# Supporting Information

## Enantioenriched β-Lactone and Aldol-Type Products from Regiodivergent Carbonylation of *Racemic cis*-Epoxides

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## General considerations

### Methods and instruments

Unless stated otherwise all synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere or in an MBraun Unilab glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven-dried glassware cooled under vacuum. High-pressure reactions were performed in a custom-designed and -fabricated, six-chamber, stainless steel, high-pressure reactor.[1] The reactor design allowed for incorporation of six 2 fluid dram glass vials. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Varian 300, 400 or 500 MHz instrument at 22° C (unless indicated otherwise) with shifts reported relative to the residual solvent peak ($CDCl_3$: 7.26 ppm ($^{1}$H), and 77.16 ppm ($^{13}$C); $C_6D_6$: 7.16 ppm ($^{1}$H) and 128.06 ppm ($^{13}$C); THF-$d_8$: 3.58 ppm ($^{1}$H) and 67.57 ppm ($^{13}$C)). $^{19}$F NMR spectra were recorded on a Varian 400 MHz instrument with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). NMR solvents were purchased from Cambridge Isotope Laboratories and stored over activated 4Å molecular sieves ($C_6D_6$) or $K_2CO_3$ ($CDCl_3$). Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589 nm (Na-line) in a 1 dm cuvette at 22 °C. GC analyses were performed on a Hewlett Packard 6890 gas chromatograph equipped with a Supelco β-Dex120 and a Supelco β-Dex225 column, and a flame ionization detector. Helium (Airgas, UHP grade) was used as carrier gas. HRMS analyses were performed at the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign. Elemental analyses were performed at Midwest Microlab, LLC.

### Chemicals

Anhydrous 1,4-dioxane, 1,2-dimethoxyethane (DME) and tetrahydropyran (THP) were purchased from Sigma-Aldrich and degassed via three freeze-pump-thaw cycles prior to use. Anhydrous toluene, dichloromethane (DCM), hexanes and tetrahydrofuran (THF) were purchased from Fischer Scientific and sparged vigorously with nitrogen for 40 minutes prior to first use. The solvents were further purified by passing them under nitrogen pressure through two packed columns of neutral alumina (tetrahydrofuran was

also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Tetrahydrofurane and dichloromethane were degassed via three freeze-pump-thaw cycles prior to use. Diethylether was dried over sodium/benzophenone and degassed via three freeze-pump-thaw cycles prior to use. Pentane and cyclohexane were dried over phosphorous pentoxide and degassed via three freeze-pump-thaw cycles prior to use. Triethylamine was dried over calcium hydride and degassed via three freeze-pump-thaw cycles prior to use. *n*-Dodecane and all epoxides used in this study were dried over calcium hydride and degassed via three freeze-pump-thaw cycles prior to use. All non-dried solvents used were reagent grade or better and used as received.

Carbon monoxide (Airgas, 99.99% min. purity) was used as received. All other chemicals were purchased from Aldrich, Alfa-Aesar or GFS Chemicals, and used as received. Flash column chromatography was performed with silica gel (particle size 40-64 μm, 230-400 mesh) using either mixtures of ethyl acetate and hexanes or mixtures of diethylether and pentane as eluent.

The following compounds were prepared according to literature procedures:

[(*R*,*R*)-salcyAl(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ ((*R*,*R*)-**2**, (*R*,*R*)-salcy = (*R*,*R*)-*N*,*N*′-*bis*(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediamine),[2]

(*R*)-$^t$BuBinamAlCl (precursor to (*R*)-**1a**, (*R*)-$^t$BuBinam = (*R*)-*N*,*N*′-*bis*(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,1'-binaphthyl-2,2'-diamine),[3]

NaCo(CO)$_4$,[4]

*rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**3a**),[5]

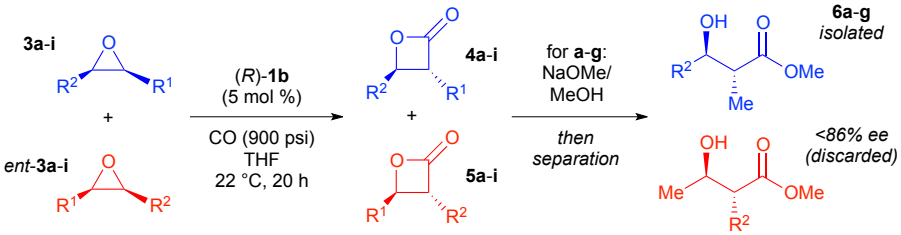
*rac*-(2*R*,3*S*)-2-ethyl-3-propyloxirane (*rac*-**3h**),[6]

*rac*-(2*R*,3*S*)-2-butyl-3-ethyloxirane (*rac*-**3i**),[7]

(*S*)-2-(benzyloxy)-1-(pyrrolidin-1-yl)propan-1-one.[8]

*Racemic* mixtures of β-lactones **4a-i** and **5a-i** were synthesized using [ClTPPAl(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ (ClTPP = *meso*-tetra(4-chlorophenyl)porphyrinato).[9]

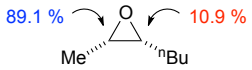
**Table S1.** Scope of the regiodivergent carbonylation of *racemic cis*-epoxides **3** using (*R*)-**1b**[a] (Detailed Table 2)



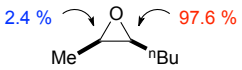

| entry | $R^1$, $R^2$ (epoxide) | | ratio[b] **4** : **5** | %ee[c] of **4** | %ee[c] of **5** | product isolated | isolated yield (%) | %ee[c] of **6** |
|---|---|---|---|---|---|---|---|---|
| 1 | Me, Et | (**3b**) | n.d. | n.d. | n.d. | **6b** | 38 | 94 |
| 2 | Me, $^n$Pr | (**3c**) | n.d. | n.d. | n.d. | **6c** | 32 | 93 |
| 3 | Me, $^n$Bu | (**3a**) | 45 : 55 | 94 | 83 | **6a** | 36 | 94 |
| 4 | Me, $^n$Pent | (**3d**) | 45 : 55 | 94 | 83 | **6d** | 36 | 94 |
| 5 | Me, $^n$Hex | (**3e**) | 45 : 55 | 95 | 83 | **6e** | 33 | 95 |
| 6 | Me, $(CH_2)_2{}^i$Pr | (**3f**) | 44 : 56 | 94 | 85 | **6f** | 36 | 94 |
| 7 | Me, $(CH_2)_3$OTBS | (**3g**) | -[d] | -[d] | -[d] | **6g** | 35 | 92 |
| 8 | Et, $^n$Pr | (**3h**) | 44 : 56 | 96 | 93 | **4h** + **5h** | 61[e] | - |
| 9 | Et, $^n$Bu | (**3i**) | 44 : 56 | 96 | 90 | **4i** + **5i** | 73[e] | - |

[a]All reactions gave full conversion by GC analysis. [b]Ratio of **4** to **5** as determined by GC analysis. [c]Enantiomeric excess determined by GC analysis. [d]Partial decomposition of the β-lactone occurred during the course of the GC analysis. [e]Isolated yield of combined β-lactones **4** and **5**. TBS = $^t$BuMe$_2$Si. Catalyst (*R*)-**1b** was generated *in situ* ($L_n$AlCl + $NaCo(CO)_4$). n.d. = not determined.

**Calculation of the theoretical enantiomeric ratio (er) and ratio of regioisomers for the reaction of *racemic* 3a with catalysts (*R*)-1b (Supplement to Table 3)**




**3a**




*ent*-**3a**

Regioselectivity of (*R*)-**1b** in the carbonylation of **3a** and *ent*-**3a** (data taken from Scheme 3)

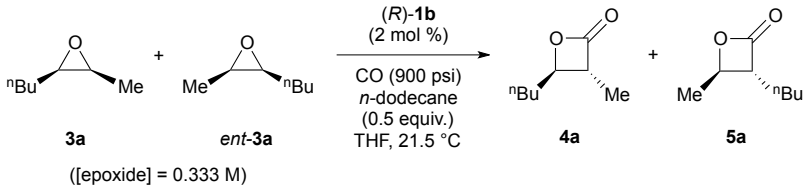
Theoretical er for β-lactone **4a** when using (*R*)-**1b**: 89.1 : 2.4 = 97.4 : 2.6 (94.8 %ee)

Theoretical er for β-lactone **5a** when using (*R*)-**1b**: 97.6 : 10.9 = 90.0 : 10.0 (80.0 %ee)

Calculation of theoretical ratio of regioisomers **4a** : **5a** when using (*R*)-**1b**:

theoretical ratio of **4a** : **5a** is (89.1 + 2.4) : (97.6 + 10.9) = 45.8 : 54.2

**Monitoring of the regiodivergent carbonylation of *racemic* 3a with catalyst (*R*)-1b (Supplement to Figure 2)**

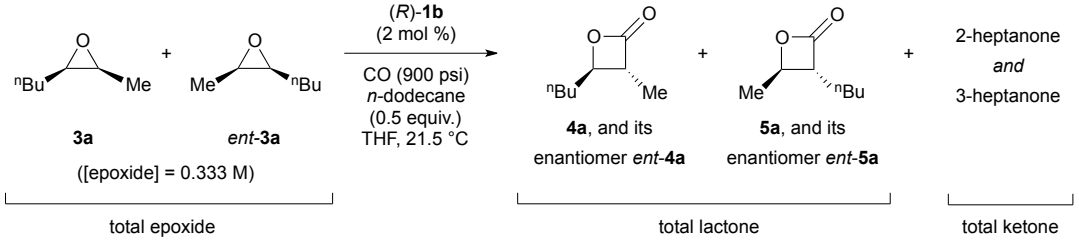


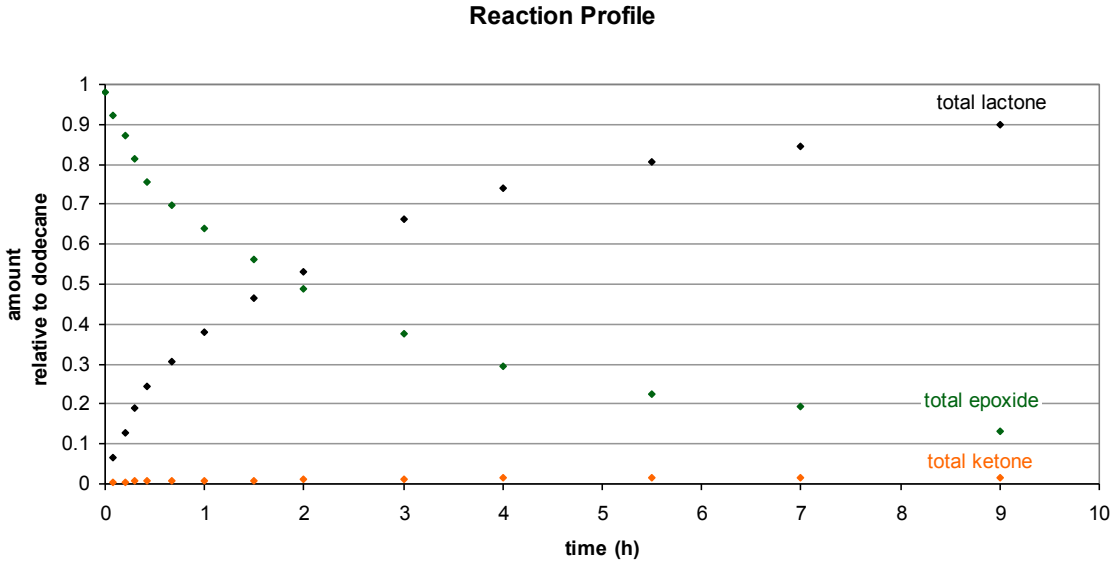

Procedure:

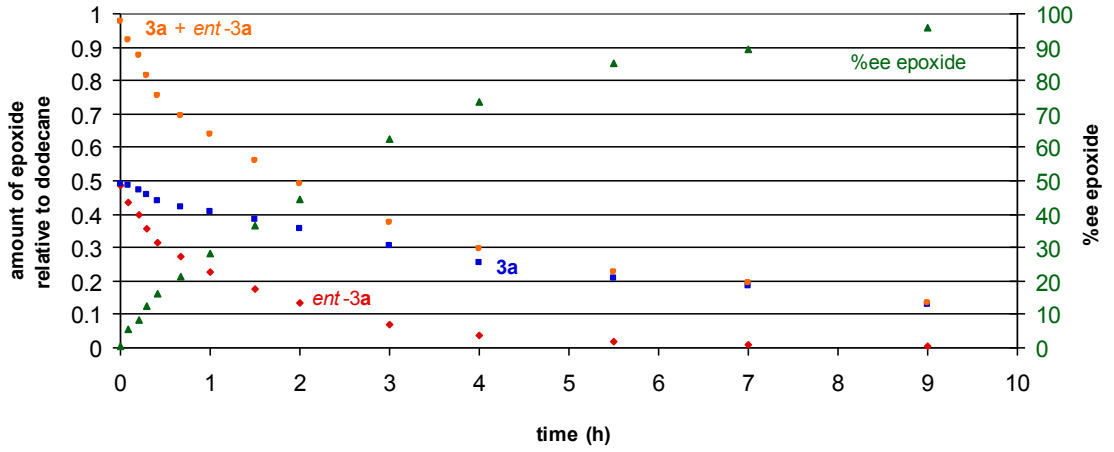
In a glovebox, the precatalyst to (*R*)-**1b**, (*R*)-**ML1** (cf. p. S27), (0.0399 M, THF, 0.10 ml, 0.00399 mmol) was placed in a 2 fluid dram glass vial, which subsequently was placed in a custom-designed and -fabricated, six-chamber, stainless steel, high-pressure reactor. *Rac*-**3a**[5] (0.399 M, THF, 0.5 ml, 0.1995 mmol; also containing *n*-dodecane (0.201 M, 0.101 mmol) and $Na[Co(CO)_4]$ (0.00830 M, 0.00415 mmol)) was placed in a syringe, the tip of which was sealed with a rubber septum. The sealed reactor and syringe were then removed from the glovebox.

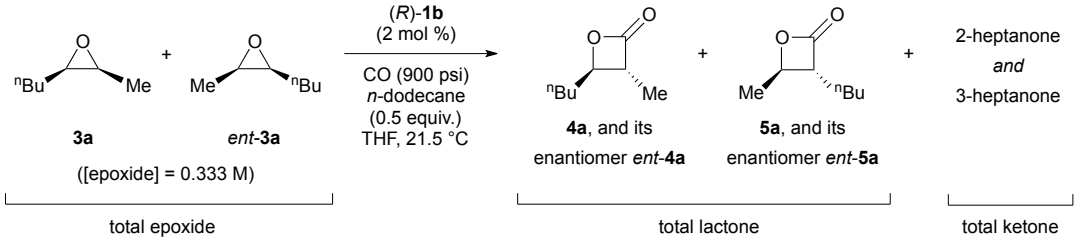
Under an atmosphere of nitrogen and stirring, the contents of the syringe was rapidly added to the glass vial containing (*R*)-**ML1** in the reactor (about 0.01 ml of liquid remained in the syringe). The reactor was immediately sealed and pressured with CO (900 psi). After an appropriate amount of time of stirring at 21.5 °C, the chamber was carefully vented, and an aliquot removed from the reaction mixture. The aliquot was passed through a short plug of silica using $Et_2O$ as eluent. The composition of the eluate was then analyzed relative to *n*-dodecane using GC (β-Dex120 and β-Dex225 columns).

Reaction profiles of major species present in the regiodivergent carbonylation of *rac*-**3a** using (*R*)-**1b**:

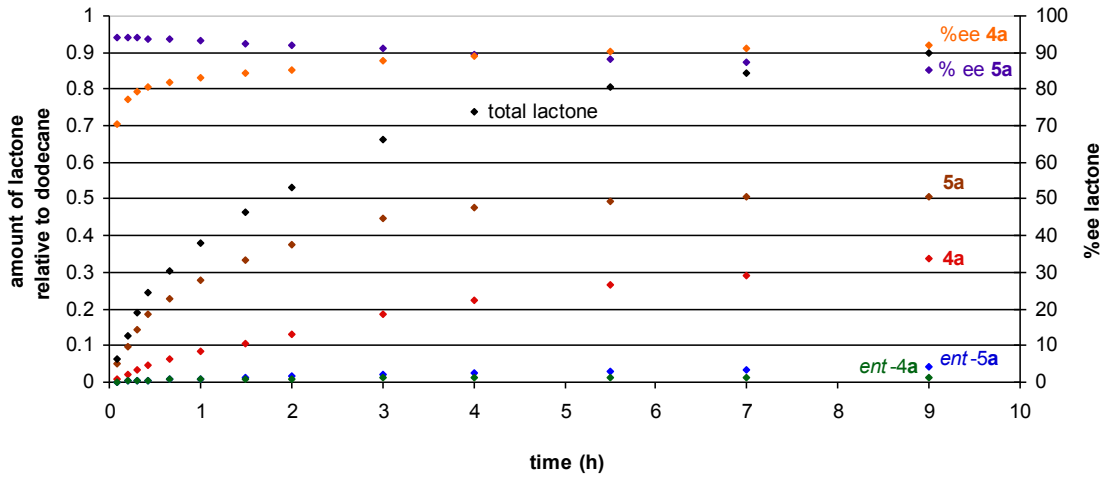


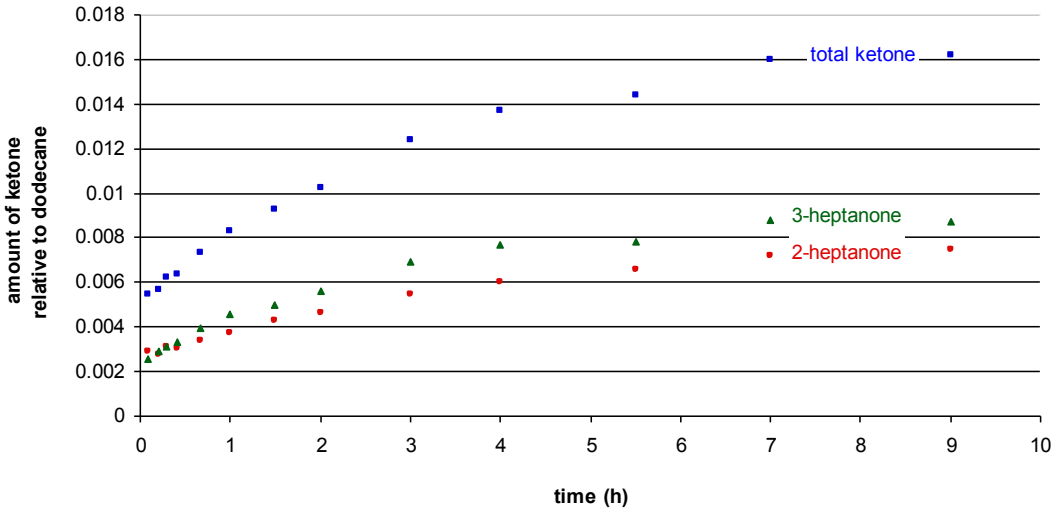






**Reaction Profile - Lactones**




**Reaction Profile - Ketone Formation**



**Plot of conversion vs. enantiomeric excess with regard to epoxide in the regio-divergent carbonylation of *rac*-3a using (*R*)-1b (Supplement to Figure 3)**

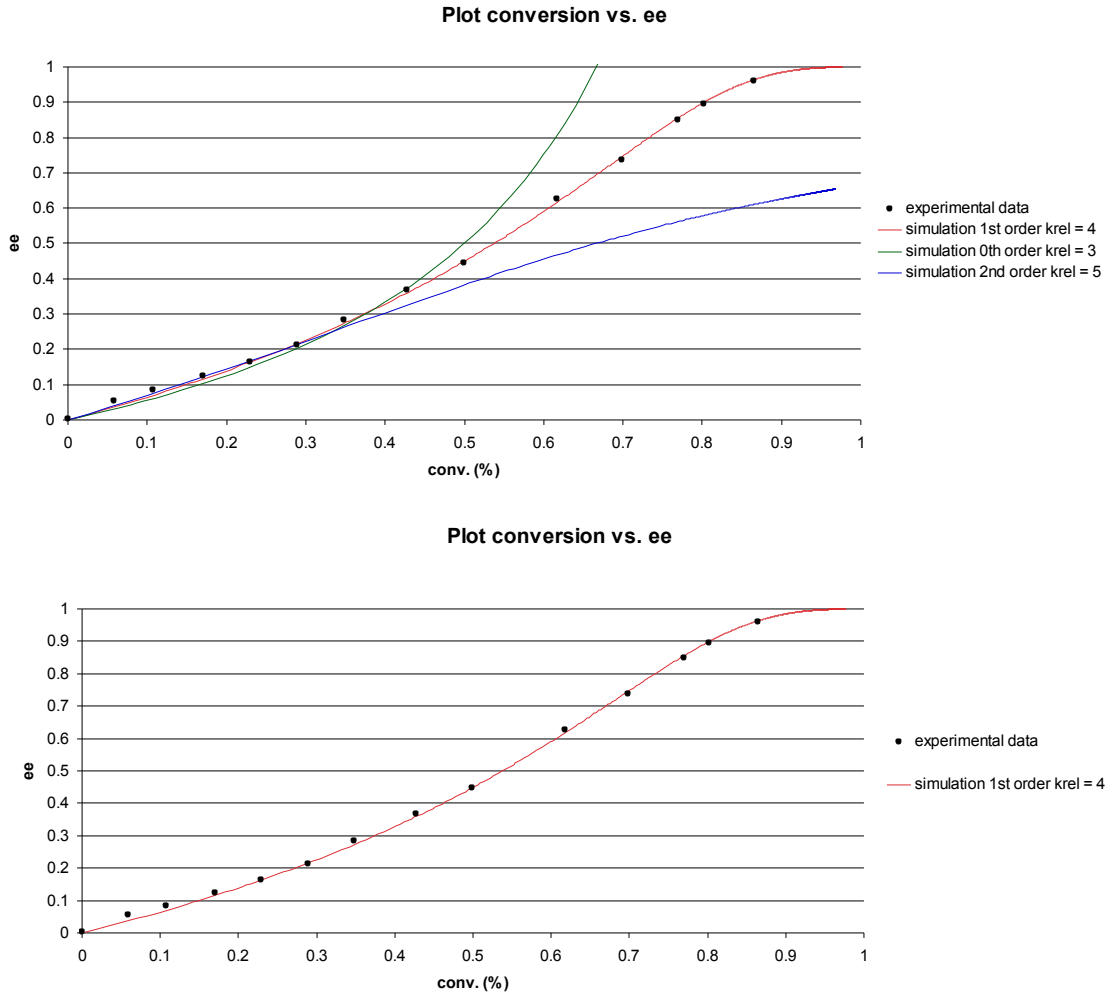
**Table S2.** Conversion and enantiomeric excess of epoxide in the regiodivergent carbonylation of *rac*-**3a** using (*R*)-**1b** and the corresponding calculated $k_{rel}$'s assuming $0^{th}$, $1^{st}$, and $2^{nd}$ order in epoxide

| conversion of total epoxide | ee of left-over epoxide | calculated $k_{rel}$ $1^{st}$ order | calculated $k_{rel}$ $0^{th}$ order | calculated $k_{rel}$ $2^{nd}$ order |
|---|---|---|---|---|
| 0 | 0.004 | - | - | - |
| 0.0586 | 0.055 | 17.0 | 16.1 | 18.0 |
| 0.107 | 0.084 | 6.1 | 5.6 | 6.7 |
| 0.170 | 0.125 | 4.7 | 4.1 | 5.3 |
| 0.229 | 0.163 | 4.0 | 3.4 | 4.8 |
| 0.289 | 0.212 | 3.9 | 3.2 | 4.9 |
| 0.348 | 0.283 | 4.3 | 3.3 | 5.8 |
| 0.427 | 0.368 | 4.2 | 3.0 | 6.4 |
| 0.499 | 0.446 | 4.0 | 2.6 | 6.8 |
| 0.617 | 0.627 | 4.1 | 2.3 | 9.9 |
| 0.699 | 0.737 | 3.9 | 1.9 | 12.8 |
| 0.770 | 0.85 | 4.0 | 1.7 | 20.8 |
| 0.802 | 0.895 | 4.0 | 1.6 | 28.3 |
| 0.864 | 0.959 | 3.9 | 1.4 | 64.7 |

In theory, the mathematical treatment of classical kinetic resolutions should also be applicable to regiodivergent carbonylation reactions as far as the starting material is concerned, because the products of the reaction should ideally have no impact on the reactivity of the starting material. Consequently, as the regiodivergent carbonylation of *rac*-**3a** by (*R*)-**1b** progresses, the selectivity factor (*s*) ($s = k_{rel}$) should remain constant irrespective of the degree of epoxide conversion. Table S2 shows that constant values for $k_{rel}$ are obtained only if one assumes that the order in epoxide in the selectivity-determining step of the regiodivergent carbonylation of *rac*-**3a** using (*R*)-**1b** is 1. Deviations are observed for small levels of conversion, but this can be attributed to the fact that measuring small amounts of epoxide conversion is prone to larger relative errors in the measurement.

The following two plots show simulated graphs for $k_{rel}$ in combination with the experimentally determined data points. Only the simulated graph for a $k_{rel}$ based on a first order assumption with respect to epoxide (with $1^{st}$ order $k_{rel} = 4.0$) reproduces the experimental data reasonably well. As a result, we assume that the order in epoxide in the

selectivity-determining step is 1 throughout most of the reaction, and that (*R*)-**1b** displays a $k_{rel}$ of approximately 4 in the regiodivergent carbonylation of *rac*-**3a**.




The simulated graphs and $k_{rel}$'s were calculated using the equations shown in Figure S1.

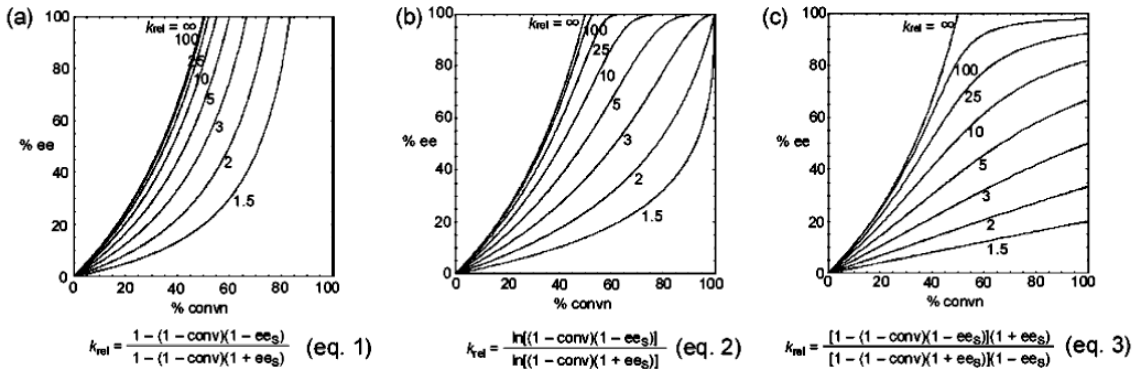



Figure S1. Variation of % ee with conversion of unreacted substrate for (a) zeroth-, (b) first-, and (c) second-order reaction. "Reprinted adapted with permission from Tokunaga, M.; Kiyosu, J.; Obora, Y.; Tsuji, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4481–4486. Copyright 2006 American Chemical Society."

## Synthetic procedures

### General procedure A: Epoxidation of alkenes to epoxides using *m*CPBA

*m*CPBA (Aldrich, ≤77 %) was added in portions at 0 °C to a solution of the corresponding alkene in DCM and the resulting mixture was stirred at the same temperature until TLC analysis indicated complete consumption of the alkene. After destroying excess *m*CPBA by adding aqueous $NaHSO_3$ at 0 °C, the reaction mixture was filtered, the organic phase washed with $NaHCO_3$ (sat., aq., 3x), dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified either *via* distillation or flash column chromatography.

### General procedure B: Carbonylation of epoxides using (*R*)-1b

In a glove box, a 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the precatalyst to (*R*)-**1b**, (*R*)-**ML1** (cf. p. S27), $NaCo(CO)_4$, and THF. After 1 minute of stirring at 22 °C, the vial was placed in a custom-made 6-well high-pressure reactor which itself was placed in a glove box freezer (-34 °C) for 30 minutes. The appropriate epoxide **3** (also cooled to -34 °C) was then added to the vial, the reactor removed from the freezer, subsequently sealed, taken out of the glove box, placed in a well-ventilated hood and pressurized with carbon monoxide (900 psi). It is important to keep the temperature of the reactor below 0 °C once it is removed from the freezer to minimize isomerization of the epoxide to ketone products. The reactor was then sealed again, placed in a 22 °C water bath (unless noted otherwise) and the reaction mixture stirred for the time indicated. The reactor was then carefully vented in a well-ventilated hood and the product isolated as indicated.

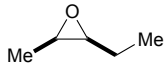
### General procedure C: Derivatization of β-hydroxymethyl esters 6 with trifluoroacetic anhydride for GC analysis

The corresponding β-hydroxymethyl ester **6** (ca. 5-10 mg) was dissolved in DCM (1 ml). Three equivalents of pyridine were added, followed by slow addition of three equivalents of trifluoroacetic anhydride at 0 °C, and the resulting reaction mixture was stirred at 22 °C. Hydrochloric acid (1M, aq.) was added as soon as TLC analysis indicated full conversion of starting material. The resulting phases were separated, the

organic phase dried with sodium sulfate, and subsequently passed through a short plug of silica gel using diethylether as eluent. The eluate was then subjected to GC analysis.

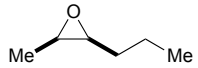
**Synthesis of starting materials**

***rac*-(2*R*,3*S*)-2-Ethyl-3-methyloxirane (*rac*-3b)**



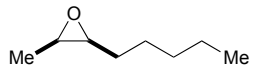

Following general procedure A, (*Z*)-pent-2-ene (7.00 g, 99.8 mmol) was reacted with *m*CPBA (27.5 g) in DCM (100 ml) to give *rac*-**3b** (0.992 g, 12 %) as a colorless liquid. The analytical data was in accordance with that reported in the literature.[10] **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.02 (qd, *J* = 5.5, 4.2 Hz, 1H), 2.84 (td, *J* = 6.4, 4.2 Hz, 1H), 1.61–1.52 (m, 1H), 1.54–1.42 (m, 1H), 1.25 (d, *J* = 5.5 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 58.3, 52.8, 21.0, 13.1, 10.5.

***rac*-(2*R*,3*S*)-2-Methyl-3-propyloxirane (*rac*-3c)**



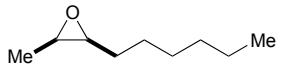

Following general procedure A, (*Z*)-hex-2-ene (5.12 g, 60.8 mmol) was reacted with *m*CPBA (17.0 g) in DCM (135 ml) to give *rac*-**3c** (1.74 g, 29 %) as a colorless liquid. The analytical data was in accordance with that reported in the literature.[11] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.01 (qd, *J* = 5.5, 4.3 Hz, 1H), 2.87 (td, *J* = 5.9, 4.1 Hz, 1H), 1.54–1.39 (m, 4H), 1.24 (d, *J* = 5.6 Hz, 3H), 0.96–0.93 (m, 3H). **$^{13}$C NM**R (126 MHz, $CDCl_3$): δ 57.0, 52.6, 29.6, 19.8, 14.1, 13.3.

***rac*-(2*R*,3*S*)-2-Methyl-3-pentyloxirane (*rac*-3d)**



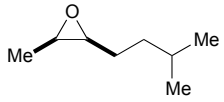

Following general procedure A, (*Z*)-oct-2-ene (5.00 g, 44.6 mmol) was reacted with *m*CPBA (12.6 g) in DCM (100 ml) to give *rac*-**3d** (3.47 g, 61 %) as a colorless liquid. The analytical data was in accordance with that reported in the literature.[12] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 2.99 (qd, *J* = 5.5, 4.4 Hz, 1H), 2.86–2.83 (m, 1H), 1.52–1.25 (m, 8H), 1.22 (d, *J* = 5.5 Hz, 3H), 0.87–0.85 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 57.2, 52.7, 31.8, 27.6, 26.20, 22.7, 14.0, 13.2.

***rac*-(2*R*,3*S*)-2-Hexyl-3-methyloxirane (*rac*-3e)**




Following general procedure A, (*Z*)-non-2-ene[13] (1.19 g, 9.43 mmol) was reacted with *m*CPBA (2.40 g) in DCM (18 ml) to give *rac*-**3e** (1.05 g, 78 %) as a colorless liquid. The analytical data was in accordance with that reported in the literature.[13] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.04 (qd, *J* = 5.5, 4.3 Hz, 1H), 2.90 (td, *J* = 5.9, 4.2 Hz, 1H), 1.58–1.24 (m, 10H), 1.27 (d, *J* = 5.4 Hz, 3H), 0.91–0.87 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 57.3, 52.7, 31.9, 29.3, 27.7, 26.5, 22.7, 14.2, 13.3.

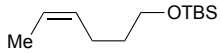
***rac*-(2*R*,3*S*)-2-Isopentyl-3-methyloxirane (*rac*-3f)**




6-Methylhept-2-yne (4.41 g, 40.0 mmol), Lindlar catalyst (Aldrich, 1.50 g), pentane (30 ml) and quinoline (freshly distilled, 1.65 g, 12.7 mmol) were placed in a Fisher-Porter tube, and the contents of the tube purged with nitrogen for 5 minutes. A $H_2$-pressure of 32 psi was applied to the tube and the reaction mixture stirred at 22 °C until TLC analysis indicated complete disappearance of starting material (during this process the tube was repressurized with $H_2$-gas as necessary). The Fisher-Porter tube was carefully vented, then HCl (1 M, aq.) was carefully added and the reaction mixture filtered through a pad of celite. The organic phase was washed with HCl (1 M, aq., 2x), then dried with sodium sulfate, filtered and concentrated under reduced pressure.

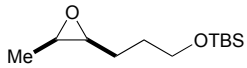
Following general procedure A, the residue was reacted with *m*CPBA (12.2 g) in DCM (80 ml) to give *rac*-**3f** (1.22 g, 24 %) as a colorless liquid. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.04 (qd, *J* = 5.5, 4.2 Hz, 1H), 2.88 (td, *J* = 6.1, 4.2 Hz, 1H), 1.64–1.35 (m, 4H), 1.32–1.23 (m, 1H), 1.27 (d, *J* = 5.5 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 57.4, 52.8, 35.5, 28.0, 25.6, 22.7, 22.5, 13.3. **IR** (neat, $cm^{-1}$): 2957, 1468, 1389, 1065, 982, 804, 790. **HRMS** (ESI) *m/z* calculated for $C_8H_{17}O^+$ ($M + H^+$) 129.1274, found 129.1276.

**(*Z*)-*Tert*-butyl(hex-4-en-1-yloxy)dimethylsilane (SM1)**



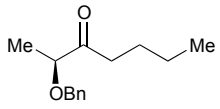

(*Z*)-Hex-4-en-1-ol (0.955 g, 9.53 mmol) and 1-methyl-1*H*-imidazole (2.47 g, 30.1 mmol) were added to a solution of *tert*-butylchlorodimethylsilane (1.80 g, 11.9 mmol) in DCM (24 ml) at 0 °C. The reaction mixture was stirred for 24 h at 22 °C, then washed with water, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM1** (1.76 g, 86 %) as a colorless liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 5.49–5.35 (m, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.12–2.06 (m, 2H), 1.61–1.54 (m, 5H), 0.90 (s, 9H), 0.05 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 130.3, 124.3, 62.8, 32.8, 26.1, 23.3, 18.5 12.9, -5.1. **IR** (neat, $cm^{-1}$): 2929, 2857, 1472, 1254, 1098, 833, 773. **Elemental analysis:** $C_{12}H_{26}OSi$ (214.42), calculated C 67.22, H 12.22; found C 67.04, H 11.97. No molecular ion peak was observed when performing EI-MS or ESI-MS analysis, consequently no HRMS data was acquired.

***rac*-*Tert*-butyldimethyl(3-(2*R*,3*S*)-3-methyloxiran-2-yl)propoxy)silane (*rac*-3g)**




Following general procedure A, (*Z*)-*tert*-butyl(hex-4-en-1-yloxy)dimethylsilane (**SM1**) (1.60 g, 7.46 mmol) was reacted with *m*CPBA (1.86 g) in DCM (20 ml) to give *rac*-**3g** (1.61 g, 94 %) as a colorless liquid. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 3.71–3.59 (m, 2H), 3.04 (td, *J* = 5.6, 4.3 Hz, 1H), 2.92 (td, *J* = 6.0, 4.1 Hz, 1H), 1.92–1.49 (m, 4H), 1.26 (d, *J* = 5.4 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 62.8, 57.0, 52.8, 29.8, 26.1, 24.3, 18.5, 13.3, -5.2. **IR** (neat, $cm^{-1}$): 2955, 2857, 1472, 1253, 1097, 833, 773. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{27}O_2Si^+$ ($M + H^+$) 231.1775, found 231.1777.

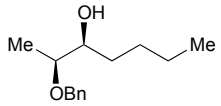
**(*S*)-2-(Benzyloxy)heptan-3-one (SM2)**




(*S*)-2-(Benzyloxy)-1-(pyrrolidin-1-yl)propan-1-one[8] (4.66 g, 20.0 mmol) was added to THF (70 ml), and the resulting mixture cooled to -78 °C. *n*-Butyllithium (Acros, 1.6 M, hexanes, 14.5 ml, 23 mmol) was added dropwise at -78 °C under vigorous stirring, and then the reaction mixture was stirred for 6 minutes at -78 °C. Ammonium chloride (sat.,

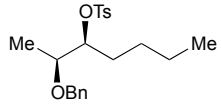
aq.) was added, and the aqueous layer extracted with $Et_2O$ (2x). The combined organic layers were dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM2** (3.17 g, 72 %) as a colorless liquid. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.31–7.14 (m, 5H), 4.45 (d, $J$ = 11.7 Hz, 1H), 4.42 (d, $J$ = 11.7 Hz, 1H), 3.85 (q, $J$ = 6.9 Hz, 1H), 2.56–2.38 (m, 2H), 1.52–1.42 (m, 2H), 1.29–1.17 (m, 2H), 1.24 (d, $J$ = 6.8 Hz, 3H), 0.82 (t, $J$ = 7.3 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 213.2, 137.8, 128.6, 128.0, 127.9, 80.8, 72.0, 37.2, 25.5, 22.5, 17.6, 14.0. **IR** (neat, $cm^{-1}$): 2958, 2933, 2872, 1716, 1454, 1368, 1113, 734. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{20}O_2Na^+$ (M + $Na^+$) 243.1356, found 243.1358. **Specific rotation**: $[\alpha]^{22}_D$ = -49.7 (*c* = 1.1, $CHCl_3$).

**(2*S*,3*S*)-2-(Benzyloxy)heptan-3-ol (SM3)**



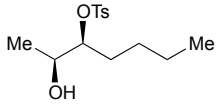

L-Selectride (Aldrich, 1.0 M, THF, 4.5 ml, 4.5 mmol) was added to a solution of (*S*)-2-(benzyloxy)heptan-3-one (**SM2**, 0.783 g, 3.55 mmol) in THF (12 ml) dropwise at -78 °C. After stirring for 2 h at -78 °C, ammonium chloride (sat., aq.) was added, and the aqueous layer extracted with $Et_2O$ (2x). The combined organic layers were washed with $NaHCO_3$ (sat., aq.), dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM3** (0.483 g, 61 %) as a colorless liquid. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.29–7.19 (m, 5H), 4.57 (d, $J$ = 11.5 Hz, 1H), 4.37 (d, $J$ = 11.5 Hz, 1H), 3.38–3.34 (m, 1H), 3.31 (q, $J$ = 6.1 Hz, 1H), 2.47 (s, 1H), 1.43–1.22 (m, 6H), 1.12 (d, $J$ = 6.0 Hz, 3H), 0.83 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 138.5, 128.6, 128.0, 127.9, 78.6, 75.1, 71.1, 32.7, 27.9, 22.9, 15.7, 14.2. **IR** (neat, $cm^{-1}$): 2932, 2860, 1454, 1375, 1072, 1027, 733. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{23}O_2^+$ (M + $H^+$) 223.1693, found 223.1699. **Specific rotation**: $[\alpha]^{22}_D$ = +27.2 (*c* = 0.90, $CHCl_3$).

**(2*S*,3*S*)-2-(Benzyloxy)heptan-3-yl 4-methylbenzenesulfonate (SM4)**




(2*S*,3*S*)-2-(Benzyloxy)heptan-3-ol (**SM3**, 0.416 g, 1.87 mmol), 4-methylbenzene-1-sulfonyl chloride (1.00 g, 5.25 mmol), and pyridine (1.96 g, 24.7 mmol) were mixed and stirred at 40 °C for 5 h. The reaction mixture was allowed to cool to 22 °C, $Et_2O$ was added and the organic phase was washed with HCl (1 M, aq., 2x). The organic layer was then dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM4** (0.632 g, 90 %) as a colorless liquid, which was stored at -15 °C to prevent discoloration of the product. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34–7.23 (m, 7H), 4.53 (qu, *J* = 4.2 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 3.66 (qd, *J* = 6.4, 4.4 Hz, 1H), 2.40 (s, 3H), 1.68 (dddd, *J* = 13.9, 9.9, 5.9, 3.8 Hz, 1H), 1.57–1.45 (m, 1H), 1.21–1.10 (m, 3H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.06–0.93 (m, 1H), 0.77 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 144.6, 138.4, 134.4, 129.7, 128.4, 127.9, 127.8, 127.7, 84.4, 74.6, 71.4, 28.7, 27.3, 22.5, 21.7, 14.6, 13.9. **IR** (neat, $cm^{-1}$): 2956, 2871, 1598, 1362, 1174, 1096, 904, 813. **HRMS** (ESI) *m/z* calculated for $C_{21}H_{28}O_4NaS^+$ ($M + Na^+$) 399.1603, found 399.1601. **Specific rotation**: $[\alpha]^{22}_D$ = -22.1 (*c* = 0.60, $CHCl_3$).

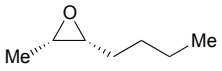
**(2*S*,3*S*)-2-Hydroxyheptan-3-yl 4-methylbenzenesulfonate (SM5)**




Palladium on carbon (Strem, 5 % Pd, 0.352 g), methanol (15 ml), and (2*S*,3*S*)-2-(benzyloxy)heptan-3-yl 4-methylbenzenesulfonate (**SM4**, 0.498 g, 1.32 mmol) were placed in a Fisher-Porter tube and the contents of the tube purged with nitrogen for 5 minutes. A $H_2$-pressure of 32 psi was applied to the tube and the reaction mixture stirred at 22 °C until TLC analysis indicated complete disappearance of starting material (during this process the tube was repressurized with $H_2$-gas as necessary). The Fisher-Porter tube was carefully vented, $Et_2O$ was added, and the resulting mixture filtered through celite. The filtrate was concentrated under reduced pressure and the residue purified *via* flash column chromatography to give **SM5** (0.309 g, 82 %) as a colorless liquid. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.45 (dt, *J* = 7.3,

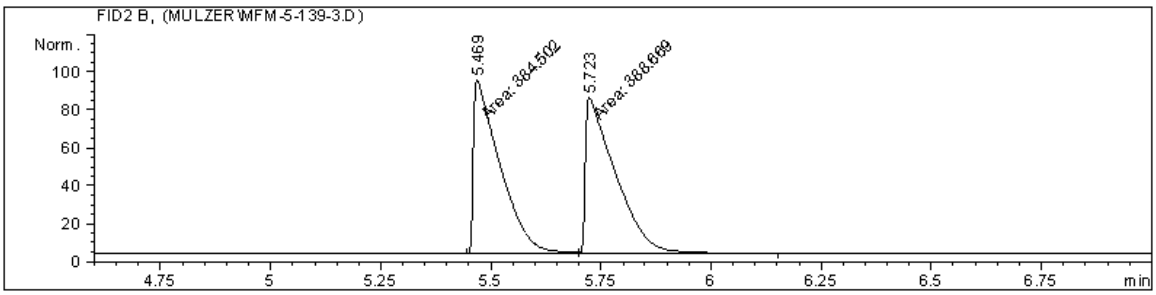
5.1 Hz, 1H), 3.84 (qd, *J* = 6.4, 5.1 Hz, 1H), 2.43 (s, 3H), 2.24 (s, 1H), 1.65 (dddd, *J* = 15.4, 7.8, 6.5, 4.9 Hz, 1H), 1.57–1.48 (m, 1H), 1.26–1.12 (m, 4H), 1.15 (d, *J* = 6.5 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 144.9, 134.2, 129.9, 127.9, 87.7, 68.2, 30.2, 26.9, 22.5, 21.7, 18.9, 13.9. **IR** (neat, $cm^{-1}$): 3531, 2957, 2872, 1356, 1173, 1096, 894, 813. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{23}O_4S^+$ ($M + H^+$) 287.1317, found 287.1312. **Specific rotation**: $[\alpha]^{22}_D$ = +4.4 (*c* = 3.9, $CHCl_3$).

