

Supporting Information

Transient Directing Groups Controlled Regiodivergent C(sp³)-H and C(sp²)-H Polyfluoroalkoxylation of Aromatic Aldehydes

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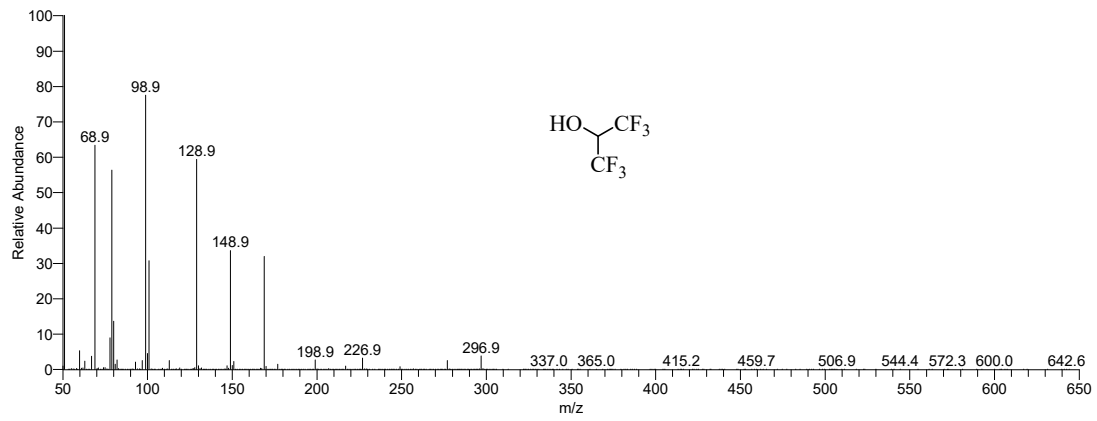
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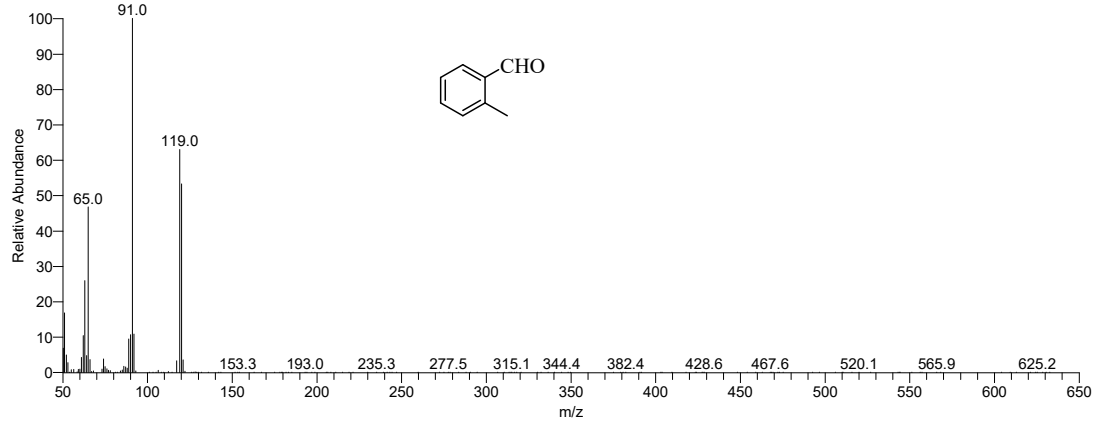
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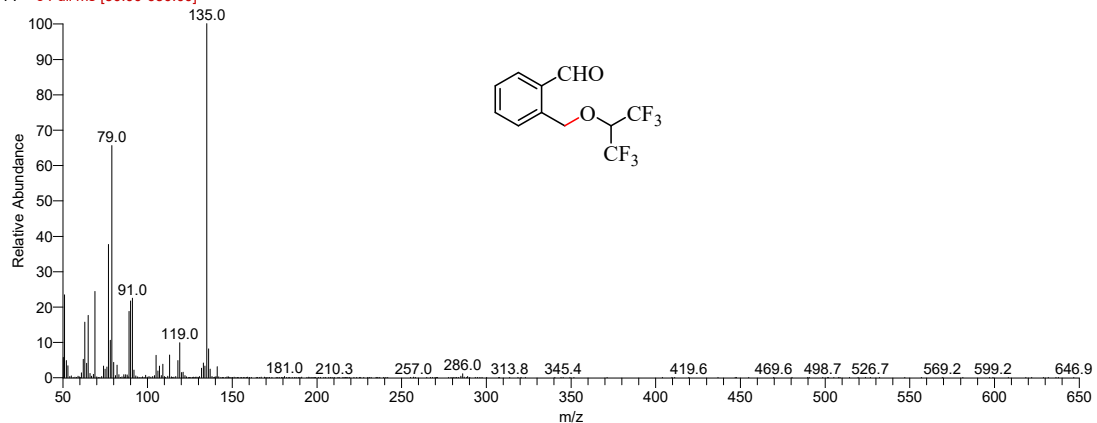
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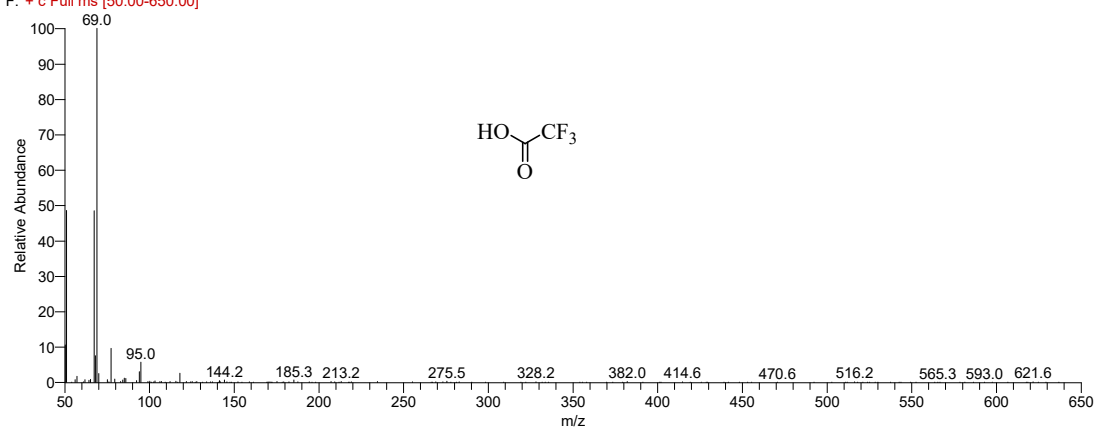
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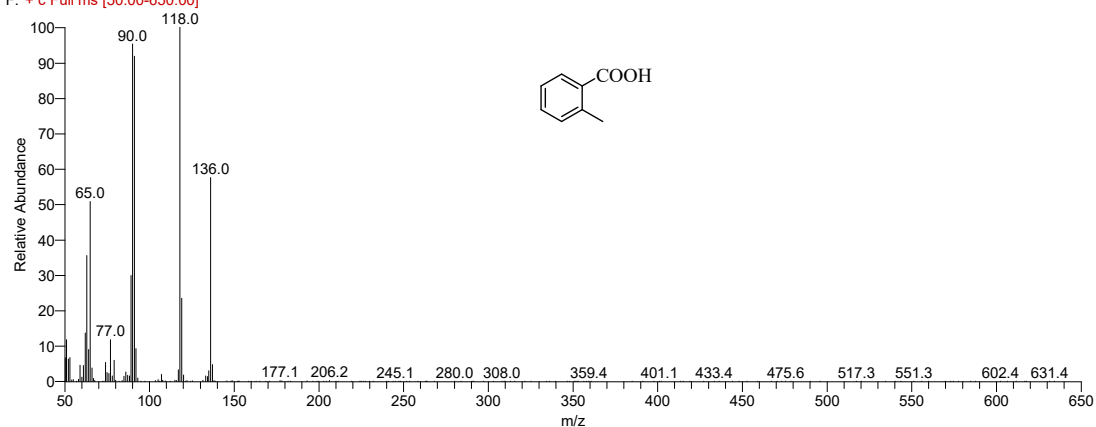
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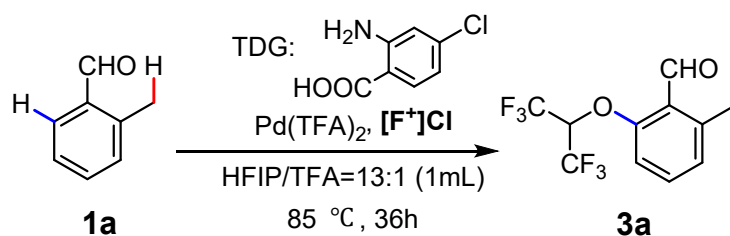
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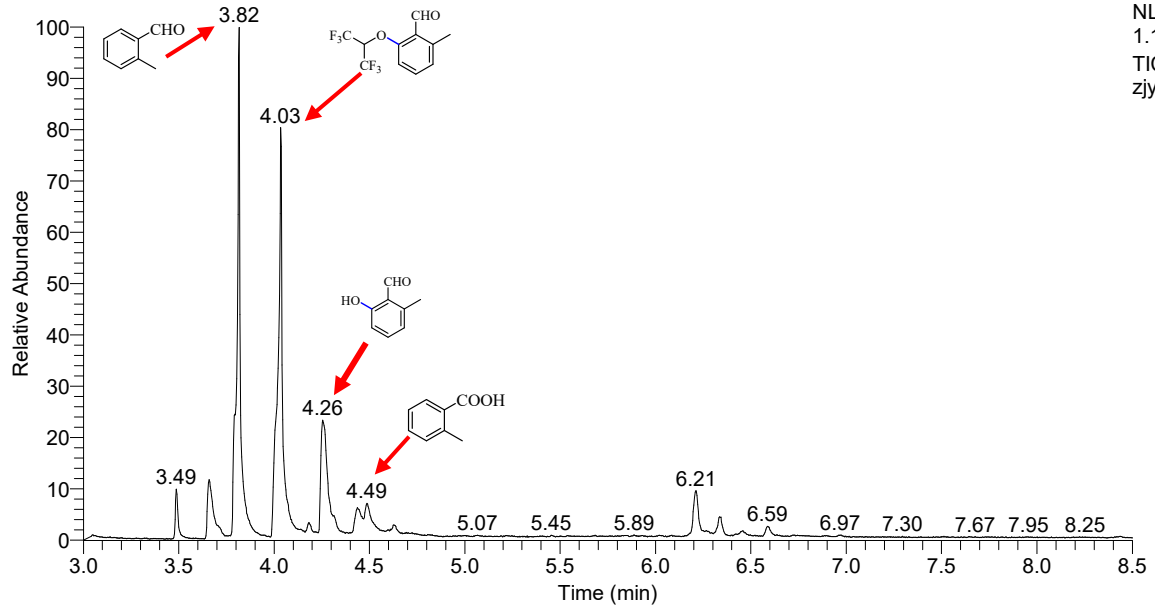
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4. GC-MS Analysis of Reaction of 1a via C(sp²)-H functionalization

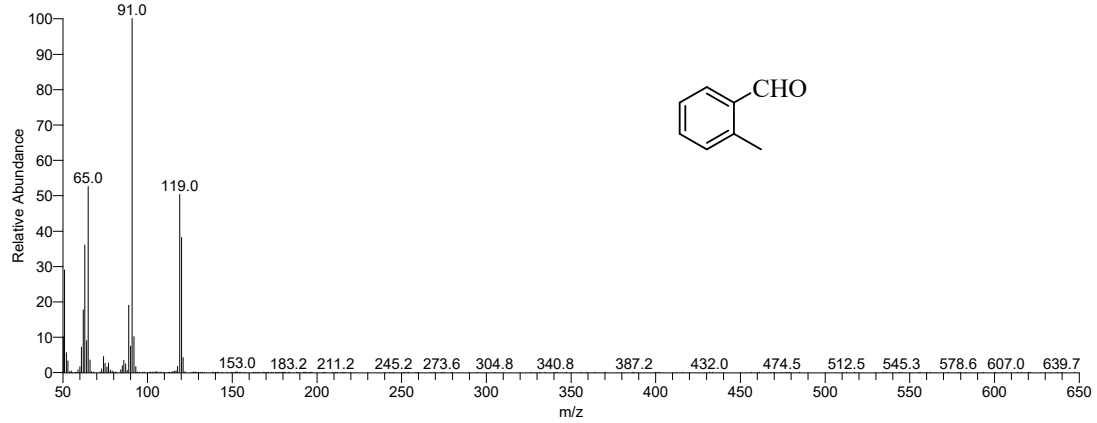


RT: 3.00 - 8.50

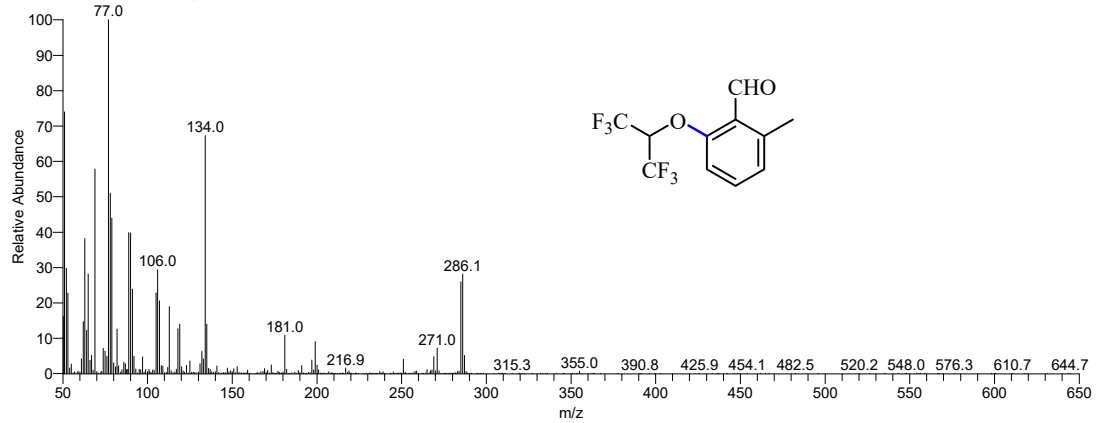


NL:
1.19E8
TIC MS
zjy-1

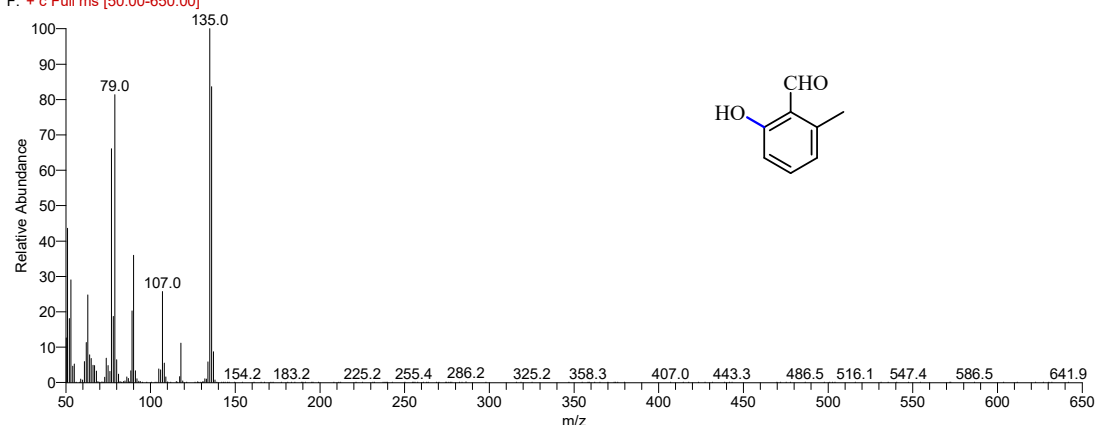
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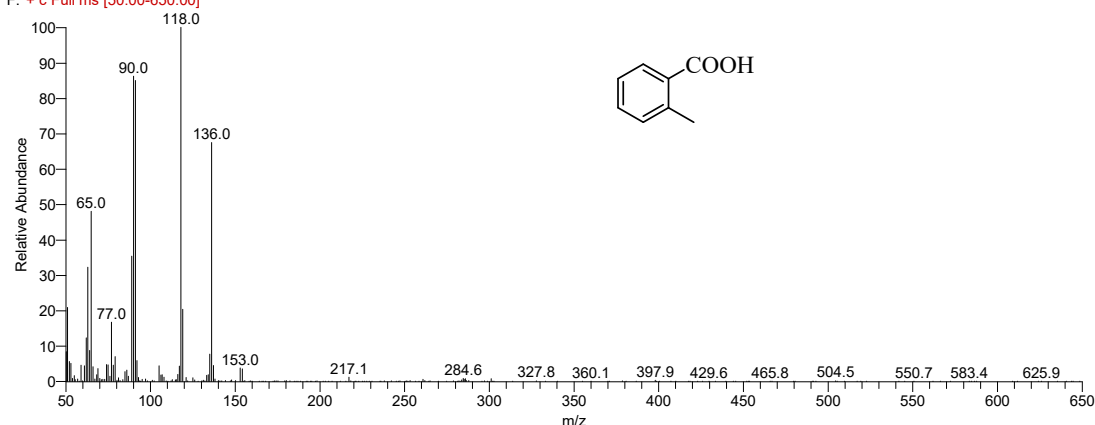
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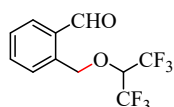
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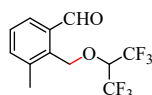
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5. Characterization Data for the Products

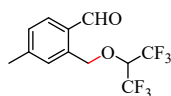


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2a**. yield:74% (M=286.17 , 21.2mg). ^1H NMR (600 MHz, CDCl_3) δ 10.11 (s, 1H), 7.87 (d, $J = 7.5, 1.1$ Hz, 1H), 7.72 (d, $J = 7.7$ Hz, 1H), 7.67 (t, $J = 7.6, 1.3$ Hz, 1H), 7.57 (t, $J = 11.0, 3.9$ Hz, 1H), 5.35 (s, 2H), 4.39-4.34 (m, $J = 11.9, 5.9$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 193.2, 137.4, 134.5, 134.2, 132.9, 128.6, 128.1, 121.6 (q, $J = 285.6$ Hz, 2C), 76.3 (sept, $J = 32.4$ Hz, 1C), 73.9; ^{19}F NMR (565 MHz, CDCl_3) δ -73.77, -73.78; Anal. Calcd. For $\text{C}_{11}\text{H}_8\text{F}_6\text{O}_2$: C, 46.17; H, 2.82%. Found: C, 46.11; H, 2.81%; MS (EI) m/z (%) 286.0(M^+ , 2), 135.0(100), 119.0(14), 105.0(7), 79.0(58),65.0(21).

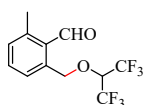


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-methylbenzaldehyde **2b**. yield:46% (M=300.20, 13.9mg). ^1H NMR (600 MHz, CDCl_3) δ 10.16 (s, 1H), 7.72-7.62 (m, 1H), 7.55-7.44 (m, 2H), 5.37 (s, 2H), 4.50-4.39 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 193.2, 140.7, 136.3, 135.0, 133.5, 132.0, 129.6, 121.6 (q, $J = 282.3$ Hz, 2C), 75.5 (sept, $J = 32.3$ Hz, 1C), 67.8, 18.9; Anal. Calcd. For

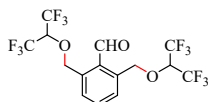
C₁₂H₁₀F₆O₂: C, 48.01; H, 3.36%. Found: C, 48.06; H, 3.35%; MS (EI) m/z (%) 300.1(M⁺, 5), 149.1(100), 133.1(13), 91.0(36), 77.0(44).



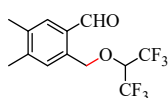
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2c**. yield: 62% (M=300.20, 18.6mg). ¹H NMR (600 MHz, CDCl₃) δ 10.04 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 5.32 (s, 2H), 4.43 – 4.30 (m, 1H), 2.47 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 192.7, 145.5, 137.3, 134.9, 130.7, 129.1, 121.6 (q, *J* = 283.2 Hz, 2C), 76.2 (sept, *J* = 32.3 Hz, 1C), 73.9, 22.0; Anal. Calcd. For C₁₂H₁₀F₆O₂: C, 48.01; H, 3.36%. Found: C, 48.03; H, 3.34%; MS (EI) m/z (%) 300.1(M⁺, 3), 149.1(100), 133.1(11), 119.1(6), 91.1(34), 77.0(41).



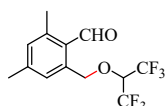
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **2d**. yield: 45% (M=300.20, 13.5mg). ¹H NMR (600 MHz, CDCl₃) δ 10.58 (s, 1H), 7.52 (dt, *J* = 15.1, 7.6 Hz, 2H), 7.27 (s, 1H), 5.26 (s, 2H), 4.39-4.29 (m, 1H), 2.70 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 192.9 (d, *J* = 10.3 Hz, 1C), 142.2, 137.9, 133.8, 131.8, 131.0, 126.2, 121.5 (d, *J* = 278.6 Hz, 2C), 76.1 ((sept, *J* = 32.4 Hz, 1C), 74.6, 19.7; Anal. Calcd. For C₁₂H₁₀F₆O₂: C, 48.01; H, 3.36%. Found: C, 48.00; H, 3.37%; MS (EI) m/z (%) 300.1(M⁺, 5), 149.1(100), 132.1(19), 91.0(43), 77.0(56).



2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2d'**. yield: 20% (M=466.04, 9.3mg). ¹H NMR (600 MHz, CDCl₃) δ 10.51 (s, 1H), 7.73-7.60 (m, 3H), 5.28 (s, 4H), 4.33-4.23 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 191.7, 138.4, 133.9, 131.0, 129.8 (2C), 121.6 (q, *J* = 282.3 Hz, 2C), 75.6 (sept, *J* = 32.6 Hz, 1C), 73.9; Anal. Calcd. For C₁₅H₁₀F₁₂O₃: C, 38.64; H, 2.16%. Found: C, 38.60; H, 2.18%; MS (EI) m/z (%) 298.1(5), 147.1(100), 119.1(24), 91.0(57), 69.0(22).

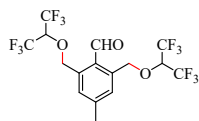


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,5-dimethylbenzaldehyde **2e**. yield: 51% (M=314.23, 16mg). ¹H NMR (600 MHz, CDCl₃) δ 10.04 (s, 1H), 7.60 (s, 1H), 7.40 (s, 1H), 5.27 (s, 2H), 4.39-4.28 (m, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 192.8, 144.0, 137.3, 135.7, 134.5, 131.2, 130.3, 121.6 (q, *J* = 283.4 Hz, 2C), 76.0 (sept, *J* = 32.4 Hz, 1C), 73.6, 20.2, 19.3; Anal. Calcd. For C₁₃H₁₂F₆O₂: C, 49.69; H, 3.85%. Found: C, 49.63; H, 3.88%; MS (EI) m/z (%) 314.1(M⁺, 2), 163.1(100), 147.1(8), 107.0(73), 91.0(55), 69.0(24).

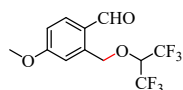


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,6-dimethylbenzaldehyde **2f**. yield: 43% (M=314.23, 13.4mg). ¹H NMR (600 MHz, CDCl₃) δ 10.51 (s, 1H), 7.32 (s, 1H), 7.07 (s, 1H), 5.24 (s, 2H), 4.40 – 4.30 (m, 1H), 2.65 (s, 3H), 2.40 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 192.4, 144.9, 142.5, 138.1, 132.4, 128.5, 127.0, 121.6 (d, *J* = 282.2 Hz, 2C), 76.1 (sept, *J* = 32.3 Hz, 1C), 74.7, 21.8, 19.6;

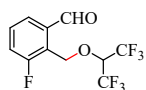
Anal. Calcd. For $C_{13}H_{12}F_6O_2$: C, 49.69; H, 3.85%. Found: C, 49.67; H, 3.83%; MS (EI) m/z (%) 314.1(M^+ , 5), 163.1(100), 147.1(11), 117.1(27), 91.0(46), 77.0(23).



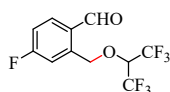
2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2f**. yield:15% ($M=480.06$, 7.2mg). 1H NMR (600 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.42 (s, 2H), 5.24 (s, 4H), 4.31-4.23 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.3, 145.3, 138.6, 130.5, 128.5, 121.4 (q, $J = 285.9$ Hz, 2C), 75.5 (sept, $J = 32.6$ Hz, 1C), 74.0, 21.9; Anal. Calcd. For $C_{16}H_{12}F_{12}O_3$: C, 40.02; H, 2.52%. Found: C, 40.05; H, 2.51%; MS (EI) m/z (%) 312.2(8), 161.1(100), 133.1(25), 105.1(31), 69.0(14).



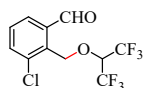
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methoxybenzaldehyde **2g**. yield:71%. ($M=316.20$, 22.4mg). 1H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.25 (s, 1H), 6.99 (dd, $J = 8.4, 2.3$ Hz, 1H), 5.36 (s, 2H), 4.43-4.31 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.7, 164.3, 140.4, 137.6, 126.2, 121.5 (q, $J = 285.9$ Hz, 2C), 113.6, 112.7, 76.4 (sept, $J = 32.4$ Hz, 1C), 74.0, 55.6; Anal. Calcd. For $C_{12}H_{10}F_6O_3$: C, 45.58; H, 3.19%. Found: C, 45.56; H, 3.18%; MS (EI) m/z (%) 316.0(M^+ , 3), 165.0(100), 149.0(11), 109.0(56), 91.0(18), 77.0(42).



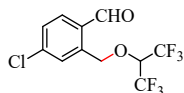
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-fluorobenzaldehyde **2h**. yield:56% ($M=304.16$, 17.0mg). 1H NMR (600 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.60 (td, $J = 7.9, 5.3$ Hz, 1H), 7.40 (t, $J = 8.7$ Hz, 1H), 5.34 (s, 2H), 4.45-4.33 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.2 (d, $J = 3.1$ Hz, 1C), 161.7 (d, $J = 251.5$ Hz, 1C), 136.2 (d, $J = 2.5$ Hz, 1C), 131.5 (d, $J = 8.9$ Hz, 1C), 128.9 (d, $J = 3.0$ Hz, 1C), 122.6 (d, $J = 14.8$ Hz, 1C), 121.4 (q, $J = 282.8$ Hz, 2C), 121.3 (d, $J = 23.6$ Hz, 1C), 75.8 (sept, $J = 32.6$ Hz, 1C), 64.1 (d, $J = 5.8$ Hz, 1C); Anal. Calcd. For $C_{11}H_7F_7O_2$: C, 43.44; H, 2.32%. Found: C, 43.41; H, 2.33%; MS (EI) m/z (%) 303.8(M^+ , 2), 153.0(100), 137.0(22), 108.0(52), 83.0(21), 68.9(33).



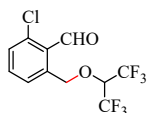
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-fluorobenzaldehyde **2i**. yield:65% ($M=304.16$, 19.9mg). 1H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.87 (dd, $J = 8.4, 5.6$ Hz, 1H), 7.48 (d, $J = 9.7$ Hz, 1H), 7.22 (td, $J = 8.2, 2.3$ Hz, 1H), 5.36 (s, 2H), 4.45-4.31 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.7, 166.3 (d, $J = 257.9$ Hz, 1C), 141.6 (d, $J = 9.2$ Hz, 1C), 137.5 (d, $J = 10.1$ Hz, 1C), 129.1 (d, $J = 2.8$ Hz, 1C), 121.4 (q, $J = 283.8$ Hz, 2C), 115.2 (d, $J = 10.9$ Hz, 1C), 115.0 (d, $J = 13.3$ Hz, 1C), 76.5 (sept, $J = 32.6$ Hz, 1C), 73.6; Anal. Calcd. For $C_{11}H_7F_7O_2$: C, 43.44; H, 2.32%. Found: C, 43.44; H, 2.31%; MS (EI) m/z (%) 304.0(M^+ , 4), 153.0(100), 137.1(16), 97.0(39), 68.0(23).



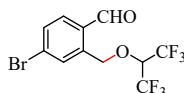
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-chlorobenzaldehyde **2j**. yield:41% (M=320.62, 13.1mg). ¹H NMR (600 MHz, CDCl₃) δ 10.22 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 5.47 (s, 2H), 4.46-4.33 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 191.0, 137.3, 136.5, 135.0, 133.2, 131.2, 130.9, 121.4 (q, *J* = 282.9 Hz, 2C), 75.7 (sept, *J* = 32.6 Hz, 1C), 67.6; Anal. Calcd. For C₁₁H₇ClF₆O₂: C, 41.21; H, 2.20%. Found: C, 41.21; H, 2.19%; MS (EI) m/z (%) 320.0(M⁺, 7), 318.9(11), 169.0(100), 153.0(17), 124.0(42),89.0(81), 77.0(54).



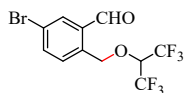
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-chlorobenzaldehyde **2k**. yield:47% (M=320.62, 15.2mg). ¹H NMR (600 MHz, CDCl₃) δ 10.05 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.72 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 5.33 (s, 2H), 4.41-4.33 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 191.9, 141.1, 139.5, 135.8, 130.9, 128.6, 128.0, 121.4 (q, *J* = 280.0 Hz, 2C), 76.4 (sept, *J* = 32.6 Hz, 1C), 73.4; Anal. Calcd. For C₁₁H₇ClF₆O₂: C, 41.21; H, 2.20%. Found: C, 41.19; H, 2.22%; MS (EI) m/z (%) 319.9(M⁺, 1), 169.0(100), 153.0(10), 113.0(39),89.0(57), 77.0(75).



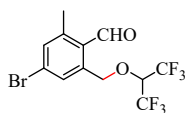
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-chlorobenzaldehyde **2l**. yield:34% (M=320.62, 11.0mg). ¹H NMR (600 MHz, CDCl₃) δ 10.63 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 5.28 (s, 2H), 4.42-4.33 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 191.3 (d, *J* = 8.7 Hz, 1C), 139.1, 138.4, 133.7, 129.2, 127.9, 125.1, 120.4 (q, *J* = 282.0 Hz, 2C), 75.7 (sept, *J* = 32.6 Hz, 1C), 73.0; Anal. Calcd. For C₁₁H₇ClF₆O₂: C, 41.21; H, 2.20%. Found: C, 41.18; H, 2.21%; MS (EI) m/z (%) 320.0(M⁺, 2), 169.0(100), 153.0(11), 113.0(29), 77.0(84).



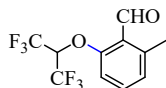
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-bromobenzaldehyde **2m**. yield:36% (M=365.07, 13.1mg). ¹H NMR (600 MHz, CDCl₃) δ 10.04 (s, 1H), 7.88 (s, 1H), 7.71 (s, 2H), 5.32 (s, 2H), 4.40 – 4.32 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 192.1, 139.3, 135.8, 131.7, 131.4, 131.0, 129.9, 121.4 (q, *J* = 286.1 Hz, 2C), 76.4 (sept, *J* = 32.6 Hz, 1C), 73.3; Anal. Calcd. For C₁₁H₇BrF₆O₂: C, 36.19; H, 1.93%. Found: C, 36.11; H, 1.91%; MS (EI) m/z (%) 365.9(8), 363.9(M⁺, 8), 212.8(100), 196.9(10), 156.9(7),104.9(7), 88.9(58),77.0(47),63.0(25).



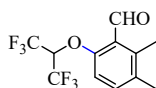
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-5-bromobenzaldehyde **2n**. yield:67% (M=365.07, 24.6mg). ¹H NMR (600 MHz, CDCl₃) δ 10.04 (s, 1H), 7.98 (d, *J* = 1.9 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 5.28 (s, 2H), 4.41-4.25 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 191.6, 137.1, 136.9, 136.3, 134.3, 129.8, 122.6, 121.4 (q, *J* = 279.8 Hz, 2C), 76.3 (sept, *J* = 32.6 Hz, 1C), 73.4; Anal. Calcd. For C₁₁H₇BrF₆O₂: C, 36.19; H, 1.93%. Found: C, 36.21; H, 1.90%; MS (EI) m/z (%) 365.9(3), 363.9(M⁺, 3), 212.9(86), 196.9(9), 156.9(12), 104.9(12), 88.9(100), 77.0(86), 63.0(53).



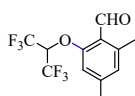
4-bromo-2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **2o**. yield:41% (M=379.10, 15.3 mg). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.50 (s, 1H), 7.71 (s, 1H), 7.44 (s, 1H), 5.23 (s, 2H), 4.37-4.29 (m, 1H), 2.67 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 191.9 (d, $J = 3.5$ Hz, 1C), 143.9, 139.9, 134.4, 129.4, 129.1, 128.9, 121.4 (q, $J = 285.6$ Hz, 2C), 76.3 (sept, $J = 32.6$ Hz, 1C), 74.0, 19.4; Anal. Calcd. For $\text{C}_{12}\text{H}_9\text{BrF}_6\text{O}_2$: C, 38.02; H, 2.39%. Found: C, 38.01; H, 2.41%; MS (EI) m/z (%) 379.9(10), 377.9(M^+ , 12), 226.9(100), 211.0(13), 181.9(6), 131.0(8), 91.0(56), 77.0(32), 63.0(19).



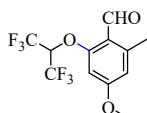
2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **3a**. yield:63% (M=286.04, 18.0 mg). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.63 (s, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.06 – 4.94 (m, 1H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 190.7 (d, $J = 10.8$ Hz, 1C), 160.5, 143.0, 134.4, 128.0, 125.2, 120.9 (q, $J = 280.5$ Hz, 2C), 112.0, 76.0 (sept, $J = 33.6$ Hz, 1C), 21.4; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -73.19, -73.20; Anal. Calcd. For $\text{C}_{11}\text{H}_8\text{F}_6\text{O}_2$: C, 46.17; H, 2.82%. Found: C, 46.16; H, 2.81%; MS (EI) m/z (%) 286.0(M^+ , 49), 270.9(14), 133.9(56), 106.0(28), 90.0(75), 77.0(100).



6-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-2,3-dimethylbenzaldehyde **3b**. yield: 51% (M=300.06, 15.2 mg). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.61 (s, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 6.83 (d, $J = 8.5$ Hz, 1H), 4.97 – 4.90 (m, 1H), 2.50 (s, 3H), 2.29 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 191.7 (d, $J = 10.4$ Hz, 1C), 158.7, 140.7, 135.6, 134.4, 125.7, 120.9 (d, $J = 285.5$ Hz, 2C), 111.4, 76.1 (sept, $J = 33.3$ Hz, 1C), 19.9, 16.3; Anal. Calcd. For $\text{C}_{12}\text{H}_{10}\text{F}_6\text{O}_2$: C, 48.01; H, 3.36%. Found: C, 48.03; H, 3.36%; MS (EI) m/z (%) 300.0(M^+ , 66), 285.0(18), 265.0(7), 213.0(12), 195.3(3), 148.0(65), 121.1(46), 91.0(100), 77.0(89).

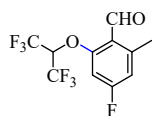


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,6-dimethylbenzaldehyde **3c**. yield: 39% (M=300.06, 11.7 mg). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.56 (s, 1H), 6.86 (s, 1H), 6.71 (s, 1H), 5.03 – 4.95 (m, 1H), 2.58 (s, 3H), 2.39 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 190.3 (d, $J = 9.8$ Hz, 1C), 160.8, 146.0, 142.9, 128.9, 122.8, 120.9 (d, $J = 282.2$ Hz, 2C), 112.7, 76.0 (sept, $J = 33.5$ Hz, 1C), 22.0, 21.4; Anal. Calcd. For $\text{C}_{12}\text{H}_{10}\text{F}_6\text{O}_2$: C, 48.01; H, 3.36%. Found: C, 48.00; H, 3.34%; MS (EI) m/z (%) 300.0(M^+ , 91), 285.0(40), 265.1(3), 195.1(11), 148.1(73), 119.9(45), 90.9(83), 77.0(100);

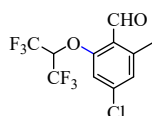


2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methoxy-6-methylbenzaldehyde **3g**. yield:37% (M=316.05, 11.8 mg). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.47 (s, 1H), 6.54 (s, 1H), 6.40 (s, 1H), 5.03 – 4.91 (m, 1H), 3.88 (s, 3H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 189.1, 164.1, 162.4, 145.6, 120.8 (q, $J = 282.9$ Hz, 2C), 118.8, 112.3, 99.1, 75.9 (sept, $J = 33.3$ Hz, 1C), 55.8, 22.3; Anal. Calcd. For

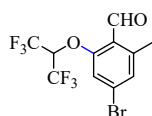
C₁₂H₁₀F₆O₃: C, 45.58; H, 3.19%. Found: C, 45.60; H, 3.17%; MS (EI) m/z (%) 315.0(M⁺, 98), 299.0(31), 269.0(5), 230.2(6), 164.0(89), 136.0(61), 121.0(32), 77.0(59).



