---- Supporting Information ----

Betti Base Derived P-Stereogenic Phosphine-Diamidophosphite Ligands with a Single Atom Spacer and their Application in Asymmetric Catalysis

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▪ General procedure for the synthesis of acetamidoacrylates

The acetamidoacrylate derivatives were synthesized following the literature procedure from the corresponding aromatic aldehyde and N-acetyl glycine.[1] The analytical data match with the previously reported data.

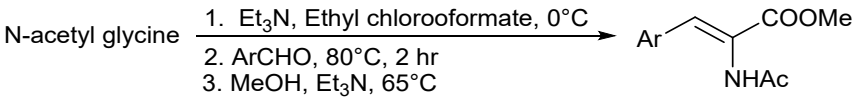

Figure S 1 *General procedure for the synthesis of dehydroamino acid derivatives*

▪ General procedure for the upscaling

The asymmetric hydrogenation upscaling experiments were performed in a stainless-steel autoclave charged with an insert suitable for up to 5 reaction vessels (10 mL each) with teflon mini stirring bars. In a typical experiment, a reaction vessel is charged with $[Rh(cod)_2]BF_4$ (1 mol%) and ligand (M/L= 1/1.1) and stirred for 10-15 mins in the appropriate solvent. The desired substrates (3.0 mmol) were added to the reaction vessel maintaining the inert atmosphere and the vessels were placed in high pressure autoclave. The autoclave was purged two times with nitrogen and three times with hydrogen. Finally, it was pressurized at the 10 bar of H_2 pressure at 25 ° C for 14 hrs. After the desired reaction time, the autoclave was depressurized, and the reaction mixture was diluted with EtOAc and filtered through a short pad of silica. The conversion was determined by GC and GC-MS measurement and the enantiomeric excess was measured by chiral HPLC.

