---- Supporting information ----

Synthesis of *P*-stereogenic phosphanorbornane-derived phosphine-phosphite ligands and their application in asymmetric catalysis

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1. General information

Chemical and solvents

All reactions were carried out using standard Schlenk techniques or under an inert atmosphere in a glove box (N_2 atmosphere), unless noted otherwise. All reagents were purchased from commercial sources and used as received, unless otherwise stated. The axially chiral diols were bought from Merck and used as received. NEt_3, $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 and distilled prior to use. THF was distilled from sodium/benzophenone. *n*-Heptane and C_6D_6 were dried over Na/benzophenone. All solvents were pre-dried with the Solvent Purification System (SPS) from MBraun (MB SPS-800, with standard MBraun drying columns).

NMR spectroscopy (LIKAT)

NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300, ^{13}C: 75, ^{31}P: 121 MHz), a Bruker Fourier 300 (^{1}H: 300, ^{13}C: 75, ^{31}P: 121 MHz) or an Avance 400 (^{1}H: 400, ^{13}C: 100, ^{31}P: 161 MHz) instrument operating at the denoted spectrometer frequency given in megahertz (MHz) for the specified nucleus.

NMR spectroscopy (Leipzig University)

The NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.63 MHz, ^{31}P: 161.98 MHz). ^{13}C{^{1}H} NMR spectra were recorded as APT spectra.

Infrared spectroscopy (Leipzig University)

IR spectra were obtained with an FTIR spectrometer (Nicolet iS5 FTIR by Thermo Scientific, Waltham, MA, USA) in the range of 400–4000 cm^{-1} in KBr.

High-resolution mass spectrometry (LIKAT)

Samples for mass spectrometry were prepared in a glove box and measured on a Finnigan MAT 95-XP (Thermo Electron) or Kratos MS-50 spectrometer and measurements were carried out in HRMS (ESI-TOF) mode.

High-resolution mass spectrometry (Leipzig University)

High-resolution mass spectra (HRMS; electrospray ionization (ESI)) were measured on a Bruker Daltonics APEX II FT-ICR spectrometer (Billerica, MA, USA).

High performance liquid chromatography (HPLC) (LIKAT)

The chiral products have been analyzed with a chiral column in Agilent 1200 series HPLC at two different wavelengths (210.8 nm and 221.0 nm).

High performance liquid chromatography (HPLC) (Leipzig University)

Chiral HPLC measurements of **9a**,**b** were performed with a Jasco LC Net II/ADC, pump system PU-4180, autosampler AS-4050, diode array detector MD-4015an HPLC column CHIRALPAK IA, 250 x 4.6 mm, 5 µm particle size with flowrate ml/min at 20 °C. Isopropanol and *n*-hexane were used as eluent.

Gas chromatography (GC) (LIKAT)

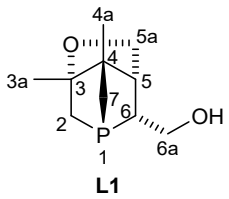
The samples have been analyzed with an Agilent HP6890 instrument with FID detector and a column. HP5 (30 m x 250 mm x 0.25 µm): front injector syringe size 10 µL, syringe 10 µL agilent G4513-80203, injection volume 1 µL, front SS inlet He, mode split heater on 250 °C pressure on 0.60993 bar, total flow on 86.971 mL/min, septum purge flow on 3 mL/min pressure 0.60993 bar, flow 1.6465 mL/min, average velocity 29.749 cm/sec run time 33.5 min.

50 m Hydrodex β-TBDAC: flow 3 mL/min, pressure 13.698 psi, avg vel. 51.506 cm/sec, initial 100 °C-hold 5 min, ramp (5 °C/min) 150 °C-hold 30 min, ramp (5 °C/min) 180 °C-hold 5°C.

Gas chromatography Mass Spectrometry (GC-MS) (LIKAT)

HP-5 (30 m x 320 µm x 0.25 µm): pressure 35.006 kPa, flow 2 mL/min, mode Split, heater On 250 °C, pressure on 35.006 kPa, total Flow On 25 mL/min, septum purge flow off, gas saver On 15 after 2 min mL/min, split ratio 10 :1, split flow 20 mL/min front injector syringe size 10 µL injection volume 1 µL temperature setpoint On (initial) 60 °C hold time 0 min post run 50 °C program #1 rate 5 °C/min #1 value 300 °C #1 hold Ttme 0 min, equilibration time 0.25 min, max temperature 325 °C.

2. NMR spectra and numbering of scheme



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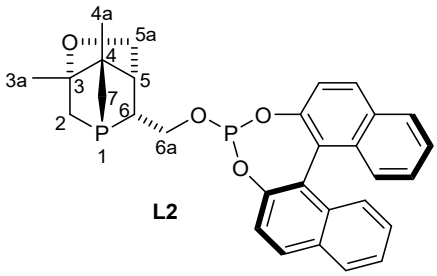

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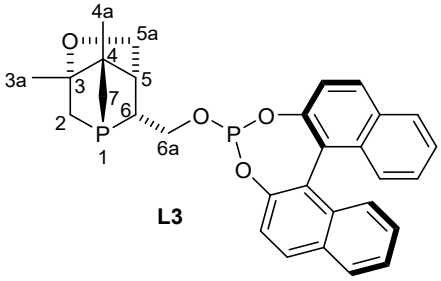
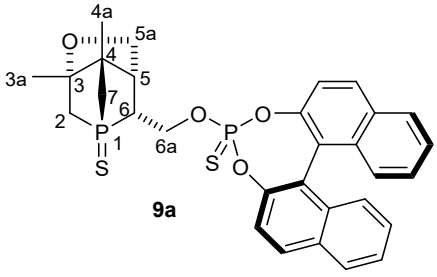
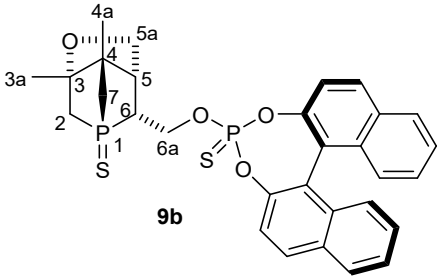


L3



9a



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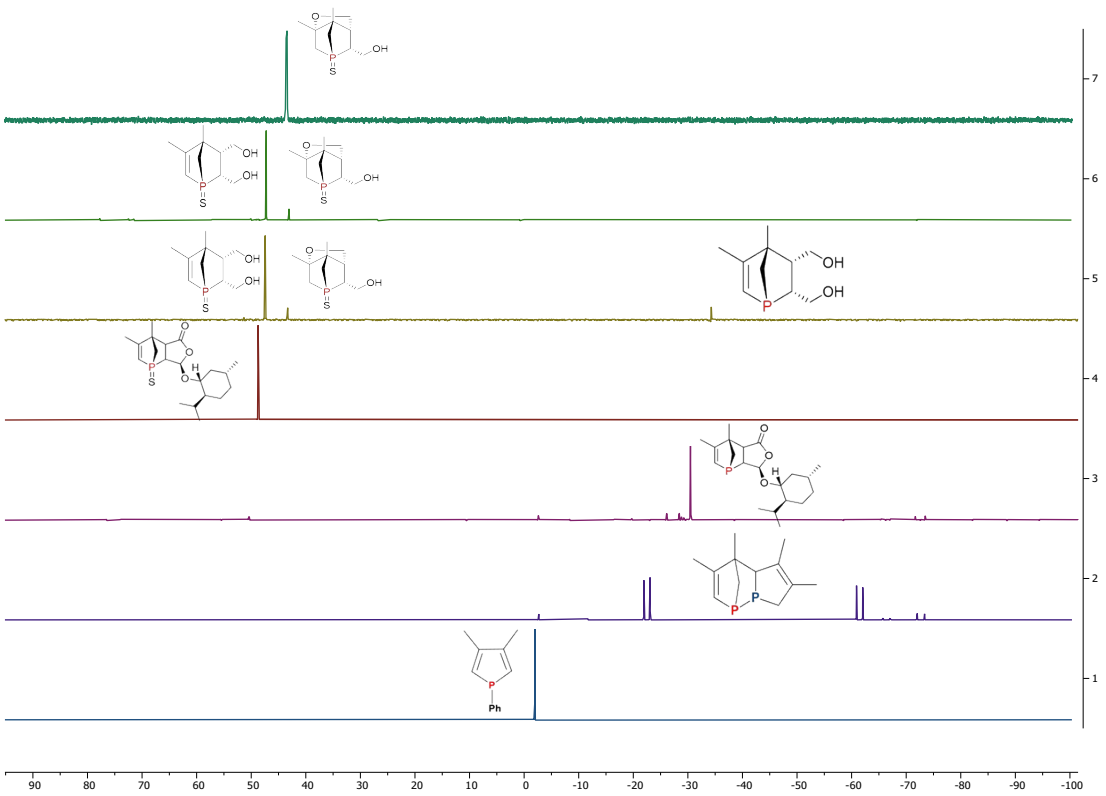

Figure S1. Synthesis of 1-phosphanorbornane alcohol: $^{31}P\{^{1}H\}$ NMR spectrum of each compound used in the synthesis as well as the final sulfur-protected product **7**.

