SUPPORTING INFORMATION

P-Chiral, *N*-Phosphoryl Sulfonamide Brønsted Acids with an Intramolecular Hydrogen Bond Interaction that Modulates Organocatalysis

Minglei Yuan,[†¶] Ifenna I. Mbaezue,[†¶] Filip Topic,[†] Youla S. Tsantrizos[†*]

[†]Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 0B8, Canada.

* Email: youla.tsantrizos@mcgill.ca

Contents:

General Experimental Methods

All reactions were carried out under anhydrous conditions and under an atmosphere of dry argon unless otherwise indicated. Compounds were purified by normal phase flash column chromatography on silica gel (SDS, 60 Å C. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by UV when applicable (λmax = 254 nm and/or 366 nm) and/or by staining with vanillin or anisadehyde in acidic ethanol and/or $KMnO_4$ in basic water followed by heating. Key compounds were fully characterized by ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR and HRMS. Chemical shifts (δ) are reported in ppm relative to the internal deuterated solvent or external H_3PO_4 (δ 0.00 ^{31}P), unless indicated otherwise. High-resolution MS spectra were recorded using electrospray ionization (ESI+/-) and Fourier transform ion cyclotron resonance mass analyzer (FTMS).

The reactions were monitored either by TLC or analytical HPLC/MS to confirm completion and homogeneity of the products. Analytical HPLC was performed using a reversed phase C18 5 μm column on a Waters Atlantis T3 instrument and the solvent system indicated below:

Solvent A: H_2O, 0.1% formic acid

Solvent B: CH_3CN, 0.1% formic acid

Mobile phase: linear gradient from 95%A and 5%B to 5%A and 95%B in 13 min, then 2 min at 100% B

Flow rate: 1 mL/min

Compounds 6-bromo-2-methylquinoline (**10a**), 2-methylquinoline (**10b**), 2-phenylquinoline (**10c**) and 4-methylquinoline (**10d**) were purchased from Sigma Aldrich. The 2-ethylquinoline (**10e**),[1] 2-isopropylquinoline (**10f**),[2] 6-nitro-2-methylquinoline (**10g**)[3] and 6-methoxy-2-methylquinoline (**10h**)[3] were synthesized according to the literature procedures indicated.

The enantiomeric purity of chiral compounds was determined by chiral HPLC using an Agilent 1100 or Agilent 1260 series instrument and the column and solvent system indicated for each compound. The absolute stereochemistry of all compounds was assigned based on several factors, including the single crystal X-ray of the previously reported key precursor compound **6**,[4] the single crystal X-ray structures of intermediate phosphinic amide **8d** (refer to SI Table 3), the single crystal X-ray structures of catalysts **5a** and **5c**, the single crystal X-ray structure of compound (*S*)-2-bromo-6-methyl-3,4-dihydro-*2H*-1λ^2-quinoline (**11a**), and by analogy with previously reported compounds in the literature.

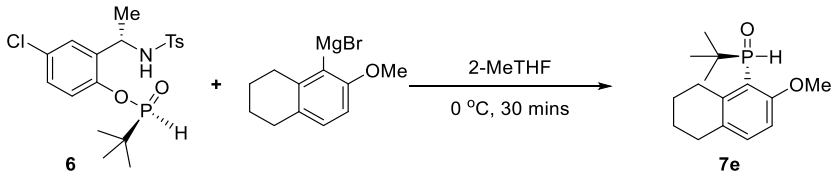
The names of all compounds were generated using ChemBioDraw Ultra 12.0.

General synthesis of secondary phosphine oxides (SPOs) **7**:

We recently reported the synthesis of SPO intermediates **6**, **7a, 7c** and **7d**.[4] The synthesis of analogs **7e** and **7f** was achieved using the same protocol.[4] The synthesis of SPO analogs **7b** was achieved using the previously reported methodology.[5]

*(S)-tert-Butyl(2-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphine oxide (***7e***)*:

Precursor compound 5-bromo-6-methoxy-1,2,3,4-tetrahydronaphthalene (used to prepare the Grignard reagent) was synthesized according to the method reported by Smith and co-workers.[6]



A three neck flask under argon was charged with SPO **6** (1 mmol) in 2-MeTHF (3 mL) and cooled to 0°C. 2-Methoxy-5,6,7,8-tetrahydronaphthalen-1-yl magnesium bromide (1 M in 2-MeTHF, 4 mmol, 4 mL) was added slowly while keeping the internal temperature <5 °C. The reaction mixture was stirred for 40 min to completion. Saturated and degassed aqueous NH_4Cl solution (5 mL) was added slowly to quench the reaction. The organic layer was collected and the aqueous residue was extracted with DCM (25 mL x3). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (deactivated with 10% water) using a solvent gradient of hexane/EtOAc (from 50:50 to 0:100, v/v) to obtained the desired product (141 mg) in 53% yield.

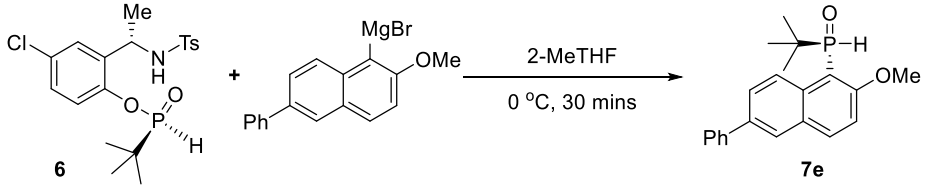
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 0.5 H), 7.17 (d, J = 8.5 Hz, 1H), 7.06 (s, 0.5 H), 6.71 (dd, J = 8.5, 5.1 Hz, 1H), 3.77 (s, 3H), 3.54 – 3.39 (m, 1H), 2.93 (dt, J = 17.0, 5.6 Hz, 1H), 2.72 (t, J = 6.2 Hz, 2H), 1.83 – 1.66 (m, 4H), 1.20 (d, J = 16.6 Hz, 9H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 36.57.

More detailed characterization and estimation of the enantiomeric purity was performed at the subsequent step, when **7e** was converted to the corresponding *P*-chiral (*tert*-butyl)-P-arylphosphinic amide **8e**.

(S)-tert-Butyl(2-methoxy-6-phenylnaphthalen-1-yl)phosphine oxide (**7f**):

The precursor 1-bromo-2-methoxy-6-phenylnaphthalene (used to prepare the Grignard reagent) was synthesized according to the method reported by Smith and co-workers.[6]



A three-neck flask under argon was charged with SPO **6** (1 mmol) dissolved in 2-MeTHF (3 mL) and cooled to 0 °C. A solution of 2-methoxy-6-phenylnaphthalen-1-yl

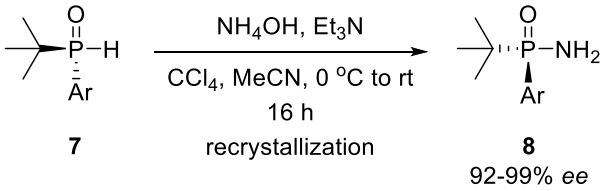
magnesium bromide (1 M in 2-MeTHF, 4 mmol, 4 ml; prepared as previously reported[6]) was added slowly, while keeping the internal temperature <5 °C. The reaction mixture was stirred for 40 min to complete the reaction. Saturated and degassed aqueous NH_4Cl solution (5 mL) was added slowly to quench the reaction. The organic layer was collected and the aqueous residue was extracted with DCM (25 mL x3). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (on deactivated silica with 10% water) eluted with a solvent gradient of hexane/EtOAc gradient (50:50 to 0:100, v/v) to obtained the desired product (189 mg) in 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 9.0 Hz, 1H), 8.54 (s, 0.5 H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.98 (s, 1H), 7.81 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (s, 0.5 H), 7.30 – 7.26 (m, 1H), 3.98 (s, 3H), 1.26 (d, *J* = 16.8 Hz, 9H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 36.19.

More detailed characterization and estimation of the enantiomeric purity was performed at the subsequent step, when **7f** was converted to the corresponding *P*-chiral (*tert*-butyl)-P-arylphosphinic amide **8f**.

General procedure for the conversion of SPOs **7** to the *P*-Chiral (*t*-butyl)-*P*-arylphosphinic amides **8**:

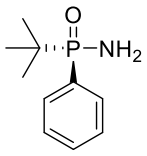


7 **8**

92-99% *ee*

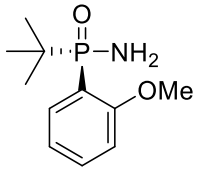
Chiral SPO **7** (1.0 mmol) was dissolved in 6 mL of degassed acetonitrile and cooled to 0 °C. CCl_4 (1.0 mL), Et_3N (2.0 mmol) and saturated aqueous solution of NH_4OH (28% in water, 0.5 mL) were sequentially added dropwise while stirring. The solution was stirred at 0 °C for 30 min and then warmed to RT and allowed to stir for 16 h. Water (5 mL) was added to the reaction mixture and then extracted with EtOAc, the organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to give the crude product. The pure product was obtained after first passing the crude through a short silica gel column and then doing a crystallization in DCM/Et_2O (1:5, v/v) at -20 °C to obtain the phosphoramide products as highly enriched single enantiomers (92-99% ee).

(R)-P-(tert-butyl)-P-phenylphosphinic amide (**8a**); characterization data consistent with previously reported.[7]



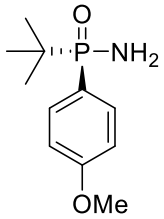
Isolated as a white solid in 82% yield (162 mg) and 96.7% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–7.84 (m, 2H), 7.57–7.52 (m, 1H), 7.49–7.43 (m, 2H), 2.72 (brs, 2H), 1.16 (d, *J* = 15.3 Hz, 9H).
^{31}P NMR (202 MHz, $CDCl_3$): δ 41.34.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*R*)-enantiomer t_R (major) = 5.88 min, (*S*)-enantiomer t_R (minor) = 7.60 min.

(R)-P-(tert-butyl)-P-(2-methoxyphenyl)phosphinic amide (**8b**):



Isolated as a white solid in 73% yield (166 mg) and 95% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (ddd, *J* = 11.9, 7.5, 1.8 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.10 – 7.02 (m, 1H), 6.93 – 6.87 (m, 1H), 3.83 (s, 3H), 3.17 (s, 2H), 1.08 (d, *J* = 15.9 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2 (d, *J* = 3.9 Hz), 135.5 (dd, *J* = 5.5, 3.0 Hz), 133.3, 121.0 (dd, *J* = 10.6, 2.5 Hz), 119.4 (d, *J* = 101.4 Hz), 110.6 (d, *J* = 7.0 Hz), 55.2, 34.3 (d, *J* = 93.7 Hz), 24.2.
^{31}P NMR (203 MHz, $CDCl_3$): δ 46.01.
HRMS: calculated for $C_{11}H_{18}NNaO_2P^+$ $[M+H]^+$: 250.0967, found: 250.0967.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*S*)-enantiomer t_R (minor) = 7.38 min, (*R*)-enantiomer t_R (major) = 10.23 min.

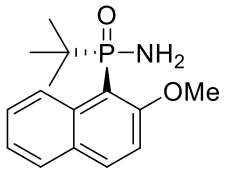
(*R*)-*P*-(*tert*-butyl)-*P*-(4-methoxyphenyl)phosphinic amide (**8c**)



Isolated as a white solid in 48% yield (109 mg) and >99% ee.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 6.92 (dd, *J* = 8.9, 2.4 Hz, 2H), 3.83 (s, 3H), 2.84 (s, 2H), 1.11 (d, *J* = 15.2 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.4 (d, *J* = 2.9 Hz), 135.0 (d, *J* = 9.6 Hz), 121.4 (d,

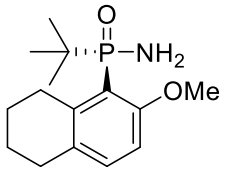
J = 123.0 Hz), 113.6 (d, *J* = 12.5 Hz), 55.2, 32.3 (d, *J* = 93.5 Hz), 24.8.
^{31}P NMR (203 MHz, $CDCl_3$): δ 41.44.
HRMS: calculated for $C_{11}H_{18}NNaO_2P^+$ $[M+H]^+$: 250.0967, found: 250.0968.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*R*)-enantiomer t_R (major) = 7.08 min, (*S*)-enantiomer t_R (minor) = 12.49 min.

(*R*)-*P*-(*tert*-butyl)-*P*-(2-methoxynaphthalen-1-yl)phosphinic amide (**8d**)



Isolated as a white solid in 42% yield (116 mg) and >99% ee.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.76 (dt, *J* = 8.2, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.6, 6.7, 1.5 Hz, 1H), 7.38 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.31 – 7.23 (m, 1H), 3.99 (s, 3H), 3.22 (s, 2H), 1.16 (d, *J* = 16.0 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7 (d, *J* = 3.2 Hz), 136.7 (d, *J* = 6.7 Hz), 134.7, 129.4 (d, *J* = 9.1 Hz), 128.0, 127.6 (d, *J* = 2.2 Hz), 127.5, 124.2, 112.8, 111.9, 111.8, 56.0, 35.9 (d, *J* = 93.2 Hz), 24.4.
^{31}P NMR (162 MHz, $CDCl_3$): δ 50.06.
HRMS: calculated for $C_{15}H_{20}NNaO_2P^+$ $[M+H]^+$: 300.1124, found: 300.1115.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*S*)-enantiomer t_R = 8.46 min, (*R*)-enantiomer t_R (single peak) = 28.96 min.

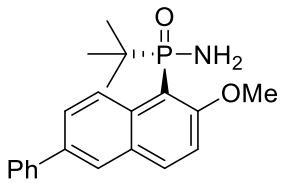
(*R*)-*P*-(tert-butyl)-*P*-(2-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphinic amide (**8e**)



Isolated as a white solid in 45% yield (126 mg) and >99% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.5 Hz, 1H), 6.72 (dd, *J* = 8.5, 4.8 Hz, 1H), 3.79 (s, 3H), 3.65 – 3.56 (m, 1H), 3.20 (dt, *J* = 17.7, 5.7 Hz, 1H), 3.12 (s, 2H), 2.72 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.77 (m, 1H), 1.75 – 1.66 (m, 2H), 1.65 – 1.55 (m, 1H), 1.13 (d, *J* = 15.8 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.09 (d, *J* = 4.6 Hz), 145.82 (d, *J* = 7.0 Hz), 133.25 (d, *J* = 2.1 Hz), 131.73 (d, *J* = 10.3 Hz), 117.61 (d, *J* = 95.2 Hz), 108.24 (d, *J* = 7.4 Hz), 55.16, 35.83 (d, *J* = 91.8 Hz), 29.87, 28.51 (d, *J* = 2.2 Hz), 24.41 (d, *J* = 0.9 Hz), 22.39 (d, *J* = 84.5 Hz).
^{31}P NMR (203 MHz, $CDCl_3$): δ 50.18.

HRMS: calculated for $C_{15}H_{24}NNaO_2P^+$ $[M+H]^+$: 304.1437, found: 304.1142.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*S*)-enantiomer t_R = 4.96 min, (*R*)-enantiomer t_R (single peak) = 6.20 min.

(*R*)-*P*-(*tert*-butyl)-*P*-(2-methoxy-6-phenylnaphthalen-1-yl)phosphinic amide (**8f**)

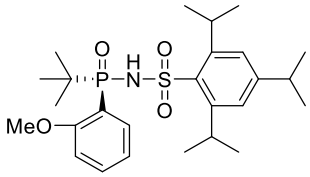


Isolated as a white solid in 60% yield (212 mg) and >99% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.64 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.94 (s, 1H), 7.80 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 9.0, 4.3 Hz, 1H), 3.95 (s, 3H), 3.31 (brs, 2H), 1.17 (d, *J* = 16.1 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7 (d, *J* = 3.2 Hz), 140.6, 136.5, 135.9 (d, *J* = 6.7 Hz), 134.9 (d, *J* = 2.1 Hz), 129.7 (d, *J* = 9.0 Hz), 128.9, 128.2 (d, *J* = 2.1 Hz), 127.3, 127.2, 127.0, 125.63, 112.4 (d, *J* = 93.6 Hz), 112.3 (d, *J* = 7.7 Hz), 56.0, 35.9 (d, *J* = 93.2 Hz), 24.4.
^{31}P NMR (203 MHz, $CDCl_3$): δ 50.11.
HRMS: calculated for $C_{21}H_{25}NO_2P^+$ $[M+H]^+$: 354.1617, found: 354.1618.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (*S*)-enantiomer t_R = 10.91 min, (*R*)-enanatiomer (single peak) t_R = 15.34 min.

General procedure for the conversion of arylphosphinic amides **8** to Brønsted acids **3b** and **4**:
A slurry of NaH (3 equiv of 60% NaH in oil) in anhydrous THF (3.0 mL) at 0 °C was added to a solution of phosphinamide **8** (0.5 mmol, 1 equiv) and the mixture was stirred for 30 min. The arylsulfonyl chloride (1.5 equiv) was added slowly, and the mixture was warmed to RT and monitored by TLC. After complete conversion (~12-15 h), NH_4Cl (0.1 g) was added portion-wise, the mixture was diluted with THF and filtered. The filtrate was concentrated and the crude residue was purified by flash column chromatography on silica gel to give the desired product. The product was dissolved in DCM (15 mL) and thoroughly washed with 4 M HCl (2x) to remove any salt impurities and completely protonate the catalyst. The organic layer was separated and concentrated under reduced pressure. The residue was taken up in toluene (5 mL), evaporated to dryness again and dried under high vacuum for 24 h to give the catalyst.

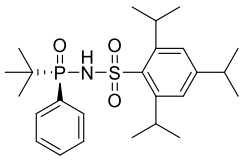
Note: Upon completion of the coupling reaction between intermediate **8** and the sulfonyl chloride, some analogs **4** were used directly in the subsequent demethylation step (without isolation/purification) to get the final catalysts **5**.

(R)-N-(tert-butyl(2-methoxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**3b**): This compound was recently reported by Han and coworkers.[8]



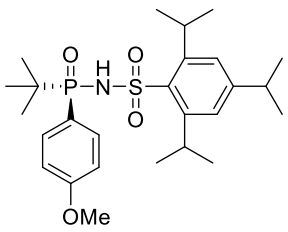
Isolated as a yellow solid in 97% yield (240 mg).
^{1}H NMR (500 MHz, CD_3OD): δ 7.74 (ddd, *J* = 7.0, 1.5 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.11 (s, 2H), 6.91 (dd, *J* = 7.8, 5.3 Hz, 1H), 6.77 (t, *J* = 7.0 Hz, 1H), 4.49 - 4.40 (m, 2H), 3.54 (s, 3H), 2.88 (hept, *J* = 6.9 Hz, 1H), 1.27 – 1.21 (m, 12H), 1.14 – 1.04 (m, 15H).
^{31}P NMR (202 MHz, CD_3OD): δ 33.97;
HRMS: calculated for $C_{26}H_{40}NO_4PSNa$ [M+Na]: 516.2308, found: 516.2305.

(R)-N-(tert-butyl(phenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**4a**):



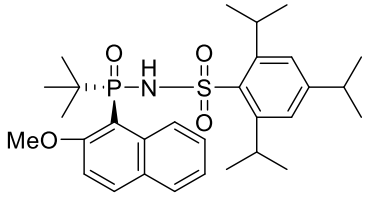
Isolated as a yellow solid in 96% yield (223 mg).
^{1}H NMR (500 MHz, CD_3OD): δ 7.66-7.62 (m, 2H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.22 (td, *J* = 8.0, 3.0 Hz, 2H), 7.04 (s, 2H), 4.51-4.45 (m, 2H), 2.88-2.82 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 6H), 1.21 (d, *J* = 6.5 Hz, 6H), 1.06 (d, *J* = 7.0 Hz, 6H), 1.01 (d, *J* = 15.5 Hz, 9H);
^{13}C NMR (125 MHz, CD_3OD): δ 150.8, 149.2, 142.7, 134.8 (d, *J* = 112.0 Hz), 134.5 (d, *J* = 8.1 Hz), 131.3 (d, *J* = 1.8 Hz), 128.1 (d, *J* = 10.9 Hz), 123.6, 35.3, 33.9 (d, *J* = 103.8 Hz), 30.2, 25.6, 25.2, 25.1, 24.33, 24.30;
^{31}P NMR (202 MHz, CD_3OD): δ 31.74;
HRMS: calculated for $C_{25}H_{38}NO_3PSNa$ $[M+Na]^+$: 486.2202, found: 486.2194.

(R)-N-(tert-butyl(4-methoxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**4b**):



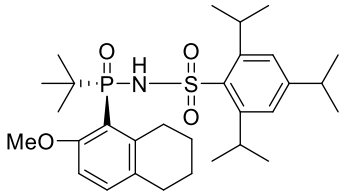
Upon completion of the coupling reaction with the sulfonyl chloride, compound **4b** was used directly in the subsequent demethylation step to get the final catalyst **5b**.

(R)-N-(tert-butyl(2-methoxynaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**4c**):



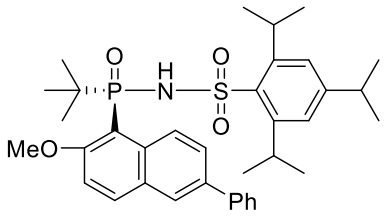
Compound was isolated as a white solid in 98% yield (173 mg).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.43 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.05 (s, 2H), 4.16 (hept, *J* = 6.5 Hz, 2H), 4.10 (s, 3H), 2.81 (hept, *J* = 7.0 Hz, 1H), 1.31 – 1.11 (m, 21H), 1.10 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.42, 152.56, 150.27, 136.80 (d, *J* = 7.6 Hz), 135.92 (d, *J* = 2.3 Hz), 135.43, 129.60 (d, *J* = 10.0 Hz), 128.28, 127.99, 127.57 (d, *J* = 2.3 Hz), 124.64, 123.75, 111.89 (d, *J* = 8.2 Hz), 110.79, 110.03, 56.53, 37.40 (d, *J* = 89.4 Hz), 34.18, 29.91, 24.91 (d, *J* = 3.4 Hz), 24.60, 23.63 (d, *J* = 5.8 Hz).
^{31}P NMR (203 MHz, $CDCl_3$): δ 43.1.
HRMS: calculated for $C_{30}H_{41}O_4NPS$: 542.2499, found: 542.2491.

(R)-N-(tert-butyl(2-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**4d**):



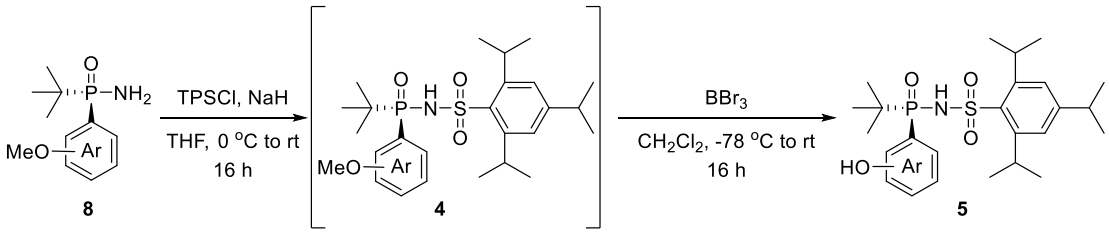
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.08 (s, 2H), 6.74 (dd, *J* = 8.5, 5.2 Hz, 1H), 4.18 (hept, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 3.40 (dt, *J* = 18.0, 6.2 Hz, 1H), 3.03 (dt, *J* = 17.9, 5.5 Hz, 1H), 2.85 (hept, *J* = 6.9 Hz, 1H), 2.74 – 2.64 (m, 2H), 1.73 – 1.56 (m, 4H), 1.26 (d, *J* = 6.7 Hz, 6H), 1.24 – 1.15 (m, 15H), 1.13 (d, *J* = 6.7 Hz, 6H).
^{31}P NMR (203 MHz, $CDCl_3$): δ 44.0.
Upon completion of the coupling reaction with the sulfonyl chloride, the crude compound **4d** was used directly in the subsequent demethylation step to get the final catalyst **5d**.

(R)-N-(tert-butyl(2-methoxy-6-phenylnaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**4e**):



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 9.2 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.95 (t, *J* = 2.1 Hz, 1H), 7.75 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.68 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.31 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.06 (s, 2H), 4.18 (hept, *J* = 6.7 Hz, 2H), 4.11 (s, 3H), 2.81 (hept, *J* = 6.8 Hz, 1H), 1.26 – 1.20 (m, 15H), 1.18 (dd, *J* = 6.9, 2.4 Hz, 6H), 1.12 (d, *J* = 6.7 Hz, 6H).
^{31}P NMR (203 MHz, $CDCl_3$): δ 43.2.
Upon completing of the coupling reaction with the sulfonyl chloride, compound **4e** the crude product was used directly in the subsequent demethylation step to get the final catalyst **5e**.

General procedure for the synthesis of Brønsted acids **5**:

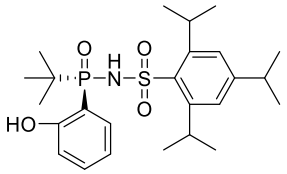


Note: Upon completion of the coupling reaction between intermediate **8** and the sulfonyl chloride, some analogs **4** were used directly in the subsequent demethylation step to get the final catalysts **5**.

Demethylation step: A solution of intermediates **3b** or **4** in dry DCM (5 mL) was cooled to -78 °C, then BBr_3 (1.2 equiv in hexane) was added slowly over a 5 min period. After the addition was finished, the reaction mixture was allowed to warm-up to RT and stirred overnight. The reaction was quenched with water and diluted with DCM. The organic fraction was washed with 1 N HCl, dried over anhydrous $MgSO_4$, concentrated and purified by flash column chromatography on silica gel. The isolated product was re-dissolved in DCM (15 mL) and thoroughly washed with 4 M HCl (15 mL x 2) to remove any metal impurities and completely protonate the catalyst. The organic layer

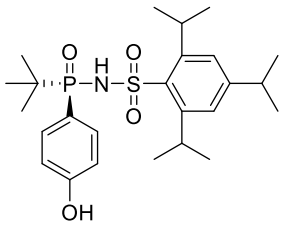
was separated and concentrated under reduced pressure. The residue was taken up in toluene (5 mL), evaporated to dryness again and allowed to dry under high vacuum for a minimum of 24 h to give (*R*)-phenolic catalyst.

(R)-N-(tert-butyl(2-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**5a**):



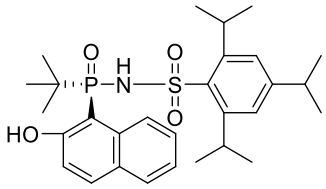
Compound was isolated as a yellow solid in 92% yield (221 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.60 (s, 1H), 7.42 (ddt, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.31-7.23 (m, 1H), 7.14 (s, 2H), 6.97 – 6.89 (m, 1H), 6.84 – 6.75 (m, 1H), 6.41 (d, *J* = 8.7 Hz, 1H), 3.91 (hept, *J* = 6.6 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.30 – 1.14 (m, 27H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6 (d, *J* = 5.0 Hz), 153.7, 150.3, 135.1 (d, *J* = 2.1 Hz), 134.2 (s), 133.0 (d, *J* = 8.4 Hz), 123.9, 118.8 (d, *J* = 12.5 Hz), 118.0 (d, *J* = 9.3 Hz), 107.5 (d, *J* = 117.5 Hz), 34.6 (d, *J* = 86.2 Hz), 34.2, 30.1, 24.7 (d, *J* = 47.0 Hz), 23.8, 23.5 (d, *J* = 4.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ 45.42.
HRMS: calculated for $C_{25}H_{39}NO_4PS^+$ $[M+H]^+$: 480.2332, found: 480.2336.

(R)-N-(tert-butyl(4-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide: (**5b**)



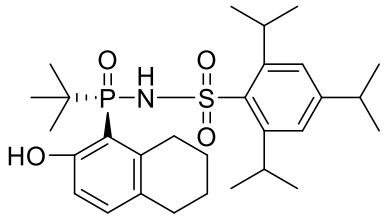
Isolated as a yellow solid, in 80% yield (193 mg).
^{1}H NMR (500 MHz, MeOD): δ 7.51–7.44 (m, 2H), 7.17 (s, 2H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 2H), 4.27–4.14 (m, 2H), 2.96–2.87 (m, 1H), 1.31–1.20 (m, 12H), 1.18–1.03 (m, 15H).
^{13}C NMR (126 MHz, MeOD): δ 161.4, 152.4, 149.6, 136.6, 134.8 (d, *J* = 11.0 Hz), 123.1, 116.5 (d, *J* = 125.4 Hz), 114.7 (d, *J* = 13.8 Hz), 34.0, 33.1 (d, *J* = 93.4 Hz), 28.9, 23.8 (d, *J* = 38.7 Hz), 23.0, 22.7 (d, *J* = 6.2 Hz).
^{31}P NMR (203 MHz, MeOD): δ 41.15.
HRMS: calculated for $C_{25}H_{39}NO_4PS^+$ $[M+H]^+$: 480.2332, found: 480.2335.

(R)-N-(tert-butyl(2-hydroxynaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**5c**):



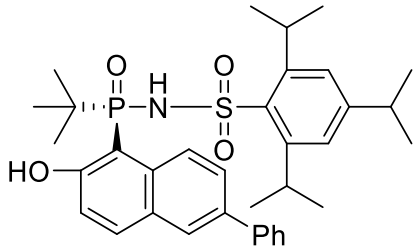
Isolated as a yellow solid in 95% yield (252 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.55 (s, 1H), 8.15 (m, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.70 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.06 (m, 3H), 6.56 (s, 1H), 3.88 (hept, *J* = 6.7 Hz, 2H), 2.88 (hept, *J* = 6.9 Hz, 1H), 1.36 – 1.14 (m, 21H), 1.11 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5 (d, *J* = 4.8 Hz), 153.4, 150.1, 136.5 (d, *J* = 2.3 Hz), 134.6, 133.6 (d, *J* = 8.6 Hz), 128.4 (d, *J* = 10.2 Hz), 128.0 (d, *J* = 197.2 Hz), 125.5 (d, *J* = 4.2 Hz), 123.9, 123.2, 120.4 (d, *J* = 11.1 Hz), 36.8 (d, *J* = 85.8 Hz), 34.2, 30.2, 24.8, 24.7 (d, *J* = 39.8 Hz), 23.5 (d, *J* = 4.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ 47.72.
HRMS: calculated for $C_{29}H_{41}NO_4PS^+$ $[M+H]^+$: 530.2488, found: 530.2496.

(R)-N-(tert-butyl(2-hydroxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**5d**):



Isolated as a yellow solid in 93% yield (248 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.50 (s, 1H), 7.17 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.19 (d, *J* = 10.9 Hz, 1H), 3.97 (hept, *J* = 6.5 Hz, 2H), 3.13 (ddd, *J* = 15.9, 10.1, 5.4 Hz, 1H), 2.95 – 2.78 (m, 2H), 2.75 – 2.67 (m, 2H), 1.98 – 1.68 (m, 4H), 1.31 (d, *J* = 6.6 Hz, 6H), 1.27 – 1.22 (m, 12H), 1.18 (d, *J* = 16.6 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9 (d, *J* = 5.6 Hz), 153.3, 150.2, 140.3 (d, *J* = 9.1 Hz), 136.0, 135.0, 128.9 (d, *J* = 10.4 Hz), 124.0, 116.4 (d, *J* = 11.0 Hz), 106.3 (d, *J* = 109.8 Hz), 36.2 (d, *J* = 83.9 Hz), 34.1, 30.3, 29.5, 24.8 (d, *J* = 84.6 Hz), 24.8 (d, *J* = 14.8 Hz), 24.3, 23.6, 22.4, 22.1.
^{31}P NMR (162 MHz, $CDCl_3$): δ 49.00.
HRMS: calculated for $C_{29}H_{45}NO_4PS^+$ $[M+H]^+$: 534.2801, found: 534.2808.

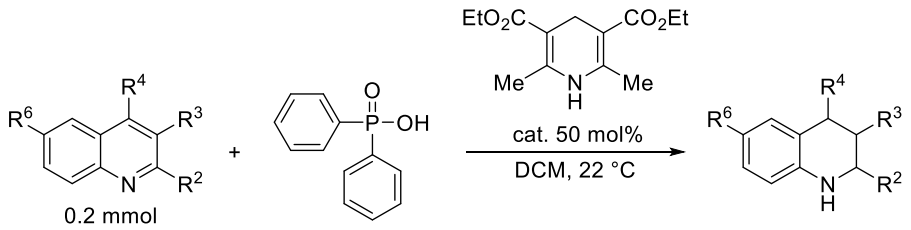
(R)-N-(tert-butyl(2-hydroxy-6-phenylnaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (**5e**):



Isolated as a yellow solid in 88% yield (267 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.49 (s, 1H), 8.30 (d, J = 8.9 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.64 (s, 1H), 7.44 – 7.30 (m, 6H), 7.17 (s, 2H), 7.13 (dd, J = 8.9, 4.7 Hz, 1H), 3.98 (hept, J = 6.7 Hz, 2H), 2.89 (hept, J = 6.9 Hz, 1H), 1.35 (d, J = 6.7 Hz, 6H), 1.28 – 1.12 (m, 21H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.2 (d, *J* = 4.3 Hz), 153.6, 150.6, 140.0, 136.8, 135.3, 134.7, 132.9 (d, *J* = 8.7 Hz), 128.6 (d, *J* = 10.1 Hz), 128.3, 126.9, 126.6 (d, *J* = 126.9 Hz), 126.3 (d, *J* = 4.1 Hz), 124.0, 120.3 (d, *J* = 10.8 Hz), 98.3 (d, *J* = 111.8 Hz), 36.9 (d, *J* = 85.1 Hz), 34.2, 30.3, 25.2, 24.6, 23.5 (d, *J* = 6.9 Hz).
^{31}P NMR (203 MHz, $CDCl_3$): δ 48.88.
HRMS: calculated for $C_{35}H_{45}NO_4PS^+$ $[M+H]^+$: 606.2801, found: 606.2803.

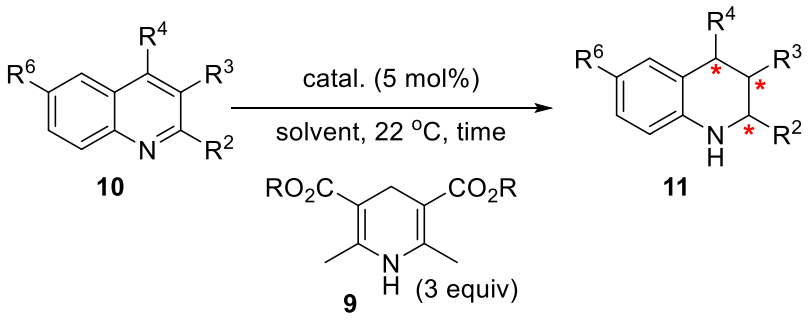
<u>General procedure for the transfer hydrogenation of quinolines **10** to the tetrahydroquinolines **11**:</u>

General procedure for the synthesis of the racemic tetrahydroquinolines:



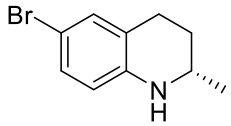
An oven dried 2 dram vial equipped with a stir bar was cooled to ambient temperature in a desiccator and subsequently charged with the requisite quinoline (0.200 mmol). 1 mL of DCM, Hantzsch ester (152 mg, 0.600 mmol) and diphenylphosphinic acid (21.8 mg, 0.500 mmol). The vial was capped under air, sealed with parafilm and the mixture was stirred at RT for 2-24 h. Progress of the reaction was monitored by TLC (20% EtOAc and 80% hexanes). The crude product was purified by flash chromatography on silica gel (using EtOAc/hexanes) to afford the desired tetrahydroquinoline.

*General procedure for the asymmetric transfer hydrogenation of quinolines **10** to the tetrahydroquinolines **11***:



An oven-dried flask was fitted with magnetic stirring bar and charged with the quinoline (reactions were typically carried out at a 0.1-0.2 mmol scale), catalyst (5 mol%), Hantzsch ester (3.0 equiv) and solvent (0.5 mL). The resulting mixture was stirred at RT (~22 °C), unless otherwise indicated and monitored by TLC. When all starting material was consumed, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using the solvent system indicated to isolate the corresponding product.

(S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (**11a**):



Reaction time: 5 h using catalyst **5c**. Known compound[9], purified using a 0-2% EtOAc/hexanes eluent gradient; isolated as white solid in 98% yield (44.2 mg) and 88% ee. The compound was crystallized from DCM/hexanes to afford the tetrahydroquinoline **11e** in 93% ee.

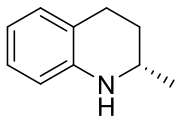
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 – 7.05 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 1H), 3.38 (dqd, *J* = 9.3, 6.3, 2.9 Hz, 1H), 2.80 (ddd, *J* = 17.0, 11.5, 5.7 Hz, 1H), 2.75 – 2.64 (dt, 1H), 1.98 – 1.87 (m, 1H), 1.55 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3): δ 143.9, 131.8, 129.5, 123.3, 115.5, 108.4, 47.2, 29.8, 26.5, 22.6.

Chiral HPLC method: Chiralpak OD-H, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (*R*)-enantiomer t_R (minor) = 8.6 min, (*S*)-enantiomer t_R (major) = 11.2 min.

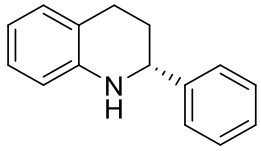
For the purpose of comparison the product was also analyzed using the same chiral HPLC column and solvent system as previously reported:[9] Chiralcel OJ-H, hexane/IPA = 95/5, 0.8 mL/min, λ = 254 nm; (*S*)-enantiomer t_R (major) = 19.04 min, (*R*)-enatiomer t_R (minor) = 23.19 min.

*(S)-2-methyl-1,2,3,4-tetrahydroquinoline (***11b**):
NMR and chiral HPLC data consistent with those previously reported.[10]



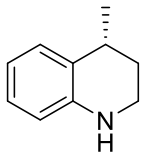
Compound was purified using a 0-1% EtOAc/hexanes as the eluent; isolated as a pale-yellow oil in 73% yield (21.6 mg) and 88% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 – 6.90 (m, 2H), 6.60 (td, *J* = 7.3, 1.2 Hz, 1H), 6.47 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.70 (broad s, 1H), 3.40 (dqd, *J* = 10.0, 6.3, 2.8 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.73 (ddd, *J* = 16.3, 5.2, 3.4 Hz, 1H), 1.93 (dddd, *J* = 12.8, 5.6, 3.4, 2.8 Hz, 1H), 1.63 – 1.55 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.9, 129.4, 126.8, 121.3, 117.1, 114.1, 47.3, 30.3, 26.7, 22.8.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (*R*)-enantiomer t_R (minor) = 6.78 min, (*S*)-enantiomer (majot) t_R = 7.79 min.

(R)-2-phenyl-1,2,3,4-tetrahydroquinoline (**11c**):
NMR and chiral HPLC data consistent with those previously reported.[10]



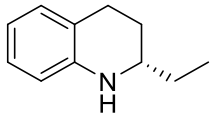
Compound was purified using a 0-3% EtOAc/hexanes eluent and isolated as a white solid 95% yield (39.9 mg) and 59.3% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.07 – 6.97 (m, 2H), 6.66 (td, *J* = 7.3, 1.2 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 4.45 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.05 (s, 1H), 2.93 (ddd, *J* = 16.2, 10.7, 5.5 Hz, 1H), 2.75 (dt, *J* = 16.3, 4.8 Hz, 1H), 2.13 (dddd, *J* = 13.1, 5.4, 4.5, 3.3 Hz, 1H), 2.00 (dddd, *J* = 13.0, 10.7, 9.3, 5.1 Hz, 1H).
^{13}C NMR (126 MHz, CDCl3): δ 144.9, 144.9, 129.4, 128.7, 127.6, 127.0, 126.7, 121.0, 117.3, 114.1, 56.4, 31.1, 26.5.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (*S*)-enantiomer t_R (minor) = 15.13 min, (*R*)-enantiomer t_R (major) = 21.39 min (major).