**(2*R*,3*S*)-2-Butyl-3-methyloxirane (3a)**

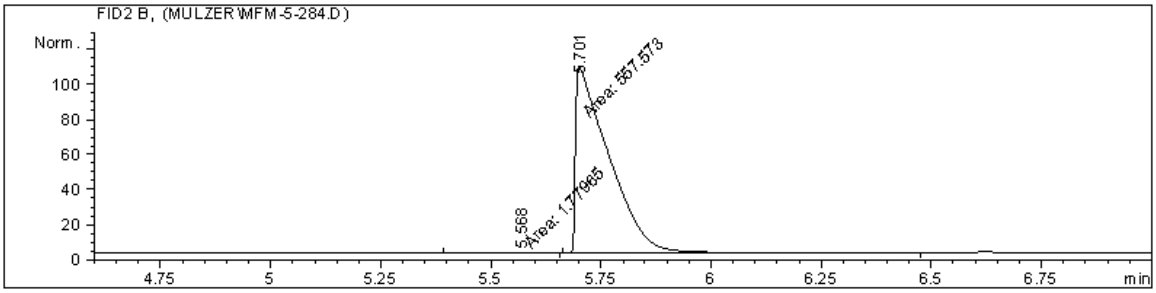



A solution of (2*S*,3*S*)-2-hydroxyheptan-3-yl 4-methylbenzenesulfonate (**SM5**, 4.46 g, 15.6 mmol) in $Et_2O$ (10 ml) was added to a suspension of sodium hydride (Aldrich, 95 %, dry, 0.560 g, 23.3 mmol) in $Et_2O$ (40 ml), and refluxed for 3 days. Upon cooling to 0 °C, $H_2O$ was added and the aqueous phase extracted with $Et_2O$ (2x). The combined organic layers were dried with sodium sulfate, filtered and concentrated under reduced pressure. Distillation of the crude product mixture provided **3a** (0.861 g, 43 %) as a colorless liquid. The analytical data was in accordance with that reported for *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**3a**) in the literature.[5] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.04 (qd, *J* = 5.5, 4.2 Hz, 1H), 2.90 (td, *J* = 5.8, 4.0 Hz, 1H), 1.56–1.32 (m, 6H), 1.26 (d, *J* = 5.5 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 57.1, 52.6, 28.7, 27.3, 22.6, 14.1, 13.2. **Specific rotation**: $[\alpha]^{22}_D$ = -7.2 (*c* = 1.0, $CHCl_3$).

The enantiomeric ratio (er) was determined to be >99 : 1 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

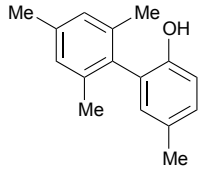



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.469 | MF | 0.0700 | 384.50156 | 91.48367 | 49.73050 |
| 2 | 5.723 | FM | 0.0788 | 388.66891 | 82.21224 | 50.26950 |




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.568 | MM | 0.1172 | 1.77965 | 0.253145 | 0.31816 |
| 2 | 5.701 | MM | 0.0871 | 557.57336 | 106.66568 | 99.68184 |

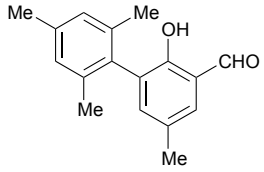
**2',4',5,6'-Tetramethyl-[1,1'-biphenyl]-2-ol (SM6)**




2-Bromo-4-methylphenol (freshly distilled, 2.33 g, 12.4 mmol) was added dropwise to a mixture of sodium hydride (Aldrich, 95%, dry, 0.380 g, 15.8 mmol) and THF (20 ml) at 0 °C, followed by stirring at 22 °C for 10 minutes. $Pd(acac)_2$ (0.170 g, 0.558 mmol, 4.50 mol %) was added, followed by mesitylmagnesium bromide (Aldrich, 1.0 M, THF, 18 ml), and the resulting mixture was refluxed for 12 h. Upon cooling to 0 °C, $H_2O$ and then HCl (2 M, aq.) were added, and the resulting mixture was filtered through a pad of celite. The resulting phases were separated and the aqueous phase extracted with $Et_2O$ (3x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM6** (2.78 g, 99 %) as an off-white solid. **MP** 66–67 °C. **$^1$H NMR**

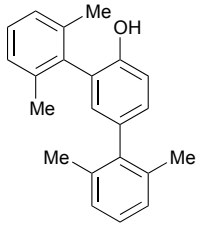
(300 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.4 Hz, 1H), 7.00 (s, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.83 (s, 1H), 4.49 (d, *J* = 0.9 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.04 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 150.3, 138.0, 137.8, 132.0, 130.5, 129.9, 129.5, 128.8, 126.3, 114.9, 21.2, 20.7, 20.4. **IR** (neat, $cm^{-1}$): 3477, 2917, 1478, 1436, 1272, 1230, 1161, 1031, 819. **HRMS** (ESI) *m/z* calculated for $C_{16}H_{18}NaO^+$ ($M + Na^+$) 249.1250, found 249.1259.

**2-Hydroxy-2',4',5,6'-tetramethyl-[1,1'-biphenyl]-3-carbaldehyde (SM7)**



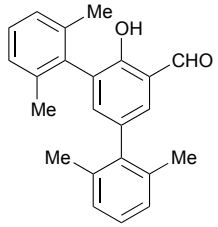

Methylmagnesium bromide (Acros, 3 M, $Et_2O$, 6.5 ml, 20 mmol) is added slowly to 2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-ol (**SM6**, 3.78 g, 16.7 mmol) in THF (40 ml) at 0 °C. After warming to 22 °C, toluene (80 ml), triethylamine (2.76 g, 27.3 mmol) and paraformaldehyde (1.28 g, 42.6 mmol) were added, and the resulting reaction mixture stirred at 80 °C for 12 h. After cooling to 0 °C, $H_2O$ and then HCl (2 M, aq.) were added, and the resulting phases were separated. The aqueous phase was extracted with $Et_2O$ (2x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to afford **SM7** (3.32 g, 78 %) as an off-white solid. **MP** 105–106 °C. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 10.95 (s, 1H), 9.93 (s, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 6.97 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 2.03 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 196.8, 156.9, 139.5, 137.4, 136.6, 132.9, 132.8, 129.8, 129.2, 128.3, 120.6, 21.3, 20.45, 20.44. **IR** (neat, $cm^{-1}$): 2917, 1643, 1454, 1320, 1224, 1103, 971, 850, 798, 742. **HRMS** (ESI) *m/z* calculated for $C_{17}H_{19}O^+$ ($M + H^+$) 255.1380, found 255.1383.

**2,2'',6,6''-Tetramethyl-[1,1':3',1''-terphenyl]-4'-ol (SM8)**




A solution of 2,4-dibromophenol (freshly sublimed, 3.80 g, 15.1 mmol) in THF (10 ml) was added dropwise to a mixture of sodium hydride (Aldrich, 95%, dry, 0.518 g, 21.6 mmol) and THF (38 ml) at 0 °C, followed by stirring at 22 °C for 10 minutes. $Pd(OAc)_2$ (0.277 g, 1.23 mmol, 8.17 mol %) was added, followed by 2,6-dimethylphenyl-magnesium bromide (Aldrich, 1.0 M, THF, 40 ml), and the resulting mixture was refluxed for 12 h. Upon cooling to 0 °C, $H_2O$ and then HCl (2 M, aq.) were added, and the resulting mixture was filtered through a pad of celite. The resulting phases were separated and the aqueous phase extracted with $Et_2O$ (2x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography to give **SM8** (3.17 g, 70 %) as a thick yellow oil. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.29–7.12 (m, 8H), 6.85 (t, *J* = 1.3 Hz, 1H), 4.68 (s, 1H), 2.16 (s, 6H), 2.15 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 151.2, 141.6, 137.9, 136.5, 134.8, 133.6, 130.4, 129.8, 128.5, 128.1, 127.4, 127.0, 126.5, 115.4, 21.1, 20.4. **IR** (neat, $cm^{-1}$): 3486, 2917, 1463, 1219, 1161, 828, 768. **HRMS** (ESI) *m/z* calculated for $C_{22}H_{22}NaO^+$ (M + $Na^+$) 325.1563, found 325.1563.

**4'-Hydroxy-2,2'',6,6''-tetramethyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde (SM9)**

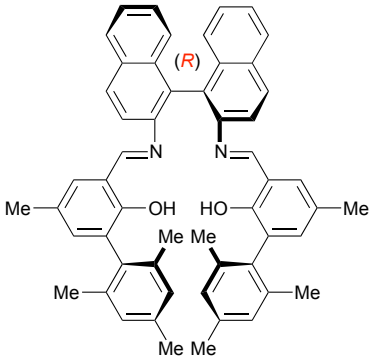



Methylmagnesium bromide (Acros, 3 M, $Et_2O$, 4.0 ml, 12.0 mmol) is added slowly to 2,2'',6,6''-tetramethyl-[1,1':3',1''-terphenyl]-4'-ol (**SM8**, 2.80 g, 9.26 mmol) in THF (20 ml) at 0 °C. After warming to 22 °C, toluene (39 ml), triethylamine (1.60 g, 15.8 mmol) and paraformaldehyde (0.810 g, 27.0 mmol) were added, and the resulting reaction

mixture stirred at 80 °C for 12 h. After cooling to 0 °C, $H_2O$ and then HCl (2 M, aq.) were added, and the resulting phases were separated. The aqueous phase was extracted with $Et_2O$ (2x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography followed by recrystallization from methanol to afford **SM9** (1.90 g, 62 %) as a colorless solid. **MP** 111–112 °C (methanol). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 11.16 (s, 1H), 9.98 (s, 1H), 7.41 (d, $J$ = 2.1 Hz, 1H), 7.23–7.13 (m, 7H), 2.12 (s, 12H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 196.9, 157.6, 139.9, 139.44, 139.44, 136.6, 136.4, 135.7, 133.3, 132.9, 130.2, 128.0, 127.7, 127.5, 120.9, 21.1, 20.6. **IR** (neat, $cm^{-1}$): 2917, 1651, 1451, 1266, 1197, 1082, 934, 767. **HRMS** (ESI) *m/z* calculated for $C_{23}H_{23}O_2^+$ ($M + H^+$) 331.1693, found 331.1688.

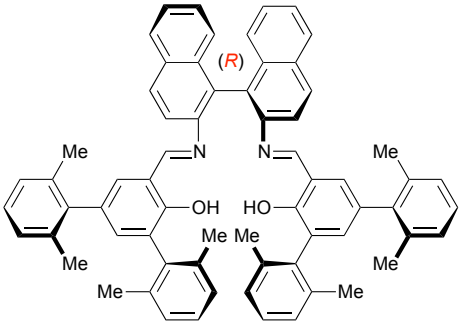
**Synthesis and metallation of salen-compounds**

**(*R*)-3,3''-(([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis-(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-ol) ((*R*)-MesBinam, (*R*)-L1)**



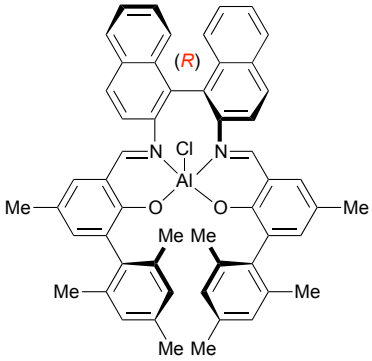

2-Hydroxy-2',4',5,6'-tetramethyl-[1,1'-biphenyl]-3-carbaldehyde (**SM7,** 254 mg, 0.999 mmol), (*R*)-[1,1'-binaphthalene]-2,2'-diamine (142 mg, 0.499 mmol) and methanol (8 ml) were mixed and then refluxed for 12 h. After allowing the reaction mixture to reach 22 °C, the resulting precipitate was isolated by filtration, washed with a small amount of cold methanol and then dried *in vacuo* at 70 °C to give (*R*)-**L1** (289 mg, 76 %) as a powder of orange color. **MP** >200 °C. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 11.91 (s, 2H), 8.26 (s, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.41–7.33 (m, 4H), 7.24–7.17 (m, 4H), 6.93 (s, 2H), 6.89 (m, 4H), 6.72 (d, *J* = 2.2 Hz, 2H), 2.31 (s, 6H), 2.25 (s, 6H), 2.04 (s, 6H), 1.87 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 164.6, 155.8, 146.4, 136.8, 136.51, 136.45, 135.3, 134.2, 133.2, 132.3, 131.7, 130.2, 128.6, 128.4, 128.2, 128.1, 127.5, 127.0, 126.9, 126.8, 125.5, 119.1, 118.7, 21.2, 20.51, 20.46, 20.45. **IR** (neat, $cm^{-1}$): 2917, 1582, 1451, 1260, 1181, 1110, 820, 745. **HRMS** (ESI) *m/z* calculated for $C_{54}H_{49}N_2O_2^+$ ($M + H^+$) 757.3789, found 757.3783. **Specific rotation**: $[\alpha]^{22}_D$ = -172.5 (*c* = 0.97, $CHCl_3$).

**(*R*)-5',5''''-((1*E*,1'*E*)-([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2,2'',6,6''tetramethyl-[1,1':3',1''-terphenyl]-4'-ol) ((*R*)-Xyl$_2$Binam, (*R*)-L2)**




4'-Hydroxy-2,2'',6,6''-tetramethyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde (**SM9**, 662 mg, 2.00 mmol), (*R*)-[1,1'-binaphthalene]-2,2'-diamine (285 mg, 1.00 mmol) and ethanol (14 ml) were mixed and then refluxed for 12 h. After allowing the reaction mixture to reach 22 °C, the resulting precipitate was isolated by filtration, washed with ethanol, then pentane, and then dried *in vacuo* at 70 °C. The obtained powder was dissolved in DCM, layered with hexane, and left standing open to the atmosphere until most of the solvent had evaporated. The resulting precipitate was isolated by filtration, washed with pentane, and then dried *in vacuo* at 70 °C to give (*R*)-**L2** (596 mg, 66 %) as a powder of orange color. **MP** 177 °C (decomp.). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 12.25 (s, 2H), 8.45 (s, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.40 (dt, *J* = 8.1, 3.9 Hz, 2H), 7.25 (d, *J* = 3.4 Hz, 4H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.11–7.05 (m, 6H), 7.00 (t, *J* = 7.8 Hz, 4H), 6.87 (d, *J* = 2.1 Hz, 2H), 6.82 (d, *J* = 2.1 Hz, 2H), 2.03 (s, 6H), 1.96 (s, 6H), 1.93 (s, 6H), 1.89 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 163.7, 156.8, 145.3, 140.7, 137.0, 136.7, 136.6, 136.5, 136.4, 135.4, 133.4, 132.4, 131.7, 131.3, 130.0, 129.0, 128.3, 127.7, 127.6, 127.4, 127.3, 127.2, 127.11, 127.10, 126.9, 126.7, 125.7, 119.2, 118.6, 21.1, 20.9, 20.46, 20.46. **IR** (neat, cm$^{-1}$): 2915, 1580, 1447, 1195, 971, 765, 744. **HRMS** (ESI) *m/z* calculated for $C_{66}H_{57}N_2O_2^+$ ($M + H^+$) 909.4415, found 909.4410. **Specific rotation**: $[\alpha]^{22}_D$ = -352.1 (*c* = 0.45, $CHCl_3$).

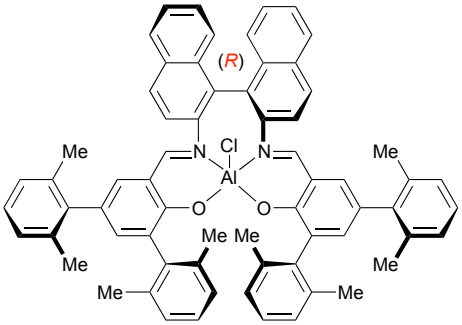
**(*R*)-MesBinamAlCl** ((*R*)-**ML1**, precursor to (*R*)-**1b**, (*R*)-MesBinam = (*R*)-3,3''-(([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-olate))




$Et_2AlCl$ (Aldrich, 1.0 M, hexanes, 1.05 ml, 1.05 mmol) was added to a solution of (*R*)-3,3''-(([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-ol) ((*R*)-MesBinam, (*R*)-**L1**, 724 mg, 0.957 mmol) in DCM (12 ml) at 0 °C. The resulting solution was stirred at 22 °C for 12 h, followed by removal of volatiles *in vacuo*. The residue was suspended in boiling cyclohexane, and filtered through celite while still hot. The filtrate was allowed to slowly reach 22 °C. The resulting precipitate was isolated by filtration, washed twice with pentane and subsequently dried *in vacuo* at 80 °C to give (*R*)-MesBinamAlCl ((*R*)-**ML1**, 394 mg, 50 %) as a bright yellow solid. **MP** >200 °C. **$^1$H NMR** (500 MHz, $CDCl_3$, -55 °C): δ 8.40 (s, 1H), 8.25 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.51 (dt, *J* = 9.9, 7.2 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.32–7.26 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.10 (s, 1H), 7.08–7.03 (m, 3H), 6.98 (s, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.79 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H), 2.19 (s, 3H), 2.15 (s, 3H), 2.06 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 1.65 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$, -55 °C): δ 174.0, 169.1, 163.3, 159.3, 144.2, 143.9, 141.1, 139.9, 138.9, 137.6, 136.9, 135.8, 135.7, 135.2, 135.1, 133.9, 133.7, 132.7, 132.5, 132.4, 132.3, 132.2, 131.91, 131.90, 129.99, 129.47, 128.5, 128.2, 127.9, 127.8, 127.75, 127.6, 127.03, 126.97, 126.85, 126.5, 126.3, 126.23, 126.22, 126.19, 126.0, 125.8, 125.5, 125.2, 119.0, 118.6, 21.7, 21.44, 21.35, 21.27, 20.5, 20.41, 20.36, 19.15. **IR** (neat, $cm^{-1}$): 2916, 1551, 1456, 1218, 977, 821, 749. **HRMS** (ESI) *m/z* calculated for $C_{54}H_{46}AlN_2O_2^+$ $(M - Cl)^+$ 781.3369, found 781.3375.

*Note*: NMR spectra collected in $CDCl_3$ at 22 °C displayed very broad resonances.

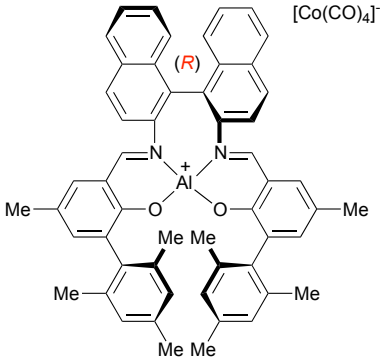
**(*R*)-Xyl$_2$BinamAlCl** ((*R*)-**ML2**, precursor to (*R*)-**1c**, (*R*)-Xyl$_2$Binam = (*R*)-5',5""-((1*E*,1'*E*)-([1,1'-binaphthalene]2,2'-diylbis(azanylylidene))bis(methanylylidene))-bis(2,2",6,6"tetramethyl-[1,1':3',1"-terphenyl]-4'-olate)




Et$_2$AlCl (Aldrich, hexanes, 1.0 M, 400 µl, 0.400 mmol) was added to a solution of (*R*)-5',5""-((1*E*,1'*E*)-([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))-bis(2,2",6,6"tetramethyl-[1,1':3',1"-terphenyl]-4'-ol) ((*R*)-Xyl$_2$Binam, (*R*)-**L2**, 327 mg, 0.360 mmol) in DCM (2 ml) at 0 °C. The reaction mixture was stirred at 22 °C for 12 h, and the resulting precipitate was isolated by filtration, washed with a small amount of DCM, and subsequently dried *in vacuo* at 80 °C to give (*R*)-Xyl$_2$BinamAlCl ((*R*)-**ML2**, 172 mg, 49 %) as a bright yellow solid. **MP** >200 °C. **$^1$H NMR** (500 MHz, $CDCl_3$, -55 °C): δ 8.49 (s, 1H), 8.29 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 8.06–8.01 (m, 3H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.58–7.52 (m, 3H), 7.37–7.28 (m, 4H), 7.20–7.03 (m, 14H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.72 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$, -55 °C): δ 174.9, 169.5, 163.9, 160.1, 144.3, 144.2, 140.56, 140.56, 140.27, 140.25, 139.5, 139.1, 137.9, 137.6, 136.9, 136.79, 136.78, 136.7, 136.4, 135.7, 134.1, 133.31, 133.31, 133.17, 133.17, 132.64, 132.63, 132.3, 132.1, 132.03, 132.00, 130.3, 129.9, 129.8, 129.1, 128.6, 127.9, 127.5, 127.3, 127.23, 127.17, 127.08, 127.05, 126.97, 126.95, 126.94, 126.86, 126.8, 126.53, 126.53, 126.4, 126.24, 126.19, 126.07, 126.07, 125.3, 119.4, 119.1, 21.74, 21.69, 21.5, 21.33, 21.25, 21.2, 20.8, 19.1. **IR** (neat, $cm^{-1}$): 2917, 1543, 1439, 1279, 1192, 1137, 881, 769, 746. **HRMS** (ESI) *m/z* calculated for $C_{66}H_{54}AlN_2O_2^+$ $(M - Cl)^+$ 933.3995, found 933.4019.

*Note*: NMR spectra collected in $CDCl_3$ at 22 °C displayed very broad resonances.

**[(*R*)-MesBinamAl]$^{+}$[Co(CO)$_4$]$^{-}$** ((*R*)-**1b**, (*R*)-MesBinam = (*R*)-3,3''-(([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-olate))




$NaCo(CO)_4$ (17.8 mg, 91.8 µmol), (*R*)-MesBinamAlCl ((*R*)-**ML1**, 75.0 mg, 91.8 µmol) and THF (4 ml) were mixed and stirred for 12 h at 22 °C. The reaction mixture was filtered through a 0.45 µm teflon syringe filter, carefully layered with hexane and then placed in a freezer at -34 °C for two days to give brown crystals of (*R*)-**1b**. A yield could not be obtained due to the unknown solvation state of (*R*)-**1b** upon isolation and drying *in vacuo*. **$^{1}$H NMR** (300 MHz, $C_6D_6$ + THF-$d_8$): δ 8.00 (s, 4H), 7.64 (d, *J* = 8.0 Hz, 4H), 7.12–7.02 (m, 6H), 6.96–6.91 (m, 2H), 6.88 (s, 2H), 6.66 (s, 2H), 6.53 (s, 2H), 2.29 (s, 6H), 1.92 (s, 6H), 1.86 (s, 6H), 1.79 (s, 6H). **$^{13}$C NMR** (126 MHz, THF-$d_8$): δ 173.2, 161.5, 146.8, 141.0, 138.8, 137.5, 135.9, 135.7, 134.2, 133.4, 133.3, 132.9, 131.6, 129.5, 129.2, 128.8, 128.0, 127.7, 127.5, 127.4, 126.9, 123.3, 120.7, 22.4, 21.2, 20.4, 20.3. **IR** (neat, cm$^{-1}$): 2916, 1878 $\nu_{(C=O)}$, 1616, 1588, 1551, 1440, 1218, 822.

Neither MS nor elemental analysis could be obtained to a satisfactory degree due to the unknown solvation state of (*R*)-**1b** in isolated form.

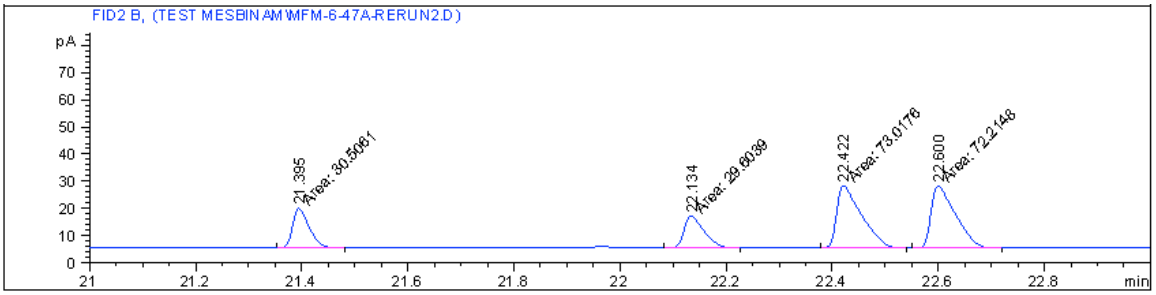
**Regiodivergent carbonylation of *racemic cis*-epoxides using (*R*)-1b**

**(3*R*,4*R*)-4-Butyl-3-methyloxetan-2-one (4a) and (3*R*,4*R*)-3-butyl-4-methyloxetan-2-one (5a)**


**4a** **5a**

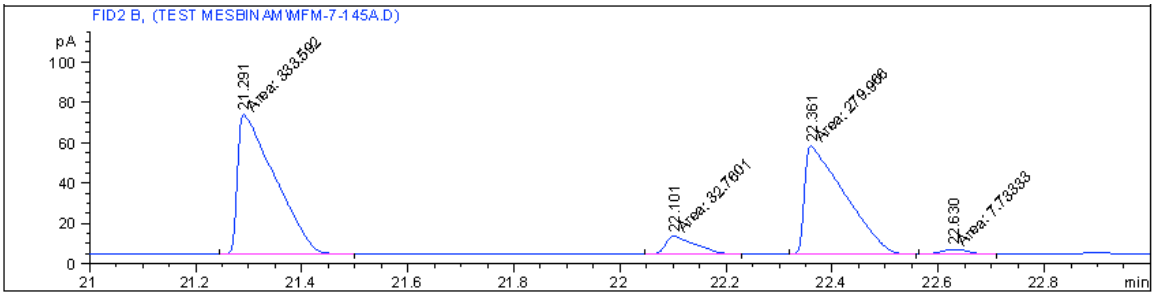
General procedure B was followed using (*R*)-**ML1** (8.2 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane[5] (*rac*-**3a**, 1.00 M, THF, 200 µl, 0.200 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was subjected to bulb-to-bulb distillation followed by flash column chromatography to give a 49 : 51 mixture of **4a** and **5a** (20.9 mg, 73 %) as a yellow oil. Analytical data for 4**a**[15] has previously been reported. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.40 (qd, *J* = 6.1, 4.0 Hz, 1H, **5a**), 4.17 (td, *J* = 6.7, 4.0 Hz, 1H, **4a**), 3.26–3.13 (m, 2H), 1.92–1.66 (m, 4H), 1.56 (d, *J* = 6.2 Hz, 3H, **5a**), 1.48–1.31 (m, 8H), 1.38 (d, *J* = 7.5 Hz, 3H, **4a**), 0.95–0.89 (m, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.2 (**4a**), 171.5 (**5a**), 79.7 (**4a**), 74.7 (**5a**), 57.6 (**5a**), 50.8 (**4a**), 33.9 (**4a**), 29.1 (**5a**), 27.5 (**5a**), 27.1 (**4a**), 22.43 (**5a**), 22.40 (**4a**), 20.4 (**5a**), 14.0 (**4a**), 13.9 (**5a**), 12.6 (**4a**). **IR** (neat, $cm^{-1}$): 2959, 2933, 2863, 1816, 1457, 1386, 1124, 828. **HRMS** (ES) *m/z* calculated for $C_8H_{14}O_2^+$ ($M^+$) 142.0994, found 142.0990. **Specific rotation**: $[\alpha]^{22}_D$ = +15.4 (*c* = 0.28, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 97.3 : 2.7 for **4a**, and 91.1 : 8.9 for **5a** by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.



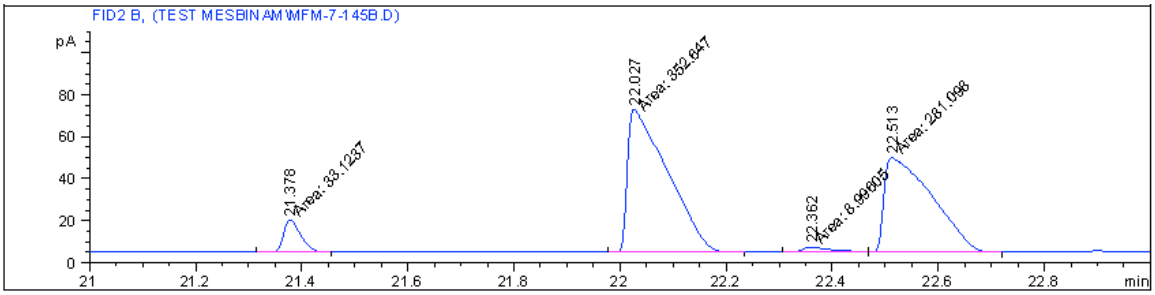

| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5a**) | 21.395 | MM | 0.0353 | 30.50614 | 14.40813 | 14.85623 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 (*ent*-**5a**) | 22.134 | MM | 0.0427 | 29.60390 | 11.56376 | 14.41684 |
| 3 (**4a**) | 22.422 | MM | 0.0534 | 73.01762 | 22.78206 | 35.55895 |
| 4 (*ent*-**4a**) | 22.600 | MM | 0.0530 | 72.21480 | 22.69843 | 35.16798 |




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5a**) | 21.291 | MM | 0.0802 | 333.59161 | 69.28416 | 51.00388 |
| 2 (*ent*-**5a**) | 22.101 | MM | 0.0621 | 32.76006 | 8.79531 | 5.00879 |
| 3 (**4a**) | 22.361 | MM | 0.0869 | 279.96649 | 53.69609 | 42.80496 |
| 4 (*ent*-**4a**) | 22.630 | MM | 0.0544 | 7.73333 | 2.36712 | 1.18237 |

Using (*S*)-**1b**, the enantiomeric ratio (er) was determined to be 96.9 : 3.1 for *ent*-**4a**, and 91.4 : 8.6 for *ent*-**5a**.

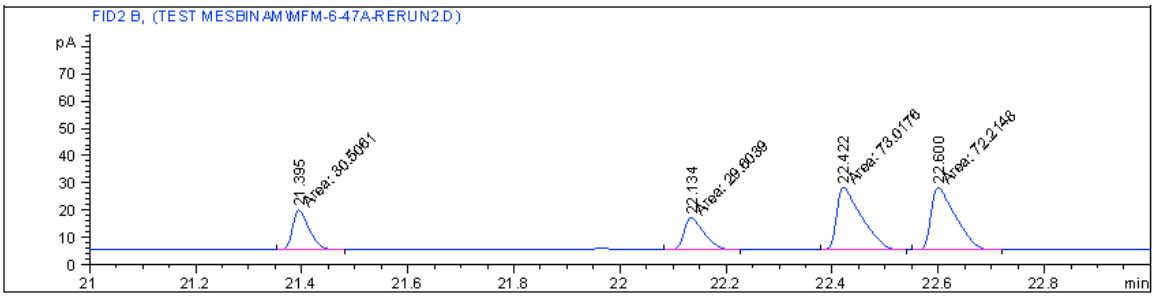



| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5a**) | 21.378 | MM | 0.0363 | 33.12371 | 15.21133 | 4.90094 |
| 2 (*ent*-**5a**) | 22.026 | MM | 0.0867 | 352.64651 | 68.80890 | 52.17713 |
| 3 (**4a**) | 22.362 | MM | 0.0604 | 8.99605 | 2.48336 | 1.33104 |
| 4 (*ent*-**4a**) | 22.513 | MM | 0.1038 | 21.097847 | 45.14734 | 41.59088 |

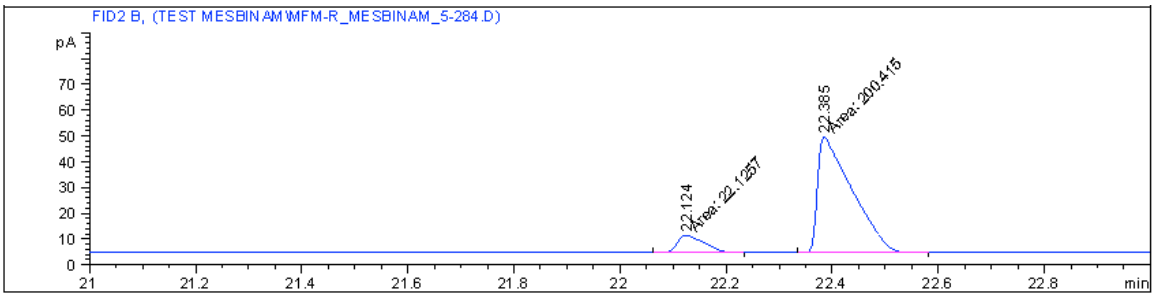
Stereochemical assignment of **4a** and **5a**:

The stereochemical identity of **4a** and **5a** was determined using a combination of $^{1}$H NMR and GC analysis. First, *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**3a**) was carbonylated using $[ClTPPAl(THF)_2]^+[Co(CO)_4]^-$ to give a corresponding *racemic* mixture of *rac*-**4a** and *rac*-**5a**. The major component in this β-lactone mixture was

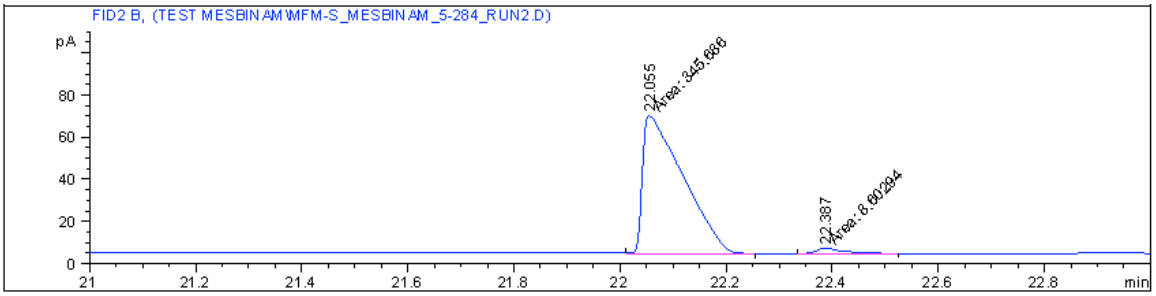
identified as *rac*-**4a** based on previously reported literature data.[15] Consequently, the two main peaks in the GC trace below (retention times 22.4 and 22.6 minutes) can be attributed to *rac*-**4a**, whereas the two minor peaks (retention times 21.4 and 22.1 minutes) stem from *rac*-**5a**.




Next, enantioenriched (2*R*,3*S*)-2-butyl-3-methyloxirane (**3a**) was carbonylated using (*R*)-**1b**, and the resulting β-lactone mixture analyzed by $^{1}$H NMR and GC (cf. Scheme 2). The main component was (3*R*,4*R*)-4-butyl-3-methyloxetan-2-one (**4a**), which allowed for identification of the main peak in the corresponding GC trace as **4a**, and the minor peak as (3*S*,4*S*)-3-butyl-4-methyloxetan-2-one (*ent*-**5a**).




Carbonylation of enantioenriched **3a** using (*S*)-**1b** yielded *ent*-**5a** as the main product and **4a** as the minor component as can be seen in the following GC trace.




In analogy, carbonylation of (2*S*,3*R*)-2-butyl-3-methyloxirane (*ent*-**3a**) using (*R*)-**1b** should give (3*R*,4*R*)-3-butyl-4-methyloxetan-2-one (**5a**) as the major product and

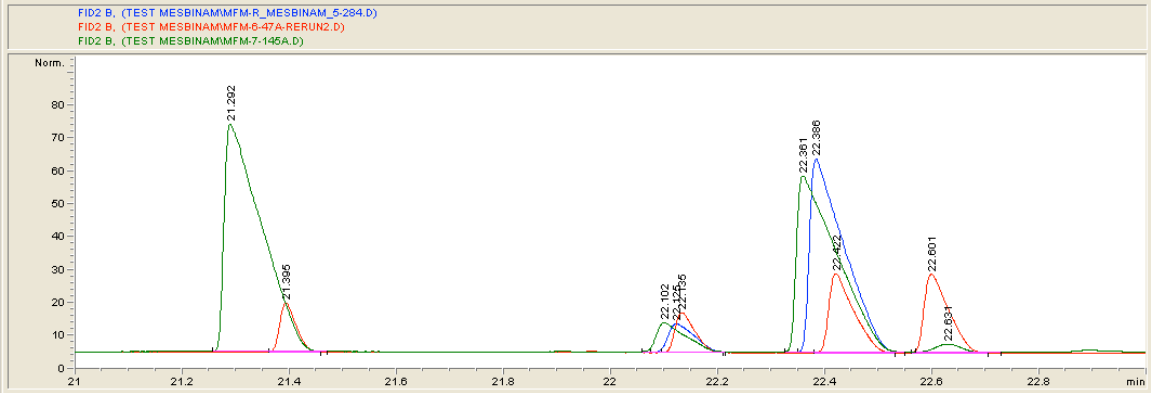
(3*S*,4*S*)-4-butyl-3-methyloxetan-2-one (*ent*-**4a**) as the minor product. Generally speaking, carbonylation of *racemic cis*-epoxides **3** using (*R*)-**1b** yields (3*R*,4*R*)-4-alkyl-3-methyloxetan-2-ones (**4**) and (3*R*,4*R*)-3-alkyl-4-methyloxetan-2-ones (**5**) as the main products, and (3*S*,4*S*)-4-alkyl-3-methyloxetan-2-ones (*ent*-**4**) and (3*S*,4*S*)-3-alkyl-4-methyloxetan-2-ones (*ent*-**5**) as the minor products.

The following chromatogram shows an overlay of some of the GC traces that were shown and discussed above:

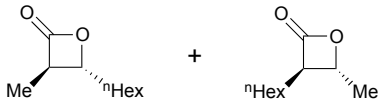
a) Carbonylation of *rac*-**3a** with $[ClTPPAl(THF)_2]^+[Co(CO)_4]^-$ (red GC trace)

b) Carbonylation of *rac*-**3a** with (*R*)-**1b** (green GC trace)

c) Carbonylation of **3a** with (*R*)-**1b** (blue GC trace)




**(3*R*,4*R*)-4-Hexyl-3-methyloxetan-2-one (4e) and (3*R*,4*R*)-3-hexyl-4-methyloxetan-2-one (5e)**

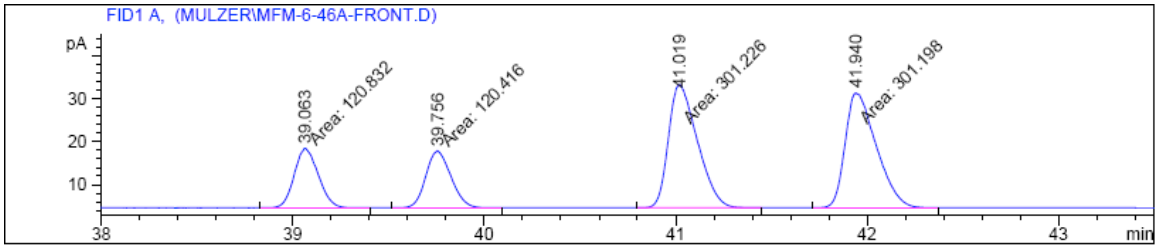



**4e** **5e**

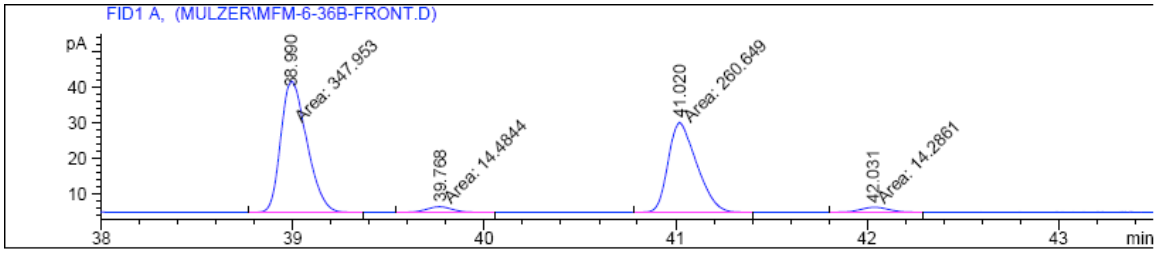
General procedure B was followed using (*R*)-**ML2** (9.7 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.03 mol %) and *rac*-(2*R*,3*S*)-2-hexyl-3-methyloxirane (*rac*-**3e**, 0.994 M, THF, 200 µl, 0.199 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was subjected to bulb-to-bulb distillation followed by flash column chromatography to give a 44 : 56 mixture of **4e** and **5e** (22.8 mg, 67 %) as a yellow oil. Analytical data for *racemic* **4e**[14] has previously been reported. **$^1$H NMR**

(300 MHz, $CDCl_3$): δ 4.40 (qd, $J$ = 6.1, 4.0 Hz, 1H, **5e**), 4.17 (td, $J$ = 6.6, 3.9 Hz, 1H, **4e**), 3.26–3.13 (m, 2H), 1.92–1.66 (m. 4H), 1.55 (d, $J$ = 6.1 Hz, 3H), 1.47–1.22 (m, 16H), 1.38 (d, $J$ = 7.6 Hz, 3H), 0.90–0.86 (m, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.2 (**4e**), 171.5 (**5e**), 79.7 (**4e**), 74.7 (**5e**), 57.7 (**5e**), 50.8 (**4e**), 34.2 (**4e**), 31.7 (**4e**), 31.6 (**5e**), 29.00 (**5e**), 28.96 (**4e**), 27.8 (**5e**), 26.9 (**5e**), 25.0 (**4e**), 22.60 (**5e**), 22.57 (**4e**), 20.4 (**5e**), 14.11 (**5e**), 14.11 (**4e**), 12.6 (**4e**). **IR** (neat, $cm^{-1}$): 2929, 2858, 1819, 1458, 1124, 828. **HRMS** (EI) *m/z* calculated for $C_{10}H_{18}O_2^+$ ($M^+$) 170.1307, found 170.1311. **Specific rotation**: $[\alpha]^{22}_D$ = +12.4 ($c$ = 0.35, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 94.8 : 5.2 for **4e**, and 96.0 : 4.0 for **5e** by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5e**) | 39.063 | MM | 0.1447 | 120.83189 | 13.91311 | 14.32215 |
| 2 (*ent*-**5e**) | 39.756 | MM | 0.1506 | 120.4157 | 13.32191 | 14.27282 |
| 3 (**4e**) | 41.019 | MM | 0.175 | 301.2261 | 28.68058 | 35.7042 |
| 4 (*ent*-**4e**) | 41.94 | MM | 0.1874 | 301.19757 | 26.7915 | 35.70082 |




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5e**) | 38.99 | MM | 0.1571 | 347.95285 | 36.91891 | 54.59175 |
| 2 (*ent*-**5e**) | 39.768 | MM | 0.1544 | 14.48438 | 1.56336 | 2.27251 |
| 3 (**4e**) | 41.02 | MM | 0.1716 | 260.64926 | 25.31508 | 40.89433 |
| 4 (*ent*-**4e**) | 42.031 | MM | 0.1687 | 14.28607 | 1.41159 | 2.2414 |

Stereochemical assignment of **4e** and **5e**:

The stereochemical identity of **4e** and **5e** was determined by first identifying the main component in the corresponding *racemic* β-lactone mixture as *racemic* **4e** based on previously reported data.[14] This allowed for the assignment of the peaks at 41.0 min and 41.9 min in the GC trace to *racemic* **4e**, and of the peaks at 39.1 min and 39.8 min to *racemic* **5e**.

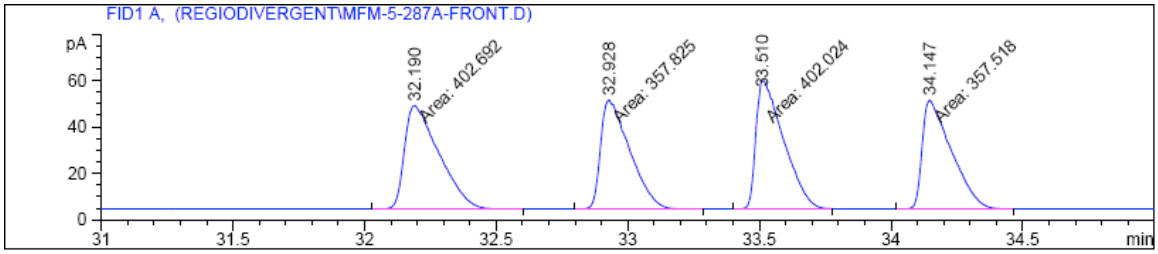
As is explained for the carbonylation of *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**3a**, p. S30), (*R*)-**1b** preferentially forms (3*R*,4*R*)-4-alkyl-3-methyloxetan-2-one (**4**) and (3*R*,4*R*)-3-alkyl-4-methyloxetan-2-one (**5**). Consequently, the major enantiomers of the two regioisomers should be (3*R*,4*R*)-4-hexyl-3-methyloxetan-2-one (**4e**) and (3*R*,4*R*)-3-hexyl-4-methyloxetan-2-one (**5e**).

