



Supporting Information

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SUPPORTING INFORMATION**Fluorine-Directed Diastereoselective Iodocyclizations**

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General Information

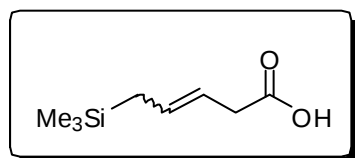
^1H NMR spectra were recorded in deuterated solvents using Bruker DPX200, DPX400, AV400 and AVC500 spectrometers, calibrated using residual undeuterated solvent as an internal reference. ^{13}C NMR spectra were recorded in deuterated solvents using Bruker DPX200, DPX400, AV400 and AVC500 spectrometers. ^{19}F spectra were recorded on a AV400 spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet. NMR were processed in either MestRe-C or ACD/SpecManager. IUPAC names were obtained using the ACD/I-lab service. Mass spectra were recorded on Micromass GCT (CI), Autospec-oeTof instruments. Optical rotations were determined on a Perkin Elmer 241 polarimeter in a 1dm cell. $[\alpha]_{\text{D}}$ values are given in $10^{-1}\text{deg cm}^2 \text{g}^{-1}$. IR spectra were recorded as thin films on NaCl plates in solution in CHCl_3 on a Bruker Tensor 27 FT-IR spectrometer. Absorptions are measured in wavenumbers and only peaks of interest are reported. All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of argon or nitrogen. Solvents were dried and purified before use according to standard procedures. All reactions were monitored by TLC using Merck Kiesegel 60 F₂₅₄ plates. Visualisation of the reaction components was achieved using U.V fluorescence (254 nm) and KMnO_4 stain. Silica gel chromatography was carried out over Merck silica gel C60 (40-60 μm).

A. SYNTHESIS OF ORGANOSILANES AND ALLYLIC FLUORIDES 1a-1d

For the synthesis of allylic fluorides (+)-**1a** and (+)-**1b** see the Supporting Information of: M. Tredwell, K. Tenza, M^a Carmen Pacheco, V. Gouverneur, *Org. Lett.* **2005**, 7, 4495-4497.

A. I. Synthesis of 3-fluoropent-4-enoic acid ($\pm$)-1c

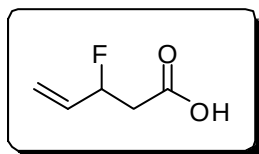
A. I. 1 Synthesis of 5-(trimethylsilyl)pent-3-enoic acid:



To a solution of 3-butenic acid (2.0 mmol, 0.17 mL) and allyltrimethylsilane (6.0 mmol, 0.95 mL) in DCM (6 mL) at reflux was added Hoveyda-Grubbs 2nd generation catalyst (3 mol%, 38 mg). The reaction was allowed to stir at reflux for 24hrs, after cooling to room temperature the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 60/40) to yield a yellow oil (307 mg, 89%); *E/Z* 3:1. NMR data of the mixture of *E/Z* isomers: ^1H NMR (400 MHz, CDCl_3): δ = 5.70-5.62 (m, 1H_Z), 5.62-5.54 (m, 1H_E), 5.46 (dt, J = 7.1, 10.9, 1H_Z), 5.34 (dt, J = 7.1, 15.2, 1H_E), 3.10 (d,

$J = 7.1$, $2H_Z$), 3.07 (d, $J = 7.1$, $2H_E$), 1.53 - 1.47 (m, $2H_E$ & Z), 0.02 (s, $9H_Z$), 0.00 (s, $9H_E$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.7$, 131.8 , 130.0_Z , 118.9 , 117.4_Z , 37.9 , 32.5_Z , 22.9 , 18.9_Z , -1.9_Z , -2.0 ; IR ($CHCl_3$): ν 2956, 1712; HRMS required for $C_8H_{15}O_2Si$ ($[M-H]^+$) 171.0841; found 171.0842.

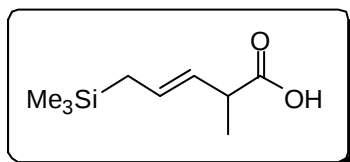
A. I. 2. Synthesis of 3-fluoropent-4-enoic acid ($\pm$)-1c:



To a solution of 5-(trimethylsilyl)pent-3-enoic acid (5.8 mmol, 1 g) in CH_3CN (20 mL) was added Selectfluor (6.4 mmol, 2.26 g). The reaction was allowed to stir for 16 hrs. Water (20 mL) was added to the reaction, the aqueous phase was then extracted with diethyl ether, dried (Na_2SO_4), filtered and the solvent removed *in vacuo* (NB: whilst removing the solvent the flask was not placed into a water bath). The crude product was purified by silica gel chromatography. to yield a brown oil (596 mg, 87%). 1H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 6.09$ - 5.94 (m, 1H), 5.45 - 5.23 (m, 3H), 2.76 - 2.67 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): $\delta = 170.6$, 136.1 (d, $J = 19.2$), 117.1 (d, $J = 12.0$), 90.0 (d, $J = 167.8$), 40.2 (d, $J = 24.8$); ^{19}F $\{^1H\}$ NMR (376.5 MHz, $(CD_3)_2CO$): $\delta = -178.2$; IR (neat): ν 2925, 1738; HRMS required for $C_5H_7O_2F$ ($[M]^+$) 118.0430 found; 118.0428.

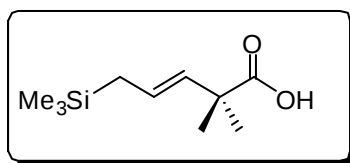
A. II. Synthesis of 3-fluoro-2,2-dimethylpent-4-enoic acid ($\pm$)-1d

A. II. 1 Synthesis of ($\pm$)-2-methyl-5-(trimethylsilyl)pent-3-enoic acid:



To a solution of 2-methylbut-3-enoic acid (2.8 mmol, 276 mg) and allyltrimethylsilane (8.4 mmol, 1.3 mL) in DCM (6 mL) at reflux was added Hoveyda-Grubbs 2nd generation catalyst (3 mol%, 53 mg). The reaction was allowed to stir at reflux for 24hrs, after cooling to room temperature the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 60/40) to yield a yellow oil. 1H NMR (400 MHz, $CDCl_3$): $\delta = 5.58$ (dt, $J = 8.2$, 15.0 , 1H), 5.32 (dd, $J = 7.9$, 15.0 , 1H), 3.18 - 3.06 (m, 1H), 1.46 (d, $J = 7.9$, 2H), 1.25 (d, $J = 7.2$, 3H), 0.00 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 184.0$, 131.3 , 128.5 , 45.0 , 24.8 , 19.6 , 0.0 ; IR ($CHCl_3$): ν 2956, 1708; HRMS required for $C_9H_{18}O_2Si$ ($[M-H]^+$) 185.0995; found 185.0998.

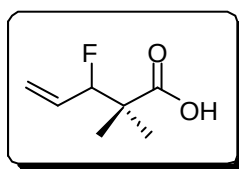
A. II. 2. Synthesis of 2,2-dimethyl-5-(trimethylsilyl)pent-3-enoic acid:



To a solution of diisopropylamine (8.7 mmol, 1.22 mL) in THF (10 mL) at $-78^\circ C$ was added *n*-BuLi (2.0 M, 4.35 mL). The mixture was allowed to stir at $-78^\circ C$ for 30 minutes. 2-Methyl-5-(trimethylsilyl)pent-3-enoic acid (3.9 mmol, 738 mg) in THF (10 mL) was added dropwise to the mixture. The

reaction was allowed to warm to 0 °C and stirred at this temperature for 30 minutes; the reaction was then cooled to -78 °C. Methyl iodide (7.92 mmol, 0.49 mL) was added and the reaction allowed to stir at -78°C for 30 minutes followed by 1 hour at room temperature. The reaction was then quenched with saturated NH₄Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic phases were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 60/40) to yield a brown oil (560 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ = 5.60-5.40 (m, 2H), 1.47 (d, *J* = 7.8, 2H), 1.30 (s, 6H), -0.01 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 183.6, 132.0, 125.9, 43.9, 25.1, 22.8, -2.0; IR (CHCl₃): ν 2956, 1702; HRMS required for C₁₀H₁₉O₂Si ([M-H]⁻) 199.1149; found 199.1154.

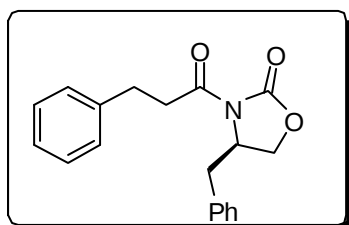
A. II. 3. Synthesis of 3-fluoro-2,2-dimethylpent-4-enoic acid (±)-1d:



To a solution of 2,2-dimethyl-5-(trimethylsilyl)pent-3-enoic acid (2.7 mmol, 540 mg) in CH₃CN (6 mL) was added Selectfluor (2.9 mmol, 1.05 g). The reaction was allowed to stir for 16 hrs. Water (6 mL) was added to the reaction, the aqueous phase was then extracted with diethyl ether, dried (Na₂SO₄), filtered and the solvent removed *in vacuo* to yield a brown oil (334 mg, 85%). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 6.04-5.90 (m, 1H), 5.44-5.33 (m, 2H), 5.06 (ddt, *J* = 1.3, 6.3, 47.0, 1H), 1.20 (s, 3H), 1.13 (s, 3H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ = 177.3, 133.0 (d, *J* = 20.0), 119.6 (d, *J* = 12.8), 97.2 (d, *J* = 173.4), 46.3 (d, *J* = 21.6), 20.8 (d, *J* = 5.6), 19.5 (d, *J* = 3.2); ¹⁹F {¹H} NMR (376.5 MHz, (CD₃)₂CO): δ = -185.6; IR (neat): ν 2984, 1707; HRMS required for C₇H₁₁O₂F ([M]⁺): 146.0743; found 146.0746.

B. SYNTHESIS OF NON-FLUORINATED ACID (2R)-2-BENZYL-4-ENOIC ACID (-)-1j

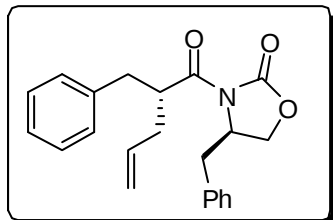
B. I. Synthesis of (4R)-4-benzyl-3-(3-phenylpropanoyl)-1,3-oxazolidin-2-one¹



To a stirred solution of (R)-4-benzyl-2-oxazolidinone (5.64 mmol, 1 g) in THF (20 mL) at -78°C was added 1 eq of *n*-BuLi (2.3 M, 2.45 mL). After 15 min, 1 eq. of hydrocinnamoyl chloride (5.6 mmol, 0.84 mL) was added directly to the solution. The solution was allowed to stir for 30 min at -78°C, then 1hr at room temperature. The reaction was quenched with saturated NH₄Cl solution, and then extracted with ethyl acetate. The solvents were removed *in vacuo* and the crude product recrystallised from hexane: ethyl acetate to yield a white solid (75%, 1.3 g). ¹H NMR (400 MHz, CDCl₃): δ = 7.37-7.15, (m, 10H), 4.71-4.64 (m, 1H), 4.22-4.14 (m, 2H), 3.38-3.31 (m, 3H), 3.08-3.0 (m, 1H), 3.04 (dd, *J* = 7.0, 13.7, 1H), 2.77 (dd, *J* = 9.7, 13.7, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 172.9, 153.9, 140.9, 135.7, 129.9, 129.4, 129.1, 128.9,

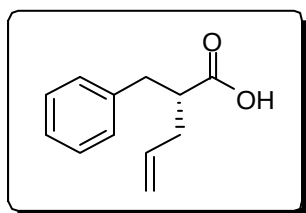
127.8, 126.7, 66.6, 55.6, 38.3, 37.6, 30.7; IR (CHCl₃): ν 1785, 1698; MS [M+H]⁺ 310.15; $[\alpha]_D^{22} = -71.3$ (c, 1.0, CHCl₃); Mp = 103-105°C.

B. II. Synthesis of (4R)-4-benzyl-3-[(2R)-2-benzylpent-4-enoyl]-1,3-oxazolidin-2-one²



To a solution of (4R)-4-benzyl-3-(3-phenylpropanoyl)-1,3-oxazolidin-2-one (2.6 mmol, 820 mg) in THF (15 mL) was added LDA (1M, 3 mL) over 10 minutes at -78°C. After 30 minutes, allyl bromide (8 mmol, 0.69 mL) was added dropwise. The reaction was then allowed to stir for 20 minutes at -78 °C, followed by 45 minutes at 0°C. The reaction was quenched by the addition of saturated NaHSO₄ solution, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 90/10) to yield a yellow oil (72%, 670 mg). ¹H NMR (400 MHz, CDCl₃): δ = 7.37-7.12 (m, 10H), 5.94-5.80 (m, 1H), 5.19-5.02 (m, 2H), 4.51-4.42 (m, 1H), 4.39-4.29 (m, 1H), 4.02 (dd, *J* = 2.1, 9.0, 1H), 3.83 (t, *J* = 8.3, 1H), 3.24 (dd, *J* = 3.1, 13.3, 1H), 3.0-2.93 (m, 1H), 2.85 (dd, *J* = 6.5, 13.3, 1H), 2.70-2.53 (m, 2H), 2.41-2.32 (m, 1H); ¹³C NMR (50 MHz, CDCl₃): δ = 175.8, 153.5, 139.4, 135.8, 135.5, 129.9, 129.6, 129.4, 128.8, 127.7, 126.9, 117.9, 66.3, 56.9, 44.4, 38.7, 38.5, 36.8; IR (CHCl₃): ν 3029, 2921, 1779, 1698, 1388, 1210; $[\alpha]_D^{22} = -108.7$ (c, 0.85, CHCl₃).

B. III. Synthesis of non-fluorinated acid (2R)-2-benzylpent-4-enoic acid (-)-1³



To a solution of (4R)-4-benzyl-3-[(2R)-2-benzylpent-4-enoyl]-1,3-oxazolidin-2-one (1.9 mmol, 660 mg) in THF/H₂O (3/1, 40 mL) at 0 °C was added H₂O₂ (50% in H₂O) (15.1 mmol, 0.87 mL) followed by LiOH (3.8 mmol, 158 mg). The mixture was allowed to warm to room temperature and stirred for 4 hrs. The mixture was cooled to 0°C and quenched with saturated Na₂SO₃ solution. After evaporation of the THF, the basic solution was extracted with DCM. The aqueous solution was then treated with 2M HCl until pH = 2 and extracted with ethyl acetate. The combined organic phases were dried (MgSO₄), filtered and the solvent removed *in vacuo*, the crude product was purified by silica gel chromatography (hexane/ethyl acetate 90/10) to yield a colourless oil (92%, 320 mg). ¹H NMR (400 MHz, CDCl₃): δ = 7.32-7.17 (m, 5H), 5.85-5.73 (m, 1H), 5.14-5.06 (m, 2H), 3.04-2.94 (m, 1H), 2.84-2.75 (m, 2H), 2.45-2.27 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ = 181.5, 139.3, 135.2, 129.4, 128.9, 127.0, 118.0, 47.5, 37.7, 36.1; MS [M-H]⁻: 189.18; $[\alpha]_D^{22} = -16.5$ (c, 0.65 CHCl₃).

NB: Absolute stereochemistry assigned by analogy with literature data.³

C. SYNTHESIS OF IODOLACTONES 2a-2d AND 2j

C. I. General procedures

C. I. 1. General procedure for condition A:

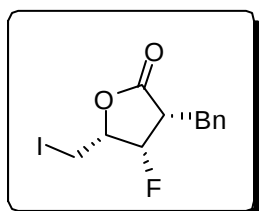
To a solution of substrate (0.3 mmol) in DCM/NaHCO₃ (1:1, 3 mL) in a darkened vessel was added iodine (0.7 mmol). The reaction mixture was then stirred for 12 hours before being quenched by the addition of saturated Na₂S₂O₃ solution/saturated NaHCO₃ solution (1:1). The aqueous layer was extracted with DCM, the combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude products were purified by silica gel chromatography (hexane/ethyl acetate 90/10 for the lactones and DCM for the ethers).

C. I. 2. General procedure for condition B:

To a solution of substrate (0.3 mmol) in CH₃CN (1 mL) in a darkened vessel was added iodine (0.8 mmol). The reaction mixture was then stirred for 12 hours and then quenched by the addition of saturated Na₂S₂O₃ solution/saturated NaHCO₃ solution (1:1). The aqueous layer was extracted with DCM, the combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude products were purified by silica gel chromatography (hexane/ethyl acetate 90/10).

C. II. Data

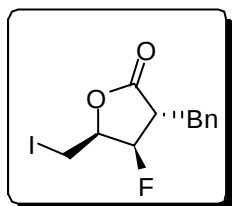
C. II. 1. Synthesis of (3*S*,4*S*,5*R*)-3-benzyl-4-fluoro-5-(iodomethyl)dihydrofuran-2(3*H*)-one (-)-2a:



Condition B: 94% yield, d.r. > 20:1. ¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.24 (m, 5H), 5.18 (dm, ²J_{HF} = 53.3, 1H), 4.53 (dm, ³J_{HF} = 25.0, 1H), 3.48-3.36 (m, 2H), 3.29-3.23 (m, 1H), 3.03-2.89 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃): δ = 174.3, 137.8, 128.9, 128.7, 126.9, 89.3 (d, J = 190.9), 80.6 (d, J = 20.0), 49.2 (d, J = 22.4), 29.3 (d, J = 6.4), -4.0 (d, J = 11.2); ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): δ = -212.6; IR (CHCl₃): ν 1783, 1117. HRMS required for C₁₂H₁₂O₂FI [M+H]⁺: 333.9866; found: 333.9876; Mp = 72-75°C [α]_D²² = -25.2 (c, 0.75, CHCl₃). *Characteristic data for minor stereoisomer*: ¹H NMR (400 MHz, CDCl₃): δ = 4.86 (dm, ³J_{HF} = 22.9, 1H, CHO); ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): δ = -188.0.

Condition B: 86% yield, d.r. > 20:1.

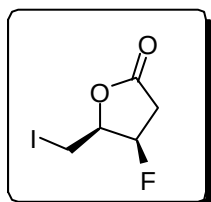
C. II. 2. Synthesis of (3*S*,4*R*,5*S*)-3-benzyl-4-fluoro-5-(iodomethyl)dihydrofuran-2(3*H*)-one (-)-2b:



Condition A: 95% yield, d.r. > 20:1. ^1H NMR (400 MHz, CDCl_3): δ = 7.40-7.20 (m, 5H), 5.14 (dd, J = 3.3, 52.0, 1H), 4.17 (dm, $^3J_{\text{HF}}$ = 24.8, 1H), 3.35-3.15 (m, 4H), 2.93 (dd, J = 8.3, 13.9, 1H); ^{13}C NMR (100.6 MHz, CDCl_3): δ = 175.3, 135.9, 129.2, 128.6, 127.8, 91.8 (d, J = 187.8), 81.0 (d, J = 20.7), 49.9 (d, J = 22.5), 33.7 (d, J = 8.2), -4.1 (d, J = 13.2); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3): δ = -194.2; IR (CHCl_3): ν 1765; HRMS required for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{FI}$ $[\text{M}+\text{H}]^+$: 333.9866; found: 333.9877; Mp = 92-94 °C. $[\alpha]_{\text{D}}^{22}$ = -22.0 (c, 0.75, CHCl_3). For X-ray data see page S38 of the Supporting Information.

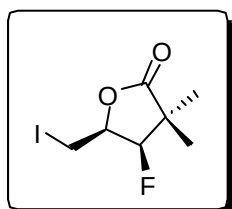
Condition B: 74% yield, d.r. > 20:1.

C. II. 3. Synthesis of 4-fluoro-5-(iodomethyl)dihydrofuran-2(3*H*)-one ($\pm$)-2c:



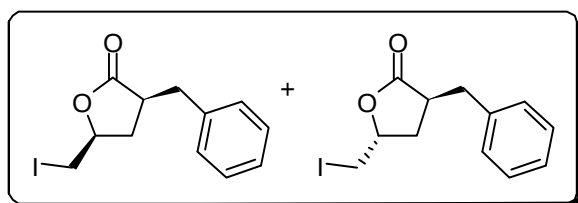
Condition B: 25% yield, d.r. > 20:1. ^1H NMR (400 MHz, CDCl_3): δ = 5.47 (dm, $^2J_{\text{HF}}$ = 53.0, 1H), 4.67 (dm, $^3J_{\text{HF}}$ = 25.0, 1H), 3.52-3.32 (m, 2H), 2.94-2.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 172.8, 88.5 (d, J = 187), 82.5 (d, J = 20.8), 37.3 (d, J = 24.8), -4.2 (d, J = 12.0); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3): δ = -197.2; IR (CHCl_3): ν 1788, 1161; HRMS required for $\text{C}_5\text{H}_6\text{O}_2\text{FI}$ $[\text{M}+\text{H}]^+$: 243.9401; found 243.9397. Condition A: 24% yield, d.r. > 20:1.

C. II. 4. Synthesis of 4-fluoro-5-(iodomethyl)-3,3-dimethyldihydrofuran-2(3*H*)-one ($\pm$)-2d:



Condition B: 72% yield, d.r. > 20:1. ^1H NMR (400 MHz, CDCl_3): δ = 4.92 (dd, J = 2.8, 52.8, 1H), 4.72 (dm, $^3J_{\text{HF}}$ = 25.0, 1H), 3.45-3.32 (m, 2H), 1.31 (d, J = 2.8, 3H), 1.27 (d, J = 1.5, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ = 178.5, 95.0 (d, J = 192.9), 79.1 (d, J = 21.1), 45.5 (d, J = 19.2), 21.7 (d, J = 5.8), 17.2 (d, J = 10.6), -3.6 (d, J = 13.4); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3): δ = -203.2; IR (CHCl_3): ν 1784, 1126; HRMS required for $\text{C}_7\text{H}_{14}\text{NO}_2\text{FI}$ $[\text{M}+\text{NH}_4]^+$: 290.0052; found 290.0053; Mp = 62-65 °C. For X-ray data see page S42 of Supporting Information. Condition A: 48% yield, d.r. > 20:1.

C. II. 5. Synthesis of (3*S*, 5*S*)-3-benzyl-5-(iodomethyl)dihydrofuran-2(3*H*)-one and (3*S*,5*R*)-3-benzyl-5-(iodomethyl)dihydrofuran-2(3*H*)-one (+)-2j:



NMR data of the mixture of diastereoisomers (ratio 2:1): ^1H NMR (400 MHz, CDCl_3): δ

= 7.39-7.15, (m, 10H), 4.41-4.30 (m, 2H), 3.38-3.10 (m, 6H), 3.10-2.96 (m, 2H), 2.88-2.76 (m, 2H), 2.53-2.44 (m, 1H), 2.25-2.07 (m, 2H), 1.71-1.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 177.8, 177.1, 138.1, 137.6, 128.9, 128.8, 128.75, 128.71, 126.9, 126.8, 76.7, 43.0, 41.1_{trans}, 36.5_{trans}, 36.0, 34.7, 32.5_{trans}, 7.4_{trans}, 6.6; IR (CHCl_3): ν 1765; HRMS required for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{I}$ ($[\text{M}+\text{NH}_4]^+$): 334.0304; found: 334.0306; $[\alpha]_{\text{D}}^{22}$ = +70.5 (c, 0.4, CHCl_3). $[\alpha]_{\text{D}}$ measured on a mixture of diastereoisomers 2:1.

NB: Stereochemistry assigned by analogy with literature data.^{4,5}

D. SYNTHESIS OF ALLYLIC FLUORIDES 1e-1i

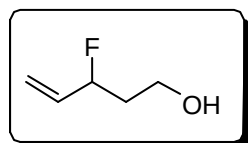
D. I. Synthesis of 3-fluoropent-4-en-1-ol ($\pm$)-1e

D. I. 1. Synthesis of 5-(trimethylsilyl)pent-3-en-1-ol:

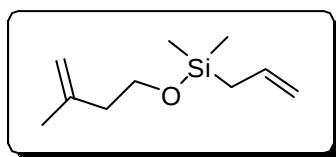


To a solution of 3-buten-1-ol (3.5 mmol, 0.32 mL) and allyltrimethylsilane (10.5 mmol, 1.67 mL) in DCM (10 mL) at reflux was added Grubbs 2nd generation catalyst (3 mol%, 89 mg). The reaction was allowed to stir at reflux for 24hrs. After cooling to room temperature the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/diethyl ether: 95/5) to give the desired compound as a mixture of *E/Z* isomers (384 mg, 69%); *E:Z*: 3:1. ^1H NMR (400 MHz, CDCl_3): δ = 5.6-5.4 (m, 1H), 5.3-5.1 (m, 1H), 3.7-3.5 (m, 2H), 2.4-2.2 (m, 2H), 1.53 (d, J = 8.6, 2H_Z), 1.46 (d, J = 8.1, 2H_E), 0.02 (s, 9H_Z), 0.00 (s, 9H_E); ^{13}C NMR (100 MHz, CDCl_3): δ = 130.3, 129.1_Z, 124.0, 122.5_Z, 62.4_Z, 62.2, 36.2, 30.6_Z, 22.9, 18.7_Z, -1.8_Z, -2.0; IR (neat): ν 3442, 2956, 1249, 1043; HRMS required for $\text{C}_8\text{H}_{19}\text{OSi}$ ($[\text{M}+\text{H}]^+$): 159.1205; found: 159.1209.

D. I. 2. Synthesis of 3-fluoropent-4-en-1-ol ($\pm$)-1e:

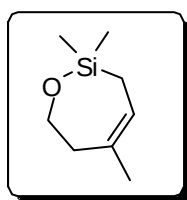


To a solution of 5-(trimethylsilyl)pent-3-en-1-ol (4.42 mmol, 700 mg) in acetone (5 mL) was added Selectfluor (4.86 mmol, 1.72g). The reaction was allowed to stir for 3 days at room temperature. The solvent was removed *in vacuo*, the crude compound was then dissolved in DCM (5 mL) and washed with water (5 mL) the organic phase was then dried (MgSO_4), filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (DCM) to yield ($\pm$)-1e (250 mg, 54%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 6.0-5.9 (m, 1H), 5.33 (ddd, J = 1.1, 1.9, 2.7, $\frac{1}{2}\text{H}$), 5.29 (ddd, J = 0.9, 1.5, 3.3, $\frac{1}{2}\text{H}$), 5.2 (d, J = 10.6, 1H), 5.1 (dm, $^2J_{\text{HF}}$ = 48.8, 1H), 3.8-3.6 (m, 2H), 1.9-1.7 (m, 2H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 137.5, (d, J = 19.6), 116.2 (d, J = 12.0), 91.0 (d, J = 165.0), 57.6 (d, J = 5.2), 38.8 (d, J = 22.0); ^{19}F { ^1H } NMR (376.5 MHz, $(\text{CD}_3)_2\text{CO}$): δ = -181.1; IR (neat): ν 356, 2954, 1618, 1053.

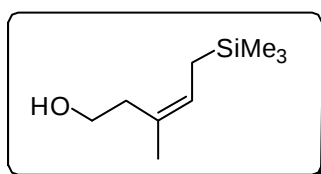
D. II. Synthesis of 3-fluoro-3-methylpent-4-en-1-ol ($\pm$)-1h**D. II. 1. Synthesis of allyl(dimethyl)[(3-methylbut-3-en-1-yl)oxy]silane:**

To a solution of 3-methyl-3-buten-1-ol (22 mmol, 2.3 mL), triethylamine (22 mmol, 3.07 mL) and DMAP (2 mg) in DCM (20 mL) was added allyl(chloro)dimethylsilane (20 mmol, 2.92 mL) dropwise.

The reaction was allowed to stir overnight at room temperature. The reaction was quenched by addition of water (20 mL), the organic phase was dried (MgSO_4), filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (petroleum ether 30-40°C) to give the desired silane (3.6 g, 100 %). ^1H NMR (200 MHz, CDCl_3): δ = 5.9-5.7 (m, 1H), 4.95-4.65 (m, 4H), 3.7 (t, J = 7.1, 2H), 2.2 (t, J = 6.9, 2H), 1.7 (s, 3H), 1.6 (d, J = 8.0, 2H), 0.1 (s, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ = 145.2, 136.5, 116.2, 114.1, 64.3, 43.5, 26.9, 25.4, 0.0; IR (neat): ν 2959, 1632; HRMS required for $\text{C}_{10}\text{H}_{21}\text{OSi}$ ($[\text{M}+\text{H}]^+$): 185.1362; found: 185.1360.

D. II. 2. Synthesis of 2,2,5-trimethyl-2,3,6,7-tetrahydro-1,2-oxasilepine:

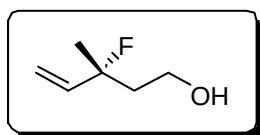
To a solution of allyl(dimethyl)[(3-methylbut-3-en-1-yl)oxy]silane (20 mmol, 3.6 g) in DCM (500 mL) at reflux was added Grubbs 2nd generation catalyst (3 mol%, 510 mg), the reaction was allowed to stir at reflux for 3 hrs. After cooling to room temperature the solvent was removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (petroleum ether 30-40°C/diethyl ether: 98/2) to yield the cyclic product (1.87 g, 60%). ^1H NMR (200 MHz, CDCl_3): δ = 5.5 (t, J = 7.1, 1H), 3.9-3.8 (m, 2H), 2.36-2.28 (m, 2H), 1.7 (d, J = 1.4, 3H), 1.5 (d, J = 7.2, 2H), 0.12 (s, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ = 136.5, 122.6, 64.1, 38.4, 26.9, 19.4, 0.0; IR (neat): ν 2923, 1436; HRMS required for $\text{C}_8\text{H}_{17}\text{OSi}$ ($[\text{M}+\text{H}]^+$): 157.1049; found: 157.1051.

D. II. 3. Synthesis of 5-(trimethylsilyl)pent-3-en-1-ol:

To a solution of 2,2,5-trimethyl-2,3,6,7-tetrahydro-1,2-oxasilepine (7.2 mmol, 1.12 g) in THF (40 mL) at -78°C was added MeLi (1M, 28.7 mL) dropwise. The reaction was warmed to 0°C and allowed to stir at this temperature for 4 hrs. The reaction was quenched by the addition of saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ solution. The aqueous layer was extracted with diethyl ether, the combined organic phases were dried (MgSO_4), filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude compound was purified by silica gel chromatography (petroleum ether 30-40°C/diethyl ether: 90/10) to give the

corresponding alcohol (900 mg, 73 %). ^1H NMR (200 MHz, CDCl_3): δ = 5.3 (t, J = 8.5, 1H), 3.6 (td, J = 2.2, 6.9, 2H), 2.28 (t, J = 6.9, 2H), 1.7 (s, 3H), 1.4 (d, J = 8.5, 2H), -0.02 (s, 9H); ^{13}C NMR (50 MHz, CDCl_3): δ = 128.4, 123.8, 60.6, 34.7, 23.4, 18.5, -1.8; IR (neat): ν 3356, 2956, 1248; HRMS required for $\text{C}_9\text{H}_{21}\text{OSi}$ ($[\text{M}+\text{H}]^+$): 173.1362; found: 173.1362.

D. II. 4. Synthesis of 3-fluoro-3-methylpent-4-en-1-ol ($\pm$)-**1h**:



To a solution of 5-(trimethylsilyl)pent-3-en-1-ol (6.1 mmol, 1.3 g) in acetone (12 mL) was added Selectfluor (6.7 mmol, 2.37 g). The reaction was allowed to stir for 3 days at room temperature. The solvent was removed *in vacuo*, the crude compound was then dissolved in DCM (10 mL) and washed with water (10 mL) the organic phase was then dried (MgSO_4), filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (DCM) to yield ($\pm$)-**1h** (510 mg, 71 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 6.0-5.9 (m, 1H), 5.2 (dt, J = 1.4, 17.4, 1H), 5.1 (dt, J = 1.1, 11.1, 1H), 3.7-3.6 (m, 2H), 2.0-1.9 (m, 2H), 1.4 (d, J = 21.9, 3H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 141.7 (d, J = 22.4), 112.6 (d, J = 11.6), 95.5 (d, J = 168.9), 57.6 (d, J = 6.0), 43.3 (d, J = 22.8), 25.5 (d, J = 24.8); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, $(\text{CD}_3)_2\text{CO}$): δ = -147.4; IR (neat): ν 3375, 2957, 1617, 1412.

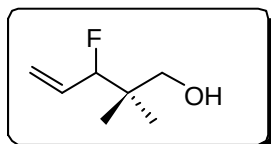
D. III. Synthesis of 3-fluoro-2,2-dimethylpent-4-en-1-ol ($\pm$)-**1f**

D. III. 1. Synthesis of 2,2-dimethyl-5-(trimethylsilyl)pent-3-en-1-ol:



To a suspension of LiAlH_4 (5 mmol, 189 mg) in diethyl ether (8 mL) was added 2,2-dimethyl-5-(trimethylsilyl)pent-3-enoic acid (2.5 mmol, 500 mg) in diethyl ether (2 mL) dropwise. The reaction was stirred for 14 hrs at room temperature. The reaction was quenched by addition of water. The aqueous layer was extracted with diethyl ether, dried (MgSO_4), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane/ether: 95/5) to give the desired alcohol (244 mg, 53%). ^1H NMR (200 MHz, CDCl_3): δ = 5.4 (dt, J = 7.8, 15.6, 1H), 5.1 (dt, J = 1.1, 15.7, 1H), 3.2 (s, 2H), 1.4 (dd, J = 1.1, 7.7, 2H), 0.9 (s, 6H), -0.07 (s, 9H); ^{13}C NMR (50 MHz, CDCl_3): δ = 137.3, 127.3, 73.7, 40.4, 26.3, 24.9, 0.02; IR (neat): ν 3363, 2956, 1248; HRMS required for $\text{C}_{10}\text{H}_{23}\text{OSi}$ ($[\text{M}+\text{H}]^+$): 187.1518; found: 187.1517.

D. III. 2. Synthesis of 3-fluoro-2,2-dimethylpent-4-en-1-ol ($\pm$)-**1f**:

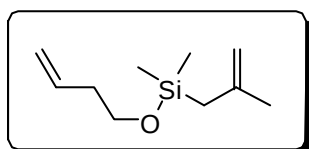


To a solution of 2,2-dimethyl-5-(trimethylsilyl)pent-3-en-1-ol (3.9 mmol, 740 mg) in acetone (5 mL) was added Selectfluor

(4.4 mmol, 1.55 g) and allowed to stir for 3 days at room temperature. The solvent was removed *in vacuo*, the crude compound was then dissolved in DCM (5 mL) and washed with water (5 mL) the organic phase was then dried (MgSO₄), filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (DCM) to yield (±)-**1f** (400 mg, 76 %). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 6.1-5.9 (m, 1H), 5.35-5.25 (m, 2H), 4.8 (ddd, *J* = 1.1, 6.4, 47.7, 1H), 3.8 (bs, 1H), 3.46 (dd, *J* = 5.4, 10.5, 1H), 3.3 (dd, *J* = 5.3, 10.4, 1H), 0.9 (s, 3H), 0.85 (s, 3H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ = 134.3 (d, *J* = 20.4), 117.9 (d, *J* = 13.2), 97.0 (d, *J* = 171.3), 67.9 (d, *J* = 4.8), 39.6 (d, *J* = 19.6), 19.9, (d, *J* = 5.2), 19.0 (d, *J* = 3.6); ¹⁹F {¹H} NMR (376.5 MHz, (CD₃)₂CO): δ = -191.4; IR (neat): ν 3376, 2969, 1475, 1109.

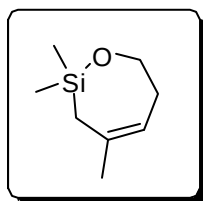
D. IV. Synthesis of 3-fluoro-4-methylpent-4-en-1-ol (±)-1i

D. IV. 1. Synthesis of (but-3-enyloxy)dimethyl(2-methylallyl)silane:



To a solution of 3-buten-1-ol (2.8 mmol, 0.24 mL), triethylamine (5.6 mmol, 0.78 mL) and DMAP (1.4 mmol, 171 mg) in DCM (5 mL) was added a solution of chlorodimethyl(2-methylallyl)silane⁶ (3.4 mmol, 500 mg) in DCM (2 mL) dropwise at 0°C. The reaction was allowed to stir overnight at room temperature. The reaction was quenched by addition of saturated NH₄Cl_(aq), the organic phase was washed with brine, dried over MgSO₄, filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (petroleum ether 30-40°C then petroleum ether 30-40°C/Et₂O: 98/2) to yield the desired silane as a colourless oil (408 mg, 79%). ¹H NMR (400 MHz, CDCl₃): δ = 5.75-5.86 (m, 1H), 5.00-5.10 (m, 2H), 4.62 (sbr, 1H), 4.53 (sbr, 1H), 3.65 (t, *J* = 6.9, 2H), 2.99 (qbr, *J* = 6.9, 2H), 1.75 (s, 3H), 1.63 (s, 2H), 0.14 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 142.7, 135.1, 116.4, 108.8, 62.3, 37.1, 28.2, 25.0, -2.2; IR (DCM): ν 3054, 1265, 909, 736; MS (CI⁺) : *m/z* = 185.13 ([M+H]⁺).