(R)-4-methyl-1,2,3,4-tetrahydroquinoline (**11d**):
NMR and chiral HPLC data consistent with those previously reported[11]



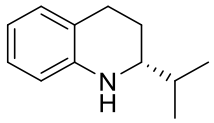
Compound purified using a 0-20% Et_2O in pentane and isolated a pale-yellow oil in 70% yield and 30% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (d, J = 7.6 Hz, 1H), 6.96 (tdd, *J* = 7.3, 1.7, 0.8 Hz, 1H), 6.63 (td, *J* = 7.4, 1.2 Hz, 1H), 6.48 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.91 (s, 1H), 3.39 – 3.23 (m, 2H), 2.92 (h, *J* = 6.6 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.68 (dddd, *J* = 13.0, 6.9, 6.1, 3.5 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, CDCl3): δ 144.3, 128.6, 126.9, 126.8, 117.1, 114.3, 39.2, 30.4, 30.0, 22.8.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 0.6 mL/min, λ = 254 nm; (*S*)-enantiomer t_R (minor) = 16.41 min, (*R*)-enantiomer t_R (major) = 17.67 min.

(S)-2-ethyl-1,2,3,4-tetrahydroquinoline (**11e**):
NMR and chiral HPLC data consistent with those previously reported.[10]



Compound was purified using a 0-2% EtOAc in hexanes and isolated as a pale-yellow oil in 72% yield (23.1 mg) and 75% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (ddt, *J* = 8.2, 7.4, 0.8 Hz, 2H), 6.60 (td, *J* = 7.4, 1.2 Hz, 1H), 6.48 (dt, *J* = 7.4, 1.3 Hz, 1H), 3.77 (s, 1H), 3.17 (dtd, *J* = 9.4, 6.4, 2.9 Hz, 1H), 2.88 – 2.77 (m, 1H), 2.73 (ddd, *J* = 16.3, 5.4, 4.0 Hz, 1H), 1.98 (dddd, *J* = 12.7, 5.6, 4.0, 2.9 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.56 – 1.49 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.9, 129.4, 126.8, 121.5, 117.0, 114.1, 53.2, 29.6, 27.7, 26.6, 10.2.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (*R*)-enantiomer t_R (minor) = 6.56 min, (*S*)-enantiomer t_R (major) = 7.91 min.

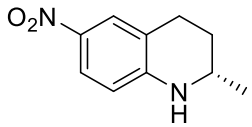
(R)-2-isopropyl-1,2,3,4-tetrahydroquinoline (**11f**):



NMR and chiral HPLC data consistent with those previously reported,[10] purified using a 0-2% EtOAc/hexanes eluent; isolated as a pale-yellow oil in 77% yield (27.0 mg) and 66% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 – 6.91 (m, 2H), 6.59 (td, *J* = 7.3, 1.2 Hz, 1H), 6.52 – 6.45 (m, 1H), 3.76 (s, 1H), 3.04 (ddd, *J* = 10.0, 5.9, 2.9 Hz, 1H), 2.81 (ddd, *J* = 16.5, 11.3, 5.5 Hz, 1H), 2.77 – 2.70 (m, 1H), 1.92 (dddd, *J* = 12.5, 5.5, 3.9, 2.9 Hz, 1H), 1.77 – 1.60 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H).

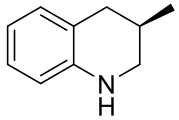
^{13}C NMR (126 MHz, $CDCl_3$): δ 145.2, 129.3, 126.8, 121.6, 116.9, 114.1, 57.4, 32.7, 26.8, 24.7, 18.7, 18.4.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (*S*)-enantiomer t_R (minor) = 5.90 min, (*R*)-enantiomer t_R (major) = 8.53 min.

(S)-2-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (**11g**):



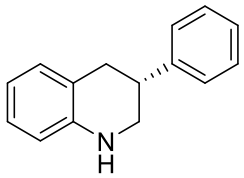
NMR and chiral HPLC data consistent with those previously reported;[12] compound was purified by flash column chromatography on silica gel (silica gel was deactivated with a 1% Et_3N in hexanes solution) using a 0-15% EtOAc/hexanes eluent gradient; isolated an orange solid in 83% yield (44.2 mg) and 86% ee. The compound was recrystallized from DCM/hexanes to afford the tetrahydroquinoline in 96% ee.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 – 7.86 (m, 2H), 6.42 – 6.32 (m, 1H), 4.53 (s, 1H), 3.55 (dqd, *J* = 9.7, 6.4, 3.4 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.00 (dtd, *J* = 12.9, 4.8, 3.4 Hz, 1H), 1.58 (dtd, *J* = 13.0, 9.8, 6.2 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 137.5, 125.9, 124.4, 119.8, 112.2, 47.6, 29.0, 26.3, 22.4.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 95/5, 1 mL/min, λ = 254 nm; (*R*)-enantiomer t_R (minor) = 19.35 min, (*S*)-enantiomer t_R (major) = 20.67 min (major).

(R)-3-methyl-1,2,3,4-tetrahydroquinoline (**11h**):



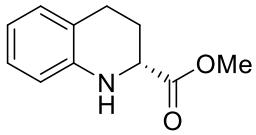
NMR and chiral HPLC data consistent with those previously reported.[13]
Compound was purified by flash column chromatography on silica gel using a 0-10% pentane/Et_2O eluent; isolated as a pale-yellow oil in 71% yield (20.9 mg) and 14% ee.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01-6.91 (m, 2H), 6.61 (td, *J* = 7.4, 1.2 Hz, 1H), 6.49 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.89 (s, 1H), 3.27 (ddd, *J* = 11.0, 3.7, 2.0 Hz, 1H), 2.90 (dd, *J* = 11.0, 9.6 Hz, 1H), 2.78 (ddd, *J* = 16.0, 5.0, 2.0 Hz, 1H), 2.43 (dd, *J* = 16.0, 10.2 Hz, 1H), 2.14 – 1.99 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 129.7, 126.8, 121.3, 117.1, 114.0, 49.0, 35.6, 27.3, 19.2.
Chiral HPLC method: Chiralcel OJ-H, hexane/IPA = 90/10, 0.5 mL/min, λ = 210 nm; (*R*)-enantiomer t_R = 30.77 min (major), (S)- enantiomer t_R = 37.77 min (minor).

(R)-3-phenyl-1,2,3,4-tetrahydroquinoline (**11i**):
The precursor 3-phenylquinoline was synthesized according to literature procedure.[14]



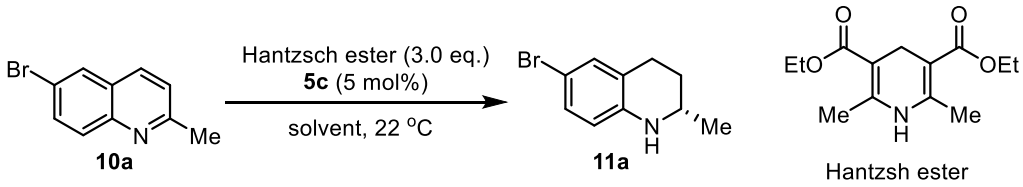
NMR and chiral HPLC data consistent with those previously reported.[15] Compound was purified by flash column chromatography on silica gel using 0-6% EtOAc/hexanes as the eluent; isolated as a pale-yellow solid in 51% yield (10.5 mg; yield based on recovered starting material) and 4% ee.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.30 – 7.22 (m, 3H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.66 (td, *J* = 7.4, 1.2 Hz, 1H), 6.57 (dd, *J* = 8.4, 1.3 Hz, 1H), 4.15 (s, 1H), 3.47 (ddd, *J* = 11.2, 3.7, 1.9 Hz, 1H), 3.35 (t, *J* = 10.7 Hz, 1H), 3.16 (tdd, *J* = 10.2, 5.8, 3.7 Hz, 1H), 3.09 – 2.93 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 144.0, 129.7, 128.8, 127.4, 127.1, 126.8, 121.6, 117.3, 114.3, 48.5, 38.8, 34.8.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1 mL/min, λ = 254 nm; (R)-enantiomer t_R = 18.81 min (major), (S)- 10.5 mg t_R = 24.04 min (minor).

Methyl (R)-1,2,3,4-tetrahydroquinoline-2-carboxylate (**11j**)



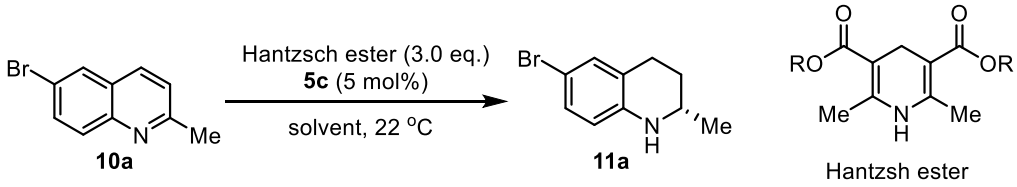
Reaction time: 4 h at 50 °C using catalyst **5c**. NMR and chiral HPLC data consistent with those previously reported.[16]
purified using a 0-8% Et_2O/hexanes eluent; isolated as a colourless oil in 71% yield (27.2 mg) and 30% ee.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.96 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.65 (td, *J* = 7.3, 1.2 Hz, 1H), 6.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.40 (s, 1H), 4.05 (dd, *J* = 8.8, 3.8 Hz, 1H), 3.78 (s, 3H), 2.90 – 2.71 (m, 2H), 2.29 (dtd, *J* = 13.0, 5.6, 3.8 Hz, 1H), 2.01 (dtd, *J* = 13.0, 9.1, 5.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 143.1, 129.3, 127.2, 120.7, 117.8, 114.7, 54.1, 52.5, 26.0, 24.8.
Chiral HPLC method: Chiralpak AD, hexane/IPA = 80/20, 1 mL/min, λ = 254 nm; (R)-t_R = 7.62 min (major), (S)-t_R = 9.04 min (minor).

Table 1: Solvent Screening and Optimization of Reaction Conditions



Entry	Solvent	Time (h)	Yield (%)	*ee* (%)
1	toluene	2	99	80
2	CH_2Cl_2	1.5	99	75
3	$CHCl_3$	0.5	99	80
4	CCl_4	1.5	99	86
5	DCE	1.5	99	78
6	cyclohexane	5	99	89
7	*n*-hexane	5	99	86
8	Et_2O	3	99	85
9	*t*-BuOMe	3	99	85
10	EtOAc	2	99	84

Table 2: Optimization of Hantzsh Ester

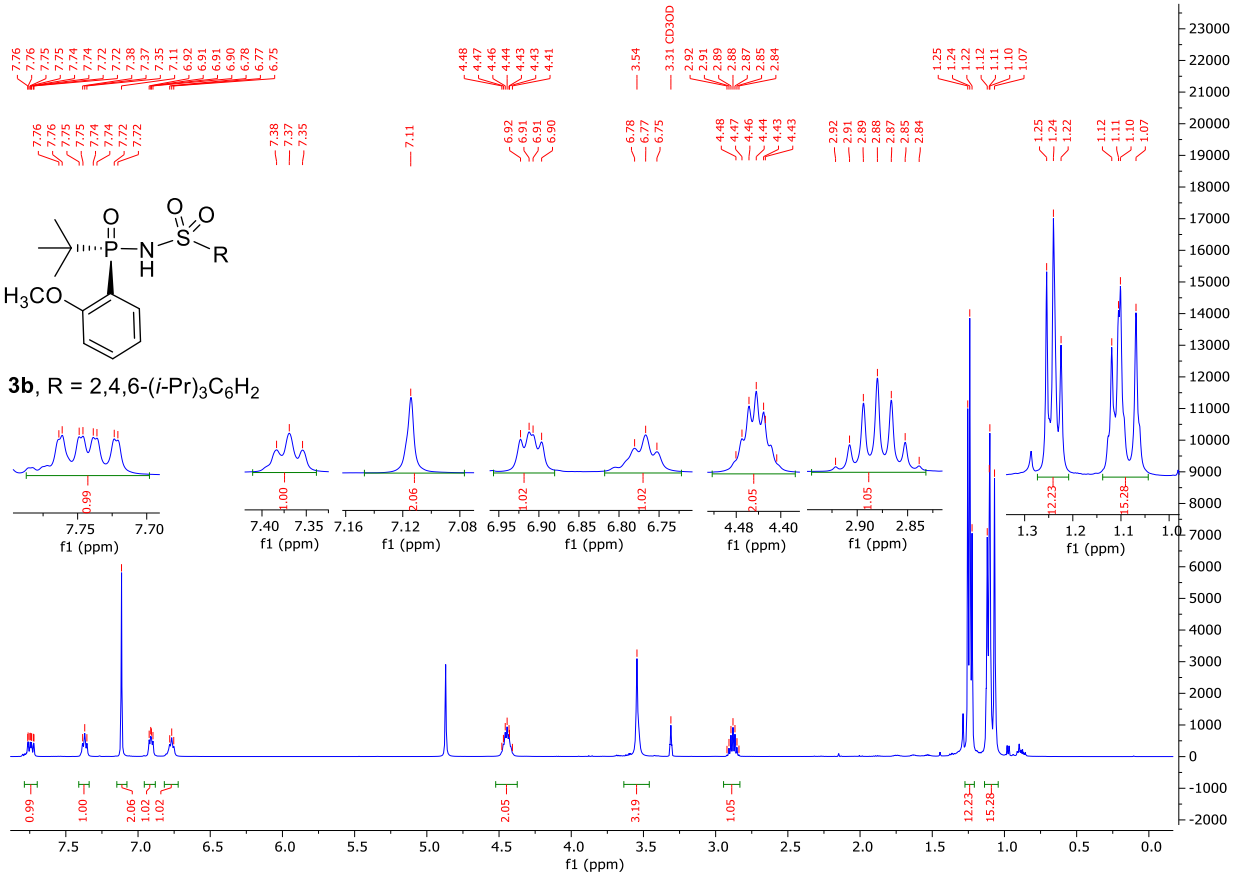


Entry	R	Time (h)	Yield (%)	*ee* (%)
1	Me	5	99	88
2	Et	5	99	89
3	*t*-Bu	3	99	85

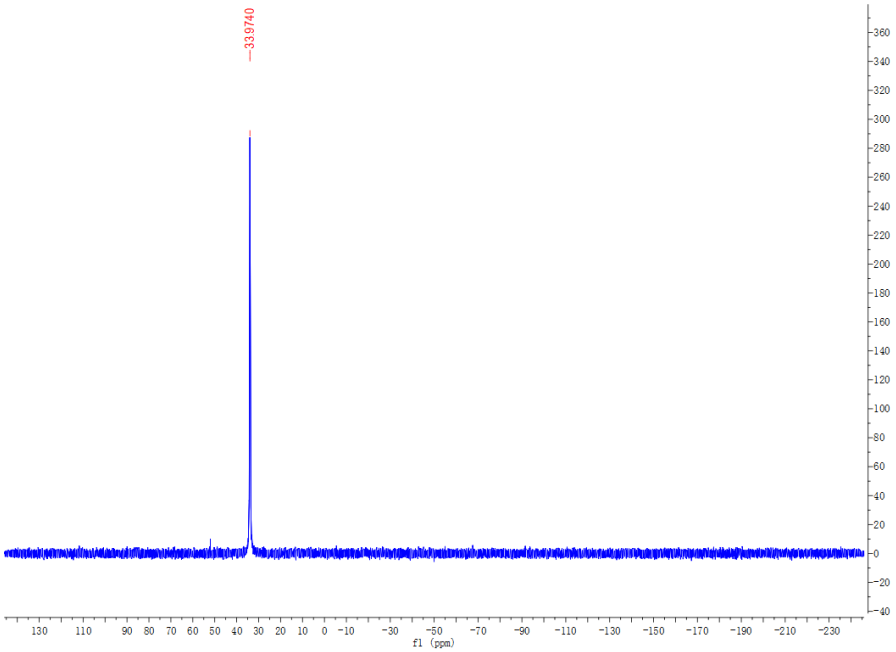
^{1}H, ^{13}C, ^{31}P NMR spectra and chiral HPLC chromatograms

Compounds Listed in Numerical Order

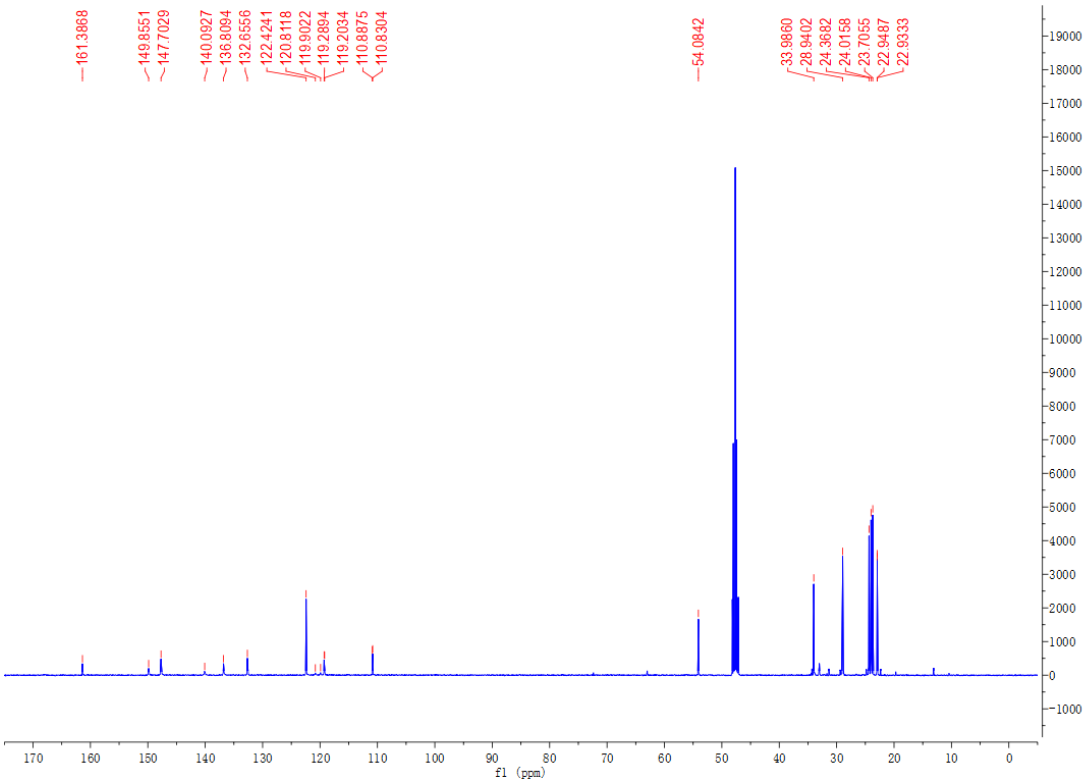
^{1}H NMR of **3b**



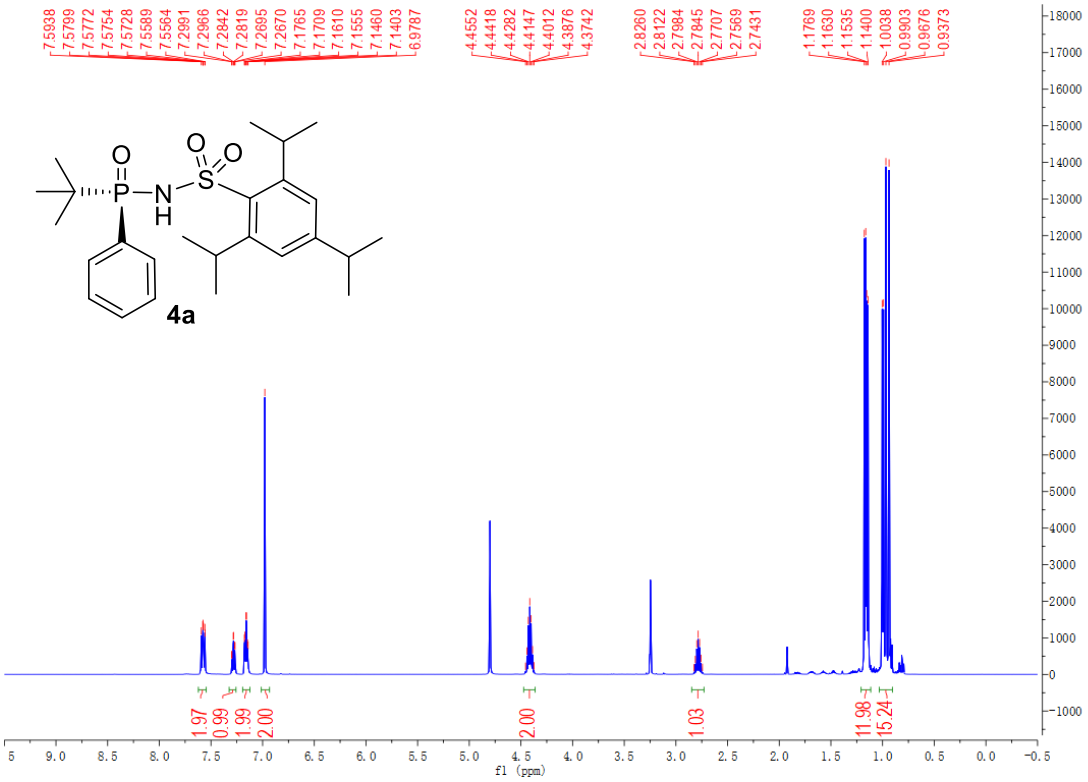
^{31}P NMR of **3b**



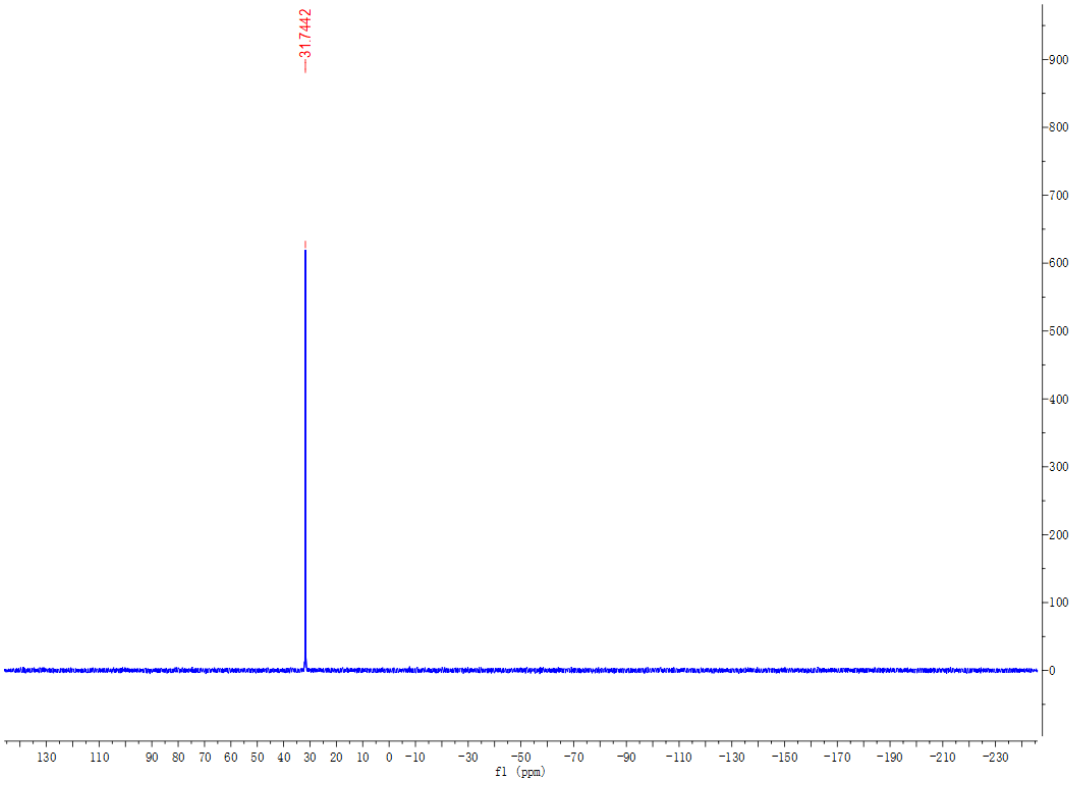
^{13}C NMR of **3b**


161.3868
149.8551
147.7029
140.0927
136.8094
132.6556
122.4241
120.8118
119.9022
119.2894
119.2034
110.8875
110.8304
54.0842
33.9860
28.9402
24.3682
24.0158
23.7055
22.9487
22.9333
f1 (ppm)

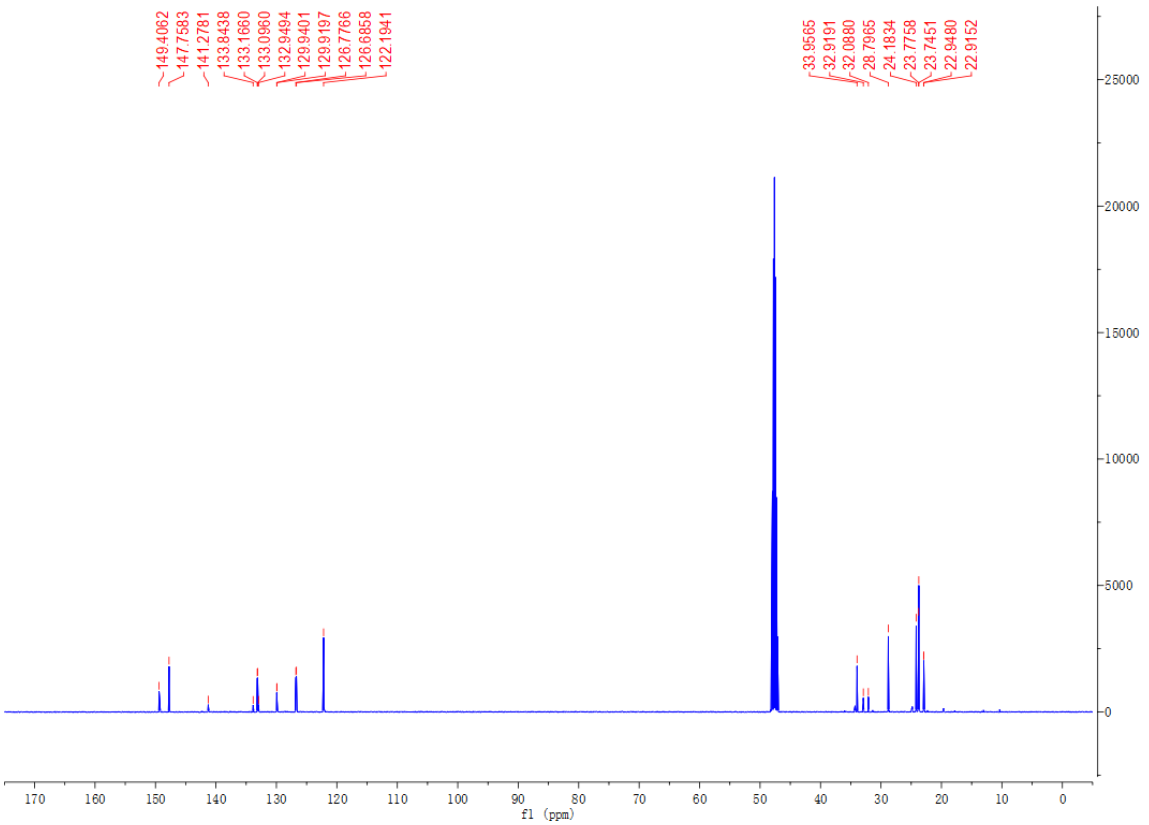
^{1}H NMR of **4a**



^{31}P NMR of **4a**

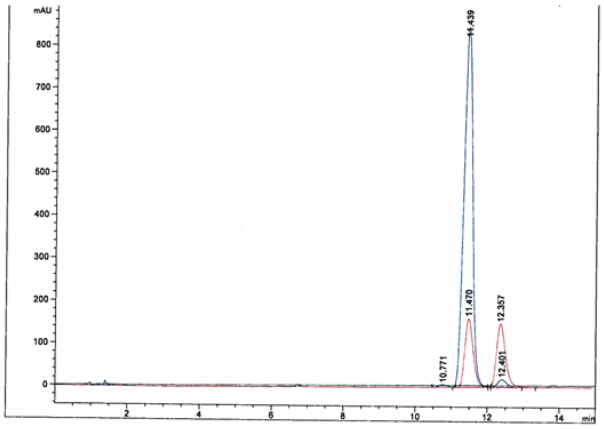


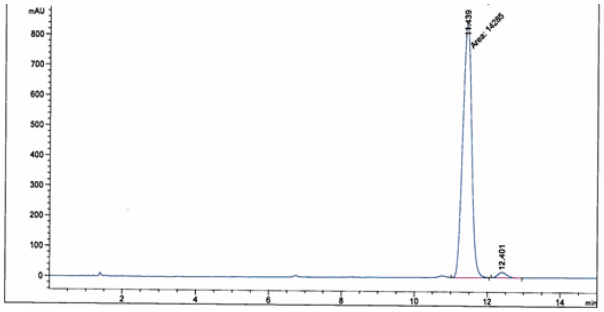
^{13}C NMR of **4a**


149.4062
147.7583
141.2781
133.8438
133.1660
133.0960
132.9494
129.9401
129.9197
126.7766
126.6858
122.1941
33.9565
32.9191
32.0880
28.7965
24.1834
23.7758
23.7451
22.9480
22.9152
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Chiral HPLC Chromatograms of **4a**

Method: HPLC instrument: Agilent 1260 HPLC; λ = 220 nm
Colum: Phenomenex Lux Cellulose-2, 4.6x100 mm
Solvent A: 0.1% (v/v) $HClO_4$ in water, Solvent B: CH_3CN; 50-90% solvent B in 15 min at a flow rate of 1.2 mL/min
Top panel, racemic (in red) superimposed with (*R*)-enantiomer (in blue); bottom panel (*R*)-**4a**; (*R*)-enantiomer t_R = 11.44 min (major), (*S*)- enantiomer t_R = 12.36 min (minor).

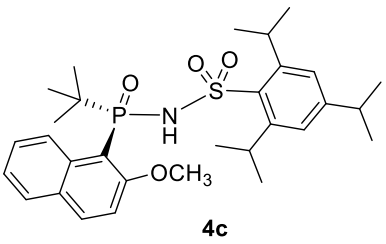




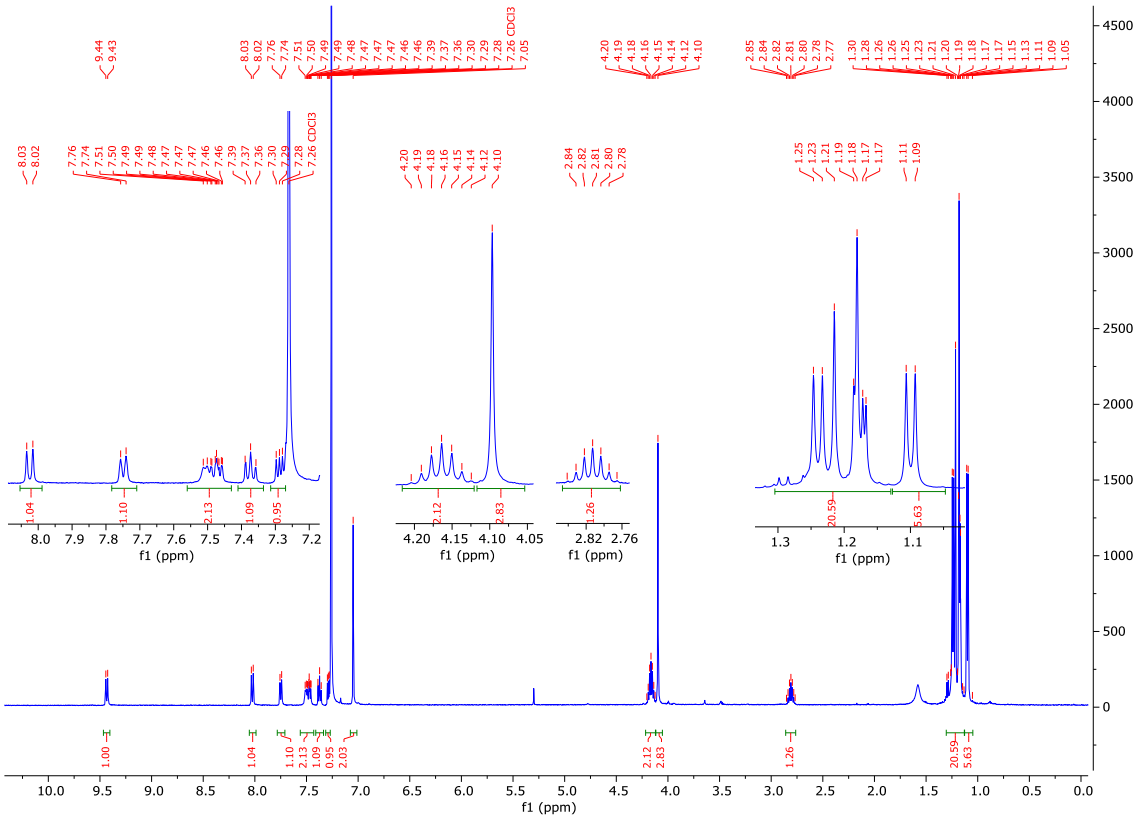
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.439	MM	0.2819	1.42850e4	844.44775	98.0089
2	12.401	BB	0.2276	290.20435	17.39890	1.9911
Totals :				1.45752e4	861.84665	

*** End of Report ***

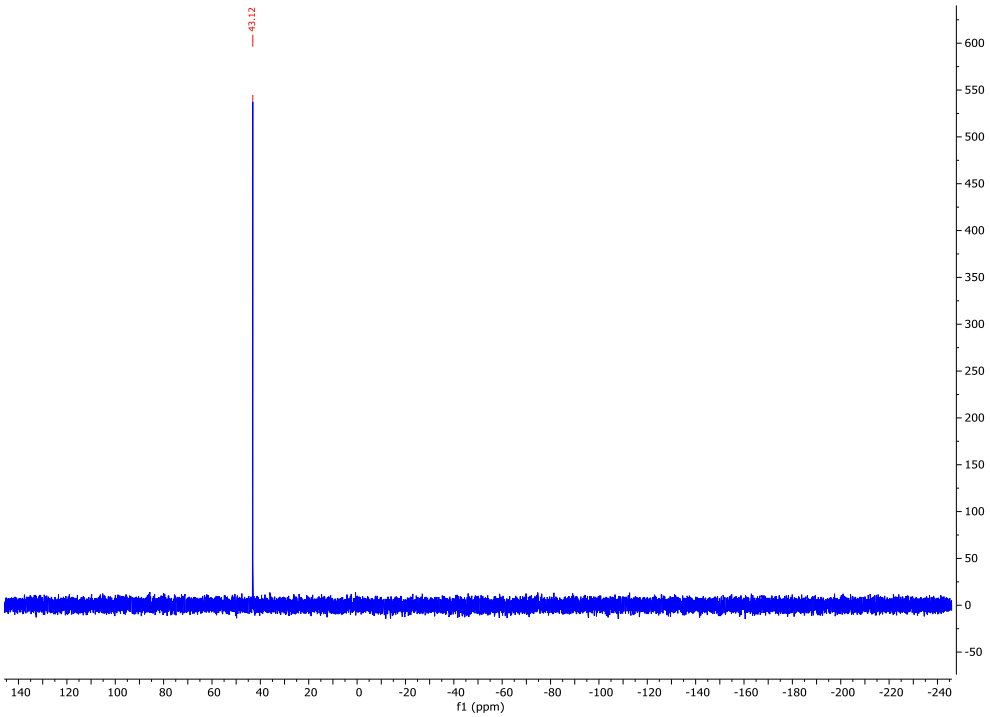
^{1}HNMR of **4c**



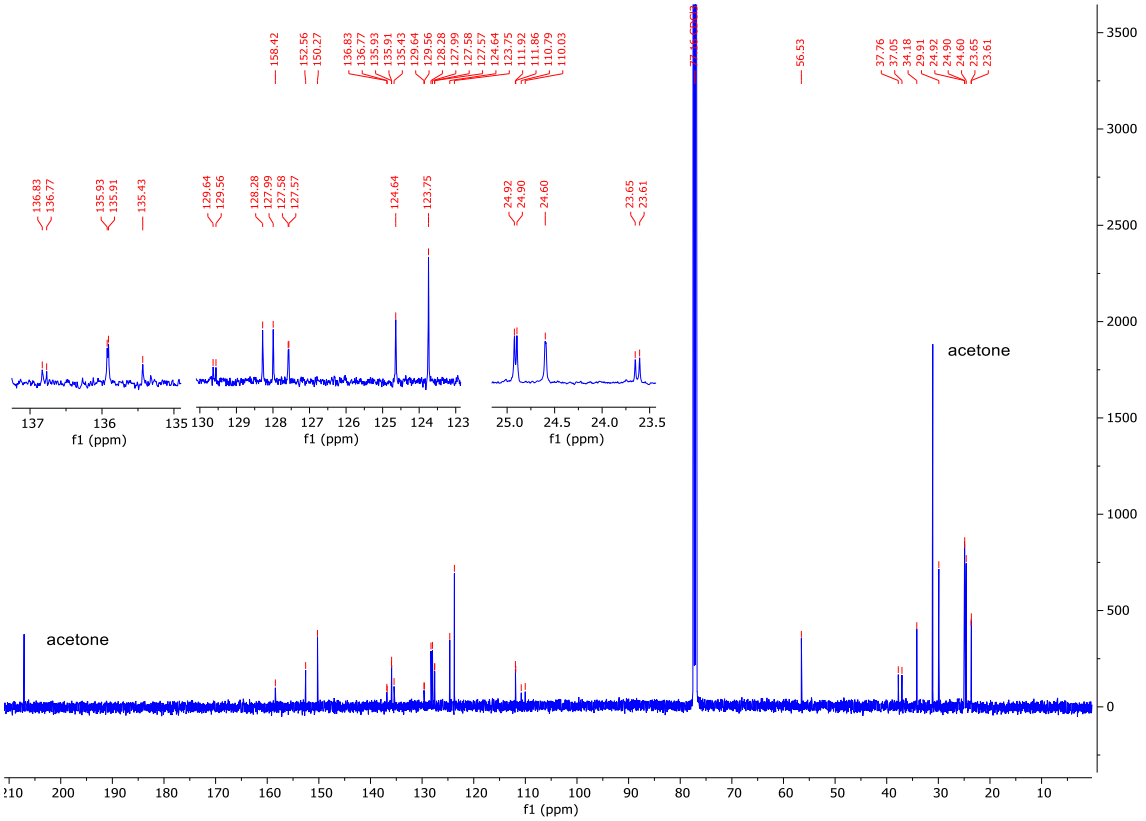
4c



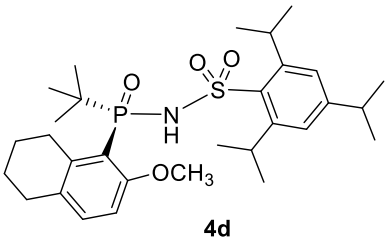
^{31}P NMR of **4c**



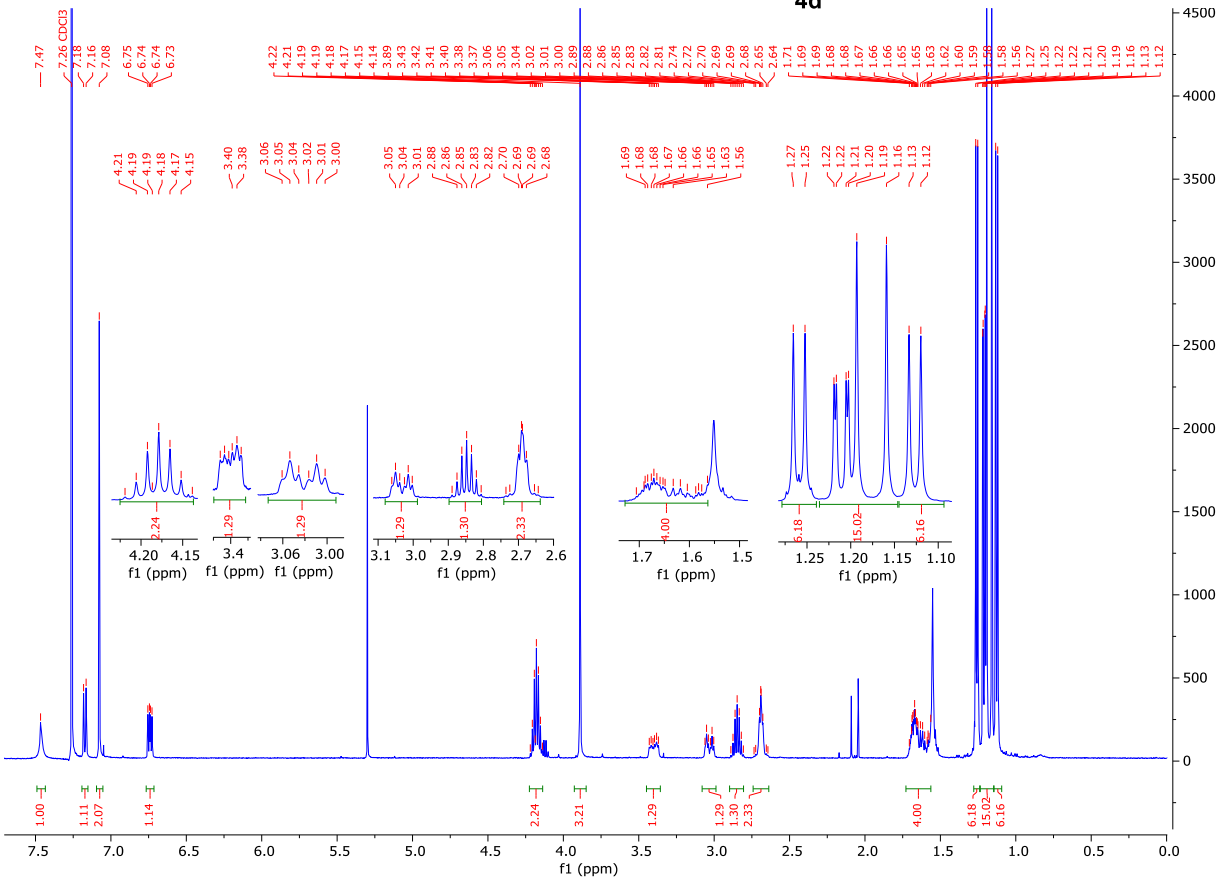
^{13}C NMR of **4c**


158.42
152.56
150.27
136.83
136.77
135.93
135.91
135.43
129.64
129.56
128.28
127.99
127.58
127.57
124.64
123.75
111.92
111.86
110.79
110.03
56.53
37.76
37.05
34.18
29.91
24.92
24.90
24.60
23.65
23.61
acetone
acetone
f1 (ppm)

