Supporting Information

Carbonylative enantioselective *meso*-desymmetrization of *cis*-epoxides to *trans*-β-lactones: effect of electronic variation on enantioselectivity

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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 1 or 2 fluid dram glass vials. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. ^{1}H NMR and ^{13}C{^{1}H} 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)). ^{19}F NMR spectra were recorded on a Varian 400 or 500 MHz instrument at 22 °C (unless indicated otherwise) with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm) or neat C_6F_6 (164.9 ppm); both external standards were recorded at 22 °C. All *J* values are given in Hertz. 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, and are given in 10^{-1} deg cm^2 g^{-1}. 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. Reported percentages of epoxide, ketone, and β-lactone are uncorrected relative areas. HRMS analyses were either performed at the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign (ESI) or on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source (Cornell University).

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). Tetrahydrofuran and dichloromethane were 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. 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, Combi-Blocks, 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:

a) catalysts and catalyst precursors

$NaCo(CO)_4$,[2]

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

(*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),[4]

(*R*)-Xyl_2BinamAlCl (precursor to (*R*)-**1b**, (*R*)-Xyl_2Binam = (*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),[5]

(*R*)-*p*MeMesBinamAlCl (precursor to (*R*)-**1c**, (*R*)-*p*MeMesBinam = (*R*)-3,3''-(([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene))bis(2',4',5,6'-tetra-methyl-[1,1'-biphenyl]-2-olate)),[5]

b) epoxides

meso-(2*R*,3*S*)-2,3-dipropyloxirane (**3a**),[6]

meso-(2*R*,3*S*)-2,3-diethyloxirane (**3c**),[7]

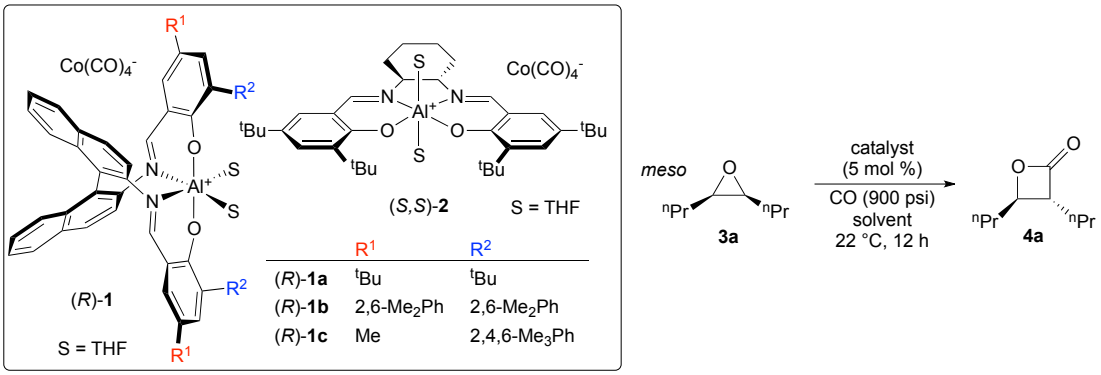
meso-(2*R*,3*S*)-2,3-dibutyloxirane (**3d**),[8]

c) others

(*Z*)-oct-4-ene-1,8-diylbis(4-methylbenzenesulfonate)[9]

Expanded Data Tables 1–4

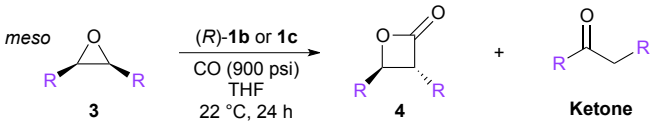
Table S1. Expanded Table 1 – Evaluation of enantiopure [Lewis acid]$^{+}$[Co(CO)$_4$]$^{-}$ catalysts and reaction parameters for the carbonylative enantioselective desymmetrization of *meso*-epoxide **3a**



Entry	Catalyst[a]	Solvent	β-Lactone **4a**[b]	
			Conv. (%)	% ee
1	(*R*)-**1c**	THF	70	94
2	(*S*,*S*)-**2**	THF	43	16
3	(*R*)-**1a**	THF	89	58
4	(*R*)-**1b**	THF	42	97
5	(*R*)-**1c**	THP	78	73
6	(*R*)-**1c**	1,4-dioxane	98	70
7	(*R*)-**1c**	DME	7	24
8	(*R*)-**1c**	toluene	98	43
9[c]	(*R*)-**1c**	THF	65	94
10[d]	(*R*)-**1c**	THF	>95	87

[a]Catalysts were generated *in situ* (L_nAlCl + $NaCo(CO)_4$), except for catalyst (*S*,*S*)-**2**. [b]Conversion to β-lactone **4a** and enantiomeric excess determined by GC analysis. [c]5 mol % $Na[Co(CO)_4]$ added. [d]Run at 40 °C.

Table S2. Expanded Table 2 – Scope of the carbonylative enantioselective desymmetrization of *meso*-epoxides **3** using catalysts (*R*)-**1b** and **1c**[a]

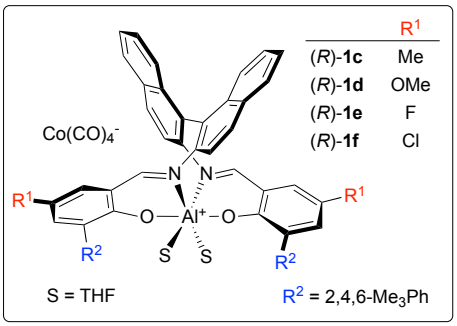


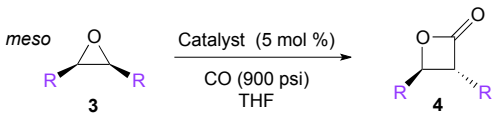
Entry	R		Catalyst[b]	mol % Catalyst	% Isol. Yield **4**	er[c] of **4**	% Ketone side product[c]
1	Me	(**4b**)	(*R*)-**1c**	2.5	95[d]	91.5 : 8.5	3
2	Et	(**4c**)	(*R*)-**1c**	4	70	97.8 : 2.2	4
3	^{n}Pr	(**4a**)	(*R*)-**1c**	7	77	96.9 : 3.1	7
4	^{n}Bu	(**4d**)	(*R*)-**1c**	8	72	95.9 : 4.1	12
5[e]	$(CH_2)_3OCH_2CF_3$	(**4e**)	(*R*)-**1c**	12.5	79	92.0 : 8.0	n.d.[f]
6	Me	(**4b**)	(*R*)-**1b**	2.5	94[d]	91.3 : 8.7	4
7	Et	(**4c**)	(*R*)-**1b**	6	74	99.0 : 1.0	1
8	^{n}Pr	(**4a**)	(*R*)-**1b**	10	76	98.6 : 1.4	6
9	^{n}Bu	(**4d**)	(*R*)-**1b**	12	72	95.6 : 4.4	19

[a]All reactions gave full conversion by GC analysis. [b]Catalysts (*R*)-**1b** and **1c** were generated *in situ* (L_nAlCl + $NaCo(CO)_4$). [c]Determined by GC analysis. [d]Yield determined by GC analysis using method of standard addition. [e]Run at 33 °C. [f]Not determined.

Note: Substrate **3e** (*meso*-2,3-bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane, p. S13) is not included in Table 2 in the manuscript. We were unable to obtain the expected 1 : 1 area ratio for the two enantiomers of the corresponding racemic β-lactone **4e** on our GC columns (p. S44). As a result, the enantiomeric ratio given for **4e** in Table S2 and on p. S44 should be viewed as an approximate value.

Table S3. Expanded Table 3 – Electronic series data including control reactions at low conversion[a]

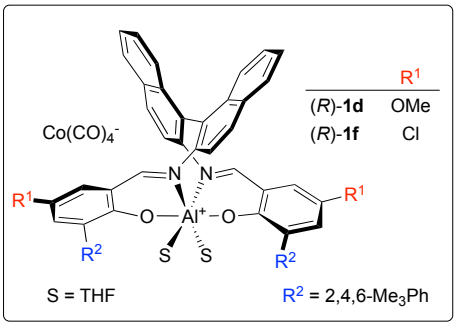


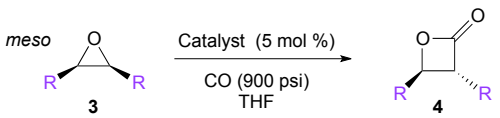


Entry	R	Catalyst	Ratio at end of reaction (%)[b] β-Lactone	Ketone	Epoxide	er of **4**
1[c,d]	Me (**4b**)	(*R*)-**1d**	94	6	<1	93.0 : 7.0
2[c,d]	Me (**4b**)	(*R*)-**1c**	97	3	<1	91.5 : 8.5
3[c,d]	Me (**4b**)	(*R*)-**1e**	84	4	12	87.9 : 12.1
4[c,d]	Me (**4b**)	(*R*)-**1f**	97	3	<1	87.9 : 12.1
5	Et (**4c**)	(*R*)-**1d**	87	5	8	97.6 : 2.4
6[c]	Et (**4c**)	(*R*)-**1c**	96	4	<1	97.8 : 2.2
7[c]	Et (**4c**)	(*R*)-**1e**	96	4	<1	98.2 : 1.8
8	Et (**4c**)	(*R*)-**1f**	96	4	<1	98.4 : 1.6
9	^{n}Pr (**4a**)	(*R*)-**1d**	58	5	36	96.0 : 4.0
10	^{n}Pr (**4a**)	(*R*)-**1c**	81	6	13	97.1 : 2.9
11	^{n}Pr (**4a**)	(*R*)-**1e**	94	3	3	97.0 : 3.0
12	^{n}Pr (**4a**)	(*R*)-**1f**	95	2	4	97.9 : 2.1
13	^{n}Bu (**4d**)	(*R*)-**1d**	64	9	27	95.1 : 4.9
14	^{n}Bu (**4d**)	(*R*)-**1c**	83	11	6	96.1 : 3.9
15	^{n}Bu (**4d**)	(*R*)-**1e**	92	4	5	96.5 : 3.5
16[c]	^{n}Bu (**4d**)	(*R*)-**1f**	84	3	14	97.9 : 2.1
17[e]	^{n}Bu (**4d**)	(*R*)-**1f**	24	1	75	98.3 : 1.7
18[f]	Me (**4b**)	(*R*)-**1f**	93[c]	7[c]	<1[c]	87.5 : 12.5
	^{n}Bu (**4d**)		38	3	59	97.4 : 2.6

[a]Reaction conditions: [**3**] = 0.5 M, 22 °C, 20 h. Conversion at end of reaction and enantiomeric ratio (er) determined by GC analysis. [b]%-Values were rounded to the nearest percent. [c]4 mol % catalyst. [d]Conversion at end of reaction determined by ^{1}H NMR spectroscopy. [e]2.5 h. [f]Both epoxides combined in one pot ([Epox]$_{total}$ = 0.5 M) for 6 h. Catalysts (*R*)-**1c–1f** were generated *in situ* (L_nAlCl + $NaCo(CO)_4$).

Table S4. Expanded Table 4 – Carbonylation with the best catalyst for each substrate at different temperatures[a]





Entry	R	Catalyst	Temp (°C)	Ratio at end of reaction (%)[b] β-Lactone	Ketone	Epoxide	er
1[c,d]	Me (**4b**)	(*R*)-**1d**	0	50	<1	50	93.7 : 6.3
2[d]	Et (**4c**)	(*R*)-**1f**	0	54	2	44	98.9 : 1.1
3[c,e]	Me (**4b**)	(*R*)-**1d**	0	96	4	<1	93.9 : 6.1
4[c,f]	Me (**4b**)	(*R*)-**1d**	22	94	6	<1	93.0 : 7.0
5	Et (**4c**)	(*R*)-**1f**	0	85	2	13	98.8 : 1.2
6	Et (**4c**)	(*R*)-**1f**	22	96	4	<1	98.4 : 1.6
7	^{n}Pr (**4a**)	(*R*)-**1f**	0	32	2	66	98.3 : 1.7
8	^{n}Pr (**4a**)	(*R*)-**1f**	22	95	2	4	97.9 : 2.1
9	^{n}Bu (**4d**)	(*R*)-**1f**	0	58	2	40	98.5 : 1.5
10[f]	^{n}Bu (**4d**)	(*R*)-**1f**	22	84	3	14	97.9 : 2.1

[a]Reaction conditions: [**3**] = 0.5 M (22 °C) or 1.5 M (0 °C), 21 h, 5 mol % catalyst. Conversion and enantiomeric ratio determined by GC analysis. [b]%-Values were rounded to the nearest percent. [c]Conversion determined by ^{1}H NMR of the crude reaction mixture. [d]5 h. [e]3 mol % catalyst. [f]4 mol % catalyst. Catalysts (*R*)-**1d** and **1f** were generated *in situ* ($L_nAlCl + NaCo(CO)_4$).

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 *via* flash column chromatography.

General procedure B: Kumada coupling of 2-bromophenols with mesitylmagnesium bromide

The appropriate brominated phenol was added dropwise to a mixture of sodium hydride (Aldrich, dry, 95%) and THF at 0 °C, followed by stirring at 22 °C for 10 minutes. $Pd(OAc)_2$ (Strem, ≥98%) was added, followed by mesitylmagnesium bromide (1 M, THF), and the resulting mixture was refluxed for 12 h. Upon cooling to 0 °C, H_2O was carefully added to destroy any residual Grignard reagent and sodium hydride. HCl (2 M, aq.) followed by celite 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.

General procedure C: Formylation of 2-arylphenols to the corresponding salicylaldehyde derivatives

Methylmagnesium bromide (Acros, 3 M, Et_2O) was added slowly to the corresponding coupled phenol in THF at 0 °C. After warming to 22 °C, toluene, triethylamine, and paraformaldehyde 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 (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 or recrystallization.

General procedure D: Imine condensation of salicylaldehydes onto (*R*)-2,2′-diamine-1,1′-binaphthalene ((*R*)-DABN)

The corresponding salicylaldehyde, (*R*)-2,2′-diamine-1,1′-binaphthalene, and methanol were mixed and then refluxed for 18 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 80 °C.

General procedure E: Metalation of salen-compounds using Et_2AlCl

Et_2AlCl (Aldrich, 0.98 M, hexanes, *pyrophoric*) was added to a solution of the corresponding salen-compound in DCM (0.04 M) at 0 °C. The resulting solution was stirred at 22 °C for 12 h. Volatiles were removed *in vacuo*, the solid was washed with hexanes, cannula filtered, and dried *in vacuo* overnight.

General procedure F: Carbonylation of epoxides using (*R*)-1b–1f

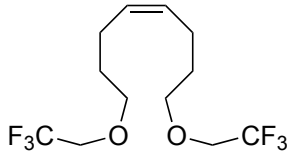
In a glove box, a 1 or 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate precursor to (*R*)-**1b–1f**, $NaCo(CO)_4$, and THF. After 1 minute of stirring at 22 °C, the vial was placed in a custom-made 6-well high-pressure reactor which itself was placed in a glove box freezer (−32 °C) for 30 minutes. The appropriate epoxide (also cooled to −32 °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 G: Carbonylation of epoxides using (*R*)-1d or (*R*)-1f at 0 °C

In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate precursor to (*R*)-**1d** or **1f**, $NaCo(CO)_4$, 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 (−32 °C) for 30 minutes. The appropriate epoxide (also cooled to −32 °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 0 °C ice bath in an insulated box and the reaction mixture stirred for 21 hours (unless otherwise noted). The reactor was then carefully vented in a well-ventilated hood and the crude reaction mixture run through a silica plug to remove the catalyst. The product was then analyzed by ^{1}H NMR spectroscopy and chiral gas chromatography.

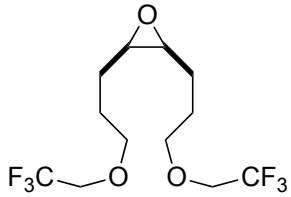
Synthesis of starting materials

(*Z*)-1,8-Bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1)



2,2,2-Trifluoroethanol (1.51 g, 15.1 mmol) was added dropwise to a mixture of sodium hydride (Aldrich, 95 %, dry, 0.480 g, 20.0 mmol) and THF (10 ml) at 0 °C. After stirring for 1 h at 22 °C, a solution of (*Z*)-oct-4-ene-1,8-diylbis(4-methylbenzene-sulfonate)[9] in THF (5 ml) was added at 0 °C, and the resulting mixture refluxed for 12 h. The reaction mixture was then cooled to 22 °C, H_2O was added, followed by extraction of the aqueous phase 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 afford **SM1** (1.38 g, 85 %) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.38 (ddd, *J* = 5.7, 4.4, 1.1, 2H), 3.79 (q, *J* = 8.8, 4H), 3.59 (t, *J* = 6.4, 4H), 2.12 (td, *J* = 7.2, 5.4, 4H), 1.67 (dt, *J* = 7.8, 6.5, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 129.7, 124.3 (d, *J* = 281.4), 72.2, 68.4 (q, *J* = 33.8), 29.5, 23.4. **^{19}F NMR** (376 MHz, $CDCl_3$, ref. $CFCl_3$): δ −74.4 (t, *J* = 8.8). **IR** (neat, cm^{-1}): 2935, 1441, 1275, 1133, 966, 827. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{18}F_6NaO_2^+$ ($M + Na^+$) 331.1103, found 331.1110.

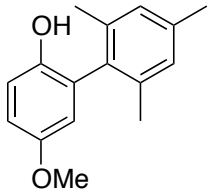
2,3-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (3e)



Following general procedure A, (*Z*)-1,8-bis(2,2,2-trifluoroethoxy)oct-4-ene (**SM1**, 1.28 g, 4.15 mmol) was reacted with *m*CPBA (1.41 g) in DCM (10 ml) to give **3e** (1.19 g, 88 %) as a colorless liquid. **^{1}H NMR** (400 MHz, C_6D_6): δ 3.23 (q, *J* = 8.8, 4H), 3.16–3.05 (m, 4H), 2.62–2.57 (m, 2H), 1.52–1.28 (m, 8H). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 124.7 (d, *J* = 279.6), 72.0, 68.1 (q, *J* = 33.4), 56.2, 27.0, 24.6. **^{19}F NMR** (376 MHz, C_6D_6, ref.

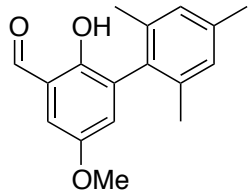
$CFCl_3$): δ −74.2 (t, *J* = 8.9). **IR** (neat, cm^{-1}): 2935, 1444, 1275, 1131, 966, 826. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{19}F_6O_3^+$ ($M + H^+$) 325.1233, found 325.1245.

5-Methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM2)



Following general procedure B, 2-bromo-4-methoxyphenol (2.86 g, 14.1 mmol) was treated with sodium hydride (0.506 g, 20.0 mmol) in THF (28 ml), followed by addition of $Pd(OAc)_2$ (0.160 g, 0.696 mmol, 4.93 mol %), and mesitylmagnesium bromide (1 M, THF, 27 ml, 27.0 mmol) to give **SM2** (3.30 g, 65 %) as a yellow oil. Analytical data for **SM2** has previously been reported.[10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.99 (s, 2H), 6.92 (d, *J* = 8.8, 1H), 6.84 (dd, *J* = 8.8, 3.0, 1H), 6.58 (d, *J* = 3.0, 1H), 4.29 (s, 1H), 3.76 (s, 3H), 2.34 (s, 3H), 2.04 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 153.5, 146.6, 137.9, 137.5, 132.2, 128.6, 127.1, 115.9, 115.0, 114.2, 55.6, 21.0, 20.2.

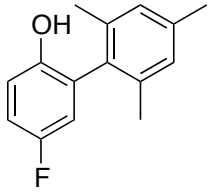
2-Hydroxy-5-methyoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM3)



Following general procedure C, 5-methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (**SM2**, 2.66 g, 11.0 mmol) was treated with methylmagnesium bromide (4.1 ml, 12.3 mmol) in THF (20 ml), followed by addition of toluene (38 ml), triethylamine (2.5 ml, 34.0 mmol), and paraformaldehyde (0.824 g, 27.5 mmol). The product was recrystallized from methanol to give **SM3** (2.90 g, 98 %) as a gold-colored powder. **MP** 59–61 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.73 (s, 1H), 9.93 (s, 1H), 7.04 (d, *J* = 3.1, 1H), 6.99 (d, *J* = 3.1, 1H), 6.97 (s, 2H), 3.84 (s, 3H), 2.33 (s, 3H), 2.03 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 196.3, 153.4, 152.6, 137.6, 136.5, 132.6, 131.2, 128.3, 126.3, 120.3, 114.5, 55.9, 21.2, 20.3. **IR** (neat, cm^{-1}): 2916, 1652, 1600, 1433, 1316, 1214, 1046, 850, 794,

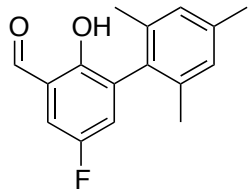
702. **HRMS** (DART) *m/z* calculated for $C_{17}H_{18}O_3^+$ (M + H^+) 271.13287, found 271.13325.

5-Fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM4)



Following general procedure B, 2-bromo-4-fluorophenol (2.30 g, 12.0 mmol) was treated with sodium hydride (0.432 g, 17.1 mmol) in THF (24 ml), followed by addition of $Pd(OAc)_2$ (0.136 g, 0.593 mmol, 4.93 mol %), and mesitylmagnesium bromide (1 M, THF, 20 ml, 20.0 mmol) to give **SM4** (0.976 g, 35 %) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.99 (s, 2H), 6.94 (m, 2H), 6.74 (dd, *J* = 8.7, 2.9, 1H), 4.45 (s, 1H), 2.34 (s, 3H), 2.02 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 157.1 (d, *J* = 238.5), 148.7 (d, *J* = 2.1), 138.6, 137.7, 131.0, 128.9, 127.6 (d, *J* = 7.8), 116.3 (d, *J* = 22.6), 116.1 (d, *J* = 8.4), 115.4 (d, *J* = 23.0), 21.17, 20.20. **^{19}F NMR** (376 MHz, $CDCl_3$, ref. C_6F_6): δ −122.7 (td, *J* = 8.4, 5.0). **IR** (neat, cm^{-1}): 3489, 2917, 1611, 1477, 1257, 1178, 1150, 783. **HRMS** (DART) *m/z* calculated for $C_{15}H_{15}FO^+$ (M^+) 230.11014, found 230.11056.

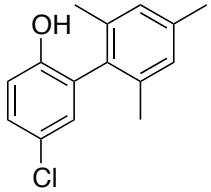
2-Hydroxy-5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM5)



Following general procedure C, 5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (**SM4**, 2.66 g, 11.6 mmol) was treated with methylmagnesium bromide (4.1 ml, 12.3 mmol) in THF (20 ml), followed by addition of toluene (38 ml), triethylamine (2.5 ml, 34.0 mmol), and paraformaldehyde (0.824 g, 27.5 mmol). The product was recrystallized from methanol to give **SM5** (0.958 g, 43 %) as white spindly crystals. **MP** 119–120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.89 (s, 1H), 9.92 (s, 1H), 7.28 (dd, *J* = 7.5, 3.1, 1H), 7.12 (dd, *J* = 8.5, 3.1, 1H), 6.97 (s, 2H), 2.33 (s, 3H), 2.02 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 195.7 (d, *J* = 2.5), 155.5 (d, *J* = 241.3), 155.3 (d, *J* = 1.5), 138.0, 136.4, 132.1

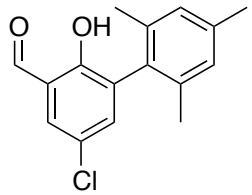
(d, J = 6.7), 131.8 (d, J = 1.2), 128.4, 126.0 (d, J = 22.8), 120.3 (d, J = 6.6), 117.2 (d, J = 22.4), 21.2, 20.3. **^{19}F NMR** (376 MHz, $CDCl_3$, ref. C_6F_6): δ −121.8 (t, J = 8.0). **IR** (neat, cm^{-1}): 2916, 1650, 1438, 1316, 1201, 1093, 985, 882, 858, 797. **HRMS** (DART) *m/z* calculated for $C_{16}H_{15}FO_2^+$ ($M + H^+$) 259.11288, found 259.11332.

5-Chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM6)



Following general procedure B, 2-bromo-4-chlorophenol (2.42 g, 11.7 mmol) was treated with sodium hydride (0.433 g, 17.1 mmol) in THF (24 ml), followed by addition of $Pd(OAc)_2$ (0.135 g, 0.588 mmol, 5.03 mol %), and mesitylmagnesium bromide (1 M, THF, 20 ml, 20.0 mmol) to give **SM6** (1.11 g, 39 %) as a light beige powder. **MP** 77–80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (dd, J = 8.7, 2.6, 1H), 7.00 (d, J = 2.6, 1H), 6.99 (s, 2H), 6.93 (d, J = 8.7, 1H), 4.62 (s, 1H), 2.34 (s, 3H), 2.02 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 151.3, 138.6, 137.7, 130.6, 129.7, 128.94, 128.90, 128.1, 125.4, 116.7, 21.2, 20.3. **IR** (neat, cm^{-1}): 3467, 3419, 2917, 1468, 1227, 1151, 852, 822, 714, 648. **HRMS** (DART) *m/z* calculated for $C_{15}H_{15}ClO^+$ $(M)^+$ 246.08059, found 246.08109.

2-Hydroxy-5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM7)



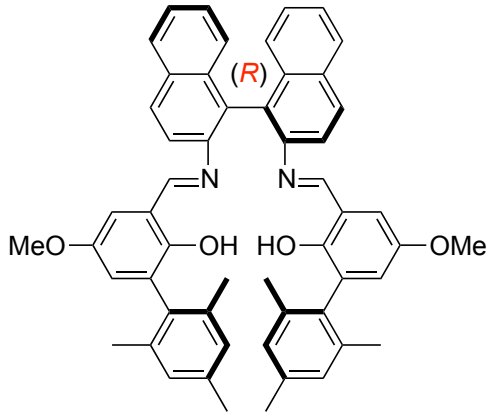
Following general procedure C, 5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (**SM6**, 1.00 g, 4.05 mmol) was treated with methylmagnesium bromide (1.5 ml, 4.6 mmol) in THF (8 ml), followed by addition of toluene (16 ml), triethylamine (0.9 ml, 6.5 mmol), and paraformaldehyde (0.334 g, 11.1 mmol). The product was purified via flash column chromatography (hexanes/EtOAc) to give **SM7** (0.730 g, 66 %) as an off-white powder. **MP** 120–122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.04 (s, 1H), 9.91 (s, 1H), 7.57 (d, J = 2.6, 1H), 7.32 (d, J = 2.6, 1H), 6.97 (s, 2H), 2.33 (s, 3H), 2.02 (s, 6H). **^{13}C{^{1}H} NMR**

(101 MHz, $CDCl_3$): δ 195.7, 157.6, 138.2, 138.0, 136.4, 132.3, 131.7, 131.5, 128.4, 124.6, 121.3, 21.2, 20.4. **IR** (neat, cm^{-1}): 2914, 1645, 1445, 1294, 1207, 1093, 852, 730. **HRMS** (DART) *m/z* calculated for $C_{16}H_{15}ClO_2^+$ ($M + H^+$) 275.08333, found 275.08377.

Synthesis of catalyst precursors to (*R*)-1d–1f

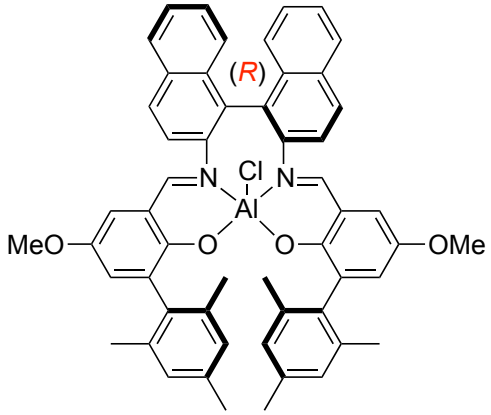
Synthesis of (*R*)-ML1 (precursor to (*R*)-1d)

(*R*)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene)) bis(methanylylidene))-bis(5-methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*OMeMesBinam, (*R*)-L1)



Following general procedure D, 2-hydroxy-5-methyoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (**SM3**, 0.217 g, 0.803 mmol) was treated with (*R*)-2,2′-diamine-1,1′-binaphthalene (0.114 g, 0.397 mmol) in methanol (2 ml). The filtered solid was recrystallized from toluene to give (*R*)-**L1** (0.245 g, 78 %) as a dark orange powder. **MP** >200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.66 (s, 2H), 8.23 (s, 2H), 7.98 (d, *J* = 8.7, 2H), 7.88 (d, *J* = 8.3, 2H), 7.38 (ddd, *J* = 8.1, 6.3, 1.6, 2H), 7.33 (d, *J* = 8.7, 2H), 7.18 (m, 4H), 6.92 (app s, 2H), 6.87 (app s, 2H), 6.69 (d, *J* = 3.0, 2H), 6.39 (d, *J* = 3.0, 2H), 3.67 (s, 6H), 2.29 (s, 6H), 2.05 (s, 6H), 1.86 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 164.2, 152.3, 151.7, 146.2, 137.0, 136.4, 136.2, 133.9, 133.2, 132.3, 130.3, 129.9, 129.1, 128.4, 128.3, 128.1, 126.84, 126.81, 125.6, 121.8, 119.0, 118.4, 114.1, 55.5, 21.2, 20.5, 20.4. **HRMS** (DART) *m/z* calculated for $C_{54}H_{48}N_2O_4^+$ (M + H^+) 789.36868, found 789.36633.

