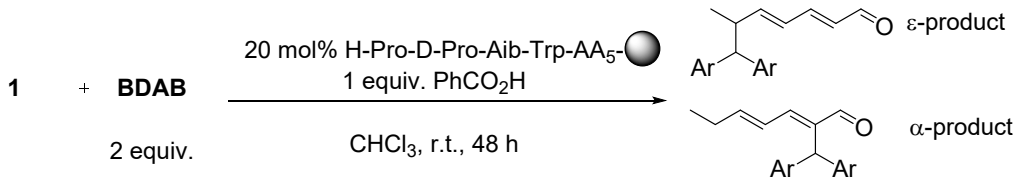
Supporting Information

for

Peptide catalyzed regio- and enantioselective ε-alkylation of γ-branched 2,4-dienals via trienamine activation

Table S1. Screening of the peptide catalysts for the reaction of dienal **1**.



Entry	AA_5	yield [a] (%)	ε:α[a]
1	Trp(6-NO_2)	16	81:19
2	Tyr	23	83:17
3	Tyr(Me)	10	52:48
4	Phe	2	<1:19
5	Phe(4-COOH)	9	78:22
6	Glu	5	79:21

[a] Determined from ^{1}H NMR spectra of the crude mixture.

Table S2. Relative Gibbs free energy of formation for the model compounds of trienamines obtained by DFT calculation

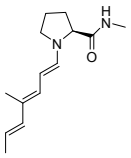
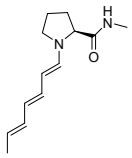
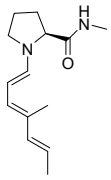
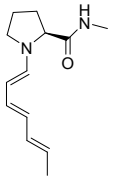
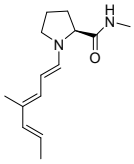
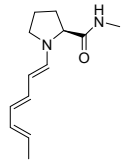
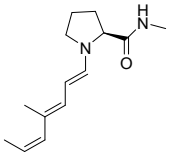
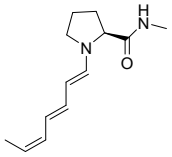
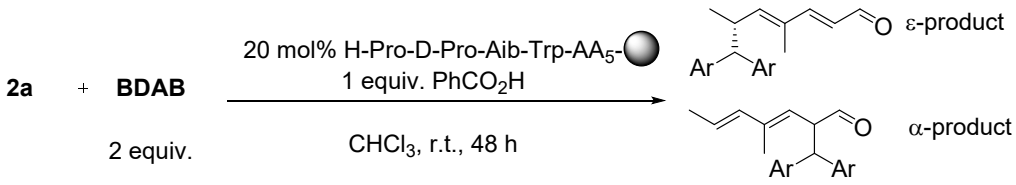
Rel. Energy ΔG (kJ/mol)	γ-methylated trienamines	γ-unsubstituted trienamines	Rel. Energy ΔG (kJ/mol)
0			0
17.97			12.68
10.77			12.88
19.31			4.38

Table S3. Screening of the peptide catalysts for the reaction of dienal **2a**.



Entry	AA_5	yield [a] (%)	ε:α[a]	ee of ε-product (%)
1	Ser	24	75:25	46
2	Tyr	38	87:13	34
3	His	8	50:50	n.d.
4	Tyr(Me)	10	40:60	46
5	Glu	8	88:12	n.d.
6	Phe	17	59:41	48

[a] Determined from ^{1}H NMR spectra of the crude mixture.

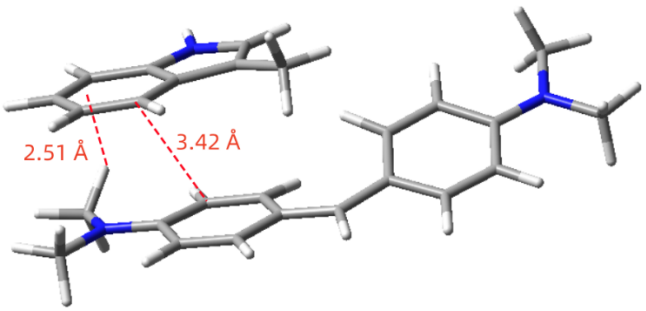


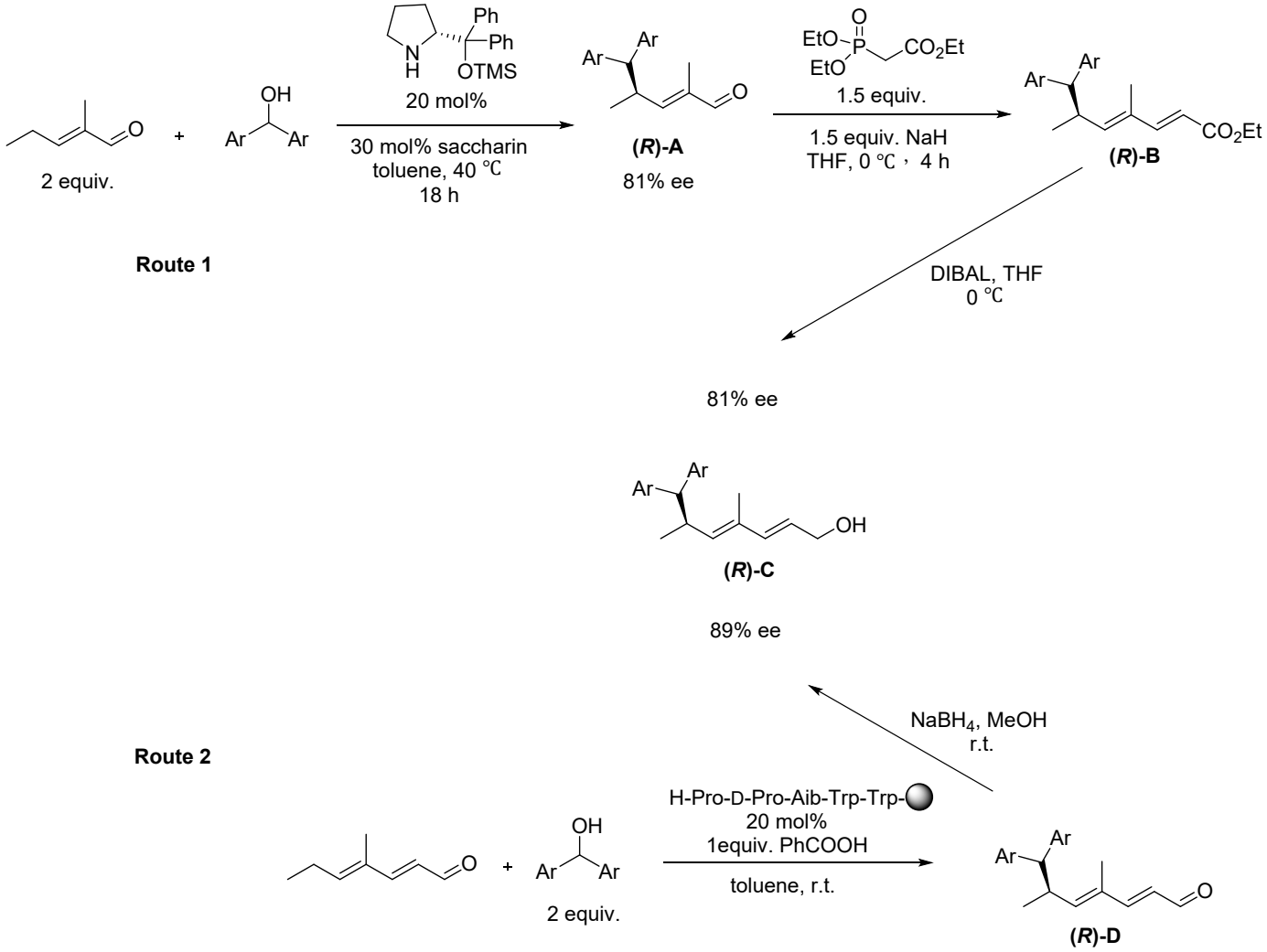
Fig. S1. Optimized structure for the complex of 3-methylindole and **BDAB**–derived cation.

Table S4. Calculated energy for the species related to Fig. S1.

Compound	Gibbs free energy of formation (Hartree/Particle)	Rel Energy (kJ/mol)
3-methylindole **(1)**	-402.9088153	-
BDAB-derived cation **(2)**	-769.2604681	-
	(sum of the above two) -1172.1692834	0
Complex of **1** and **2**	-1172.1814671	-31.99

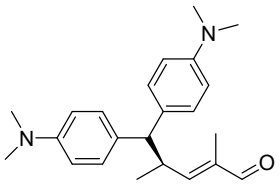
Determination of the absolute configuration of the ε-product

We synthesized γ-substituted enal (*R*)-**A** using the (*R*)-diphenylprolinol derived catalyst according to the procedure reported by Melchiorre's group.[1] Compound (*R*)-**A** was then converted to (*R*)-**B** via a Horner-Wadsworth-Emmons reaction, followed by DIBAL reduction to yield an alcohol (*R*)-**C** (route 1).
On the other hand, we synthesized the ε-substituted dienal **D** using a peptide catalyst having (*S*)-prolyl group at N-terminus. The product was reduced with $NaBH_4$ to give an alcohol **C** (route 2). Thus obtained **C** was proved to have (*R*)-configuration by comparison of chiral HPLC trace with that of (*R*)-**C** obtained by route 1**.**



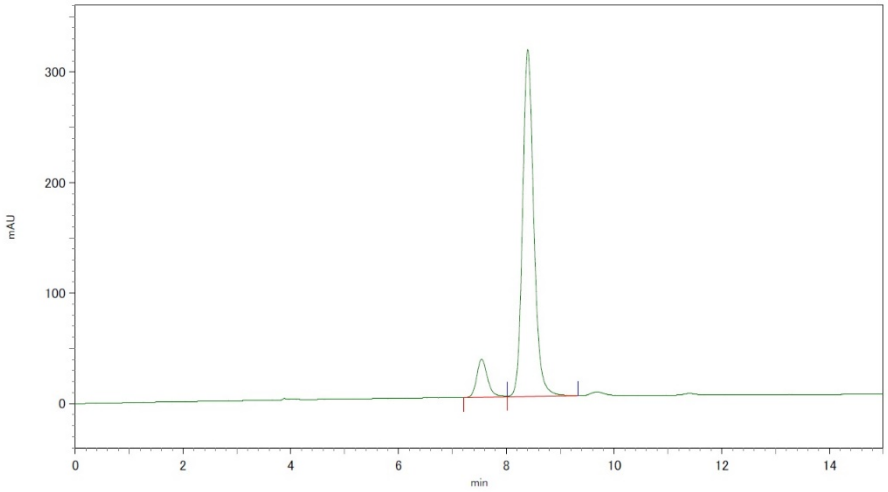
Scheme S2. Determination of the absolute configuration of the ε-alkylated product.

HPLC traces of the compounds related to Scheme S2.



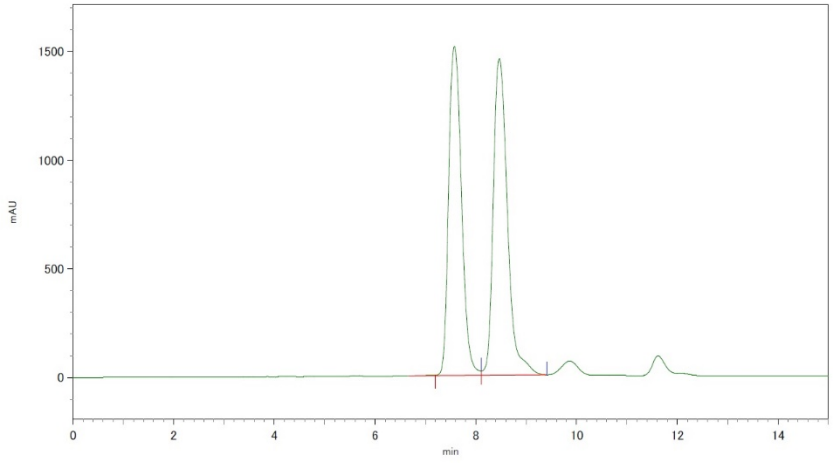
(*R*)-A

Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

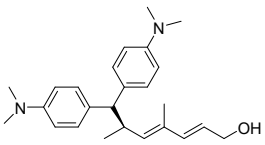


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	7.537	482908	9.60
	8.393	4547946	90.40
Total		5030854	100.00

Racemic sample:



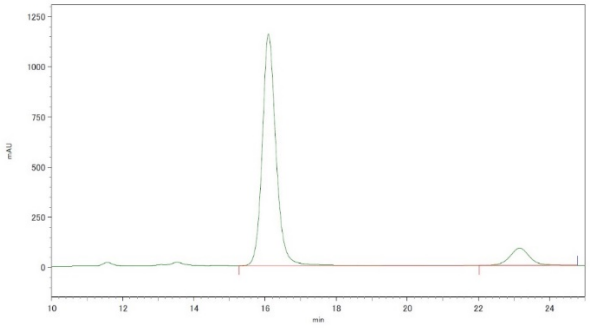
1: 290 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	7.570	26890143	48.60
	8.461	28442191	51.40
Total		55332334	100.00



c

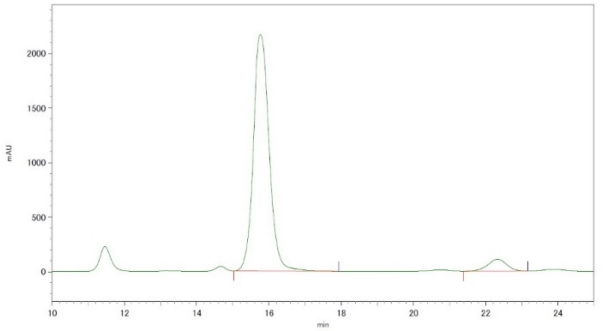
Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

From route 1 ((*R*)-**C**):



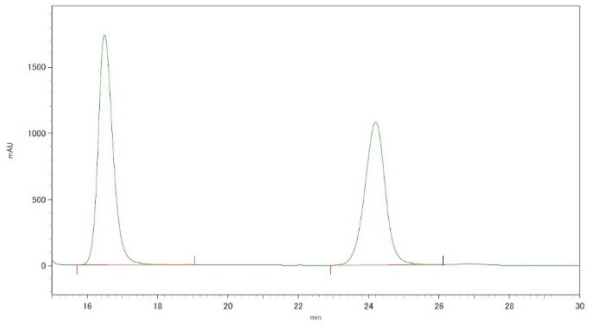
1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	16.091	30922084	90.43
	23.155	3271981	9.57
Total		34194065	100.00

Product from route 2:



1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	15.762	65508750	94.27
	22.325	3978484	5.73
Total		69487234	100.00

Racemic sample:



1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	16.487	50640857	53.53
	24.196	43966070	46.47
Total		94606927	100.00

General information

A part of chemicals and solvents were purchased from commercial suppliers and used as received: enals and dienals (TCI, Japan), BDAB (TCI, Japan), $CHCl_3$ and toluene (Wako, Japan). Products were purified by preparative TLC (PTLC).

NMR spectra were recorded on a JEOL JNM-ECZ600R (600 MHz for ^{1}H and 151 MHz for ^{13}C). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26 and TMS δ 0.00), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), dq (doublet of quartet), dd (doublet of doublet), m (multiplet). Coupling constants were reported in Hertz (Hz). High-resolution MALDI-TOFMS measurements were performed on a JMS-S3000 Spiral-TOF mass spectrometer. HPLC charts were recorded on a Shimadzu CLASS-VP system using Chiralcel IA column (25 cm) and IA guard (1 cm).

DFT calculations on trienamine intermediates of at the has been conducted.

Theoretical calculation study

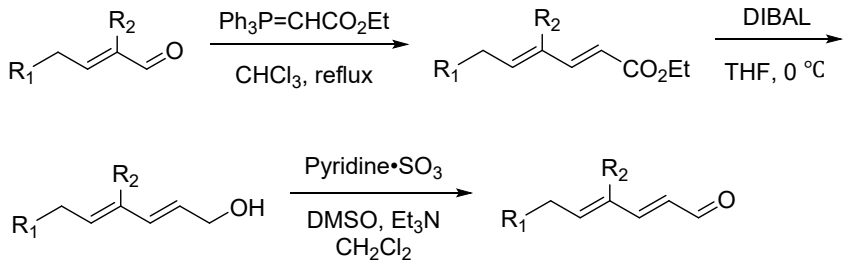
Calculation was performed based on density functional theory (DFT) using Gaussian 16 software. For the calculation of trienamine model compounds shown in Table S2, B3LYP/6-31G(d) level of theory was employed. The interaction of 3-methylindole with the **BDAB**-derived cation was calculated at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level in toluene (smd) (Fig. S1 and Table S4).

Preparation of peptide catalysts.

Resin-supported peptides were synthesized according to the previous report.[2] As a resin, TentaGel S-NH2 (AnaSpec, Inc., product number: 22798, 0.24 mmol/g amine loading) was used. The coupling reaction of an amino acid was performed with 3.0 equiv each of an N-α-9-fluorenylmethoxycarbonyl (Fmoc) amino acid, *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate (HATU), and 1-hydroxy-7-azabenzotriazole (HOAt) along with 6.0 equiv of diisopropylethylamine in N,N-dimethylformamide (DMF) for 60 min. After washing the resin with DMF, completion of the peptide bond formation was confirmed by the Kaiser test or the chloranil test. To remove the Fmoc group, the resin was soaked in 20% piperidine/DMF solution for 20 min and washed with DMF. This cycle, the coupling of an Fmoc-protected amino acid and removal of the Fmoc group, was repeated until an intended sequence was introduced on the resin. After the Fmoc group on the terminal prolyl residue was removed, the resin was washed with DMF and dichloromethane (DCM), and dried under reduced pressure. To convert the supported peptide to the salt of trifluoroacetic acid (TFA), the resin was soaked in TFA for a few minutes. Then, the resin was washed successively with DCM, DMF, and DCM, and dried under reduced pressure.

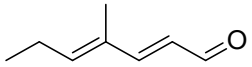
Preparation of substrates 2a-2f.

Substrates **2a-2f** were synthesized according to the scheme shown below.[3,4]



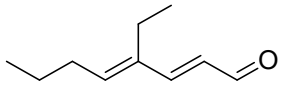
Scheme S1. Preparation of dienals

(*2E,4E*)-4-Methylhepta-2,4-dienal (2a)



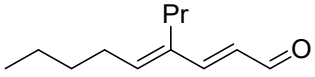
^{1}H NMR ($CDCl_3$) δ = 9.56 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 6.04 (t, *J* = 7.6 Hz, 1H), 2.26 (p, *J* = 7.6 Hz, 2H), 1.82 (s, 3H), 1.07 (t, *J* = 7.6 Hz, 3H).

(*2E,4E*)-4-Ethylocta-2,4-dienal (2b)



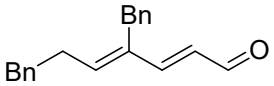
^{1}H NMR ($CDCl_3$) δ = 9.51 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 5.93 (t, *J* = 7.6 Hz, 1H), 2.25 (q, *J* = 7.6 Hz, 1H), 2.16 (t, *J* = 7.6 Hz, 1H), 1.47-1.40 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.6 Hz, 3H).

(*2E,4E*)-4-Propylnona-2,4-dienal (2c)



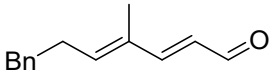
^{1}H NMR ($CDCl_3$) δ = 9.55 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 6.02 (t, *J* = 7.6 Hz, 1H), 2.28-2.21 (m, 4H), 1.46-1.34 (m, 6H), 0.96-0.91 (m, 2H).

(*2E,4E*)-4-Benzyl-7-phenylhepta-2,4-dienal (2d)



^{1}H NMR ($CDCl_3$) δ = 9.47 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 2H), 7.25-7.15 (m, 6H), 7.09 (d, *J* = 15.8 Hz, 1H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.26 (t, *J* = 6.9 Hz, 1H), 6.02 (dd, *J* = 8.3 Hz, 15.8 Hz, 1H), 3.61 (s, 2H), 2.78 (d, *J* = 6.9 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H).

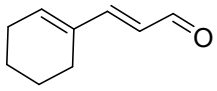
(*2E,4E*)-4-methyl-7-phenylhepta-2,4-dienal (2e)



^{1}H NMR ($CDCl_3$) δ = 9.54 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22-7.17 (m, 4H), 7.09 (d, *J* = 15.2

Hz, 1H), 6.08 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 6.04 (t, *J* = 7.6 Hz, 1H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.74 (s, 3H).

3-(Cyclohexen-1-yl)-2-propenal (2f)

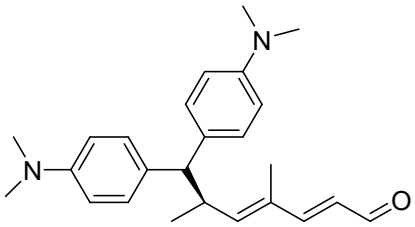


^{1}H NMR ($CDCl_3$) δ = 9.56 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 15.8 Hz, 1H), 6.32 (t, *J* = 3.4 Hz, 1H), 6.08 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 2.29-2.25 (m, 2H), 2.21-2.16 (m, 2H), 1.75-1.70 (m, 2H), 1.68-1.63 (m, 2H).

General procedure for the alkylation of dienals.

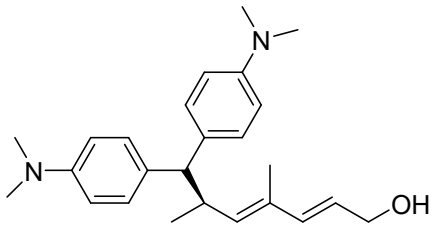
Toluene (1.0 mL) was added to a round-bottomed flask containing dienal (0.10 mmol), BDAB (0.20 mmol), and benzoic acid (0.10 mmol), and resin-supported peptide (0.02 mmol). Then, the peptide catalyst was filtered off and washed with chloroform. After removal of the solvent, the residue was purified by preparative TLC using hexanes/ethyl acetate (7:3) as eluent to afford the alkylated product.

(*R*)-7,7-Bis(4-(dimethylamino)phenyl)-4,6-dimethylhepta-2,4-dienal (3a)



27.1 mg (yield 72%). yellow solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.47 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 6.01 (dd, *J* = 7.6 Hz, 15.1 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 3.57 (d, *J* = 10.3 Hz, 1H), 3.35-3.27 (m, 1H), 2.89 (s, 6H), 2.85 (s, 6H), 1.80 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.3, 158.4, 150.3, 149.0, 148.8, 132.4, 131.8, 128.6, 128.5, 126.4, 112.8, 112.6, 56.4, 40.7, 40.6, 38.0, 19.5, 12.5; HRMS (MALDI-TOF) m/z: calculated for $C_{25}H_{32}N_2O[H]^+$: 377.2587, found 377.2592.

The enantiomeric excess was determined by chiral HPLC analysis of the corresponding alcohol obtained by $NaBH_4$ reduction of the aldehyde.

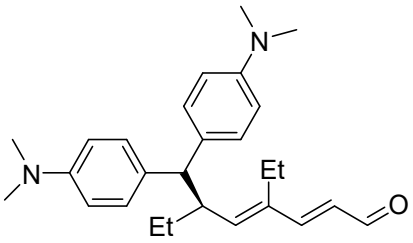


^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 2H), 6.12 (d, *J* = 15.2 Hz, 1H), 6.01 (dt, *J* = 15.8 Hz, 6.2 Hz, 1H), 5.31 (d, *J* = 8.9 Hz, 1H), 4.12 (d, *J* = 6.2 Hz, 2H), 3.51 (d, *J* = 9.6 Hz, 1H), 3.27-3.20 (m, 1H), 2.88 (s, 6H), 2.85 (s, 6H), 1.74 (s,

3H), 0.90 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.8, 148.6, 139.5, 139.5, 137.3, 131.2, 128.7, 124.5, 112.9, 112.7, 64.1, 56.7, 40.8, 37.0, 20.1, 12.6; HRMS (MALDI-TOF) m/z: calculated for $C_{25}H_{34}N_2O[Na]^+$: 401.2563, found 401.2578.

Chiralcel IA and IA guard column (2-propanol/hexane = 5/95, 1 mL/min); t_R = 16.5 min (major), 24.2 min (minor).

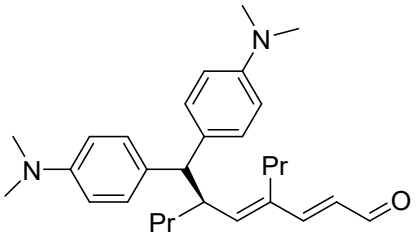
(*R*)-6-(Bis(4-(dimethylamino)phenyl)methyl)-4-ethylocta-2,4-dienal (3b)



29.1 mg (yield 72%). yellow solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.47 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 6.2 Hz, 2H), 7.04 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 15.8 Hz, 1H), 6.67 (d, J = 8.3 Hz, 2H), 6.57 (d, J = 8.9 Hz, 2H), 6.02 (dd, J = 8.3 Hz, 15.8 Hz, 1H), 5.72 (d, J = 10.3 Hz, 1H), 3.65 (d, J = 9.6 Hz, 1H), 3.13 (dq, J = 3.4 Hz, 10.3 Hz, 1H), 2.89 (s, 6H), 2.83 (s, 6H), 2.30-2.21 (m, 2H), 1.67-1.59 (m, 1H), 1.23-1.14 (m, 1H), 0.93 (t, J = 7.6 Hz, 3H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.5, 157.5, 149.0, 148.9, 148.5, 139.4, 132.5, 132.1, 128.7, 128.5, 126.3, 112.8, 112.6, 55.0, 44.9, 40.7, 26.5, 20.2, 12.9, 11.6; HRMS (MALDI-TOF) m/z: calculated for $C_{27}H_{36}N_2O[H]^+$: 405.2900, found 405.2901.

The enantiomeric excess was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel IA and IA guard column (2-propanol/hexane = 5:95, 1 mL/min); t_R = 13.7 min (major), 25.2 min (minor).

