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Supporting Information

DIASTEREOSELECTIVE SYNTHESIS OF TRIFLUOROMETHYLATED 1,3 DIOXANES BY INTRAMOLECULAR OXA-MICHAEL REACTION

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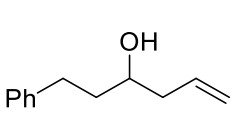
GENERAL METHODS

^{1}H NMR, ^{13}C NMR and ^{19}F spectra were recorded in $CDCl_3$ as solvent on 300 MHz or 400 MHz spectrometer. The coupling constant *J* is given in Hz. The chemical shifts are expressed in parts per million (ppm) referenced to TMS and trifluoracetic acid (^{19}F). Data are reported as follows: *δ*, chemical shift; multiplicity (recorded as br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet and m, multiplet). FTIR spectral values are reported in wave number (cm^{-1}). Optical rotations were measured on digital polarimeter using a 1 mL cell with a 1 dm path length. Mass spectrometry (MS) was performed in electron impact (EI; 70 eV) mode. Mass spectrums data are reported as m/z. High resolution mass spectrometry (HRMS) was performed on a Q-TOF LC/MS instrument. Solvents for reactions were distilled prior to use: THF and diethyl ether were distilled from Na and benzophenone; DCM from CaH_2. All air– or moisture–sensitive reactions were conducted under a nitrogen or argon atmosphere in flame– dried or oven–dried glassware with magnetic stirring. Column chromatography was carried out using silica gel 60 (230– 400 mesh).

Known compounds were found to be identical to those described in literature, in consequence in some cases only ^{1}H NMR spectra is shown.

TYPICAL PROCEDURE FOR FORMATION OF HOMOALLYLIC ALCOHOLS

To a solution of allyl bromide (2 equiv) in THF (0.96 M) was added Zn dust (2 equiv) and the aldehyde (1 equiv) at 0°C. This mixture was vigorously stirred and an aqueous solution of NH_4Cl (sat) (equal volumes with THF) was added dropwise over a period of 30 min. The reaction mixture was stirred at room temperature for 12 to 24 h (followed by TLC), then, water was added and 5% aqueous HCl to dissolve the suspension. The aqueous layer was extracted with DCM and the organic phases were washed with aqueous $NaHCO_3$ (sat), water and NaCl (sat). The organic layer was dried over $MgSO_4$ and the solvent was evaporated *in vacuo.* The crude mixture was purified using flash chromatography to afford the pure product. The known products obtained by this procedure are listed below.



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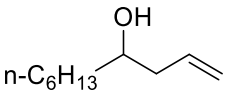

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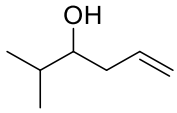

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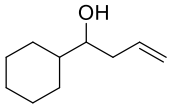

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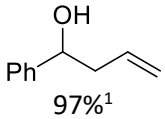

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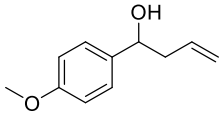

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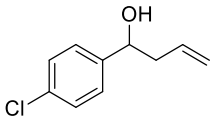
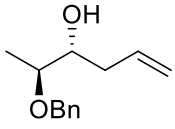


66%[1]

(2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol[5]



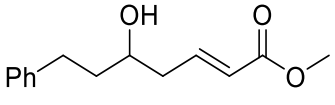
The typical procedure for formation of homoallylic alcohols was applied to (S)-2-(benzyloxy)propanal[6] (1.2 mmol, 200 mg). The crude extract was purified by flash chromatography to afford a mixture of diasteroisomers *syn* (m) and *anti* (M) (1:1.8) as a yellow oil (164 mg, 66%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.22 – 7.50 (m, 5H), 5.72 – 5.98 (m, 1H), 5.05 – 5.26 (m, 2H), 4.56 (m, 2H), 3.76 – 3.81 (m, 0.5H), 3.49 – 3.61 (m, 1H), 3.41 – 3.49 (m, 0.5H), 2.25 (t, *J* = 6.8 Hz, 1.5H), 2.12 – 2.22 (m, 0.5H), 1.20 (dd, *J* = 6.1, 3.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
138.7 (M), 138.5 (m), 135.2 (M), 135.0 (m), 128.7, 128.7, 128.1, 128.0, 127.9, 117.9 (M), 117.5 (m), 77.8 (m), 77.4 (M), 74.5 (m), 72.8 (M), 71.3 (m), 71.0 (M), 37.8 (m), 37.2 (M), 15.7 (m), 14.0.

GENERAL PROCEDURE FOR CROSS-METATHESIS REACTION

To a solution of homoallylic alcohol (1 equiv) and methyl acrylate (3.2 equiv) in dry DCM (0.34 M) under Argon was added Grubb´s II catalyst (0.025 equiv). The mixture was heated at reflux and stirred overnight. The mixture was cooled at room temperature and concentrated *in vacuo.* The crude mixture was purified using flash chromatography to afford the pure product.

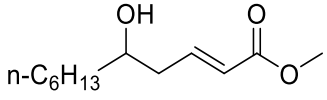
Methyl (*E*)-5-hydroxy-7-phenylhept-2-enoate (1a)



The general procedure for cross-metathesis reaction was applied to 1-phenylhex-5-en-3-ol (2.8 mmol, 500 mg). The crude residue was purified by column chromatography with petroleum ether/AcOEt (8:2) to give a brown oil (550 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):
7.17 – 7.38 (m, 5H), 6.99 - 7.07 (m, 1H), 5.96 (dt, *J* = 15.7, 1.4 Hz, 1H), 3.83 – 3.86 (m, 1H), 3.78 (s, 3H), 2.78 - 2.88 (m, 2H), 2.41 – 2.48 (m, 2H), 1.78 – 1.96 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):
166.6, 145.1, 141.5, 128.4, 128.3, 125.9, 123.5, 69.7, 51.4, 40.3, 38.6, 31.9.
IR: 3493, 3022, 2942, 1720, 1656, 1437, 1325, 1273, 1172, 1033, 977, 700.
HRMS: Calculated for $C_{14}H_{18}O_3Na$: 257.1154; found: 257.1148.

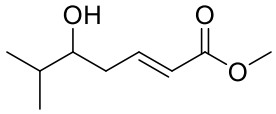
Methyl (*E*)-5-hydroxyundec-2-enoate[5] (1b)



The general procedure for cross-metathesis reaction was applied to dec-1-en-4-ol (1.3 mmol, 200 mg) The crude residue was purified by column chromatography with CH_2Cl_2/AcOEt (9.5:0.5) to give a brown oil (270 mg, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.00 (dt, *J* = 15.2, 7.4 Hz, 1H), 5.91 (d, *J* = 15.7 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.73 (s, 3H), 2.23 – 2.46 (m, 2H), 1.94 (s, 1H), 1.21 – 1.55 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H).

(*E*)-Ethyl 5-Hydroxy-2-methyl-7-phenylhept-2-enoate (1c)

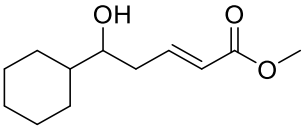


The general procedure for cross-metathesis reaction was applied to 2-methylhex-5-en-3-ol (0.89 mmol, 102 mg). The crude residue was purified by column chromatography with petroleum ether/AcOEt (8:2) to give a yellow oil (140 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):
6.95 (dt, *J* = 15.6, 7.6 Hz, 1H), 5.86 (dt, *J* = 15.6, 1.2 Hz, 1H), 3.67 (s, 3H), 3.46 (m, 1H), 2.35 (m, 1H), 2.25 (m, 1H), 1.63 (m, 1H), 1.44 (d, *J* = 4.4 Hz, 1H), 0.88 (d, *J* = 0.8 Hz, 3H), 0.87 (d, *J* = 0.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):
166.8, 146.2, 123.3, 75.3, 51.5, 37.2, 33.4, 18.7, 17.3.

IR: 3457, 2955, 2878, 1713, 1659, 1435, 1273, 1211, 1165, 1042.
MS (CI): 155.3, 173.3 ($M + H^+$, 100%).

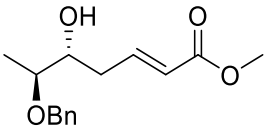
Methyl (*E*)-5-cyclohexyl-5-hydroxypent-2-enoate[5] (1d)



The general procedure for cross-metathesis reaction was applied to 1-cyclohexylbut-3-en-1-ol (1.3 mmol, 200 mg). The crude residue was purified by column chromatography with pentane/AcOEt (9:1) to give a brown oil (260 mg, 95%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
6.29 – 7.91 (m, 1H), 5.92 (d, *J* = 15.7 Hz, 1H), 3.74 (s, 3H), 3.41 – 3.61 (m, 1H), 2.20 – 2.58 (m, 2H), 1.59 - 2.00 (m, 6H), 0.76 - 1.36 (m, 6H).

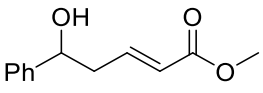
Methyl (5*R*,6*S*,*E*)-6-(benzyloxy)-5-hydroxyhept-2-enoate[5] (1e)



The general procedure for cross-metathesis reaction was applied to (2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol (0.97 mmol, 200 mg) The crude residue was purified by column chromatography with CH_2Cl_2/AcOEt (9.5:0.5) to give the product as a brown oil (70 mg, 27%). $[\alpha]_D^{23.2}$ = 27.3 (c=0.01 g/mL in CH_3Cl).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.20 – 7.49 (m, 5H), 7.09 – 6.92 (m, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 4.56 (m, 2H), 3.79 – 3.93 (m, 1H), 3.73 (s, 3H), 3.41 – 3.61 (m, 1H), 2.39 (t, *J* = 6.8 Hz, 2H), 2.15 (d, *J* = 4.5 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H).

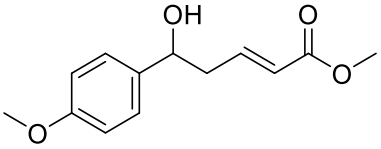
Methyl (*E*)-5-hydroxy-5-phenylpent-2-enoate[5] (1f)



The general procedure for cross-metathesis reaction was applied to 1-phenylbut-3-en-1-ol (1.2 mmol, 200 mg). The crude residue was purified by column chromatography with pentane/AcOEt (6:4) to give a brown oil (250 mg, 100%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.23 – 7.48 (m, 5H), 6.97 (dt, *J* = 15.3, 7.3 Hz, 1H), 5.90 (d, *J* = 15.3 Hz, 1H), 4.81 (t, *J* = 5.8 Hz, 1H), 3.71 (s, 3H), 2.61 - 2.70 (m, 2H), 2.31 (bs, 1H).

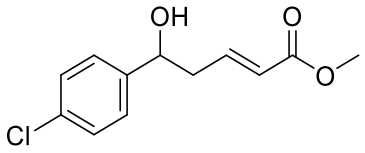
Methyl (*E*)-5-hydroxy-5-(4-methoxyphenyl)pent-2-enoate[7] (1g)



The general procedure for cross-metathesis reaction was applied to 1-(4-methoxyphenyl)but-3-en-1-ol (1.1 mmol, 200 mg) The crude residue was purified by column chromatography with CH_2Cl_2/cyclohexane (8:2) to give a brown oil (226 mg, 85%)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.23 – 7.34 (m, 2H), 6.82 - 7.05 (m, 3H), 5.89 (d, *J* = 15.7 Hz, 1H), 4.77 (t, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 2.54- 2.79 (m, 2H), 2.10 (d, *J* = 8.5 Hz, 1H).

Methyl (*E*)-5-(4-chlorophenyl)-5-hydroxypent-2-enoate[7] (1h)

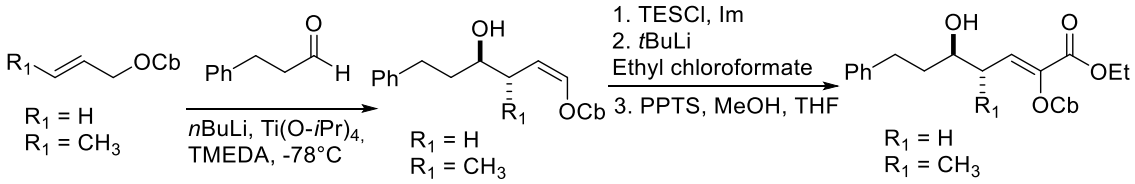


The general procedure for cross-metathesis reaction was applied to 1-(4-chlorophenyl)but-3-en-1-ol (1.1 mmol, 200 mg) The crude residue was purified by column chromatography with CH_2Cl_2/cyclohexane (8:2) to give a brown oil (239 mg, 91%).

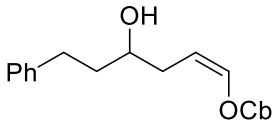
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)

7.31 (q, *J* = 8.3 Hz, 4H), 6.78 – 6.98 (m, 1H), 5.89 (d, *J* = 15.7 Hz, 1H), 4.81 (t, *J* = 6.0 Hz, 1H), 3.71 (s, 3H), 2.61 (m, 2H).

SYNTHESIS OF *O*-CARBAMATES



(*Z*)-4-hydroxy-6-phenylhex-1-en-1-yl diisopropylcarbamate



To a solution of allyl carbamate[8] (2.2 mmol, 400 mg) in dry Et_2O (6 mL) at -78°C was added freshly distilled TMEDA (2.4 mmol, 0.35 mL) dropwise over a period of 2 min, then 1.9 M *n*BuLi in hexane (2.4 mmol, 1.2 mL) was added. After 30 min freshly distilled Ti(*i*OPr)$_4$ (8.7 mmol, 2.6 mL) was added dropwise, the resulting mixture became clear red-orange and was stirred for 40 min. Then, a solution of hydrocinnamaldehyde (2.4 mmol, 0.31 mL) in Et_2O was added dropwise and the resulting mixture was stirred at -78°C for 90 min and quenched with 4M aqueous HCl solution until the white solid was totally dissolved. The aqueous phase was extracted 3 times with Et_2O and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated on *vacuo*. The crude residue was purified by flash chromatography using petroleum ether/Et_2O (7:3) to give as pale yellow oil (320 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

7.18 – 7.33 (m, 5H), 7.13 (dt, *J* = 6.5, 1.4 Hz, 1H), 4.79 (dd, *J* = 14.1, 7.6 Hz, 1H), 4.07 (bs, 1H), 3.82 (bs, 1H,), 3.66 – 3.74 (m, 1H), 2.86 – 2.77 (m, 1H), 2.66 – 2.72 (m, 1H), 2.32 – 2.43 (m, 2H), 1.74 – 1.94 (m, 2H), 1.61 (d, *J* = 4.5 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 12H).

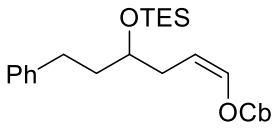
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

153.1, 142.3, 137.8, 128.7, 126.1, 106.5, 70.9, 47.2, 46.1, 38.8, 33.6, 32.3, 21.8, 20.6.

IR: 3459, 2971, 2931, 1684, 1437, 1370, 1437, 1237, 1132, 1055, 761, 699.

HRMS: Calculated for $C_{19}H_{29}NNaO_3$: 342.2045; Found: 342.2029.

(*Z*)-4-((3-ethylpentan-3-yl)oxy)-6-phenylhex-1-en-1-yl diisopropylcarbamate



To a solution of carbamate (1.1 mmol, 350 mg), imidazole (3.3 mmol, 223 mg) and dry CH_2Cl_2 (5.5 mL) was added chlorotriethylsilane (0.3 mL, 1.7 mmol) to 0°C. The reaction mixture was stirred for 2 h and heated to room temperature overnight. The reaction mixture was quenched with MeOH. Water was added and the aqueous phase was extracted three times with

CH_2Cl_2. The organic phase was washed with NaCl sat, dried with $MgSO_4$ and purified with flash chromatography using petroleum ether/Et_2O (9:1). The product was obtained as pale yellow oil (295 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

7.25 – 7.29 (m, 2H), 7.15 – 7.18 (m, 3H), 7.07 (dt, *J* = 6.5, 1.5 Hz, 1H), 4.78 (m, 1H), 4.02 (brs, 1H), 3.87 (brs, 1H), 3.75 – 3.83 (m, 1H), 2.69 – 2.76 (m, 1H), 2.57 – 2.64 (m, 1H), 2.30 – 2.50 (m, 2H), 1.69 – 1.85 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 12H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H).

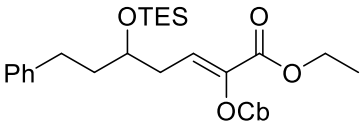
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

153.0, 142.8, 136.6, 128.6, 126.0, 106.9, 71.8, 46.8, 46.3, 39.1, 33.4, 32.1, 21.8, 20.7, 6.7, 5.4.

IR: 2956,2875, 1707, 1433, 1369, 1307, 1287, 1210, 1061, 726, 698.

HRMS: Calculated for $C_{25}H_{43}NNaO_3Si$: 456.2910; found: 456.2928.

Ethyl (*Z*)-2-((diisopropylcarbamoyl)oxy)-7-phenyl-5-((triethylsilyl)oxy)hept-2-enoate



To a solution of protected carbamate (0.66 mmol, 290 mg) in 4.1 mL of dry THF at -78°C was slowly added a solution of 0.90 M *t*BuLi in pentane (0.73 mmol, 0.82 mL). After stirring for 1 hour at -78 °C, a solution of ethyl chloroformate (0.73 mmol, 0.70 mL) in THF was added dropwise. The resulting solution was stirred at -78°C for 5 h, and quenched with NH_4Cl (sat). Water and Et_2O were added. The aqueous phase was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ concentrated *in vacuo* and purified with flash chromatography using cychlohexane/CH_2Cl_2 (7:3). The product was obtained as pale yellow oil (290 mg, 92%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.06 – 7.32 (m, 5H), 6.57 (t, *J* = 7.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.02 – 4.14 (m, 1H), 3.78 – 3.99 (m, 2H), 2.53 – 2.82 (m, 2H), 2.38 – 2.48 (m, 2H), 1.76- 1.85 (m, 2H), 1.18 – 1.42 (m, 15H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H).

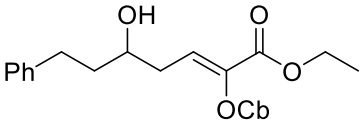
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

162.9, 153.1, 142.5, 139.9, 128.6, 128.6, 126.8, 126.0, 71.0, 61.4, 47.1, 46.5, 39.4, 34.2, 31.9, 21.7, 20.7, 14.4, 7.2, 5.2.

IR: 2954, 2933, 2358, 2341, 1716, 1521, 1456, 1367, 1290, 1087, 1043, 1006, 723.

HRMS: Calculated for $C_{28}H_{48}NO_5Si$: 506.3302; found: 506.3303.

Ethyl (Z)-2-((diisopropylcarbamoyl)oxy)-5-hydroxy-7-phenylhept-2-enoate (6b)



The protected alcohol (0.25 mmol, 150 mg) was dissolved in MeOH (0.75 mL) and THF (0.19 mL) with pyridinium-*p*-toluensulfanate (PPTS) (15 mg, 0.059 mmol) at 0°C. The reaction mixture was stirred for 2 h, and quenched with $NaHCO_3$ (sat). Water was added and the product was extracted with AcOEt, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude product was purified by flash chromatography using pentane/AcOEt (9:1) to give the product as pale yellow oil (91 mg, 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.13 – 7.33 (m, 5H), 6.61 (t, *J* = 7.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.89 – 4.07 (m, 2H), 3.69 – 3.83 (m, 1H), 2.60 – 2.91 (m, 3H), 2.29 – 2.51 (m, 2H), 1.76 – 1.85 (m, 2H), 1.22 – 1.35 (m, 15H).

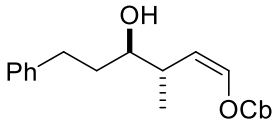
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

162.6, 153.7, 142.2, 140.4, 128.7, 128.6, 127.5, 126.1, 69.8, 61.6, 47.2, 46.6, 39.3, 34.4, 32.2, 21.6, 20.6, 14.4.

IR: 3398, 2954, 2875, 2357, 1701, 1454, 1261, 1068, 1047, 1002, 740, 734.

HRMS: Calculated for $C_{22}H_{34}NO_5$: 392.2437; found: 392.2436.

(3*R,4*S**,*Z*)-4-hydroxy-3-methyl-6-phenylhex-1-en-1-yl diisopropylcarbamate**



To a solution of crotyl carbamate[9] (2.0 mmol, 400 mg) in dry Et_2O (5.7 mL) at -78°C was added freshly distilled TMEDA (2.2 mmol, 0.30 mL) dropwise over a period of 2 min, then 1.9 M *n*BuLi in hexane (2.2 mmol, 1.7mL) was added. After 30 min freshly distilled Ti(*i*OPr)$_4$ (8.0 mmol, 2.4 mL) was added dropwise, the resulting mixture became clear red-orange and was stirred 40 min. Then, a solution of hydrocinnamaldehyde (2.2 mmol, 0.30 mL) in Et_2O was added dropwise and the resulting mixture was stirred at -78°C for 90 min and quenched with 4N aqueous HCl aqueous solution until the white solid was totally dissolved. The aqueous phase was extracted 3 times with Et_2O and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated *on vacuo*. The crude residue was purified by flash chromatography using petroleum ether/Et_2O (7:3) to give as pale yellow oil (340 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

7.23 – 7.30 (m, 2H), 7.15 – 7.23 (m, 3H), 7.12 (dd, *J* = 6.5, 0.7 Hz, 1H), 4.67 (dd, *J* = 10.0, 6.5 Hz, 1H), 4.08 (bs, 1H), 3.80 (bs, 1H), 3.43 – 4.49 (m, 1H), 2.60 – 2.99 (m, 3H), 1.67 – 1.95 (m, 2H), 1.60 (d, *J* = 3.9 Hz, 1H), 1.24 (d, *J* = 6.7 Hz, 12H), 1.04 (d, *J* = 6.9 Hz, 3H).

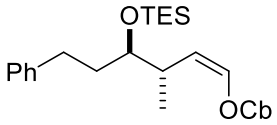
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

153.1, 142.6, 136.7, 128.7, 128.7, 126.1, 112.4, 74.9, 47.2, 46.2, 36.8, 36.7, 32.3, 21.9, 20.7, 17.6.

IR: 3478, 2969, 2934, 1687, 1437,1370, 1259, 1209, 1135, 1209.

HRMS: Calculated for $C_{20}H_{31}NNaO_3$: 356.2202; found: 356.2182.

(3*R,4*S**,*Z*)-3-methyl-6-phenyl-4-((triethylsilyl)oxy)hex-1-en-1-yl diisopropylcarbamate**



To a solution of carbamate (0.99 mmol, 330 mg), imidazole (2.9 mmol, 202 mg) and dry CH_2Cl_2 (5 mL) was added chlorotriethylsilane (0.25 mL, 1.5 mmol) to 0°C. The reaction mixture was stirred for 2 h and heated to room temperature overnight. The reaction mixture was quenched with MeOH. Water was added and the aqueous phase was extracted three times with CH_2Cl_2. The organic phase was washed with NaCl sat, dried with $MgSO_4$ and purified with flash chromatography using petroleum ether/Et_2O (9:1). The product was obtained as pale yellow oil (277 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

7.24 – 7.31 (m, 2H), 7.15 – 7.19 (m, 3H), 7.03 (dd, *J* = 6.5, 0.7 Hz, 1H), 4.75 (dd, *J* = 10, 6.5 Hz, 1H), 4.00 (brs, 1H), 3.92 (brs, 1H), 3.63 – 3.67 (m, 1H), 2.85 – 2.91 (m, 1H), 2.53 – 2.70 (m, 2H), 1.67 – 1.78 (m, 2H), 1.25 (d, *J* = 6.9 Hz, 12H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H).

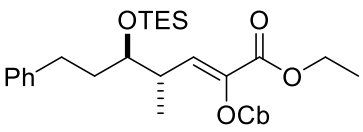
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

153.1, 142.9, 135.3, 128.6, 128.6, 126.0, 112.7, 75.5, 46.8, 46.2, 37.0, 35.5, 32.6, 21.7, 20.7, 17.3, 7.3, 5.6.

IR: 2958, 2875, 1708, 1433, 1369, 1306, 1288, 1212, 1135, 1057, 736.

HRMS: Calculated for $C_{26}H_{45}NNaO_3Si$: 470.3066; Found: 470.3076.

Ethyl (4*R,5*S**,*Z*)-2-((diisopropylcarbamoyl)oxy)-4-methyl-7-phenyl-5-((triethylsilyl)oxy)hept-2-enoate**



To a solution of protected carbamate (0.60 mmol, 280 mg) in 4.1 mL of dry THF at -78°C was slowly added a solution of 0.90 M *t*-BuLi in pentane (0.70 mL, 0.69 mmol). After stirring for 1 hour at -78 °C, a solution of ethyl chloroformate (0.65 mL, 0.69 mmol) in THF was added dropwise. The resulting solution was stirred at -78°C for 5 h, and quenched with NH_4Cl (sat). Water and Et_2O were added. The aqueous phase was extracted with Et_2O The combined organic phases were dried over $MgSO_4$ concentrated *in vacuo* and purified with flash chromatography using cyclohexene/CH_2Cl_2 (6:4). The product was obtained as pale yellow oil (273 mg, 84%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.11 – 7.37 (m, 5H), 6.45 (d, *J* = 10.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.85 - 4.08 (m, 2H), 3.66 – 3.71 (m, 1H), 2.74 – 2.85 (m, 1H), 2.50 – 2.69 (m, 2H), 1.74 (q, *J* = 8.1 Hz, 2H), 1.24 - 1.31 (m, 15H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H).

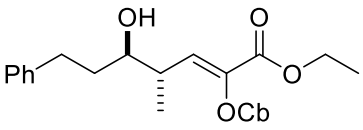
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

163.1, 153.1, 142.7, 138.8, 132.0, 128.6, 126.0, 75.0, 61.4, 47.0, 46.6, 36.9, 36.5, 32.4, 21.7, 20.7, 16.1, 14.4, 7.3, 5.4.

IR: 2962, 2935, 2357, 2320, 1716, 1521, 1506, 1471, 1456, 1435, 1288, 1234, 1288, 1234, 1083, 1031, 1006, 742, 725.

HRMS: Calculated for $C_{29}H_{50}NO_5Si$: 520.3458; found: 520.3440.

Ethyl (4*R,5*S**,*Z*)-2-((diisopropylcarbamoyl)oxy)-5-hydroxy-4-methyl-7-phenylhept-2-enoate (6c)**



The protected alcohol (0.28 mmol, 150 mg) was dissolved in MeOH (1 mL) and THF (0.27 mL) with PPTS (14 mg, 0.057 mmol) at 0°C. The reaction mixture was stirred for 2 h, and quenched with $NaHCO_3$ (sat). Water was added and the product was extracted with AcOEt, dried over MgSO4, filtered and concentrated *in vacuo.* The crude product was purified by flash chromatography using pentane/AcOEt (8:2) to give the product as pale yellow oil (86 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.12 – 7.38 (m, 5H), 6.48 (d, *J* = 10.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.87 - 4.08 (m, 2H), 3.46 – 3.56 (m, 1H), 2.61 – 2.91 (m, 3H), 2.57 (d, *J* = 4.4 Hz, 1H), 1.60 – 1.97 (m, 2H), 1.21 – 1.39 (m, 15H), 1.06 (d, *J* = 6.8 Hz, 3H).

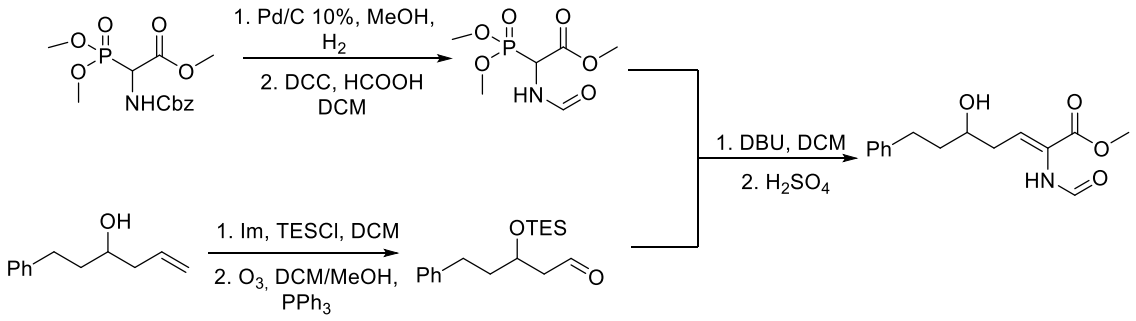
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)

162.7, 153.3, 142.5, 139.2, 132.9, 128.8, 128.6, 126.0, 74.2, 61.6, 47.2, 46.6, 37.7, 37.1, 31.9, 21.7, 21.6, 20.7, 20.6, 16.9, 14.4.

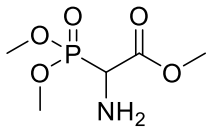
IR: 3487, 2970, 1705, 1452, 1436, 1369,1292, 1230, 1126, 1082, 1043, 987, 761.

HRMS: Calculated for $C_{23}H_{36}NO_5$: 406.2593; found: 406.2586.

SYNTHESIS OF *N*-CARBAMATE



Methyl 2-amino-2-(dimethoxyphosphoryl)acetate[10]

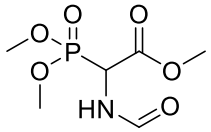


A mixture of benzyloxycarbonyl-α-phosphonoglycine trimethyl ester (4.5 mmol, 1500 mg) and Pd/C (10% mol, 15 mg) in MeOH (0.1 M) was allowed to stir for 12 hours in hydrogen atmosphere. The mixture reaction was filtered through a short pad of celite and concentrated under reduced pressure. The crude extract was obtained as pale yellow oil (890 mg, 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

3.96 (d, *J* = 21.3 Hz, 1H), 3.86 (d, *J* = 2.6 Hz, 3H), 3.83 (d, *J* = 2.6 Hz, 6H), 1.78 (bs, 2H).

Methyl 2-(dimethoxyphosphoryl)-2-formamidoacetate[11]

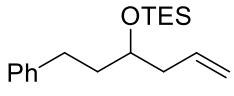


To a solution of free amine (341 mg, 1.5 mmol) in dry dichloromethane (1 mL), a solution of formic acid (0.060 mL, 1.5 mmol) in dicholomethane (1.5 mL) were added at -10°C. Then, the cyclohexylcarbodiimide (342 mg, 1.7 mmol) was added and the mixture reaction was stirred to room temperature overnight. The precipitated urea was filtered and washed with cool DCM and the filtrate was washed with 1 mL of $KHSO_4$ 1 N, and with 1 mL of $NaHCO_3$ (sat), dried with Na_2SO_4 and concentrated *in vaccuo.* To remove traces of urea, the residue was dissolved in DCM (3 mL) the mixture was kept at -10°C overnight and washed with cool DCM. The product was purified with AcOEt to afford white solid (331 mg, 96 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

8.26 (s, 1H), 6.75 (bs, 1H), 5.29 (dd, *J* = 21.8, 9.1 Hz), 3.79 – 3.88 (m, 9H).

Triethyl((1-phenylhex-5-en-3-yl)oxy)silane[12]

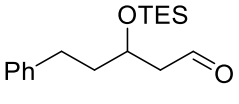


To a solution of 1-phenylhex-5-en-3-ol (21 mmol, 4 g), imidazole (68 mmol, 4.6 g) and dry CH_2Cl_2 (60 mL) was added chlorotriethylsilane (34 mmol, 5.7 mL) to 0°C. The reaction mixture was stirred for 2 h and heated to room temperature overnight. The reaction mixture was quenched with MeOH. Water was added and the aqueous phase was extracted three times with CH_2Cl_2. The organic phase was washed with brine, dried with anhydrous $MgSO_4$ and purified with flash chromatography using cyclohexane/CH_2Cl_2 (9:1). The product was obtained as yellow oil (646 mg, 98 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.11 – 7.36 (m, 5H), 5.83 (m, 1H), 5.01 (m, 2H), 3.71 – 3.84 (m, 1H), 2.60 - 2.72 (m, 2H), 2.23 – 2.34 (m, 2H), 1.67 – 1.87 (m, 2H), 0.95 - 0.99 (t, 7.9 Hz, 9H), 0.58 – 0,64 (q, 7.9 Hz, 6H).

5-phenyl-3-((triethylsilyl)oxy)pentanal



A solution of protected alcohol (15 mmol, 4.4 g) in DCM (180 mL) and MeOH (45 mL) was cooled at -78°C. O_3 was burbled until the solution was turned pale blue, then O_2 was burbled until the coloration disappeared completely. PPh_3 (17 mmol, 4.3 g) was added, and the mixture was stirred at -78°C for 30 min. The reaction mixture was warmed up to room temperature for 3 hours. Then the solvent was evaporated *in vacuo.* Purification was done by flash chromatography using cyclohexane/CH_2Cl_2 (6:4) to give a pale yellow oil (4.4 g, 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

9.82 (t, *J* = 2.4 Hz, 1H), 6.95 - 7.45 (m, 5H), 4.24 – 4.30 (m, 1H), 2.43 - 2.80 (m, 4H), 1.84 – 1.89 (m, 2H), 0.96 (t, *J*=7.9, 9H), 0.61 (q, *J*=7.9, 6H).

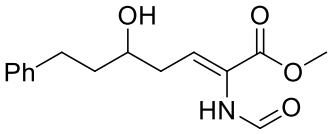
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

201.8, 141.6, 128.4, 128.2, 125.9, 67.6, 50.9, 39.6, 31.5, 6.8, 4.9.

IR: 1954, 2876, 1711, 1456, 1413, 1101, 1005, 744, 698.

HRMS: Calculated, $C_{17}H_{28}OSiNa$: 315.1756; found: 315.1766.

Methyl (*Z*)-2-formamido-5-hydroxy-7-phenylhept-2-enoate (6d)



To a solution of methyl 2-(dimethoxyphosphoryl)-2-formamidoacetate (2.1 mmol, 466 mg) in dry DCM (5.5 mL) was added DBU (1.9 mmol, 0.29 mL) at 0°C. After 30 minutes of stirring a solution of 5-phenyl-3-((triethylsilyl)oxy)pentanal (1.9 mmol, 550 mg) in dry DCM was added dropwise at 0°C. The reaction was stirred to room temperature overnight. Then, a solution 1M of H_2SO_4 (10 mL) was added to mixture reaction. This mixture reaction was stirred by 4 hours, the aqueous layer was extracted with ethyl acetate and dried over $MgSO_4$, filtered and concentered *in vaccuo.* The crude mixture was purified by column chromatography using CH_2Cl_2/AcOEt (8:2) to obtain the product as yellow oil (410 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

The presence of two rotamers was observed in NMR spectra in a 0,73 (M):0,27 (m) ratio.

8.26 (m) (d, *J* = 10.5 Hz, 1H), 8.21 (M) (s, 1H), 7.76 (m) (d, *J* = 10.5 Hz, 1H), 7.48 (M) (s, 1H), 7.14 – 7.33 (m, 5H), 6.82 (M) (t, *J* = 7.6 Hz, 1H), 6.68 (m) (t, *J* = 7.6 Hz, 1H), 3.81 – 3.91 (m, 1H), 3.80 (m) (s, 3H) 3.78 (M) (s, 3H), 3.12 (s, 1H), 2.60 – 2.87 (m, 2H), 2.36- 2.45 (m, 2H), 1.79 – 1.86 (m, 2H).

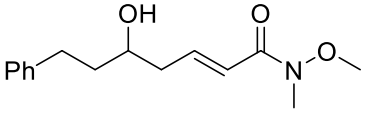
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

164.4 (M), 164.4 (m), 159.5, 141.7, 134.8 (M), 130.8 (m), 128.5, 128.3, 128.3, 126.0, 125.8, 125.2, 70.5 (m), 69.7 (M), 52.6 (m), 52.5 (M), 39.4 (M), 38.8 (m), 36.6 (M), 35.3 (m), 31.9.

IR: 3380, 2929, 2859, 1721, 1779, 1652, 1495, 1436, 1394, 1282, 1278, 1207, 1057, 911, 748, 966.

HRMS: Calculated for: $C_{15}H_{19}NNaO_4$: 300.1212; found: 300.1206.

(*E*)-5-hydroxy-*N*-methoxy-*N*-methyl-7-phenylhept-2-enamide (8)



To a solution of methyl (*E*)-5-hydroxy-7-phenylhept-2-enoate **1a** (0.85 mmol, 200 mg), imidazole (2.5 mmol, 174 mg) and dry CH_2Cl_2 (2 mL) was added chlorotriethylsilane (1.27 mmol,0.20 mL,) to 0°C. The reaction mixture was stirred for 2 h and heated to room temperature overnight. The reaction was quenched with MeOH. Water was added and the aqueous phase was extracted three times with CH_2Cl_2. The organic phase was washed with brine, dried with anhydrous $MgSO_4$. The crude protected alcohol was dissolved with dry THF (4 mL) and

Me(OMe)NH**.**HCl (0.86 mmol, 84 mg) at –10 °C, the mixture was treated with LiHMDS (1.7 mL, 1.0 M in THF) 3 min. After stirring for 15 min at –10 °C, the mixture was warmed to rt and stirred for 6 h. The mixture was diluted with Et_2O, washed with saturated NH_4Cl and brine, dried ($MgSO_4$) and concentrated *in vaccuo.* The crude protected alcohol was dissolved in MeOH/THF (4:1) and a catalytic amount of pyridinium p-toluenesulfonate was added and after stirring over night the reaction mixture was quenched with $NaHCO_3$. Water was added and the product was extracted with AcOEt, washed with brine and dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography using AcOEt/CH_2Cl_2 to afford the corresponding weinreb amide as pale yellow oil (60 mg, 27%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

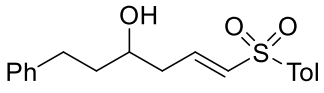
7.14 – 7.38 (m, 5H), 6.93 – 7.00 (m, 1H), 6.49 (d, *J* = 15.4 Hz, 1H), 3.76 – 3.85 (m, 1H), 3.70 (s, 3H), 3.24 (s, 3H), 2.64 – 2.76 (m, 2H), 2.33 – 2.50 (m, 2H), 1.69 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

166.9, 143.5, 142.1, 128.8, 128.7, 126.2, 122.1, 70.2, 62.0, 41.0, 39.0, 23.2, 32.3.

HRMS: Calculated for $C_{15}H_{22}NO_3$: 438.1892; Found: 438.1884

(*E*)-1-phenyl-6-tosylhex-5-en-3-ol[13] (10)



To a solution of 1-phenylhex-5-en-3-ol (1.7 mmol, 300 mg) in 3.4 mL of acetonitrile at room temperature was added a solution of freshly prepared tosyl iodide (3.4 mmol, 605 mg) in acetonitrile. The resulting solution was stirred for 1 h 30 min at room temperature until completion of the reaction and then concentrated to a brown oil. The crude mixture of β-iodosulfones was treated with a solution of DBU (2.0 mmol, 305 mg) in 4 mL of 3:1 toluene/THF at room temperature. The mixture was stirred for 1 h 30 min at room temperature and quenched by the addition of 3 mL of a saturated aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with 5 mL of ether and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo.* The crude mixture was purified by flash chromatography using CH_2Cl_2 /cyclohexane (8:2) to give the sulfone as white solid (170 mg, 30%).

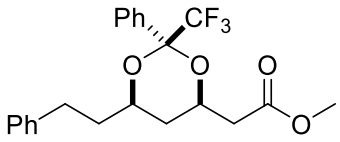
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

7.66 – 7.89 (m, 2H), 7.24 – 7.37 (m, 5H), 7.06 – 7.21 (m, 2H), 6.93 – 7.01 (m, 1H), 6.39 (dt, *J* = 15.1, 1.4 Hz, 1H), 3.77 – 3.81 (m, 1H), 2.65 – 2.81 (m, 2H), 2.43 (s, 3H), 2.36 – 2.42 (m, 2H), 1.67 – 1.87 (m, 2H).

SYNTHESIS OF TRIFLUOROMETHYLATED 1,3 DIOXANES

To a solution of homoallylic alcohol (1 equiv) in THF (0.1 M) at 0°C was added trifluoroacetophenone (1.1 equiv) followed by *t*BuOK (0.1 equiv) and the resulting mixture was stirred for 15 min at 0°C. A second portion of trifluoroacetophenone and *t*BuOK was added, after 15 min a third addition was made. The reaction was then stirred at 0°C for 4 hours and quenched with a saturated aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with AcOEt and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vaccuo*. The crude residue was then purified by column chromatography.