(*R*)-*p*OMeMesBinamAlCl ((*R*)-**ML1**, (*R*)-*p*OMeMesBinam = (*R*)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-olate))

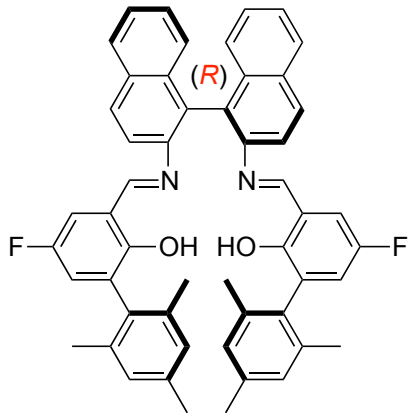


General Procedure F was followed using Et_2AlCl (Aldrich, hexanes, 0.98 M, 265 µl, 0.260 mmol), (*R*)-3,3′′-(([1,1′-binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*OMeMesBinam, (*R*)-**L1**, 0.183 g, 0.232 mmol), and DCM (6 ml) to give (*R*)-*p*OMeMesBinamAlCl ((*R*)-**ML1**, 0.152 g, 76 %) as a reddish-orange solid. **MP** >200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, -55 °C): δ 8.41 (s, 1H), 8.27 (s, 1H), 8.04 (d, *J* = 8.6, 1H), 7.97 (d, *J* = 8.2, 1H), 7.92 (m, 2H), 7.62 (d, *J* = 8.5, 1H), 7.51 (m, 2H), 7.41 (d, *J* = 8.5, 1H), 7.30 (m, 2H), 7.12 (d, *J* = 8.4, 1H), 7.08 (s, 1H), 7.04 (d, *J* = 8.6, 1H), 6.97 (s, 1H), 6.89 (m, 2H), 6.89 (s, 1H), 6.76 (s, 1H), 6.61 (d, *J* = 2.9, 1H), 6.51 (d, *J* = 2.9, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H), 2.05 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.62 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, -55 °C): δ 173.5, 168.9, 161.1, 156.5, 150.0, 149.6, 144.1, 143.9, 138.9, 137.7, 136.8, 136.2, 135.9, 135.4, 135.3, 134.6, 133.9, 133.6, 132.4, 132.2, 131.9, 130.0, 129.7, 129.5, 128.6, 128.2, 127.9, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.6, 126.34, 126.26, 126.2, 126.0, 125.6, 125.2, 118.1, 117.9, 113.1, 111.2, 55.6, 55.4, 21.6, 21.5, 21.4, 21.2, 20.4, 19.1. **HRMS** (DART) *m/z* calculated for $C_{54}H_{46}AlClN_2O_4^+$ $(M - Cl)^+$ 813.32675, found 813.32322.

Note: NMR spectra collected in $CDCl_3$ at 22 °C displayed very broad resonances. One ^{13}C peak not observed due to pseudohomotopic aryl peaks.

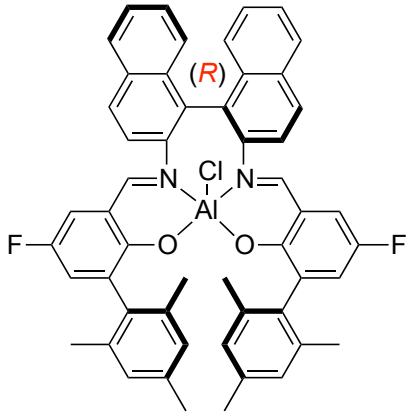
Synthesis of (*R*)-ML2 (precursor to (*R*)-1e)

(*R*)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))-bis(5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*FMesBinam, (*R*)-L2)



Following general procedure F, 2-hydroxy-5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (**SM5**, 0.207 g, 0.801 mmol) was treated with (*R*)-2,2′-diamine-1,1′-binaphthalene (0.114 g, 0.395 mmol) in methanol (3 ml) to give (*R*)-**L2** (0.282 g, 92 %) as an orange powder. **MP** >200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.94 (s, 2H), 8.31 (s, 2H), 7.99 (d, *J* = 8.8, 2H), 7.88 (d, *J* = 8.0, 2H), 7.39 (m, 2H), 7.37 (d, *J* = 8.8, 2H) 7.22 (m, 2H), 7.15 (app d, *J* = 8.4, 2H), 6.91 (s, 2H), 6.87 (s, 2H), 6.81 (dd, *J* = 8.7, 3.1, 2H), 6.69 (dd, *J* = 8.3, 3.1, 2H), 2.29 (s, 6H), 1.96 (s, 6H), 1.81 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 162.9, 155.1 (d, *J* = 237.9), 154.3, 145.1, 137.3, 136.4, 136.3, 133.2, 133.1, 132.5, 130.5 (d, *J* = 7.1), 130.4, 128.4, 128.3, 128.2, 127.7, 127.0, 126.7, 125.9, 121.6 (d, *J* = 22.5), 119.0, 118.9, 118.2, 21.2, 20.3, 20.3. **^{19}F NMR** (376 MHz, $CDCl_3$, ref. C_6F_6): δ −124.3 (t, *J* = 8.4). **HRMS** (DART) *m/z* calculated for $C_{52}H_{42}F_2N_2O_2^+$ ($M + H^+$) 765.32871, found 765.32939.

(*R*)-*p*FMesBinamAlCl ((*R*)-**ML2**, (*R*)-*p*FMesBinam = (*R*)-3,3″-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-olate))

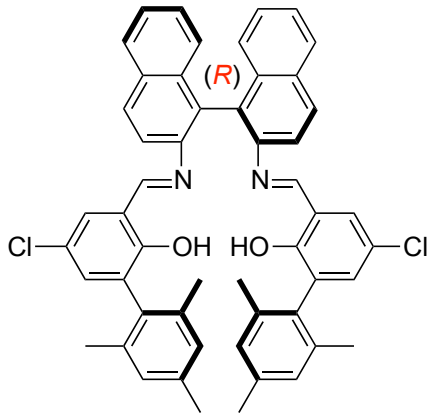


General Procedure F was followed using Et_2AlCl (Aldrich, hexanes, 0.98 M, 400 µl, 0.393 mmol), (*R*)-3,3″-(([1,1′-binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*FMesBinam, (*R*)-**L2**, 0.265 g, 0.346 mmol), and DCM (10 ml) to give (*R*)-*p*FMesBinamAlCl ((*R*)-**ML2**, 0.214 g, 75 %) as an orange solid. **MP** >200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, -55 °C): δ 8.40 (s, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 8.5, 1H), 7.95 (m, 3H), 7.59 (d, *J* = 8.5, 1H), 7.52 (m, 2H), 7.38 (d, *J* = 8.5, 1H), 7.30 (m, 2H), 7.12 (d, *J* = 8.4, 1H), 7.07 (s, 1H), 7.05 (d, *J* = 8.7, 1H), 6.99 (m, 2H), 6.96 (s, 1H), 6.85 (m, 2H), 6.81 (dd, *J* = 8.0, 3.1, 1H), 6.77 (s, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.02 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H), 1.58 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, -55 °C): δ 173.6, 168.4, 161.8, 157.8, 153.6 (d, *J* = 237.0), 153.2 (d, *J* = 236.1), 143.6, 143.5, 138.6, 137.4, 136.7, 136.5, 136.2, 135.8 (d, *J* = 7.3), 135.3, 134.4 (d, *J* = 6.6), 133.9, 133.0, 132.6, 132.3, 131.9, 131.8, 130.3, 129.7, 128.6, 128.2, 127.9, 127.7, 127.5, 127.3, 127.1, 126.59, 126.57, 126.11, 126.06, 125.9, 125.2, 125.1, 118.12, 118.05, 118.0, 116.9, 116.7, 116.2, 116.0, 21.45, 21.43, 21.37, 21.2, 20.3, 19.0. **^{19}F NMR** (470 MHz, $CDCl_3$, −55 °C, ref. C_6F_6): δ 125.25, 125.83. **HRMS** (DART) *m/z* calculated for $C_{52}H_{40}AlClF_2N_2O_2^+$ $(M - Cl)^+$ 789.28677, found 789.28306.

Note: NMR spectra collected in $CDCl_3$ at 22 °C displayed very broad resonances. One ^{13}C peak not observed due to pseudohomotopic aryl peaks.

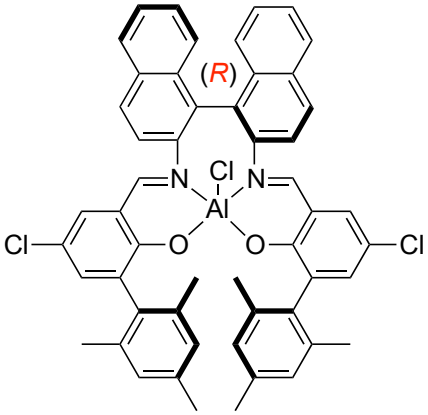
Synthesis of (*R*)-ML3 (precursor to (*R*)-1f)

(*R*)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))-bis(5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*ClMesBinam, (*R*)-L3)



Following general procedure D, 2-hydroxy-5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (**SM7**, 0.500 g, 1.92 mmol) was treated with (*R*)-2,2′-diamine-1,1′-binaphthalene (0.261 g, 0.910 mmol) in methanol (4.5 ml) to give (*R*)-**L1** (0.684 g, 94 %) as a light orange powder. **MP** >200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.14 (s, 2H), 8.30 (s, 2H), 7.99 (d, *J* = 8.8, 2H), 7.88 (d, *J* = 8.2, 2H), 7.38 (m, 4H), 7.21 (m, 2H), 7.14 (d, *J* = 8.4, 2H), 7.01 (d, *J* = 2.6, 2H), 6.99 (d, *J* = 2.6, 2H), 6.90 (s, 2H), 6.86 (s, 2H), 2.29 (s, 6H), 1.94 (s, 6H), 1.80 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 162.7, 156.7, 144.8, 137.3, 136.4, 136.3, 134.1, 133.2, 132.8, 132.5, 130.9, 130.4, 129.2, 128.39, 128.36, 128.3, 128.2, 127.1, 126.7, 125.9, 123.2, 120.0, 118.1, 21.2, 20.4, 20.3. **HRMS** (DART) *m/z* calculated for $C_{52}H_{42}Cl_2N_2O_2^+$ ($M + H^+$) 797.26961, found 797.27019.

(*R*)-*p*ClMesBinamAlCl ((*R*)-**ML3**, (*R*)-*p*ClMesBinam = (*R*)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-olate))

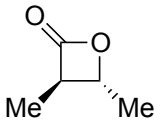


General Procedure F was followed using Et_2AlCl (Aldrich, hexanes, 0.98 M, 335 µl, 0.329 mmol), (*R*)-3,3′′-(([1,1′-binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((*R*)-*p*ClMesBinam, (*R*)-**L3**, 0.231 g, 0.289 mmol), and DCM (7.5 ml) to give (*R*)-*p*ClMesBinamAlCl ((*R*)-**ML3**, 0.185 g, 72 %) as a yellow solid. **MP** >200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, -55 °C): δ 8.53 (s, 1H), 8.34 (s, 1H), 3.17 (d, *J* = 8.4, 1H), 8.08 (m, 3H), 7.69 (d, *J* = 8.5, 1H), 7.65 (m, 2H), 7.49 (d, *J* = 8.6, 1H), 7.43 (m, 2H), 7.39 (s, 1H), 7.29 (m, 1H), 7.26 (s, 1H), 7.24 (m, 2H), 7.20 (s, 1H), 7.17 (d, *J* = 8.7, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 6.89 (s, 1H), 2.57 (s, 3H), 2.51 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.70 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, -55 °C): δ 173.6, 168.3, 163.6, 159.8, 143.4, 143.3, 138.9, 138.5, 137.9, 137.4, 136.7, 136.4, 136.2, 136.0, 135.3, 134.7, 133.7, 132.7, 132.6, 132.3, 131.8, 131.7, 131.5, 131.4, 130.4, 129.7, 128.6, 128.2, 127.93, 127.91, 127.7, 127.3, 127.1, 127.0, 126.63, 126.58, 126.3, 126.0, 125.7, 125.0, 121.6, 120.9, 119.7, 119.5, 21.5, 21.42, 21.36, 21.2, 20.3, 19.1. **HRMS** (DART) *m/z* calculated for $C_{52}H_{40}AlCl_3N_2O_2^+$ $(M - Cl)^+$ 821.22767, found 821.22470.

Note: NMR spectra collected in $CDCl_3$ at 22 °C displayed very broad resonances. Two ^{13}C peaks not observed due to pseudohomotopic aryl peaks.

Carbonylative desymmetrization of *meso*-epoxides using (*R*)-1b–f

(3*R*,4*R*)-3,4-Dimethyloxetan-2-one (4b)

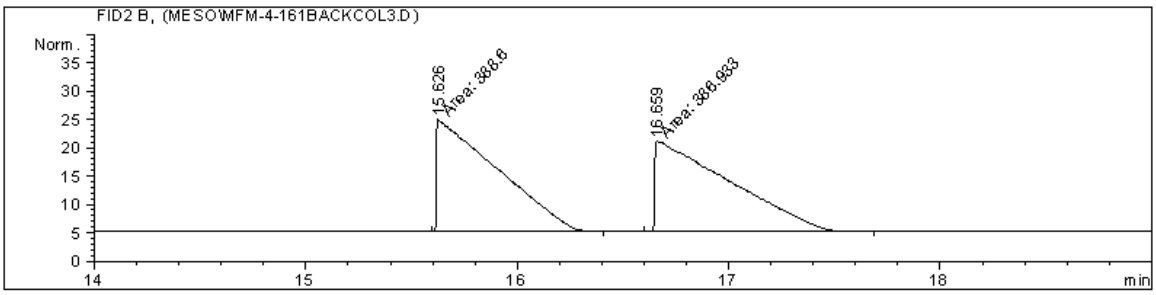


Using (*R*)-**1b**:

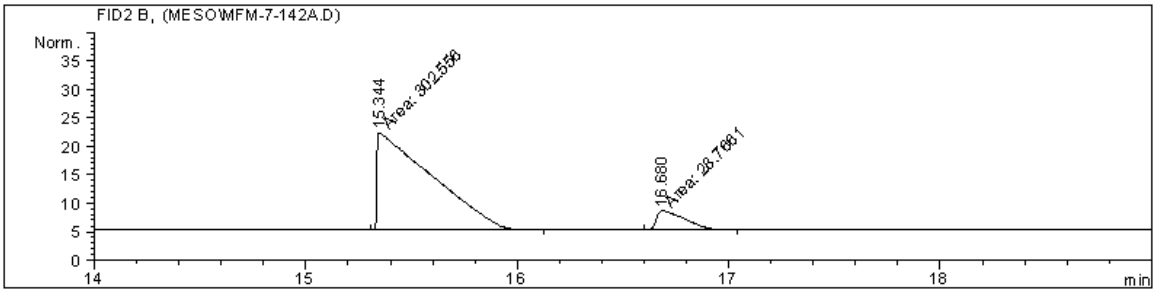
General procedure F was followed using (*R*)-Xyl_2BinamAlCl[5] (precursor to (*R*)-**1b**, 4.8 mg, 0.0050 mmol, 2.5 mol %), $NaCo(CO)_4$ (0.025 M, THF, 200 µl, 0.0050 mmol, 2.5 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 14.3 mg, 0.198 mmol). The reaction mixture was stirred for 24 h at 22 °C. The volatility of **4b** interfered with its quantitative isolation, thus the yield of the reaction was determined using the method of standard addition. To this end, the crude reaction mixture was filtered through a short plug of silica gel using THF as eluent. The entire eluate was placed in a volumetric flask and diluted with THF to a total volume of 5 ml. A 0.5 ml aliquot of this solution was then analyzed via GC analysis. Additional 0.5 ml aliquots from this stock solution were subsequently treated with increasing amounts of independently isolated **4b**, and the resulting mixtures also analyzed via GC analysis. The observed increase in signal for **4b** was then used to determine that the yield of **4b** was approximately 18.7 mg (94 %).

Analytical data for **4b** has previously been reported.[11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.35 (qd, J = 6.1, 4.0, 1H), 3.22 (qd, J = 7.5, 4.0, 1H), 1.56 (d, J = 6.3, 3H), 1.39 (d, J = 7.7, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 171.9, 76.2, 52.3, 20.1, 12.4. **Specific rotation**: $[\alpha]^{22}_D$ = +43.7 (c = 0.22, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 91.3 : 8.7 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	15.626	MM	0.3279	388.60034	19.74989	50.10750
2	16.659	MM	0.4058	386.93295	15.89145	49.89250

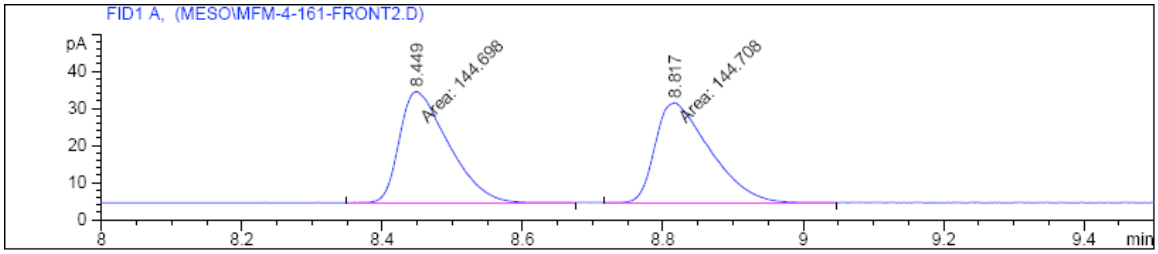


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.344	MM	0.2965	302.55566	17.00768	91.31778
2	16.680	MM	0.1480	28.76610	3.23954	8.68222

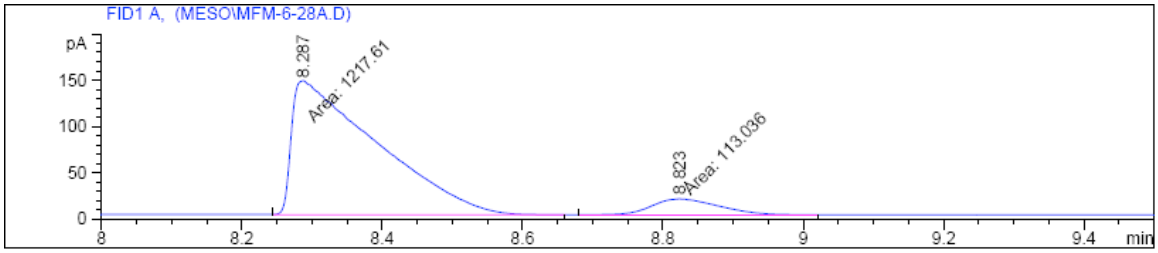
Using (*R*)-**1c**:

General procedure F was followed using (*R*)-*p*MeMesBinamAlCl[5] (precursor to (*R*)-**1c**, 0.025 M, THF, 400 µl, 0.010 mmol, 2.5 mol %), $NaCo(CO)_4$ (0.025 M, THF, 400 µl, 0.010 mmol, 2.5 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 28.7 mg, 0.398 mmol). After stirring at 22 °C for 24 h, the yield of **4b** was determined as described above to be approximately 37.8 mg (95 %).

The enantiomeric ratio (er) was determined to be 91.5 : 8.5 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.449	MM	0.0808	144.69809	29.85658	49.99824
2	8.817	MM	0.0897	144.70828	26.88497	50.00176

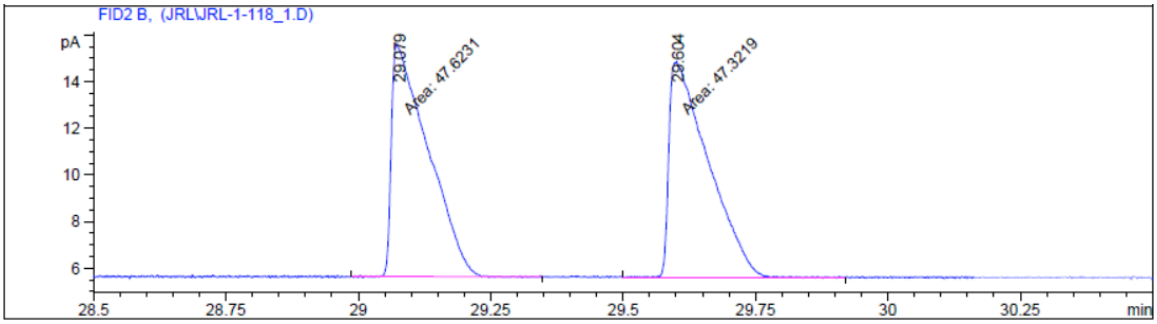


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.287	MM	0.14	1217.60522	144.94244	91.50513
2	8.823	MM	0.1098	113.03628	17.16434	8.49487

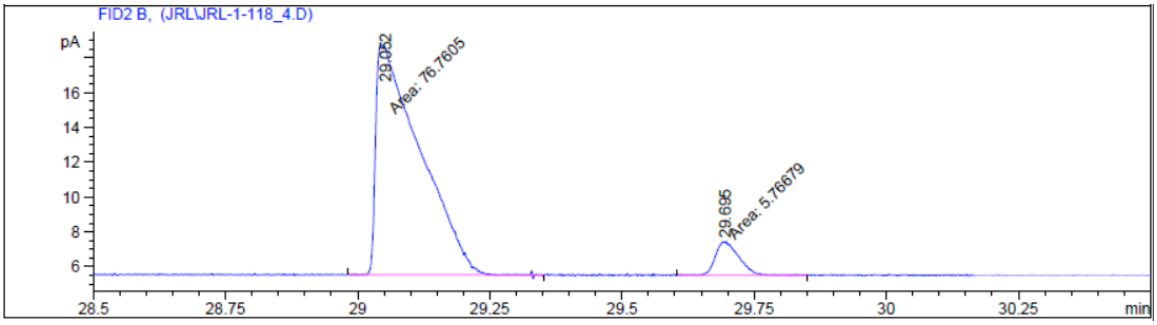
Using (*R*)-**1d**:

General procedure F was followed using (*R*)-**ML1** (precursor to (*R*)-**1d**, 5.9 mg, 0.0069 mmol, 4.2 mol %), $NaCo(CO)_4$ (1.3 mg, 0.0067 mmol, 4.1 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 11.8 mg, 0.164 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 93.0 : 7.0 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	29.079	MM	0.0821	47.62315	9.66924	50.15866
2	29.604	MM	0.0868	47.32187	9.08220	49.84134

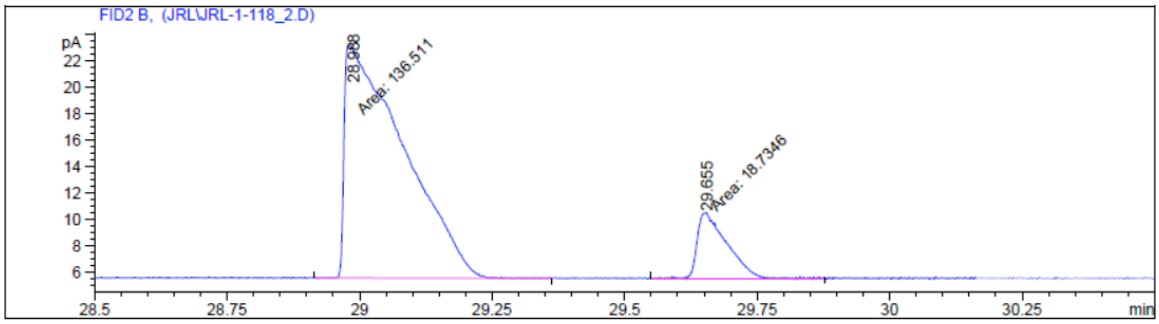


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.052	MM	0.0959	76.76054	13.34069	93.01227
2	29.695	MM	0.0510	5.76679	1.88377	6.98773

Using (*R*)-**1e**:

General procedure F was followed using (*R*)-**ML2** (precursor to (*R*)-**1e**, 5.7 mg, 0.0069 mmol, 4.4 mol %), $NaCo(CO)_4$ (2.7 mg, 0.014 mmol, 8.9 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 11.3 mg, 0.157 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 87.9 : 12.1 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

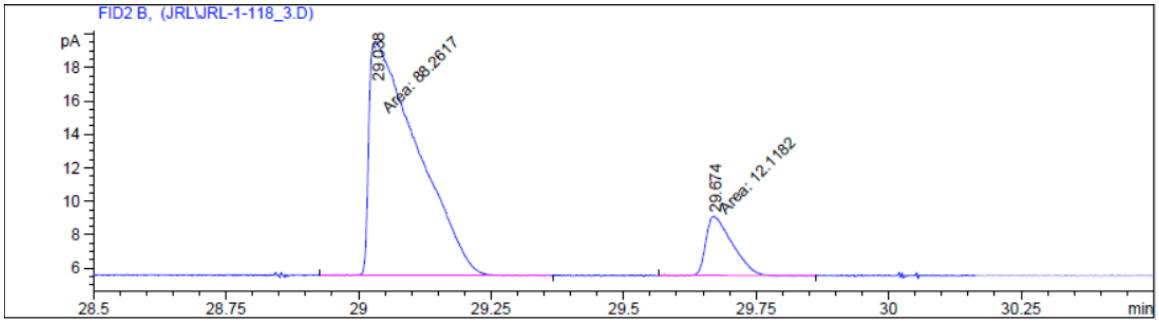


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.988	MM	0.1210	136.51096	18.80851	87.93225
2	29.655	MM	0.0655	18.73464	4.76909	12.06775

Using (*R*)-**1f**:

General procedure F was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.1 mg, 0.0071 mmol, 4.4 mol %), $NaCo(CO)_4$ (1.3 mg, 0.0067 mmol, 4.2 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 11.6 mg, 0.161 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^{1}H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 87.9 : 12.1 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	29.038	MM	0.1030	88.26166	14.27975	87.92765
2	29.674	MM	0.0577	12.11820	3.49899	12.07235

Stereochemical assignment of **4b**:

The stereochemical identity of **4b** was determined by two methods. First, the specific rotation of **4b** was compared under identical conditions to that reported in the literature for (3*S*,4*S*)-3,4-dimethyloxetan-2-one[11] and found to be of the opposite sign. Second, a *racemic* mixture of *trans*-3,4-dimethyloxetan-2-one was kinetically resolved to enantiopure (3*R*,4*R*)-3,4-dimethyloxetan-2-one by adapting a published procedure[12] using Lipase PS and benzyl alcohol. The β-lactone isolated from this reaction was identical with **4b** with regard to the sign of its specific rotation, and its GC retention time (Figures S1 and S2).

