Catalyzing the Hydrodefluorination of CF_3-substituted Alkenes by $PhSiH_3$. H• Transfer from a Nickel Hydride

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Supporting Information

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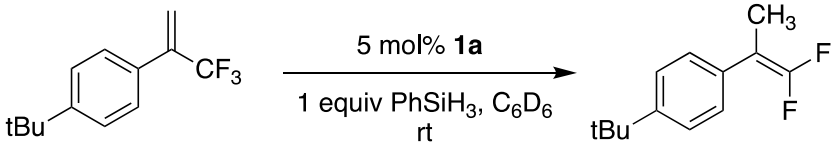
NMR Spectrum for $PhSiF_3$ formation



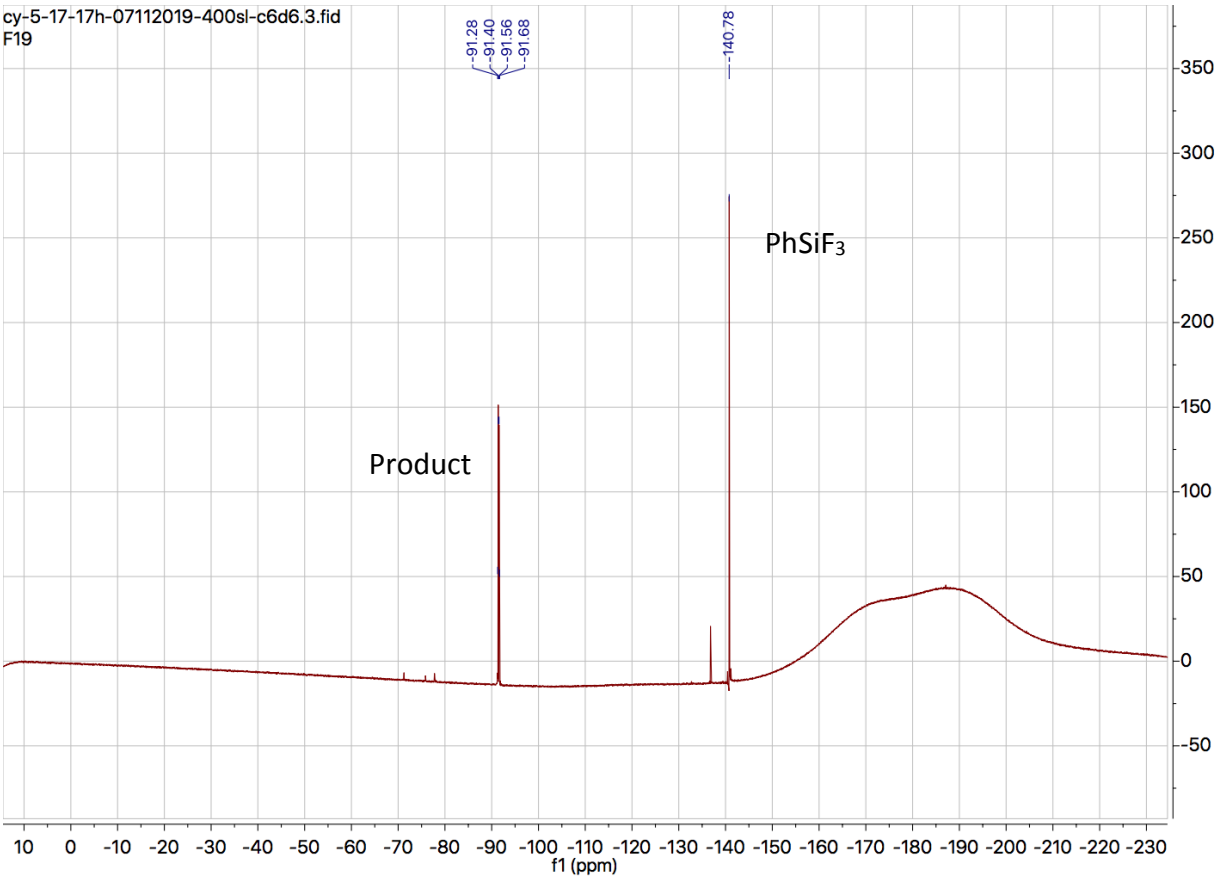
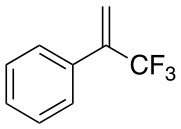


Figure S1. ^{19}F-NMR before workup. The peak at -140.8 ppm matches well with reported chemical shift value for $PhSiF_3$. [1]

Synthesis of Substrates



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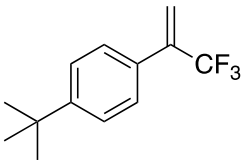

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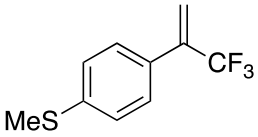

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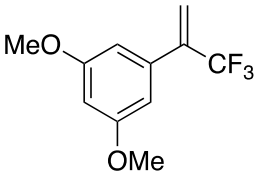

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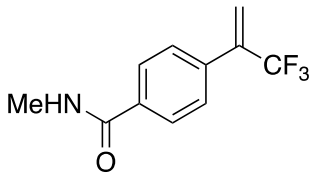

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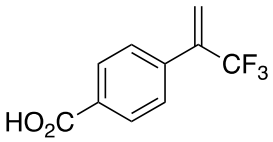

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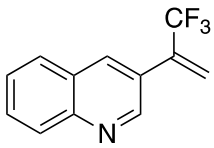

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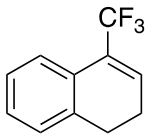

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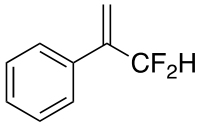

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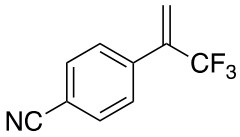

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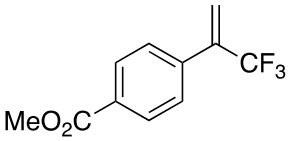

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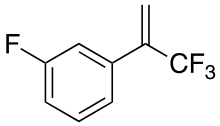

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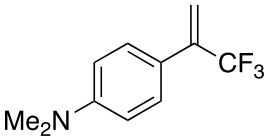

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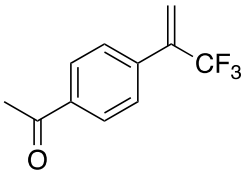

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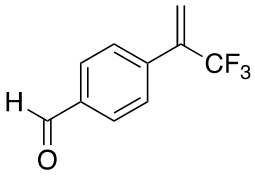
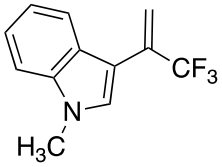


2o



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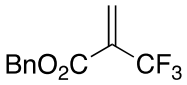

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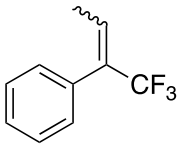

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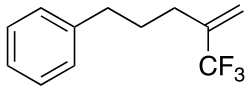
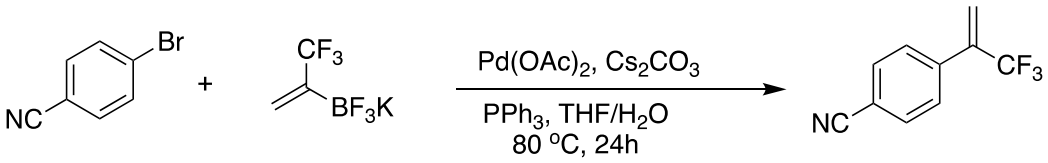


2s

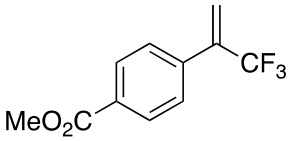
The substrates **2a**[2], **2b**[3], **2c**[4], **2d**[5], **2e-f**[4], **2g-2i, 2s**[6], **2r**[7] and **2q**[8] were prepared by literature methods. Substrates **2j, 2k, 2n,** and **2o** were synthesized by modifying the method reported by the Molander group.[9] Substrates **2l, 2m,** and **2p** were synthesized by Wittig reaction.

General procedure for the synthesis of **2j, 2k, 2n,** and **2o**

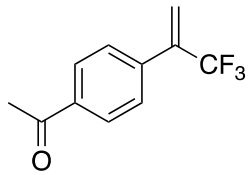


4-(3,3,3-trifluoroprop-1-en-2-yl)benzonitrile, 2j

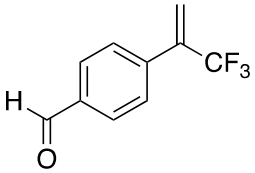
To a 50 mL oven-dried Schlenk flask was added 4-bromobenzonitrile (273 mg, 1.5 mmol, 1 equiv), Cs_2CO_3 (1.47g, 4.5 mmol, 3 equiv), potassiumtrifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (455 mg, 2.25 mmol, 1.5 equiv), $Pd(OAc)_2$ (17 mg, 0.075 mmol, 0.05 equiv),and PPh_3 (47 mg, 0.18 mmol, 0.12equiv).The Schlenk flask was evacuated and then refilled with argon. A mixture of degassed THF (9 mL) and degassed deionized H_2O (4.5 mL) were added via syringe. The reaction mixture was allowed to stir at 80 ^oC for 24h. Once complete the reaction was cooled to room temperature and diluted in EtOAc (25 mL). The reaction mixture was transferred to a separatory funnel and further diluted with deionized H_2O (25 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with 1M aqNaOH (25 mL), deionized H_2O (25 mL), and brine (25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo by rotary evaporation. Further purification was achieved by SiO_2 column (5% EtOAc in hexanes) to give the desired product **2j** (177mg, 60%). The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[8]



methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate, 2k was prepared according to the general procedure. The desired product was purified by flash column with 2.5% EtOAc in hexanes. The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[4]

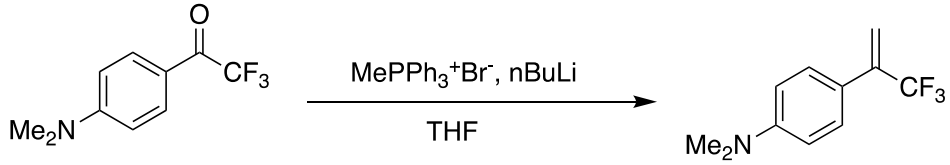


1-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one, 2n was prepared according to the general procedure. The desired product was purified by flash column with 10% EtOAc in hexanes. The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[10]



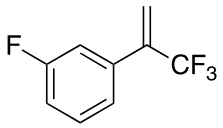
4-(3,3,3-trifluoroprop-1-en-2-yl)benzaldehyde, 2o was prepared according to the general procedure. The desired product was purified by flash column with 10% EtOAc in hexanes. The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[8]

General Procedure for the synthesis of **2l, 2m,** and **2p**

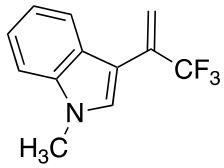


N,N-dimethyl-4-(3,3,3-trifluoroprop-1-en-2-yl)aniline, 2m

To a 50 ml oven-dried Schlenk flask, were added methyl triphenylphosphonium bromide (1.79 g, 5 mmol, 1.25 equiv) and dry THF (10 ml). nBuLi (4 mmol, 1 equiv) was added dropwise at 0 ^{o}C. After stirring the mixture for 10 min, 1-(4-(dimethylamino)phenyl)-2,2,2-trifluoroethan-1-one (872 mg, 4 mmol, 1 equiv) in dry THF (10 ml) was added at -78 ^{o}C. The reaction mixture was allowed to stir at rt for 3h. Once complete the reaction was cooled to room temperature and diluted with diethyl ether. The reaction mixture was quenched by NH_4Cl (aq) and then transferred to a separatory funnel. The layers were separated, and the aq layer was extracted with ether. The combined organic layers were washed with deionized H_2O (25 mL), and brine (25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo by rotary evaporation. Further purification was achieved by SiO_2 column (5% EtOAc in hexanes) to give the desired product **2m** (570mg, 66%). The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[6]

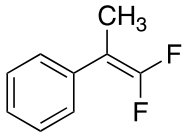


1-fluoro-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene, 2l was prepared according to the general procedure. The desired product was purified by flash column with pure hexanes. The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[11]

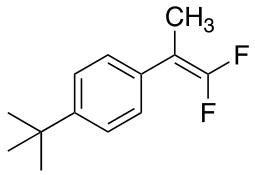


1-methyl-3-(3,3,3-trifluoroprop-1-en-2-yl)-1H-indole, 2p was prepared according to the general procedure. The desired product was purified by flash column with 10% EtOAc in hexanes. The ^{1}H-NMR spectrum was in agreement with that reported in the reference.[12]

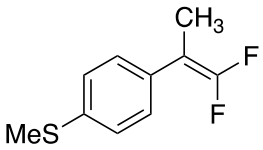
Product Purification and Characterization



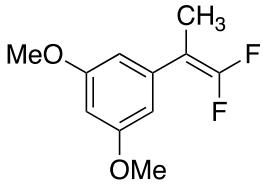
(1,1-difluoroprop-1-en-2-yl)benzene, 3a Flash column chromatography was done using pure hexane. Product was obtained with 88% yield. Spectral data matches the reported data in the literature.[13]



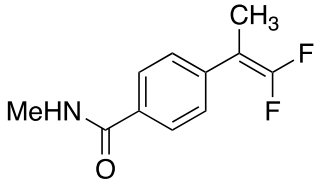
1-(tert-butyl)-4-(1,1-difluoroprop-1-en-2-yl)benzene, 3b Flash column chromatography was done using pure hexane. Product was obtained with 91% yield. Spectral data matches the reported data in the literature.[14]



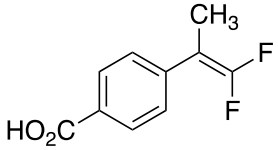
(4-(1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane, 3c Flash column chromatography was done using pure hexane. Product was obtained with 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (m, 4H), 2.51 (s, 3H), 1.98 (t, *J* = 3.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) AB system (δ_A = -90.20, δ_B = -90.44, $^{2}J_{F,F}$ = 43.7 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.45 (dd, *J* = 290.0, 286.1 Hz), 137.29, 131.60 (t, *J* = 3.8 Hz), 127.96 – 127.66 (m), 126.49, 87.03 (dd, *J* = 22.6, 14.6 Hz), 15.80, 13.11. HRMS-ASAP+ (m/z): calcd for $C_{10}H_{11}F_2S$ $[M+H]^+$: 201.0549, found: 201.0542



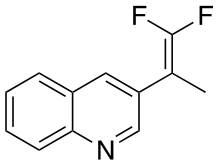
1-(1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene, 3d Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.54 (dd, *J* = 2.3, 1.1 Hz, 2H), 6.41 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 6H), 1.97 (t, *J* = 3.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) AB system (δ_A = -89.48, δ_B = -89.89, $^{2}J_{F,F}$ = 42.6 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.67, 153.51 (dd, *J* = 290.5, 285.9 Hz), 136.86 (t, *J* = 4.2 Hz), 105.96 (dd, *J* = 4.8, 3.4 Hz), 99.09, 87.63 (dd, *J* = 22.9, 14.0 Hz), 55.33, 13.33 (t, *J* = 1.8 Hz). HRMS-ASAP+ (m/z): calcd for $C_{11}H_{13}F_2O_2$ $[M+H]^+$: 215.0884, found: 215.0880



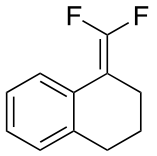
4-(1,1-difluoroprop-1-en-2-yl)-*N*-methylbenzamide, 3e Flash column chromatography was done using 50% ethyl acetate/hexanes mixture. Product was obtained with 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (m, 2H), 7.41 (m, 2H), 6.51 (br, 1H), 3.01 (d, *J* = 4.9 Hz, 3H), 1.99 (t, *J* = 3.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.81, 153.74 (dd, *J* = 292.1, 287.3 Hz), 137.98 (t, *J* = 4.5 Hz), 133.06, 127.47 (dd, *J* = 5.1, 3.3 Hz), 126.94, 87.16 (dd, *J* = 23.2, 13.6 Hz), 26.81, 12.94 (t, *J* = 1.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) ABX3 system (δ_A = -88.29, δ_B = -88.87, $^{2}J_{F,F}$ = 39.4 Hz, $^{4}J_{H,F}$ = 3.9 Hz). HRMS-ASAP+ (m/z): calcd for $C_{11}H_{12}F_2NO$ $[M+H]^+$: 212.0887, found: 212.0881



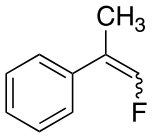
4-(1,1-difluoroprop-1-en-2-yl)benzoic acid, 3f Flash column chromatography was done using 50% ethyl acetate/hexanes mixture. Product was obtained with 82% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.77 (br, 1H), 8.13 (m, 2H), 7.51 (m, 2H), 2.04 (t, *J* = 3.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.92, 153.95 (dd, *J* = 293.1, 288.0 Hz), 140.59 (t, J = 5 Hz), 130.28, 127.82, 127.46 (dd, *J* = 5.2, 3.4 Hz), 87.33 (dd, *J* = 23.4, 13.2 Hz), 12.90. ^{19}F NMR (376 MHz, Chloroform-*d*) AB system (δ_A = -87.12, δ_B = -87.70, $^{2}J_{F,F}$ = 36.5 Hz). HRMS-ESI (m/z): calcd for $C_{10}H_7F_2O_2$ $[M-H]^-$: 197.0414, found: 197.0439



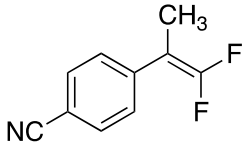
3-(1,1-difluoroprop-1-en-2-yl)quinoline, 3g Flash column chromatography was done using 20% ethyl acetate/hexanes mixture. Product was obtained with 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.98 (m, 1H), 8.21 – 8.01 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 2.04-2.18 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) AB system (δ_A = -87.91, δ_B = -88.88, $^{2}J_{F,F}$ = 39.3 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.00 (dd, *J* = 291.6, 288.3 Hz), 149.66 (d, *J* = 6.6 Hz), 146.89, 133.83 (t, *J* = 4.1 Hz), 129.54, 129.19, 128.12 (t, *J* = 4.1 Hz), 127.76, 127.66, 127.02, 85.29 (dd, *J* = 24.4, 14.6 Hz), 12.98 (t, *J* = 1.8 Hz). HRMS-ASAP+ (m/z): calcd for $C_{12}H_{10}F_2N$ $[M+H]^+$: 206.0781, found: 206.0777



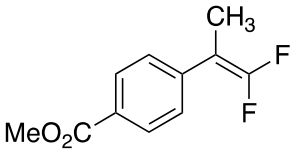
1-(difluoromethylene)-1,2,3,4-tetrahydronaphthalene, 3h The reaction was carried out at 70 ^{o}C. Flash column chromatography was done using pure hexanes. Product was obtained with 75% yield. Spectral data matches the reported data in the literature.[15]