**(3*R*,4*R*)-3-Ethyl-4-propyloxetan-2-one (4h) and (3*R*,4*R*)-4-ethyl-3-propyloxetan-2-one (5h)**

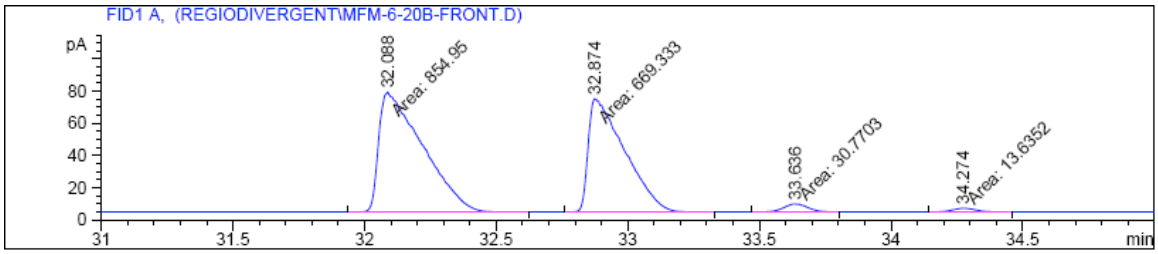

**4h** **5h**

General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.1 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.08 mol %) and *rac*-(2*R*,3*S*)-2-ethyl-3-propyloxirane[6] (*rac*-**3h**, 0.985 M, THF, 200 µl, 0.197 mmol). After stirring at 22 °C for 18.5 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give a 44 : 56 mixture of **4h** and **5h** (17.0 mg, 61 %) as a yellow oil. Analytical data for **4h**[16] and **5h**[15] has previously been reported. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.22 (ddd, *J* = 7.3, 6.1, 4.0 Hz, 1H, **4h**), 4.15 (td, *J* = 6.6, 4.0 Hz, 1H, **5h**), 3.20–3.09 (m, 2), 1.94–1.62 (m, 8H), 1.51–1.35 (m, 4H), 1.01 (t, *J* = 7.6 Hz, 3H, **4h**), 0.99 (t, *J* = 7.5 Hz, 3H, **5h**), 0.96 (t, *J* = 7.7 Hz, 3H, **4h**), 0.93 (t, *J* = 7.4 Hz, 3H, **5h**). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.7 (**4h**), 171.6 (**5h**), 79.3 (**5h**), 77.5 (**4h**), 57.6 (**4h**), 55.6 (**5h**), 36.6 (**4h**), 30.0 (**5h**), 27.6 (**5h**), 21.1 (**4h**), 20.4 (**5h**), 18.5 (**4h**), 13.83 (**4h**), 13.83 (**5h**), 11.3 (**4h**), 9.2 (**5h**). **IR** (neat, $cm^{-1}$): 2964, 2936, 2877, 1814, 1463, 1383, 1124, 868, 821. **HRMS** (ESI) *m/z* calculated for $C_8H_{15}O_2^+$ ($M + H^+$) 143.1067, found 143.1074. **Specific rotation**: $[\alpha]^{22}_D$ = +11.6 (*c* = 0.26, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 98.0 : 2.0 for **4h**, and 96.5 : 3.5 for **5h** by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5h**) | 32.19 | MM | 0.1508 | 402.69193 | 44.50388 | 26.49188 |
| 2 (**4h**) | 32.928 | MM | 0.1273 | 357.82501 | 46.8356 | 23.54022 |
| 3 (*ent*-**5h**) | 33.51 | MM | 0.121 | 402.02359 | 55.39784 | 26.44791 |
| 4 (*ent*-**4h**) | 34.147 | MM | 0.1273 | 357.51758 | 46.7909 | 23.51999 |




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5h**) | 32.088 | MM | 0.1915 | 854.95007 | 74.40437 | 54.50094 |
| 2 (**4h**) | 32.874 | MM | 0.1588 | 669.33313 | 70.25794 | 42.66832 |
| 3 (*ent*-**5h**) | 33.636 | MM | 0.1044 | 30.77026 | 4.91322 | 1.96153 |
| 4 (*ent*-**4h**) | 34.274 | MM | 0.0997 | 13.63518 | 2.27972 | 0.86921 |

Stereochemical assignment of **4h** and **5h**:

The stereochemical identity of **4h** and **5h** was determined by first identifying the main component in the corresponding *racemic* β-lactone mixture as *racemic* **5h** based on previously reported analytical data.[15,16] As is explained for the carbonylation of *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**3a**, p. S30), (*R*)-**1b** preferentially forms (3*R*,4*R*)-4-alkyl-3-methyloxetan-2-one (**4**) and (3*R*,4*R*)-3-alkyl-4-methyloxetan-2-one (**5**). Assuming that this preference is not altered by substituting the methyl-group with an ethyl-group, and given that the elution profile of **4h** and **5h** in the GC trace resembles that of **4a** and **5a** (i.e. the major enantiomer elutes first for both regioisomers), the major

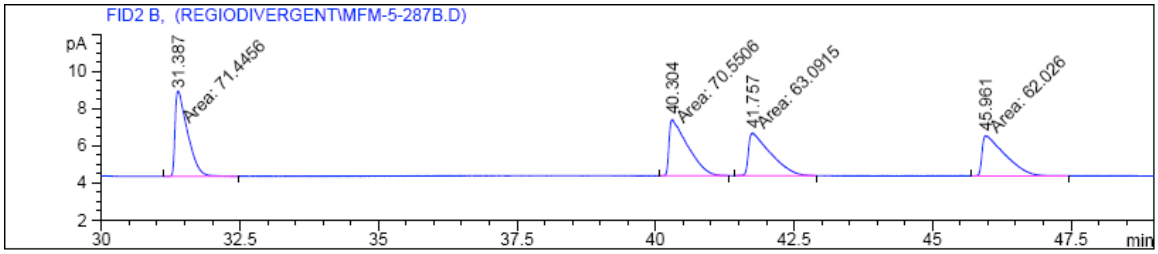
enantiomers of the two regioisomers should be (3*R*,4*R*)-3-ethyl-4-propyloxetan-2-one (**4h**) and (3*R*,4*R*)-4-ethyl-3-propyloxetan-2-one (**5h**). The sign of the specific rotation further supports this assignment, because it is identical to that of β-lactone mixture of **4a** and **5a**.

**(3*R*,4*R*)-4-Butyl-3-ethyloxetan-2-one (4i) and (3*R*,4*R*)-3-butyl-4-ethyloxetan-2-one (5i)**

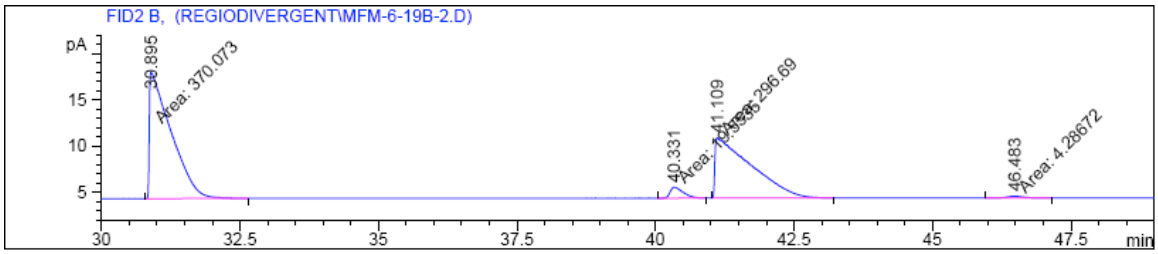

**4i** **5i**

General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-butyl-3-ethyloxirane[7] (*rac*-**3i**, 1.00 M, THF, 200 µl, 0.200 mmol). After stirring at 22 °C for 18.5 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give a 44 : 56 mixture of **4i** and **5i** (22.8 mg, 73 %) as a yellow oil. Analytical data for *racemic* **4i** has previously been reported.[17] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.22–4.17 (m, 1H, **4i**), 4.17–4.11 (m, 1H, **5i**), 3.17–3.07 (m, 2H), 1.92–1.62 (m, 8H), 1.44–1.26 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.90–0.86 (m, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.6 (**4i**), 171.5 (**5i**), 79.2 (**5i**), 77.7 (**4i**), 57.5 (**4i**), 55.7 (**5i**), 34.2 (**4i**), 29.2 (**5i**), 27.6 (**5i**), 27.5 (**5i**), 27.1 (**4i**), 22.41 (**4i**), 22.38 (**5i**), 21.1 (**4i**), 13.9 (**4i**), 13.8 (**5i**), 11.3 (**4i**), 9.1 (**5i**). **IR** (neat, $cm^{-1}$): 2960, 2993, 2863, 1816, 1462, 1382, 1123, 851. **HRMS** (ESI) *m/z* calculated for $C_9H_{17}O_2^+$ ($M + H^+$) 157.1223, found 157.1233. **Specific rotation**: $[\alpha]^{22}_D$ = +5.2 (*c* = 0.35, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 98.6 : 1.4 for **4i**, and 95.0 : 5.0 for **5i** by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.




| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5i**) | 31.387 | MM | 0.2586 | 71.44564 | 4.60474 | 26.74727 |
| 2 (*ent*-**5i**) | 40.304 | MM | 0.3871 | 70.55064 | 3.03754 | 26.4122 |
| 3 (**4i**) | 41.757 | MM | 0.4551 | 63.09148 | 2.3104 | 23.6197 |
| 4 (*ent*-**4i**) | 45.961 | MM | 0.4795 | 62.02603 | 2.15614 | 23.22083 |

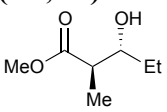



| Peak # (*compound*) | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 (**5i**) | 30.895 | MM | 0.4506 | 370.07291 | 13.68907 | 53.58688 |
| 2 (*ent*-**5i**) | 40.331 | MF | 0.2743 | 19.55349 | 1.1881 | 2.83136 |
| 3 (**4i**) | 41.109 | FM | 0.7601 | 296.6904 | 6.50563 | 42.96103 |
| 4 (*ent*-**4i**) | 46.483 | MM | 0.3529 | 4.28672 | 2.02E-01 | 0.62072 |

Stereochemical assignment of **4i** and **5i**:

The stereochemical identity of **4i** and **5i** was determined by first identifying the main component in the corresponding *racemic* β-lactone mixture as *racemic* **5i** based on previously reported analytical data.[17] The identity of **4i** and **5i** was then further assigned based on the assignment made for **4h** and **5h** (see p. S35).

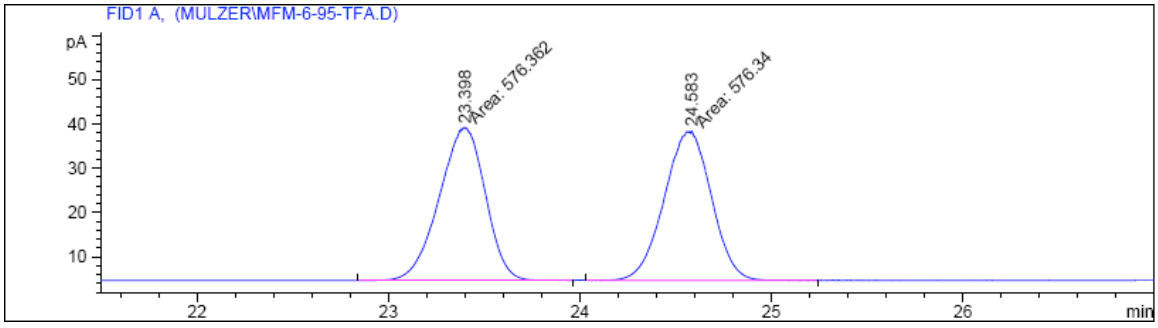
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylpentanoate (6b)**



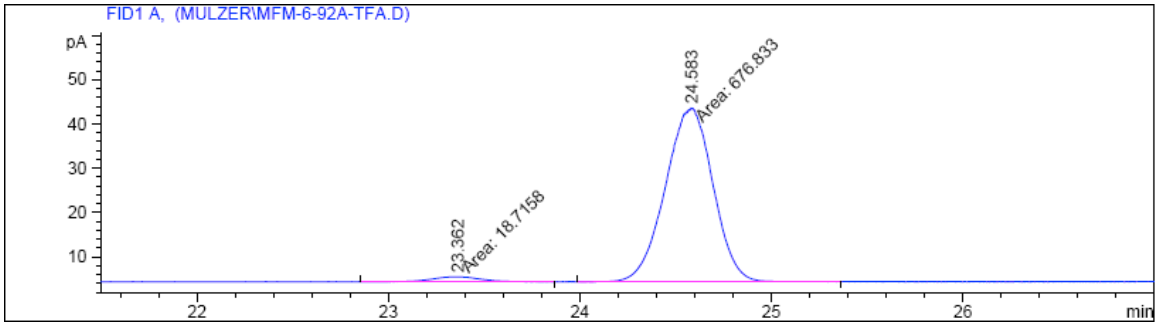

General procedure B was followed using (*R*)-**ML1** (8.3 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-ethyl-3-methyloxirane (*rac*-**3b**, 0.998 M, THF, 200 µl, 0.200 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium

methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **6b** (11.1 mg, 38 %) as a yellow oil. Analytical data for this compound has previously been reported.[18] $\boldsymbol{R_f}$ = 0.40 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.29. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.59 (dtd, *J* = 8.5, 6.5, 3.9 Hz, 1H), 2.56 (d, *J* = 6.7 Hz, 1H), 2.55 (td, *J* = 7.2, 6.5 Hz, 1H), 1.54 (dtt, *J* = 14.1, 7.5, 4.0 Hz, 1H), 1.47–1.36 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 176.6, 74.8, 51.83, 44.9, 27.7, 14.4, 9.9. **Specific rotation**: $[\alpha]^{22}_D$ = -6.8 (*c* = 0.99, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 2.7 : 97.3 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6b** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 23.398 | MM | 0.2783 | 576.36206 | 34.51988 | 50.00097 |
| 2 | 24.583 | MM | 0.285 | 576.33972 | 33.70103 | 49.99903 |

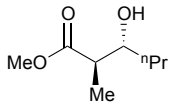



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 23.362 | MM | 0.2794 | 18.71581 | 1.11647 | 2.6908 |
| 2 | 24.583 | MM | 0.2879 | 676.83282 | 39.18534 | 97.3092 |

Stereochemical assignment of **6b**:

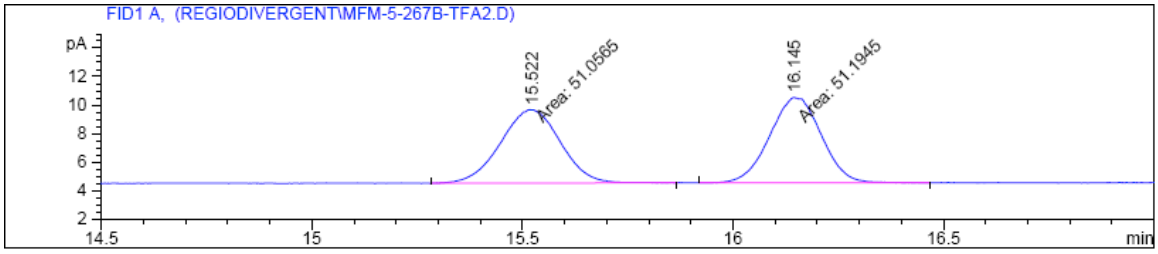
The stereochemical identity of **6b** was determined by comparing the specific rotation of **6b** under identical conditions to that reported in the literature for (2*R*,3*R*)-methyl 3-hydroxy-2-methylpentanoate.[18] The literature known compound and **6b** displayed the same sign of rotation.

**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylhexanoate (6c)**

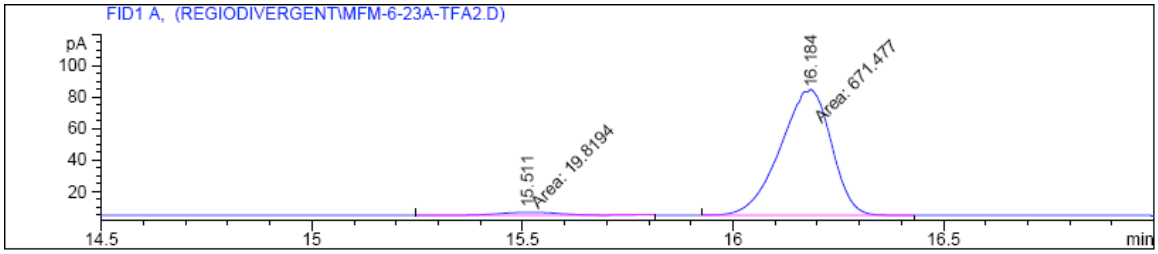



General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.1 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.08 mol %) and *rac*-(2*R*,3*S*)-2-methyl-3-propyloxirane (*rac*-**3c**, THF, 0.983 M, 200 µl, 0.197 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **6c** (10.1 mg, 32 %) as a yellow oil. Analytical data for this compound has previously been reported.[19] $\boldsymbol{R_f}$ = 0.38 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.25. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.69–3.65 (m, 1H), 2.56–2.49 (m, 1H), 2.48 (broad s, 1H), 1.56–1.36 (m, 4H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 176.6, 73.3, 51.9, 45.4, 37.1, 18.9, 14.5, 14.2. **Specific rotation**: $[\alpha]^{22}_D$ = -3.4 (*c* = 1.6, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 2.9 : 97.1 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6c** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.522 | MM | 0.1655 | 51.05653 | 5.14305 | 49.93251 |
| 2 | 16.145 | MM | 0.1422 | 51.19454 | 5.9997 | 50.06749 |

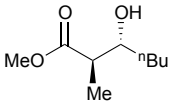



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.511 | MM | 0.1742 | 19.81944 | 1.89599 | 2.867 |
| 2 | 16.184 | MM | 0.14 | 671.47723 | 79.93716 | 97.133 |

Stereochemical assignment of **6c**:

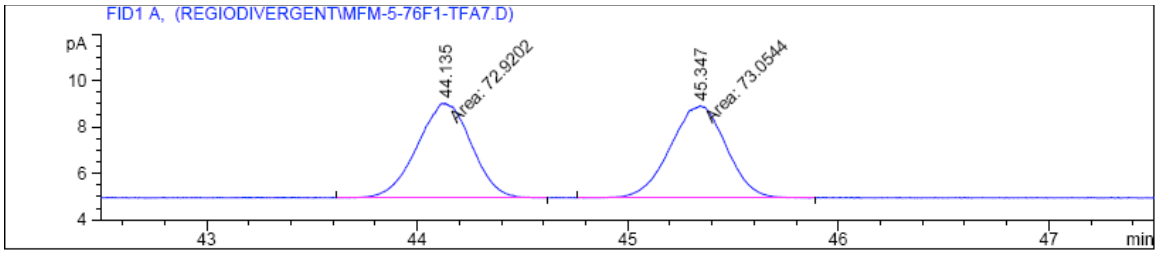
The stereochemical identity of **6c** was determined by comparing the specific rotation of **6c** under identical conditions to that reported in the literature for (2*R*,3*R*)-methyl 3-hydroxy-2-methylhexanoate.[19] The literature known compound and **6c** displayed the same sign of rotation.

**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylheptanoate (6a)**

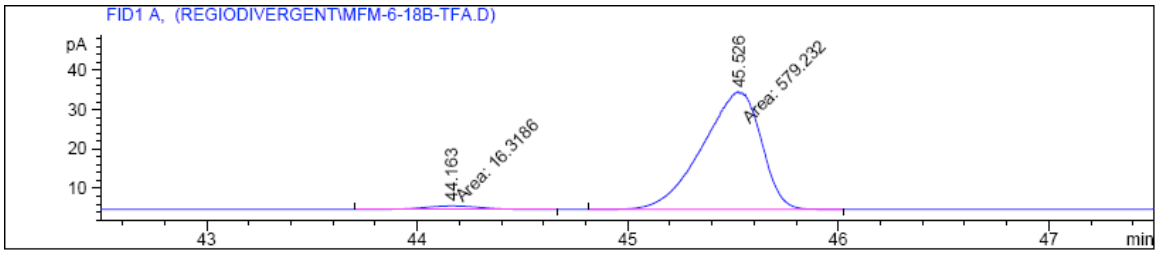



General procedure B was followed using (*R*)-**ML1** (8.2 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane[5] (*rac*-**3a**, 1.00 M, THF, 200 µl, 0.200 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **6a** (12.5 mg, 36 %) as a yellow oil. Analytical data for this compound has previously been reported.[20] $\boldsymbol{R_f}$ = 0.40 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.29. $\boldsymbol{R_f}$ = 0.37 (20 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.24. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.65 (ddd, *J* = 8.4, 6.3, 3.0 Hz, 1H), 2.56–2.49 (m, 1H), 2.49 (broad s, 1H). 1.52–1.25 (m, 6H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 176.6, 73.5, 51.9, 45.3, 34.6, 27.8, 22.8, 14.5, 14.2. **Specific rotation**: $[\alpha]^{22}_D$ = -4.7 (*c* = 1.1, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 2.7 : 97.3 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6a** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 44.135 | MM | 0.2983 | 72.92017 | 4.07483 | 49.95404 |
| 2 | 45.347 | MM | 0.3074 | 73.05435 | 3.96065 | 50.04596 |

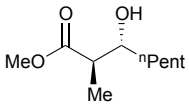



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 44.163 | MM | 0.2998 | 16.31861 | 9.07E-01 | 2.74009 |
| 2 | 45.526 | MM | 0.3227 | 579.23212 | 29.91504 | 97.25991 |

Stereochemical assignment of **6a**:

The stereochemical identity of **6a** was determined by comparing the specific rotation of **6a** under identical conditions to that reported in the literature for (2*R*,3*R*)-methyl 3-hydroxy-2-methylheptanoate.[20] The literature known compound and **6a** displayed the same sign of rotation.

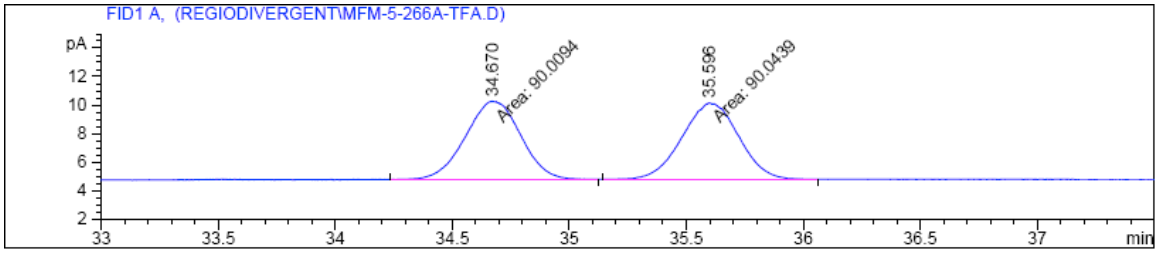
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methyloctanoate (6d)**



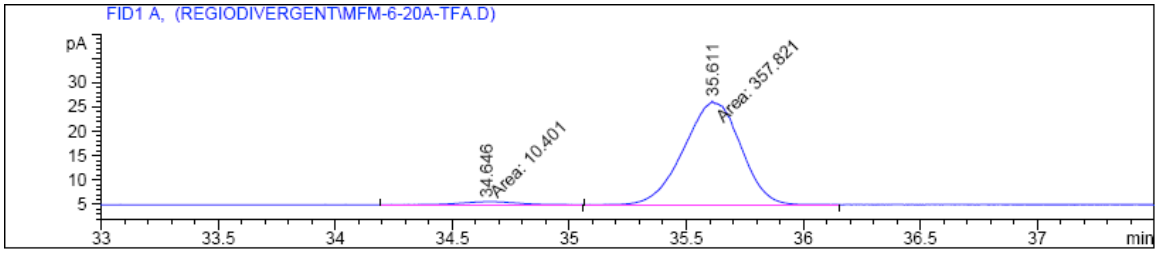

General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-

methyl-3-pentyloxirane (*rac*-**3d**, 1.00 M, THF, 200 µl, 0.200 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **6d** (12.9 mg, 34 %) as a yellow oil. Analytical data for this compound has previously been reported.[21] $\boldsymbol{R_f}$ = 0.51 (25 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.34. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.66 (dt, *J* = 6.6, 4.1 Hz, 1H), 2.57–2.50 (m, 1H), 2.48 (broad s, 1H), 1.52–1.25 (m, 8H), 1.22 (d, *J* = 7.2 Hz, 3H), 0.91–0.87 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 176.6, 73.5, 51.8, 45.3, 34.8, 31.9, 25.3, 22.7, 14.5, 14.2. **Specific rotation**: $[\alpha]^{22}_D$ = -4.9 (*c* = 1.5, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 2.8 : 97.2 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6d** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 34.67 | MM | 0.2729 | 90.00943 | 5.49704 | 49.99044 |
| 2 | 35.596 | MM | 0.2798 | 90.04386 | 5.36409 | 50.00956 |

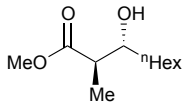



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 34.646 | MM | 0.2728 | 10.40101 | 6.35E-01 | 2.82466 |
| 2 | 35.611 | MM | 0.2806 | 357.82089 | 21.25685 | 97.17534 |

Stereochemical assignment of **6d**:

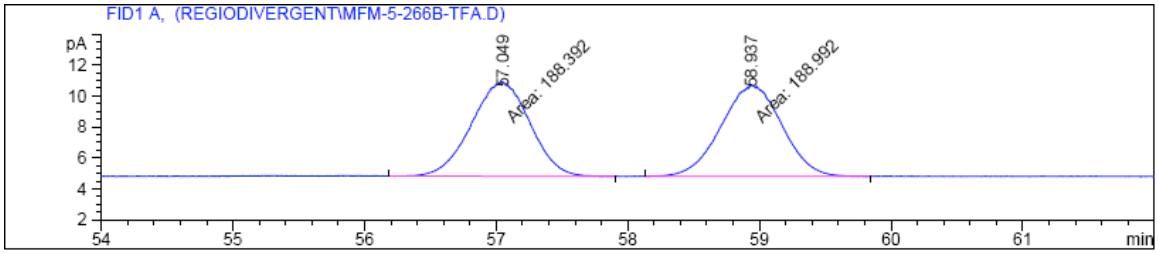
The stereochemical identity of **6d** was determined by comparing the specific rotation of **6d** under identical conditions to that reported in the literature for (2*R*,3*R*)-methyl 3-hydroxy-2-methyloctanoate.[21] The literature known compound and **6d** displayed the same sign of rotation.

**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylnonanoate (6e)**

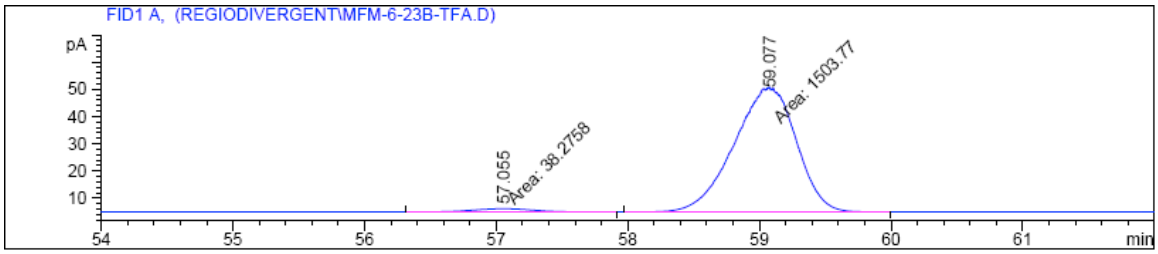



General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.0 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.00 mol %) and *rac*-(2*R*,3*S*)-2-hexyl-3-methyloxirane (*rac*-**3e**, 0.991 M, THF, 200 µl, 0.198 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **3e** (13.3 mg, 33 %) as a yellow oil. Analytical data for this compound has previously been reported.[22] $\boldsymbol{R_f}$ = 0.46 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.27. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.65 (td, *J* = 7.2, 6.1, 2.8 Hz, 1H), 2.57–2.49 (m, 1H), 2.48 (broad s, 1H), 1.52–1.24 (m, 10H), 1.21 (d, *J* = 7.3 Hz, 3H), 0.90–0.86 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 176.7, 73.5, 51.9, 45.3, 34.9, 31.9, 29.4, 25.6, 22.8, 14.5, 14.2. **Specific rotation**: $[\alpha]^{22}_D$ = -4.3 (*c* = 1.0, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 2.5 : 97.5 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6e** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 57.049 | MM | 0.515 | 188.39207 | 6.09693 | 49.92051 |
| 2 | 58.937 | MM | 0.531 | 188.99207 | 5.93201 | 50.07949 |

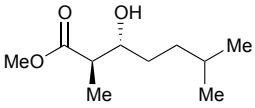



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 57.055 | MM | 0.5185 | 38.27585 | 1.23033 | 2.48215 |
| 2 | 59.077 | MM | 0.5464 | 1503.76831 | 45.86915 | 97.51785 |

Stereochemical assignment of **6e**:

The stereochemical identity of **6e** was determined by comparing the specific rotation of **6e** under identical conditions to that reported in the literature for (2*R*,3*R*)-methyl 3-hydroxy-2-methylnonanoate.[22] The literature known compound and **6e** displayed the same sign of rotation.

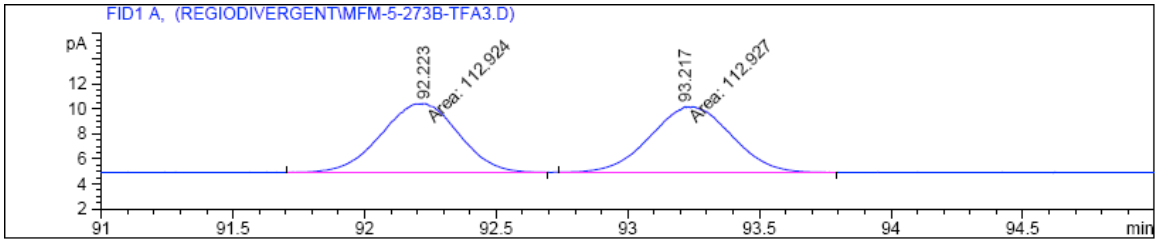
**(2*R*,3*R*)-Methyl 3-hydroxy-2,6-dimethylheptanoate (6f)**



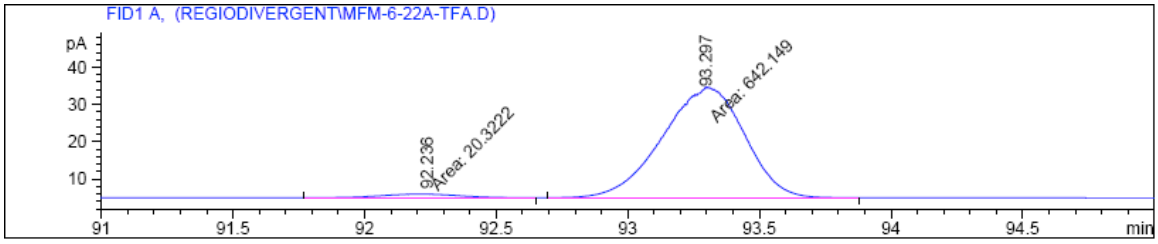

General procedure B was followed using (*R*)-**ML1** (8.3 mg, 0.010 mmol, 5.1 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.08 mol %) and *rac*-(2*R*,3*S*)-2-isopentyl-3-methyloxirane (*rac*-**3f**, 0.983 M, THF, 200 µl, 0.197 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column

chromatography to give **6f** (13.4 mg, 36 %) as a yellow oil. $R_f$ = 0.48 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.29. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.62 (ddd, *J* = 8.1, 6.3, 3.8 Hz, 1H), 2.53 (p, *J* = 7.0 Hz, 1H), 2.50 (broad s, 1H), 1.60–1.16 (m, 5H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.8 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 176.6, 73.7, 51.8, 45.2, 34.7, 32.7, 28.1, 22.8, 22.5, 14.5. **IR** (neat, $cm^{-1}$): 3458, 2953, 2870, 1720, 1460, 1196, 1169, 1025. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{20}NaO_3^+$ (M + $Na^+$) 211.1305, found 211.1307. **Specific rotation**: $[\alpha]^{22}_D$ = -6.6 (*c* = 1.2, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 3.1 : 96.9 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6f** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 92.223 | FM | 0.3413 | 112.92448 | 5.51484 | 49.99934 |
| 2 | 93.217 | MF | 0.3572 | 112.92747 | 5.26861 | 50.00066 |



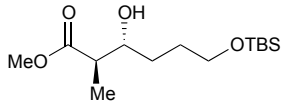

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 92.236 | MF | 0.3406 | 20.32217 | 9.94E-01 | 3.06763 |
| 2 | 93.297 | MF | 0.3594 | 642.14899 | 29.77535 | 96.93237 |

Stereochemical assignment of **6f**:

The stereochemical identity of **6f** was determined by comparing the order of elution of the two enantiomers during GC analysis with that of **6a-e**. Furthermore, the specific

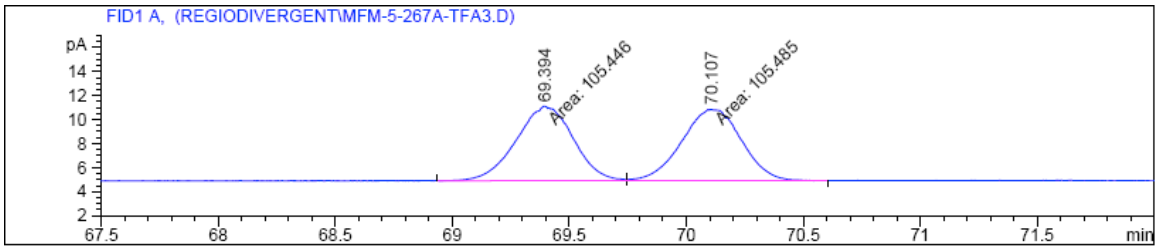
rotation of **6f** was compared under identical conditions to that of **6a-e**. Compounds **6a-e** and **6f** displayed the same sign of rotation.

**(2*R*,3*R*)-Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-2-methylhexanoate (6g)**

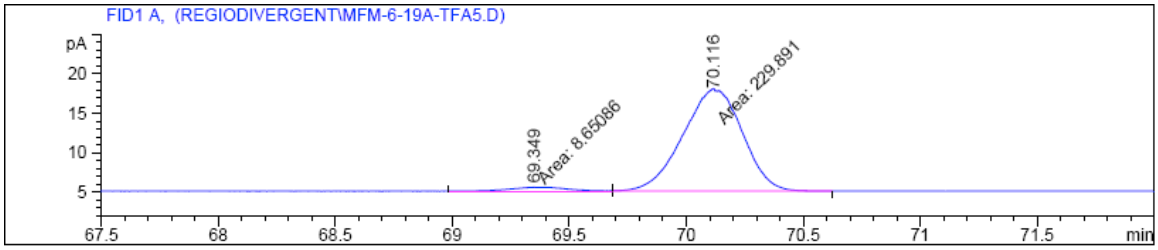



General procedure B was followed using (*R*)-**ML1** (8.4 mg, 0.010 mmol, 5.1 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 5.05 mol %) and *rac-tert*-butyldimethyl(3-((2*R*,3*S*)-3-methyloxiran-2-yl)propoxy)silane (*rac*-**3g**, 0.991 M, THF, 200 µl, 0.198 mmol). After stirring at 22 °C for 20 h, the crude reaction mixture was treated with methanol (0.4 ml) and sodium methoxide (ca. 14.0 mg, ca. 0.259 mmol), stirred for 5 minutes at 22 °C and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give **6g** (20.0 mg, 35 %) as a yellow oil. $R_f$ = 0.33 (50 % $Et_2O$ in pentane); $R_f$ of discarded isomer = 0.27. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.73–3.63 (m, 1H), 3.69 (s, 3H), 3.65 (t, *J* = 5.8 Hz, 2H), 3.13 (broad s, 1H), 2.54 (p, *J* = 7.1 Hz, 1H), 1.71–1.60 (m, 3H), 1.52–1.39 (m, 1H), 1.18 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 176.4, 73.1, 63.3, 51.8, 45.5, 31.6, 29.0, 26.1, 18.4, 14.1, -5.2. **IR** (neat, $cm^{-1}$): 2952, 2857, 1739, 1462, 1254, 1093, 833, 774. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{31}O_4Si^+$ ($M + H^+$) 291.1986, found 291.1991. **Specific rotation**: $[\alpha]^{22}_D$ = -3.6 (*c* = 2.7, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 3.6 : 96.4 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material. Prior to GC analysis, ester **6g** was derivatized following general procedure C.




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 69.394 | MF | 0.2833 | 105.44571 | 6.20387 | 49.99075 |
| 2 | 70.107 | FM | 0.2959 | 105.48472 | 5.94137 | 50.00925 |

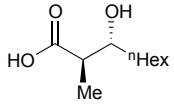



| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 69.349 | MF | 0.2862 | 8.65086 | 5.04E-01 | 3.62655 |
| 2 | 70.116 | FM | 0.2941 | 229.89117 | 13.02643 | 96.37345 |

Stereochemical assignment of **6g**:

The stereochemical identity of **6g** was determined by comparing the order of elution of the two enantiomers during GC analysis with that of **6a-e**. Furthermore, the specific rotation of **6g** was compared under identical conditions to that of **6a-e**. Compounds **6a-e** and **6g** displayed the same sign of rotation.

**(2*R*,3*R*)-3-Hydroxy-2-methylnonanoic acid (7)**




(2*R*,3*R*)-Methyl 3-hydroxy-2-methylnonanoate (**6e**) was converted into **7** using a previously published method.[23] Ester **6e** (12 mg, 0.059 mmol) was dissolved in a mixture of THF, methanol and water (1:1:1, 0.9 ml), and lithium hydroxide monohydrate (13 mg, 0.31 mmol) was added. The mixture was stirred at 22 °C until no more starting material was detected by TLC. Water was added and the reaction mixture extracted with DCM once. The aqueous phase was acidified using hydrochloric acid (1 M, aq.), and then extracted with $Et_2O$ (3x). The organic phase was dried with sodium sulfate and subsequently concentrated under reduced pressure to give **7** as a colorless oil (10 mg, 90 %). The analytical data matched that reported in the literature.[23] **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.68 (broad s, 1H), 3.70 (m, 1H), 2.56 (p, $J$ = 7.1 Hz, 1H), 1.71–1.11 (m, 11H), 1.24 (d, $J$ = 7.2 Hz, 3H), 0.96–0.81 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 181.2, 73.5, 45.4, 34.7, 31.9, 29.3, 25.5, 22.8, 14.4, 14.2. $[\alpha]^{22}_D$ = +3.8 ($c$ = 0.90, $CHCl_3$).

**Crystallographic data for (*R*)-1b**

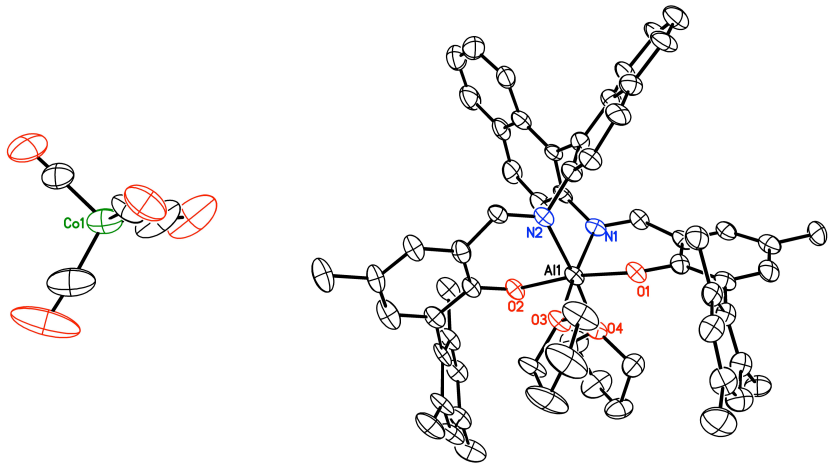



**Table S3.** Crystal data and structure refinement for (*R*)-**1b**

| | | |
|---|---|---|
| Identification code | (*R*)-**1b** | |
| Empirical formula | $C_{66}H_{62}AlCoN_2O_8$ | |
| Formula weight | 1097.09 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 11.5495(11) Å | α = 90° |
| | b = 21.268(2) Å | β = 90° |
| | c = 28.170(3) Å | γ = 90° |
| Volume | 6919.5(12) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.053 $Mg/m^3$ | |
| Absorption coefficient | 0.308 $mm^{-1}$ | |
| F(000) | 2304 | |
| Crystal size | 0.35 x 0.20 x 0.15 $mm^3$ | |
| Theta range for data collection | 1.45 to 23.84° | |
| Index ranges | -7<=h<=13, -20<=k<=24, -30<=l<=31 | |
| Reflections collected | 22724 | |

| | |
|---|---|
| Independent reflections | 10625 [R(int) = 0.0439] |
| Completeness to theta = 23.26° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9552 and 0.8997 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10625 / 54 / 713 |
| Goodness-of-fit on $F^2$ | 0.977 |
| Final R indices [I>2sigma(I)] | R1 = 0.0576, wR2 = 0.1370 |
| R indices (all data) | R1 = 0.0864, wR2 = 0.1481 |
| Absolute structure parameter | 0.02(2) |
| Largest diff. peak and hole | 0.263 and -0.357 e.$Å^{-3}$ |

*Note*: The A level alerts in the Checkcif-file are caused by the presence of empty spaces in the structure, i. e. the place where disordered THF solvent molecules (removed from the model by using the SQUEEZE option in the program PLATON) used to reside.

