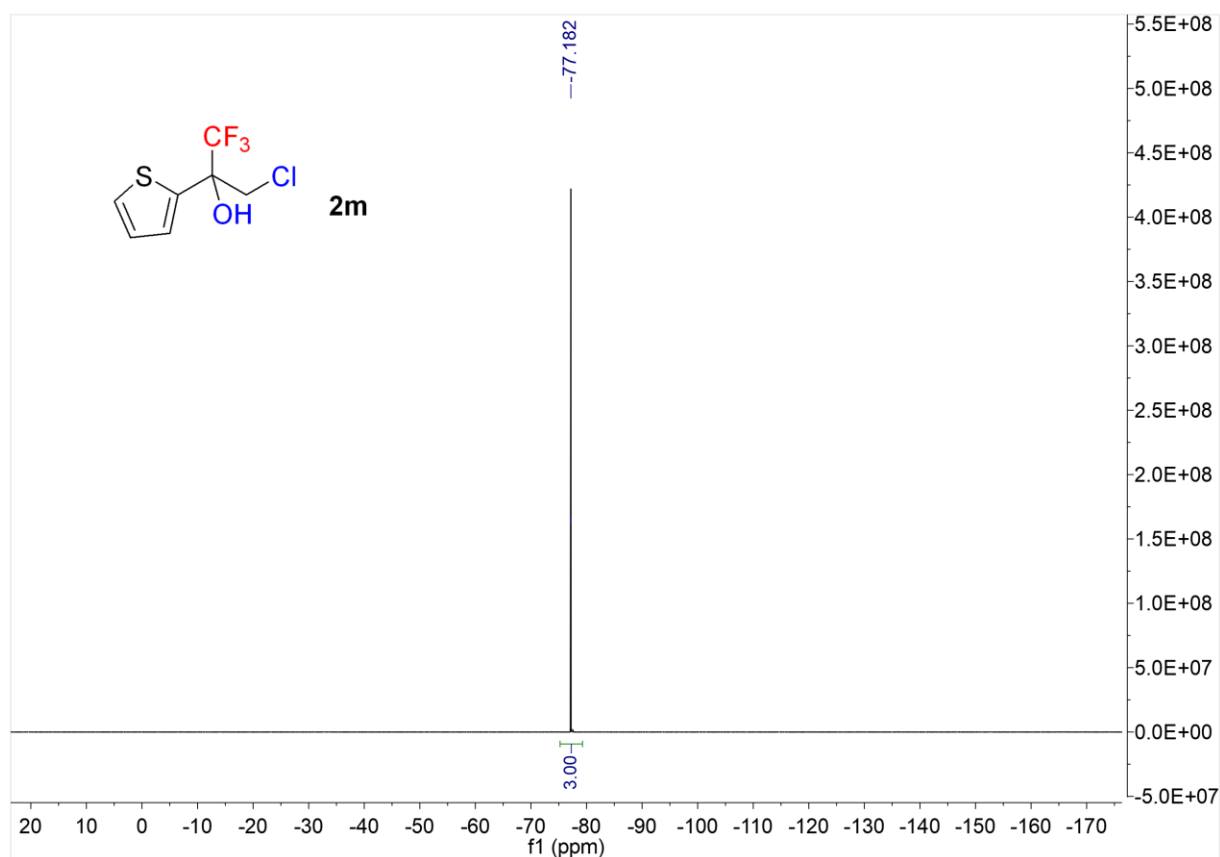
^1H NMR spectrum of **2m** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **2m** (400 MHz, CDCl_3)



^{19}F NMR spectrum of **2m** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **2m**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

670 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

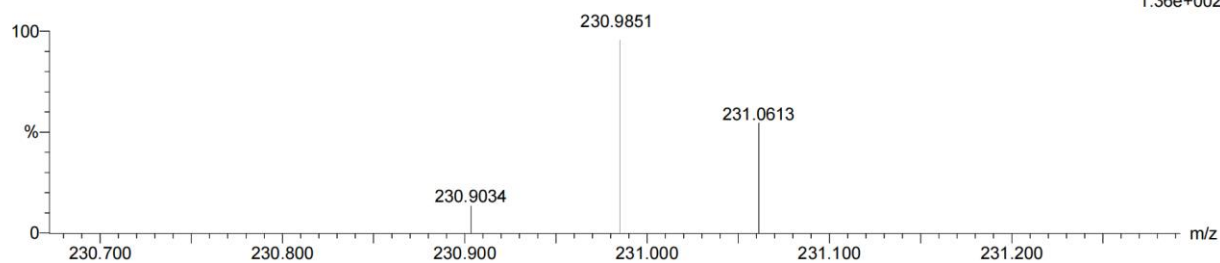
Elements Used:

C: 7-7 H: 7-7 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 S: 1-6 Cl: 1-3

6

241205-17-3 66 (0.422)

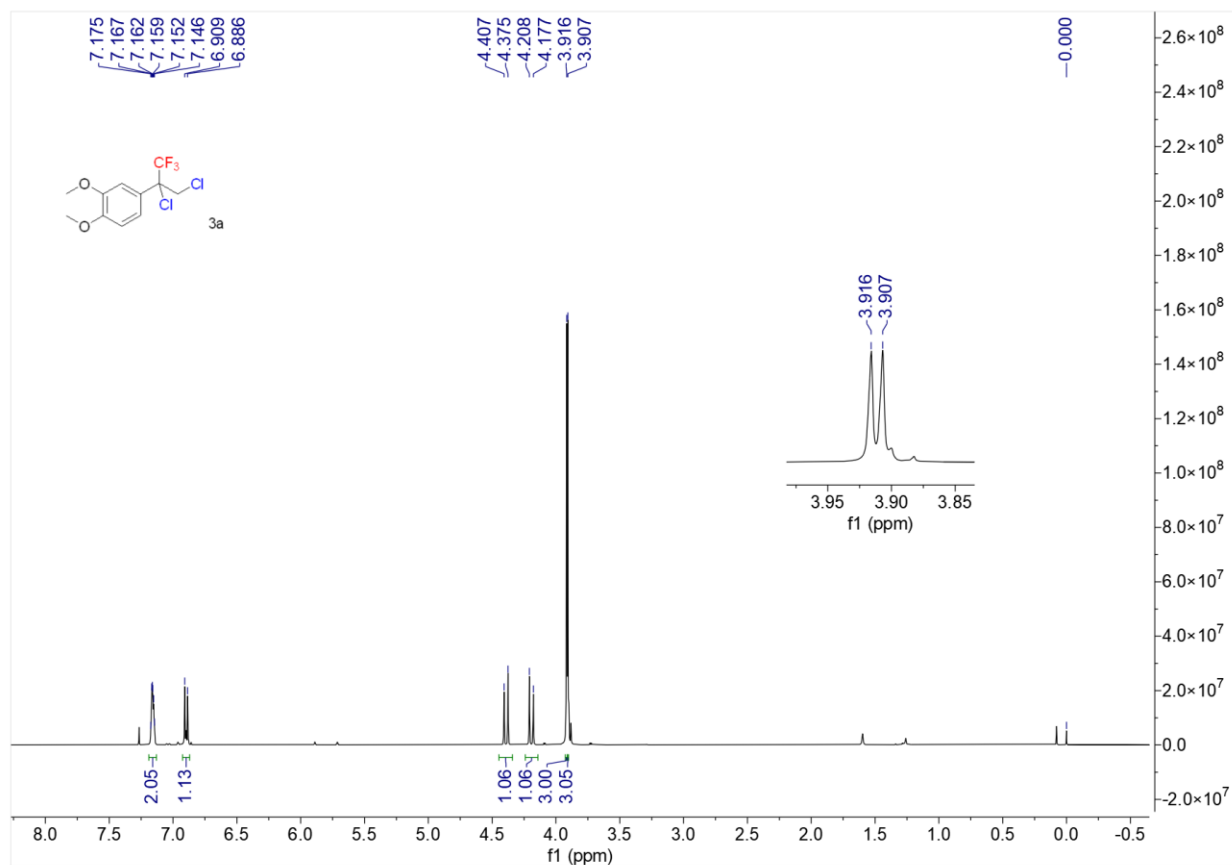
1: TOF MS ES+
1.36e+002



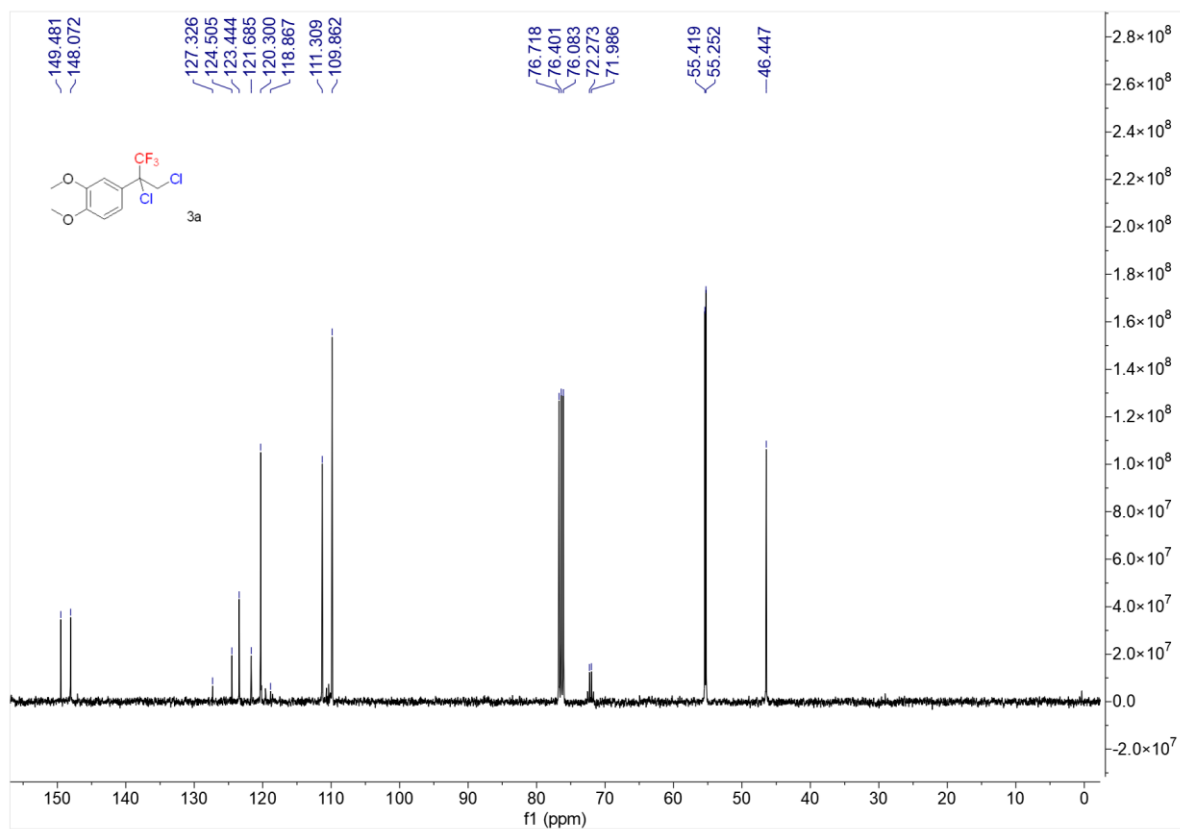
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
230.9851	230.9858	-0.7	-3.0	2.5	33.0	n/a	n/a	C7 H7 O F3 S Cl

