SUPPORTING INFORMATION

For

Regio- and Stereoretentive Synthesis of Branched, Linear (*E*)- and (*Z*)- Allyl Fluorides from Allyl Carbonates under Ir-Catalysis

Table of Contents

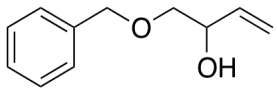
1. General Experimental Information

All NMR spectra were recorded on Bruker DPX250, AV400, AVC500, AVB500 and DRX500 spectrometers. Proton and carbon-13 NMR spectra are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using the Bruker internal referencing procedure (edlock). Fluorine-19 NMR spectra are referenced relative to $CFCl_3$ in $CDCl_3$. Coupling constants (*J*) are reported in units of hertz (Hz). High resolution mass spectra (HRMS, *m*/*z*) were recorded on a Bruker MicroTOF spectrometer using positive electrospray ionization (ESI^+) or on a Micromass GCT spectrometer using field ionization (FI^+) or chemical ionization (CI^+). Infrared spectra were recorded either as the neat compound on NaCl discs or as a KBr pellet using a Bruker Tensor 27 FT-IR spectrometer. Absorptions are reported in wavenumbers (cm^{-1}) and only peaks of interest are reported. Melting points of solids were measured on a Griffin apparatus and are uncorrected. Chiral HPLC was performed on DIONEX P680 using OD, IA chiralcel columns. IUPAC names were obtained using the ACD/I-Lab service. All reactions were performed in flame-dried apparatus with magnetic stirring under an inert atmosphere. All solvents were dried on a column of alumina prior to use. Flash column chromatography was performed over Merck silica gel C60 (40-60 μm) using eluent systems as described for each experiment. TBAF(*t*BuOH)$_4$ was prepared according to the procedure of Kim.[1] Iridium complexes IrCODacac[2] and [Ir(COD)(κ2-P^C)(P^C)][3] were prepared according to literature procedures.

2. Experimental Procedures and Characterization Data

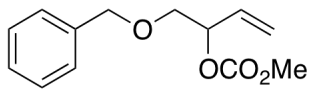
2.1 Synthesis of branched allylic carbonates

1-(Benzyloxy)but-3-en-2-ol, 4a



To a solution of benzyloxyacetaldehyde (5.0 g, 33.3 mmol) in THF (150 mL) at 0 °C was added vinylmagnesium bromide solution (1M in THF, 50 mL, 50 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 5 h at room temperature. The reaction was quenched by addition of water. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (4.52 g, 76%). ^1H NMR (400MHz, $CDCl_3$): δ 7.40-7.29 (m, 5H), 5.85 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.38 (dt, *J* = 17Hz, 2Hz, 1H), 5.21 (dt, *J* = 11Hz, 2Hz, 1H), 4.59 (s, 2H), 4.40-4.34 (m, 1H), 3.57 (dd, *J* = 10Hz, 3Hz, 1H), 3.57 (dd, *J* = 10Hz, 8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 137.8, 136.5, 128.5, 127.8, 127.7, 116.5, 74.0, 73.4, 71.5. Data are in agreement with literature.[4]

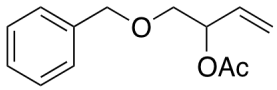
1-(Benzyloxy)but-3-en-2-yl methyl carbonate, 1a



To a solution of **4a** (2.67 g, 15.0 mmol) and pyridine (3.60 mL, 45 mmol) in DCM (65 mL) at 0° C was added methyl chloroformate (2.31 mL, 30 mmol). The reaction mixture was allowed

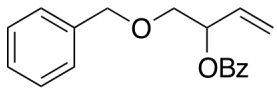
to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%: Et_2O/ 9:1) to yield the title compound (3.04 g, 86%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.38-7.28 (m, 5H), 5.85 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.41 (d, *J* = 17Hz, 1H), 5.35-5.31 (m, 1H), 5.30 (d, *J* = 11Hz, 1H), 4.59 (s, 2H), 3.80 (s, 3H), 3.65-3.57 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.2, 137.8, 132.7, 128.4, 127.7, 127.6, 118.7, 77.0, 73.3, 71.2, 54.8. Data are in agreement with literature.[5]

1-(Benzyloxy)but-3-en-2-yl acetate



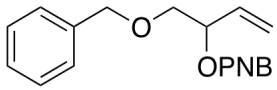
To a solution of **4a** (0.10 g, 0.56 mmol) and triethylamine (86 μL, 0.62 mmol) in DCM (4 mL) at 0 °C was added acetyl chloride (44 μL, 0.62 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of sat. aqueous $NaHCO_3$ solution. The organic phase was washed with water and brine, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane) to yield the title compound (0.11 g, 89%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H), 5.83 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.49 (tdt, *J* = 6Hz, 5Hz, 1Hz, 1H), 5.31 (dt, *J* = 11Hz, 1Hz, 1H), 5.23 (dt, *J* = 11Hz, 1Hz, 1H), 4.55 (d, *J* = 3Hz, 2H), 3.57-3.54 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 170.2, 137.9, 133.3, 128.4, 127.7, 127.6, 117.9, 73.2, 73.1, 71.2, 21.2; IR *v* 2863, 1739, 1233, 1094; HRMS calc for $C_{13}H_{16}NaO_3$ $[M+Na]^+$ 243.0997 found 243.0992.

1-(Benzyloxy)but-3-en-2-yl benzoate



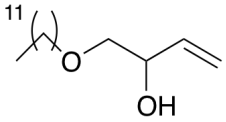
To a solution of **4a** (0.18 g, 1 mmol) and pyridine (0.08 mL, 1 mmol) in DCM (6 mL) at 0 °C was added benzoyl chloride (0.12 mL, 1 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%: Et_2O/ 9:1) to yield the title compound (0.26 g, 92%). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.10 (d, *J* = 9Hz, 2H), 7.58 (t, *J* = 7Hz, 1H), 7.46 (t, *J* = 8Hz, 2H), 7.35-7.28 (m, 5H), 5.98 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.76 (dd, *J* = 10Hz, 5Hz, 1H), 5.44 (d, *J* = 17Hz, 1H), 5.31 (d, *J* = 11Hz, 1H), 4.63 (q, *J* = 12Hz, 2H), 3.76 (dd, *J* = 11Hz, 7Hz, 1H), 3.72 (dd, *J* = 11Hz, 5 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 165.7, 138.0, 133.4, 133.0, 130.3, 129.7, 128.4, 128.3, 127.7, 127.6, 118.0, 73.7, 73.2, 71.3. Data are in agreement with literature.[6]

1-(Benzyloxy)but-3-en-2-yl 4-nitrobenzoate



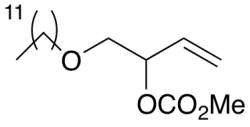
To a solution of **4a** (0.18 g, 1 mmol) and triethylamine (0.14 mL, 1 mmol) in DCM (6 mL) at 0 °C was added *p*-nitrobenzoyl chloride (0.19 mL, 1 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 4 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%: Et_2O/ 9:1) to yield the title compound (0.27 g, 82%). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.32-8.23 (m, 4H), 7.32-7.25 (m, 5H), 5.96 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.79-5.76 (m, 1H), 5.46-5.32 (m, 2H), 4.61 (d, *J* = 5Hz, 2H), 3.73 (dd, *J* = 5Hz, 2Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 163.9, 151.0, 137.7, 135.7, 132.6, 130.8, 128.4, 127.8, 127.6, 123.5, 118.9, 74.9, 73.2, 71.1; IR (DCM) *ν* 1724, 1525, 1267, 1100; HRMS calc for $C_{18}H_{17}NNaO_5$ $[M+Na]^+$ 350.0999 found 350.1003.

1-(Dodecyloxy)but-3-en-2-ol



To a solution of but-3-ene-1,2-diol (0.84 mL, 10.0 mmol) in THF (15 mL) and DMF (4 mL) at 0 °C was carefully added sodium hydride (0.30 g, 7.5 mmol). After being stirred for 20 min at 0 °C, 1-bromododecane (0.85 mL, 5.0 mmol) was added at 0 °C, and the resulting mixture was allowed to warm to room temperature and stirred for 24 h at room temperature. The reaction was quenched by addition of sat. aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with EtOAc, the combined organic phases were washed with water and dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (0.26 g, 20%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.82 (ddd, J = 17Hz, 11Hz, 6Hz, 1H), 5.34 (dt, J = 17Hz, 2Hz, 1H), 5.16 (dt, J = 11Hz, 2Hz, 1H), 4.32-4.26 (m, 1H), 3.46-3.40 (m, 3H), 3.29 (dd, J = 10Hz, 8Hz, 1H), 1.57-1.51 (m, 2H), 1.30-1.22 (m, 18H), 0.84 (t, J = 7Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 136.9, 116.4, 74.7, 71.7, 71.6, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 26.3, 22.8, 14.3. IR ($CDCl_3$) ν 3441, 1116; HRMS calc for $C_{16}H_{32}NaO_2$ $[M+Na]^+$ 279.2295, found 279.2300.

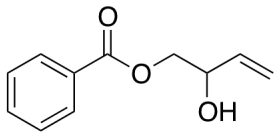
1-(Dodecyloxy)but-3-en-2-yl methyl carbonate, 1c



To a solution of 1-(dodecyloxy)but-3-en-2-ol (0.26 g, 1.0 mmol) and pyridine (0.24 mL, 3 mmol) in DCM (20 ml) at 0 °C was added dropwise methyl chloroformate (0.15 mL, 2 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried

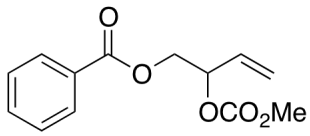
($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.28 g, 90%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.36 (dt, *J* = 17Hz, 1Hz, 1H), 5.27-5.24 (m, 2H), 3.77 (s, 3H), 3.51-3.38 (m, 4H), 1.55-1.50 (m, 2H), 1.28-1.20 (m, 18H), 0.86 (t, *J* = 7Hz, 3H); ^{13}C NMR (125MHz, $CDCl_3$): δ 155.4, 133.1, 118.8, 77.6, 72.1, 71.9, 54.9, 32.1, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 26.2, 22.9, 14.3; IR ($CDCl_3$) ν 1752, 1264; HRMS calc for $C_{18}H_{34}NaO_4$ $[M+Na]^+$ 337.2349, found 337.2346.

2-Hydroxybut-3-en-1-yl benzoate



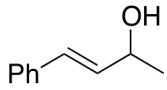
To a solution of butene-1,2-diol (0.33 mL, 4.0 mmol) in pyridine (2 mL) at -35 °C was added a solution of benzoyl chloride (0.56 mL, 4.8 mmol) in pyridine (1 mL). The reaction mixture was stirred for 12 h at -35 °C. The reaction was quenched by addition of water. The aqueous phase was extracted 3 times with DCM, the combined organic phases were washed with 2M $HCl_{(aq)}$ and $NaHCO_3$ solution, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.66 g, 85%). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.04-8.01 (m, 2H), 7.56-7.52 (m, 1H), 7.43-7.39 (m, 2H), 5.92 (ddd, *J* = 17Hz, 10Hz, 6Hz, 1H), 5.42 (d, *J* = 17Hz, 1H), 5.26 (d, *J* = 10Hz, 1H), 4.53-4.49 (m, 1H), 4.39 (dd, *J* = 11Hz, 4Hz, 1H), 4.27 (dd, *J* = 11Hz, 6Hz, 1H), 2.58 (brs, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.7, 136.2, 133.2, 129.8, 129.7, 128.4, 117.2, 71.1, 68.3. Data are in agreement with literature.[7]

2-[(Methoxycarbonyl)oxy]but-3-en-1-yl benzoate, 1d



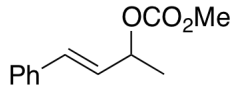
To a solution of 2-hydroxybut-3-en-1-yl benzoate (0.20 g, 1.04 mmol) and pyridine (0.25 mL, 3.12 mmol) in DCM (5 mL) at 0 °C was added methyl chloroformate (0.16 mL, 2.08 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.23 g, 89%). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.01 (d, *J* = 8Hz, 2H), 7.55 (t, *J* = 8Hz, 1H), 7.44-7.40 (m, 2H), 5.89 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.50-5.45 (m, 2H), 5.35 (d, *J* = 11Hz, 1H), 4.49 (dd, *J* = 12Hz, 4Hz, 1H), 4.37 (dd, *J* = 12Hz, 7Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.1, 155.1, 133.2, 131.7, 129.7, 129.6, 128.4, 119.7, 76.2, 65.1, 55.0; IR (CH_2Cl_2) ν 1752, 1735, 1264; HRMS calc for $C_{13}H_{14}O_5^+$ $[M]^+$ 250.0841, found 250.0841.

(3*E*)-4-Phenylbut-3-en-2-ol



To a solution of (3*E*)-4-phenyl-3-butene-2-one (1.02 mL, 7 mmol) in MeOH (4 mL) at 0 °C was added sodium borohydride (0.28 g, 7.35 mmol). The reaction mixture was stirred for 2 h at 0 °C. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with EtOAc, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : EtOAc/ 5:5) to yield the title compound (0.96 g, 93%) as a yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.39 (dt, *J* = 7Hz, 2Hz, 2H), 7.32 (dt, *J* = 7Hz, 2Hz, 2H), 7.24 (tt, *J* = 7Hz, 2Hz, 1H), 6.57 (d, *J* = 16Hz, 1H), 6.27 (dd, *J* = 16Hz, 7Hz, 1H), 4.55-4.43 (m, 1H), 2.11 (brs, 1H), 1.38 (d, *J* = 7Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 136.7, 133.6, 129.3, 128.6, 127.6, 126.4, 68.8, 23.4. Data are in agreement with literature.[8]

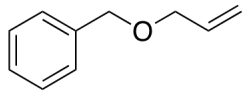
Methyl (3*E*)-4-phenylbut-3-en-2-yl carbonate, 1e



To a solution of (3*E*)-4-phenylbut-3-en-2-ol (0.15 g, 1.01 mmol) and pyridine (0.25 mL, 3.03 mmol) in DCM (5 mL) at 0 °C was added methyl chloroformate (0.16 mL, 2.02 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.19 g, 94%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.25 (m, 1H), 6.67 (d, *J* = 16Hz, 1H), 6.22 (dd, *J* = 16Hz, 7Hz, 1H), 5.42-5.35 (m, 1H), 3.80 (s, 3H), 1.49 (d, *J* = 7Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.1, 136.1, 132.3, 128.6, 128.1, 128.0, 126.6, 75.3, 54.6, 20.5. Data are in agreement with literature.[9]

2.2 Synthesis of *E* linear allylic carbonates:

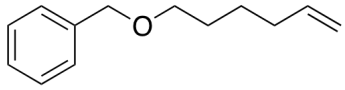
Allyl benzyl ether



To a solution of allyl alcohol (0.6 mL, 10.3 mmol) and pyridine (1.9 mL, 23.2 mmol) in DCM (17 mL) at 0 °C was added benzyl chloride (2.0 mL, 17.4 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 5 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (1.29 g, 78%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.37 (d, *J* = 4Hz, 4H), 7.34-7.28 (m, 1H), 6.02-5.93 (ddt, *J* = 17Hz, 10Hz, 6Hz, 1H), 5.33 (ddt, *J* = 17Hz, 3Hz, 1Hz, 1H), 5.22 (ddt, *J* = 10Hz, 3Hz, 1Hz, 1H), 4.54 (s, 2H) (dt,

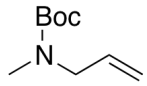
J = 6Hz, 1Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.3, 134.7, 128.4, 127.7, 127.6, 117.1, 72.1, 71.1. Data are in agreement with literature.[10]

Benzyl hex-5-en-1-yl ether



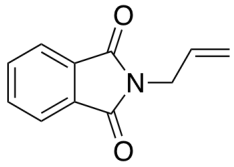
To a solution of NaH (0.7 g, 17.4 mmol) in DMF (12 mL) at 0 °C was added hex-5-en-1-ol (1.4 mL, 11.6 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 20 min. Benzyl bromide (2.1 mL, 17.4 mmol) was added and the mixture was allowed to stir for 1.5 h. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (1.04 g, 47%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.36 (d, *J* = 4Hz, 4H), 7.33-7.28 (m, 1H), 5.87-5.77 (m, 1H), 5.02 (dd, *J* = 17Hz, 2Hz, 1H), 4.96 (dd, *J* = 10Hz, 1Hz, 1H), 4.52 (s, 2H), 3.49 (t, *J* = 7Hz, 2H), 2.11-2.06 (m, 2H), 1.69-1.62 (m, 2H), 1.53-1.46 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.8, 138.7, 128.3, 127.6, 127.5, 114.5, 72.9, 70.2, 33.6, 29.2, 25.5. Data are in agreement with literature.[11]

***tert*-Butyl allyl(methyl)carbamate**



To a solution of *N*-methylprop-2-en-1-amine (0.5 mL, 5.0 mmol) and triethylamine (1.5 mL, 11.0 mmol) in anhydrous DCM (6 mL) at 0 °C was added di-*tert*-butyl malonate (1.3 mL, 5.5 mmol) in 2 portions. The reaction mixture was allowed to warm to room temperature and stirred overnight at room temperature. The solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography (petroleum ether 30-40% /diethyl ether: 9/1) to yield the title compound (0.58 g, 68%) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$): δ 5.81-5.71 (m, 1H), 5.14-5.10 (m, 2H), 3.81 (brs, 2H), 2.82 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$): 155.7, 133.6, 116.1, 79.3, 51.4, 33.6, 28.3. Data are in agreement with literature.[12]

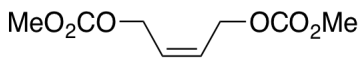
2-Allyl-1*H*-isoindole-1,3(2*H*)-dione



To a suspension of potassium phthalimide (1.9 g, 10.0 mmol) and tetrabutylammonium bromide (64 mg, 0.2 mmol) in anhydrous DMF (10 mL) at room temperature was added dropwise allylbromide (0.9 mL, 10.0 mmol). The reaction mixture was stirred overnight at room temperature and then poured into 10 mL of water. The solid was filtered and washed with water. The crude product is purified by recrystallization from hexane to yield the title

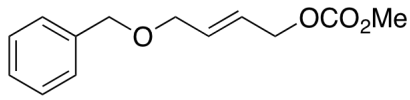
compound (1.3 g, 70%) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.89-7.85 (m, 2H), 7.75-7.71 (m, 2H), 5.95-5.85 (m, 1H), 5.26 (dd, *J* = 17Hz, 1Hz, 1H), 5.21 (dd, *J* = 10Hz, 1Hz, 1H), 4.31 (d, *J* = 6Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 168.0, 134.0, 132.1, 131.5, 123.3, 117.7, 40.0. Data are in agreement with literature.[13]

(2*Z*)-But-2-ene-1,4-diyl dimethyl biscarbonate



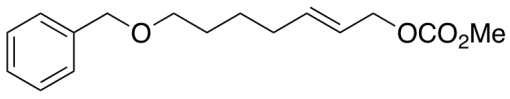
To a solution of *cis*-2-butene-1,4-diol (4.1 mL, 0.05 mol) and pyridine (24.3 mL, 0.3 mol) in DCM (220 mL) at 0 °C was added methyl chloroformate (15.4 mL, 0.2 mol). The reaction mixture was allowed to warm to room temperature and stirred for 16 h at room temperature. The reaction was quenched by addition of $HCl_{(aq)}$. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 8:2) to yield the title compound (9.82 g, 96%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.81 (t, *J* = 4Hz, 2H), 4.76 (d, *J* = 4Hz, 4H), 3.79 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.5, 128.0, 63.2, 54.9. Data are in agreement with literature.[14]

(2*Z*)-4-(Benzyloxy)but-2-en-1-yl methyl carbonate, (*E*)-1b



To a solution of allyl benzyl ether (1.48 g, 10 mmol) and (2*Z*)-but-2-ene-1,4-diyl dimethyl biscarbonate (4.08 g, 20 mol) in DCM (35 mL) at 50 °C was added Grubbs-Hoveyda 2nd generation catalyst (0.3 g, 0.5 mmol) in 3 portions over 24 h. The reaction mixture was stirred for further 48 h at 50 °C. The mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (1.02 g, 43%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.36-7.29 (m, 5H), 5.85-5.78 (m, 1H), 5.63-5.56 (m, 1H), 4.57 (d, *J* = 7Hz, 2H), 4.51 (s, 2H), 3.79 (s, 3H), 3.48 (t, *J* = 6 Hz, 2H), 2.12-2.06 (m, 2H), 1.67-1.60 (m, 2H), 1.53-1.44 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.6, 138.0, 131.7, 128.4, 127.7, 127.6, 125.8, 72.4, 69.6, 67.7, 54.8. Data are in agreement with literature.[15]

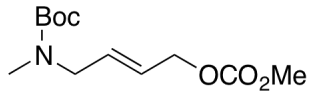
(2*E*)-7-(Benzyloxy)hept-2-en-1-yl methyl carbonate, (*E*)-1f



To a solution of benzyl hex-5-en-1-yl ether (0.95 g, 5 mmol) and (2*Z*)-but-2-ene-1,4-diyl dimethyl biscarbonate (2.04 g, 10 mol) in DCM (18 mL) at 50 °C was added Grubbs-Hoveyda 2nd generation catalyst (0.16 g, 0.3 mmol) in 3 portions over 24 h. The reaction mixture was stirred for further 48 h at 50 °C. The mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (1.06 g, 76%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.35-7.25 (m, 5H), 5.98-5.85 (m, 2H), 4.66 (d, *J* = 5Hz, 2H), 4.53 (s, 2H), 4.06 (dd,

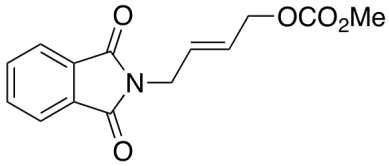
J = 5Hz, 1Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.7, 138.6, 137.0, 128.3, 127.6, 127.5, 123.5, 72.9, 70.1, 68.6, 54.7, 32.0, 29.2, 25.4; IR (CH_2Cl_2) ν 1750, 1264; HRMS calc for $C_{16}H_{22}NaO_4$ $[M+Na]^+$ 301.1410, found 301.1407.

(2*E*)-4-[(*tert*-Butoxycarbonyl)(methyl)amino]but-2-en-1-yl methyl carbonate, (*E*)-1g



To a solution of *tert*-butyl allyl(methyl)carbamate (0.43 g, 2.5 mmol) and (2*Z*)-but-2-ene-1,4-diyl dimethyl biscarbonate (1.02 g, 5.0 mol) in DCM (9 mL) at 50 °C was added Grubbs-Hoveyda 2nd generation catalyst (78 mg, 0.13 mmol) in 3 portions over 24 h. The reaction mixture was stirred for further 48 h at 50 °C. The mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (190 mg, 30%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.73 (dt, *J* = 16Hz, 5Hz, 1H), 5.65 (dt, *J* = 16Hz, 6Hz, 1H), 4.60 (dd, *J* = 6Hz, 1Hz, 2H), 3.80 (brs, 2H), 3.76 (s, 3H), 2.78 (brs, 3H), 1.42 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.5, 131,1, 127.9, 125.3, 79.6, 67.6, 67.0, 54.8, 33.8, 28.4; IR (CH_2Cl_2) ν 1749, 1687, 1264, 1152, 907; HRMS calc for $C_{12}H_{21}NNaO_5$ $[M+Na]^+$ 282.1312, found 282.1316.

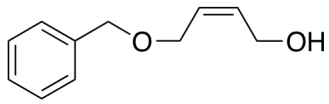
(2*E*)-4-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)but-2-en-1-yl methyl carbonate, (*E*)-1h



To a solution of 2-allyl-1*H*-isoindole-1,3(2*H*)-dione (0.94 g, 5.0 mmol) and (2*Z*)-but-2-ene-1,4-diyl dimethyl biscarbonate (2.04 g, 10 mol) in DCM (18 mL) at 50 °C was added Grubbs-Hoveyda 2nd generation catalyst (0.16 g, 0.3 mmol) in 3 portions over 24 h. The reaction mixture was stirred for further 48 h at 50 °C. The mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (0.51 g, 37%) as a grey solid. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79-7.78 (m, 2H), 7.72-7.67 (m, 2H), 5.84 (dt, *J* = 16Hz, 6Hz, 1H), 5.77 (dt, *J* = 16Hz, 5Hz, 1H), 4.57 (d, *J* = 5Hz, 2H), 4.27 (d, *J* = 6Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 170.0, 155.6, 134.2, 132.2, 128.5, 127.2, 123.6, 67.3, 55.0, 38.9; IR (CH_2Cl_2) ν 1749, 1715, 1395, 1264, 907; HRMS calc for $C_{14}H_{13}NO_5$ $[M]^+$ 275.0794, found 275.0797. Mp 91-93 °C.

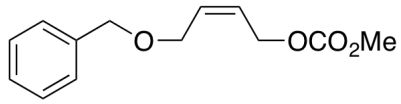
2.3 Synthesis of *Z* linear allylic carbonates:

(2*Z*)-4-(Benzyloxy)but-2-en-1-ol, (*Z*)-4b



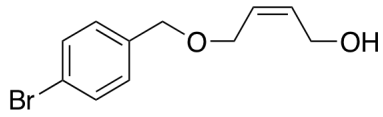
To a solution of (*Z*)-but-2-ene-1,4-diol (2.46 mL, 30 mmol) in THF (35 mL) at 0 °C was carefully added sodium hydride (421 mg, 10.5 mmol). After being stirred for 1 h at room temperature, benzyl bromide (1.18 mL, 10 mmol) was added, and the resulting mixture was stirred at 75 °C for 1 h. The reaction was then quenched at room temperature by addition of sat. aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with DCM, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : EtOAc, 9:1) to yield the title compound (1.25 g, 70%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 5.87-5.80 (m, 1H), 5.79-5.72 (m, 1H), 4.54 (s, 2H), 4.18 (t, J = 6Hz, 2H), 4.11 (d, *J* = 6Hz, 2H), 1.95 (t, *J* = 6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 137.9, 132.4, 128.5, 128.3, 127.9, 127.8, 72.5, 65.7, 58.8. Data are in agreement with literature.[16]

(2*Z*)-4-(Benzyloxy)but-2-en-1-yl methyl carbonate, (*Z*)-1b



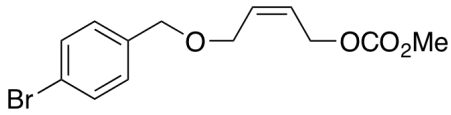
To a solution of (*Z*)-**4b** (1.25 g, 7.0 mmol) and pyridine (1.70 mL, 21 mmol) in DCM (20 ml) at 0 °C was added dropwise methyl chloroformate (1.08 mL, 14 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (1.5 g, 91%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 5.89-5.83 (m, 1H), 5.78-5.71 (m, 1H), 4.71 (d, *J* = 7Hz, 2H), 4.53 (s, 2H), 4.15 (dt, *J* = 6Hz, 1Hz , 2H), 3.79 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.6, 137.9, 131.4, 128.4, 127.8, 127.7, 126.0, 72.5, 65.6, 63.6, 54.8. Data are in agreement with literature.[17]

(2*Z*)-4-[(4-Bromobenzyl)oxy]but-2-en-1-ol



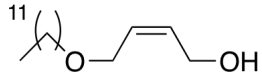
To a solution of (*Z*)-but-2-ene-1,4-diol (1.25 mL, 15 mmol) in THF (15 mL) at 0 °C was carefully added sodium hydride (0.21 g, 5.3 mmol). After being stirred for 1.5 h at room temperature, 4-bromobenzyl bromide (1.25 mL, 5 mmol) was added, and the resulting mixture was stirred at 90 °C for 1 h. The reaction was then cooled to room temperature and quenched by addition of sat. aqueous NH_4Cl solution and extracted 3 times with DCM. The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield the title compound (0.88 g, 68%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.47 (d, *J* = 8Hz, 2H), 7.21 (d, *J* = 8Hz, 2H), 5.81 (ddd, *J* = 6Hz, 6Hz, 11Hz, 1H), 5.71 (ddd, *J* = 6Hz, 6Hz, 11Hz, 1H), 4.46 (s, 2H), 4.16 (d, *J* = 6Hz, 2H), 4.08 (d, *J* = 6Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 136.9, 132.5, 131.6, 129.4, 127.9, 121.6, 71.6, 65.8, 58.6. Data are in agreement with literature.[18]

(2*Z*)-4-[(4-Bromobenzyl)oxy]but-2-en-1-yl methyl carbonate, (*Z*)-1i



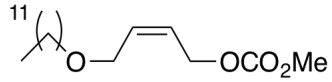
To a solution of (2*Z*)-4-[(4-bromobenzyl)oxy]but-2-en-1-ol (0.74 g, 3.0 mmol) and pyridine (0.73 mL, 9.0 mmol) in DCM (10 mL) at 0 °C was added dropwise methyl chloroformate (0.46 mL, 6.0 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.81 g, 86%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45 (d, *J* = 8Hz, 2H), 7.22 (d, *J* = 8Hz, 2H), 5.79 (ddd, *J* = 6Hz, 6Hz, 11Hz, 1H), 5.71 (ddd, *J* = 6Hz, 7Hz, 11Hz, 1H), 4.67 (d, *J* = 7Hz, 2H), 4.44 (s, 2H), 4.11 (d, *J* = 6Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.6, 137.0, 131.5, 131.1, 129.4, 126.2, 121.6, 71.6, 65.8, 63.5, 54.8; IR ($CDCl_3$) ν 1749, 1265; HRMS calc for $C_{13}H_{15}{}^{79}BrNaO_4$ $[M+Na]^+$ 337.0046, found 337.0051.

(2*Z*)-4-(Dodecyloxy)but-2-en-1-ol



To a solution of (*Z*)-butene-1,4-diol (2.18 mL, 26.5 mmol) in THF (40 mL) and DMF (10 mL) at 0 °C was carefully added sodium hydride (792 mg, 19.8 mmol). After being stirred for 20 min at 0 °C, 1-bromododecane (2.25 mL, 13.2 mmol) was added at 0 °C, and the resulting mixture was allowed to warm to room temperature and stirred for 24 h at room temperature. The reaction was quenched by addition of sat. aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with EtOAc, the combined organic phases were washed with water and dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (1.67 g, 50%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.85-5.79 (m, 1H), 5.74-5.68 (m, 1H), 4.20 (d, J = 6Hz, 2H), 4.04 (d, J = 6Hz, 2H), 3.44 (t, J = 7Hz, 2H), 2.10 (s, 1H), 1.62-1.55 (m, 2H), 1.35-1.25 (m, 18H), 0.88 (t, J = 7Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 132.1, 128.6, 70.9, 66.5, 58.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 26.2, 22.7, 14.1; IR ($CDCl_3$) ν 3379, 1108, 1030; HRMS calc for $C_{16}H_{32}NaO_2$ $[M+Na]^+$ 279.2295, found 279.2294.

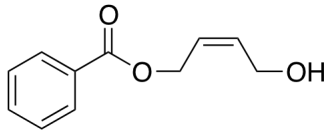
(2*Z*)-4-(Dodecyloxy)but-2-en-1-yl methyl carbonate, (*Z*)-1j



To a solution of (*Z*)-4-(dodecyloxy)but-2-en-1-ol (1.63 g, 6.36 mmol) and pyridine (1.6 mL, 20 mmol) in DCM (20 ml) at 0 °C was added dropwise methyl chloroformate (1.0 mL, 13 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica

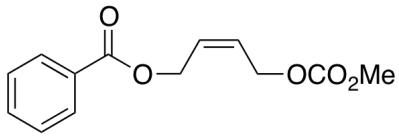
gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (1.88 g, 94%). ^1H NMR (400MHz, $CDCl_3$): δ 5.84-5.78 (m, 1H), 5.74-5.68 (m, 1H), 4.73 (d, J = 7Hz, 2H), 4.08 (dt, J = 6Hz, 1Hz, 2H), 3.79 (s, 3H), 3.42 (t, J = 7Hz, 2H), 1.61-1.54 (m, 2H), 1.35-1.25 (m, 18H), 0.89 (t, J = 7Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.7, 131.8, 125.6, 70.8, 66.4, 63.7, 54.8, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 26.2, 22.7, 14.1; IR ($CDCl_3$) ν 1751, 1262; HRMS calc for $C_{18}H_{34}NaO_4$ $[M+Na]^+$ 337.2349, found 337.2353.

(Z)-4-Hydroxybut-2-en-1-yl benzoate



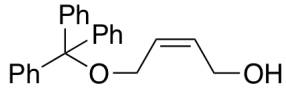
To a solution of (*Z*)-but-2-ene-1,4-diol (0.82 mL, 10.0 mmol) and pyridine (0.49 mL, 6.0 mmol) in DCM (20 ml) at 0 °C was added dropwise benzoyl chloride (0.58 mL, 5.0 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 3 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 2 times with DCM, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (0.78 g, 81%). ^1H NMR (400MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.60-7.55 (m, 1H), 7.47-7.43 (m, 2H), 5.93 (dtt, J = 11Hz, 7Hz, 1Hz, 1H), 5.78 (dtt, J = 11Hz, 7Hz, 1Hz, 1H), 4.95 (d, J = 7Hz, 2H), 4.36 (d, J = 7Hz, 2H), 1.60 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.7, 133.6, 133.1, 130.0, 129.6, 128.4, 125.6, 60.6, 58.5. Data are in agreement with literature.[19]

(Z)-4-((Methoxycarbonyl)oxy)but-2-en-1-yl benzoate, (*Z*)-1k



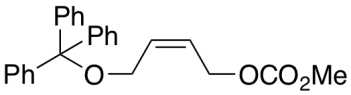
To a solution of (*Z*)-4-hydroxybut-2-en-1-yl benzoate (0.16 g, 0.83 mmol) and pyridine (0.20 mL, 2.5 mmol) in DCM (3 ml) at 0 °C was added dropwise methyl chloroformate (0.13 mL, 1.7 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (0.20 g, 96%). ^1H NMR (400MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.42 (m, 2H), 5.95-5.89 (m, 1H), 5.86-5.80 (m, 1H), 4.94 (d, J = 6Hz, 2H), 4.82 (d, J = 6Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.2, 155.6, 133.1, 129.9, 129.6, 128.7, 128.4, 127.6, 63.3, 60.4, 54.9. IR ($CDCl_3$) ν 1748, 1718, 1445, 1258; HRMS calc for $C_{13}H_{14}NaO_5$ $[M+Na]^+$ 273.0733, found 273.0732.

(2*Z*)-4-(Trityloxy)but-2-en-1-ol



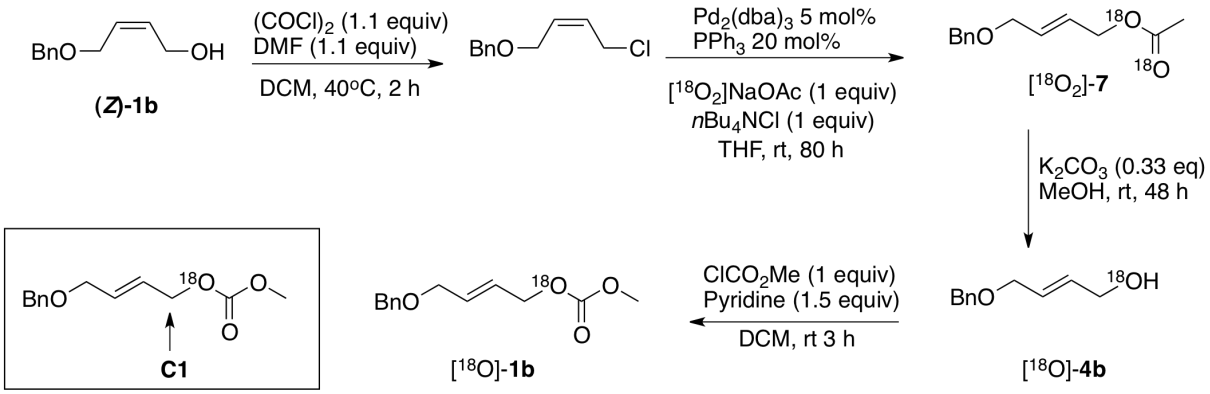
To a solution of (*Z*)-2-butene-1,4-diol (0.16 mL, 2 mmol) in pyridine (4 mL) was added dropwise trityl chloride (0.56 g, 2 mmol). The reaction mixture was stirred overnight at room temperature. The reaction was quenched by addition of water. The aqueous phase was extracted 3 times with DCM, the combined organic phases were washed with 2M HCl aqueous solution and $NaHCO_3$ solution, dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.40 g, 60%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.52-7.49 (m, 6H), 7.37-7.32 (m, 6H), 7.29-7.25 (m, 3H), 5.85-5.79 (m, 1H), 5.77-5.71 (m, 1H), 4.03 (d, *J* = 6Hz, 2H), 3.74 (d *J* = 6Hz, 2H), 1.86 (br s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 144.0, 131.2, 128.8, 128.6, 127.9, 127.1, 87.2, 60.2, 58.7. Data are in agreement with literature.[20]

Methyl (2*Z*)-4-(trityloxy)but-2-en-1-yl carbonate, (*Z*)-1l

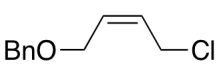


To a solution of (*Z*)-4-trityloxy-but-2-en-1-ol (0.32 g, 0.97 mmol) and pyridine (0.24 mL, 2.91 mmol) in DCM (5 mL) at 0 °C was added dropwise methyl chloroformate (0.15 mL, 1.94 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 9:1) to yield the title compound (0.31 g, 81%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.51-7.46 (m, 6H), 7.36-7.32 (m, 6H), 7.29-7.25 (m, 3H), 5.91 (dddt, *J* = 12 Hz, 11Hz, 5Hz, 1Hz, 1H), 5.68 (dddt, *J* = 13 Hz, 11Hz, 7Hz, 2Hz, 1H), 4.59 (dt, *J* = 7Hz, 1Hz, 2H), 3.78 (s, 3H), 3.79-3.76 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.6, 143.9, 131.6, 128.6, 127.9, 127.1, 124.9, 87.1, 63.9, 60.3, 54.8; IR (CH_2Cl_2) ν 1749, 1448, 1264; HRMS calc for $C_{25}H_{24}NaO_4$ $[M+Na]^+$ 411.1567, found 441.1565.

2.4 Synthesis of [^{18}O]-1b:[21]

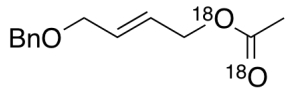


Benzyl (2*Z*)-4-chlorobut-2-en-1-yl ether



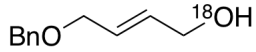
To a solution of oxalyl chloride (0.19 mL, 2.2 mmol) in DCM (8 mL) at 0 °C was added DMF (0.17 mL, 2.2 mmol) dropwise. The resulting white suspension was allowed to warm to room temperature, and after 10 min cooled again to 0 °C. Alcohol (*Z*)-**4b** (0.3 g, 2 mmol) was added and the reaction mixture stirred for 3 h at reflux. The reaction was cooled to room temperature and poured into a saturated solution of NaCl. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O/ 8:2) to yield the title compound (0.34 g, 86%, *Z*/*E* 99/1). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.37-7.24 (m, 5H), 5.84-5.75 (m, 2H), 4.52 (s, 2H), 4.16-4.14 (m, 2H), 4.12-4.10 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 137.9, 130.8, 128.5, 128.5, 127.8, 127.8, 72.4, 65.1, 39.2. Data are in agreement with literature.[22]

(2*E*)-4-(Benzyloxy)but-2-en-1-yl [$^{18}O_2$]-acetate, [$^{18}O_2$]-7



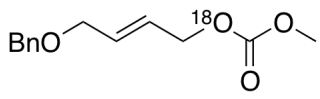
To a solution of benzyl (2*Z*)-4-chlorobut-2-en-1-yl ether (0.29 g, 1.5 mmol) in THF (4 mL) at room temperature was added $Pd_2(dba)_3$ (69 mg, 5 mol%), PPh_3 (81 mg, 20 mol%), nBu$_4$NCl (0.48 g, 1.5 mmol) and [$^{18}O_2$]-NaOAc . The reaction mixture was stirred for 80 h at room temperature. The solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%) to yield **[$^{18}O_2$]-7** (0.31 g, 98% yield, *E*/*Z* 66/34, 98% ^{18}O incorporation calculated from ^{13}C NMR). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.38-7.29 (m, 5H), 5.90-5.87 (m, 2H), 4.59 (d, *J* = 4Hz, 2H), 4.54 (s, 2H), 4.05 (d, *J* = 4Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 170.7, 138.1, 130.9, 128.4, 127.7, 127.6, 126.6, 72.4, 69.8, 64.2, 20.9. HRMS calc for $C_{13}H_{16}NaO^{18}O_2$ $[M+Na]^+$ 247.1077, found 247.1082.

(2*E*)-4-(Benzyloxy)-[^{18}O]-but-2-en-1-ol, [^{18}O]-4b



To a solution of allylic acetate **[$^{18}O_2$]-7** (0.25 mg, 1.2 mmol) in MeOH (4 mL) at room temperature was added K_2CO_3 (55 mg, 0.4 mmol). The reaction mixture was stirred for 3 days at room temperature. The reaction was filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40% : Et_2O)/ 5:5) to yield **[^{18}O]-4b** (0.12 g, 57% yield, *E*/*Z* 66/34, 98% ^{18}O incorporation calculated from ^{13}C NMR). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.33-7.25 (m, 5H), 5.91 (dt, *J* = 16Hz, 5Hz, 1H), 5.83 (dt, *J* = 16Hz, 5Hz, 1H), 4.51 (s, 2H), 4.15 (dd, *J* = 5Hz, 1Hz, 2H), 4.03 (dd, *J* = 5Hz, 1Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.2, 132.1, 128.4, 127.9, 127.7, 127.6, 72.3, 70.1, 63.0. HRMS calc for $C_{11}H_{14}NaO^{18}O$ $[M+Na]^+$ 203.0928, found 203.0921. Data are in agreement with literature.[23]

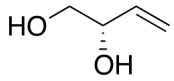
(2*E*)-4-(Benzyloxy)but-2-en-1-yl) [^{18}O]-methyl carbonate, [^{18}O]-1b



To a solution of **[^{18}O]-4b** (90 mg, 0.5 mmol) and pyridine (0.12 mL, 1.5 mmol) in DCM (2 mL) at 0 °C was added methyl chloroformate (77 µL, 1 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 8 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether 30-40%: Et_2O/ 9:1) to yield **[^{18}O]-1b** (77 mg, 64% yield, *E*/*Z* 81/19, 98% ^{18}O incorporation calculated from ^{13}C NMR). The NMR data are in agreement with substrate (*E*)-**1b**. HRMS calc for $C_{13}H_{16}NaO_3{}^{18}O$ $[M+Na]^+$ 261.0983, found 261.1011.

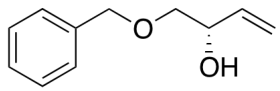
2.5 Synthesis of enantiopure allyl carbonate (*S*)-1a:

(*S*)-3-Butene-1,2-diol



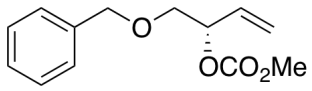
(*R*, *R*)-Jacobsen's catalyst (86 mg, 0.14 mmol) was added to a mixture of butadiene monoxide (2.3 mL, 28.52 mmol) and acetic acid (32 µL, 0.57 mmol) and cooled to 0 °C. H_2O (0.23 mL, 12.83 mmol) was added dropwise and the reaction mixture was stirred at 4 °C for 16 h. The crude reaction was purified directly by flash column chromatography (30-50 % EtOAc : pet ether) and the product afforded as a clear oil (1.0 g, 40 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87-5.76 (ddd, *J* = 17Hz, 11Hz, 6Hz, 1H), 5.32 (d, *J* = 17Hz, 1H), 5.18 (d, *J* = 11Hz, 1H), 4.28-4.20 (m, 1H), 3.95 (br s, 2H), 3.75 (br s, 1H), 3.50 (dd, *J* = 11Hz, 8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 137.0, 116.6, 73.2, 66.1. Data are in agreement with literature.[24]

(2*S*)-1-(Benzyloxy)but-3-en-2-ol, (*S*)-4a



To a solution of (*S*)-3-butene-1,2-diol (0.89 g, 10.1 mmol) in THF (30 mL) at 0 °C was added sodium hydride (0.25 g, 10.6 mmol) portionwise. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h at room temperature. Benzyl bromide (1.24 mL, 10.6 mmol, 1.05 equiv.) was subsequently added and the reaction mixture was stirred under reflux conditions for 1 h before being cooled to 0 °C. The mixture was carefully quenched by addition of 1M HCl aqueous solution. The aqueous phases were extracted 3 times with DCM, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (0.79 g, 44%, *ee* 97%). Chiral HPLC: (OD, Hexane/ *i*-PrOH= 95/5, 1.0 mL/ min, 259 nm) t_R (major-isomer)= 12.6 min, t_R (minor-isomer)= 14.4 min. Data are in agreement with literature.[4]

(2*S*)-1-(Benzyloxy)but-3-en-2-yl methyl carbonate, (*S*)-1a



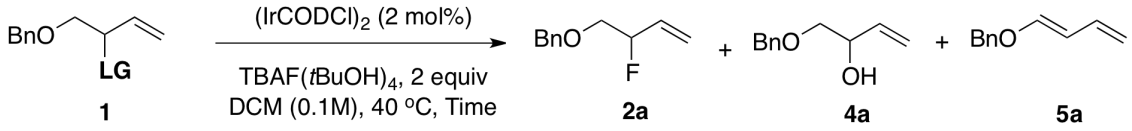
To a solution of (*S*)-**4a** (0.40 g, 2.21 mmol) and pyridine (0.53 mL, 6.57 mmol) in DCM (10 mL) at 0 °C was added dropwise methyl chloroformate (0.36 mL, 3.69 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h at room temperature. The reaction was quenched by addition of 1M HCl aqueous solution. The aqueous phase was extracted 3 times with Et_2O, the combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (hexane : Et_2O/ 9:1) to yield the title compound (0.33 g, 62%, *ee* 95%). Chiral HPLC: (OD, Hexane/ *i*-PrOH= 95/5, 1.0 mL/ min, 259 nm) t_R (minor-isomer)= 6.9 min, t_R (major- isomer)= 9.4 min. Data are in agreement with literature.[4]

General procedure for the initial studies (Table 1)

To a solution of [Ir]/Ligand (4 mol%, Ir/Ligand: 1/2) in dry solvent (THF, DMF, Toluene or DCM, 1 mL) **1a** (0.1 mmol) was added, followed by addition of the fluorinating source (2 eq, 0.2 mmol). The reaction was allowed to stir at the indicated temperature until TLC indicated complete conversion of the starting material and no longer then 24 h. The solvent was removed *in vacuo* and ^{1}H NMR and ^{19}F NMR of the crude mixture were recorded to determine the conversion of the starting material and the product distribution.

Procedure for the screening of leaving groups

To a solution of allylic derivative (0.1 mmol) in dry DCM (1 mL) was added $[Ir(COD)Cl]_2$ (2 mol%), followed by addition of TBAF(*t*BuOH)$_4$ (2 eq, 0.2 mmol). The reaction was allowed to stir at 40 °C until TLC indicated complete conversion of the starting material and no longer than 24 h. The solvent was removed *in vacuo* and ^{1}H NMR and ^{19}F NMR of the crude mixture recorded to determine the conversion of the starting material and the product distribution.



Entry	Leaving group	Time (h)	Product ratio[a] **1** : **2a** : **4a** : **5a**
1	OCO_2Me	2	0 : 80 : 13 : 7
2	OBz	24	90 : 10 : 0 : 0
3	OPNB	24	56 : 31 : 10 : 3
4	OAc	24	94 : 6 : 0 : 0

[a] Determined by 1H NMR of the crude mixture.

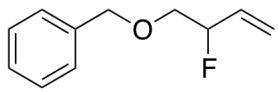
General Procedure (A) for the synthesis of allylic fluorides (Scheme 1, Scheme 2 and Table 2)

To a solution of allylic carbonate (0.2 mmol) and TBAF(*t*BuOH)$_4$ (2 eq, 0.4 mmol) in dry DCM (8 mL) was added a solution of $[Ir(COD)Cl]_2$ (2 mol%) in dry DCM (2 mL) in 4

portions over 45 min. The reaction was allowed to stir at 40 °C until TLC indicated complete conversion of the starting material and no longer than 24 h. Additional portions of catalyst (up to 4 mol%) were added to reactions which did not show completion after few hours. The solvent was removed *in vacuo* and ^{1}H NMR and ^{19}F NMR of the crude mixture recorded. Crude products were purified by silica gel column chromatography.

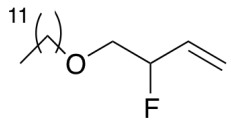
2.6 Synthesis of branched allylic fluorides:

Benzyl 2-fluorobut-3-en-1-yl ether, 2a



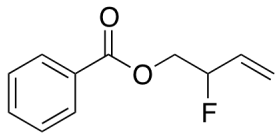
Following the general procedure A, the reaction was carried out on 47 mg of **1a** and 2 mol% of $[Ir(COD)Cl]_2$ for 3 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 83% of conversion into **2a** (b/l: >20/1). Silica gel column chromatography (hexane) yielded **2a** (21 mg, 57%, b/l: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.42-7.36 (m, 4H), 7.35-7.31 (m, 1H), 5.95 (dddd, *J* = 18Hz, 15Hz, 11Hz, 6Hz, 1H), 5.45 (dq, *J* = 17Hz, 1Hz, 1H) 5.34 (dt, *J* = 11Hz, 1Hz, 1H) 5.85 (dm, *J* = 49Hz, 1H), 4.64 (s, 2H), 3.68 (dd, *J* = 2Hz, 5Hz, 1H), 3.62 (dd, *J* = 5Hz, 1Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 138.5, 133.5 (d, *J* = 20Hz), 128.7, 128.1, 128.0, 118.5 (d, *J* = 11Hz), 92.3 (d, *J* = 171Hz), 73.7, 72.5 (d, *J* = 23Hz); ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -184.76. Data are in agreement with literature.[10]

Dodecyl 2-fluorobut-3-en-1-yl ether, 2c



Following the general procedure A, the reaction was carried out on 63 mg of **1c** and 2 mol% of $[Ir(COD)Cl]_2$ for 3 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 95% of conversion into **2c** (b/l: >20/1). Silica gel column chromatography (hexane) yielded **2c** (33 mg, 64%, b/l: >20/1) as a colourless oil. %). ^{1}H NMR (500MHz, CD_2Cl_2): δ 5.90 (dddd, *J* = 14Hz, 12Hz, 9Hz, 5Hz, 1H), 5.40 (dq, *J* = 14Hz, 1Hz, 1H), 5.29 (dt, J = 9Hz, 1Hz, 1H), 5.02 (dm, *J* = 40Hz 1H), 3.57 (d, *J* = 4Hz, 1H), 3.52-3.51 (m, 1H), 3,47 (t, *J* = 5Hz, 2H), 1.60-1.54 (m, 2H), 1.31-1.22 (m, 18H), 0.89 (t, J = 6Hz, 3H); ^{13}C NMR (125MHz, CD_2Cl_2):δ 133.7 (d, *J* = 15Hz), 118.3 (d, *J* = 9Hz), 92.8 (d, *J* = 136Hz), 73.0 (d, *J* = 18Hz), 72.1, 32.3, 30.1, 30.0, 30.0, 29.9, 29.8, 26.5, 23.1, 14.3; ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -184.72; IR (CH_2Cl_2) ν 1265, 1125; HRMS calc for $C_{16}H_{35}FNO^{+}$ $[M+NH_4]^{+}$ 276.2697, found 276.2700.

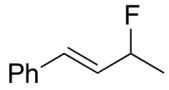
2-Fluorobut-3-en-1-yl benzoate, 2d



Following the general procedure A, the reaction was carried out on 50 mg of **1d** and 4 mol% of $[Ir(COD)Cl]_2$ for 24 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 58% of

conversion into **2d** (b/l: >20/1). Silica gel column chromatography (hexane) yielded **2d** (13 mg, 32%, b/l: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 8.06-8.04 (m, 2H), 7.60 (t, *J* = 8Hz, 1H), 7.49-7.45 (m, 2H), 6.05-5.93 (m, 1H), 5.52 (dt, *J* = 17Hz, 2Hz, 1H), 5.40 (dd, *J* = 11Hz, 2Hz, 1H), 5.25 (dm, *J* = 49Hz, 1H), 4.55-4.36 (m, 2H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 166.4, 133.6, 132.7 (d, *J* = 19Hz), 130.4, 130.1, 129.0, 119.8 (d, *J* = 11Hz), 91.4 (d, *J* = 171Hz), 66.3 (d, *J* = 23Hz); ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -186.01. Data are in agreement with literature.[10]

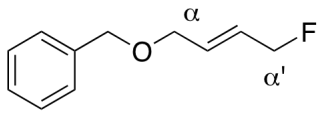
[(2*E*)-4-Fluoropent-2-en-1-yl]benzene, 2e



Following the general procedure A, the reaction was carried out on 41 mg of **1e** and 4 mol% of $[Ir(COD)Cl]_2$ for 24 h. A NMR yield of the crude mixture showed the formation of 66% of **2e** as single regioisomer (*E*/*Z*: >20/1), employing 1-fluoro-3-nitrobenzene as internal standard (21 μL, 0.2 mmol). ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.43-7.17 (m, 5H), 6.53 (dd, *J* = 16Hz, 6Hz, 1H), 6.26 (ddd, *J* = 16Hz, 12Hz, 7Hz, 1H), 5.21 (dm, *J* = 48Hz, 1H), 1.48 (dd, *J* = 24Hz, 7Hz, 3H); ^{19}F {^{1}H}NMR (376.5MHz, $CDCl_3$): δ -163.47; HRMS calc for $C_{10}H_{11}F$ $[M]^+$ 150.0845, found 150.0844. Data are in agreement with literature.[10]

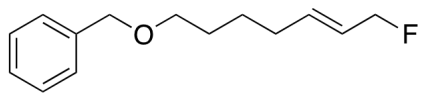
2.7 Synthesis of *E* linear allylic fluoride:

Benzyl (2*E*)-4-fluorobut-2-en-1-yl ether, (*E*)-2b



Following the general procedure A, the reaction was carried out on 47 mg of (*E*)-**1b** and 2 mol% of $[Ir(COD)Cl]_2$ for 5 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 86% of conversion into (*E*)-**2b** (l/b: >20/1, *E*/*Z*: >20/1). Silica gel column chromatography (hexane) yielded (*E*)-**2b** (20 mg, 55%, l/b: >20/1, *E*/*Z*: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.35-7.33 (m, 4H), 7.31-7.27 (m, 1H), 5.95-5.93 (m, 2H), 4.87 (dd, *J* = 47Hz, 4Hz, 2H), 4.52 (s, 2H), 4.07-4.05 (m, 2H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 138.8, 132.0 (d, *J* = 9Hz), 128.7, 128.0, 127.9, 127.0 (d, *J* = 13Hz), 83.3 (d, *J* = 129Hz, **Cα'**), 72.7, 70.0 (d, *J* = 1Hz, **Cα**); ^{19}F {^{1}H}NMR (376.5MHz, $CDCl_3$): δ -212.73. IR (CD_2Cl_2) ν 1216, 952. HRMS calc for $C_{11}H_{13}FNaO$ $[M+Na]^+$ 203.0843, found 203.0841. The geometry of the alkene was assigned by examining the chemical shift of the carbons in α and α' position of (*E*)-**2b** and (*Z*)-**2b**. For the (*E*)-allyl fluorides the chemical shifts of α and α' are consistently higher.