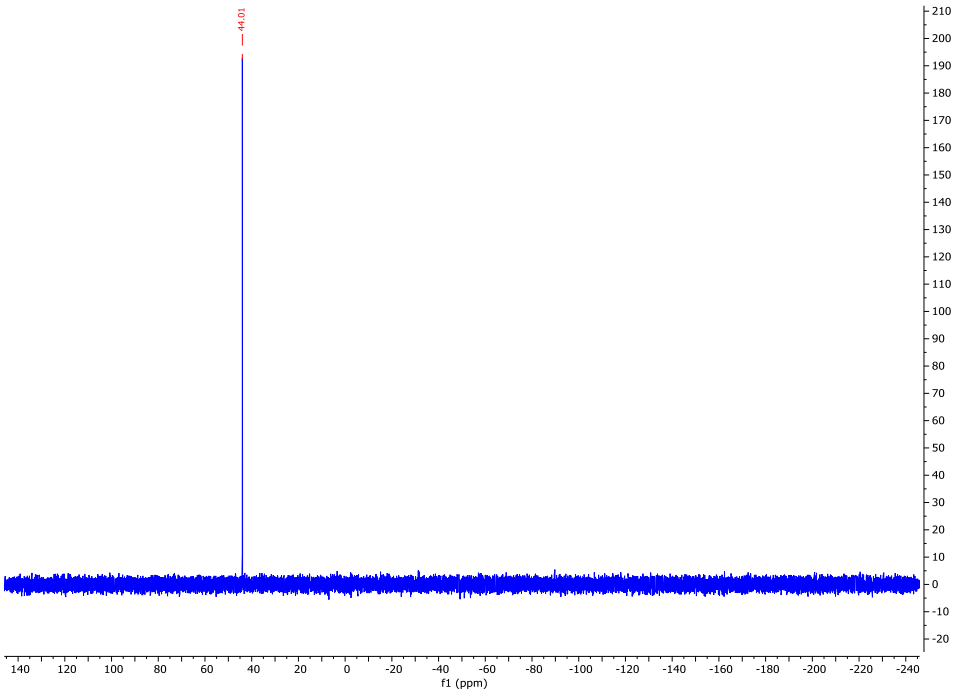
^{1}HNMR of **4d**



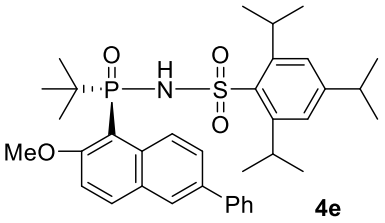
4d



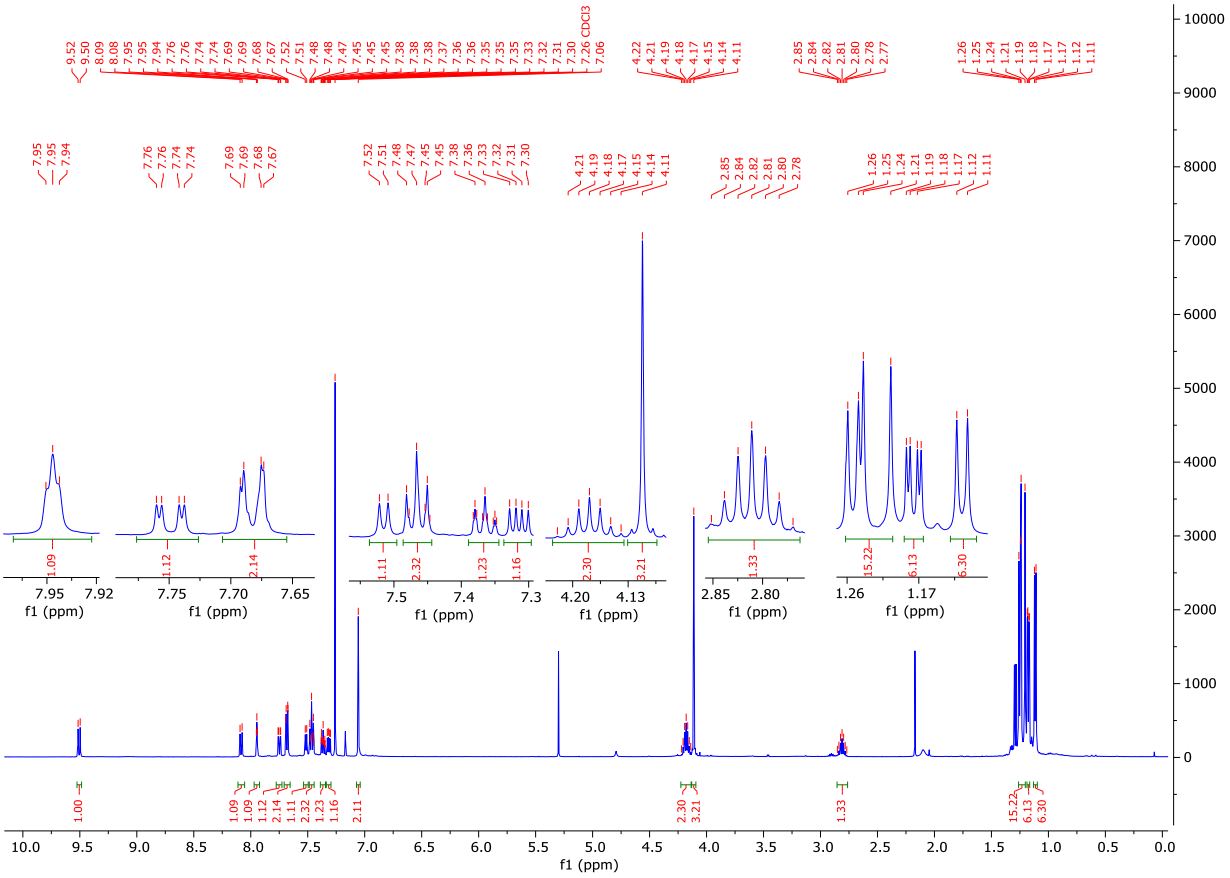
^{31}P NMR of **4d**



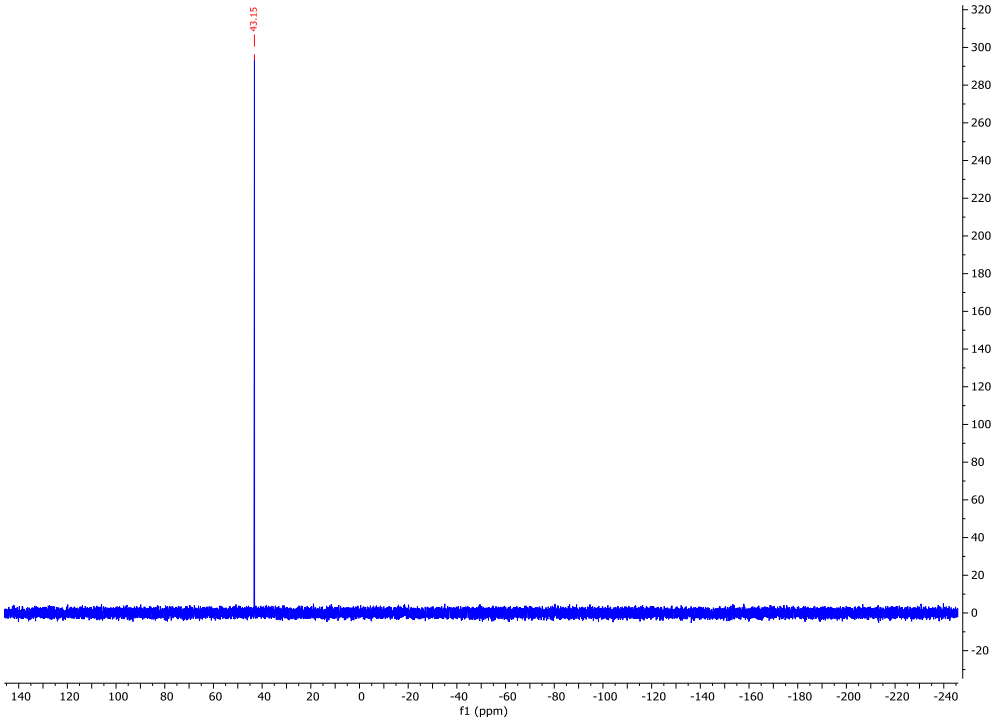
^{1}H NMR of **4e**



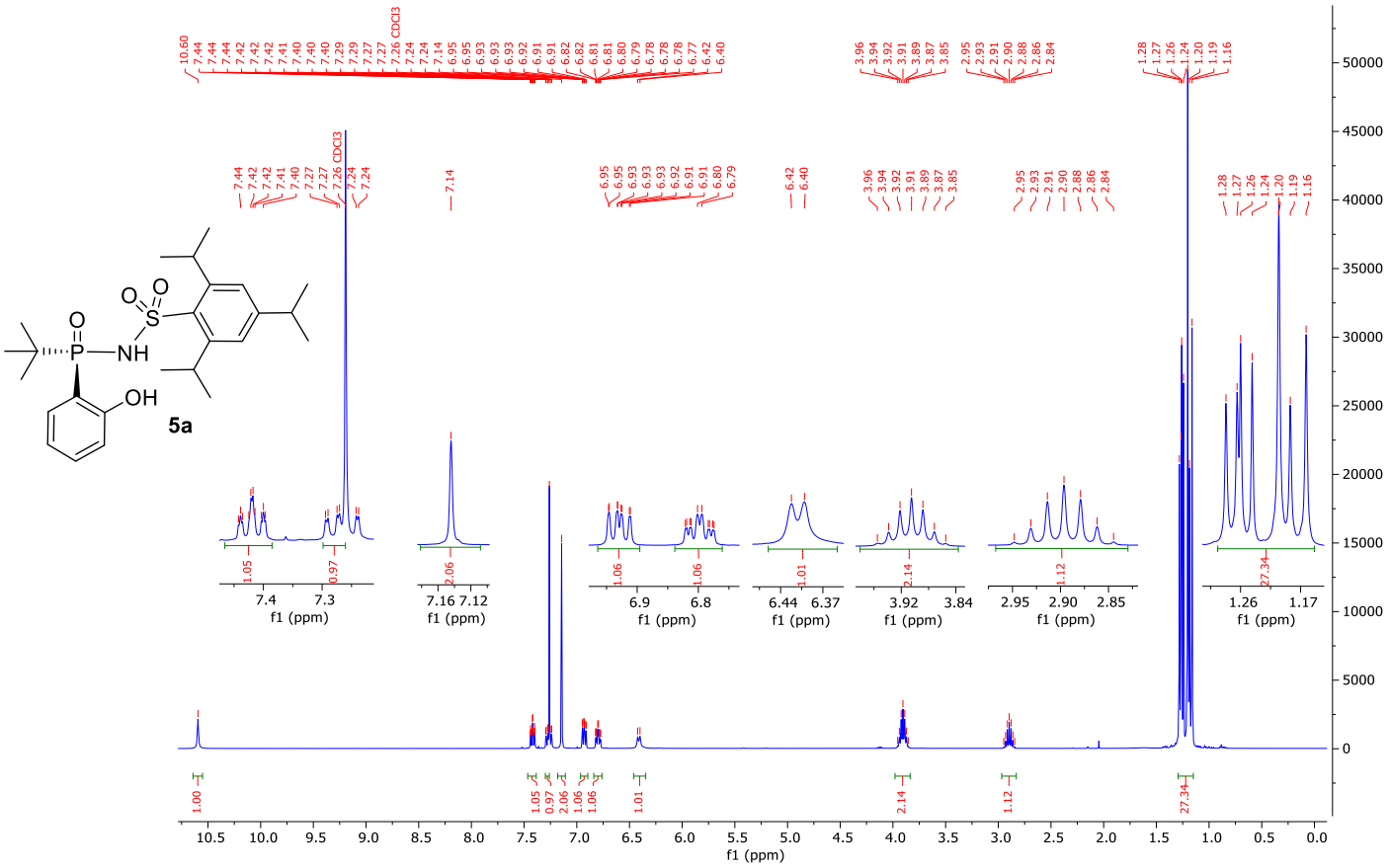
4e



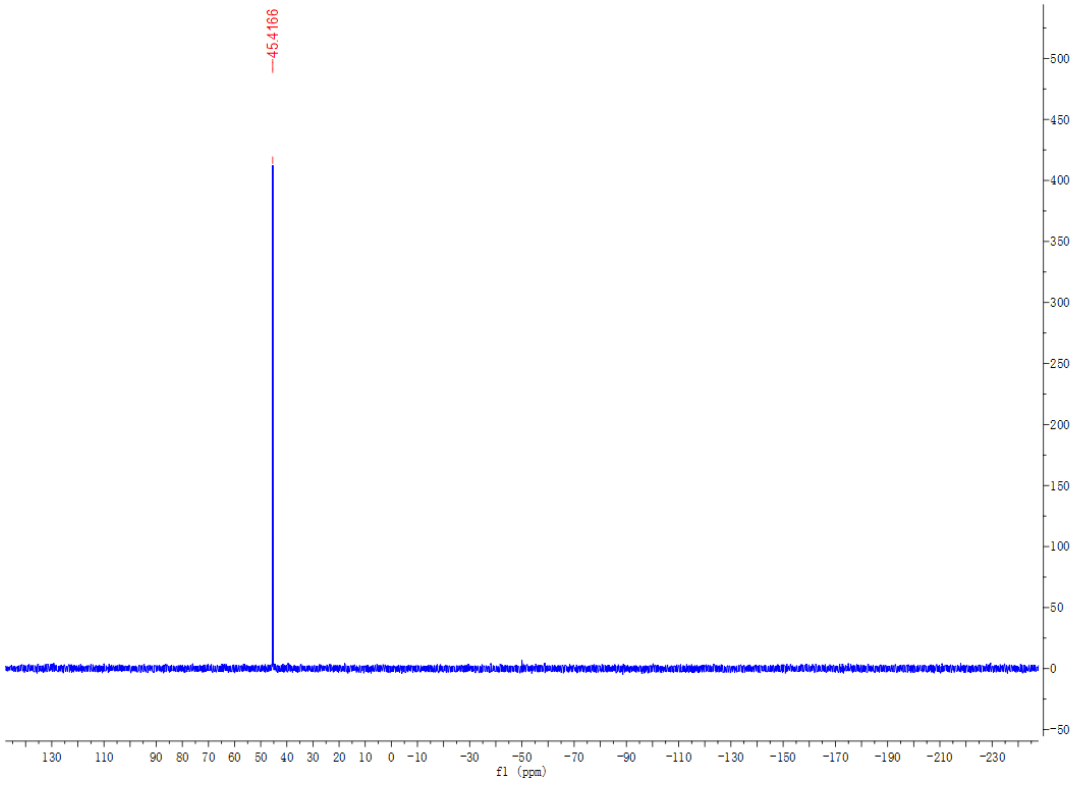
^{31}P NMR of **4e**



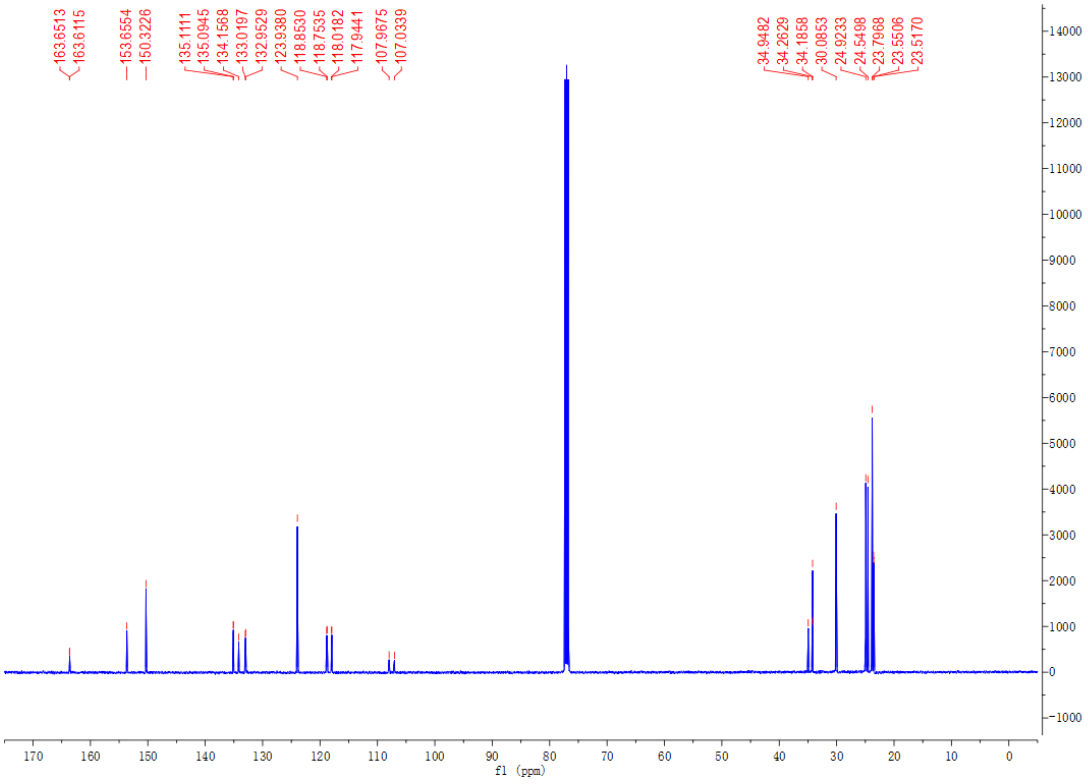
^{1}H NMR of **5a**



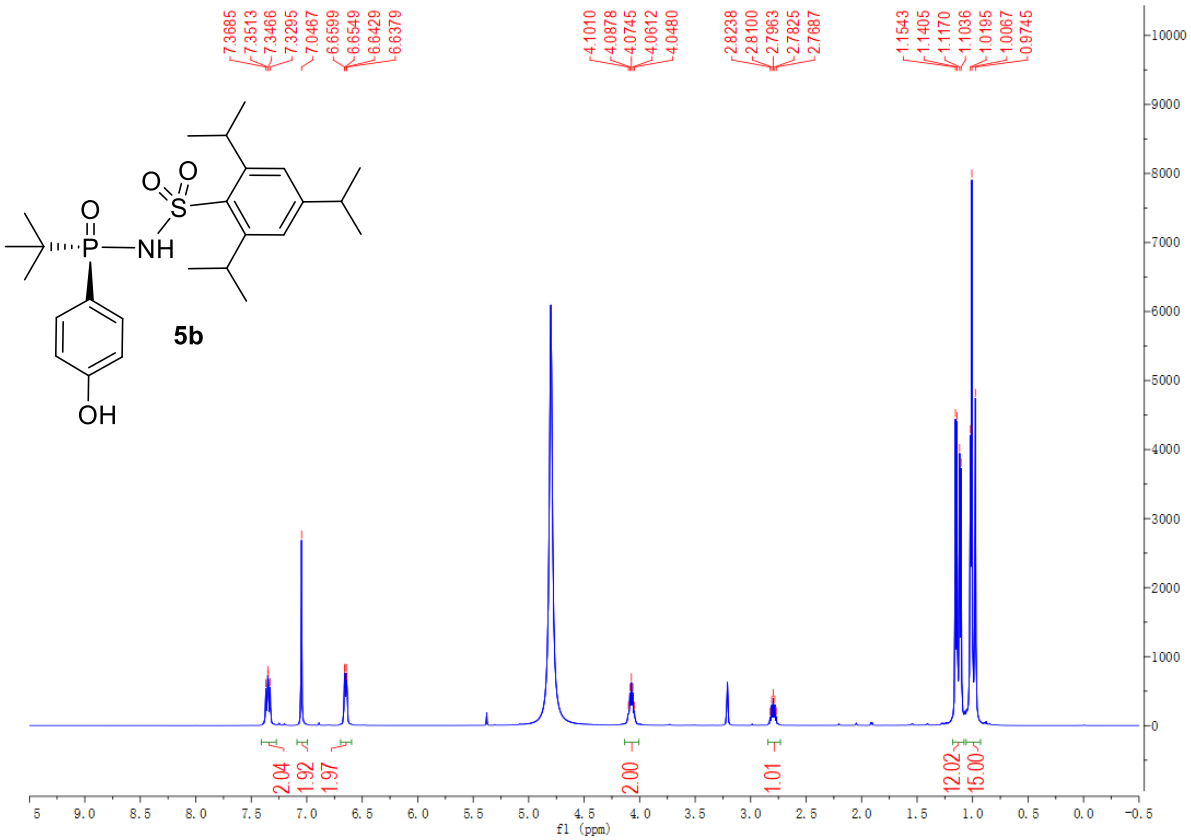
^{31}P NMR of **5a**



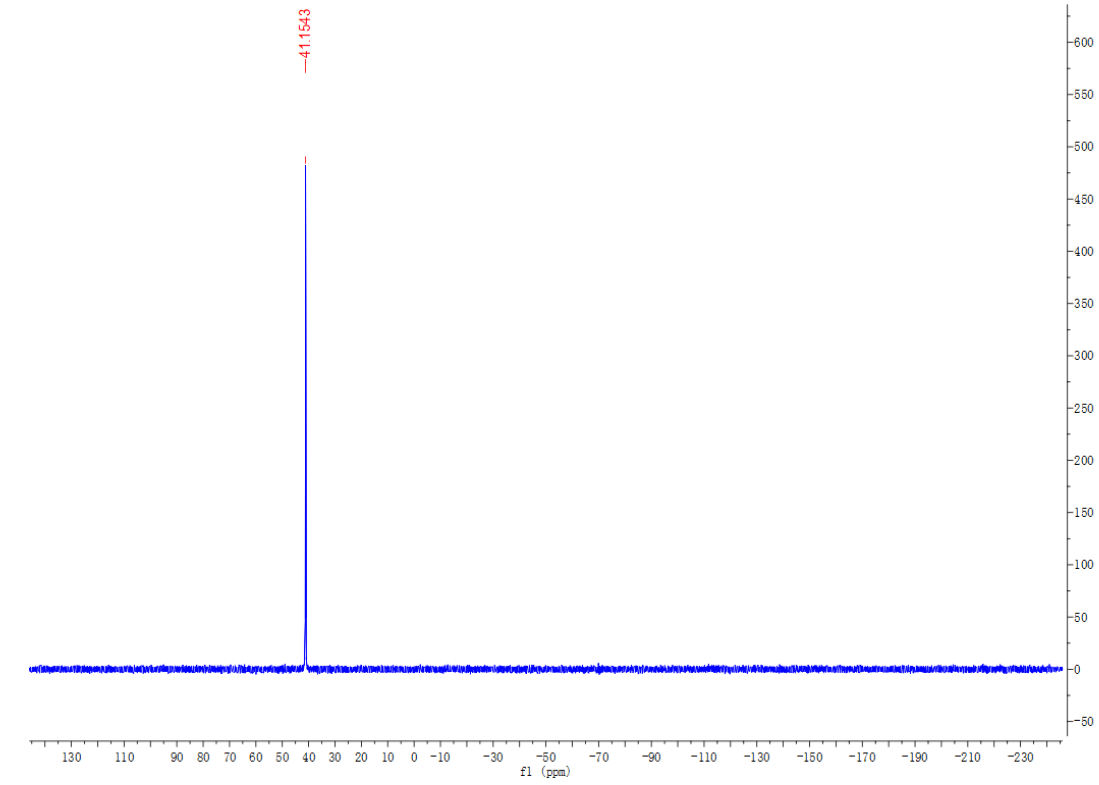
^{13}C NMR of **5a**


163.6513
163.6115
153.6554
150.3226
135.1111
135.0945
134.1568
133.0197
132.9529
123.9380
118.8530
118.7535
118.0182
117.9441
107.9675
107.0339
34.9482
34.2629
34.1858
30.0853
24.9233
24.5498
23.7968
23.5506
23.5170
f1 (ppm)

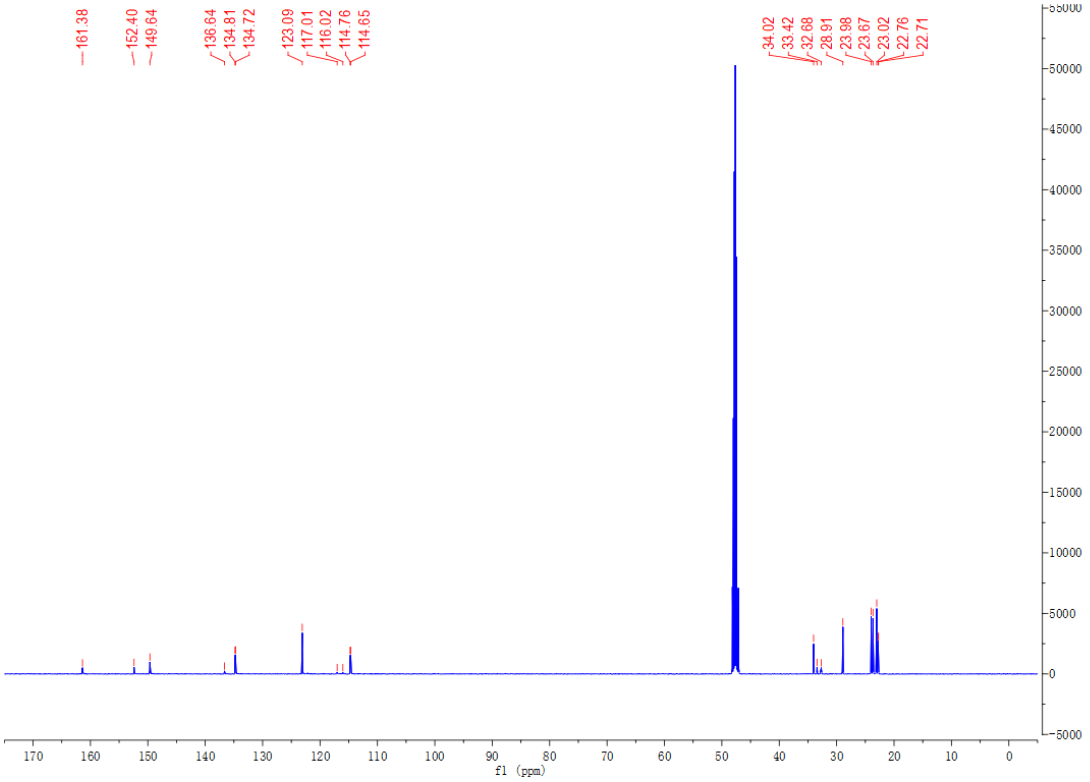
^{1}H NMR of **5b**



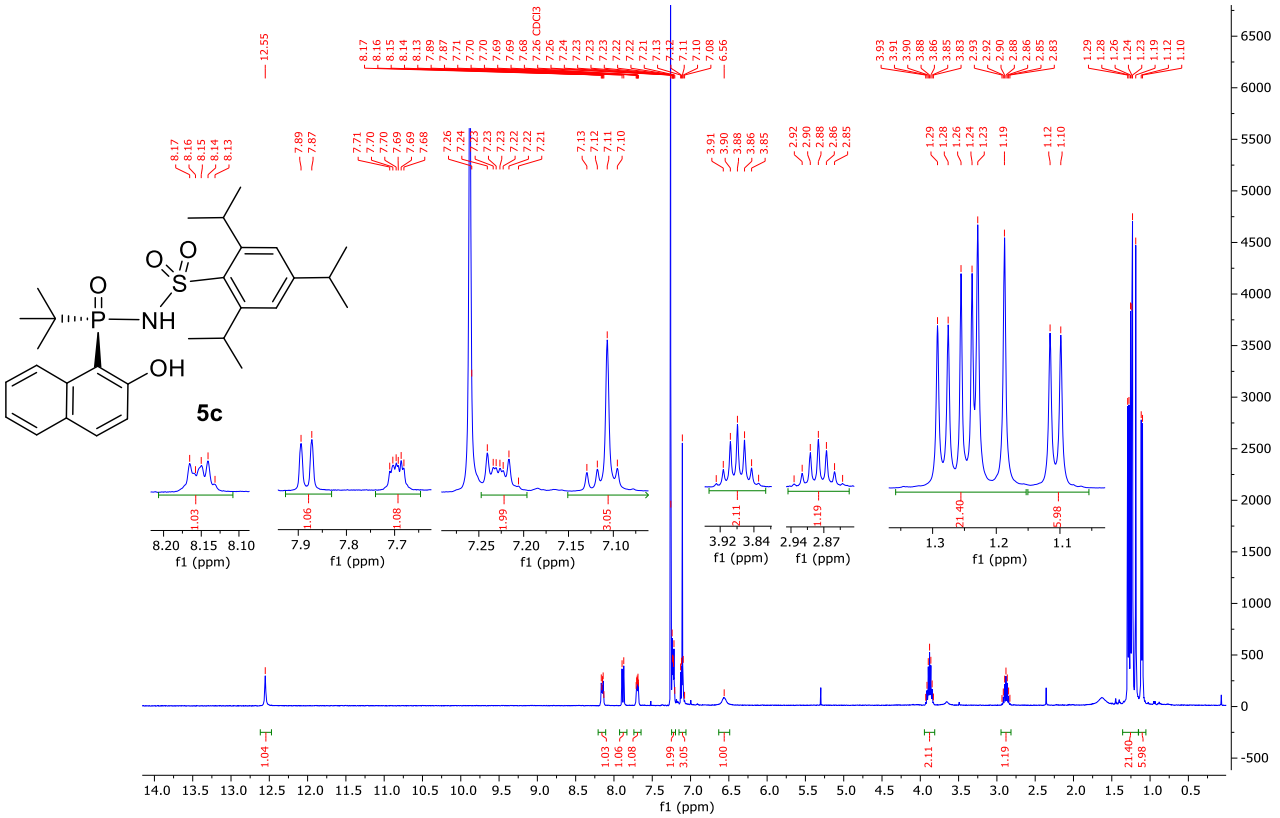
^{31}P NMR of **5b**



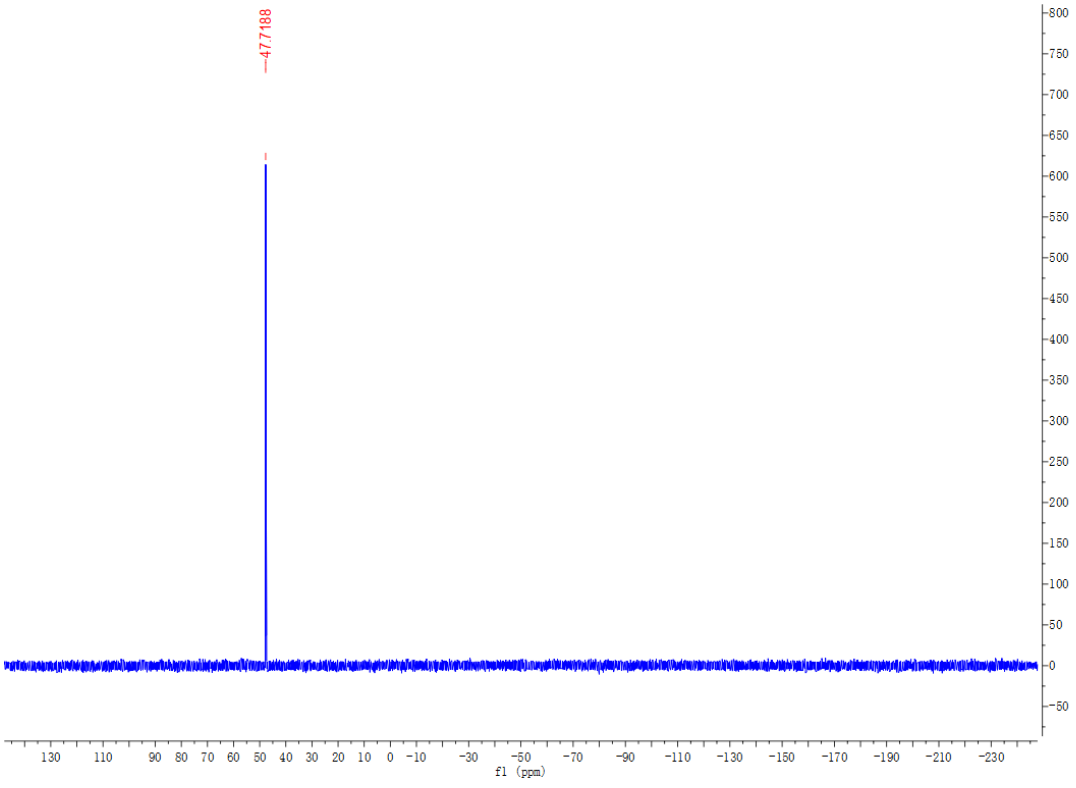
^{13}C NMR of **5b**


161.38
152.40
149.64
136.64
134.81
134.72
123.09
117.01
116.02
114.76
114.65
34.02
33.42
32.68
28.91
23.98
23.67
23.02
22.76
22.71
f1 (ppm)

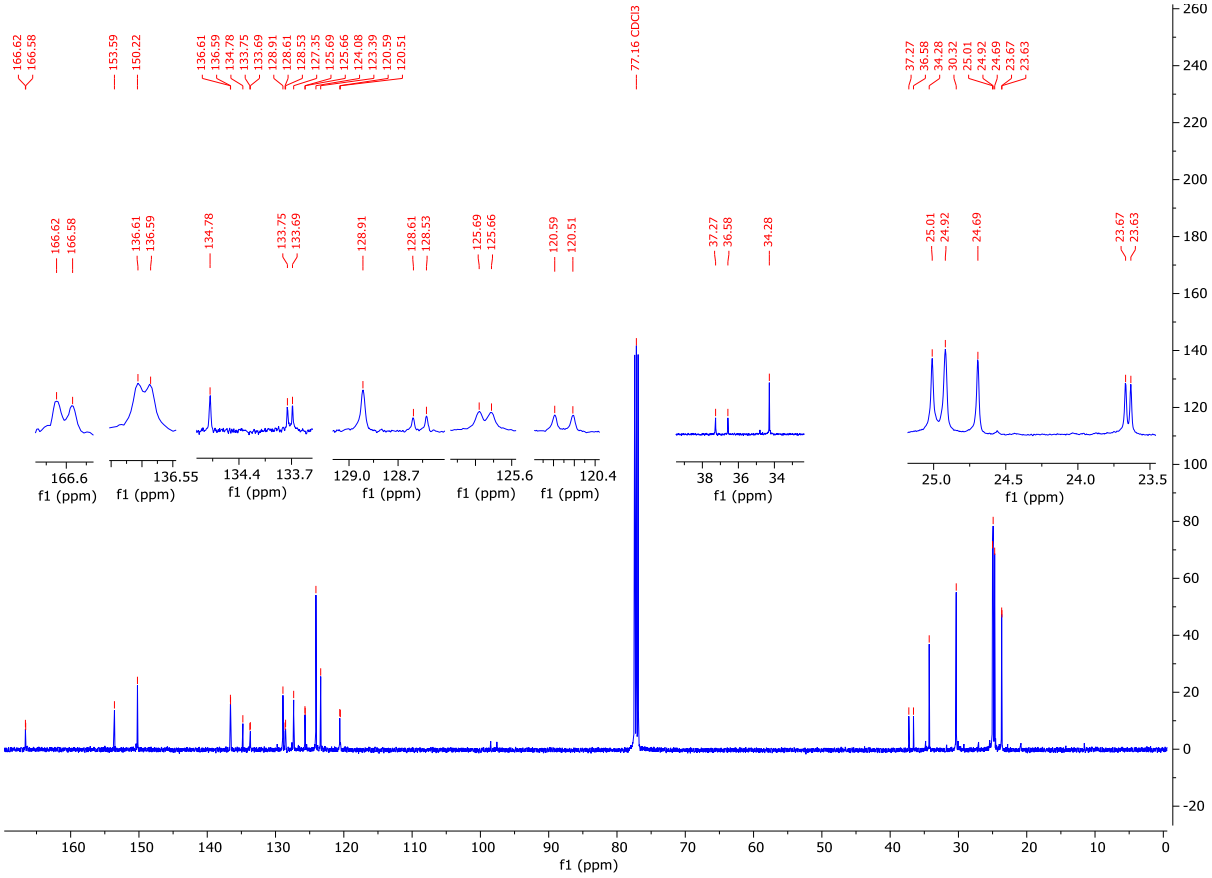
^{1}H NMR of **5c**



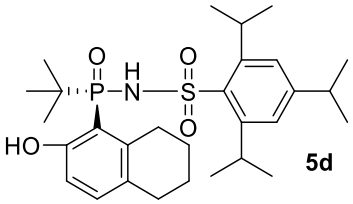
^{31}P NMR of **5c**



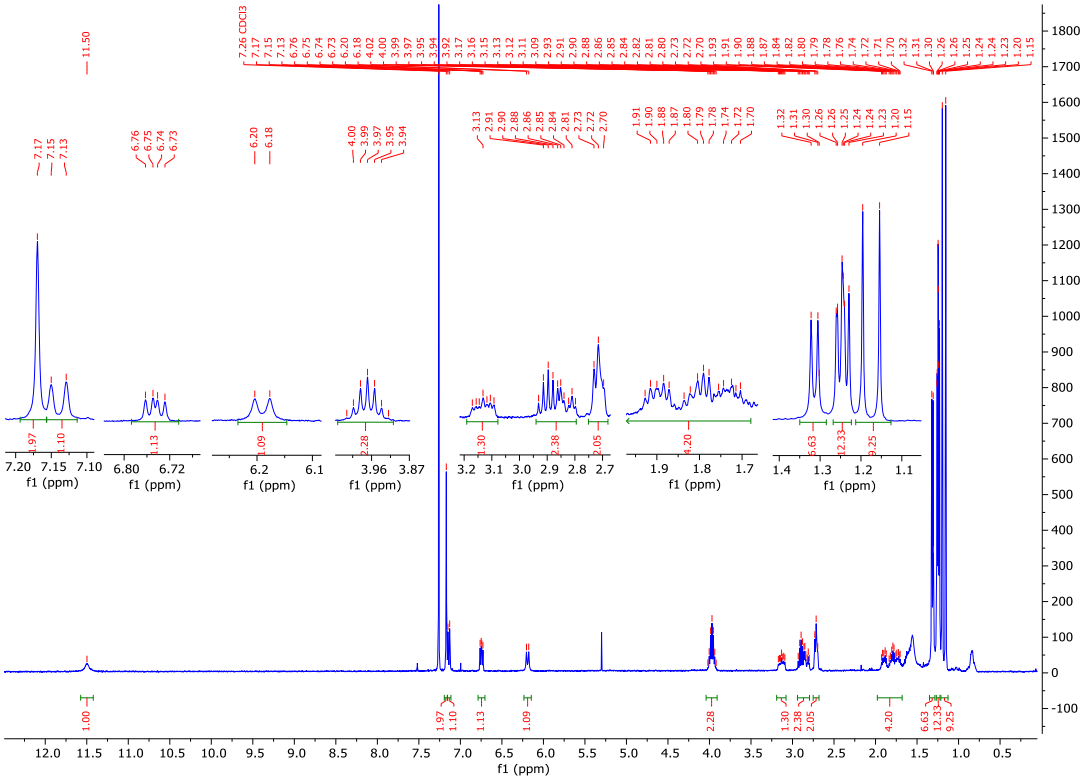
^{13}C NMR of **5c**


166.62
166.58
153.59
150.22
136.61
136.59
134.78
133.75
133.69
128.91
128.61
128.53
127.35
125.69
125.66
124.08
123.39
120.59
120.51
77.16 CDCl3
37.27
36.58
34.28
30.32
25.01
24.92
24.69
23.67
23.63
f1 (ppm)

