Ligand-controlled diastereodivergent, enantio- and regioselective copper-catalyzed hydroxyalkylboration of 1,3-dienes with ketones

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Electronic Supplementary Information

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1 General Information

All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. All metal salts were purchased from commercial suppliers and used as received. All solvents were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (*tert*-butyl methyl ether, cyclohexane, CH_2Cl_2, ethyl acetate, and *n*-pentane) were distilled prior to use. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on Bruker AV 400, Bruker AV 500 and Bruker AV 700 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetra-methylsilane and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.0 ppm for ^{13}C NMR, $CHDCl_2$: δ = 5.32 ppm for ^{1}H NMR and CD_2Cl_2: δ = 53.84 ppm for ^{13}C NMR). ^{11}B, and ^{19}F NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.[1] Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a Schmidt & Haensch Polatronic H532 polarimeter with $[\alpha]_\lambda$ values reported in 10^{-1} (° cm^2 g^{-1}); concentration *c* is in g/100 mL and λ as indicated. Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an *Agilent Technologies* 1290 Infinity instrument with a chiral stationary phase using *Daicel* Chiralcel columns. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

Ligands: L18,[2] **L19**,[3] and phosphoramidite ligands[4] **L1** and **L21**–**26** were prepared according to literature procedures. Other ligands were directly purchased from Alfa Aesar, Sigma Aldrich, Solvias, TCI, and Strem. Solvias AG is acknowledged for a generous gift of Josiphos ligands used in this work.

Dienes: 2a and **2c** were purchased from Acros; **2b** was purchased from TCI and used as a toluene solution (15 %); **2d**[5a] and **2f**[5b] were prepared according to the literature; **2f** was purchased from AlfaAesar.

Ketones: Commercially available ketones were purchased from Alfa Aesar, Sigma Aldrich, ABCR, TCI and were used as received.

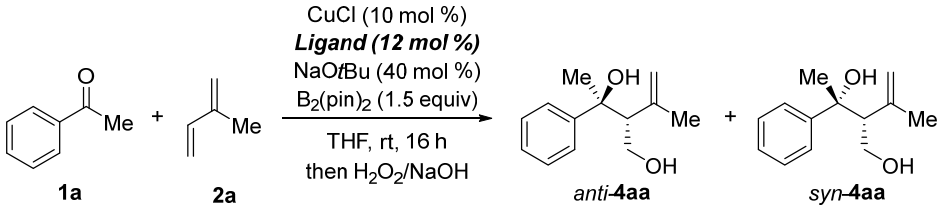
Racemic products: *rac*-**L1** was employed to prepare corresponding racemates of **4ad**, **4ae**, **4af**, and **4nc**; *rac*-BINAP or Ph_3P were employed to prepare other racemates.

2 Optimization Study

General procedure for the optimization reactions:

In a nitrogen-filled glovebox, to a flame-dried Schlenk tube was added the copper salt (20 μmol, 10 mol%), the ligand (24 μmol, 12 mol%), and the base (80 μmol, 40 mol%). The tube was taken out of the glovebox, evacuated, and backfilled with N_2 (3 times) followed by the addition of the solvent (1.0 mL). After stirring for 30 min at room temperature, $B_2(pin)_2$ (78 mg, 0.30 mmol, 1.5 equiv.) in THF (1.0 mL) was added. After stirring at room temperature for about 1 min, it was cooled to indicated reaction temperature, isoprene **2a** (100 μL, 1.0 mmol, 5.0 equiv.) was added via syringe, followed by acetophenone (**1a**, 24 mg, 0.20 mmol, 1.0 equiv.). After the indicated reaction time, the reaction was quenched by 0.3 mL saturated ammonium chloride water solution. To the mixture was then added 1.0 mL THF, 3 M NaOH (0.6 mL), and 30% H_2O_2 (0.6 mL) at 0 °C. After stirring at 0 °C for 30 min, brine (10 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. It was then analyzed by ^1H NMR spectroscopy to obtain the NMR yield and diastereoselectivity with CH_2Br_2 as an internal standard. The residue was purified by column chromatography on silica gel (5:1 to 3:1 *n*-pentane/EtOAc) to afford the target compound. The enantiomeric exess was determined by HPLC analysis on a chiral stationary phase.

Table S1. Screening of chiral ligands for enantioselective copper-catalyzed borylative coupling of 1,3-diene and ketone [a]



1a **2a** *anti*-**4aa** *syn*-**4aa**

Entry	Ligand	Conversion [%][b]	Yield [%][b]	d.r. (*anti*:*syn*)[c]	*ee* [%][d]	
					anti-**4aa**	*syn*-**4aa**
1	**L1**	100	53	**71**:29	60	21
2	**L2**	100	75	42:58	43	32[e]
3	**L3**	100	92	35:65	6	35
4	**L4**	100	93	28:72	35[e]	32[e]
5	**L5**	100	84	44:56	13	22
6	**L6**	89	45	23:**77**	22[e]	61
7	**L7**	100	98	23:**77**	13[e]	80
8	**L8**	91	80	22:**78**	72[e]	88
9	**L9**	100	98	23:**77**	74[e]	88
10	**L10**	100	65	28:72	71[e]	87
11[f]	**L11**	80	37	47:53	0	37
12	**L12**	60	29	49:51	—	—
13	**L13**	100	98	25:75	32[e]	64
14	**L14**	100	98	29:71	0	44
15	**L15**	100	83	60:40	38	12[e]
16	**L16**	100	81	58:42	44[e]	26[e]
17	**L17**	100	36	50:50	0	0
18[g]	**L18**	100	98	40:60	8[e]	4
19	**L19**	100	41	61:39	0	0
20	**L20**	67	39	33:67	0	0

[a] All reactions were performed on a 0.20 mmol scale. [b] Determined by ^{1}H NMR

spectrocopy with CH_2Br_2 as an internal standard. [c] Determined by ^1H NMR spectroscopy. [d] Determined by HPLC analysis on a chiral stationary phase. [e] The other enantiomer was obtained. [f] RT, 49 h. [g] 10 mol% **L18**·CuCl was used.

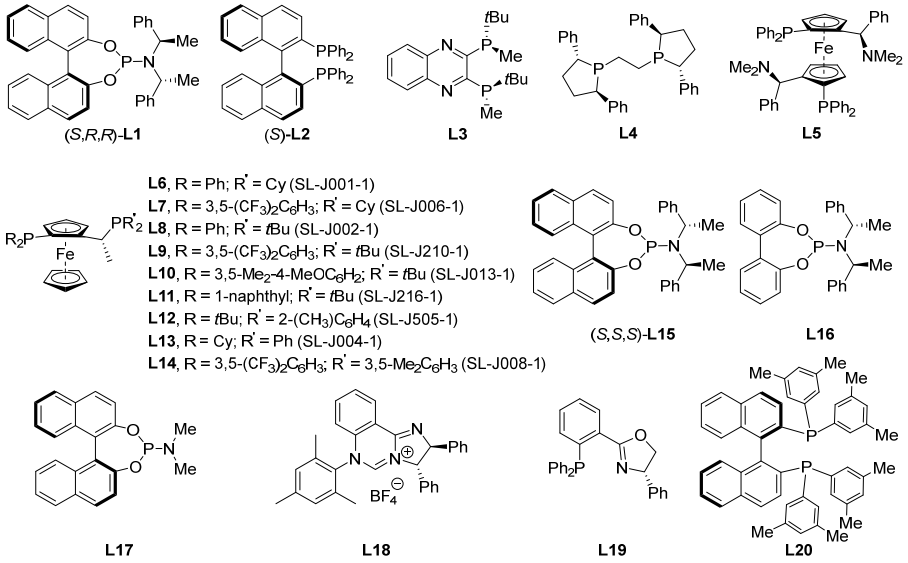
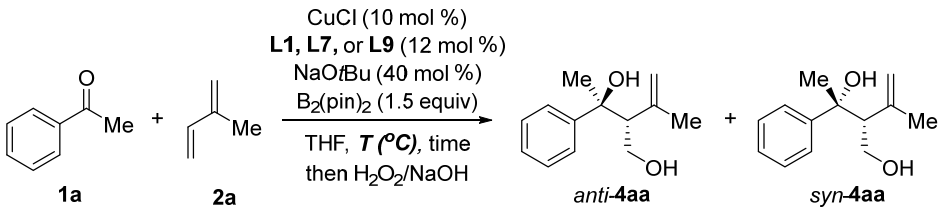


Table S2. Examining the effect of temperature on the borylative coupling of 1,3-diene and ketone [a]

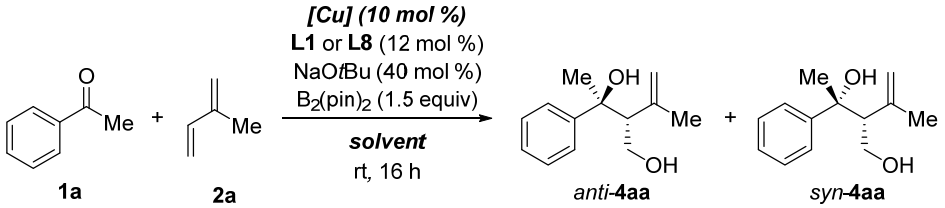


Ligand	Temperature [°C]	Time [h]	Yield [%][b]	dr (*anti*:*syn*)[c]	*ee* [%][d]	
					anti-**4aa**	*syn*-**4aa**
L1	25	16	53	71:29	60	21
L1	–15	64	85	71:29	77	41
L1	–30	71	98	76:24	86	52
L7	25	16	98	23:77	13[e]	80
L7	–15	17	98	11:89	22[e]	86
L7	–30	71	84	21:79	23[e]	84
L9	25	16	98	23:77	74[e]	88
L9	0	15	97	18:82	79[e]	92

L9	–10	18	91	16:84	79[e]	93
L9	–20	23	61	15:85	79[e]	94
L9	–30	34	99	15:85	79[e]	94
L9[f]	–20	37	85	20:80	75[e]	93
L9[g]	–20	45	98	13:87	71[e]	93

[a] All reactions were performed on a 0.20 mmol scale. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis on a chiral stationary phase. [e] The other enantiomer was obtained. [f] 0.4 mmol scale, CuCl (5 mol%) and **L9** (6 mol%) were used. [g] 0.4 mmol scale, CuOAc (5 mol%), **L9** (6 mol%) and toluene/THF (8:2) were used.

Table S3. Screening of copper catalysts and solvents in the borylative coupling of 1,3-diene and ketone [a]

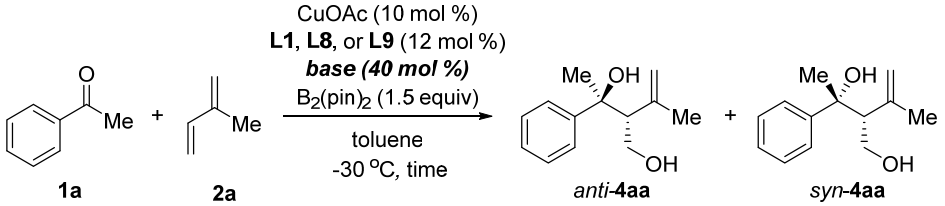


1a **2a** *anti*-**4aa** *syn*-**4aa**

Ligand	Copper catalyst	solvents	Yield [%][b]	dr (*anti*:*anti*)[c]	*ee* [%][d]	
					anti-**4aa**	*syn*-**4aa**
L1	CuCl	THF	53	71:29	60	21
L1	CuOAc	THF	88	66:34	64	10
L1	$(CuOTf)_2{\cdot}C_6H_6$ [e]	THF	92	66:34	61	23
L1	$Cu(CH_3CN)_4PF_6$	THF	93	66:34	59	21
L1	CuCl	*t*BuOMe	83	70:30	67	24
L1	CuCl	Toluene	98	71:29	67	24
L1	CuOAc	Toluene	96	68:32	68	30
L8	CuCl	THF	80	22:78	72[f]	88
L8	CuCl	*t*BuOMe	97	30:70	63[f]	85
L8	CuCl	Toluene	80	29:71	69[f]	88

[a] All reactions were performed on a 0.2 mmol scale. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis on a chiral stationary phase. [e] 5 mol% $(CuOTf)_2{\cdot}C_6H_6$ was used. [f] The other enantiomer was obtained.

Table S4. Screening of bases in the borylative coupling of 1,3-diene and ketone [a]

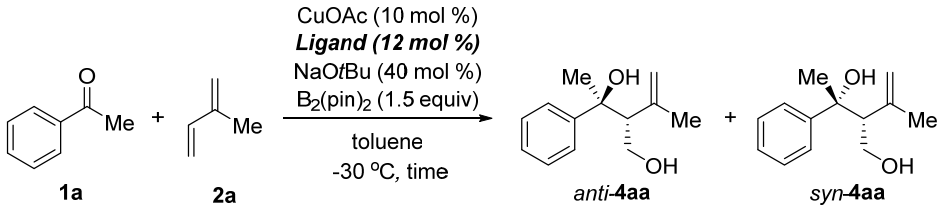


1a **2a** *anti*-**4aa** *syn*-**4aa**

Ligand	Base	time [h]	Yield [%][b]	dr (*anti*:*syn*)[c]	*ee* [%][d]	
					anti-**4aa**	*syn*-**4aa**
L1	*t*BuOK	64	82	77:23	89	63
L1	*t*BuOK[e]	64	84	82:18	89	63
L1	*t*BuONa	64	94	80:20	90	64
L1	MeOK	64	89	78:22	90	65
L8[f]	*t*BuOK	57	54	32:68	6[g]	64
L8[f]	*t*BuONa	57	65	25:75	36[g]	82
L8[f]	MeOK	57	28	19:81	64[g]	90
L8[f]	MeONa	57	44	34:66	8[g]	65
L8[f]	MeOLi	57	10	—	—	—
L9[h]	*t*BuOK	14	66	19:81	76	88
L9[h]	*t*BuONa	16	98	23:77	74	88
L9[h]	MeOK	14	68	19:81	75	89

[a] All reactions were performed on a 0.1 mmol scale. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis on a chiral stationary phase. [e] 12 mol% $NaBAr^F{}_4$ was used. [f] Run at –15 °C and THF was used instead of toluene. [g] The other enantiomer was obtained. [h] Run at rt and THF was used instead of toluene.

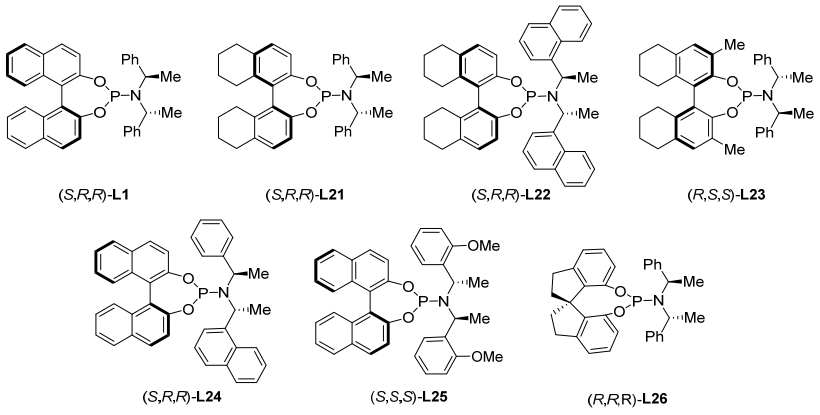
Table S5. Further examining phosphoramidite ligands for borylative coupling of 1,3-diene and ketone under optimized reaction conditions [a]



1a **2a** *anti*-**4aa** *syn*-**4aa**

Entry	Ligand	Conversion [%][b]	Yield [%][b]	dr (*anti*:*syn*)[c]	*ee* [%][d]	
					anti-**3aa**	*syn*-**3aa**
1	**L1**	100	94	80:20	90	64
2	**L21**	100	94	79:21	87	64
3	**L22**	78	70	67:33	47	5
4	**L23**	100	97	71:29	55[e]	44[e]
5	**L24**	85	81	78:22	61	37
6	**L25**	89	73	71:29	26[e]	37[e]
7	**L26**	100	98	67:33	80	58

[a] All reactions were performed on a 0.15 mmol scale. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis on a chiral stationary phase. [e] The other enantiomer was obtained.



(*S*,*R*,*R*)-**L1** (*S*,*R*,*R*)-**L21** (*S*,*R*,*R*)-**L22** (*R*,*S*,*S*)-**L23**

(*S*,*R*,*R*)-**L24** (*S*,*S*,*S*)-**L25** (*R*,*R*R)-**L26**

3 Experimental Details for the Asymmetric Difunctionalization of Isoprene and Its Derivatives

3.1 General Procedure for Asymmetric *Anti*-Selective Borylative Coupling of 1,3-Dienes and Ketones (Condition A)

In a nitrogen-filled glovebox, to a flame-dried Schlenk tube was added CuOAc (2.5 mg, 20 μmol, 10 mol%), ligand **L1** (13 mg, 24 μmol, 12 mol%), NaO*t*Bu (8.0 mg, 80 μmol, 40 mol%). The tube was taken out of the glovebox, evacuated, and backfilled with N_2 (3 times) followed by the addition of toluene (1.0 mL). After stirring for 30 min at room temperature, $B_2(pin)_2$ (78 mg, 0.30 mmol, 1.5 equiv.) in toluene (0.5 mL) was added. After stirring at room temperature for about 1 min, it was cooled to –30 °C. 1,3-diene **2** (1.0 mmol, 5.0 equiv.) was added via syringe, followed by ketone **1** (0.20 mmol, 1.0 equiv.) in toluene (0.5 mL). After the indicated reaction time, the reaction was quenched by 0.3 mL saturated ammonium chloride water solution. The mixture was concentrated *in vacuo*. To the residue was then added 2.0 mL THF, 3 M NaOH (0.6 mL) ,and 30% H_2O_2 (0.6 mL) at 0 °C. After stirring at 0 °C for 30 min, brine (10 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. It was then analyzed by ^1H NMR spectroscopy to obtain the NMR yield and diastereoselectivity with CH_2Br_2 as an internal standard. The crude product was purified by column chromatography on silica gel (5:1 to 3:1 cyclohexane/EtOAc) to afford target compound.

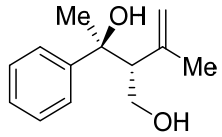
3.2 General Procedure for Asymmetric *Syn*-Selective Borylative Coupling of 1,3-Dienes and Ketones (Condition B)

In a nitrogen-filled glovebox, to a flame-dried Schlenk tube was added CuOAc (2.5 mg, 20 μmol, 5 mol%), ligand **L9** (20 mg, 24 μmol, 6 mol%), NaO*t*Bu (16.0 mg, 160 μmol, 40 mol%). The tube was taken out of the glovebox, evacuated, and backfilled with N_2 (3 times) followed by the addition of toluene/THF (2.0 mL, 8/2, v/v). After stirring for 30 min at room temperature, $B_2(pin)_2$ (152 mg, 0.60 mmol, 1.5 equiv.) in toluene/THF (1.0 mL, 8/2, v/v) was added. After stirring at room temperature for about 1 min, it was cooled to –20 °C. 1,3-diene **2** (2.0 mmol, 5.0 equiv.) was added via syringe, followed by ketone **1** (0.40 mmol, 1.0 equiv.) in toluene/THF (0.5 mL, 8/2, v/v). After the

indicated reaction time, the reaction was quenched by 0.3 mL saturated ammonium chloride water solution. The mixture was concentrated *in vacuo*. To the residue was then added 5.0 mL THF, 3 M NaOH (1.2 mL) ,and 30% H_2O_2 (1.2 mL) at 0 °C. After stirring at 0 °C for 30 min, brine (10 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. It was then analyzed by ^{1}H NMR spectroscopy to obtain the NMR yield and diastereoselectivity with CH_2Br_2 as an internal standard. The crude product was purified by column chromatography on silica gel (5:1 to 3:1 *n*-pentane/EtOAc) to afford target compound.

Note: *The diastereomers have different* $\boldsymbol{R_f}$ *value except for* ***4oa****. The major diasteromer can be partially separated by flash chromatography on silica gel. Yields are combined isolated material.*

3.3 Characterization Data of the Chiral Tertiary Homoallylic Alcohols (*anti*-4)



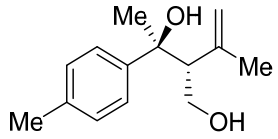
anti-**4aa**
$C_{13}H_{18}O_2$
M = 206.29 g/mol

(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4aa**): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 64 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4aa** as a colorless oil (37.2 mg, 90% yield, *anti*:*syn* = 80:20, *anti*-**4aa**: 90% *ee*).

$\mathbf{R_f}$ = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.66 (s, 3H), 1.82 (s, 3H), 2.46 (broad s, 1H), 2.87 (t, *J* = 6.40 Hz, 1H), 3.12 (broad s, 1H), 4.03 (d, *J* = 6.40 Hz, 1H), 4.88 (s, 1H), 5.11–5.12 (m, 1H), 7.40–7.44 (m, 1H), 7.48–7.52 (m, 2H), 7.56–7.59 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.2, 28.8, 58.1, 62.4, 76.2, 115.1, 125.4, 126.7, 127.8, 143.9, 146.4 ppm. **HRMS** (APCI) for $C_{13}H_{17}O$ $[M\text{-}OH]^+$: calculated 189.1274, found 189.1273.

Optical rotation: $[\alpha]_D^{20}$= -67.4 (*c* 1.0, $CHCl_3$, 90% *ee*). The enantiomeric excess of *anti*-**4aa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel

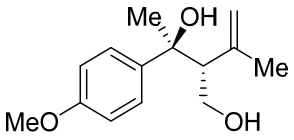
ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 34.4 min (minor), t_R = 37.1 min (major).



anti-**4ba**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*anti*-**4ba**): Prepared from 1-(*p*-tolyl)ethan-1-one (**1b**, 26.8 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 62 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ba** as a colorless oil (37.6 mg, 85% yield, *anti*:*syn* = 88:12, *anti*-**4ba**: 92% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.49 (s, 3H), 1.62 (s, 3H), 2.33 (s, 3H), 2.69 (t, *J* = 6.56 Hz, 1H), 3.83–3.85 (m, 2H), 4.72 (s, 1H), 4.94–4.95 (m, 1H), 7.13 (d, *J* = 7.92 Hz, 2H), 7.28 (d, *J* = 7.92 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.9, 24.3, 28.9, 58.2, 62.5, 76.1, 115.0, 125.3, 128.5, 136.3, 143.4, 144.0 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ $[M\text{-}OH]^+$: calculated 203.1436, found 203.1430. Optical rotation: $[\alpha]_D^{20}$= -46.0 (*c* 0.75, $CHCl_3$, 92% *ee*). The enantiomeric excess of *anti*-**4ba** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 18.7 min (minor), t_R = 25.9 min (major).

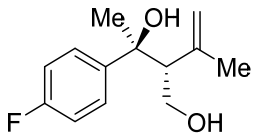


anti-**4ca**
$C_{14}H_{20}O_3$
M = 236.31 g/mol

(2*R*,3*S*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ca**): Prepared from 1-(4-methoxyphenyl)ethan-1-one (**1c**, 30.0 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 90 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ba** as

a colorless oil (36.4 mg, 77% yield, *anti*:*syn* = 77:23, *anti*-**4ca**: 81% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.50 (s, 3H), 1.61 (s, 3H), 2.67 (t, *J* = 6.60 Hz, 1H), 3.77–3.85 (m, 2H), 3.80 (s, 3H), 4.67 (s, 1H), 4.94–4.95 (m, 1H), 6.85 (d, *J* = 8.88 Hz, 2H), 7.31 (d, *J* = 8.88 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.3, 28.9, 55.2, 58.3, 62.6, 76.0, 113.1, 115.1, 126.7, 138.4, 144.0, 158.3 ppm. **HRMS** (APCI) for $C_{14}H_{19}O_2$ [M-OH]$^+$: calculated 219.1335, found 219.1382. Optical rotation: $[\alpha]_D^{20}$= -48.6 (*c* 0.7, $CHCl_3$, 81% *ee*). The enantiomeric excess of *anti*-**4ca** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 93:7, flow rate 0.4 mL/min): t_R = 50.8 min (minor), t_R = 54.9 min (major).



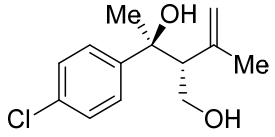
anti-**4da**
$C_{13}H_{17}FO_2$
M = 224.28 g/mol

(2*R*,3*S*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4da**): Prepared from 1-(4-fluorophenyl)ethan-1-one (**1d**, 44.1 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 67 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4da** as a colorless oil (41.7 mg, 94% yield, *anti*:*syn* = 88:12, *anti*-**4da**: 91% *ee*).

R_f = 0.32 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.51 (s, 3H), 1.62 (s, 3H), 2.25 (broad s, 1H), 2.64 (t, *J* = 6.25 Hz, 1H), 3.06 (broad s, 1H), 3.79–3.87 (m, 2H), 4.66 (s, 1H), 4.92 (s, 1H), 6.97–7.01 (m, 2H), 7.34–7.37 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.2, 29.1, 58.1, 62.5, 76.1, 114.5 (d, *J* = 21.22 Hz), 115.4, 127-2 (d, *J* = 7.93 Hz), 142.2 (d, *J* = 2.68 Hz), 143.6, 161.7 (d, *J* = 244.90 Hz) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.60. **HRMS** (APCI) for $C_{13}H_{16}FO$ [M-OH]$^+$: calculated 207.11797, found 207.1179.

Optical rotation: $[\alpha]_D^{20}$= -77.9 (*c* 1.0, $CHCl_3$, 91% *ee*). The enantiomeric excess of *anti*-**4da** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 98:2, flow rate 0.3

mL/min): t_R = 73.0 min (minor), t_R = 77.5 min (major).

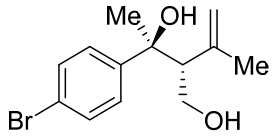


anti-**4ea**
$C_{13}H_{17}ClO_2$
M = 240.73 g/mol

(2*R*,3*S*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ea**): Prepared from 1-(4-chlorophenyl)ethan-1-one (**1e**, 31.0 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 66 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ea** as a colorless oil (41.2 mg, 86% yield, *anti*:*syn* = 81:19, *anti*-**4ea**: 93% *ee*).

R_f = 0.32 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55 (s, 3H), 1.65 (s, 3H), 2.33 (broad s, 1H), 2.67 (t, *J* = 6.17 Hz, 1H), 3.22 (broad s, 1H), 3.83–3.93 (m, 2H), 4.71 (s, 1H), 4.95–4.96 (m, 1H), 7.31 (d, *J* = 8.97 Hz, 2H), 7.37 (d, *J* = 8.97 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.3, 29.1, 57.8, 62.4, 76.1, 115.5, 127.0, 127.8, 132.5, 143.5, 145.0 ppm. **HRMS** (APCI) for $C_{13}H_{16}ClO$ $[M\text{-}OH]^+$: calculated 223.0890, found 223.0885.

Optical rotation: $[\alpha]_D^{20}$= -91.5 (*c* 1.0, $CHCl_3$, 93% *ee*). The enantiomeric excess of *anti*-**4ea** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 25.4 min (minor), t_R = 33.2 min (major).



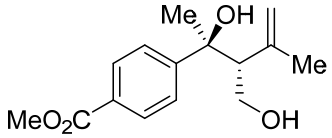
anti-**4fa**
$C_{13}H_{17}BrO_2$
M = 285.18 g/mol

(2*R*,3*S*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4fa**): Prepared from 1-(4-bromophenyl)ethan-1-one (**1f**, 40.0 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 86 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4fa** as a

colorless oil (49.4 mg, 87% yield, *anti*:*syn* = 80:20, *anti*-**4fa**: 93% *ee*).

R_f = 0.32 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.52 (s, 3H), 1.61 (s, 3H), 2.12 (broad s, 1H), 2.63 (t, *J* = 6.18 Hz, 1H), 3.06 (broad s, 1H), 3.81–3.91 (m, 2H), 4.69 (s, 1H), 4.92–4.93 (m, 1H), 7.27 (d, *J* = 8.56 Hz, 2H), 7.43 (d, *J* = 8.65 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.3, 29.1, 57.7, 62.4, 76.1, 115.5, 120.7, 127.3, 130.8, 143.5, 145.6 ppm. **HRMS** (APCI) for $C_{13}H_{16}BrO$ [M-OH]$^+$: calculated 267.0385, found 267.0386.

Optical rotation: $[\alpha]_D^{20}$= -91.8 (*c* 0.65, $CHCl_3$, 93% *ee*). The enantiomeric excess of *anti*-**4fa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.0 min (minor), t_R = 36.4 min (major).



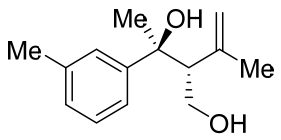
anti-**4ga**
$C_{15}H_{20}O_4$
M = 264.32 g/mol

4-((2*S*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*anti*-**4ga):** Prepared from methyl 4-acetylbenzoate (**1g**, 35.6 mg, 0.20 mmol) according to **Condition A** with isoprene **2a** and $B_2(Pin)_2$ at –30 °C for 86 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ga** as a white solid (50.2 mg, 95% yield, *anti*:*syn* = 62:38, *anti*-**4ga**: 89% *ee*).

R_f = 0.34 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.48 (s, 3H), 1.65 (s, 3H), 2.10 (broad s, 1H), 2.68 (t, *J* = 5.75 Hz, 1H), 3.16 (broad s, 1H), 3.84–3.96 (m, 2H), 3.91 (s, 3H), 4.72 (s, 1H), 4.90–4.91 (m, 1H), 7.47 (d, *J* = 8.44 Hz, 2H), 7.98 (d, *J* = 8.46 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.2, 29.1, 52.1, 57.6, 62.3, 76.3, 115.6, 125.4, 128.5, 129.1, 143.4, 151.9, 167.0 ppm. **HRMS** (APCI) for $C_{15}H_{19}O_3$ [M-OH]$^+$: calculated 247.1334, found 247.1340.

Optical rotation: $[\alpha]_D^{20}$= -26.0 (*c* 1.0, $CHCl_3$, 89% *ee*). The enantiomeric excess of *anti*-**4ga** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.4

mL/min): t_R = 82.2 min (minor), t_R = 99.0 min (major).

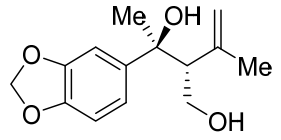


anti-**4ha**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*anti*-**4ha):** Prepared from 1-(*m*-tolyl)ethan-1-one (**1h**, 26.8 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 67 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ha** as a colorless oil (39.7 mg, 90% yield, *anti*:*syn* = 84:16, *anti*-**4ha**: 92% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.48 (s, 3H), 1.62 (s, 3H), 2.19 (broad s, 1H), 2.35 (s, 3H), 2.70 (t, *J* = 6.45 Hz, 1H), 2.81 (broad s, 1H), 3.84 (d, *J* = 6.41 Hz, 2H), 4.73 (s, 1H), 4.95–4.96 (m, 1H), 7.04–7.06 (m, 1H), 7.16–7.21 (m, 3H), ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 24.3, 28.7, 58.2, 62.4, 76.0, 115.1, 122.5, 126.0, 127.4, 127.7, 137.3, 144.0, 146.4 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ $[M\text{-}OH]^+$: calculated 203.1436, found 203.1432.

Optical rotation: $[\alpha]_D^{20}$= -61.8 (*c* 1.0, $CHCl_3$, 92% *ee*). The enantiomeric excess of *anti*-**4ha** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel AS-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 33.0 min (major), t_R = 36.5 min (minor).



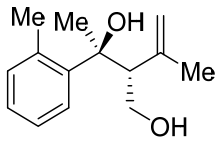
anti-**4ia**
$C_{14}H_{18}O_4$
M = 250.29 g/mol

(2*R*,3*S*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ia):** Prepared from 1-(benzo[d][1,3]dioxol-5-yl)ethan-1-one (**1i**, 32.8 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 90 h (***Note:*** 15 mol% CuOAc and 18 mol% **L1** were used). Purification by flash column

chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ia** as a colorless oil (47.6 mg, 95% yield, *anti*:*syn* = 71:29, *anti*-**4ia**: 85% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.53 (s, 3H), 1.59 (s, 3H), 2.18 (broad s, 1H), 2.64 (t, *J* = 6.39 Hz, 1H), 2.87 (broad s, 1H), 3.82 (d, *J* = 6.36 Hz, 2H), 4.72 (s, 1H), 4.956–4.963 (m, 1H), 5.94 (s, 2H), 6.75 (d, *J* = 8.16 Hz, 1H), 6.84 (dd, *J* = 8.12, 1.81 Hz, 1H), 6.91 (d, *J* = 1.84 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.2, 29.0, 58.2, 62.4, 76.1, 100.9, 106.5, 107.5, 115.2, 118.6, 140.7, 143.9, 146.1, 147.3 ppm. **HRMS** (APCI) for $C_{14}H_{17}O_3$ $[M\text{-}OH]^+$: calculated 233.1178, found 233.1173.

Optical rotation: $[\alpha]_D^{20}$= -61.4 (*c* 1.0, $CHCl_3$, 85% *ee*). The enantiomeric excess of *anti*-**4ia** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 41.1 min (minor), t_R = 43.8 min (major).



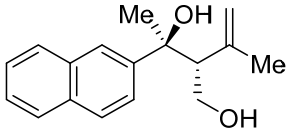
anti-**4ja**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*anti*-**4ja):** Prepared from 1-(*o*-tolyl)ethan-1-one (**1j**, 26.8 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 70 h (*Note: (R,S,S)-**L1** was used*). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ja** as a colorless oil (37.5 mg, 85% yield, *anti*:*syn* = 46:54, *anti*-**4ja**: 29% *ee*; *syn*-**4ja**: 72% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55-1.56 (m, 3H), 1.69 (s, 3H), 2.56 (s, 3H), 3.02 (dd, *J* = 8.46, 4.37 Hz, 1H), 3.78 (dd, *J* = 11.05, 4.35 Hz, 1H), 3.92 (dd, *J* = 11.05, 8.46 Hz, 1H), 4.93–4.94 (m, 1H), 5.04–5.05 (m, 1H), 7.12–7.17 (m, 3H), 7.39–7.43 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 22.7, 23.9, 27.4, 55.9, 61.9, 76.3, 115.1, 125.6, 126.1, 127.0, 132.7, 134.7, 144.6, 144.8 ppm. **HRMS**

(APCI) for $C_{14}H_{19}O$ [M-OH]$^+$: calculated 203.1436, found 203.1430.

Optical rotation: $[\alpha]_D^{20}$= +14.5 (*c* 0.6, CH_2Cl_2, 29% *ee*). The enantiomeric excess of *anti*-**4ja** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:iPrOH = 96:4, flow rate 0.4 mL/min): t_R = 36.3 min (minor), t_R = 49.0 min (major).

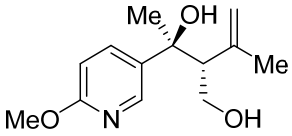


anti-**4ka**
$C_{17}H_{20}O_2$
M = 256.35 g/mol

(2*R*,3*S*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ka):** Prepared from 1-(naphthalen-2-yl)ethan-1-one (**1k**, 34.1 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 66 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ka** as a colorless oil (48.7 mg, 95% yield, *anti*:*syn* = 82:18, *anti*-**4ka**: 91% *ee*).

R_f = 0.33 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.48 (s, 3H), 1.72 (s, 3H), 2.82 (t, *J* = 6.17 Hz, 1H), 3.88–3.95 (m, 2H), 4.76 (s, 1H), 4.92–4.93 (m, 1H), 7.45–7.52 (m, 3H), 7.79–7.87 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.3, 29.0, 57.9, 62.4, 76.3, 115.3, 123.8, 124.1, 125.8, 126.0, 127.39, 127.41, 128.2, 132.2, 132.9, 143.9, 144.1 ppm. **HRMS** (APCI) for $C_{17}H_{19}O$ [M-OH]$^+$: calculated 239.1436, found 239.1431.

Optical rotation: $[\alpha]_D^{20}$= -85.0 (*c* 1.0, $CHCl_3$, 91% *ee*). The enantiomeric excess of *anti*-**4ka** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 43.8 min (minor), t_R = 55.6 min (major).



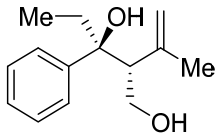
anti-**4la**
$C_{13}H_{19}NO_3$
M = 237.30 g/mol

(2*R*,3*S*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4la):**

Prepared from 1-(6-methoxypyridin-3-yl)ethan-1-one (**1l**, 30.2 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 90 h (***Note:*** 15 mol% CuOAc and 18 mol% **L1** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4la** as a colorless oil (33.2 mg, 70% yield, *anti*:*syn* = 42:58, *anti*-**4la**: 78% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.59 (s, 3H), 1.62 (s, 3H), 2.61 (t, *J* = 6.34 Hz, 1H), 3.36 (broad s, 1H), 3.77–3.87 (m, 2H), 3.92 (s, 3H), 4.60 (s, 1H), 4.92–4.93 (m, 1H), 6.69 (d, *J* = 8.70 Hz, 1H), 7.63 (dd, *J* = 8.67, 2.60 Hz, 1H), 8.17 (d, *J* = 2.50 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.3, 29.1, 53.4, 57.8, 62.7, 75.4, 109.6, 115.6, 134.3, 136.7, 143.2, 144.1, 163.0 ppm. **HRMS** (APCI) for $C_{13}H_{18}NO_2$ $[M\text{-}OH]^+$: calculated 220.1338, found 220.1334.

Optical rotation: $[\alpha]_D^{20}$= -62.6 (*c* 0.5, $CHCl_3$, 78% *ee*). The enantiomeric excess of *anti*-**4la** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 36.9 min (major), t_R = 41.1 min (minor).



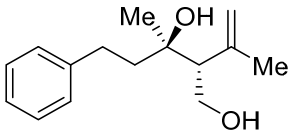
anti-**4ma**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*anti*-4ma): Prepared from propiophenone (**1m**, 26.8 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 67 h (***Note:*** 15 mol% CuOAc and 18 mol% **L1** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ma** as a colorless oil (41.0 mg, 93% yield, *anti*:*syn* = 70:30, *anti*-**4ma**: 87% *ee*, *syn*-**4ma**: 78% *ee*).

R_f = 0.36 (cyclohexane/EtOAc = 5/1**^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.33 Hz, 3H), 1.60 (s, 3H), 2.18 (q, *J* = 7.33 Hz, 2H), 2.42 (broad s, 1H), 2.90 (t, *J* = 6.33 Hz, 1H), 3.02 (broad s, 1H), 4.03–4.12 (m, 2H), 4.89 (s, 1H), 5.08–5.09 (m, 1H), 7.38–7.42 (m, 1H), 7.47–7.52 (m, 4H), ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.7, 24.4, 32.9, 57.6,

62.3, 78.9, 115.0, 126.1, 126.5, 127.7, 143.9, 144.1 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ [M-OH]$^+$: calculated 203.1436, found 203.1432.

Optical rotation: $[\alpha]_D^{20}$= -33.7 (*c* 1.0, $CHCl_3$, 87% *ee*). The enantiomeric excess of *anti*-**4ma** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:iPrOH = 95:5, flow rate 0.6 mL/min): tR = 15.8 min (minor), tR = 22.7 min (major).

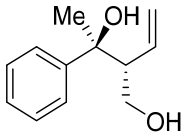


anti-**4oa**
$C_{15}H_{22}O_2$
M = 234.34 g/mol

(2*R*,3*R*)-3-Methyl-5-phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*anti*-4oa): Prepared from 4-phenylbutan-2-one (**1o**, 29.6 mg, 0.20 mmol) according to **Condition A** with isoprene (**2a**) and $B_2(Pin)_2$ at –30 °C for 66 h (***Note:*** 15 mol% CuOAc and 18 mol% **L1** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4oa** as a colorless oil (28.2 mg, 60% yield, *anti*:*syn* = 65:35, *anti*-**4oa**: 87% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.31 (s, 3H), 1.87 (s, 3H), 1.76–1.89 (m, 2H), 2.43 (t, *J* = 6.79 Hz, 1H), 2.64 (broad s, 1H), 2.67–2.81 (m, 2H), 3.95–4.00 (m, 2H), 4.06 (s, 1H), 4.91 (s, 1H), 5.04-5.05 (m, 1H), 7.17-7.21 (m, 3H), 7.27-7.31 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.2, 25.9, 30.1, 41.8, 57.2, 62.4, 74.4, 115.3, 125.8, 128.3, 128.4, 142.5, 144.2 ppm. **HRMS** (APCI) for $C_{15}H_{21}O$ [M-OH]$^+$: calculated 217.1588, found 217.1592.

Optical rotation: $[\alpha]_D^{20}$= -31.9 (*c* 0.75, $CHCl_3$, 87% *ee*). The enantiomeric excess of *anti*-**4oa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 38.3 min (minor), t_R = 89.2 min (major).

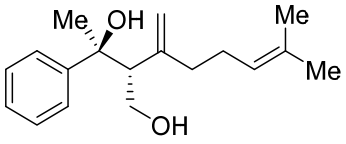


anti-**4ab**
$C_{12}H_{16}O_2$
M = 192.26 g/mol

(2*R*,3*S*)-3-Phenyl-2-vinylbutane-1,3-diol (*anti*-4ab): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition A** with buta-1,3-diene (**2b**) and $B_2(Pin)_2$ at –30 °C for 86 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ab** as a colorless oil (35.4 mg, 92% yield, *anti*:*syn* = 57:43, *anti*-**4ab**: 66% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.62 (s, 3H), 2.63 (dt, *J* = 9.08, 5.93 Hz, 1H), 3.61–3.69 (m, 2H), 5.11–5.16 (m, 2H), 5.48–5.58 (m, 1H), 7.22–7.27 (m, 1H), 7.31–7.41 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.7, 56.2, 63.5, 76.8, 119.1, 125.6, 126.9, 128.0, 135.4, 145.4 ppm. **HRMS** (APCI) for $C_{12}H_{15}O$ $[M\text{-}OH]^+$: calculated 175.1123, found 175.1118.

Optical rotation: $[\alpha]_D^{20}$= -20.4 (*c* 0.5, $CHCl_3$, 66% *ee*). The enantiomeric excess of *anti*-**4ab** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.4 mL/min): t_R = 46.8 min (major), t_R = 52.9 min (minor).



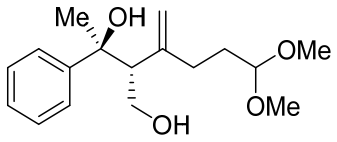
anti-**4ac**
$C_{18}H_{26}O_2$
M = 274.40 g/mol

(2*R*,3*S*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*anti*-4ac): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition A** with myrcene (**2c**) and $B_2(Pin)_2$ at –30 °C for 67 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ac** as a colorless oil (46.7 mg, 85% yield, *anti*:*syn* = 60:40, *anti*-**4ac**: 93% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.63

(s, 3H), 1.64 (s, 3H), 1.67–1.80 (m, 2H), 1.87–2.04 (m, 2H), 2.23 (broad s, 1H), 2.69 (t, *J* = 6.46 Hz, 1H), 2.99 (broad s, 1H), 3.79–3.87 (m, 2H), 4.75 (s, 1H), 4.89–4.93 (m, 1H), 4.97 (s, 1H), 7.21–7.25 (m, 1H), 7.29–7.33 (m, 2H), 7.36–7.39 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 17.7, 25.6, 26.1, 28.5, 38.2, 56.7, 62.8, 76.1, 113.3, 123.7, 125.5, 126.7, 127.7, 131.9, 146.3, 147.6 ppm. **HRMS** (APCI) for $C_{18}H_{25}O$ [M-OH]$^+$: calculated 257.1905, found 257.1902.

Optical rotation: $[\alpha]_D^{20}$= -29.7 (*c* 1.0, $CHCl_3$, 93% *ee*). The enantiomeric excess of *anti*-**4ac** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 22.2 min (minor), t_R = 35.2 min (major).



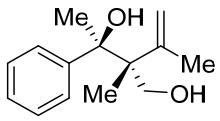
anti-**4ad**
$C_{17}H_{26}O_4$
M = 294.39 g/mol

(2*R*,3*S*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*anti*-**4ad**): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition A** with 6,6-dimethoxy-3-methylenehex-1-ene (**2d**) and $B_2(Pin)_2$ at –30 °C for 86 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ad** as a colorless oil (46.3 mg, 78% yield, *anti*:*syn* = 68:32, *anti*-**4ad**: 93% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.44–1.59 (m, 2H), 1.61 (s, 3H), 1.64–1.83 (m, 2H), 2.36 (broad s, 1H), 2.63 (t, *J* = 5.65 Hz, 1H), 3.14 (broad s, 1H), 3.20 (s, 3H), 3.21 (s, 3H), 3.79–3.88 (m, 2H), 4.16 (t, *J* = 5.65 Hz, 1H), 4.78 (s, 1H), 4.92–4.93 (m, 1H), 7.20–7.24 (m, 1H), 7.28–7.33 (m, 2H), 7.36–7.39 (m, 2H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 29.0, 30.9, 33.2, 52.8, 53.0, 57.3, 63.1, 76.5, 104.6, 113.5, 125.9, 126.9, 128.1, 147.3, 147.9 ppm. **HRMS** (APCI) for $C_{15}H_{20}O_2$ [M-$(OMe)_2$]$^+$: calculated 232.1463, found 232.1412.

Optical rotation: $[\alpha]_D^{20}$= -84.0 (*c* 1.0, CH_2Cl_2, 93% *ee*). The enantiomeric excess of *anti*-**4ad** was determined by HPLC analysis on a chiral stationary phase (Daicel

Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 27.9 min (major), t_R = 30.6 min (minor).

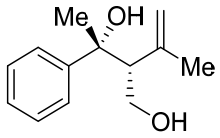


anti-**4ae**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*R*)-2-Methyl-3-phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ae): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition A** with 2,3-dimethylbuta-1,3-diene (**2e**) and $B_2(Pin)_2$ at –30 °C for 66 h (***Note:*** 15 mol% CuOAc and 18 mol% **L1** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ae** as a colorless oil (35.3 mg, 80% yield, *anti*:*syn* = 57:43, *anti*-**4ae** = 80% *ee*).

R_f = 0.62 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.45 (s, 3H), 1.57 (s, 3H), 1.81 (s, 3H), 3.89 (d, *J* = 11.01 Hz, 1H), 3.95 (d, *J* = 11.01 Hz, 1H), 4.97 (s, 1H), 5.28–5.29 (m, 1H), 7.42–7.50 (m, 3H), 7.56–7.58 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.5, 23.0, 25.3, 50.8, 67.8, 78.4, 115.6, 126.76, 126.83, 127.2, 145.4, 147.0 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ $[M\text{-}OH]^+$: calculated 203.1436, found 203.1435. Optical rotation: $[\alpha]_D^{20}$= +5.2 (*c* 0.75, $CHCl_3$, 80% *ee*). The enantiomeric excess of *anti*-**4ae** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.3 mL/min): t_R = 40.3 min (minor), t_R = 43.7 min (major).

3.4 Characterization Data of the Chiral Tertiary Homoallylic Alcohols (*syn*-4)



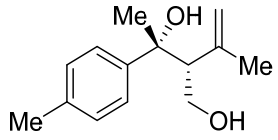
syn-**4aa**
$C_{13}H_{18}O_2$
M = 206.29 g/mol

(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4aa**): Prepared from acetophenone (**1a**, 48.1 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**)

and $B_2(Pin)_2$ at –20 °C for 45 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4aa** as a colorless oil (74.4 mg, 90% yield, *syn*:*anti* = 87:13, *syn*-**4aa**: 93% *ee*).

R_f = 0.39 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.57 (s, 3H), 1.75 (s, 3H), 2.04 (broad s, 1H), 2.58 (t, *J* = 5.71 Hz, 1H), 2.90 (broad s, 1H), 3.60–3.70 (m, 2H), 4.99 (s, 1H), 5.07–5.08 (m, 1H), 7.23–7.28 (m, 1H), 7.33–7.37 (m, 2H), 7.44–7.47 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.4, 28.3, 58.1, 62.8, 76.6, 115.0, 124.9, 126.7, 128.1, 144.4, 147.5 ppm. **HRMS** (APCI) for $C_{13}H_{17}O$ $[M\text{-}OH]^+$: calculated 189.1274, found 189.1271.

Optical rotation: $[\alpha]_D^{20}$= -35.8 (*c* 1.0, $CHCl_3$, 93% *ee*). The enantiomeric excess of *syn*-**4aa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 38.7 min (major), t_R = 42.6 min (minor).



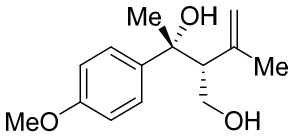
syn-**4ba**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*syn*-**4ba**): Prepared from 1-(*p*-tolyl)ethan-1-one (**1b**, 53.7 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ba** as a colorless oil (71.9 mg, 82% yield, *syn*:*anti* = 85:15, *syn*-**4ba**: 95% *ee*).

R_f = 0.39 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.74 (s, 3H), 2.15 (broad s, 1H), 2.34 (s, 3H), 2.55 (t, *J* = 5.87 Hz, 1H), 2.89 (broad s, 1H), 3.59–3.68 (m, 2H), 4.95 (s, 1H), 5.04–5.05 (m, 1H), 7.15 (d, *J* = 8.04Hz, 2H), 7.33 (d, *J* = 8.23 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.9, 24.3, 28.2, 58.1, 62.8, 76.5, 114.8, 124.8, 128.8, 136.2, 144.5 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ $[M\text{-}OH]^+$: calculated 203.1436, found 203.1434.

Optical rotation: $[\alpha]_D^{20}$= -35.9 (*c* 1.0, $CHCl_3$, 95% *ee*). The enantiomeric excess of *syn*-

4ba was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 21.3 min (major), t_R = 25.8 min (minor).

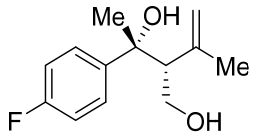


syn-**4ca**
$C_{14}H_{20}O_3$
M = 236.31 g/mol

(2*R*,3*R*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ca**): Prepared from 1-(4-methoxyphenyl)ethan-1-one (**1c**, 60.1 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 37 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ca** as a colorless oil (84.4 mg, 89% yield, *syn*:*anti* = 83:17, *syn*-**4ca**: 96% *ee*).

R_f = 0.33 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55 (s, 3H), 1.70 (s, 3H), 2.10 (broad s, 1H), 2.54 (t, *J* = 5.80 Hz, 1H), 2.81 (broad s, 1H), 3.62–3.69 (m, 2H), 3.80 (s, 3H), 4.94 (s, 1H), 5.04 (s, 1H), 6.87 (d, *J* = 8.86 Hz, 2H), 7.36 (d, *J* = 8.86 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 28.1, 55.2, 58.3, 62.9, 76.4, 113.4, 114.7, 126.1, 139.6, 144.5, 158.3 ppm. **HRMS** (APCI) for $C_{14}H_{19}O_2$ $[M\text{-}OH]^+$: calculated 219.1335, found 219.1379.

Optical rotation: $[\alpha]_D^{20}$= -40.8 (*c* 1.0, $CHCl_3$, 96% *ee*). The enantiomeric excess of *syn*-**4ca** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 93:7, flow rate 0.4 mL/min): 57.6 min (major), t_R = 62.1 min (minor).



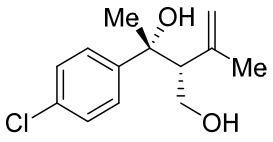
syn-**4da**
$C_{13}H_{17}FO_2$
M = 224.28 g/mol

(2*R*,3*R*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4da**): Prepared from 1-(4-fluorophenyl)ethan-1-one (**1d**, 55.3 mg, 0.40 mmol) according to **Condition**

B with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4da** as a colorless oil (82.2 mg, 92% yield, *syn*:*anti* = 86:14, *syn*-**4da**: 95% *ee*).

R_f = 0.36 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55 (s, 3H), 1.70 (s, 3H), 2.11 (broad s, 1H), 2.52 (t, *J* = 5.92 Hz, 1H), 3.06 (broad s, 1H), 3.60–3.69 (m, 2H), 4.95 (s, 1H), 5.05–5.06 (m, 1H), 6.98–7.04 (m, 2H), 7.38–7.43 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 28.0, 58.1, 62.8, 76.4, 114.8 (d, *J* = 21.09 Hz), 114.9, 126.7 (d, *J* = 7.84 Hz), 143.2 (d, *J* = 3.08 Hz), 144.2, 161.6 (d, *J* = 245.35 Hz) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.65. **HRMS** (APCI) for $C_{13}H_{16}FO$ $[M\text{-}OH]^+$: calculated 207.11797, found 207.1183.

Optical rotation: $[\alpha]_D^{20}$= -35.8 (*c* 1.0, $CHCl_3$, 95% *ee*). The enantiomeric excess of *syn*-**4da** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 98:2, flow rate 0.3 mL/min): t_R = 81.8 min (major), t_R = 98.3 min (minor).

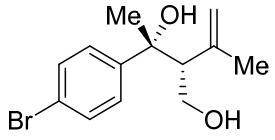


syn-**4ea**
$C_{13}H_{17}ClO_2$
M = 240.73 g/mol

(2*R*,3*R*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ea**): Prepared from 1-(4-chlorophenyl)ethan-1-one (**1e**, 61.8 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 39 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ea** as a colorless oil (78.6 mg, 82% yield, *syn*:*anti* = 84:16, *syn*-**4ea**: 92% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.53 (s, 3H), 1.71-1.72 (s, 3H), 2.12 (broad s, 1H), 2.51 (t, *J* = 5.91 Hz, 1H), 3.17 (broad s, 1H), 3.58–3.68 (m, 2H), 4.95 (s, 1H), 5.05–5.06 (m, 1H), 7.30 (d, *J* = 8.63 Hz, 2H), 7.38 (d, *J* = 8.71 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 28.0, 57.8, 62.8, 76.5, 115.1, 126.5, 128.2, 132.5, 144.1, 146.1 ppm. **HRMS** (APCI) for $C_{13}H_{16}ClO$ $[M\text{-}OH]^+$: calculated 223.0890, found 223.0888.

Optical rotation: $[\alpha]_D^{20}$= -38.5 (*c* 1.0, $CHCl_3$, 92% *ee*). The enantiomeric excess of *syn*-**4ea** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 27.0 min (minor), t_R = 38.6 min (major).

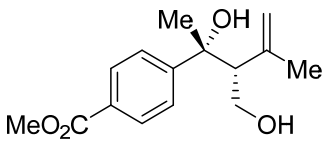


syn-**4fa**
$C_{13}H_{17}BrO_2$
M = 285.18 g/mol

(2*R*,3*R*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4fa**): Prepared from 1-(4-bromophenyl)ethan-1-one (**1f**, 79.6 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4fa** as a colorless oil (97.6 mg, 86% yield, *syn*:*anti* = 83:17, *syn*-**4fa**: 92% *ee*).

R_f = 0.36 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.52 (s, 3H), 1.73 (s, 3H), 2.08 (broad s, 1H), 2.51 (t, *J* = 5.84 Hz, 1H), 3.14 (broad s, 1H), 3.57–3.68 (m, 2H), 4.96 (s, 1H), 5.06–5.07 (m, 1H), 7.32 (d, *J* = 8.59 Hz, 2H), 7.45 (d, *J* = 8.57 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 28.0, 57.8, 62.8, 76.5, 115.1, 120.6, 126.9, 131.1, 144.0, 146.6 ppm. **HRMS** (APCI) for $C_{13}H_{16}BrO$ $[M\text{-}OH]^+$: calculated 267.0385, found 267.0377.

Optical rotation: $[\alpha]_D^{20}$= -32.9 (*c* 1.0, $CHCl_3$, 92% *ee*). The enantiomeric excess of *syn*-**4fa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.4 min (major), t_R = 34.8 min (minor).



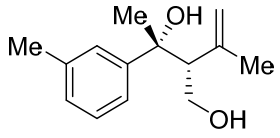
syn-**4ga**
$C_{15}H_{20}O_4$
M = 264.32 g/mol

4-((2*R*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*syn*-

4ga): Prepared from methyl 4-acetylbenzoate (**1g**, 35.6 mg, 0.20 mmol) according to **Condition B** with isoprene **2a** and $B_2(Pin)_2$ at –20 °C in THF for 29 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ga** as a white solid (40.1 mg, 76% yield, *syn*:*anti* = 82:18, *syn*-**4ga**: 82% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.56 (s, 3H), 1.76 (s, 3H), 1.90 (broad s, 1H), 2.58 (t, *J* = 5.89 Hz, 1H), 3.11 (s, 1H), 3.56–3.69 (m, 2H), 3.91 (s, 3H), 5.01 (s, 1H), 5.09–5.10 (m, 1H), 7.54 (d, *J* = 8.53 Hz, 2H), 8.01 (d, *J* = 8.55 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 28.2, 52.1, 57.7, 62.8, 76.7, 115.3, 125.1, 128.6, 129.5, 144.0, 152.8, 167.0 ppm. **HRMS** (APCI) for $C_{15}H_{19}O_3$ [M-OH]$^+$: calculated 247.1334, found 247.1332.

Optical rotation: $[\alpha]_D^{20}$= -22.3 (*c* 1.0, $CHCl_3$, 82% *ee*). The enantiomeric excess of *syn*-**4ga** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.4 mL/min): t_R = 93.0 min (minor), t_R = 112.9 min (major).

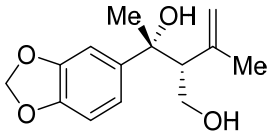


syn-**4ha**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*syn*-**4ha**): Prepared from 1-(*m*-tolyl)ethan-1-one (**1h**, 53.7 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ha** as a colorless oil (82.0 mg, 93% yield, *syn*:*anti* = 87:13, *syn*-**4ha**: 92% *ee*).

R_f = 0.38 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.77 (s, 3H), 2.00 (broad s, 1H), 2.36 (s, 3H), 2.57 (t, *J* = 5.40 Hz, 1H), 2.82 (broad s, 1H), 3.57–3.68 (m, 2H), 4.99 (s, 1H), 5.07–5.08 (m, 1H), 7.05–7.07 (m, 1H), 7.20–7.27 (m, 3H), ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 24.4, 28.5, 58.1, 62.7, 76.5, 114.9, 121.9, 125.5, 127.4, 128.0, 137.7, 144.5, 147.4 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ [M-OH]$^+$: calculated 203.1436, found 203.1432.

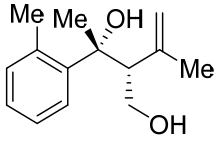
Optical rotation: $[\alpha]_D^{20}$= -29.0 (*c* 1.0, $CHCl_3$, 92% *ee*). The enantiomeric excess of *syn*-**4ha** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel AS-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.1 min (major), t_R = 67.2 min (minor).



syn-**4ia**
$C_{14}H_{18}O_4$
M = 250.29 g/mol

(2*R*,3*R*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ia**): Prepared from 1-(benzo[d][1,3]dioxol-5-yl)ethan-1-one (**1i**, 65.7 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h (***Note:*** 10 mol% CuOAc and 12 mol% **L9** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ia** as a colorless oil (90.1 mg, 90% yield, *syn*:*anti* = 86:14, *syn*-**4ia**: 91% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.51 (s, 3H), 1.72 (s, 3H), 2.16 (broad s, 1H), 2.50 (t, *J* = 5.91 Hz, 1H), 2.97 (broad s, 1H), 3.61–3.70 (m, 2H), 4.94 (s, 1H), 5.03–5.04 (m, 1H), 5.94 (s, 2H), 6.76 (d, *J* = 8.10 Hz, 1H), 6.70 (dd, *J* = 8.10, 1.83 Hz, 1H), 6.95 (d, *J* = 1.83 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.4, 28.2, 58.2, 62.8, 76.6, 100.9, 106.0, 107.7, 114.8, 118.1, 141.8, 144.4, 146.1, 147.5 ppm. **HRMS** (APCI) for $C_{14}H_{17}O_3$ $[M\text{-}OH]^+$: calculated 233.1178, found 233.1174. Optical rotation: $[\alpha]_D^{20}$= -34.7 (*c* 1.0, $CHCl_3$, 91% *ee*). The enantiomeric excess of *syn*-**4ia** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 48.5 min (minor), t_R = 51.9 min (major).

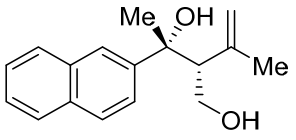


syn-**4ja**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*syn***-4ja):** Prepared from 1-(*o*-tolyl)ethan-1-one (**1j**, 26.8 mg, 0.20 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 70 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ja** as a colorless oil (38.8 mg, 88% yield, *syn*:*anti* = 86:14, *anti*-**4ja**: 80% *ee*; *syn*-**4ja**: 98% *ee*).

R_f = 0.38 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.43 (s, 3H), 1.65-1.66 (m, 3H), 2.27 (broad s, 1H), 2.58 (s, 3H), 2.79 (broad s, 1H), 2.94 (t, *J* = 6.31 Hz, 1H), 3.67–3.76 (m, 2H), 4.89 (s, 1H), 5.02–5.03 (m, 1H), 7.12–7.17 (m, 3H), 7.44–7.47 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 22.7, 24.5, 26.9, 55.0, 63.1, 78.0, 114.7, 125.7, 126.5, 127.1, 132.7, 134.9, 144.47, 144.49 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ [M-OH]$^+$: calculated 203.1436, found 203.1428.

Optical rotation: $[\alpha]_D^{20}$= -41.0 (*c* 1.0, CH_2Cl_2, 98% *ee*). The enantiomeric excess of *syn*-**4ja** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 49.5 min (major), t_R = 63.3 min (minor).



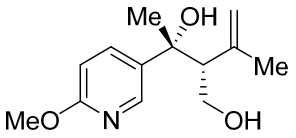
syn-**4ka**
$C_{17}H_{20}O_2$
M = 256.35 g/mol

(2*R*,3*R*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ka**): Prepared from 1-(naphthalen-2-yl)ethan-1-one (**1k**, 68.1 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ka** as a colorless oil (93.2 mg, 91% yield, *syn*:*anti* = 86:14, *syn*-**4ka**: 89% *ee*).

R_f = 0.36 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.63 (s, 3H), 1.79 (s, 3H), 2.10 (broad s, 1H), 2.70 (dd, *J* = 6.44, 5.23 Hz, 1H), 3.15 (broad s, 1H), 3.61 (dd, *J* = 11.05, 5.10 Hz, 1H), 3.69 (dd, *J* = 6.66, 5.23 Hz, 1H), 5.03 (s, 1H), 5.09–5.10 (m, 1H), 7.45–7.54 (m, 3H), 7.81–7.86 (m, 3H), 7.95–7.96 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.4, 28.4, 57.7, 62.8, 76.8, 115.1, 123.4, 123.5, 125.8, 126.1, 127.4,

127.8, 128.2, 132.2, 133.1, 144.3, 144.9 ppm. **HRMS** (APCI) for $C_{17}H_{19}O$ [M-OH]$^+$: calculated 239.1436, found 239.1432.

Optical rotation: $[\alpha]_D^{20}$= -29.6 (*c* 1.0, $CHCl_3$, 89% *ee*). The enantiomeric excess of *syn*-**4ka** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 46.5 min (major), t_R = 48.9 min (minor).

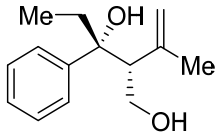


syn-**4la**
$C_{13}H_{19}NO_3$
M = 237.30 g/mol

(2*R*,3*R*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4la**): Prepared from 1-(6-methoxypyridin-3-yl)ethan-1-one (**1l**, 60.5 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4la** as a colorless oil (77.6 mg, 82% yield, *syn*:*anti* = 90:10, *syn*-**4la**: 90% *ee*).

R_f = 0.30 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.56 (s, 3H), 1.67 (s, 3H), 2.49 (t, *J* = 6.09 Hz, 1H), 3.42 (broad s, 1H), 3.71 (d, *J* = 6.16 Hz, 2H), 3.92 (s, 3H), 4.90 (s, 1H), 5.02–5.03 (m, 1H), 6.70 (d, *J* = 8.75 Hz, 1H), 7.66 (dd, *J* = 8.69, 2.57 Hz, 1H), 8.21(d, *J* = 2.40 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 27.4, 53.4, 58.0, 62.9, 75.5, 110.0, 115.1, 135.7, 136.2, 143.7, 143.9, 163.1 ppm. **HRMS** (APCI) for $C_{13}H_{18}NO_2$ [M-OH]$^+$: calculated 220.1338, found 220.1334.

Optical rotation: $[\alpha]_D^{20}$= -35.0 (*c* 1.0, $CHCl_3$, 90% *ee*). The enantiomeric excess of *syn*-**4la** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 47.2 min (major), t_R = 51.0 min (minor).

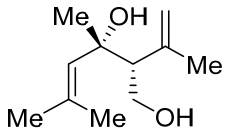


syn-**4ma**
$C_{14}H_{20}O_2$
M = 220.31 g/mol

(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*syn*-**4ma**): Prepared from propiophenone (**1m**, 53.7 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 54 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ma** as a colorless oil (84.7 mg, 96% yield, *syn*:*anti* = 92:8, *syn*-**4ma**: 64% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.61 (t, *J* = 7.40 Hz, 3H), 1.88 (s, 3H), 1.89 (q, *J* = 7.40 Hz, 2H), 2.59 (dd, *J* = 7.26, 4.37 Hz, 1H), 3.49 (dd, *J* = 11.04, 4.37 Hz, 1H), 3.64 (dd, *J* = 10.99, 7.23 Hz, 1H), 5.04 (s, 1H), 5.11–5.12 (m, 1H), 7.21–7.26 (m, 1H), 7.32–7.41 (m, 4H), ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.3, 24.5, 33.1, 58.4, 62.6, 79.1, 115.2, 125.5, 126.5, 128.1, 144.68, 144.74 ppm. **HRMS** (APCI) for $C_{14}H_{19}O$ $[M\text{-}OH]^+$: calculated 203.1436, found 203.1435.

Optical rotation: $[\alpha]_D^{20}$= -19.8 (*c* 1.0, $CHCl_3$, 64% *ee*). The enantiomeric excess of *syn*-**4ma** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 26.8 min (major), t_R = 32.0 min (minor).



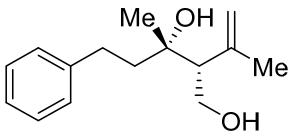
syn-**4na**
$C_{11}H_{20}O_2$
M = 184.28 g/mol

(2*R*,3*S*)-3,5-Dimethyl-2-(prop-1-en-2-yl)hex-4-ene-1,3-diol (*syn*-**4na**): Prepared from 4-methylpent-3-en-2-one (**1n**, 20.0 mg, 0.20 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 60 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4na** as a colorless oil (25.8 mg, 70% yield, *syn*:*anti* = 95:5, *syn*-**4na**: 90% *ee*).

R_f = 0.45 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.30 (s, 3H), 1.71

(d, *J* = 1.41 Hz, 3H), 1.82–1.83 (m, 3H), 1.86 (d, *J* = 1.36 Hz, 3H), 2.21 (broad s, 2H), 2.38–2.42 (m, 1H), 3.75–3.76 (m, 2H), 4.85–4.86 (m, 1H), 4.99–5.00 (m, 1H), 5.21–5.23 (m, 1H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 18.9, 24.1, 27.7, 27.9, 58.5, 63.0, 75.6, 114.9, 131.4, 134.1, 145.1 ppm. **HRMS** (APCI) for $C_{11}H_{19}O$ [M-OH]$^+$: calculated 167.1436, found 167.1428.

Optical rotation: $[\alpha]_D^{20}$= -8.6 (*c* 0.5, CH_2Cl_2, 90% *ee*). The enantiomeric excess of *syn*-**4na** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.3 mL/min): t_R = 39.2 min (minor), t_R = 41.1 min (major).

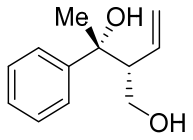


syn-**4oa**
$C_{15}H_{22}O_2$
M = 234.34 g/mol

(2*R*,3*S*)-3-Methyl-5-phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*syn*-**4oa**): Prepared from 4-phenylbutan-2-one (**1o**, 59.3 mg, 0.40 mmol) according to **Condition B** with isoprene (**2a**) and $B_2(Pin)_2$ at –20 °C for 54 h (***Note:*** 10 mol% CuOAc and 12 mol% **L9** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4oa** as a colorless oil (86.2 mg, 92% yield, *syn*:*anti* = 63:37, *syn*-**4oa**: 92% *ee*).

R_f = 0.35 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.83 (s, 3H), 1.76–1.89 (m, 2H), 2.43 (t, J = 6.76 Hz, 1H), 2.64 (broad s, 1H), 2.67–2.81 (m, 2H), 3.80–3.88 (m, 2H), 4.89 (s, 1H), 5.00–5.01 (m, 1H), 7.17-7.21 (m, 3H), 7.27-7.31 (m, 2H) ppm. ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 23.8, 25.9, 29.9, 43.5, 56.4, 62.9, 75.0, 115.1, 125.8, 128.3, 128.4, 142.4, 143.9 ppm. **HRMS** (APCI) for $C_{15}H_{21}O$ [M-OH]$^+$: calculated 217.1588, found 217.1590.

Optical rotation: $[\alpha]_D^{20}$= -32.7 (*c* 1.0, $CHCl_3$, 92% *ee*). The enantiomeric excess of *syn*-**4oa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 50.7 min (minor), t_R = 64.7 min (major).

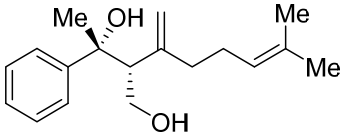


syn-**4ab**
$C_{12}H_{16}O_2$
M = 192.26 g/mol

(2*R*,3*R*)-3-Phenyl-2-vinylbutane-1,3-diol (*syn*-**4ab**): Prepared from acetophenone (**1a**, 48.1 mg, 0.40 mmol) according to **Condition B** with buta-1,3-diene (**2b**) and $B_2(Pin)_2$ at –20 °C for 35 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ab** as a colorless oil (65.4 mg, 85% yield, *syn*:*anti* = 80:20, *syn*-**4ab**: 95% *ee*).

R_f = 0.44 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.42 (s, 3H), 2.34 (broad s, 1H), 2.42 (dt, *J* = 9.18, 4.51 Hz, 1H), 3.27 (broad s, 1H), 3.45–3.53 (m, 2H), 5.09 (ddd, *J* = 17.27, 1.88 and 0.72 Hz, 1H), 5.18 (dd, *J* = 10.37, 1.89 Hz, 1H), 5.97 (ddd, *J* = 17.26, 10.36 and 9.70 Hz, 1H), 7.14–7.18 (m, 1H), 7.24–7.28 (m, 2H), 7.33–7.36 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.5, 55.3, 64.3, 77.0, 118.9, 124.8, 126.7, 128.2, 135.8, 147.4 ppm. **HRMS** (APCI) for $C_{12}H_{15}O$ $[M\text{-}OH]^+$: calculated 175.1123, found 175.1116.

Optical rotation: $[\alpha]_D^{20}$= -27.5 (*c* 1.0, $CHCl_3$, 95% *ee*). The enantiomeric excess of *syn*-**4ab** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.4 mL/min): t_R = 55.4 min (major), t_R = 63.4 min (minor).



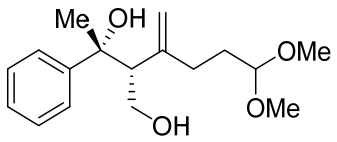
syn-**4ac**
$C_{18}H_{26}O_2$
M = 274.40 g/mol

(2*R*,3*R*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ac**): Prepared from acetophenone (**1a**, 48.1 mg, 0.40 mmol) according to **Condition B** with myrcene (**2c**) and $B_2(Pin)_2$ at –20 °C for 39 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ac** as a

colorless oil (98.8 mg, 90% yield, *syn*:*anti* = 88:12, *syn*-**4ac**: 90% *ee*).

R_f = 0.44 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.60 (s, 3H), 1.64 (s, 3H), 1.72 (s, 3H), 1.86–1.99 (m, 2H), 2.04–2.22 (m, 2H), 2.25 (broad s, 1H), 2.61 (t, *J* = 5.98 Hz, 1H), 3.11 (broad s, 1H), 3.66 (d, *J* = 5.88 Hz, 2H), 5.06–5.10 (m, 1H), 5.13 (s, 1H), 5.17 (s, 1H), 7.26–7.30 (m, 1H), 7.35–7.39 (m, 2H), 7.47–7.50 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 17.7, 25.6, 26.2, 27.7, 38.6, 56.6, 63.2, 76.8, 112.9, 123.7, 125.0, 126.7, 128.1, 132.0, 147.3, 148.1 ppm. **HRMS** (APCI) for $C_{18}H_{25}O$ [M-OH]$^+$: calculated 257.1905, found 257.1990.

Optical rotation: $[\alpha]_D^{20}$= -35.8 (*c* 1.0, $CHCl_3$, 90% *ee*). The enantiomeric excess of *syn*-**4ac** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 23.7 min (major), t_R = 31.4 min (minor).



syn-**4ad**

$C_{17}H_{26}O_4$

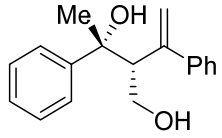
M = 294.39 g/mol

(2*R*,3*R*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ad**): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition B** with 6,6-dimethoxy-3-methylenehex-1-ene (**2d**) and $B_2(Pin)_2$ at –20 °C for 56 h (***Note:*** 8 mol% CuOAc and 10 mol% **L9** were used). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 2/1 afforded **4ad** as a colorless oil (42.4 mg, 72% yield, *syn*:*anti* = 93:7, *syn*-**4ad**: 91% *ee*).