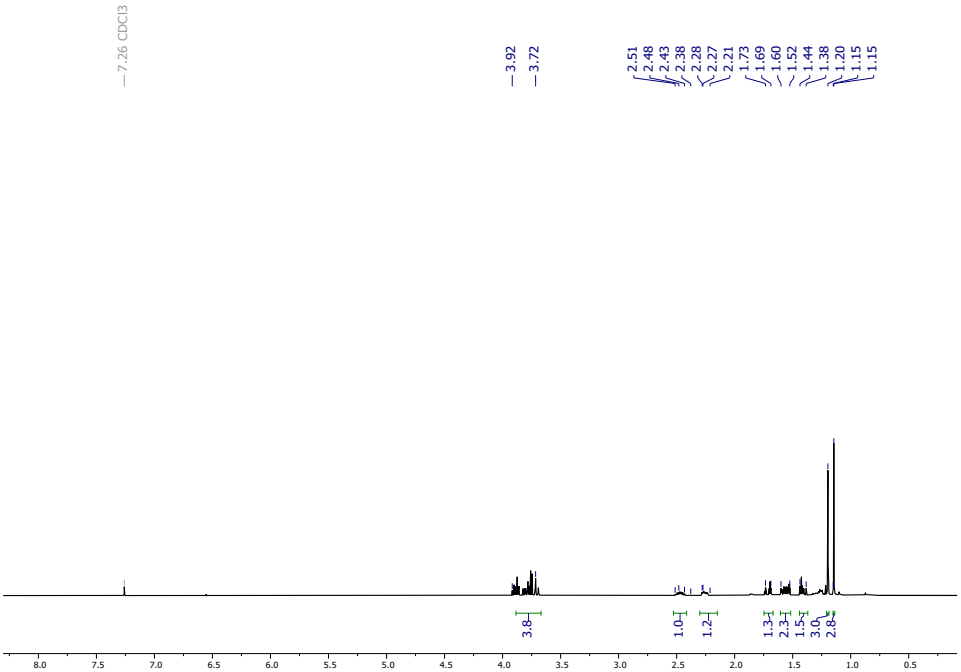

Figure S2. ^{1}H NMR spectrum of **L1** ($CDCl_3$).

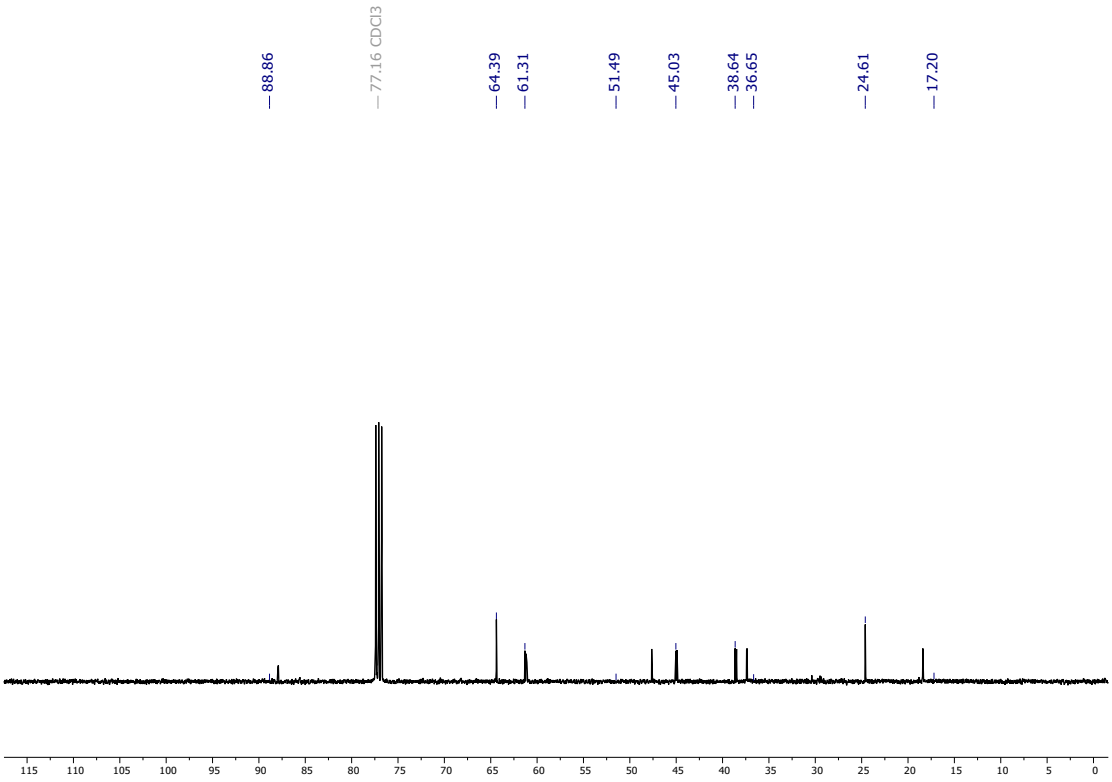

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **L1** ($CDCl_3$).

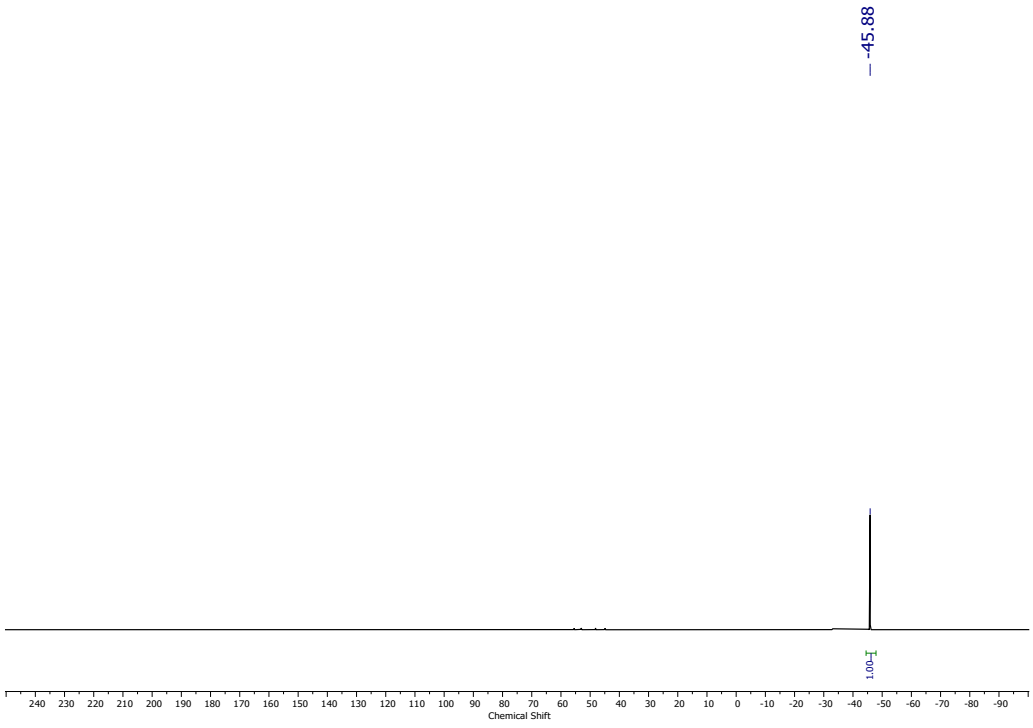

Figure S4. $^{31}P\{H\}$ NMR spectrum of **L1** ($CDCl_3$).

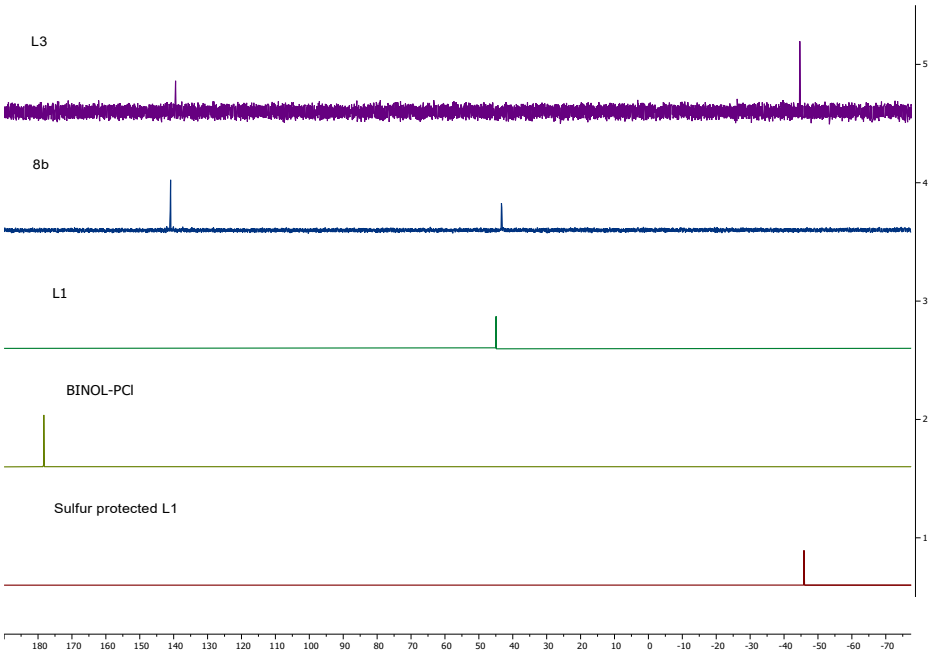

Figure S5. $^{31}P\{^{1}H\}$ NMR spectra of each step in the ligand synthesis, shown exemplarily for **L3** ($CDCl_3$).