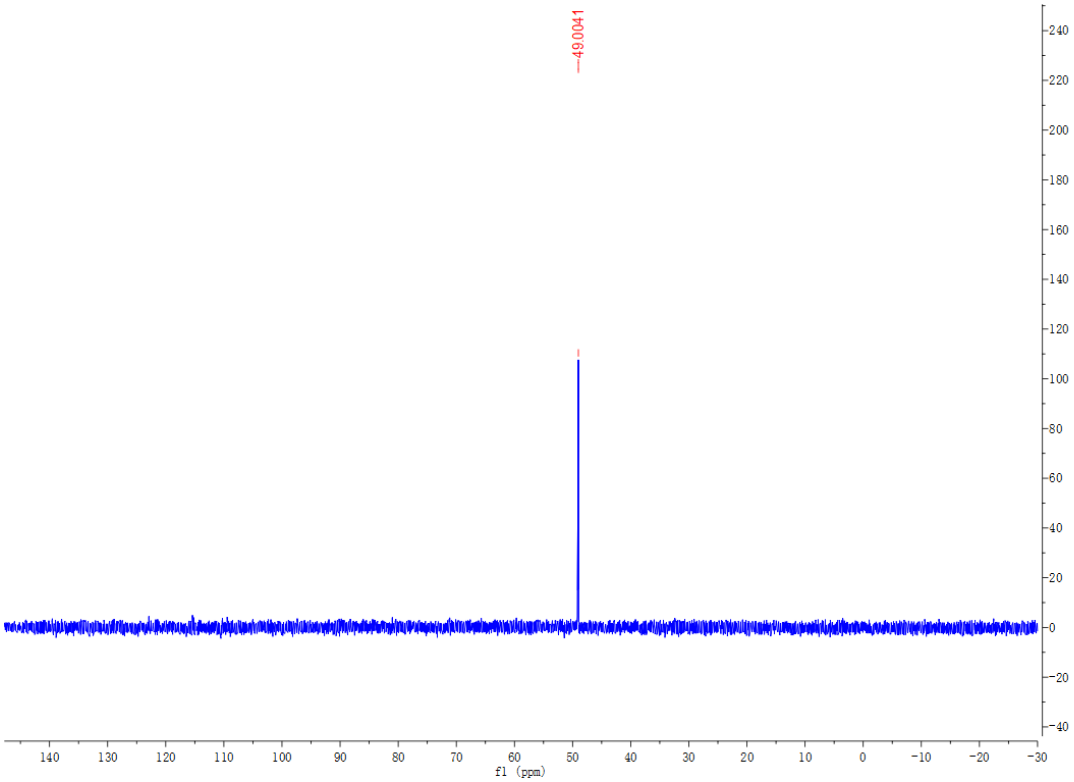
^{1}H NMR of **5d**



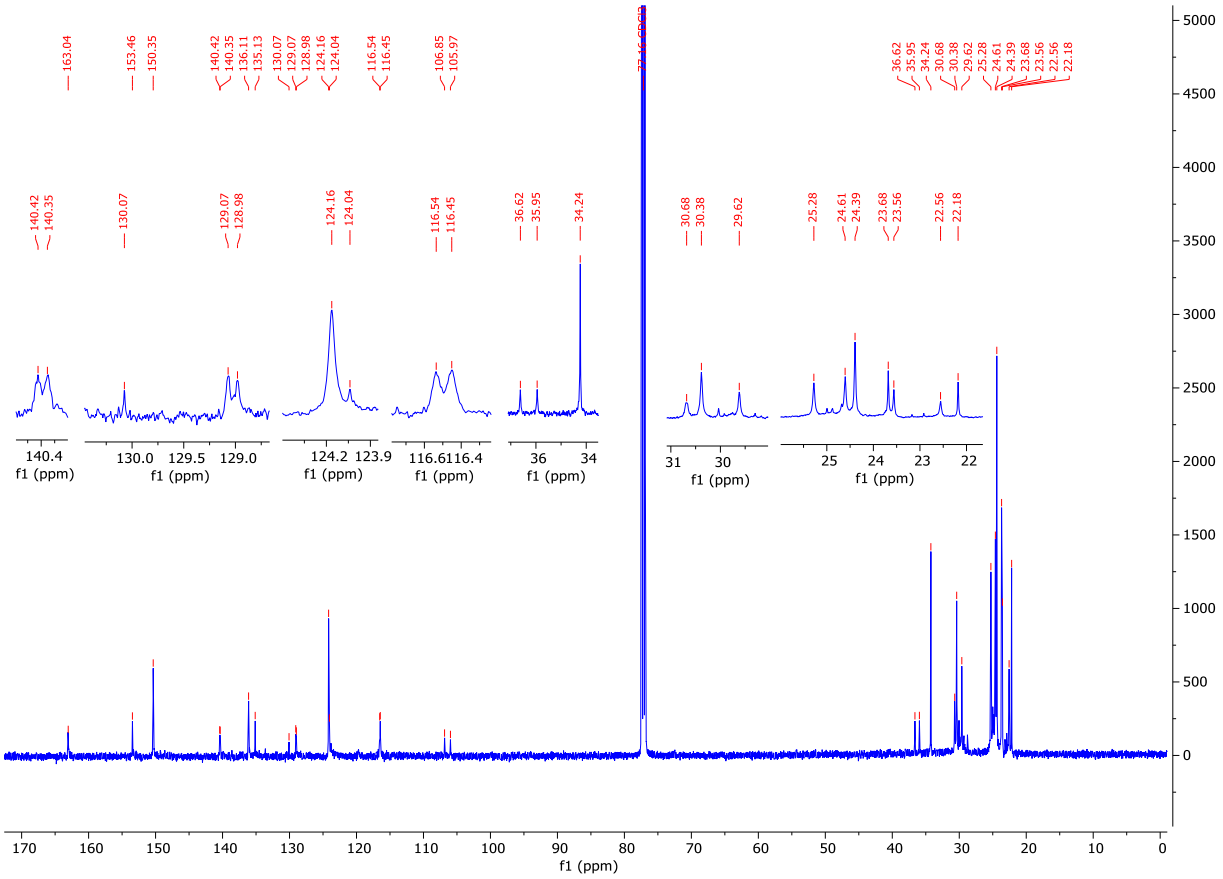
5d



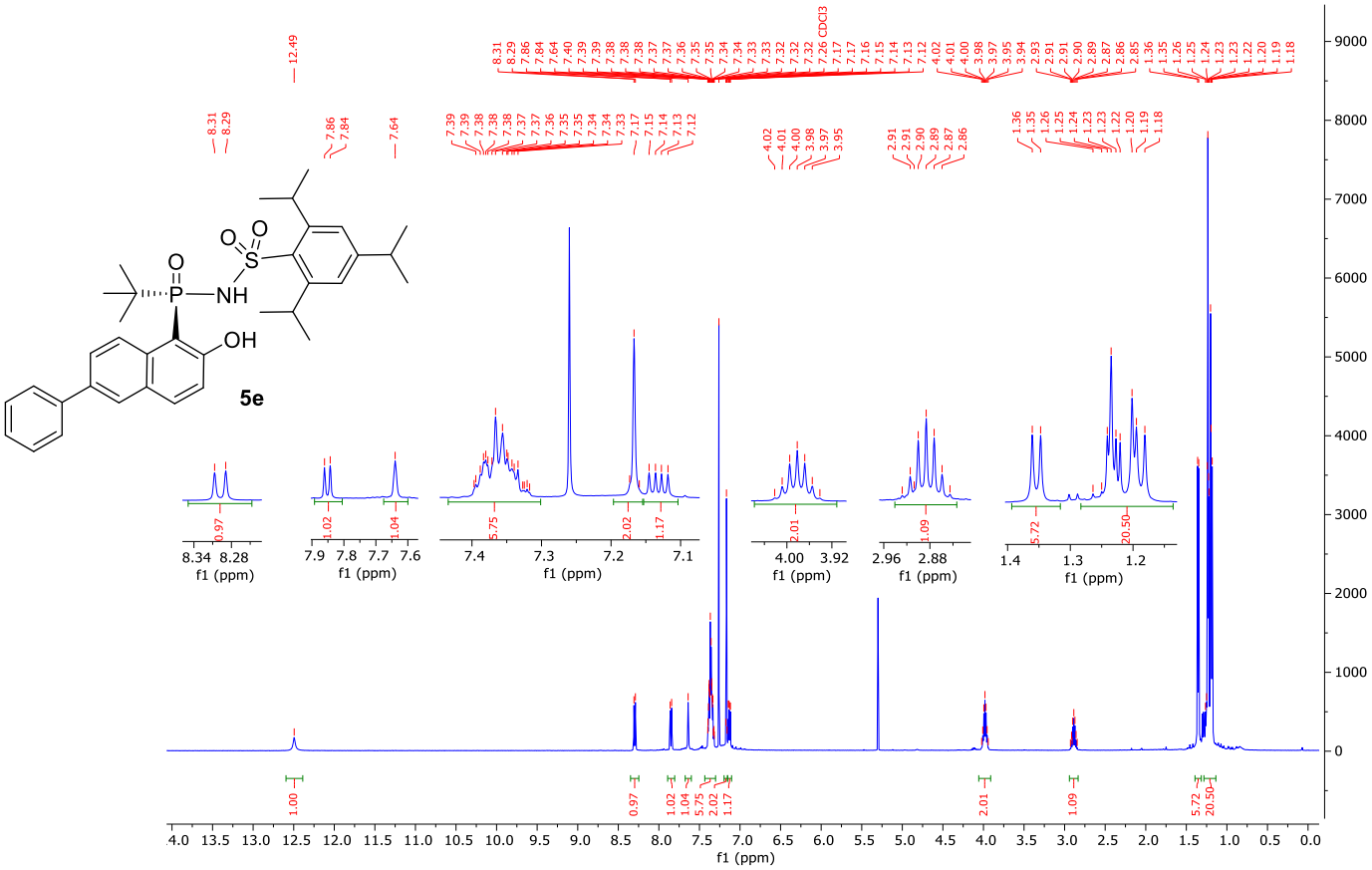
^{31}P NMR of **5d**



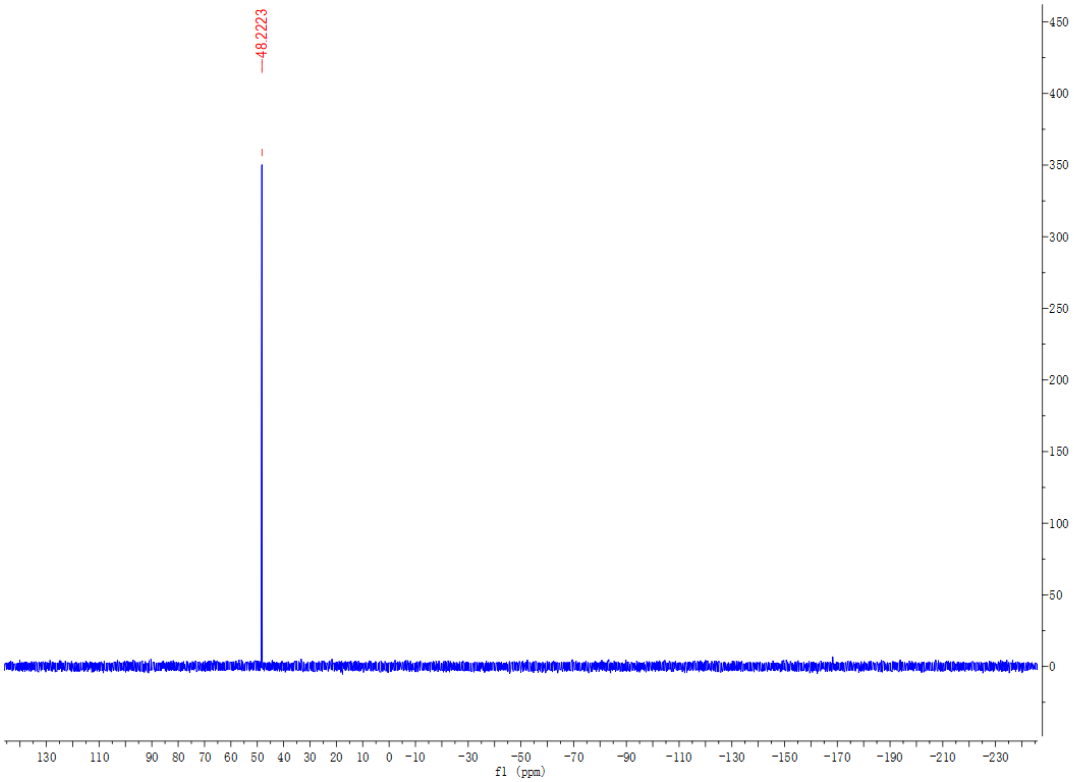
^{13}C NMR of **5d**


163.04
153.46
150.35
140.42
140.35
136.11
135.13
130.07
129.07
128.98
124.16
124.04
116.54
116.45
106.85
105.97
36.62
35.95
34.24
30.68
30.38
29.62
25.28
24.61
24.39
23.68
23.56
22.56
22.18
f1 (ppm)

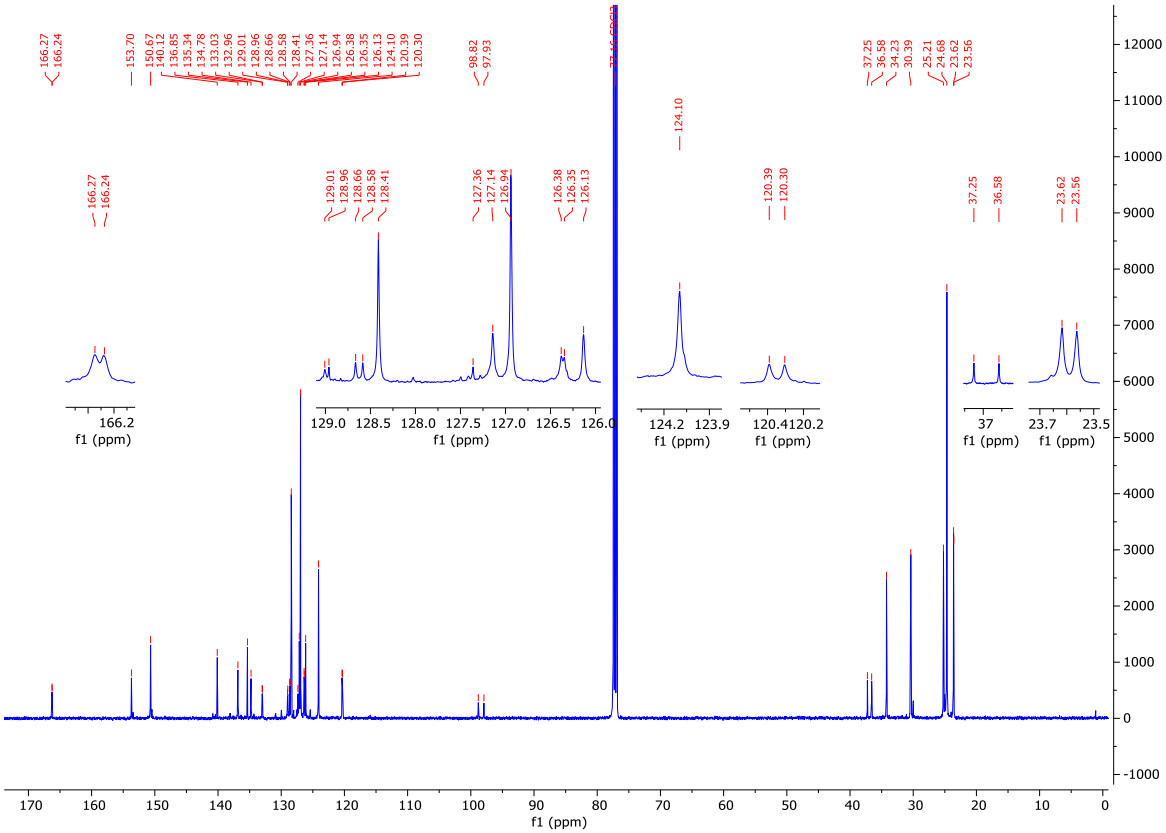
^{1}H NMR of **5e**



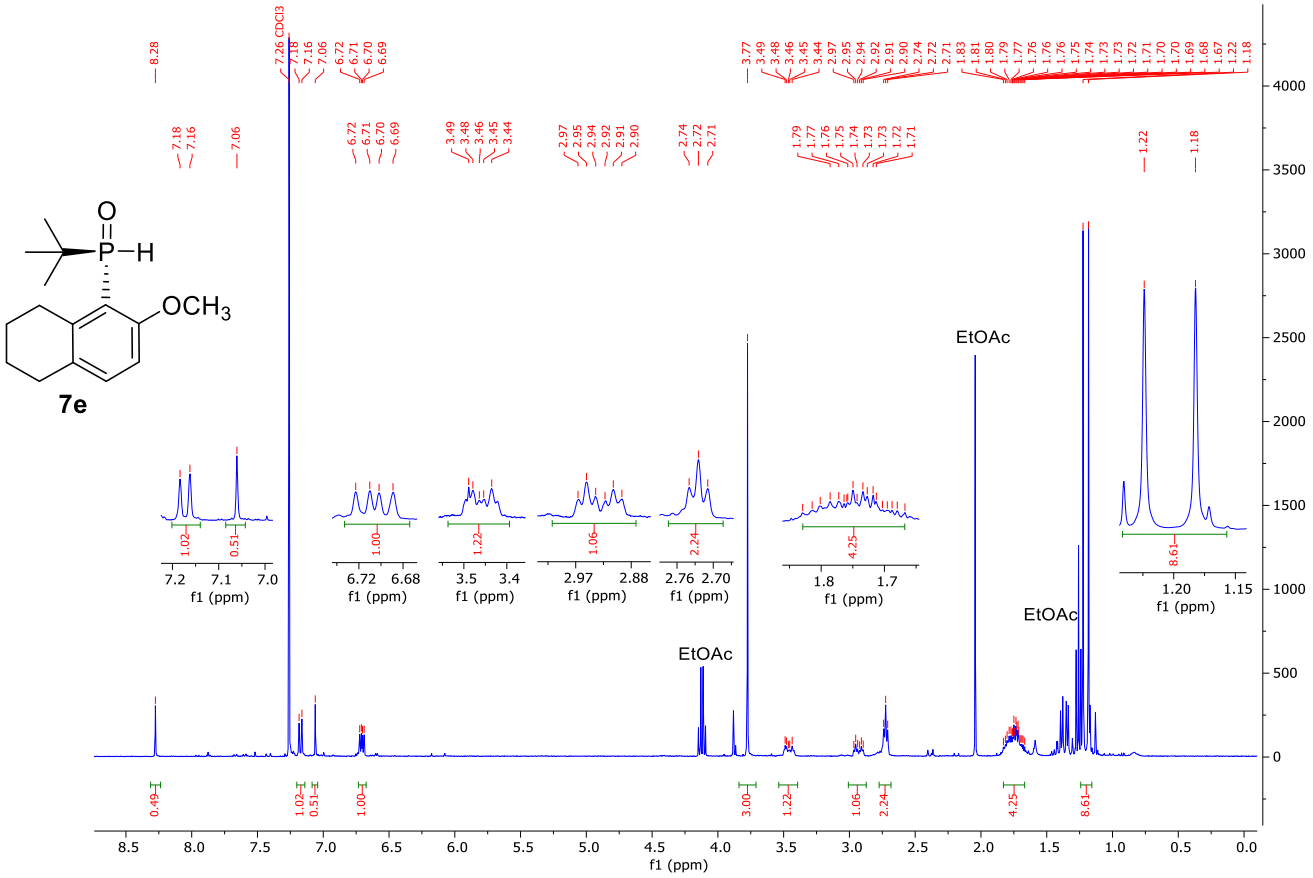
^{31}P NMR of **5e**



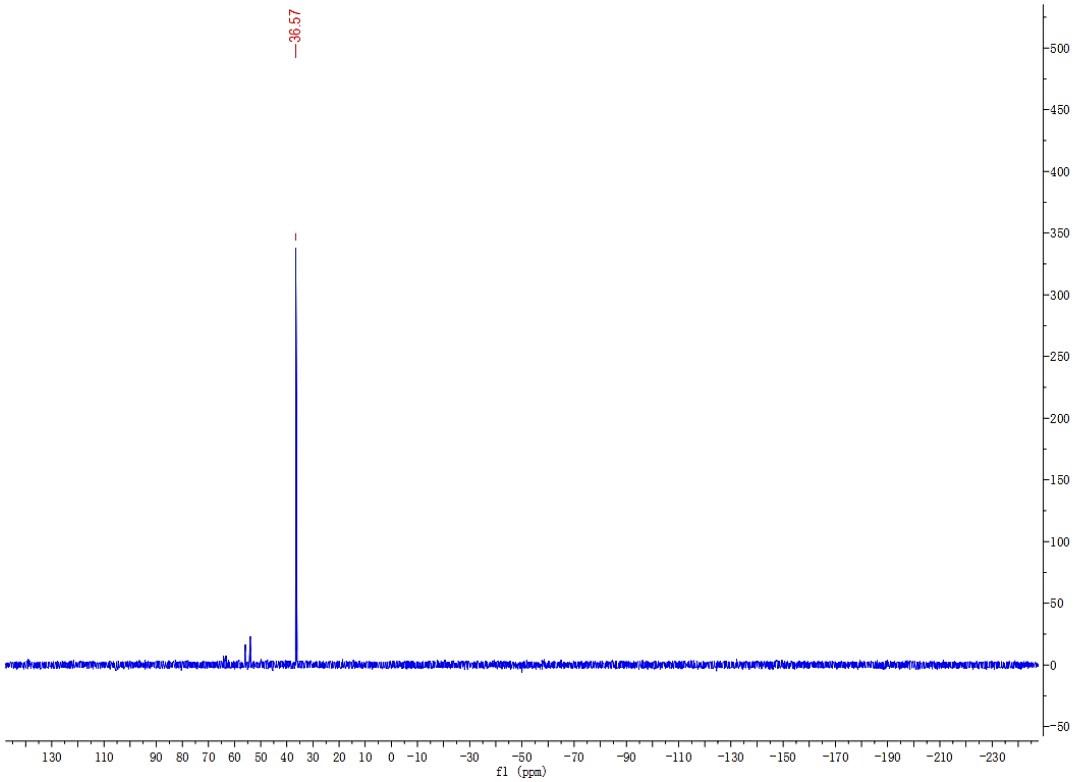
^{13}C NMR of **5e**


166.27
166.24
153.70
150.67
140.12
136.85
135.34
134.78
133.03
132.96
129.01
128.96
128.66
128.58
128.41
127.36
127.14
126.94
126.38
126.35
126.13
124.10
120.39
120.30
98.82
97.93
77.46
37.25
36.58
34.23
30.39
25.21
24.68
23.62
23.56
f1 (ppm)

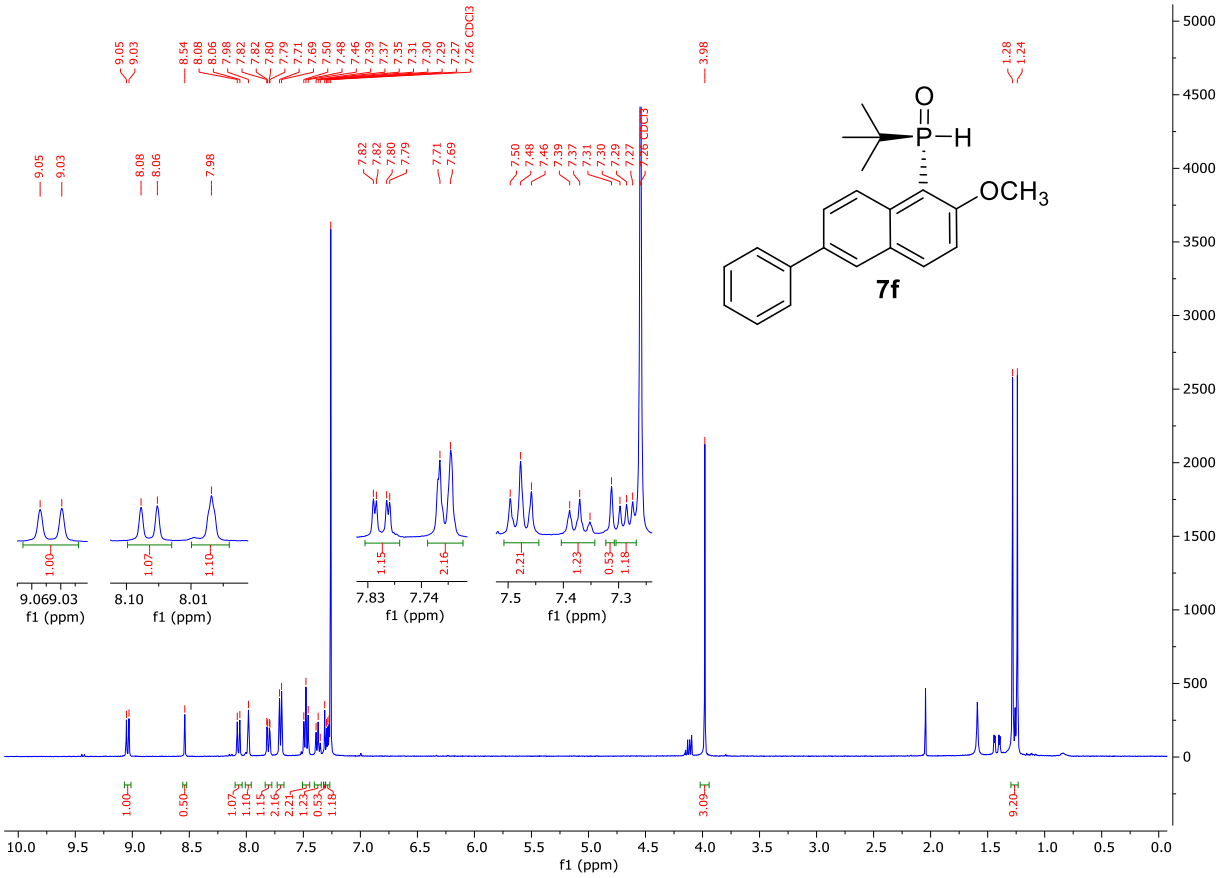
^{1}H-NMR of **7e**



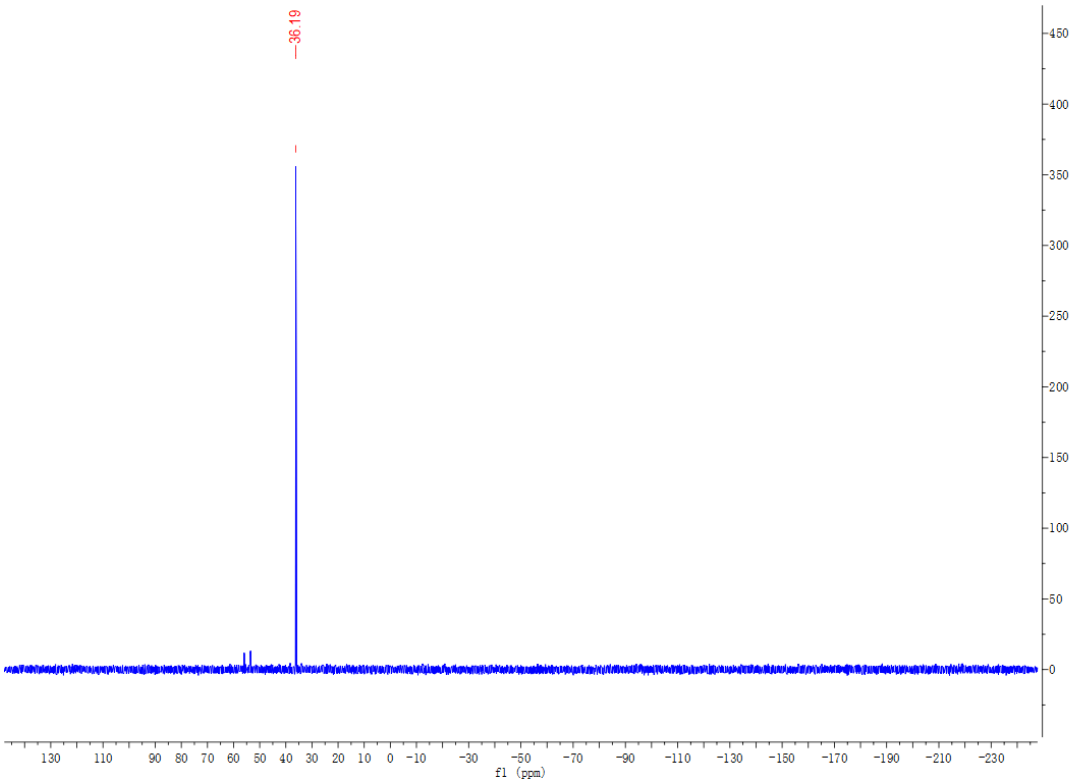
^{31}P-NMR of **7e**



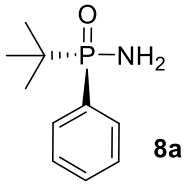
^{1}H-NMR of **7f**



^{31}P-NMR of **7f**

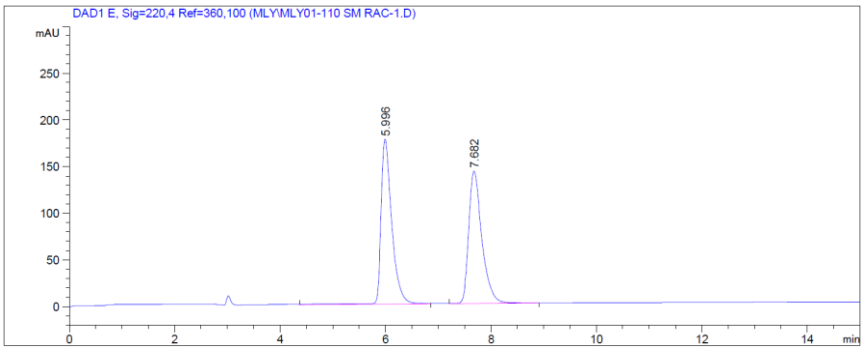


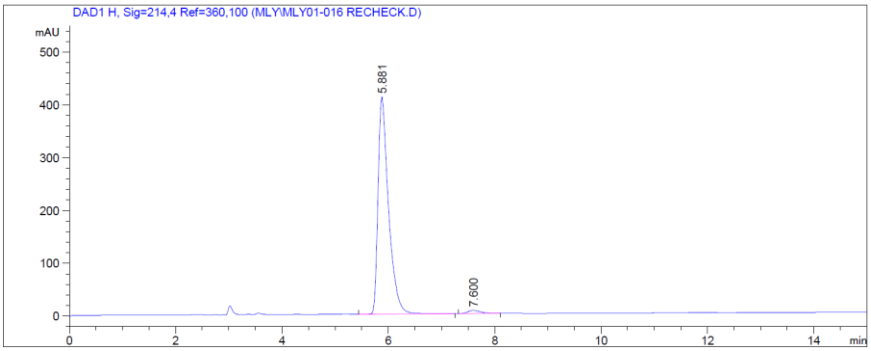
^{1}H-NMR, ^{13}C and ^{31}P NMR spectra of compound **8a** were consistent with those previously reported.[7]



8a

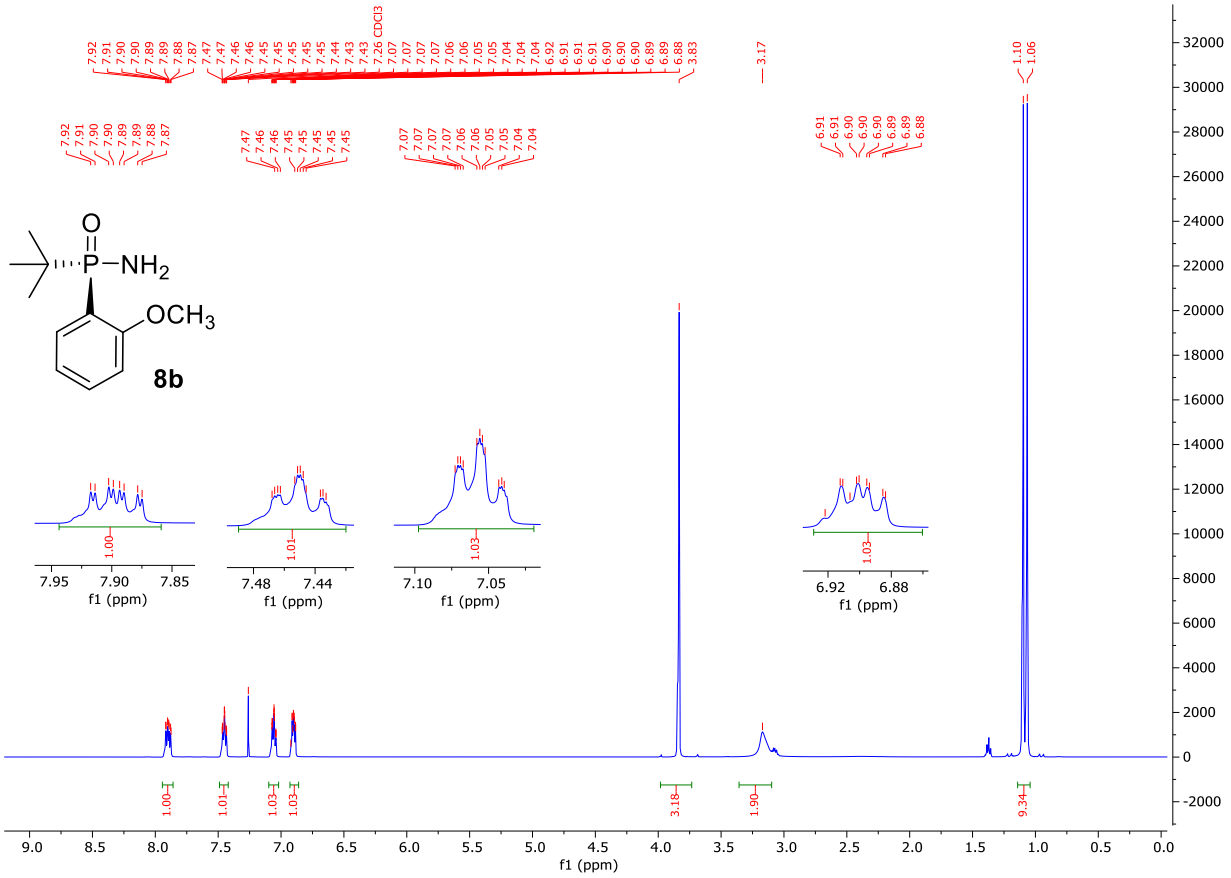
Chiral HPLC chromatograms of **8a**



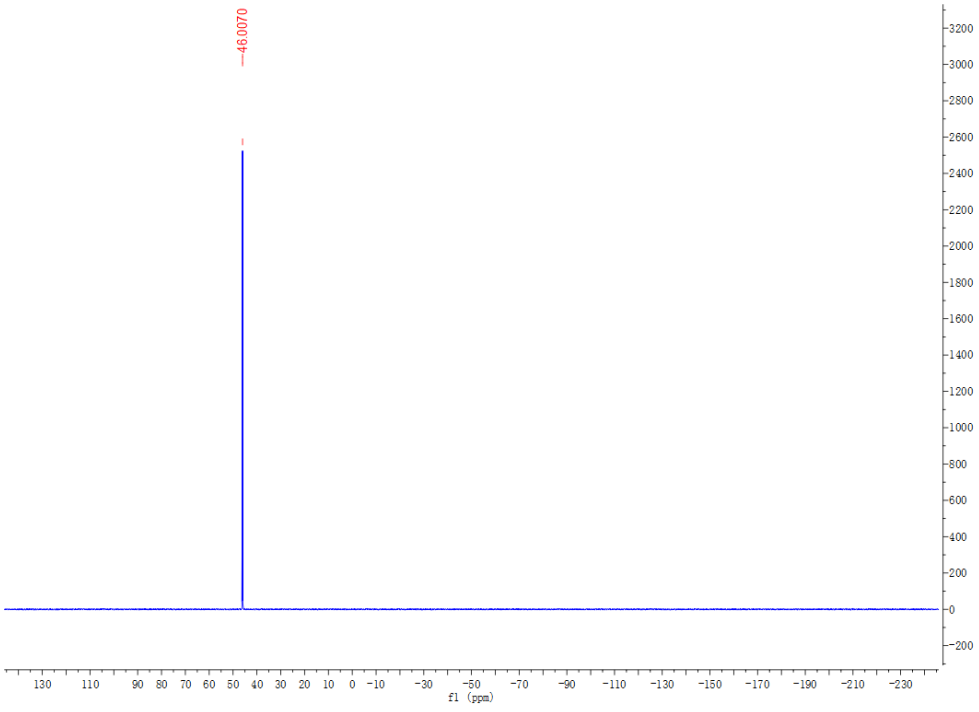


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.881	BB	0.2069	5673.06494	411.40399	98.3002
2	7.600	BB	0.2540	98.09958	5.90015	1.6998