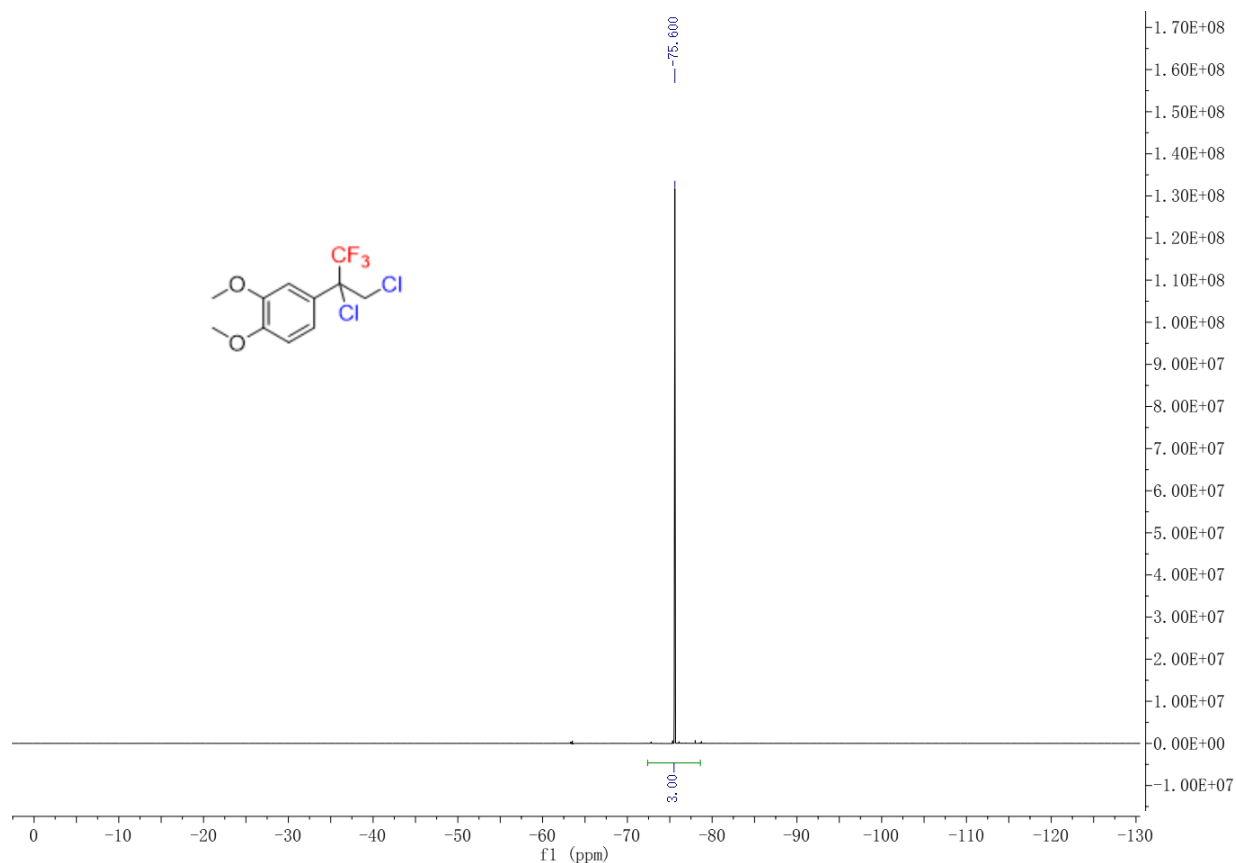
^1H NMR spectrum of **3a** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3a** (100 MHz, CDCl_3)



¹⁹F NMR spectrum of **3a** (367 MHz, CDCl₃)



HRMS (ESI) spectrum of **3a**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1827 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

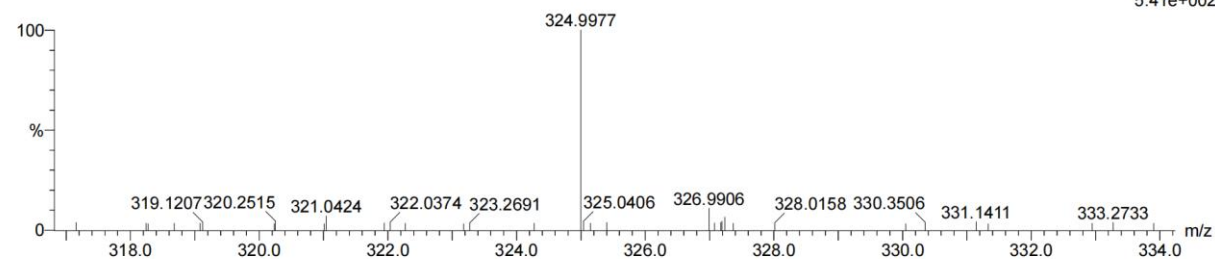
Elements Used:

C: 11-11 H: 11-11 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 Cl: 1-5

14

240308-3-6 10 (0.072)

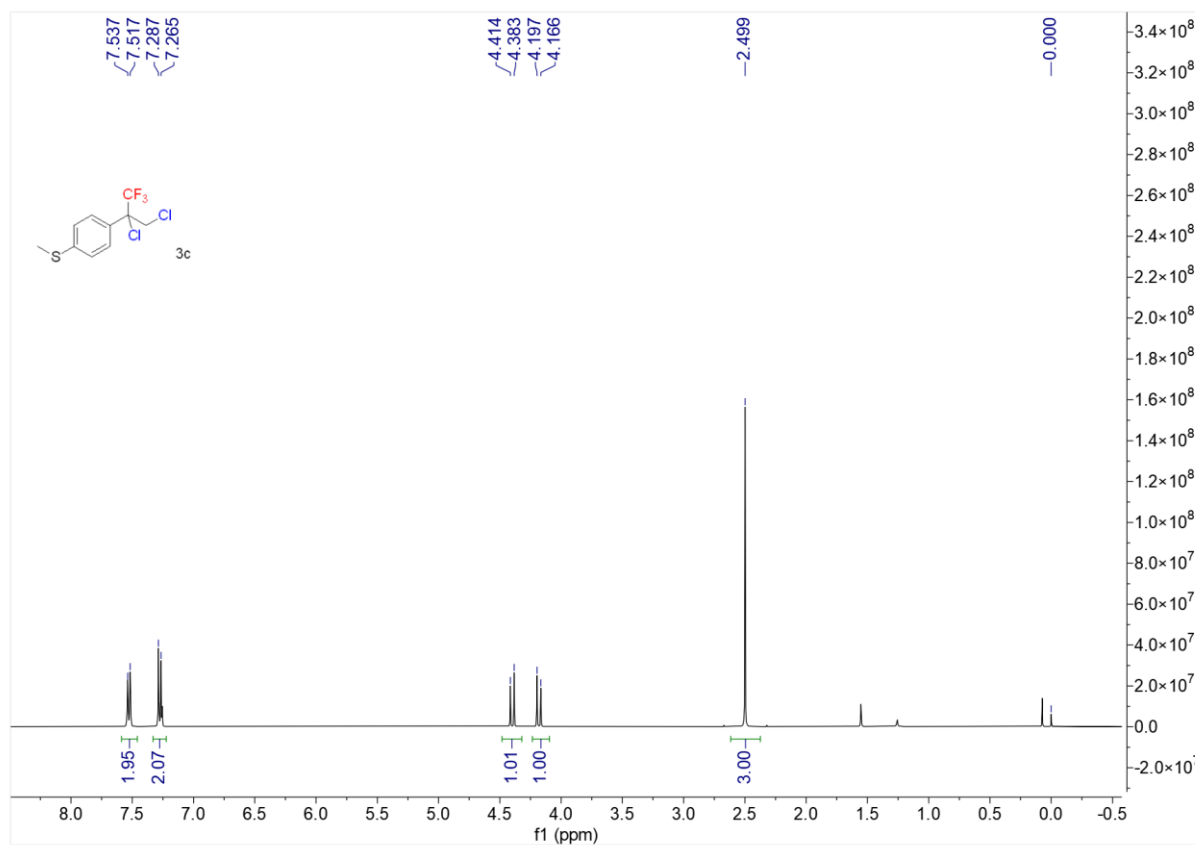
1: TOF MS ES+
5.41e+002



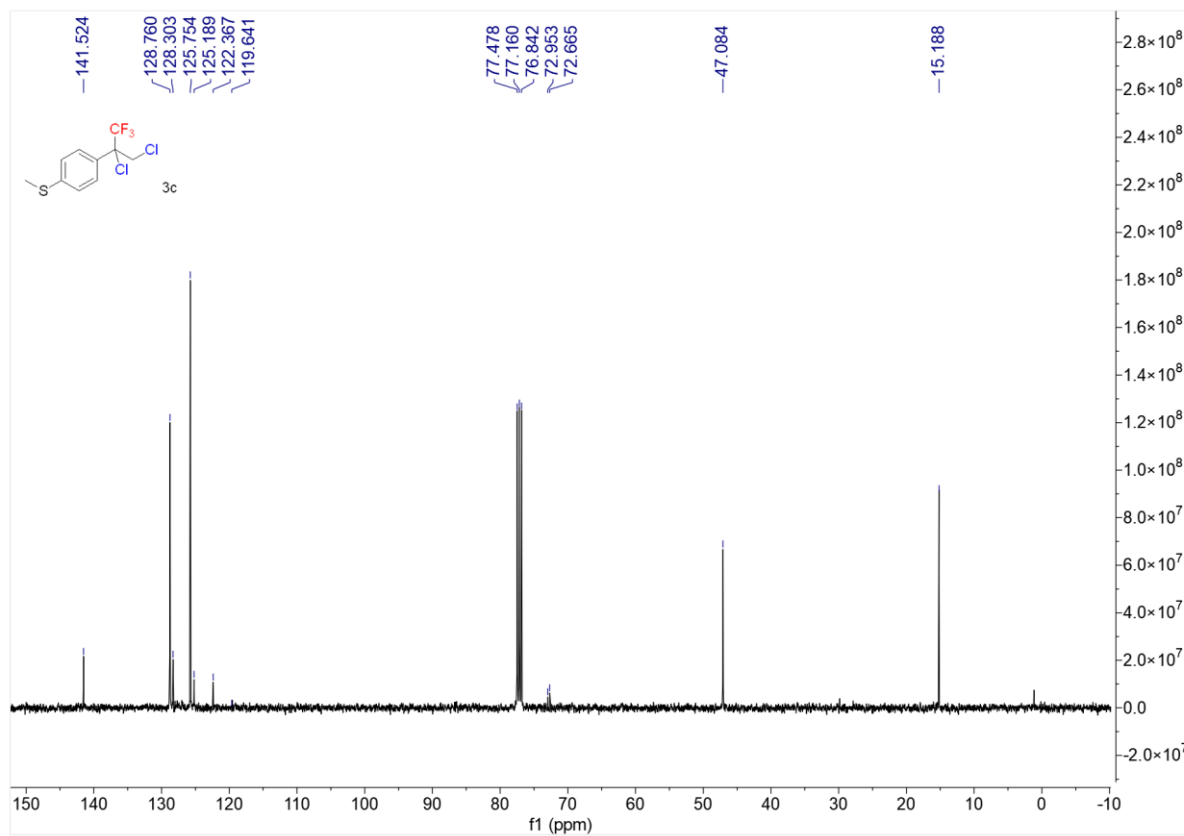
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
324.9977	324.9986	-0.9	-2.8	3.5	71.3	n/a	n/a	C11 H11 O2 F3 Na Cl2