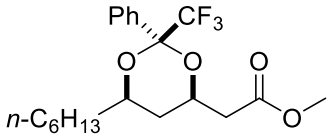
Methyl 2-((2*R,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2a)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1a** (0.59 mmol, 140 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (7:3) to afford ketal as white solid (193mg, 79%), mp: 99-101 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.36 – 7.64 (m, 5H), 7.18 – 7.37 (m, 5H), 4.23 – 4.32 (m, 1H), 3.80 – 3.88 (m, 1H), 3.77 (s, 3H), 2.92 - 3.06 (m, 1H), 2.70 – 2.83 (m, 1H), 2.78 (dd, *J* = 16.1, 8.1 Hz, 1H), 2.51 (dd, *J* = 16.1, 4.9 Hz, 1H), 1.94 - 2.14 (m, 1H), 1.93 – 1.78 (m, 1H), 1.50 – 1.64 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.1, 141.7, 132.3, 130.1, 129.3, 129.0, 128.7, 128.6, 126.3, 121.8 (q, $J_{C\text{-}F}$ = 284.6 Hz), 98.9 (q, $J_{C\text{-}F}$ = 32.0 Hz), 70.4, 67.8, 52.1, 40.7, 37.4, 36.1, 31.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.51
IR: 2949, 1738, 1497, 1484, 1398, 1358, 1337, 1217, 1188, 1177, 1109, 1092, 1061, 1032.
HRMS: Calculated for $C_{22}H_{24}F_3O_4$: 409.4254; Found: 409.4267.

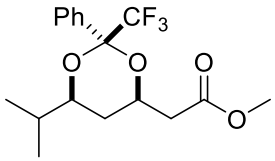
Methyl 2-((2*R,4*R**,6*R**)-6-hexyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2b)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1b** (0.46 mmol, 100 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (7:3) to afford ketal as white solid (145 mg, 80%), mp: 93-95 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.37 – 7.65 (m, 5H), 4.15 – 4.36 (m, 1H), 3.61 – 3.78 (m, 1H), 3.74 (s, 3H), 2.74 (dd, *J* = 16.1, 8.1 Hz, 1H), 2.48 (dd, *J* = 16.1, 4.9 Hz, 1H), 1.25 – 1.82 (m, 12H), 0.90 (t, *J* = 6.3 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.2, 132.5, 130.0, 129.4, 128.9, 121.78 (q, $J_{C\text{-}F}$ = 284.5 Hz), 98.79 (q, $J_{C\text{-}F}$ = 31.8 Hz), 71.0, 67.8, 52.1, 40.7, 36.1, 36.0, 32.1, 29.5, 25.1, 22.9, 14.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.61.
IR: 2953, 2926, 2856m 2360, 1740, 1330, 1174, 1107, 977, 856, 725.
HRMS: Calculated for $C_{20}H_{31}F_3NO_4$: 406.2205; Found: 406.2204.

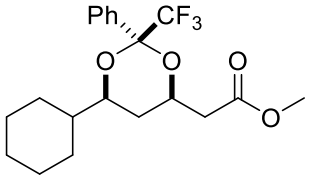
Methyl 2-((2*R,4*S**,6*R**)-6-isopropyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2c)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1c** (0.31 mmol, 53 mg). The crude mixture was purified by column chromatography using petroleum ether/AcOEt (9:1) to afford ketal as white solid (86 mg, 81%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):
7.50 (m, 2H), 7.37 (m, 3H), 4.16 (m, 1H), 3.68 (s, 3H), 3.40 (m, 1H), 2.68 (dd, *J* = 16.1, 8.0 Hz, 1H), 2.42 (dd, *J* = 16.1, 4.9 Hz, 1H), 1.72 (sp, *J* = 6.8 Hz, 1H), 1.44 (m, 2H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): (quaternary carbons were not detected)
170.9, 132.3, 129.7, 129.1, 128.7, 75.4, 67.6, 51.8, 40.6, 32.8, 18.0, 17.8.
MS (CI): 347.4 ($M + H^+$, 68%).
IR: 2893, 1744, 1443, 1380, 1327, 1240, 1185, 1103, 1057.

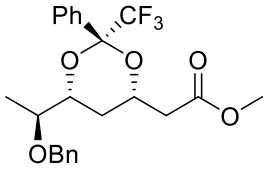
Methyl 2-((2*R,4*S**,6*R**)-6-cyclohexyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2d)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1d** (0.66 mmol, 140 mg). The crude mixture was purified by column chromatography using pentane/AcOEt (9:1) to afford ketal as white solid (210 mg, 82%), mp: 94-96 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.37 – 7.75 (m, 5H), 4.17 – 4.33 (m, 1H), 3.76 (s, 3H), 3.49 – 3.56 (m, 1H,), 2.78 (dd, *J* = 16.1, 8.1 Hz, 1H), 2.51 (dd, *J* = 16.1, 4.8 Hz, 1H), 0.95 - 1.88 (m, 11H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.1, 132.5, 130.0, 129.4, 128.9, 121.8 (q, $J_{C\text{-}F}$ = 284.7 Hz), 98.7 (q, $J_{C\text{-}F}$= 31.8 Hz), 75.0, 67.9, 52.0, 42.6, 40.8, 33.2, 28.7, 28.2, 26.6, 26.2, 26.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.59.
IR: 2926, 2368, 1743, 1327, 1176, 1114, 1062, 979, 729
HRMS: Calculated for $C_{20}H_{25}F_3NaO_4$: 409.1603; Found: 409.1618.

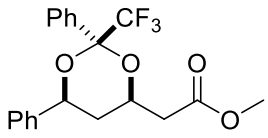
Methyl 2-((2*R*,4*S*,6*R*)-6-((S)-1-(benzyloxy)ethyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate. (2e)



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1e** (0.24 mmol, 65 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (1:9) to afford ketal as pale yellow oil (75 mg, 70%). $[\alpha]_D^{24.3}$ = -6.5 (c=0.01 g/mL in $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.24 – 7.69 (m, 10H), 4.61 – 4.72(m, 2H), 4.26 – 4.34 (m, 1H), 3.78 (s, 3H), 3.53 – 3.75 (m, 2H), 2.80 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.54 (dd, *J* = 16.2, 4.7 Hz, 1H), 1.59 – 1.82 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.1, 138.7, 131.9, 130.2, 129.4, 129.0, 128.7, 128.0, 127.9, 121.7 ($J_{C\text{-}F}$ =283. Hz), 98.7 ($J_{C\text{-}F}$ =32 Hz), 76.5, 74.1, 71.8, 67.8, 52.1, 40.8, 31.6, 16.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.52.
IR: 2929, 2357, 1739, 1450, 1436, 1332, 1224, 1188, 1107, 983, 7725.
HRMS: Calculated for $C_{23}H_{29}F_3NO_5$: 456.1996; Found: 456.1998.

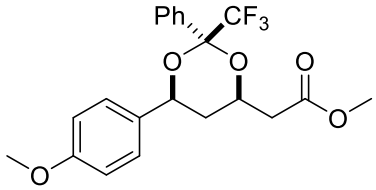
Methyl 2-((2*R,4*S**,6*R**)-2,6-diphenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2f)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1f** (0.67 mmol, 140 mg). The crude mixture was purified by column chromatography using pentane/AcOEt (9:1) to afford ketal as white solid (173 mg, 67%; 80% brsm), mp: 116-118 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.27 – 7.74 (m, 5H), 4.81 – 4,86 (m, 1H), 4.38 – 4.52 (m, 1H), 3.74 (s, 3H), 2.80 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.52 (dd, *J* = 16.2, 4.9 Hz, 1H), 1.80 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.0, 140.5, 132.0, 130.3, 129.4, 129.2, 128.9, 128.5, 126.0, 121.7 (q, $J_{C\text{-}F}$ = 284.5 Hz), 99.2 (q, $J_{C\text{-}F}$ = 32.2 Hz), 72.8, 68.0, 52.2, 40.6, 38.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.49.
IR: 2924, 1722, 1328, 1190, 1161, 1116, 1051, 719.
HRMS: Calculated for $C_{20}H_{23}F_3NO_4$: 398.1579; Found: 398.1567.

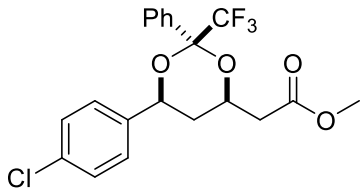
Methyl 2-((2*R,4*S**,6*R**)-6-(4-methoxyphenyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2g)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1g** (0.42 mmol, 100 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (7:3) to afford ketal as white solid (125mg, 70%), mp: 81- 83°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.65 (d, *J* = 6.4 Hz, 2H), 7.48 (d, *J* = 6.4 Hz, 3H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.77 (dd, *J* = 10.9, 2.8 Hz, 1H), 4.39 - 4.45 (m, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.80 (dd, *J* = 16.2, 8.0 Hz, 1H), 2.52 (dd, *J* = 16.2, 4.9 Hz, 1H), 1.63 – 1.98 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
171.0, 159.8, 132.6, 132.1, 130.2, 129.4, 129.1, 127.5, 114.2, 121.76 (q, $J_{C\text{-}F}$ =284.6 Hz), 99.2 (q, $J_{C\text{-}F}$= 32.1 Hz), 72.6, 68.1, 55.5, 52.1, 40.6, 38.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.50.
IR: 2953, 1739, 1614, 1450, 1385, 1263, 1164, 1105, 1031, 979.
HRMS: Calculated for $C_{21}H_{25}F_3NO_5$: 428.1685; Found: 428.1690.

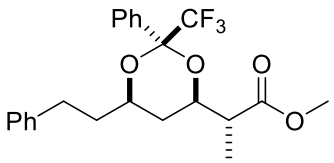
Methyl 2-((2*R,4*S**,6*R**)-6-(4-chlorophenyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2h)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1h** (0.42 mmol, 100 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (7:3) to afford ketal as white solid (110 mg, 63%), mp: 127-129°C.

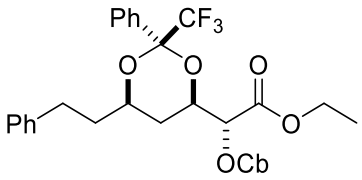
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.20 – 7.79 (m, 9H), 4.64 – 4.98 (m, 1H), 4.40 – 4.45 (m, 1H), 3.75 (s, 3H), 2.80 (dd, *J* = 16.3, 7.9 Hz, 1H), 2.56 (dd, *J* = 16.3, 5.0 Hz, 1H), 1.76 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
170.8, 139.0, 134.3, 131.9, 130.4, 129.3, 129.2, 129.1, 127.4, 121.4 (q, $J_{C\text{-}F}$ =283.8 Hz), 99.4 (q, $J_{C\text{-}F}$= 32.1 Hz), 72.3, 68.1, 52.1, 40.6, 38.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.48
IR: 1724, 1490, 1440, 1330, 1226, 1192, 1174, 1161, 1122, 1083, 1014, 985, 829.
HRMS: Calculated for $C_{20}H_{22}ClF_3NO_4$: 432.1189; Found: 432.1200.

Methyl 2-((2*R,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)propanoate (7a)**



To a solution of homoallylic alcohol (0.14 mmol, 36 mg) in THF (1 mL) at 0°C were added trifluoroacetophenone (0.59 mmol, 80 µL) and *t*BuOK in THF (0.10 mmol, 0.10 mL). The mixture was warmed to room temperature and stirred for 3 days. The mixture was quenched with a saturated aqueous solution of NH_4Cl (2 mL) and diluted with diethyl ether and water. The aqueous phase was then extracted with diethyl ether. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was analysed by ^{1}H NMR and revealed a mixture of **7d** (50%), the two diastereoisomers **7d´** and **7d´´** (4.5:1, 27% conversion by NMR) the hemiacetal (7.1% by NMR) and the elimination product (15% by NMR). The crude mixture was purified by column chromatography using petroleum ether/AcOEt (9:1) to afford a mixture of two inseparable *syn*-diastereoisomers.
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):
7.39-7.42 (m, 2H), 7.33-7.37 (m, 3H), 7.20-7.24 (m, 2H), 7.11-7.16 (m, 3H), 3.87 (ddd, *J* = 11.4, 7.2, 2.4 Hz, 1H), 3.68-3.74 (m, 1H), 3.62 (s, 3H), 2.84-2.92 (m, 1H), 2.62-2.69 (m, 1H), 2.57 (dq, *J* = 7.2, 7.1 Hz, 1H), 1.89-1.97 (m, 1H), 1.72-1.80 (m, 1H), 1.42-1.55 (m, 1H), 1.32-1.37 (m, 1H, H-4), 1.30 (d, *J* = 7.1 Hz, 2.45H, **7d´´**), 1.05 (d, *J* = 7.1 Hz, 0.55H **7d´**).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):
174.7, 174.1, 141.42, 132.2, 129.8, 129.1, 129.0, 128.7, 128.5, 128.4, 126.0, 121.5, (q, *J* = 283 Hz), 98.5 (q, *J* = 32 Hz), 72.0, 71.6, 70.2, 70.1, 51.8, 44.9, 37.3, 37.2, 34.1, 33.1, 31.1, 12.8, 12.4.
IR: 3028, 2990, 2953, 2886, 2361, 2332, 1736, 1497, 1452, 1435, 1387, 1362, 1329, 1263, 1225, 1188, 1123, 1105, 1063.
HRMS (EI): Calculated. for $C_{23}H_{25}F_3O_4$: 422.4443; Found: 422.4457.

Ethyl (*R)-2-((diisopropylcarbamoyl)oxy)-2-((2*R**,4*S**,6R*)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl) acetate (7b)**

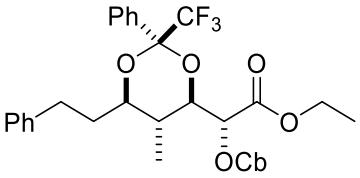


The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **6a** (0.23 mmol, 90 mg). The crude mixture was purified by column chromatography using cyclohexane:CH_2Cl_2 (9:1) to afford ketal as pale yellow oil (70 mg, 54 %; 80 % brsm).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.13 – 7.61 (m, 10H), 5.17 (d, *J* = 3.3 Hz, 1H), 4.09 – 4.34 (m, 4H), 3.67 – 3.95 (m, 2H), 2.89 - 3.12 (m, 1H), 2.69 - 2.79 (m, 1H), 1.78 - 2.18 (m, 2H), 1.16 – 1.47 (m, 17H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
168.3, 154.8, 141.5, 131.9, 130.2, 129.2, 129.1, 128.7, 128.6, 126.3, 121.6 ($J_{C\text{-}F}$ =283. Hz), 98.8 ($J_{C\text{-}F}$ =32.2. Hz) 74.8, 70.9, 70.4, 61.8, 47.3, 45.8, 37.5, 31.8, 31.3, 21.7, 21.6, 14.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.34
IR: 2970, 2933, 2356, 2341, 1734, 1697, 1558, 1506, 1436, 1301, 1188, 1120, 1064, 1031, 763, 723
HRMS: Calculated for $C_{30}H_{38}F_3NO_5$: 566.2729; Found: 566.2736.

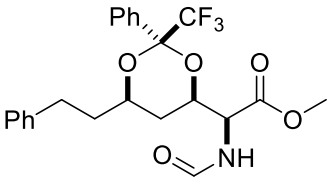
Ethyl (*R)-2-((diisopropylcarbamoyl)oxy)-2-((2*R**,4*R**,5*R**,6*R**)-5-methyl-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (7c)**



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **6b** (0.19 mmol, 76 mg). The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (9:1) to afford ketal as pale yellow oil (101 mg, 90 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):
7.13 – 7.64 (m, 10H), 5.29 (d, *J* = 1.6 Hz, 1H), 4.07 – 4.40 (m, 3H), 3.86 (brs, 1H), 3.84 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.43 (m, 1H), 3.00 – 3.17 (m, 1H), 2.67 – 2.88 (m, 1H), 2.14 – 2.40 (m, 1H), 1.74 – 1.94 (m, 2H), 1.18 – 1.54 (m, 15H), 0.82 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):
167.9, 154.9, 141.9, 131.9, 130.2, 129.2, 129.0, 128.8, 128.7, 126.3, 123.2 ($J_{C\text{-}F}$ =284.7 Hz), 98.3 ($J_{C\text{-}F}$ =32.1 Hz), 77.1, 75.5, 73.3, 61.7, 47.3, 46.0, 34.6, 34.4, 31.3, 21.8, 21.4, 14.4, 11.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):
-85.54.
IR: 2970, 2929, 2343, 1734, 1697, 1456, 1436, 1369, 1300, 1190, 1122, 1083, 981, 762, 731.
HRMS: Calculated for $C_{31}H_{41}F_3NO_6$: 580.2886; Found: 580.2892.

Methyl (*R)-2-formamido-2-((2*R**,4*S**,6*S**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (7d)**



To a solution of homoallylic alcohol **6d** (0.29 mmol, 80 mg, 1 equiv) in THF (0.1 M) at 0°C was added trifluoroacetophenone (0.32 mmol, 0.045 mL, 1.1 equiv) followed by *t*BuOK (0.32 mmol, 35 mg, 1.1 equiv) and the resulting mixture was stirred for 15 min at 0°C. A second portion of trifluoroacetophenone (1.1 equiv) and *t*BuOK (0.1 equiv) was added, after 15 min a third portion of trifluoroacetophenone (1.1 equiv) and *t*BuOK (0.1 equiv) was made. The resulting mixture was then stirred at 0°C for 4 h 30 min and quenched with a saturated aqueous NH_4Cl solution. The aqueous phase was extracted 3 times with AcOEt and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was then purified by column chromatography using CH_2Cl_2/AcOEt (9:1) to give the product as white solid (101 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):
After purification, the presence of two isomers was observed in the NMR spectra, in a [0.75(M):0.25(m)] ratio.
8.41(M) (s, 1H), 8.28 (m) (s, 1H) 7.11 – 7.51 (m, 10H), 6.71 (m) (d, *J* = 4.2 Hz, 1H), 6.47 (M) (d, *J* = 9.5 Hz, 1H), 4.85 (M) (dd, *J* = 9.5, 2.1 Hz, 1H), 4.74 (m) (dd, *J* = 9.5, 3.1 Hz, 1H), 4.44 (M) (dt, *J* = 10.2, 2.1

Hz, 1H), 4.07 (m) (dt, 1H, 10.2, 2.1 Hz), 3.89 (M) (s, 3H), 3.86 (m) (s, 1H), 3.75 – 3.93 (m, 1H), 2.88 - 2,96 (m, 2H), 1.85 – 2.06 (m, 2H), 1.55 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):

169.7 (M), 169.2 (m), 161.6, (M), 160,7 (m), 141.4 (m), 141,3 (M), 131.7 (m), 131.6 (M), 130.1, 128.8, 128.7, 128.6, 128.4, 128.2, 126.0, 121.5 (q, $J_{C\text{-}F}$ = 285.4 Hz), 98.8 (q, J = 32.3 Hz), 72.5 (m), 71.2 (M), 70.6, 70.2 (M), 54.8 (m), 53.5 (M), 53.1 (M), 53.1 (m), 37.3 (m), 37.2 (M), 32.8 (m), 82.3 (M), 31.3 (m), 31,2 (M).

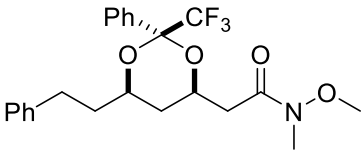
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):

-85.63 (m), -85.90 (M)

IR: 3315, 2953, 3029, 1749, 1666, 1540, 1326, 1192, 1120, 985

HRMS: Calculated for $C_{23}H_{24}F_3NO_5Na$: 474.1504; Found: 474.1503.

_N_-methoxy-_N_-methyl-2-((2R*,4R*,6R*)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetamide (9)



The typical procedure for conjugate intramolecular addition reaction was applied to (*E*)-5-hydroxy-*N*-methoxy-*N*-methyl-7-phenylhept-2-enamide **8** (0.19 mmol, 50 mg). The crude mixture was purified by column chromatography using pentane/AcOEt (7:3) to afford ketal as pale yellow oil (67 mg, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.72 – 7.07 (m, 10H), 4.21 – 4.47 (m, 1H), 3.75 – 3.84 (m, 1H), 3.75 (s, 3H), 3.23 (s, 3H), 2.89 - 3.11 (m, 2H), 2.73 (dd, J = 15.7, 8.2 Hz, 1H), 2.46 (dd, J = 15.7, 5.1 Hz, 1H,), 1.94 – 2.09 (m, 1H), 1.77 – 1.88 (m, 1H), 1.52 – 1.61 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

171.2, 141.8, 132.4, 130.0, 129.4, 129.0, 128.7, 128.6, 126.33, 121.9 (q, $J_{C\text{-}F}$= 280.1 Hz), 98.9 (q, $J_{C\text{-}F}$ = 31.9 Hz). 70.6, 68.3, 61.7, 38.2, 37.6, 36.5, 32.4, 31.4.

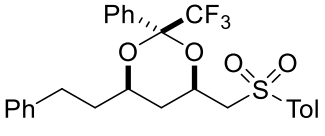
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):

-88.44.

IR: 2939, 1682, 1477, 1464, 1378, 1363, 1337, 1223, 1138, 1116, 1132, 1033, 1001.

HRMS: Calculated for $C_{23}H_{27}F_3NO_4$: 438.1892; Found: 438.1884

(2R*,4R*,6R*)-4-phenethyl-2-phenyl-6-(tosylmethyl)-2-(trifluoromethyl)-1,3-dioxane (11)



The typical procedure for conjugate intramolecular addition reaction was applied to (E)-1-phenyl-6-tosylhex-5-en-3-ol **10** (0.15 mmol, 50 mg). The crude mixture was purified by column chromatography using Pentane/AcOEt (9:1) to afford ketal as pale yellow oil (58 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

7.84 (d, J = 8.3 Hz, 2H), 7.11 – 7.57 (m, 12H), 4.36 – 4.43 (m, 1H), 3.76 - 3.82 (m, 1H), 3.59 (dd, J = 14.7, 6.8 Hz, 1H), 3.24 (dd, J = 14.7, 4.8 Hz, 1H), 2.79 - 3.07 (m, 1H), 2.66 – 2.72 (m, 1H), 2.46 (s, 3H), 1.92 - 2.02 (m, 1H), 1.75 – 1.87 (m, 1H), 1.57 - 1.59 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

145.2, 141.5, 137.6, 131.6, 130.2, 129.1, 128.8, 128.6, 128.2, 126.4, 99.0 (q, $J_{C\text{-}F}$ = 32 Hz), 70.2, 66.3, 61.8, 37.3, 36.3, 31.2, 21.9.

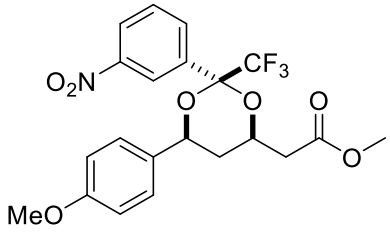
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):

-85.43.

IR: 2933, 1602, 1333, 1358, 1217, 1138, 1177, 1111, 1009, 1022

HRMS: Calculated for $C_{27}H_{31}F_3NO_4S$: 522.1926; found: 522.1927

Methyl 2-((2S*,4R*,6S*)-6-(4-methoxyphenyl)-2-(3-nitrophenyl)-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (13)



The typical procedure for conjugate intramolecular addition reaction was applied to homoallylic alcohol **1g** (0.21 mmol, 50 mg) and *m*-nitrotrifluoracetophenone[14]. The crude mixture was purified by column chromatography using cyclohexane/CH_2Cl_2 (1:1) to afford ketal as pale yellow oil (57 mg, 60 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

8.53 (s, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.86 - 7.06 (m, 2H), 4.55 – 4.83 (m, 1H), 4.34 – 4.38 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.83 (dd, *J* = 16.5, 8.6 Hz), 2.55 (dd, *J* = 16.5, 4.1 Hz, 1H), 1.75 – 1.91 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):

170.7, 160.2, 149.4, 135.6, 135.0, 131.8, 130.4, 127.6, 125.4, 124.7, 121.4 (q, $J_{C\text{-}F}$= 284.9 Hz), 114.5, 98.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 73.3, 68.6, 55.7, 52.4, 40.6, 37.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):

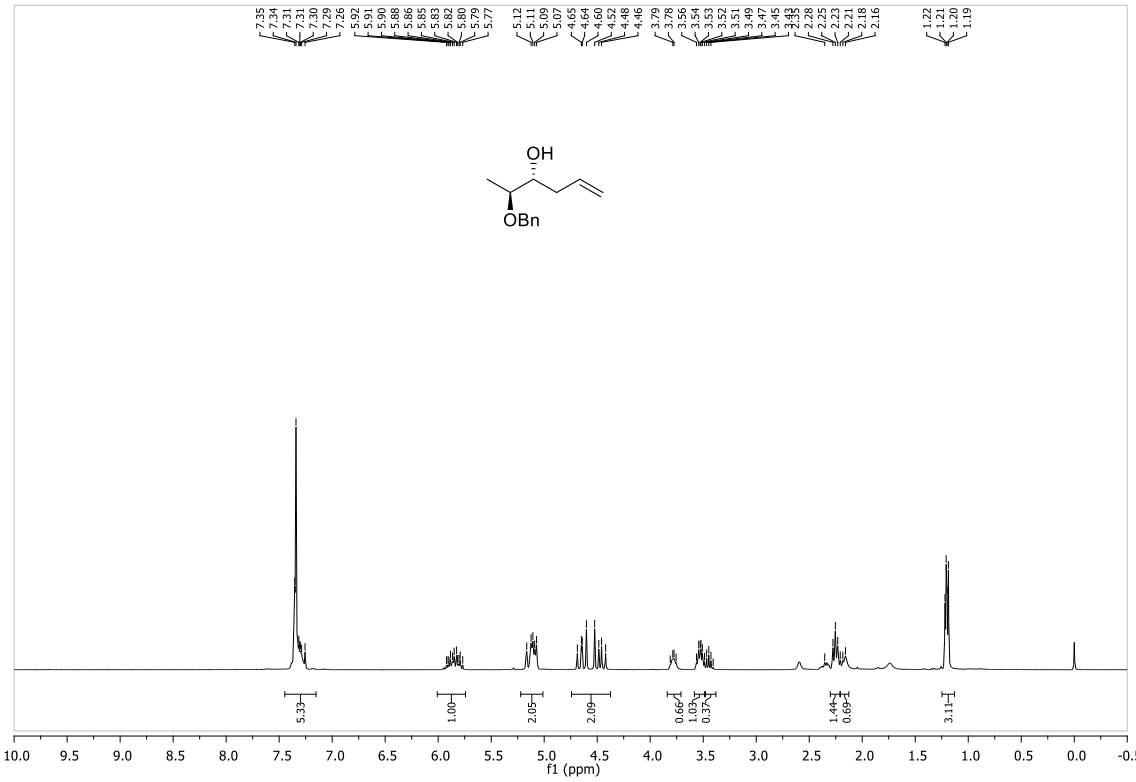
-85.26.

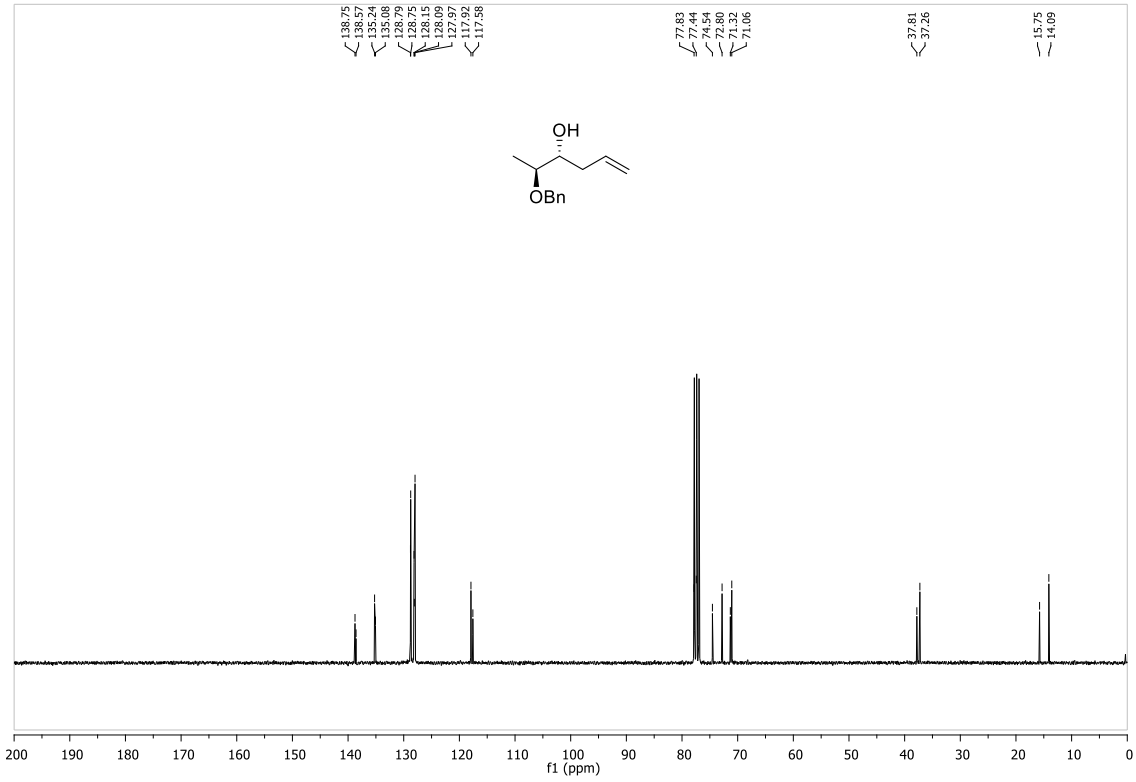
IR: 2960, 1745, 1632, 1618, 1532, 1450, 1355, 1320, 1282, 1142, 1105, 1033, 965.

HRMS: Calculated for $C_{21}H_{24}F_3N_2O_7$: 473.1536; Found: 473.1538.

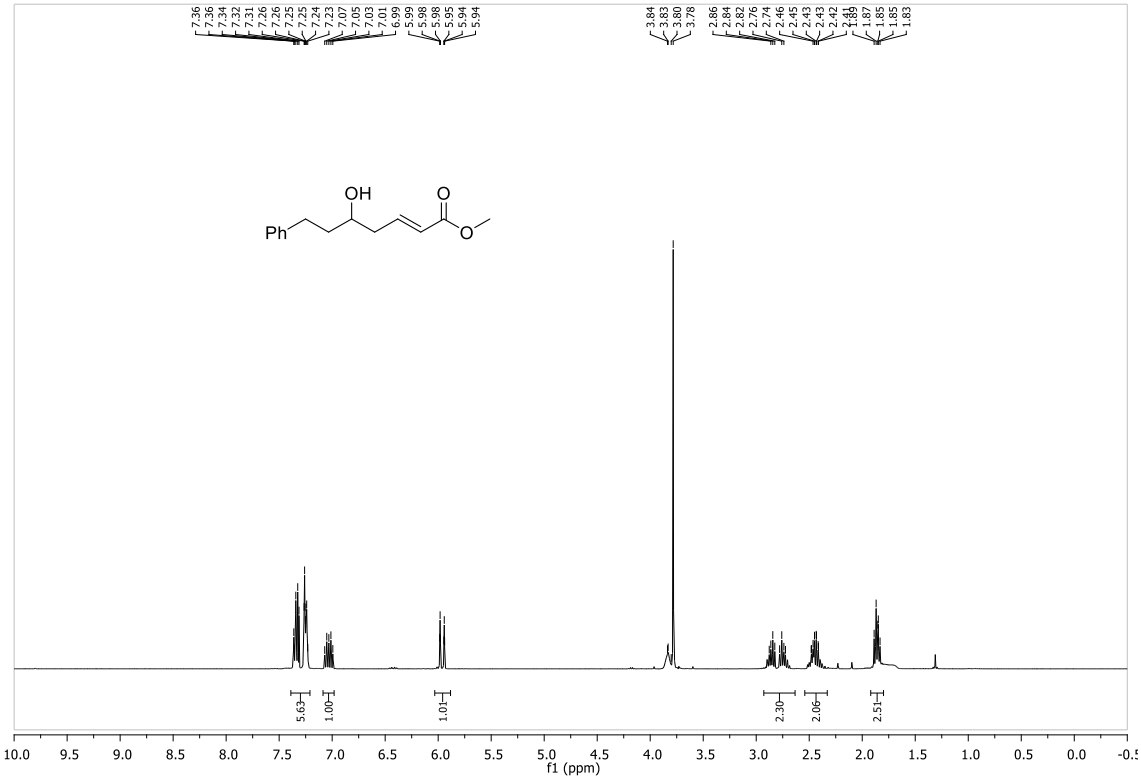
COPY OF NMR SPECTRA

(2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol

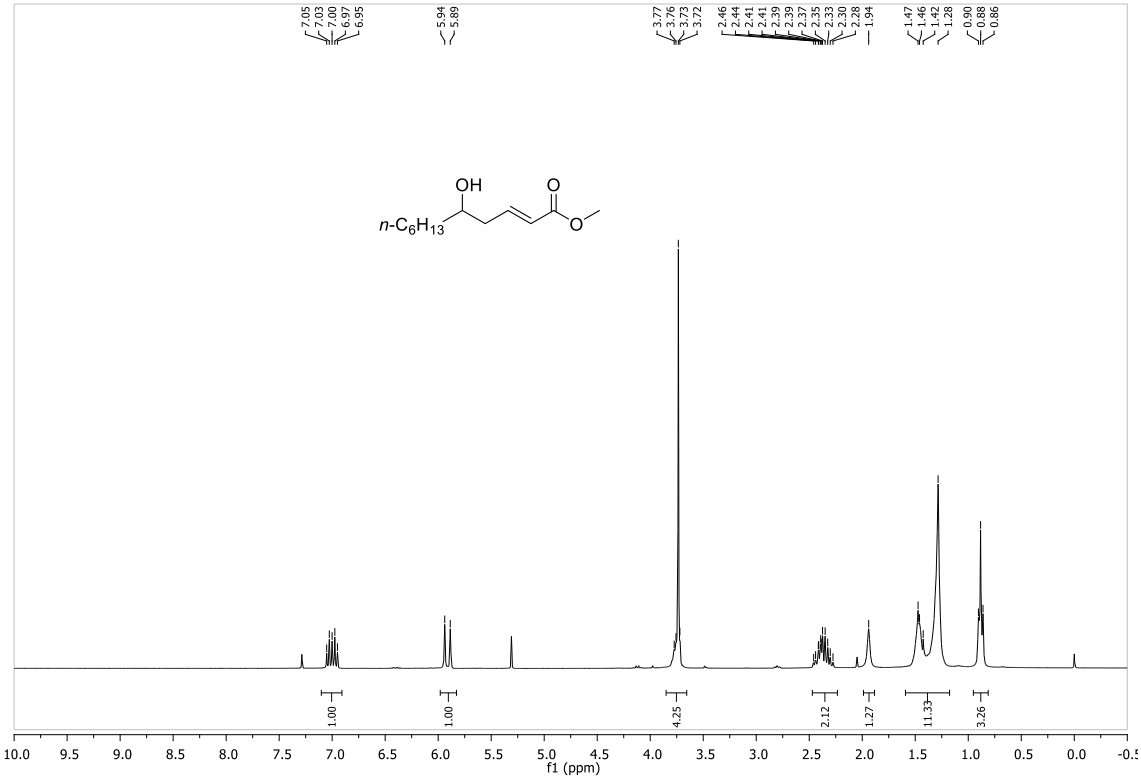




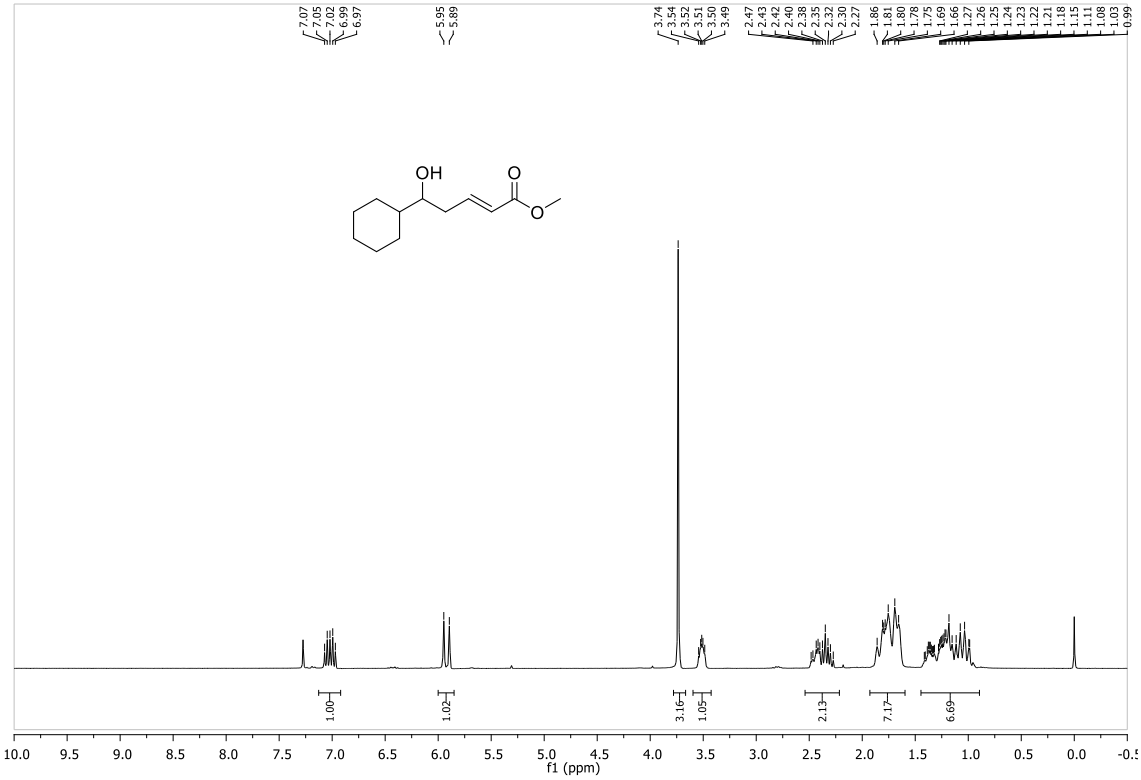
Methyl (*E*)-5-hydroxy-7-phenylhept-2-enoate (1a)



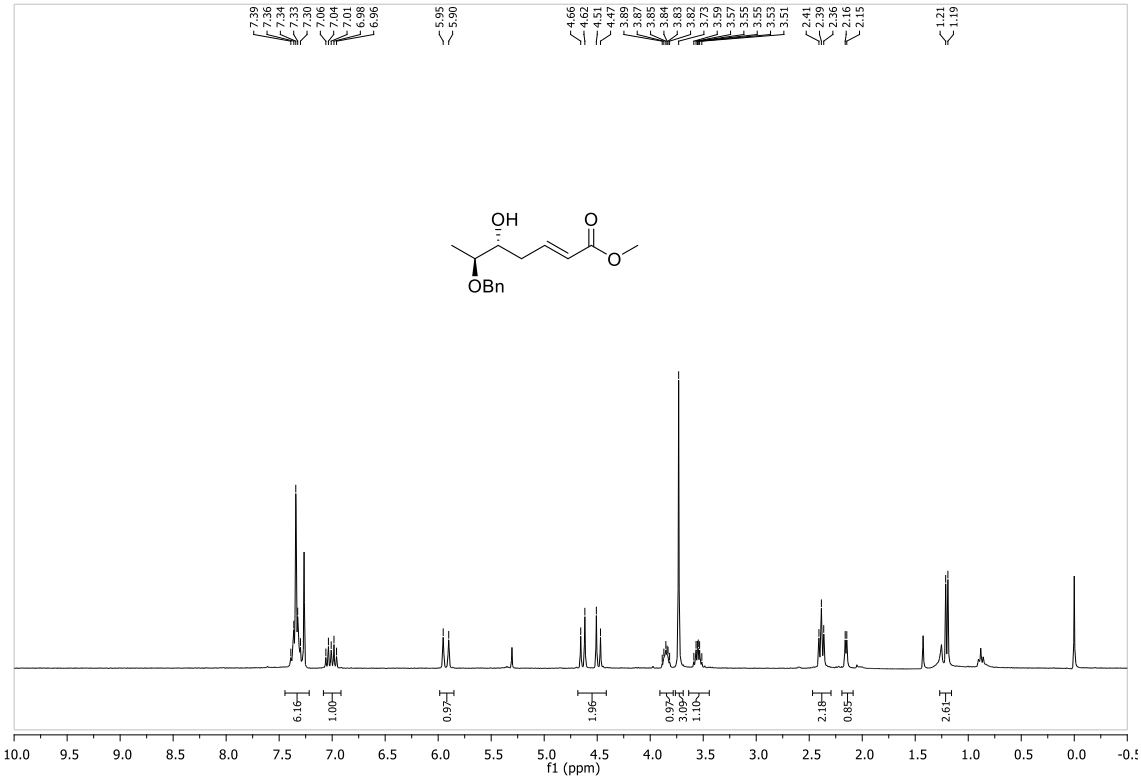
Methyl (*E*)-5-hydroxyundec-2-enoate (1b)