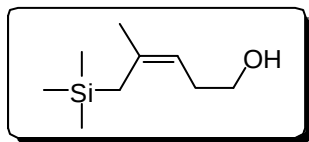
D. IV. 2. Synthesis of 2,2,4-trimethyl-2,3,6,7-tetrahydro-1,2-oxasilepine:



To a solution of (but-3-enyloxy)dimethyl(2-methylallyl)silane (1.1 mmol, 200 mg) in DCM (109 mL) at reflux was added Hoveyda-Grubbs 2nd generation catalyst (7 mg, 1 mol%), the reaction was allowed to stir at reflux for 1h30. After cooling to room temperature the solvent was removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (petroleum ether 30-40°C/Et₂O: 95/5) to give the cyclic product as a colourless oil (145 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ = 5.44 (t, *J* = 7.4, 1H), 3.78-3.82 (m, 2H), 2.23-2.29 (m, 2H), 1.75 (s, 3H), 1.59 (s, 2H), 0.12 (s, 6H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ =

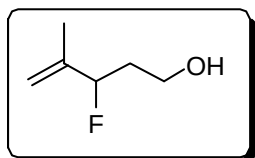
139.3, 122.8, 65.7, 33.3, 28.6, 25.7, -0.9; IR (DCM): ν 3055, 2987, 2306, 1702, 1422, 1265, 896, 736; HRMS required for $C_8H_{17}OSi$ ($[M+H]^+$): 157.1049; found: 157.1041.

D. IV. 3. Synthesis of 4-methyl-5-(trimethylsilyl)pent-3-en-1-ol:

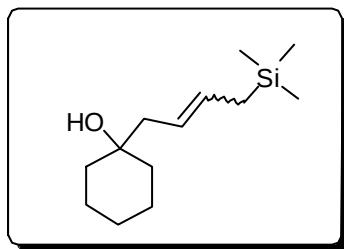


To a solution of 2,2,4-trimethyl-2,3,6,7-tetrahydro-1,2-oxasilepine (2.3 mmol, 765 mg) in THF (12 mL) at -78°C was added MeLi (1.6M/Et₂O, 9.2 mmol, 5.8 mL) dropwise. The reaction was warmed to 0°C and allowed to stir at this temperature for 3 hrs. The reaction was quenched by the addition of saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ solution. The aqueous layer was extracted with diethyl ether, the combined organic phases were washed with brine, dried over MgSO_4 , filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude compound was purified by silica gel chromatography (petroleum ether $30\text{--}40^\circ\text{C}/\text{Et}_2\text{O}$: 80/20) to give the corresponding alcohol as a colourless oil (210 mg, 53%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 5.06 (t, J = 6.14, 1H), 3.43–3.54 (m, 3H), 2.17 (qbr, J = 7.00, 2H), 1.69 (d, J = 1.28, 3H), 1.58 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 136.1, 120.3, 63.6, 34.3, 27.5, 24.6, 0.37; IR (DCM): ν 3579 (broad), 3392, 2256, 1703, 1248, 1033, 962; HRMS required for $C_9H_{21}OSi$ ($[M+H]^+$): 173.1362; found: 173.1364.

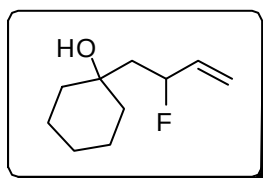
D. IV. 4. Synthesis of 3-fluoro-4-methylpent-4-en-1-ol ($\pm$)-**1i**:



To a solution 4-methyl-5-(trimethylsilyl)pent-3-en-1-ol (1.2 mmol, 200 mg) in acetone (6 mL) was added Selectfluor (1.3 mmol, 452 mg) and NaHCO_3 (1.3 mmol, 108 mg). The reaction was allowed to stir for 24h at room temperature. The solvent was carefully removed *in vacuo* and the crude compound then dissolved in DCM and brine. The aqueous phase was extracted three times with DCM. The combined organic layers were then washed with brine, dried over Na_2SO_4 , filtered and the solvent removed *in vacuo* (caution: volatile compound). The crude product was purified by silica gel chromatography (DCM/Et₂O: 90/10) to yield ($\pm$)-**1i** as a colourless oil (96 mg, 70 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 4.97–5.13 (m, J = 48.2, 2H), 4.91–4.94 (m, 1H), 3.60–3.69 (m, 3H), 1.76–1.94 (m, 2H), 1.74 (s, 3H); ^{13}C NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 145.3 (d, J = 17.6), 113.1 (d, J = 10.1), 94.1 (d, J = 168.6), 58.7 (d, J = 3.8), 38.1 (d, J = 22.6), 17.8; ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, $(\text{CD}_3)_2\text{CO}$): δ = -181.46; IR (DCM): ν 3055, 2987, 2306, 1702, 1265, 738; HRMS required for $C_6H_{15}\text{NOF}$ ($[M+\text{NH}_4]^+$): 136.1138; found 136.1139.

D. V. Synthesis of 1-(2-fluorobut-3-enyl)cyclohexanol ($\pm$)-1g**D. V. 1. Synthesis of 1-(4-(trimethylsilyl)but-2-enyl)cyclohexanol:**

To a solution of 1-allylcyclohexanol (3.6 mmol, 500 mg) and allyltrimethylsilane (11.0 mmol, 1.7 mL) in DCM (12 mL) at reflux was added Grubbs 2nd generation catalyst (2.5 mol %, 75 mg). The reaction was allowed to stir at reflux for 24hrs, after which time an additional (2.5 mol%, 75 mg) of Grubbs 2nd generation catalyst was added to the reaction mixture and allowed to stir at reflux for a further 24hrs. After cooling to room temperature the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane then hexane/diethyl ether 90/10) to give the compound as a *E/Z* mixture of isomers (643 mg, 79 %); *E:Z* = 95:5. ¹H NMR (400 MHz, CDCl₃): δ = 5.58-5.68 (m, *J* = 9.4, 0.2H)_Z, 5.45-5.55 (m, *J* = 15.4, 1H), 5.37-5.43 (m, *J* = 9.4, 0.2H)_Z, 5.26-5.35 (m, *J* = 15.4, 1H), 2.16 (d, *J* = 8.0, 0.12H)_Z, 2.13 (d, *J* = 7.5, 2H), 1.20-1.66 (m, 14H), 0.06 (s, 0.5H)_Z, -0.02 (s, 9H); ¹³C NMR (50 MHz, CDCl₃): δ = 131.2, 129.3_Z, 122.8, 121.5_Z, 70.9, 45.5, 37.3, 25.8, 23.1_Z, 22.2, 18.6_Z, -1.78_Z, -1.94; IR (DCM): ν 2977, 2863, 1382, 1350, 1123, 1076; HRMS required for C₁₃H₂₆NaOSi ([M+Na]⁺): 249.1651; found : 249.1645.

D. V. 2. Synthesis of 1-(2-fluorobut-3-enyl)cyclohexanol ($\pm$)-1g:

To a solution of 1-(4-(trimethylsilyl)but-2-enyl)cyclohexanol (3.1 mmol, 540 mg) in acetone (10 mL) was added Selectfluor (3.5 mmol, 1.22 g). The reaction was allowed to stir for 3.5 days at room temperature. The solvent was then carefully removed *in vacuo* and the crude compound dissolved in DCM and brine. The aqueous phase was extracted three times with DCM. The combined organic layers were then washed with brine, dried over Na₂SO₄, filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether 30-40°C then petroleum ether 30-40°C/Et₂O: 80/20) to yield ($\pm$)-**1g** as a colourless oil (252 mg, 47 %). ¹H NMR (400 MHz, CDCl₃): δ = 5.85-5.98 (m, *J*_{trans} = 17.0, *J*_{cis} = 10.6, 1H), 5.18-5.38 (m, *J*_{trans} = 17.2, *J*_{cis} = 10.6, 3H), 1.89-2.01 (m, *J* = 9.7, *J* = 15.4, 1H), 1.76-1.80 (m, 1H), 1.58-1.70 (m, 5H), 1.42-1.55 (m, 5.8H), 1.23-1.34 (m, 1.4H); ¹³C NMR (125.8 MHz, (CD₃)₂CO): δ = 137.3 (d, *J* = 18.9), 116.7 (d, *J* = 12.6), 91.4 (d, *J* = 164.8), 70.9, 46.9 (d, *J* = 20.1), 38.1, 25.9, 22.4 (d, *J* = 12.6). ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): δ = - 175.7; IR (DCM): ν 3054, 2987, 1265, 737; HRMS required for C₁₀H₂₁NOF ([M+NH₄]⁺): 190.1607; found: 196.1615.

E. SYNTHESIS OF IODOETHERS 2e-2i

E. I. General procedures

E. I. 1. General procedure for conditions A & B: see C. I. 1. and C. I. 2.

E. I. 2. General procedure for condition C:

To a solution of substrate (0.48 mmol) in CH₃CN (2.4 mL) in a darkened vessel was added *N*-iodosuccinimide (0.58 mmol). The reaction mixture was then stirred for 12 hours and quenched by the addition of saturated Na₂S₂O₃ solution/saturated NaHCO₃ solution (1:1). The aqueous layer was extracted with DCM, the combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude products were purified by silica gel chromatography (DCM).

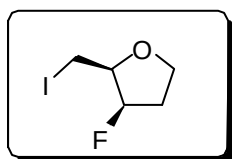
E. I. 3. Procedure for condition D:

To a solution of substrate (0.48 mmol) in CH₃CN (2.4 mL) in a darkened vessel was added *N*-bromosuccinimide (0.58 mmol). The reaction mixture was then stirred for 12 hours before being quenched by the addition of saturated Na₂S₂O₃ solution/saturated NaHCO₃ solution (1:1). The aqueous layer was extracted with DCM, the combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude products were purified by silica gel chromatography (DCM).

E. II. Data

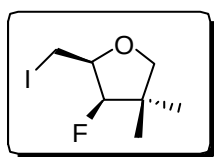
NB: all the cyclised compounds (excepted (±)-2g) are volatile.

E. II.1. Synthesis of 3-fluoro-2-(iodomethyl)tetrahydrofuran (±)-2e:

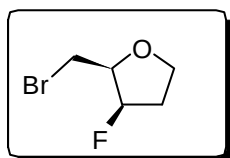


Condition A: 52 % yield; d.r = 12:1; *NMR data for the major syn diastereoisomer*: ¹H NMR (400 MHz, C₆D₆): δ = 4.76 (dm, ²J_{H-F} = 54.2, 1H), 3.87-3.80 (m, 1H), 3.6 (dddd, ³J_{H-F} = 2.7, 5.9, 8.8, 26.3, 1H), 3.52-3.45 (m, 1H), 3.2-3.1 (m, 2H), 1.80-1.65 (m, 1H), 1.45-1.25 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 92.8 (d, J = 184.1), 83.0 (d, J = 18.8), 67.4, 33.7 (d, J = 21.6), -0.65 (d, J = 12.8); ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): δ = -195.8; IR (neat): ν 2980, 1434, 1115; HRMS required for C₅H₉OFI ([M+H]⁺): 230.9682; found: 230.9678. *Characteristic data for minor diastereoisomer*: ¹H NMR (400 MHz, C₆D₆): δ = 4.69 (dm, ²J_{H-F} = 54.4), 4.02 (dddd, J = 1.4, 4.6, 7.3, 26.0); ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): δ = -176.0.

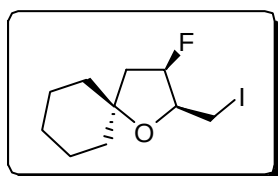
Condition C: 81 % yield, d.r. = 5:1.

E. II. 2. Synthesis of 3-fluoro-2-(iodomethyl)-4,4-dimethyltetrahydrofuran ($\pm$)-2f:

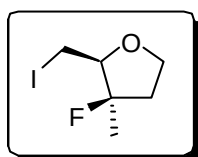
Condition A: 92 % yield, d.r. > 20:1; *NMR data for the major syn diastereoisomer:* ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 4.7 (dd, $^2J_{\text{H-F}}$ = 2.9, 54.1, 1H), 4.4 (dddd, $^3J_{\text{H-F}}$ = 3.0, 6.1, 8.7, 28.2, 1H), 3.75-3.60 (m, 2H), 3.31-3.20 (m, 2H), 1.1 (s, 6H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 99.3 (d, J = 188.5), 82.3 (d, J = 18.9), 78.6, 44.2 (d, J = 17.6), 23.9 (d, J = 6.8), 18.2 (d, J = 9.2), 0.59 (d, J = 16.4); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, $(\text{CD}_3)_2\text{CO}$): δ = -203.1; IR (neat): ν 2953, 1052; HRMS required for $\text{C}_7\text{H}_{12}\text{FINaO}$ ($[\text{M}+\text{Na}]^+$): 280.9809; found: 280.9804.

E. II.3. Synthesis of 2-(bromomethyl)-3-fluorotetrahydrofuran ($\pm$)-2k:

Condition D: 80 % yield; d.r. = 7:1; *NMR data for the major syn diastereoisomer:* ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 5.30 (dm, $^2J_{\text{H-F}}$ = 52.0, 1H), 3.96-4.12 (m, 2H), 3.89 (td, $^3J_{\text{H-F}}$ = 4.0, 8.0, 1H), 3.39-3.58 (m, 2H), 2.08-2.39 (m, 2H); ^{13}C NMR (125.8 MHz, C_6D_6): δ = 93.0 (d, J = 176.0), 82.7 (d, J = 20.1), 67.2, 33.7 (d, J = 22.0), 27.9 (d, J = 13.8); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, C_6D_6): δ = -194.9; IR (neat): ν 3054, 2987, 1265, 896, 736; HRMS required for $\text{C}_5\text{H}_{12}\text{NOFBr}$ ($[\text{M}+\text{NH}_4]^+$): 200.0086; found: 200.0093; *Characteristic data for minor diastereoisomer:* ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3): δ = -175.9.

E. II. 4. Synthesis of 3-fluoro-2-(iodomethyl)-1-oxaspiro[4.5]decane ($\pm$)-2g:

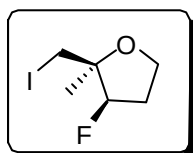
Procedure A: 69 % yield. d.r. = 12:1 ; *NMR data for the major syn diastereoisomer:* ^1H NMR (400 MHz, CDCl_3): δ = 5.23 (ddd, $^2J_{\text{H-F}}$ = 53.7, 4.7, 2.6, 1H), 4.18 (dddd, $^3J_{\text{H-F}}$ = 26.4, 8.7, 6.6, 2.5, 1H), 3.23-3.33 (m, 2H), 2.23 (dd, J = 25.9, 14.8, 1H), 1.94 (ddd, J = 40.7, 14.8, 4.8, 1H), 1.26-1.73 (m, 12H) ; ^{13}C NMR (100 MHz, CDCl_3): δ = 94.1 (d, J = 183.2), 84.3, 81.3 (d, J = 19.0), 38.2 (d, J = 23.2), 25.6, 25.2, 23.5, 0.1 (d, J = 11.2); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CD_2Cl_2): δ = -191.8; IR (DCM): ν 3054, 1265, 737, 705; HRMS required for $\text{C}_{10}\text{H}_{17}\text{OFI}$ ($[\text{M}+\text{H}]^+$): 299.0308; found: 299.0308. *Characteristic data for minor anti diastereoisomer:* ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, C_6D_6): δ = -171.4.

E. II. 5. Synthesis of 3-fluoro-2-(iodomethyl)-3-methyltetrahydrofuran ($\pm$)-2h:

Condition A: 88 % yield, d.r. = 9:1; *NMR data for the major syn diastereoisomer:* ^1H NMR (400 MHz, C_6D_6): δ = 3.65-3.73 (m, 1H), 3.5 (dm, $^3J_{\text{H-F}}$ = 21.5, 1H), 3.32-3.37 (m, 1H), 3.0-3.13 (m, 2H), 1.73-1.85 (m, 1H), 1.25-1.41 (m, 1H), 0.9 (d, $^3J_{\text{H-F}}$ = 20.8,

3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 100.5 (d, J = 182.0), 85.7 (d, J = 20.0), 65.1, 40.2 (d, J = 23.4), 21.6 (d, J = 26.2), 0.35 (d, J = 11.9); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, C_6D_6): δ = -157.6; IR (neat): ν 2987, 1048; HRMS required for $\text{C}_6\text{H}_{11}\text{FIO}$ ($[\text{M}+\text{H}]^+$): 244.9839; found: 244.9845. *Characteristic data for minor diastereoisomer*: ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, C_6D_6): δ = -137.2.

E. II. 6. Synthesis of 3-fluoro-2-(iodomethyl)-2-methyltetrahydrofuran ($\pm$)-**2i**:



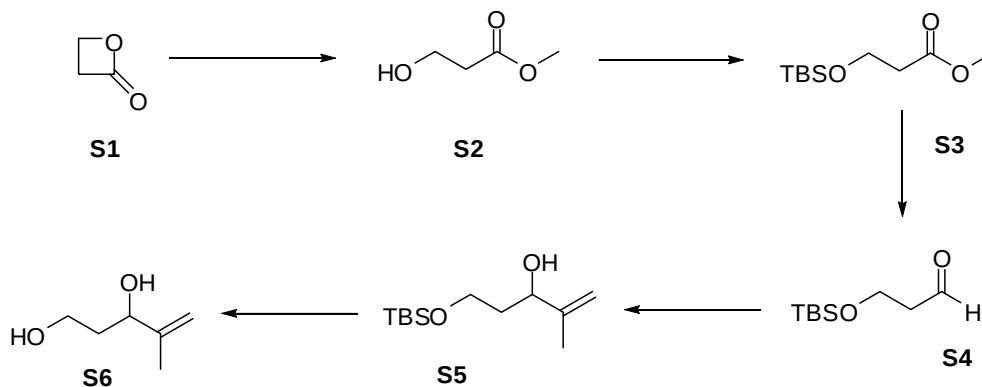
Condition A: 69 % yield. d.r. = 9:1; *NMR data for the major syn diastereoisomer*: ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 5.03 (dd, $^2J_{\text{H-F}}$ = 53.9, 1H), 3.09-4.04 (m, 2H), 3.28-3.41 (m, 2H), 2.32-2.55 (m, 1H), 2.13-2.28 (m, 1H), 1.30 (d, $^4J_{\text{H-F}}$ = 1.62, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 97.2 (d, J = 183.2), 84.2 (d, J = 17.3), 66.8, 33.5 (d, J = 21.9), 24.3 (d, J = 4.8), 9.38 (d, J = 13.8); ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, CD_2Cl_2): δ = -185.32; IR (DCM): ν 3051, 2280, 1265, 740, 705; HRMS required for $\text{C}_6\text{H}_{15}\text{NOFI}$ ($[\text{M}+\text{NH}_4]^+$): 262.0104; found: 262.0091; *Characteristic data for minor anti diastereoisomer*: ^{19}F $\{^1\text{H}\}$ NMR (376.5 MHz, C_6D_6): δ = -184.1.

F. ATTEMPT OF PREPARATION OF THE *anti*-3-FLUORO-2-(IODOMETHYL)-2-METHYLTETRAHYDROFURAN *anti*-($\pm$)-**2i**

To access *anti*-($\pm$)-**2i** we prepared *syn*-2-(iodomethyl)-2-methyltetrahydrofuran-3-ol ($\pm$)-**2l** and attempted a DAST-mediated fluorination ($\text{S}_{\text{N}}2$).

F. I. Synthesis of 2-(iodomethyl)-2-methyltetrahydrofuran-3-ol ($\pm$)-**2l**

F. I. 1. Synthesis of 4-methylpent-4-en-1,3-diol **S6**:

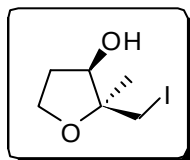


a) NaOMe 0.1 eq., MeOH, 50°C, 1h, 69%; b) TBDMSCl 1.1 eq., Imidazole 1.8 eq., DCM, rt, 15h, 66%; c) DibalH 1.1 eq., DCM, -78°C, 1.5h, 72%; d) $\text{CH}_2\text{CHMeMgBr}$ 1.8 eq., THF, 0°C, 5 min, 63%; e) TBAF 1.5 eq., DCM, rt, 6h, 73%.

The preparation of the required diol **S6** was achieved from commercial β -propiolactone **S1** by adapting literature procedures.^{7, 8} Thus, the methylester **S3** was

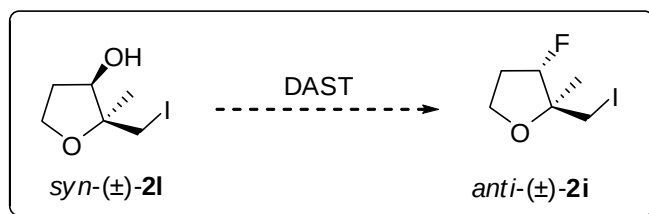
obtained by ring-opening and TBS protection of the lactone **S1**. Subsequent DibalH reduction gave the aldehyde **S4**⁷ which was then added to isopropenylmagnesium bromide to form the alcohol **S5**.⁸ TBAF deprotection of the TBS group furnished the desired diol **S6**.

F. I. 2. Synthesis of 2-(iodomethyl)-2-methyltetrahydrofuran-3-ol ($\pm$)-**2I**:⁹



To a solution of 4-methylpent-4-en-1,3-diol **S6** (1.2 mmol, 144 mg) in DCM/NaHCO₃ (1:1, 8 mL) in a darkened vessel, was added iodine (2.7 mmol, 693 mg). The reaction mixture was allowed to stir for 12 hours, after which it was quenched by the addition of saturated aqueous Na₂S₂O₃ solution. The aqueous layer was then extracted three times with DCM and the combined organic extracts were washed with brine, dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography (DCM then DCM/Et₂O: 90/10) to give the desired product as a yellow solid (290 mg, 99 %). d.r. = 15:1. *NMR data for the major syn diastereoisomer* : ¹H NMR (400 MHz, (CD₃)₂CO) : δ = 4.28 (d, *J* = 4.9, 1H), 4.14-4.20 (m, 1H), 3.87-3.94 (m, 1H), 3.78-3.84 (m, 1H), 3.37-3.46 (m, 2H), 2.25-2.34 (m, 1H), 1.92-1.99 (m, 1H), 1.26 (s, 3H); ¹³C NMR (125.8 MHz, C₆D₆) : δ = 83.3, 76.6, 66.0, 34.6, 24.7, 11.7; MS (CI⁺): *m/z* = 260.03 ([M+NH₄]⁺).

F. II. Attempt of fluorination of ($\pm$)-**2I**



To a solution of 2-(iodomethyl)-2-methyltetrahydrofuran-3-ol ($\pm$)-**2I** (0.2 mmol, 50 mg) in DCM (2 mL) was added dropwise a solution of DAST (1.2 to 2.5 eq.) in DCM (1 mL) (**Table 1**). The reaction mixture was quenched by addition of aqueous saturated NaHCO₃, and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with brine, dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude mixture was analyzed by ¹H and ¹⁹F NMR by comparison with NMR data obtained for compound ($\pm$)-**2i**.

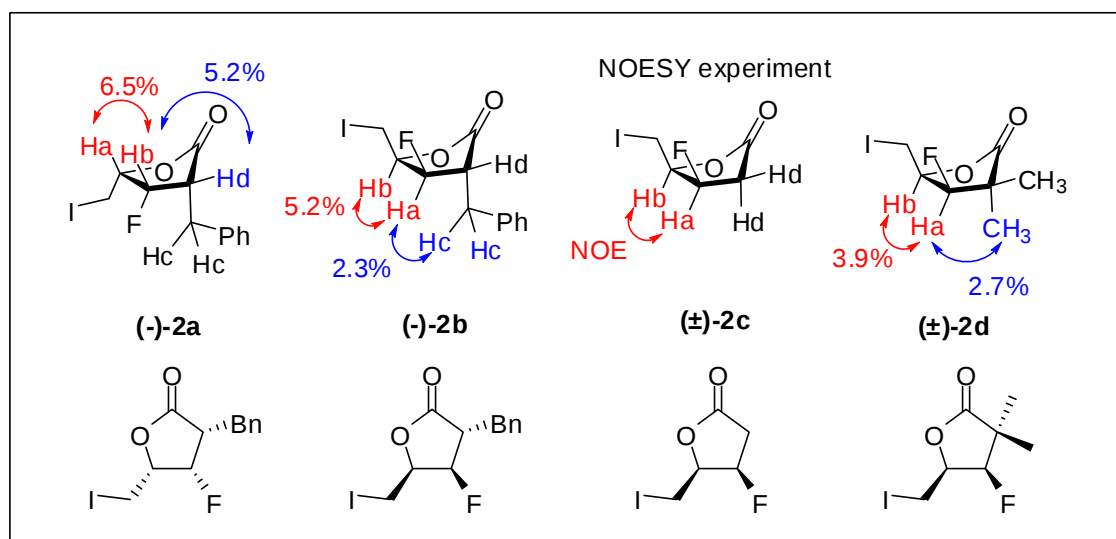
Table 1: different conditions used for the fluorination of ($\pm$)-**2l**.

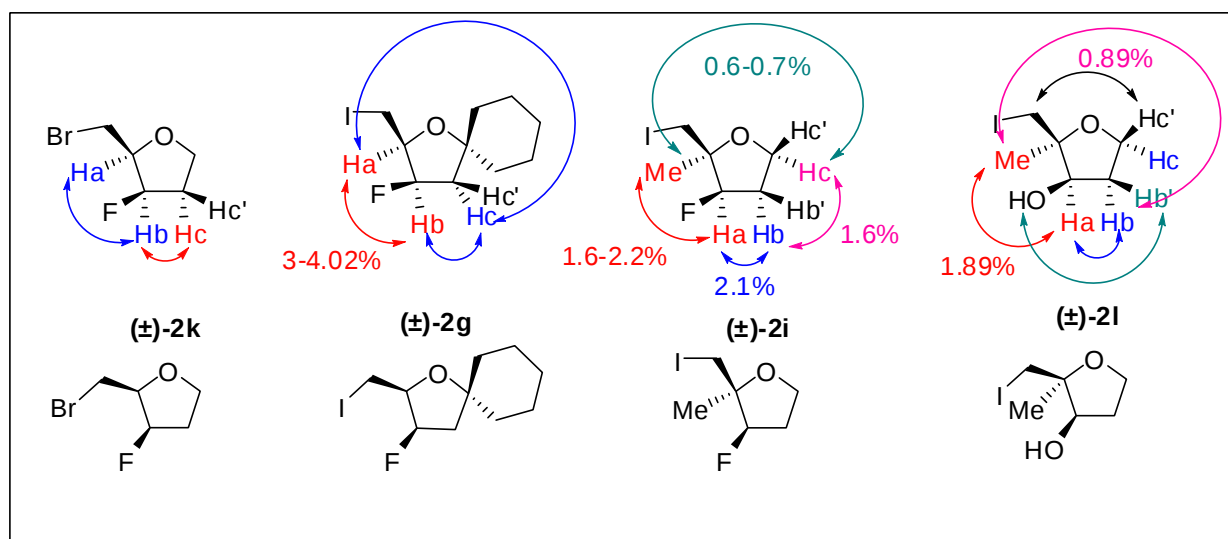
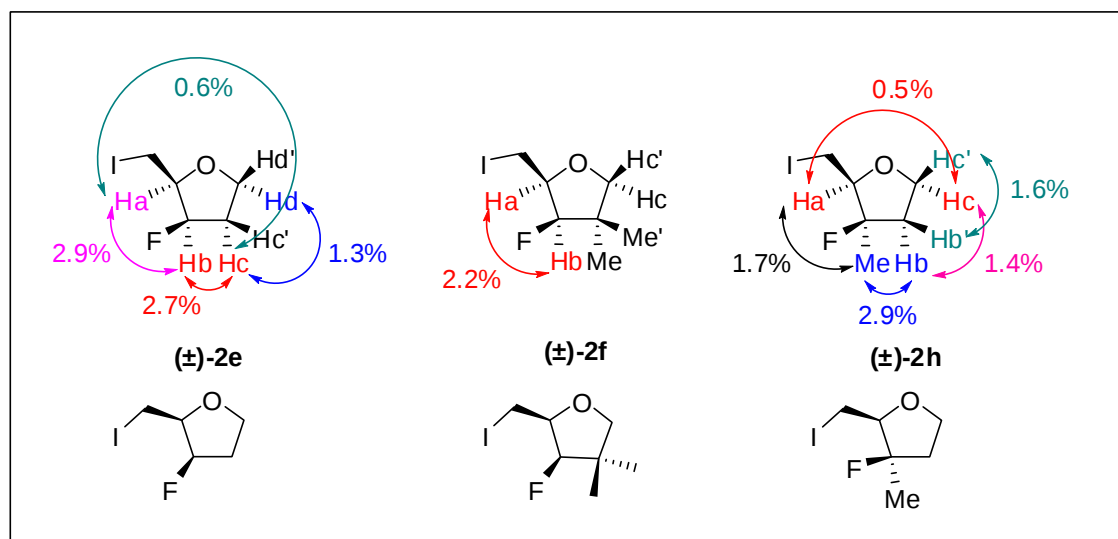
Entry	DAST	Conditions	Results
1	1.2 eq.	-70°C, 1h then 15°C, 4h30.	no reaction
2	2.5 eq.	-20°C, 4h	no more starting material, no trace of <i>anti</i> -($\pm$)- 2i

Treatment of *syn*-($\pm$)-**2l** does not deliver *anti*-($\pm$)-**2i**.

G. NMR ASSIGNMENT OF RELATIVE STEREOCHEMISTRY FOR COMPOUNDS ($\pm$)-**2a-2l**

The relative stereochemistry was assigned by NOE experiments for ($\pm$)-**2a-2l** and by X-ray diffraction analysis for ($\pm$)-**2d** and (-)-**2b**. Selected NOE enhancements are shown below. In all cases, a strong NOE enhancement was observed between protons H_a and H_b, indicating a *syn* relationship. NOE studies on the iodoethers derivatives also revealed a *syn* relationship between the fluorine and iodomethyl substituents.





H. CALCULATIONS

Quantum mechanical investigations were performed using Gaussian 03.¹⁰ All structures were optimized using density functional theory with the B3LYP¹¹ functional. The basis sets 3-21G(d) and 6-31G(d) were employed for all atoms except iodine, for which the LANL2DZ¹² basis set was implemented. B3LYP with the LANL2DZ basis set has been shown to effectively model the geometries and energies of compounds that contain iodine.¹³

Carboxylates, **14** and **15** (from **1a** and **1b**, respectively), were investigated, **Table 2**. Both diastereomers prefer the bulky R group in the first skew (S_1) position by *c.* 2 kcal/mol over the second skew (S_2) orientation and 3 kcal/mol over the eclipsed position. Isomers **14** _{S_1} and **15** _{S_1} orient the hydrogen of the β carbon above the olefin, and the carboxylate group away from the olefin, Figure 1. Previous studies show that conformers with fluoro eclipsing the olefin are more stable,¹⁴ but the

conformational preference of the β carbon predominates in this study. Isomer **15_{S1}** is more stable than **14_{S1}** by 5 kcal/mol, indicating a preference for fluoro and olefin eclipsed in agreement with previous studies.

Table 2. Relative energies (kcal/mol) of deprotonated substrates **1a** and **1b** and their rotamers (B3LYP/6-31G(d) + LANL2DZ).

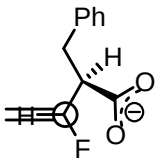
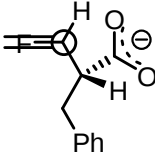
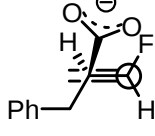
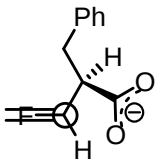
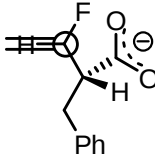
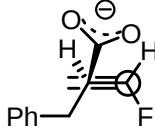
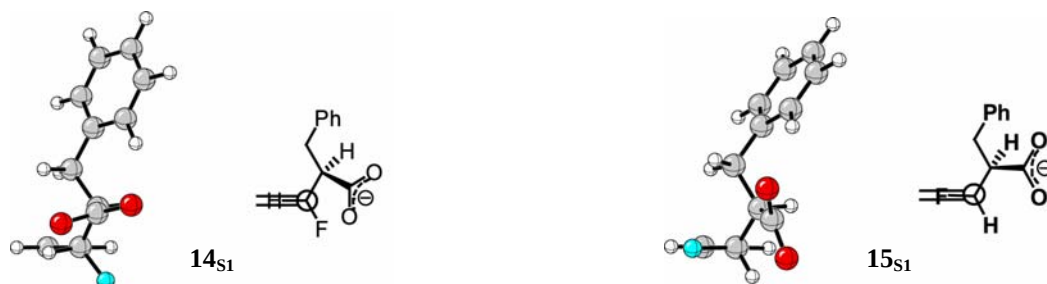
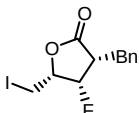
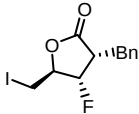
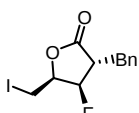
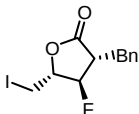
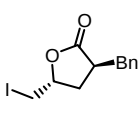
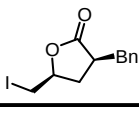
compd	substrate	relative energy
14_{S1}		4.7
14_{S2}		6.3
14_{eclipsed}		6.8
15_{S1}		0.0
15_{S2}		1.8
15_{eclipsed}		2.5

Figure 1. Most stable rotamers of **14** and **15**.

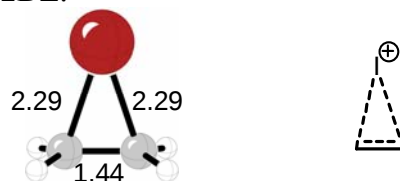


The conformational preferences of the products were also investigated, **Table 3**. The more stable product, with the iodomethyl and fluoro groups *syn*, is the major product observed experimentally. Energy differences between isomers of the products are within 1 kcal/mol. The energy differences in **2a**, **2b**, and **2c** are not great enough to explain the high diastereoselectivity observed in the iodolactonizations.

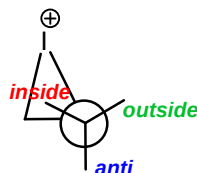
Table 3. Relative energies (kcal/mol) of isomeric products (B3LYP/6-31G(d) + LANL2DZ).

compound	substrate	relative energy
2a_{major}		0.0
2a_{minor}		1.0
2b_{major}		2.3
2b_{minor}		2.8
2j_{major}		0.0
2j_{minor}		0.8

Since investigations of carboxylates and cyclized products do not explain selectivity, geometry optimizations of an unsubstituted iodonium ion at B3LYP/6-31G(d) + LANL2DZ were undertaken. The iodonium complex lies between iodonium ion and iodonium- π complex, **Figure 2**. The carbon-carbon bond length (1.44 Å) is between those of a single bond and double bond (1.54 Å and 1.34 Å, respectively) and the carbon-iodine bond is longer than an sp^3 carbon-iodine bond (2.29 Å versus 2.20 Å). Calculated bond distances agree with previous experimental results¹⁵ and are an improvement from earlier theoretical studies.¹⁶

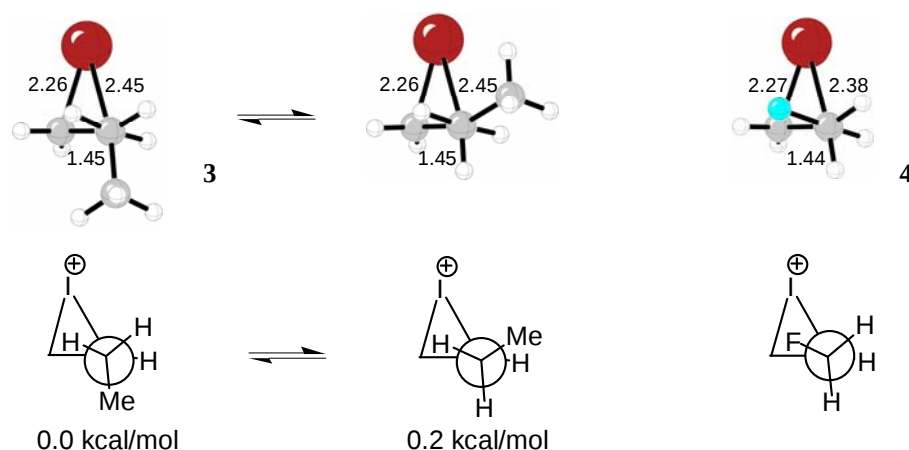
Figure 2. Calculated structure of an unsubstituted ethylene iodonium ion using B3LYP/6-31G(d) + LANL2DZ.

Rotamers of substituted iodonium ions were investigated, **Table 4**. Ethyliodonium was substituted with ethyl and fluoromethyl groups to investigate their individual rotational preferences. Substituted alkanes prefer an eclipsed arrangement.¹⁷ Staggered conformers are more stable in transition structures,¹⁸ such as formation of onium ions.¹⁹ The inside, outside and anti positions relative to the staggered iodonium ion were investigated.