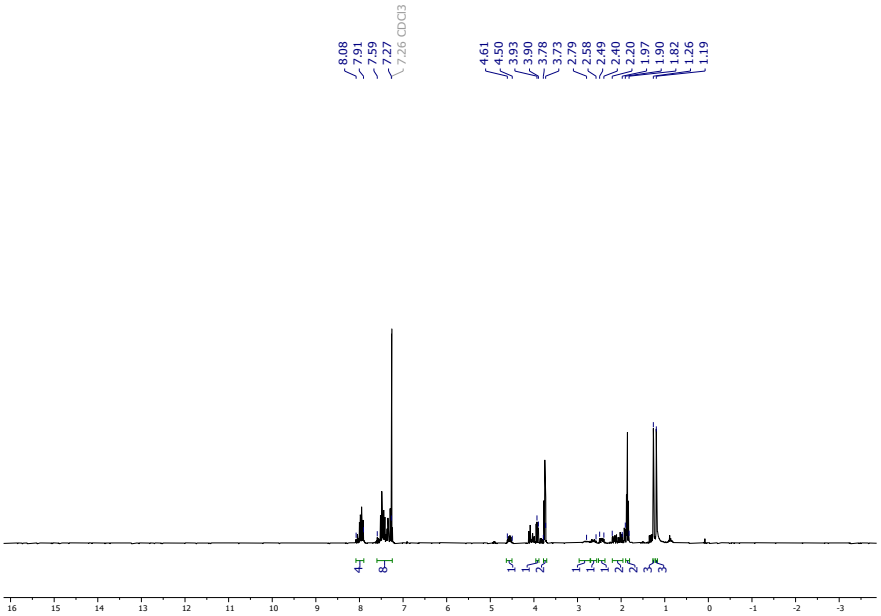

Figure S6. ^{1}H NMR spectrum of **L2** ($CDCl_3$).

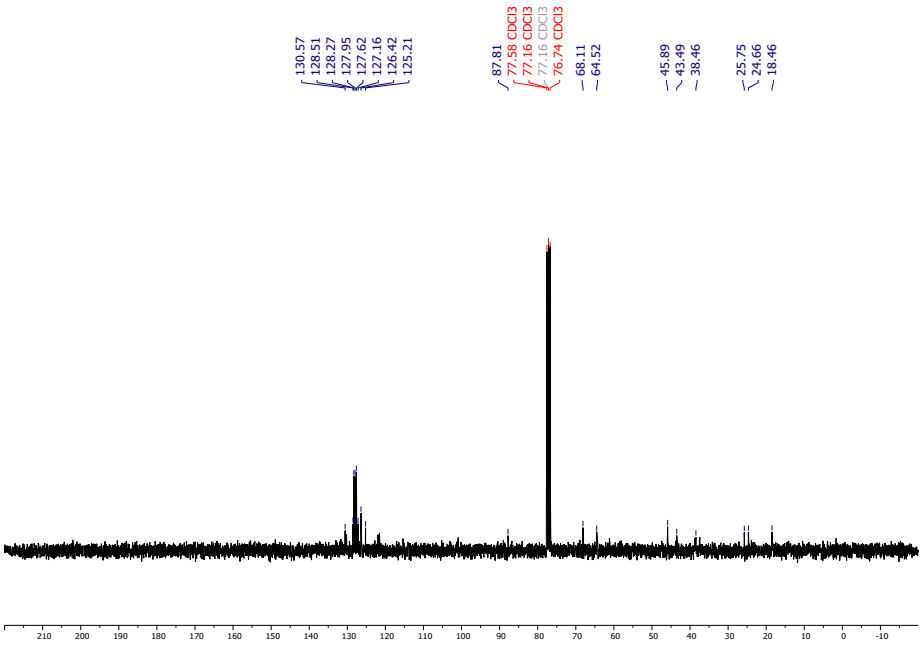

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **L2** ($CDCl_3$).

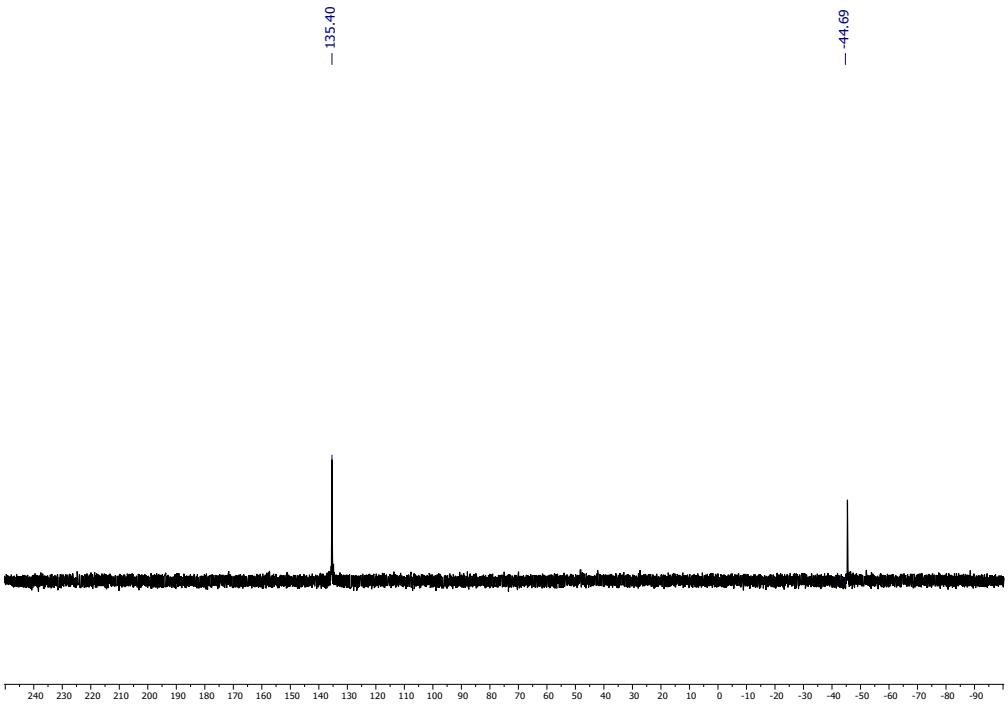

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **L2** ($CDCl_3$).

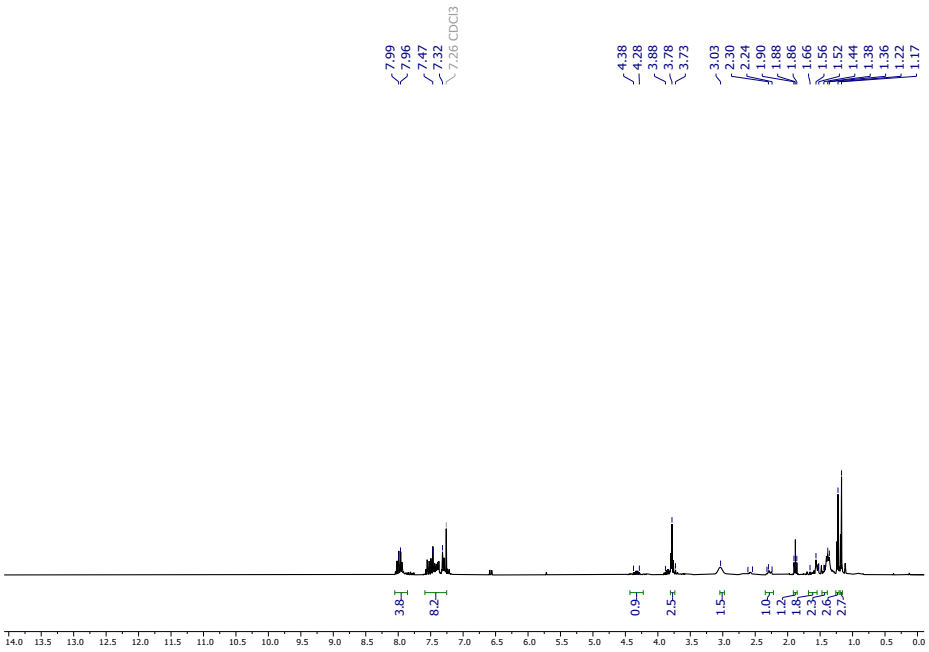

Figure S9. ^{1}H NMR spectrum of **L3** ($CDCl_3$).

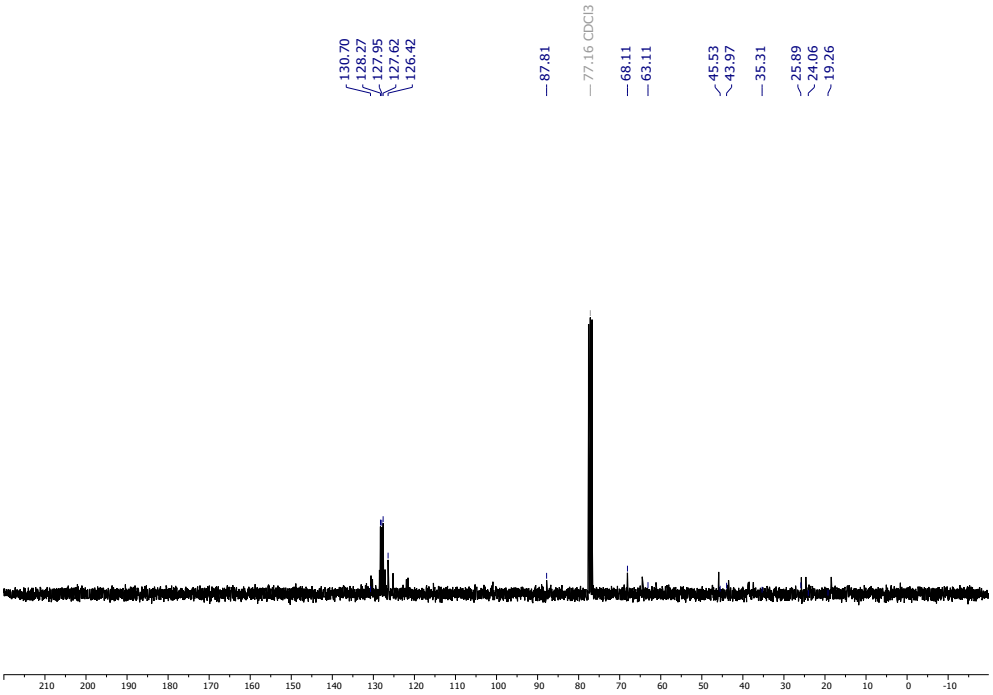

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **L3** ($CDCl_3$).