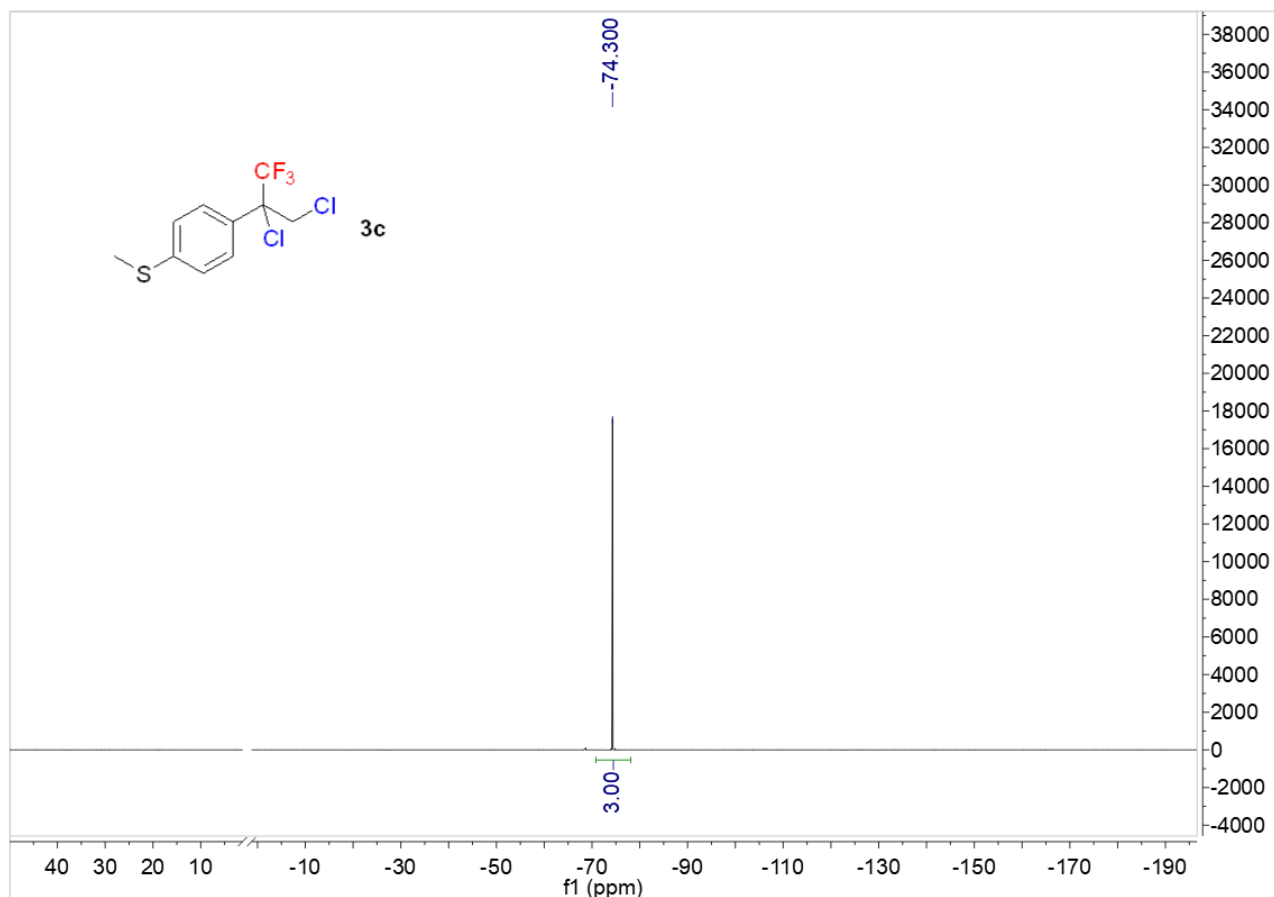
^1H NMR spectrum of **3c** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3c** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **3c** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **3c**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1544 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

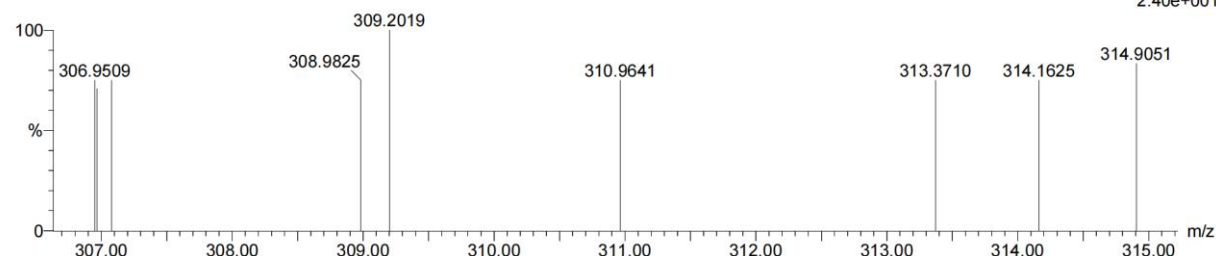
Elements Used:

C: 10-10 H: 9-9 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 S: 1-2 Cl: 1-5

31

240308-3-18 9 (0.069)