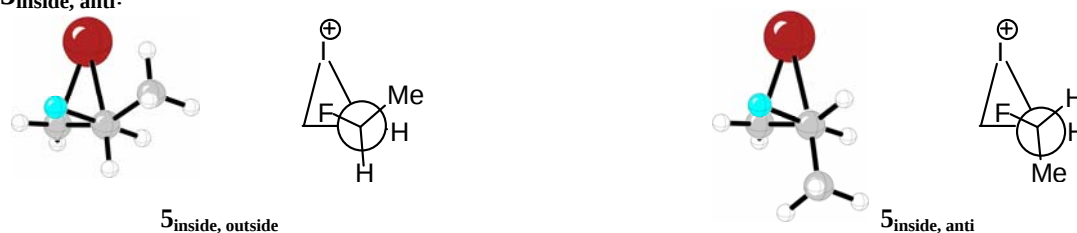
Table 4. Relative energies (kcal/mol) of the iodonium rotamers (B3LYP/6-31G(d) + LANL2DZ).

compound	substituents	relative energy	inside	outside	anti
3 _{outside}	methyl	0.0	H	Me	H
3 _{anti}		0.2	H	H	Me
3 _{inside}		0.7	Me	H	H
4 _{inside}	fluoro	0.0	F	H	H
4 _{outside}		3.2	H	F	H
4 _{anti}		5.3	H	H	F
5 _{inside, outside}	fluoro, methyl	0.0	F	Me	H
5 _{inside, anti}		0.0	F	H	Me
5 _{outside, anti}		2.9	H	F	Me
5 _{outside, inside}		4.1	Me	F	H
5 _{anti, outside}		5.2	H	Me	F
5 _{anti, inside}		6.6	Me	H	F

An allylic methyl group shows little conformational preference, **9**. Rotamers that place the methyl group outside or anti are equally stable, Figure 3. The rotamer with methyl inside is slightly higher in energy (0.7 kcal/mol), since the inside position is the most sterically demanding. Methyl prefers to reside in the less sterically crowded outside or anti positions.

Figure 3. Most stable rotamers for allylic methyl, **3**, and fluoride, **4**.

Fluoro prefers to reside inside by 3 kcal/mol with respect to outside, and 5 kcal/mol with respect to anti, **4**. When both fluoro and methyl are present, **5_{inside, outside}** and **5_{inside, anti}** are equal in energy, since both contain fluoro inside, and methyl has no conformational preference for outside versus *anti*. The energy difference between the other rotamers of **11** arise from the methyl group orientation; *anti* is favored over inside for steric reasons. The most stable isomers of **5** are shown in **Figure 4**.

Figure 4. Most stable rotamers with fluoride and methyl substituents, **5_{inside, outside}** and **5_{inside, anti}**.

An anti fluoride substituent aligns the electron-withdrawing σ_{CF}^* orbital with the alkene π orbital, destabilizing the iodonium ion. An inside fluoro minimizes the interaction between the σ_{CF}^* and the π orbitals. Fluoro inside also enables the fluoro lone pairs to stabilize the partially positive iodonium ion. Previous studies have shown that allylic fluorides prefer to reside inside in polar cycloaddition transition states (with nitrile oxides) and prefer inside or outside in nonpolar cycloaddition transition states (with butadiene).²⁰ In iodonium ions, anti fluoro destabilizes the iodonium ion and is disfavored; inside fluoro is stabilizing and preferred.

Diastereomers **16** and **17** were investigated, **Table 5**. The structures are models of **1** and **3** in which the carboxylate group present in **1** or **3** is replaced with a methyl group. Geometry optimizations were also attempted with a carboxylate group, but these led directly to product formation via cleavage of the iodonium ion.

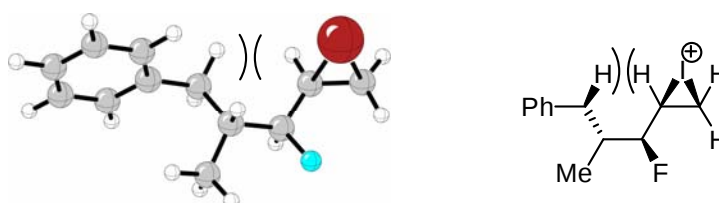
Stereochemistries of the fluoro substituent chiral center and the iodonium chiral center produces four possible diastereomers. Their relative energies are given in **Table 5**.

Table 5. Relative energies of the most stable rotamers of **16** and **17** (B3LYP/6-31G(d) + LANL2DZ).

compound	substrate	relative energy (kcal/mol)
16(S)		0.0
16(R)		2.6
17(R)		0.1
17(S)		1.7

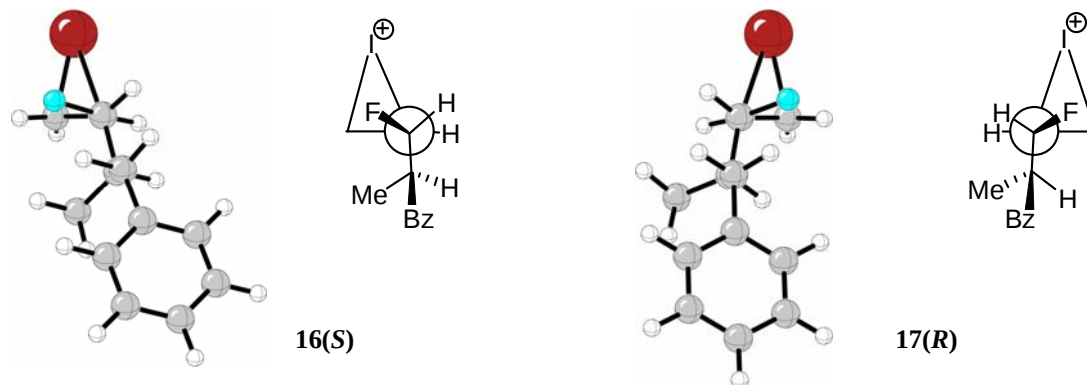
The most stable rotamers consistently have inside fluoro substitution. Alkyl anti (**16(S)** and **17(R)**) is significantly more stable than alkyl outside (**16(R)** and **17(S)**), since the anti position is the least sterically demanding location for the large alkyl group. An outside alkyl has steric interactions with the iodonium ion, **Figure 5**.

Figure 5. Example of destabilizing steric effects in **16(R)**.



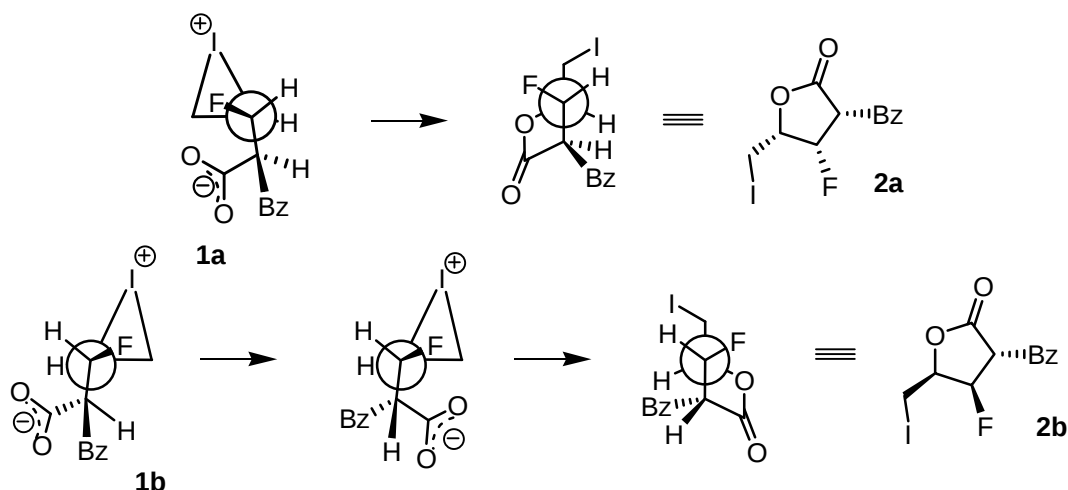
Similar destabilizing steric interactions have been observed in hydroborations of substituted alkenes.²¹ Fluoro inside and alkyl *anti* are favored in both **16** and **17**. The lowest energy conformers of **16(S)** and **17(R)** are shown in **Figure 6**.

Figure 6. Most stable rotamers of **16** and **17**.



The most stable conformers of **1a** and **1b** may easily form the major products of Gouverneur's iodolactonization, **Scheme 1**. In Scheme 1, the proposed conformers have fluoro inside and the large alkyl group *anti*, as is favored. Iodolactonizations occur by carboxylate attack on the back-side of the iodonium ion. In **1a**, the carboxylate may cleave the iodonium ion and give the experimentally observed major stereoisomer. In **1b**, the β carbon must rotate so that the carboxylate may attack the iodonium ion. After rotation, cleavage produces the experimentally observed major product. Conformational preferences lead to the formation of the major product and explain the high stereoselectivity observed in these iodolactonizations.

Scheme 1. Formation of major products from experimental substrates **1a** and **1b**.

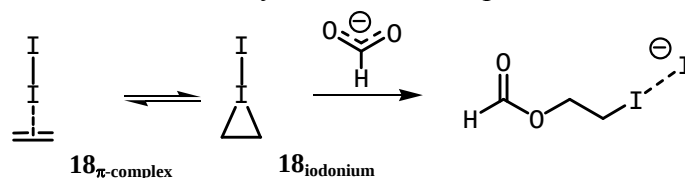


An allylic fluoride dictates which iodonium ion is more stable. Without fluoro substitution neither iodonium ion is predicted to be favored and both *syn* and *anti*

products are expected. Absence of an allylic fluoride results in poor stereoselectivity in agreement with experiments.

While the conformational preferences of α -fluoro and α -methyl substituents of an iodonium ion were enlightening, transition structures could not be found without incorporating a second iodine molecule for stabilization. Formate attack on an I_2 -ethylene complex was investigated, **Scheme 2**.

Scheme 2. Addition of formate to ethylene-iodine complex.



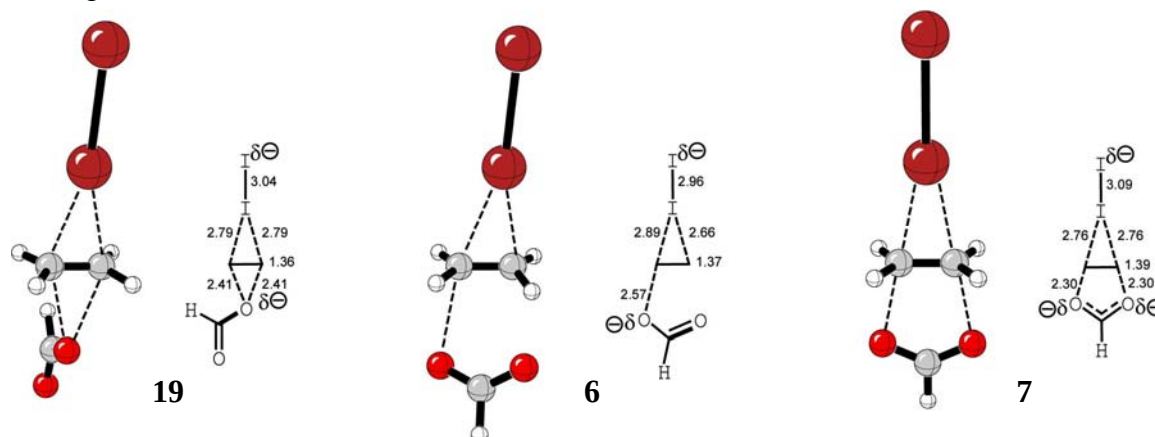
The iodine- π complex, **18 π -complex**, is loosely associated, **Figure 7**. Formation of the iodine- π complex from separate I_2 and ethylene is exothermic by 4.6 kcal/mol, but endergonic by 3.1 kcal/mol at standard state. The carbon-carbon bond length is the same as an uncoordinated alkene (1.34 Å) and the carbon-iodine bonds are long, 3.14 Å. This is a marked difference from the iodonium complex between I^+ and ethylene. With a single iodine cation present, the carbon-carbon bond length (1.44 Å) is between those of a single bond and double bond (1.54 Å and 1.34 Å, respectively) and the carbon-iodine bond is only slightly longer than sp^3 carbon-iodine bonds (2.29 Å versus 2.20 Å).

Figure 7. Ethylene-iodine complex (**18**) compared calculated iodonium ion.

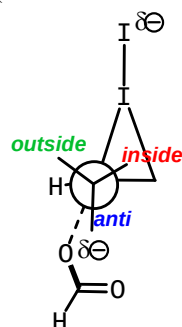


A number of transition structures were located for formate addition to the iodine- π complex, **Figure 8**. One transition structure located, **19**, is completely symmetric and is a transition structure between isomeric products. The asymmetric transition structure, **6**, is 8 kcal/mol more stable. A third transition structure, the transition structure for the dyotropic rearrangement between isomeric products, **7**, is the most stable transition structure.

Figure 8. Isomeric transition structures located for formate addition to the iodine- π complex.



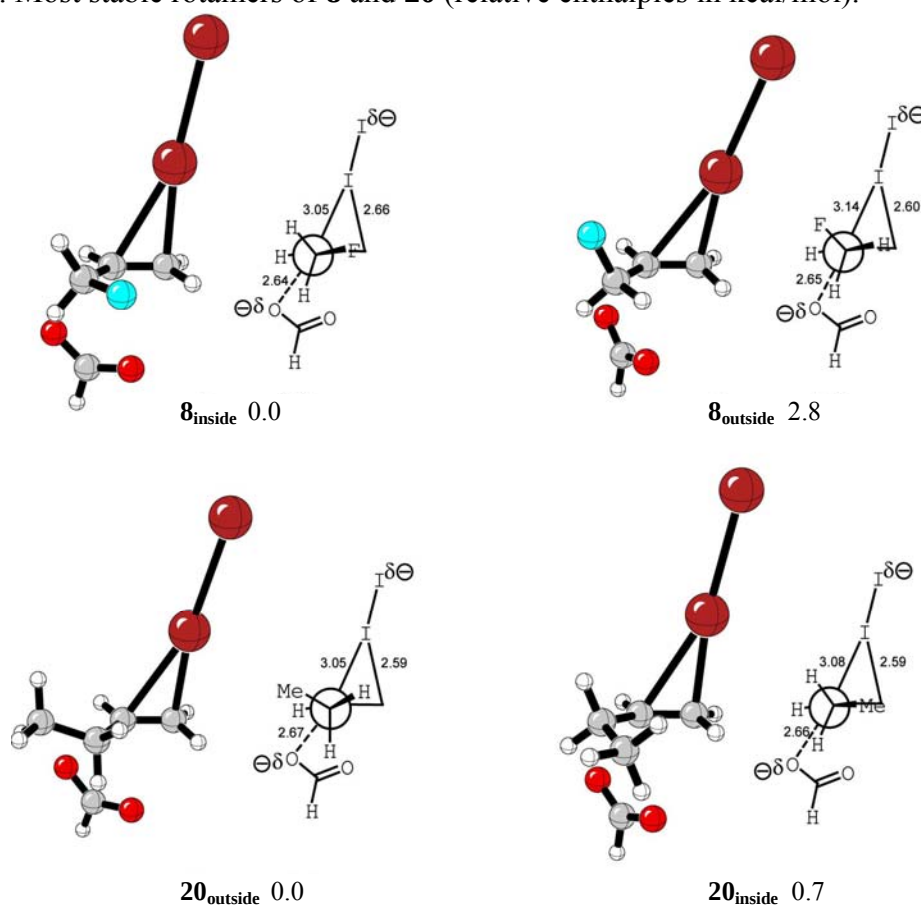
Conformational preferences of fluoromethyl, ethyl, and fluoroethyl groups during direct nucleophilic attack on substituted ethylene-iodine complexes were investigated, **Table 6**. In these transition structures, one formate oxygen attacks the more substituted carbon. The forming bond distances are between 2.6Å and 2.8Å. The formate attacks the alkene at an angle around 110°, indicating attack on the backside of the carbon-iodine σ^* bond.²² The second oxygen has more conformational flexibility and may be proximal or distal to the alkene. Orienting the second oxygen proximal to the alkene provides a stabilizing electrostatic interaction between the negatively charged oxygen and the positively charged carbons of the iodine- π complex. Transition structures with the second oxygen proximal to the alkene are at least 4 kcal/mol more stable than those with the second oxygen distal to the alkene.

Table 6. Relative enthalpies of rotamers of formate attack on substituted ethylene-iodine complexes (B3LYP/6-31G(d) + LANL2DZ).

compound	substituents	relative energy	inside	outside	anti
20_{anti}	methyl	0.0	H	H	Me
20_{outside}		0.7	H	Me	H
20_{inside}		N/A	Me	H	H
8_{inside}	fluoro	0.0	F	H	H
8_{outside}		0.8	H	F	H
8_{anti}		N/A	H	H	F
9_{inside,anti}	fluoro, methyl	0.0	F	H	Me
9_{inside,outside}		0.3	F	Me	H
9_{outside,inside}		1.3	Me	F	H
9_{outside,anti}		1.5	H	F	Me
9_{anti,inside}		2.8	Me	H	F
9_{anti,outside}		N/A	H	Me	F

The inside, outside and anti positions for fluoromethyl, ethyl, and fluoroethyl groups relative to the staggered ethylene-iodine complex were investigated.

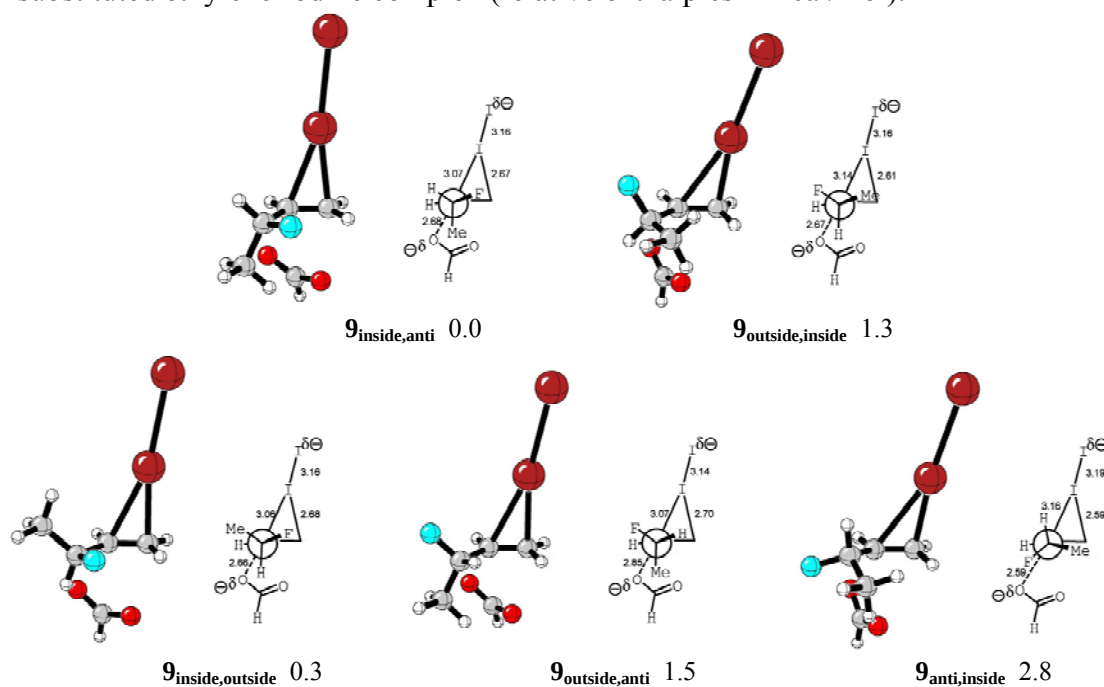
Recall that substituted iodonium ions prefer to have fluoro inside by at least 3 kcal/mol. Similarly, in the study of substituted ethylene-iodine complexes fluoro prefers to reside inside over outside by 1 kcal/mol, **8_{inside}** versus **8_{outside}** in **Figure 10**. The rotamer with fluoro anti, **8_{anti}**, optimizes to **8_{outside}**. An allylic methyl group shows a slight preference for anti versus outside orientation. Rotamers with methyl inside are sterically hindered and optimize to **20_{anti}**.

Figure 10. Most stable rotamers of **8** and **20** (relative enthalpies in kcal/mol).

When both fluoro and methyl are present, **9_{inside,anti}** and **9_{inside,outside}** are equal in energy, since both contain fluoro inside, and methyl has little conformational preference, **Figure 11**. Rotamers with fluoro inside, **9_{inside,anti}** and **9_{inside,outside}**, are preferred over those with fluoro outside, **9_{outside,inside}** and **9_{outside,anti}**, by 1 kcal/mol. Only one rotamer with fluoro anti was located, **9_{anti,inside}**, and it is 3 kcal/mol less stable than those with fluoro inside. Rotamer **9_{anti,outside}** optimizes to **9_{outside,anti}**.

Again, an anti fluoride substituent aligns the electron-withdrawing σ_{CF}^* orbital with one of the carbon-iodine bonds, destabilizing the $\text{I}_2\text{-}\pi$ complex. Preference for fluoro inside is smaller in the $\text{I}_2\text{-}\pi$ complex than in the iodonium ion since the $\text{I}_2\text{-}\pi$ complex is neutral compared to the positively charged iodonium ion. An inside fluoro minimizes the interaction between the σ_{CF}^* and the C-I bond. Fluoro inside also enables the fluoro lone pairs to stabilize the partial positive charge on iodine in the $\text{I}_2\text{-}\pi$ complex. In $\text{I}_2\text{-}\pi$ complexes, anti fluoro destabilizes the iodonium ion and is disfavored; inside fluoro is stabilizing and preferred.

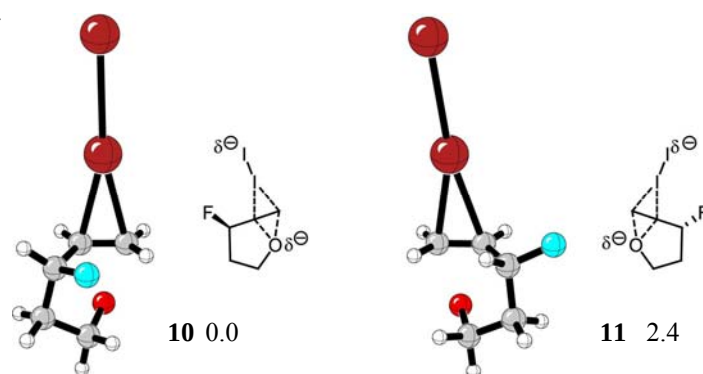
Figure 11. Intermolecular transition structure isomers for addition of formate to substituted ethylene-iodine complex (relative enthalpies in kcal/mol).



Finally, transition structures for the etherification of **1e** were located, **Figure 12**. As predicted, the transition structure that has fluorine inside is more stable than the transition structure with fluorine outside. The transition structure with fluorine inside leads to the experimentally observed major product.

Conformational preferences lead to formation of the major product and explain the high stereoselectivity observed in these iodolactonizations. An allylic fluoride dictates which transition structure of formate attack on the iodine- π complex is most stable. Without fluoro substitution neither iodonium ion is predicted to be favored and both syn and anti products are expected. Absence of an allylic fluoride results in poor stereoselectivity in agreement with experiments since a methyl substituent has little conformational preference in the iodine- π complex.

Figure 12. Transition structure isomers for intramolecular addition of substituted ethylene-iodine complex (relative enthalpies at B3LYP/6-31G(d) + LANL2DZ in kcal/mol).



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Table 7. Cartesian coordinates and energies for stationary points.

<u>1) 14_{SI}</u> E = -714.603109			C	-2.417208	0.530733	0.165604	H	-0.004758	0.743842	1.708313		
H (0 K) = -714.816036			C	-1.095407	-0.178286	-0.084188	C	-1.466991	-0.182917	0.454500		
H (298 K) = -714.588188			H	-0.788948	-0.014700	-1.124030	C	-2.152072	-1.405064	0.500336		
G (298 K) = -714.645586			C	-1.298811	-1.740276	0.164221	C	-2.137670	0.932435	-0.078986		
C	-2.941236	1.469118	-0.284838	O	-1.796796	-2.012127	1.282884	C	-3.464175	-1.522066	0.032837	
C	-3.297127	2.372888	0.630658	O	-0.898456	-2.499059	-0.750779	H	-1.649043	-2.279856	0.910349	
H	-2.951236	1.732340	-1.344053	C	-0.011364	0.336823	0.897457	C	-3.446392	0.816857	-0.546710	
H	-3.591237	3.384888	0.359797	H	-0.180421	1.385568	1.177076	H	-1.590486	1.873062	-0.111052	
H	-3.298302	2.134992	1.692803	H	-0.143326	-0.247906	1.819544	C	-4.118863	-0.408484	-0.493890	
C	-2.474936	0.072652	0.004280	C	1.420479	0.211024	0.408924	H	-3.972514	-2.483829	0.080882	
C	-1.005329	-0.201370	-0.320690	C	2.375010	1.169930	0.781855	H	-3.948444	1.692136	-0.955685	
H	-0.825558	0.012528	-1.381974	C	1.837577	-0.857696	-0.404270	H	-5.140635	-0.493387	-0.859619	
C	-0.707356	-1.742772	-0.042840	C	3.706060	1.072299	0.370874	F	2.727686	-0.266072	1.437699	
O	-0.378775	-2.422075	-1.032870	H	2.066820	2.008338	1.405296	<u>6) 15_{eclisped}</u> E = -714.606530				
O	-0.813895	-2.058918	1.174366	C	3.167929	-0.952609	-0.817204	H (0 K) = -714.819728				
C	-0.095079	0.672987	0.573527	H	1.103712	-1.604345	-0.710165	H (298 K) = -714.591802				
H	-0.379345	1.731671	0.501371	C	4.109732	0.005670	-0.433515	G (298 K) = -714.648596				
H	-0.282232	0.345995	1.603963	H	4.424142	1.832375	0.674538	C	-2.343619	2.035336	-0.342103	
C	1.384992	0.547385	0.277717	H	3.470317	-1.786992	-1.447415	C	-1.437282	2.704262	-1.056972	
C	2.083512	1.581362	-0.359827	H	5.144958	-0.076000	-0.759868	H	-3.193082	2.577715	0.078619	
C	2.100120	-0.603804	0.650515	F	-3.432408	-0.080168	-0.613271	H	-1.534764	3.773726	-1.232882	
C	3.452562	1.481174	-0.620935	H	-2.697684	0.357739	1.212689	H	-0.568907	2.216950	-1.491755	
H	1.544549	2.481000	-0.653644	<u>4) 15_{SI}</u> E = -714.610586			C	-2.388231	0.556249	-0.061688		
C	3.466491	-0.705756	0.391881	H (0 K) = -714.823778			H	-3.119231	0.064127	-0.716709		
H	1.559906	-1.412833	1.134756	H (298 K) = -714.595889			C	-1.100209	-0.247246	-0.185421		
C	4.151379	0.334301	-0.243320	G (298 K) = -714.652775			H	-0.672685	0.006056	-1.166166		
H	3.971058	2.299925	-1.117211	C	2.327012	-1.704138	-0.829184	C	-1.457632	-1.798871	-0.294350	
H	4.000558	-1.607244	0.685695	C	2.678122	-2.809876	-0.169103	O	-2.429606	-2.048766	-1.044472	
H	5.218077	0.250039	-0.442769	H	1.976978	-1.772305	-1.860344	O	-0.719022	-2.586398	0.349002	
F	-3.275638	-0.774550	-0.795369	H	2.624909	-3.793336	-0.630413	C	-0.082650	0.086194	0.934323	
H	-2.652104	-0.203374	1.050854	H	3.031239	-2.757101	0.856140	H	-0.316054	1.059641	1.382977	
<u>2) 14_{S2}</u> E = -714.600520			C	2.353838	-0.310815	-0.278084	H	-0.211707	-0.681570	1.704160		
H (0 K) = -714.813346			H	3.017150	0.336201	-0.868146	C	1.362562	0.094409	0.483691		
H (298 K) = -714.585591			C	0.993419	0.397524	-0.268931	C	2.122019	1.273003	0.501670		
G (298 K) = -714.643975			H	0.557690	0.229531	-1.265214	C	1.980519	-1.085178	0.030649		
C	0.372328	1.992894	-0.452236	C	1.221031	1.974241	-0.180074	C	3.456535	1.284899	0.085603	
C	0.219850	3.149863	0.195839	O	2.153981	2.396685	-0.901784	H	1.657962	2.195617	0.846876	
H	-0.395705	1.662173	-1.149420	O	0.435165	2.608031	0.568098	C	3.311651	-1.074069	-0.385420	
H	-0.660913	3.771440	0.051663	C	0.045709	-0.170732	0.814931	H	1.375152	-1.989929	0.015490	
H	0.972550	3.502323	0.893939	H	0.372885	-1.174717	1.113782	C	4.058899	0.108132	-0.360229	
C	1.549879	1.074524	-0.316039	H	0.138885	0.487792	1.684582	H	4.023352	2.214352	0.110758	
C	1.289506	-0.333825	0.225750	C	-1.408797	-0.240484	0.400559	H	3.772371	-1.997578	-0.732435	
H	1.067720	-0.256632	1.296829	C	-2.062290	-1.472599	0.257097	H	5.097824	0.111066	-0.685345	
C	2.596034	-1.236880	0.051834	C	-2.142055	0.932439	0.145886	F	-2.890732	0.434268	1.261296	
O	3.296942	-0.970232	-0.953994	C	-3.405083	-1.543469	-0.124520	<u>7) 2a_{major}</u> E = -726.175931250				
O	2.699648	-2.147473	0.904308	H	-1.507515	-2.390267	0.446757	C	-1.235229	1.380157	-0.298568	
C	0.160396	-1.122749	-0.478526	C	-3.481815	0.862723	-0.235551	C	-0.096159	0.408309	-0.001062	
H	0.345057	-1.121624	-1.561283	H	-1.617159	1.880455	0.250509	C	1.141146	1.192847	-0.468573	
H	0.305121	-2.159865	-0.145606	C	-4.122812	-0.372947	-0.372191	O	0.798600	2.585599	-0.263788	
C	-1.283923	-0.745345	-0.210228	H	-3.888342	-2.513829	-0.227745	C	-2.515157	1.233705	0.542932	
C	-2.191870	-0.555756	-1.262855	H	-4.032745	1.781912	-0.428254	F	-0.014880	0.206389	1.381514	
C	-1.777278	-0.630986	1.099814	H	-5.168902	-0.421698	-0.669529	C	2.423018	0.938921	0.302016	
C	-3.535432	-0.256342	-1.024741	F	2.867121	-0.353507	1.033595	C	-0.556927	2.741656	-0.136274	
H	-1.834761	-0.645932	-2.287306	<u>5) 15_{S2}</u> E = -714.607714			O	-1.066257	3.812181	0.055567		
C	-3.117164	-0.334240	1.345180	H (0 K) = -714.820827			I	3.246768	-1.048866	-0.151697		
H	-1.094847	-0.775782	1.933256	H (298 K) = -714.592913			C	-4.676352	-2.413739	-0.336192		
C	-4.006144	-0.143218	0.283599	G (298 K) = -714.650117			C	-5.023020	-1.220490	-0.972727		
H	-4.213477	-0.111192	-1.863711	C	2.326078	-1.881608	-0.211658	C	-4.329302	-0.044561	-0.681110	
H	-3.470461	-0.250609	2.371092	C	2.965288	-2.450460	-1.235754	C	-3.280280	-0.040152	0.248064	
H	-5.050934	0.091415	0.475484	H	1.728096	-2.497750	0.461750	C	-2.941668	-1.244904	0.882070	
F	2.482434	1.683678	0.546515	H	2.895128	-3.516876	-1.440629	C	-3.633612	-2.422062	0.592830	
H	2.058941	0.935184	-1.280436	H	3.571730	-1.861813	-1.921652	H	-1.488590	1.283129	-1.365098	
<u>3) 14_{eclisped}</u> E = -714.599699			C	2.335277	-0.409843	0.081594	H	-0.189021	-0.571300	-0.472414		
H (0 K) = -714.813167			H	3.070310	0.118322	-0.533976	H	1.294638	1.034468	-1.542761		
H (298 K) = -714.584994			C	0.998049	0.305402	-0.121932	H	-5.217831	-3.329253	-0.558565		
G (298 K) = -714.641497			H	0.633419	-0.012361	-1.109108	H	-5.837899	-1.202365	-1.691718		
C	-2.527979	1.999888	-0.172853	C	1.253847	1.878047	-0.260175	H	-4.611625	0.884054	-1.173101	
C	-1.601912	2.783792	-0.726494	O	2.244674	2.178257	-0.963377	H	-2.129692	-1.255043	1.604628	
H	-3.513316	2.420908	0.040179	O	0.425221	2.624573	0.320015	H	-3.360366	-3.345312	1.097103	
H	-1.808540	3.828169	-0.953431	C	-0.046924	-0.058261	0.964414	H	-2.238774	1.277071	1.600757	
H	-0.608675	2.420090	-0.974278	H	0.226151	-0.993718	1.470573	H	-3.135720	2.112590	0.340266	
									H	3.198593	1.647032	0.016578

H 2.254033 0.956972 1.375975

8) *2a_{minor}* E = -726.174341984

C -1.026042 1.341280 -0.244889
C -0.058637 0.566943 0.647669
C 1.274995 1.306709 0.452184
O 0.910784 2.660956 0.097226
C -2.505405 1.358057 0.182314
F -0.434646 0.715088 1.986274
C 2.164011 0.778348 -0.667647
C -0.402090 2.737084 -0.291408
O -0.914640 3.772611 -0.618471
I 3.100527 -1.143943 -0.156098
C -4.414485 -2.503337 -0.258614
C -4.530031 -1.542838 -1.265137
C -3.919223 -0.296192 -1.116275
C -3.184297 0.011389 0.036591
C -3.075289 -0.961680 1.041317
C -3.685355 -2.208443 0.895490
H -0.956788 0.932252 -1.263593
H 1.821335 1.352884 1.396664
H -4.892484 -3.472772 -0.370662
H -5.100804 -1.760468 -2.164125
H -4.022197 0.7051414 -1.900254
H -2.506208 -0.735706 1.939099
H -3.594225 -2.948498 1.686309
H 0.000558 -0.502276 0.437172
H -2.562528 1.705392 1.218333
H -3.007776 2.110578 -0.434155
H 1.616884 0.604947 -1.594948
H 2.990037 1.462968 -0.852708

9) *2b_{major}* E = -726.172337003

C -1.545646 -2.167889 -0.597276
O -0.557605 -1.570318 -1.325585
O -2.385625 -2.866611 -1.100808
C -1.412081 -1.781041 0.876188
C 0.245648 -0.690325 -0.499715
C -0.030288 -1.133511 0.950032
C 1.679725 -0.835630 -0.972463
F 0.895744 -2.111181 1.320642
C -2.608794 -0.912168 1.348071
I 2.986627 0.670668 -0.043719
C -2.953483 2.933821 -0.615865
C -3.430532 1.779484 -1.241447
C -3.328490 0.541677 -0.605183
C -2.743126 0.435871 0.666565
C -2.276101 1.603353 1.287306
C -2.377747 2.843244 0.652476
H -0.119560 0.329957 -0.651790
H 0.056223 -0.308046 1.660214
H -1.405241 -2.698600 1.473043
H -3.036151 3.897593 -1.110678
H -3.888537 1.841930 -2.224854
H -3.706934 -0.350889 -1.096735
H -1.839096 1.543798 2.282153
H -2.012094 3.736617 1.151529
H 2.097778 -1.801833 -0.701278
H 1.757521 -0.662102 -2.043984
H -3.513490 -1.507762 1.181952
H -2.511996 -0.771315 2.430782

10) *2b_{minor}* E = -726.171420627

C 1.265252 1.636672 0.902610
C 0.020325 0.754970 0.876086
C -0.861137 1.392646 -0.219131
O 0.051056 2.138164 -1.063634
C 2.602659 0.994452 1.329744
C -1.590788 0.436238 -1.147242
C 1.285889 2.258033 -0.490175
O 2.196373 2.812934 -1.046155
C 3.630889 -2.625621 -0.816843
C 3.916001 -1.375843 -1.371802
C 3.591615 -0.207210 -0.681096
C 2.974067 -0.268832 0.577949
C 2.698044 -1.529887 1.126702
C 3.021222 -2.700114 0.436484
F -0.634564 0.762183 2.098583
I -3.158263 -0.701918 -0.110876
H 1.045362 2.466224 1.591964

H 3.887686 -3.534263 -1.354673
H 4.398156 -1.308786 -2.343531
H 3.818020 0.761571 -1.116992
H 2.233319 -1.595424 2.108492
H 2.801651 -3.667130 0.881200
H 3.379980 1.754975 1.195830
H 2.542450 0.779773 2.402514
H 0.261911 -0.284975 0.633056
H -1.557553 2.097131 0.248115
H -2.102345 0.974542 -1.943647
H -0.913283 -0.303431 -1.574532

11) *2c_{major}* E = -626.944570034

C -0.401569 2.758462 -0.131548
O 0.893690 2.665871 0.302172
O -0.895834 3.808568 -0.447279
C -1.042674 1.370457 -0.136725
C 1.248368 1.293270 0.611626
C -0.096277 0.553257 0.753252
C 2.151970 0.816512 -0.521934
C -2.525078 1.416232 0.279312
I 3.094278 -1.120287 -0.066587
C -4.481794 -2.418224 -0.199868
C -4.058465 -2.001397 1.062809
C -3.437033 -0.760323 1.219054
C -3.227118 0.083527 0.120699
C -3.662658 -0.345640 -1.141802
C -4.283192 -1.584509 -1.303158
H 1.812684 1.323386 1.546343
H -0.429646 0.599755 1.796219
H -0.988769 1.008923 -1.174112
H -4.967969 -3.382080 -0.323616
H -4.214641 -2.639363 1.928751
H -3.118420 -0.430979 2.208407
H -3.521602 0.302021 -2.005039
H -4.617757 -1.896396 -2.289120
H 1.610840 0.666266 -1.456742
H 2.978689 1.507863 -0.678441
H -2.589434 1.753427 1.321415
H -3.014023 2.185435 -0.329357
H -0.026416 -0.500222 0.474975