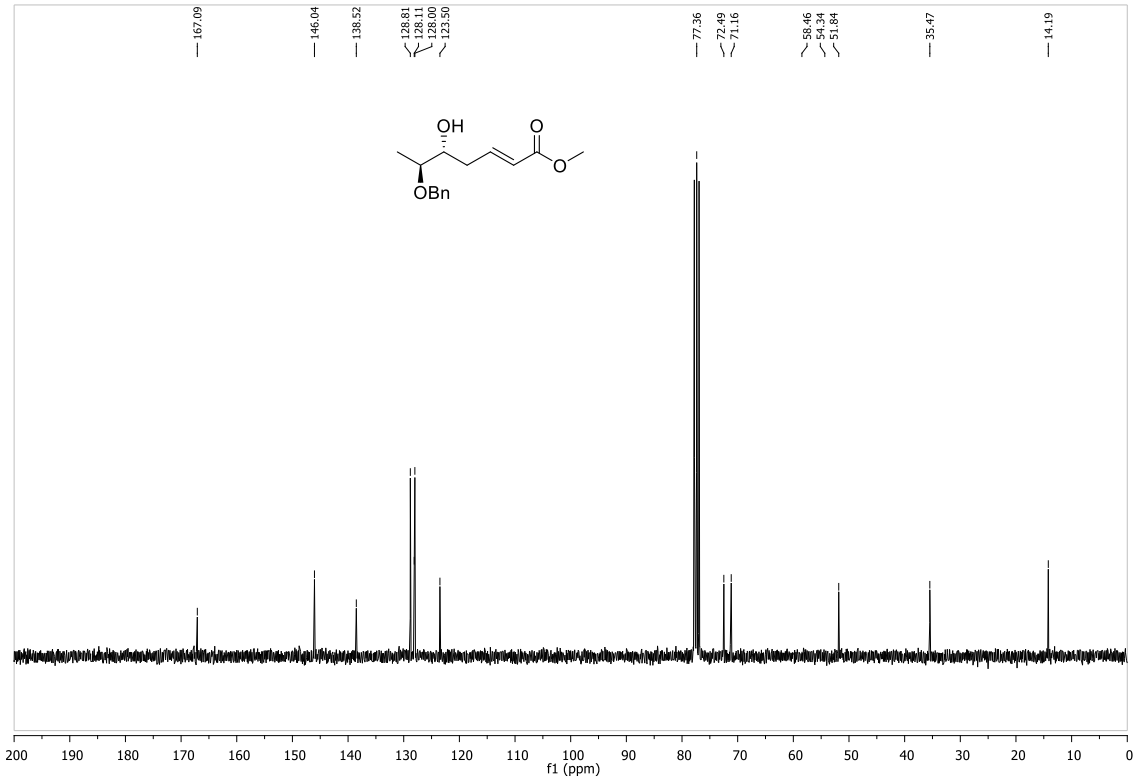


Methyl (*E*)-5-cyclohexyl-5-hydroxypent-2-enoate (1d)

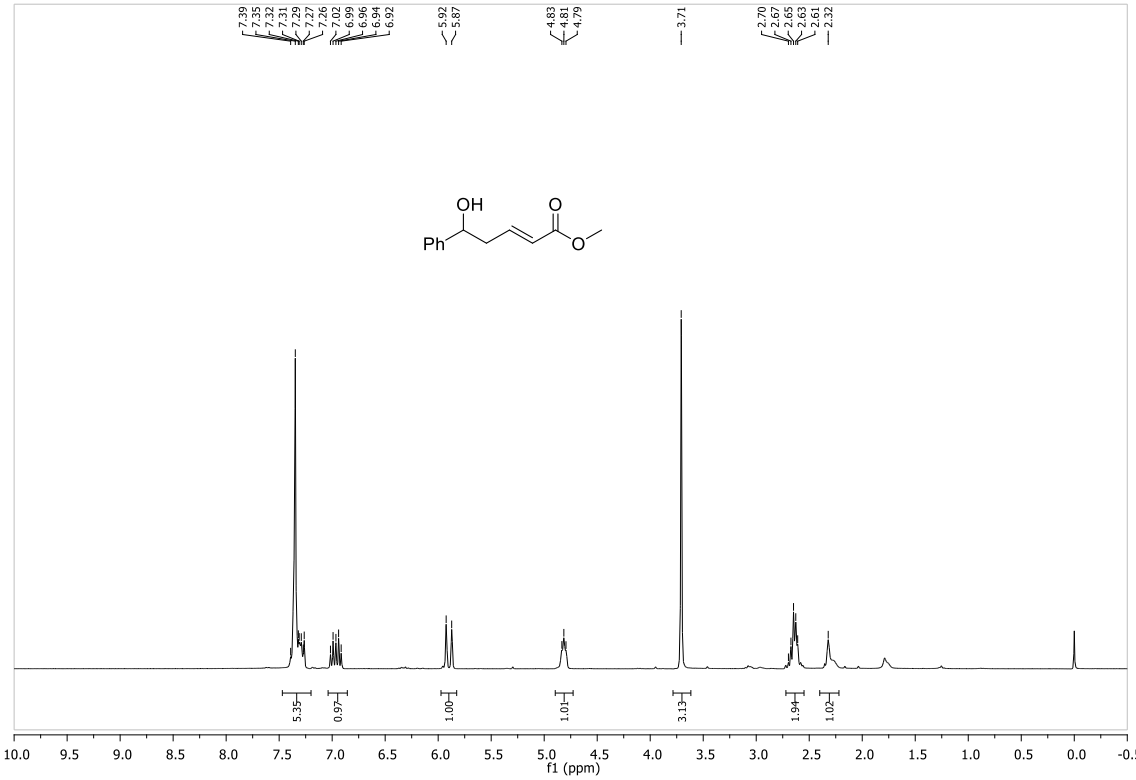


Methyl (5*R*,6*S*,*E*)-6-(benzyloxy)-5-hydroxyhept-2-enoate (1e)

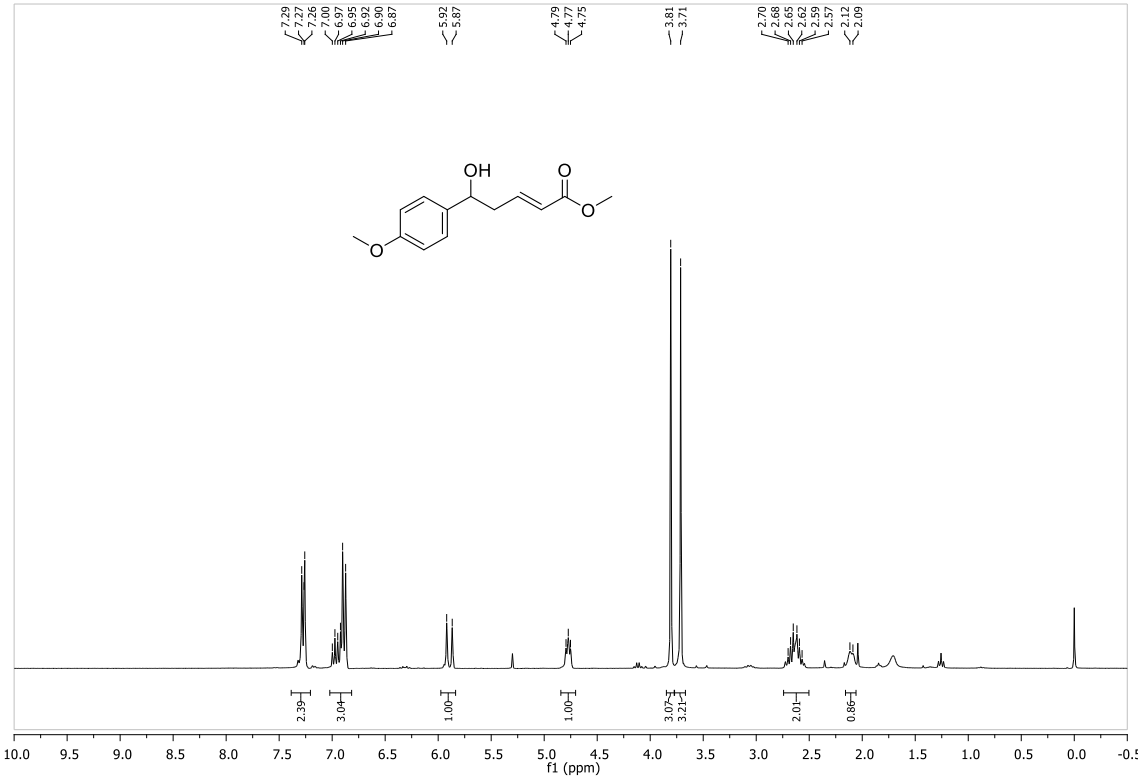




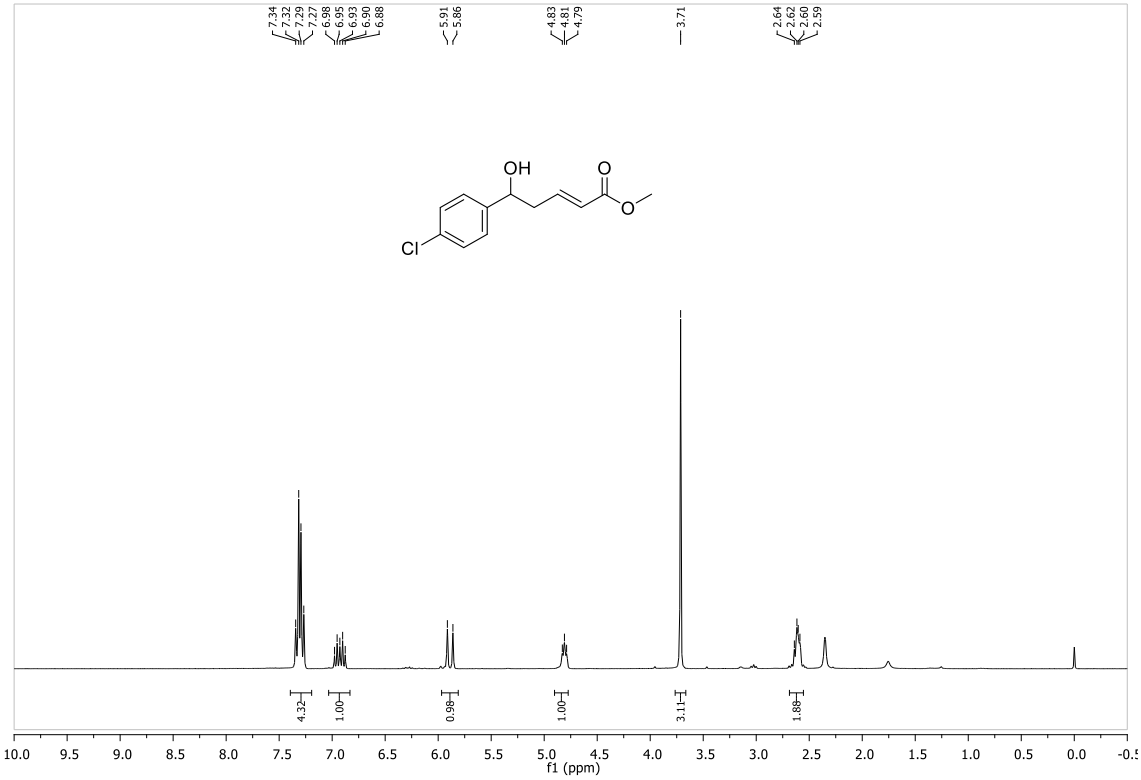
Methyl (*E*)-5-hydroxy-5-phenylpent-2-enoate (1f)



Methyl (*E*)-5-hydroxy-5-(4-methoxyphenyl)pent-2-enoate (1g)

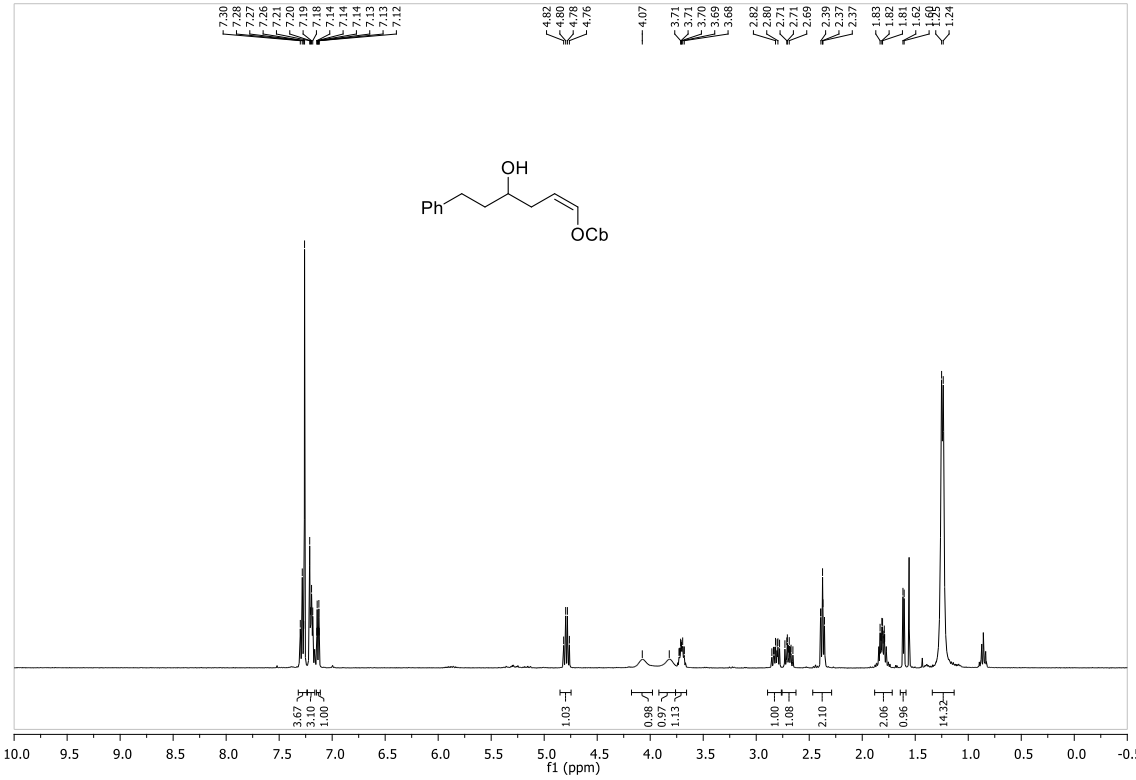


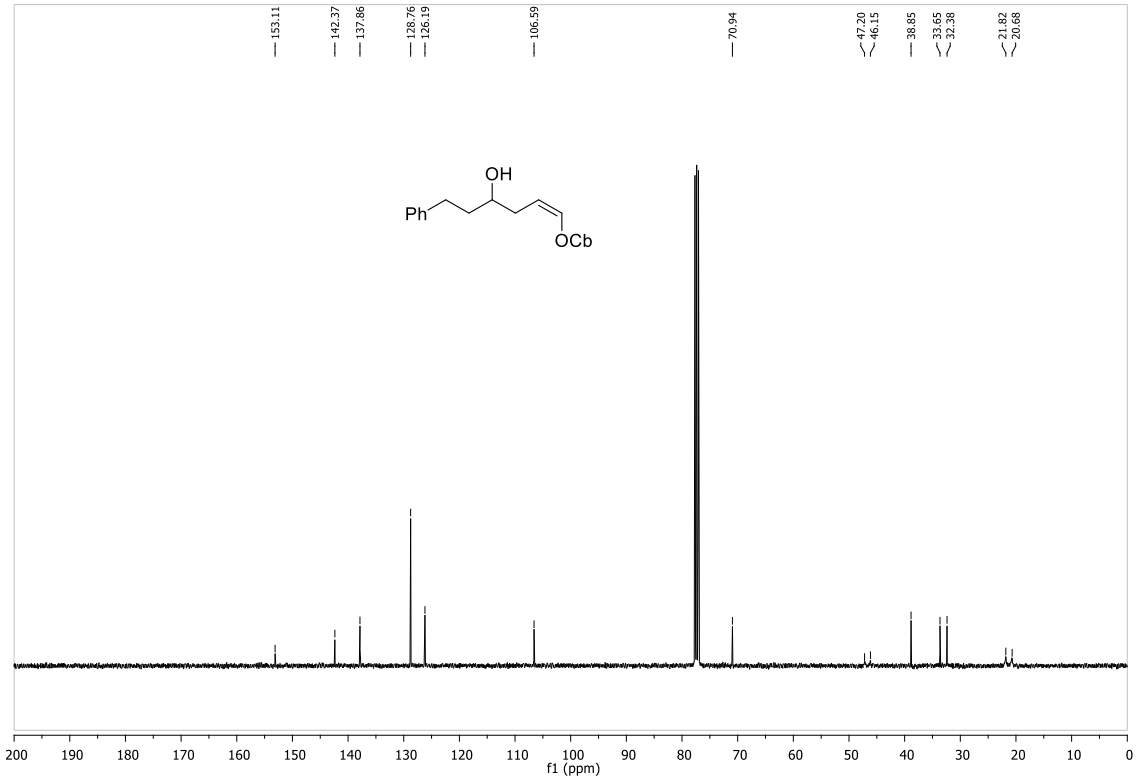
Methyl (*E*)-5-(4-chlorophenyl)-5-hydroxypent-2-enoate (1h)



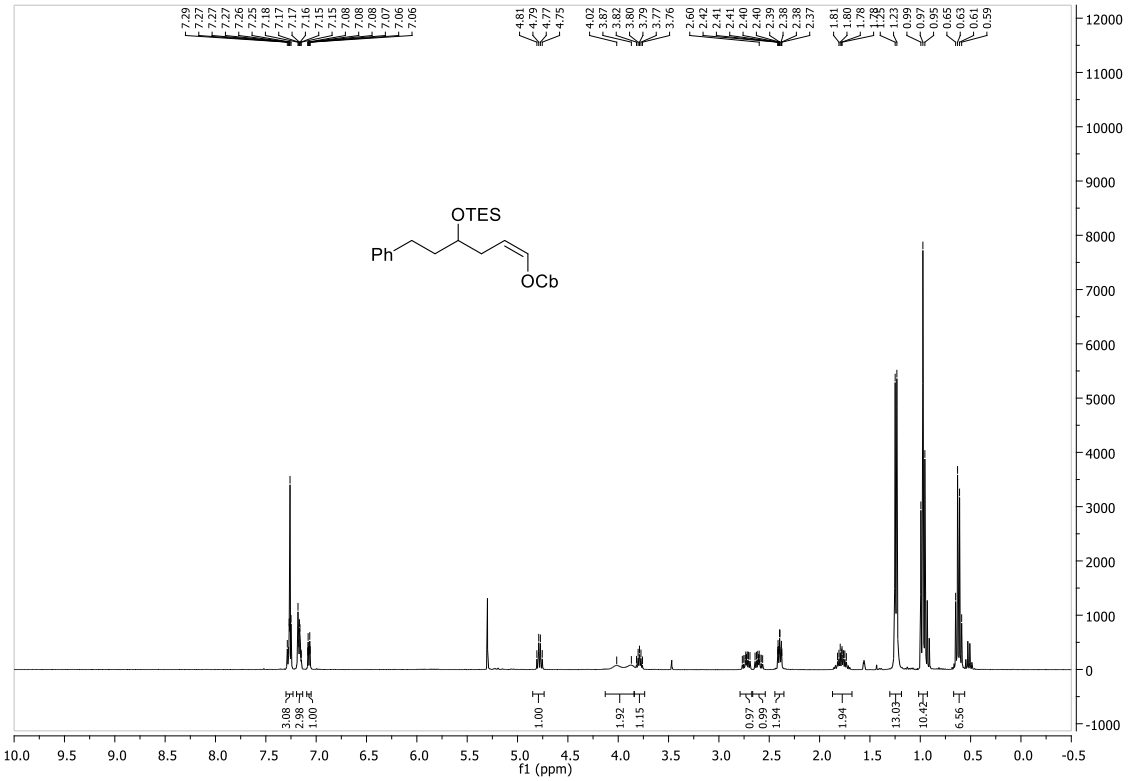
SYNTHESIS OF *O*-CARBAMATES

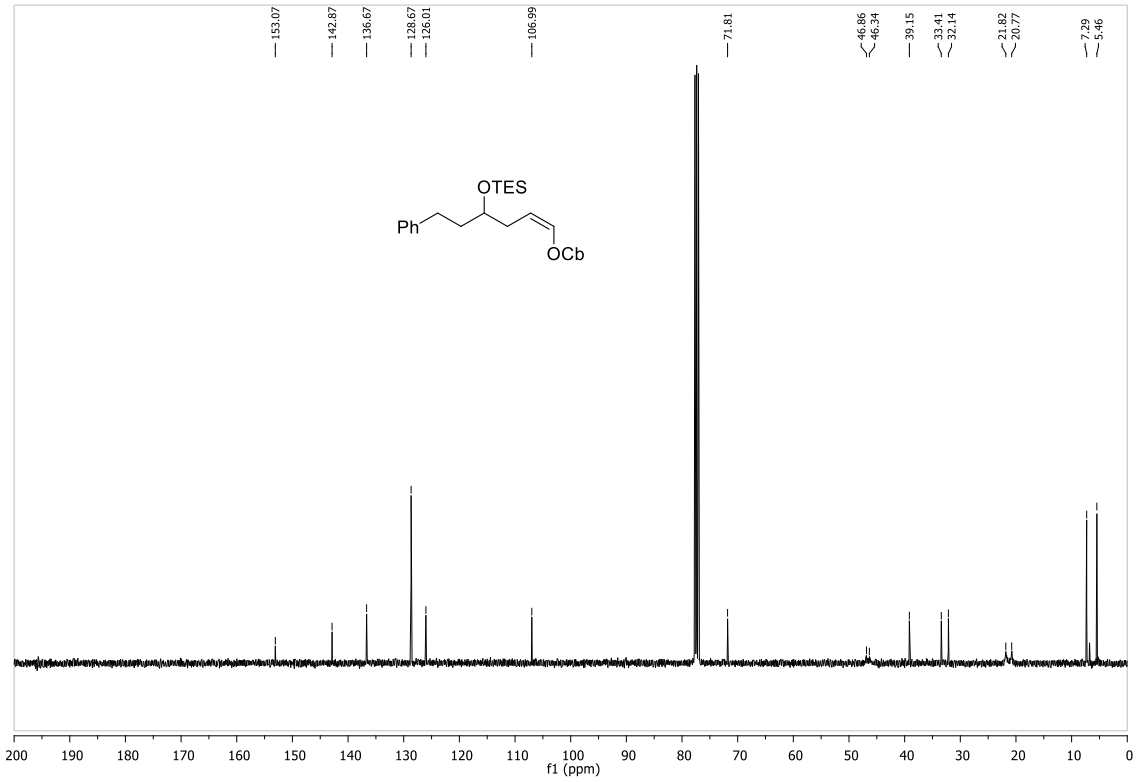
(*Z*)-4-hydroxy-6-phenylhex-1-en-1-yl diisopropylcarbamate



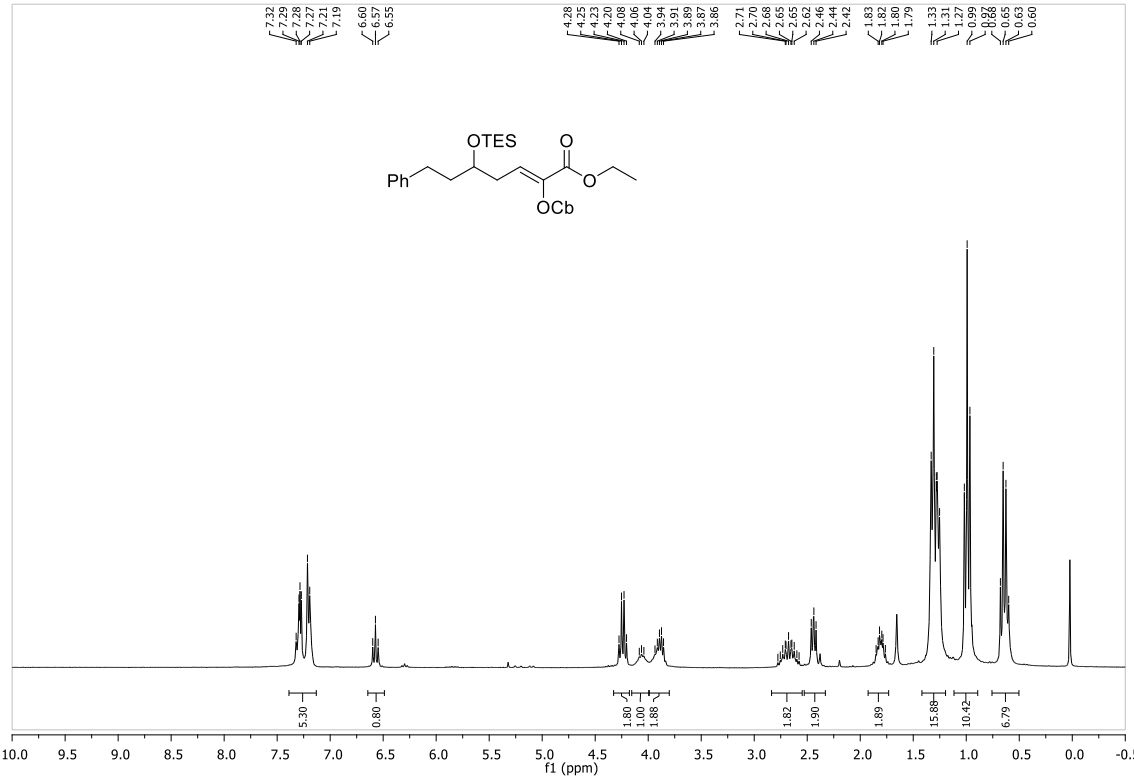


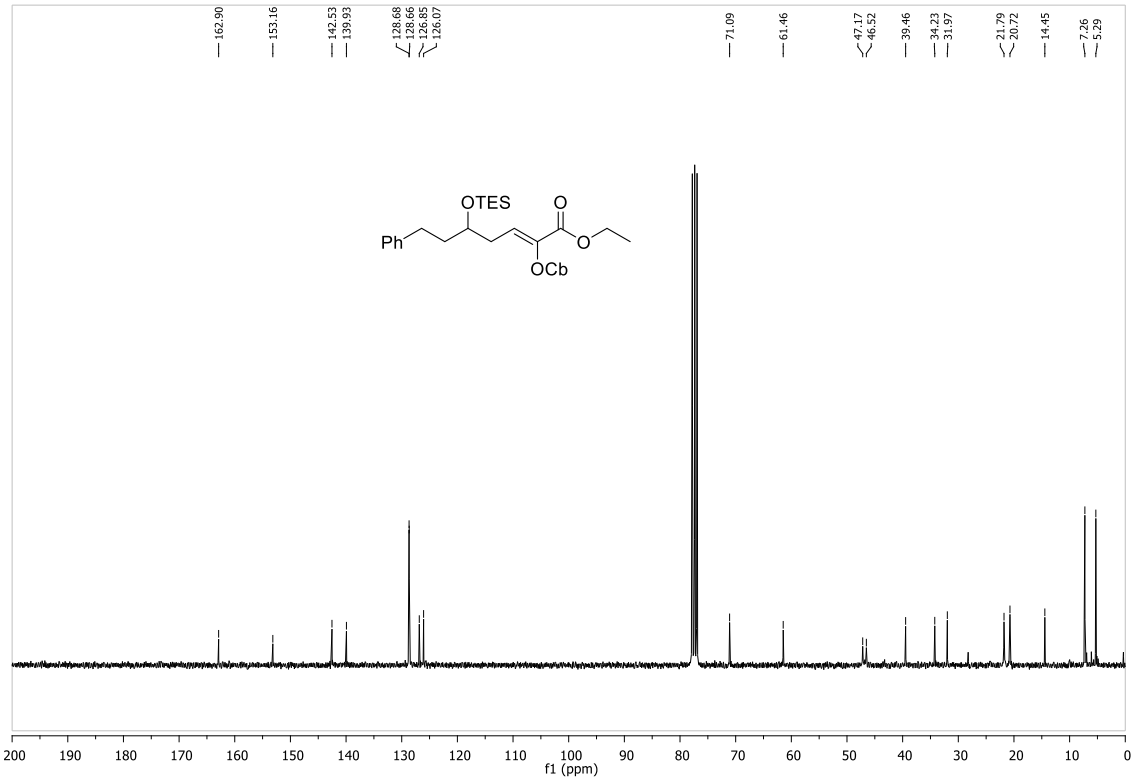
(*Z*)-4-((3-ethylpentan-3-yl)oxy)-6-phenylhex-1-en-1-yl diisopropylcarbamate



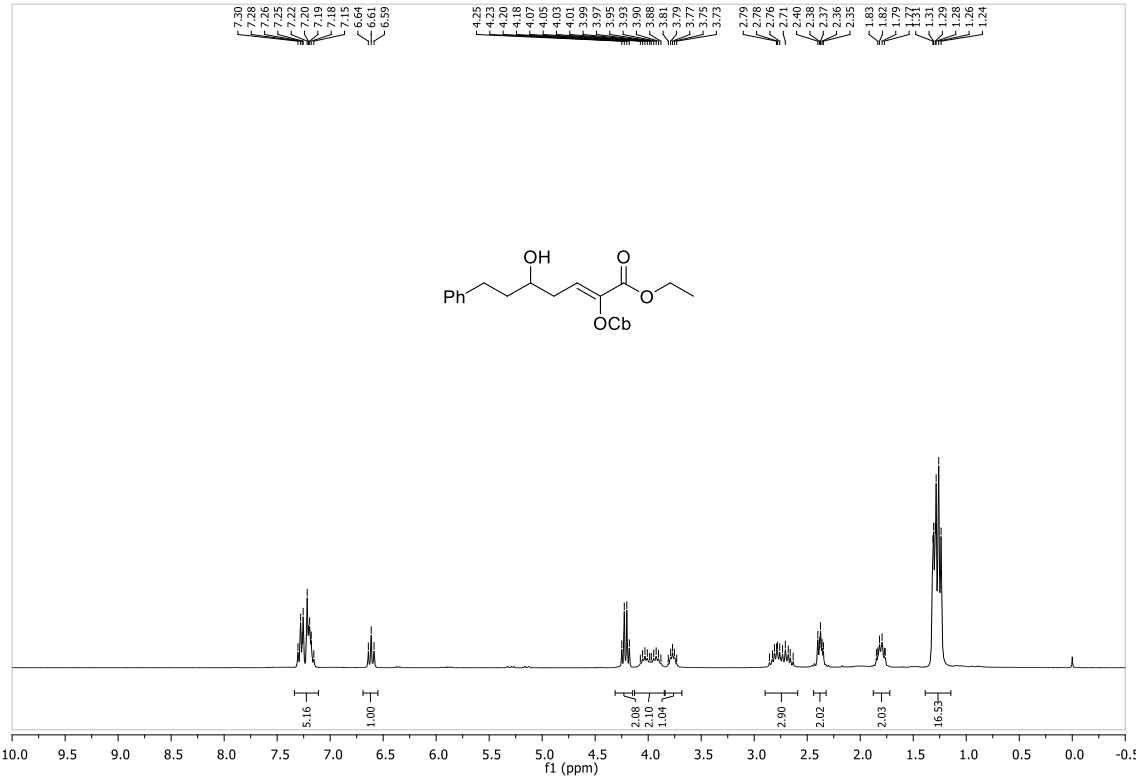


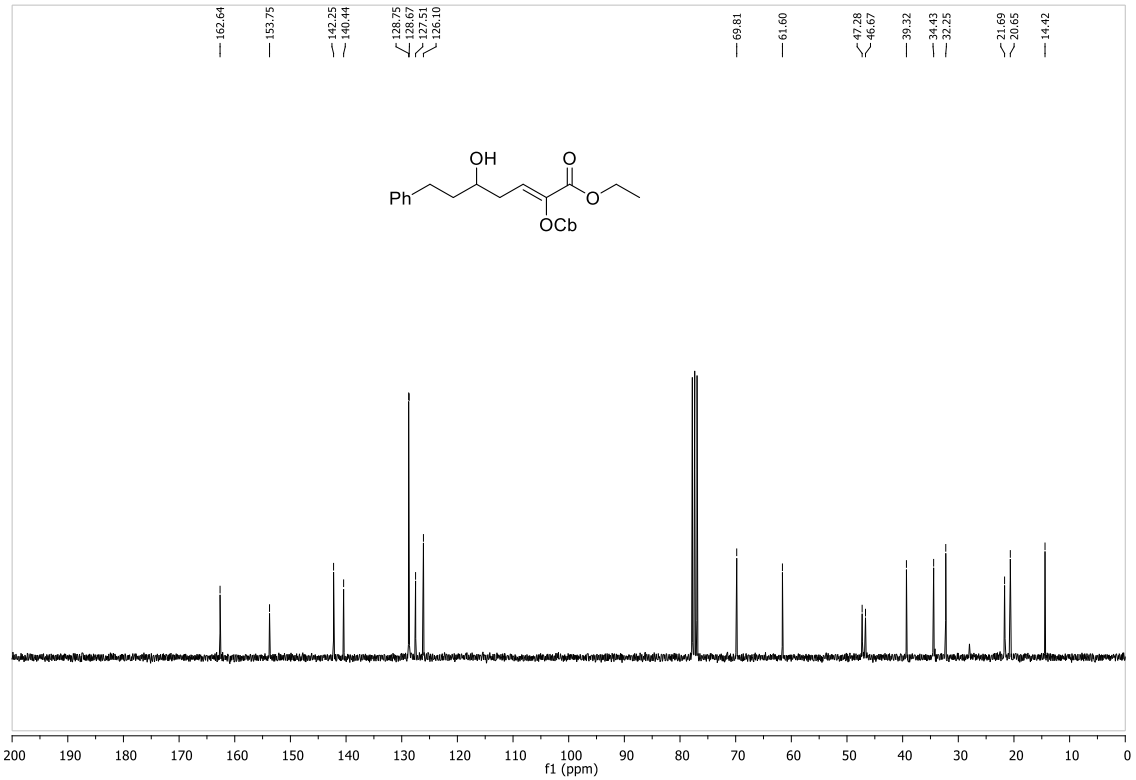
Ethyl (*Z*)-2-((diisopropylcarbamoyl)oxy)-7-phenyl-5-((triethylsilyl)oxy)hept-2-enoate



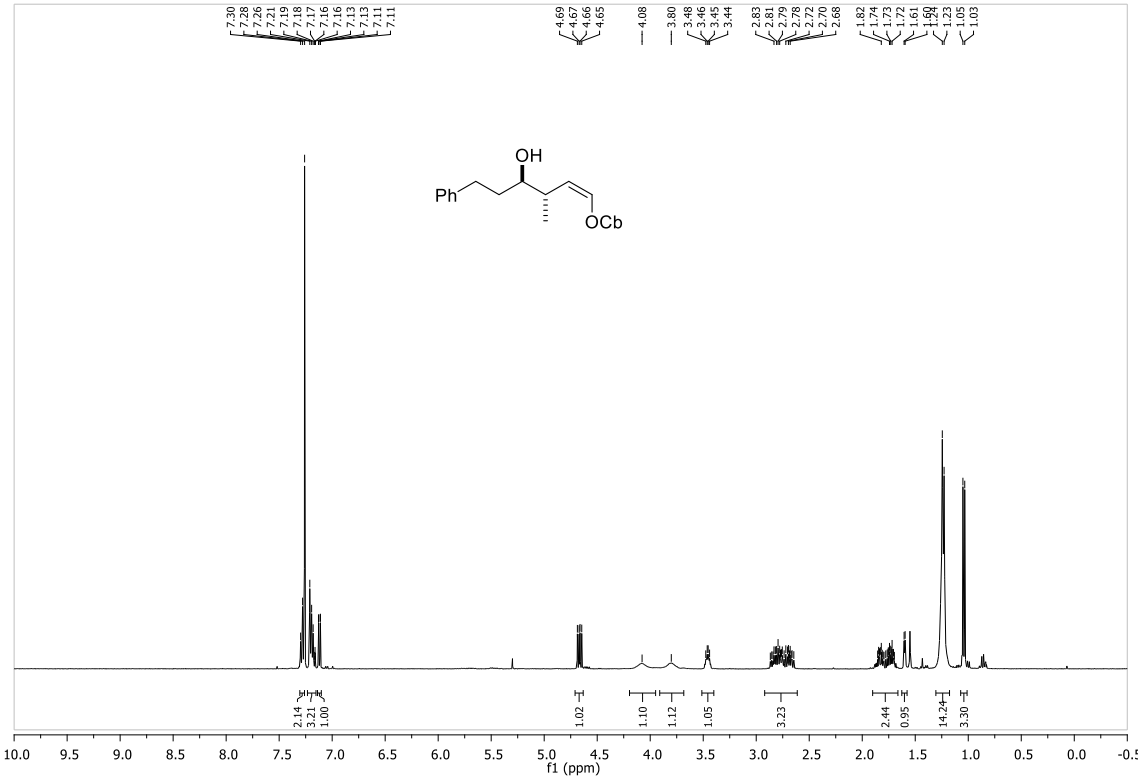


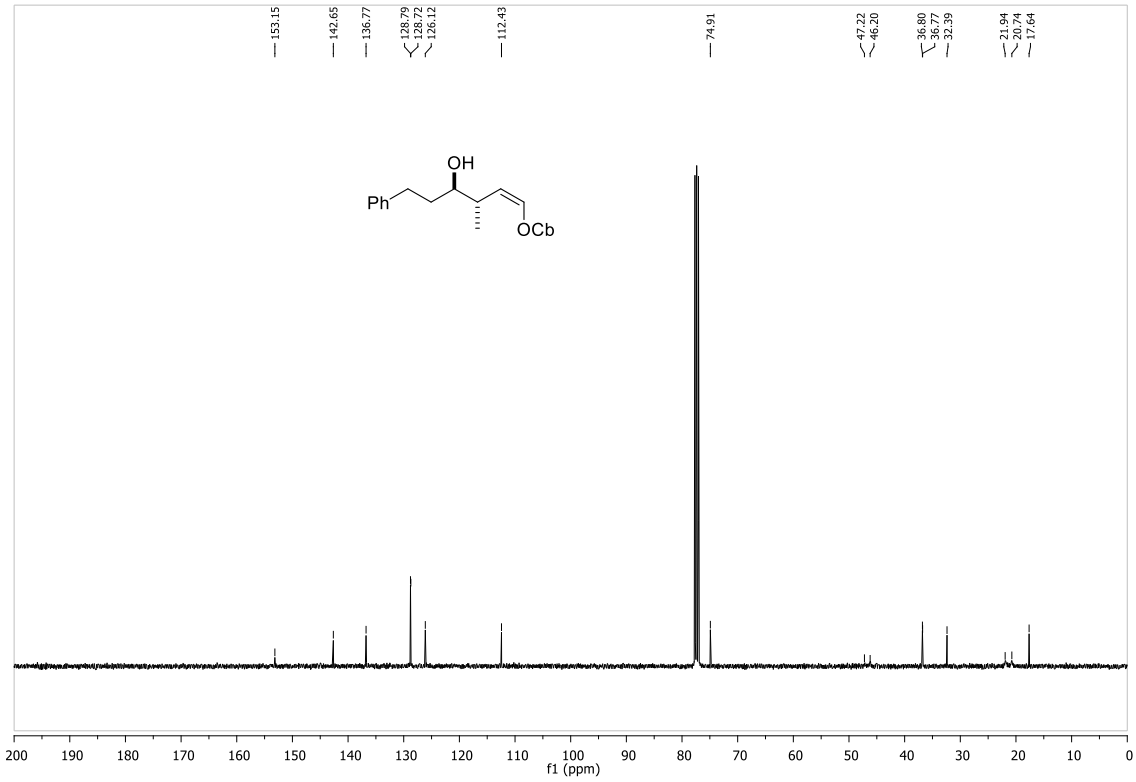
Ethyl (*Z*)-2-((diisopropylcarbamoyl)oxy)-5-hydroxy-7-phenylhept-2-enoate (6b)