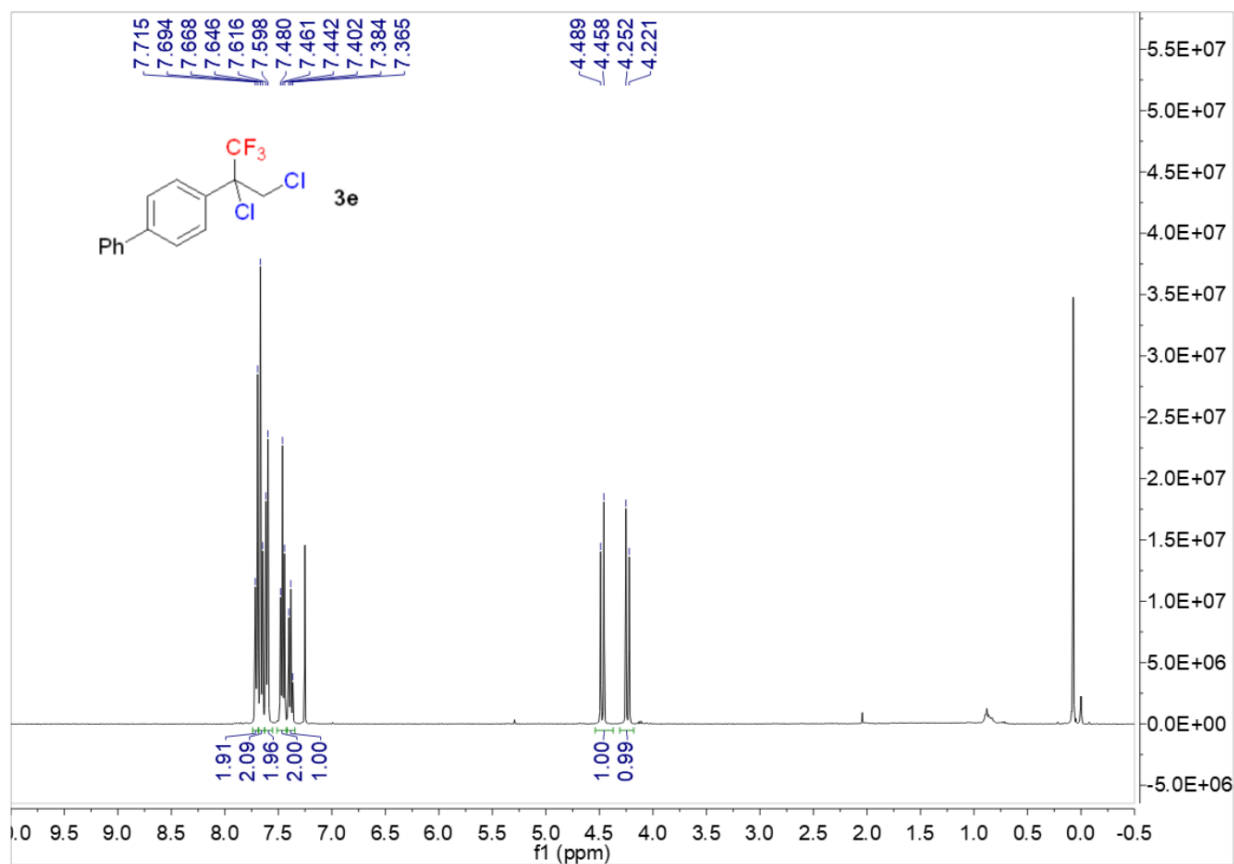
1: TOF MS ES+
2.40e+001



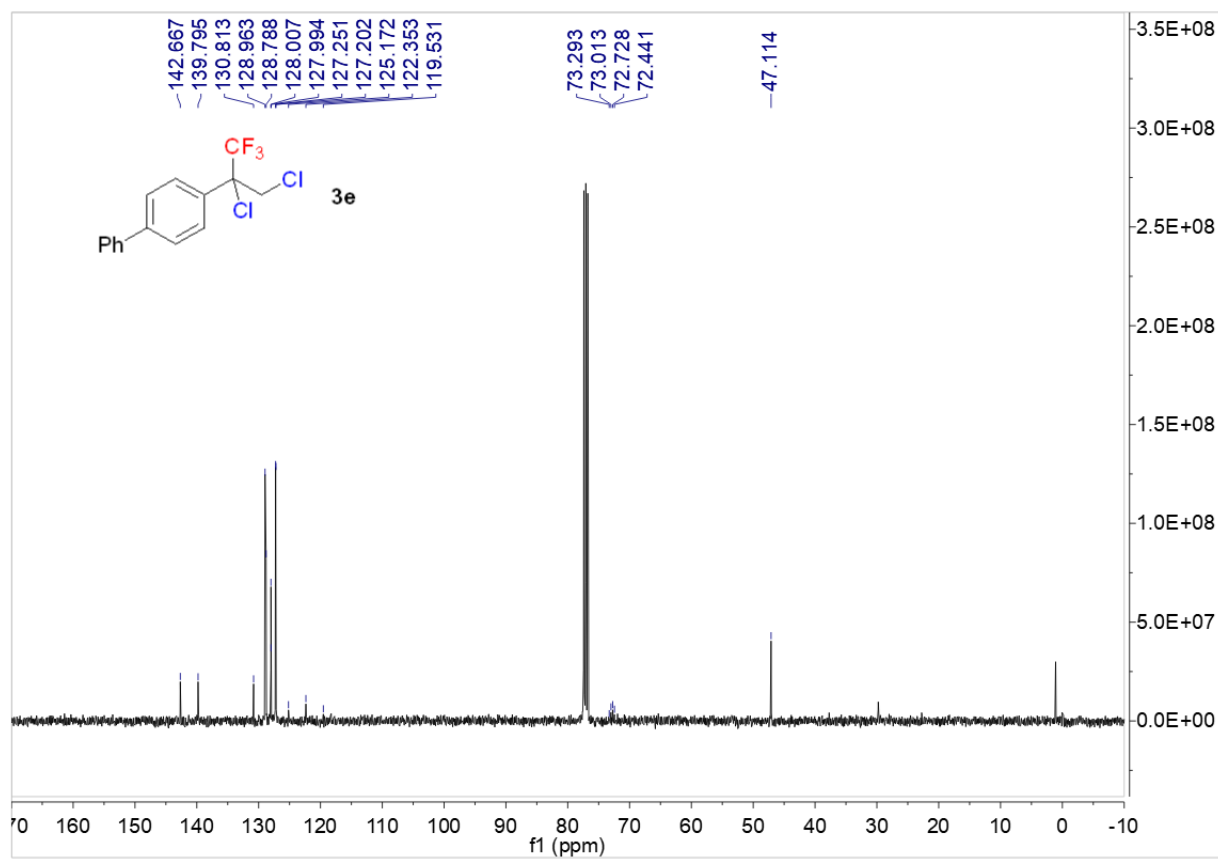
Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
310.9641	310.9652	-1.1	-3.5	3.5	20.1	n/a	n/a	$\text{C}_{10}\text{H}_9\text{F}_3\text{NaSCl}_2$

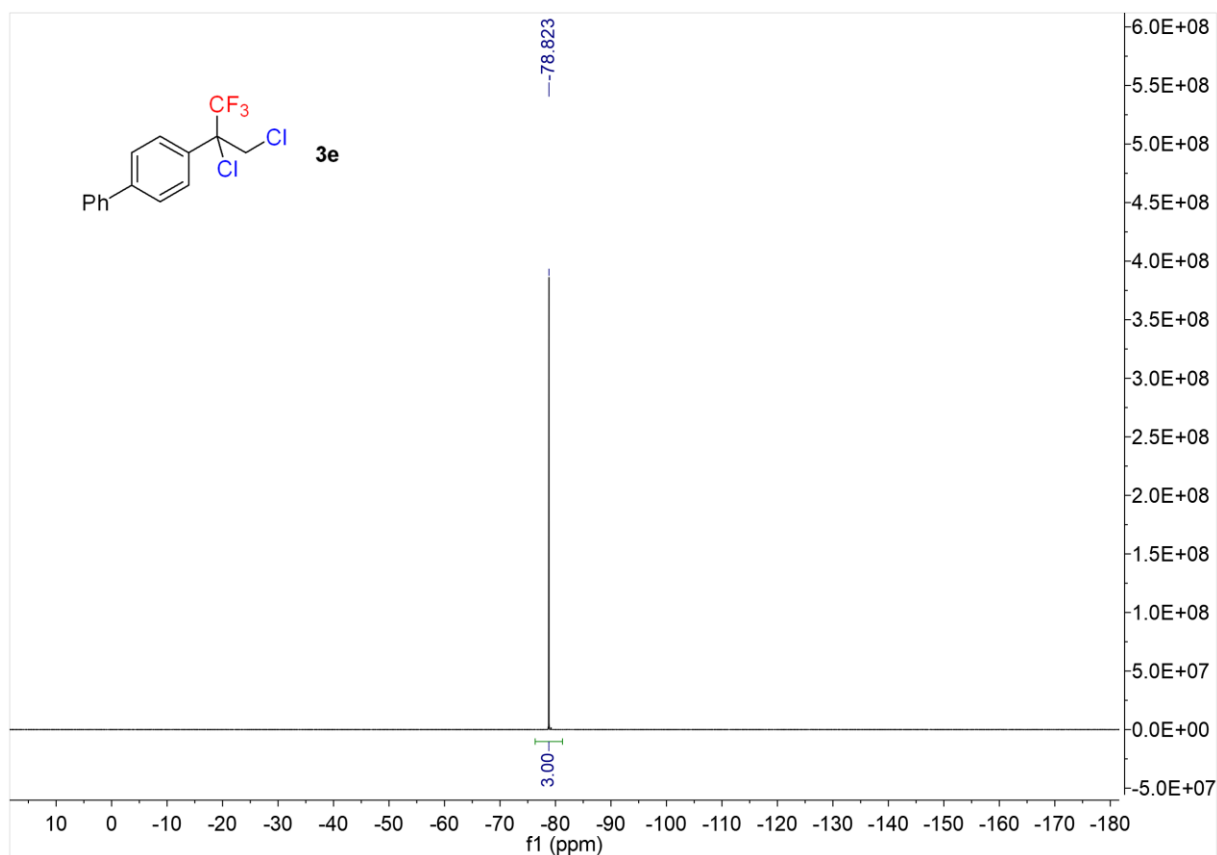
^1H NMR spectrum of **3e** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3e** (100 MHz, CDCl_3)



¹⁹F NMR spectrum of **3e** (367 MHz, CDCl₃)



HRMS (ESI) spectrum of **3e**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1801 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

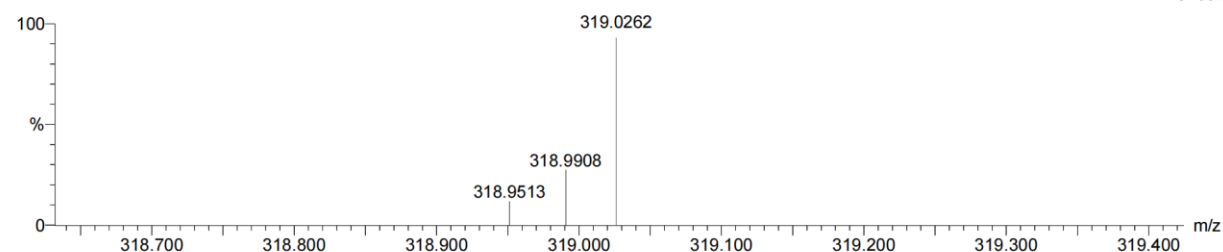
Elements Used:

C: 15-15 H: 12-12 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-4 40 (0.266)