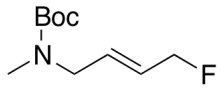
Benzyl (5*E*)-7-fluorohept-5-en-1-yl ether, (*E*)-2f



Following the general procedure A, the reaction was carried out on 56 mg of (*E*)-**1f** and 2 mol% of $[Ir(COD)Cl]_2$ for 16 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 70% of

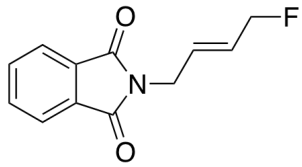
conversion into (*E*)-**2f** (l/b: >20/1, *E*/*Z*: >20/1). Silica gel column chromatography (hexane) yielded (*E*)-**2f** (30 mg, 68%, l/b: >20/1, *E*/*Z*: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.35-7.33 (m, 4H), 7.30-7.25 (m, 1H), 5.89-5.81 (m, 1H), 5.74-5.65 (m, 1H), 4.78 (dd, *J* = 47Hz, 6Hz, 2H), 4.48 (s, 2H), 3.48 (t, *J* = 6Hz, 2H), 2.11 (dt, *J* = 14Hz, 6Hz, 2H), 1.66-1.59 (m, 2H), 1.53-1.46 (m, 2H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 139.4, 137.7 (d, *J* = 12Hz), 128.6, 127.9, 127.7, 125.2 (d, *J* = 16Hz), 84.1 (d, *J* = 158Hz), 73.1, 70.6, 32.3, 29.6, 25.9; ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -207.74; IR (CH_2Cl_2) ν 1265, 1108; HRMS calc for $C_{14}H_{19}OF$ $[M]^+$ 222.1420, found 222.1420.

tert-Butyl [(2*E*)-4-fluorobut-2-en-1-yl]methylcarbamate, (*E*)-2g



Following the general procedure A, the reaction was carried out on 63 mg of (*E*)-**1g** and 2 mol% of $[Ir(COD)Cl]_2$ for 16 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 85% of conversion into (*E*)-**2g** (l/b: >20/1, *E*/*Z*: >20/1). Silica gel column chromatography (hexane) yielded (*E*)-**2g** (26 mg, 64%, l/b: >20/1, *E*/*Z*: >20/1) as a yellow oil. ^{1}H NMR (500MHz, CD_2Cl_2): δ 5.76-5.74 (m, 2H), 4.84 (dm, *J* = 47Hz, 2H), 3.83 (br s, 2H), 2.80 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 156.0, 131.7, 126.9 (d, *J* = 17Hz), 83.2 (d, *J* = 161Hz), 79.8, 50.7, 50.0 (rotamer), 34.3, 28.7; ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -211.68, -211.81 (rotamer). IR (CH_2Cl_2) ν 1696, 1454, 1248, 1151; HRMS calc for $C_{10}H_{22}FN_2O_2^+$ $[M+NH_4]^+$ 221.1660, found 221.1664.

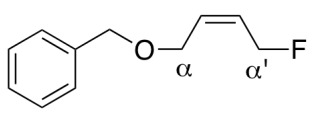
2-[(2*E*)-4-Fluorobut-2-en-1-yl]-1*H*-isoindole-1,3(2*H*)-dione, (*E*)-2h



Following the general procedure A, the reaction was carried out on 58 mg of (*E*)-**1h** and 2 mol% of $[Ir(COD)Cl]_2$ for 16 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 66% of conversion into **2c** (l/b: 15/1, *E*/*Z*: >20/1). Silica gel column chromatography (hexane) yielded (*E*)-**2h** (21 mg, 48%, l/b: >20/1, *E*/*Z*: >20/1) as a yellow oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.86-7.83 (m, 2H), 7.75-7.73 (m, 2H), 5.91-5.81 (m, 2H), 4.82 (dd, *J* = 46Hz, 4Hz, 2H), 4.30 (d, *J* = 5Hz, 2H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 168.1, 134.5, 132.5, 128.7 (d, *J* = 12Hz), 128.1 (d, *J* = 17Hz), 123.6, 83.9 (d, *J* = 162Hz), 39.0; ^{19}F {^{1}H}NMR (376.5MHz, CD_2Cl_2): δ -214.14; IR (CH_2Cl_2) ν 1709, 1427, 1393, 1061; HRMS calc for $C_{12}H_{10}NO_2F$ $[M]^+$ 219.0696, found 219.0702.

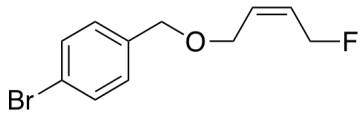
2.8 Synthesis of *Z* linear allylic fluoride:

Benzyl (2*Z*)-4-fluorobut-2-en-1-yl ether, (*Z*)-2b



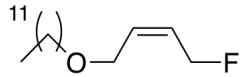
Following the general procedure A, the reaction was carried out on 47 mg of (*Z*)-**1b** and 2 mol% of $[Ir(COD)Cl]_2$ for 4 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 87% of conversion into (*Z*)-**2b** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane) yielded (*Z*)-**2b** (23 mg, 64%, l/b: >20/1, *Z*/*E*: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.41-7.32 (m, 5H), 5.92-5.79 (m, 2H), 5.00 (dd, *J* = 5Hz, 46Hz, 2H), 4.53 (s, 2H), 4.15-4.13 (m, 2H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 138.7, 131.5 (d, *J* = 10Hz), 128.7, 128.1, 128.0, 127.3 (d, *J* = 20Hz), 79.3 (d, *J* = 158Hz, **Cα'**), 72.7, 66.2 (**Cα**); ^{19}F {^{1}H}NMR (376.5MHz, $CDCl_3$): δ -213.10. IR (CD_2Cl_2) ν 1092, 1008; HRMS calc for $C_{11}H_{13}FO$ $[M]^+$ 180.0950, found 180.0947. The geometry of the alkene was assigned by examining the chemical shift of the carbons in α and α' position of (*E*)-**2b** and (*Z*)-**2b**. For the (*Z*)-allyl fluorides the chemical shifts of α and α' are consistently lower.

4-Bromobenzyl (2*Z*)-4-fluorobut-2-en-1-yl ether, (*Z*)-2i



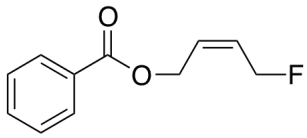
Following the general procedure A, the reaction was carried out on 63 mg of (*Z*)-**1i** and 2 mol% of $[Ir(COD)Cl]_2$ for 16 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 87% of conversion into (*Z*)-**2i** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane) yielded (*Z*)-**2i** (27 mg, 52%, l/b: >20/1, *Z*/*E*: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 7.52 (d, *J* = 9Hz, 2H), 7.26 (d, *J* = 9Hz, 2H), 5.89-5.79 (m, 2H), 4.99 (dd, *J* = 5Hz, 47Hz, 2H), 4.48 (s, 2H), 4.14-4.12 (m, 2H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 137.8, 131.8, 131.3 (d, *J* = 10Hz), 129.7, 127.4 (d, *J* = 19Hz), 121.7, 79.3 (d, *J* = 157Hz), 71.9, 66.3; ^{19}F {^{1}H}NMR (376.5MHz, $CDCl_3$): δ -213.14. IR (CD_2Cl_2) ν 1217, 1011; HRMS calc for $C_{11}H_{12}{}^{79}BrFO$ $[M]^+$ 258.0056, found 258.0051.

Dodecyl (2*Z*)-4-fluorobut-2-en-1-yl ether, (*Z*)-2j



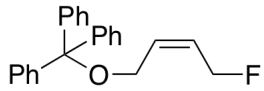
Following the general procedure A, the reaction was carried out on 63 mg of (*Z*)-**1j** and 2 mol% of $[Ir(COD)Cl]_2$ for 3 h. ^{1}H NMR and ^{19}F NMR of the crude mixture showed 81% of conversion into (*Z*)-**2j** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane) yielded (*Z*)-**2j** (34 mg, 65%, l/b: >20/1, *Z*/*E*: >20/1) as a colourless oil. ^{1}H NMR (400MHz, CD_2Cl_2): δ 5.83-5.76 (m, 2H), 5.01 (dd, *J* = 5Hz, 47Hz, 2H), 4.05 (t, *J* = 5Hz, 2H), 3.42 (t, *J* = 7Hz, 2H), 1.58 (m, 2H), 1.30 (s, 18H), 0.92 (t, *J* = 7Hz, 3H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 132.0 (d, *J* = 10Hz), 126.8 (d, *J* = 19Hz), 79.4 (d, *J* = 158Hz), 71.1, 66.8, 32.3, 30.1, 30.0, 30.0, 29.9, 29.9, 29.8, 29.7, 26.6, 23.1, 14.2; ^{19}F {^{1}H}NMR (376.5MHz, $CDCl_3$): δ -212.98. IR (CD_2Cl_2) ν 1109, 1011; HRMS calc for $C_{16}H_{31}FNaO$ $[M+Na]^+$ 281.2251, found 281.2249.

(2*Z*)-4-Fluorobut-2-en-1-yl benzoate, (*Z*)-2k



Following the general procedure A, the reaction was carried out on 66 mg of (*Z*)-**1k** and 2 mol% of $[Ir(COD)Cl]_2$ for 24 h. ^1H NMR and ^{19}F NMR of the crude mixture showed 71% of conversion into (*Z*)-**2k** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane) yielded (*Z*)-**2k** (25 mg, 65%, l/b: >20/1, *Z*/*E*: >20/1) as a colourless oil. ^1H NMR (400MHz, CD_2Cl_2): δ 8.04-8.02 (m, 2H), 7.59 (t, *J* = 8Hz, 1H), 7.48-7.44 (m, 2H), 5.94-5.89 (m, 2H), 5.09 (dd, *J* = 47Hz, 5Hz, 2H), 4.90 (dd, *J* = 5Hz, 3Hz, 2H); ^{13}C NMR (125MHz, CD_2Cl_2): δ 166.6, 133.6, 130.6, 130.0, 129.1, 129.0, 128.9 (d, *J* = 10Hz), 79.4 (d, *J* = 159Hz), 61.0; ^{19}F {^1H}NMR (376.5MHz, CD_2Cl_2): δ -214.52. IR (CD_2Cl_2) ν 1735, 1471, 1268, 1105; HRMS calc for $C_{11}H_{15}FNO_2^+$ $[M+NH_4]^+$ 212.1081, found 212.1086.

(2*Z*)-4-Fluorobut-2-en-1-yl trityl ether, (*Z*)-2l



Following the general procedure A, the reaction was carried out on 78 mg of (*Z*)-**1l** and 4 mol% of $[Ir(COD)Cl]_2$ for 5 h. ^1H NMR and ^{19}F NMR of the crude mixture showed 99% of conversion into (*Z*)-**2l** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane) yielded (*Z*)-**2l** (33 mg, 50%, l/b: >20/1, *Z*/*E*: 18/1) as a colourless oil. ^1H NMR (400MHz, CD_2Cl_2): δ 7.46-7.44 (m, 6H), 7.35-7.31 (m, 6H), 7.28-7.24 (m, 3H), 5.92-5.85 (m, 1H), 5.80-5.70 (m, 1H), 4.80 (dd, *J* = 47Hz, 6Hz, 2H), 3.70 (br s, 2H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 144.4, 131.8 (d, *J* = 11Hz), 128.9, 128.3, 127.5, 126.5 (d, *J* = 19Hz), 87.5, 79.3 (d, *J* = 157Hz), 60.6; ^{19}F {^1H}NMR (376.5MHz, CD_2Cl_2): δ -212.80; IR (CD_2Cl_2) ν 1490, 1448, 1264, 1059, 1010; HRMS calc for $C_{23}H_{25}FNO^+$ $[M+NH_4]^+$ 350.1920, found 350.1926.

General Procedure (B) for the dimethyl malonate substitution (Scheme 1 and Scheme 2)

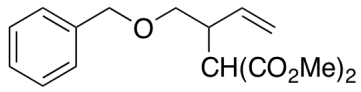
To a solution of allylic carbonate (0.2 mmol) in THF (1 mL) was added $[Ir(COD)Cl]_2$ (2 mol%). A solution of sodium dimethyl malonate (0.4 mmol) in THF (1 mL), prepared from dimethyl malonate (0.4 mmol) and NaH (0.4 mmol) was then added in one portion. The reaction was allowed to stir at 40 °C for 24 h. The reaction was quenched by the addition of distilled water. The aqueous layer was extracted 2 times with Et_2O (2 x 5 mL), the combined organic extracts were dried (Na_2SO_4) and the solvent removed *in vacuo*. ^1H NMR of the crude mixtures were recorded to determine the conversion of the starting material and the product distribution. Crude products were purified by silica gel column chromatography.

Starting from **1a** (47 mg) and following the general procedure B, ^1H NMR of the crude mixture showed 100% of conversion into **3a**/(*E*)-**3b** mixture (b/l: 67/33, *E*/*Z*: >20/1). Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded **3a** (25 mg, 42%) and (*E*)-**3b** (15 mg, 25%, *E*/*Z*: >20/1).

Starting from (*E*)-**1b** (47 mg) and following the general procedure B, ^1H NMR of the crude mixture showed 94% of conversion into **3a**/(*E*)-**3b** mixture (b/l: 55/45, *E*/*Z*: >20/1). Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded **3a** (25 mg, 42%) and (*E*)-**3b** (6 mg, 11 %, *E*/*Z*: >20/1).

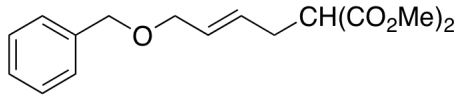
Starting from (*Z*)-**1b** (47 mg) and following the general procedure B, ^{1}H NMR of the crude mixture showed 65% of conversion into (*Z*)-**3b** (l/b: >20/1, *Z*/*E*: >20/1). Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded (*Z*)-**3b** (29 mg, 50%, *Z*/*E*, >20/1).

Dimethyl [1-(benzyloxy)but-3-en-2-yl]malonate, 3a



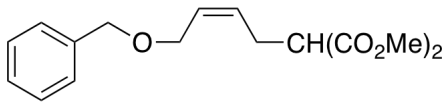
Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded the title compound as a colourless oil. ^{1}H NMR (400MHz, CD_3Cl): δ 7.37-7.28 (m, 5H), 5.86 (ddd, *J* = 18Hz, 9Hz, 6Hz, 1H), 5.18 (d, *J* = 18Hz, 1H), 5.13 (d, *J* = 9Hz, 1H), 4.48 (s, 2H), 3.71 (d, *J* = 4Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.60-3.51 (m, 2H), 3.19-3.12 (m, 1H); ^{13}C NMR (100MHz, CD_2Cl_2): δ 168.8, 168.6, 138.0, 135.4, 128.3, 127.7, 127.6, 118.2, 73.1, 71.0, 53.2, 52.4, 52.3, 44.0. IR (CD_2Cl_2) ν 1750, 1326, 1175; HRMS calc for $C_{16}H_{20}NaO_5$ $[M+Na]^+$ 315.1203, found 315.1202.

Dimethyl [(2*E*)-4-(benzyloxy)but-2-en-1-yl]malonate, (*E*)-3b



Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded the title compound as a colourless oil. ^{1}H NMR (400MHz, CD_3Cl): δ 7.37-7.29 (m, 5H), 5.76-5.64 (m, 2H), 4.48 (s, 2H), 3.97 (d, *J* = 4Hz, 2H), 3.74 (s, 6H), 3.47 (t, *J* = 7Hz, 1H), 2.67 (dd, *J* = 7Hz, 6Hz, 2H); ^{13}C NMR (100MHz, CD_3Cl): δ 169.2, 138.2, 129.8, 129.1, 128.4, 127.7, 127.6, 71.9, 70.3, 52.5, 51.5, 31.5. IR (CD_2Cl_2) ν 1735, 1437, 1273; HRMS calc for $C_{16}H_{20}NaO_5$ $[M+Na]^+$ 315.1203, found 315.1197.

Dimethyl [(2*Z*)-4-(benzyloxy)but-2-en-1-yl]malonate, (*Z*)-3b



Silica gel column chromatography (hexane: diethyl ether, 9:1) yielded the title compound as a colourless oil. ^{1}H NMR (400MHz, CD_3Cl): δ 7.36-7.28 (m, 5H), 5.73 (dddt, *J* = 11Hz, 6Hz, 4Hz, 2Hz, 1H), 5.53 (dddt, *J* = 11Hz, 8Hz, 5Hz, 1Hz, 1H), 4.52 (s, 2H), 4.12 (d, *J* = 6Hz, 2H), 3.74 (s, 6H), 3.43 (t, *J* = 8Hz, 1H), 2.67 (dd, *J* = 8Hz, 8Hz, 2H); ^{13}C NMR (100MHz, CD_3Cl): δ 169.2, 138.2, 129.6, 128.4, 128.0, 127.8, 127.6, 72.4, 65.7, 52.6, 51.4, 27.1. IR (CH_2Cl_2) ν 1735, 1437, 1276. HRMS calc for $C_{16}H_{20}NaO_5$ $[M+Na]^+$ 315.1203, found 315.1208.

General procedure (C) for the dimethyl malonate substitution with TBAF(*t*BuOH)$_4$ as additive (Scheme 3)

To a solution of allylic carbonate (0.1 mmol) in THF (0.5 mL) was added a solution of sodium dimethyl malonate (0.2 mmol) in THF (0.5 mL), prepared from dimethyl malonate (0.2 mmol)

and NaH (0.2 mmol). TBAF(*t*BuOH)$_4$ (0.2 mmol) was then added, followed by the addition of [Ir(COD)Cl]$_2$ (2 mol%) in one portion. The reaction was allowed to stir at 40 °C for 24 h. The solvent was removed *in vacuo*. ^{1}H NMR and ^{19}F NMR of the crude mixtures were recorded to determine the conversion of the starting material and the product distribution.

Starting from **1a** (24 mg) and following the general procedure C, ^{1}H NMR of the crude mixture showed 74% of conversion into **3a** (b/l: 91/9, *E*/*Z*: >20/1).

Starting from (*E*)-**1b** (24 mg) and following the general procedure C, ^{1}H NMR of the crude mixture showed 53% of conversion into (*E*)-**3b** (l/b: >20/1, *E*/*Z*: >20/1).

Starting from (*Z*)-**1b** (24 mg) and following the general procedure C, ^{1}H NMR of the crude mixture showed 37% of conversion into (*Z*)-**3b** (l/b: >20/1, *Z*/*E*: >20/1).

Procedure for the dimethyl malonate substitution with Bu$_4$NCl as additive

To a solution of allylic carbonate (*E*)-**1b** (0.1 mmol) in THF (0.5 mL) was added a solution of sodium dimethyl malonate (0.2 mmol) in THF (0.5 mL), prepared from dimethyl malonate (0.2 mmol) and NaH (0.2 mmol). Bu$_4$NCl (0.2 mmol) was then added, followed by the addition of [Ir(COD)Cl]$_2$ (2 mol%) in one portion. The reaction was allowed to stir at 40 °C for 24 h. The solvent was removed *in vacuo*. ^{1}H NMR of the crude mixture was recorded and showed 25 % of conversion into (*E*)-**3b** (l/b: 16/, *E*/*Z*: >20/1).

General procedure (D) for the dimethyl malonate substitution of allyl fluoride (Scheme 1 and 3)

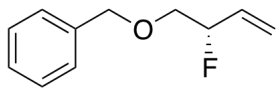
To a solution of allylic fluoride (0.1 mmol) in THF (0.5 mL) was added [Ir(COD)Cl]$_2$ (2 mol%). A solution of sodium dimethyl malonate (0.2 mmol) in THF (0.5 mL), prepared from dimethyl malonate (0.2 mmol) and NaH (0.2 mmol) was then added in one portion. The reaction was allowed to stir at 40 °C for 24 h. The solvent was removed *in vacuo*. ^{1}H NMR and ^{19}F NMR of the crude mixtures were recorded to determine the conversion of the starting material and the product distribution.

Starting from **2a** (18 mg) and following the general procedure D, ^{1}H NMR of the crude mixture showed 56% of conversion into **3a** (b/l: 79/21, *E*/*Z*: >20/1).

Starting from (*E*)-**2b** (18 mg) and following the general procedure D, ^{1}H NMR of the crude mixture showed 46% of conversion into (*E*)-**3b** (l/b: 87/13, *E*/*Z*: >20/1).

Starting from (*Z*)-**2b** (18 mg) and following the general procedure D, ^{1}H NMR of the crude mixture showed 69% of conversion into (*Z*)-**3b** (l/b: >20/1, *Z*/*E*: >20/1).

Benzyl (2*S*)-2-fluorobut-3-en-2-yl ether, (*S*)-2a



Following the general procedure A, the reaction was carried out on 48 mg of (*S*)-**1a** and 2 mol% of [Ir(COD)Cl]$_2$ for 2 h. Silica gel column chromatography (hexane) yielded (*S*)-**2a** (17

mg, 46%, *ee* 37%) and (*S*)-**4a** (15 mg, 43%, *ee* 20%). When the reaction was carried out at room temperature for 24 h, silica gel column chromatography (hexane) yielded (*S*)-**1a** (16 mg, 33%, *ee* 93%), (*S*)-**2a** (12 mg, 34%, *ee* 48%) and (*S*)-**4a** (7 mg, 20%, *ee* 65%). Chiral HPLC for (*S*)-**2a**: (IA, Hexane/ *i*-PrOH= 99.5/0.5, 1.3 mL/ min, 210 nm) t_R (major-isomer)= 6.9 min, t_R (minor- isomer)= 8.1 min. The absolute configuration of (*S*)-**2a** was determined by synthesizing the title compound following a literature procedure. Chiral HPLC traces were identical to those obtained from our iridium protocol. Data are in agreement with literature.[25]

Procedure for testing racemization of (*S*)-1b

To a solution of (*S*)-**1a** (0.1 mmol, *ee* 95%) in DCM (5 mL) was added $[Ir(COD)Cl]_2$ (2 mol%). The reaction was allowed to stir at 40 °C for 2 h. The solvent was removed *in vacuo*. ^{1}H NMR of the crude mixture was recorded and showed 77% of (*S*)-**1a** (*ee* 87%) and 22% of diene **5a**.

Procedure for testing racemization of (*S*)-2b

To a solution of (*S*)-**2a** (0.1 mmol, *ee* 37%) in DCM (5 mL) was added $[Ir(COD)Cl]_2$ (2 mol%) and TBAF(*t*BuOH)$_4$ (0.2 mmol). The reaction was allowed to stir at 40 °C for 2 h. The solvent was removed *in vacuo*. ^{1}H NMR of the crude mixture was recorded and showed 100% of (*S*)-**1a** (*ee* 35%).

3. [18F]-Labeling Experiments:

3.1 Radiochemistry

[^{18}F]Fluoride was produced by PETNET Solutions at Mount Vernon Hospital (UK) via the ^{18}O(p,n)18F reaction and delivered as [^{18}F]fluoride in [^{18}O]water. Radiosynthesis and azeotropic drying was performed on a NanoTek® automated microfluidic device (Advion). [^{18}F]Fluoride was separated from ^{18}O-enriched water using an anion exchange cartridges (MP1, ORTG, Tennessee) and eluted with either a solution of tetraethylammonium bicarbonate (7 mg) in acetonitrile/water (9:1, 0.5 mL) or a solution of K_2CO_3 (3 mg)/K_{222} (15 mg) in acetonitrile/water (4:1, 0.5mL). The complex was dried with six cycles of azeotropic evaporation. The resultant [^{18}F]tetraethylammonium fluoride or [^{18}F]KF/K_{222} was dissolved in anhydrous acetonitrile for use in radiofluorination reactions. HPLC analysis was performed with a Dionex Ultimate 3000 system equipped with a LabLogic Flow-RAM NaI/PMT detector. Radio-TLC was performed on Merck Kiesegel 60 F254 plates. Analysis was performed using a plastic scintillator/PMT detector. TLC yields are calculated based on conversion of [^{18}F]fluoride to product.

3.2 General Radiochemical Procedure

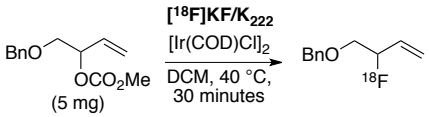
To a glass V-vial containing a magnetic stirrer bar was added [^{18}F]Et_4NF (~ 30 MBq in 30 µL MeCN). To this vial was added a mixture of substrate (5 mg in 440 µL of DCM) with $[Ir(COD)Cl]_2$ (60 µL of a 1 mg/mL solution in DCM). The reaction mixture was then heated at 40 °C for 30 minutes. Upon cooling an aliquot was of the crude reaction mixture was taken and analysed by radio-TLC and radio-HPLC (equipped with Nova-Pak C18 column).
HPLC gradient (1 ml/min): 0-2 min 5 % MeCN 95 % H_2O isocratic
2-2.5 min 5 % MeCN to 40 % MeCN linear gradient
2.5-14 min 40 % MeCN to 95 % MeCN linear gradient

14-15 min 95 % MeCN to 5 % MeCN linear gradient
15-16 min 5 % MeCN 95 % H_2O isocratic.

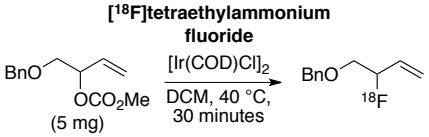
The radiofluorination of (*Z*)-**1b** was found to be rather capricious, giving variable yields. The specific activity was not measured for any of the products due to co-elution of the starting carbonate with the desired [^{18}F]products.

3.3 Radiochemical optimisation

All optimisation reactions were performed following the general procedure. For each reaction the total volume was made up to be 500 μL.

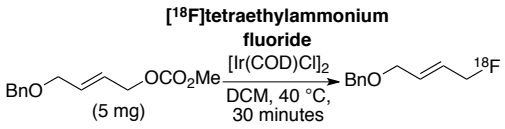


Ir loading (1mg/ml in DCM)	RCY (TLC)
500 μL	7 %
250 μL	8 %
125 μL	23 %
60 μL	44 %
10 μL	14 %
0	0 %

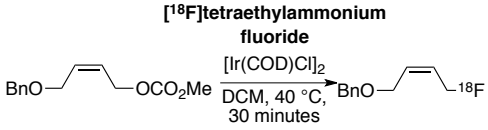


Ir loading (1mg/ml in DCM)	RCY (TLC)
500 μL	4 %
250 μL	21 %
125 μL	61 %
60 μL	68 %
0	0 %
60 μL	44 %[a]

a) reaction time of 15 minutes

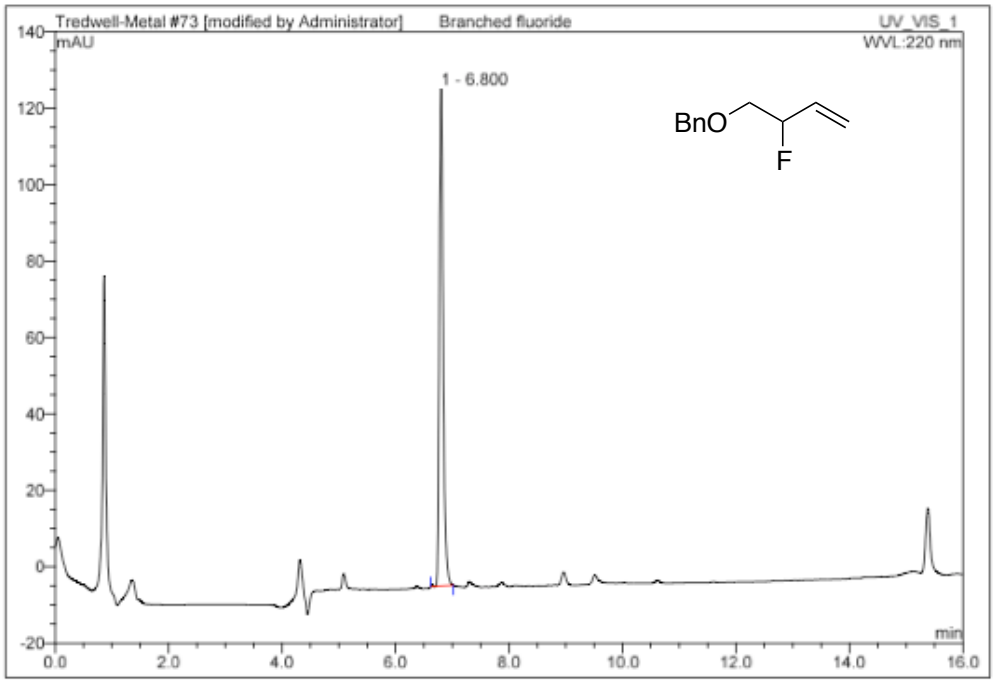


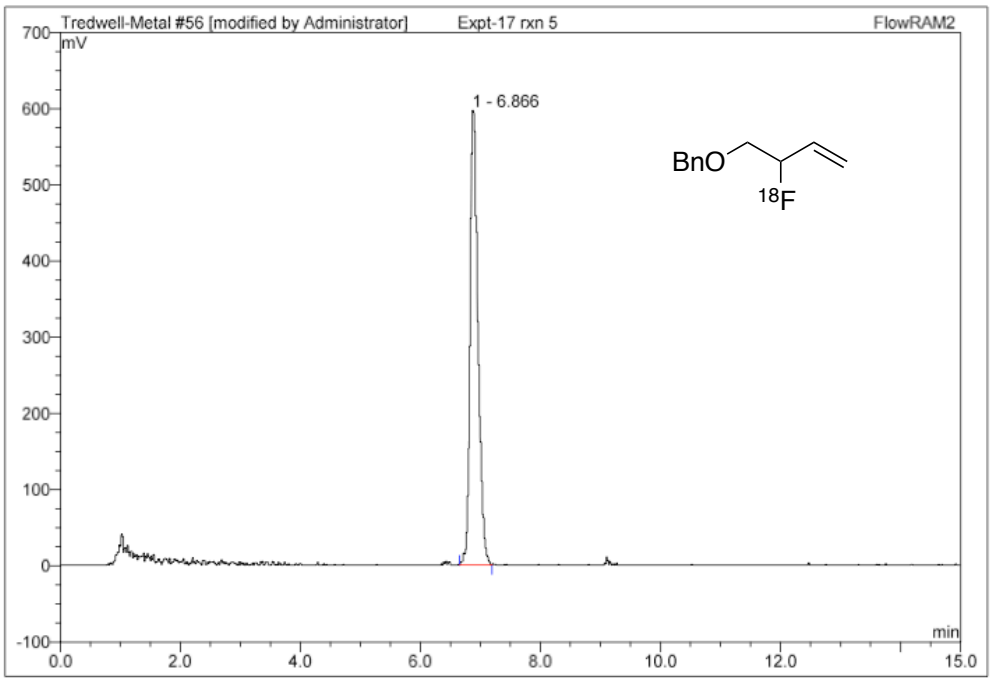
Ir loading (1mg/ml in DCM)	RCY (TLC)
60 μL	30 %
60 μL	74 %
60 μL	65 %
125 μL	40 %
125 μL	62 %
125 μL	62 %

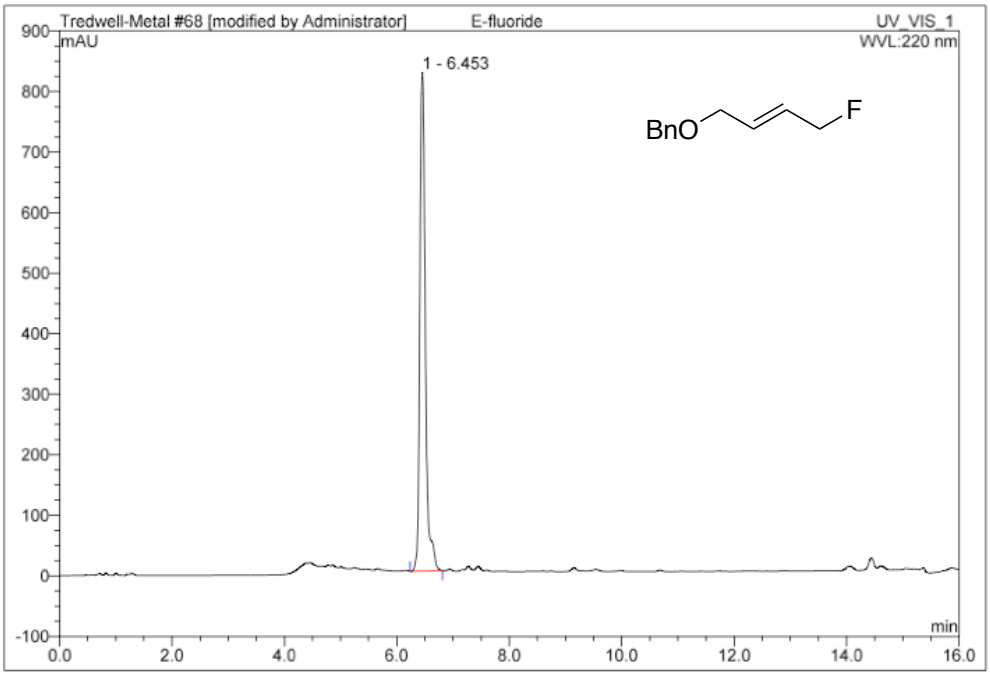


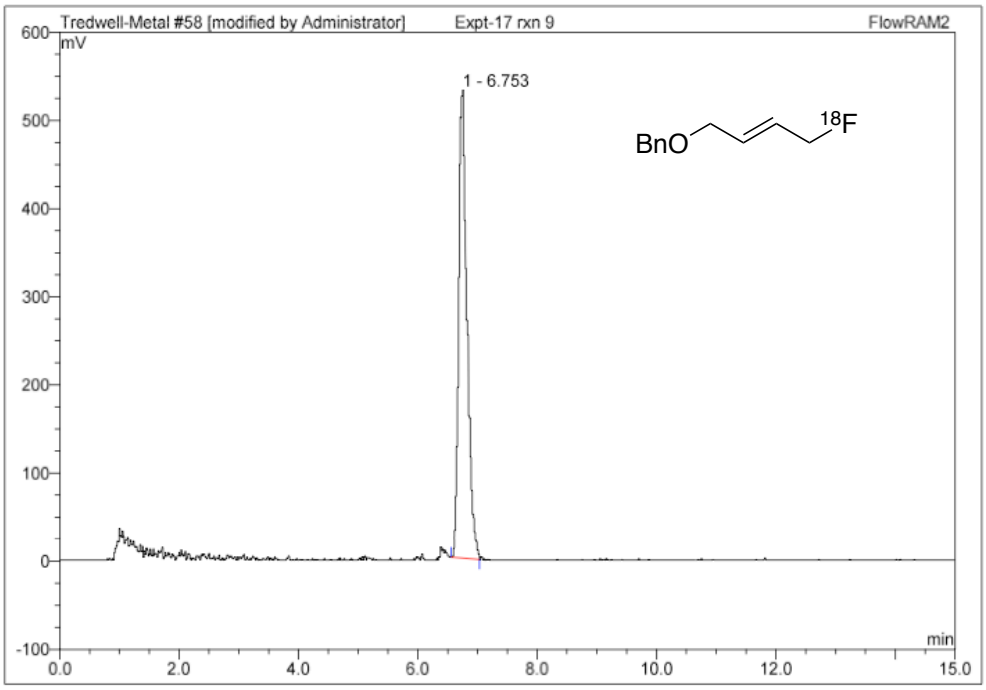
Ir loading (1mg/ml in DCM)	RCY (TLC)
60 μL	0 %
60 μL	14 %
60 μL	7 %
125 μL	11 %
125 μL	37 %
125 μL	8 %

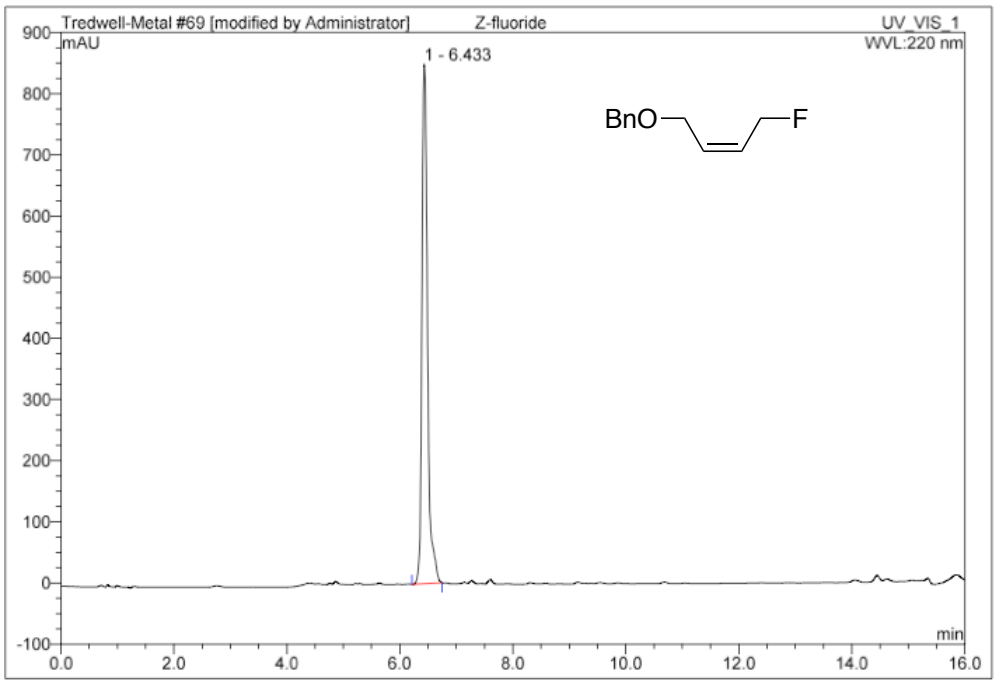
3.4 Radio-HPLC Traces

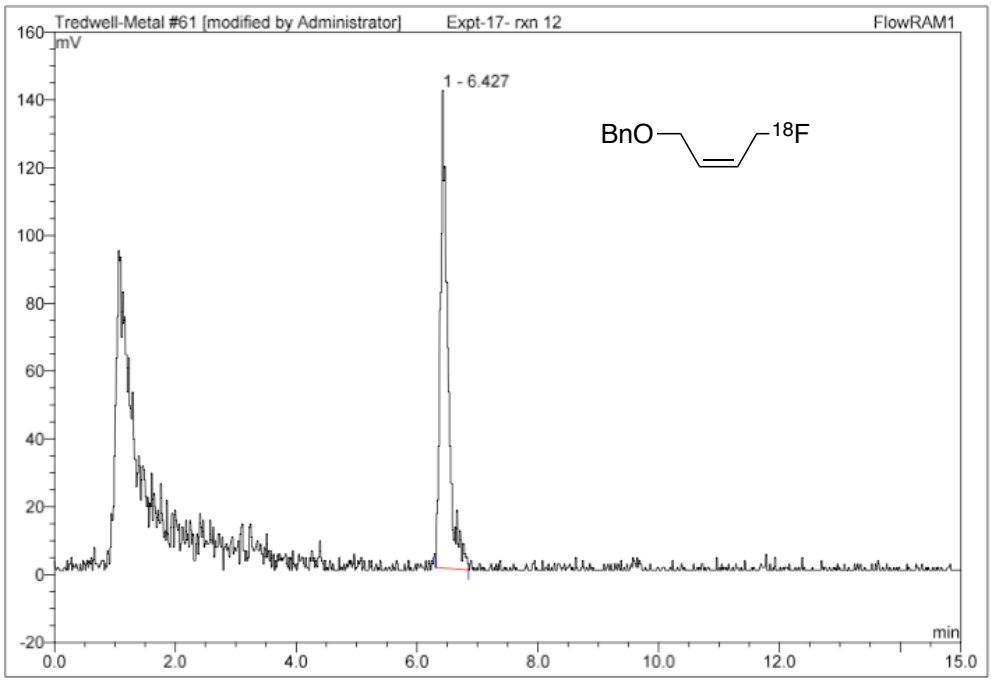





Tredwell-Metal #68 [modified by Administrator]
E-fluoride
UV_VIS_1
WVL:220 nm
mAU
1 - 6.453
BnO
F
min

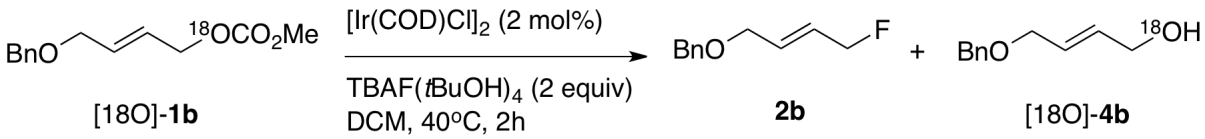

Tredwell-Metal #58 [modified by Administrator]
Expt-17 rxn 9
FlowRAM2
mV
1 - 6.753
BnO
18F
min


Tredwell-Metal #69 [modified by Administrator]
Z-fluoride
UV_VIS_1
WVL:220 nm
mAU
1 - 6.433
BnO
F
min

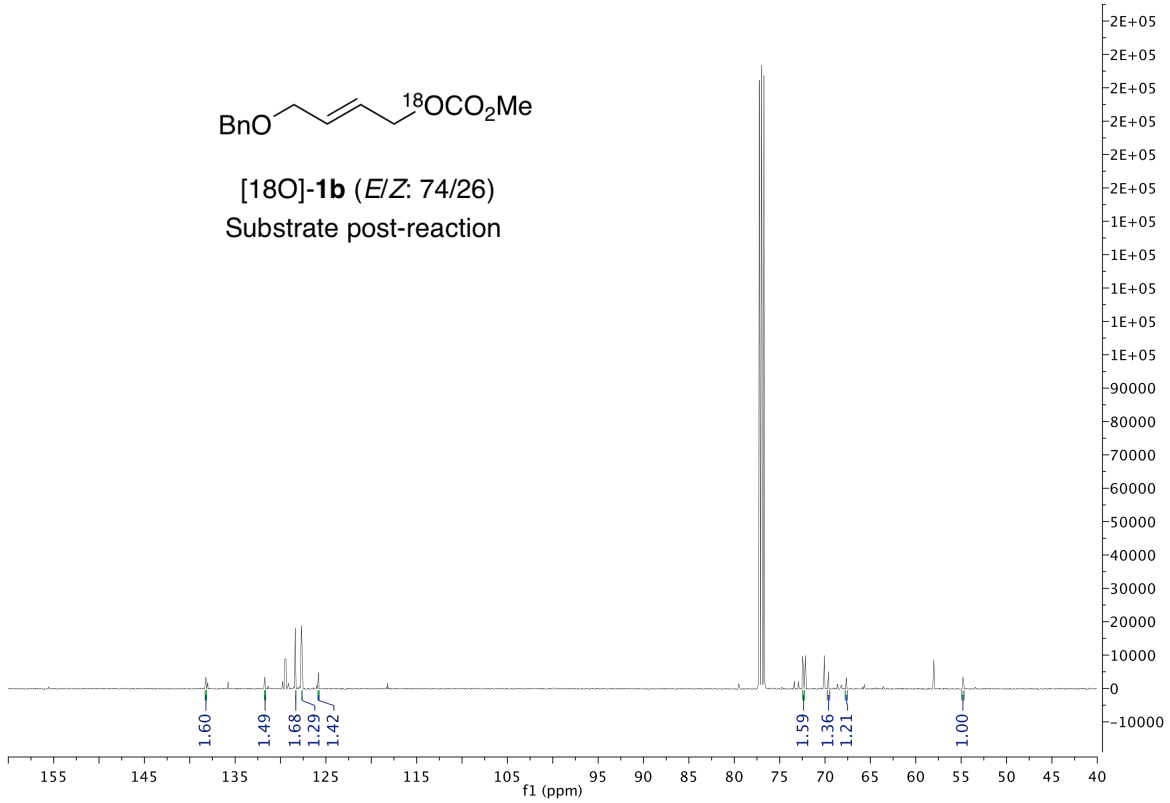

Tredwell-Metal #61 [modified by Administrator]
Expt-17- rxn 12
FlowRAM1
mV
1 - 6.427
BnO
18F
min

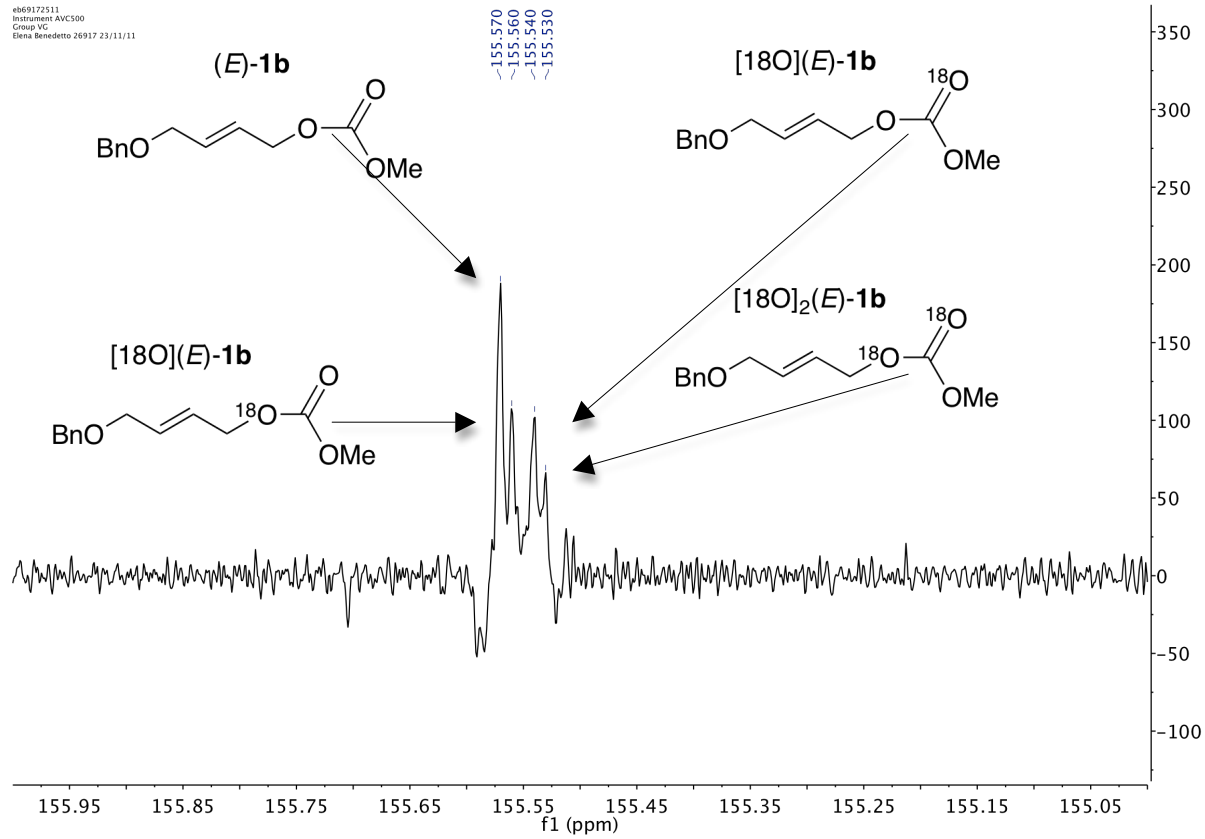
4. [18O]-Labeling Experiments:

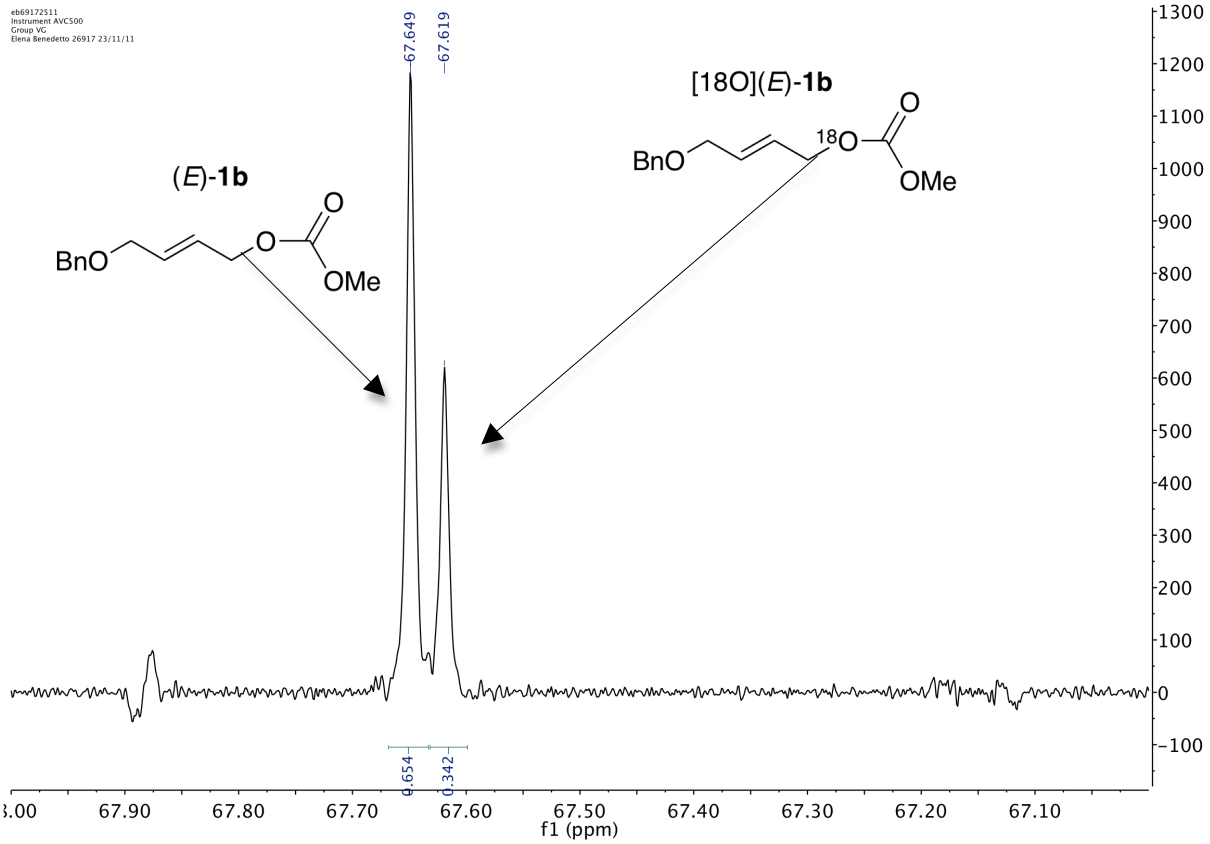
4.1 Procedure for fluorination of [18O]-1b:

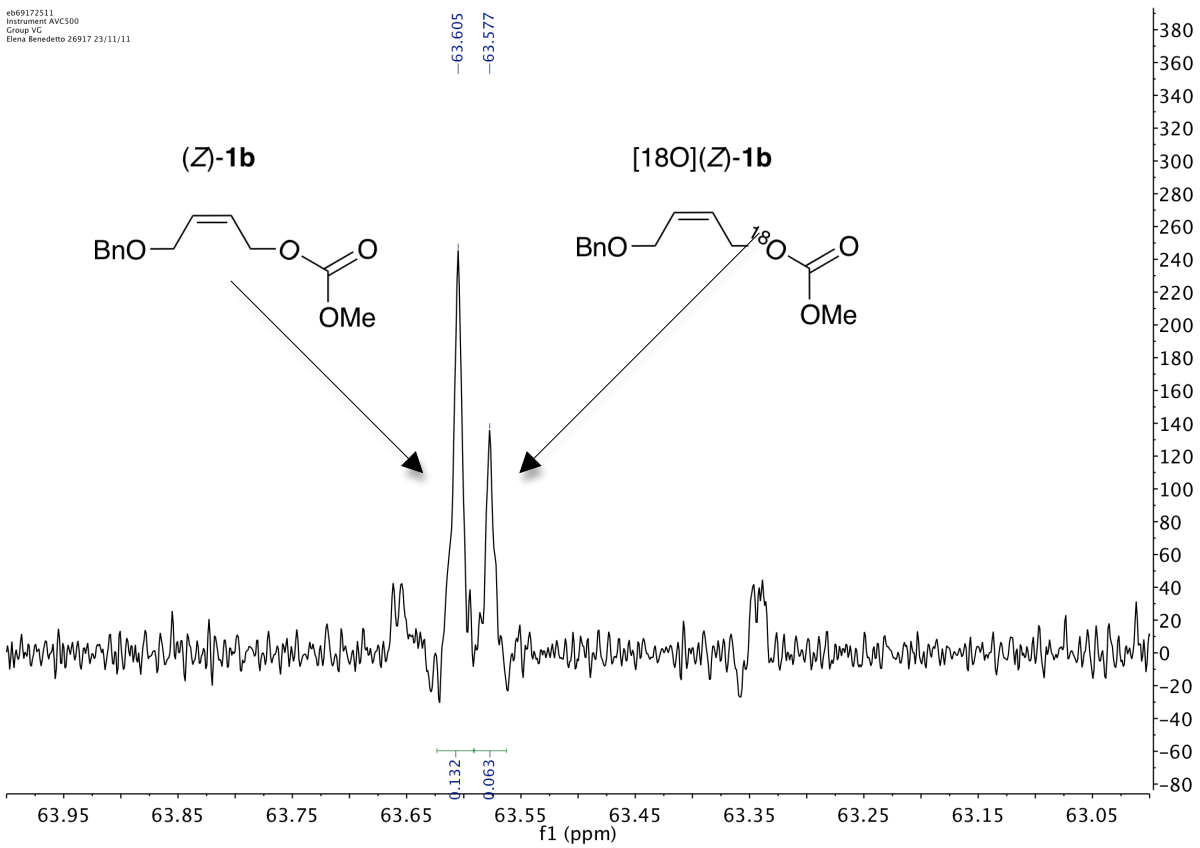


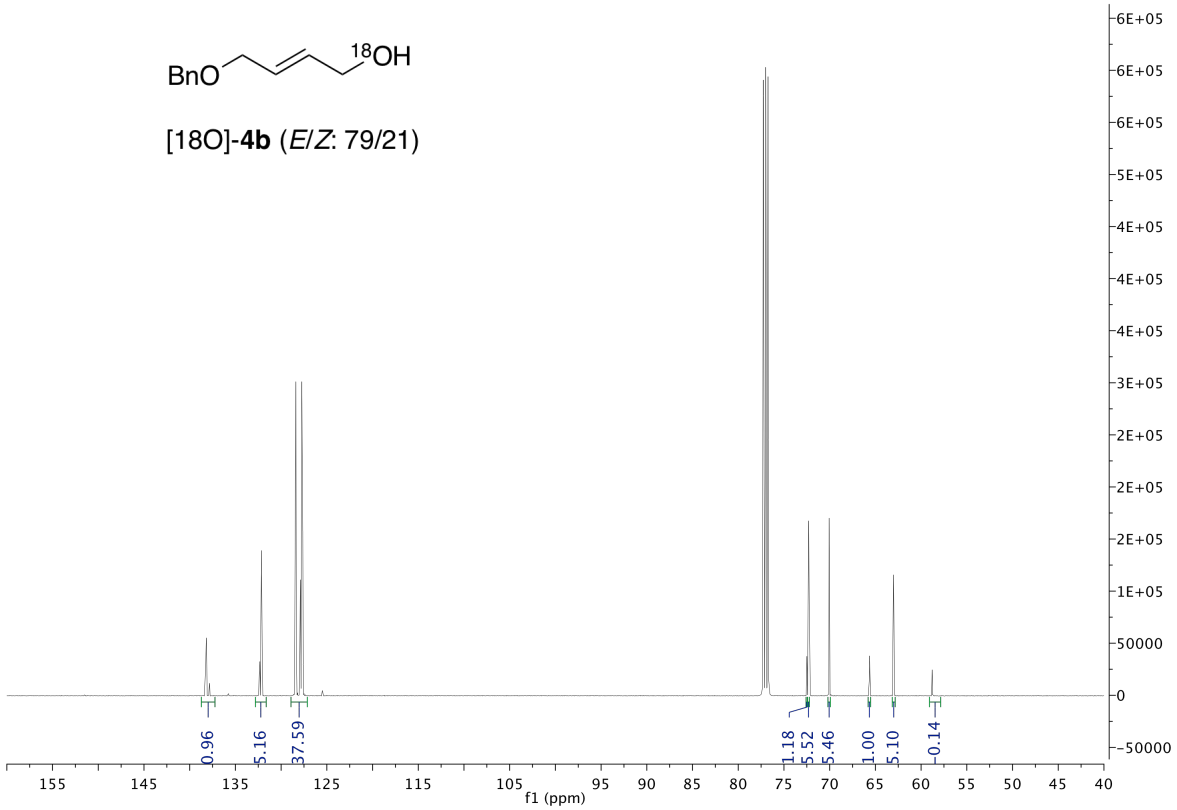
To a solution of [18O]-**1b** (48 mg, 0.2 mmol, *E/Z*: 81/19, 98% ^{18}O incorporation) and TBAF(*t*-BuOH)$_4$ (2 eq, 0.4 mmol) in dry DCM (2 mL) was added [Ir(COD)Cl]$_2$ (2.7 mg, 0.004 mmol). The reaction was allowed to stir at 40 °C for 2 h and the solvent was removed *in vacuo*. The crude reaction mixture was purified by silica gel column chromatography (hexane) to yield **2b** (8 mg, 22%), [18O]-**4b** (10 mg, 28%, *E/Z*: 79/21, 33% ^{18}O incorporation calculated from ^{13}C NMR) and recovered [18O]-**1b** (9 mg, 18%, *E/Z*: 74/26, 34% ^{18}O incorporation calculated from ^{13}C NMR).