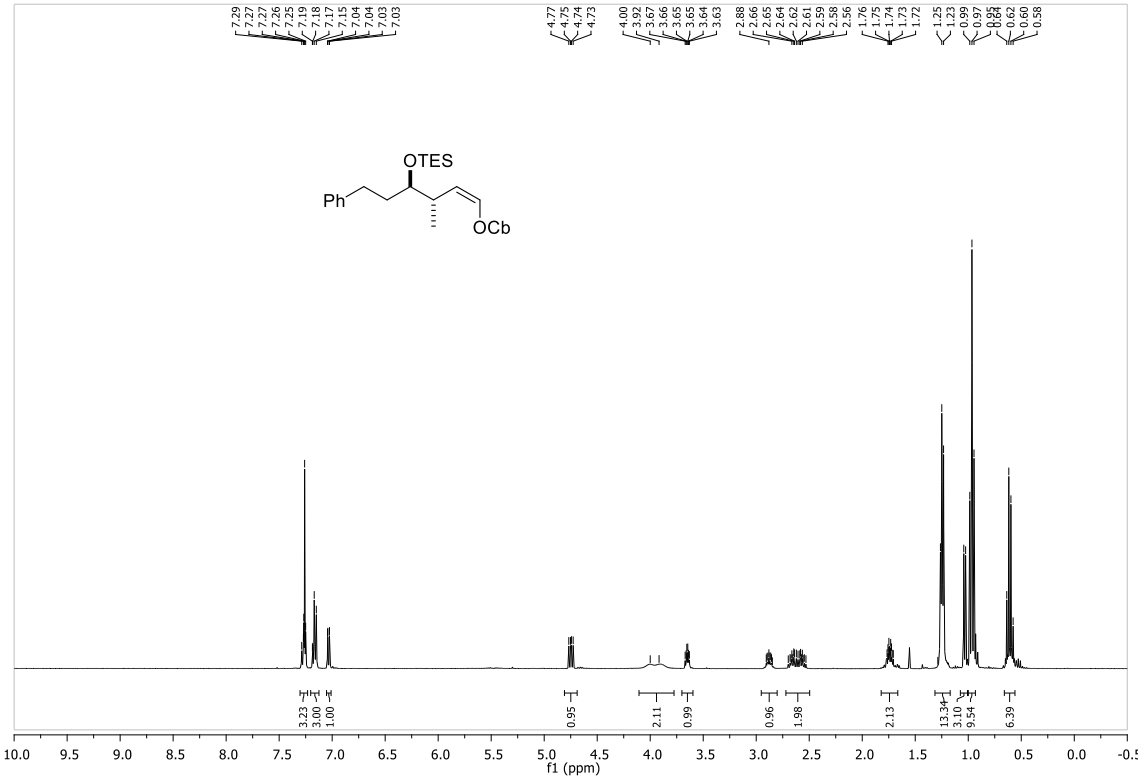


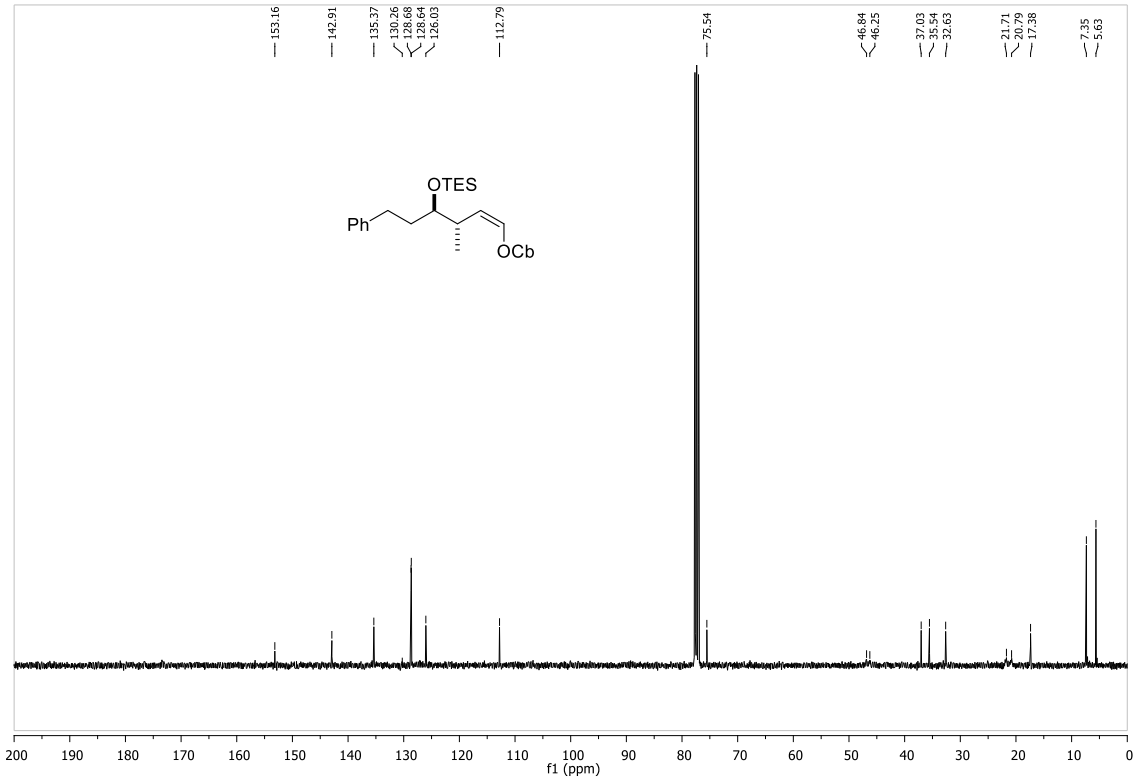
(3*R,4*S**,*Z*)-4-hydroxy-3-methyl-6-phenylhex-1-en-1-yl diisopropylcarbamate**



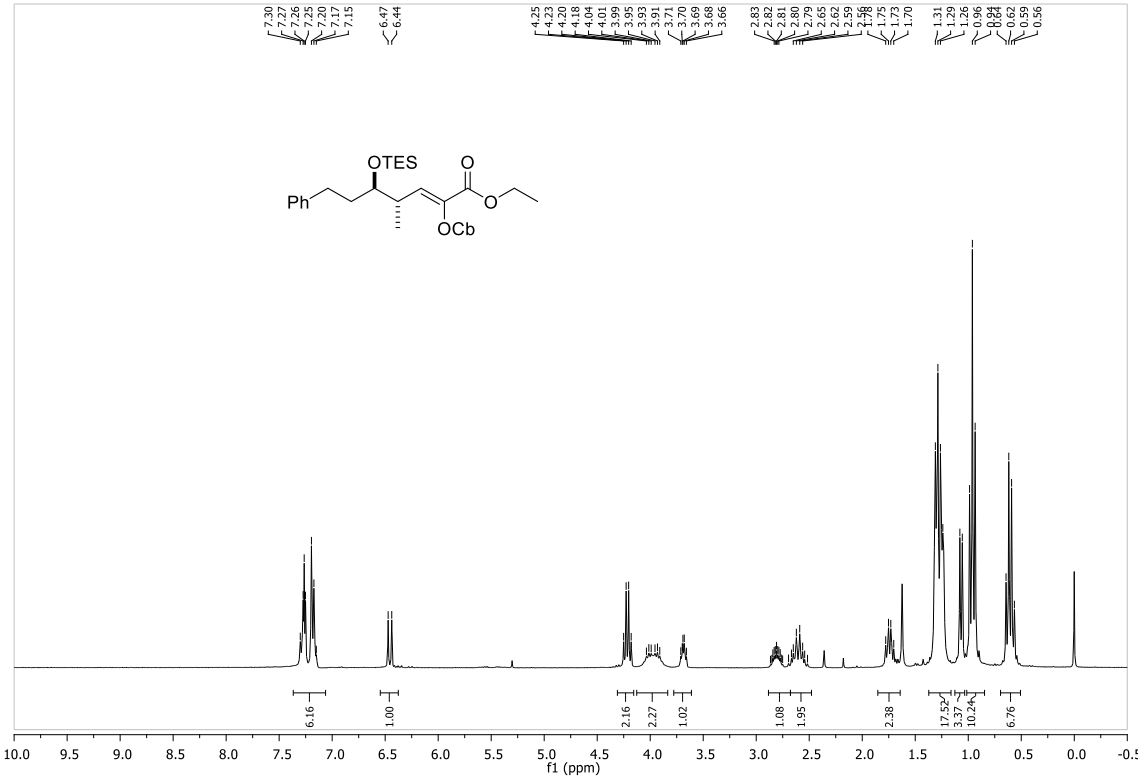


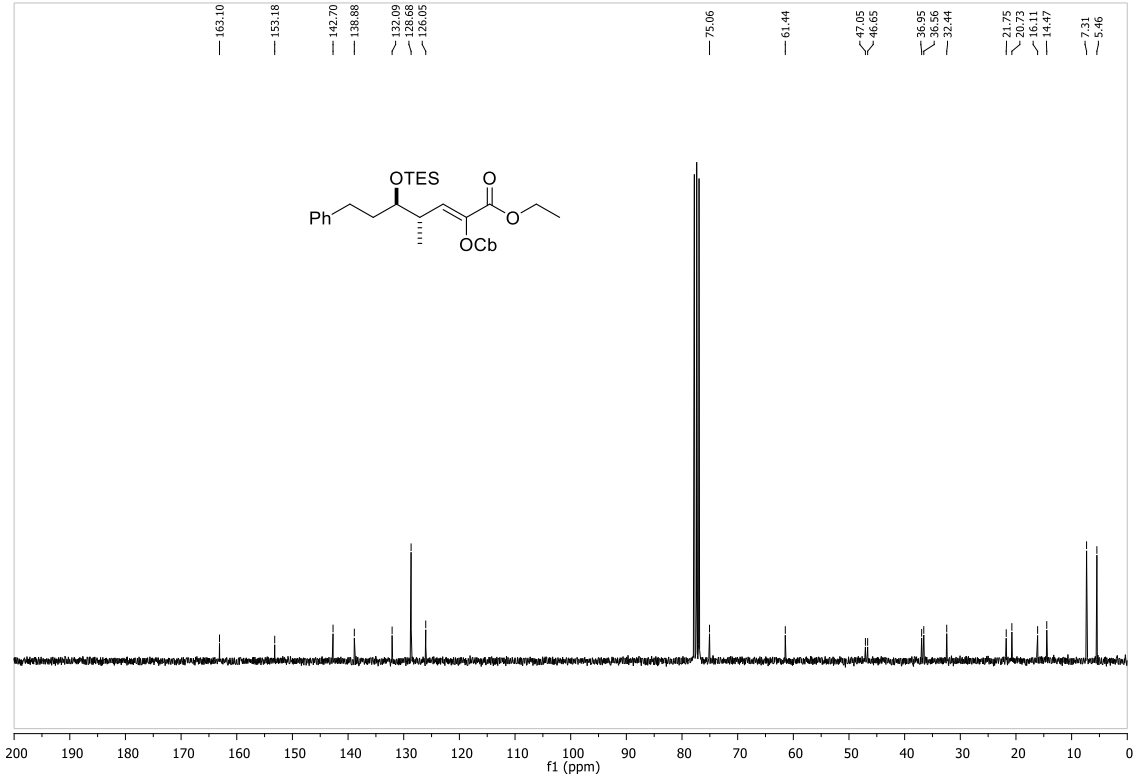
(3*R,4*S**,*Z*)-3-methyl-6-phenyl-4-((triethylsilyl)oxy)hex-1-en-1-yl diisopropylcarbamate**



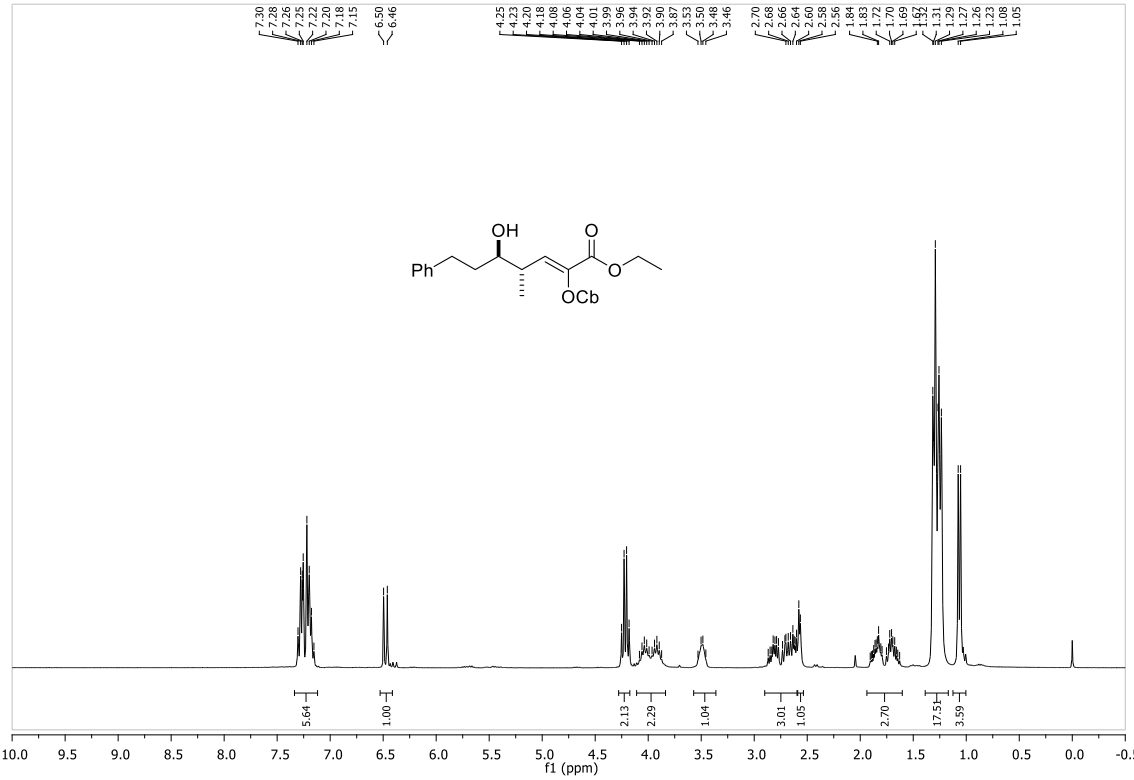


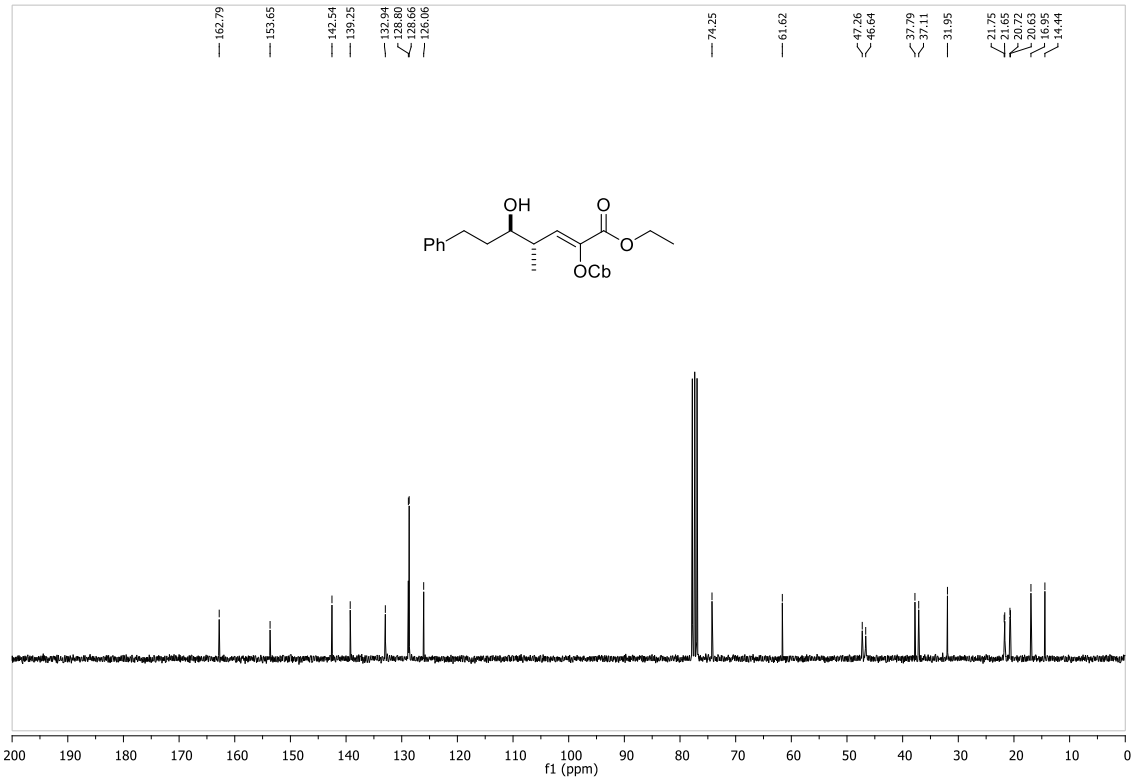
Ethyl (4*R,5*S**,*Z*)-2-((diisopropylcarbamoyl)oxy)-4-methyl-7-phenyl-5-((triethylsilyl)oxy)hept-2-enoate**





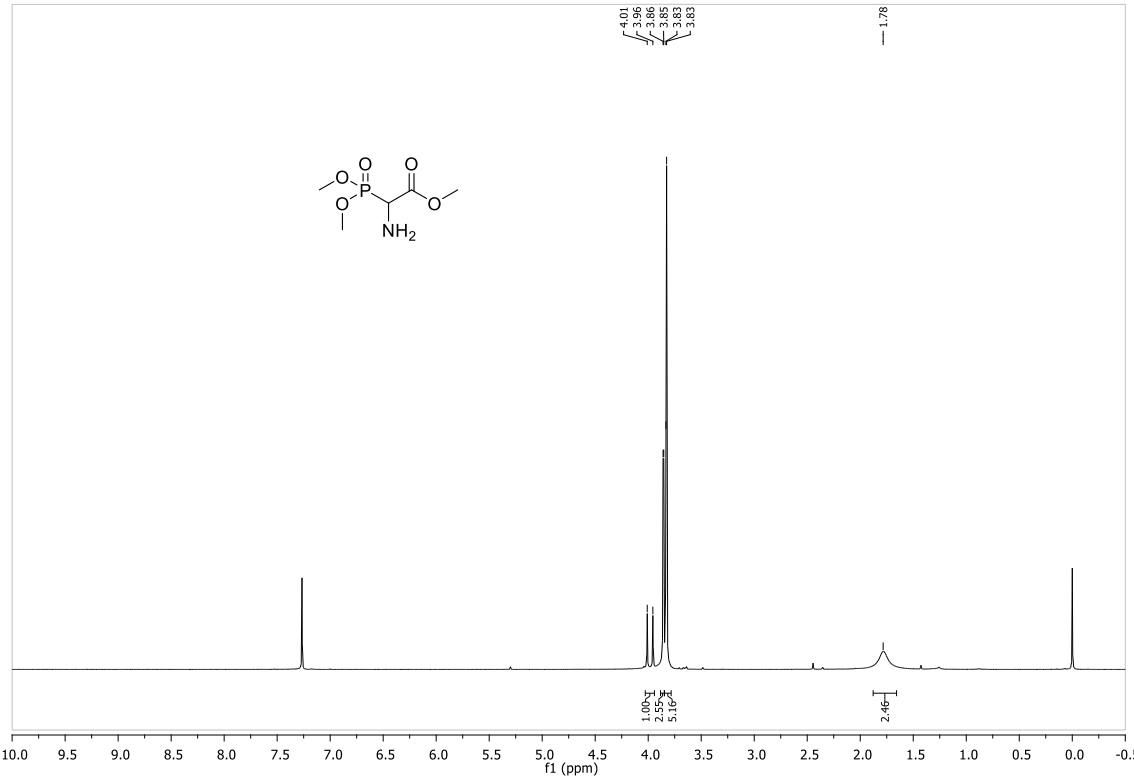
Ethyl (4*R,5*S**,*Z*)-2-((diisopropylcarbamoyl)oxy)-5-hydroxy-4-methyl-7-phenylhept-2-enoate (6c)**



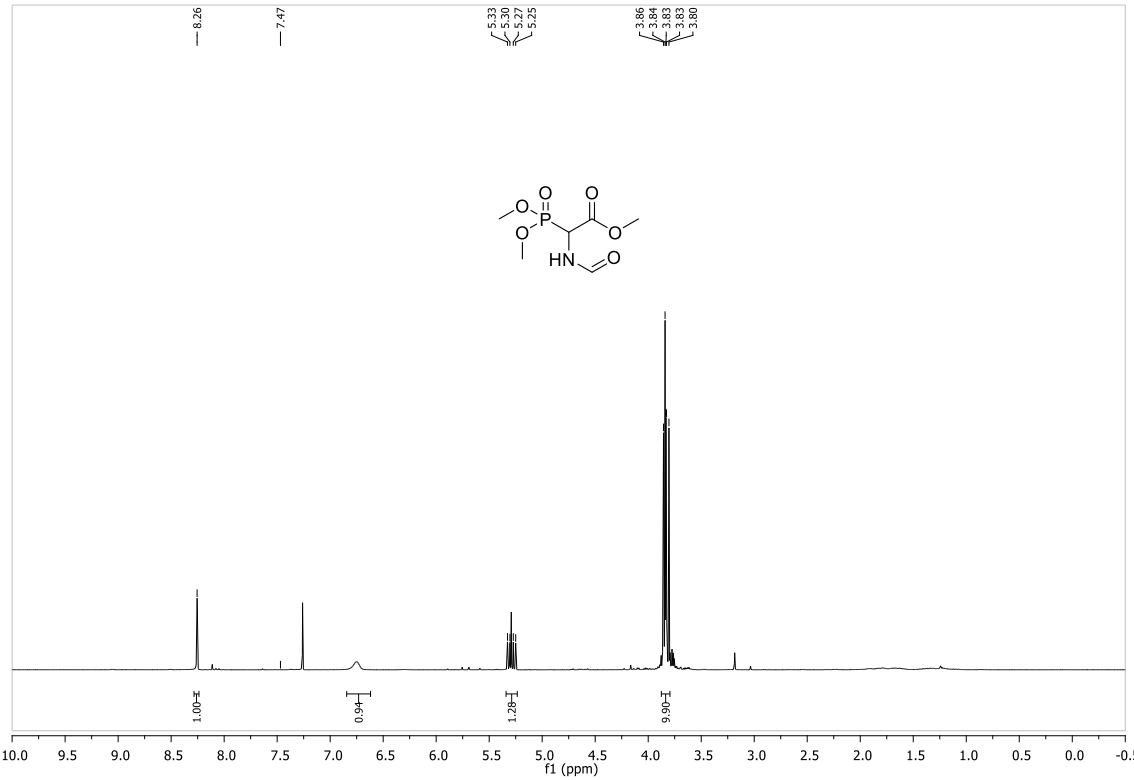


SYNTHESIS OF *N*-CARBAMATE

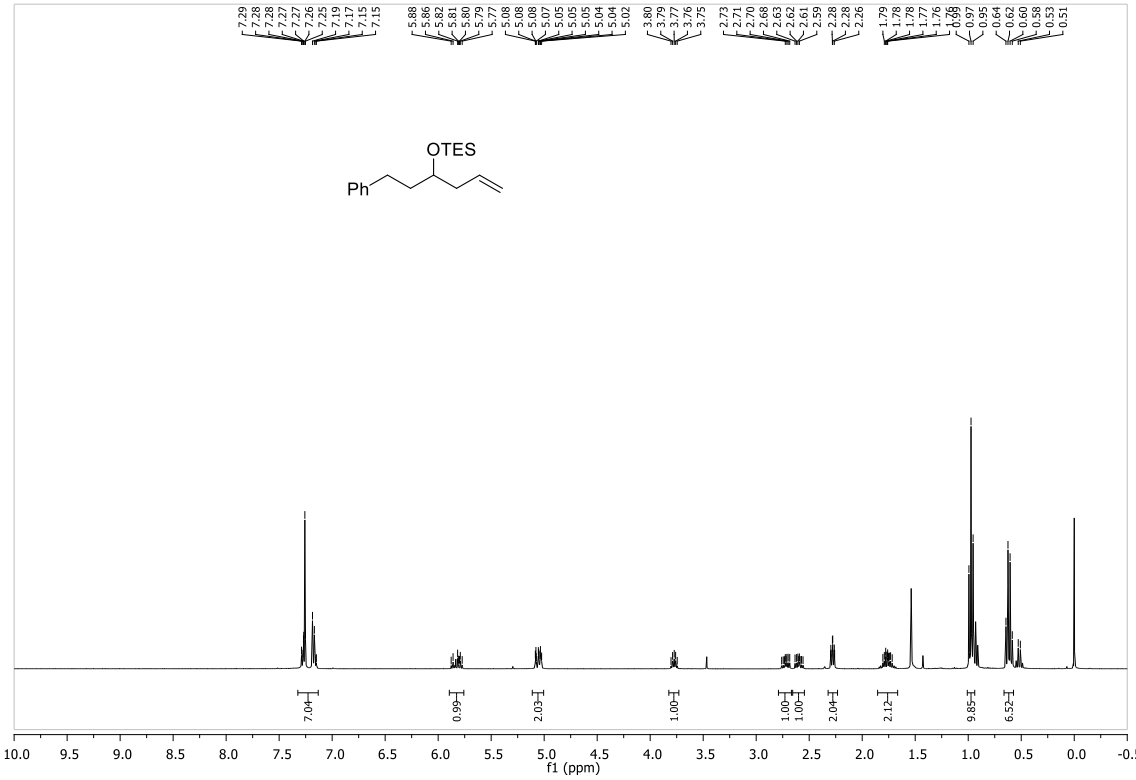
Methyl 2-amino-2-(dimethoxyphosphorylacetate)



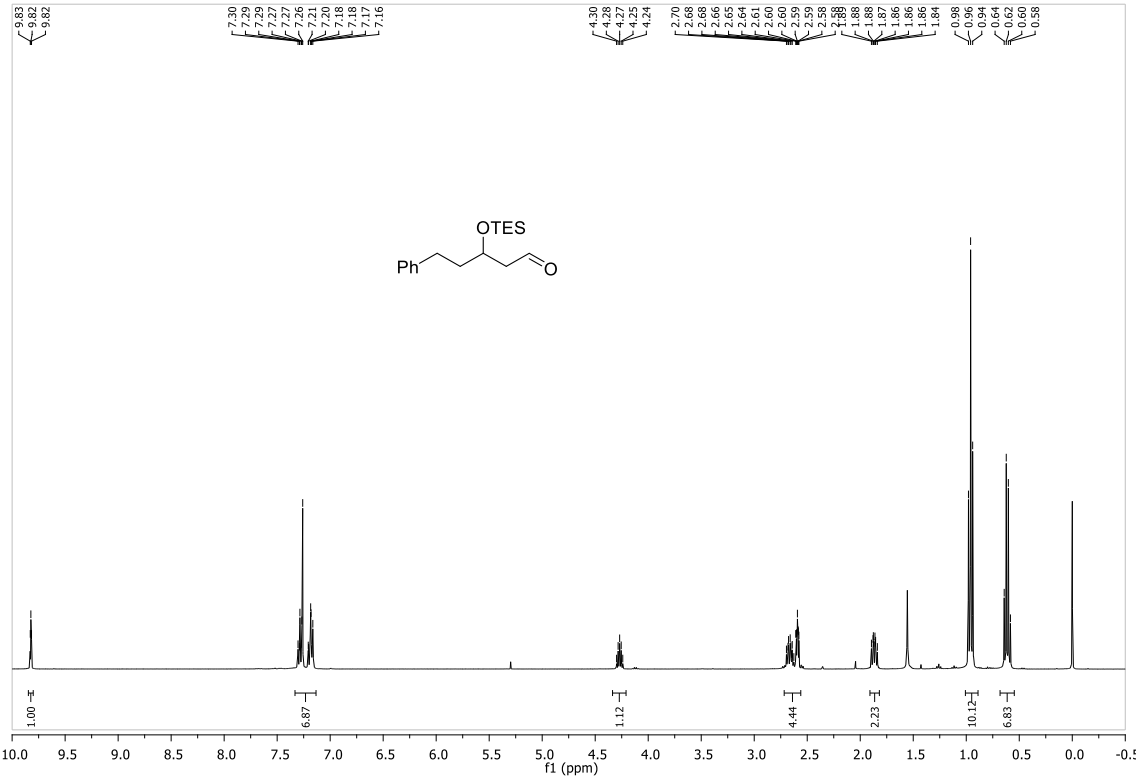
Methyl 2-(dimethoxyphosphoryl)-2-formamidoacetate

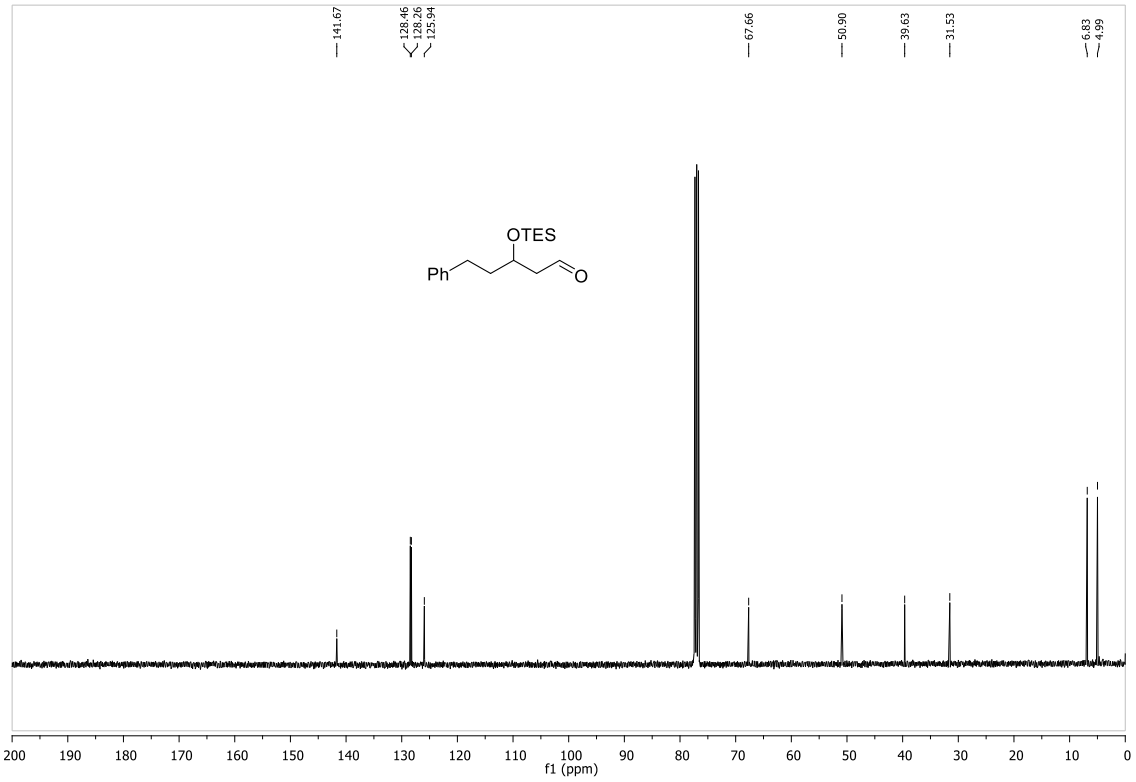


Triethyl((1-phenylhex-5-en-3-yl)oxy)silane

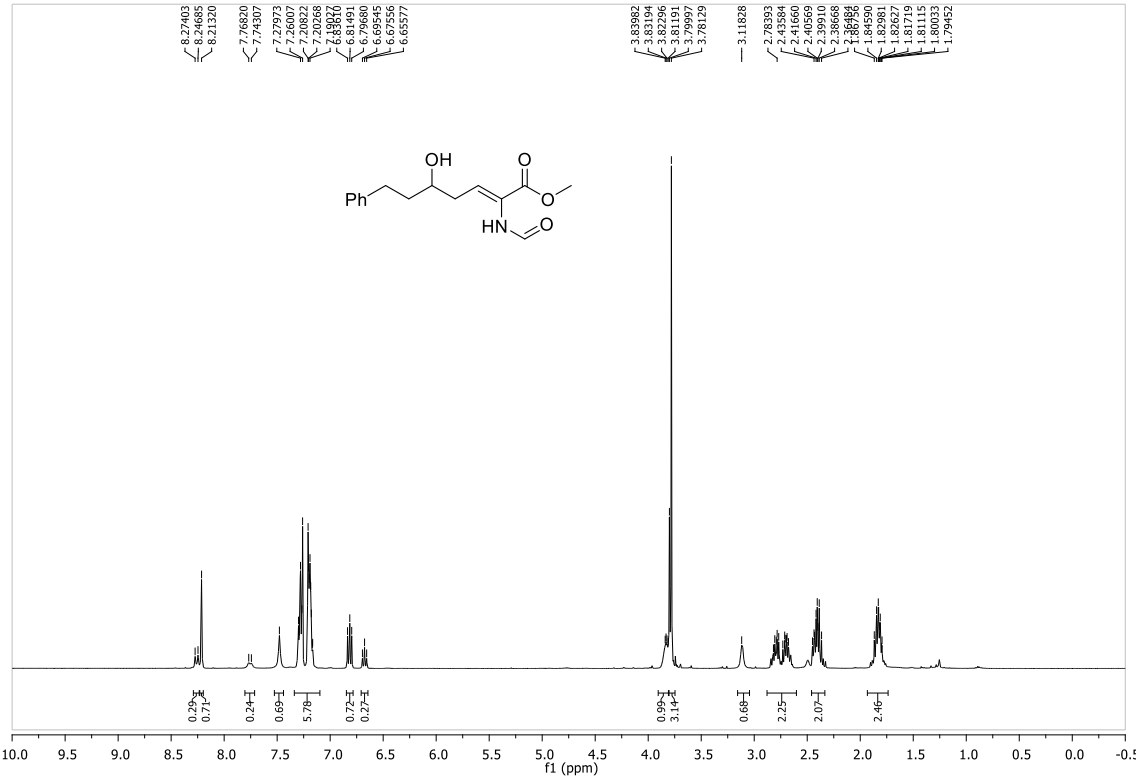


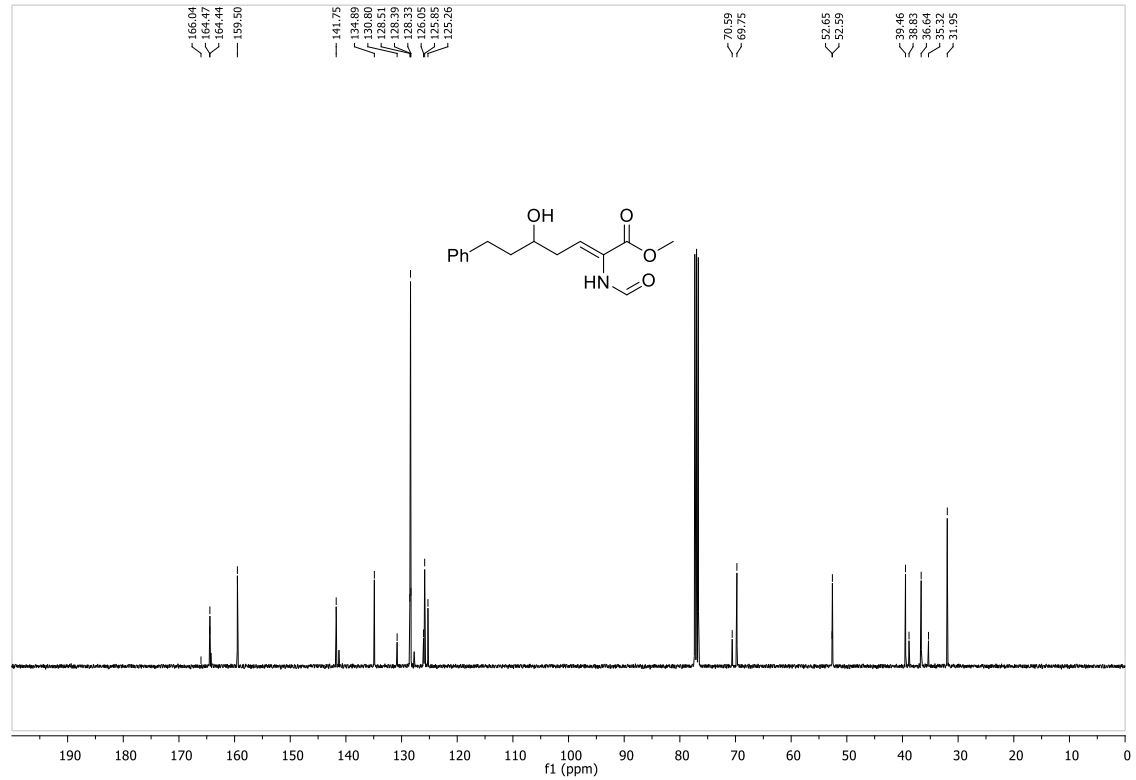
5-Phenyl-3-((triethylsilyl)oxy)pentanal



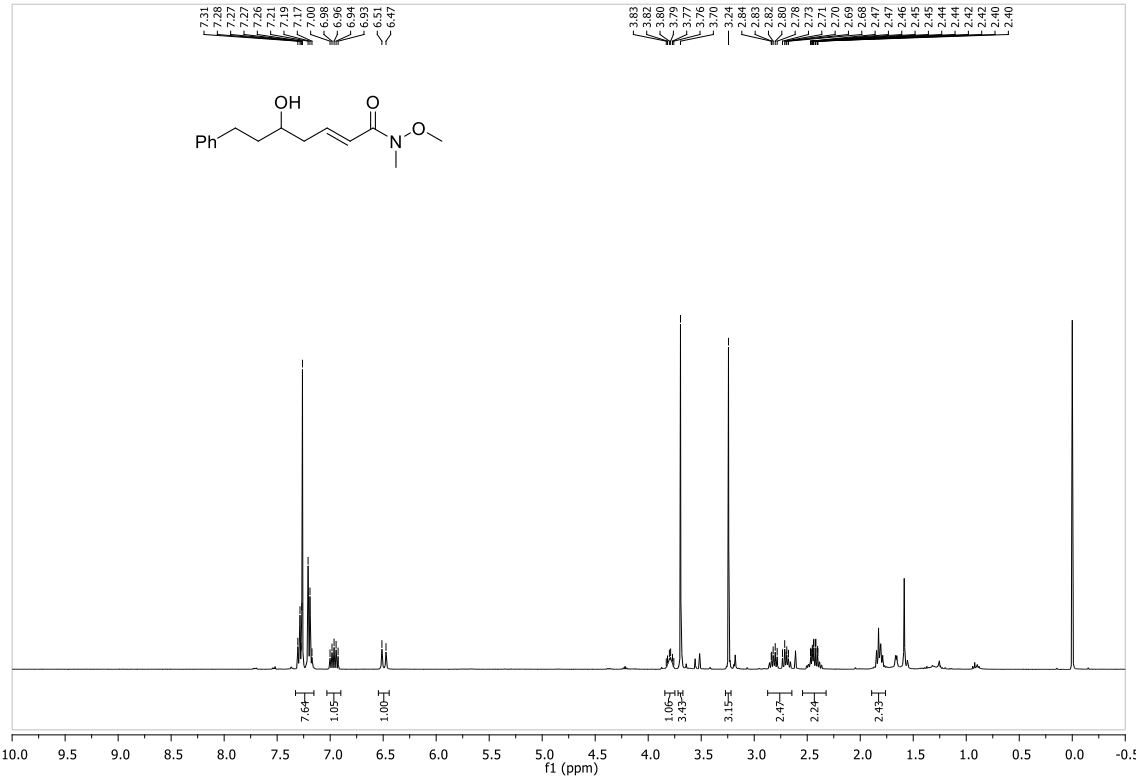


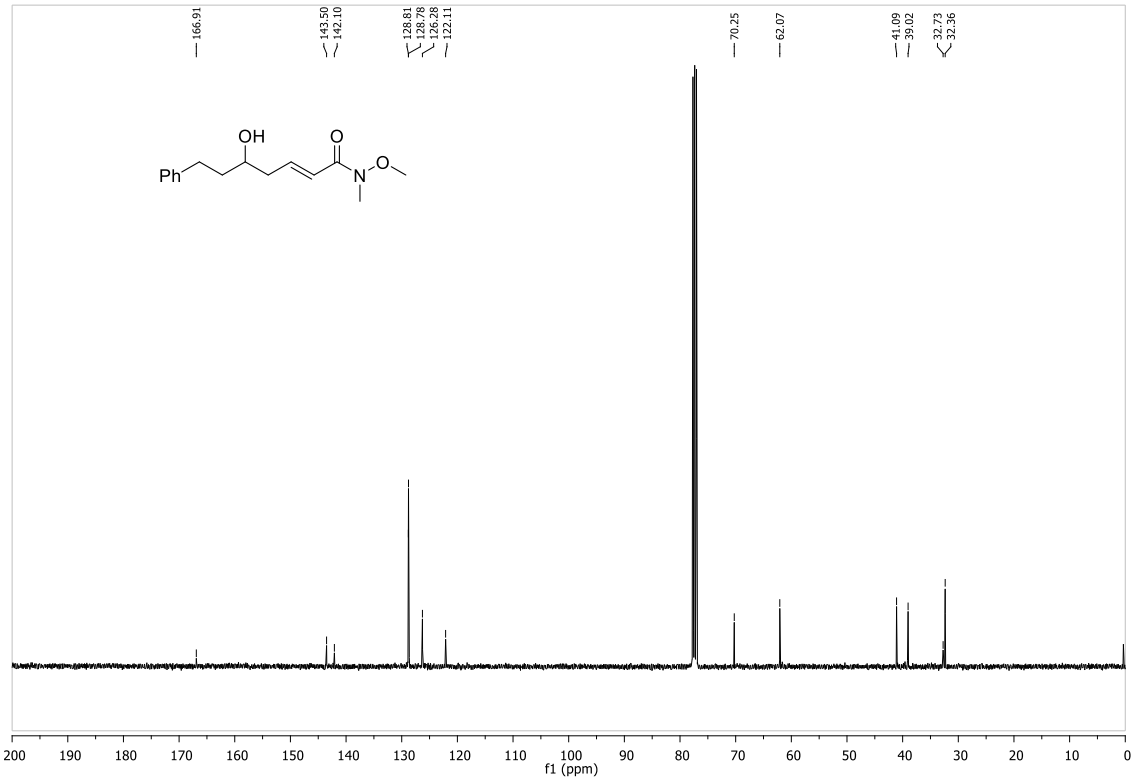
Methyl (*Z*)-2-formamido-5-hydroxy-7-phenylhept-2-enoate (6d)