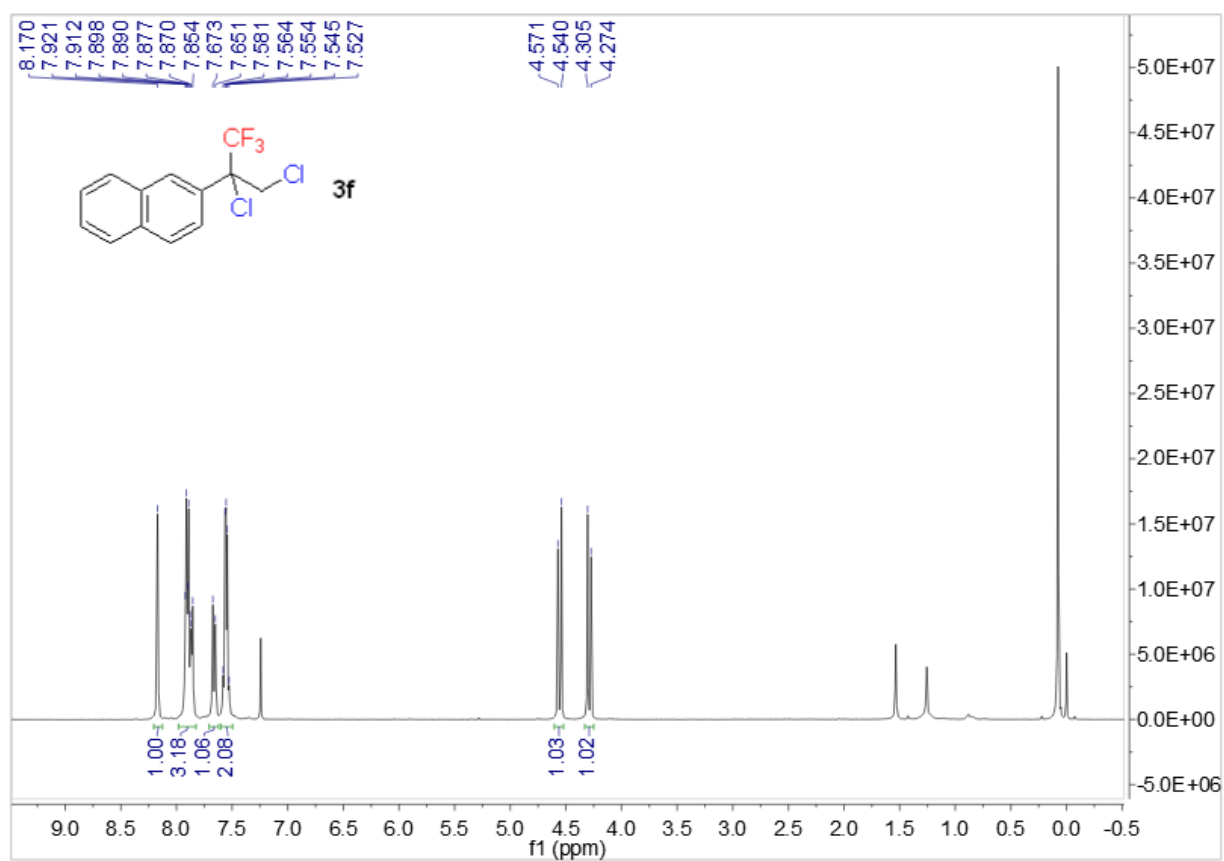
1: TOF MS ES+
1.47e+002



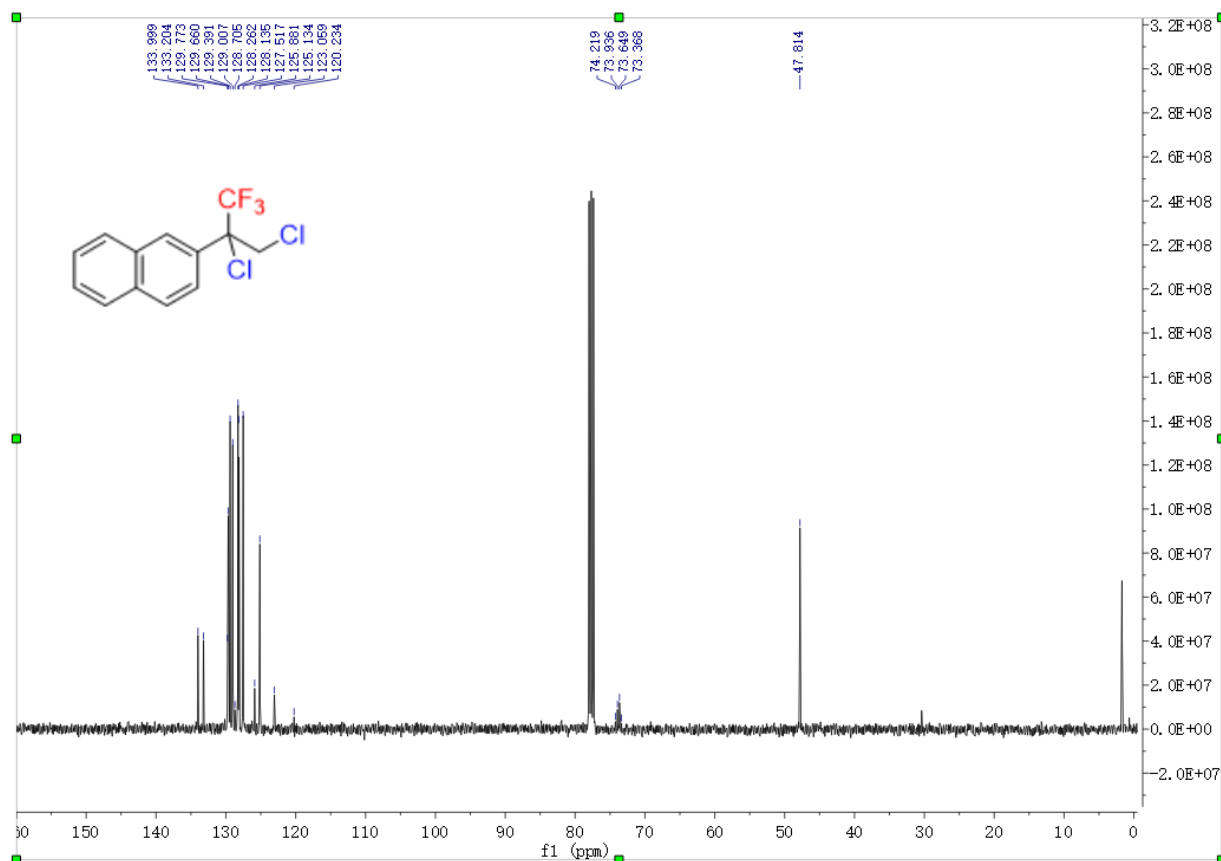
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
319.0262	319.0268	-0.6	-1.9	7.5	37.1	n/a	n/a	C15 H12 F3 Cl2

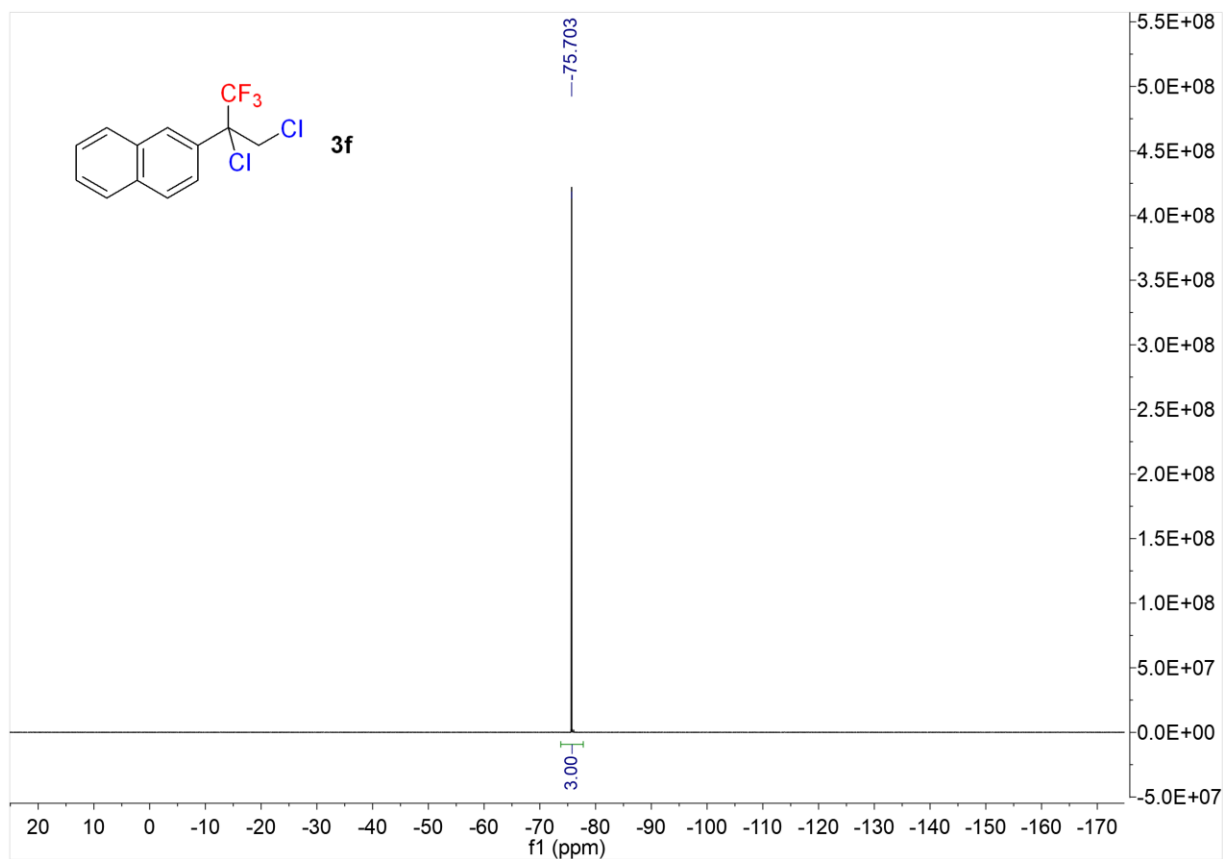
^1H NMR spectrum of **3f** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3f** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **3f** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **3f**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1682 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

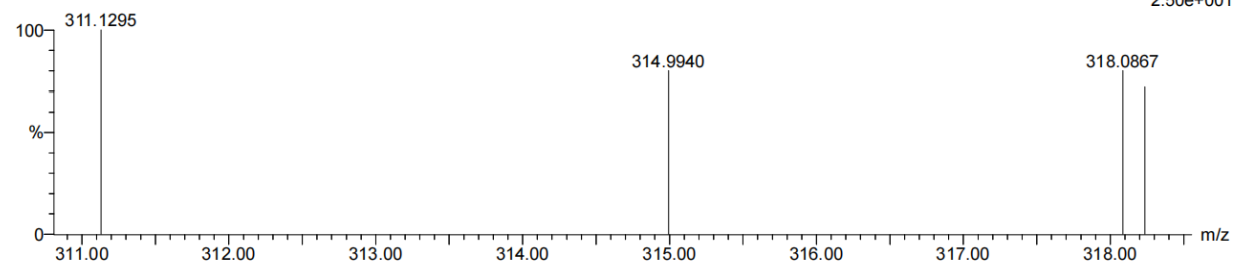
Elements Used:

C: 13-13 H: 9-9 N: 0-100 O: 0-100 Na: 0-1 Cl: 1-5 F: 3-6

14

240308-3-2 83 (0.353)