R_f = 0.34 (cyclohexane/EtOAc = 2/1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.52 (s, 3H), 1.58–1.78 (m, 2H), 1.85–1.99 (m, 2H), 2.30 (broad s, 1H), 2.54 (t, *J* = 6.05 Hz, 1H), 3.20 (broad s, 1H), 3.25 (s, 3H), 3.26 (s, 3H), 3.54–3.64 (m, 2H), 4.29 (t, *J* = 5.63 Hz, 1H), 5.07 (s, 1H), 5.11 (s, 1H), 7.22–7.26 (m, 1H), 7.31–7.36 (m, 2H), 7.43–7.46 (m, 2H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 28.1, 31.0, 33.4, 52.9, 53.0, 57.5, 63.5, 77.0, 104.6, 113.1, 125.4, 127.0, 128.4, 148.1, 148.3 ppm. **HRMS** (APCI) for $C_{15}H_{20}O_2$ [M-

$(OMe)_2]^+$: calculated 232.1463, found 232.1412.

Optical rotation: $[\alpha]_D^{20}$= -52.9 (*c* 1.0, CH_2Cl_2, 91% *ee*). The enantiomeric excess of *syn*-**4ad** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 42.2 min (minor), t_R = 50.7 min (major).

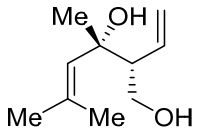


syn-**4af**
$C_{18}H_{20}O_2$
M = 268.36 g/mol

(2*R*,3*R*)-3-phenyl-2-(1-phenylvinyl)butane-1,3-diol (*syn*-**4af**): Prepared from acetophenone (**1a**, 24.0 mg, 0.20 mmol) according to **Condition B** with buta-1,3-dien-2-ylbenzene (**2e**) and $B_2(Pin)_2$ at –5 °C for 60 h (***Note**: 10 mol% CuOAc, 12 mol% **L9**, 50 mol% NaOtBu and 2.0 equiv. $B_2(pin)_2$ were used*). Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4ae** as a colorless oil (37.6 mg, 70% yield, *syn*:*anti* > 98:2, *syn*-**4ae**: 85% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.46 (s, 3H), 2.03 (broad s, 1H), 2.89 (broad s, 1H), 3.28 (dd, *J* = 6.66, 5.00 Hz, 1H), 3.67 (dd, *J* = 11.28, 4.96 Hz, 1H), 3.79 (dd, *J* = 11.33, 6.76 Hz, 1H), 5.55 (s, 2H), 7.19–7.22 (m, 1H), 7.25–7.37 (m, 7H), 7.43–7.45 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 29.3, 55.6, 63.5, 76.9, 116.3, 124.8, 126.5, 126.7, 127.4, 128.2, 128.4, 144.5, 146.9, 148.1 ppm. **HRMS** (APCI) for $C_{18}H_{19}O$ [M-OH]$^+$: calculated 251.1436, found 251.1428.

Optical rotation: $[\alpha]_D^{20}$= -149.0 (*c* 0.5, $CHCl_3$, 85% *ee*). The enantiomeric excess of *syn*-**4af** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 69.9 min (minor), t_R = 83.7 min (major).

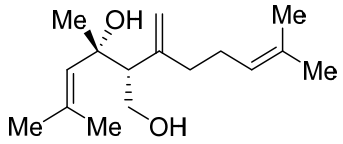


syn-**4nb**
$C_{10}H_{18}O_2$
M = 170.25 g/mol

(2*R*,3*S*)-3,5-Dimethyl-2-vinylhex-4-ene-1,3-diol (*syn*-**4nb**): Prepared from 4-methylpent-3-en-2-one (**1n**, 20.0 mg, 0.20 mmol) according to **Condition B** with buta-1,3-diene (**2b**) and $B_2(Pin)_2$ at –20 °C for 80 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 afforded **4nb** as a colorless oil (28.3 mg, 83% yield, *syn*:*anti* = 96:4, *syn*-**4nb**: 92% *ee*).

R_f = 0.45 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.30 (s, 3H), 1.71 (d, *J* = 1.36 Hz, 3H), 1.86 (d, *J* = 1.28 Hz, 3H), 2.40 (dt, *J* = 9.07, 5.77 Hz, 1H), 3.77 (dd, *J* = 10.64, 5.62 Hz, 1H), 3.85 (dd, *J* = 10.79, 5.91 Hz, 1H), 5.13–5.22 (m, 2H), 5.23–5.24 (m, 1H), 5.83 (ddd, *J* = 17.20, 10.45 and 9.20 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.9, 26.8, 27.5, 55.7, 63.7, 75.4, 118.8, 130.3, 134.5, 136.0 ppm. **HRMS** (APCI) for $C_{10}H_{17}O$ $[M\text{-}OH]^+$: calculated 154.1358, found 154.1306.

Optical rotation: $[\alpha]_D^{20}$= -4.7 (*c* 1.0, CH_2Cl_2, 92% *ee*). The enantiomeric excess of *syn*-**4nb** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.3 mL/min): t_R = 42.6 min (minor), t_R = 44.9 min (major).



syn-**4nc**
$C_{16}H_{28}O_2$
M = 252.40 g/mol

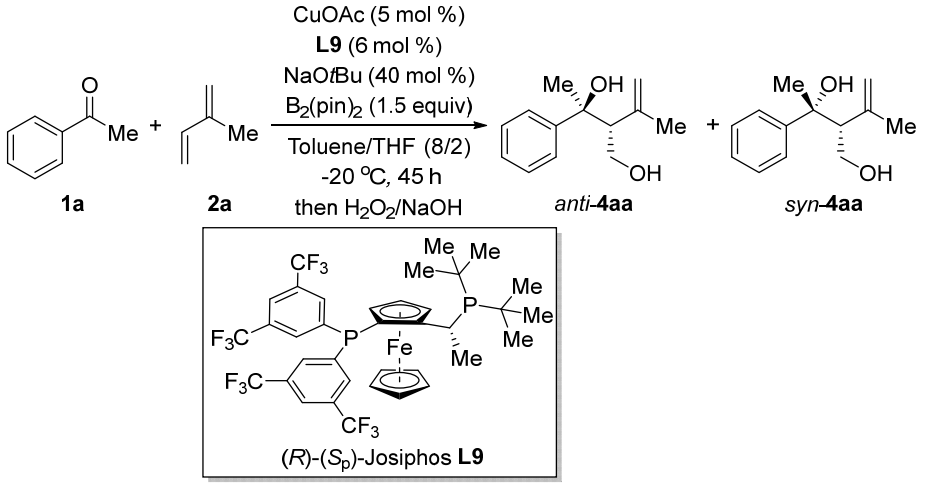
(2*R*,3*S*)-3,5-Dimethyl-2-(6-methylhepta-1,5-dien-2-yl)hex-4-ene-1,3-diol (*syn*-**4nc**): Prepared from 4-methylpent-3-en-2-one (**1n**, 20.0 mg, 0.20 mmol) according to **Condition B** with myrcene (**2c**) and $B_2(Pin)_2$ at –20 °C for 56 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 5/1 afforded **4nc** as a colorless oil (37.7 mg, 75% yield, *syn*:*anti* > 98:2, *syn*-**4nc**: 92% *ee*).

R_f = 0.40 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.61

(s, 3H), 1.68 (s, 3H), 1.70 (d, *J* = 1.36 Hz, 3H), 1.87 (d, *J* = 1.32 Hz, 3H), 2.07–2.19 (m, 4H), 2.22 (broad s, 1H), 2.33 (broad s, 1H), 2.45 (t, *J* = 6.48 Hz, 1H), 3.75–3.81 (m, 1H), 3.85–3.90 (m, 1H), 4.99 (s, 1H), 5.04 (s, 1H), 5.07–5.11 (m, 1H), 5.20–5.21 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 17.7, 18.8, 25.6, 26.4, 27.4, 27.5, 38.6, 56.1, 63.3, 75.6, 112.6, 123.8, 130.6, 132.0, 133.9, 148.3 ppm. **HRMS** (APCI) for $C_{16}H_{27}O$ [M-OH]$^+$: calculated 235.2062, found 235.2052.

Optical rotation: $[\alpha]_D^{20}$= -22.2 (*c* 1.0, CH_2Cl_2, 92% *ee*). The enantiomeric excess of *syn*-**4nc** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.25 mL/min): t_R = 62.4 min (major), t_R = 65.0 min (minor).

4 Scale-up Experiment (1.0 mmol)

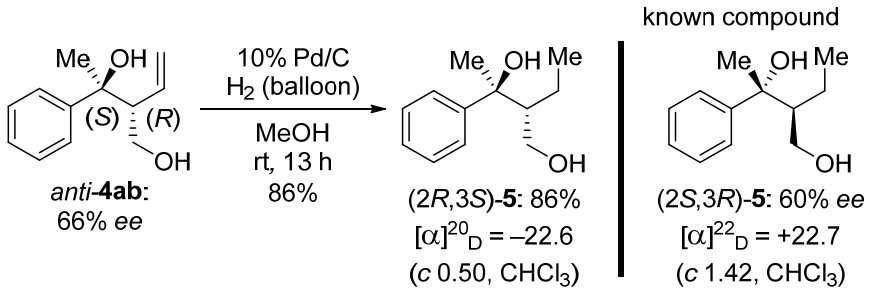


In a nitrogen-filled glovebox, to a flame-dried Schlenk tube was added CuOAc (6.1 mg, 50 μmol, 5 mol%), ligand **L9** (49 mg, 60 μmol, 6 mol%), NaO*t*Bu (40.0 mg, 400 μmol, 40 mol%). The tube was taken out of the glovebox, evacuated, and backfilled with N_2 (3 times) followed by the addition of toluene/THF (3.0 mL, 8/2, v/v). After stirring for 30 min at room temperature, $B_2(pin)_2$ (381 mg, 1.50 mmol, 1.5 equiv.) in toluene/THF (3.0 mL, 8/2, v/v) was added. After stirring at room temperature for about 1 min, it was cooled to –20 °C. isoprene **2a** (0.5 mL, 5.0 mmol, 5.0 equiv.) was added via syringe, followed by acetophenone **1a** (121 mg, 1.0 mmol, 1.0 equiv.) in toluene/THF (2.0 mL, 8/2, v/v). The resulting solution was stirred at –20 °C for 45 h. The reaction was then

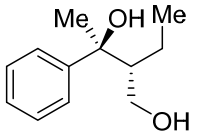
quenched by 0.6 mL saturated ammonium chloride water solution. The mixture was concentrated *in vacuo*. To the residue was then added 15.0 mL THF, 3 M NaOH (3.0 mL) ,and 30% H_2O_2 (3.0 mL) at 0 °C. After stirring at 0 °C for 30 min, brine (20 mL) was added. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. It was then analyzed by ^{1}H NMR spectroscopy to obtain the diastereoselectivity. The crude product was purified by column chromatography on silica gel (5:1 to 3:1 *n*-pentane/EtOAc) to afford **4aa** as a a colorless oil (183.5 mg, 89% yield, *syn*:*anti* = 87:13, *anti*-**4aa** = 71% *ee*, *syn*-**4aa** = 93% *ee*).

5 Determination of the Absolute Configurations of the Products

The absolute configuration of *anti*-**4ab** was confirmed by converting *anti*-**4ab** into compound (2*R*,3*S*)-**5**. Based on comparison of the sign of the optical rotation of **5** [(2*S*,3*R*)-**5** is a known compound,[6] $[\alpha]_D^{22}$ = +22.7 (*c* 1.42, $CHCl_3$), 60% *ee*], the absolute configuration of *anti*-**4ab** was determined to be *R*,*S*. The absolute configurations of other *anti*-products were deduced by analogy.



To a solution of *anti*-**4ab** (12.0 mg, 0.06 mmol, 1.00 equiv.) and MeOH (1.5 mL) was added 10% palladium on carbon (1.2 mg, 10% by weight). The mixture was stirred under a hydrogen gas atmosphere (balloon) for 13 h at room temperature. The mixture was filtered through a pad of Celite and concentrated. The residue was purified by column chromatography on silica gel (5:1 *n*-pentane/EtOAc) to afford target product (2*R*,3*S*)-**5** as a colorless oil (10.4 mg, 86% yield).



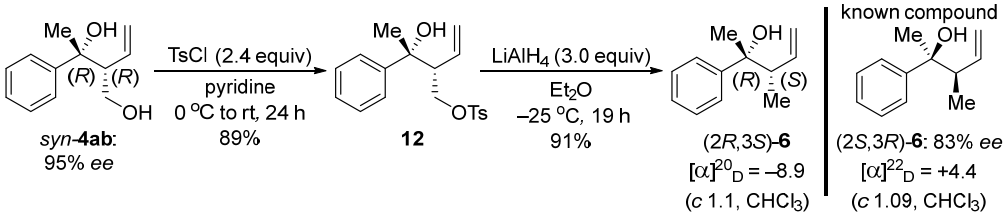
(2*R*,3*S*)-**5**
$C_{12}H_{18}O_2$
M = 194.27 g/mol

(2*R*,3*S*)-2-ethyl-3-phenylbutane-1,3-diol ((2*R*,3*S*)-**5):**

R_f = 0.5 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.75 (t, *J* = 7.47 Hz, 3H), 1.13–1.22 (m, 2H), 1.58 (s, 3H), 1.58–1.63 (m, 1H), 3.66 (dd, *J* = 11.26, 4.87 Hz, 1H), 3.97 (dd, *J* = 11.30, 2.53 Hz, 2H), 7.14–7.33 (m, 5H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 12.6, 18.7, 29.7, 51.0, 61.5, 78.5, 124.9, 126.5, 128.0, 146.9 ppm. **HRMS** (APCI) for $C_{12}H_{17}O_2$ [M-H]$^+$: calculated 193.12231, found. 193.12269.

Optical rotation: $[\alpha]_D^{20}$= –22.6 (*c* 0.5, $CHCl_3$).

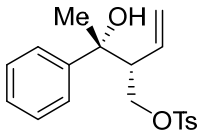
The absolute configuration of *syn*-**4ab** was determined after conversion to compound (2*R*,3*S*)-**6**, which can also be generated from the reported catalytic asymmetric allylation acetphenone with crotylborate [(2*S*,3*R*)-**6** is known compound,[7] $[\alpha]_D^{22}$= +4.4 (*c* 1.09, $CHCl_3$), 83% *ee*]. Based on comparison of the sign of the optical rotation of **6**, the absolute configuration of *syn*-**4ab** was determined to be *R*,*R*. The absolute configurations of other *syn*-products were deduced by analogy.



To a stirred solution of *syn*-**4ab** (50.0 mg, 0.26 mmol, 1.0 equiv.) in pyridine (2.5 mL) at 0 °C was added tosyl chloride (62.0 mg, 0.31 mmol, 1.2 equiv.) in one portion. After being stirred at 0 °C for 8 h, an additional portion of tosyl chloride (62.0 mg, 0.31 mmol, 1.2 equiv.) was added. The mixture was stirred an additional 16 h at room temperature. The mixture was concentrated under vacuum to remove the pyridine. The mixture was quenched with brine (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried, and concentrated. The residue was purified by column chromatography on silica gel

(cyclohexane/EtOAc = 5/1) to afford target product **12** (80.2 mg, 89% yield) as a white solid.

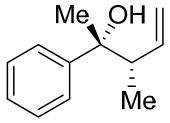
To a flame-dried Schlenk tube was added tosylate **12** (62.0 mg, 0.18 mmol, 1.0 equiv.) and Et_2O (5 mL). The tube was cooled to –25 °C. Lithium aluminum hydride (21.0 mg, 0.54 mmol, 3.0 equiv.) was added in one portion. After stirring at –25 °C for 19 h, H_2O (21 μL), 15% aqueous NaOH (21 μL), and H_2O (63 μL) were added successively. Filtration and evaporation gave crude product. The residue was purified by column chromatography on silica gel (10:1 *n*-pentane/EtOAc) to afford (2*R*,3*S*)-**6** as a colorless oil (28.6 mg, 91% yield).



12
$C_{19}H_{22}O_4S$
M = 346.44 g/mol

(*R*)-2-((*R*)-1-Hydroxy-1-phenylethyl)but-3-en-1-yl 4-methylbenzenesulfonate (12):

R_f = 0.48 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.39 (s, 3H), 1.82 (s, 1H), 2.35 (s, 3H), 2.59-2.64 (m, 1H), 3.82 (dd, *J* = 10.06, 3.81 Hz, 1H), 3.89 (dd, *J* = 10.06, 8.68 Hz, 1H), 5.04–5.09 (m, 1H), 5.18 (dd, *J* = 10.33, 1.53 Hz, 1H), 5.62–5.71 (m, 1H), 7.14–7.24 (m, 7H), 7.53 (d, *J* = 8.34 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 29.4, 53.9, 70.3, 75.2, 120.4, 124.6, 126.9, 127.9, 128.3, 129.6, 132.8, 134.0, 144.5, 145.9 ppm. **HRMS** (APCI) for $C_{19}H_{22}O_4SNa$ $[M+Na]^+$: calculated 369.1137, found. 369.1127. Optical rotation: $[\alpha]_D^{20}$= +18.6 (*c* 1.0, CH_2Cl_2).



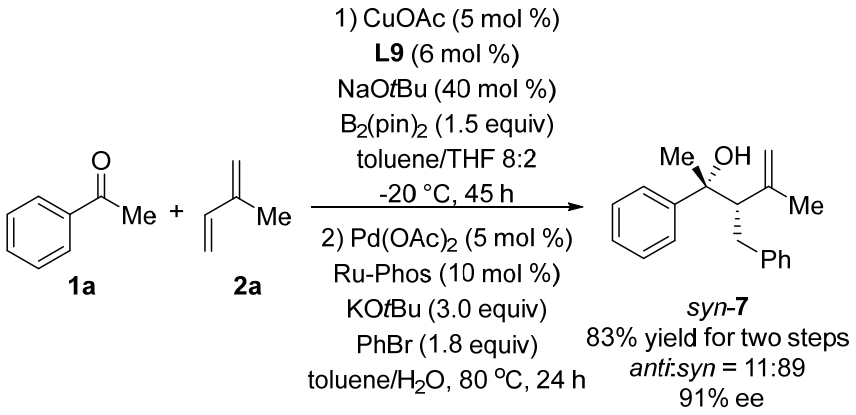
(*2R,3S*)-**6**
$C_{12}H_{16}O$
M = 176.26 g/mol

(2*R*,3*S*)-3-Methyl-2-phenylpent-4-en-2-ol ((2*R*,3*S*)-**6):**

R_f = 0.5 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (d, *J* = 6.99 Hz, 3H), 1.54 (s, 3H), 1.87 (s, 1H), 2.55 (q, *J* = 6.72 Hz, 1H), 5.09–5.12 (m, 1H), 5.13–5.14 (m, 1H), 5.78–5.87 (m, 1H), 7.22–7.26 (m, 1H), 7.32–7.36 (m, 2H), 7.39–7.42 (m,

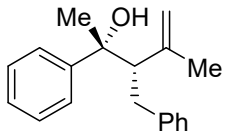
2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.8, 28.5, 48.9, 75.8, 116.3, 125.2, 126.4, 127.9, 139.9, 146.9 ppm. **HRMS** (APCI) for $C_{12}H_{15}$ $[M\text{-}OH]^+$: calculated 159.1174, found. 159.1166. Optical rotation: $[\alpha]_D^{20}$= -8.9 (*c* 1.1, $CHCl_3$).

6 Transformations of the Products



In a nitrogen-filled glovebox, to a flame-dried Schlenk tube was added CuOAc (2.5 mg, 20 μmol, 5 mol%), ligand **L9** (20 mg, 24 μmol, 6 mol%), NaO*t*Bu (16.0 mg, 160 μmol, 40 mol%). The tube was taken out of the glovebox, evacuated, and backfilled with N_2 (3 times) followed by the addition of toluene/THF (2.0 mL, 8/2, v/v). After stirring for 30 min at room temperature, $B_2(pin)_2$ (152 mg, 0.60 mmol, 1.5 equiv.) in toluene/THF (1.0 mL, 8/2, v/v) was added. After stirring at room temperature for about 1 min, it was cooled to –20 °C. Isoprene **2a** (200 μL, 2.0 mmol, 5.0 equiv.) was added via syringe, followed by acetophenone **1a** (48.1 mg, 0.40 mmol, 1.0 equiv.) in toluene/THF (0.5 mL, 8/2, v/v). After stirring at -20 °C for 45 h, The reaction was quenched by passing the mixture through a short plug of celite and eluting with Et_2O. The filtrate was concentrated in *vacuo* to provide a crude mixture as a yellow oil, which was used in the next step without further purification. $Pd(OAc)_2$ (5.0 mg, 20 μmol, 5 mol%), RuPhos (19 mg, 40 μmol, 10 mol%), KO*t*Bu (135 mg, 1.2 mmol, 3.0 equiv.), and bromobenzene (112 mg, 0.72 mmol, 1.8 equiv.) were added to a solution of unpurifed mixture obtained from previous step in toluene (3.0 mL) and water (0.3 mL). The solution was stirred at 80 °C for 24 h. Then, the reaction was quenched by passing the mixture through a short plug of celite and eluting with Et_2O. The filtrate was concentrated and purified by silica gel chromatography (5:1 cyclohexane/EtOAc) to afford **7** (88.0 mg, 83% yield for

two steps, *syn*:*anti* = 89:11, *syn*-**7** = 91% *ee*) as a colorless oil.

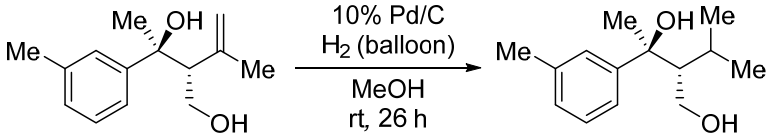


syn-**7**
$C_{19}H_{22}O$
M = 266.38 g/mol

(2*R*,3*S*)-3-Benzyl-4-methyl-2-phenylpent-4-en-2-ol (*syn*-7):

R_f = 0.48 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55 (s, 3H), 1.67 (s, 3H), 1.99 (broad s, 1H), 2.57 (dd, *J* = 13.15, 2.03 Hz, 1H), 2.67 (t, *J* = 13.06 Hz, 1H), 2.73 (dd, *J* = 11.70, 2.25 Hz, 1H), 4.84 (s, 1H), 4.96 (s, 1H), 6.94 (d, *J* = 7.11 Hz, 2H), 7.07–7.10 (m, 1H), 7.14–7.17 (m, 2H), 7.24–7.28 (m, 1H), 7.36–7.40 (m, 2H), 7.52–7.53 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 23.9, 29.9, 34.4, 59.3, 76.3, 114.9, 124.9, 125.5, 126.5, 127.9, 128.1, 128.7, 141.2, 144.8, 147.7 ppm. **HRMS** (APCI) for $C_{19}H_{21}$ $[M\text{-}OH]^+$: calculated 249.1643, found. 249.1646.

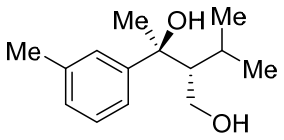
Optical rotation: $[\alpha]_D^{20}$= -29.6 (*c* 1.0, CH_2Cl_2, 91% *ee*). The enantiomeric excess of *syn*-**7** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 14.0 min (major), t_R = 15.5 min (minor).



anti-**4ha**
ee = 92%
d.r. > 98:2

anti-**8**
ee = 90%
d.r. > 98:2

To a solution of *anti*-**4ha** (13.0 mg, 0.06 mmol, 1.00 equiv.) in1.5 mL MeOH was added 10% palladium on carbon (1.3 mg, 10% by weight). The mixture was stirred under a hydrogen gas atmosphere (balloon) for 26 h at room temperature. The mixture was filtered through a pad of Celite and concentrated. The residue was purified by column chromatography on silica gel (5:1 *n*-pentane/EtOAc) to afford target product *anti*-**8** as a colorless oil (11.6 mg, 87 % yield, 90% *ee*).

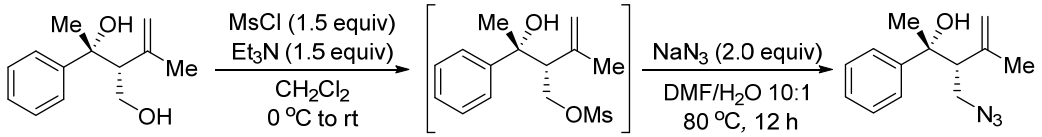


anti-**8**
$C_{14}H_{22}O_2$
M = 222.33 g/mol

(2*R*,3*S*)-2-Isopropyl-3-(*m*-tolyl)butane-1,3-diol (*anti*-8):

R_f = 0.3 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.68 (d, *J* = 6.86 Hz, 3H), 0.85 (d, *J* = 6.98 Hz, 3H), 1.69 (s, 3H), 1.72–1.79 (m, 2H), 2.37 (s, 3H), 2.75 (broad s, 1H), 3.15 (broad s, 1H), 3.93–4.01 (m, 2H), 7.05–7.09 (m, 1H), 7.20–7.23 (m, 2H), 7.28 (s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.6, 21.7, 24.4, 26.8, 30.5, 53.9, 60.5, 79.2, 122.3, 125.9, 127.3, 127.9, 137.6, 147.0 ppm. **HRMS** (APCI) for $C_{14}H_{21}O$ $[M\text{-}OH]^+$: calculated 205.1585, found. 205.1592.

Optical rotation: $[\alpha]_D^{20}$= -76.8 (*c* 0.25, CH_2Cl_2, 90% *ee*). The enantiomeric excess of *anti*-**8** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.3 mL/min): t_R = 26.4 min (minor), t_R = 27.9 min (major).

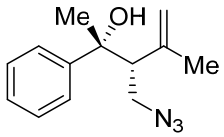


syn-**4aa**
93% *ee*
d.r. > 98:2

syn-**9**
93% *ee*
d.r. > 98:2

Compound *syn*-**4aa** (20.6 mg, 0.10 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (1.0 mL) at 0 °C. Et_3N (21 µL, 0.15 mmol, 1.5 equiv.) was added, followed by the addition of MsCl (12 µL, 0.15 mmol, 1.5 equiv.). Then the reaction mixture was stired for 50 min at room temperature, before being poured into saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated and washed with saturated aqueous NaCl, dried over $MgSO_4$. The filterate was concentrated under reduced pressure. The resulting residue was dissolved in 1.5 mL DMF/H_2O (10:1) and NaN_3 (13 mg, 0.20 mmol, 2.0 equiv.) was added. The solution was stired at 80 °C for 12 h. Then it was cooled to room temperature, diluted with H_2O (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layers were concentrated under reduced pressure to give crude

reaction mixture, which was purified by flash column chromatography (10:1 *n*-pentane/EtOAc) to afford *syn*-**9** (18.7 mg, 81% for two steps, 93% *ee*) as a colorless oil.

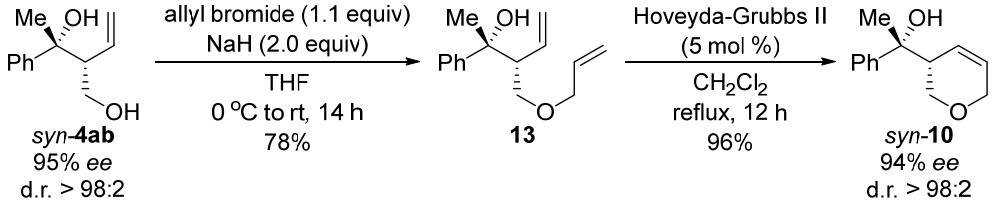


syn-**9**
$C_{13}H_{17}N_3O$
M = 231.29 g/mol

(2*R*,3*R*)-3-(Azidomethyl)-4-methyl-2-phenylpent-4-en-2-ol (*syn*-9):

R_f = 0.45 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.50 (s, 3H), 1.87 (s, 3H), 2.02 (s, 1H), 2.65 (dd, *J* = 11.03, 3.96 Hz, 1H), 3.11 (dd, *J* = 12.57, 3.99 Hz, 1H), 3.41 (dd, *J* = 12.44, 11.01 Hz, 1H), 5.03 (s, 1H), 5.14–5.15 (m, 1H), 7.24–7.28 (m, 1H), 7.34–7.38 (m, 2H), 7.42–7.45 (m, 2H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 23.2, 30.4, 51.0, 57.0, 75.8, 116.1, 125.1, 127.1, 128.6, 144.3, 147.5 ppm. **HRMS** (APCI) for $C_{13}H_{18}NO$ $[M+H-N_2]^+$: calculated 204.13829, found. 204.13838.

Optical rotation: $[\alpha]_D^{20}$= -18.6 (*c* 0.5, CH_2Cl_2, 93% *ee*). The enantiomeric excess of *syn*-**9** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 15.1 min (major), t_R = 16.3 min (minor).



syn-**4ab**
95% *ee*
d.r. > 98:2

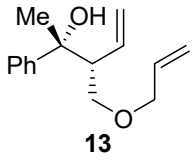
13

syn-**10**
94% *ee*
d.r. > 98:2

To a suspension of NaH (18 mg of 60% dispersion in mineral oil, 0.44 mmol, 2.0 equiv.) in THF (1.5 mL) was added dropwise a solution of *syn*-**4ab** (42.0 mg, 0.22 mmol, 1.0 equiv.) in THF (0.6 mL) at 0 ºC. The mixture was stirred for 30 min at room temperature and then allyl bromide (21.0 µL, 0.24 mmol, 1.1 equiv.) was added dropwise at 0 ºC. The reaction mixture was stirred for 14 hours at room temperature, at which point the reaction was quenched with water and extracted with diethyl ether (5 mL ×3). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed

in vacuo. The obtained residue was purified by flash column chromatography on silica gel (10:1 *n*-pentane/EtOAc) to furnish **13** (39.7 mg, 78 % yield) as a colorless oil.

To a stirred solution of **13** (31 mg, 0.13 mmol, 1.0 equiv) in CH_2Cl_2 (7 mL, 0.02 M) was added Hoveyda-Grubbs II catalyst (4.2 mg, 0.007 mmol, 5 mol%). After stirring at 40 °C for 12 h, it was cooled to room temperature and the reaction solvent was removed *in vacuo*. The obtained residue was purified by flash column chromatography on silica gel (5:1 *n*-pentane/EtOAc) to furnish *syn*-**10** (26.3 mg, 96% yield, 95% *ee*) as a colorless oil.

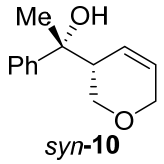


13

$C_{15}H_{20}O_2$

M = 232.32 g/mol

(2*R*,3*R*)-3-((allyloxy)methyl)-2-phenylpent-4-en-2-ol (13): R_f = 0.40 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.46 (s, 3H), 2.56 (dt, *J* = 9.26, 3.61 Hz, 1H), 3.31 (dd, *J* = 9.06, 3.67 Hz, 1H), 3.42 (dd, *J* = 9.12, 3.67 Hz, 1H), 3.73–3.83 (m, 2H), 4.25 (s, 1H), 5.11–5.20 (m, 3H), 5.22 (dd, *J* = 10.33, 1.99 Hz, 1H), 5.74–5.83 (m, 1H), 6.14–6.23 (m, 1H), 7.21–7.26 (m, 1H), 7.32–7.36 (m, 2H), 7.42–7.45 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.4, 53.8, 72.4, 72.9, 76.6, 117.3, 117.8, 124.9, 126.4, 128.0, 133.9, 136.5, 148.1 ppm. **HRMS** (APCI) for $C_{15}H_{19}O$ [M-OH]$^+$: calculated 215.1436, found. 215.1429.



syn-**10**

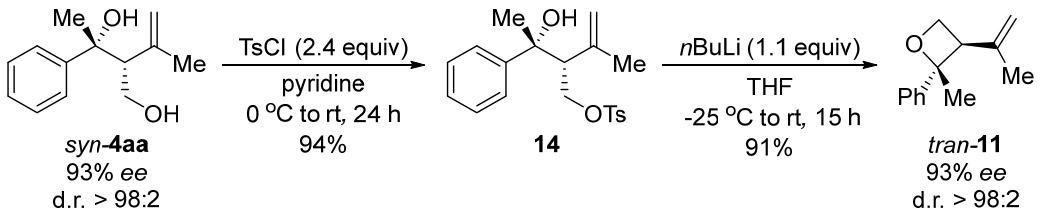
$C_{13}H_{16}O_2$

M = 204.27 g/mol

(*R*)-1-((*R*)-3,6-Dihydro-2H-pyran-3-yl)-1-phenylethan-1-ol (*syn*-10): R_f = 0.30 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.56 (s, 3H), 2.43–2.46 (m, 1H), 3.48 (dd, *J* = 11.67, 3.98 Hz, 1H), 3.56 (s, 1H), 3.71–3.75 (m, 1H), 4.07–4.13 (m, 1H), 4.16–4.21 (m, 1H), 5.97–6.01 (m, 1H), 6.04–6.09 (m, 1H), 7.22–7.27 (m, 1H),

7.33–7.38 (m, 2H), 7.46–7.49 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.0, 43.6, 66.0, 66.4, 76.9, 124.2, 125.0, 126.5, 128.2, 129.3, 147.8 ppm. **HRMS** (APCI) for $C_{13}H_{15}O$ [M-OH]$^+$: calculated 187.1123, found. 187.1114.

Optical rotation: $[\alpha]_D^{20}$= -43.3 (*c* 1.0, CH_2Cl_2, 94% *ee*). The enantiomeric excess of *syn*-**10** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.5 mL/min): t_R = 30.6 min (minor), t_R = 35.9 min (major).



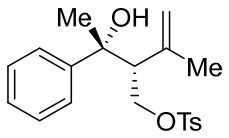
syn-**4aa**
93% *ee*
d.r. > 98:2

14

tran-**11**
93% *ee*
d.r. > 98:2

To a stirred solution of *syn*-**4aa** (42.0 mg, 0.20 mmol, 1.0 equiv.) in pyridine (2.5 mL) at 0 °C was added tosyl chloride (45.8 mg, 0.24 mmol, 1.2 equiv.) in one portion. After being stirred at 0 °C for 8 h, an additional portion of tosyl chloride (45.8 mg, 0.24 mmol, 1.2 equiv.) was added. The mixture was stirred an additional 16 h at room temperature. The mixture was concentrated under vacuum to remove the pyridine. The mixture was quenched with brine (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried, and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc = 5/1) to afford target product **14** (67.8 mg, 94% yield) as a white solid.

To a flame-dried Schlenk tube was added tosylate **14** (37.5 mg, 0.10 mmol, 1.0 equiv.) and THF (1.5 mL). The tube was cooled to –25 °C. 2.5 M *n*BuLi (48.0 μL, 0.11 mmol, 1.1 equiv.) was added via syringe. After stirring at –25 °C for 1 h, it was warmed to room temperature and stirred an additional 14 h at room temperature. Then it was quenched by *aq* NH_4Cl (0.2 mL). $MgSO_4$ (100 mg) were added and the mixture was filtered. Careful rotary evaparator concentration provided the crude volatile **11**. The residue was purified by column chromatography on silica gel (20:1 *n*-pentane/Et_2O) to afford *trans*-**11** (17.1 mg, 91% yield, 93% *ee*) as a colorless oil.

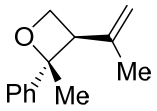


14

$C_{20}H_{24}O_4S$

M = 360.47 g/mol

(*R*)-2-((*R*)-1-Hydroxy-1-phenylethyl)-3-methylbut-3-en-1-yl 4-methylbenzene sulfonate (14): R_f = 0.45 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.66 (s, 3H), 1.74 (broad s, 1H), 2.35 (s, 3H), 2.66 (dd, *J* = 10.54, 3.96 Hz, 1H), 3.77 (dd, *J* = 10.20, 3.91 Hz, 1H), 4.05 (t, *J* = 10.34 Hz, 1H), 4.75 (s, 1H), 4.95–4.96 (m, 1H), 7.14–7.18 (m, 3H), 7.19–7.27 (m, 4H), 7.50 (d, *J* = 8.32 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 23.1, 29.9, 55.9, 69.8, 75.2, 115.9, 124.5, 126.9, 127.9, 128.3, 129.6, 132.8, 142.1, 144.4, 146.2 ppm. **HRMS** (APCI) for $C_{20}H_{23}O_4S$ $[M-H]^+$: calculated 359.13116, found. 359.13104.



trans-**11**

$C_{13}H_{16}O$

M = 188.27 g/mol

(2*R*,3*R*)-2-Methyl-2-phenyl-3-(prop-1-en-2-yl)oxetane (*trans*-11):

R_f = 0.45 (cyclohexane/EtOAc = 20/1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.54 (s, 3H), 1.81 (s, 3H), 3.54 (t, *J* = 7.86 Hz, 1H), 4.52 (dd, *J* = 8.38, 6.26 Hz, 1H), 4.69 (dd, *J* = 7.75, 6.35 Hz, 1H), 4.96 (s, 1H), 5.14 (s, 1H), 7.24–7.29 (m, 1H), 7.36–7.40 (m, 2H), 7.45–7.48 (m, 2H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 23.2, 23.9, 52.4, 67.4, 89.0, 112.8, 124.2, 127.2, 128.7, 141.8, 149.2 ppm. **HRMS** (APCI) for $C_{13}H_{17}O$ $[M+H]^+$: calculated 189.12739, found:189.12771.

Optical rotation: $[\alpha]_D^{20}$= +62.5 (*c* 0.4, CH_2Cl_2, 93% *ee*). The enantiomeric excess of *trans*-**11** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.25 mL/min): t_R = 21.9 min (major), t_R = 25.5 min (minor).

7 Proposed Catalytic Cycle and Model for the Stereochemical Outcome

Based on literature reports,[8] a plausible mechanism is depicted in Figure S1. The boron nucleophile Cu–B(pin)[9] is formed by the reaction of the copper (pre)catalyst and the base with $B_2(pin)_2$. A formal migratory insertion of 1,3-diene **2b** into the copper–boron bond then leads to the thermodynamically more stable (*Z*)-allylcopper complex **B**,[10] which can undergo diastereoselective addition to the ketone **1a** to afford intermediates **C** and **D**. Subsequent transmetalation with $B_2(pin)_2$ regenerates Cu–B(pin) and releases the product **E** (Figure S1, top). Hydrolysis eventually affords the tertiary homoallylic alcohol **3ab**. However, the corresponding (*E*)-allylcopper complex cannot be excluded as the actual carbon nucleophile. For example, Hoveyda and co-workers reported a copper-catalyzed borylative coupling of 1,3-dienes and α,β-unsaturated acceptors.[8c] Based on DFT calculations, a catalytic cycle that involves the participation of the (*E*)-allylcopper complex was proposed, and another plausible catalytic cycle could therefore be operative (Figure S1, bottom).

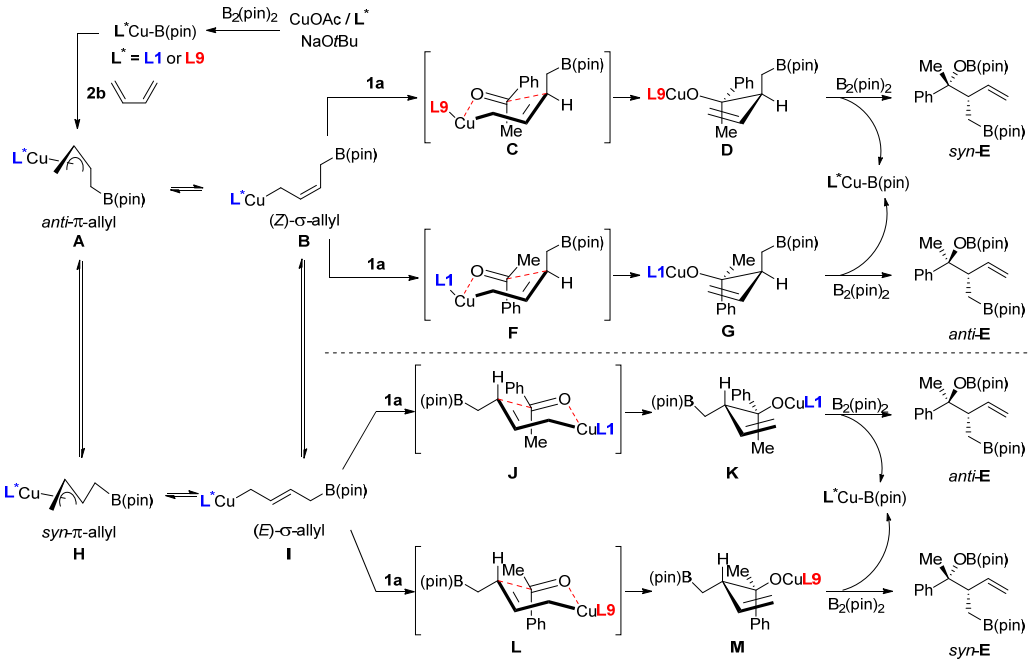


Figure S1. Proposed catalytic cycle.

The enantio- and diastereoselectivity are both determined in the ketone addition step, which proceeds through a six-membered Zimmerman−Traxler-type transition state.[11] The stereochemical course will be sensitive to the steric environment around the

copper catalyst, thereby leading to a dramatic switch in diastereoselectivity depending on the chiral ligand structure. We did not find sufficiently convincing literature support to derive mechanistic models to rationalize the stereochemical outcome with **L1** as the ligand. One issue is the copper/ligand ratio. Feringa and co-workers reported the molecular structure of a copper–MonoPhos complex where three chiral phosphoramidite ligands are bound to the copper center creating a C_3-symmetrical complex.[12] It is therefore hard to show models. In turn, Liu, Buchwald, and co-workers recently reported a copper-catalyzed enantioselective reductive coupling of ketones and 1,3-dienes with a josiphos chiral ligand.[8a] In that work, a stereochemical model has been provided to explain the diastereo- and enantioselectivity of the process. Based on those computations, we propose a stereochemical model that accounts for the observed enantioselectivity of the *syn*-products (Figure S2).

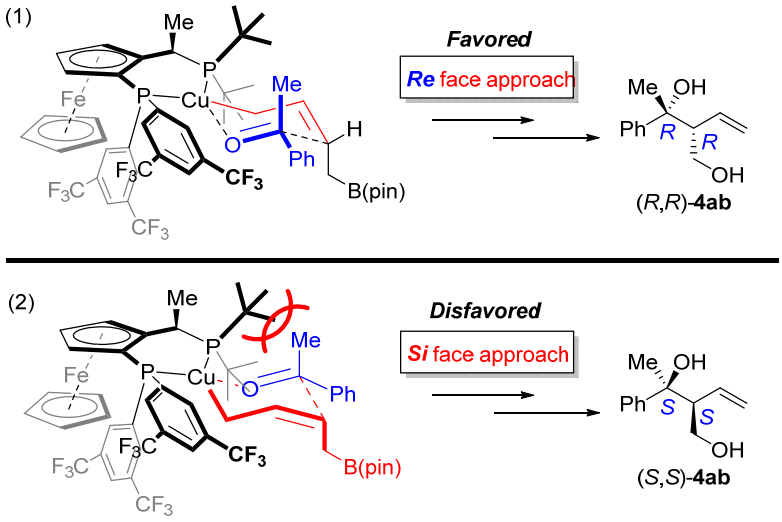
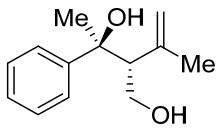


Figure S2. A plausible model for the stereochemical outcome.

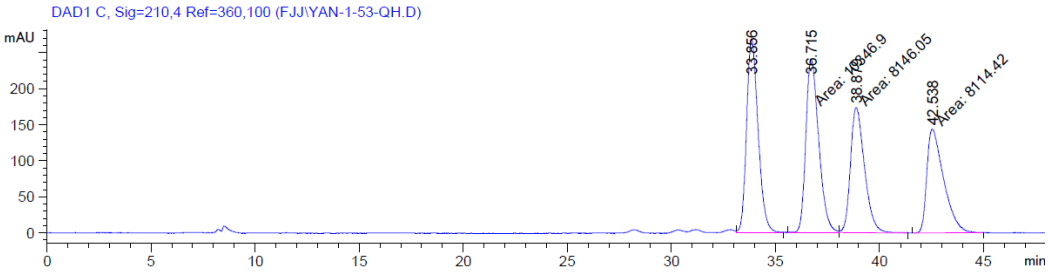
As can be seen from Table 1 in the manuscript, replacing the cyclohexyl substituents on a phosphorus atom of **L6** (or **L7**) with bulkier *t*Bu groups markedly enhanced the enantioselectivity (**L6** *vs* **L8** and **L7** *vs* **L9**). However, a slight modification of the substituents on the other phosphorus atom from 3,5-$(CF_3)_2C_6H_3$ group (as in **L9**) to smaller phenyl- (as in **L8**) or 3,5-Me_2-4-$MeOC_6H_2$ group (as in **L10**) produced similar enantioselectivity, albeit with significantly decreased reactivity. The model depicted in Figure S2 is in agreement with the stereochemical information observed in these experiments.

8 HPLC Traces



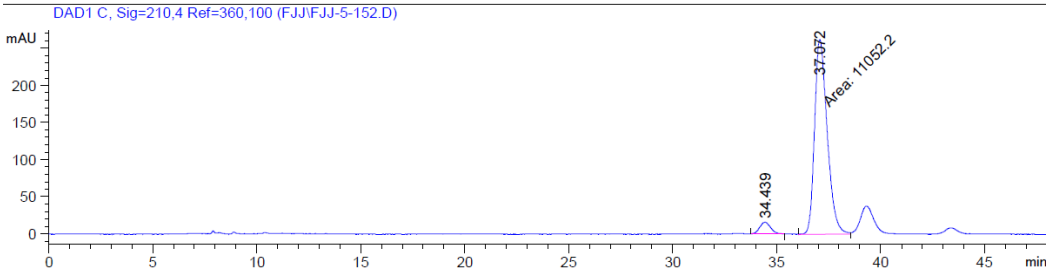
anti-**4aa**

(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4aa**): The enantiomeric excess of *anti*-**4aa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 34.4 min (minor), t_R = 37.1 min (major).



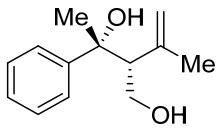
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.856	VB	0.6013	1.03414e4	268.53079	27.9884
2	36.715	MF	0.7164	1.03469e4	240.72768	28.0034
3	38.879	FM	0.7824	8146.05420	173.51753	22.0469
4	42.538	MM	0.9384	8114.42236	144.12112	21.9613



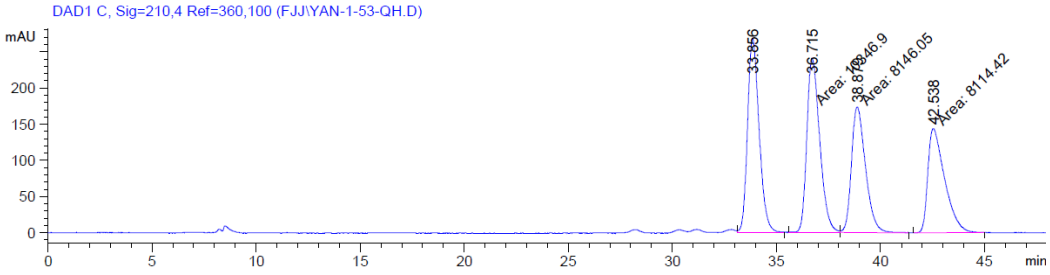
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.439	BB	0.4426	586.77441	16.04716	5.0414
2	37.072	MF	0.7038	1.10522e4	261.70926	94.9586



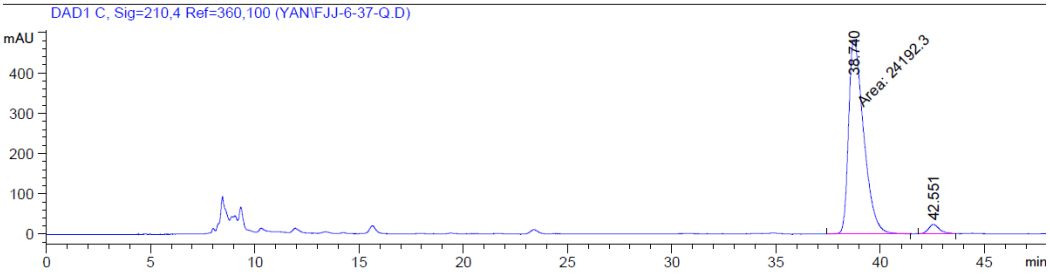
syn-**4aa**

(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4aa**): The enantiomeric excess of *syn*-**4aa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 38.7 min (major), t_R = 42.6 min (minor).



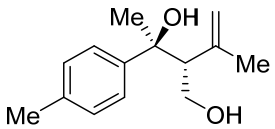
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.856	VB	0.6013	1.03414e4	268.53079	27.9884
2	36.715	MF	0.7164	1.03469e4	240.72768	28.0034
3	38.879	FM	0.7824	8146.05420	173.51753	22.0469
4	42.538	MM	0.9384	8114.42236	144.12112	21.9613



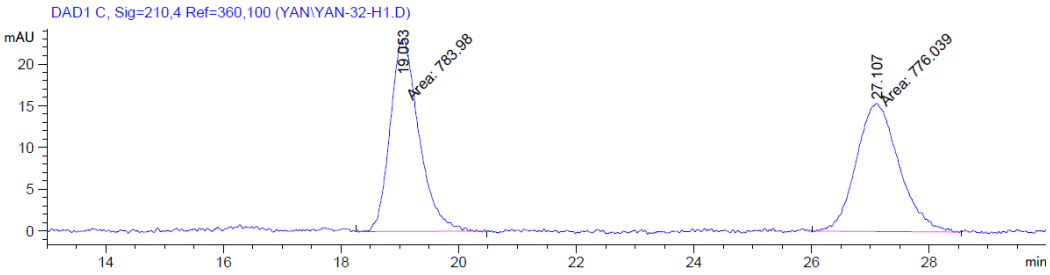
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.740	MM	0.8360	2.41923e4	482.29706	96.5096
2	42.551	VV	0.4524	874.94977	23.60606	3.4904



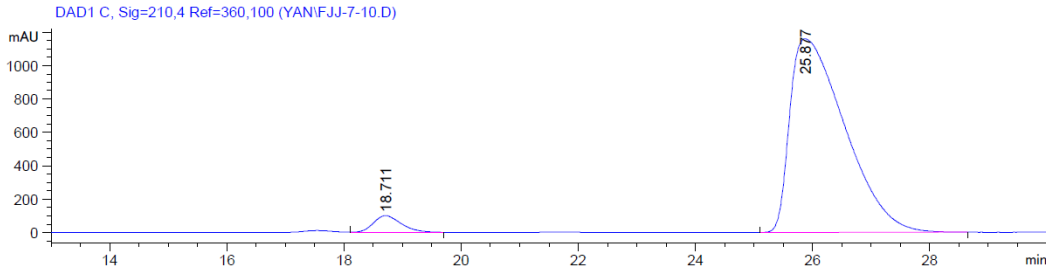
anti-**4ba**

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*anti*-**4ba**): The enantiomeric excess of *anti*-**4ba** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 18.7 min (minor), t_R = 25.9 min (major).



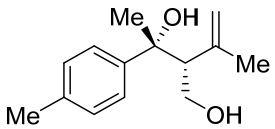
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.053	MM	0.5666	783.98047	23.06146	50.2545
2	27.107	MM	0.8427	776.03906	15.34871	49.7455



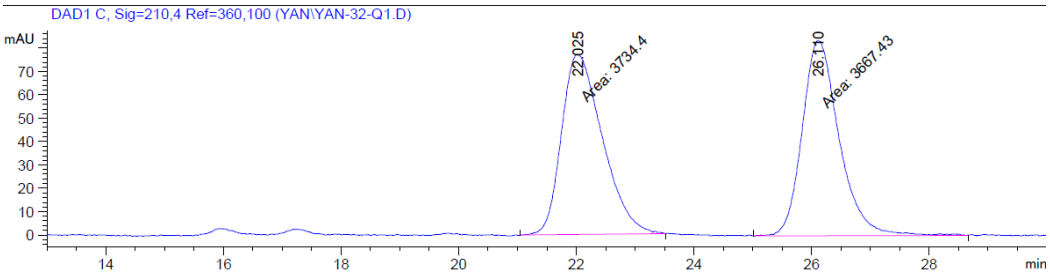
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.711	VV	0.4903	3365.65796	100.61079	4.2580
2	25.877	BB	0.7990	7.56776e4	1160.15002	95.7420



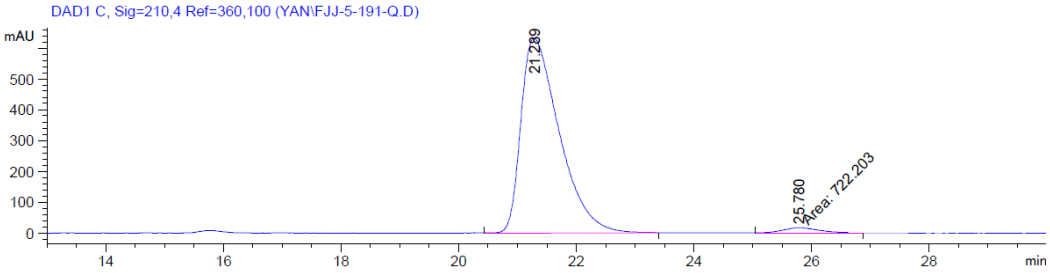
syn-**4ba**

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*syn*-**4ba**): The enantiomeric excess of *syn*-**4ba** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 21.3 min (major), t_R = 25.8 min (minor).



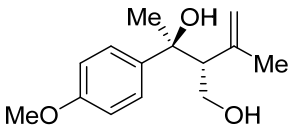
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.025	MM	0.8060	3734.40405	77.21961	50.4524
2	26.110	MM	0.7319	3667.43091	83.51577	49.5476



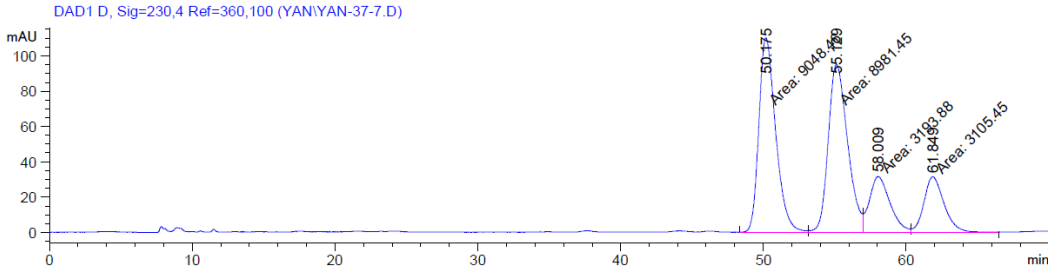
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.289	VV	0.6556	2.86231e4	632.96753	97.5389
2	25.780	MM	0.7216	722.20313	16.67959	2.4611



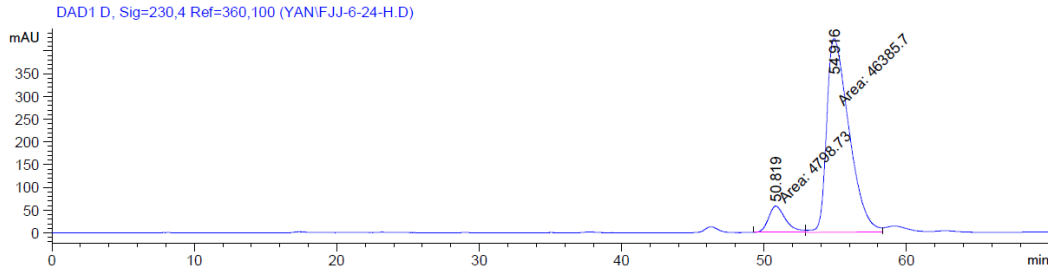
anti-**4ca**

(2*R*,3*S*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ca**): The enantiomeric excess of *anti*-**4ca** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 93:7, flow rate 0.4 mL/min): t_R = 50.8 min (minor), t_R = 54.9 min (major).



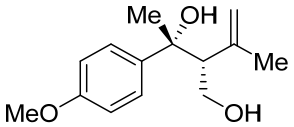
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.175	MF	1.3676	9048.46289	110.27201	37.1917
2	55.129	FM	1.5735	8981.45020	95.13177	36.9163
3	58.009	MF	1.6825	3193.87573	31.63785	13.1277
4	61.849	FM	1.6481	3105.45410	31.40460	12.7643



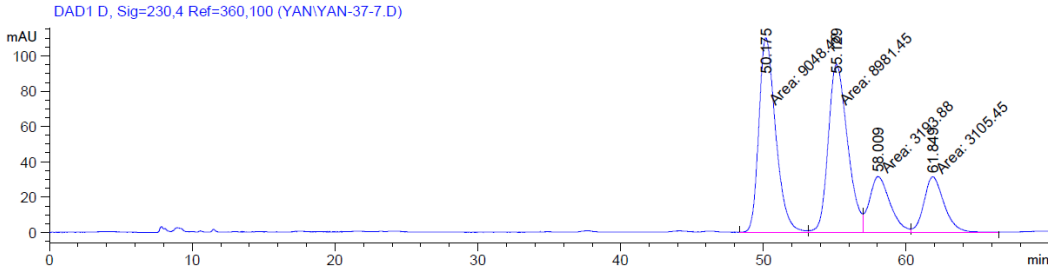
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.819	MF	1.3879	4798.72900	57.62648	9.3754
2	54.916	MF	1.8158	4.63857e4	425.76315	90.6246



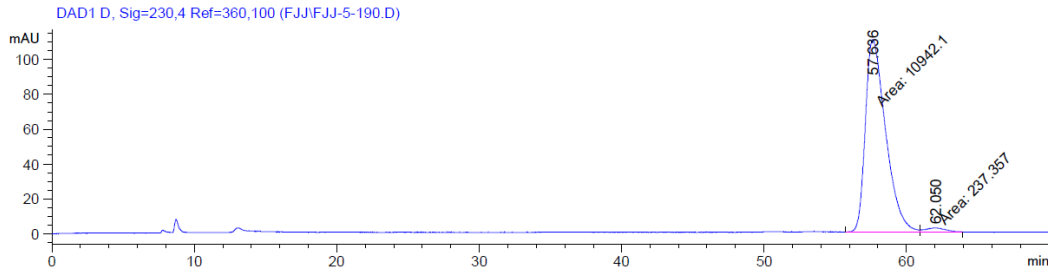
syn-**4ca**

(2*R*,3*R*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ca**): The enantiomeric excess of *syn*-**4ca** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 93:7, flow rate 0.4 mL/min): t_R = 57.6 min (major), t_R = 62.1 min (minor).



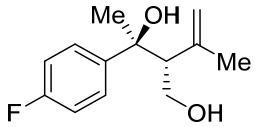
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.175	MF	1.3676	9048.46289	110.27201	37.1917
2	55.129	FM	1.5735	8981.45020	95.13177	36.9163
3	58.009	MF	1.6825	3193.87573	31.63785	13.1277
4	61.849	FM	1.6481	3105.45410	31.40460	12.7643



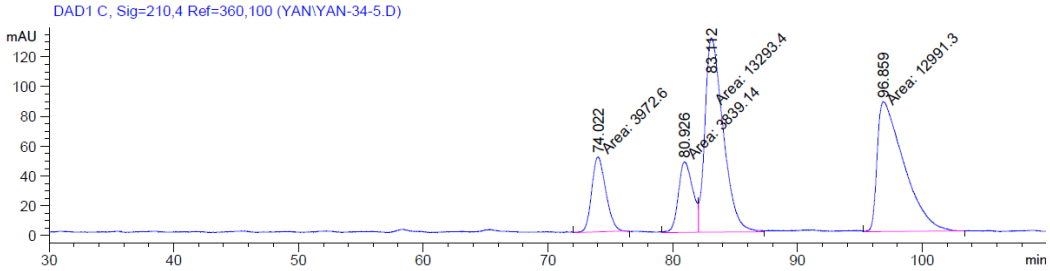
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.636	MF	1.6518	1.09421e4	110.40554	97.8768
2	62.050	FM	1.6162	237.35686	2.44764	2.1232



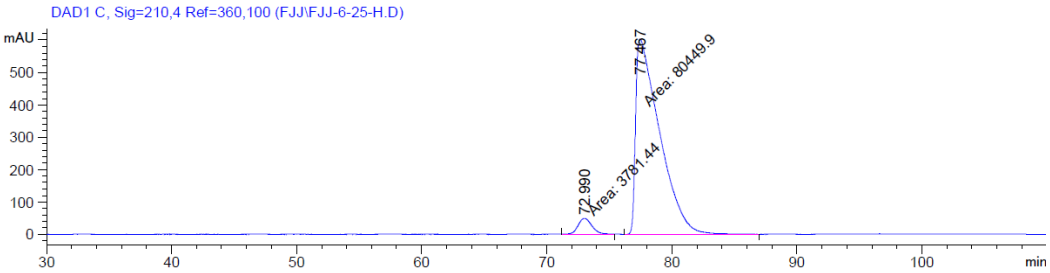
anti-**4da**

(2*R*,3*S*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4da**): The enantiomeric excess of *anti*-**4da** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 98:2, flow rate 0.3 mL/min): t_R = 73.0 min (minor), t_R = 77.5 min (major).



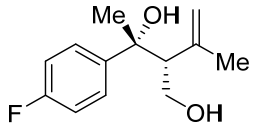
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	74.022	MM	1.3161	3972.59814	50.30923	11.6511
2	80.926	MF	1.3445	3839.13794	47.59168	11.2596
3	83.112	FM	1.6939	1.32934e4	130.79370	38.9878
4	96.859	MM	2.4812	1.29913e4	87.26418	38.1015



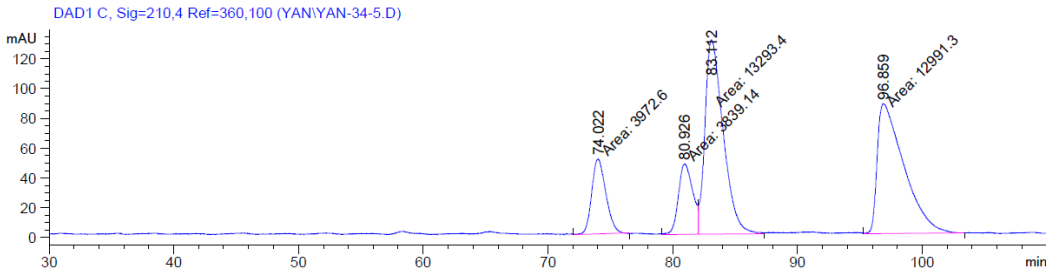
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	72.990	MF	1.2806	3781.44458	49.21444	4.4894
2	77.467	MM	2.2202	8.04499e4	603.93115	95.5106



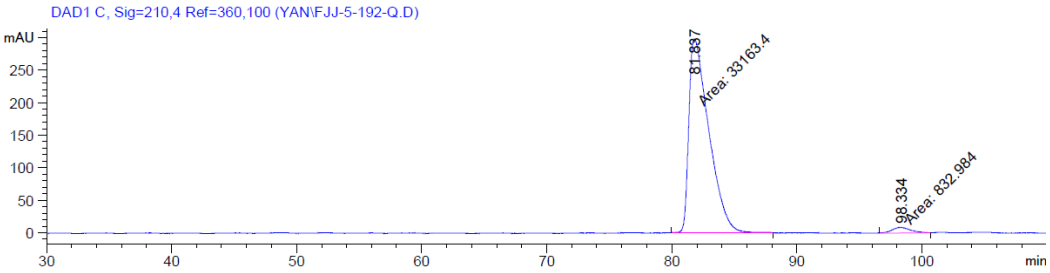
syn-**4da**

(2*R*,3*R*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4da**): The enantiomeric excess of *syn*-**4da** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 98:2, flow rate 0.3 mL/min): t_R = 81.8 min (major), t_R = 98.3 min (minor).



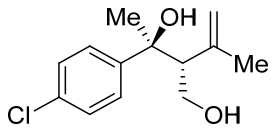
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	74.022	MM	1.3161	3972.59814	50.30923	11.6511
2	80.926	MF	1.3445	3839.13794	47.59168	11.2596
3	83.112	FM	1.6939	1.32934e4	130.79370	38.9878
4	96.859	MM	2.4812	1.29913e4	87.26418	38.1015



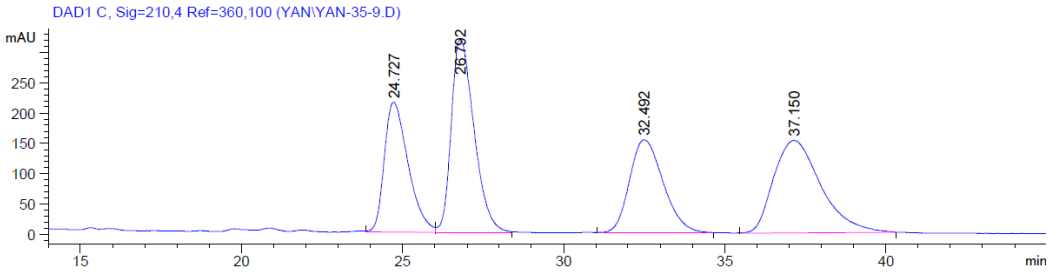
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	81.837	MM	1.8540	3.31634e4	298.13193	97.5498
2	98.334	MM	1.6652	832.98364	8.33711	2.4502



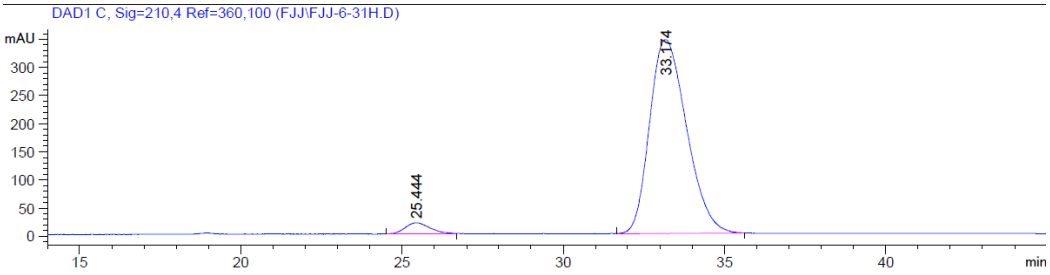
anti-**4ea**

(2*R*,3*S*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ea**): The enantiomeric excess of *anti*-**4ea** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 25.4 min (minor), t_R = 33.2 min (major).



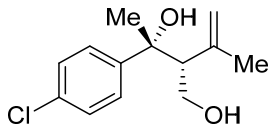
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.727	VV	0.7347	1.09745e4	213.87502	20.6348
2	26.792	VV	0.7227	1.56393e4	318.60571	29.4055
3	32.492	BB	0.9013	1.11046e4	152.89886	20.8792
4	37.150	BB	1.2012	1.54664e4	152.24208	29.0805



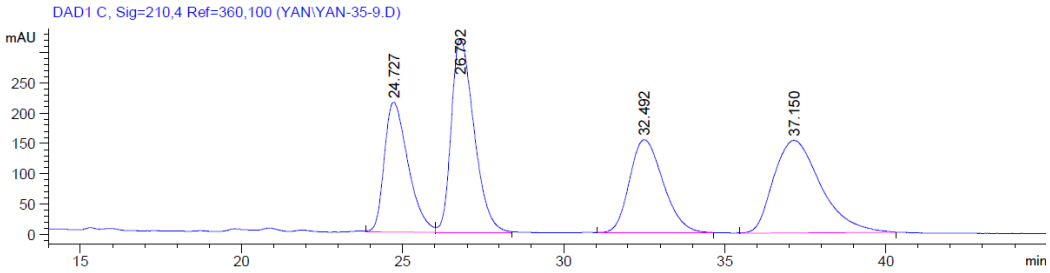
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.444	VV	0.6423	1065.11511	19.71410	3.7305
2	33.174	VV	0.9687	2.74864e4	344.54700	96.2695



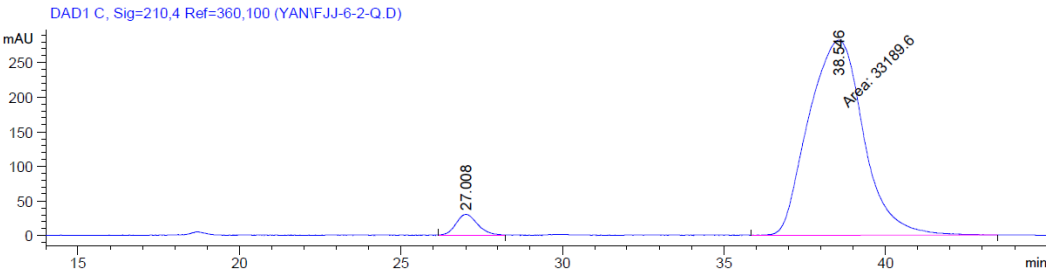
syn-**4ea**

(2*R*,3*R*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ea**): The enantiomeric excess of *syn*-**4ea** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 27.0 min (minor), t_R = 38.6 min (major).



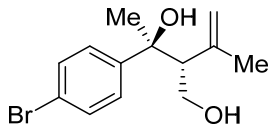
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.727	VV	0.7347	1.09745e4	213.87502	20.6348
2	26.792	VV	0.7227	1.56393e4	318.60571	29.4055
3	32.492	BB	0.9013	1.11046e4	152.89886	20.8792
4	37.150	BB	1.2012	1.54664e4	152.24208	29.0805



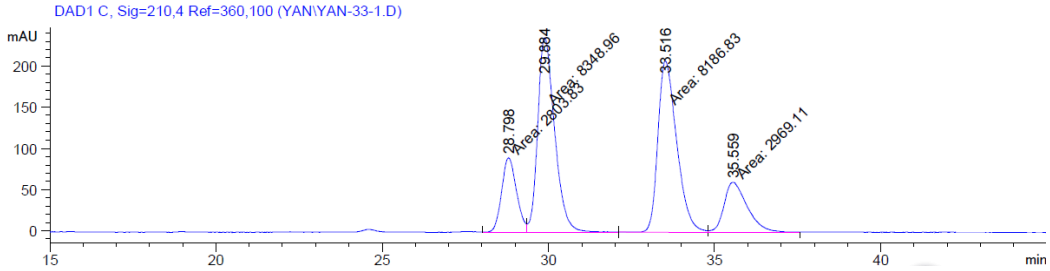
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.008	BB	0.5457	1398.11743	30.10945	4.0422
2	38.546	MM	1.9592	3.31896e4	282.33713	95.9578



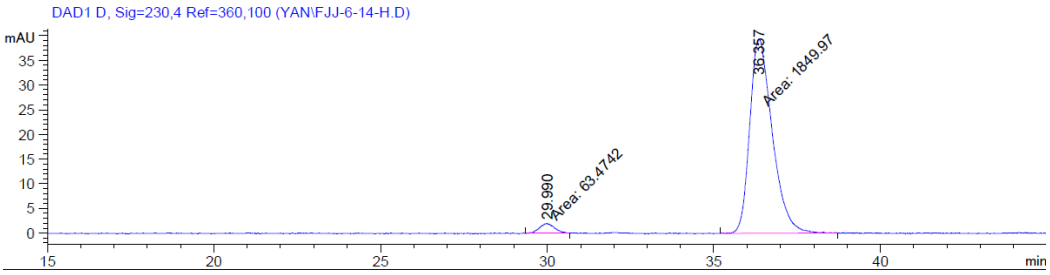
anti-**4fa**

(2*R*,3*S*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4fa**): The enantiomeric excess of *anti*-**4fa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.0 min (minor), t_R = 36.4 min (major).



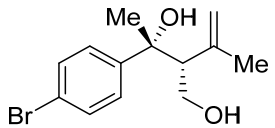
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.798	MF	0.5192	2803.83008	90.00201	12.5683
2	29.884	MF	0.5899	8348.96387	235.87181	37.4246
3	33.516	FM	0.6565	8186.82666	207.82611	36.6979
4	35.559	FM	0.8145	2969.10913	60.75273	13.3092



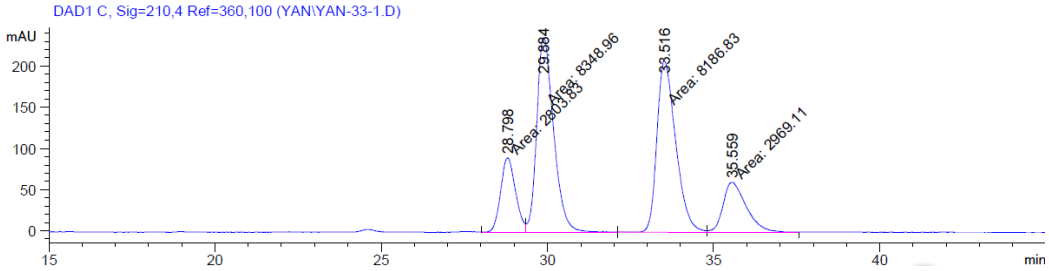
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.990	MM	0.5300	63.47422	1.99610	3.3173
2	36.357	MM	0.7839	1849.97266	39.33429	96.6827



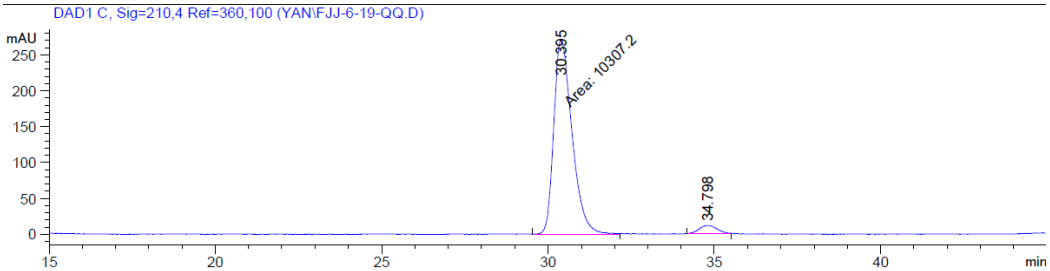
syn-**4fa**

(2*R*,3*R*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4fa**): The enantiomeric excess of *syn*-**4fa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.4 min (major), t_R = 34.8 min (minor).