12) *2c_{minor}* E = -626.945825328

C 1.197555 1.559324 1.113175
C -0.014016 0.628892 0.974366
C -0.905412 1.370884 -0.036853
O 0.008849 2.161805 -0.842029
C 2.555361 0.929445 1.499936
C -1.677695 0.505237 -1.016934
C 1.225235 2.282817 -0.233342
O 2.128609 2.905697 -0.729428
I -3.254501 -0.646252 0.000789
C 3.770598 -2.457947 -0.914364
C 3.142040 -2.660702 0.315252
C 2.756418 -1.565751 1.091429
C 2.987042 -0.253081 0.654682
C 3.623803 -0.062831 -0.581704
C 4.011170 -1.155760 -1.358612
H 0.975059 2.340689 1.856170
H -0.532372 0.440235 1.917104
H -1.586362 2.068655 0.464519
H 4.075947 -3.307758 -1.518990
H 2.956328 -3.669564 0.674548
H 2.277570 -1.731954 2.054422
H 3.813825 0.947320 -0.932232
H 4.507110 -0.988420 -2.311172
H 3.305828 1.725632 1.437762
H 2.499077 0.624473 2.551576
H -2.197286 1.104654 -1.763002
H -1.035341 -0.229790 -1.501750
H 0.296929 -0.335990 0.558699

13) *Unsubstituted Iodonium Ion*

C -1.664128 0.720681 0.000014
H -1.822779 1.262812 0.929306
H -1.822850 1.262698 -0.929334
C -1.664149 -0.720680 0.000093
H -1.822903 -1.262779 -0.929196
H -1.822786 -1.262664 0.929469
I 0.514358 -0.000001 -0.000017

14) *3_{outside}* E = -168.318437376

C 0.108149 1.707199 -0.062290
H 0.168133 2.028949 -1.099905
H -0.409505 2.375354 0.622331
C 1.140214 0.834791 0.454679
H 1.192713 0.725674 1.538718
I -1.005697 -0.255621 -0.015324
C 2.285770 0.334748 -0.339047
H 3.054007 1.108702 -0.128631
H 2.081376 0.395227 -1.413466
C 2.841670 -1.034917 0.076125
H 3.772284 -1.229981 -0.461814
H 3.055617 -1.075786 1.148913
H 2.132512 -1.831178 -0.170790

15) *3_{anti}* E = -168.318124245

C 0.522715 1.346902 -0.186841
H 0.701685 1.515033 -1.246877
H 0.242902 2.218495 0.400566
C 1.199533 0.245773 0.463913
H 1.202133 0.250340 1.554235
I -1.179850 -0.124842 -0.004078
C 2.137871 -0.671759 -0.221727
H 1.928489 -0.738300 -1.293301
H 2.085821 -1.672747 0.126260
C 3.570706 -0.093955 0.013043
H 4.278841 -0.775138 -0.468084
H 3.688486 0.897083 -0.433772
H 3.818761 -0.039890 1.076765

16) *3_{inside}* E = -168.317324596

C -0.486415 1.290321 0.760420
H -0.884082 0.884533 1.686823
H 0.024635 2.247681 0.832543
C -1.120333 0.934689 -0.490153
H -0.846297 1.536364 -1.356995
I 1.031788 -0.181076 -0.033416
C -2.300383 0.048540 -0.640790
H -2.252201 -0.449581 -1.616883
H -3.111877 0.797450 -0.769167
C -2.650940 -0.921014 0.486999
H -3.576550 -1.443712 0.233549
H -1.872176 -1.679294 0.620899
H -2.817787 -0.411645 1.441402

17) *4_{inside}* E = -228.215474785

C 0.595840 1.352812 -0.594752
H 1.006618 1.022351 -1.545606
H 0.126225 2.332365 -0.558500
C 1.127997 0.770290 0.614111
H 0.945390 1.271424 1.564161
I -0.985549 -0.155470 0.017098
C 2.249951 -0.218252 0.067718
H 3.163922 0.371208 0.766082
H 2.165318 -0.981046 1.348976
F 2.331546 -0.800608 -0.667089

18) *4_{outside}* E = -228.210414820

C 0.201808 1.713031 -0.047532
H 0.274906 2.041845 -1.082657
H -0.283488 2.393545 0.648282
C 1.129666 0.725609 0.454814
H 1.216996 0.602556 1.533939
I -0.972400 -0.231263 -0.017544
C 2.259785 0.170126 -0.359257
H 2.022288 0.098818 -1.426385
H 3.087799 0.890986 -0.232320
F 2.630127 -1.047048 0.133422

19) *4_{anti}* E = -228.206900855

C 0.582497 1.403509 -0.185622
H 0.782550 1.547006 -1.245881
H 0.287594 2.279862 0.387219
C 1.123777 0.247074 0.492186
H 1.180382 0.285520 1.579475
I -1.107514 -0.125061 -0.007997
C 2.087162 -0.701569 -0.198311
H 2.088935 -1.687852 0.272027
H 1.886301 -0.789020 -1.270590
F 3.301316 -0.077930 0.005784

20) 5_{inside, outside} E = -267.541243347

C	0.013949	1.659883	0.313939
H	0.287756	2.072231	-0.653709
H	-0.586638	2.278733	0.975671
C	0.855302	0.626492	0.872007
H	0.767122	0.402585	1.934335
I	-1.170735	-0.231820	-0.070926
C	2.103569	0.167182	0.181783
H	2.882150	0.779416	0.681382
F	2.050963	0.541799	-1.143820
C	2.457421	-1.306528	0.314624
H	3.436073	-1.477813	-0.139410
H	2.504699	-1.605300	1.366430
H	1.717688	-1.921778	-0.205382

21) 5_{inside, anti} E = -267.541282318

C	-0.305739	1.105172	0.929466
H	-0.589952	0.559160	1.825299
H	0.079127	2.114110	1.053184
C	-0.923251	0.723881	-0.318787
H	-0.862527	1.410502	-1.161683
I	1.322503	-0.092484	-0.094008
C	-1.966132	-0.350607	-0.380068
F	-1.836919	-1.165039	0.725619
H	-1.850147	-0.958075	-1.283807
C	-3.347833	0.328987	-0.374431
H	-3.501237	0.928674	-1.275995
H	-4.096787	-0.468315	-0.353684
H	-3.481120	0.956341	0.511471

22) 5_{outside, anti} E = -267.536607984

C	0.135301	1.601221	-0.001692
H	0.273188	1.932788	-1.029013
H	-0.251675	2.336844	0.699673
C	0.910554	0.486286	0.491883
H	0.956398	0.328661	1.569149
I	-1.320574	-0.136501	-0.029509
C	1.964447	-0.215740	-0.315091
H	1.708290	-0.239629	-1.380418
F	2.066329	-1.506171	0.150719
C	3.292995	0.524175	-0.092169
H	4.068445	-0.047872	-0.611758
H	3.268645	1.536019	-0.507693
H	3.550412	0.567615	0.969962

23) 5_{outside, inside} E = -267.534773252

C	0.010451	1.698480	-0.120616
H	-0.210163	2.045193	0.885887
H	0.590026	2.369367	-0.750617
C	-0.846923	0.714520	-0.741715
H	-0.753160	0.571920	-1.817795
I	1.190337	-0.230258	0.049563
C	-2.125158	0.182994	-0.156073
F	-2.440866	-0.967660	-0.841279
H	-2.847020	0.969927	-0.459500
C	-2.222119	-0.046968	1.342150
H	-1.540952	-0.842597	1.656784
H	-2.013977	0.864971	1.910874
H	-3.242345	-0.360317	1.576549

24) 5_{anti, outside} E = -267.532981701

C	0.098376	1.620016	0.006608
H	0.237162	1.948540	-1.021489
H	-0.318014	2.343003	0.704544
C	0.867849	0.501445	0.501841
H	0.945552	0.383390	1.582391
I	-1.306450	-0.173462	-0.027561
C	1.974226	-0.132532	-0.330366
F	2.980239	0.807759	-0.090658
H	1.725277	-0.100470	-1.396883
C	2.423823	-1.505685	0.114695
H	1.658661	-2.259735	-0.093680
H	3.327287	-1.775881	-0.438649
H	2.658106	-1.514669	1.183750

25) 5_{anti, inside} E = -267.530754907

C	0.273942	-1.030514	1.081501
H	0.547738	-0.416559	1.935636
H	-0.134788	-2.016015	1.293142

C	0.860641	-0.766283	-0.211921
H	0.784896	-1.557087	-0.956938
I	-1.310653	0.108259	-0.095598
C	1.993223	0.228192	-0.464471
H	1.921006	0.601009	-1.490580
F	3.064993	-0.665129	-0.401644
C	2.197225	1.352626	0.527800
H	3.107602	1.890862	0.250565
H	1.368230	2.066484	0.506457
H	2.334782	0.975620	1.545740

26) 16(S) E = -577.220267776

C	2.167257	0.845507	1.090547
H	2.011663	1.799414	0.595310
H	2.508025	0.879773	2.122119
C	1.346055	-0.261821	0.668970
H	1.311576	-1.153924	1.291457
I	3.791457	-0.228824	-0.061918
C	0.369139	-0.163414	-0.428536
F	0.622672	0.959077	-1.189172
H	0.397742	-1.047379	-1.077218
C	-1.069662	-0.070215	0.209592
H	-1.215436	-0.987107	0.794240
C	-2.085932	-0.085681	-0.978124
H	-1.921986	0.809719	-1.585903
H	-1.861628	-0.955047	-1.609691
C	-3.511814	-0.147890	-0.492746
C	-4.050247	-1.358280	-0.020883
C	-4.324679	0.998074	-0.496166
C	-5.366281	-1.422450	0.429518
H	-3.439760	-2.259128	-0.026133
C	-5.643283	0.935011	-0.047903
H	-3.925325	1.938173	-0.869071
C	-6.165907	-0.274283	0.419029
H	-5.773780	-2.366101	0.780005
H	-6.264457	1.825503	-0.068487
H	-7.193318	-0.324625	0.767091
C	-1.223288	1.158754	1.117278
H	-0.975534	2.078757	0.577440
H	-2.259448	1.239088	1.453587
H	-0.597777	1.099008	2.016018

27) 16(R) E = -577.216071522

C	3.069068	0.989088	0.845010
H	3.481720	1.631397	0.071975
H	3.695736	0.777292	1.707504
C	1.633207	0.954921	0.995965
H	1.218838	0.544114	1.914091
I	2.602395	-1.002563	-0.115118
C	0.728580	1.760213	0.133050
H	0.500320	2.631439	0.784039
F	1.448420	2.215135	-0.955543
C	-0.616749	1.143079	-0.318680
H	-0.355420	0.307171	-0.981940
C	-1.417704	0.593443	0.889690
H	-0.817568	-0.158578	1.421666
H	-1.607506	1.410419	1.599073
C	-2.735025	-0.041798	0.488047
C	-2.756222	-1.308040	-0.114700
C	-3.948838	0.622354	0.705350
C	-3.962291	-1.894985	-0.496659
H	-1.824229	-1.846779	-0.277380
C	-5.157808	0.036622	0.325636
H	-3.951228	1.600352	1.181044
C	-5.166959	-1.222208	-0.278082
H	-3.963189	-2.878634	-0.957286
H	-6.091051	0.562052	0.505934
H	-6.107214	-1.679601	-0.571168
C	-1.394327	2.191441	-1.126331
H	-2.307230	1.745153	-1.525950
H	-1.684376	0.642249	-0.497474
H	-0.799910	2.566808	-1.962767

28) 17(R) E = -577.220079963

C	2.031692	-0.641532	1.241656
H	1.747787	-1.643974	0.933792
H	2.367241	-0.521937	2.268525
C	1.366129	0.464371	0.598222
H	1.457220	1.454612	1.036911
I	3.784752	-0.035109	-0.053124

C	0.384169	0.276522	-0.482306
F	0.544937	-0.977744	-1.036635
H	0.486854	1.034707	-1.268014
C	-1.061609	0.405443	0.139733
H	-1.153944	-0.377949	0.901734
C	-2.073112	0.087879	-1.012781
H	-2.025235	0.903644	-1.745396
H	-1.749200	-0.827344	-1.514724
C	-3.476606	-0.074307	-0.486600
C	-3.879429	-1.293528	0.086752
C	-4.402972	0.980111	-0.553258
C	-5.173172	-1.455658	0.575743
H	-3.178530	-2.124602	0.131206
C	-5.699978	0.817848	-0.068275
H	-4.112158	1.923475	-1.009382
C	-6.086748	-0.398762	0.500983
H	-5.474787	-2.406280	1.005550
H	-6.410438	1.635962	-0.140556
H	-7.097126	-0.525954	0.878076
C	-1.298205	1.785060	0.771494
H	-1.068541	2.595047	0.067968
H	-2.351268	1.878065	1.046631
H	-0.715096	1.942319	1.684791

29) 17(S) E = -577.217616128

C	-3.147281	1.227102	-0.386460
H	-3.104391	1.298258	-1.469741
H	-4.083543	1.502893	0.091891
C	-1.917996	1.403775	0.346088
H	-1.973114	1.590419	1.416219
I	-2.775954	-0.936723	0.158989
C	-0.613826	1.631355	-0.318170
H	-0.435063	2.714227	-0.147471
F	-0.756741	1.421176	-1.675245
C	0.617832	0.862367	0.231092
C	0.760998	1.035355	1.748872
H	-0.056739	0.569870	2.310453
H	1.686793	0.557604	2.078348
H	0.820770	2.094044	2.032081
H	0.432978	-0.194687	-0.002543
C	1.882535	1.320942	-0.543839
H	1.643974	1.362193	-1.611419
H	2.141053	2.340802	-0.229628
C	3.053820	0.389252	-0.319334
C	4.072026	0.705652	0.591818
C	3.130973	-0.824243	-1.022533
C	5.139884	-0.169006	0.797447
H	4.039743	1.650633	1.129526
C	4.195019	-1.700897	-0.816794
H	2.360846	-1.074715	-1.749688
C	5.201971	-1.375849	0.096251
H	5.926581	0.095138	1.498138
H	4.245704	-2.631041	-1.375388
H	6.034898	-2.054723	0.253381

30) Unsubstituted Iodine- π Complex

C	-3.867204	0.673200	0.000018
H	-3.882112	1.243394	0.924662
H	-3.882072	1.243281	-0.924697
C	-3.867496	-0.672918	0.000098
H	-3.882596	-1.243103	-0.924549
H	-3.882633	-1.242993	0.924813
I	-0.878759	-0.000071	0.000014
I	2.047393	0.000028	-0.000032

31) 19 E = -290.503689

	H (0 K) = -290.578757	
	H (298 K) = -290.491925	
	G (298 K) = -290.546243	
C	-2.670819	0.279624 -0.681886
H	-2.770800	-0.642186 -1.242938
H	-2.659047	1.206226 -1.241538
C	-2.670795	0.279820 0.681887
H	-2.659016	1.206585 1.241271
I	0.088815	0.096919 -0.000003
I	3.272931	-0.109121 0.000001
C	-5.709971	-0.459051 0.000118
O	-6.937021	-0.601875 -0.000055
O	-5.054527	0.640093 -0.000082
H	-2.770771	-0.641831 1.243204

H -5.070997 -1.390191 0.000503

32) 6

E = -290.51361

H (0 K) = -290.58931

H (298 K) = -290.50236

G (298 K) = -290.55578

C 2.473848 -0.035867 0.814954
H 2.509152 -0.981413 1.344825
H 2.506424 0.854974 1.432801
C 2.978226 0.026969 -0.482225
H 3.071855 0.975896 -0.987447
I 0.000185 -0.008063 0.184470
I -3.189796 0.006118 -0.138692
C 5.764478 0.004351 -0.186133
O 5.223278 -1.122728 -0.277643
O 5.240496 1.142391 -0.217656
H 3.071784 -0.868326 -1.077403
H 6.880634 -0.008066 -0.056188

33) 7

E = -290.51707

H (0 K) = -290.59323

H (298 K) = -290.50596

G (298 K) = -290.55774

C -2.772997 -0.691838 0.000257
H -2.771486 -1.254777 0.922341
H -2.771466 -1.254875 -0.921771
C -2.772980 0.691798 0.000187
H -2.771448 1.254739 -0.921901
I -0.051086 -0.000014 0.000132
I 3.192599 0.000010 -0.000110
C -5.630585 0.000029 -0.000545
O -5.099879 1.138210 0.000051
O -5.099920 -1.138168 0.000003
H -2.771455 1.254834 0.922212
H -6.756617 0.000053 -0.001879

34) 8_{inside}

E = -429.03662

H (0 K) = -429.13319

H (298 K) = -429.02313

G (298 K) = -429.08200

C 2.635438 -0.029644 0.376715
H 2.698714 -0.700247 1.221905
C 2.200931 -0.480178 -0.849165
H 2.247483 0.178142 -1.706858
I -0.357820 -0.179138 -0.187271
I -3.506968 -0.016714 0.140442
C 5.521185 -0.794686 0.189582
O 4.991641 -0.740538 1.329714
O 5.038814 -0.523025 -0.932914
H 2.138951 -1.544166 -1.039136
H 6.597188 -1.133147 0.181091
C 2.930987 1.403903 0.663661
H 3.961287 1.467534 1.023363
F 2.773480 2.205611 -0.456113
H 2.253912 1.773658 1.447423

35) 8_{outside}

E = -429.03353

H (0 K) = -429.12968

H (298 K) = -429.01972

G (298 K) = -429.08022

C -2.551677 0.418287 -0.137348
H -2.721841 0.199227 -1.186430
C -2.398785 -0.628561 0.727125
H -2.334438 -0.470311 1.798540
I 0.271685 -0.119478 0.082109
I 3.431265 -0.126581 -0.057226
C -5.349993 -1.074234 -0.187657
O -4.638869 -1.772844 -0.933075
O -5.024878 -0.182957 0.655040
H -2.510777 -1.638924 0.357224
H -6.464608 -1.243214 -0.252545
C -2.761265 1.828182 0.302523
F -2.267389 2.731636 -0.633383
H -2.291320 2.028680 1.272233
H -3.846534 1.965314 0.389029

36) 8_{anti}

N/A

37) 20_{anti}

E = -369.08988

H (0 K) = -369.22270

H (298 K) = -369.07591

G (298 K) = -369.13496

C 2.645386 0.199761 0.216412
H 2.734158 0.105441 1.290564
C 2.063491 -0.857163 -0.481854
H 2.095307 -0.853132 -1.565732
I -0.406176 -0.298922 -0.103909
I -3.582532 0.124787 0.092864
C 5.328819 -0.960548 0.183949
O 4.815863 -0.784791 1.314159
O 4.919909 -0.594149 -0.944698
H 2.051624 -1.834155 -0.011743
H 6.301296 -1.528151 0.179883
C 2.874823 1.558538 -0.363120
C 4.115964 2.282988 0.174723
H 5.013837 1.775479 -0.180931
H 4.123976 3.324091 -0.170881
H 4.132977 2.284321 1.269950
H 1.979782 2.150131 -0.106637
H 2.911480 1.495158 -1.455406

38) 20_{outside}

E = -369.09042

H (0 K) = -369.22286

H (298 K) = -369.07631

G (298 K) = -369.13583

C 2.640129 0.090803 0.062946
H 2.766321 0.229623 1.128115
C 2.079442 -1.097558 -0.385601
H 2.066195 -1.320741 -1.447383
I -0.377784 -0.349818 -0.060235
I -3.533429 0.132136 0.095590
C 5.504140 -0.660447 0.413399
O 5.030724 0.156716 1.242146
O 4.965158 -1.195594 -0.583967
H 2.051668 -1.951925 0.280606
H 6.578245 -0.952866 0.592925
C 2.962243 1.245855 -0.837458
C 3.169993 2.565111 -0.089902
H 3.967131 2.437925 0.648624
H 3.455400 3.365391 -0.782963
H 2.254969 2.879072 0.426564
H 2.174364 1.339309 -1.597390
H 3.877221 0.959816 -1.368676

39) 20_{inside}

N/A

40) 9_{inside,anti}

E = -468.32893

H (0 K) = -468.45387

H (298 K) = -468.31423

G (298 K) = -468.37527

C 2.447286 0.011944 0.337104
H 2.524625 -0.515085 1.276922
C 1.996377 -0.640986 -0.786463
H 2.022993 -0.143781 -1.747255
I -0.566638 -0.221116 -0.170855
I -3.699090 0.001136 0.146438
C 5.171173 -1.415689 0.125567
O 4.599452 -1.289965 1.240136
O 4.933884 -0.860190 -0.970594
H 1.925146 -1.721460 -0.781687
H 6.034132 -2.142989 0.123257
C 2.751891 1.477561 0.366888
C 4.200667 1.792268 0.725016
H 4.843514 1.369810 -0.049791
H 4.329152 2.878756 0.791765
H 4.468550 1.322206 1.674055
H 2.072569 1.947281 1.094736
F 2.465761 2.057205 -0.872547

41) 9_{inside,outside}

E = -468.32869

H (0 K) = -468.45321

H (298 K) = -468.31369

G (298 K) = -468.37632

C -2.543555 -0.024295 -0.233433
H -2.639597 -0.238127 -1.287977
C -2.063203 -0.978992 0.631731
H -2.077120 -0.796347 1.698705
I 0.478038 -0.317136 0.119966

I 3.615045 0.003647 -0.144682
C -5.386121 -1.030668 -0.497093
O -4.926116 -0.268939 -1.387885
O -4.871987 -1.415239 0.577284
H -1.964127 -2.004364 0.300558
H -6.426356 -1.420065 -0.698181
C -2.938050 1.355271 0.203228
H -4.031309 1.377078 0.179642
C -2.377257 2.466741 -0.677305
H -2.727054 2.334729 -1.706428
H -2.728328 3.437363 -0.311635
H -1.283481 2.457451 -0.666863
F -2.535788 1.579143 1.524912

42) 9_{outside,inside}

E = -468.32687

H (0 K) = -468.45194

H (298 K) = -468.31218

G (298 K) = -468.37345

C 2.611583 -0.116448 0.358059
H 2.676928 -0.522981 1.358255
C 2.006271 -0.871838 -0.629553
H 2.040563 -0.549710 -1.663329
I -0.490925 -0.303835 -0.107595
I -3.634599 0.008711 0.066432
C 5.366333 -1.063145 0.068074
O 4.877511 -1.252049 1.203368
O 4.880630 -0.460391 -0.924447
H 1.892926 -1.937785 -0.466718
H 6.395568 -1.487909 -0.097543
C 3.011175 1.332356 0.253260
F 2.232013 2.032514 1.202229
H 4.047878 1.403194 0.588103
C 2.841939 1.994105 -1.100378
H 1.802478 1.939395 -1.439912
H 3.120878 3.050247 -1.022637
H 3.498494 1.503827 -1.822936

43) 9_{outside,anti}

E = -468.32680

H (0 K) = -468.45138

H (298 K) = -468.31186

G (298 K) = -468.37377

C 2.478312 0.098384 0.093949
H 2.688868 -0.114151 1.135123
C 1.983029 -0.882685 -0.725683
H 1.902709 -0.725473 -1.796684
I -0.568619 -0.243774 -0.122887
I -3.693221 0.002811 0.108560
C 5.191425 -1.411665 0.419530
O 4.819337 -0.808000 1.452545
O 4.752532 -1.357972 -0.758701
H 1.941223 -1.907730 -0.380702
H 6.061928 -2.116770 0.560970
C 2.781333 1.490696 -0.374253
C 4.276650 1.758949 -0.499152
H 4.763387 1.544534 0.454947
H 4.714430 1.092472 -1.244930
H 4.428237 2.808278 -0.779469
H 2.270486 1.687982 -1.325554
F 2.251866 2.389733 0.566503

44) 9_{anti,inside}

E = -468.32444

H (0 K) = -468.44928

H (298 K) = -468.30978

G (298 K) = -468.37128

C 2.536111 -0.077622 0.355677
H 2.619540 -0.494082 1.348792
C 1.919765 -0.827063 -0.638216
H 1.949838 -0.491391 -1.667978
I -0.573759 -0.337657 -0.144418
I -3.723087 0.104109 0.108927
C 5.230893 -1.157351 0.046766
O 4.629833 -1.389500 1.119547
O 4.865531 -0.496136 -0.953956
H 1.862510 -1.899907 -0.493871
H 6.252329 -1.621870 -0.038263
C 2.777899 1.405510 0.286334
C 3.150418 1.995519 -1.062579
H 2.341434 1.842415 -1.785365
H 3.306793 3.074002 -0.951679
H 4.058888 1.509261 -1.421133

H	1.844203	1.870449	0.646007
F	3.760432	1.737812	1.221324

45) 9_{anti, outside}
N/A

46) 21_{inside} E = -391.046755
 H (0 K) = -391.171168
 H (298 K) = -391.035016
 G (298 K) = -391.088669

C	-2.495406	-1.181362	0.507613
H	-2.614279	-0.768305	1.497099
H	-2.283220	-2.231344	0.390727
C	-2.595970	-0.341989	-0.585630
H	-2.467211	-0.700269	-1.594616
C	-3.072441	1.072850	-0.370775
H	-2.508176	1.785514	-0.978021
C	-4.583514	1.121208	-0.654763
H	-4.752581	0.913831	-1.715632
I	0.188756	-0.323335	0.022906
I	3.597204	0.174935	-0.033574
C	-5.182436	-0.032786	0.185787
O	-4.490160	-1.237125	-0.183347
F	-2.912180	1.411680	1.012378
H	-4.986729	2.107622	-0.395975
H	-6.264245	-0.119979	-0.023521
H	-5.069937	0.242501	1.247273

47) 21_{outside} E = -391.043189
 H (0 K) = -391.167009
 H (298 K) = -391.031247
 G (298 K) = -391.085547

C	2.396472	-1.358065	0.009168
H	2.406947	-1.472483	1.084616
H	2.185234	-2.228820	-0.590608
C	2.691361	-0.142826	-0.584480
H	2.663703	-0.026848	-1.657716
C	3.140292	1.039450	0.233103
C	4.668382	0.962464	0.432773
H	4.997382	1.664097	1.209059
I	-0.185749	-0.291892	-0.150305
I	-3.578132	0.130290	0.123781
C	5.020498	-0.507467	0.729642
O	4.457384	-1.307026	-0.325235
H	2.625036	1.037712	1.199921
F	2.840625	2.248297	-0.459466
H	5.118067	1.239936	-0.525678
H	4.644197	-0.769405	1.738325
H	6.118402	-0.619059	0.763704

Table 1: Crystal data and refinement details

Crystal identification	ARC1394
Chemical formula	C ₁₂ H ₁₂ FI ₂ O ₂
Formula weight	334.13
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> (Å)	9.3877(4)
<i>b</i> (Å)	5.9073(3)
<i>c</i> (Å)	11.1222(6)
α (°)	90
β (°)	106.906(3)
γ (°)	90
Cell volume (Å ³)	590.14(5)
<i>Z</i>	2
Calculated density (Mg/m ³)	1.880
Absorption coefficient (mm ⁻¹)	2.709
<i>F</i> ₀₀₀	324
Crystal size (mm)	0.04 x 0.04 x 0.20
Description of crystal	Colourless needle
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.58, 0.90
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-12 ≤ <i>h</i> ≤ 11, -7 ≤ <i>k</i> ≤ 7, 0 ≤ <i>l</i> ≤ 14
Reflections measured	4664
Unique reflections	2483
<i>R</i> _{int}	0.029
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	2358
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	146
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.1063
<i>R</i>	0.0253
w <i>R</i>	0.0277
Residual electron density (min,max) (eÅ ⁻³)	-0.79, 0.88

Table 2: Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
O(1)	0.7473(3)	-0.0579(5)	0.3217(3)	0.0273
O(2)	0.8505(3)	0.2254(4)	0.4496(3)	0.0205
C(1)	0.7357(4)	0.1287(6)	0.3616(3)	0.0197
C(2)	0.6045(3)	0.2908(12)	0.3248(3)	0.0199
C(3)	0.6388(4)	0.4544(6)	0.4343(3)	0.0199
C(4)	0.8088(4)	0.4516(7)	0.4840(4)	0.0194
C(5)	0.5983(4)	0.4027(7)	0.1978(4)	0.0229
C(6)	0.4451(4)	0.4916(7)	0.1291(3)	0.0208
C(7)	0.3501(4)	0.3578(6)	0.0365(3)	0.0255
C(8)	0.2063(4)	0.4326(8)	-0.0249(4)	0.0313
C(9)	0.1570(5)	0.6388(9)	0.0046(4)	0.0331
C(10)	0.2513(4)	0.7754(12)	0.0957(4)	0.0306
C(11)	0.3953(4)	0.7005(7)	0.1579(4)	0.0242
F(1)	0.5808(2)	0.3627(4)	0.5281(2)	0.0277
C(12)	0.8760(4)	0.4710(6)	0.6239(4)	0.0221
I(1)	0.83706(2)	0.80334(14)	0.685926(17)	0.0261

Table 3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(21)	0.5042	0.2203	0.3111	0.0238
H(31)	0.5966	0.6091	0.4109	0.0249
H(41)	0.8458	0.5866	0.4478	0.0241
H(51)	0.6703	0.5317	0.2138	0.0280
H(52)	0.6277	0.2878	0.1434	0.0280
H(71)	0.3851	0.2081	0.0141	0.0309
H(81)	0.1385	0.3355	-0.0908	0.0364
H(91)	0.0535	0.6905	-0.0394	0.0400
H(101)	0.2162	0.9262	0.1165	0.0378
H(111)	0.4629	0.7982	0.2235	0.0292
H(121)	0.9857	0.4434	0.6457	0.0263
H(122)	0.8297	0.3558	0.6667	0.0263

Table 4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0285(14)	0.0211(15)	0.0298(14)	-0.0035(12)	0.0047(11)	0.0017(12)
O(2)	0.0171(12)	0.0188(14)	0.0242(13)	-0.0008(10)	0.0037(10)	0.0020(9)
C(1)	0.0168(16)	0.0219(19)	0.0196(17)	0.0017(14)	0.0041(13)	0.0007(13)
C(2)	0.0150(12)	0.0229(19)	0.0215(13)	0.002(3)	0.0050(10)	0.001(2)
C(3)	0.0176(15)	0.0226(19)	0.0221(16)	0.0027(14)	0.0101(13)	0.0015(14)

C(4)	0.0184(16)	0.0158(18)	0.0262(18)	-0.0008(15)	0.0097(14)	-0.0003(14)
C(5)	0.0224(17)	0.0242(18)	0.0234(17)	0.0027(15)	0.0088(14)	0.0014(14)
C(6)	0.0209(16)	0.024(2)	0.0183(16)	0.0045(14)	0.0067(13)	0.0004(14)
C(7)	0.0282(17)	0.030(3)	0.0187(15)	-0.0026(13)	0.0081(13)	-0.0007(14)
C(8)	0.0247(18)	0.046(3)	0.0206(18)	-0.0007(18)	0.0022(14)	-0.0066(18)
C(9)	0.0231(19)	0.049(3)	0.028(2)	0.0129(19)	0.0083(16)	0.0062(18)
C(10)	0.0336(17)	0.032(4)	0.0287(16)	0.008(2)	0.0132(14)	0.012(2)
C(11)	0.0291(19)	0.0189(18)	0.0249(18)	0.0010(15)	0.0085(15)	0.0021(15)
F(1)	0.0221(9)	0.0413(19)	0.0231(10)	0.0011(9)	0.0118(8)	-0.0056(9)
C(12)	0.0228(16)	0.0198(18)	0.0233(17)	0.0009(14)	0.0059(14)	0.0007(15)
I(1)	0.03121(11)	0.02371(12)	0.02344(10)	-0.00181(17)	0.00791(7)	0.00085(17)

Table 5: Bond lengths (Å)

O(1) - C(1)	1.205(5)	C(5) - C(6)	1.513(5)
O(2) - C(1)	1.354(4)	C(6) - C(7)	1.395(5)
O(2) - C(4)	1.474(5)	C(6) - C(11)	1.390(6)
C(1) - C(2)	1.519(6)	C(7) - C(8)	1.395(6)
C(2) - C(3)	1.514(7)	C(8) - C(9)	1.376(7)
C(2) - C(5)	1.545(5)	C(9) - C(10)	1.392(7)
C(3) - C(4)	1.530(5)	C(10) - C(11)	1.399(6)
C(3) - F(1)	1.417(4)	C(12) - I(1)	2.147(4)
C(4) - C(12)	1.504(5)		

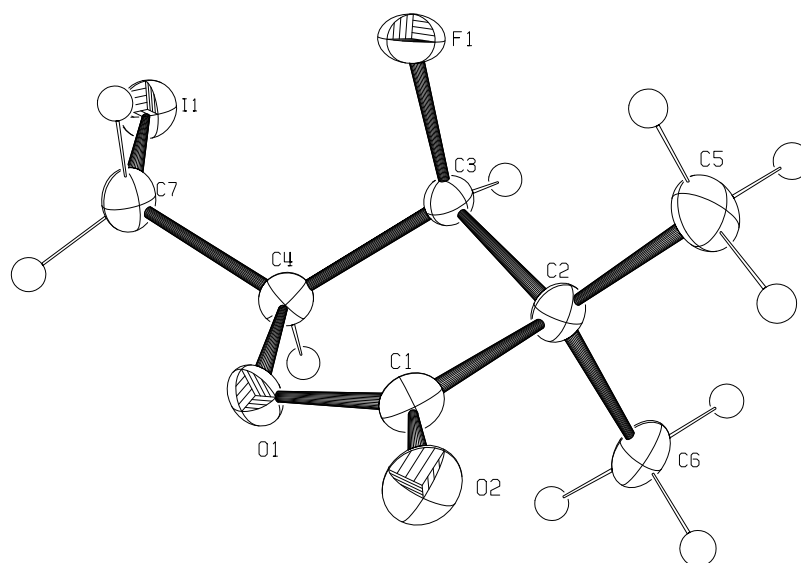
Note – H atoms have been excluded

Table 6: Bond angles (°)

C(1) - O(2) - C(4)	110.8(3)	C(3) - C(4) - C(12)	117.0(3)
O(1) - C(1) - O(2)	120.9(3)	C(2) - C(5) - C(6)	112.8(3)
O(1) - C(1) - C(2)	129.1(4)	C(5) - C(6) - C(7)	119.1(3)
O(2) - C(1) - C(2)	110.0(3)	C(5) - C(6) - C(11)	121.8(3)
C(1) - C(2) - C(3)	102.7(3)	C(7) - C(6) - C(11)	119.2(3)
C(1) - C(2) - C(5)	109.1(3)	C(6) - C(7) - C(8)	120.1(4)
C(3) - C(2) - C(5)	113.9(5)	C(7) - C(8) - C(9)	120.5(4)
C(2) - C(3) - C(4)	103.8(3)	C(8) - C(9) - C(10)	120.0(4)
C(2) - C(3) - F(1)	108.1(3)	C(9) - C(10) - C(11)	119.6(5)
C(4) - C(3) - F(1)	108.3(3)	C(6) - C(11) - C(10)	120.6(4)
O(2) - C(4) - C(3)	104.1(3)	C(4) - C(12) - I(1)	110.0(3)
O(2) - C(4) - C(12)	105.9(3)		

Note – H atoms have been excluded

I. II. Single-crystal X-ray diffraction report for 4-fluoro-5-(iodomethyl)-3,3-dimethyldihydrofuran-2(3H)-one ($\pm$)-2d



Crystals of 4-fluoro-5-(iodomethyl)-3,3-dimethyldihydrofuran-2(3H)-one were grown by recrystallisation from hexane/DCM. A polycrystalline aggregate was cut to give a fragment having dimensions approximately 0.08 x 0.14 x 0.16 mm. This was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N₂ using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package¹.

Examination of the systematic absences of the intensity data showed the space group to be *P* 2₁/*n*. The structure was solved using the direct-methods program SIR92², which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite³. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give *R* = 0.0292, *wR* = 0.0281.