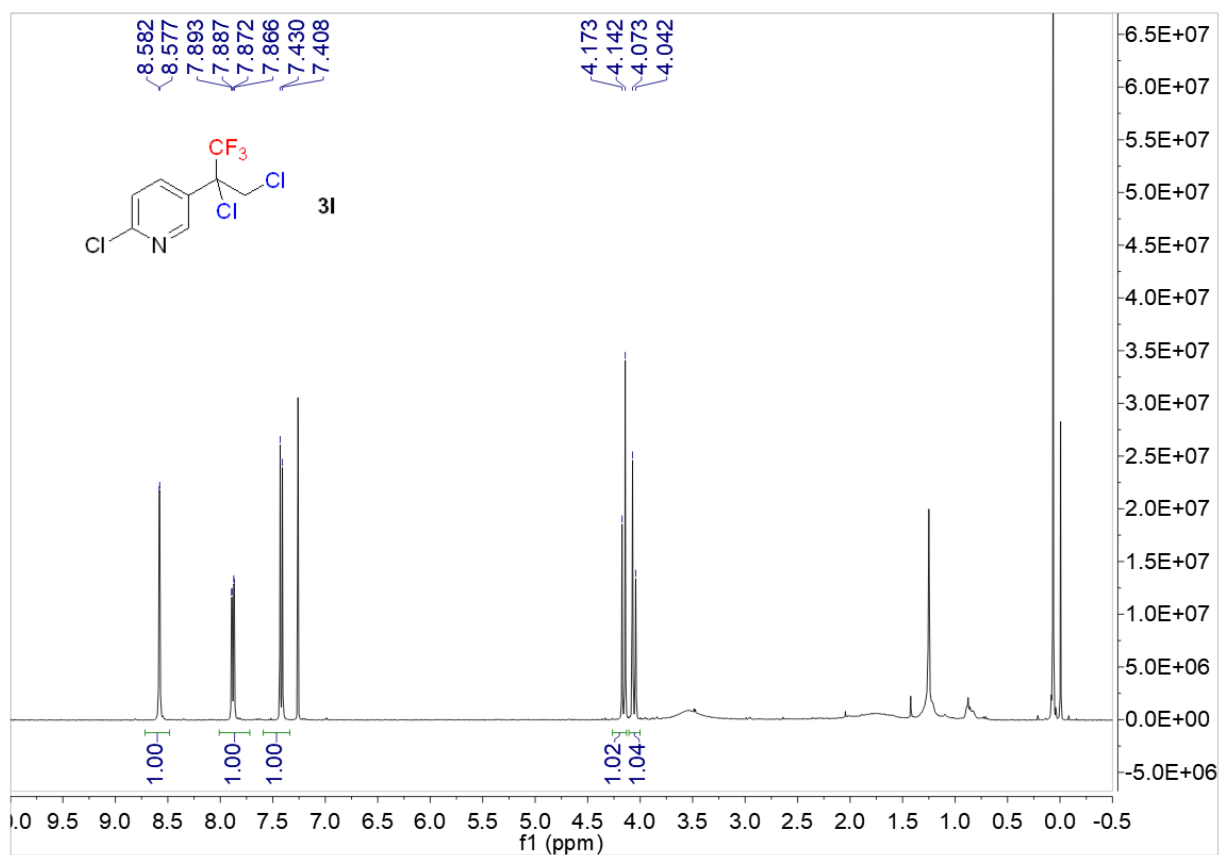
1: TOF MS ES+
2.50e+001



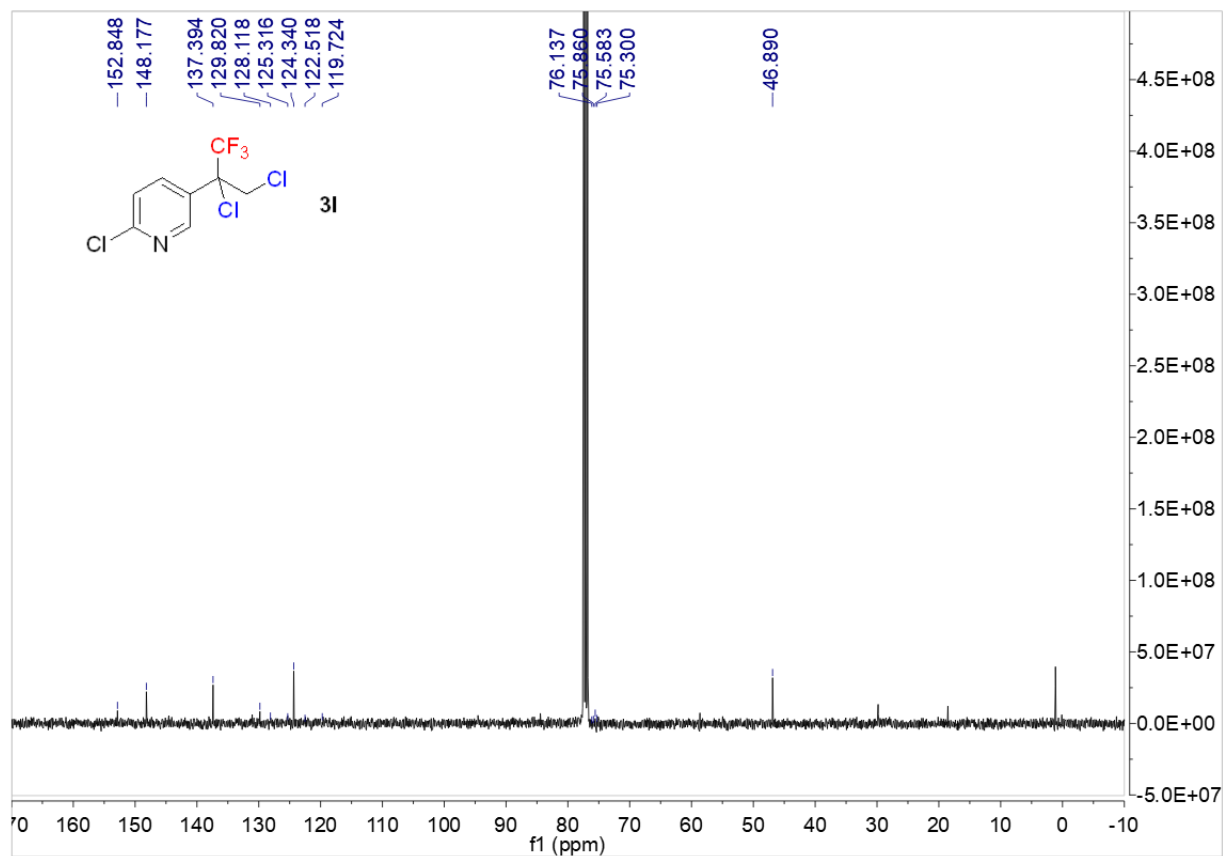
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
314.9940	314.9931	0.9	2.9	6.5	14.4	n/a	n/a	C13 H9 Na Cl2 F3

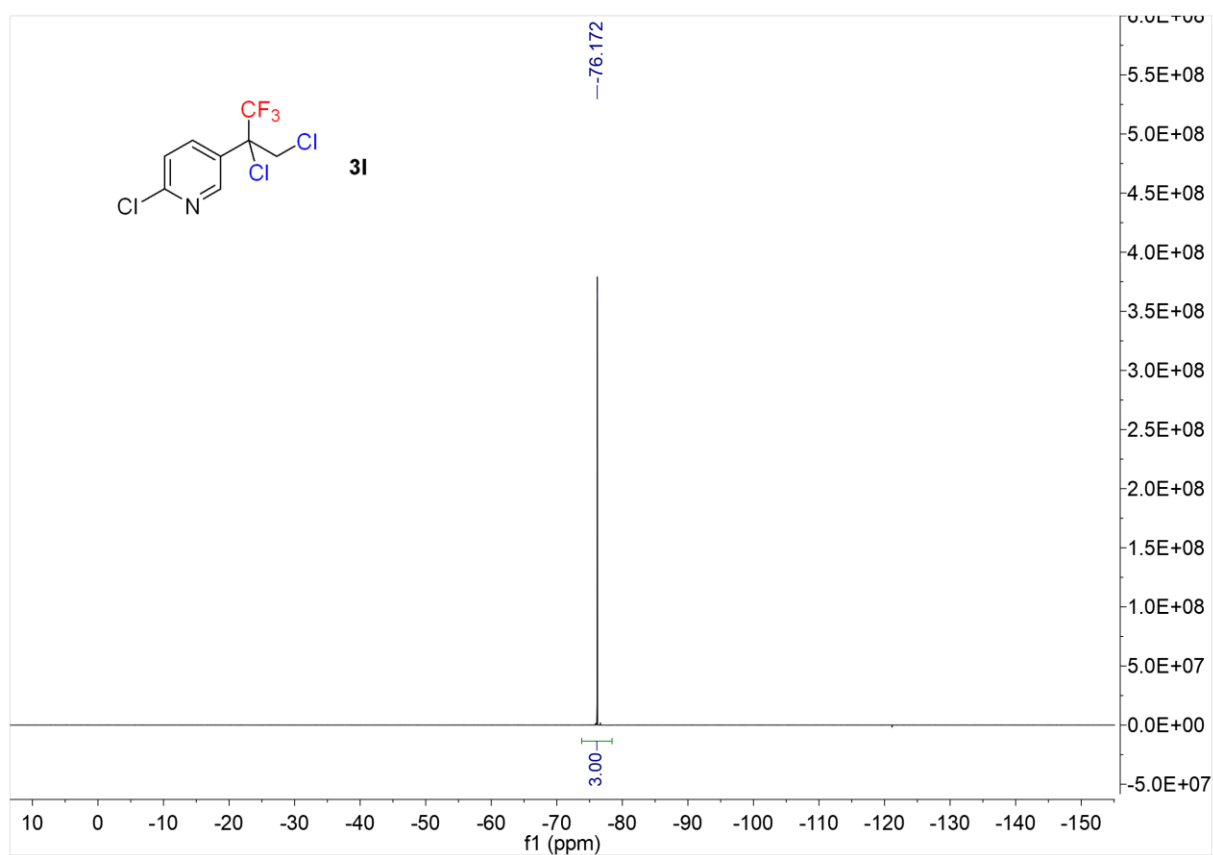
^1H NMR spectrum of **3I** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3I** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **3I** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **3I**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1075 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

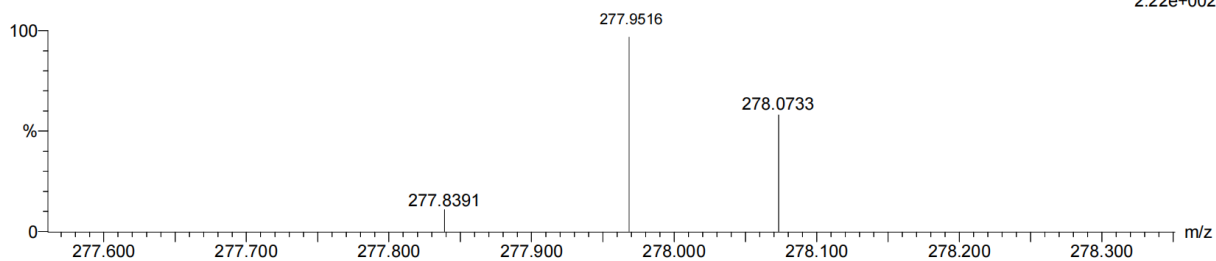
Elements Used:

C: 8-8 H: 6-6 N: 0-100 O: 0-100 F: 1-3 Na: 0-1 Cl: 1-3

6

241205-17-7 24 (0.162)