(*R*)-6-(Bis(4-(dimethylamino)phenyl)methyl)-4-propylnona-2,4-dienal (3c)

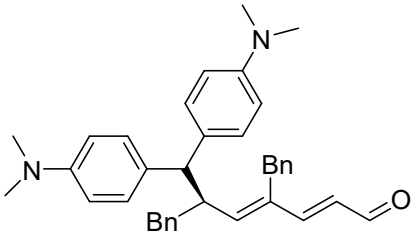


19.9 mg (yield 46%). yellow solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.47 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 15.8 Hz, 1H), 6.68 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 8.3 Hz, 2H), 5.99 (dd, J = 7.6 Hz, 15.4 Hz, 1H), 5.74 (d, J = 10.3 Hz, 1H), 3.65 (d, J = 9.6 Hz, 1H), 3.19 (dq, J = 3.4 Hz, 9.6 Hz, 1H), 2.90 (s, 6H), 2.83 (s, 6H), 2.20-2.08 (m, 2H), 1.59-1.49 (m, 1H), 1.33-1.11 (m, 5H), 0.92 (t, J = 7.6 Hz, 3H), 0.81 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.5, 158.0, 149.3, 149.0, 148.9, 138.0, 132.5, 132.0, 128.8, 128.6, 126.3, 112.8, 112.6, 55.1, 43.4, 40.8, 40.7, 36.1, 29.5, 21.7, 20.4, 14.6, 14.3; HRMS (MALDI-TOF) m/z: calculated for $C_{29}H_{40}N_2O[H]^+$: 433.3213, found 433.3209.

The enantiomeric excess was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel IA and IA guard column (2-propanol/hexane = 5:95, 1 mL/min); t_R = 12.8 min

(major), 26.1 min (minor).

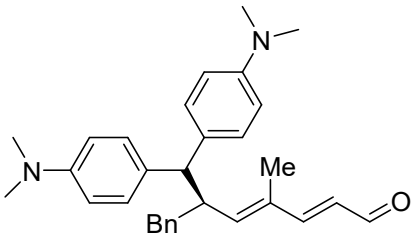
(*R*)-4,6-Dibenzyl-7,7-(bis(4-dimethylamino)phenyl)hepta-2,4-dienal (3d)



42.3 mg (yield 80%). White solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.36 (d, *J* = 7.6 Hz, 1H), 7.27-7.21 (m, 4H, containing the peak of $CHCl_3$), 7.10-7.00 (m, 7H), 6.93 (d, *J* = 15.8 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 4H), 6.04 (d, *J* = 10.3 Hz, 1H), 5.68 (dd, *J* = 7.6 Hz, 15.8 Hz, 1H), 3.78 (d, *J* = 10.3 Hz, 1H), 3.50 (dq, *J* = 2.8 Hz, 10.3 Hz, 1H), 2.93 (s, 6H), 2.89 (s, 6H), 2.42 (dq, *J* = 10.3 Hz, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.3, 156.8, 149.2, 149.0, 149.0, 136.2, 129.5, 128.8, 128.7, 128.2, 128.2, 128.0, 127.9, 126.1, 125.9, 113.0, 112.6, 55.3, 46.9, 40.7, 40.4, 32.2; HRMS (MALDI-TOF) m/z: calculated for $C_{37}H_{40}N_2O[H]^+$: 529.3213, found 529.3189.

The enantiomeric excess was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel IA and IA guard column (2-propanol/hexane = 5:95, 1 mL/min); t_R = 13.9 min (major), 15.4 min (minor).

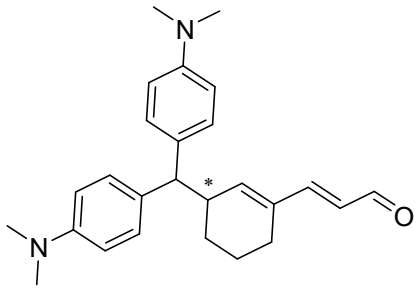
(*R*)-6-Benzyl-7,7-(bis(4-dimethylamino)phenyl)-4-methylhepta-2,4-dienal (3e)



32.1 mg (yield 71%). Green plate. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.44 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 6.9 Hz, 2H), 6.93 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 5.83 (dd, *J* = 8.3 Hz, 15.8 Hz, 1H), 5.75 (d, *J* = 10.3 Hz, 1H), 3.74 (d, *J* = 10.3 Hz, 1H), 3.47 (dq, *J* = 3.4 Hz, 10.3 Hz, 1H), 2.95 (dd, *J* = 2.8 Hz, 13.1 Hz, 1H), 2.92 (s, 6H), 2.84 (s, 6H), 2.34 (dd, *J* = 10.3 Hz, 13.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.3, 158.0, 149.1, 147.2, 140.0, 124.2, 129.3, 128.6, 128.4, 128.0, 126.4, 125.8, 113.0, 112.6, 55.1, 46.3, 40.7, 40.7, 40.2, 12.2; HRMS (MALDI-TOF) m/z: calculated for $C_{31}H_{36}N_2O[Na]^+$: 475.2720, found 475.2732.

The enantiomeric excess was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel IA and IA guard column (2-propanol/hexane = 5:95, 1 mL/min); t_R = 23.0 min (minor), 24.7 min (major).

3-(3-(Bis(4-(dimethylamino)phenyl)methyl)cyclohexen-1-yl)-2-propenal (3f)

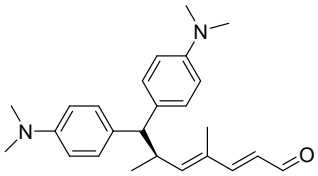


19.0 mg (yield 49%). yellow solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.47 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 15.8 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.15 (s, 1H), 6.06 (dd, *J* = 8.3 Hz, 15.8 Hz, 1H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.10-3.04 (m, 1H), 2.91 (s, 6H), 2.89 (s, 6H), 2.23-2.17 (m, 1H), 2.14-2.07 (m, 1H), 1.89-1.83 (m, 1H), 1.71-1.65 (m, 1H), 1.62-1.52 (m, 1H), 1.20 (dq, *J* = 2.8 Hz, 9.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 151 MHz) δ 194.4, 156.8, 149.1, 149.0, 144.9, 135.7, 131.8, 128.7, 128.3, 126.1, 112.9, 112.8, 56.3, 41.1, 40.7, 27.8, 24.5, 21.2; HRMS (MALDI-TOF) m/z: calculated for $C_{26}H_{32}N_2O[H]^+$: 389.2587, found 389.2592.

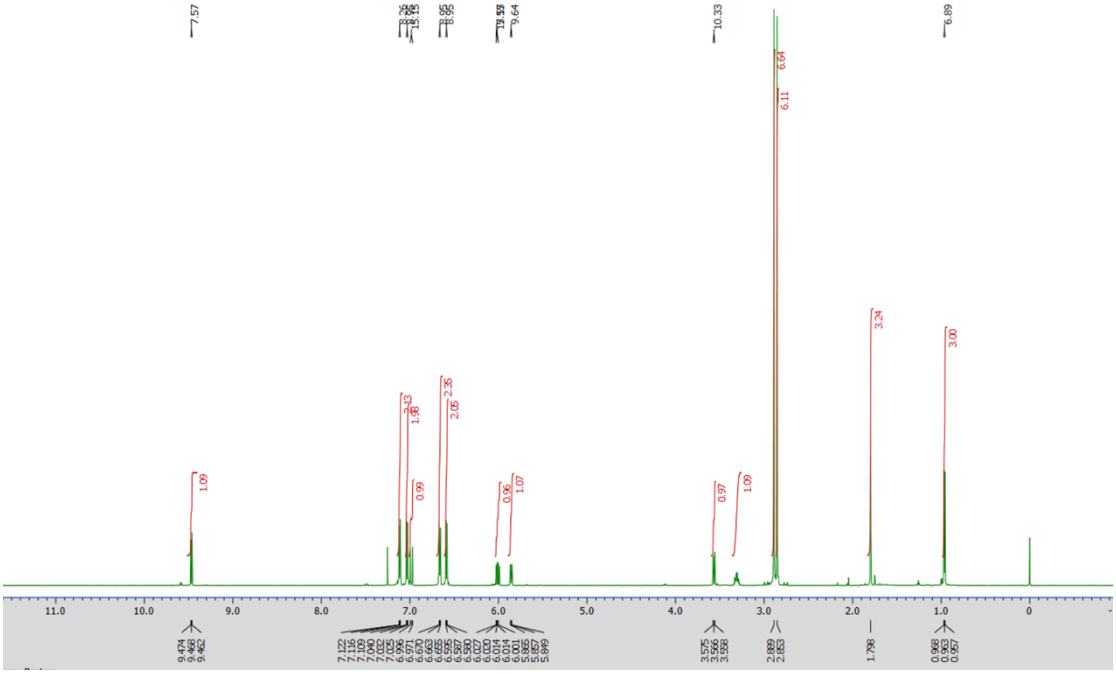
The enantiomeric excess was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel IA and IA guard column (2-propanol/hexane = 10:90, 1 mL/min); t_R = 8.9 min (major), 19.3 min (minor).

^{1}H and ^{13}C NMR spectra

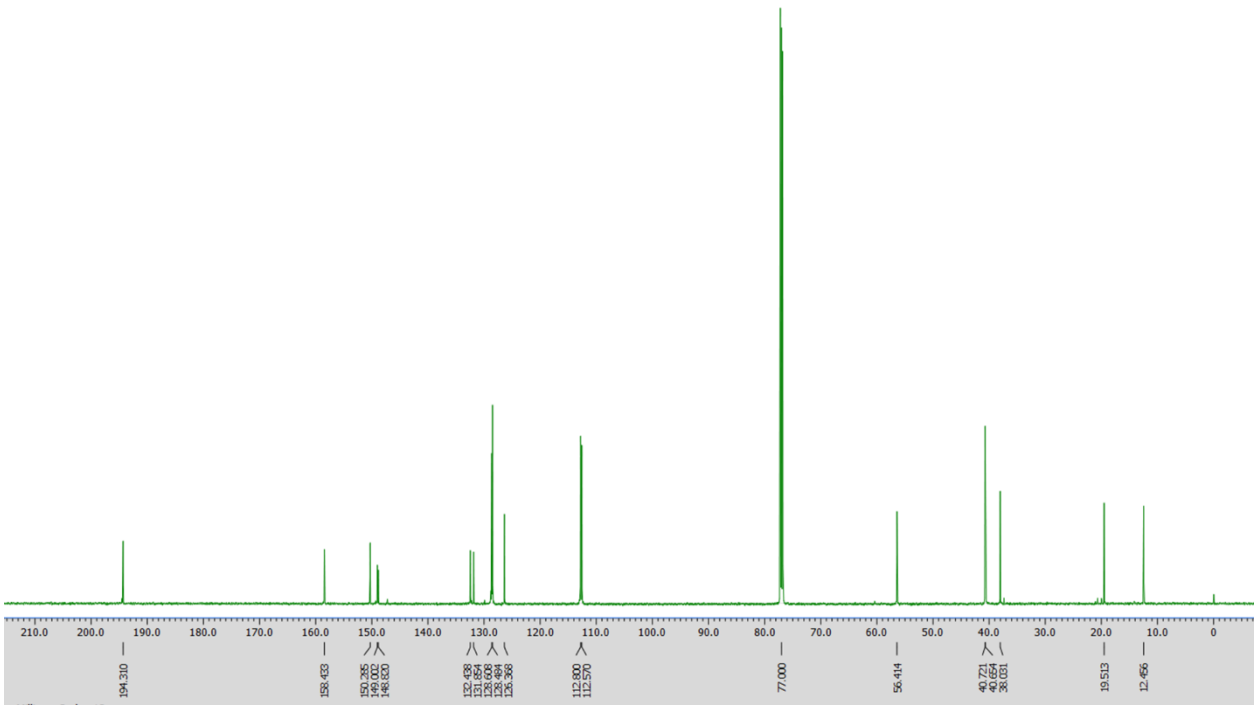
(*R*)-7,7-Bis(4-(dimethylamino)phenyl)-4,6-dimethylhepta-2,4-dienal (3a)



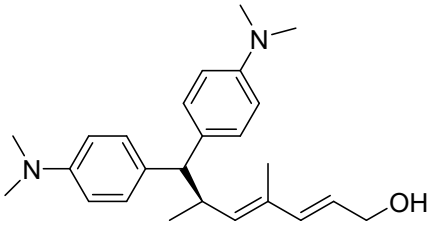
^{1}H-NMR (600 MHz, $CDCl_3$):