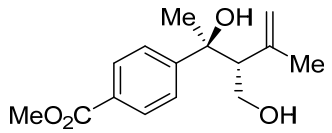
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.798	MF	0.5192	2803.83008	90.00201	12.5683
2	29.884	MF	0.5899	8348.96387	235.87181	37.4246
3	33.516	FM	0.6565	8186.82666	207.82611	36.6979
4	35.559	FM	0.8145	2969.10913	60.75273	13.3092



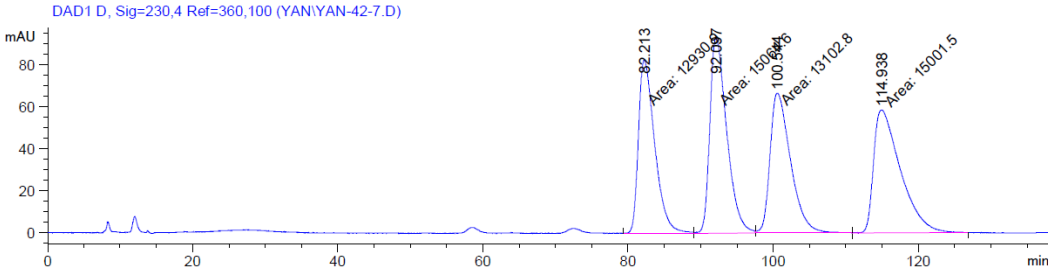
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.395	MM	0.6335	1.03072e4	271.19241	95.8321
2	34.798	BV	0.4531	448.27396	11.96480	4.1679



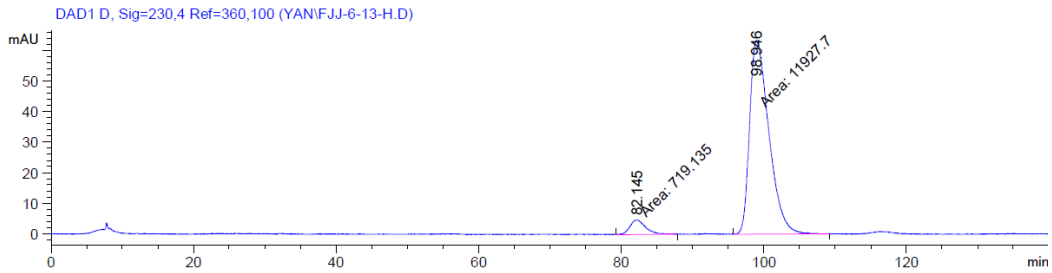
anti-**4ga**

4-((2*S*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*anti*-4ga): The enantiomeric excess of *anti*-**4ga** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.4 mL/min): t_R = 82.2 min (minor), t_R = 99.0 min (major).



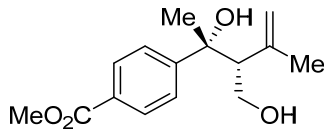
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.213	MF	2.6014	1.29309e4	82.84698	23.0498
2	92.097	MF	2.6935	1.50646e4	93.21604	26.8532
3	100.544	MF	3.2704	1.31028e4	66.77424	23.3563
4	114.938	FM	4.2710	1.50015e4	58.54039	26.7407



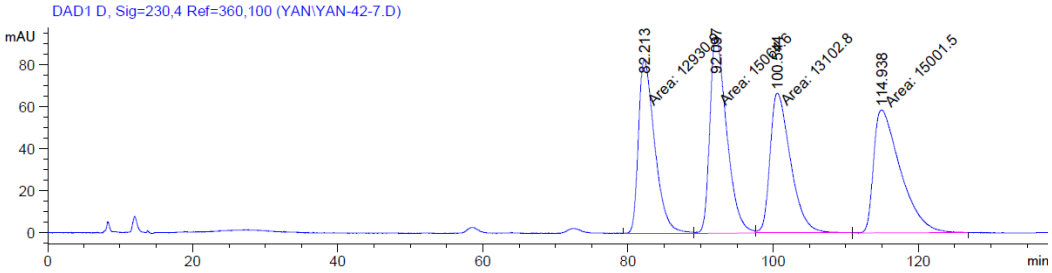
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.145	MM	2.5233	719.13525	4.74995	5.6863
2	98.946	MM	3.1342	1.19277e4	63.42724	94.3137



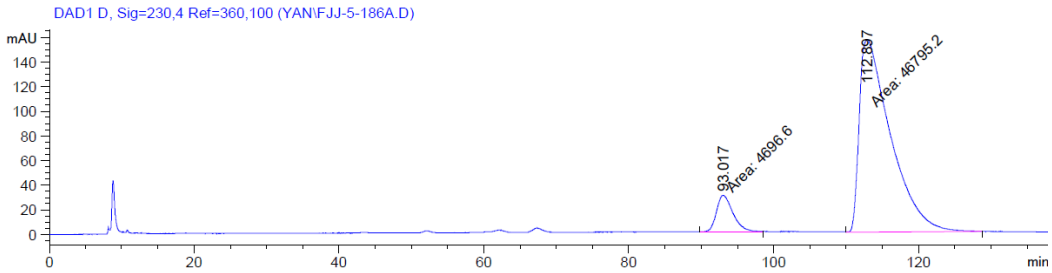
syn-**4ga**

4-((2*R*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*syn*-**4ga**): The enantiomeric excess of *syn*-**4ga** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.4 mL/min): t_R = 93.0 min (minor), t_R = 112.9 min (major).



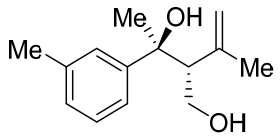
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	82.213	MF	2.6014	1.29309e4	82.84698	23.0498
2	92.097	MF	2.6935	1.50646e4	93.21604	26.8532
3	100.544	MF	3.2704	1.31028e4	66.77424	23.3563
4	114.938	FM	4.2710	1.50015e4	58.54039	26.7407



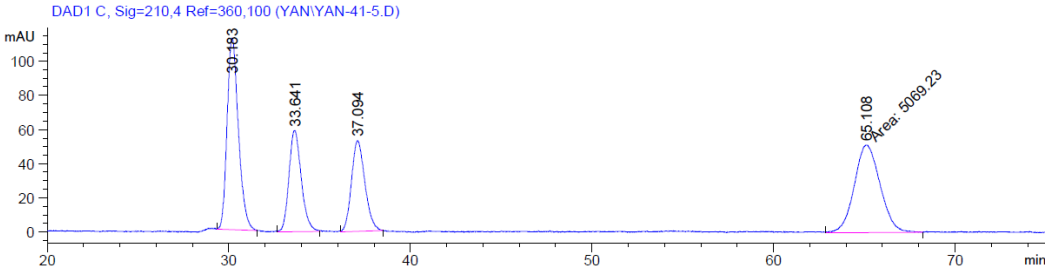
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	93.017	MM	2.6355	4696.60205	29.70082	9.1211
2	112.897	MM	4.9947	4.67952e4	156.15024	90.8789



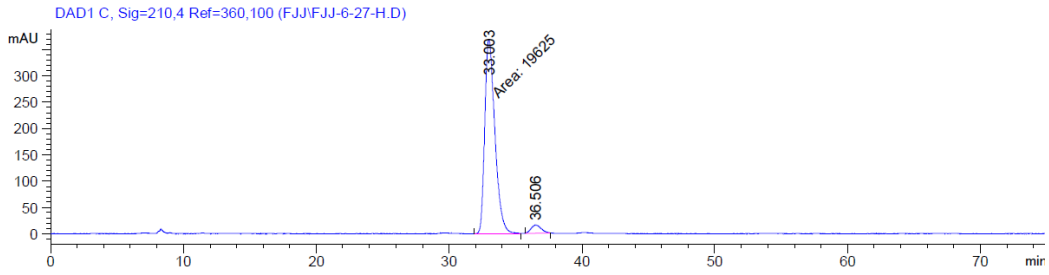
anti-**4ha**

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*anti*-4ha): The enantiomeric excess of *anti*-**4ha** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel AS-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 33.0 min (major), t_R = 36.5 min (minor).



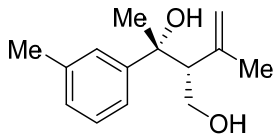
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.183	VB	0.6228	4866.54248	112.47483	31.4755
2	33.641	VV	0.5753	2790.24072	59.26205	18.0465
3	37.094	VB	0.6260	2735.33691	53.18371	17.6914
4	65.108	MM	1.6449	5069.23486	51.36318	32.7865



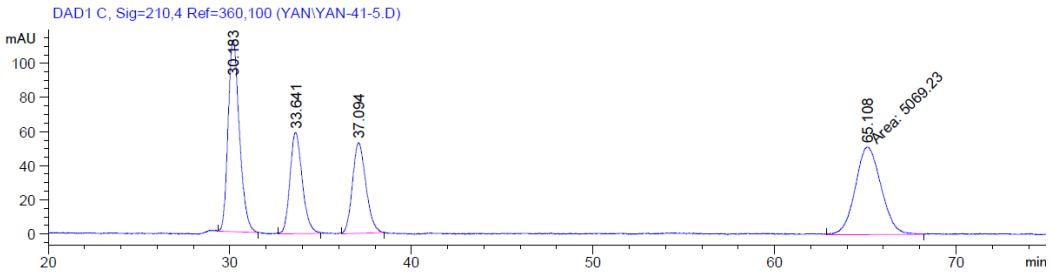
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.003	MM	0.8858	1.96250e4	369.26688	95.8958
2	36.506	VB	0.6217	839.92010	15.96771	4.1042



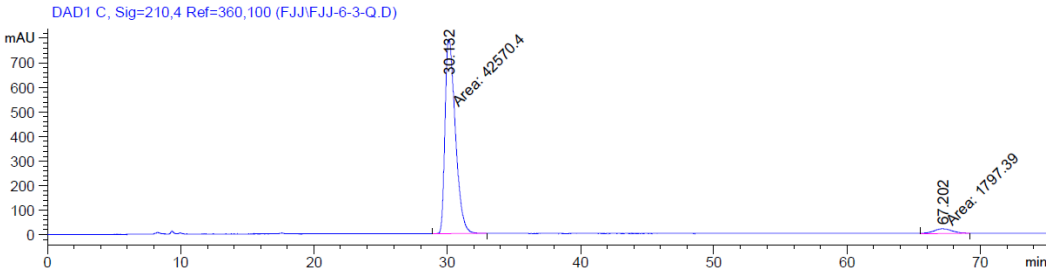
syn-**4ha**

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*syn*-**4ha**): The enantiomeric excess of *syn*-**4ha** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel AS-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 30.1 min (major), t_R = 67.2 min (minor).



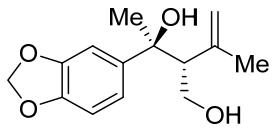
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.183	VB	0.6228	4866.54248	112.47483	31.4755
2	33.641	VV	0.5753	2790.24072	59.26205	18.0465
3	37.094	VB	0.6260	2735.33691	53.18371	17.6914
4	65.108	MM	1.6449	5069.23486	51.36318	32.7865



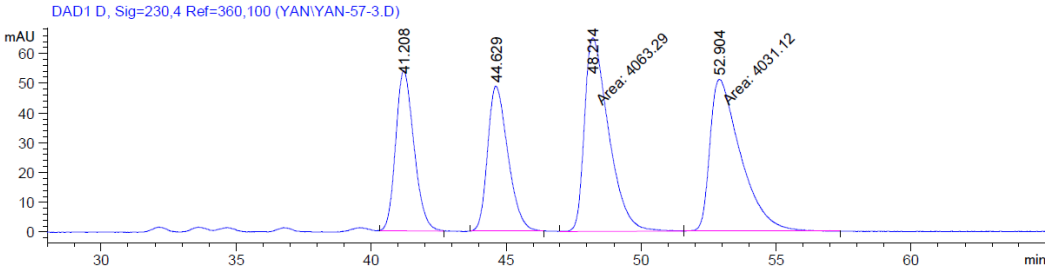
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.132	MM	0.8954	4.25704e4	792.38373	95.9489
2	67.202	MM	1.6167	1797.39172	18.52912	4.0511



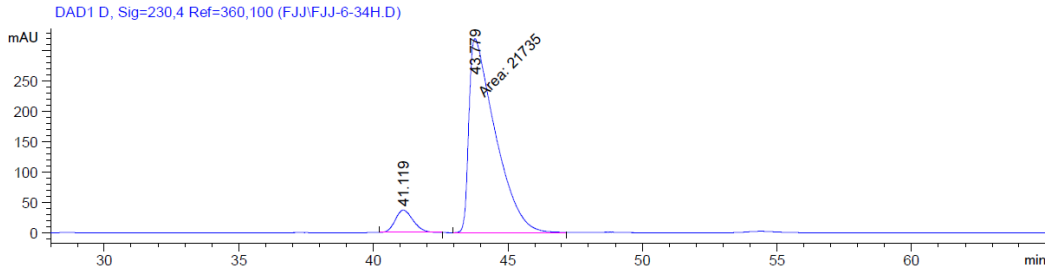
anti-**4ia**

(2*R*,3*S*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ia**): The enantiomeric excess of *anti*-**4ia** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 41.1 min (minor), t_R = 43.8 min (major).



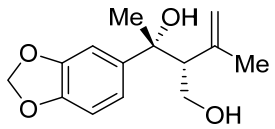
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.208	BB	0.6442	2522.46631	53.68176	19.1705
2	44.629	BB	0.7103	2541.17700	48.57903	19.3127
3	48.214	MF	1.0428	4063.29053	64.93948	30.8806
4	52.904	FM	1.3177	4031.11621	50.98620	30.6361



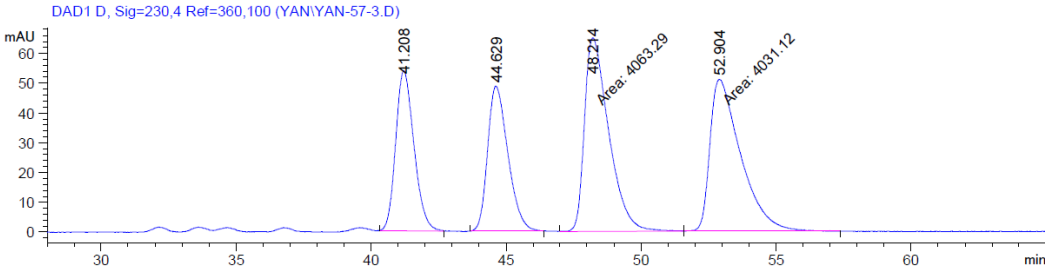
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.119	BB	0.6765	1726.10229	36.98433	7.3573
2	43.779	MM	1.1320	2.17350e4	320.00214	92.6427



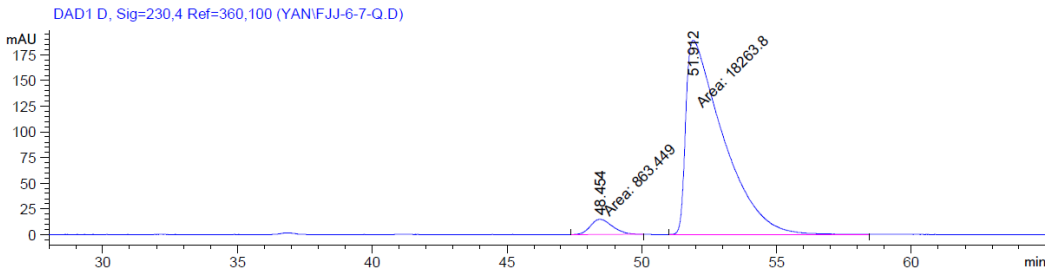
syn-**4ia**

(2*R*,3*R*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ia**): The enantiomeric excess of *syn*-**4ia** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 48.5 min (minor), t_R = 51.9 min (major).



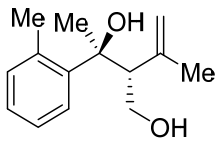
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.208	BB	0.6442	2522.46631	53.68176	19.1705
2	44.629	BB	0.7103	2541.17700	48.57903	19.3127
3	48.214	MF	1.0428	4063.29053	64.93948	30.8806
4	52.904	FM	1.3177	4031.11621	50.98620	30.6361



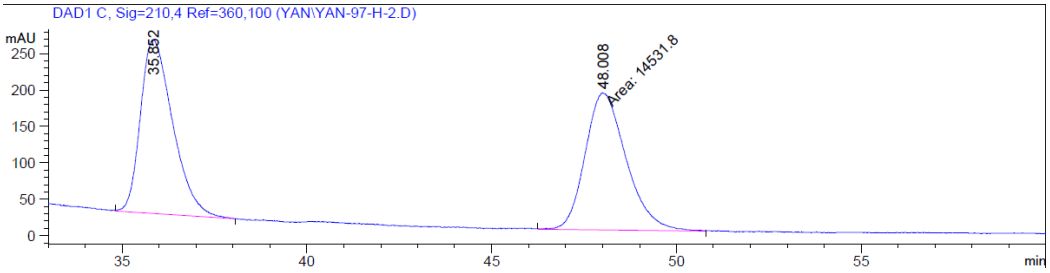
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.454	MM	0.9619	863.44904	14.96026	4.5142
2	51.912	MM	1.6109	1.82638e4	188.95515	95.4858



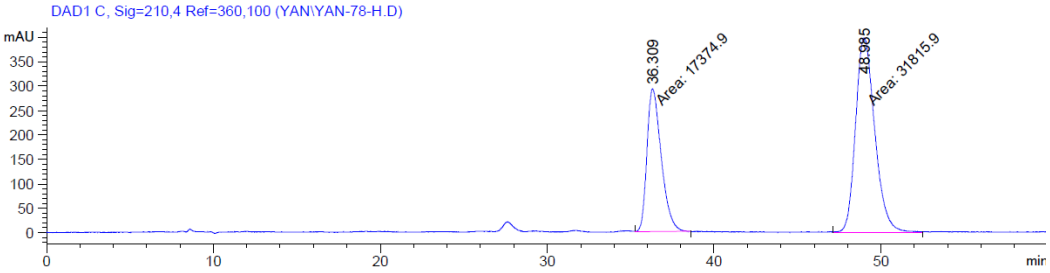
anti-**4ja**

(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*anti*-4ja): The enantiomeric excess of *anti*-**4ja** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 36.3 min (minor), t_R = 49.0 min (major).



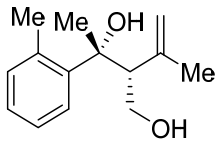
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.852	VB	0.7252	1.44863e4	238.98204	49.9216
2	48.008	MM	1.2862	1.45318e4	188.30243	50.0784



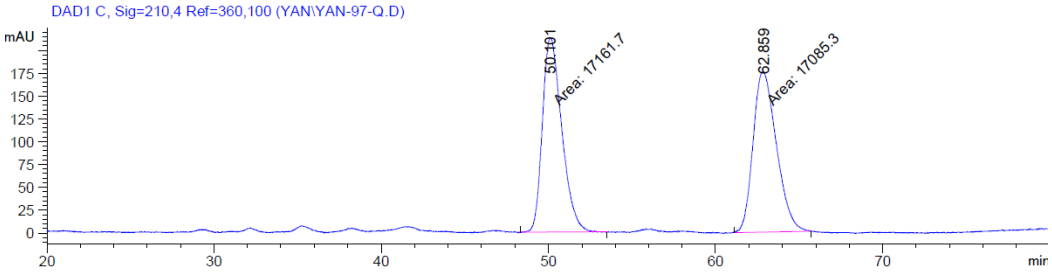
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.309	MM	0.9918	1.73749e4	291.98779	35.3215
2	48.985	MM	1.3321	3.18159e4	398.07559	64.6785



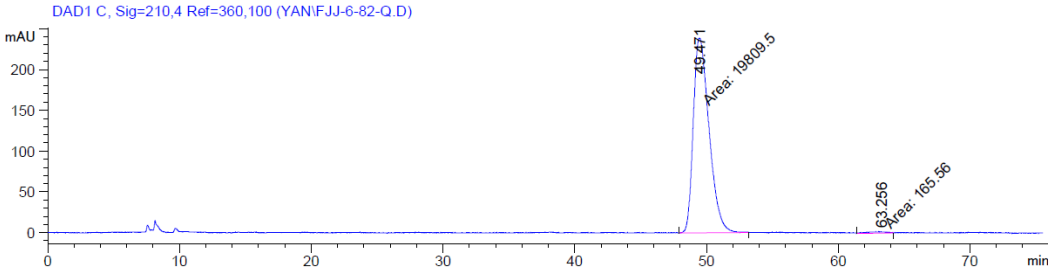
syn-**4ja**

(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*syn*-**4ja**): The enantiomeric excess of *syn*-**4ja** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 49.5 min (major), t_R = 63.3 min (minor).



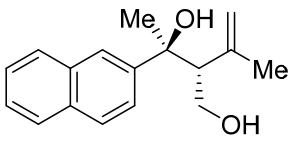
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.101	MM	1.3449	1.71617e4	212.67732	50.1116
2	62.859	MM	1.6188	1.70853e4	175.90973	49.8884



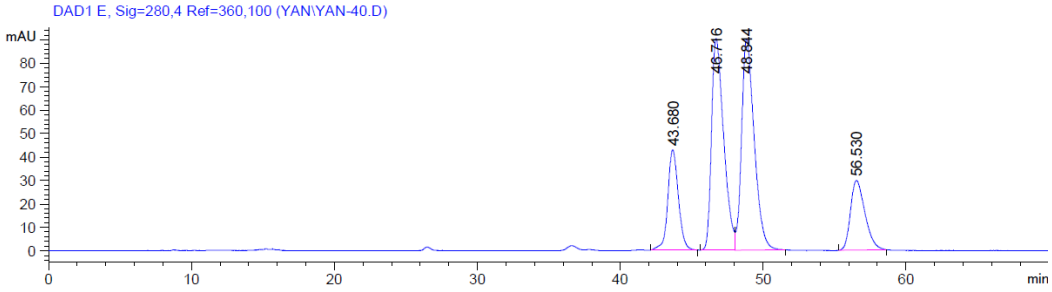
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.471	MM	1.3822	1.98095e4	238.86757	99.1712
2	63.256	MM	1.5127	165.55965	1.82411	0.8288



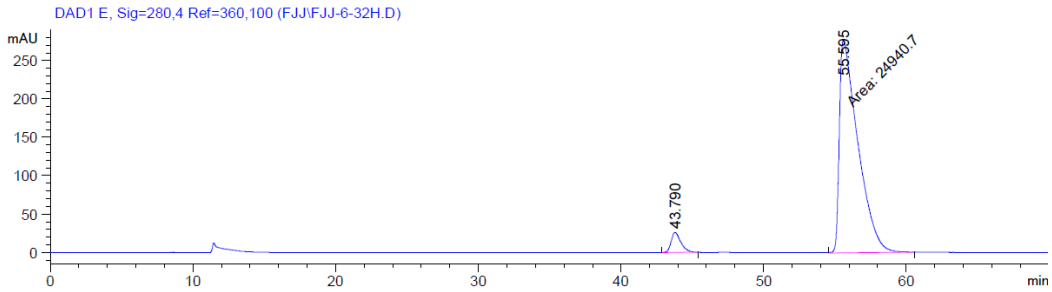
anti-**4ka**

(2*R*,3*S*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ka): The enantiomeric excess of *anti*-**4ka** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 43.8 min (minor), t_R = 55.6 min (major).

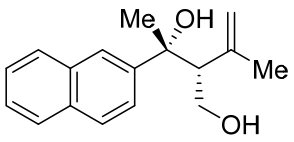


Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.680	BB	0.7347	2206.51294	42.85769	14.5415
2	46.716	BV	0.8383	5329.39063	90.33796	35.1222
3	48.844	VB	0.9088	5544.68066	89.99050	36.5410
4	56.530	BB	0.9029	2093.28809	29.67883	13.7953

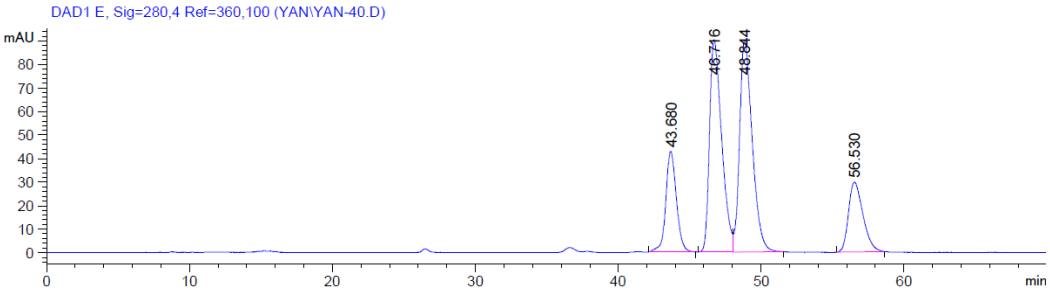


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.790	BB	0.6672	1234.38098	26.12593	4.7159
2	55.595	MM	1.5040	2.49407e4	276.38004	95.2841



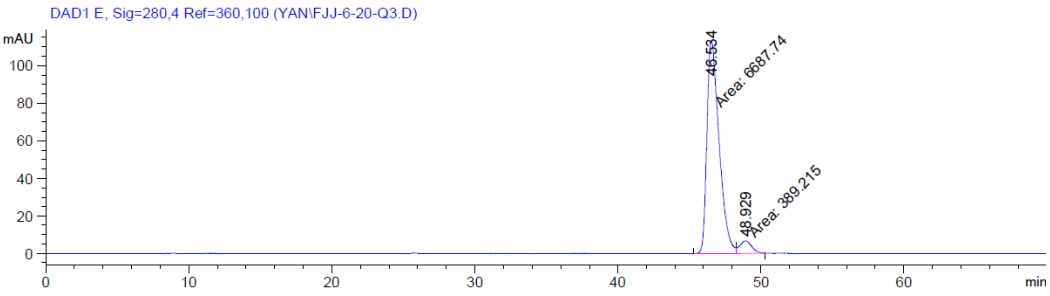
syn-**4ka**

(2*R*,3*R*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ka**): The enantiomeric excess of *syn*-**4ka** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 46.5 min (major), t_R = 48.9 min (minor).



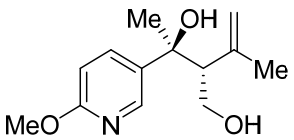
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.680	BB	0.7347	2206.51294	42.85769	14.5415
2	46.716	BV	0.8383	5329.39063	90.33796	35.1222
3	48.844	VB	0.9088	5544.68066	89.99050	36.5410
4	56.530	BB	0.9029	2093.28809	29.67883	13.7953



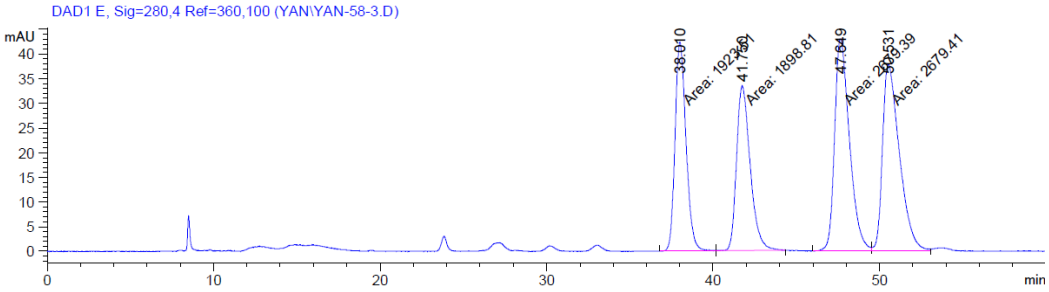
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.534	MF	0.9847	6687.73682	113.19811	94.5002
2	48.929	FM	0.9761	389.21548	6.64585	5.4998



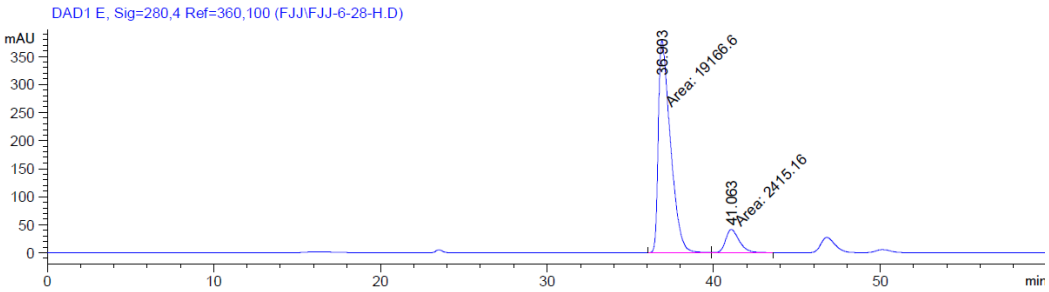
anti-**4la**

(2*R*,3*S*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4la**): The enantiomeric excess of *anti*-**4la** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 36.9 min (major), t_R = 41.1 min (minor).



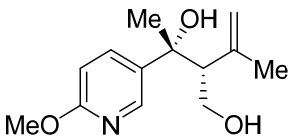
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.010	MF	0.7580	1923.51257	42.29352	20.9507
2	41.750	FM	0.9480	1898.81323	33.38183	20.6817
3	47.649	MF	1.0367	2679.38623	43.07478	29.1837
4	50.531	MF	1.1797	2679.40820	37.85402	29.1839



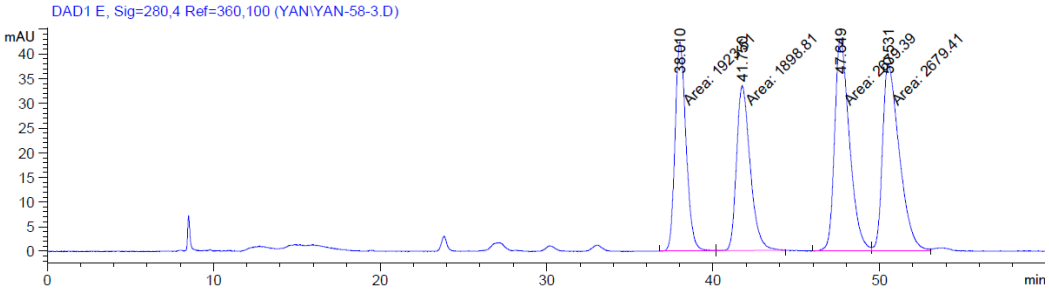
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.903	MF	0.8436	1.91666e4	378.65662	88.8093
2	41.063	MF	0.9682	2415.16211	41.57422	11.1907



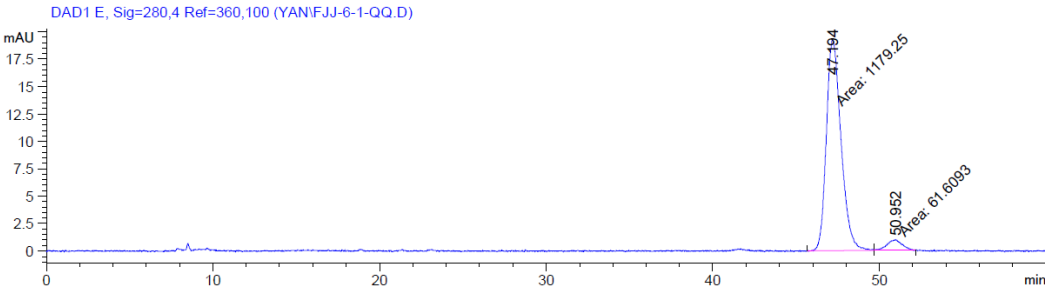
syn-**4la**

(2*R*,3*R*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4la**): The enantiomeric excess of *syn*-**4la** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 47.2 min (major), t_R = 51.0 min (minor).



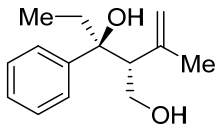
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.010	MF	0.7580	1923.51257	42.29352	20.9507
2	41.750	FM	0.9480	1898.81323	33.38183	20.6817
3	47.649	MF	1.0367	2679.38623	43.07478	29.1837
4	50.531	MF	1.1797	2679.40820	37.85402	29.1839



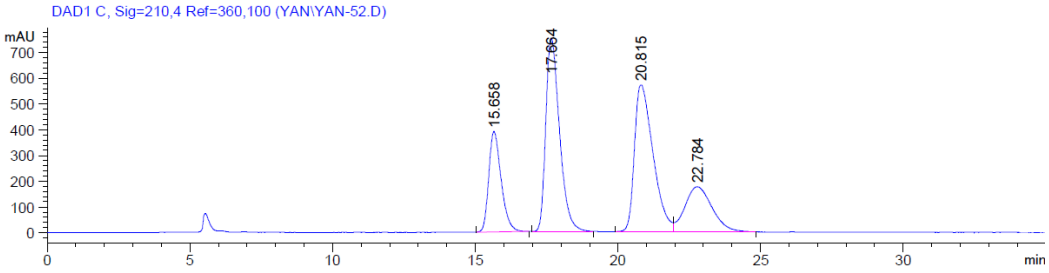
Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.194	MF	1.0212	1179.24988	19.24644	95.0349
2	50.952	FM	1.0733	61.60931	9.56719e-1	4.9651



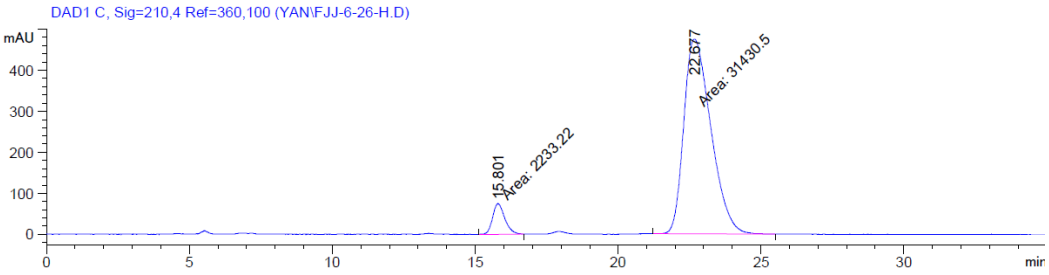
anti-**4ma**

(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*anti*-4ma): The enantiomeric excess of *anti*-**4ma** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 15.8 min (minor), t_R = 22.7 min (major).



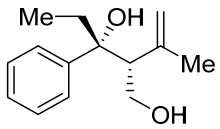
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.658	BB	0.4585	1.17986e4	390.53555	15.8477
2	17.664	BB	0.4967	2.51956e4	752.44653	33.8424
3	20.815	BV	0.6457	2.58302e4	571.08765	34.6948
4	22.784	VB	0.7939	1.16254e4	175.25348	15.6151



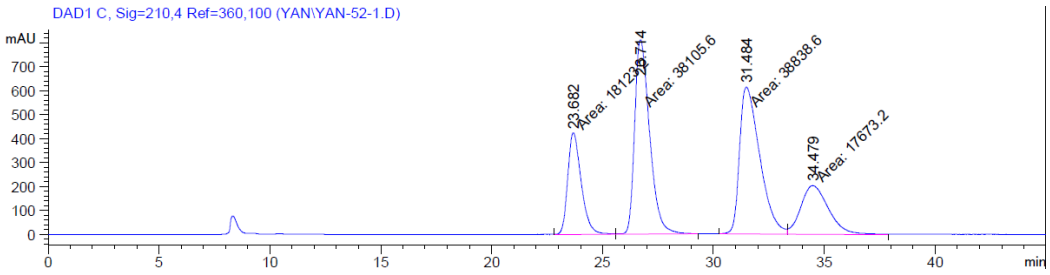
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.801	MM	0.4964	2233.22290	74.97643	6.6339
2	22.677	MM	1.1013	3.14305e4	475.65314	93.3661



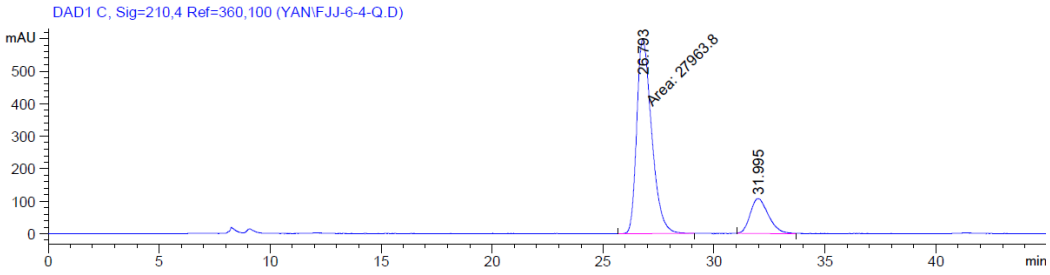
syn-**4ma**

(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*syn*-**4ma**): The enantiomeric excess of *syn*-**4ma** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.4 mL/min): t_R = 26.8 min (major), t_R = 32.0 min (minor).



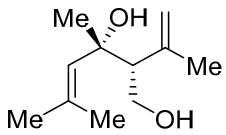
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.682	MF	0.7099	1.81232e4	425.48965	16.0751
2	26.714	FM	0.7827	3.81056e4	811.38147	33.7994
3	31.484	MF	1.0548	3.88386e4	613.67798	34.4495
4	34.479	FM	1.4517	1.76732e4	202.89993	15.6760



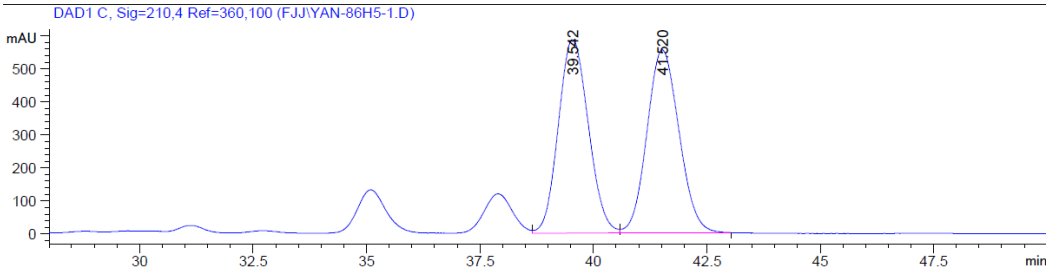
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.793	MM	0.7782	2.79638e4	598.91937	82.0515
2	31.995	VV	0.7209	6117.00146	107.33590	17.9485



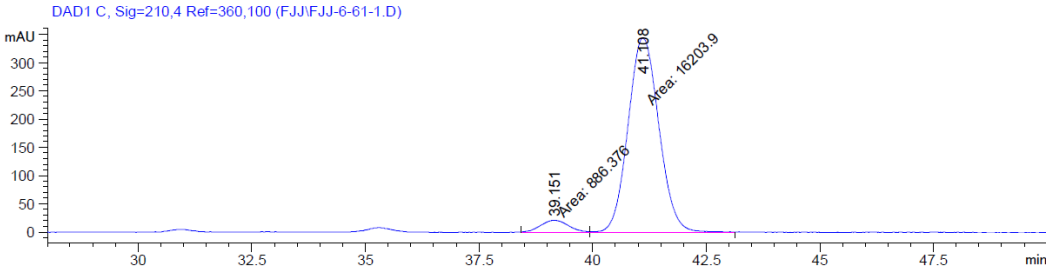
syn-**4na**

(2*R*,3*S*)-3,5-Dimethyl-2-(prop-1-en-2-yl)hex-4-ene-1,3-diol (*syn*-**4na**): The enantiomeric excess of *syn*-**4na** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.3 mL/min): t_R = 39.2 min (minor), t_R = 41.1 min (major).



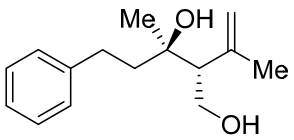
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.542	VV	0.6684	2.69663e4	586.56995	49.6962
2	41.520	VB	0.7099	2.72960e4	554.87317	50.3038



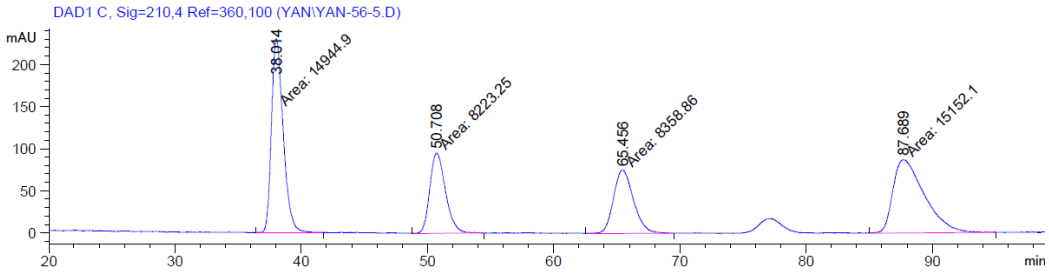
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.151	MF	0.7000	886.37561	21.10277	5.1864
2	41.108	FM	0.7851	1.62039e4	343.99725	94.8136



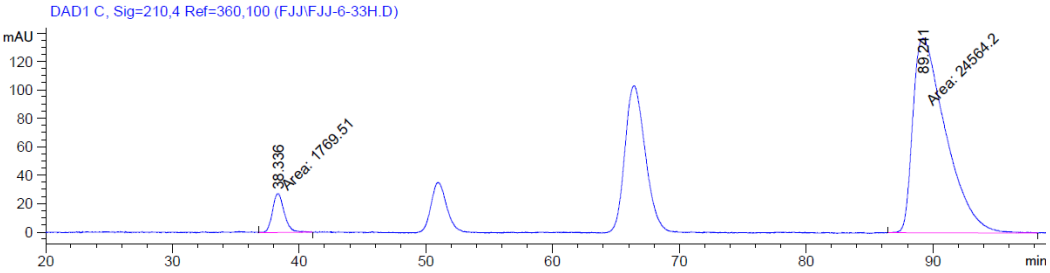
anti-**4oa**

(2*R*,3*R*)-3-Methyl-5-phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*anti*-4oa): The enantiomeric excess of *anti*-**4oa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 38.3 min (minor), t_R = 89.2 min (major).



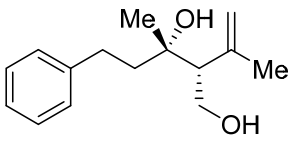
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.014	MM	1.0810	1.49449e4	230.42384	32.0163
2	50.708	MM	1.4354	8223.24902	95.48369	17.6166
3	65.456	MM	1.8470	8358.86133	75.42542	17.9071
4	87.689	MM	2.8972	1.51521e4	87.16428	32.4601



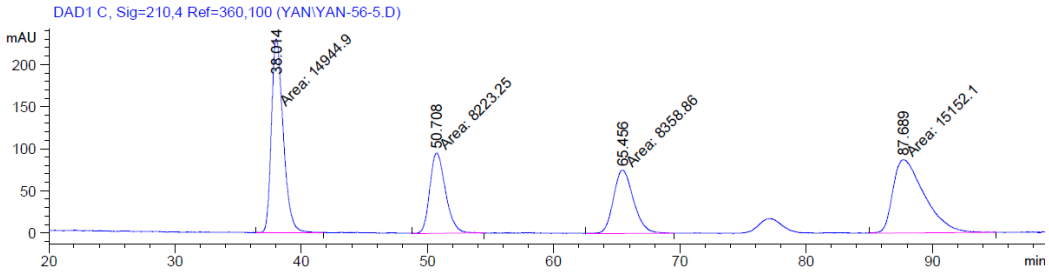
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.336	MM	1.0810	1769.51477	27.28125	6.7196
2	89.241	MM	2.9936	2.45642e4	136.75821	93.2804



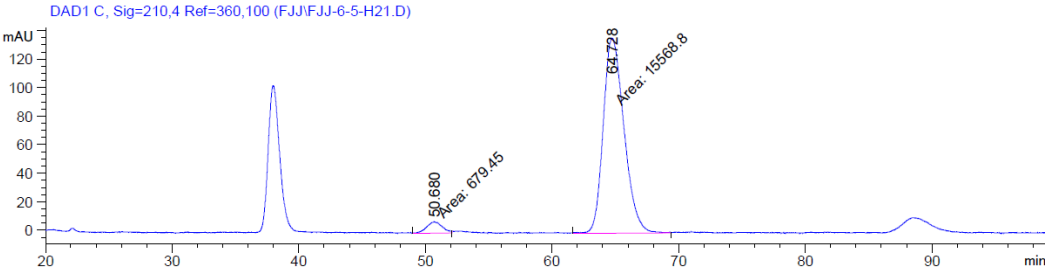
syn-**4oa**

(2*R*,3*S*)-3-Methyl-5-phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*syn*-**4oa**): The enantiomeric excess of *syn*-**4oa** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 50.7 min (minor), t_R = 64.7 min (major).



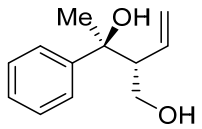
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.014	MM	1.0810	1.49449e4	230.42384	32.0163
2	50.708	MM	1.4354	8223.24902	95.48369	17.6166
3	65.456	MM	1.8470	8358.86133	75.42542	17.9071
4	87.689	MM	2.8972	1.51521e4	87.16428	32.4601



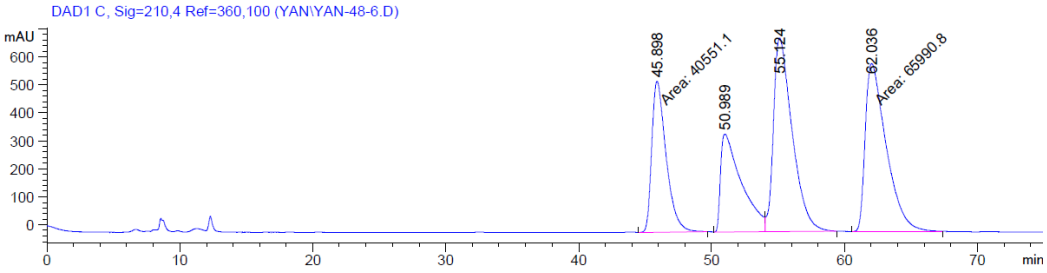
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.680	MF	1.3929	679.44989	8.12986	4.1817
2	64.728	MM	1.8956	1.55688e4	136.88451	95.8183



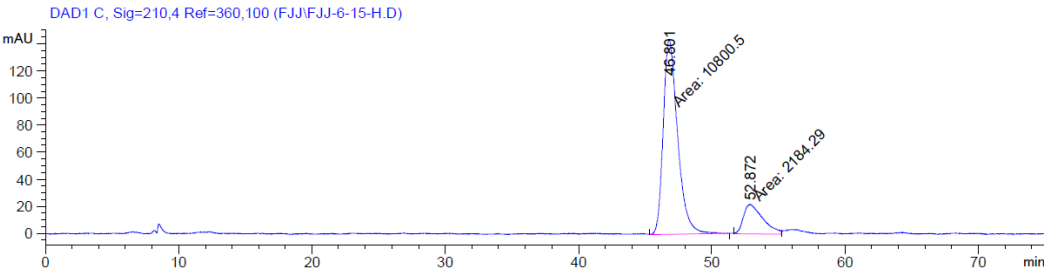
anti-**4ab**

(2*R*,3*S*)-3-Phenyl-2-vinylbutane-1,3-diol (*anti*-4ab): The enantiomeric excess of *anti*-**4ab** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.4 mL/min): t_R = 46.8 min (major), t_R = 52.9 min (minor).



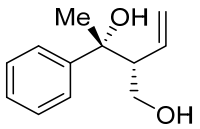
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.898	MM	1.2534	4.05511e4	539.20087	19.0696
2	50.989	BV	1.3967	3.82744e4	349.76962	17.9990
3	55.124	VV	1.1617	6.78309e4	691.91504	31.8983
4	62.036	MM	1.8311	6.59908e4	600.65033	31.0330



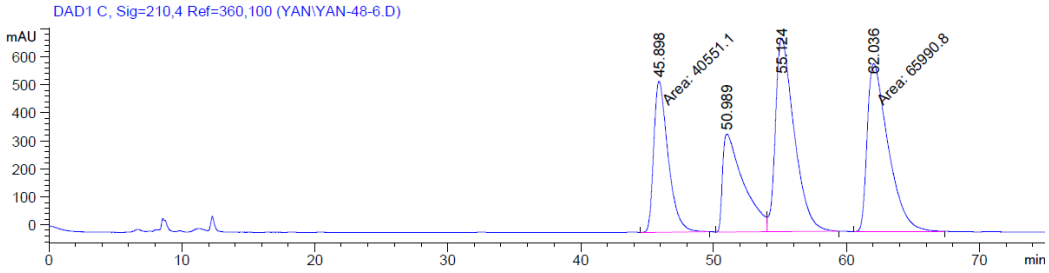
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.801	MM	1.2527	1.08005e4	143.69597	83.1780
2	52.872	MF	1.6842	2184.28833	21.61506	16.8220



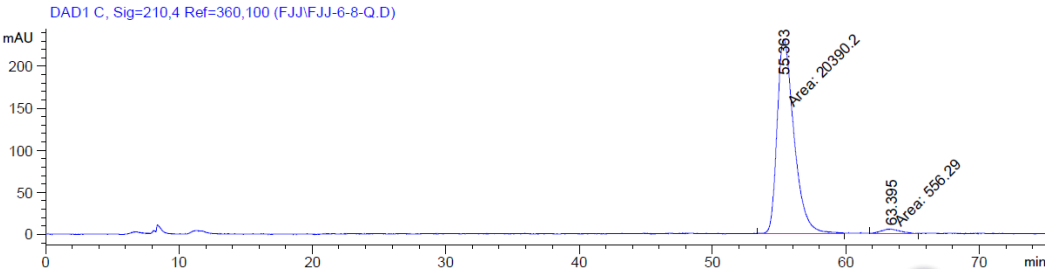
syn-**4ab**

(2*R*,3*R*)-3-Phenyl-2-vinylbutane-1,3-diol (*syn*-**4ab**): The enantiomeric excess of *syn*-**4ab** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.4 mL/min): t_R = 55.4 min (major), t_R = 63.4 min (minor).



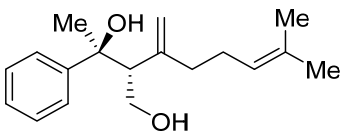
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.898	MM	1.2534	4.05511e4	539.20087	19.0696
2	50.989	BV	1.3967	3.82744e4	349.76962	17.9990
3	55.124	VV	1.1617	6.78309e4	691.91504	31.8983
4	62.036	MM	1.8311	6.59908e4	600.65033	31.0330



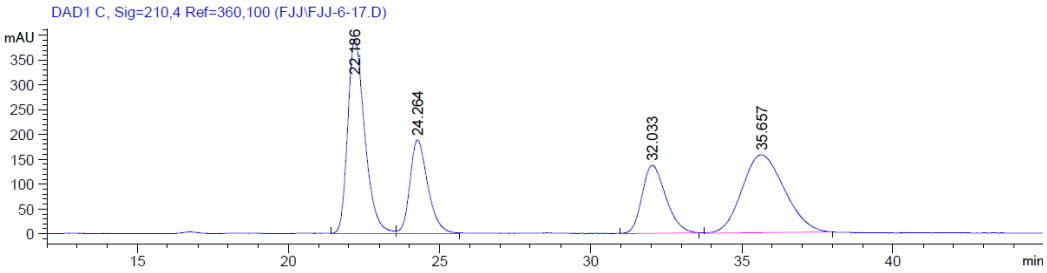
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.363	MM	1.4670	2.03902e4	231.64612	97.3442
2	63.395	MM	1.7103	556.28955	5.42094	2.6558



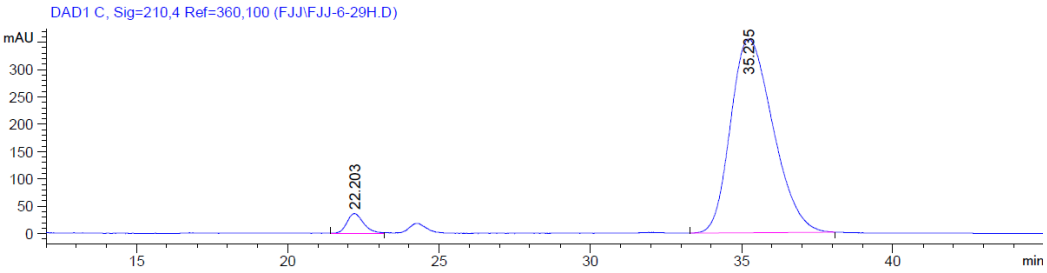
anti-**4ac**

(2*R*,3*S*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*anti*-**4ac**): The enantiomeric excess of *anti*-**4ac** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 22.2 min (minor), t_R = 35.2 min (major).



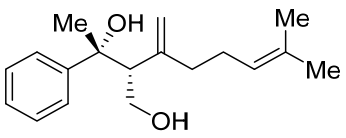
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.186	BV	0.5921	1.53128e4	391.65991	33.4858
2	24.264	VB	0.5879	7667.82373	187.97578	16.7679
3	32.033	VV	0.7294	7517.20459	137.15277	16.4385
4	35.657	BB	1.1547	1.52314e4	156.60896	33.3078



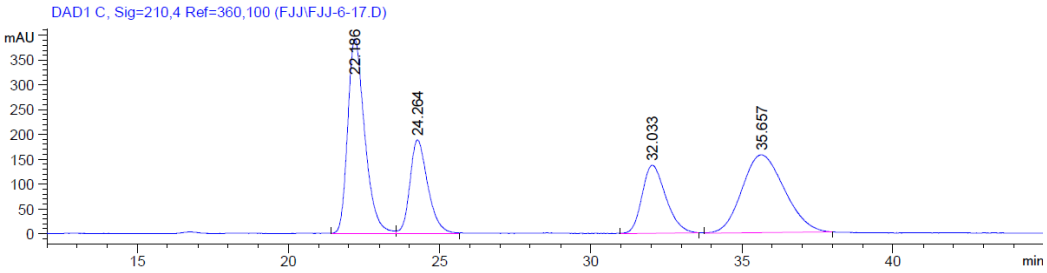
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.203	BV	0.4579	1348.72400	35.60748	3.7643
2	35.235	BB	1.1438	3.44807e4	354.18423	96.2357



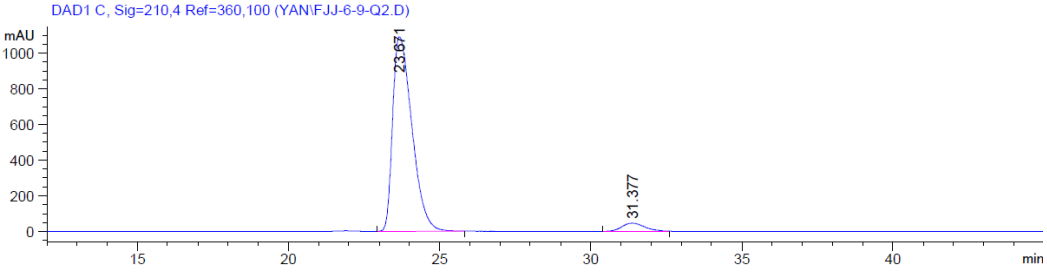
syn-**4ac**

(2*R*,3*R*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ac**): The enantiomeric excess of *syn*-**4ac** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 23.7 min (major), t_R = 31.4 min (minor).



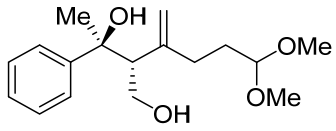
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.186	BV	0.5921	1.53128e4	391.65991	33.4858
2	24.264	VB	0.5879	7667.82373	187.97578	16.7679
3	32.033	VV	0.7294	7517.20459	137.15277	16.4385
4	35.657	BB	1.1547	1.52314e4	156.60896	33.3078



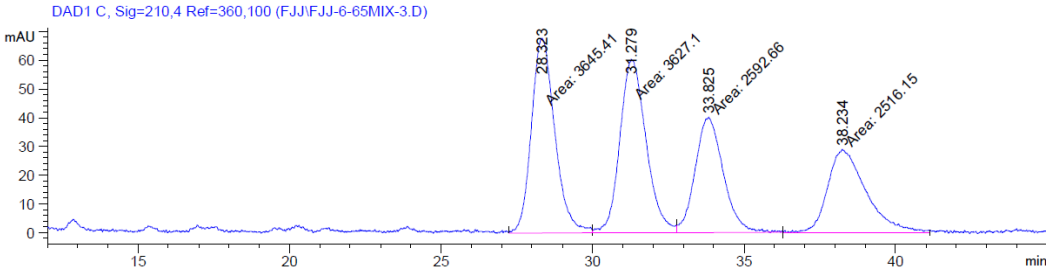
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.671	VV	0.6241	4.84861e4	1091.79065	95.1507
2	31.377	BV	0.6220	2471.06616	46.95186	4.8493



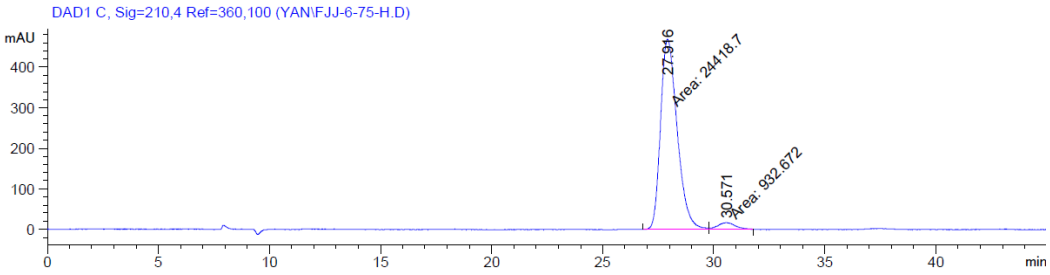
anti-**4ad**

(2*R*,3*S*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*anti*-4ad): The enantiomeric excess of *anti*-**4ad** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 27.9 min (major), t_R = 30.6 min (minor).



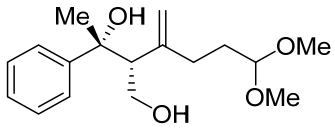
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.323	MF	0.8965	3645.40698	67.77480	29.4428
2	31.279	MF	1.0028	3627.10498	60.28340	29.2950
3	33.825	MF	1.0803	2592.66016	39.99982	20.9401
4	38.234	FM	1.4530	2516.14722	28.86229	20.3221



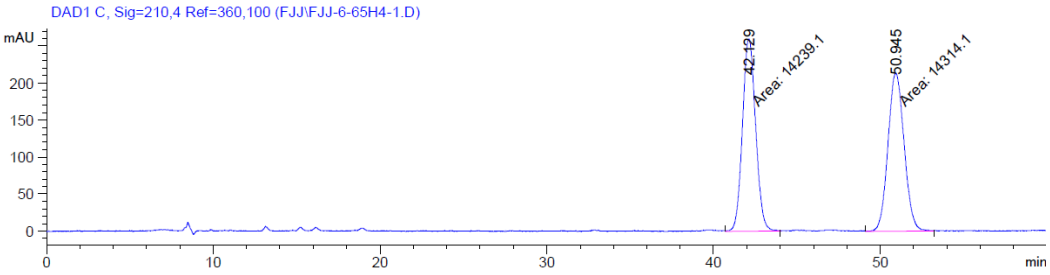
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.916	MF	0.8661	2.44187e4	469.89258	96.3210
2	30.571	FM	0.9310	932.67212	16.69679	3.6790



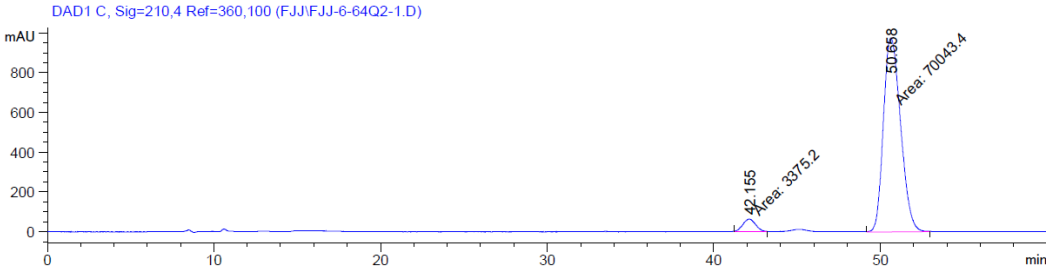
syn-**4ad**

(2*R*,3*R*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ad**): The enantiomeric excess of *syn*-**4ad** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 92:8, flow rate 0.4 mL/min): t_R = 42.2 min (minor), t_R = 50.7 min (major).



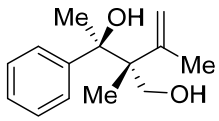
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.129	MM	0.9144	1.42391e4	259.52118	49.8686
2	50.945	MM	1.1198	1.43141e4	213.05009	50.1314



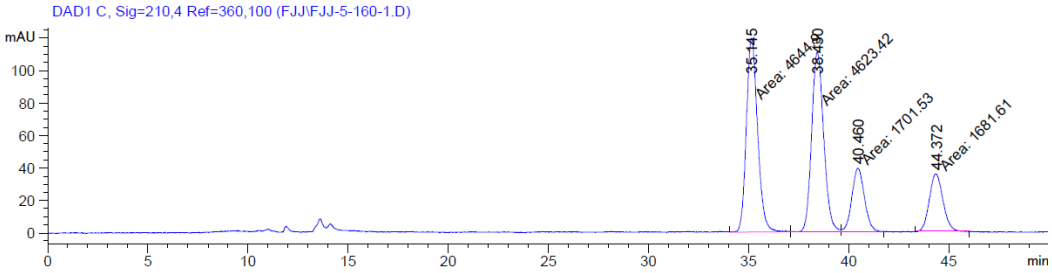
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.155	MM	0.8872	3375.19995	63.40290	4.5972
2	50.658	MM	1.1956	7.00434e4	976.38129	95.4028



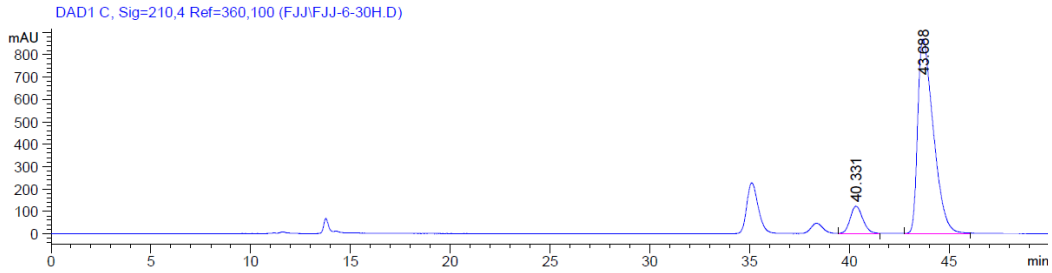
anti-**4ae**

(2*R*,3*R*)-2-Methyl-3-phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ae): The enantiomeric excess of *anti*-**4ae** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.3 mL/min): t_R = 40.3 min (minor), t_R = 43.7 min (major).



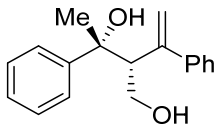
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.145	MF	0.6480	4644.89941	119.45889	36.7143
2	38.430	MF	0.6954	4623.42236	110.80334	36.5446
3	40.460	MF	0.7247	1701.53040	39.13168	13.4493
4	44.372	FM	0.7895	1681.60522	35.49865	13.2918



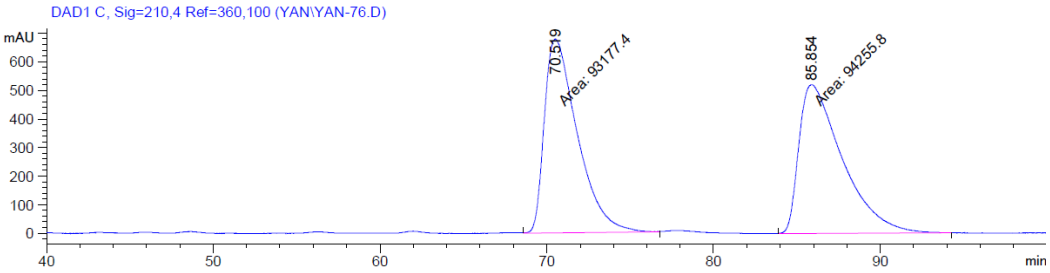
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.331	BV	0.6113	5311.11816	121.66339	10.0944
2	43.688	BV	0.7232	4.73032e4	868.87836	89.9056



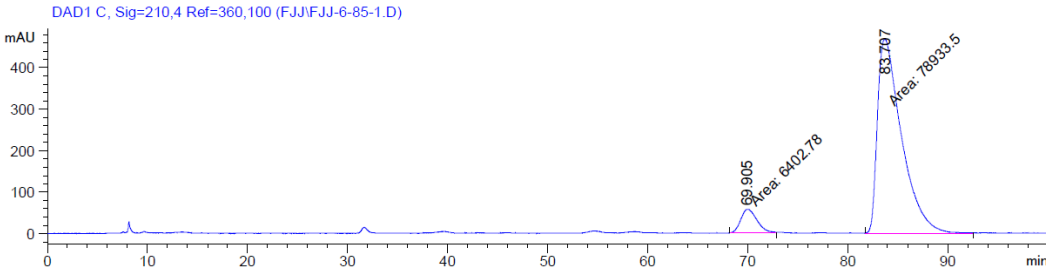
syn-**4af**

(2*R*,3*R*)-3-Phenyl-2-(1-phenylvinyl)butane-1,3-diol (*syn*-**4af**): The enantiomeric excess of *syn*-**4af** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.4 mL/min): t_R = 69.9 min (minor), t_R = 83.7 min (major).



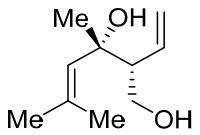
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	70.519	MM	2.2896	9.31774e4	678.25775	49.7123
2	85.854	MM	3.0231	9.42558e4	519.63550	50.2877



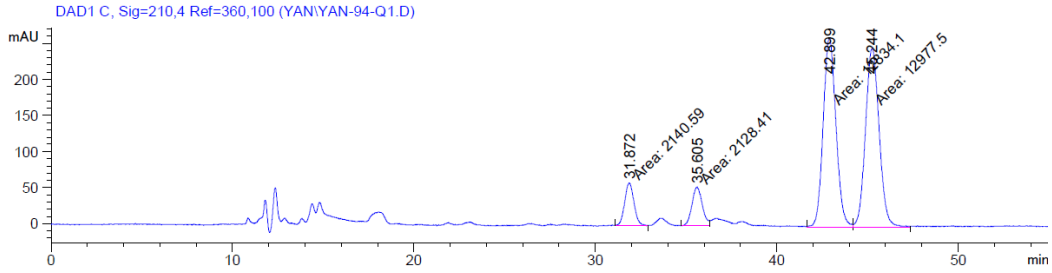
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.905	MM	1.8815	6402.77588	56.71734	7.5030
2	83.707	MM	2.8011	7.89335e4	469.66379	92.4970



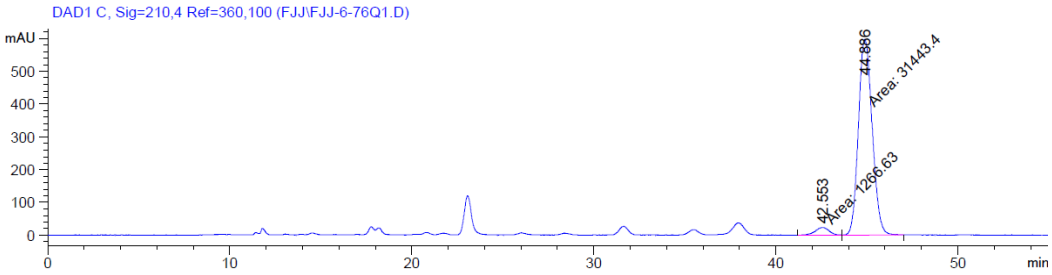
syn-**4nb**

(2*R*,3*S*)-3,5-Dimethyl-2-vinylhex-4-ene-1,3-diol (*syn*-**4nb**): The enantiomeric excess of *syn*-**4nb** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.3 mL/min): t_R = 42.6 min (minor), t_R = 44.9 min (major).



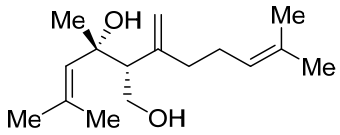
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.872	MF	0.6020	2140.58838	59.26796	7.1162
2	35.605	MF	0.6604	2128.40576	53.71402	7.0757
3	42.899	MF	0.8154	1.28341e4	262.33636	42.6657
4	45.244	FM	0.8750	1.29775e4	247.19064	43.1425



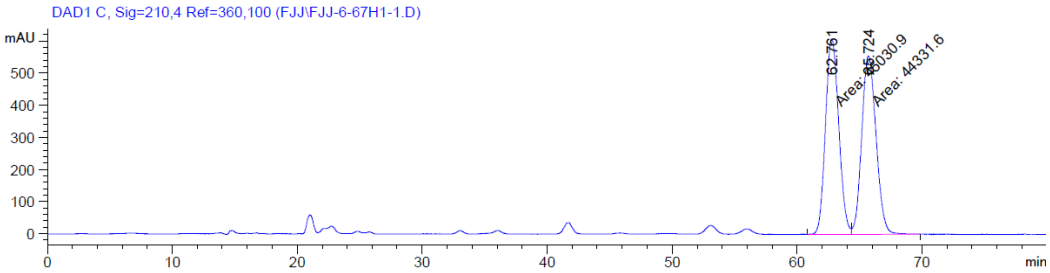
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.553	MF	0.8827	1266.62622	23.91700	3.8723
2	44.886	FM	0.8766	3.14434e4	597.86255	96.1277



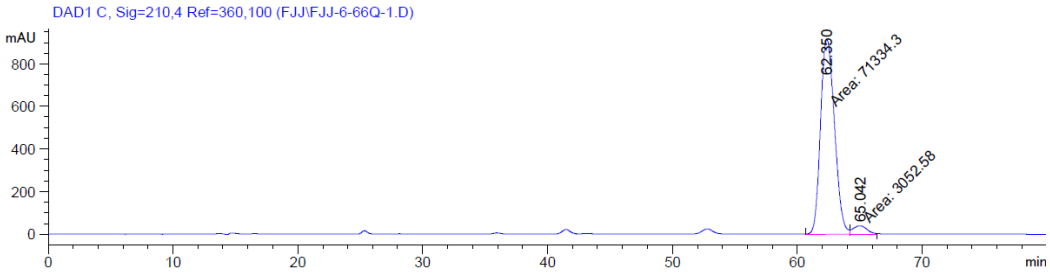
syn-**4nc**

(2*R*,3*S*)-3,5-Dimethyl-2-(6-methylhepta-1,5-dien-2-yl)hex-4-ene-1,3-diol (*syn*-**4nc**): The enantiomeric excess of *syn*-**4nc** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.25 mL/min): t_R = 62.4 min (major), t_R = 65.0 min (minor).



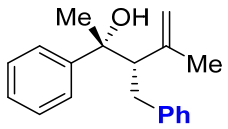
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	62.761	MF	1.2328	4.50309e4	608.78876	50.3913
2	65.724	FM	1.3301	4.43316e4	555.50104	49.6087



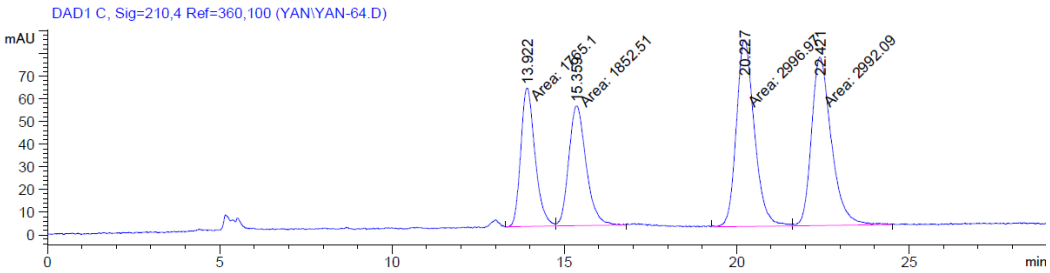
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	62.350	MF	1.2958	7.13343e4	917.53394	95.8963
2	65.042	FM	1.2670	3052.58325	40.15623	4.1037



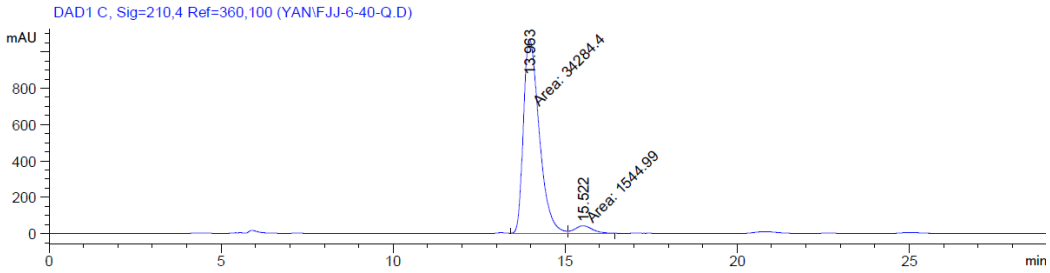
syn-**7**

(2*R*,3*S*)-3-Benzyl-4-methyl-2-phenylpent-4-en-2-ol (*syn*-7): The enantiomeric excess of *syn*-**7** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 14.0 min (major), t_R = 15.5 min (minor).