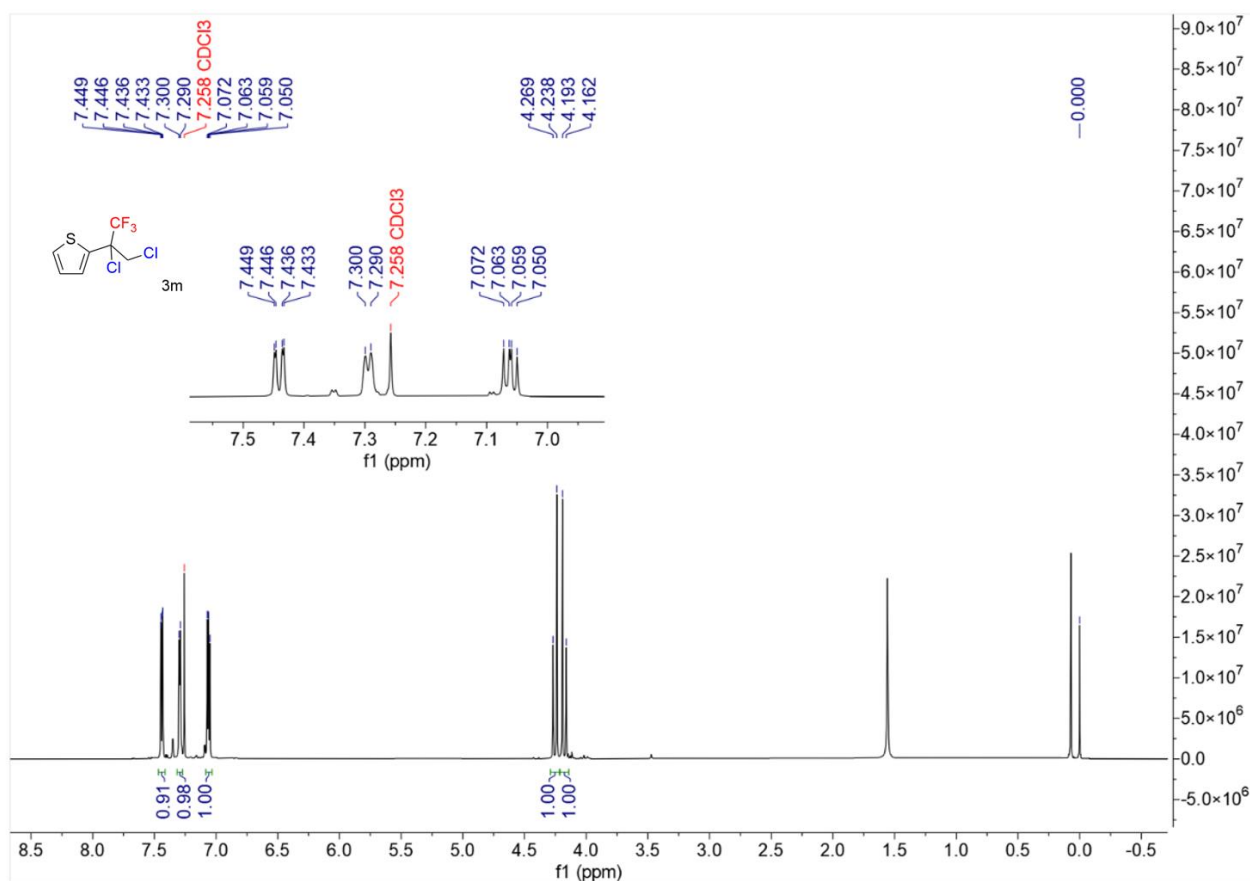
1: TOF MS ES+
2.22e+002



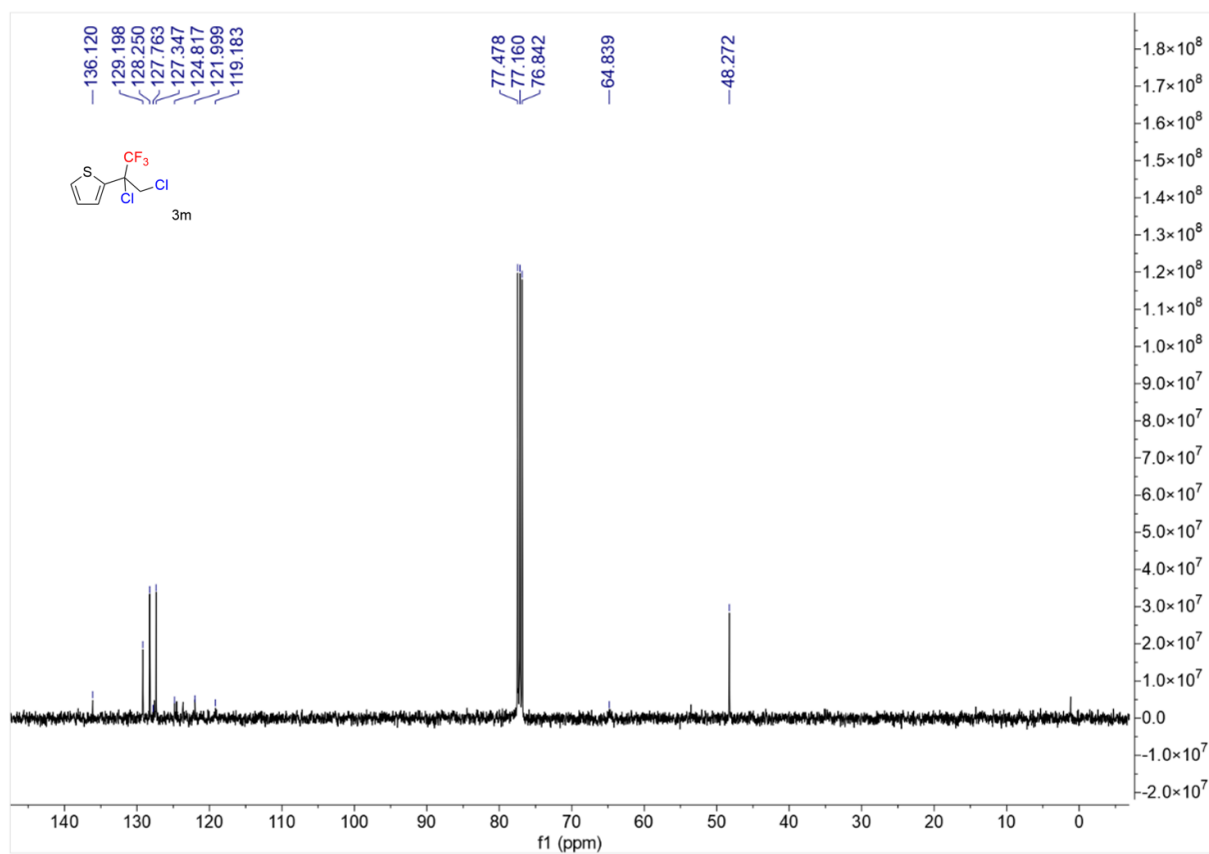
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
277.9516	277.9518	-0.2	-0.7	3.5	68.8	n/a	n/a	C8 H6 N F3 Cl3

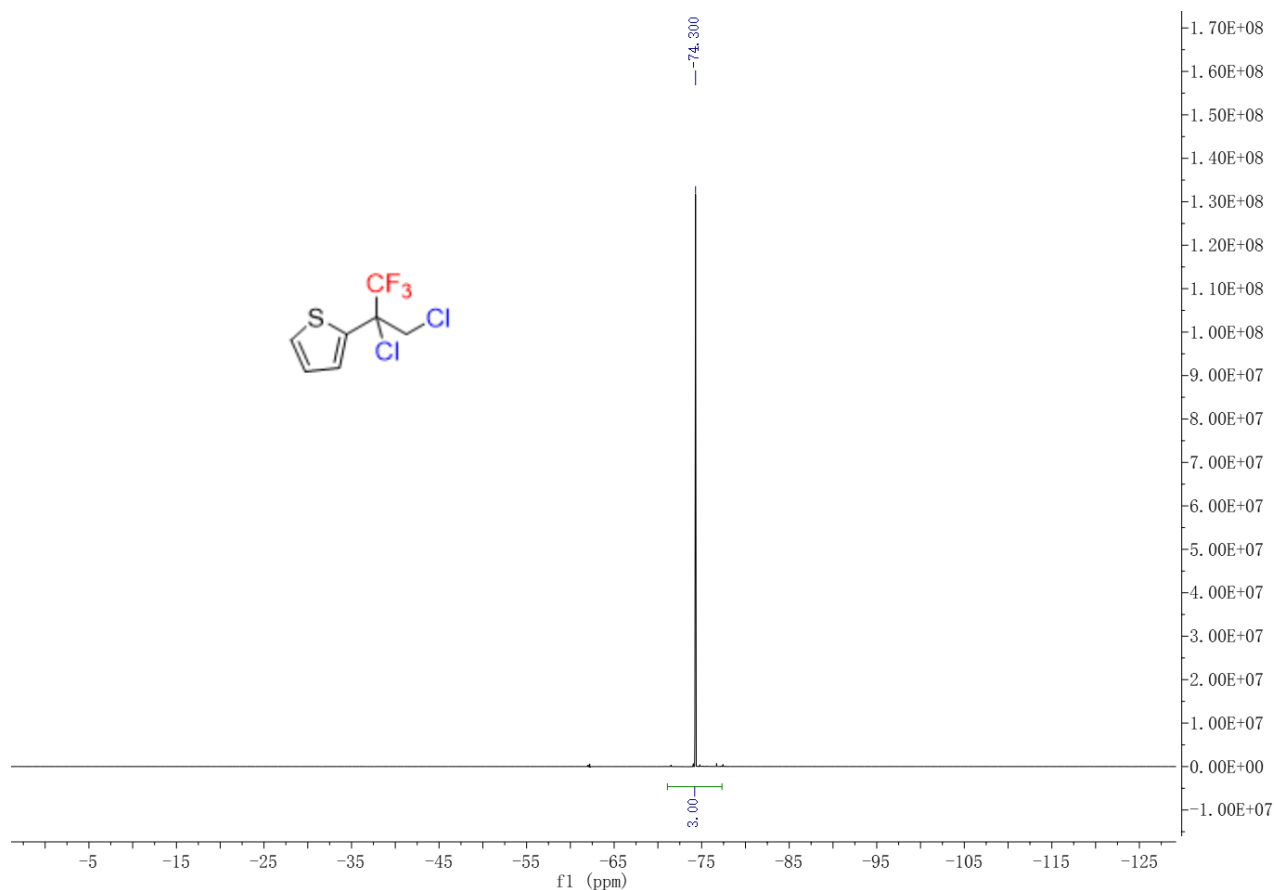
^1H NMR spectrum of **3m** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3m** (100 MHz, CDCl_3)



¹⁹F NMR spectrum of **3m** (367 MHz, CDCl₃)



HRMS (ESI) spectrum of **3m**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

555 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

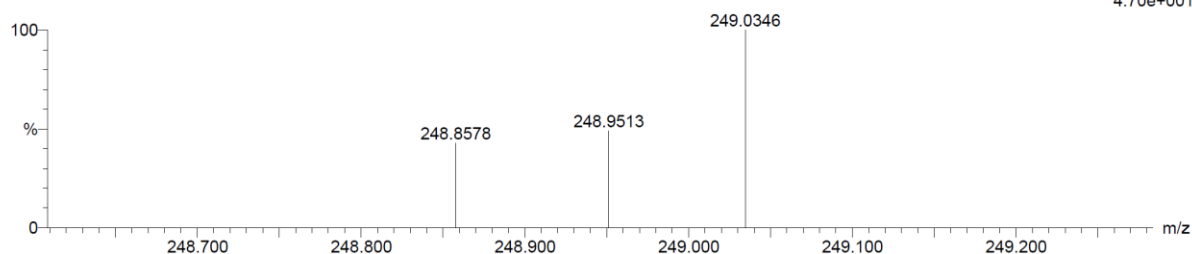
Elements Used:

C: 7-7 H: 6-6 N: 0-100 O: 0-100 F: 1-3 S: 1-3 Cl: 1-3

15

250721-7-4 79 (0.455)