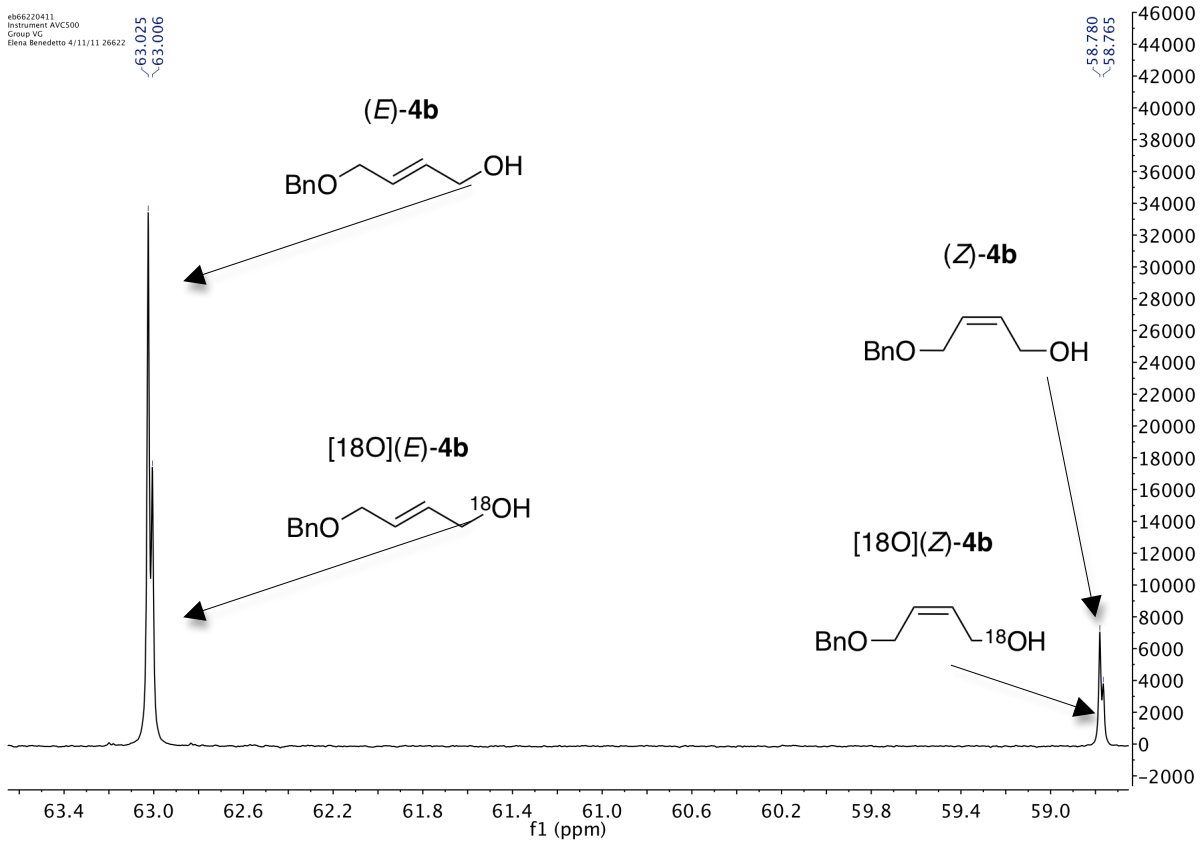



eb69172511
Instrument AVC500
Group VG
Elena Benedetto 26917 23/11/11
(E)-1b
[18O](E)-1b
[18O]2(E)-1b
[18O](E)-1b
155.570
155.560
155.540
155.530
155.95
155.85
155.75
155.65
155.55
155.45
155.35
155.25
155.15
155.05
f1 (ppm)

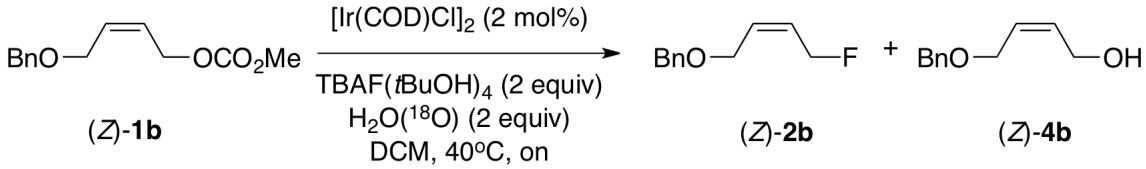

eb69172511
Instrument AVC500
Group VG
Elena Benedetto 26917 23/11/11
67.649
67.619
(E)-1b
[18O](E)-1b
0.654
0.342
67.90
67.80
67.70
67.60
67.50
67.40
67.30
67.20
67.10
f1 (ppm)


eb69172511
Instrument AVC500
Group VG
Elena Benedetto 26917 23/11/11
63.605
63.577
(Z)-1b
[18O](Z)-1b
BnO
O
O
OMe
18O
0.132
0.063
f1 (ppm)

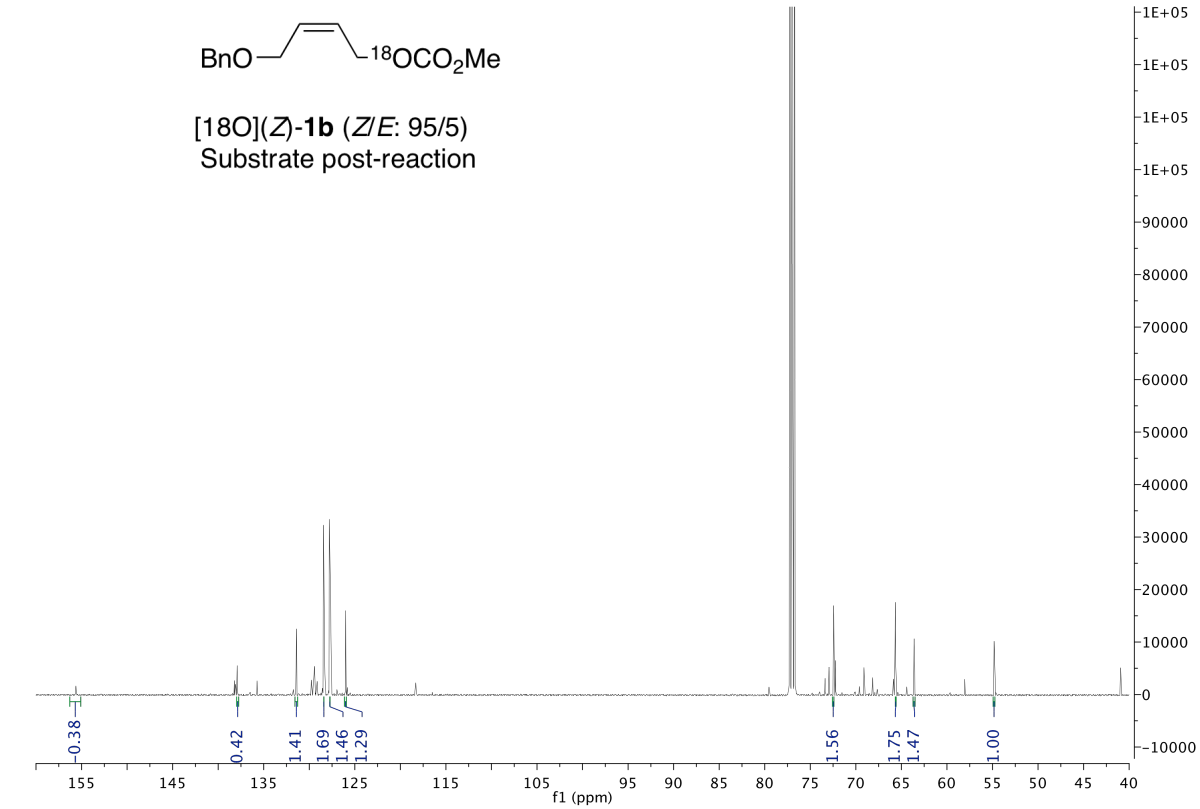

BnO
18OH
[18O]-4b (E/Z: 79/21)
0.96
5.16
37.59
1.18
5.52
5.46
1.00
5.10
0.14
f1 (ppm)

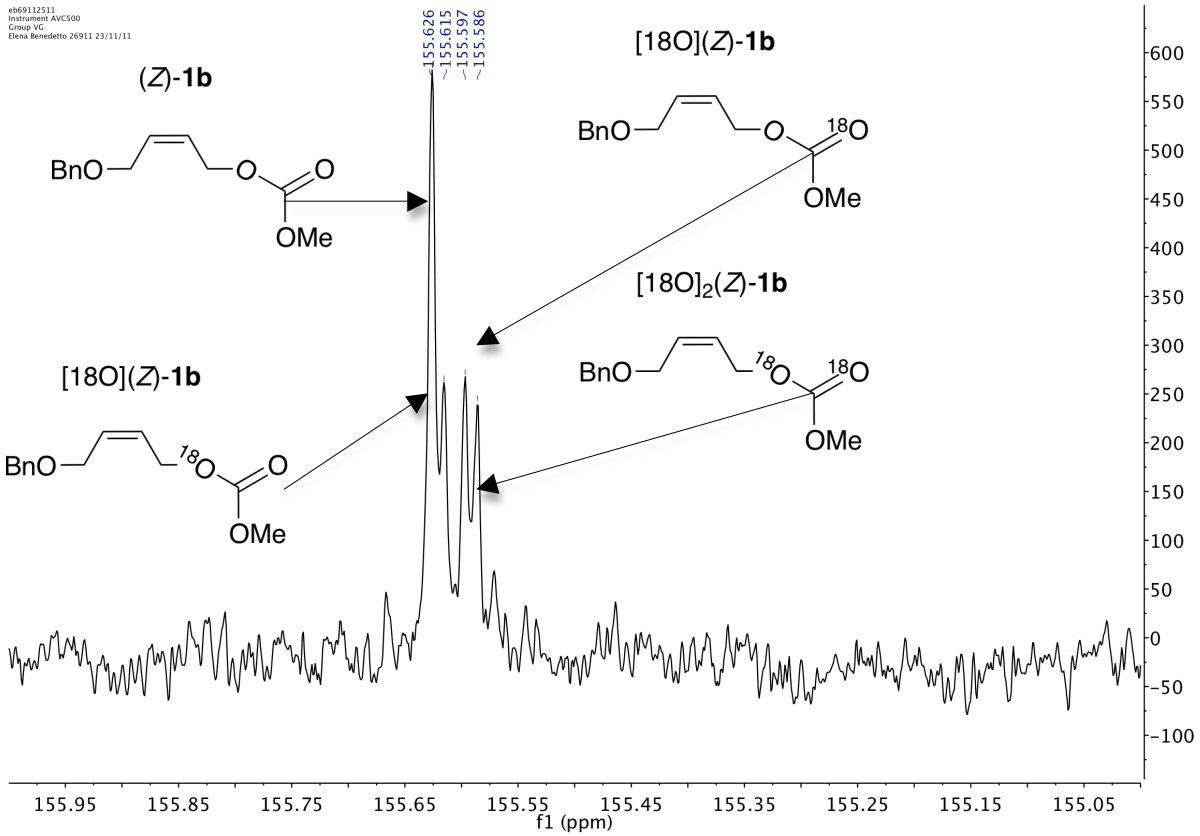


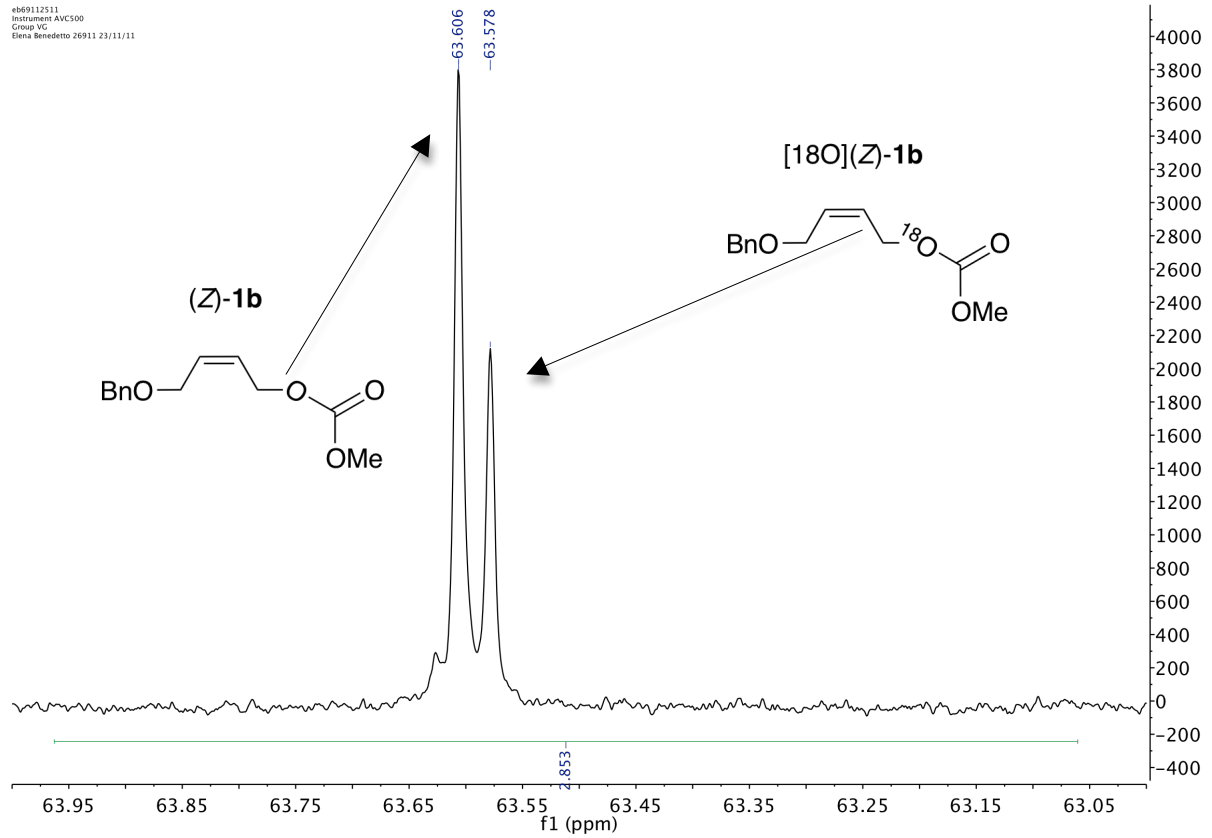
4.2 Procedure for fluorination of (Z)-1b in the presence of [18O]-H_2O:

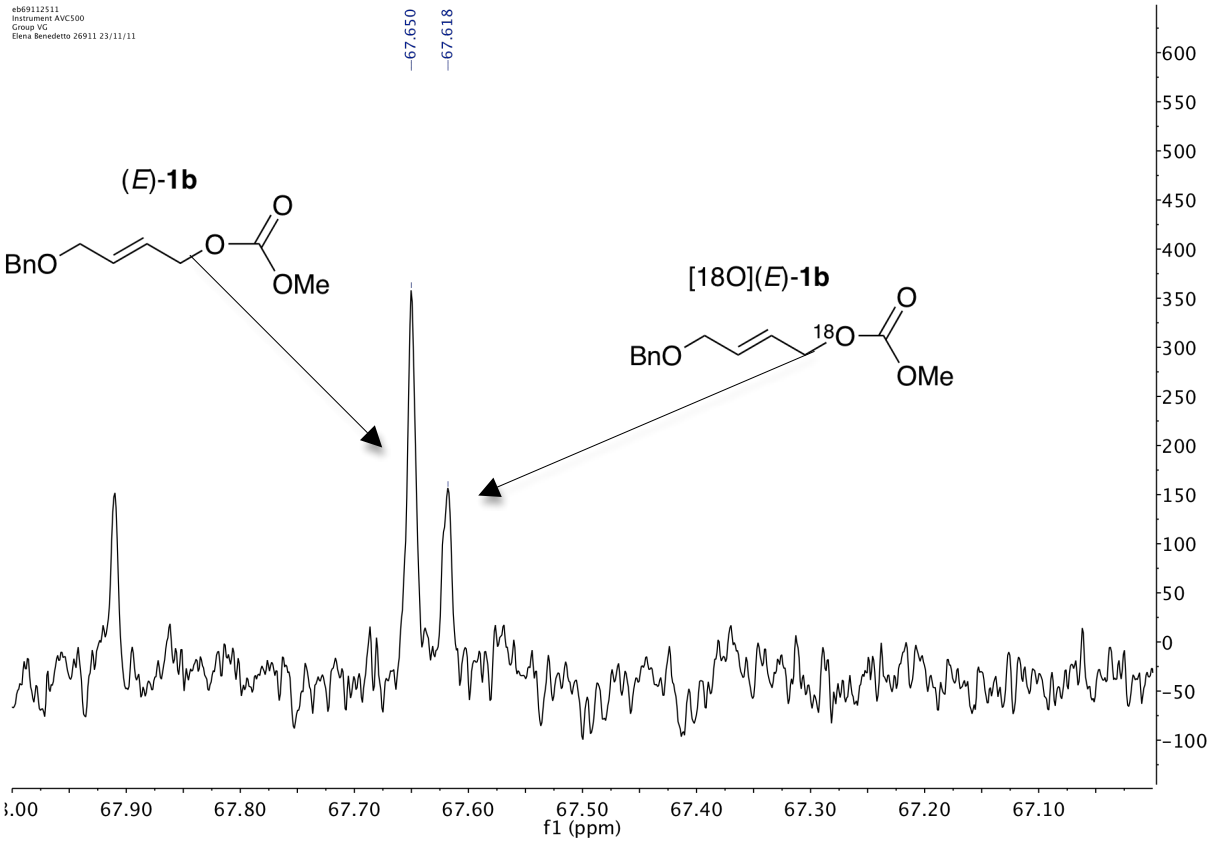


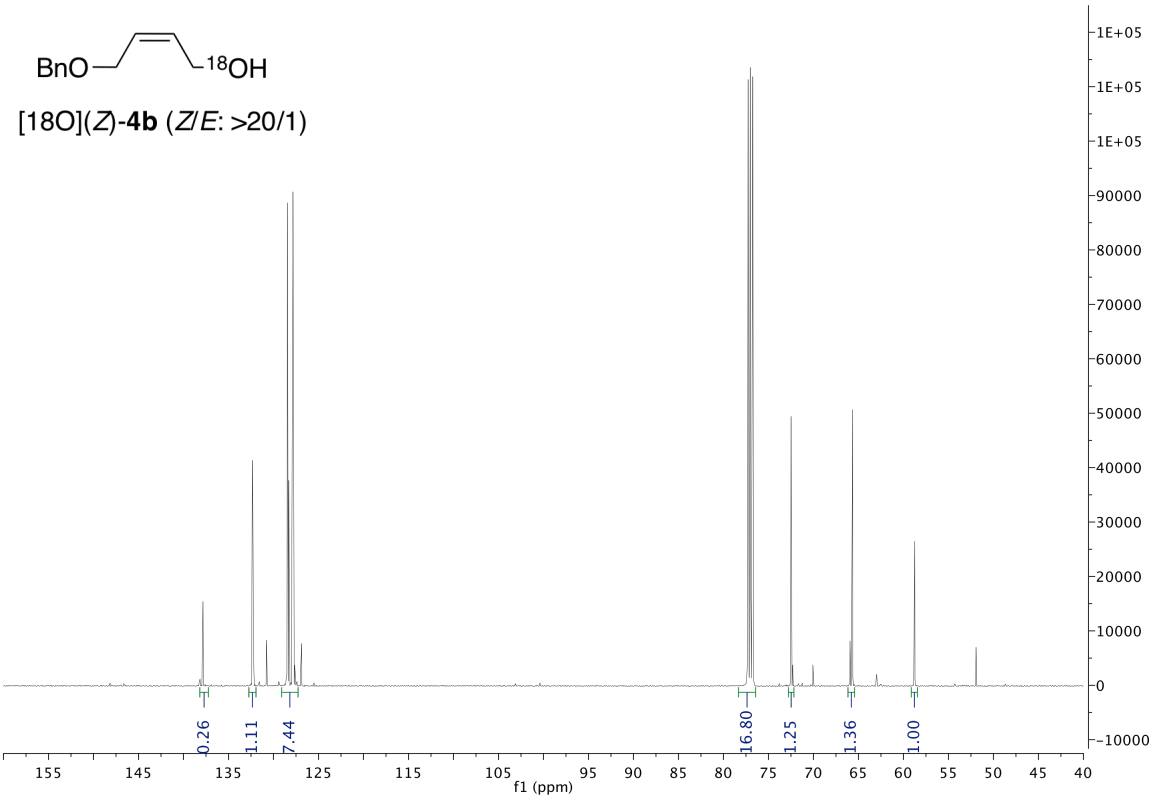
To a solution of (*Z*)-**1b** (47 mg, 0.2 mmol, *Z*/*E*: >20/1, 0% ^{18}O incorporation) and TBAF(*t*BuOH)$_4$ (2 eq, 0.4 mmol) in dry DCM (2 mL) was added [18O]-H_2O (8 μL, 0.4 mmol) and [Ir(COD)Cl]$_2$ (2.7 mg, 0.004 mmol). The reaction was allowed to stir at 40 °C overnight and the solvent was removed *in vacuo*. The crude reaction mixture was purified by silica gel column chromatography (hexane) to yield (*Z*)-**2b** (7 mg, 21%), (*Z*)-**4b** (15 mg, 41%, *Z*/*E*: >20/1, 53% ^{18}O incorporation calculated from ^{13}C NMR) and recovered (*Z*)-**1b** (7 mg, 15%, *Z*/*E*: 95/5, 35% ^{18}O incorporation calculated from ^{13}C NMR).

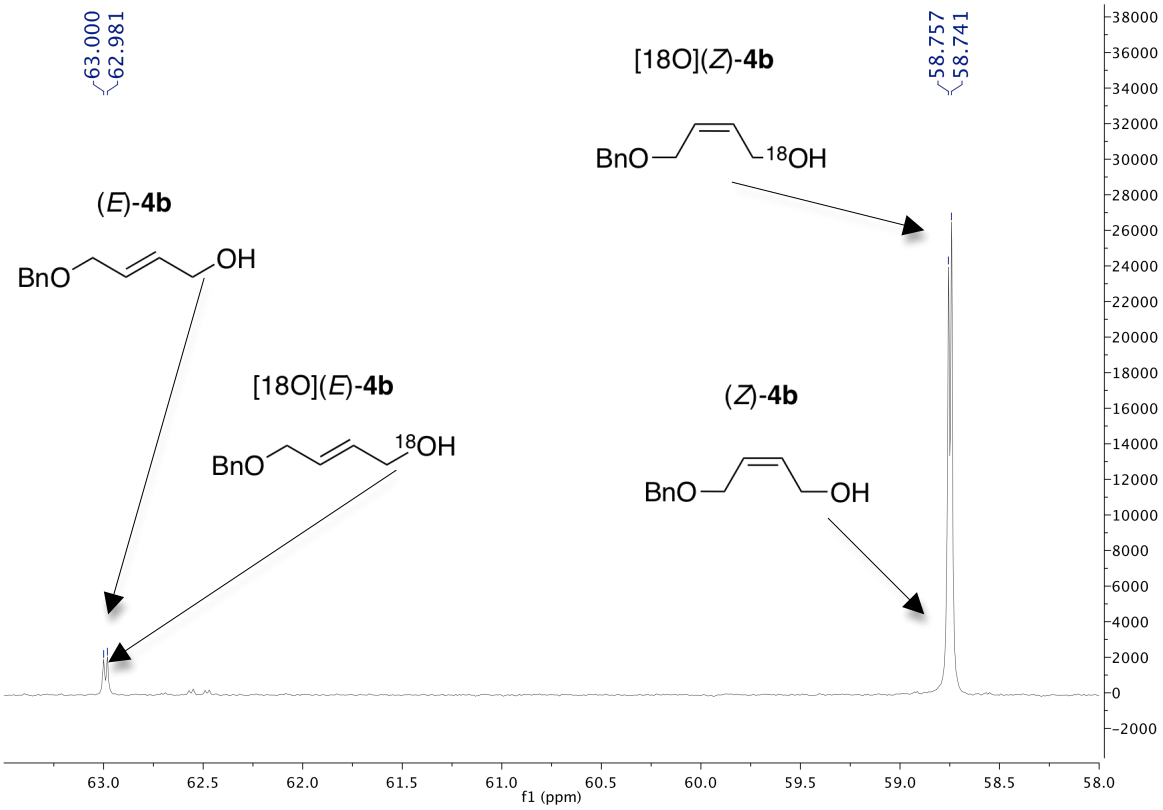

BnO
18OCO2Me
[18O](Z)-1b (Z/E: 95/5)
Substrate post-reaction
0.38
0.42
1.41
1.69
1.46
1.29
1.56
1.75
1.47
1.00
f1 (ppm)


155.626
155.615
155.597
155.586
(Z)-1b
[18O](Z)-1b
[18O]2(Z)-1b
[18O](Z)-1b
BnO
OMe
f1 (ppm)

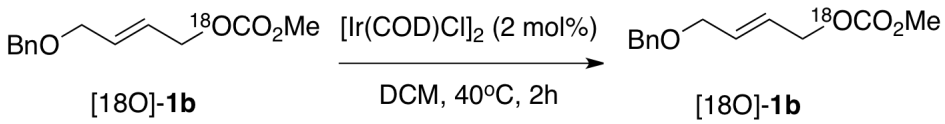

eb69112511
Instrument AVC500
Group VG
Elena Benedetto 26911 23/11/11
63.606
63.578
2.853
(Z)-1b
BnO
O
O
OMe
[18O](Z)-1b
BnO
18O
O
OMe
f1 (ppm)


eb69112511
Instrument AVC500
Group VG
Elena Benedetto 26911 23/11/11
67.650
67.618
(E)-1b
BnO
O
O
OMe
[18O](E)-1b
BnO
18O
O
OMe
f1 (ppm)



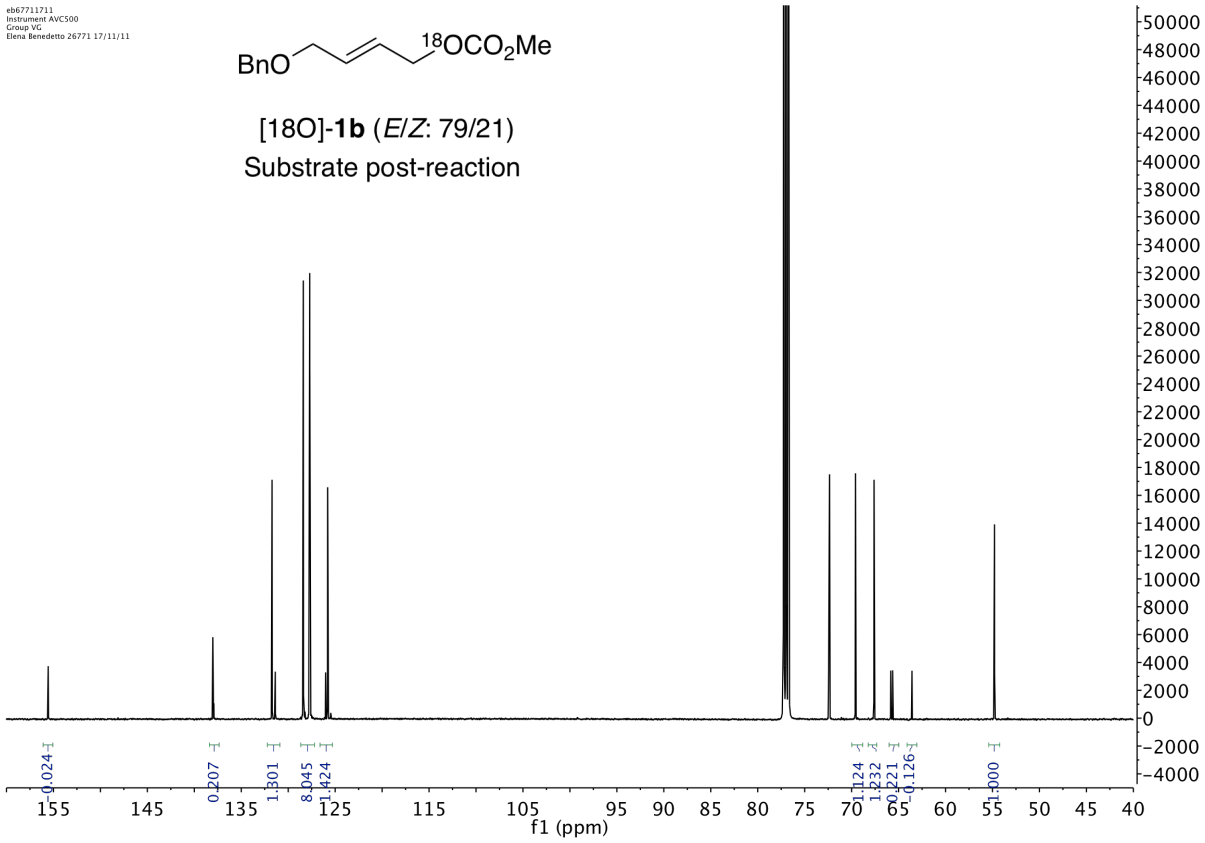


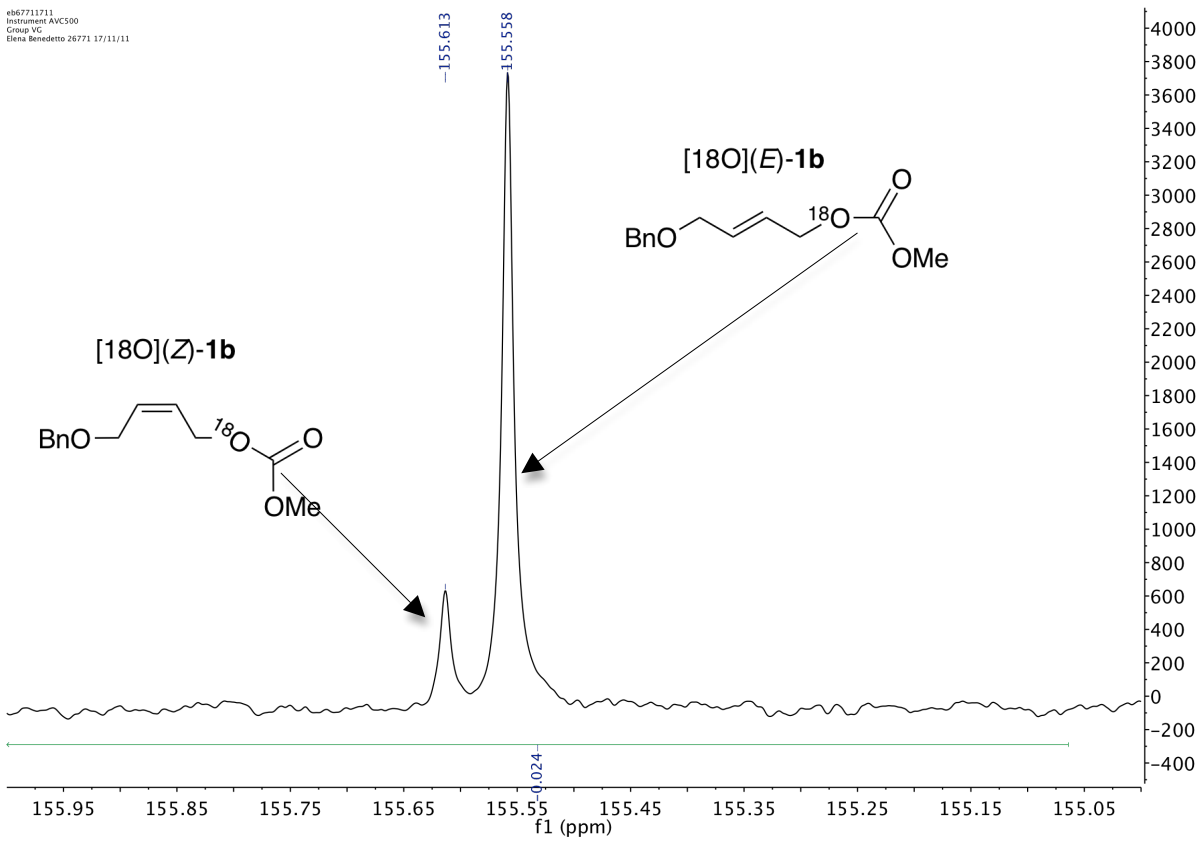
4.3 Procedure for scrambling test:

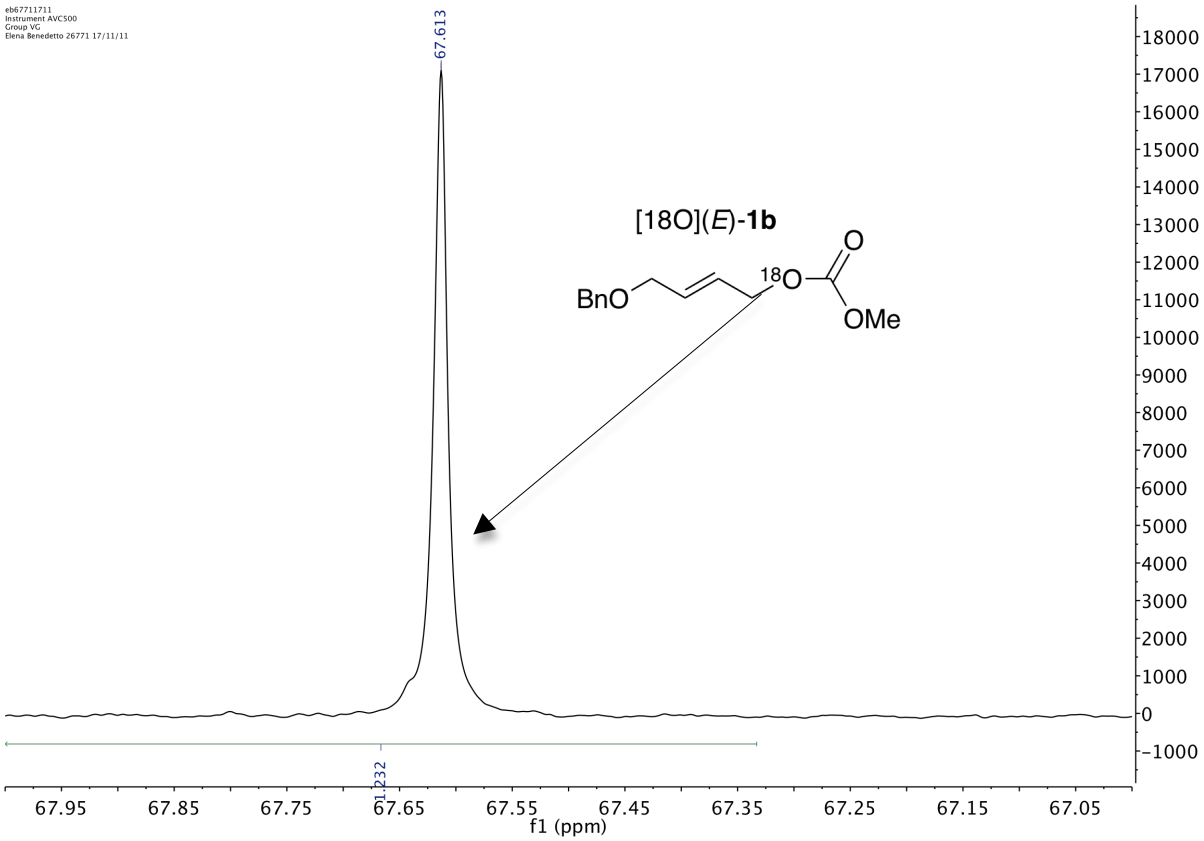


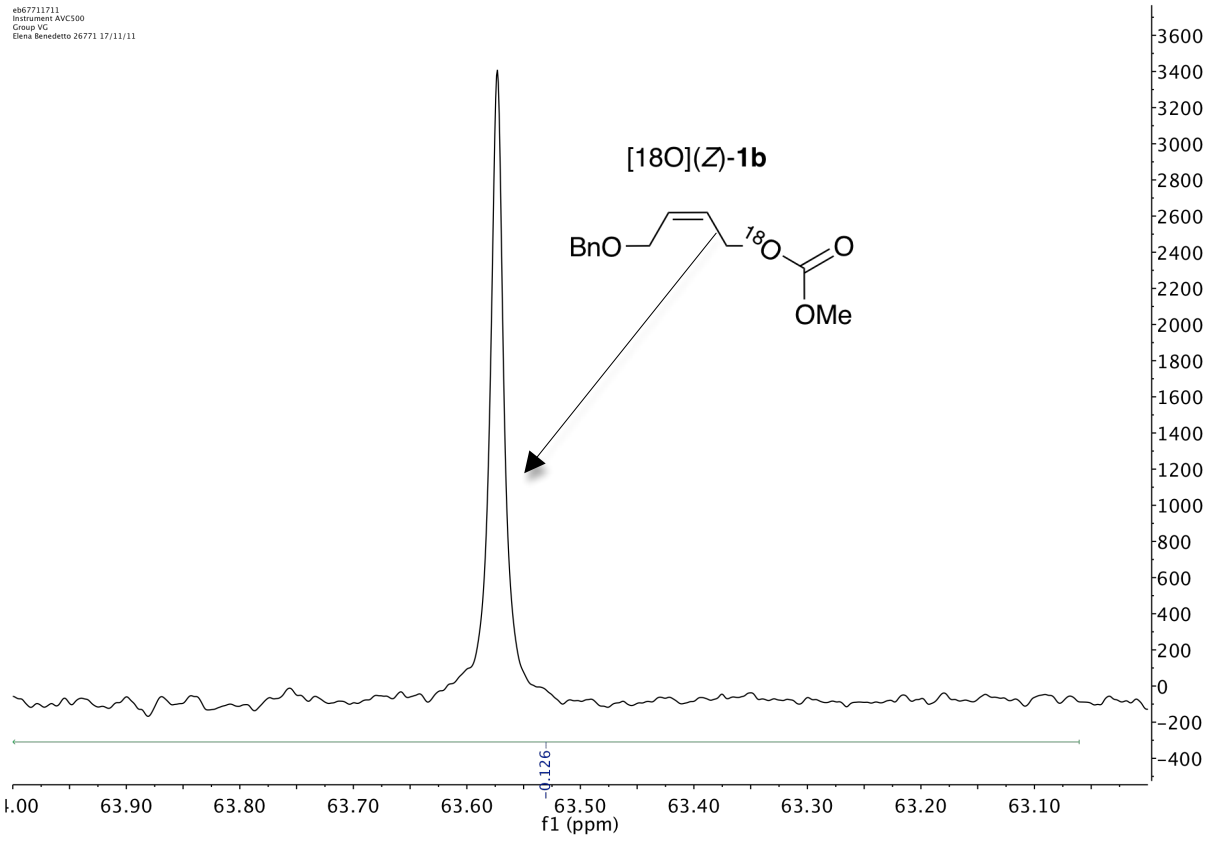
[18O]-**1b** [18O]-**1b**

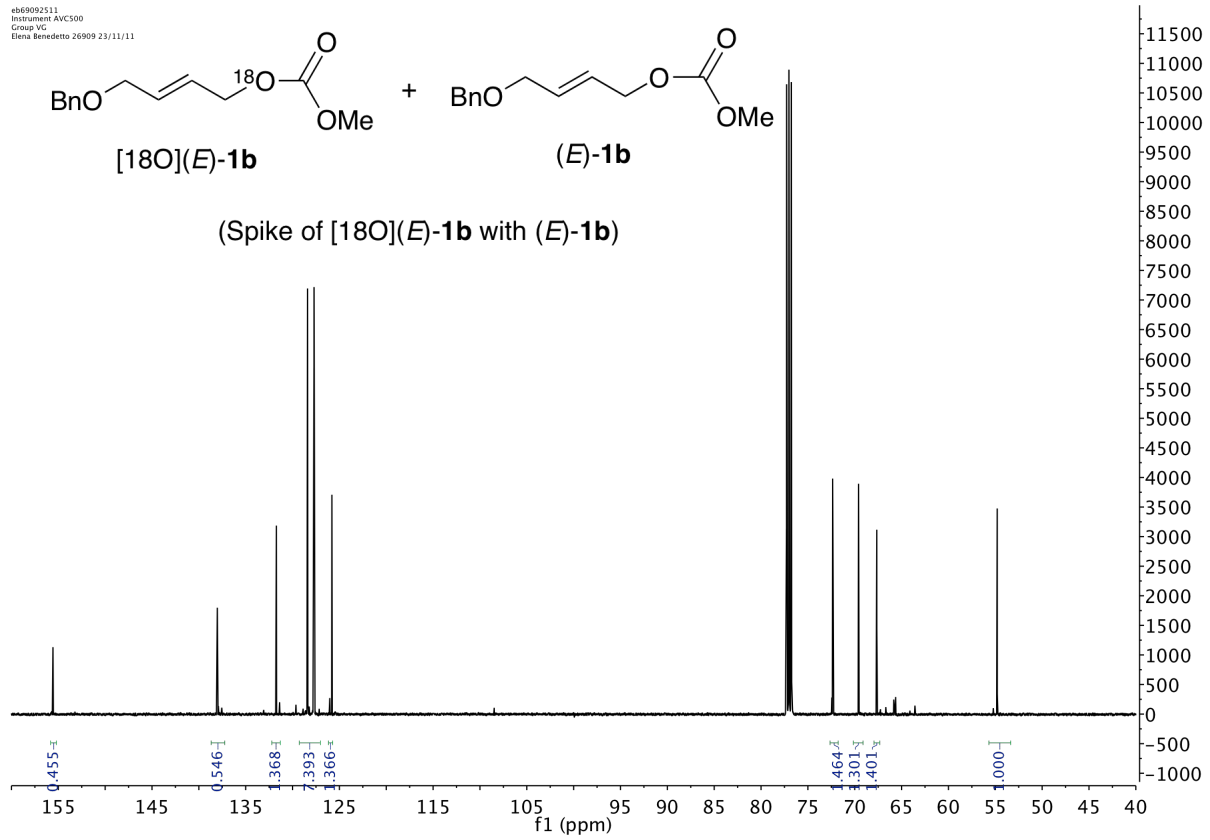
To a solution of [18O]-**1b** (12 mg, 0.05 mmol, *E/Z*: 81/19, $^{18}O/^{16}O$: 98/2) in dry DCM (0.5 mL) was added $[Ir(COD)Cl]_2$ (0.7 mg, 0.001 mmol). The reaction was allowed to stir at 40 °C for 2 h. The crude reaction mixture was filtered and solvent was removed *in vacuo*. A ^{1}H NMR and a quantitative ^{13}C NMR of the crude mixture was recorded. 100% of recovered [18O]-**1b** (*E/Z*: 79/21, 98% ^{18}O incorporation calculated from ^{13}C NMR) was detected.

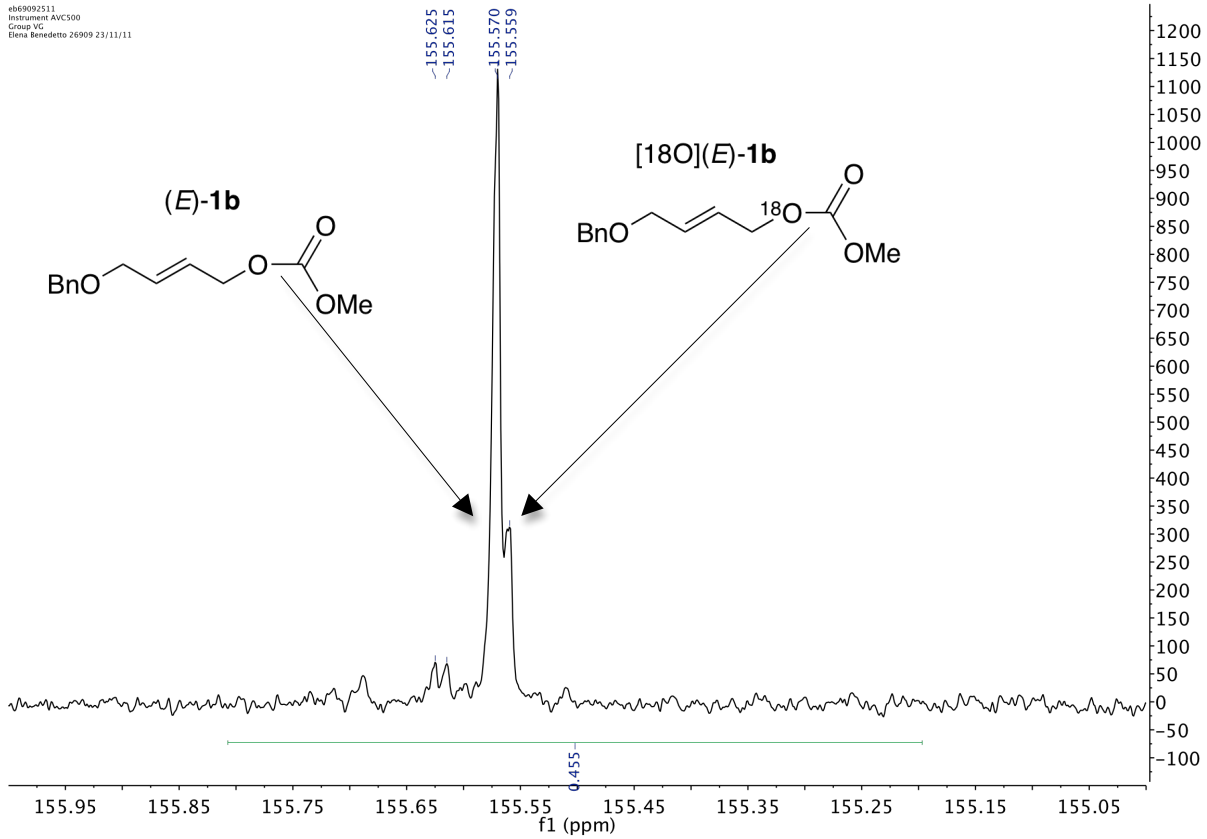



eb67711711
Instrument AVC500
Group VG
Elena Benedetto 26771 17/11/11
155.613
155.558
[18O](E)-1b
BnO
18O
O
OMe
[18O](Z)-1b
BnO
18O
O
OMe
0.024
155.95
155.85
155.75
155.65
155.55
155.45
155.35
155.25
155.15
155.05
f1 (ppm)


eb67711711
Instrument AVC500
Group VG
Elena Benedetto 26771 17/11/11
67.613
[18O](E)-1b
BnO
18O
O
OMe
1.232
67.95
67.85
67.75
67.65
67.55
67.45
67.35
67.25
67.15
67.05
f1 (ppm)


eb67711711
Instrument AVC500
Group VG
Elena Benedetto 26771 17/11/11
[18O](Z)-1b
BnO
18O
O
OMe
0.126
63.90
63.80
63.70
63.60
63.50
63.40
63.30
63.20
63.10
f1 (ppm)


eb69092511
Instrument AVC500
Group VG
Elena Benedetto 26909 23/11/11
BnO
18O
O
OMe
[18O](E)-1b
+
BnO
O
O
OMe
(E)-1b
(Spike of [18O](E)-1b with (E)-1b)
0.455
0.546
1.368
7.393
1.366
1.464
1.301
1.401
1.000
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
f1 (ppm)


eb69092511
Instrument AVC500
Group VG
Elena Benedetto 26909 23/11/11
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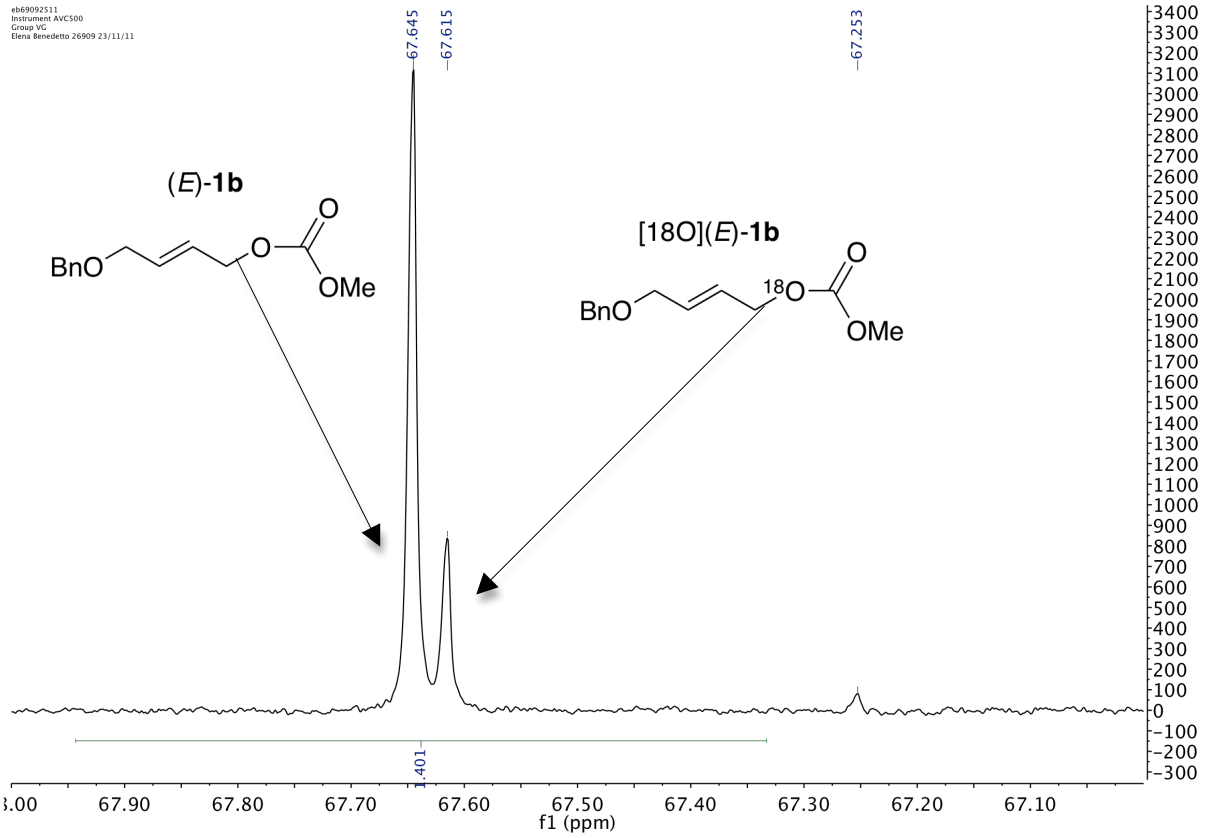
155.615
155.570
155.559
(E)-1b
BnO
O
O
OMe
[18O](E)-1b
BnO
18O
O
OMe
0.455
155.95
155.85
155.75
155.65
155.55
155.45
155.35
155.25
155.15
155.05
f1 (ppm)


eb69092511
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Group VG
Elena Benedetto 26909 23/11/11
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67.615
67.253
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BnO
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O
OMe
[18O](E)-1b
BnO
18O
O
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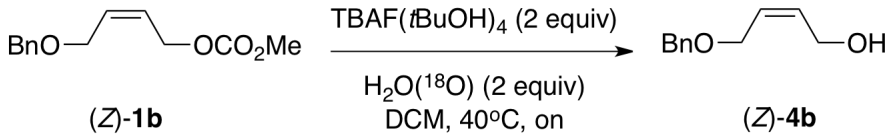
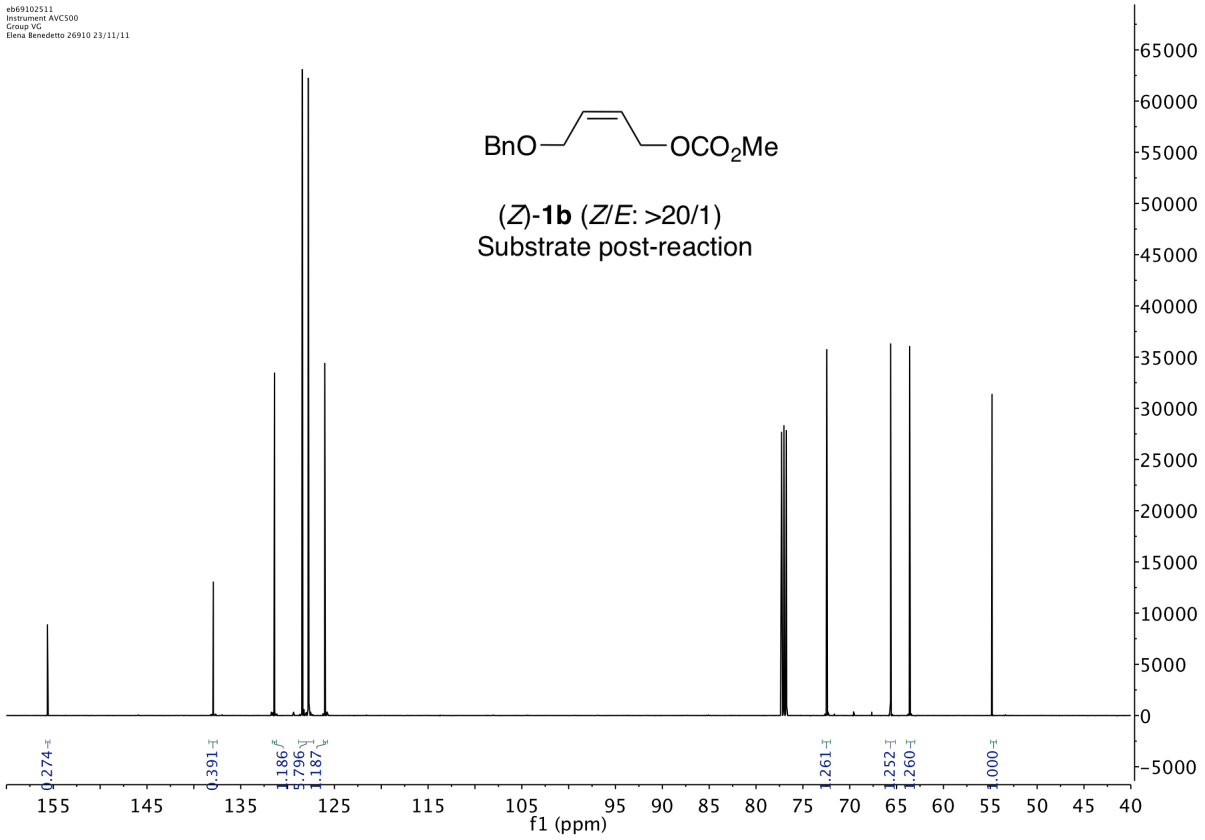
1.401
67.90
67.80
67.70
67.60
67.50
67.40
67.30
67.20
67.10
f1 (ppm)

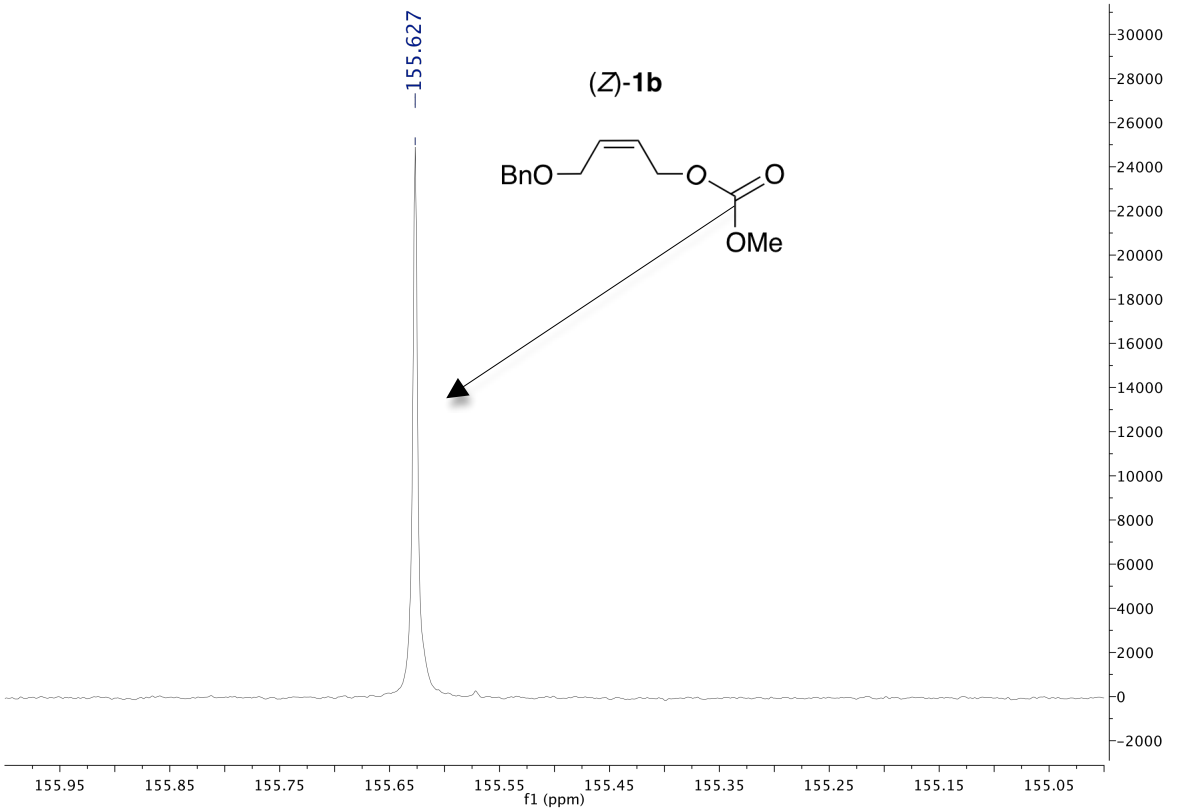
4.4 Procedure for test reaction in the presence of [18O]-H_2O:

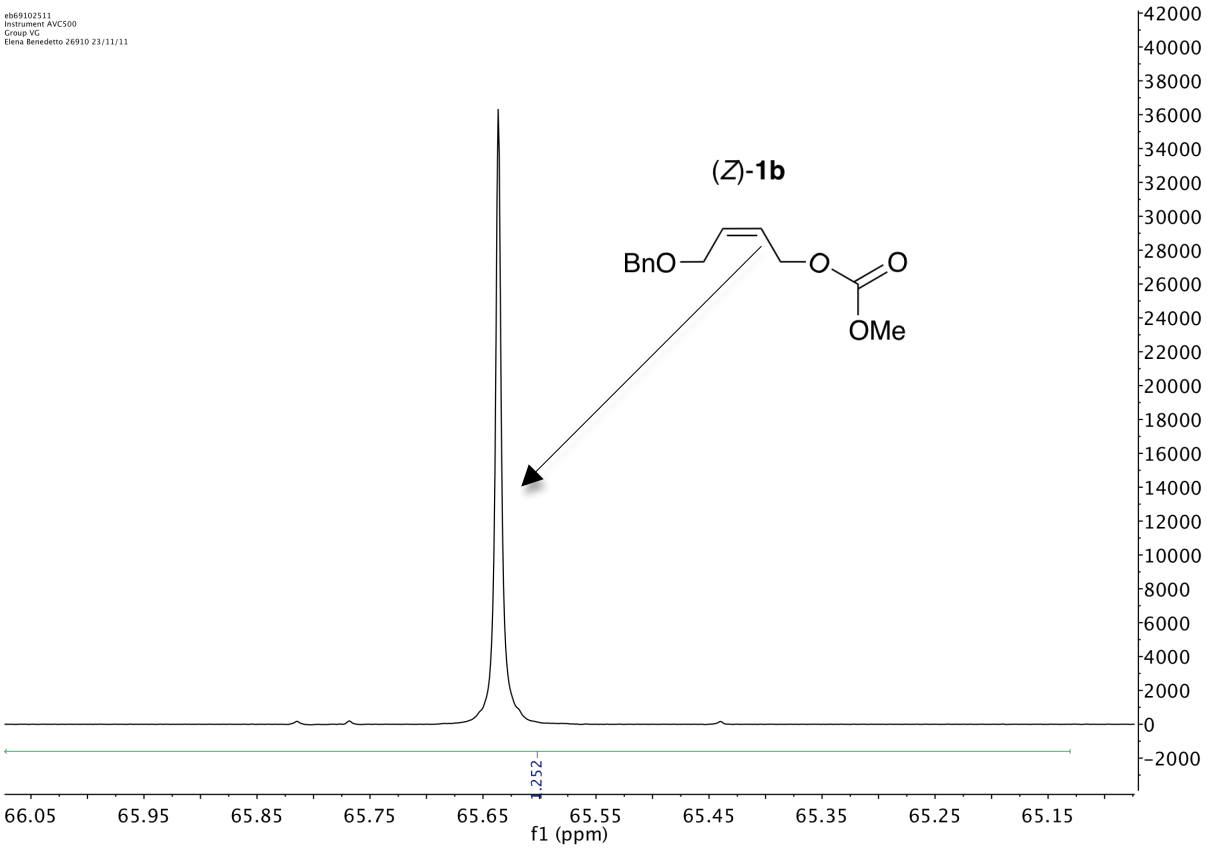


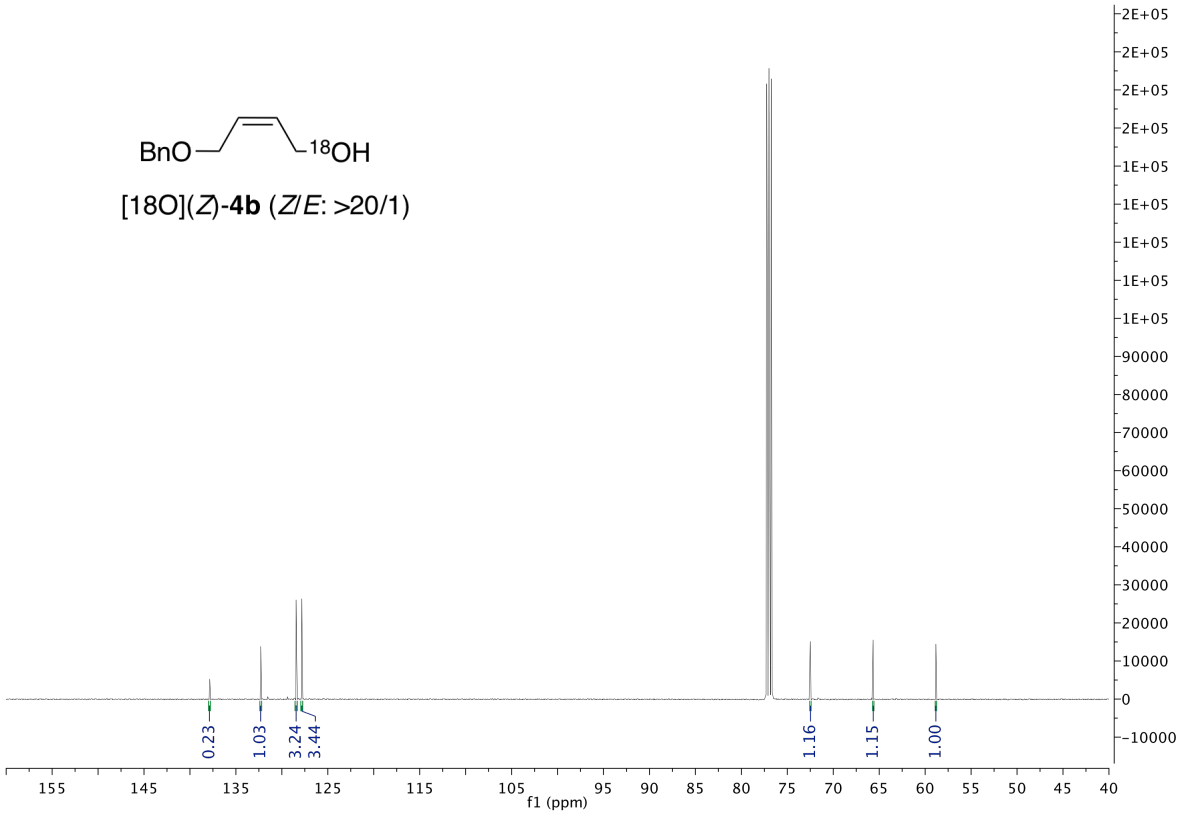
(*Z*)-**1b** (*Z*)-**4b**

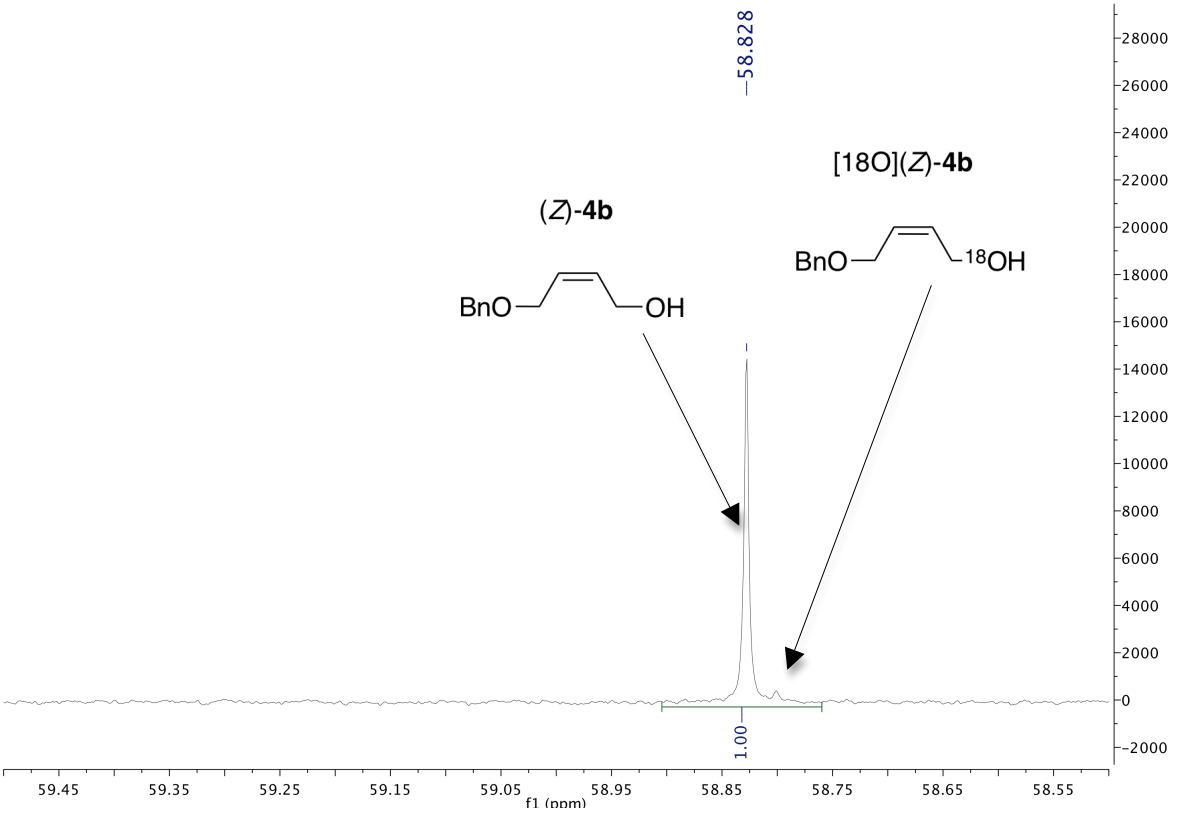
To a solution of (*Z*)-**1b** (47 mg, 0.2 mmol, *Z*/*E*: >20/1, 0% ^{18}O incorporation) and TBAF(*t*BuOH)$_4$ (2 eq, 0.4 mmol) in dry DCM (2 mL) was added [18O]-H_2O (8 μL, 0.4 mmol) and [Ir(COD)Cl]$_2$ (2.7 mg, 0.004 mmol). The reaction was allowed to stir at 40 °C overnight and the solvent was removed *in vacuo*. The crude reaction mixture was purified by silica gel column chromatography (hexane) to yield (*Z*)-**4b** (4 mg, 11%, *Z*/*E*: >20/1, 2% ^{18}O incorporation calculated from ^{13}C NMR) and recovered (*Z*)-**1b** (31 mg, 66%, *Z*/*E*: >20/1, 0% ^{18}O incorporation calculated from ^{13}C NMR).



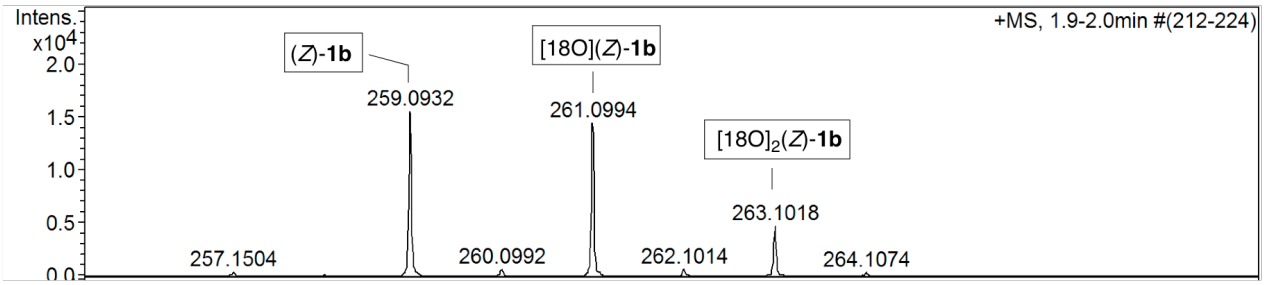

155.627
(Z)-1b
BnO
O
O
OMe
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
155.95
155.85
155.75
155.65
155.55
155.45
155.35
155.25
155.15
155.05
f1 (ppm)


eb69102511
Instrument AVC500
Group VG
Elena Benedetto 26910 23/11/11
(Z)-1b
BnO
O
O
OMe
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.252
66.05
65.95
65.85
65.75
65.65
65.55
65.45
65.35
65.25
65.15
f1 (ppm)





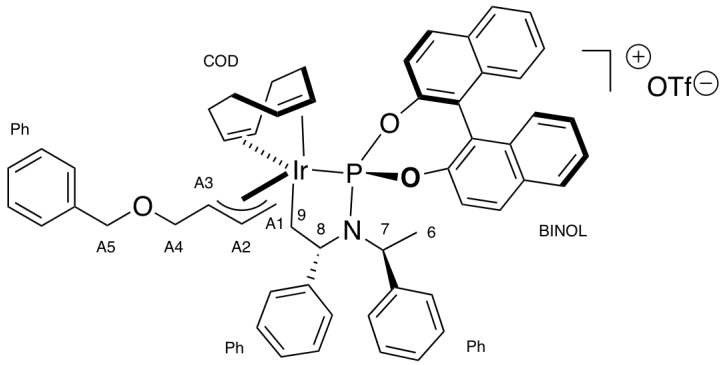
4.5 ES-MS of recovered (*Z*)-1b following experiment 3.2:



(*Z*)-**1b**: HRMS calc for $C_{13}H_{16}NaO_4$ $[M+Na]^+$ 259.0941, found 259.0932. Relative abundance determined by the intensity of the peak: 46%.
[18O](*Z*)-**1b**: HRMS calc for $C_{13}H_{16}NaO_3{}^{18}O$ $[M+Na]^+$ 261.0983, found 261.0994. Relative abundance determined by the intensity of the peak: 41%.
$[18O]_2$(*Z*)-**1b**: HRMS calc for $C_{13}H_{16}NaO_2{}^{18}O_2$ $[M+Na]^+$ 263.1026, found 263.1018. Relative abundance determined by the intensity of the peak: 13%.

5. NMR Experiments

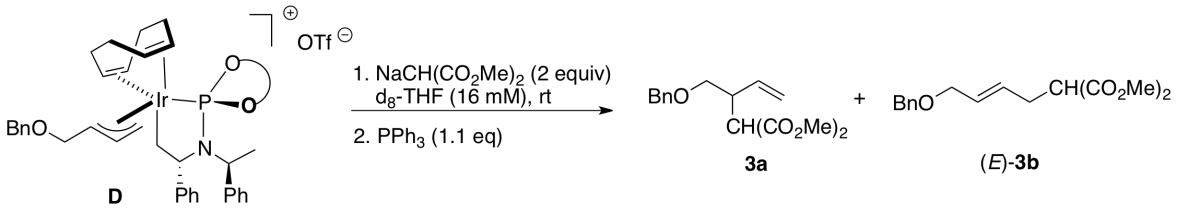
5.1 Synthesis of [(Allyl)Ir(COD)(P,C-L)(L)], D



To a solution of $[Ir(COD)Cl]_2$ (0.17 g, 0.25 mmol) in THF (13 mL) was added (*S*,*S*,*S*)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis(1-phenylethyl)amine (*S*,*S*,*S*)-L (0.27 g, 0.5 mmol) at room temperature. After being stirred for 30 min at room temperature, carbonate **1a** (0.24 g, 1 mmol) and AgOTf (0.13 g, 0.5 mmol) were added, and the resulting mixture stirred for 20 h. The reaction was filtered trough celite and the solvent removed *in vacuo*. The crude product was purified by silica gel column chromatography (DCM: iPrOH/97:3) to yield the title complex **D** as a pale yellow powder (0.39 g, 70%). The product was isolated as a mixture of isomers 94:6 (ratio determined by ^{31}P NMR spectroscopy). ^1H NMR (500 MHz, d_8-THF): δ = 8.34 (d, *J* = 9 Hz, 1H; BINOL), 8.30 (d, *J* = 9 Hz, 1H; BINOL), 8.09 (d, *J* = 8 Hz, 2H; 2 BINOL), 8.03 (d, *J* = 9Hz, 1H; BINOL), 7.99 (d, *J* = 9Hz, 1H; BINOL), 7.56–7.52 (m, 2H; 2 BINOL), 7.36–7.24 (m, 17H; 13 Ph, 4 BINOL), 7.12-7.10 (m, 2H, 2 Ph), 5.25–5.20 (m, 1H; cod-CH), 4.97–4.92 (m, 1H; 3A-H), 4.83–4.75 (m, 1H; 2A-H), 4.67–4.61 (m, 2H, A5-H), 4.56–4.49 (m, 1H; A4-H'), 4.24–4.16 (m, 2H; A4-H, cod-CH), 3.91–3.82 (m, 2H; 7-H, 8-H), 3.50–3.46 (m, 1H; cod-CH), 3.38–3.35 (m, 1H; cod-CH), 3.27–3.21 (m, 1H; cod-CH2), 2.96–2.93 (m, 2H ; 1A-H, cod-CH2), 2.43–2.33 (m, 3H; 1A-H', 2 cod-CH2), 2.32-2.30 (m, 1H, 9-H), 2.09–2.05 (m, 1H; cod- CH2), 1.73–1.71 (m,

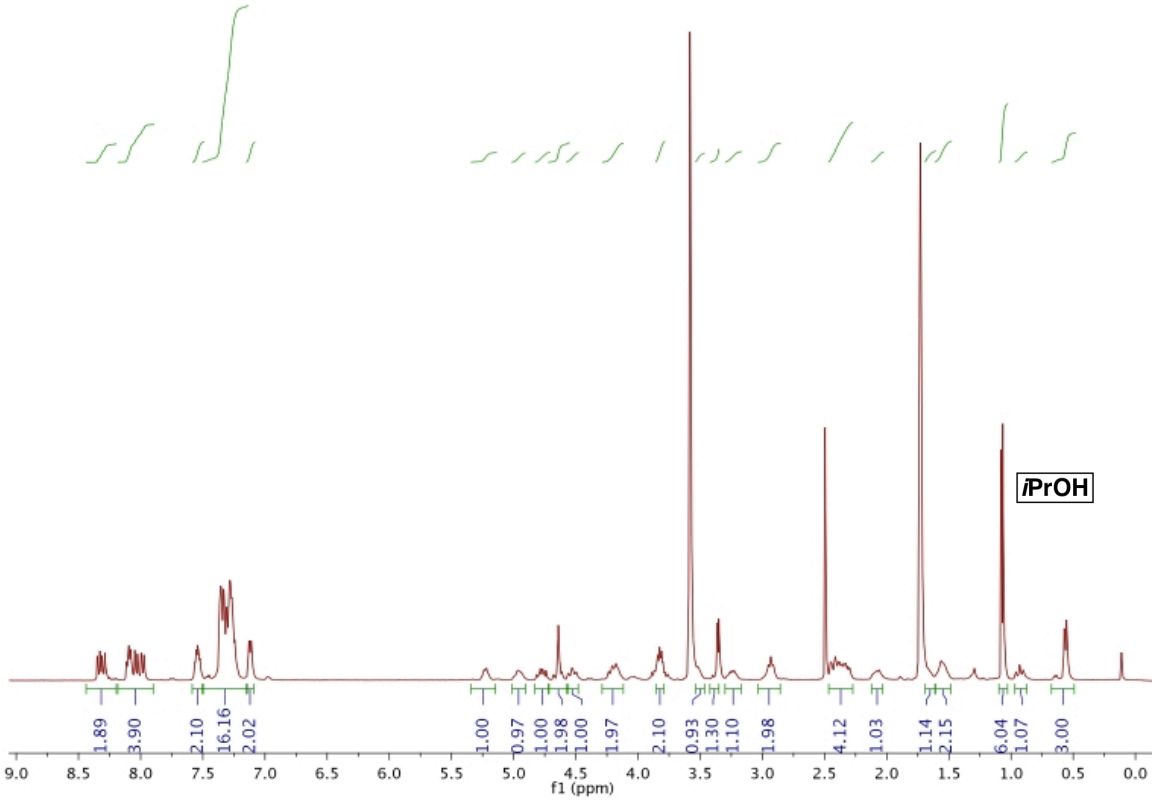
1H; cod-CH2), 1.60-1.50 (m, 2H; 2 cod-CH2), 0.95 (t, J = 12 Hz, 1H; 9-H'), 0.57 (d, J = 7 Hz, 3H; 3 6-H); ^{13}C NMR (125 MHz, d$_8$-THF): δ = 150.1 (d, J_{CP}= 16Hz; BINOL), 149.0 (d, J_{CP}= 8Hz; BINOL), 144.0 (d, J_{CP}= 12Hz; BINOL), 141.6 (s; BINOL), 139.5 (s; A-Ph), 134.2 (d, J_{CP}= 2Hz; BINOL), 133.7 (s; BINOL), 133.3, 133.1, 132.6 (s, 3xPh), 129.9, 129.8, 129.7, 129.4, 129.3, 129.2, 129.1, 129.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.1 (s; 8xPh, 8xBINOL), 124.0 (s; BINOL), 123.8 (d, J_{CP}= 3Hz; BINOL), 123.3 (d, J_{CP}= 3Hz, BINOL), 122.6 (s; BINOL), 122.5 (d, J_{CP}= 1Hz; BINOL), 121.4 (s; BINOL), 101.5 (d, J_{CP}= 3Hz; CH-cod), 101.4 (d, J_{CP}= 4Hz, C2), 93.4 (d, J_{CP}= 3Hz; CH-cod), 89.0 (d, J_{CP}= 5Hz; CH-cod), 83.1 (d, J_{CP}= 6Hz; CH-cod), 76.0 (d, J_{CP}= 29Hz; C3), 73.9 (s; C5), 69.8 (d, J_{CP}= 3Hz; C4), 66.9 (d, J_{CP}= 33Hz; C8), 61.1 (d, J_{CP}= 5Hz; C7), 45.5 (s; C1), 37.8 (s; CH2-cod), 35.5 (s, CH2-cod), 28.8 (s; CH2-cod), 26.4 (s; CH2-cod), 19.2 (s; C6), 14.5 (d, J_{CP}= 7Hz; C9); ^{31}P NMR (97 MHz): 123.07 (minor isomer), 121.00 (major isomer); ^{19}F {^{1}H}NMR (376.5MHz, d$_8$-THF): δ -80.59 (-OTf); m/z [$C_{55}H_{53}IrNO_3P$]$^+$: 999.34.
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.29 (d, J = 9 Hz, 1H; BINOL), 8.20 (d, J = 9 Hz, 1H; BINOL), 8.08 (t, J = 8 Hz, 2H; 2 BINOL), 7.81 (d, J = 9Hz, 1H; BINOL), 7.66 (d, J = 9Hz, 1H; BINOL), 7.61–7.55 (m, 2H; 2 BINOL), 7.40–7.31 (m, 15H; 11 Ph, 4 BINOL), 7.11-7.08 (m, 4H, 4 Ph), 5.13–5.09 (m, 1H; cod-CH), 4.65–4.59 (m, 4H; 3A-H, 2A-H, 2 5A-H), 4.54–4.48 (m, 1H; 4A-H), 4.22–4.16 (m, 1H, cod-CH), 4.11–4.07 (m, 1H; A4-H'), 3.87–3.79 (m, 1H; 7-H), 3.68–3.65 (m, 1H; 8-H), 3.37–3.32 (m, 1H; cod-CH), 3.29–3.26 (m, 1H; cod-CH2), 3.15–3.10 (m, 1H; cod-CH), 2.86–2.77 (m, 2H ; 1A-H, cod-CH2), 2.50–2.43 (m, 1H; cod-CH2), 2.35-2.27 (m, 2H; 9-H, cod-CH2), 2.15–2.11 (m, 1H; cod-CH2), 2.00–1.98 (m, 1H; 1A-H'), 1.68-1.55 (m, 3H; 3 cod-CH2), 0.95 (t, J = 12 Hz, 1H; 9-H'), 0.55 (d, J = 8 Hz, 3H; 3 6-H).

5.2 Procedure for the dimethyl malonate substitution of [(Allyl)Ir(COD)(P,C-L)(L)] (D) in THF:[26]

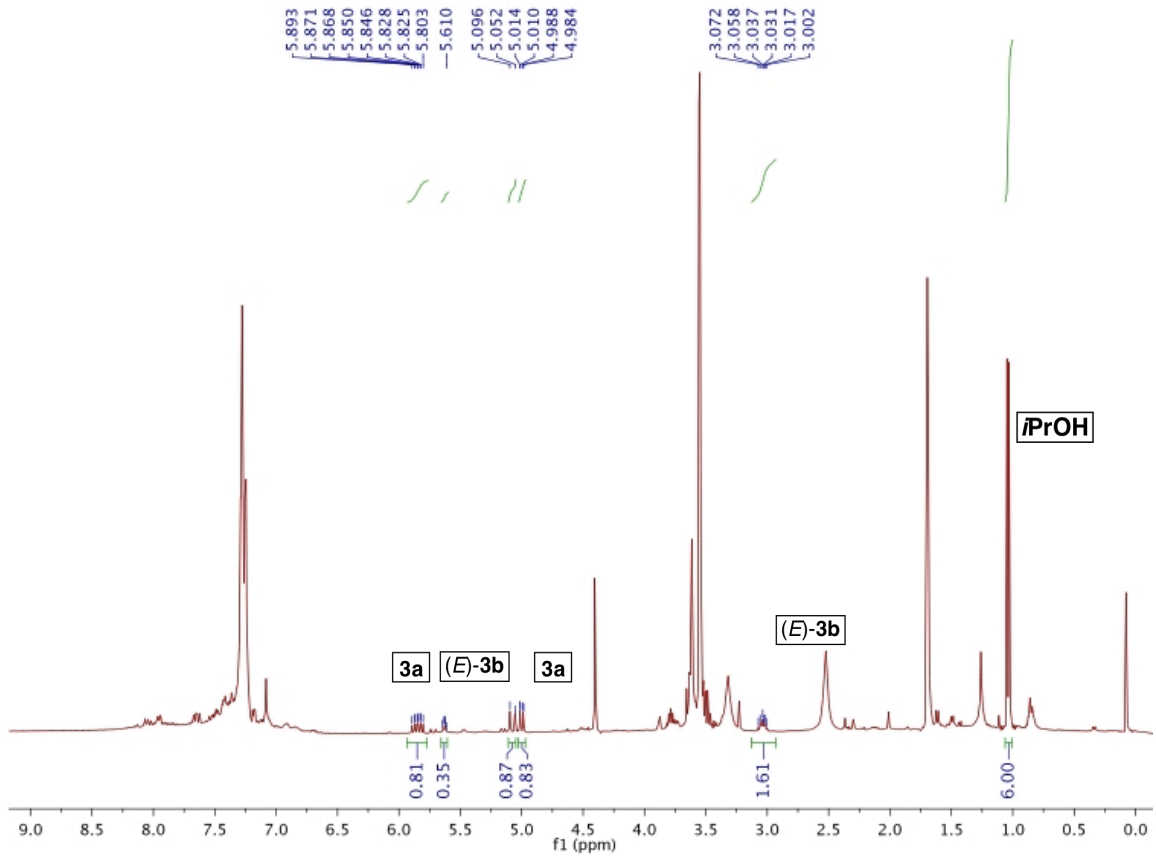


The complex **D** (12 mg, 0.01 mmol) was dissolved in d$_8$-THF (0.3 mL) in an NMR tube under N_2 atmosphere, and a ^{1}H NMR recorded. A solution of sodium dimethyl malonate (0.02 mmol) in d$_8$-THF (0.3 mL), prepared from dimethyl malonate (3 μL, 0.02 mmol) and NaH (1 mg, 0.02 mmol), was then added to the mixture and the reaction allowed to react at room temperature. After 5 min a second ^{1}H NMR showed completion, PPh_3 (3mg, 0.01 mmol) was added and a ^{1}H NMR recorded. From the crude reaction mixture was observed the formation of the **3a** (81%) and (*E*)-**3b** (17%). The conversion was determined using an internal standard, *i*PrOH present in the complex **D**, deriving from the flash chromatography purification. When the reaction was repeated on 0.05 mmol scale of complex **D** (57 mg), the substituted product **3a** was isolated in 79% yield (12 mg).

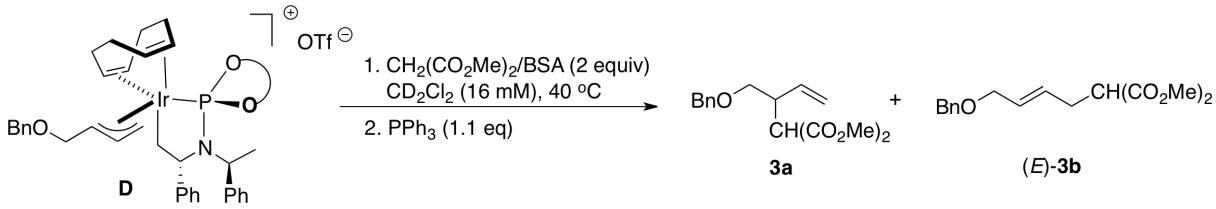
Complex D with internal standard *i*PrOH in d_8-THF:



Reaction mixture in d_8-THF after addition of PPh_3:

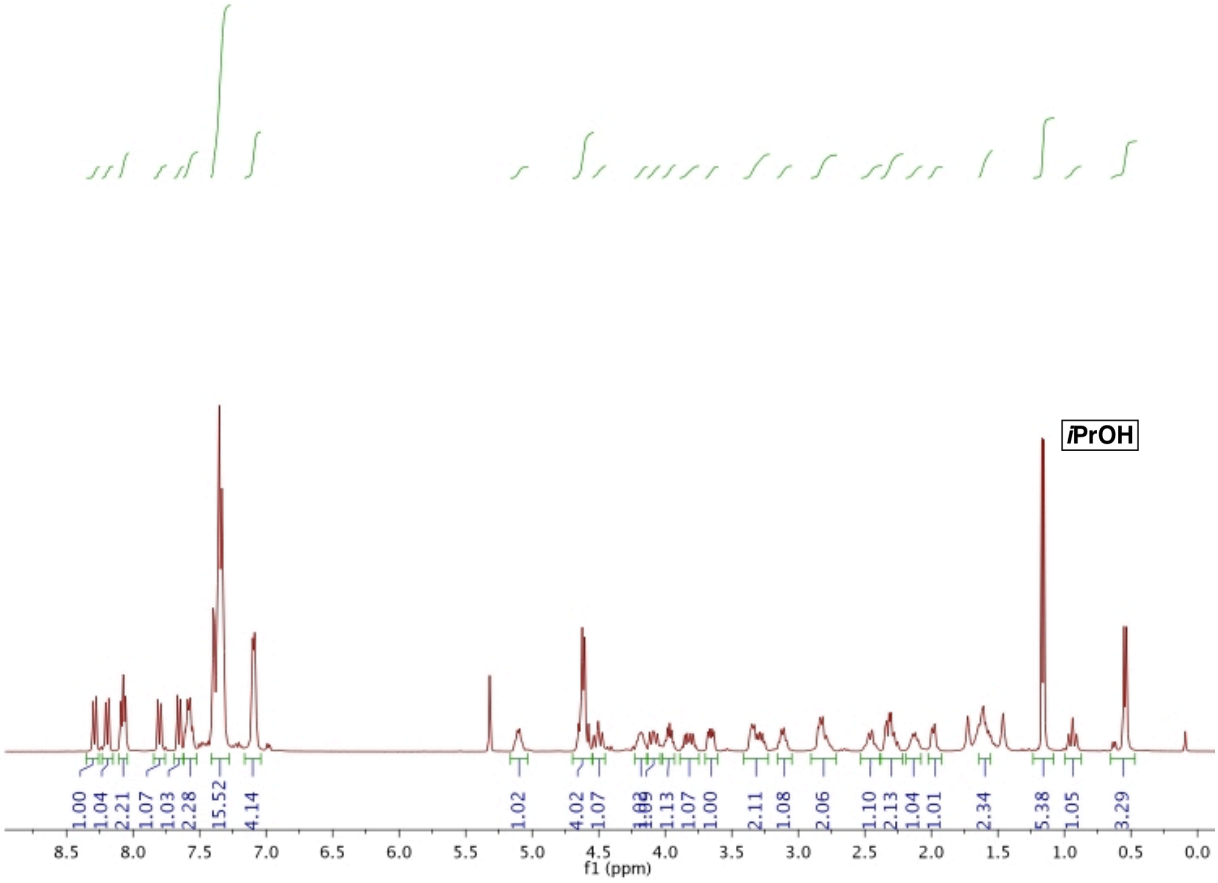


5.3 Procedure for the dimethyl malonate substitution of [(Allyl)Ir(COD)(P,C-L)(L)] (D) in DCM:

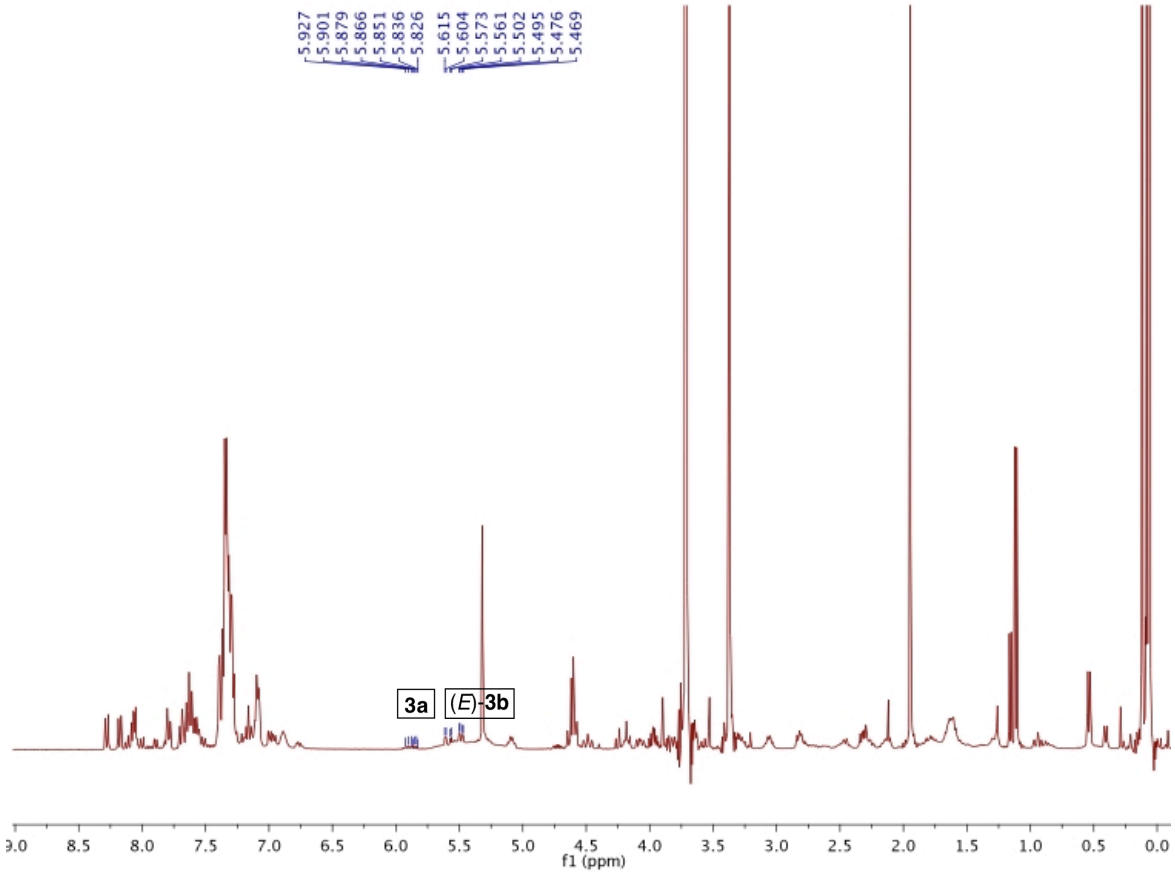


The complex **D** (12 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (0.3 mL) in an NMR tube under N_2 atmosphere, and a ^1H NMR recorded. A solution of dimethyl malonate (0.02 mmol) in CD_2Cl_2 (0.3 mL), prepared from dimethyl malonate (3 µL, 0.02 mmol) and BSA (5 µL, 0.02 mmol), was then added to the mixture and the reaction allowed to react at room temperature, and monitored by ^1H NMR spectroscopy. After 1h at rt still no product was observed in the crude reaction mixture by ^1H NMR. The mixture was subsequently warmed to 40 °C and monitored by ^1H NMR. After 18 h reacting at 40 °C, PPh_3 (3mg, 0.01 mmol) was added and a last ^1H NMR recorded. From the crude reaction mixture was observed the formation of traces of the **3a** and (*E*)-**3b**, in addition to the un-reacted complex **D**.

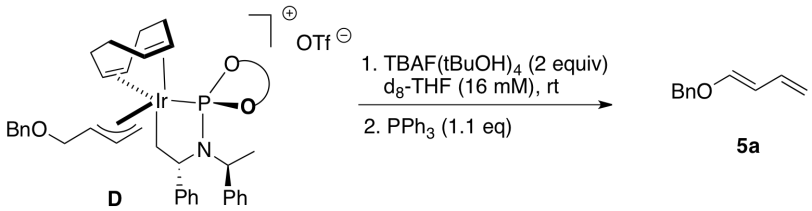
Complex D with internal standard *i*PrOH in d_2-DCM:



Reaction mixture in d_2-DCM after addition of PPh_3:

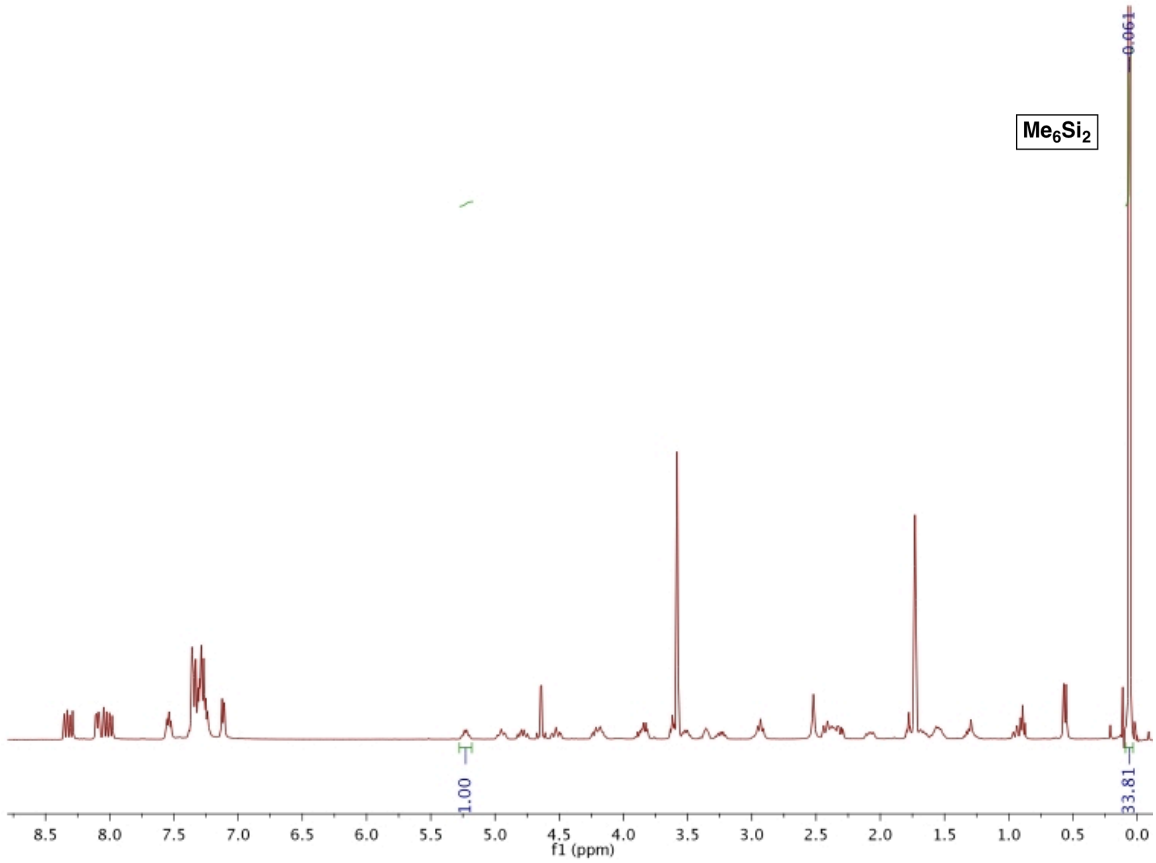


5.4 Procedure for fluorination of [(Allyl)Ir(COD)(P,C-L)(L)] (D) in d_8-THF:

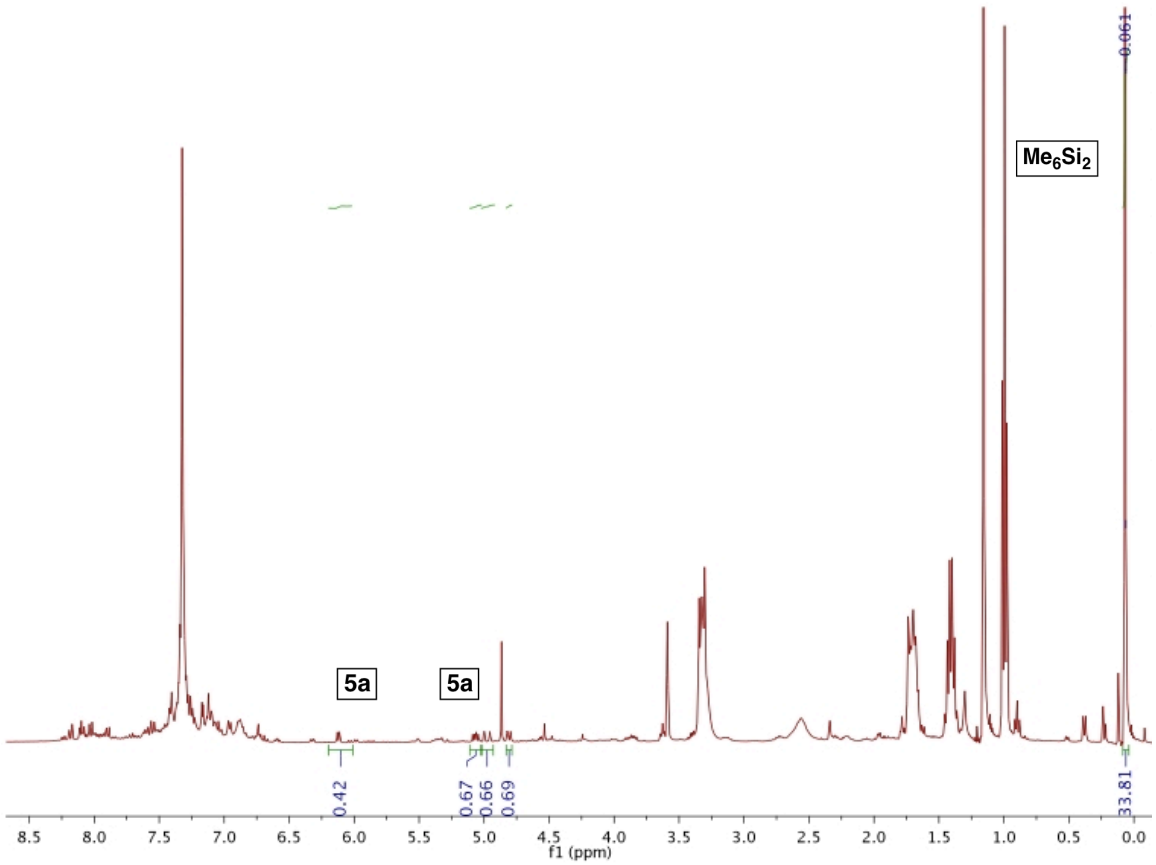


The complex **D** (12 mg, 0.01 mmol) was dissolved in d_8-THF (0.6 mL) in an NMR tube under N_2 atmosphere, and a ^1H NMR recorded. TBAF(tBuOH)$_4$, (6mg, 0.02 mmol) was added to the mixture and the reaction allowed to react at room temperature, and monitored by ^1H NMR and ^{19}F NMR spectroscopy. After 5 min, the ^1H NMR showed complete consumption of starting material, PPh_3 (3mg, 0.01 mmol) was added and a second ^1H and ^{19}F NMR recorded. From the crude reaction mixture no formation of the fluorinated products **2a** or (*E*)-**2b** was detected, but formation of 67% of diene **5a**, and decomposition of the initial complex was observed. The conversion was determined using as internal standard Me_6Si_2 (3.9 μL, 0.019 mmol).

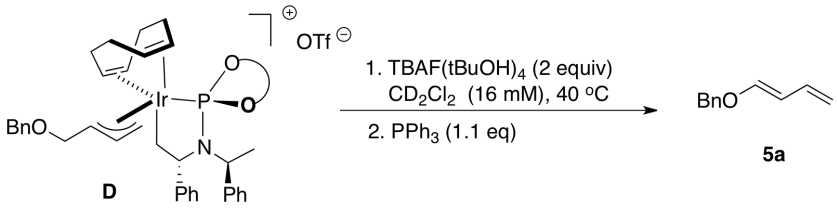
Complex D with internal standard Me_6Si_2 in d_8-THF:



Reaction mixture in d_8-THF after addition of PPh_3:

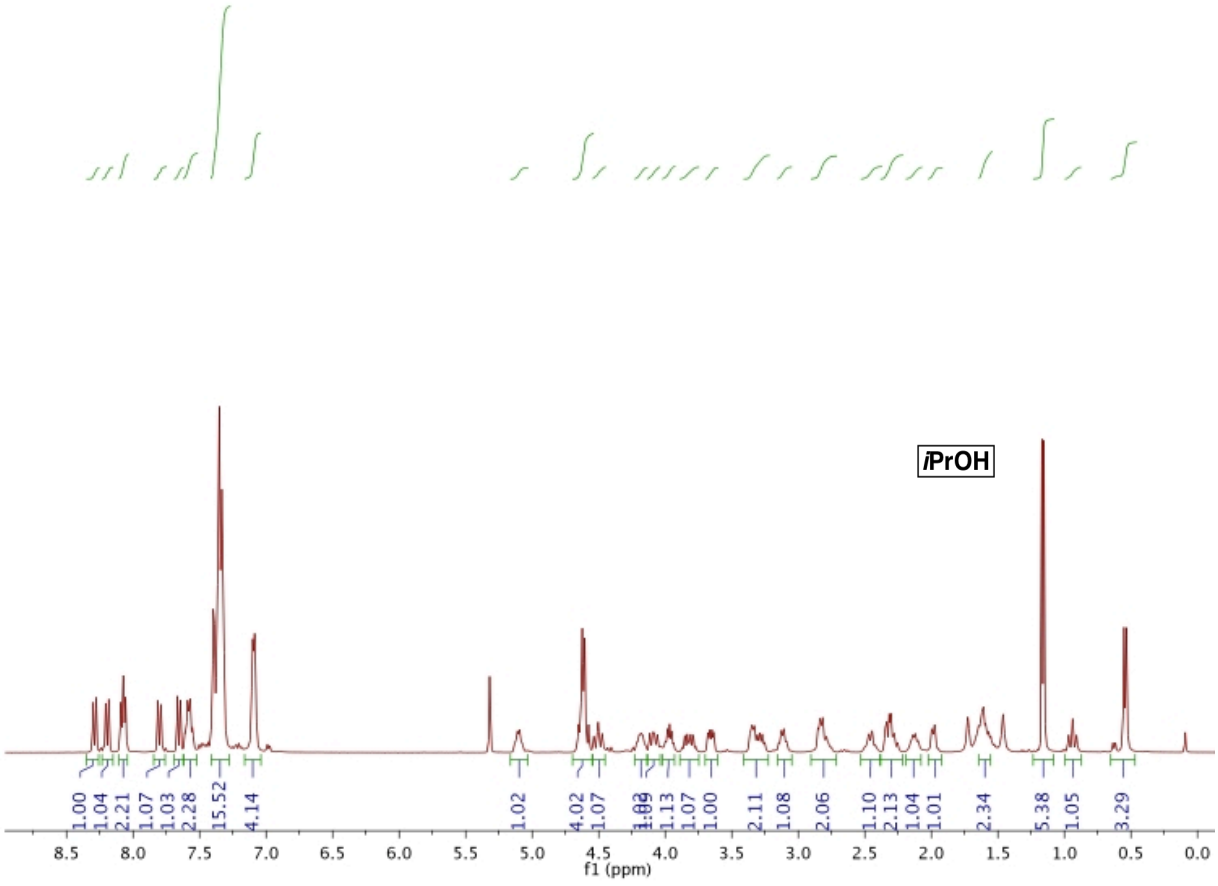


5.5 Procedure for fluorination of [(Allyl)Ir(COD)(P,C-L)(L)] (D) in d_2-DCM:

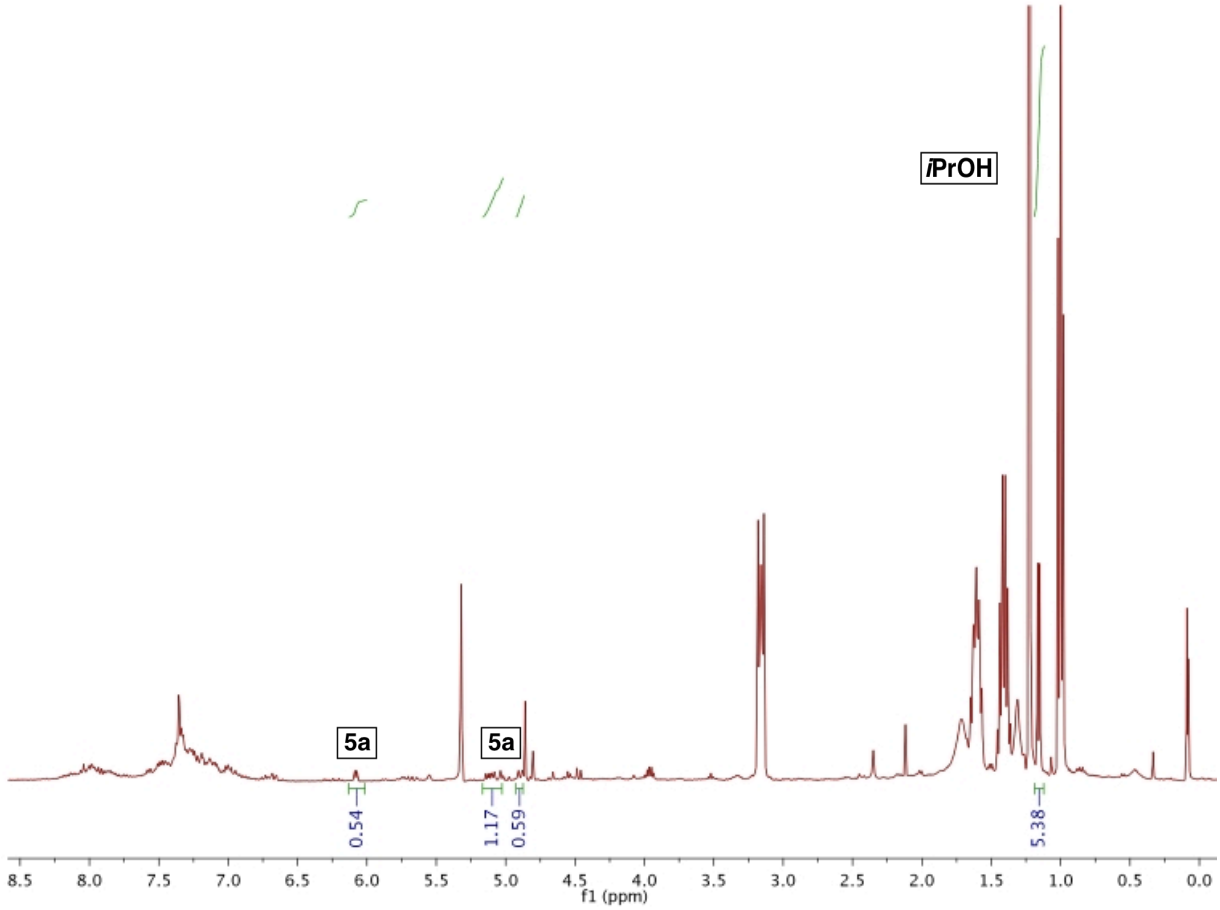


The complex **D** (12 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (0.6 mL) in an NMR tube under N_2 atmosphere, and a ^{1}H NMR recorded. TBAF(*t*BuOH)$_4$, (6 mg, 0.02 mmol) was added to the mixture and the reaction allowed to react at room temperature, and monitored by ^{1}H NMR and ^{19}F NMR spectroscopy. After 1 h at rt still no consumption of the starting material was observed in the crude reaction mixture by ^{1}H NMR. The mixture was subsequently warmed to 40 °C and monitored by ^{1}H NMR. After 30 min PPh_3 (3mg, 0.01 mmol) was added and the last ^{1}H and ^{19}F NMR recorded. From the crude mixture no formation of the fluorinated products **2a** or (*E*)-**2b** was detected, but formation of 59% of diene **5a**, and decomposition of the initial complex was observed. The conversion was determined using as internal standard, *i*PrOH present in the complex **D**, deriving from the flash chromatography purification.