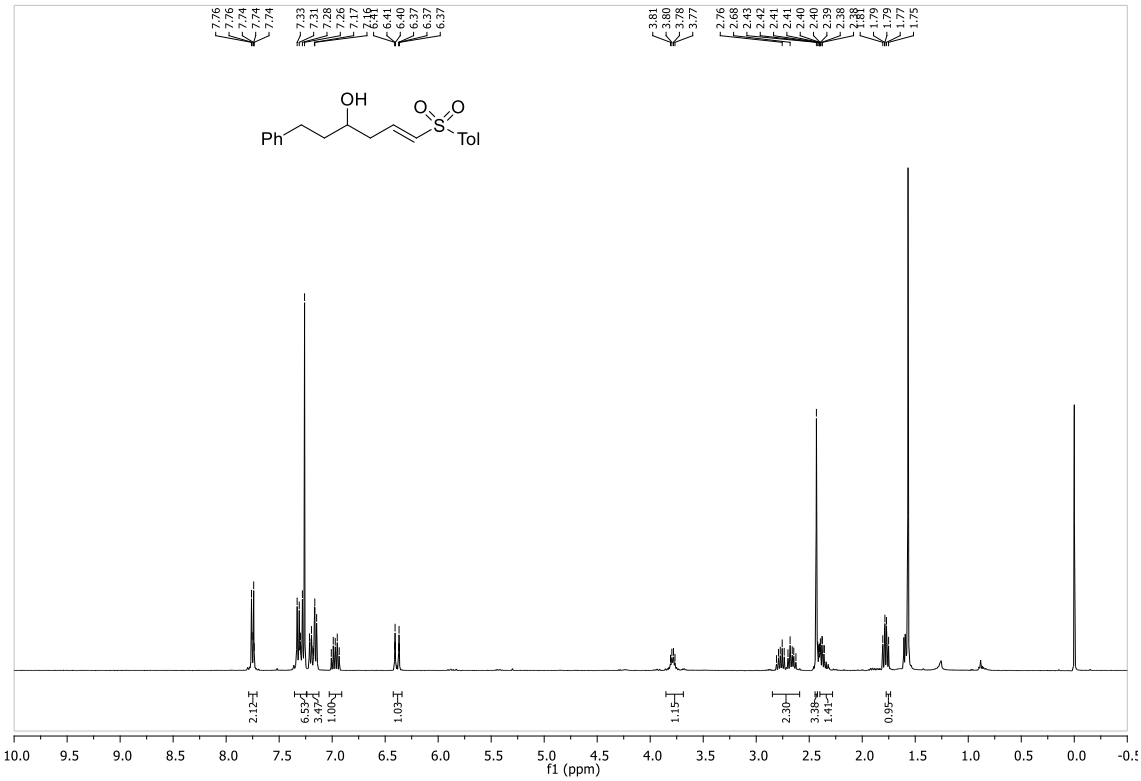


(*E*)-5-hydroxy-*N*-methoxy-*N*-methyl-7-phenylhept-2-enamide (8)



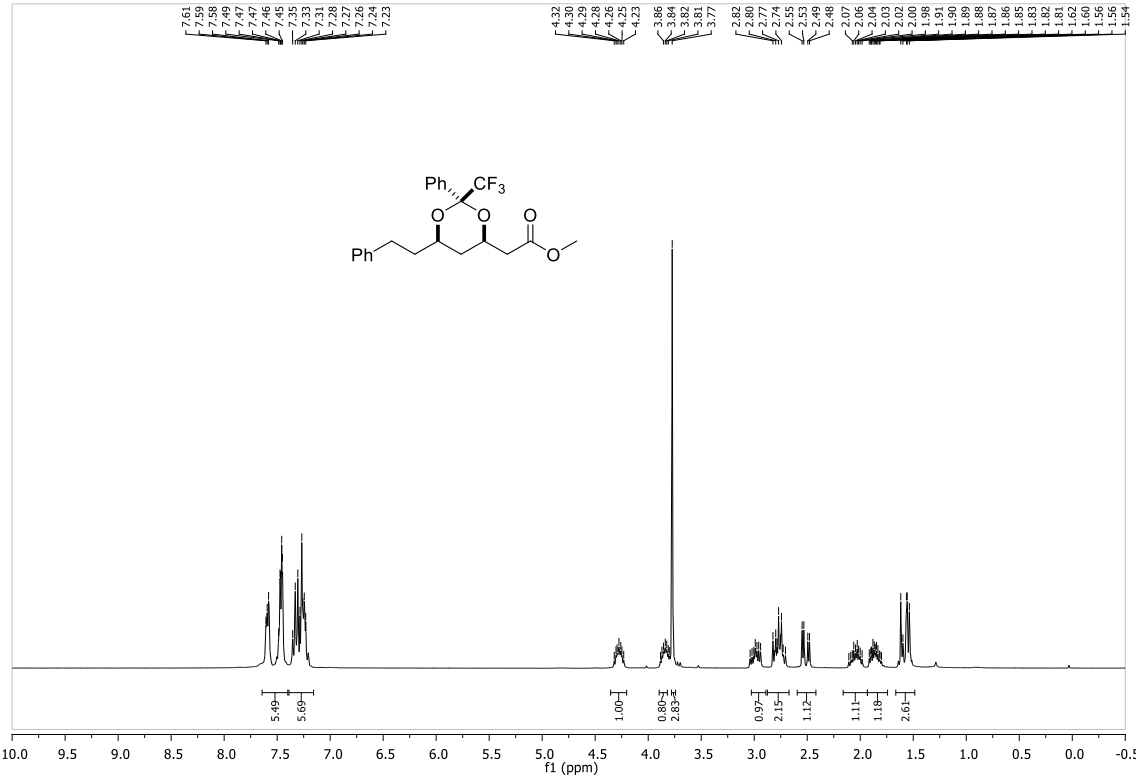


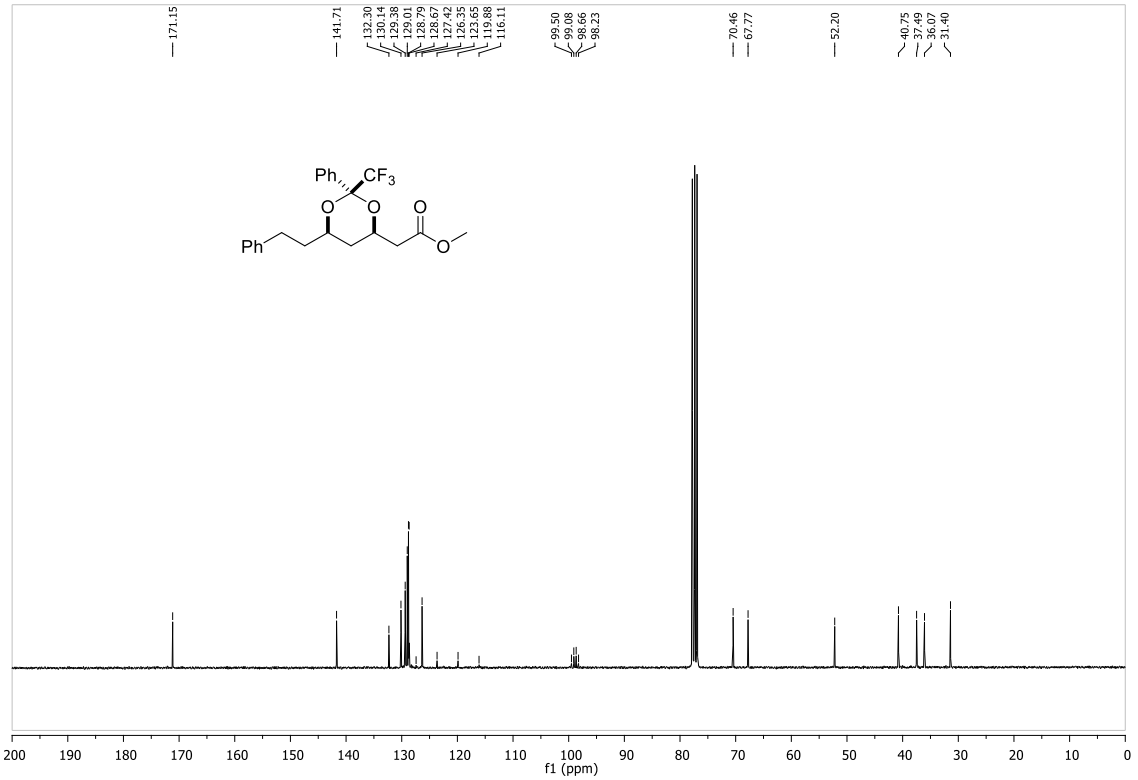
(*E*)-1-phenyl-6-tosylhex-5-en-3-ol (10)

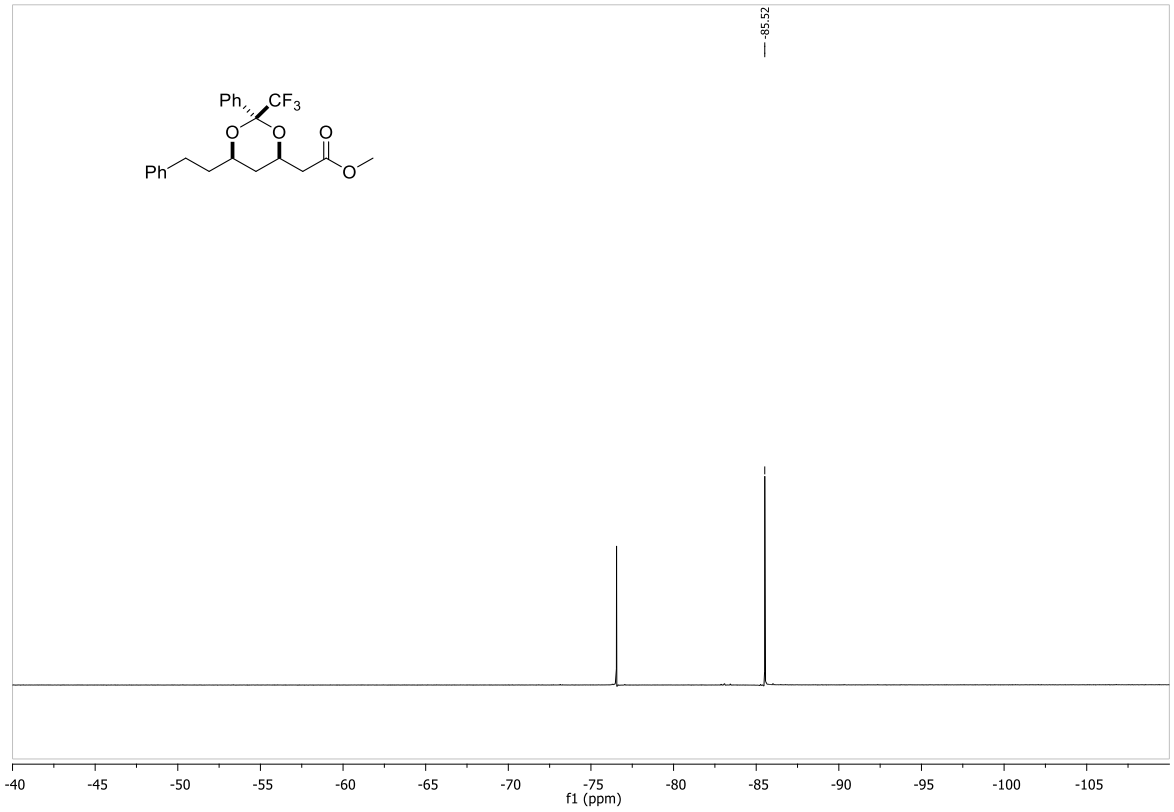


TRILUOROMETHYLATED 1,3 DIOXANES

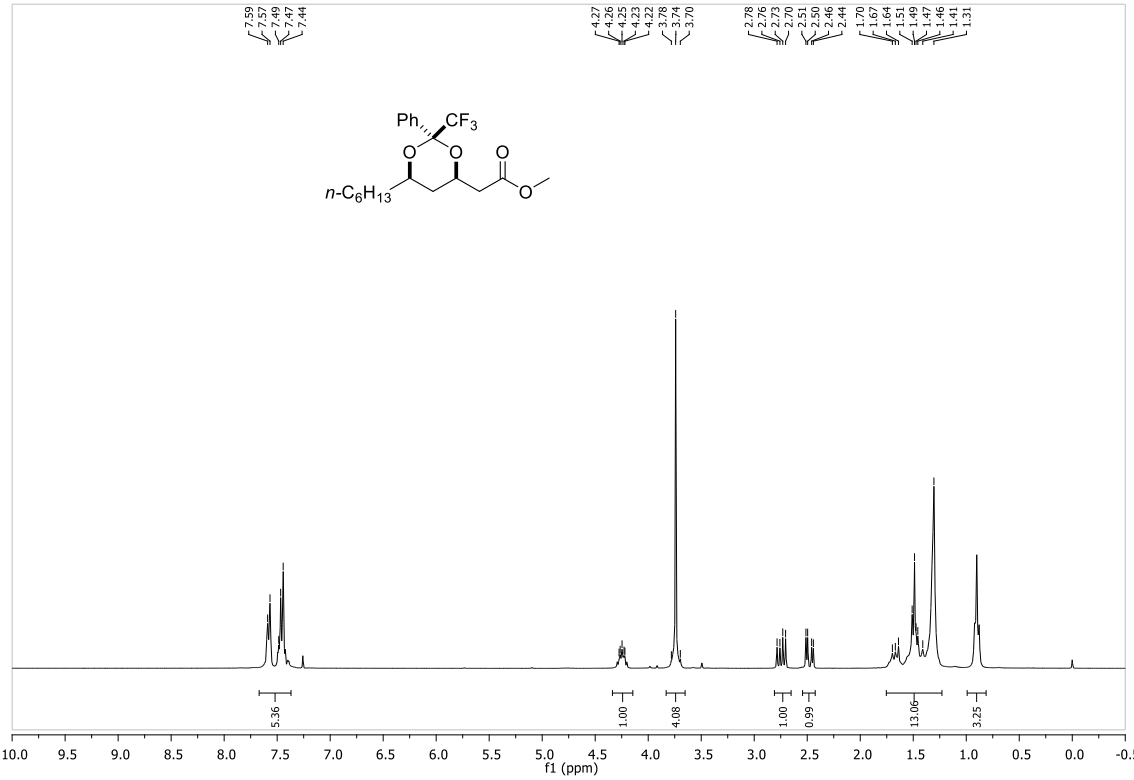
Methyl 2-((2*R,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2a)**

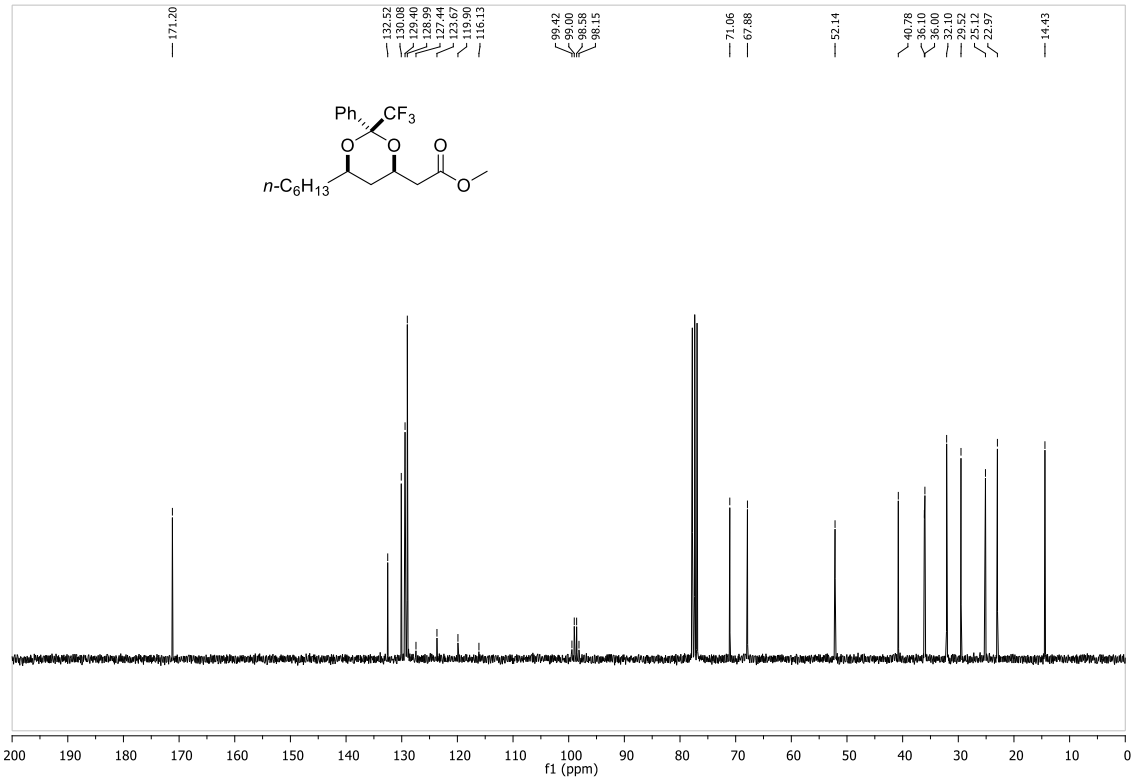


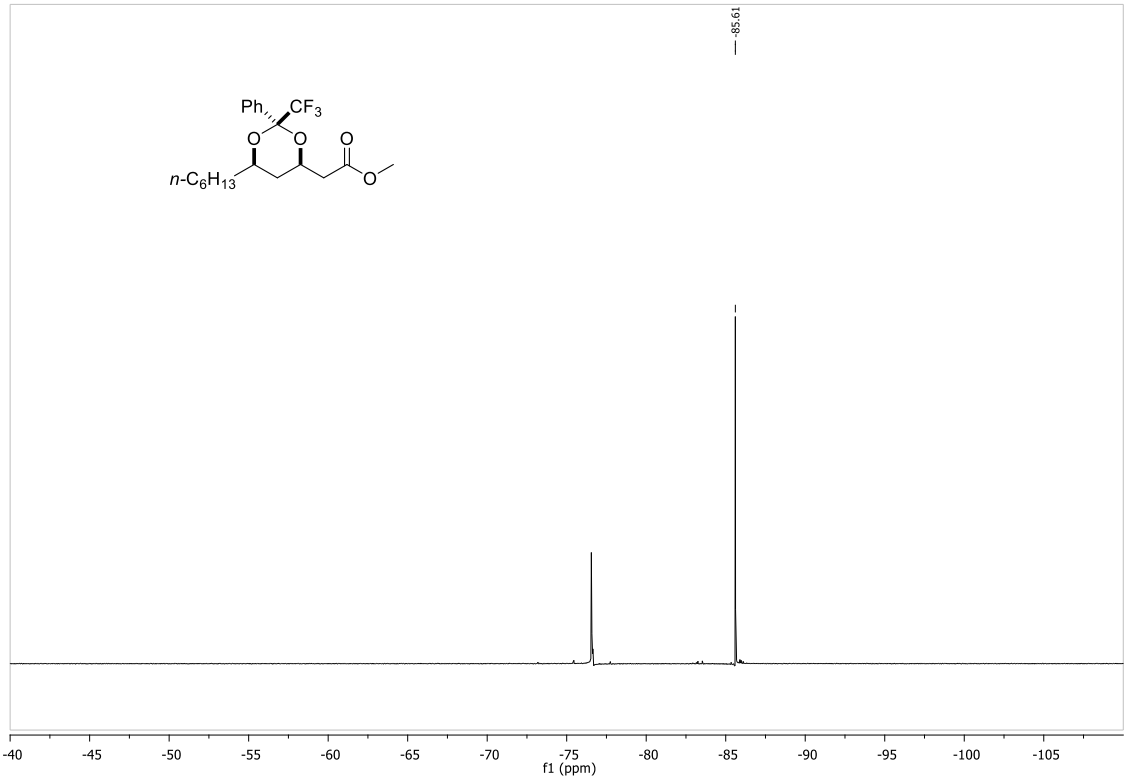



-85.52
Ph
CF3
O
O
O
O
Ph
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

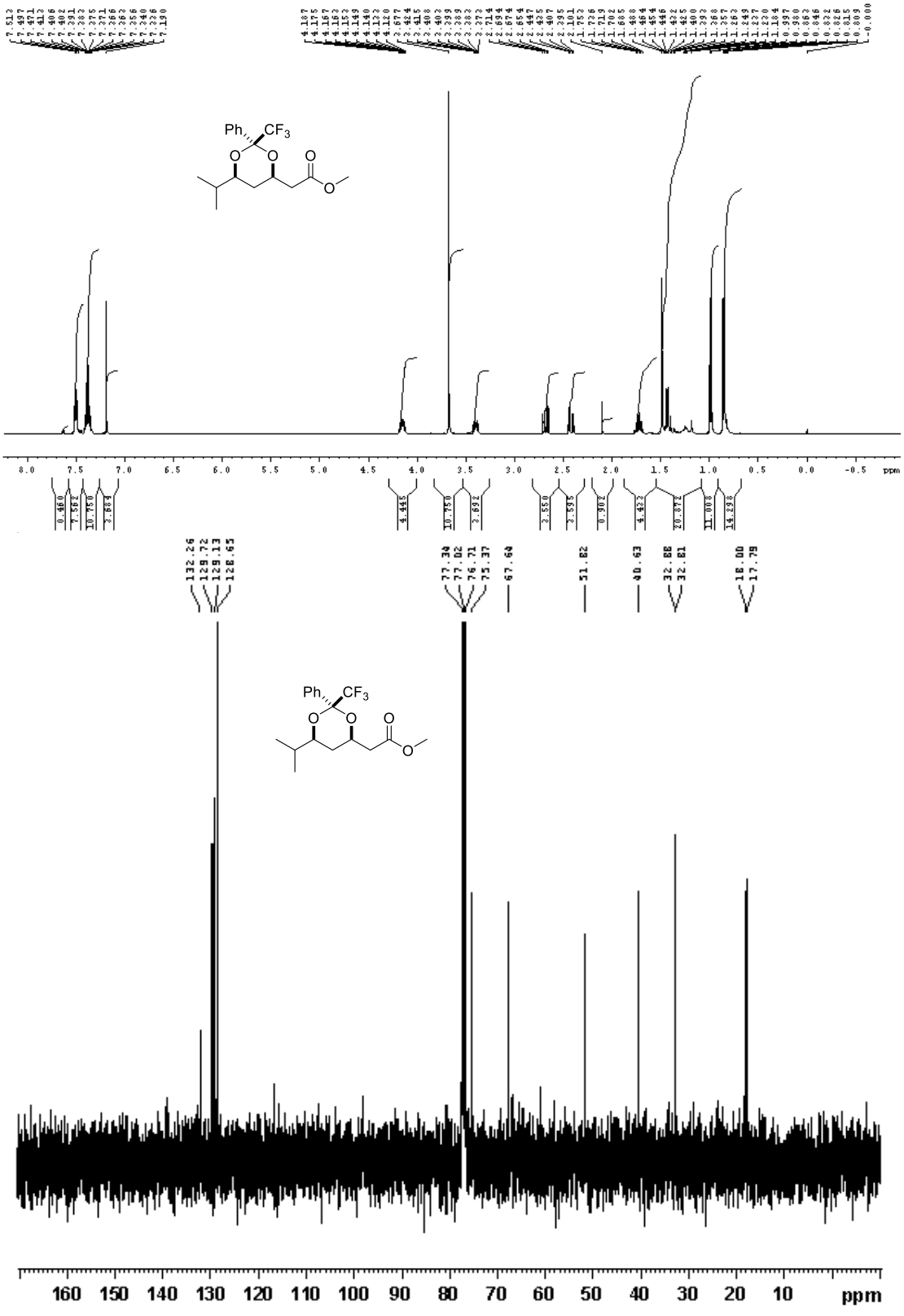
Methyl 2-((2*R,4*R**,6*R**)-6-hexyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2b)**



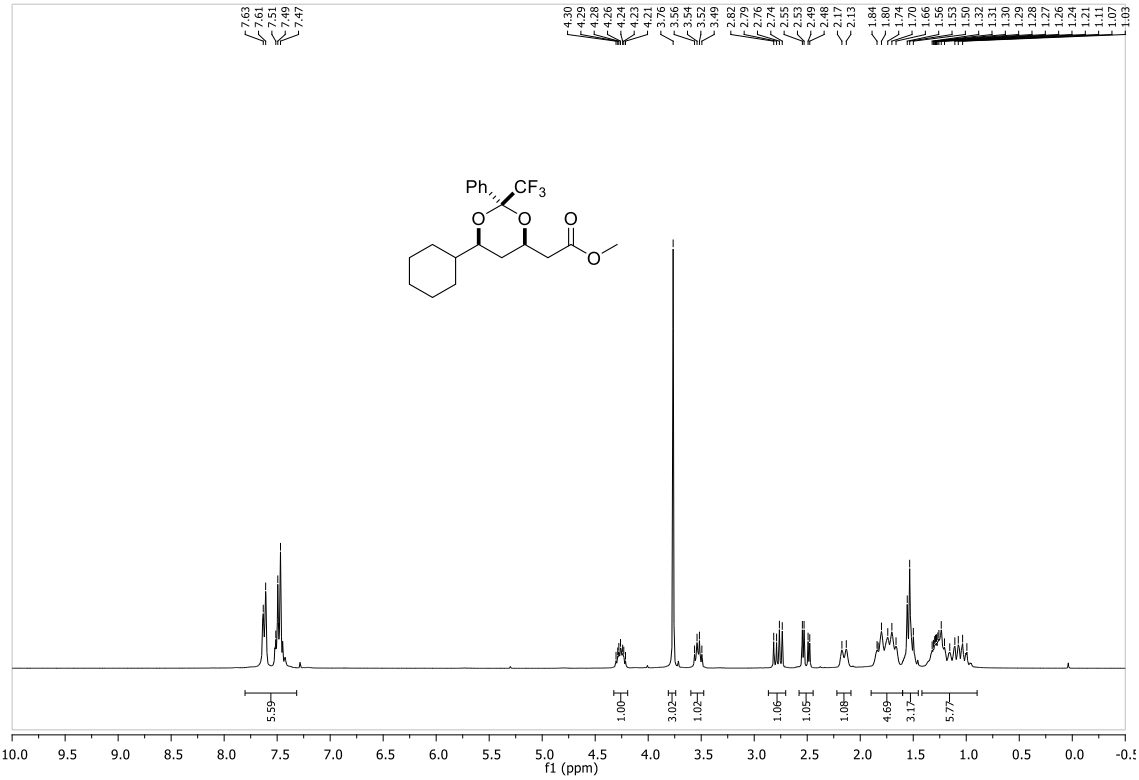


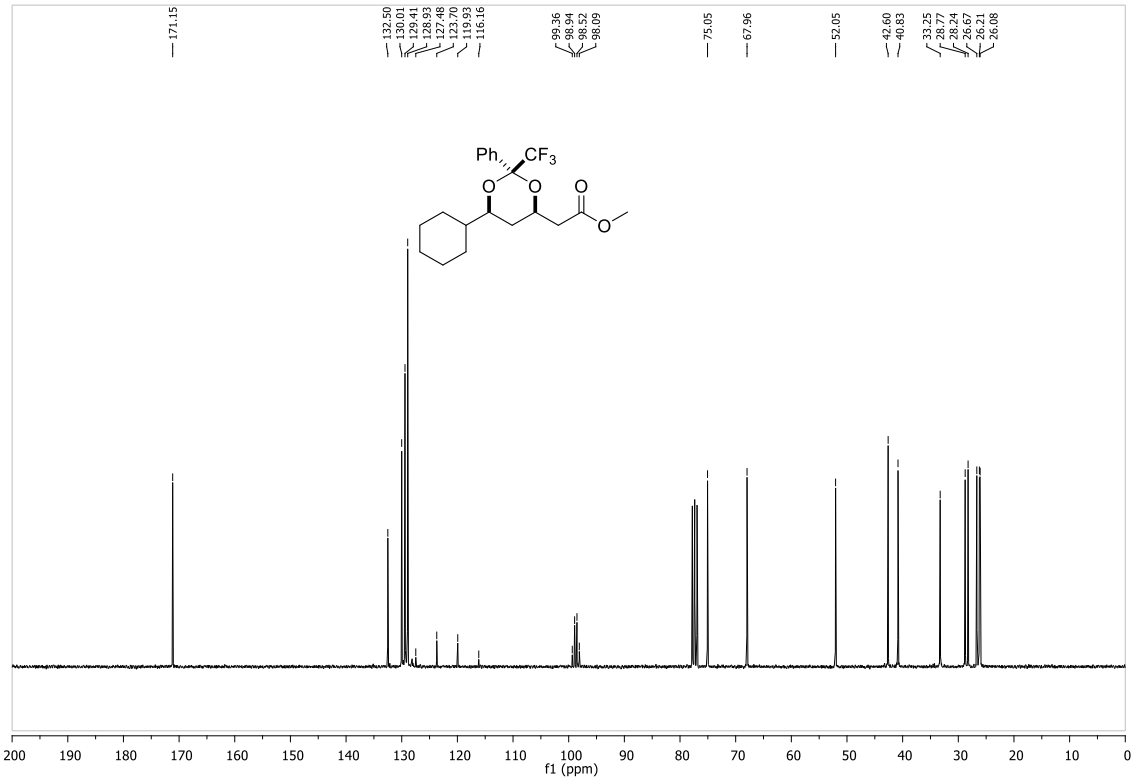

-85.61
Ph
CF3
O
O
O
O
n-C6H13
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

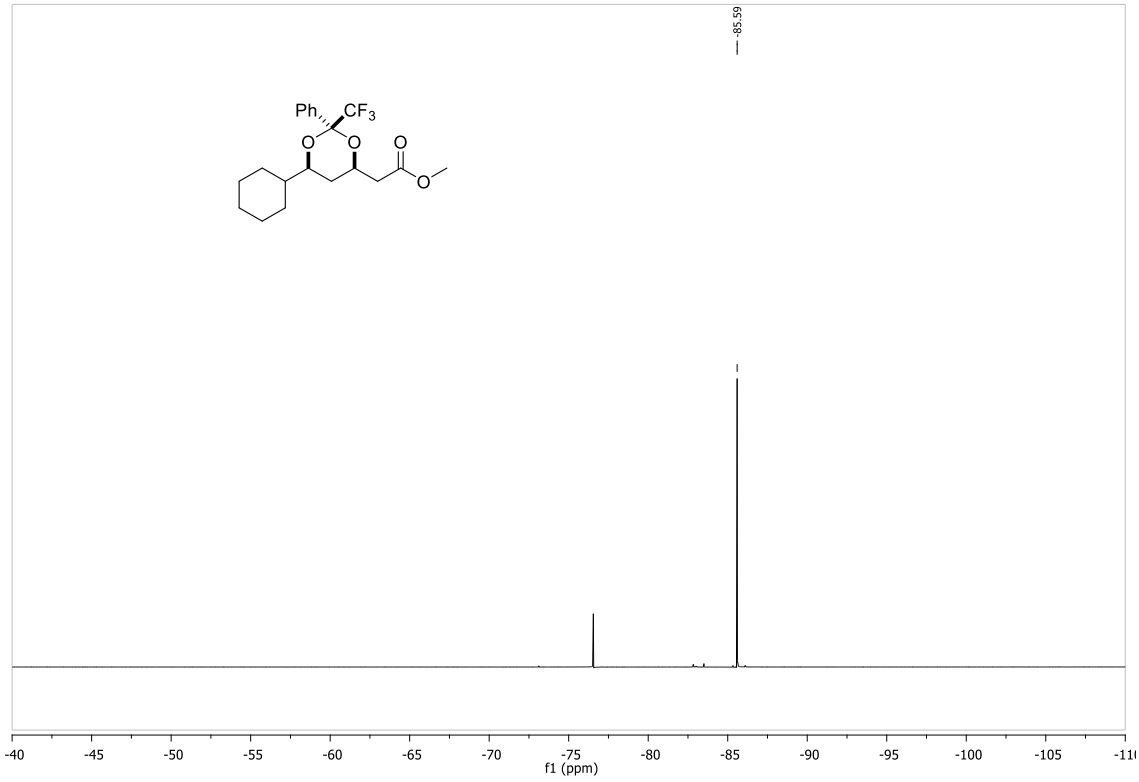
Methyl 2-((2*R,4*S**,6*R**)-6-isopropyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2c)**



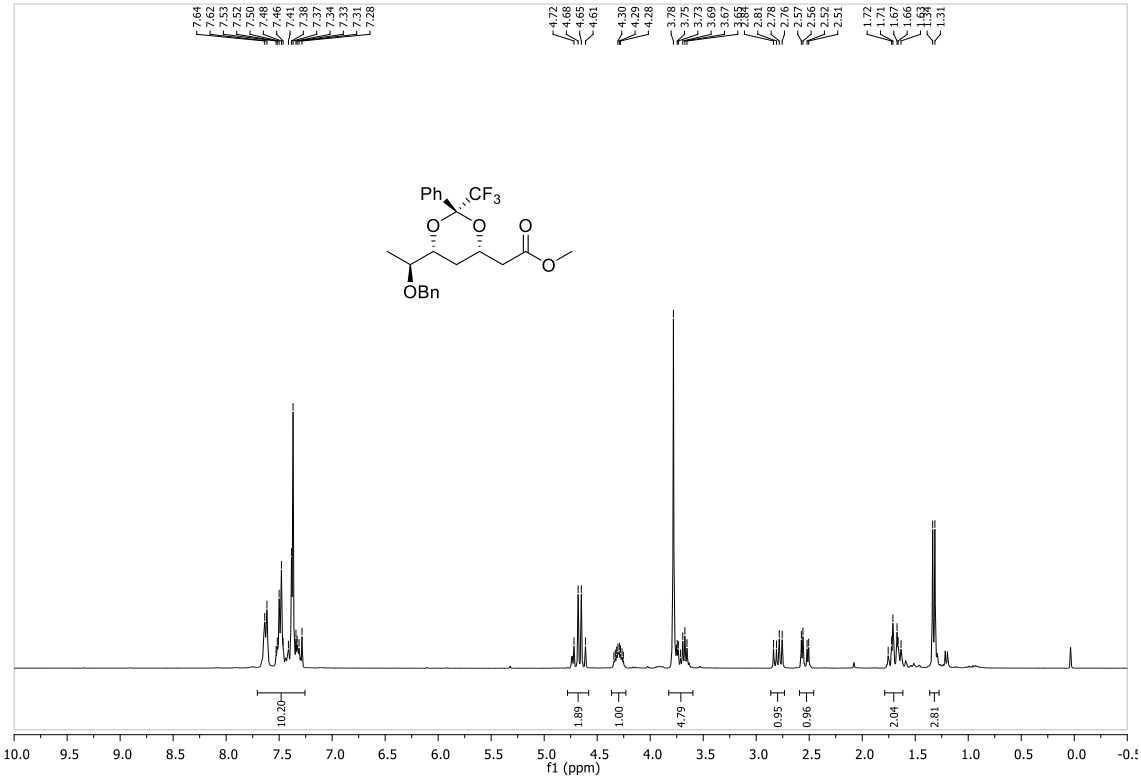
Methyl 2-((2*R,4*S**,6*R**)-6-cyclohexyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2d)**