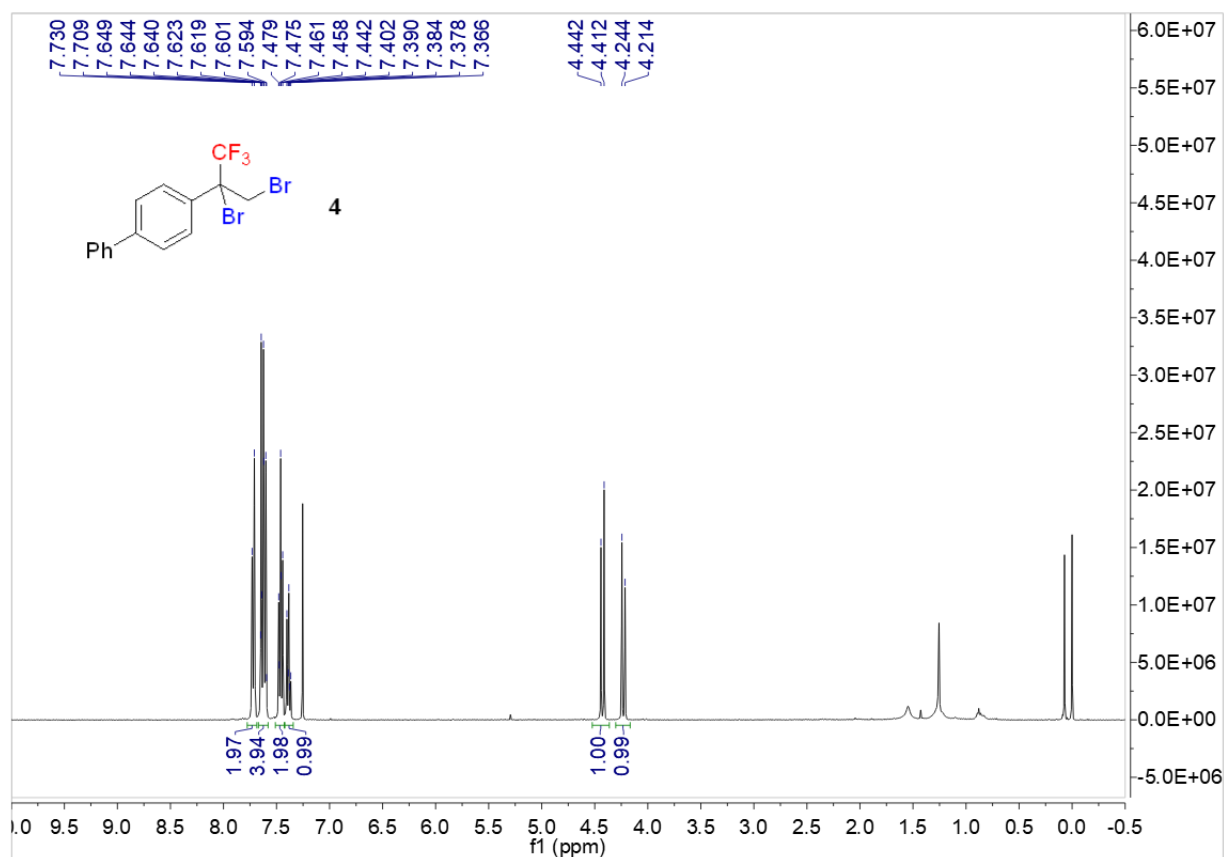
1: TOF MS ES+
4.70e+001



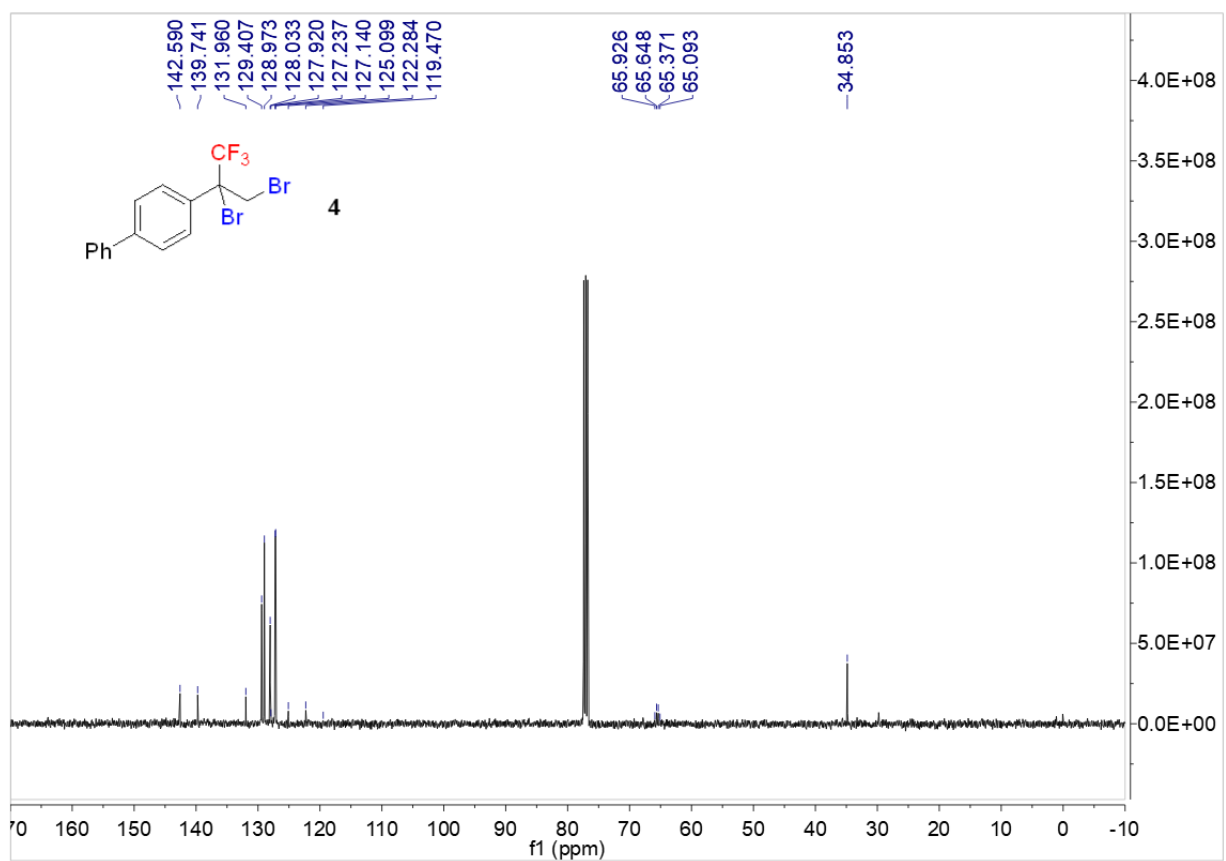
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
248.9513	248.9519	-0.6	-2.4	2.5	22.3	n/a	n/a	C7 H6 F3 S Cl2

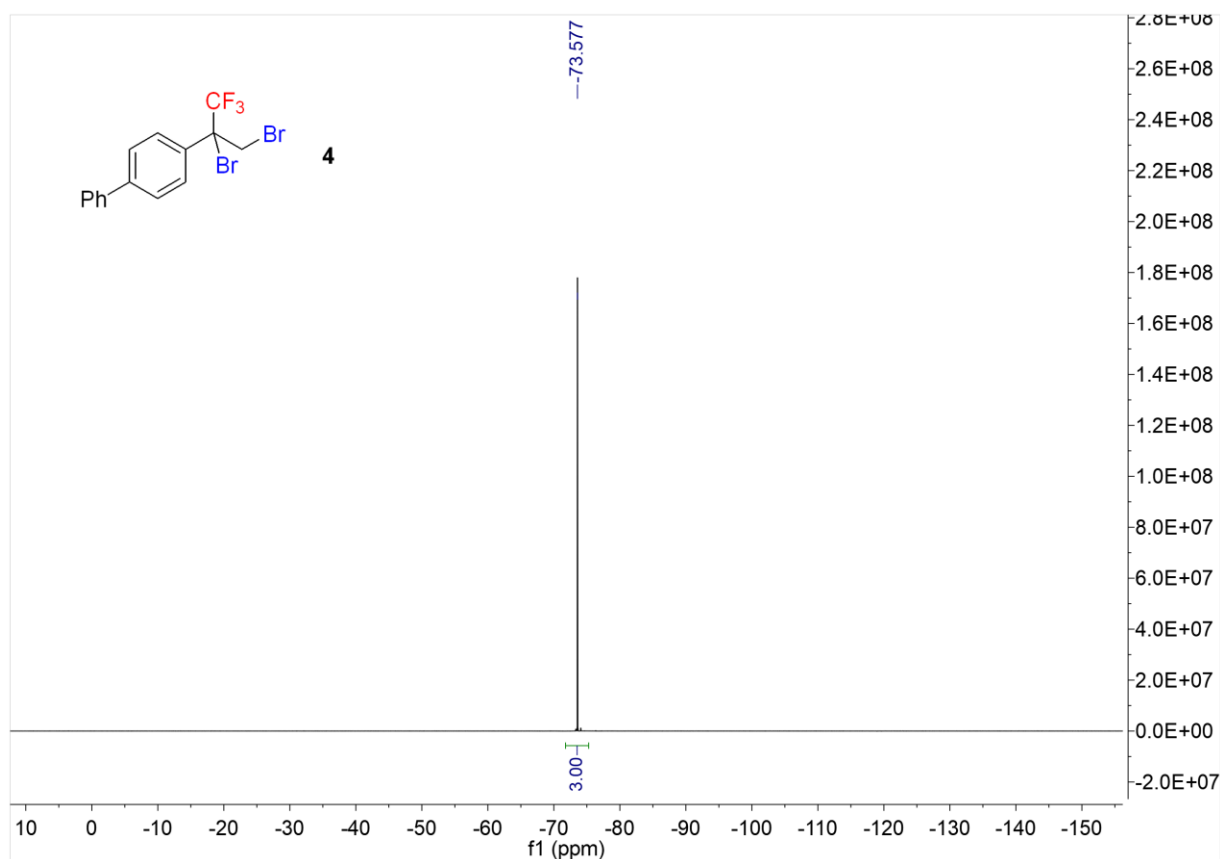
^1H NMR spectrum of **4** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **4** (100 MHz, CDCl_3)



^{19}F NMR spectrum of **4** (367 MHz, CDCl_3)



HRMS (ESI) spectrum of **4**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1672 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

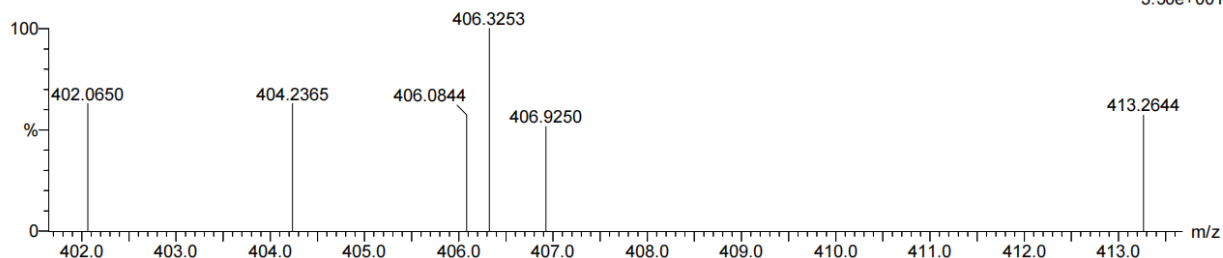
Elements Used:

C: 15-15 H: 12-12 N: 0-100 O: 0-100 F: 3-6 Na: 0-1 Br: 1-4

14

240308-3-11 88 (0.371)

1: TOF MS ES+
3.50e+001



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
406.9250	406.9258	-0.8	-2.0	7.5	15.5	n/a	n/a	C15 H12 F3 Br2

7. References

- (1) Y. Q. Guo, Y. P. Cao, H. J. Song, Y. X. Liu and Q. M. Wang, *Chem. Commun.* 2021, **57**, 9768.
- (2) F. L. Chen, X. F. Xu, Y. L. He, S. L. Zhu, *Angew. Chem., Int. Ed.* 2020, **59**, 5398.
- (3) Y. F. Chen, N. N. Ni, D. P. Cheng, X. L. Xu, *Tetrahedron Lett.* 2020, **61**, 152425.
- (4) Y. Li, B. Zhao, K. Dai, D. H. Tu, B. Wang, Y. Y. Wang, Z. T. Liu, Z. W. Liu, J. Lu, *Tetrahedron.* 2016, **72**, 5684.
- (5) W. J. Yue, C. S. Day and R. Martin, *J. Am. Chem. Soc.* 2021, **143**, 6395.