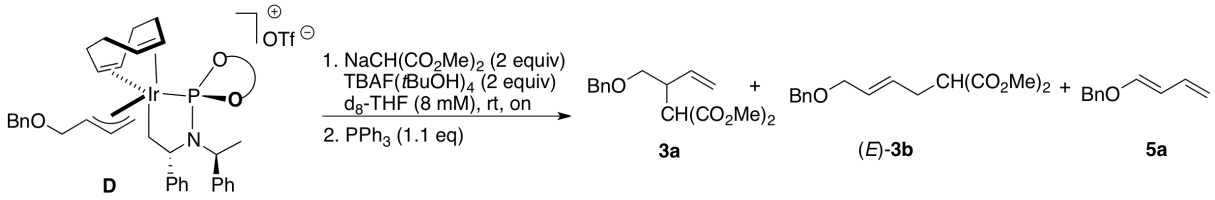
Complex D with internal standard *i*PrOH in d_2-DCM:



Reaction mixture in d_2-DCM after addition of PPh_3:

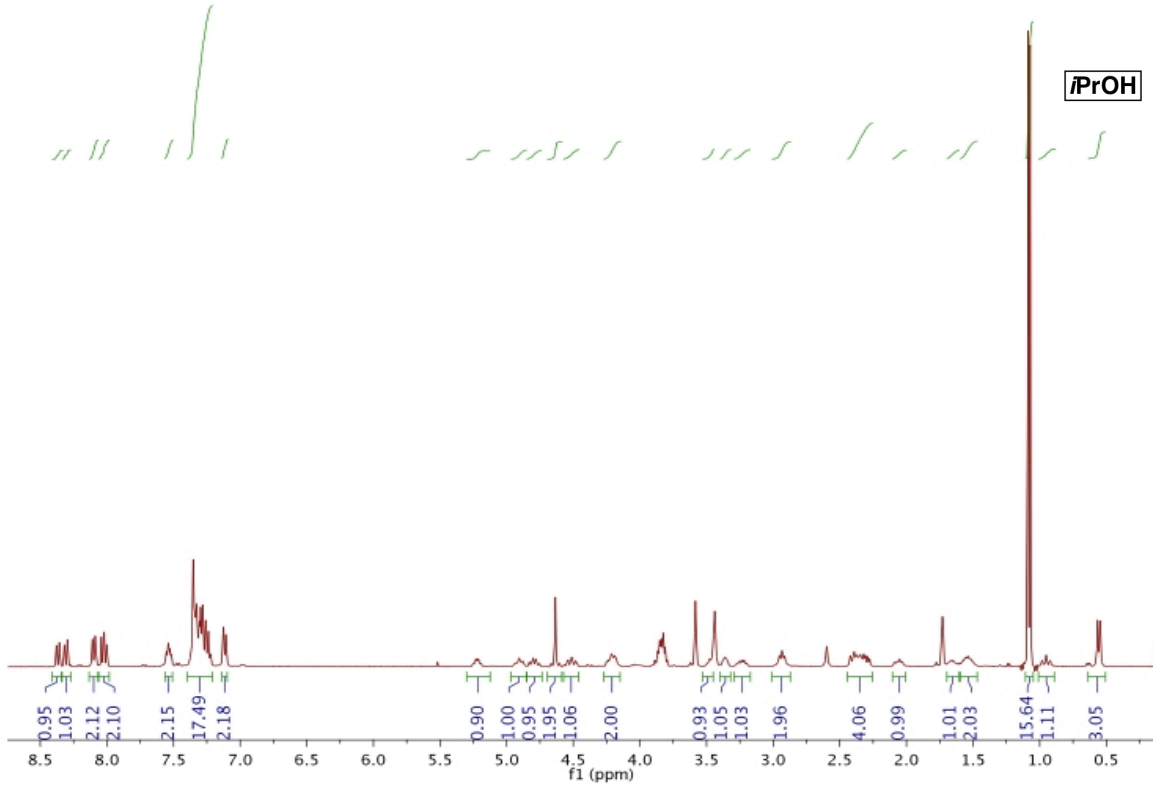


5.6 General Procedure for the dimethyl malonate substitution of [(Allyl)Ir(COD)(P,C-L)(L)] (D) in the presence of TBAF(*t*BuOH)$_4$:

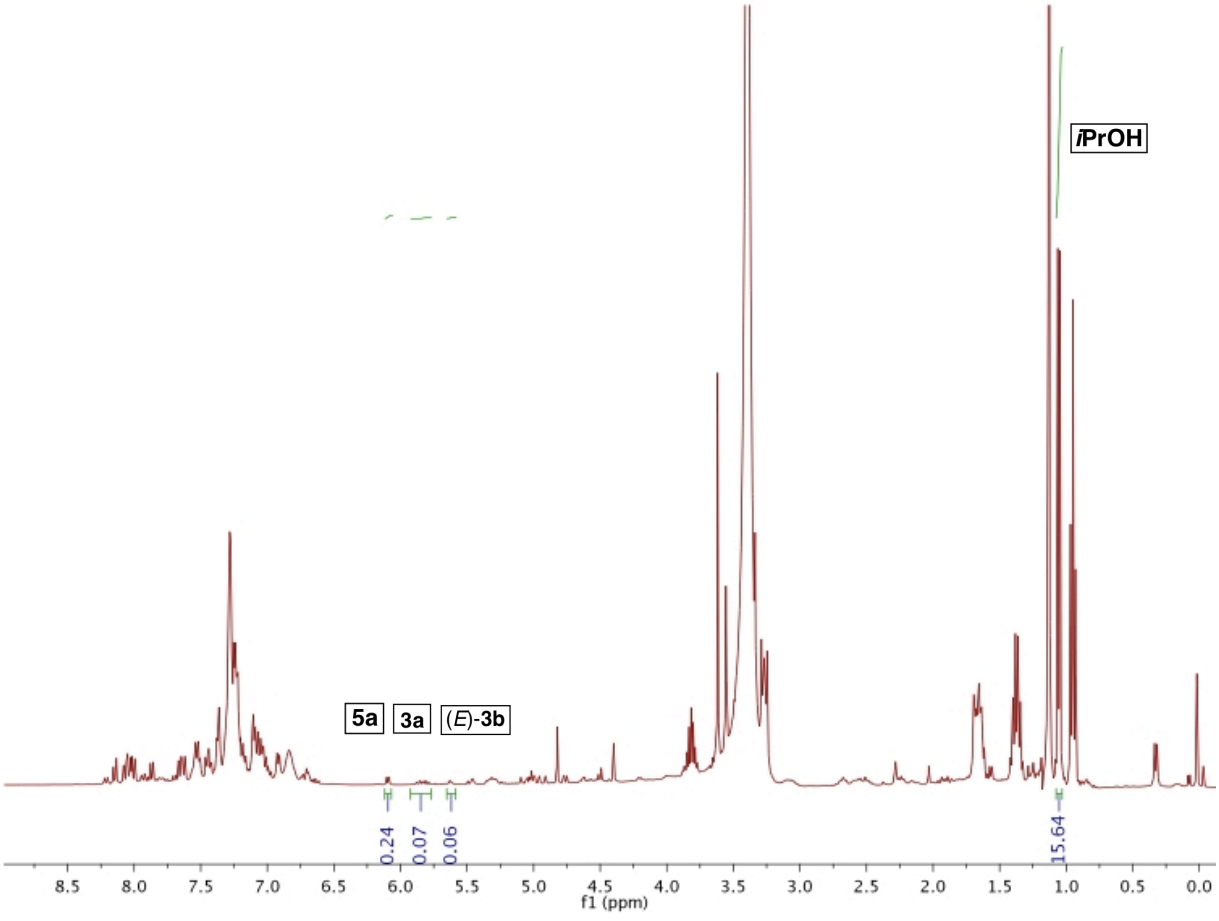


The complex **D** (12 mg, 0.01 mmol) was dissolved in d_8-THF (0.3 mL) in an NMR tube under N_2 atmosphere, and a ^{1}H NMR recorded. A solution of sodium dimethyl malonate (0.02 mmol) in d_8-THF (0.3 mL), prepared from dimethyl malonate (3 μL, 0.02 mmol) and NaH (1 mg, 0.02 mmol) was then added to the mixture, followed by the addition of TBAF(*t*BuOH)$_4$, (6mg, 0.02 mmol) and the reaction allowed to react at room temperature, and monitored by ^{1}H and ^{19}F NMR spectroscopy. After 5 min the ^{1}H NMR showed consumption of starting material, PPh_3 (3mg, 0.01 mmol) was added and the second ^{1}H and ^{19}F NMR recorded. From the crude mixture no formation of the fluorinated products **2a** or (*E*)-**2b** was detected. Only 7% of **3a**, 3% of (*E*)-**3b** and 23% of **5a** were observed, and complete decomposition of initial allyl-Ir complex. The conversion was determined using as internal standard, *i*PrOH present in the complex **D**, deriving from the flash chromatography purification.

Complex D with internal standard *i*PrOH in d_8-THF:



Reaction mixture after addition of PPh_3:



6. References

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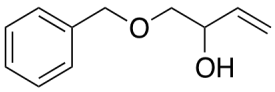
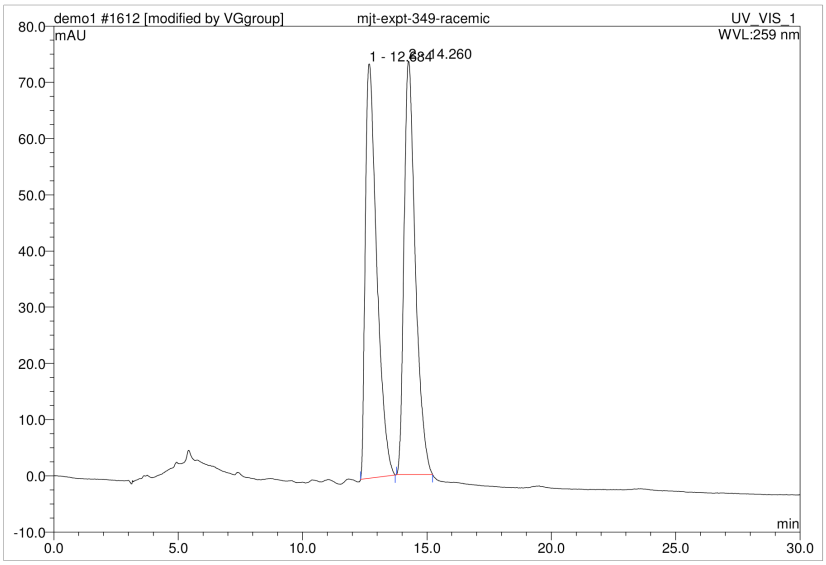
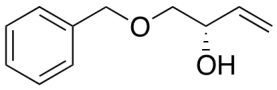
7. HPLC Traces



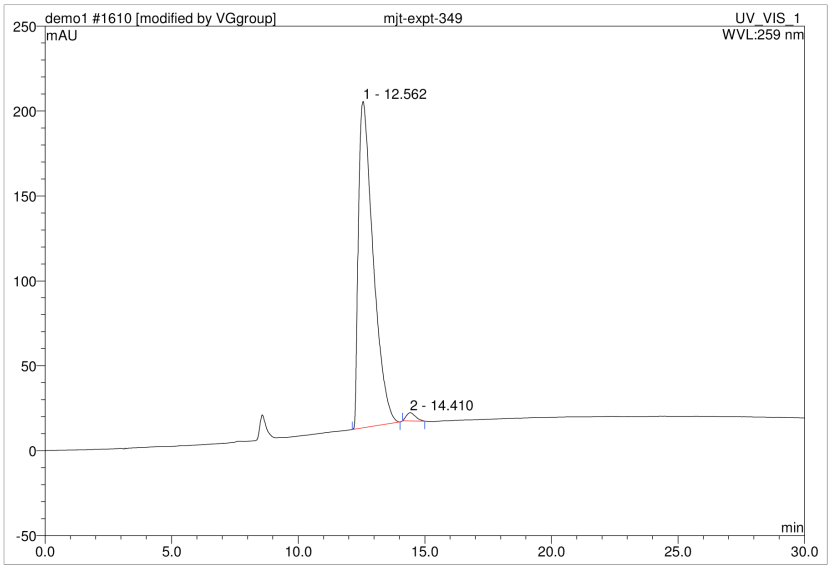
Racemic **4a**



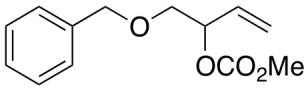
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount um	Type
1	12.68	n.a.	73.726	39.411	50.33	n.a.	BMB*
2	14.26	n.a.	73.534	38.892	49.67	n.a.	BMB*
Total:			147.261	78.302	100.00	0.000	



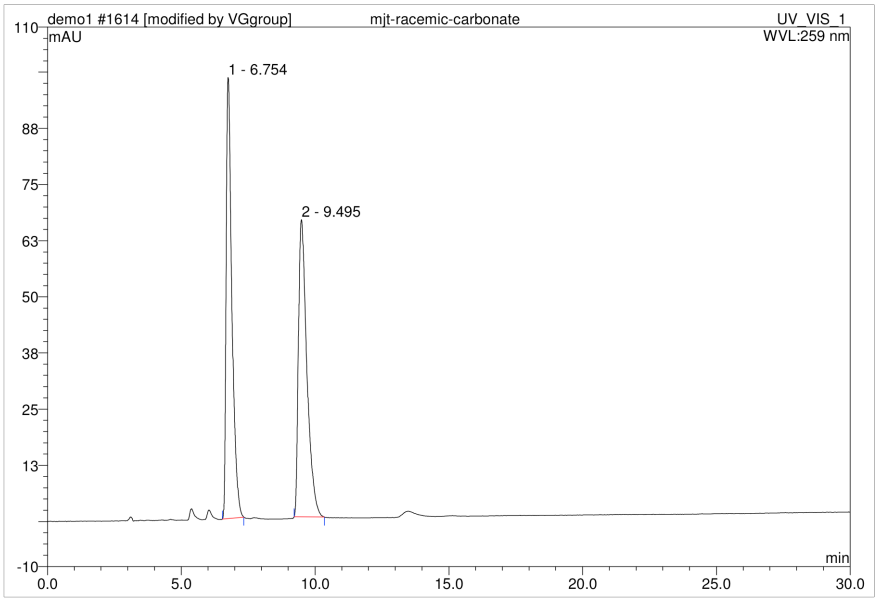
Enantioenriched (*S*)-**4a (97% ee)**



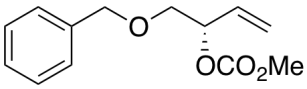
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount um	Type
1	12.56	n.a.	192.278	129.706	98.48	n.a.	BMB
2	14.41	n.a.	4.778	2.004	1.52	n.a.	BMB*
Total:			197.056	131.710	100.00	0.000	



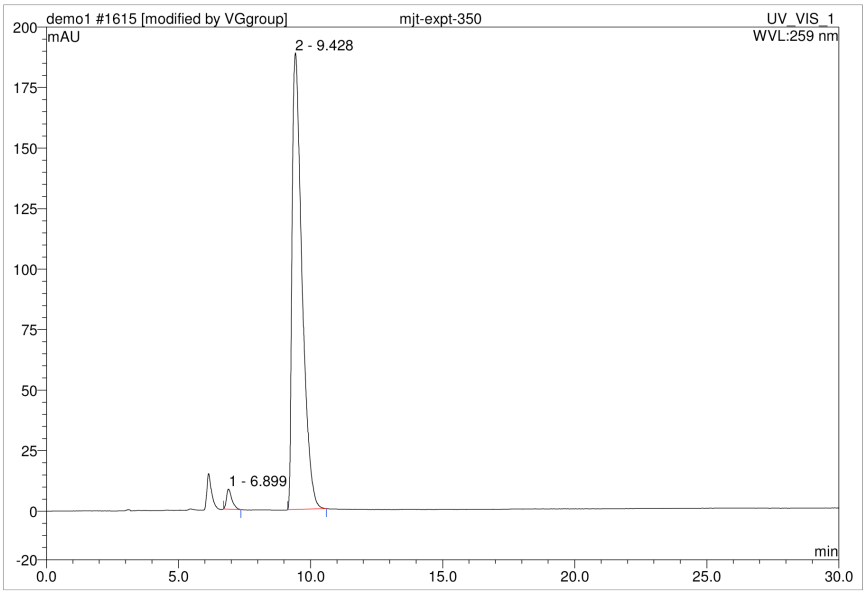
Racemic **1a**



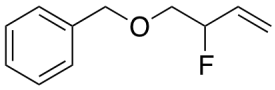
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount um	Type
1	6.75	n.a.	98.242	24.297	50.08	n.a.	BMB*
2	9.50	n.a.	66.150	24.215	49.92	n.a.	BMB*
Total:			164.392	48.512	100.00	0.000	



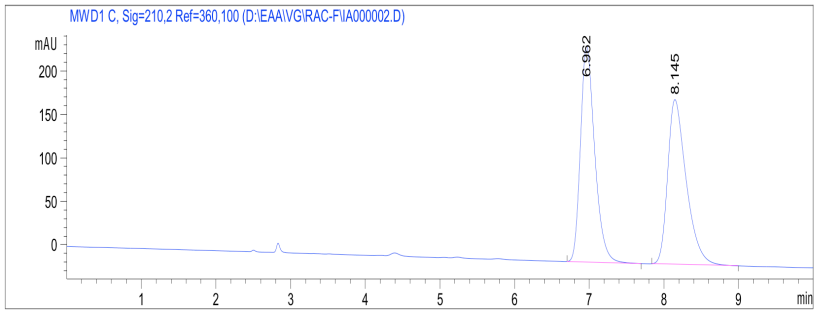
Enantioenriched (*S*)-**1a (95% ee)**



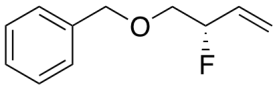
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount um	Type
1	6.90	n.a.	8.332	1.977	2.35	n.a.	BMB*
2	9.43	n.a.	188.567	82.176	97.65	n.a.	BMB*
Total:			196.899	84.153	100.00	0.000	



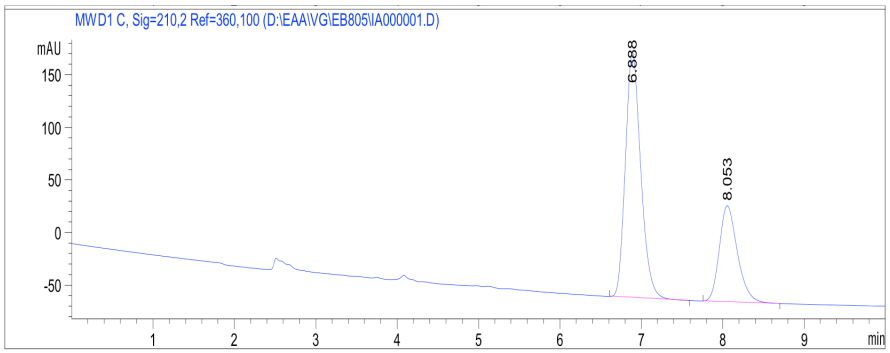
Racemic **2a**



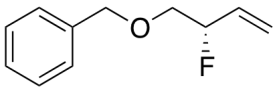
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.962	BB	0.2007	3293.89893	248.38553	50.0625
2	8.145	BB	0.2601	3285.67261	189.65283	49.9375
Totals :				6579.57153	438.03836	



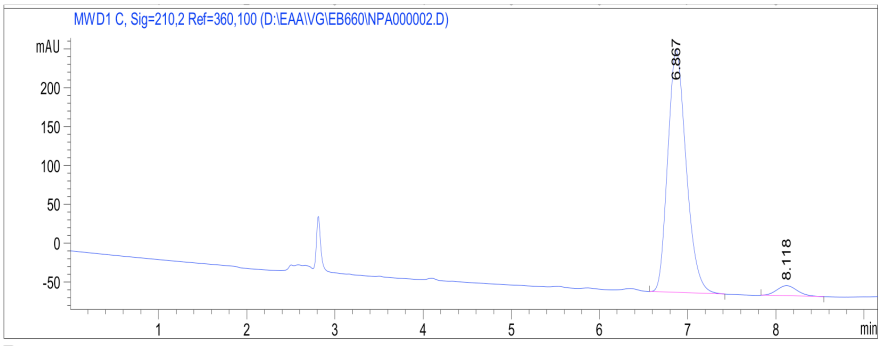
Enantioenriched (*S*)-**2a (37% ee)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.888	VB	0.2003	3064.39453	233.24889	68.4562
2	8.053	BB	0.2364	1412.03491	91.31494	31.5438
Totals :				4476.42944	324.56383	

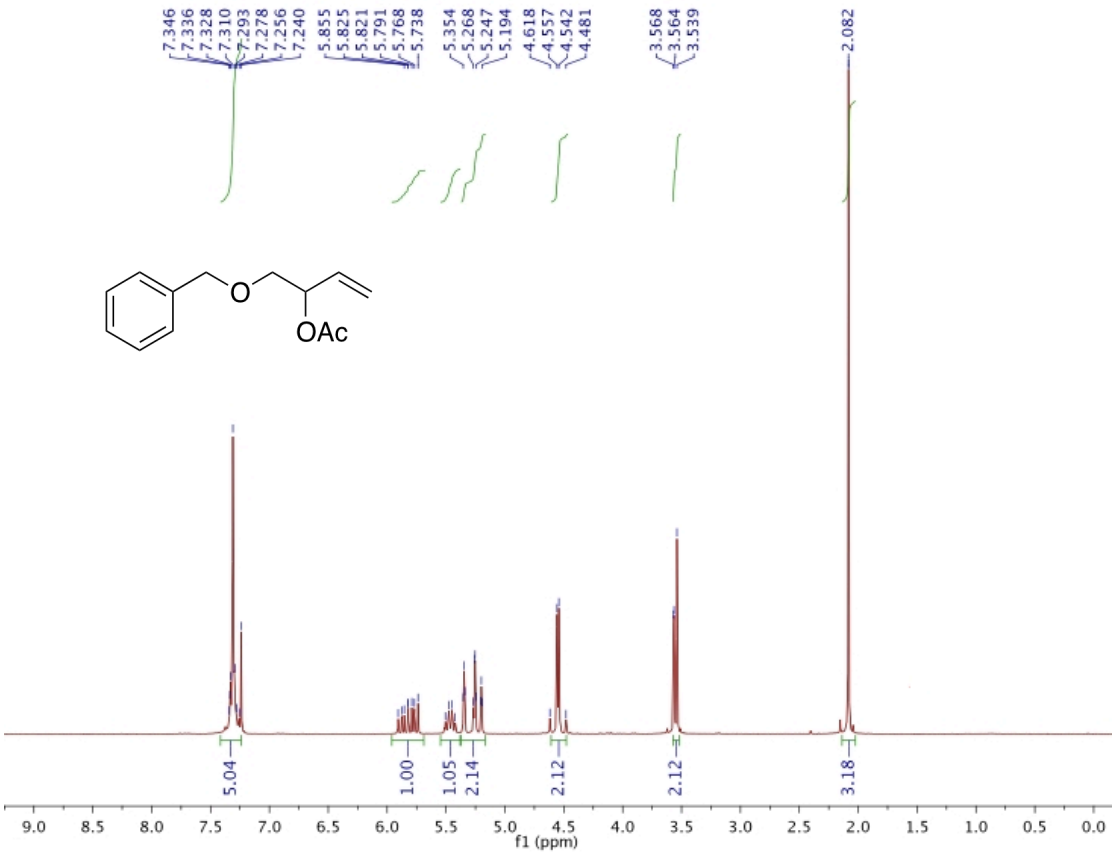


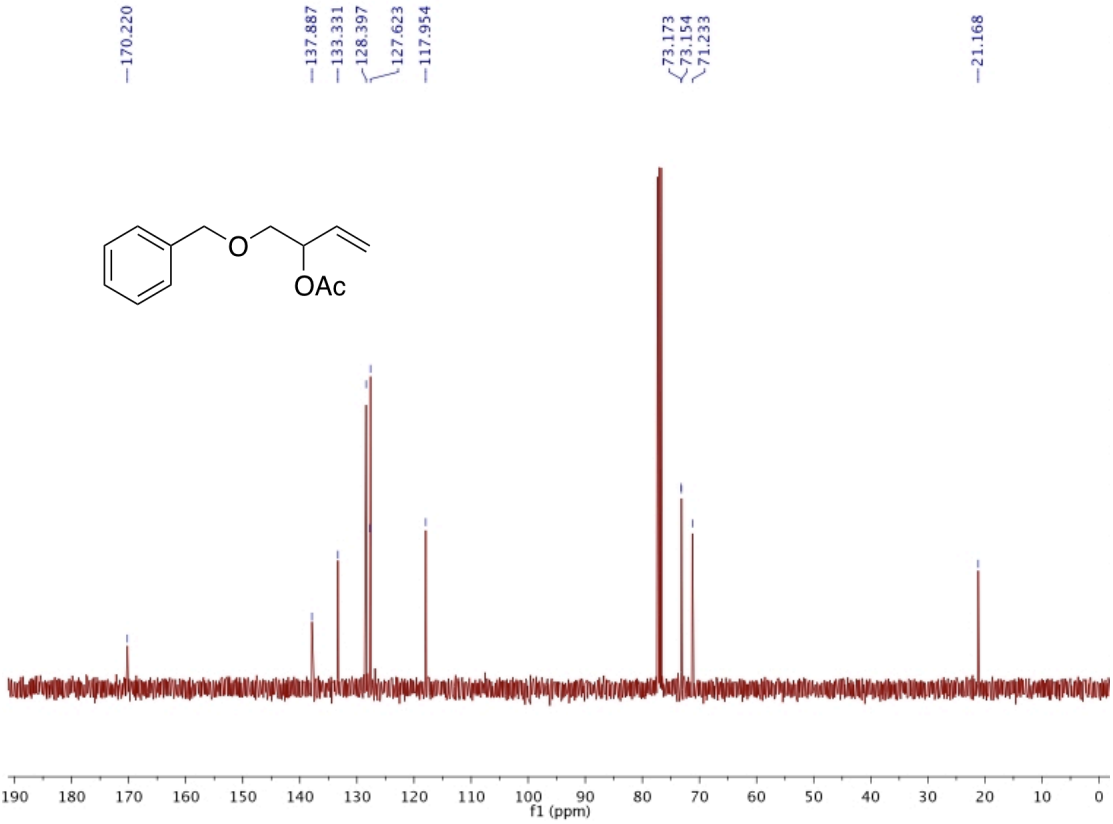
REFERENCE: Enantioenriched (*S*)-**2a (91% ee)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.867	VB	0.2260	4544.19336	311.93356	95.4448
2	8.118	BB	0.2460	216.87724	13.24431	4.5552
Totals :				4761.07060	325.17788	

8. NMR Spectra of novel compounds




170.220
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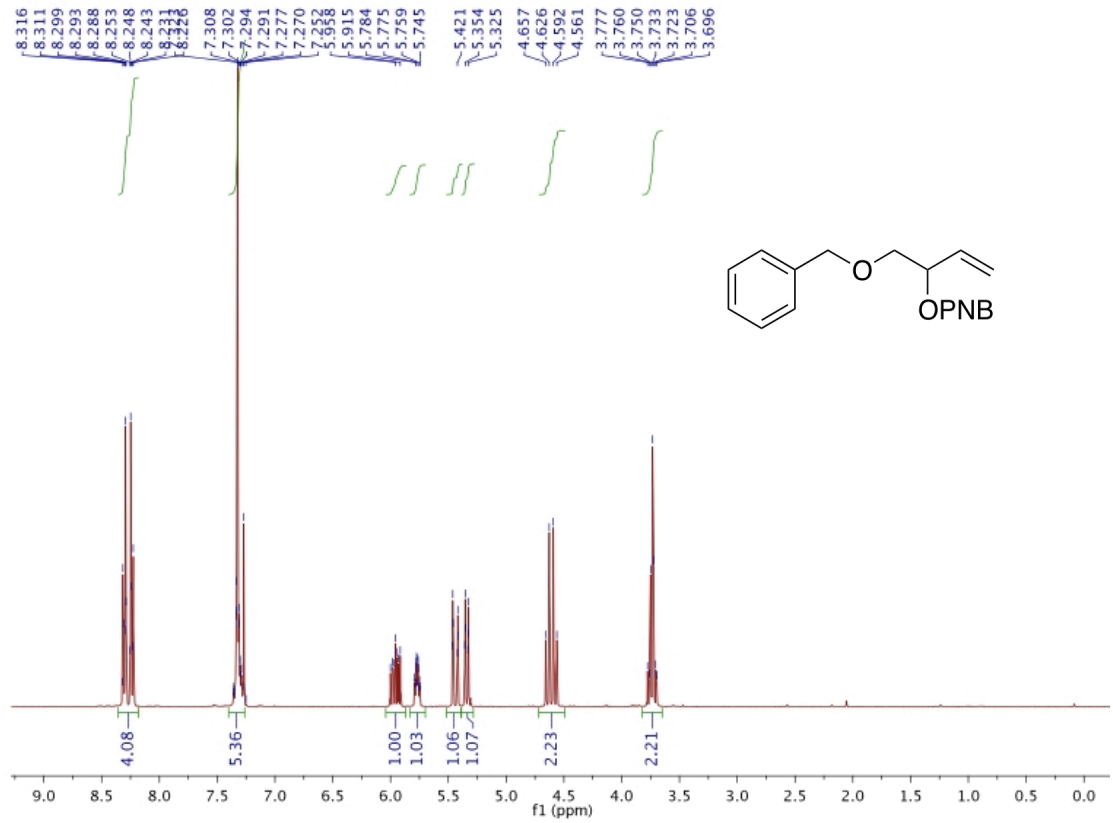
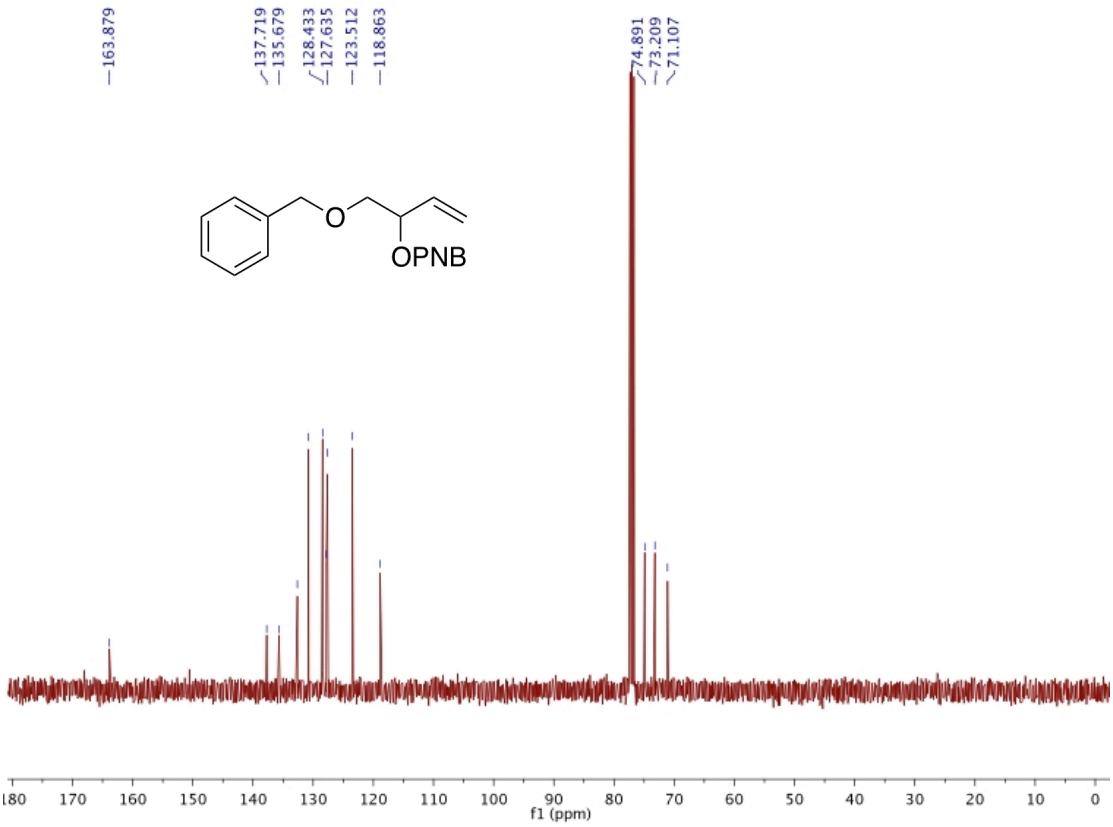
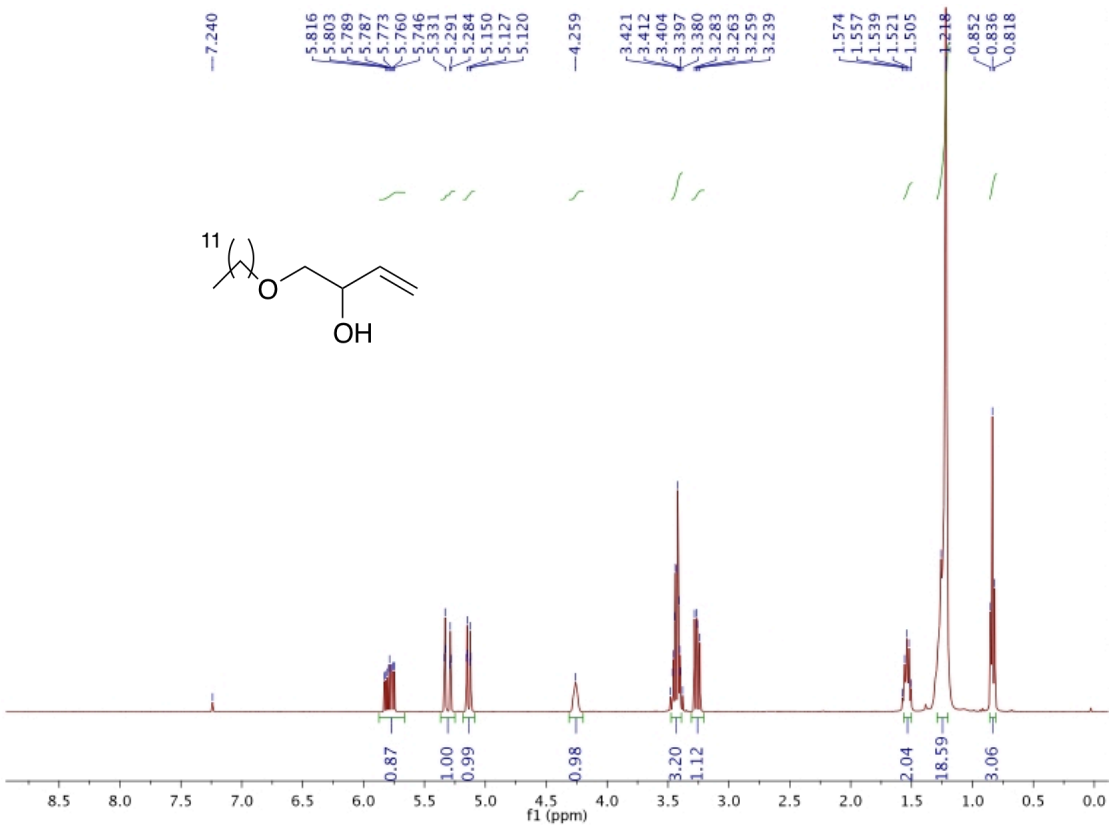
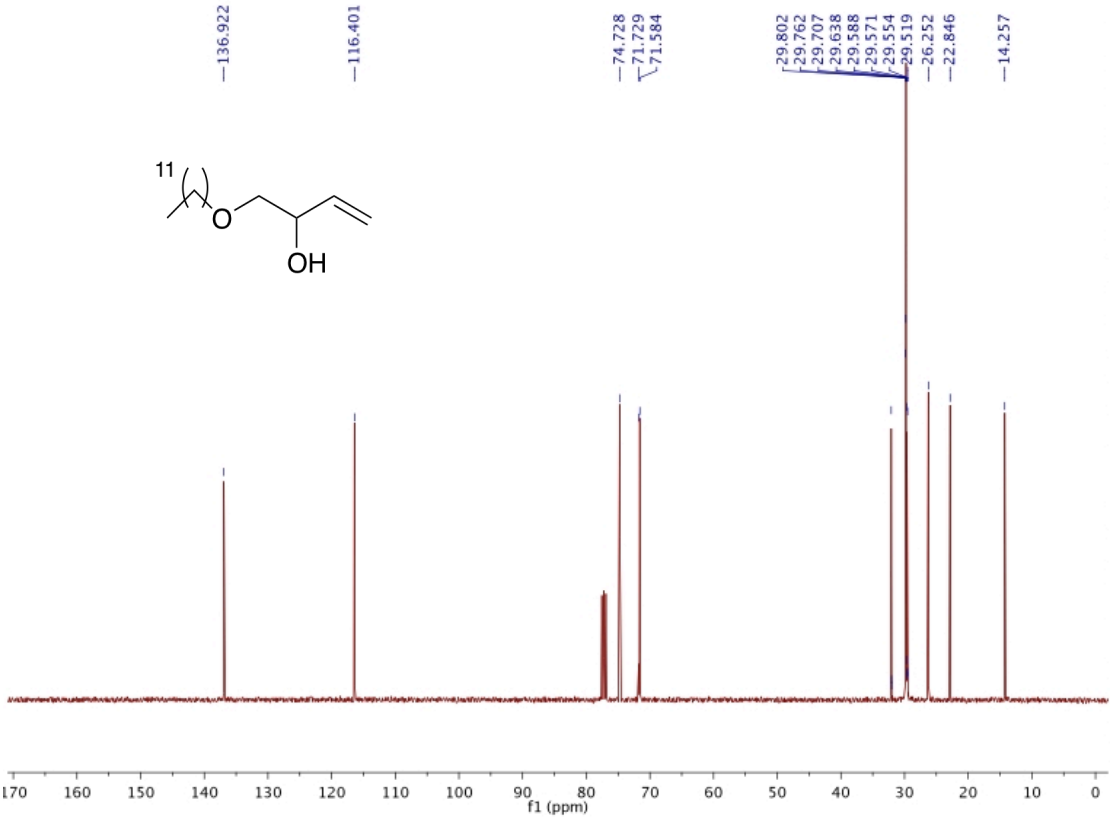
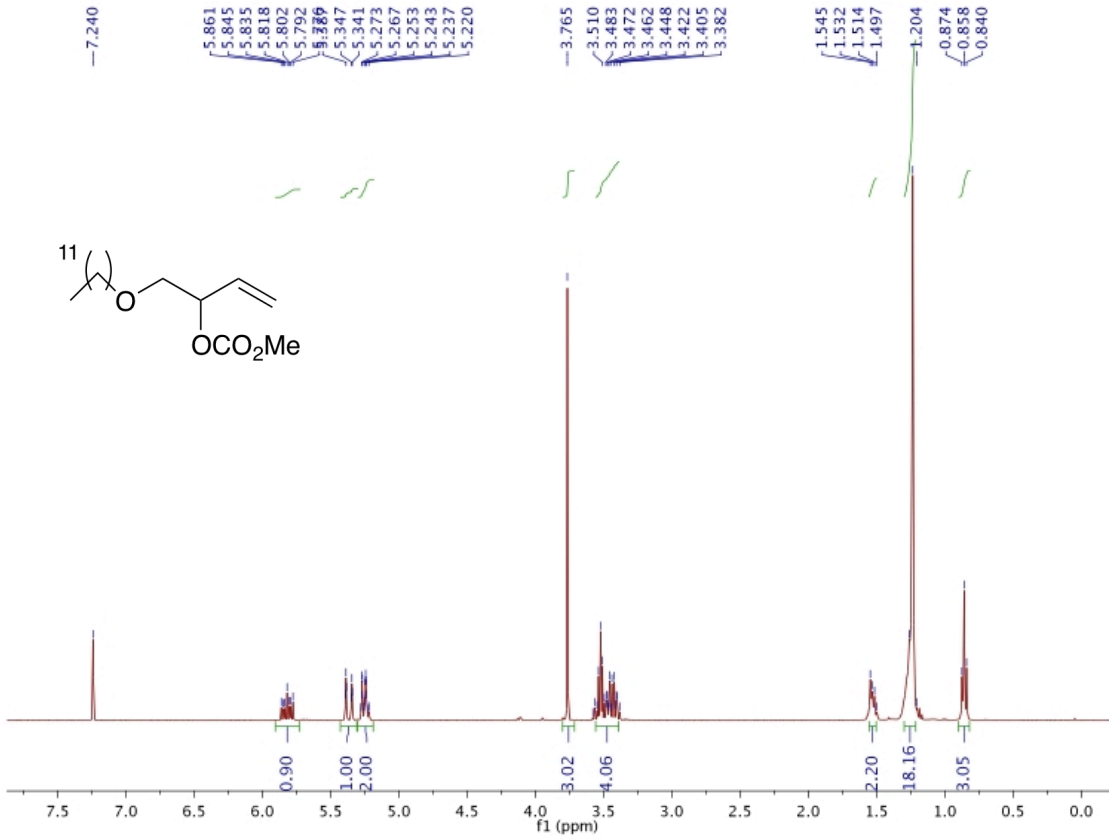
133.331
128.397
127.623
117.954
73.173
73.154
71.233
21.168
O
OAc
f1 (ppm)


8.316
8.311
8.299
8.293
8.288
8.253
8.248
8.243
7.308
7.302
7.294
7.291
7.277
7.270
5.958
5.915
5.784
5.775
5.759
5.745
5.421
5.354
5.325
4.657
4.626
4.592
4.561
3.777
3.760
3.750
3.733
3.723
3.706
3.696
O
OPNB
4.08
5.36
1.00
1.03
1.06
1.07
2.23
2.21
f1 (ppm)






136.922
116.401
74.728
71.729
71.584
29.802
29.762
29.707
29.638
29.588
29.571
29.554
29.519
26.252
22.846
14.257
11
O
OH
f1 (ppm)


7.240
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5.845
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5.818
5.802
5.792
5.347
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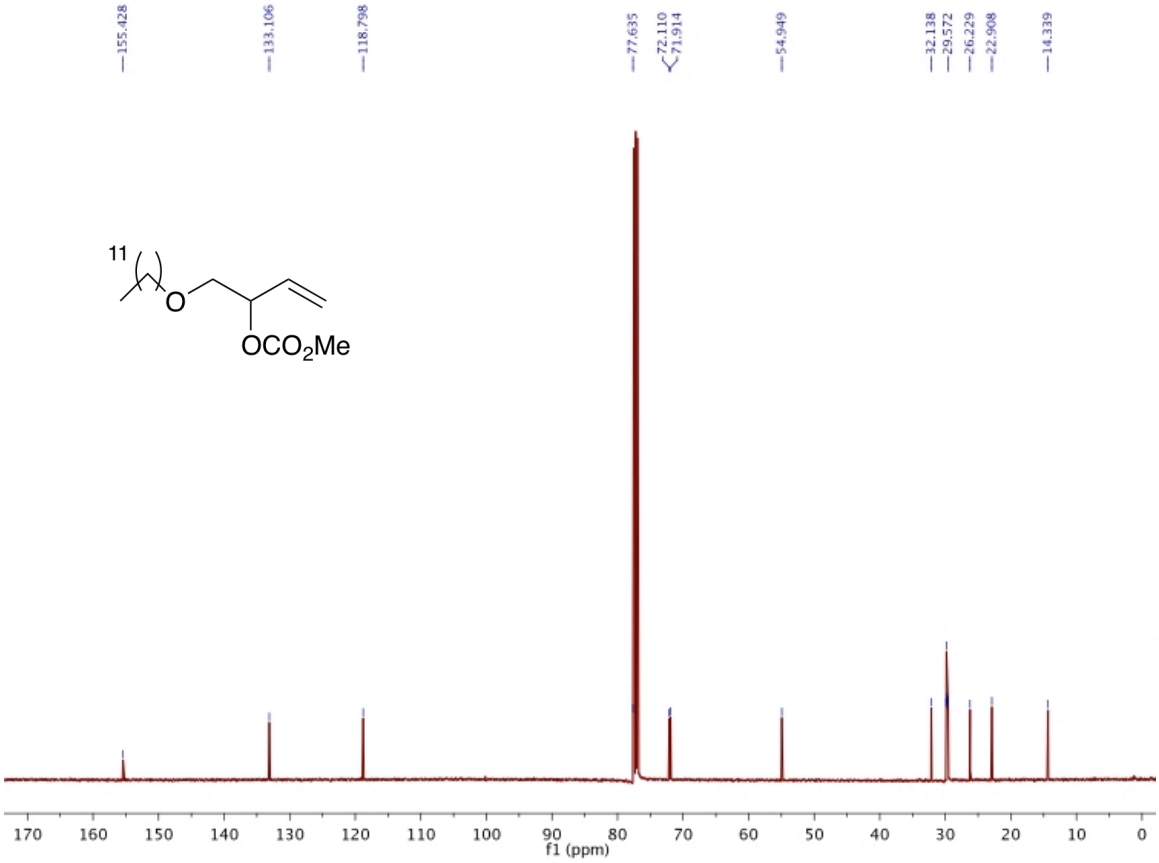
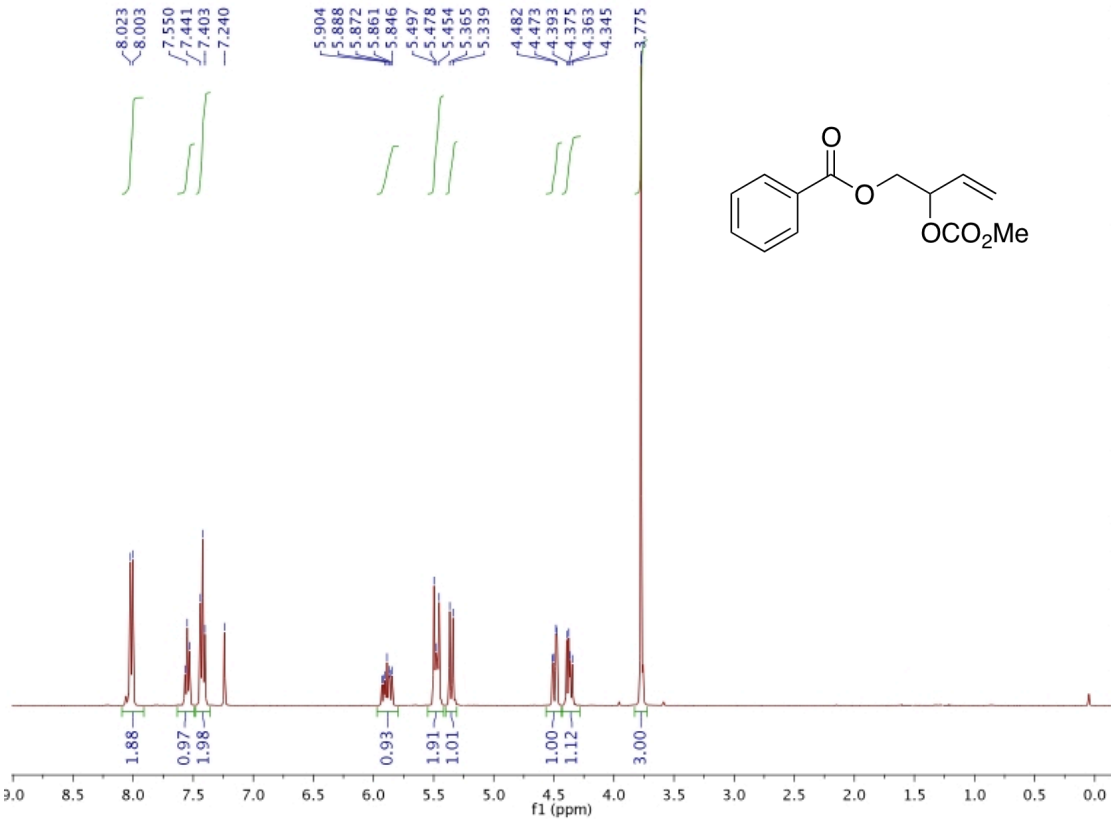
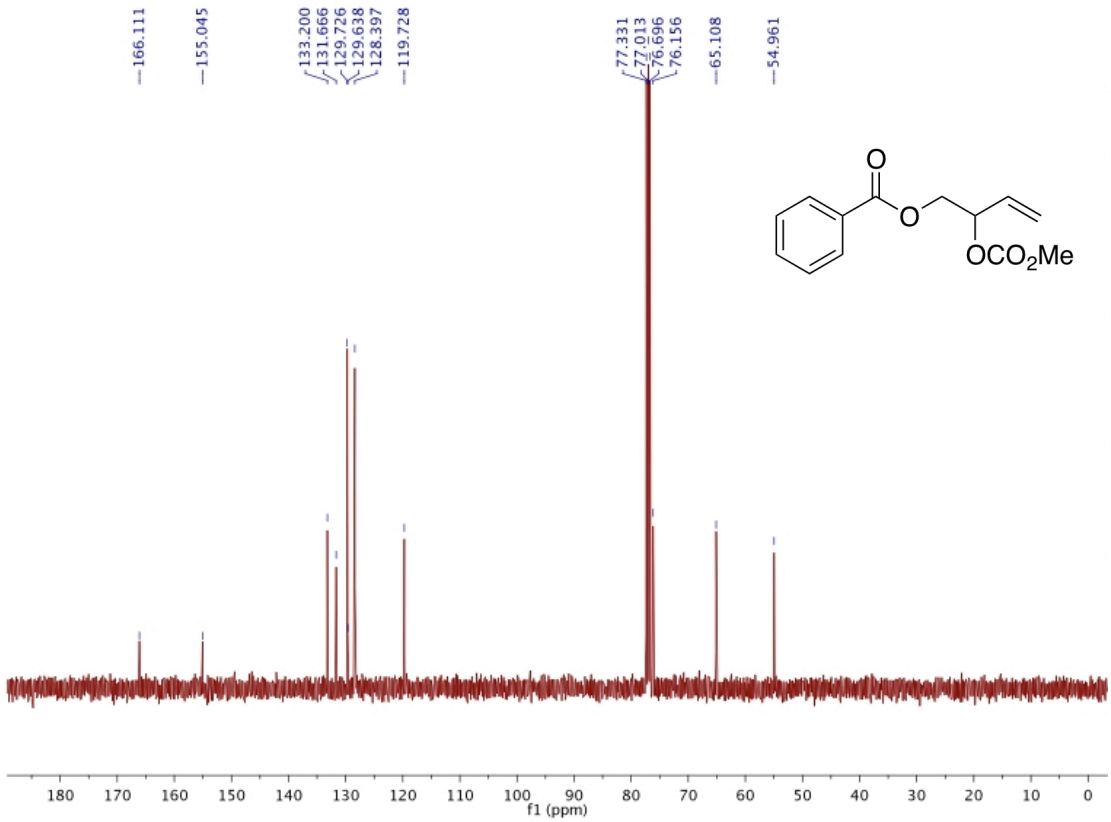
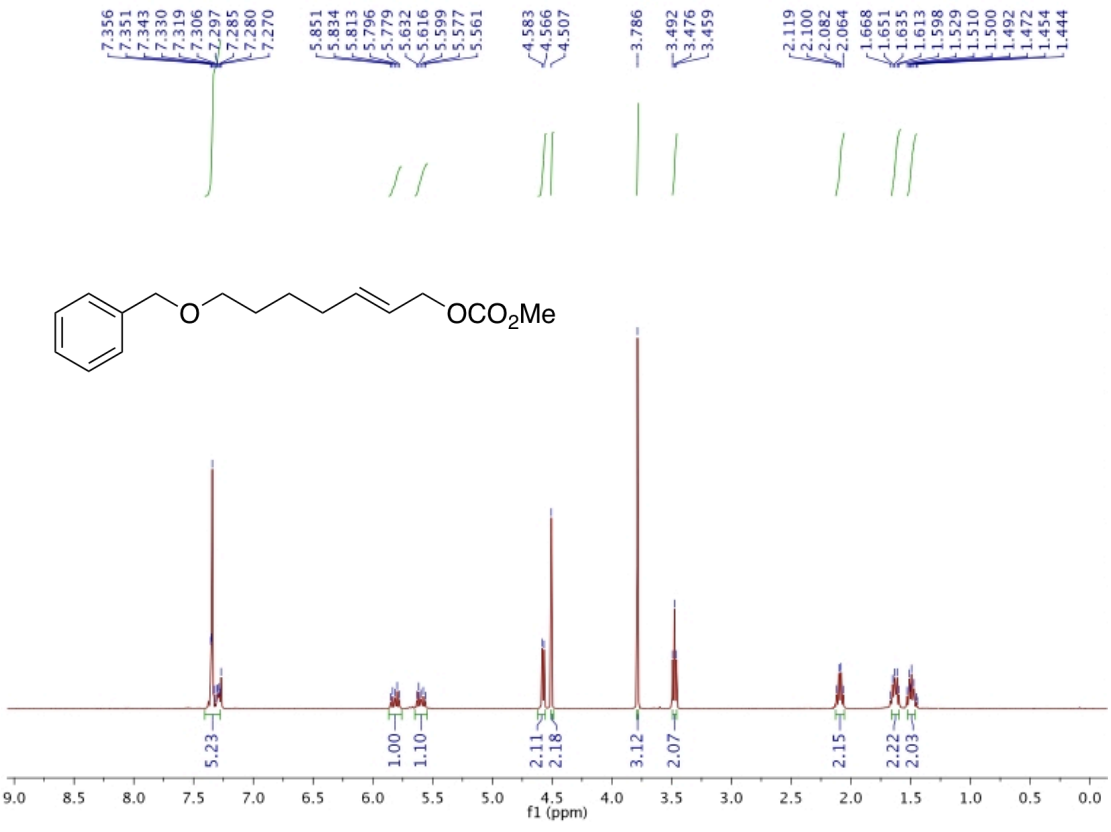
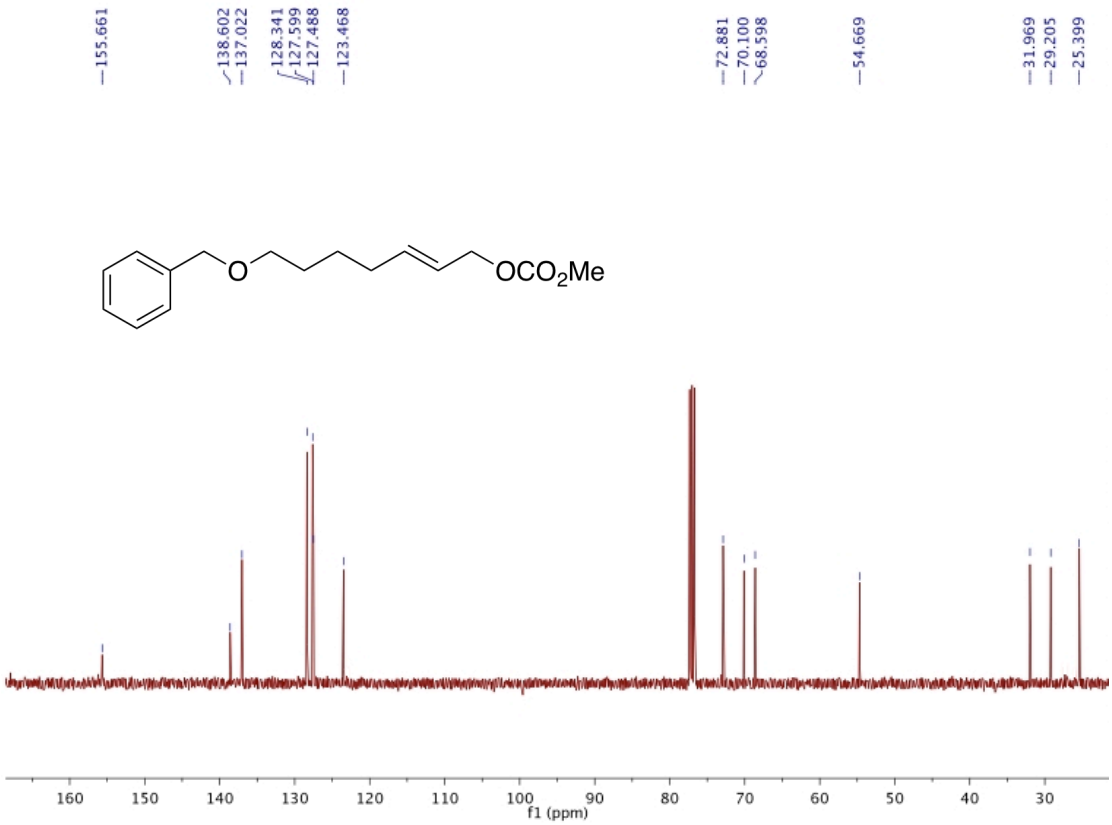
5.273
5.267
5.253
5.243
5.237
5.220
3.765
3.510
3.483
3.472
3.462
3.448
3.422
3.405
3.382
1.545
1.532
1.514
1.497
1.204
0.874
0.858
0.840
11
O
OCO2Me
0.90
1.00
2.00
3.02
4.06
2.20
18.16
3.05
f1 (ppm)

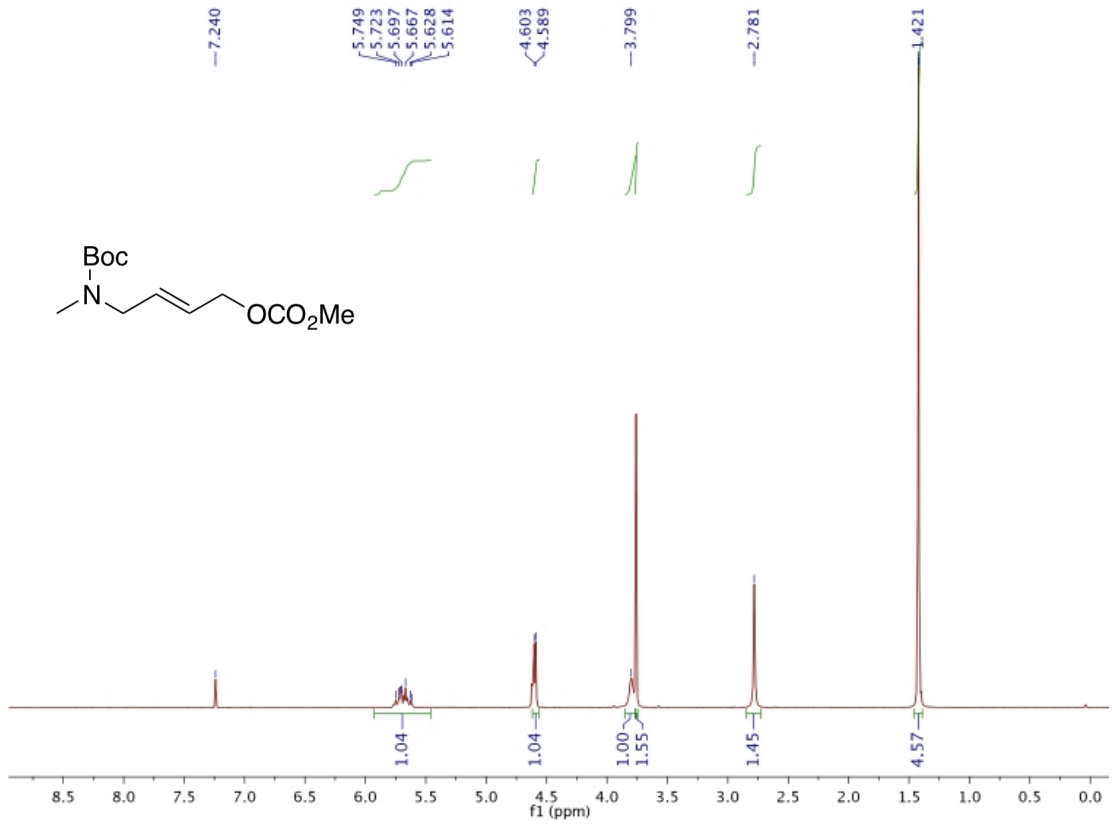

155.428
133.106
118.798
77.635
72.110
71.914
54.949
32.138
29.572
26.229
22.908
14.339
11
O
OCO2Me
f1 (ppm)