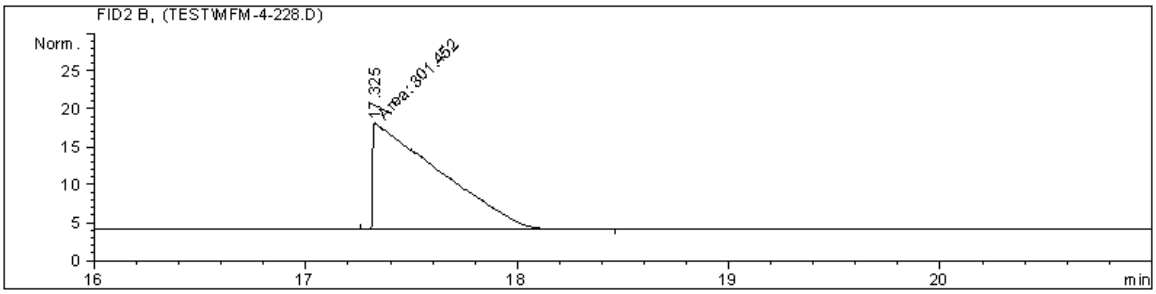


Figure S1 GC trace (β-Dex225 column) of (3*R*,4*R*)-3,4-dimethyloxetan-2-one obtained from kinetic resolution using Lipase PS

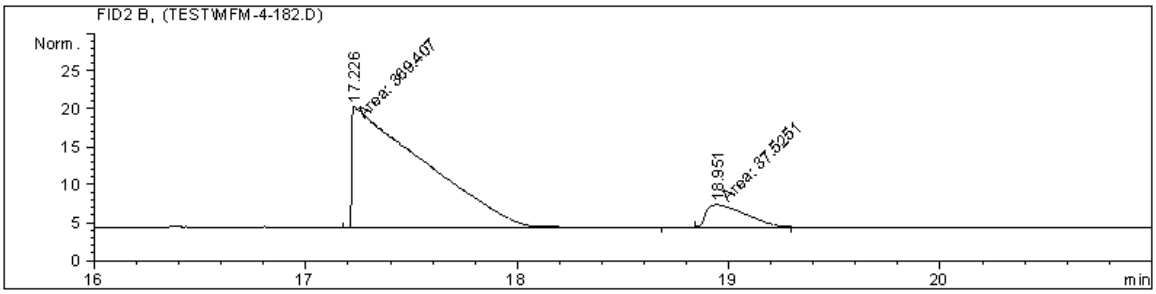
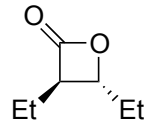


Figure S2 GC trace (β-Dex225 column) of isolated β-lactone **4b**

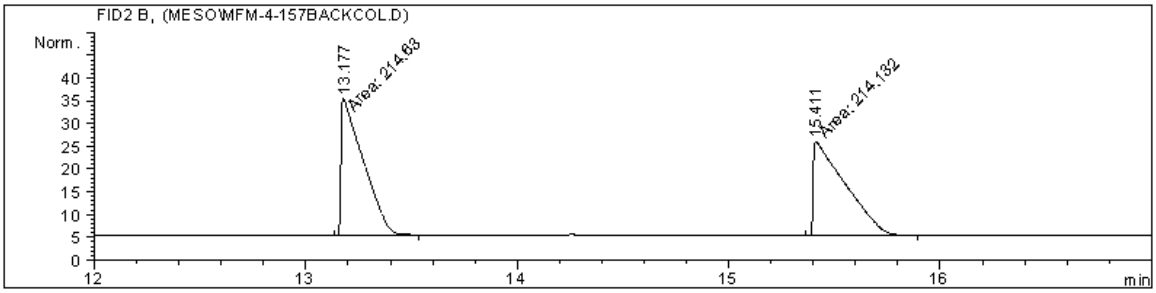
(3*R*,4*R*)-3,4-Diethyloxetan-2-one (4c)



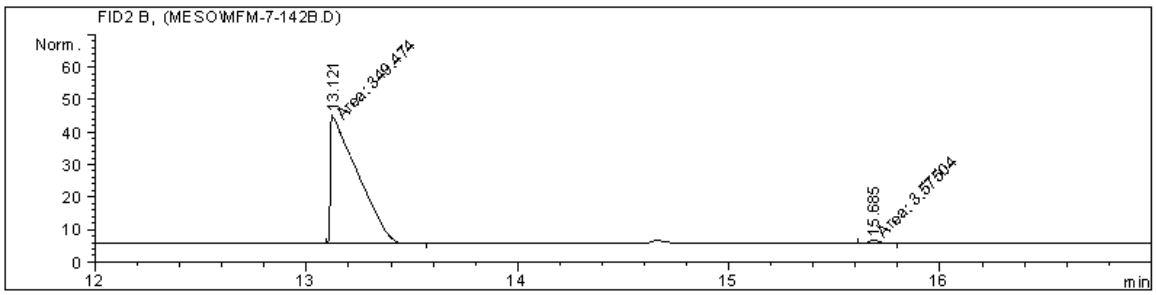
Using (*R*)-**1b**:

General procedure F was followed using (*R*)-Xyl$_2$BinamAlCl[5] (precursor to (*R*)-**1b**, 29.1 mg, 0.0300 mmol, 10.1 mol %), NaCo(CO)$_4$ (0.0500 M, THF, 600 µl, 0.0300 mmol, 10.1 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 29.8 mg, 0.298 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4c** (28.2 mg, 74 %) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.17 (td, *J* = 6.6, 3.9, 1H), 3.12 (ddd, *J* = 8.5, 6.5, 4.0, 1H), 1.93–1.69 (m, 4H), 1.02 (t, *J* = 7.5, 3H), 0.99 (t, *J* = 7.4, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 171.5, 78.8, 57.2, 27.6, 21.2, 11.4, 9.2. **IR** (neat, cm^{-1}): 2969, 2939, 2880, 1812, 1461, 1386, 1120, 1062, 954. **HRMS** (ESI) *m/z* calculated for $C_7H_{13}O_2^+$ (M + H$^+$) 129.0916, found 129.0922. **Specific rotation**: $[\alpha]^{22}_D$ = +23.6 (*c* = 0.51, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 99.0 : 1.0 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	13.177	MM	0.1198	214.62965	29.85584	50.05800
2	15.411	MM	0.1736	214.13228	20.56300	49.94200

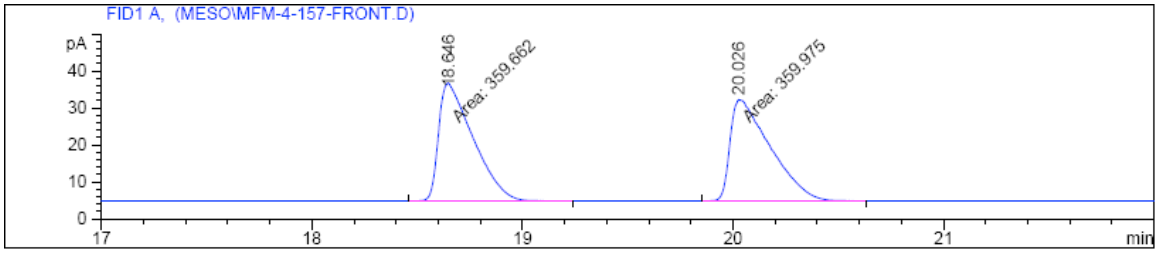


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.121	MM	0.1478	349.47379	39.40045	98.98738
2	15.685	MM	0.0654	3.57504	0.910499	1.01262

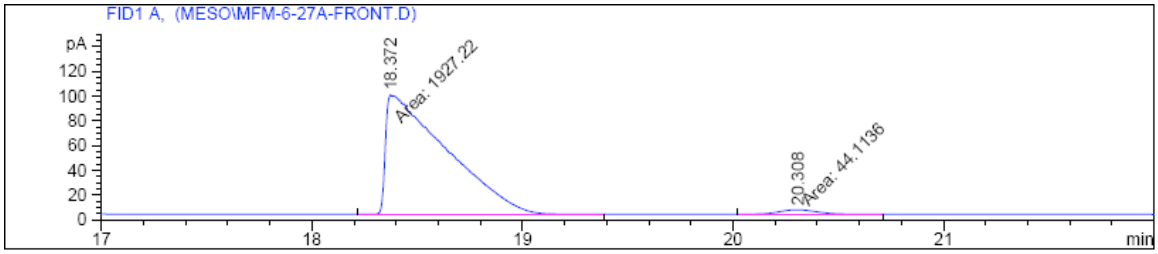
Using (*R*)-**1c**:

General procedure F was followed using (*R*)-*p*MeMesBinamAlCl[5] (precursor to (*R*)-**1c**, 8.2 mg, 0.010 mmol, 3.9 mol %), $NaCo(CO)_4$ (0.0500 M, THF, 200 µl, 0.0100 mmol, 3.91 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 1.28 M, THF, 200 µl, 0.256 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4c** (23.0 mg, 70 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 97.8 : 2.2 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.646	MM	0.1879	359.66174	31.89876	49.97826
2	20.026	MM	0.2194	359.97464	27.34226	50.02174

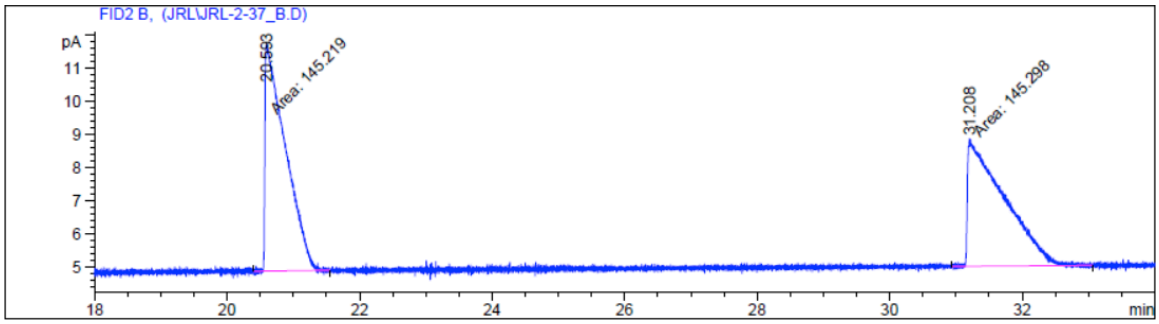


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.372	MM	0.3339	1927.21753	96.18916	97.76224
2	20.308	MM	0.2035	44.11358	3.61259	2.23776

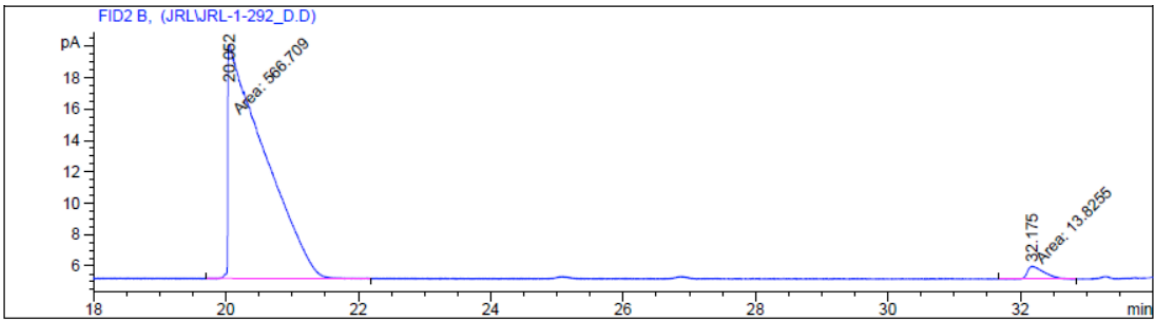
Using (*R*)-**1d**:

General procedure F was followed using (*R*)-**ML1** (precursor to (*R*)-**1d**, 5.9 mg, 0.0069 mmol, 5.4 mol %), $NaCo(CO)_4$ (1.4 mg, 0.0072 mmol, 5.6 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 12.9 mg, 0.129 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^{1}H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 97.6 : 2.4 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	20.593	MM	0.3477	145.21936	6.96069	49.98645
2	31.208	MM	0.6370	145.29810	3.80148	50.01355

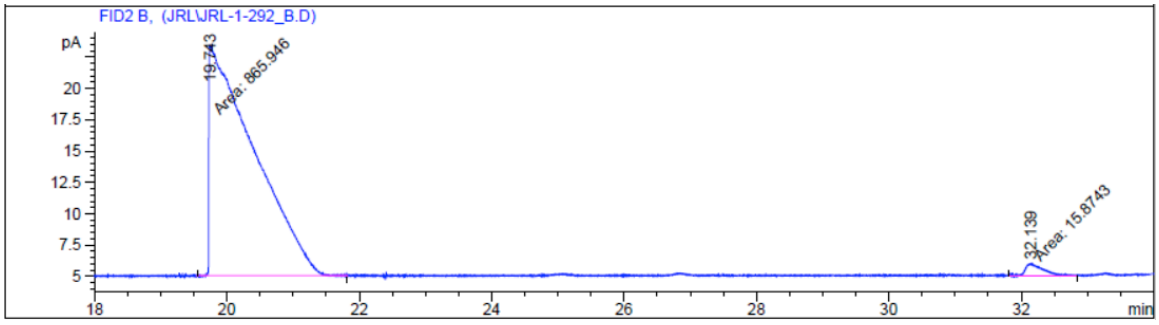


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.052	MM	0.6328	566.70917	14.92557	97.61849
2	32.175	MM	0.2907	13.82550	7.92559e-1	2.38151

Using (*R*)-**1e**:

General procedure F was followed using (*R*)-**ML2** (precursor to (*R*)-**1e**, 5.8 mg, 0.0070 mmol, 3.9 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 4.3 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 17.9 mg, 0.179 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^{1}H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 98.2 : 1.8 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

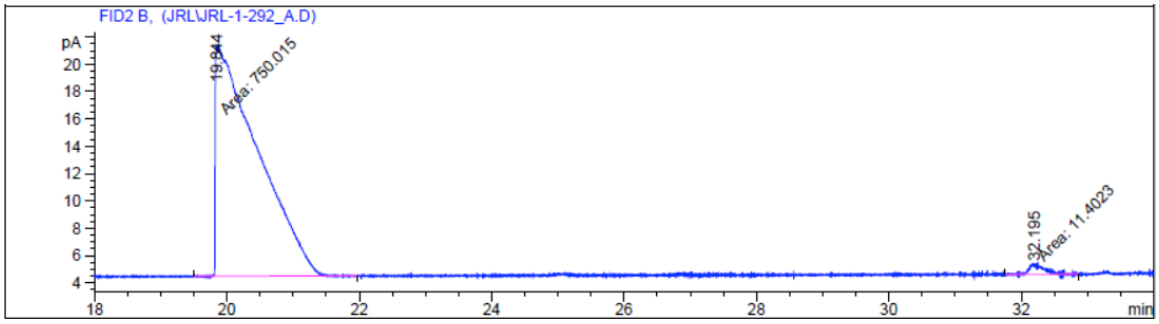


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.743	MM	0.7137	865.94617	20.22080	98.19983
2	32.139	MM	0.2856	15.87426	9.26470e-1	1.80017

Using (*R*)-**1f**:

General procedure F was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.4 mg, 0.0075 mmol, 4.7 mol %), $NaCo(CO)_4$ (1.3 mg, 0.0067 mmol, 4.2 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 15.9 mg, 0.159 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 98.5 : 1.5 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

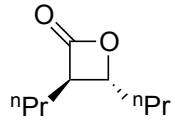


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.844	MM	0.7259	750.01532	17.22082	98.50248
2	32.195	MM	0.2695	11.40235	7.05162e-1	1.49752

Stereochemical assignment of **4c**:

The stereochemical identity of **4c** was determined by comparing the order of elution of the two enantiomers during GC analysis with that of **4b** and **4a**.

(3*R*,4*R*)-3,4-Dipropyloxetan-2-one (4a)

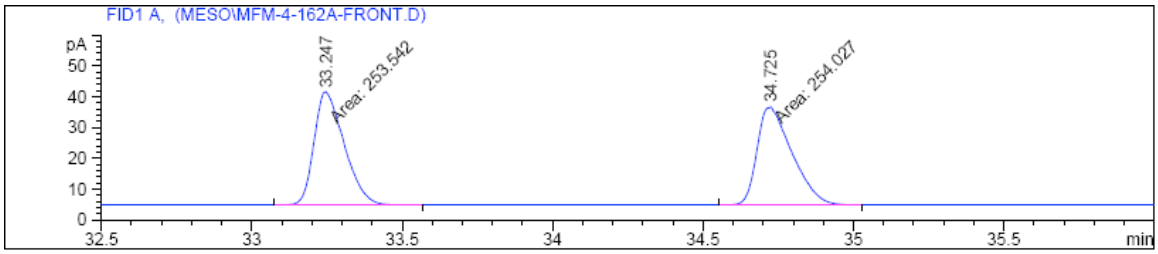


Using (*R*)-**1b**:

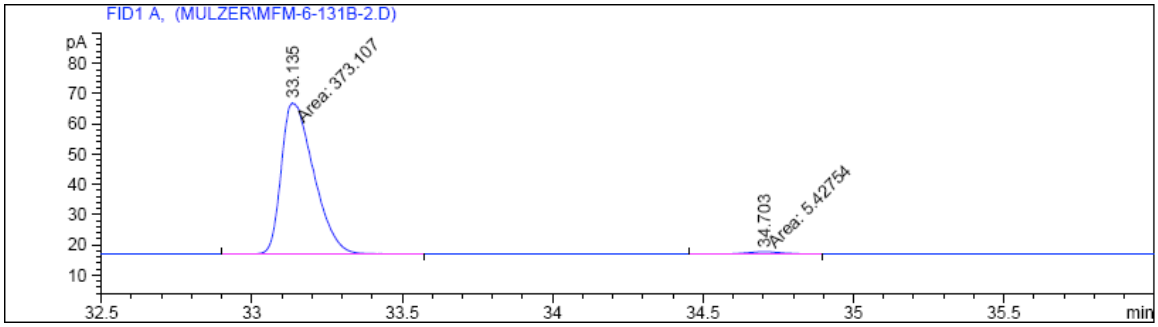
General procedure F was followed using (*R*)-Xyl_2BinamAlCl[5] (precursor to (*R*)-**1b**, 9.7 mg, 0.010 mmol, 10 mol %), $NaCo(CO)_4$ (1.00 M, THF, 100 µl, 0.0100 mmol, 10.0 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 1.00 M, THF, 100 µl, 0.100 mmol). After

stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4a** (11.9 mg, 76 %) as a yellow oil. Analytical data for **4a** has previously been reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.22 (ddd, *J* = 7.4, 5.9, 4.0, 1H), 3.17 (ddd, *J* = 8.8, 6.6, 4.0, 1H), 1.88–1.77 (m, 2H), 1.75–1.64 (m, 2H), 1.51–1.37 (m, 4H), 0.97 (t, *J* = 7.4, 3H), 0.94 (t, *J* = 7.3, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 171.7, 78.1, 56.1, 36.6, 30.1, 20.4, 18.5, 13.86, 13.86. **Specific rotation**: $[\alpha]^{22}_D$ = +30.3 (*c* = 1.29, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 98.6 : 1.4 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.247	MM	0.1152	253.54163	36.67054	49.95223
2	34.725	MM	0.1338	254.02655	31.6324	50.04777

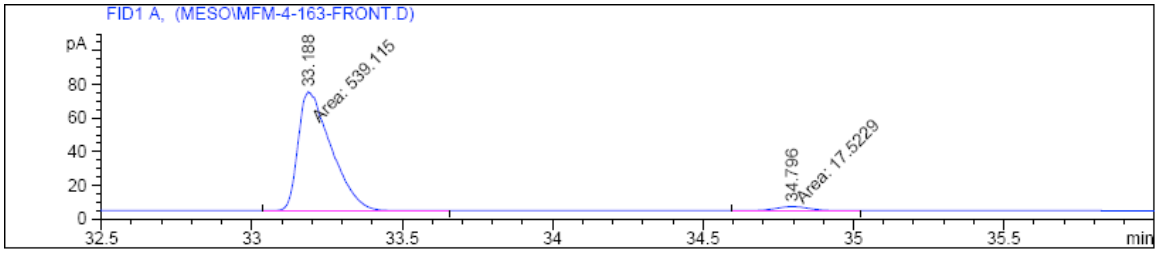


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.135	MM	0.1248	373.10696	49.82232	98.56617
2	34.703	MM	0.1251	5.42754	0.722884	1.43383

Using (*R*)-**1c**:

General procedure F was followed using (*R*)-*p*MeMesBinamAlCl[5] (precursor to (*R*)-**1c**, 14.3 mg, 0.0175 mmol, 7.00 mol %), $NaCo(CO)_4$ (0.100 M, THF, 175 µl, 0.0175 mmol, 7.00 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 1.00 M, THF, 250 µl, 0.250 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4a** (30.1 mg, 77 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 96.9 : 3.1 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.

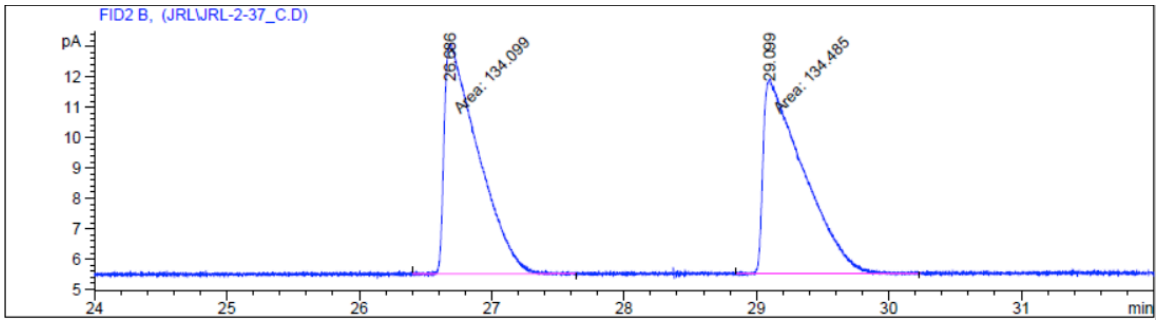


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.188	MM	0.1271	539.11475	70.71523	96.852
2	34.796	MM	0.123	17.52294	2.37393	3.148

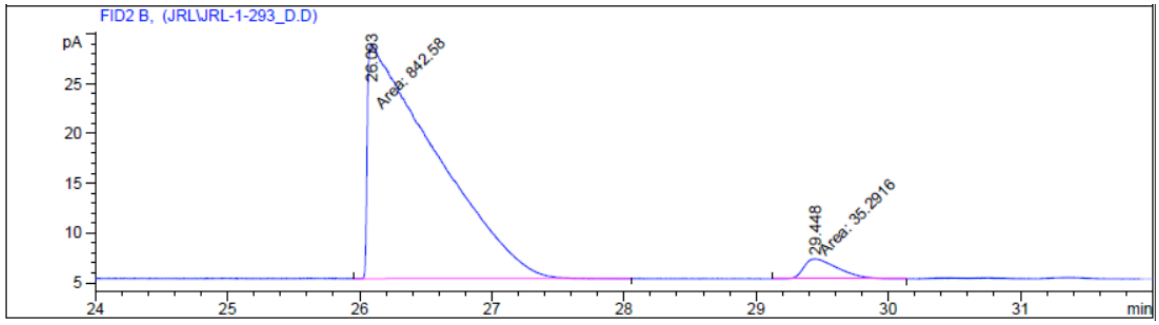
Using (*R*)-**1d**:

General procedure F was followed using (*R*)-**ML1** (precursor to (*R*)-**1d**, 5.9 mg, 0.0069 mmol, 5.0 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 5.6 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 17.7 mg, 0.138 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 96.0 : 4.0 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	26.686	MM	0.2965	134.09883	7.53866	49.92820
2	29.099	MM	0.3501	134.48454	6.40236	50.07180

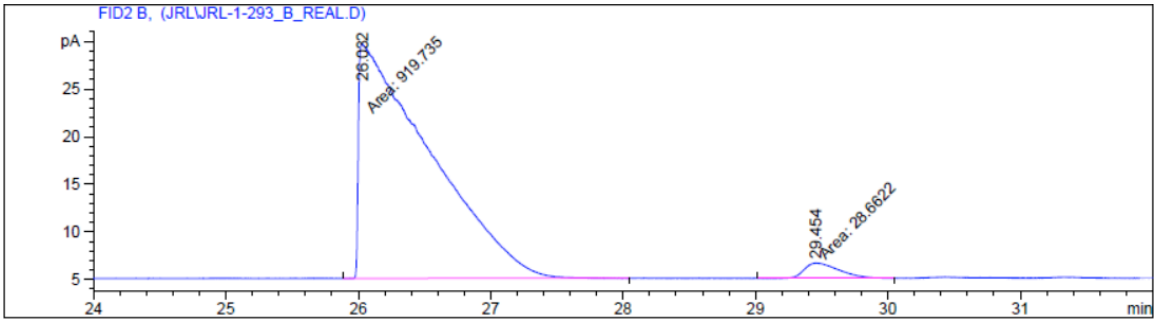


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.093	MM	0.5974	842.58002	23.50514	95.97987
2	29.448	MM	0.2939	35.29161	2.00165	4.02013

Using (*R*)-**1e**:

General procedure F was followed using (*R*)-**ML2** (precursor to (*R*)-**1e**, 5.8 mg, 0.0070 mmol, 5.4 mol %), $NaCo(CO)_4$ (2.3 mg, 0.012 mmol, 9.2 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 16.5 mg, 0.129 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.0 : 3.0 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

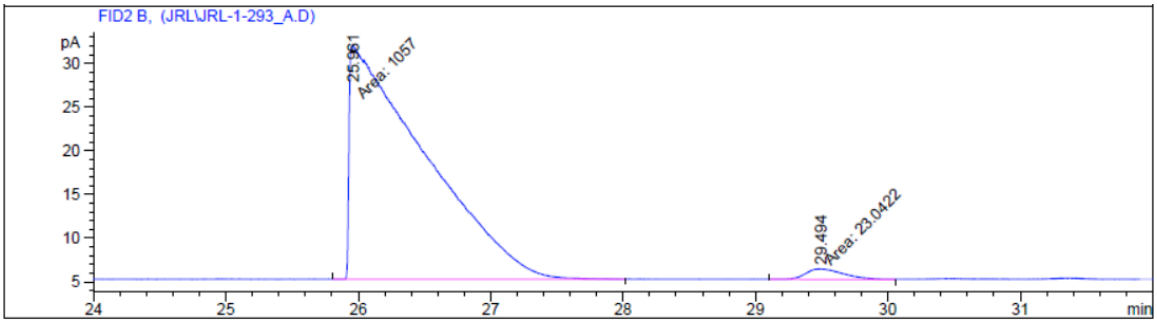


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.032	MM	0.6245	919.73505	24.54473	96.97783
2	29.454	MM	0.2987	28.66216	1.59935	3.02217

Using (*R*)-**1f**:

General procedure F was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.1 mg, 0.0071 mmol, 5.4 mol %), $NaCo(CO)_4$ (1.6 mg, 0.0082 mmol, 6.3 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 16.9 mg, 0.132 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^{1}H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.9 : 2.1 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

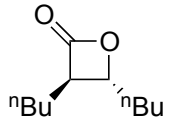


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.961	MM	0.6543	1056.99536	26.92523	97.86654
2	29.494	MM	0.3241	23.04221	1.18481	2.13346

Stereochemical assignment of **4a**:

The stereochemical identity of **4a** was determined by comparing the specific rotation of **4a** under identical conditions to that reported in the literature for (3*R*,4*R*)-3,4-dipropyl-oxetan-2-one.[13] The literature known compound (95 % ee, $[\alpha]^{22.3}_D$ = +36.8 (*c* = 1.630, $CHCl_3$)) and **4a** (97 % ee, $[\alpha]^{22}_D$ = +30.3 (*c* = 1.29, $CHCl_3$)) displayed the same sign and approximately the same magnitude of rotation.

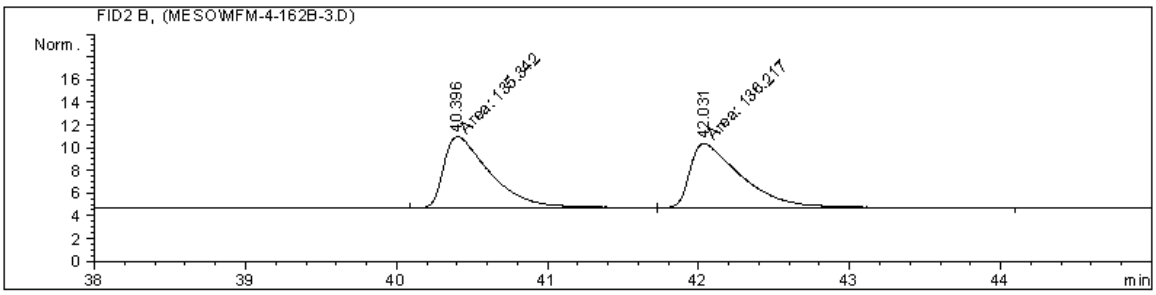
(3*R*,4*R*)-3,4-Dibutyloxetan-2-one (4d)



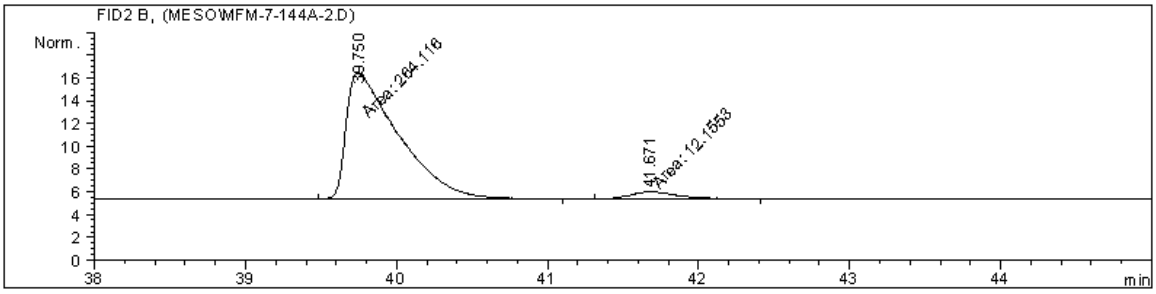
Using (*R*)-**1b**:

General procedure F was followed using (*R*)-Xyl_2BinamAlCl[5] (precursor to (*R*)-**1b**, 23.3 mg, 0.0240 mmol, 12.1 mol %), $NaCo(CO)_4$ (0.120 M, THF, 200 µl, 0.0240 mmol, 12.1 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 0.994 M, THF, 200 µl, 0.199 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4d** (26.4 mg, 72 %) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.20 (ddd, *J* = 7.4, 6.0, 4.0, 1H), 3.15 (ddd, *J* = 8.7, 6.6, 3.9, 1H), 1.89–1.65 (m, 4H), 1.44–1.29 (m, 8H), 0.91 (t, *J* = 7.0, 3H), 0.90 (t, *J* = 7.0, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 171.8, 78.3, 56.2, 34.2, 29.2, 27.7, 27.2, 22.50, 22.46, 14.0, 13.9. **IR** (neat, cm^{-1}): 2957, 2931, 2861, 1817, 1466, 1125, 1064, 838. **HRMS** (ESI) *m/z* calculated for $C_{11}H_{21}O_2^+$ (M + H^+) 185.1542, found 185.1543. **Specific rotation**: $[\alpha]^{22}_D$ = +25.0 (*c* = 0.76, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 95.6 : 4.4 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	40.396	MF	0.2578	135.34154	6.30441	49.8388
2	42.031	FM	0.3962	136.21703	5.72963	50.16120

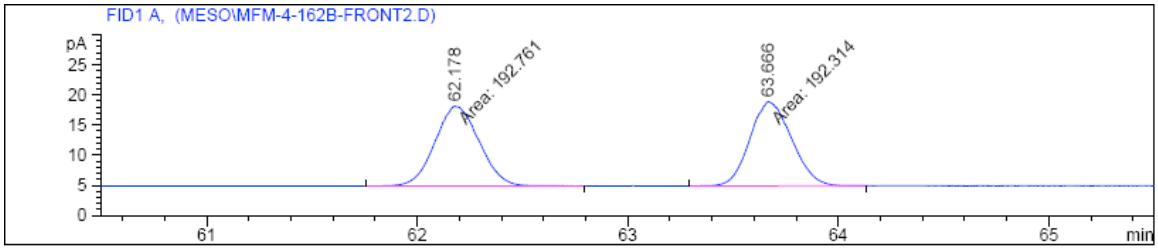


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.750	MM	0.3960	264.11627	11.11648	95.60022
2	41.671	MM	0.3387	12.15534	0.598054	4.39978

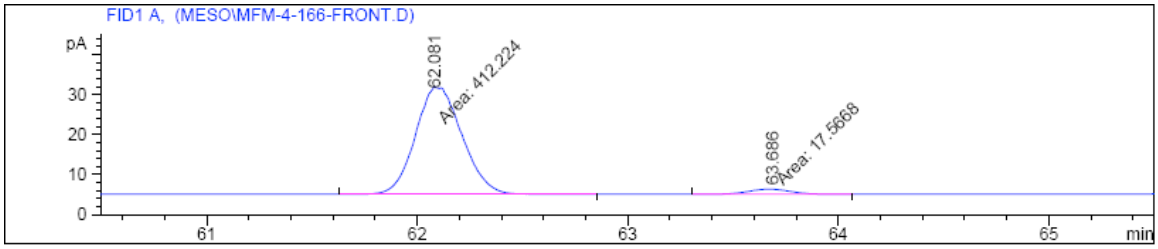
Using (*R*)-**1c**:

General procedure F was followed using (*R*)-*p*MeMesBinamAlCl[5] (precursor to (*R*)-**1c**, 13.1 mg, 0.0160 mmol, 8.04 mol %), $NaCo(CO)_4$ (0.0800 M, THF, 200 µl, 0.0160 mmol, 8.00 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 0.994 M, THF, 200 µl, 0.199 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give **4d** (26.7 mg, 72 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 95.9 : 4.1 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	62.178	MM	0.2419	192.76053	13.28018	50.05796
2	63.666	MM	0.2295	192.31415	13.96905	49.94204