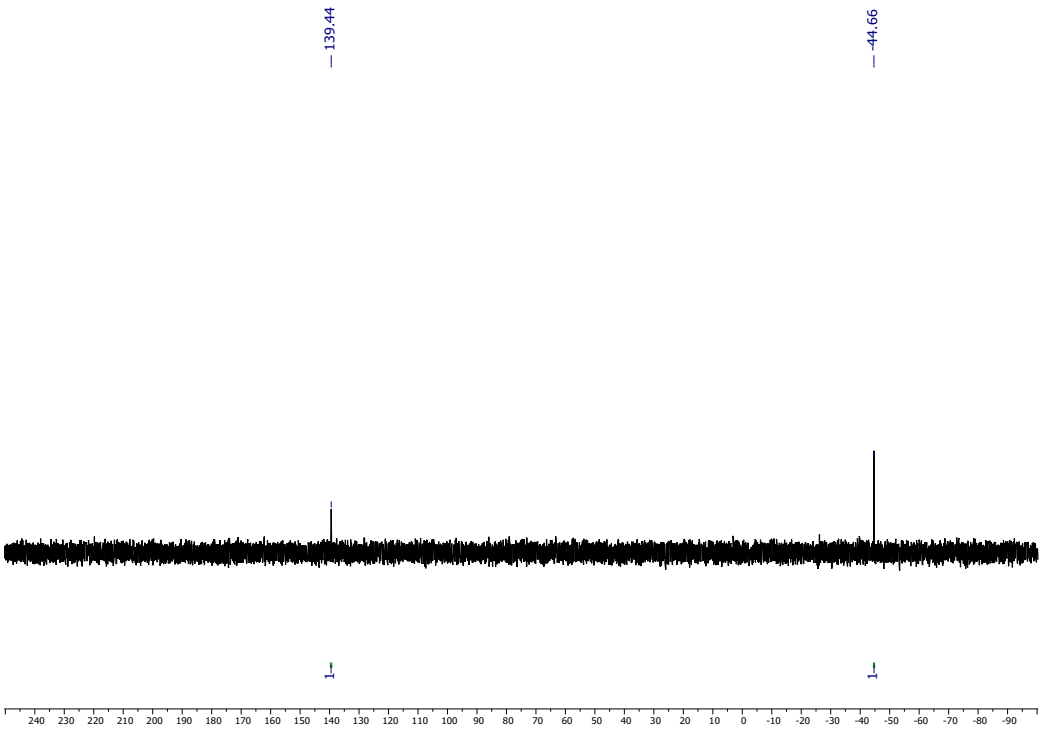

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **L3** ($CDCl_3$).

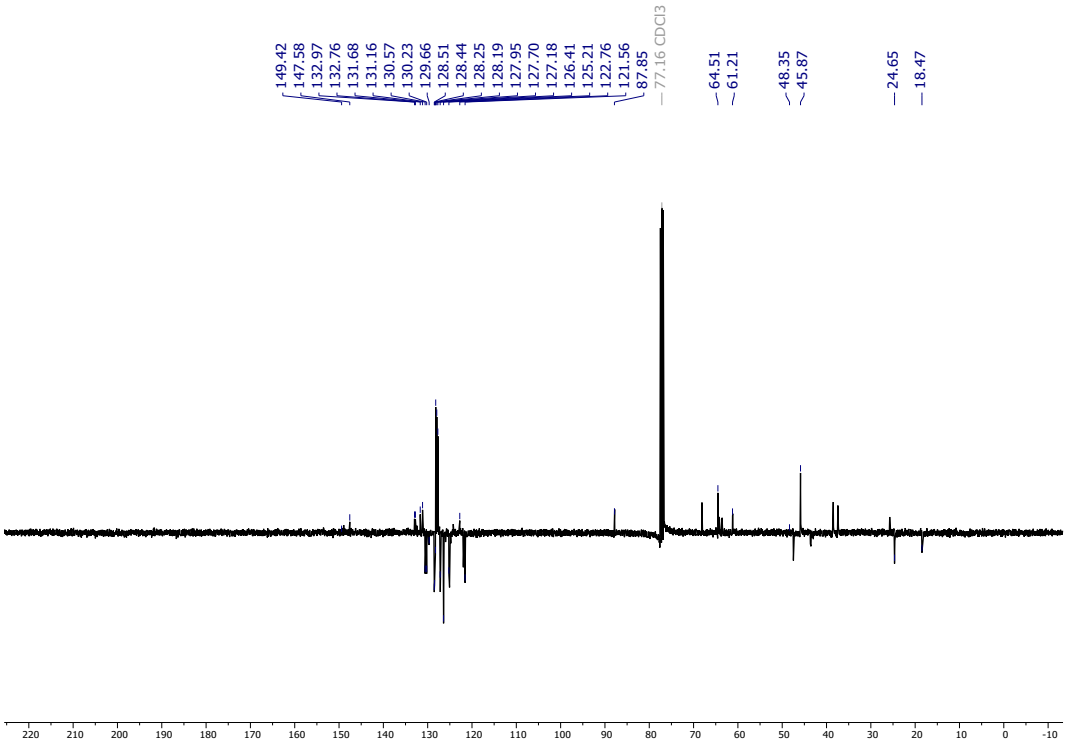

Figure S12. APT spectrum of **L3** ($CDCl_3$).

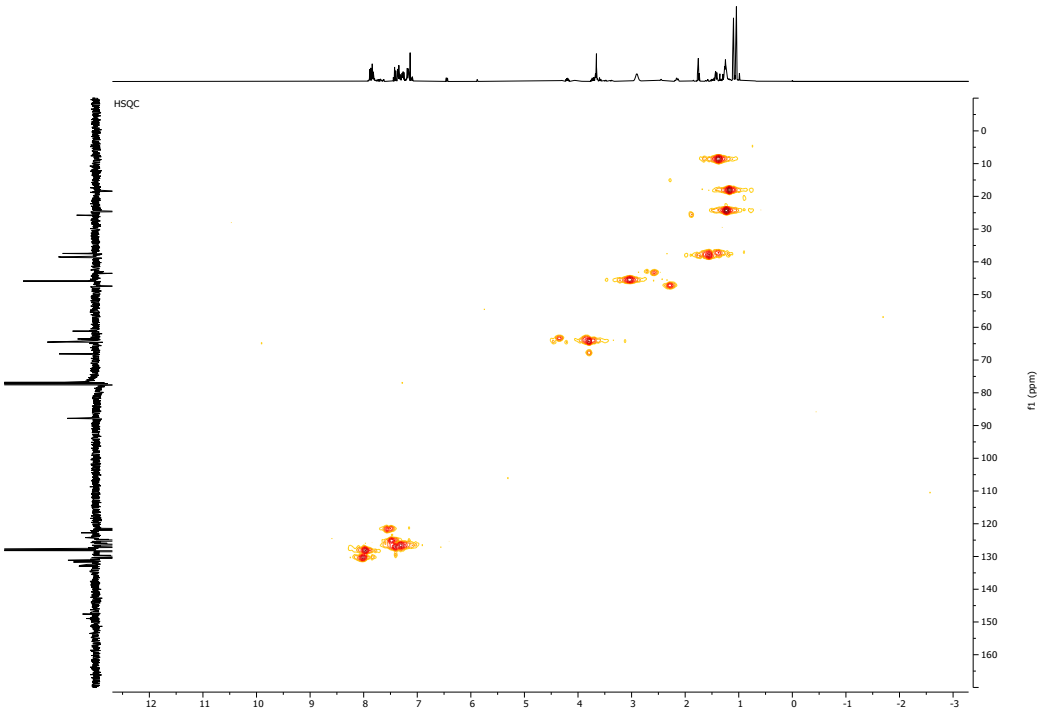

Figure S13. HSQC spectrum of **L3** ($CDCl_3$).

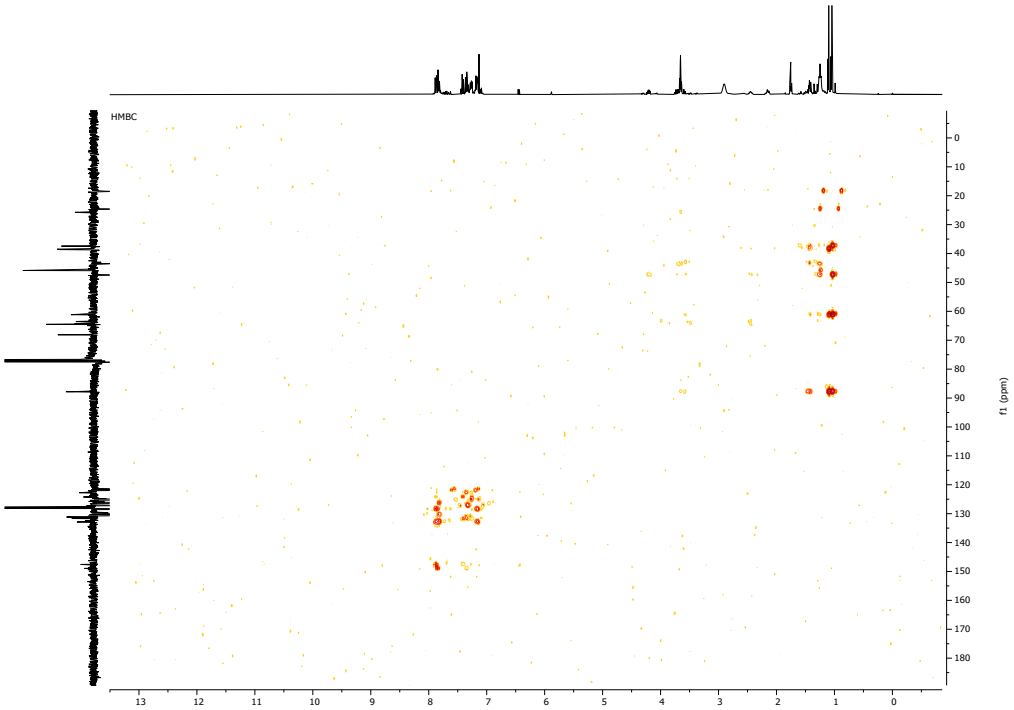

Figure S14. HMBC spectrum of **L3** ($CDCl_3$).

