Supporting Information

α-Amido sulphones as useful intermediates in the preparation of *C*-chiral α-aminophosphonates and α-aminophosphonic acids

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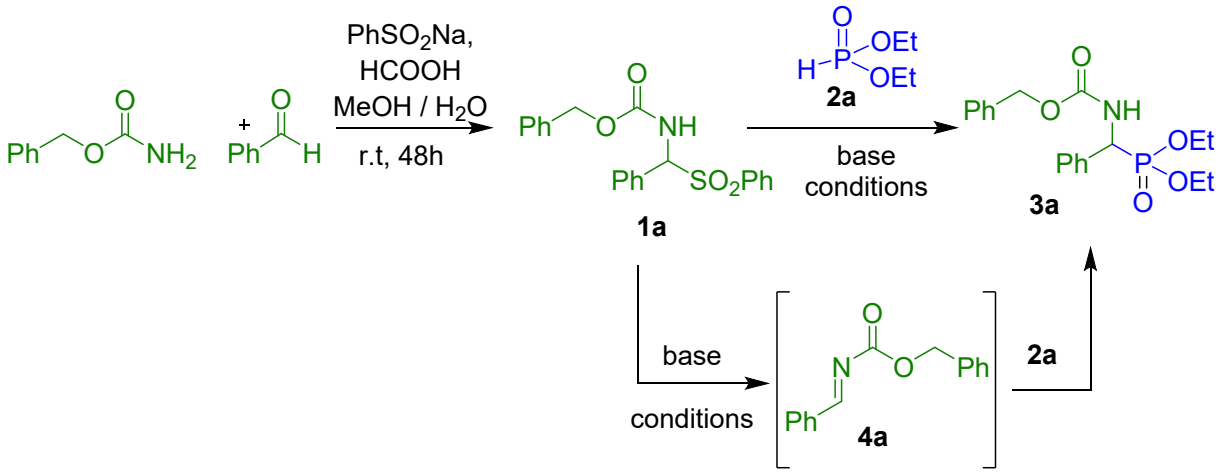
1. General information

All the substrates and solvents were of analytical grade purchased from Polish suppliers (Sigma Aldrich and POCh) and used without further purification. Unless otherwise specified solvents were removed using rotary evaporator. The ^{1}H, ^{13}C and ^{31}P NMR spectra were collected on a Jeol 400yh instrument (400 MHz for ^{1}H NMR, 162 MHz for ^{31}P NMR and 101 MHz for ^{13}C NMR) and were processed with dedicated software (Delta 5.0.5). Samples of the product were diluted with $CDCl_3$, DMSO-d_6 or D_2O with referenced to the respective residual ^{1}H or ^{13}C signals of the solvents. Coupling constant were reported in Hertz (Hz). Multiplicities are reported with the abbreviations: s (singlet), brs (broad singlet), d (doublet), t (triplet), m (multiplet) and the reported J values are those observed from the splitting patterns in the spectrum and may not reflect the true coupling constant values. Analytical thin layer chromatography was performed on SIL G/UV254 plates and visualization was accomplished by UV light (254 nm). Column chromatography (FC) was performed using Sigma-Aldrich® silica gel high purity-grade (SiO_2 70-230 mesh). The optical rotations were measured on a Bellingham+Stanley ADP440+ polarimeter and $[\alpha]_D^T$ values are given in deg cm^3 g^{-1} dm^{-1}; concentrations, c, are listed in 0.05g 5 mL^{-1}. Mass spectra were recorded using a water LCT Premier XE mass spectrometer (electrospray ionization, ESI) (Water, Milford, MA, USA) and melting point were determined on SRS melting point apparatus OptiMelt MPA 100 (Stanford Research System, Sunnyvale, CA USA) and are reported at Faculty of Chemistry Wroclaw University of Science and Technology

2. Optimization of the reaction

2.1 Optimization of the reaction for the non-asymmetric hydrophoshonylation of α-amido sulphones with non-chiral phosphonates