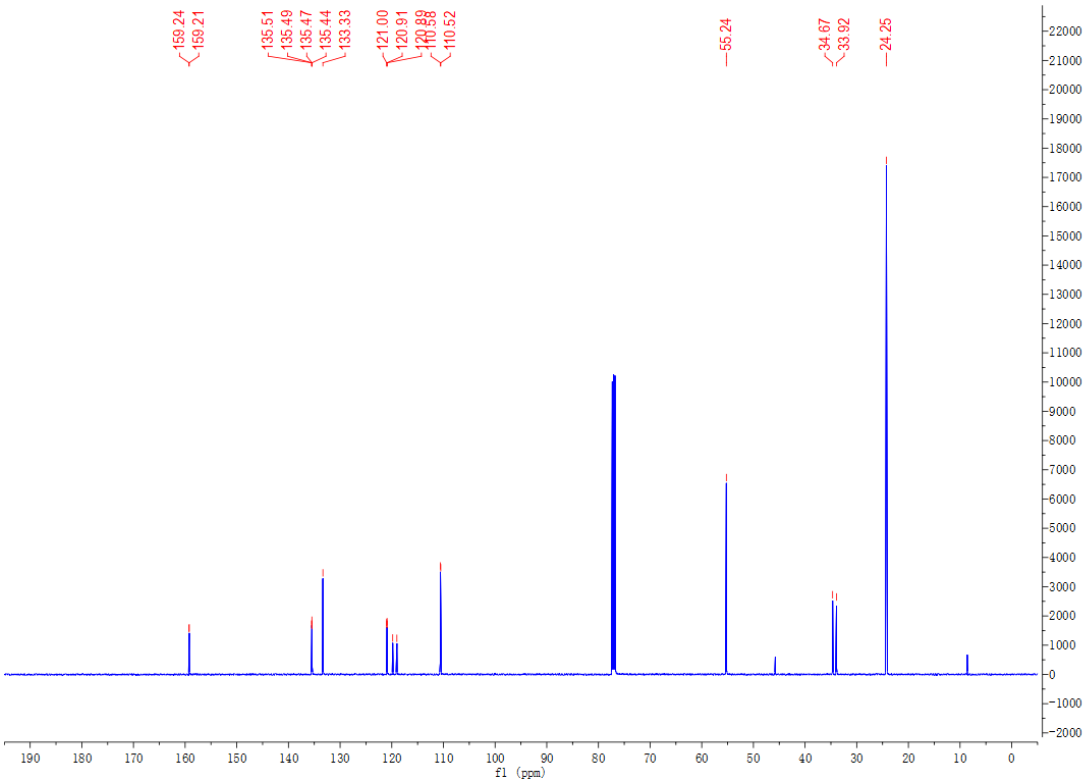
^{1}H NMR of **8b**



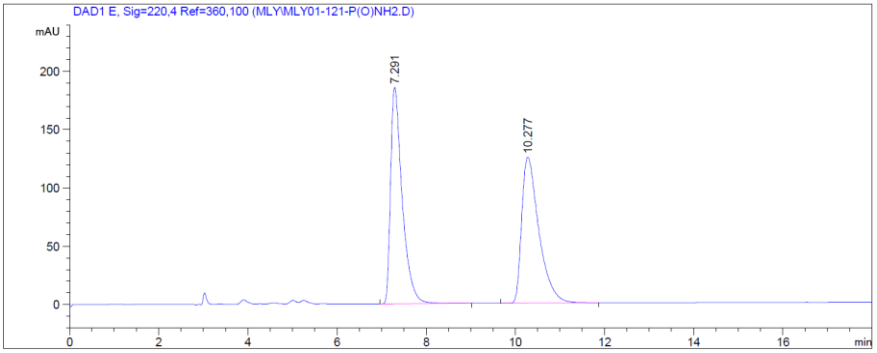
^{31}P NMR of **8b**

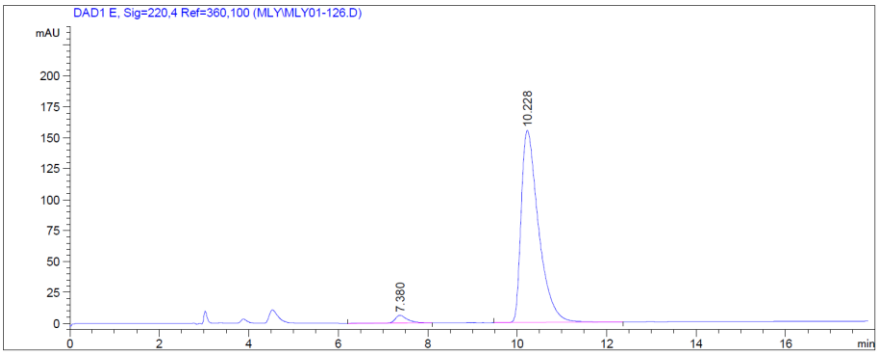


^{13}C NMR of **8b**



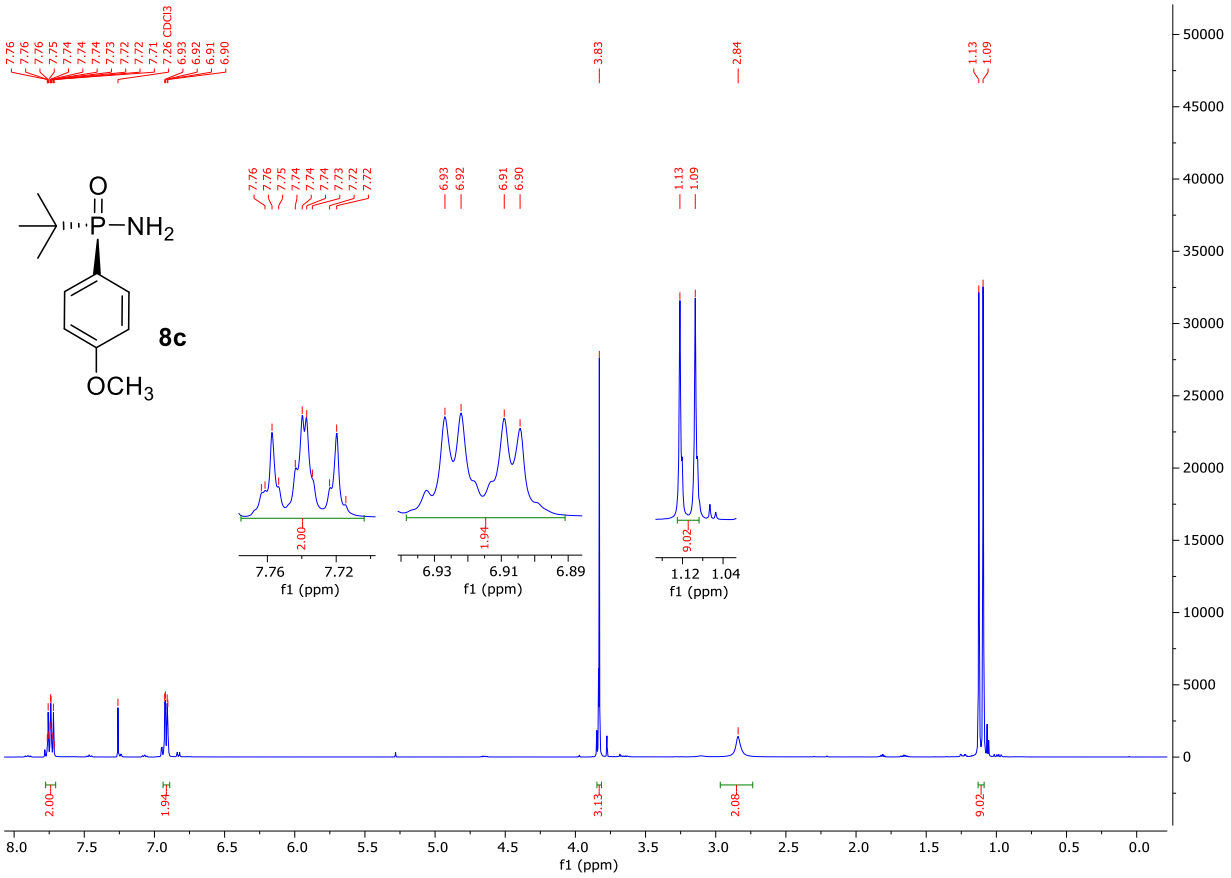
Chiral HPLC chromatograms of **8b**



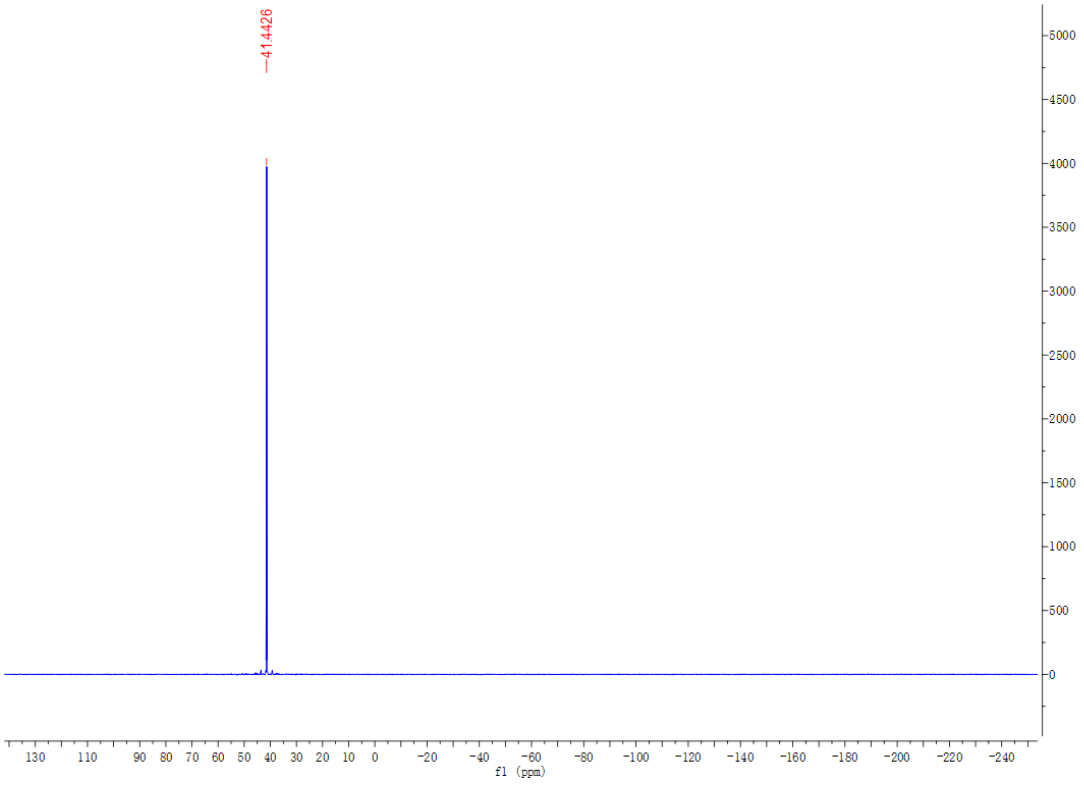


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.380	BB	0.2838	118.71608	6.18996	2.7608
2	10.228	BB	0.4025	4181.28223	155.10017	97.2392

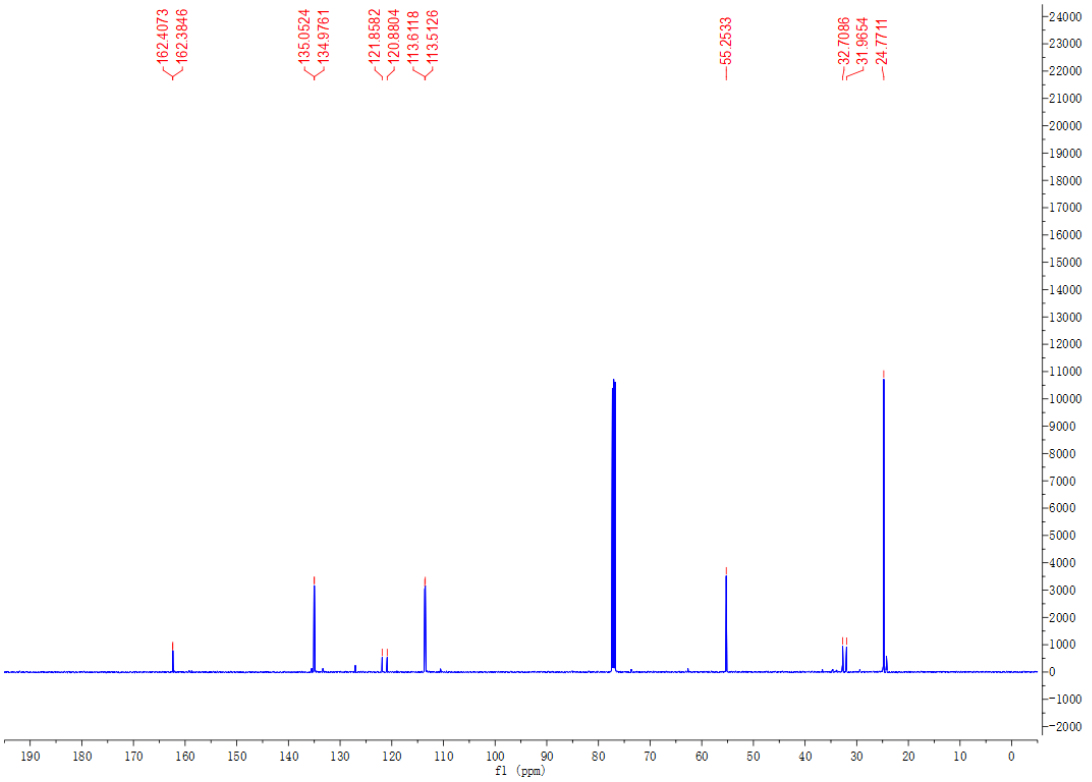
^{1}H NMR of **8c**



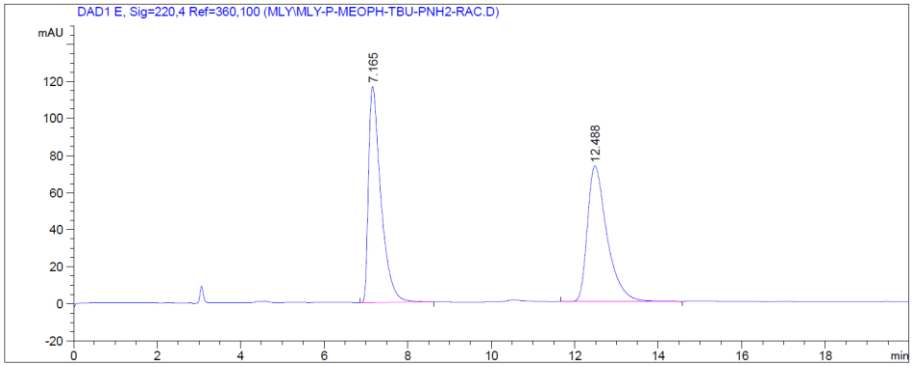
^{31}P NMR of **8c**

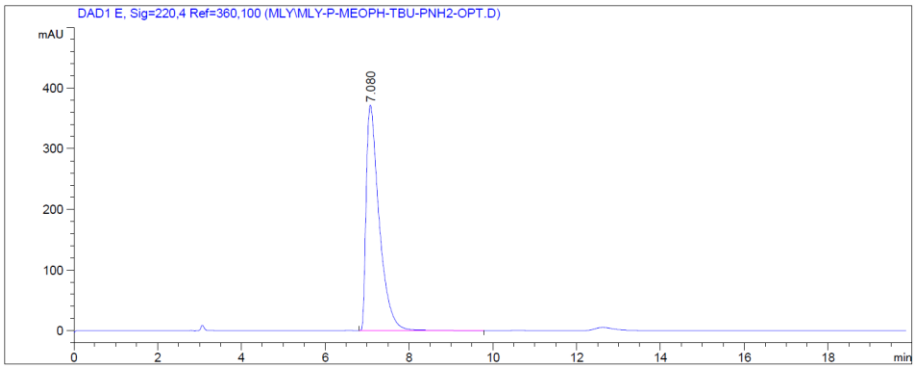


^{13}C NMR of **8c**



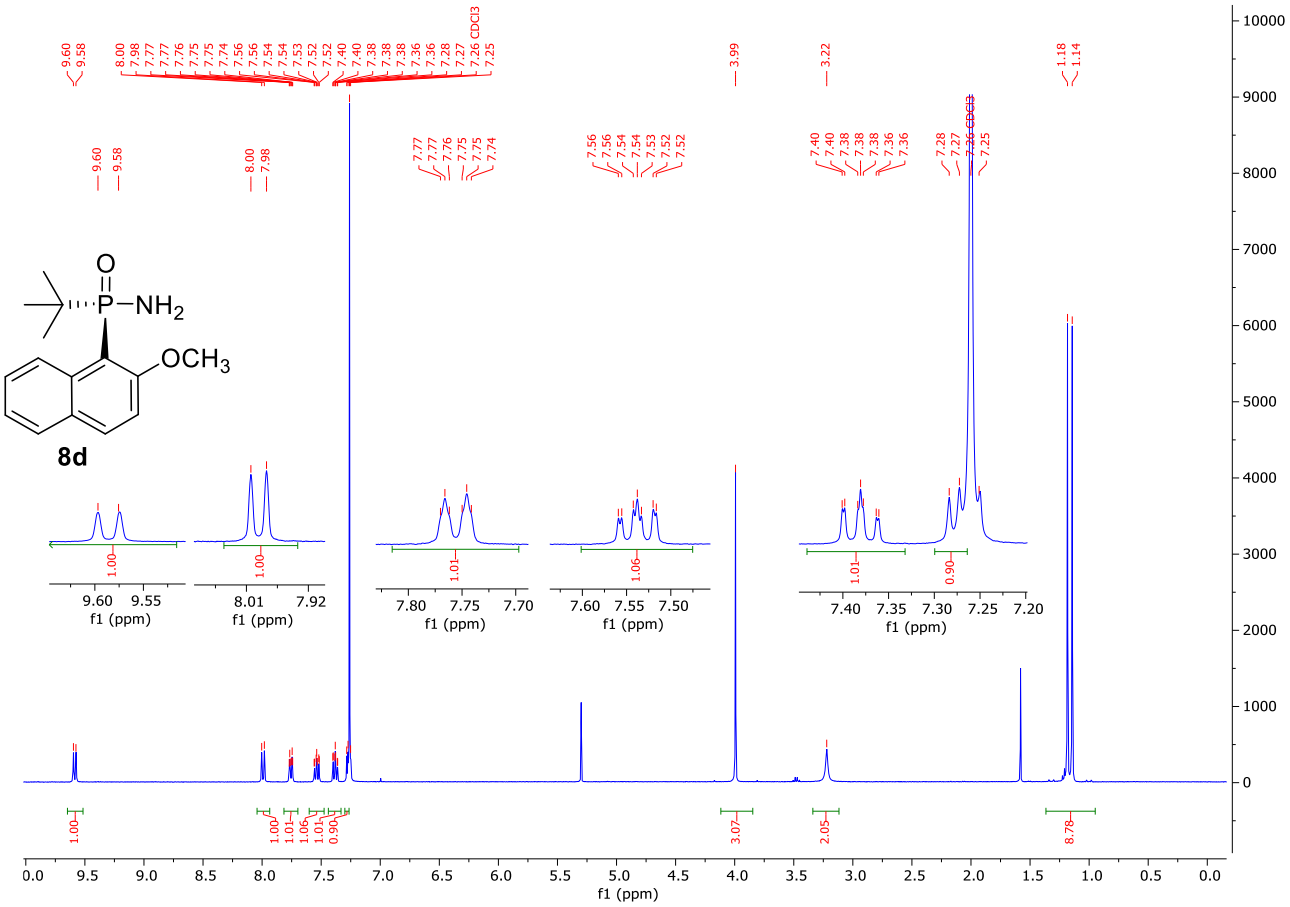
Chiral HPLC chromatograms of **8c**



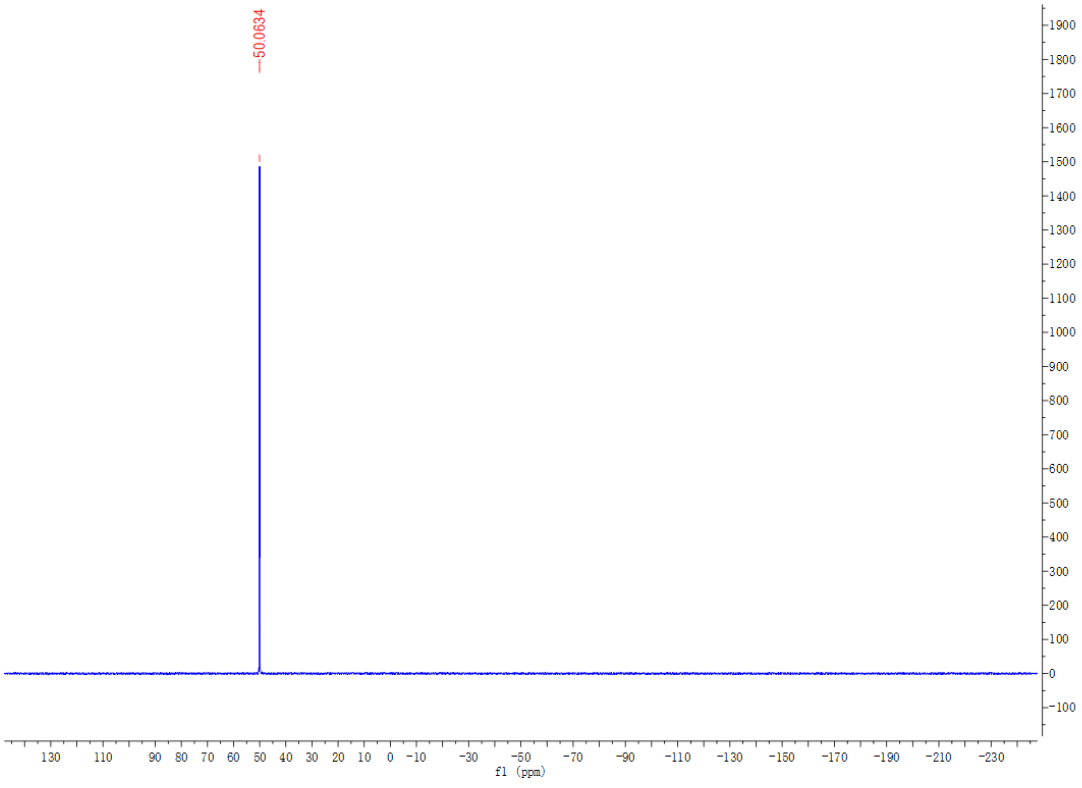


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.080	VV	0.3243	8036.97559	371.68729	100.0000

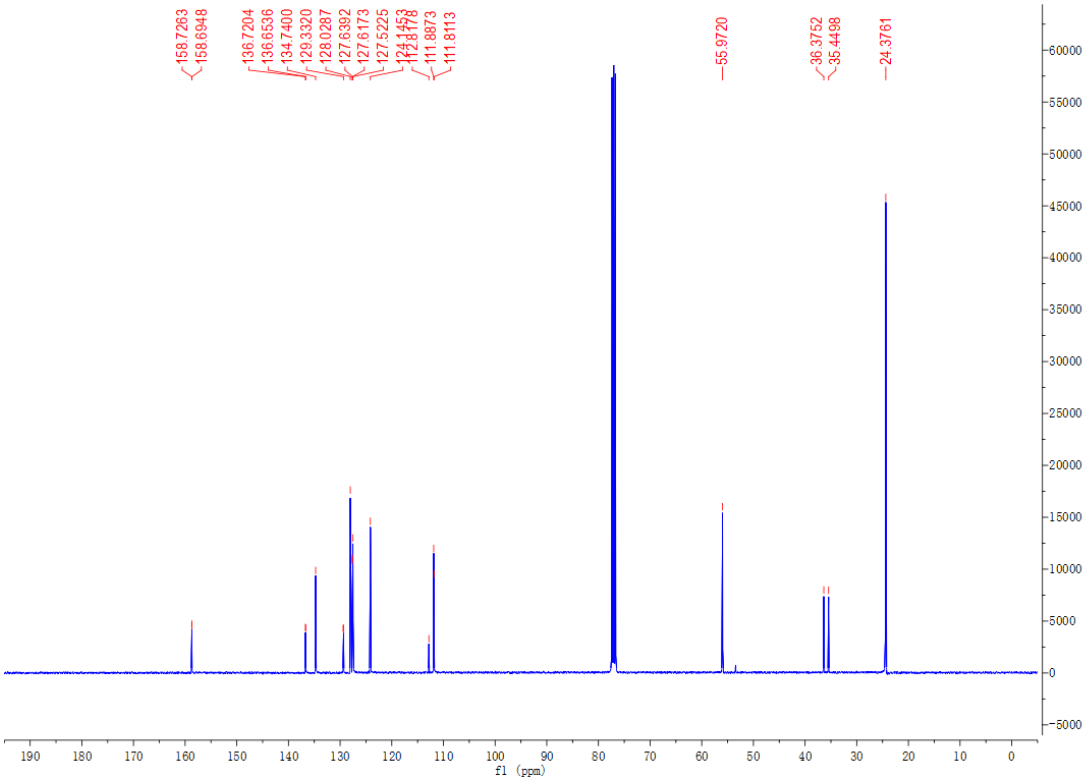
^{1}H NMR of **8d**



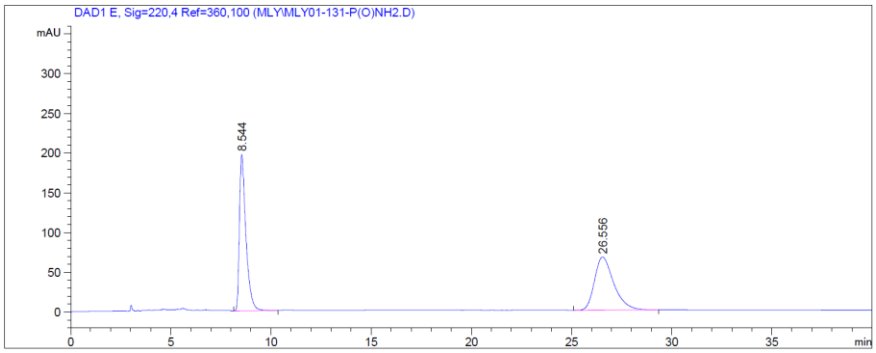
^{31}P NMR of **8d**

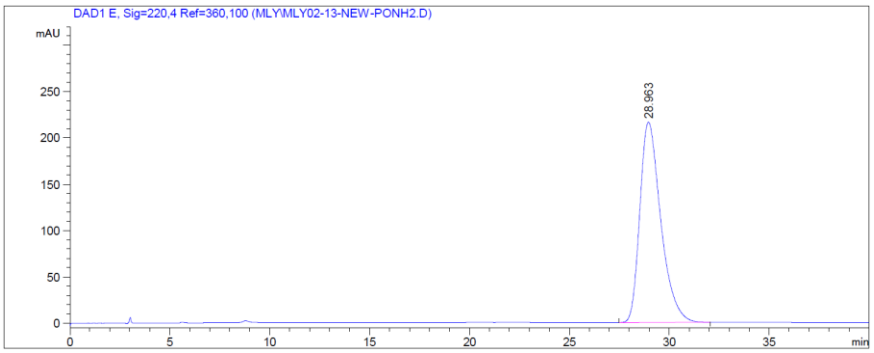


^{13}C NMR of **8d**



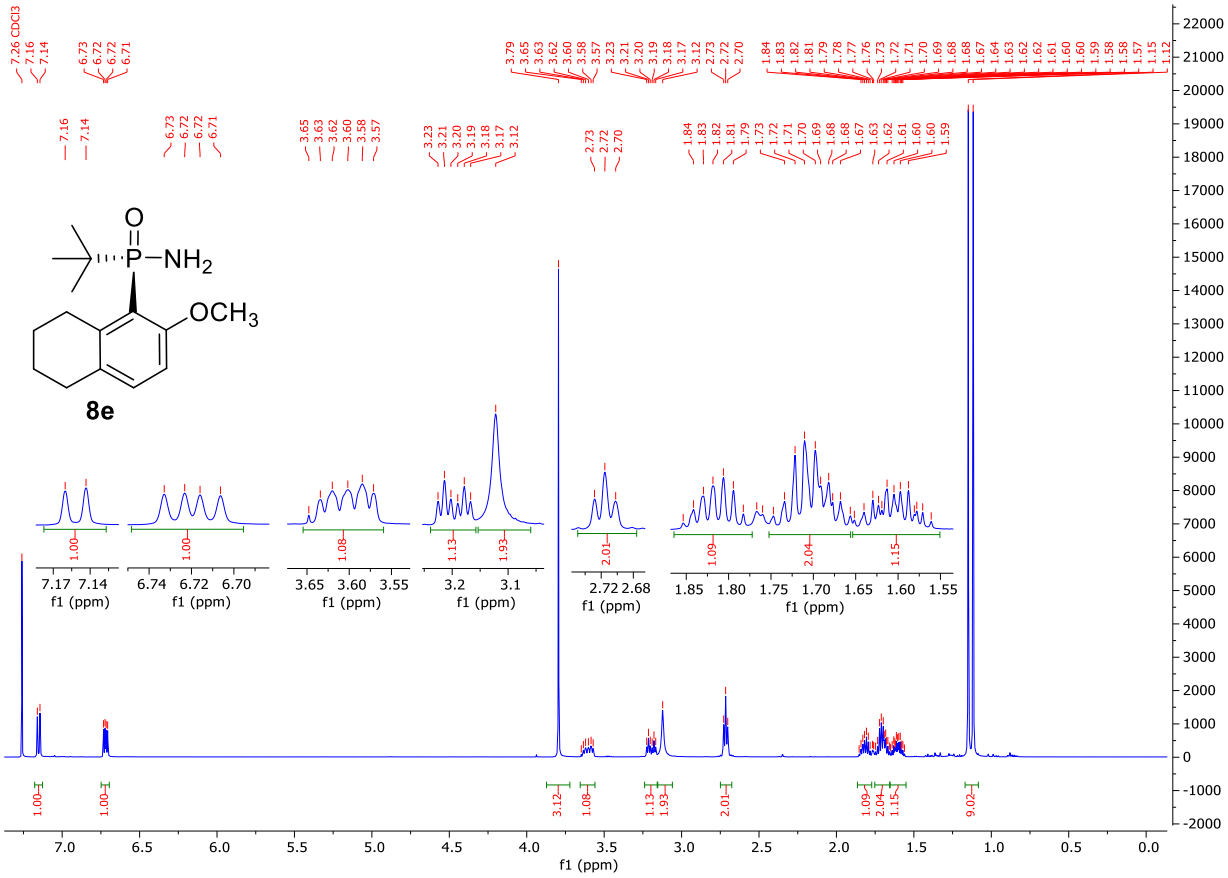
Chiral HPLC chromatograms of **8d**



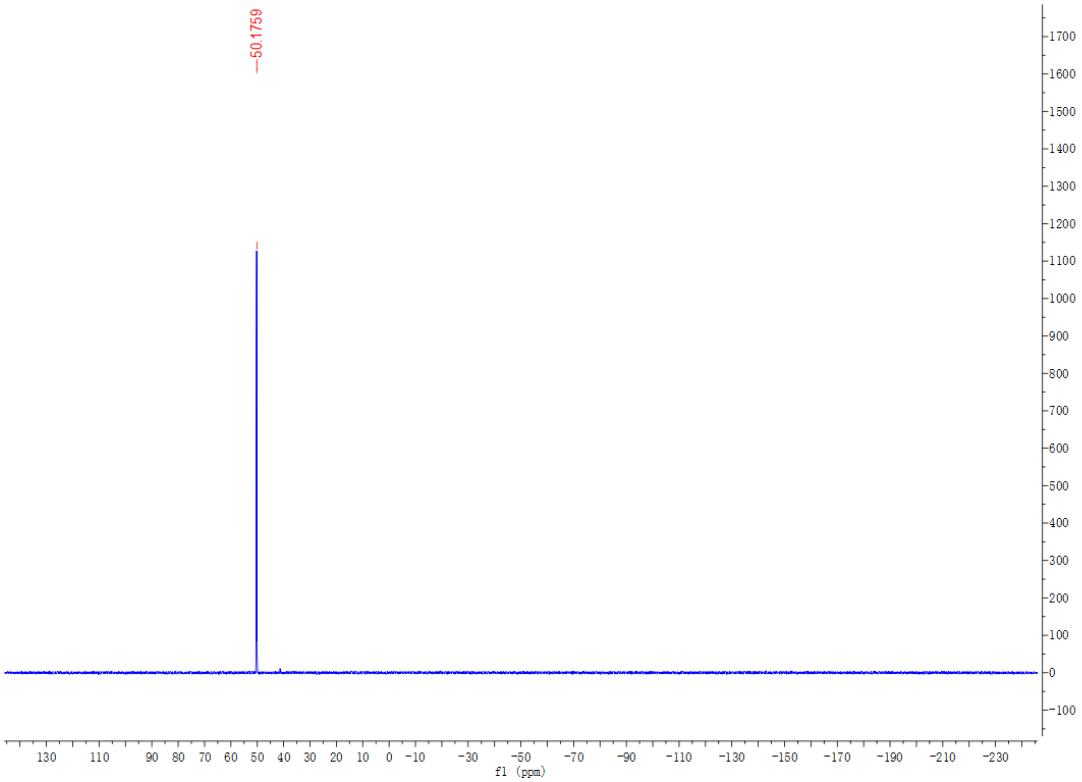


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.963	BB	1.0990	1.57264e4	216.10506	100.0000

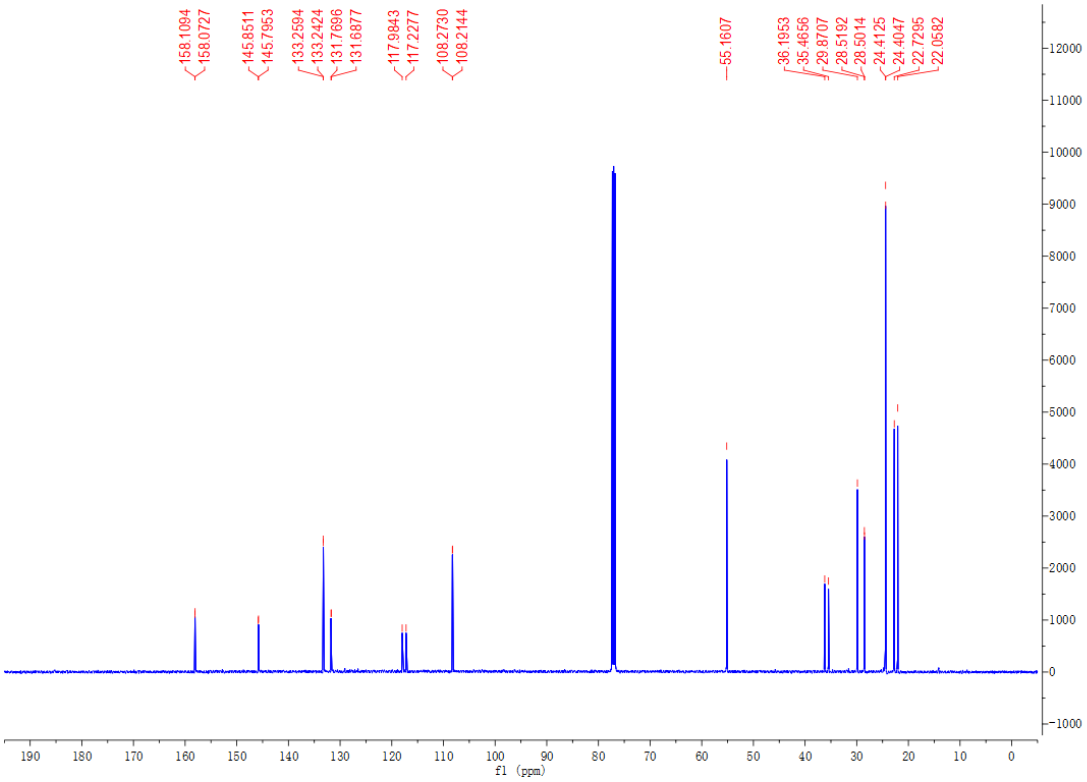
^{1}H NMR of **8e**



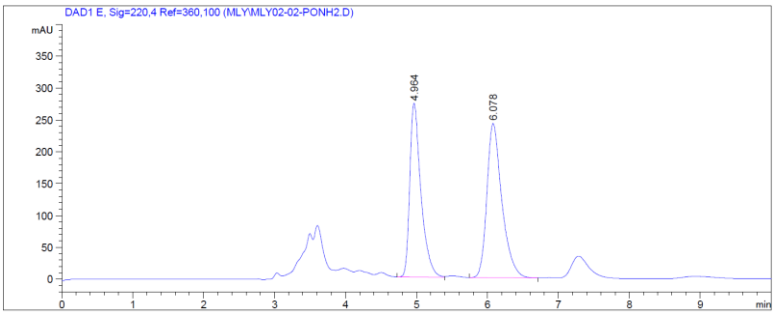
^{31}P NMR of **8e**

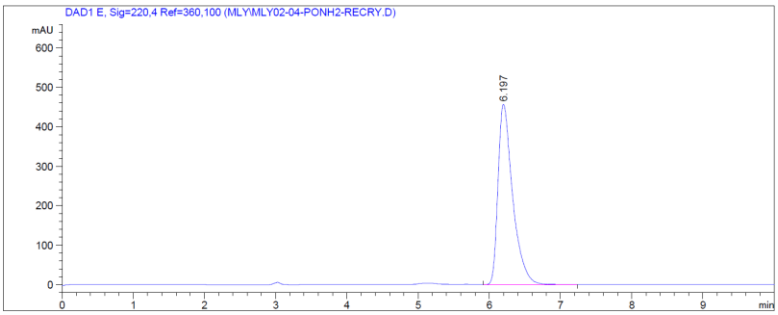


^{13}C NMR of **8e**



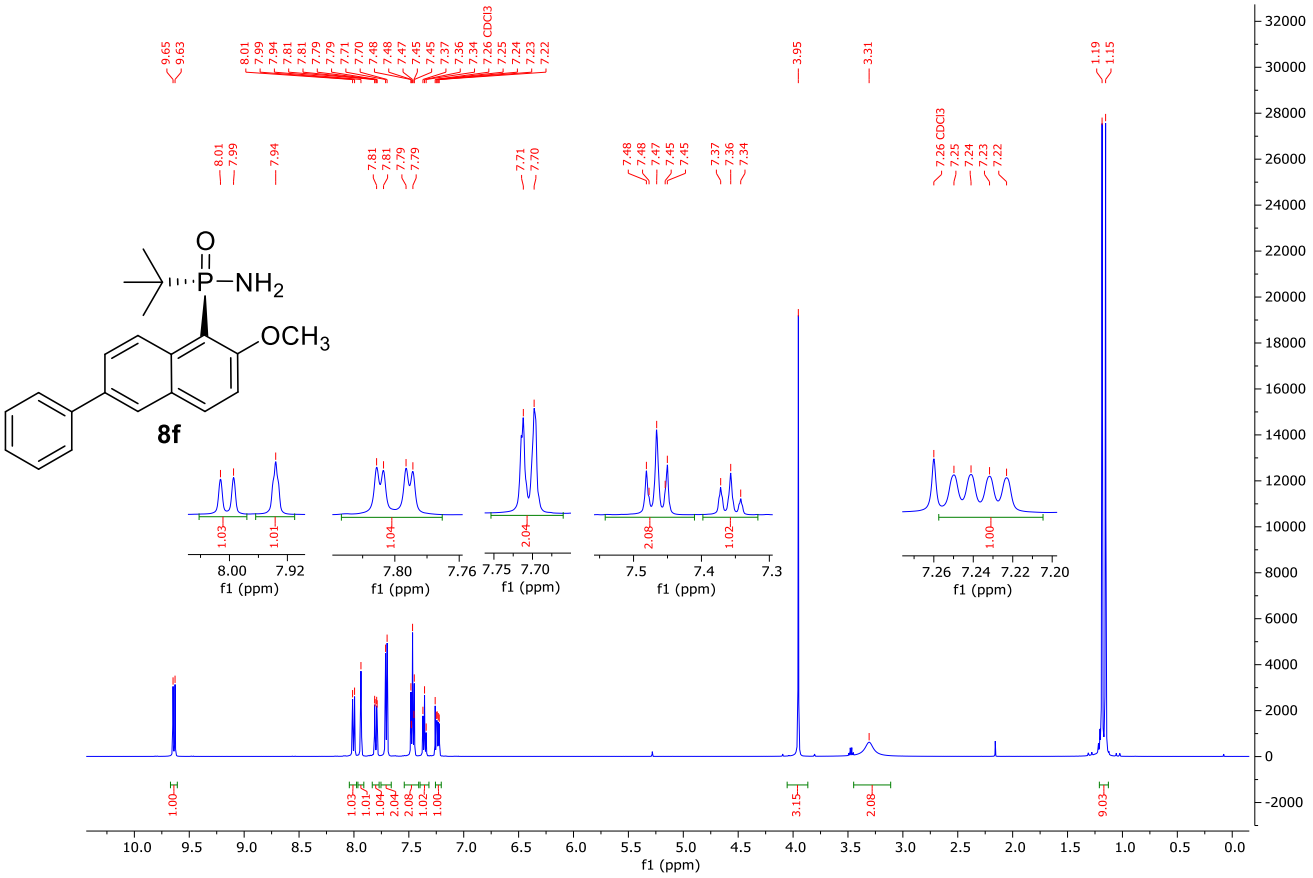
Chiral HPLC chromatograms of **8e**



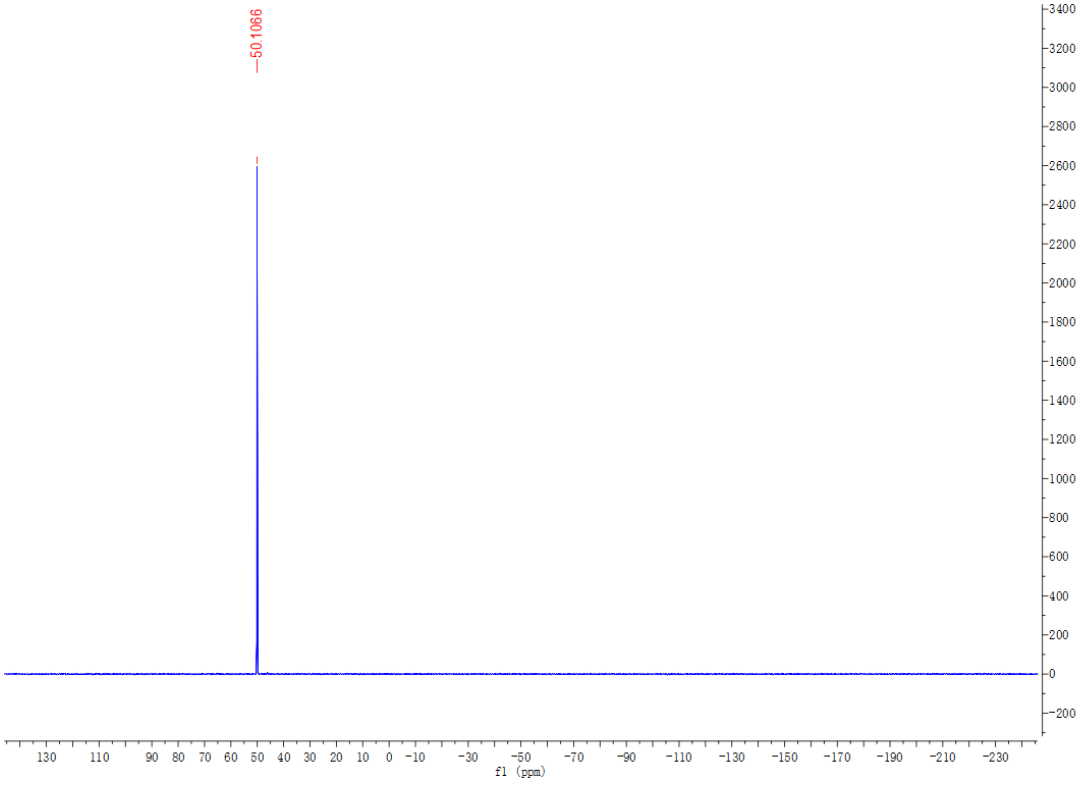


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.197	BV	0.2148	6538.37207	457.20520	100.0000