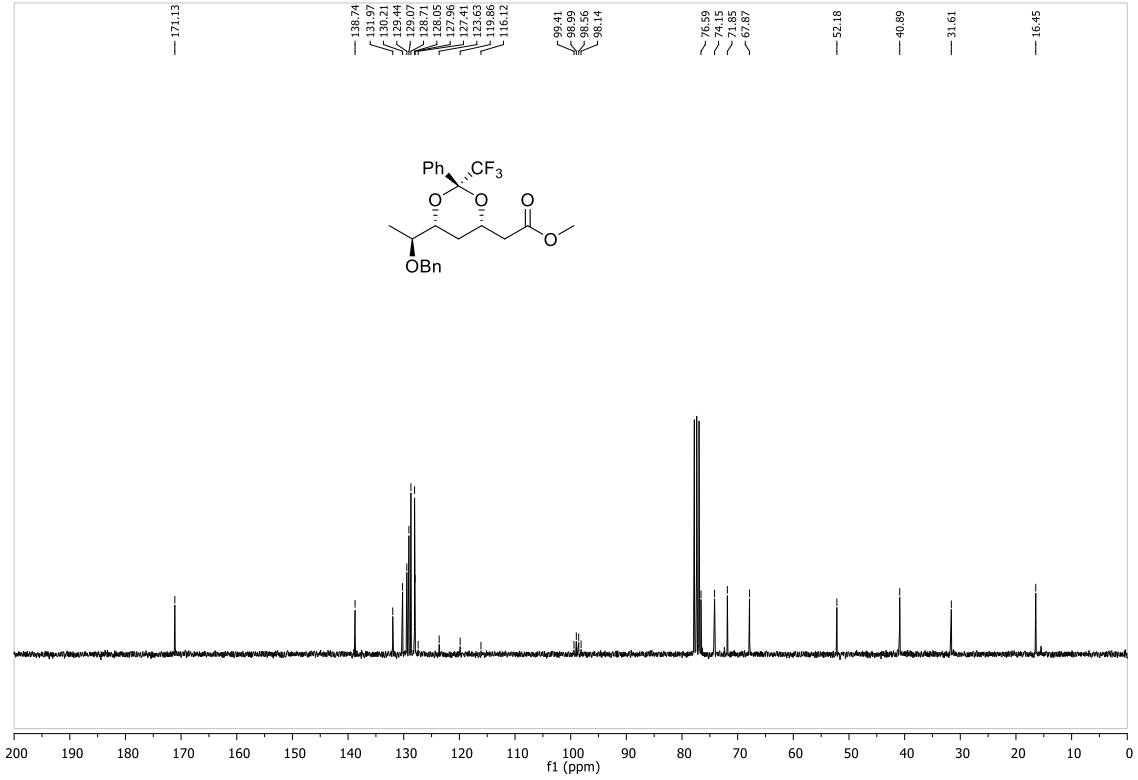


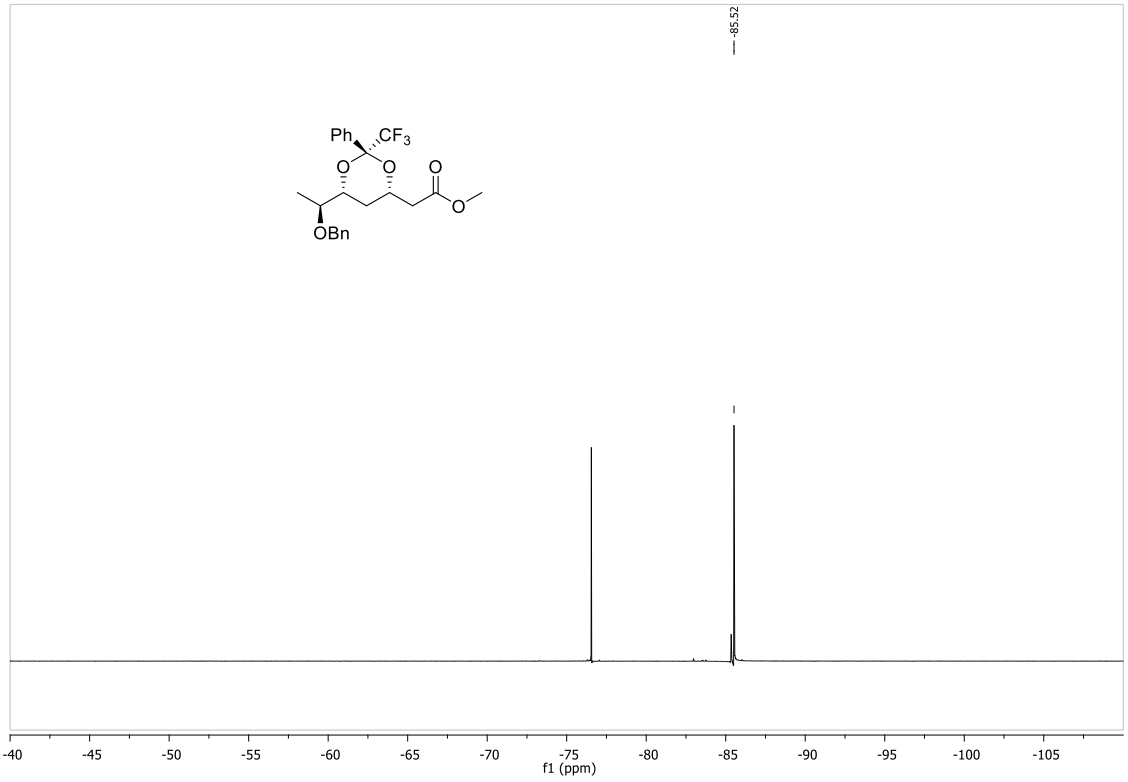



-85.59
Ph
CF3
O
O
O
O
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

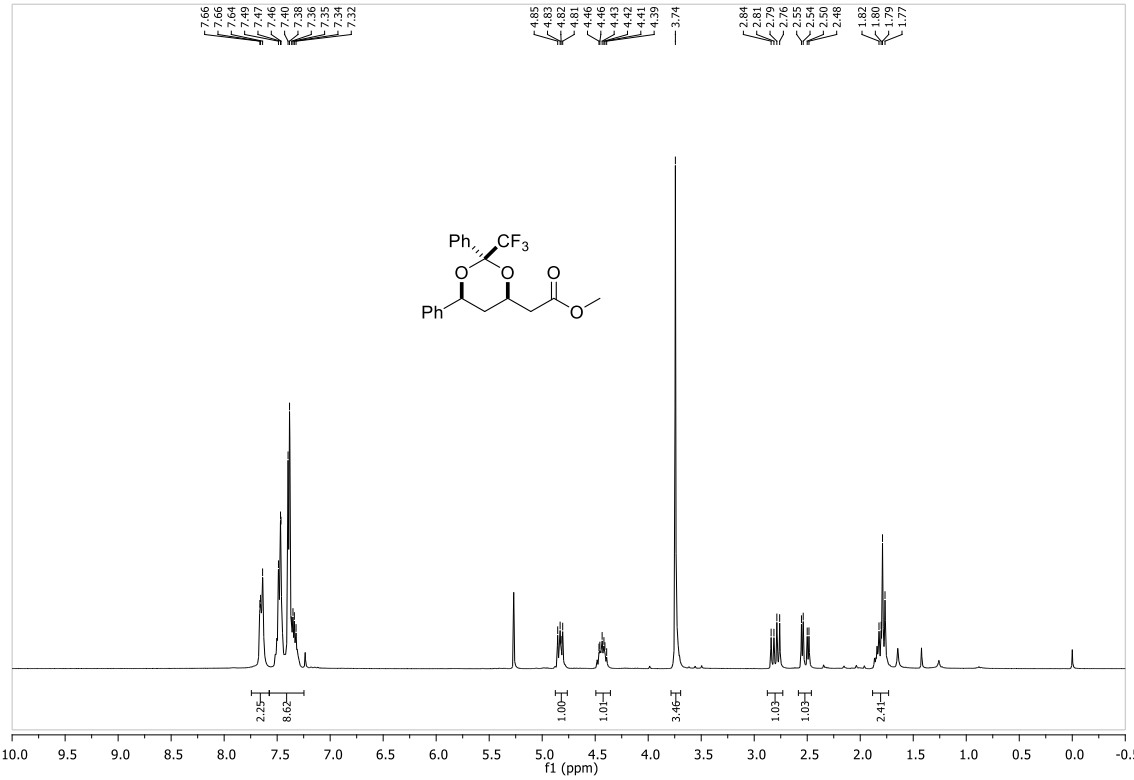
Methyl 2-((2*R*,4*S*,6*R*)-6-((*S*)-1-(benzyloxy)ethyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2e)

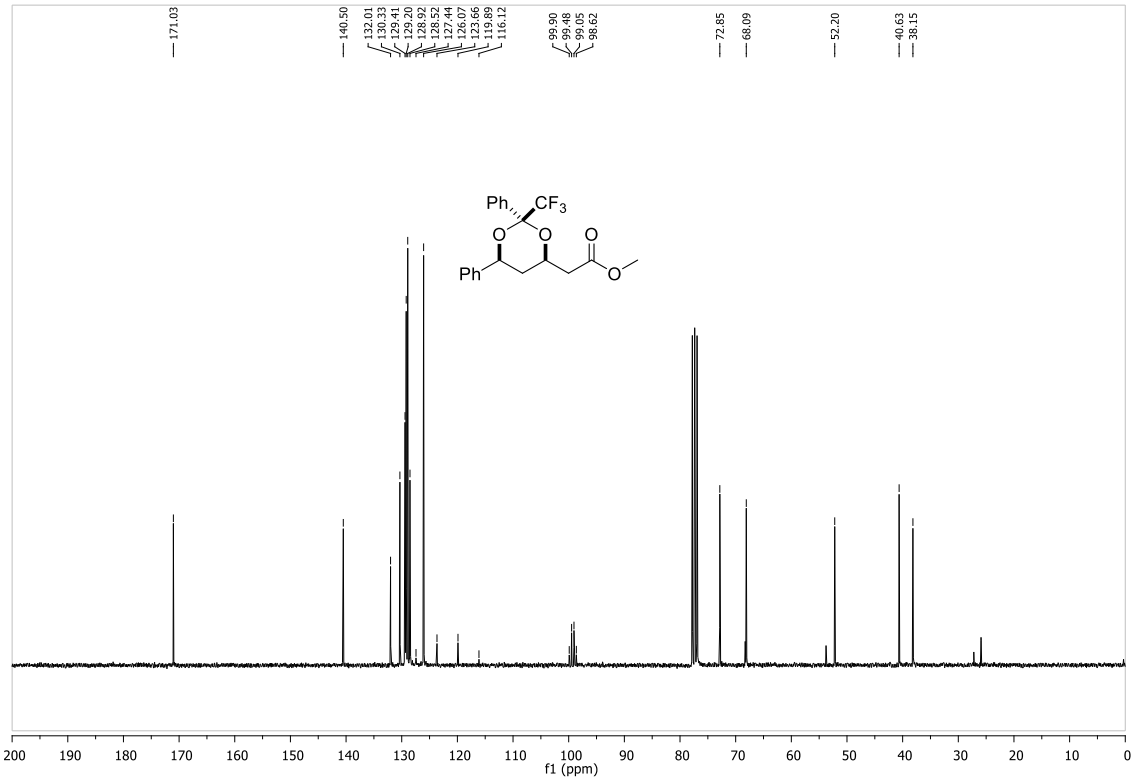


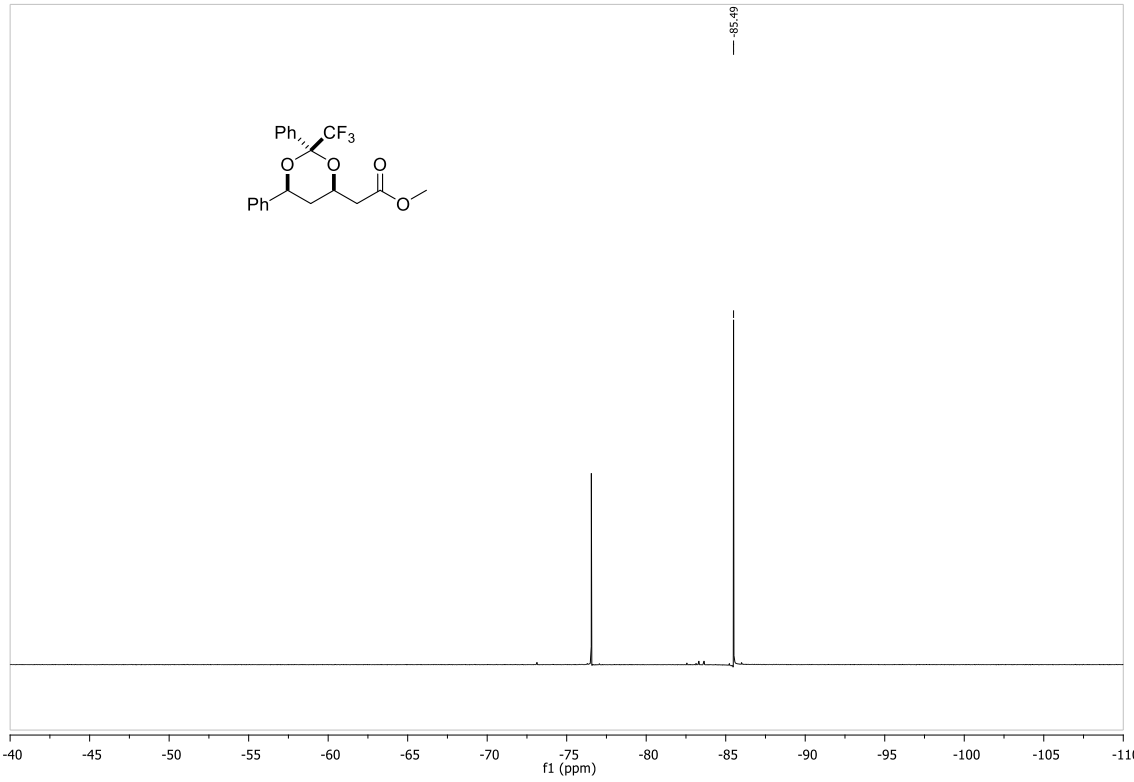



-85.52
Ph
CF3
O
O
O
O
OBn
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

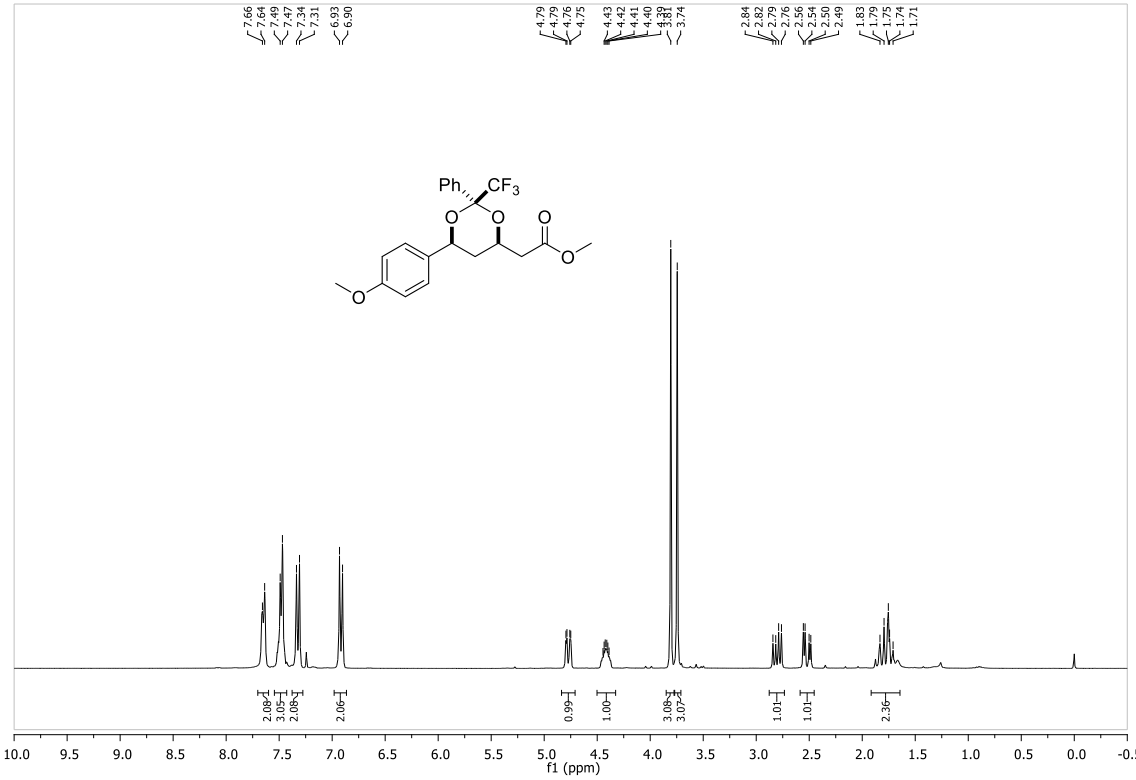
Methyl 2-((2*R,4*S**,6*R**)-2,6-diphenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2f)**

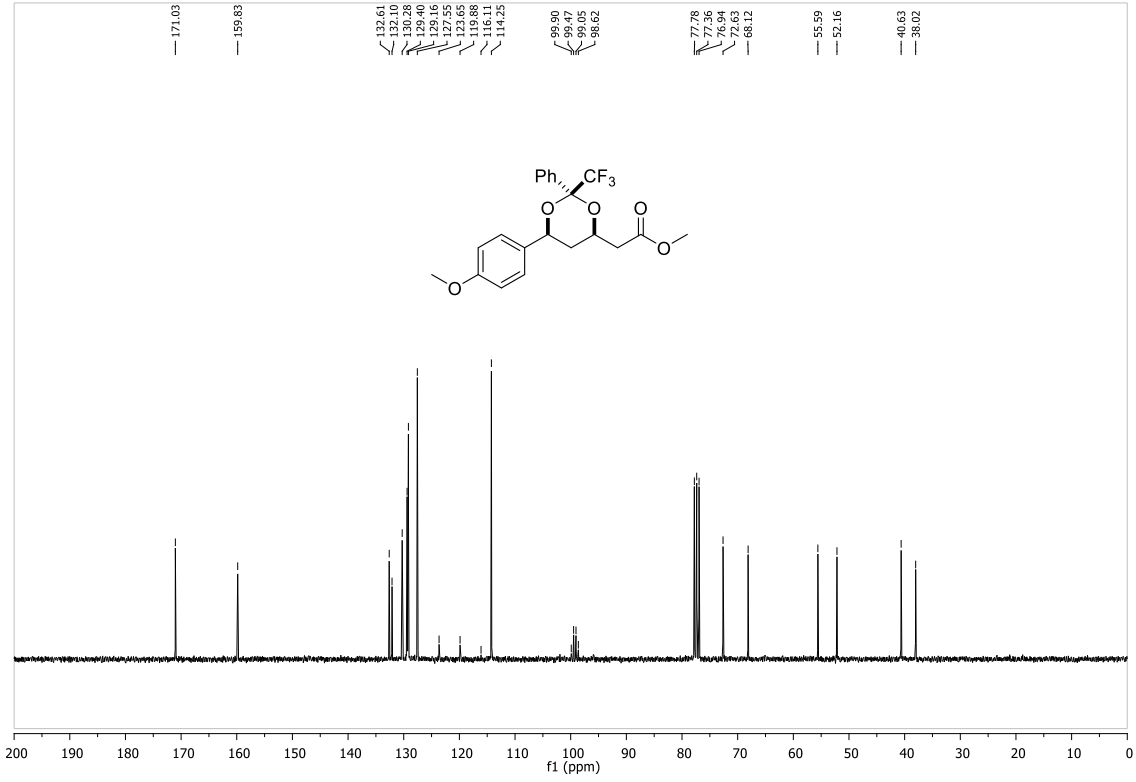


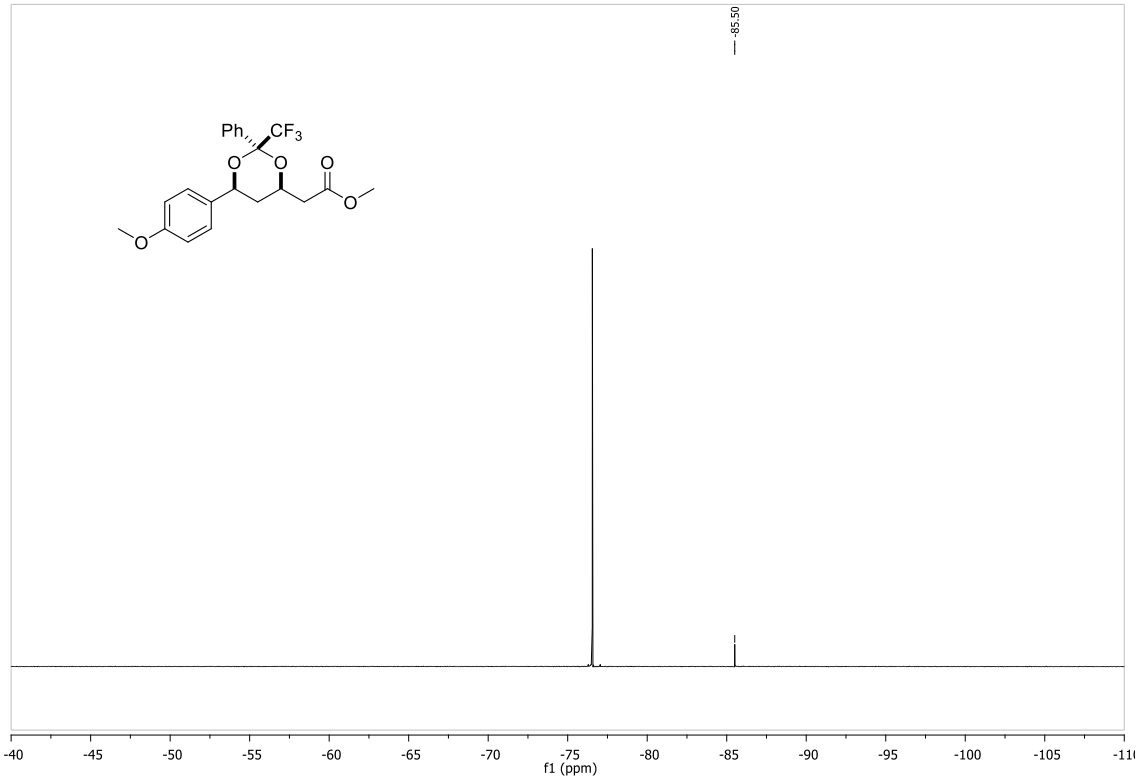



-85.49
Ph
CF3
O
O
O
Ph
O
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

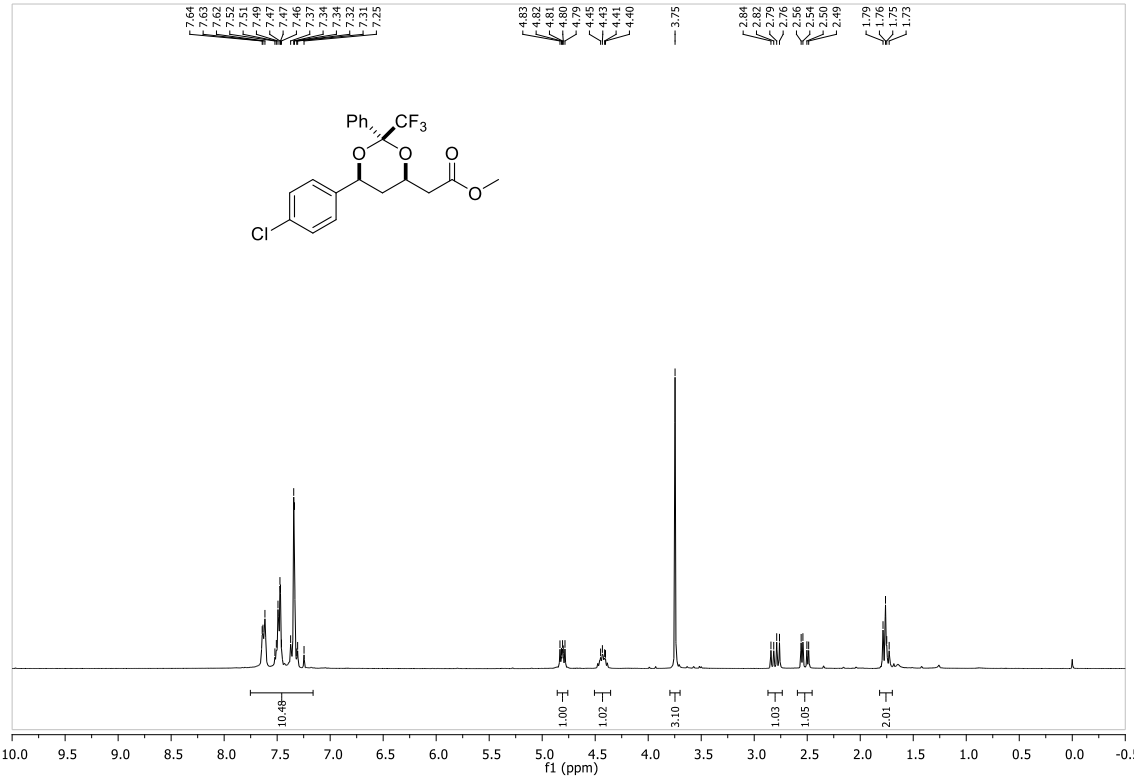
Methyl 2-((2*R,4*S**,6*R**)-6-(4-methoxyphenyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2g)**

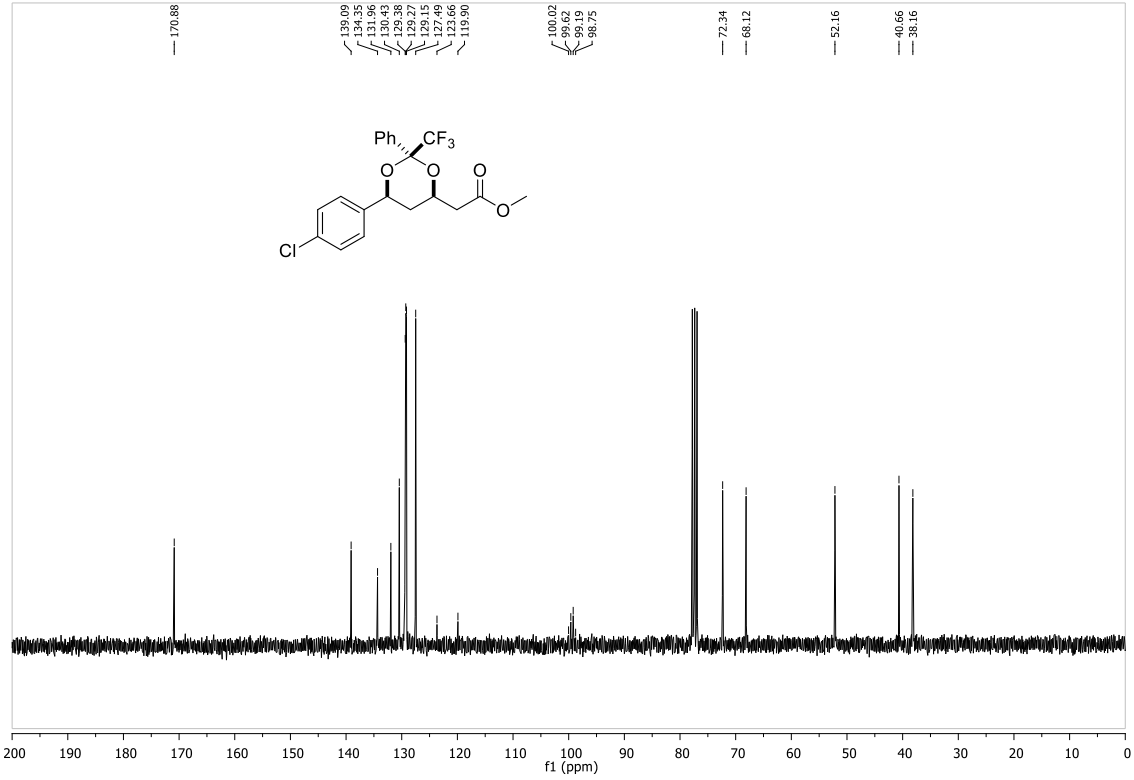


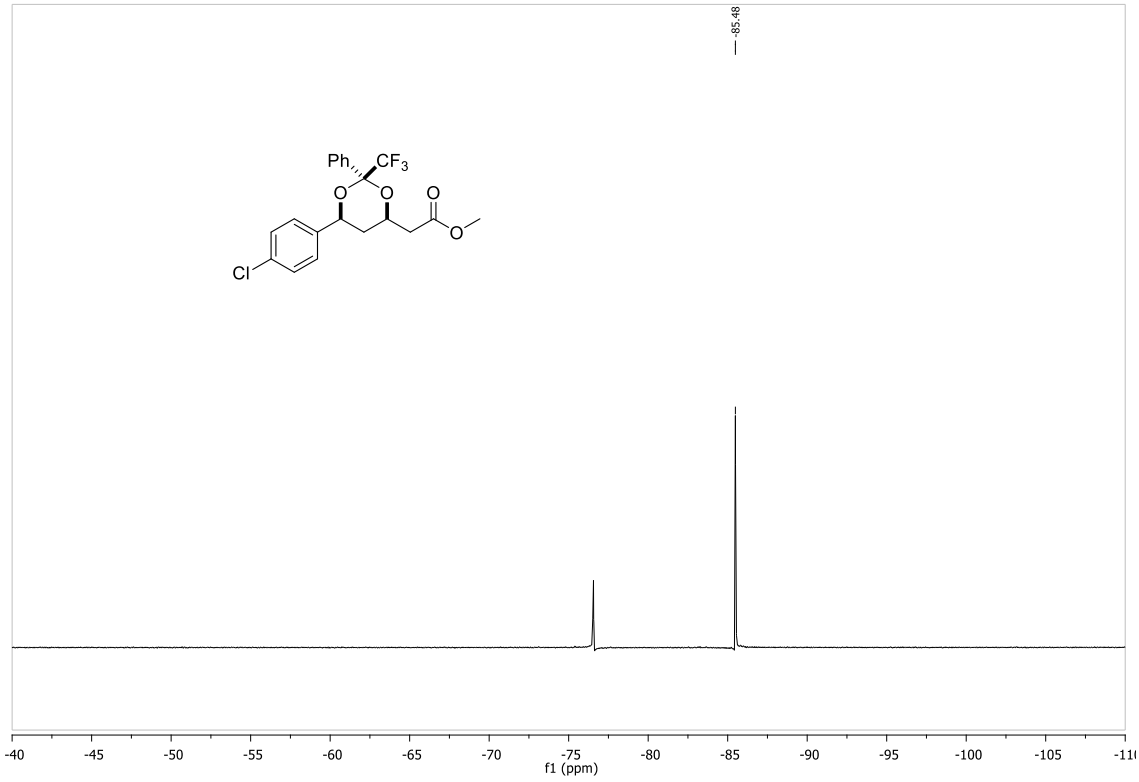



-85.50
Ph
CF3
O
O
O
O
O
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

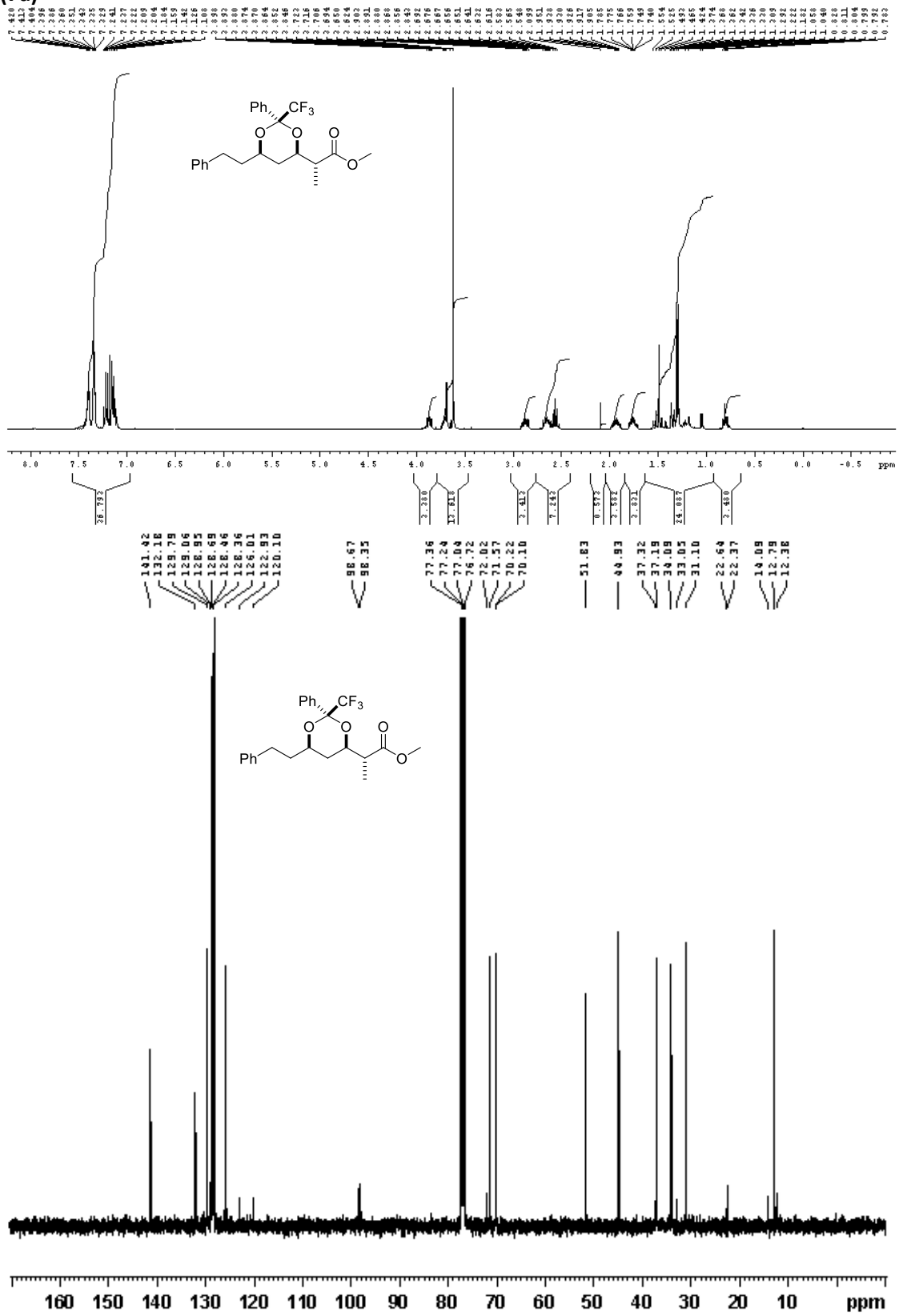
Methyl 2-((2*R,4*S**,6*R**)-6-(4-chlorophenyl)-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2h)**



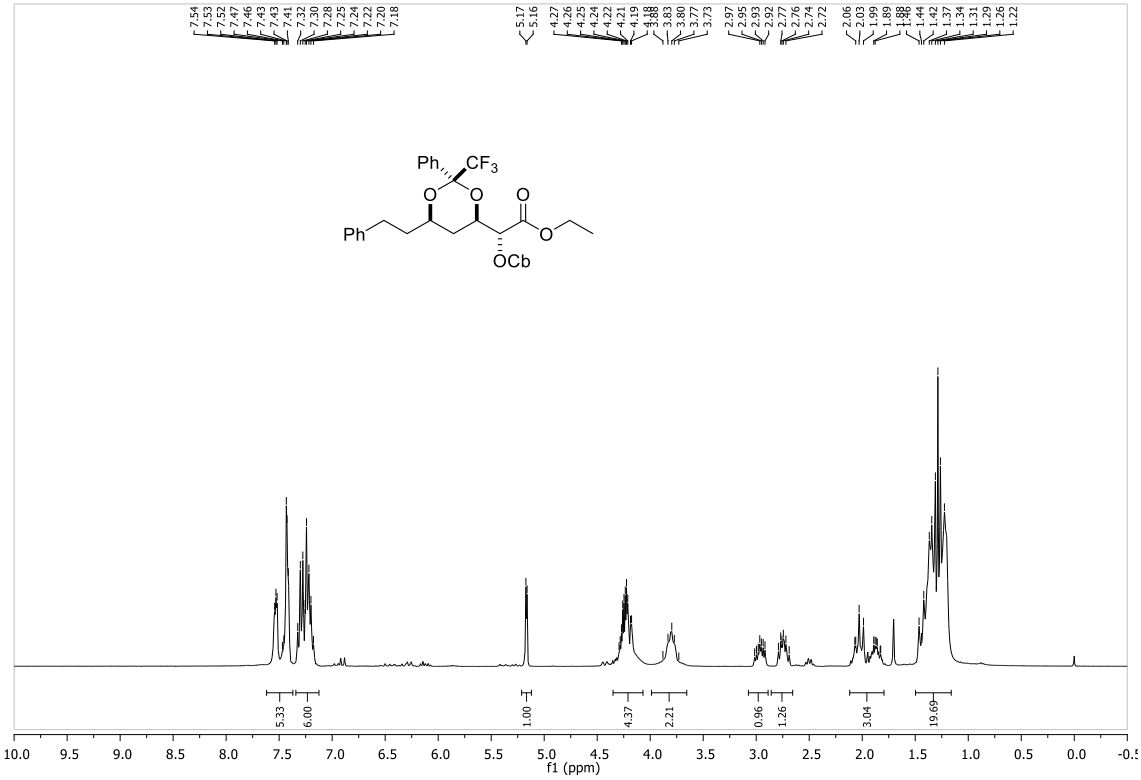


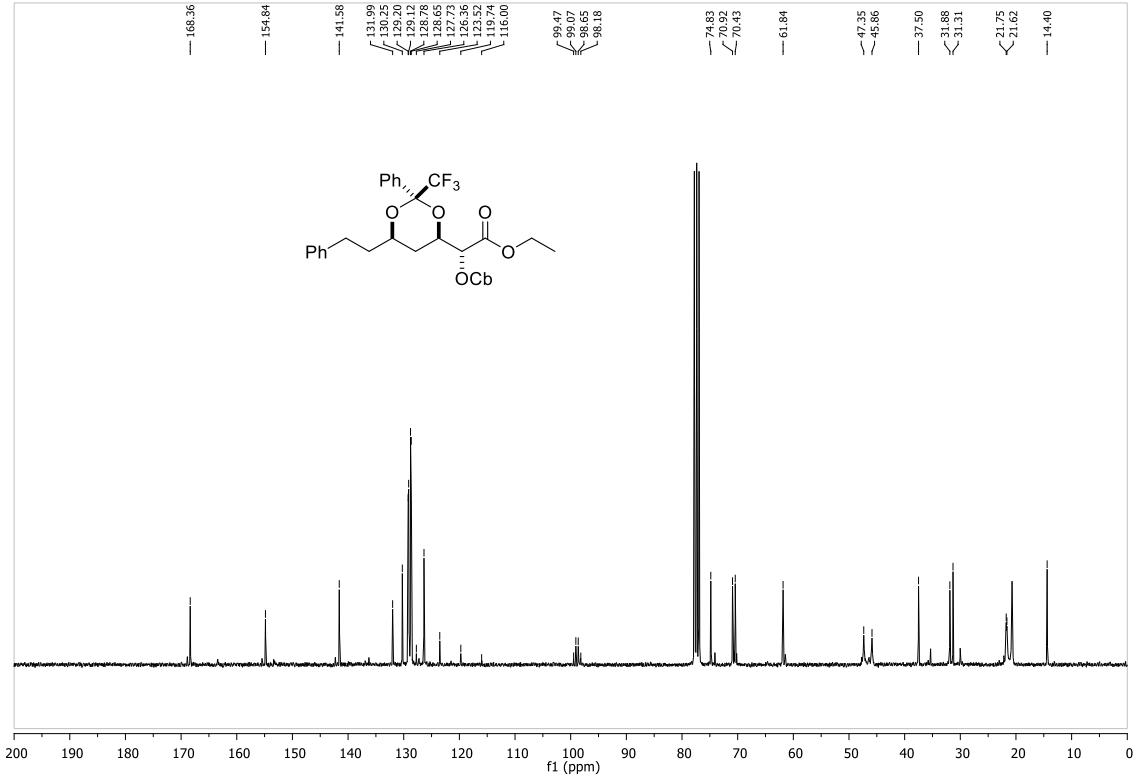

-85.48
Ph
CF3
O
O
O
O
Cl
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

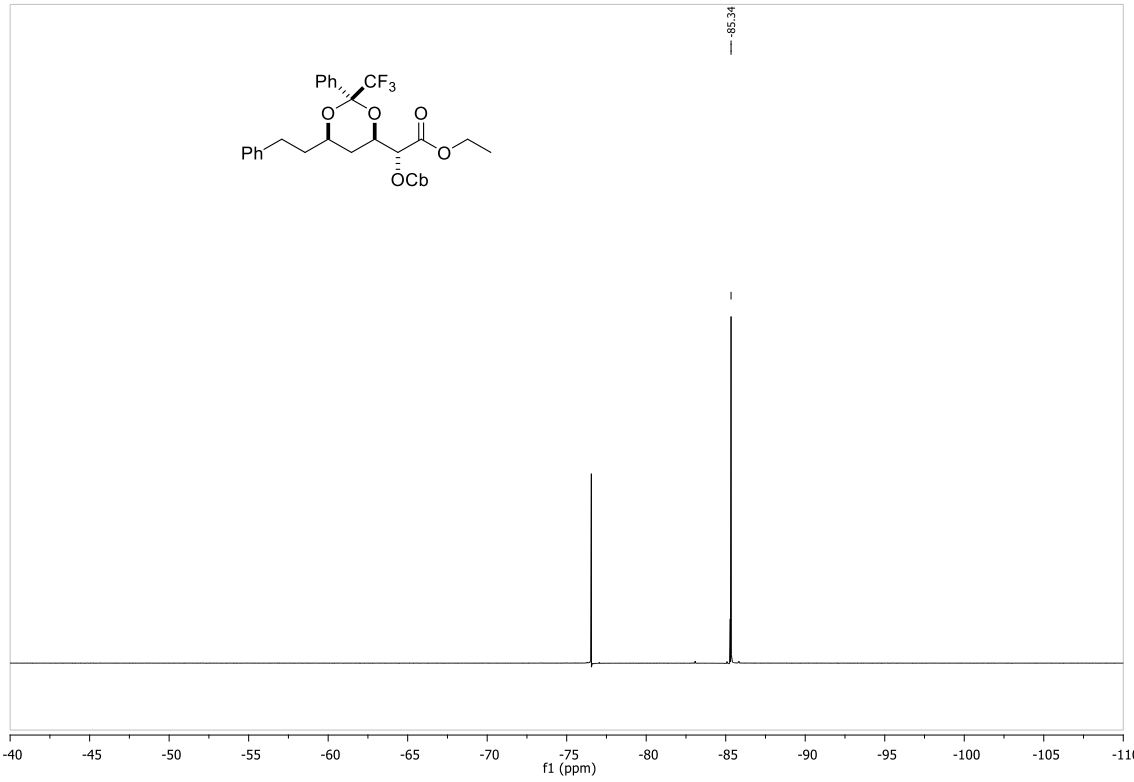
Methyl 2-((2*R,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)propanoate (7a)**