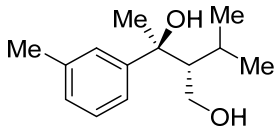
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.922	MF	0.4818	1765.10364	61.06294	18.3737
2	15.359	FM	0.5840	1852.50989	52.86738	19.2836
3	20.227	MF	0.6068	2996.96851	82.32286	31.1967
4	22.421	FM	0.6708	2992.09204	74.33650	31.1460



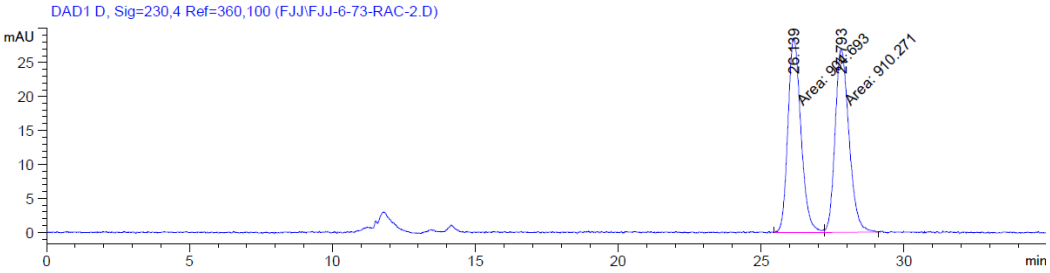
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.963	MF	0.5337	3.42844e4	1070.64587	95.6879
2	15.522	FM	0.6098	1544.98755	42.22543	4.3121



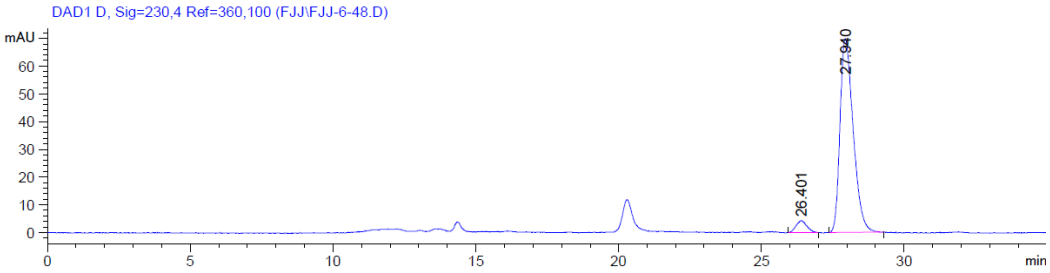
anti-**8**

(2*R*,3*S*)-2-Isopropyl-3-(*m*-tolyl)butane-1,3-diol (*anti*-8): The enantiomeric excess of *anti*-**8** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel ID column, column temperature 20 °C, solvent Heptane:*i*PrOH = 96:4, flow rate 0.3 mL/min): t_R = 26.4 min (minor), t_R = 27.9 min (major).



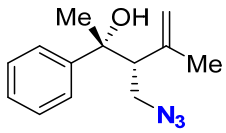
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.139	MF	0.5270	904.69330	28.61263	49.8463
2	27.793	FM	0.5646	910.27069	26.86940	50.1537



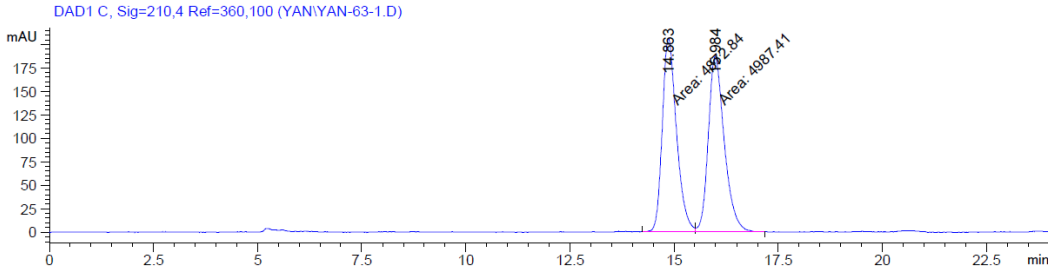
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.401	BB	0.3499	114.27889	4.27402	4.8504
2	27.940	BB	0.4760	2241.77173	69.92561	95.1496



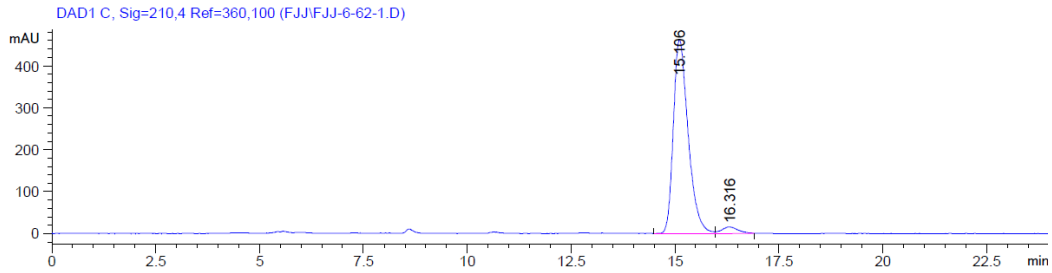
syn-**9**

(2*R*,3*R*)-3-(Azidomethyl)-4-methyl-2-phenylpent-4-en-2-ol (*syn*-9): The enantiomeric excess of *syn*-**9** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:*i*PrOH = 95:5, flow rate 0.6 mL/min): t_R = 15.1 min (major), t_R = 16.3 min (minor).



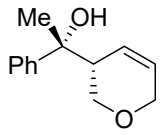
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.863	MF	0.3935	4872.83838	206.37277	49.4190
2	15.984	FM	0.4453	4987.40576	186.65556	50.5810



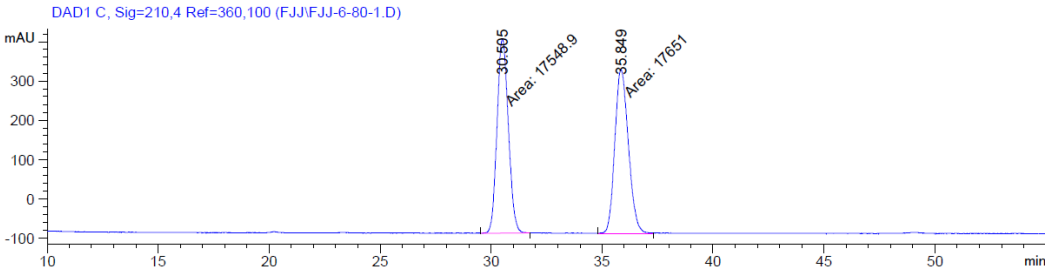
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.106	BV	0.3768	1.14547e4	462.71332	96.2708
2	16.316	VV	0.3352	443.71857	16.01588	3.7292



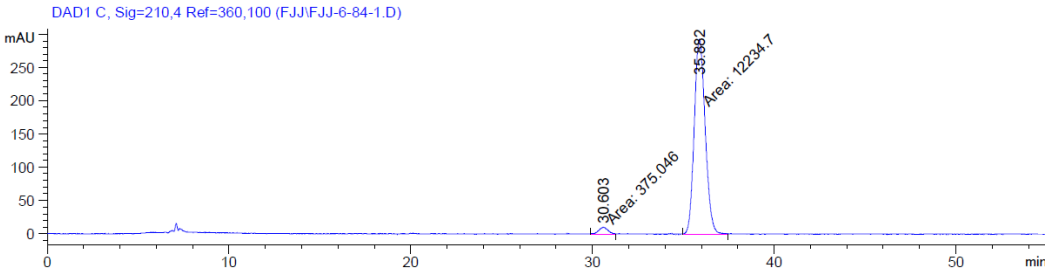
syn-**10**

(*R*)-1-((*R*)-3,6-Dihydro-2H-pyran-3-yl)-1-phenylethan-1-ol (*syn*-10): The enantiomeric excess of *syn*-**10** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.5 mL/min): t_R = 30.6 min (minor), t_R = 35.9 min (major).



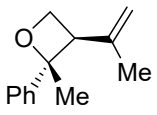
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.505	MM	0.5917	1.75489e4	494.33951	49.8550
2	35.849	MM	0.7065	1.76510e4	416.39059	50.1450



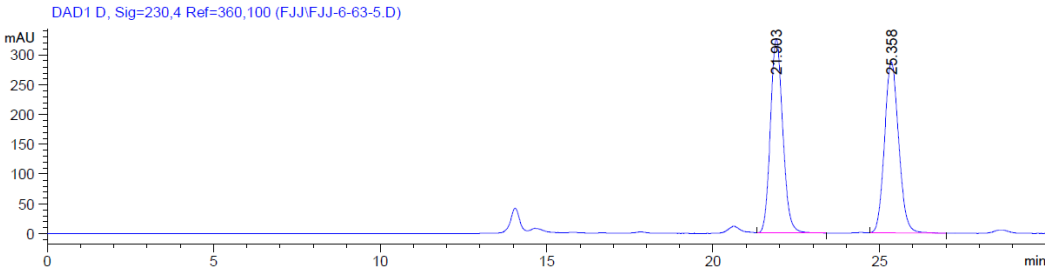
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.603	MM	0.5908	375.04608	10.58073	2.9743
2	35.882	MM	0.6962	1.22347e4	292.89719	97.0257



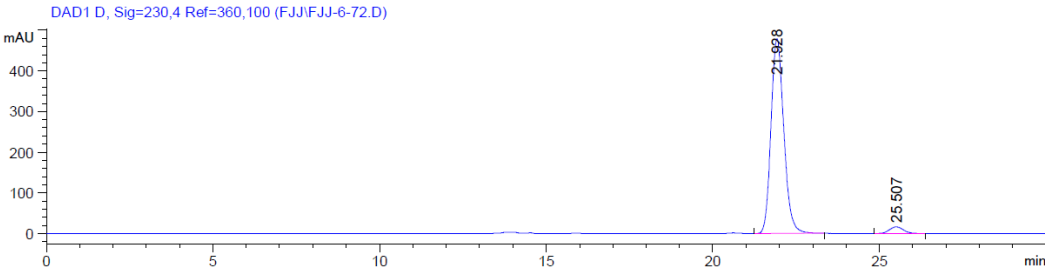
trans-**11**

(2*R*,3*R*)-2-Methyl-2-phenyl-3-(prop-1-en-2-yl)oxetane (*trans*-11): The enantiomeric excess of *trans*-**11** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IC column, column temperature 20 °C, solvent Heptane:*i*PrOH = 97:3, flow rate 0.25 mL/min): t_R = 21.9 min (major), t_R = 25.5 min (minor).



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.903	VB	0.4024	8460.58496	326.45944	49.9850
2	25.358	BB	0.4661	8465.66309	286.99872	50.0150

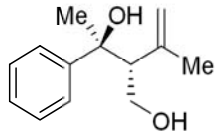


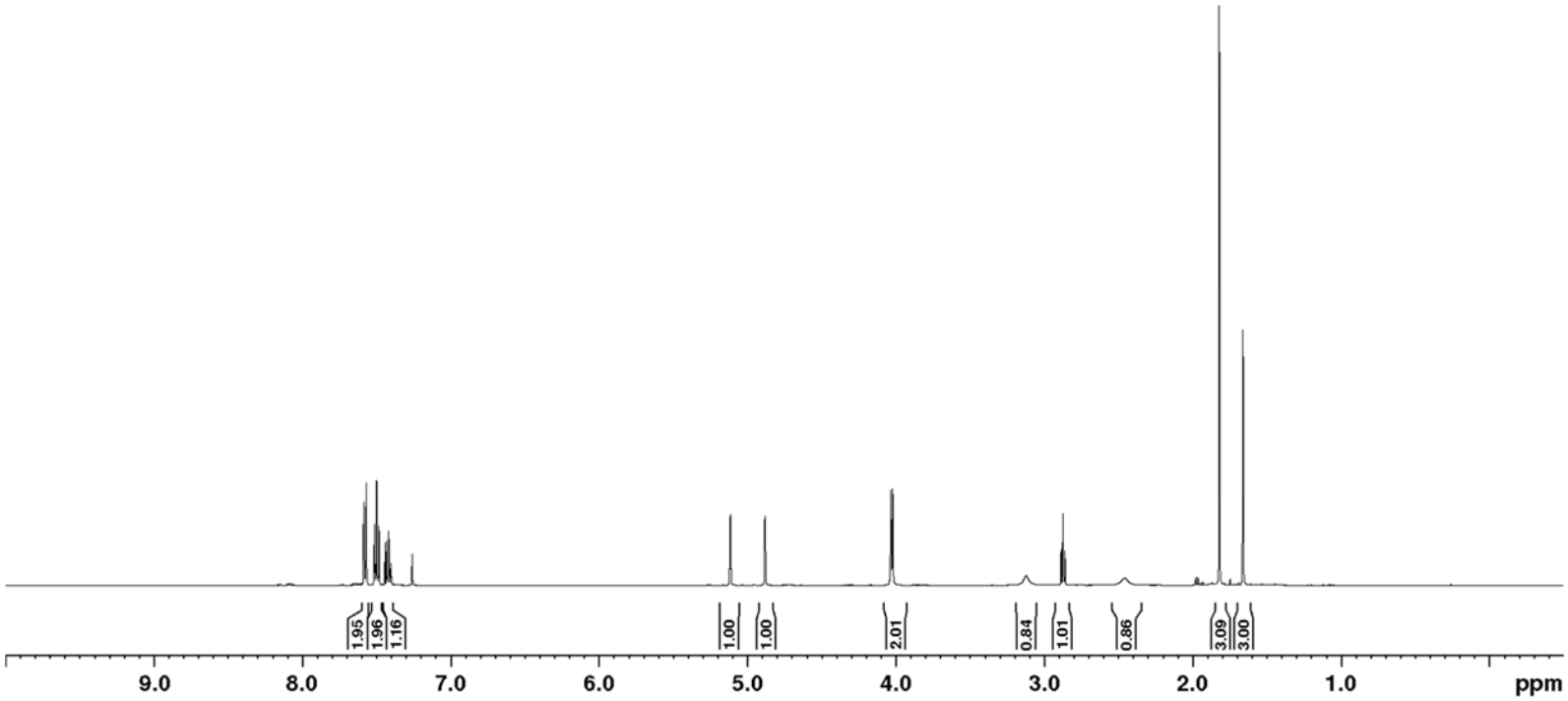
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.928	BB	0.4162	1.28136e4	478.81979	96.3584
2	25.507	BB	0.4100	484.25931	16.51861	3.6416

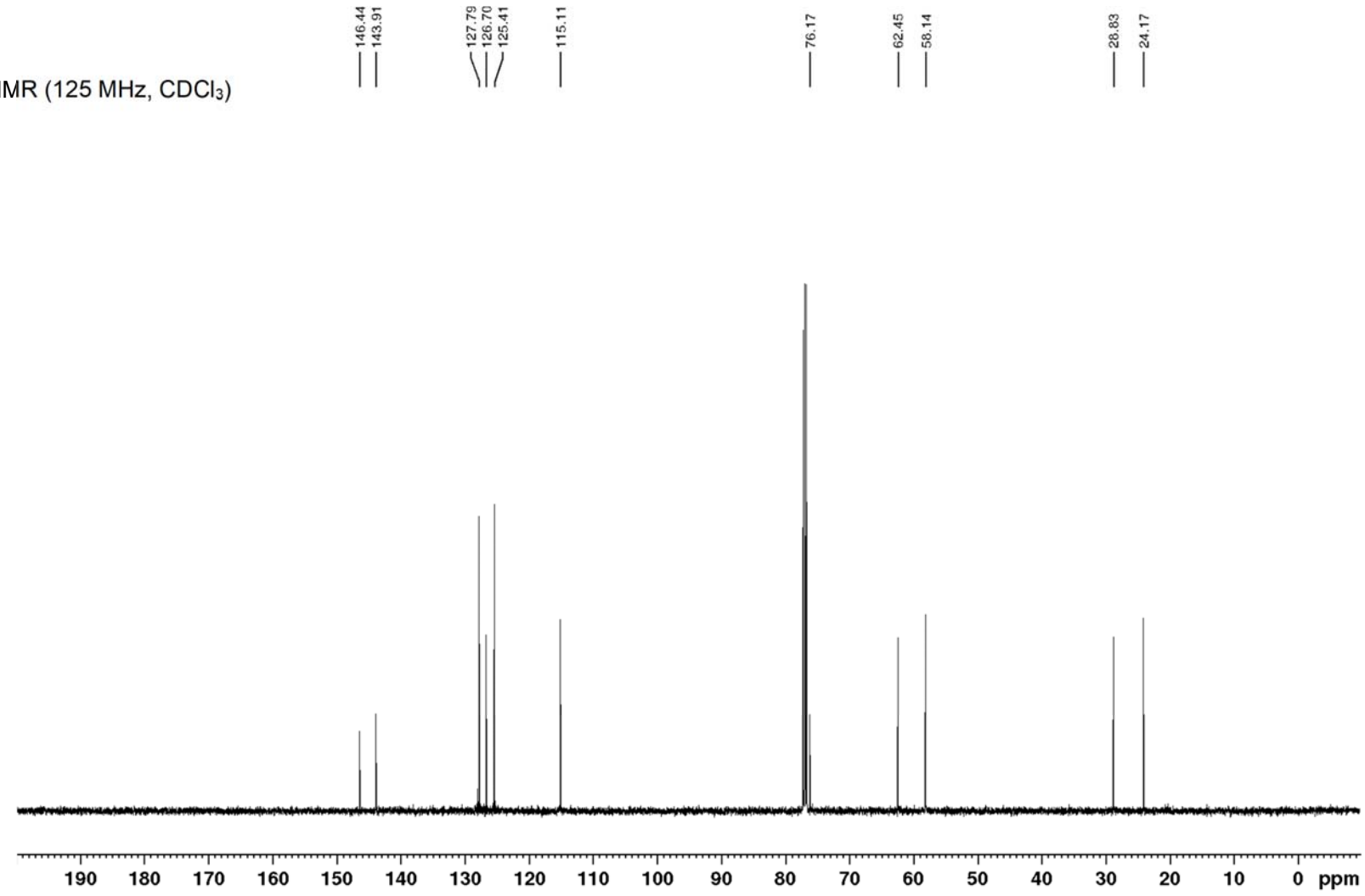
9 NMR Spectra

(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4aa**): ^{1}H NMR (500 MHz, $CDCl_3$)

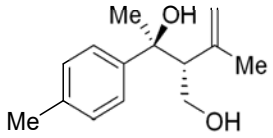


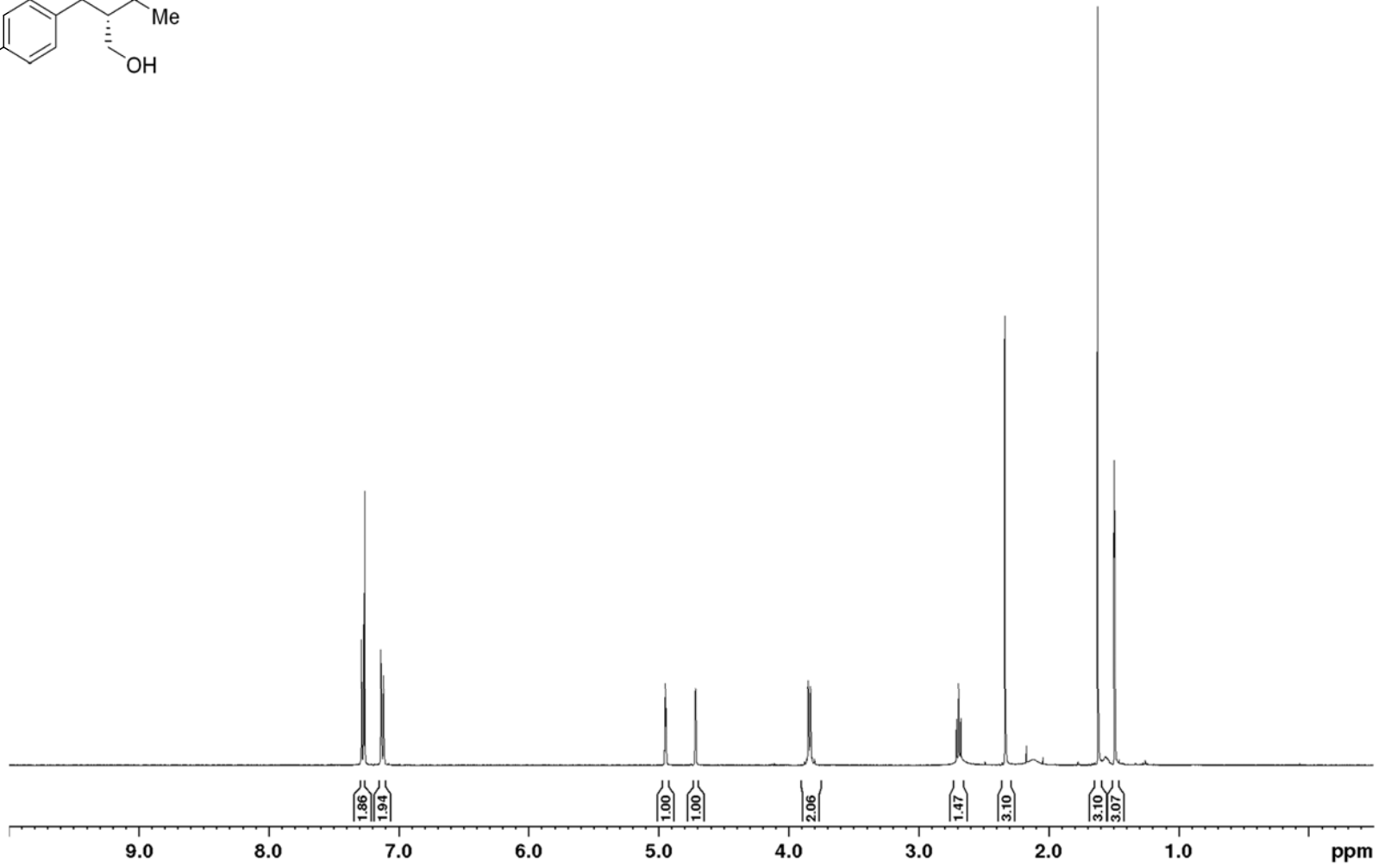


^{13}C NMR (125 MHz, $CDCl_3$)

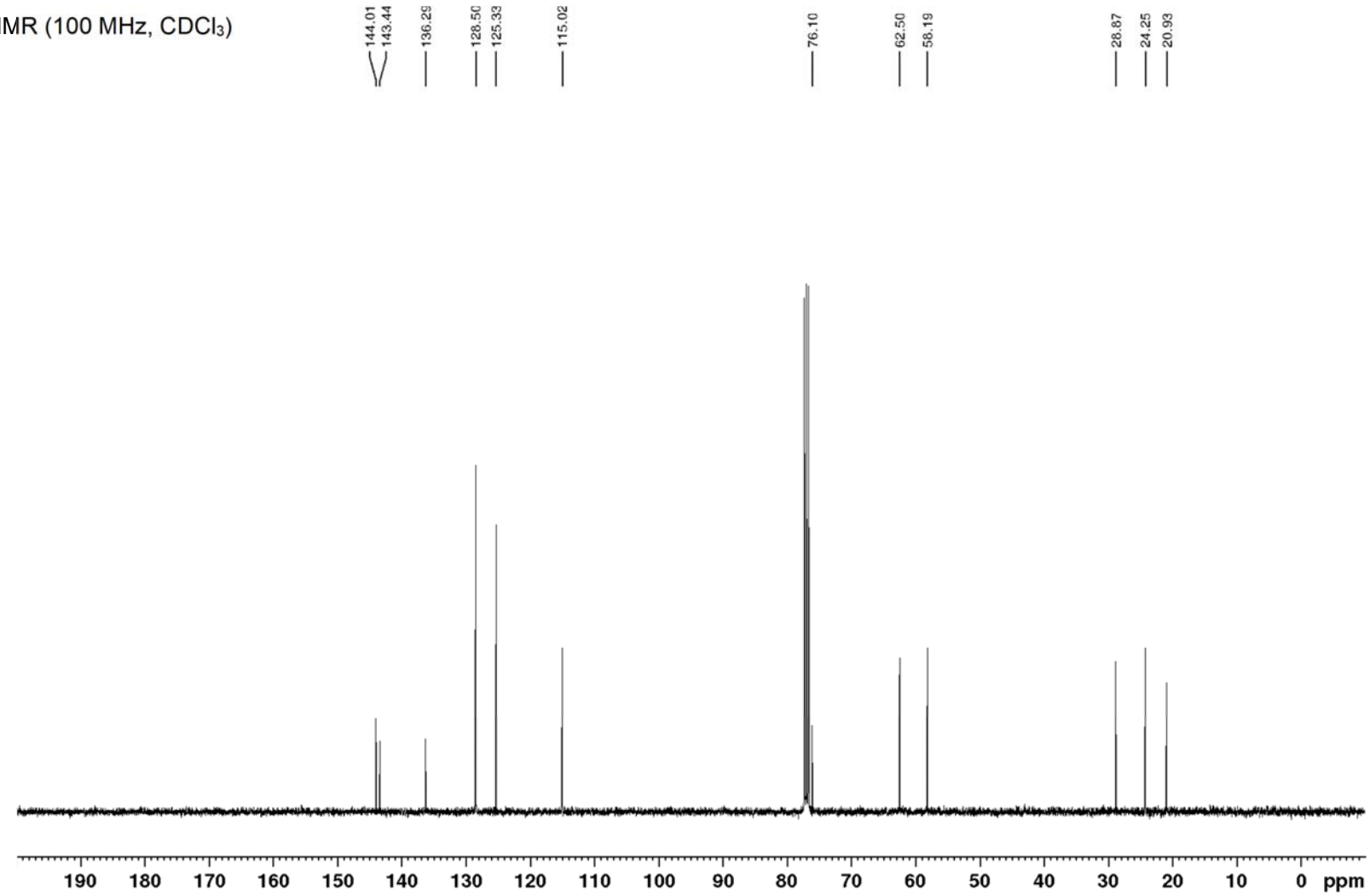


(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*anti*-**4ba**): ^{1}H NMR (400 MHz, $CDCl_3$)

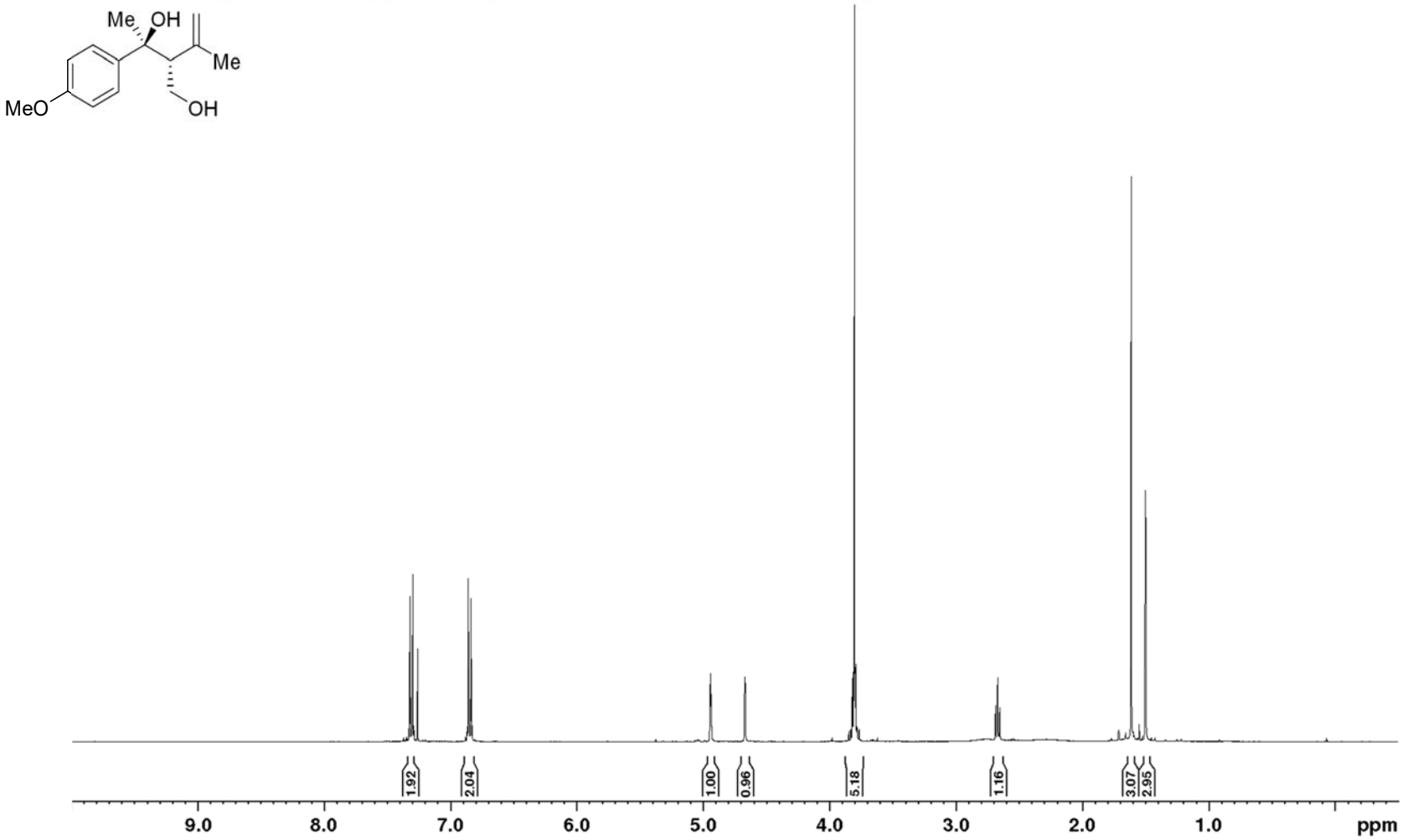




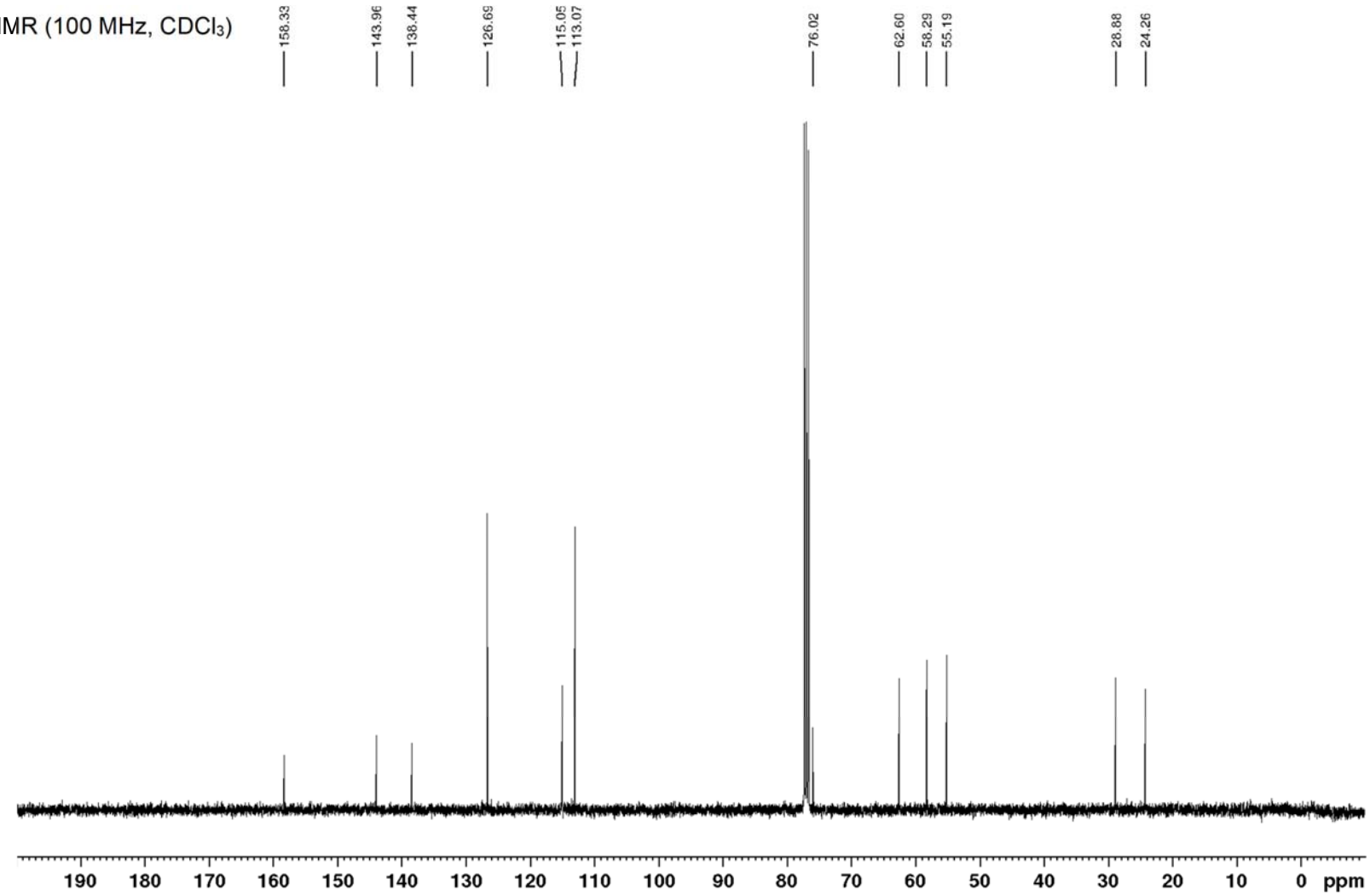
^{13}C NMR (100 MHz, $CDCl_3$)



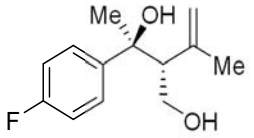
(2*R*,3*S*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ca**): ^{1}H NMR (400 MHz, $CDCl_3$)

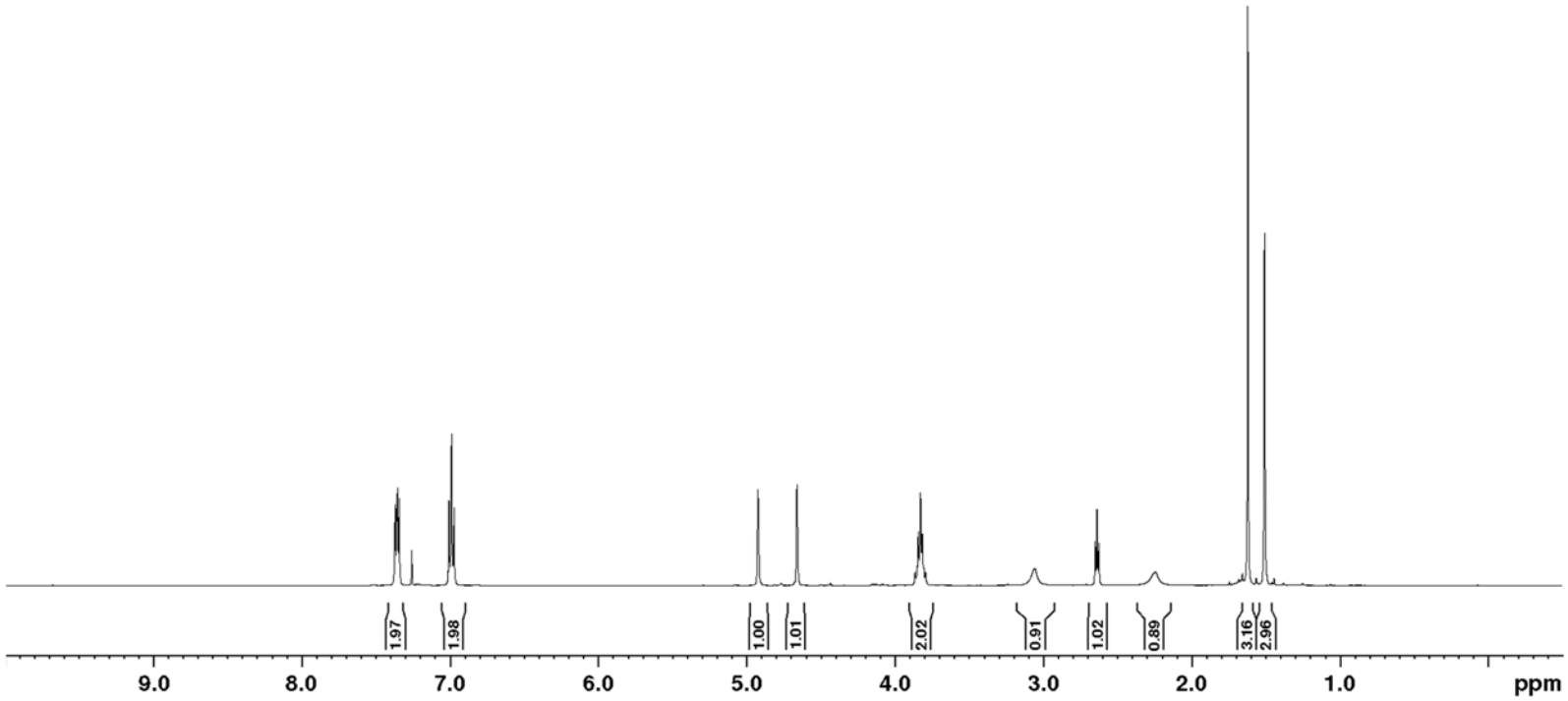


^{13}C NMR (100 MHz, $CDCl_3$)

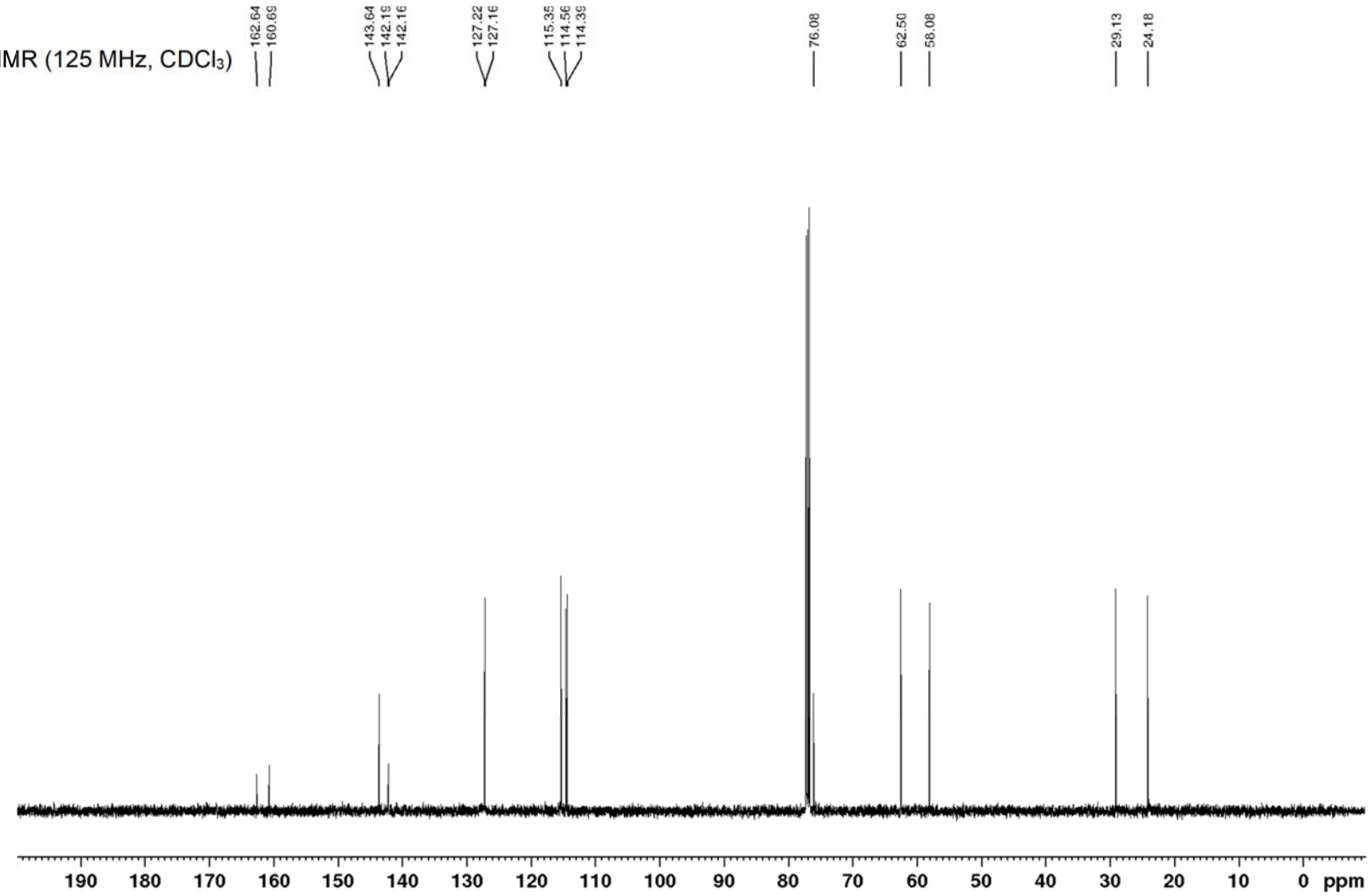


(2*R*,3*S*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4da**): ^{1}H NMR (500 MHz, $CDCl_3$)

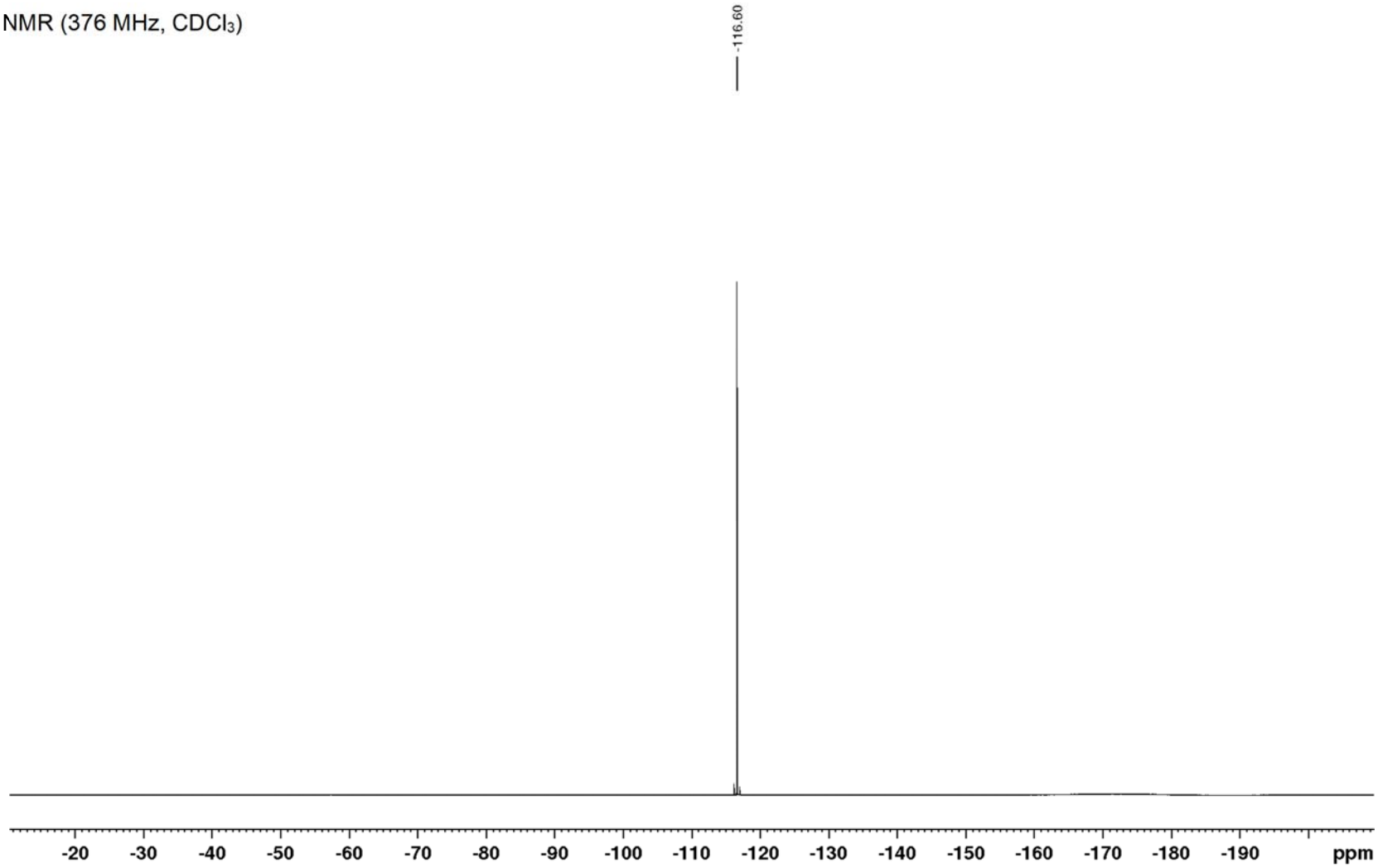




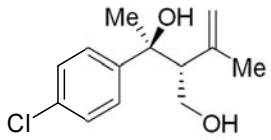
^{13}C NMR (125 MHz, $CDCl_3$)

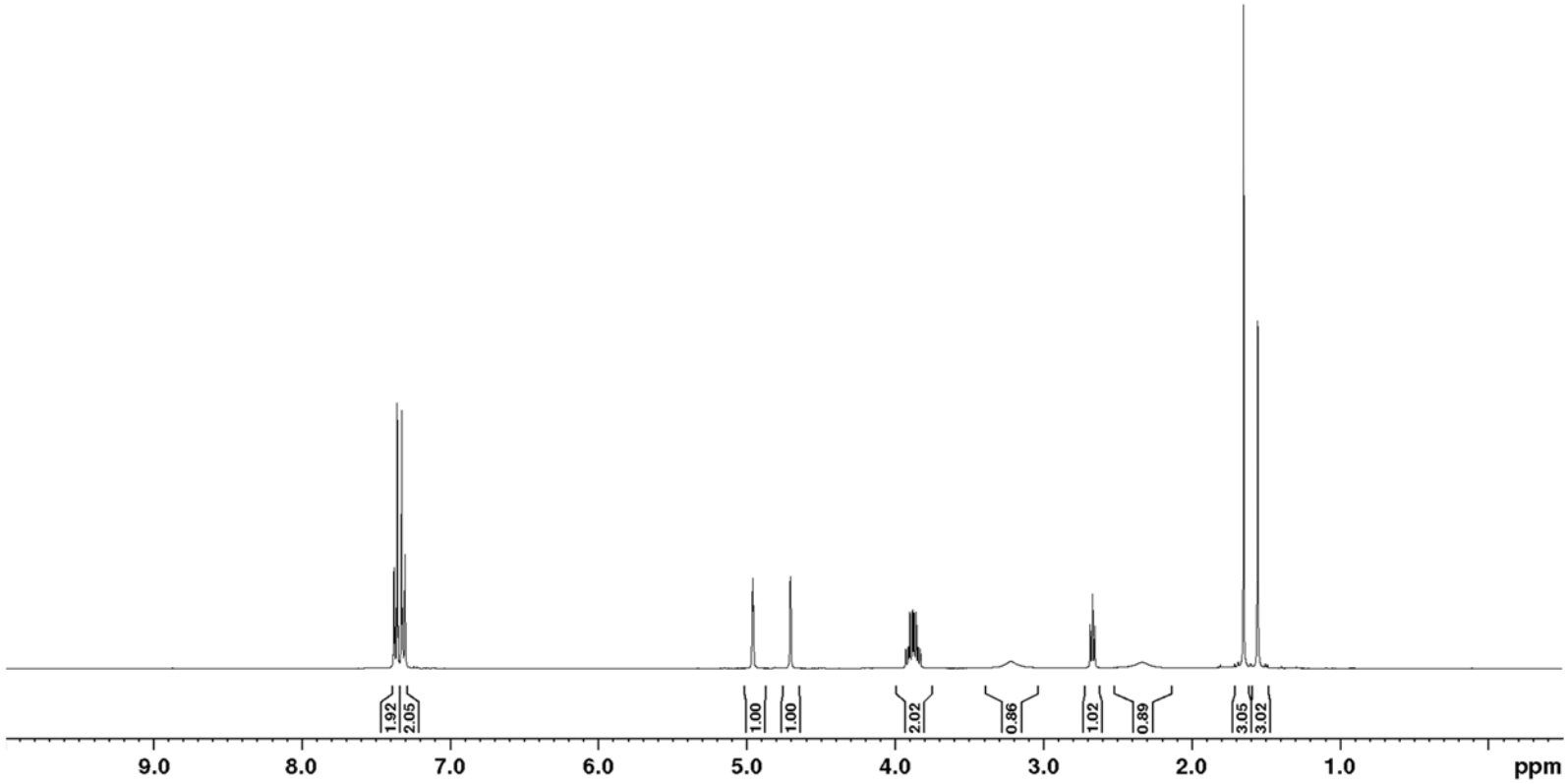


^{19}F NMR (376 MHz, $CDCl_3$)

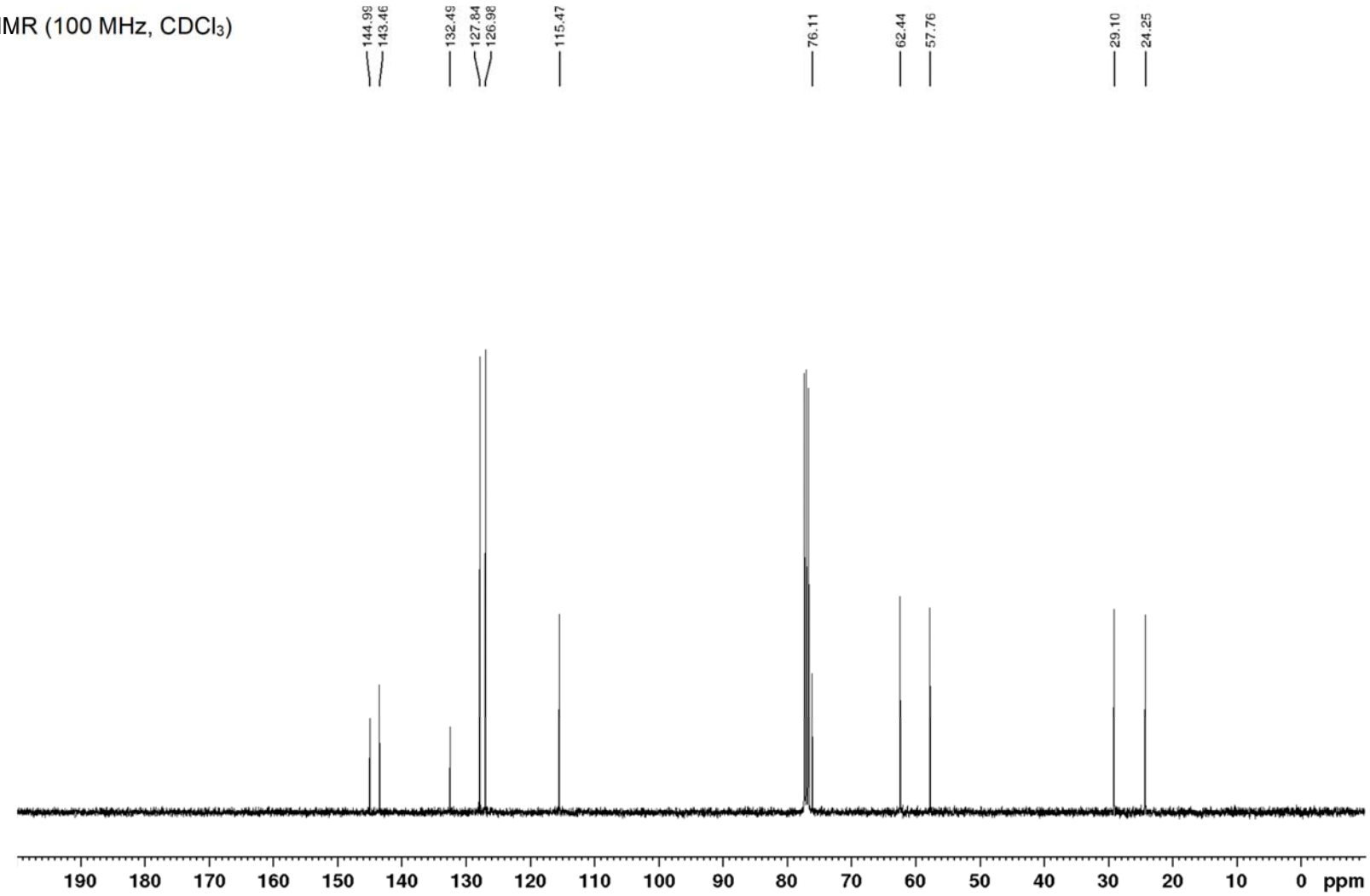


(2*R*,3*S*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4ea**): ^{1}H NMR (400 MHz, $CDCl_3$)

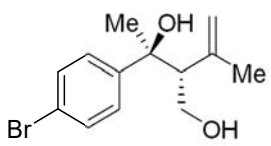




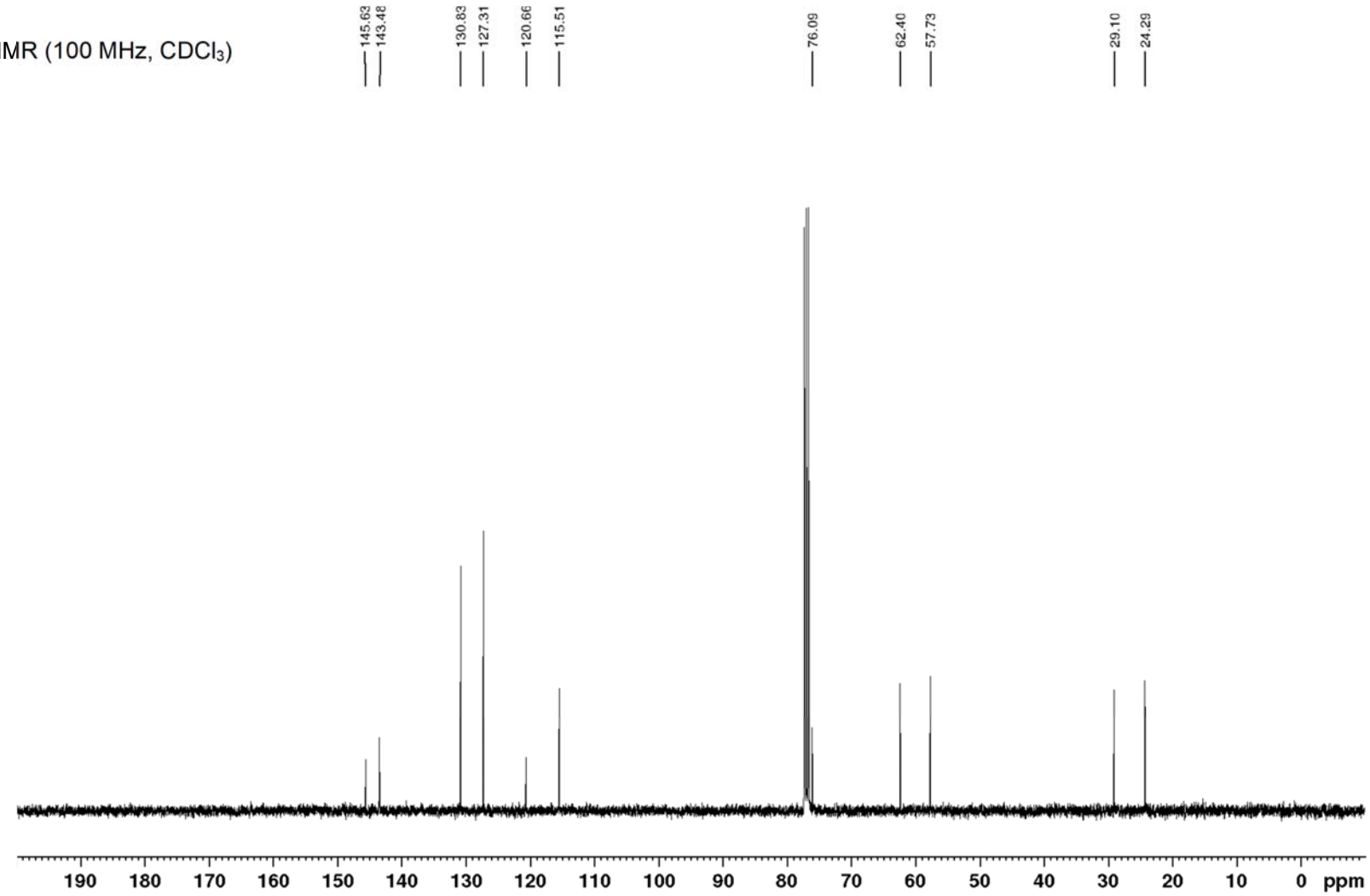
^{13}C NMR (100 MHz, $CDCl_3$)



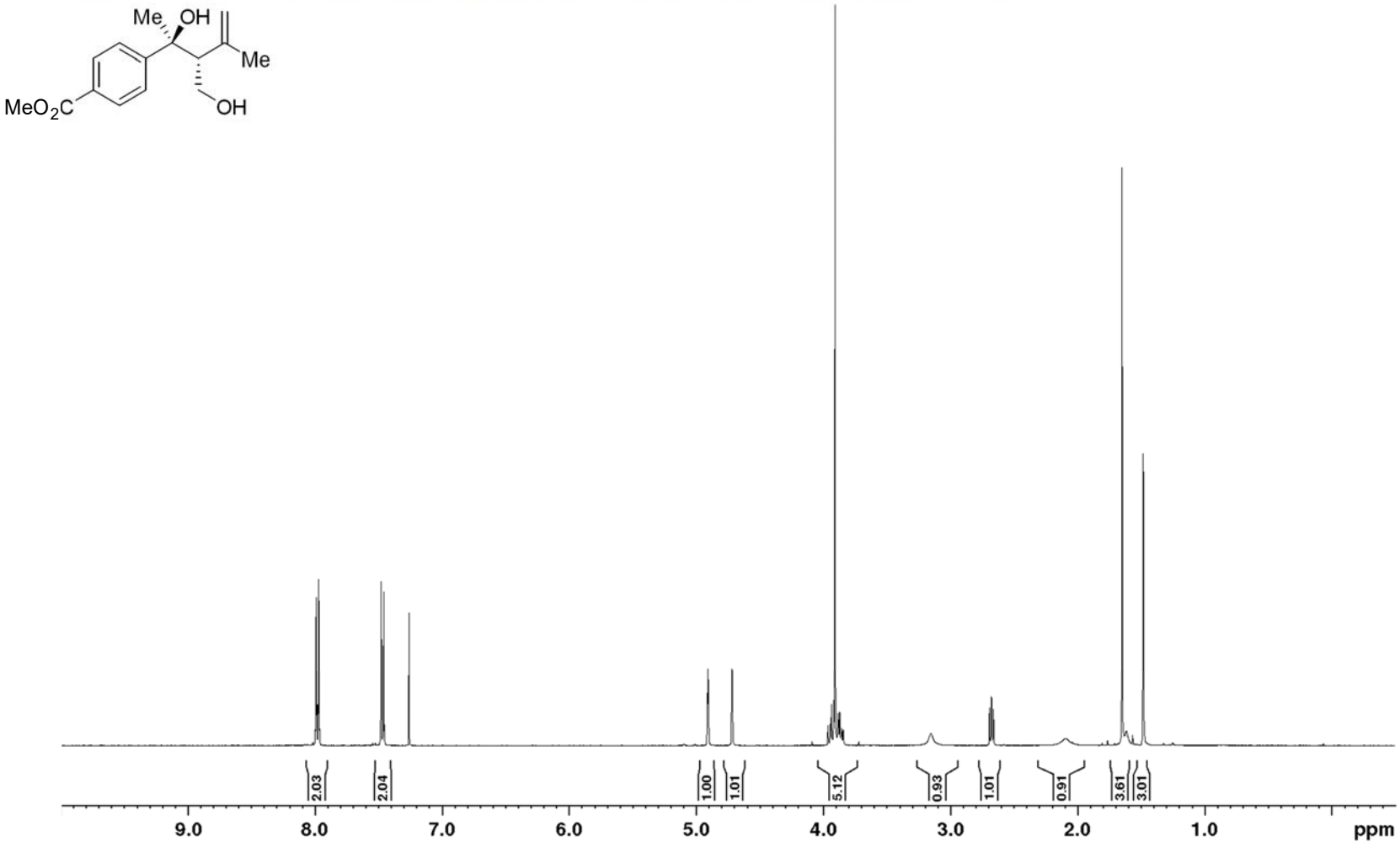
(2*R*,3*S*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-**4fa**): ^{1}H NMR (400 MHz, $CDCl_3$)



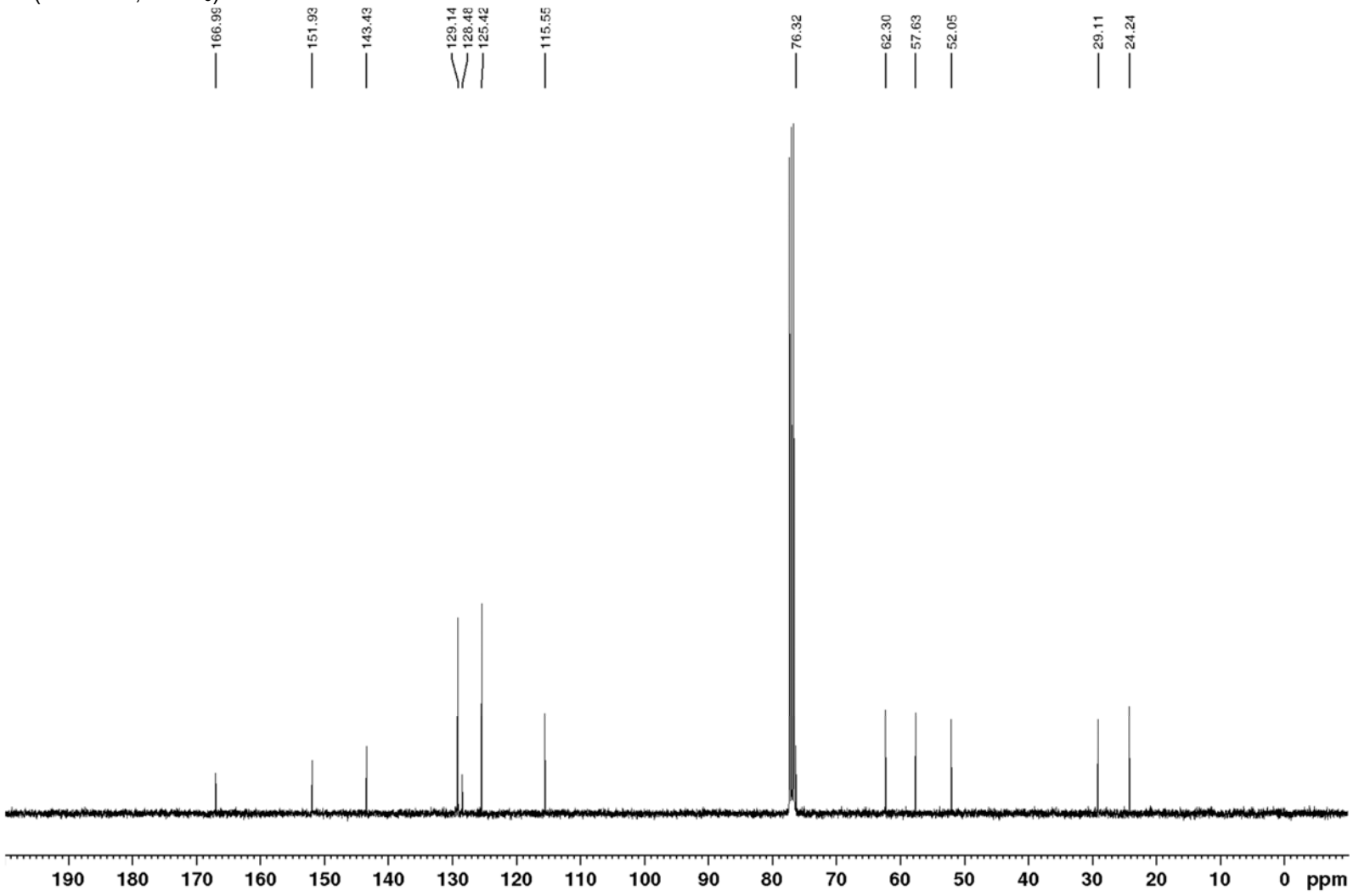
^{13}C NMR (100 MHz, $CDCl_3$)



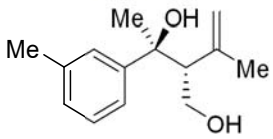
4-((2*S*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*anti*-4ga): ^{1}H NMR (400 MHz, $CDCl_3$)



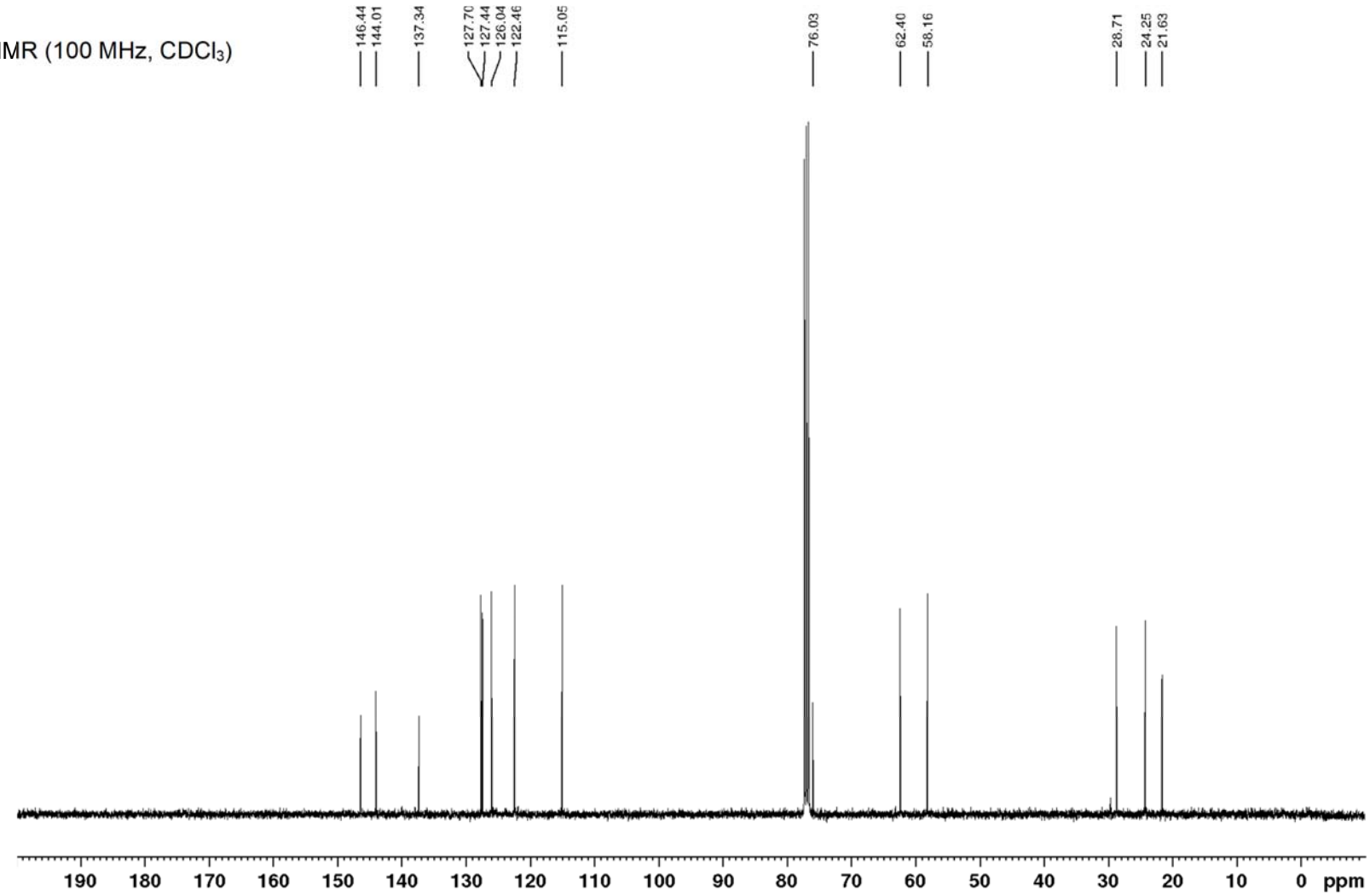
^{13}C NMR (100 MHz, $CDCl_3$)



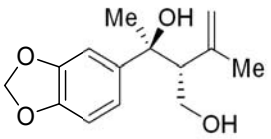
(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*anti*-4ha): ^{1}H NMR (400 MHz, $CDCl_3$)

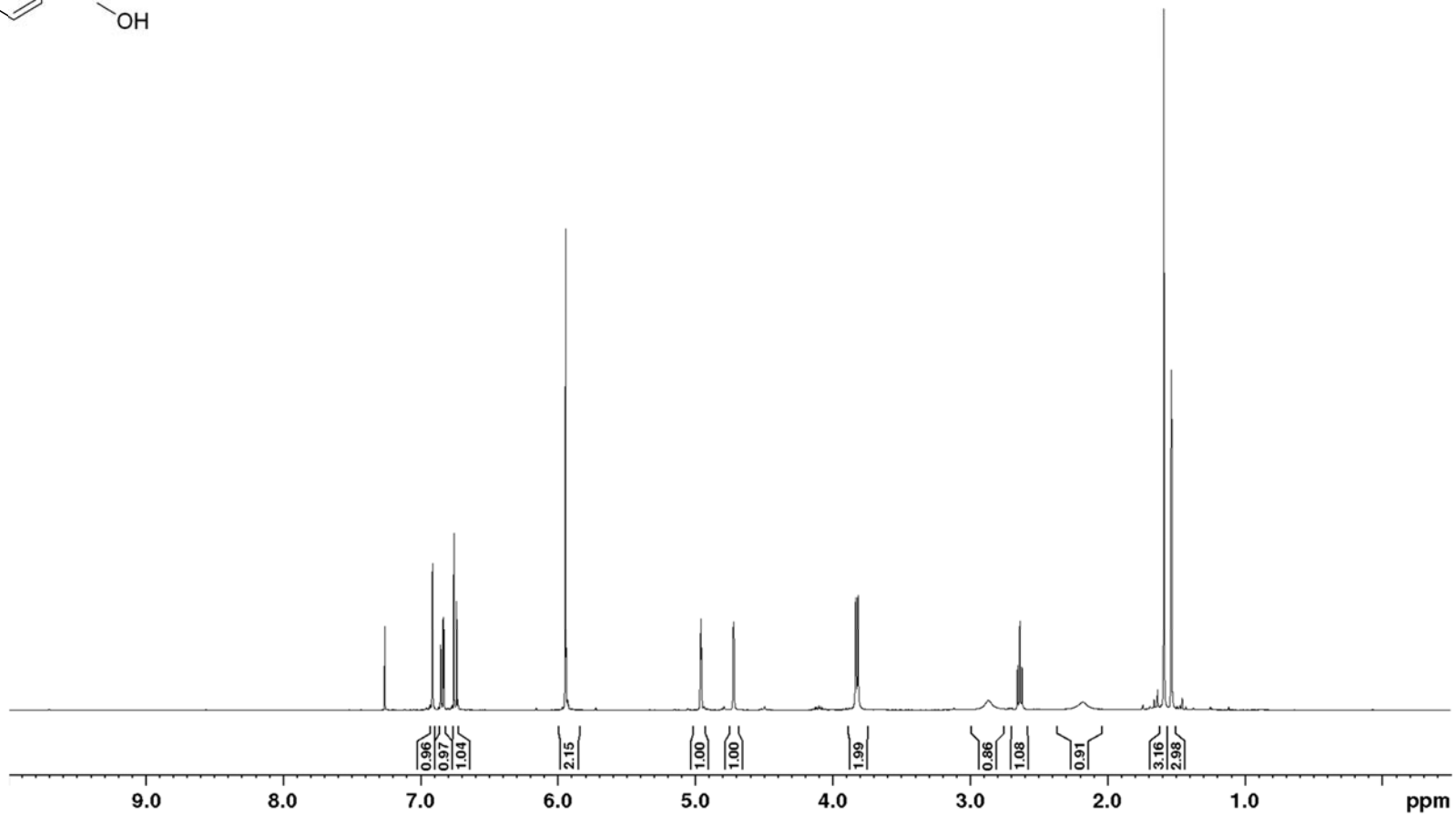


^{13}C NMR (100 MHz, $CDCl_3$)