- **NMR Spectra of the ligands**

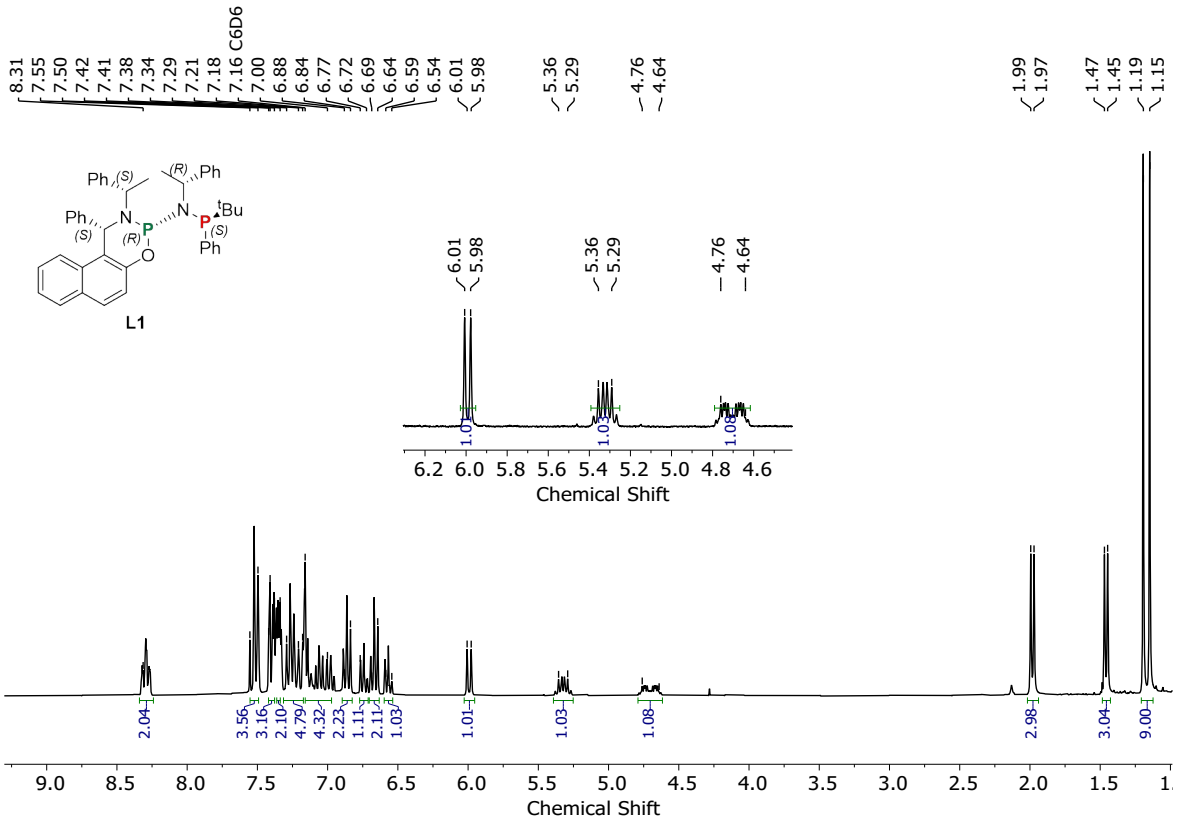

Figure S 2 *^{1}H NMR of* ***(S,S,R$_P$,R,S$_P$)- L1***

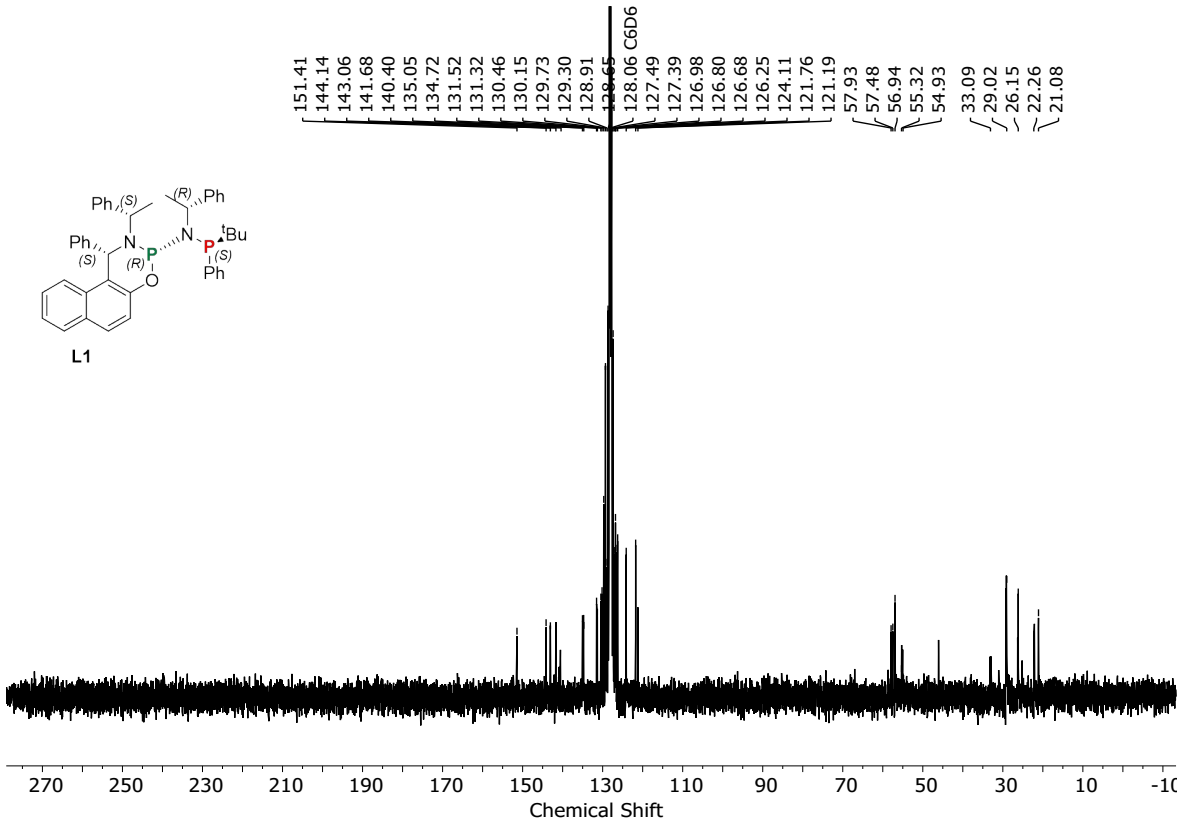

Figure S 3 L1 *^{13}C NMR of* ***(S,S,R$_P$,R,S$_P$)- L1***

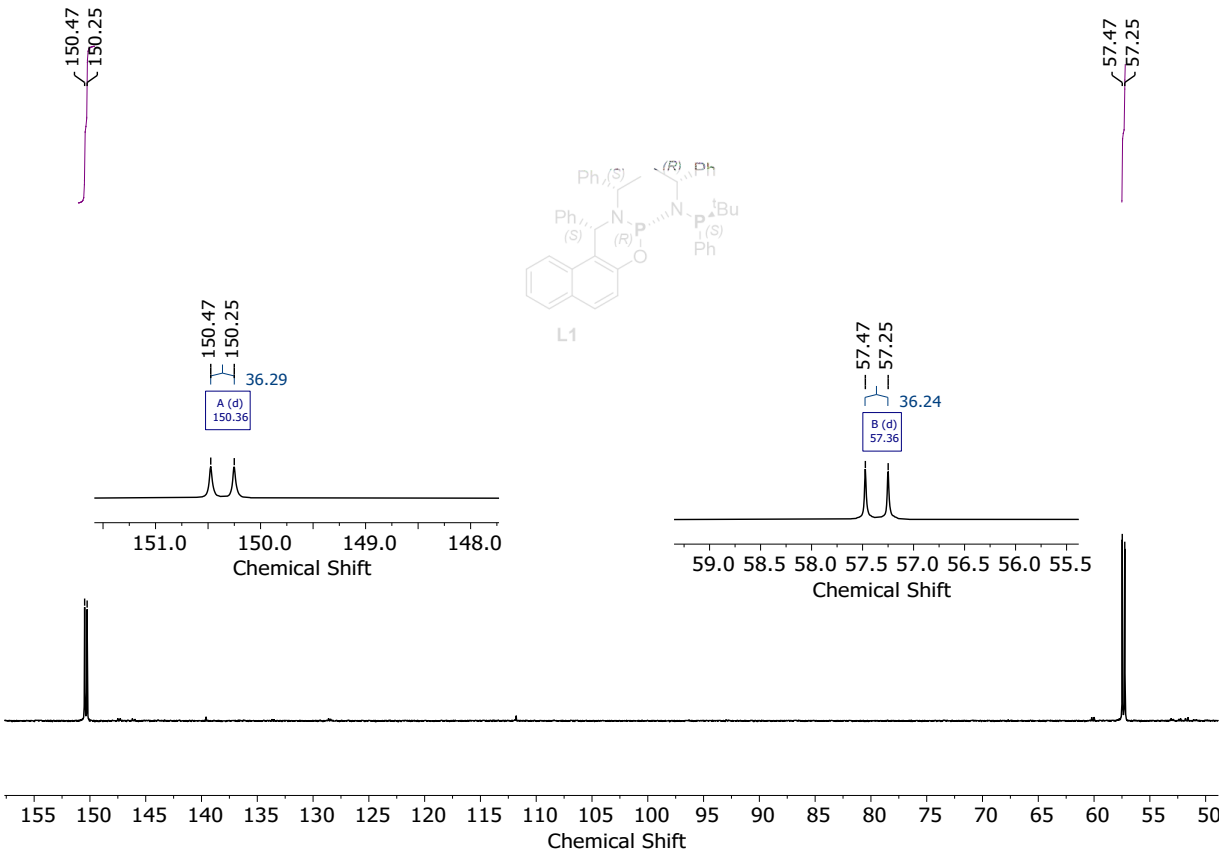

Figure S 4 *^{31}P {H} NMR of* ***(S,S,R_P,R,S_P)- L1***

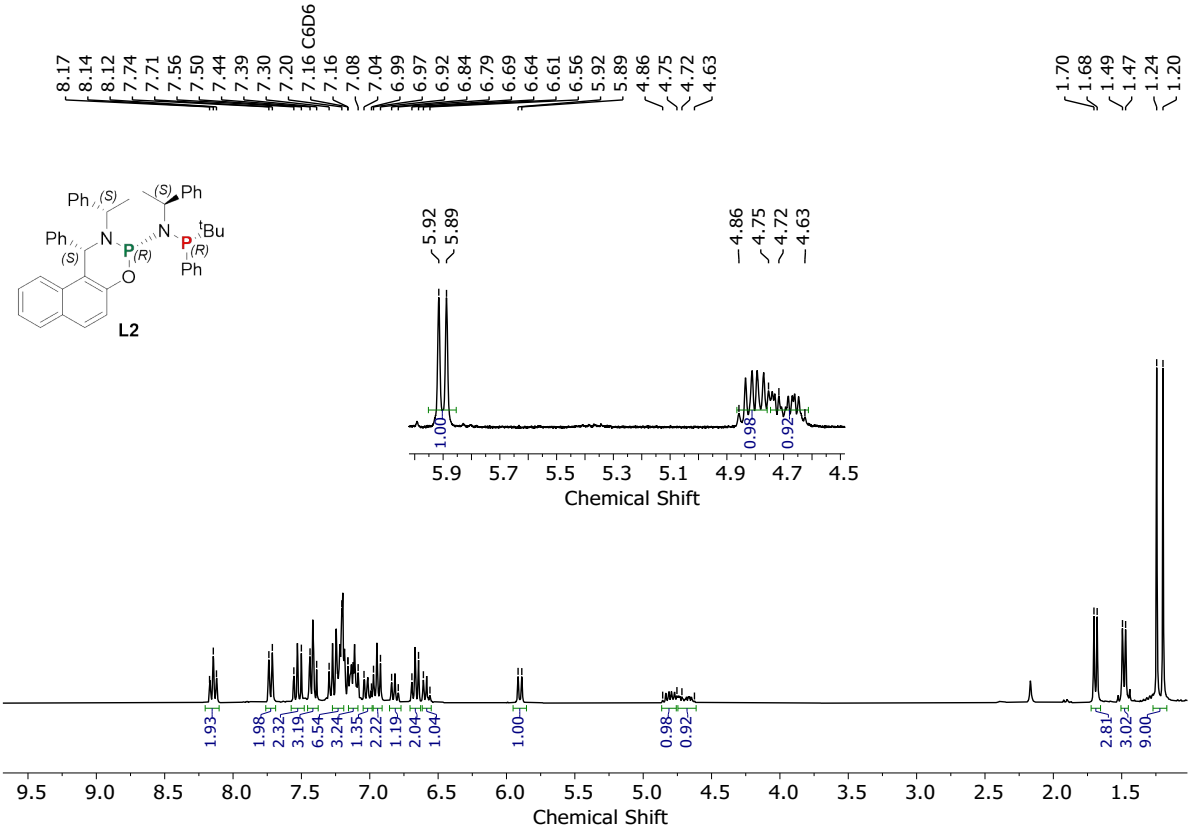

Figure S 5 *^{1}H NMR of* ***(S,S,R_P,S,R_P)- L2***

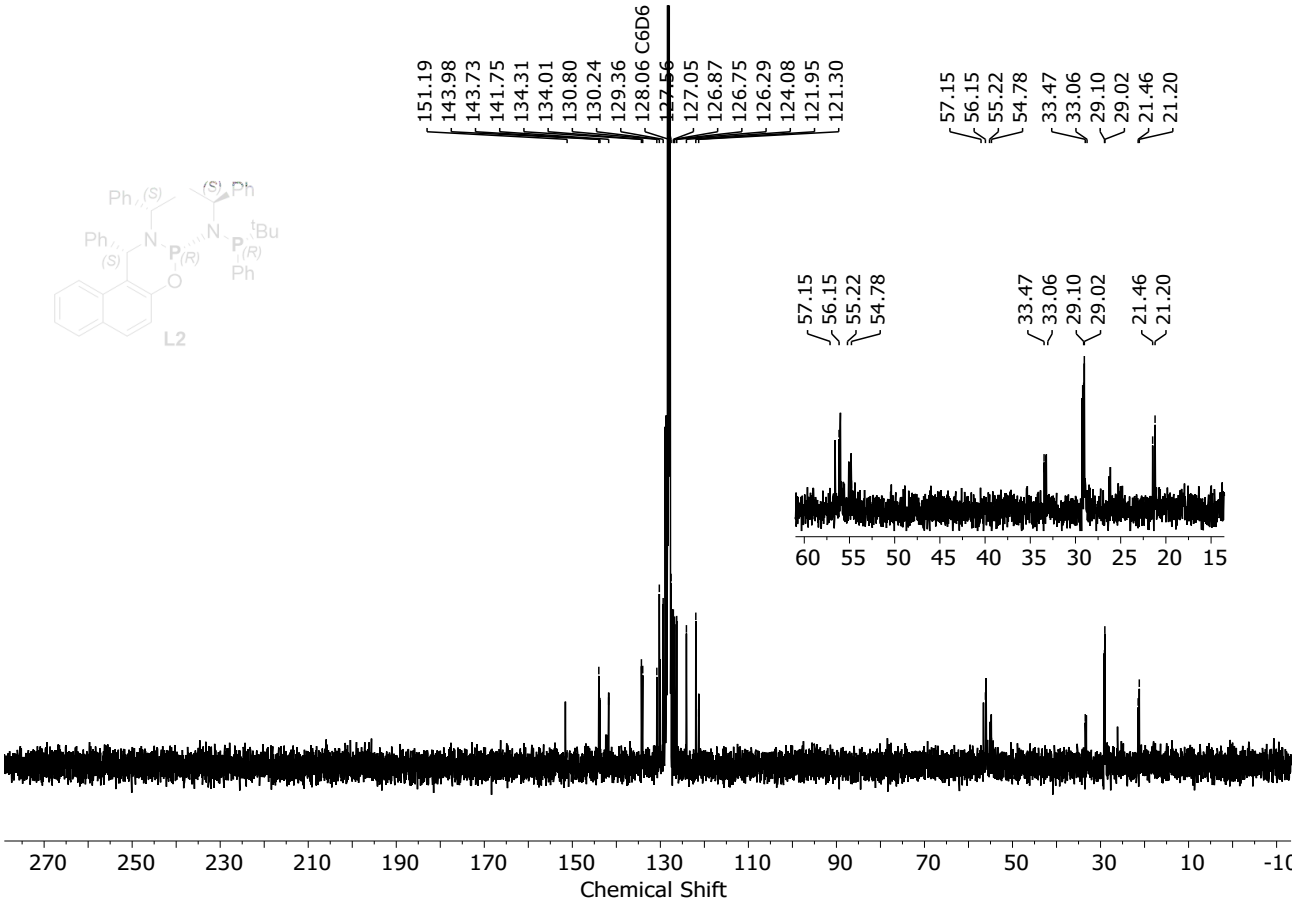

Figure S 6 *^{13}C NMR of* ***(S,S,R_P,S,R_P)- L2***

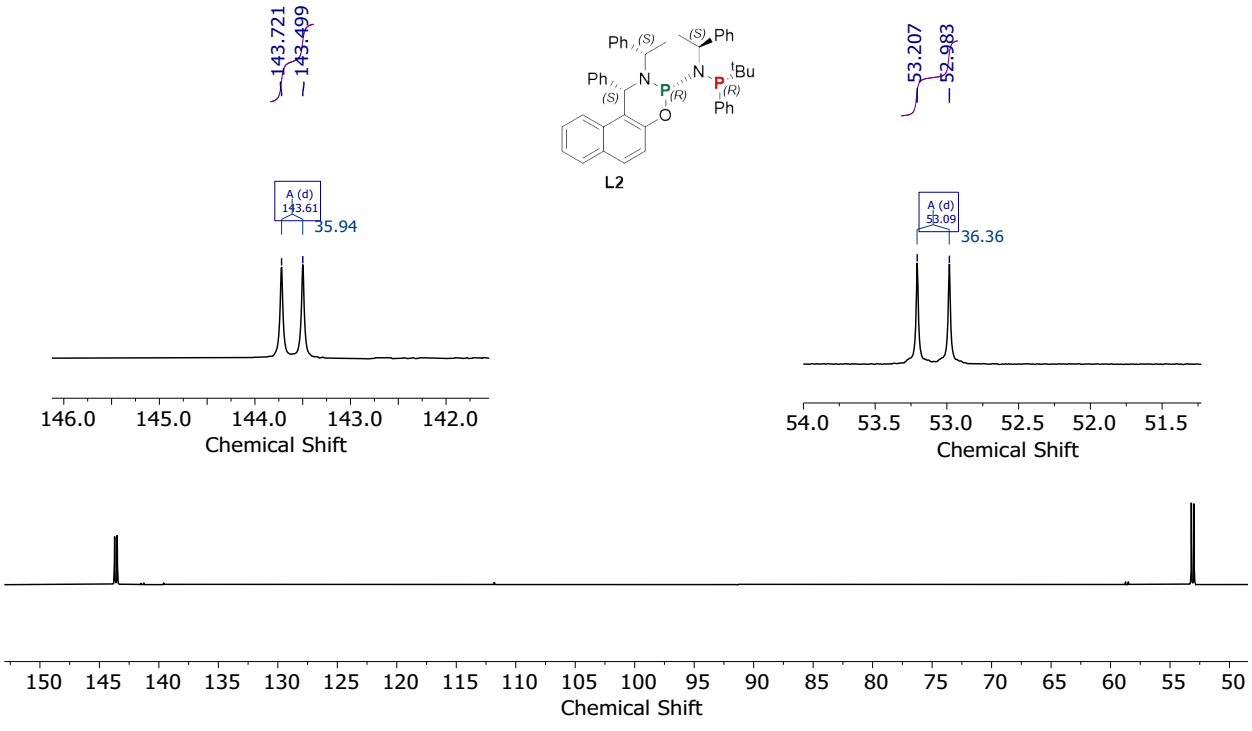

Figure S 7 *^{31}P {H} NMR of* ***(S,S,R_P,S,R_P)- L2***

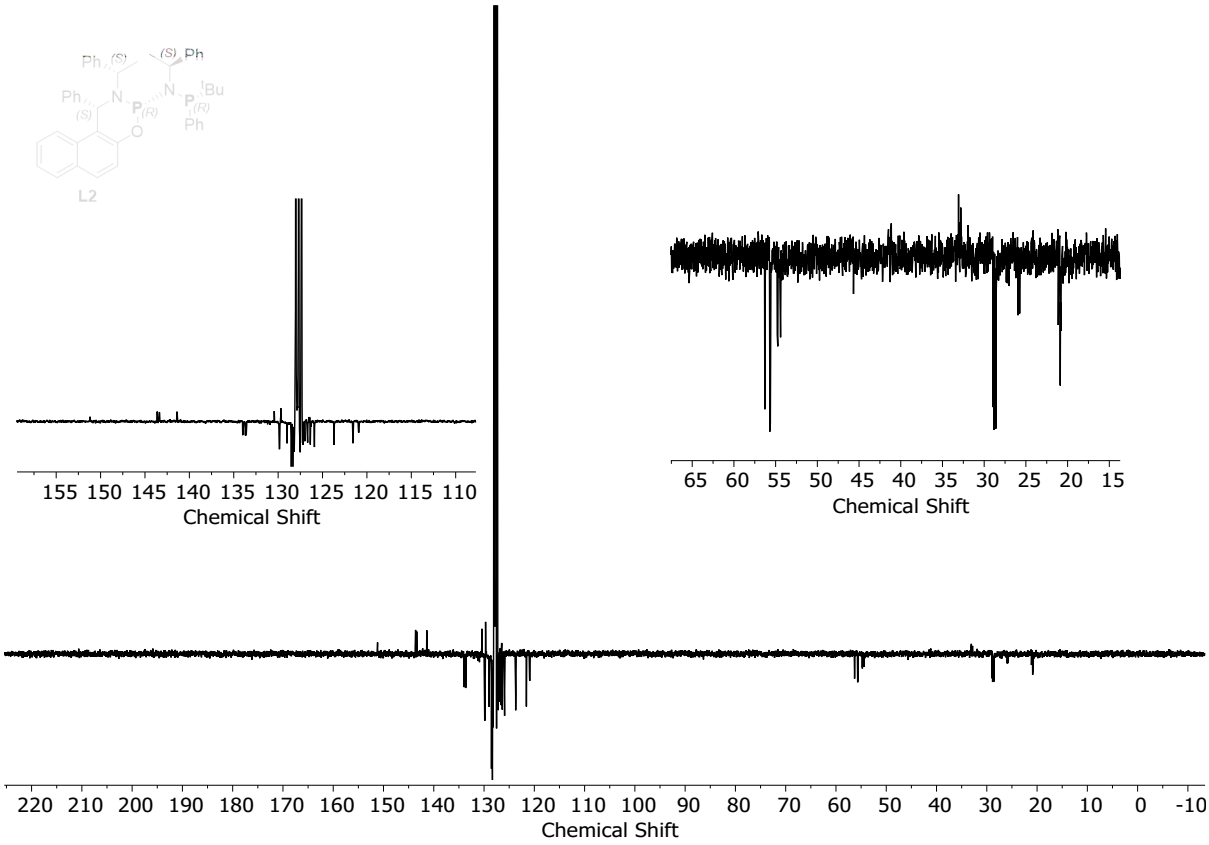