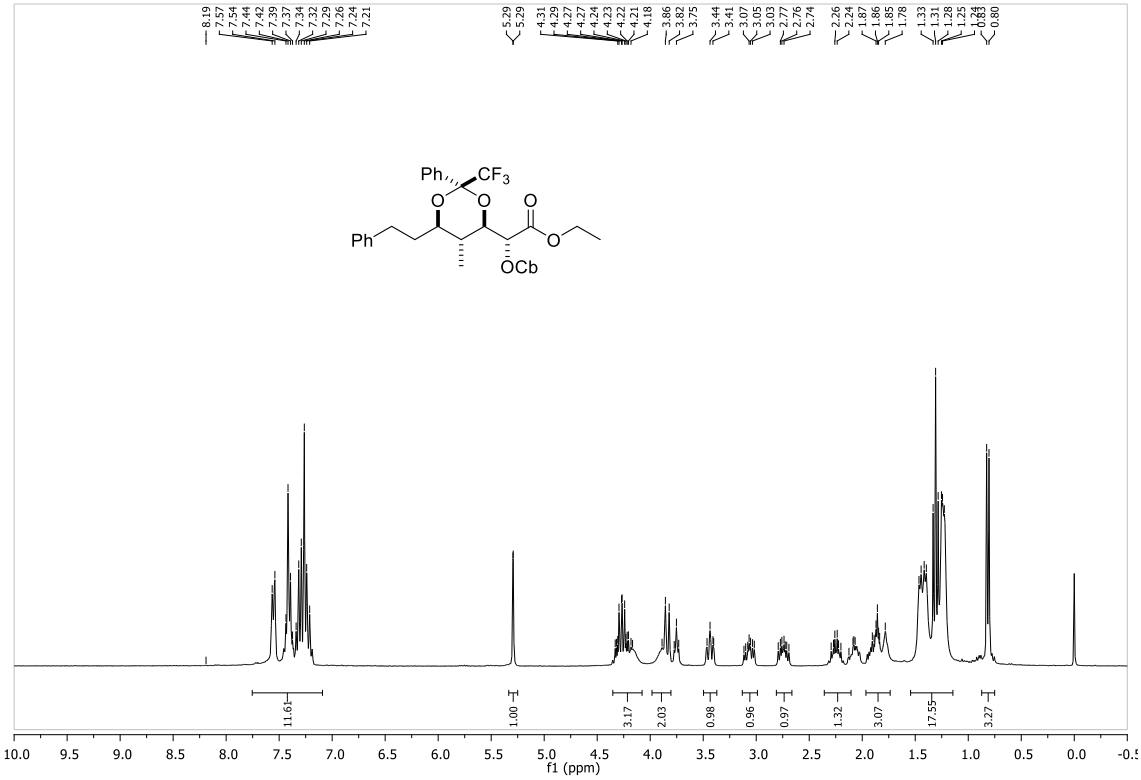
Ethyl (*R)-2-((diisopropylcarbamoyl)oxy)-2-((2*R**,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl) acetate (7b)**

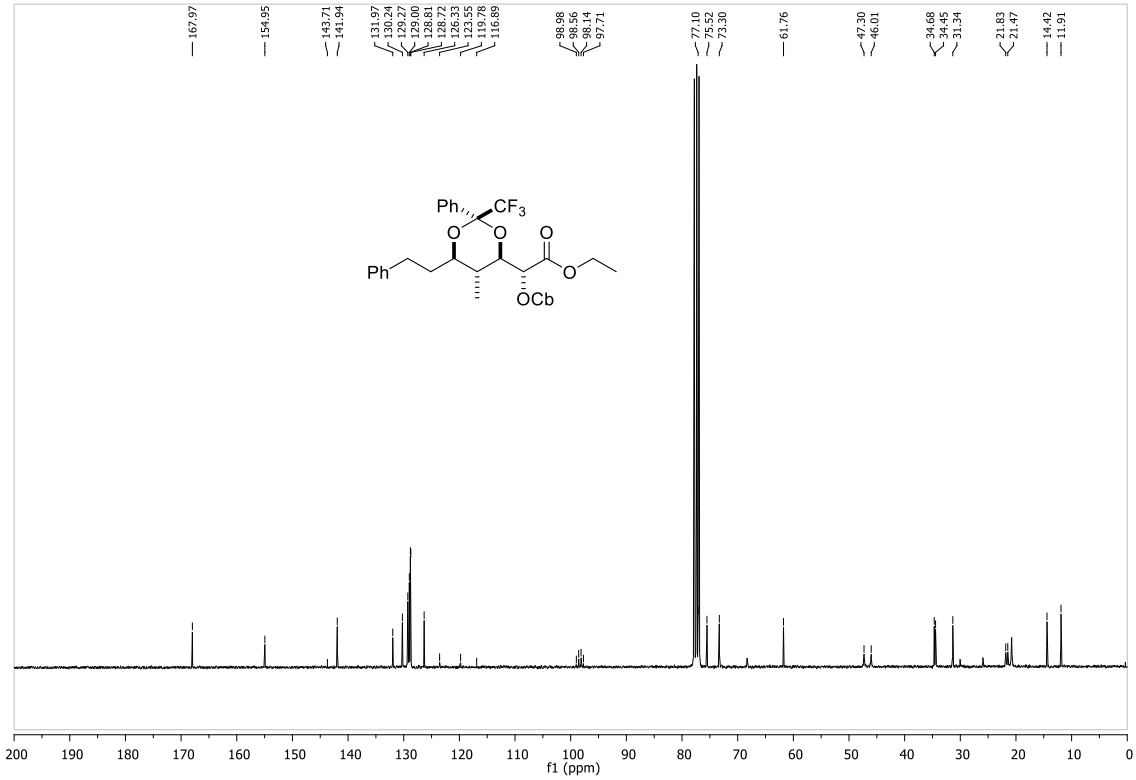


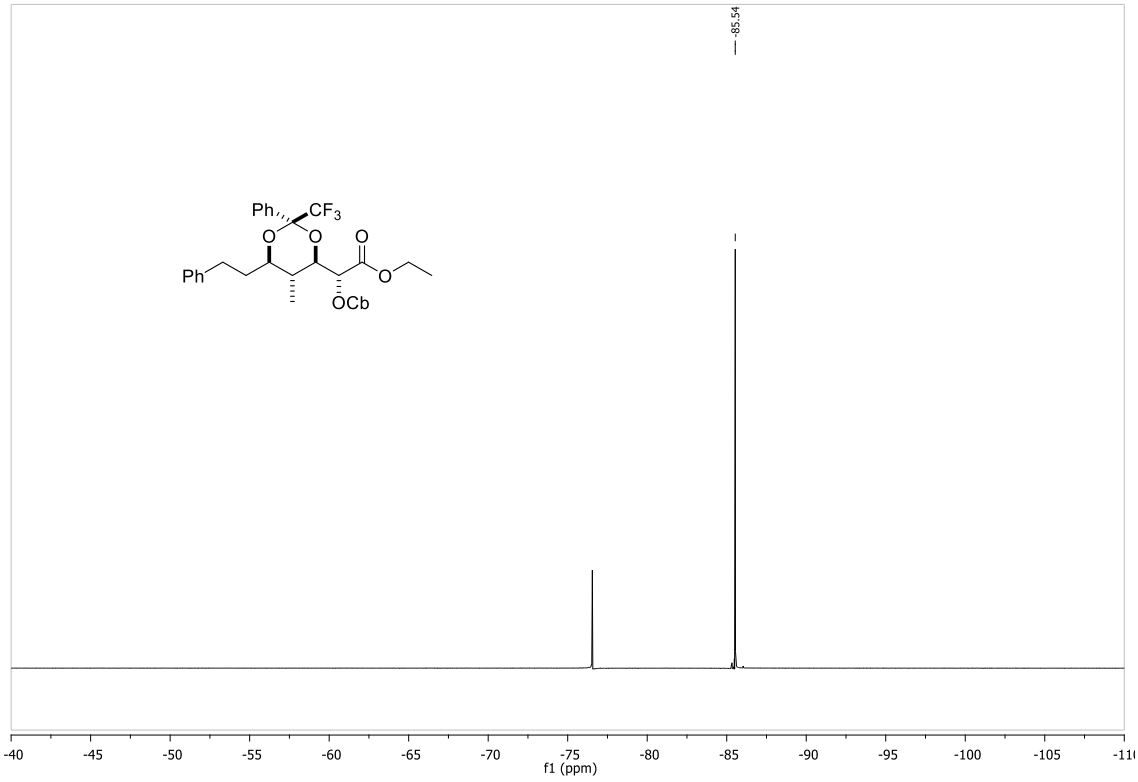



-85.34
Ph
CF3
O
O
O
Ph
O
OCb
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

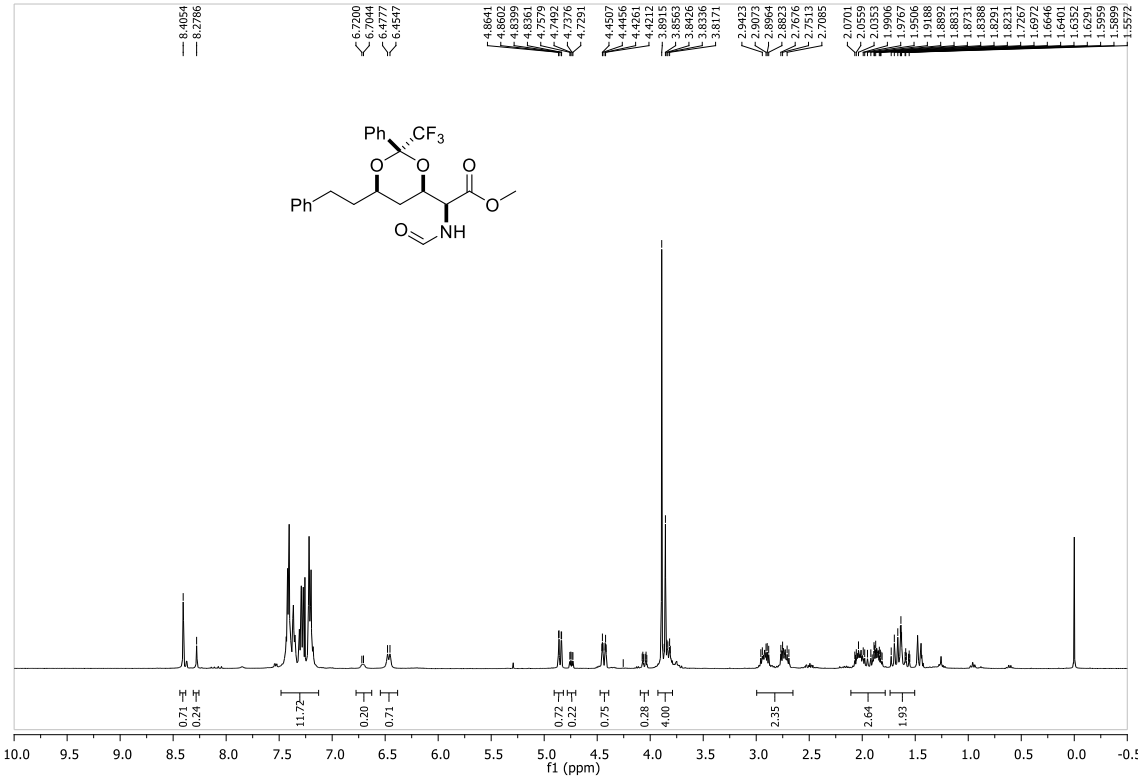
Ethyl (*R)-2-((diisopropylcarbamoyl)oxy)-2-((2*R**,4*R**,5*R**,6*R**)-5-methyl-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (7c)**

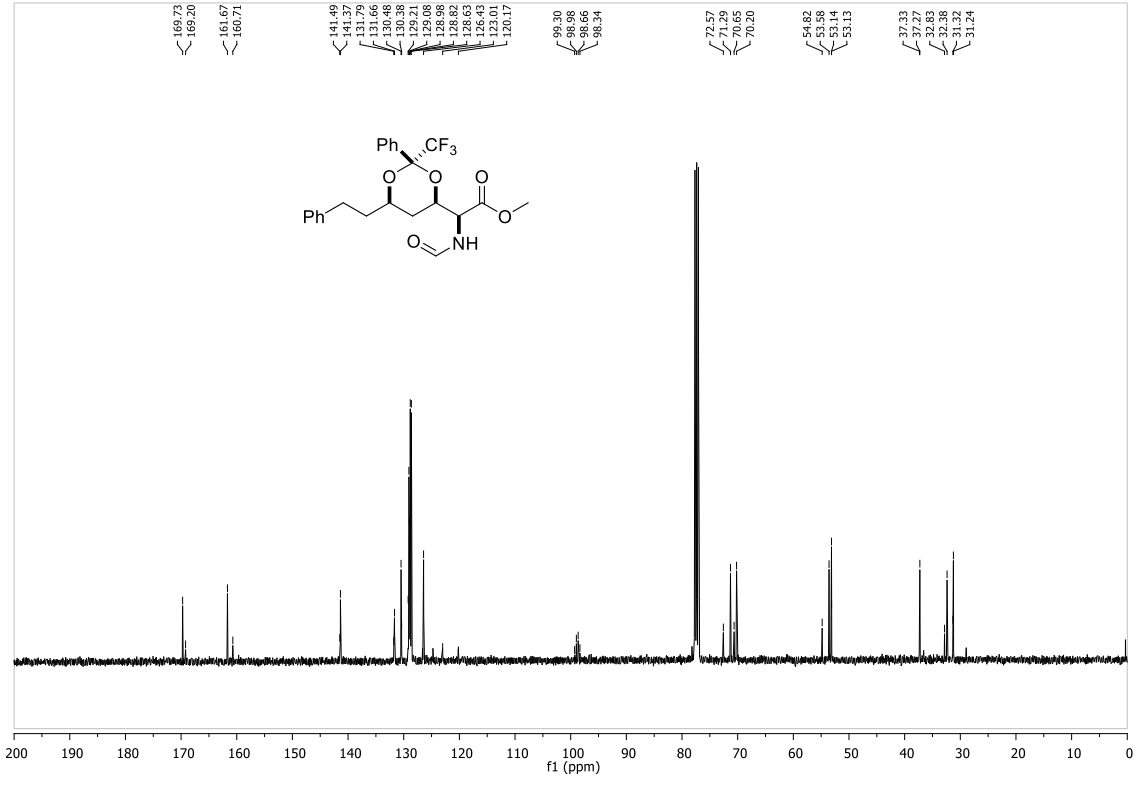


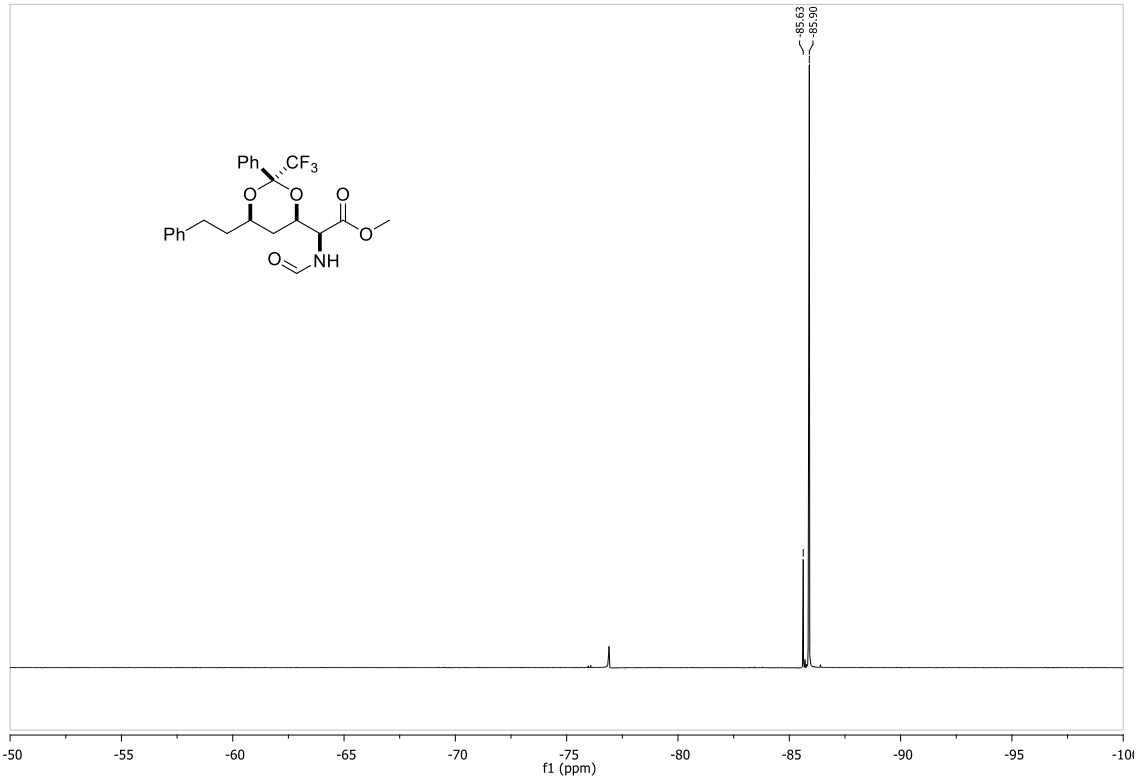



-85.54
Ph
CF3
O
O
O
Ph
O
OCb
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

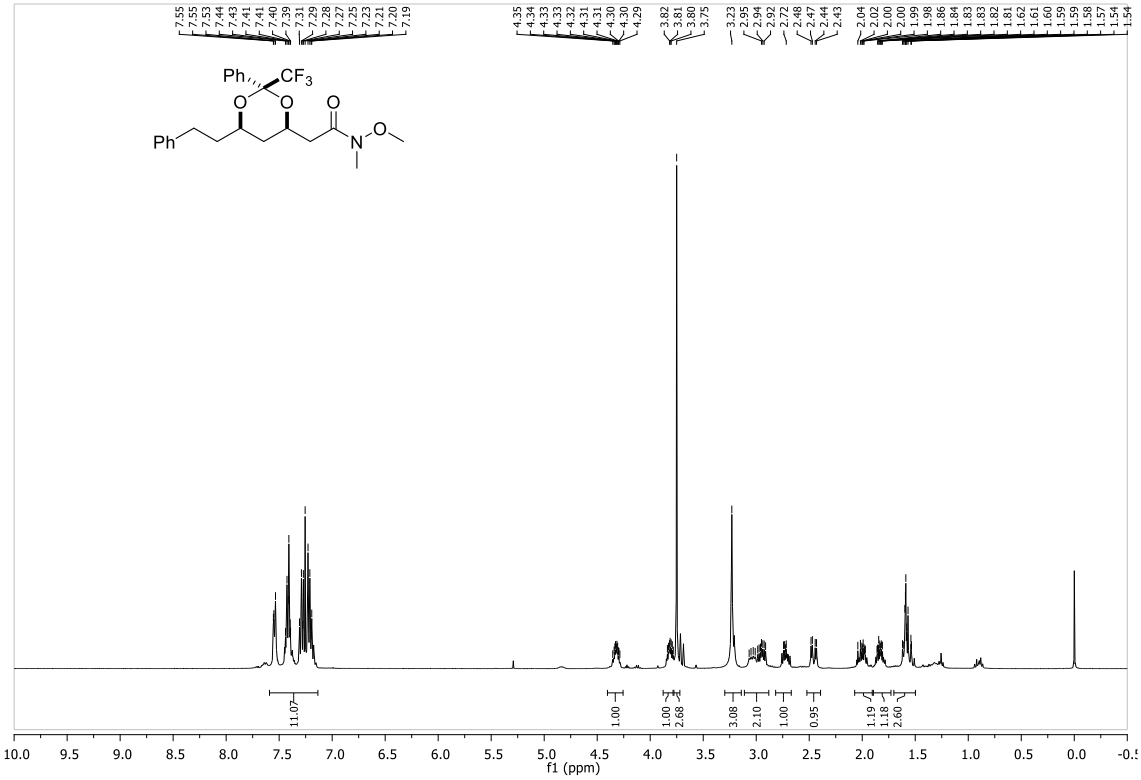
Methyl (*R)-2-formamido-2-((2*R**,4*S**,6*S**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (7d)**

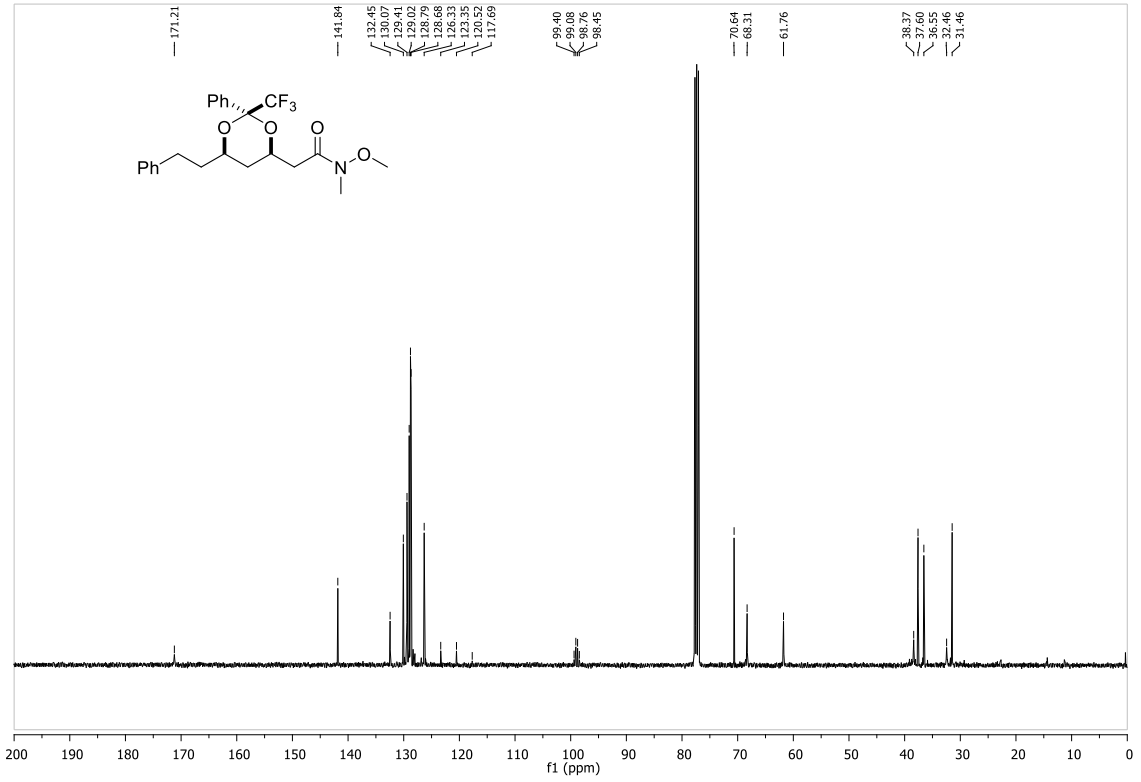


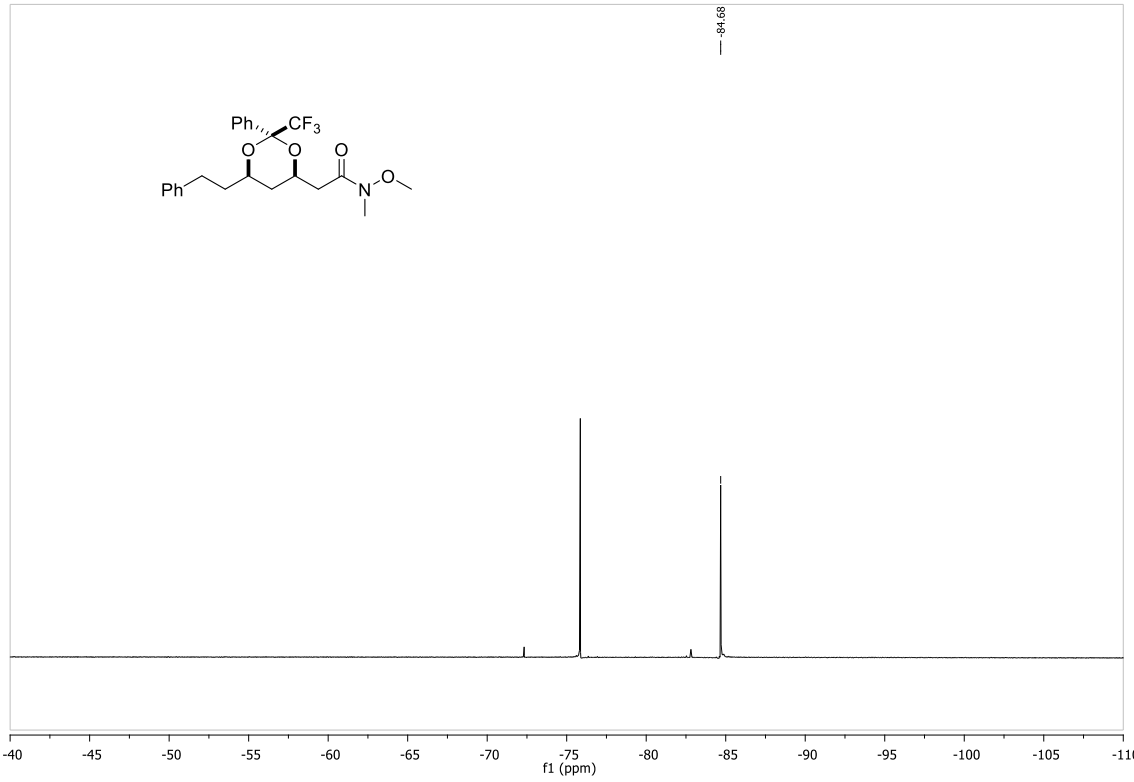



-85.63
-85.90
Ph
CF3
O
O
O
O
Ph
O
NH
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

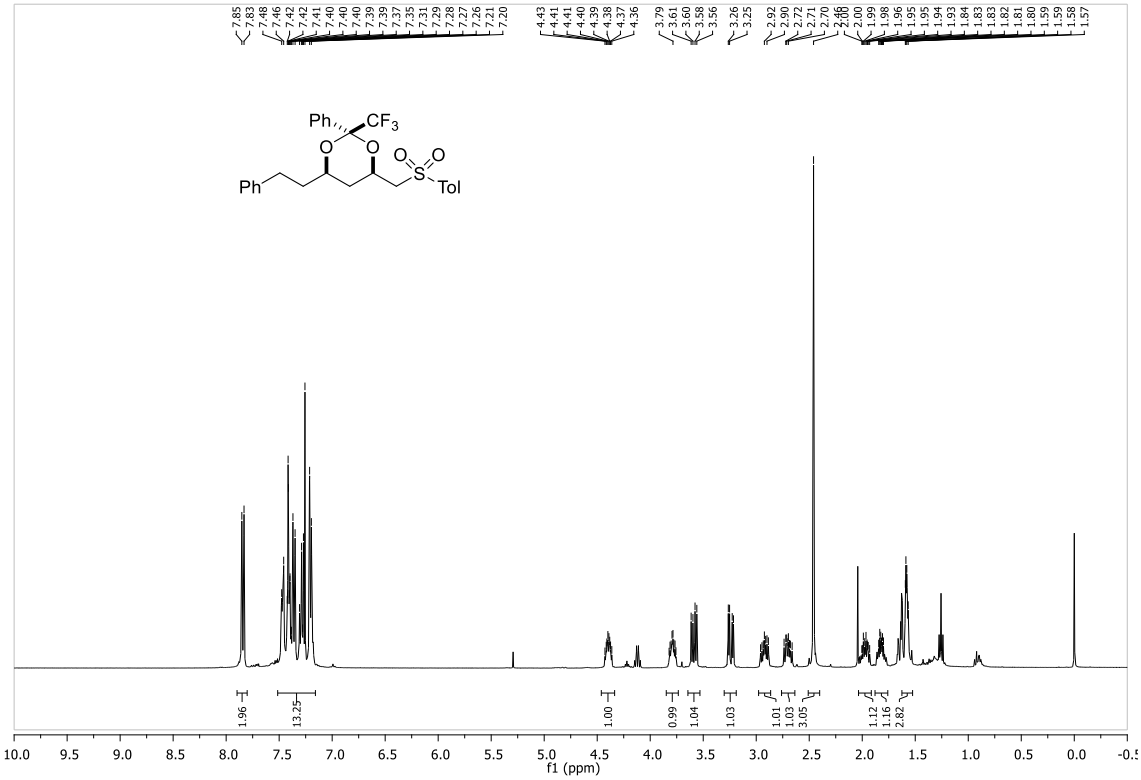
***N*-methoxy-*N*-methyl-2-((2R*,4R*,6R*)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetamide (9)**

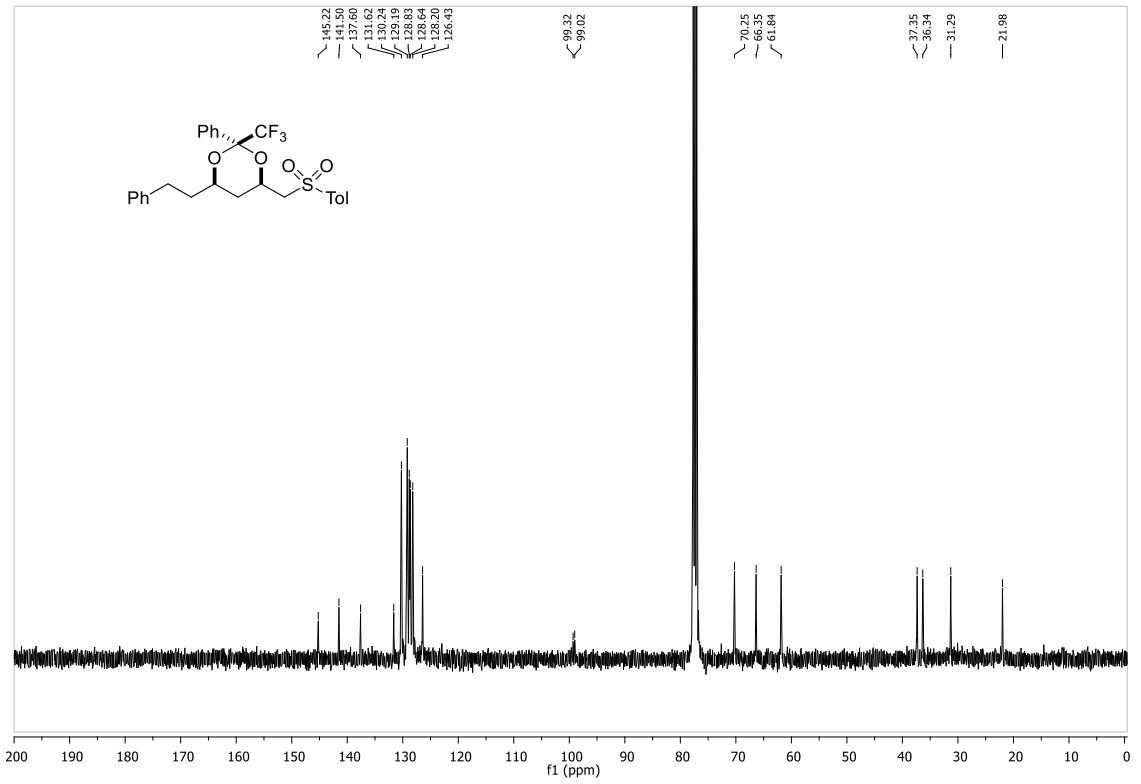


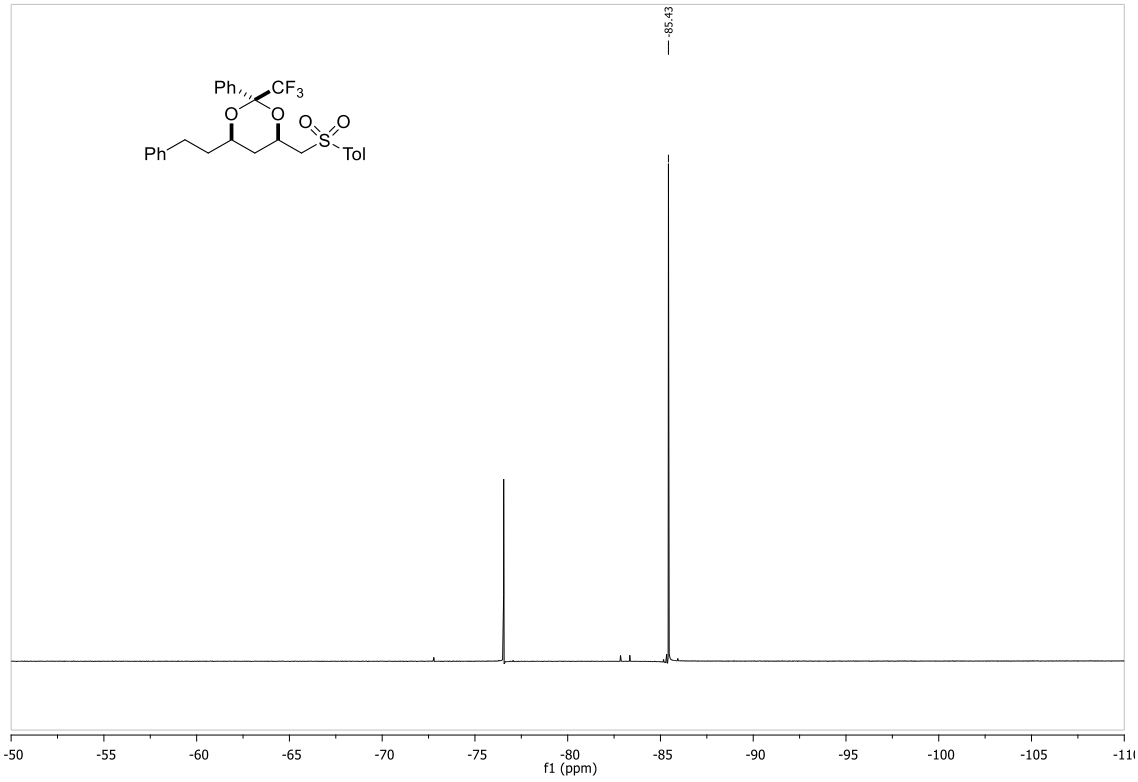



-84.68
Ph
CF3
O
O
O
N
O
Ph
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

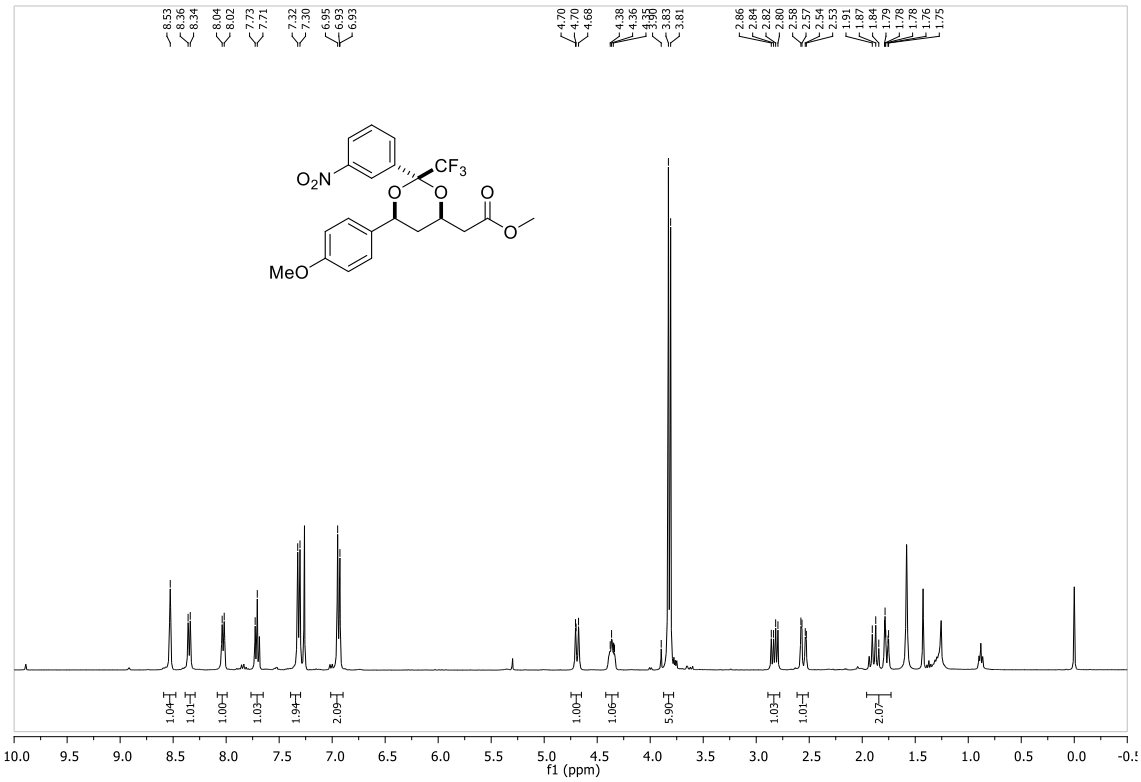
(2R*,4R*,6R*)-4-phenethyl-2-phenyl-6-(tosylmethyl)-2-(trifluoromethyl)-1,3-dioxane (11)

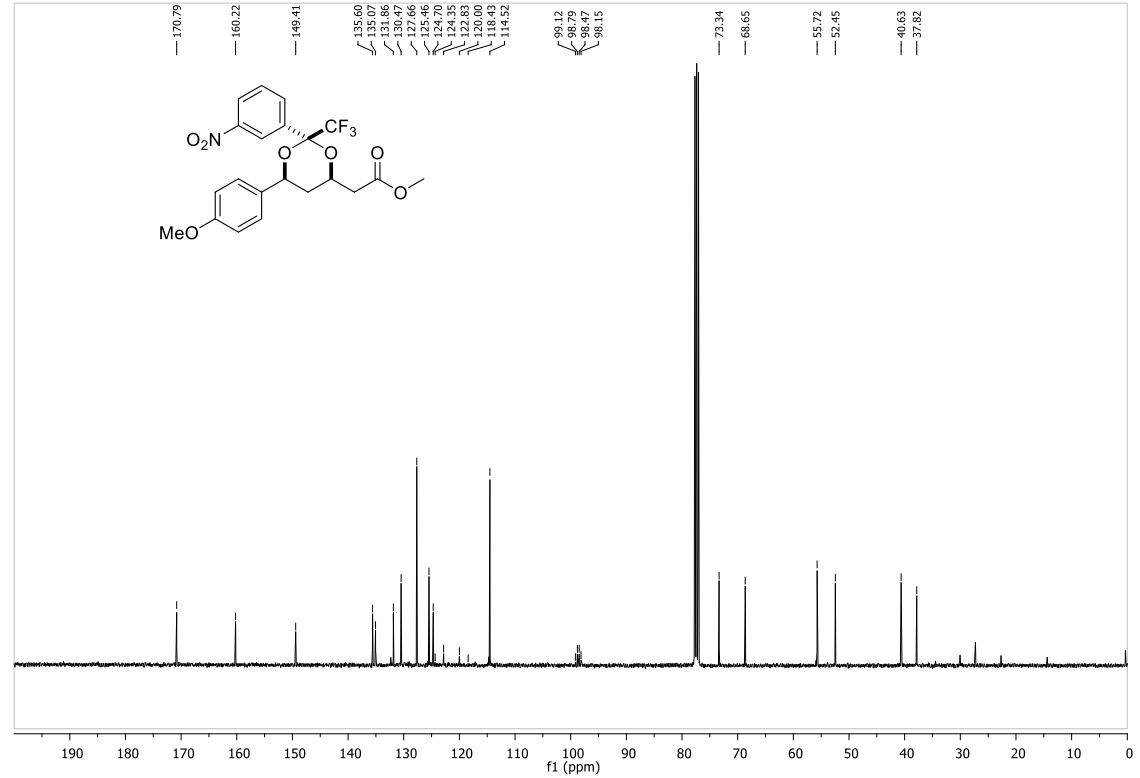


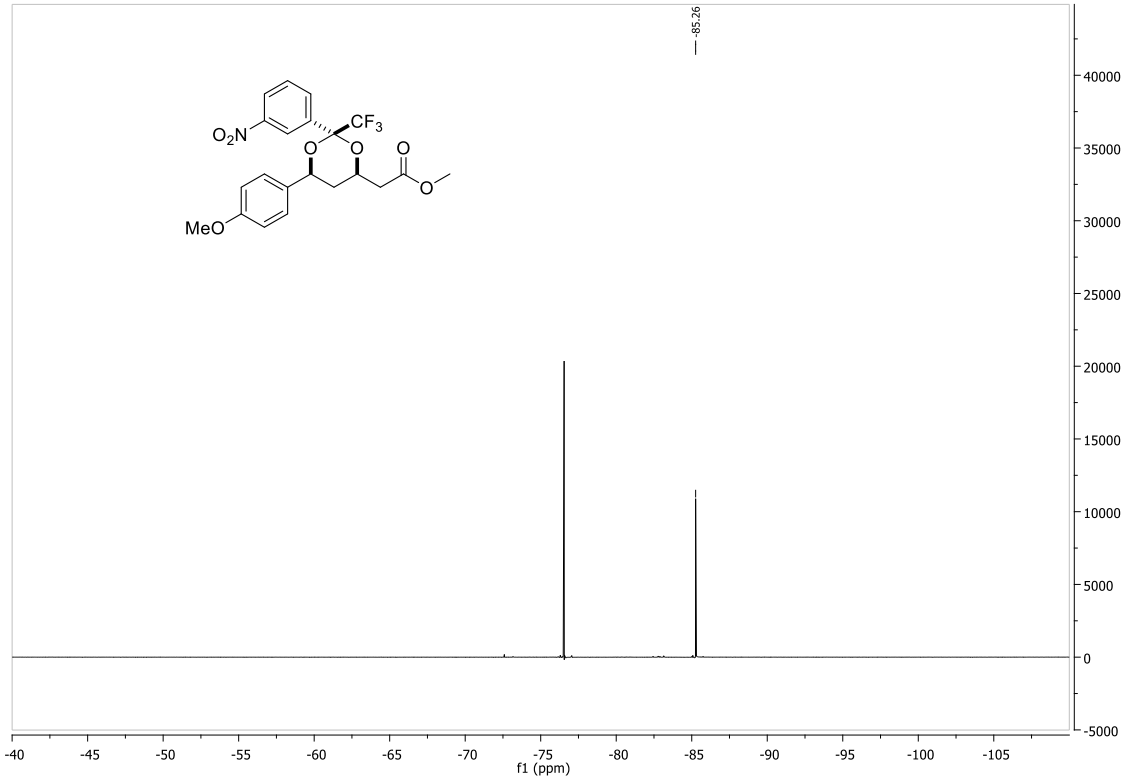



-85.43
Ph
CF3
O
O
O
O
S
Ph
Tol
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

Methyl 2-((2S*,4R*,6S*)-6-(4-methoxyphenyl)-2-(3-nitrophenyl)-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (13)






-85.26
O_2N
CF_3
O
O
O
O
MeO
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)

X-RAY ANALYSIS

X-Ray Analysis for the products: CCDC 1511482 and CCDC 1510756 contains the supplementary crystallographic data for the product. These data can be obtained free of charge from The Cambridge Crystallographic Data.