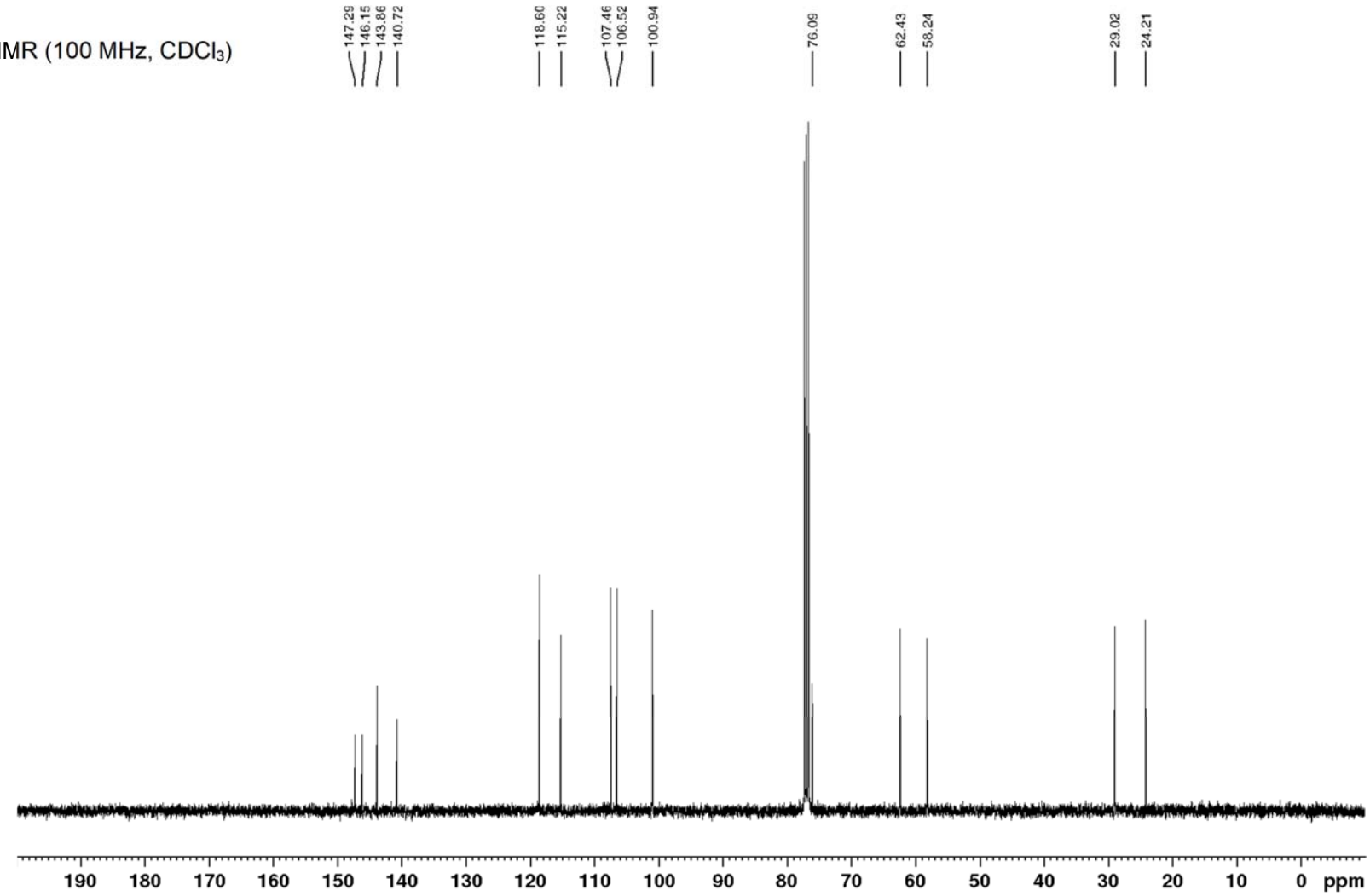


(2*R*,3*S*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ia): ^{1}H NMR (400 MHz, $CDCl_3$)

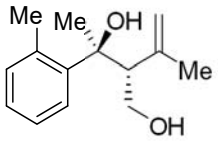


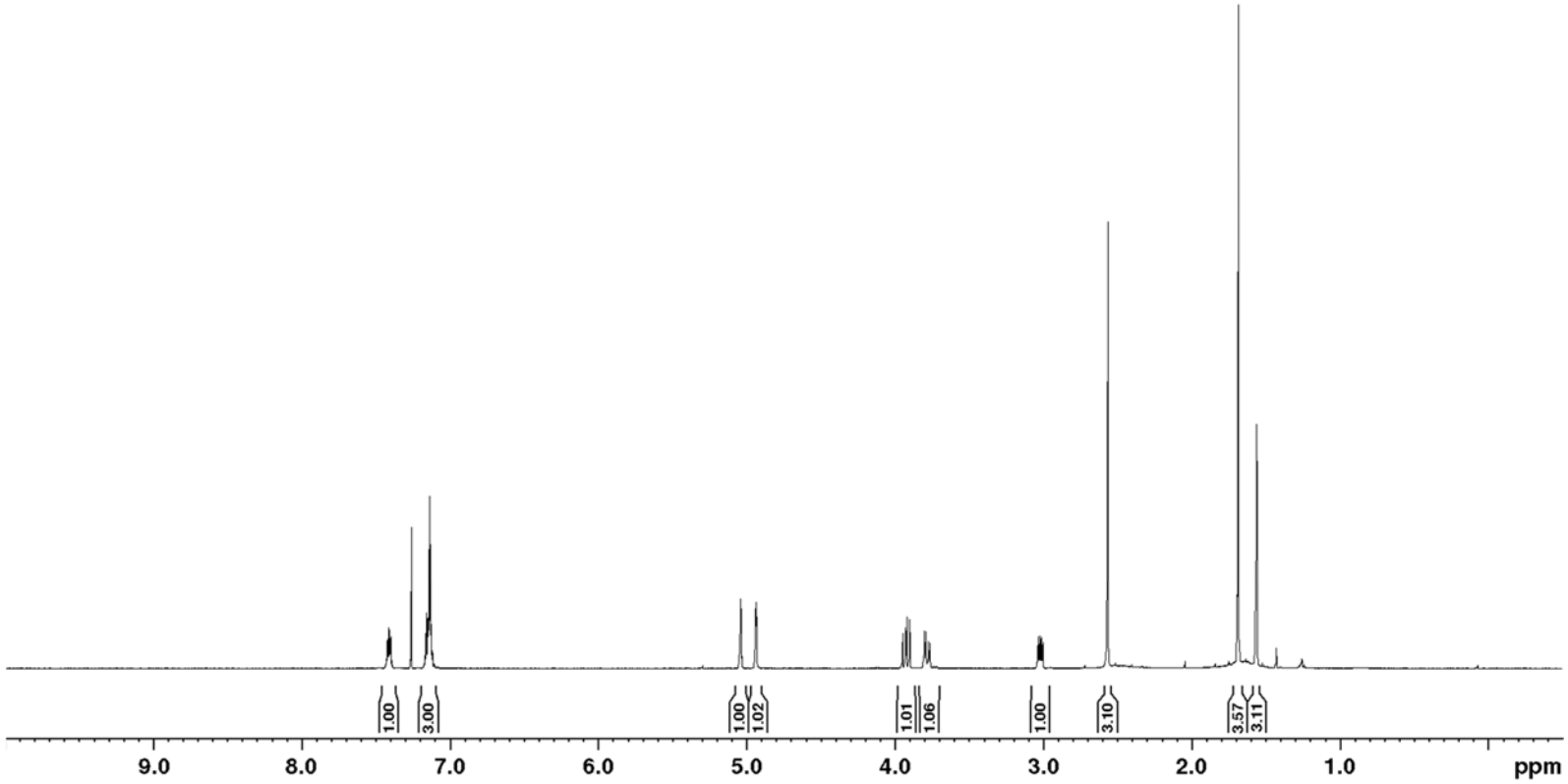


^{13}C NMR (100 MHz, $CDCl_3$)

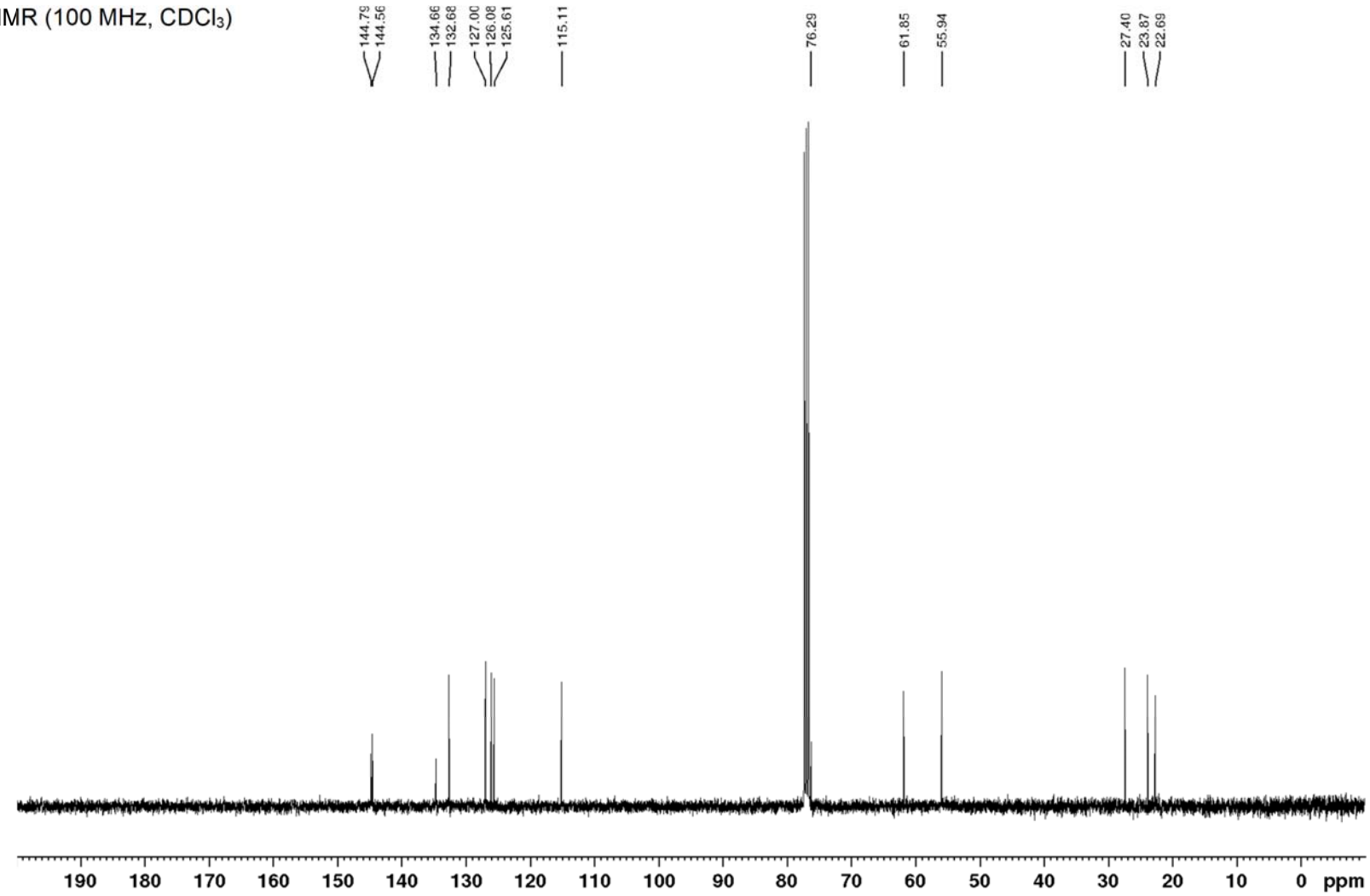


(2*R*,3*S*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*anti*-4ja): ^{1}H NMR (400 MHz, $CDCl_3$)

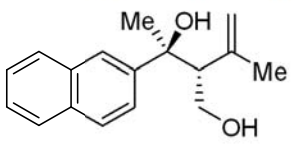




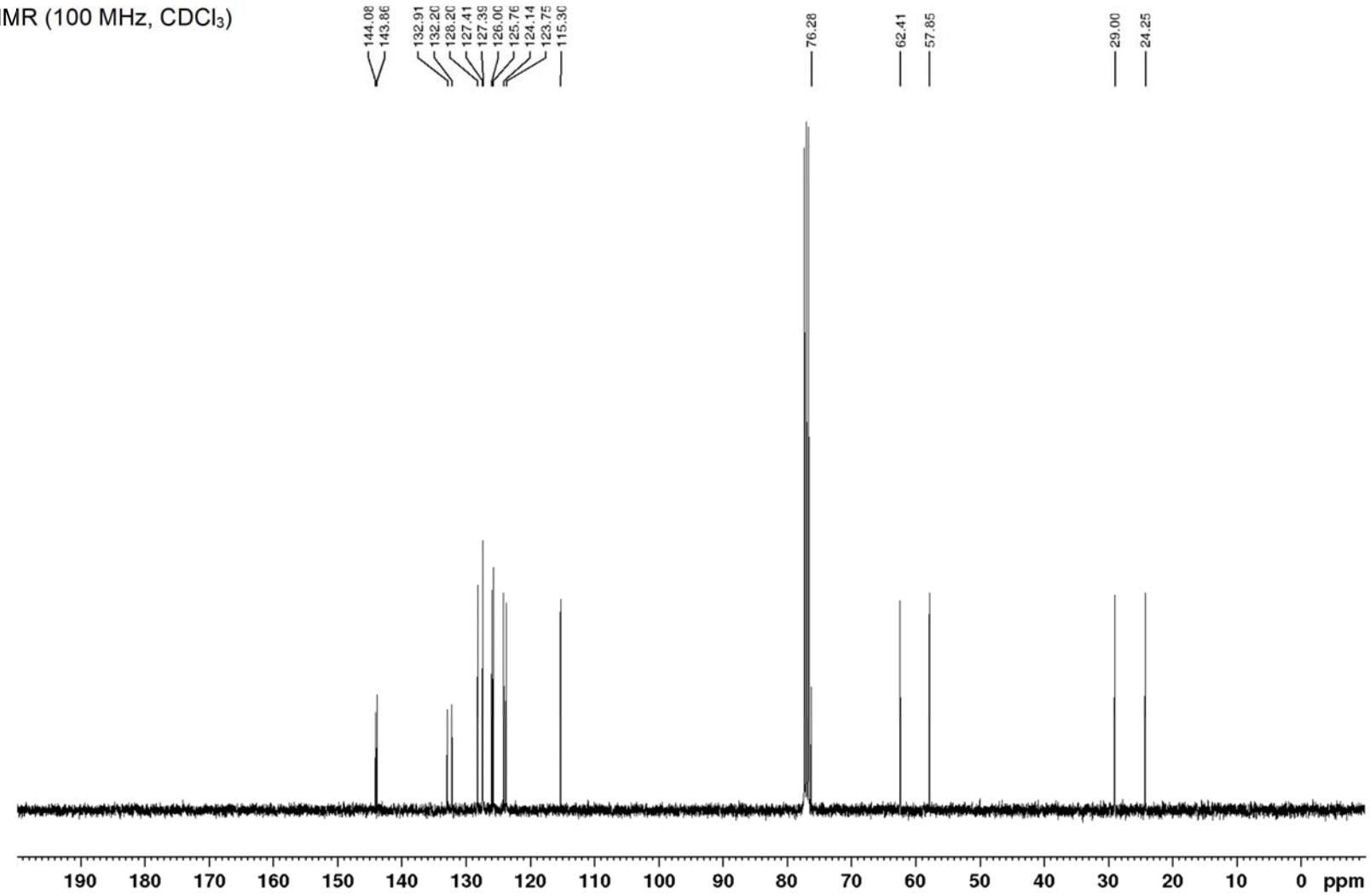
^{13}C NMR (100 MHz, $CDCl_3$)



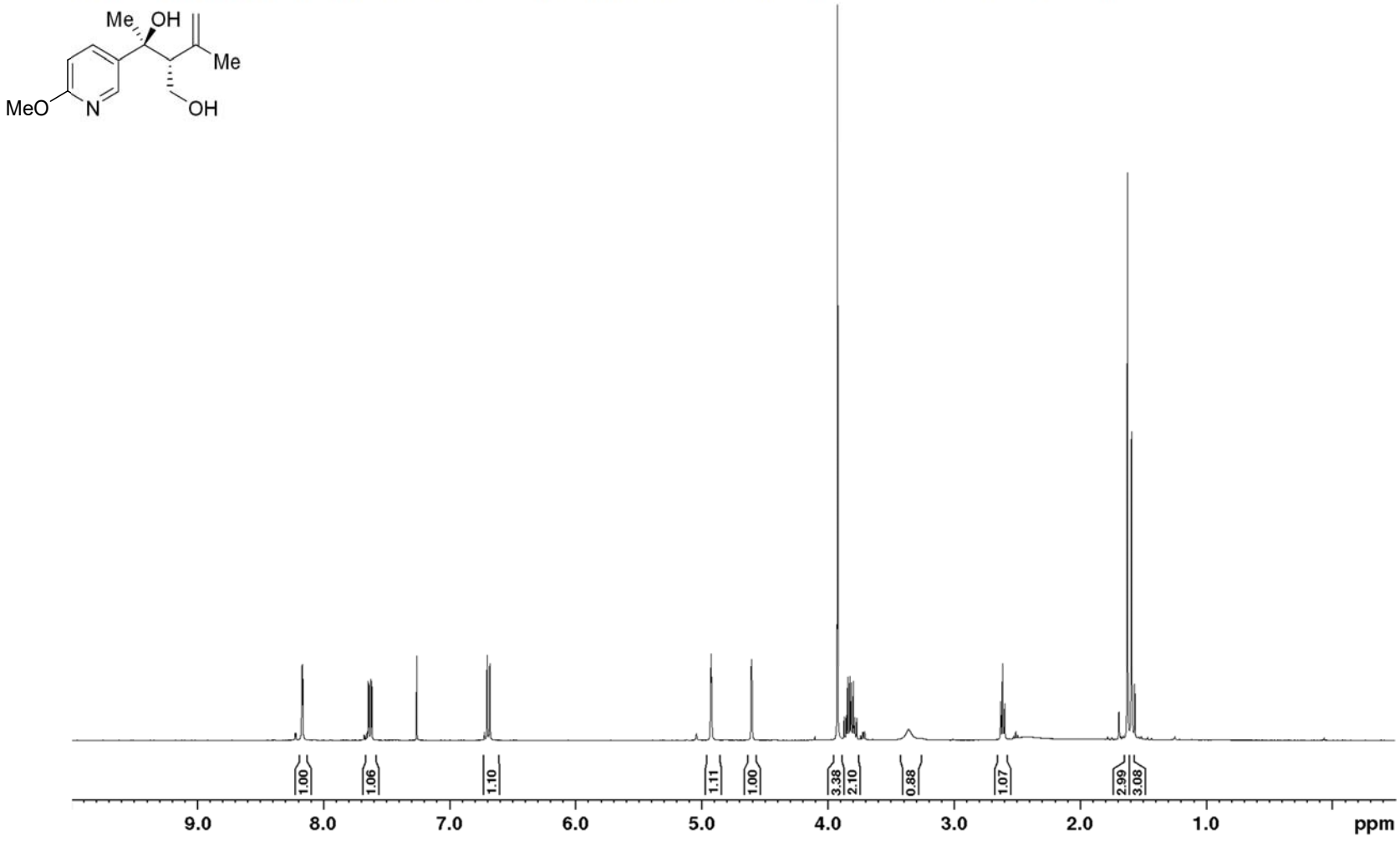
(2*R*,3*S*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ka): ^{1}H NMR (400 MHz, $CDCl_3$)



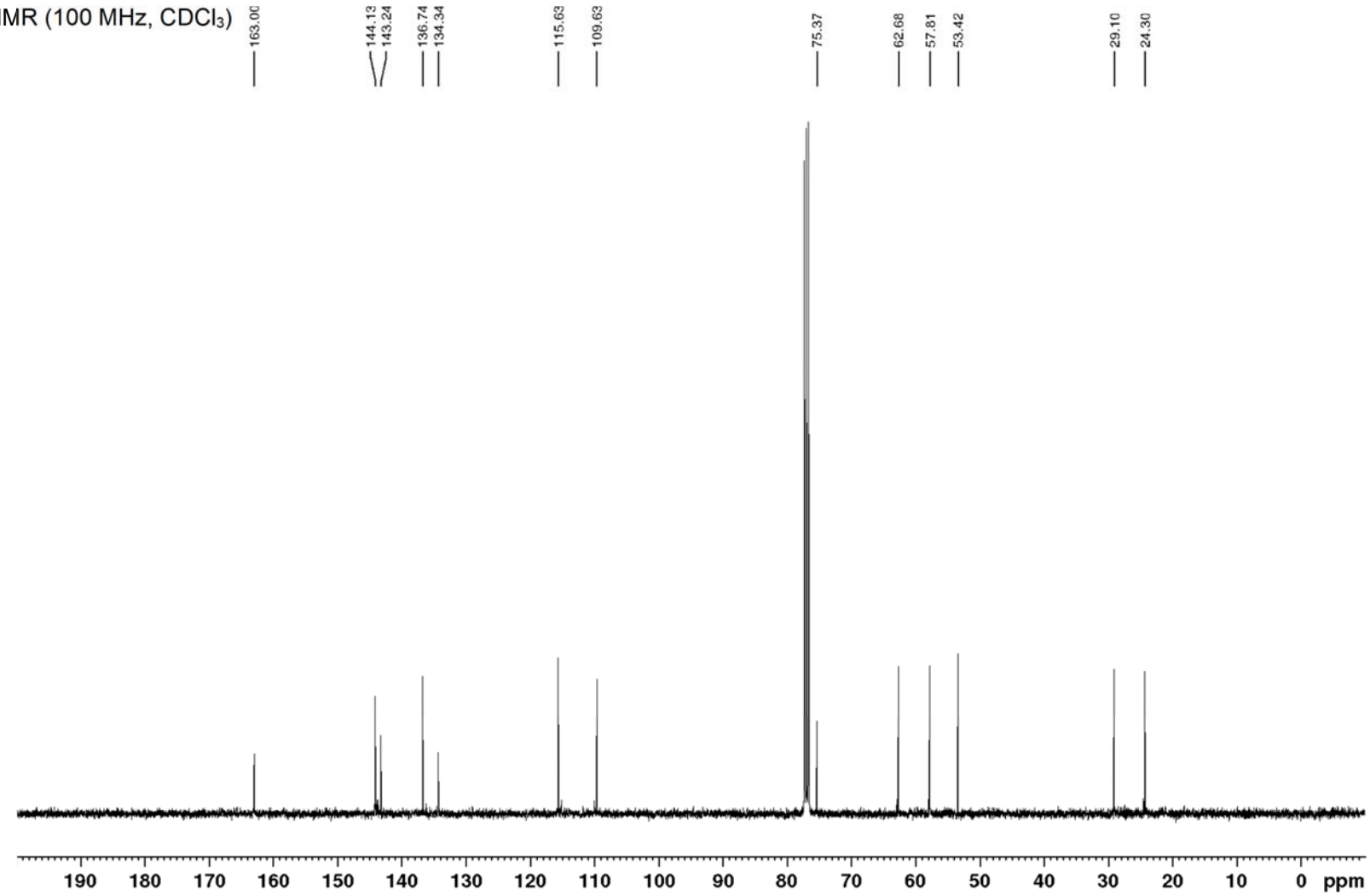
^{13}C NMR (100 MHz, $CDCl_3$)



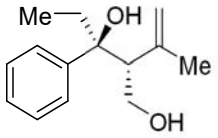
(2*R*,3*S*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4la): ^{1}H NMR (400 MHz, $CDCl_3$)

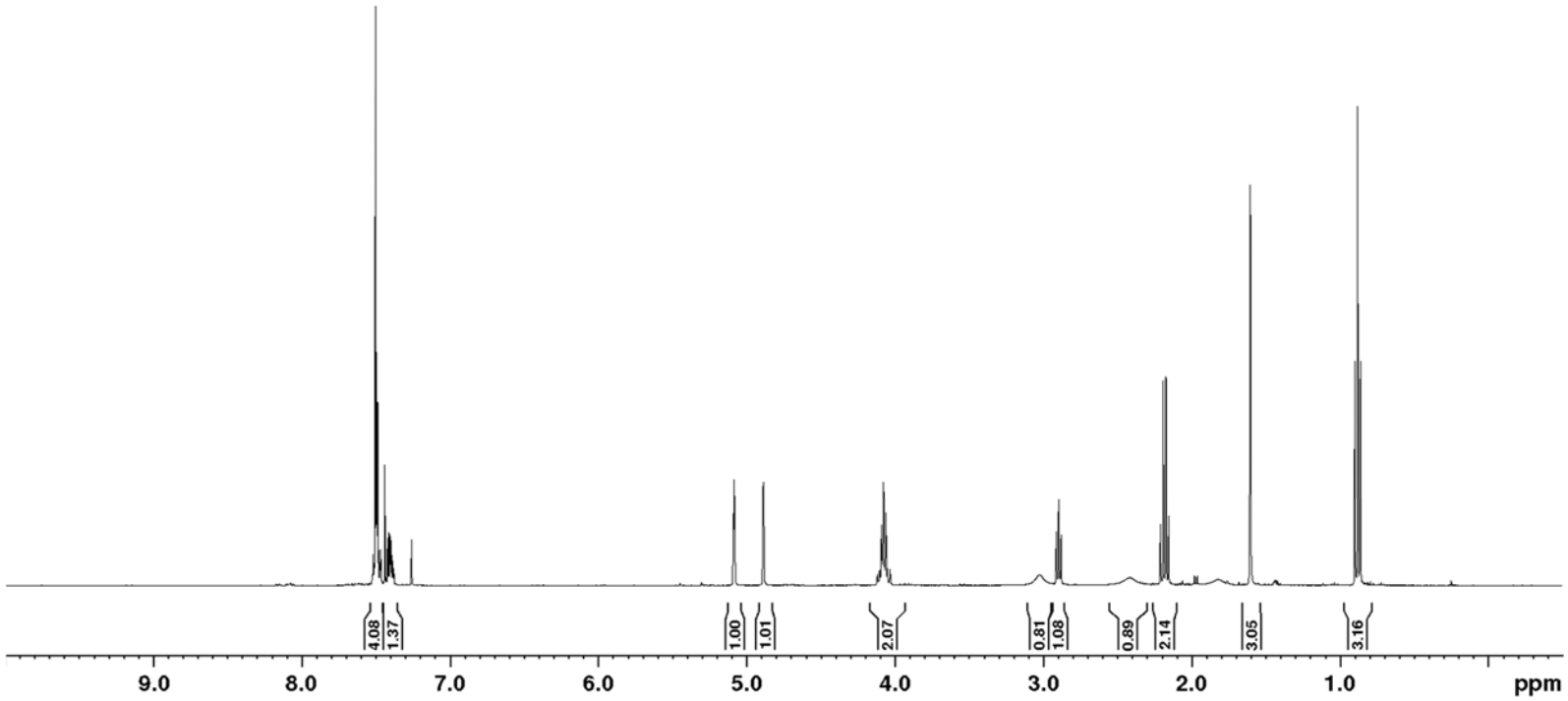


^{13}C NMR (100 MHz, $CDCl_3$)

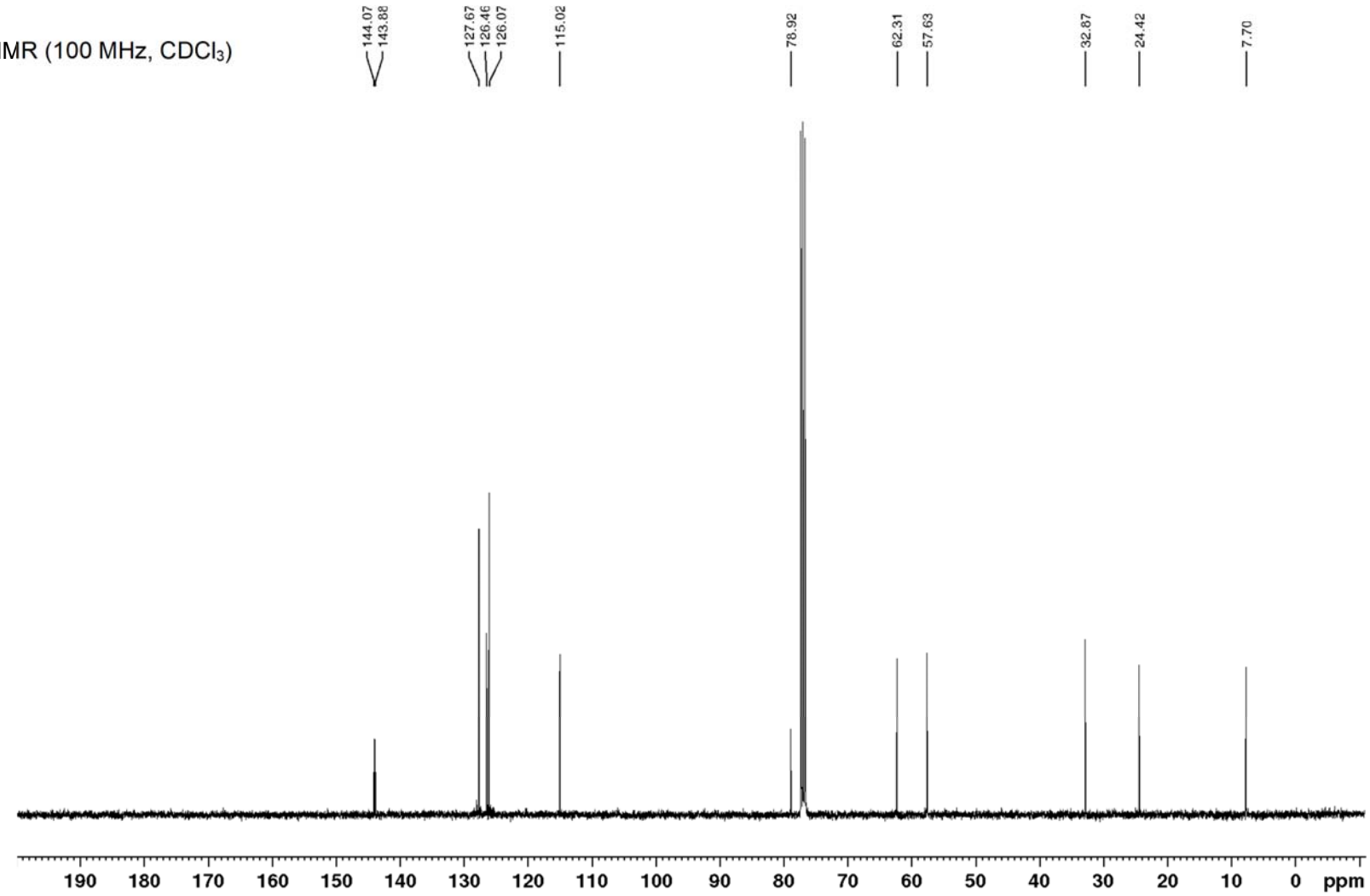


(2*R*,3*S*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*anti*-4ma): ^{1}H NMR (400 MHz, $CDCl_3$)

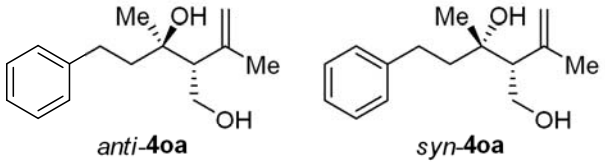




^{13}C NMR (100 MHz, $CDCl_3$)

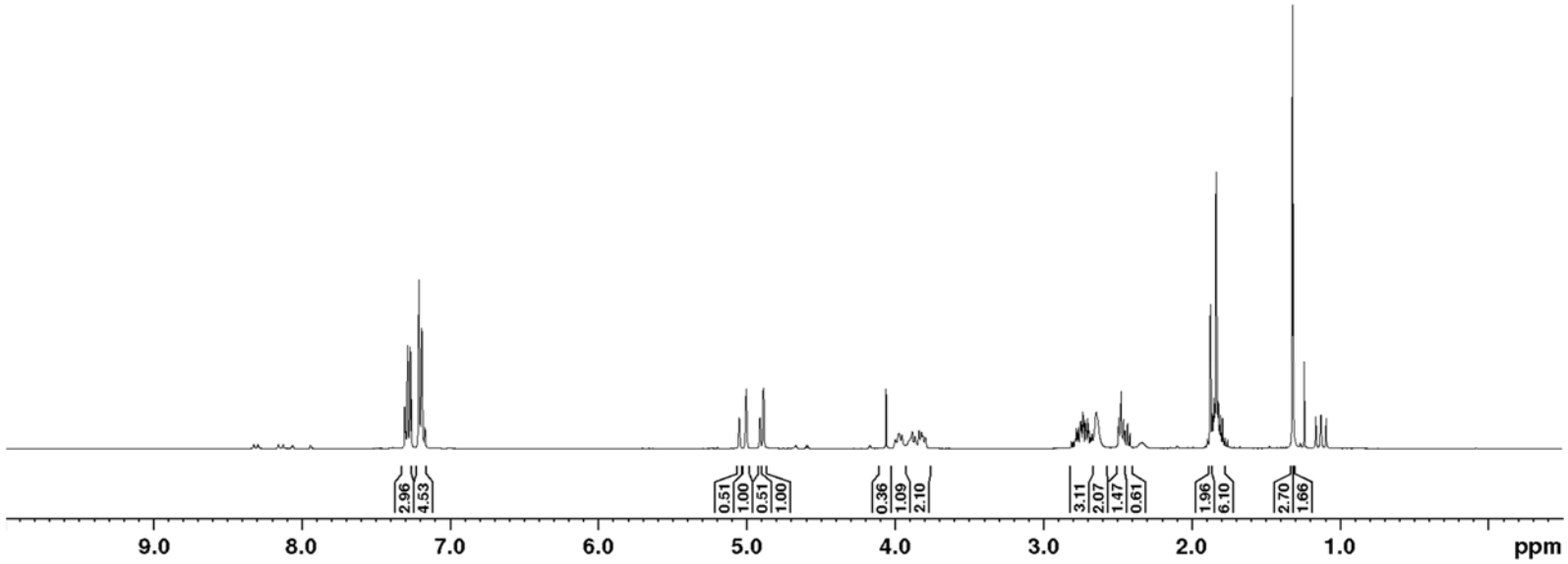


3-Methyl-5-phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (4oa): ^{1}H NMR (400 MHz, $CDCl_3$)

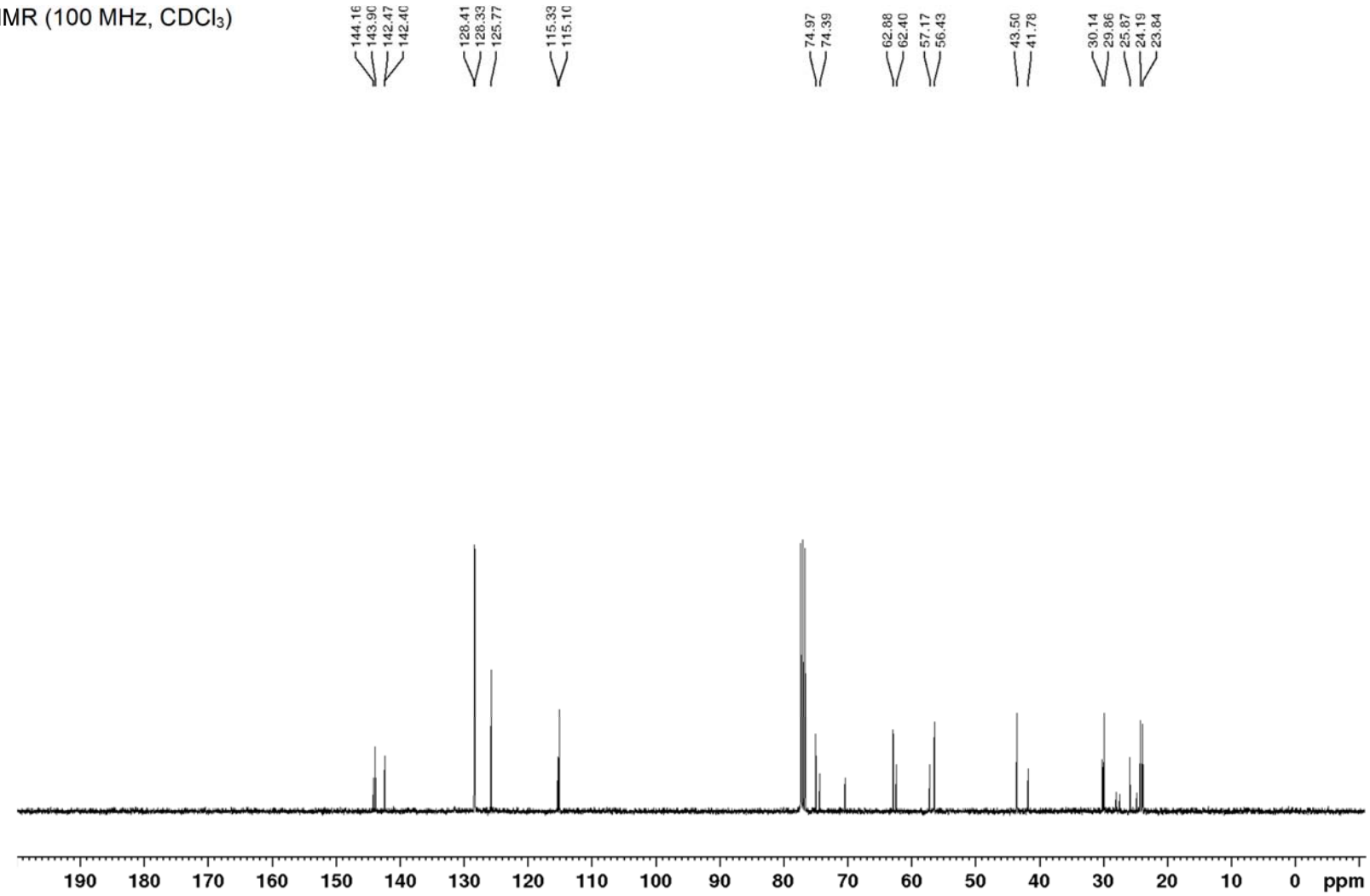


anti-**4oa** *syn*-**4oa**

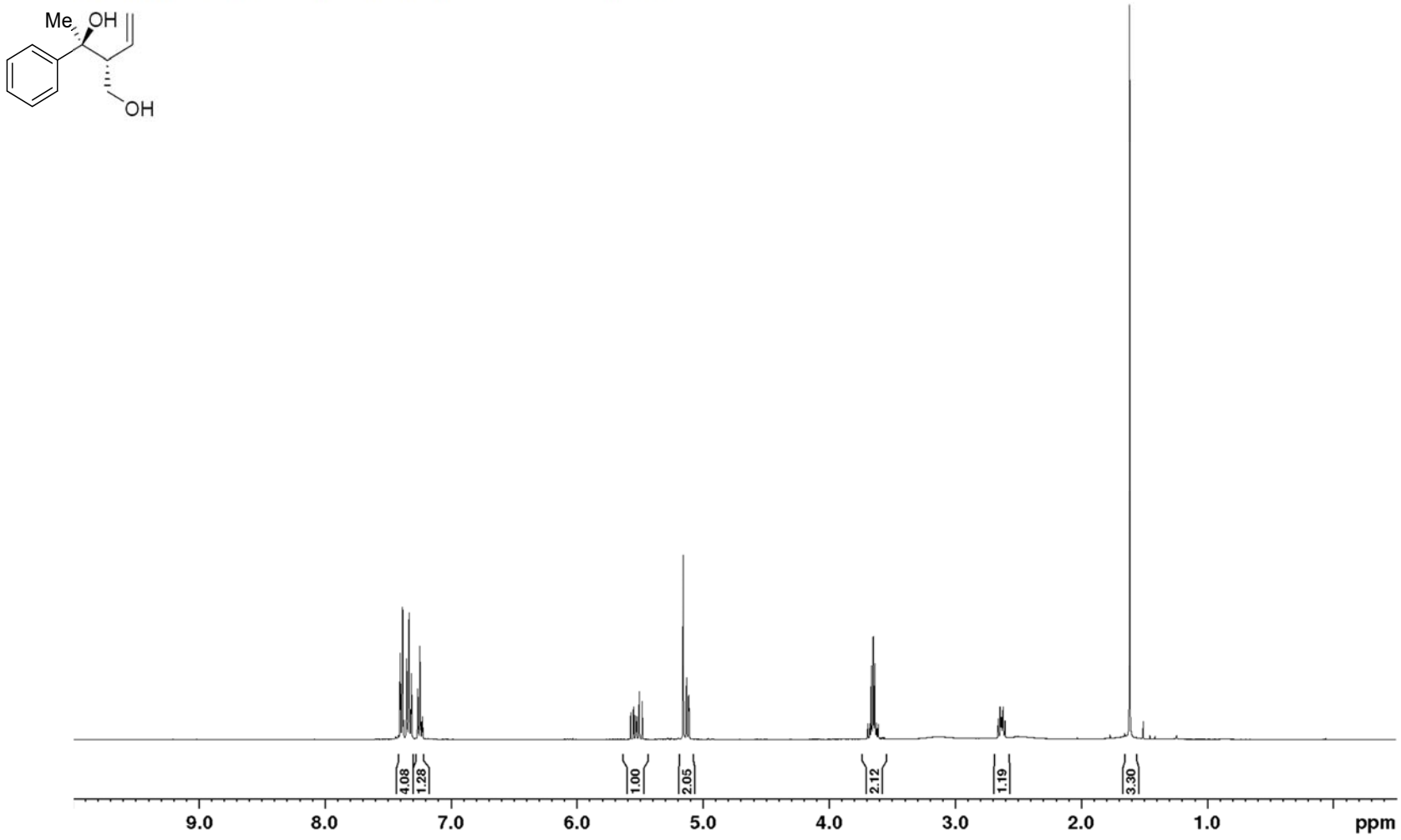
anti-**4oa** : *syn*-**4oa** = 1:2



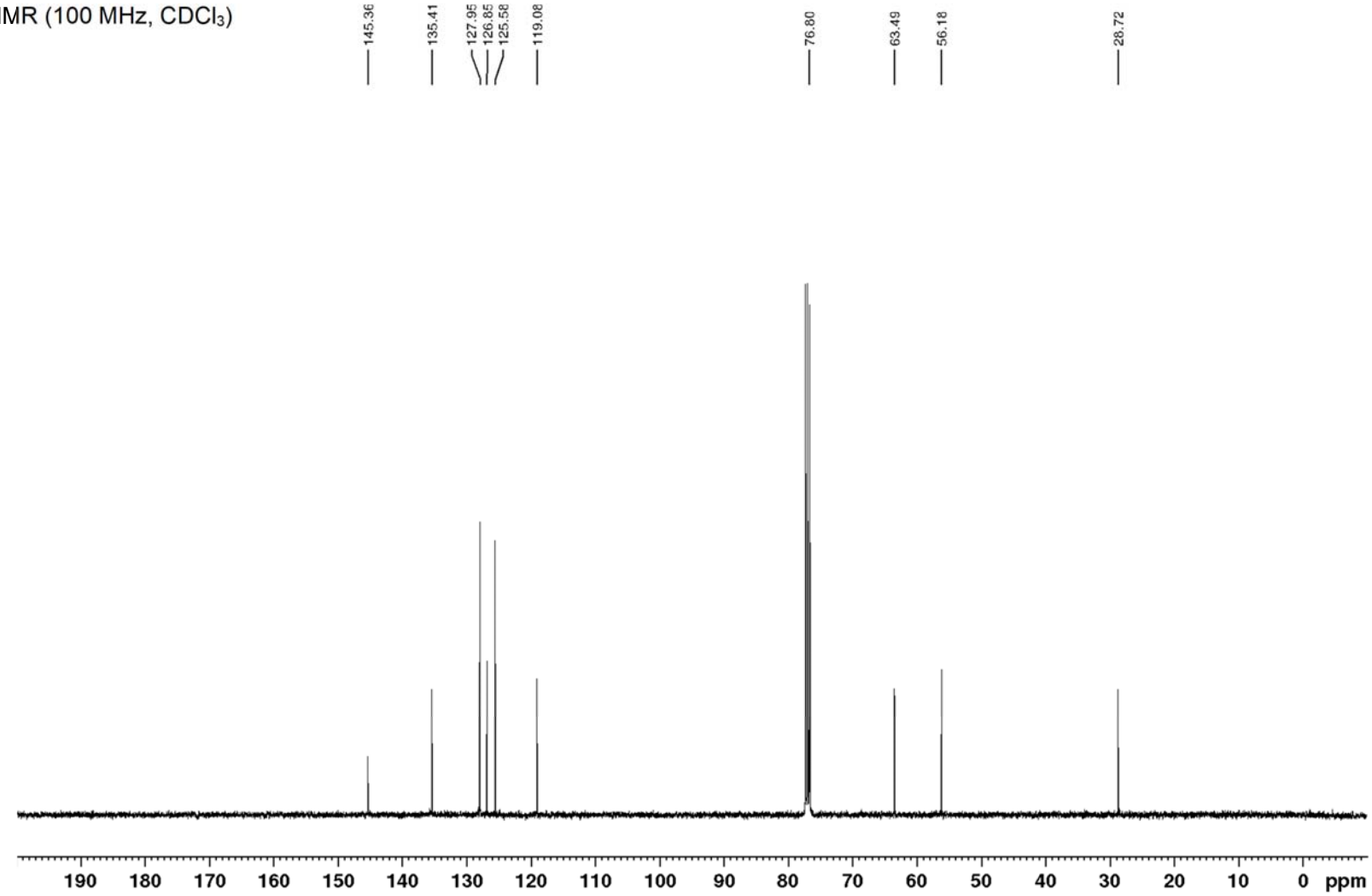
^{13}C NMR (100 MHz, $CDCl_3$)



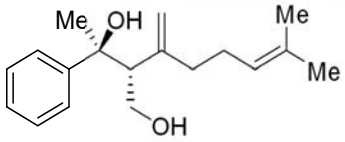
(2*R*,3*S*)-3-Phenyl-2-vinylbutane-1,3-diol (*anti*-4ab): ^{1}H NMR (400 MHz, $CDCl_3$)

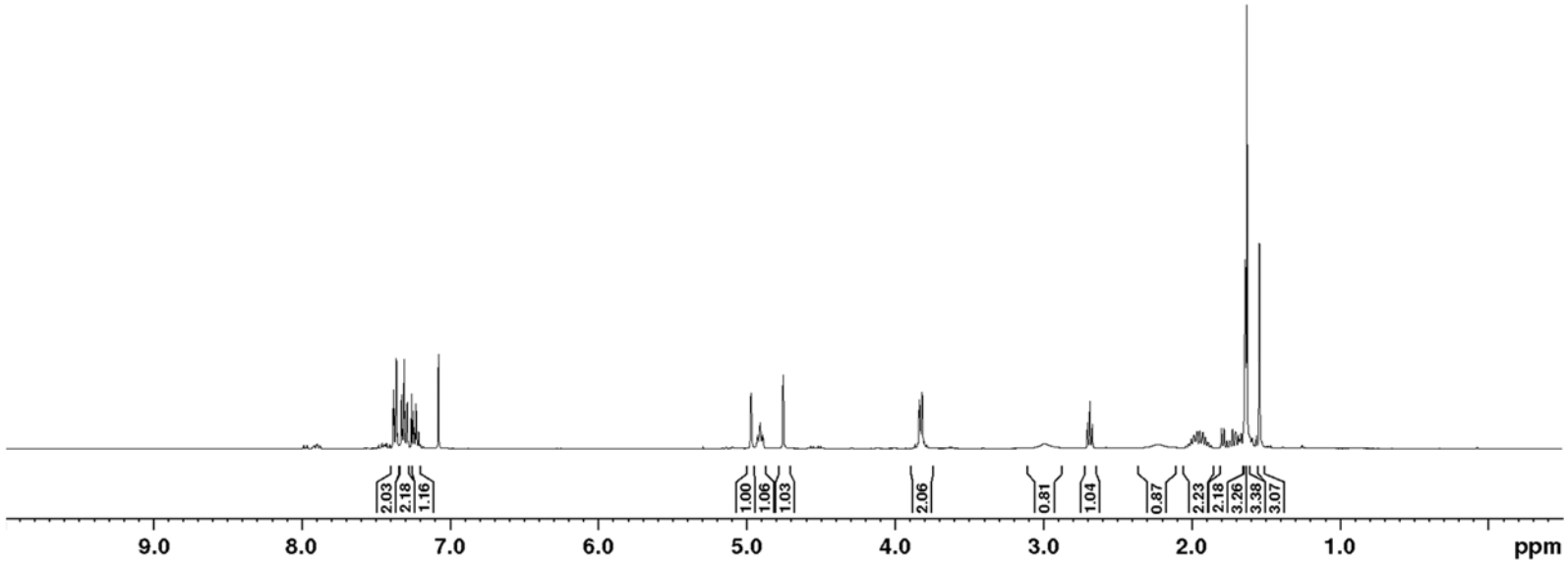


^{13}C NMR (100 MHz, $CDCl_3$)

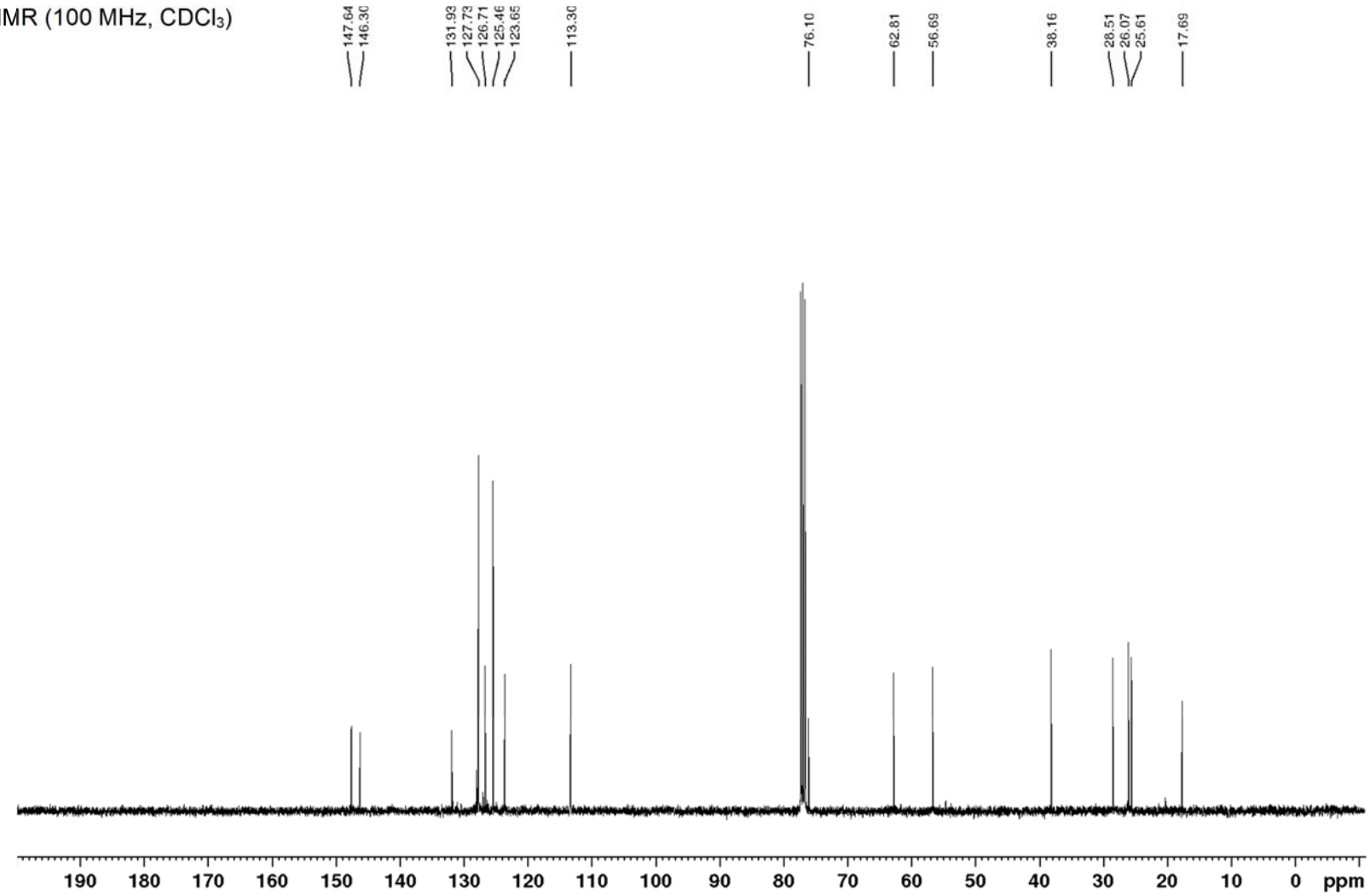


(2*R*,3*S*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*anti*-4ac): ^{1}H NMR (400 MHz, $CDCl_3$)

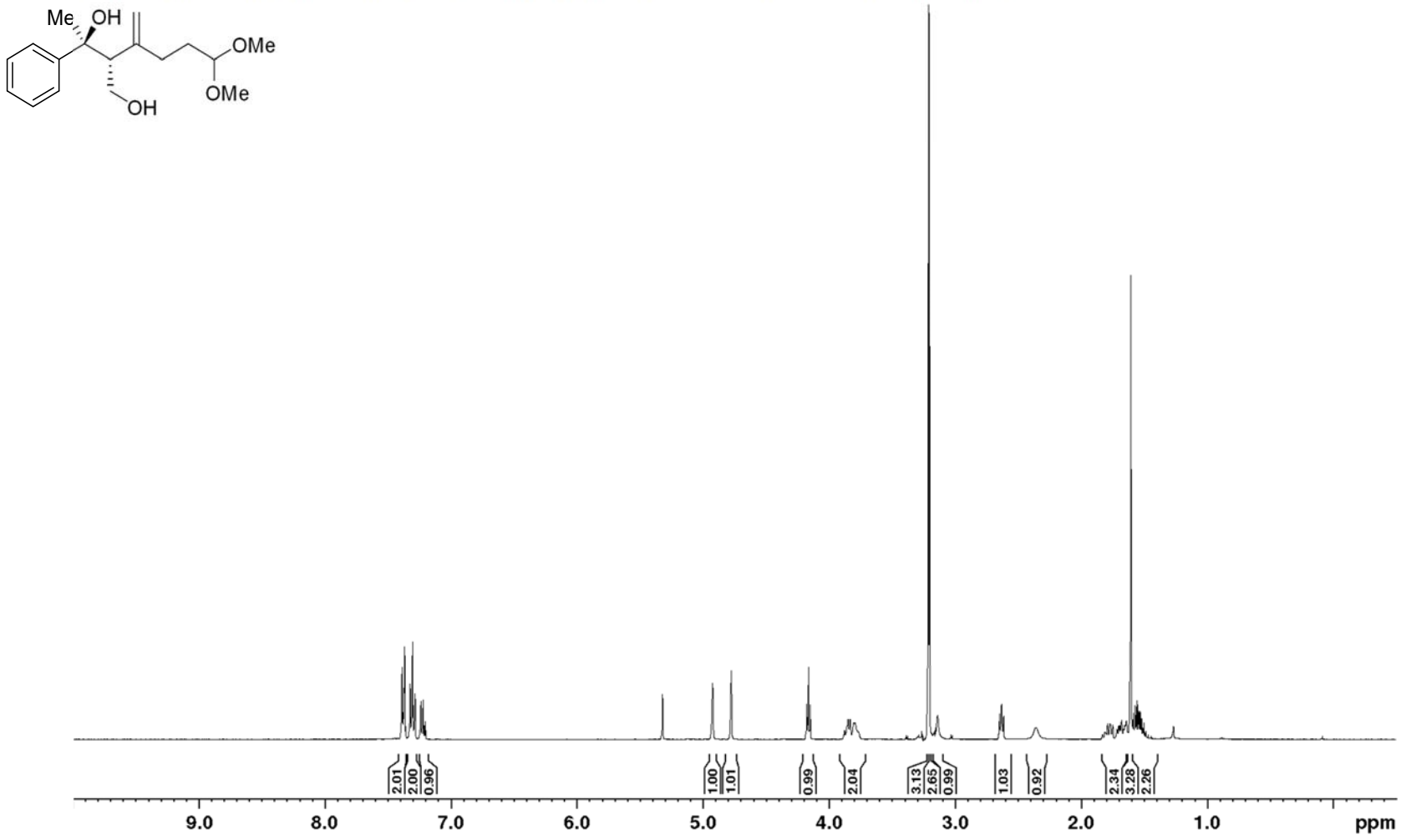




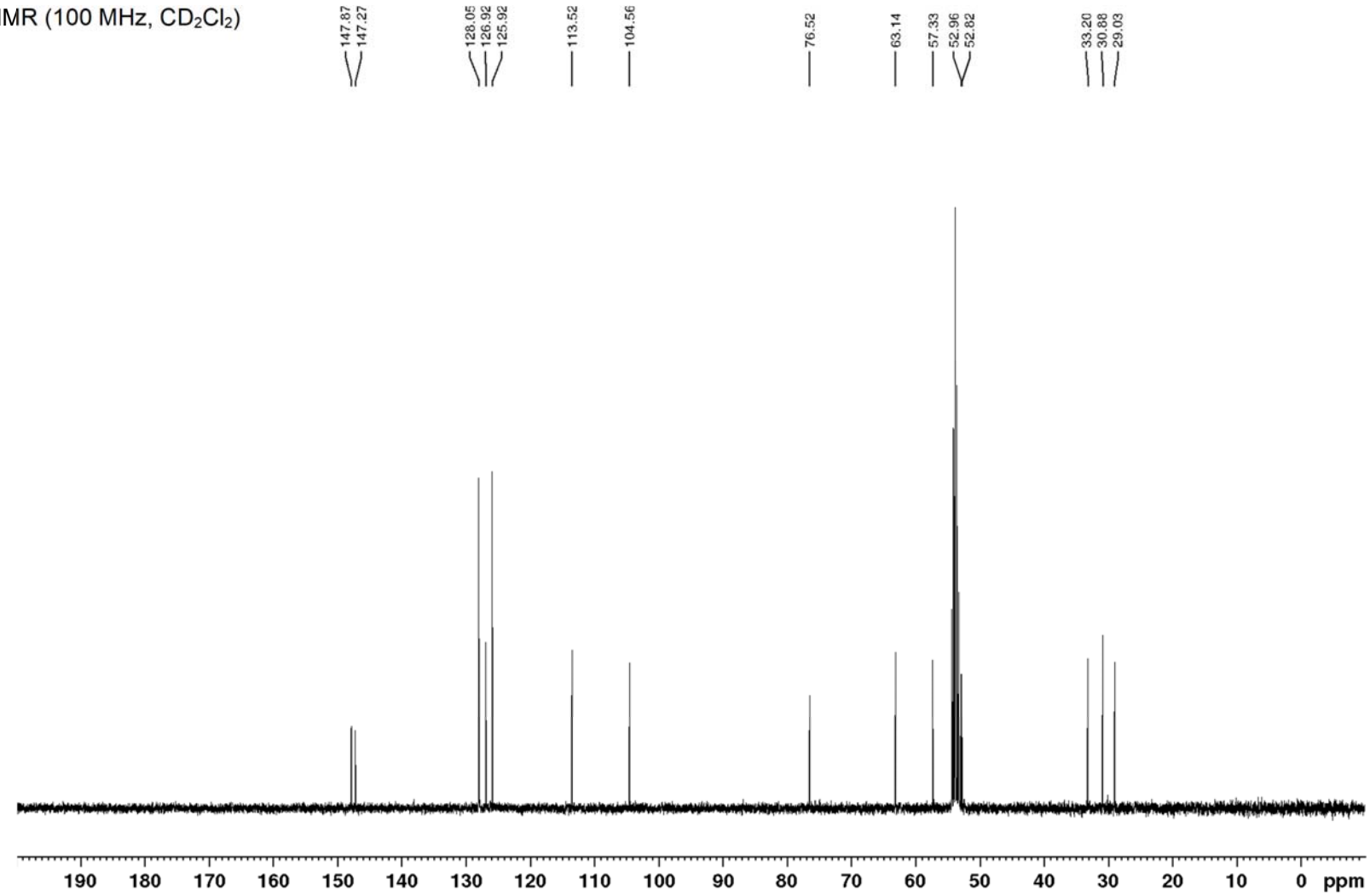
^{13}C NMR (100 MHz, $CDCl_3$)



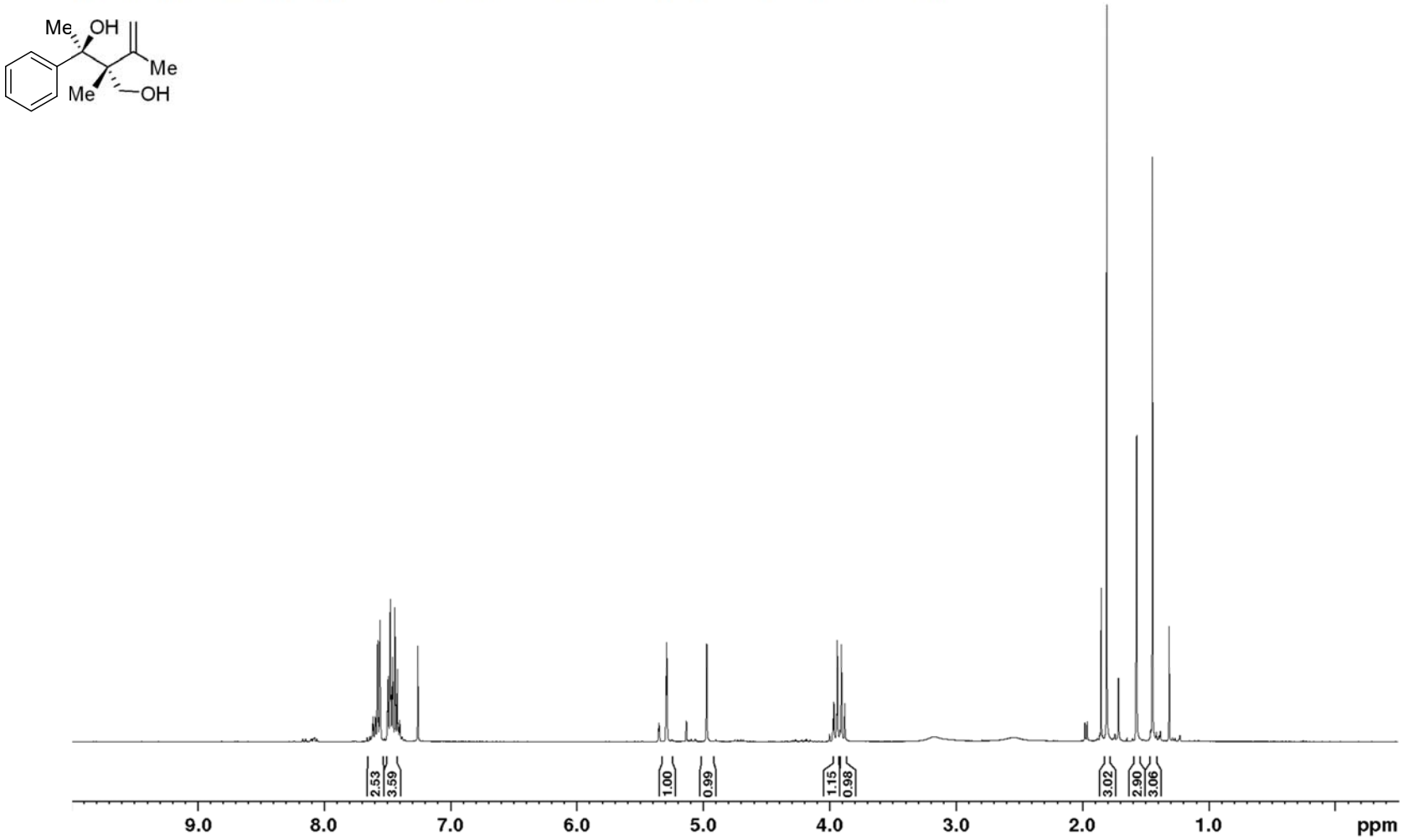
(2*R*,3*S*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*anti*-**4ad**): ^{1}H NMR (400 MHz, CD_2Cl_2)



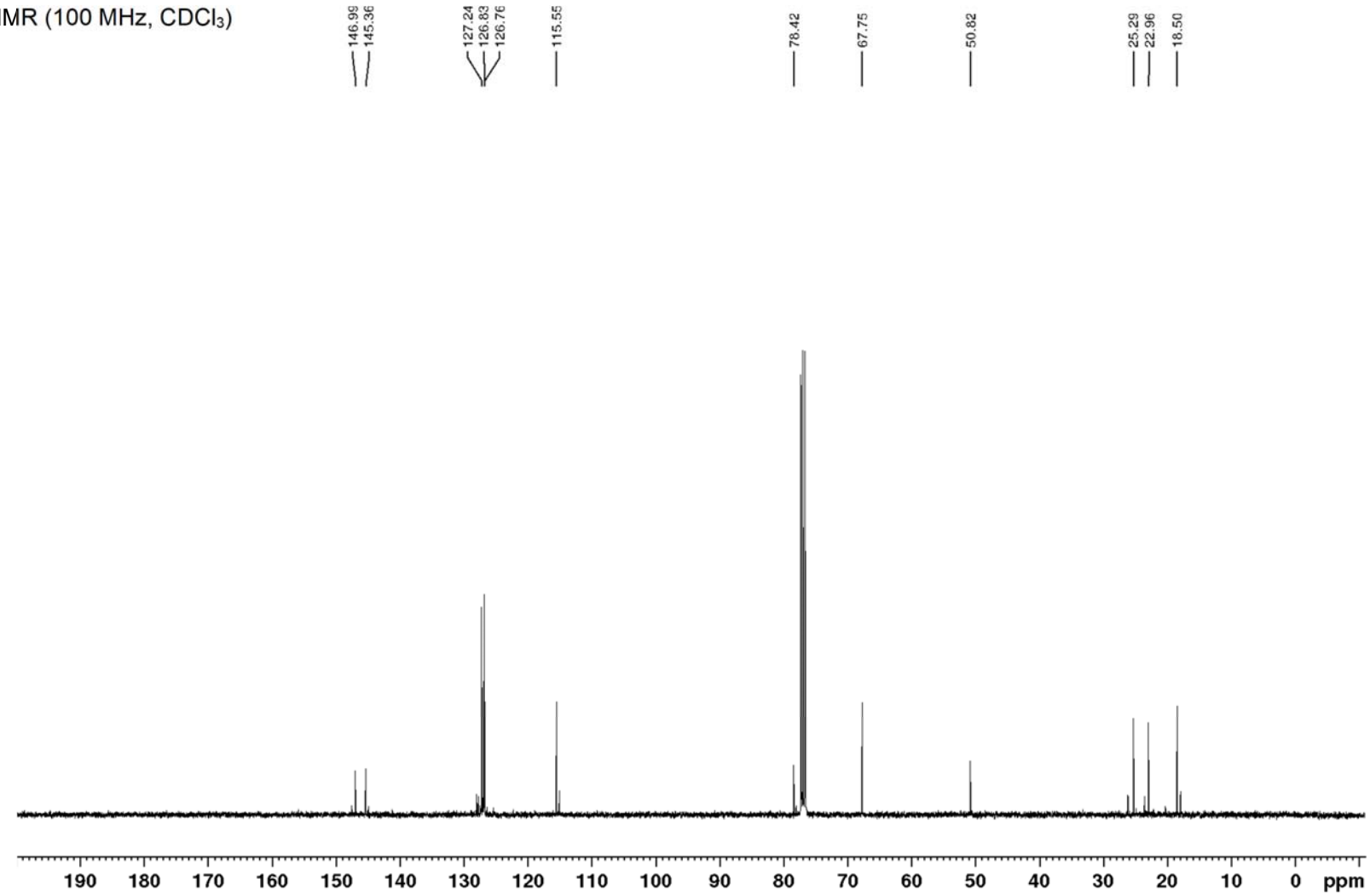
^{13}C NMR (100 MHz, CD_2Cl_2)



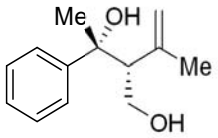
(2*R*,3*R*)-2-Methyl-3-phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*anti*-4ae): ^{1}H NMR (400 MHz, $CDCl_3$)

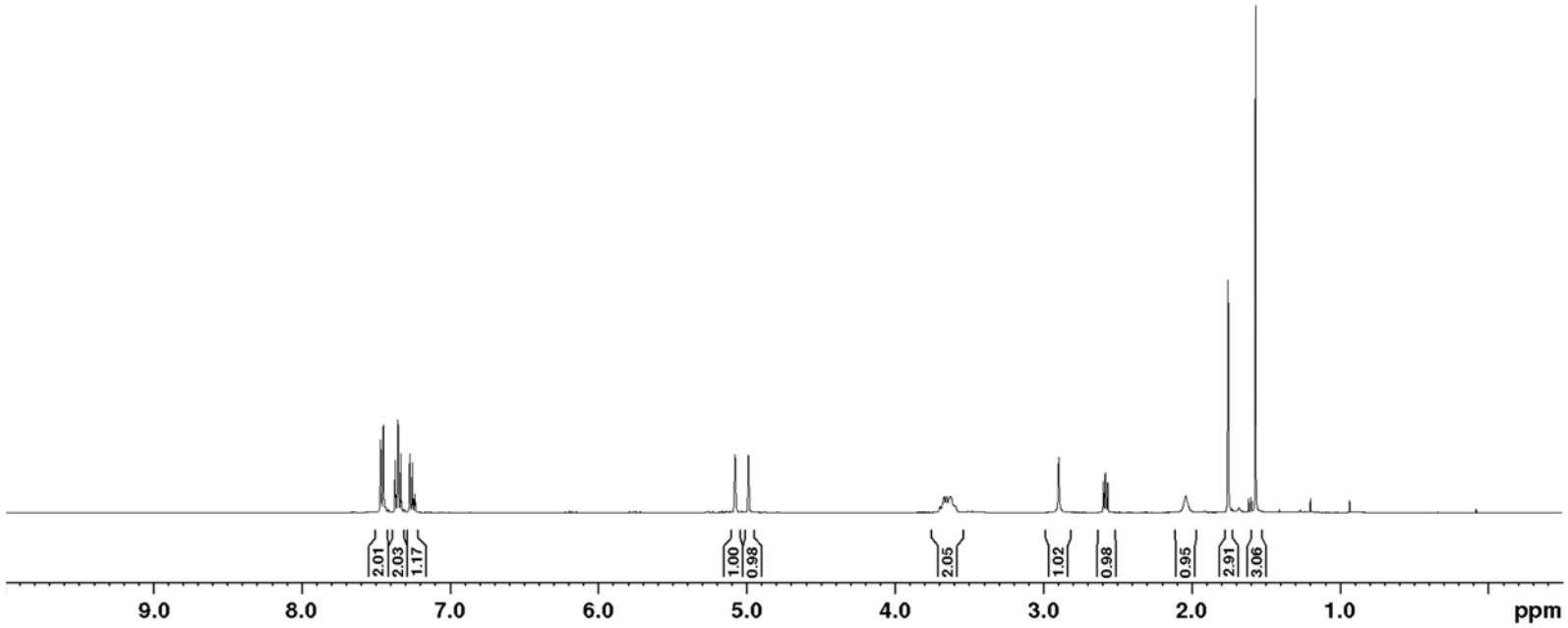


^{13}C NMR (100 MHz, $CDCl_3$)

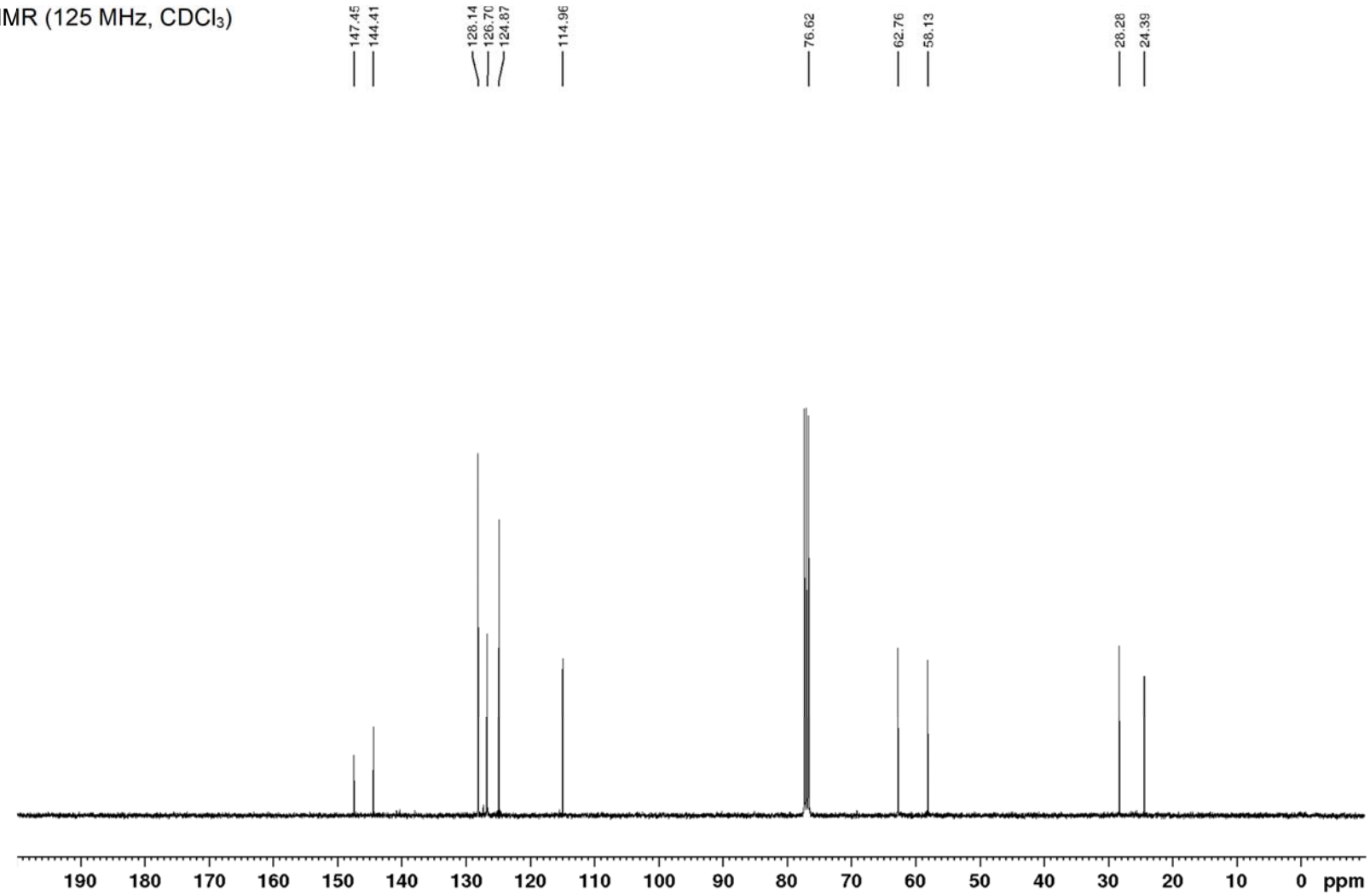


(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4aa**): ^{1}H NMR (500 MHz, $CDCl_3$)