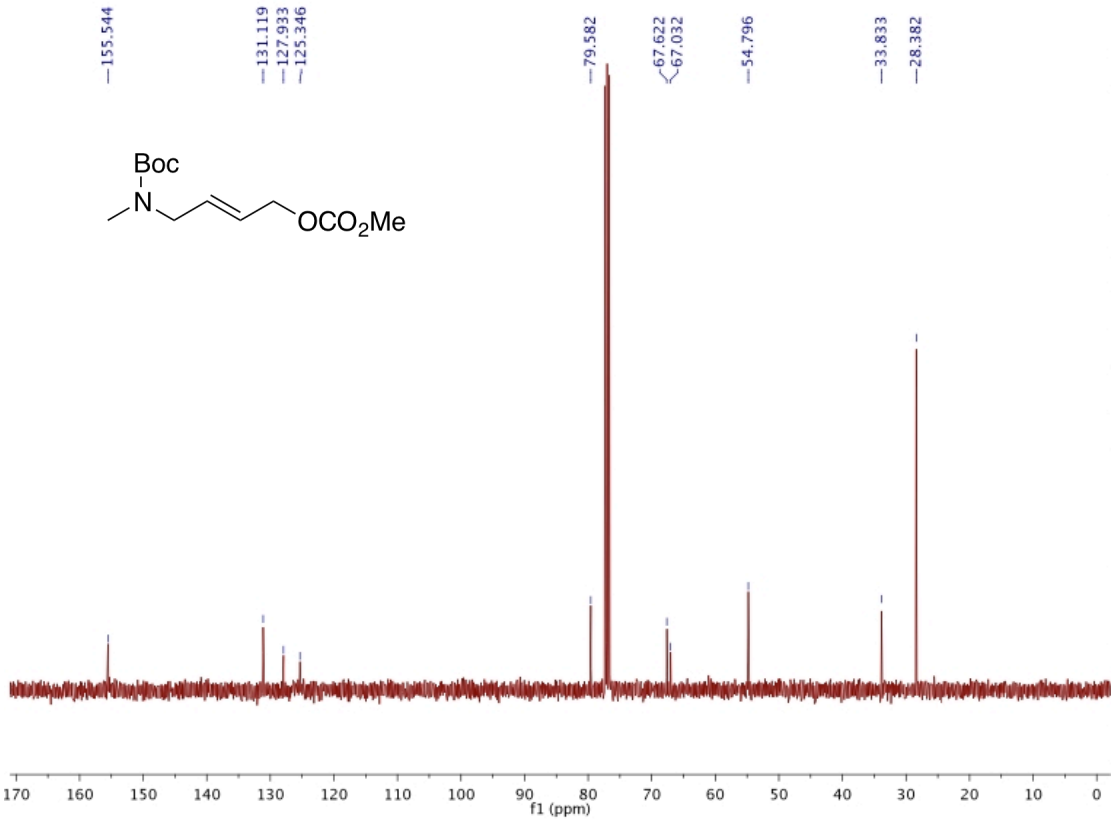

8.023
8.003
7.550
7.441
7.403
7.240
5.904
5.888
5.872
5.861
5.846
5.497
5.478
5.454
5.365
5.339
4.482
4.473
4.393
4.375
4.363
4.345
3.775
O
O
OCO2Me
1.88
0.97
1.98
0.93
1.91
1.01
1.00
1.12
3.00
f1 (ppm)

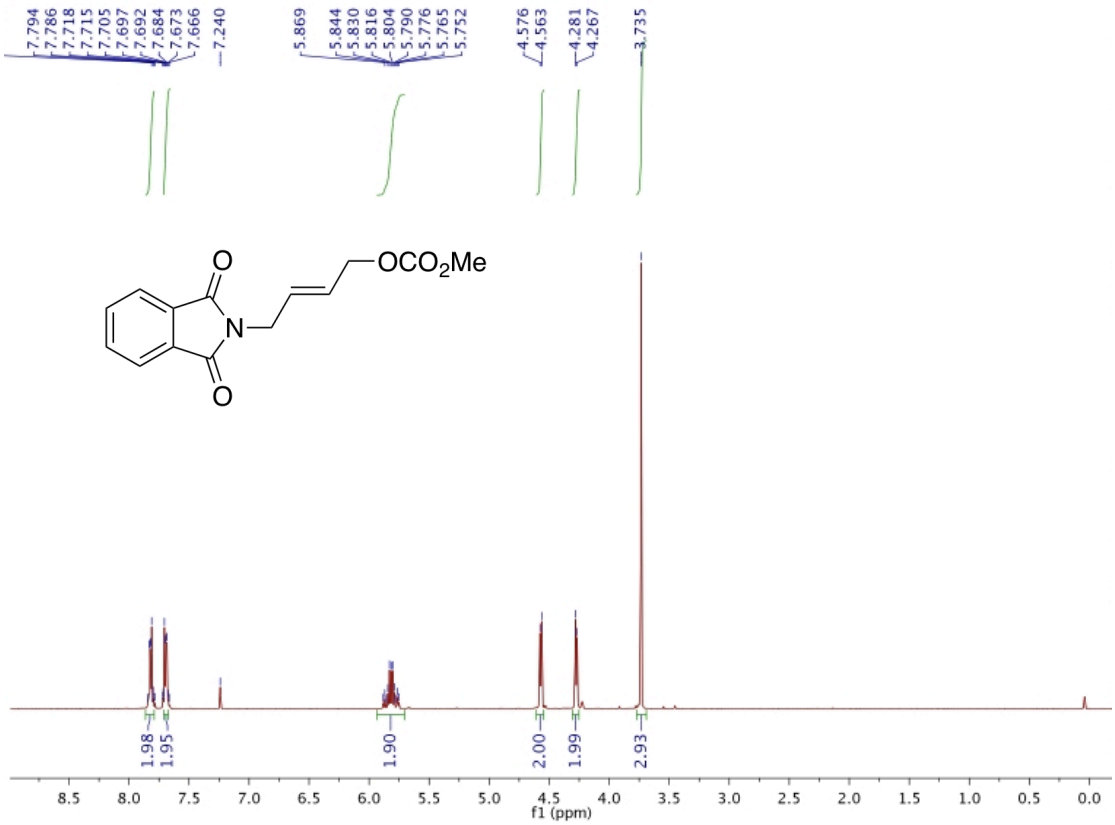

166.111
155.045
133.200
131.666
129.726
129.638
128.397
119.728
77.331
77.013
76.696
76.156
65.108
54.961
O
O
OCO2Me
f1 (ppm)

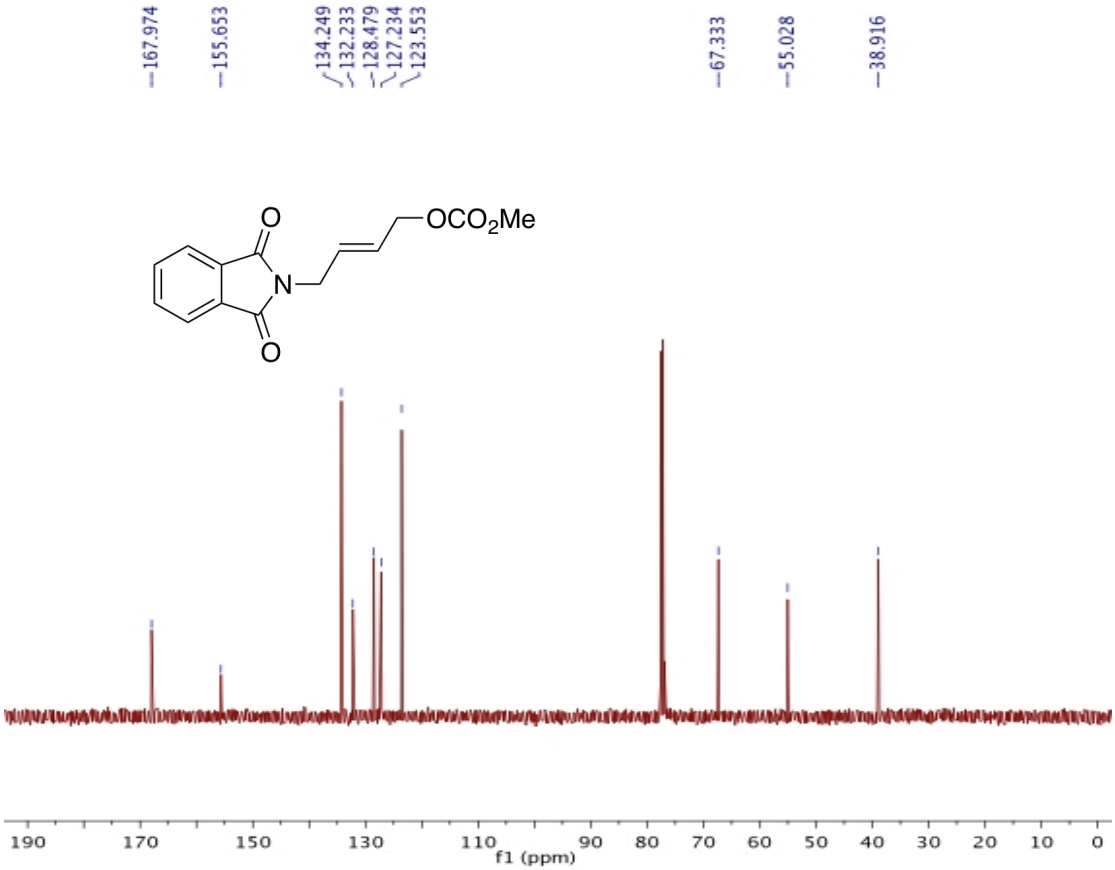

7.356
7.351
7.343
7.330
7.319
7.306
7.297
7.285
7.280
7.270
5.851
5.834
5.813
5.796
5.779
5.632
5.616
5.599
5.577
5.561
4.583
4.566
4.507
3.786
3.492
3.476
3.459
2.119
2.100
2.082
2.064
1.668
1.651
1.635
1.613
1.598
1.529
1.510
1.500
1.492
1.472
1.454
1.444
O
OCO2Me
5.23
1.00
1.10
2.11
2.18
3.12
2.07
2.15
2.22
2.03
f1 (ppm)

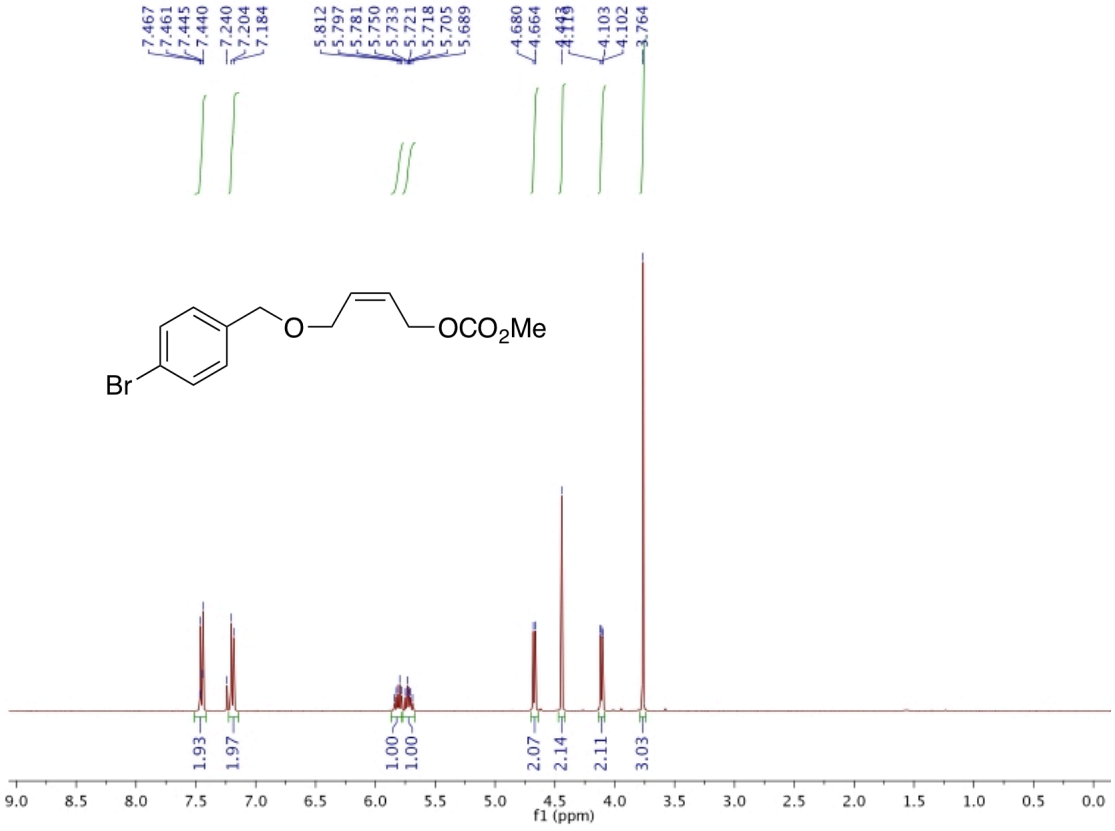

155.661
138.602
137.022
128.341
127.599
127.488
123.468
72.881
70.100
68.598
54.669
31.969
29.205
25.399
O
OCO2Me
f1 (ppm)

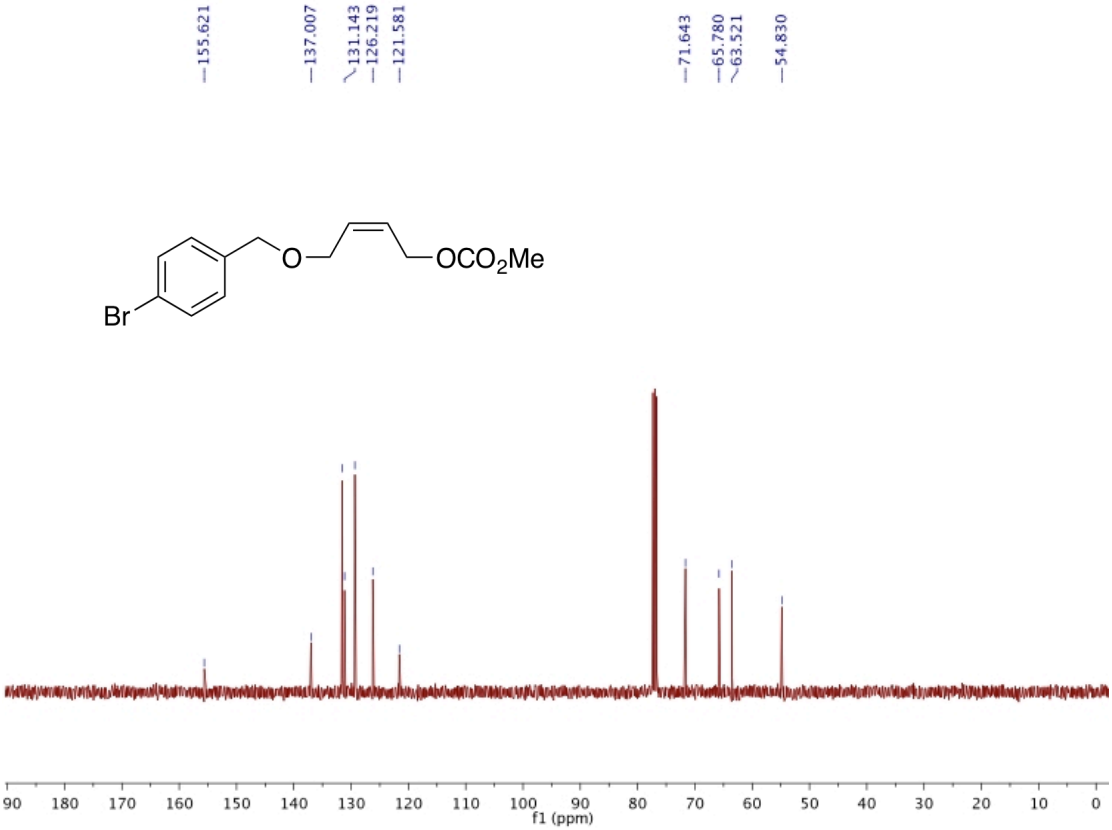

7.240
5.749
5.723
5.697
5.667
5.628
5.614
4.603
4.589
3.799
2.781
1.421
Boc
N
OCO2Me
1.04
1.04
1.00
1.55
1.45
4.57
f1 (ppm)

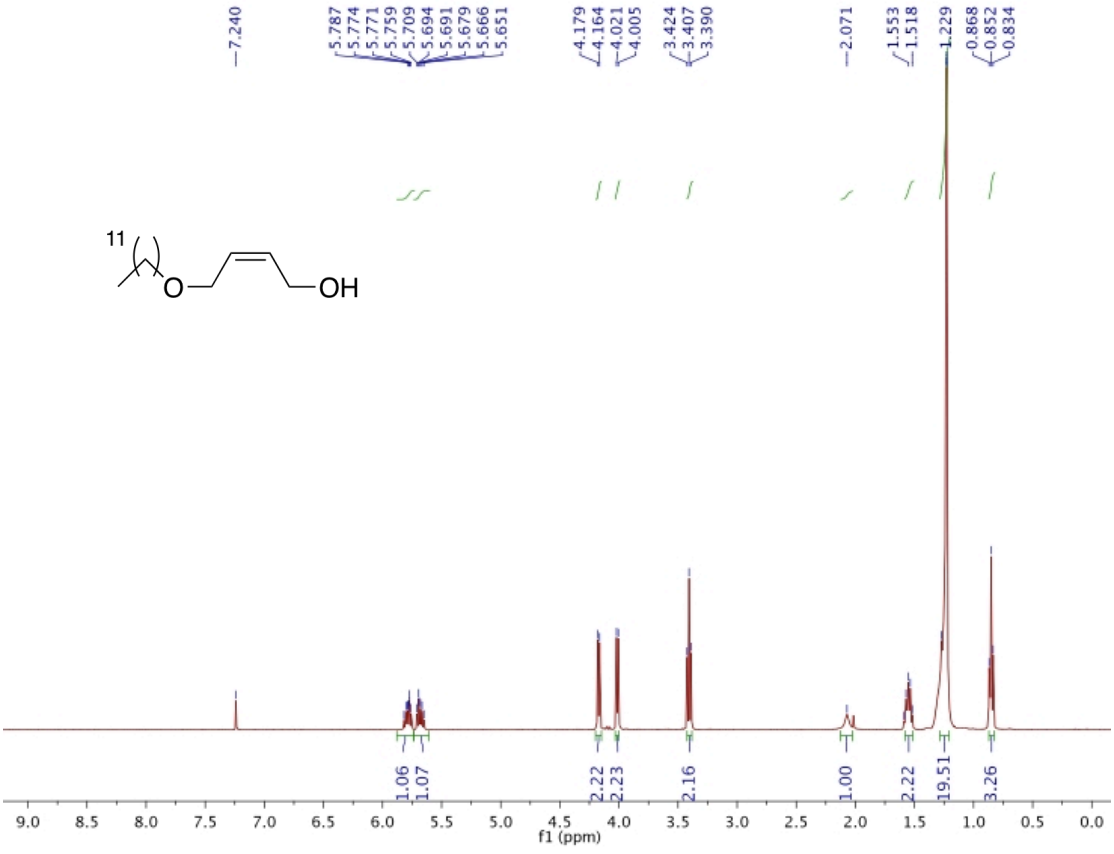

155.544
131.119
127.933
125.346
79.582
67.622
67.032
54.796
33.833
28.382
Boc
N
OCO2Me
f1 (ppm)


7.794
7.786
7.718
7.715
7.705
7.697
7.692
7.684
7.673
7.666
7.240
5.869
5.844
5.830
5.816
5.804
5.790
5.776
5.765
5.752
4.576
4.563
4.281
4.267
3.735
O
N
O
OCO2Me
1.98
1.95
1.90
2.00
1.99
2.93
f1 (ppm)






155.621
137.007
131.143
126.219
121.581
71.643
65.780
63.521
54.830
Br
O
OCO2Me
f1 (ppm)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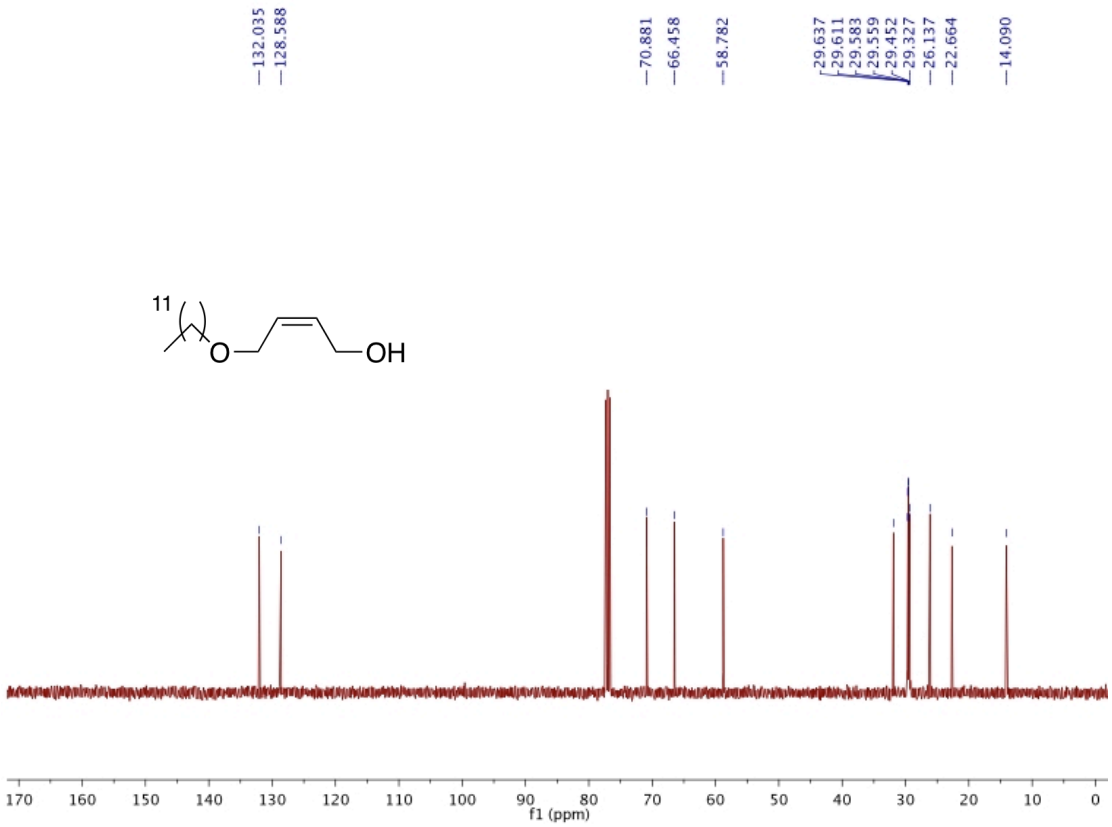
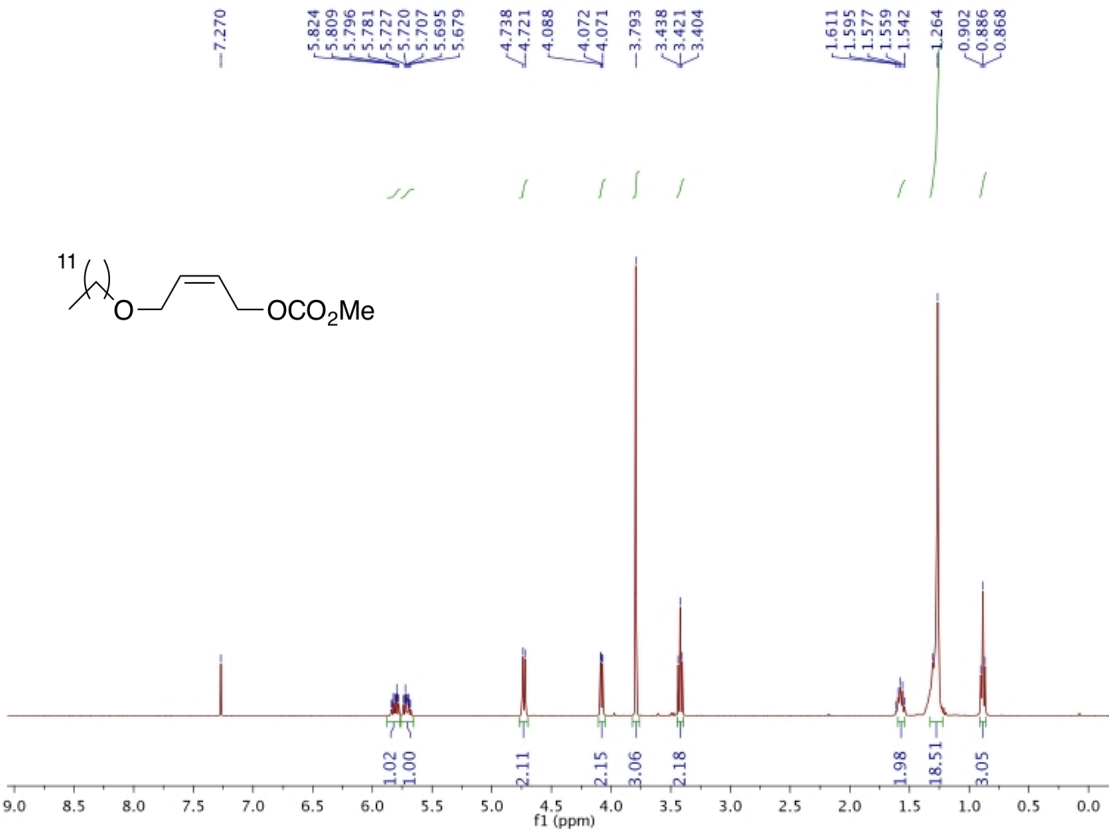
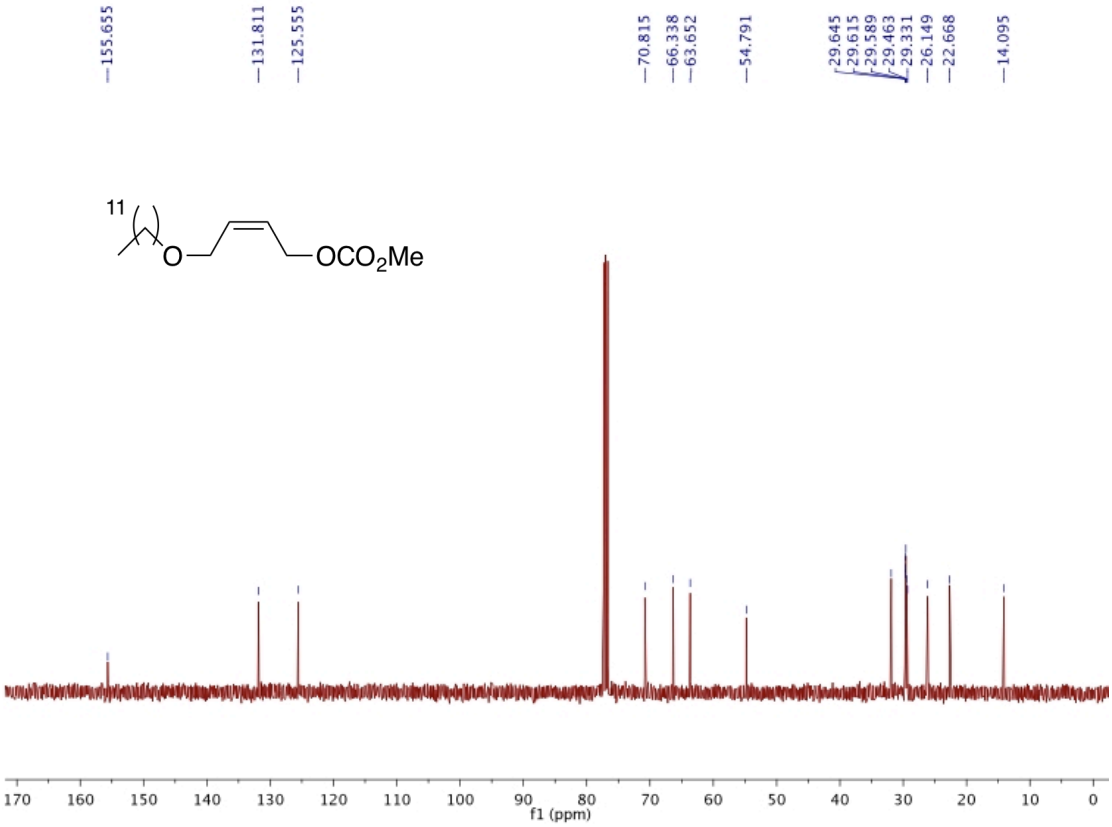
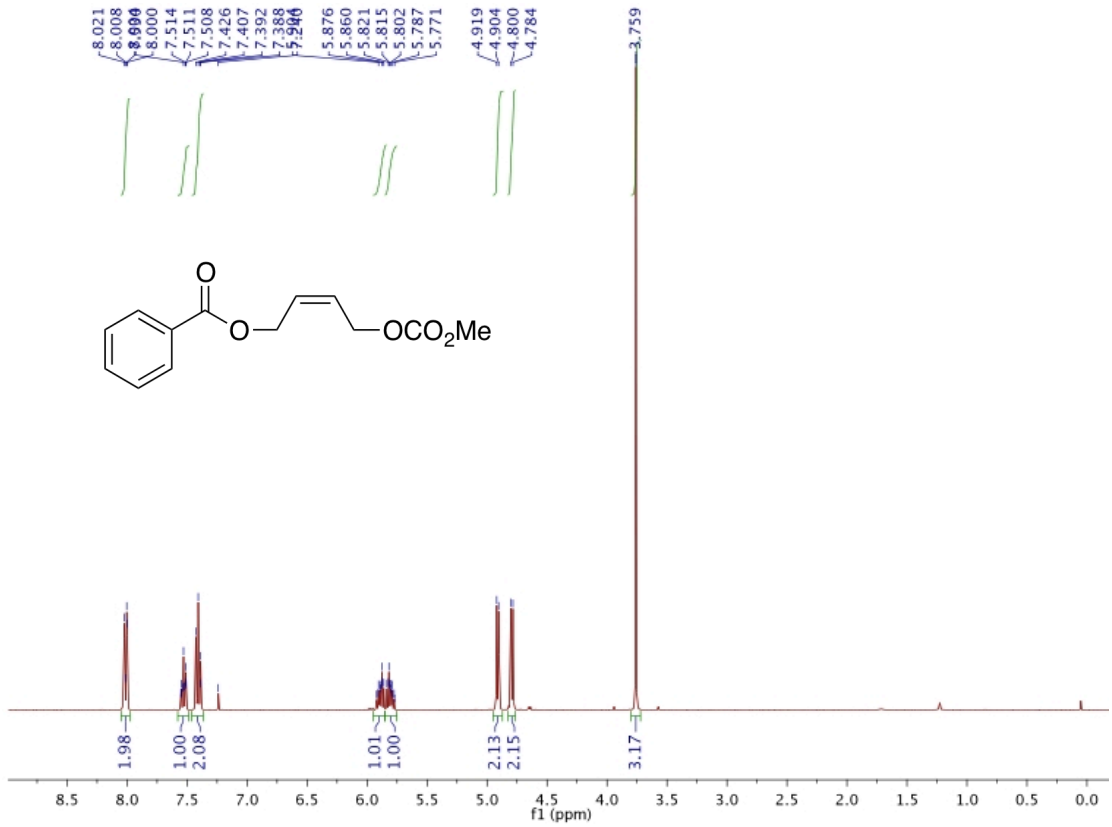
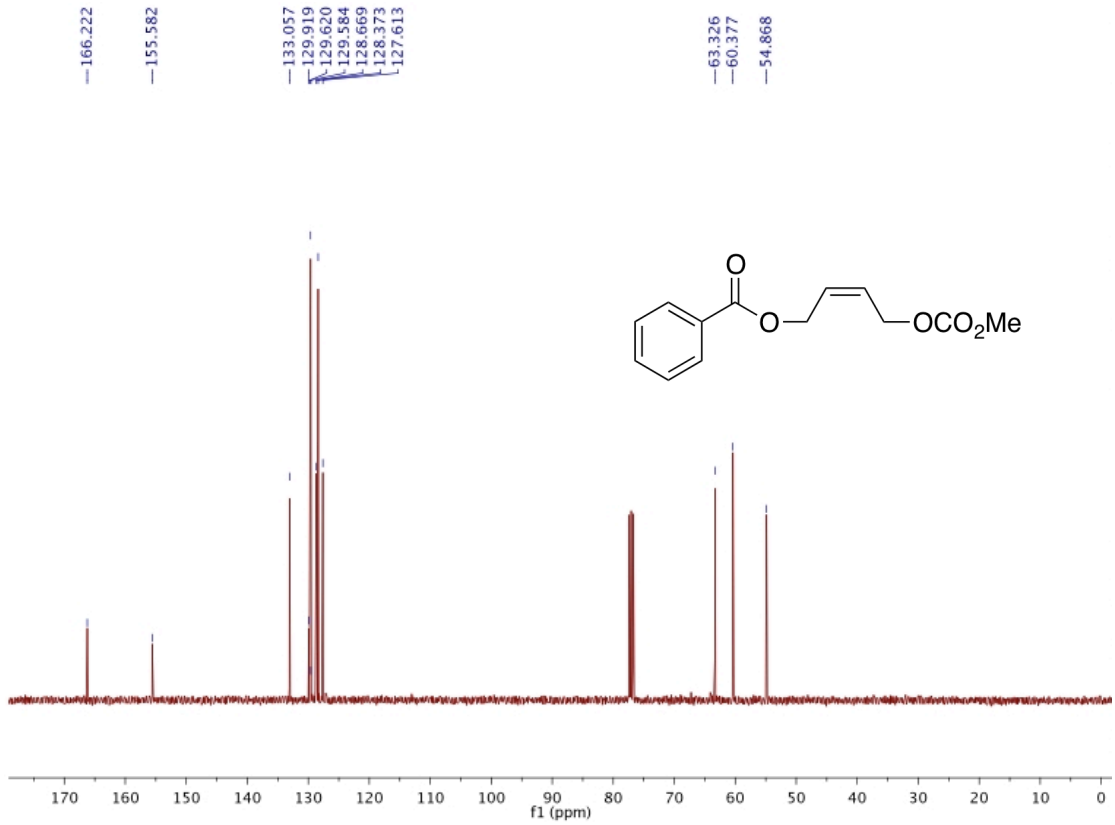
5.787
5.774
5.771
5.759
5.709
5.694
5.691
5.679
5.666
5.651
4.179
4.164
4.021
4.005
3.424
3.407
3.390
2.071
1.553
1.518
1.229
0.868
0.852
0.834
11
O
OH
1.06
1.07
2.22
2.23
2.16
1.00
2.22
19.51
3.26
f1 (ppm)

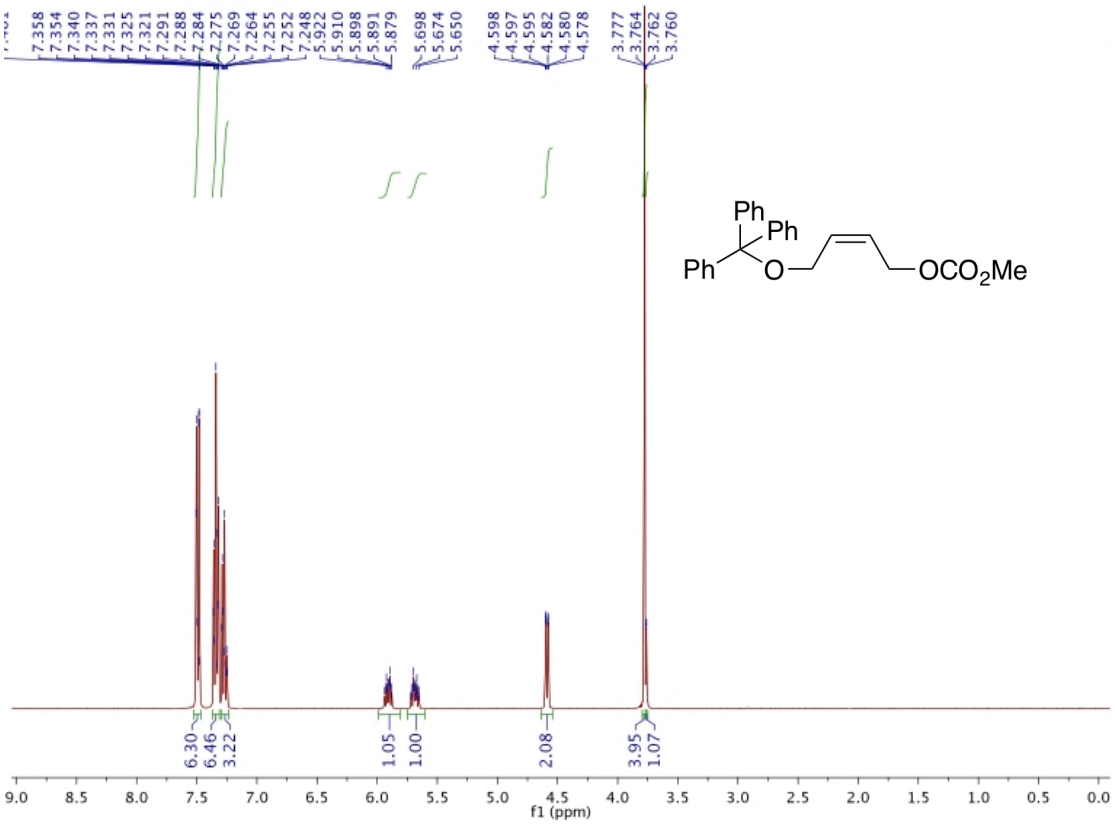









166.222
155.582
133.057
129.919
129.620
129.584
128.669
128.373
127.613
63.326
60.377
54.868
O
O
OCO2Me
f1 (ppm)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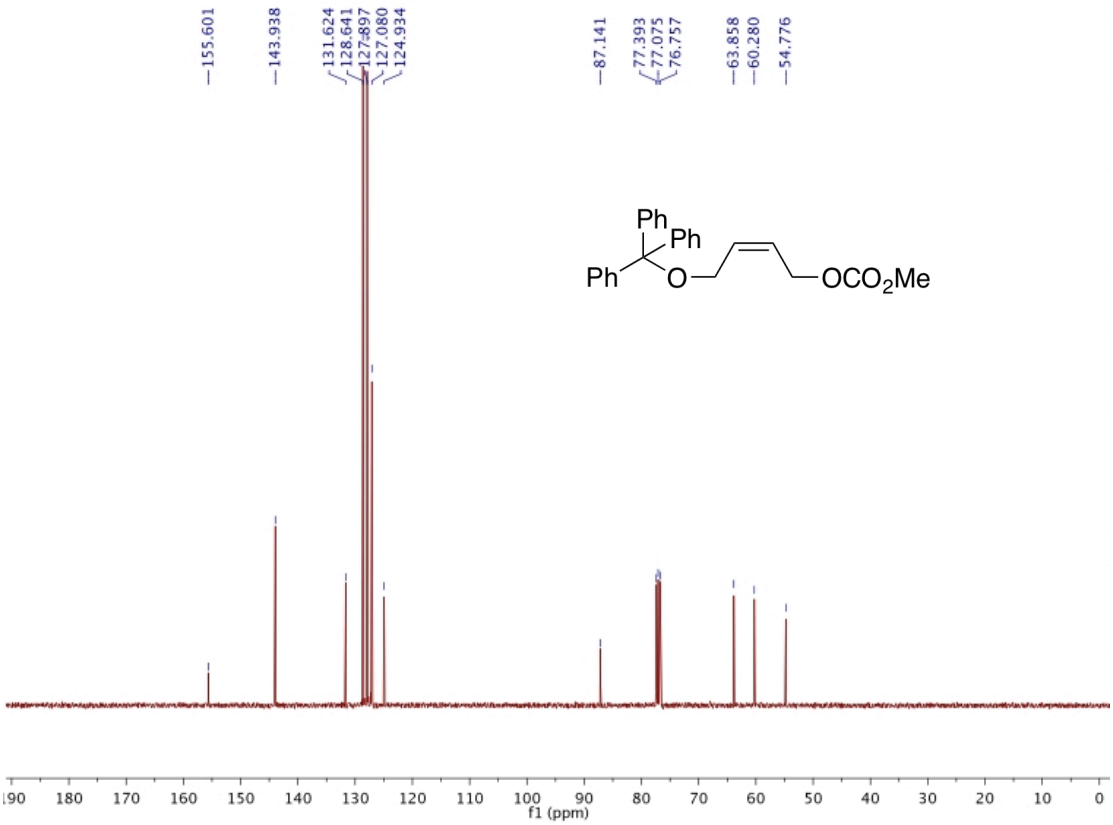
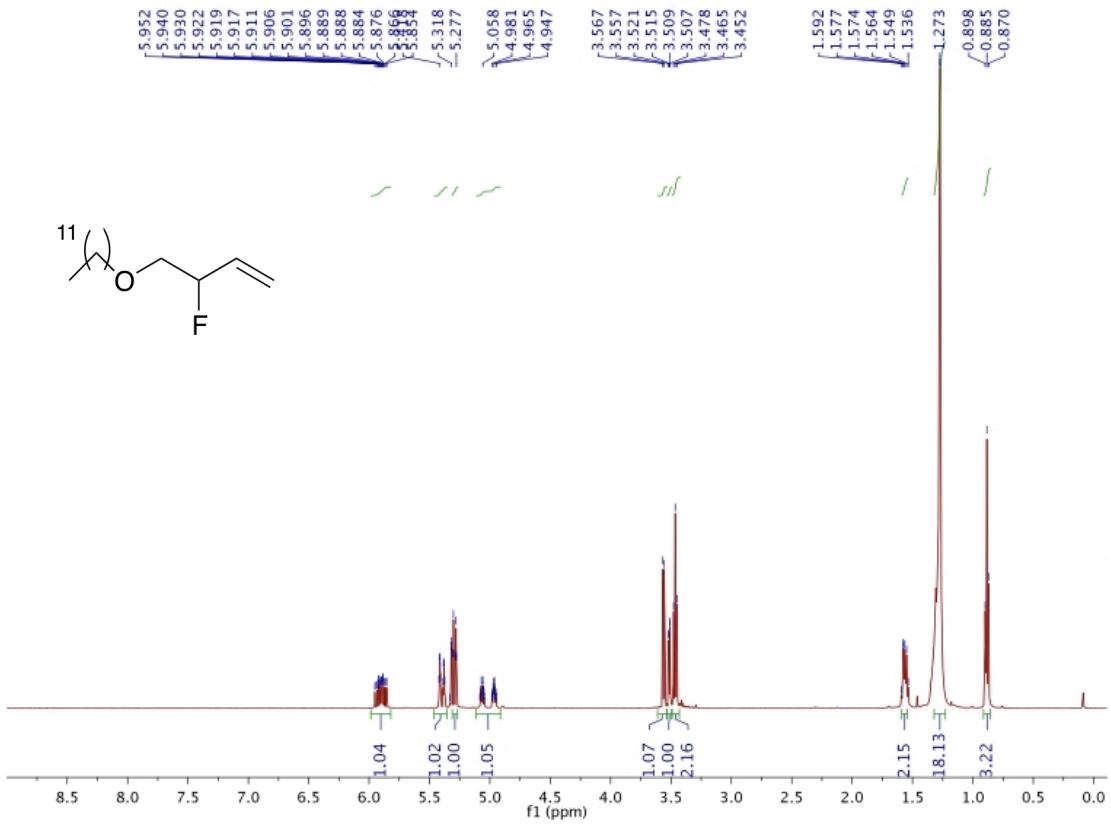
7.354
7.340
7.337
7.331
7.325
7.321
7.291
7.288
7.284
7.275
7.269
7.264
7.255
7.252
7.248
5.922
5.910
5.898
5.891
5.879
5.698
5.674
5.650
4.598
4.597
4.595
4.582
4.580
4.578
3.777
3.764
3.762
3.760
Ph
Ph
Ph
O
OCO2Me
6.30
6.46
3.22
1.05
1.00
2.08
3.95
1.07
f1 (ppm)


155.601
143.938
131.624
128.641
127.897
127.080
124.934
87.141
77.393
77.075
76.757
63.858
60.280
54.776
Ph
Ph
Ph
O
OCO2Me
f1 (ppm)

: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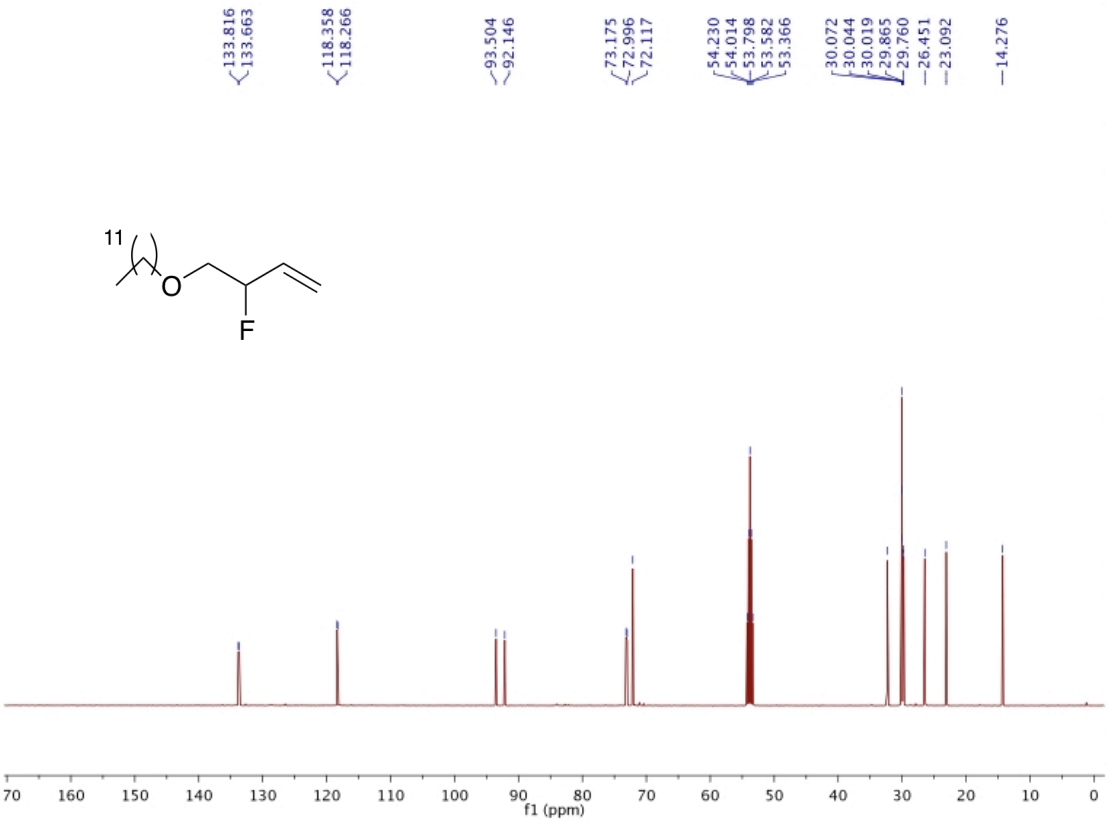
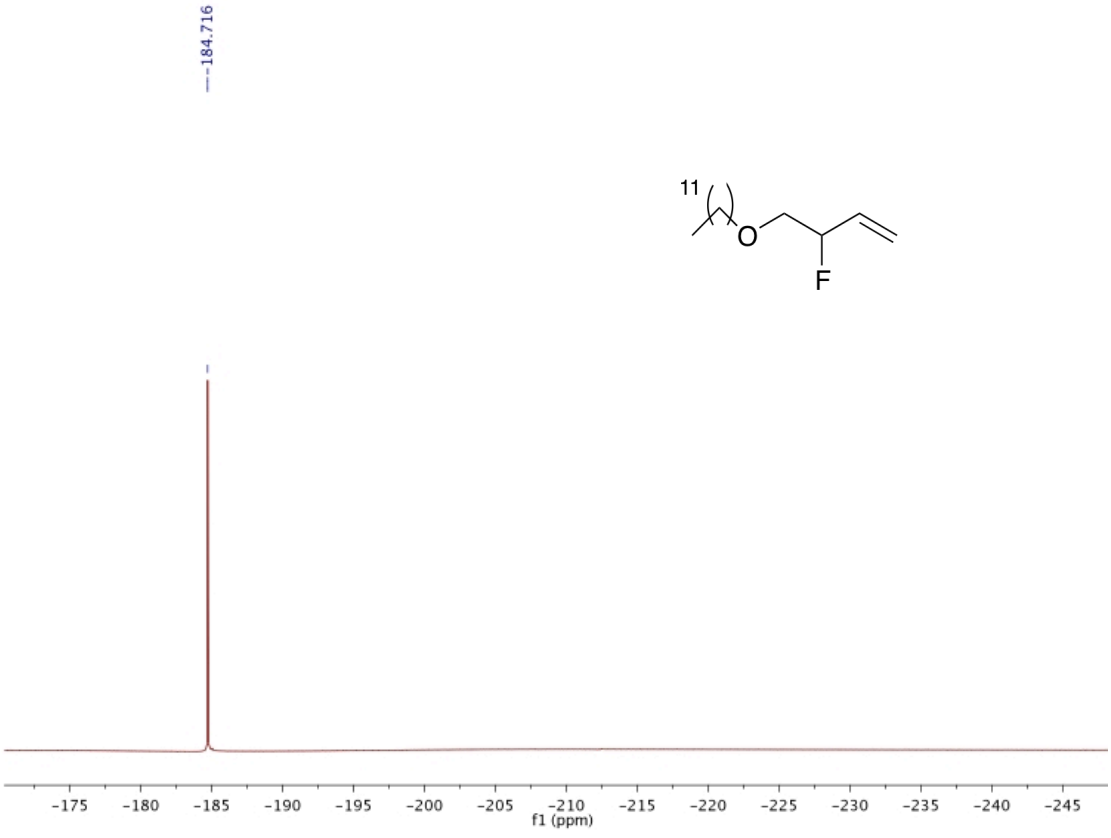
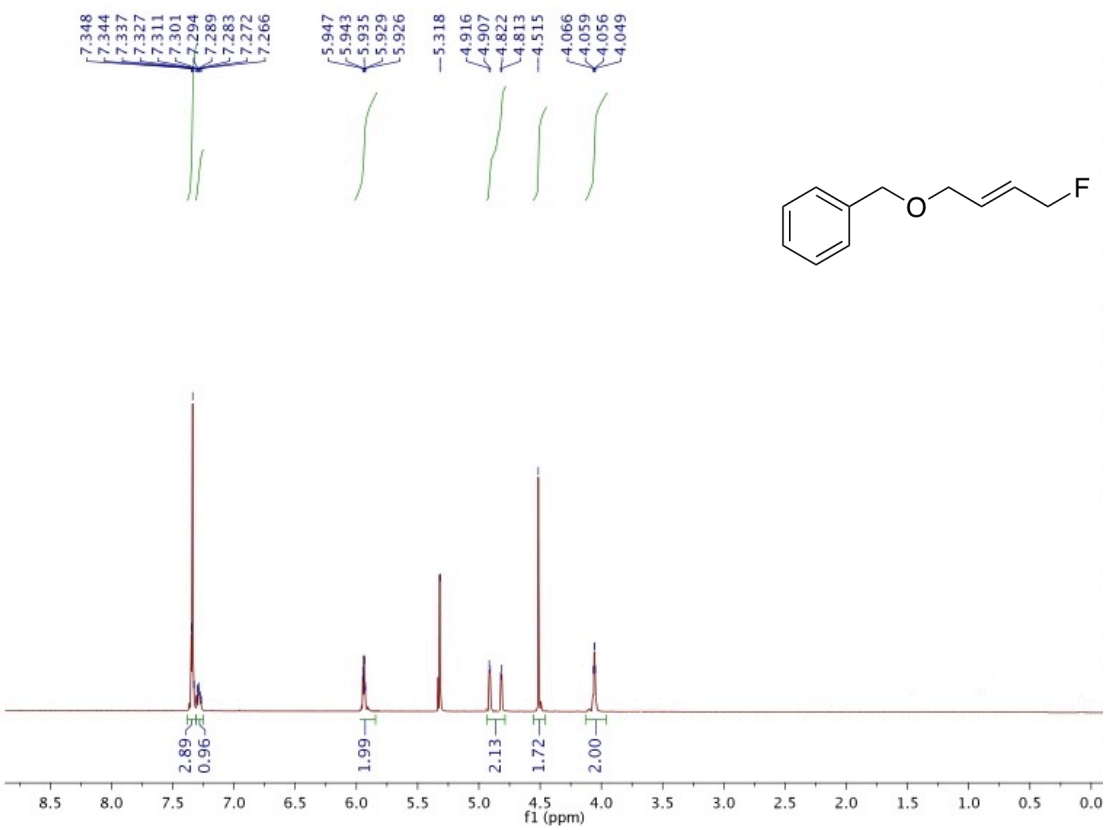
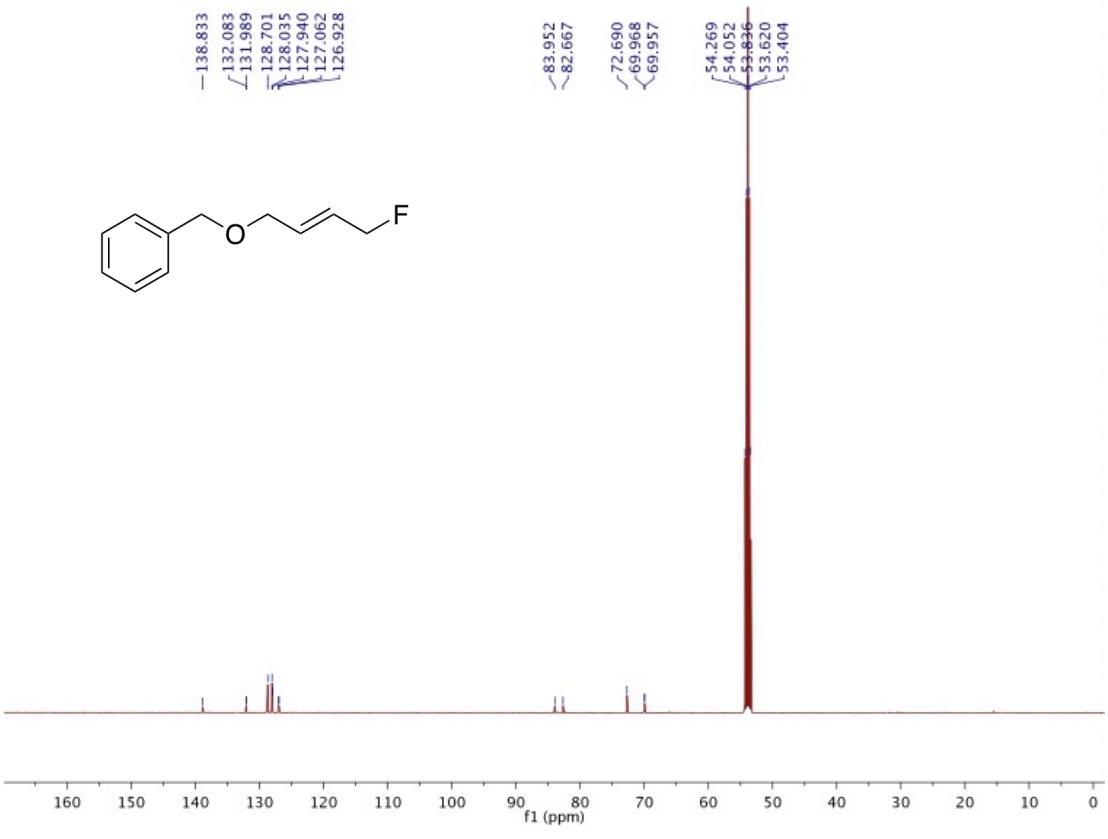
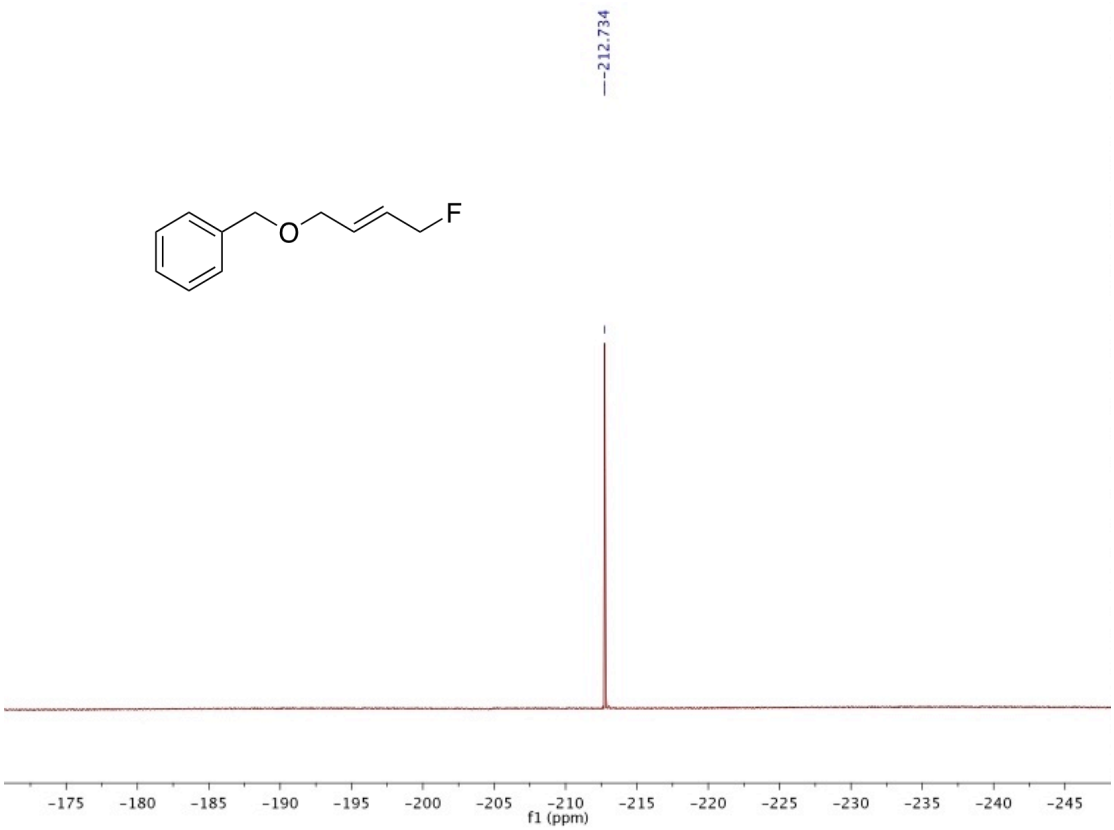
5.940
5.930
5.922
5.919
5.917
5.911
5.906
5.901
5.896
5.889
5.888
5.884
5.876
5.318
5.277
5.058
4.981
4.965
4.947
3.567
3.557
3.521
3.515
3.509
3.507
3.478
3.465
3.452
1.592
1.577
1.574
1.564
1.549
1.536
1.273
0.898
0.885
0.870
11
O
F
1.04
1.02
1.00
1.05
1.07
1.00
2.16
2.15
18.13
3.22
f1 (ppm)