Attached is a thermal ellipsoid plot (ORTEP-3⁴) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

Table 1: Crystal data and refinement details

Crystal identification	ARC1323
Chemical formula	C ₇ H ₁₀ FIO ₂
Formula weight	272.06
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.3702(3)
<i>b</i> (Å)	5.9546(2)
<i>c</i> (Å)	18.0184(7)
α (°)	90
β (°)	93.134(2)
γ (°)	90
Cell volume (Å ³)	896.72(6)
<i>Z</i>	4
Calculated density (Mg/m ³)	2.015
Absorption coefficient (mm ⁻¹)	3.539
<i>F</i> ₀₀₀	520
Crystal size (mm)	0.08 x 0.14 x 0.16
Description of crystal	Colourless fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.57, 0.97
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 7, 0 ≤ <i>l</i> ≤ 23
Reflections measured	7386
Unique reflections	2223
<i>R</i> _{int}	0.042
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	1476
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	100
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.1021
<i>R</i>	0.0292
w <i>R</i>	0.0281
Residual electron density (min,max) (eÅ ⁻³)	-0.86, 0.82

Table 2: Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
O(1)	0.3061(3)	0.2925(5)	0.19027(16)	0.0256
C(1)	0.4528(5)	0.3731(7)	0.1770(2)	0.0240
C(2)	0.5479(5)	0.2020(6)	0.1358(2)	0.0224
C(3)	0.4138(5)	0.0571(7)	0.1004(2)	0.0210
C(4)	0.2838(5)	0.0700(6)	0.1562(2)	0.0217
O(2)	0.4940(4)	0.5571(5)	0.19876(19)	0.0344
C(5)	0.6586(6)	0.3092(8)	0.0822(3)	0.0374
C(6)	0.6454(5)	0.0629(8)	0.1944(3)	0.0312
F(1)	0.3563(3)	0.1563(5)	0.03328(13)	0.0309
C(7)	0.1117(5)	0.0658(7)	0.1255(3)	0.0275
I(1)	0.04840(3)	-0.26776(5)	0.089092(17)	0.0318

Table 3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(31)	0.4485	-0.0997	0.0895	0.0252
H(41)	0.2965	-0.0655	0.1887	0.0260
H(51)	0.7184	0.1892	0.0565	0.0452
H(52)	0.7362	0.4097	0.1102	0.0452
H(53)	0.5942	0.3992	0.0444	0.0452
H(61)	0.7099	-0.0523	0.1689	0.0371
H(62)	0.7186	0.1644	0.2245	0.0371
H(63)	0.5709	-0.0137	0.2277	0.0371
H(71)	0.0399	0.1132	0.1652	0.0330
H(72)	0.0990	0.1716	0.0825	0.0330

Table 4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0256(14)	0.0237(15)	0.0280(15)	-0.0068(12)	0.0064(11)	-0.0018(12)
C(1)	0.028(2)	0.0177(18)	0.026(2)	0.0011(16)	-0.0022(17)	-0.0034(16)
C(2)	0.0206(18)	0.0178(18)	0.029(2)	-0.0031(15)	-0.0014(15)	-0.0028(15)
C(3)	0.0200(19)	0.0214(18)	0.0214(19)	0.0015(15)	0.0004(15)	-0.0013(15)
C(4)	0.025(2)	0.0148(17)	0.025(2)	-0.0019(16)	0.0000(16)	-0.0021(15)
O(2)	0.0367(18)	0.0210(15)	0.0448(19)	-0.0082(14)	-0.0034(15)	-0.0039(13)
C(5)	0.034(2)	0.040(3)	0.038(3)	-0.001(2)	0.011(2)	-0.017(2)
C(6)	0.024(2)	0.027(2)	0.042(3)	-0.0019(19)	-0.0068(19)	0.0026(17)
F(1)	0.0334(14)	0.0395(14)	0.0194(12)	0.0024(10)	-0.0006(10)	-0.0053(11)
C(7)	0.022(2)	0.024(2)	0.037(2)	-0.0044(18)	0.0026(18)	-0.0076(17)
I(1)	0.02915(14)	0.02942(15)	0.03667(15)	-0.00071(16)	0.00009(10)	-0.00973(14)

Table 5: Bond lengths (Å)

O(1) - C(1)	1.352(5)	C(2) - C(6)	1.540(6)
O(1) - C(4)	1.468(4)	C(3) - C(4)	1.523(6)
C(1) - C(2)	1.513(6)	C(3) - F(1)	1.407(5)
C(1) - O(2)	1.208(5)	C(4) - C(7)	1.514(6)
C(2) - C(3)	1.527(5)	C(7) - I(1)	2.149(4)
C(2) - C(5)	1.515(6)		

Note – H atoms have been excluded

Table 6: Bond angles (°)

C(1) - O(1) - C(4)	110.0(3)	C(5) - C(2) - C(6)	110.1(4)
O(1) - C(1) - C(2)	110.8(3)	C(2) - C(3) - C(4)	103.4(3)
O(1) - C(1) - O(2)	120.7(4)	C(2) - C(3) - F(1)	109.3(3)
C(2) - C(1) - O(2)	128.4(4)	C(4) - C(3) - F(1)	108.8(3)
C(1) - C(2) - C(3)	101.0(3)	O(1) - C(4) - C(3)	104.1(3)
C(1) - C(2) - C(5)	112.7(4)	O(1) - C(4) - C(7)	105.3(3)
C(3) - C(2) - C(5)	115.7(3)	C(3) - C(4) - C(7)	117.2(4)
C(1) - C(2) - C(6)	107.4(3)	C(4) - C(7) - I(1)	109.9(3)
C(3) - C(2) - C(6)	109.4(3)		

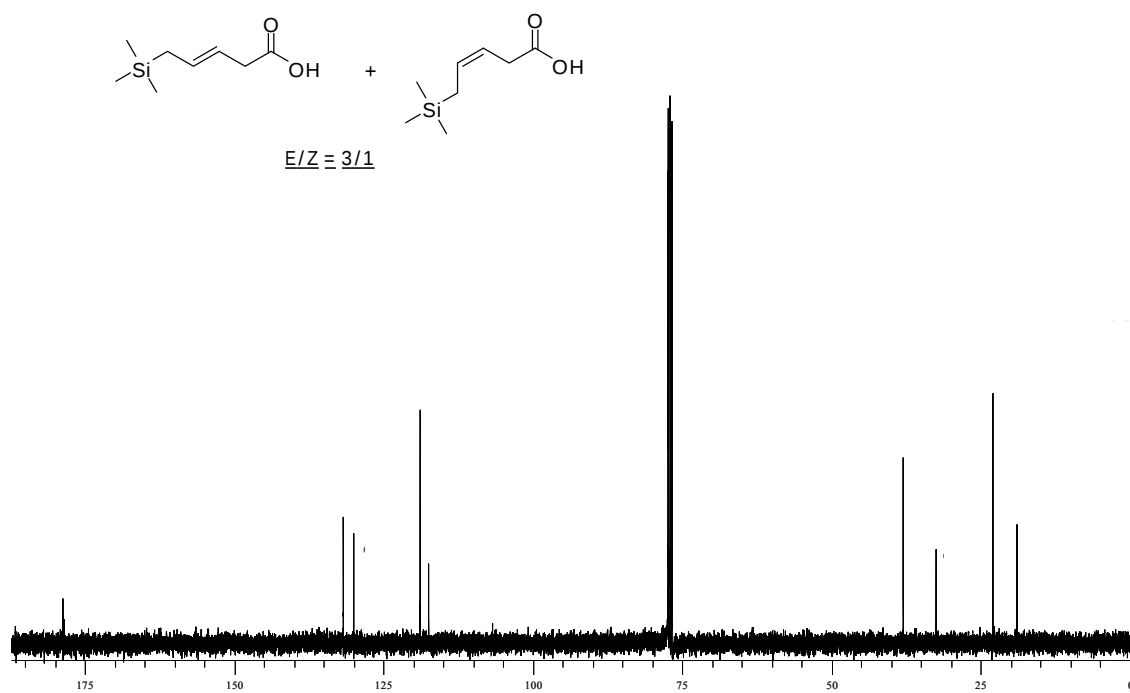
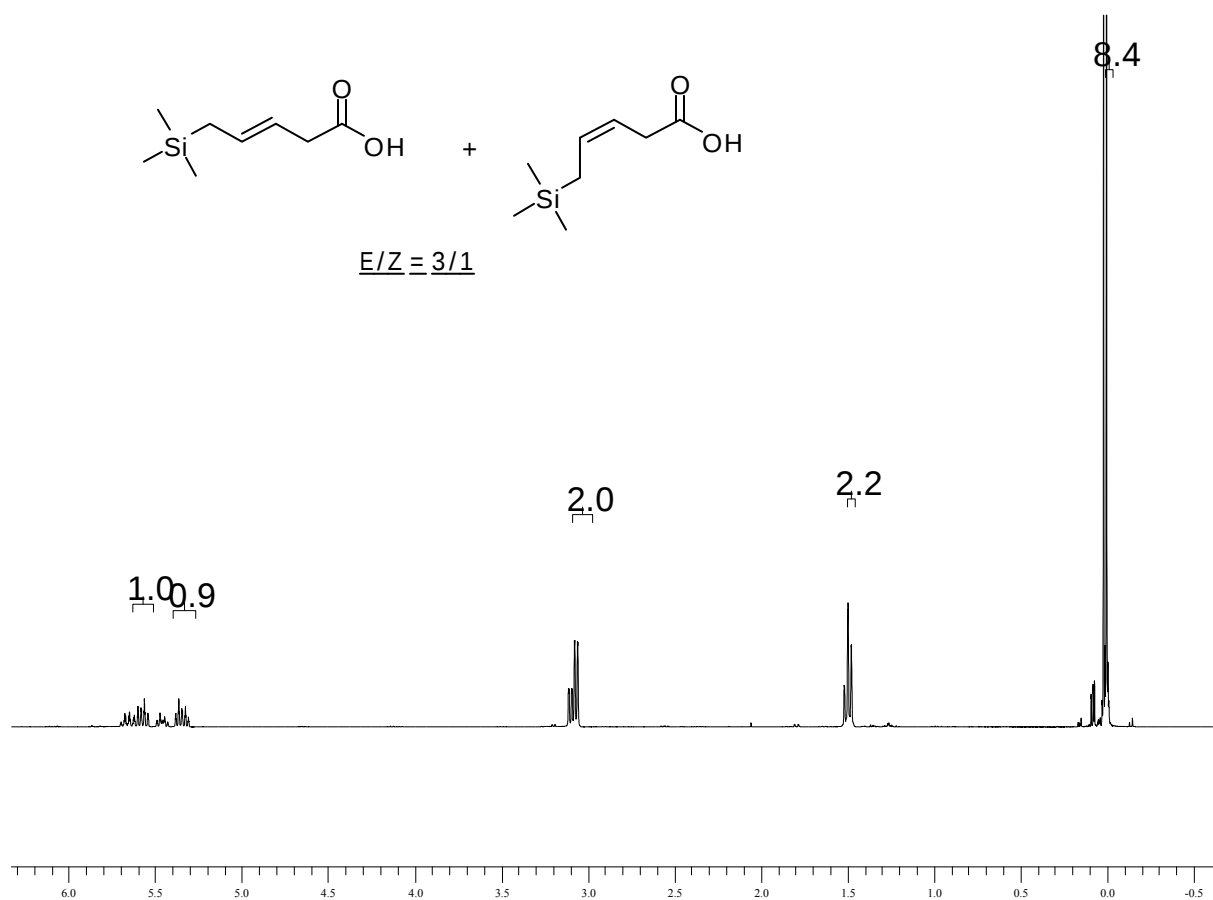
Note – H atoms have been excluded

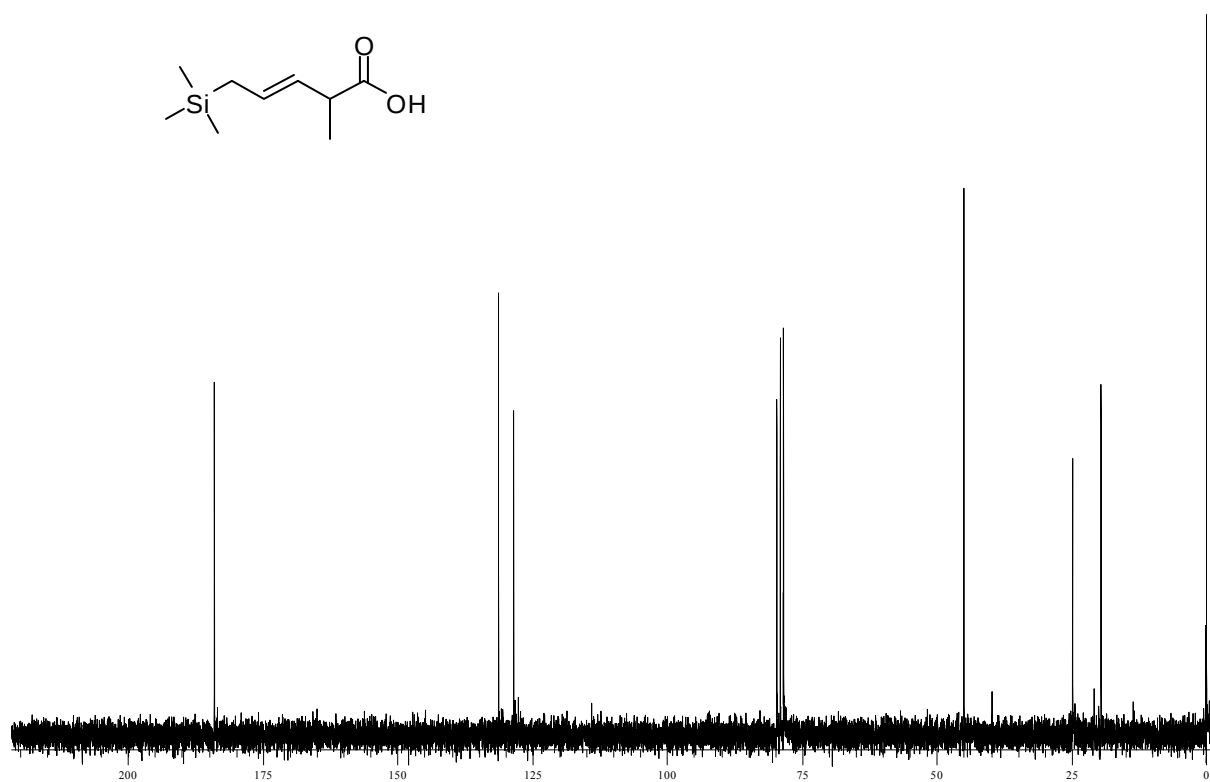
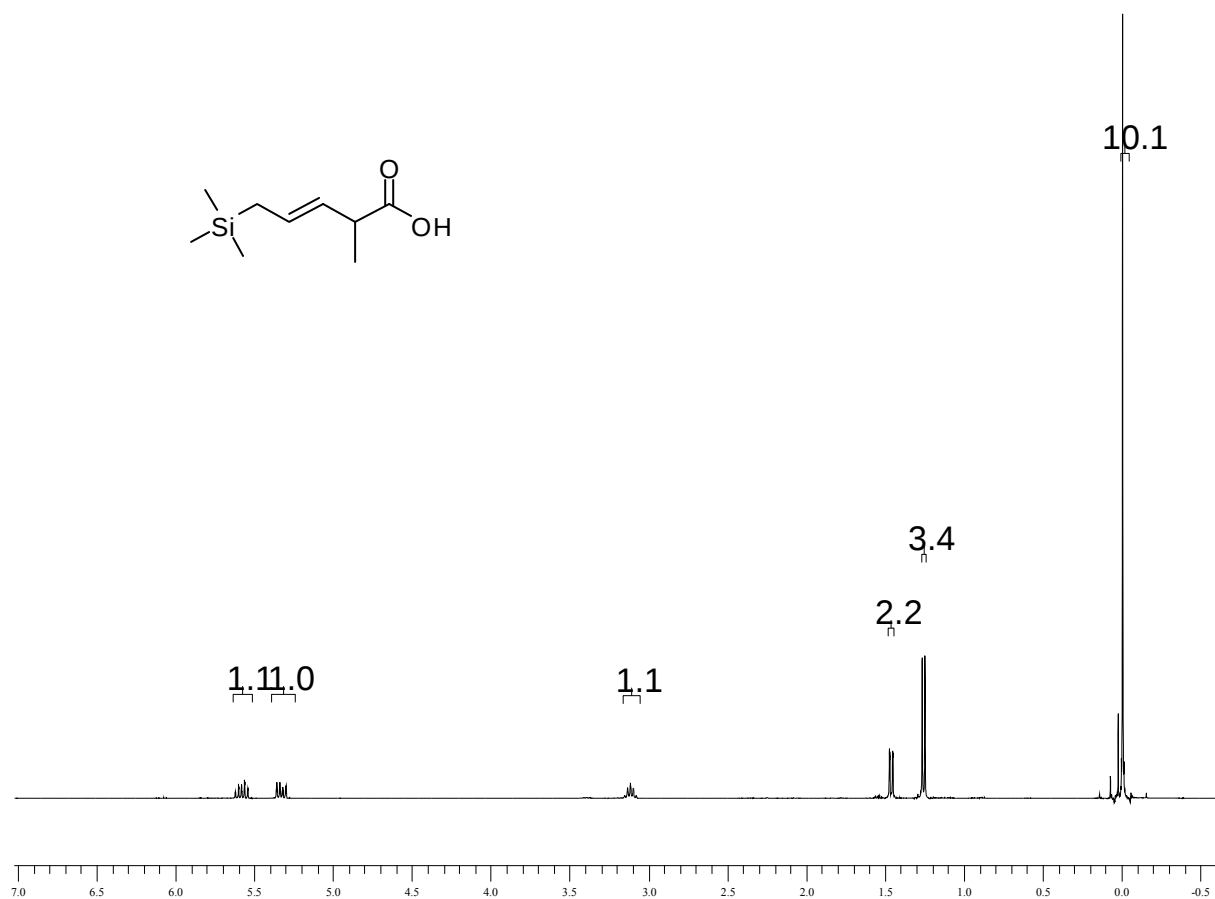
References:

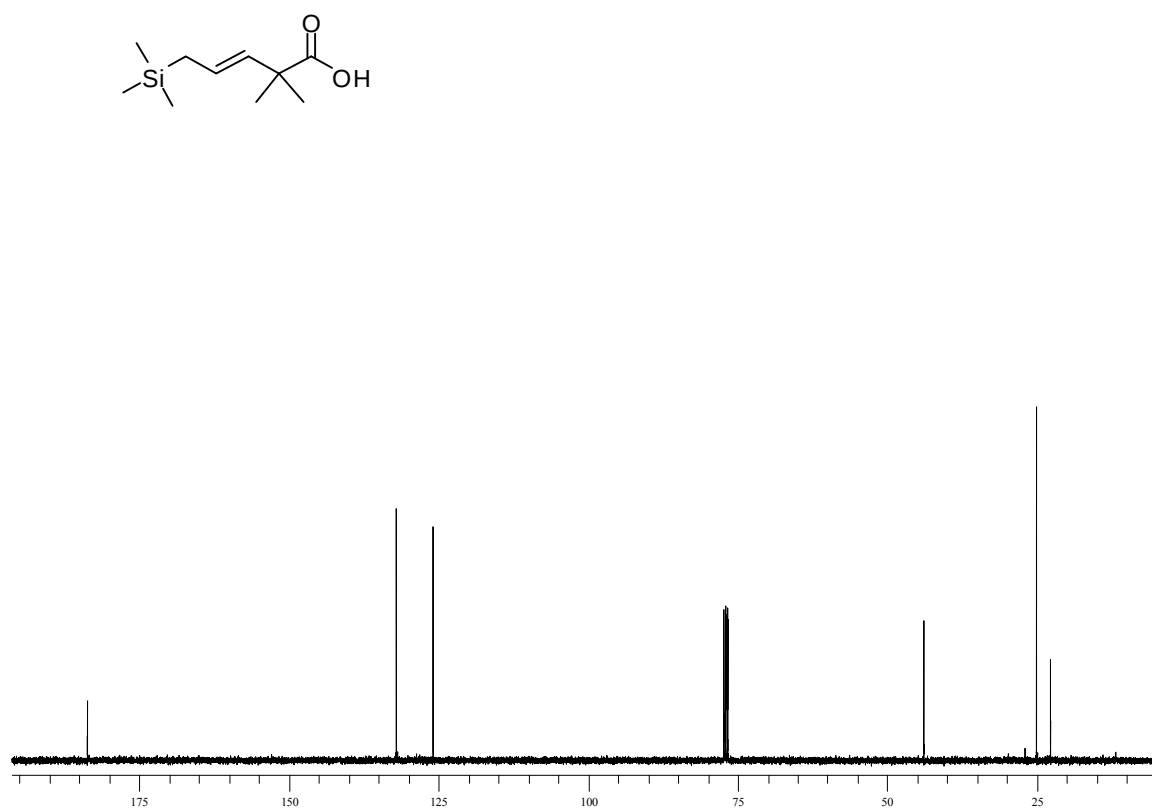
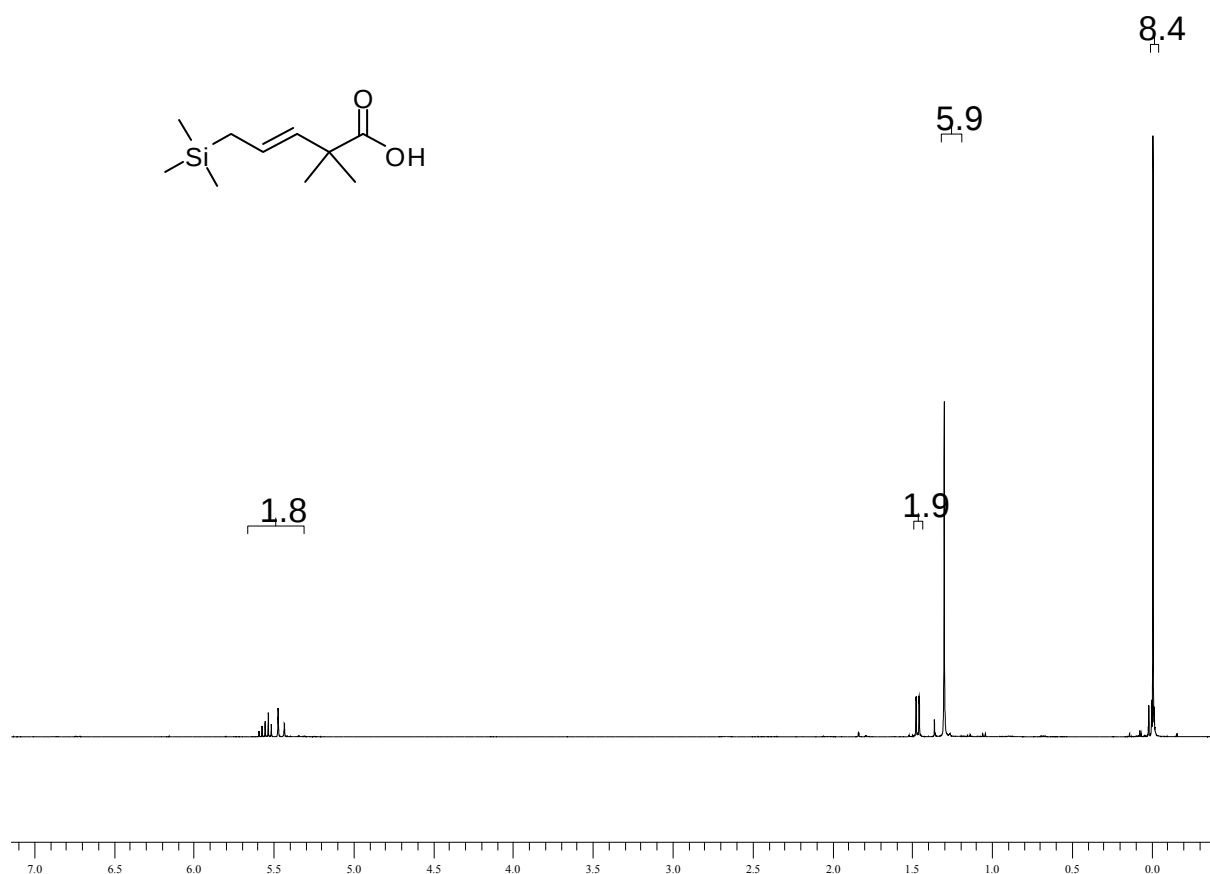
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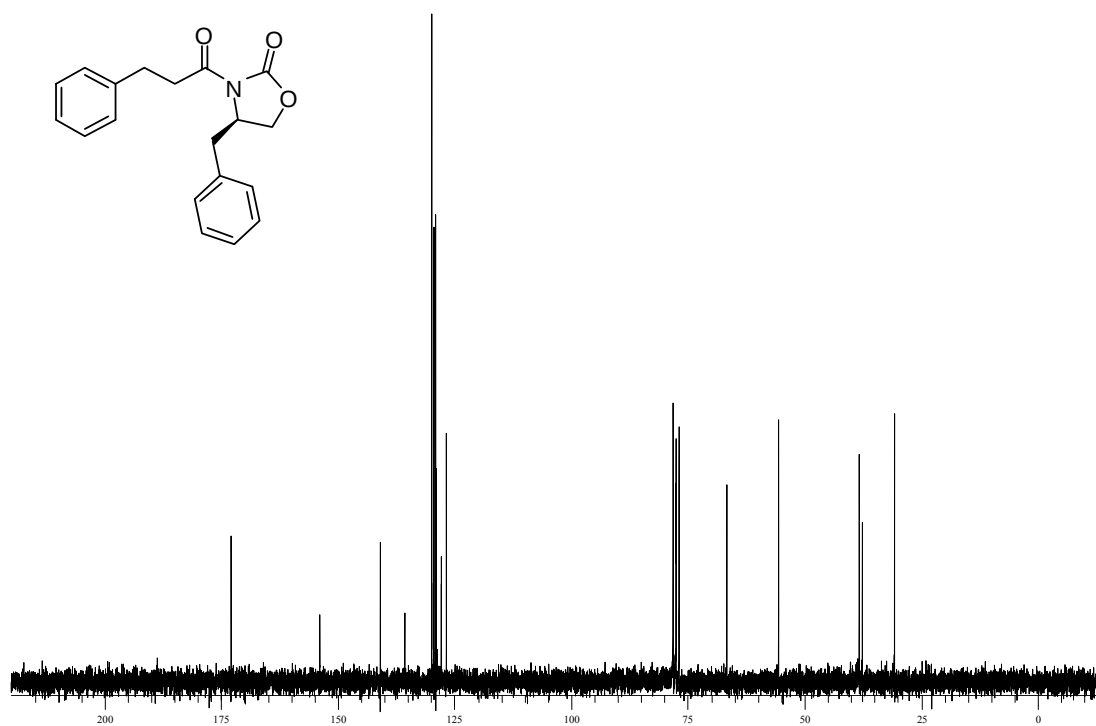
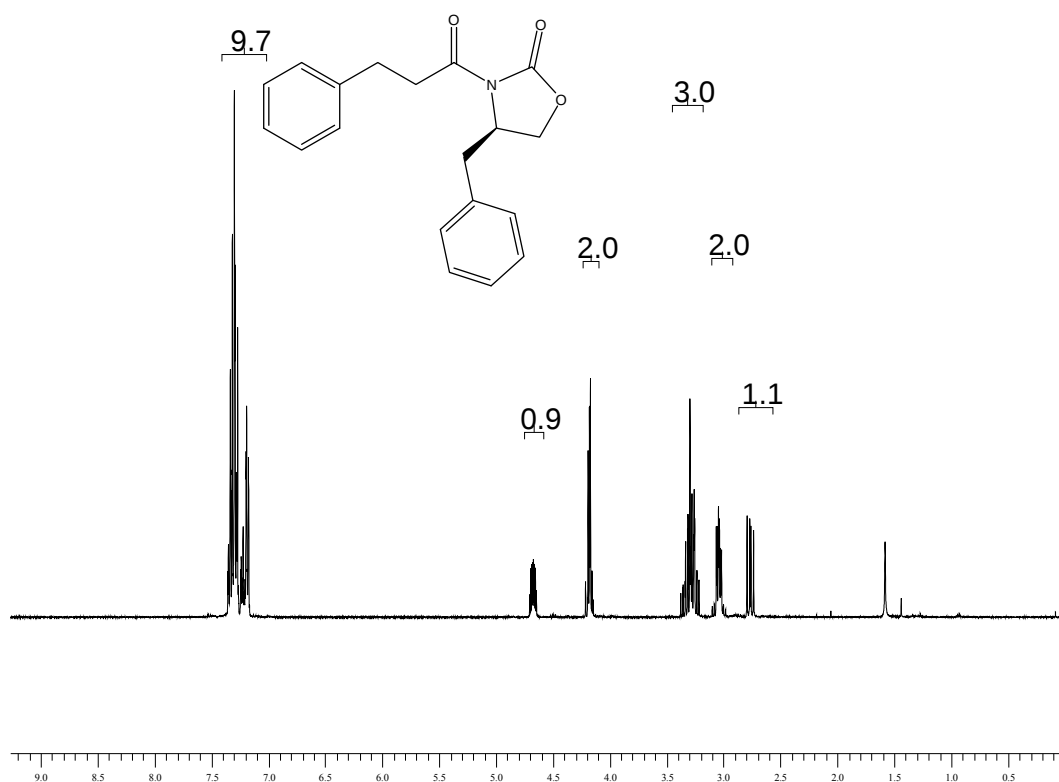
J. NMR SPECTRA**J. I. Iodolactones**

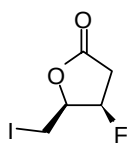
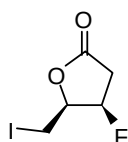
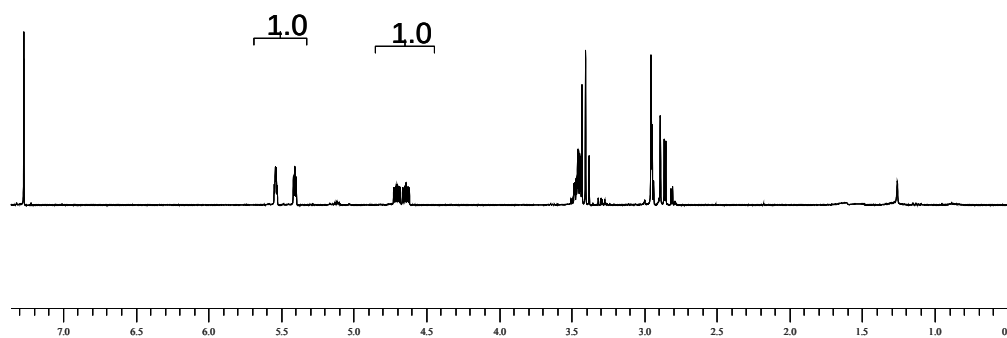
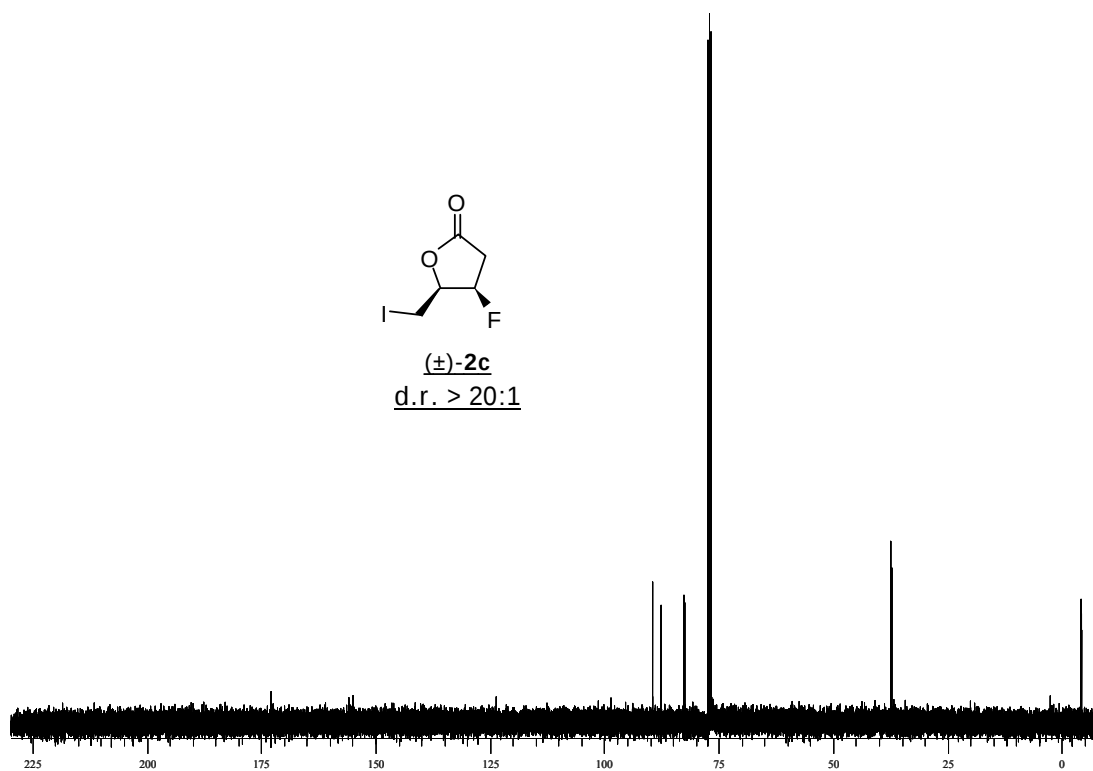
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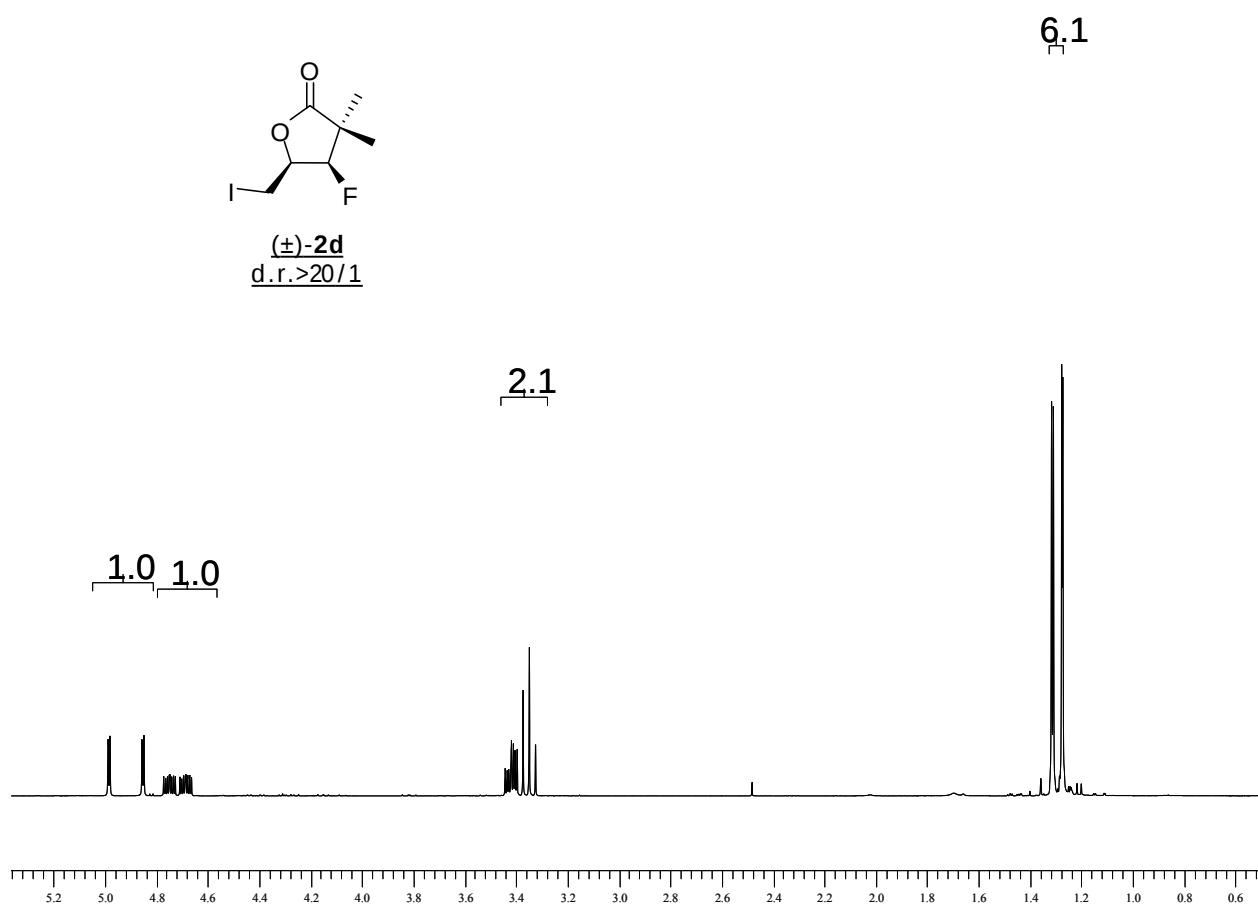
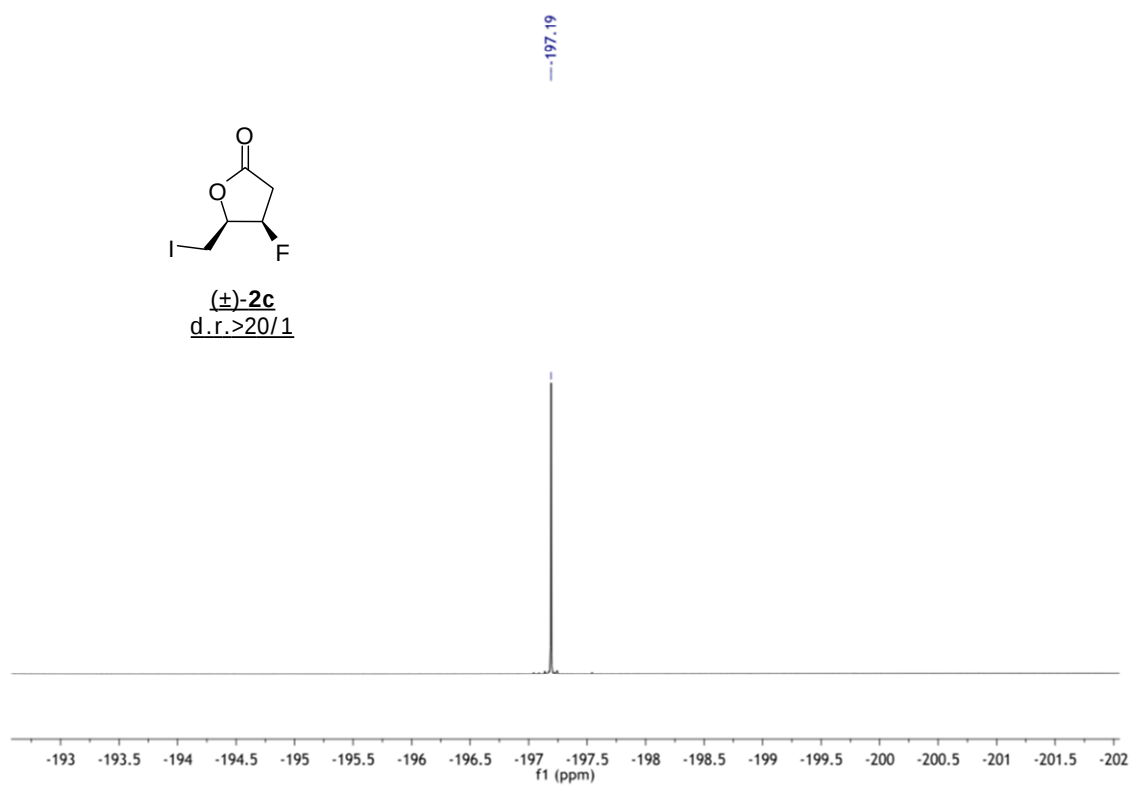