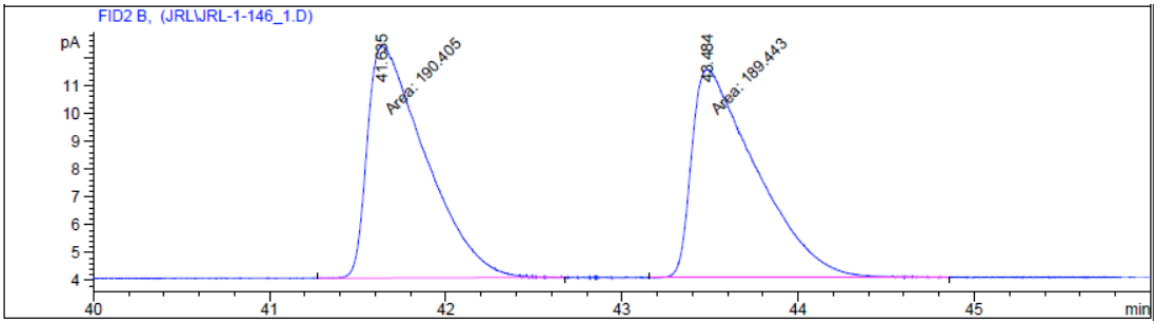


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	62.081	MM	0.2552	412.22443	26.91874	95.91271
2	63.686	MM	0.2309	17.5668	1.2679	4.08729

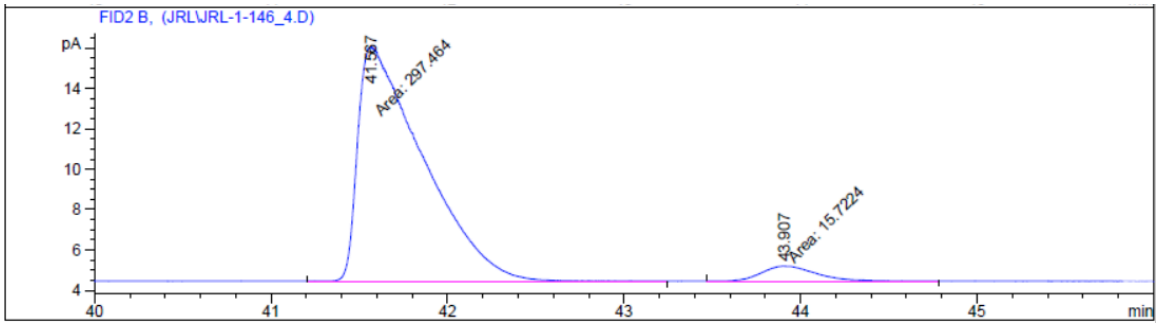
Using (*R*)-**1d**:

General procedure F was followed using (*R*)-**ML1** (precursor to (*R*)-**1d**, 5.9 mg, 0.0069 mmol, 4.6 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 5.1 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 23.5 mg, 0.150 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 95.0 : 5.0 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	41.635	MM	0.3793	190.40520	8.36624	50.12667
2	43.484	MM	0.4239	189.44292	7.44791	49.87333

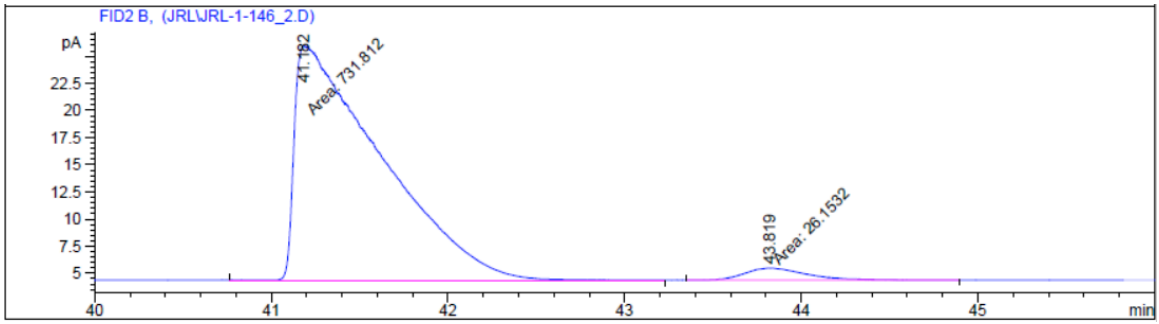


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.567	MM	0.4277	297.46405	11.59227	94.97985
2	43.907	MM	0.3530	15.72243	7.42406e-1	5.02015

Using (*R*)-**1e**:

General procedure F was followed using (*R*)-**ML2** (precursor to (*R*)-**1e**, 5.8 mg, 0.0070 mmol, 4.6 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 5.0 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 24.0 mg, 0.154 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^1H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 96.5 : 3.5 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

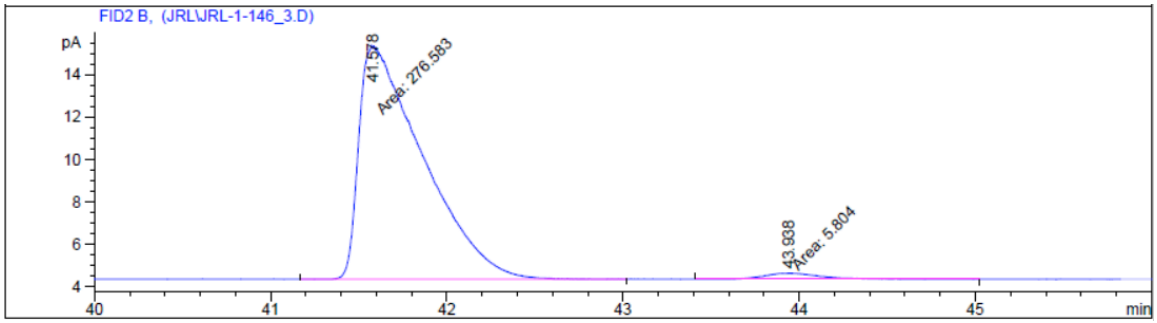


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.182	MM	0.5638	731.81244	21.63292	96.54955
2	43.819	MM	0.3988	26.15322	1.09292	3.45045

Using (*R*)-**1f**:

General procedure F was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 5.9 mg, 0.0069 mmol, 3.7 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 4.2 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 28.8 mg, 0.184 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO_2 and analyzed by ^{1}H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.9 : 2.1 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

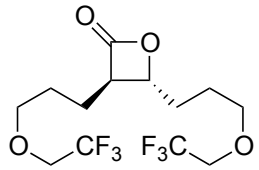


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.578	MM	0.4225	276.58276	10.91018	97.94466
2	43.938	MM	0.3543	5.80400	2.73024e-1	2.05534

Stereochemical assignment of **4d**:

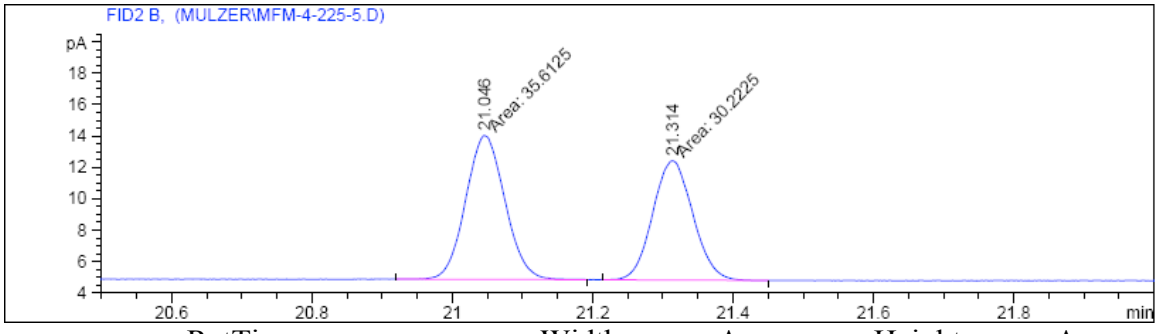
The stereochemical identity of **4d** was determined by comparing the order of elution of the two enantiomers during GC analysis with that of **4b** and **4a**.

(3*R*,4*R*)-3,4-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxetan-2-one (4e)

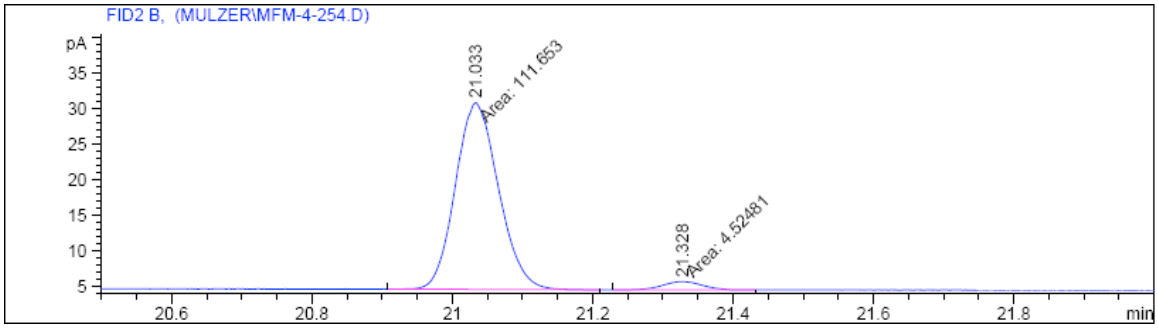


General procedure F was followed using (*R*)-*p*MeMesBinamAlCl[5] (precursor to (*R*)-**1c**, 25.5 mg, 0.0312 mmol, 12.5 mol %), $NaCo(CO)_4$ (0.0624 M, THF, 500 µl, 0.0312 mmol, 12.5 mol %) and *meso*-2,3-bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (**3e**, 80.4 mg, 0.248 mmol). After stirring at 33 °C for 24 h, the crude reaction mixture was subjected to flash column chromatography to give **4e** (68.6 mg, 79 %) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.29 (td, *J* = 6.6, 4.1, 1H), 3.81 (qd, *J* = 8.7, 2.5, 4H), 3.70–3.60 (m, 4H), 3.25 (td, *J* = 7.6, 4.0, 1H), 1.98–1.65 (m, 8H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 171.1, 124.0 (q, *J* = 279.6), 77.7, 72.02, 71.95, 68.45 (q, *J* = 34.0), 68.44 (q, *J* = 34.0), 55.9, 31.2, 27.0, 25.4, 24.7. *Note*: The two CF_3-groups are pseudohomotopic, thus only one signal was observed. **^{19}F NMR** (376 MHz, $CDCl_3$, ref. $CFCl_3$): δ -74.3 (td, *J* = 8.9, 2.6). **IR** (neat, cm^{-1}): 2923, 2853, 1816, 1445, 1275, 1121, 966, 826. **HRMS** (ESI) *m/z* calculated for $C_{13}H_{19}F_6O_4^+$ ($M + H^+$) 353.1182, found 353.1197. **Specific rotation**: $[\alpha]^{22}_D$ = +19.8 (*c* = 1.52, $CHCl_3$).

The enantiomeric ratio (er) was determined to be 92.0 : 8.0 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	21.046	MM	0.0647	35.6125	9.17749	54.09353
2	21.314	MM	0.0662	30.22254	7.60377	45.90647



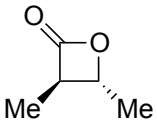
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	21.033	MM	0.071	111.65323	26.22412	96.10528
2	21.328	MM	0.065	4.52481	1.16045	3.89472

Stereochemical assignment of **4e**:

The stereochemical identity of **4e** was determined by comparing the order of elution of the two enantiomers during GC analysis with that of **4a**–**d**.

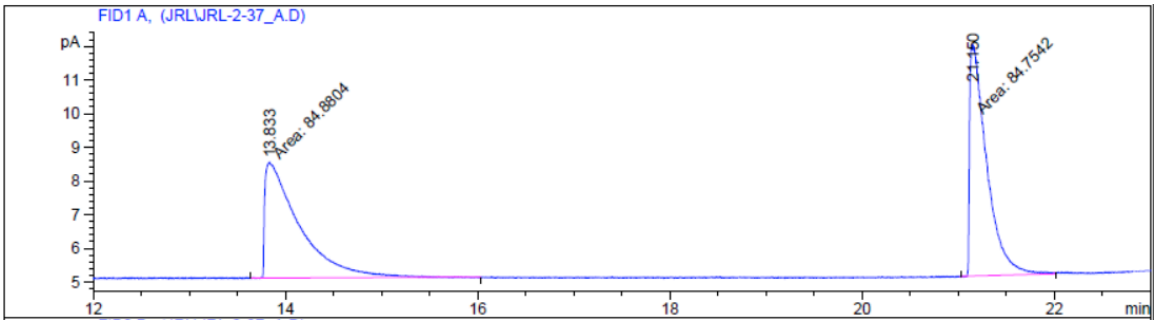
Carbonylative desymmetrization of *meso*-epoxides using (*R*)-1d or (*R*)-1f at 0 °C

(3*R*,4*R*)-3,4-Dimethyloxetan-2-one (4b)

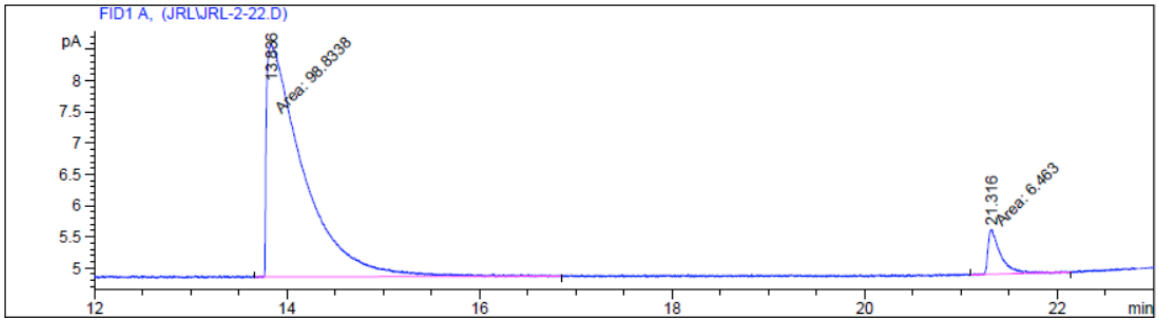


General procedure G was followed using (*R*)-**ML1** (precursor to (*R*)-**1d**, 5.0 mg, 0.0059 mmol, 3.3 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 4.3 mol %) and *meso*-(2*R*,3*S*)-2,3-dimethyloxirane (**3b**, 12.9 mg, 0.179 mmol).

The enantiomeric ratio (er) was determined to be 93.9 : 6.1 by GC analysis (β-Dex120 column) in comparison to authentic *racemic* material.

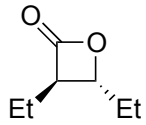


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.833	MM	0.4114	84.88037	3.43889	50.03718
2	21.150	MM	0.2055	84.75423	6.87440	49.96282



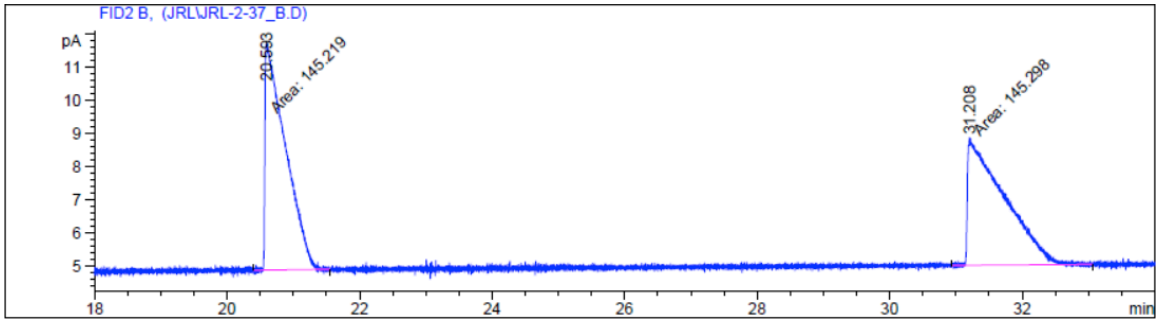
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.836	MM	0.4403	98.83379	3.74093	93.86211
2	21.316	MM	0.1501	6.46300	7.17660e-1	6.13789

(3*R*,4*R*)-3,4-Diethyloxetan-2-one (4c)

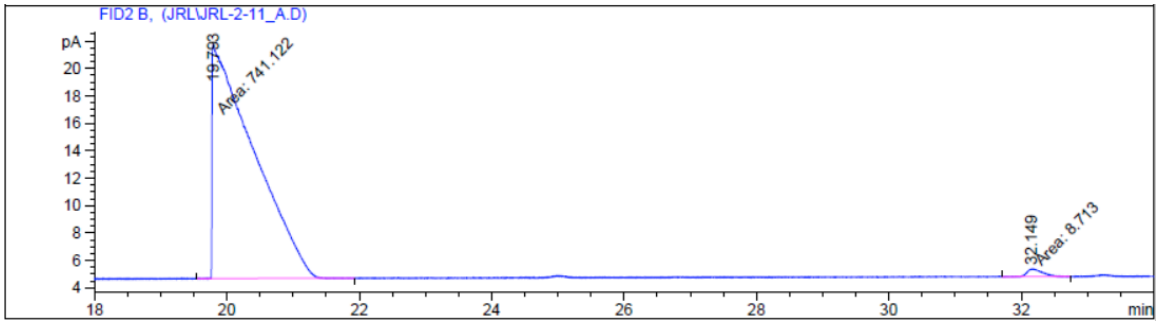


General procedure G was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.3 mg, 0.0073 mmol, 4.6 mol %), $NaCo(CO)_4$ (1.5 mg, 0.0077 mmol, 4.9 mol %) and *meso*-(2*R*,3*S*)-2,3-diethyloxirane[7] (**3c**, 15.9 mg, 0.159 mmol).

The enantiomeric ratio (er) was determined to be 98.8 : 1.2 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

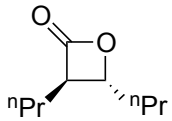


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.593	MM	0.3477	145.21936	6.96069	49.98645
2	31.208	MM	0.6370	145.29810	3.80148	50.01355



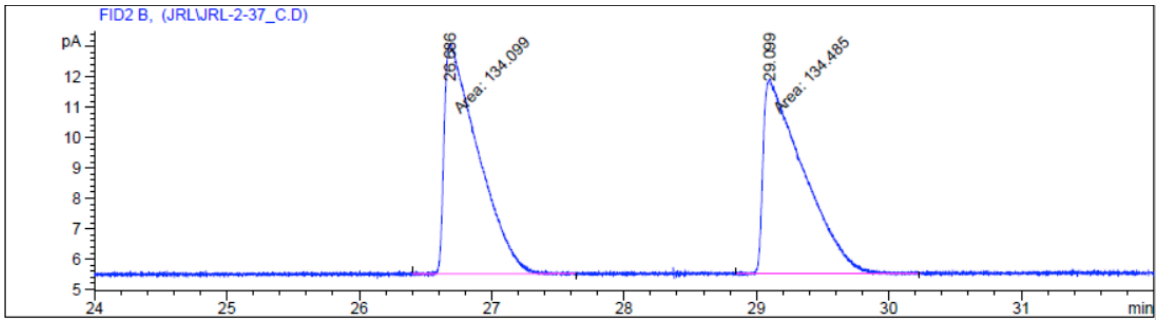
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.793	MM	0.7261	741.12238	17.01032	98.83801
2	32.149	MM	0.2639	8.71300	5.50337e-1	1.16199

(3*R*,4*R*)-3,4-Dipropyloxetan-2-one (4a)

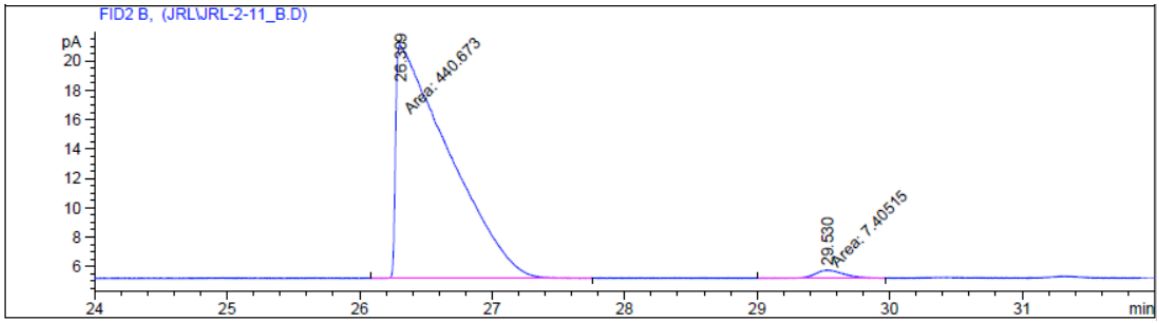


General procedure G was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.5 mg, 0.0076 mmol, 5.2 mol %), $NaCo(CO)_4$ (1.7 mg, 0.0088 mmol, 6.0 mol %) and *meso*-(2*R*,3*S*)-2,3-dipropyloxirane[6] (**3a**, 18.6 mg, 0.145 mmol).

The enantiomeric ratio (er) was determined to be 98.3 : 1.7 by GC analysis (β-Dex225 column) in comparison to authentic *racemic* material.

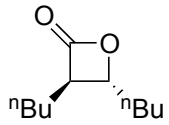


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.686	MM	0.2965	134.09883	7.53866	49.92820
2	29.099	MM	0.3501	134.48454	6.40236	50.07180



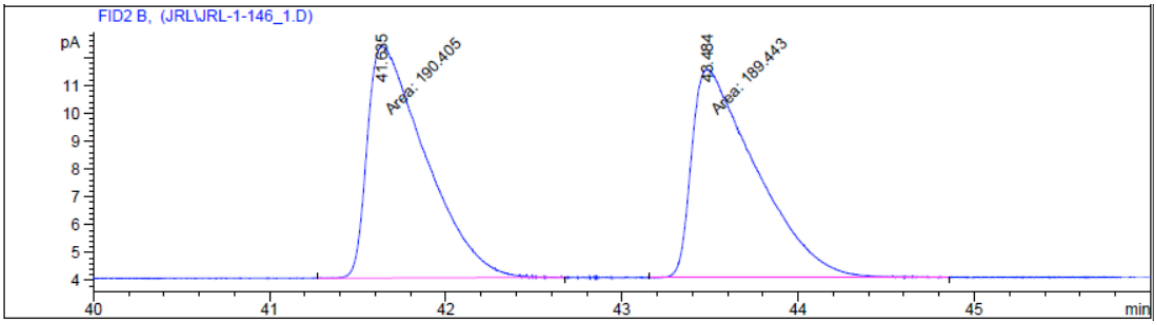
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.309	MM	0.4648	440.67282	15.80125	98.34735
2	29.530	MM	0.2271	7.40515	5.43382e-1	1.65265

(3*R*,4*R*)-3,4-Dibutyloxetan-2-one (4d)

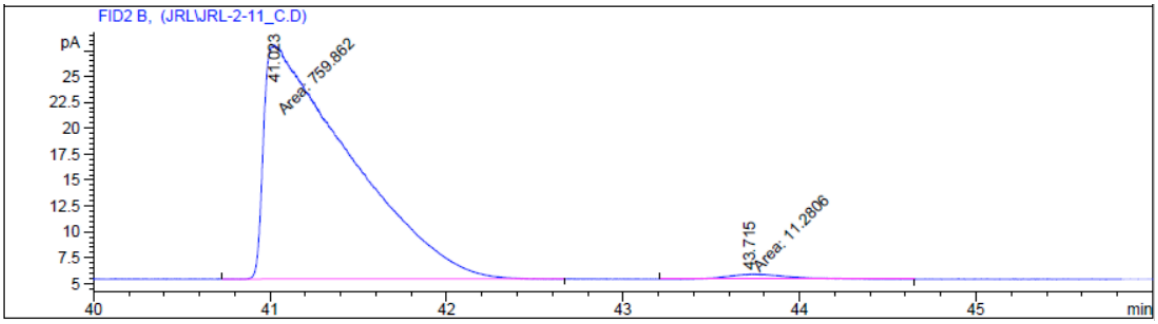


General procedure G was followed using (*R*)-**ML3** (precursor to (*R*)-**1f**, 6.4 mg, 0.0075 mmol, 4.8 mol %), $NaCo(CO)_4$ (1.8 mg, 0.0093 mmol, 6.0 mol %) and *meso*-(2*R*,3*S*)-2,3-dibutyloxirane[8] (**3d**, 24.1 mg, 0.154 mmol).

The enantiomeric ratio (er) was determined to be 98.5 : 1.5 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	41.635	MM	0.3793	190.40520	8.36624	50.12667
2	43.484	MM	0.4239	189.44292	7.44791	49.87333



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.023	MM	0.5614	759.86176	22.55735	98.53716
2	43.715	MM	0.4130	11.28061	4.55275e-1	1.46284

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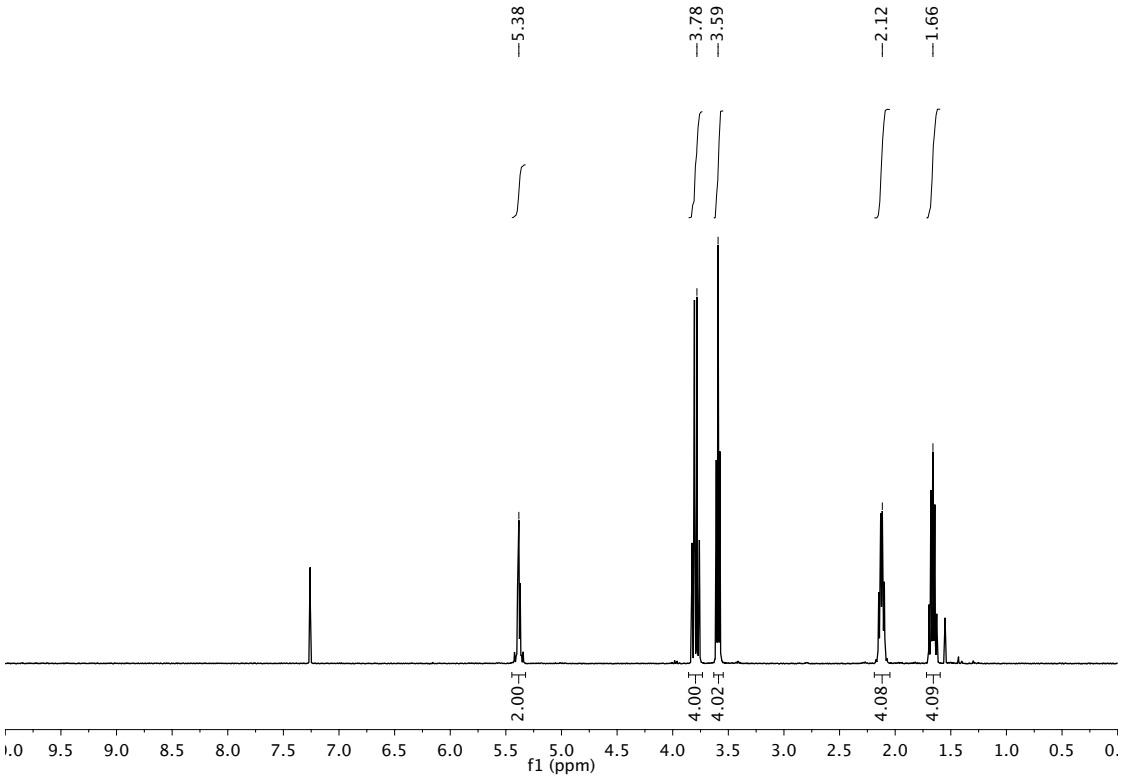
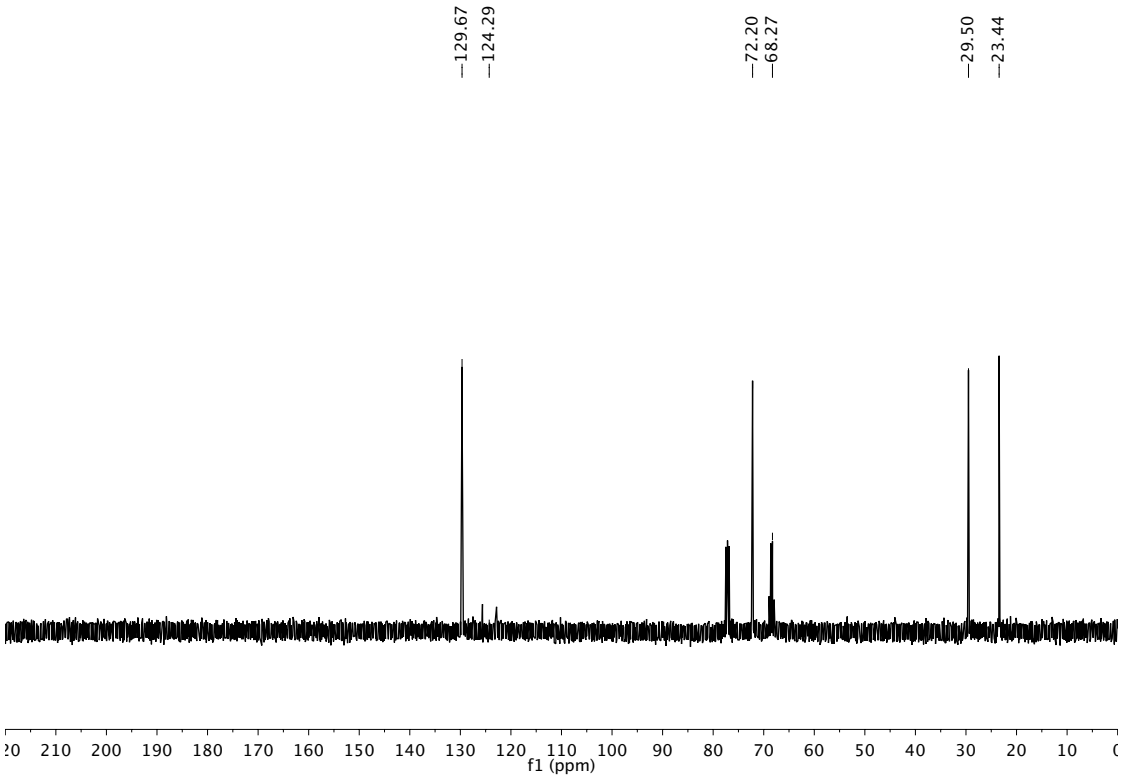
Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