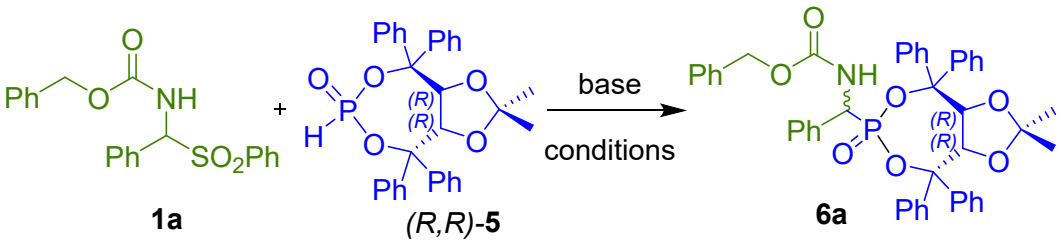


Entry	Conditions	Conversion (%)[b]
1.	no base, r.t, 24h, THF	**0**
2.	K_2CO_3 (4 equiv), r.t., 24h, THF	**30%[b]**
3.	**K_2CO_3 (4 equiv), 66°C, 4h, THF**	**99%[b][95%][c]**
4.	Pyridine (4 equiv), 66°C, 4h, THF	**0**

5.	Cs_2CO_3 (4 equiv), 66°C, 4h, THF	**74**
6.	Et_3N (4 equiv), 66°C, 4h, THF	**0**
7.	NaOH (4 equiv), 66°C, 4h, THF	**81**
8.	Diisopropylamine (4 equiv), 66°C, 4h, THF	**5**
9.	L-proline (4 equiv), 66°C, 4h, THF	**0**
10.	K_2CO_3 (4 equiv), 64°C, 4h, MeOH	**0**
11.	K_2CO_3 (4 equiv), 77°C, 4h, ethyl acetate	**42 (56)[d]**
12.	K_2CO_3 (4 equiv), 80°C, 4h, 2-methyl THF	**66 (89)[d]**
13.	K_2CO_3 (4 equiv), 82°C, 4h, acetonitrile	**50 (94)[d]**
14.	K_2CO_3 (4 equiv), 101°C, 4h, 1,4-dioxane	**54 (80)[d]**
15.	K_2CO_3 (2 equiv), 66°C, 4h, THF	**60**
16.	K_2CO_3 (6 equiv), 66°C, 4h, THF	**97**

[a]General reaction conditions (unless otherwise stated): α-amido sulphone **1a** (2.4 mmol), *H*-phosphonate **2a** (2.4 mmol), base (9.6 mmol). [c]Conversion based on the ^{31}P NMR spectra of the crude reaction mixture. [c]Isolated yield in square bracket. [d]Reaction time 8h.

2.2 Optimization of the reaction of the asymmetric hydrophoshonylation of α-amido sulphones with chiral TADDOL derived *H*- phosphonate *(R,R)*-5

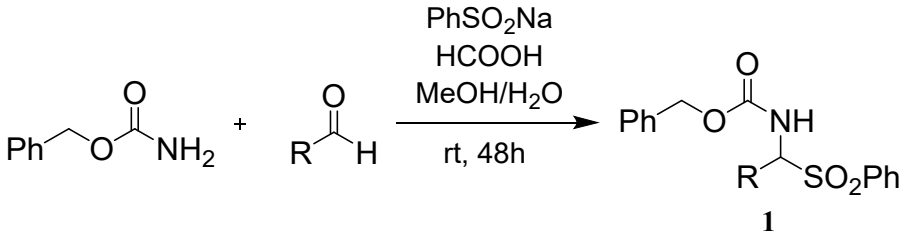


Entry	Conditions	Diastereomeric ratio *dr* (%)[b] /Conversion [%][b]
1.	K_2CO_3 (4 equiv), 66°C, 4h, THF	35:65 [80]
2.	Cs_2CO_3 (4 equiv), 66°C, 4h, THF	33:67 [97]
3.	NaOH (4 equiv), 66°C, 4h, THF	36:64 [87]
4.	KOH (4 equiv), 66°C, 4h, THF	34:66 [90]
5.	Pyridine (4 equiv), 66°C, 4h, THF	-
6.	Et_3N (4 equiv), 66°C, 4h, THF	-
7.	Cs_2CO_3 (4 equiv), 80°C, 4h, 2-methyl THF	36:64 [89]
8.	Cs_2CO_3 (4 equiv), 110°C, 4h, toluene	65:35 [97]
9.	Cs_2CO_3 (4 equiv), 82°C, 4h, acetonitrile	45:55 [84]
10.	KOH (2.5 equiv), Fe_2O_3, r.t., 5 days, CH_2Cl_2	60:40 [80][c]
11.	KOH (2.5 equiv), Al_2O_3, r.t., 5 days, CH_2Cl_2	25:75 [89][c]
12.	KOH (2.5 equiv), ZnO, r.t., 5 days, CH_2Cl_2	30:70 [76][c]
13.	KOH (2.5 equiv), MgO, r.t., 5 days, CH_2Cl_2	35:65 [74][c]
14.	K_2CO_3 (2.5 equiv), Al_2O_3, r.t., 5 days, CH_2Cl_2	22:78 [98][c]
15.	NaOH (2.5 equiv), Al_2O_3, r.t., 5 days, CH_2Cl_2	40:60 [98][c]
16.	n-BuLi (1 equiv), 12h, -78°C, THF	- [d]
17.	LDA (1 equiv), 12h, -78°C, THF	- [d]
18.	$ZnEt_2$ / (TMEDA) (1 equiv), 12h, -78°C, THF	100 [74][d]
19.	**KOH (3 equiv), -78°C, 5 days, THF**	**100 [95]**