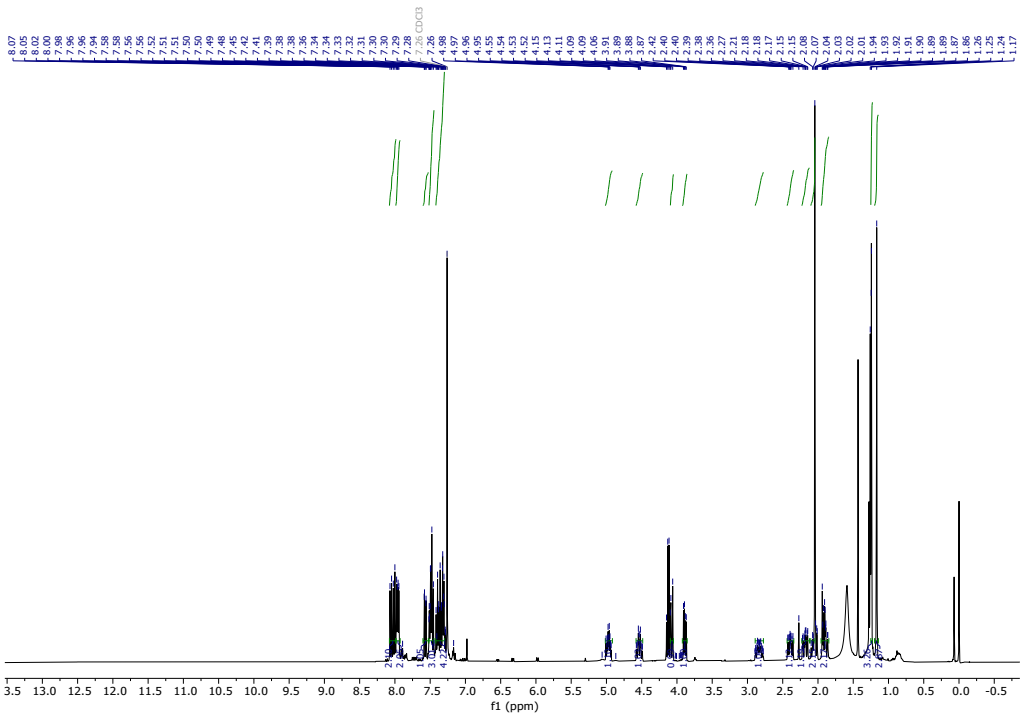

Figure S15. ^{1}H NMR spectrum of **9a** in $CDCl_3$.

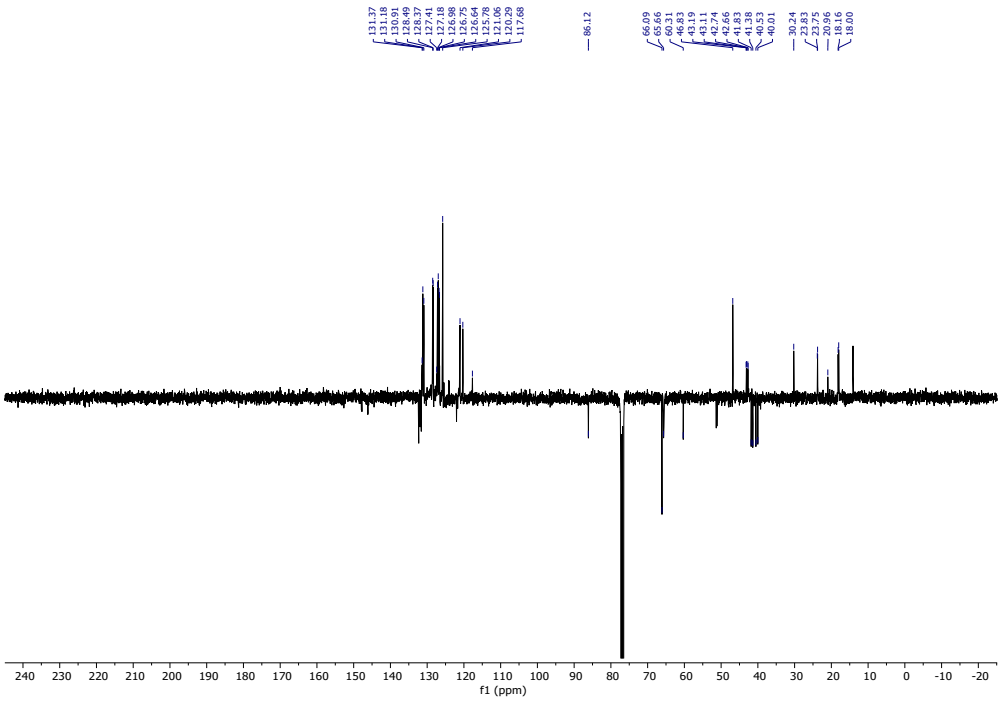

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$.

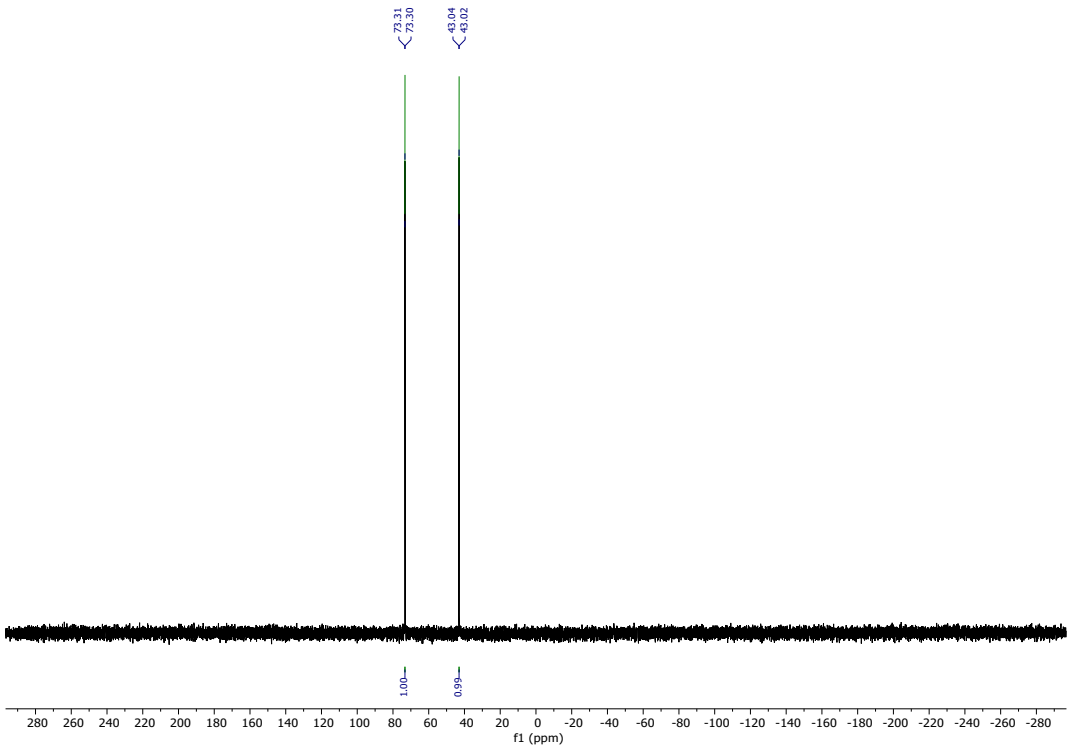

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$.