Figure S 8** APT of **(S,S,R_P,S,R_P)- L2

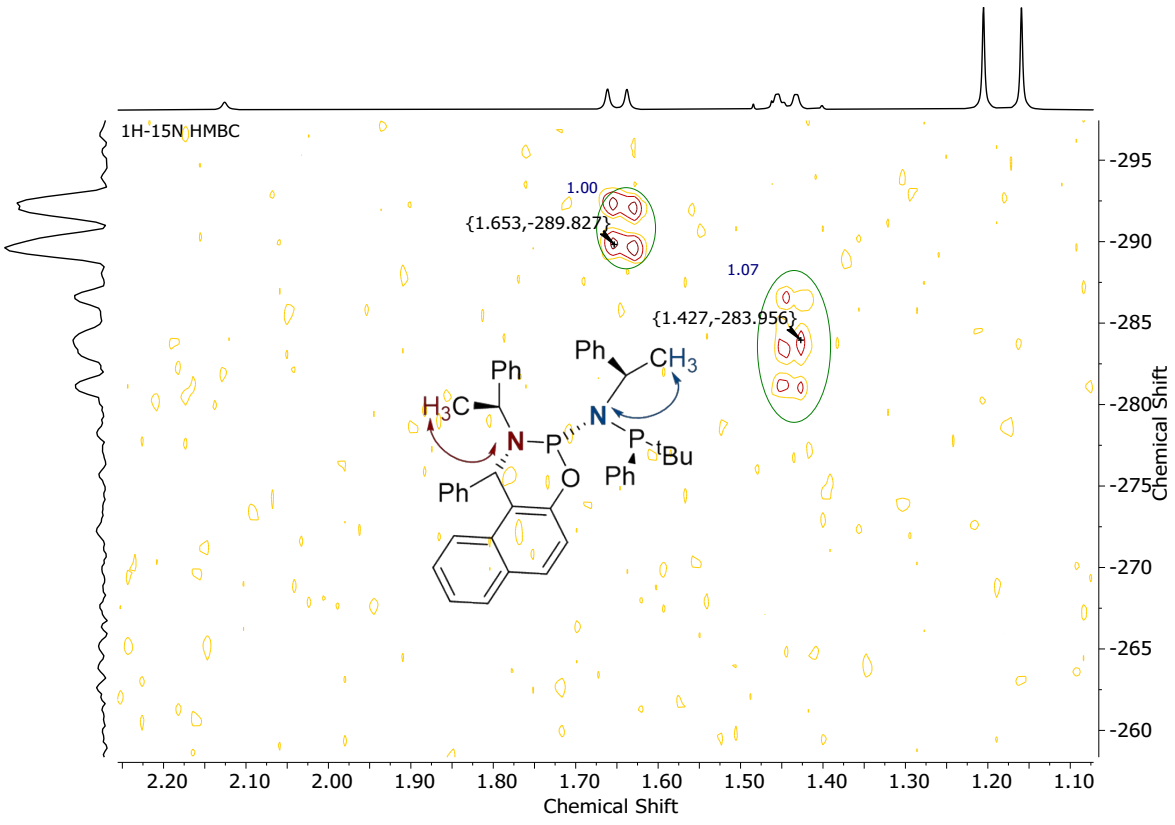

Figure S 9** ^{1}H-^{15}N-HMBC of **(S,S,R_P,S,R_P)- L2

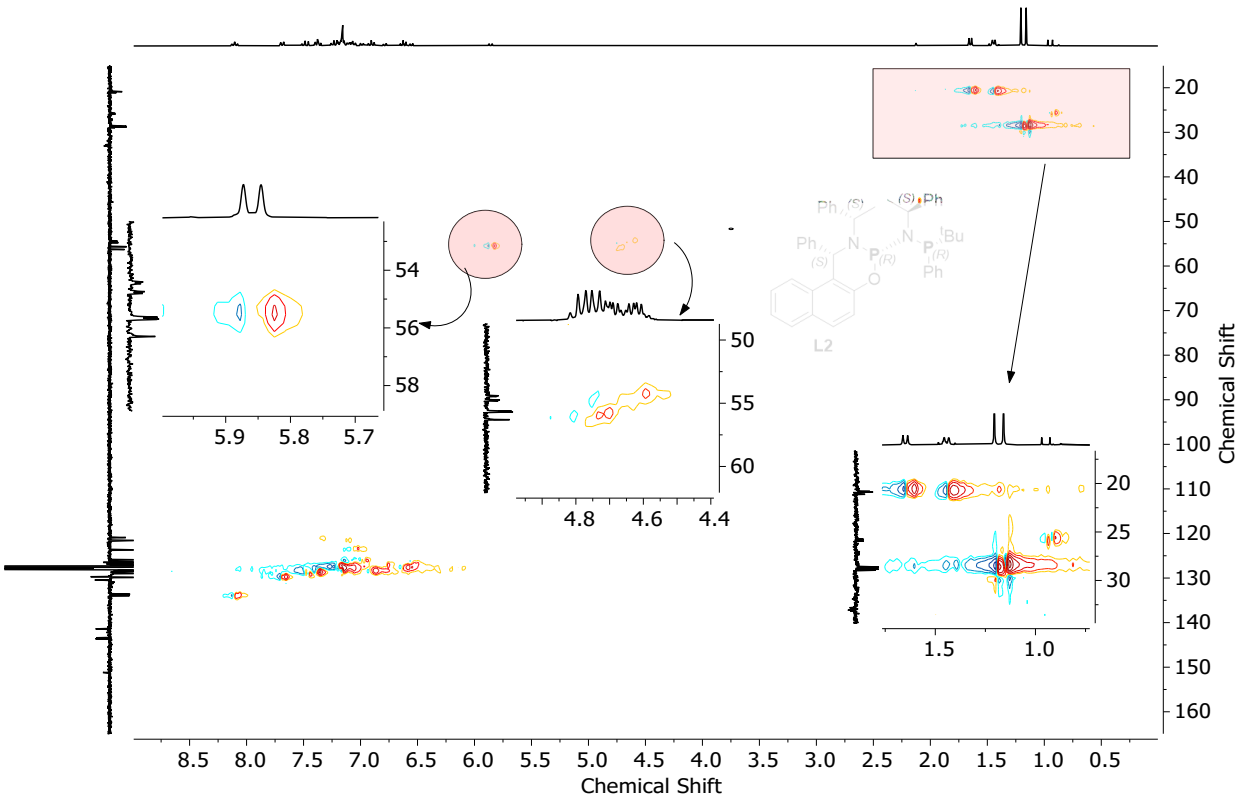

Figure S 10 *^{1}H-^{13}C-HSQC of* ***(S,S,R$_P$,S,R$_P$)- L2***

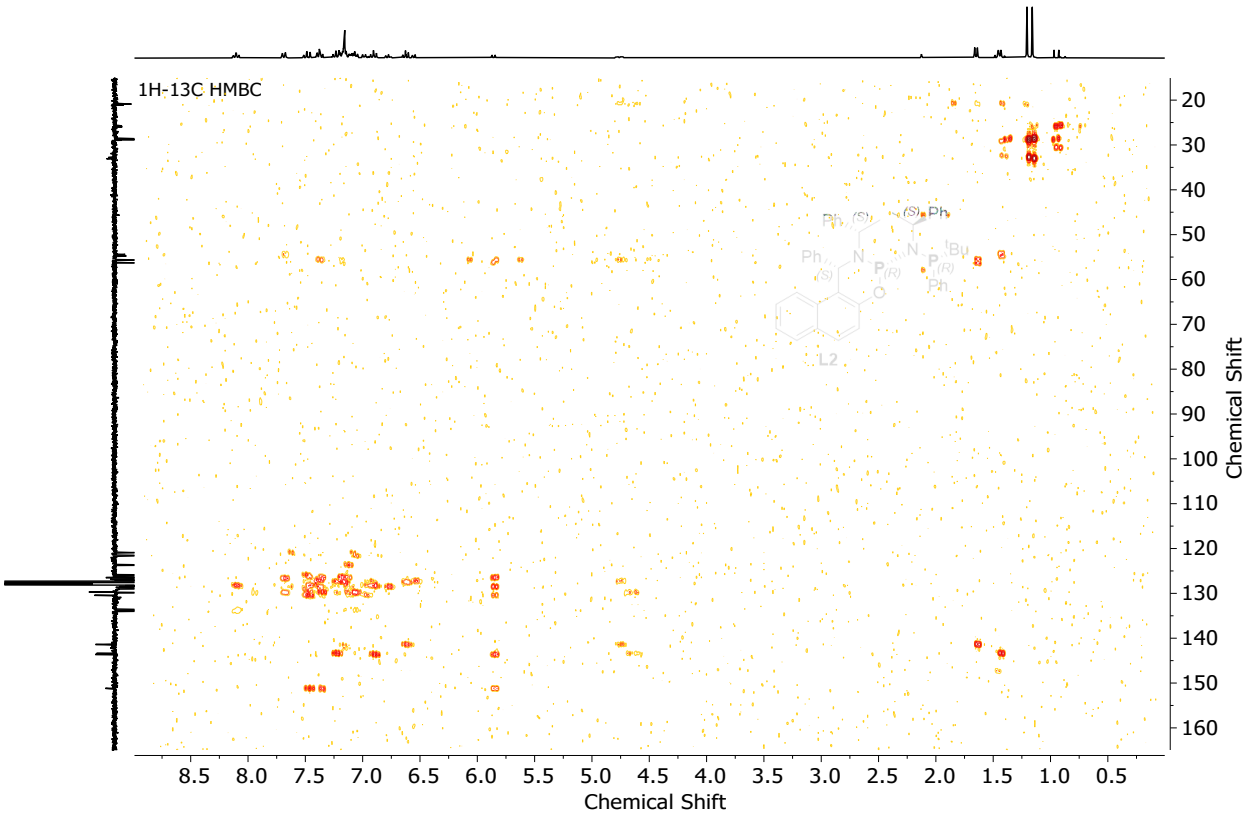

Figure S 11 *^{1}H-^{13}C-HMBC of* ***(S,S,R$_P$,S,R$_P$)- L2***

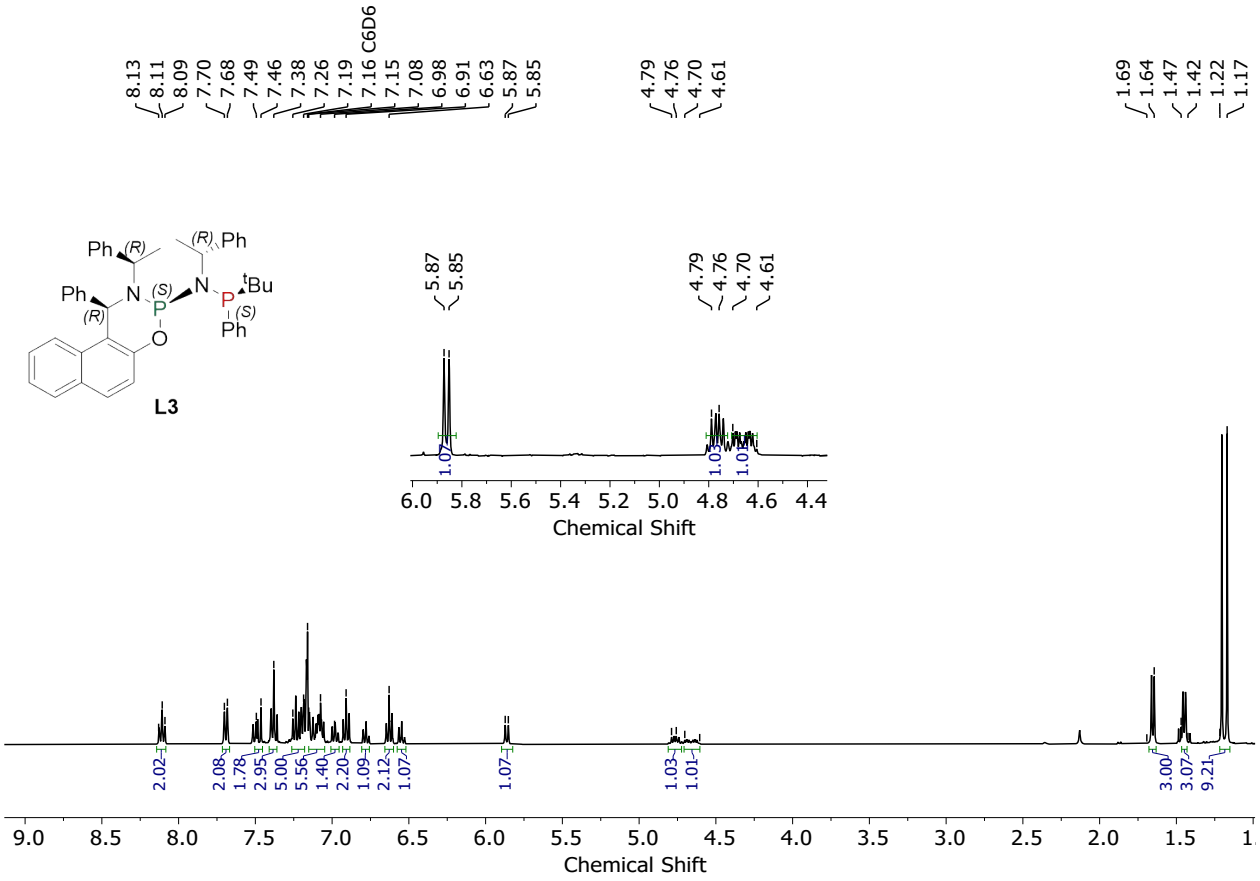

Figure S 12 *^{1}H NMR of* ***(R,R,S$_P$,R,S$_P$)- L3***

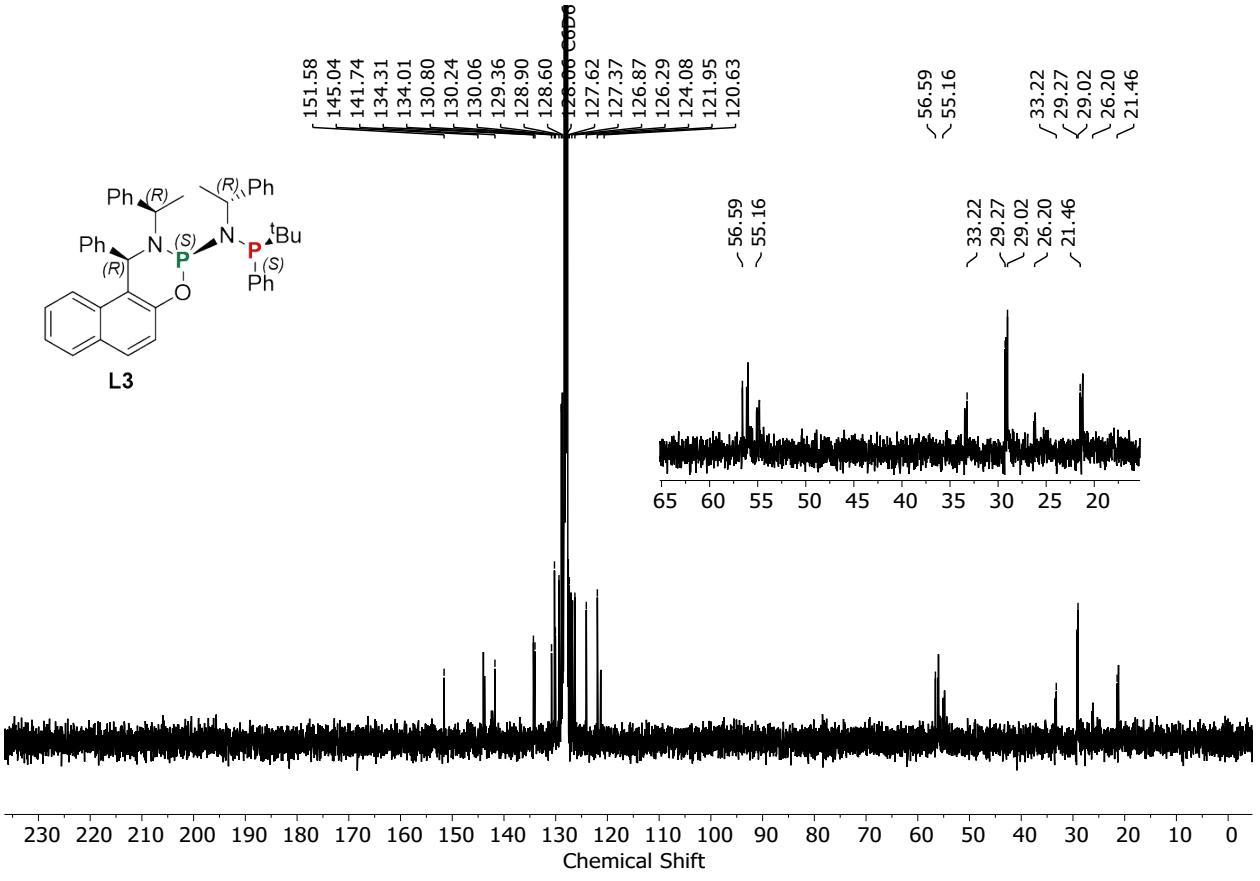

Figure S 13 *^{13}C NMR of* ***(R,R,S$_P$,R,S$_P$)- L3***

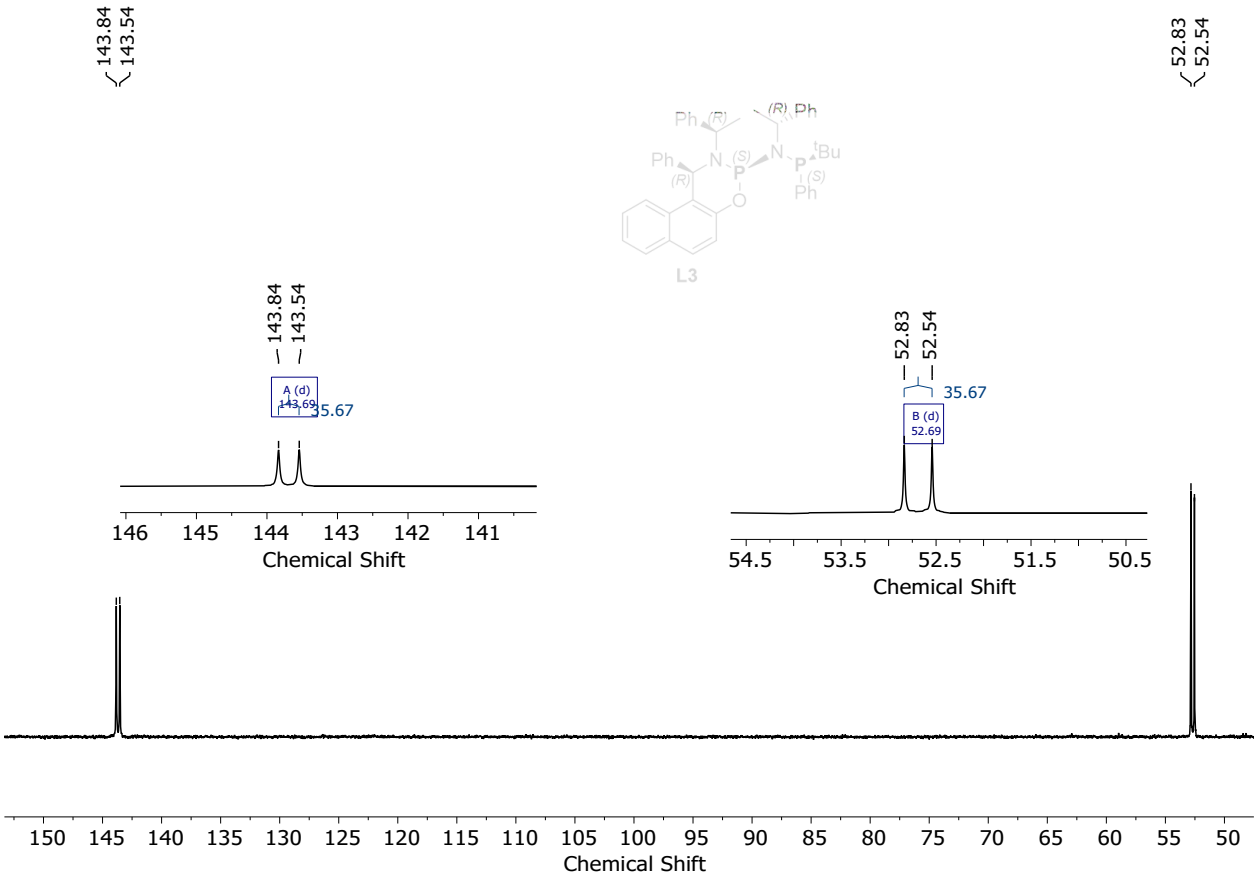

Figure S 14 *^{31}P {H} NMR of* ***(R,R,S_P,R,S_P)- L3***