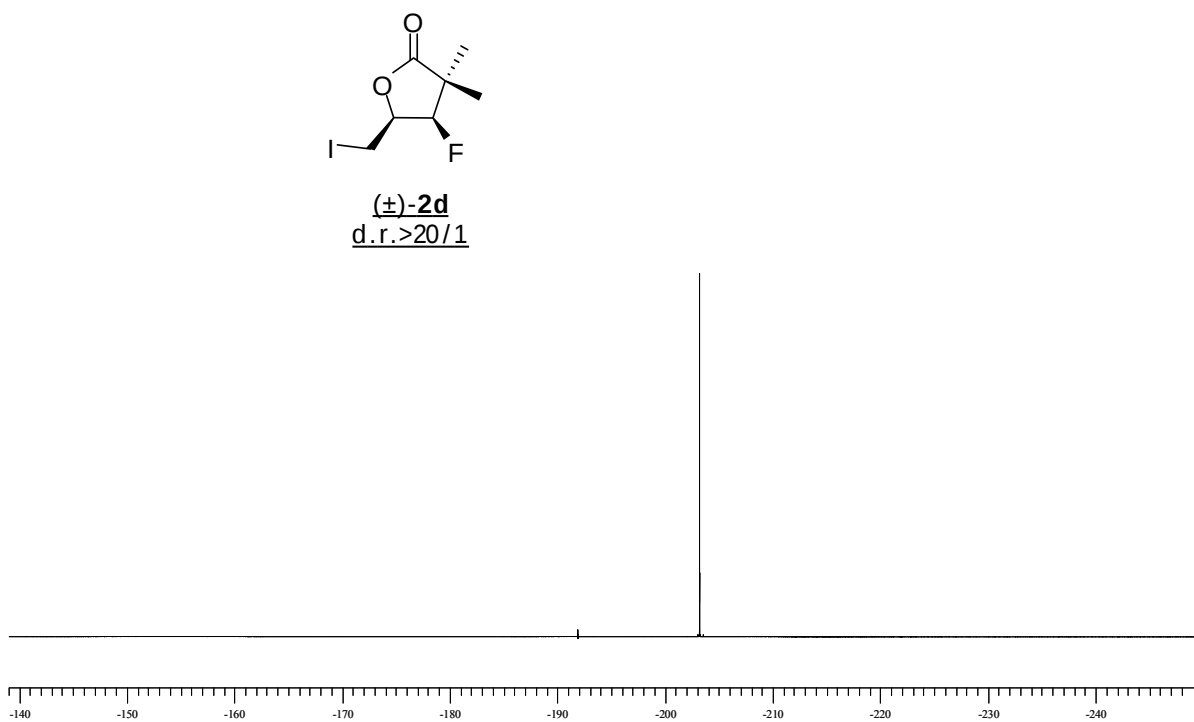
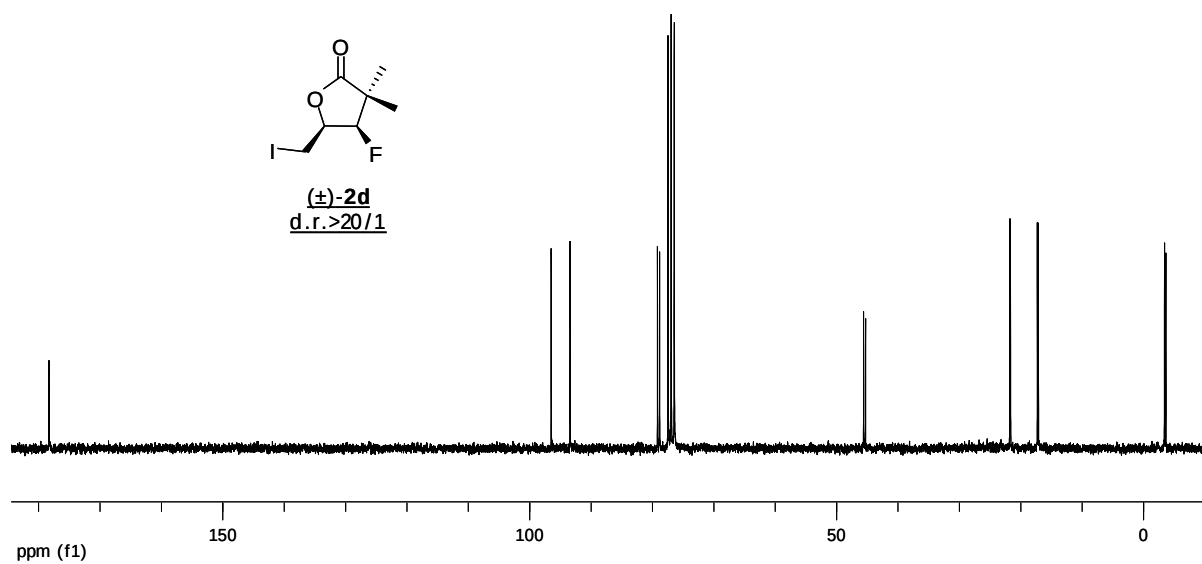


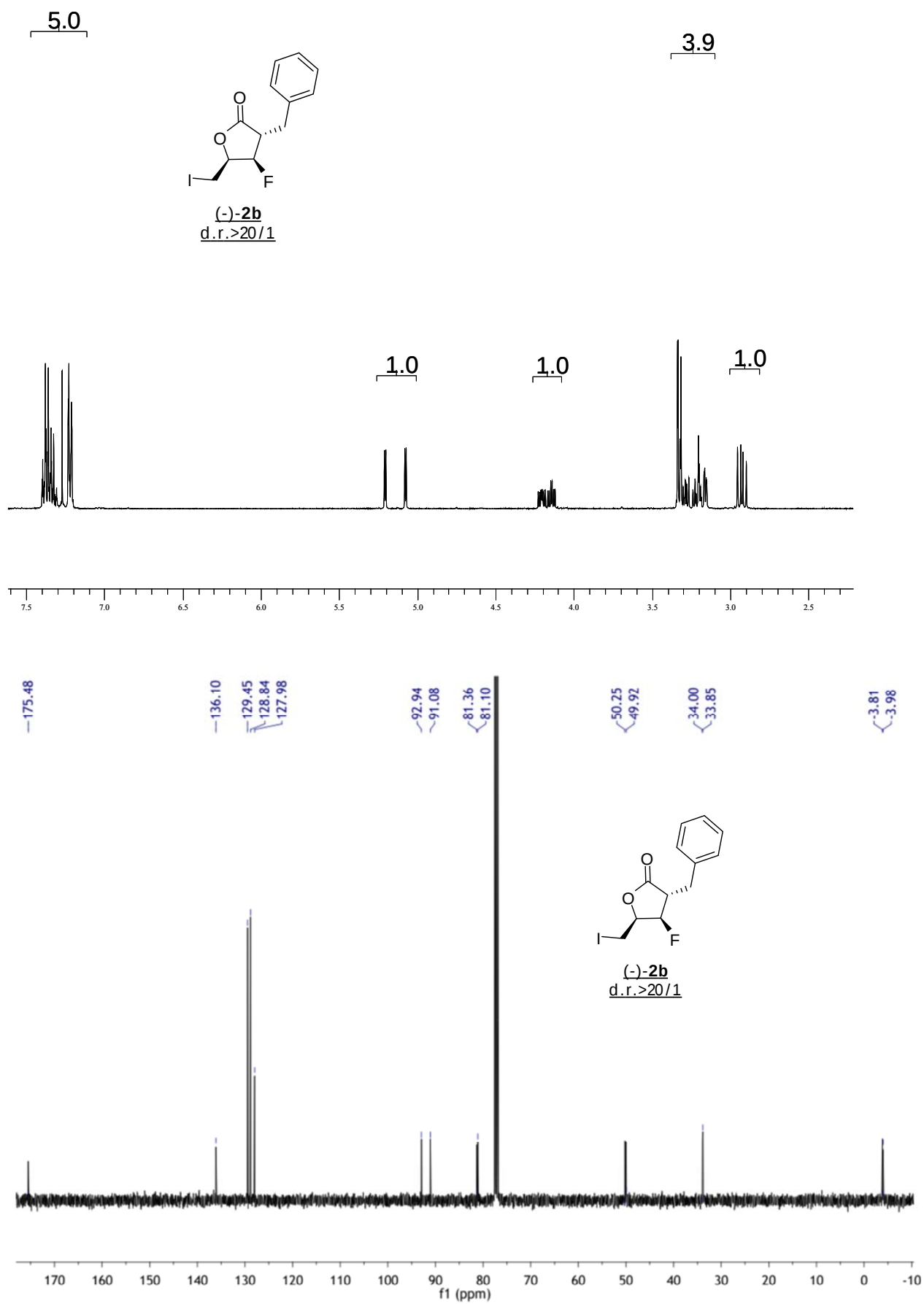


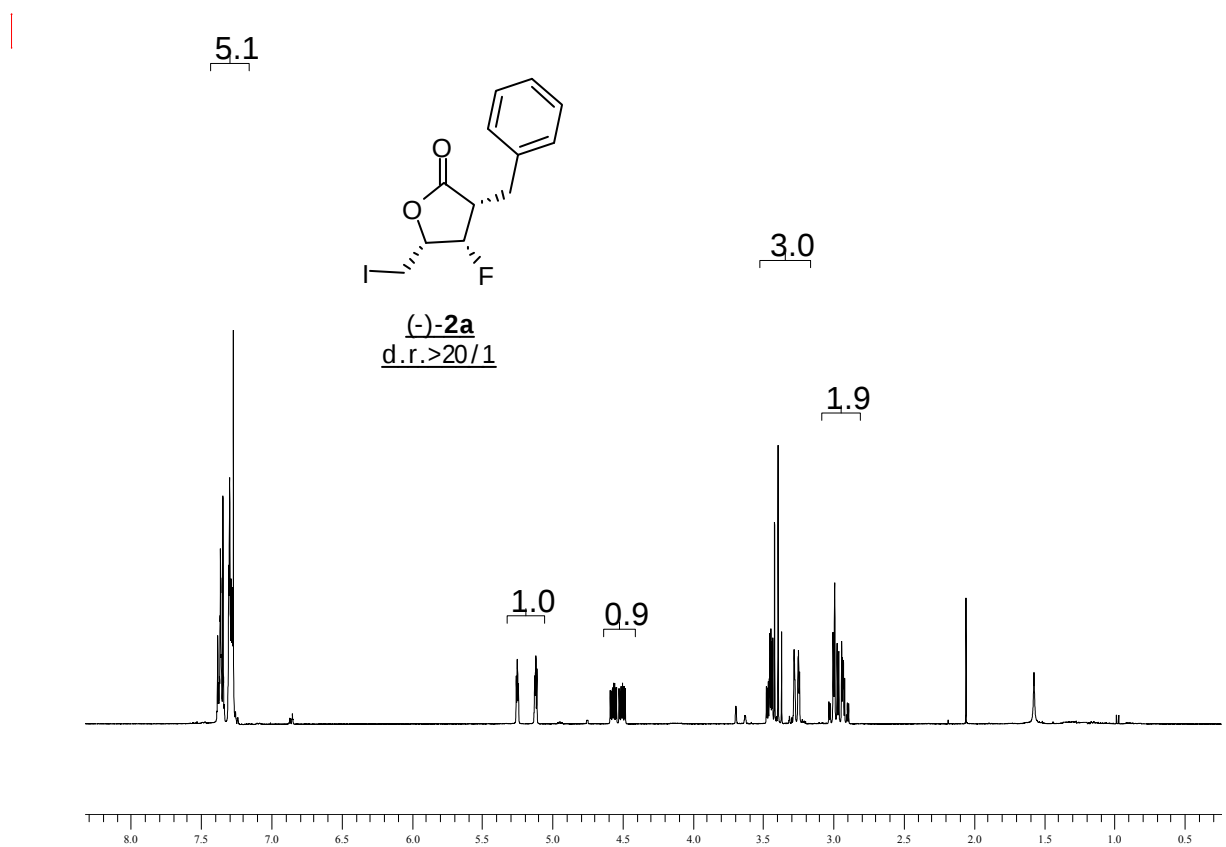
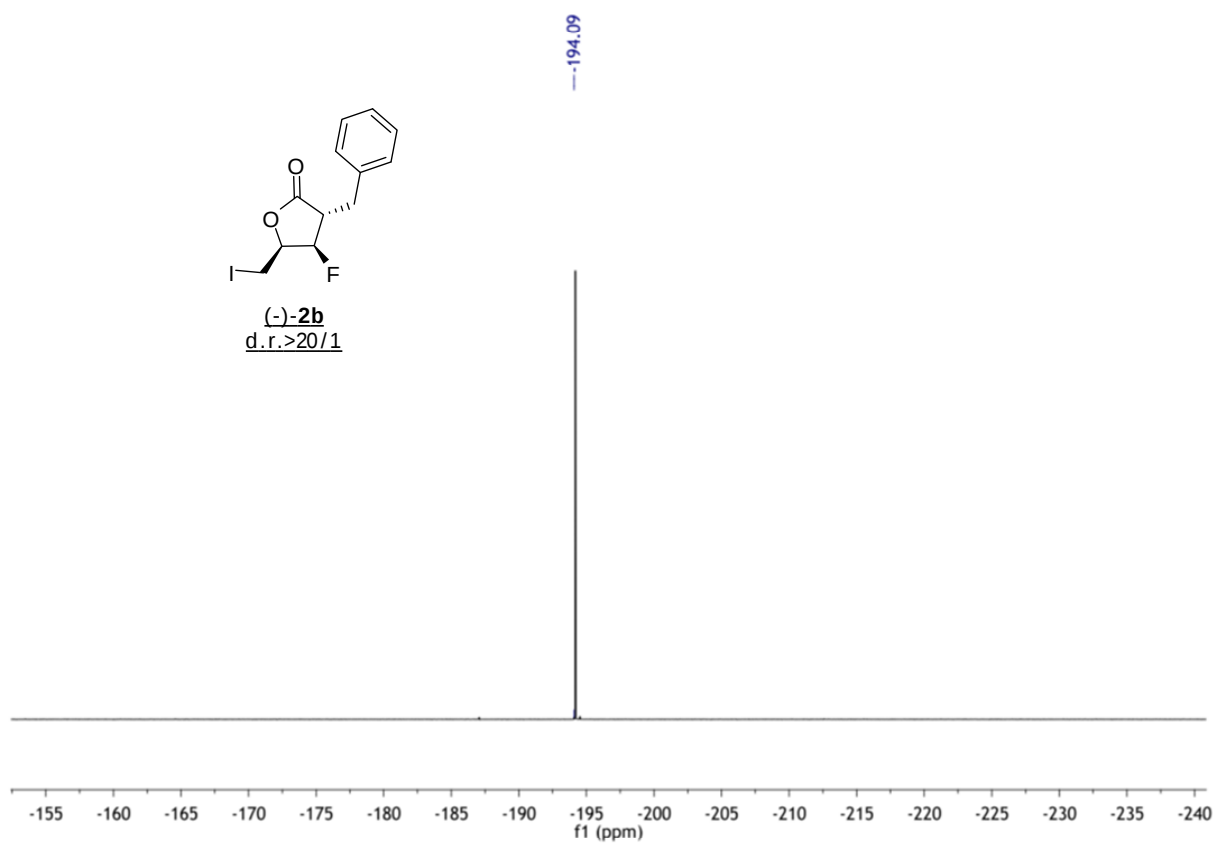


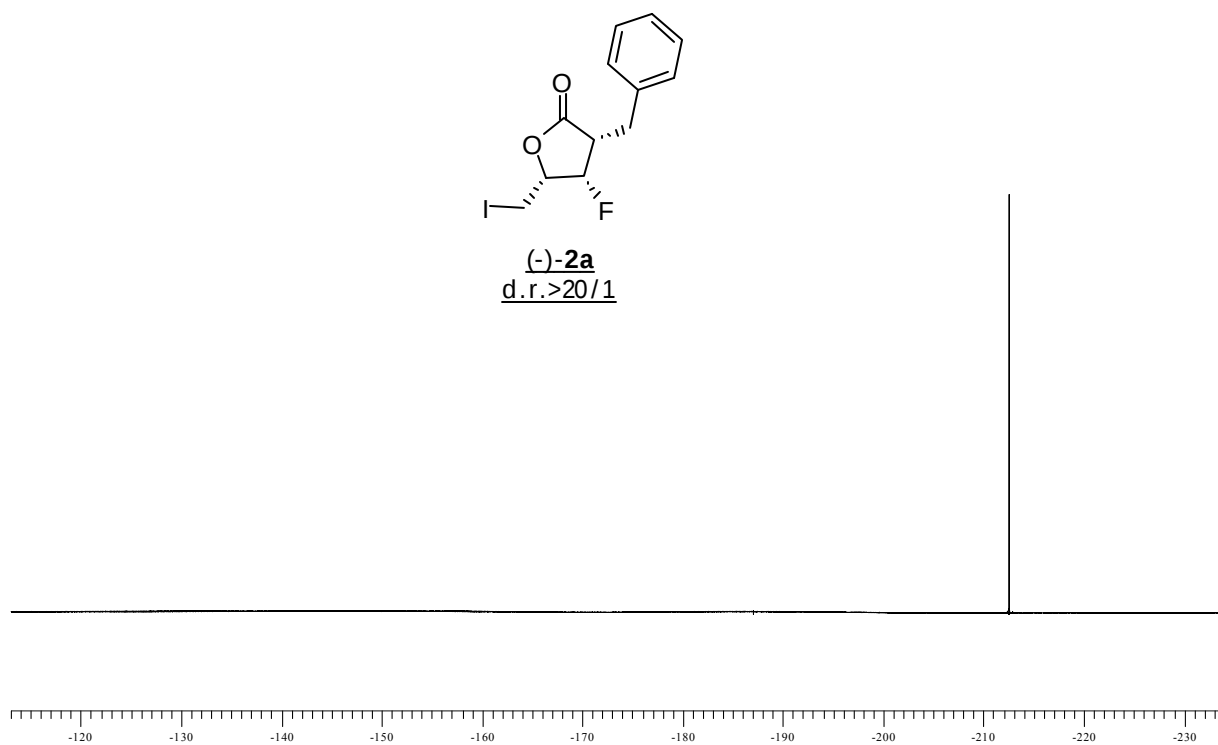
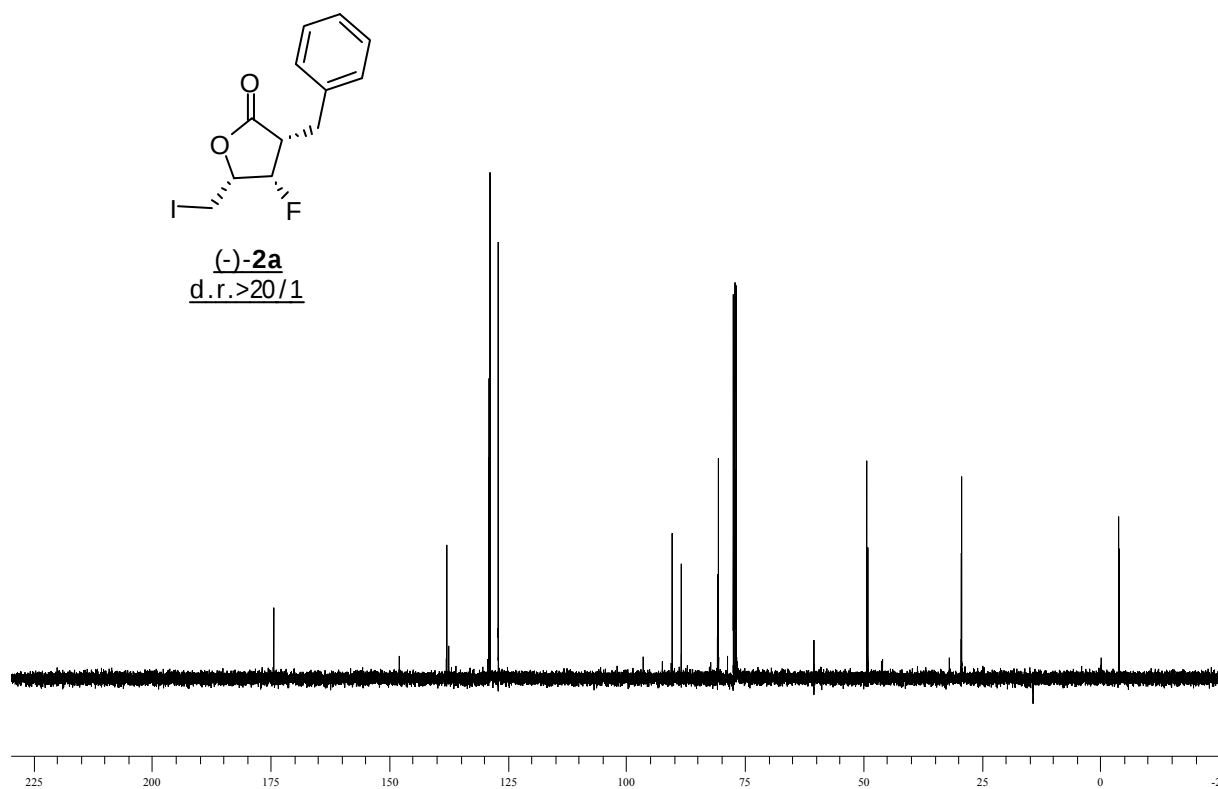
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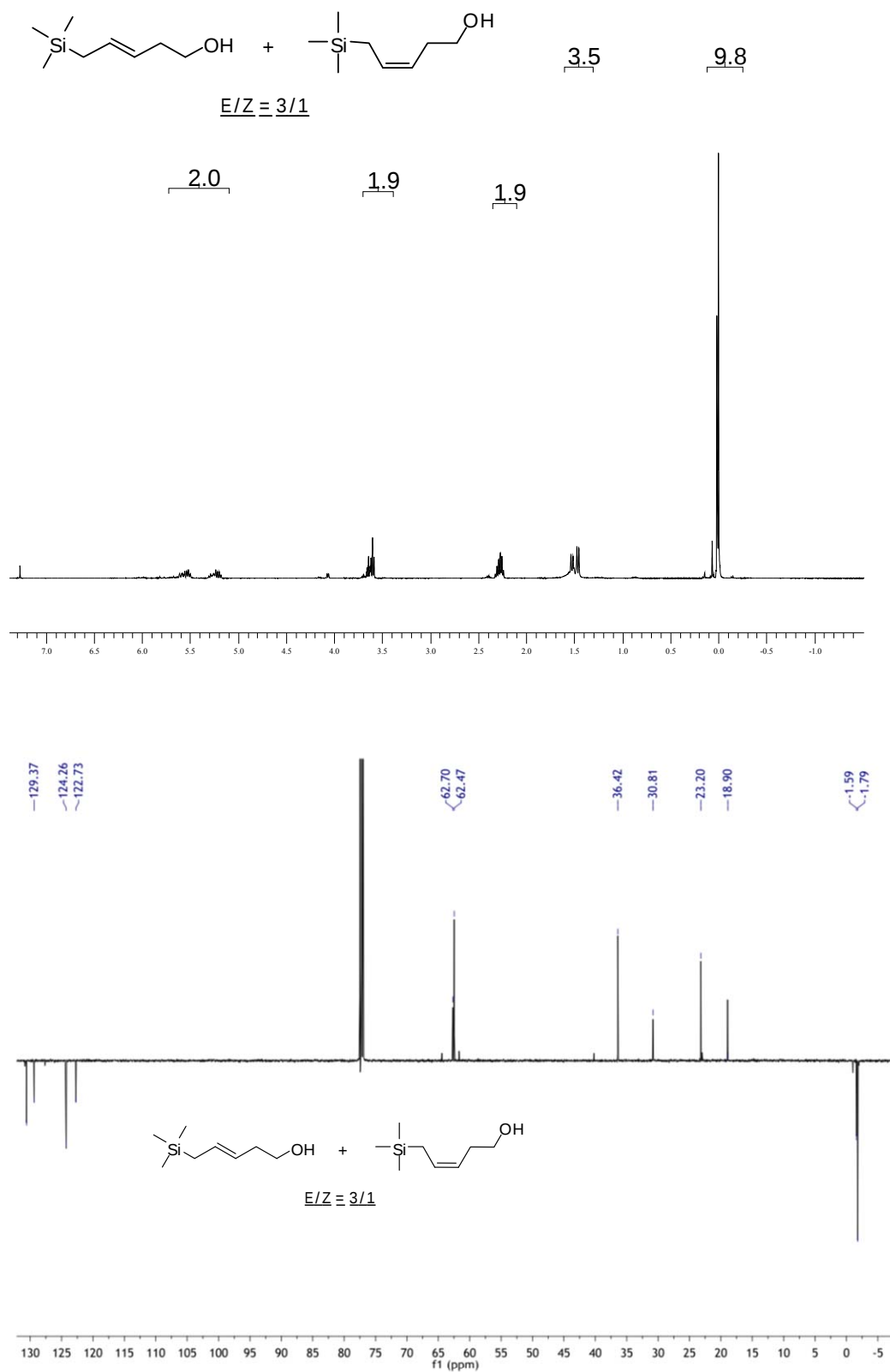


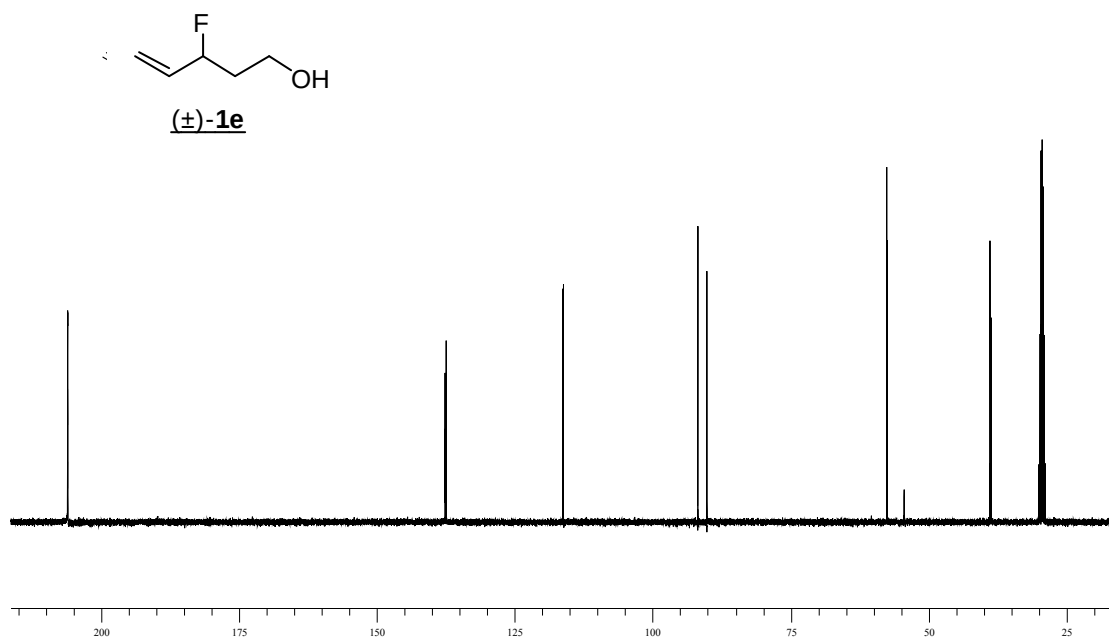
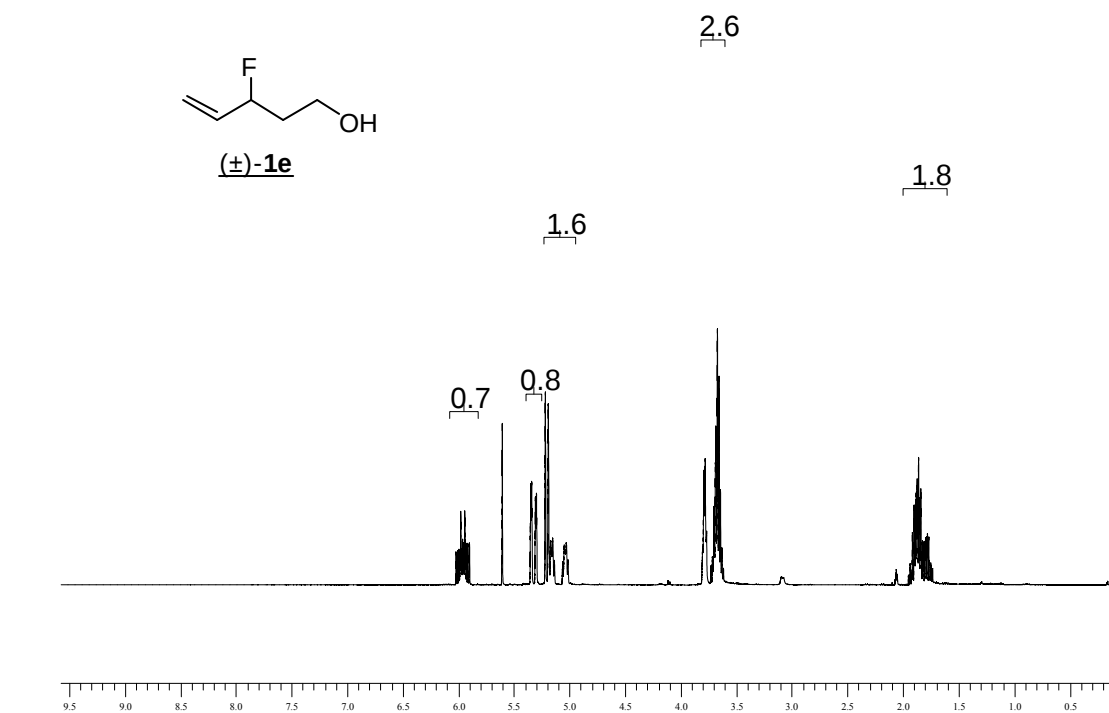


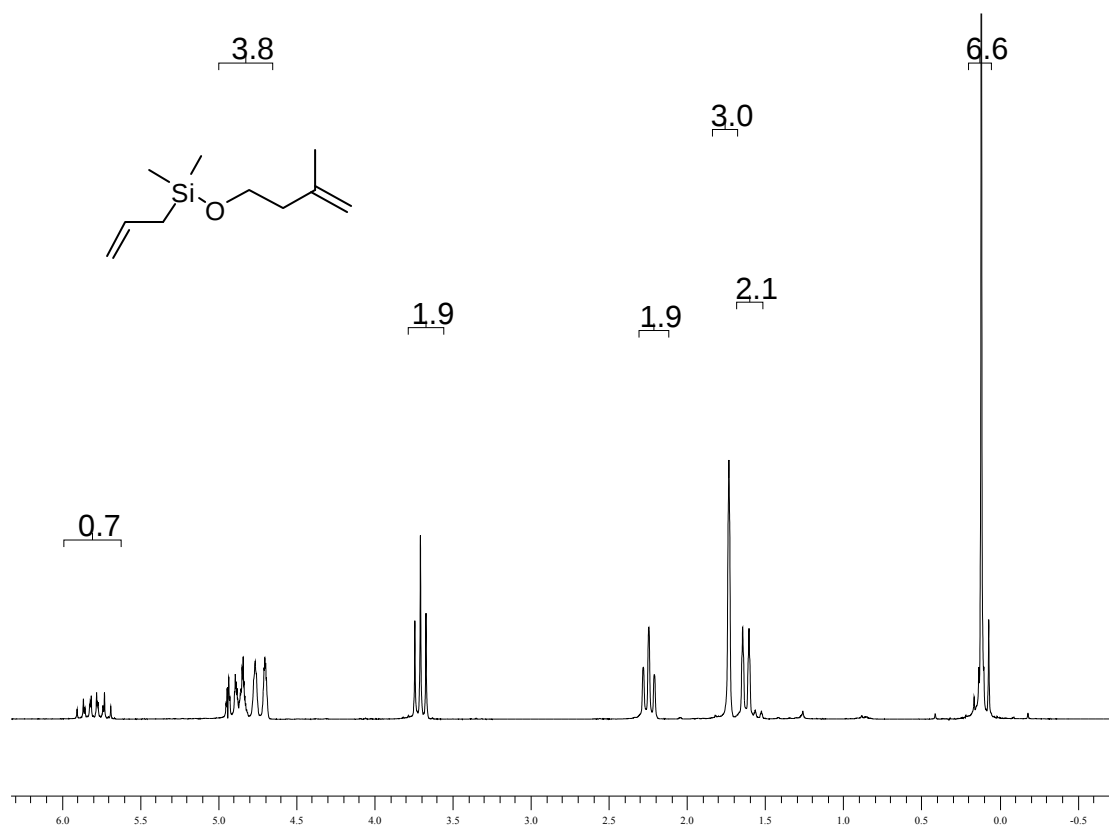
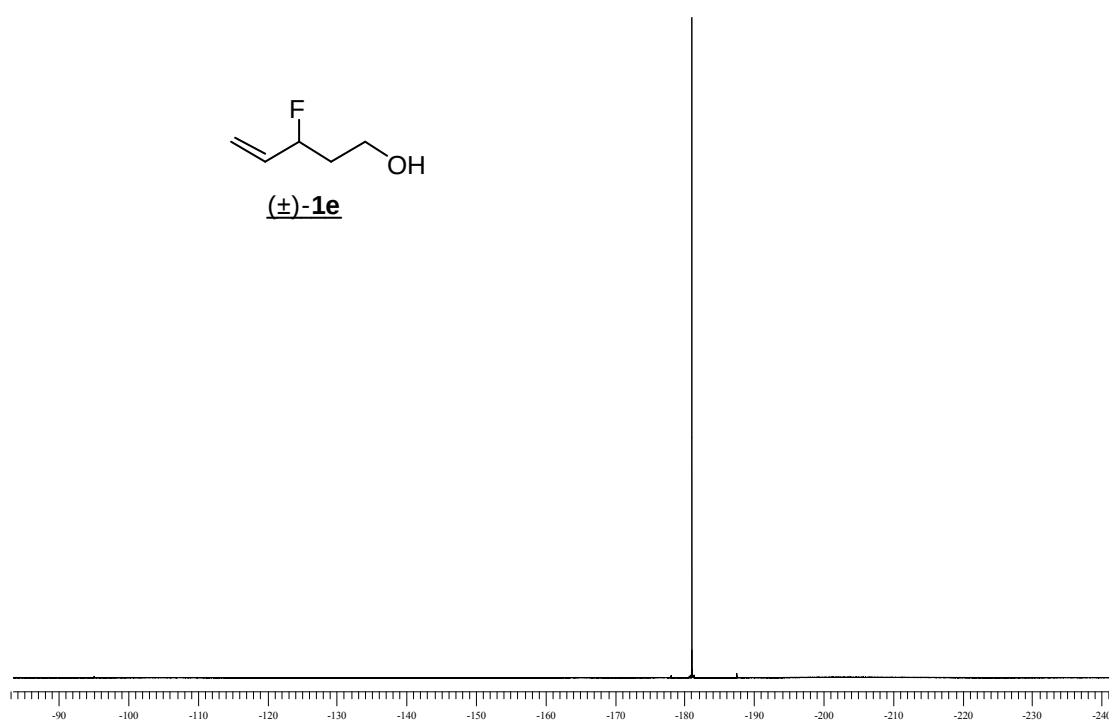