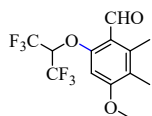
4-fluoro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3i**. yield:46% (M=304.03, 14.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.45 (s, 1H), 6.72 (dd, *J* = 8.9, 1.8 Hz, 1H), 6.59 (dd, *J* = 9.2, 2.0 Hz, 1H), 4.98 – 4.76 (m, 1H), 2.56 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 188.0 (d, *J* = 4.9 Hz, 1C), 164.3 (d, *J* = 257.6 Hz, 1C), 160.8 (d, *J* = 11.1 Hz, 1C), 145.3 (d, *J* = 10.6 Hz, 1C), 120.8 (d, *J* = 3.1 Hz, 1C), 119.7 (q, *J* = 282.2 Hz, 2C), 114.0 (d, *J* = 20.9 Hz, 1C), 99.4 (d, *J* = 25.6 Hz, 1C), 75.0 (sept, *J* = 33.8 Hz, 1C), 20.9 (d, *J* = 1.3 Hz, 1C); Anal. Calcd. For C₁₁H₇F₇O₂: C, 43.44; H, 2.32%. Found: C, 43.46; H, 2.33%; MS (EI) m/z (%) 303.0(M⁺, 90), 288.9(21), 268.9(7), 199.0(15), 152.0(100), 124.0(58), 96.0(73), 68.9(83).



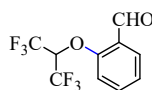
4-chloro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3k**. yield:38% (M=320.00, 12.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.53 (s, 1H), 7.07 (s, 1H), 6.94 (s, 1H), 5.05 – 4.90 (m, 1H), 2.60 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 188.4 (d, *J* = 9.5 Hz, 1C), 159.7, 143.6, 139.0, 127.2, 122.6, 119.7 (q, *J* = 282.6 Hz, 2C), 111.9, 75.1 (sept, *J* = 33.8 Hz, 1C), 20.4; Anal. Calcd. For C₁₁H₇ClF₆O₂: C, 41.21; H, 2.20%. Found: C, 41.20; H, 2.21%; MS (EI) m/z (%) 319.9(M⁺, 50), 318.9(55), 304.8(13), 285.0(32), 168.0(60), 113.0(35), 89.0(50), 77.0(100).



4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3m**. yield:33% (M=363.95, 12.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.54 (s, 1H), 7.25 (s, 1H), 7.09 (s, 1H), 5.02 – 4.90 (m, 1H), 2.59 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 189.6 (d, *J* = 7.2 Hz, 1C), 160.5, 144.6, 131.2, 128.4, 124.0, 120.7 (q, *J* = 282.9 Hz, 2C), 115.9, 76.1 (sept, *J* = 33.8 Hz, 1C), 21.3; Anal. Calcd. For C₁₁H₇BrF₆O₂: C, 36.19; H, 1.93%. Found: C, 36.22; H, 1.92%; MS (EI) m/z (%) 363.9(M⁺, 40), 285.0(57), 265.0(21), 211.9(48), 134.0(14), 105.0(26), 77.0(100).

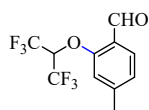


6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-2,3-dimethylbenzaldehyde **3p**. yield: 47% (M=330.07, 15.4 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.50 (s, 1H), 6.36 (s, 1H), 4.98 – 4.87 (m, 1H), 3.90 (s, 3H), 2.55 (s, 3H), 2.13 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 190.1 (d, *J* = 9.5 Hz, 1C), 162.2, 160.8, 142.2, 123.2, 120.9 (d, *J* = 280.2 Hz, 2C), 119.1, 95.0, 76.5 (sept, *J* = 33.3 Hz, 1C), 55.8, 16.5, 11.2; Anal. Calcd. For C₁₃H₁₂F₆O₃: C, 47.28; H, 3.66%. Found: C, 47.31; H, 3.65%; MS (EI) m/z (%) 330.1(M⁺, 97), 313.0(40), 244.2(11), 179.1 (100), 150.1(40), 135.0(32), 107.0(32), 91.0(92) 77.0(83).

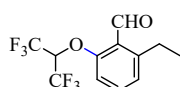


2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3r**.¹ yield:45% (M=272.03, 12.2 mg). ¹H NMR

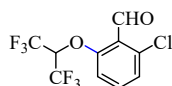
(600 MHz, CDCl₃) δ 10.48 (s, 1H), 7.94 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.72 – 7.59 (m, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.06 – 4.94 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 188.0 (d, *J* = 9.2 Hz, 1C), 159.15, 136.08, 129.10, 126.76, 124.81, 120.9 (q, *J* = 284.9 Hz, 2C), 114.82, 76.0 (sept, *J* = 33.6 Hz, 1C).



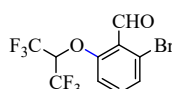
2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methylbenzaldehyde **3s**. yield:52% (M=286.04, 14.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.40 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.88 (s, 1H), 5.05 – 4.92 (m, 1H), 2.45 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 187.8, 159.2, 147.9, 129.0, 125.7, 124.5, 120.9 (q, *J* = 282.3 Hz, 2C), 115.3, 75.9 (sept, *J* = 33.6 Hz, 1C), 22.2; Anal. Calcd. For C₁₁H₈F₆O₂: C, 46.17; H, 2.82%. Found: C, 46.16; H, 2.80%; MS (EI) *m/z* (%) 286.1(M⁺, 73), 271.0(39), 251.0(11), 217.0(10), 181.1(16), 134.0(97), 91.0(48), 77.0(100).



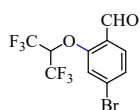
2-ethyl-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3t**. yield:66% (M=300.06, 19.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.61 (s, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.05 – 4.93 (m, 1H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 190.6 (d, *J* = 9.8 Hz, 1C), 160.5, 149.2, 134.6, 126.4, 124.8, 120.9 (d, *J* = 285.6 Hz, 2C), 111.9, 76.0 (sept, *J* = 33.6 Hz, 1C), 26.9, 15.4; Anal. Calcd. For C₁₂H₁₀F₆O₂: C, 48.01; H, 3.36%. Found: C, 47.98; H, 3.37%; MS (EI) *m/z* (%) 300.0(M⁺, 63), 271.0(17), 195.0(12), 148.1(41), 121.1(60), 103.0(100), 91.0(68), 77.0(98).



2-chloro-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3u**.² yield:47% (M=305.99, 14.4 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.48 (s, 1H), 7.50 (t, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 5.06 – 4.93 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 187.4 (d, *J* = 9.8 Hz, 1C), 158.72, 136.71, 134.46, 127.36, 124.84, 120.7 (d, *J* = 282.9 Hz, 2C), 114.12, 76.2 (sept, *J* = 33.5 Hz, 1C).

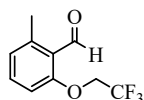


2-bromo-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3v**.³ yield:51% (M=349.94, 17.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.38 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.07 – 4.94 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 188.5, 158.6, 134.6, 130.7, 126.1, 124.7, 120.7 (d, *J* = 282.5 Hz, 2C), 114.9, 76.2 (sept, *J* = 33.8 Hz, 1C).

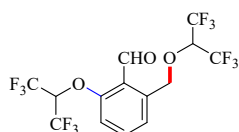


4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3w**.⁴ yield:34% (M=349.94, 11.9 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.39 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 1.3 Hz, 1H), 5.05 – 4.94 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 186.9, 159.0, 130.3, 130.3,

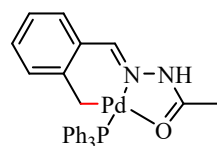
128.5, 125.6, 120.7 (d, $J = 285.0$ Hz, 2C), 118.6, 76.1 (sept, $J = 33.8$ Hz, 1C).



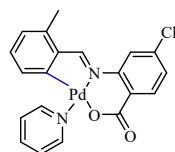
2-methyl-6-(2,2,2-trifluoroethoxy)benzaldehyde **4**. yield:52% (M=218.18, 11.3 mg). ^1H NMR (600 MHz, CDCl_3) δ 10.66 (s, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 4.45 (q, $J = 7.9$ Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 191.4, 160.7, 142.7, 134.3, 126.2, 124.1, 123.1 (d, $J = 276.5$ Hz, 2C), 110.2, 66.4 (q, $J = 35.9$ Hz, 1C), 21.4; Anal. Calcd. For $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_2$: C, 55.05; H, 4.16%. Found: C, 55.06; H, 4.18%; MS (EI) m/z (%) 218.0(M^+ , 100), 201.1(27), 134.0(28), 118.1(37), 90.0(70), 77.0(76).



2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **5**. Total yield: 27% (M=452.03, 12.4 mg). ^1H NMR (600 MHz, CDCl_3) δ 10.58 (s, 1H), 7.69 (t, $J = 8.1$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 5.31 (s, 2H), 5.07-4.97 (m, 1H), 4.42-4.31 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 190.2 (d, $J = 8.3$ Hz, 1C), 160.3, 140.6, 135.8, 123.1, 122.9, 122.1 (d, $J = 104.3$ Hz, 2C), 120.2(d, $J = 104.1$ Hz, 2C), 113.9, 76.6 (sept, $J = 32.4$ Hz, 1C), 76.1 (sept, $J = 33.6$ Hz, 1C), 74.2.



Intermediate **6**. yield:48% (M=543.08, 26.1 mg). ^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, $J = 9.4$ Hz, 1H), 7.65-7.60 (m, 6H), 7.50-7.44 (m, 4H), 7.44-7.39 (m, 6H), 7.32 (d, $J = 7.4$ Hz, 1H), 7.14 (t, $J = 7.3$ Hz, 1H), 7.10 (t, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 7.4$ Hz, 1H), 2.94 (d, $J = 6.2$ Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 178.1 (d, $J = 4.7$ Hz, 1C), 148.5, 143.7, 134.5, 134.5, 134.4, 132.9, 132.5, 132.2, 132.1, 132.1, 132.0, 131.9, 131.1, 130.8, 130.7, 130.7, 130.2, 128.9, 128.7, 128.6, 128.5, 128.5, 124.8, 26.5 (d, $J = 5.3$ Hz, 1C), 19.3; HRMS (ESI): m/z [$\text{M}+2\text{H}$] $^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{OPPd}$ 545.0818, found 545.0826.



Intermediate **7**. yield:65% (M=455.99, 29.7 mg). ^1H NMR (600 MHz, CDCl_3) δ 8.84 (d, $J = 5.0$ Hz, 2H), 8.71 (s, 1H), 8.26 (d, $J = 8.5$ Hz, 1H), 7.91 (t, $J = 7.7$ Hz, 1H), 7.47 (dd, $J = 7.4, 6.6$ Hz, 2H), 7.40 (d, $J = 1.7$ Hz, 1H), 7.30 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.5$ Hz, 1H), 6.28 (d, $J = 7.6$ Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.9, 169.3, 160.8, 152.6, 145.5, 144.0, 141.0, 138.6, 136.4, 136.3, 133.0, 131.8, 130.9, 128.3, 127.0, 125.6, 117.6, 20.2.

Reference:

[1] CAS Registry Number: 1988549-39-8.

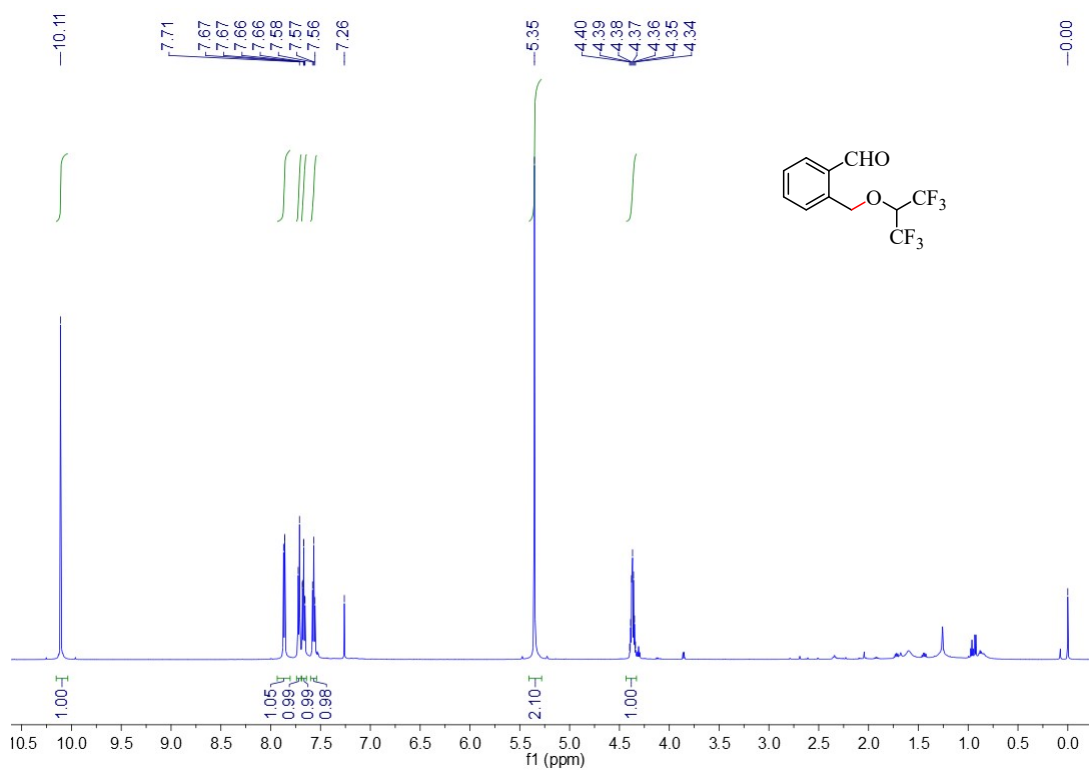
[2] CAS Registry Number: 1990191-30-4.

[3] CAS Registry Number: 1779119-70-8.

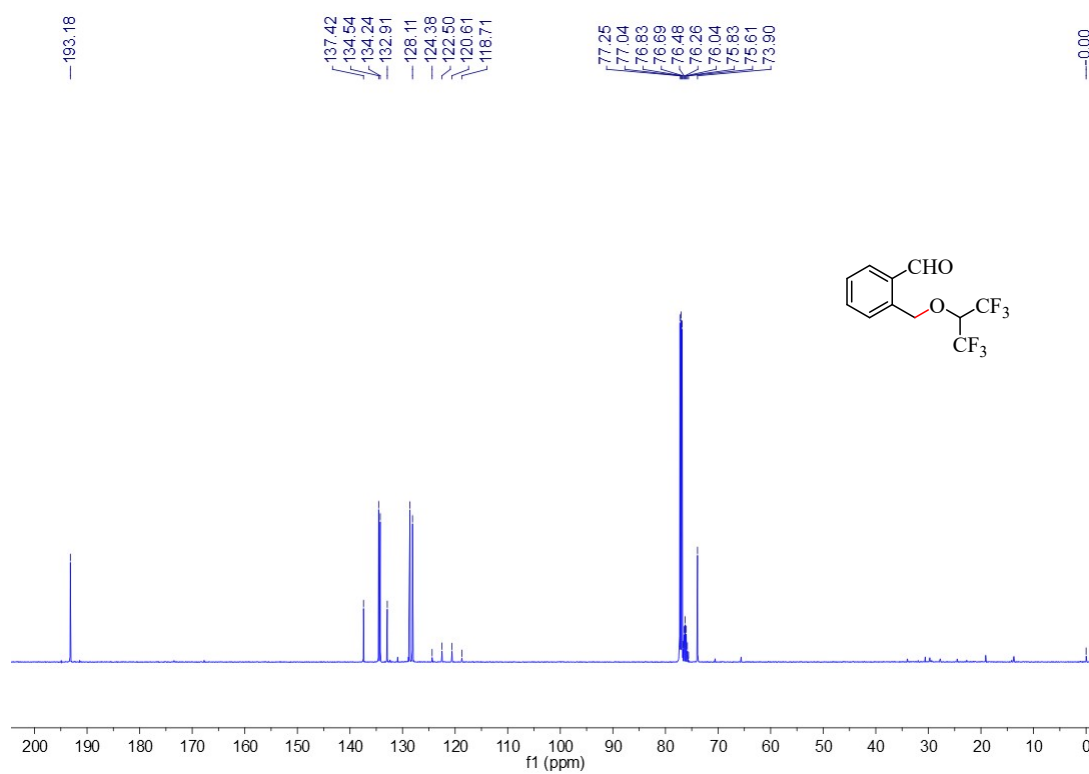
[4] CAS Registry Number: 1707604-69-0.

6. ¹H NMR, ¹³C NMR and MS Spectra of the Products

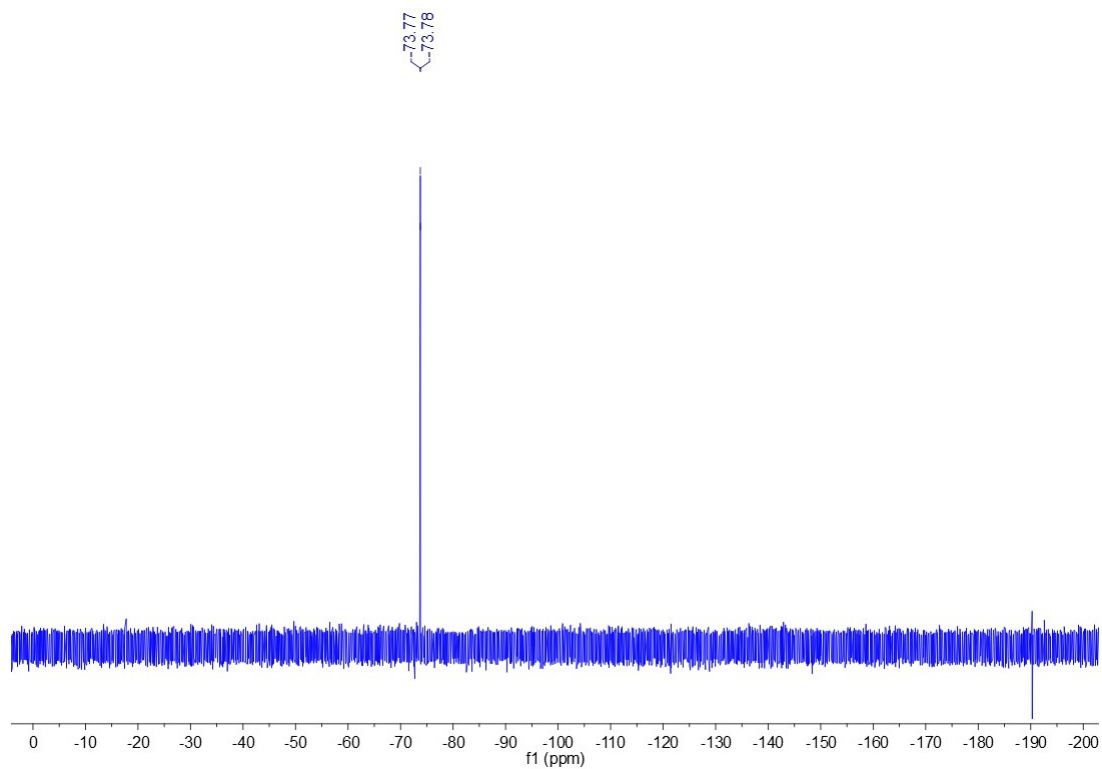
¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2a**



¹³C NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2a**

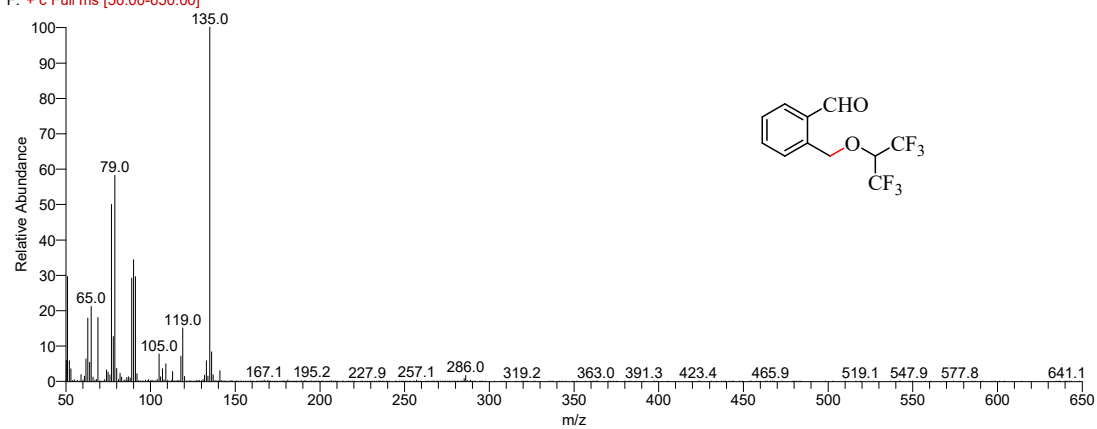


^{19}F NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2a**

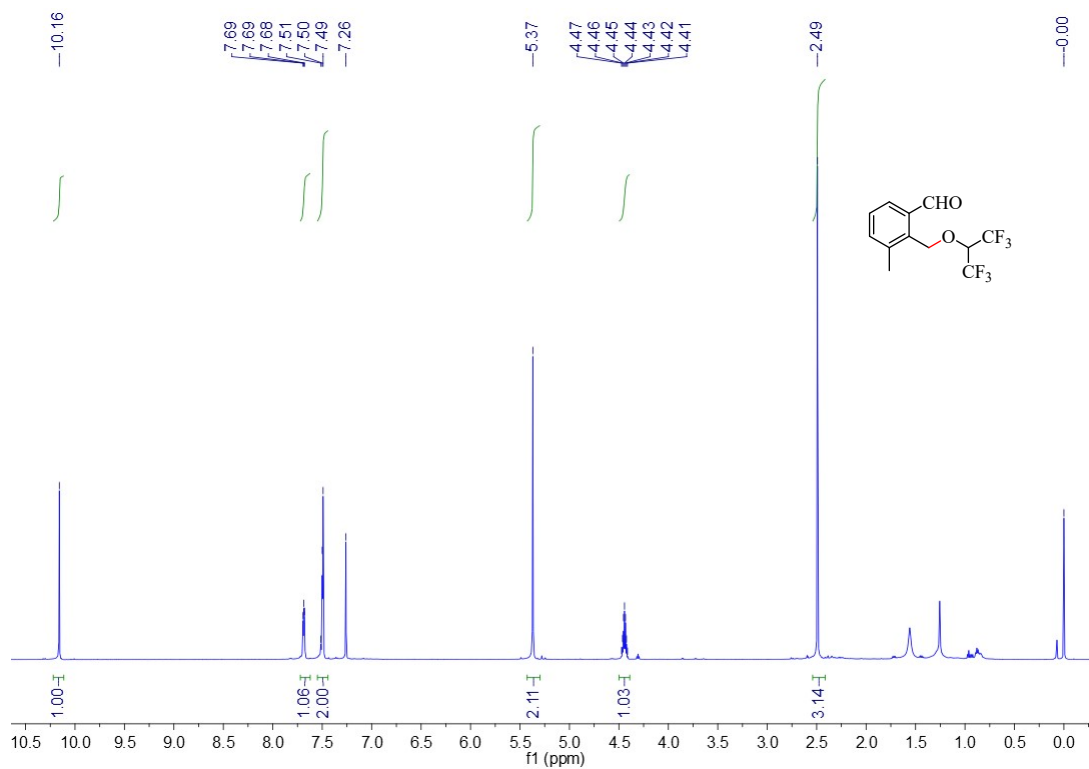


MS(EI) of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2a**

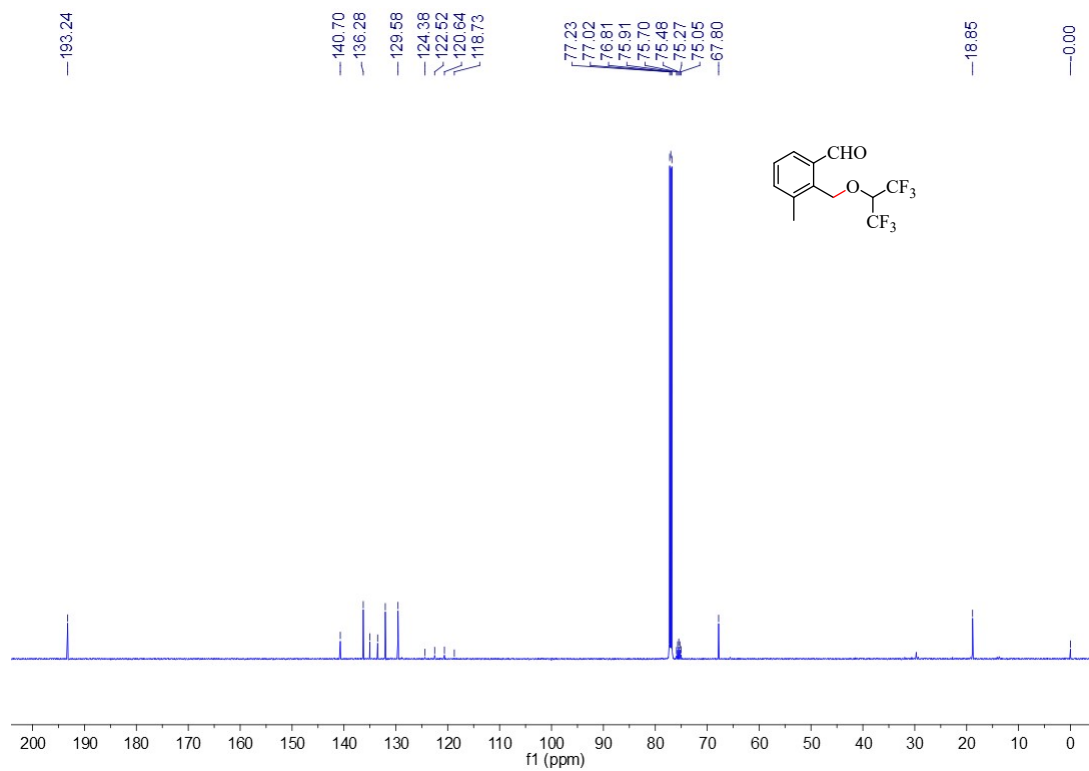
2a #1591 RT: 5.33 AV: 1 AV: 5 SB: 12 1584-1589 1593-1598 NL: 3.77E7
F: + c Full ms [50.00-650.00]



¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-methylbenzaldehyde **2b**

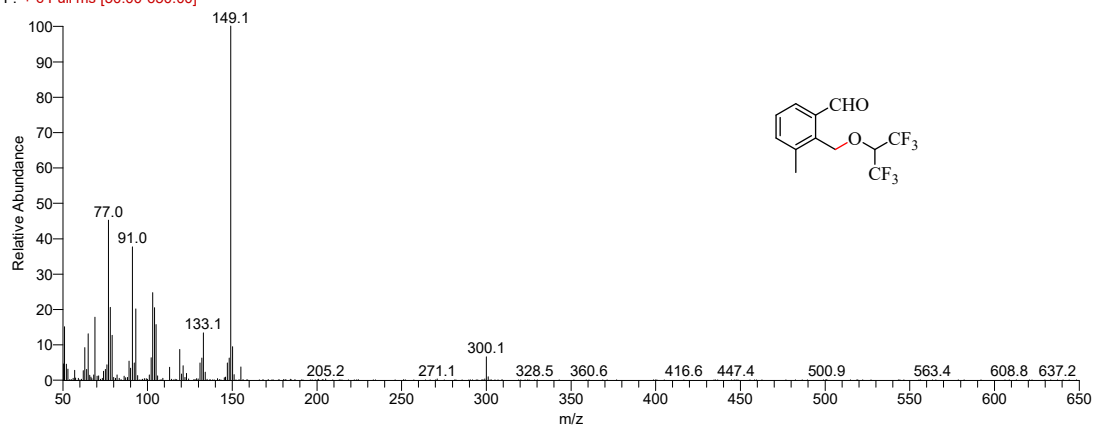


¹³C NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-methylbenzaldehyde **2b**

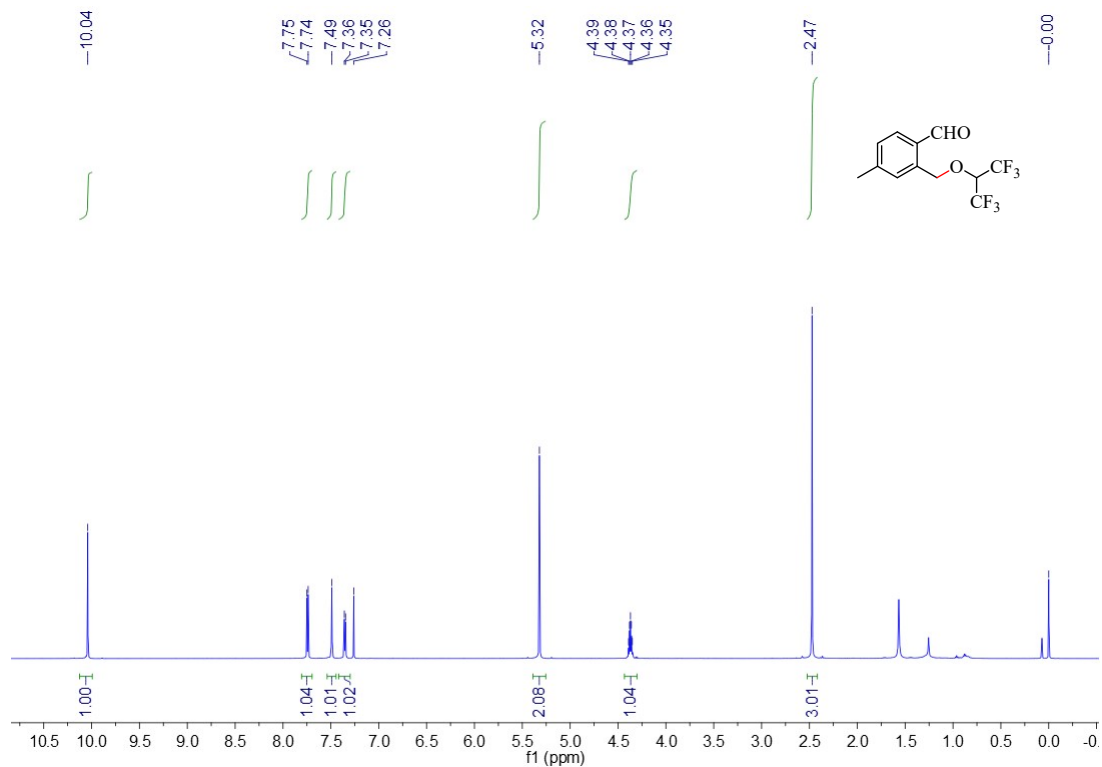


MS(EI) of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-3-methylbenzaldehyde **2b**

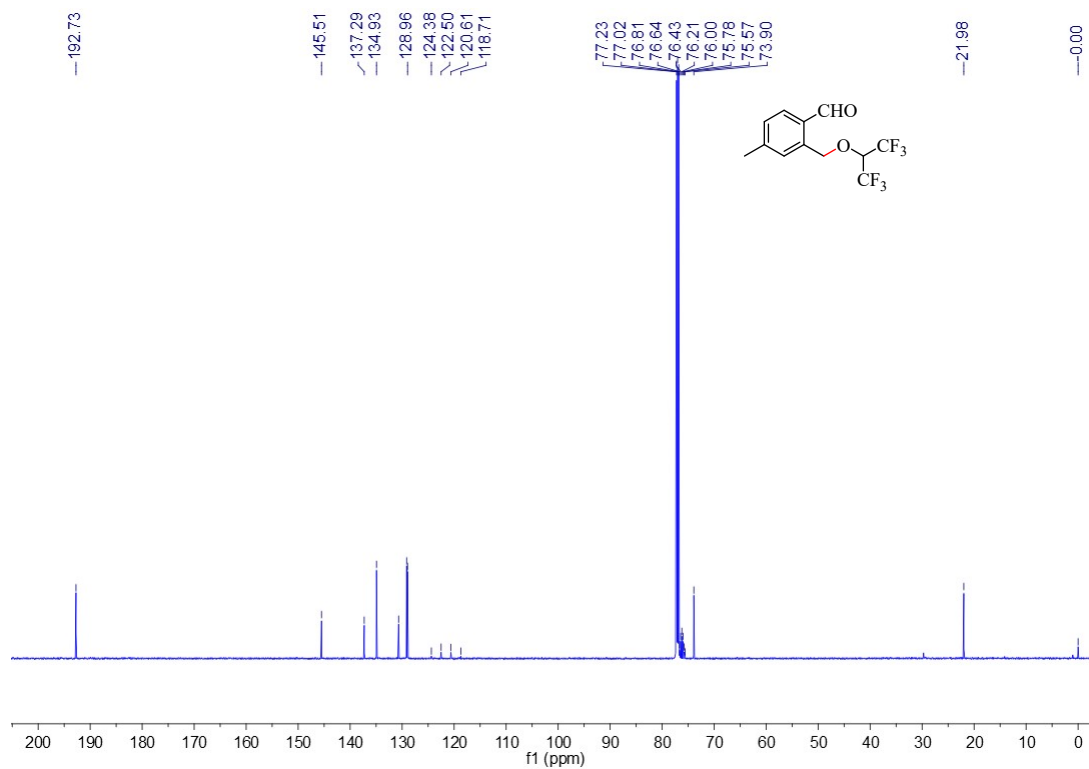
2b #1303 RT: 4.38 AV: 1 SB: 12 1296-1301 1305-1310 NL: 8.38E5
F: + c Full ms [50.00-650.00]



¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2c**

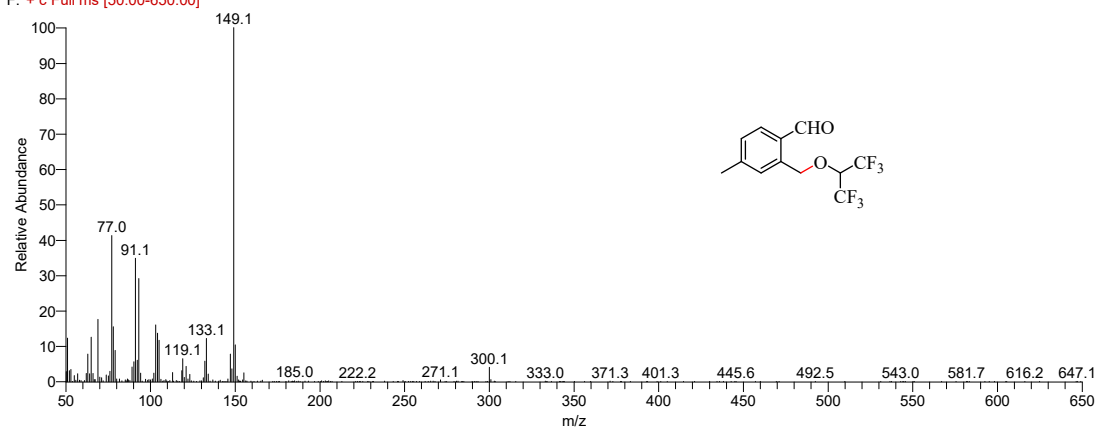


¹³C NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2c**

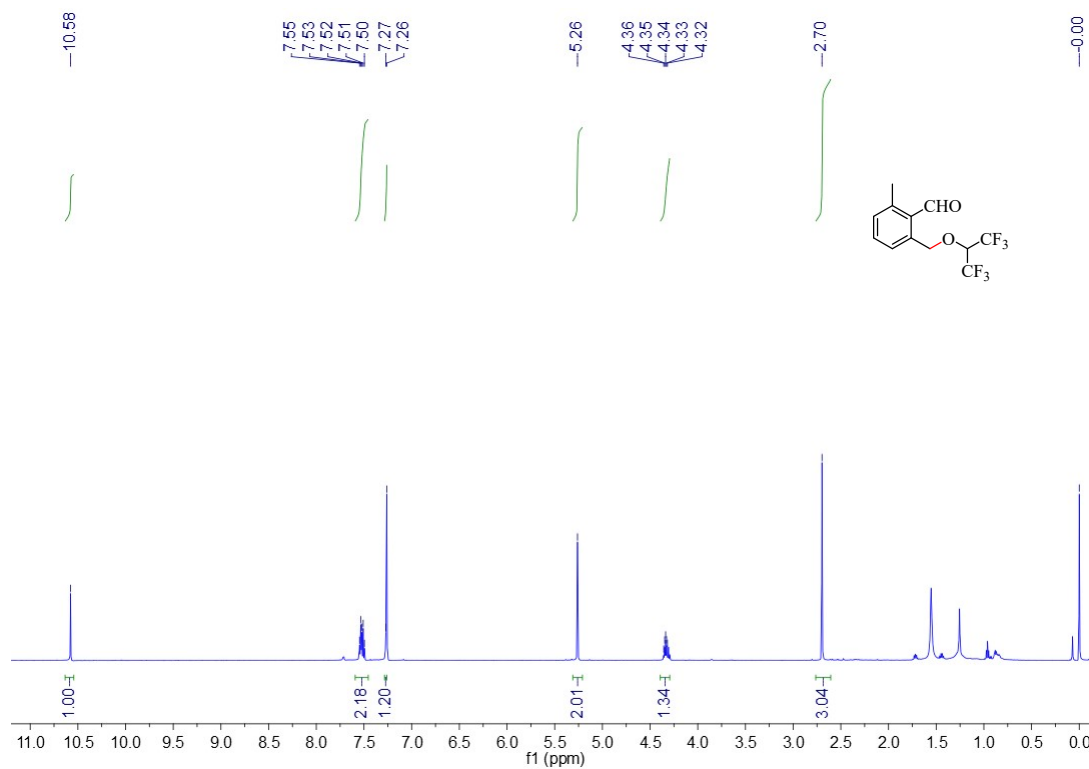


MS(EI) of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2c**

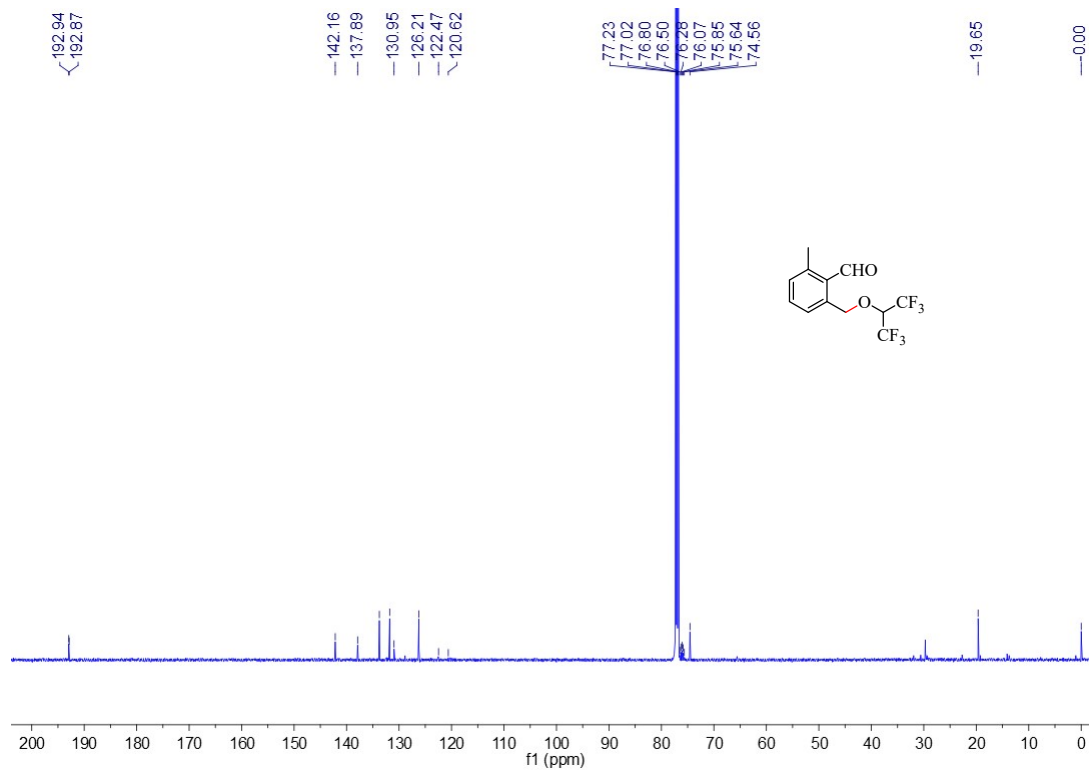
2c #1305 RT: 4.38 AV: 1 AV: 5 SB: 12 1298-1303 1307-1312 NL: 8.04E5
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-6-methylbenzaldehyde **2d**

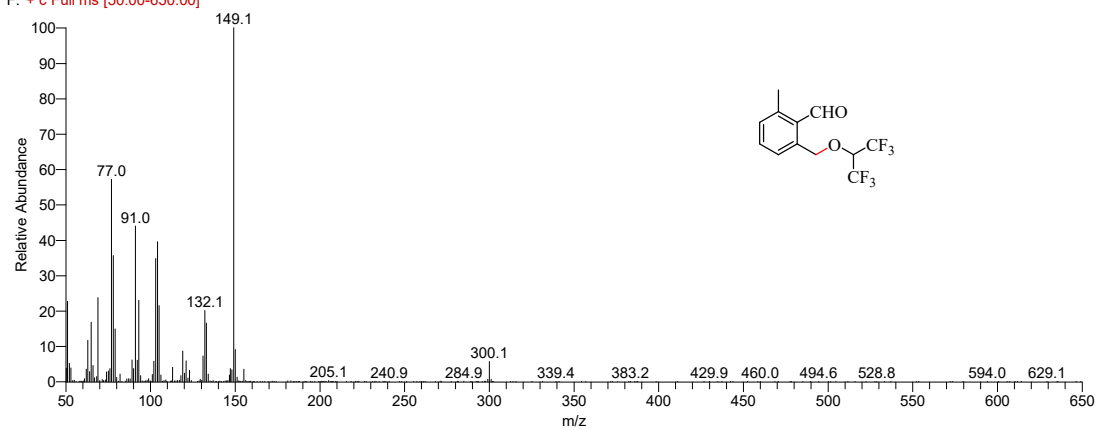


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-6-methylbenzaldehyde **2d**

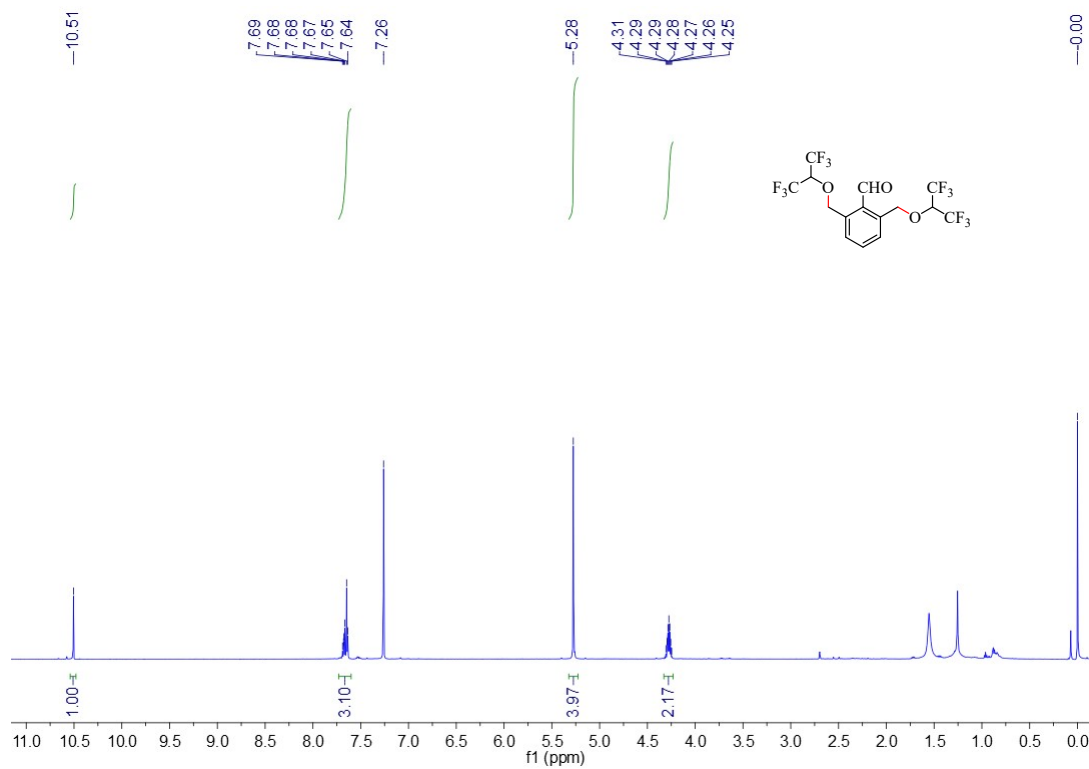


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-6-methylbenzaldehyde **2d**

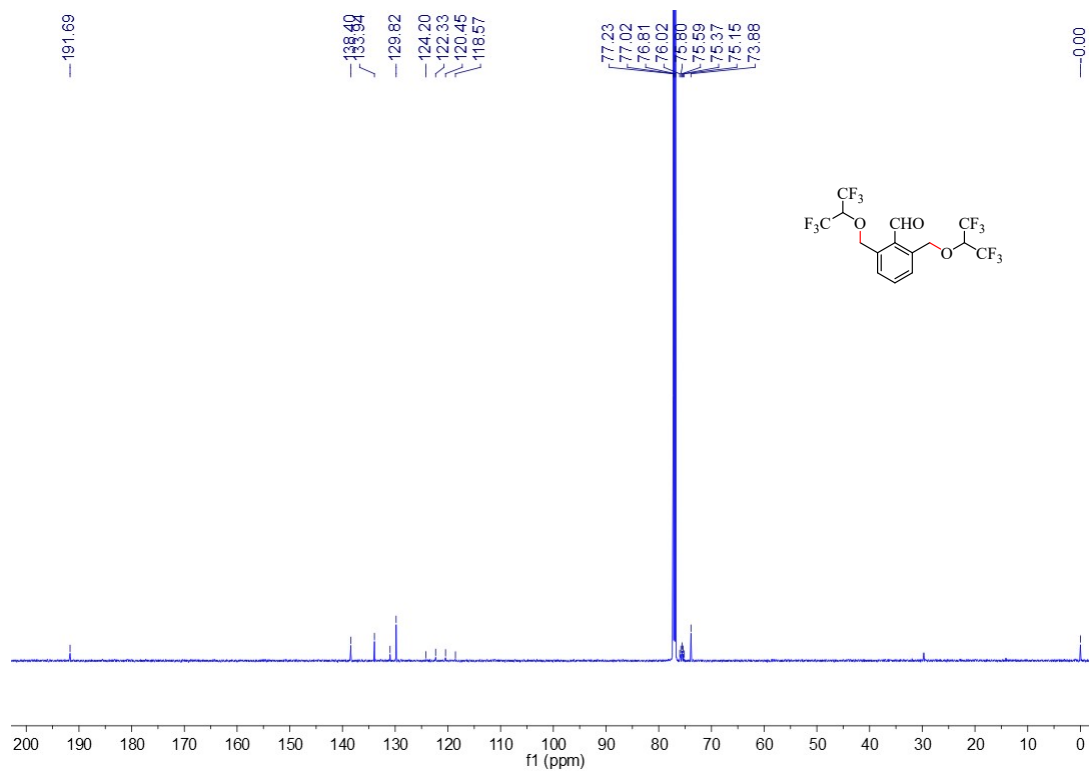
2d #1332 RT: 4.47 AV: 1 AV: 5 SB: 12 1325-1330 1334-1339 NL: 3.18E6
F: + c Full ms [50.00-650.00]



¹H NMR of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2d'**

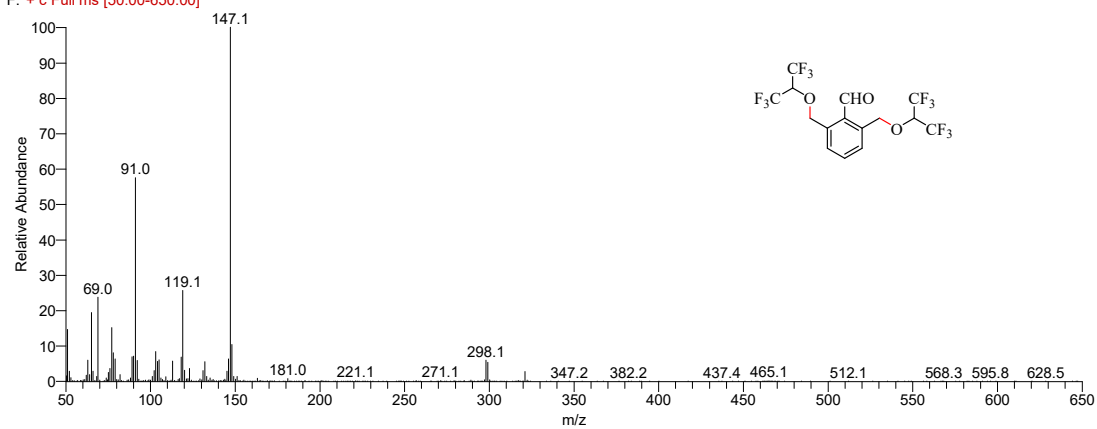


^{13}C NMR of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2d'**

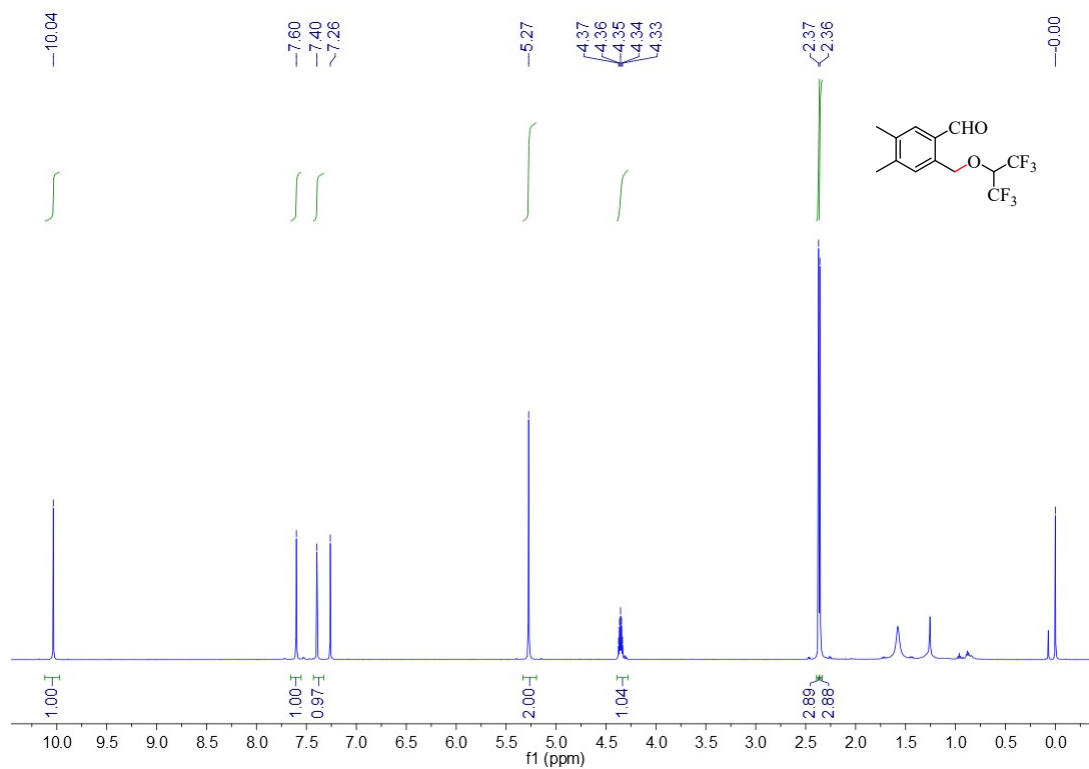


MS(EI) of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **2d'**

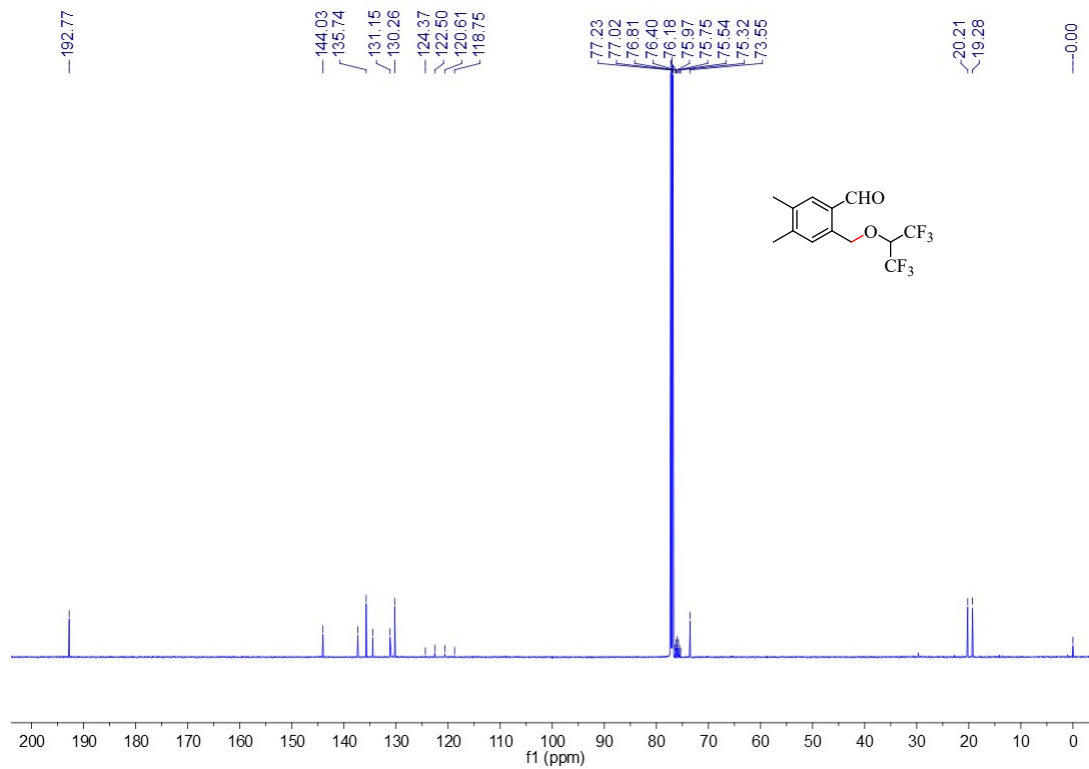
2d2 #1391 RT: 4.67 AV: 1 AV: 5 SB: 12 1384-1389 1393-1398 NL: 5.50E6
F: + c Full ms [50.00-650.00]



¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,5-dimethylbenzaldehyde **2e**

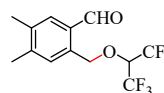
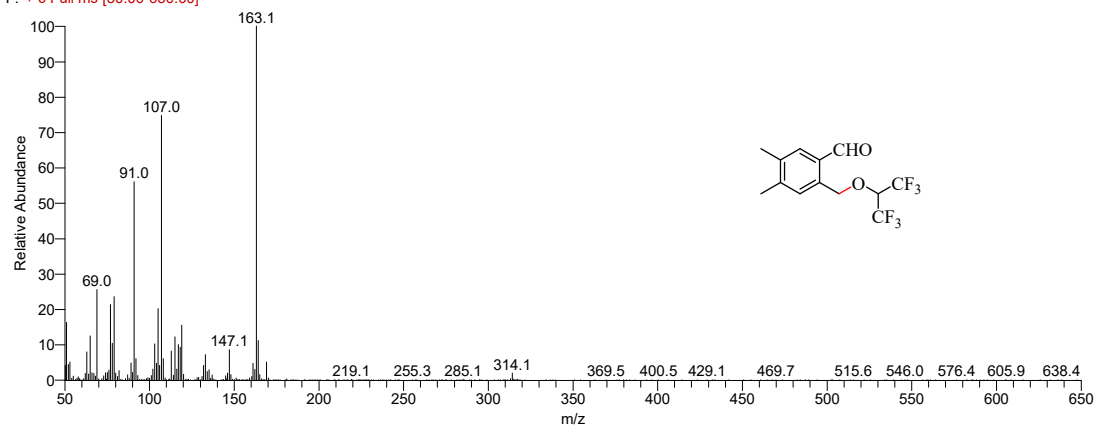


¹³C NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,5-dimethylbenzaldehyde **2e**

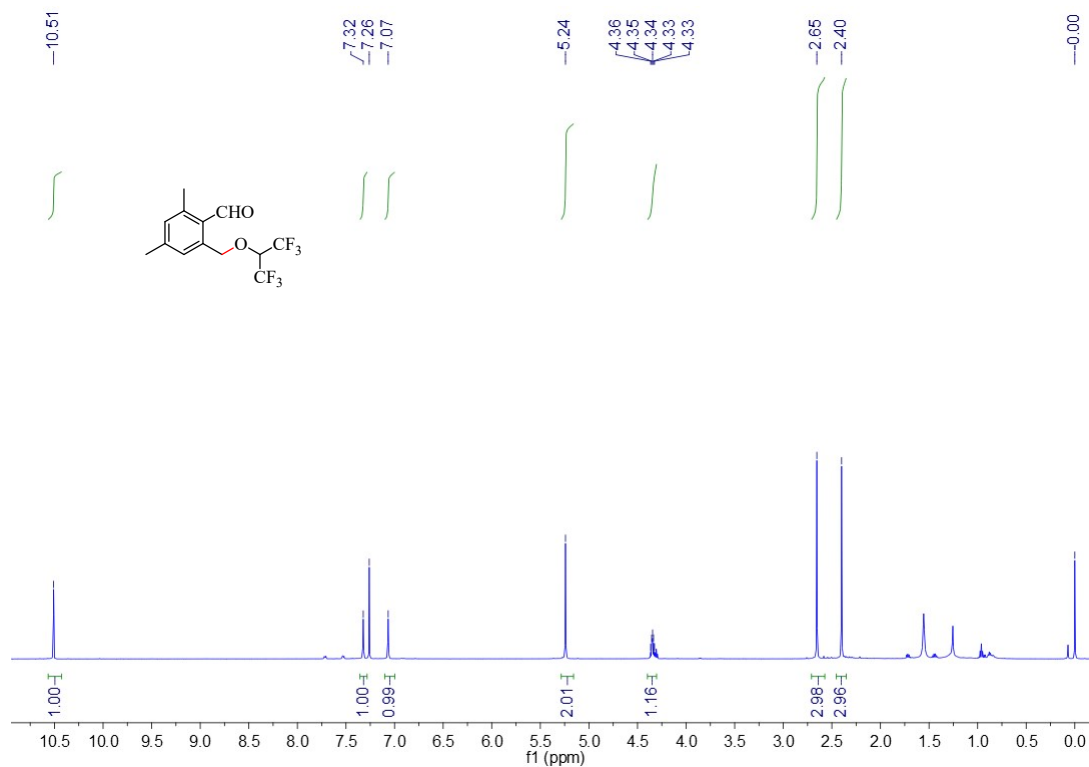


MS(EI) of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,5-dimethylbenzaldehyde **2e**

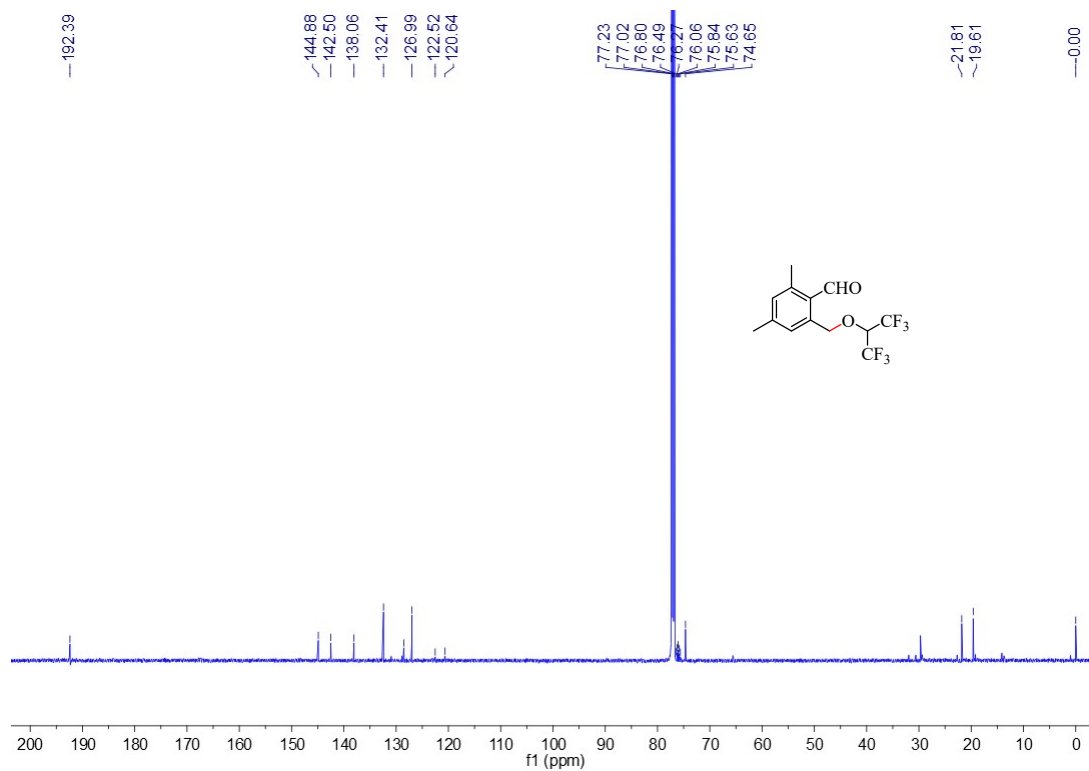
2e #1417 RT: 4.75 AV: 1 AV: 5 SB: 12 1410-1415 1419-1424 NL: 5.34E6
 F: + c Full ms [50.00-650.00]



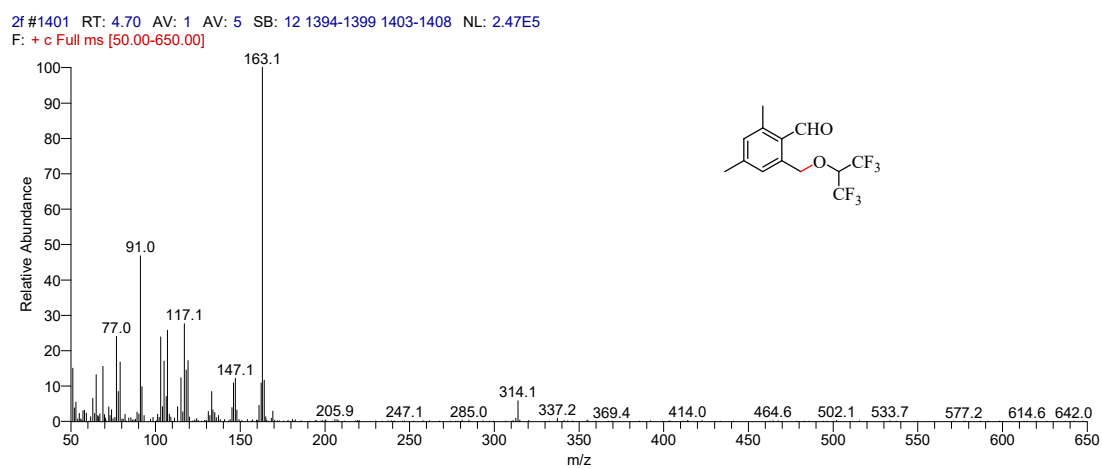
¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4,6-dimethylbenzaldehyde **2f**



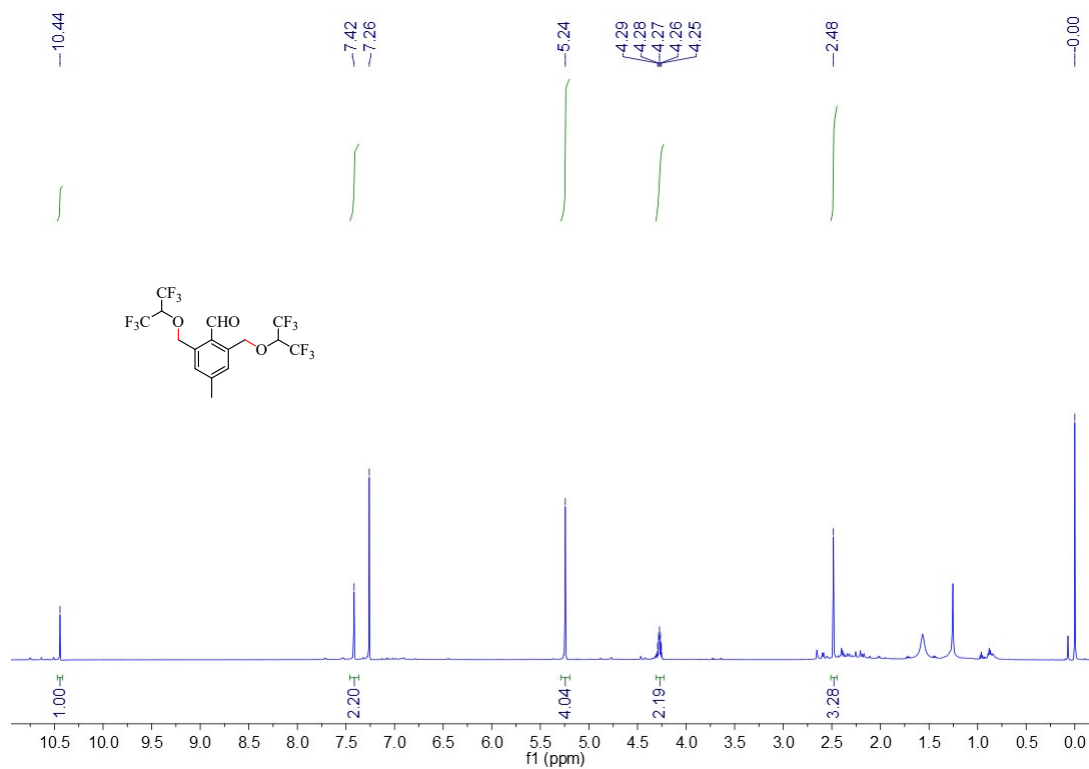
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4,6-dimethylbenzaldehyde **2f**



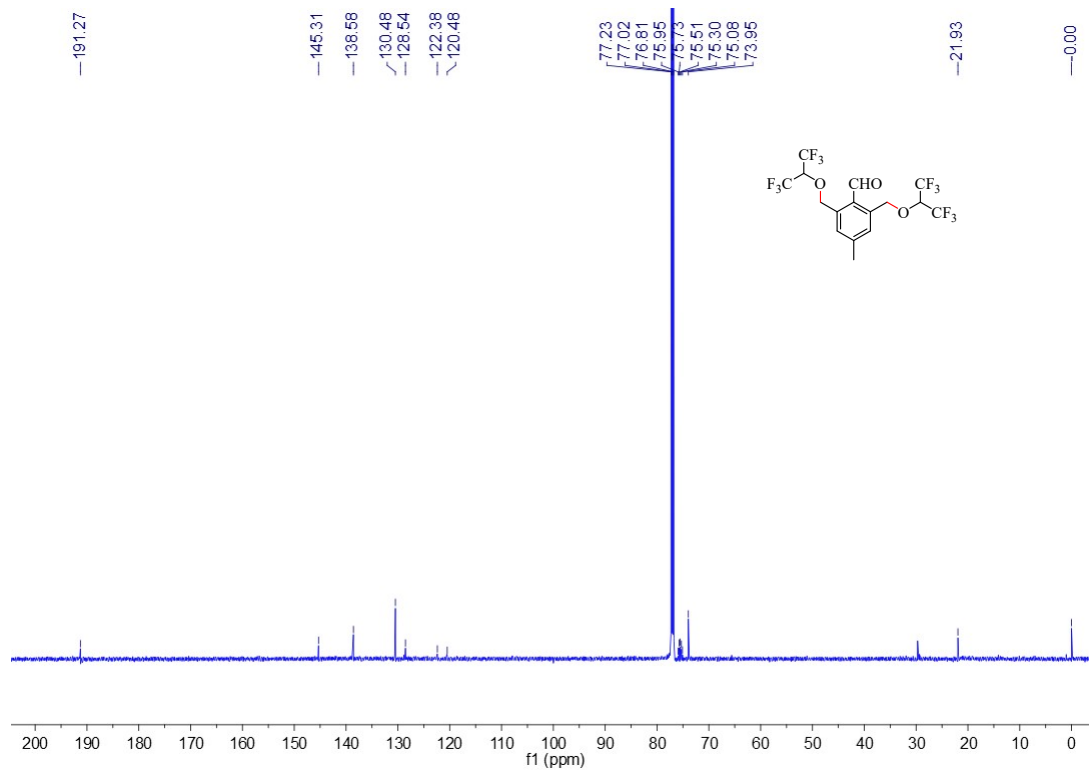
MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4,6-dimethylbenzaldehyde **2f**



¹H NMR of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2f**

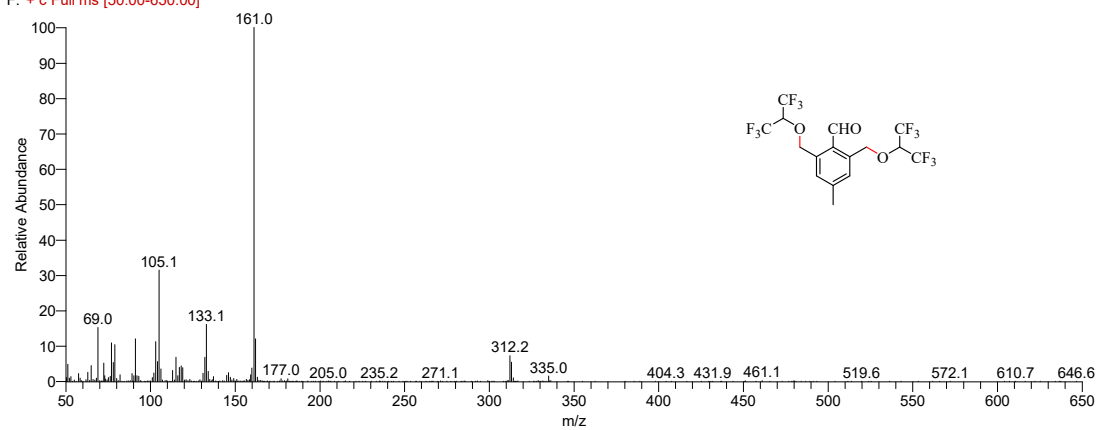


¹³C NMR of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2f**

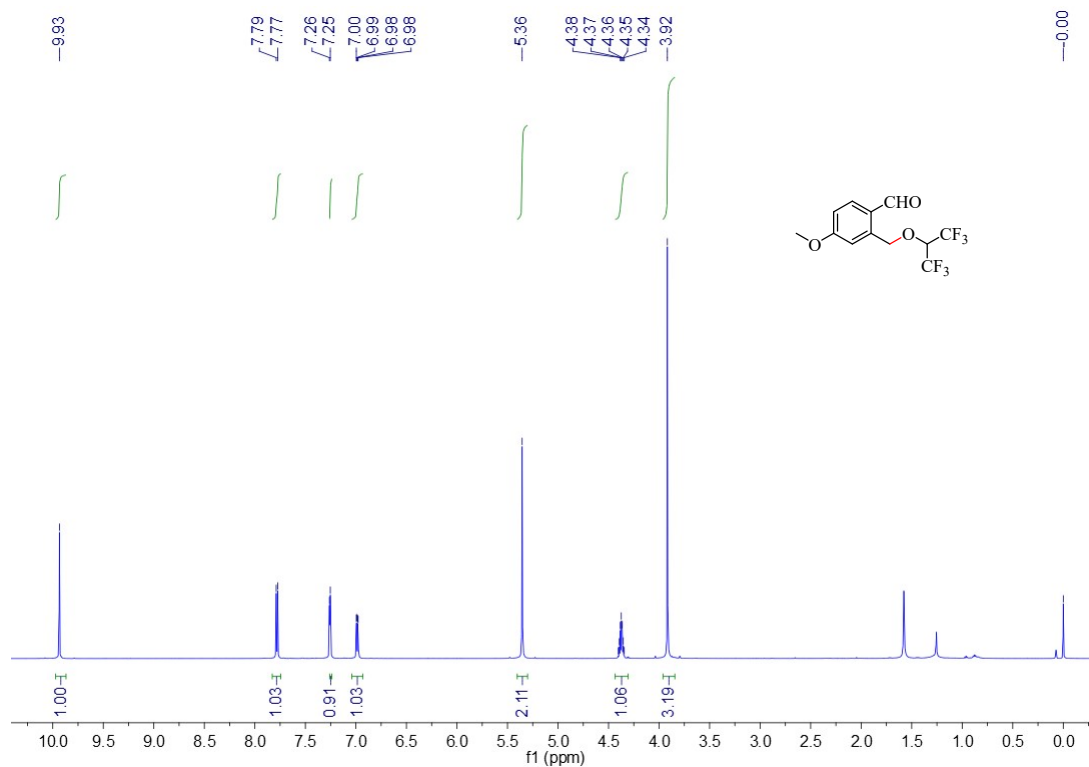


MS(EI) of 2,6-bis(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methylbenzaldehyde **2f**