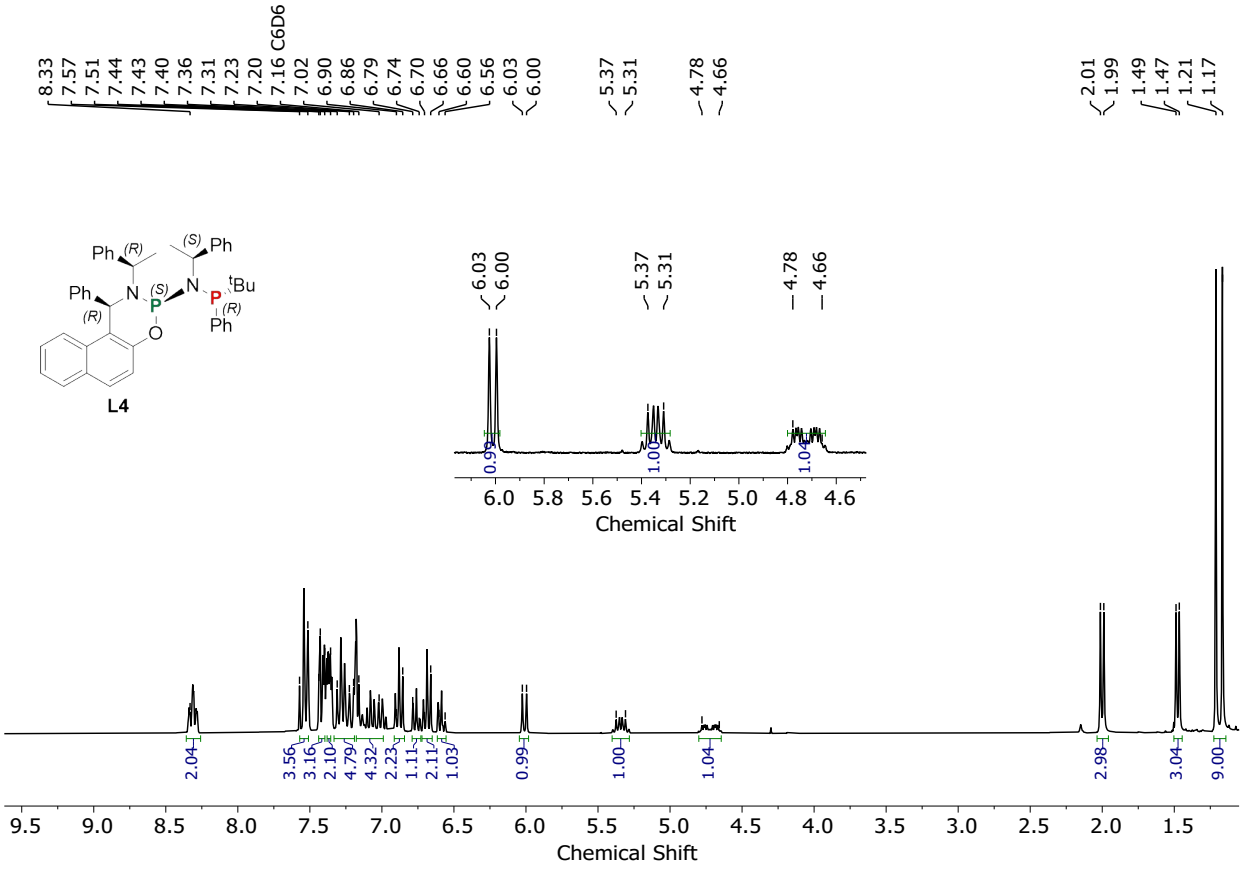

Figure S 15 *^{1}H NMR of* ***(R,R,S_P,S,R_P)- L4***

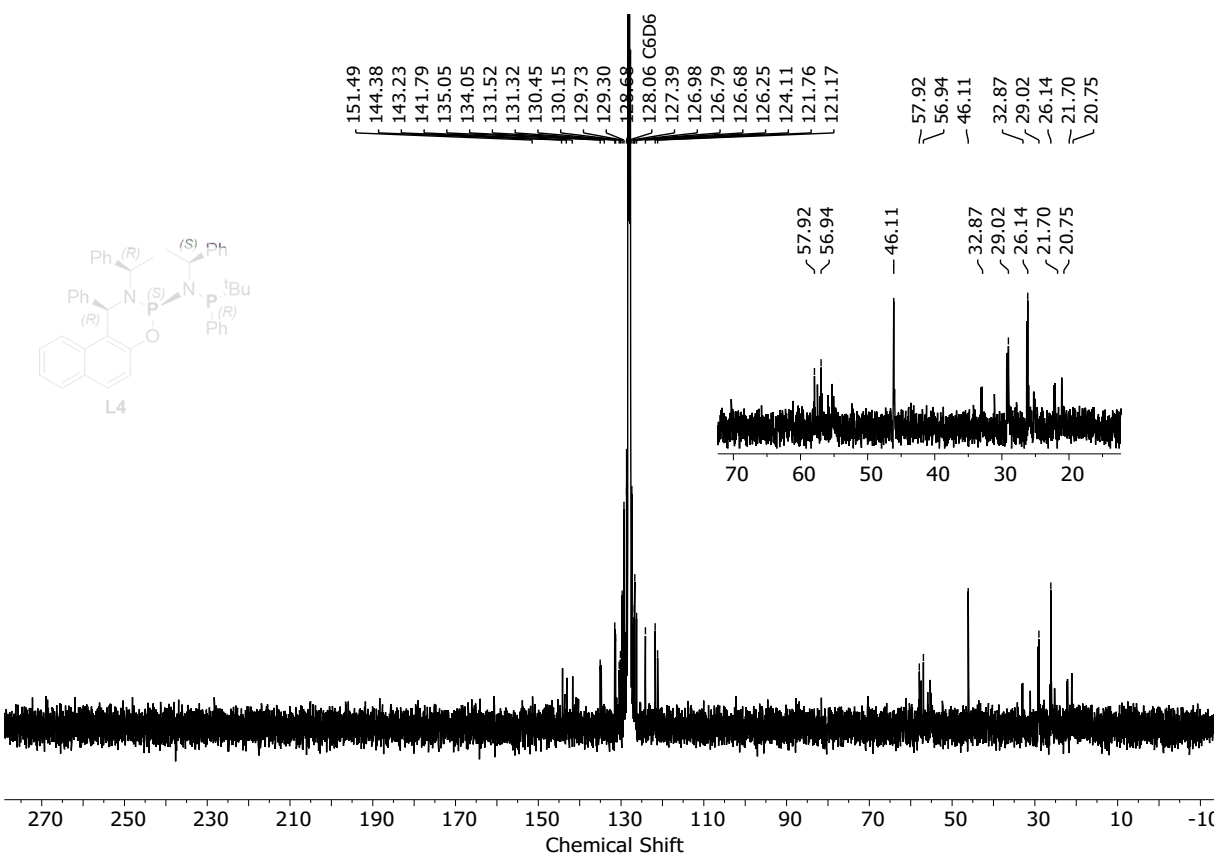

Figure S 16 *^{13}C NMR of* ***(R,R,S$_P$,S,R$_P$)- L4***

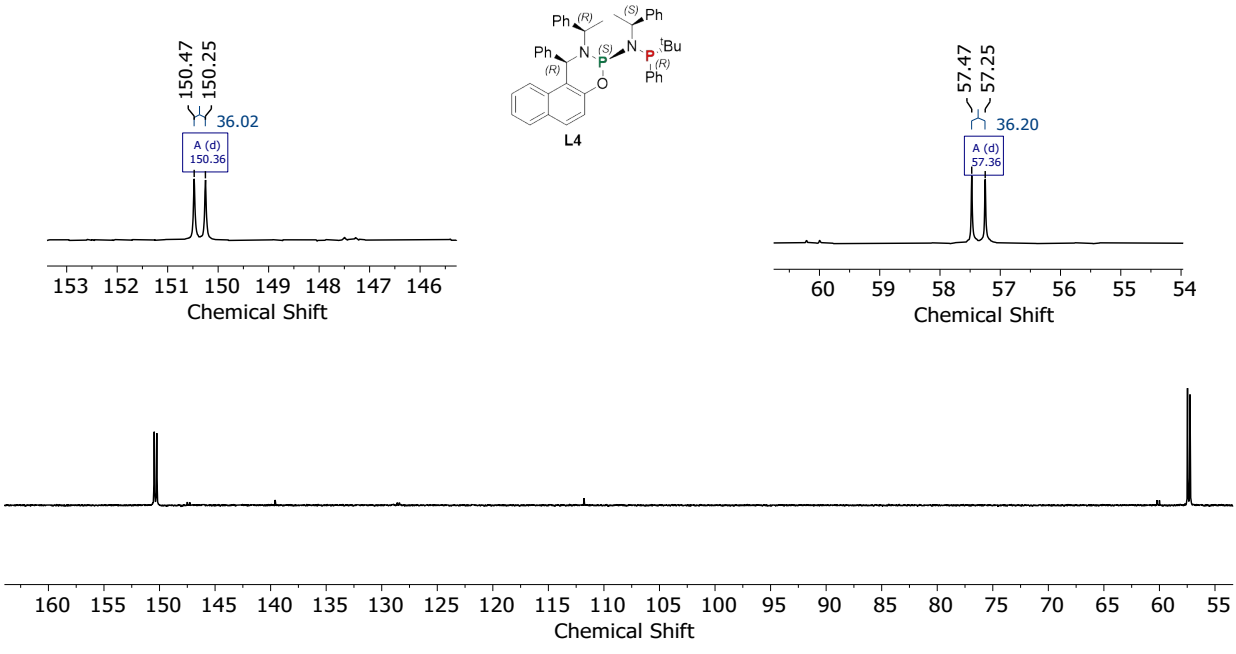

Figure S 17 *^{31}P {H} NMR of* ***(R,R,S$_P$,S,R$_P$)- L4***

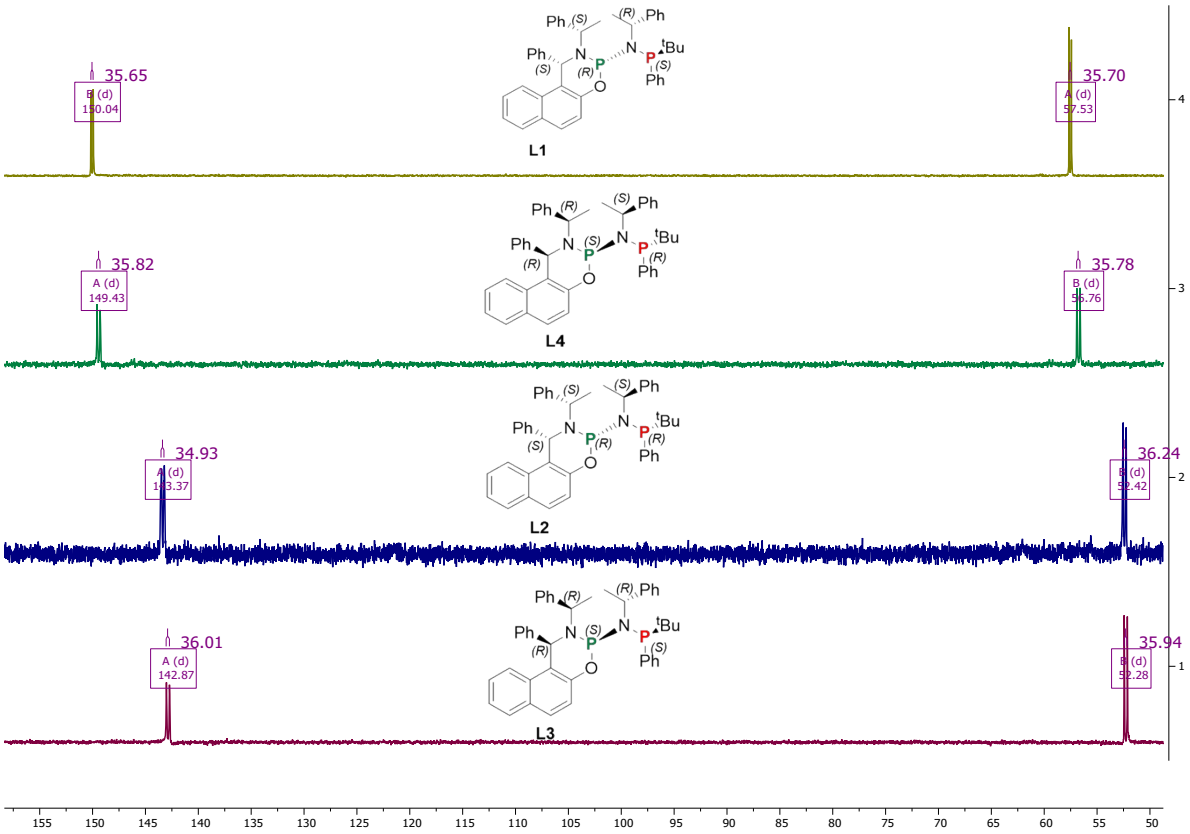

Figure S 18 *^{31}P {H} NMR of the possible ligand combination*

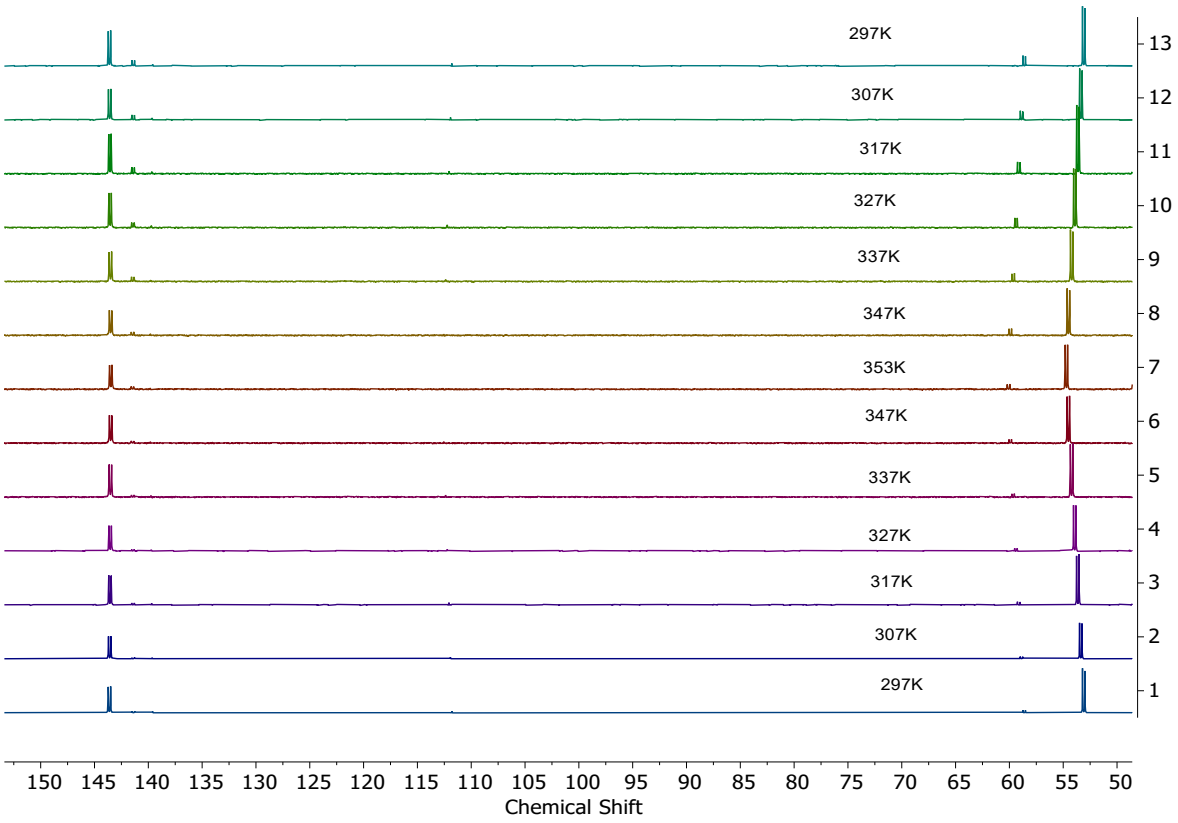

Figure S 19 *Temperature dependent epimerization of S,S,R_P,S,R_P-**L2.***

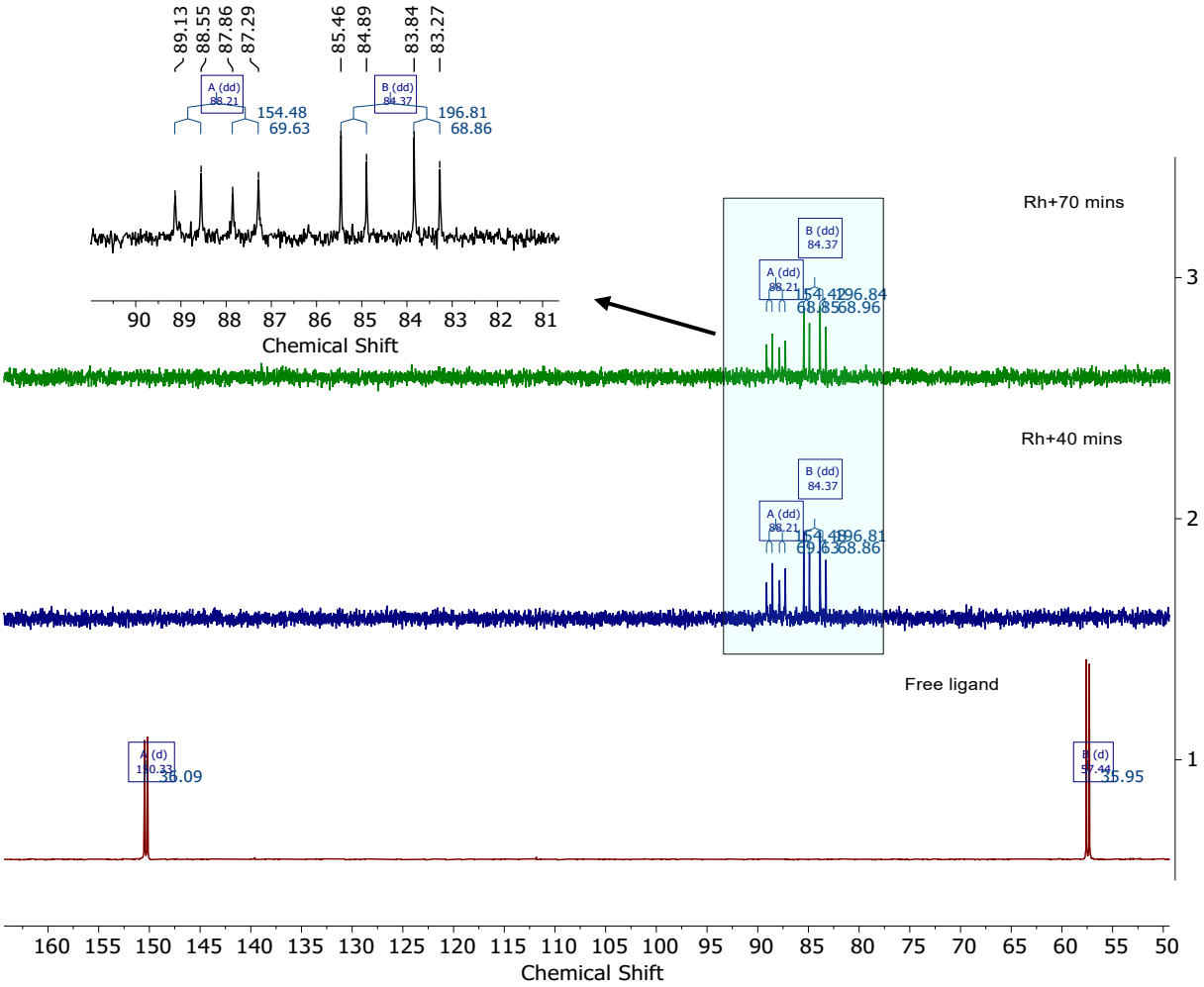

Figure S 20 *^{31}P NMR of In-situ Complexation studies using L2/Rh system (in Methanol-d_4).*