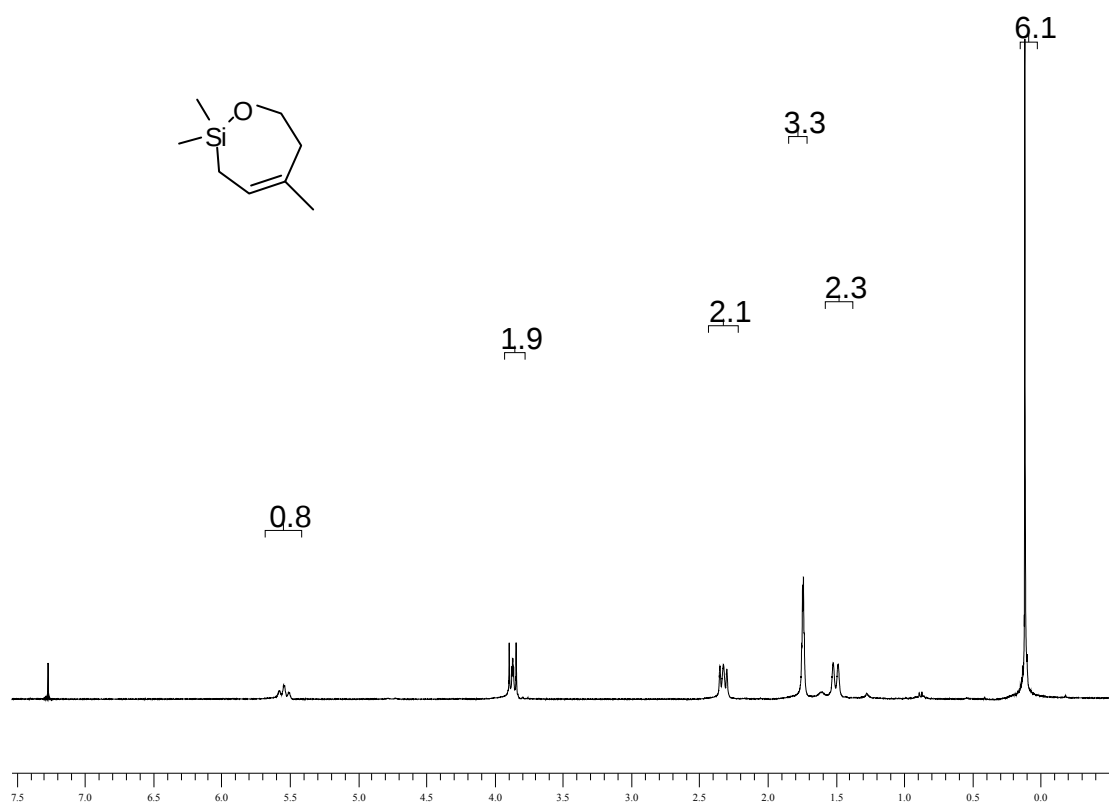
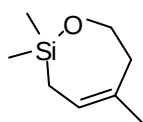
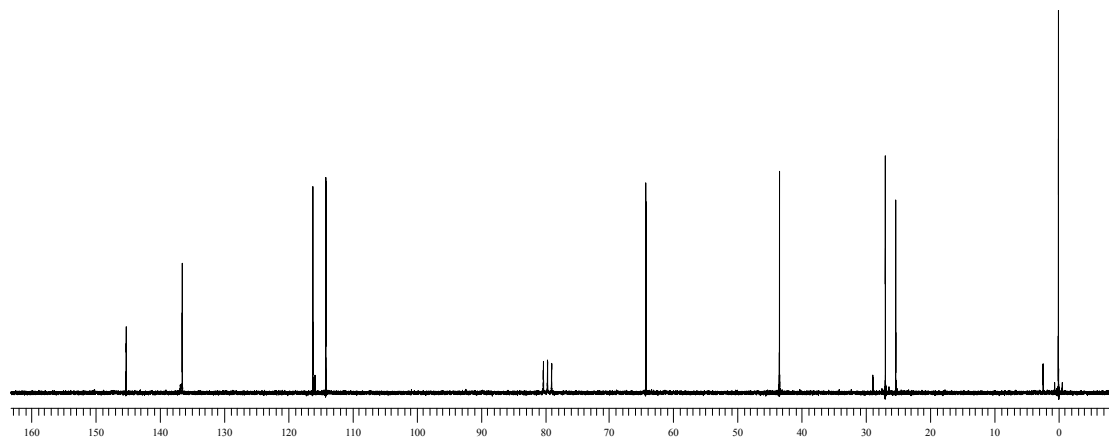
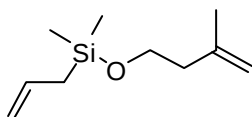
J. II. Iodoethers

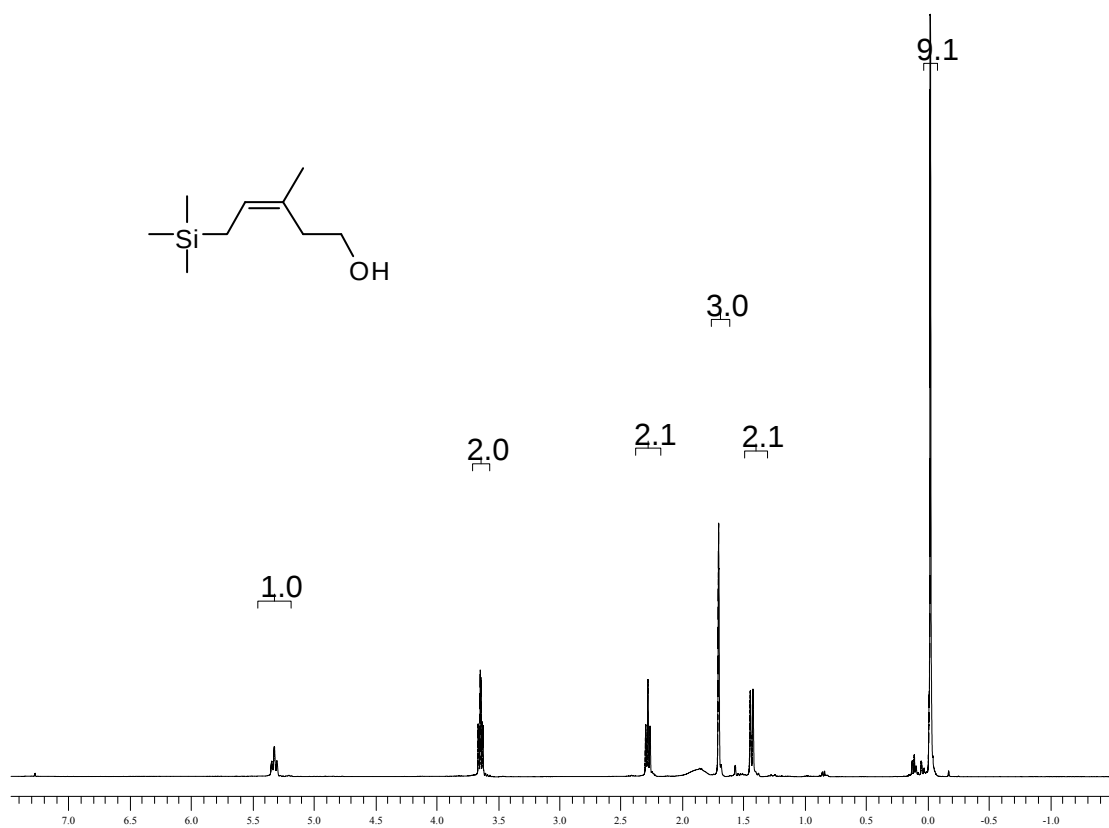
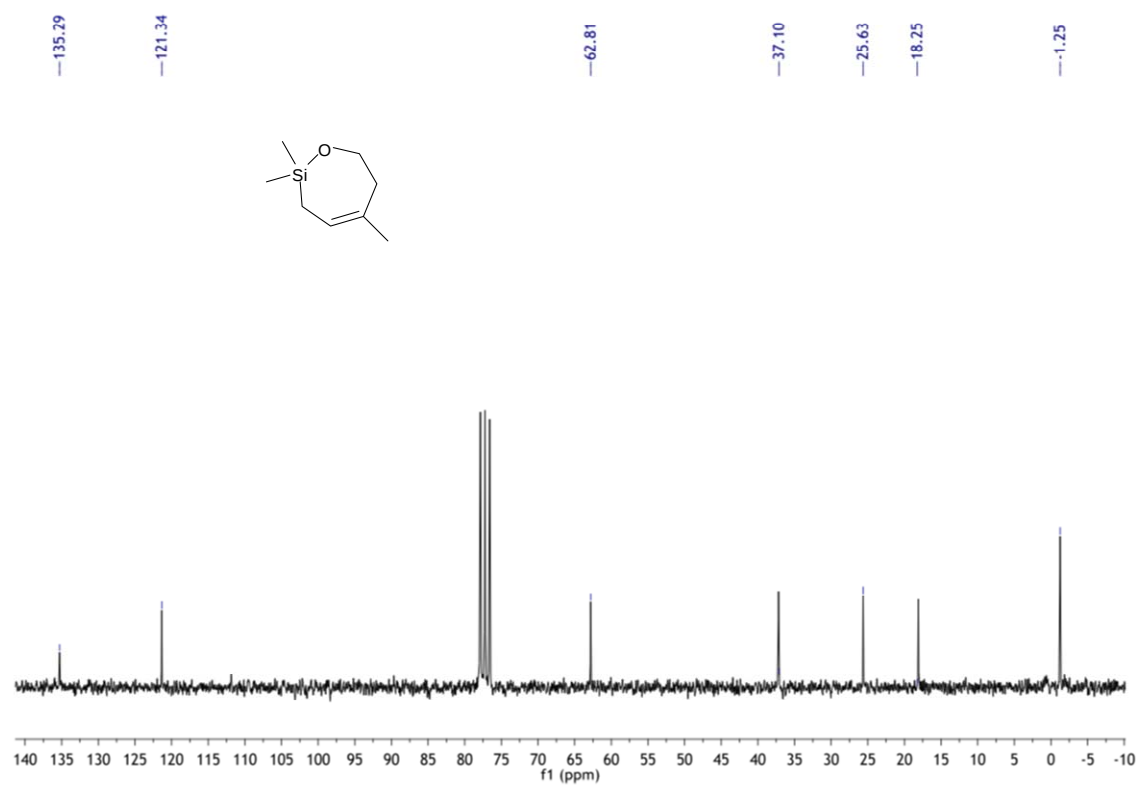
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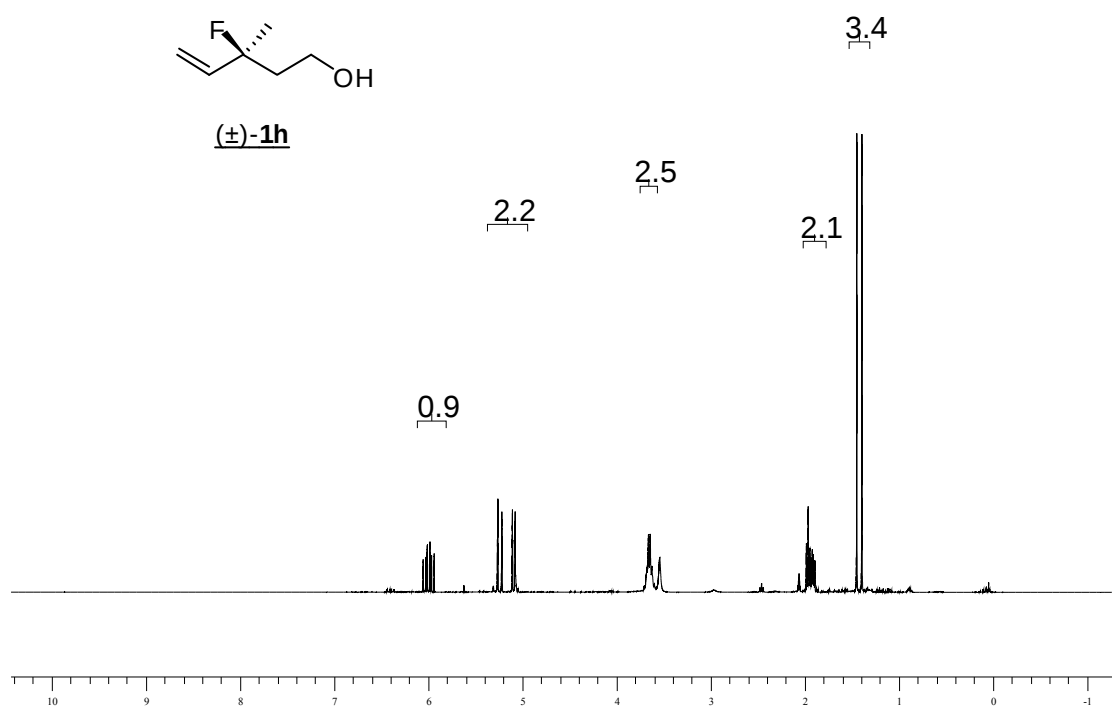
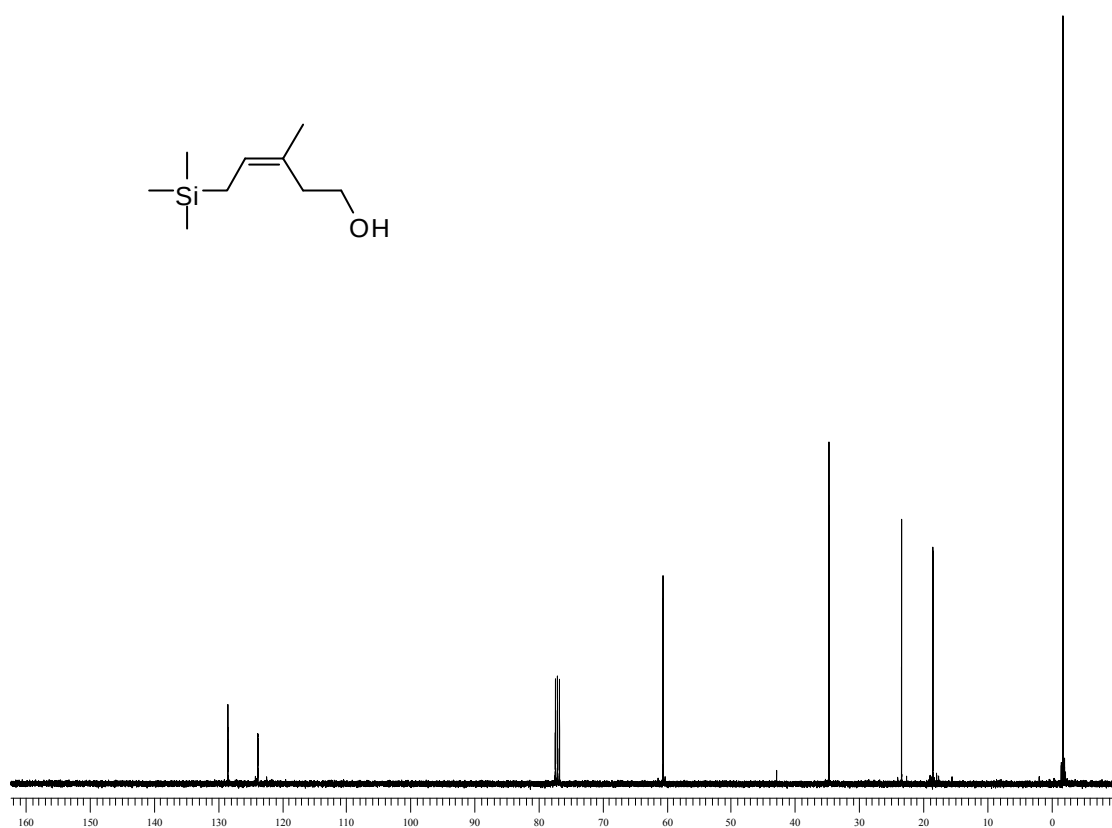


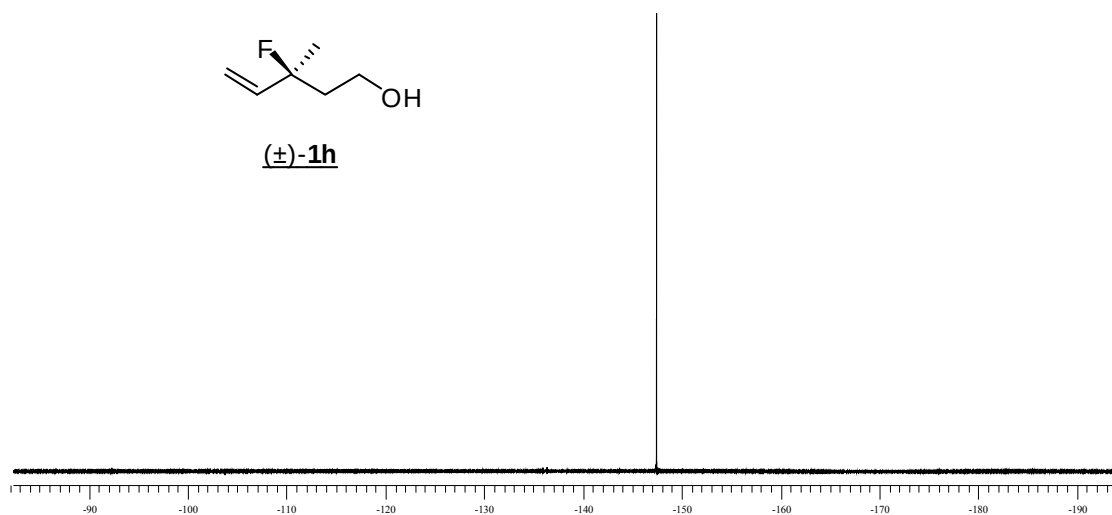
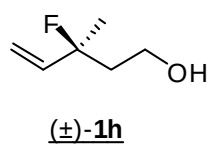
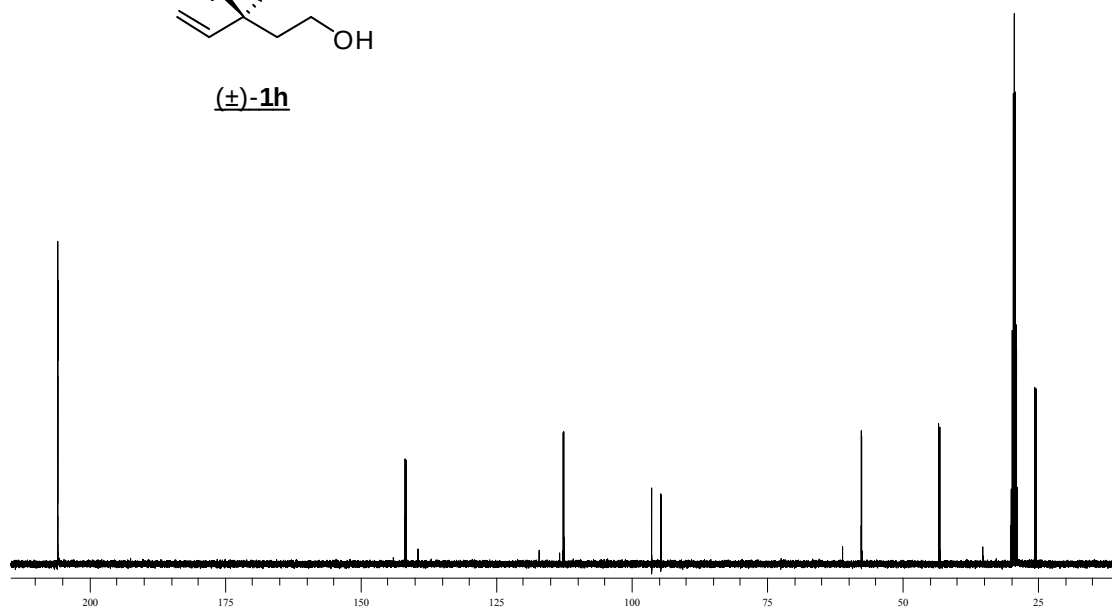
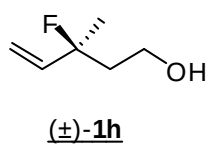


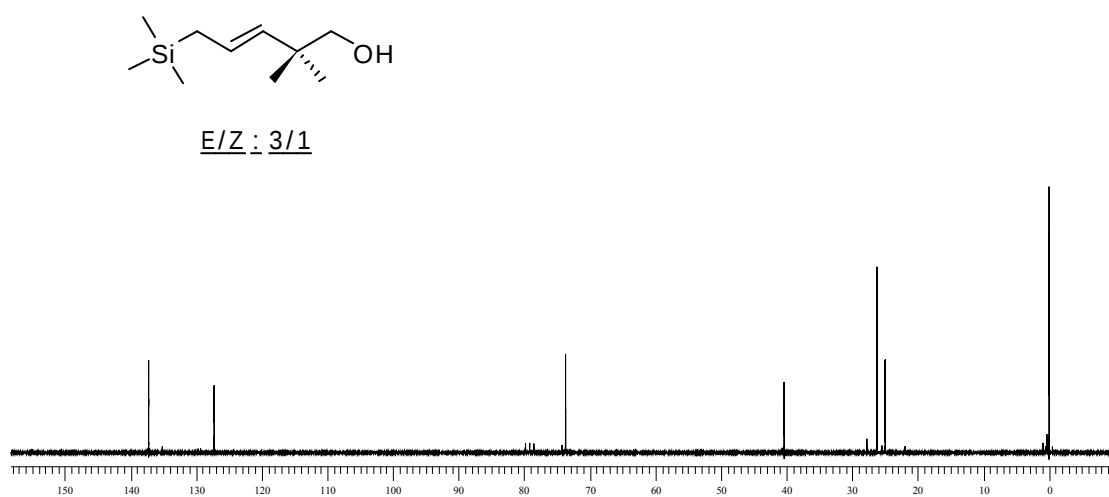
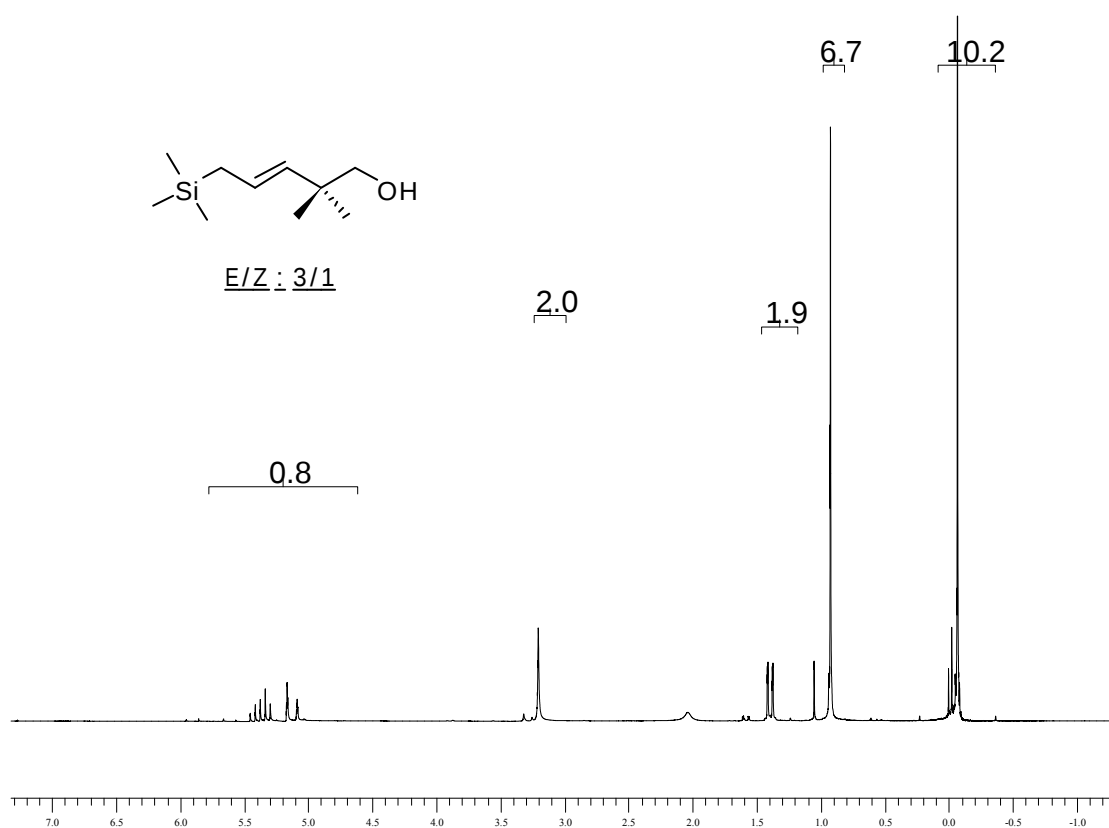


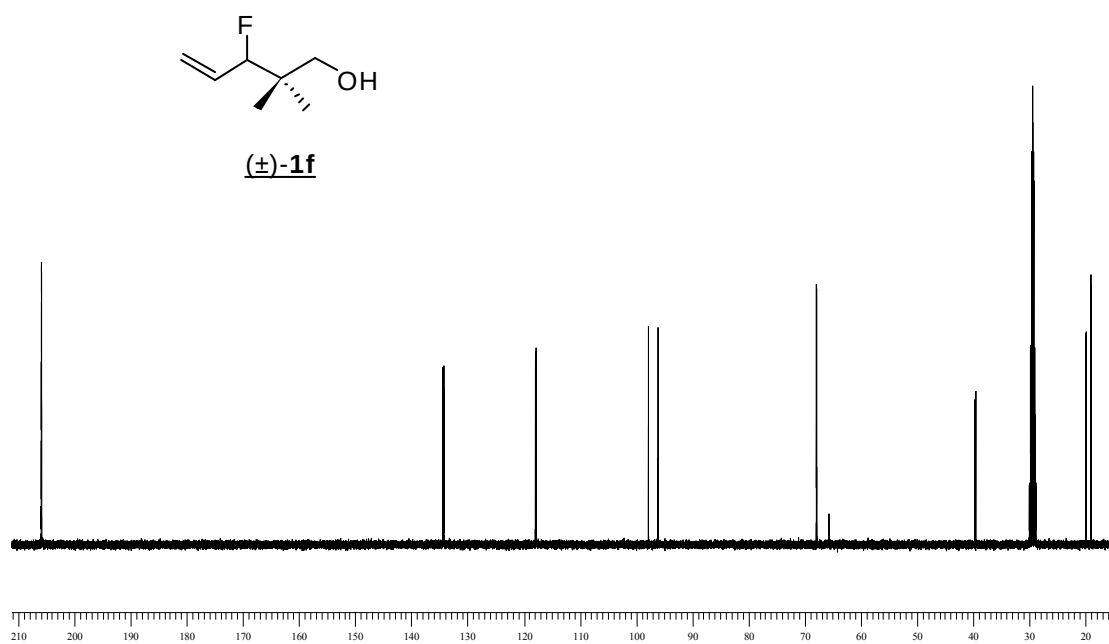
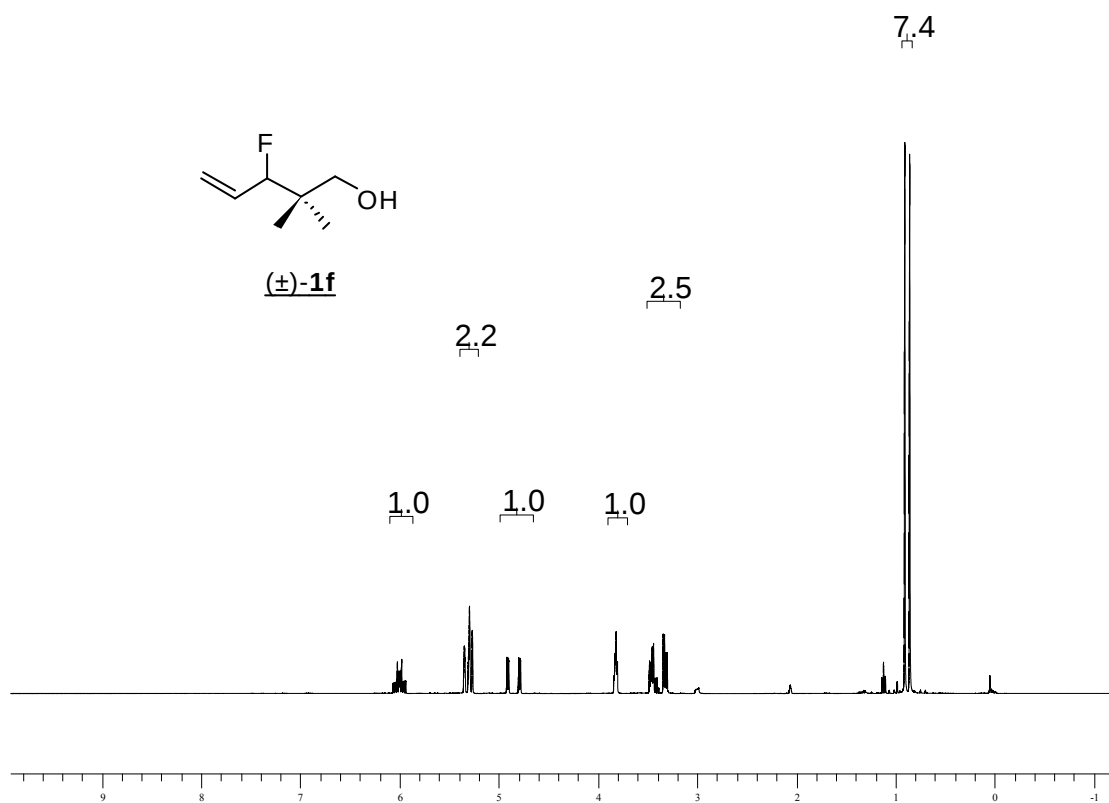


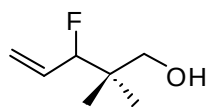




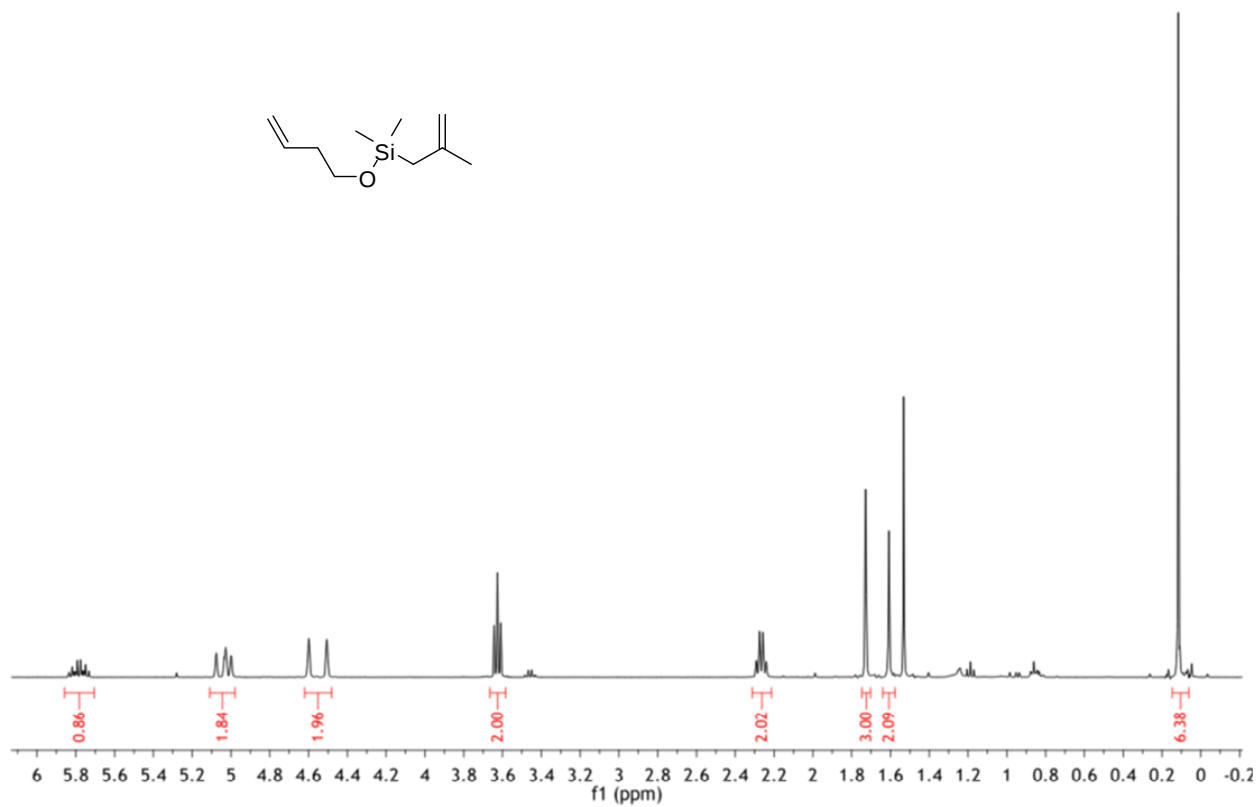
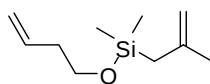
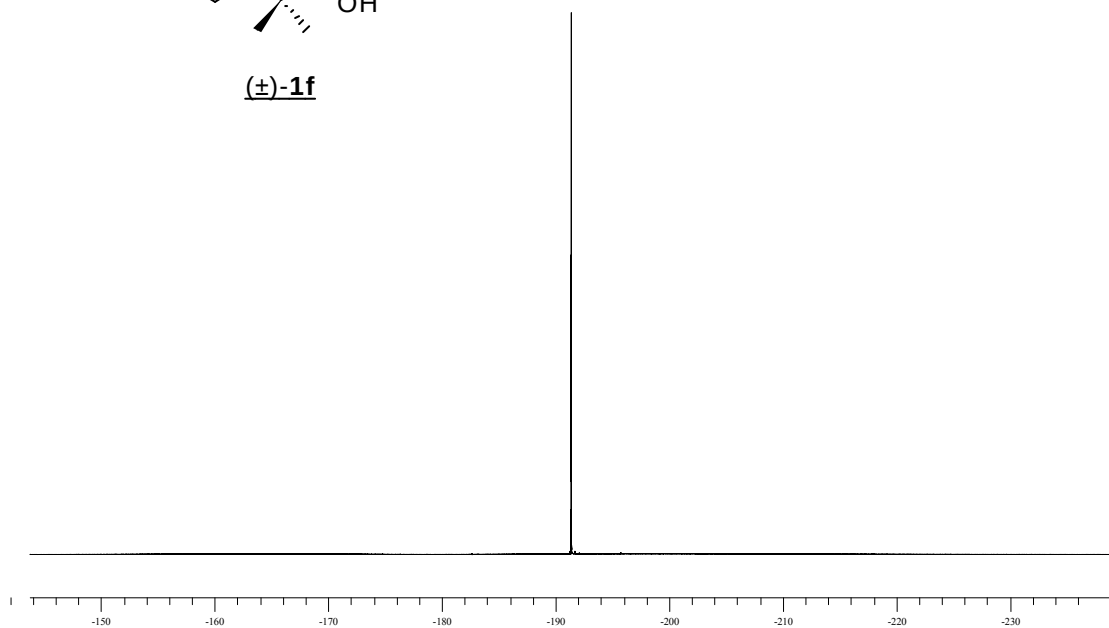