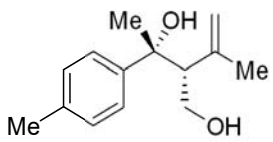




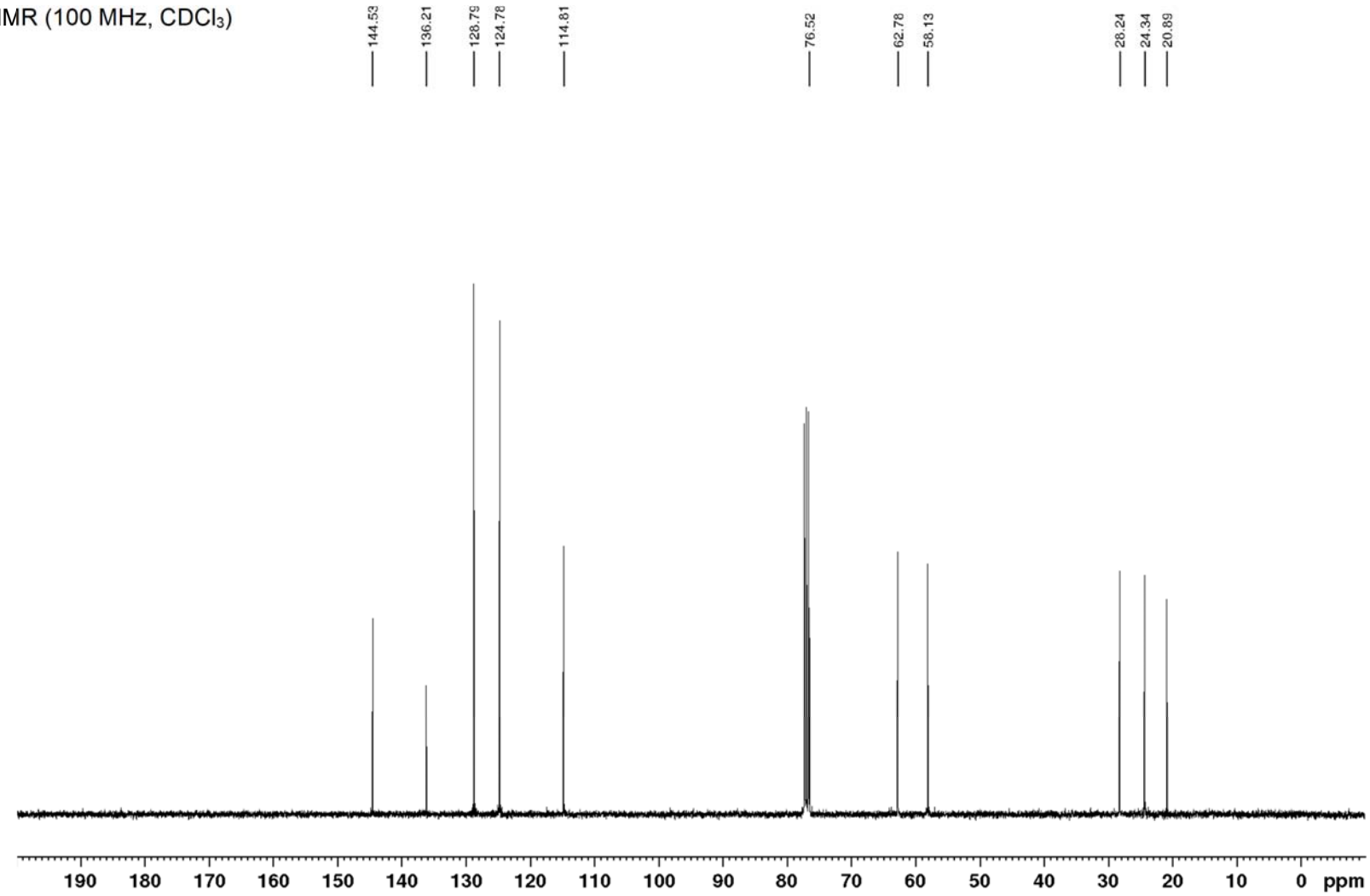
^{13}C NMR (125 MHz, $CDCl_3$)



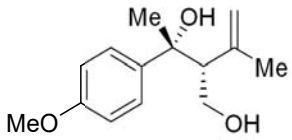
(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*p*-tolyl)butane-1,3-diol (*syn*-**4ba**): ^{1}H NMR (400 MHz, $CDCl_3$)

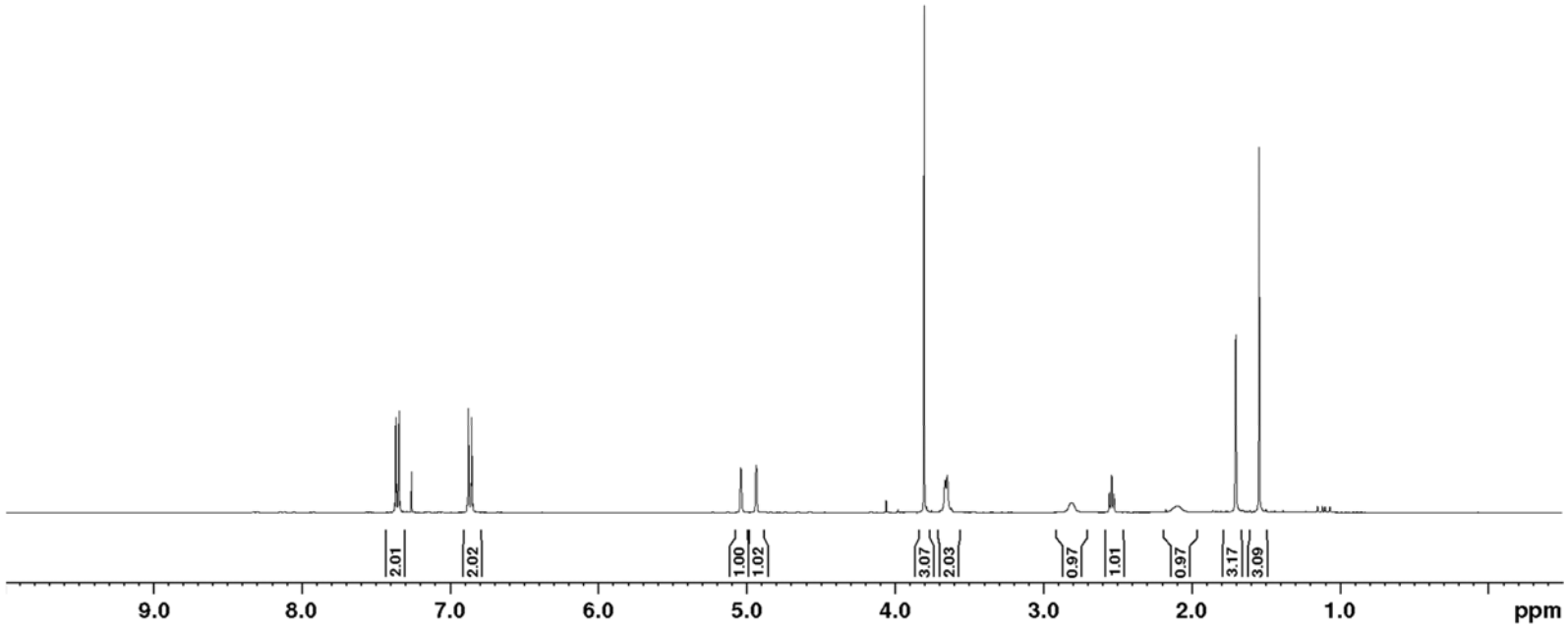


^{13}C NMR (100 MHz, $CDCl_3$)

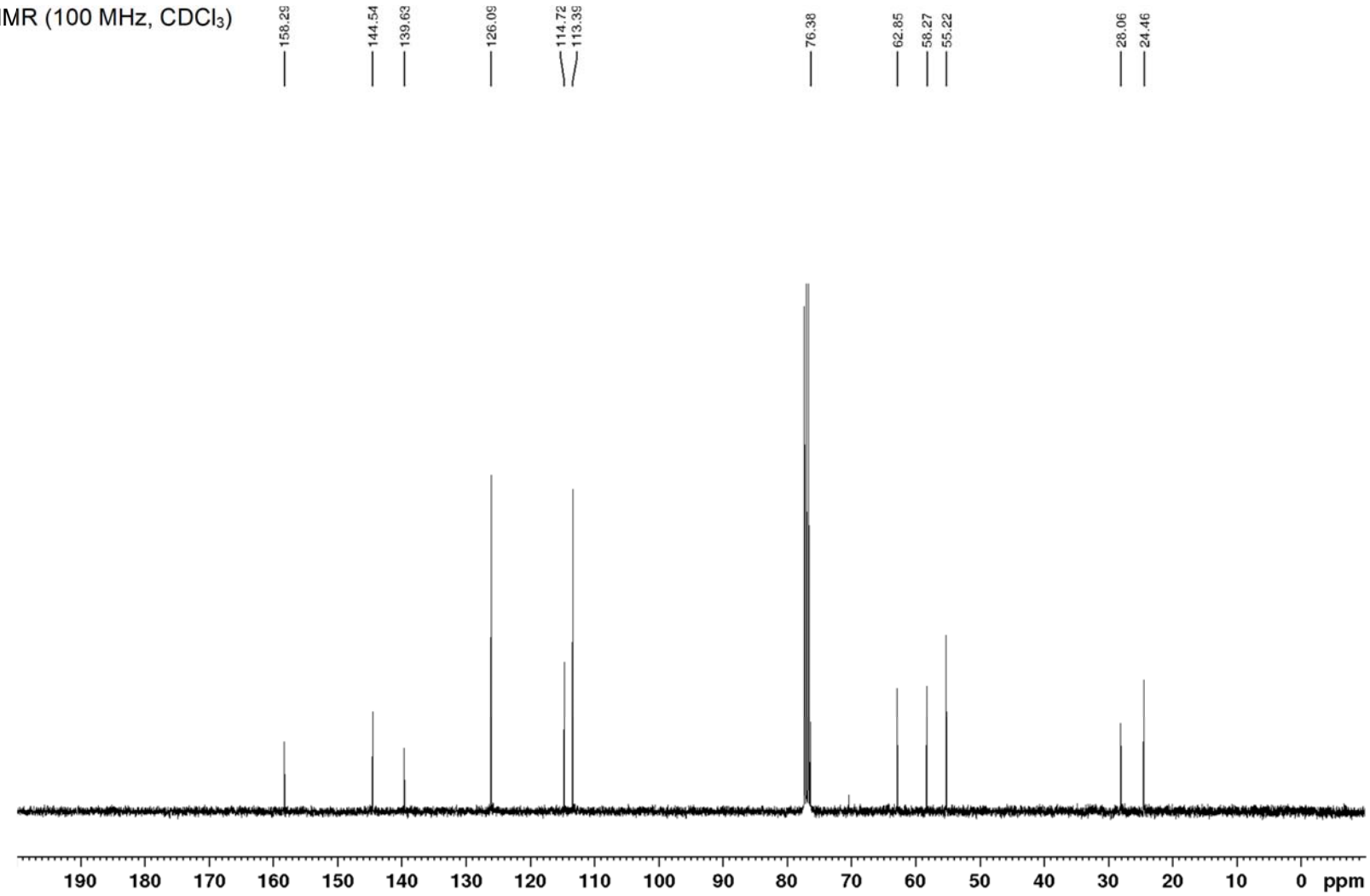


(2*R*,3*R*)-3-(4-Methoxyphenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ca**): ^{1}H NMR (400 MHz, $CDCl_3$)

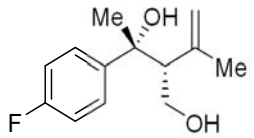


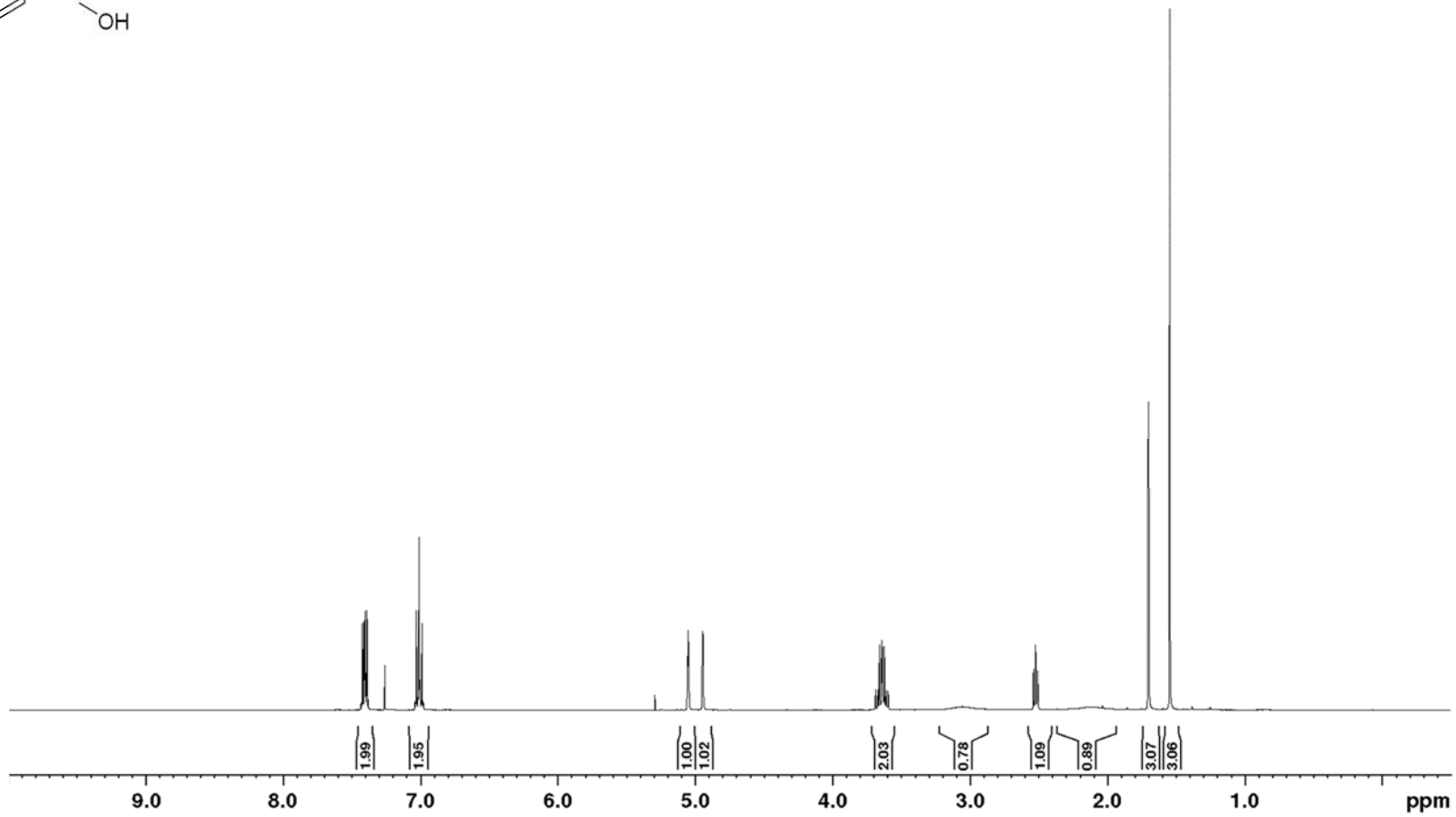


^{13}C NMR (100 MHz, $CDCl_3$)

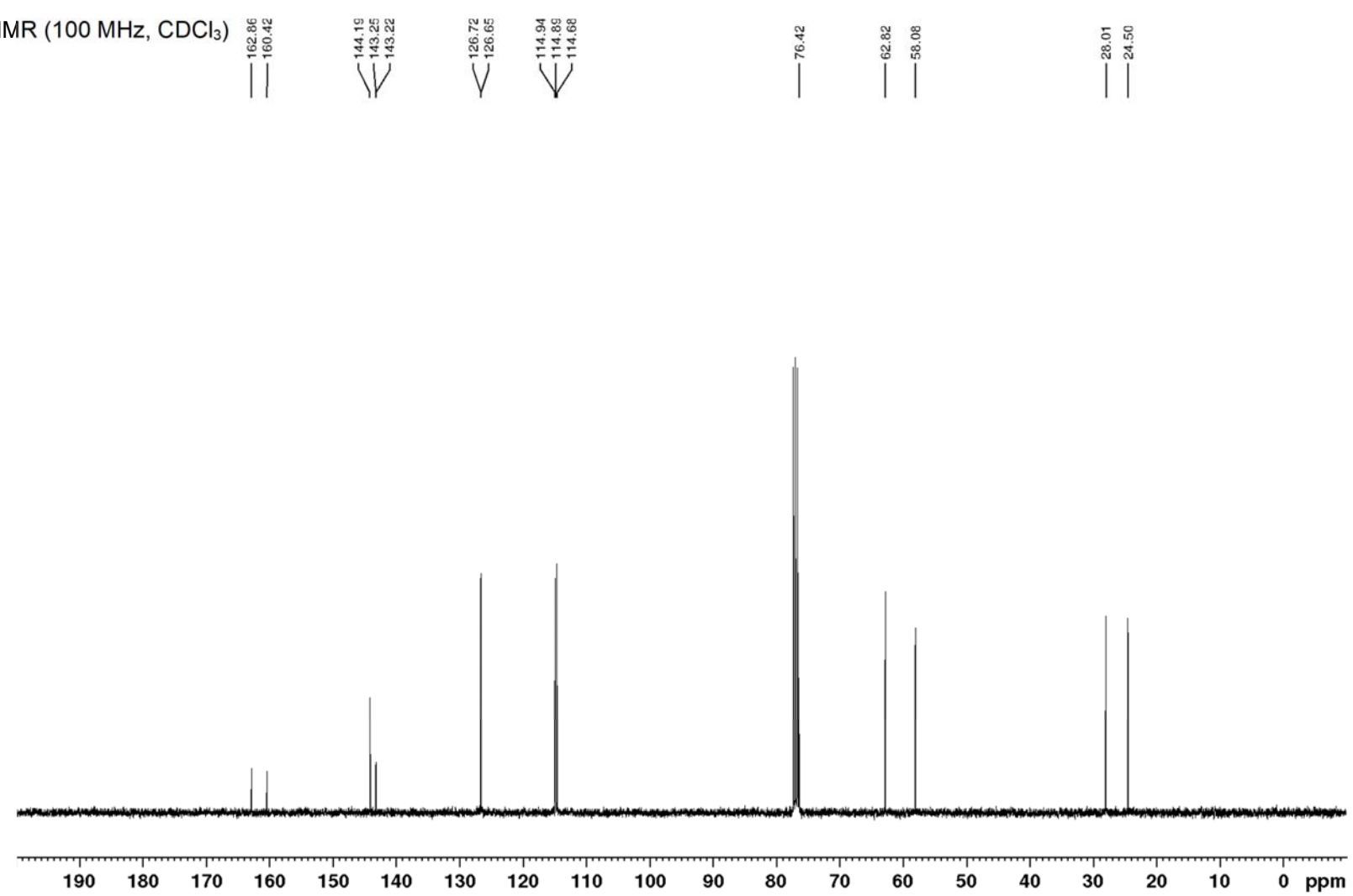


(2*R*,3*R*)-3-(4-Fluorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4da**): ^{1}H NMR (400 MHz, $CDCl_3$)

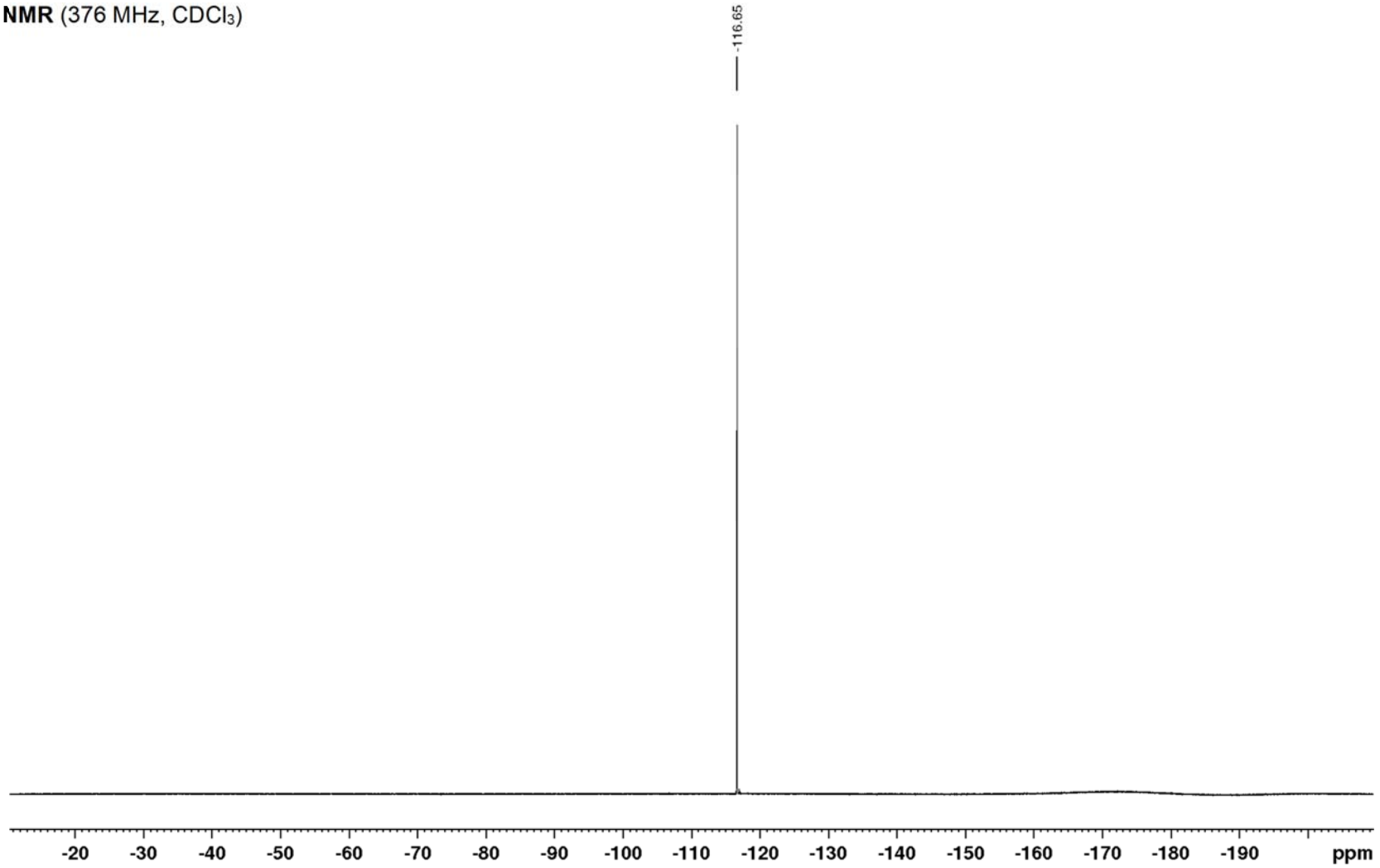




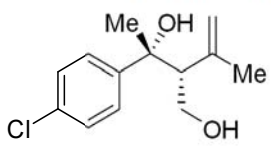
^{13}C NMR (100 MHz, $CDCl_3$)



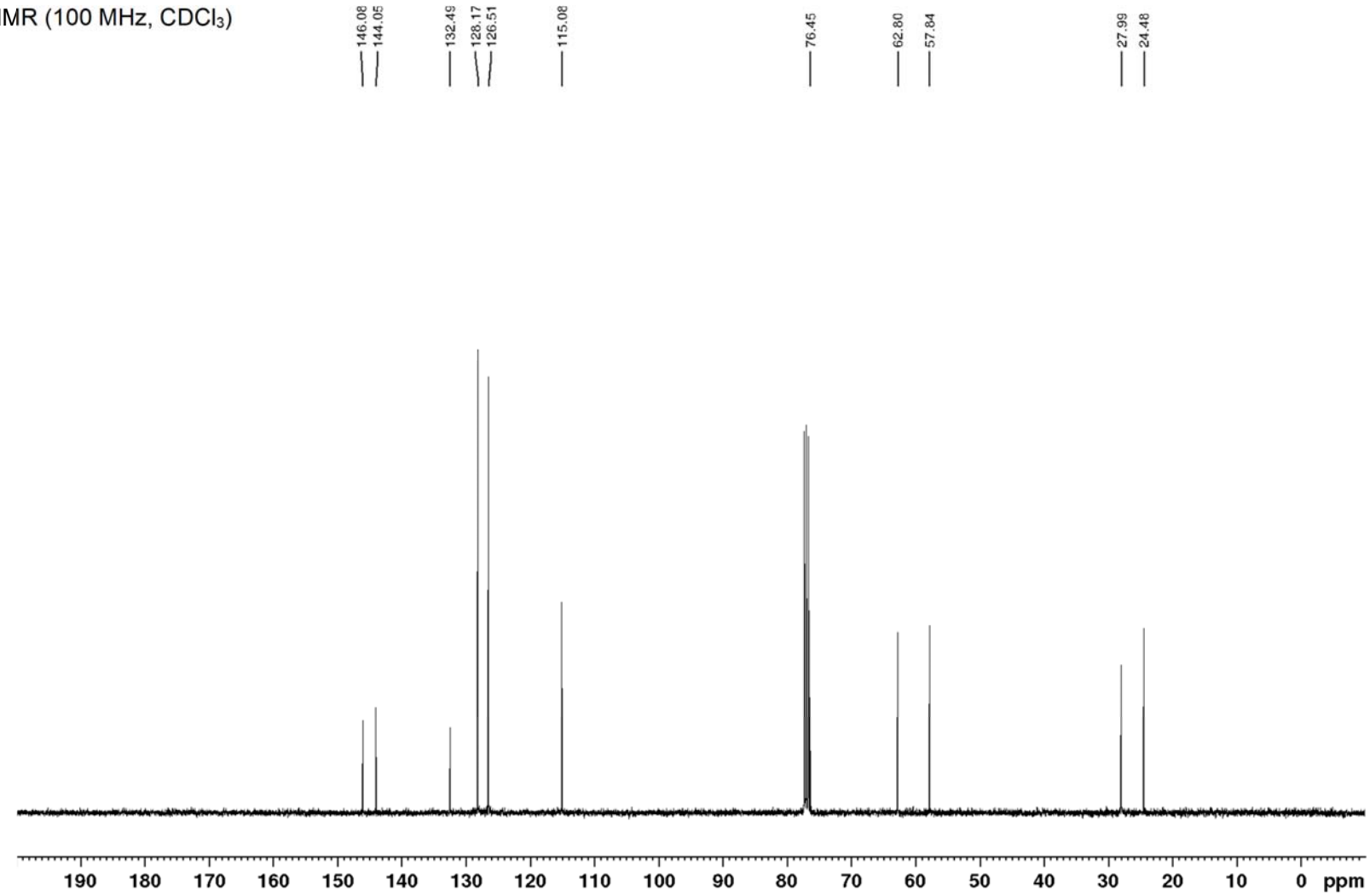
^{19}F NMR (376 MHz, $CDCl_3$)



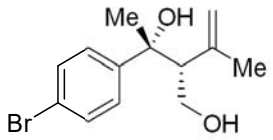
(2*R*,3*R*)-3-(4-Chlorophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ea**): ^{1}H NMR (400 MHz, $CDCl_3$)

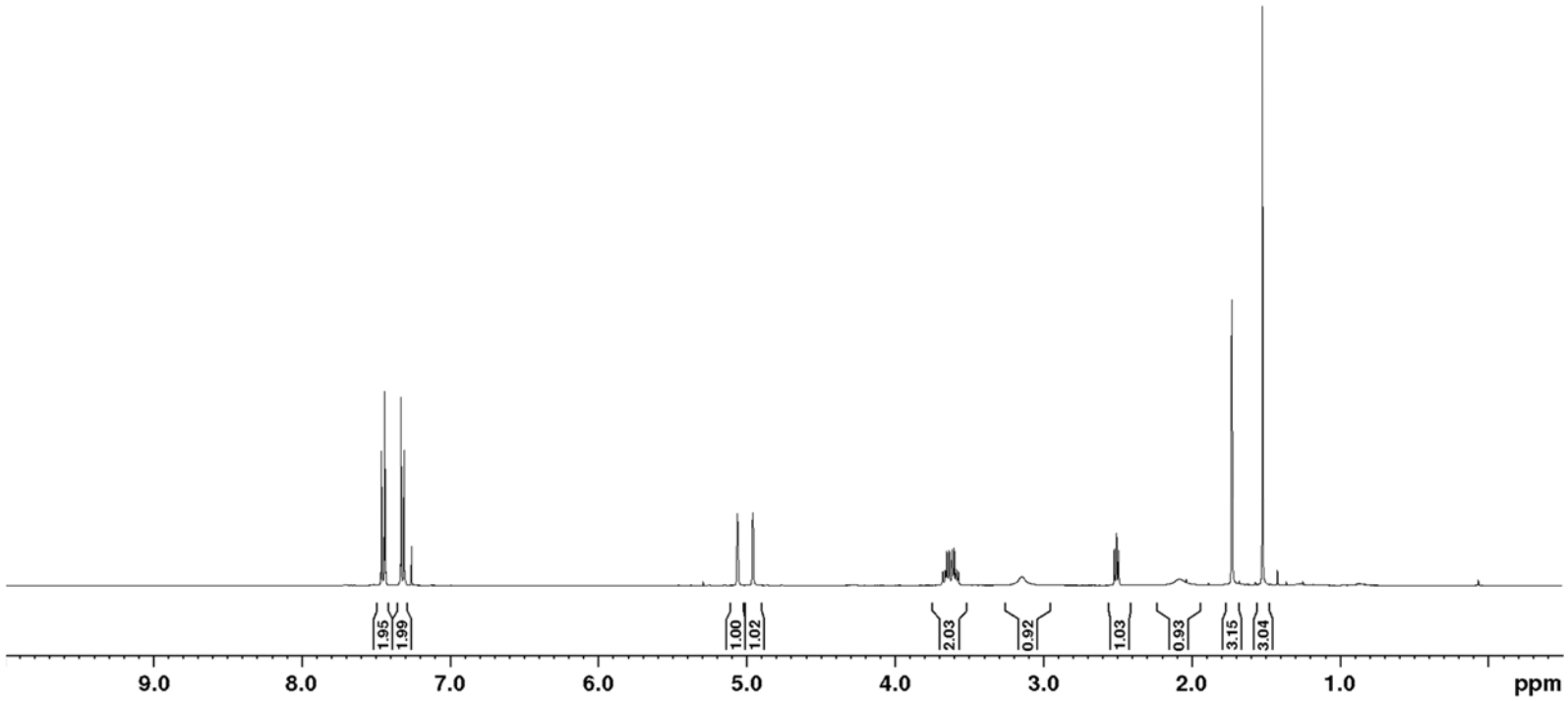


^{13}C NMR (100 MHz, $CDCl_3$)

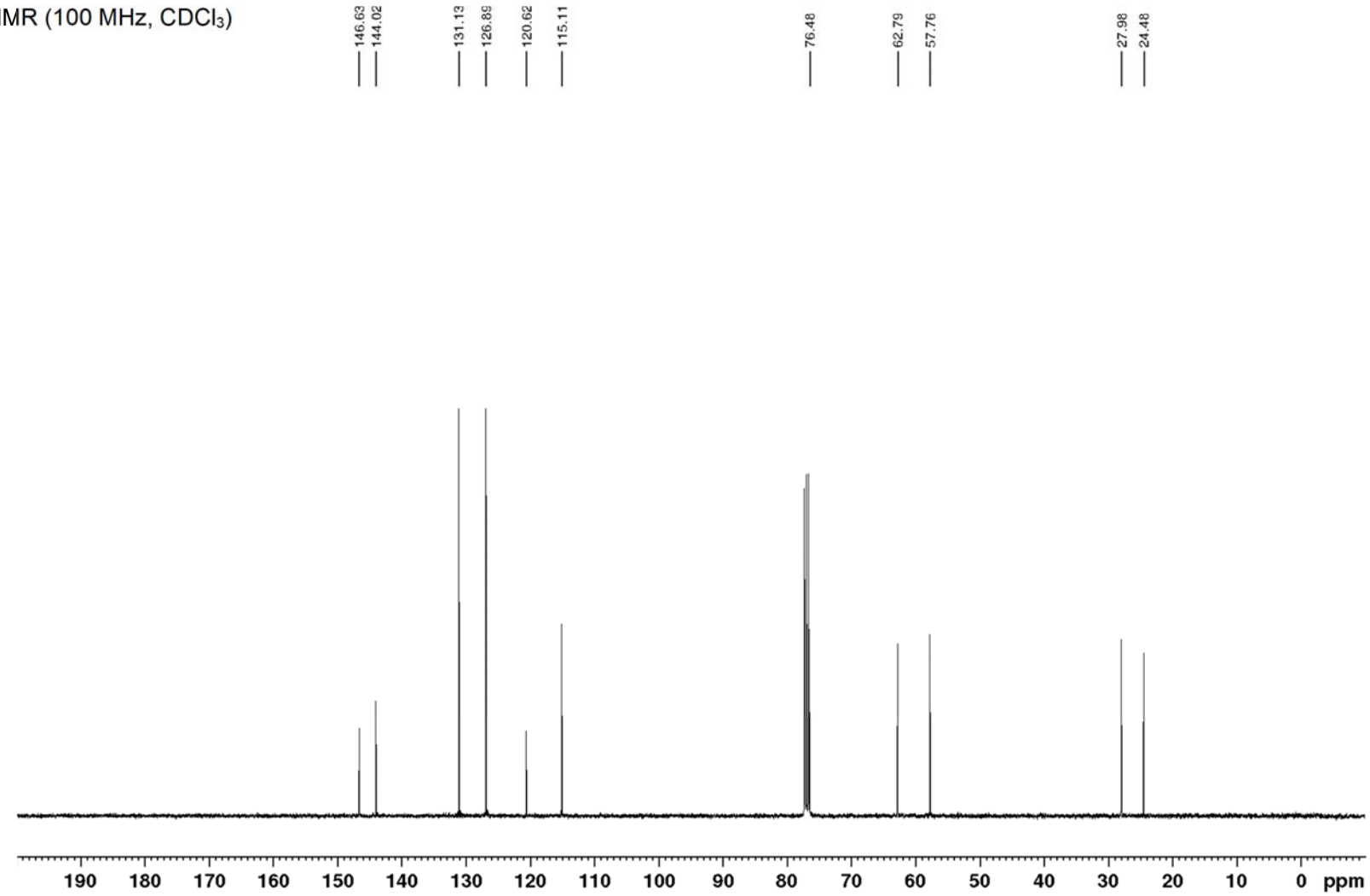


(2*R*,3*R*)-3-(4-Bromophenyl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4fa**): ^{1}H NMR (400 MHz, $CDCl_3$)

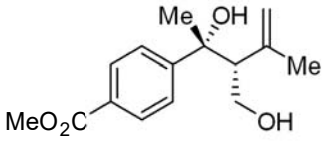


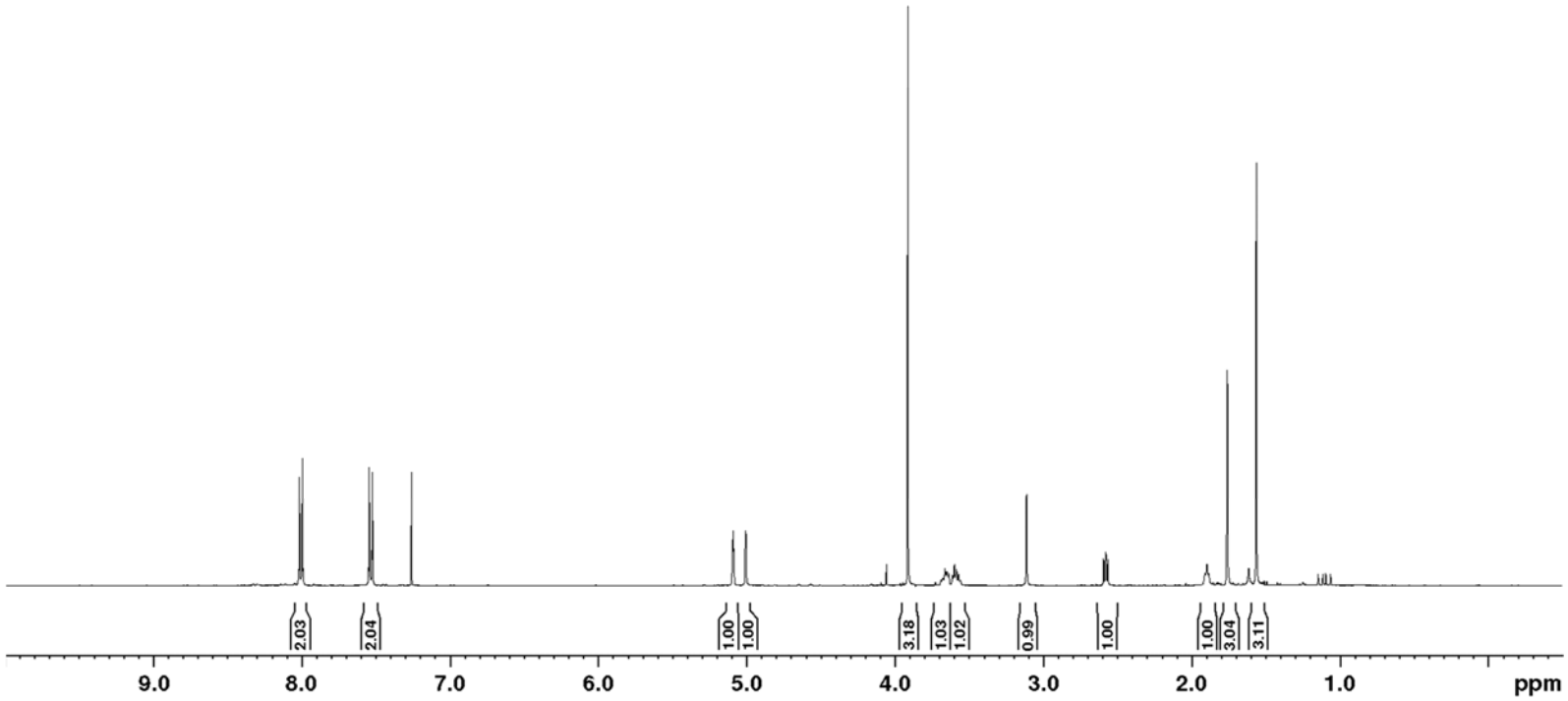


^{13}C NMR (100 MHz, $CDCl_3$)

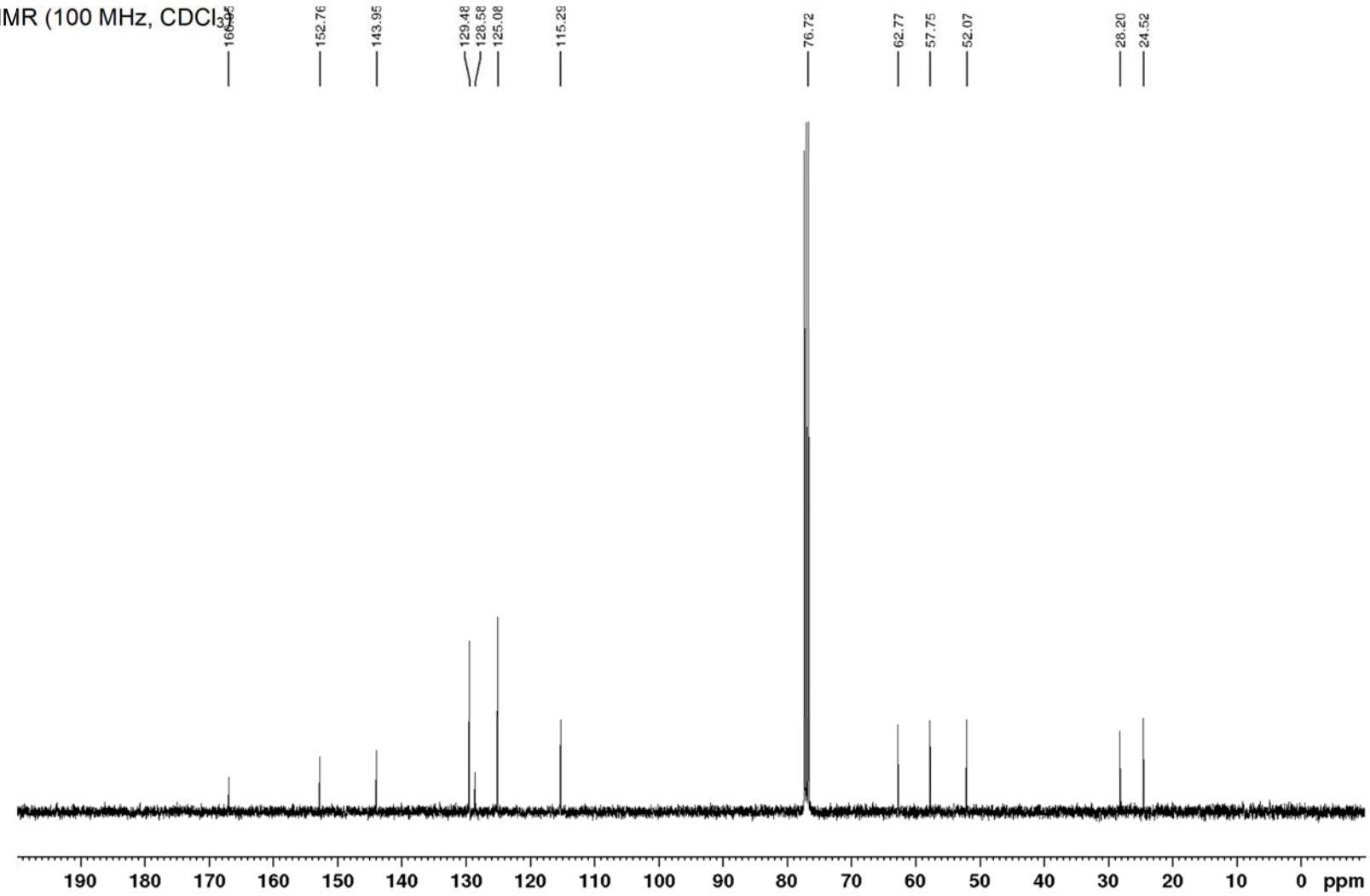


4-((2*R*,3*R*)-2-Hydroxy-3-(hydroxymethyl)-4-methylpent-4-en-2-yl)benzoate (*syn*-**4ga**): ^{1}H NMR (400 MHz, $CDCl_3$)

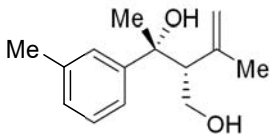


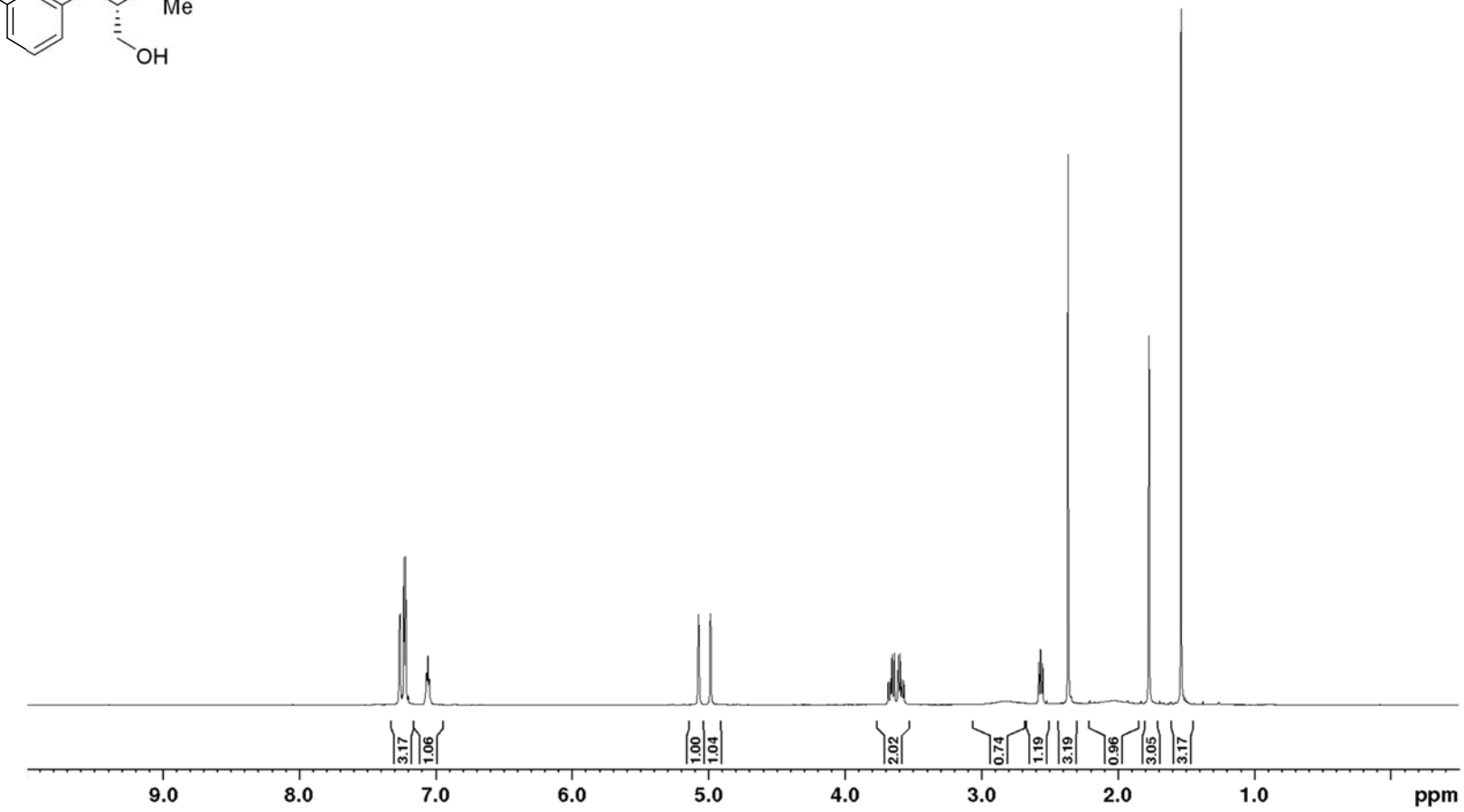


^{13}C NMR (100 MHz, $CDCl_3$)

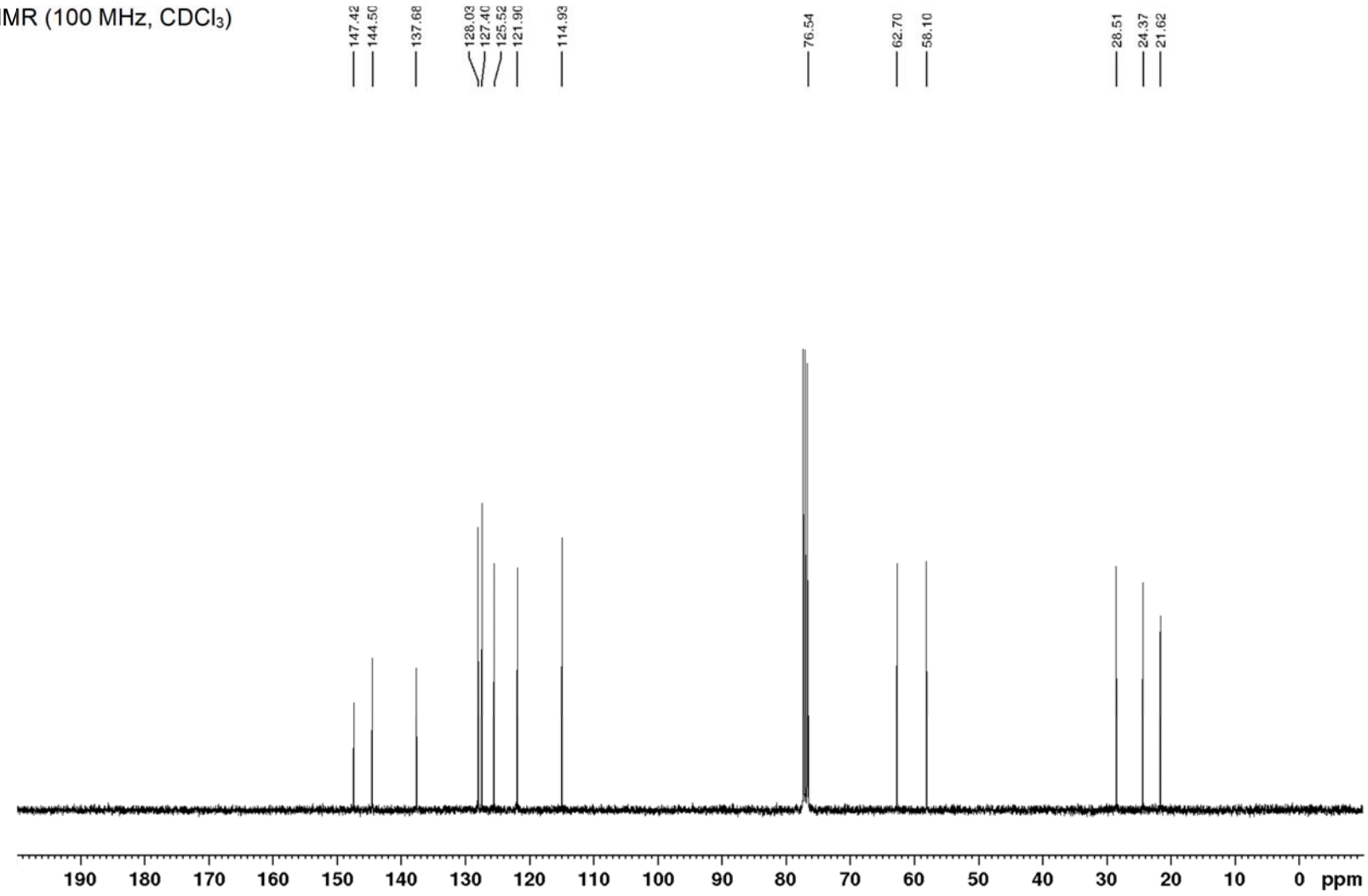


(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*m*-tolyl)butane-1,3-diol (*syn*-**4ha**): ^{1}H NMR (400 MHz, $CDCl_3$)

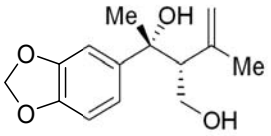


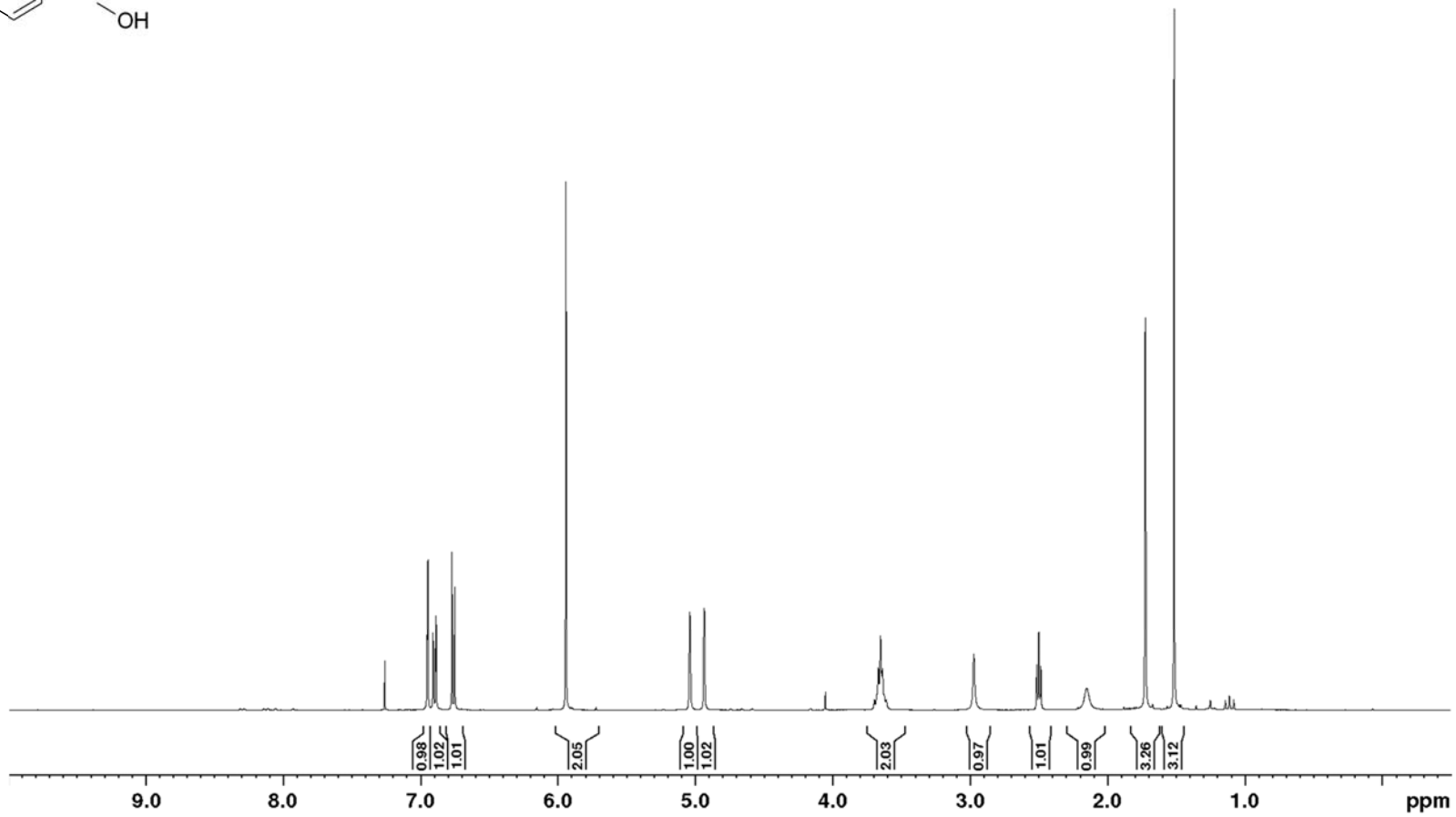


^{13}C NMR (100 MHz, $CDCl_3$)

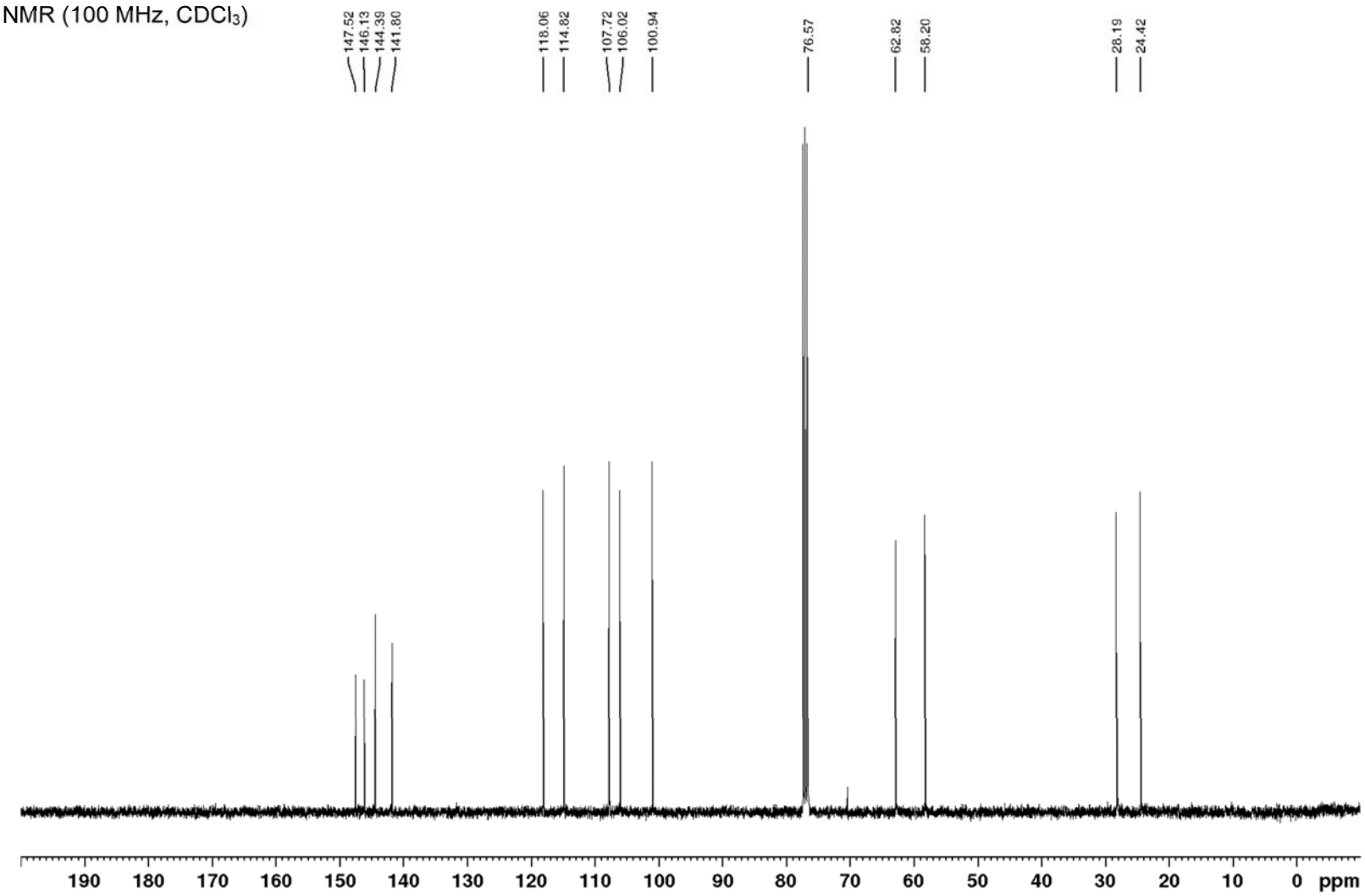


(2*R*,3*R*)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4ia**): ^{1}H NMR (400 MHz, $CDCl_3$)

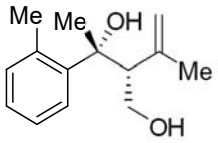


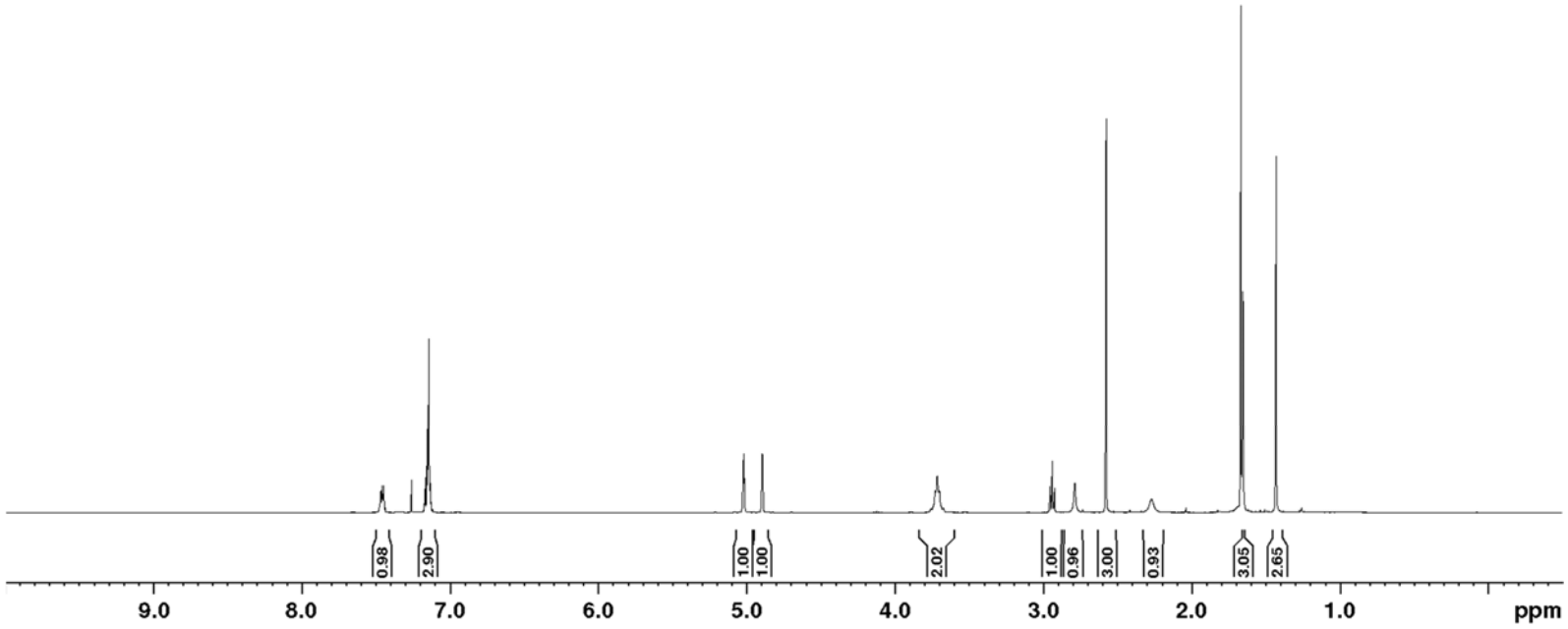


^{13}C NMR (100 MHz, $CDCl_3$)

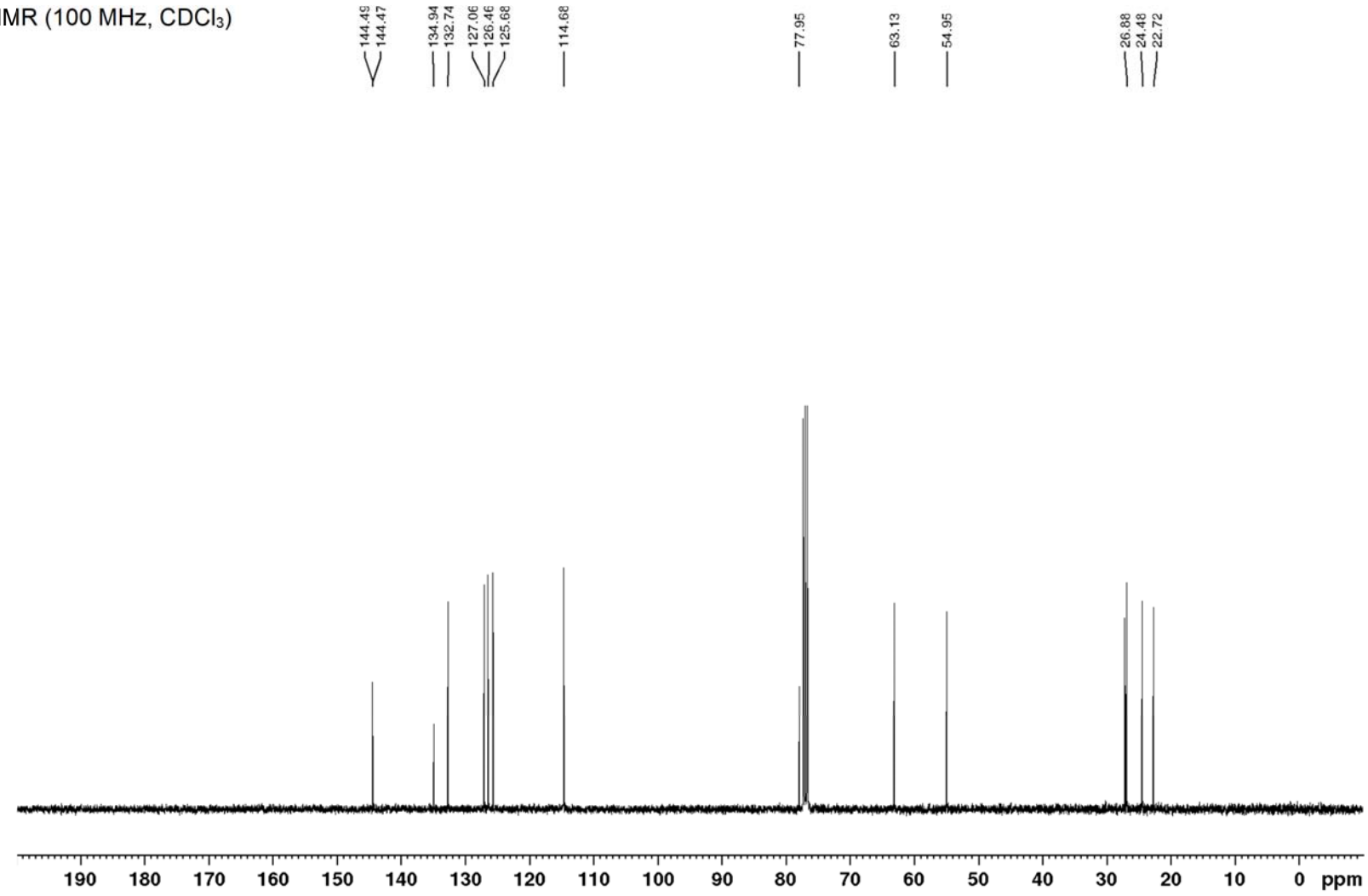


(2*R*,3*R*)-2-(Prop-1-en-2-yl)-3-(*o*-tolyl)butane-1,3-diol (*syn*-**4ja**): ^{1}H NMR (400 MHz, $CDCl_3$)

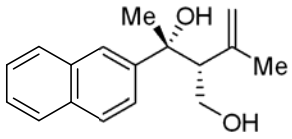


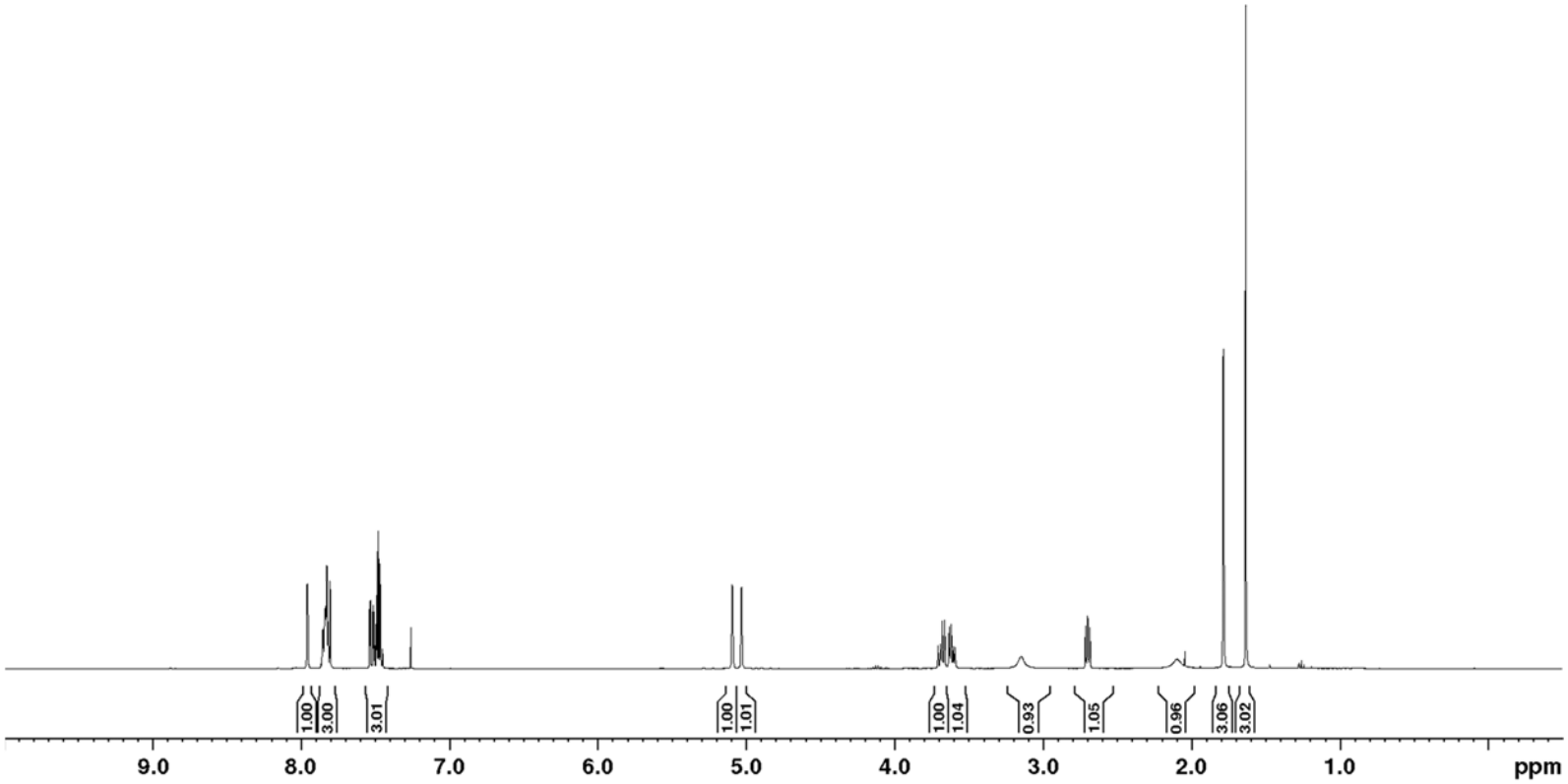


^{13}C NMR (100 MHz, $CDCl_3$)

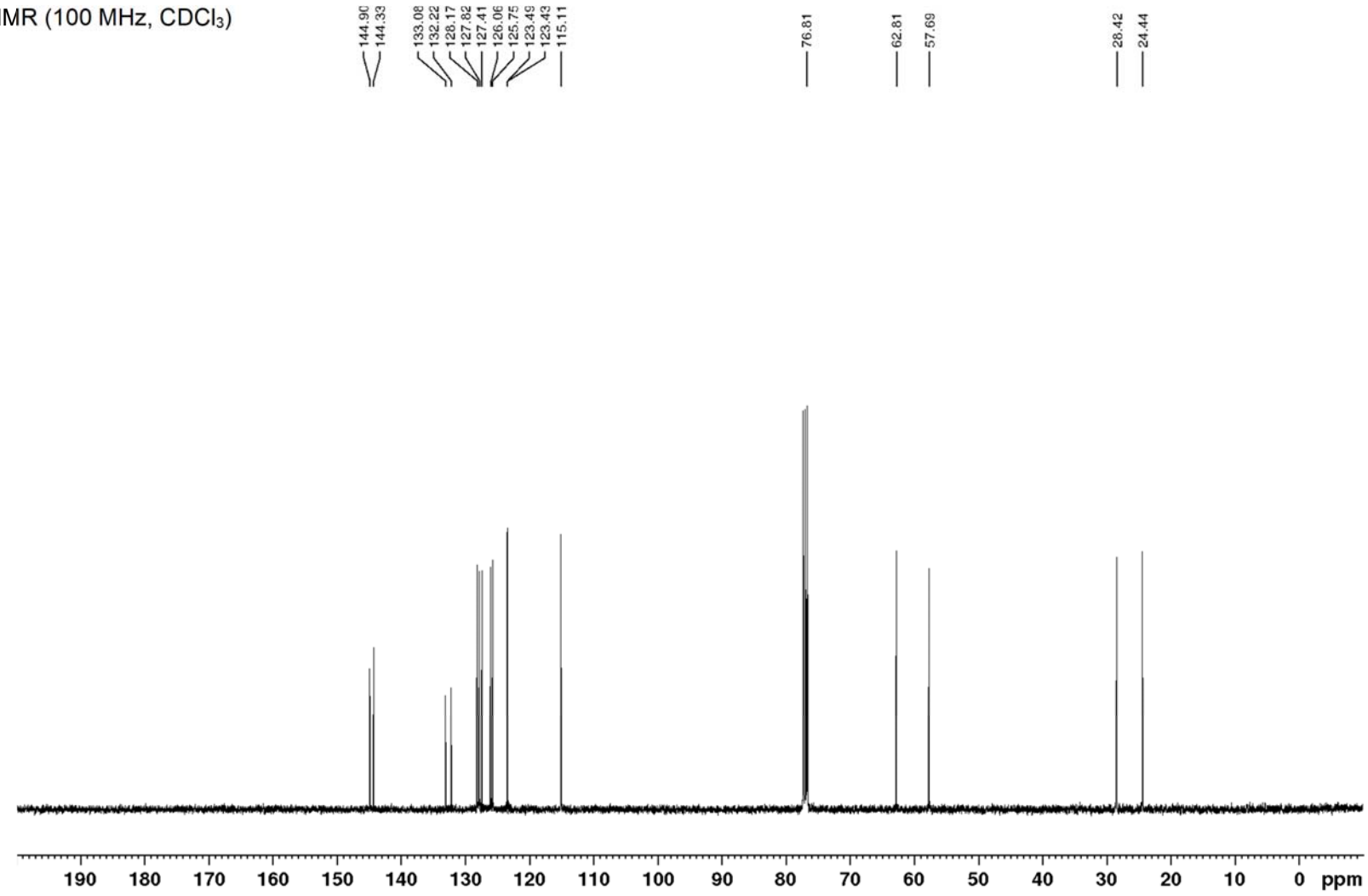


(2*R*,3*R*)-3-(Naphthalen-2-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-4ka): ^{1}H NMR (400 MHz, $CDCl_3$)