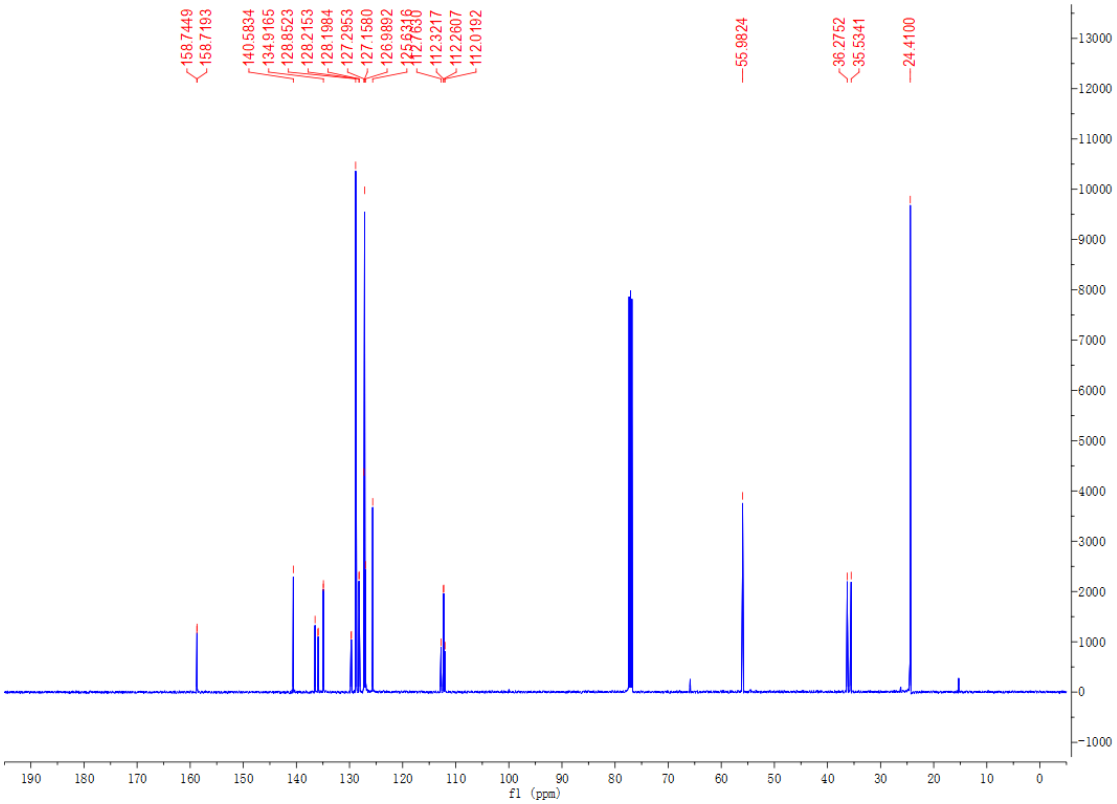
^{1}H NMR of **8f**



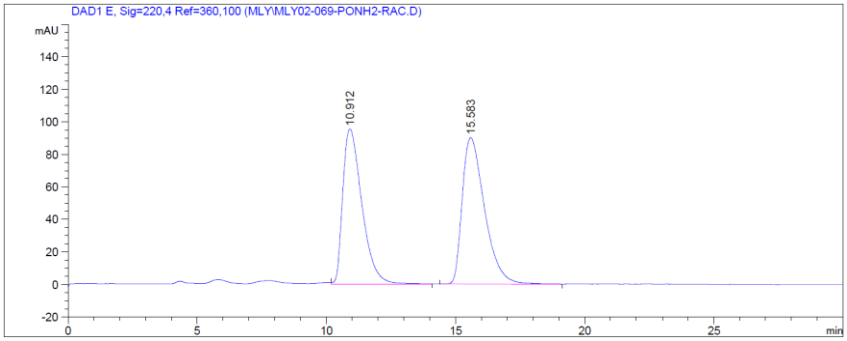
^{31}P NMR of **8f**

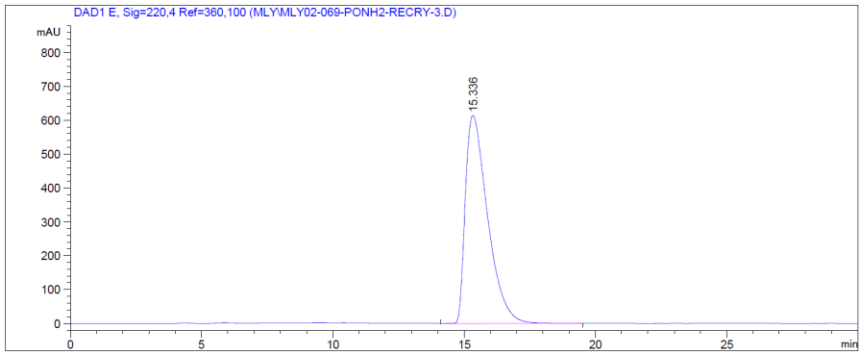


^{13}C NMR of **8f**



Chiral HPLC chromatograms of **8f**

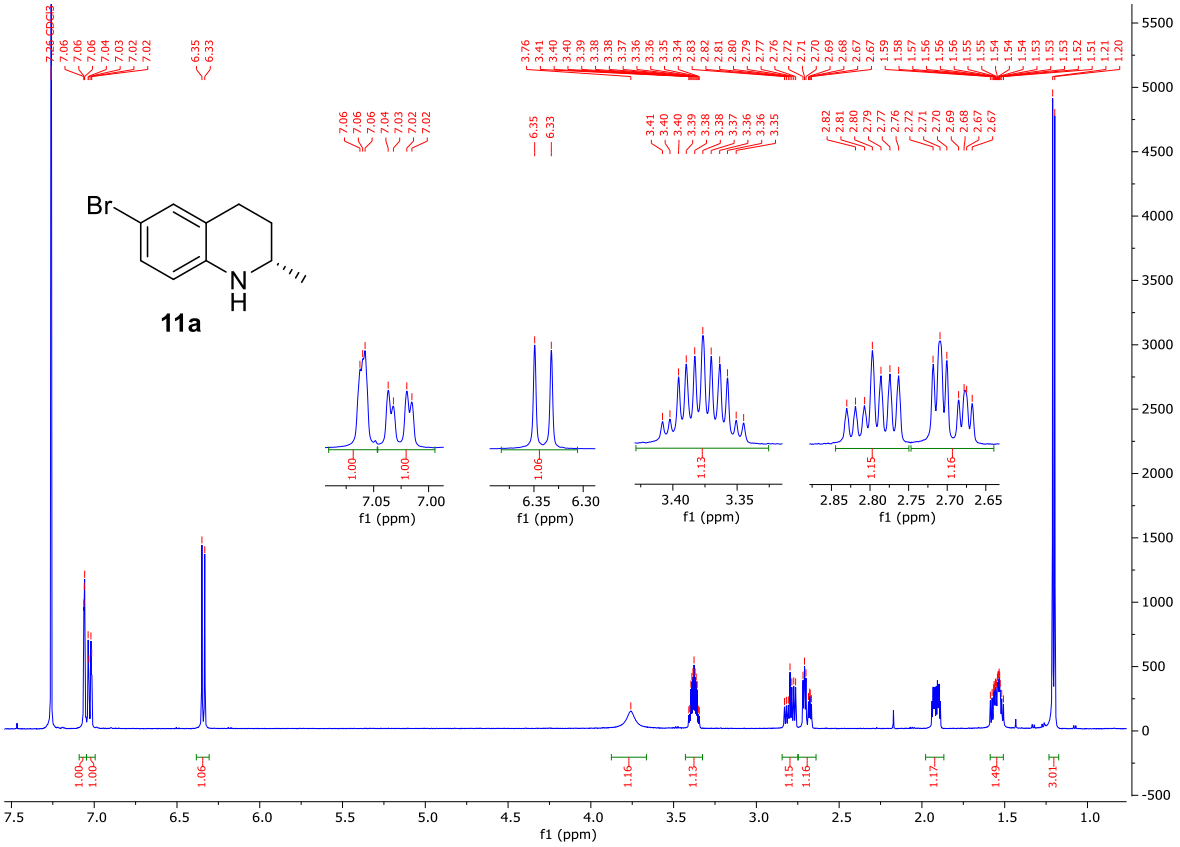


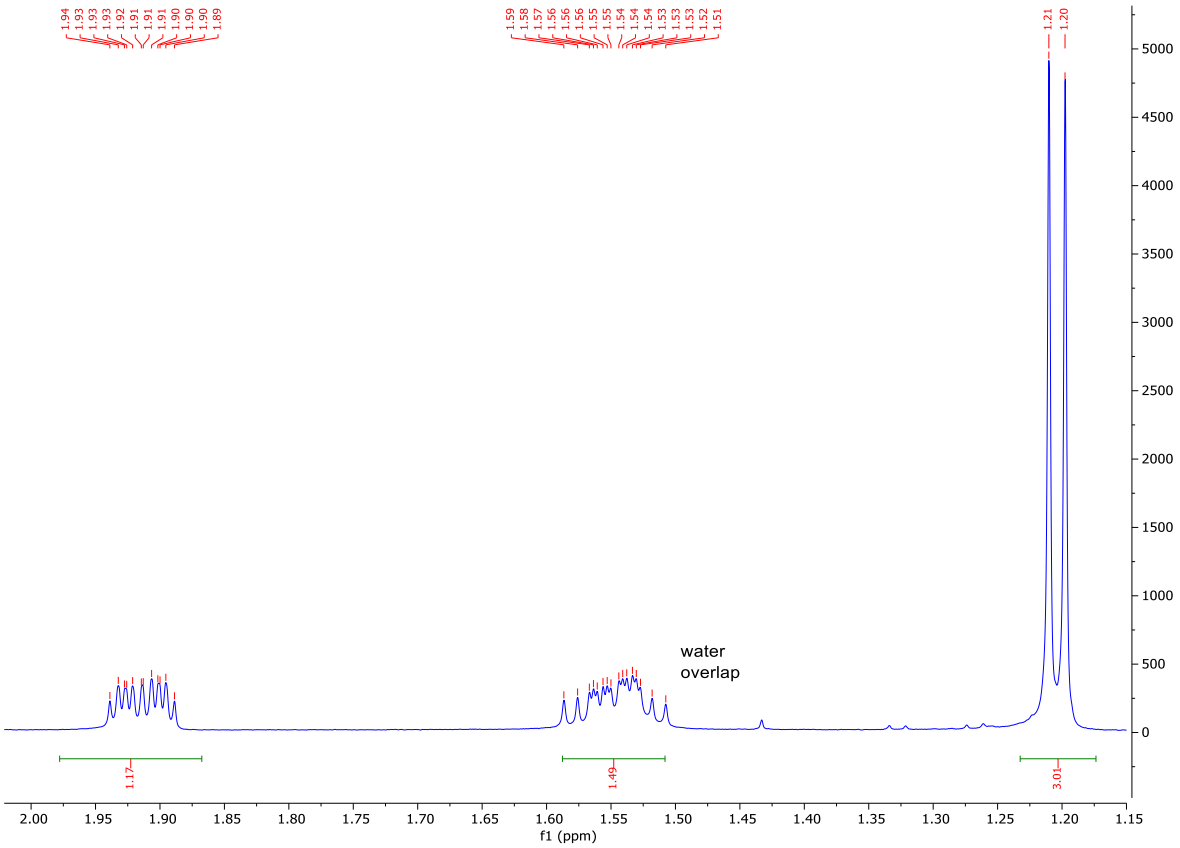


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.336	BV	0.9039	3.62257e4	614.41528	100.0000

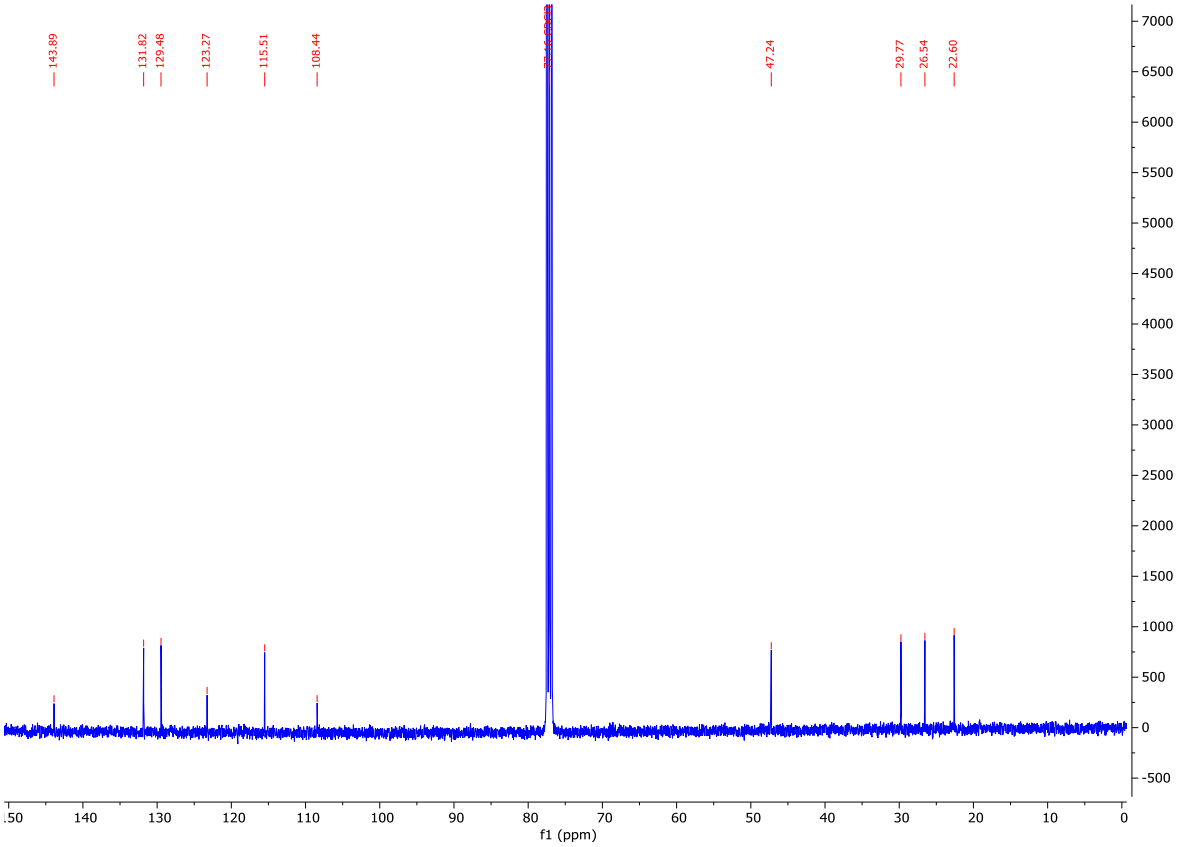
(*S*)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (**11a**)

^{1}H NMR of **11a**

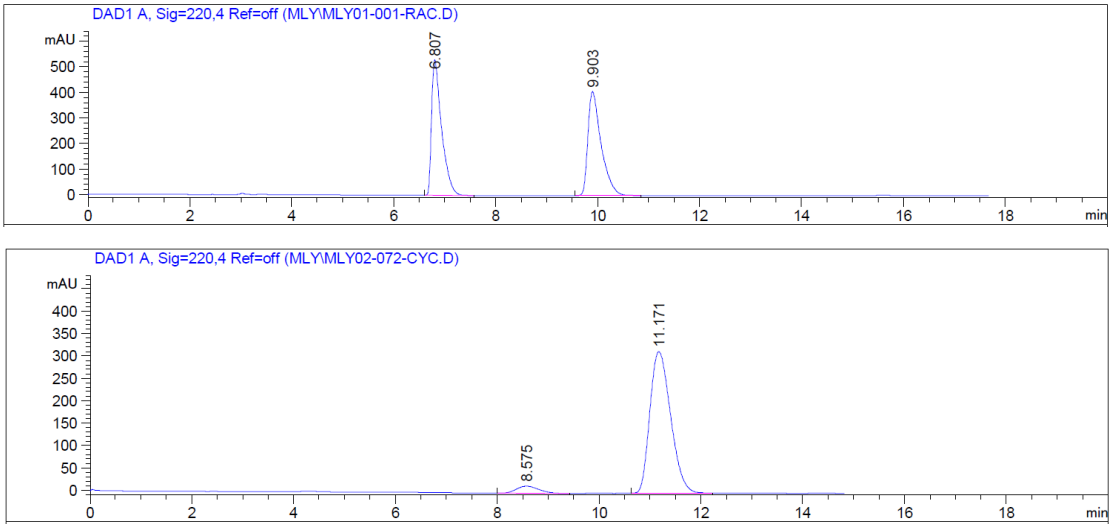




^{13}C NMR of **11a**



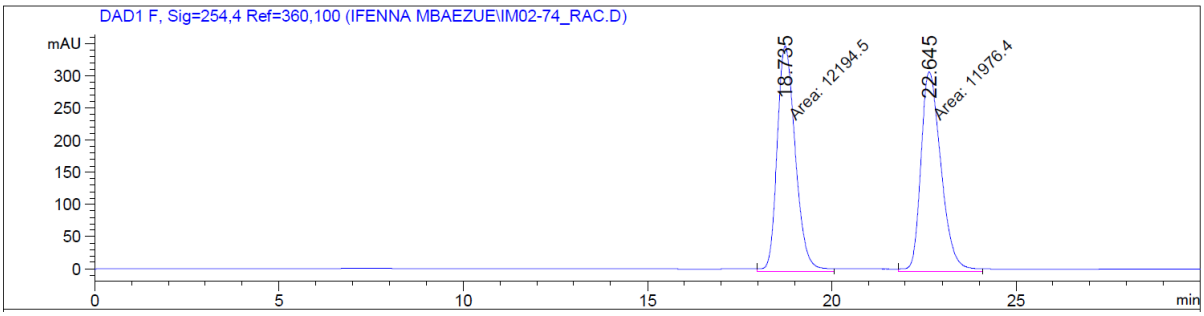
Chiral HPLC Chromatograms of **11a**

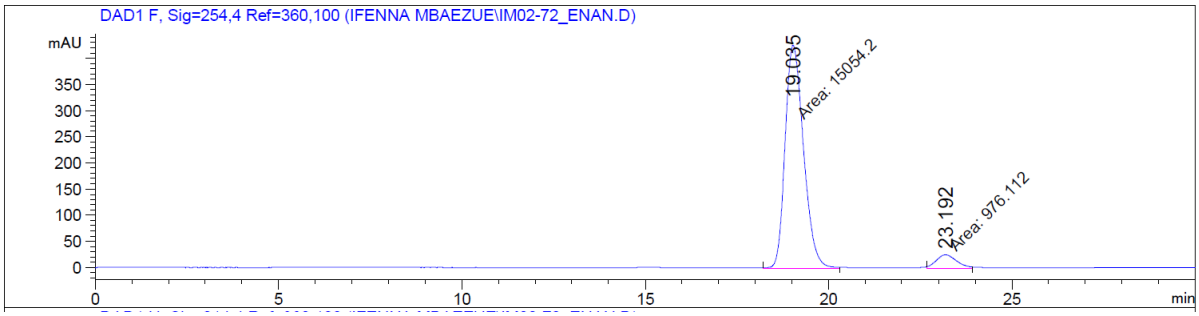


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.575	BB	0.4773	492.90408	16.00656	5.2228
2	11.171	BB	0.4480	8944.63574	316.22061	94.7772

For comparison compound **11a** was also analyzed using a chiracel OJ-H comlun in comparison with the literature.[9]

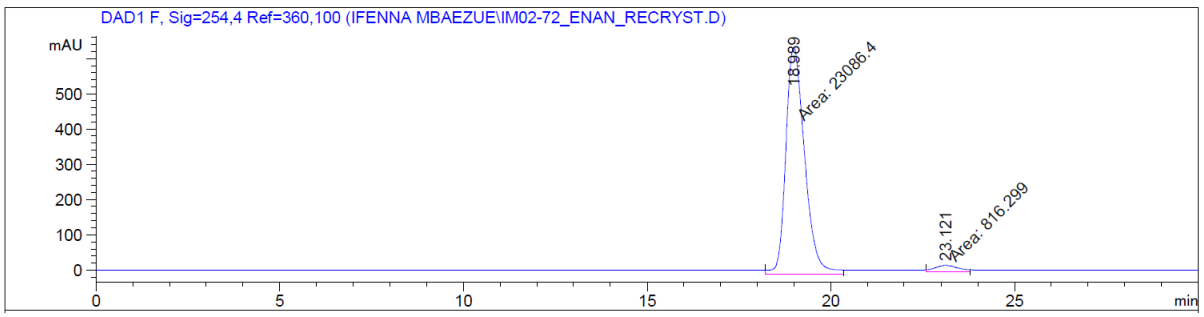
Chiral HPLC Chromatograms of **11a**





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.035	MM	0.5867	1.50542e4	427.68332	93.9108
2	23.192	MM	0.6424	976.11206	25.32313	6.0892

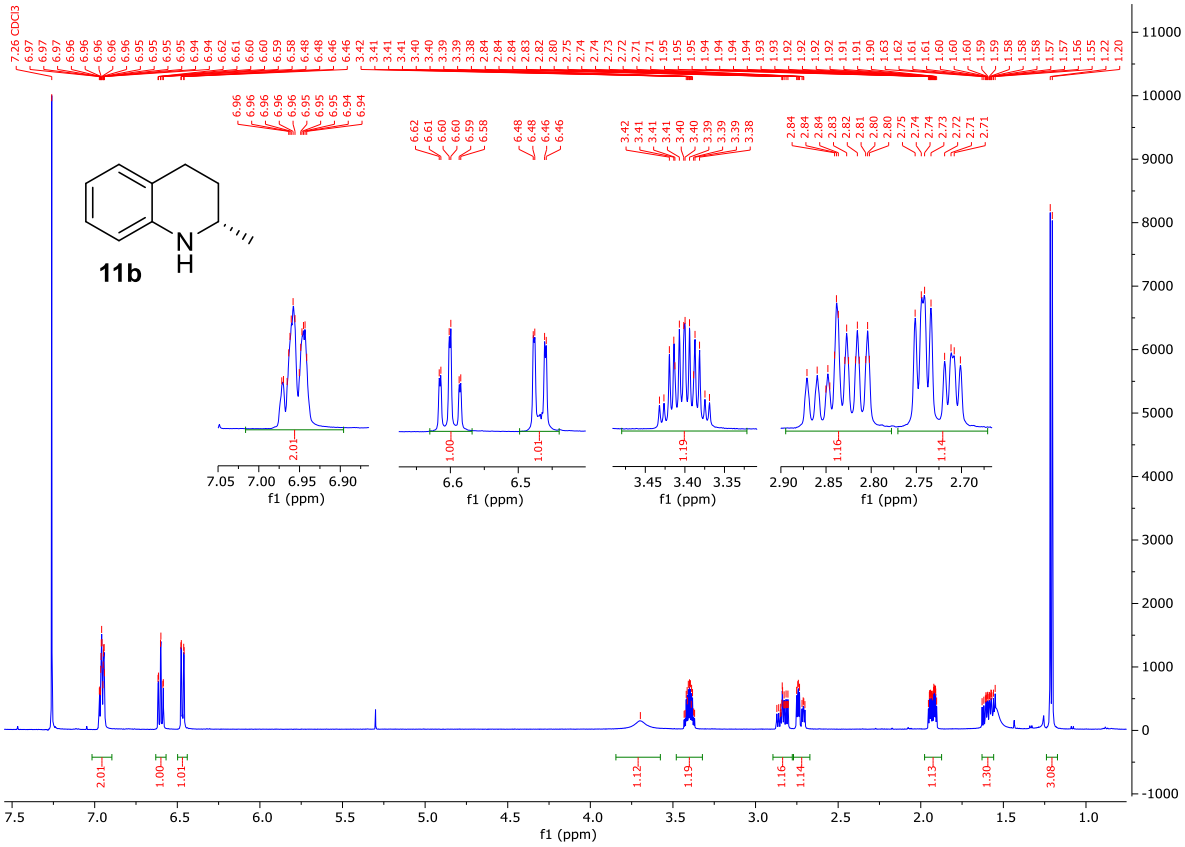
Chiral HPLC Chromatogram of crystallized product **11a**

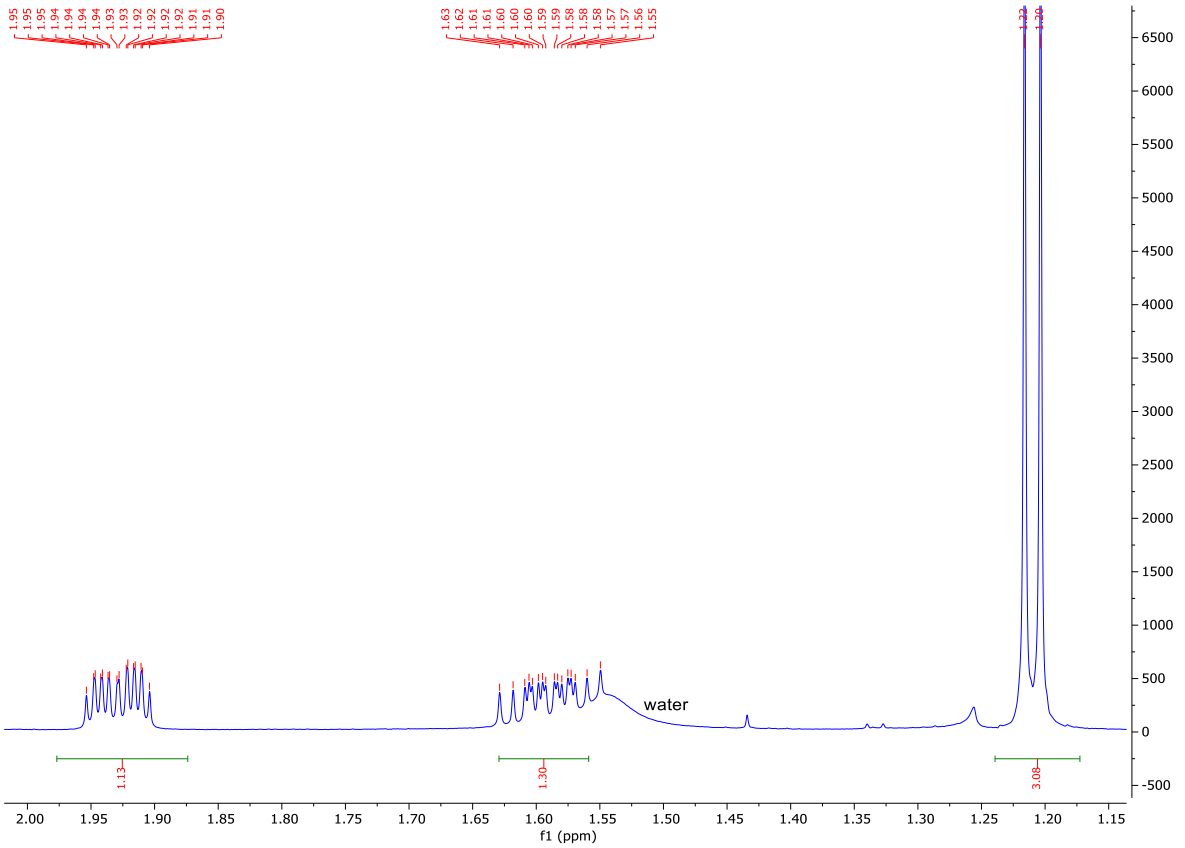


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.989	MM	0.5980	2.30864e4	643.44177	96.5849
2	23.121	MM	0.7581	816.29865	17.94708	3.4151

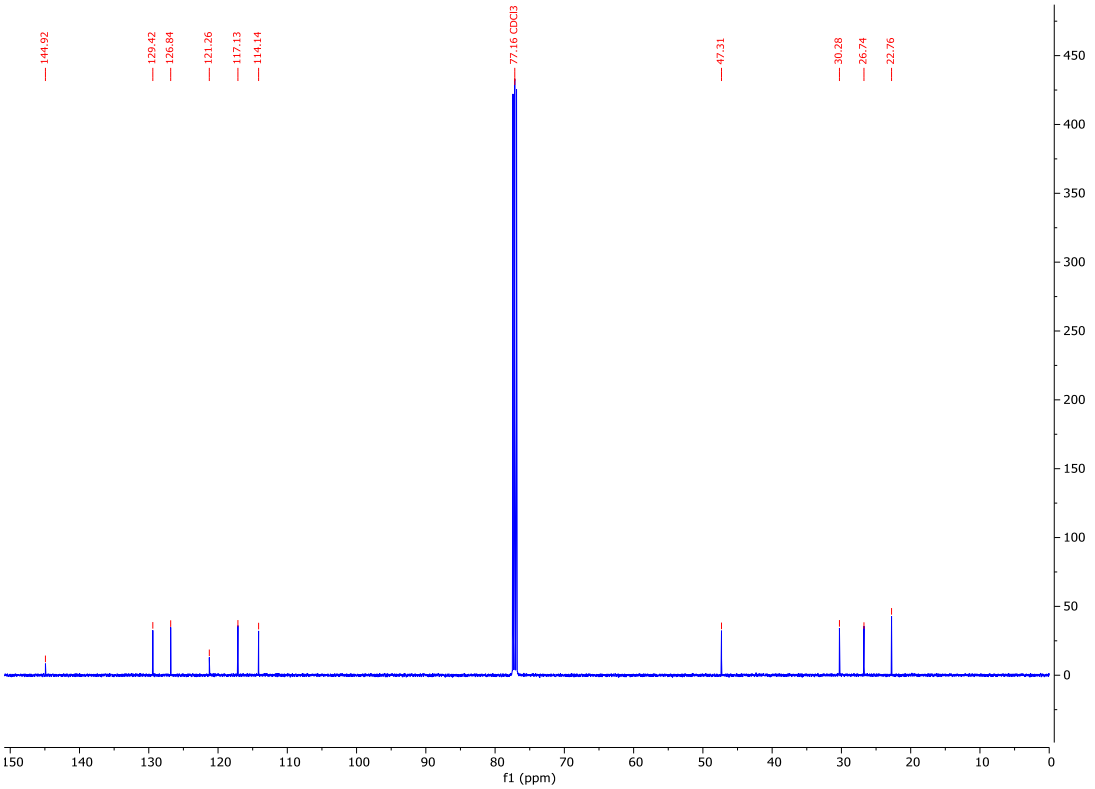
(*S*)-2-methyl-1,2,3,4-tetrahydroquinoline (**11b**)

^{1}H NMR of **11b**

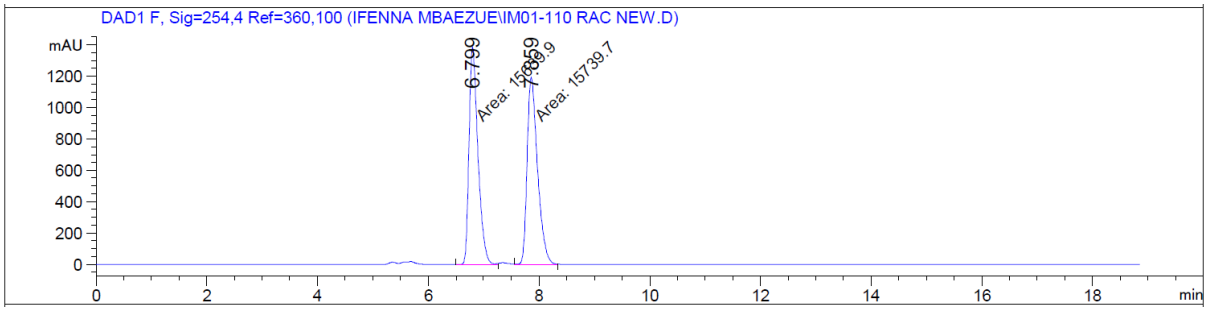


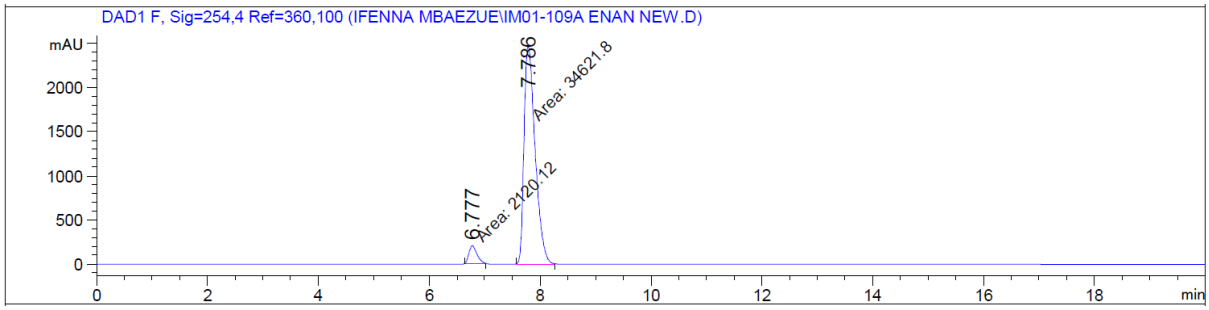


^{13}C NMR of **11b**



Chiral HPLC Chromatograms of **11b**

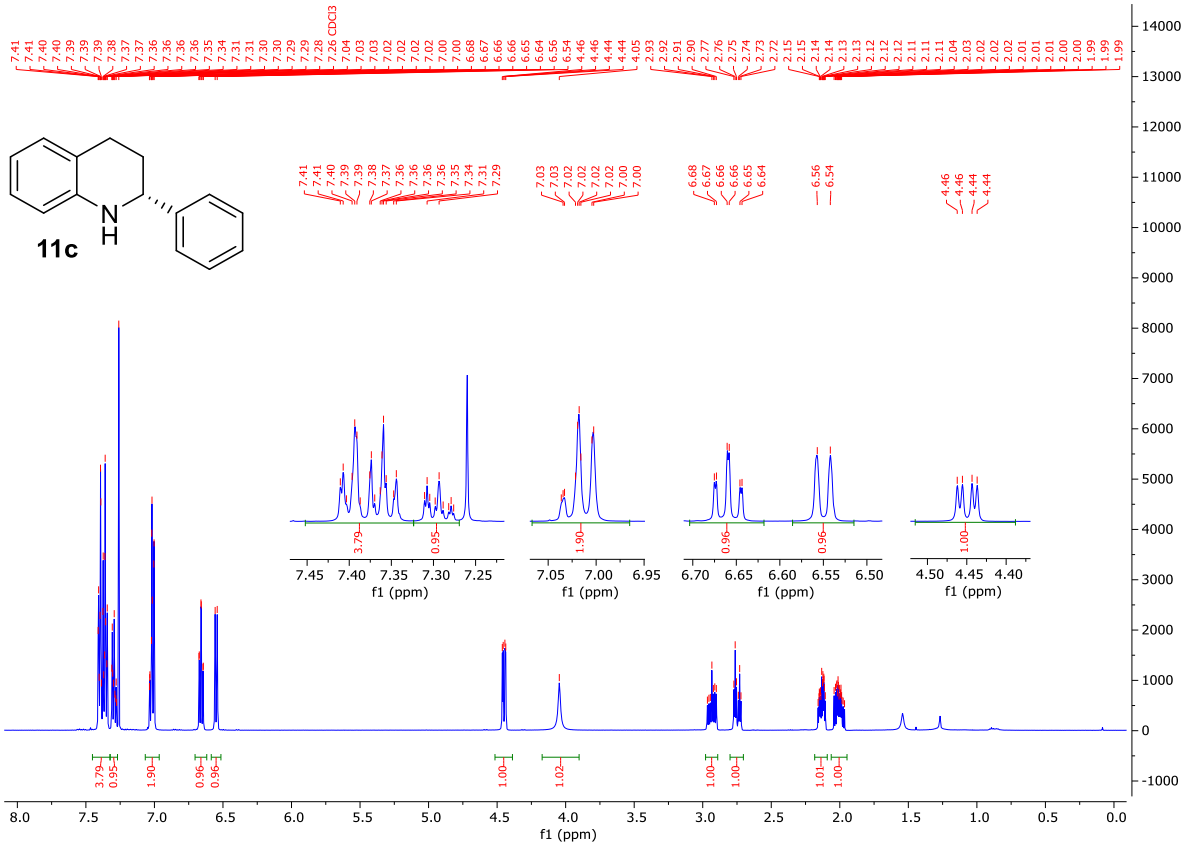


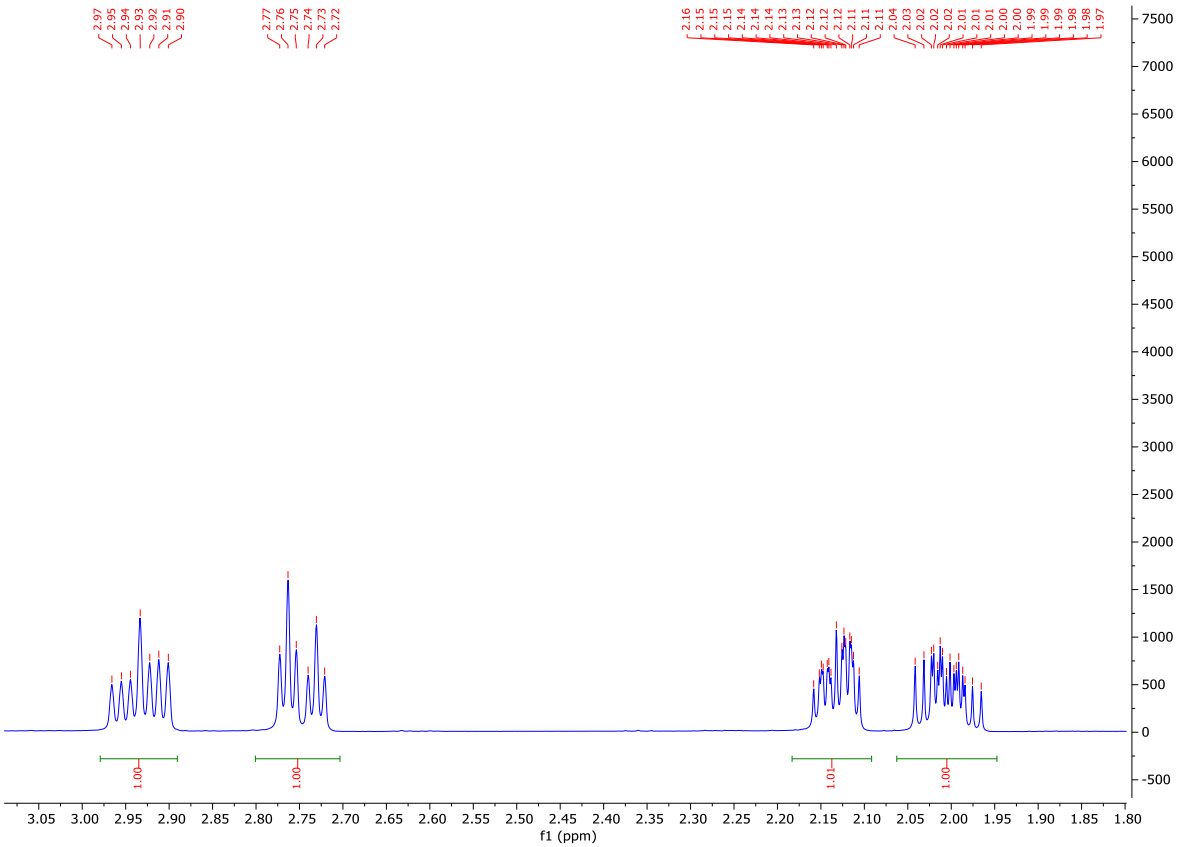


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.777	MM	0.1708	2120.12207	206.83456	5.7703
2	7.786	MM	0.2332	3.46218e4	2474.55640	94.2297