[a]General reaction conditions (unless otherwise stated): α-amido sulphone **1a** (2.4 mmol), *H*-phosphonate *(R,R)*-**5** (2.4 mmol), base (9,6 mmol). [b]Diastereoselectivy and conversion based on the ^{31}P NMR spectra of the crude reaction mixture. – no reaction. [c]For 6.5 g of metal oxide for 6 mmol of base. [d]The imine was first generated by

reacting of **1a** with K_2CO_3 (2 equiv) at 66°C for 4h in THF and after filtration the filtrate containing the imine was transferred to a separate flask and cooled to -78°C followed by addition of a base and *(R,R)*-**5.**

3. General procedure for the preparation of the sulfones and spectra characterization



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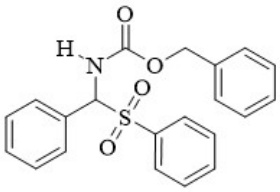
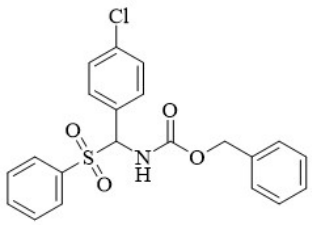
The synthesis of the sulphones was carried out according to the protocol reported by Tillman et al[1]. In a 100 mL flask, the corresponding aldehyde (9.4 mmol, 1.5 equ.) was added to a rapidly stirred suspension of benzyl carbamate (6.3 mmol, 1 equ.) and benzenesulfinic acid sodium salt (12.5 mmol, 2 equ.) in methanol (6mL) and water (12mL), followed by formic acid (0.94 mL). The reaction mixture was stirred for 48 h at room temperature. The resulting precipitate formed during the reaction was filtered and washed with water and diethyl ether, then dried in vacuo to yield the sulfone which was used without further purification. Spectral data for **1a**,[2] **1j**[2], **1b**[3] and **1d**[4] agree with those previously reported in the literature.

Benzyl (phenyl(phenylsulfonyl)methyl)carbamate (1a)



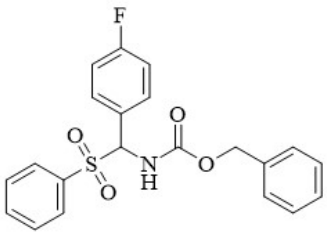
White solid; 1.98g, 55% yield; mp: 154-156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.30 (m, 10H), 7.22 (brs, 2H), 6.16 (d, *J* = 10.7 Hz, 1H), 5.97 (d, *J* = 10.8 Hz, 1H), 4.96 – 4.88 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 154.77, 136.50, 135.57, 134.59, 134.23, 130.04, 129.82, 129.52, 129.10, 128.89, 128.67, 128.35, 124.94, 74.60, 67.77. HRMS (ESI) calculated for $C_{21}H_{19}NO_4SNa$ $[M^+Na]^+$: 404.0933 found 404.0933

Benzyl ((4-chlorophenyl)(phenylsulfonyl)methyl)carbamate (1b)



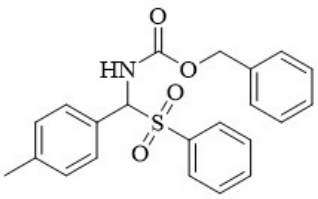
White solid; 1.48g, 38% yield; mp: 152-153 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 9.14 (d, *J* = 10.7 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.24 (m, 3H), 7.15 (d, *J* = 6.5 Hz, 2H), 6.14 (d, *J* = 10.7 Hz, 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 4.80 (d, *J* = 12.6 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6), δ: 155.67, 136.97, 136.78, 134.87 (d, *J* = 13.7 Hz), 132.02, 129.92 – 129.49 (m), 128.90, 128.75, 128.24, 125.01, 74.60, 66.64. HRMS (ESI) calculated for $C_{21}H_{18}ClNO_4SNa$ $[M^+Na]^+$: 438.0543 found 438.0544.