7.348
7.344
7.337
7.327
7.311
7.301
7.294
7.289
7.283
7.272
7.266
5.947
5.943
5.935
5.929
5.926
5.318
4.916
4.907
4.822
4.813
4.515
4.066
4.059
4.056
4.049
O
F
2.89
0.96
1.99
2.13
1.72
2.00
f1 (ppm)


138.833
132.083
131.989
128.701
128.035
127.940
127.062
126.928
83.952
82.667
72.690
69.968
69.957
54.269
54.052
53.836
53.620
53.404
O
F
f1 (ppm)


-212.734
O
F
-175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245
f1 (ppm)


7.365
7.346
7.340
7.332
7.297
7.290
7.275
5.821
5.805
5.739
5.723
5.704
5.700
5.684
5.662
5.646
4.847
4.831
4.729
4.713
4.477
3.493
3.478
3.462
2.147
2.131
2.114
2.097
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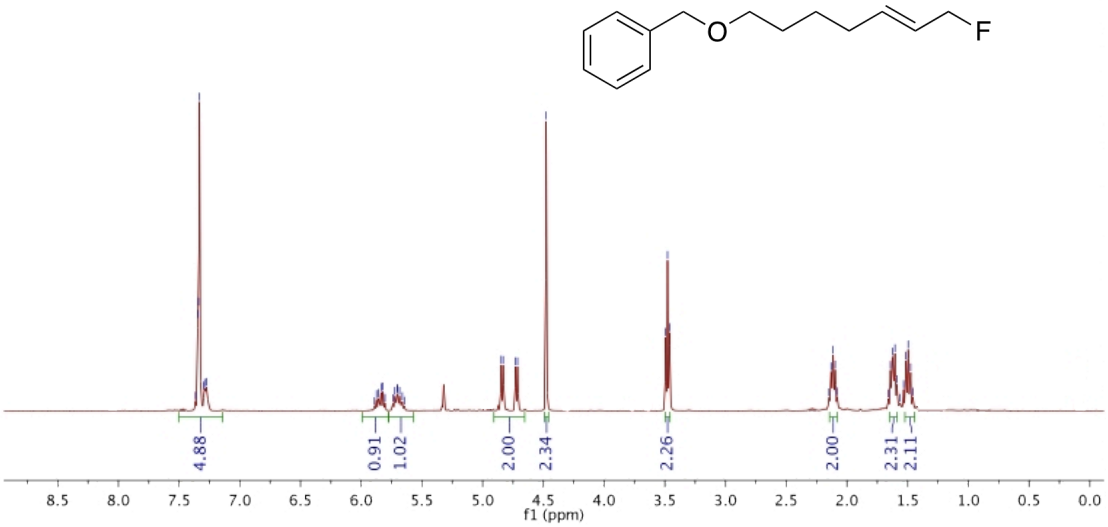
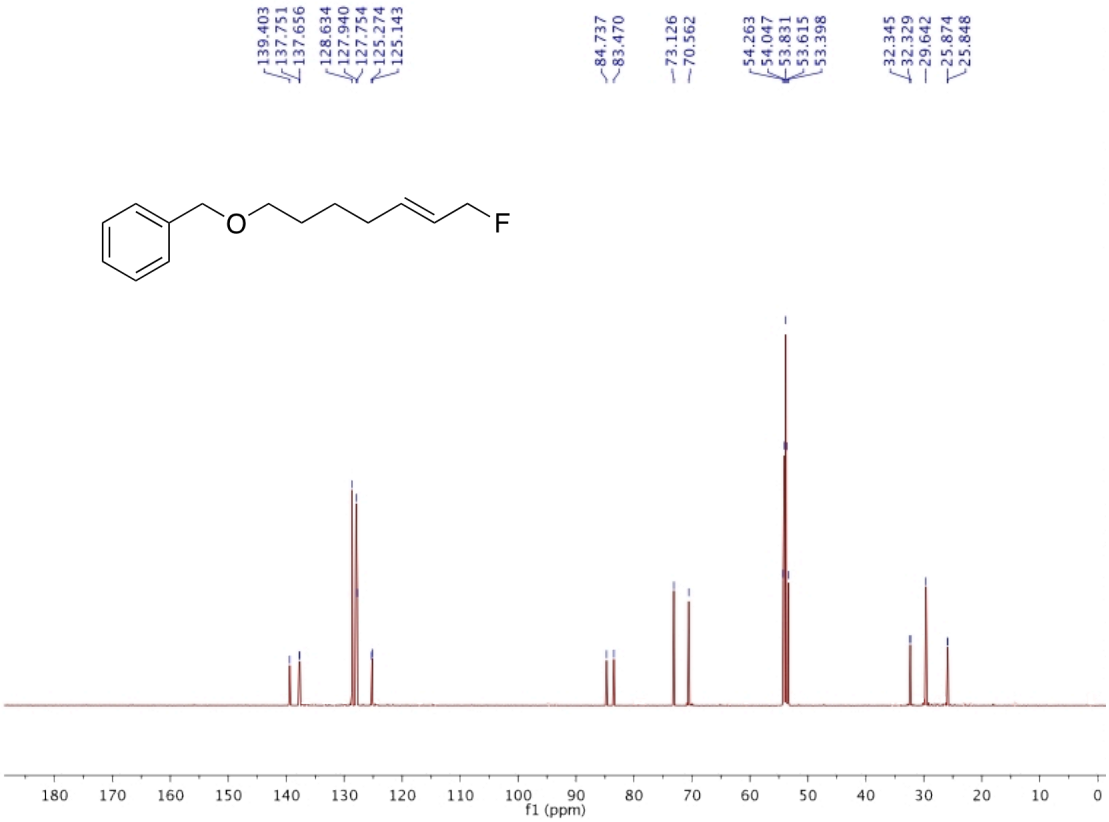
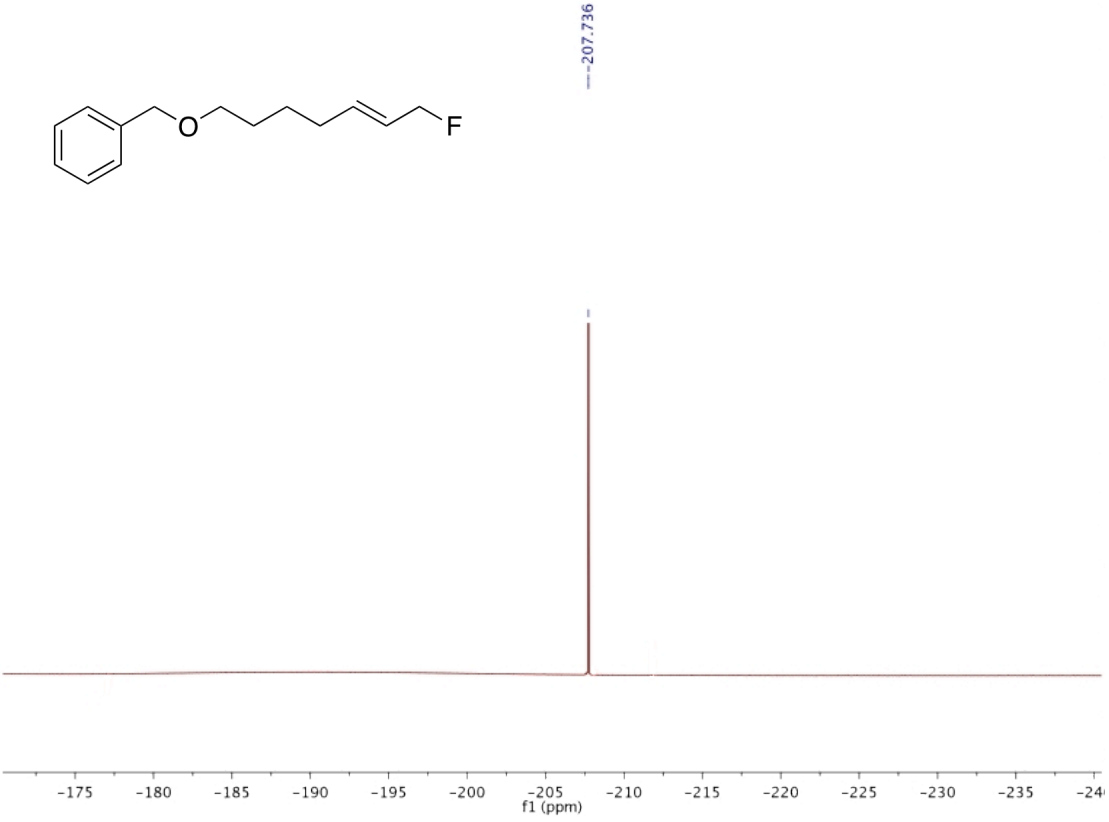
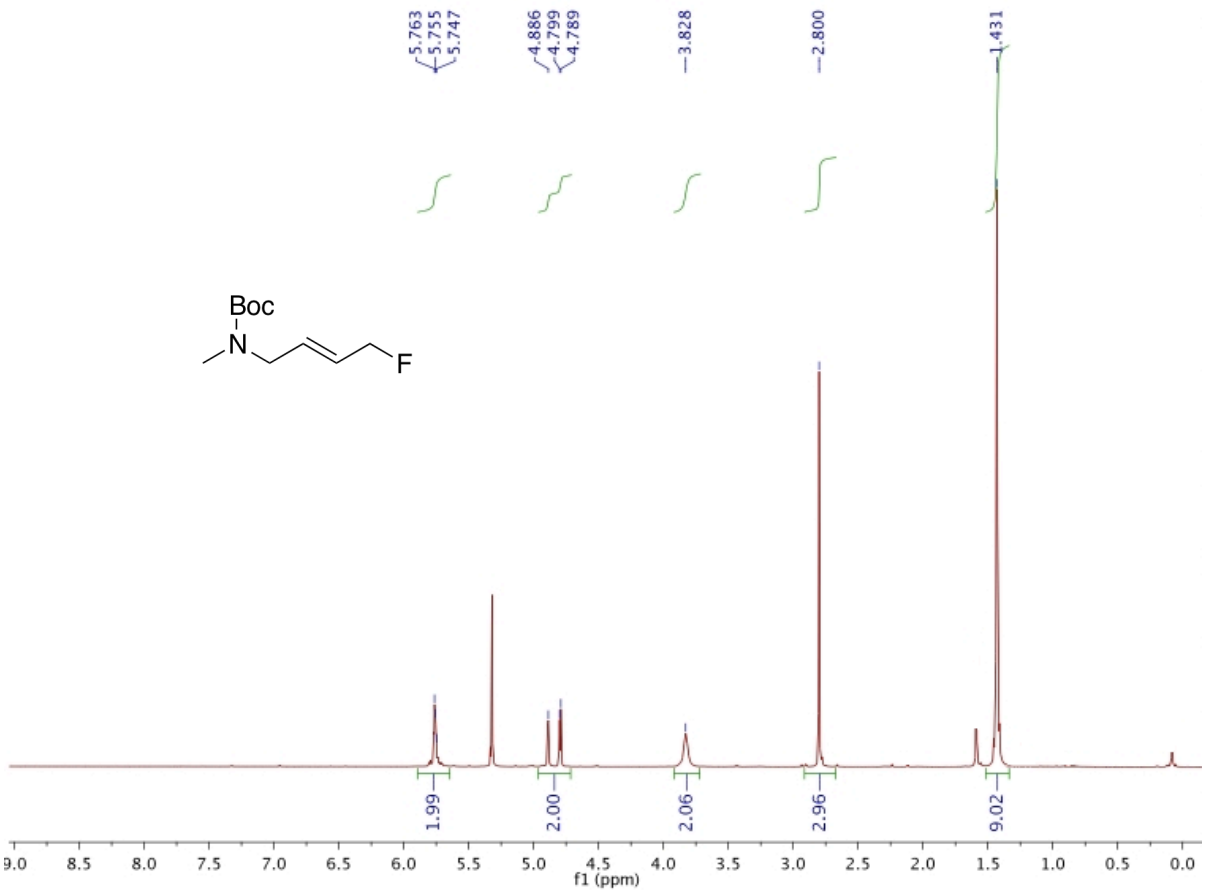
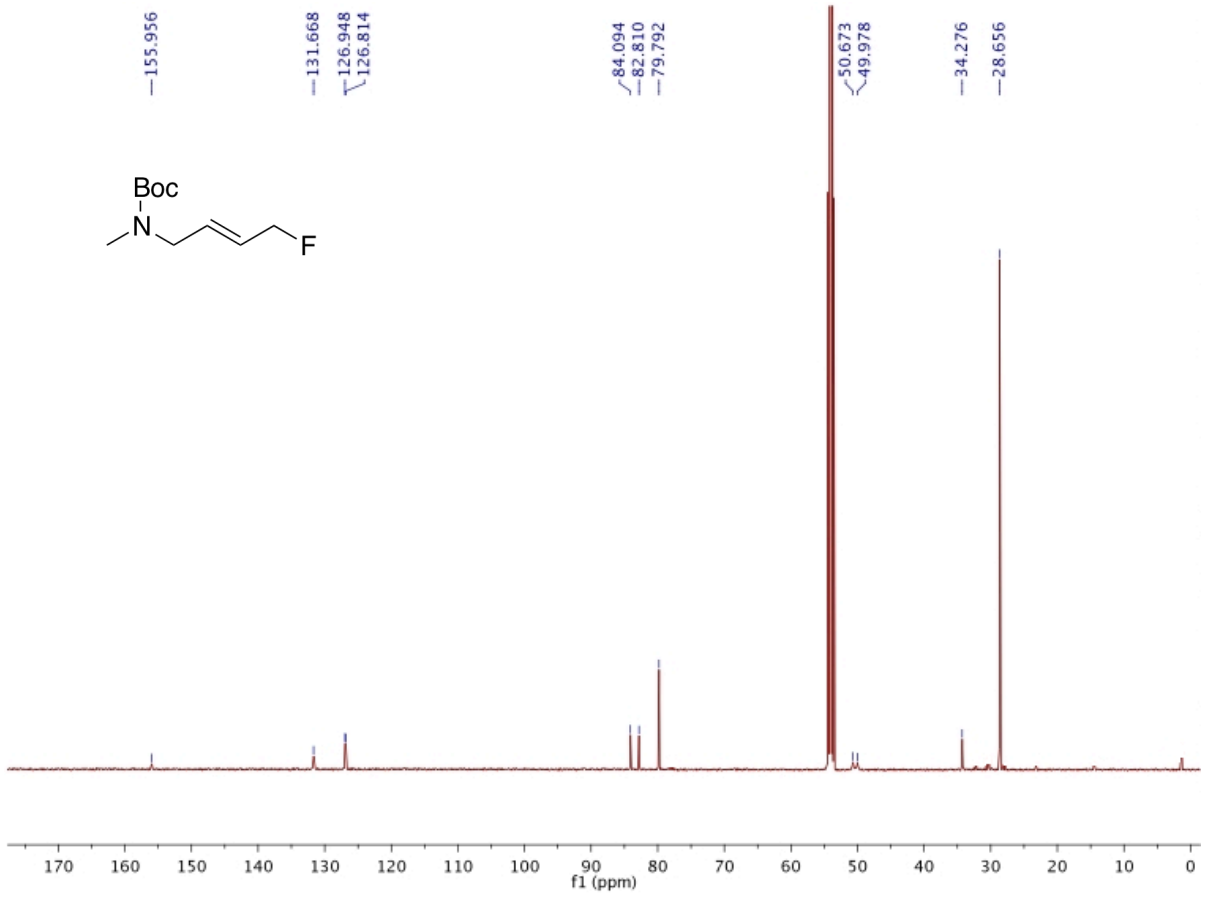
1.562
1.533
1.514
1.496
1.475
1.457

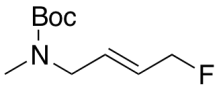

O
F
4.88
0.91
1.02
2.00
2.34
2.26
2.00
2.31
2.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

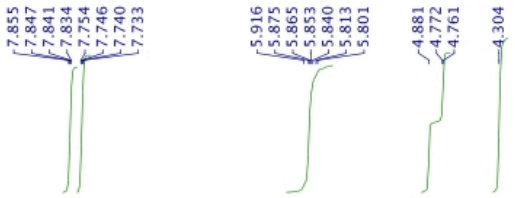


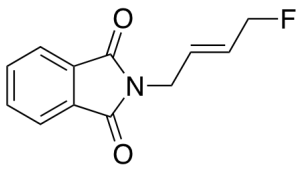


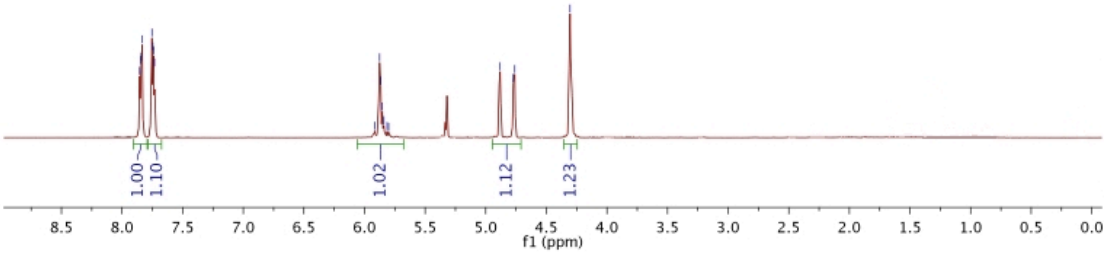


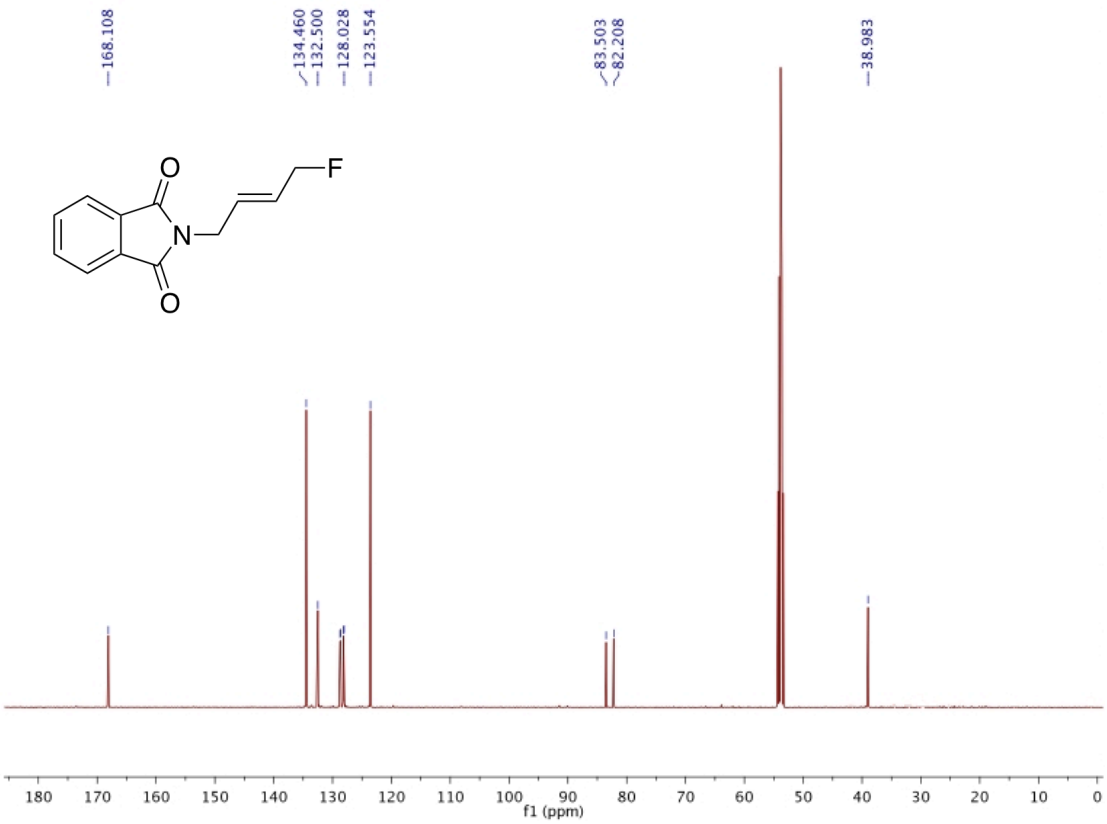


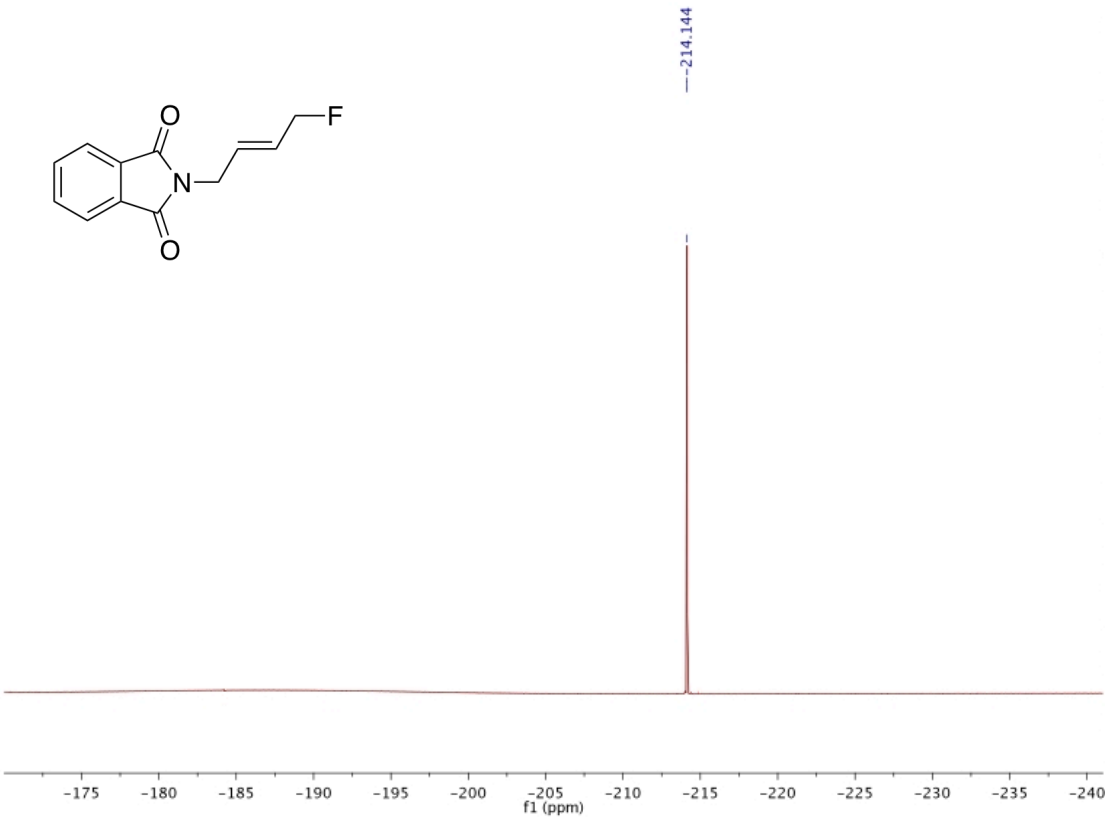


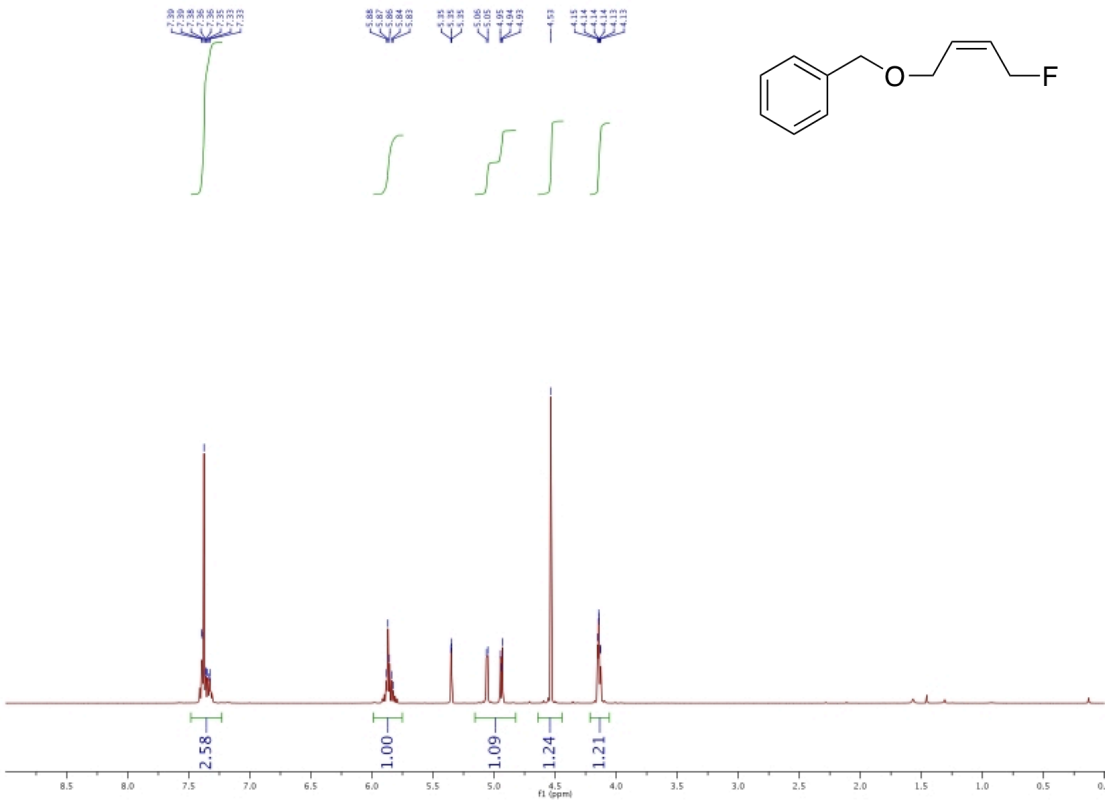


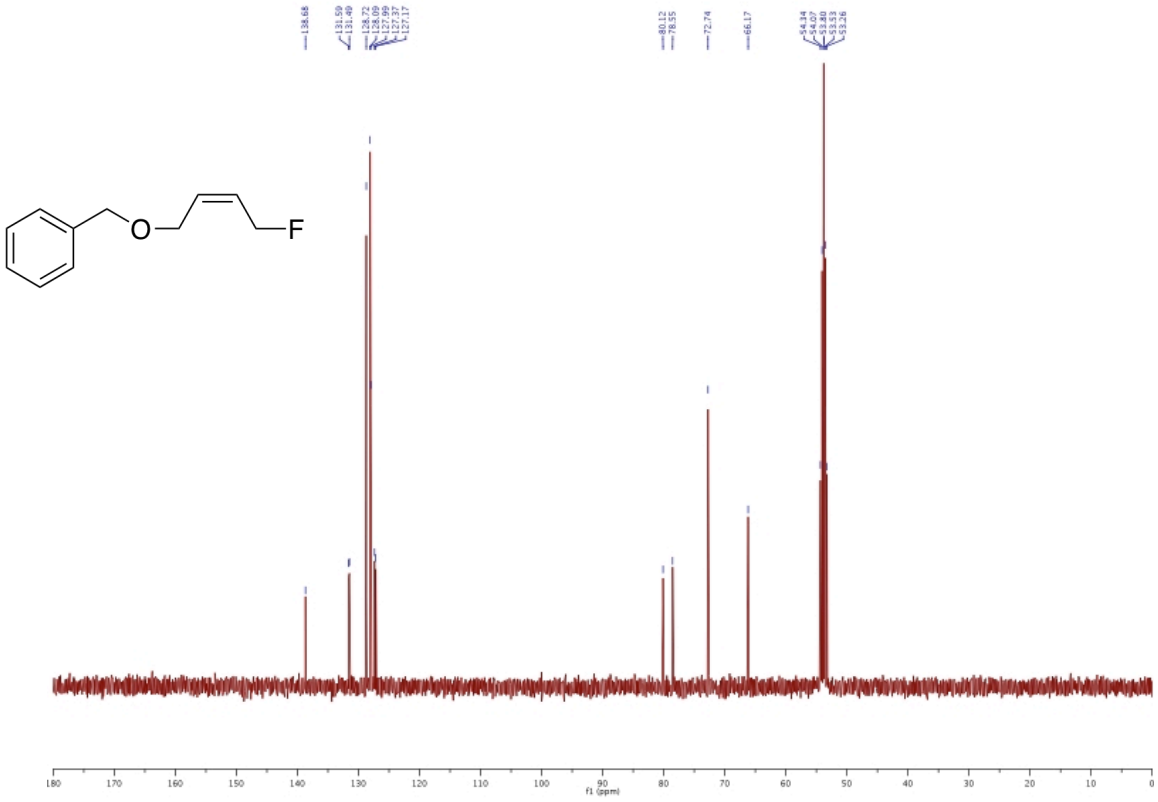


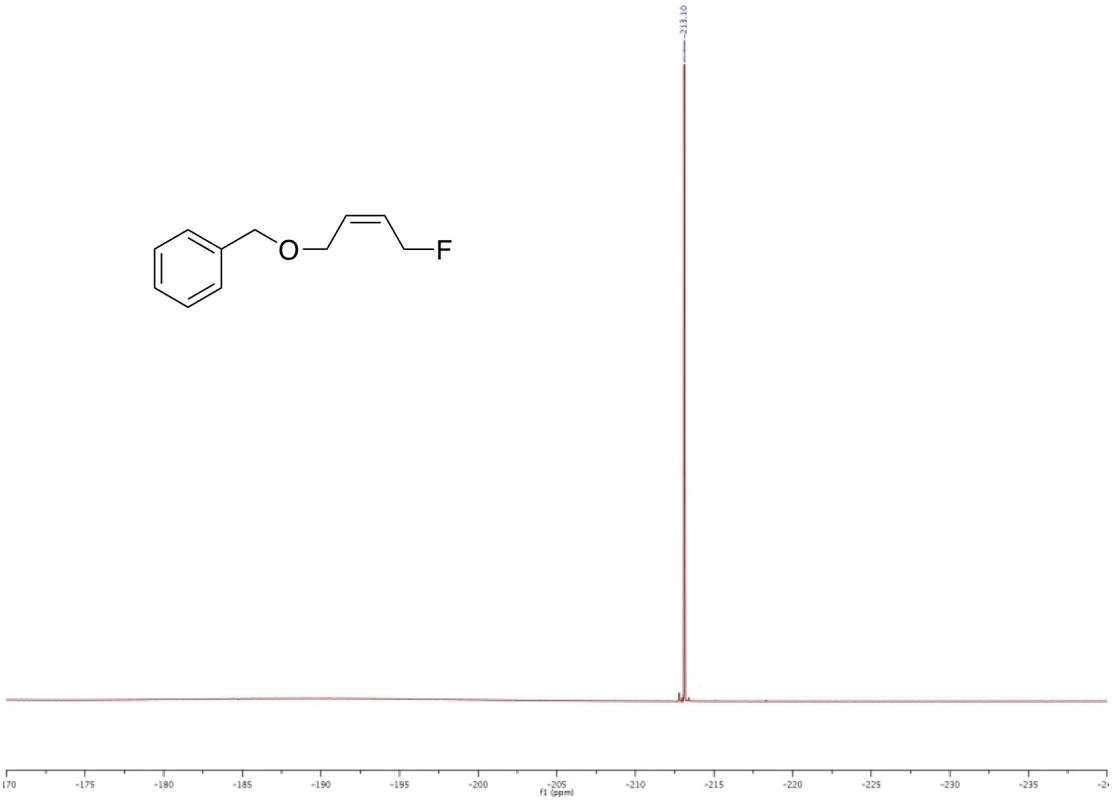


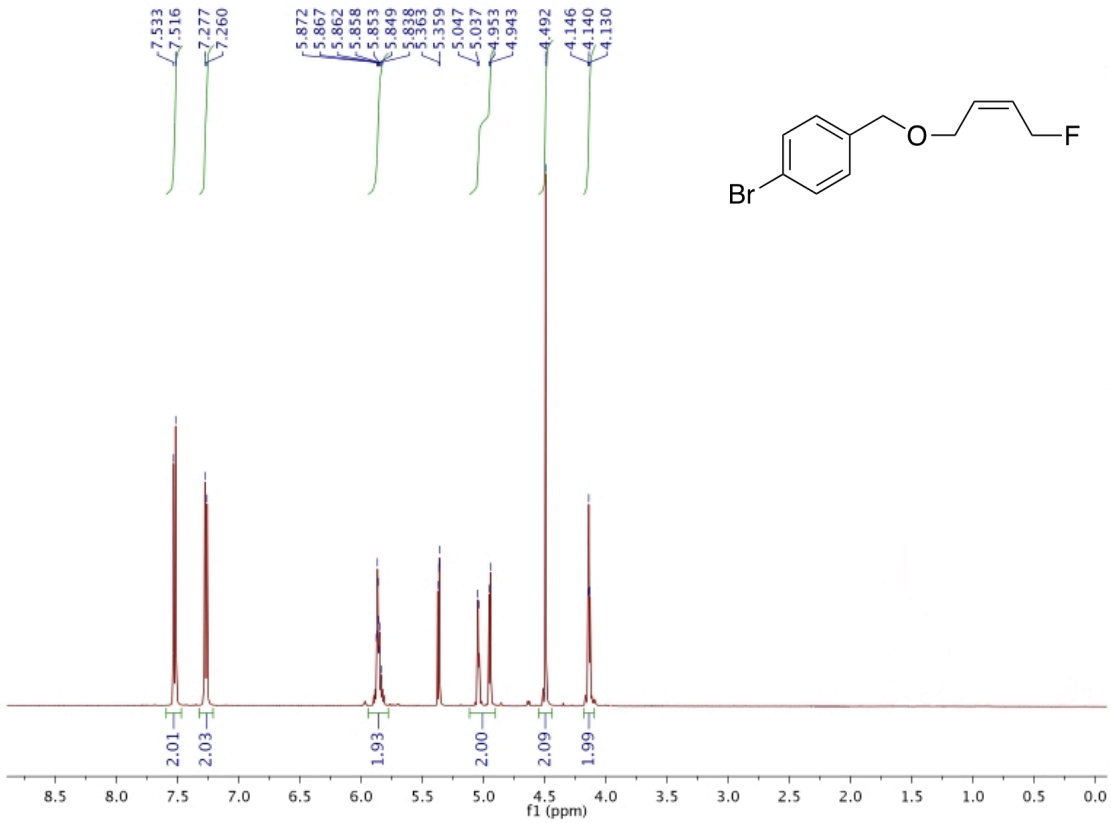


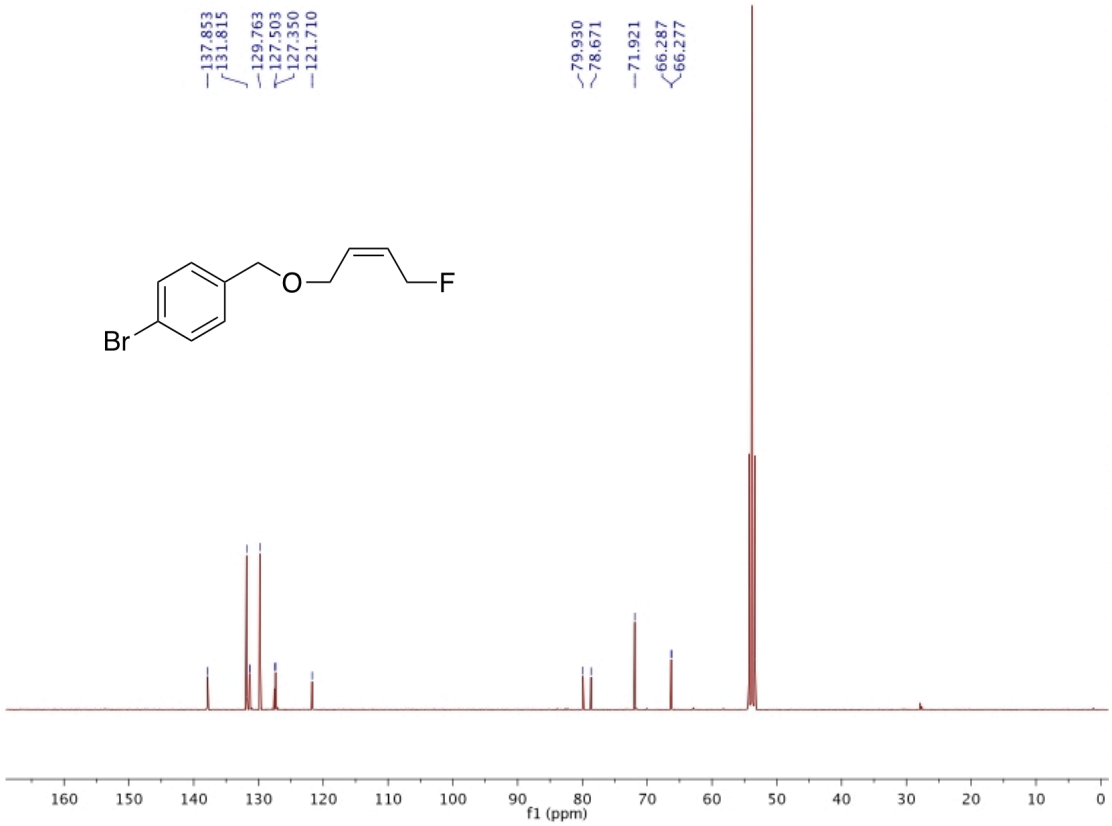


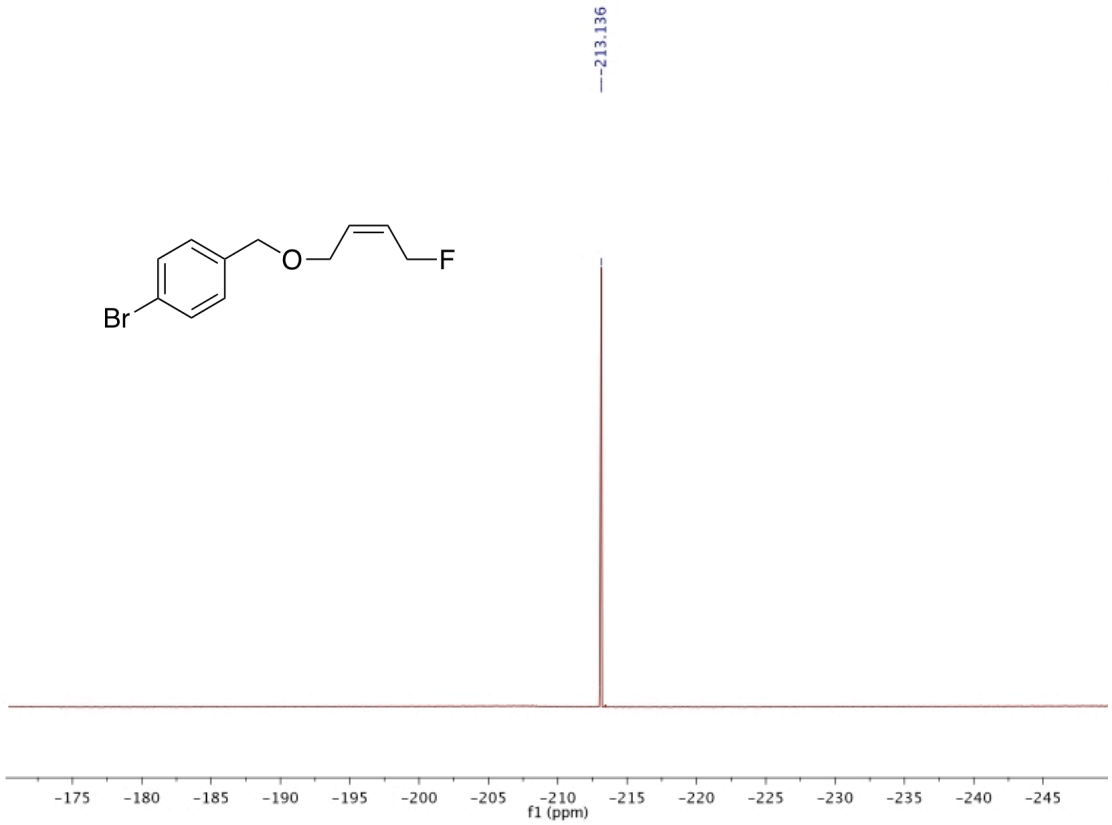

O
F
2.58
1.00
1.09
1.24
1.21
f1 (ppm)

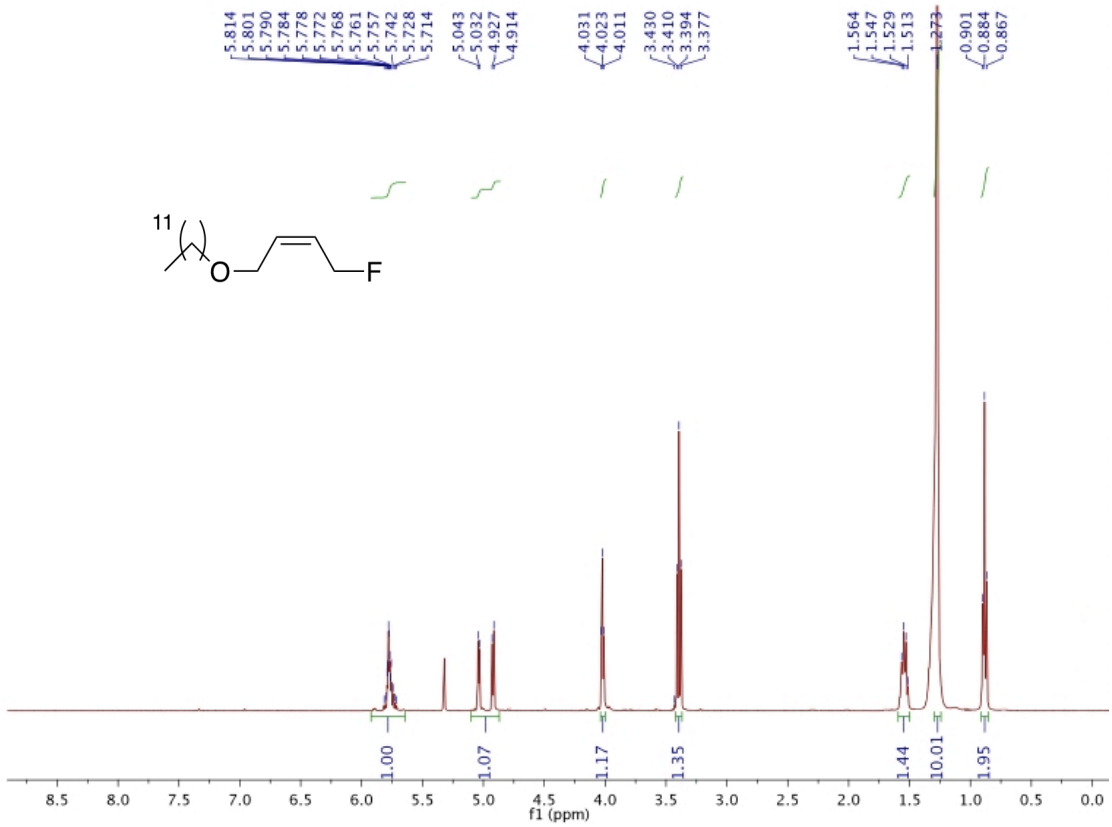

O
F
f1 (ppm)


O
F
f1 (ppm)


7.533
7.516
7.277
7.260
5.872
5.867
5.862
5.858
5.853
5.849
5.838
5.363
5.359
5.047
5.037
4.953
4.943
4.492
4.146
4.140
4.130
O
F
Br
2.01
2.03
1.93
2.00
2.09
1.99
f1 (ppm)






5.814
5.801
5.790
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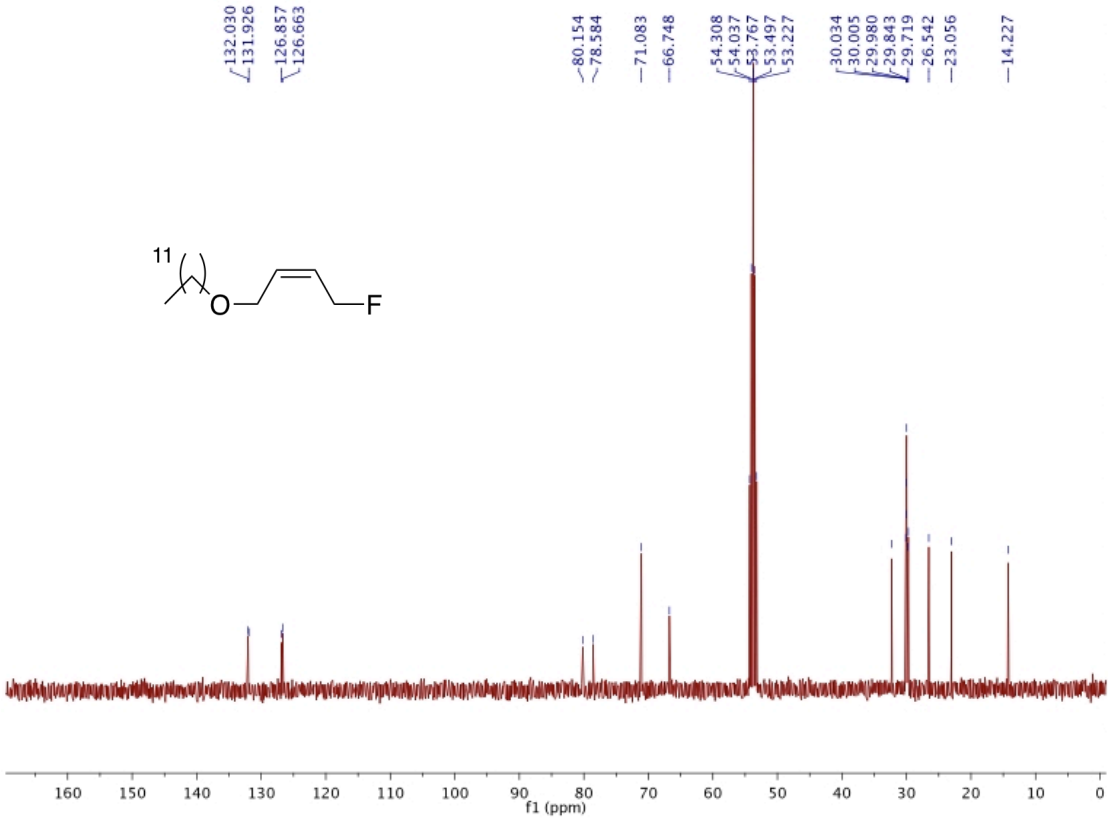
5.778
5.772
5.768
5.761
5.757
5.742
5.728
5.714
5.043
5.032
4.927
4.914
4.031
4.023
4.011
3.430
3.410
3.394
3.377
1.564
1.547
1.529
1.513
1.273
0.901
0.884
0.867
11
O
F
1.00
1.07
1.17
1.35
1.44
10.01
1.95
f1 (ppm)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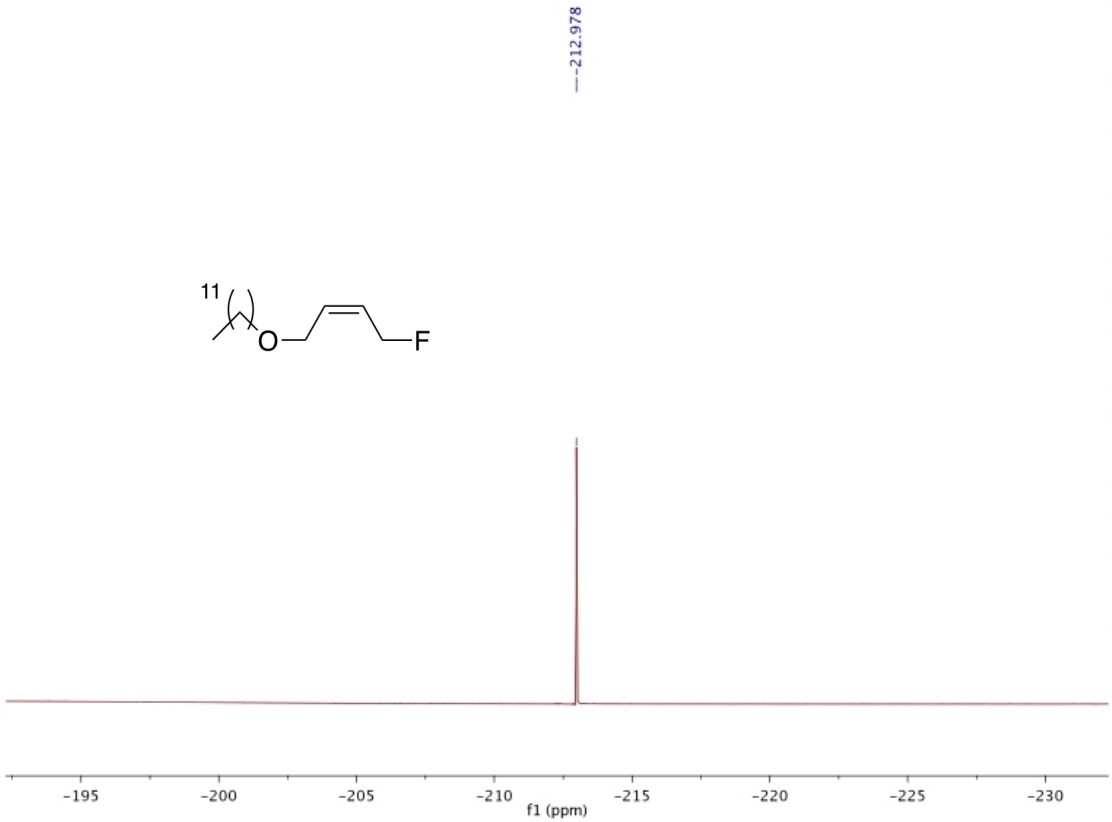
71.083
66.748
54.308
54.037
53.767
53.497
53.227
30.034
30.005
29.980
29.843
29.719
26.542
23.056
14.227
11
O
F
f1 (ppm)


-212.978
11
O
F
-195
-200
-205
-210
-215
-220
-225
-230
f1 (ppm)


8.039
8.021
7.607
7.589
7.570
7.482
7.462
7.443
5.929
5.926
5.920
5.915
5.908
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5.890
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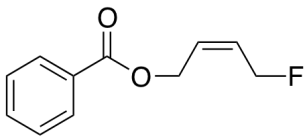
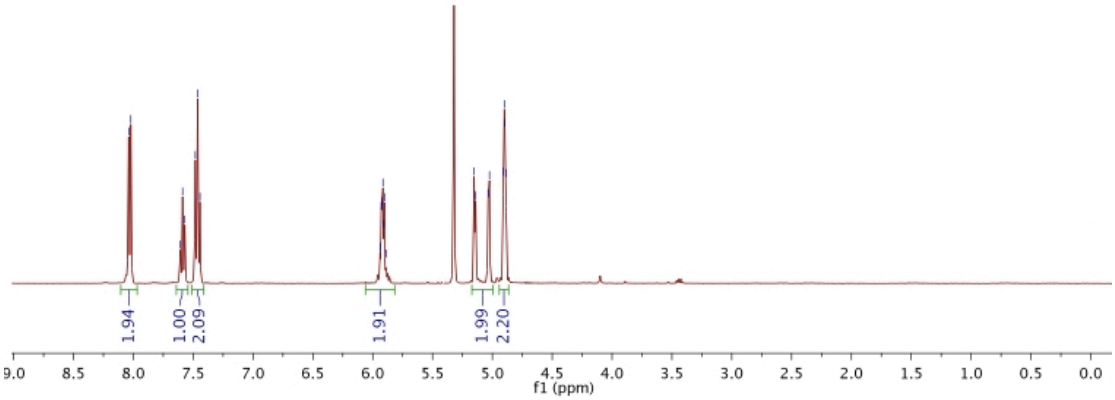
5.141
5.036
5.024
4.908
4.900
4.896
4.888