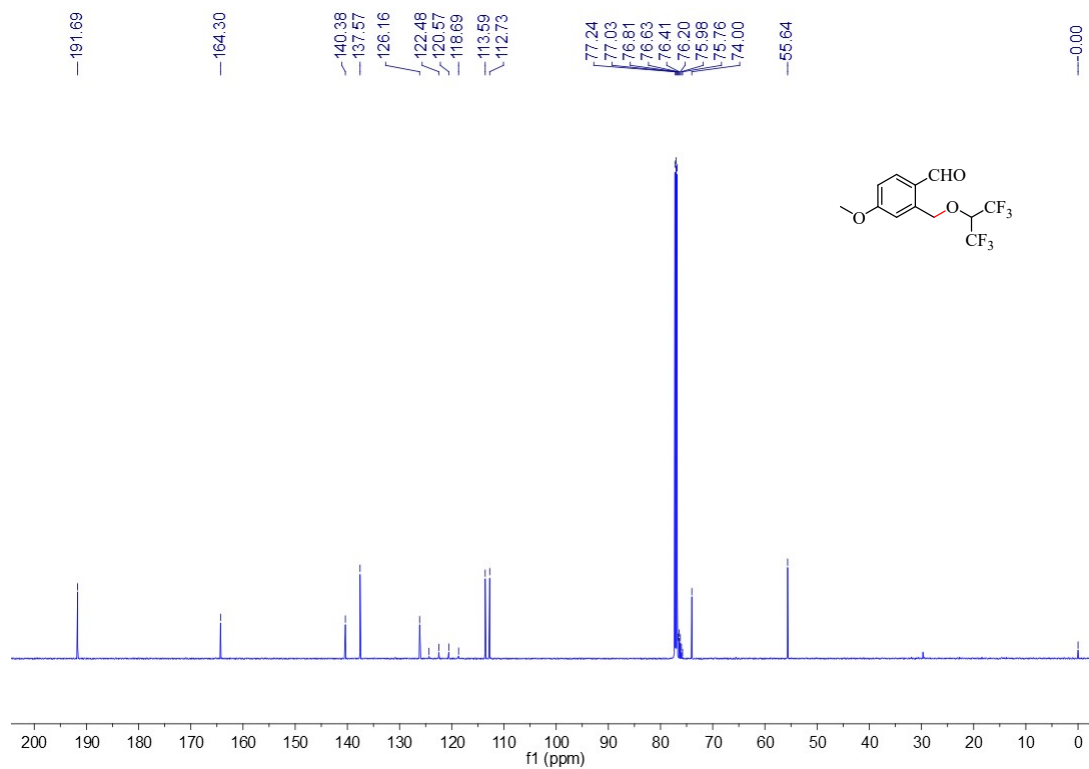
2f2 #1426 RT: 4.78 AV: 1 AV: 5 SB: 12 1419-1424 1428-1433 NL: 2.20E6
 F: + c Full ms [50.00-650.00]



¹H NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methoxybenzaldehyde **2g**

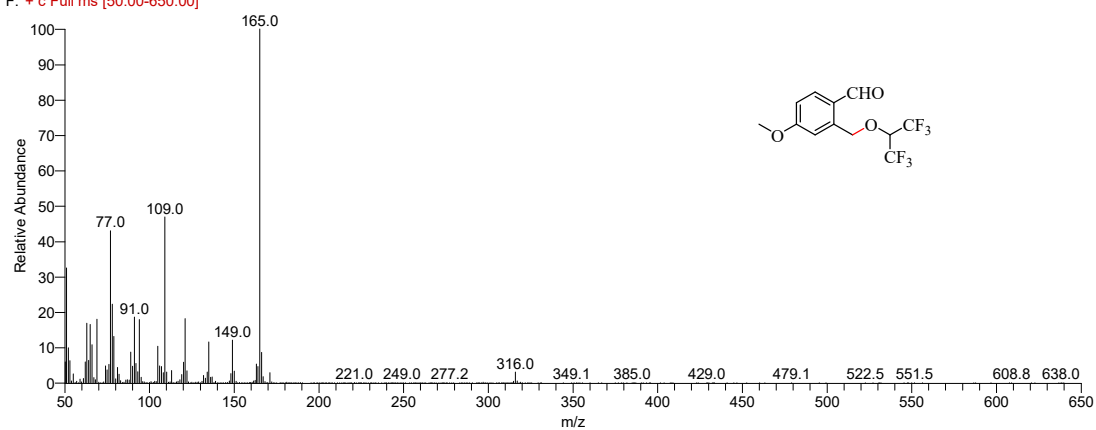


¹³C NMR of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methoxybenzaldehyde **2g**

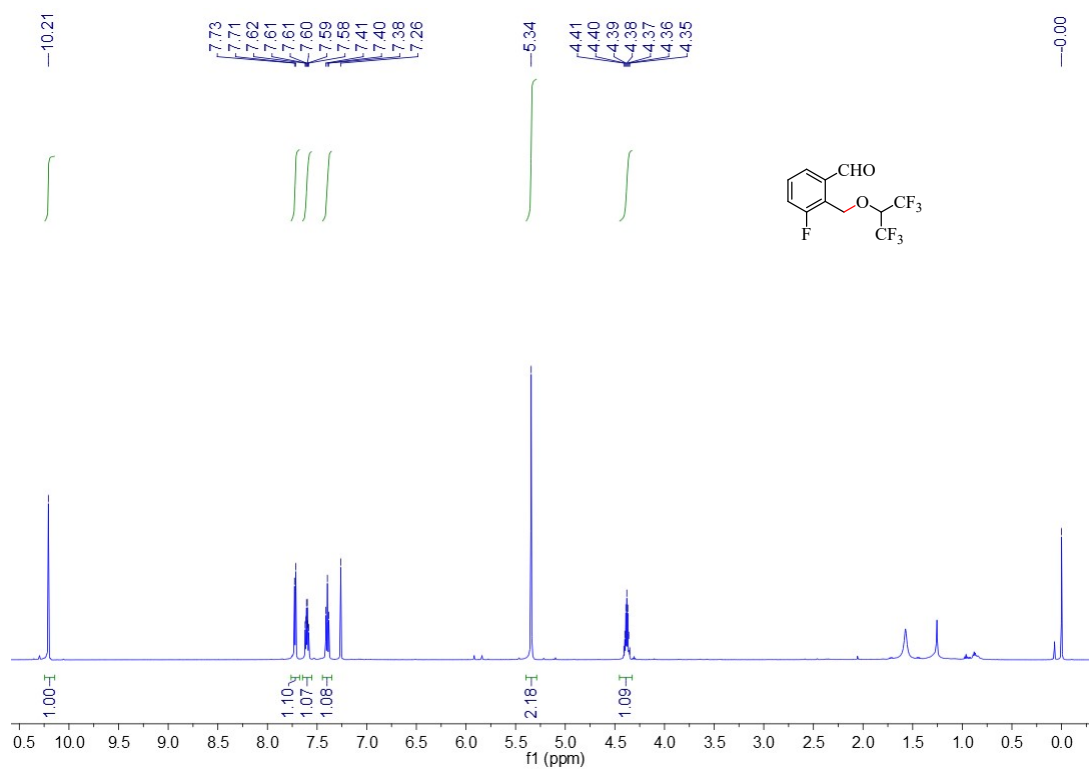


MS(EI) of 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-4-methoxybenzaldehyde **2g**

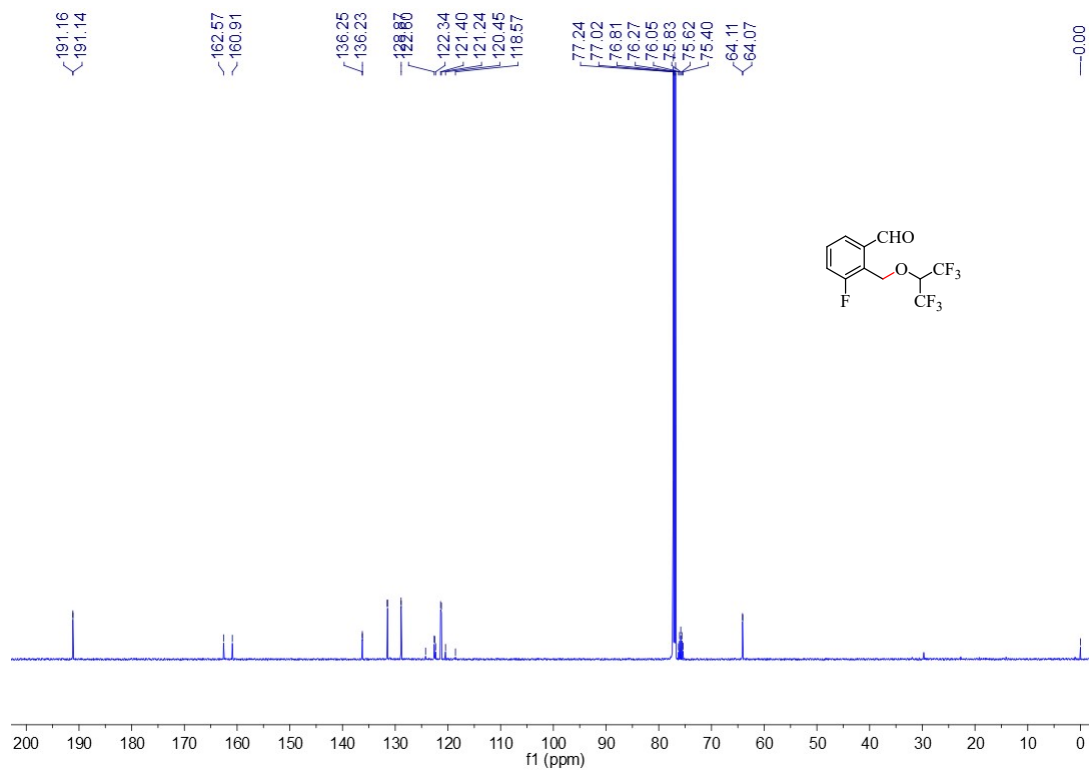
2g #1433 RT: 4.80 AV: 1 AV: 5 SB: 12 1426-1431 1435-1440 NL: 2.44E7
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-fluorobenzaldehyde **2h**

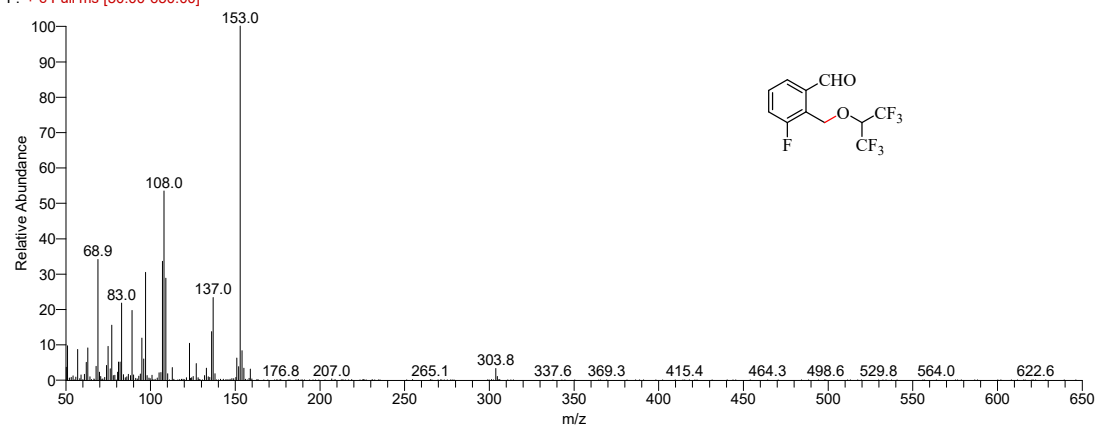


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-fluorobenzaldehyde **2h**

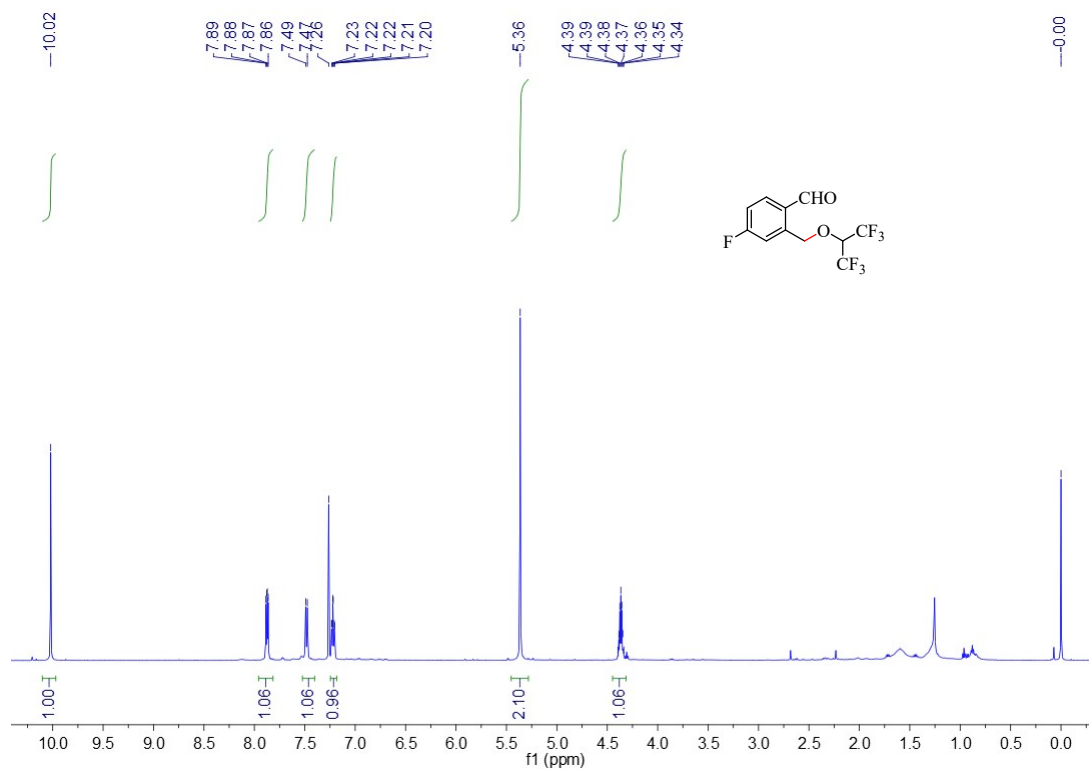


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-fluorobenzaldehyde **2h**

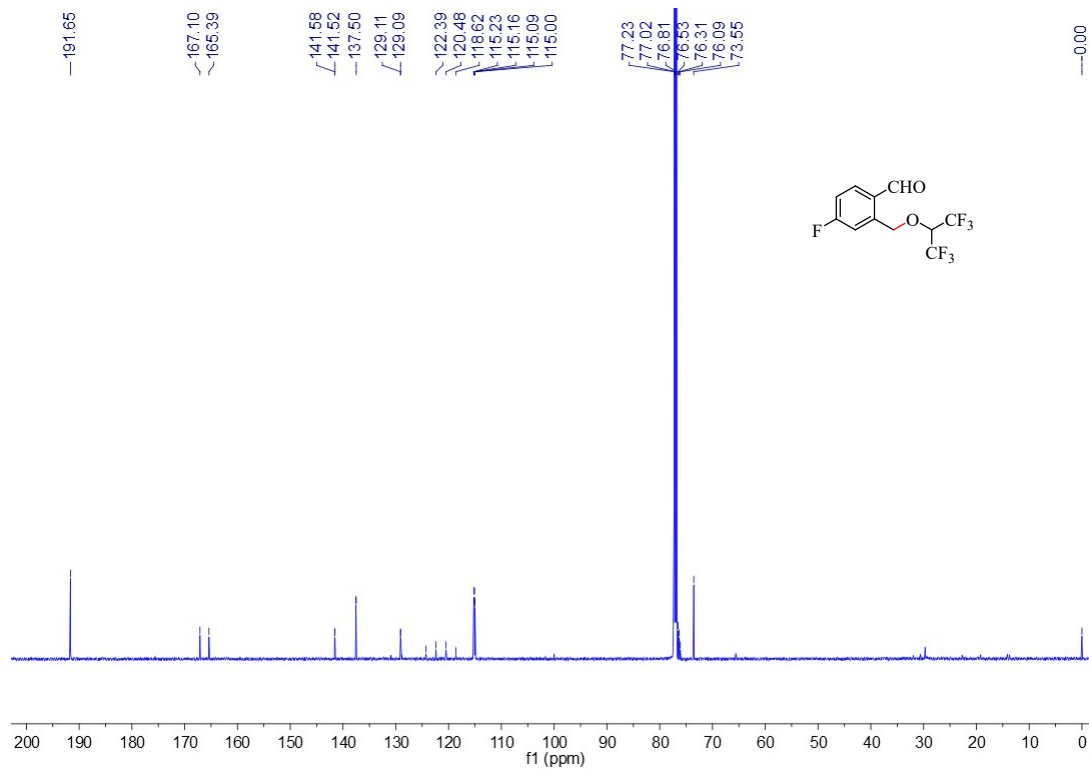
2h #1231 RT: 4.14 AV: 1 SB: 12 1224-1229 1233-1238 NL: 9.00E5
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-fluorobenzaldehyde **2i**

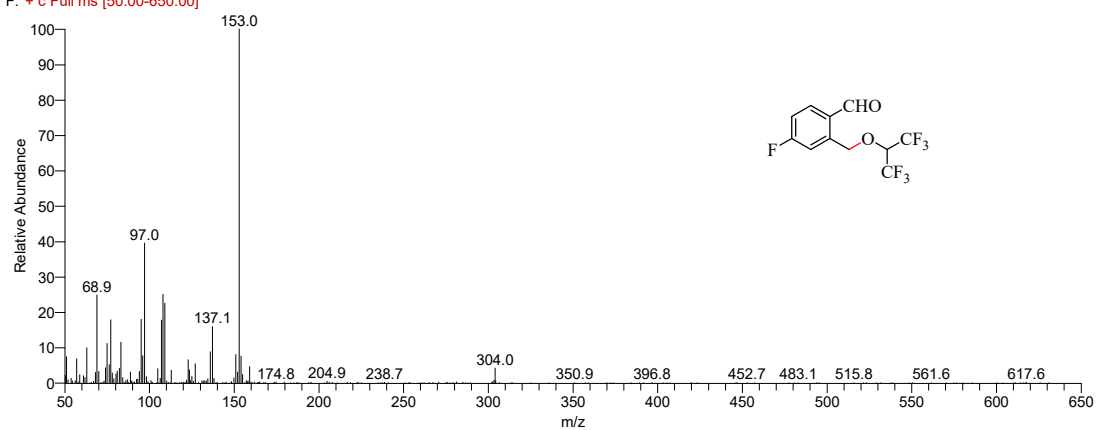


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-fluorobenzaldehyde **2i**

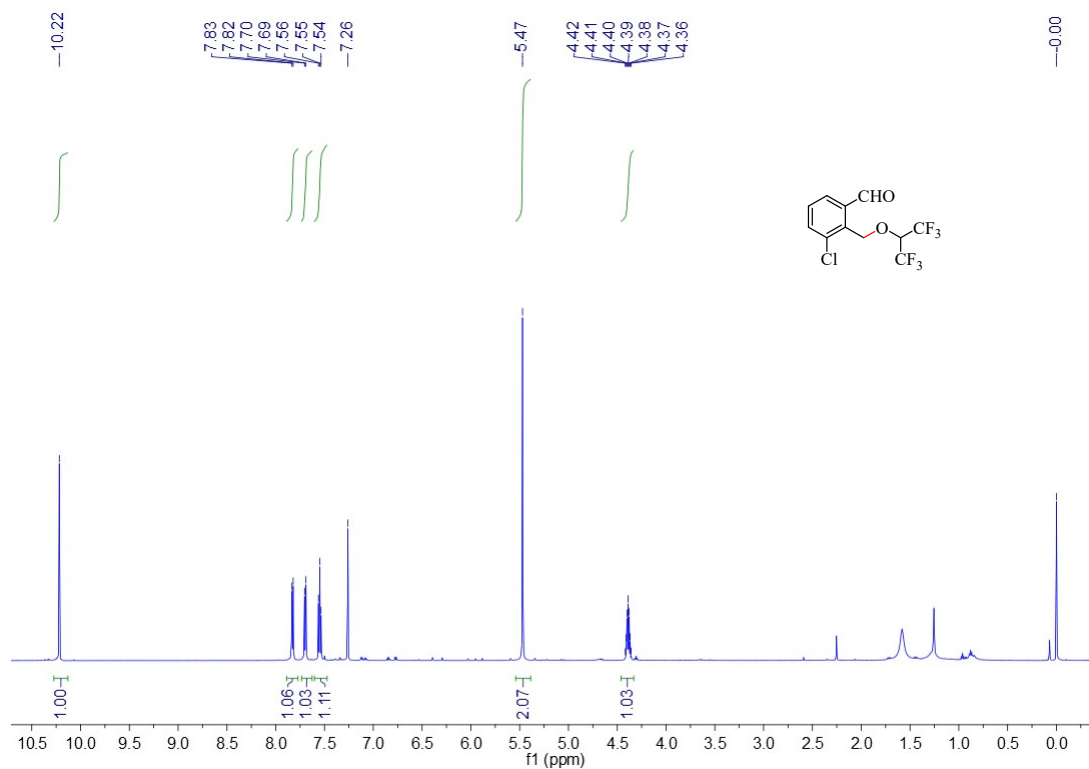


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-fluorobenzaldehyde **2i**

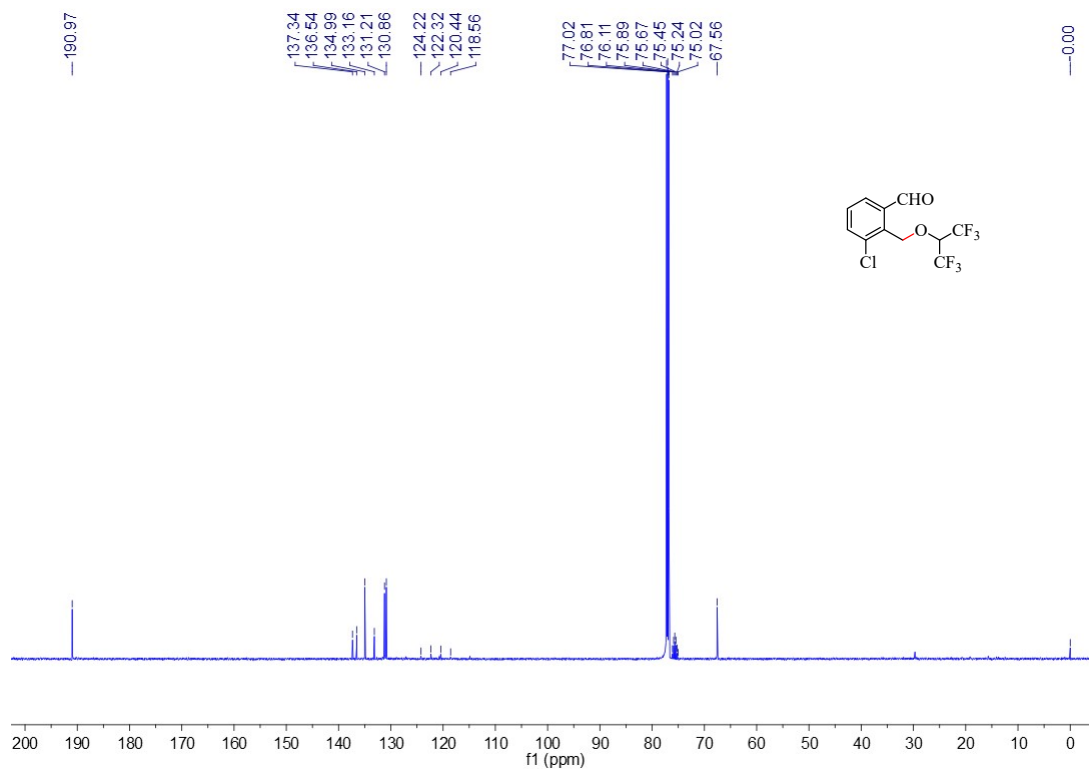
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F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-chlorobenzaldehyde **2j**

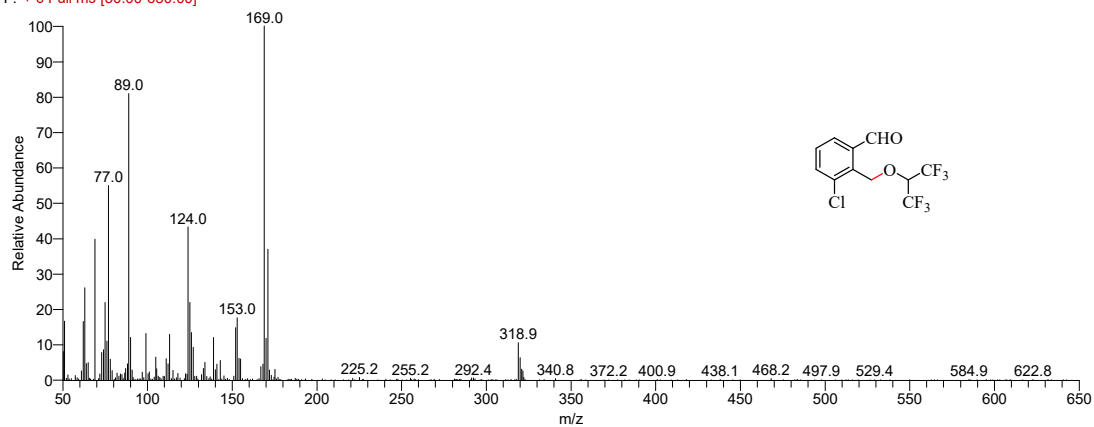


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-chlorobenzaldehyde **2j**

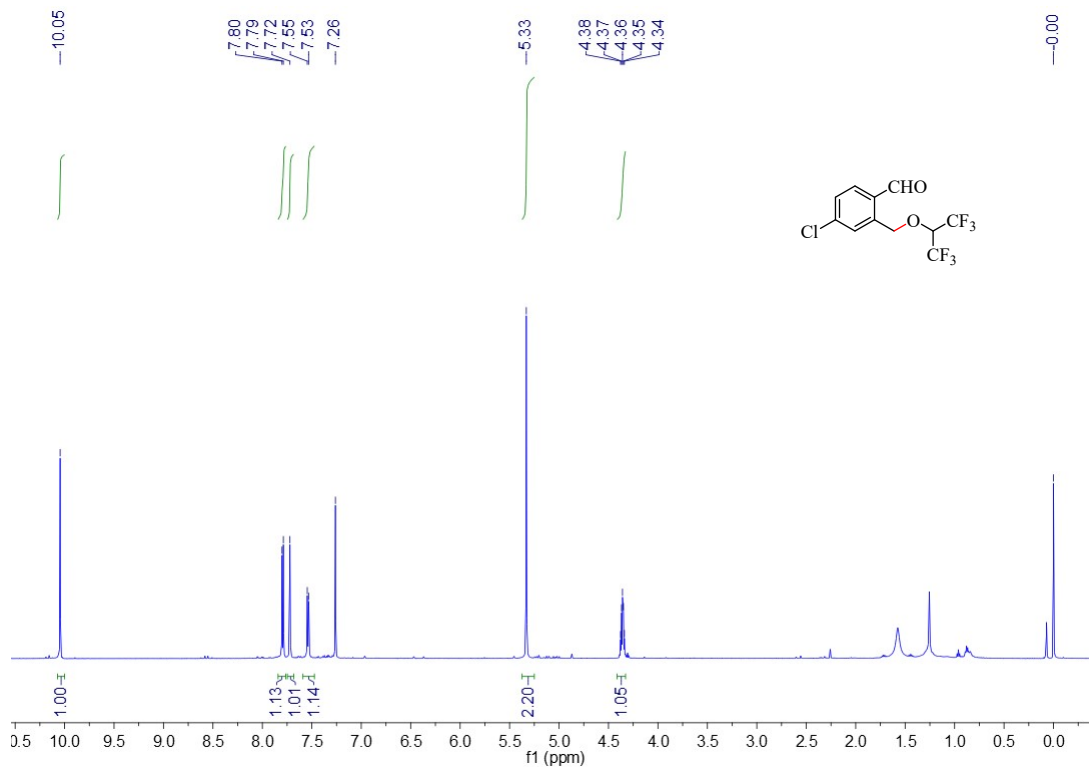


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-3-chlorobenzaldehyde **2j**

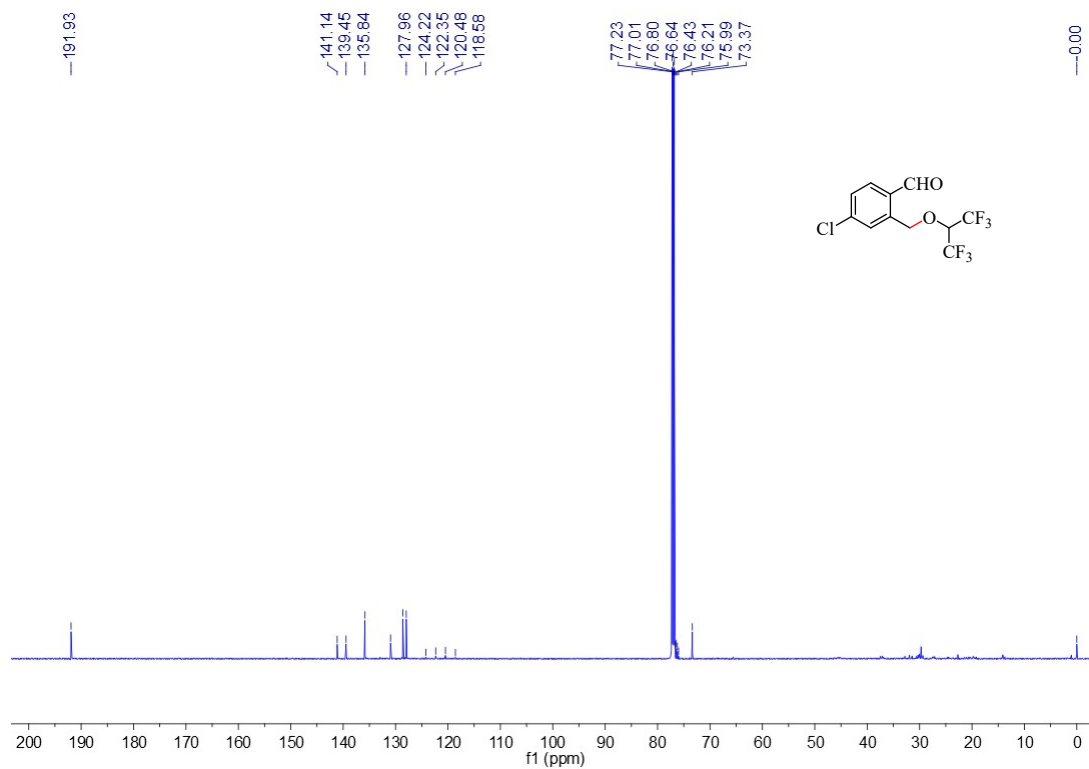
2j #1376 RT: 4.62 AV: 1 AV: 5 SB: 12 1369-1374 1378-1383 NL: 3.17E5
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-chlorobenzaldehyde **2k**

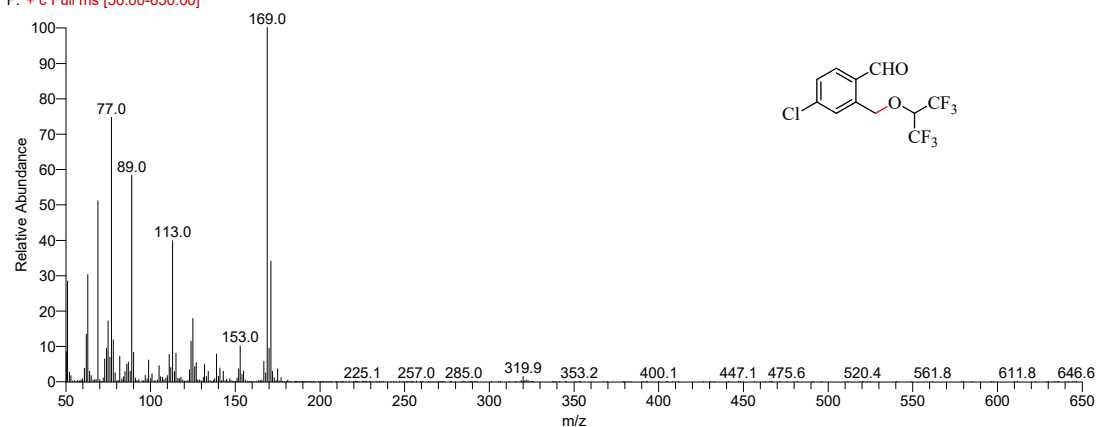


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-chlorobenzaldehyde **2k**

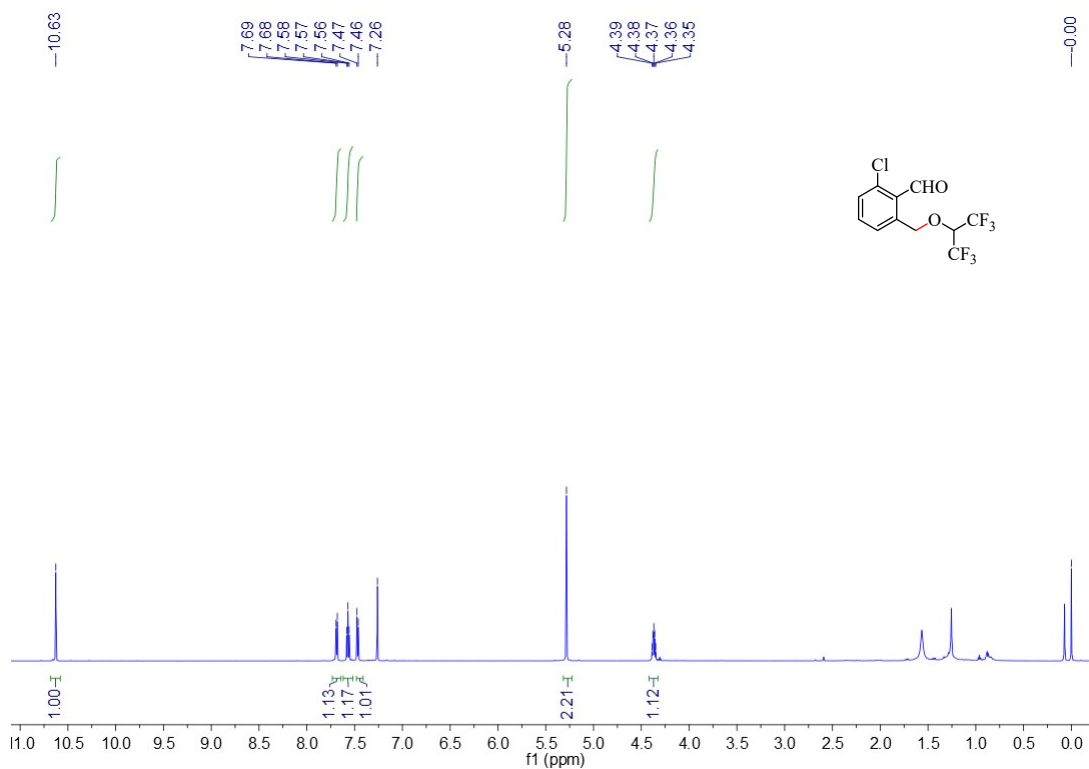


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-chlorobenzaldehyde **2k**

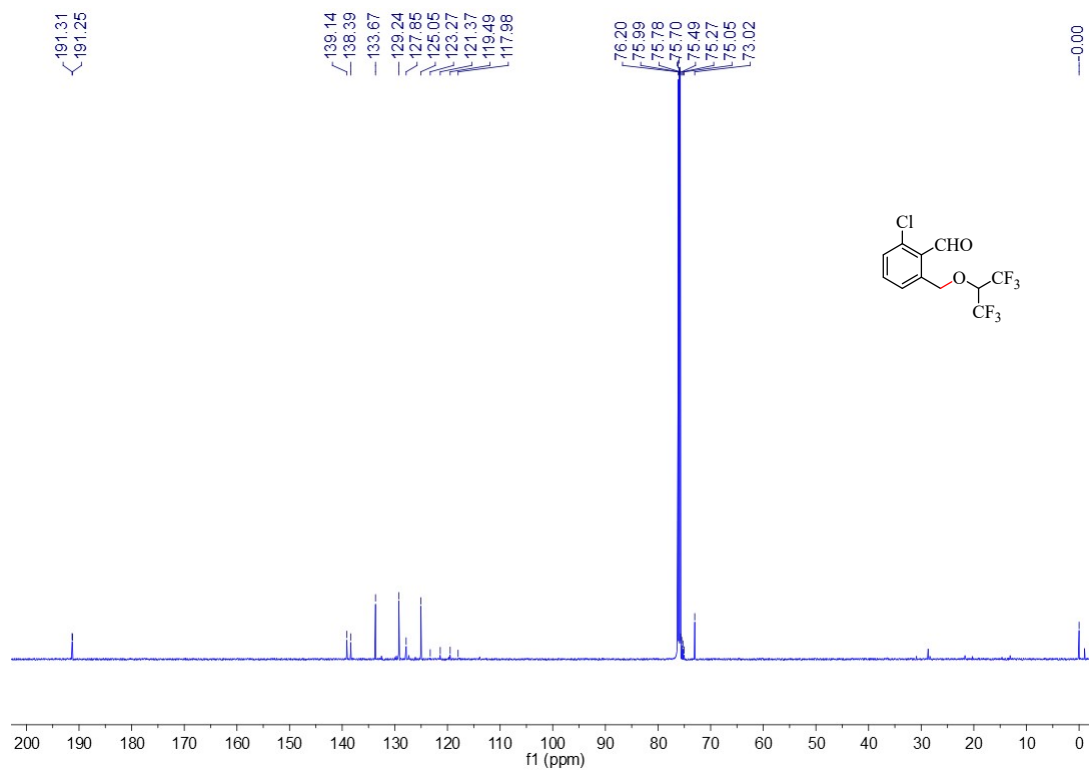
2k #1367 RT: 4.59 AV: 1 AV: 5 SB: 12 1360-1365 1369-1374 NL: 5.91E6
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl-6-chlorobenzaldehyde **21**