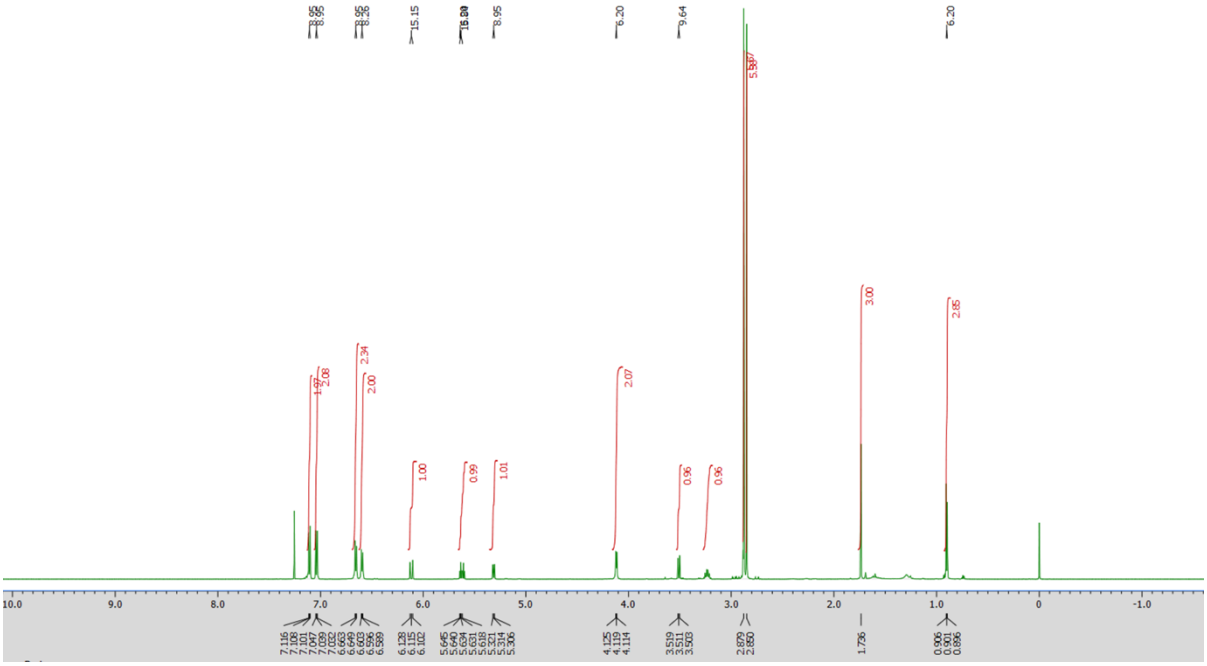
^{13}C-NMR (151 MHz, $CDCl_3$):



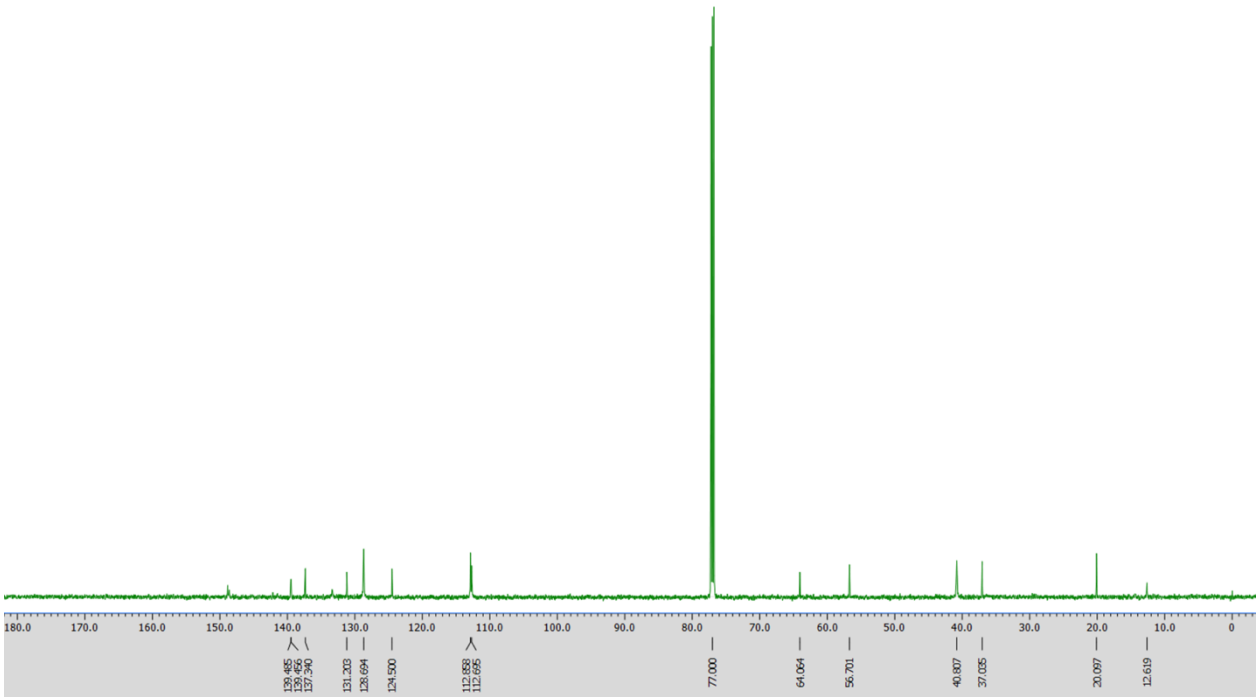
Alcohol prepared by the $NaBH_4$ reduction of **3a**



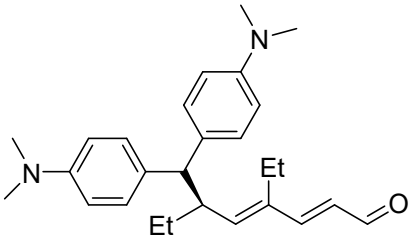
^{1}H-NMR (600 MHz, $CDCl_3$):



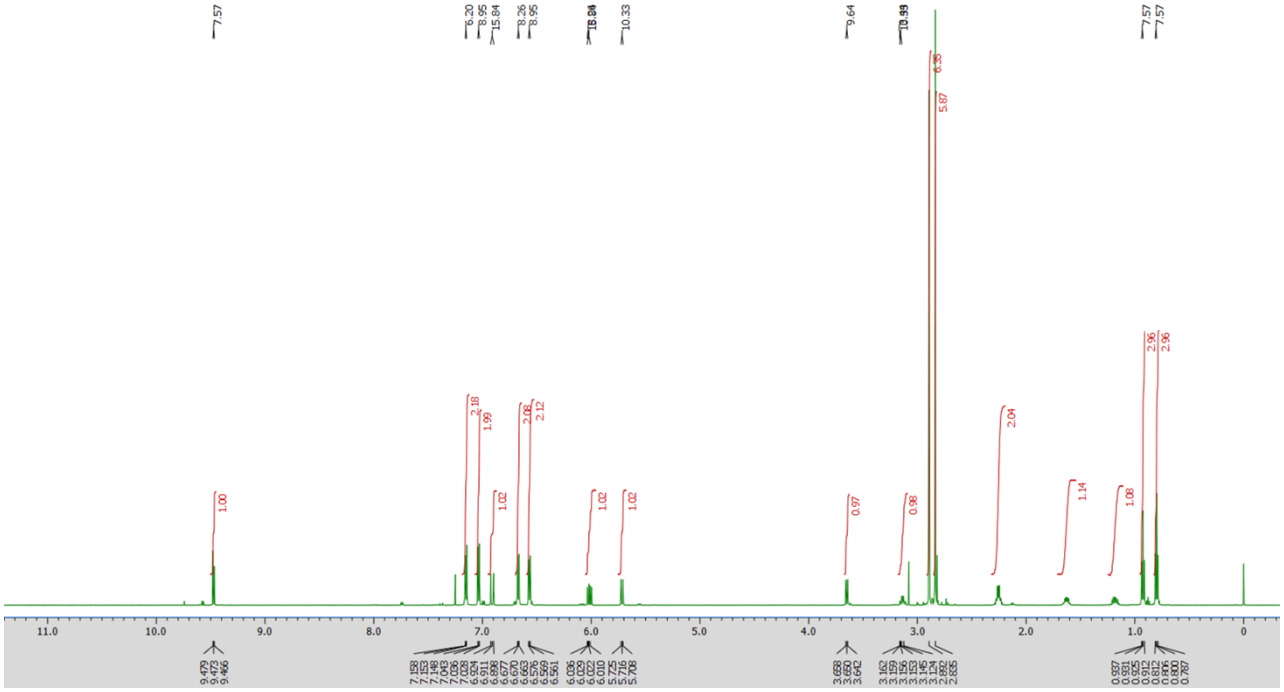
^{13}C-NMR (151 MHz, $CDCl_3$):



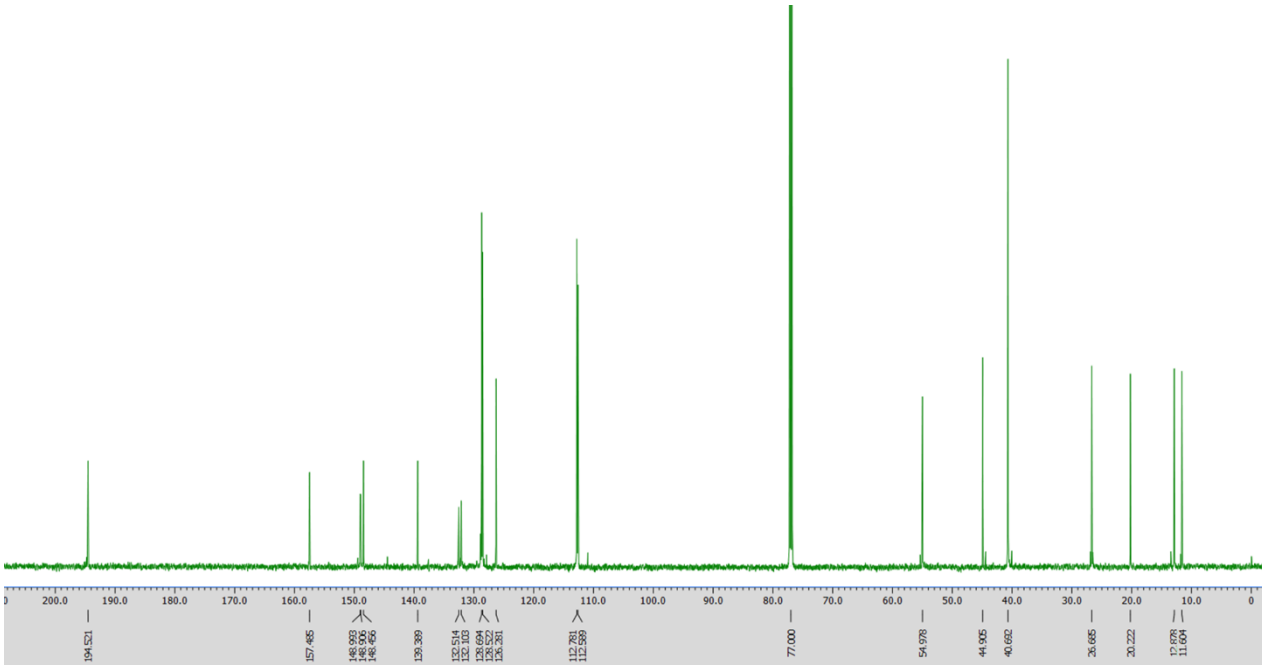
(*R*)-6-(Bis(4-(dimethylamino)phenyl)methyl)-4-ethylocta-2,4-dienal (3b)



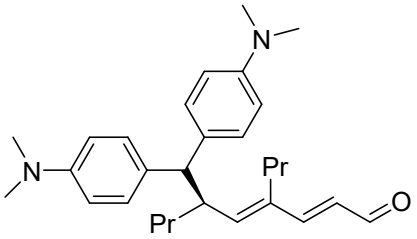
^{1}H-NMR (600 MHz, $CDCl_3$):