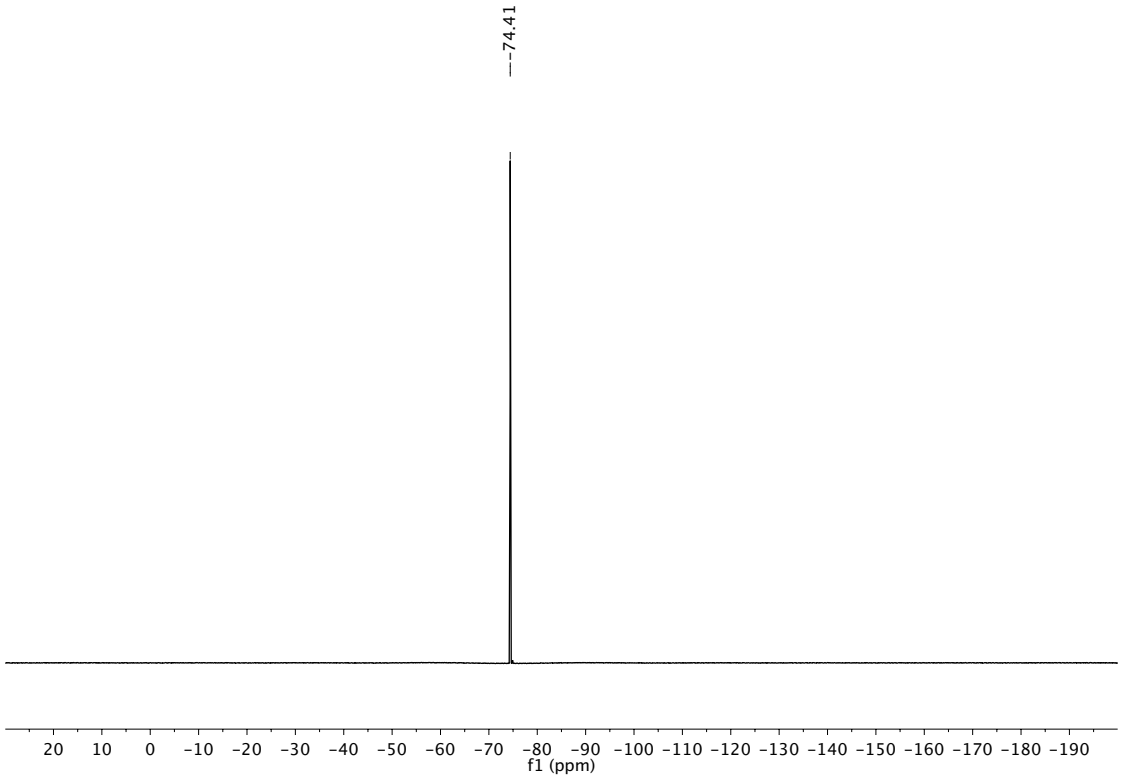
(*Z*)-1,8-Bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1), **^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



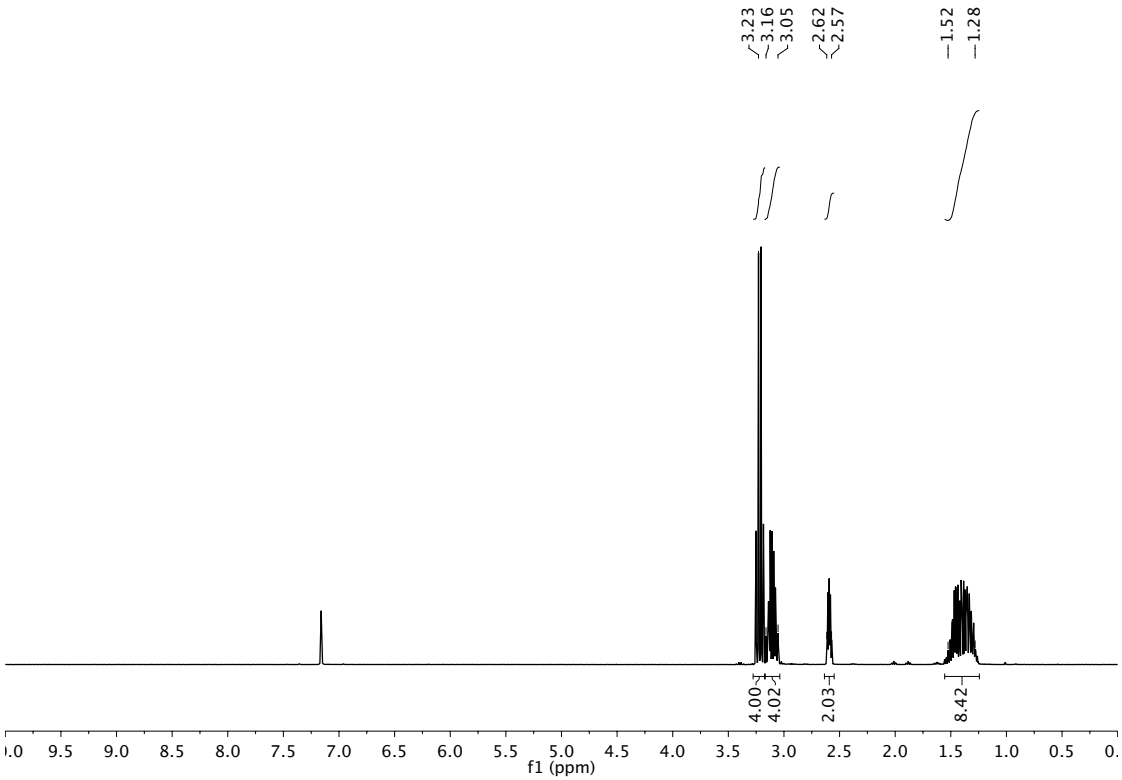
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$)



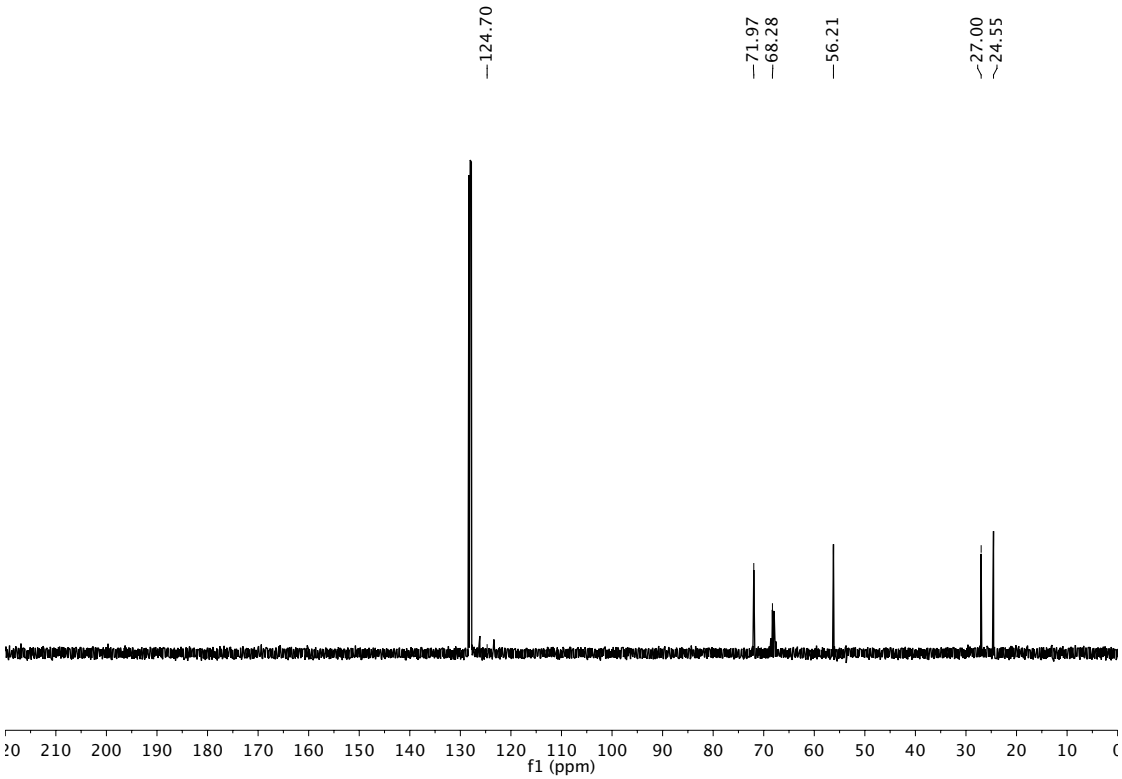
^{19}F NMR spectrum (376 MHz, $CDCl_3$)



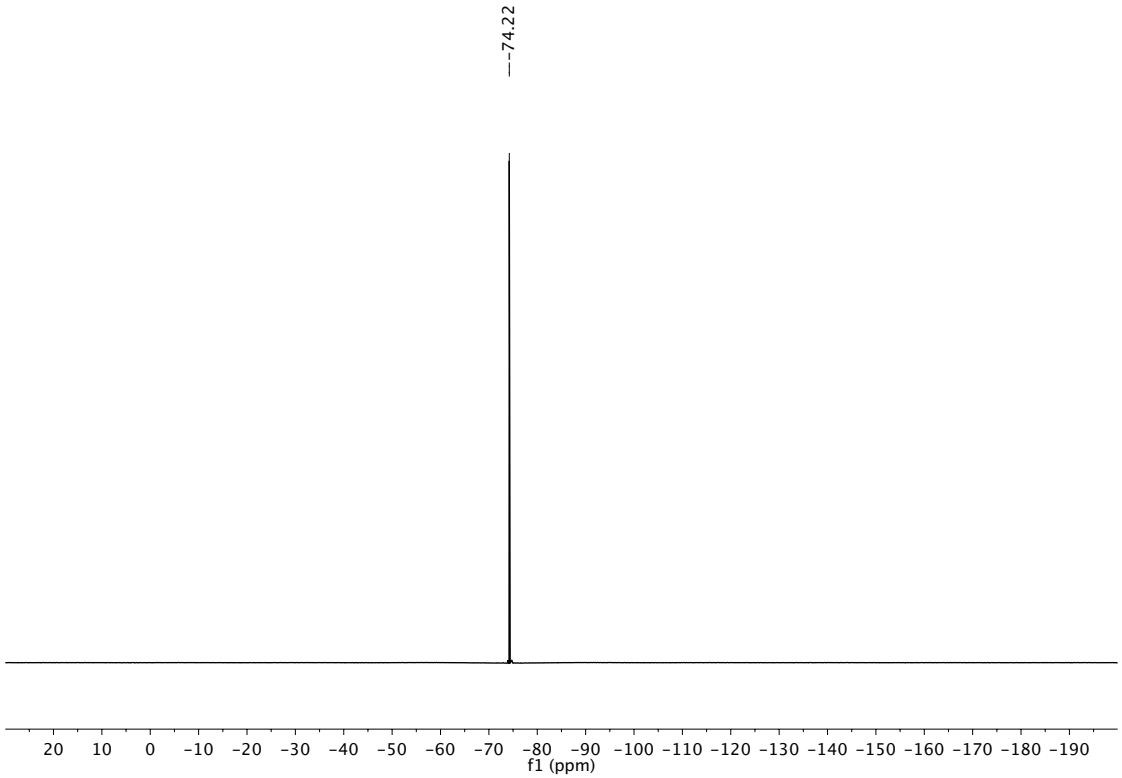
2,3-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (3e), **^{1}H NMR spectrum** (400 MHz, C_6D_6)



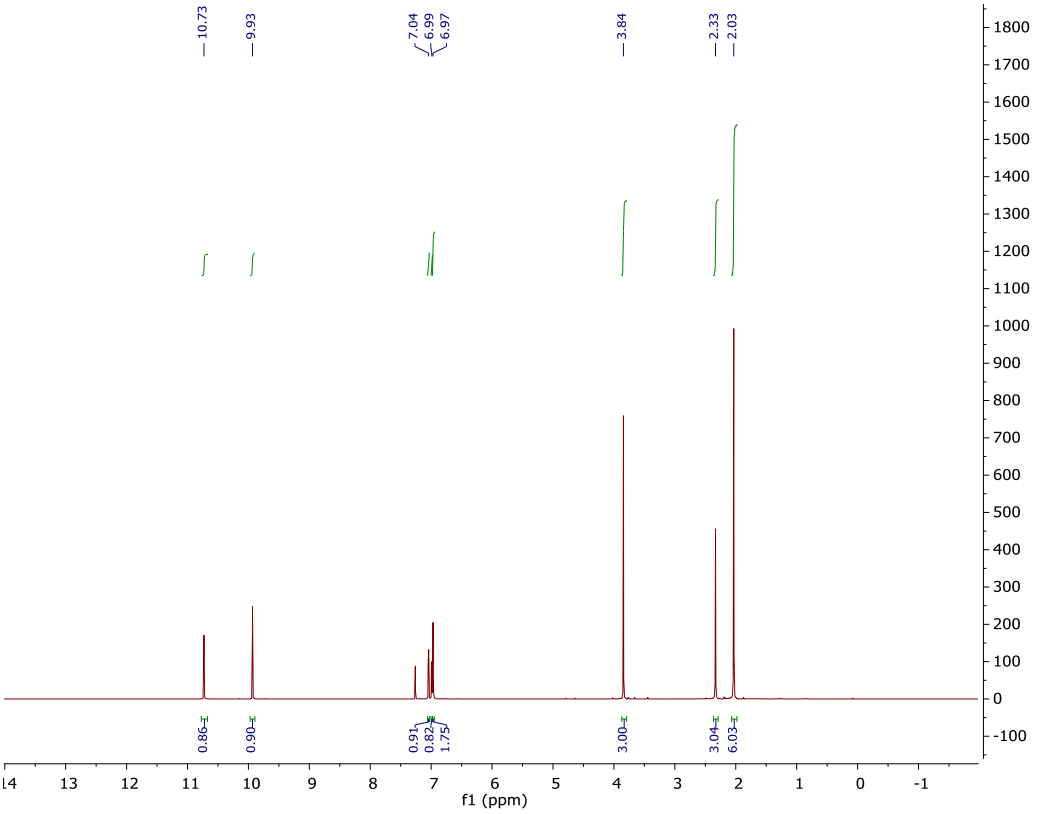
^{13}C{^{1}H} NMR spectrum (101 MHz, C_6D_6)



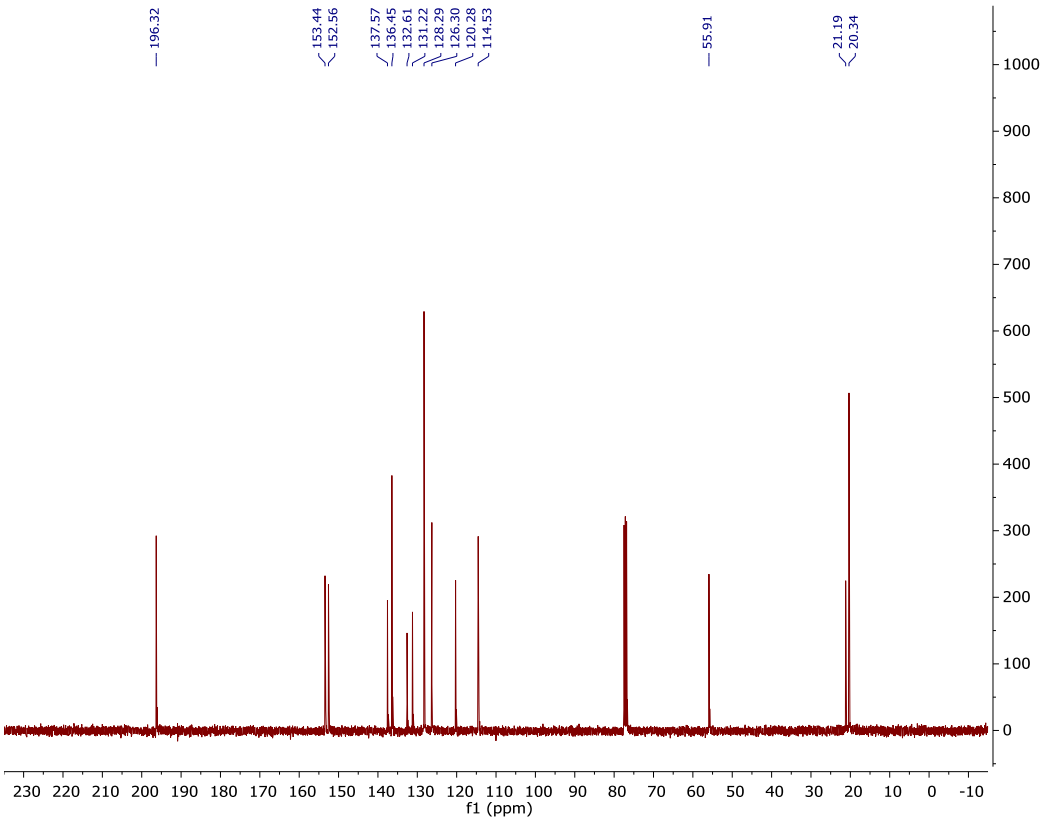
^{19}F NMR spectrum (376 MHz, C_6D_6)



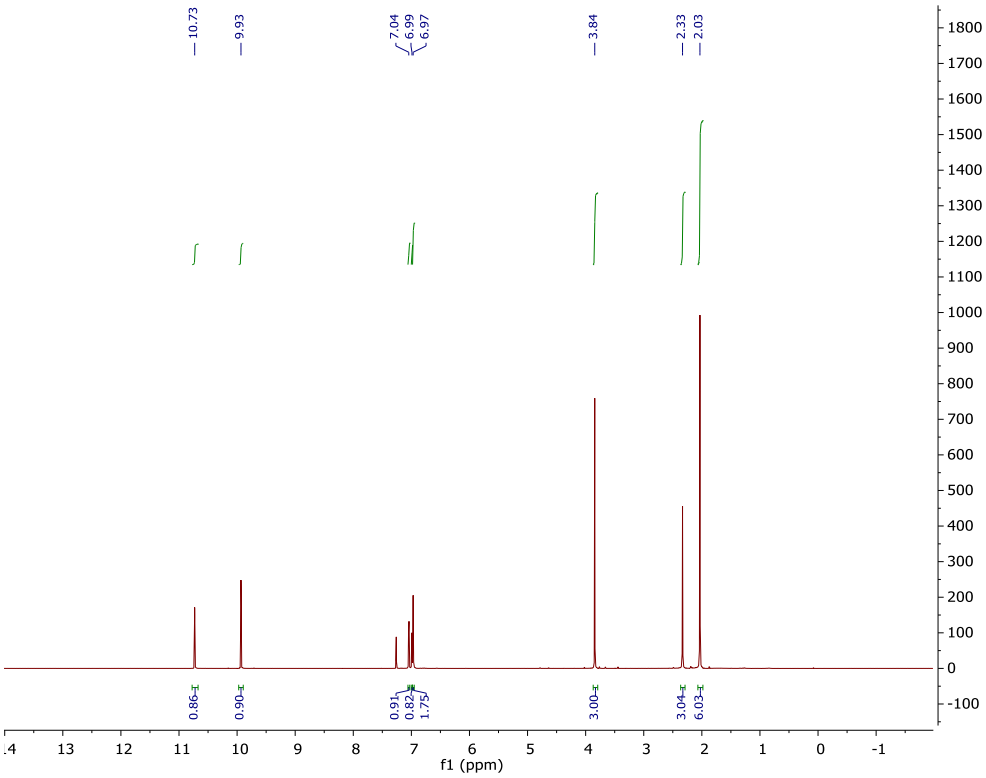
5-Methoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM2), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



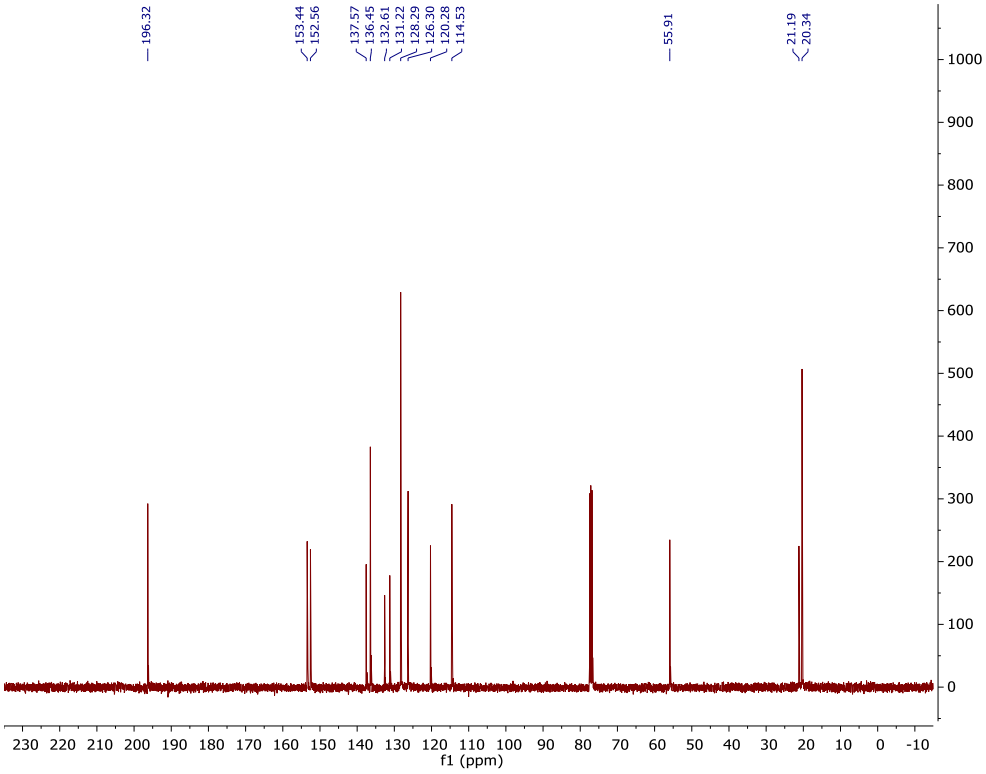
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



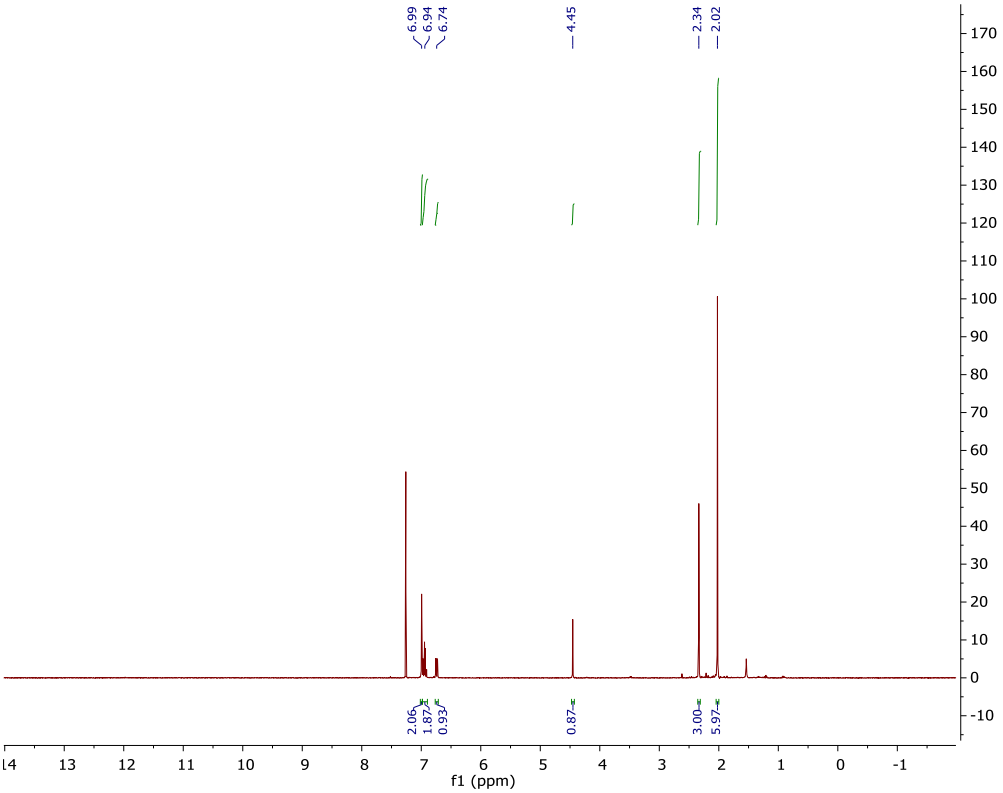
2-Hydroxy-5-methyoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM3), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



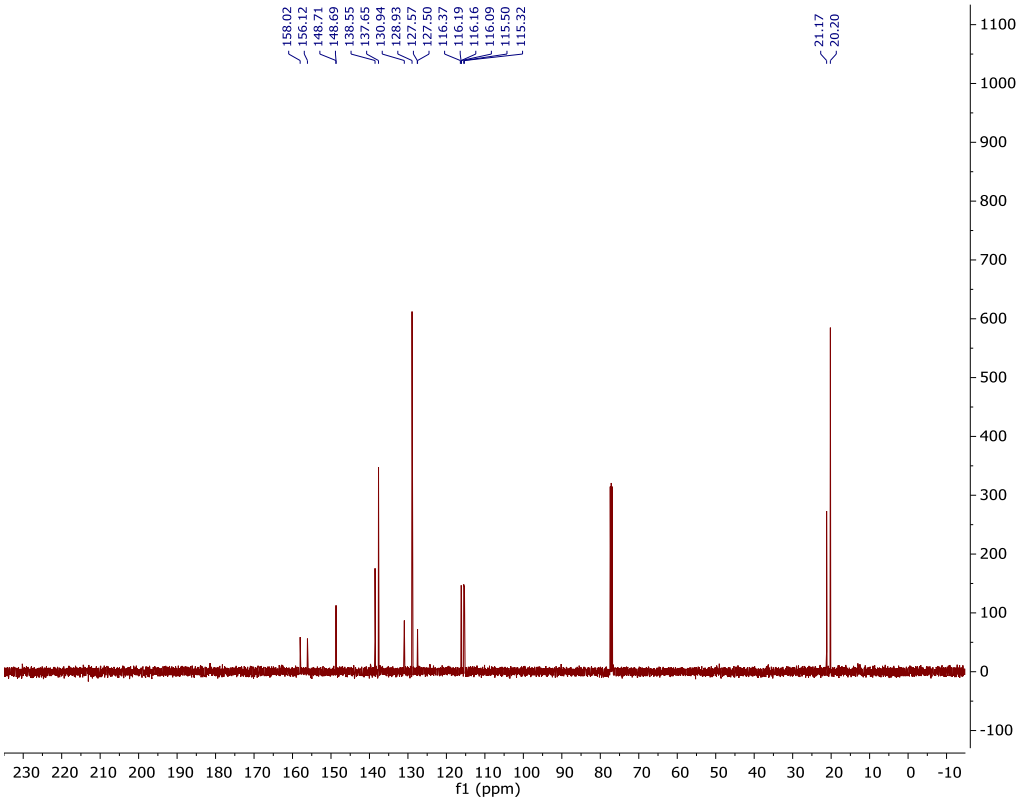
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



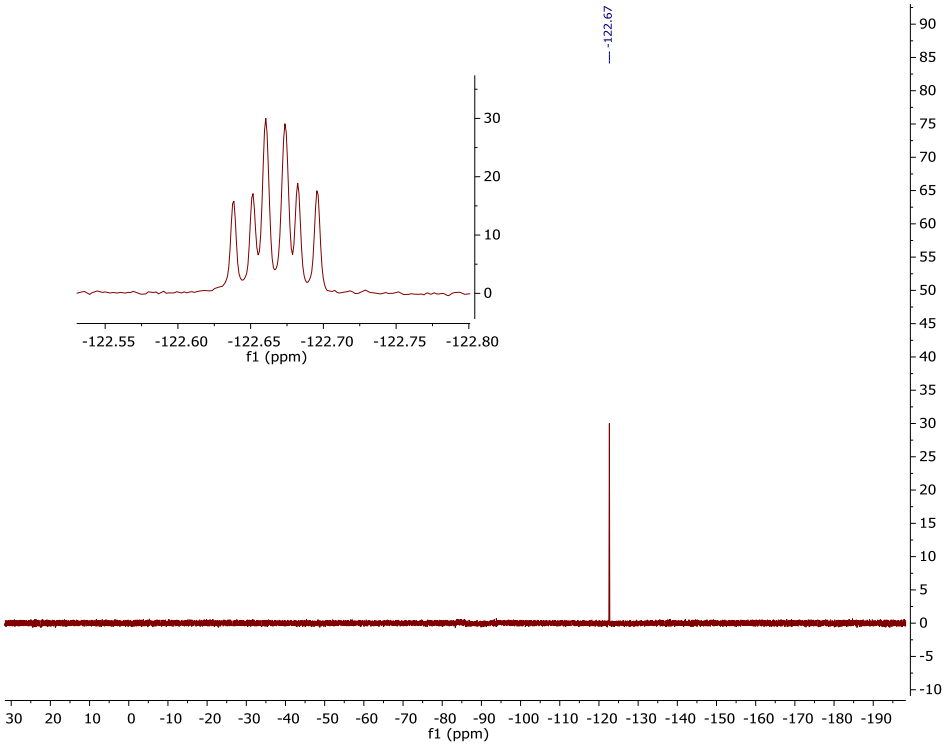
5-Fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM4), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