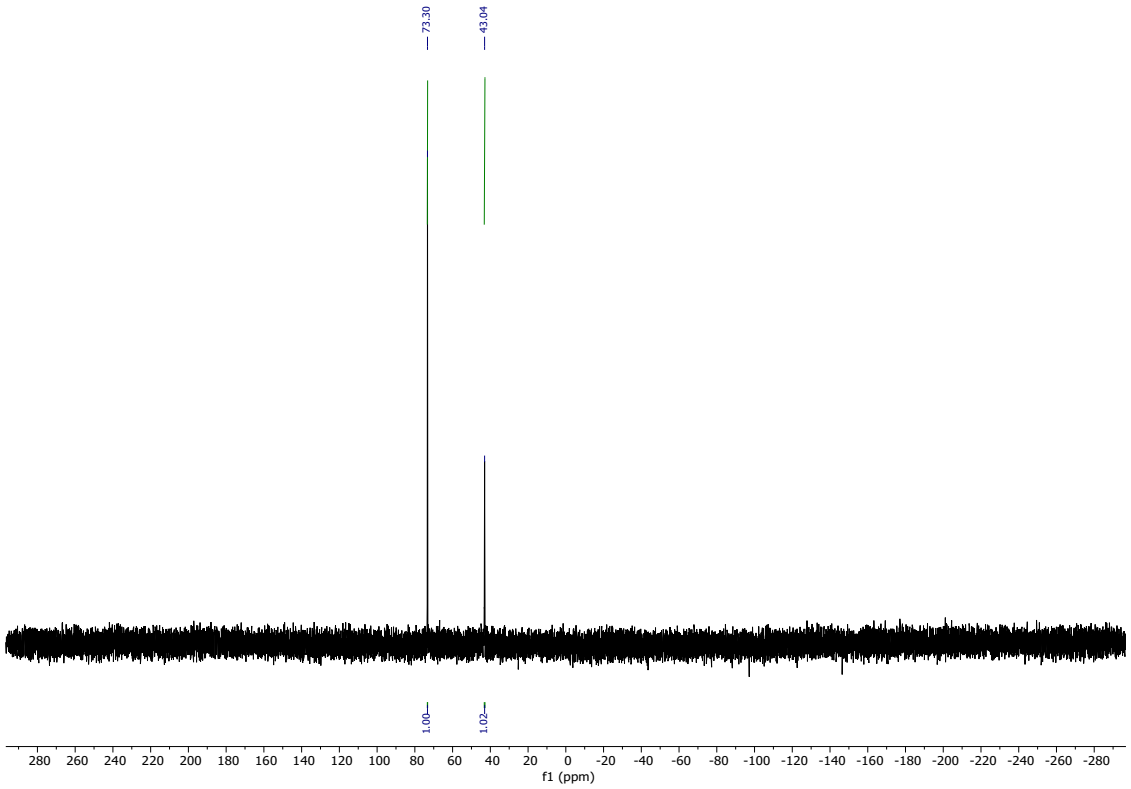

Figure S18. ^{31}P NMR spectrum of **9a** in $CDCl_3$.

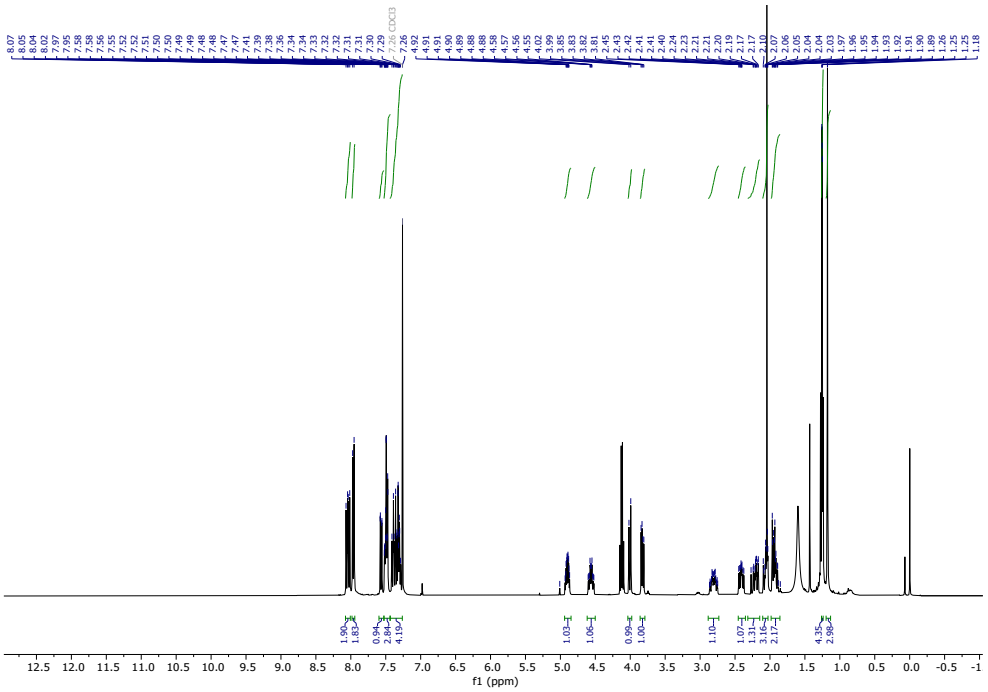

Figure S19. ^{1}H NMR spectrum of **9b** in $CDCl_3$.

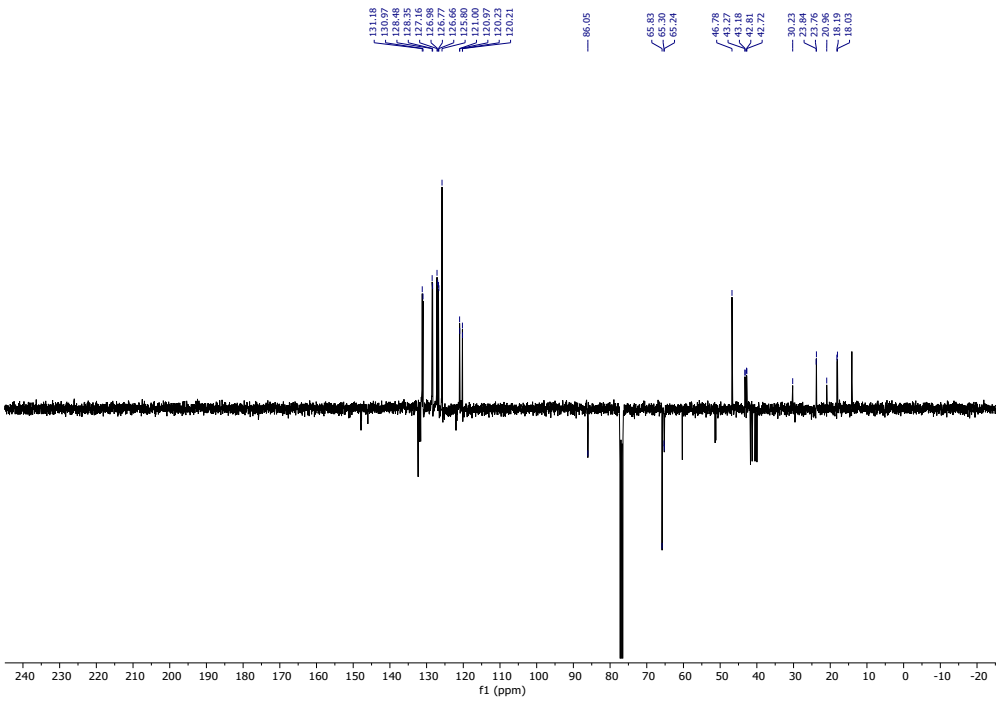

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **9b** in $CDCl_3$.

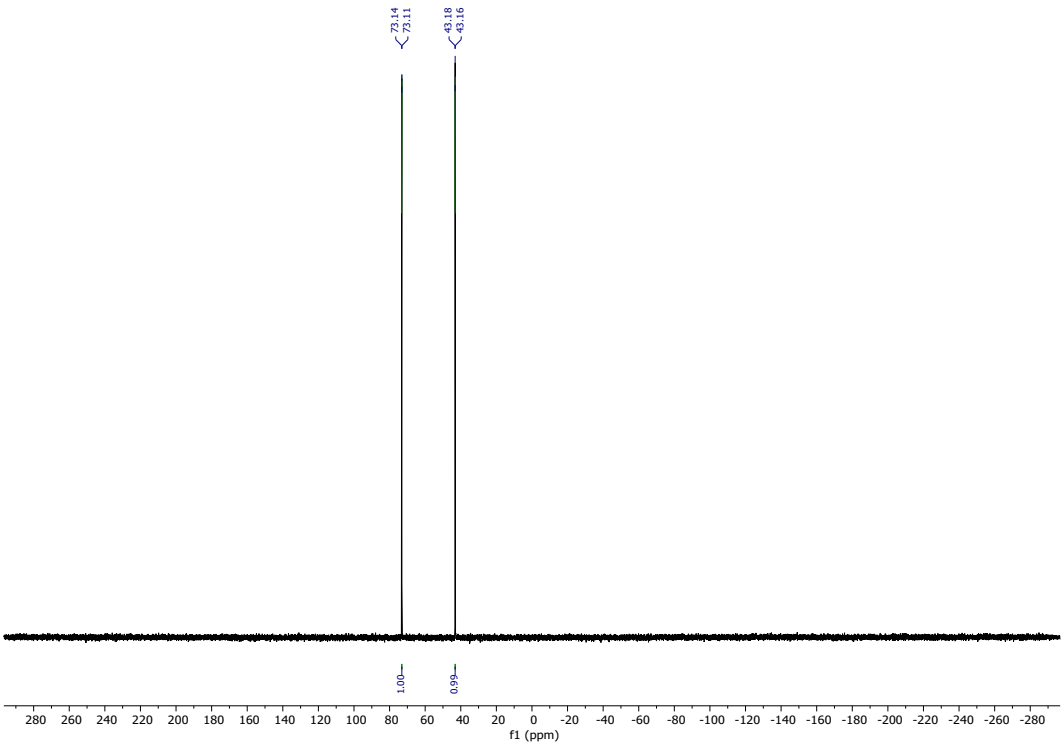

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **9b** in $CDCl_3$.