(E/Z = 2:1)

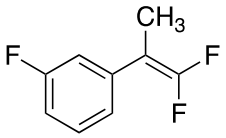
(1-fluoroprop-1-en-2-yl)benzene, 3i The reaction was carried out at 50 ^{o}C. Flash column chromatography was done using pure hexanes. Product was obtained with 77% yield. Spectral data matches the reported data in the literature.[16]



4-(1,1-difluoroprop-1-en-2-yl)benzonitrile, 3j Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 80% yield. Spectral data matches the reported data in the literature.[17]

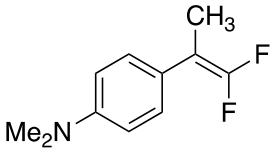


methyl 4-(1,1-difluoroprop-1-en-2-yl)benzoate, 3k Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 90% yield. Spectral data matches the reported data in the literature.[18]

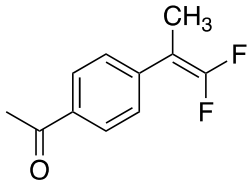


1-(1,1-difluoroprop-1-en-2-yl)-3-fluorobenzene, 3l Flash column chromatography was done using pure hexanes. Product was obtained with 86% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 (td, J = 8.0, 6.2 Hz, 1H), 7.18 (ddt, J = 7.9, 2.0, 1.0 Hz, 1H), 7.11 (ddt, J = 10.6, 2.6, 1.1 Hz, 1H), 6.99 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H), 1.99 (t, J = 3.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-d) ABX3 system (δA = -93.09, δB = -93.21, $^{2}J_{F,F}$ = 50.3 Hz, $^{4}J_{H,F}$ = 3.9 Hz), δ -113.17 (td, *J* = 9.8, 6.5

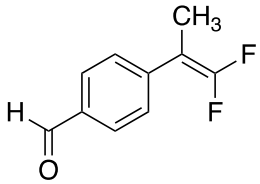
Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.99, 161.55, 153.70 (dd, *J* = 291.3, 286.8 Hz), 129.77 (d, *J* = 8.5 Hz), 123.08 (dt, *J* = 4.9, 3.1 Hz), 114.50 (ddd, *J* = 22.6, 5.2, 3.4 Hz), 113.94 (d, *J* = 21.0 Hz), 86.95 (ddd, *J* = 22.9, 14.2, 2.4 Hz), 13.01 (t, *J* = 1.7 Hz). HRMS-ASAP+ (m/z): calcd for $C_9H_8F_3$ $[M+H]^+$: 173.0578, found: 173.0568



4-(1,1-difluoroprop-1-en-2-yl)-N,N-dimethylaniline, 3m Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 86% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.01 (s, 6H), 1.99 (t, J = 3.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-d) AB system (δA = -88.90, δB = -89.09, $^2J_{F,F}$ = 50.3 Hz). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.18 (t, J = 286.3 Hz), 149.48, 128.16 (t, J = 4.0 Hz), 122.59, 112.31, 87.04 (dd, J = 18.8, 17.9 Hz), 40.47, 13.21 (t, J = 1.7 Hz). HRMS-ASAP+ (m/z): calcd for $C_{11}H_{14}F_2N$ $[M+H]^+$: 198.1094, found: 198.1096

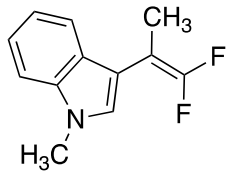


1-(4-(1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one, 3n Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 53% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 1H), 7.52 – 7.45 (m, 1H), 2.62 (s, 2H), 2.03 (t, *J* = 3.4 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-d) ABX3 system (δA = -87.38, δB = -87.98, $^2J_{F,F}$ = 37.2 Hz, $^4J_{H,F}$ = 3.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.47, 153.89 (dd, *J* = 292.9, 288.0 Hz), 139.80 (t, *J* = 4.7 Hz), 135.61, 128.40, 127.52 (dd, *J* = 5.1, 3.4 Hz), 87.28 (dd, *J* = 23.6, 13.3 Hz), 26.56, 12.91 (t, J = 2.3 Hz). HRMS-ASAP+ (m/z): calcd for $C_{11}H_{11}F_2O$ $[M+H]^+$: 197.0778, found: 197.0781

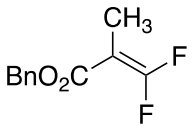


4-(1,1-difluoroprop-1-en-2-yl)benzaldehyde, 3o Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 50% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 7.95 – 7.82 (m, 2H), 7.60 – 7.51 (m, 2H), 2.05 (t, *J* = 3.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-d) ABX3 system (δA = -86.61, δB = -87.34, $^2J_{F,F}$ = 35.6 Hz, $^4J_{H,F}$ = 3.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.62, 154.02 (dd, *J* = 293.5, 288.5 Hz), 141.26,

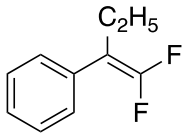
134.93, 129.73, 127.96 (dd, *J* = 5.3, 3.4 Hz), 87.38 (t, J = 13.1, 23.6 Hz), 12.91 (t, *J* = 1.7 Hz). HRMS-ASAP+ (m/z): calcd for $C_{10}H_9F_2O$ $[M+H]^+$: 183.0621, found: 183.0621



3-(1,1-difluoroprop-1-en-2-yl)-1-methyl-1*H*-indole, 3p Flash column chromatography was done using 5% ethyl acetate/hexanes mixture. Product was obtained with 85% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (ddt, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.37 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.31 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.08 (s, 1H), 3.82 (s, 3H), 2.11 (t, *J* = 3.3 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-d) ABX3 system (δA = -89.10, δB = -93.85, $^2J_{F,F}$ = 48.7 Hz, $^4J_{H,F}$ = 3.3 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.87 (dd, *J* = 286.7, 284.3 Hz), 136.85, 127.47 (t, *J* = 4.1 Hz), 126.31 (d, *J* = 2.4 Hz), 121.89, 120.46 (d, *J* = 4.8 Hz), 119.51, 109.44, 108.97 (dd, *J* = 4.4, 3.2 Hz), 81.64 (dd, *J* = 25.5, 17.9 Hz), 32.84, 14.19 (t, *J* = 2.7 Hz). HRMS-ASAP+ (m/z): calcd for $C_{12}H_{12}F_2N$ $[M+H]^+$: 208.0938, found: 208.0930



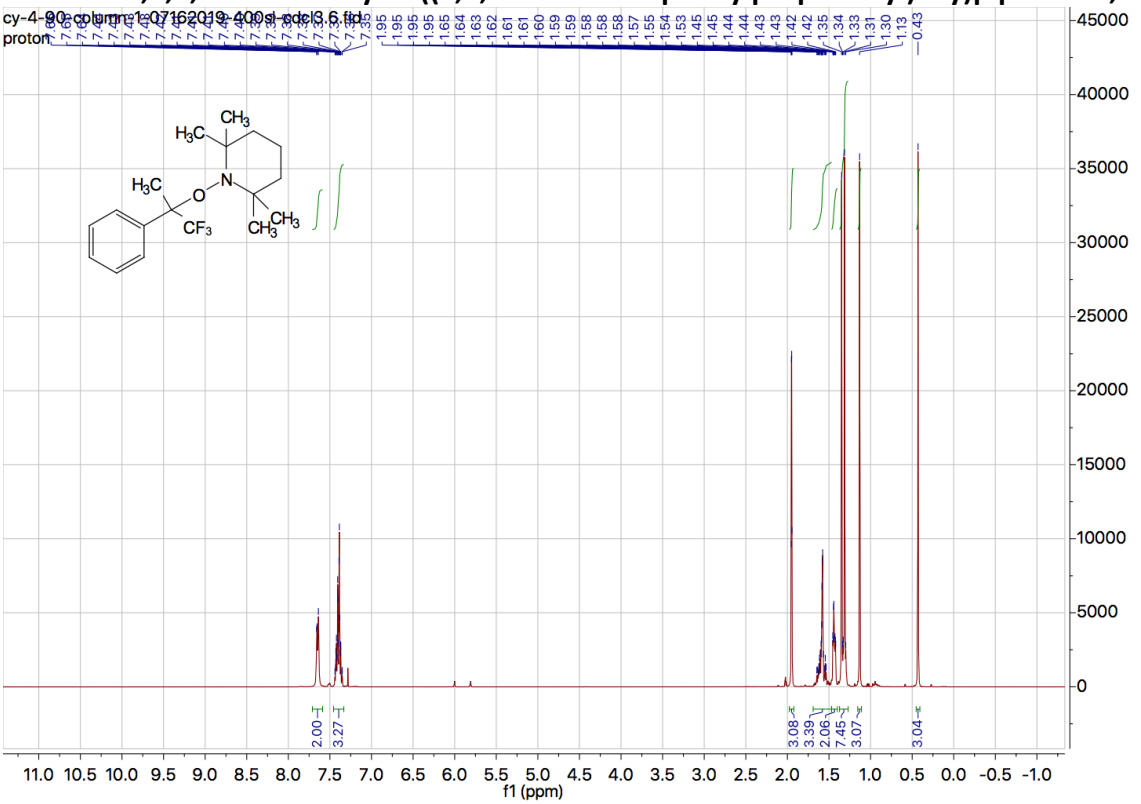
benzyl 3,3-difluoro-2-methylacrylate, 3q Flash column chromatography was done using 20% dichloromethane/hexanes mixture. Product was obtained with 85% yield. Spectral data matches the reported data in the literature.[8]



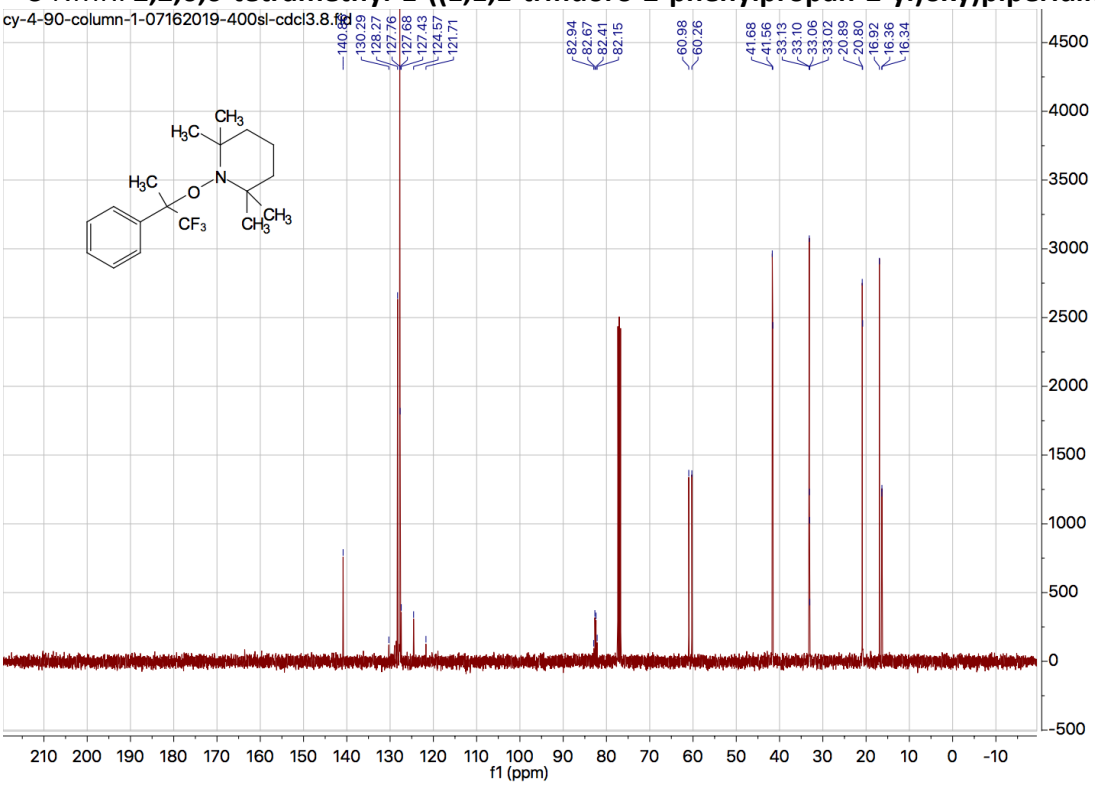
(1,1-difluorobut-1-en-2-yl)benzene, 3r The reaction was carried out at 95 °C for 10 days with a mixture of Z/E isomers (Z:E = 1: 0.84). Reaction progress was monitored by ^{19}F-NMR. The Z isomer of the starting material showed no conversion. The yield from the E isomer was determined by ^{19}F-NMR to be 91%. Spectral data matches the reported data in the literature.[19]

NMR Assignment of compound 6

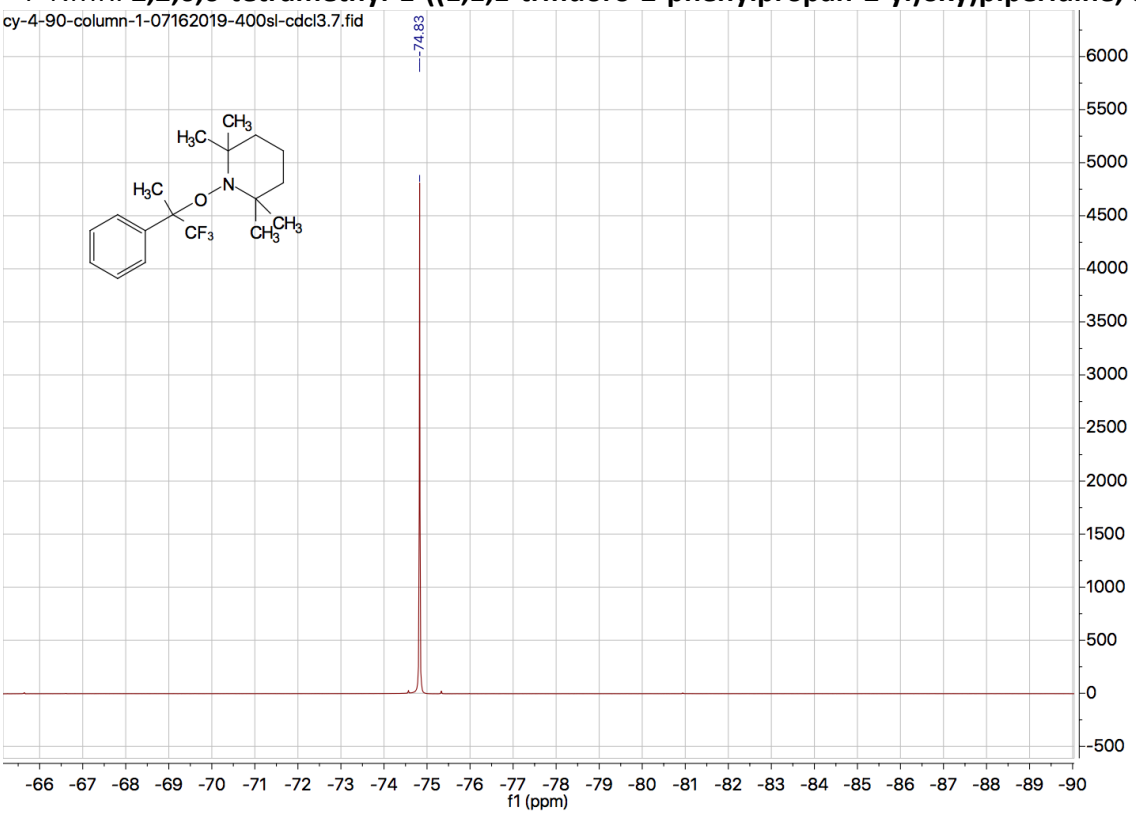
^{1}H-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**

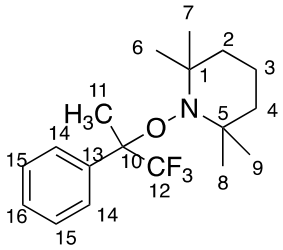


^{13}C-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**



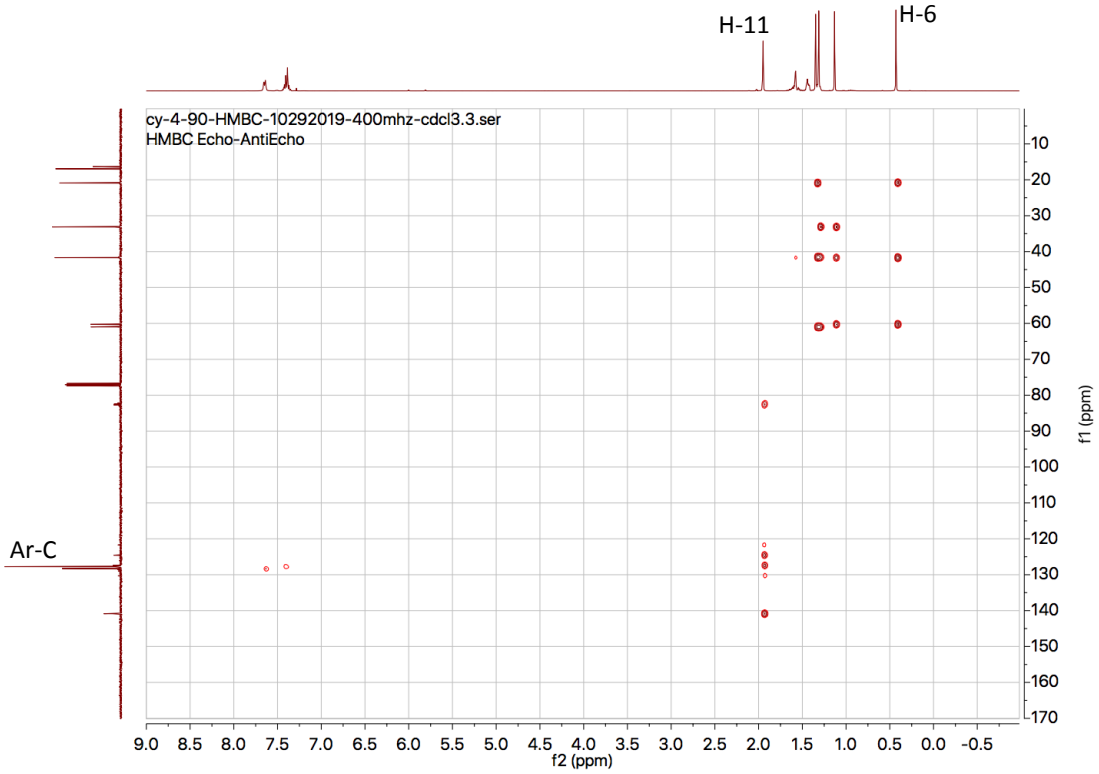
^{19}F-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**