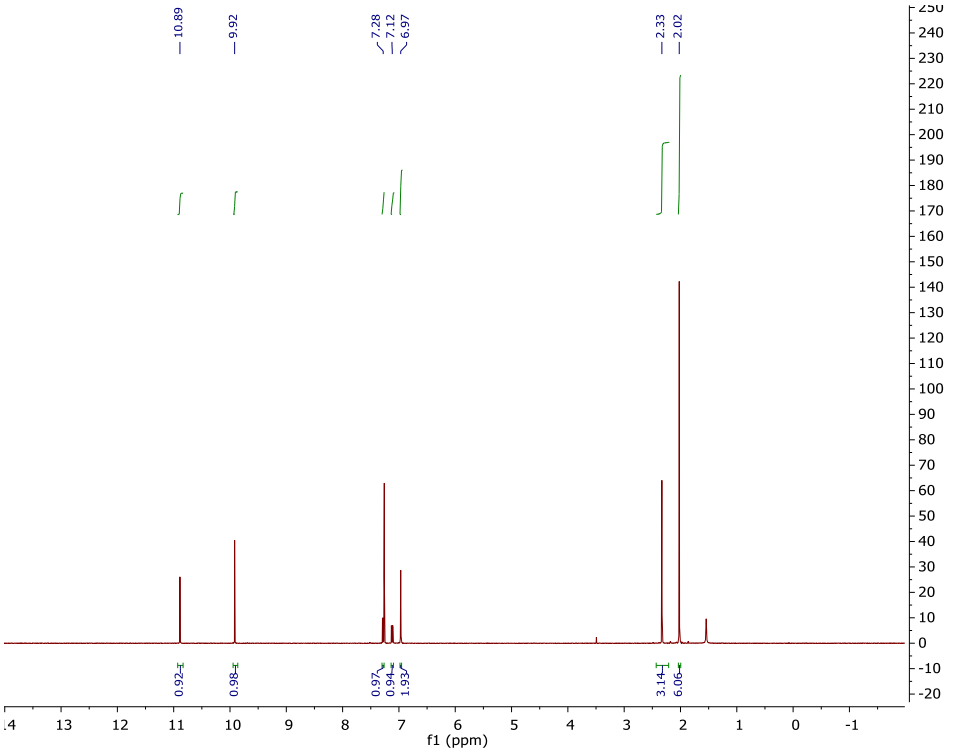
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$)



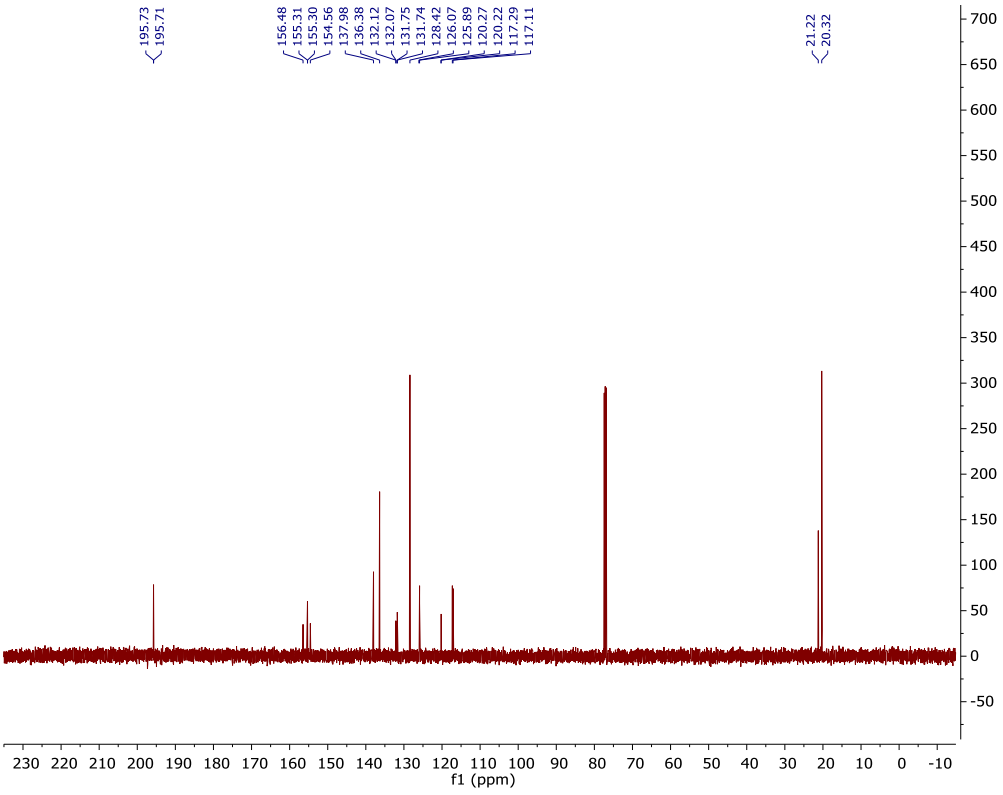
^{19}F NMR spectrum (376 MHz, $CDCl_3$, ref. C_6F_6)



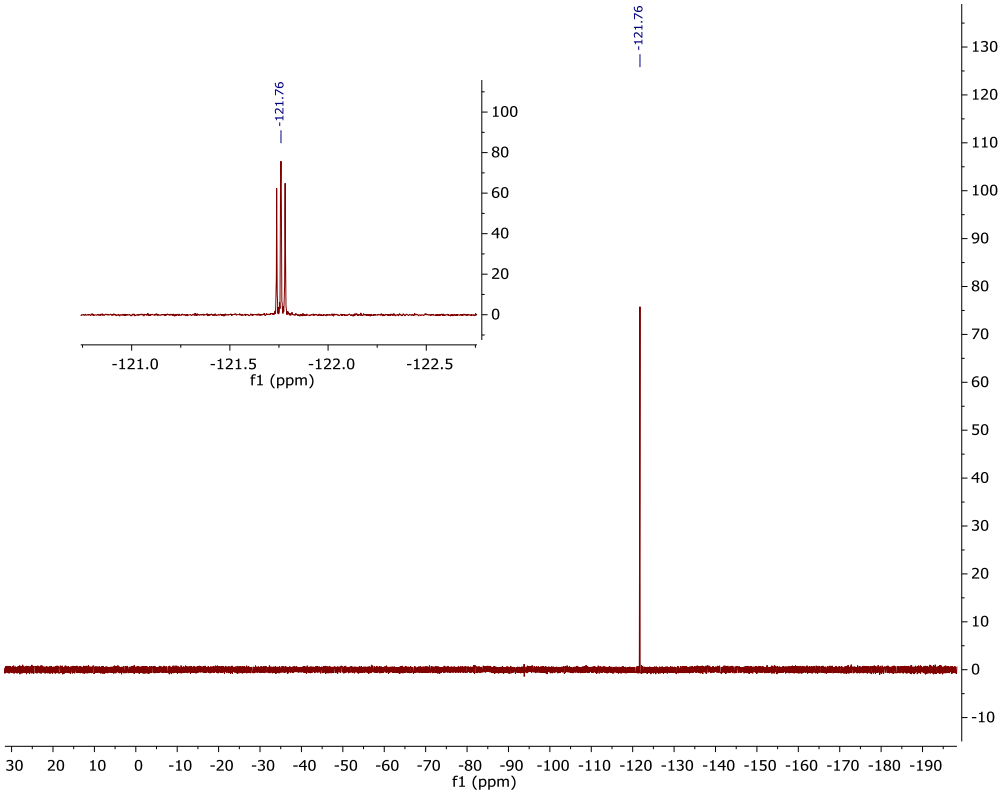
2-Hydroxy-5-fluoro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM5), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



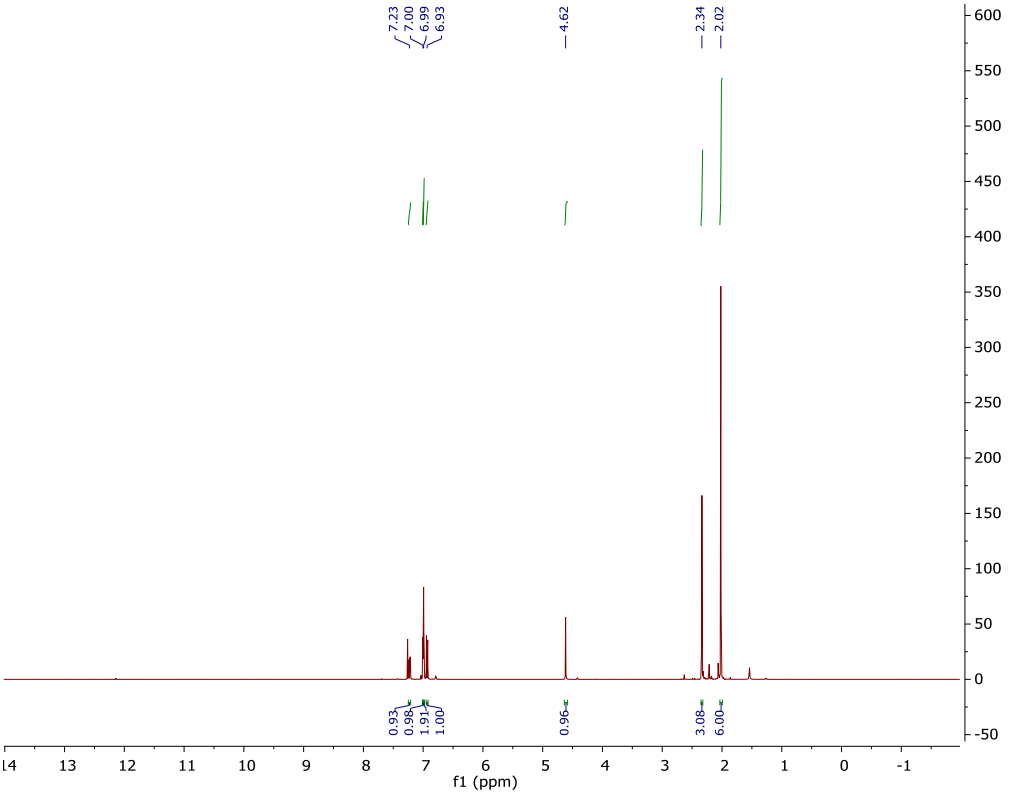
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$)



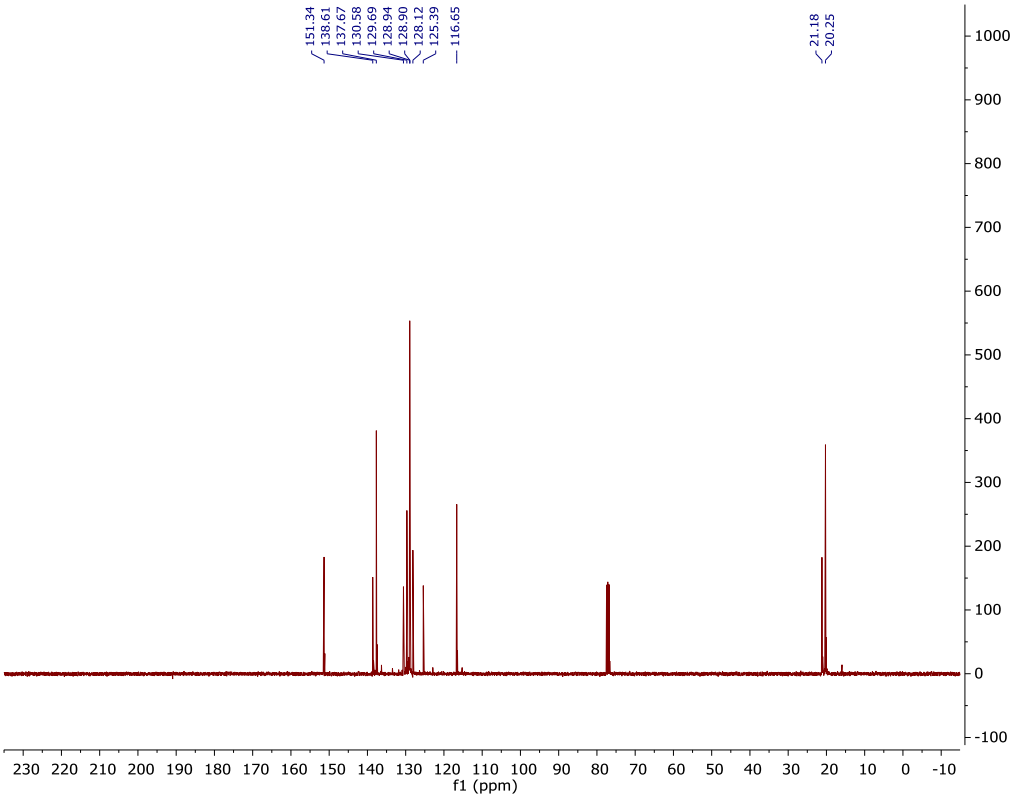
^{19}F NMR spectrum (376 MHz, $CDCl_3$, ref. C_6F_6)



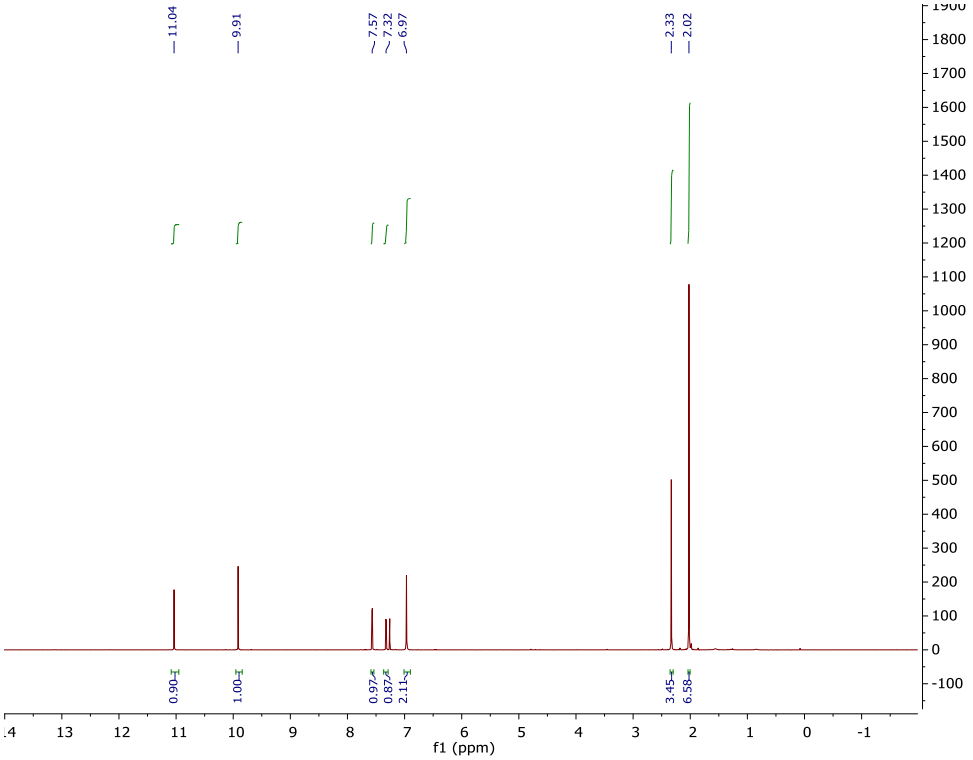
5-Chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol (SM6), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



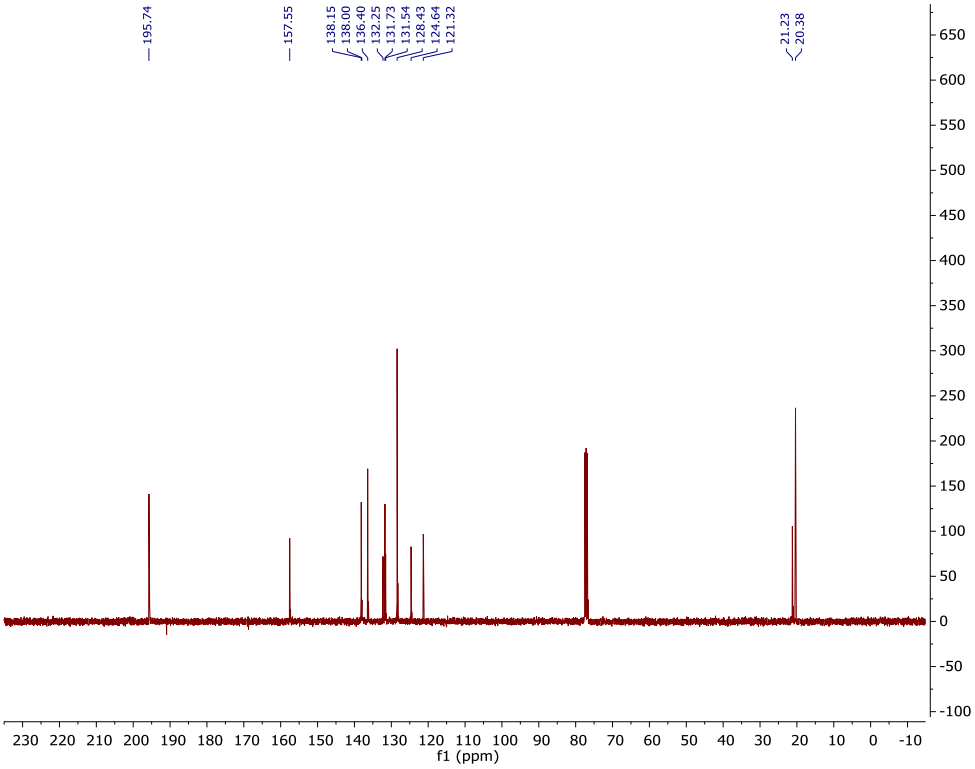
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



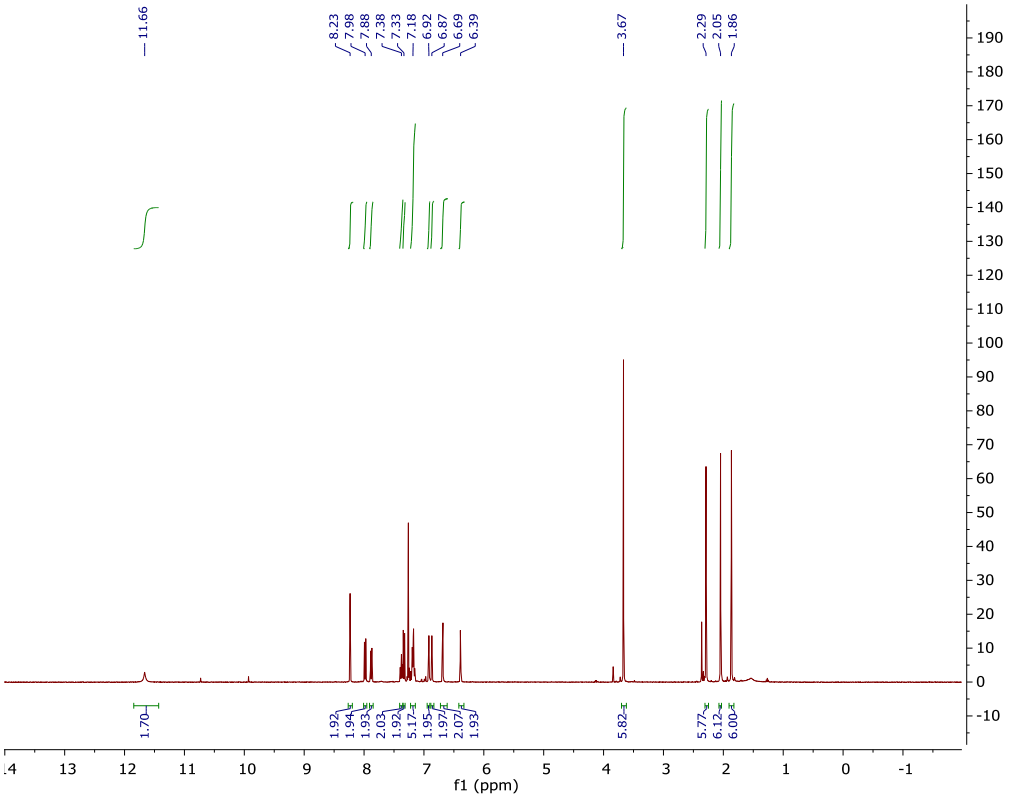
2-Hydroxy-5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM7), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



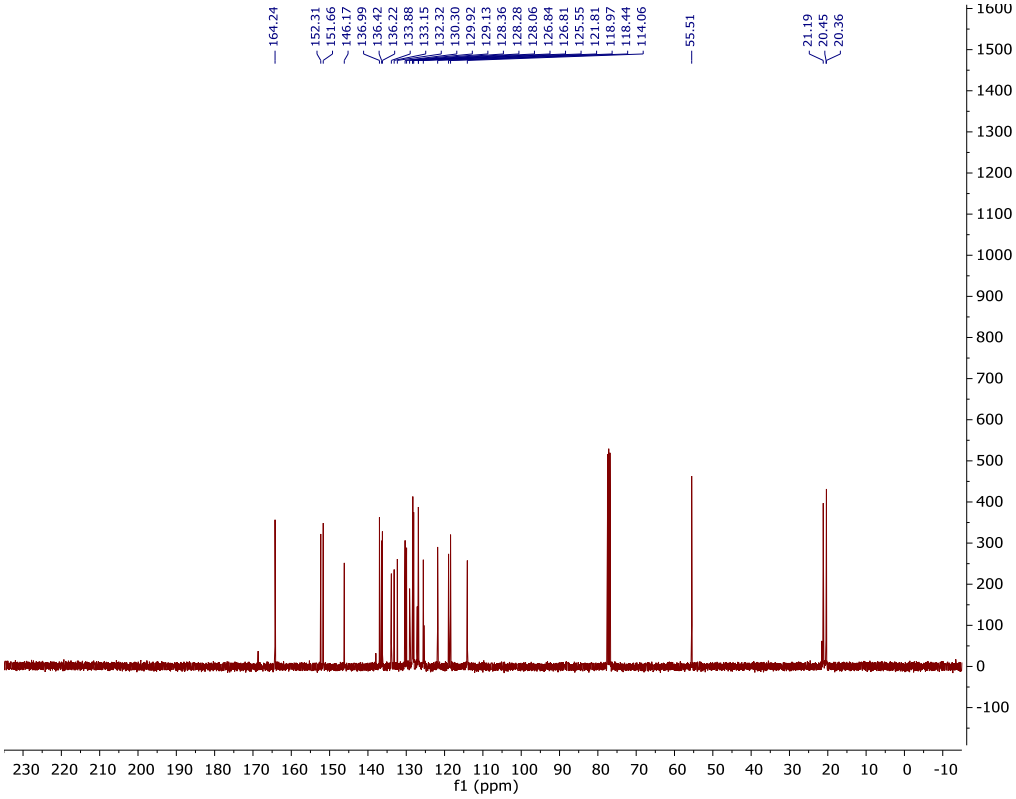
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



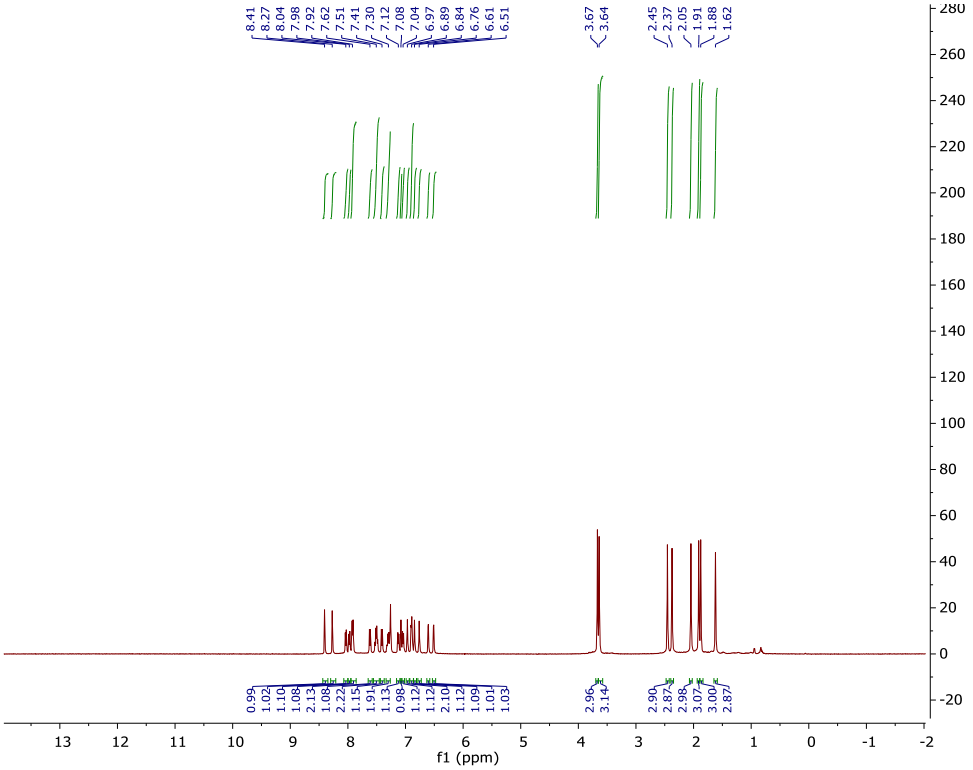
(*R*)-*p*OMeMesBinam ((*R*)-L1), ^{1}H NMR spectrum (400 HMz, $CDCl_3$)



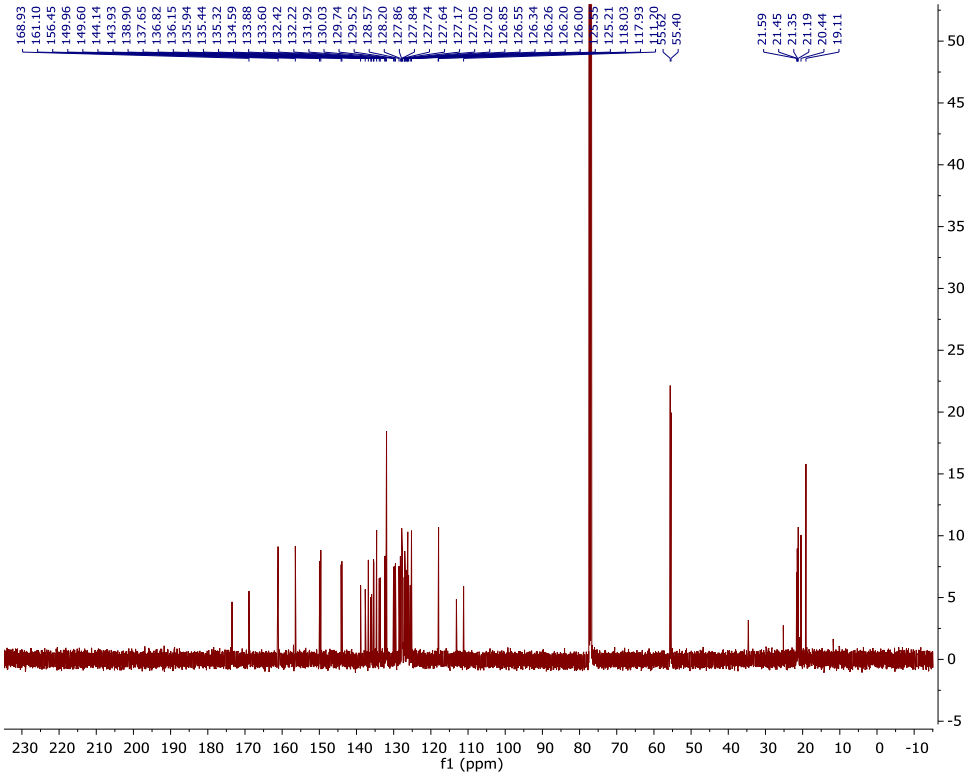
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



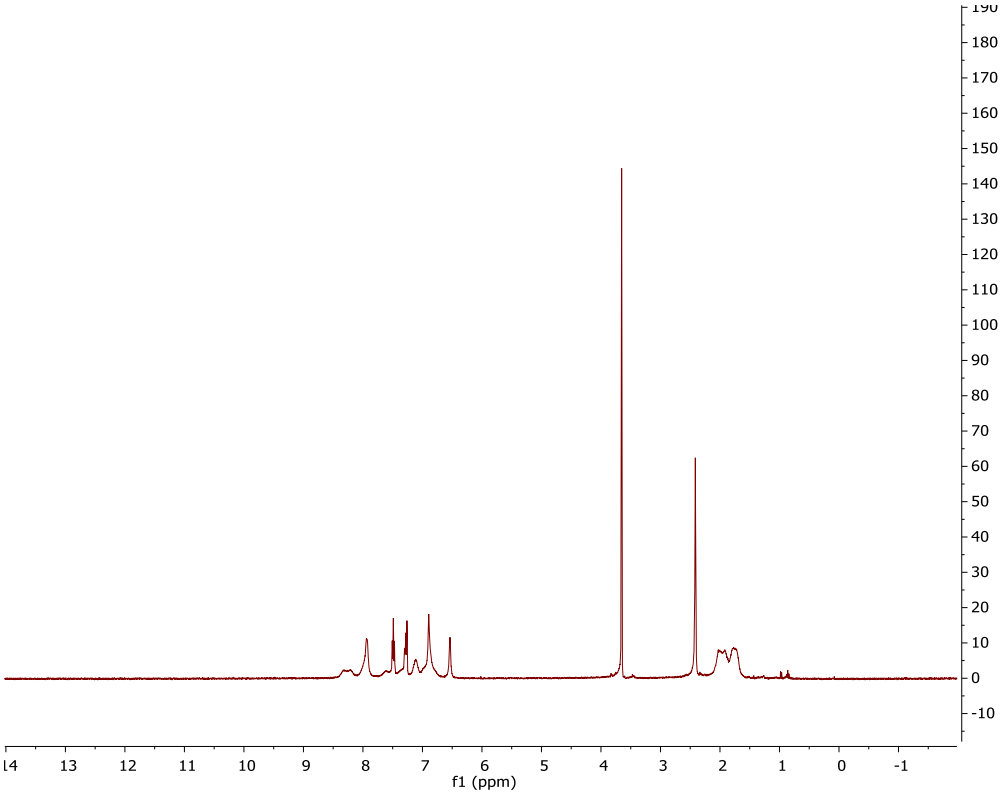
(*R*)-*p*OMeMesBinamAlCl ((*R*)-ML1, precursor to (*R*)-1d), ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −55 °C)