**Table S4.** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for (*R*)-**1b**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Al(1) | 726(1) | 5441(1) | -2037(1) | 30(1) |
| O(1) | 153(2) | 5974(1) | -2482(1) | 33(1) |
| O(2) | 1488(2) | 4890(1) | -1661(1) | 33(1) |
| O(3) | 2237(2) | 5840(1) | -2184(1) | 36(1) |
| O(4) | 939(2) | 4809(1) | -2539(1) | 35(1) |
| N(1) | -933(3) | 5143(1) | -1913(1) | 32(1) |
| N(2) | 506(3) | 5989(1) | -1462(1) | 32(1) |
| C(1) | -1264(3) | 4968(2) | -1449(2) | 35(1) |
| C(2) | -1312(4) | 4318(2) | -1317(2) | 44(1) |
| C(3) | -1673(4) | 4156(2) | -876(2) | 49(1) |
| C(4) | -1992(4) | 4620(2) | -531(2) | 45(1) |
| C(5) | -2320(5) | 4453(3) | -65(2) | 70(2) |
| C(6) | -2530(5) | 4900(3) | 275(2) | 65(2) |
| C(7) | -2402(5) | 5520(3) | 152(2) | 61(1) |
| C(8) | -2115(4) | 5707(2) | -299(2) | 47(1) |
| C(9) | -1896(4) | 5258(2) | -664(2) | 40(1) |
| C(10) | -1569(4) | 5426(2) | -1127(2) | 31(1) |
| C(11) | -1559(4) | 6100(2) | -1284(2) | 34(1) |
| C(12) | -2573(4) | 6482(2) | -1271(2) | 43(1) |
| C(13) | -3693(4) | 6221(2) | -1204(2) | 43(1) |
| C(14) | -4644(4) | 6600(2) | -1215(2) | 57(1) |
| C(15) | -4543(5) | 7246(2) | -1288(2) | 60(2) |
| C(16) | -3491(5) | 7527(2) | -1349(2) | 58(2) |
| C(17) | -2470(5) | 7143(2) | -1351(2) | 45(1) |
| C(18) | -1371(5) | 7397(2) | -1437(2) | 50(1) |
| C(19) | -403(4) | 7025(2) | -1487(2) | 38(1) |
| C(20) | -509(4) | 6378(2) | -1408(2) | 38(1) |
| C(21) | -1771(4) | 5215(2) | -2209(2) | 34(1) |
| C(22) | -1720(4) | 5544(2) | -2665(2) | 34(1) |
| C(23) | -2677(4) | 5526(2) | -2957(2) | 40(1) |
| C(24) | -2749(4) | 5871(2) | -3362(2) | 43(1) |
| C(25) | -1767(4) | 6239(2) | -3481(2) | 44(1) |
| C(26) | -795(4) | 6285(2) | -3197(2) | 37(1) |

| | | | | |
|---|---|---|---|---|
| C(27) | -766(4) | 5936(2) | -2770(2) | 34(1) |
| C(28) | -3796(4) | 5868(3) | -3678(2) | 58(1) |
| C(29) | 235(4) | 6646(2) | -3362(2) | 36(1) |
| C(30) | 599(4) | 7208(2) | -3119(2) | 41(1) |
| C(31) | 1567(5) | 7511(2) | -3279(2) | 48(1) |
| C(32) | 2216(5) | 7311(2) | -3649(2) | 56(1) |
| C(33) | 1845(5) | 6774(2) | -3905(2) | 54(1) |
| C(34) | 836(4) | 6462(2) | -3760(2) | 43(1) |
| C(35) | -51(4) | 7446(2) | -2695(2) | 47(1) |
| C(36) | 3336(5) | 7626(3) | -3792(3) | 81(2) |
| C(37) | 469(5) | 5894(2) | -4056(2) | 51(1) |
| C(38) | 1185(4) | 5994(2) | -1101(2) | 33(1) |
| C(39) | 2152(4) | 5566(2) | -1040(2) | 39(1) |
| C(40) | 2251(4) | 5013(2) | -1316(2) | 32(1) |
| C(41) | 3118(4) | 4591(2) | -1208(2) | 39(1) |
| C(42) | 3885(4) | 4710(2) | -843(2) | 57(2) |
| C(43) | 3798(4) | 5273(2) | -557(2) | 46(1) |
| C(44) | 2917(4) | 5679(2) | -673(2) | 48(1) |
| C(45) | 4629(5) | 5383(2) | -156(2) | 67(2) |
| C(46) | 3307(4) | 3994(2) | -1486(2) | 38(1) |
| C(47) | 4257(4) | 3898(2) | -1786(2) | 44(1) |
| C(48) | 4336(4) | 3356(2) | -2046(2) | 53(1) |
| C(49) | 3522(4) | 2865(2) | -2015(2) | 48(1) |
| C(50) | 2633(4) | 2953(2) | -1693(2) | 42(1) |
| C(51) | 2478(4) | 3489(2) | -1439(2) | 39(1) |
| C(52) | 5217(4) | 4381(2) | -1827(2) | 63(2) |
| C(53) | 3637(5) | 2284(2) | -2313(2) | 73(2) |
| C(54) | 1486(4) | 3552(2) | -1106(2) | 49(1) |
| C(55) | 2393(5) | 6511(2) | -2302(2) | 70(2) |
| C(56) | 3546(6) | 6591(3) | -2447(3) | 108(3) |
| C(57) | 4066(5) | 5951(3) | -2535(3) | 102(3) |
| C(58) | 3318(4) | 5525(2) | -2251(2) | 55(1) |
| C(59) | 1172(5) | 4915(2) | -3035(2) | 49(1) |
| C(60) | 1825(5) | 4343(2) | -3200(2) | 62(2) |
| C(61) | 1264(17) | 3833(3) | -2899(4) | 81(4) |
| C(61') | 1920(30) | 3865(12) | -2740(13) | 37(7) |
| C(62) | 965(5) | 4126(2) | -2451(2) | 58(2) |
| Co(1) | 7534(1) | 6396(1) | 1570(1) | 70(1) |
| O(5) | 9850(7) | 5880(3) | 1426(4) | 210(4) |
| O(6) | 7190(5) | 6208(2) | 2574(2) | 100(2) |

| | | | | |
|---|---|---|---|---|
| O(7) | 7495(4) | 7677(2) | 1220(2) | 97(2) |
| O(8) | 5705(6) | 5694(3) | 1104(2) | 167(3) |
| C(63) | 8901(7) | 6078(3) | 1468(3) | 117(3) |
| C(64) | 7331(6) | 6308(2) | 2174(2) | 69(2) |
| C(65) | 7500(5) | 7179(3) | 1370(2) | 72(2) |
| C(66) | 6446(8) | 5967(4) | 1289(3) | 120(3) |

**Table S5.** Bond lengths [Å] and angles [°] for (*R*)-**1b**

| | | | |
|---|---|---|---|
| Al(1)-O(2) | 1.810(3) | C(19)-C(20) | 1.399(6) |
| Al(1)-O(1) | 1.814(3) | C(21)-C(22) | 1.464(6) |
| Al(1)-O(4) | 1.966(3) | C(22)-C(23) | 1.378(6) |
| Al(1)-O(3) | 1.985(3) | C(22)-C(27) | 1.414(6) |
| Al(1)-N(2) | 2.013(4) | C(23)-C(24) | 1.356(6) |
| Al(1)-N(1) | 2.048(4) | C(24)-C(25) | 1.418(6) |
| O(1)-C(27) | 1.339(5) | C(24)-C(28) | 1.502(6) |
| O(2)-C(40) | 1.336(5) | C(25)-C(26) | 1.382(6) |
| O(3)-C(58) | 1.429(5) | C(26)-C(27) | 1.413(6) |
| O(3)-C(55) | 1.475(5) | C(26)-C(29) | 1.490(6) |
| O(4)-C(59) | 1.440(5) | C(29)-C(34) | 1.375(6) |
| O(4)-C(62) | 1.476(4) | C(29)-C(30) | 1.440(6) |
| N(1)-C(21) | 1.287(5) | C(30)-C(31) | 1.366(7) |
| N(1)-C(1) | 1.411(5) | C(30)-C(35) | 1.500(6) |
| N(2)-C(38) | 1.286(5) | C(31)-C(32) | 1.352(7) |
| N(2)-C(20) | 1.442(5) | C(32)-C(33) | 1.417(7) |
| C(1)-C(10) | 1.376(6) | C(32)-C(36) | 1.511(7) |
| C(1)-C(2) | 1.433(6) | C(33)-C(34) | 1.404(7) |
| C(2)-C(3) | 1.354(6) | C(34)-C(37) | 1.527(6) |
| C(3)-C(4) | 1.431(7) | C(38)-C(39) | 1.450(6) |
| C(4)-C(9) | 1.414(6) | C(39)-C(44) | 1.381(6) |
| C(4)-C(5) | 1.414(7) | C(39)-C(40) | 1.416(6) |
| C(5)-C(6) | 1.370(8) | C(40)-C(41) | 1.378(6) |
| C(6)-C(7) | 1.371(7) | C(41)-C(42) | 1.380(6) |
| C(7)-C(8) | 1.371(7) | C(41)-C(46) | 1.508(6) |
| C(8)-C(9) | 1.426(6) | C(42)-C(43) | 1.446(7) |
| C(9)-C(10) | 1.405(6) | C(43)-C(44) | 1.373(6) |
| C(10)-C(11) | 1.500(6) | C(43)-C(45) | 1.502(6) |
| C(11)-C(20) | 1.393(6) | C(46)-C(47) | 1.400(6) |
| C(11)-C(12) | 1.427(6) | C(46)-C(51) | 1.446(6) |
| C(12)-C(13) | 1.421(6) | C(47)-C(48) | 1.367(7) |
| C(12)-C(17) | 1.428(6) | C(47)-C(52) | 1.516(6) |
| C(13)-C(14) | 1.363(6) | C(48)-C(49) | 1.408(6) |
| C(14)-C(15) | 1.395(7) | C(49)-C(50) | 1.383(7) |
| C(15)-C(16) | 1.366(7) | C(49)-C(53) | 1.500(7) |
| C(16)-C(17) | 1.434(7) | C(50)-C(51) | 1.357(6) |
| C(17)-C(18) | 1.400(7) | C(51)-C(54) | 1.488(6) |
| C(18)-C(19) | 1.377(6) | C(55)-C(56) | 1.403(8) |

| | | | |
|---|---|---|---|
| C(56)-C(57) | 1.508(8) | C(21)-N(1)-Al(1) | 123.7(3) |
| C(57)-C(58) | 1.486(7) | C(1)-N(1)-Al(1) | 119.6(3) |
| C(59)-C(60) | 1.506(6) | C(38)-N(2)-C(20) | 114.1(3) |
| C(60)-C(61) | 1.522(9) | C(38)-N(2)-Al(1) | 124.4(3) |
| C(60)-C(61') | 1.65(3) | C(20)-N(2)-Al(1) | 121.3(3) |
| C(61)-C(62) | 1.450(10) | C(10)-C(1)-N(1) | 119.5(4) |
| C(61')-C(62) | 1.48(3) | C(10)-C(1)-C(2) | 120.1(4) |
| Co(1)-C(64) | 1.729(7) | N(1)-C(1)-C(2) | 120.4(4) |
| Co(1)-C(63) | 1.740(8) | C(3)-C(2)-C(1) | 119.7(4) |
| Co(1)-C(66) | 1.743(7) | C(2)-C(3)-C(4) | 121.8(4) |
| Co(1)-C(65) | 1.759(6) | C(9)-C(4)-C(5) | 120.5(5) |
| O(5)-C(63) | 1.180(8) | C(9)-C(4)-C(3) | 117.6(4) |
| O(6)-C(64) | 1.156(6) | C(5)-C(4)-C(3) | 121.8(4) |
| O(7)-C(65) | 1.141(6) | C(6)-C(5)-C(4) | 121.5(5) |
| O(8)-C(66) | 1.159(7) | C(5)-C(6)-C(7) | 118.2(5) |
| | | C(8)-C(7)-C(6) | 122.6(5) |
| O(2)-Al(1)-O(1) | 170.76(15) | C(7)-C(8)-C(9) | 121.1(5) |
| O(2)-Al(1)-O(4) | 85.34(13) | C(10)-C(9)-C(4) | 120.7(4) |
| O(1)-Al(1)-O(4) | 88.65(13) | C(10)-C(9)-C(8) | 123.3(4) |
| O(2)-Al(1)-O(3) | 88.37(12) | C(4)-C(9)-C(8) | 116.0(4) |
| O(1)-Al(1)-O(3) | 84.80(12) | C(1)-C(10)-C(9) | 120.0(4) |
| O(4)-Al(1)-O(3) | 91.85(13) | C(1)-C(10)-C(11) | 118.7(4) |
| O(2)-Al(1)-N(2) | 87.97(14) | C(9)-C(10)-C(11) | 121.2(4) |
| O(1)-Al(1)-N(2) | 98.45(14) | C(20)-C(11)-C(12) | 118.6(4) |
| O(4)-Al(1)-N(2) | 172.30(14) | C(20)-C(11)-C(10) | 119.1(4) |
| O(3)-Al(1)-N(2) | 91.76(13) | C(12)-C(11)-C(10) | 122.1(4) |
| O(2)-Al(1)-N(1) | 98.86(14) | C(13)-C(12)-C(17) | 118.8(4) |
| O(1)-Al(1)-N(1) | 88.31(14) | C(13)-C(12)-C(11) | 121.8(4) |
| O(4)-Al(1)-N(1) | 91.67(13) | C(17)-C(12)-C(11) | 119.3(5) |
| O(3)-Al(1)-N(1) | 172.19(13) | C(14)-C(13)-C(12) | 120.0(4) |
| N(2)-Al(1)-N(1) | 85.59(14) | C(13)-C(14)-C(15) | 121.3(5) |
| C(27)-O(1)-Al(1) | 132.1(2) | C(16)-C(15)-C(14) | 121.6(5) |
| C(40)-O(2)-Al(1) | 128.3(2) | C(15)-C(16)-C(17) | 118.9(5) |
| C(58)-O(3)-C(55) | 108.5(3) | C(18)-C(17)-C(12) | 118.7(4) |
| C(58)-O(3)-Al(1) | 126.5(2) | C(18)-C(17)-C(16) | 121.8(4) |
| C(55)-O(3)-Al(1) | 124.6(3) | C(12)-C(17)-C(16) | 119.5(5) |
| C(59)-O(4)-C(62) | 108.4(3) | C(19)-C(18)-C(17) | 122.2(4) |
| C(59)-O(4)-Al(1) | 127.9(2) | C(18)-C(19)-C(20) | 118.6(4) |
| C(62)-O(4)-Al(1) | 123.6(3) | C(11)-C(20)-C(19) | 122.2(4) |
| C(21)-N(1)-C(1) | 115.4(3) | C(11)-C(20)-N(2) | 119.4(3) |

| | | | |
|---|---|---|---|
| C(19)-C(20)-N(2) | 118.4(4) | C(41)-C(42)-C(43) | 121.5(4) |
| N(1)-C(21)-C(22) | 126.6(4) | C(44)-C(43)-C(42) | 116.1(4) |
| C(23)-C(22)-C(27) | 121.1(4) | C(44)-C(43)-C(45) | 123.7(5) |
| C(23)-C(22)-C(21) | 118.6(4) | C(42)-C(43)-C(45) | 120.3(4) |
| C(27)-C(22)-C(21) | 119.8(4) | C(43)-C(44)-C(39) | 122.9(5) |
| C(24)-C(23)-C(22) | 122.4(4) | C(47)-C(46)-C(51) | 117.7(4) |
| C(23)-C(24)-C(25) | 116.6(4) | C(47)-C(46)-C(41) | 123.5(4) |
| C(23)-C(24)-C(28) | 123.1(4) | C(51)-C(46)-C(41) | 118.8(4) |
| C(25)-C(24)-C(28) | 120.4(4) | C(48)-C(47)-C(46) | 120.0(4) |
| C(26)-C(25)-C(24) | 123.5(4) | C(48)-C(47)-C(52) | 118.8(5) |
| C(25)-C(26)-C(27) | 118.3(4) | C(46)-C(47)-C(52) | 121.2(4) |
| C(25)-C(26)-C(29) | 120.3(4) | C(47)-C(48)-C(49) | 123.2(5) |
| C(27)-C(26)-C(29) | 121.2(4) | C(50)-C(49)-C(48) | 115.8(4) |
| O(1)-C(27)-C(22) | 121.8(4) | C(50)-C(49)-C(53) | 123.0(4) |
| O(1)-C(27)-C(26) | 120.2(4) | C(48)-C(49)-C(53) | 121.2(5) |
| C(22)-C(27)-C(26) | 118.0(4) | C(51)-C(50)-C(49) | 123.9(4) |
| C(34)-C(29)-C(30) | 118.5(4) | C(50)-C(51)-C(46) | 119.2(4) |
| C(34)-C(29)-C(26) | 120.7(4) | C(50)-C(51)-C(54) | 120.6(4) |
| C(30)-C(29)-C(26) | 120.8(4) | C(46)-C(51)-C(54) | 120.1(4) |
| C(31)-C(30)-C(29) | 118.3(4) | C(56)-C(55)-O(3) | 107.3(4) |
| C(31)-C(30)-C(35) | 120.9(4) | C(55)-C(56)-C(57) | 108.5(5) |
| C(29)-C(30)-C(35) | 120.8(4) | C(58)-C(57)-C(56) | 103.2(5) |
| C(32)-C(31)-C(30) | 124.0(4) | O(3)-C(58)-C(57) | 107.1(4) |
| C(31)-C(32)-C(33) | 118.5(4) | O(4)-C(59)-C(60) | 105.5(4) |
| C(31)-C(32)-C(36) | 122.7(5) | C(59)-C(60)-C(61) | 101.0(5) |
| C(33)-C(32)-C(36) | 118.7(5) | C(59)-C(60)-C(61') | 106.7(10) |
| C(34)-C(33)-C(32) | 119.0(5) | C(61)-C(60)-C(61') | 31.8(9) |
| C(29)-C(34)-C(33) | 121.4(4) | C(62)-C(61)-C(60) | 106.4(6) |
| C(29)-C(34)-C(37) | 122.1(4) | C(62)-C(61')-C(60) | 98.9(17) |
| C(33)-C(34)-C(37) | 116.5(4) | C(61')-C(62)-O(4) | 106.9(11) |
| N(2)-C(38)-C(39) | 124.0(4) | C(61')-C(62)-C(61) | 34.9(11) |
| C(44)-C(39)-C(40) | 120.3(4) | O(4)-C(62)-C(61) | 106.2(4) |
| C(44)-C(39)-C(38) | 118.2(4) | C(64)-Co(1)-C(63) | 104.1(4) |
| C(40)-C(39)-C(38) | 121.2(4) | C(64)-Co(1)-C(66) | 107.0(3) |
| O(2)-C(40)-C(41) | 120.8(4) | C(63)-Co(1)-C(66) | 112.1(4) |
| O(2)-C(40)-C(39) | 120.6(4) | C(64)-Co(1)-C(65) | 114.6(3) |
| C(41)-C(40)-C(39) | 118.5(4) | C(63)-Co(1)-C(65) | 109.6(3) |
| C(40)-C(41)-C(42) | 120.8(4) | C(66)-Co(1)-C(65) | 109.5(4) |
| C(40)-C(41)-C(46) | 122.5(4) | O(5)-C(63)-Co(1) | 175.8(9) |
| C(42)-C(41)-C(46) | 116.7(4) | O(6)-C(64)-Co(1) | 175.6(5) |

| | |
|---|---|
| O(7)-C(65)-Co(1) | 176.9(6) |
| O(8)-C(66)-Co(1) | 178.4(9) |

Symmetry transformations used to generate equivalent atoms.

**Table S6.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for (*R*)-**1b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2$ $a^{*2}U^{11}$ + ... + 2 h k a*b*$U^{12}$]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Al(1) | 26(1) | 19(1) | 46(1) | 1(1) | -1(1) | -1(1) |
| O(1) | 25(2) | 21(1) | 53(2) | 1(1) | -4(2) | -2(1) |
| O(2) | 30(2) | 19(1) | 52(2) | 5(1) | -5(2) | 0(1) |
| O(3) | 23(2) | 24(1) | 62(2) | 6(1) | 0(1) | -3(1) |
| O(4) | 40(2) | 15(1) | 51(2) | 1(1) | 6(2) | 5(1) |
| N(1) | 33(2) | 15(2) | 47(2) | -3(2) | 3(2) | 2(2) |
| N(2) | 25(2) | 25(2) | 46(2) | 2(2) | 0(2) | -1(2) |
| C(1) | 15(2) | 37(2) | 53(3) | 8(2) | 3(2) | 2(2) |
| C(2) | 35(3) | 26(2) | 70(4) | 10(2) | -1(3) | -1(2) |
| C(3) | 48(3) | 42(3) | 57(3) | 28(3) | 1(3) | -1(2) |
| C(4) | 33(3) | 47(3) | 55(3) | 26(2) | 0(2) | 6(2) |
| C(5) | 59(4) | 82(4) | 68(4) | 37(3) | 5(3) | 25(3) |
| C(6) | 60(4) | 78(4) | 56(4) | 17(3) | -5(3) | 13(3) |
| C(7) | 49(3) | 85(4) | 50(3) | 4(3) | 2(3) | 2(3) |
| C(8) | 37(3) | 57(3) | 49(3) | 6(2) | -6(2) | 6(2) |
| C(9) | 26(2) | 41(3) | 53(3) | 5(2) | 2(2) | 5(2) |
| C(10) | 27(2) | 27(2) | 39(3) | 5(2) | 4(2) | 8(2) |
| C(11) | 31(3) | 33(2) | 37(3) | 3(2) | 0(2) | -2(2) |
| C(12) | 47(3) | 35(2) | 47(3) | 3(2) | 1(3) | 14(2) |
| C(13) | 27(3) | 45(3) | 58(3) | 11(2) | 1(2) | 6(2) |
| C(14) | 31(3) | 60(3) | 78(4) | 15(3) | 7(3) | 14(2) |
| C(15) | 51(4) | 49(3) | 80(4) | 11(3) | 6(3) | 16(3) |
| C(16) | 49(3) | 46(3) | 78(4) | 15(3) | 18(3) | 24(3) |
| C(17) | 46(3) | 35(2) | 52(3) | 8(2) | 8(3) | 5(2) |
| C(18) | 62(4) | 24(2) | 64(4) | 1(2) | 5(3) | 19(2) |
| C(19) | 38(3) | 22(2) | 53(3) | 0(2) | 0(2) | -1(2) |
| C(20) | 43(3) | 22(2) | 49(3) | 3(2) | 0(2) | 7(2) |
| C(21) | 31(3) | 21(2) | 50(3) | 2(2) | -3(2) | -4(2) |
| C(22) | 30(3) | 16(2) | 56(3) | -5(2) | -3(2) | 3(2) |
| C(23) | 37(3) | 33(2) | 50(3) | -4(2) | 1(2) | 9(2) |
| C(24) | 34(3) | 40(2) | 56(3) | -12(2) | -2(2) | 4(2) |
| C(25) | 54(3) | 26(2) | 51(3) | -2(2) | -5(3) | 14(2) |
| C(26) | 39(3) | 20(2) | 52(3) | 1(2) | 4(2) | 8(2) |
| C(27) | 41(3) | 20(2) | 41(3) | -3(2) | -4(2) | 5(2) |
| C(28) | 31(3) | 89(4) | 55(3) | 3(3) | -16(3) | 5(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(29) | 48(3) | 18(2) | 41(3) | 6(2) | -2(2) | -2(2) |
| C(30) | 54(3) | 23(2) | 44(3) | 8(2) | -3(3) | 5(2) |
| C(31) | 69(4) | 24(2) | 51(3) | 0(2) | -2(3) | -6(2) |
| C(32) | 49(3) | 47(3) | 71(4) | 16(3) | 4(3) | -17(3) |
| C(33) | 63(4) | 38(3) | 62(4) | 3(2) | 13(3) | 3(3) |
| C(34) | 52(3) | 28(2) | 48(3) | 8(2) | 0(3) | -6(2) |
| C(35) | 55(3) | 34(3) | 53(3) | -2(2) | -3(3) | 9(2) |
| C(36) | 56(4) | 77(4) | 108(5) | 14(4) | 22(4) | -14(3) |
| C(37) | 55(3) | 41(3) | 56(3) | -14(2) | 8(3) | -1(2) |
| C(38) | 29(2) | 28(2) | 42(3) | 4(2) | 2(2) | 3(2) |
| C(39) | 27(3) | 41(3) | 49(3) | 7(2) | -6(2) | -9(2) |
| C(40) | 31(3) | 19(2) | 46(3) | 9(2) | -1(2) | 0(2) |
| C(41) | 26(2) | 31(2) | 59(3) | 3(2) | -3(2) | -9(2) |
| C(42) | 35(3) | 38(3) | 98(4) | 24(3) | -15(3) | -15(2) |
| C(43) | 38(3) | 37(3) | 62(3) | 11(2) | -21(2) | -6(2) |
| C(44) | 37(3) | 40(3) | 66(4) | 11(2) | -12(3) | 0(2) |
| C(45) | 54(3) | 50(3) | 98(5) | 9(3) | -36(3) | -7(3) |
| C(46) | 20(2) | 28(2) | 67(3) | 12(2) | -13(2) | 4(2) |
| C(47) | 20(2) | 27(2) | 87(4) | 8(2) | -1(2) | 4(2) |
| C(48) | 27(3) | 45(3) | 88(4) | 13(3) | 7(3) | 7(2) |
| C(49) | 42(3) | 25(2) | 77(4) | 11(2) | -1(3) | 7(2) |
| C(50) | 38(3) | 21(2) | 67(3) | 11(2) | -1(3) | -5(2) |
| C(51) | 24(2) | 25(2) | 68(3) | 13(2) | -4(2) | -5(2) |
| C(52) | 27(3) | 44(3) | 118(5) | 16(3) | 4(3) | -7(2) |
| C(53) | 54(4) | 43(3) | 124(6) | -6(3) | 18(4) | -1(3) |
| C(54) | 41(3) | 28(2) | 79(4) | 10(2) | -2(3) | -7(2) |
| C(55) | 46(3) | 26(2) | 138(5) | 7(3) | 17(4) | -11(2) |
| C(56) | 72(5) | 50(4) | 201(8) | 45(4) | 30(5) | 12(3) |
| C(57) | 44(4) | 73(4) | 189(8) | 32(5) | 48(4) | 3(3) |
| C(58) | 28(3) | 48(3) | 90(4) | 16(3) | 18(3) | 13(2) |
| C(59) | 69(4) | 31(2) | 49(3) | 1(2) | 1(3) | 4(2) |
| C(60) | 80(4) | 44(3) | 61(3) | -10(2) | 20(3) | 10(3) |
| C(61) | 135(11) | 35(4) | 74(6) | 1(3) | 19(7) | 7(4) |
| C(62) | 85(4) | 11(2) | 79(4) | 4(2) | 19(3) | 9(2) |
| Co(1) | 68(1) | 57(1) | 85(1) | -14(1) | 27(1) | -16(1) |
| O(5) | 149(6) | 117(5) | 363(12) | -12(6) | 133(7) | 57(4) |
| O(6) | 157(5) | 57(2) | 85(3) | -10(2) | 24(4) | 38(3) |
| O(7) | 66(3) | 61(2) | 164(5) | 15(3) | 11(3) | 6(2) |
| O(8) | 190(7) | 203(6) | 109(4) | -51(4) | 54(4) | -151(6) |
| C(63) | 129(8) | 79(5) | 142(7) | -28(5) | 60(6) | -2(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(64) | 79(4) | 51(3) | 76(5) | -17(3) | 10(4) | 3(3) |
| C(65) | 37(3) | 63(4) | 115(5) | -6(3) | 2(4) | 5(3) |
| C(66) | 174(9) | 102(6) | 84(5) | -32(4) | 46(6) | -91(6) |

**Table S7.** Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for (*R*)-**1b**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | -1092 | 4001 | -1537 | 53 |
| H(3A) | -1716 | 3724 | -793 | 59 |
| H(5A) | -2396 | 4021 | 16 | 84 |
| H(6A) | -2759 | 4784 | 586 | 78 |
| H(7A) | -2516 | 5832 | 388 | 74 |
| H(8A) | -2061 | 6143 | -369 | 57 |
| H(13A) | -3779 | 5782 | -1151 | 52 |
| H(14A) | -5390 | 6420 | -1172 | 68 |
| H(15A) | -5224 | 7497 | -1295 | 72 |
| H(16A) | -3435 | 7970 | -1389 | 69 |
| H(18A) | -1290 | 7840 | -1461 | 60 |
| H(19A) | 321 | 7203 | -1573 | 45 |
| H(21A) | -2495 | 5036 | -2123 | 41 |
| H(23A) | -3308 | 5263 | -2873 | 48 |
| H(25A) | -1778 | 6465 | -3771 | 53 |
| H(28A) | -4389 | 5591 | -3543 | 88 |
| H(28B) | -3578 | 5715 | -3994 | 88 |
| H(28C) | -4105 | 6296 | -3704 | 88 |
| H(31A) | 1798 | 7884 | -3120 | 58 |
| H(33A) | 2274 | 6628 | -4171 | 65 |
| H(35A) | 471 | 7463 | -2421 | 71 |
| H(35B) | -697 | 7162 | -2625 | 71 |
| H(35C) | -352 | 7868 | -2761 | 71 |
| H(36A) | 3434 | 8015 | -3609 | 121 |
| H(36B) | 3315 | 7725 | -4131 | 121 |
| H(36C) | 3986 | 7343 | -3727 | 121 |
| H(37A) | -246 | 5716 | -3926 | 76 |
| H(37B) | 1082 | 5576 | -4049 | 76 |
| H(37C) | 335 | 6027 | -4385 | 76 |
| H(38A) | 1045 | 6295 | -858 | 40 |
| H(42A) | 4483 | 4416 | -778 | 69 |
| H(44A) | 2831 | 6054 | -493 | 57 |
| H(45A) | 5387 | 5502 | -284 | 101 |
| H(45B) | 4706 | 4997 | 32 | 101 |
| H(45C) | 4337 | 5722 | 47 | 101 |

| | | | | |
|---|---|---|---|---|
| H(48A) | 4971 | 3309 | -2257 | 64 |
| H(50A) | 2100 | 2619 | -1646 | 51 |
| H(52A) | 5042 | 4740 | -1621 | 95 |
| H(52B) | 5275 | 4525 | -2157 | 95 |
| H(52C) | 5952 | 4191 | -1730 | 95 |
| H(53A) | 3862 | 1929 | -2111 | 110 |
| H(53B) | 4229 | 2351 | -2557 | 110 |
| H(53C) | 2893 | 2192 | -2466 | 110 |
| H(54A) | 981 | 3894 | -1211 | 74 |
| H(54B) | 1777 | 3644 | -786 | 74 |
| H(54C) | 1047 | 3157 | -1100 | 74 |
| H(55A) | 1858 | 6634 | -2560 | 84 |
| H(55B) | 2228 | 6775 | -2021 | 84 |
| H(56A) | 3989 | 6813 | -2197 | 129 |
| H(56B) | 3576 | 6845 | -2741 | 129 |
| H(57A) | 4038 | 5841 | -2877 | 123 |
| H(57B) | 4880 | 5934 | -2425 | 123 |
| H(58A) | 3198 | 5123 | -2420 | 66 |
| H(58B) | 3683 | 5435 | -1940 | 66 |
| H(59A) | 1644 | 5299 | -3079 | 59 |
| H(59B) | 440 | 4963 | -3215 | 59 |
| H(60A) | 2664 | 4380 | -3134 | 74 |
| H(60B) | 1707 | 4265 | -3544 | 74 |
| H(61C) | 561 | 3668 | -3058 | 98 |
| H(61D) | 1810 | 3480 | -2848 | 98 |
| H(61A) | 1772 | 3421 | -2830 | 45 |
| H(61B) | 2673 | 3899 | -2577 | 45 |
| H(62A) | 198 | 3977 | -2340 | 70 |
| H(62B) | 1549 | 4022 | -2205 | 70 |

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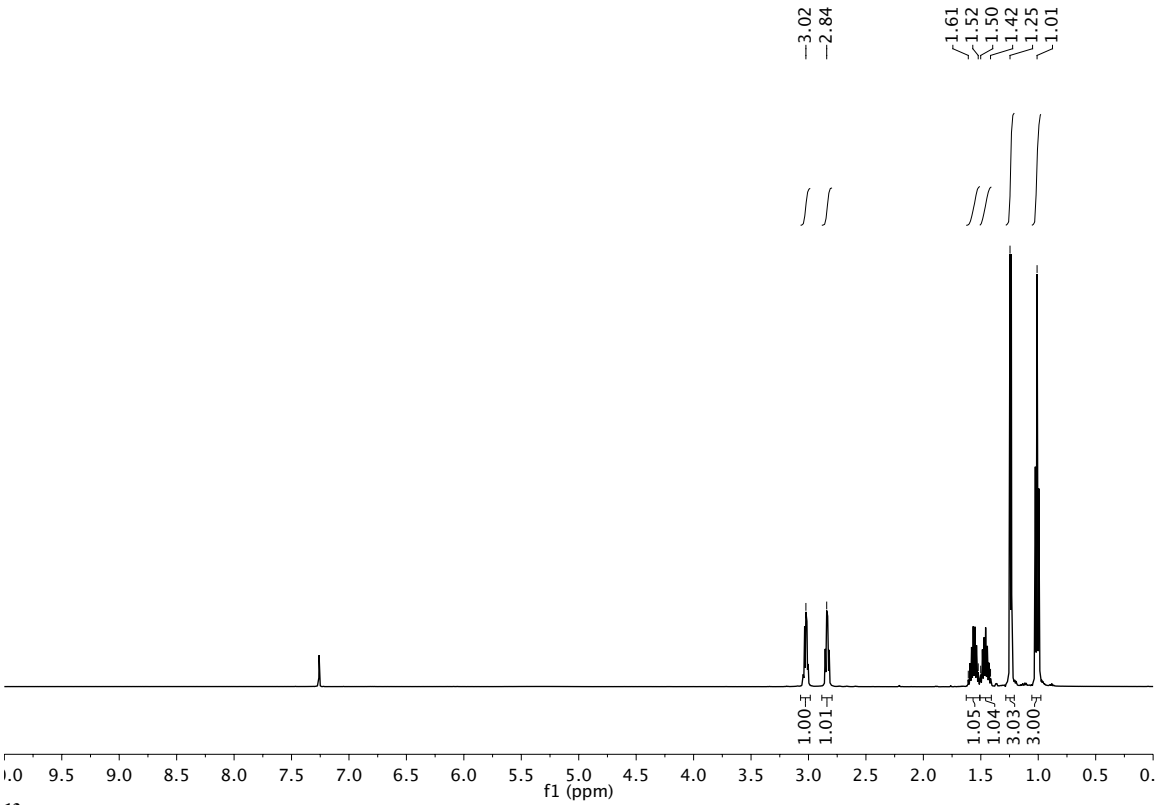
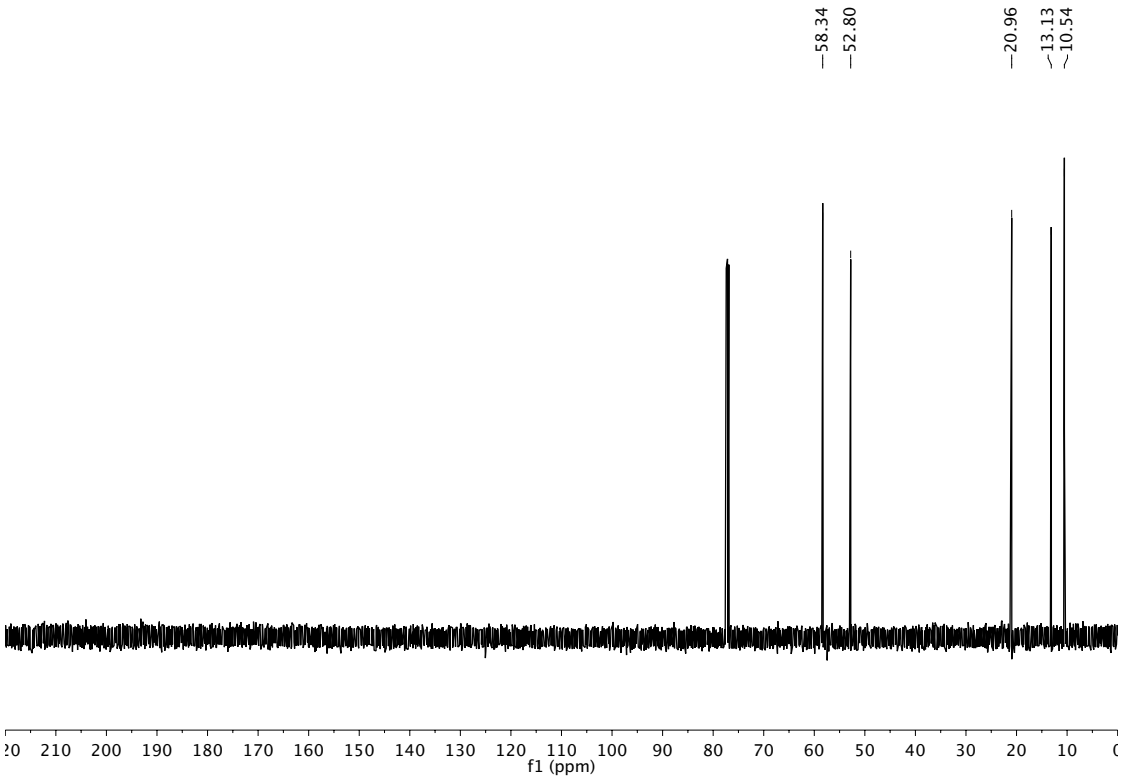
## Copies of $^{1}$H and $^{13}$C NMR spectra

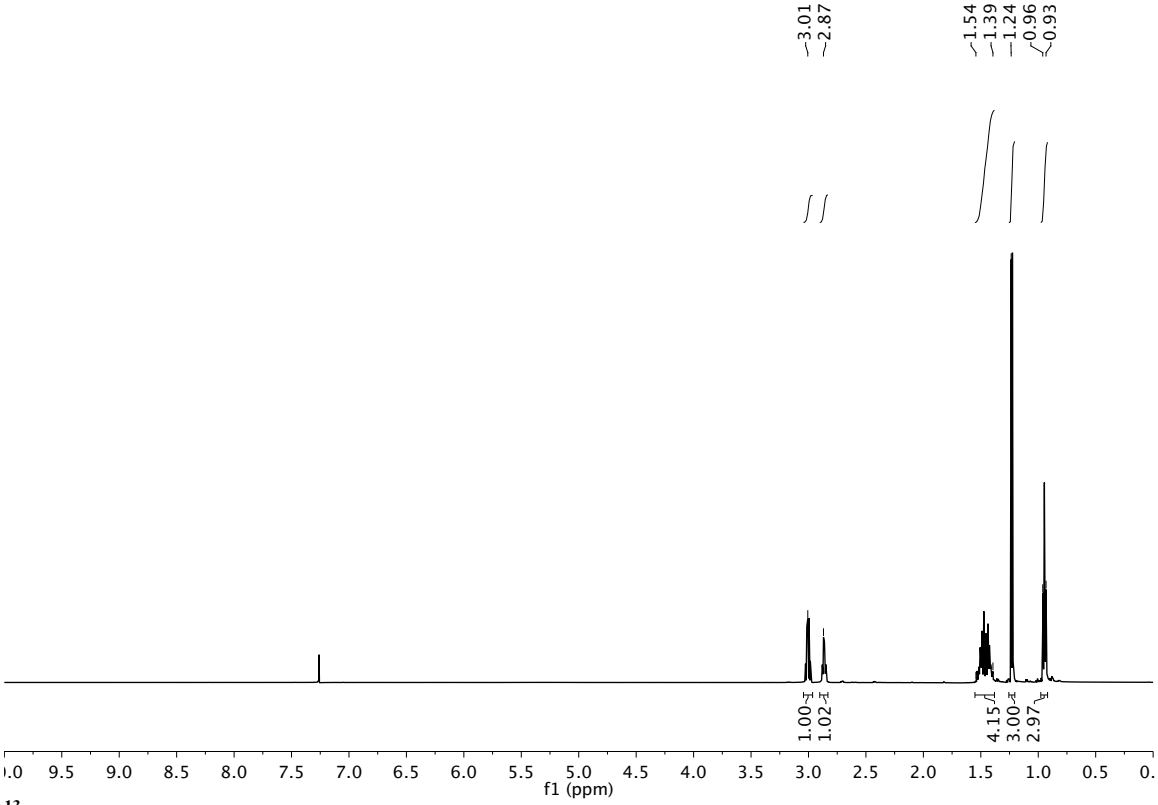
***rac*-(2*R*,3*S*)-2-Ethyl-3-methyloxirane (*rac*-3b)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



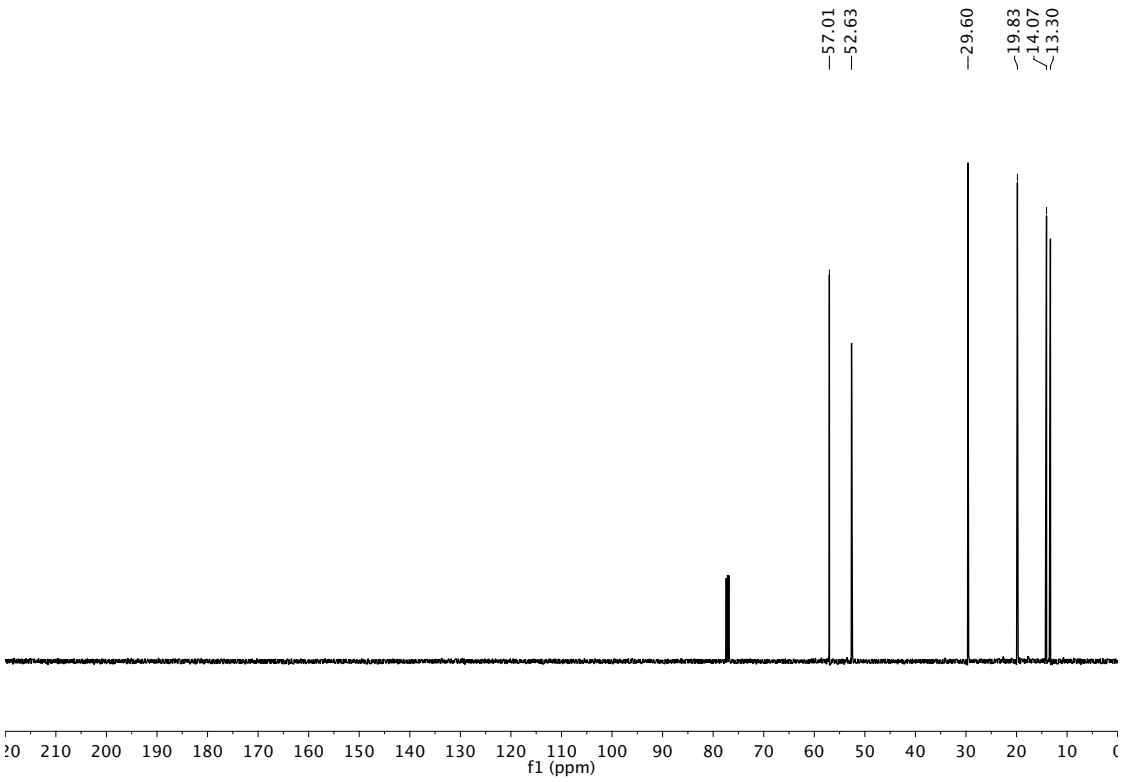

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



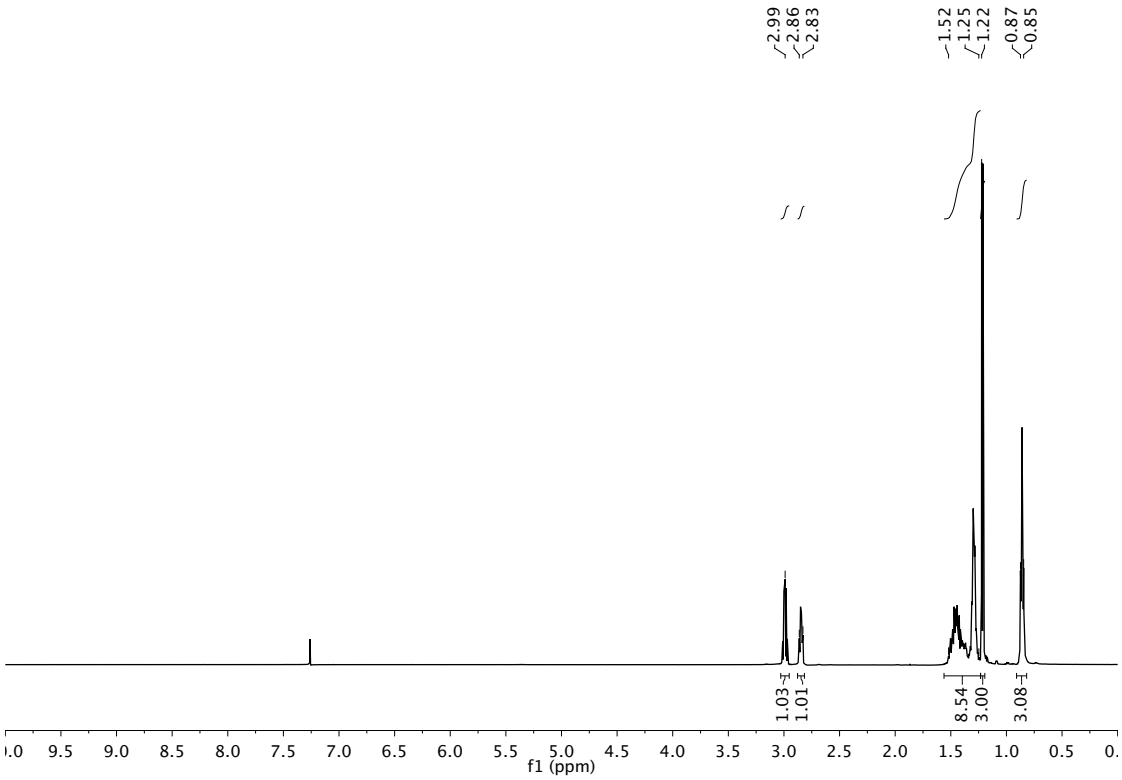
***rac*-(2*R*,3*S*)-2-Methyl-3-propyloxirane (*rac*-3c)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