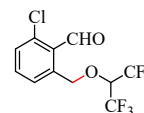
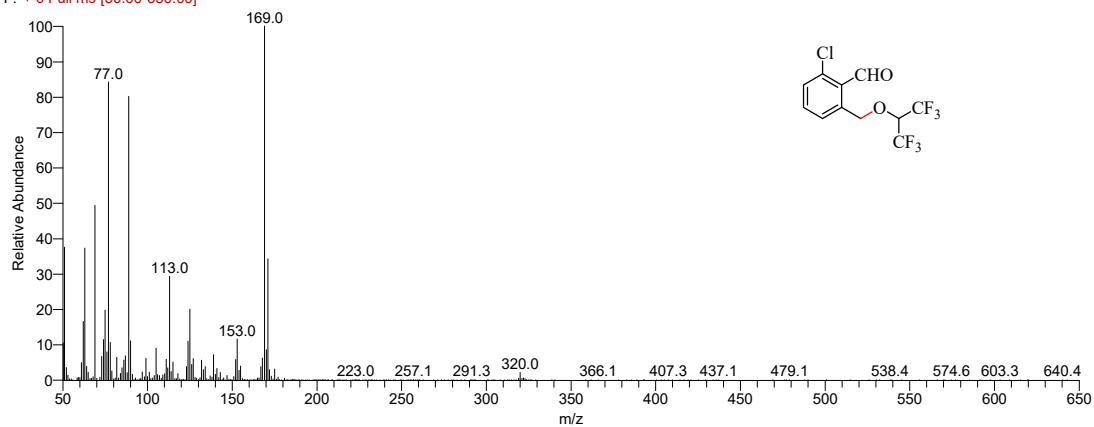


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl-6-chlorobenzaldehyde **21**

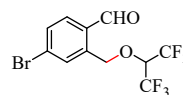
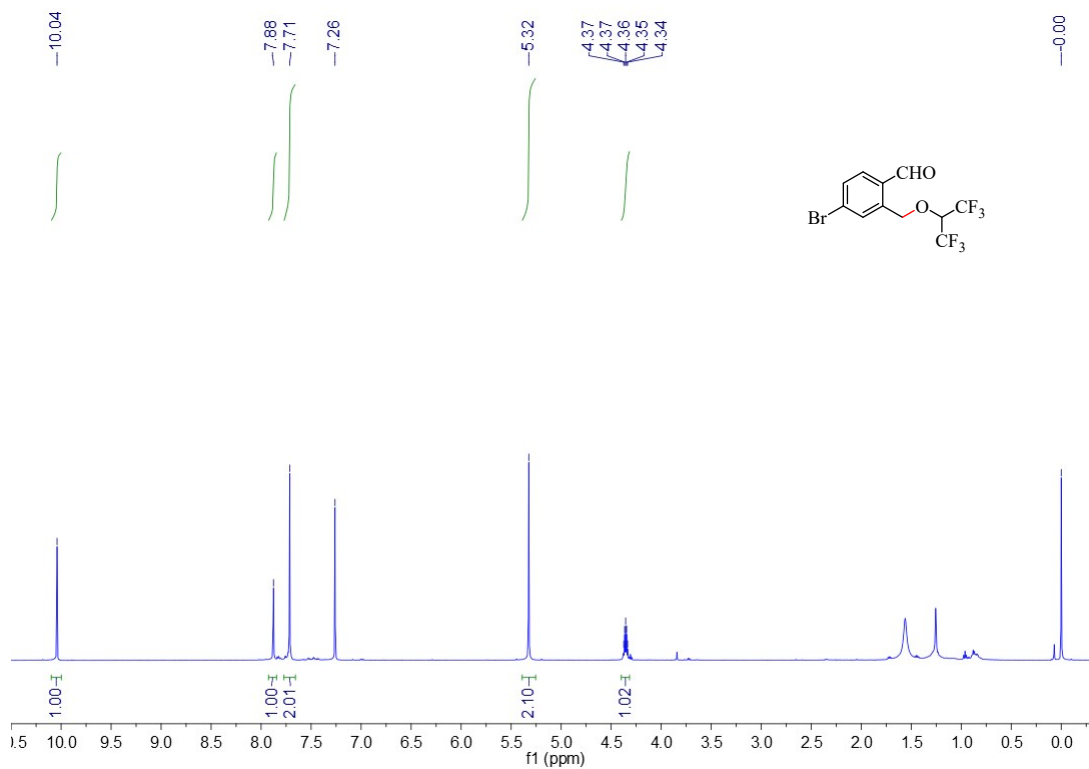


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-6-chlorobenzaldehyde **2l**

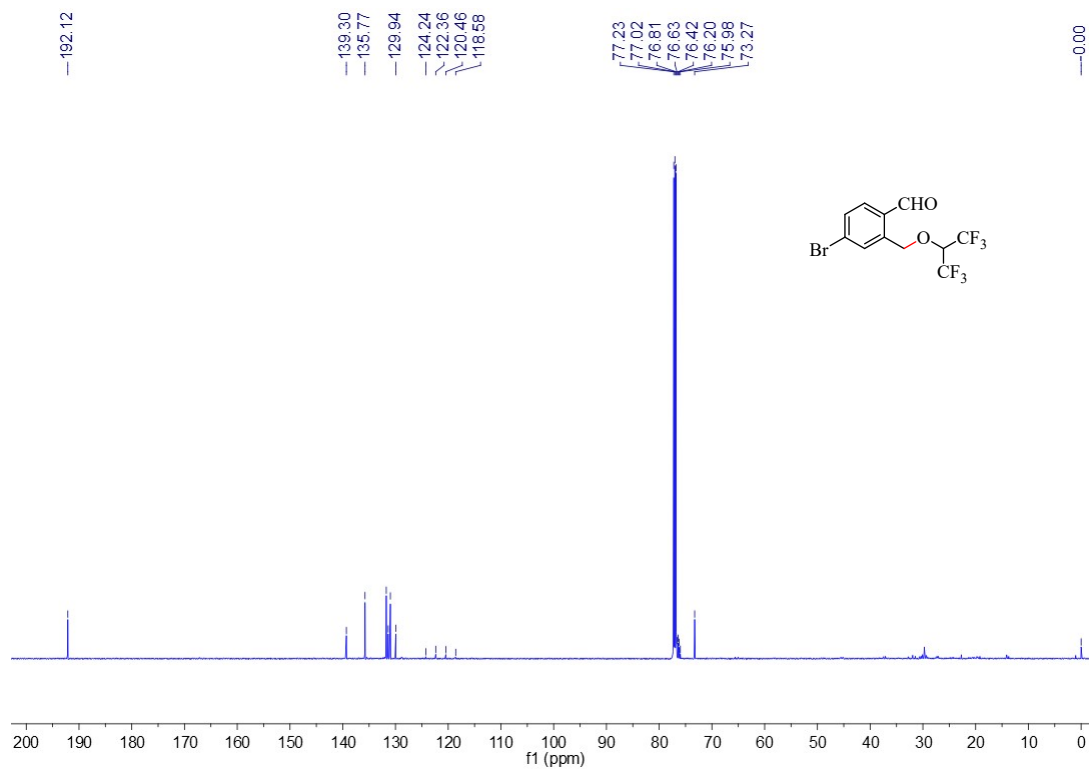
2l #1348 RT: 4.52 AV: 1 AV: 5 SB: 12 1341-1346 1350-1355 NL: 7.48E6
 F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-bromobenzaldehyde **2m**

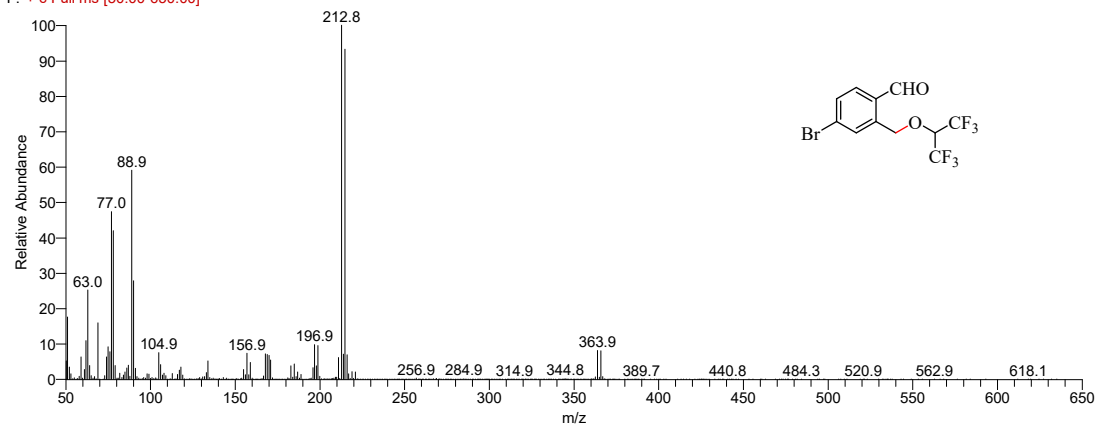


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-bromobenzaldehyde **2m**

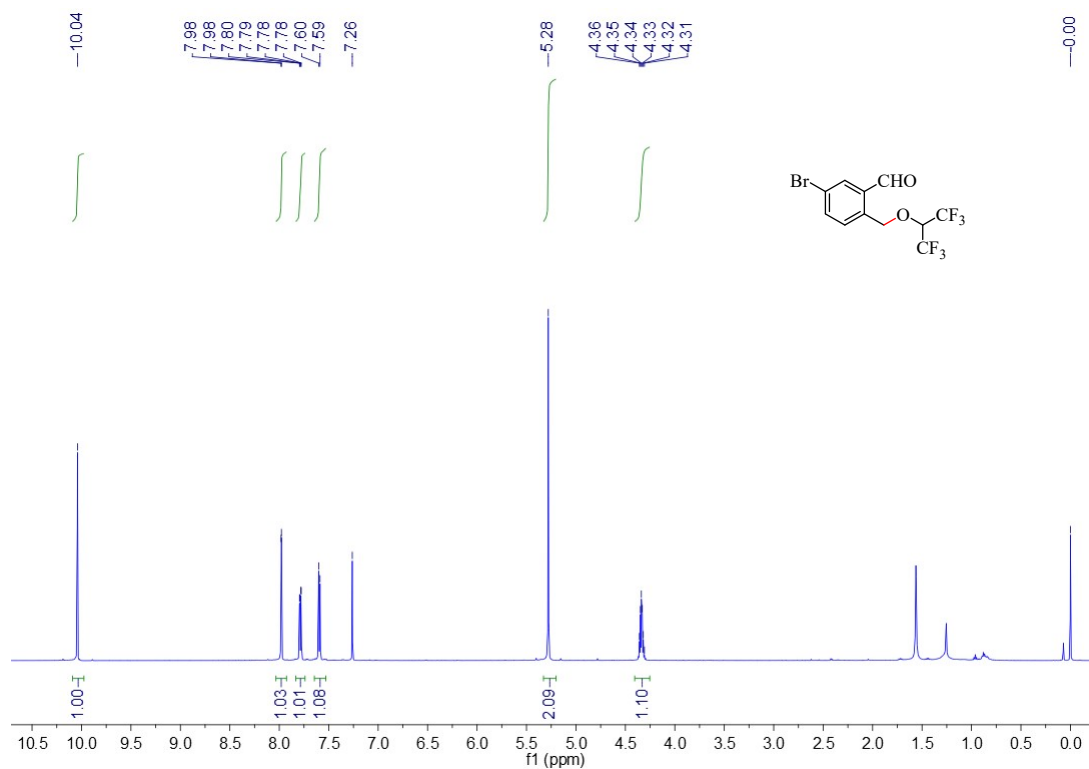


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-4-bromobenzaldehyde **2m**

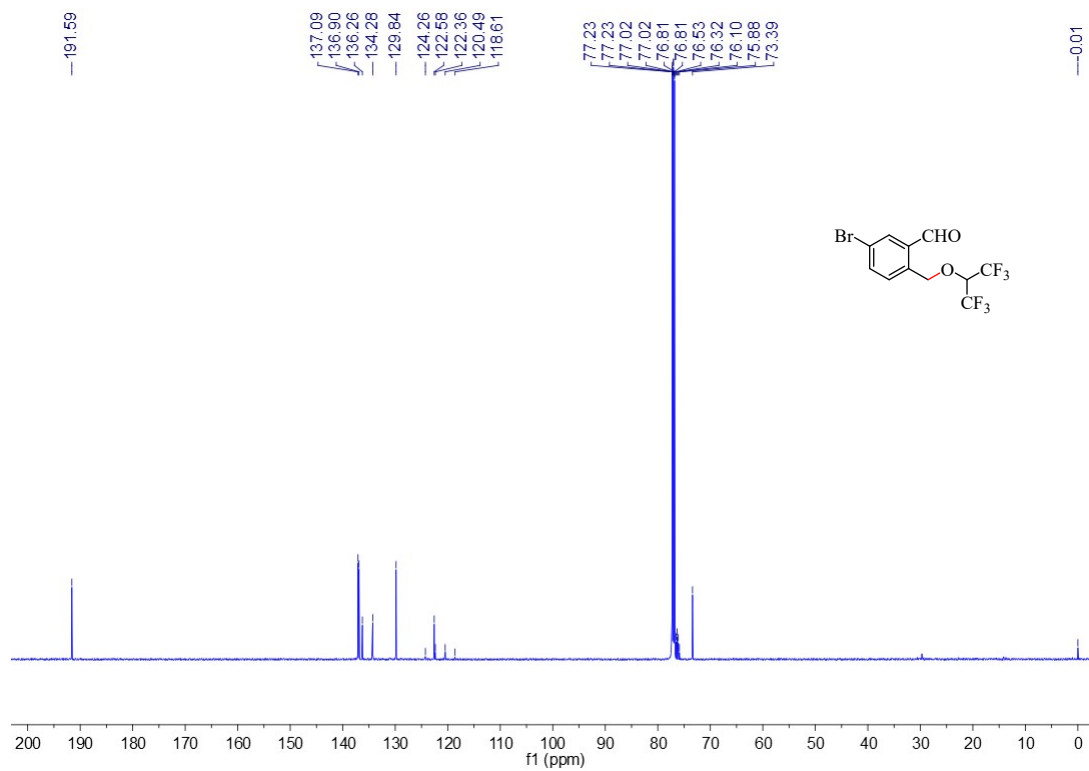
2m #1452 RT: 4.87 AV: 1 AV: 5 SB: 12 1445-1450 1454-1459 NL: 9.53E7
F: + c Full ms [50.00-650.00]



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl-5-bromobenzaldehyde **2n**

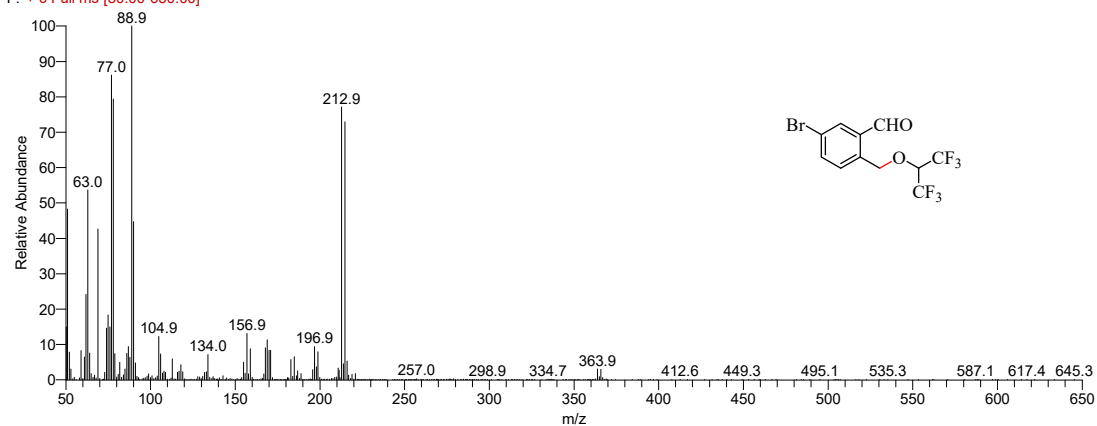


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl-5-bromobenzaldehyde **2n**

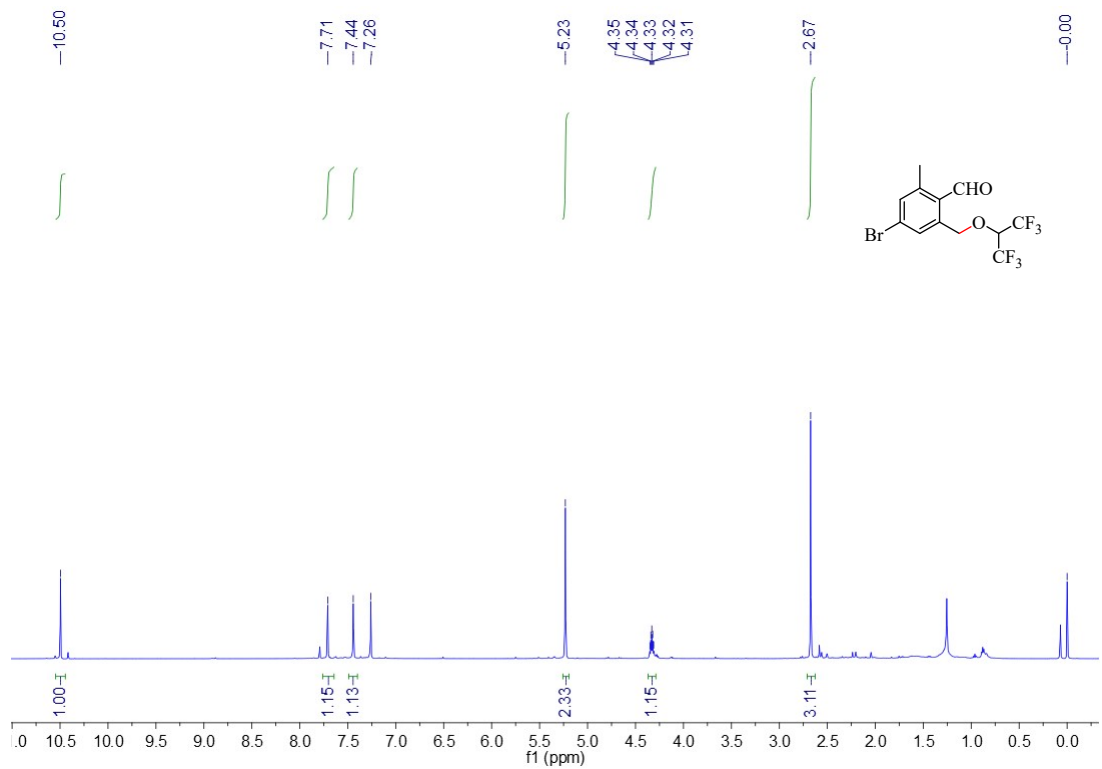


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yloxy)methyl)-5-bromobenzaldehyde **2n**

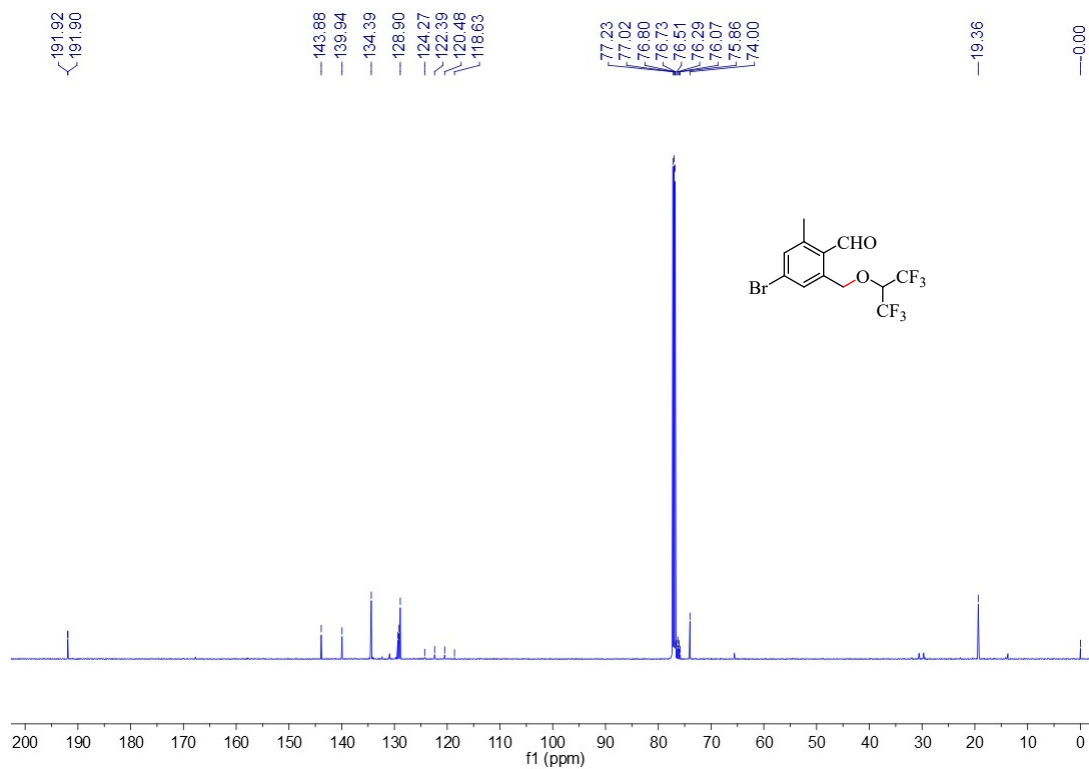
2n #1447 RT: 4.85 AV: 1 AV: 5 SB: 12 1440-1445 1449-1454 NL: 1.45E7
F: + c Full ms [50.00-650.00]



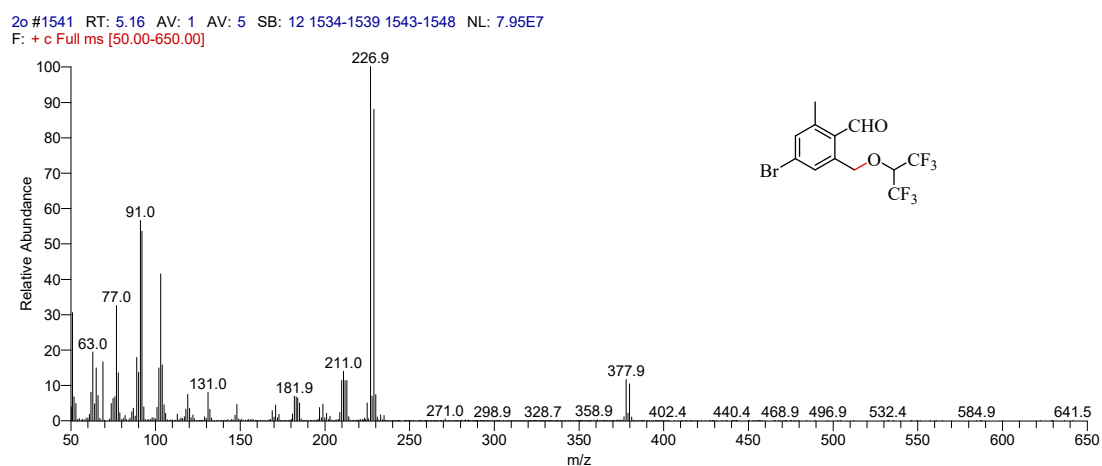
¹H NMR of 4-bromo-2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **2o**



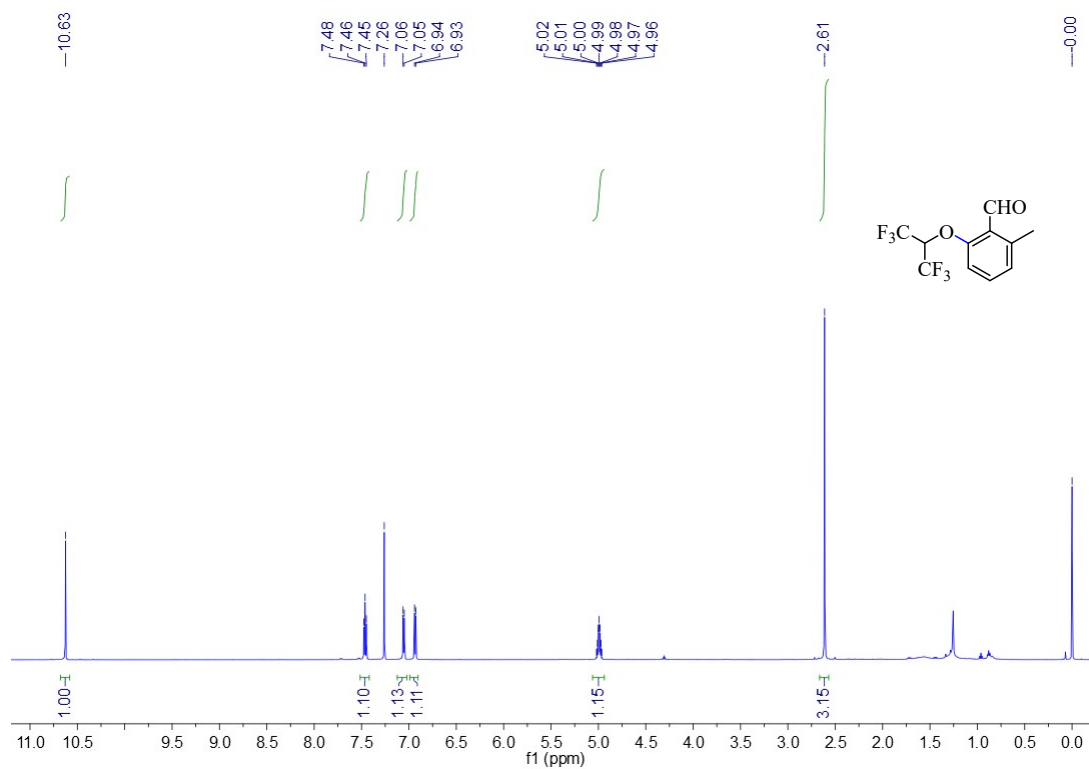
¹³C NMR of 4-bromo-2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **2o**



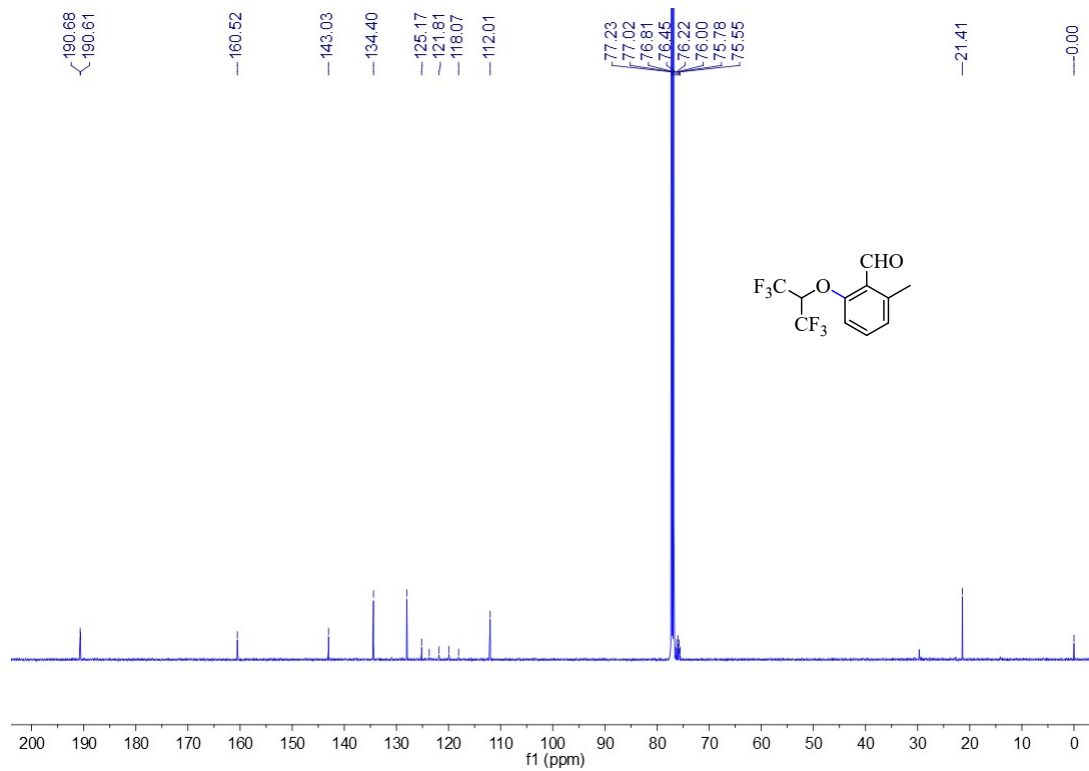
MS(EI) of 4-bromo-2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)-6-methylbenzaldehyde **2o**



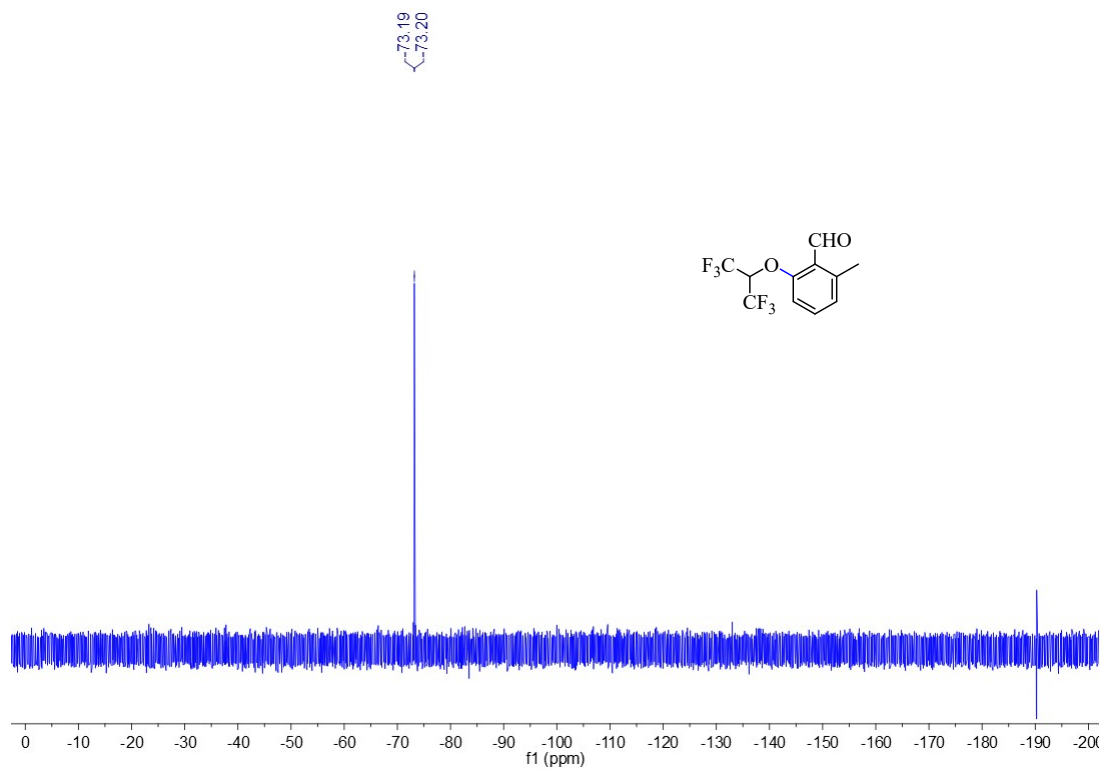
¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3a**



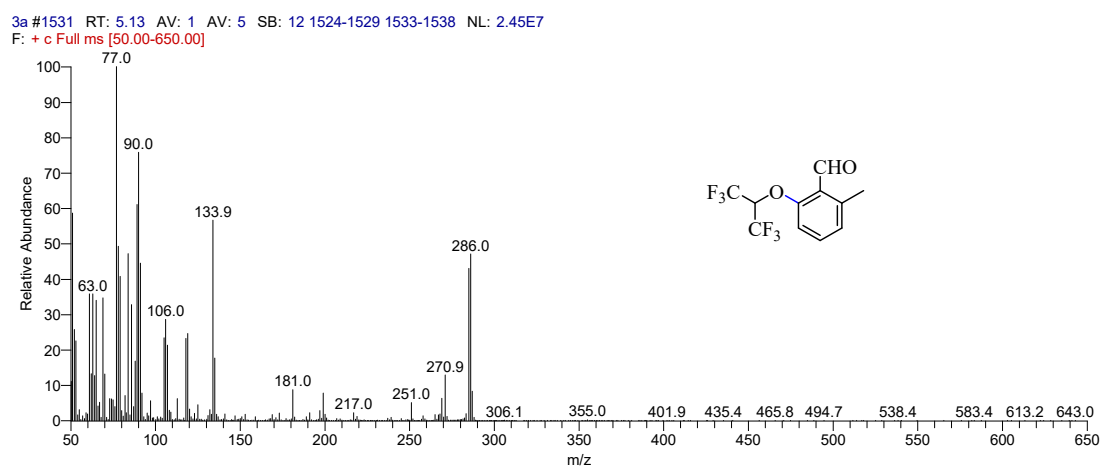
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3a**