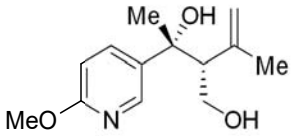


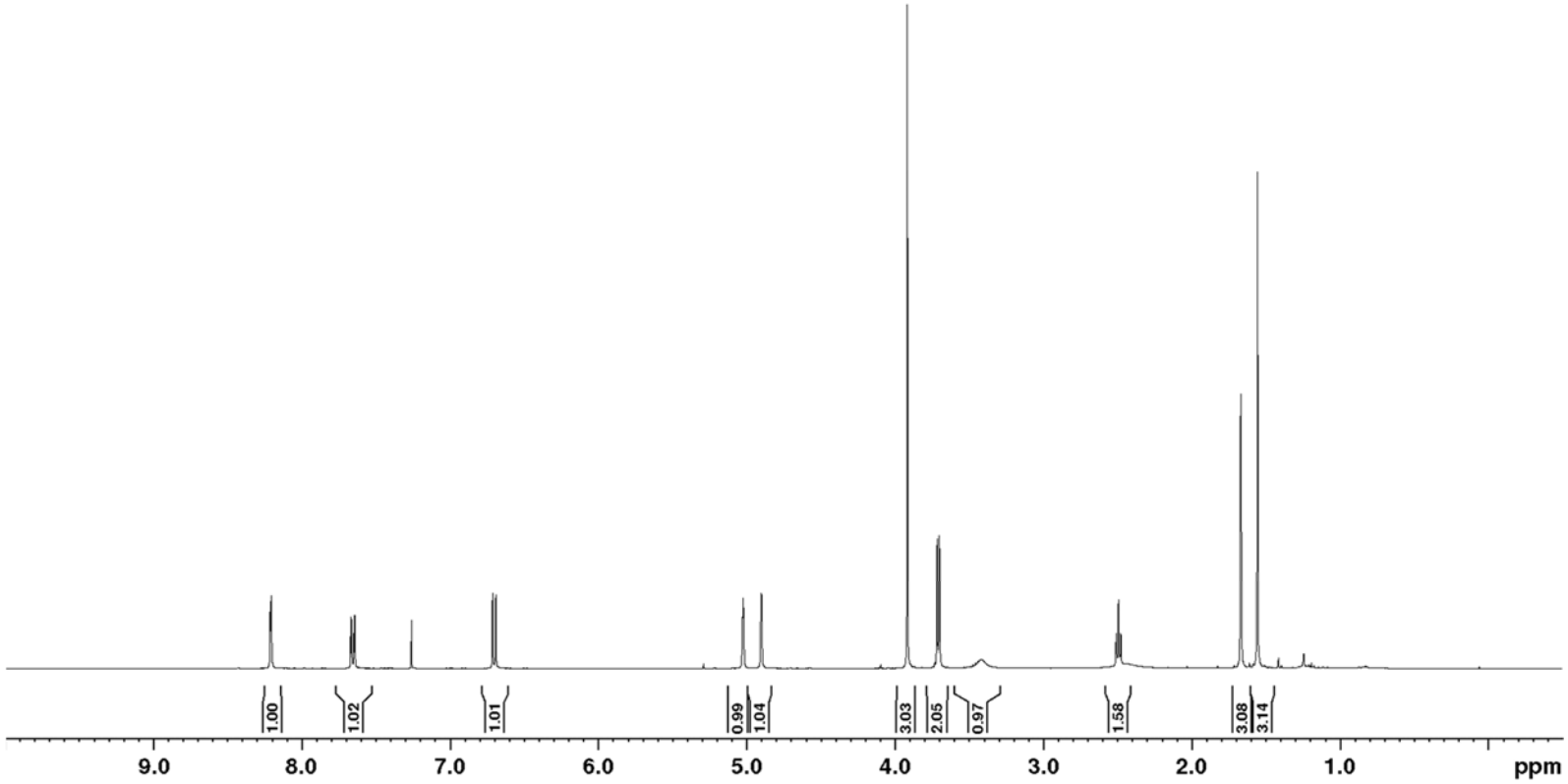


^{13}C NMR (100 MHz, $CDCl_3$)

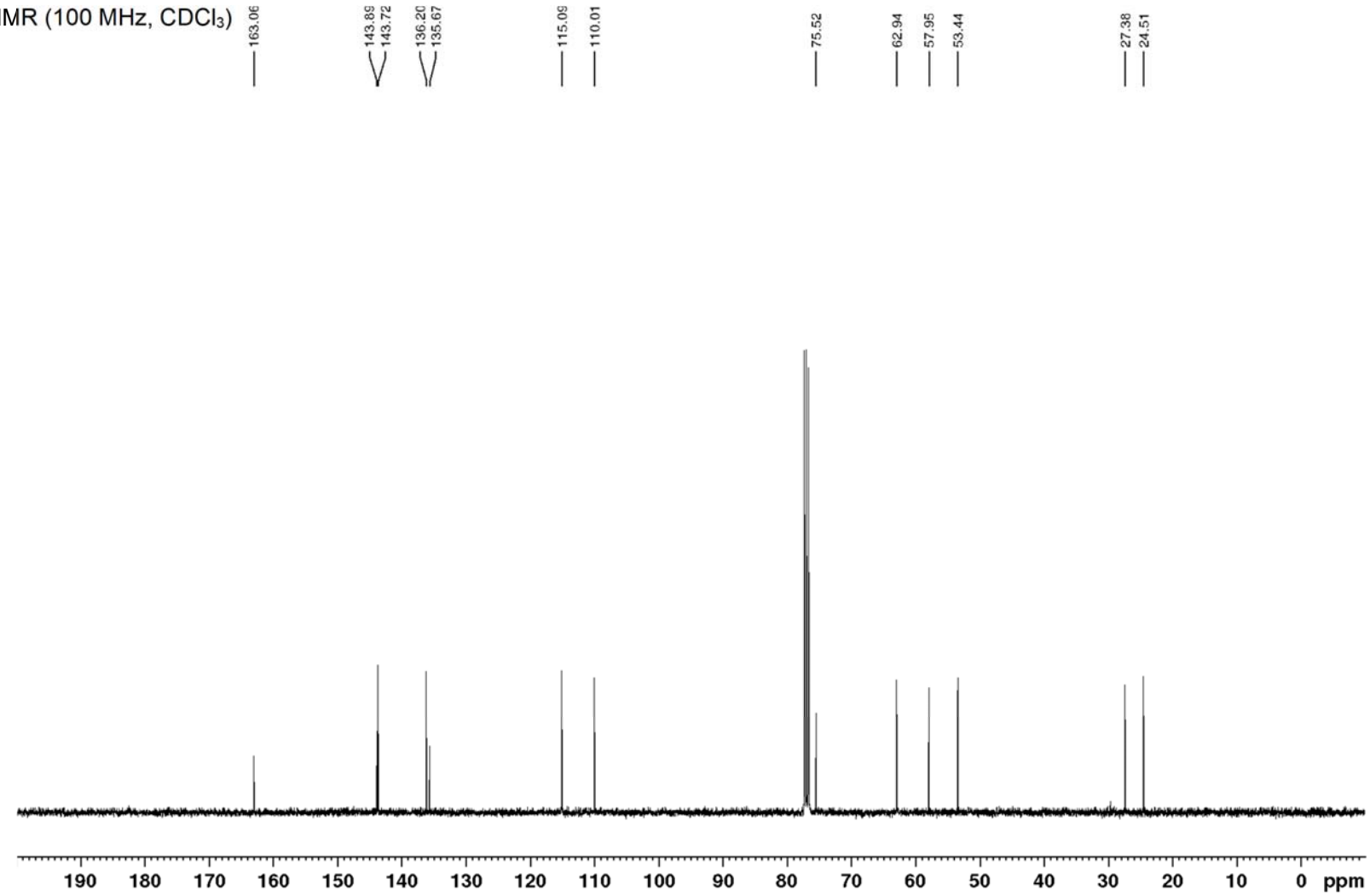


(2*R*,3*R*)-3-(6-Methoxypyridin-3-yl)-2-(prop-1-en-2-yl)butane-1,3-diol (*syn*-**4la**): ^{1}H NMR (400 MHz, $CDCl_3$)

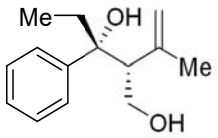


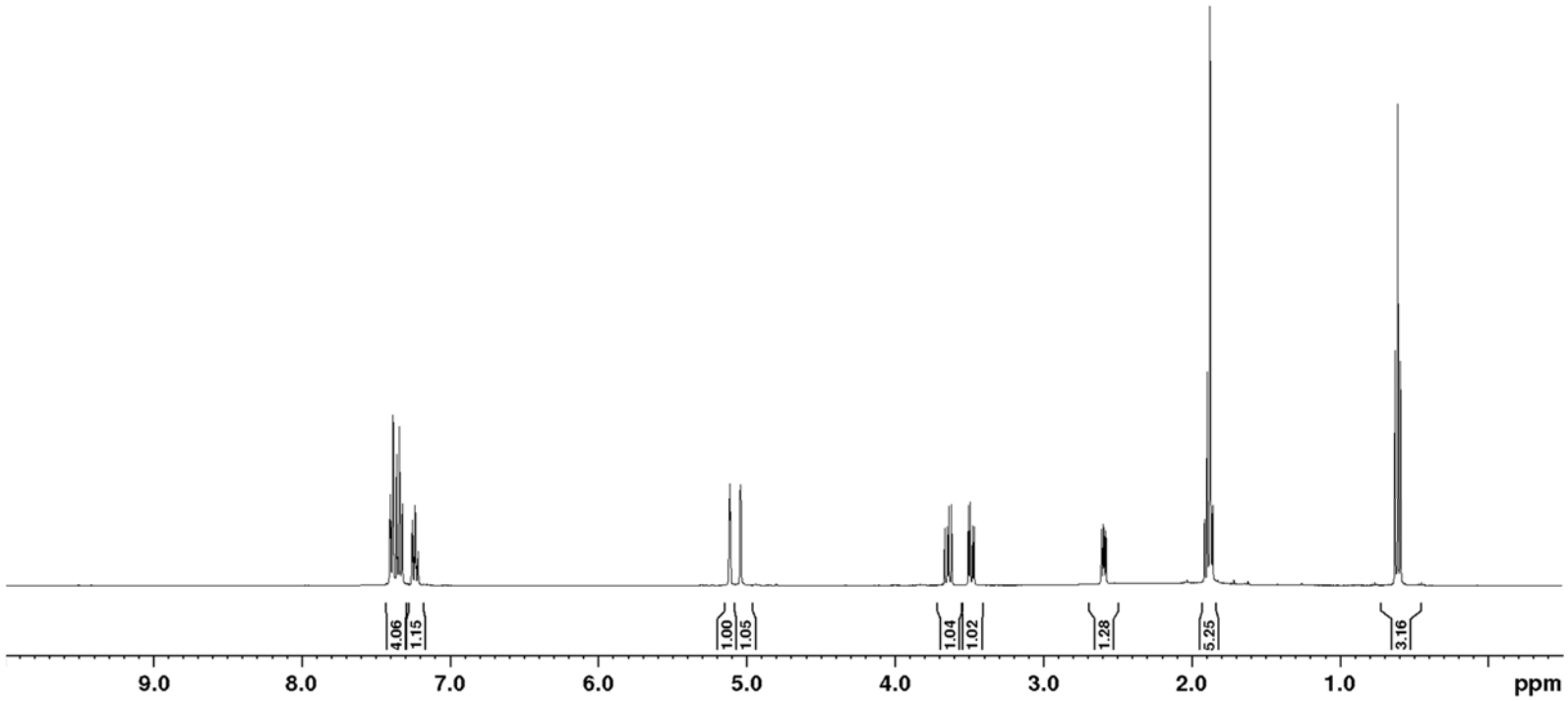


^{13}C NMR (100 MHz, $CDCl_3$)

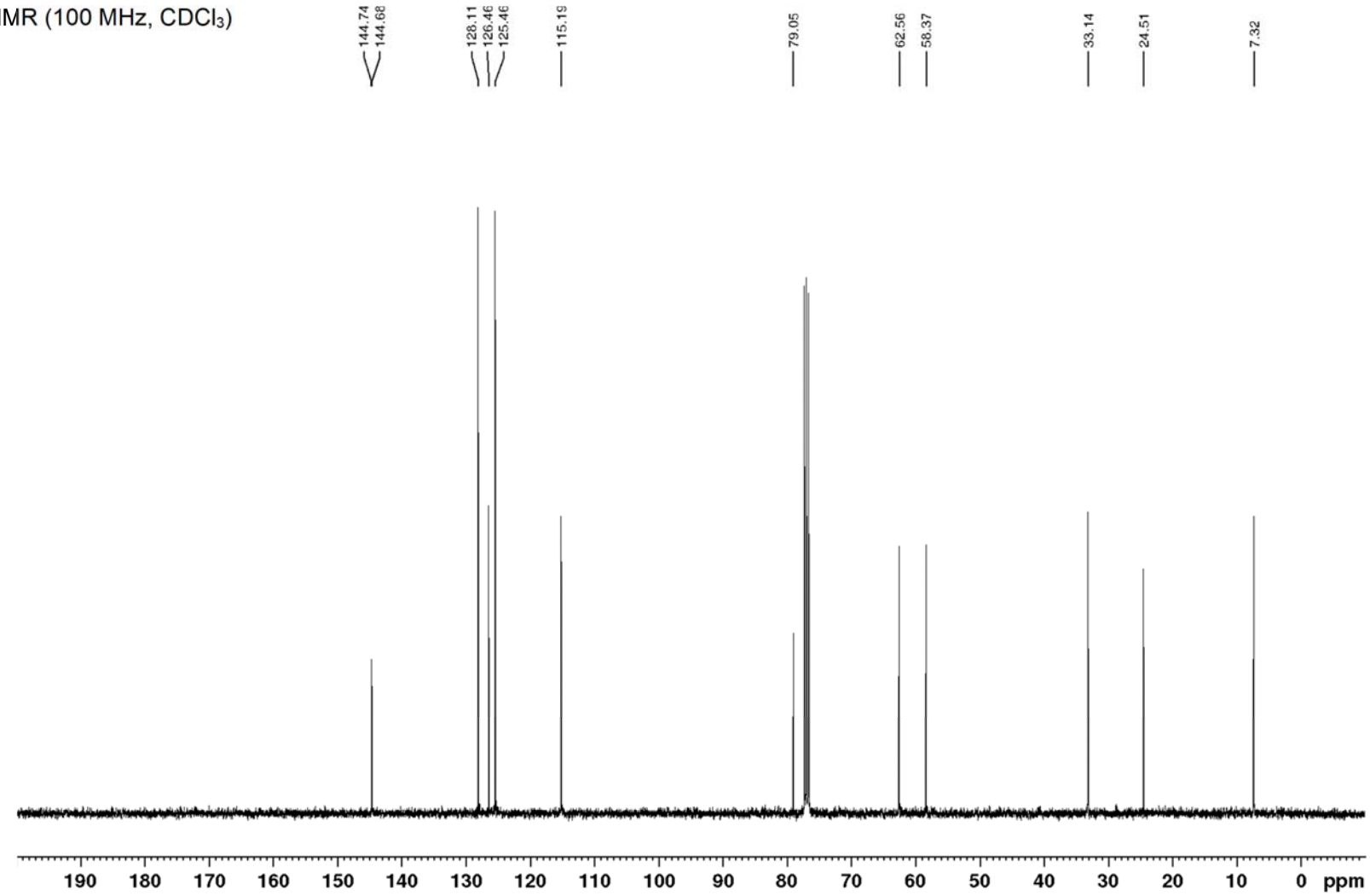


(2*R*,3*R*)-3-Phenyl-2-(prop-1-en-2-yl)pentane-1,3-diol (*syn*-**4ma**): ^{1}H NMR (400 MHz, $CDCl_3$)

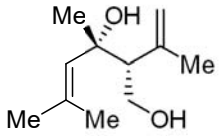


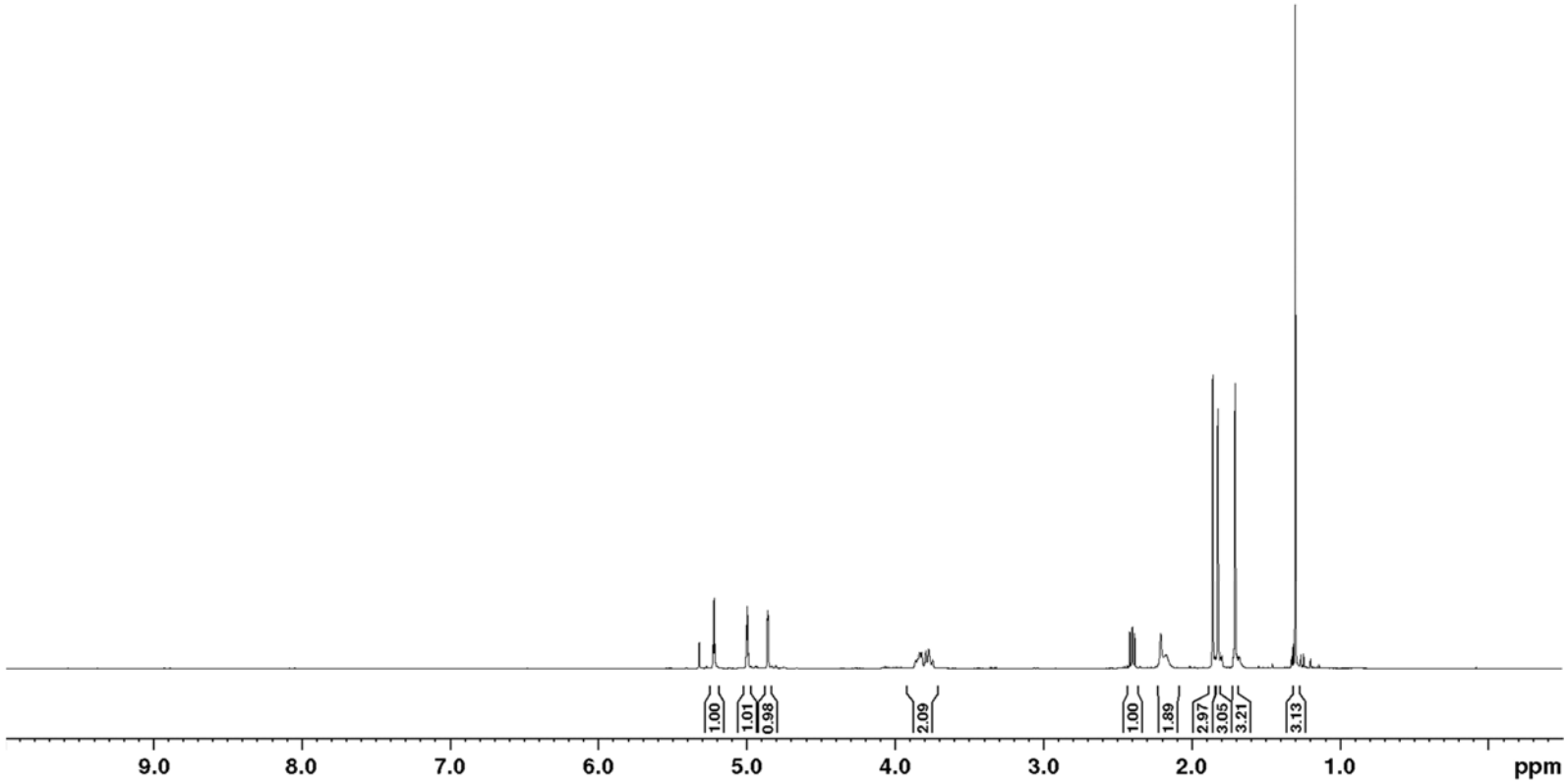


^{13}C NMR (100 MHz, $CDCl_3$)

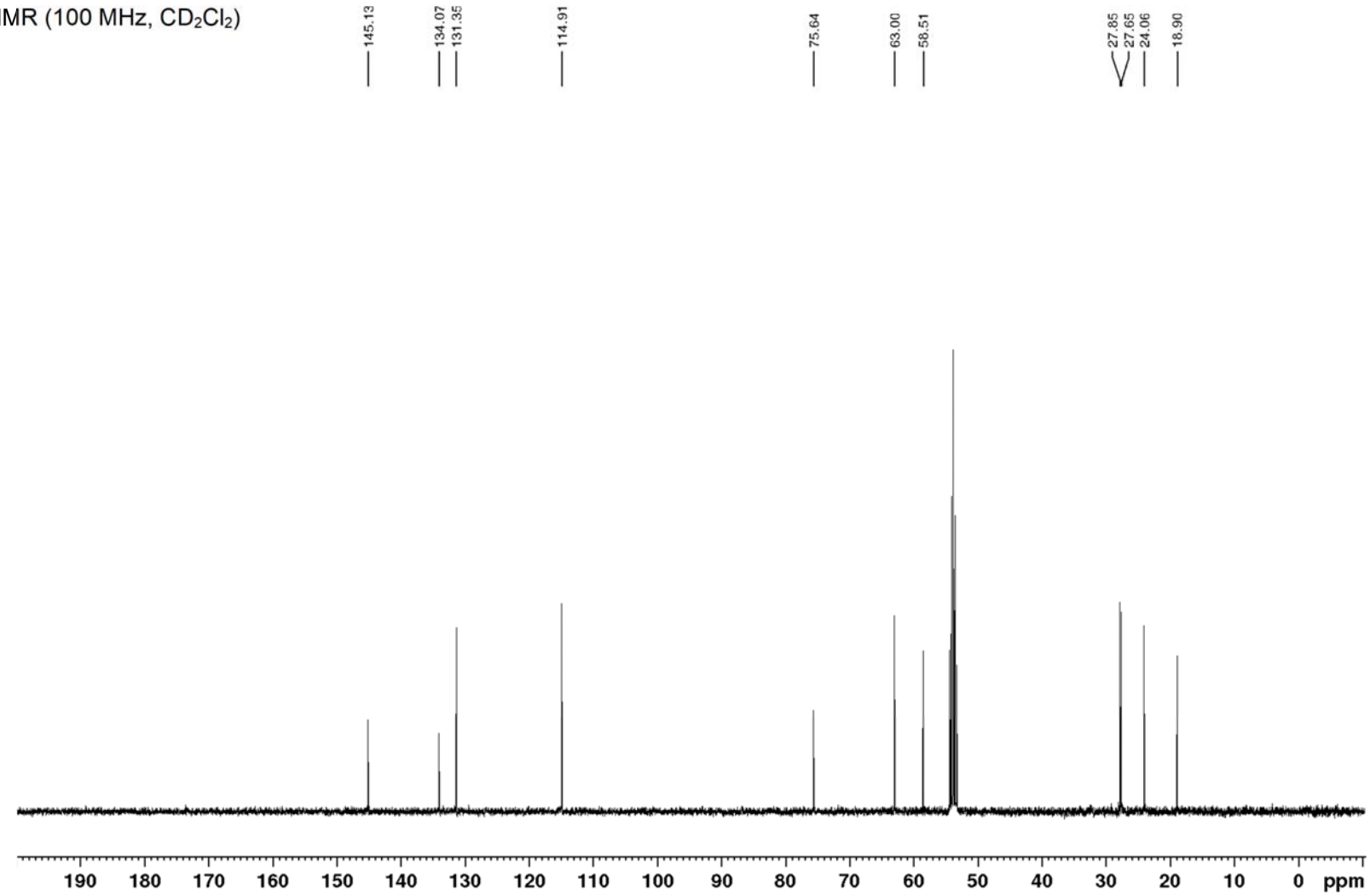


(2*R*,3*S*)-3,5-Dimethyl-2-(prop-1-en-2-yl)hex-4-ene-1,3-diol (*syn*-**4na**): ^{1}H NMR (400 MHz, CD_2Cl_2)

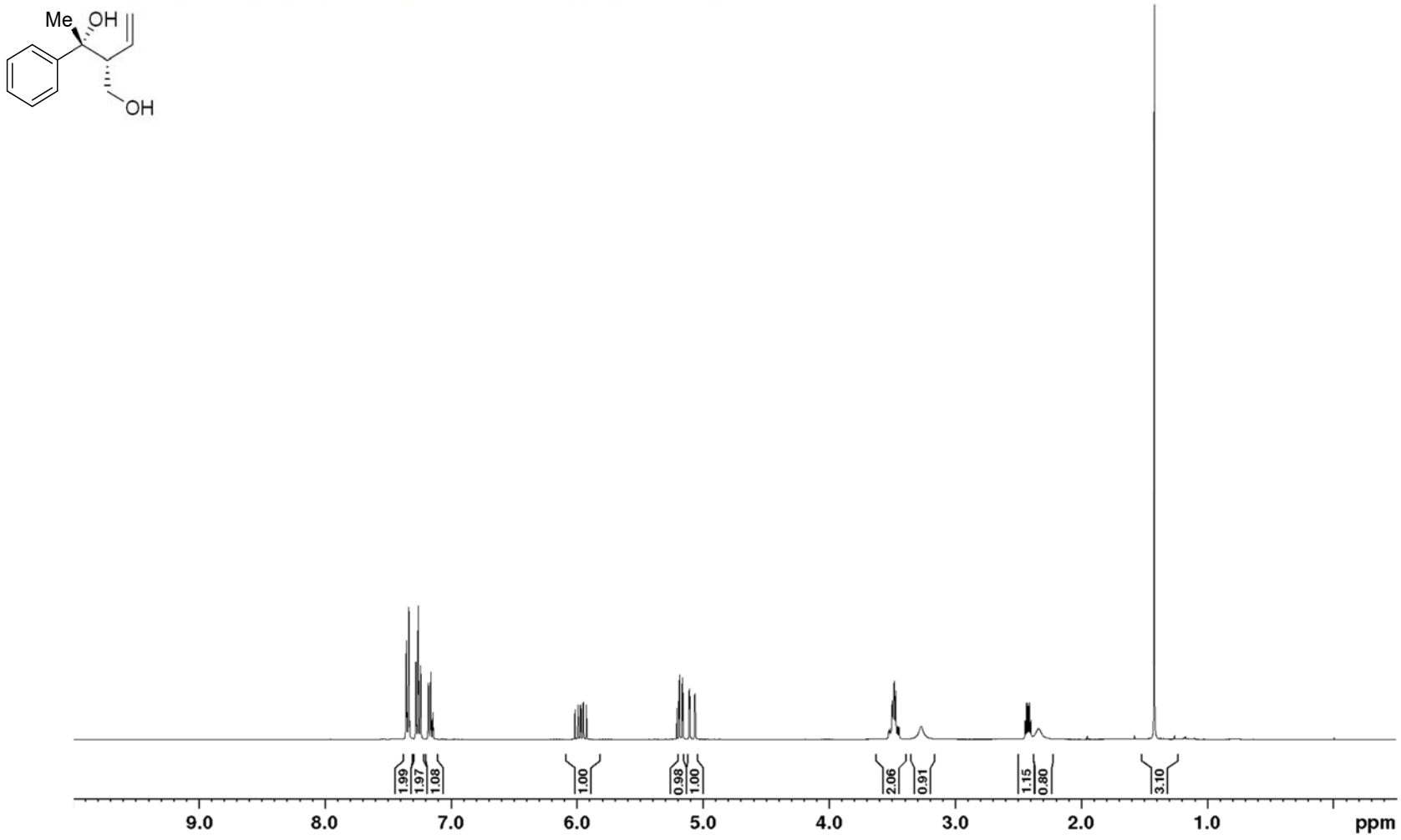




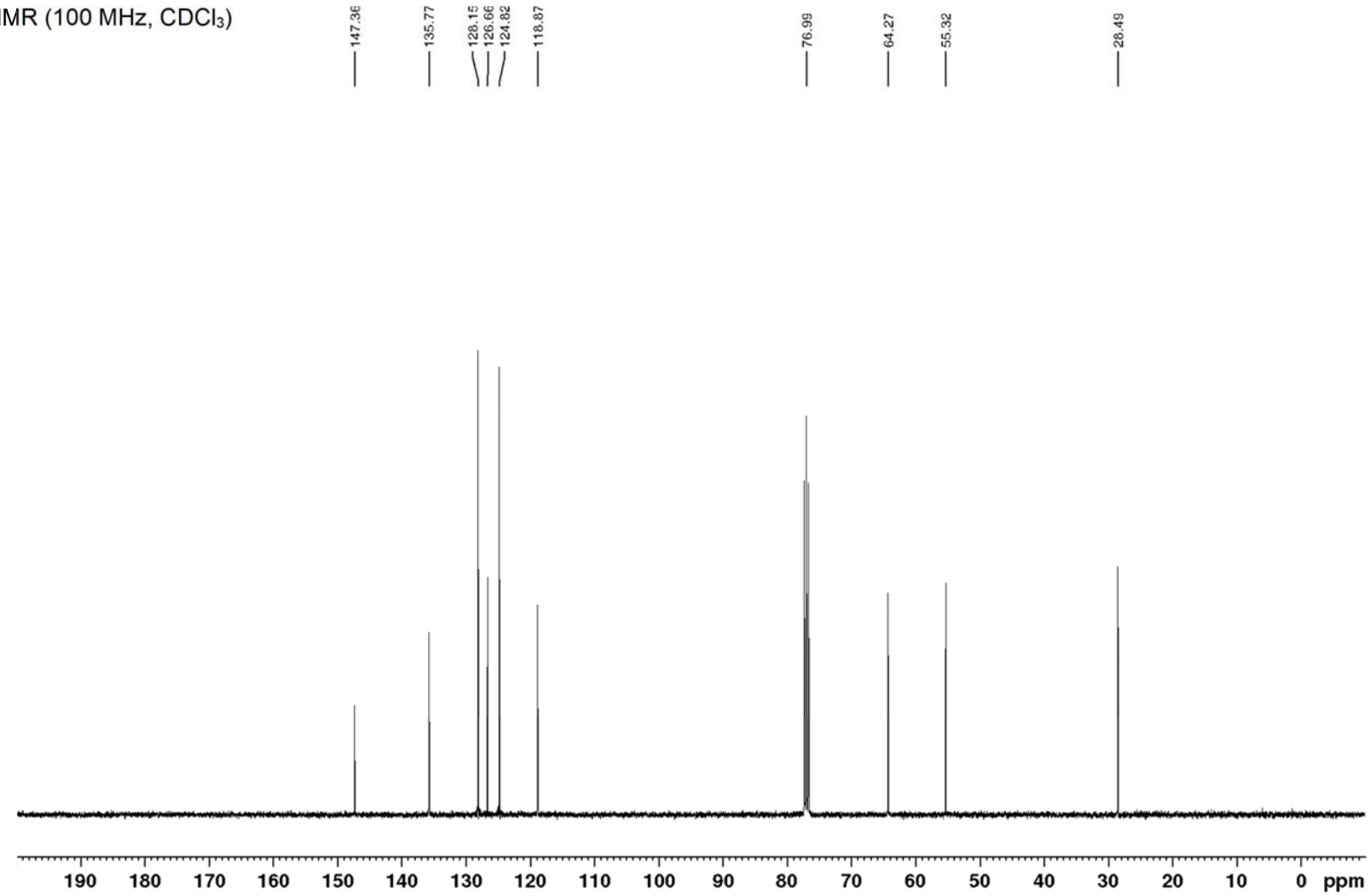
^{13}C NMR (100 MHz, CD_2Cl_2)



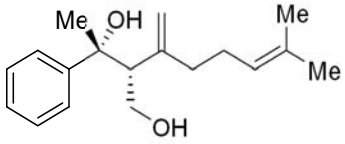
(2*R*,3*R*)-3-Phenyl-2-vinylbutane-1,3-diol (*syn*-**4ab**): ^{1}H NMR (400 MHz, $CDCl_3$)

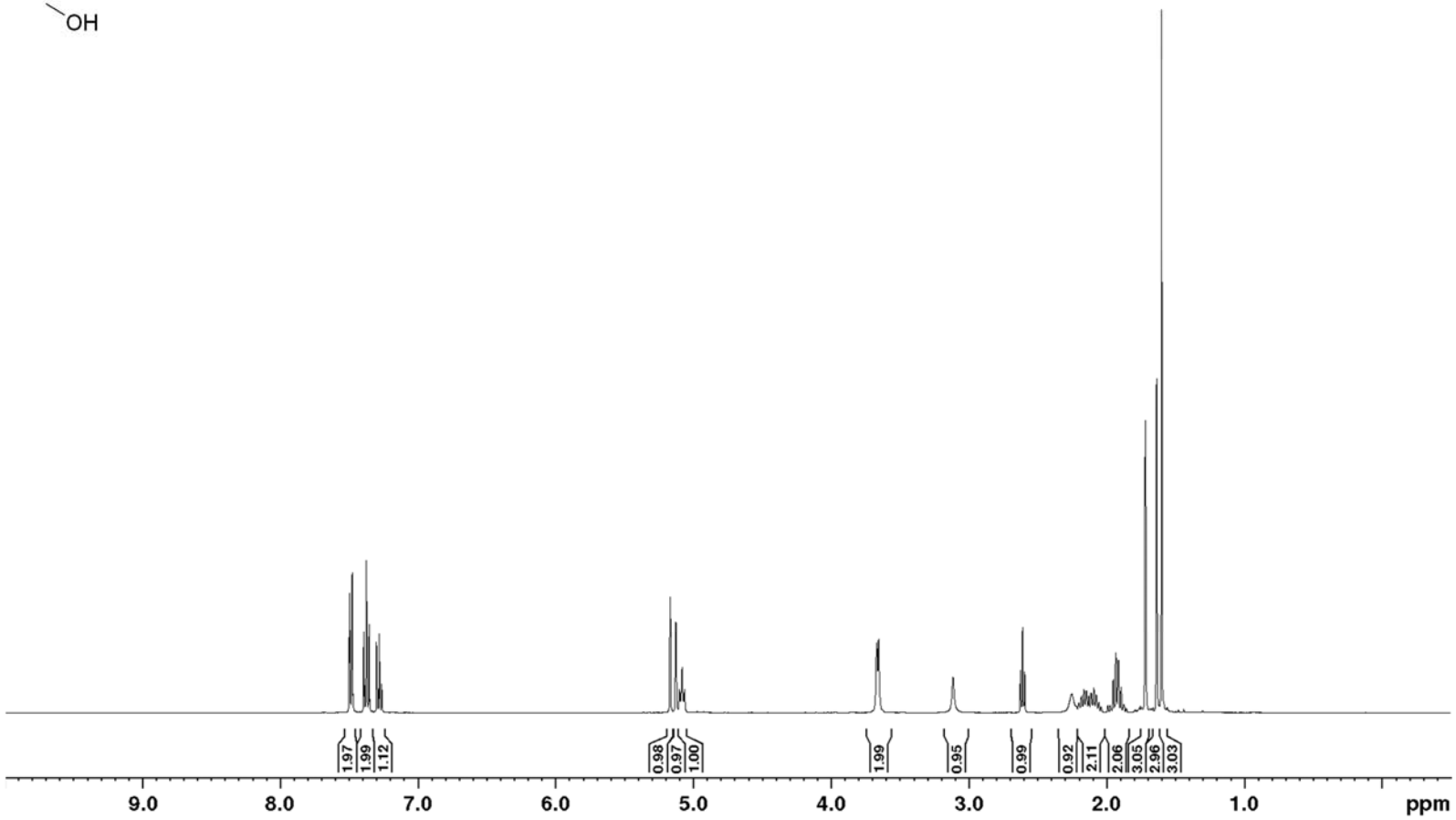


^{13}C NMR (100 MHz, $CDCl_3$)

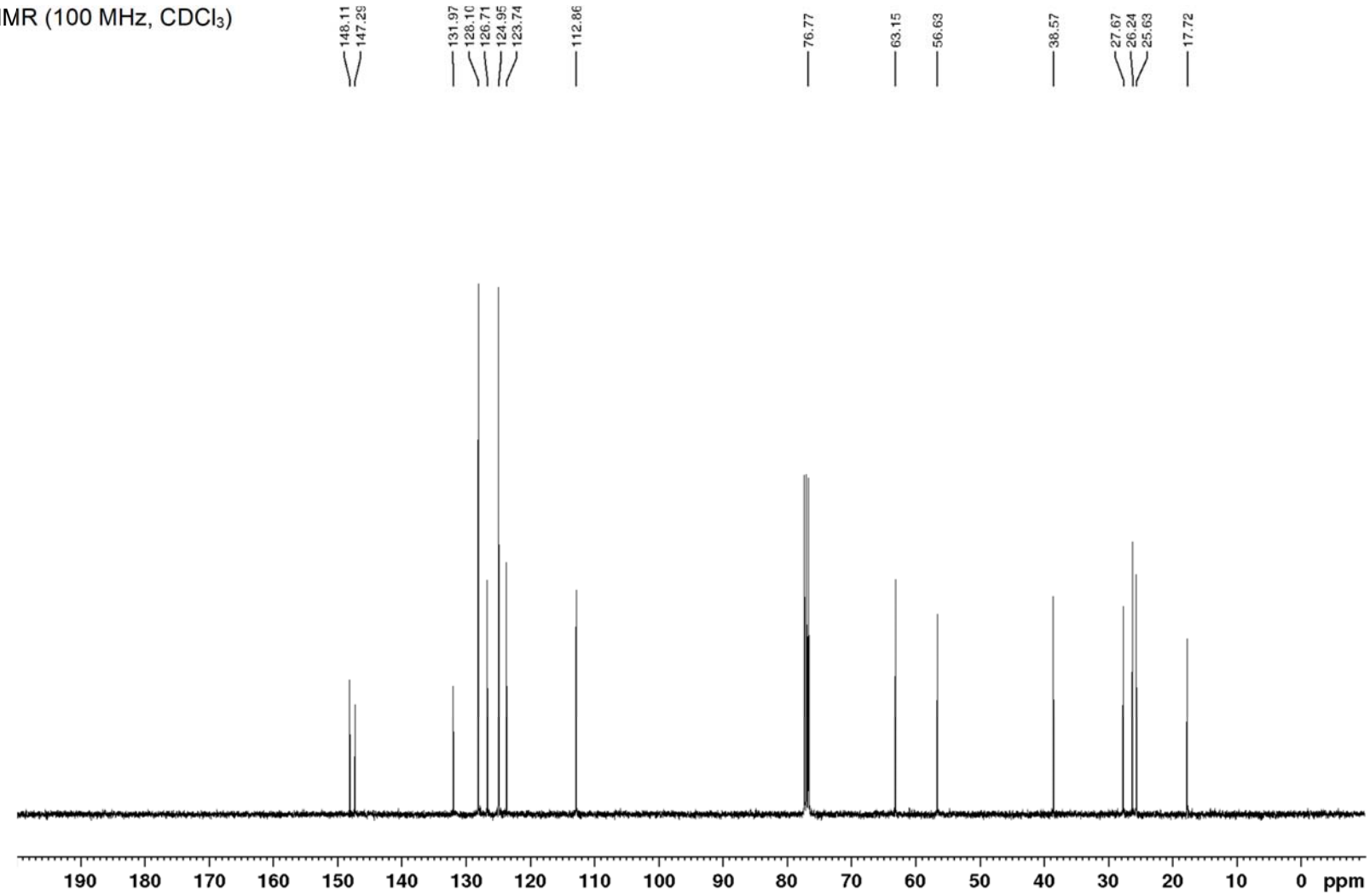


(2*R*,3*R*)-2-(6-Methylhepta-1,5-dien-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ac**): ^{1}H NMR (400 MHz, $CDCl_3$)

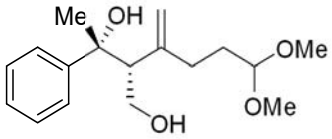


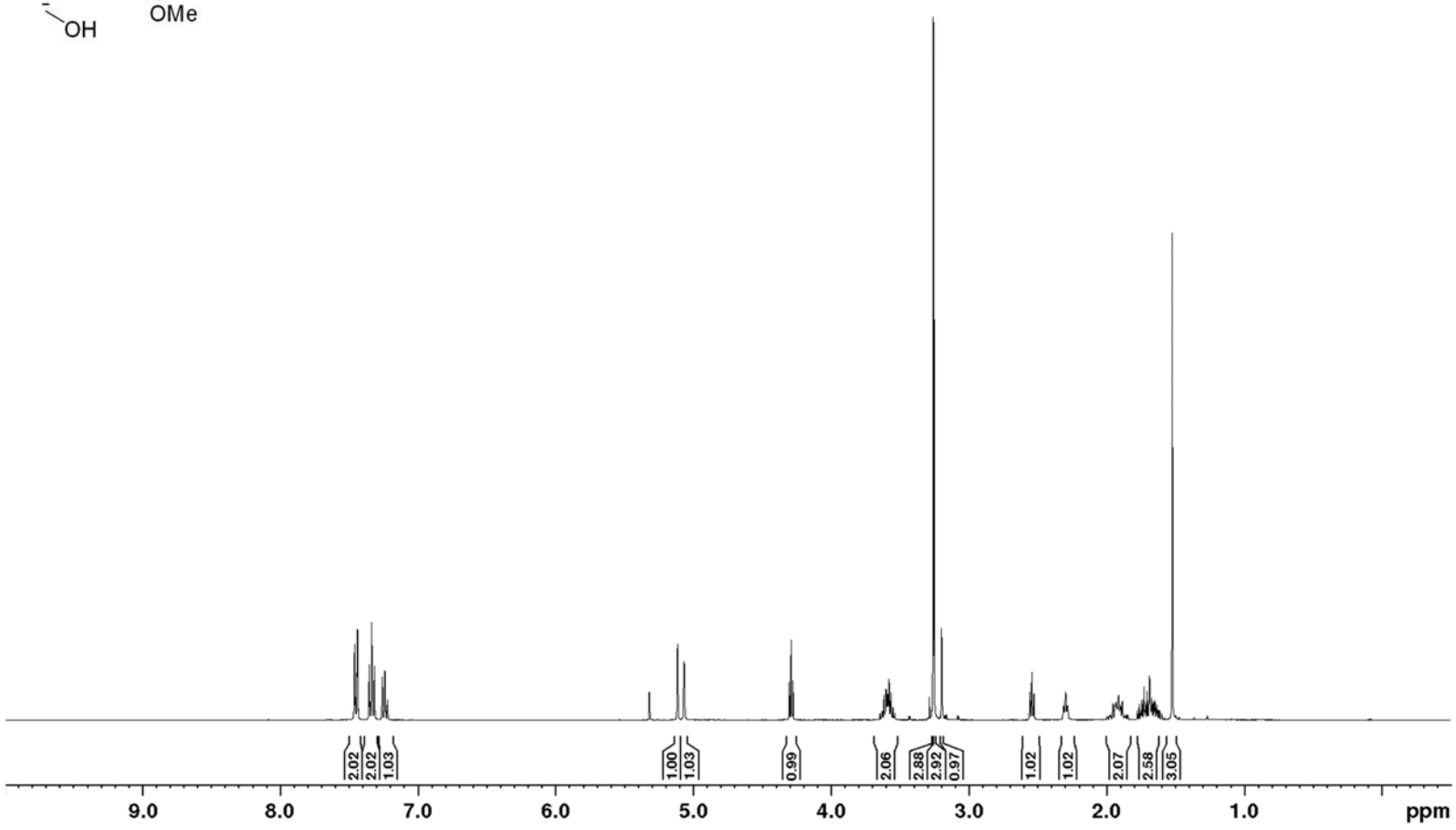


^{13}C NMR (100 MHz, $CDCl_3$)

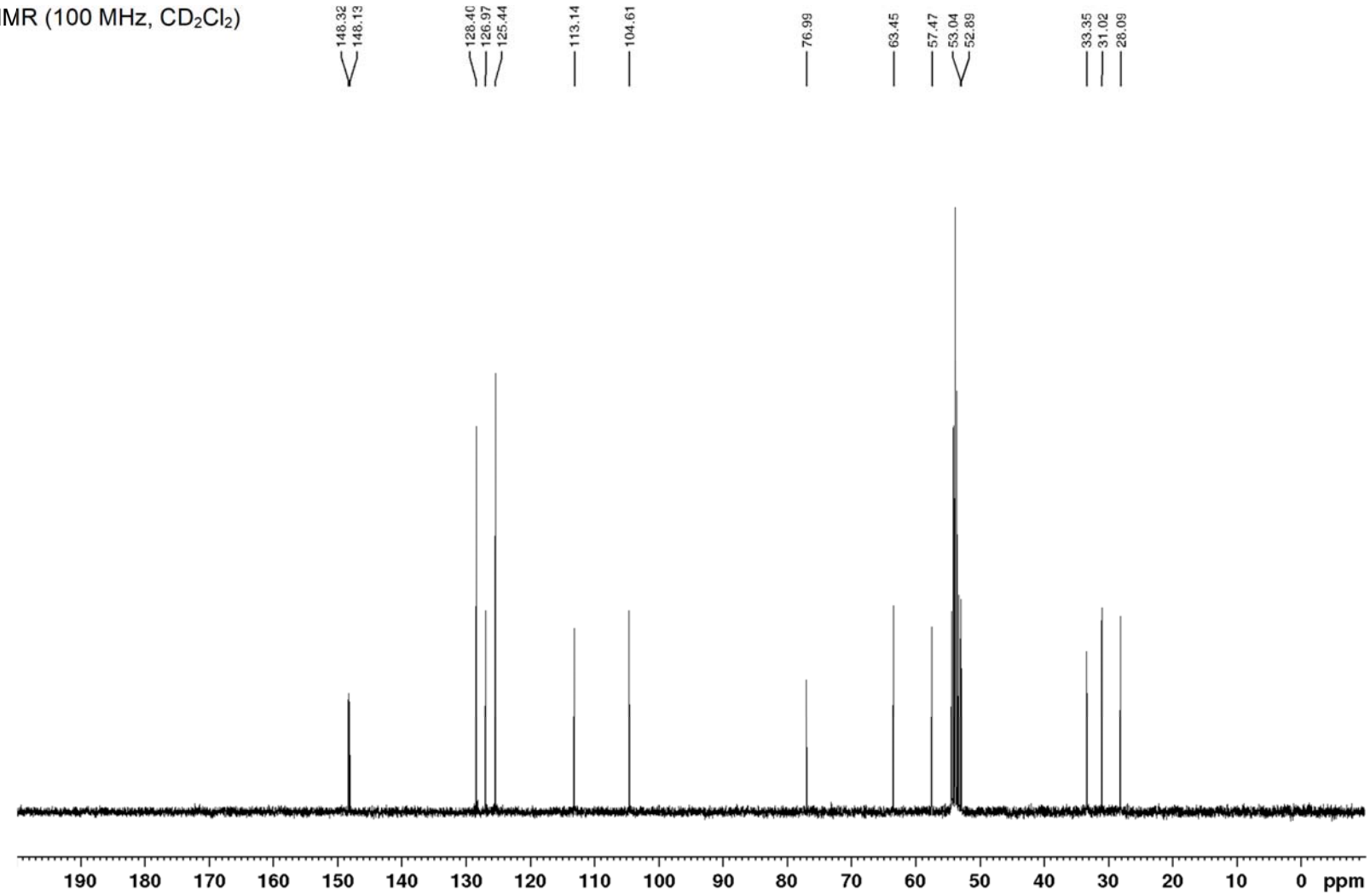


(2*R*,3*R*)-2-(5,5-Dimethoxypent-1-en-2-yl)-3-phenylbutane-1,3-diol (*syn*-**4ad**): ^{1}H NMR (400 MHz, CD_2Cl_2)

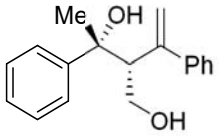


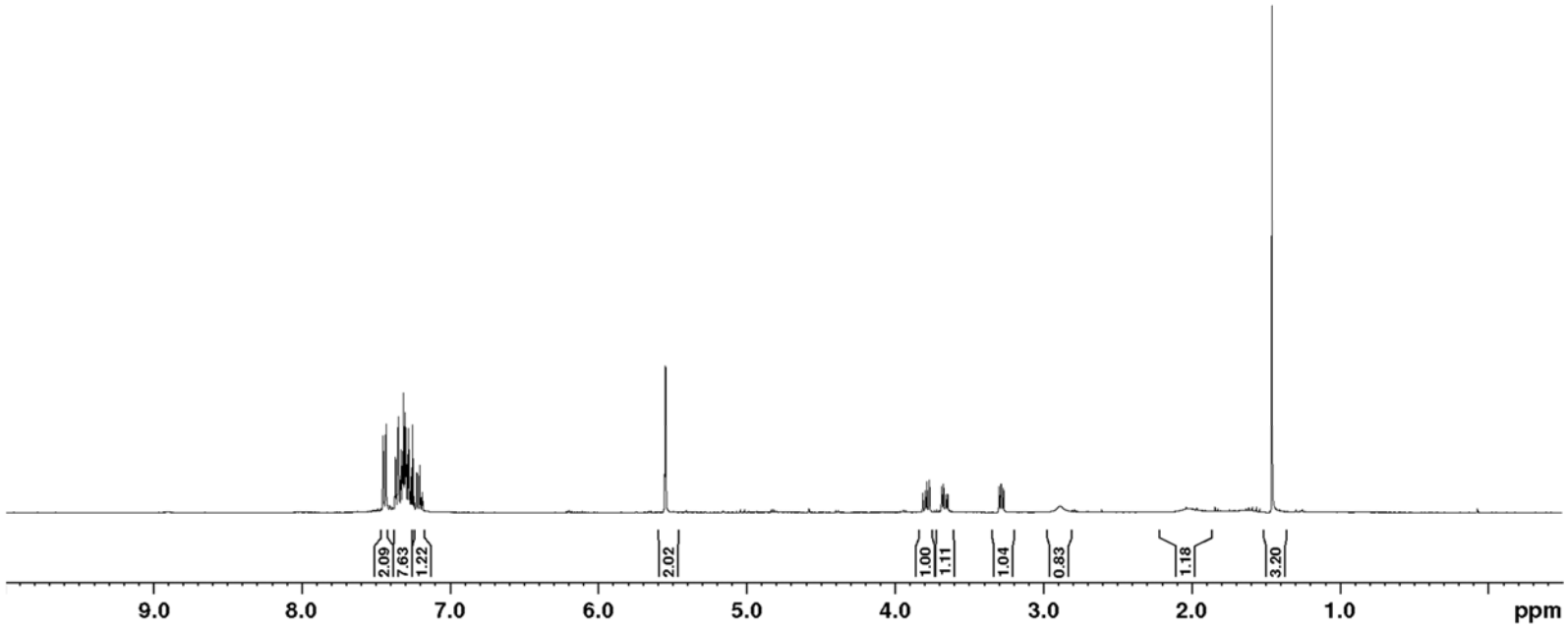


^{13}C NMR (100 MHz, CD_2Cl_2)

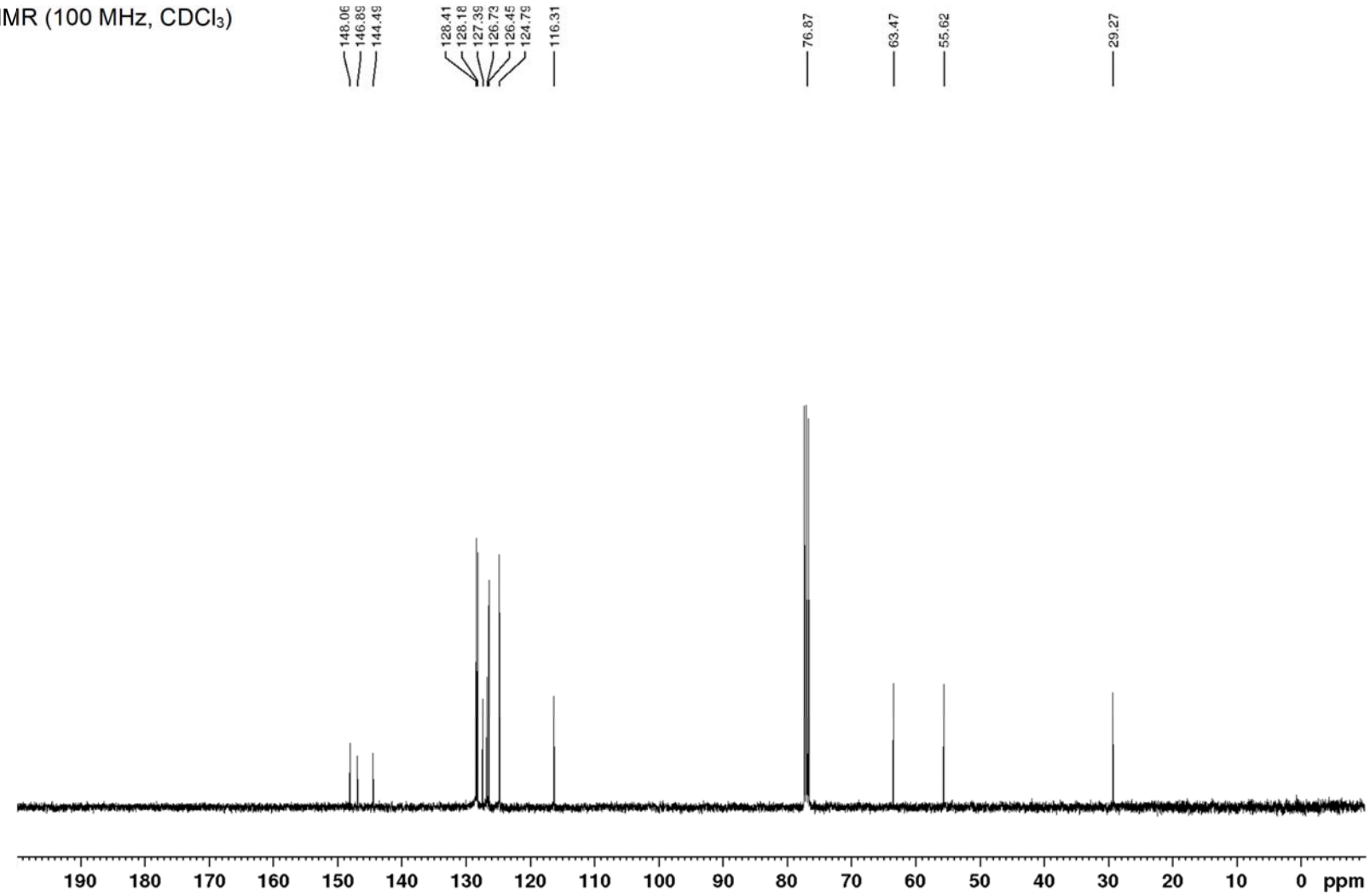


(2*R*,3*R*)-3-Phenyl-2-(1-phenylvinyl)butane-1,3-diol (*syn*-**4af**): ^{1}H NMR (400 MHz, $CDCl_3$)

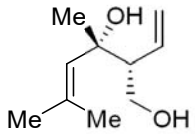


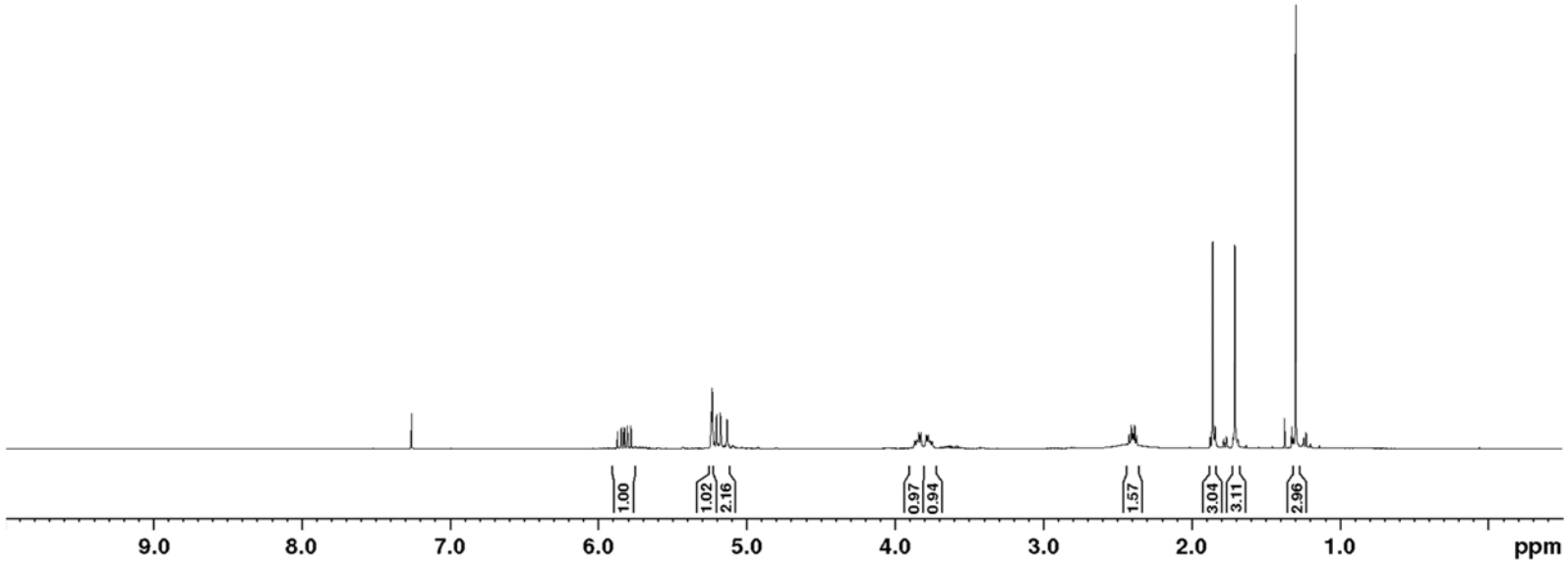


^{13}C NMR (100 MHz, $CDCl_3$)

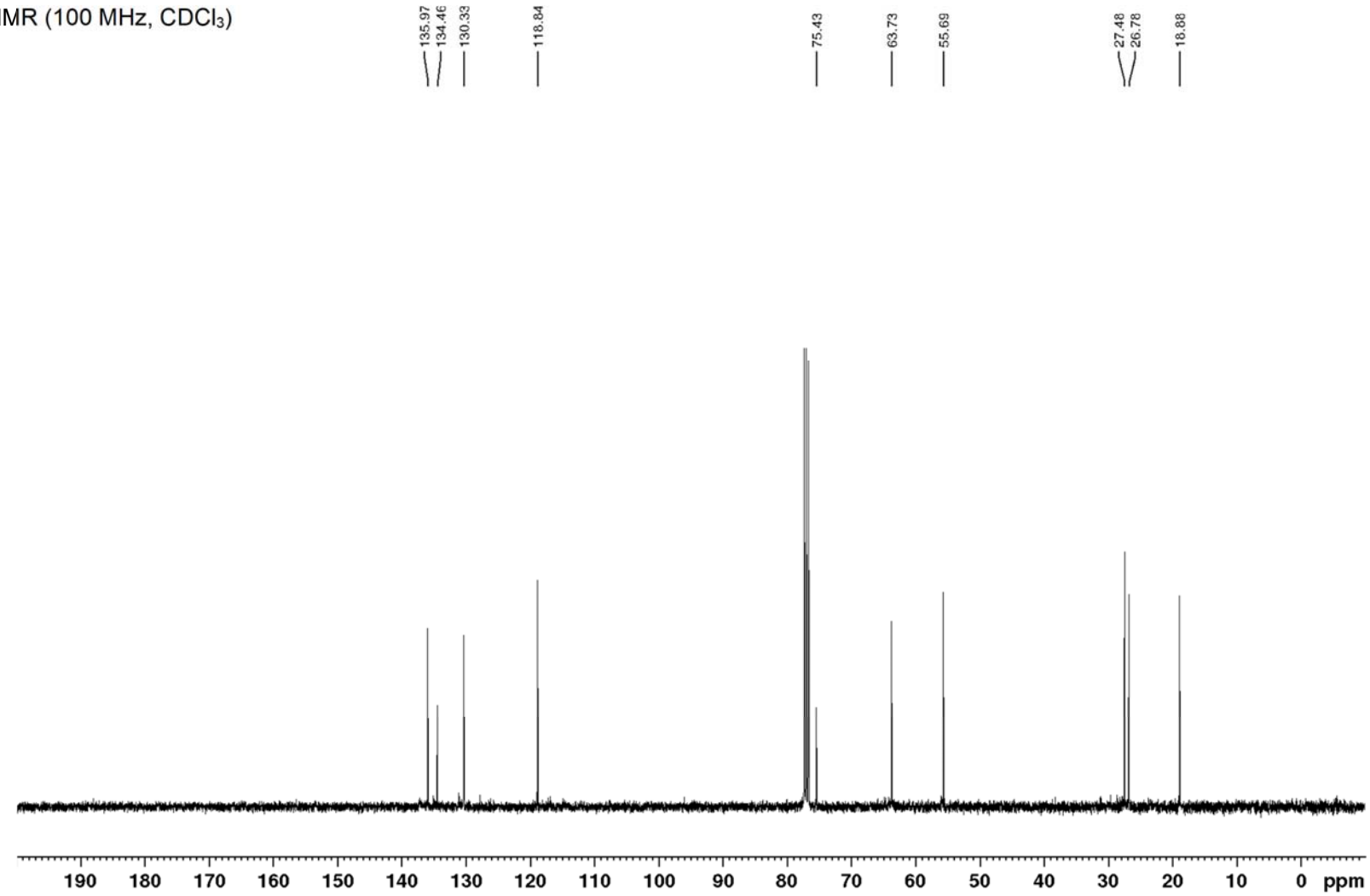


(2*R*,3*S*)-3,5-Dimethyl-2-vinylhex-4-ene-1,3-diol (*syn*-**4nb**): ^{1}H NMR (400 MHz, $CDCl_3$)

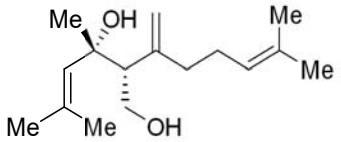


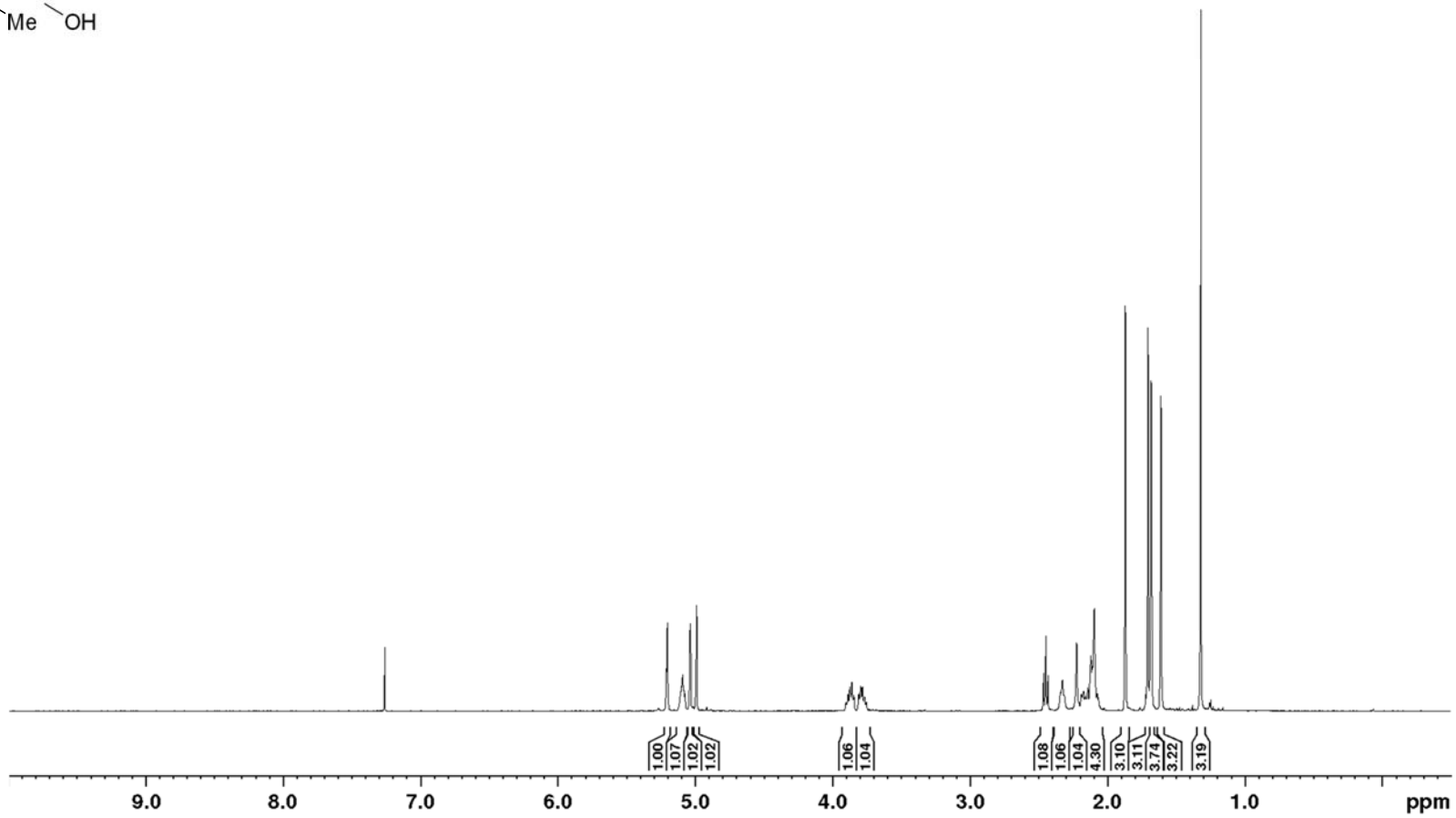


^{13}C NMR (100 MHz, $CDCl_3$)

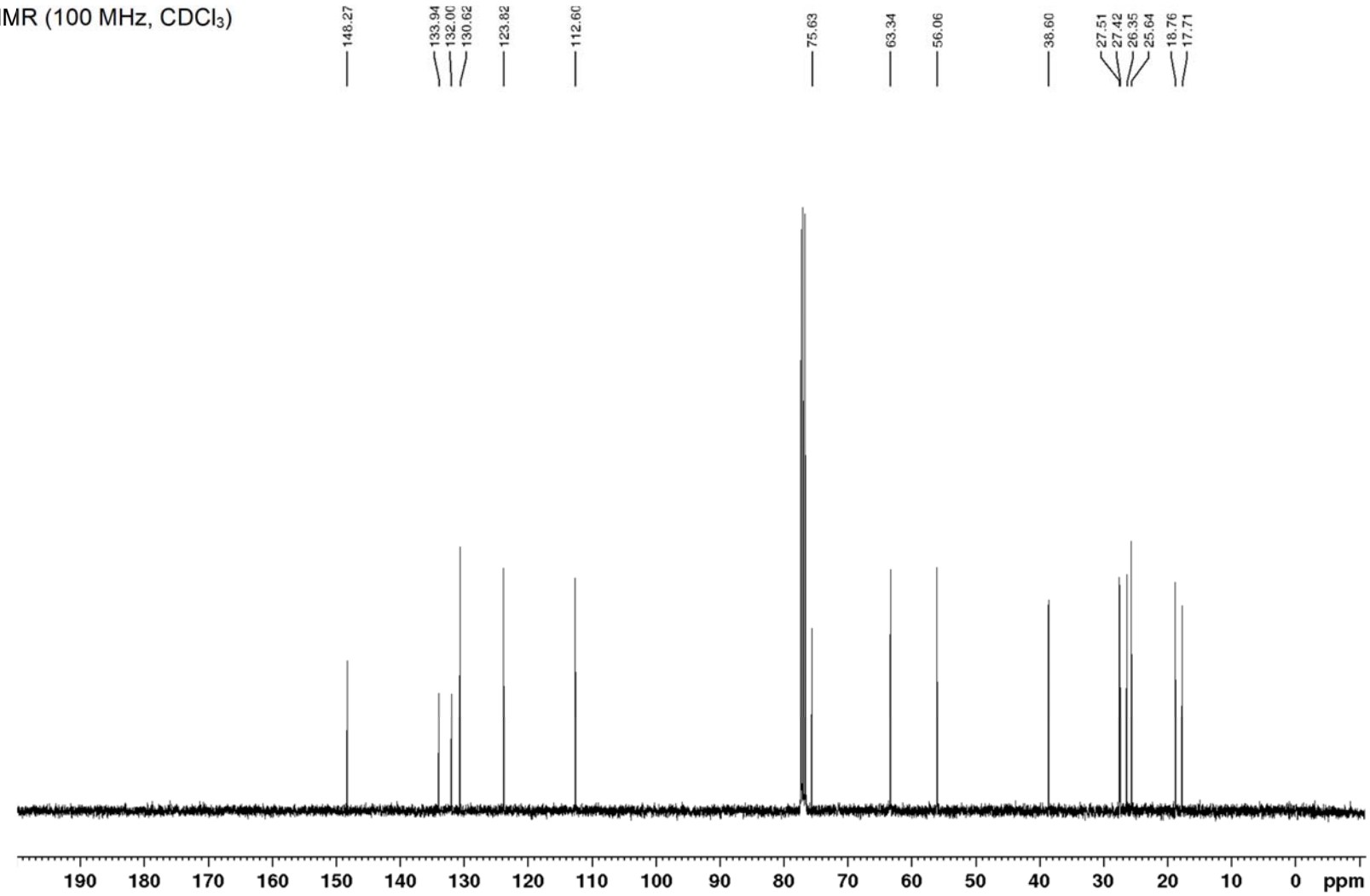


(2*R*,3*S*)-3,5-Dimethyl-2-(6-methylhepta-1,5-dien-2-yl)hex-4-ene-1,3-diol (*syn*-**4nc**): ^{1}H NMR (400 MHz, $CDCl_3$)

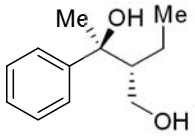


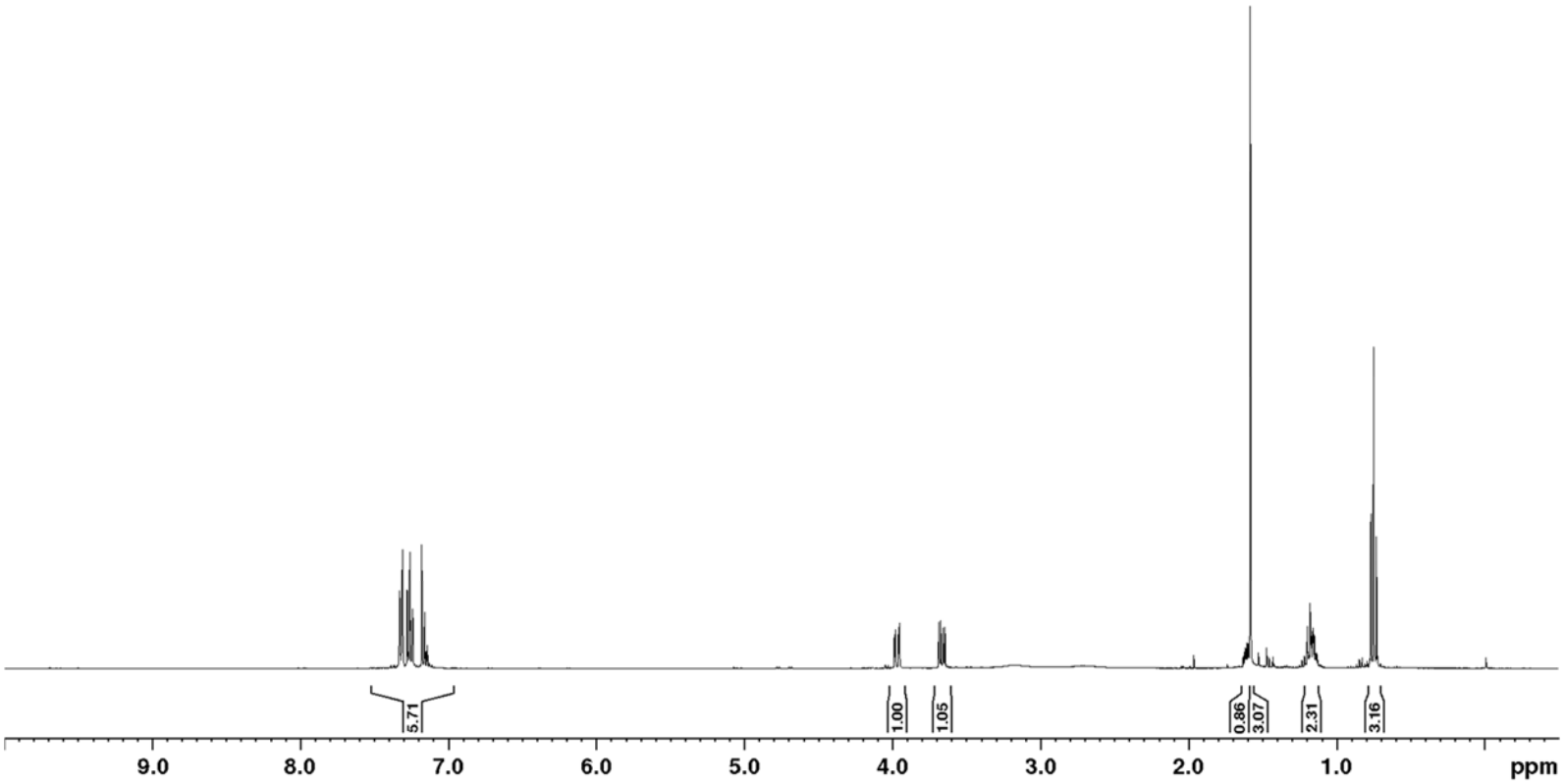


^{13}C NMR (100 MHz, $CDCl_3$)