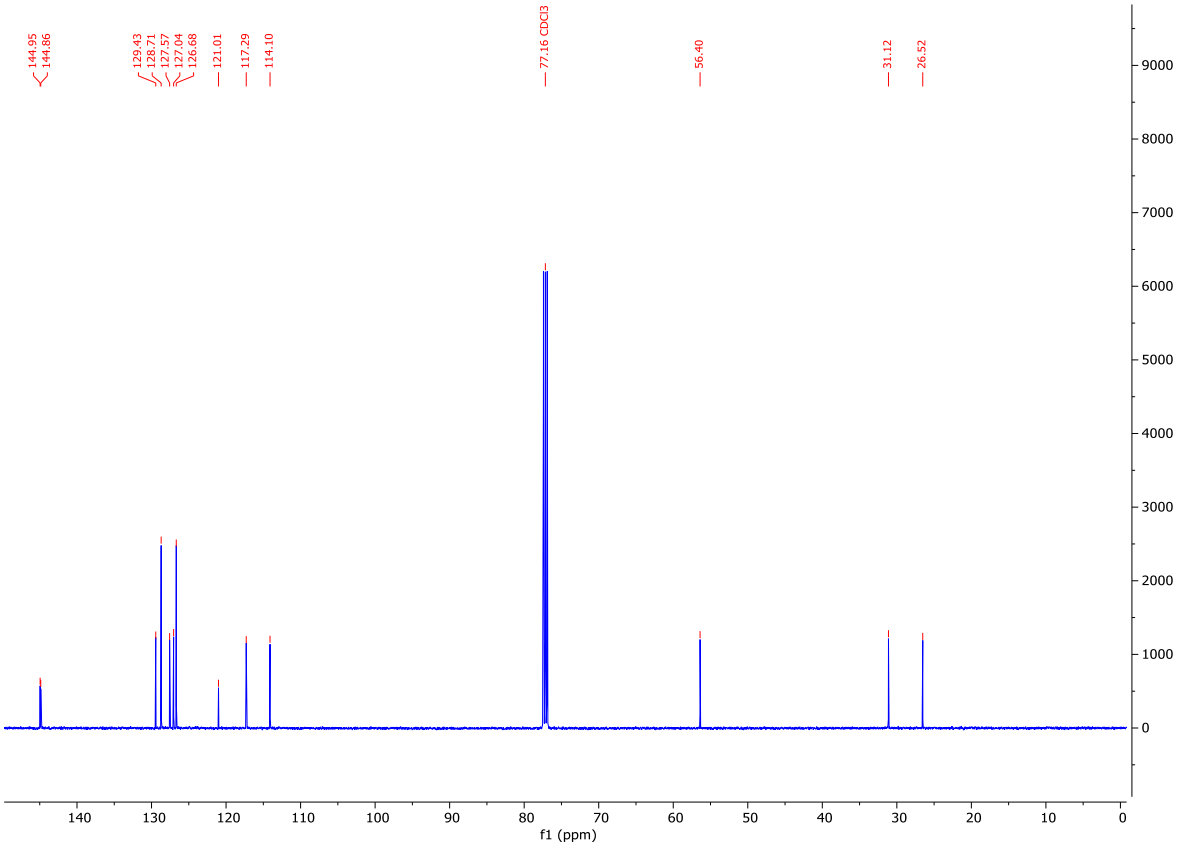
(*R*)-2-phenyl-1,2,3,4-tetrahydroquinoline (**11c**)

^{1}H NMR of **11c**

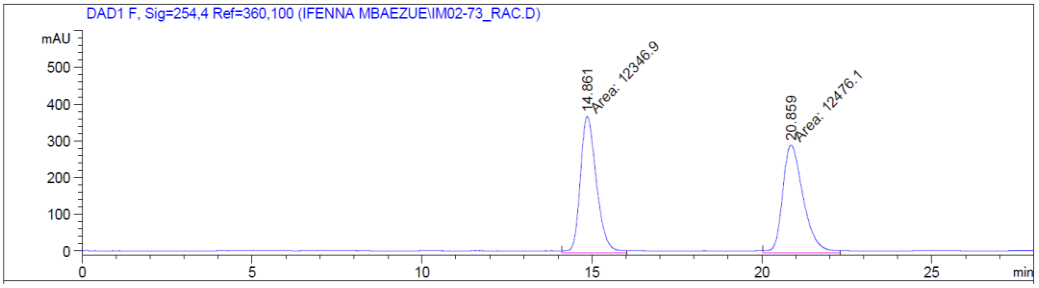


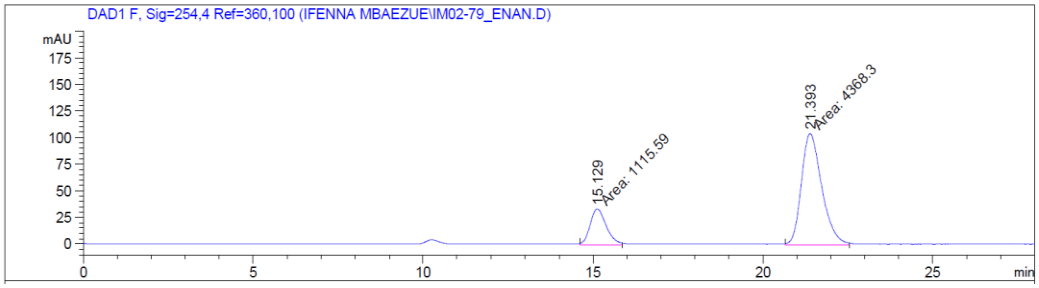


^{13}C NMR of **11c**



Chiral HPLC Chromatograms of **11c**

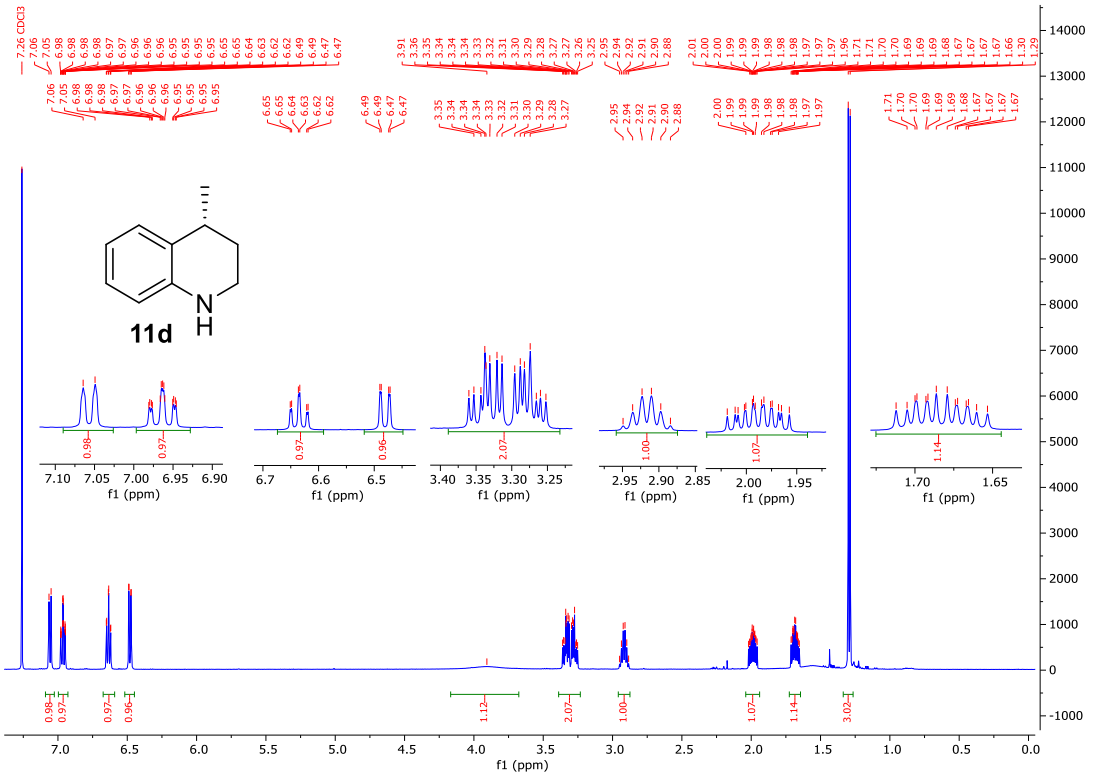




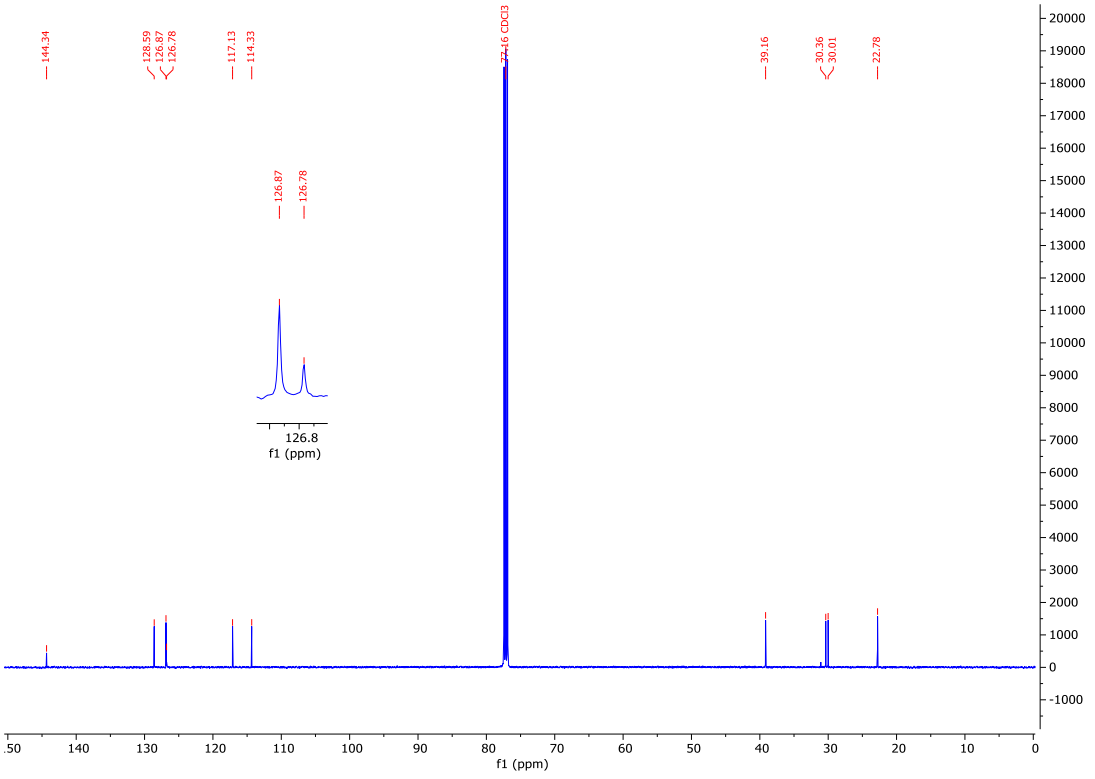
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.129	MM	0.5518	1115.59338	33.69407	20.3431
2	21.393	MM	0.6967	4368.30176	104.49825	79.6569

(*R*)-4-methyl-1,2,3,4-tetrahydroquinoline (**11d**)

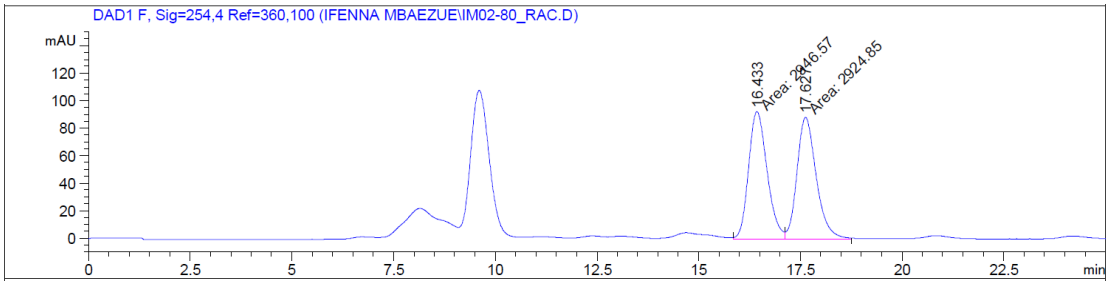
^{1}H NMR of **11d**

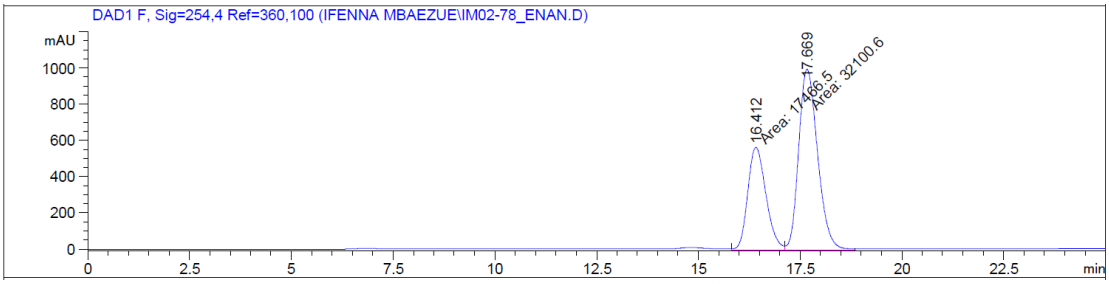


^{13}C NMR of **11d**



Chiral HPLC Chromatograms of **11d**

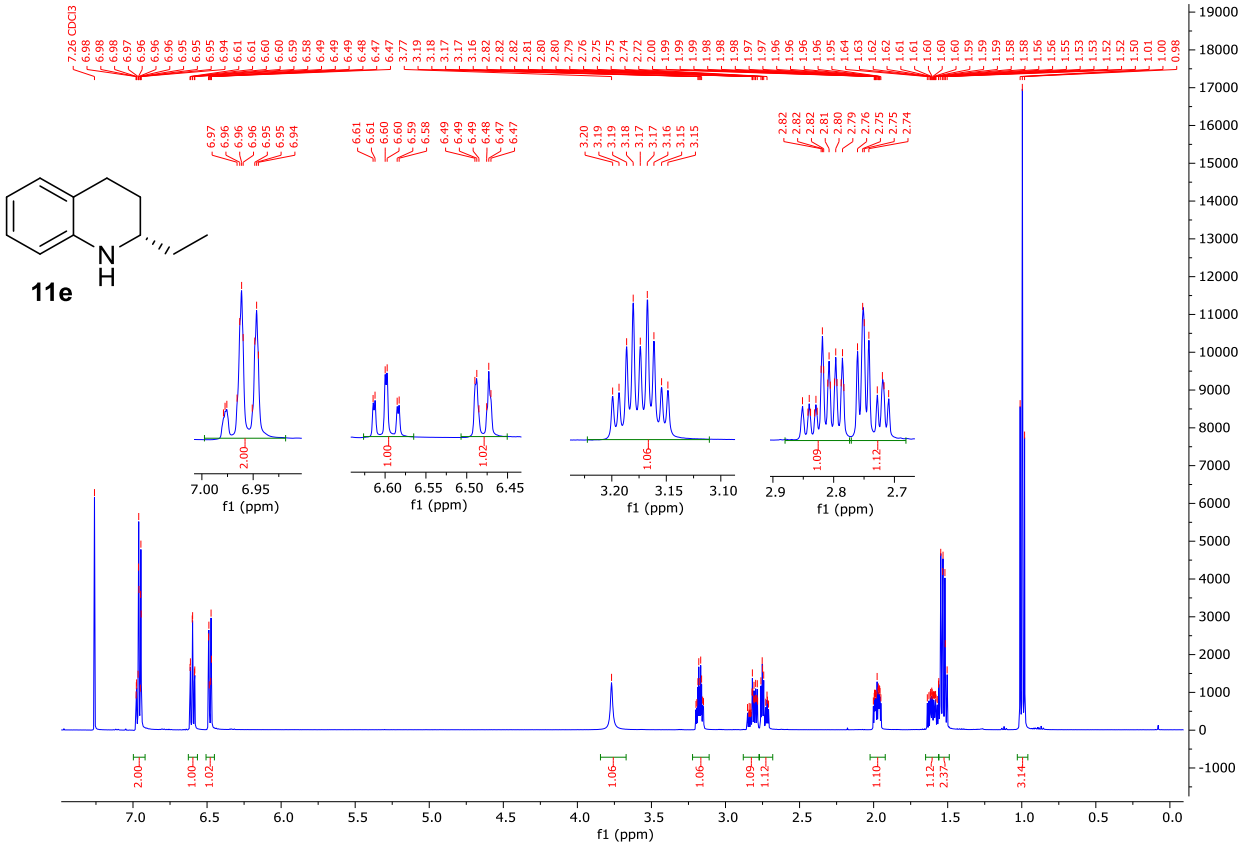


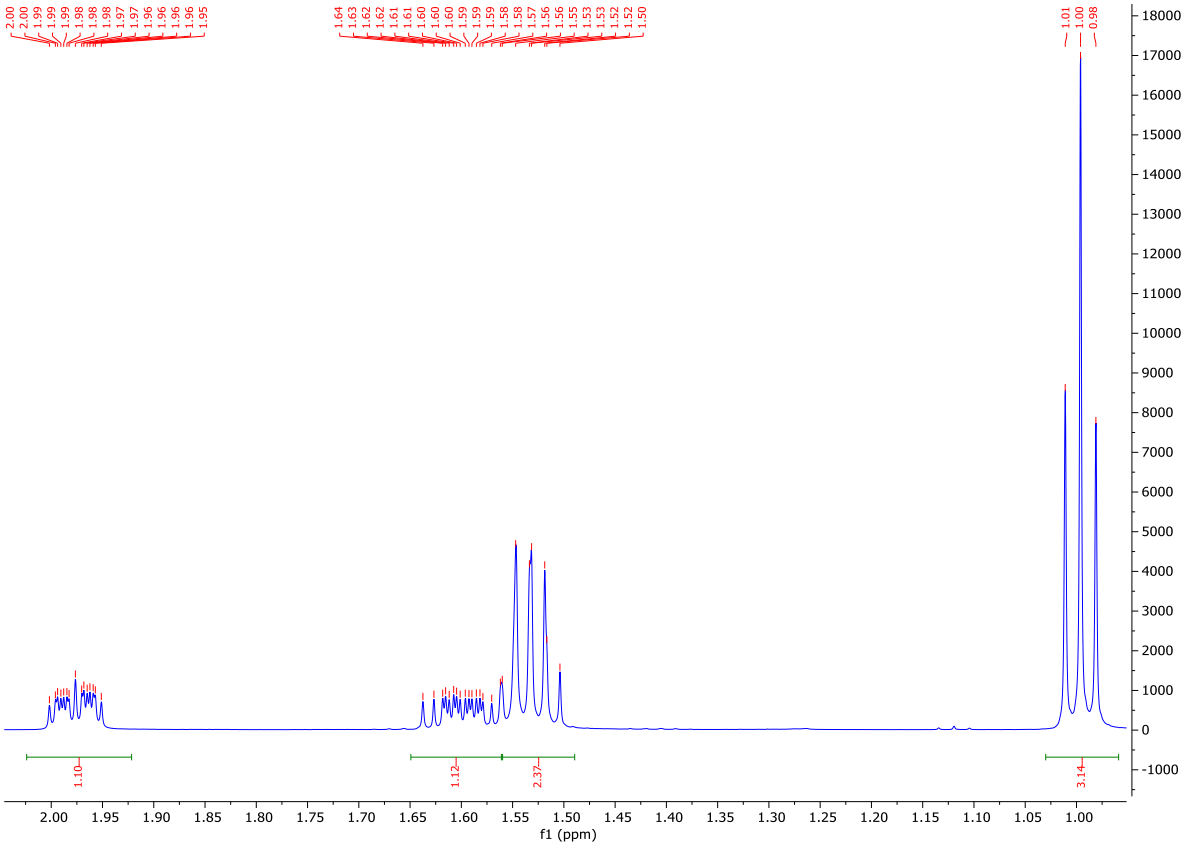


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.412	MM	0.5150	1.74665e4	565.20856	35.2382
2	17.669	MM	0.5373	3.21006e4	995.67267	64.7618

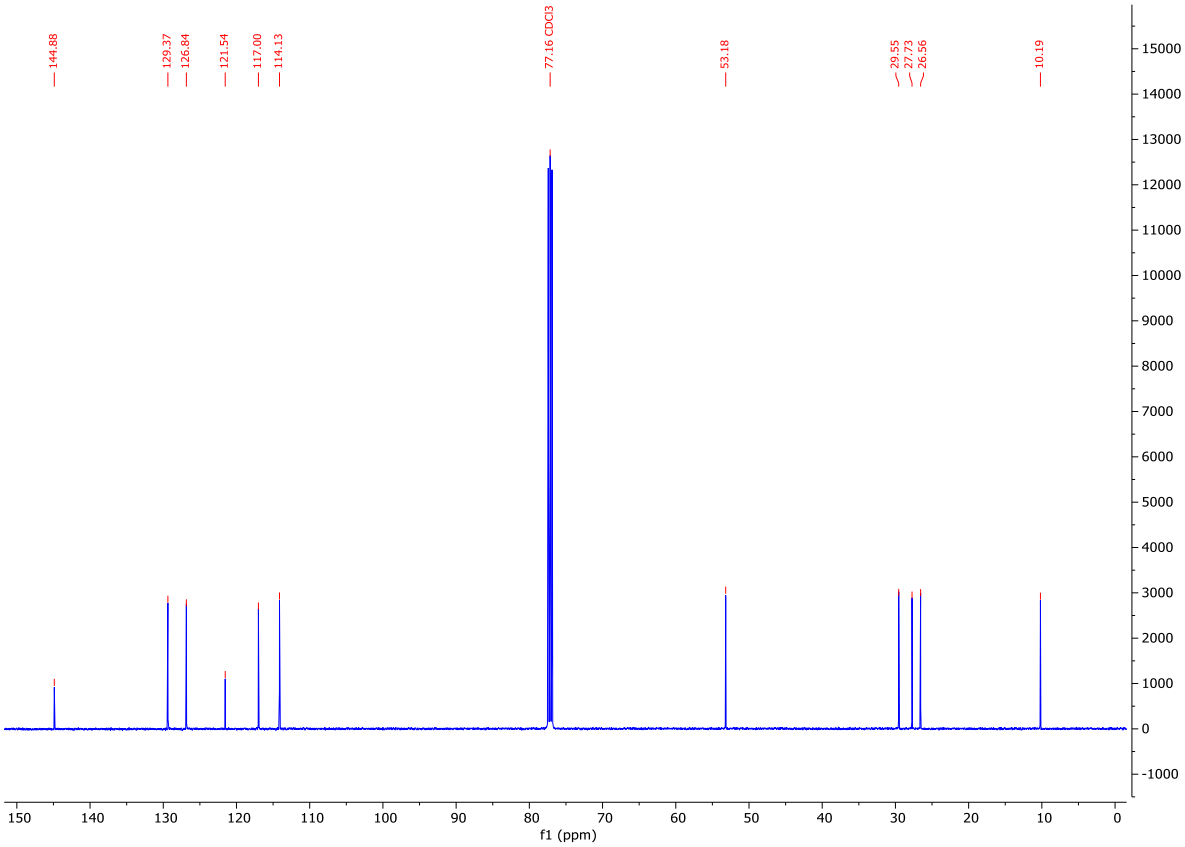
(*S*)-2-ethyl-1,2,3,4-tetrahydroquinoline (**11e**)

^{1}H NMR of **11e**

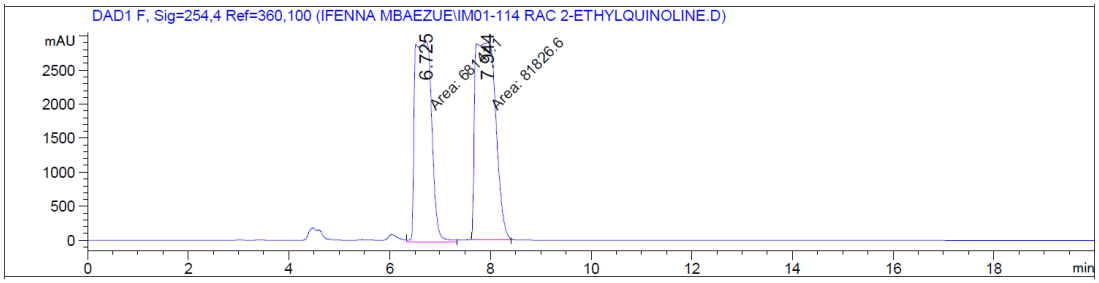


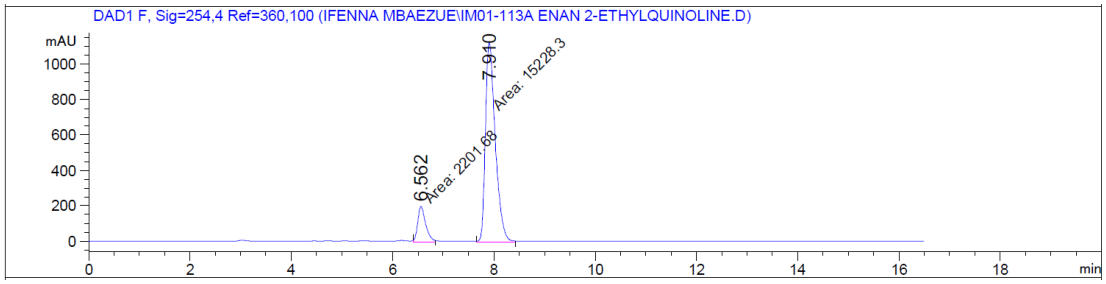


^{13}C NMR of **11e**



Chiral HPLC Chromatograms of **11e**

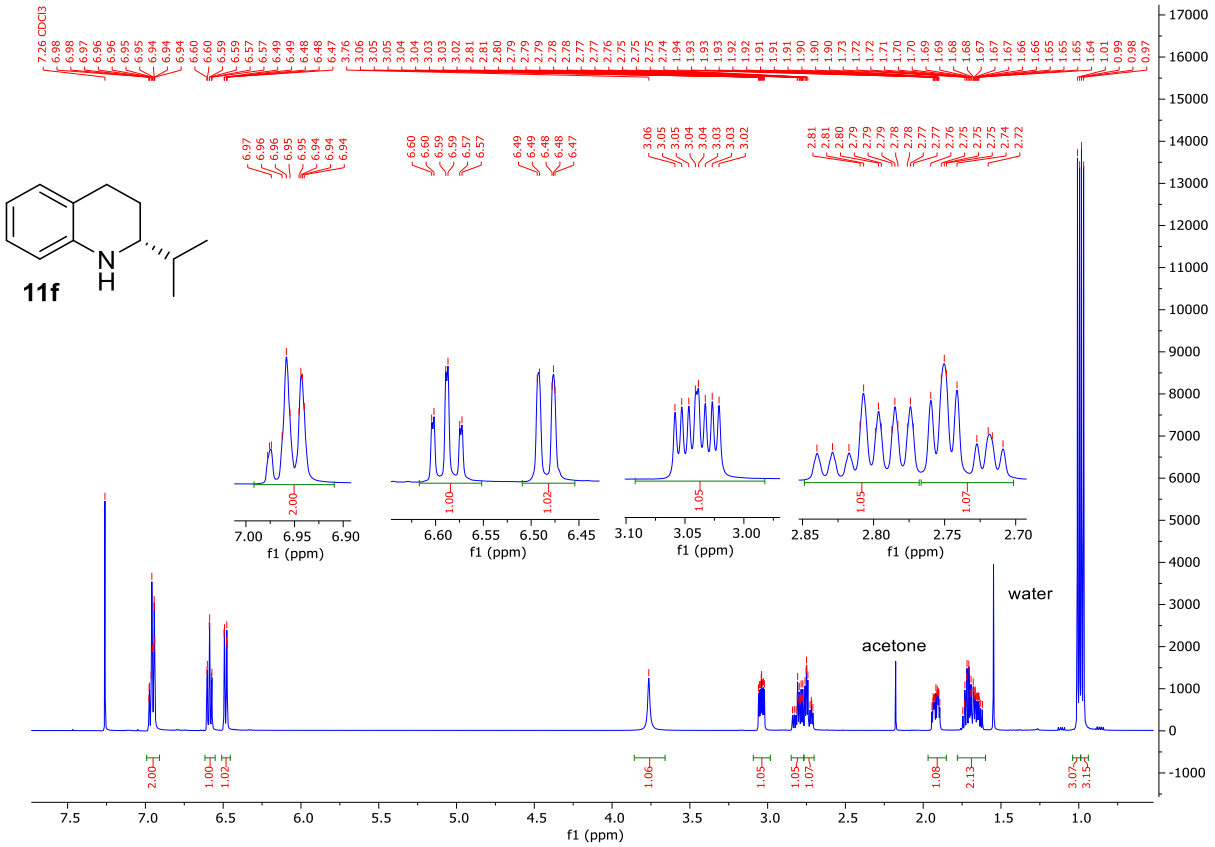


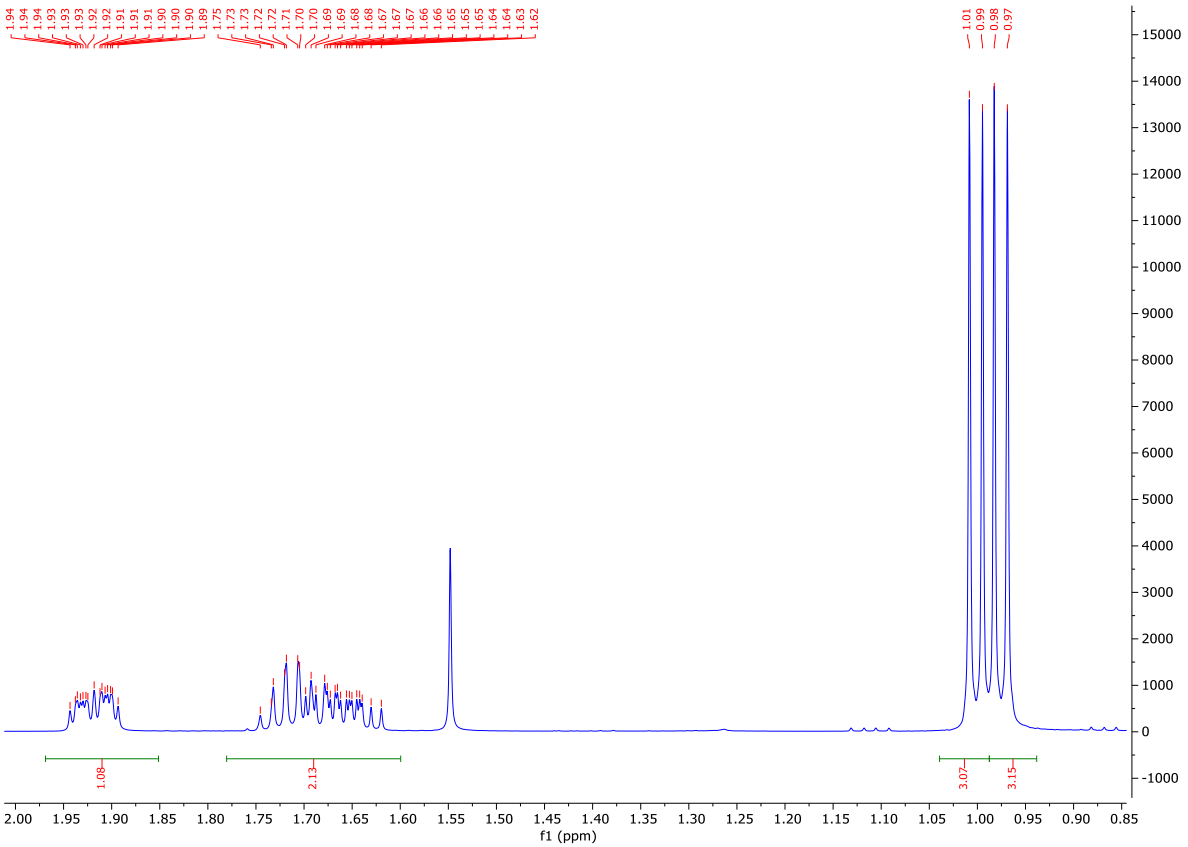


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.562	MM	0.1823	2201.67993	201.33543	12.6316
2	7.910	MM	0.2248	1.52283e4	1129.25708	87.3684

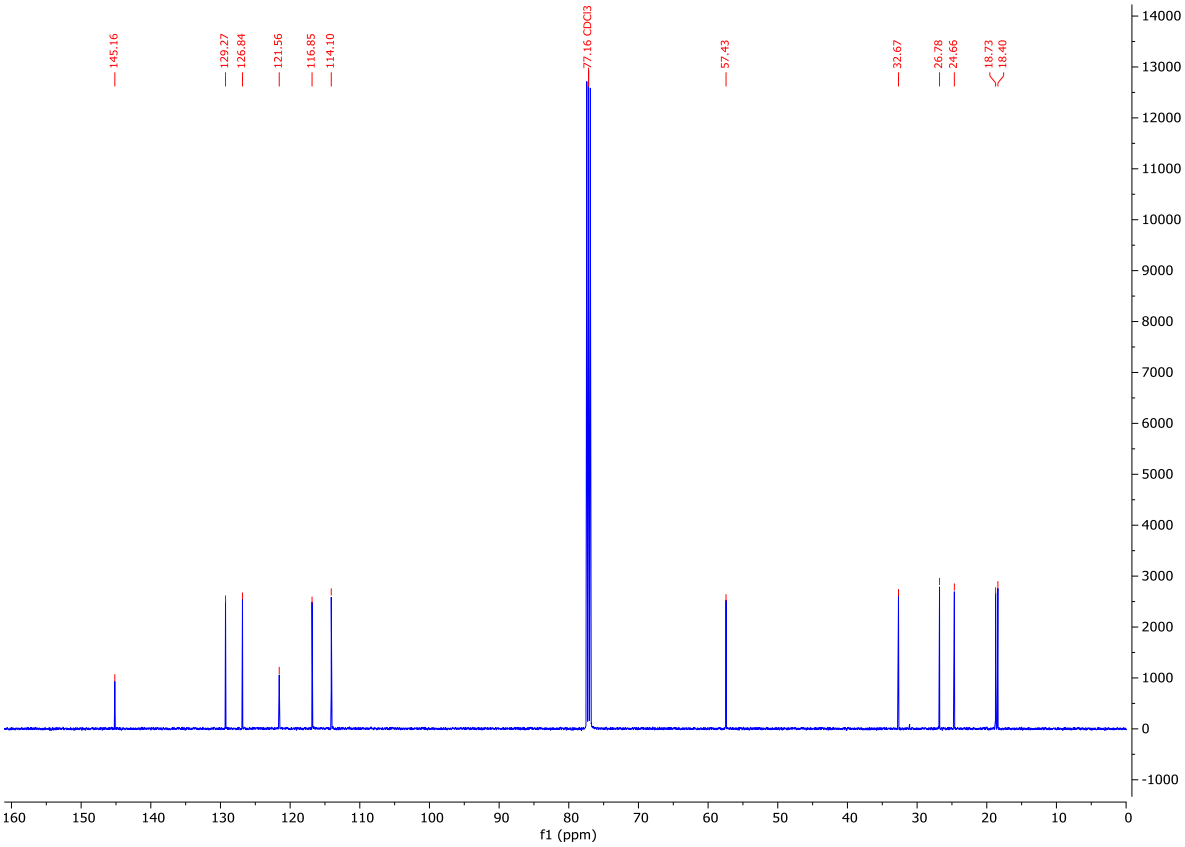
(*R*)-2-isopropyl-1,2,3,4-tetrahydroquinoline (**11f**)