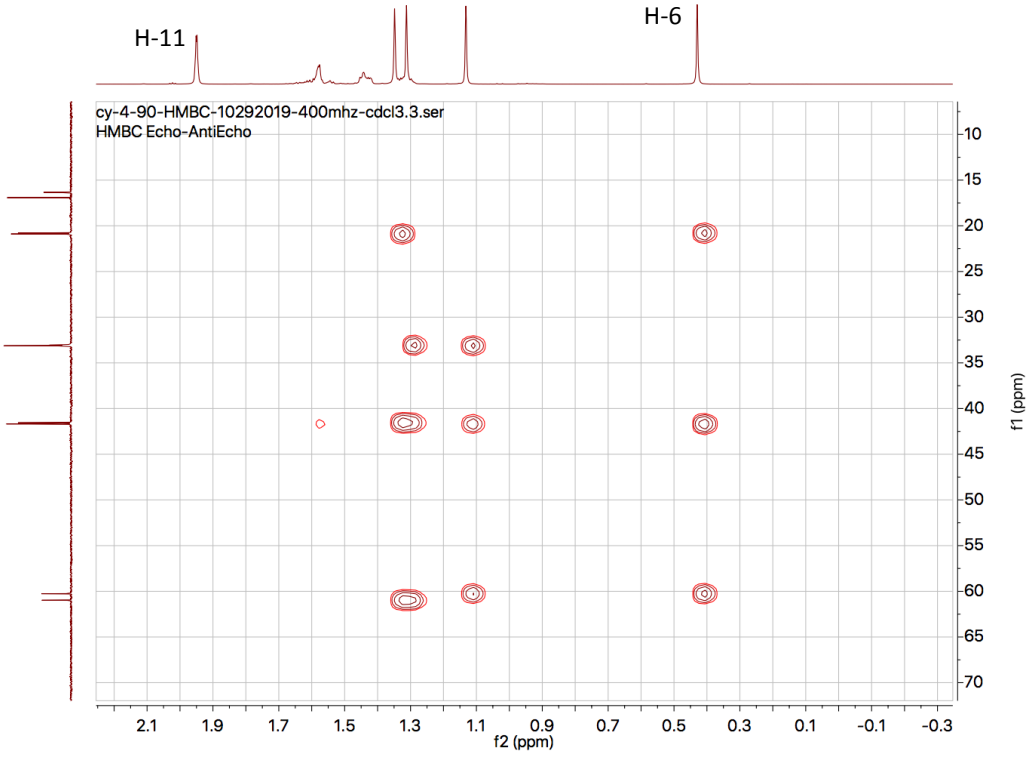


^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.62 (m, 2H, Ar-H), 7.46 – 7.34 (m, 3H, Ar-H), 1.95 (q, J = 1.2 Hz, 3H, H-11), 1.69 – 1.50 (m, 3H), 1.47 - 1.41 (m, 2H), 1.29 – 1.36 (m, 7H), 1.13 (s, 3H), 0.43 (s, 3H, H-6). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.86 (C-13), 128.27 (Ar-C), 127.76 (Ar-C), 127.68 (Ar-C), 126.00 (q, J = 287.6 Hz, C-12), 82.54 (q, J = 26.4 Hz, C-10), 60.98 (C-1), 60.26 (C-5), 41.68 (C-2), 41.56 (C-4), 33.13 (C-3), 33.08 (q, J = 4.1 Hz, C-6), 20.89 (C-7), 20.80 (C-8), 16.92 (C-9), 16.35 (q, J = 1.7 Hz, C-11). ^{19}F NMR (376 MHz, Chloroform-d) δ -74.83.

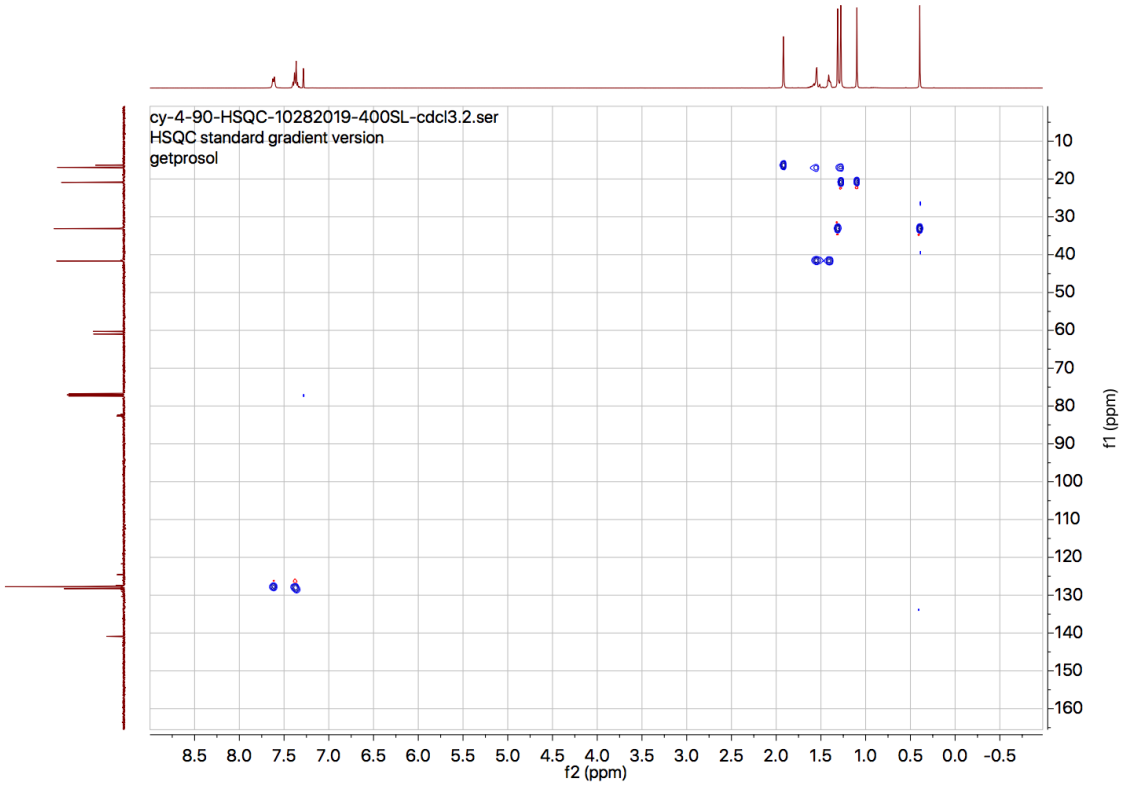
HMBC spectrum of compound **6**



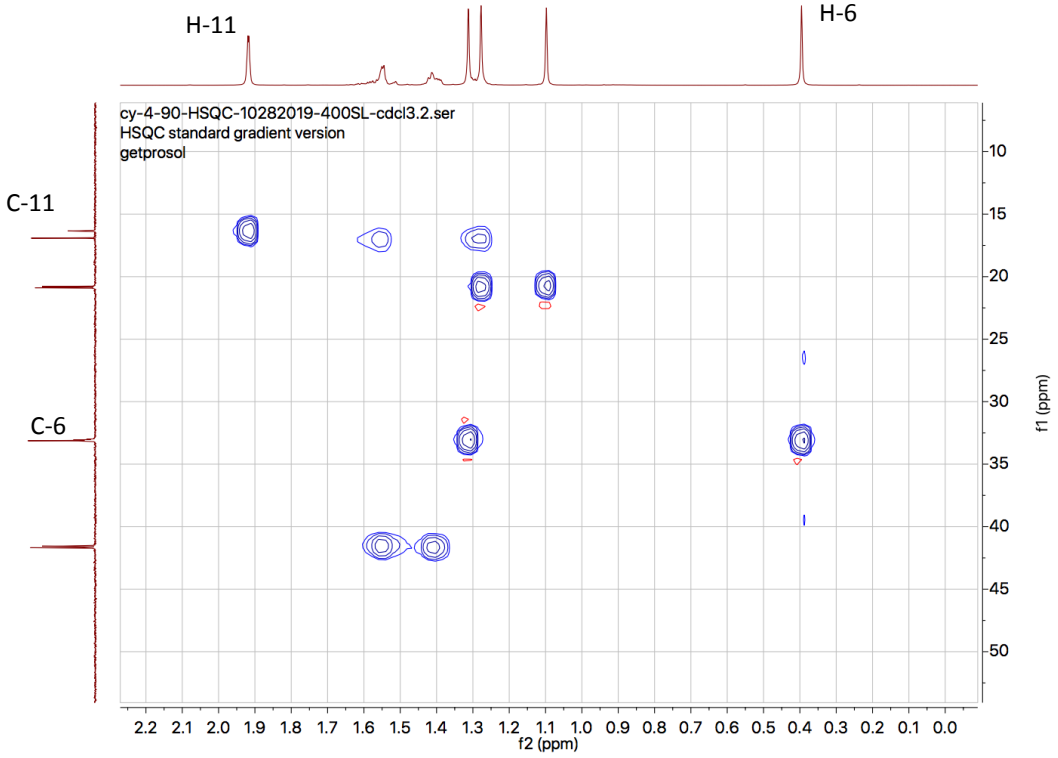
Zoom-in HMBC spectrum of compound **6**



HSQC spectrum of compound **6**

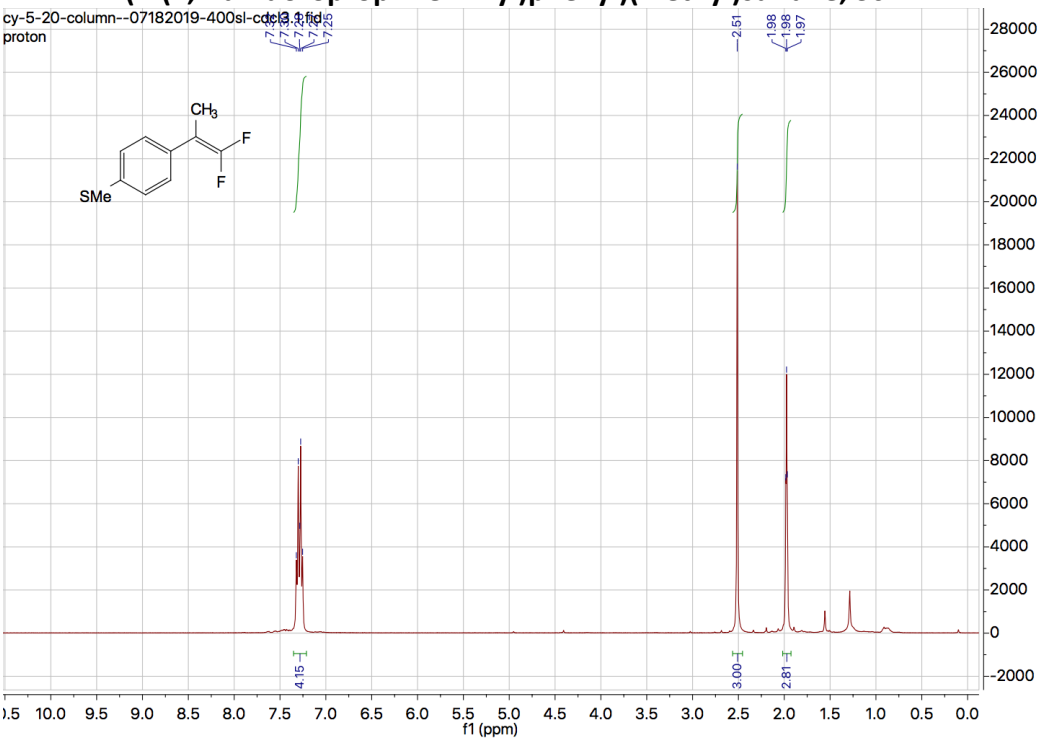


Zoom-in HSQC spectrum of compound **6**

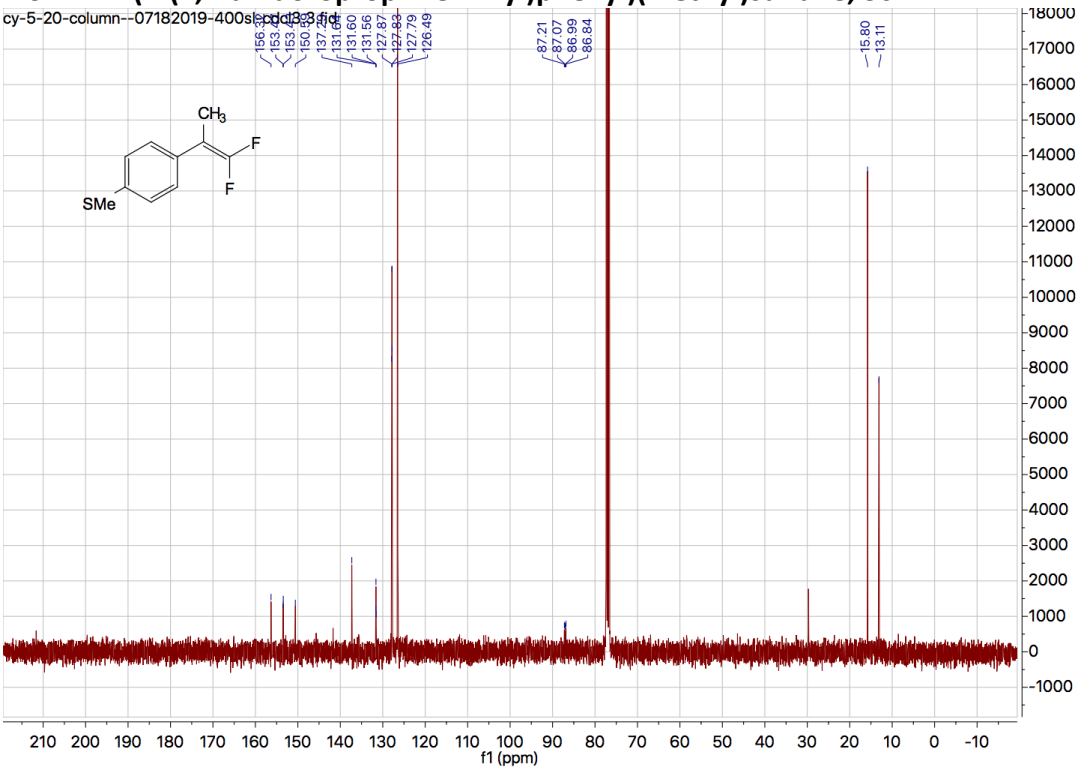


NMR Spectra

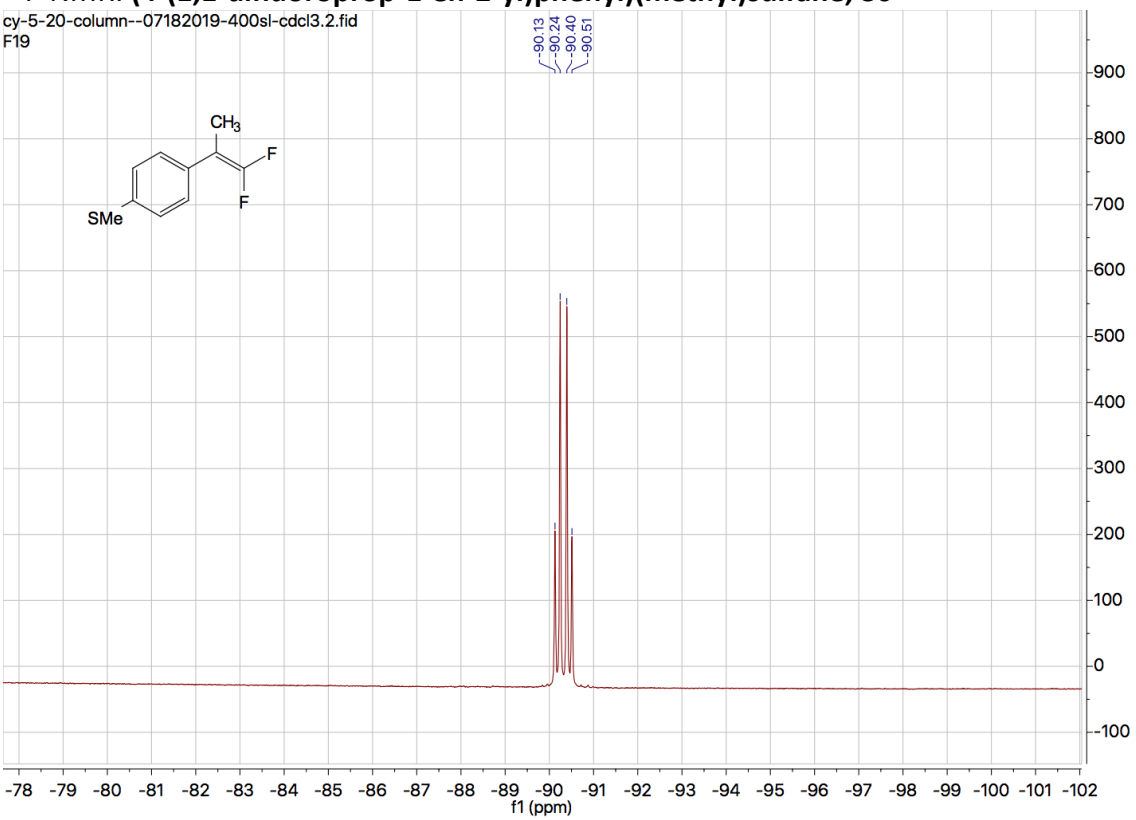
^{1}H-NMR: **(4-(1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane, 3c**