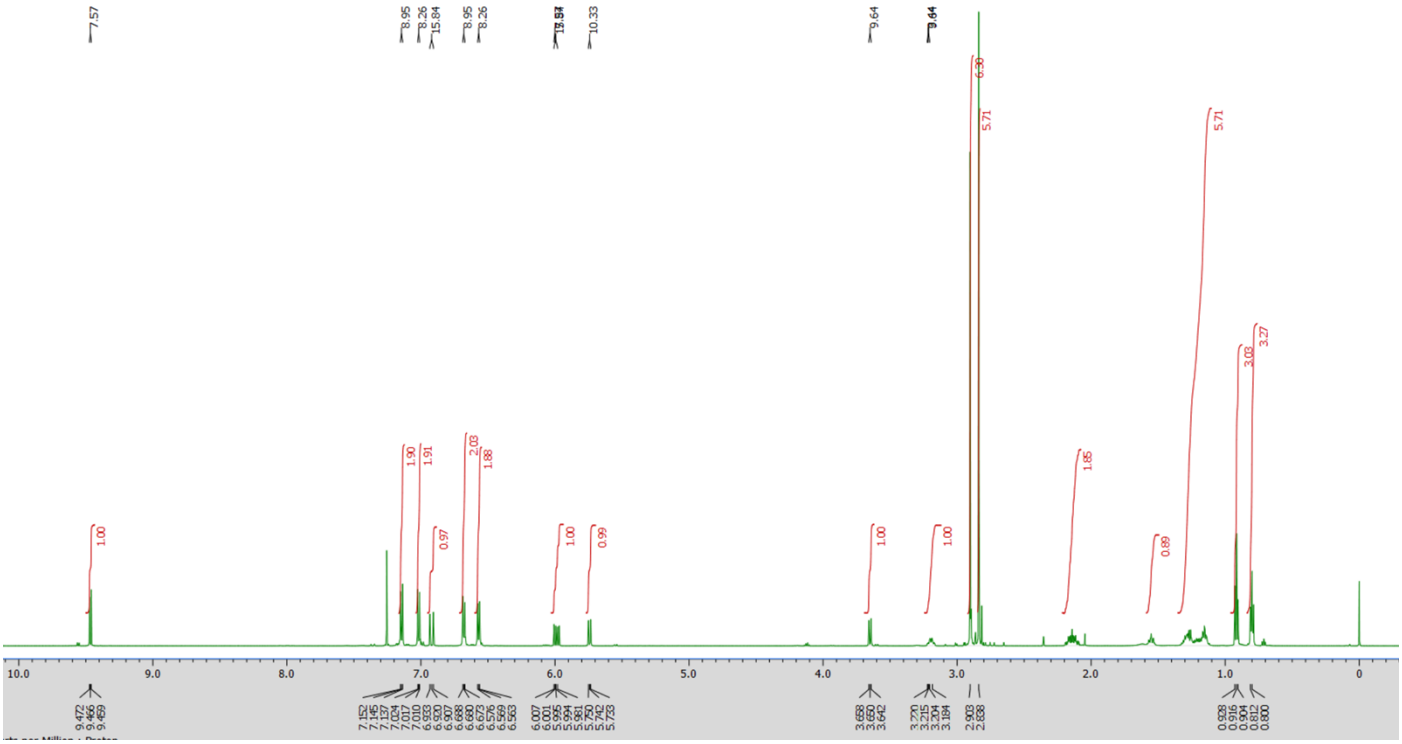
^{13}C-NMR (151 MHz, $CDCl_3$):



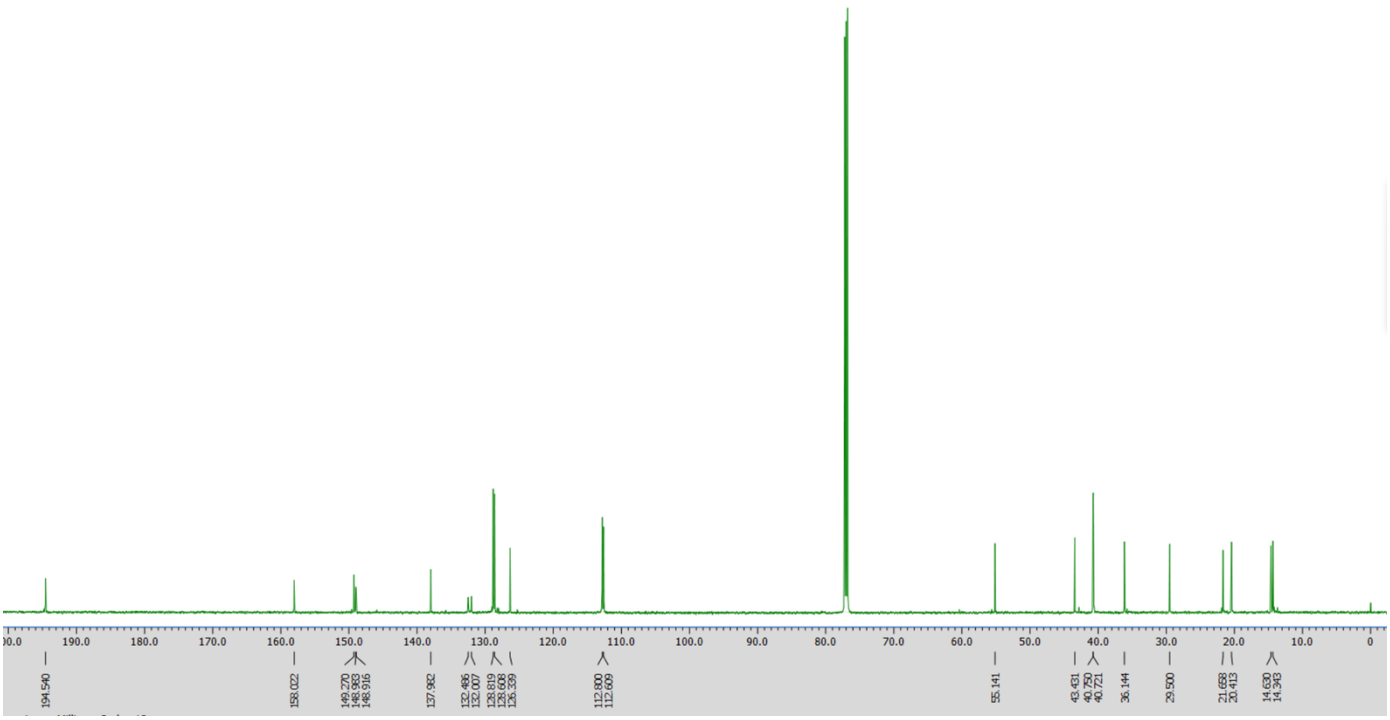
(*R*)-6-(Bis(4-(dimethylamino)phenyl)methyl)-4-propylnona-2,4-dienal (3c)



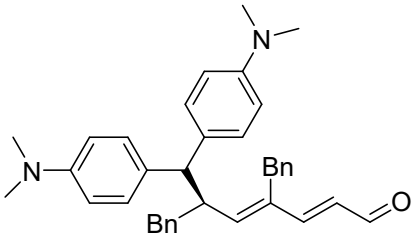
^{1}H-NMR (600 MHz, $CDCl_3$):



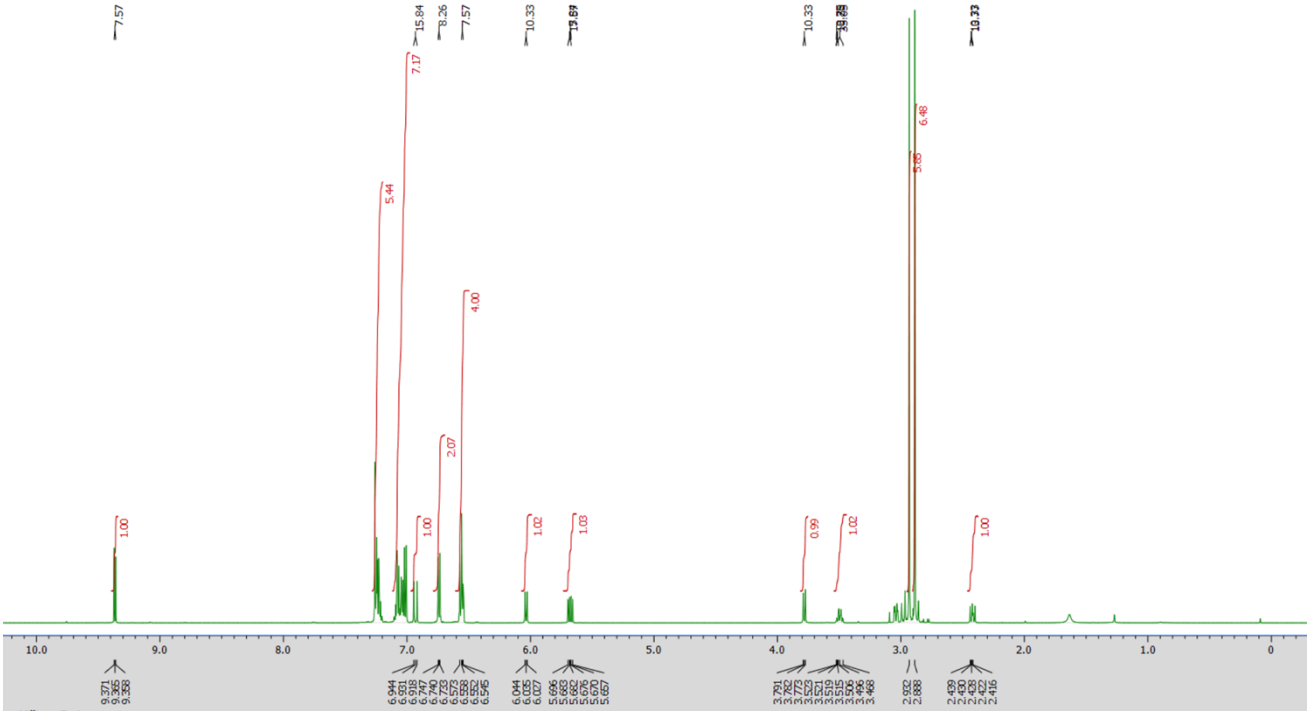
^{13}C-NMR (151 MHz, $CDCl_3$):



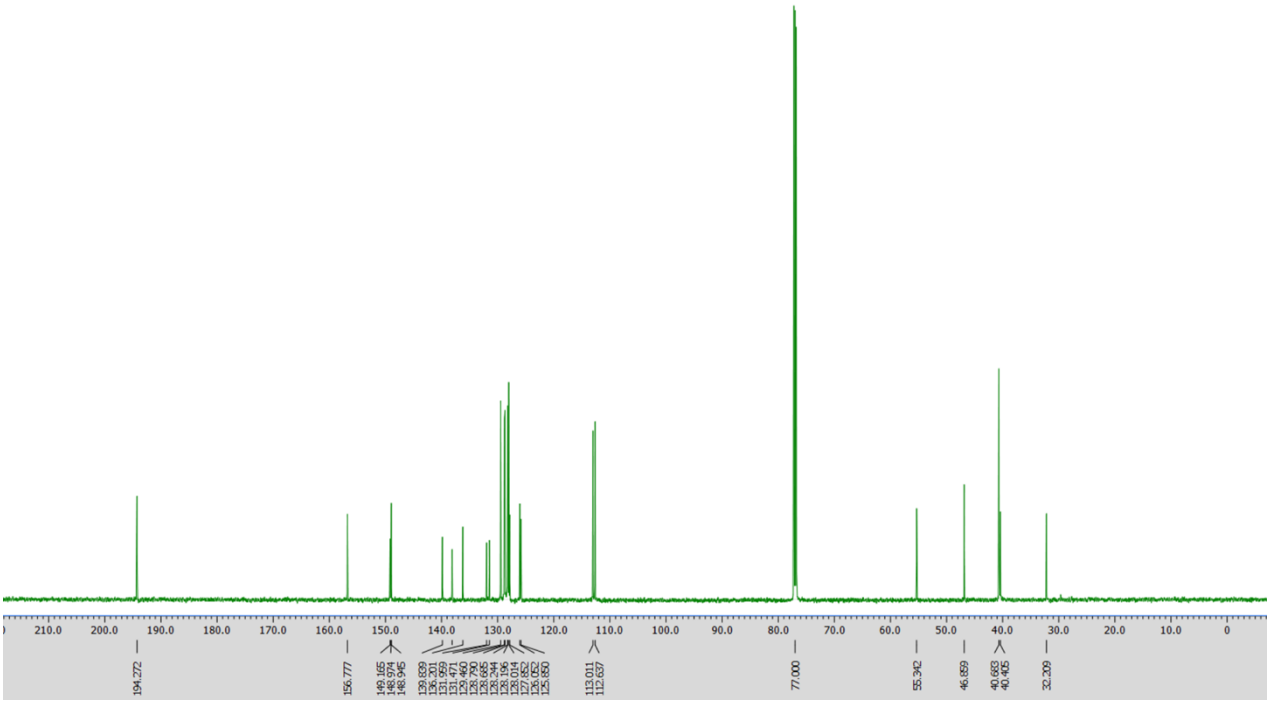
(*R*)-4,6-Dibenzyl-7,7-(bis(4-dimethylamino)phenyl)hepta-2,4-dienal (3d)



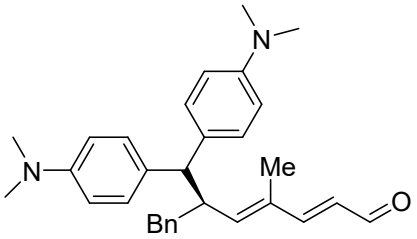
^{1}H-NMR (600 MHz, $CDCl_3$):