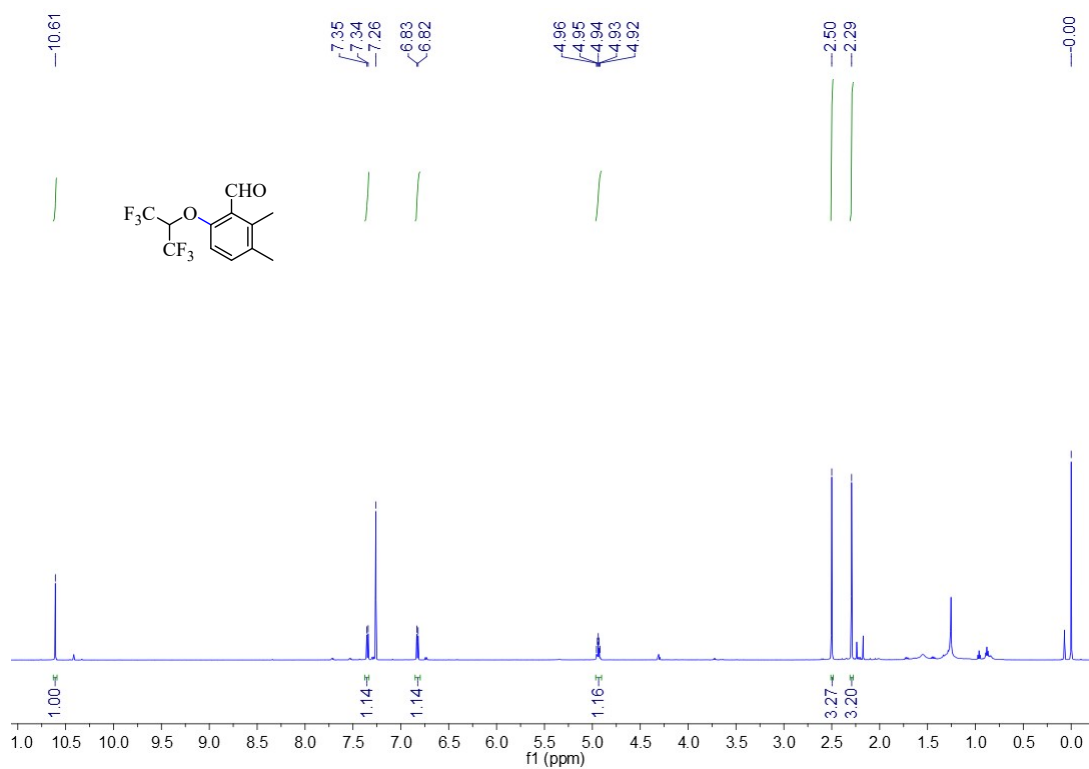
^{19}F NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3a**



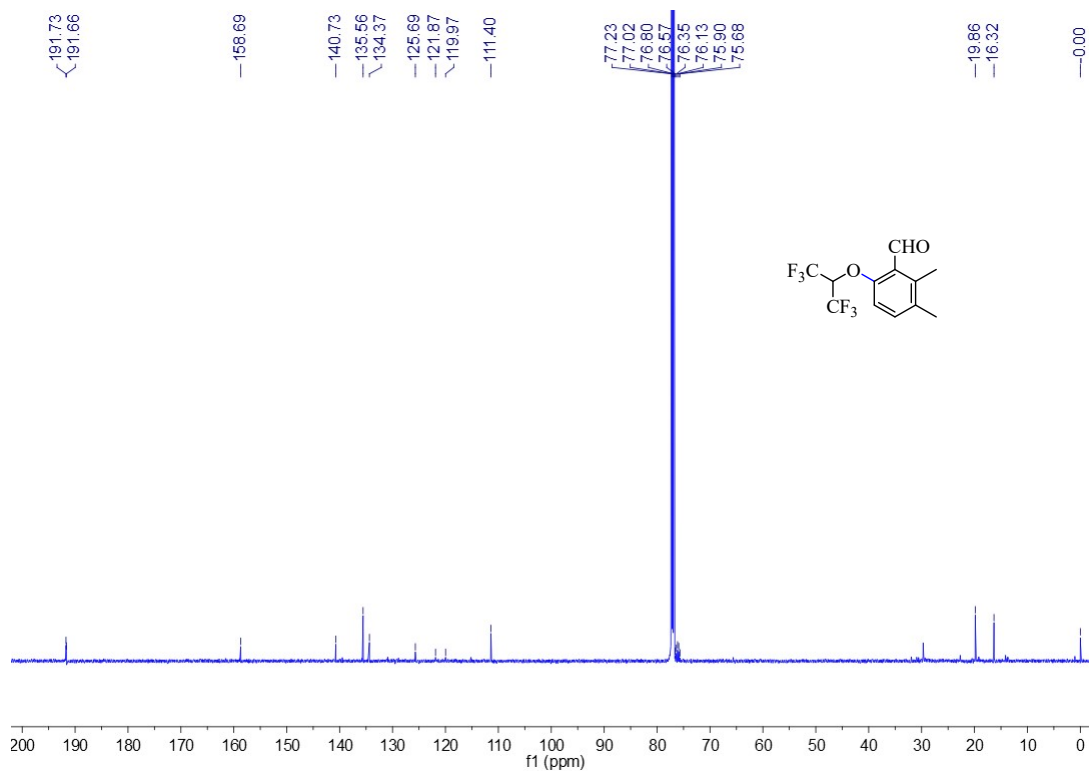
MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3a**



¹H NMR of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2,3-dimethylbenzaldehyde **3b**

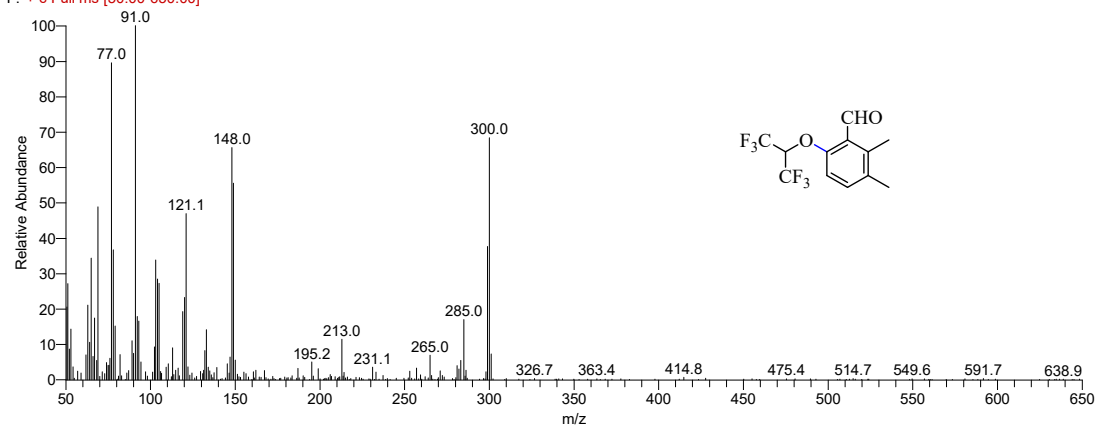


¹³C NMR of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2,3-dimethylbenzaldehyde **3b**

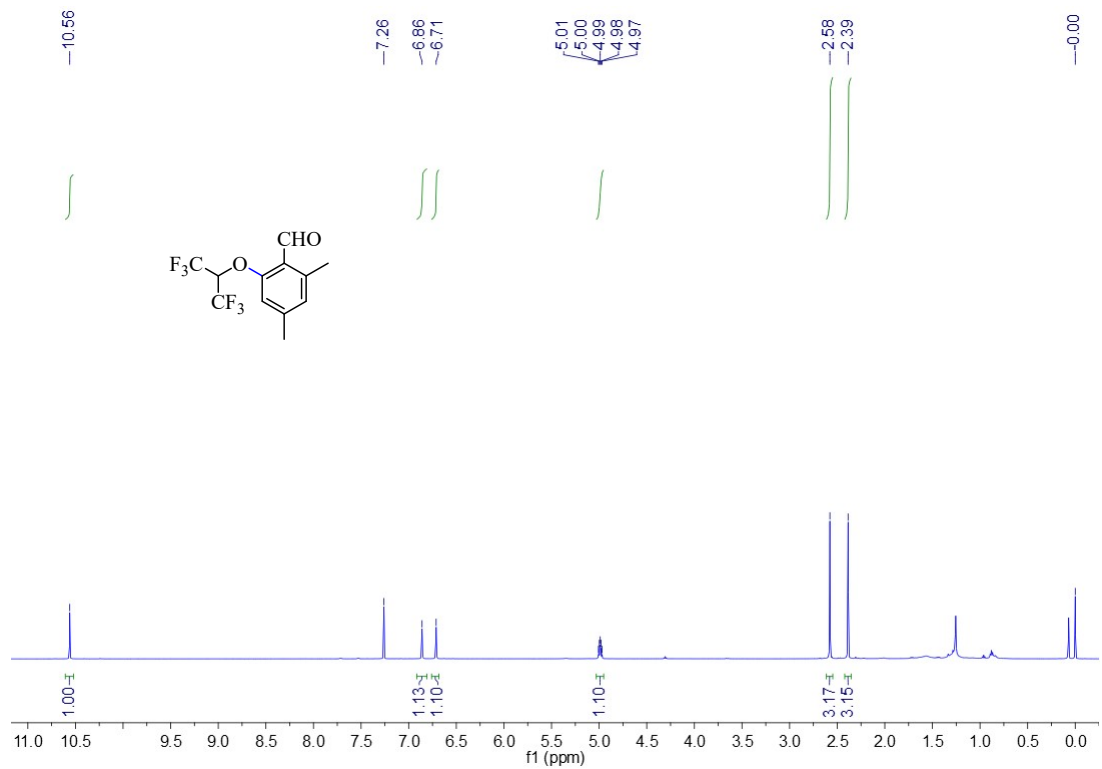


MS(EI) of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2,3-dimethylbenzaldehyde **3b**

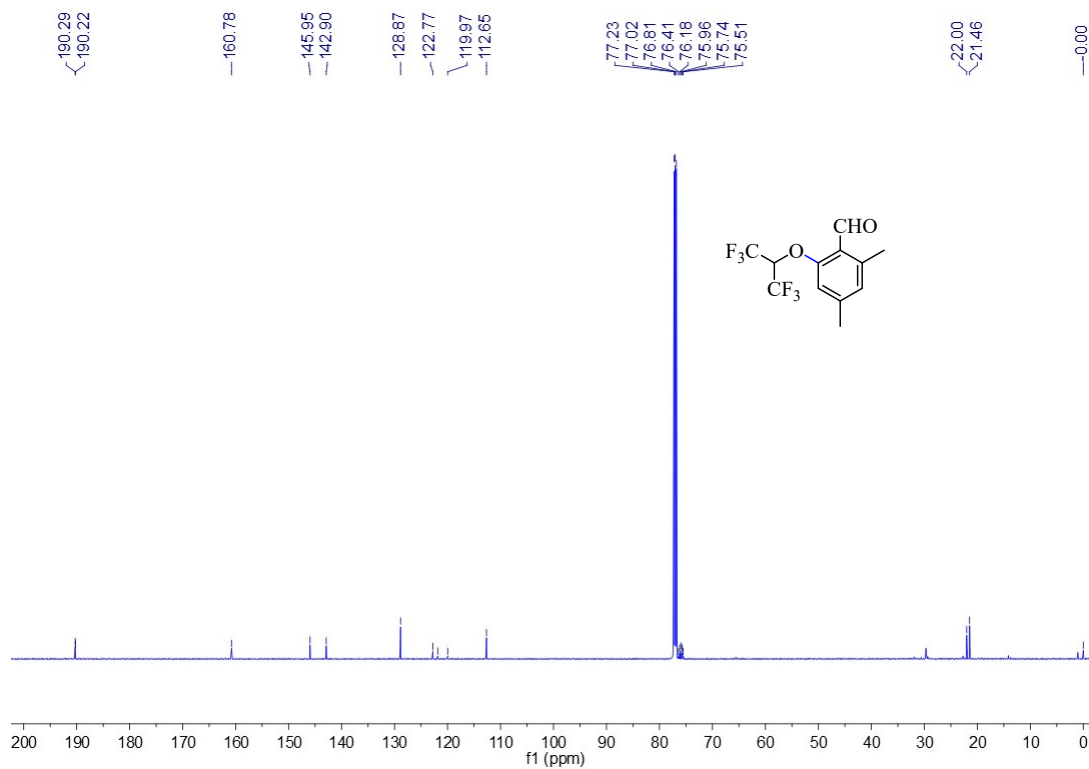
3b #1704 RT: 5.70 AV: 1 AV: 5 SB: 12 1697-1702 1706-1711 NL: 1.60E5
F: + c Full ms [50.00-650.00]



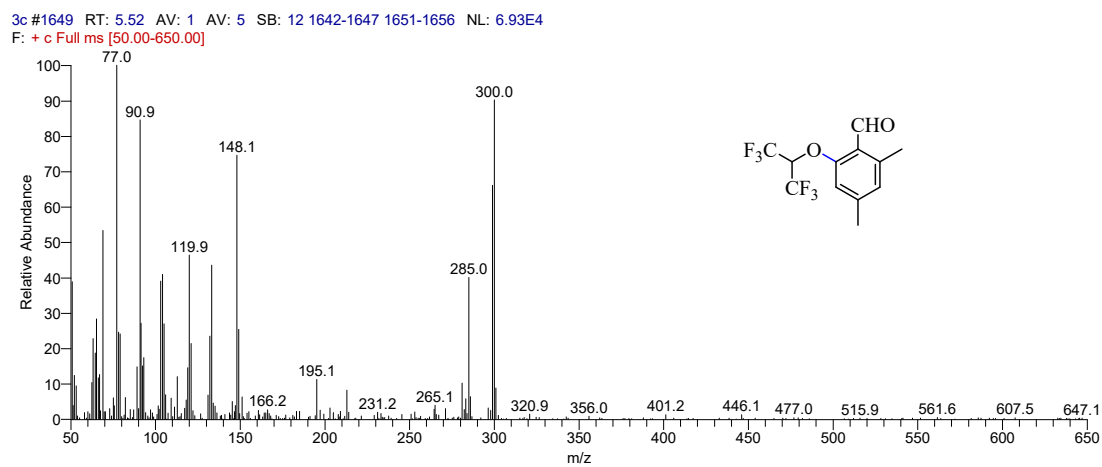
¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4,6-dimethylbenzaldehyde **3c**



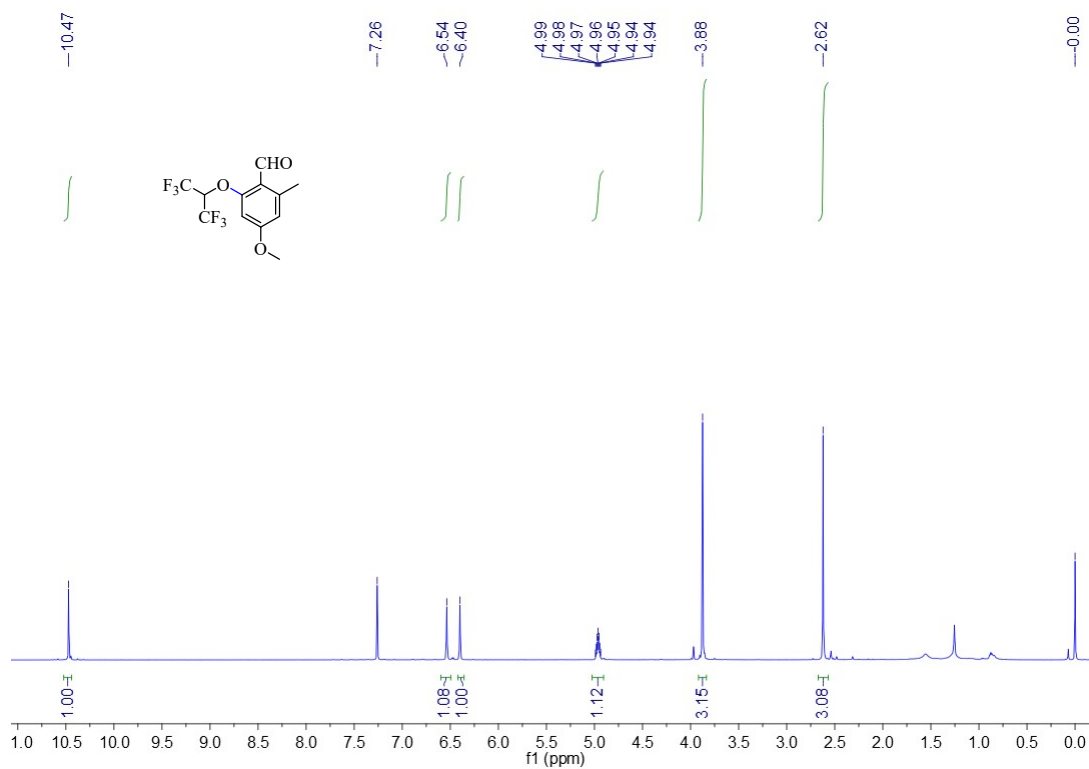
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4,6-dimethylbenzaldehyde **3c**



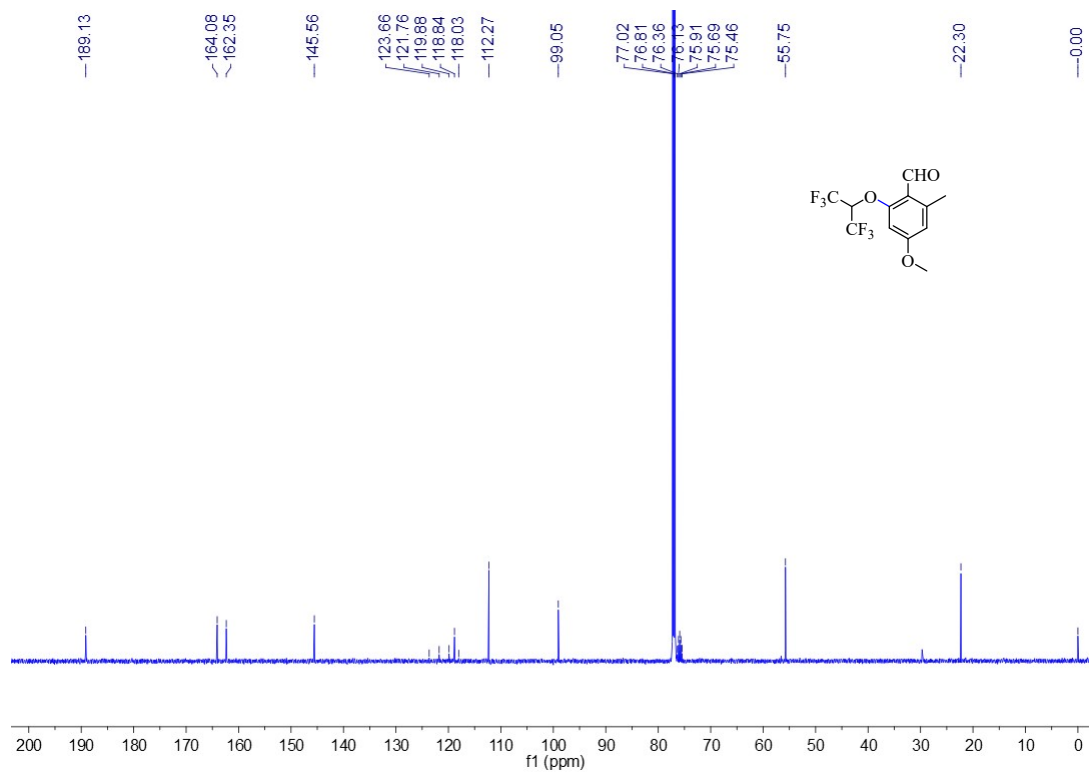
MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4,6-dimethylbenzaldehyde **3c**



¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-6-methylbenzaldehyde **3g**

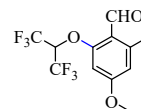
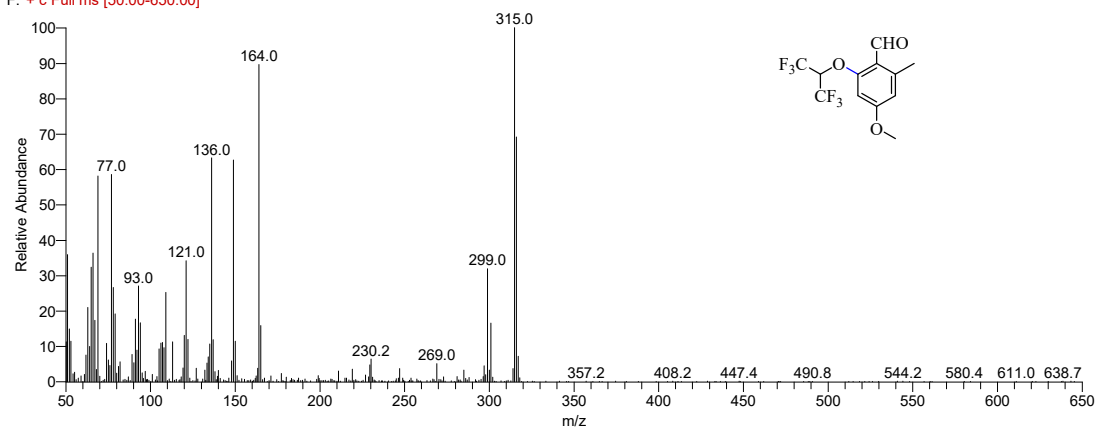


¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-6-methylbenzaldehyde **3g**

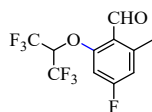
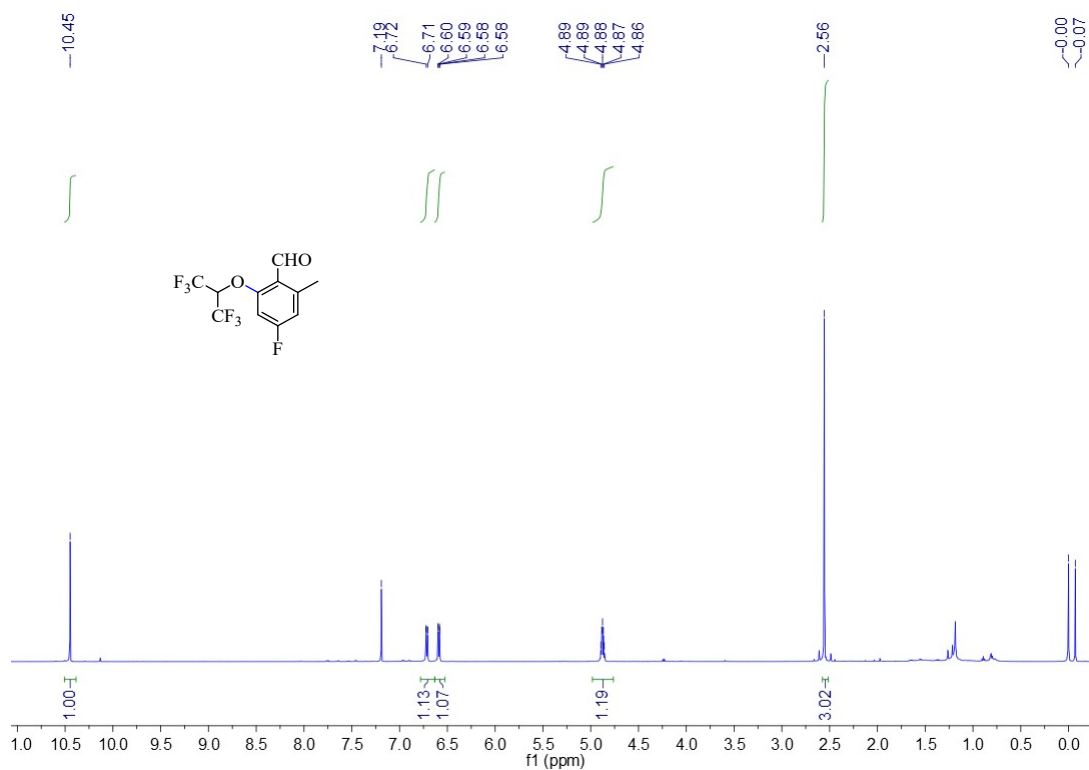


MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-6-methylbenzaldehyde **3g**

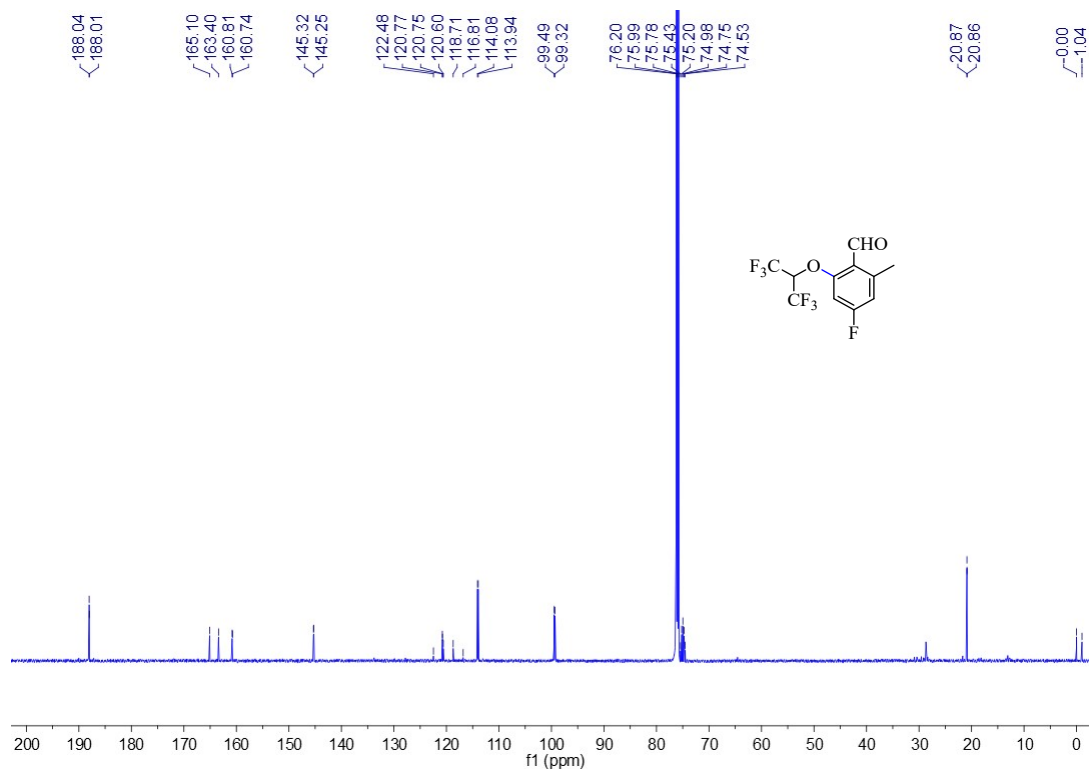
3d #1853 RT: 6.19 AV: 1 AV: 5 SB: 12 1846-1851 1855-1860 NL: 3.05E5
 F: + c Full ms [50.00-650.00]



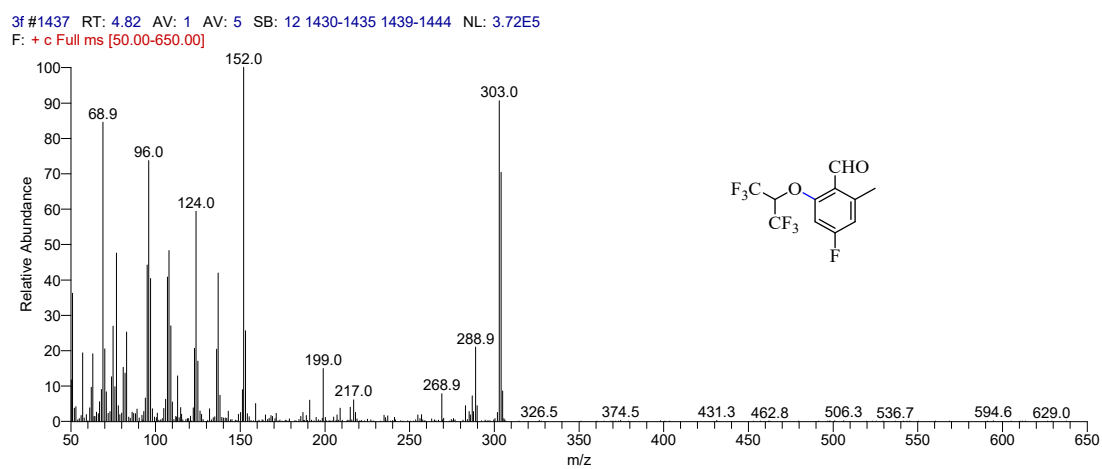
¹H NMR of 4-fluoro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3i**



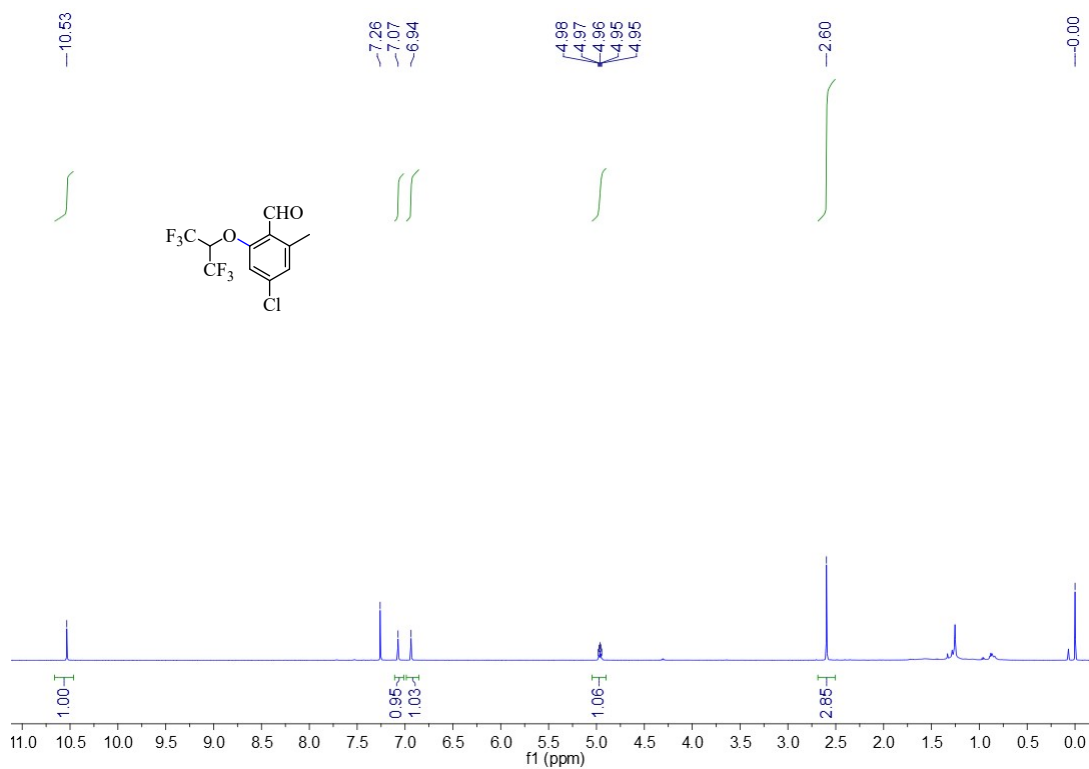
¹³C NMR of 4-fluoro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3i**



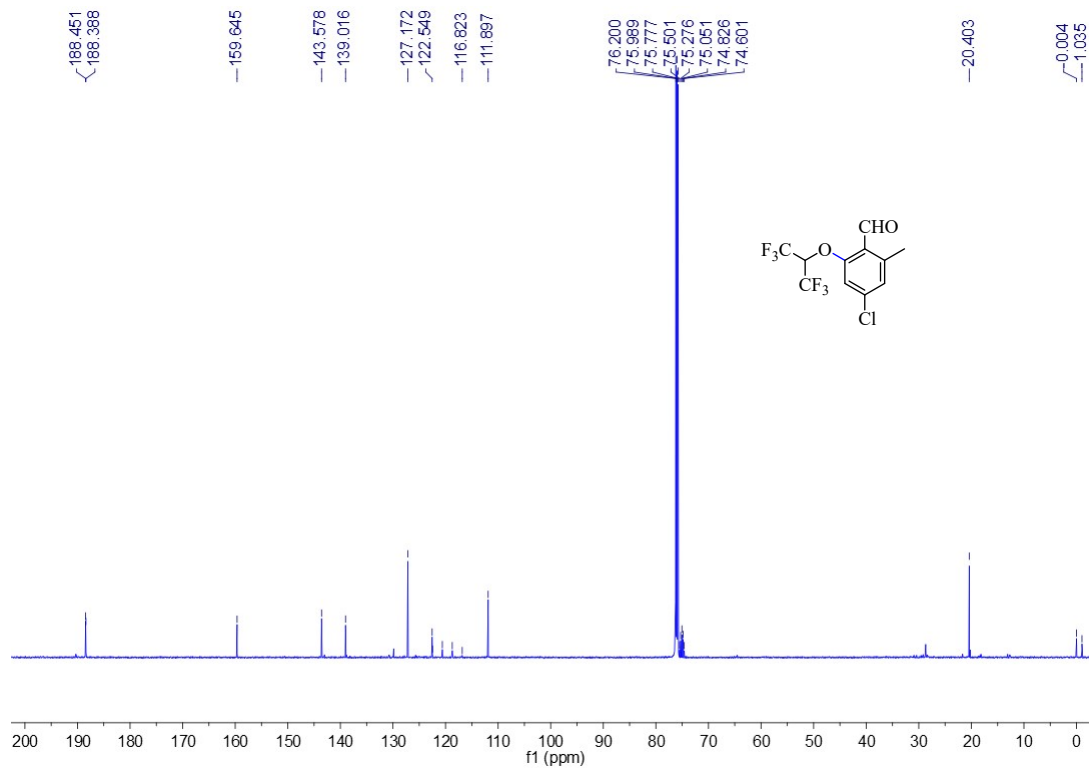
MS(EI) of 4-fluoro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3i**