O
O
F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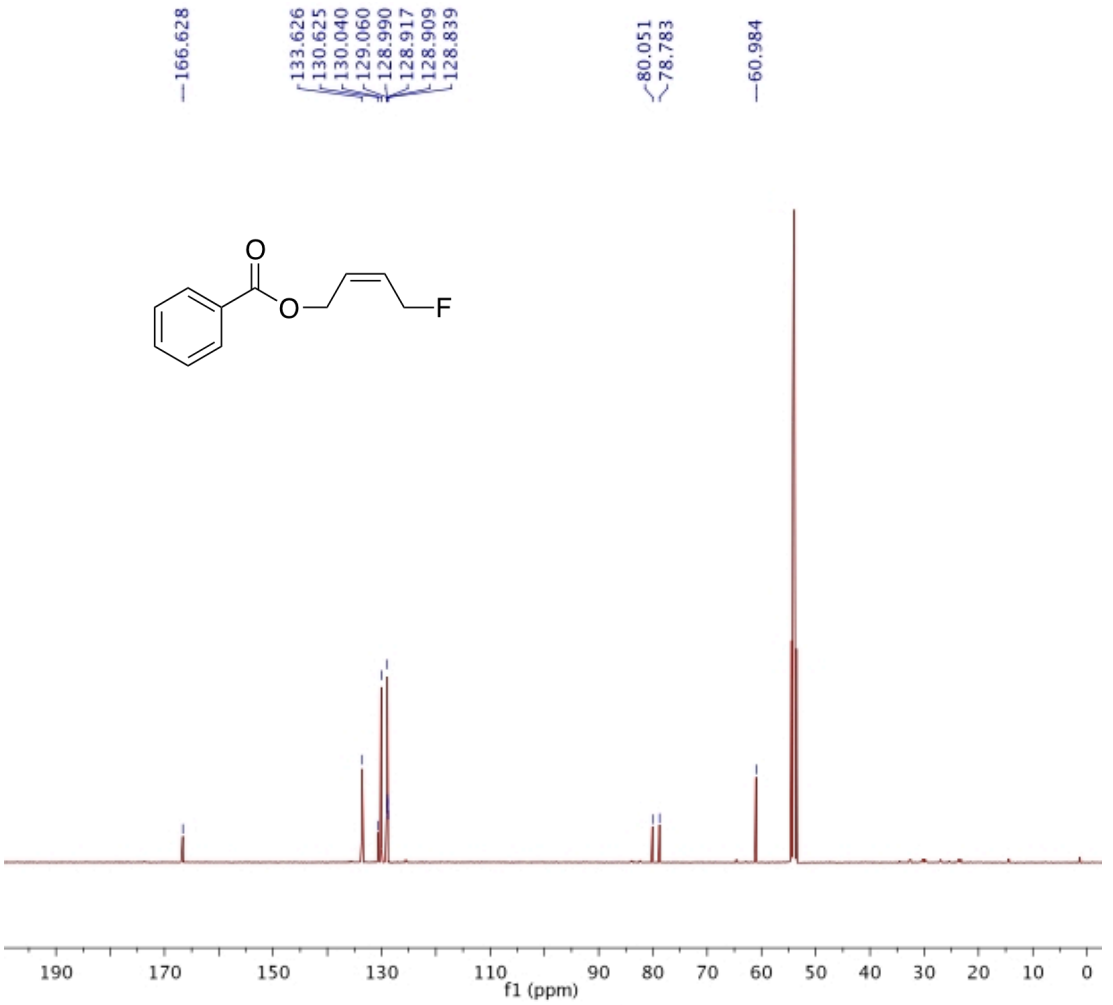
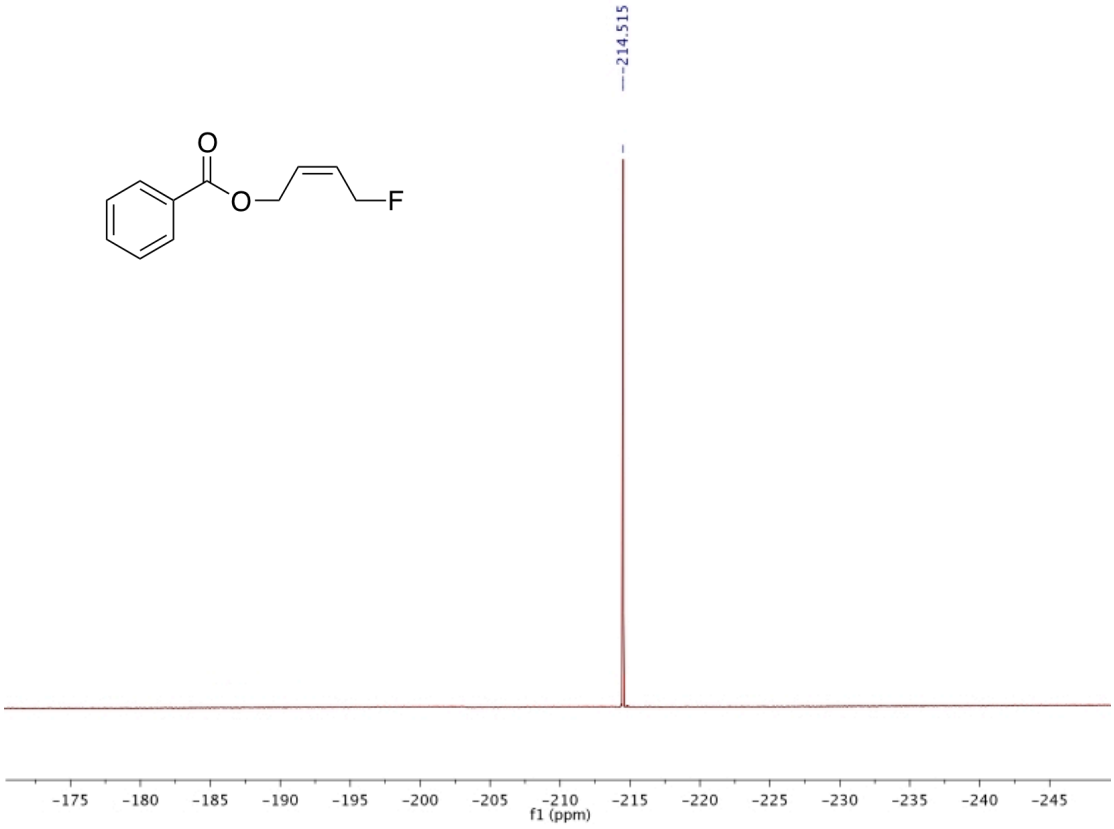
1.00
2.09
1.91
1.99
2.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.628
133.626
130.625
130.040
129.060
128.990
128.917
128.909
128.839
80.051
78.783
60.984
O
O
F
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-214.515
O
O
F
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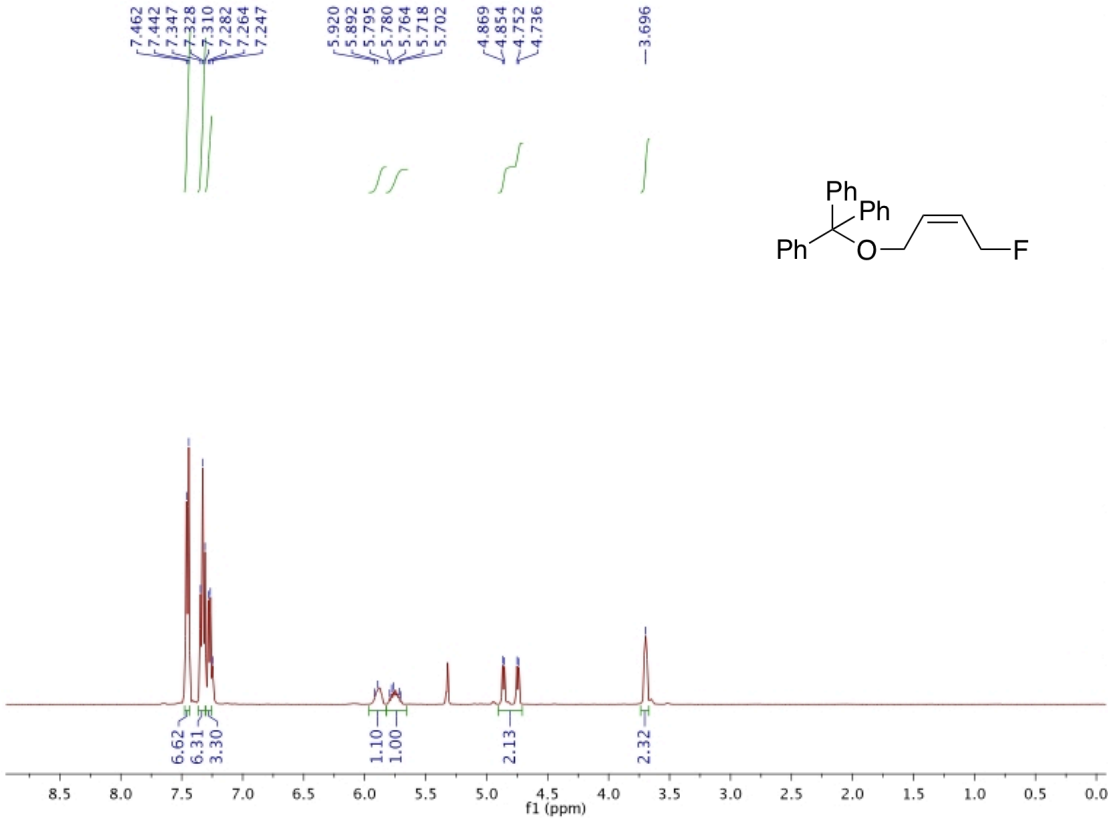
-180
-185
-190
-195
-200
-205
-210
-215
-220
-225
-230
-235
-240
-245
f1 (ppm)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7.328
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7.282
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7.247
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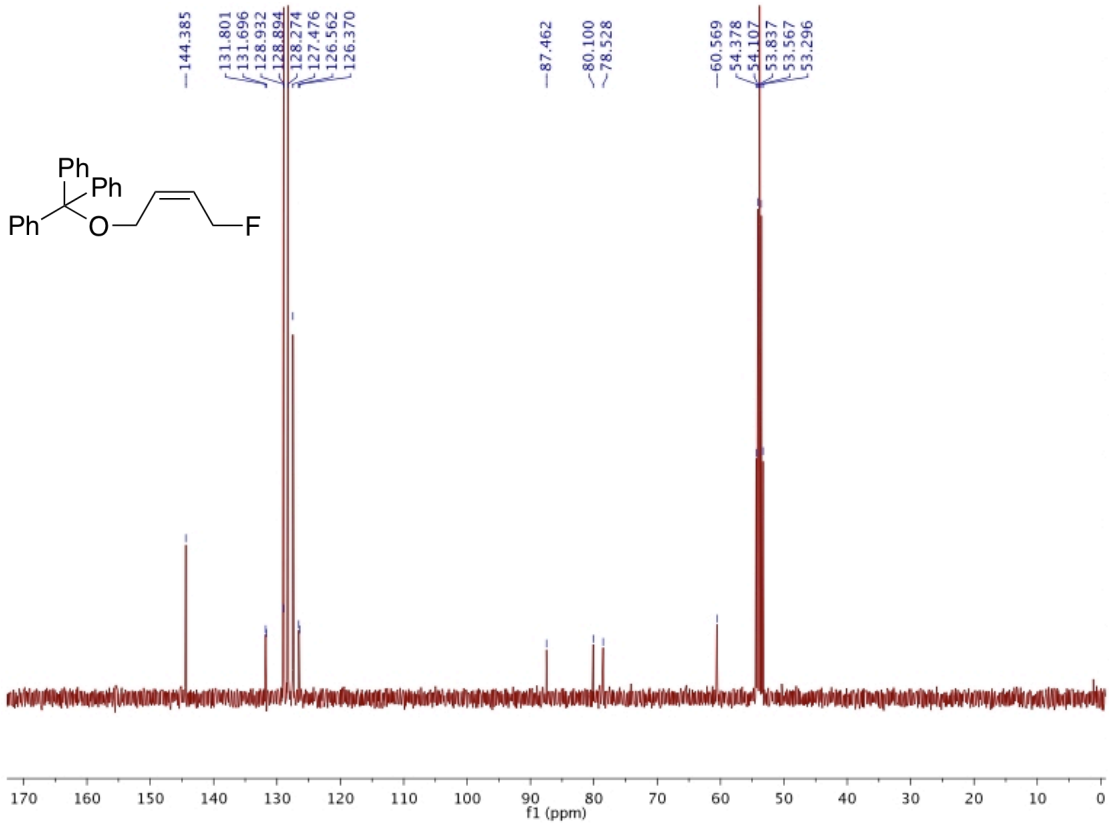
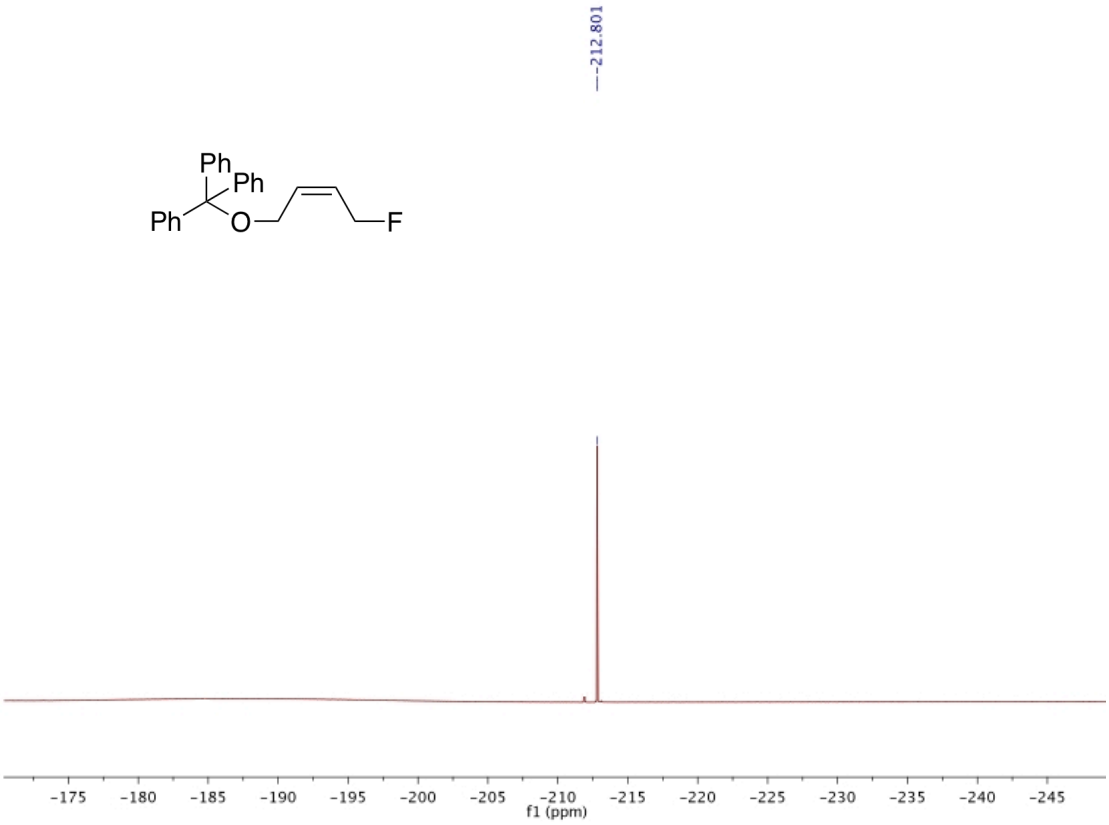
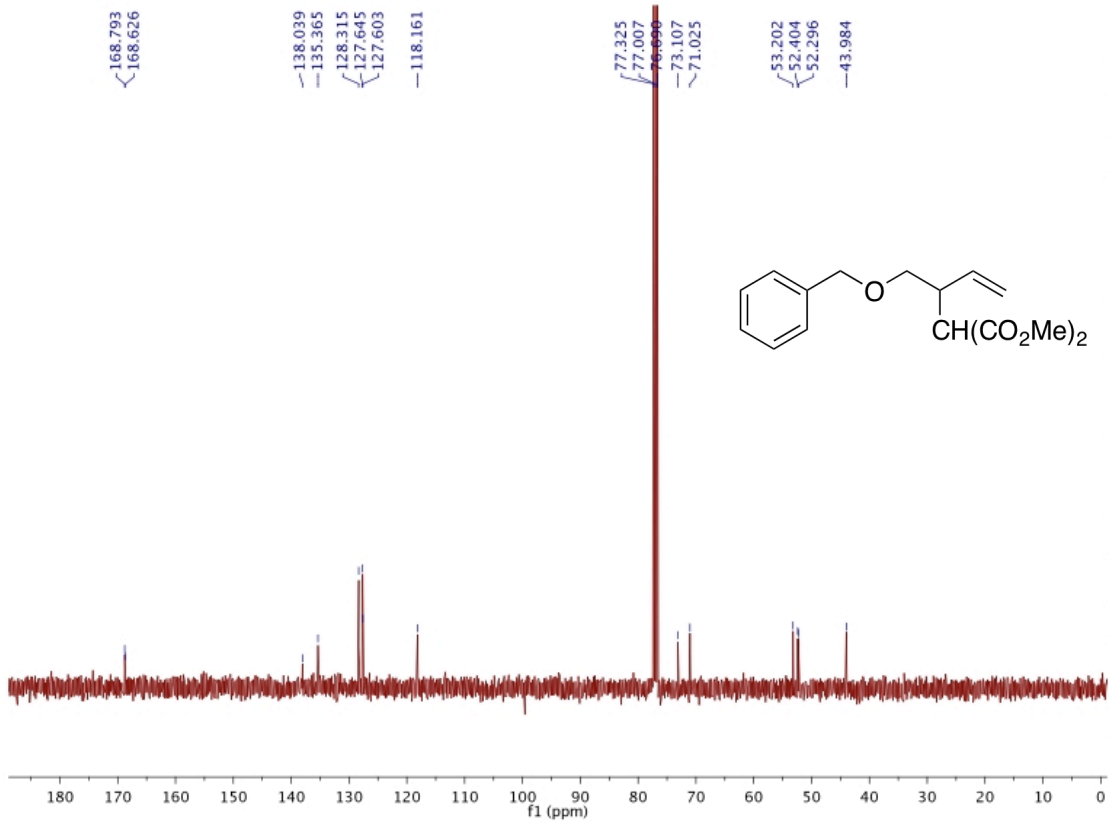
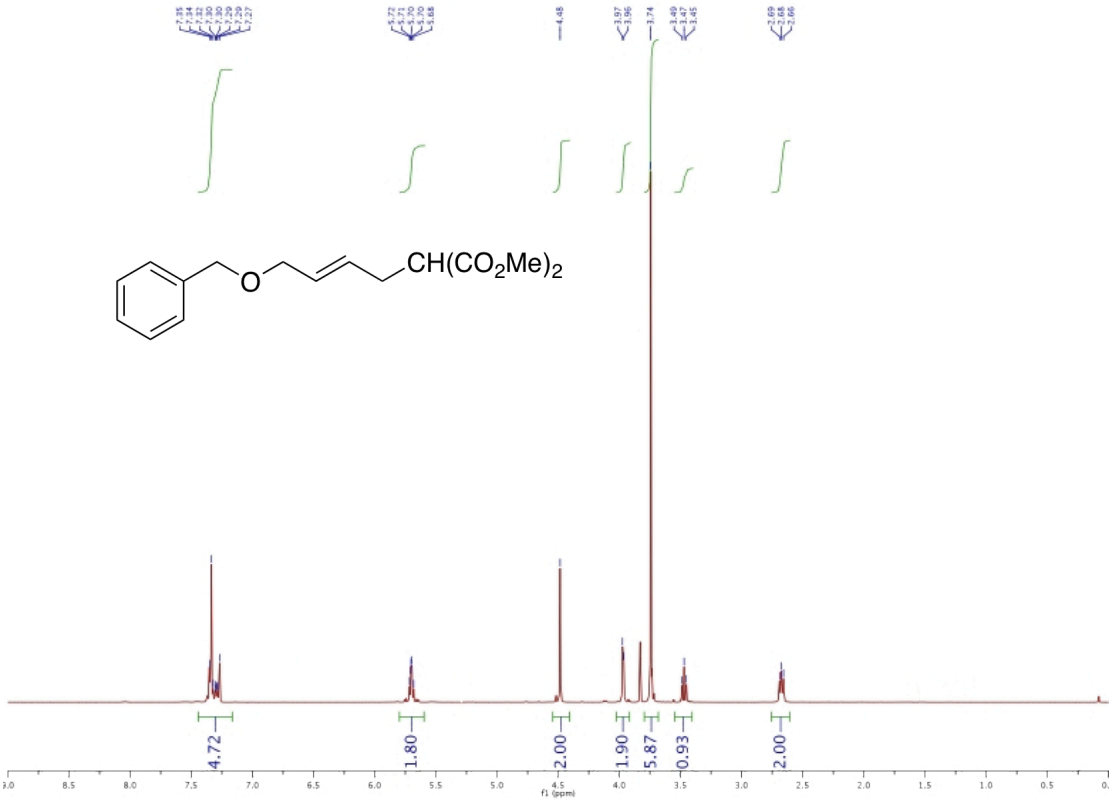
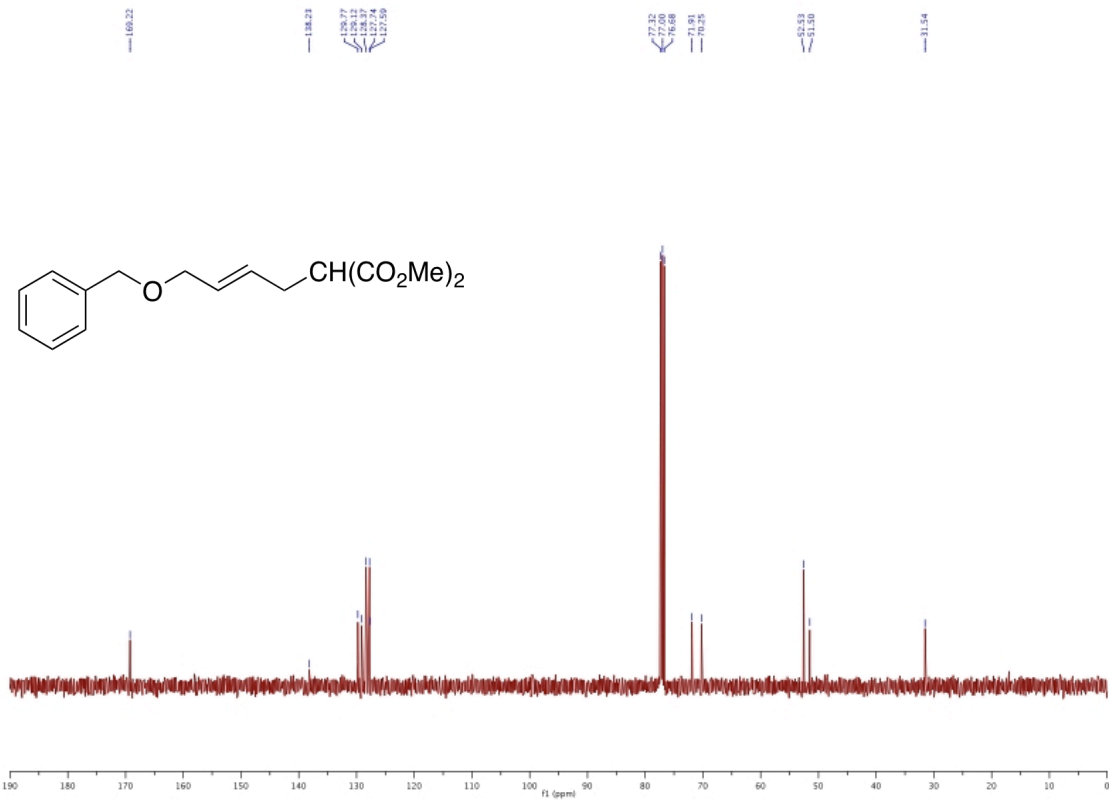
5.892
5.795
5.780
5.764
5.718
5.702
4.869
4.854
4.752
4.736
3.696
Ph
Ph
Ph
O
F
6.62
6.31
3.30
1.10
1.00
2.13
2.32
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

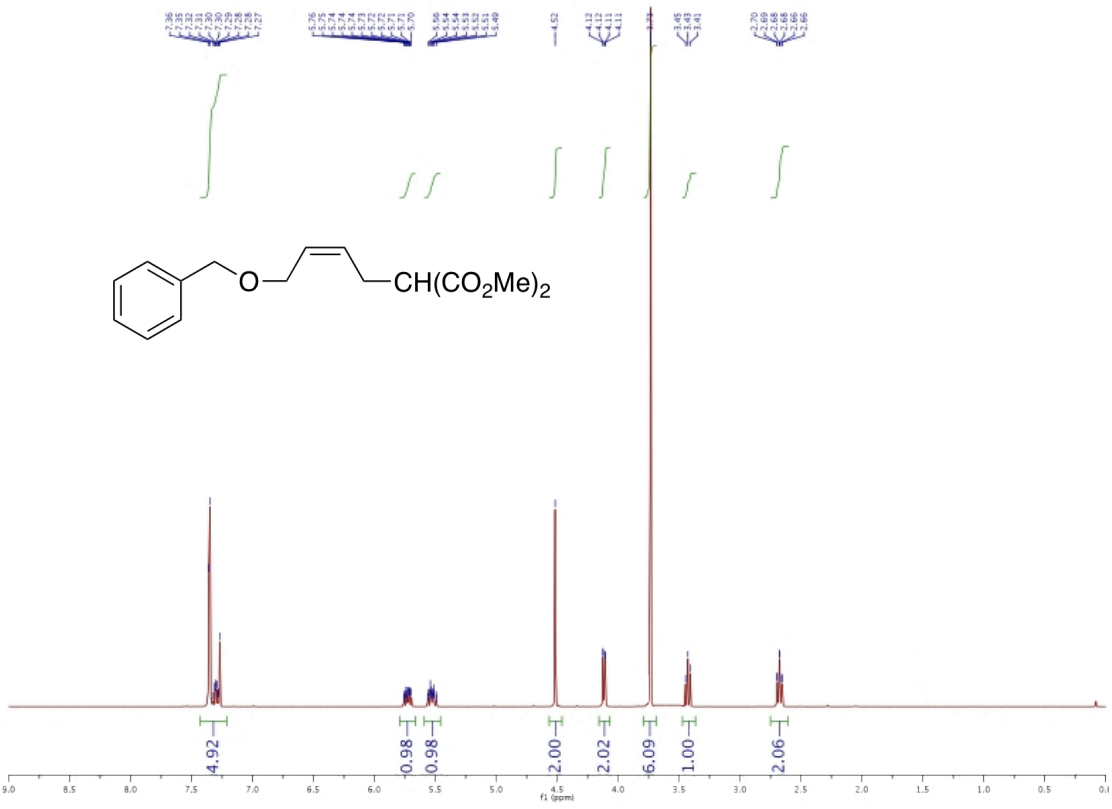

144.385
131.801
131.696
128.932
128.894
128.274
127.476
126.562
126.370
87.462
80.100
78.528
60.569
54.378
54.107
53.837
53.567
53.296
Ph
Ph
Ph
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

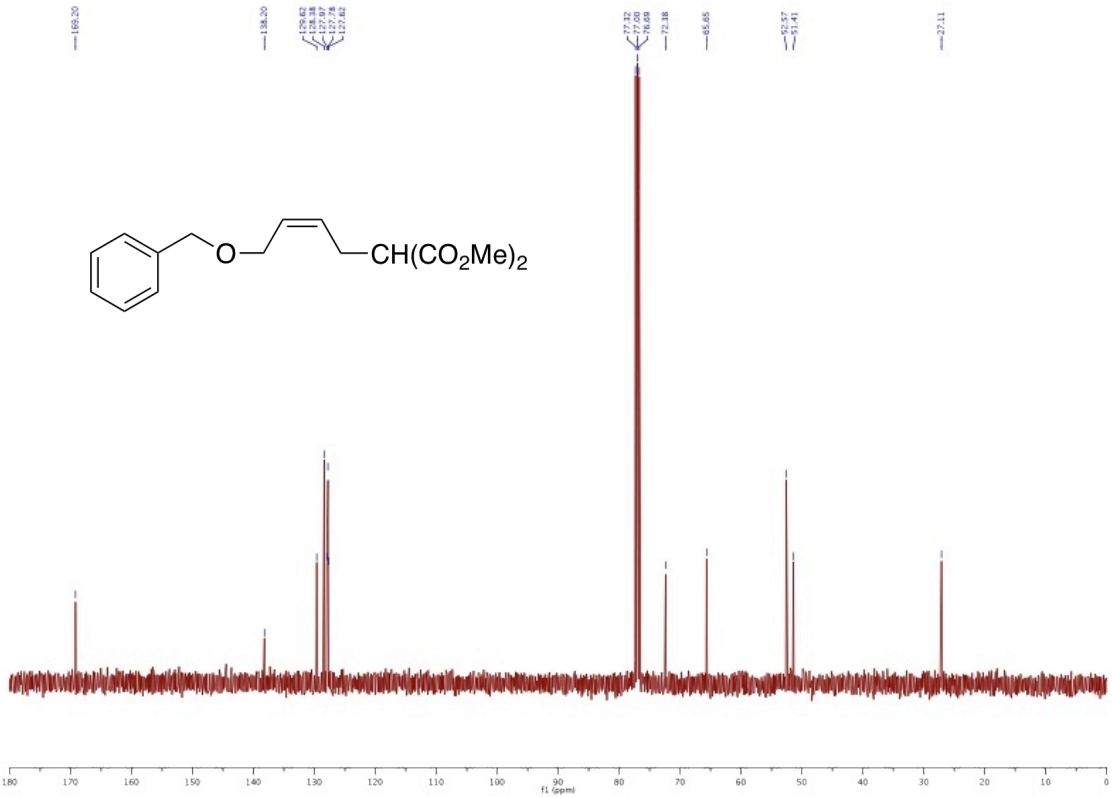

-212.801
Ph
Ph
Ph
O
F
f1 (ppm)
7.365
7.345
7.328
7.317
7.301
7.283
7.270
5.904
5.880
5.858
5.837
5.814
5.199
5.155
5.147
5.121
4.481
3.665
3.585
3.562
3.536
3.496
3.194
3.175
3.158
3.142
3.122
O
CH(CO2Me)2
5.58
1.00
2.12
2.12
1.11
2.98
3.03
2.22
1.04
f1 (ppm)

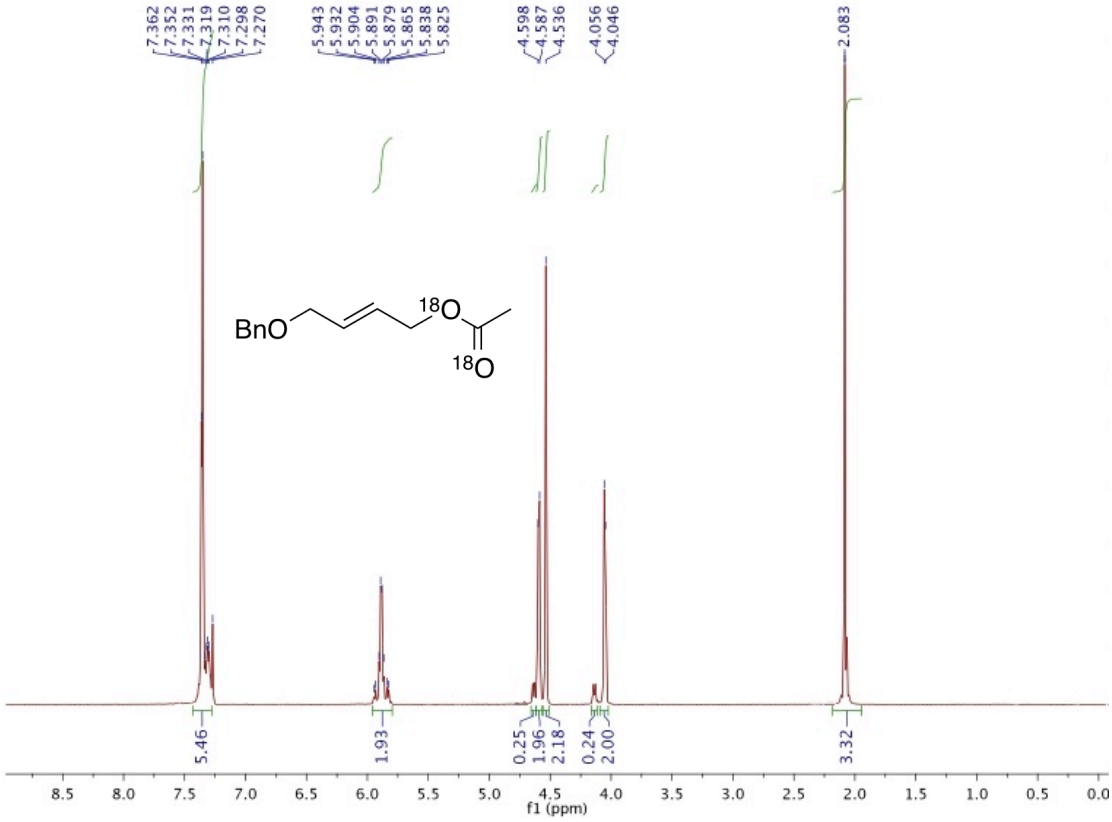

168.793
168.626
138.039
135.365
128.315
127.645
127.603
118.161
77.325
77.007
76.690
73.107
71.025
53.202
52.404
52.296
43.984
O
CH(CO2Me)2
f1 (ppm)

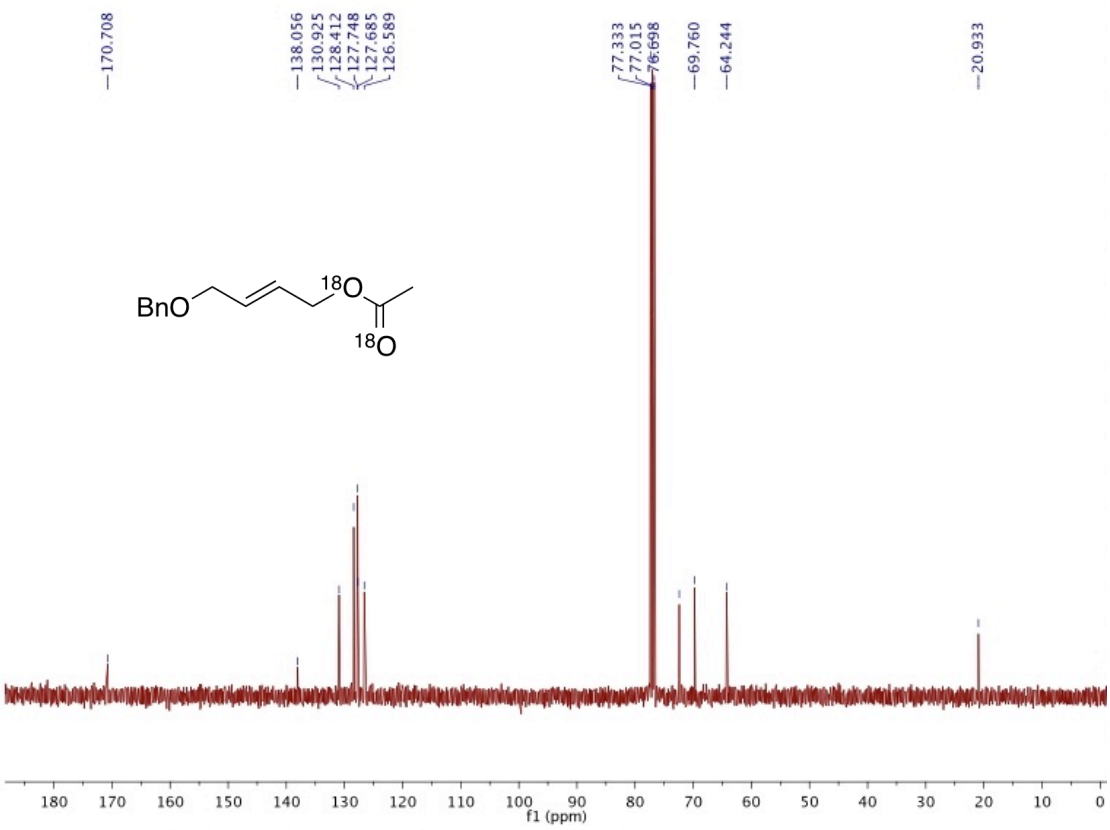

O
CH(CO2Me)2
4.72
1.80
2.00
1.90
5.87
0.93
2.00
f1 (ppm)

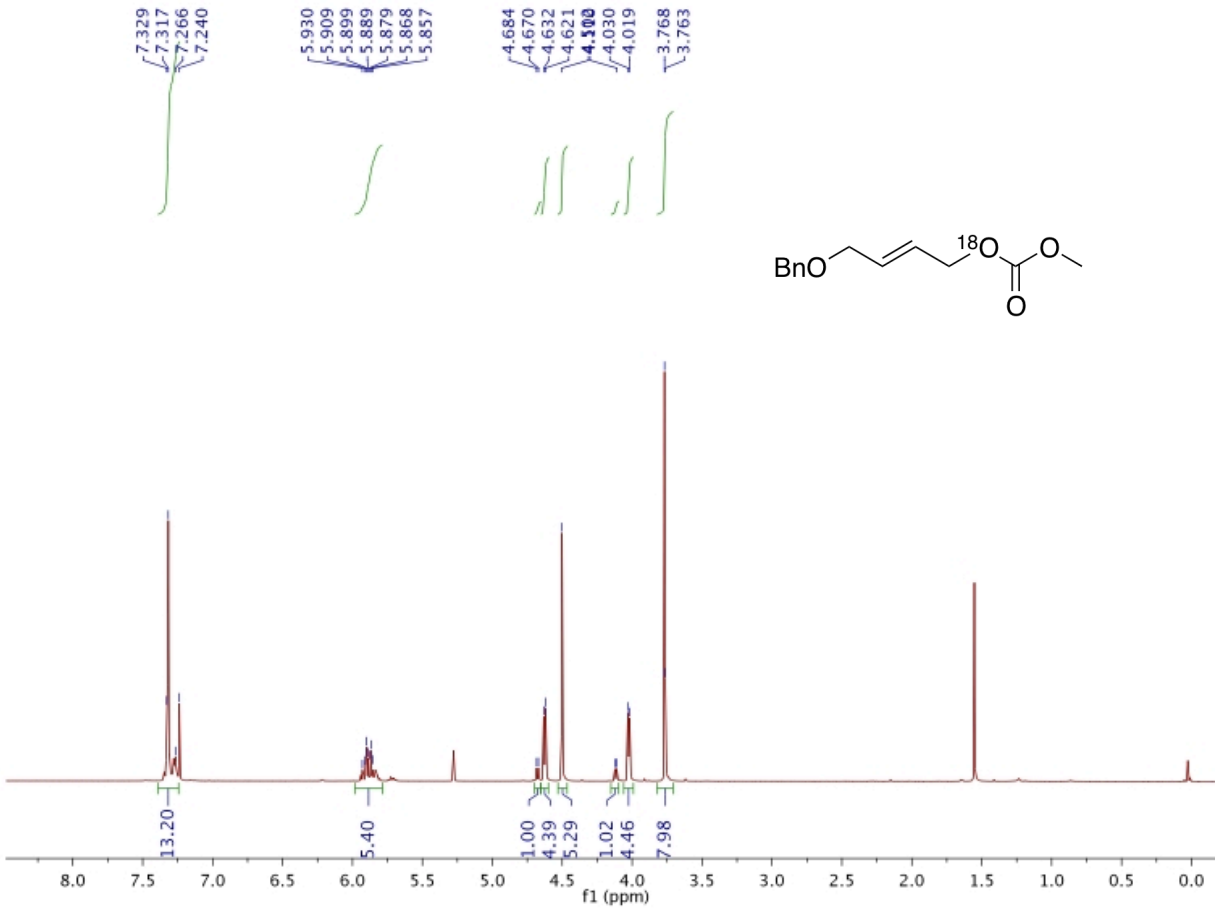

CH(CO2Me)2
O

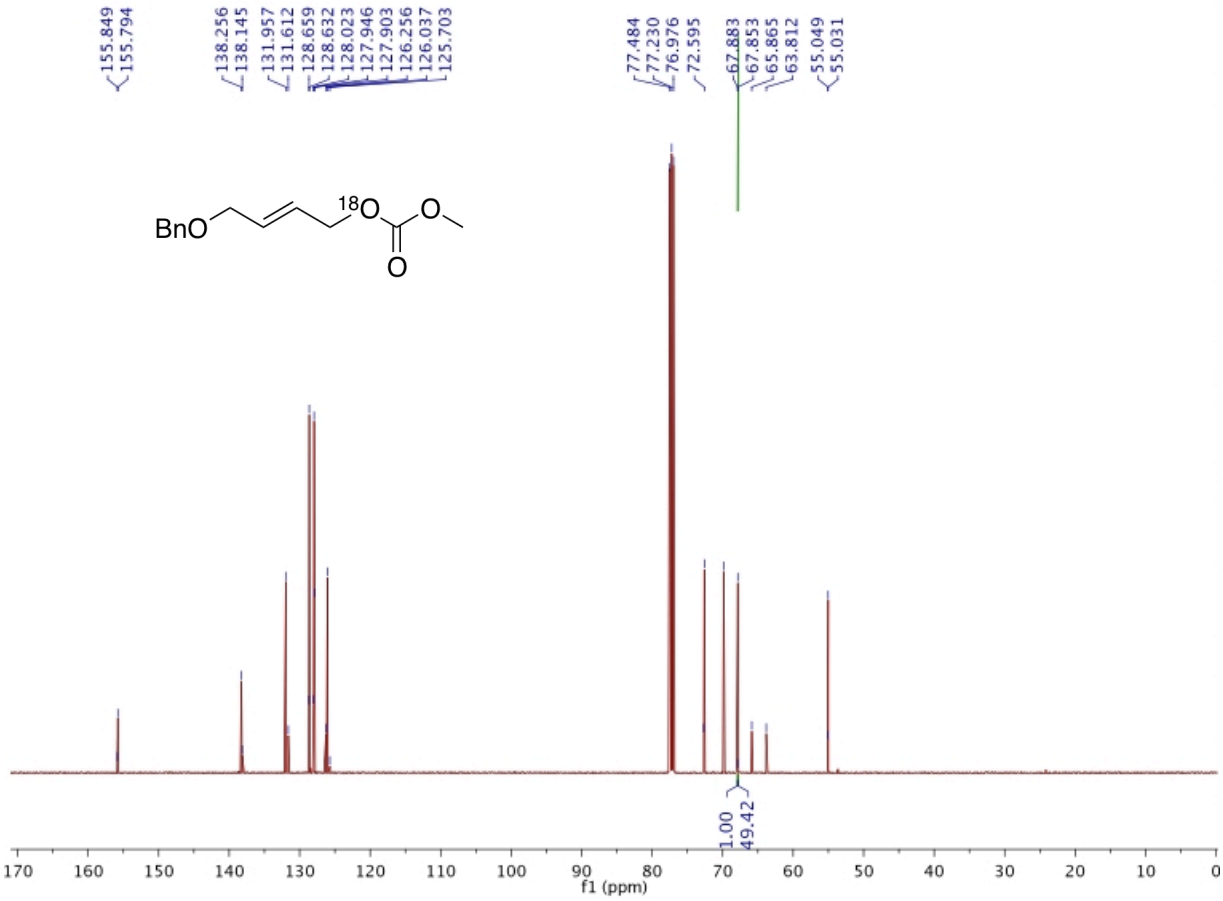

CH(CO2Me)2
O
4.92
0.98
0.98
2.00
2.02
6.09
1.00
2.06

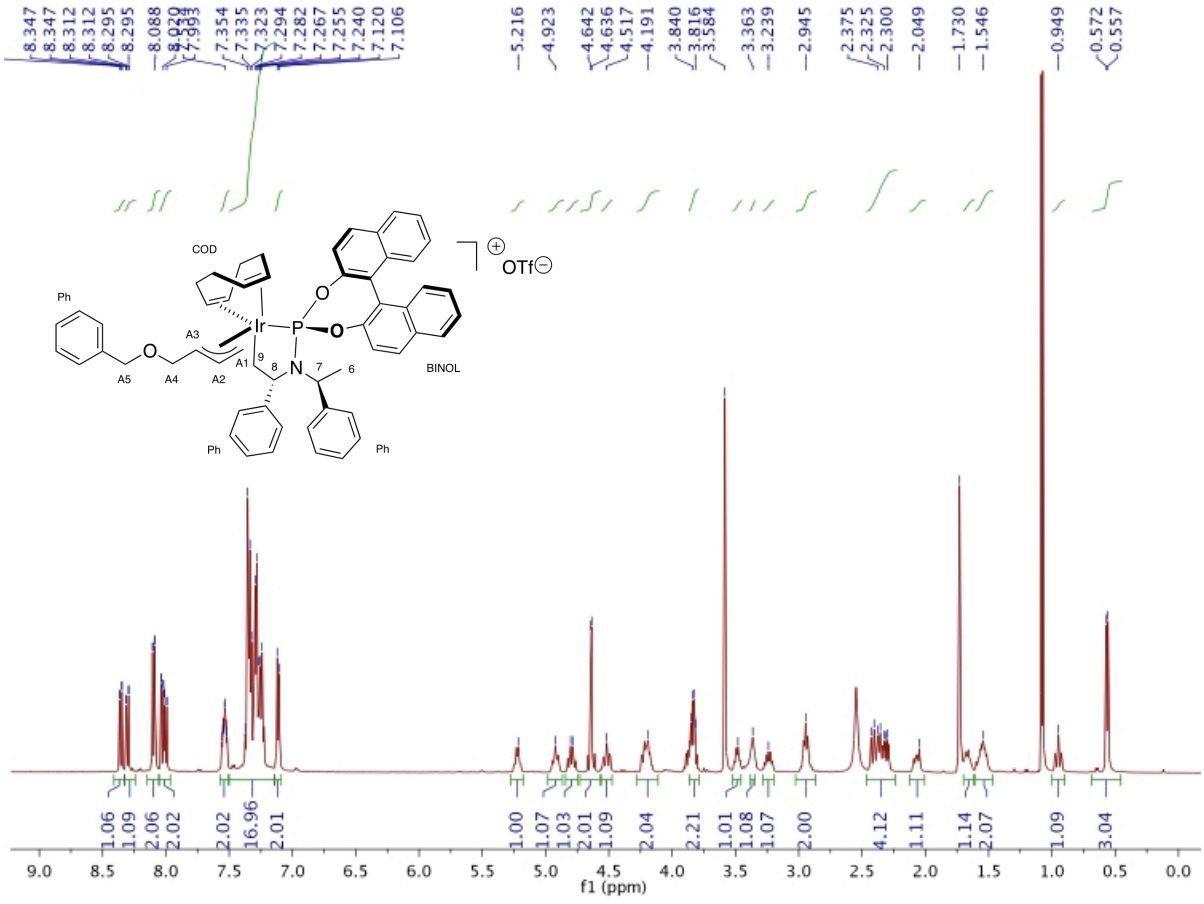


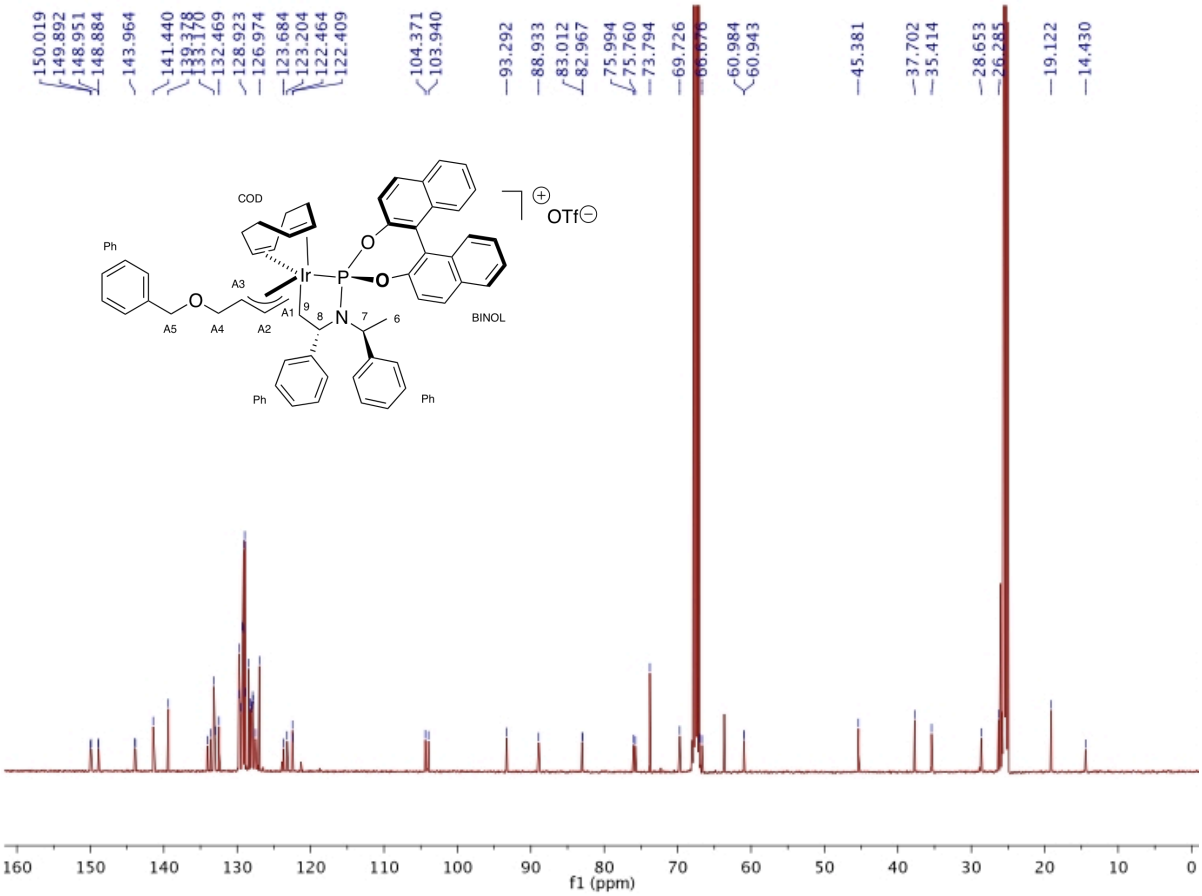


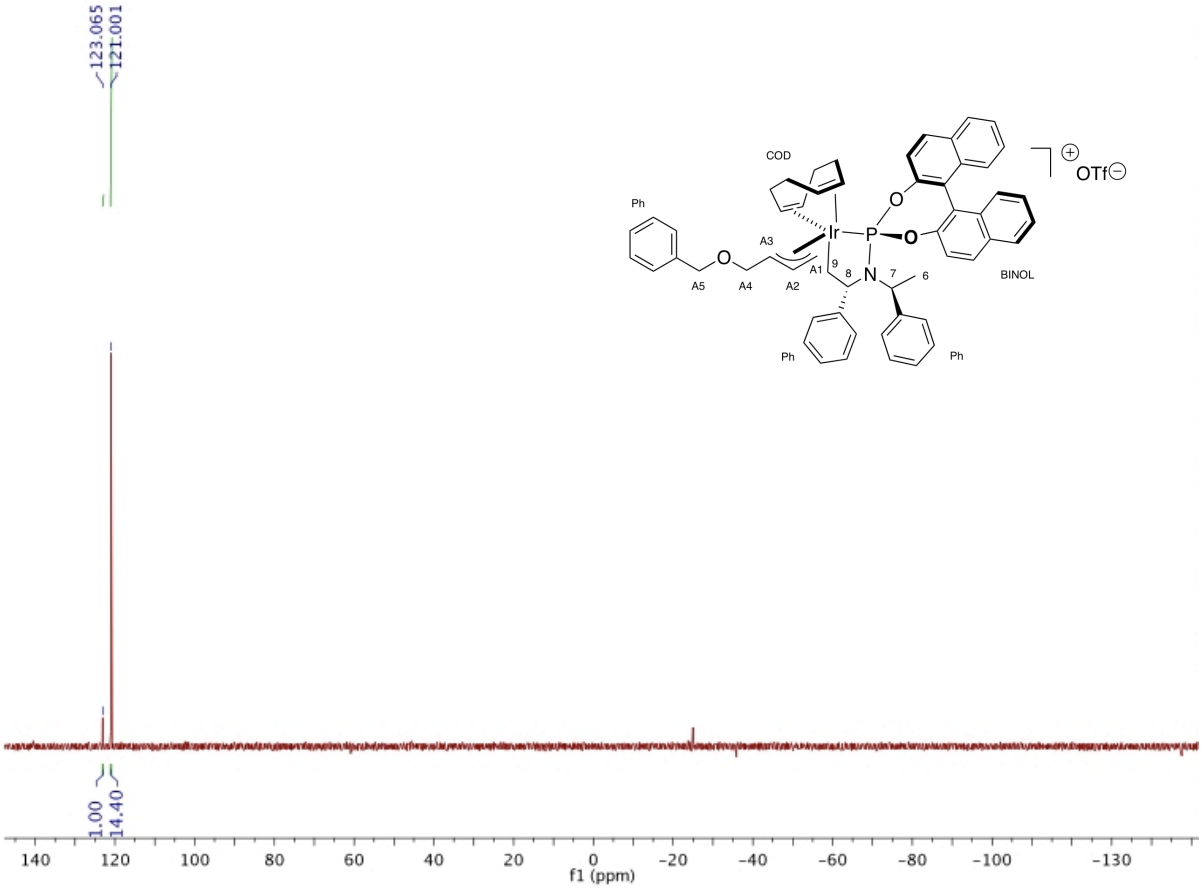

170.708
138.056
130.925
128.412
127.748
127.685
126.589
77.333
77.015
76.698
69.760
64.244
20.933
BnO
18O
18O
f1 (ppm)

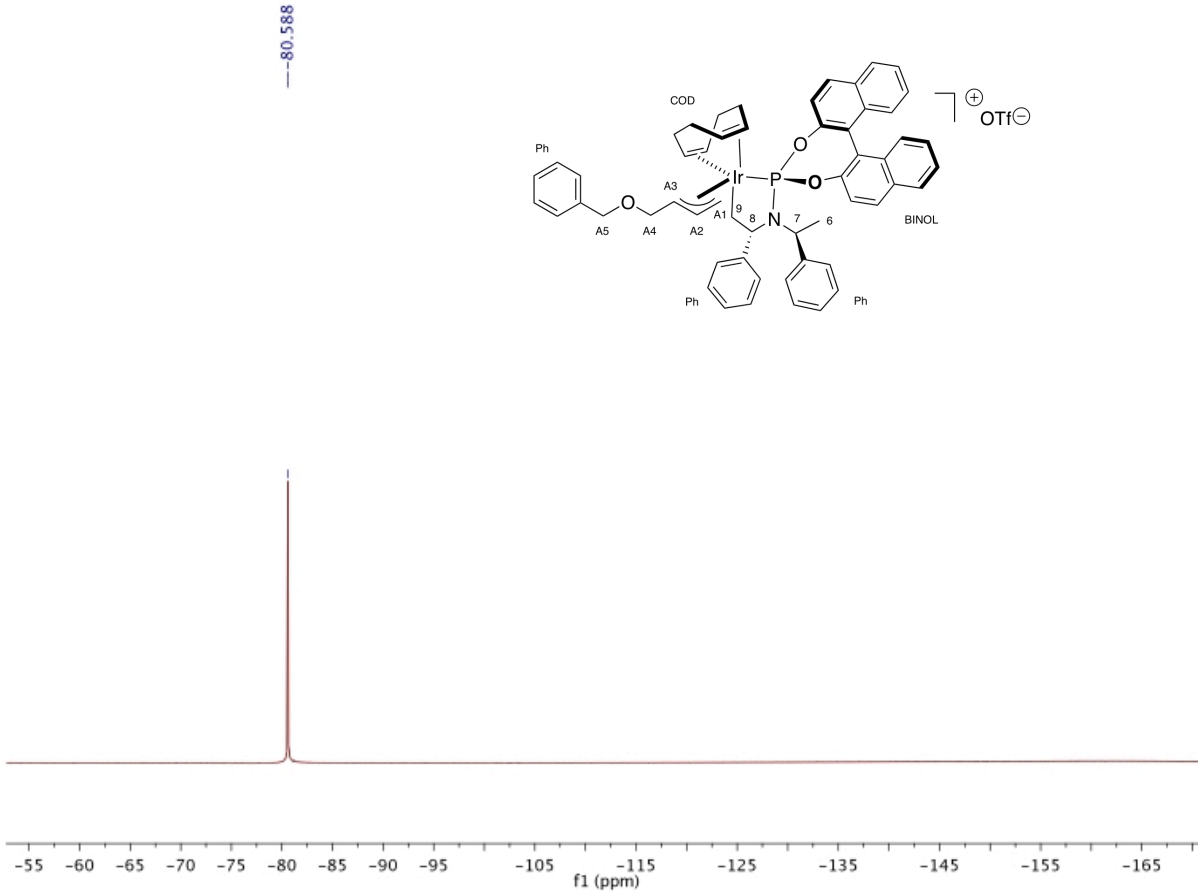

7.329
7.317
7.266
7.240
5.930
5.909
5.899
5.889
5.879
5.868
5.857
4.684
4.670
4.632
4.621
4.030
4.019
3.768
3.763
BnO
18O
O
O
13.20
5.40
1.00
4.39
5.29
1.02
4.46
7.98
f1 (ppm)


155.849
155.794
138.256
138.145
131.957
131.612
128.659
128.632
128.023
127.946
127.903
126.256
126.037
125.703
77.484
77.230
76.976
72.595
67.883
67.853
65.865
63.812
55.049
55.031
BnO
18O
O
O
1.00
49.42
f1 (ppm)


8.347
8.347
8.312
8.312
8.295
8.295
8.088
7.354
7.335
7.323
7.294
7.282
7.267
7.255
7.240
7.120
7.106
5.216
4.923
4.642
4.636
4.517
4.191
3.840
3.816
3.584
3.363
3.239
2.945
2.375
2.325
2.300
2.049
1.730
1.546
0.949
0.572
0.557
COD
OTf
Ph
Ir
P
O
A3
A1
A5
A4
A2
N
BINOL
Ph
Ph
1.06
1.09
2.06
2.02
2.02
16.96
2.01
1.00
1.07
1.03
2.01
1.09
2.04
2.21
1.01
1.08
1.07
2.00
4.12
1.11
1.14
2.07
1.09
3.04
f1 (ppm)


150.019
149.892
148.951
148.884
143.964
141.440
139.378
133.170
132.469
128.923
126.974
123.684
123.204
122.464
122.409
104.371
103.940
93.292
88.933
83.012
82.967
75.994
75.760
73.794
69.726
66.676
60.984
60.943
45.381
37.702
35.414
28.653
26.285
19.122
14.430
COD
OTf
Ph
A3
A1
A5
A4
A2
Ir
P
O
N
9
8
7
6
BINOL
Ph
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


123.065
121.001
COD
OTf
Ph
A3
A1
A5
A4
A2
Ir
P
O
N
9
8
7
6
BINOL
Ph
Ph
1.00
14.40
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
f1 (ppm)


-80.588
COD
Ph
Ir
P
O
N
A1
A2
A3
A4
A5
BINOL
OTf
Ph
Ph
-55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165
f1 (ppm)