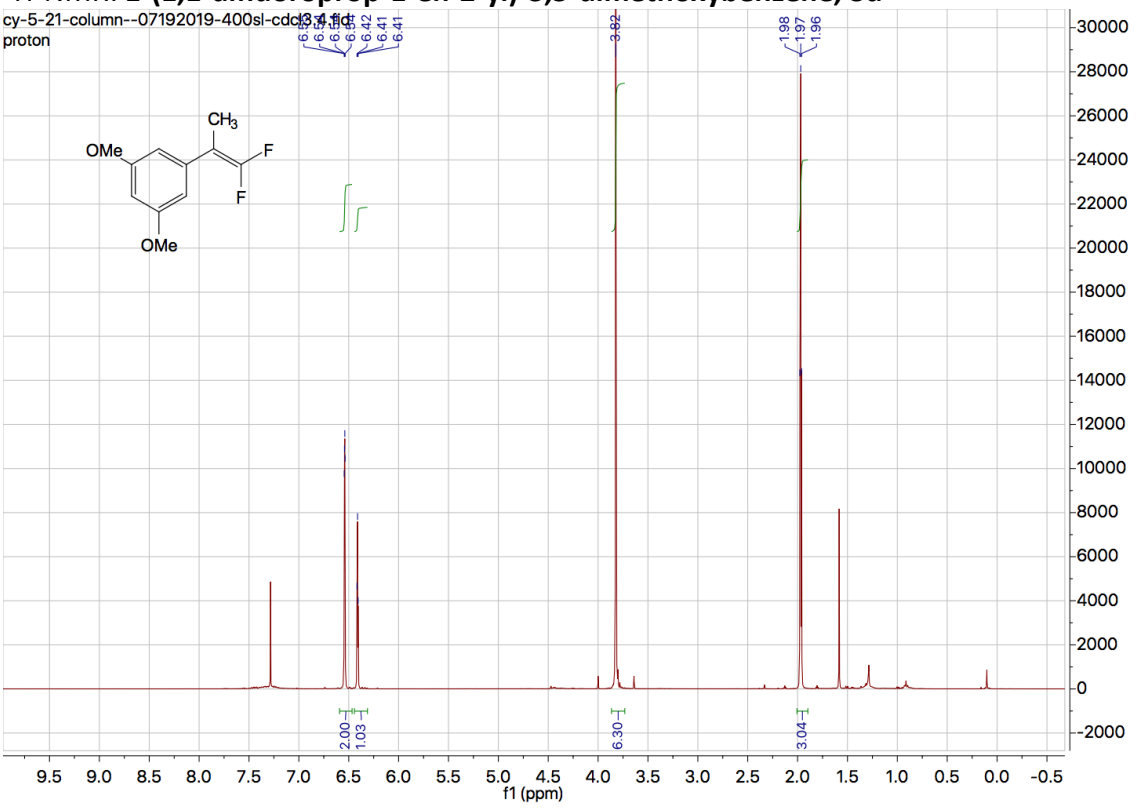
^{13}C-NMR: **(4-(1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane, 3c**



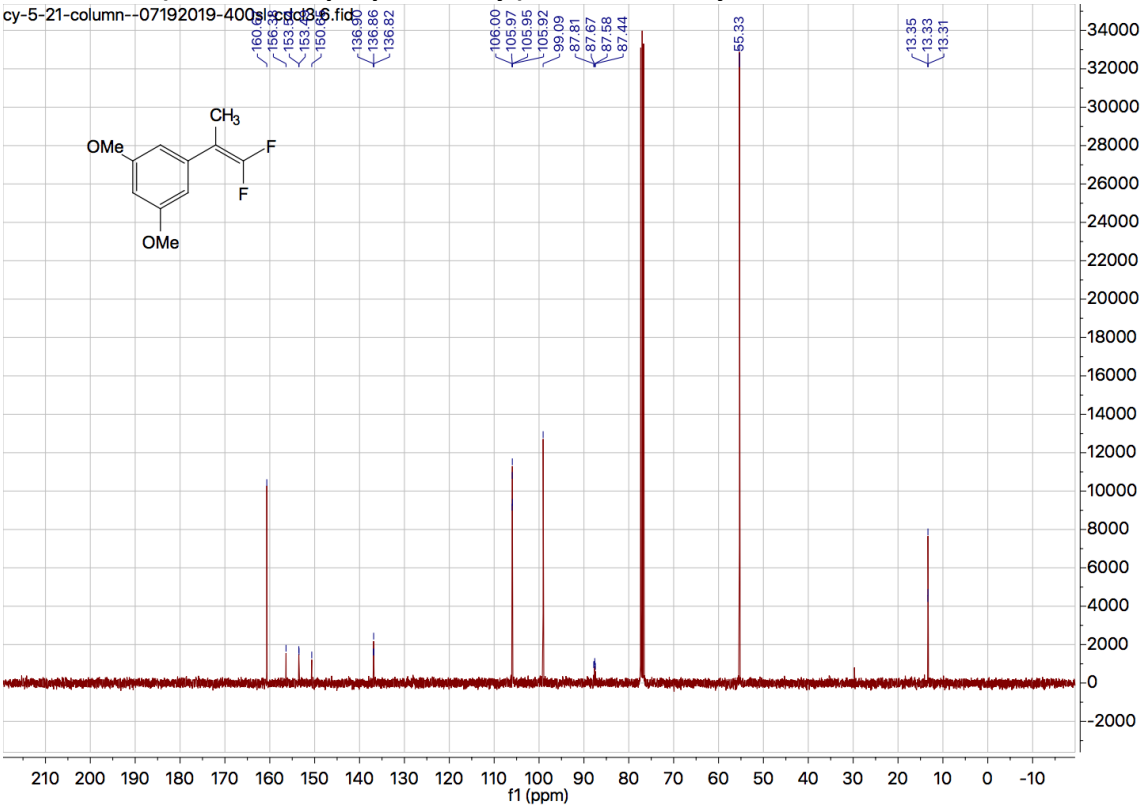
^{19}F-NMR: **(4-(1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane, 3c**



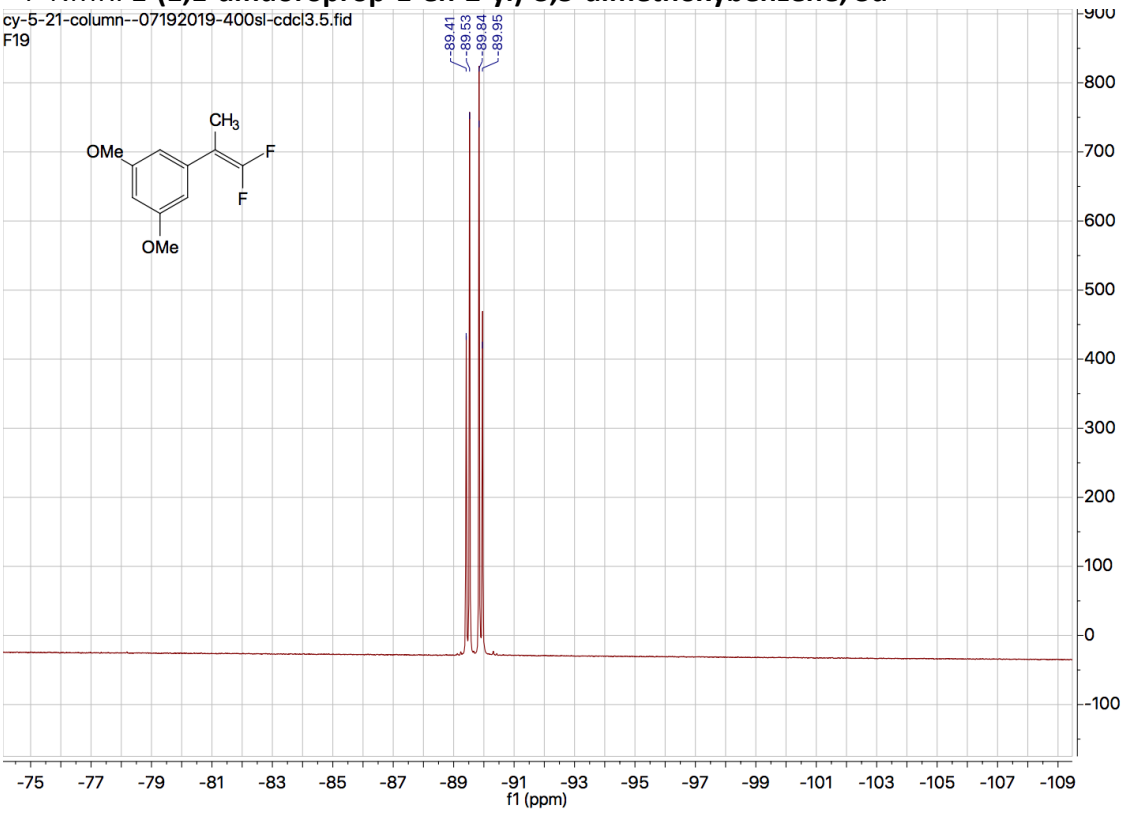
^{1}H-NMR: **1-(1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene, 3d**



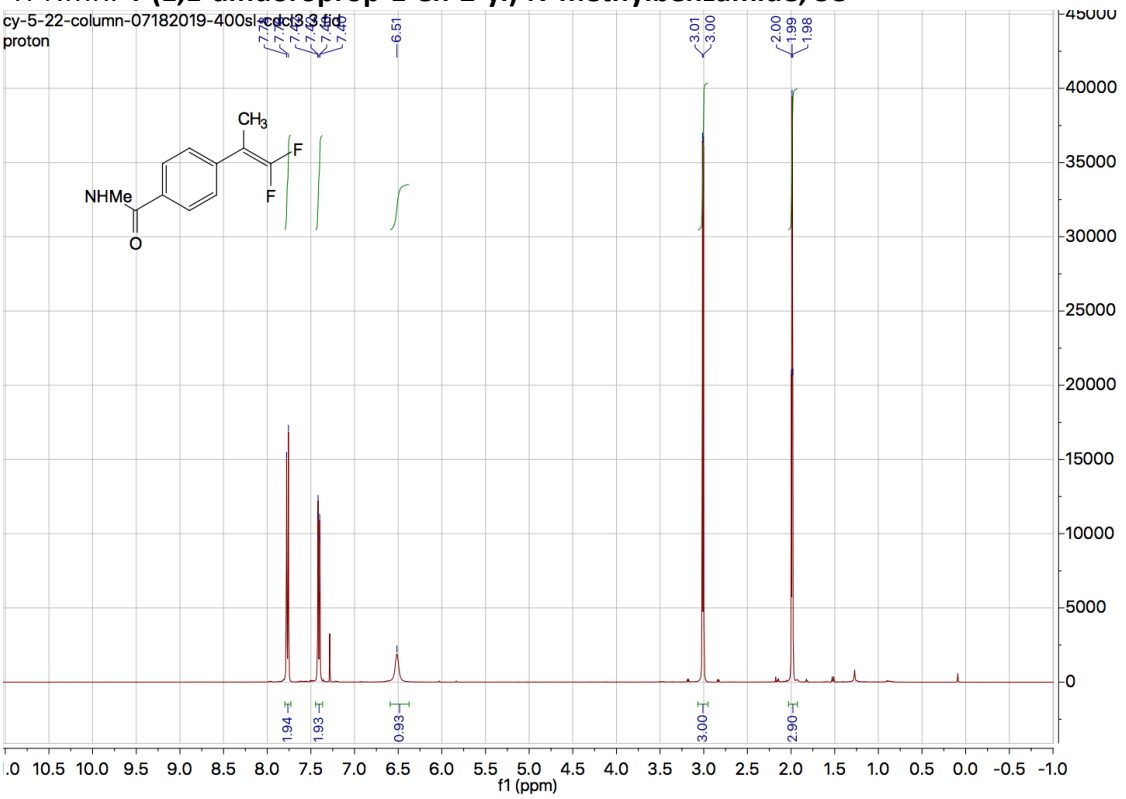
^{13}C-NMR: **1-(1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene, 3d**



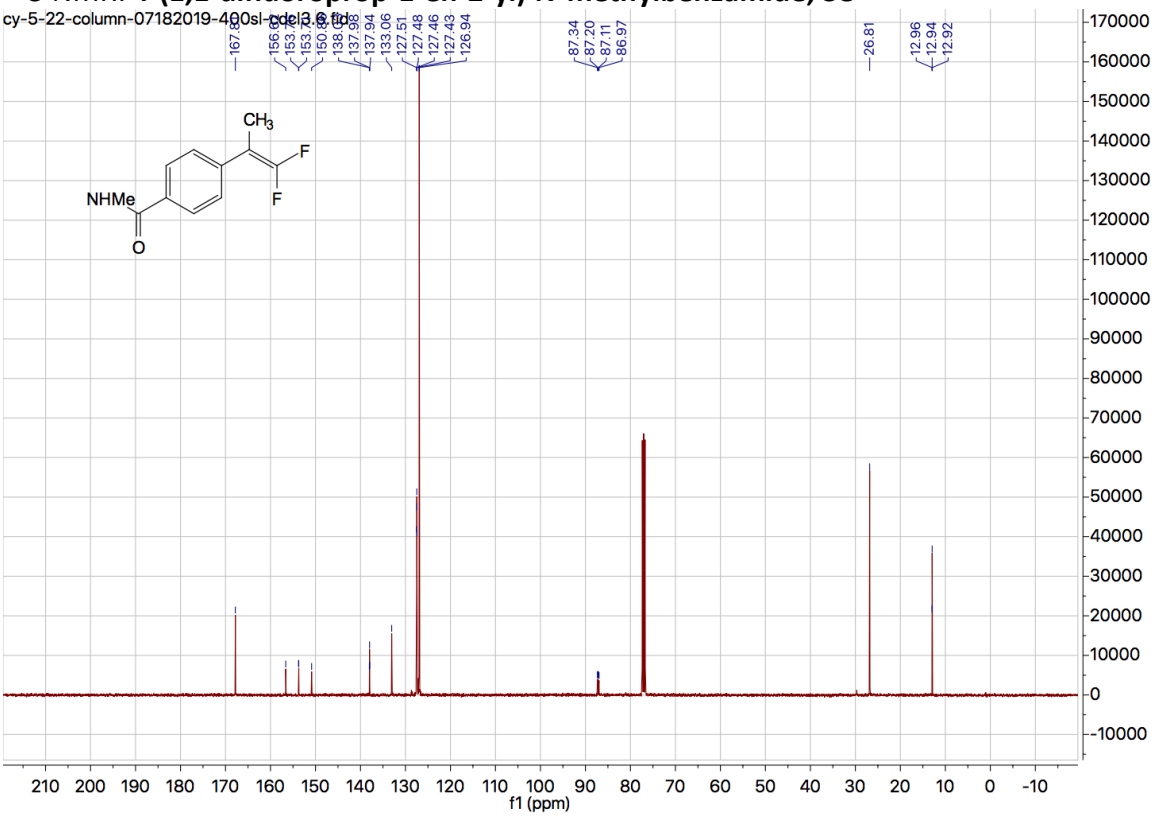
^{19}F-NMR: **1-(1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene, 3d**



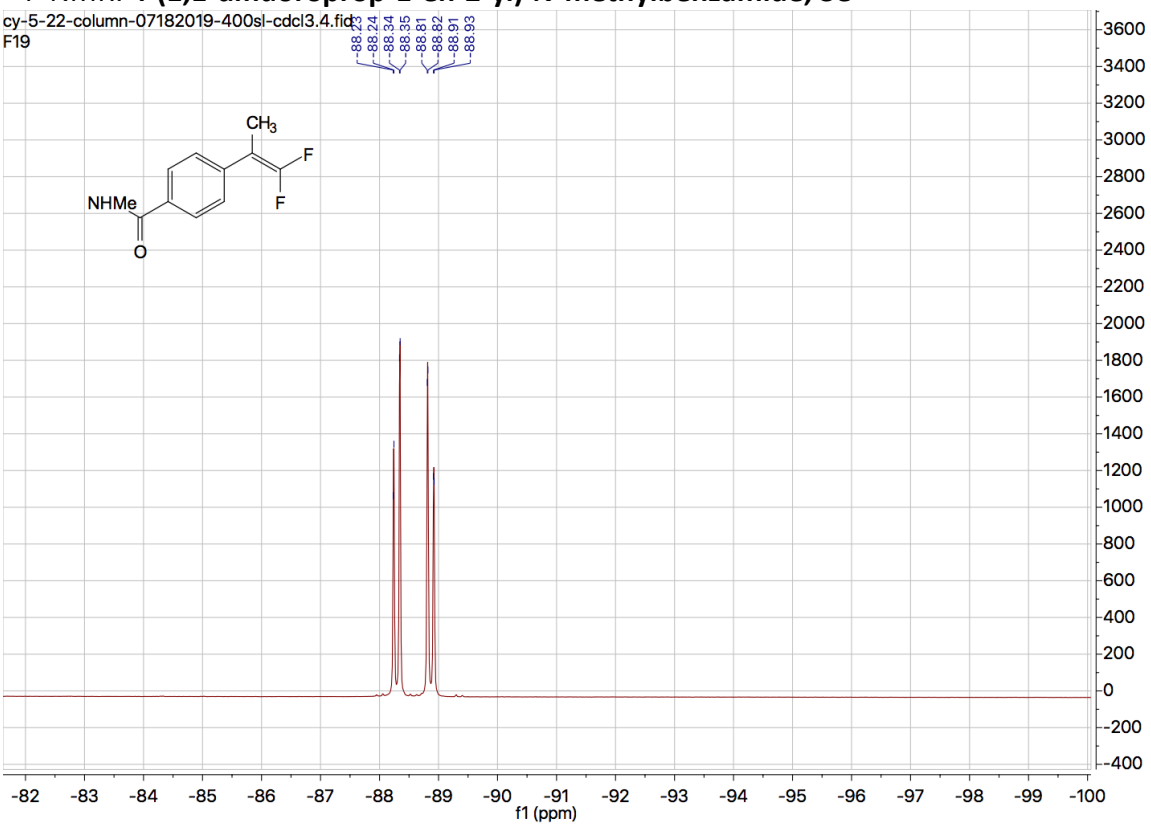
^{1}H-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*-methylbenzamide, 3e**



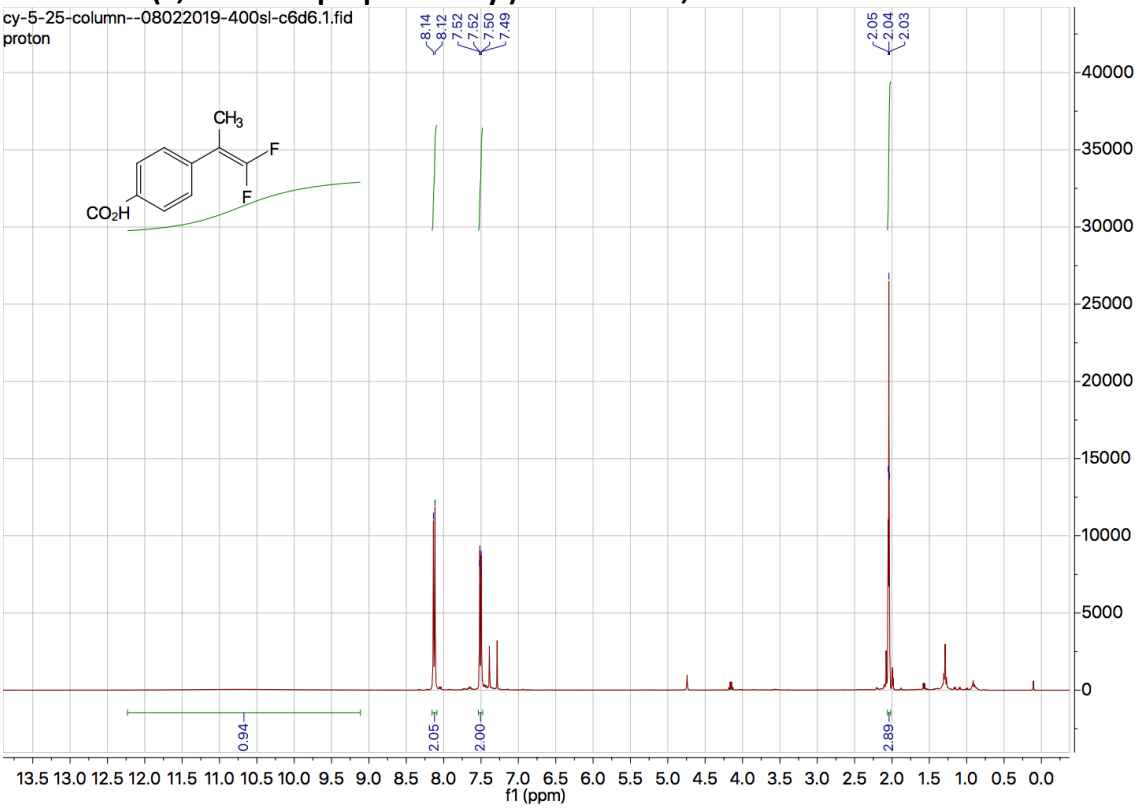
^{13}C-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*-methylbenzamide, 3e**