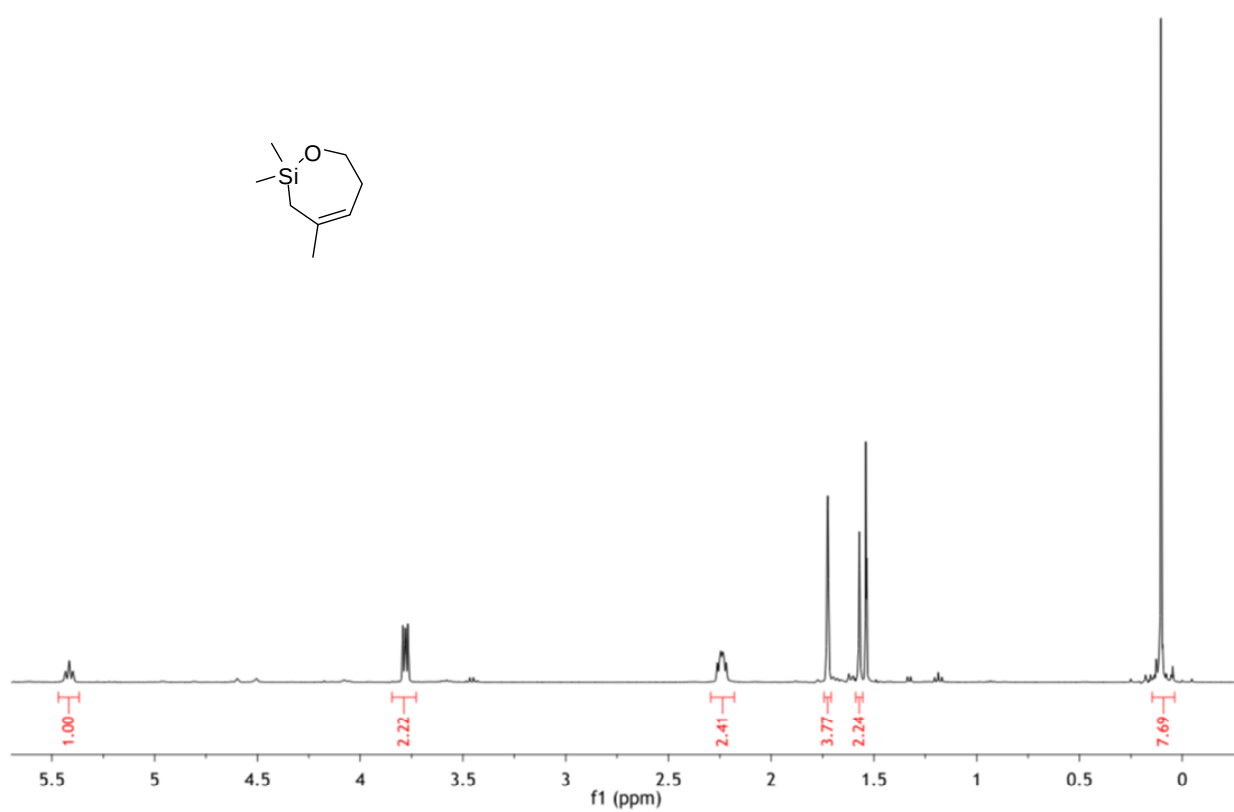
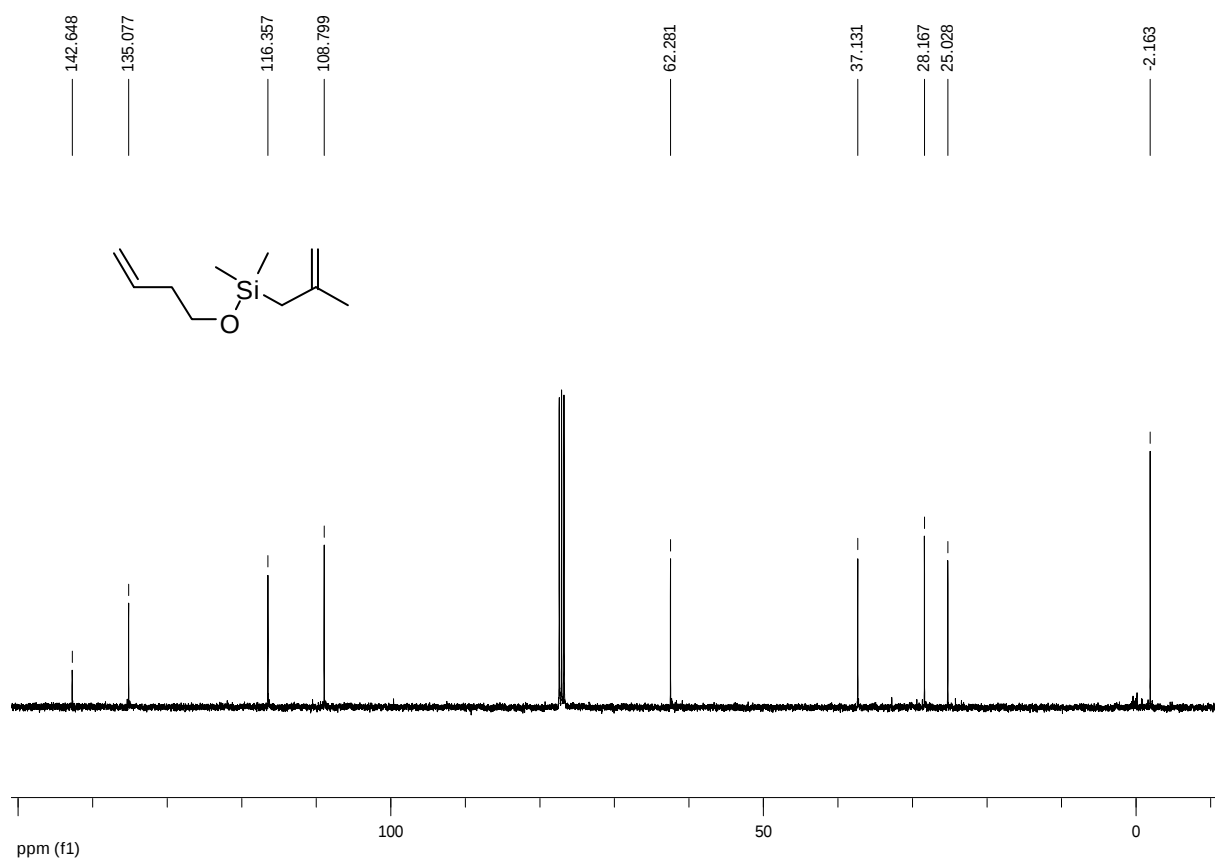


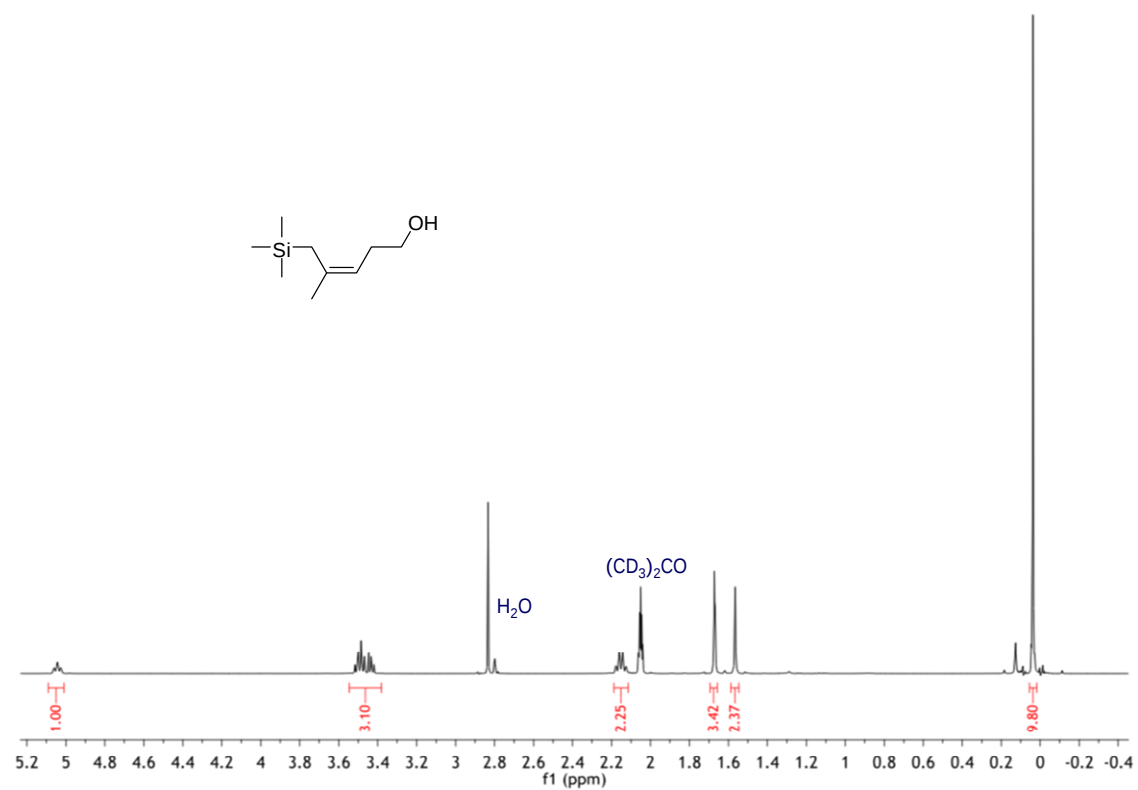
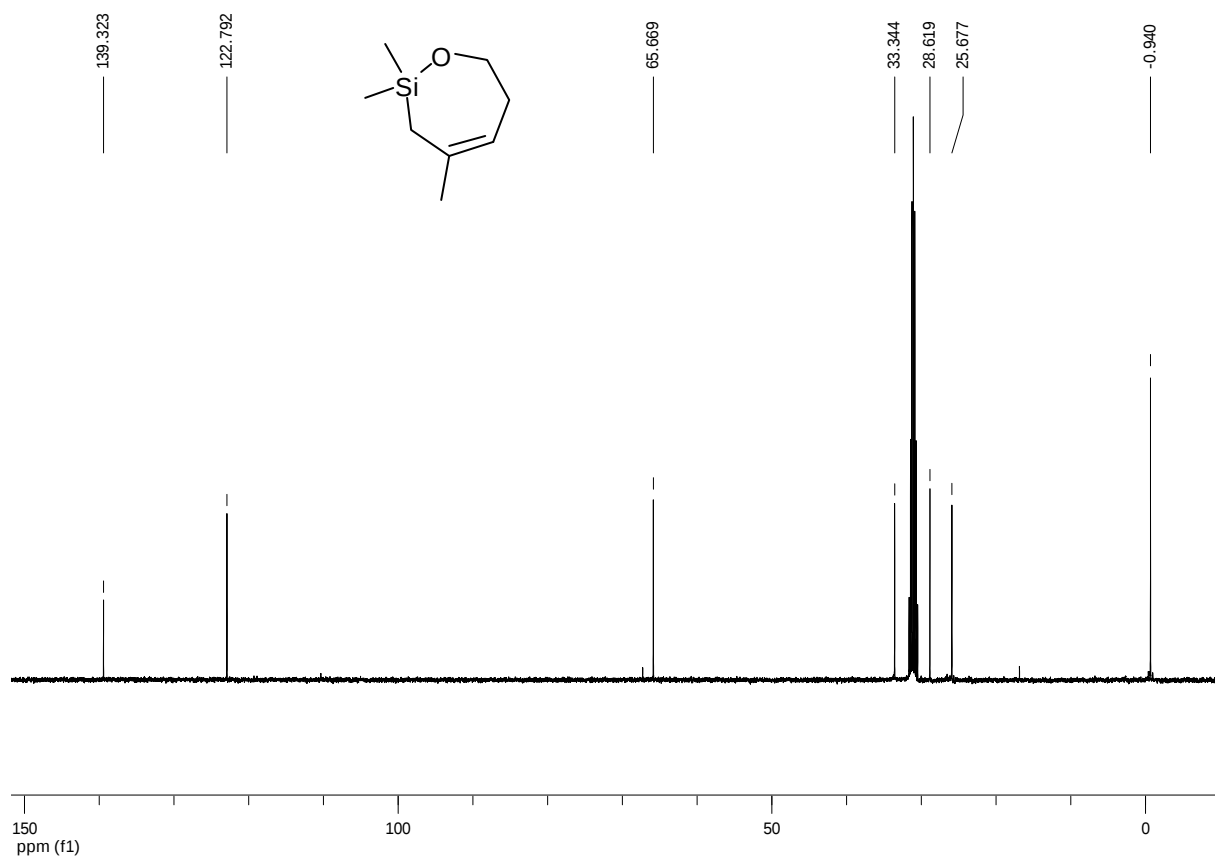


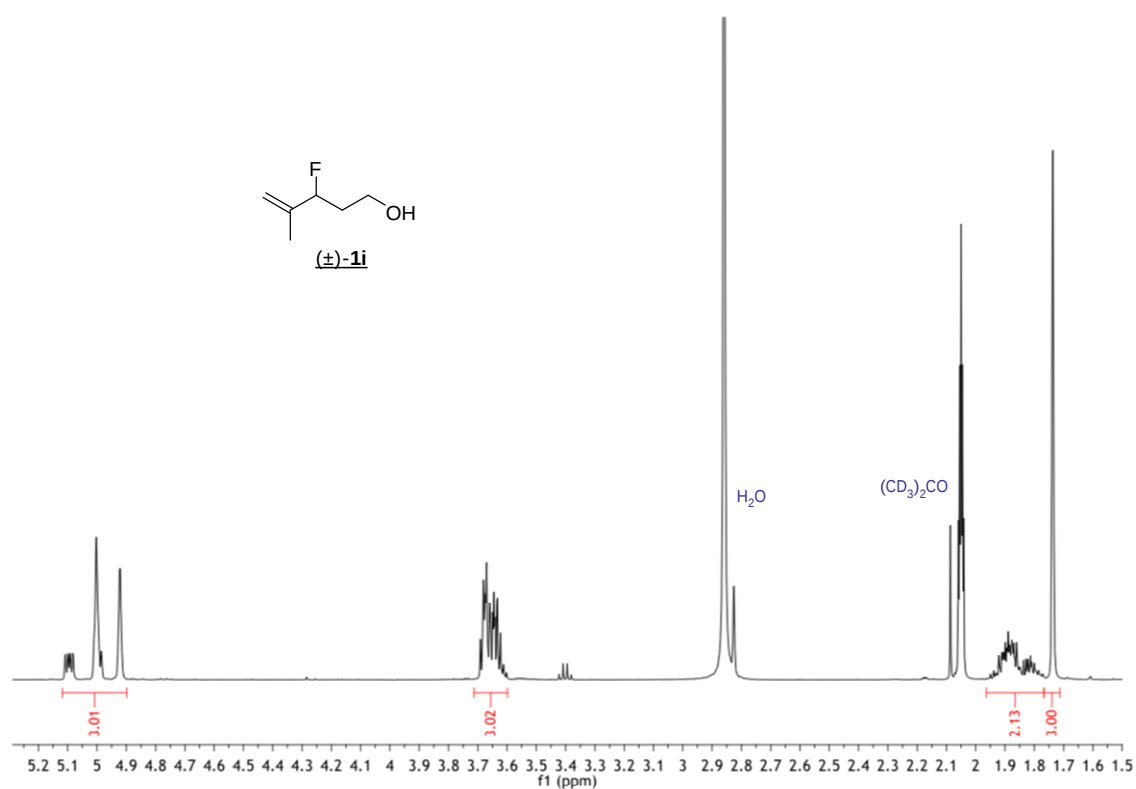
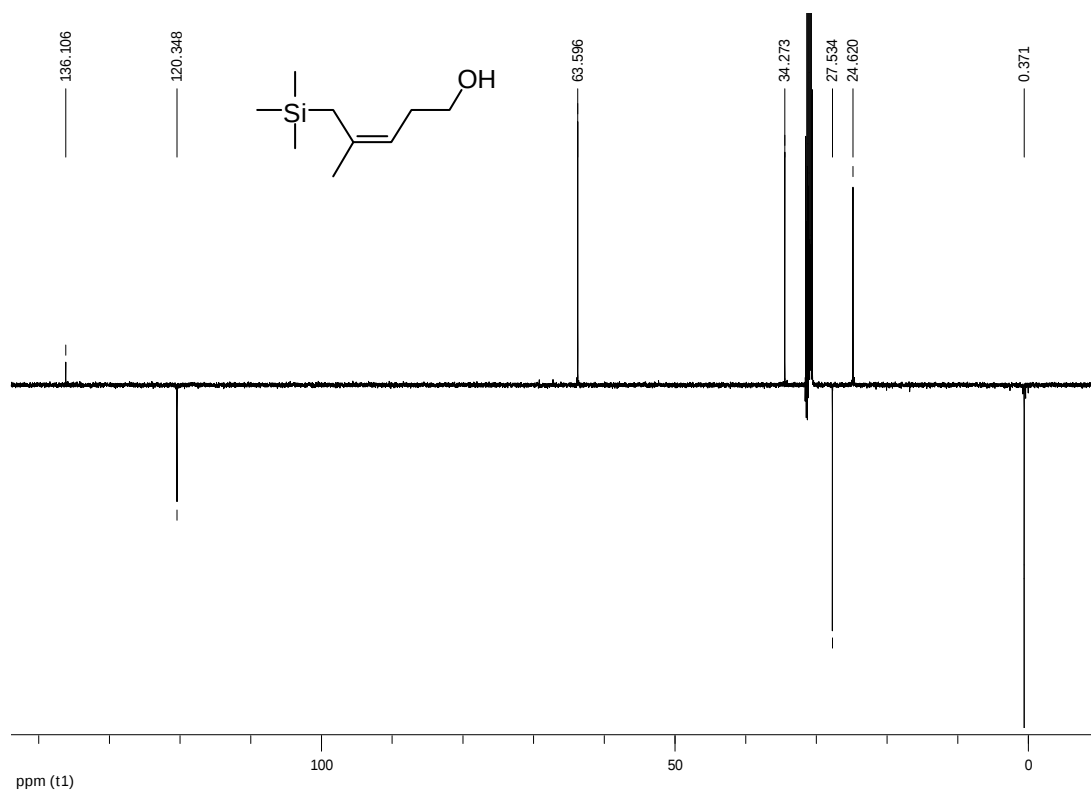


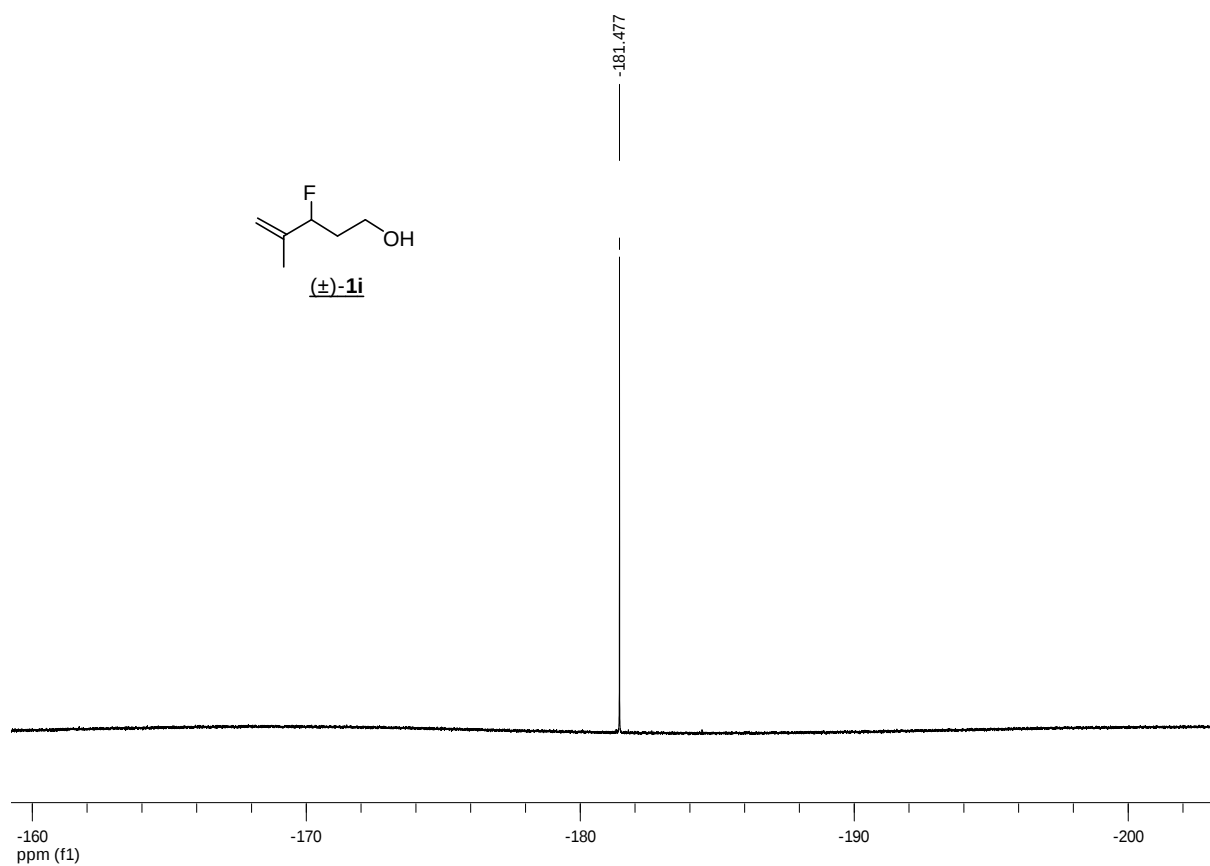
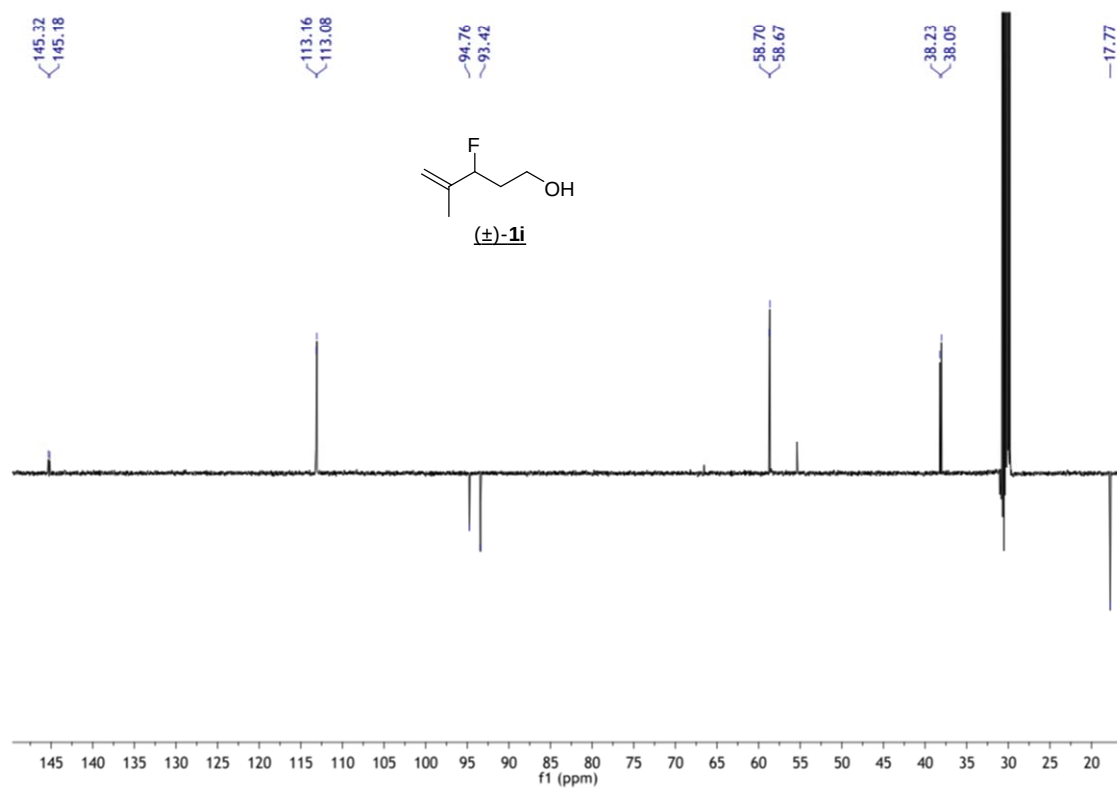
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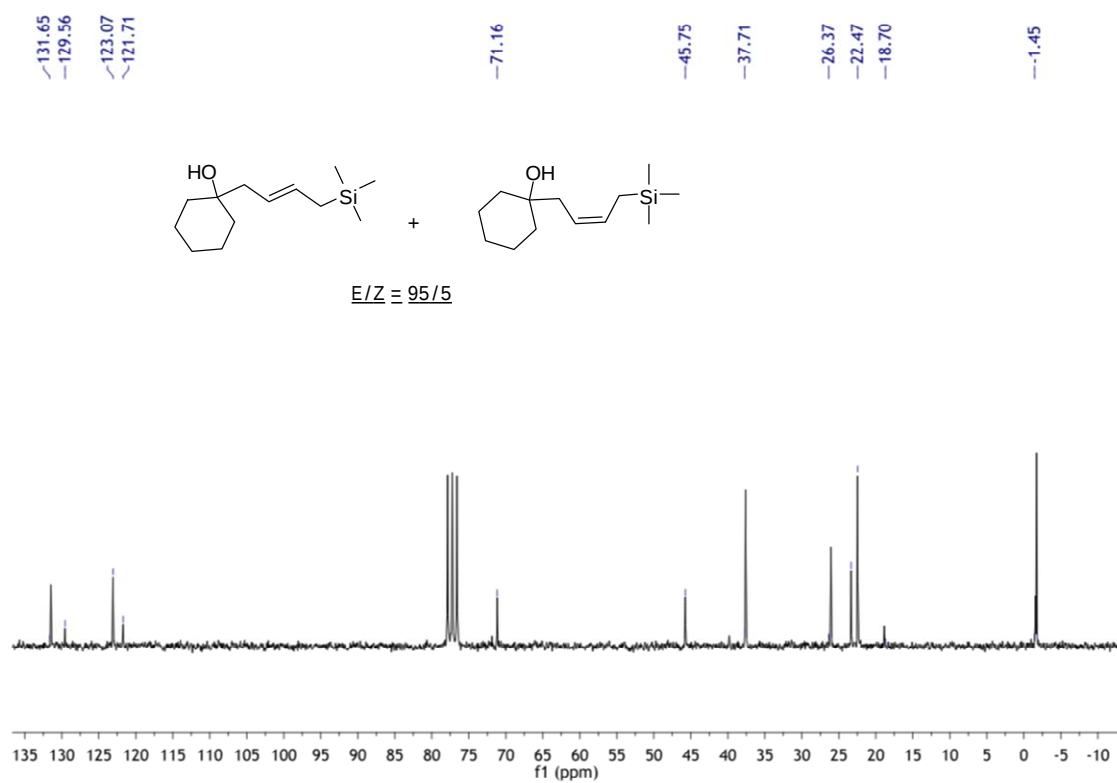
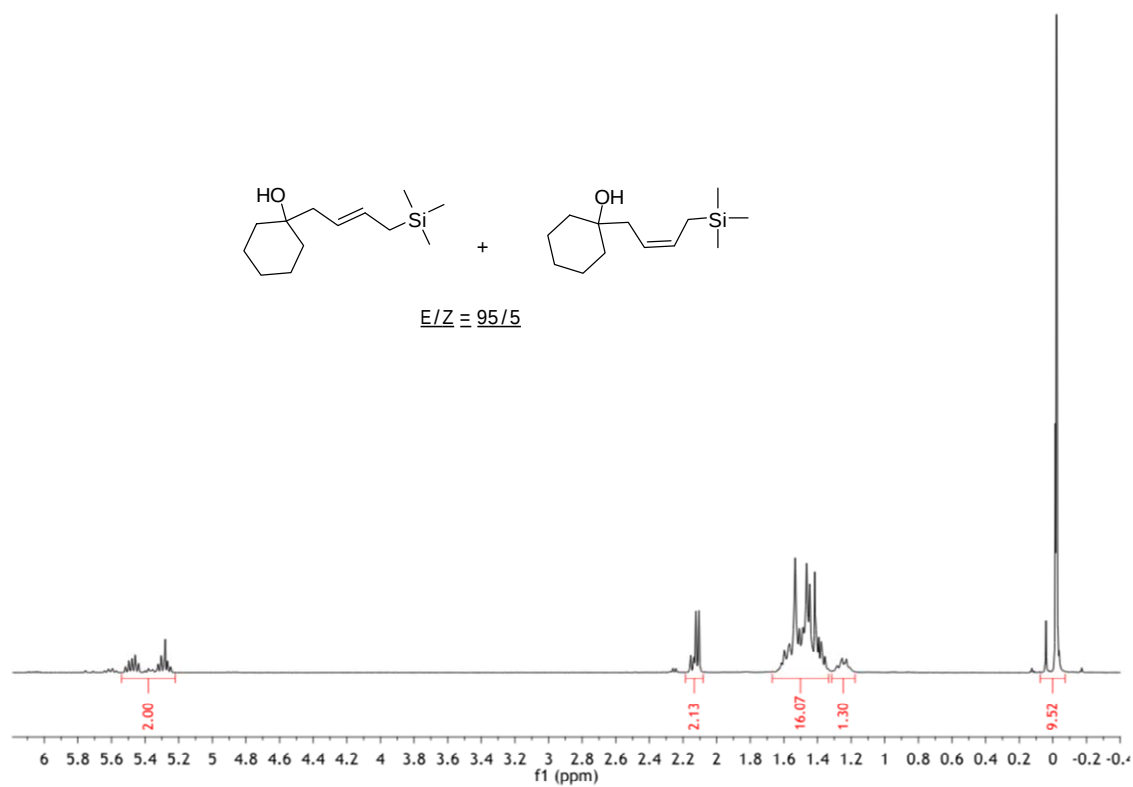


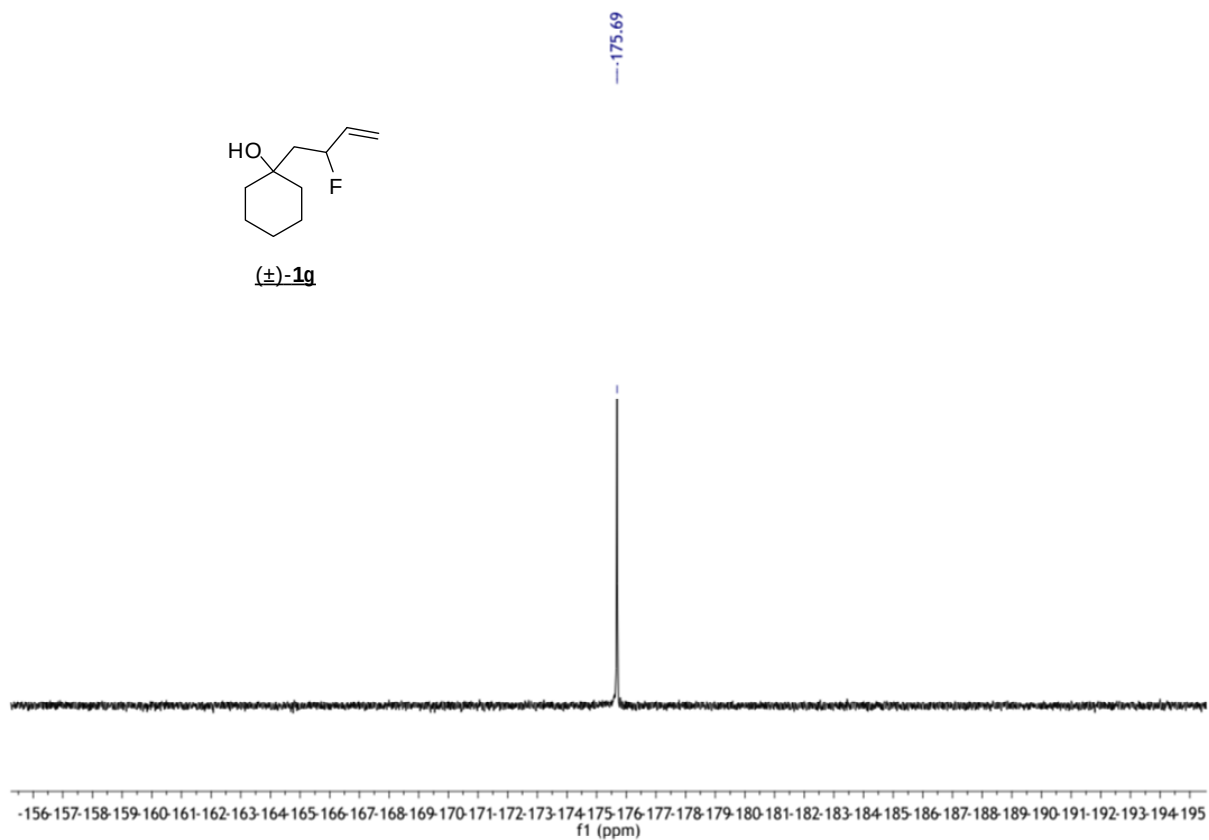
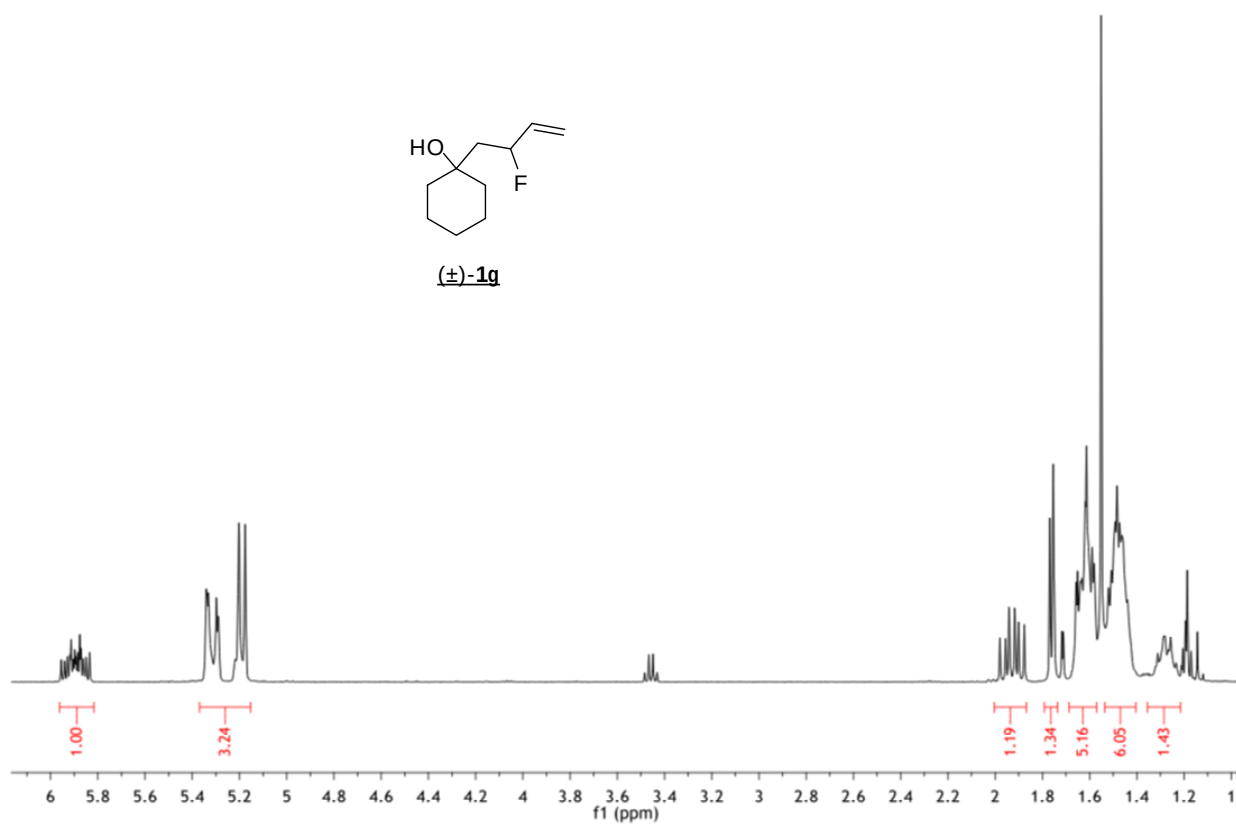


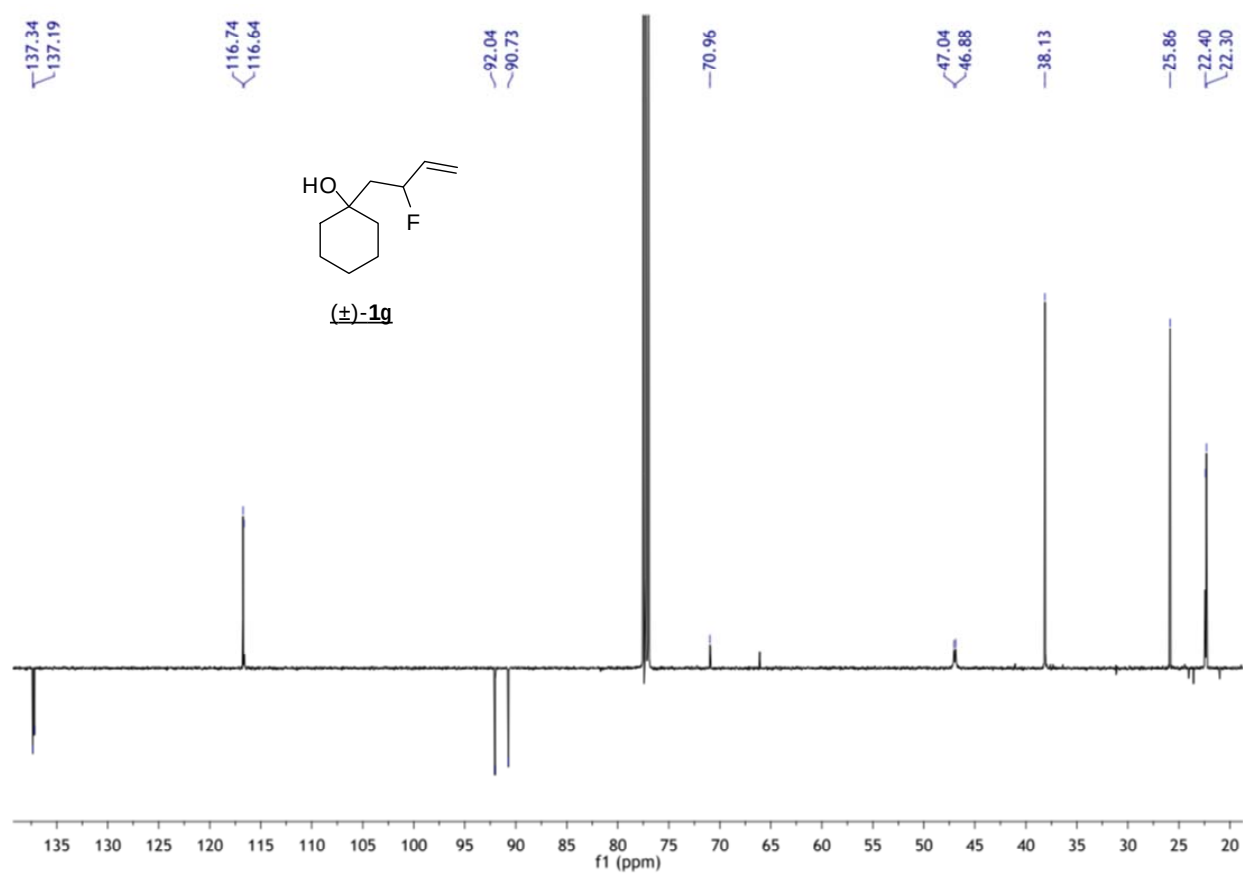












J. II. 2. Iodoethers (±)-2e-2i