- **HRMS of the ligands**

ESI-TOF Accurate Mass Report

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Last modified: Friday, June 04, 2021 08:24:26

Sample Summary:

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58	21060404	SDC-L-1	'hakraborttty	666.2929	C43H44N2OP2	667.3007	667.3005	-0.3	-0.2

Figure S 21 *HRMS of* ***(S,S,R_P,R,S_P)- L1***

ESI-TOF Accurate Mass Report

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Last modified: Friday, June 04, 2021 08:27:01

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Figure S 22** HRMS of **(S,S,Rp,S,Rp)- L2

ESI-TOF Accurate Mass Report

Results file: E:\Projects\2006.PRO\SampleDB\2006.rpt
Last modified: Monday, June 22, 2020 16:34:04

Sample Summary:

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172	20062212	SDC-152	Chakrabortty	666.2929	C43H44N2OP2	667.3007	667.3020	1.9	1.3

Figure S 23 *HRMS of* ***(R,R,S$_P$,R,S$_P$)- L3***

ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2106.PRO\SampleDB\2106.rpt
Last modified: Friday, June 04, 2021 08:32:18

Sample Summary:

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61	21060407	SDC-L-4	hakraborttty	666.2929	C43H44N2OP2	667.3007	667.3016	1.3	0.9

***Figure S 24** HRMS of (R,R,S$_p$,S,R$_p$)- L4*

▪ NMR of the hydrogenated products

All the hydrogenated products have been characterized and matched with the literature reports.[2, 3]