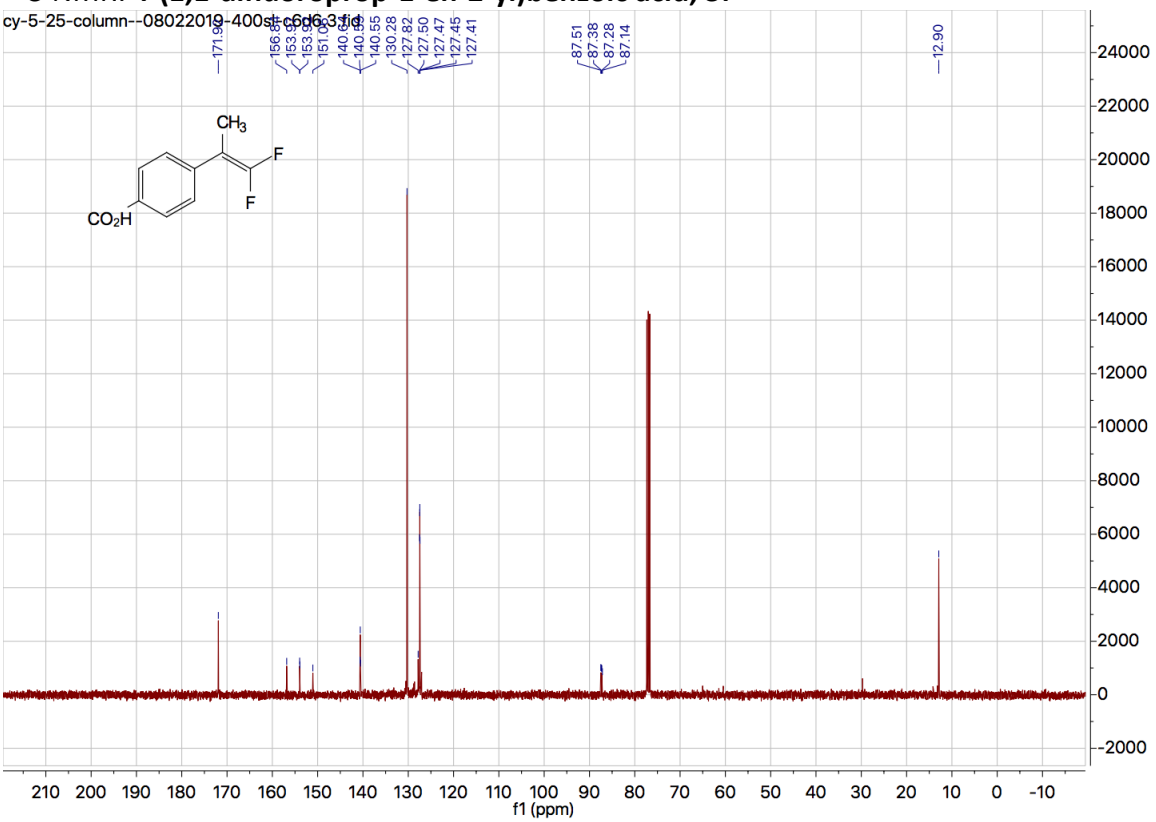
^{19}F-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*-methylbenzamide, 3e**



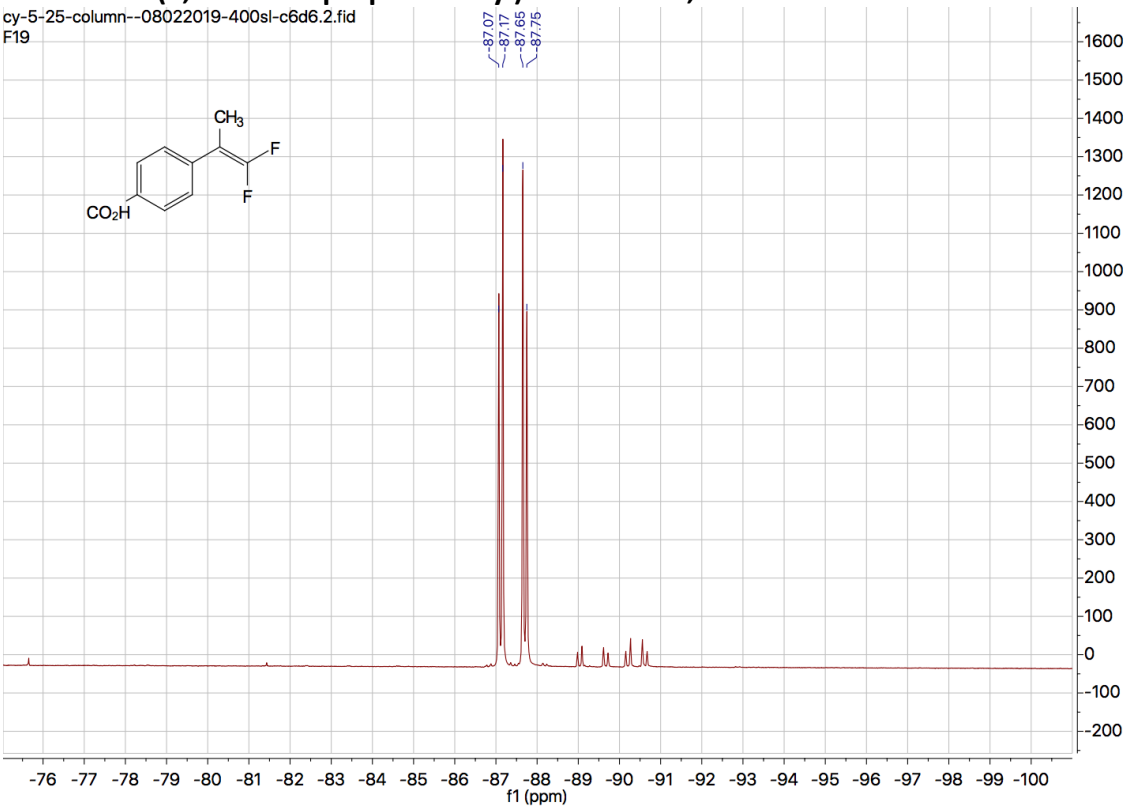
^{1}H-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzoic acid, 3f**



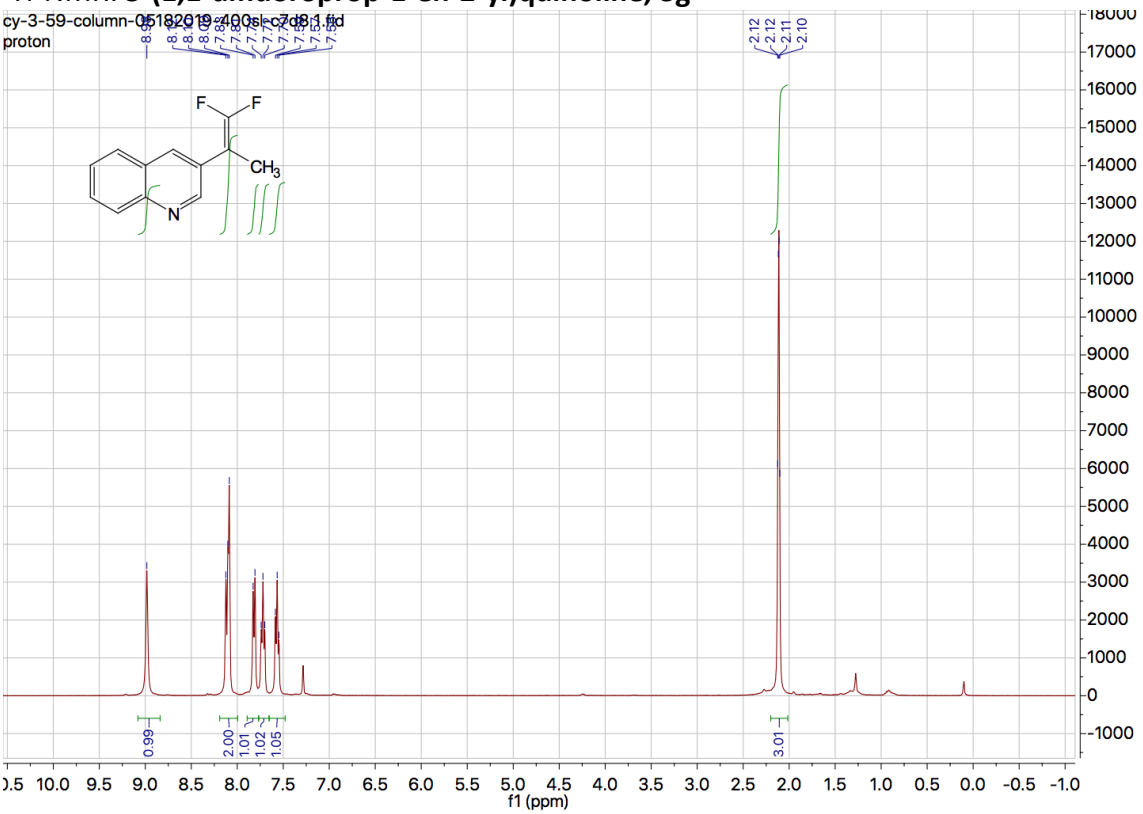
^{13}C-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzoic acid, 3f**



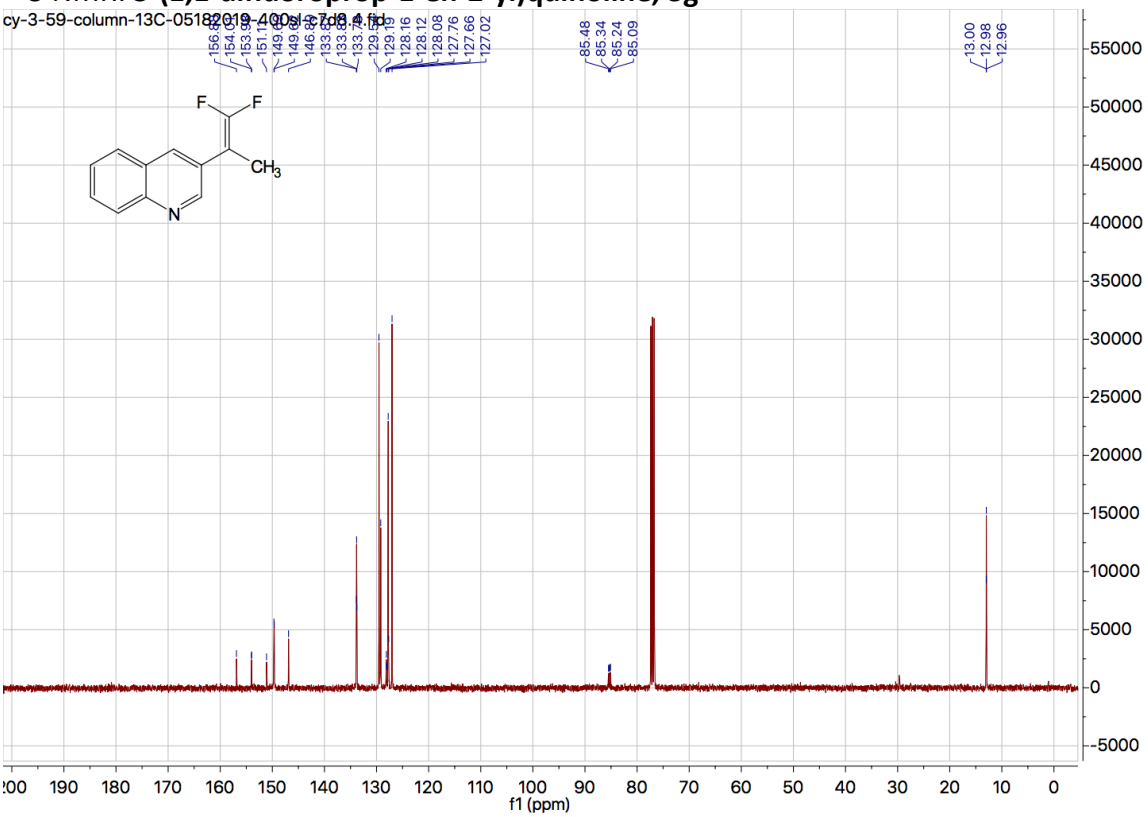
^{19}F-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzoic acid, 3f**



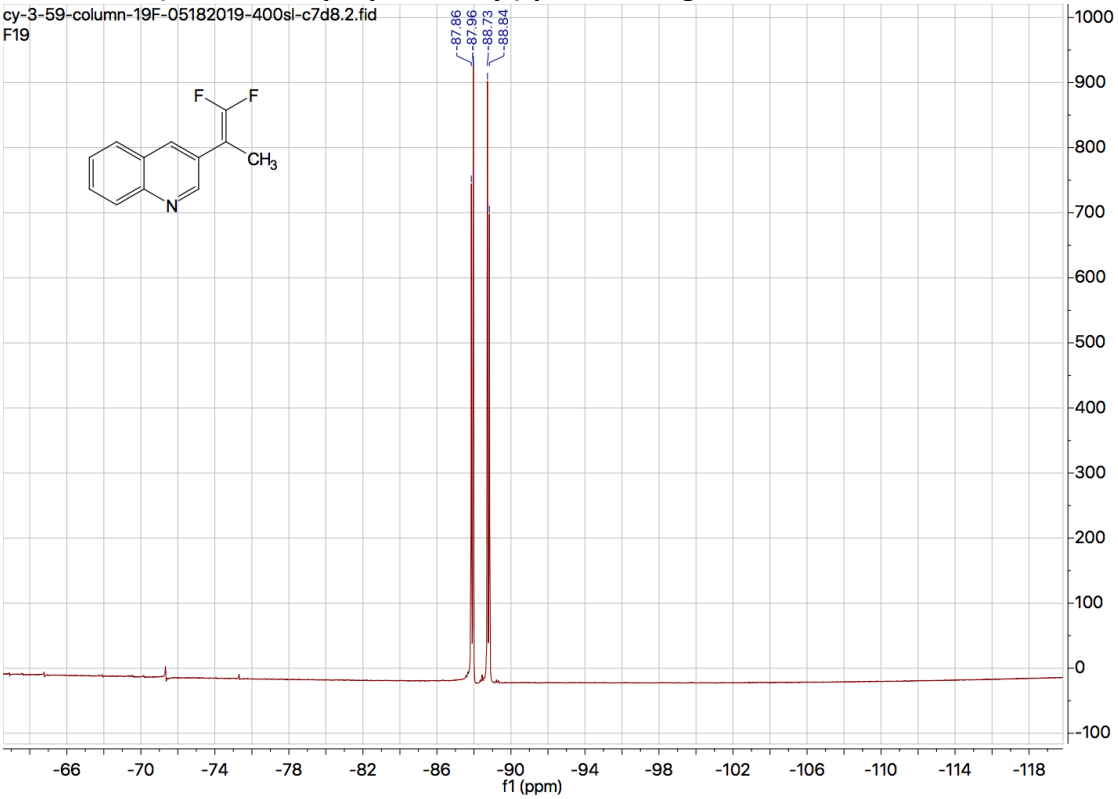
^{1}H-NMR: **3-(1,1-difluoroprop-1-en-2-yl)quinoline, 3g**



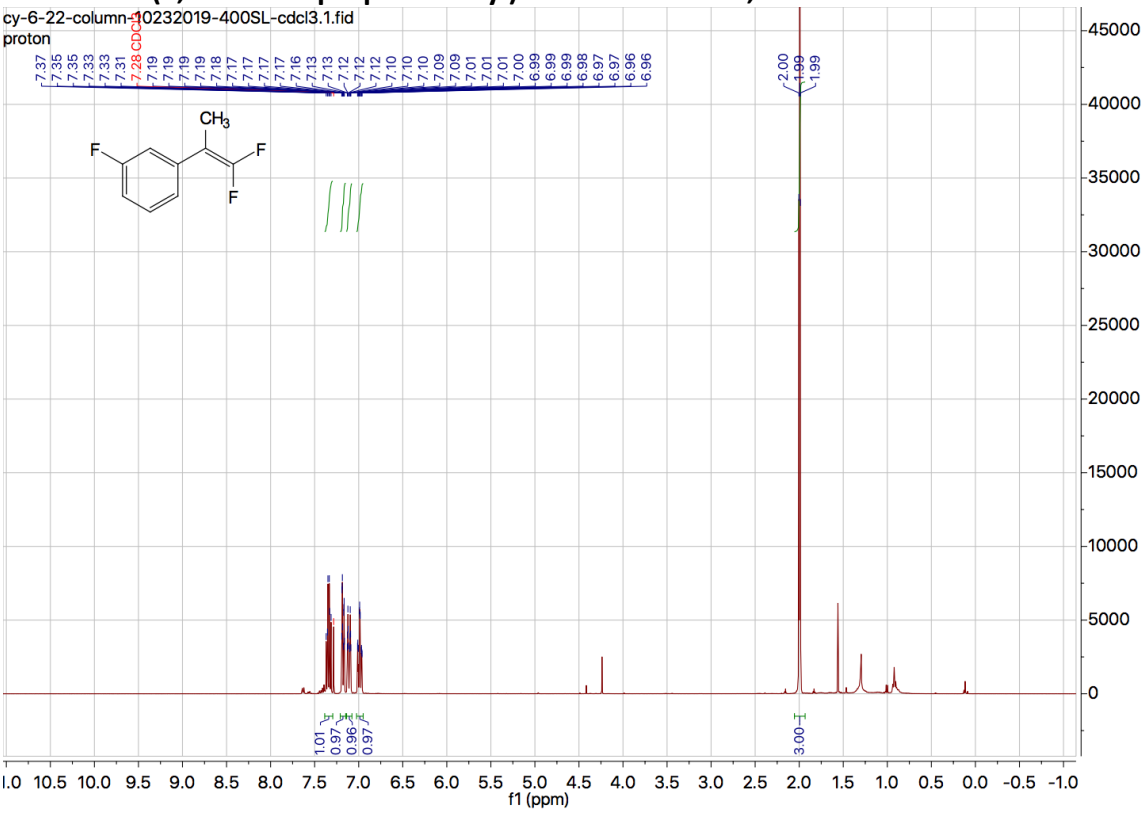
^{13}C-NMR: **3-(1,1-difluoroprop-1-en-2-yl)quinoline, 3g**