¹H NMR of 4-chloro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3k**

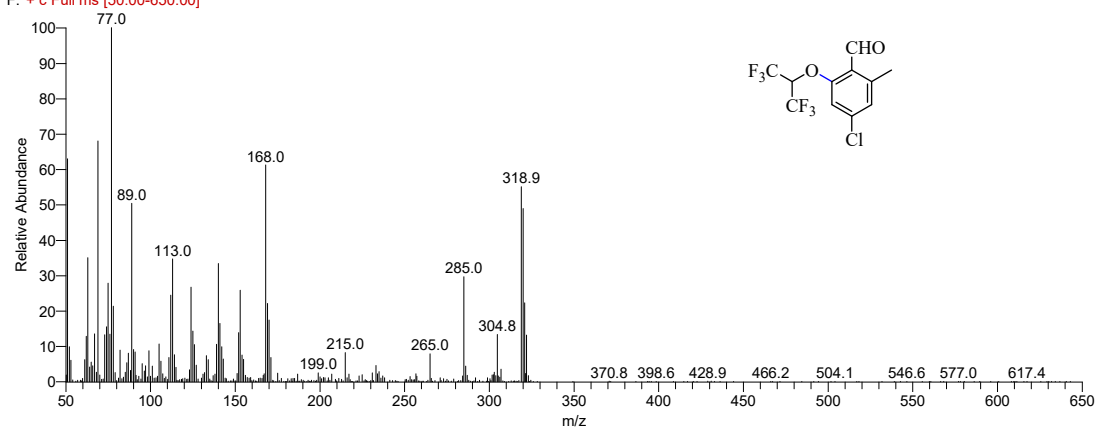


¹³C NMR of 4-chloro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3k**

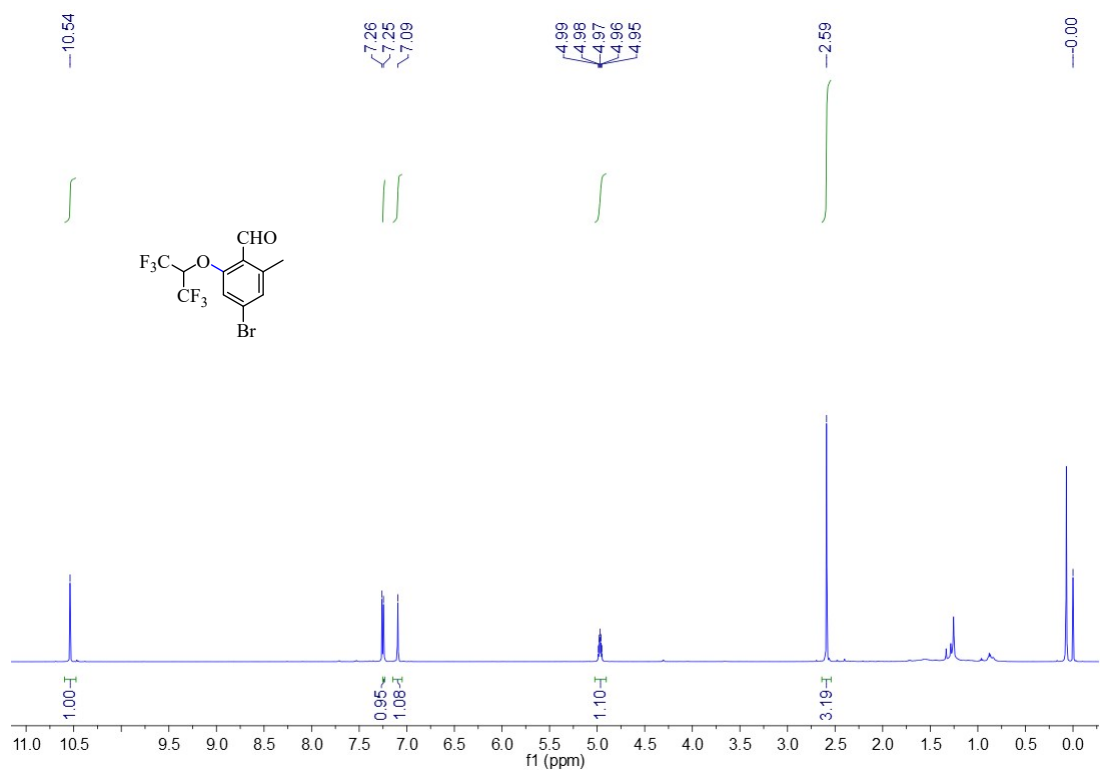


MS(EI) of 4-chloro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3k**

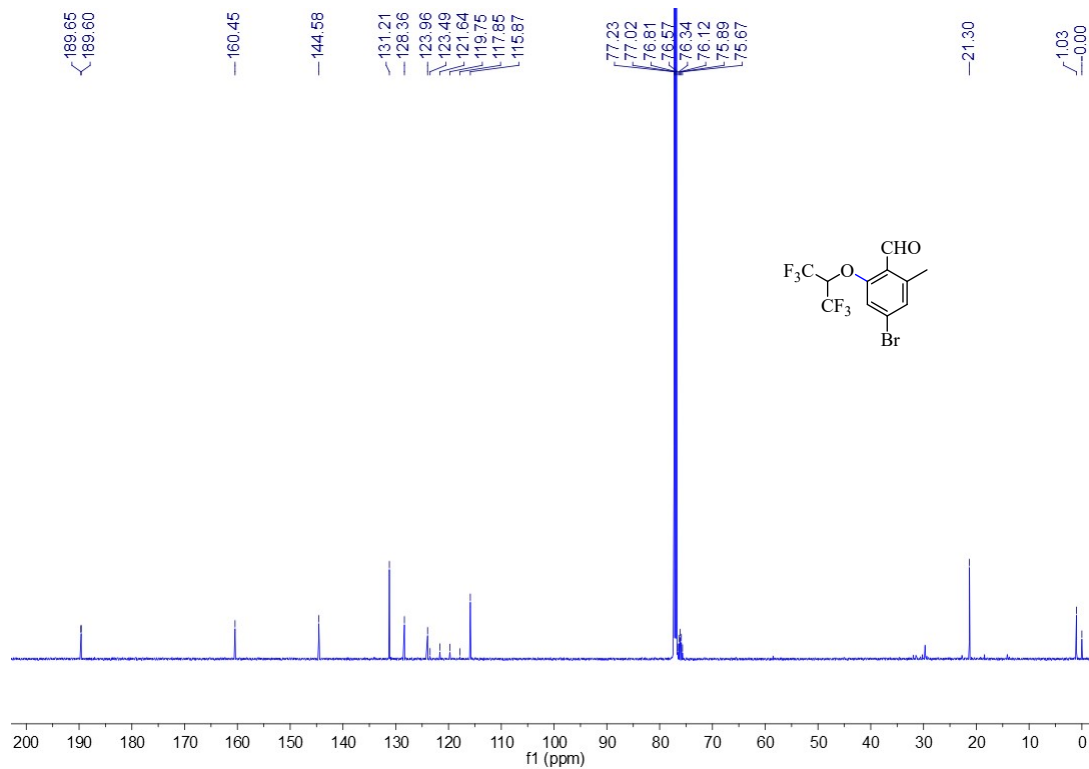
3g #1679 RT: 5.62 AV: 1 AV: 5 SB: 12 1672-1677 1681-1686 NL: 5.22E5
F: + c Full ms [50.00-650.00]



¹H NMR of 4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3m**

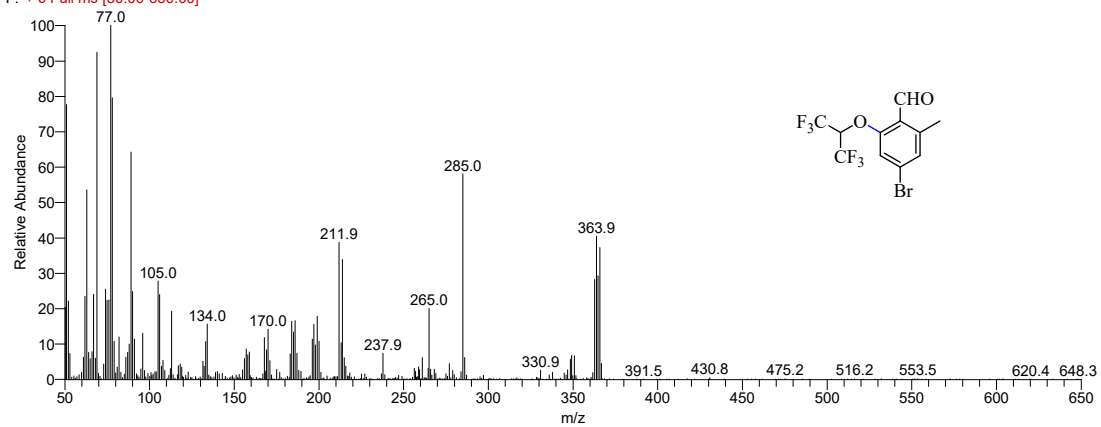


¹³C NMR of 4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3m**

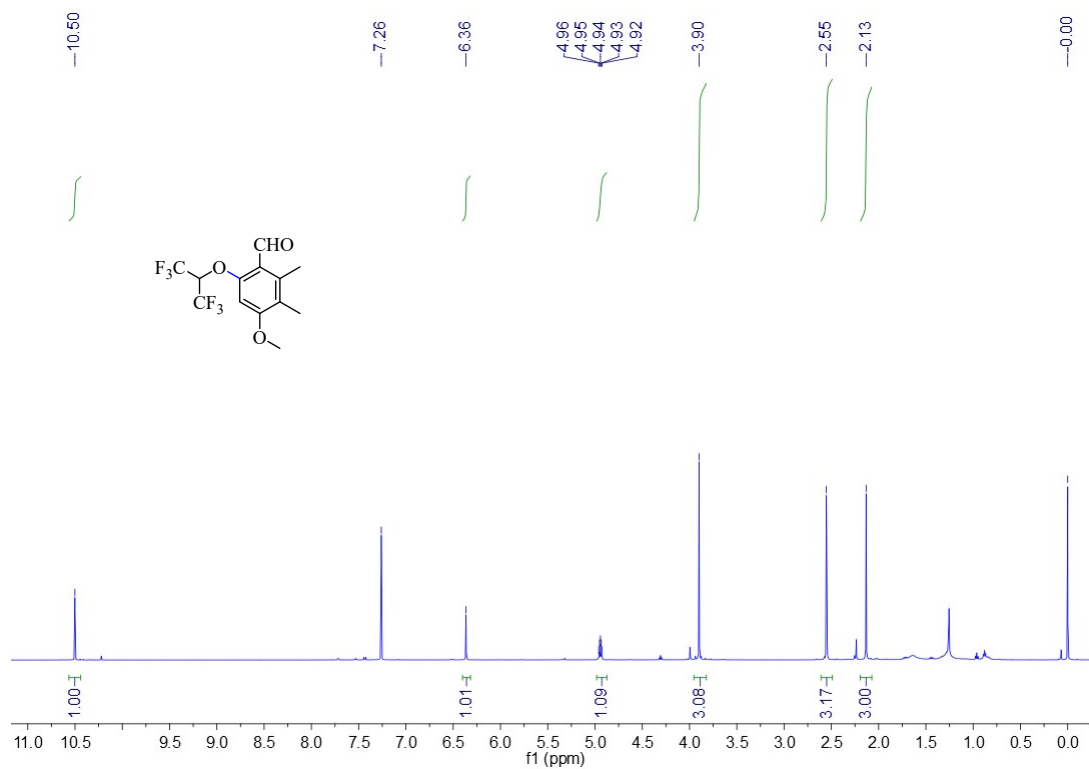


MS(EI) of 4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-methylbenzaldehyde **3m**

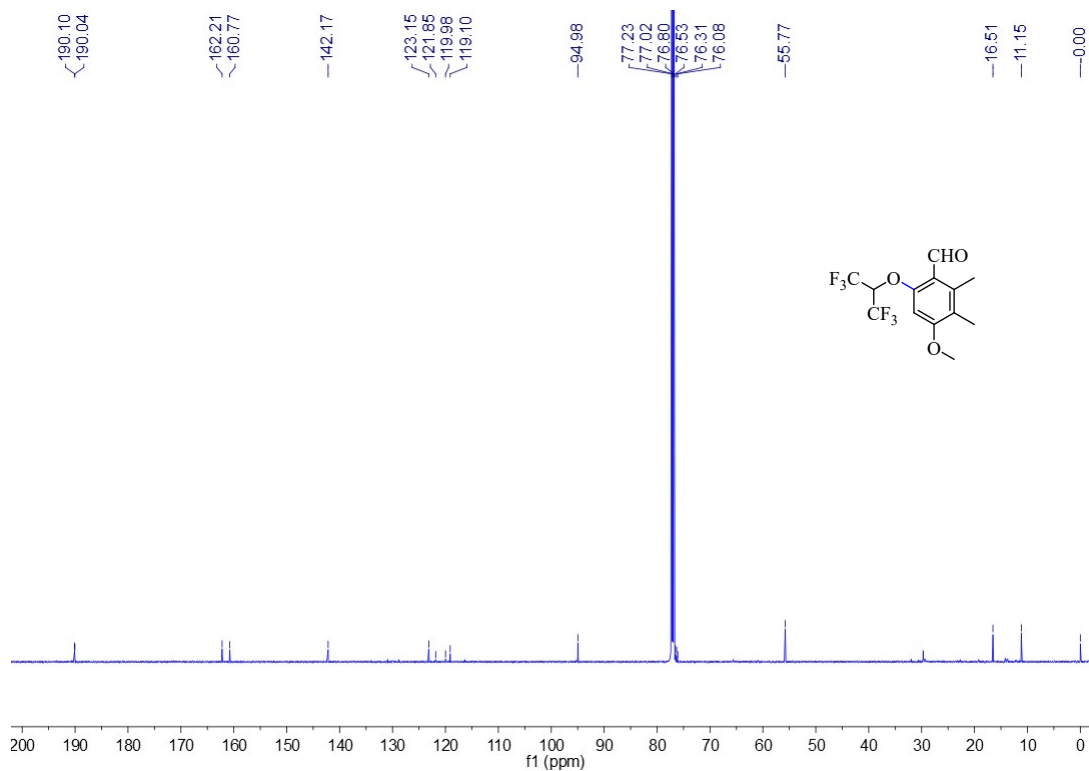
3h #1801 RT: 6.02 AV: 1 AV: 5 SB: 12 1794-1799 1803-1808 NL: 3.82E5
F: + c Full ms [50.00-650.00]



¹H NMR of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-2,3-dimethylbenzaldehyde **3p**

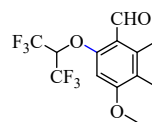
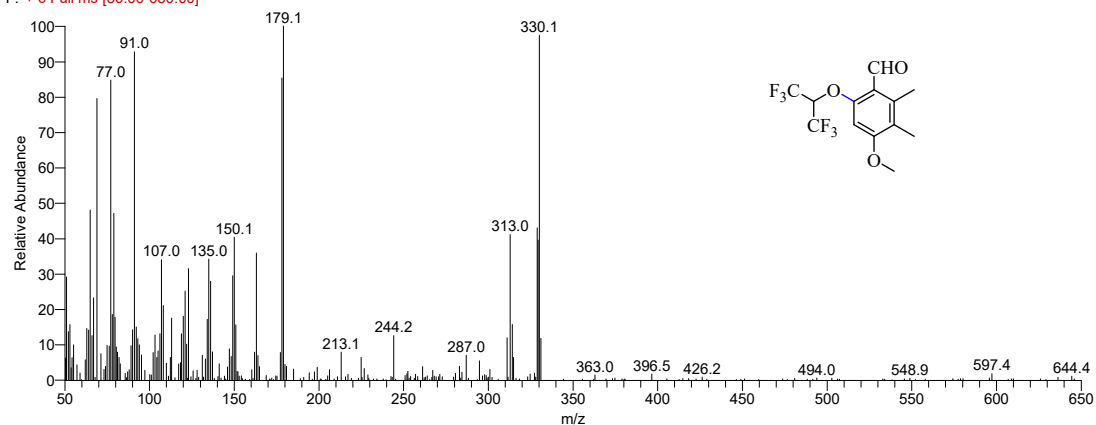


¹³C NMR of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-2,3-dimethylbenzaldehyde **3p**

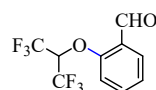
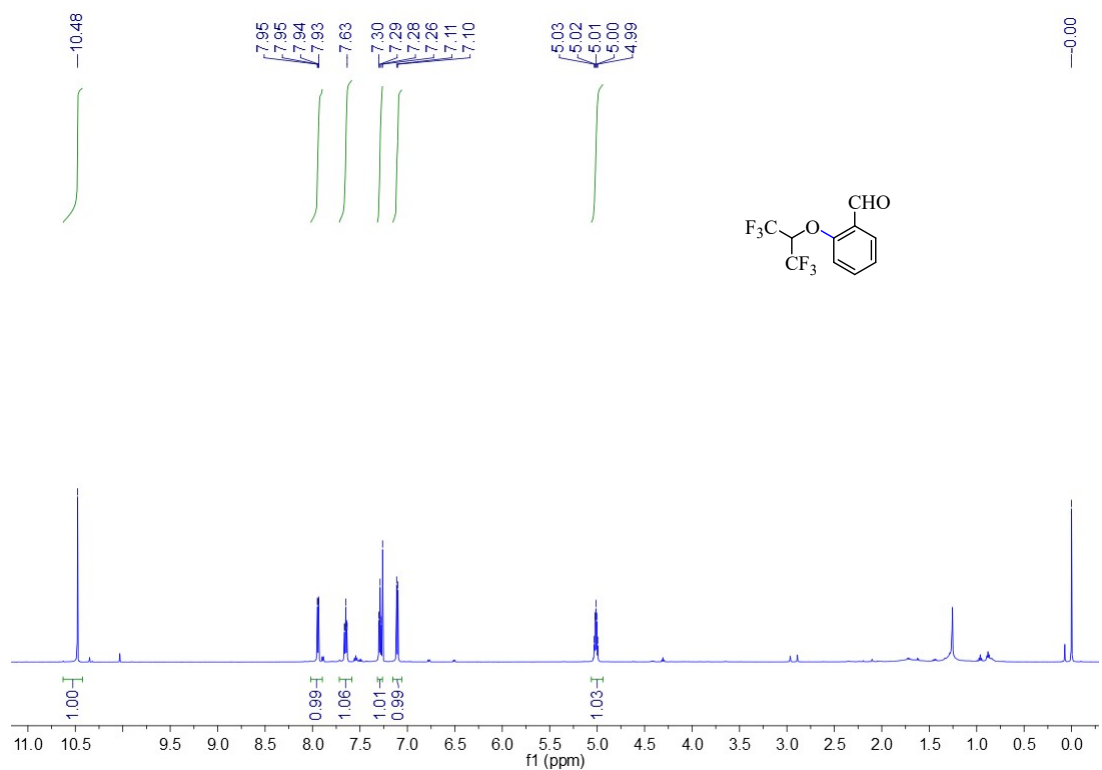


MS(EI) of 6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxy-2,3-dimethylbenzaldehyde **3p**

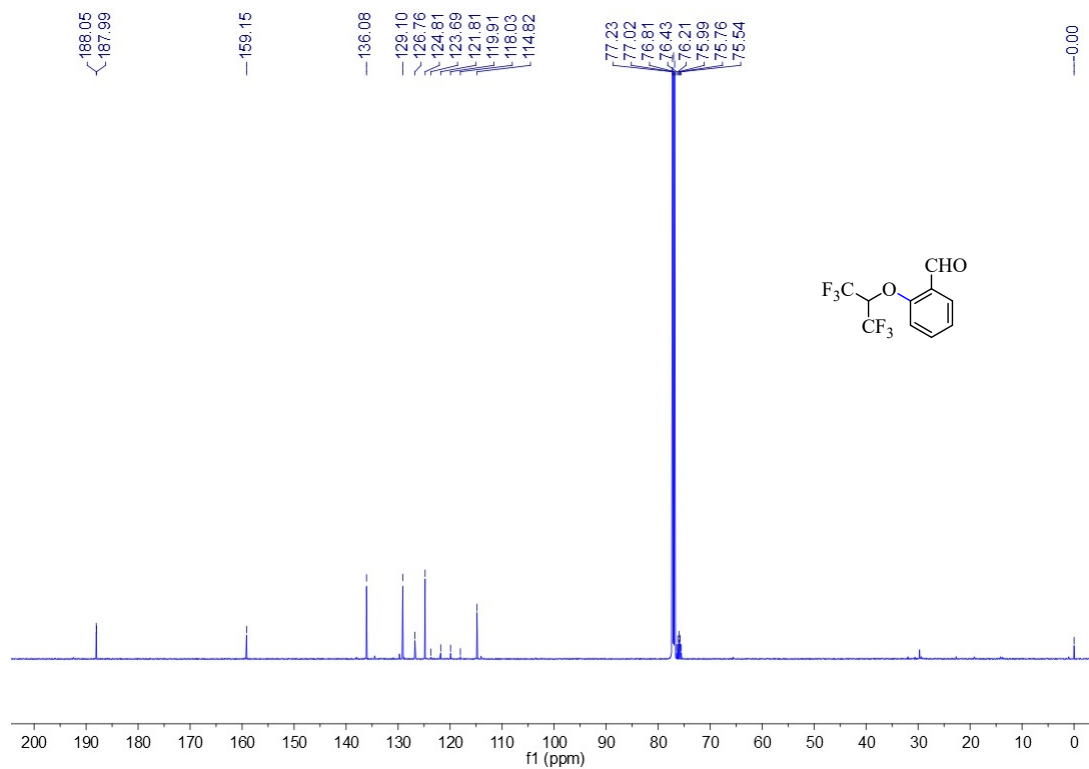
3e #1988 RT: 6.64 AV: 1 AV: 5 SB: 12 1981-1986 1990-1995 NL: 5.52E4
 F: + c Full ms [50.00-650.00]



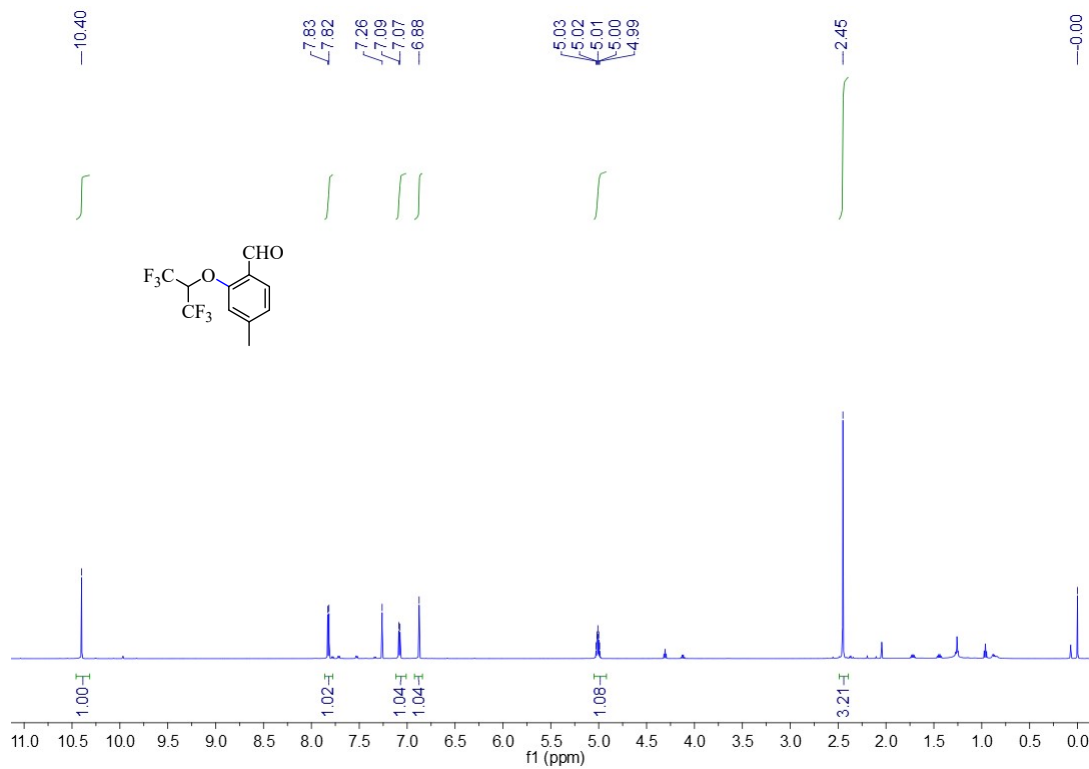
¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3r**



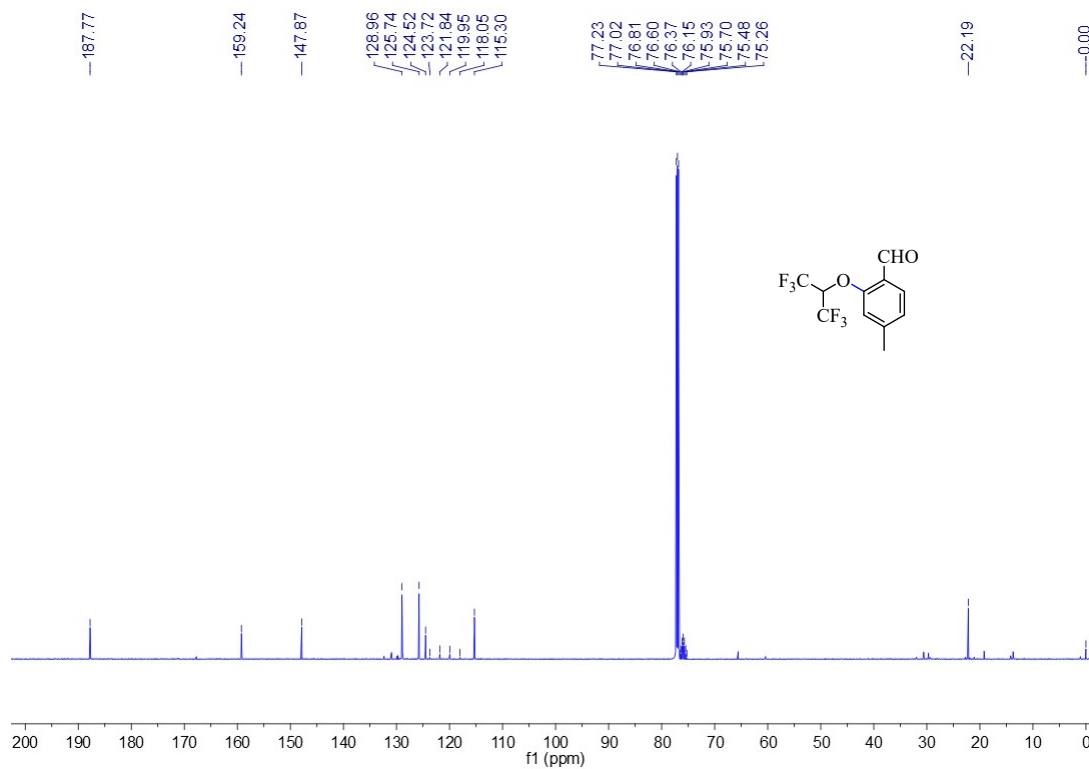
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3r**



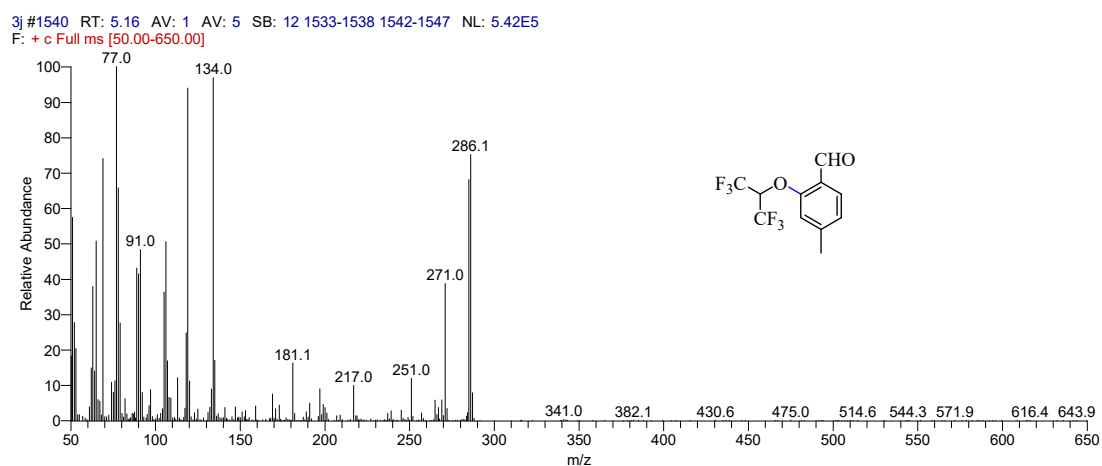
¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methylbenzaldehyde **3s**



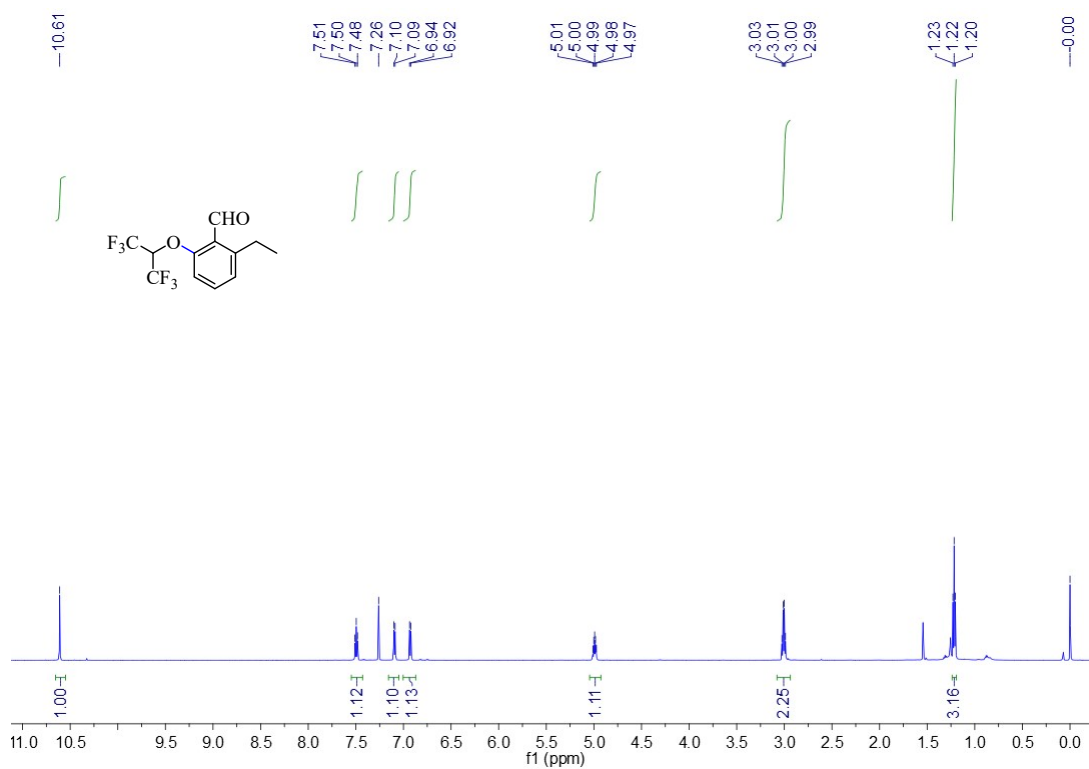
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methylbenzaldehyde **3s**



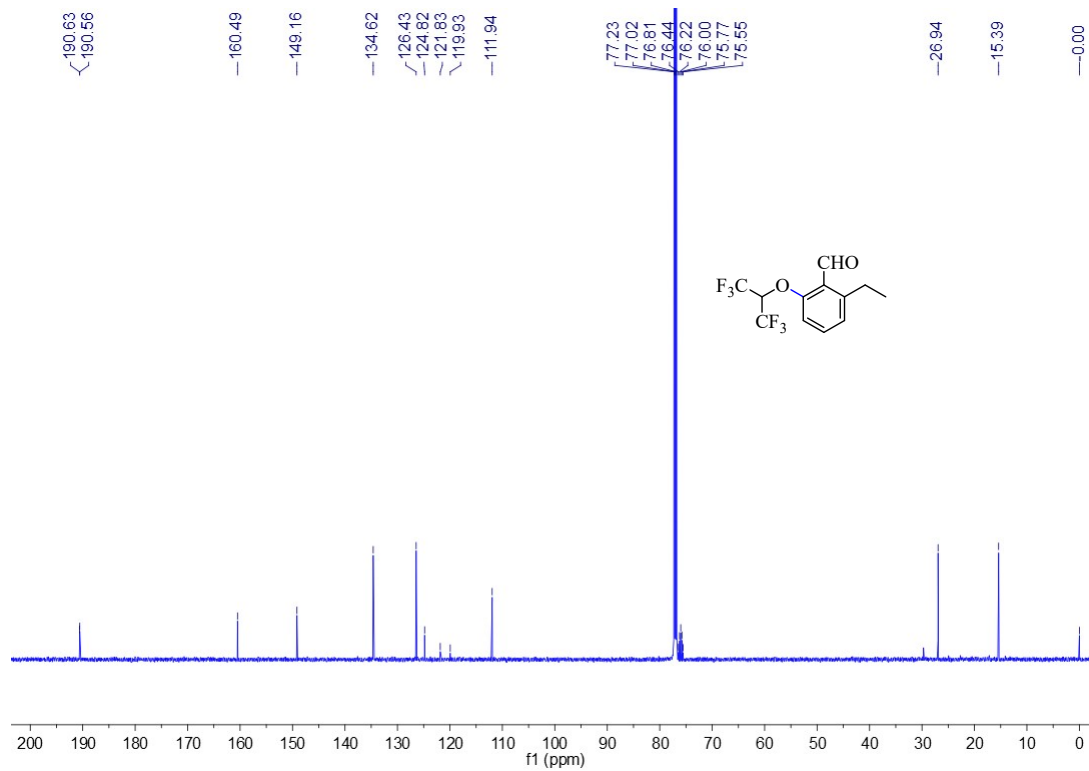
MS(EI) of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methylbenzaldehyde **3s**



¹H NMR of 2-ethyl-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3t**

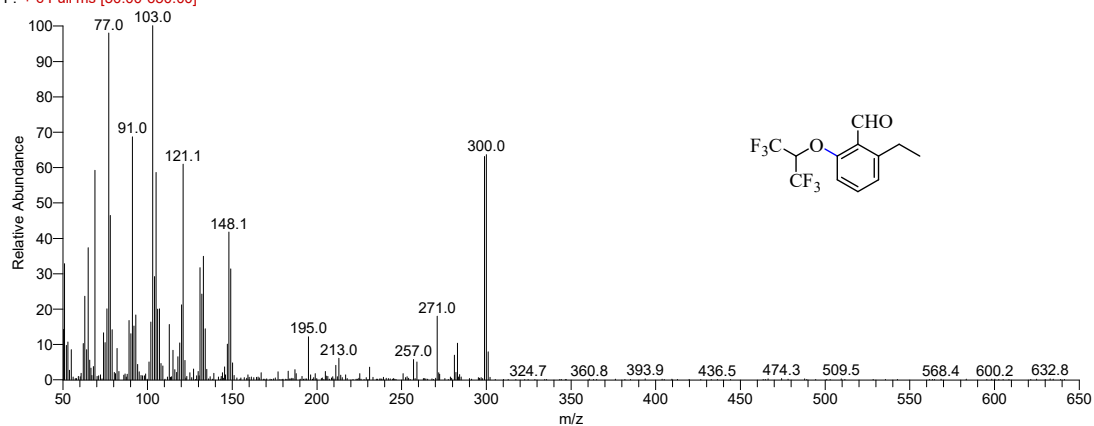


¹³C NMR of 2-ethyl-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3t**

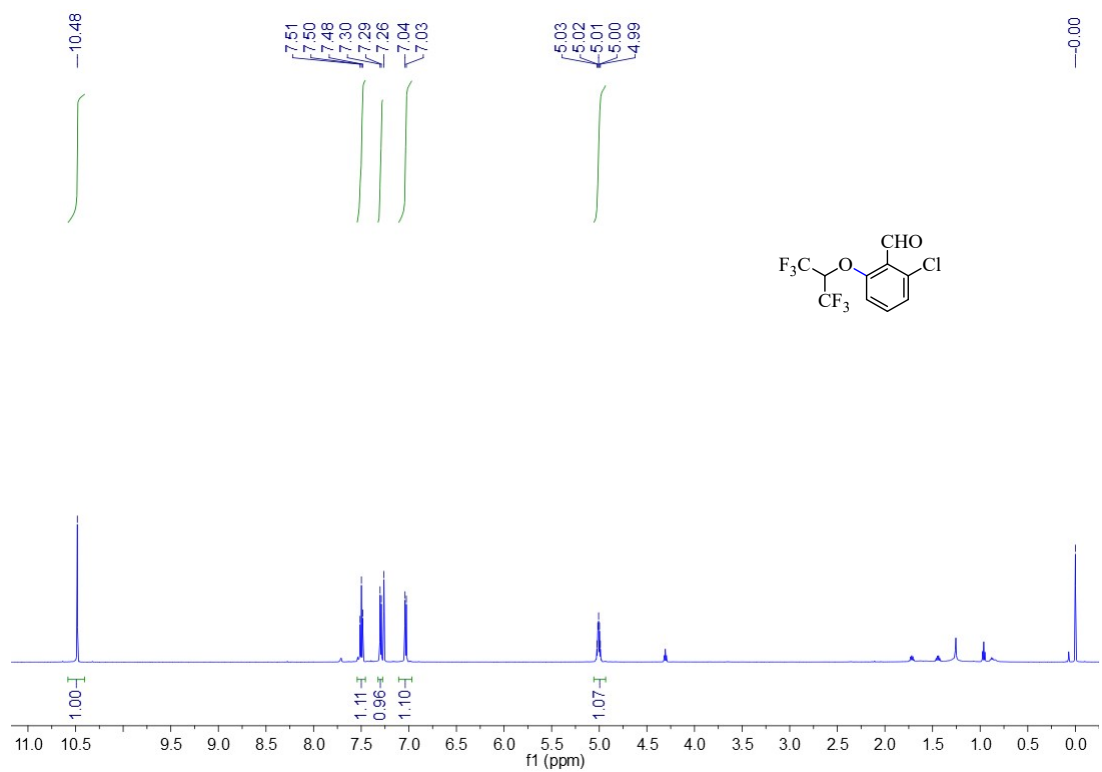


MS(EI) of 2-ethyl-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3t**

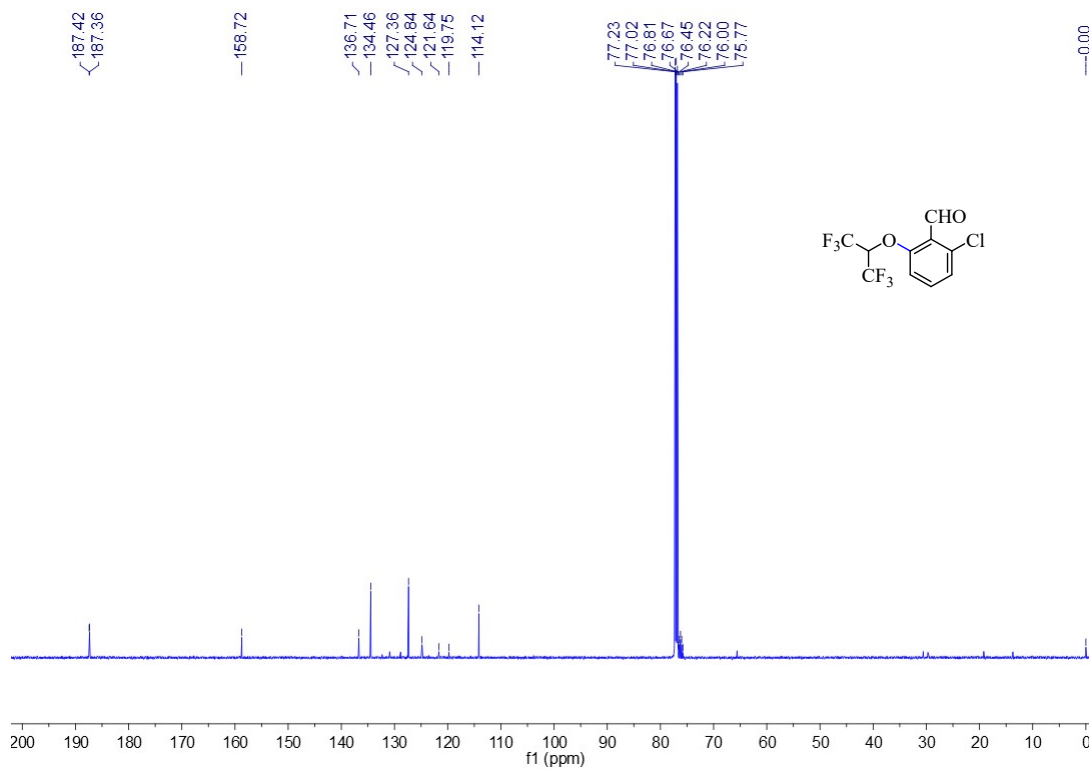
3k #1603 RT: 5.37 AV: 1 AV: 5 SB: 12 1596-1601 1605-1610 NL: 2.32E5
 F: + c Full ms [50.00-650.00]