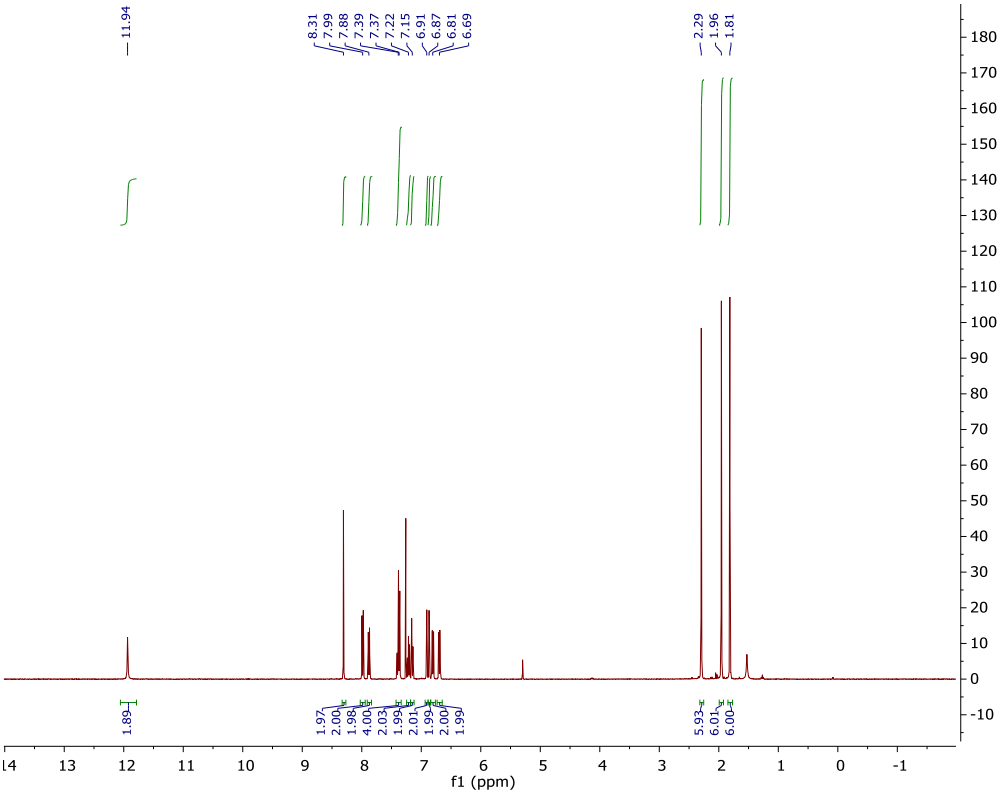
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$, −55 °C)



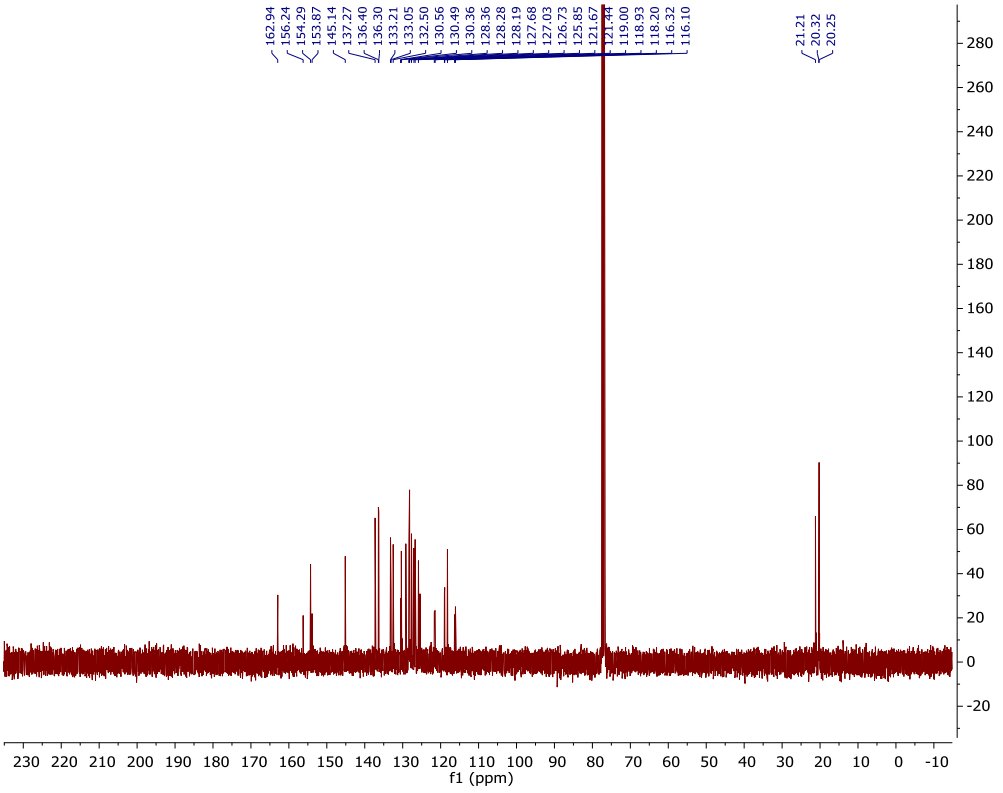
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 22 °C)



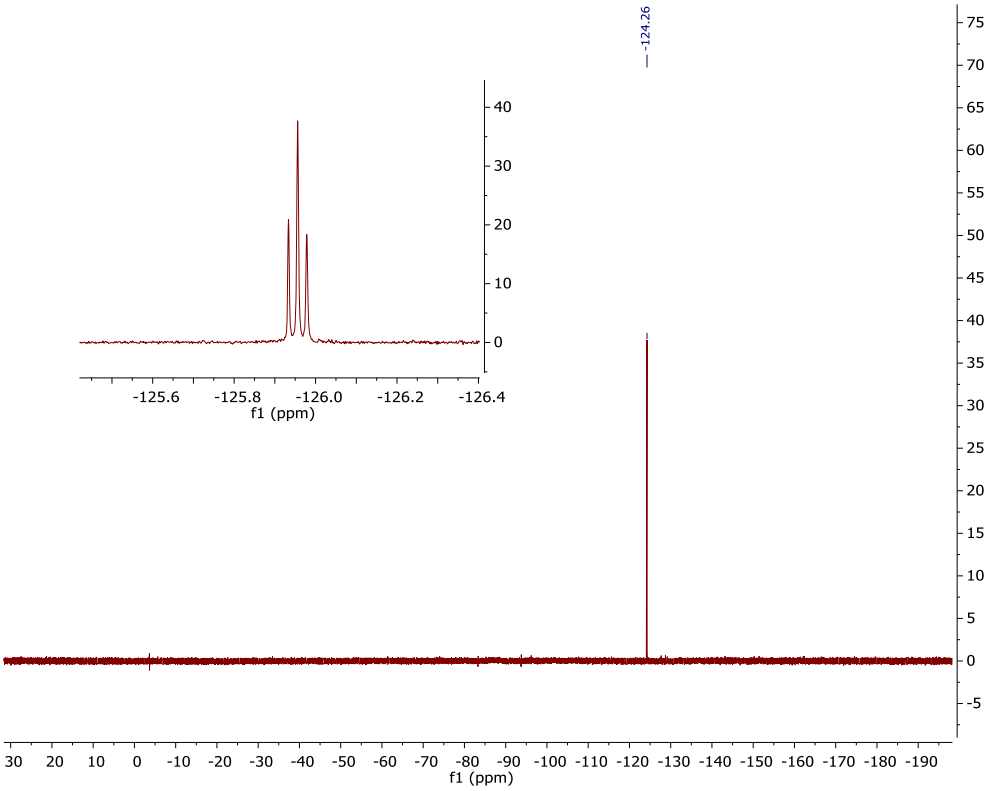
(*R*)-*p*FMesBinam ((*R*)-L2), ^{1}H NMR spectrum (400 HMz, $CDCl_3$)



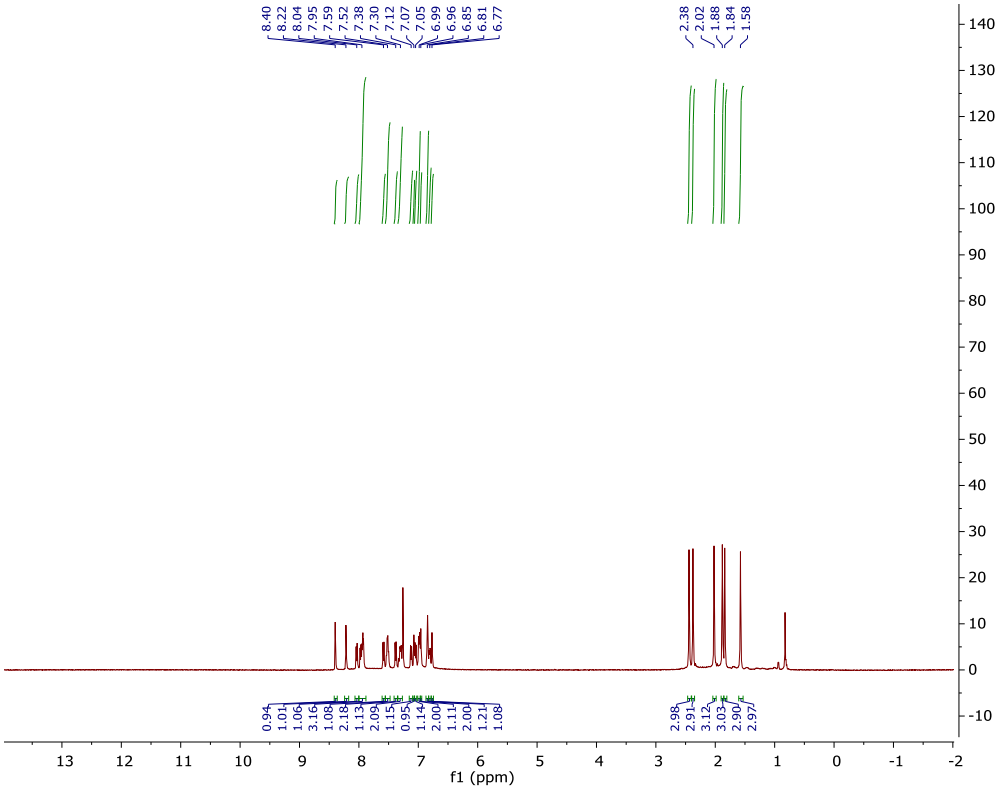
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$)



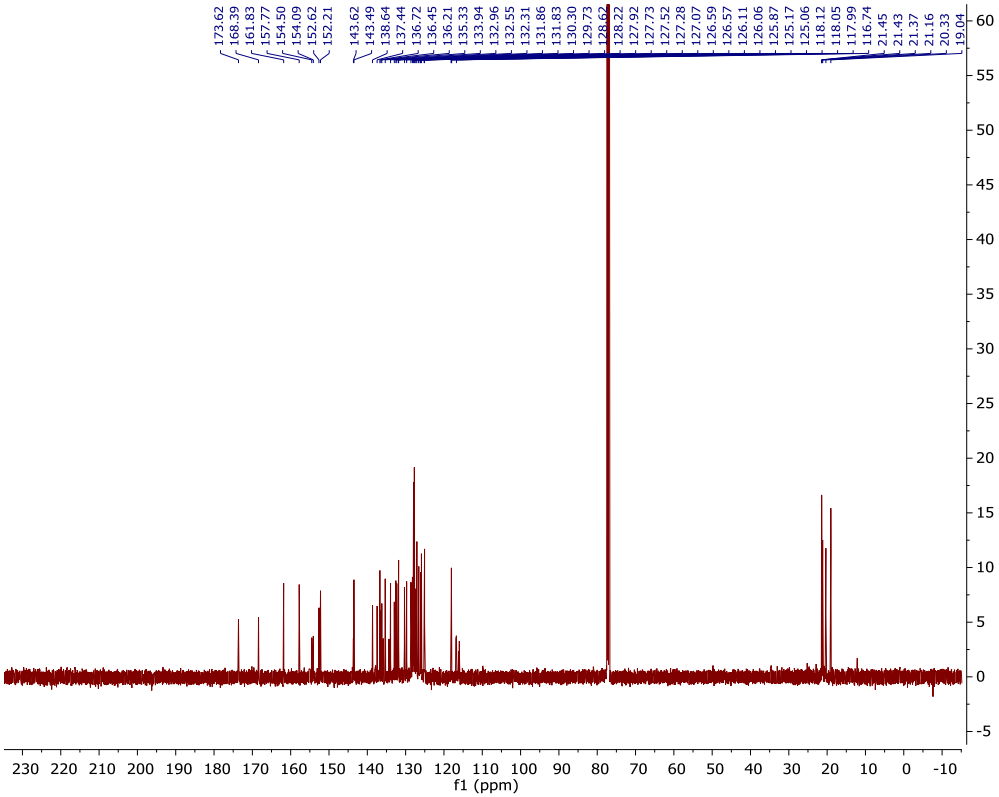
^{19}F NMR spectrum (376 MHz, $CDCl_3$, ref. C_6F_6)



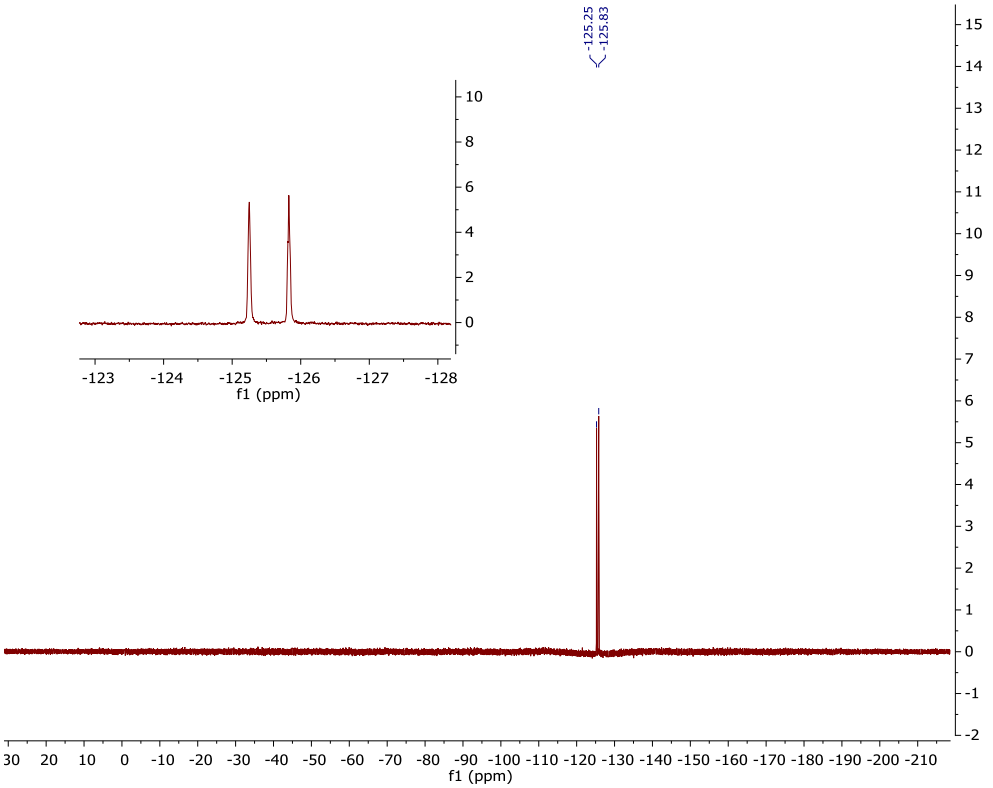
(*R*)-*p*FMesBinamAlCl ((*R*)-ML2, precursor to (*R*)-1e), ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −55 °C)



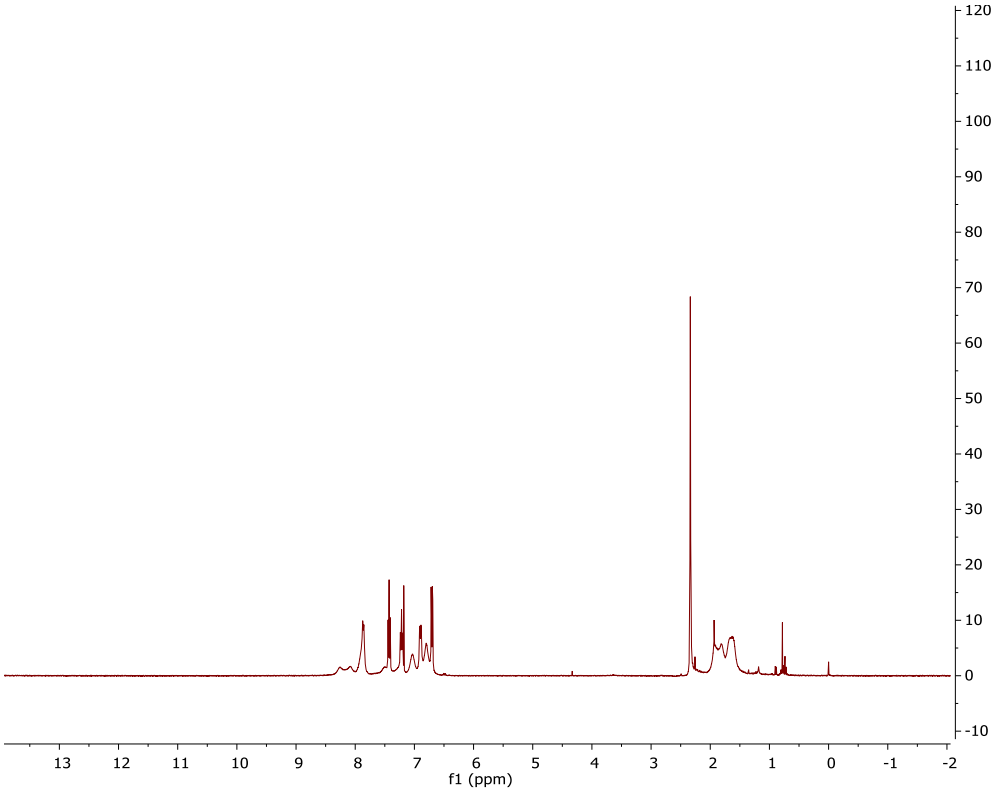
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$, −55 °C)



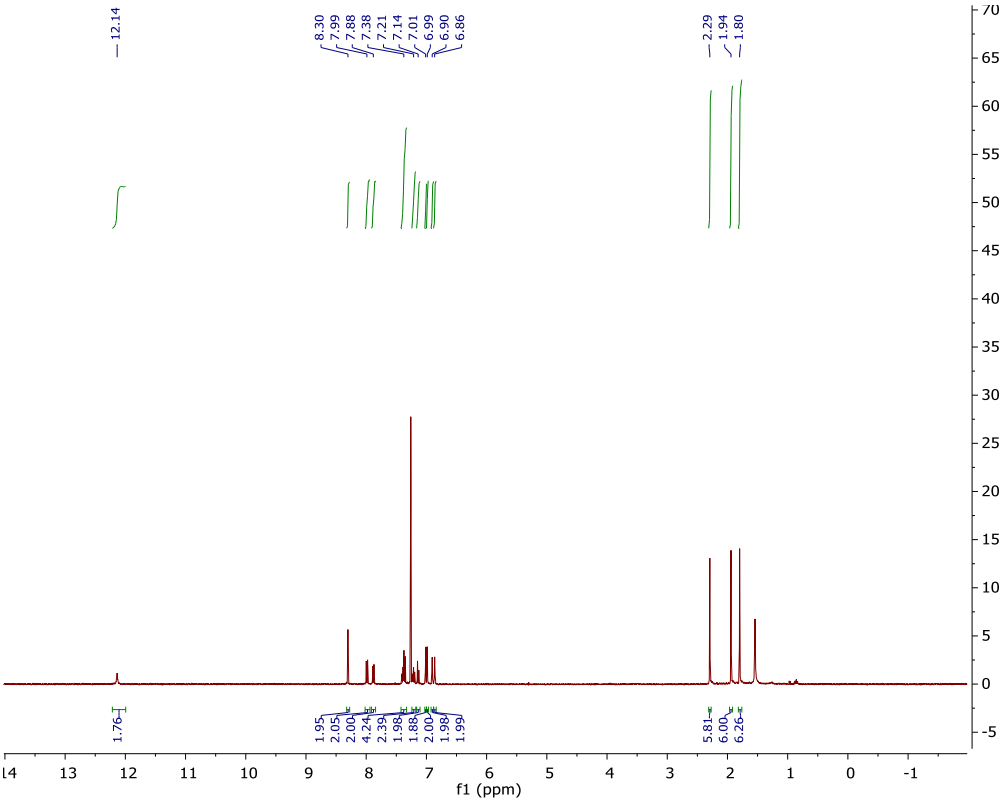
^{19}F NMR spectrum (470 MHz, $CDCl_3$, −55 °C, ref. C_6F_6)



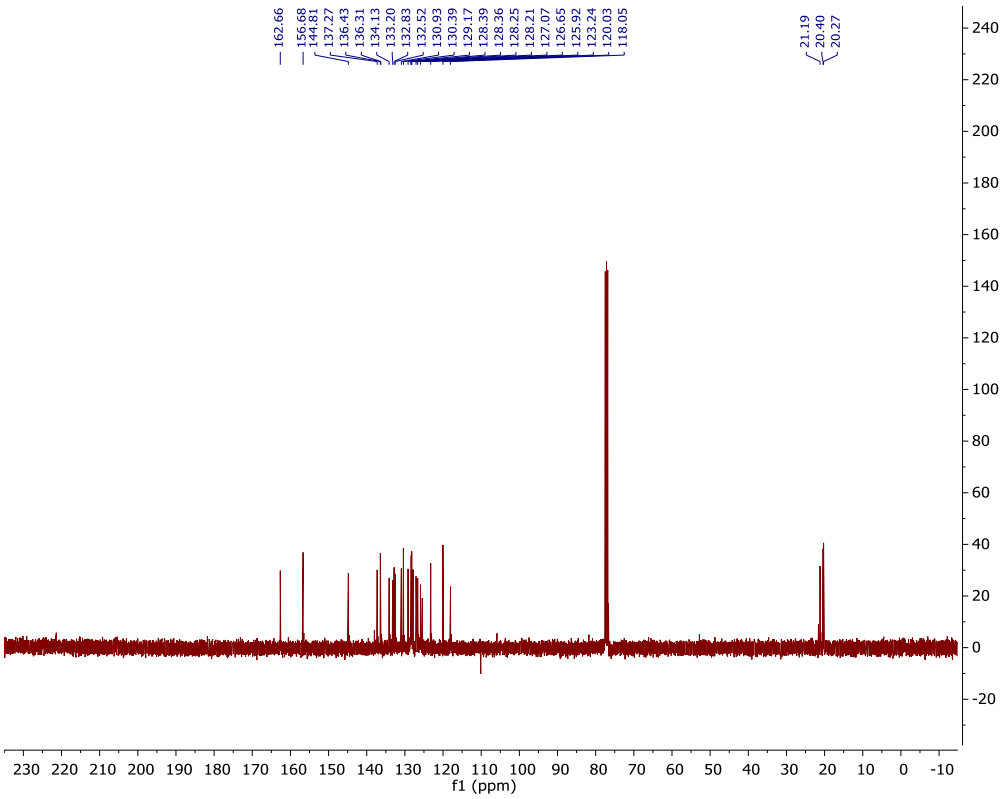
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 22 °C)



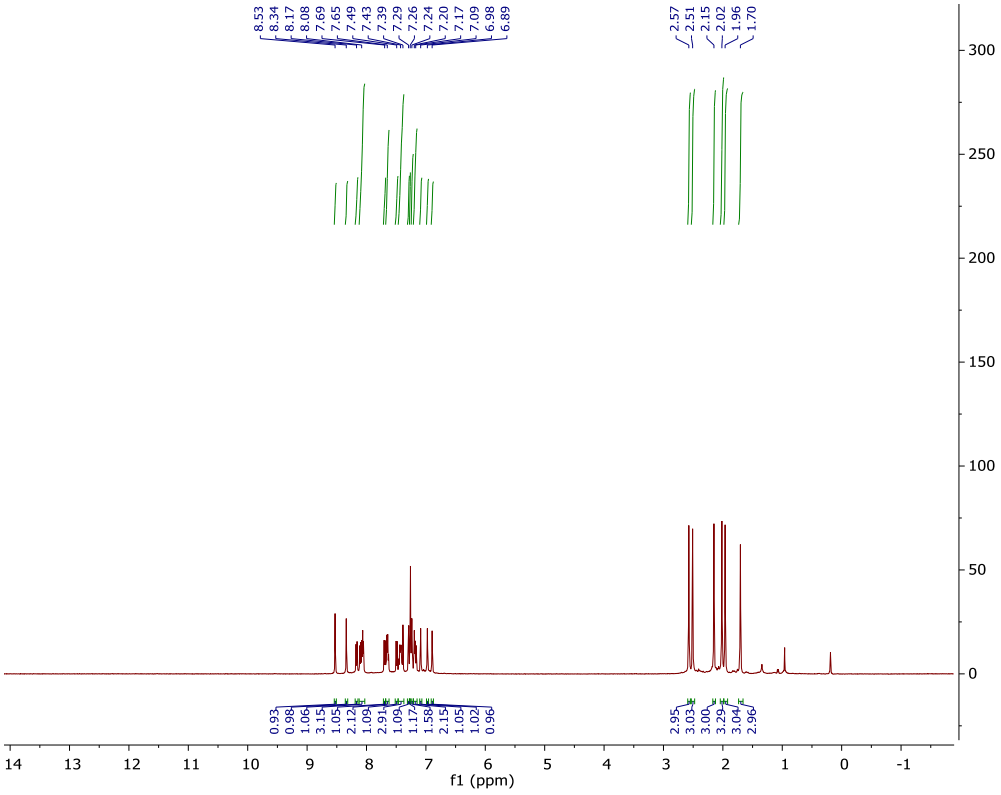
(*R*)-*p*ClMesBinam (*R*)-L3), ^{1}H NMR spectrum (400 HMz, $CDCl_3$)



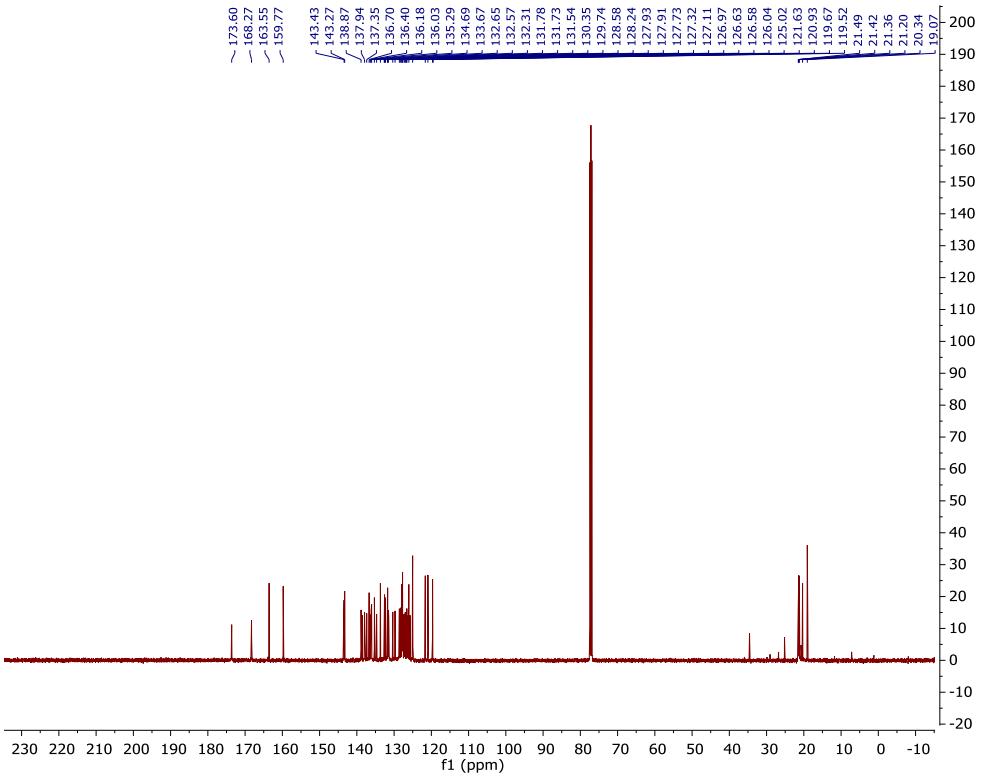
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$)