^{1}H NMR of **11f**

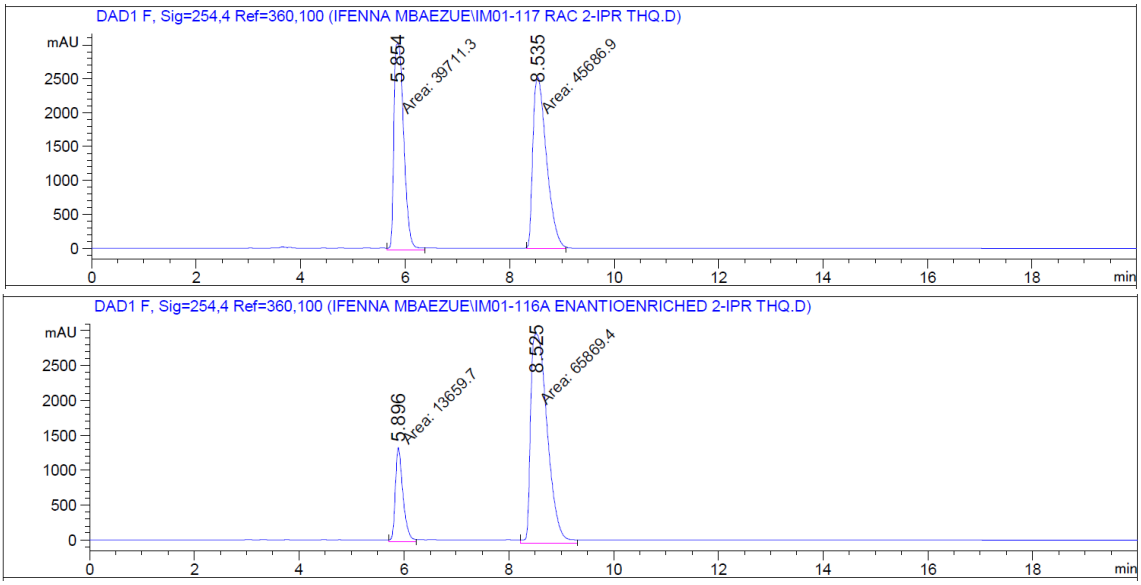




^{13}C NMR of **11f**



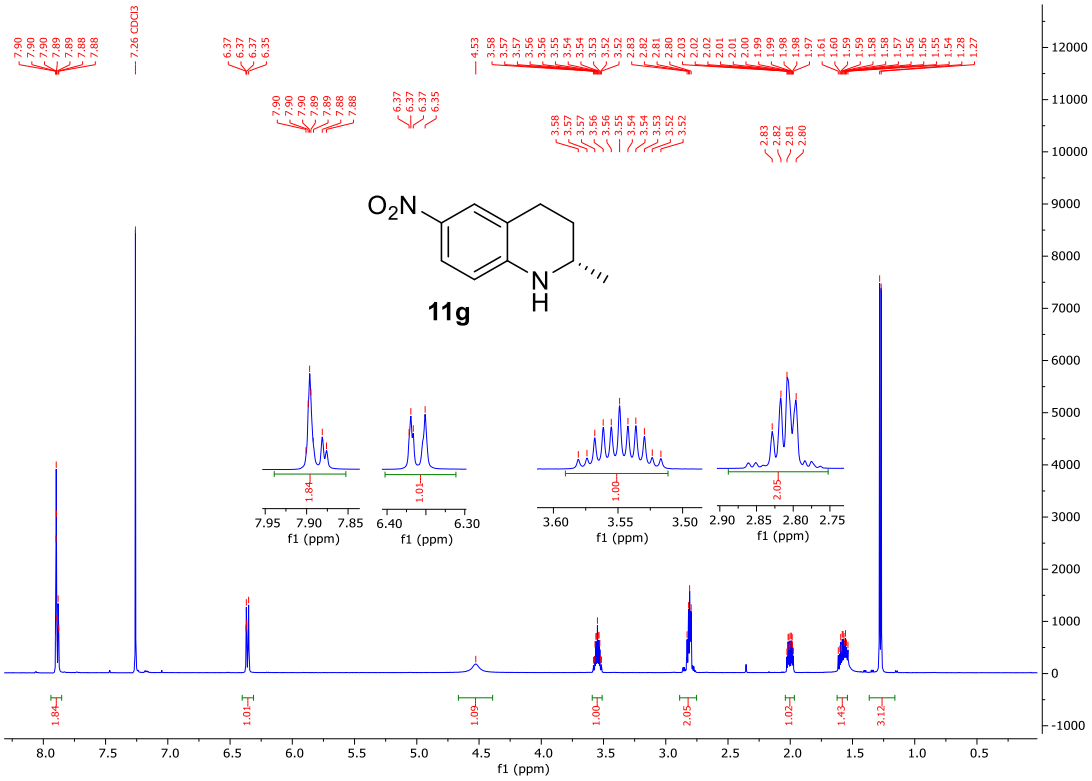
Chiral HPLC Chromatograms of **11f**

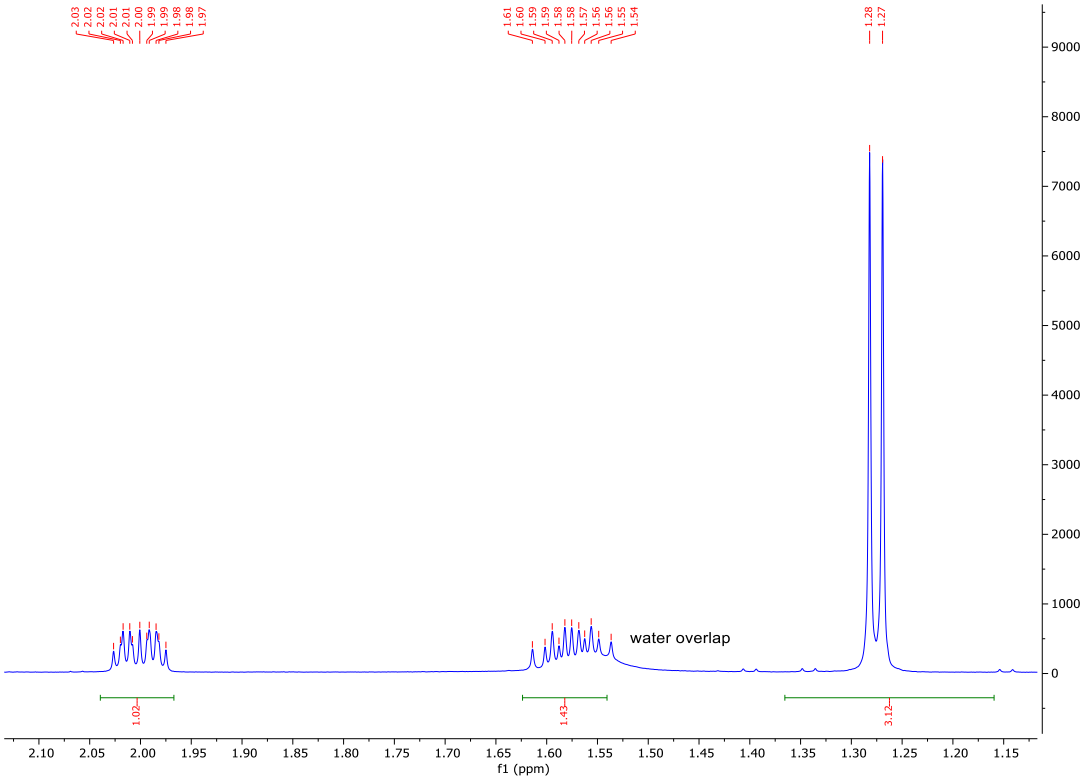


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.896	MM	0.1692	1.36597e4	1345.61450	17.1757
2	8.525	MM	0.3666	6.58694e4	2994.45923	82.8243

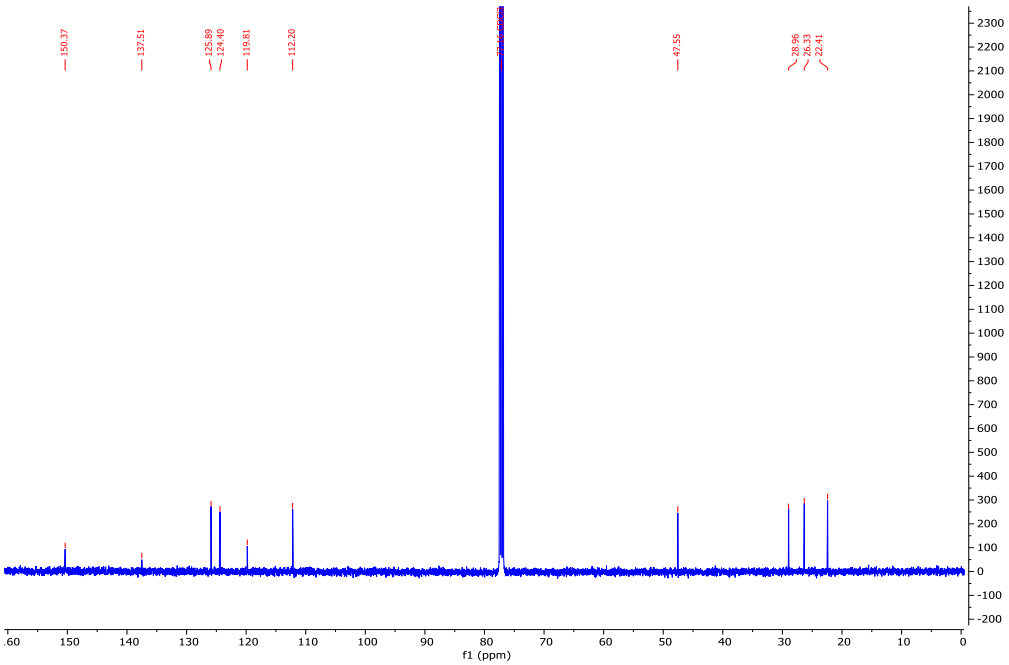
(*S*)-2-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (**11g**)

^{1}H NMR of **11g**

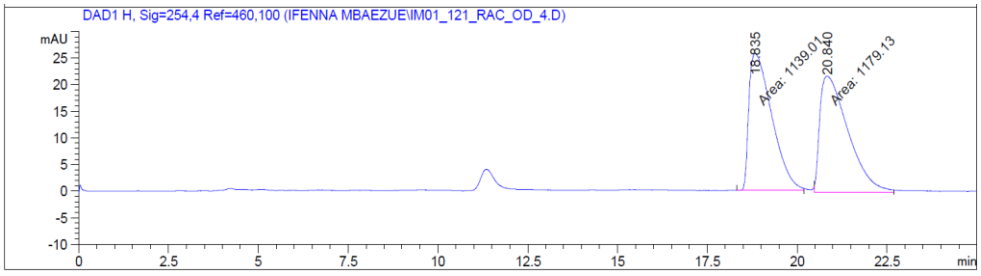


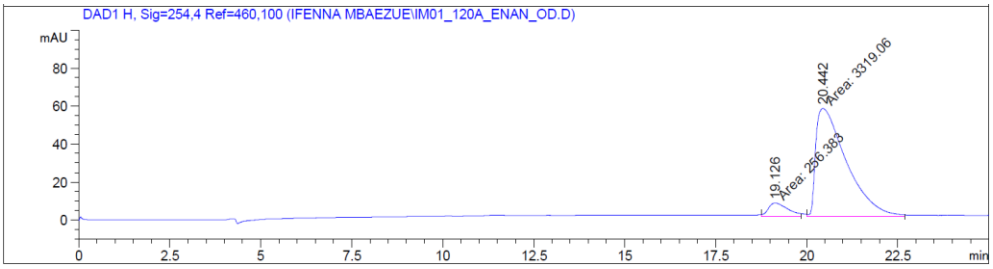


^{13}C NMR of **11g**



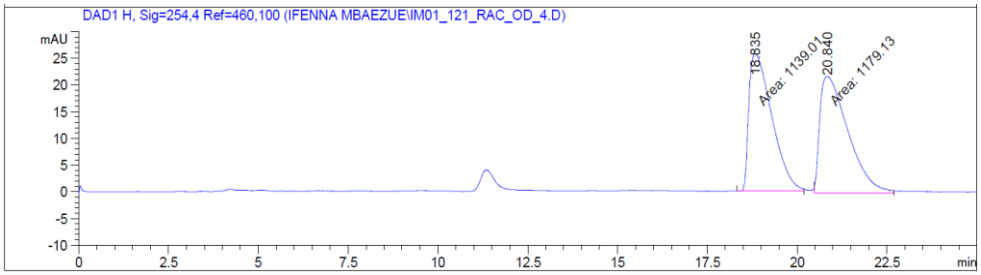
Chiral HPLC Chromatogram of **11g**

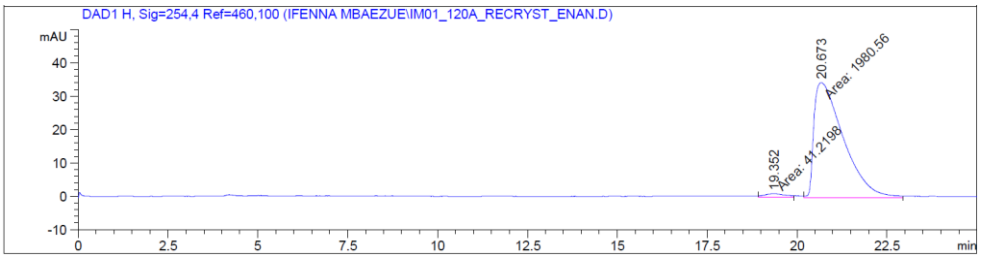




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.126	MM	0.6119	256.38251	6.98332	7.1706
2	20.442	MM	0.9745	3319.06494	56.76318	92.8294

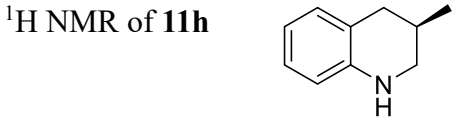
Chiral HPLC Chromatogram of crystallized product **11g**

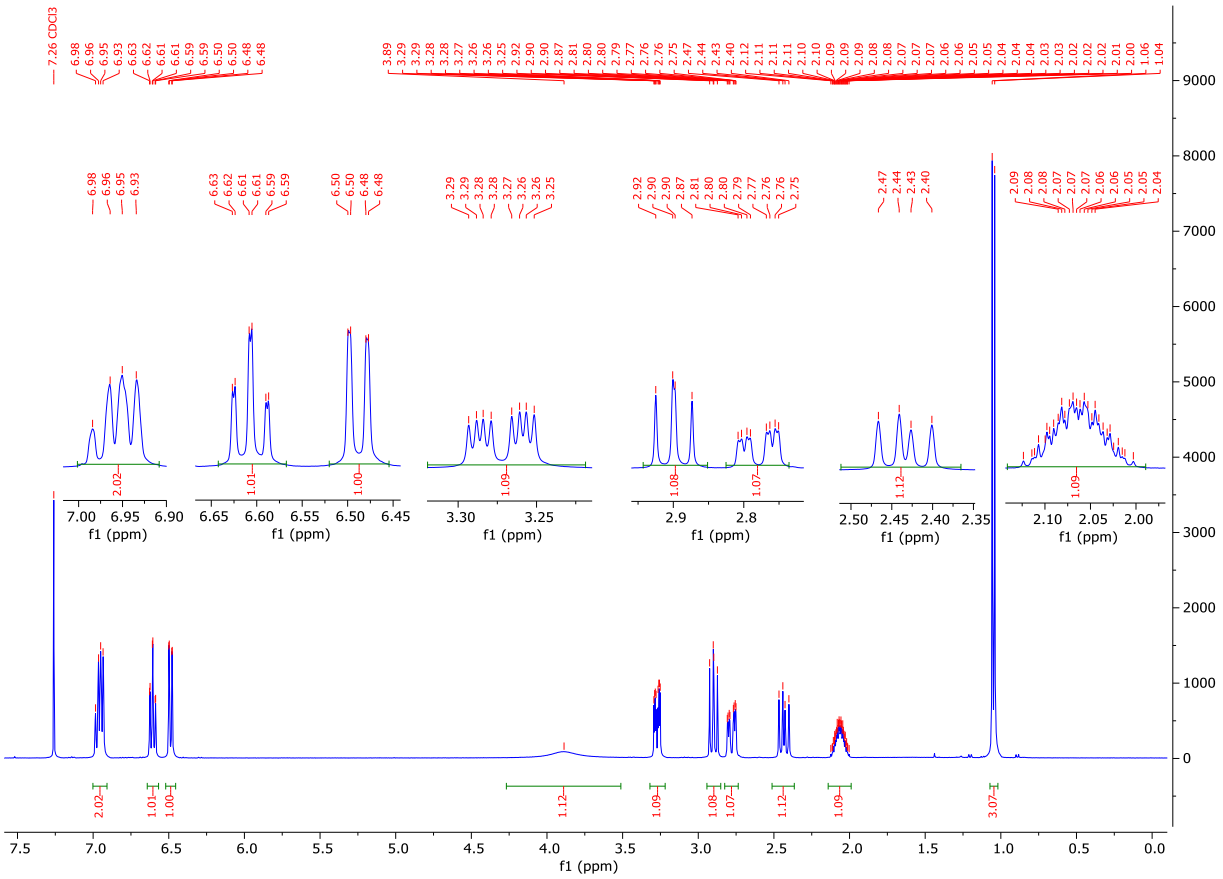




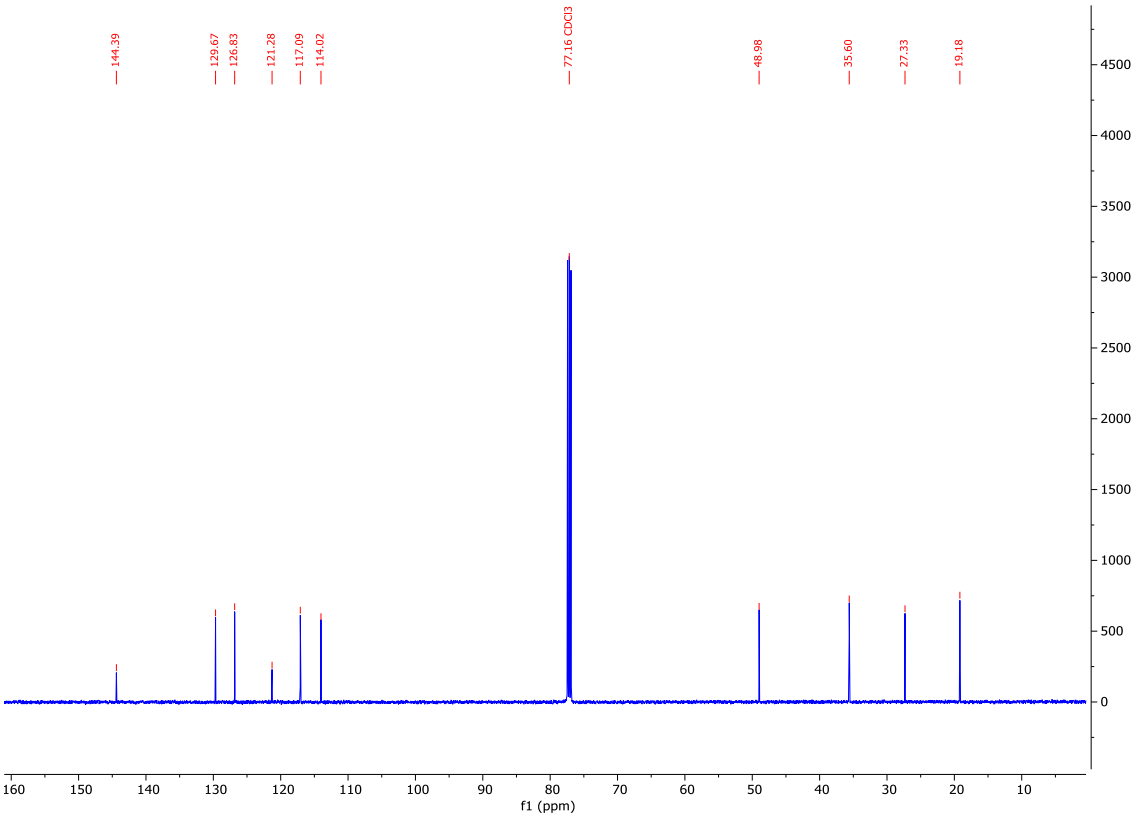
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.352	MM	0.6727	41.21978	1.02125	2.0388
2	20.673	MM	0.9551	1980.56396	34.56263	97.9612

^{1}H NMR of **11h**

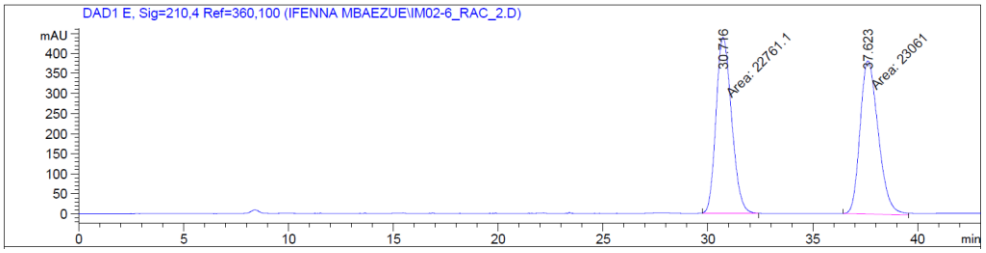




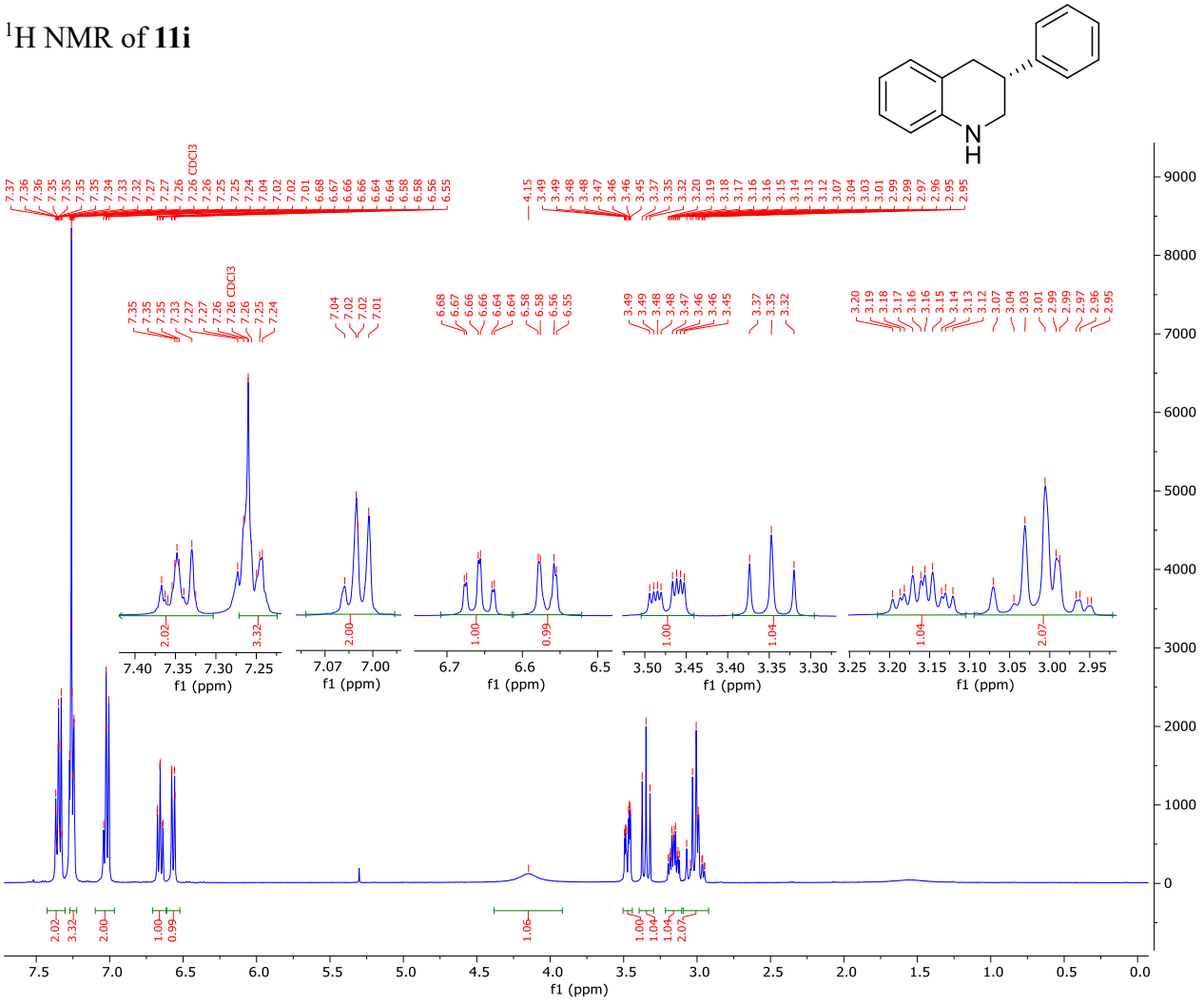
^{13}C NMR of **11h**



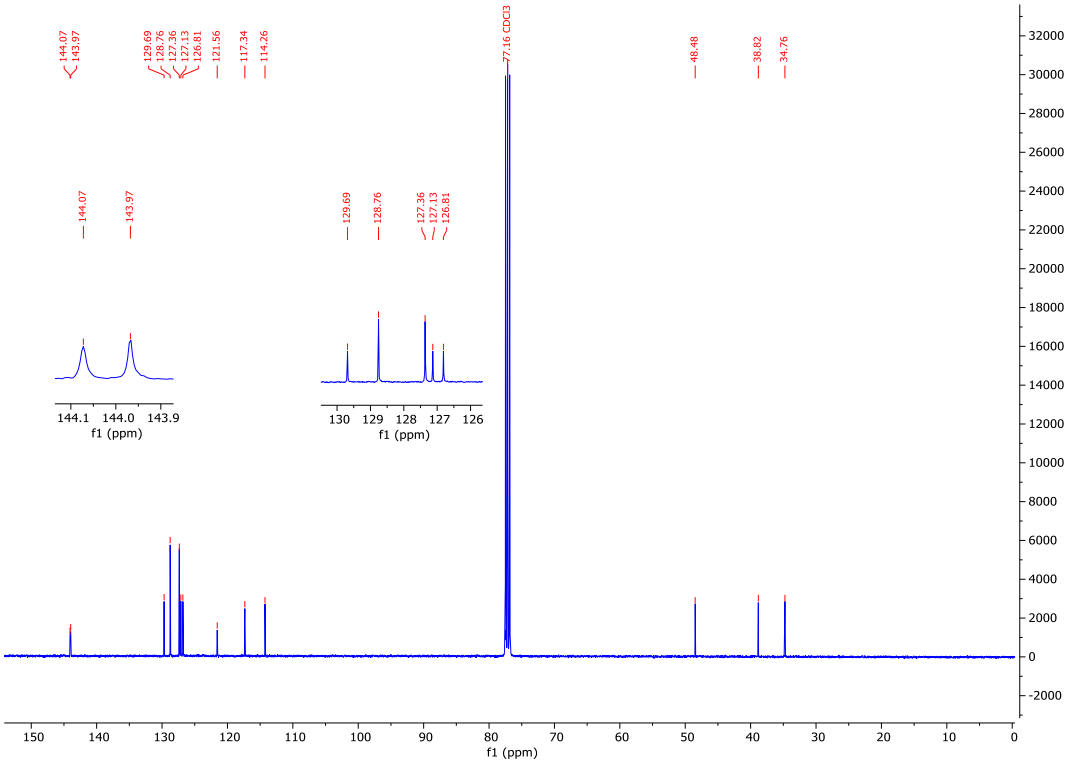
Chiral HPLC Chromatograms of **11h**



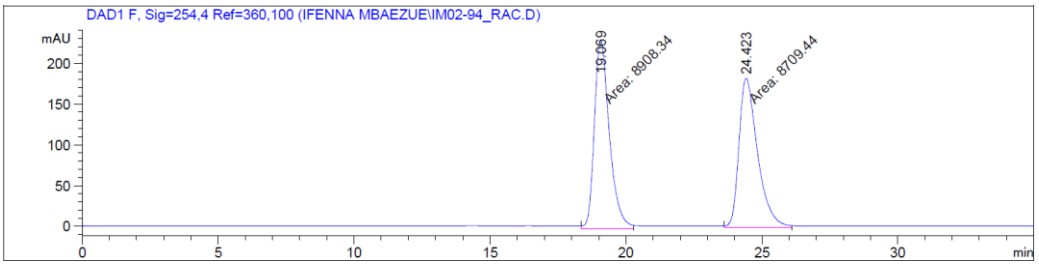
^{1}H NMR of **11i**

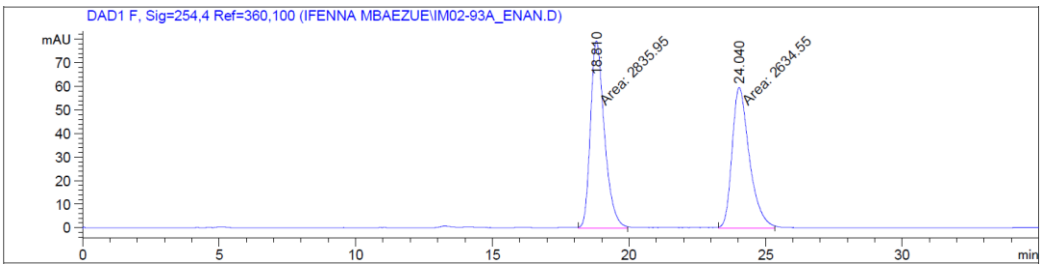


^{13}C NMR of **11i**



Chiral HPLC Chromatograms of **11i**

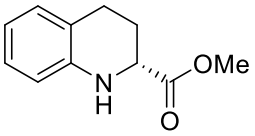


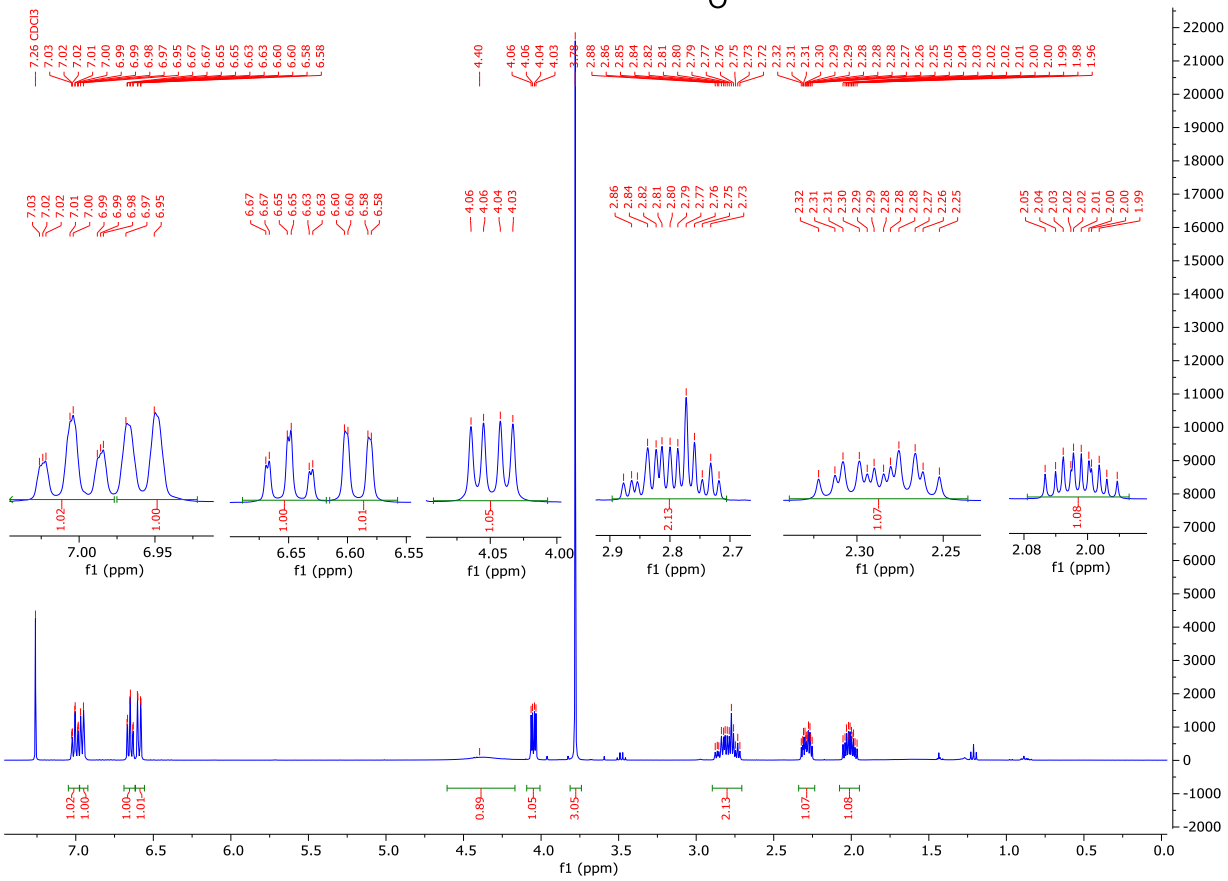


Signal 6: DAD1 F, Sig=254,4 Ref=360,100

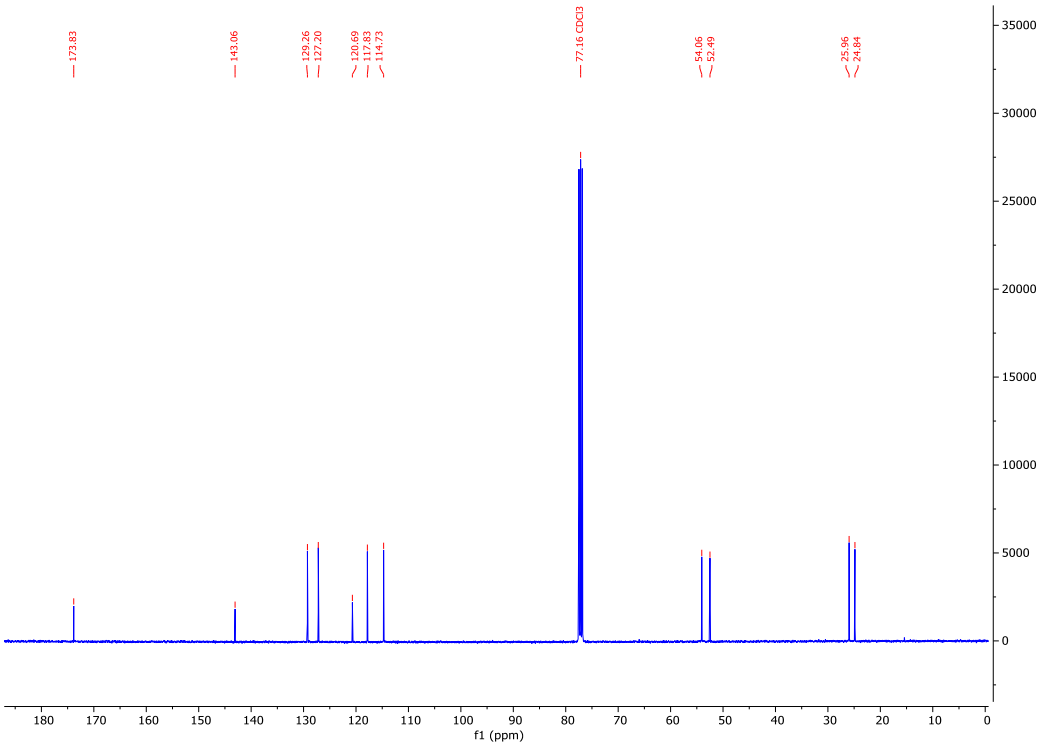
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.810	MM	0.5948	2835.94873	79.46480	51.8408
2	24.040	MM	0.7355	2634.54956	59.70087	48.1592
Totals :				5470.49829	139.16567	

^{1}H NMR of **11j**

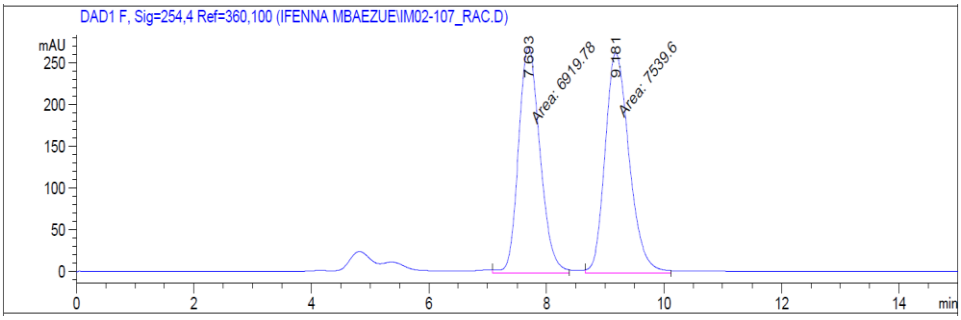


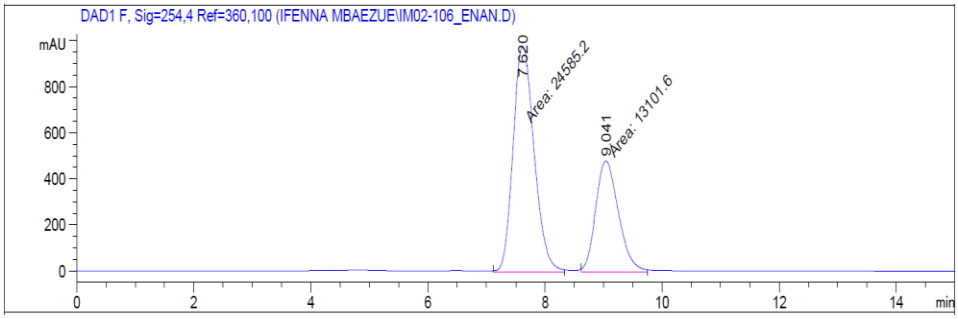


^{13}C NMR of **11j**



Chiral HPLC Chromatograms of **11j**





Signal 6: DAD1 F, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.620	MM	0.4169	2.45852e4	982.85883	65.2355
2	9.041	MM	0.4524	1.31016e4	482.72311	34.7645
Totals :				3.76868e4	1465.58194	

X-Ray Data Collection and Structural Refinement Statistics

The X-ray data were collected on a Bruker D8 Venture dual-source diffractometer equipped with a PHOTON II detector and an Oxford Cryostream 800 cooling system, using mirror-monochromatized Cu*K*α radiation (λ = 1.54184 Å) from a microfocus source, in a series of φ- and ω-scans. APEX3 software was used for data collection, integration and reduction.[17] Semi-empirical absorption correction was applied using SADABS-2016/2.[18]

The structures were solved using SHELXT-2014/5 (**5a_123K**, **11a_253K**) or SHELXT-2018/2 (**5c_253K**, **8d_253K**)[19] and refined by full-matrix least-squares using SHELXL-2018/3[20] within Olex2[21] and WinGX[22] packages. All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 (or 1.5 in case of methyl groups) times larger than the respective parent atoms. Nitrogen- and oxygen-bound hydrogen atoms were found in the difference electron density map and were modelled as constrained, with isotropic displacement parameters 1.2 (for nitrogen-bound) or 1.5 (for oxygen-bound) times larger than those of the respective parent atoms. In case of **11a_253K**, the amino group was instead allowed to refine as a rigid body to allow for the partial sp^3 character of the nitrogen, i.e. the out-of-plane position of the attached hydrogen atom. For disordered moieties, 1,2- and 1,3-interatomic distances were restrained to be equal and the anisotropic displacement parameters of the atoms were restrained to be equal for bonded and spatially close atoms. In case of **5c_253K**, the minor disorder component of the 2,4,6-triisopropylbenzenesulfonyl group was partially refined as a rigid body including the benzene ring with the attached secondary carbon atoms of isopropyl groups and the sulfonyl (–SO_2–) group. The occupancies of the disordered moieties were either allowed to refine freely (**5c_253K**) or were fixed to 0.5 as required by the proximity of a two-fold rotation axis (**8d_253K**).

CCDC 1935843–1935846 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table 3. Crystallographic data

Complex	**5a_123K**	**5c_253K**	**8d_253K**	**11a_253K**
CCDC Number	1935843	1935844	1935845	1935846
Empirical formula	$C_{25}H_{38}NO_4PS$	$C_{30}H_{44}NO_5PS$	$C_{31}H_{42}Cl_2N_2O_4P_2$	$C_{10}H_{12}BrN$
Formula weight	479.59	561.69	639.50	226.12
T/K	123.0(1)	253.0(1)	253.0(1)	253.0(1)
Crystal system	Monoclinic	Orthorhombic	Tetragonal	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P4_12_12$	$P2_12_12_1$
a/Å	10.6790(7)	10.5840(6)	10.7127(2)	16.0321(5)
b/Å	12.0178(8)	15.7917(8)	10.7127(2)	6.1532(2)
c/Å	11.2241(7)	18.4493(10)	27.9476(6)	9.7828(3)
α/°	90	90	90	90
β/°	112.3257(14)	90	90	90
γ/°	90	90	90	90
V/Å^3	1332.50(15)	3083.6(3)	3207.32(14)	965.06(5)
Z	2	4	4	4
ρ_{calc}/g cm^{-3}	1.195	1.210	1.324	1.556
μ/mm^{-1}	1.878	1.721	3.070	5.338
Max. and min. transmission	0.7543 and 0.5780	0.7536 and 0.6107	0.7536 and 0.6332	0.7543 and 0.5764
F(000)	516.0	1208.0	1352.0	456.0
Crystal color and shape	colorless, prism	yellow, lath	colorless, prism	colorless, block
Crystal size/mm^3	0.655×0.634×0.502	0.644×0.628×0.384	0.314×0.283×0.221	0.337×0.312×0.294
2θ range for data collection /°	8.952 to 161.056	7.368 to 145.612	8.84 to 144.914	10.594 to 161.068
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 14$, $-14 \le l \le 14$	$-13 \le h \le 13$, $-19 \le k \le 19$, $-22 \le l \le 22$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-34 \le l \le 32$	$-20 \le h \le 20$, $-7 \le k \le 7$, $-12 \le l \le 12$
Reflections collected	31499	60068	45989	25154
Reflections [R_{int}]	5643 [0.0313]	6006 [0.0411]	3167 [0.0835]	2073 [0.0457]
Data completeness (%)	99.5 to 2θ = 135.500°	97.6 to 2θ = 135.358°	99.2 to 2θ = 135.500°	97.6 to 2θ = 135.358°
Data/restraints/parameters	5643/1/300	6006/981/483	3167/20/208	2073/0/114
Goodness-of-fit on F^2	1.034	1.137	1.054	1.145
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0271, wR_2 = 0.0709	R_1 = 0.0437, wR_2 = 0.1133	R_1 = 0.0278, wR_2 = 0.0741	R_1 = 0.0656, wR_2 = 0.1579
Final R indices [all data]	R_1 = 0.0273, wR_2 = 0.0711	R_1 = 0.0440, wR_2 = 0.1137	R_1 = 0.0280, wR_2 = 0.0744	R_1 = 0.0662, wR_2 = 0.1581
Largest diff. peak/hole (e Å^{-3})	0.346/−0.258	0.477/−0.282	0.253/−0.190	0.475/−0.632
Flack parameter x	0.014(9)	0.029(4)	−0.007(5)	0.050(18)
Extinction coefficient	0.0090(10)	0.0130(15)	-	0.014(2)

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