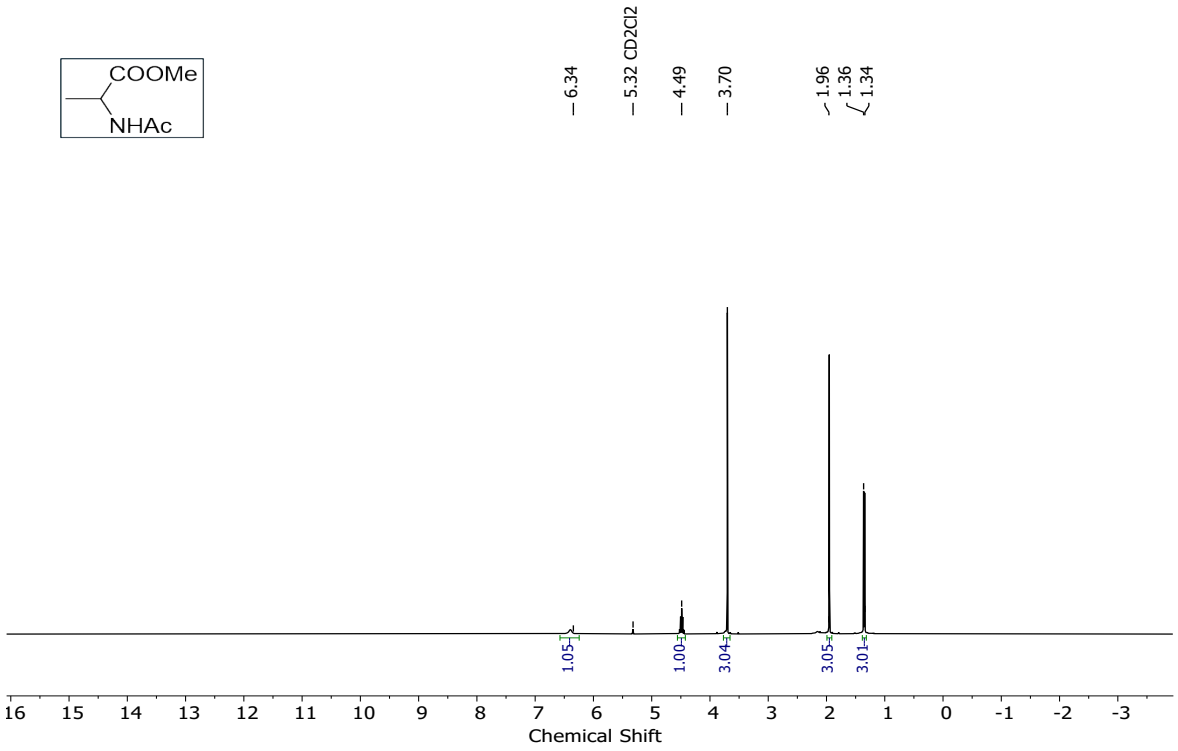


Figure S 25 *^{1}H NMR of* ***1b***

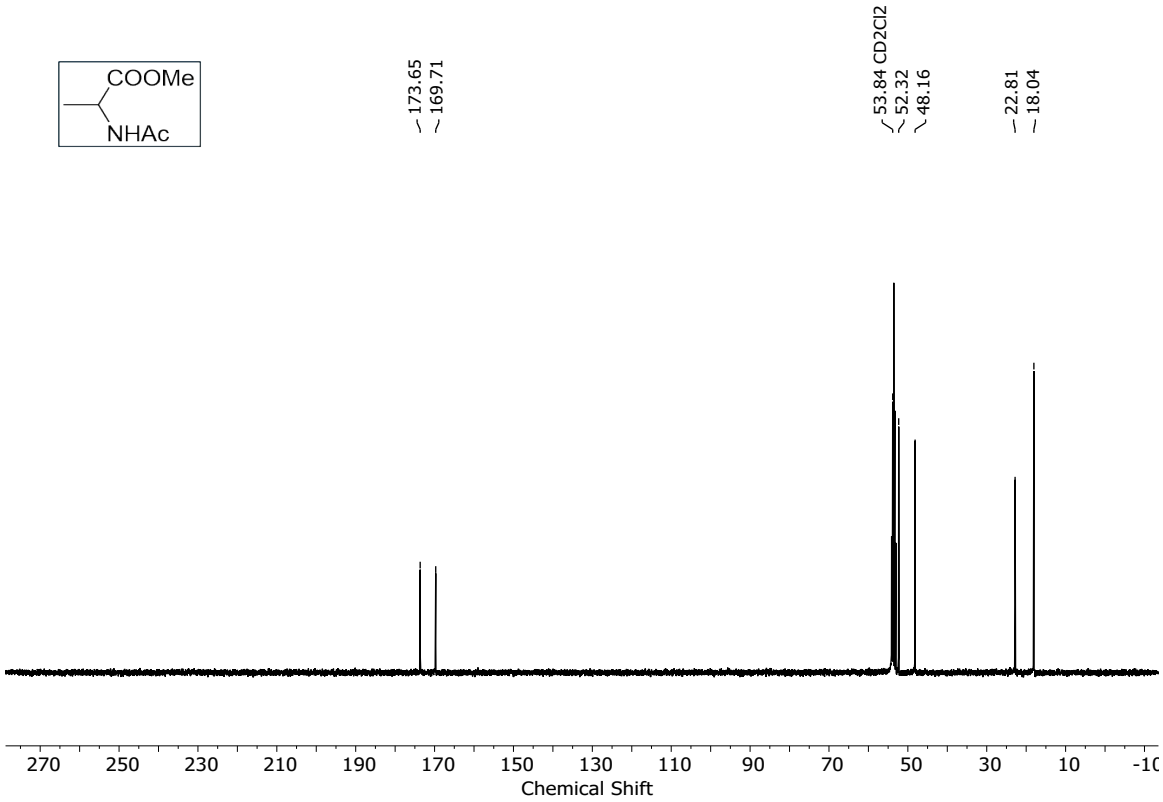


Figure S 26 *^{13}C NMR of* ***1b***

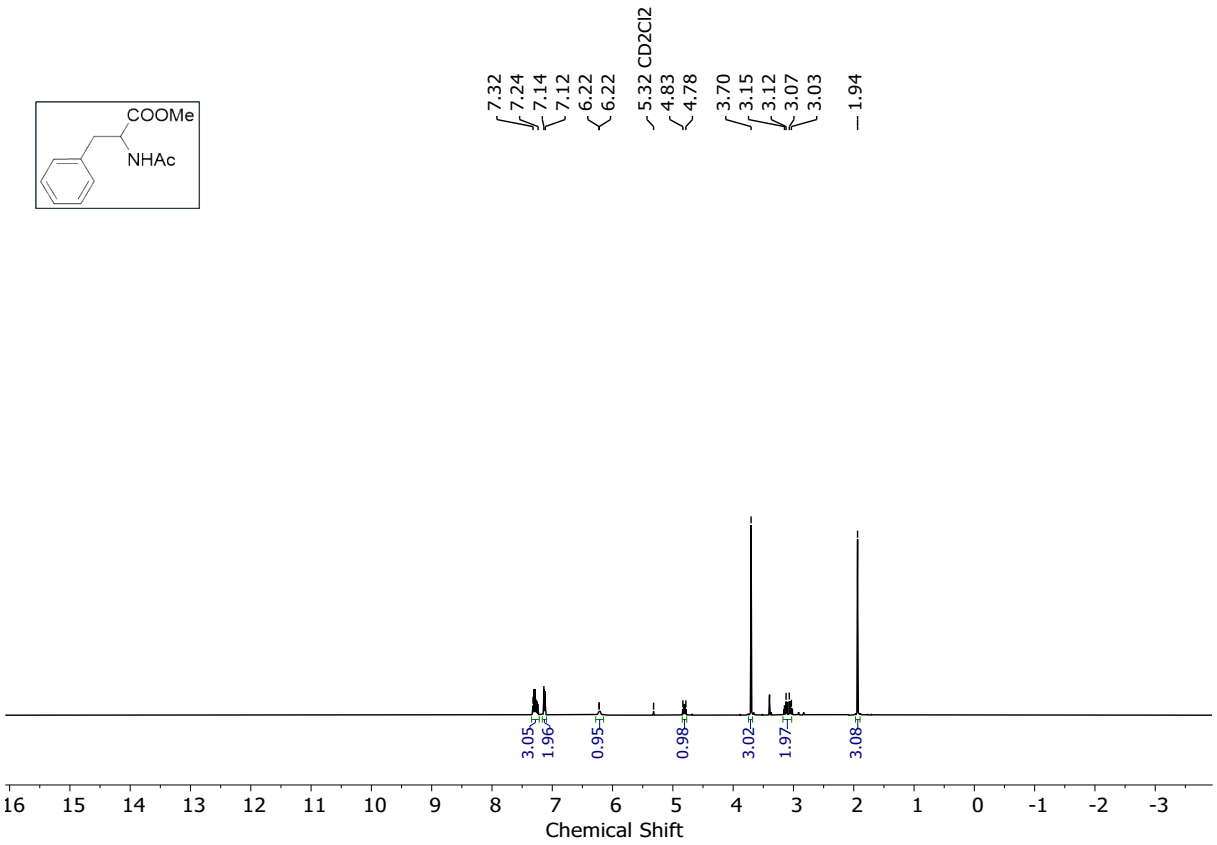


Figure S 27 *^{1}H NMR of* ***1c***

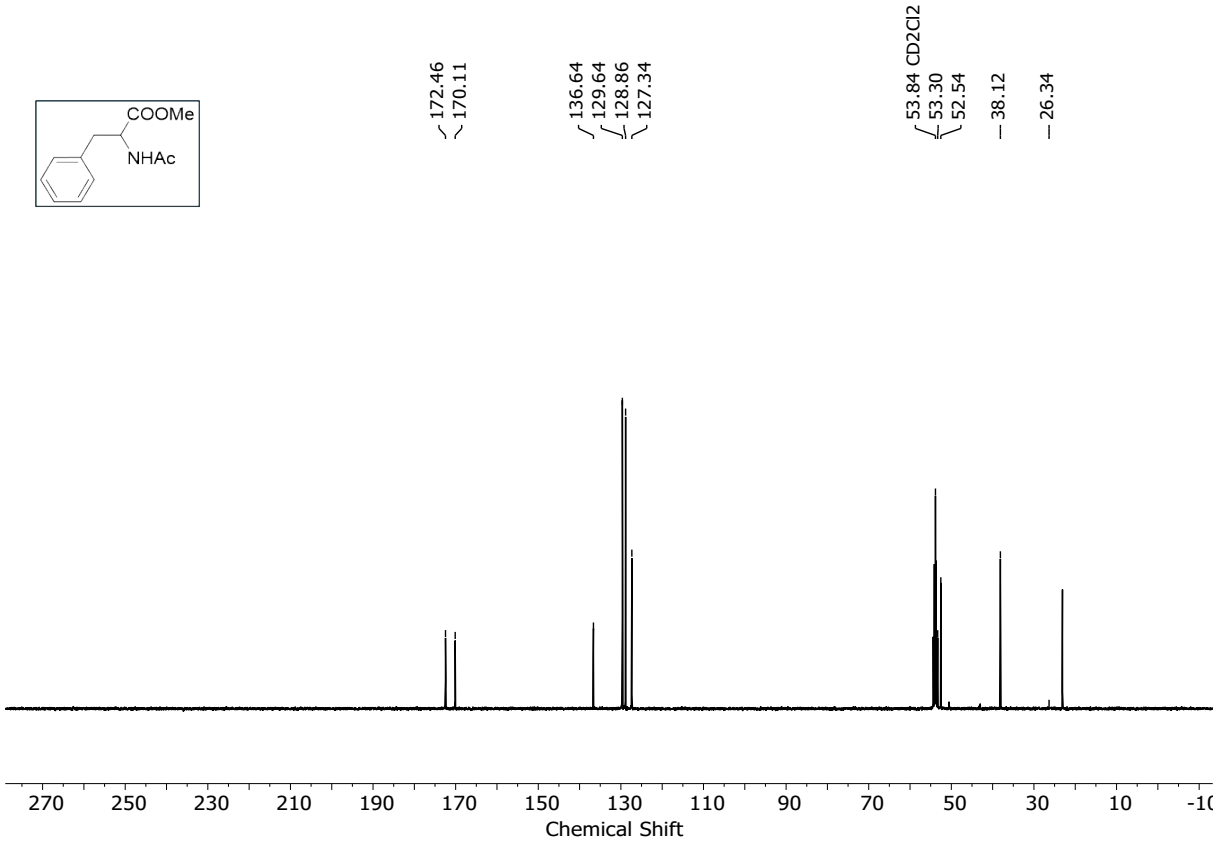


Figure S 28 *^{13}C NMR of* ***1c***

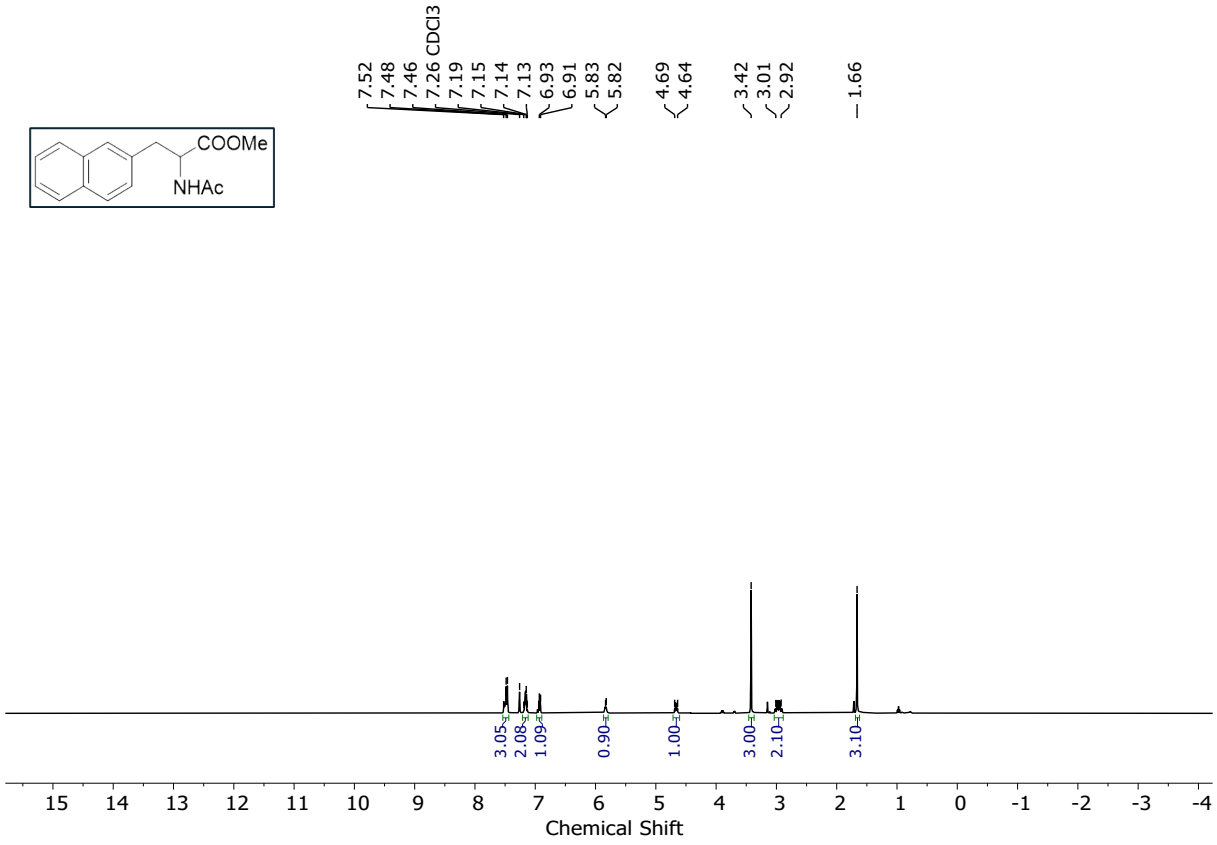


Figure S 29 *^{1}H NMR of* ***1d***

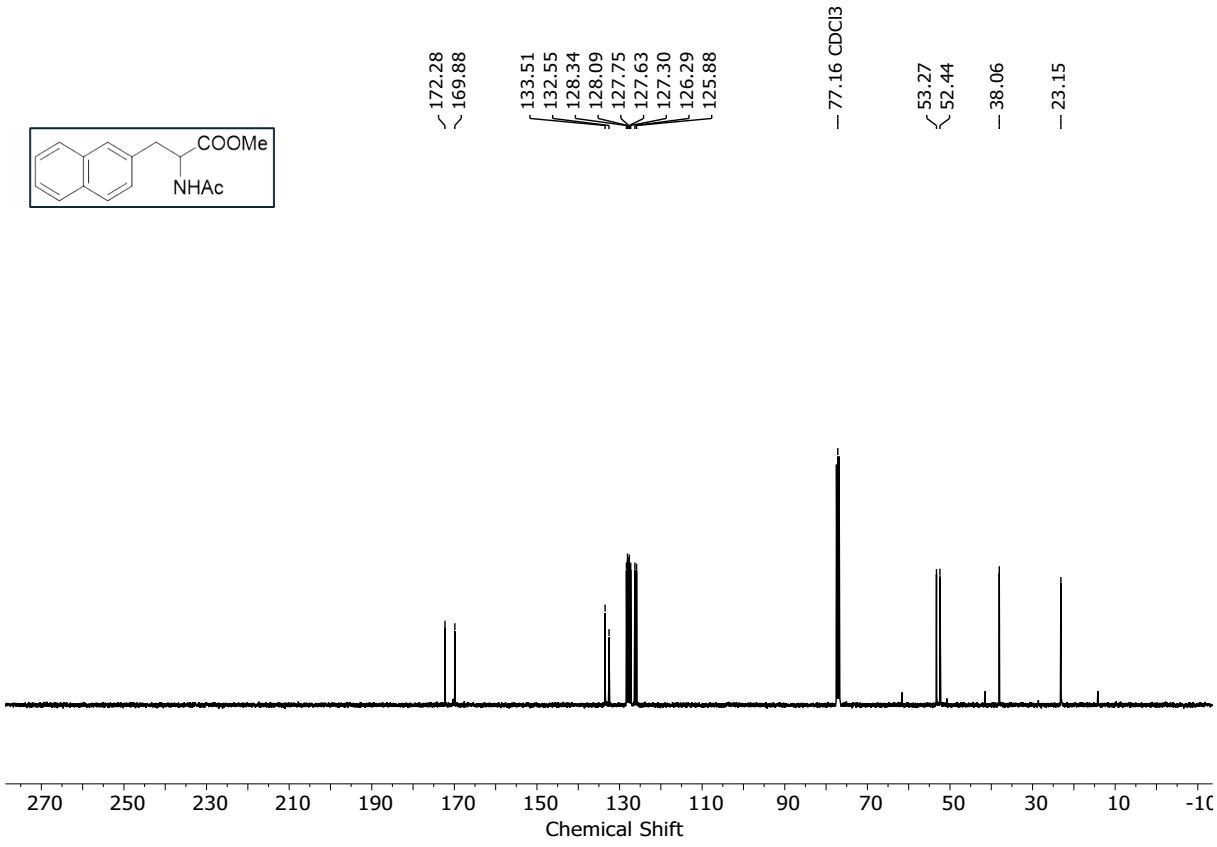


Figure S 30 *^{13}C NMR of* ***1d***

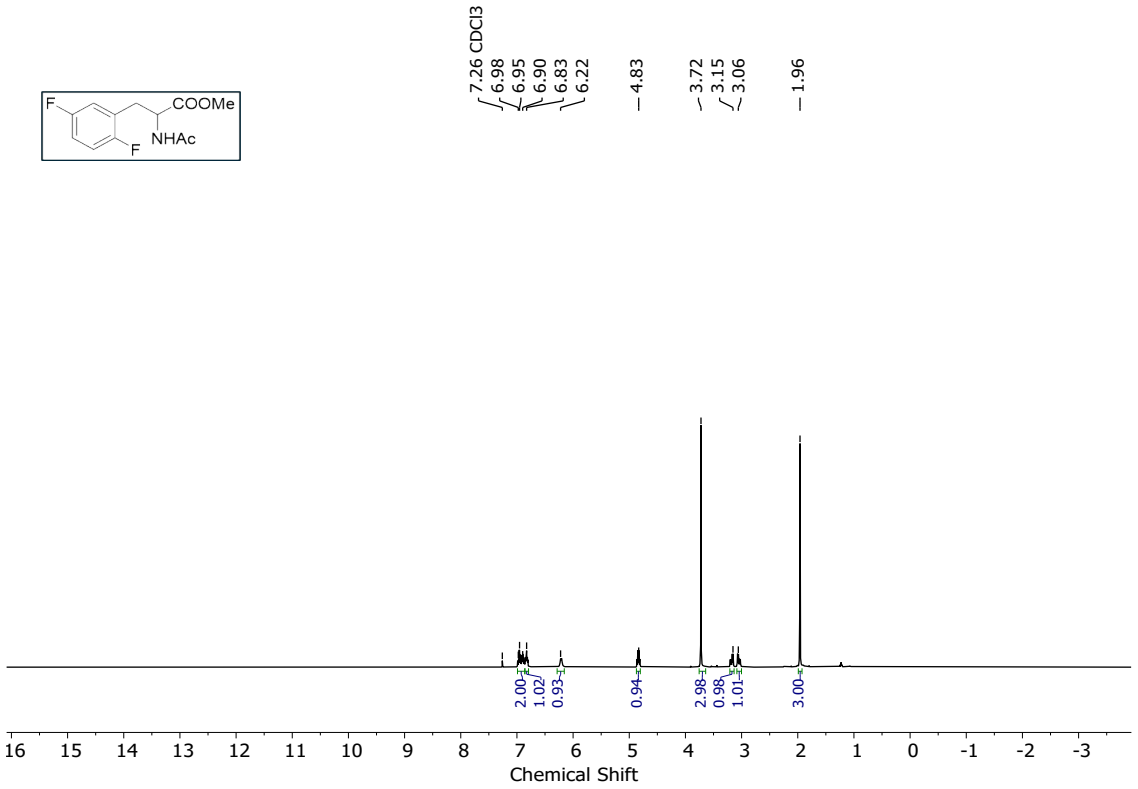


Figure S 31 *[1]H NMR of* ***1e***

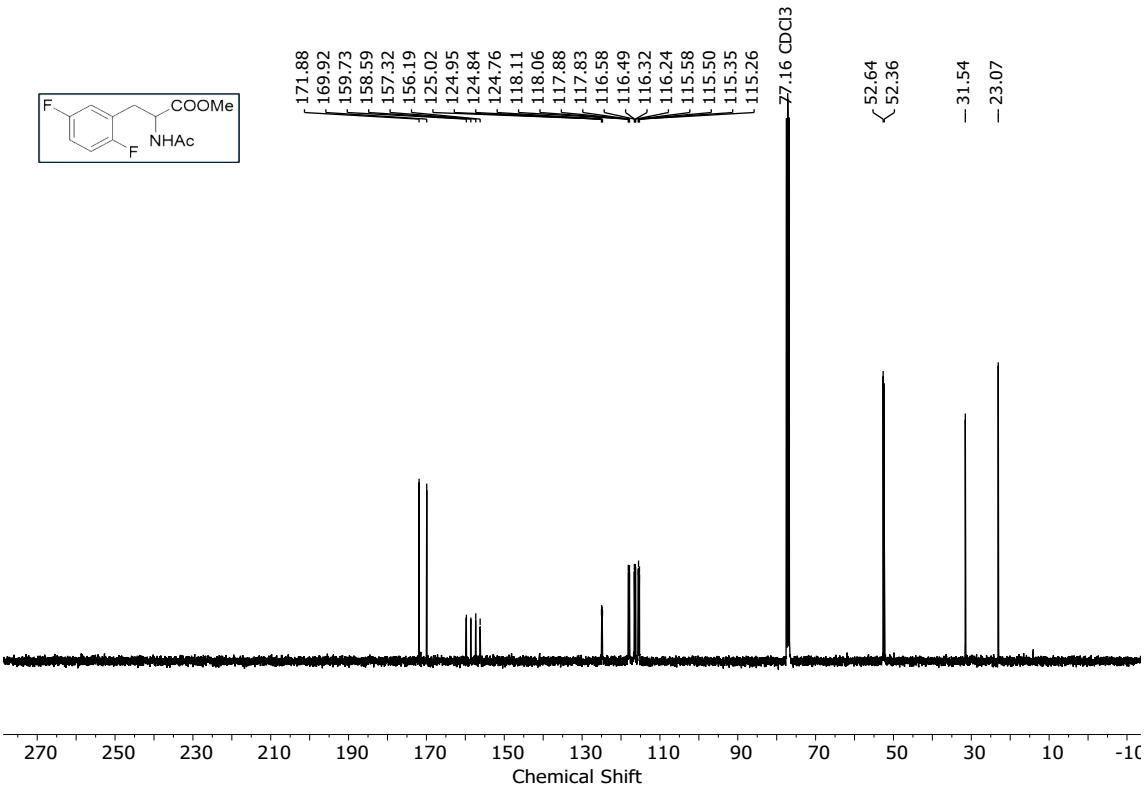


Figure S 32 *[13]C NMR of* ***1e***

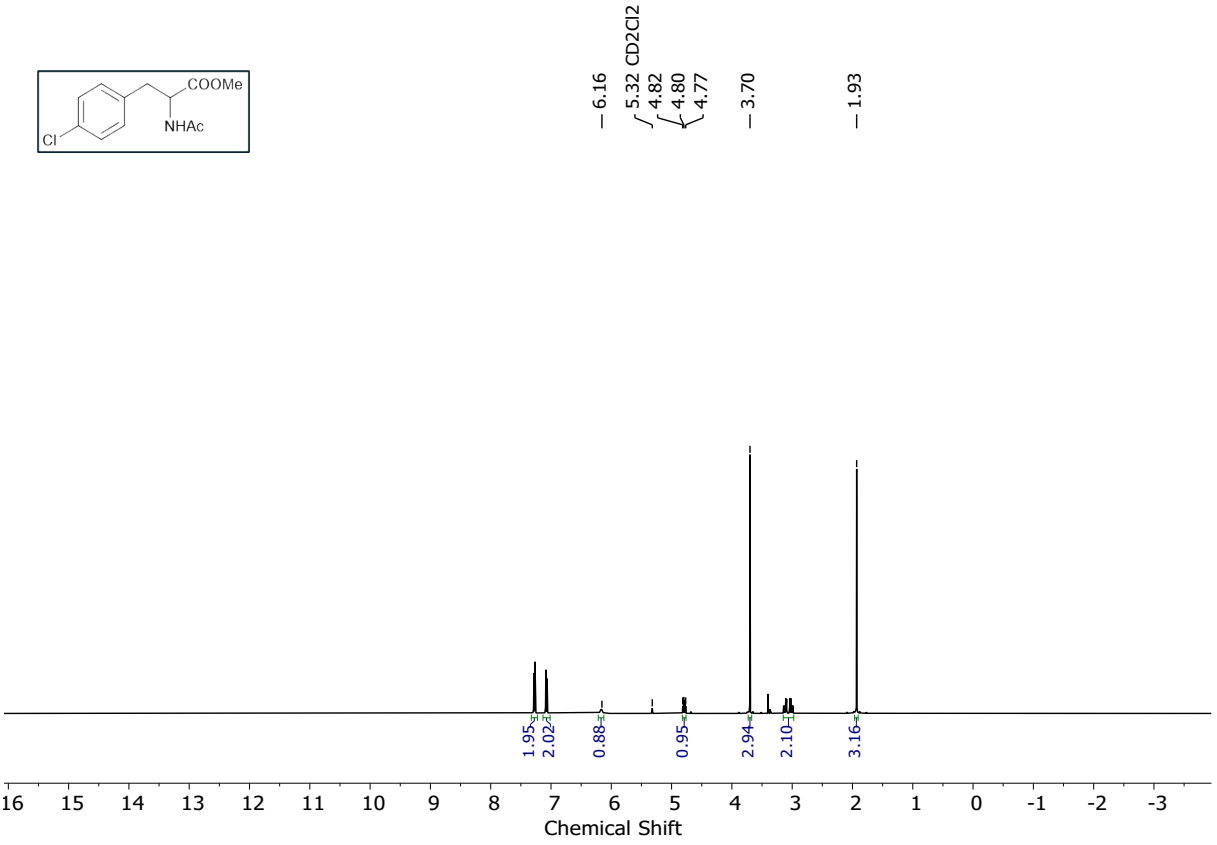


Figure S 33 *^{1}H NMR of* ***1f***