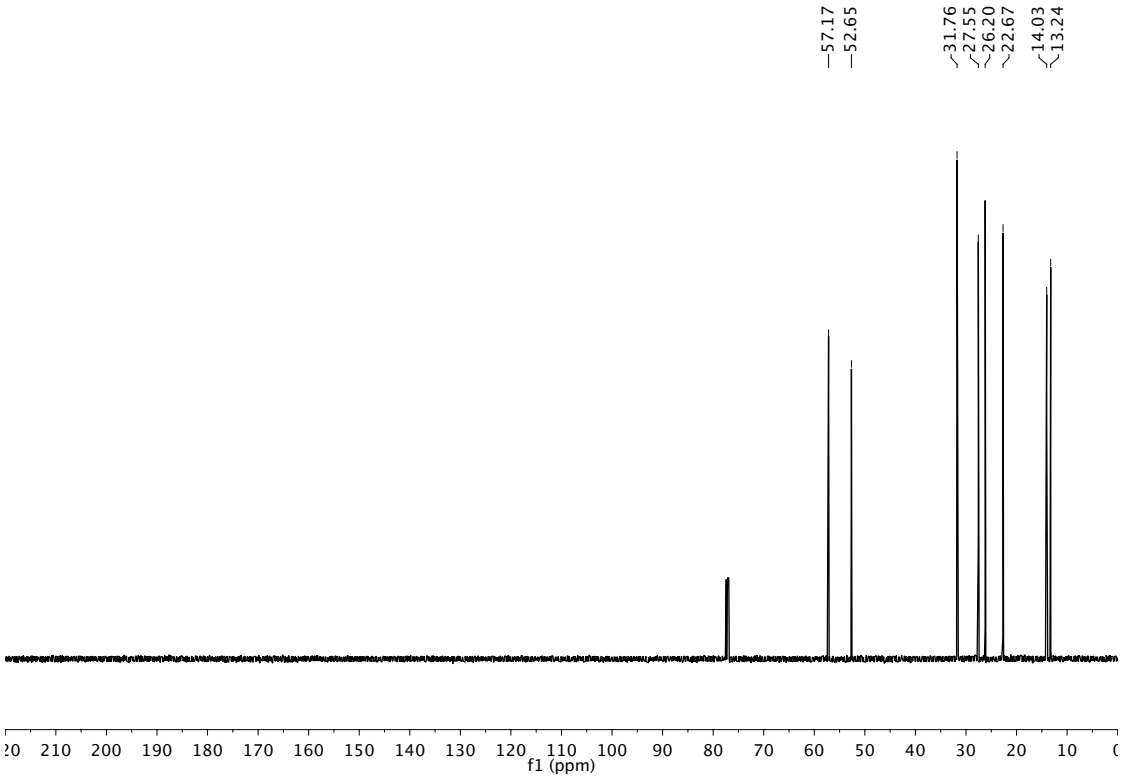

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



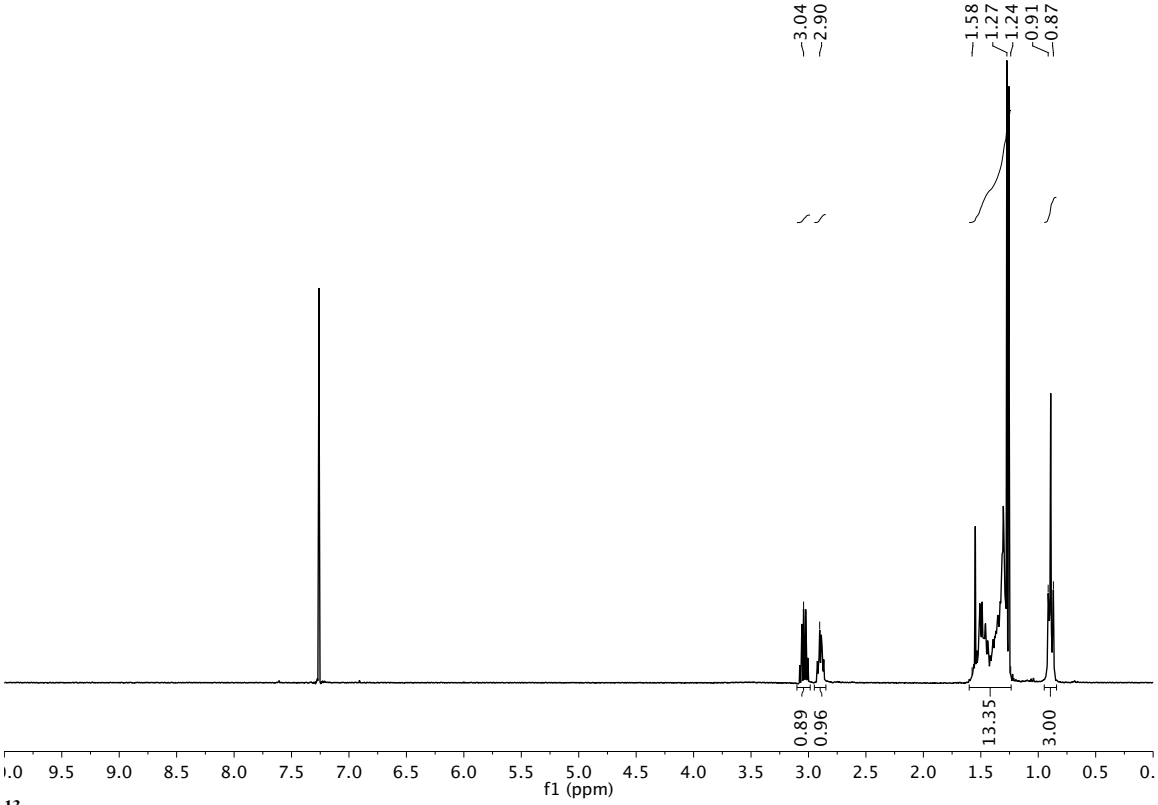
***rac*-(2*R*,3*S*)-2-Methyl-3-pentyloxirane (*rac*-3d)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



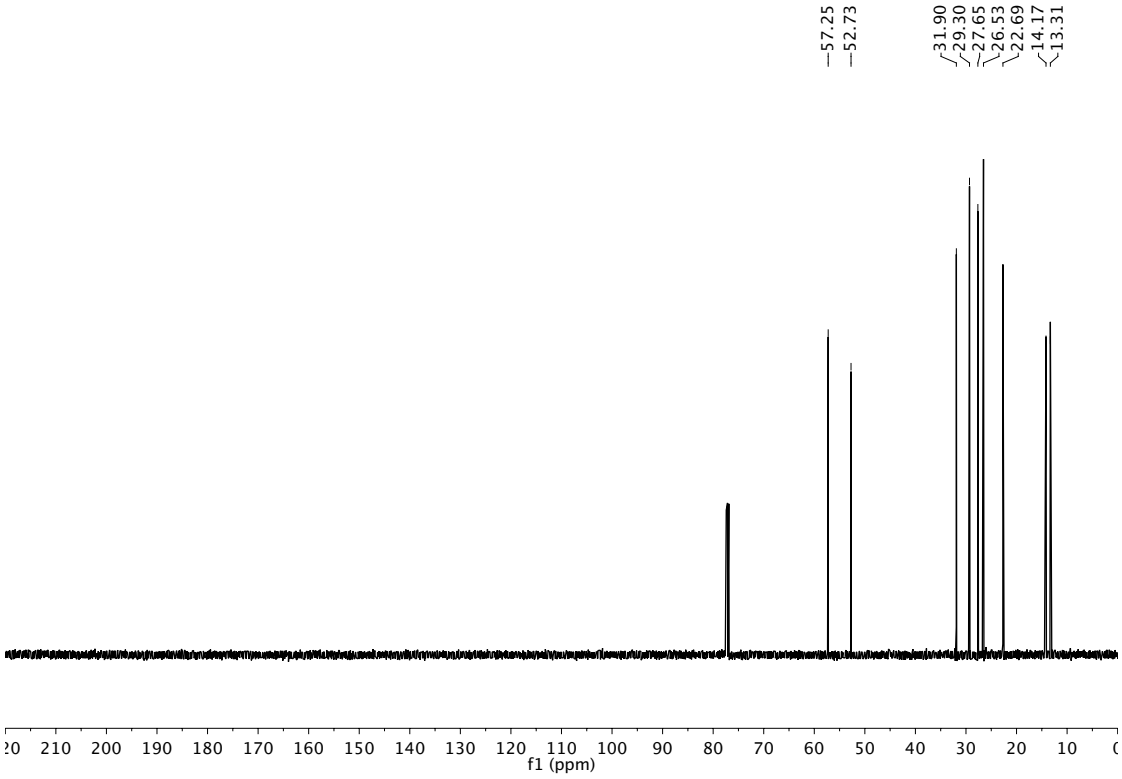

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



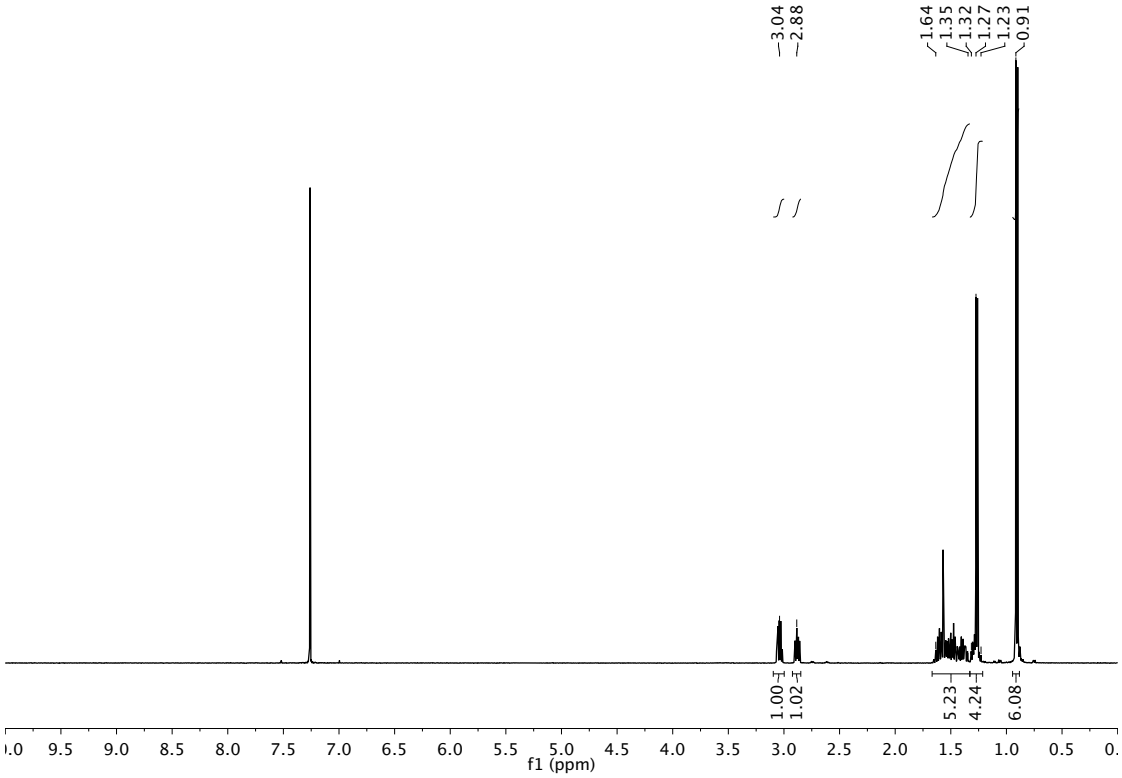
***rac*-(2*R*,3*S*)-2-Hexyl-3-methyloxirane (*rac*-3e)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



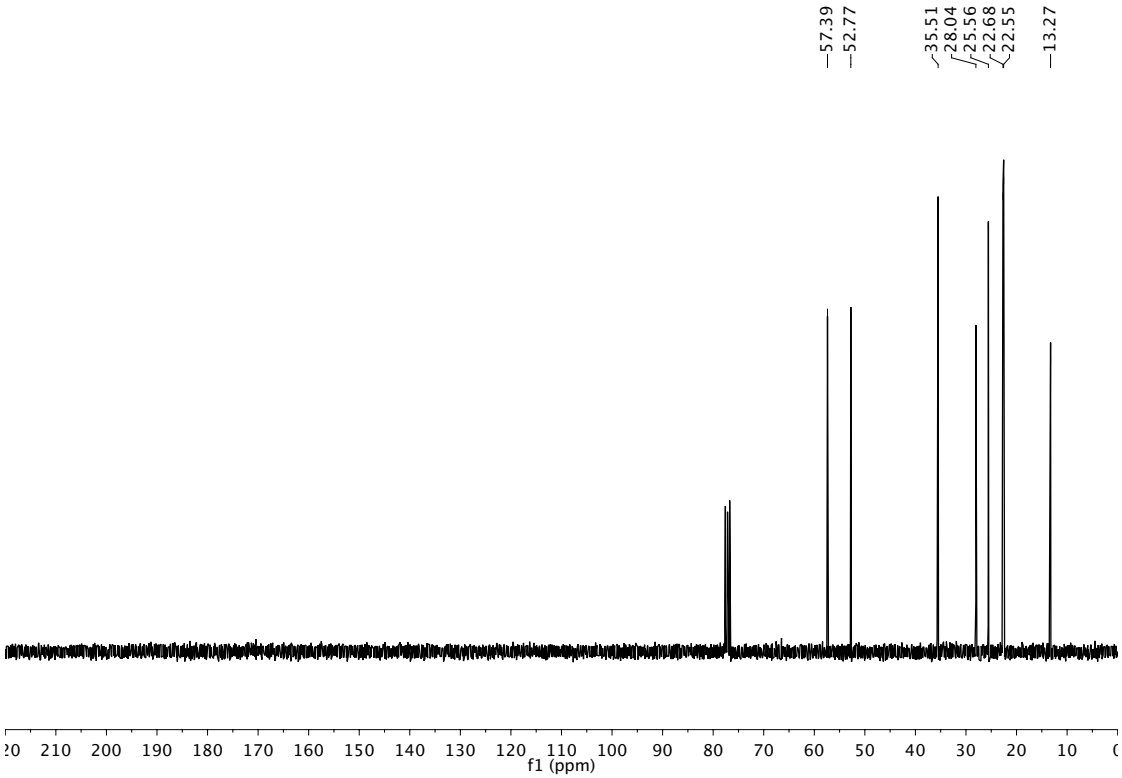

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



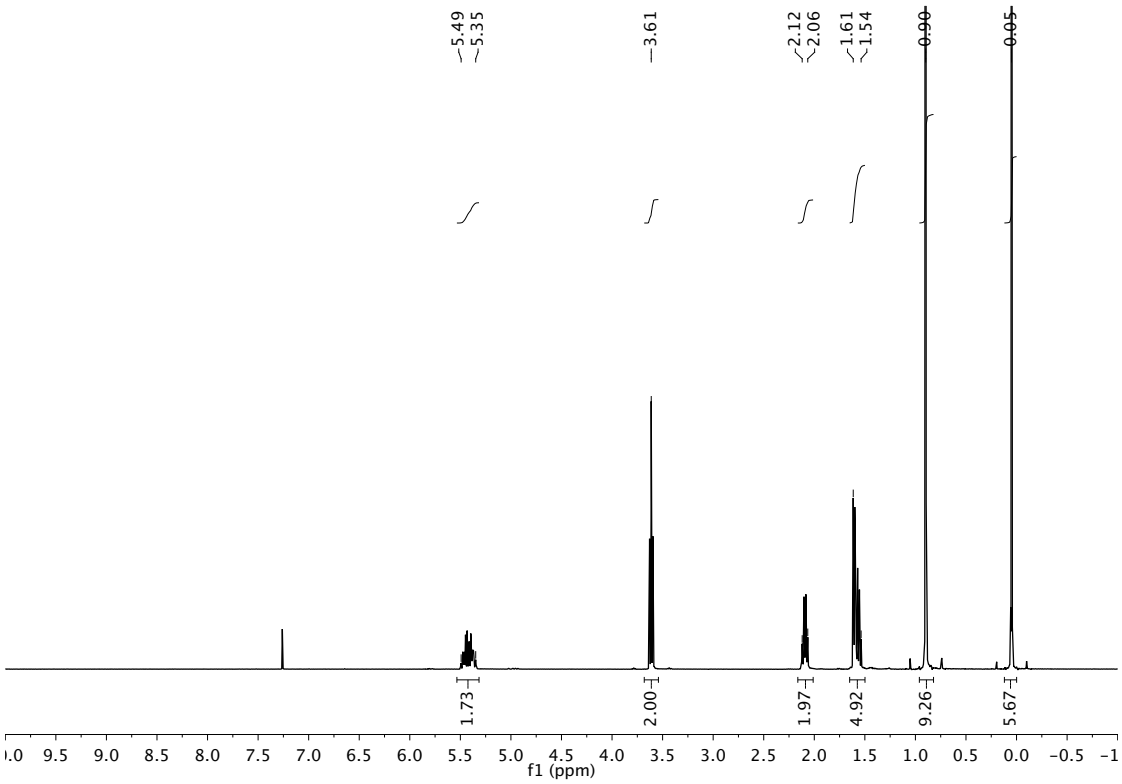
***rac*-(2*R*,3*S*)-2-Isopentyl-3-methyloxirane (*rac*-3f)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



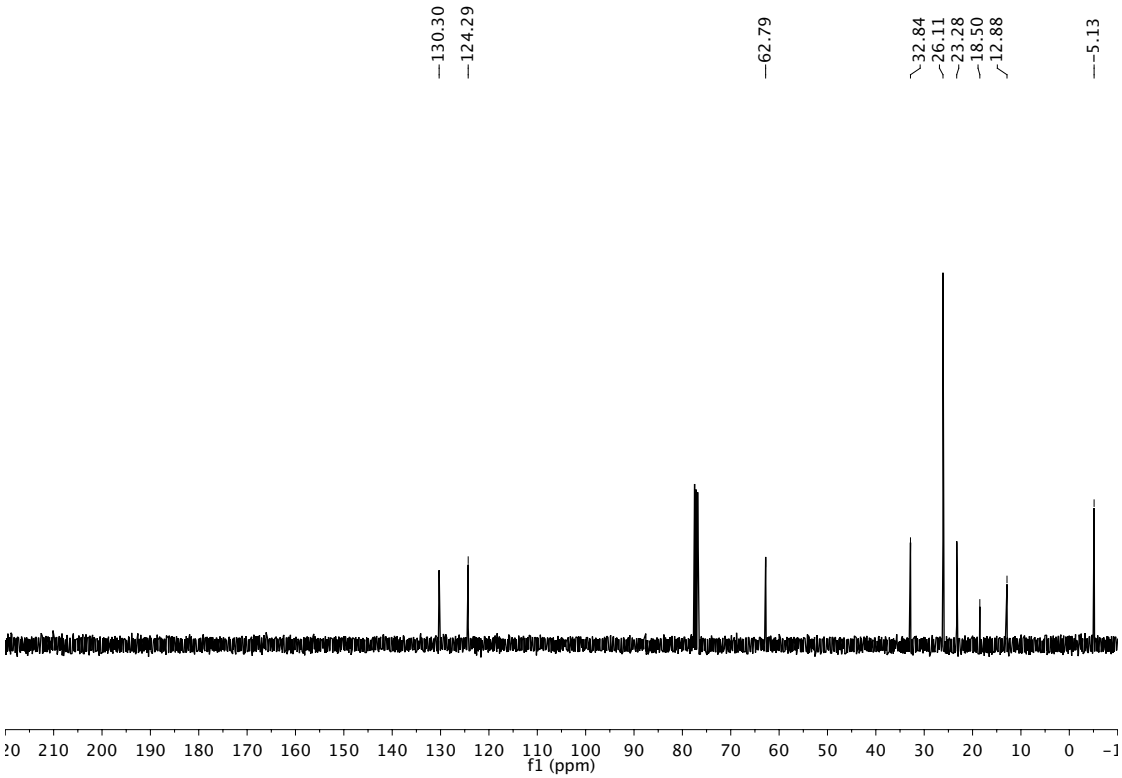

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



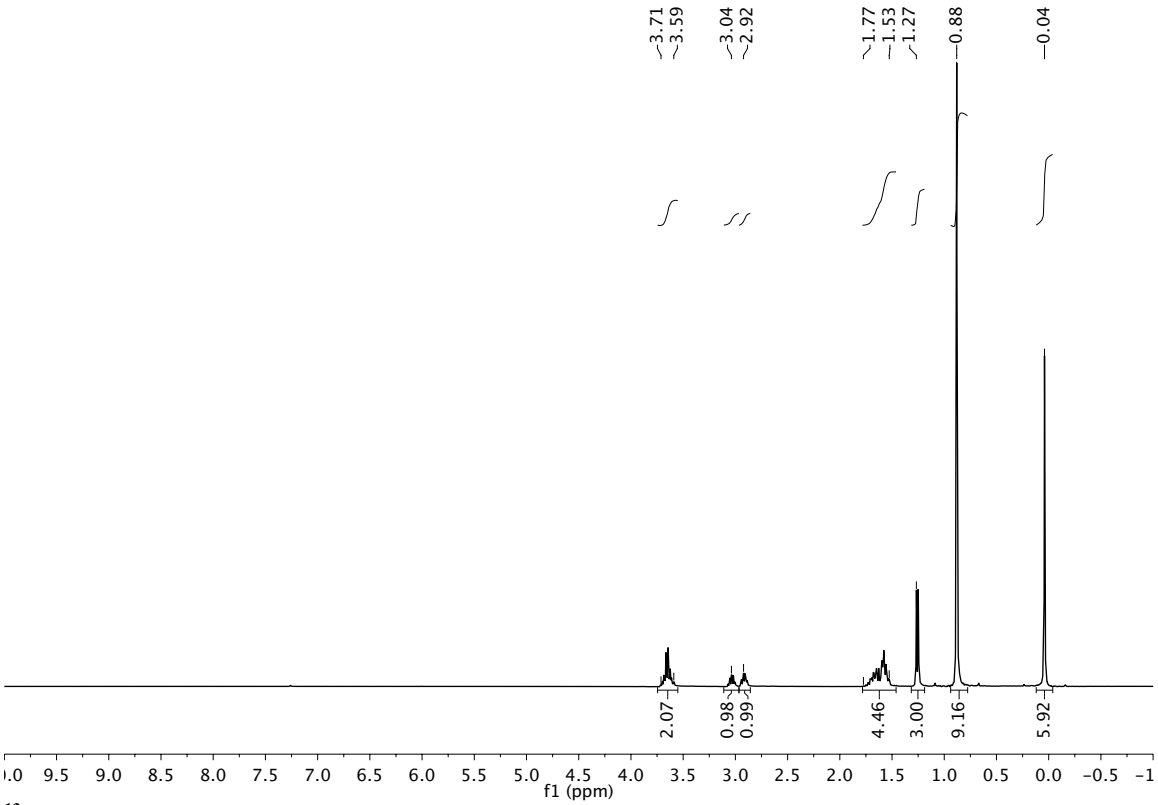
**(*Z*)-*Tert*-butyl(hex-4-en-1-yloxy)dimethylsilane (SM1)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



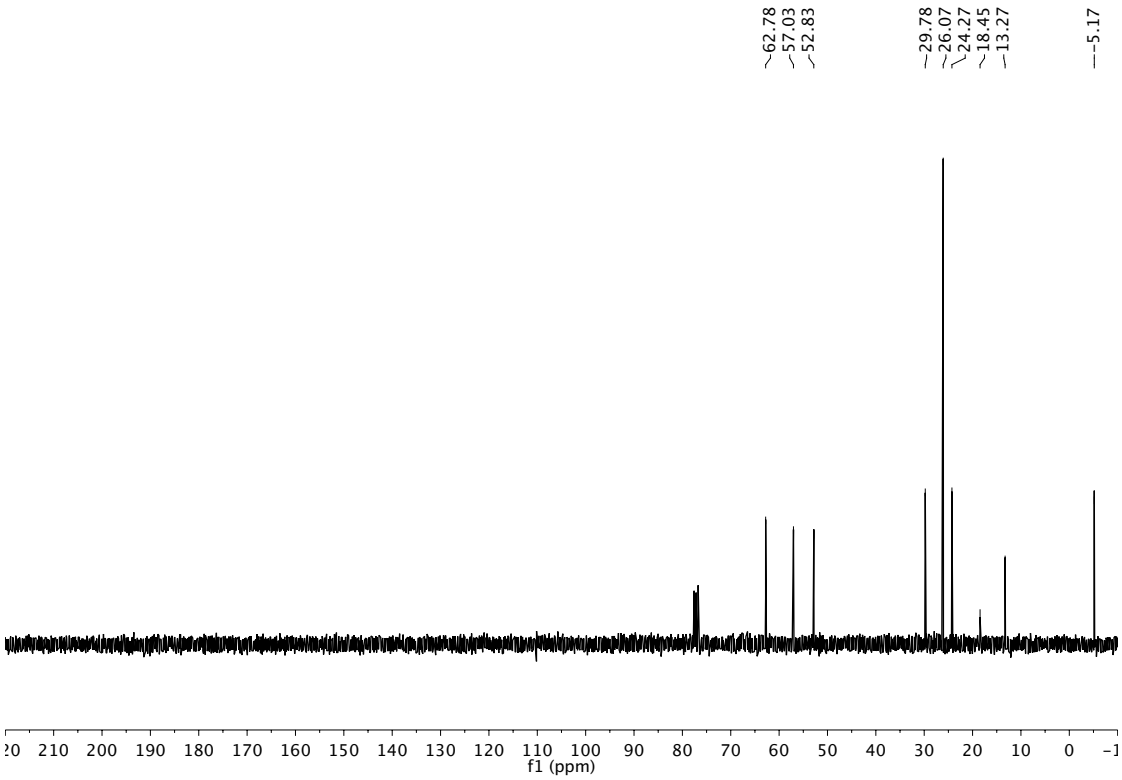

**$^{13}$C NMR spectrum** (101 MHz, $CDCl_3$)



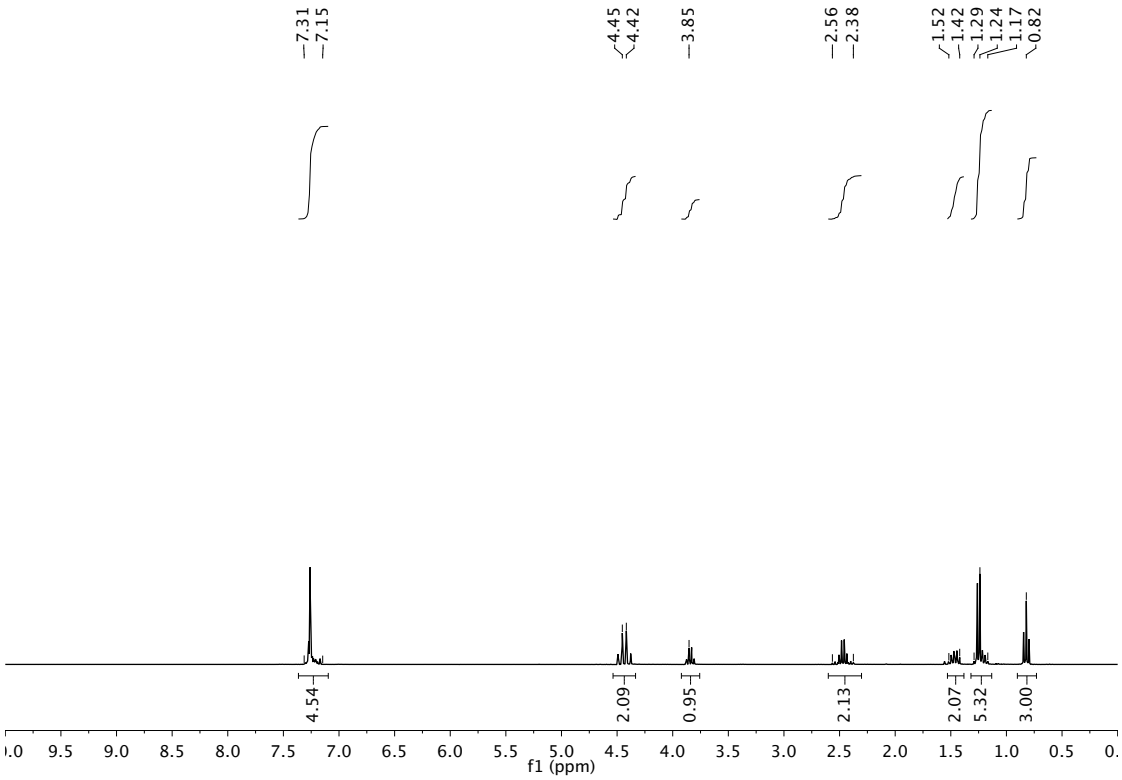
***rac*-*Tert*-butyldimethyl(3-((2*R*,3*S*)-3-methyloxiran-2-yl)propoxy)silane (*rac*-3g)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



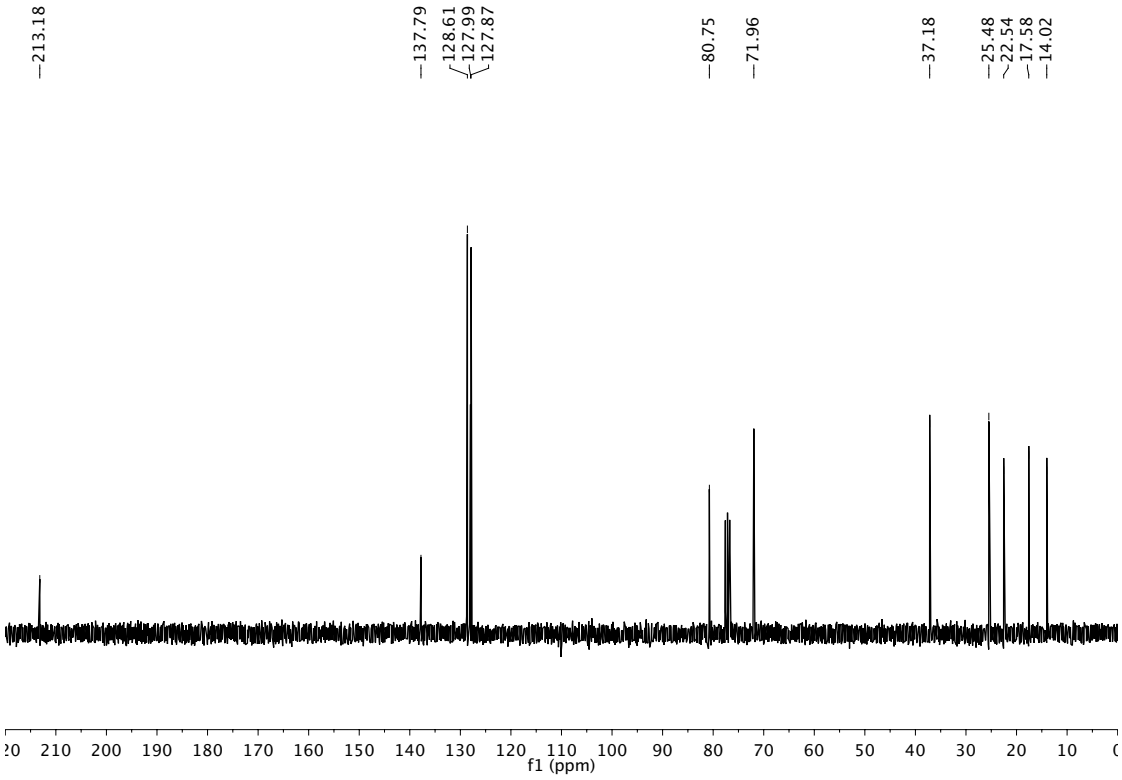

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



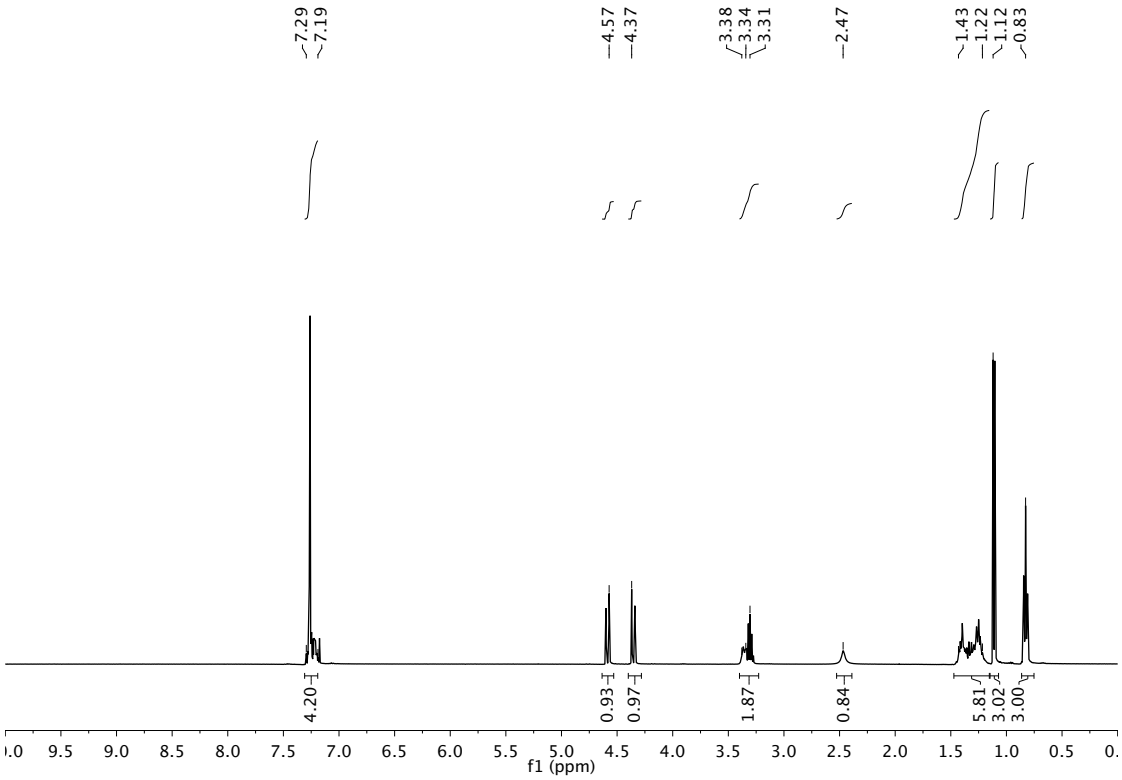
**(*S*)-2-(Benzyloxy)heptan-3-one (SM2)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



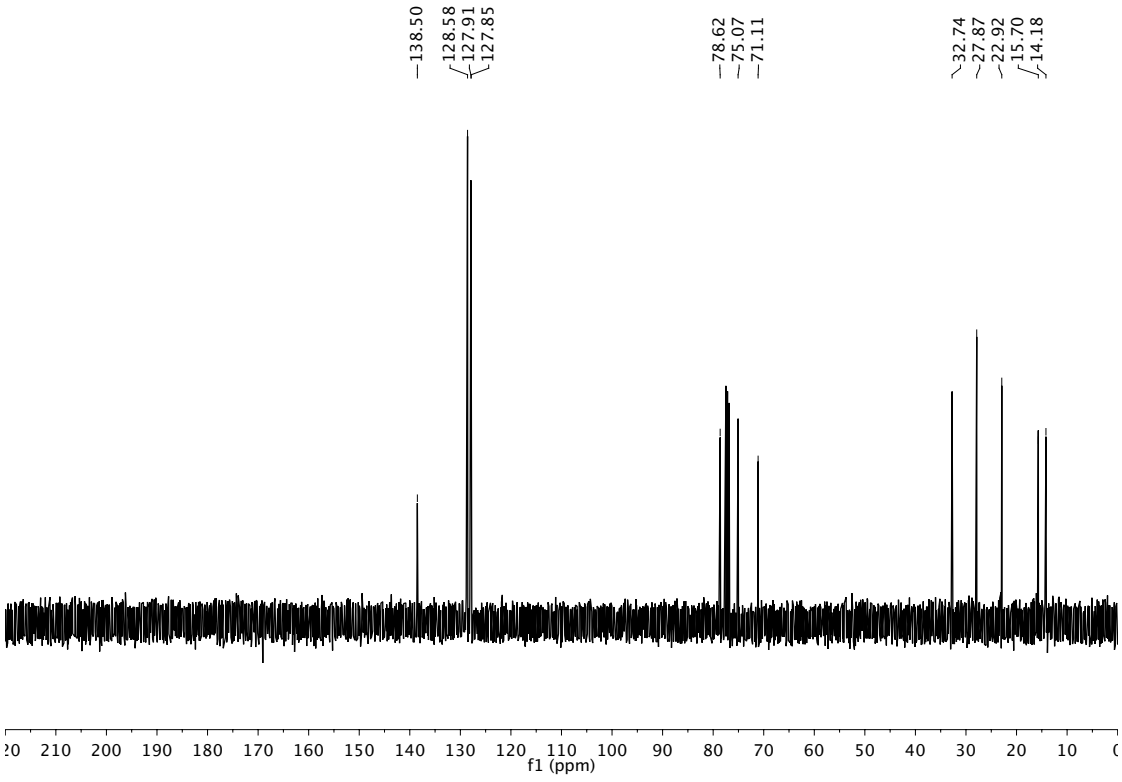

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



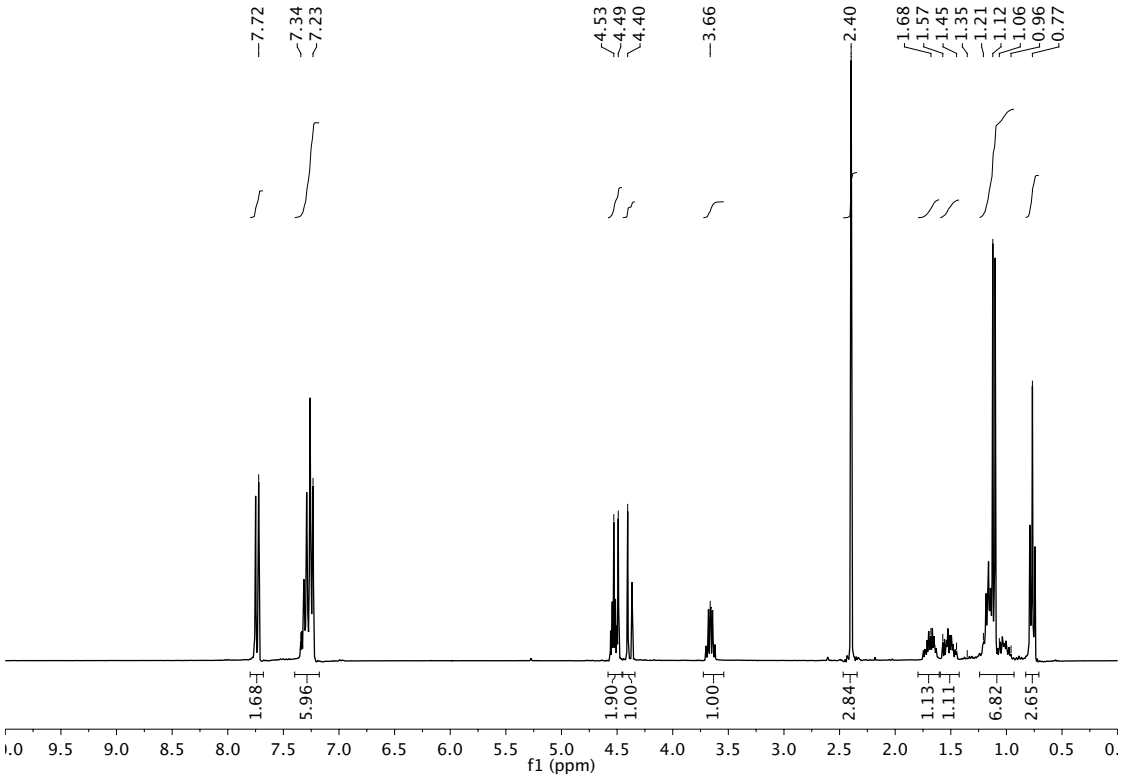
**(2*S*,3*S*)-2-(Benzyloxy)heptan-3-ol (SM3)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



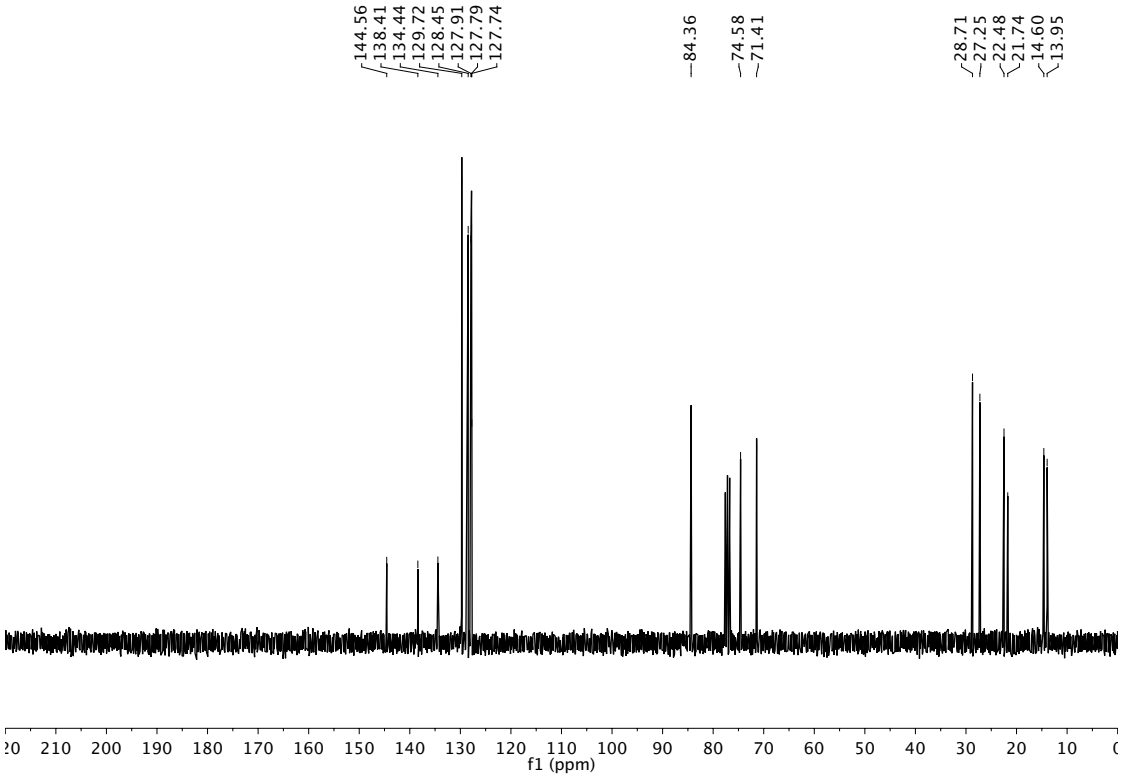

**$^{13}$C NMR spectrum** (101 MHz, $CDCl_3$)



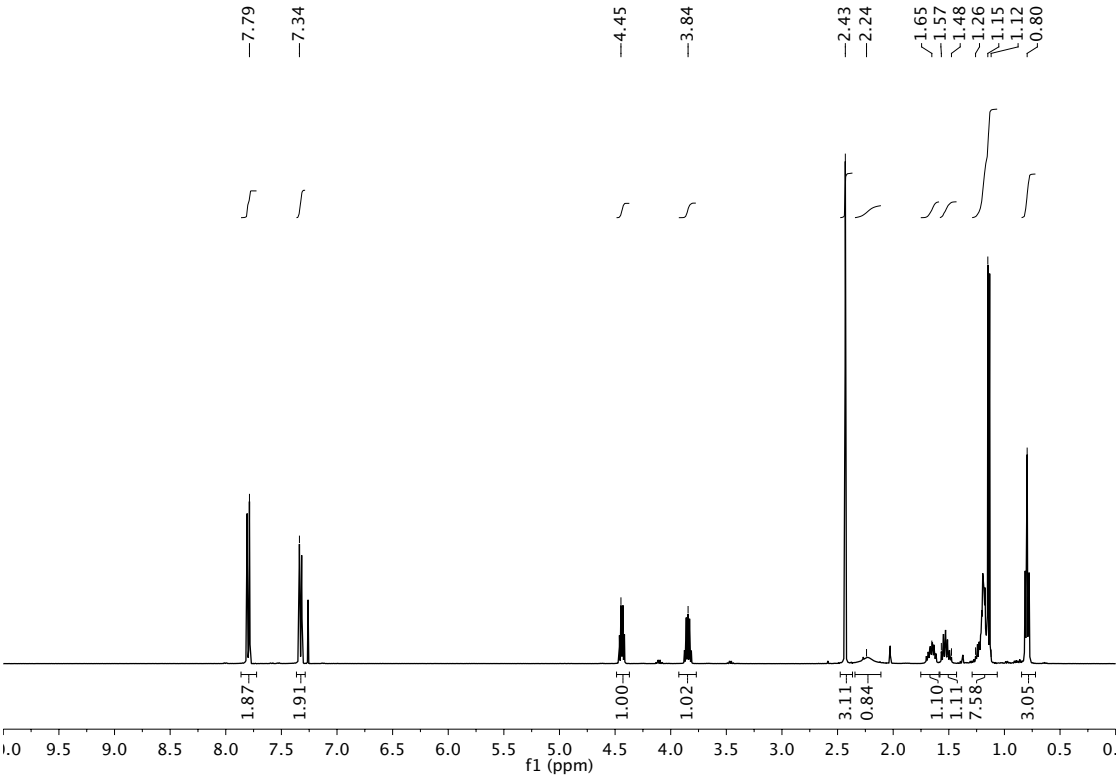
**(2*S*,3*S*)-2-(Benzyloxy)heptan-3-yl 4-methylbenzenesulfonate (SM4)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