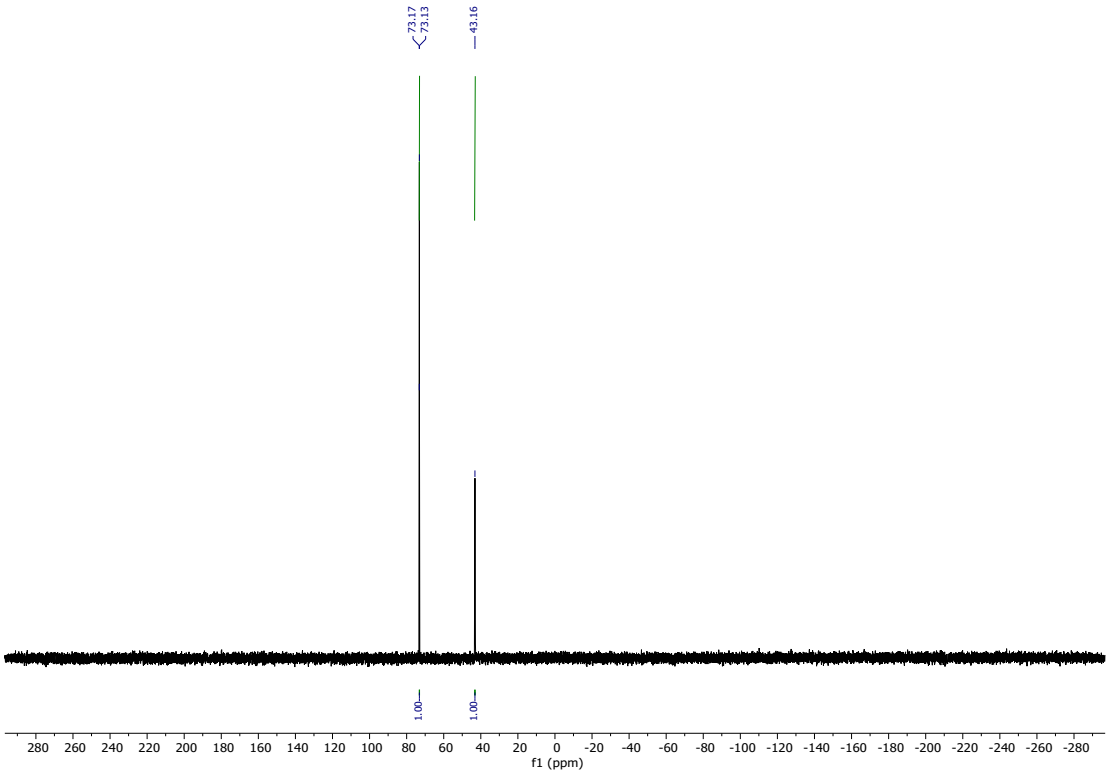

Figure S22. ^{31}P NMR spectrum of **9b** in $CDCl_3$.

3. Chiral HPLC reports

The chemical and optical purity of **9a**,**b** was confirmed by HPLC using a chiral column. Overall, chemical purities were in the range of 98-100%. **9a**: Eluent: 20% *i*PrOH, 80% *n*-hexane

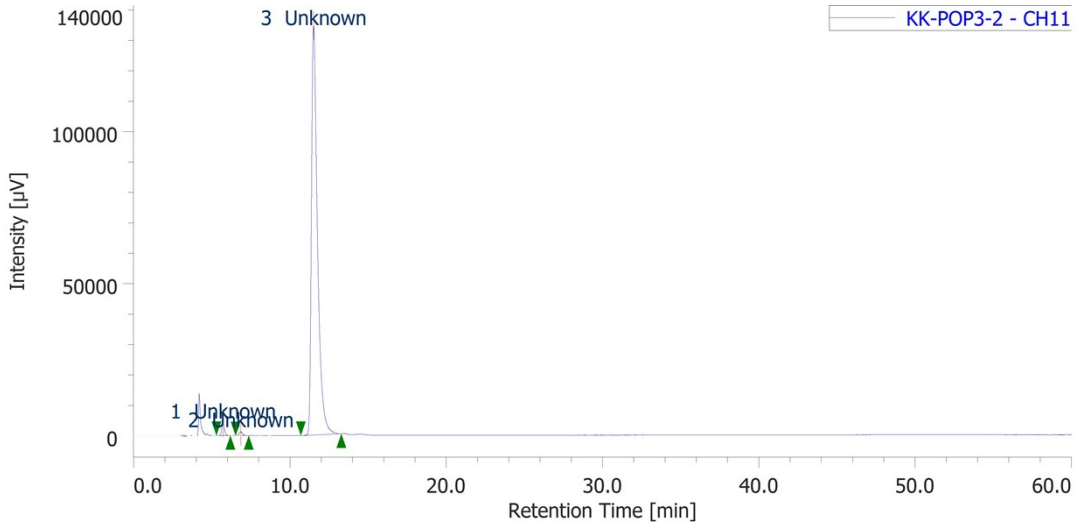

Figure S23. Chromatogram of **9a**.

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	5.710	50524	4117	1.375	2.941	N/A	5258	3.415	1.216	
2	Unknown	11	6.847	18112	1326	0.493	0.947	N/A	6039	9.210	1.235	
3	Unknown	11	11.507	3606815	134514	98.133	96.111	N/A	4830	N/A	1.746	

9b:

Eluent: 20% *i*PrOH, 80% *n*-hexane

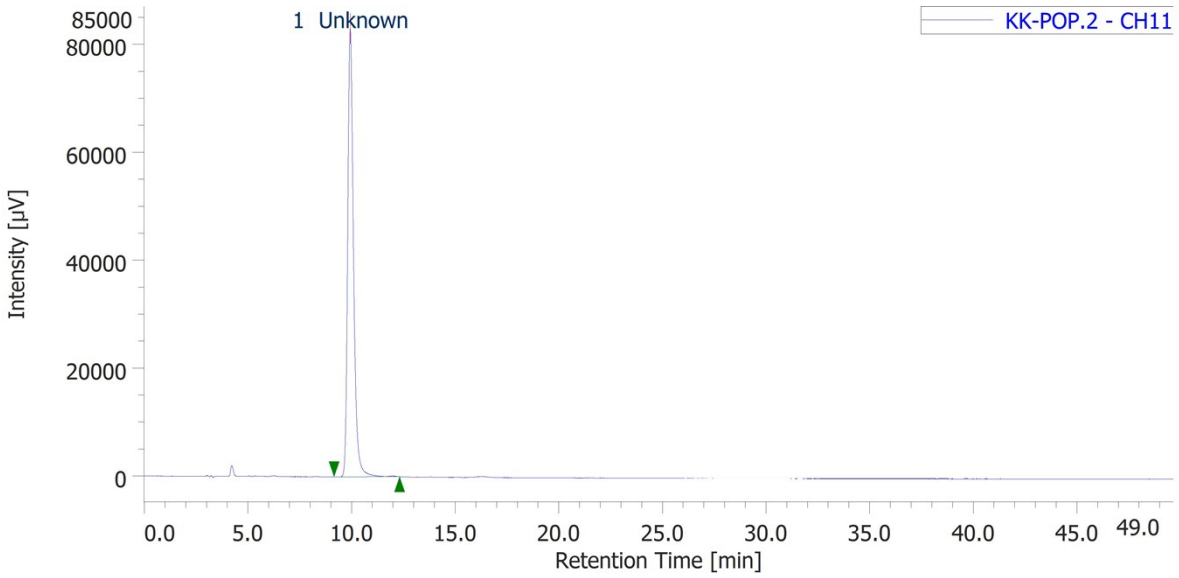

Figure S24. Chromatogram of **9b**.

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
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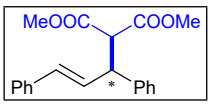

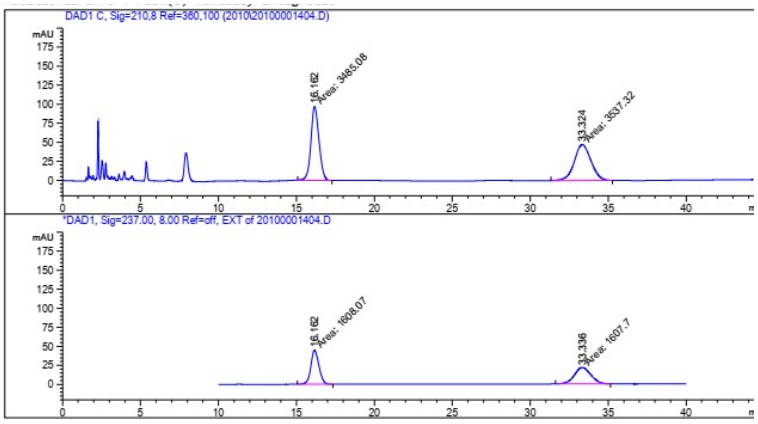


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Figure S25. Racemic P1.

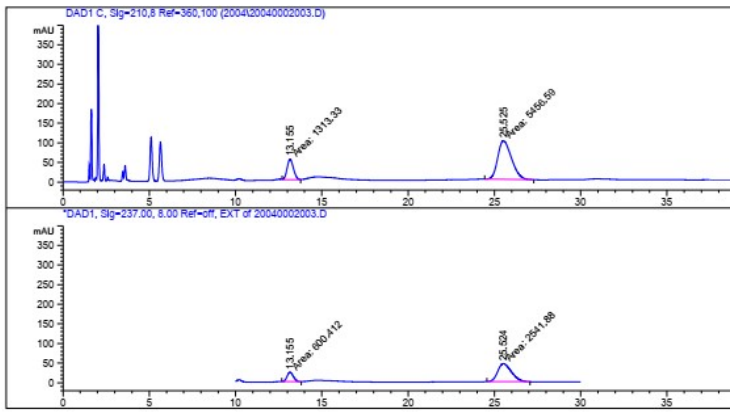


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Figure S26. Enantioenriched P1.