^{19}F-NMR: **3-(1,1-difluoroprop-1-en-2-yl)quinoline, 3g**



^{1}H-NMR: **1-(1,1-difluoroprop-1-en-2-yl)-3-fluorobenzene, 3l**



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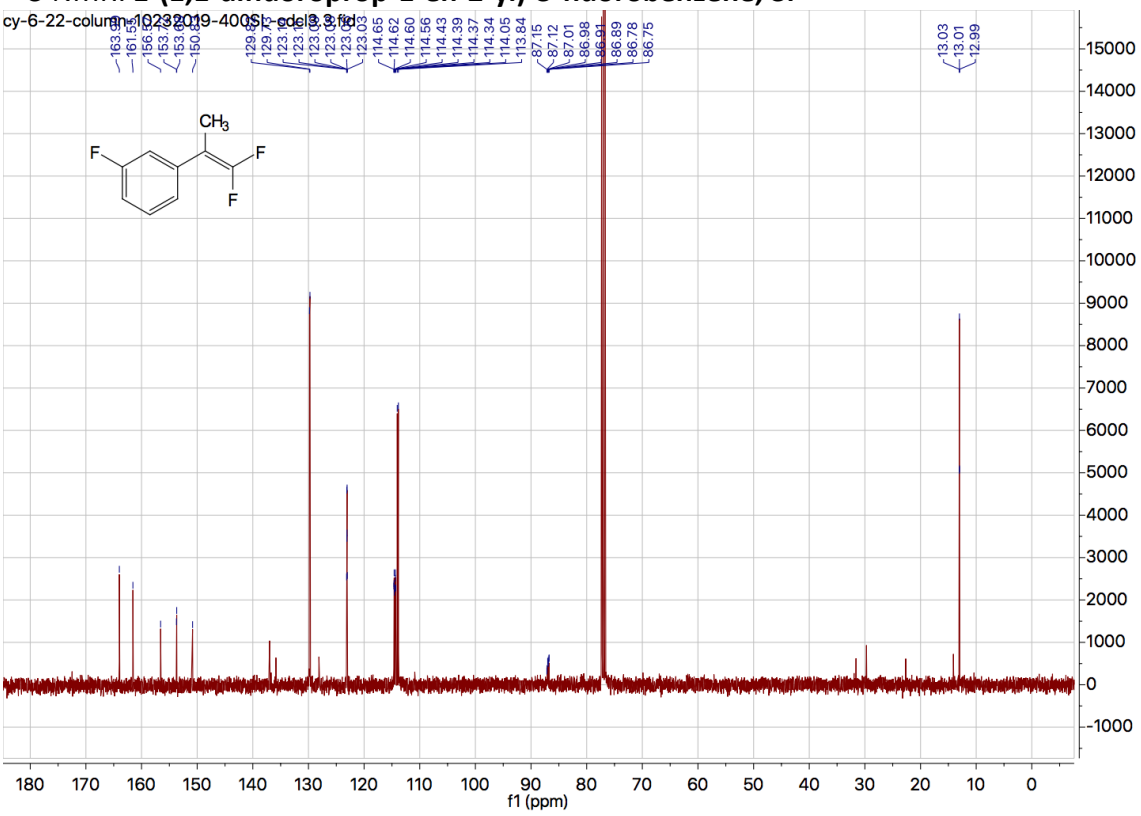
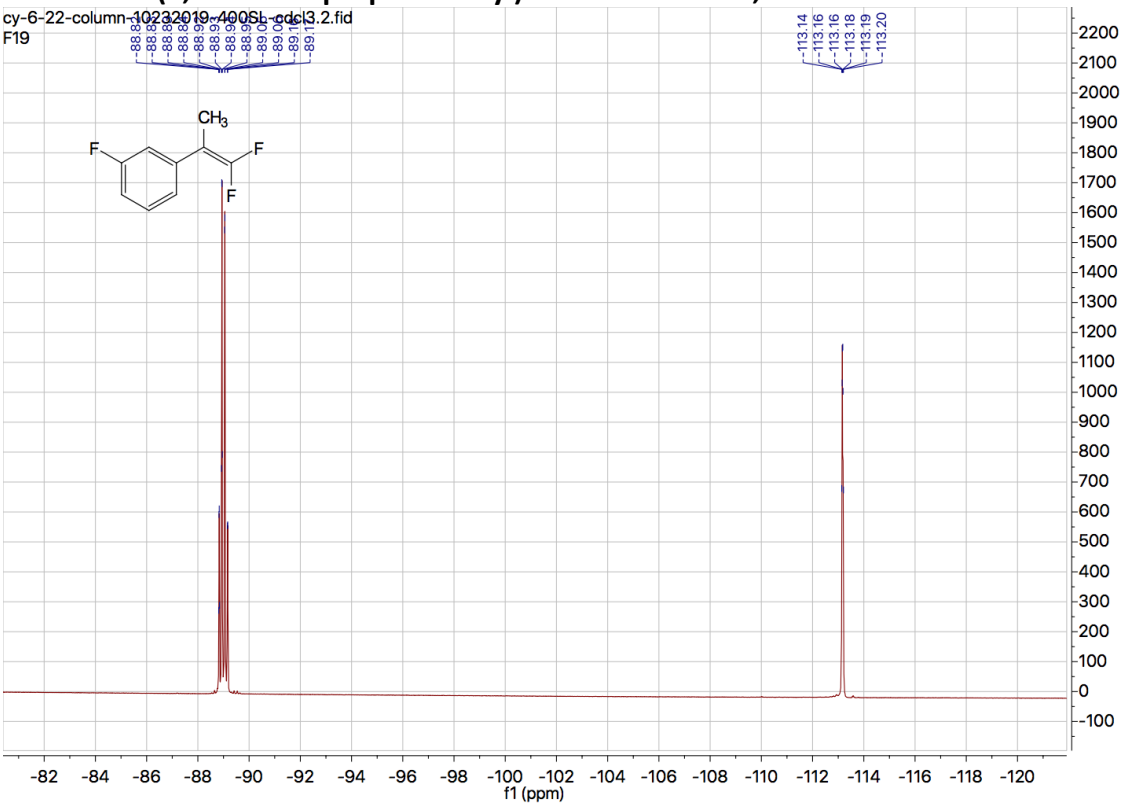
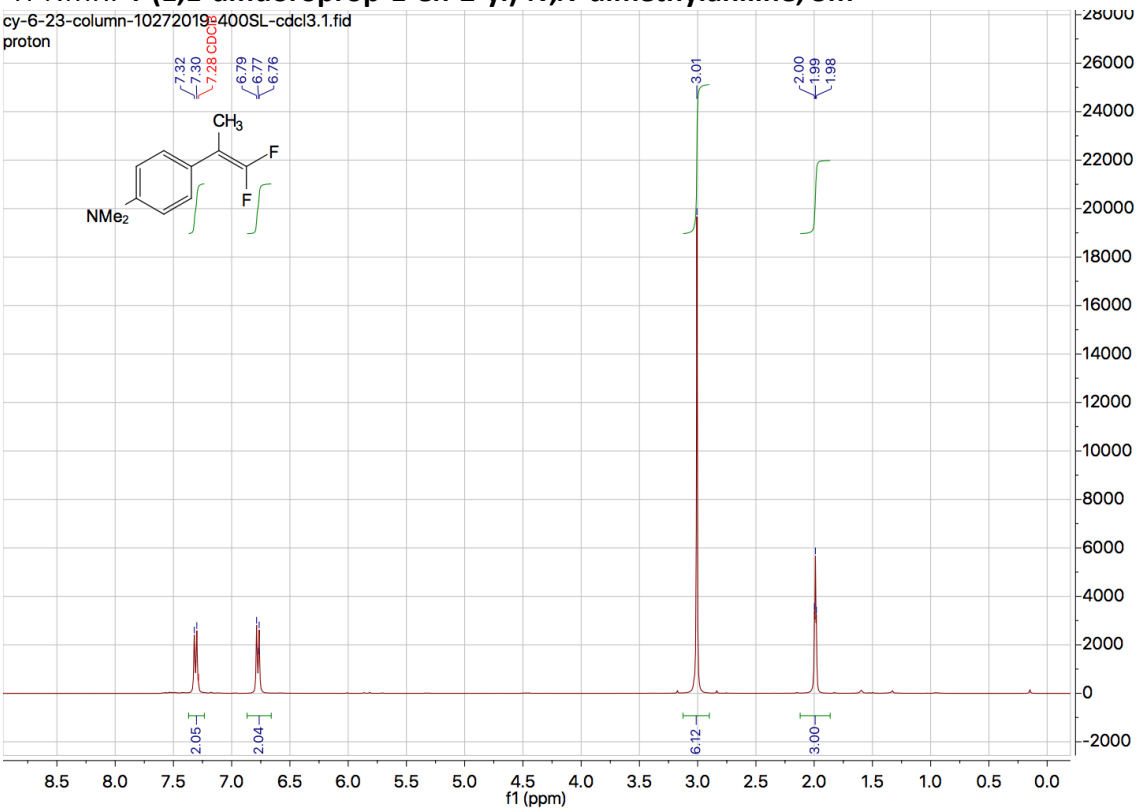


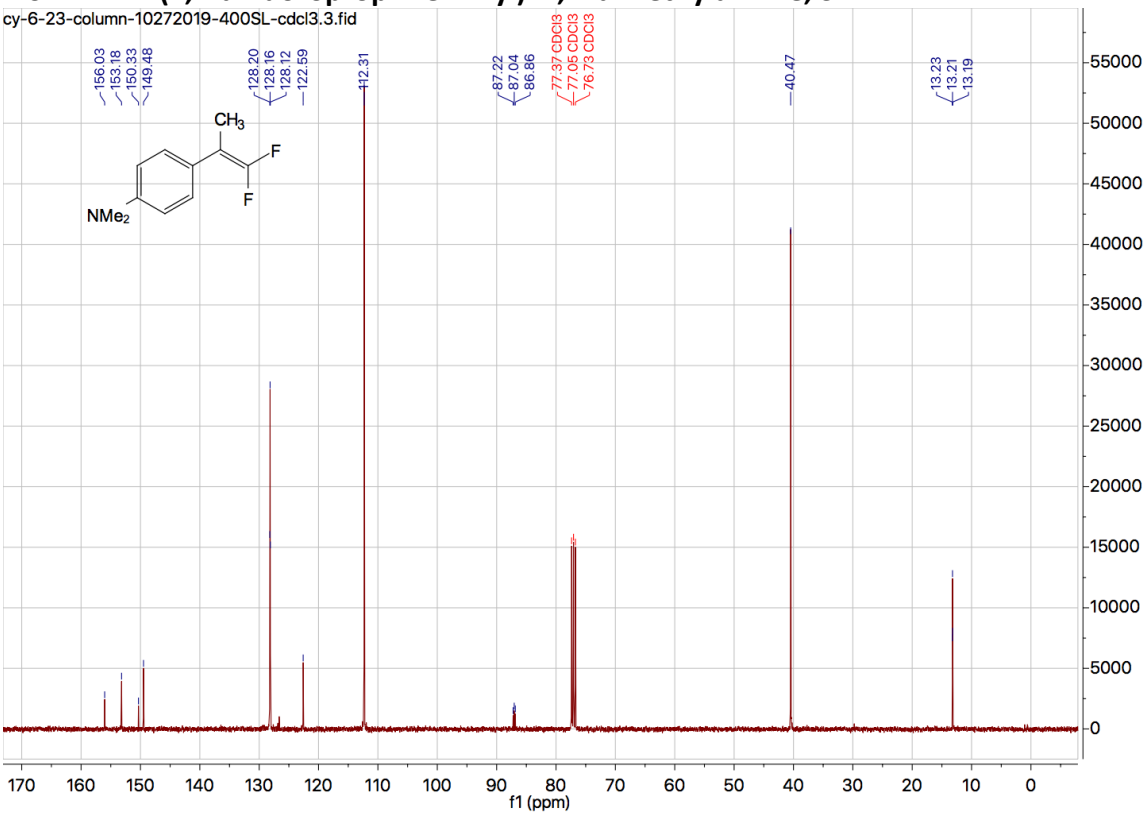
^{19}F-NMR: **1-(1,1-difluoroprop-1-en-2-yl)-3-fluorobenzene, 3l**



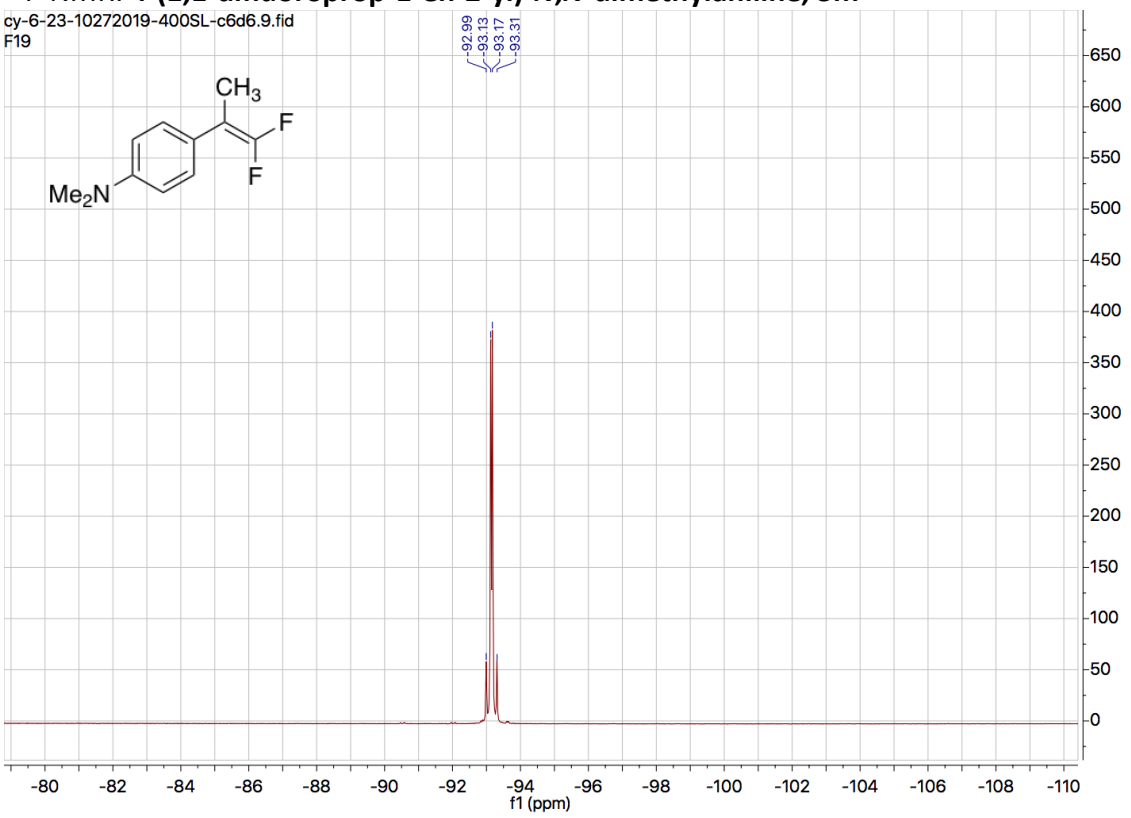
^{1}H-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*,*N*-dimethylaniline, 3m**



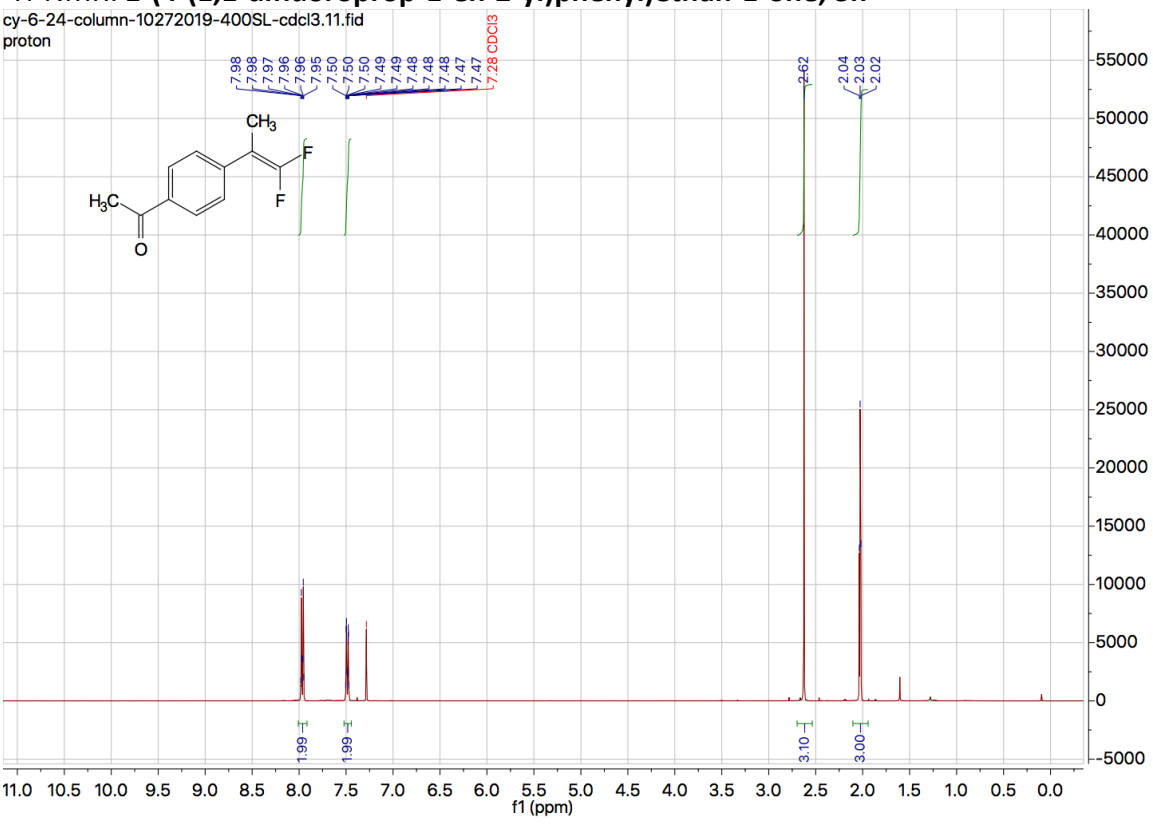
^{13}C-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*,*N*-dimethylaniline, 3m**