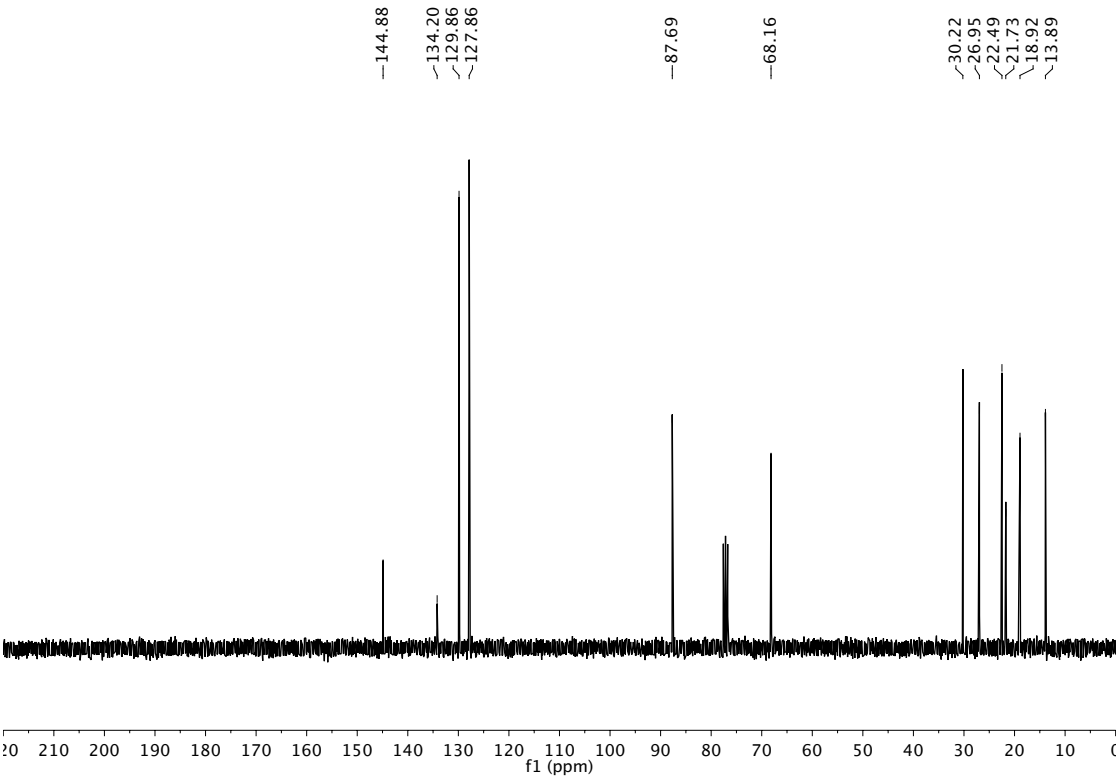

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



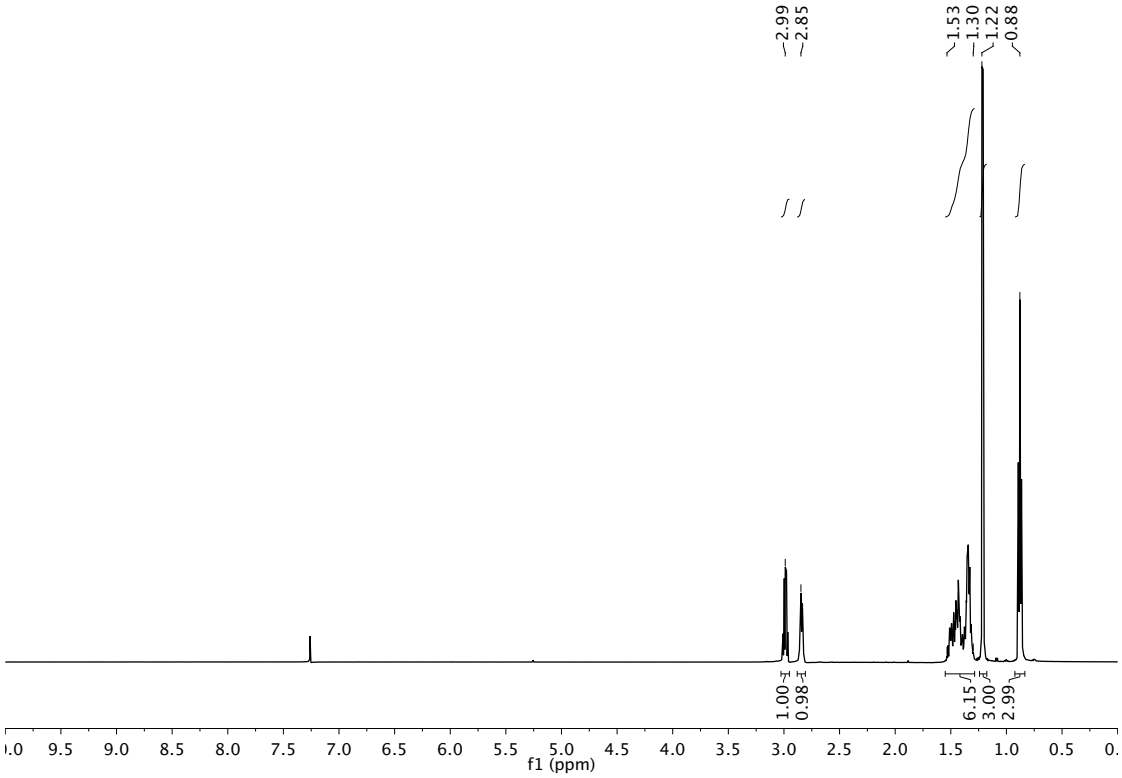
**(2*S*,3*S*)-2-Hydroxyheptan-3-yl 4-methylbenzenesulfonate (SM5)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



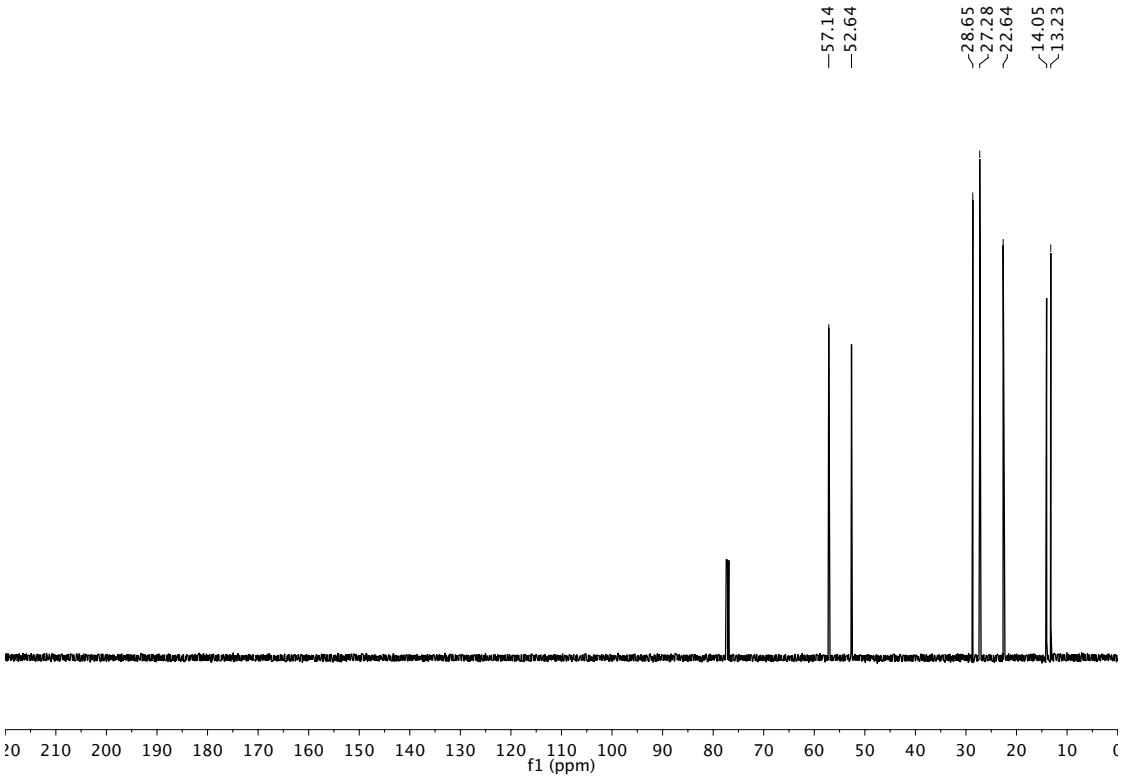

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



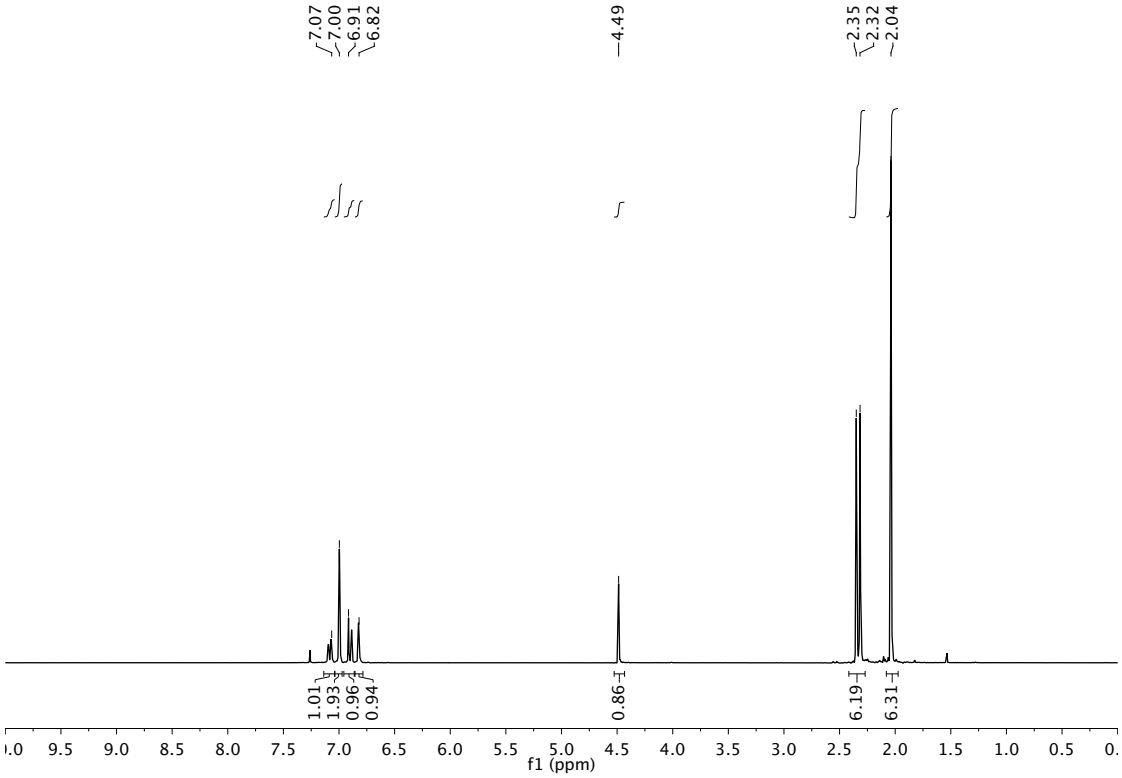
**(2*R*,3*S*)-2-Butyl-3-methyloxirane (3a)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



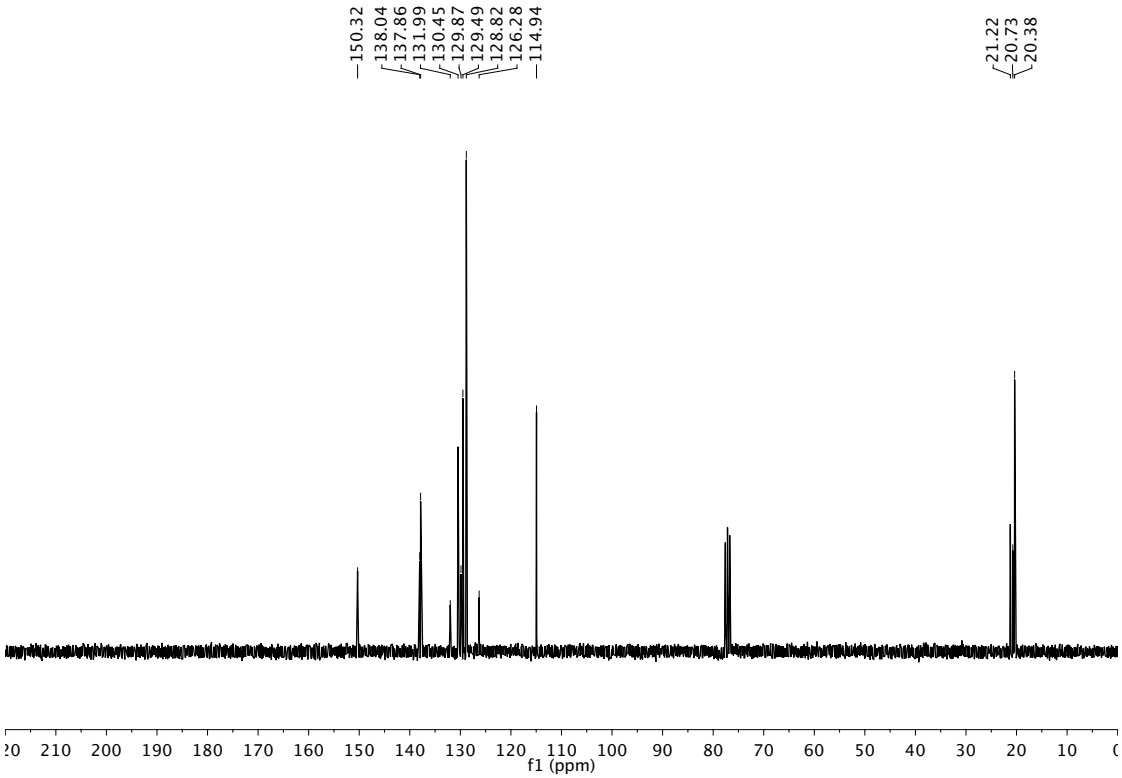

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



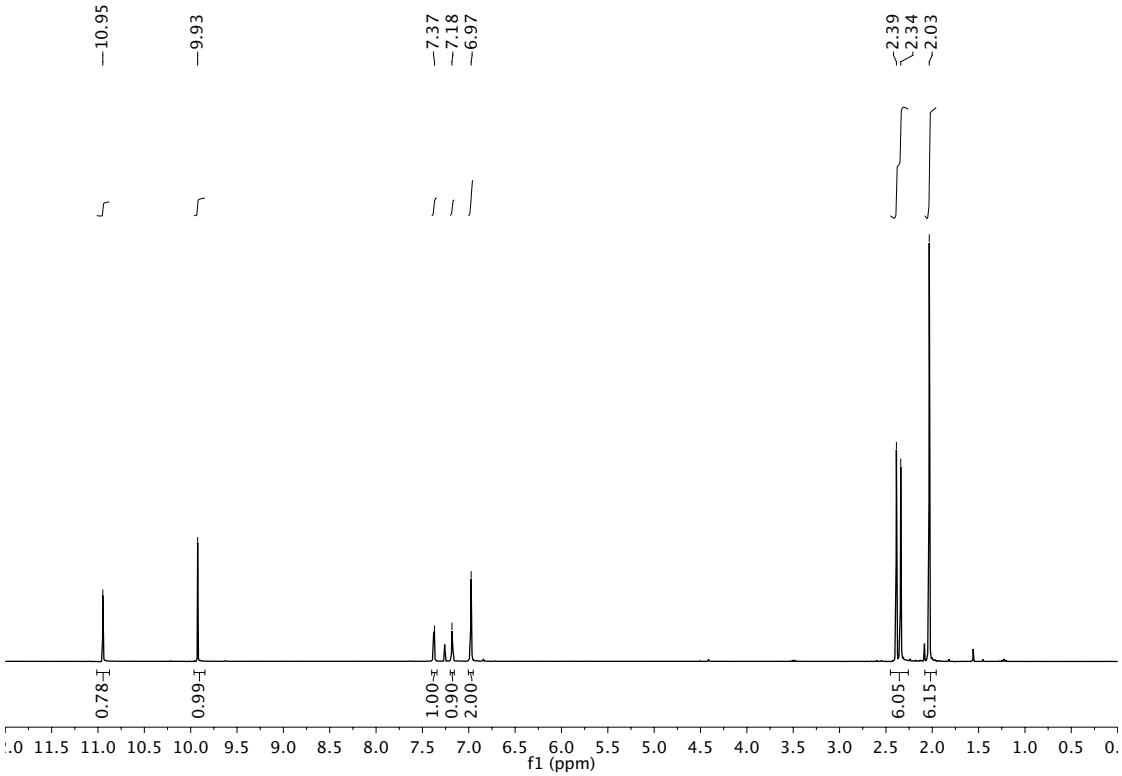
**2',4',5,6'-Tetramethyl-[1,1'-biphenyl]-2-ol (SM6)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



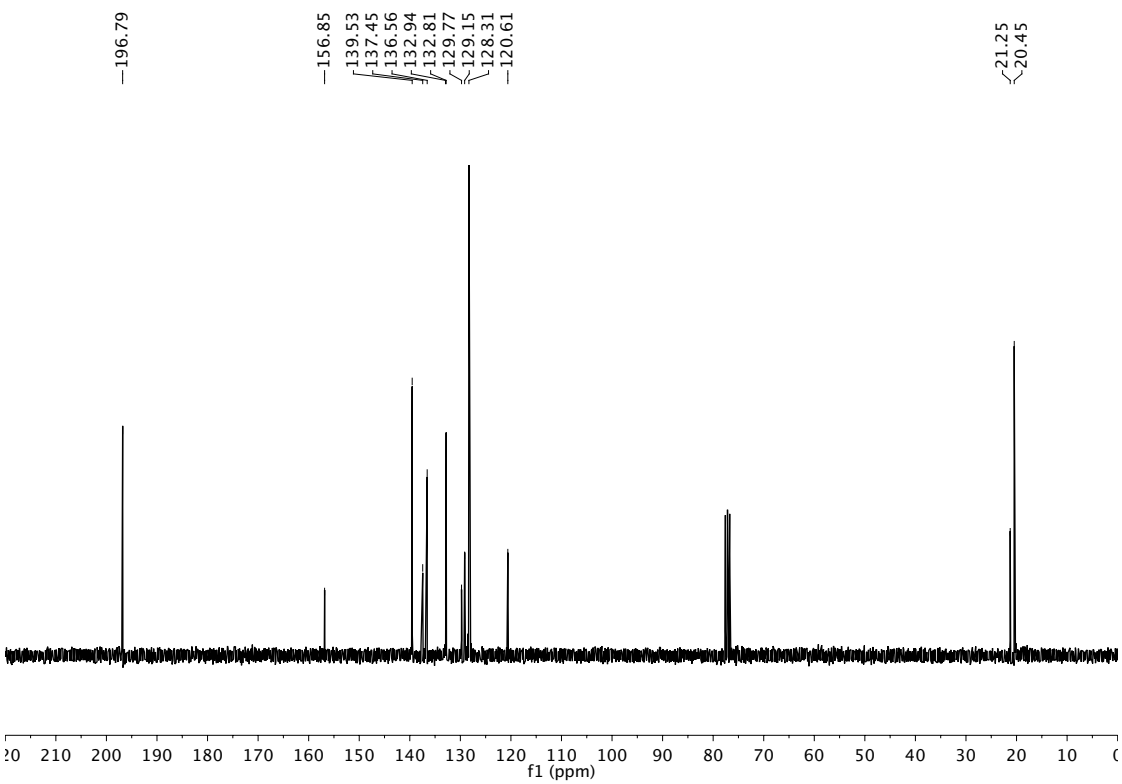

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



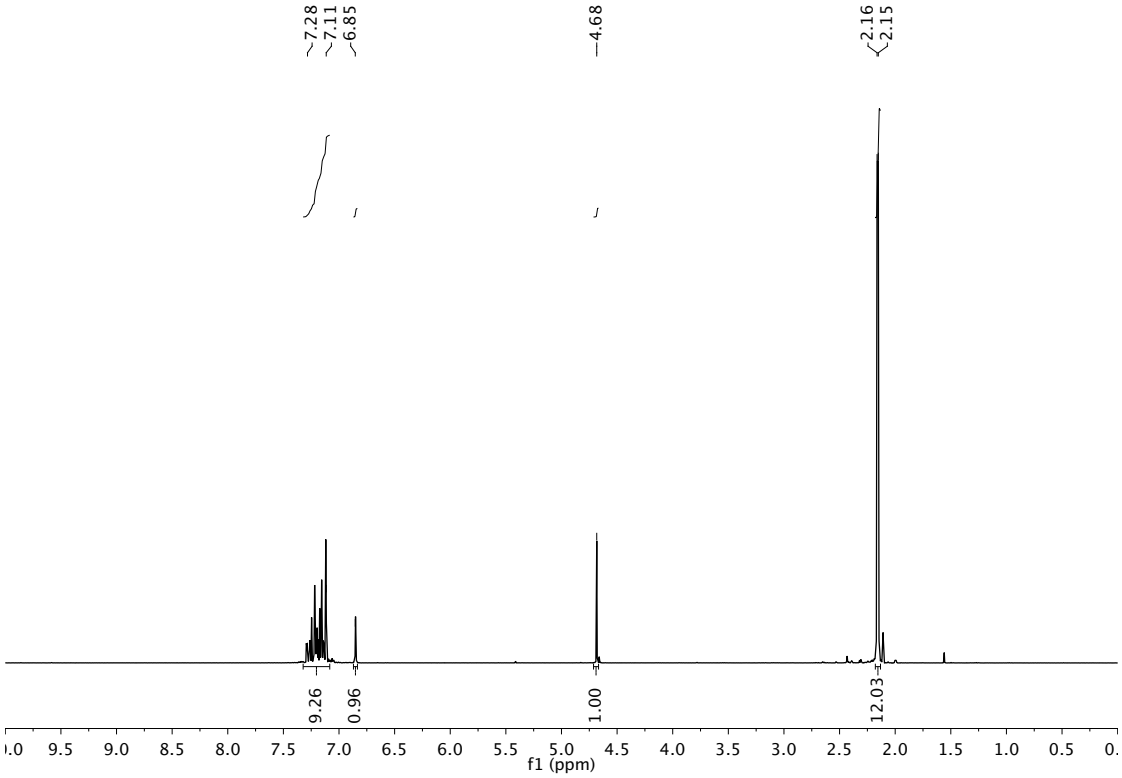
**2-Hydroxy-2',4',5,6'-tetramethyl-[1,1'-biphenyl]-3-carbaldehyde (SM7)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



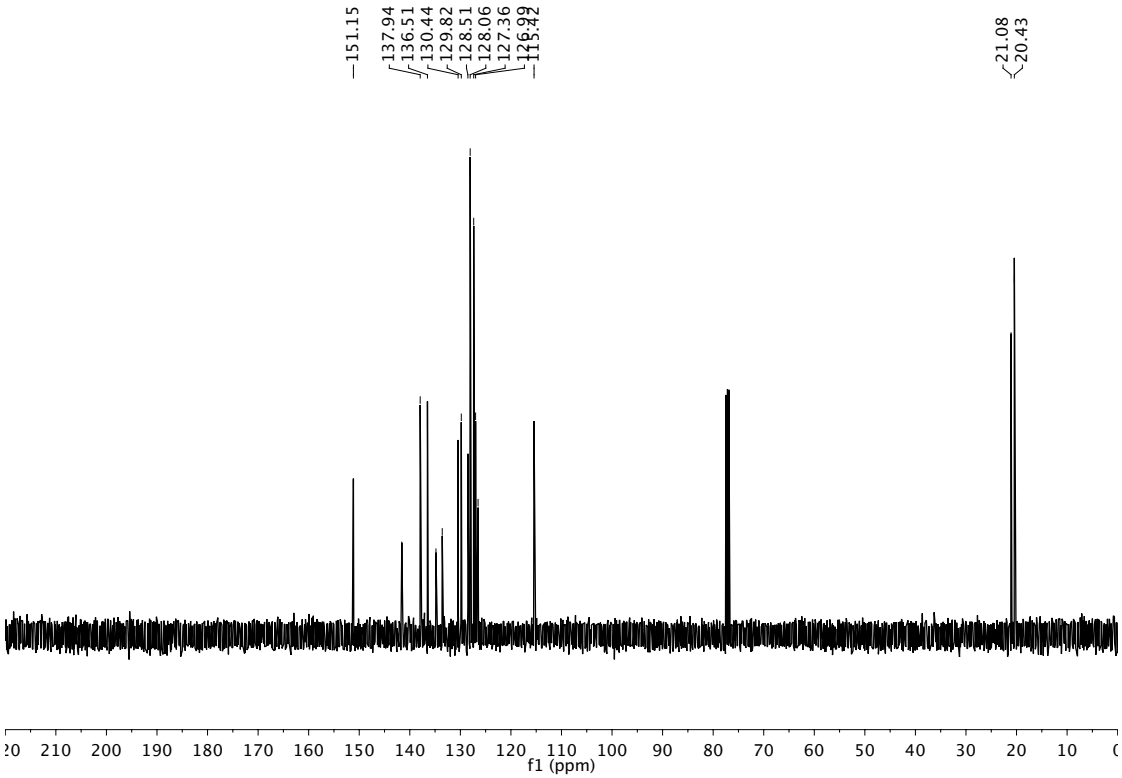

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



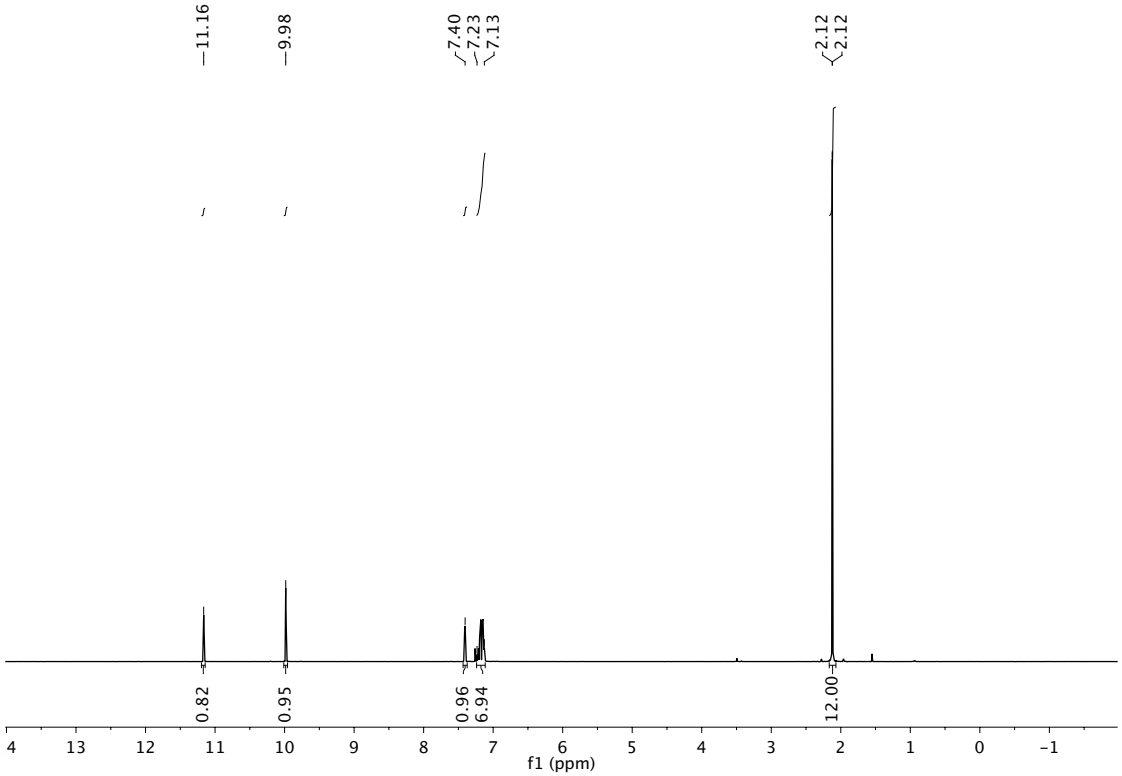
**2,2'',6,6''-Tetramethyl-[1,1':3',1''-terphenyl]-4'-ol (SM8)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



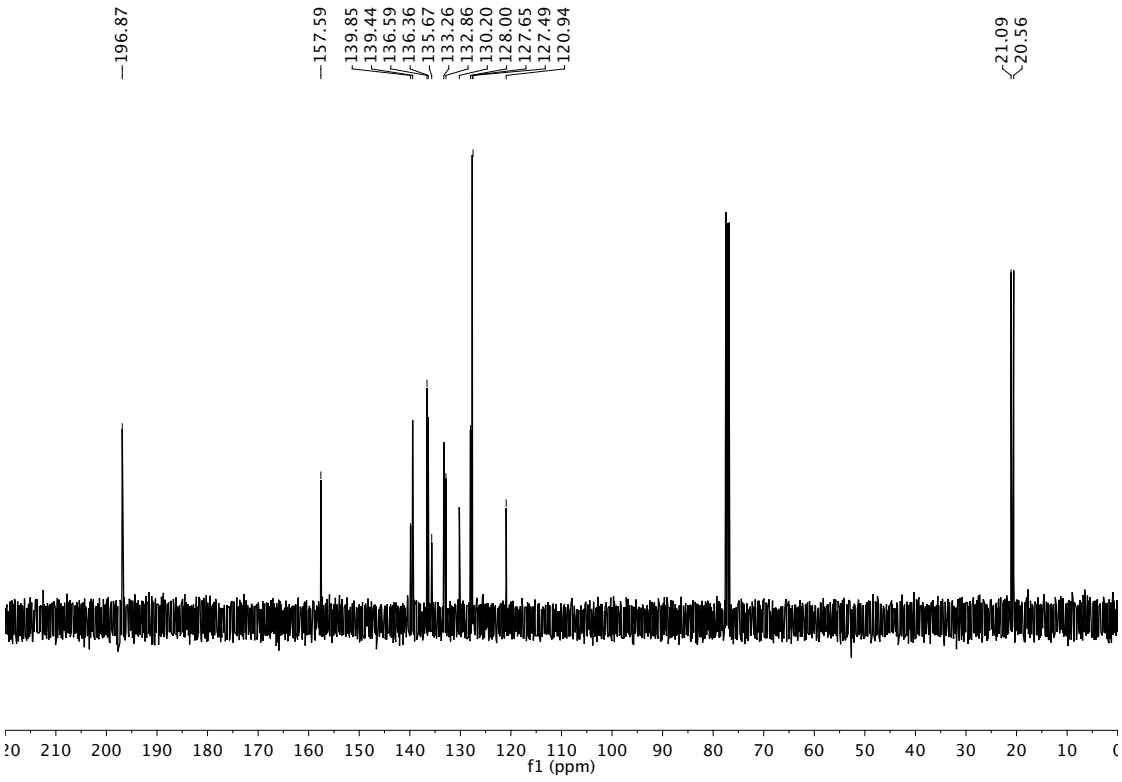

**$^{13}$C NMR spectrum** (101 MHz, $CDCl_3$)



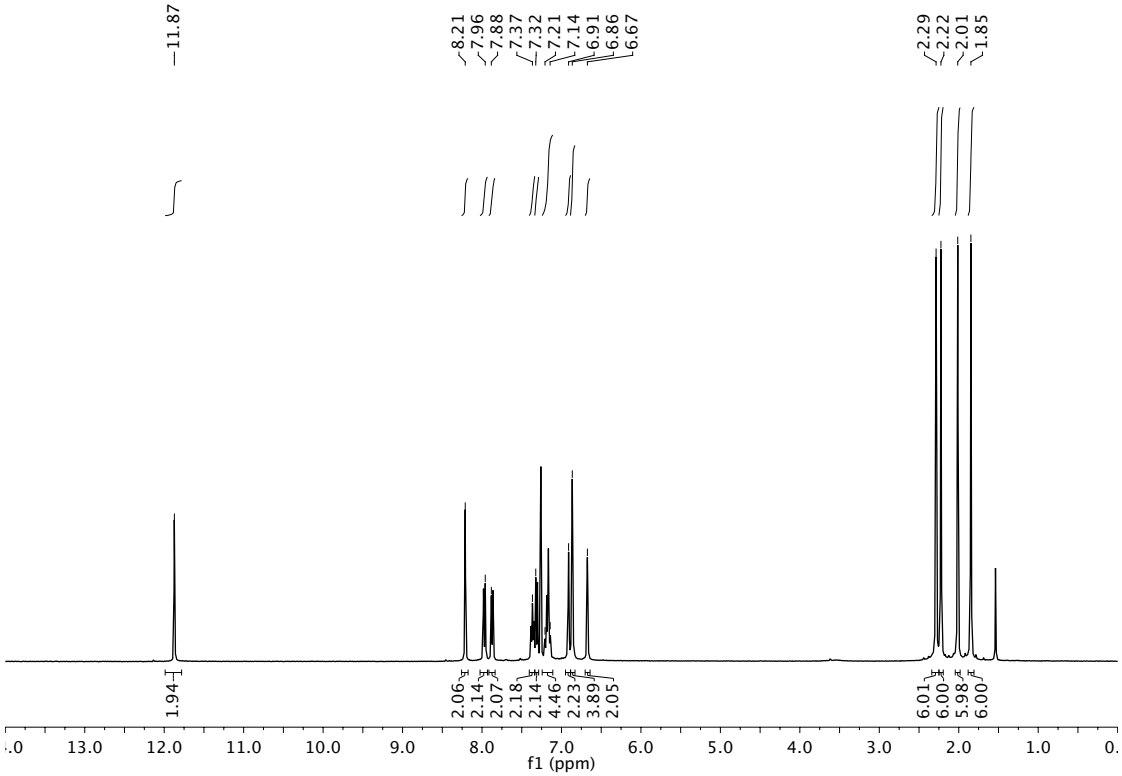
**4'-Hydroxy-2,2'',6,6''-tetramethyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde (SM9)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



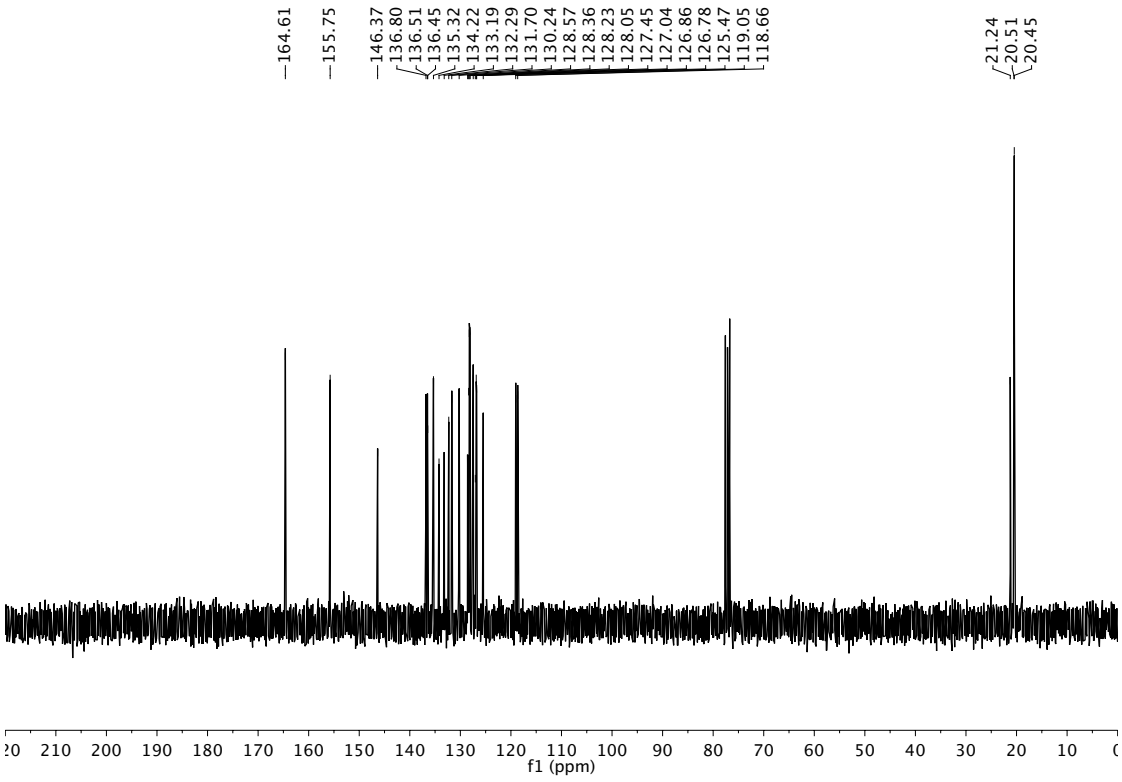

**$^{13}$C NMR spectrum** (101 MHz, $CDCl_3$)



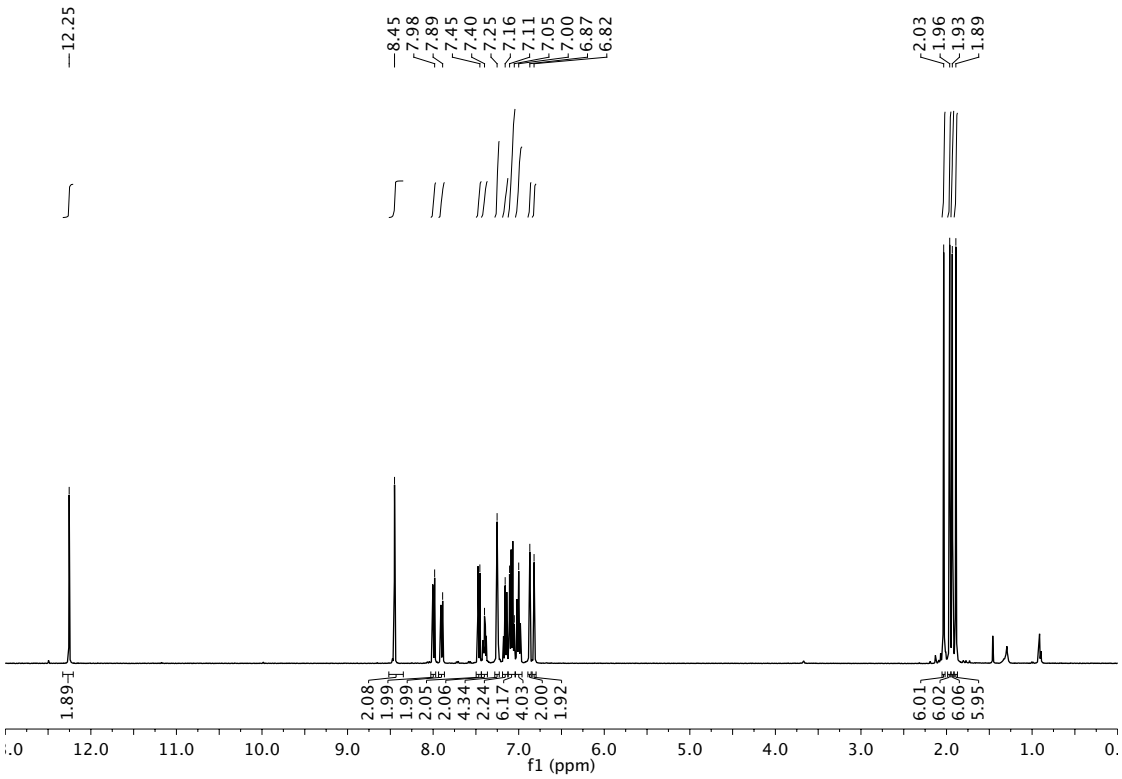
**(*R*)-3,3''-(([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-ol) ((*R*)-MesBinam, (*R*)-L1)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



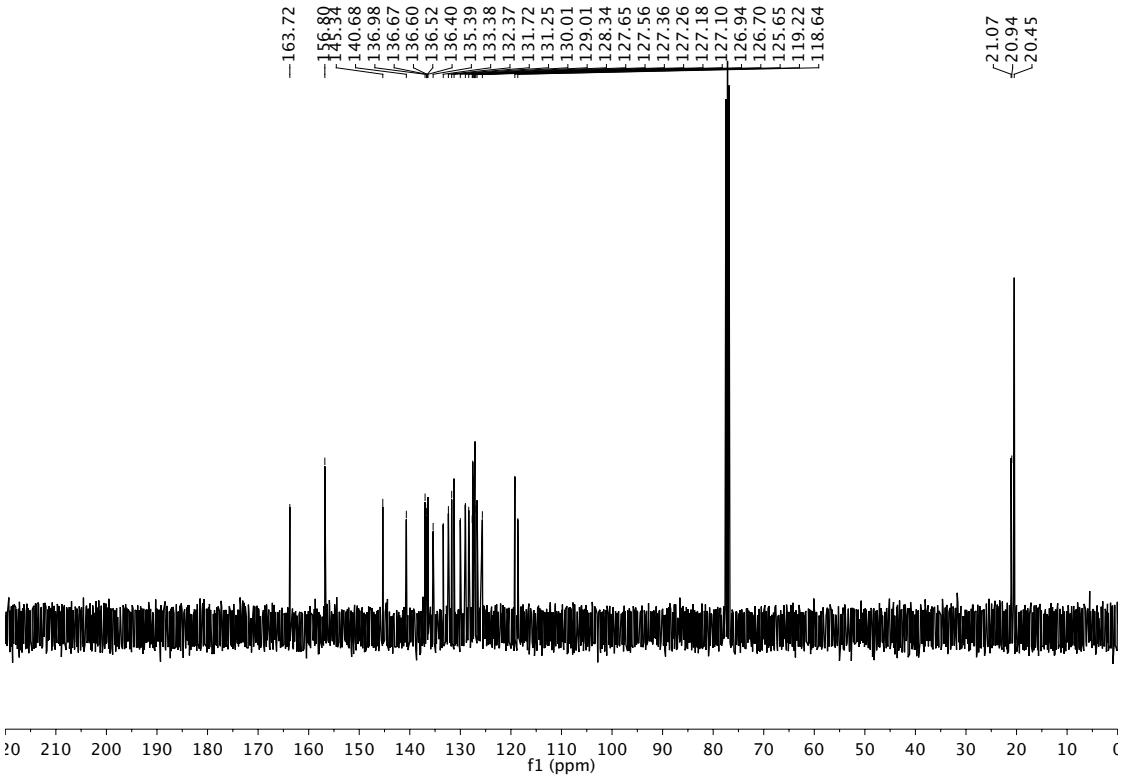

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



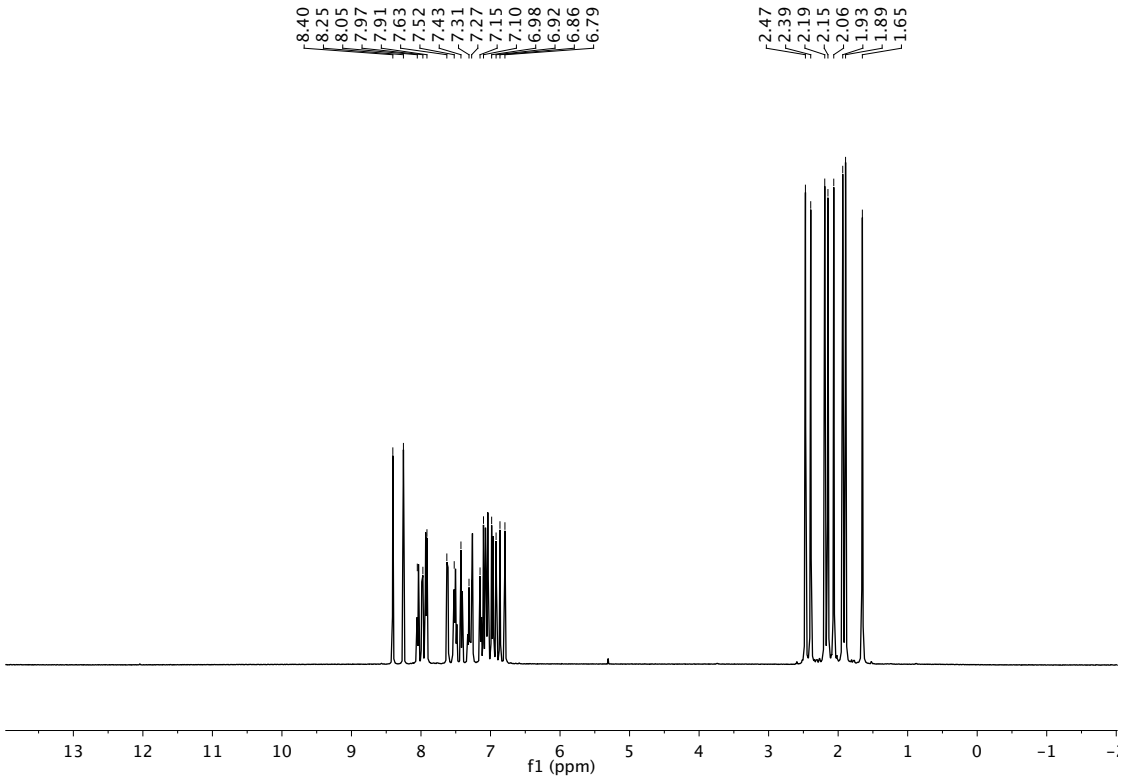
**(*R*)-5',5''''-((1*E*,1'*E*)-([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2,2'',6,6''-tetramethyl-[1,1':3',1''-terphenyl]-4'-ol) ((*R*)-Xyl$_2$Binam, (*R*)-L2)**, **$^1$H NMR spectrum** (400 MHz, $CDCl_3$)