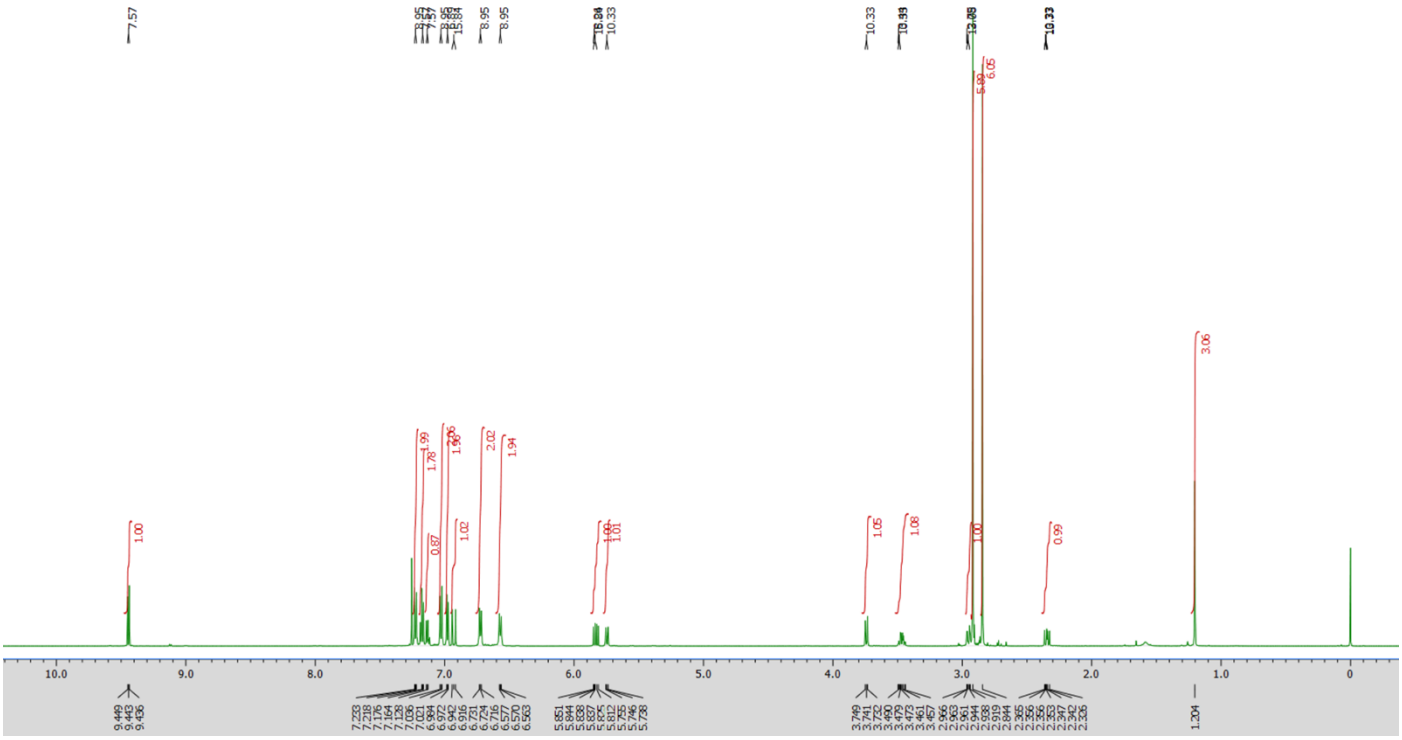
^{13}C-NMR (151 MHz, $CDCl_3$):



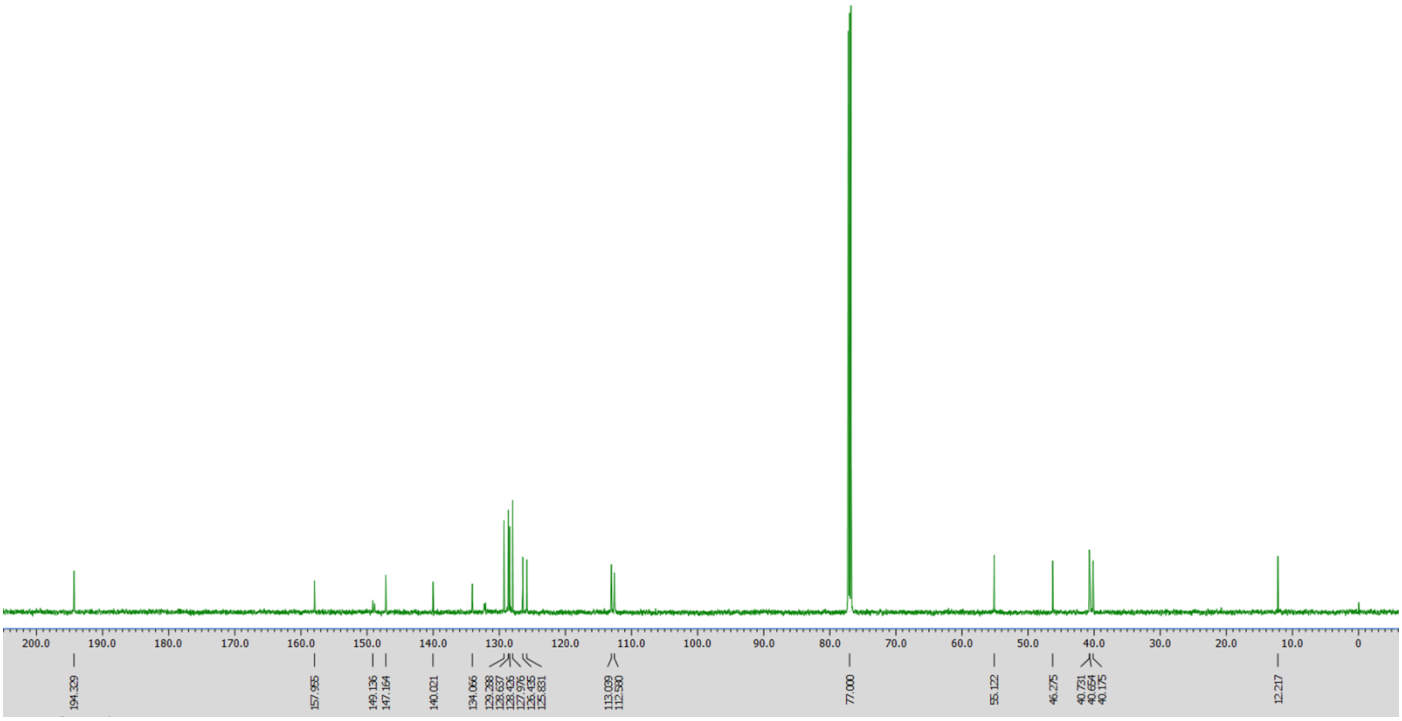
(*R*)-6-Benzyl-7,7-(bis(4-dimethylamino)phenyl)-4-methylhepta-2,4-dienal (3e)



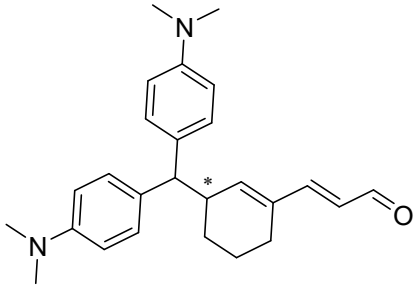
^{1}H-NMR (600 MHz, $CDCl_3$):



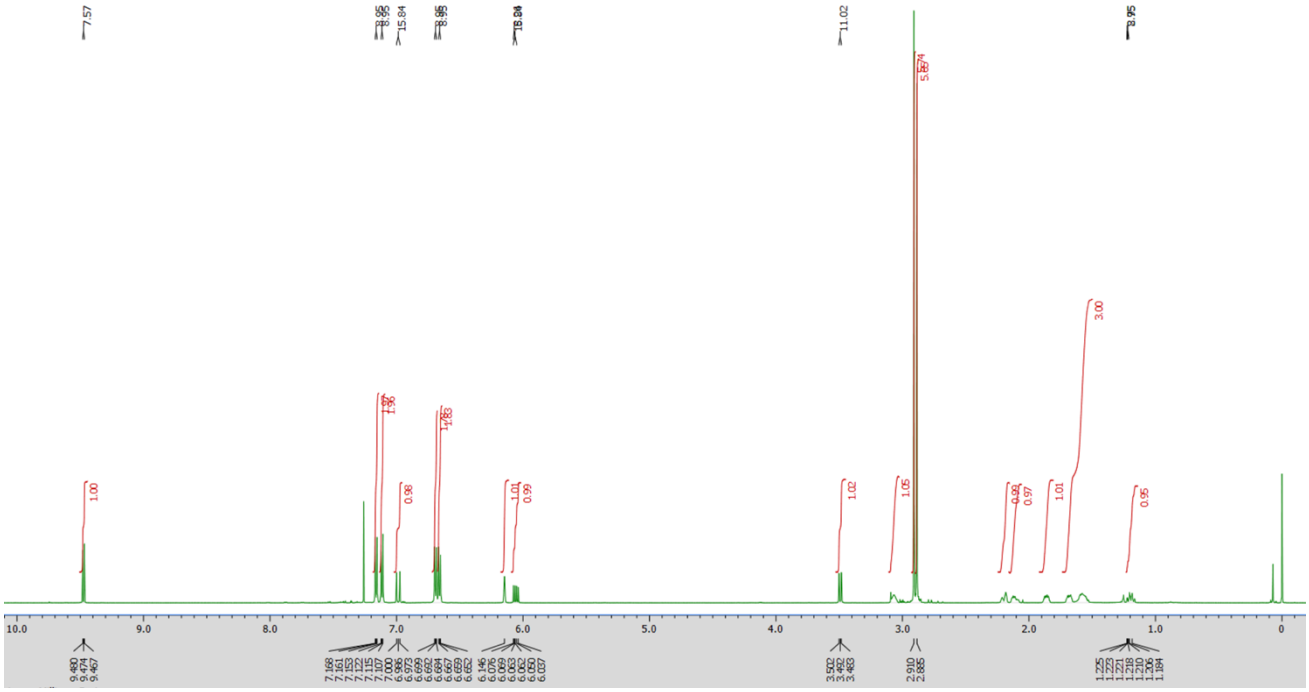
^{13}C-NMR (151 MHz, $CDCl_3$):



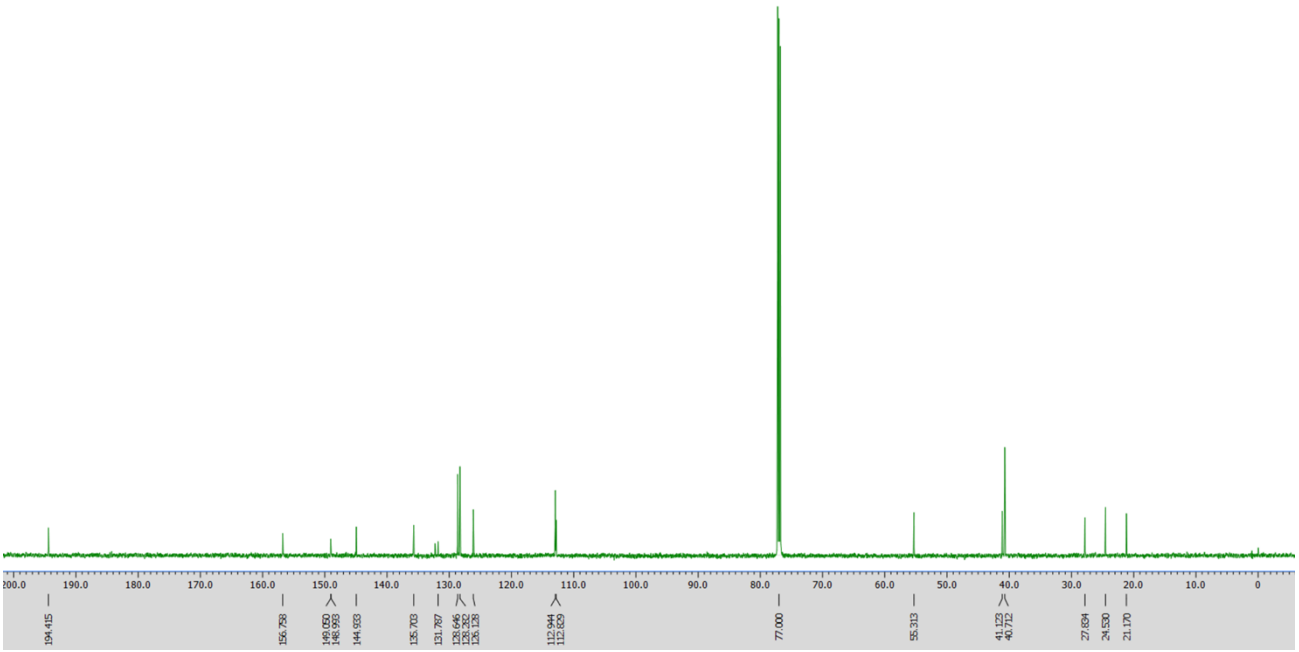
3-(3-(Bis(4-(dimethylamino)phenyl)methyl)cyclohexen-1-yl)-2-propenal (3f)



^{1}H-NMR (600 MHz, $CDCl_3$):

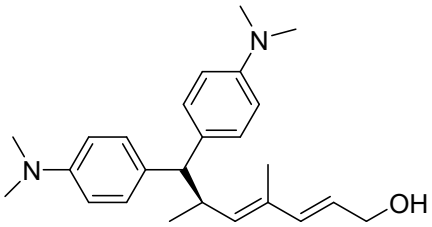


^{13}C-NMR (151 MHz, $CDCl_3$):