Methyl (*R)-2-formamido-2-((2*R**,4*S**,6*S**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (7d) (CCDC 1511482)**

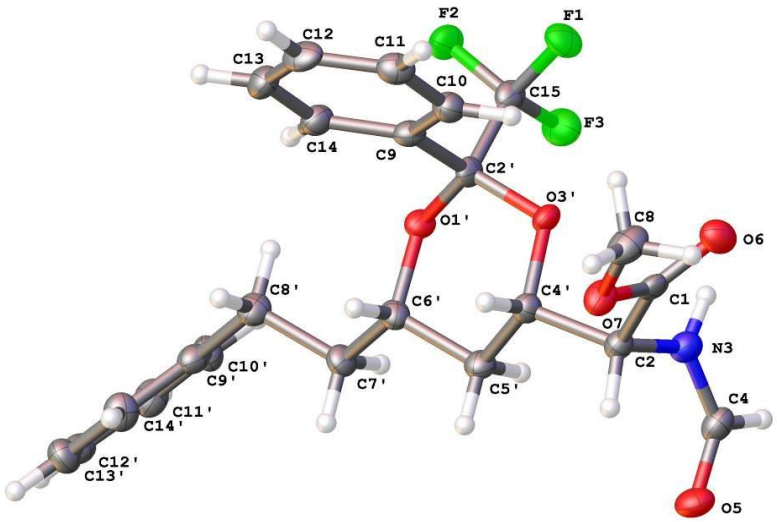


Table 1. Crystal data

Molecular Formula:$C_{23}H_{24}F_3NO_5$
Molecular weight*:* M_r = 451.43
Crystal habit: Tablet, colourless
Crystal system: Monoclinic, $P2_1/c$
Crystal dimensions: 0.42 × 0.33 × 0.12 mm
a = 8.898 (3) Å
b = 26.042 (7) Å
c = 9.427 (2) Å
β = 91.704 (6)°
V = 2183.5 (10) Å^3
Z = 4
F(000) = 944
D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2565 reflections

θ = 2.3–25.2°
μ = 0.11 mm^{-1}
T = 100 K

Table 2. Data collection

Bruker APEX-II CCD diffractometer	2472 reflections with *I* > 2(*I*)
ϕ and ω scans	R_{int} = 0.117
Absorption correction: multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.1485 before and 0.1092 after correction. The Ratio of minimum to maximum transmission is 0.6020. The λ/2 correction factor is 0.00150.	θ_{max} = 25.3°, θ_{min} = 1.6°
T_{min} = 0.449, T_{max} = 0.745	*h* = -10→10
12762 measured reflections	*k* = -31→31
3903 independent reflections	*l* = -10→11

Table 3. Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.078	H-atom parameters constrained
$wR(F^2)$ = 0.198	$w = 1/[\sigma^2(F_o^2) + (0.089P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
3903 reflections	$\Delta\rangle_{max}$ = 0.45 e Å^{-3}
290 parameters	$\Delta\rangle_{min}$ = -0.32 e Å^{-3}
0 restraints	

Table 4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*Y*	*z*	U_{iso}*/U_{eq}
F2	0.6276 (3)	0.44084 (8)	0.6640 (2)	0.0298 (6)
F1	0.6004 (3)	0.36064 (8)	0.7041 (2)	0.0297 (6)
F3	0.8081 (3)	0.38874 (9)	0.6278 (2)	0.0331 (6)
O3'	0.6440 (3)	0.33565 (9)	0.4342 (2)	0.0203 (6)

O1'	0.6814 (3)	0.42287 (9)	0.3876 (2)	0.0211 (6)
O7	0.4463 (3)	0.23346 (10)	0.2755 (3)	0.0268 (7)
O5	0.9575 (3)	0.24270 (11)	0.1392 (3)	0.0311 (7)
O6	0.5963 (3)	0.21087 (10)	0.4580 (3)	0.0296 (7)
N3	0.8348 (4)	0.25951 (12)	0.3422 (3)	0.0248 (8)
H3	0.8461	0.2627	0.4327	0.030*
C1	0.5749 (5)	0.23375 (14)	0.3490 (4)	0.0218 (9)
C9	0.4326 (5)	0.39370 (14)	0.4531 (4)	0.0209 (9)
C15	0.6601 (5)	0.39424 (14)	0.6152 (4)	0.0232 (9)
C2'	0.6009 (5)	0.38611 (13)	0.4644 (4)	0.0207 (9)
C9'	0.7719 (5)	0.55260 (14)	0.1168 (4)	0.0241 (9)
C14	0.3720 (5)	0.44111 (15)	0.4212 (4)	0.0252 (9)
H14	0.4352	0.4686	0.4033	0.030*
C10	0.3374 (5)	0.35290 (15)	0.4819 (4)	0.0254 (9)
H10	0.3774	0.3208	0.5037	0.031*
C6'	0.6768 (5)	0.41421 (14)	0.2357 (4)	0.0226 (9)
H6'	0.5721	0.4164	0.2009	0.027*
C7'	0.7655 (5)	0.45696 (14)	0.1694 (4)	0.0245 (9)
H7'A	0.7686	0.4513	0.0678	0.029*
H7'B	0.8680	0.4561	0.2073	0.029*
C5'	0.7348 (5)	0.36100 (14)	0.2075 (4)	0.0227 (9)
H5'A	0.8388	0.3581	0.2402	0.027*
H5'B	0.7294	0.3539	0.1065	0.027*
C2	0.6883 (5)	0.26744 (14)	0.2785 (4)	0.0217 (9)
H2	0.6917	0.2575	0.1783	0.026*
C4'	0.6389 (5)	0.32332 (13)	0.2857 (4)	0.0216 (9)
H4'	0.5348	0.3261	0.2495	0.026*
C12	0.1243 (5)	0.40765 (16)	0.4442 (4)	0.0296 (10)
H12	0.0206	0.4123	0.4408	0.036*
C8'	0.6988 (5)	0.50975 (14)	0.1966 (4)	0.0264 (9)
H8'A	0.5926	0.5090	0.1705	0.032*
H8'B	0.7077	0.5170	0.2974	0.032*
C10'	0.9007 (5)	0.57553 (15)	0.1677 (4)	0.0275 (10)
H10'	0.9450	0.5640	0.2524	0.033*

C12'	0.9024 (5)	0.63281 (14)	-0.0294 (4)	0.0280 (10)
H12'	0.9452	0.6600	-0.0778	0.034*
C4	0.9533 (5)	0.24745 (14)	0.2676 (4)	0.0266 (10)
H4	1.0430	0.2420	0.3186	0.032*
C14'	0.7110 (5)	0.56995 (15)	-0.0105 (4)	0.0293 (10)
H14'	0.6248	0.5544	-0.0485	0.035*
C11'	0.9669 (5)	0.61569 (15)	0.0954 (4)	0.0294 (10)
H11'	1.0546	0.6308	0.1315	0.035*
C13	0.2179 (5)	0.44811 (15)	0.4155 (4)	0.0279 (10)
H13	0.1777	0.4801	0.3924	0.033*
C11	0.1845 (5)	0.35999 (16)	0.4780 (4)	0.0271 (10)
H11	0.1211	0.3327	0.4983	0.032*
C13'	0.7754 (5)	0.60991 (15)	-0.0823 (4)	0.0298 (10)
H13'	0.7318	0.6213	-0.1675	0.036*
C8	0.3299 (5)	0.20227 (16)	0.3345 (5)	0.0354 (11)
H8A	0.2467	0.1998	0.2677	0.053*
H8B	0.2969	0.2177	0.4207	0.053*
H8C	0.3687	0.1685	0.3544	0.053*

Table 5. Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F2	0.0399 (16)	0.0191 (11)	0.0306 (13)	0.0004 (11)	0.0044 (10)	-0.0036 (9)
F1	0.0382 (16)	0.0253 (12)	0.0258 (12)	-0.0071 (11)	0.0056 (10)	0.0045 (10)
F3	0.0226 (14)	0.0434 (14)	0.0332 (13)	0.0015 (12)	0.0003 (10)	0.0006 (11)
O3'	0.0221 (16)	0.0158 (13)	0.0232 (14)	0.0032 (11)	0.0058 (11)	-0.0010 (10)
O1'	0.0214 (16)	0.0190 (13)	0.0233 (14)	-0.0022 (12)	0.0065 (11)	0.0016 (11)
O7	0.0227 (17)	0.0217 (14)	0.0363 (16)	-0.0020 (12)	0.0075 (12)	0.0025 (12)
O5	0.0291 (18)	0.0356 (16)	0.0292 (16)	0.0027 (14)	0.0099 (12)	-0.0043 (13)
O6	0.0383 (19)	0.0246 (14)	0.0260 (15)	-0.0040 (14)	0.0037 (12)	0.0003 (12)

N3	0.025 (2)	0.0237 (17)	0.0255 (18)	0.0007 (15)	0.0035 (14)	-0.0015 (14)
C1	0.027 (2)	0.0173 (18)	0.021 (2)	0.0037 (18)	0.0060 (17)	-0.0056 (17)
C9	0.021 (2)	0.0230 (19)	0.019 (2)	-0.0017 (18)	0.0047 (15)	-0.0020 (16)
C15	0.026 (2)	0.0170 (19)	0.027 (2)	-0.0012 (18)	0.0084 (17)	0.0029 (16)
C2'	0.026 (2)	0.0116 (17)	0.025 (2)	-0.0008 (17)	0.0051 (16)	0.0022 (15)
C9'	0.026 (2)	0.0208 (19)	0.026 (2)	0.0005 (18)	0.0074 (17)	-0.0006 (16)
C14	0.028 (3)	0.022 (2)	0.026 (2)	0.0009 (19)	0.0056 (17)	-0.0016 (16)
C10	0.029 (2)	0.025 (2)	0.023 (2)	0.0006 (19)	0.0031 (17)	0.0007 (17)
C6'	0.021 (2)	0.023 (2)	0.024 (2)	0.0004 (17)	0.0049 (16)	0.0039 (16)
C7'	0.028 (2)	0.0210 (19)	0.025 (2)	-0.0008 (18)	0.0051 (17)	0.0052 (16)
C5'	0.022 (2)	0.023 (2)	0.023 (2)	0.0006 (18)	0.0056 (16)	0.0007 (16)
C2	0.023 (2)	0.0196 (19)	0.023 (2)	0.0022 (17)	0.0027 (16)	-0.0008 (16)
C4'	0.024 (2)	0.0189 (19)	0.022 (2)	0.0003 (17)	0.0019 (16)	-0.0006 (16)
C12	0.016 (2)	0.045 (3)	0.028 (2)	0.004 (2)	0.0050 (17)	-0.0044 (19)
C8'	0.024 (2)	0.024 (2)	0.031 (2)	-0.0022 (19)	0.0072 (17)	0.0024 (17)
C10'	0.030 (3)	0.025 (2)	0.027 (2)	0.0021 (19)	0.0000 (18)	0.0059 (17)
C12'	0.035 (3)	0.0193 (19)	0.031 (2)	0.0001 (19)	0.0143 (19)	0.0023 (17)
C4	0.025 (2)	0.022 (2)	0.033 (2)	0.0027 (19)	0.0030 (18)	-0.0034 (18)
C14'	0.029 (3)	0.025 (2)	0.034 (2)	-0.0037 (19)	-0.0017 (18)	0.0002 (18)
C11'	0.025 (3)	0.025 (2)	0.038 (2)	-0.0014 (19)	0.0031 (19)	0.0006 (18)
C13	0.026 (3)	0.028 (2)	0.030 (2)	0.007 (2)	0.0030 (18)	-0.0011 (18)
C11	0.027 (3)	0.030 (2)	0.025 (2)	-0.0070 (19)	0.0044 (17)	-0.0016 (17)

C13'	0.037 (3)	0.026 (2)	0.026 (2)	0.001 (2)	0.0024 (19)	0.0046 (18)
C8	0.027 (3)	0.030 (2)	0.050 (3)	-0.002 (2)	0.013 (2)	-0.004 (2)

Table 6. Geometric parameters (Å, º)

F2—C15	1.333 (4)	C7'—H7'A	0.9700
F1—C15	1.333 (4)	C7'—H7'B	0.9700
F3—C15	1.326 (5)	C7'—C8'	1.522 (5)
O3'—C2'	1.401 (4)	C5'—H5'A	0.9700
O3'—C4'	1.436 (4)	C5'—H5'B	0.9700
O1'—C2'	1.409 (4)	C5'—C4'	1.507 (5)
O1'—C6'	1.449 (4)	C2—H2	0.9800
O7—C1	1.320 (5)	C2—C4'	1.522 (5)
O7—C8	1.440 (5)	C4'—H4'	0.9800
O5—C4	1.218 (5)	C12—H12	0.9300
O6—C1	1.198 (4)	C12—C13	1.375 (6)
N3—H3	0.8600	C12—C11	1.385 (6)
N3—C2	1.434 (5)	C8'—H8'A	0.9700
N3—C4	1.322 (5)	C8'—H8'B	0.9700
C1—C2	1.507 (6)	C10'—H10'	0.9300
C9—C2'	1.511 (6)	C10'—C11'	1.389 (6)
C9—C14	1.377 (5)	C12'—H12'	0.9300
C9—C10	1.391 (6)	C12'—C11'	1.368 (6)
C15—C2'	1.515 (5)	C12'—C13'	1.360 (6)
C9'—C8'	1.504 (5)	C4—H4	0.9300
C9'—C10'	1.366 (6)	C14'—H14'	0.9300
C9'—C14'	1.378 (5)	C14'—C13'	1.376 (6)
C14—H14	0.9300	C11'—H11'	0.9300
C14—C13	1.382 (6)	C13—H13	0.9300
C10—H10	0.9300	C11—H11	0.9300
C10—C11	1.373 (6)	C13'—H13'	0.9300
C6'—H6'	0.9800	C8—H8A	0.9600
C6'—C7'	1.511 (5)	C8—H8B	0.9600
C6'—C5'	1.505 (5)	C8—H8C	0.9600

C2'—O3'—C4'	114.0 (3)	N3—C2—C1	110.1 (3)
C2'—O1'—C6'	113.7 (3)	N3—C2—H2	108.2
C1—O7—C8	115.0 (3)	N3—C2—C4'	112.3 (3)
C2—N3—H3	118.6	C1—C2—H2	108.2
C4—N3—H3	118.6	C1—C2—C4'	109.8 (3)
C4—N3—C2	122.7 (3)	C4'—C2—H2	108.2
O7—C1—C2	110.7 (3)	O3'—C4'—C5'	109.2 (3)
O6—C1—O7	124.1 (4)	O3'—C4'—C2	104.9 (3)
O6—C1—C2	125.2 (4)	O3'—C4'—H4'	109.0
C14—C9—C2'	120.9 (3)	C5'—C4'—C2	115.6 (3)
C14—C9—C10	119.4 (4)	C5'—C4'—H4'	109.0
C10—C9—C2'	119.6 (3)	C2—C4'—H4'	109.0
F2—C15—C2'	112.2 (3)	C13—C12—H12	120.0
F1—C15—F2	106.6 (3)	C13—C12—C11	120.0 (4)
F1—C15—C2'	111.4 (3)	C11—C12—H12	120.0
F3—C15—F2	107.0 (3)	C9'—C8'—C7'	114.2 (3)
F3—C15—F1	106.6 (3)	C9'—C8'—H8'A	108.7
F3—C15—C2'	112.6 (3)	C9'—C8'—H8'B	108.7
O3'—C2'—O1'	112.8 (3)	C7'—C8'—H8'A	108.7
O3'—C2'—C9	112.6 (3)	C7'—C8'—H8'B	108.7
O3'—C2'—C15	103.4 (3)	H8'A—C8'—H8'B	107.6
O1'—C2'—C9	113.1 (3)	C9'—C10'—H10'	119.3
O1'—C2'—C15	102.7 (3)	C9'—C10'—C11'	121.4 (4)
C9—C2'—C15	111.3 (3)	C11'—C10'—H10'	119.3
C10'—C9'—C8'	121.3 (3)	C11'—C12'—H12'	120.1
C10'—C9'—C14'	117.8 (4)	C13'—C12'—H12'	120.1
C14'—C9'—C8'	120.9 (4)	C13'—C12'—C11'	119.7 (4)
C9—C14—H14	119.7	O5—C4—N3	126.9 (4)
C9—C14—C13	120.6 (4)	O5—C4—H4	116.5
C13—C14—H14	119.7	N3—C4—H4	116.5
C9—C10—H10	120.0	C9'—C14'—H14'	119.4
C11—C10—C9	120.1 (4)	C13'—C14'—C9'	121.2 (4)
C11—C10—H10	120.0	C13'—C14'—H14'	119.4
O1'—C6'—H6'	108.7	C10'—C11'—H11'	120.2

O1'—C6'—C7'	107.1 (3)	C12'—C11'—C10'	119.6 (4)
O1'—C6'—C5'	108.6 (3)	C12'—C11'—H11'	120.2
C7'—C6'—H6'	108.7	C14—C13—H13	120.1
C5'—C6'—H6'	108.7	C12—C13—C14	119.8 (4)
C5'—C6'—C7'	114.8 (3)	C12—C13—H13	120.1
C6'—C7'—H7'A	109.1	C10—C11—C12	120.2 (4)
C6'—C7'—H7'B	109.1	C10—C11—H11	119.9
C6'—C7'—C8'	112.6 (3)	C12—C11—H11	119.9
H7'A—C7'—H7'B	107.8	C12'—C13'—C14'	120.3 (4)
C8'—C7'—H7'A	109.1	C12'—C13'—H13'	119.8
C8'—C7'—H7'B	109.1	C14'—C13'—H13'	119.8
C6'—C5'—H5'A	110.1	O7—C8—H8A	109.5
C6'—C5'—H5'B	110.1	O7—C8—H8B	109.5
C6'—C5'—C4'	108.1 (3)	O7—C8—H8C	109.5
H5'A—C5'—H5'B	108.4	H8A—C8—H8B	109.5
C4'—C5'—H5'A	110.1	H8A—C8—H8C	109.5
C4'—C5'—H5'B	110.1	H8B—C8—H8C	109.5
F2—C15—C2'—O3'	-179.2 (3)	C14—C9—C10—C11	0.2 (5)
F2—C15—C2'—O1'	63.3 (4)	C10—C9—C2'—O3'	29.9 (5)
F2—C15—C2'—C9	-58.0 (4)	C10—C9—C2'—O1'	159.2 (3)
F1—C15—C2'—O3'	-59.8 (4)	C10—C9—C2'—C15	-85.8 (4)
F1—C15—C2'—O1'	-177.2 (3)	C10—C9—C14—C13	-1.0 (5)
F1—C15—C2'—C9	61.5 (4)	C6'—O1'—C2'—O3'	53.4 (4)
F3—C15—C2'—O3'	60.0 (4)	C6'—O1'—C2'—C9	-75.8 (4)
F3—C15—C2'—O1'	-57.5 (4)	C6'—O1'—C2'—C15	164.1 (3)
F3—C15—C2'—C9	-178.8 (3)	C6'—C7'—C8'—C9'	-172.5 (3)
O1'—C6'—C7'—C8'	-61.5 (4)	C6'—C5'—C4'—O3'	-57.7 (4)
O1'—C6'—C5'—C4'	57.7 (4)	C6'—C5'—C4'—C2	-175.6 (3)
O7—C1—C2—N3	-168.4 (3)	C7'—C6'—C5'—C4'	177.5 (3)
O7—C1—C2—C4'	67.4 (4)	C5'—C6'—C7'—C8'	177.9 (3)
O6—C1—C2—N3	12.7 (5)	C2—N3—C4—O5	1.9 (6)
O6—C1—C2—C4'	-111.4 (4)	C4'—O3'—C2'—O1'	-53.2 (4)
N3—C2—C4'—O3'	-57.9 (4)	C4'—O3'—C2'—C9	76.3 (4)

N3—C2—C4'—C5'	62.5 (4)	C4'—O3'—C2'—C15	-163.4 (3)
C1—C2—C4'—O3'	65.0 (4)	C8'—C9'—C10'—C11'	-178.9 (4)
C1—C2—C4'—C5'	-174.7 (3)	C8'—C9'—C14'—C13'	178.5 (4)
C9—C14—C13—C12	1.0 (6)	C10'—C9'—C8'—C7'	-83.7 (5)
C9—C10—C11—C12	0.6 (6)	C10'—C9'—C14'—C13'	-1.7 (6)
C2'—O3'—C4'—C5'	55.9 (4)	C4—N3—C2—C1	126.1 (4)
C2'—O3'—C4'—C2	-179.6 (3)	C4—N3—C2—C4'	-111.2 (4)
C2'—O1'—C6'—C7'	179.2 (3)	C14'—C9'—C8'—C7'	96.2 (5)
C2'—O1'—C6'—C5'	-56.4 (4)	C14'—C9'—C10'—C11'	1.3 (6)
C2'—C9—C14—C13	-177.9 (3)	C11'—C12'—C13'—C14'	0.5 (7)
C2'—C9—C10—C11	177.1 (3)	C13—C12—C11—C10	-0.6 (6)
C9'—C10'—C11'—C12'	0.0 (6)	C11—C12—C13—C14	-0.2 (6)
C9'—C14'—C13'—C12'	0.8 (7)	C13'—C12'—C11'—C10'	-0.9 (6)
C14—C9—C2'—O3'	-153.2 (3)	C8—O7—C1—O6	-1.1 (5)
C14—C9—C2'—O1'	-23.9 (5)	C8—O7—C1—C2	-179.9 (3)
C14—C9—C2'—C15	91.1 (4)		

Methyl 2-((2*R,4*R**,6*R**)-6-phenethyl-2-phenyl-2-(trifluoromethyl)-1,3-dioxan-4-yl)acetate (2a) CCDC 1510756**

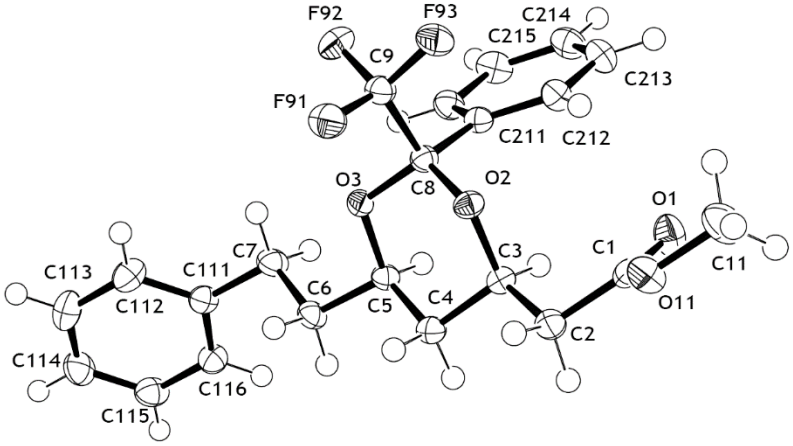


Table 7: Crystal data

Molecular formula:$C_{22}H_{23}F_3O_4$
Molecular weight :408.4
Crystal habit: colourless plate
Crystal dimensions: 0.5 x 0.4 x 0.1 mm
Crystal system: triclinic
Space group: P -1
a (Å): 8.8528(7)
b (Å): 10.3527(8)
c (Å): 14.1556(11)
α (°): 73.562(4)
β (°): 72.631(4)
γ (°): 64.671(4)
V ($Å^3$) : 1100.90(15)
Z : 2
d ($g.cm^{-3}$) : 1.232
F (000): 428
μ (cm^{-1}): 0.1
Absorption corrections : multi-scan; 0.689 min, 0.746 max

Diffractometer: APEX-II CCD
X-ray source: MoK\a
λ (Å): 0.71073
Monochromator : graphite
T (K) :100(2)
Scan mode: phi and omega oscillation scans
Maximum θ: 29.955
HKL ranges: -12 12; -14 14; -19 19
Reflections measured: 9912
Unique data: 6433
Rint: 0.0631
Reflections used: 5276
Criterion: >2\s(I)
Refinement type: Fsqd
Hydrogen atoms:constr
Parameters refined: 263
Reflections / parameter: 20
wR2: 0.1087
R1: 0.0411
GoF: 1.08

Table 8: Atomic coordinates and equivalent isotropic displacement parameters

Atom	x (Å)	y (Å)	z (Å)	U(eq) (Å²)
F91	0.41379(8)	0.26721(7)	0.83281(5)	0.02265(15)
F92	0.57746(8)	0.37483(7)	0.73011(5)	0.02175(14)
F93	0.43504(8)	0.44396(7)	0.87190(5)	0.02194(14)
O1	0.65405(10)	0.22470(9)	1.18170(6)	0.02340(17)
O2	0.59935(9)	0.18037(8)	0.97751(5)	0.01457(14)
O3	0.74937(9)	0.10497(8)	0.82322(5)	0.01459(14)

O11	0.40774(10)	0.18823(8)	1.24665(6)	0.02087(16)
C1	0.56561(13)	0.15864(11)	1.18948(7)	0.01631(19)
C2	0.61959(14)	0.03224(11)	1.13754(8)	0.01773(19)
H2A	0.5172	0.0182	1.135	0.021
H2B	0.6908	-0.0575	1.1764	0.021
C3	0.72004(12)	0.05913(11)	1.03150(7)	0.01498(18)
H3	0.8133	0.0878	1.0336	0.018
C4	0.79684(13)	-0.06957(11)	0.97736(8)	0.01630(19)
H4A	0.7069	-0.1034	0.9791	0.02
H4B	0.8849	-0.1507	1.0113	0.02
C5	0.87667(12)	-0.02282(10)	0.86859(7)	0.01455(18)
H5	0.9742	0.0024	0.8679	0.017
C6	0.93961(13)	0.13606(11)	- 0.80299(8)	0.01624(19)
H6A	0.8425	-0.159	0.802	0.019
H6B	1.0246	-0.2262	0.8327	0.019
C7	1.02110(14)	-0.08566(11)	0.69455(8)	0.0188(2)
H7A	0.9355	0.0035	0.6644	0.023
H7B	1.117	-0.0611	0.6956	0.023
C8	0.67543(12)	0.22032(10)	0.87678(7)	0.01381(18)
C9	0.52326(12)	0.32768(11)	0.82765(8)	0.01606(19)
C11	0.34646(15)	0.30970(13)	1.29781(9)	0.0257(2)
H11A	0.4207	0.2888	1.344	0.039
H11B	0.2297	0.3251	1.3359	0.039
H11C	0.3476	0.3974	1.2481	0.039
C111	1.08650(13)	-0.19952(11)	0.62960(7)	0.01659(19)
C112	1.00272(14)	-0.18409(13)	0.55552(8)	0.0221(2)
H112	0.9042	-0.0994	0.5446	0.026
C113	1.06083(16)	-0.29057(14)	0.49726(9)	0.0259(2)
H113	1.0006	-0.279	0.4481	0.031
C114	1.20644(16)	-0.41354(13)	0.51080(8)	0.0246(2)

H114	1.2472	-0.4857	0.4704	0.03
C115	1.29230(14)	-0.43036(12)	0.58401(8)	0.0219(2)
H115	1.392	-0.5144	0.5937	0.026
C116	1.23259(13)	-0.32465(11)	0.64296(8)	0.0183(2)
H116	1.2917	-0.3375	0.693	0.022
C211	0.79579(12)	0.29643(10)	0.86756(7)	0.01442(18)
C212	0.76314(13)	0.38069(11)	0.93794(8)	0.01732(19)
H212	0.6713	0.3852	0.9944	0.021
C213	0.86562(14)	0.45847(12)	0.92532(9)	0.0210(2)
H213	0.8431	0.5164	0.9731	0.025
C214	1.00080(14)	0.45131(12)	0.84285(9)	0.0216(2)
H214	1.0703	0.5044	0.8344	0.026
C215	1.03401(13)	0.36680(12)	0.77314(9)	0.0212(2)
H215	1.1268	0.3614	0.7172	0.025
C216	0.93144(13)	0.28957(11)	0.78493(8)	0.01774(19)
H216	0.9539	0.2323	0.7368	0.021

Table 9: Bond lengths (Å)

F91 C9	1.3369(11)	C8 C211	1.5332(13)
F92 C9	1.3410(12)	C8 C9	1.5410(14)
F93 C9	1.3348(12)	C11 H11A	0.98
O1 C1	1.2070(13)	C11 H11B	0.98
O2 C8	1.4104(11)	C11 H11C	0.98
O2 C3	1.4484(12)	C111 C112	1.3940(15)
O3 C8	1.4059(11)	C111 C116	1.4002(14)
O3 C5	1.4520(11)	C112 C113	1.3914(16)
O11 C1	1.3419(12)	C112 H112	0.95
O11 C11	1.4481(13)	C113 C114	1.3872(18)
C1 C2	1.5103(14)	C113 H113	0.95
C2 C3	1.5166(14)	C114 C115	1.3917(17)
C2 H2A	0.99	C114 H114	0.95

C2 H2B	0.99	C115 C116	1.3900(15)
C3 C4	1.5220(14)	C115 H115	0.95
C3 H3	1	C116 H116	0.95
C4 C5	1.5250(14)	C211 C212	1.3932(14)
C4 H4A	0.99	C211 C216	1.3967(14)
C4 H4B	0.99	C212 C213	1.3965(14)
C5 C6	1.5151(13)	C212 H212	0.95
C5 H5	1	C213 C214	1.3926(16)
C6 C7	1.5352(14)	C213 H213	0.95
C6 H6A	0.99	C214 C215	1.3859(16)
C6 H6B	0.99	C214 H214	0.95
C7 C111	1.5104(14)	C215 C216	1.3953(15)
C7 H7A	0.99	C215 H215	0.95
C7 H7B	0.99	C216 H216	0.95

Table 10: Angles (deg)

C8 O2 C3	112.05(7)	F93 C9 F91	107.12(8)
C8 O3 C5	113.73(7)	F93 C9 F92	107.56(8)
C1 O11 C11	115.10(8)	F91 C9 F92	107.46(8)
O1 C1 O11	123.67(10)	F93 C9 C8	111.67(8)
O1 C1 C2	124.30(9)	F91 C9 C8	112.15(8)
O11 C1 C2	112.03(9)	F92 C9 C8	110.64(8)
C1 C2 C3	110.76(8)	O11 C11 H11A	109.5
C1 C2 H2A	109.5	O11 C11 H11B	109.5
C3 C2 H2A	109.5	H11A C11 H11B	109.5
C1 C2 H2B	109.5	O11 C11 H11C	109.5
C3 C2 H2B	109.5	H11A C11 H11C	109.5
H2A C2 H2B	108.1	H11B C11 H11C	109.5
O2 C3 C2	105.29(8)	C112 C111 C116	118.08(10)
O2 C3 C4	109.44(8)	C112 C111 C7	121.19(9)
C2 C3 C4	114.46(8)	C116 C111 C7	120.72(9)

O2 C3 H3	109.2	C113 C112 C111	121.15(10)
C2 C3 H3	109.2	C113 C112 H112	119.4
C4 C3 H3	109.2	C111 C112 H112	119.4
C3 C4 C5	108.98(8)	C114 C113 C112	120.16(10)
C3 C4 H4A	109.9	C114 C113 H113	119.9
C5 C4 H4A	109.9	C112 C113 H113	119.9
C3 C4 H4B	109.9	C113 C114 C115	119.46(10)
C5 C4 H4B	109.9	C113 C114 H114	120.3
H4A C4 H4B	108.3	C115 C114 H114	120.3
O3 C5 C6	106.67(7)	C116 C115 C114	120.21(10)
O3 C5 C4	108.91(8)	C116 C115 H115	119.9
C6 C5 C4	114.24(8)	C114 C115 H115	119.9
O3 C5 H5	109	C115 C116 C111	120.92(10)
C6 C5 H5	109	C115 C116 H116	119.5
C4 C5 H5	109	C111 C116 H116	119.5
C5 C6 C7	112.64(8)	C212 C211 C216	119.84(9)
C5 C6 H6A	109.1	C212 C211 C8	120.00(8)
C7 C6 H6A	109.1	C216 C211 C8	120.02(9)
C5 C6 H6B	109.1	C211 C212 C213	119.88(9)
C7 C6 H6B	109.1	C211 C212 H212	120.1
H6A C6 H6B	107.8	C213 C212 H212	120.1
C111 C7 C6	112.64(8)	C214 C213 C212	120.11(10)
C111 C7 H7A	109.1	C214 C213 H213	119.9
C6 C7 H7A	109.1	C212 C213 H213	119.9
C111 C7 H7B	109.1	C215 C214 C213	120.04(10)
C6 C7 H7B	109.1	C215 C214 H214	120
H7A C7 H7B	107.8	C213 C214 H214	120
O3 C8 O2	112.60(8)	C214 C215 C216	120.15(10)
O3 C8 C211	113.51(8)	C214 C215 H215	119.9
O2 C8 C211	112.63(8)	C216 C215 H215	119.9
O3 C8 C9	103.80(7)	C215 C216 C211	119.98(10)
O2 C8 C9	104.11(7)	C215 C216 H216	120

C211 C8 C9	109.31(8)	C211 C216 H216	120

Table 11: Anisotropic displacement parameters (Å²)

Atom	U11	U22	U33	U23	U13	U12
F91	0.0183(3)	0.0203(3)	0.0321(4)	-0.0013(3)	-0.0113(3)	-0.0079(2)
F92	0.0226(3)	0.0227(3)	0.0163(3)	0.0013(2)	-0.0060(2)	-0.0067(3)
F93	0.0194(3)	0.0150(3)	0.0267(3)	-0.0065(2)	-0.0051(2)	-0.0001(2)
O1	0.0241(4)	0.0296(4)	0.0229(4)	-0.0103(3)	-0.0013(3)	-0.0147(3)
O2	0.0140(3)	0.0145(3)	0.0131(3)	-0.0011(2)	-0.0018(2)	-0.0049(3)
O3	0.0156(3)	0.0122(3)	0.0153(3)	-0.0040(2)	-0.0047(2)	-0.0025(3)
O11	0.0200(4)	0.0191(4)	0.0232(4)	-0.0063(3)	0.0006(3)	-0.0087(3)
C1	0.0188(4)	0.0168(4)	0.0122(4)	0.0000(3)	-0.0047(3)	-0.0063(4)
C2	0.0222(5)	0.0167(5)	0.0146(4)	-0.0016(4)	-0.0026(4)	-0.0091(4)
C3	0.0164(4)	0.0143(4)	0.0138(4)	-0.0011(3)	-0.0041(3)	-0.0055(3)
C4	0.0182(4)	0.0135(4)	0.0159(4)	-0.0019(3)	-0.0045(3)	-0.0046(3)
C5	0.0142(4)	0.0119(4)	0.0163(4)	-0.0028(3)	-0.0043(3)	-0.0028(3)
C6	0.0168(4)	0.0133(4)	0.0174(4)	-0.0048(3)	-0.0023(3)	-0.0041(3)
C7	0.0214(5)	0.0140(4)	0.0180(4)	-0.0039(4)	-0.0020(4)	-0.0047(4)
C8	0.0139(4)	0.0129(4)	0.0131(4)	-0.0025(3)	-0.0021(3)	-0.0039(3)
C9	0.0160(4)	0.0140(4)	0.0178(4)	-0.0023(3)	-0.0043(3)	-0.0049(3)
C11	0.0245(5)	0.0214(5)	0.0289(6)	-0.0098(4)	0.0017(4)	-0.0078(4)
C111	0.0172(4)	0.0163(5)	0.0144(4)	-0.0031(3)	-0.0004(3)	-0.0063(4)
C112	0.0192(5)	0.0243(5)	0.0188(5)	-0.0028(4)	-0.0047(4)	-0.0046(4)
C113	0.0282(6)	0.0349(6)	0.0180(5)	-0.0067(4)	-0.0061(4)	-0.0128(5)
C114	0.0324(6)	0.0235(5)	0.0183(5)	-0.0086(4)	-0.0002(4)	-0.0111(5)
C115	0.0227(5)	0.0173(5)	0.0202(5)	-0.0043(4)	-0.0012(4)	-0.0041(4)
C116	0.0171(4)	0.0183(5)	0.0181(4)	-0.0035(4)	-0.0036(4)	-0.0054(4)
C211	0.0135(4)	0.0130(4)	0.0159(4)	-0.0014(3)	-0.0035(3)	-0.0046(3)
C212	0.0171(4)	0.0174(5)	0.0176(4)	-0.0045(4)	-0.0010(3)	-0.0074(4)
C213	0.0226(5)	0.0194(5)	0.0246(5)	-0.0070(4)	-0.0041(4)	-0.0096(4)
C214	0.0194(5)	0.0189(5)	0.0286(5)	-0.0036(4)	-0.0043(4)	-0.0100(4)

C215	0.0163(4)	0.0207(5)	0.0239(5)	-0.0037(4)	0.0005(4)	-0.0076(4)
C216	0.0175(4)	0.0163(5)	0.0179(4)	-0.0043(4)	-0.0012(4)	-0.0058(4)

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