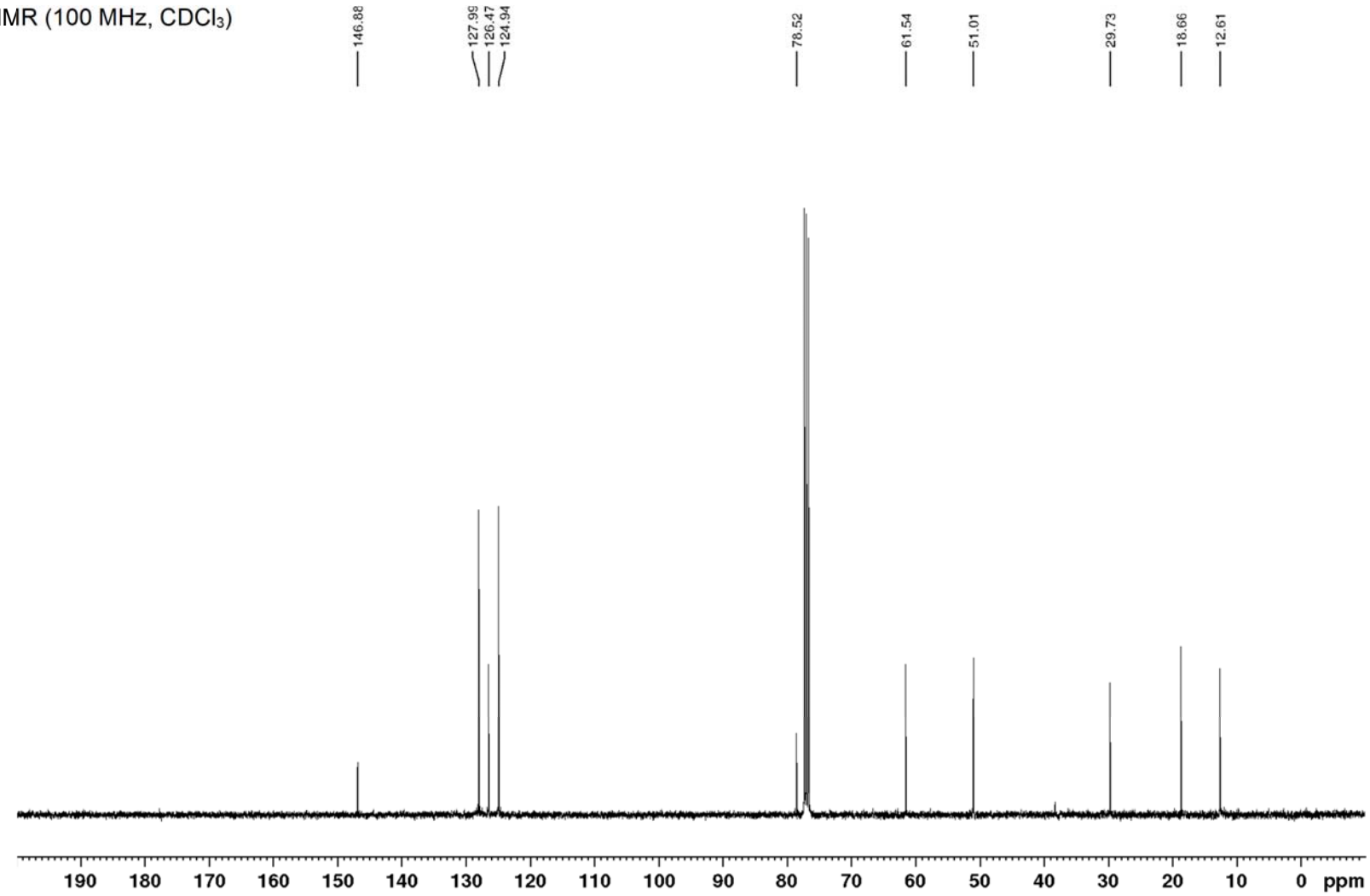


(2*R*,3*S*)-2-ethyl-3-phenylbutane-1,3-diol ((2*R*,3*S*)-5): ^{1}H NMR (400 MHz, $CDCl_3$)

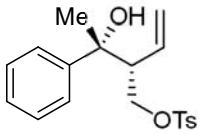


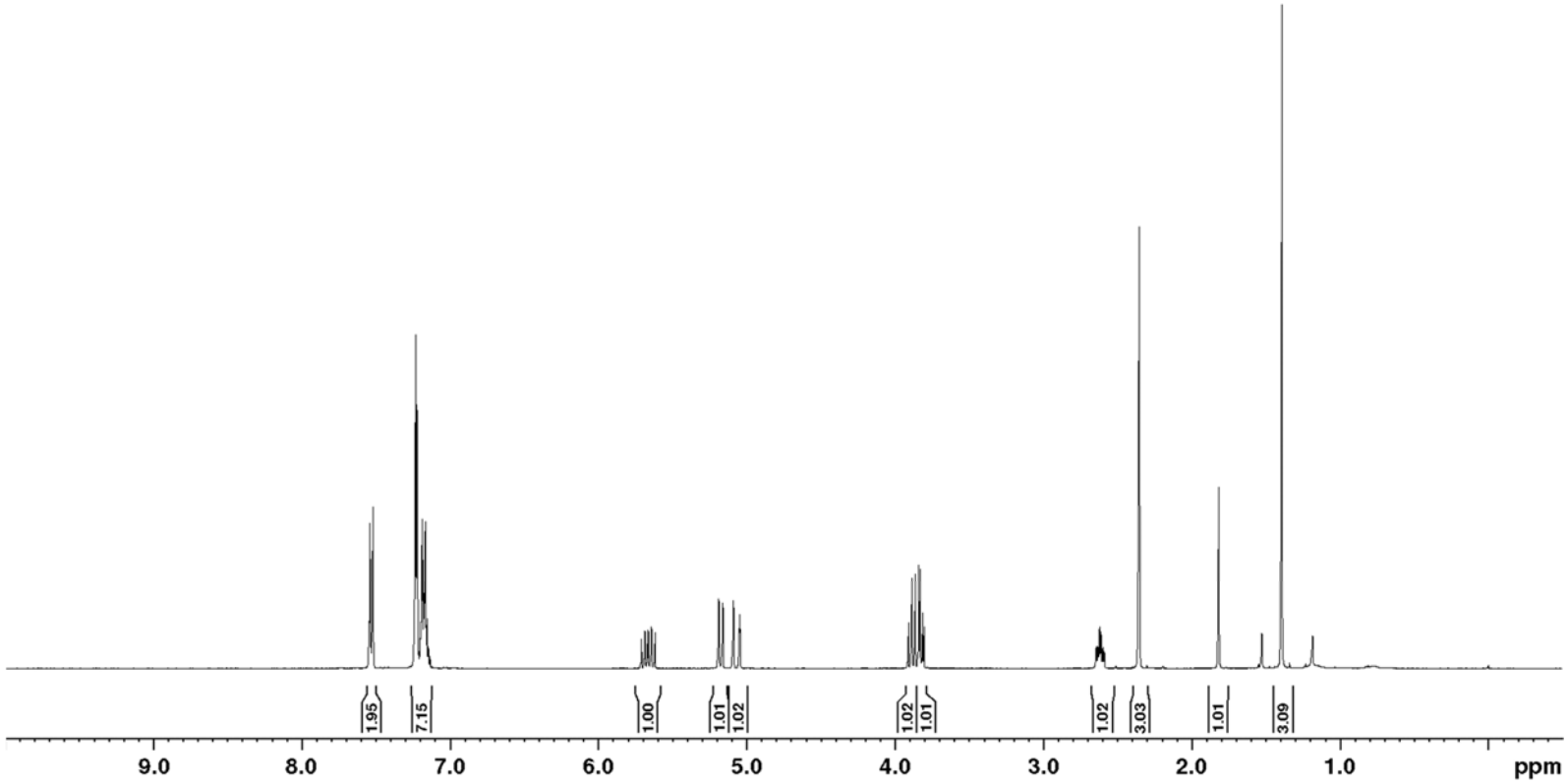


^{13}C NMR (100 MHz, $CDCl_3$)

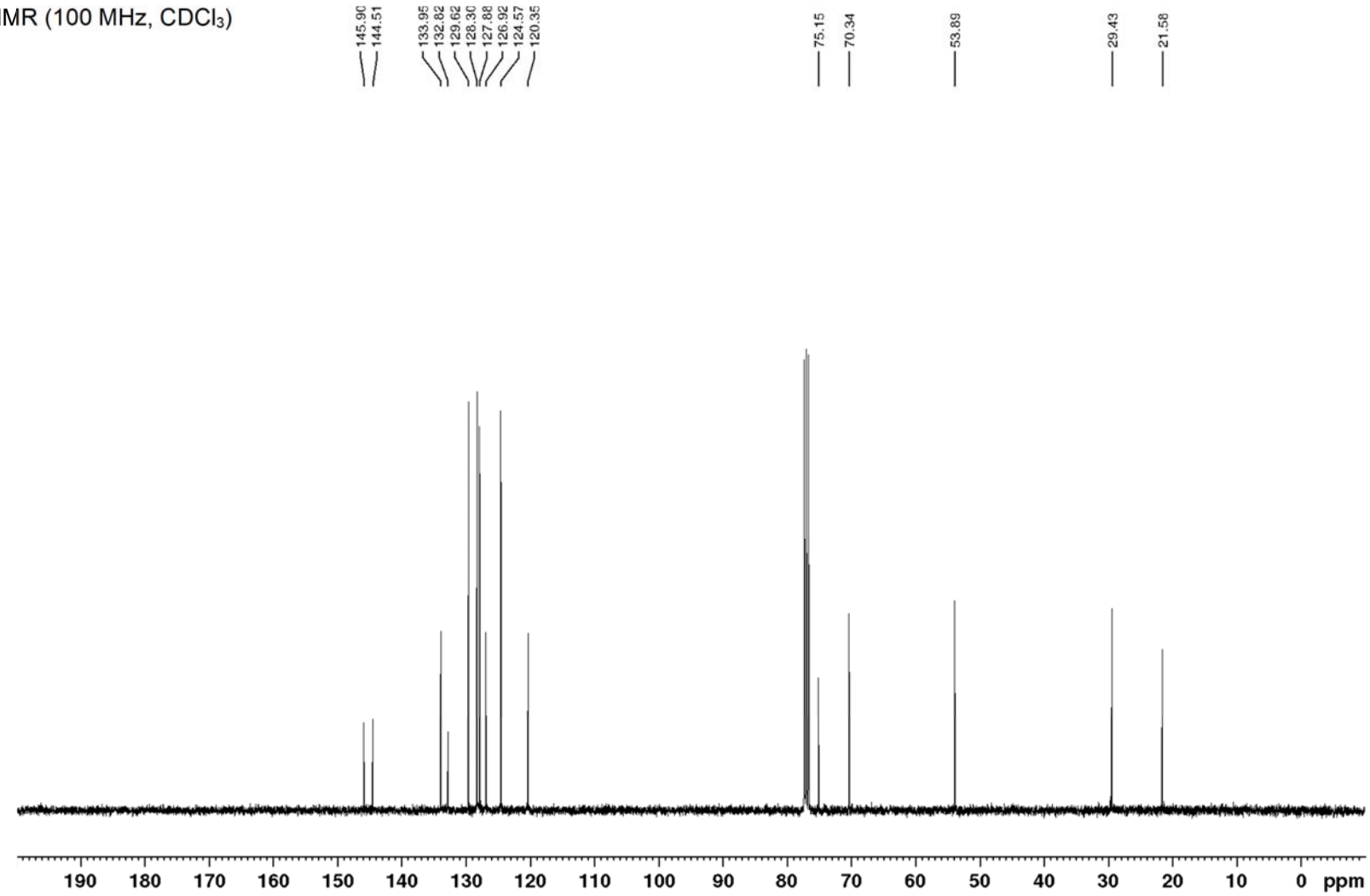


(*R*)-2-((*R*)-1-Hydroxy-1-phenylethyl)but-3-en-1-yl 4-methylbenzenesulfonate (12): ^{1}H NMR (400 MHz, $CDCl_3$)

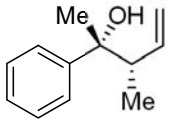


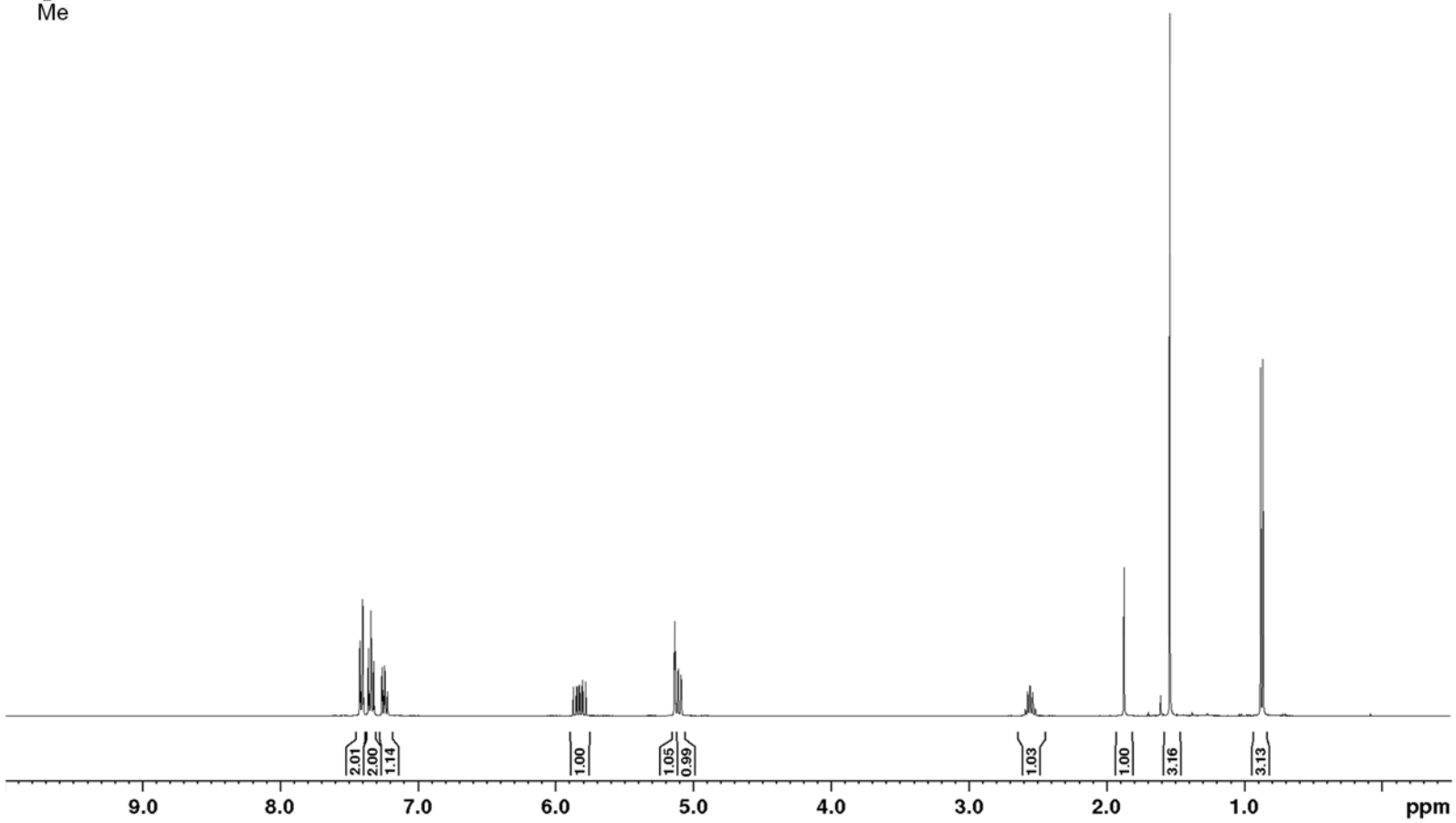


^{13}C NMR (100 MHz, $CDCl_3$)

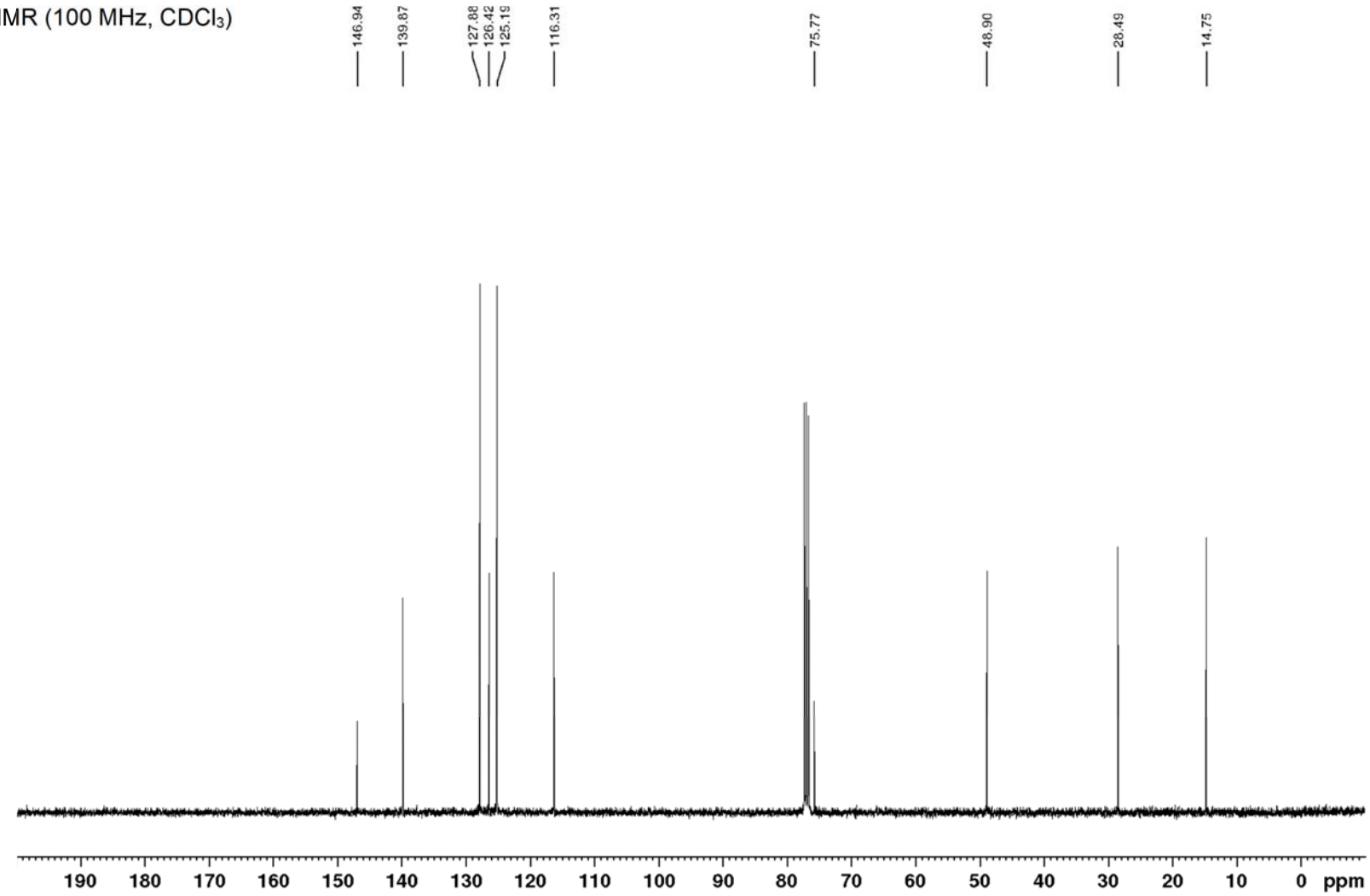


(2*R*,3*S*)-3-Methyl-2-phenylpent-4-en-2-ol ((2*R*,3*S*)-6): ^{1}H NMR (400 MHz, $CDCl_3$)

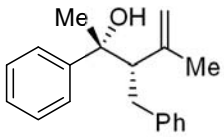


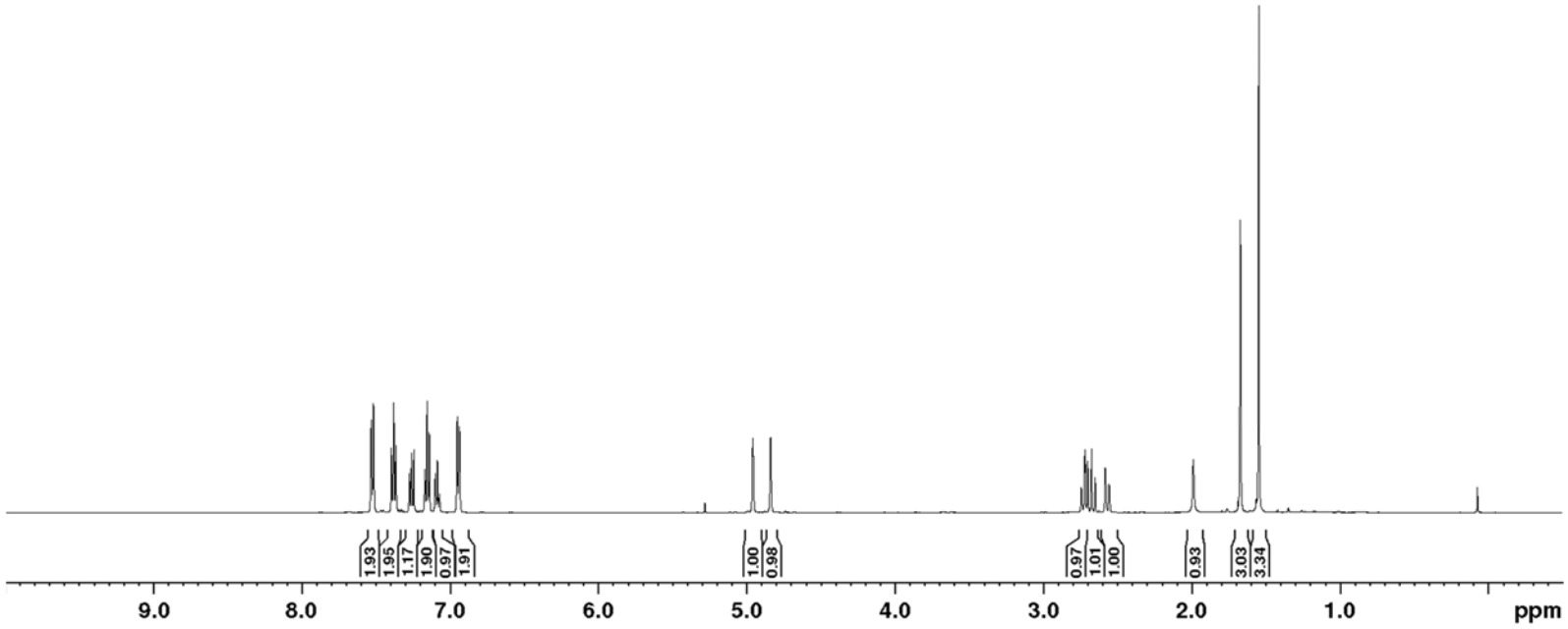


^{13}C NMR (100 MHz, $CDCl_3$)

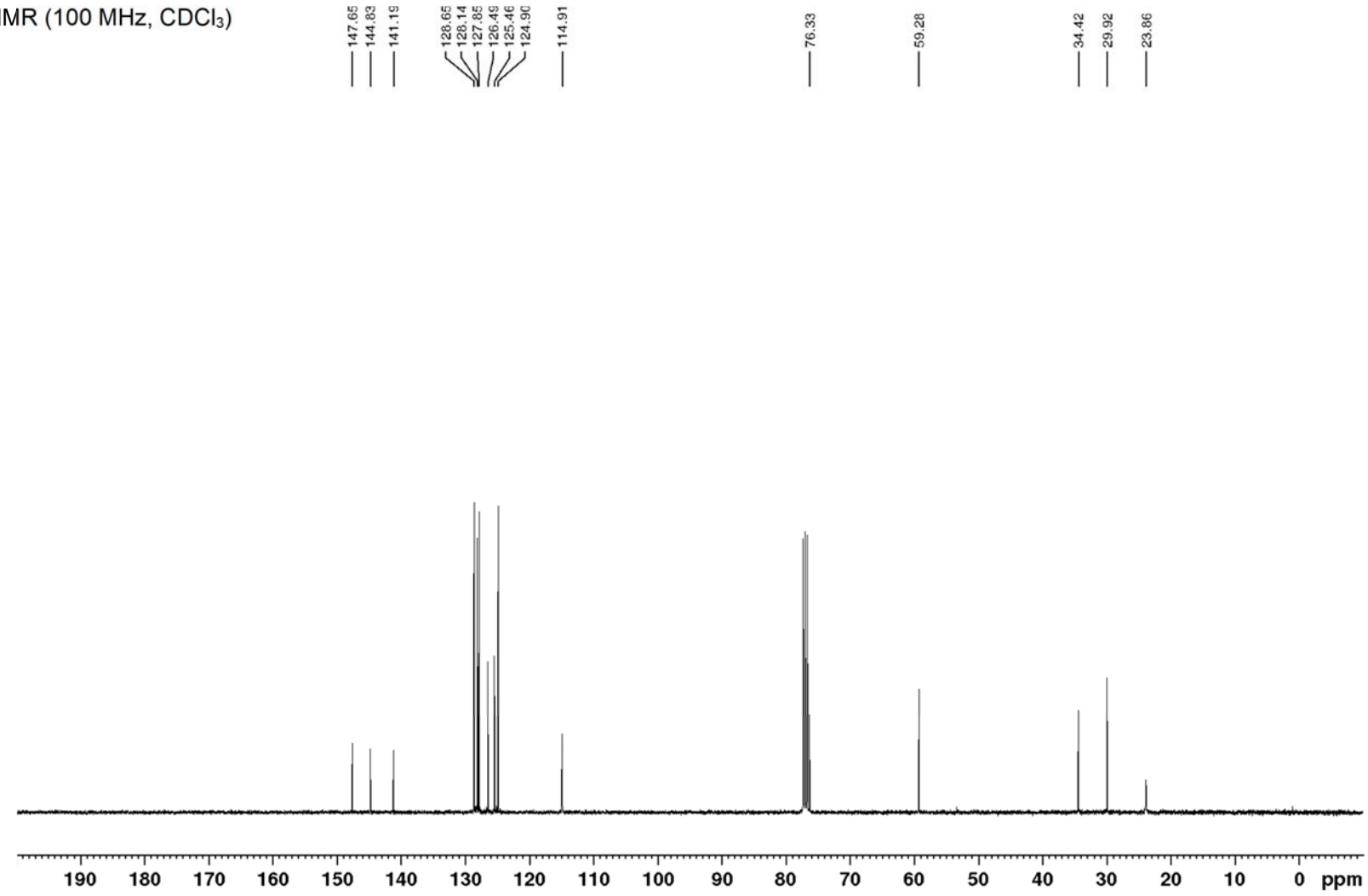


(2*R*,3*S*)-3-Benzyl-4-methyl-2-phenylpent-4-en-2-ol (*syn*-7): ^{1}H NMR (400 MHz, $CDCl_3$)

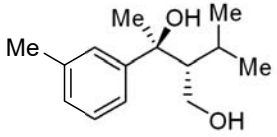


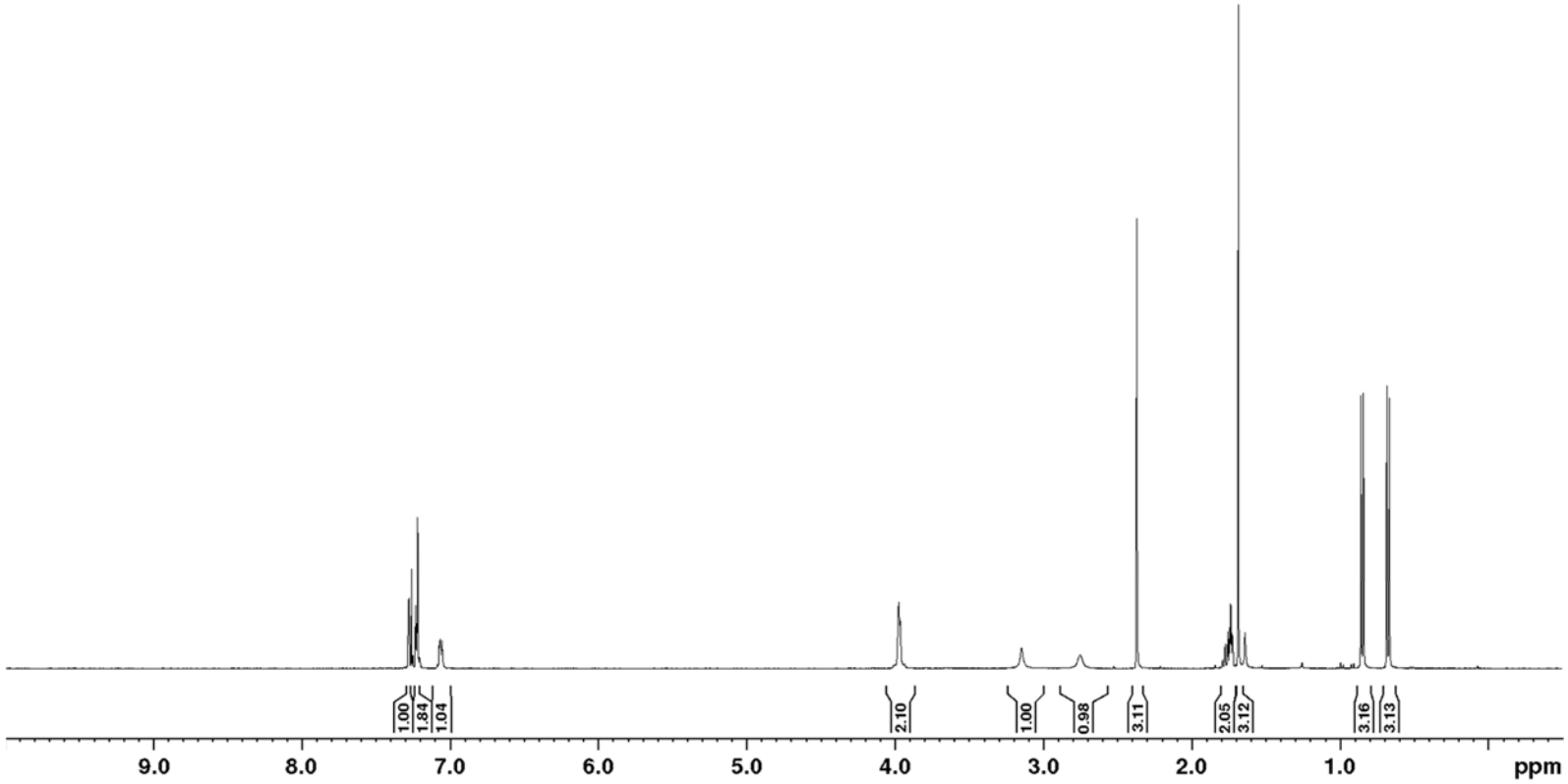


^{13}C NMR (100 MHz, $CDCl_3$)

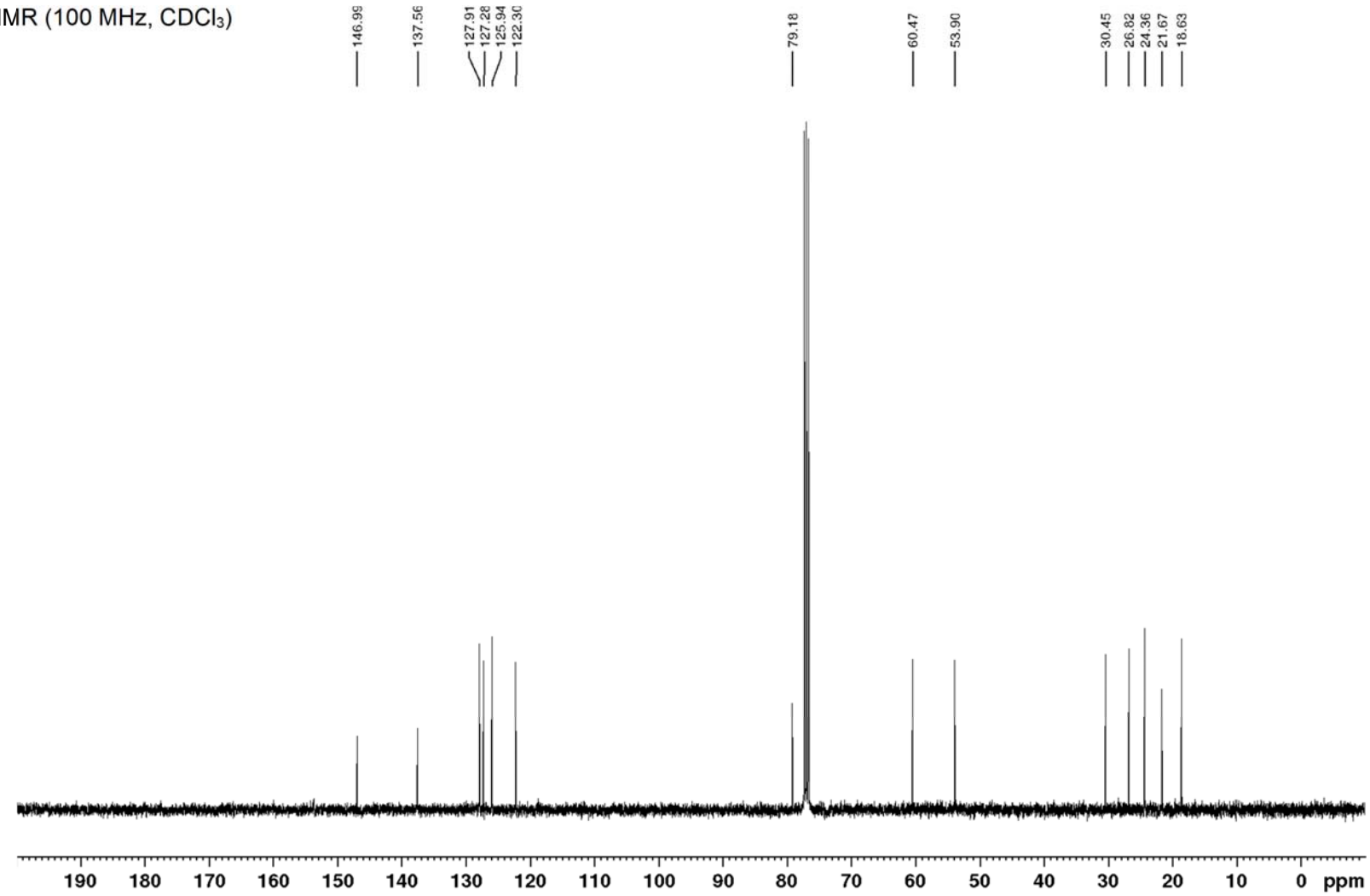


(2*R*,3*S*)-2-Isopropyl-3-(m-tolyl)butane-1,3-diol (*anti*-8): ^{1}H NMR (400 MHz, $CDCl_3$)

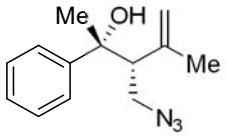


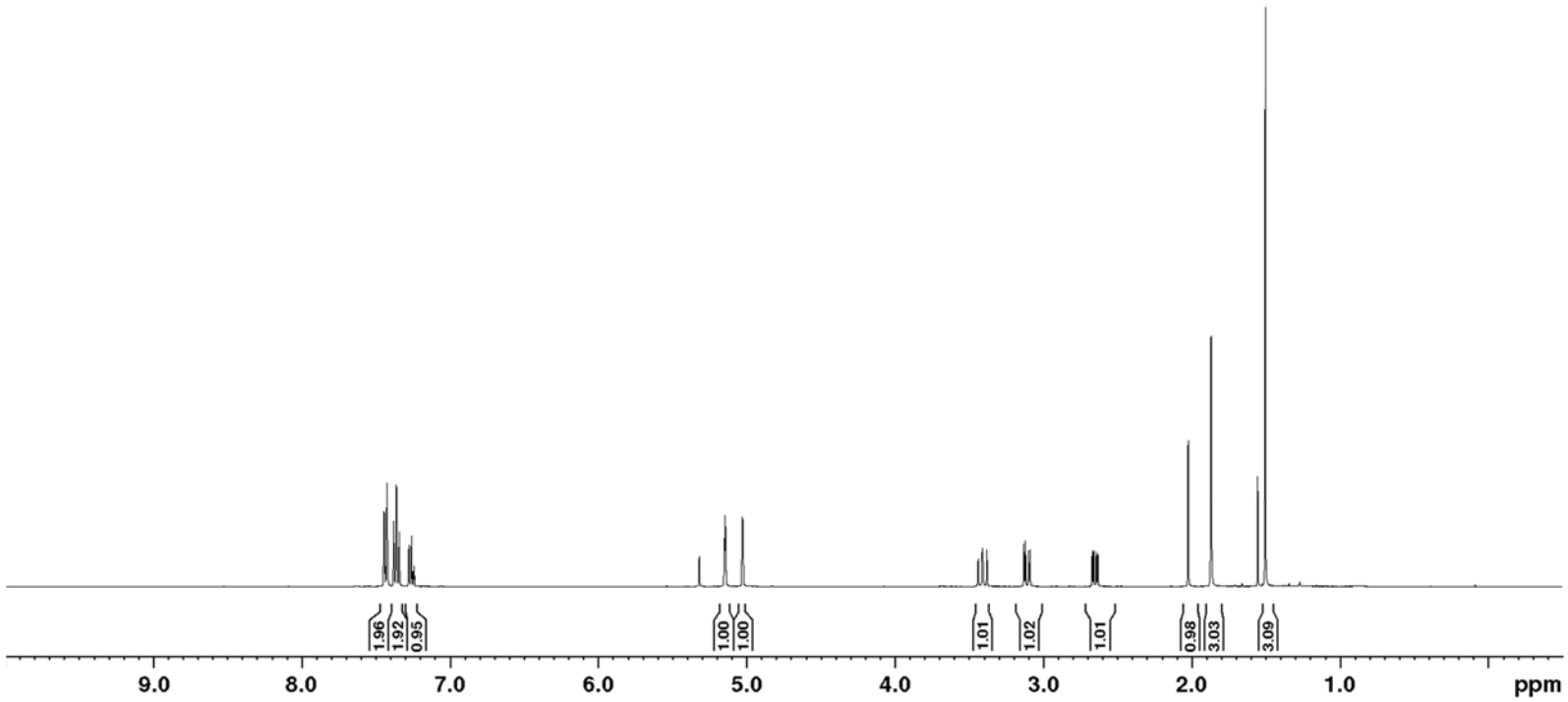


^{13}C NMR (100 MHz, $CDCl_3$)

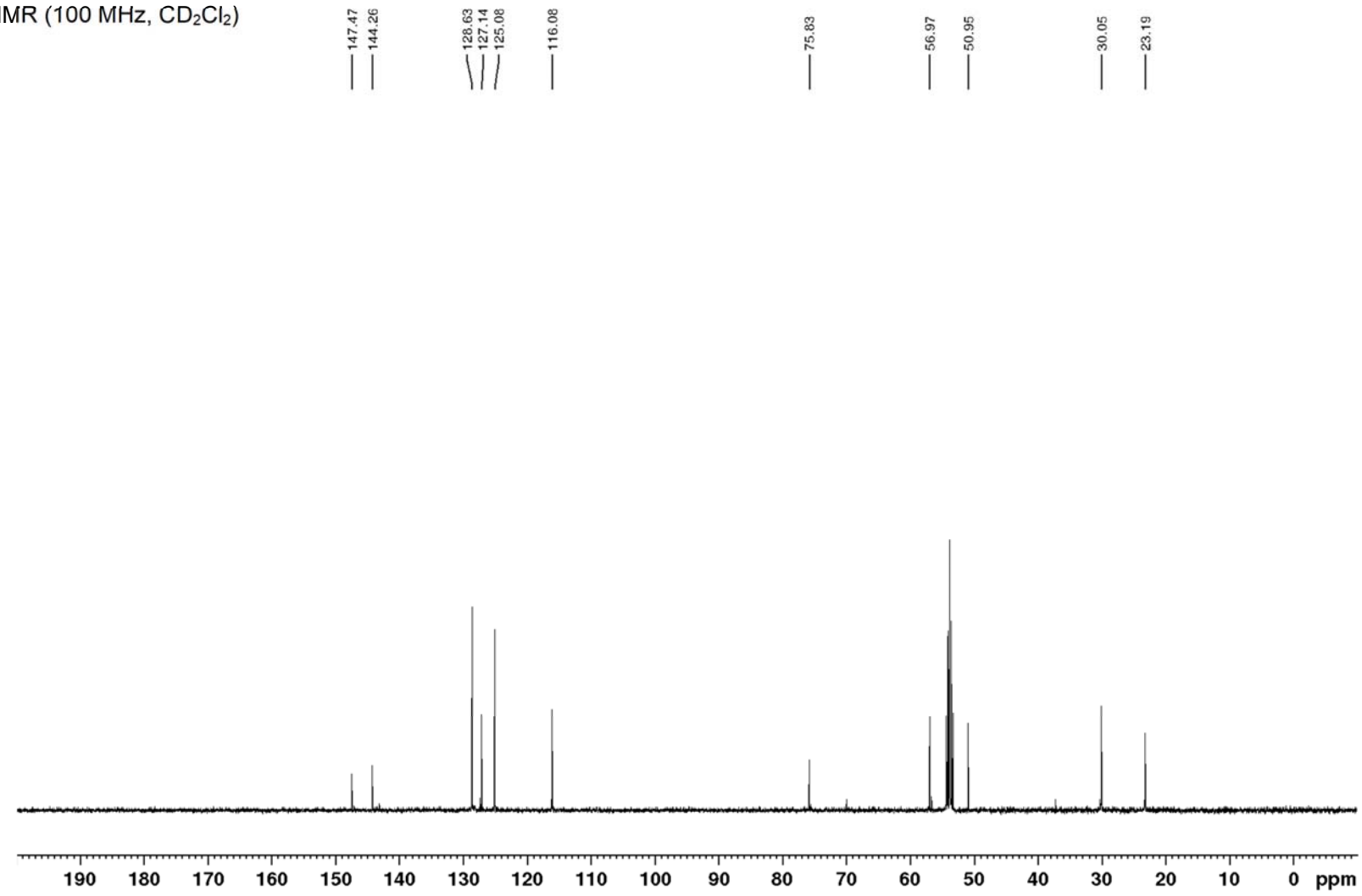


(2*R*,3*R*)-3-(Azidomethyl)-4-methyl-2-phenylpent-4-en-2-ol (*syn*-9): ^{1}H NMR (400 MHz, CD_2Cl_2)

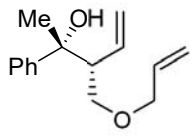


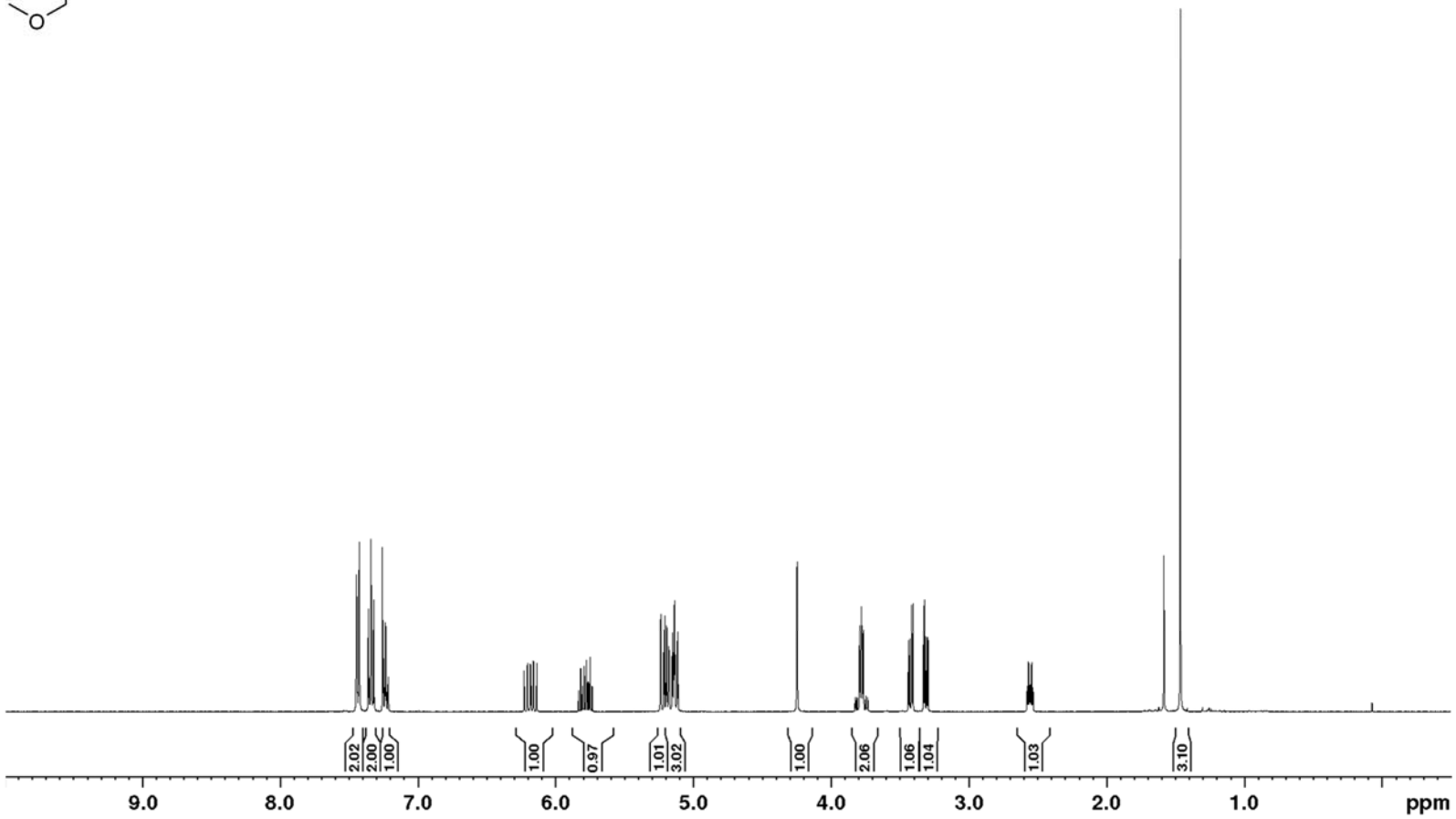


^{13}C NMR (100 MHz, CD_2Cl_2)

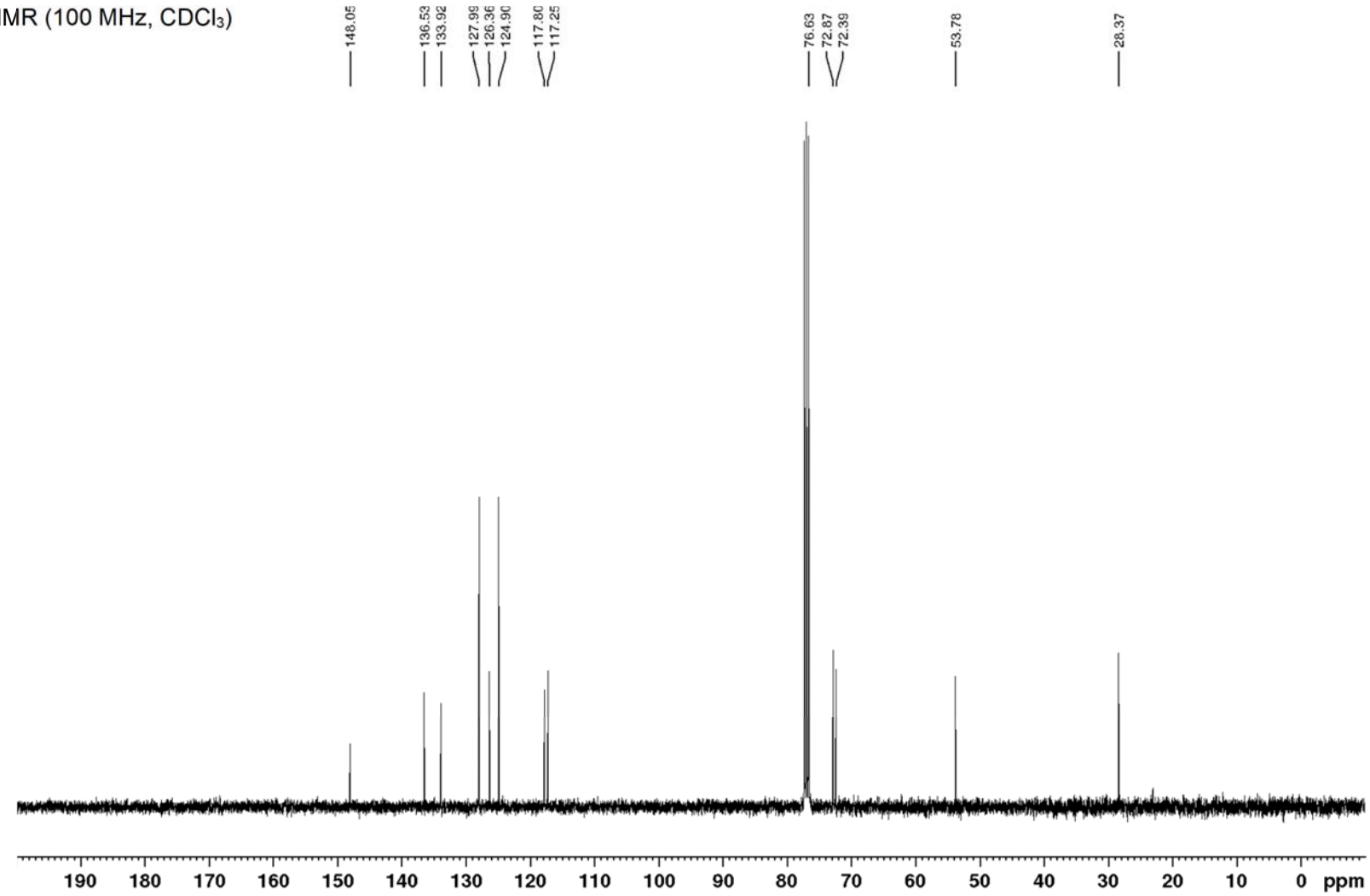


(2*R*,3*R*)-3-((Allyloxy)methyl)-2-phenylpent-4-en-2-ol (13): ^{1}H NMR (400 MHz, $CDCl_3$)

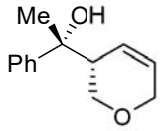


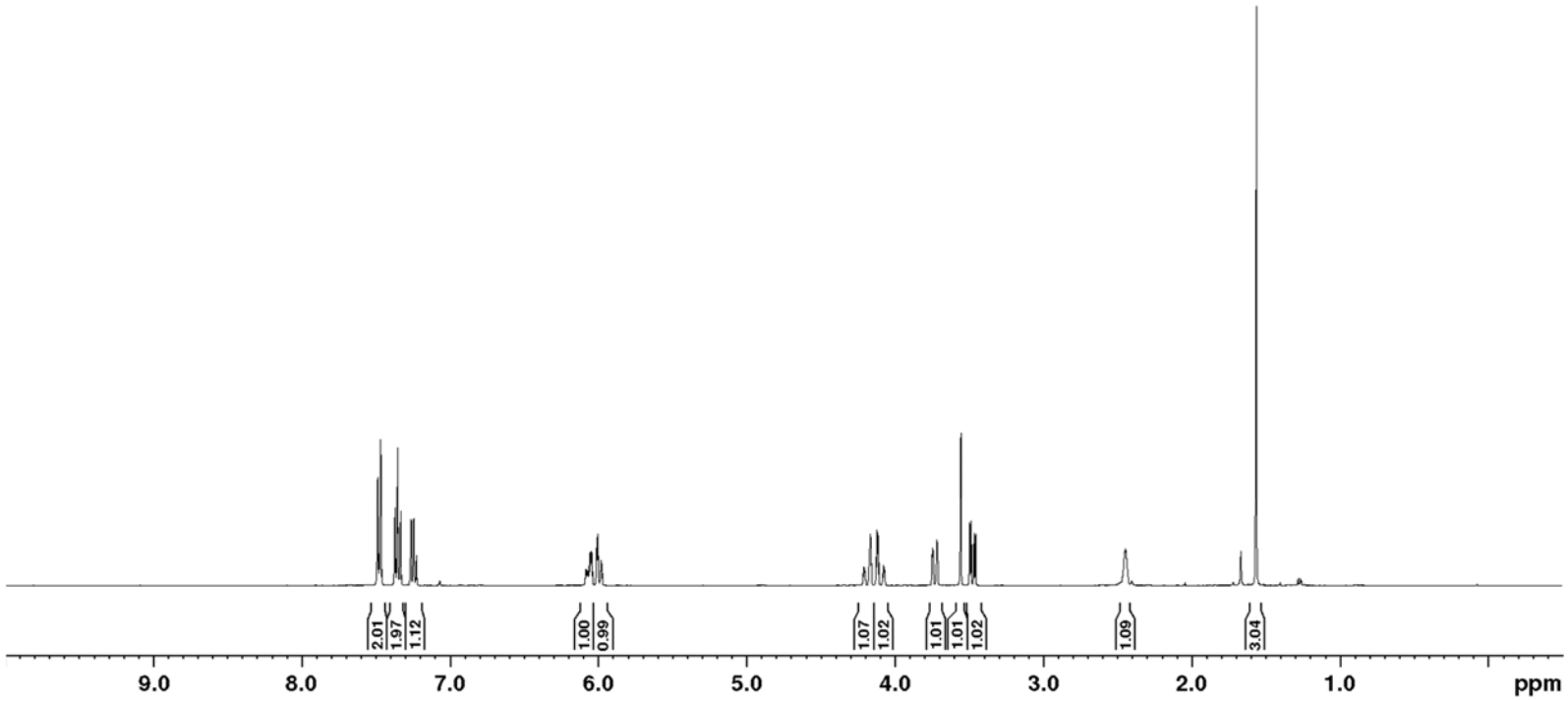


^{13}C NMR (100 MHz, $CDCl_3$)

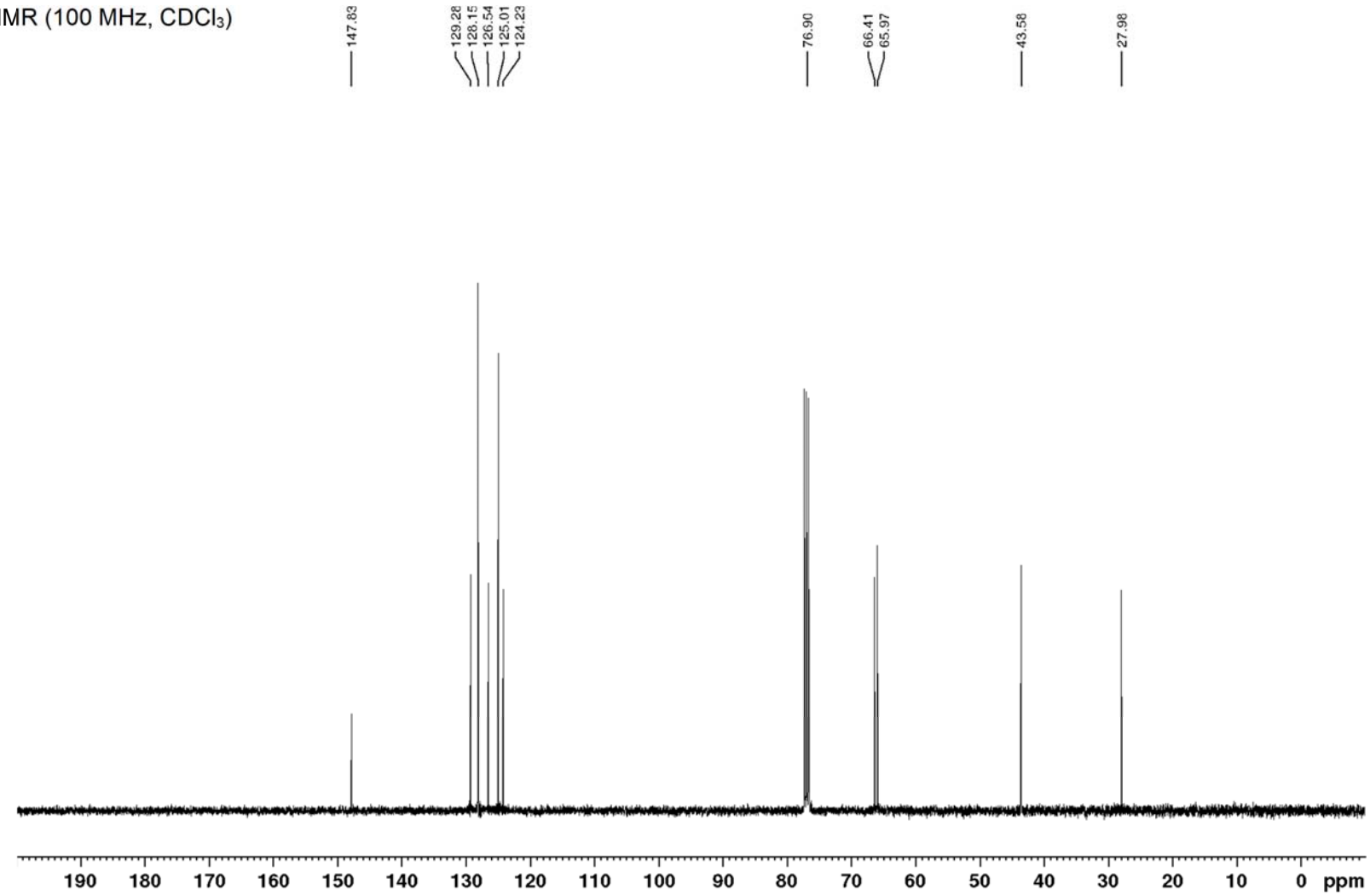


(*R*)-1-((*R*)-3,6-Dihydro-2H-pyran-3-yl)-1-phenylethan-1-ol (*syn*-10): ^{1}H NMR (400 MHz, $CDCl_3$)

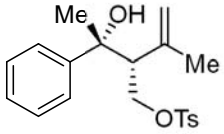


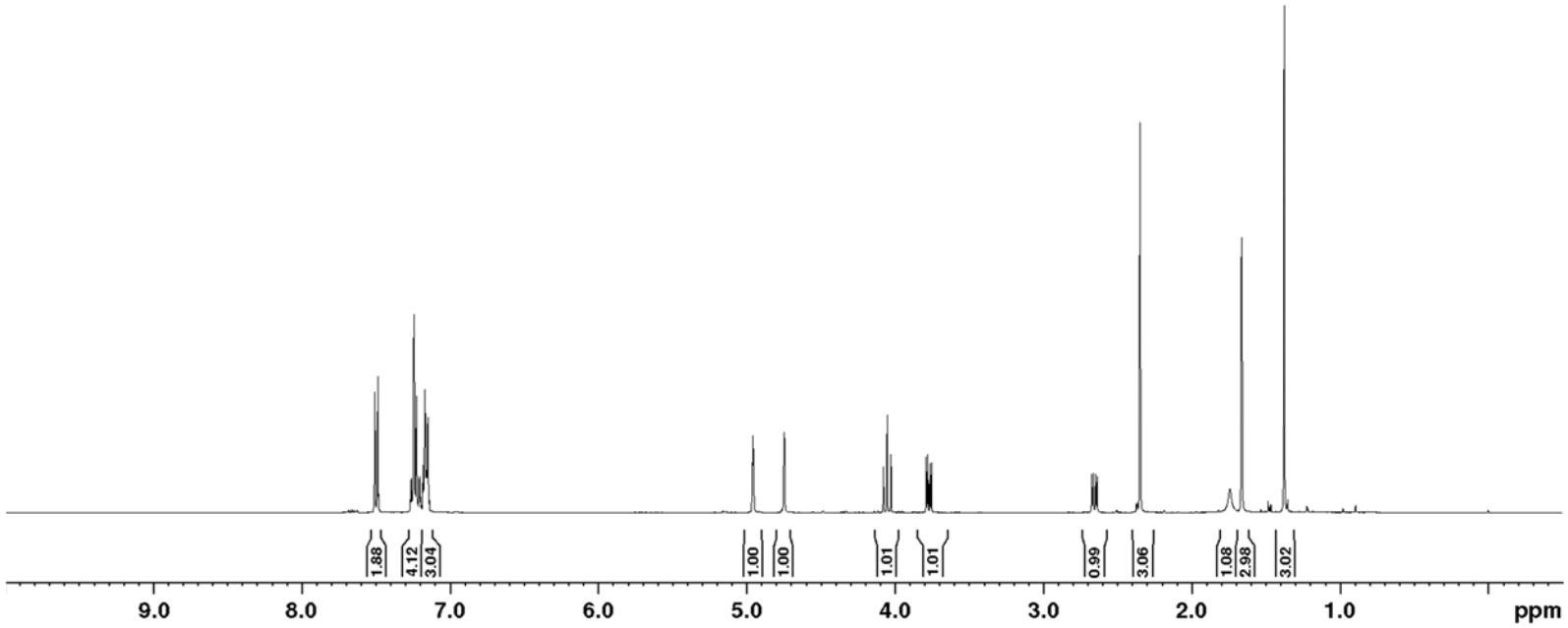


^{13}C NMR (100 MHz, $CDCl_3$)

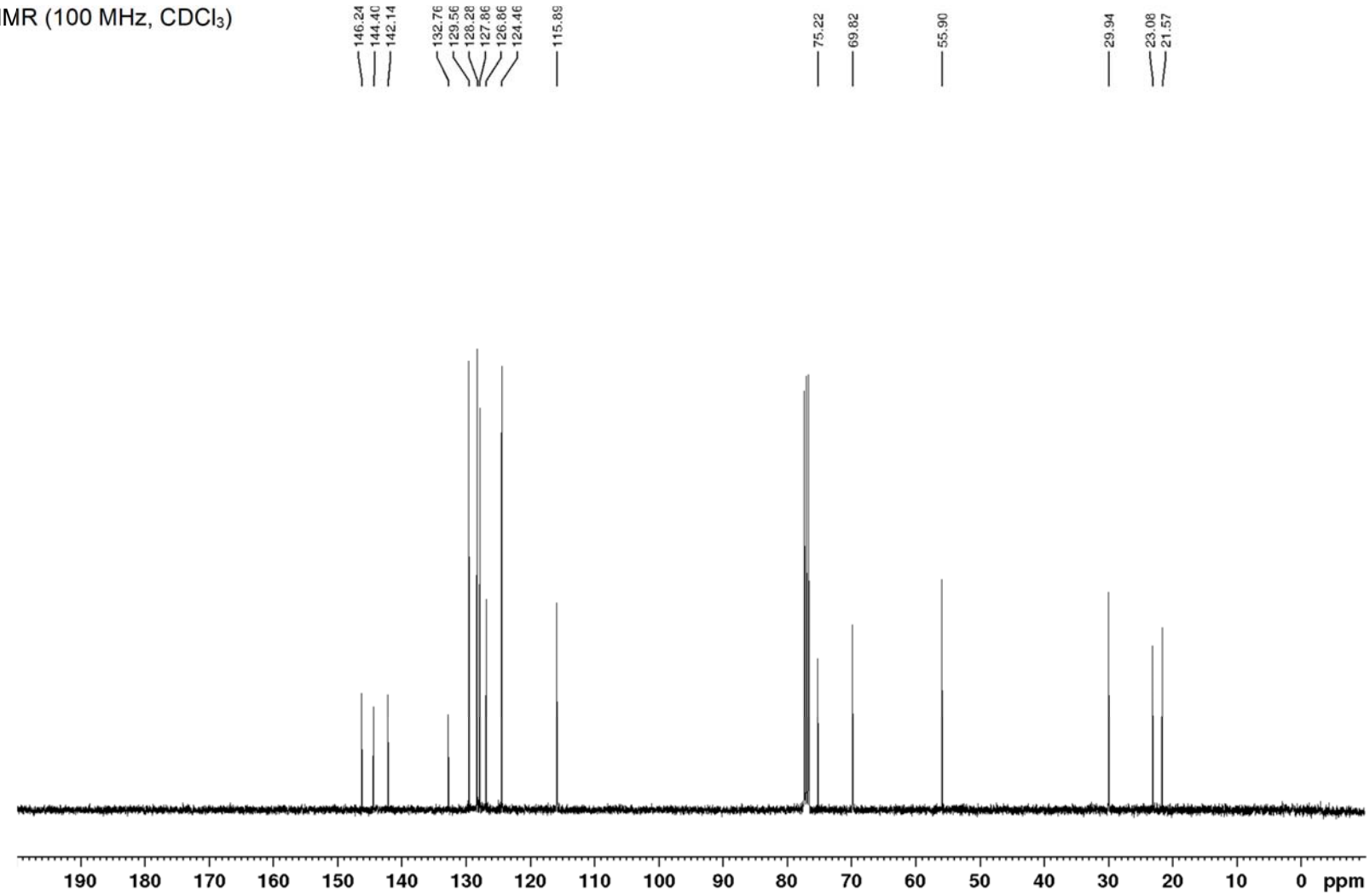


(*R*)-2-((*R*)-1-Hydroxy-1-phenylethyl)-3-methylbut-3-en-1-yl 4-methylbenzenesulfonate (14): ^{1}H NMR (400 MHz, $CDCl_3$)

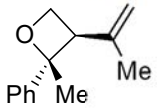


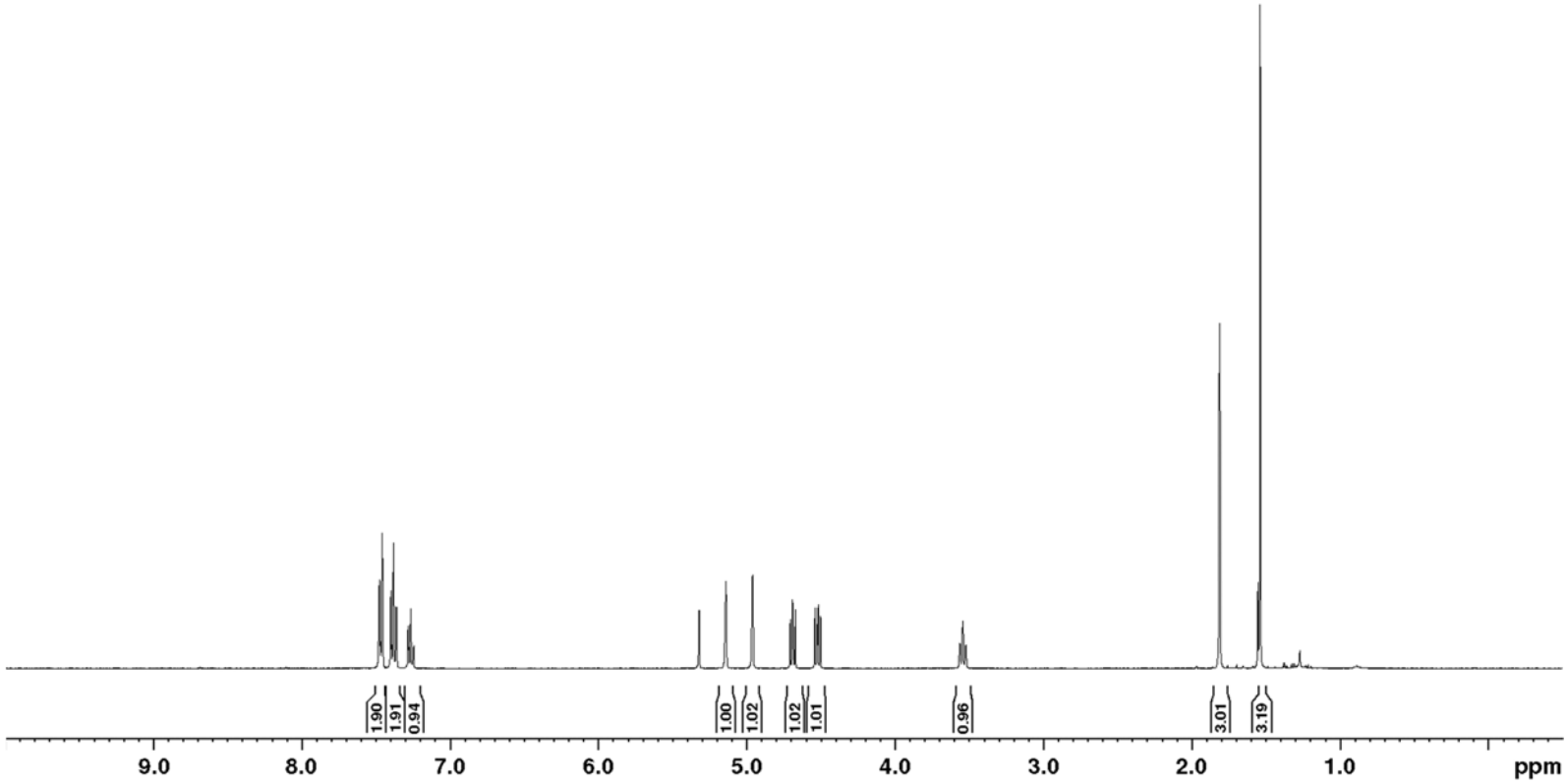


^{13}C NMR (100 MHz, $CDCl_3$)

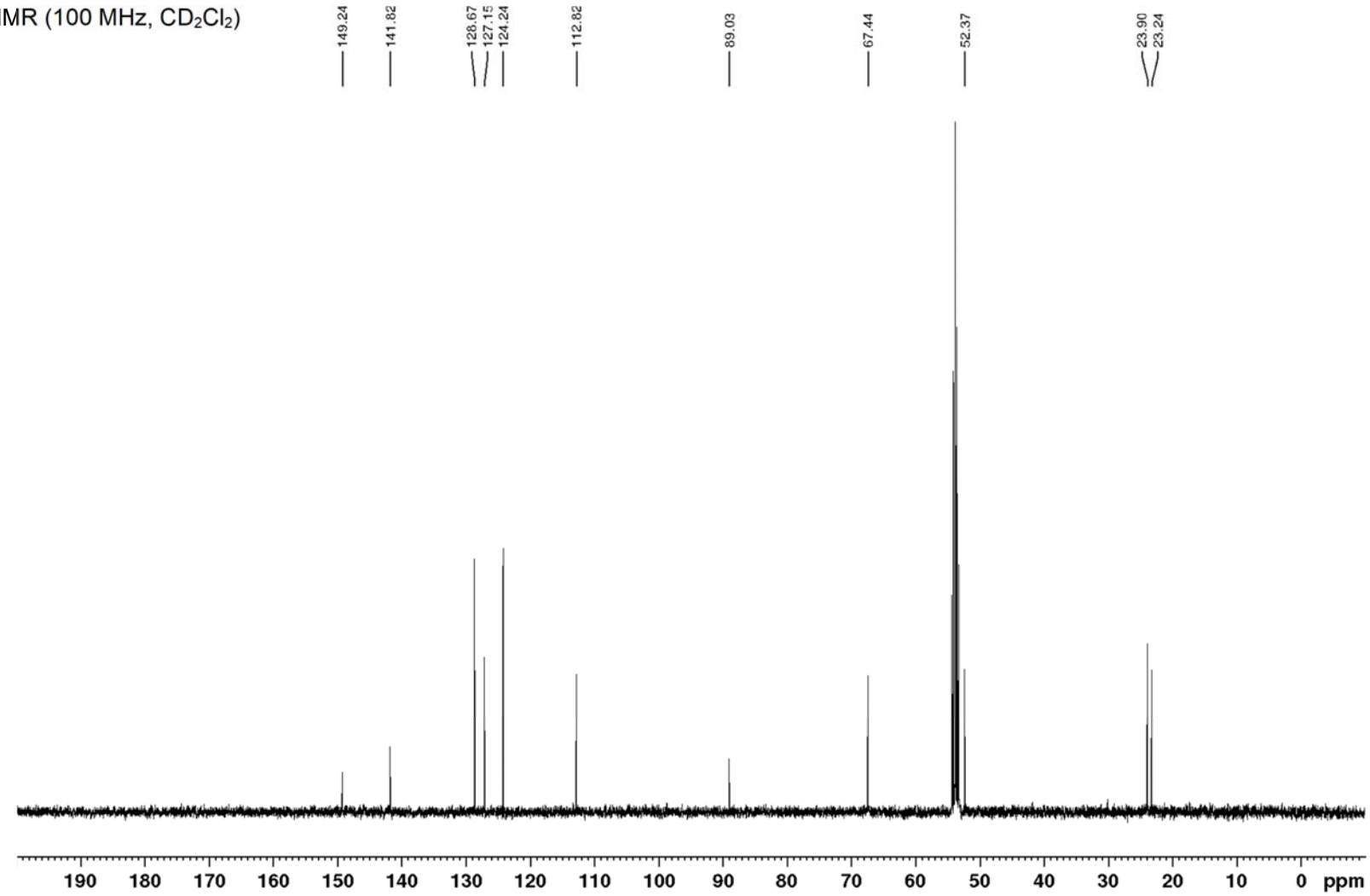


(2*R*,3*R*)-2-Methyl-2-phenyl-3-(prop-1-en-2-yl)oxetane (*trans*-11): ^{1}H NMR (400 MHz, CD_2Cl_2)





^{13}C NMR (100 MHz, CD_2Cl_2)



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