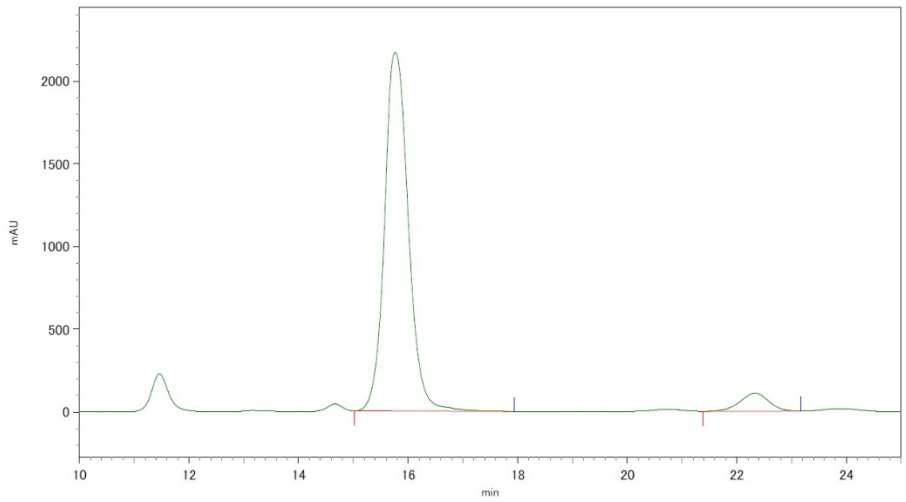


HPLC traces for the products / racemic samples

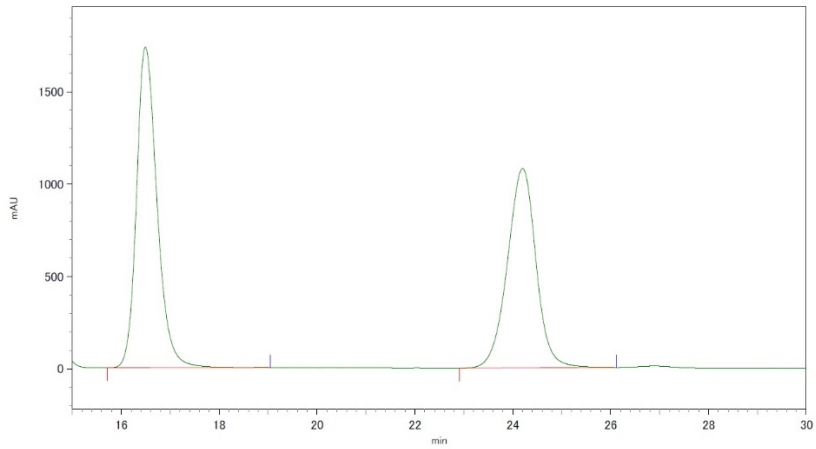
Alcohol derived from 3a



Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

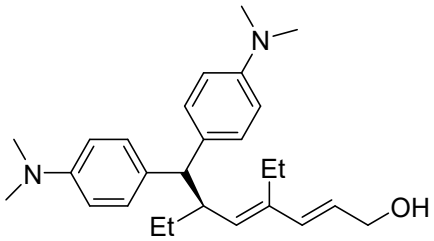


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	15.762	65508750	94.27
	22.325	3978484	5.73
Total		69487234	100.00

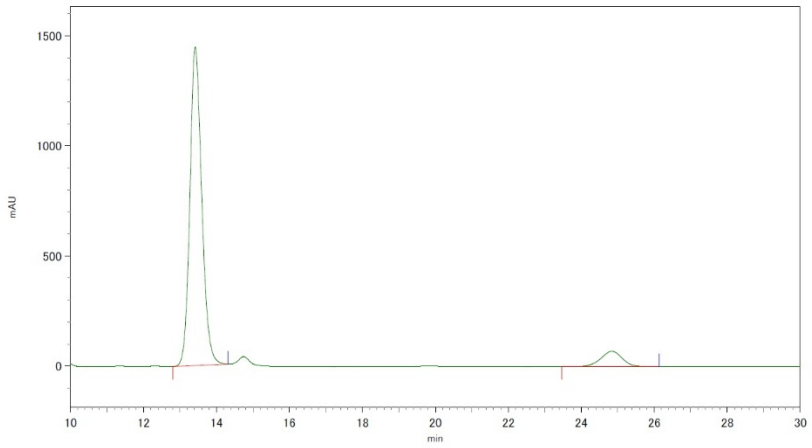


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	16.487	50640857	53.53
	24.196	43966070	46.47
Total		94606927	100.00

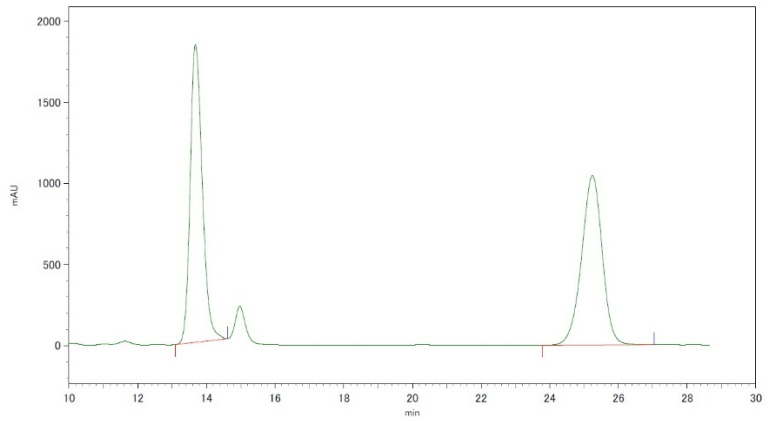
Alcohol derived from 3b



Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

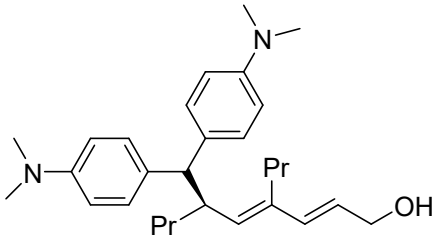


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	13.416	32622251	91.85
	24.836	2895998	8.15
Total		35518249	100.00

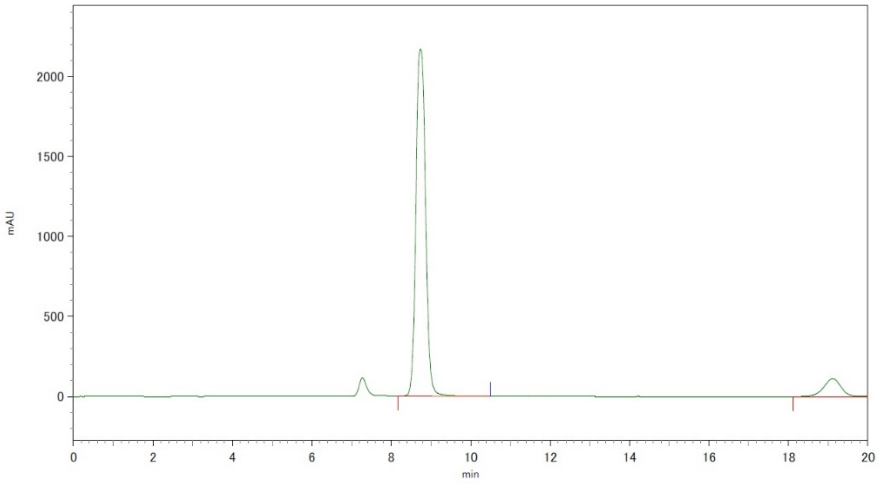


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	13.676	44973843	50.77
	25.239	43602205	49.23
Total		88576049	100.00

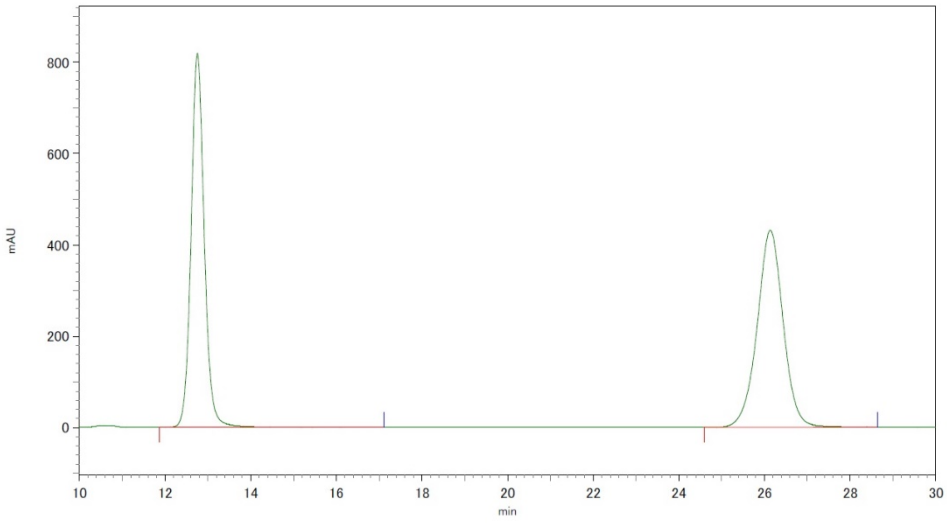
Alcohol derived from 3c



Chiralpak IA, hexane/2-propanol = 90:10, 1.0 mL min^{-1}

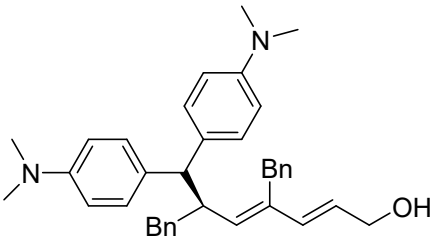


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	8.733	36430985	91.48
	19.110	3394320	8.52
	Total	39825305	100.00

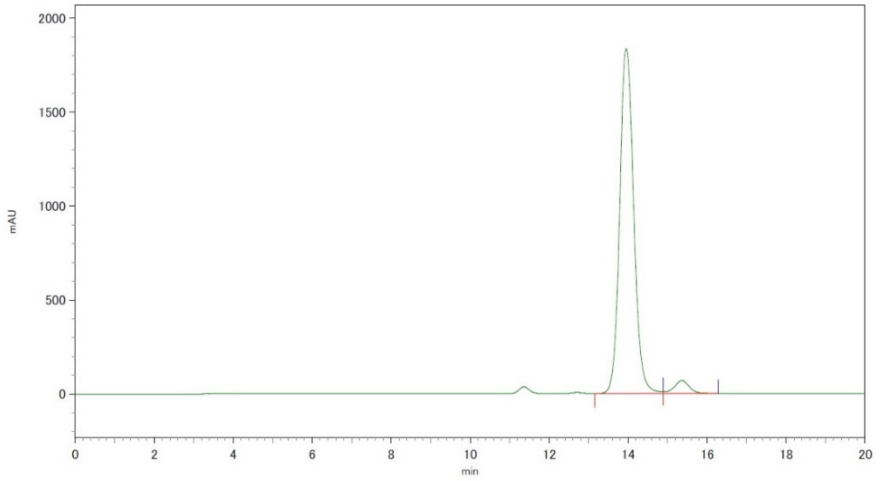


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	12.750	17594225	49.06
	26.129	18271183	50.94
	Total	35865408	100.00

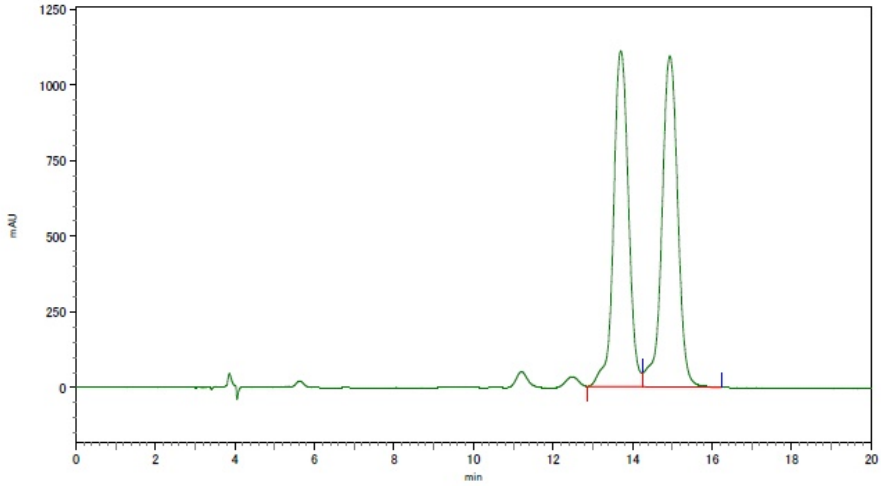
Alcohol derived from 3d



Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

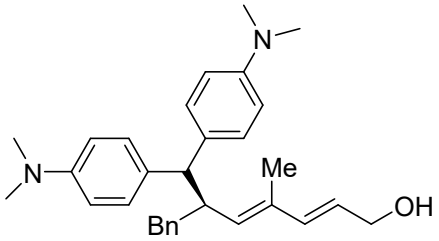


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	13.949	45203074	96.10
	15.357	1832022	3.90
	Total	47035097	100.00