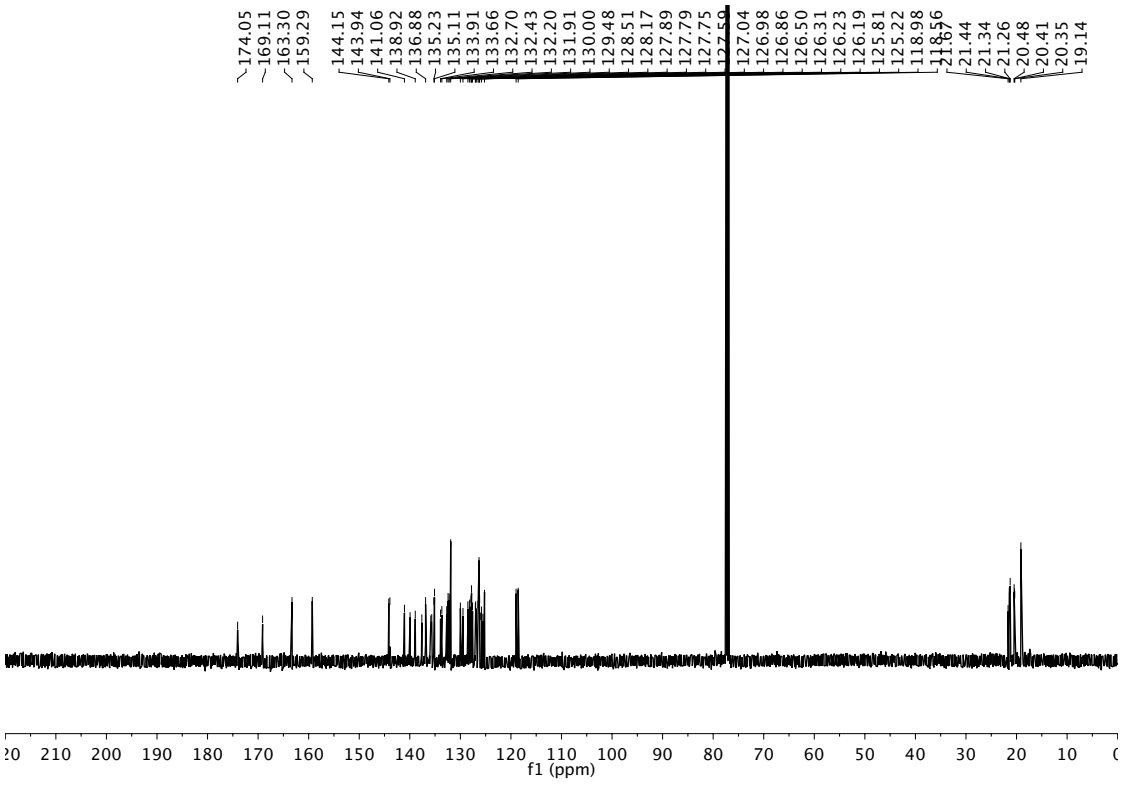

**$^{13}$C NMR spectrum** (101 MHz, $CDCl_3$)



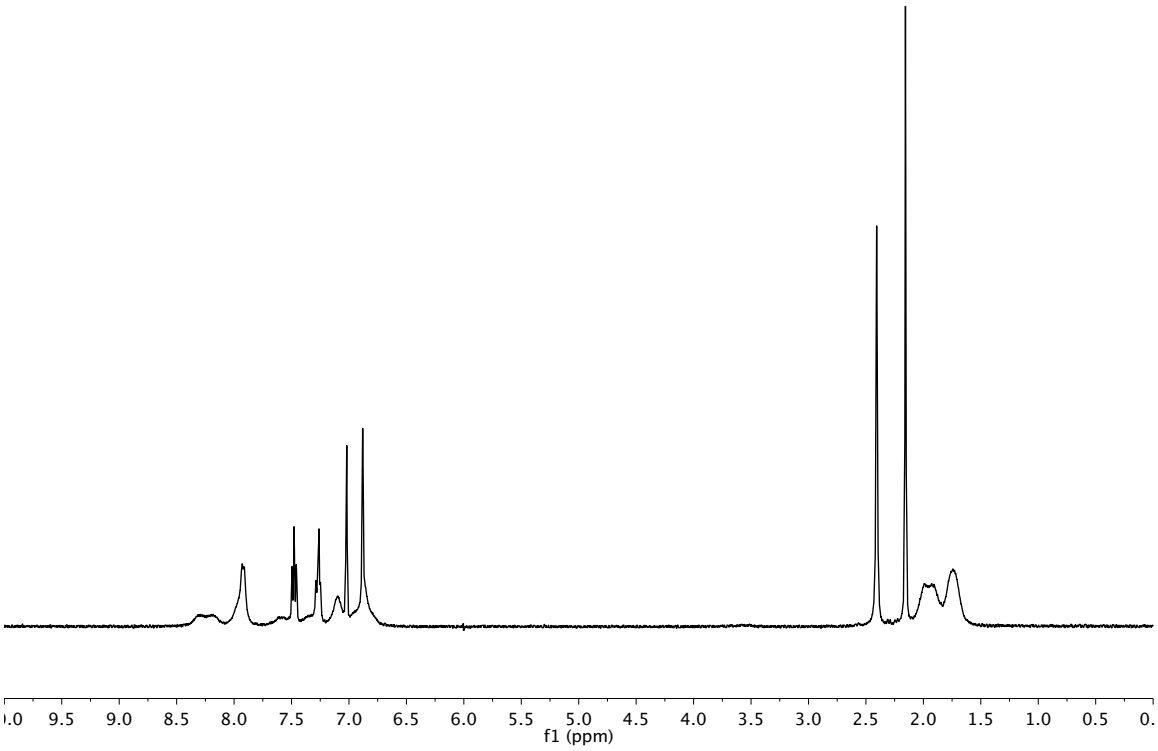
**(*R*)-MesBinamAlCl ((*R*)-ML1, precursor to (*R*)-1b)**, **$^{1}$H NMR spectrum** (500 MHz, $CDCl_3$, -55 °C)



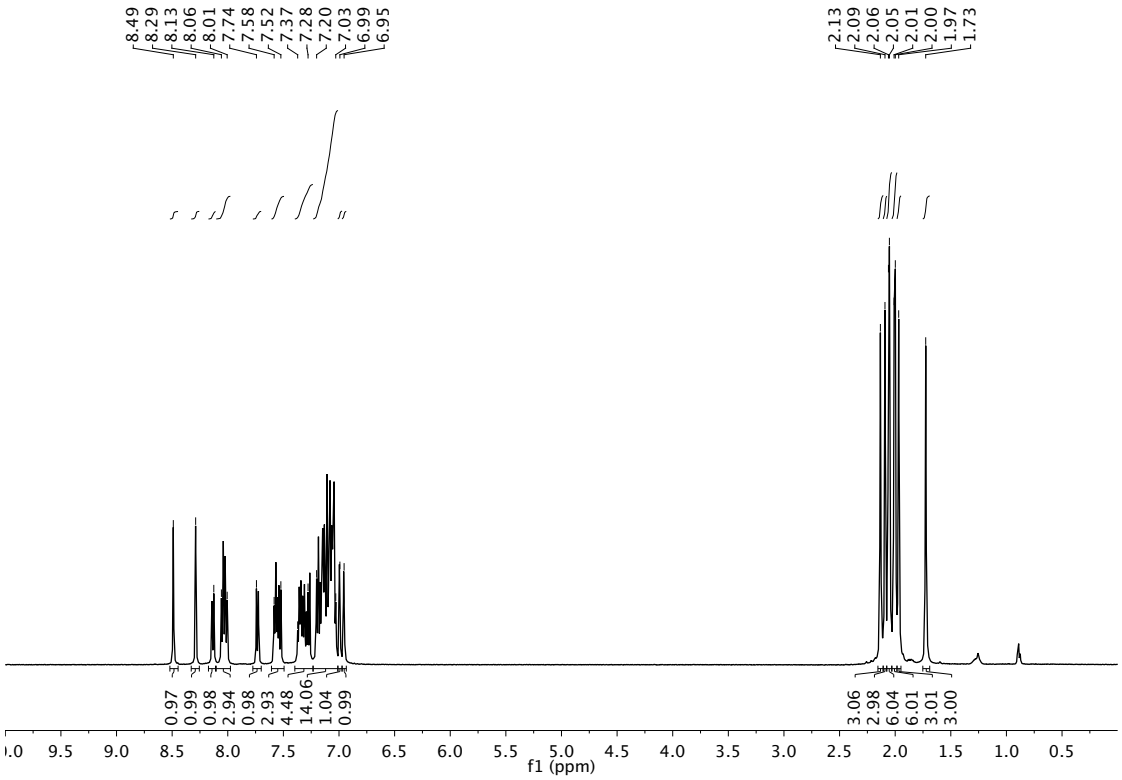

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$, -55 °C)



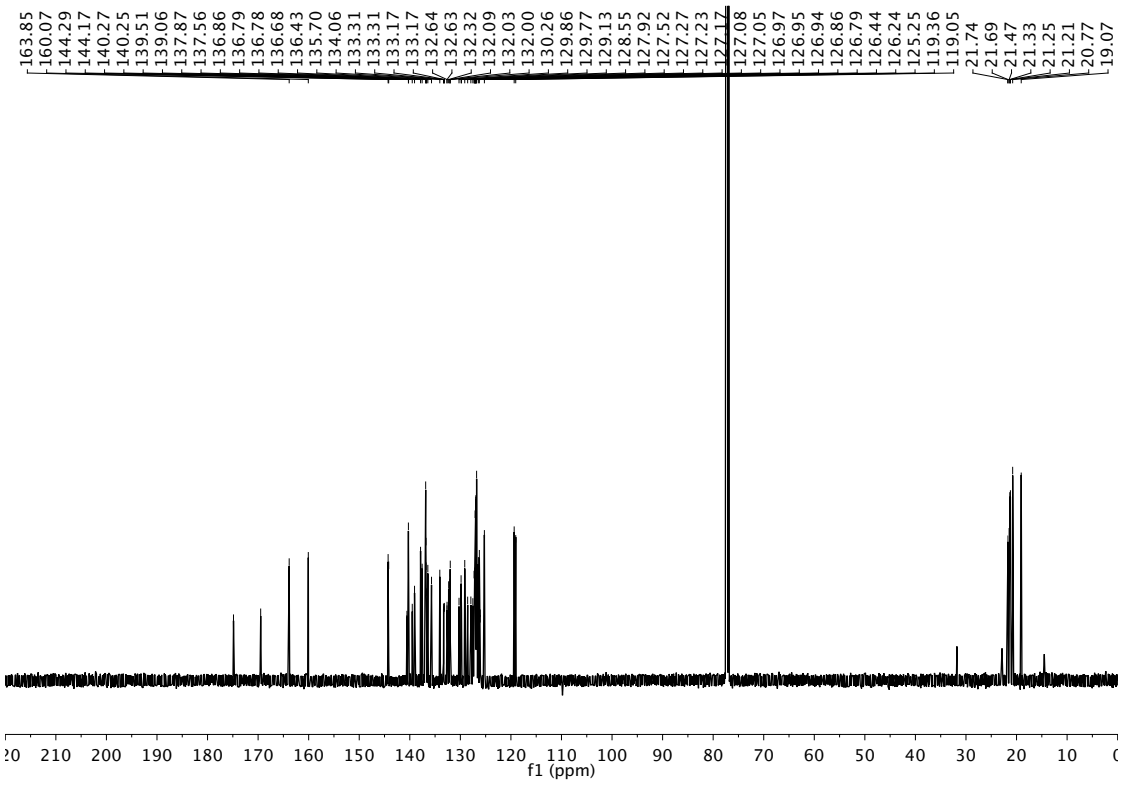
**(*R*)-MesBinamAlCl ((*R*)-ML1, precursor to (*R*)-1b)**, **$^1$H NMR spectrum** (500 MHz, $CDCl_3$, 22 °C)



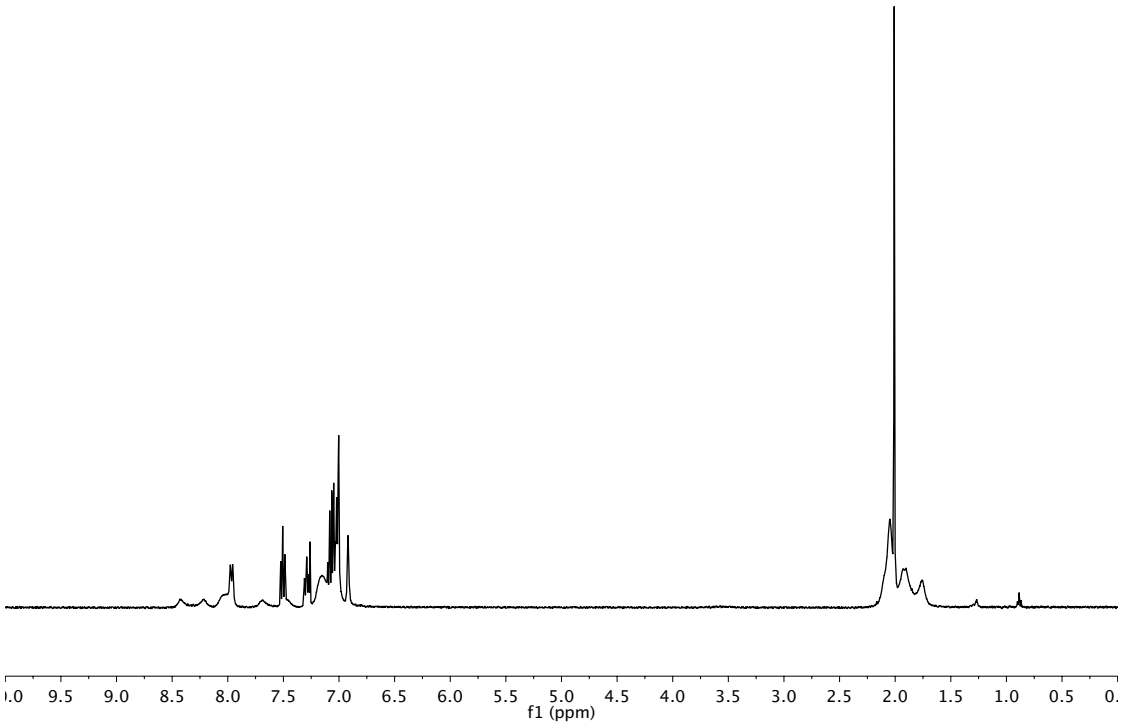
**(*R*)-Xyl$_2$BinamAlCl ((*R*)-ML2, precursor to (*R*)-1c), $^1$H NMR spectrum** (500 MHz, $CDCl_3$, -55 °C)



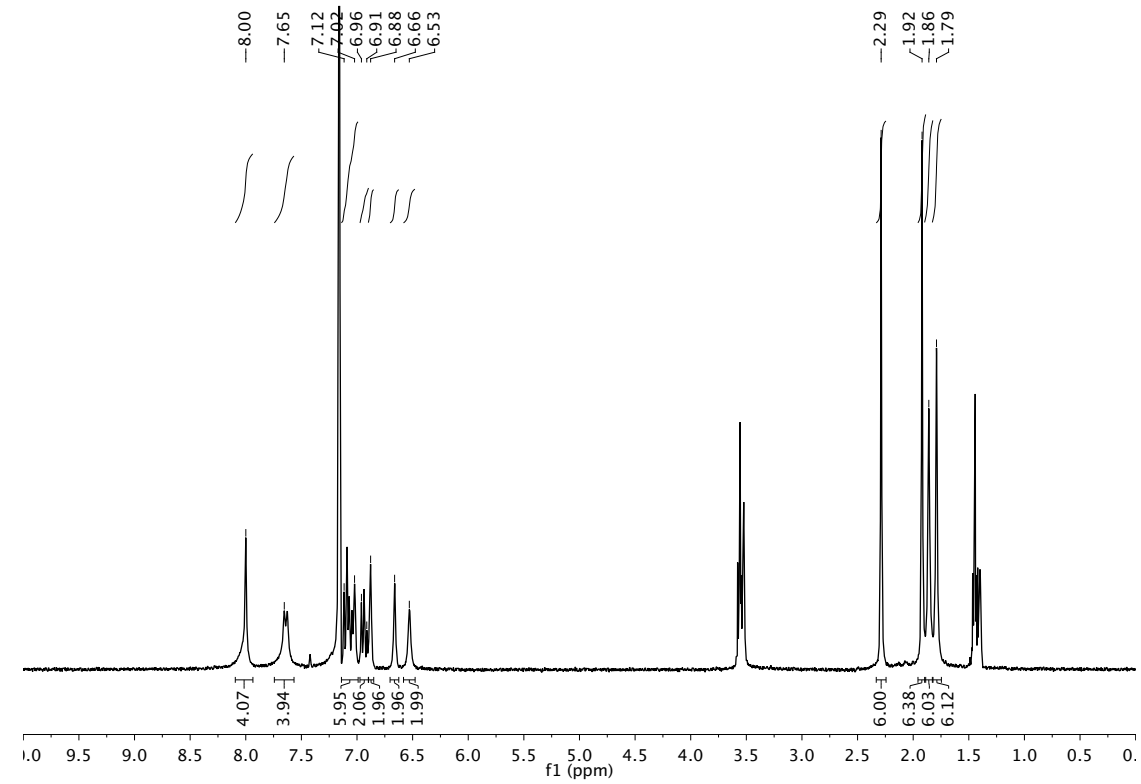

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$, -55 °C)



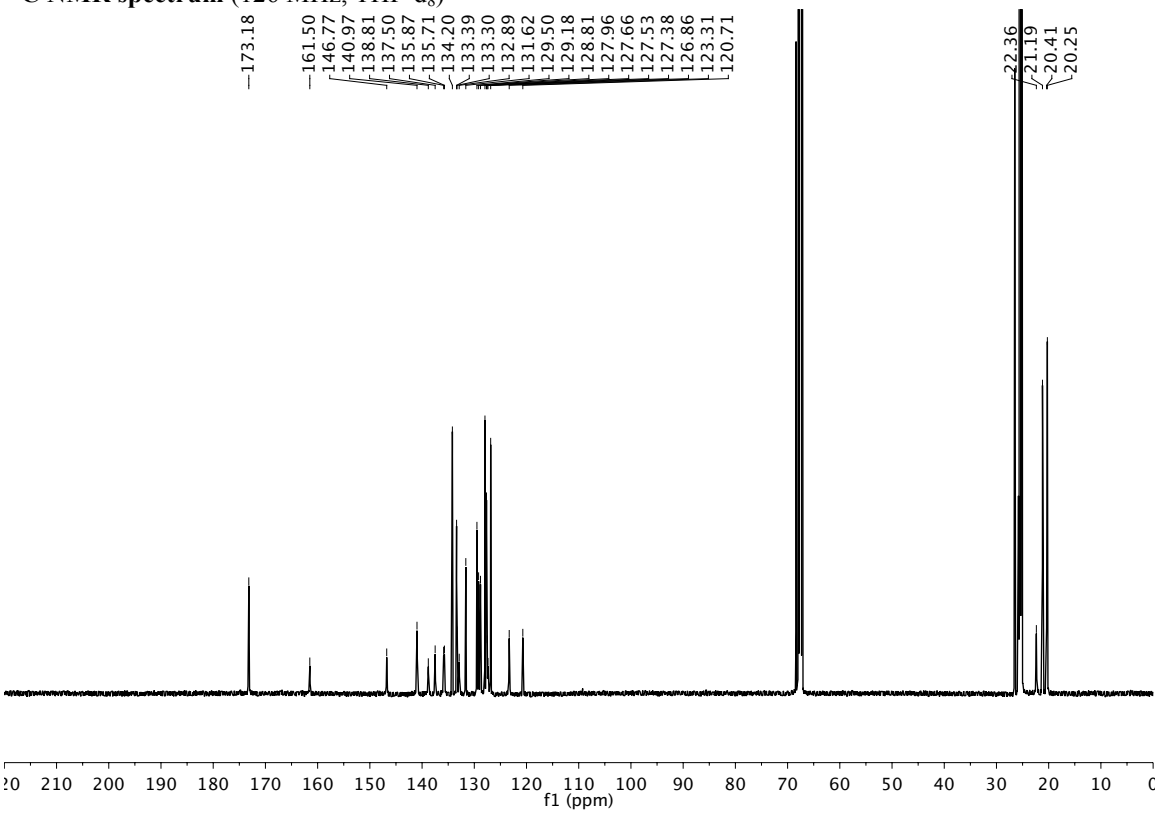
**(*R*)-Xyl$_2$BinamAlCl ((*R*)-ML2, precursor to (*R*)-1c), $^1$H NMR spectrum** (500 MHz, $CDCl_3$, 22 °C)



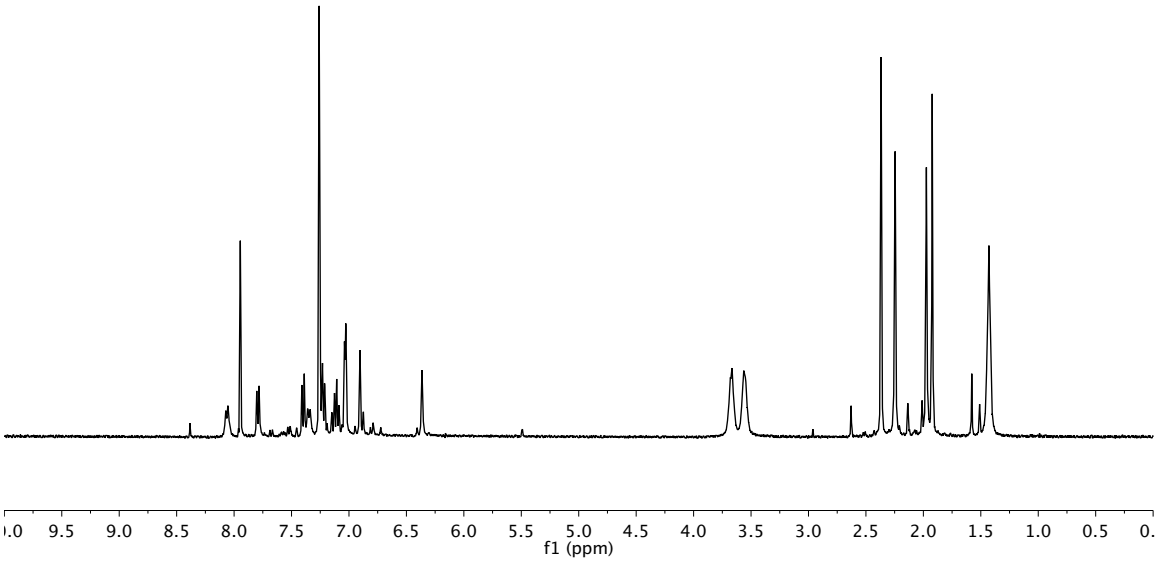
**[(*R*)-MesBinamAl]$^{+}$[Co(CO)$_4$]$^{-}$ ((*R*)-1b)**, **$^{1}$H NMR spectrum** (300 MHz, $C_6D_6$ + THF-$d_8$)



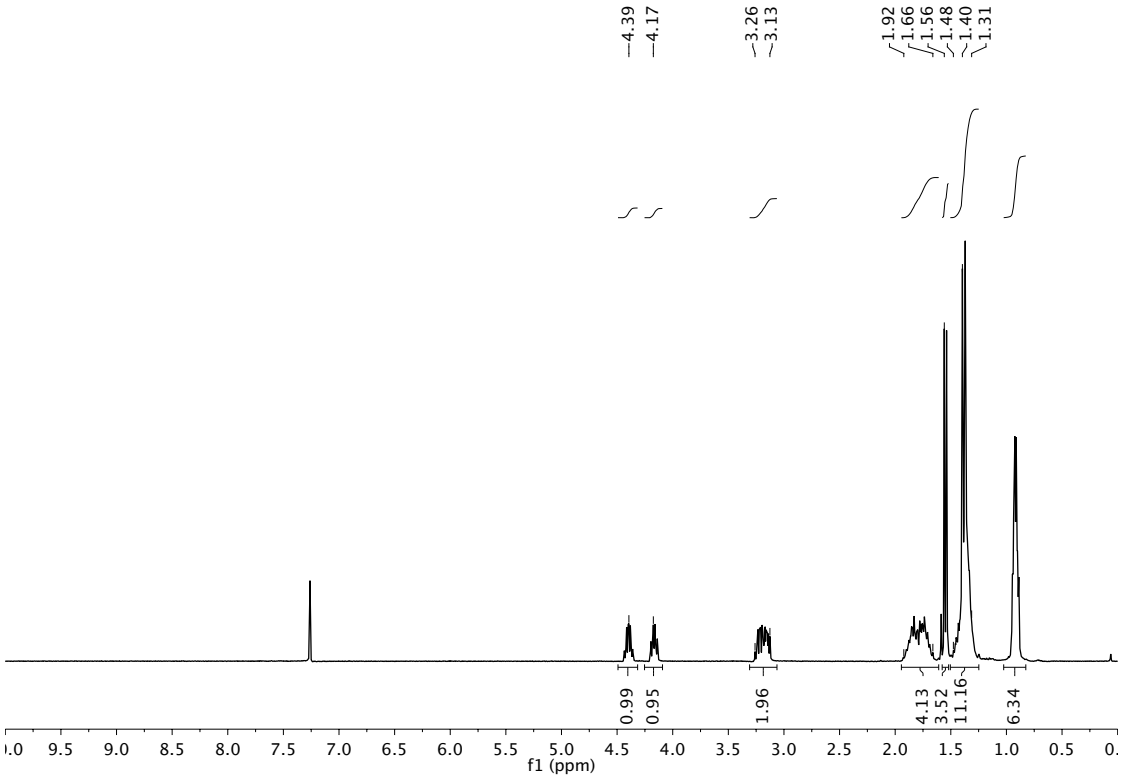

**$^{13}$C NMR spectrum** (126 MHz, THF-$d_8$)



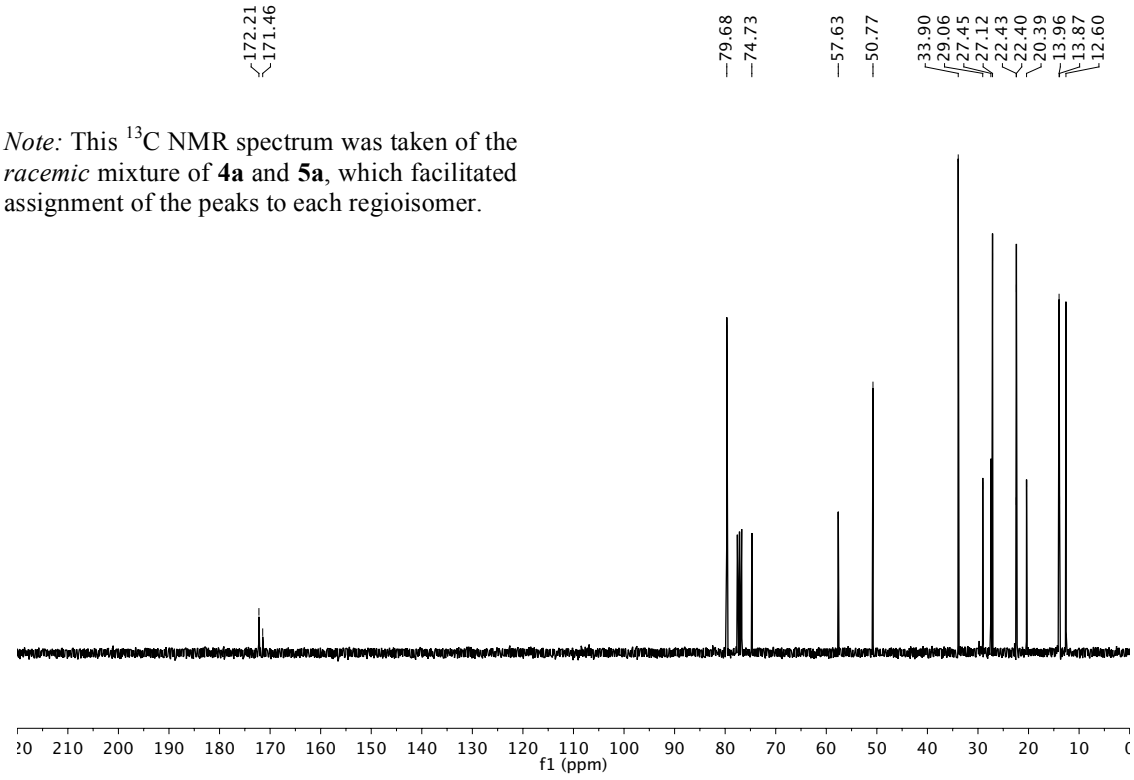
**[(*R*)-MesBinamAl]$^{+}$[Co(CO)$_4$]$^{-}$ ((*R*)-1b)**, **$^{1}$H NMR spectrum** (300 MHz, $C_6D_6$, no additional THF added)



**(3*R*,4*R*)-4-Butyl-3-methyloxetan-2-one (4a) and (3*R*,4*R*)-3-butyl-4-methyloxetan-2-one (5a)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)

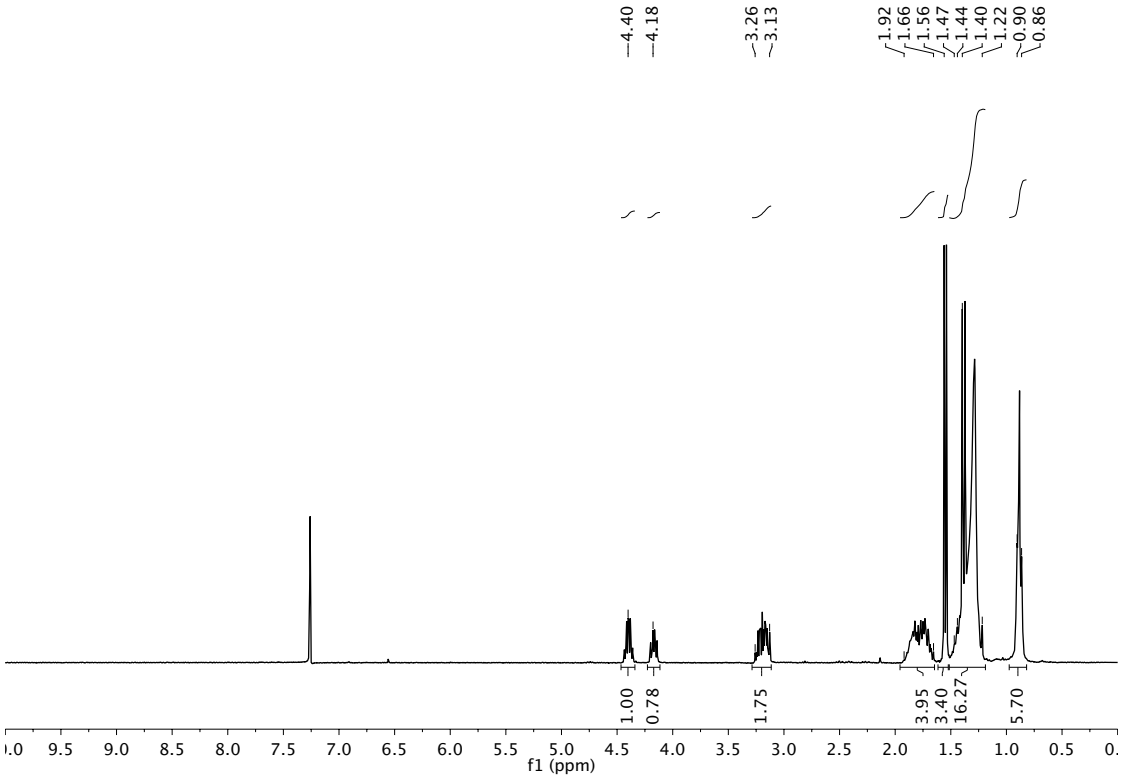



**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)

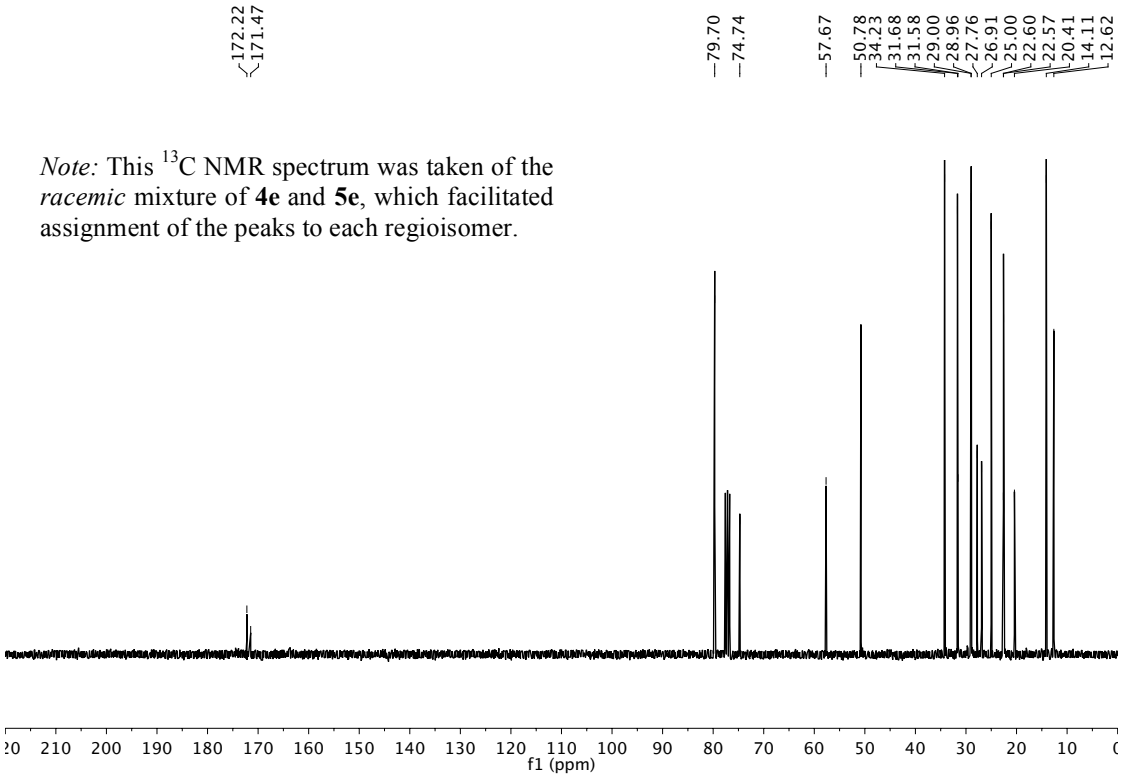



*Note:* This $^{13}$C NMR spectrum was taken of the *racemic* mixture of **4a** and **5a**, which facilitated assignment of the peaks to each regioisomer.

**(3*R*,4*R*)-4-Hexyl-3-methyloxetan-2-one (4e) and (3*R*,4*R*)-3-hexyl-4-methyloxetan-2-one (5e)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)

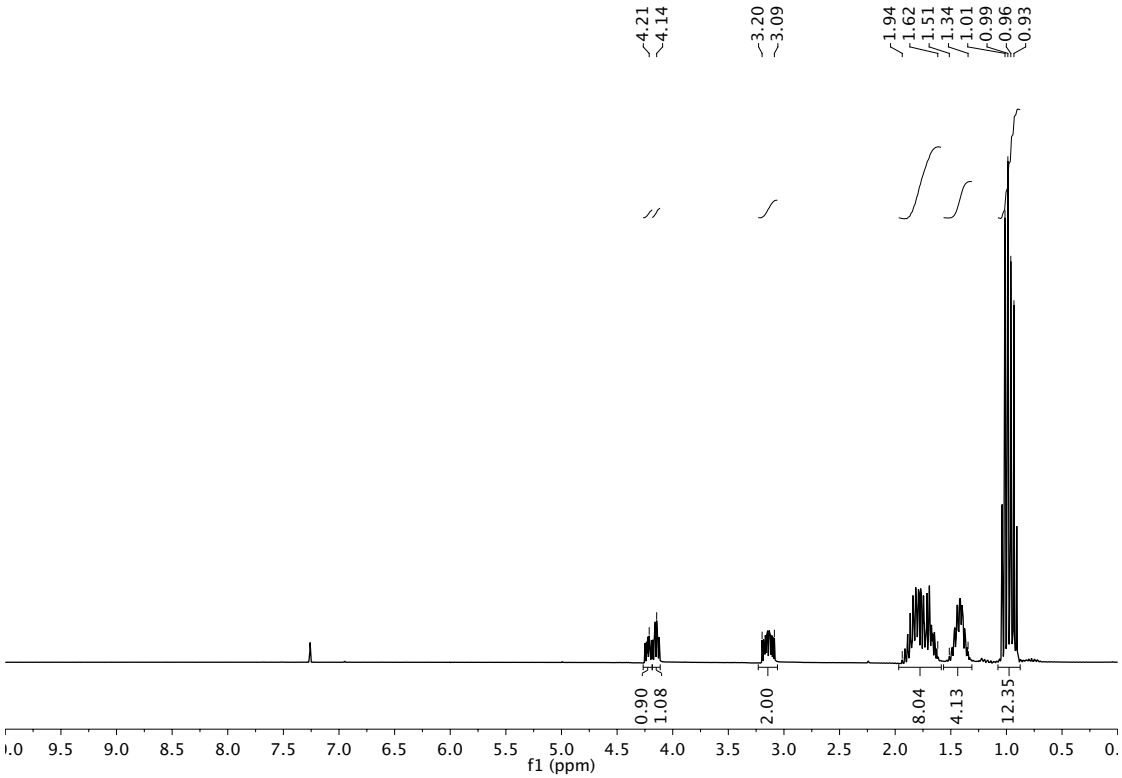



**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)

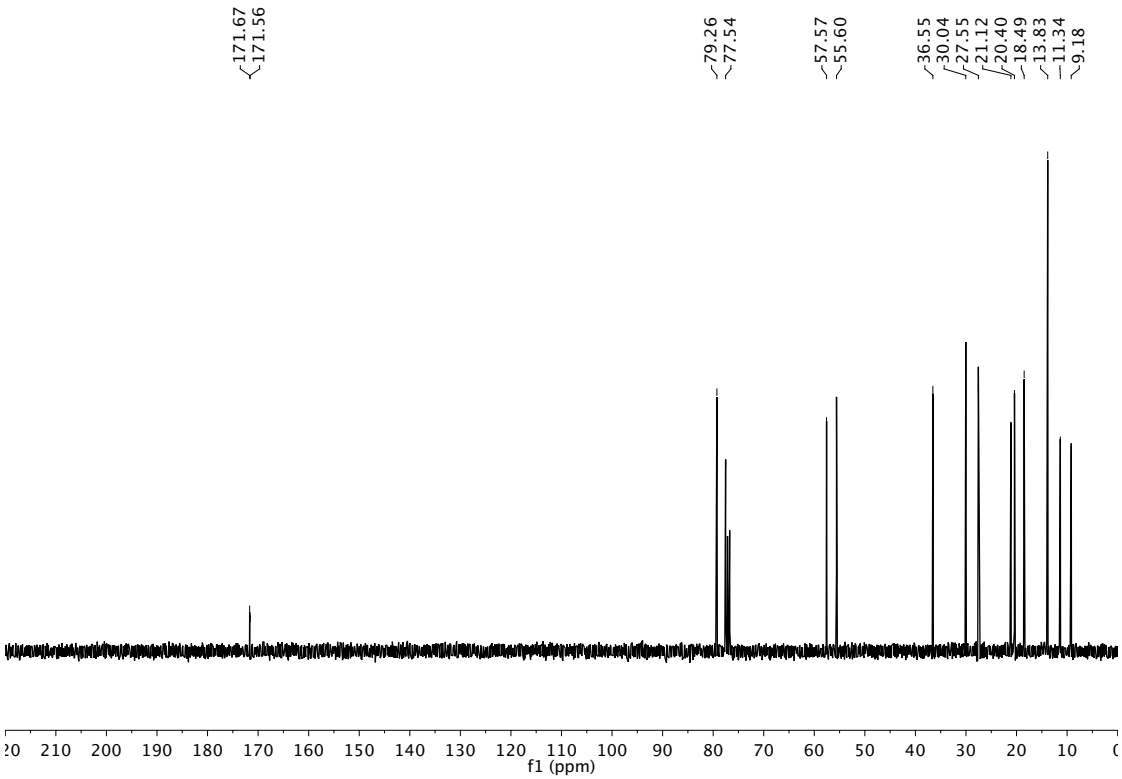



*Note:* This $^{13}$C NMR spectrum was taken of the *racemic* mixture of **4e** and **5e**, which facilitated assignment of the peaks to each regioisomer.