^{19}F-NMR: **4-(1,1-difluoroprop-1-en-2-yl)-*N*,*N*-dimethylaniline, 3m**



^{1}H-NMR: **1-(4-(1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one, 3n**



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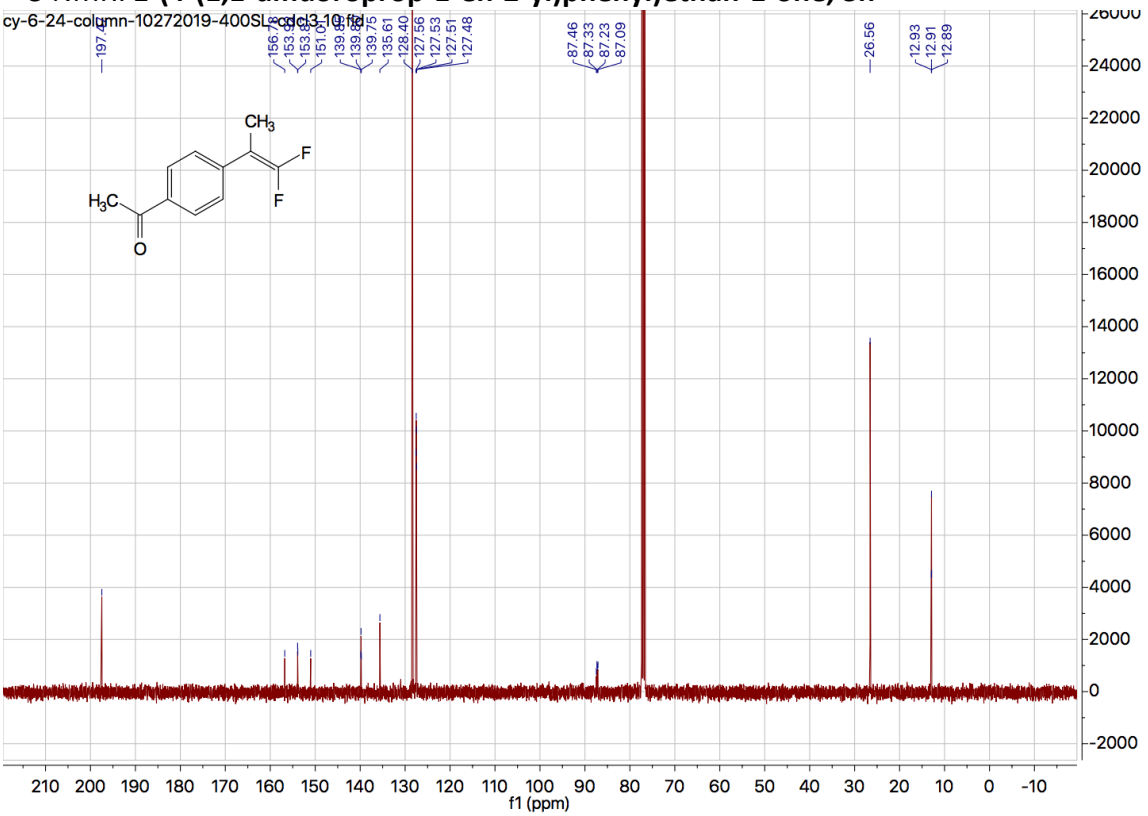
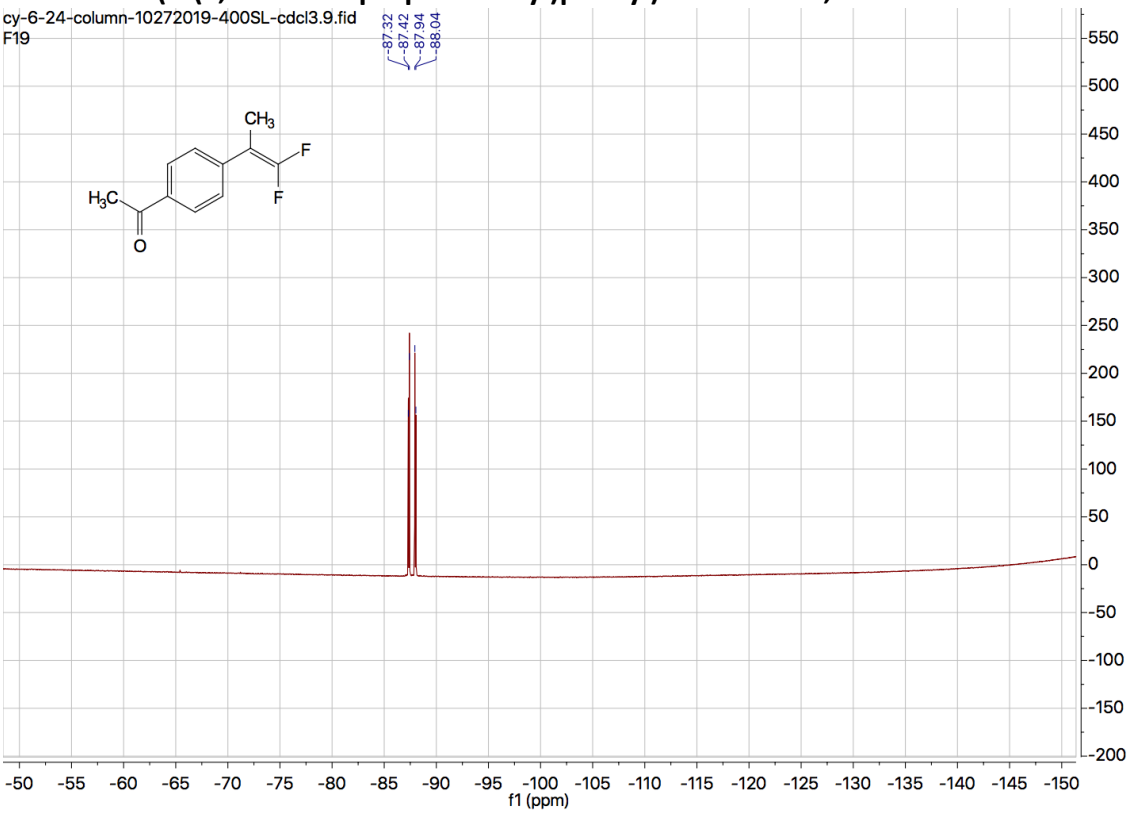
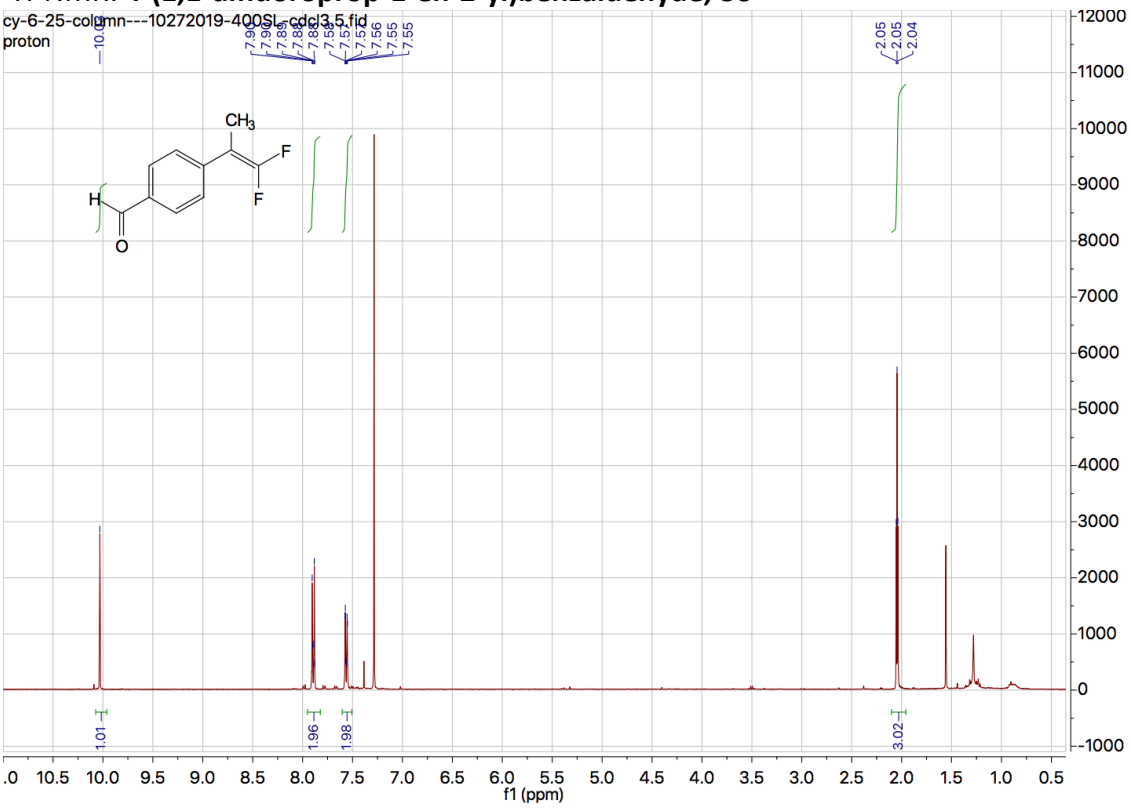


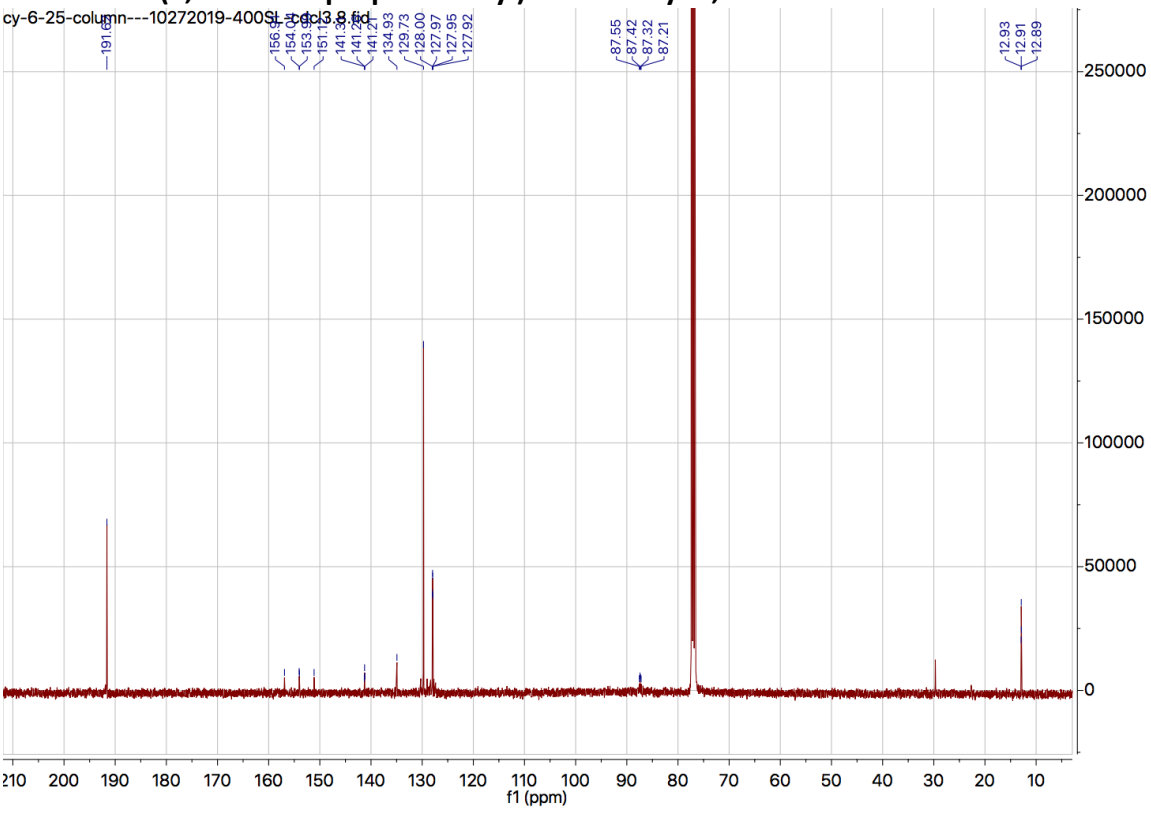
^{19}F-NMR: **1-(4-(1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one, 3n**



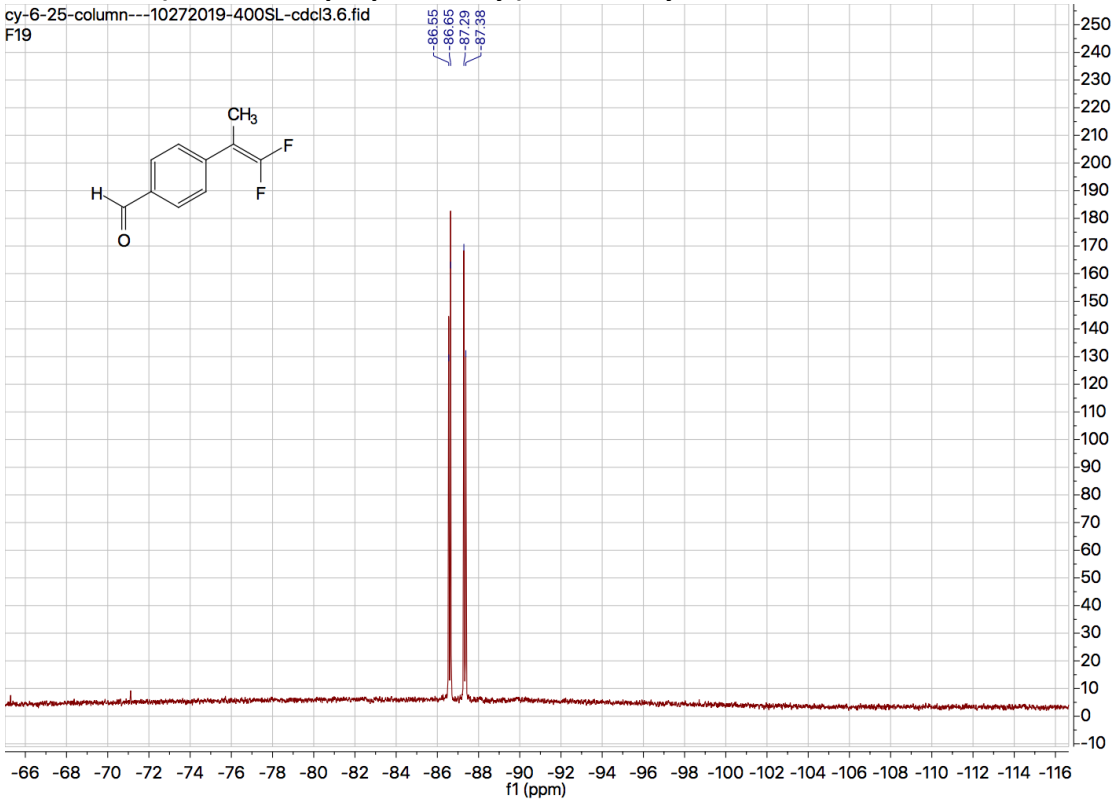
^{1}H-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzaldehyde, 3o**



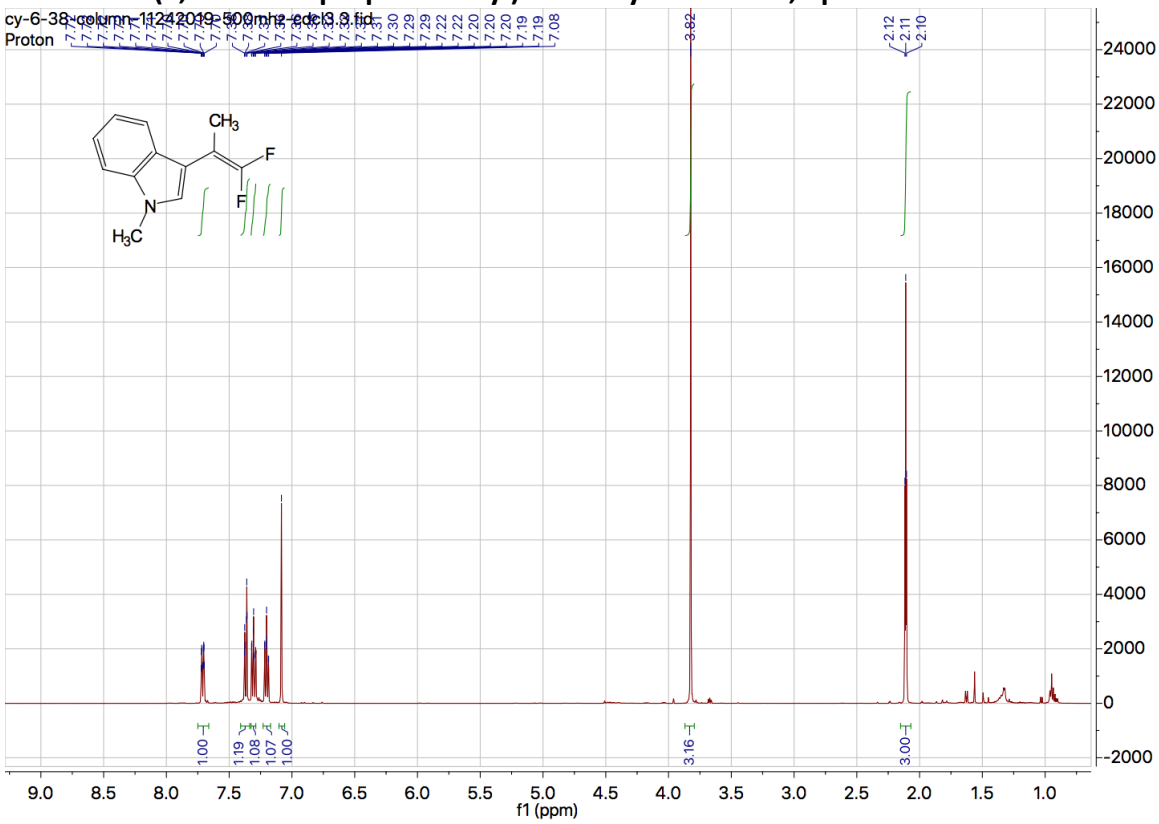
^{13}C-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzaldehyde, 3o**