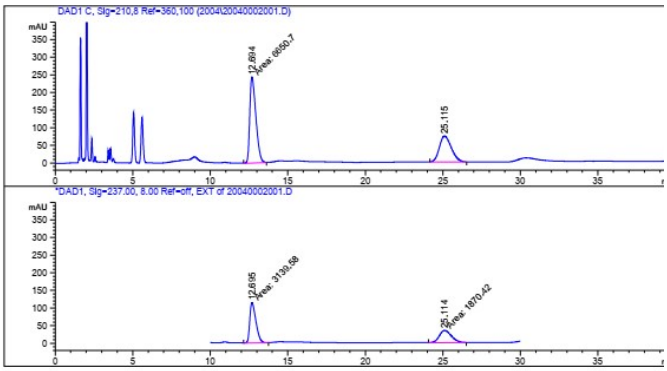


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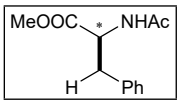
Figure S27. Enantioenriched P1.



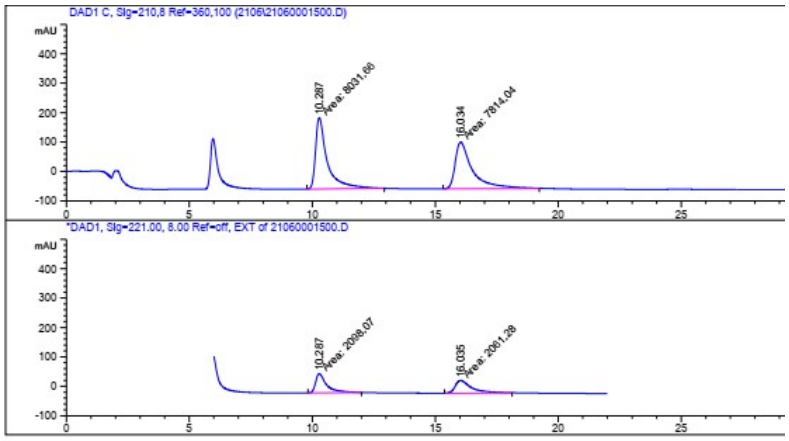



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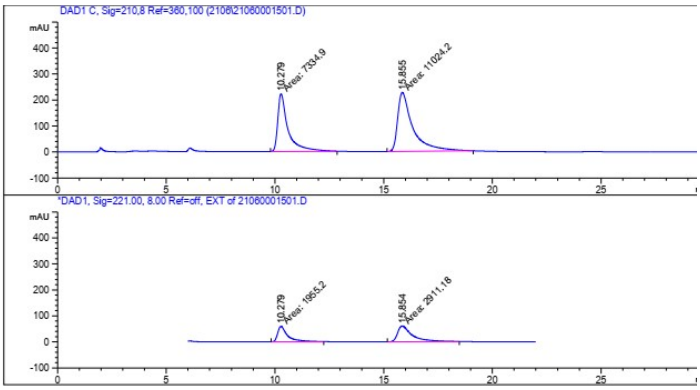
Figure S28. Racemic P3.

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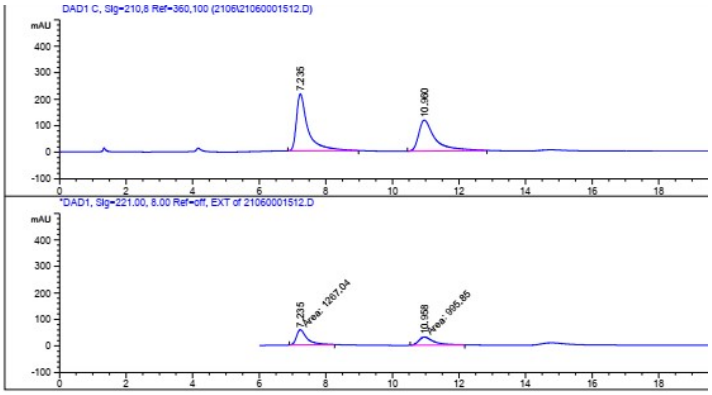
----|-------|----|-------|----------|----------|--------|
   1  10.279 MM    0.5497 7334.89551  222.40221  39.9524
   2  15.855 MM    0.8088 1.10242e4   227.16539  60.0476

Totals :                  1.83591e4   449.56760
```

Figure S29. Enantioenriched P3.




```
=====================================================================
                    Area Percent Report
=====================================================================

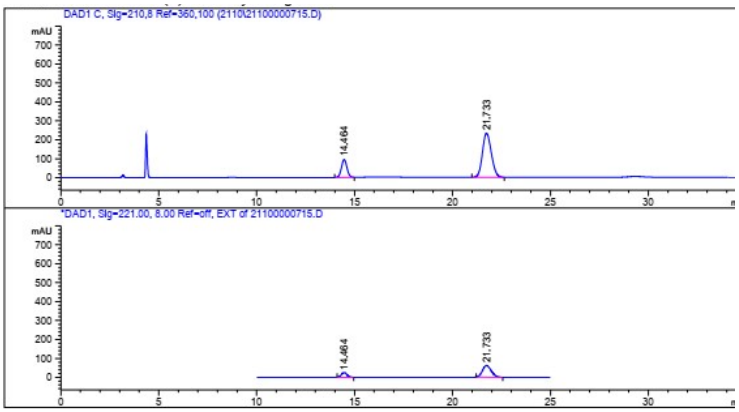
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.235 BB    0.3474 5185.61182  214.98224  56.2914
   2  10.960 BB    0.4958 4026.47803  116.91271  43.7086

Totals :                  9212.08984  331.89495
```

Figure S30. Enantioenriched P3.




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

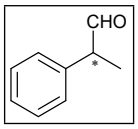

Signal 1: DAD1 C, Sig=210,8 Ref=360,100

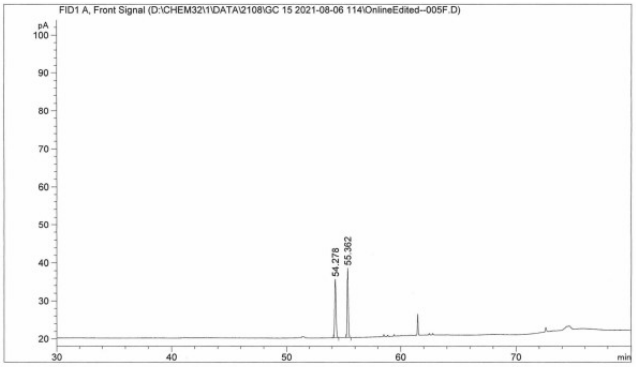
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.464 BB    0.3042 1855.39697   94.85580  20.0586
   2  21.733 BB    0.4954 7394.50293  233.56657  79.9414

Totals :                  9249.89990  328.42237
```

Figure S31. Enantioenriched P3.

4. GC traces






```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

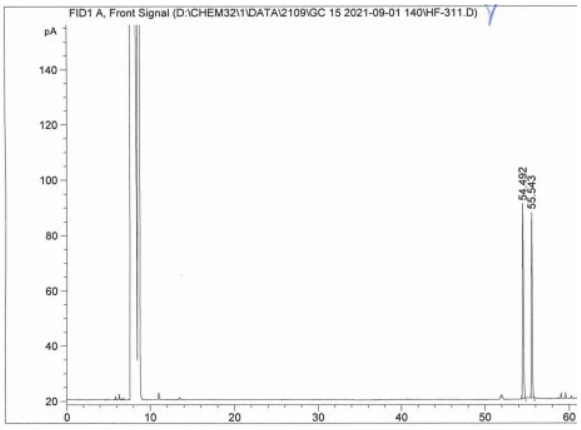

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]     [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  54.278 BB    0.1121  125.12329   15.35218 50.36129
   2  55.362 BB    0.0950  123.32803   18.21740 49.63871

Totals :                  248.45132   33.56958

=====================================================================
                    *** End of Report ***
```

Figure S32. Racemic P2.



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	54.492	BB	0.1165	588.93976	70.48726	55.34556
2	55.543	BB	0.0946	475.17398	67.08473	44.65444
Totals :				1064.11374	137.57199	

*** End of Report ***

Figure S33. Enantioenriched P2.

5. X-ray crystallography data

The data was collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation and ω-scan rotation. Data reduction was performed with CrysAlisPro [1], including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved with SHELXT [2] using dual-space methods and refined with SHELXL [3]. Hydrogen atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with DIAMOND-4 [4].

CCDC deposition number 2302227 for 9b contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Table S1. Crystal data and structure refinement for **9b**.

Empirical formula	$C_{30}H_{28}O_4P_2S_2$	
Formula weight	578.58	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 743.04(1) pm	α = 90°
	b = 1677.05(3) pm	β = 90°
	c = 2253.42(3) pm	γ = 90°
Volume	2.80802(7) nm^3	
Z	4	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.339 mm^{-1}	
F(000)	1208	
Crystal size	0.52 x 0.20 x 0.13 mm^3	
Theta range for data collection	2.178 to 27.712°	
Index ranges	$-9 \le h \le 8$, $-21 \le k \le 21$, $-29 \le l \le 29$	
Reflections collected	39714	
Independent reflections	6143 [R(int) = 0.0619]	
Completeness to theta = 25.350°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.88899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6143 / 0 / 455	
Goodness-of-fit on F^2	1.031	

Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0765
R indices (all data)	R1 = 0.0458, wR2 = 0.0813
Absolute structure parameter	0.02(4)
Residual electron density	0.298 and -0.259 e·Å^{-3}

6. References

[1] Rigaku Corporation. CrysAlisPro Software System; Rigaku Oxford Diffraction: Wroclaw, Poland, 1995–2023.

[2] G. M. Sheldrick *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71** , 3–8.

[3] G. M. Sheldrick *Acta Crystallogr., Sect. C: Found. Adv.*, 2015, **71** , 3–8.

[4] Crystal Impact GbR, version 4.6.8; DIAMOND 4; Brandenburg, K: Bonn, Germany.