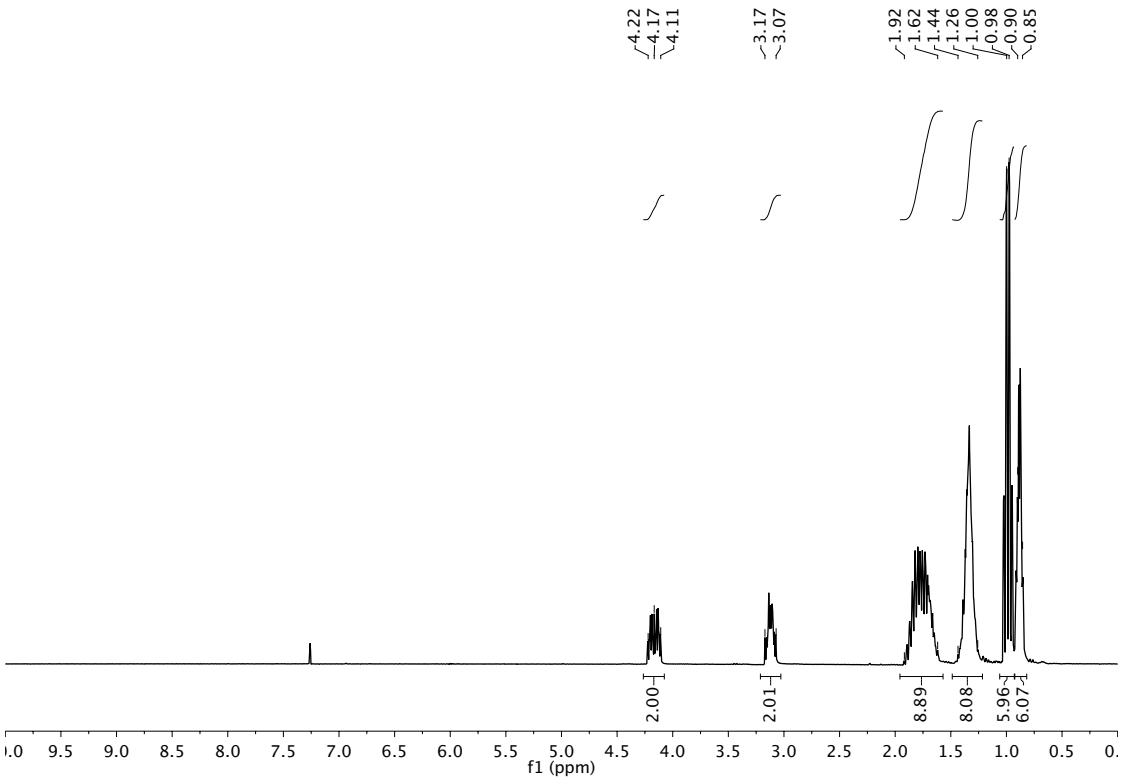
**(3*R*,4*R*)-3-Ethyl-4-propyloxetan-2-one (4h) and (3*R*,4*R*)-4-ethyl-3-propyloxetan-2-one (5h)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



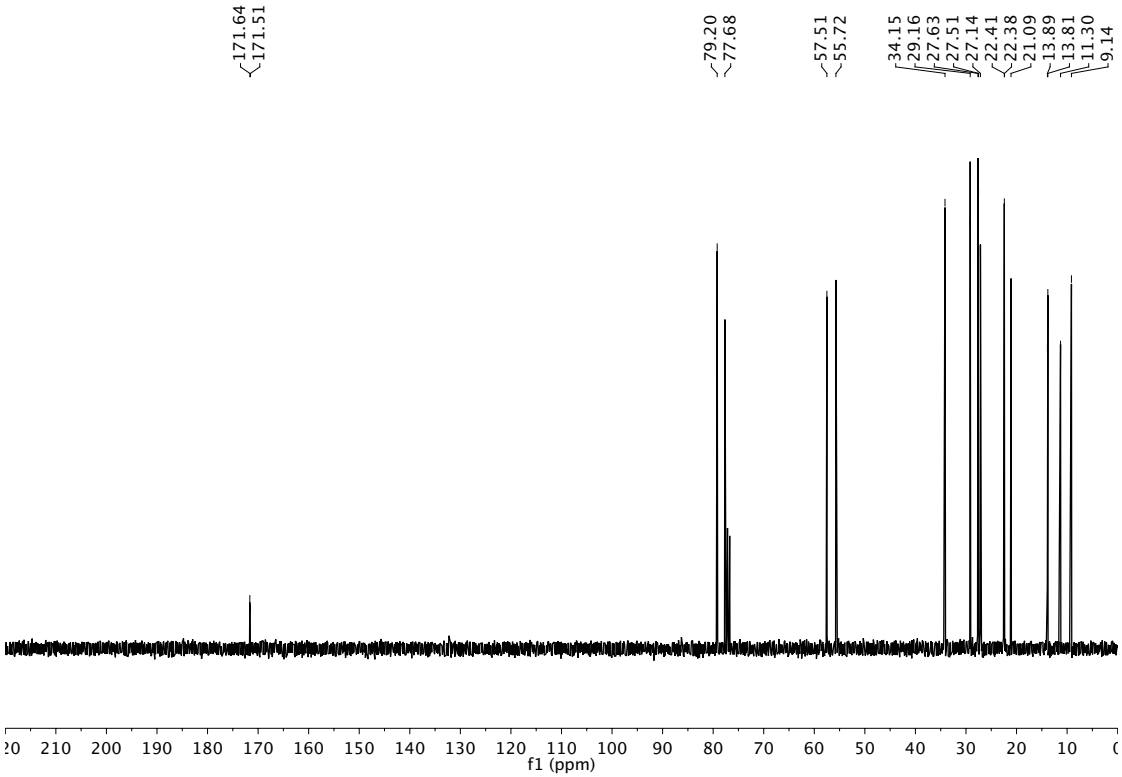

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



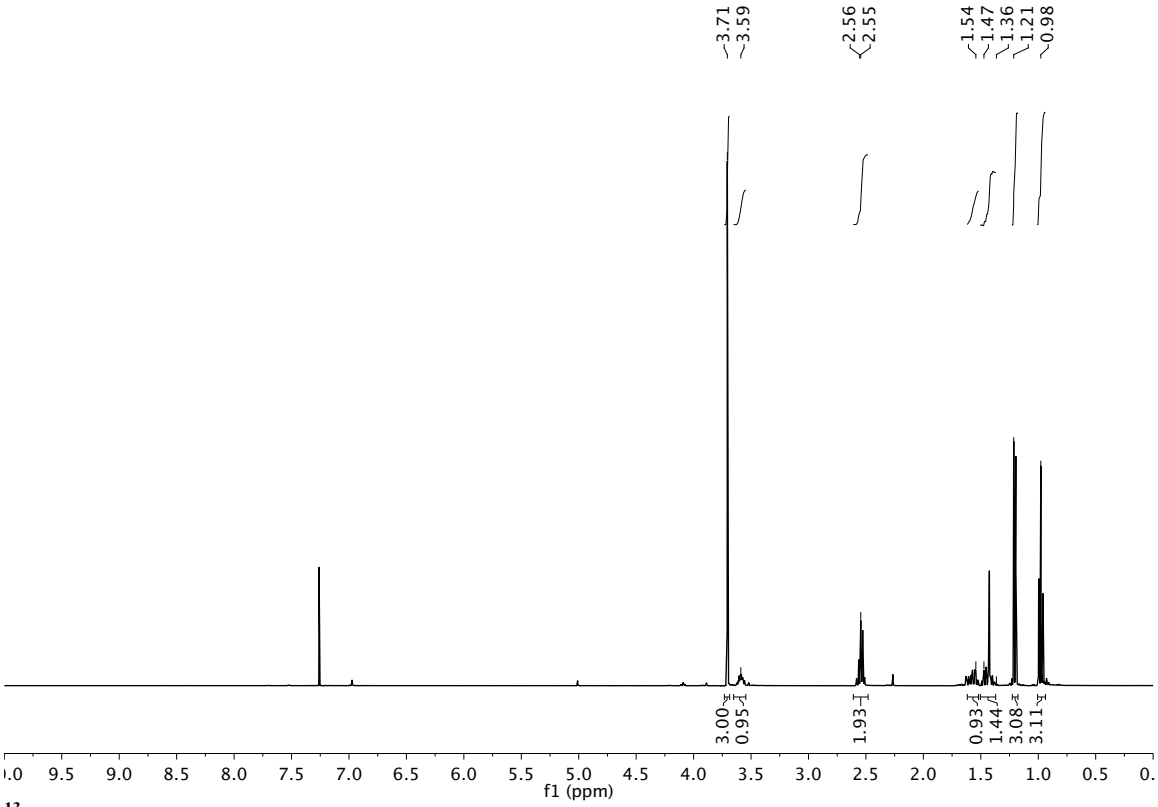
**(3*R*,4*R*)-4-Butyl-3-ethyloxetan-2-one (4i) and (3*R*,4*R*)-3-butyl-4-ethyloxetan-2-one (5i)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



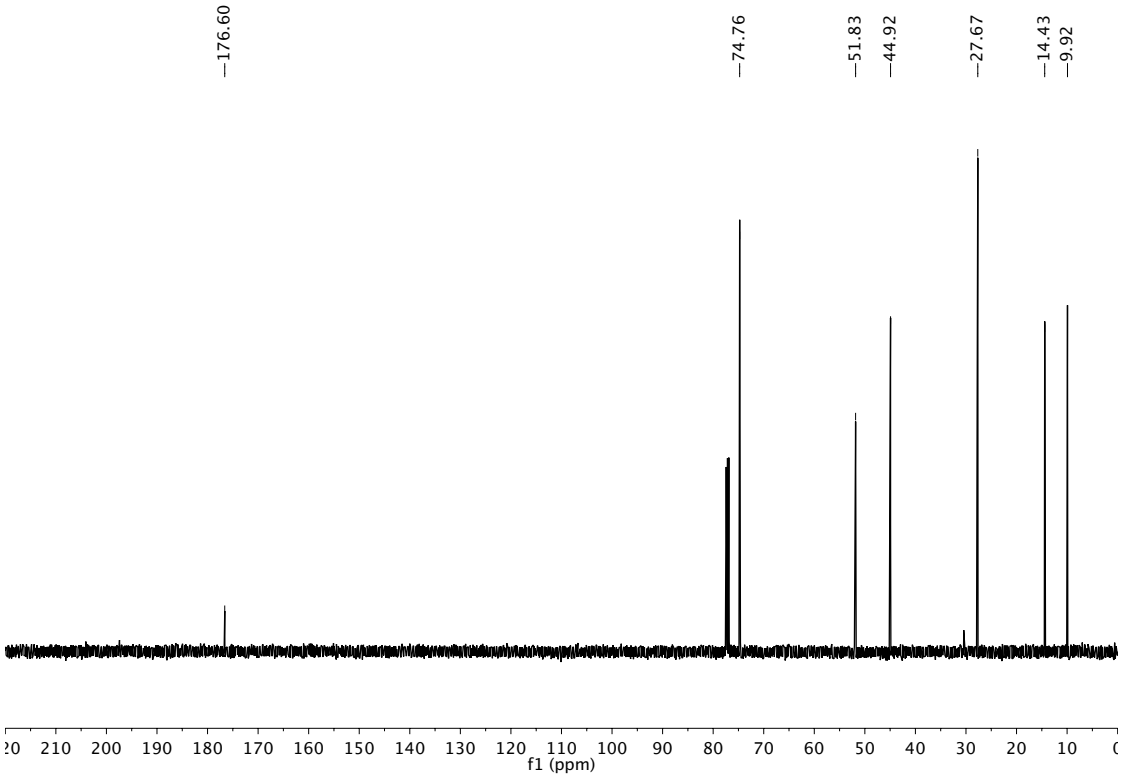

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



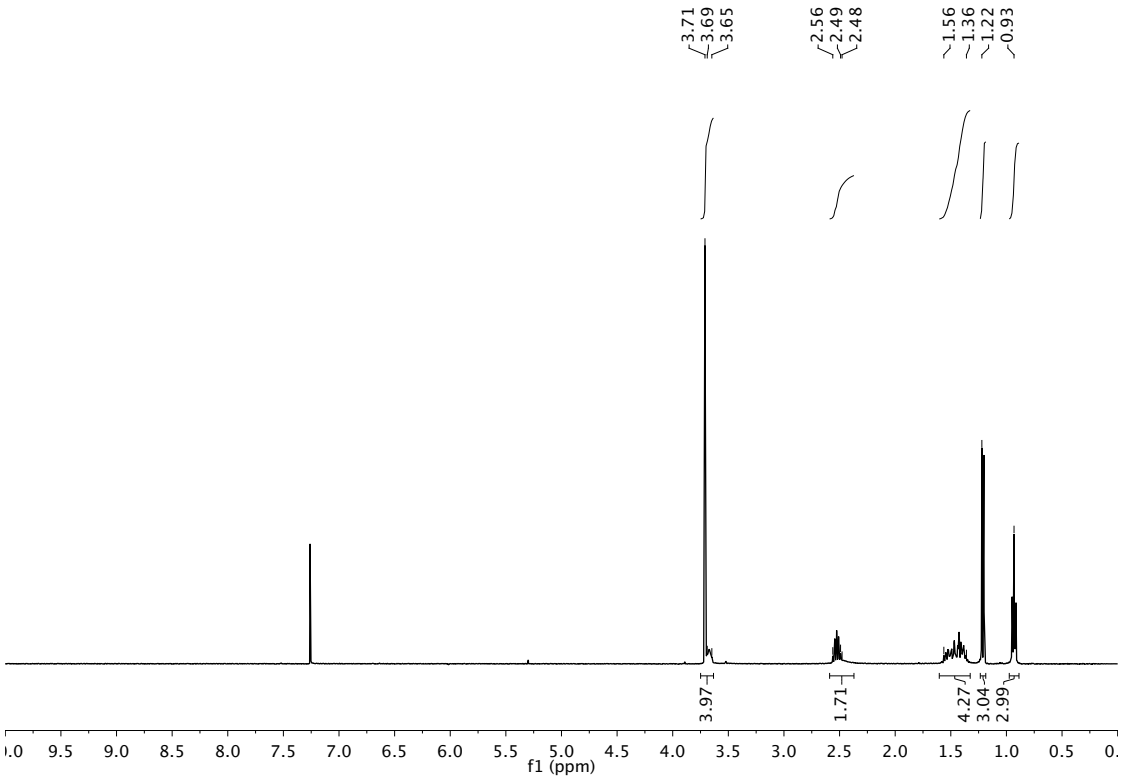
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylpentanoate (6b)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



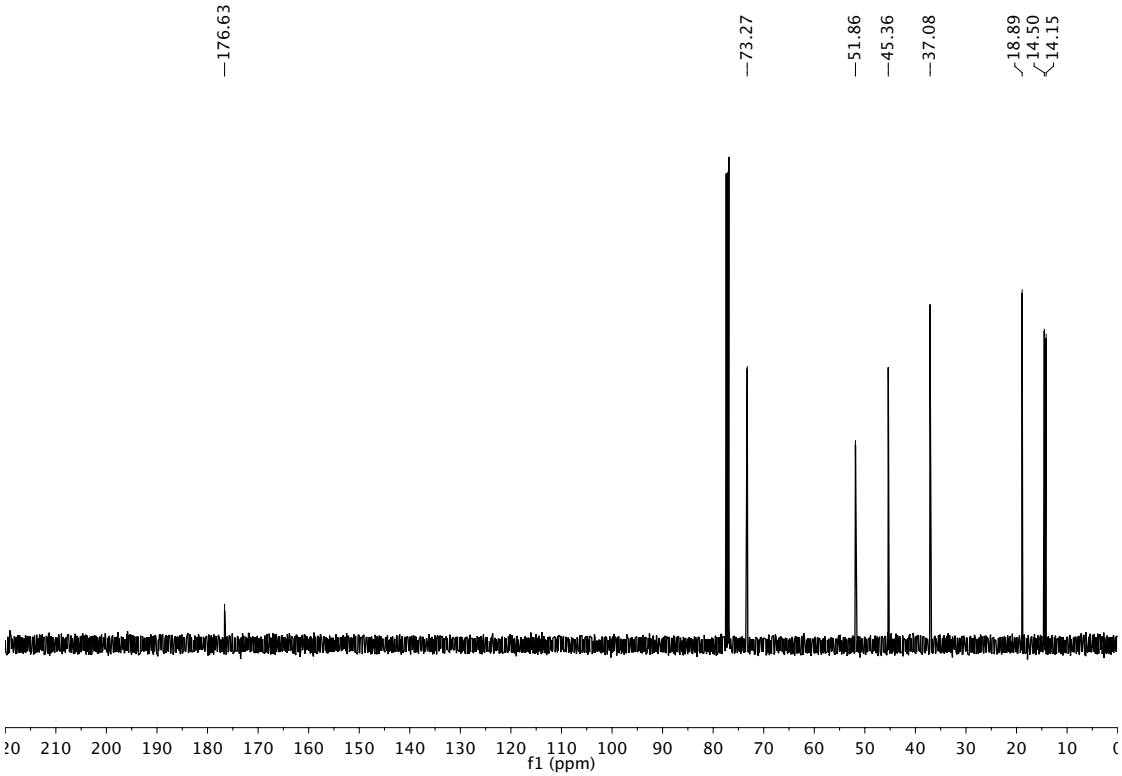

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



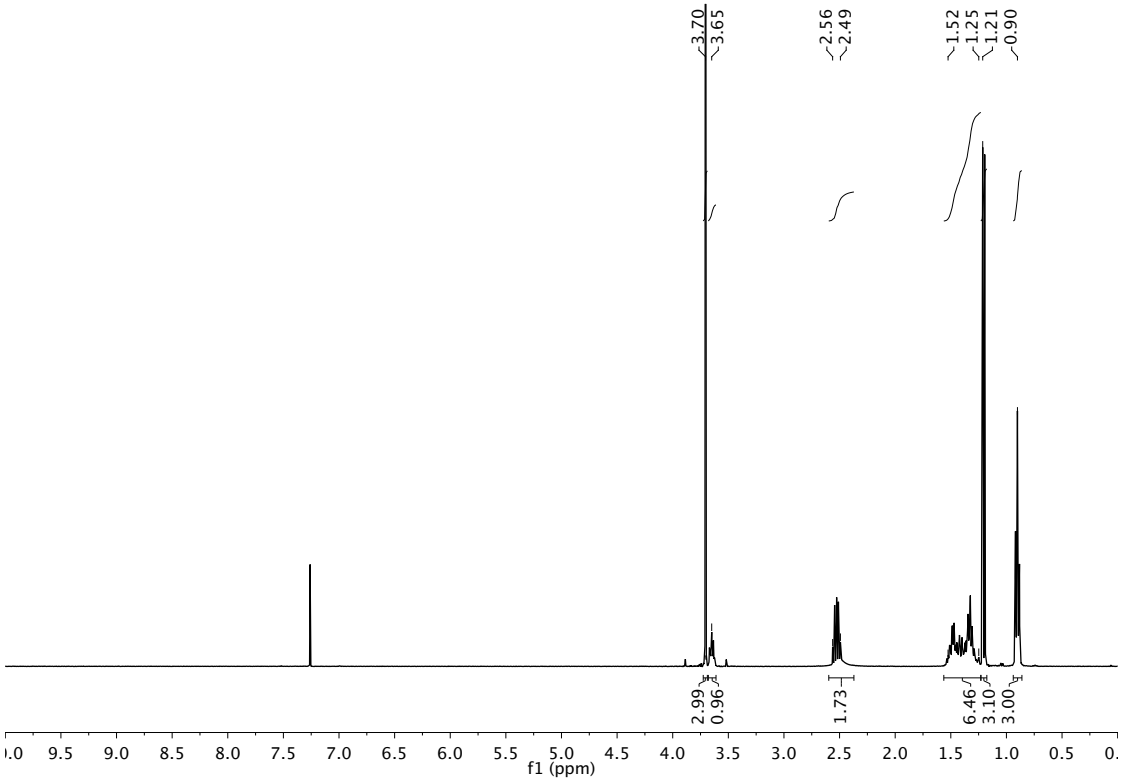
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylhexanoate (6c)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



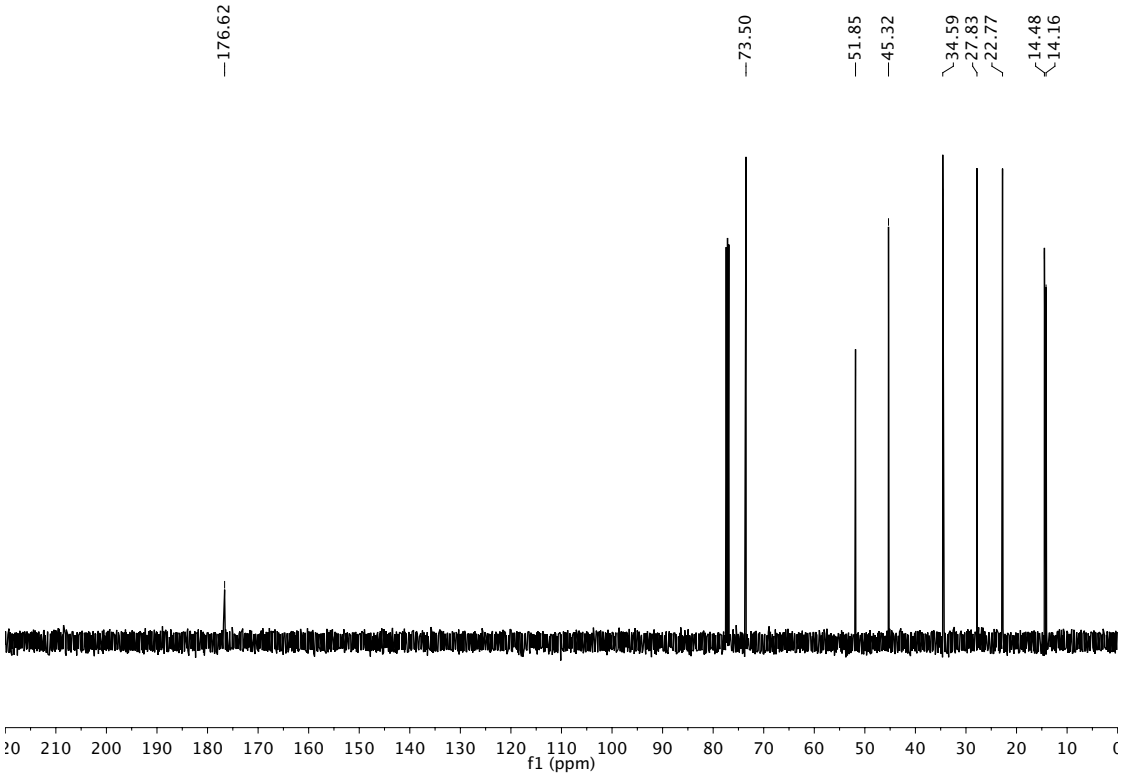

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



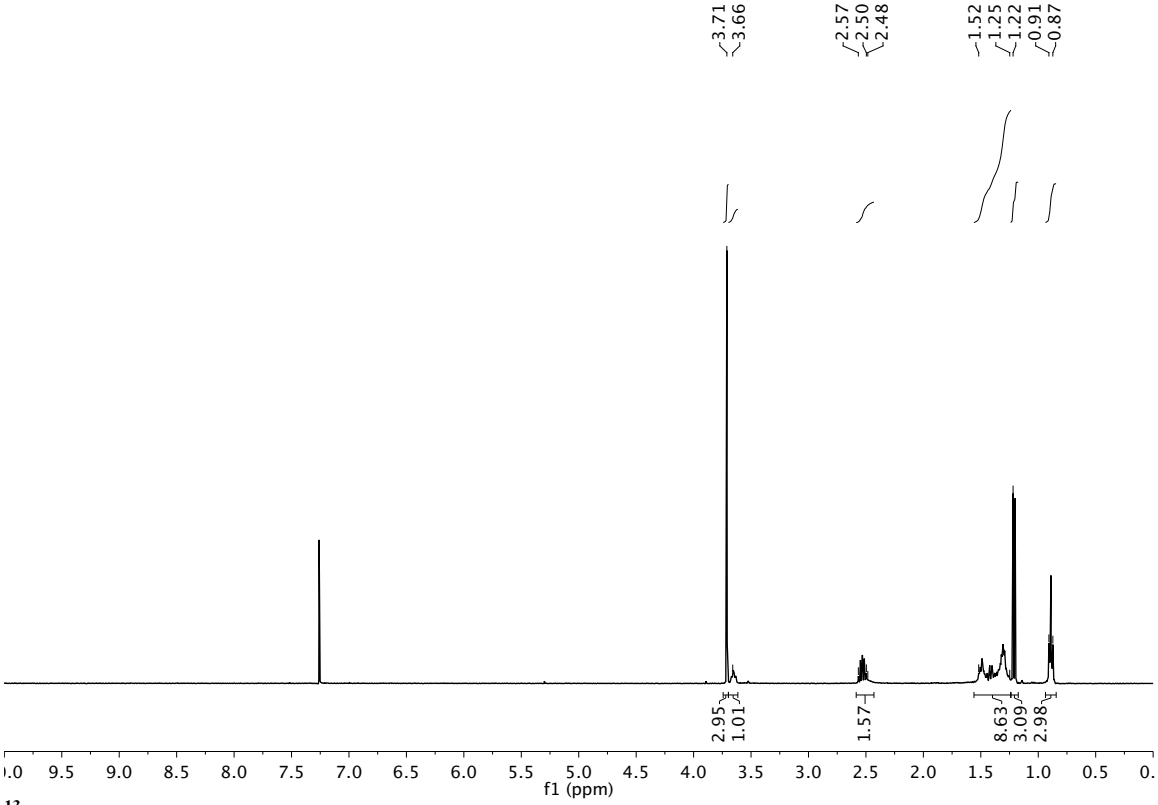
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylheptanoate (6a)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



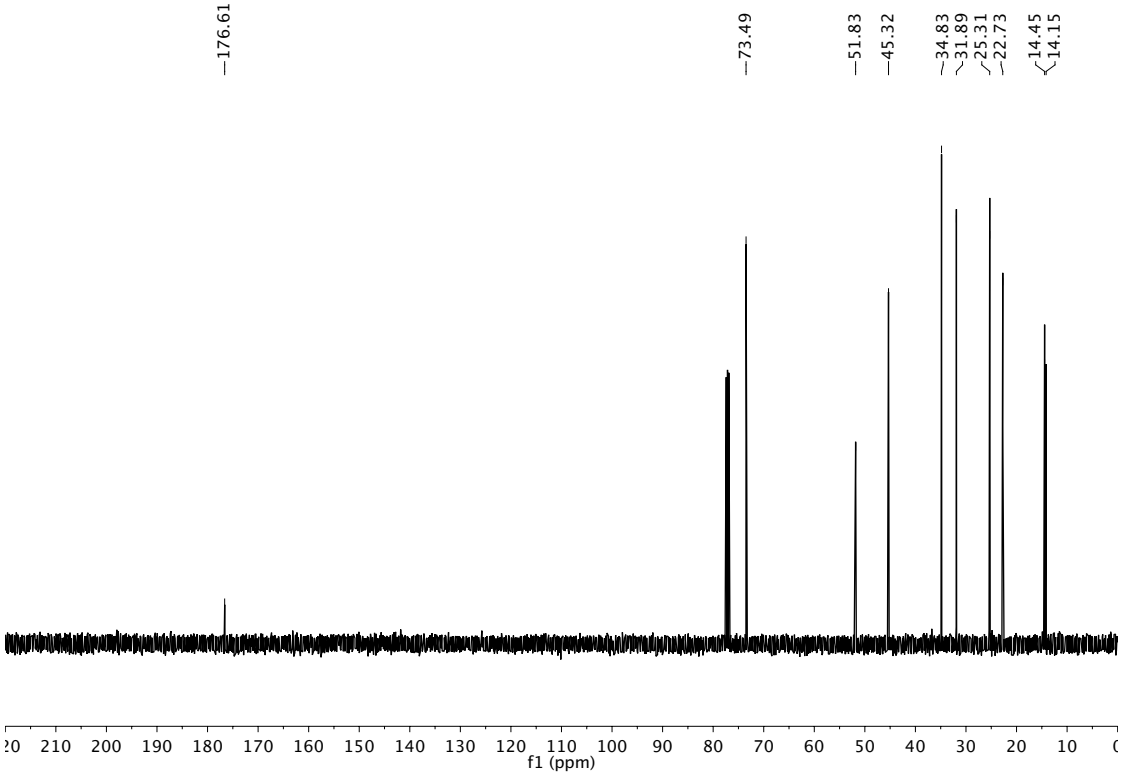

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



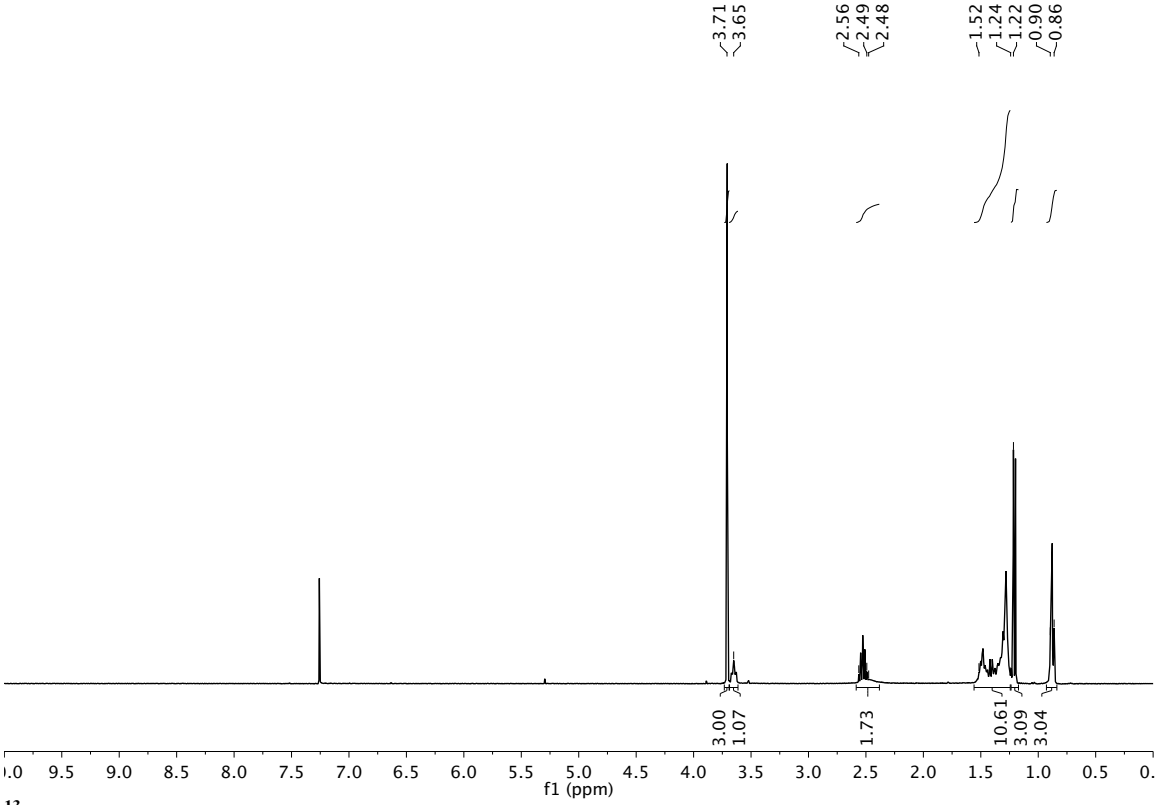
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methyloctanoate (6d)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



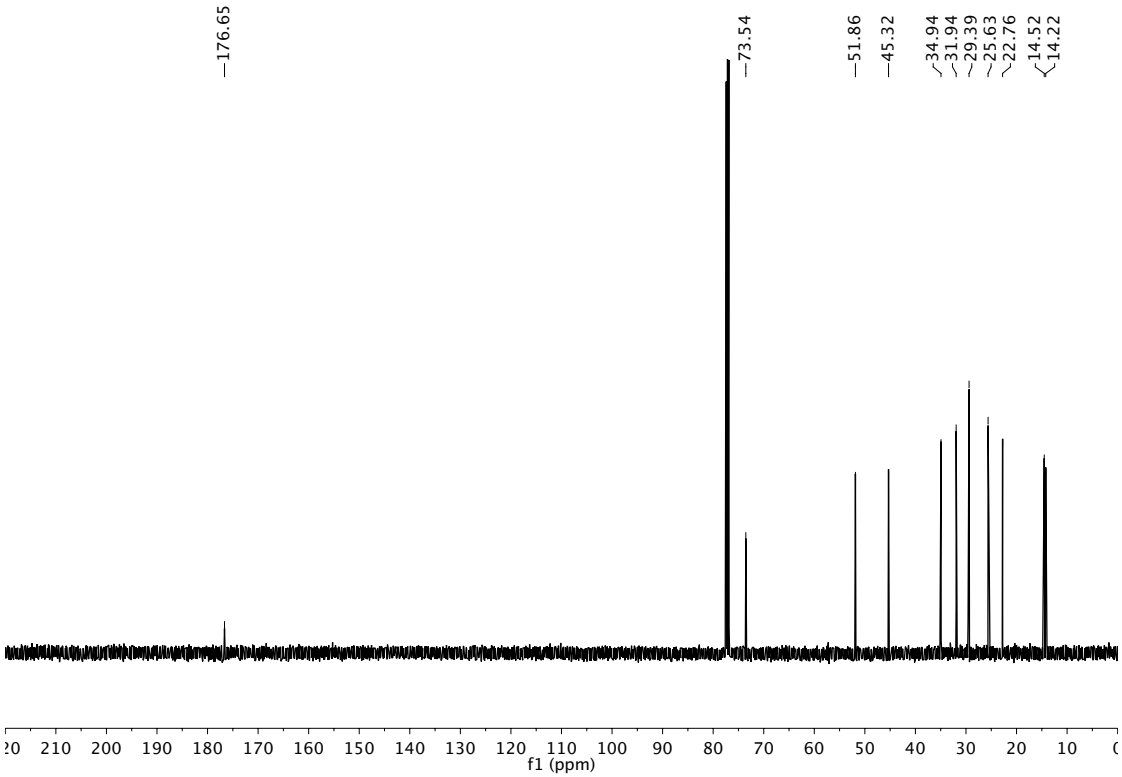

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



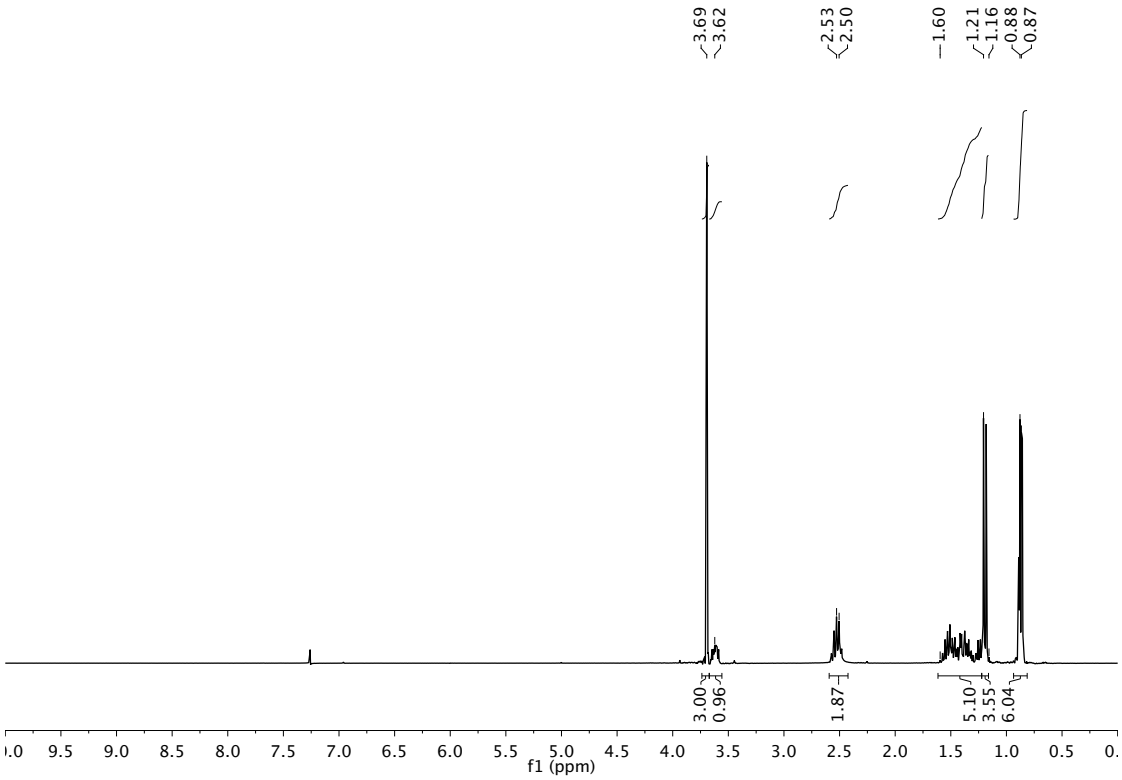
**(2*R*,3*R*)-Methyl 3-hydroxy-2-methylnonanoate (6e)**, **$^{1}$H NMR spectrum** (400 MHz, $CDCl_3$)



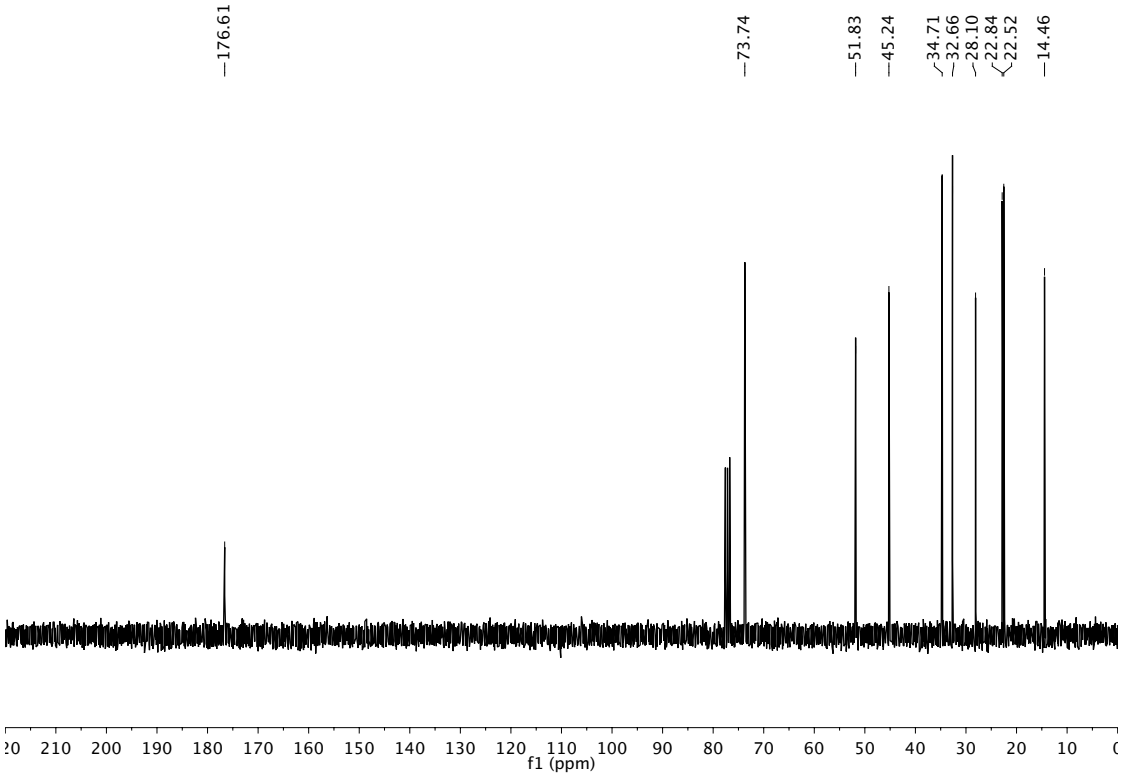

**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)



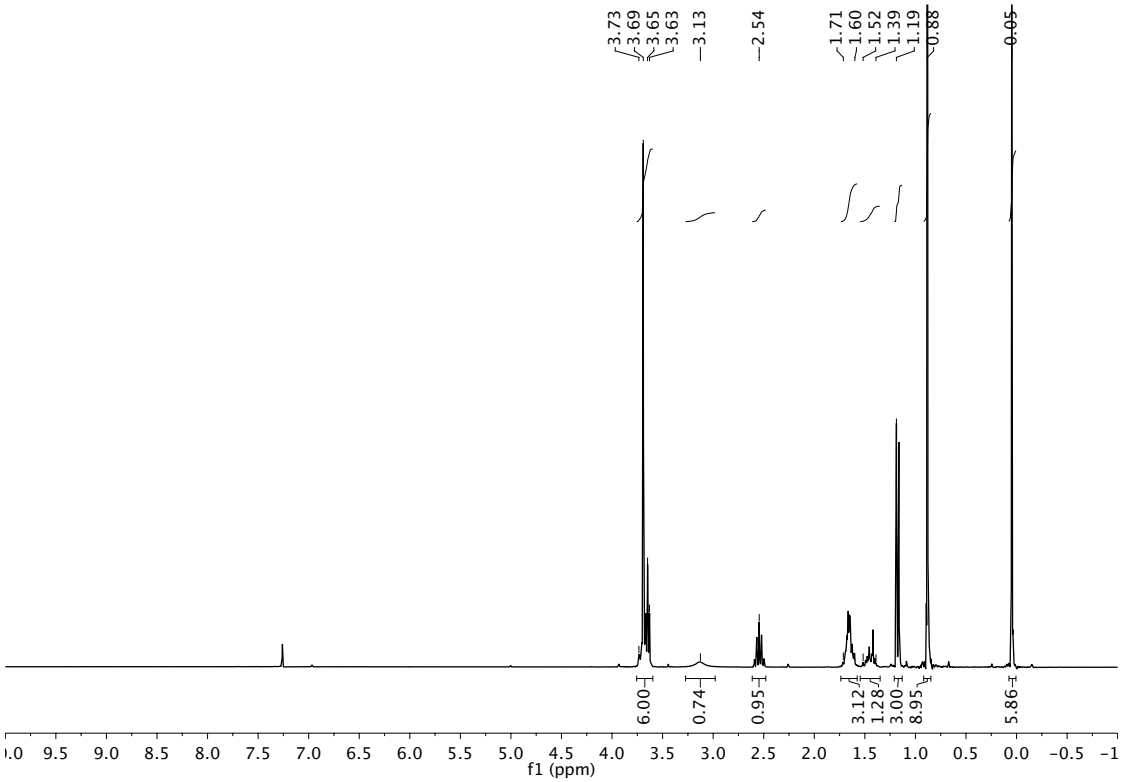
**(2*R*,3*R*)-Methyl 3-hydroxy-2,6-dimethylheptanoate (6f)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)



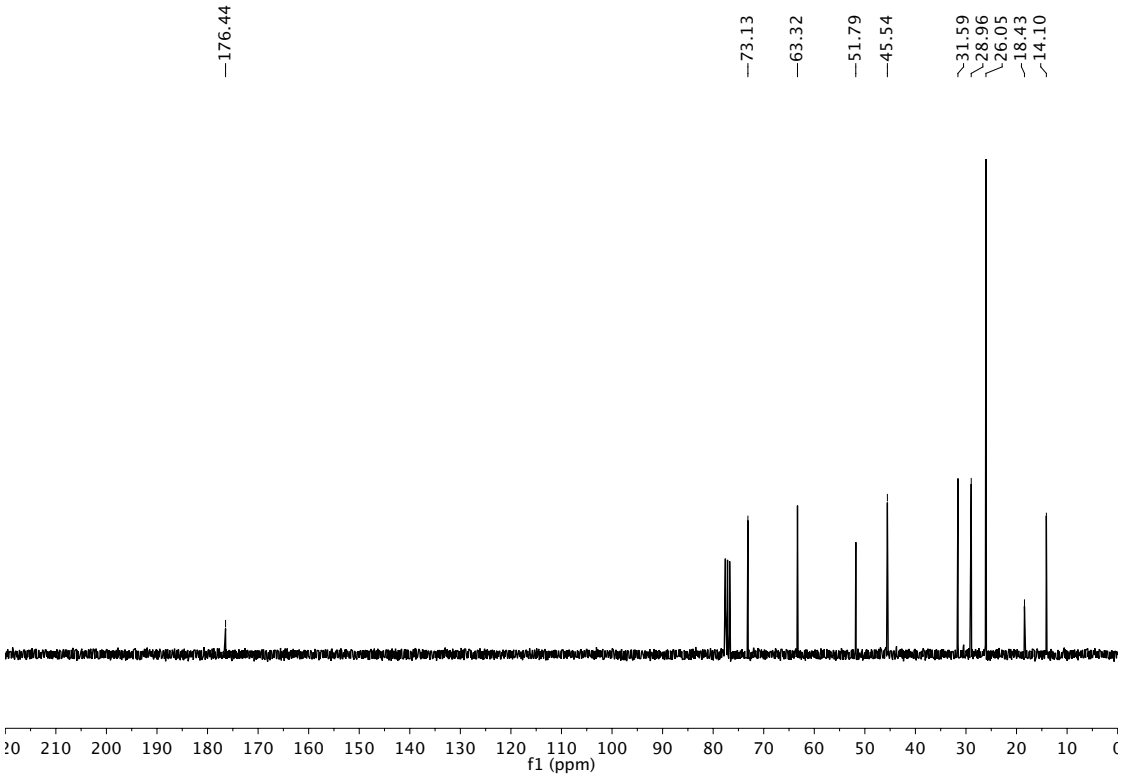

**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



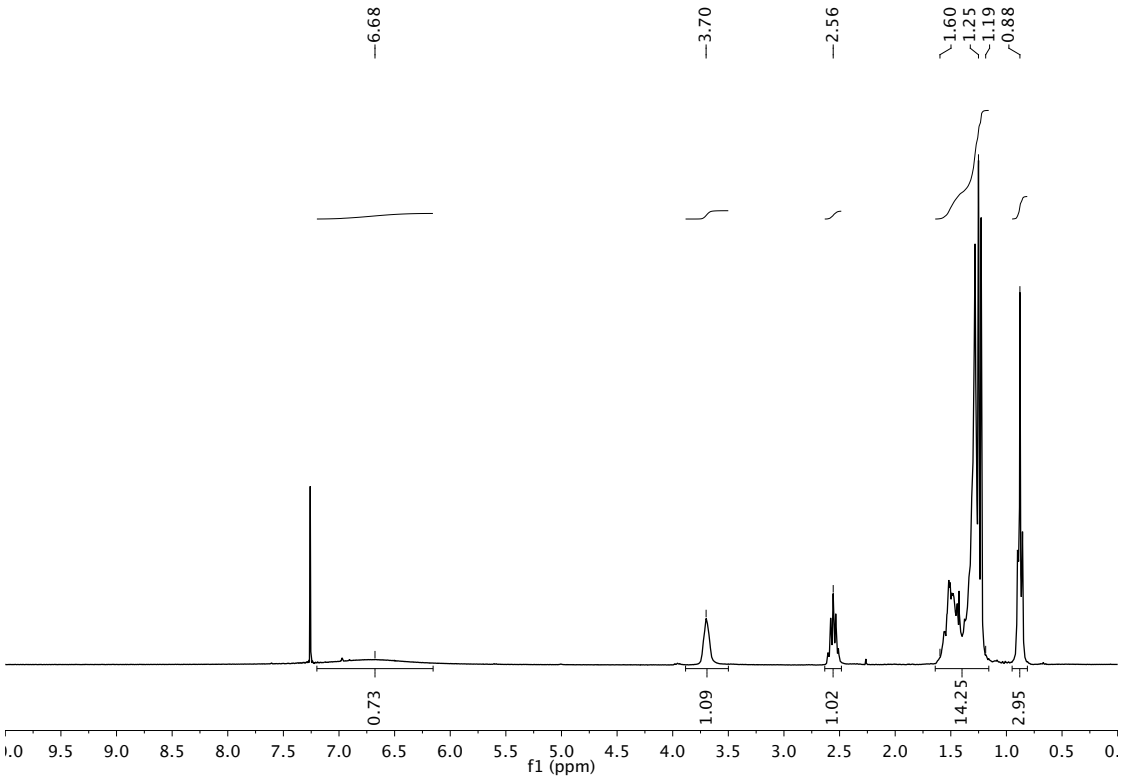
**(2*R*,3*R*)-Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-2-methylhexanoate (6g)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)




**$^{13}$C NMR spectrum** (75 MHz, $CDCl_3$)



**(2*R*,3*R*)-3-Hydroxy-2-methylnonanoic acid (7)**, **$^{1}$H NMR spectrum** (300 MHz, $CDCl_3$)




**$^{13}$C NMR spectrum** (126 MHz, $CDCl_3$)