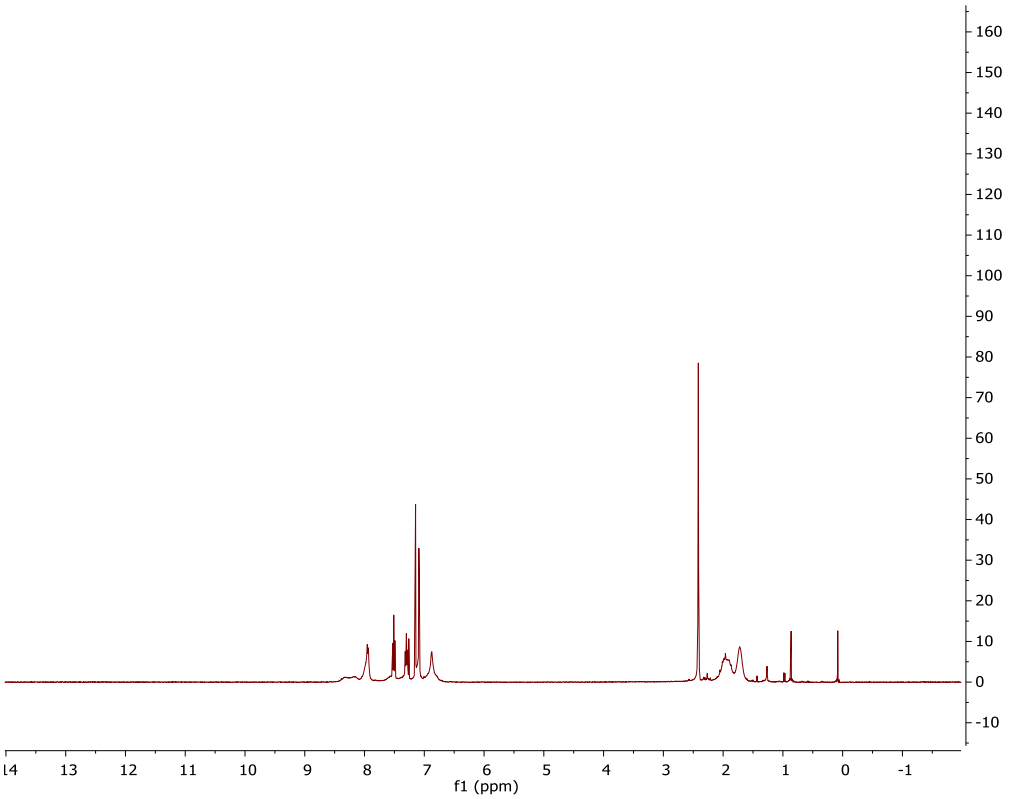
(*R*)-*p*ClMesBinamAlCl ((*R*)-ML3, precursor to (*R*)-1f), ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −55 °C)



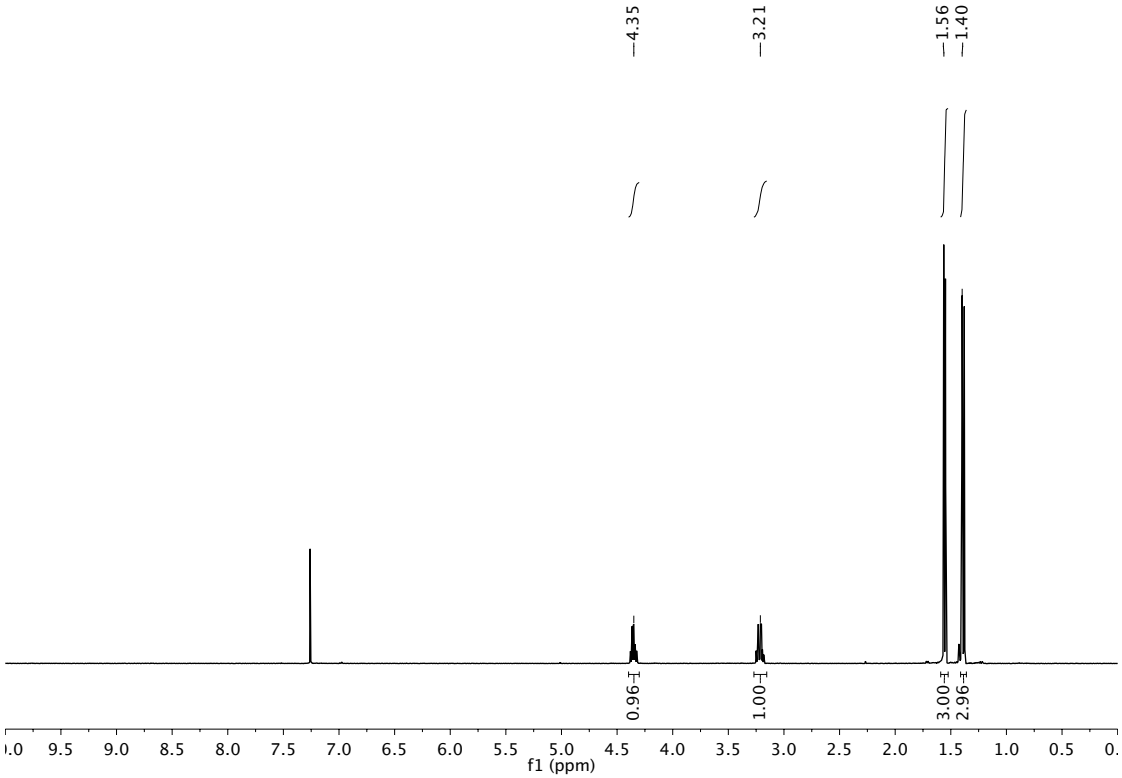
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$, −55 °C)



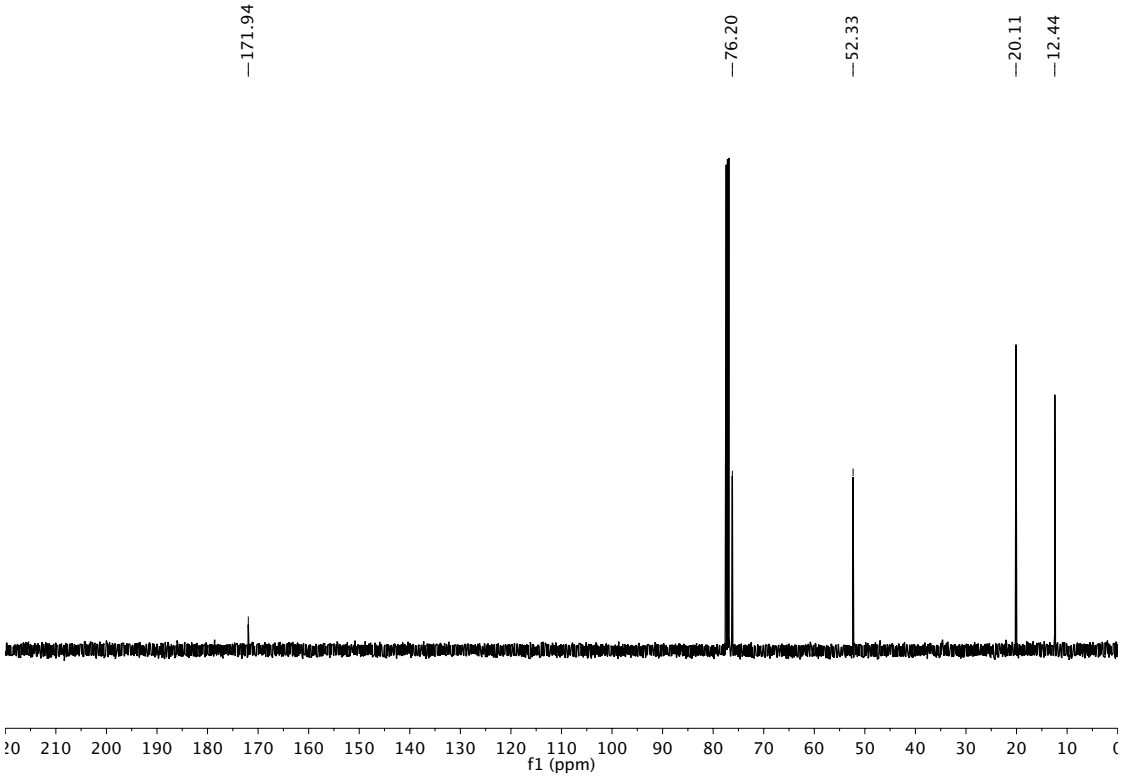
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 22 °C)



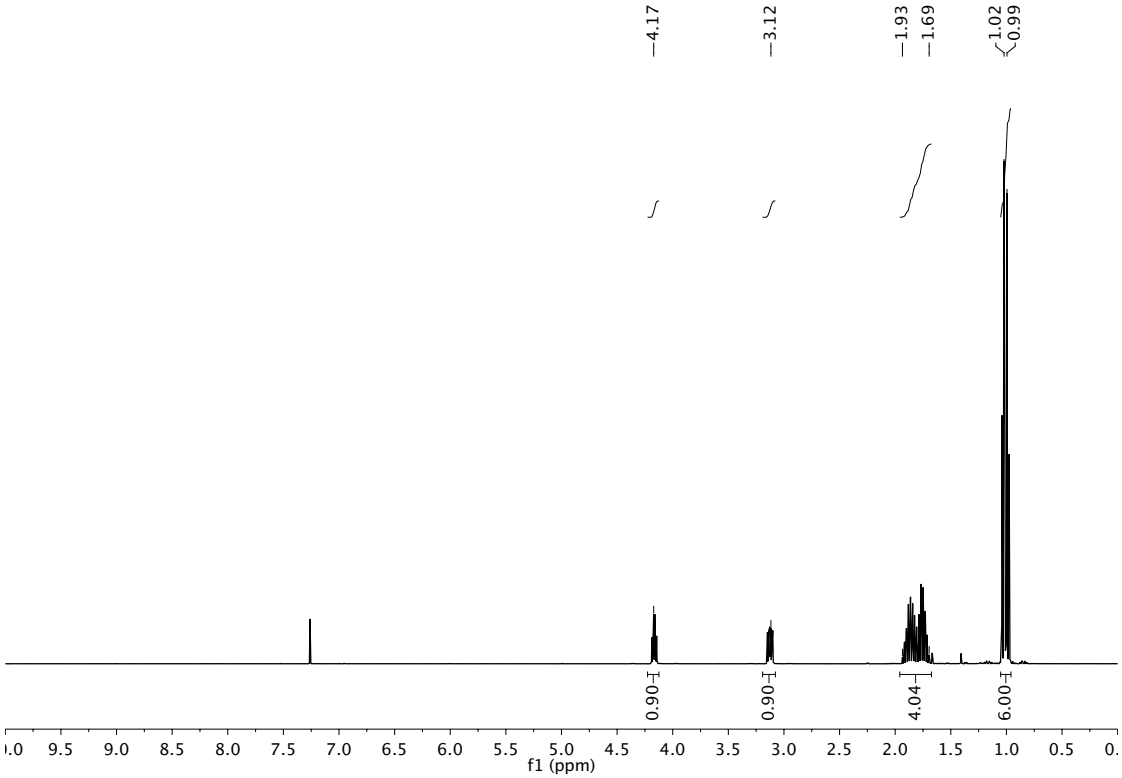
(3*R*,4*R*)-3,4-Dimethyloxetan-2-one (4b), **^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



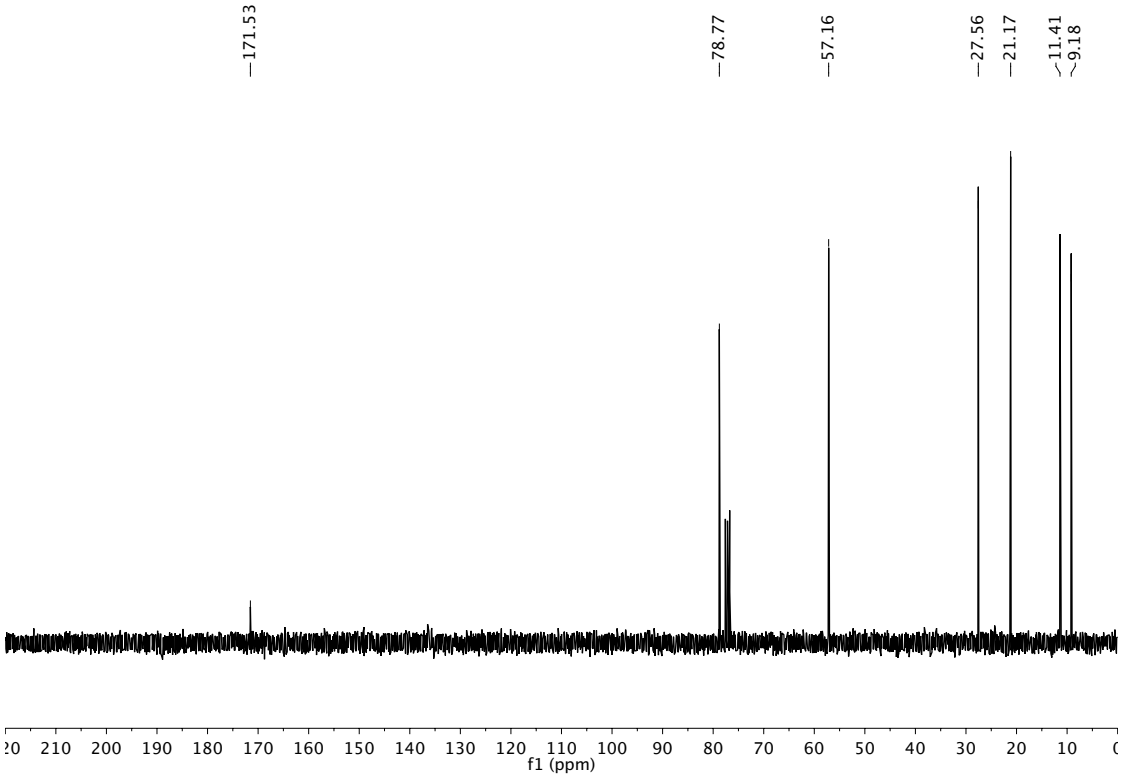
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$)



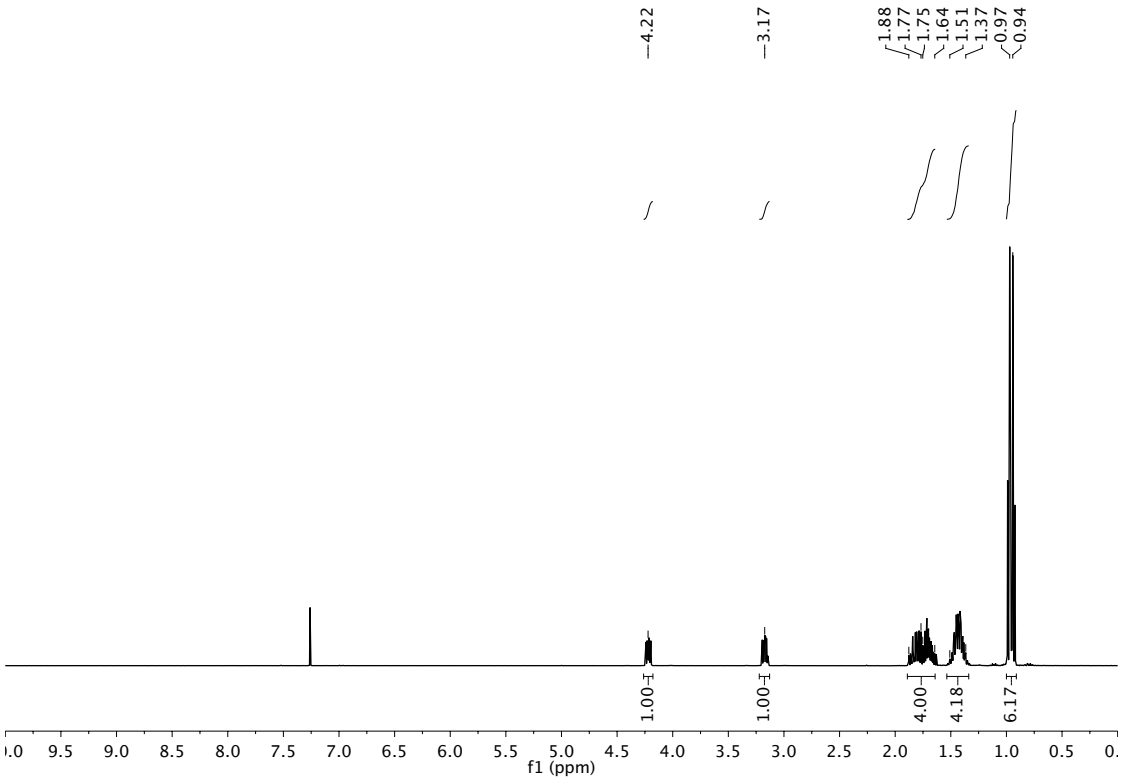
(3*R*,4*R*)-3,4-Diethyloxetan-2-one (4c), **^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



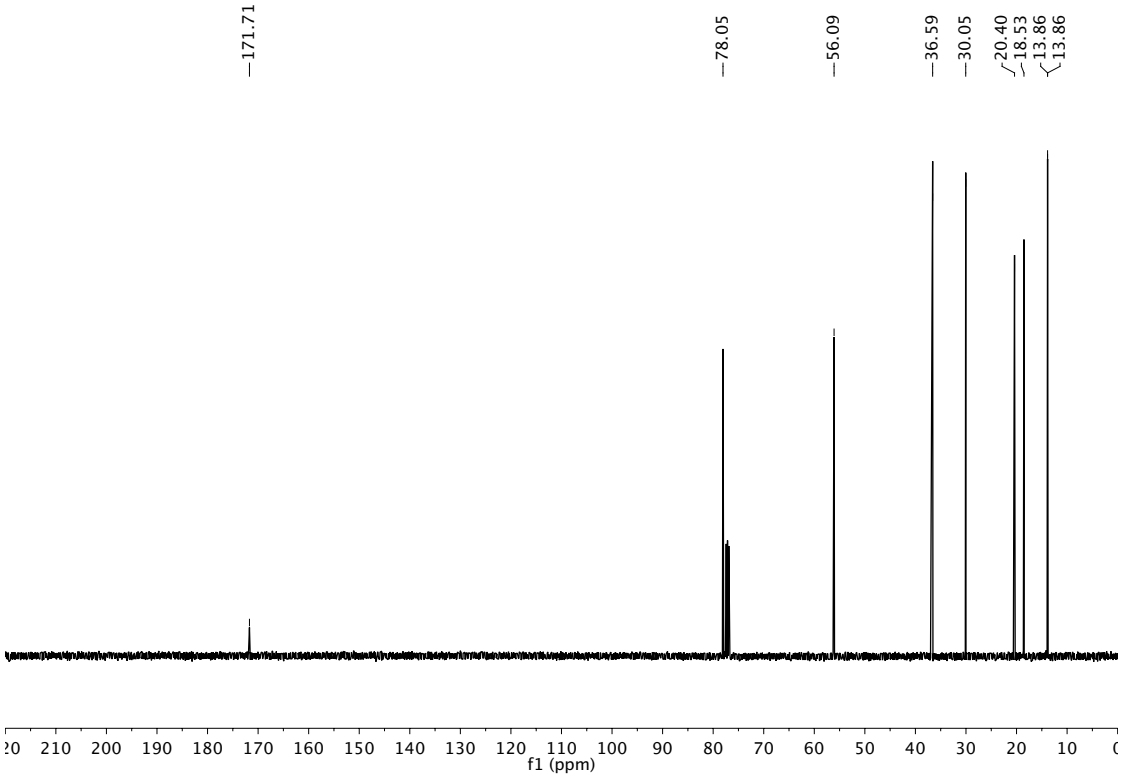
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$)



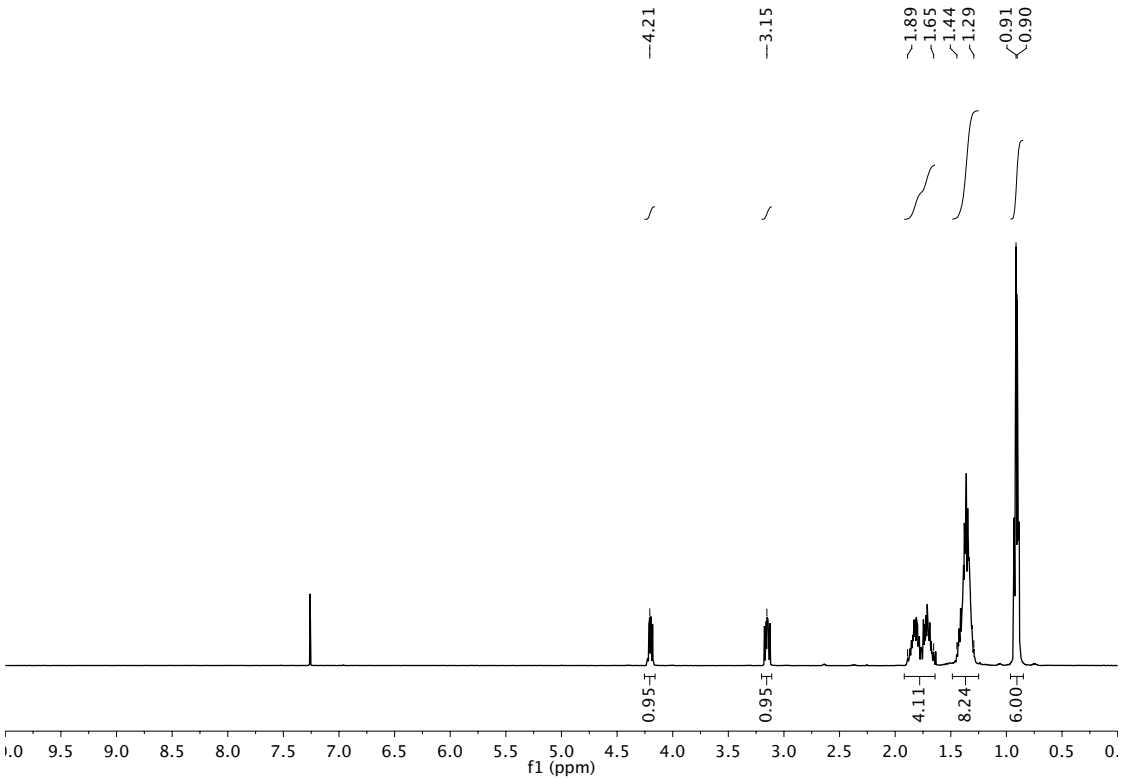
(3*R*,4*R*)-3,4-Dipropyloxetan-2-one (4a), **^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



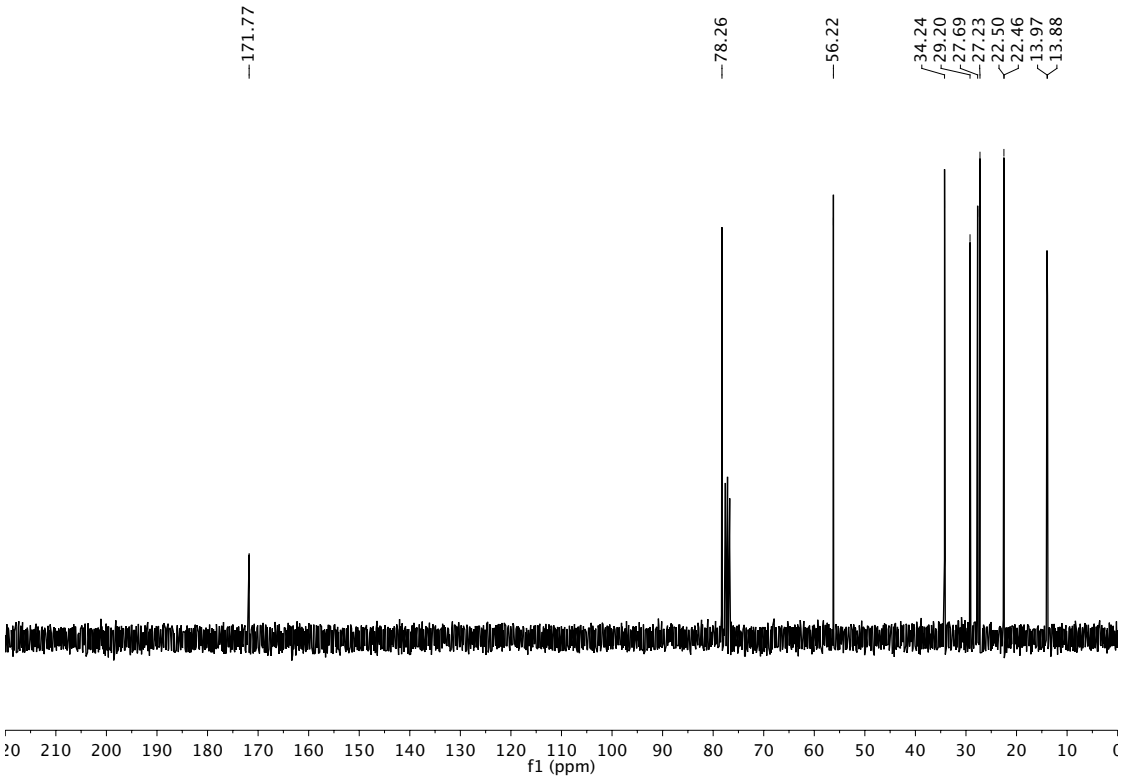
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$)



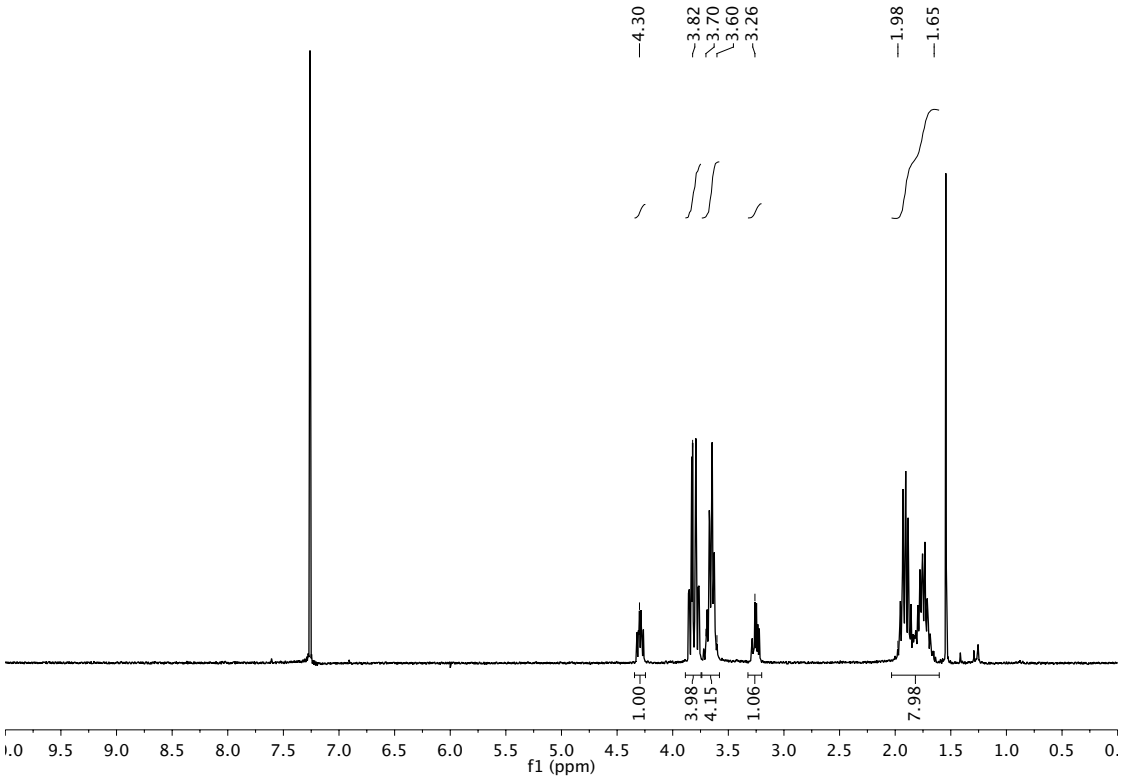
(3*R*,4*R*)-3,4-Dibutyloxetan-2-one (4d), **^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



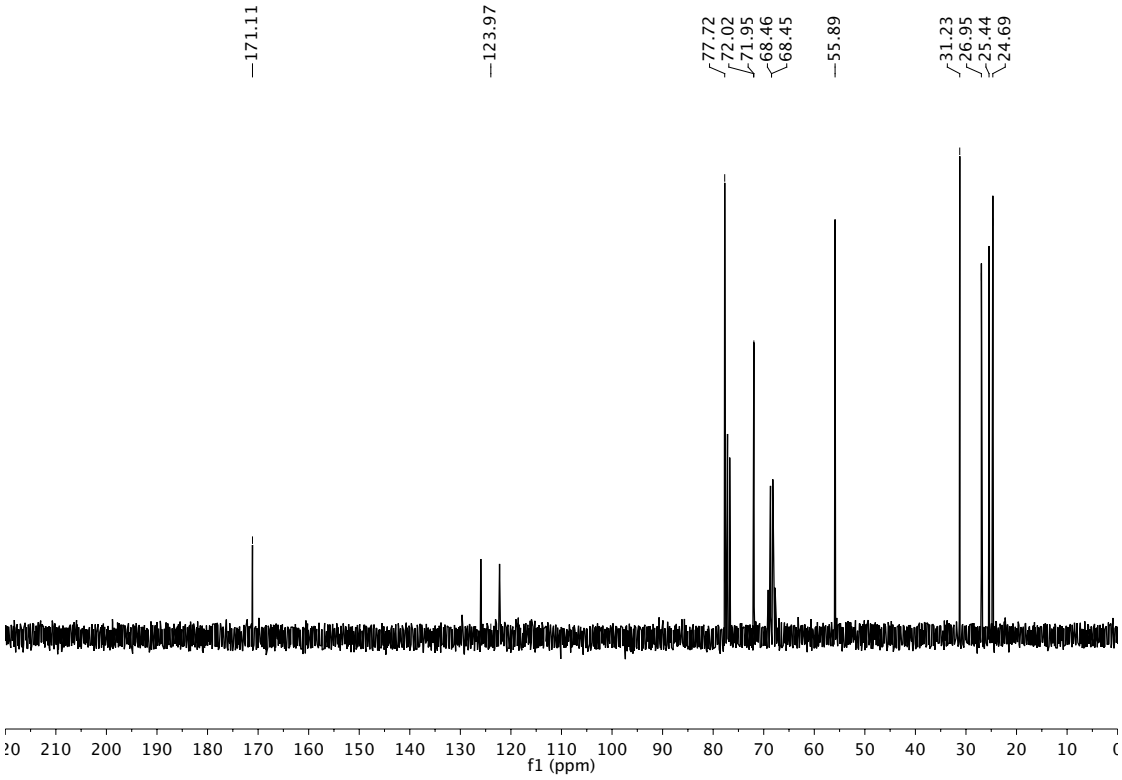
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$)



(3*R*,4*R*)-3,4-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxetan-2-one (4e), **^{1}H NMR spectrum** (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$)



^{19}F NMR spectrum (376 MHz, $CDCl_3$)