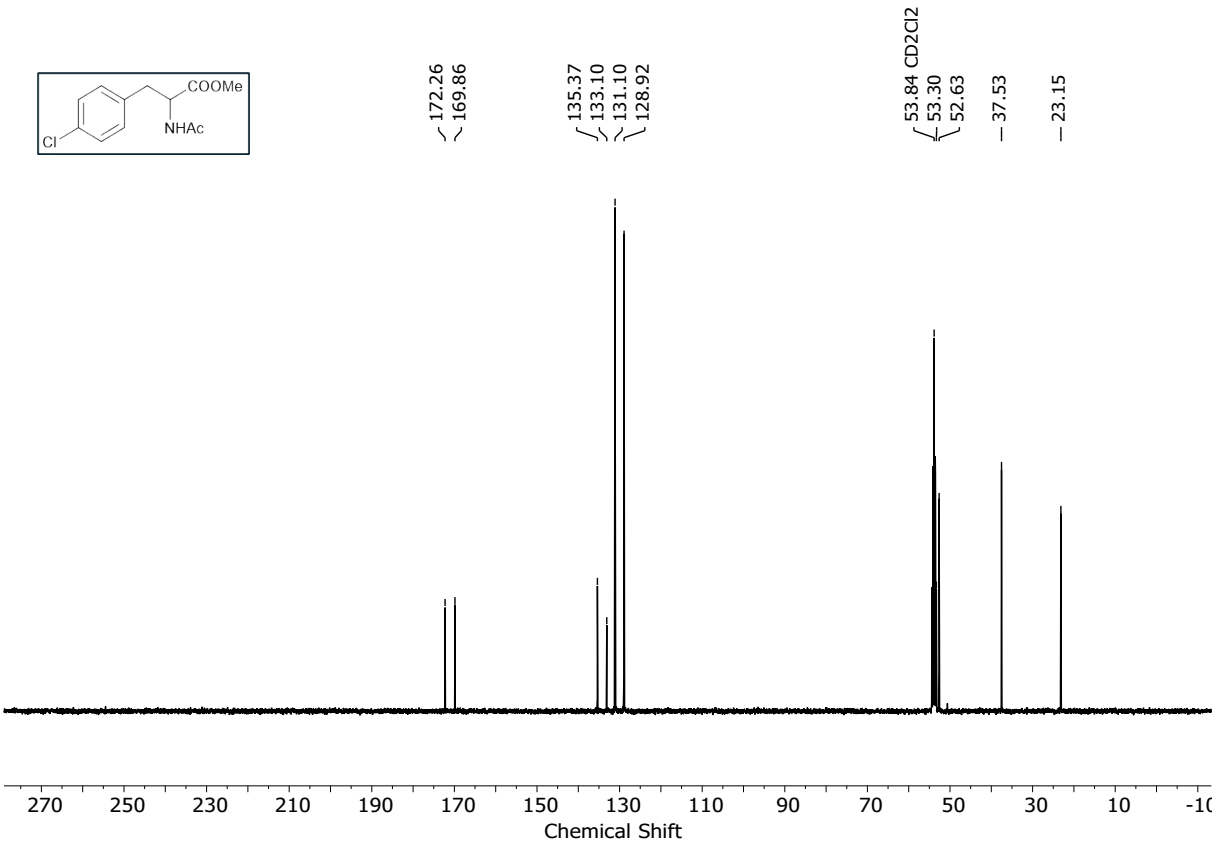


Figure S 34 *^{13}C NMR of* ***1f***

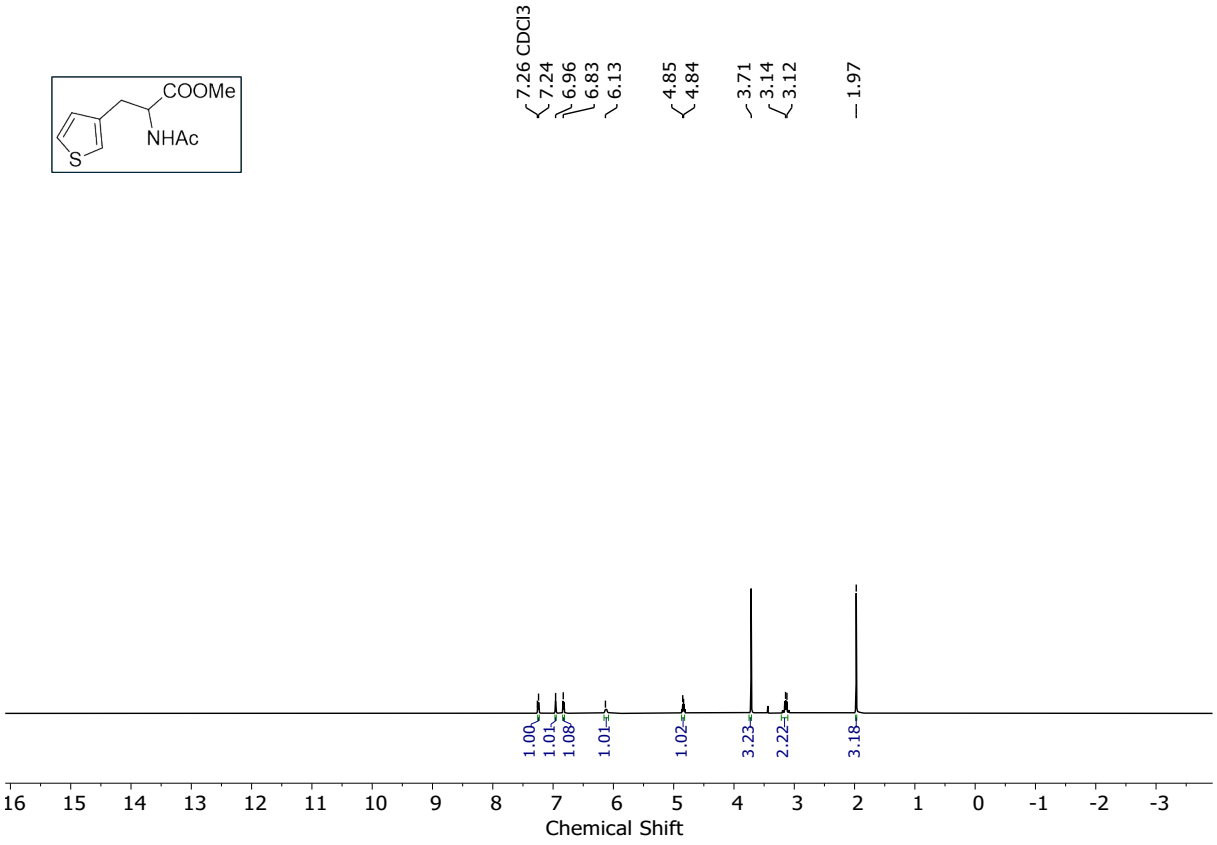


Figure S 35 *[1]H NMR of* ***1g***

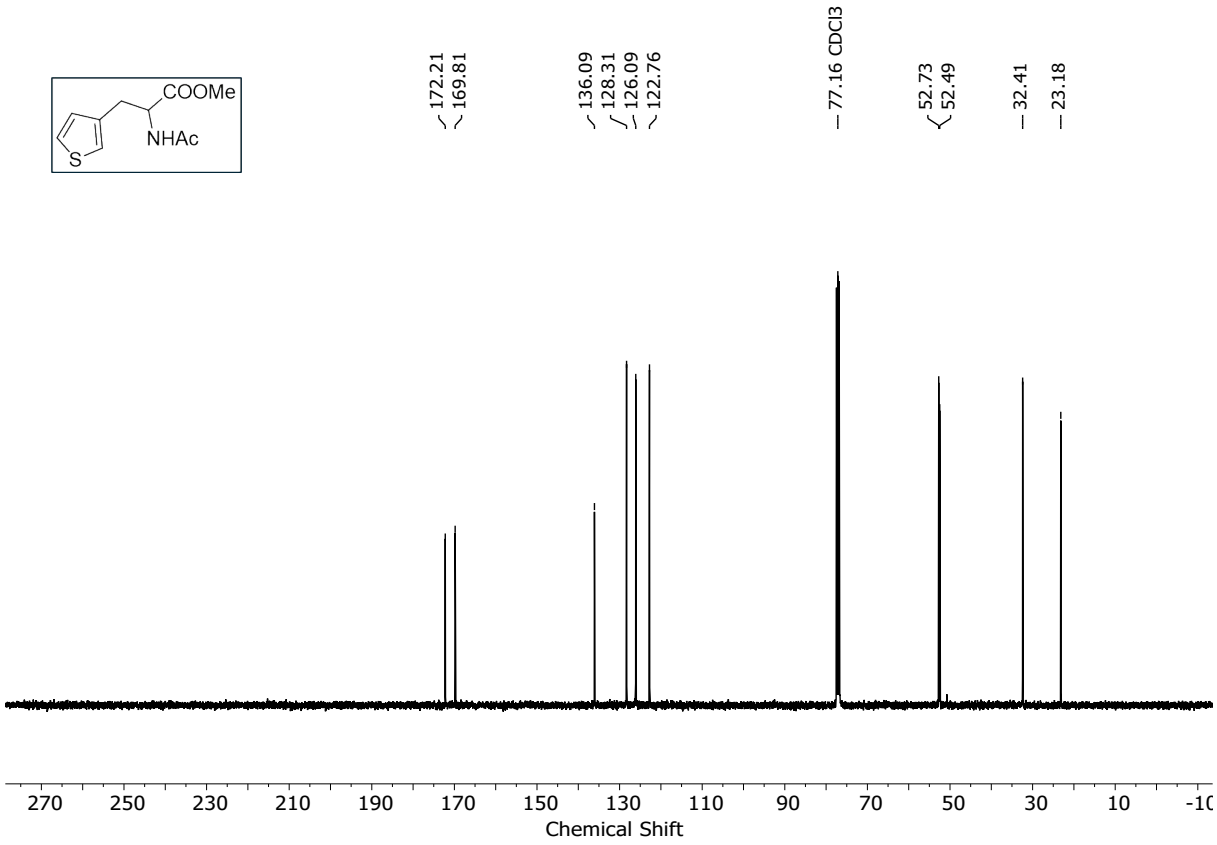


Figure S 36 *[13]C NMR of* ***1g***

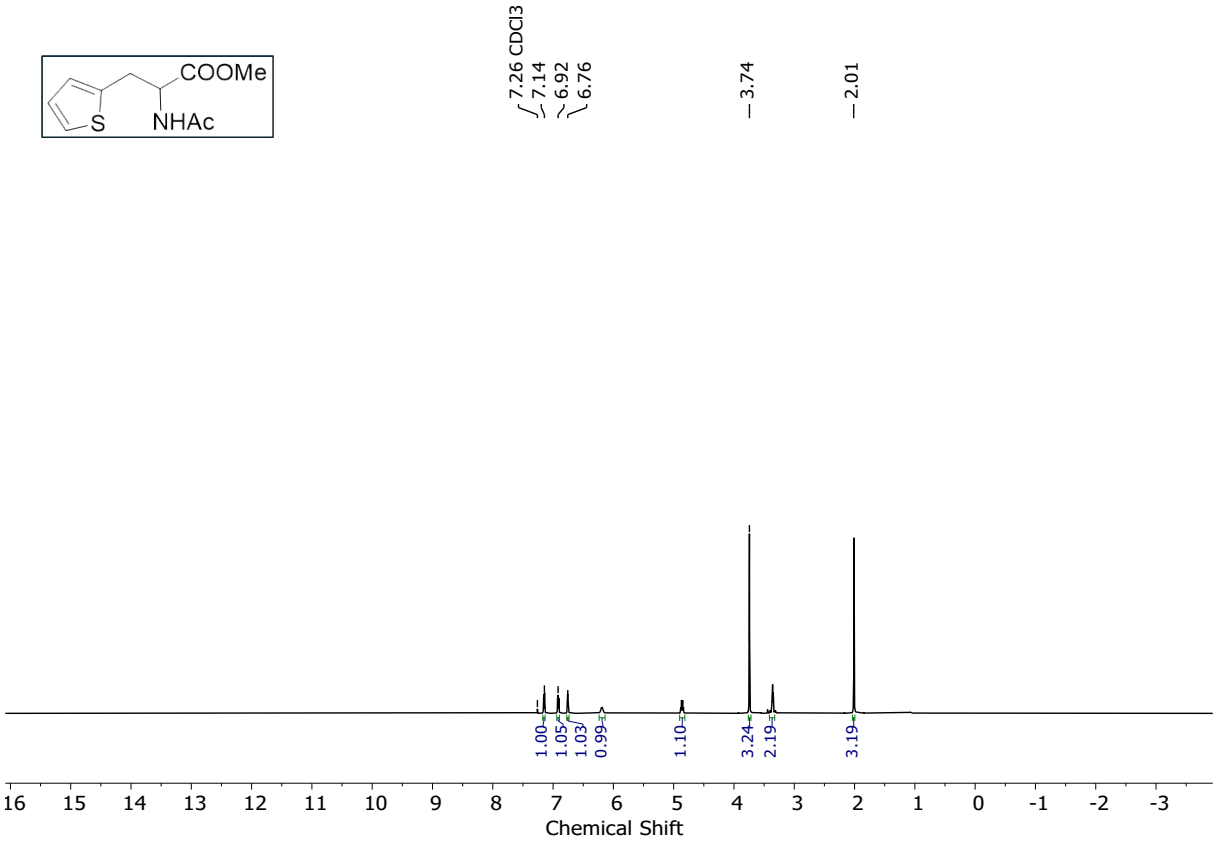


Figure S 37 *^{1}H NMR of* ***1h***

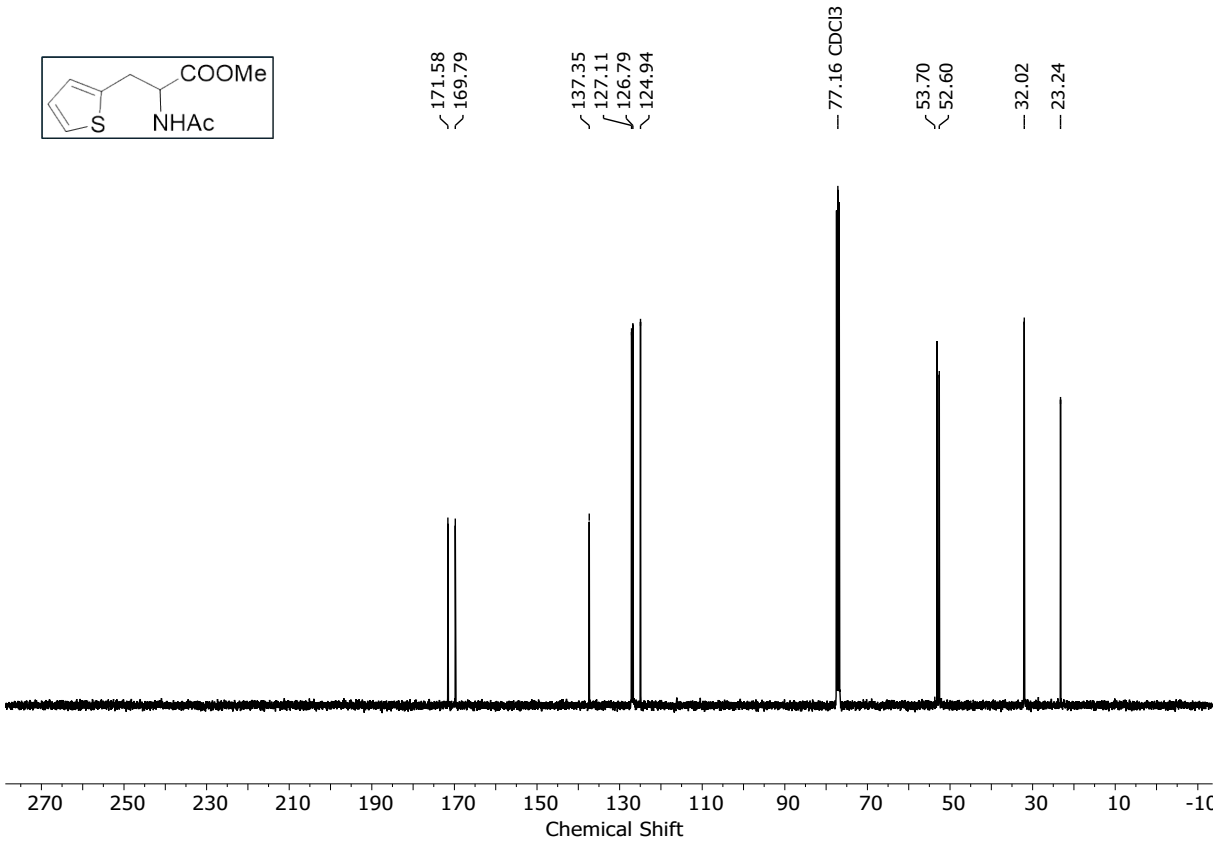


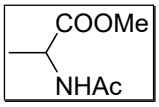
Figure S 38 *^{13}C NMR of* ***1h***

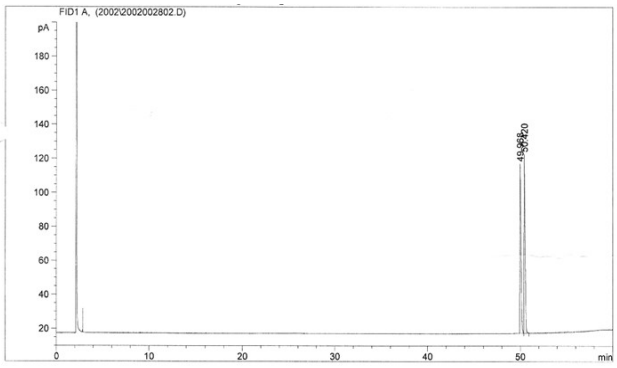
- **HPLC Traces for enantiomeric excess determination of the product**

Method Information for HPLC

Substrate	Column
1b	25m Lipodex E 90/40-6-200/10
1a, 1c-1h	Chiralcel OJ-H Heptan/EtOH 95:5
2a	AD-H, Heptan/EtOH 90:10