^{19}F-NMR: **4-(1,1-difluoroprop-1-en-2-yl)benzaldehyde, 3o**



^{1}H-NMR: **3-(1,1-difluoroprop-1-en-2-yl)-1-methyl-1*H*-indole, 3p**



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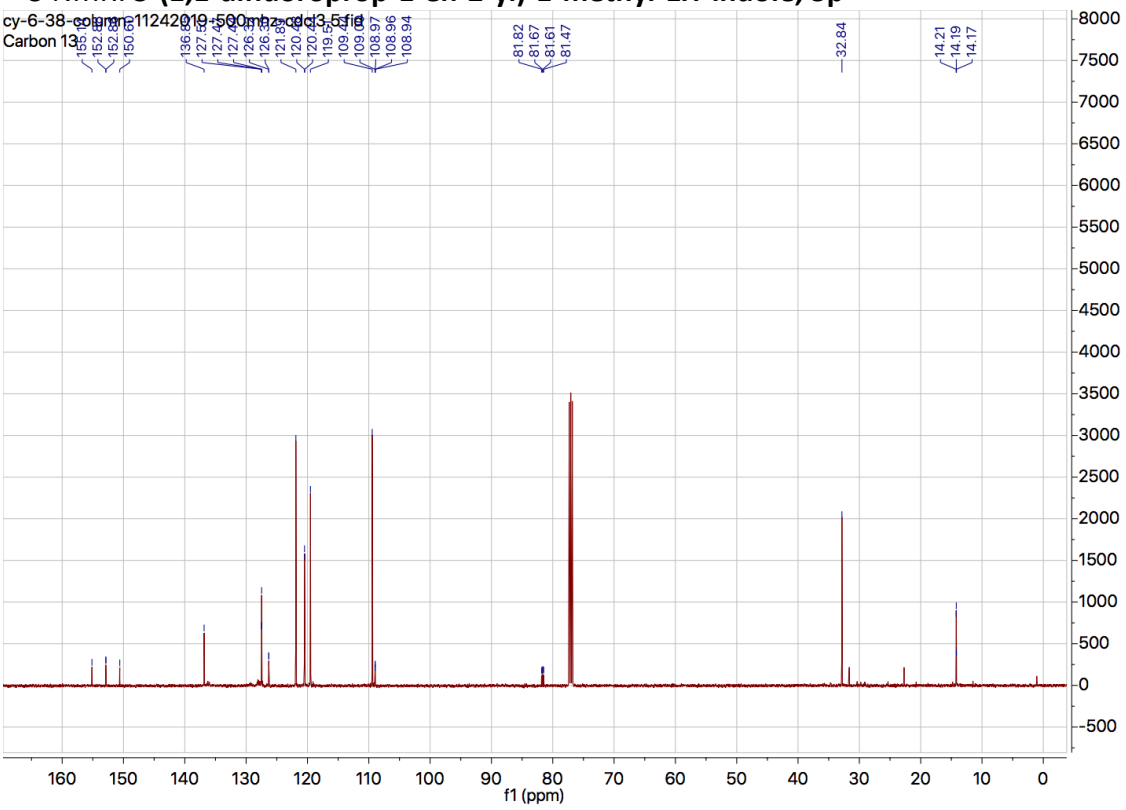
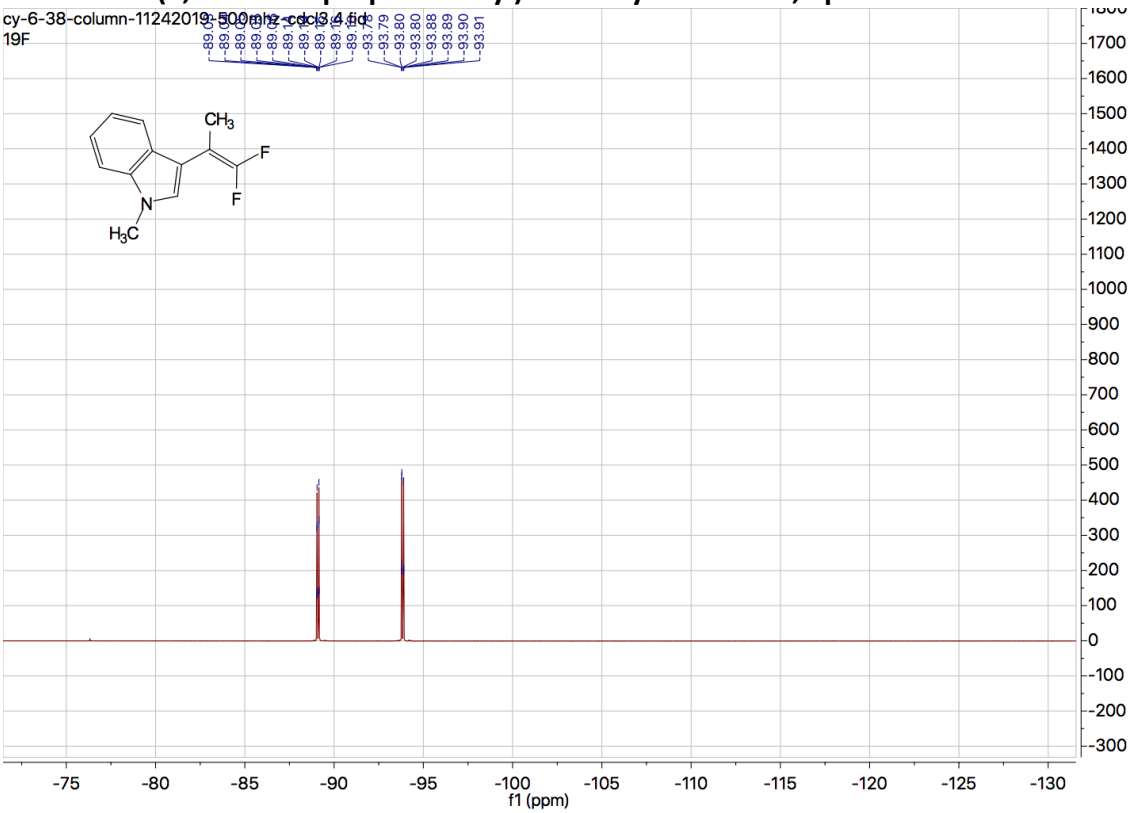
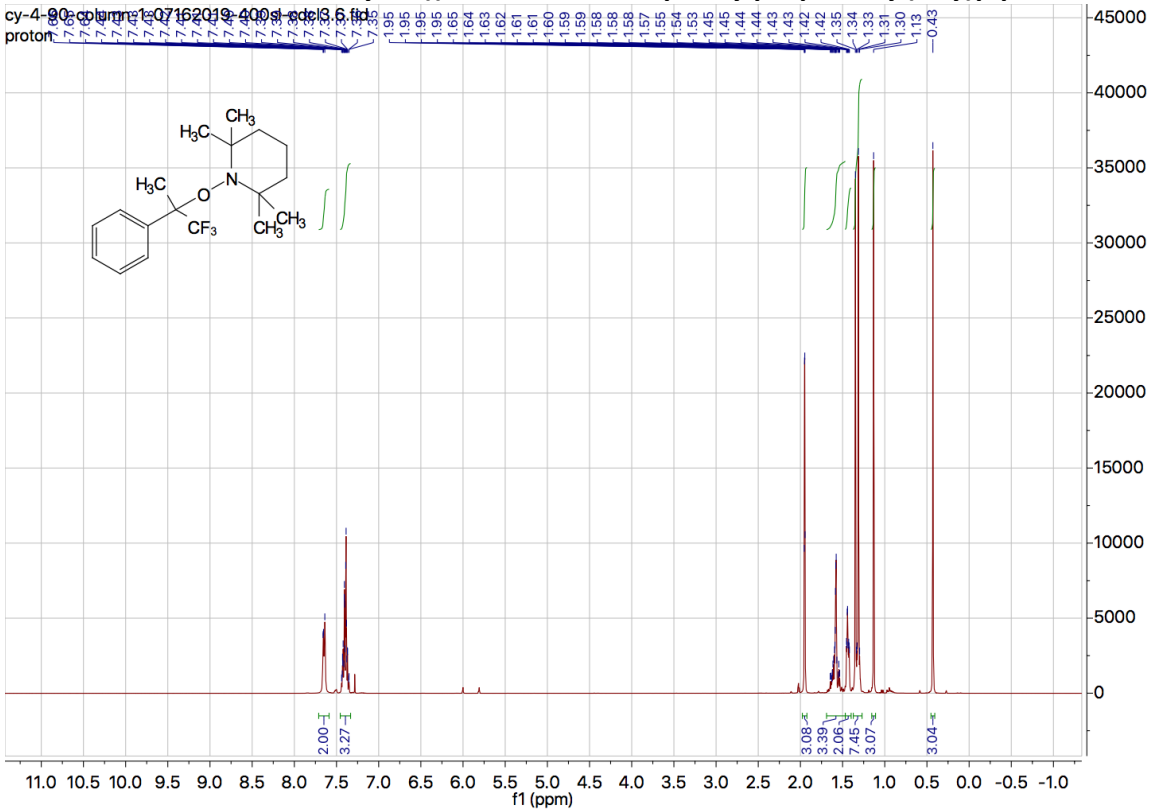


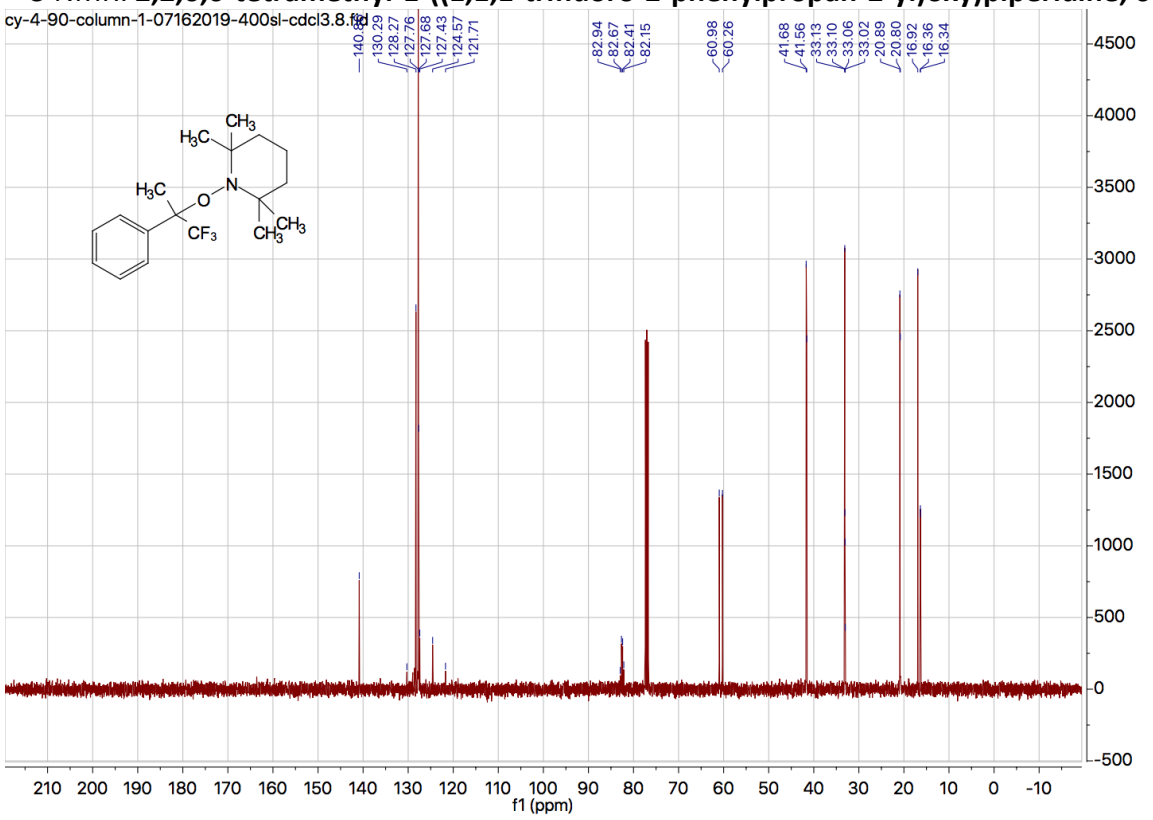
^{19}F-NMR: **3-(1,1-difluoroprop-1-en-2-yl)-1-methyl-1*H*-indole, 3p**



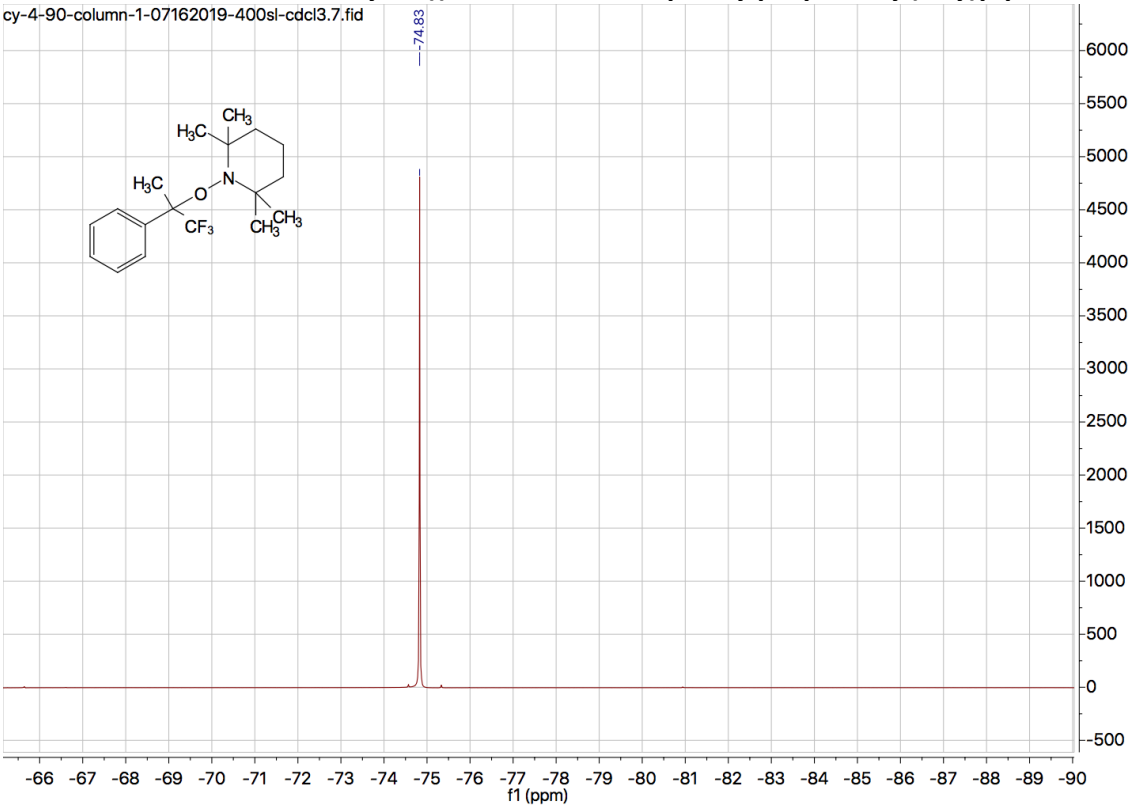
^{1}H-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**



^{13}C-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**



^{19}F-NMR: **2,2,6,6-tetramethyl-1-((1,1,1-trifluoro-2-phenylpropan-2-yl)oxy)piperidine, 6**



Crystal Structure of Compound **6**

Table S1. Crystal, intensity, collection, and refinement data of **6**

lattice	Orthorhombic
formula	C18 H26 F3 N O
formula weight	329.40
space group	$P\,2_12_12_1$
a/Å	6.3624(3)
b/Å	10.6132(4)
c/Å	25.6176(11)
α/°	90
β/°	90
γ/°	90
V/Å^3	1729.84 (13)
Z	4
temperature (K)	200
radiation (λ, Å)	0.71073
ρ (calcd.) g cm^{-3}	1.265
μ (Mo Kα), mm^{-1}	0.099
θ max, deg.	30.518
no. of data collected	28510
no. of data	5290
no. of parameters	213
R_1 [$I > 2\sigma(I)$]	0.0414
wR_2 [$I > 2\sigma(I)$]	0.0981
R_1 [all data]	0.0541
wR_2 [all data]	0.1069
GOF	1.029
R_{int}	0.061

The structure of **6** has been confirmed by single-crystal X-ray diffraction (Figure 2). The fact that the CF_3 group is not disordered suggests an attractive interaction between one of its F's and something else. However, the shortest distance between an F and the carbon of the closest methyl (3.143(3) Å) is long in comparison with the F–C distances in compounds reported to have intramolecular [C–F•••H-C] contacts: for example, the F–C distance is 2.996(3) Å in **7** [20] and 2.963(6) Å in **8** (Figure 3).[21] The interactions in **7** and **8** are reflected in the ^{19}F–^{1}H and ^{19}F–^{13}C coupling constants that are observed in both cases — but we see no such coupling in **6**. The interaction between the CF_3 and the closest piperidine methyl in **6** is therefore insignificant.

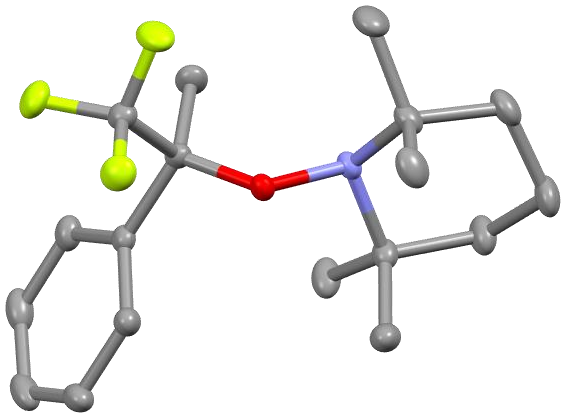
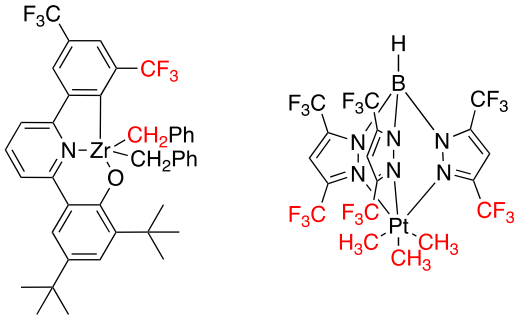


Figure S1. Molecular structure of TEMPO-adduct **6**. Hydrogen atoms are omitted for clarity.



7 **8**

Figure S2. Compounds reported to have intramolecular [C–F•••H-C] contacts.

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