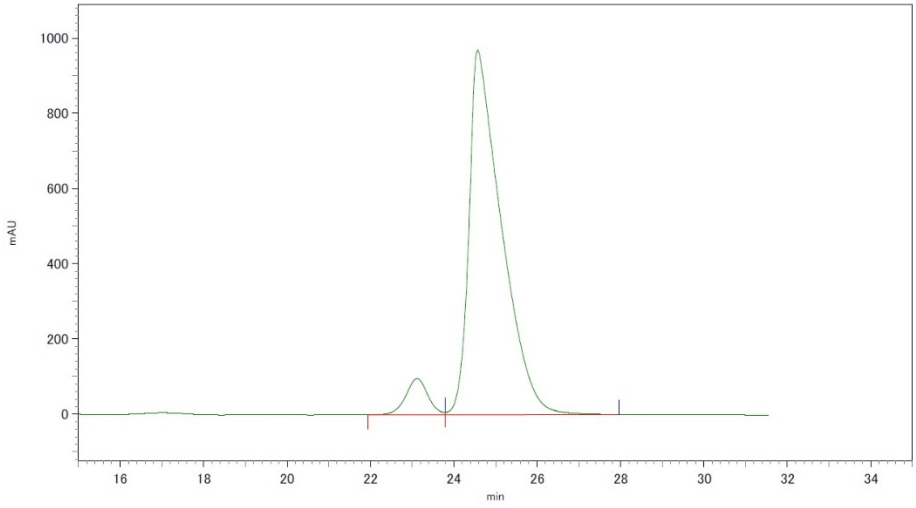


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	13.700	28960476	48.81
	14.931	30372711	51.19
	Total	59333186	100.00

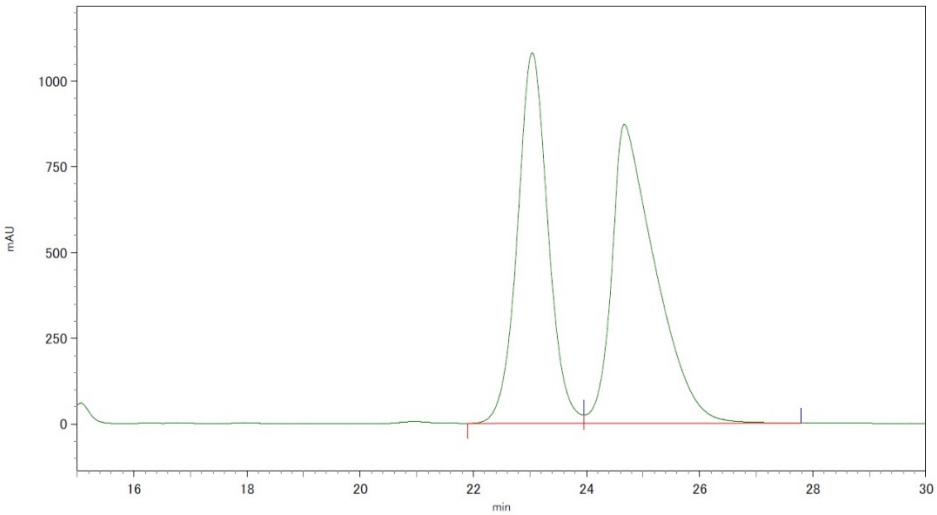
Alcohol derived from 3e



Chiralpak IA, hexane/2-propanol = 95:5, 1.0 mL min^{-1}

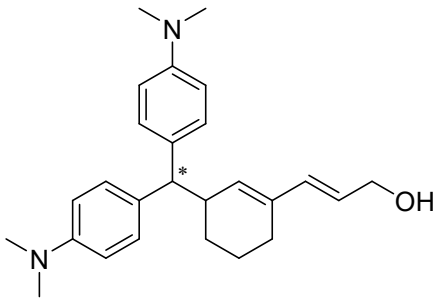


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	23.114	3574832	6.38
	24.566	52476925	93.62
Total		56051757	100.00

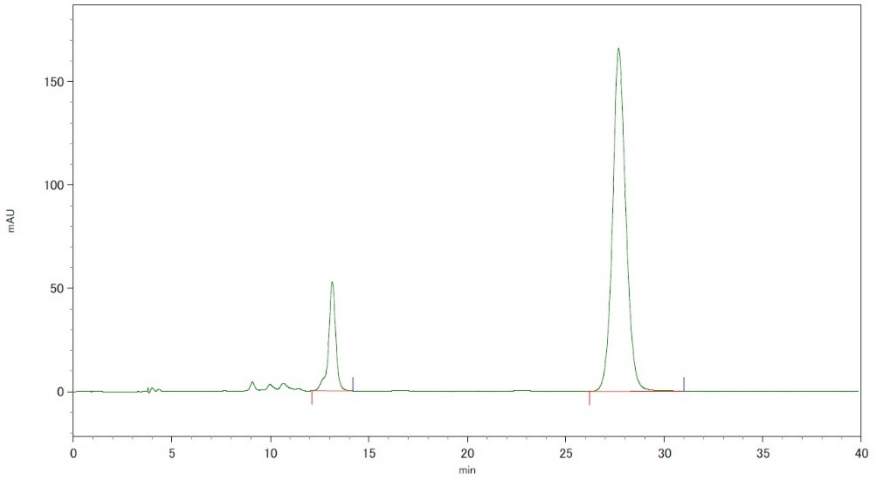


1: 254 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	23.035	40574550	46.46
	24.662	46763566	53.54
Total		87338116	100.00

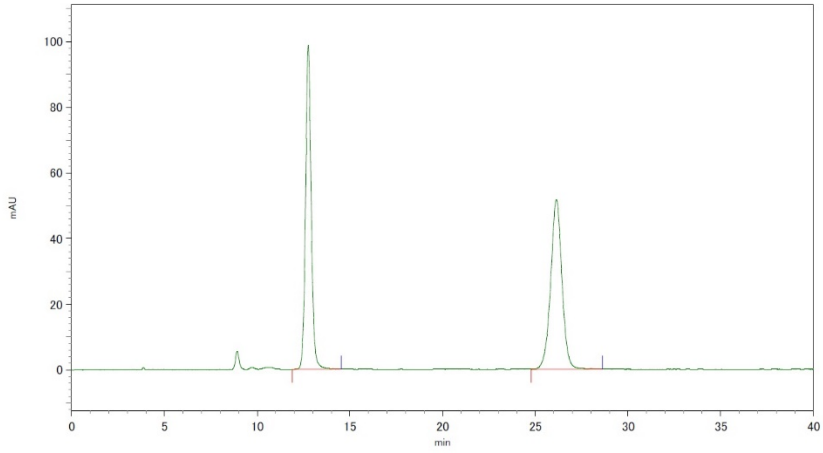
Alcohol derived from 3f



Chiralpak IA, hexane/2-propanol = 90:10, 1.0 mL min^{-1}



1: 290 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	13.137	1334547	14.63
	27.676	7789890	85.37
Total		9124437	100.00



1: 290 nm, 8 nm	(Retention time) 保持時間	(Area) 面積	(Area%) 面積%
	12.750	2097592	48.95
	26.128	2187460	51.05
Total		4285052	100.00

Coordinates for DFT optimized species related to Fig S1 and Table S4

3-methylindole

C	0.17406900	-0.38846500	-0.00000600
C	1.60520500	-0.22236900	-0.00003600
C	-0.67100200	-1.50988400	0.00002200
C	-0.40178500	0.90576900	-0.00001100
C	-1.78665400	1.10530800	0.00001400
C	-2.04202700	-1.31774900	0.00005700
C	-2.59321100	-0.02034800	0.00005500
H	-2.21126700	2.10490400	0.00001200
H	-0.25183500	-2.51280800	0.00003200
H	-2.70706000	-2.17597600	0.00008700
H	-3.67246200	0.09907100	0.00008400
C	1.82941000	1.12624900	-0.00002600
C	2.62502700	-1.31704400	-0.00003300
N	0.63173000	1.80902800	-0.00006500
H	2.76621300	1.66711200	-0.00006000
H	0.53341400	2.81322200	0.00017900
H	2.52387500	-1.95920400	0.88243000
H	2.52320000	-1.95981300	-0.88197200
H	3.63961200	-0.90850100	-0.00056400

BDAB-derived cation

C	-1.27667700	0.90510500	0.03920800
C	-0.00000100	1.49185000	-0.00001500
C	-2.40475200	1.72747600	-0.24548300
C	-1.54206700	-0.44926200	0.39408600
C	-2.81223700	-0.95436700	0.39865500
C	-3.67956100	1.23482900	-0.27294900
C	-3.93006900	-0.13859400	0.03299700
H	-0.73219600	-1.08364300	0.73734900
H	-2.96972800	-1.97700100	0.71626900
H	-2.23513500	2.77570100	-0.47855000
H	-4.49972600	1.89609500	-0.52075900
N	-5.17495800	-0.64043300	0.00902100
H	-0.00000100	2.58318800	-0.00000800
C	1.27667700	0.90510600	-0.03923400
C	1.54207500	-0.44925800	-0.39411200
C	2.40474700	1.72747900	0.24547400
C	3.67955700	1.23483700	0.27295300
C	2.81224800	-0.95435800	-0.39867000

C	3.93007300	-0.13858300	-0.03300400
H	2.23512400	2.77570100	0.47855100
H	4.49971600	1.89610400	0.52078400
H	0.73221000	-1.08364900	-0.73737500
H	2.96974600	-1.97699600	-0.71627100
N	5.17496000	-0.64042900	-0.00901600
C	6.31003300	0.21939400	0.30588900
C	5.41487000	-2.04214800	-0.33238600
C	-5.41488500	-2.04215200	0.33238400
C	-6.31002900	0.21941200	-0.30582900
H	6.39497700	1.03675900	-0.41769300
H	6.21212800	0.64094700	1.31158100
H	7.22326400	-0.37162800	0.26805900
H	4.82890900	-2.69619600	0.32061400
H	5.15793800	-2.25551600	-1.37573700
H	6.46966600	-2.26442600	-0.18249900
H	-6.39495300	1.03675000	0.41778700
H	-6.21213700	0.64100300	-1.31150600
H	-7.22326400	-0.37160400	-0.26800600
H	-4.82890500	-2.69619900	-0.32059800
H	-5.15799200	-2.25552500	1.37574300
H	-6.46967600	-2.26442600	0.18245300

Complex of 3-methylindole and BDAB-derived cation

C	-2.07641900	1.50111000	1.02836400
C	-0.65168900	1.70815700	1.01277300
C	-2.96212800	0.93724000	1.96104000
C	-2.59515100	2.02630600	-0.18043300
C	-3.96574500	2.02697700	-0.46765600
C	-4.31711300	0.92246300	1.67661700
C	-4.81350100	1.46556600	0.47243100
H	-4.34928800	2.46394500	-1.38543300
H	-2.58680000	0.52644800	2.89483000
H	-5.01526600	0.50415900	2.39585700
H	-5.88376700	1.45589500	0.28592100
C	-0.37453500	2.32667000	-0.17775900
C	0.30638100	1.35880000	2.10654500
N	-1.53115600	2.50328500	-0.90655500
H	0.57243300	2.68270700	-0.56131100
H	-1.59827700	3.01818000	-1.77246500

H	0.05123900	1.88268400	3.03482800
H	0.29252600	0.28439300	2.32594700
H	1.33124200	1.63324500	1.83993600
C	-0.04755200	-1.67833400	0.22433400
C	1.23772000	-1.82670700	0.75448400
C	-1.13989100	-2.25700500	0.94106100
C	-0.36085500	-1.03576500	-1.01318600
C	-1.64430000	-0.93699300	-1.46590200
C	-2.43165700	-2.14106400	0.52159500
C	-2.73831300	-1.45015100	-0.69532900
H	0.44140600	-0.68393800	-1.65180000
H	-1.82647400	-0.48364000	-2.43151100
H	-0.92839900	-2.78838200	1.86574800
H	-3.22593000	-2.58191100	1.10978600
N	-4.00149900	-1.33053300	-1.12121600
H	1.31368800	-2.55180900	1.56666900
C	2.45872500	-1.19847100	0.41908800
C	2.57356700	0.00990300	-0.32073300
C	3.66613900	-1.77382600	0.89870600
C	4.89548400	-1.24880300	0.60104100
C	3.79323300	0.56421400	-0.60917600
C	5.00424000	-0.06444400	-0.18606100
H	3.61104900	-2.67894100	1.49840600
H	5.78541300	-1.74163300	0.97032200
H	1.67523000	0.54868300	-0.60317400
H	3.83082100	1.50593700	-1.14270700
N	6.20603300	0.45613000	-0.49861500
C	7.42669800	-0.16407400	-0.00095000
C	6.30007700	1.65228000	-1.32374800
C	-4.29769900	-0.72344700	-2.41215600
C	-5.10096400	-1.91291000	-0.36085700
H	7.43762200	-0.18626200	1.09414100
H	7.52907000	-1.18778000	-0.37726200
H	8.28241900	0.41644100	-0.34076900
H	5.78396300	1.50757700	-2.27827100
H	5.86933500	2.52205200	-0.81469600
H	7.34926300	1.85750200	-1.53056400
H	-5.06464200	-3.00804800	-0.38512900
H	-5.06779000	-1.57061800	0.67607500
H	-6.04180900	-1.58360100	-0.79910500

H	-3.80715600	0.24819700	-2.49846100
H	-3.97005600	-1.36895600	-3.23538800
H	-5.37321700	-0.57086400	-2.49050700

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