- **Asymmetric Hydrogenation**





Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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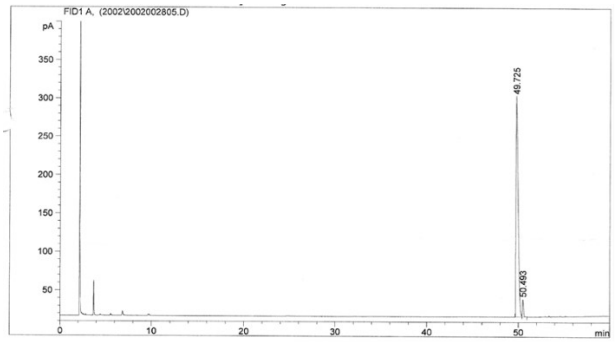
2	50.420	VB	0.1073	836.89764	105.11221	49.91779

Figure S 39 HPLC traces of racemic **1b**



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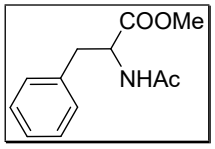
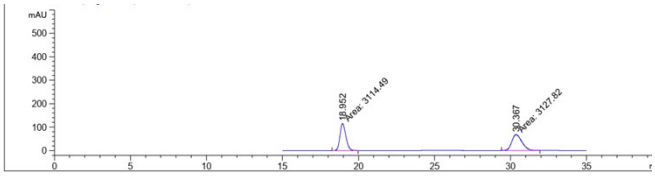
1	49.725	BV	0.2083	4816.83594	287.48532	95.93251
2	50.493	VB	0.1139	204.23126	22.84838	4.06749

Figure S 40 HPLC traces of enantioenriched product **1b** using *Rh/S,S,R_P,S,R_P-**L2** catalytic system*



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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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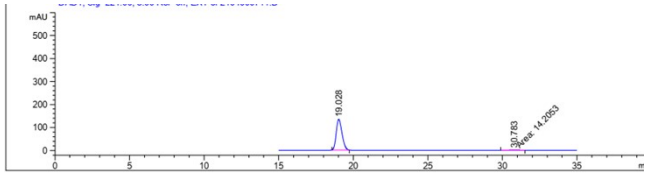
Figure S 41 HPLC traces of racemic **1c**

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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
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   2  30.784 MM    0.8223   58.93432    1.19445   0.4288
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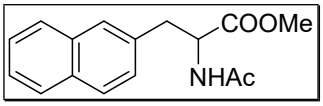
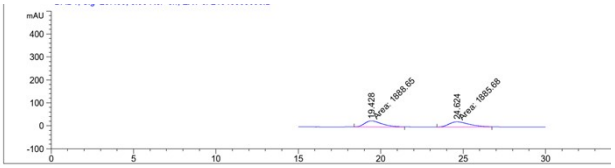
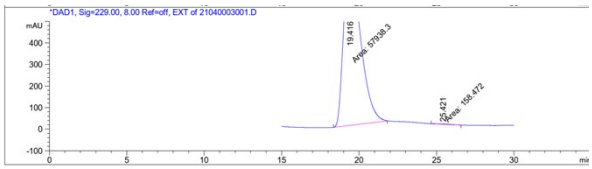
Figure S 42 HPLC traces of enantioenriched product **1c** using *Rh/S,S,R$_P$,S,R$_P$-**L2** catalytic system*





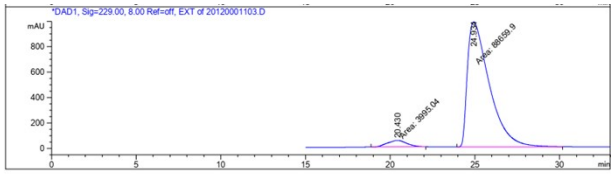

```
=====================================================================
                        Area Percent Report
=====================================================================

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  19.433 MM    1.1908 1.89320e4   264.98242  49.9287
   2  24.630 BB    1.2766 1.89861e4   224.06425  50.0713

Totals :                 3.79181e4   489.04668
```

Figure S 43 HPLC traces of racemic **1d**



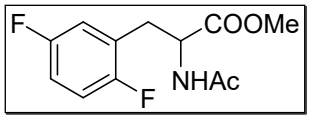

```
================================================================================
                            Area Percent Report
================================================================================

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  19.416 BB    1.0688 3.14055e4   446.39917  99.8249
   2  25.601 MM    1.1473   55.08820 8.00269e-1   0.1751

Totals :                  3.14606e4   447.19944
```

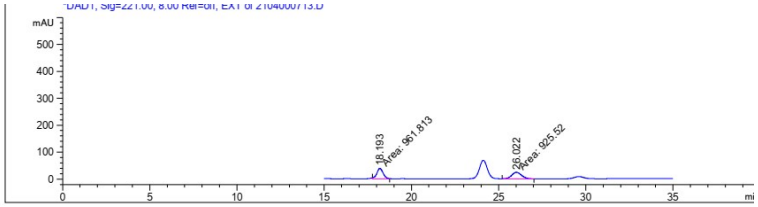
Figure S 44 HPLC traces of enantioenriched product **1d** using *Rh/S,S,R_P,S,R_P-**L2** catalytic system*




```
================================================================================
                            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  20.422 MM    1.3975 2180.02466   25.99930   3.9637
   2  24.932 MM    1.3352 5.28197e4   659.33752  96.0363

Totals :                  5.49998e4   685.33682
```

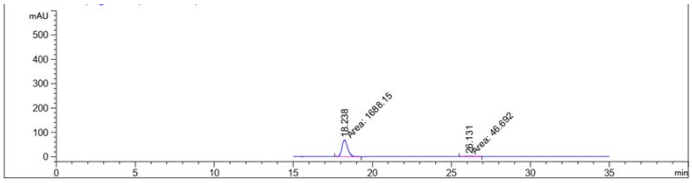
Figure S 45 HPLC traces of enantioenriched product **1d** using *Rh/ R,R,S_P,R,S_P-**L3** catalytic system.*





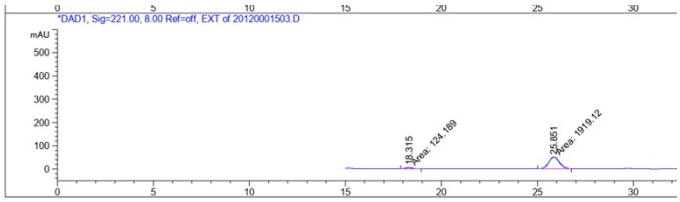

```
================================================================================
                            Area Percent Report
================================================================================

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  18.195 MM    0.4107 4881.18945  198.06927  50.6214
   2  26.022 BB    0.5994 4761.34473  123.59566  49.3786
```

Figure S 46 HPLC traces of racemic **1e**



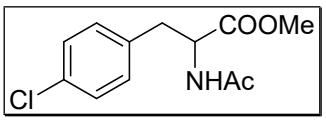

```
=====================================================================
                      Area Percent Report
=====================================================================

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  18.238 MM    0.4090 8634.70410  351.87573  97.1938
   2  26.132 BB    0.5647  249.30283    6.54036   2.8062
```

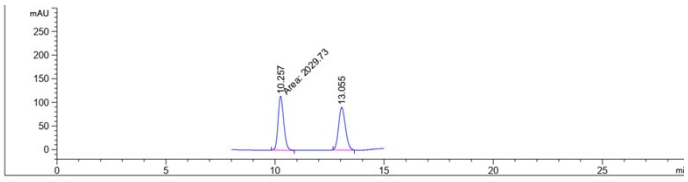
Figure S 47 HPLC traces of enantioenriched product **1e** using *Rh/S,S,R_P,S,R_P-**L2** catalytic system*




```
=====================================================================
                      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  18.314 BB    0.3693  610.08331   25.85602   5.9443
   2  25.850 BB    0.5967 9653.21973  252.11436  94.0557

Totals :                  1.02633e4   277.97038
```

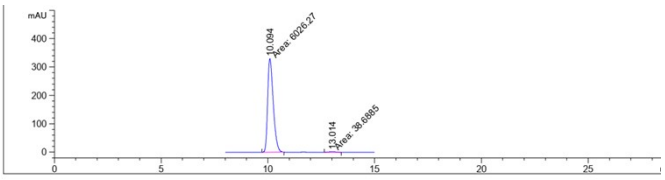
Figure S 48 HPLC traces of enantioenriched product **1e** using *Rh/ R,R,S_P,R,S_P-**L3** catalytic system.*





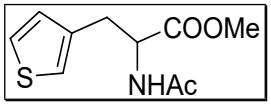

```
=====================================================================
                      Area Percent Report
=====================================================================

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  10.257 MM    0.2975 1483.22229   83.10563  50.7891
   2  13.055 MM    0.3647 1437.13403   65.68080  49.2109
```

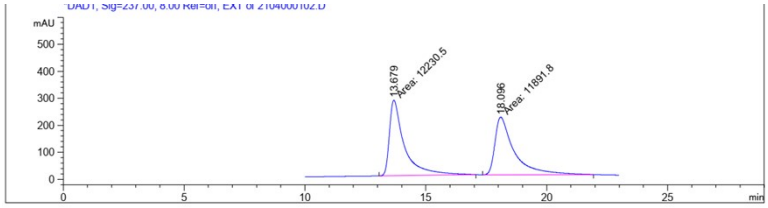
Figure S 49 HPLC traces of racemic **1f**




```
=====================================================================
                      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  10.094 MM    0.3004 7780.92529  431.75073  99.4528
   2  13.009 BB    0.3065   42.81082    2.07715   0.5472
```

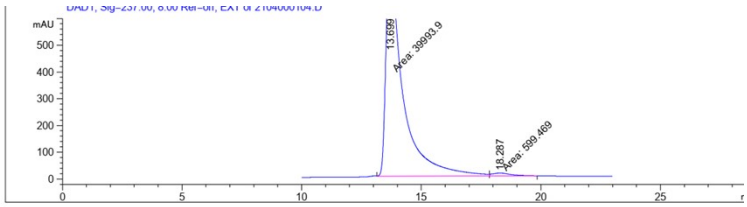
Figure S 50 *HPLC traces of enantioenriched product* ***1f*** *using Rh/S,S,R_P,S,R_P-**L2** catalytic system*





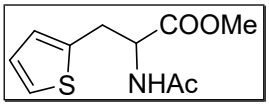

```
=====================================================================
                      Area Percent Report
=====================================================================

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  13.678 MM    0.7358 8787.10645  199.05054  50.9399
   2  18.096 MM    0.9297 8462.84668  151.71397  49.0601
```

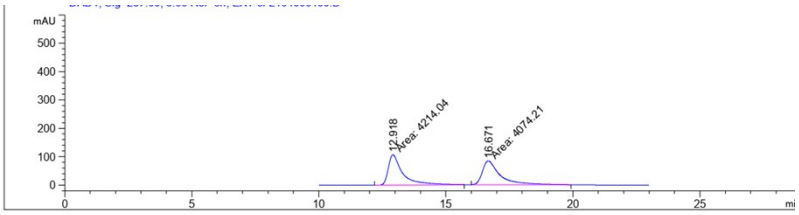
Figure S 51 HPLC traces of racemic **1g**




```
=====================================================================
                      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  13.698 MF    0.8000 2.86061e4   595.94580  98.3492
   2  18.287 FM    0.9872  480.16110    8.10677   1.6508
```

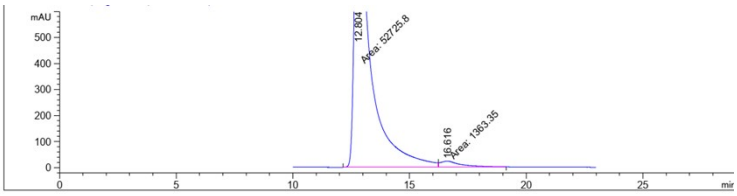
Figure S 52 *HPLC traces of enantioenriched product* **1g** *using Rh/S,S,R_P,S,R_P-**L2** catalytic system*






```
======================================================================
                    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  12.917 MM    0.6342 1556.58765   40.90533  50.8042
   2  16.671 MM    0.7738 1507.30933   32.46615  49.1958
```

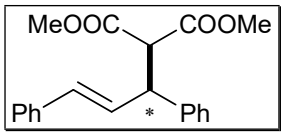
Figure S 53 HPLC traces of racemic **1h**

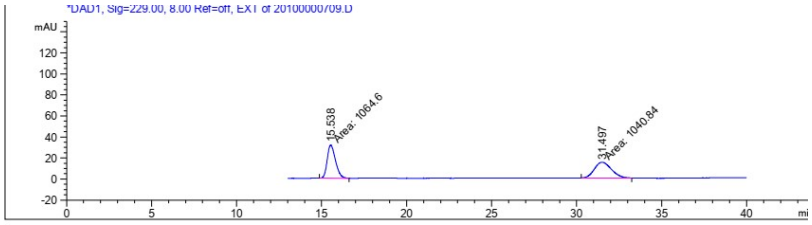



```
======================================================================
                    Area Percent Report
======================================================================

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  12.804 MF    0.7356 2.02327e4   458.38684  97.5042
   2  16.617 FM    1.0103  517.89771    8.54386   2.4958
```

Figure S 54 HPLC traces of enantioenriched product **1h** using *Rh/S,S,R_P,S,R_P-**L2** catalytic system*

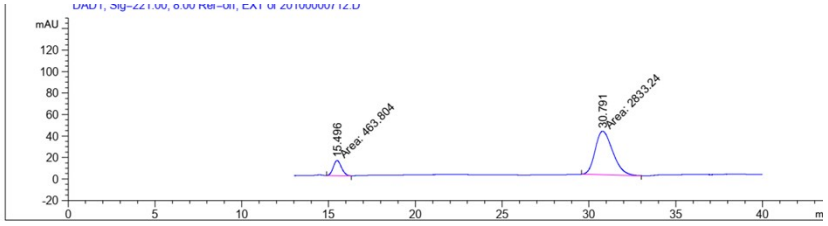
- **Asymmetric Allylic substitution**






```
=====================================================================
                      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  15.537 BB    0.5236 3770.37988  111.77082  50.3355
   2  31.491 BB    1.0424 3720.12598   53.55556  49.6645

Totals :                  7490.50586  165.32639
```

Figure S 55 HPLC traces of racemic **2a**




```
=====================================================================
                      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  15.492 BB    0.4981 1005.13135   31.01613  13.7832
   2  30.791 MM    1.1699 6287.32129   89.57087  86.2168

Totals :                  7292.45264  120.58700
```

Figure S 56 HPLC traces of enantioenriched product **2a** using *Pd/ R,R,S_P,S,R_P-**L4** catalytic system.*

▪ X-ray Crystallographic data

Single crystals were prepared under argon and measured under a continuous flow of nitrogen on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. Acta Cryst. 2008, A64, 112.) and refined by full-matrix least-squares procedures on F^2

(SHELXL-2018: Sheldrick, G. M. Acta Cryst. 2015, C71, 3.). XP (Bruker AXS) was used for graphical representations.

CCDC 2091899 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Crystal data of *S*,*S*,R_P,*R*,S_P-**L1**: $C_{43}H_{44}N_2OP_2$, M = 666.74, orthorhombic, space group $P2_12_12_1$, a = 10.0784(3), b = 11.7543(3), c = 30.5885(7) Å, V = 3623.65(16) Å^3, T = 150(2) K, Z = 4, 30024 reflections measured, 6377 independent reflections (R_{int} = 0.0251), final R values ($I > 2\sigma(I)$): R_1 = 0.0246, wR_2 = 0.0645, final R values (all data): R_1 = 0.0247, wR_2 = 0.0646, 438 parameters, largest diff. peak/hole: 0.38/-0.25 eÅ^{-3}, Flack parameter x = -0.002(4).

Reference

1. B. Roy, E. Das, A. Roy and D. Mal, *Organic & Biomolecular Chemistry*, 2020, **18**, 3697-3706.
2. M. Biosca, P. de la Cruz-Sanchez, O. Pamies and M. Dieguez, *J Org Chem*, 2020, **85**, 4730-4739.
3. M. van den Berg, A. J. Minnaard, R. M. Haak, M. Leeman, E. P. Schudde, A. Meetsma, B. L. Feringa, A. H. M. de Vries, C. E. P. Maljaars, C. E. Willans, D. Hyett, J. A. F. Boogers, H. J. W. Henderickx and J. G. de Vries, *Advanced Synthesis & Catalysis*, 2003, **345**, 308-323.