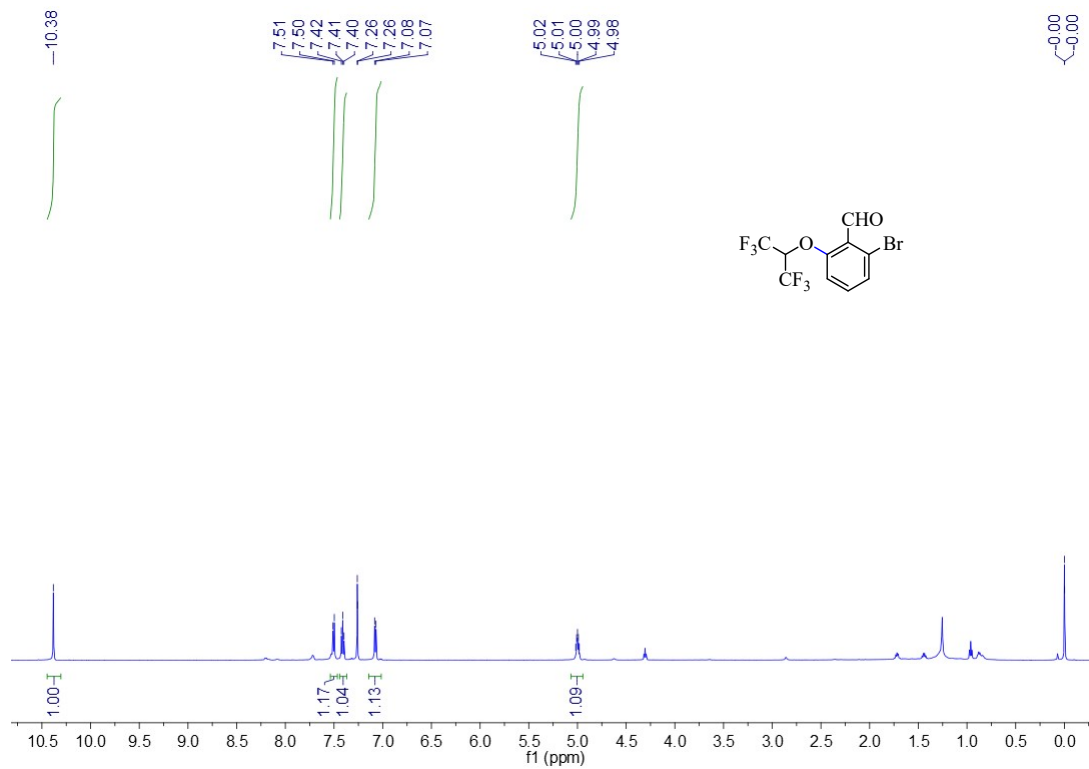
¹H NMR of 2-chloro-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3u**



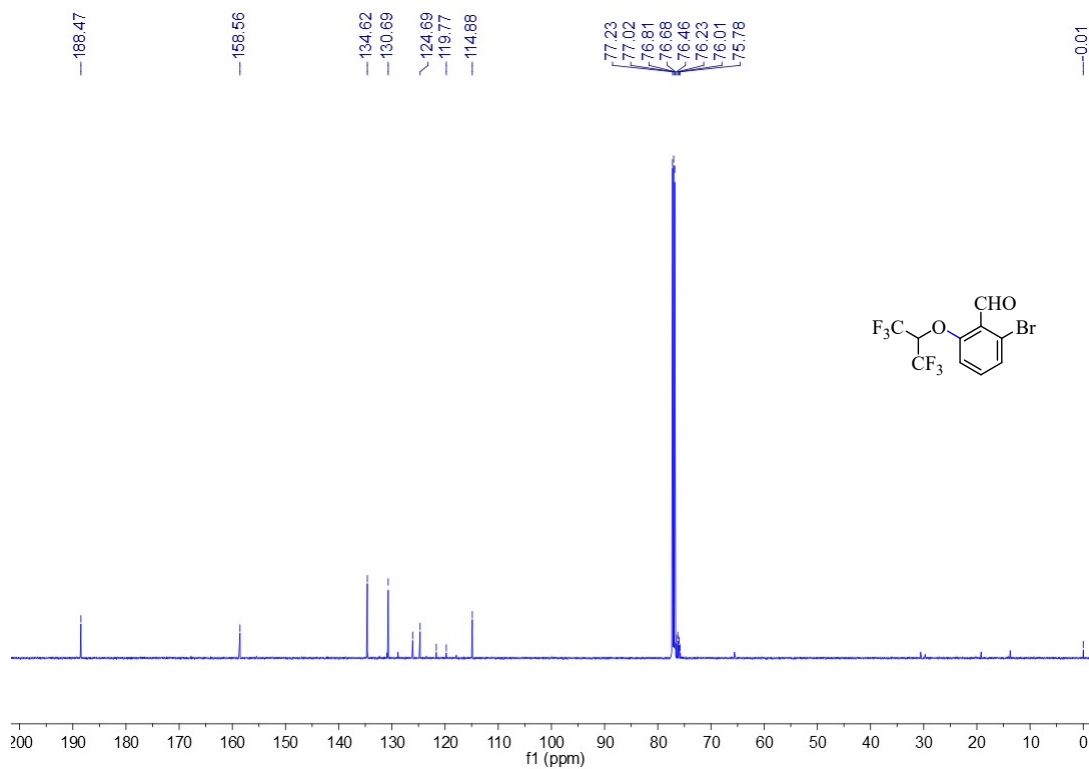
¹³C NMR of 2-chloro-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3u**



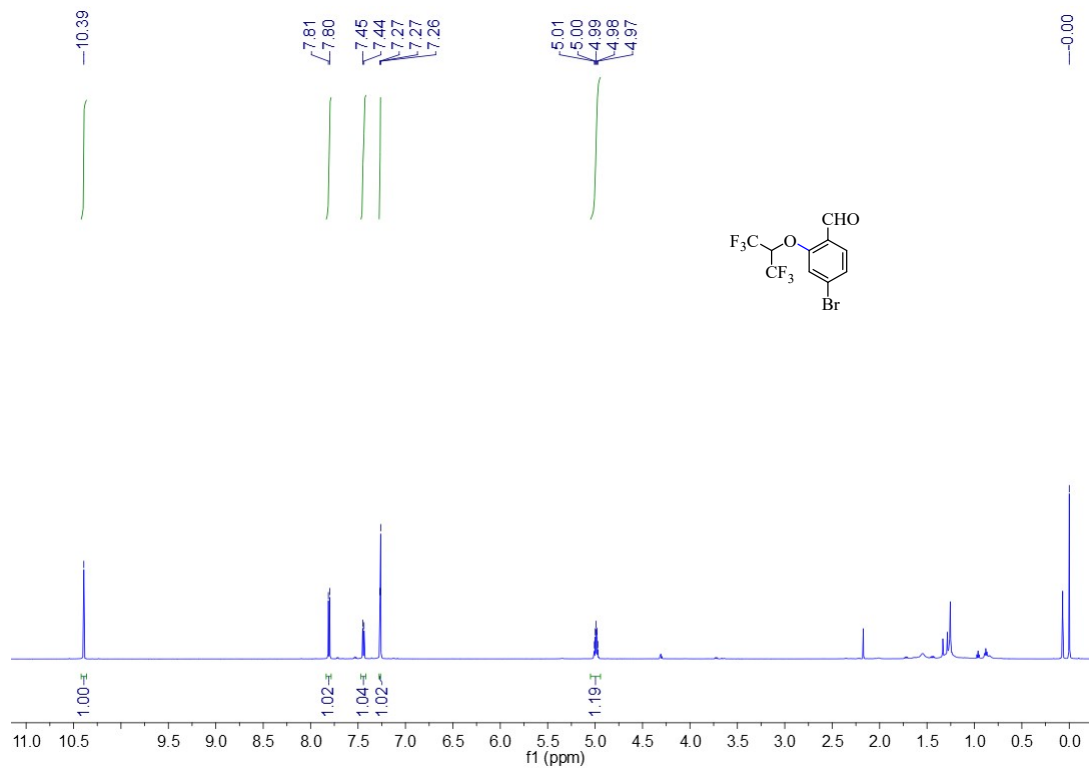
¹H NMR of 2-bromo-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3v**



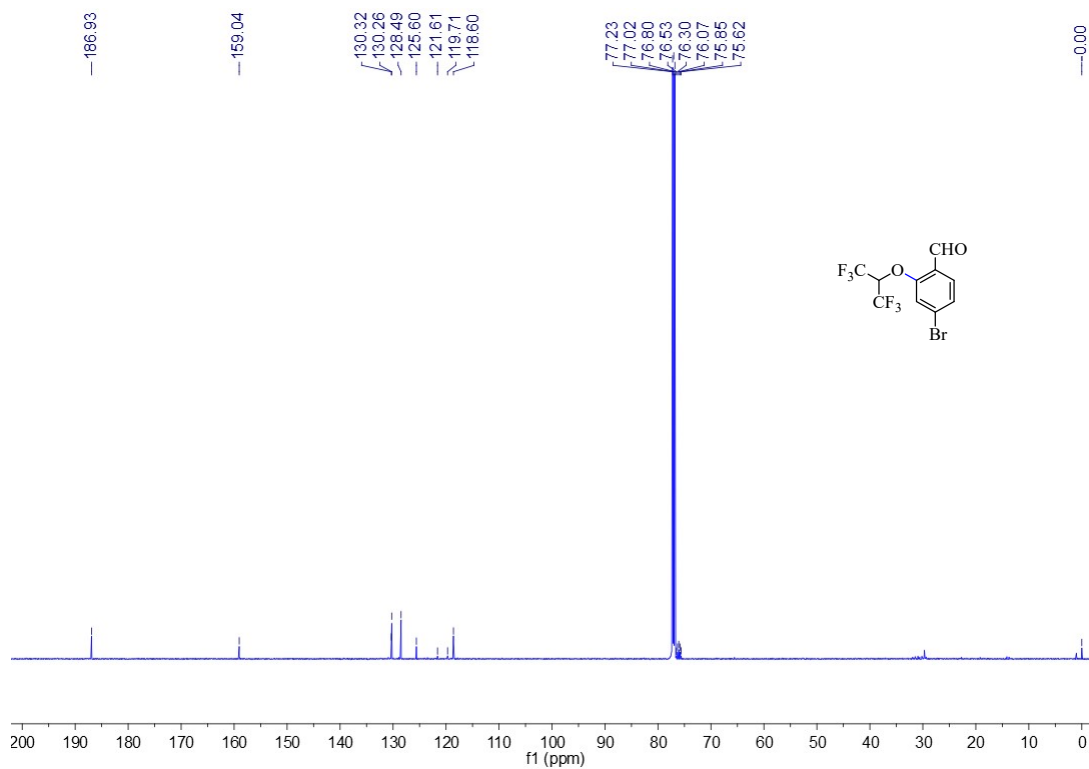
¹³C NMR of 2-bromo-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3v**



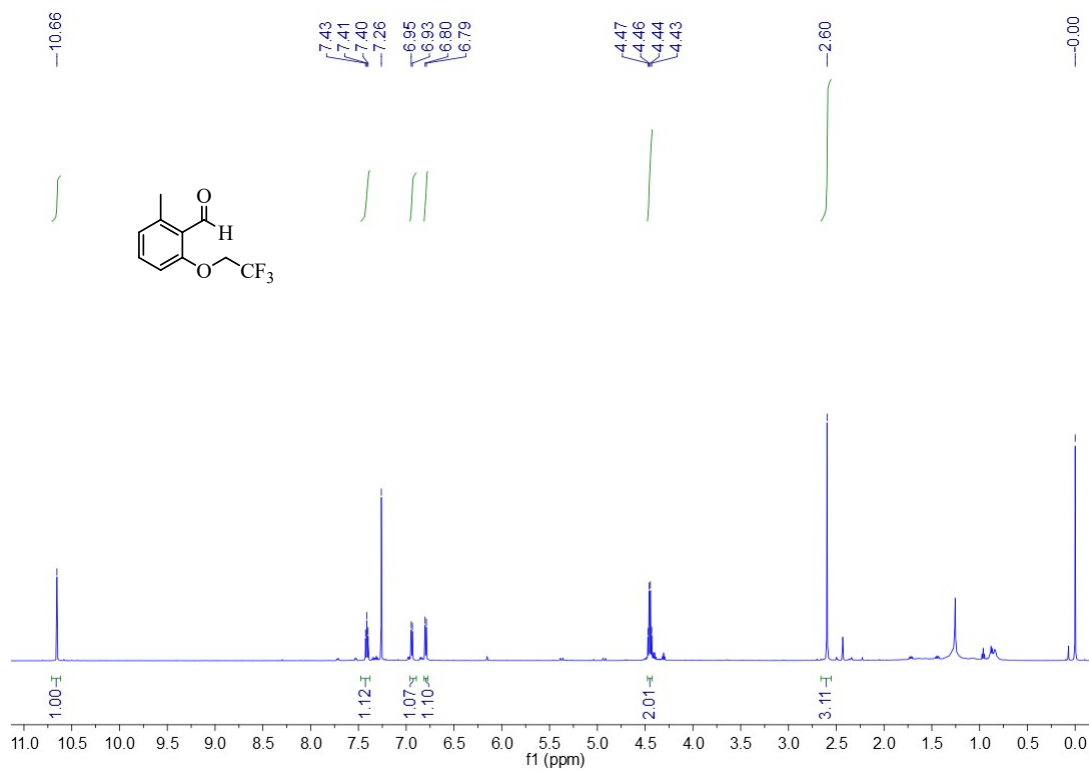
¹H NMR of 4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3w**



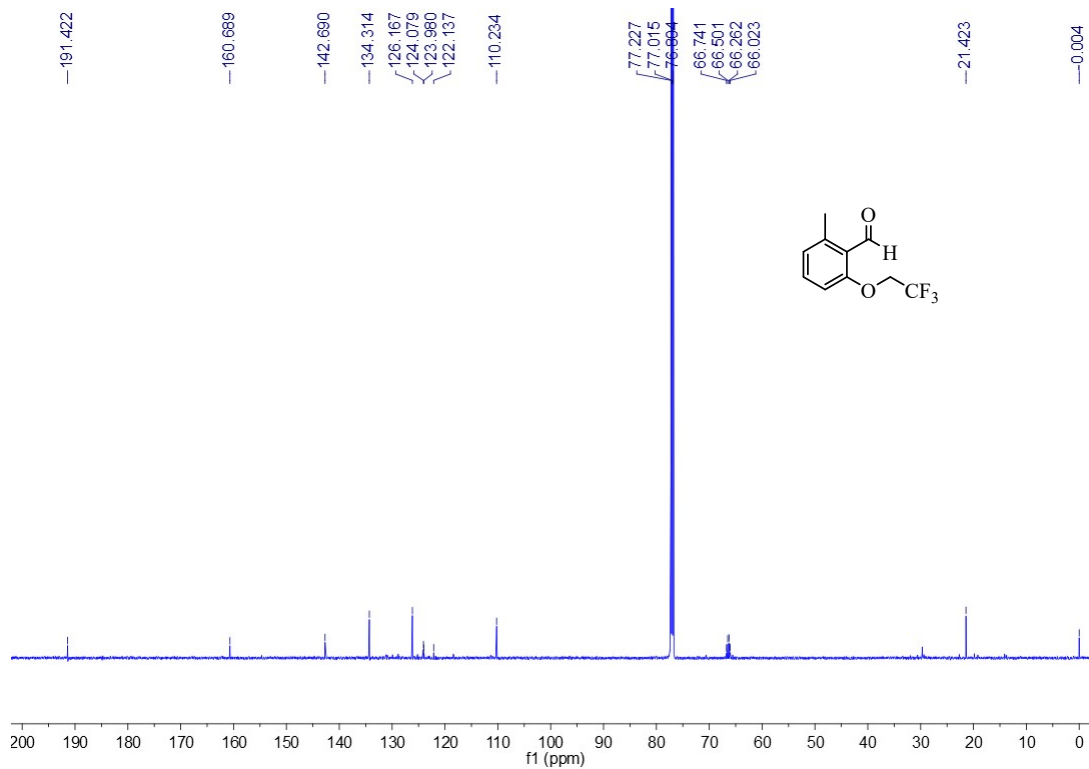
¹³C NMR of 4-bromo-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzaldehyde **3w**



¹H NMR of 2-methyl-6-(2,2,2-trifluoroethoxy)benzaldehyde **4**

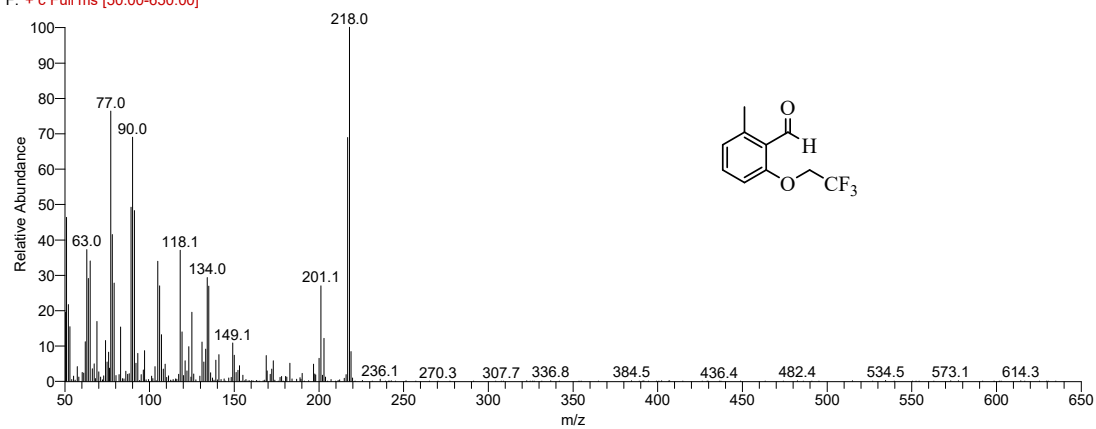


¹³C NMR of 2-methyl-6-(2,2,2-trifluoroethoxy)benzaldehyde 4

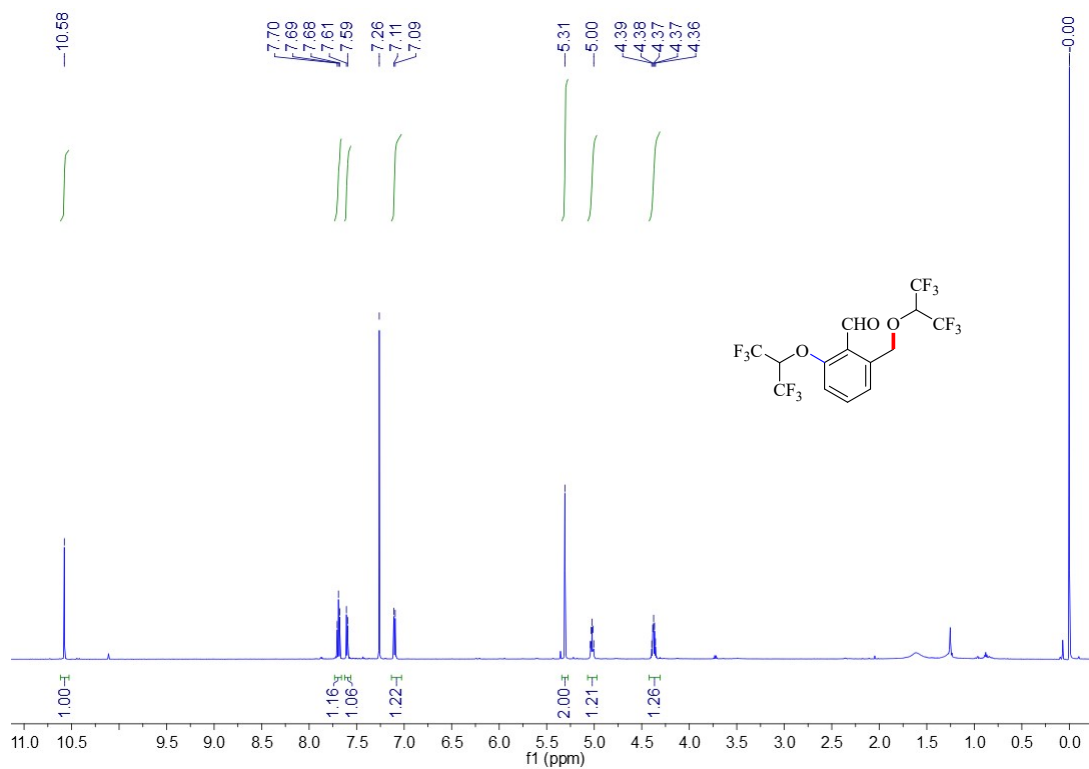


MS(EI) of 2-methyl-6-(2,2,2-trifluoroethoxy)benzaldehyde 4

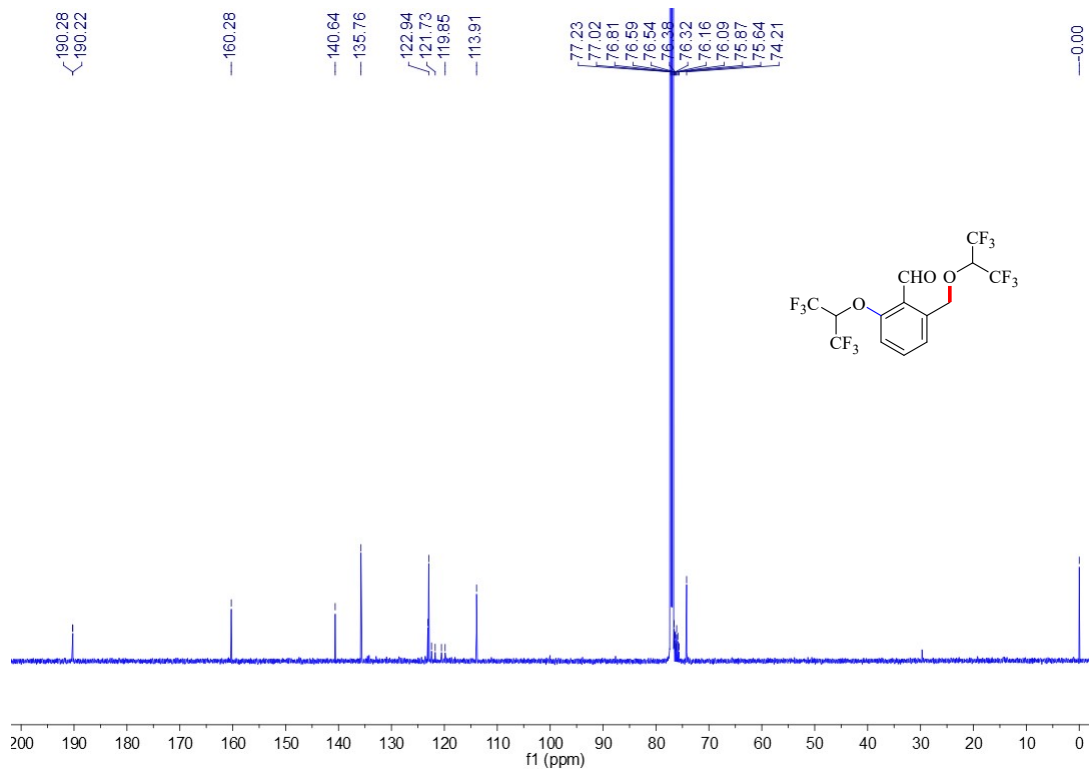
4a #1711 RT: 5.72 AV: 1 AV: 5 SB: 12 1704-1709 1713-1718 NL: 2.37E5
F: + c Full ms [50.00-650.00]



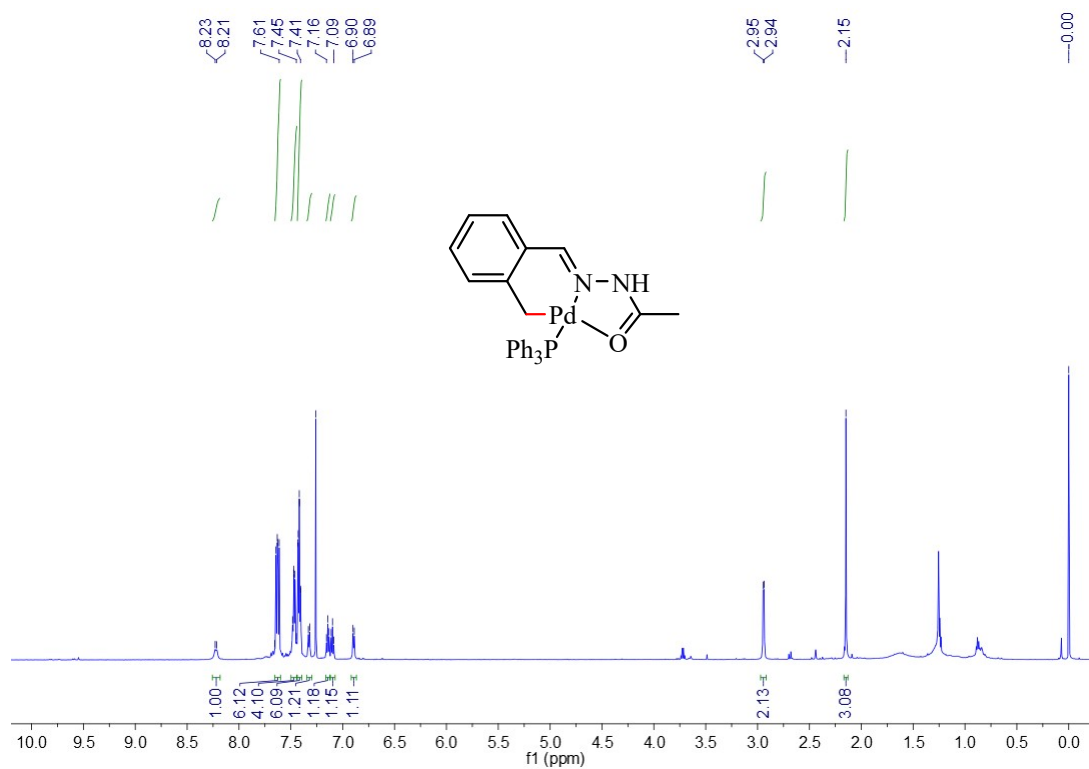
¹H NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **5**



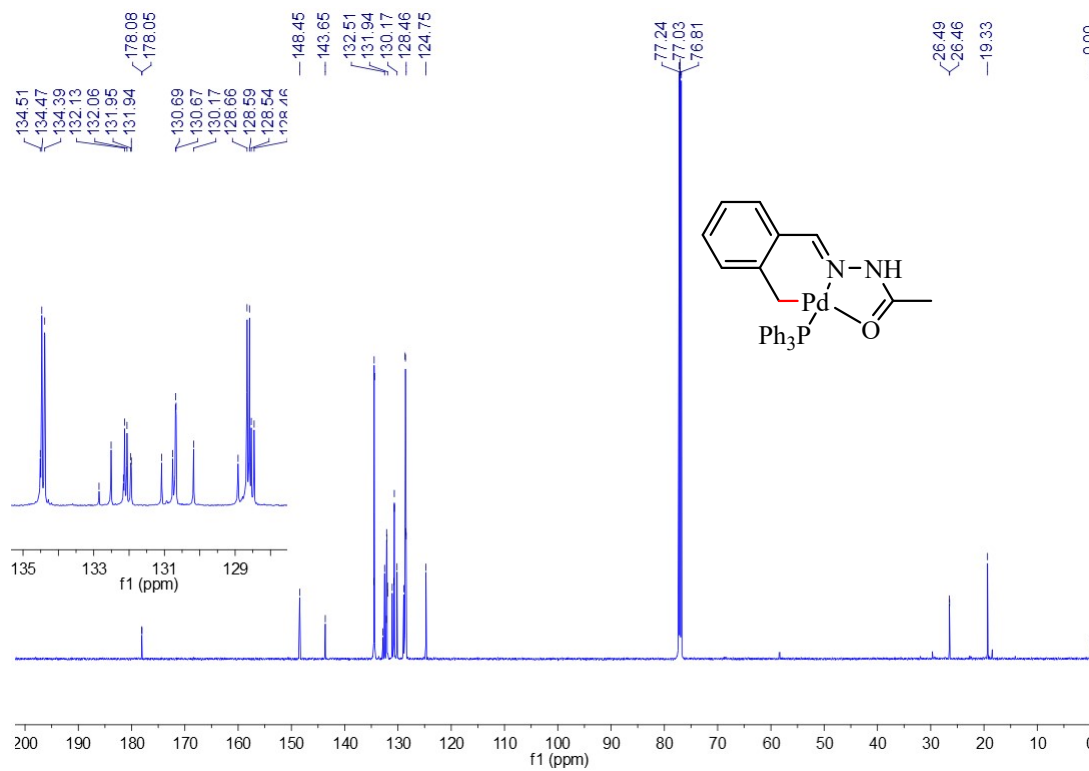
¹³C NMR of 2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-6-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzaldehyde **5**



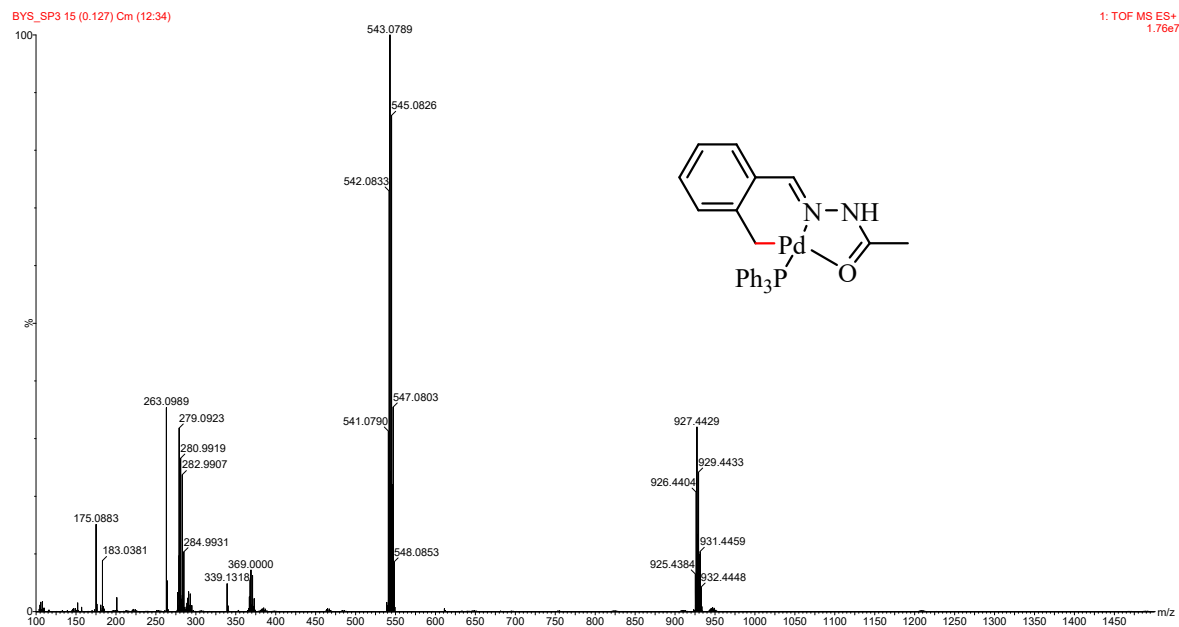
¹H NMR of Intermediate 6



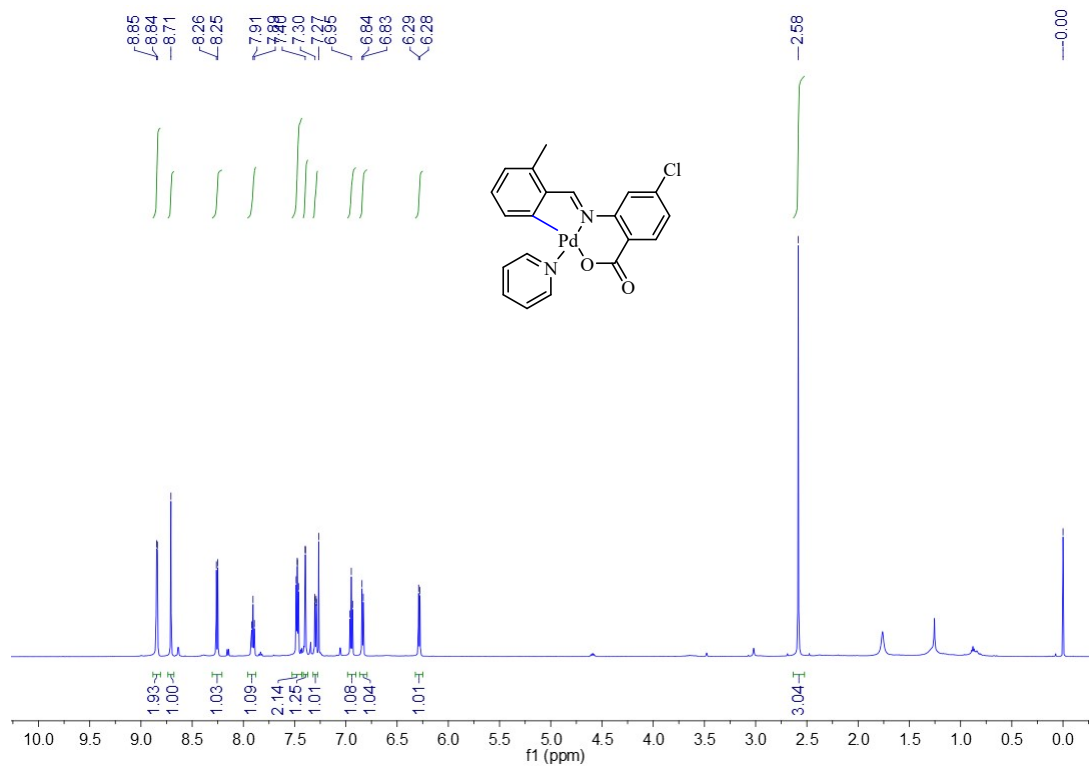
¹³C NMR of Intermediate 6



HRMS(ESI) of Intermediate 6



¹H NMR of Intermediate 7



¹³C NMR of Intermediate 7