Benzyl ((4-fluorophenyl)(phenylsulfonyl)methyl)carbamate (1c)



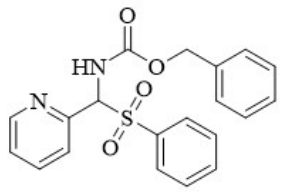
White solid; 1.64g, 44% yield; mp: ;162-164 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 9.12 (d, *J* = 10.7 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.74 – 7.63 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.13 (m, 7H), 6.12 (d, *J* = 10.7 Hz, 1H), 4.94 – 4.78 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 164.52, 162.07, 155.68, 137.02, 136.79, 134.74, 132.48 (d, *J* = 8.5 Hz), 129.63 (d, *J* = 6.7 Hz), 128.90, 128.49, 128.26, 128.07, 127.97, 127.13, 124.79, 115.67 (d, *J* = 21.7 Hz), 74.54, 66.62. HRMS (ESI) calculated for $C_{21}H_{18}FNO_4SNa$ $[M^+Na]^+$: 422.0838 found 422.0829.

Benzyl ((phenylsulfonyl)(p-tolyl)methyl)carbamate (1d)



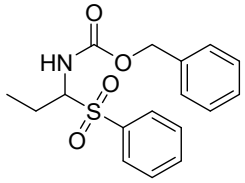
White solid; 2.20g, 59% yield, mp: 157-158 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 9.08 (d, *J* = 10.7 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.24 (m, 3H), 7.19 – 7.10 (m, 4H), 6.00 (d, *J* = 10.7 Hz, 1H), 4.87 – 4.77 (m, 2H), 2.28 (s, 3H).; **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 155.73, 139.49, 137.30, 136.85, 134.62, 130.27, 130.10, 129.62, 129.56, 129.25, 128.89, 128.46, 128.21, 127.68, 75.24, 66.54, 21.36. HRMS (ESI) calculated for $C_{22}H_{21}NO_4SNa$ $[M^+Na]^+$: 418.1089 found 418.1091.

Benzyl ((phenylsulfonyl)(pyridin-2-yl)methyl)carbamate (1e)



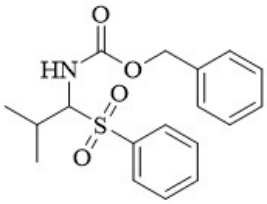
White solid; 1.51g, 42% yield; mp: 144-146 °C. **^{1}H NMR** (400 MHz, , $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.77 (t, *J* = 6.7 Hz, 4H), 7.66 – 7.55 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 3H), 7.38 – 7.29 (m, 5H), 7.25 (d, *J* = 5.7 Hz, 2H), 7.05 (d, *J* = 9.1 Hz, 1H), 6.08 (d, *J* = 9.2 Hz, 1H), 5.03 – 4.89 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 155.73, 150.35, 149.53, 137.50, 137.12, 136.84, 134.81, 129.68, 129.59, 128.90, 128.47, 128.20, 125.16, 125.02, 76.86, 66.74. HRMS (ESI) calculated for $C_{20}H_{18}N_2O_4SNa$ $[M^+Na]^+$: 405.0885 found 405.0892.

Benzyl (1-(phenylsulfonyl)propyl)carbamate (1f)



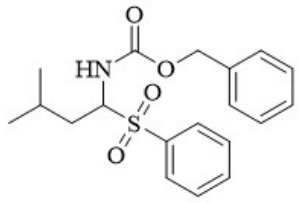
White solid; 2.15g, 68% yield; mp: 96-98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.24 (m, 3H), 7.21 – 7.13 (m, 2H), 5.28 (d, *J* = 10.8 Hz, 1H), 4.93 – 4.74 (m, 3H), 2.36 – 2.22 (m, 1H), 1.84 – 1.68 (m, 1H), 1.06 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.17, 136.73, 135.76, 134.09, 129.52 – 128.96 (m), 128.70 – 127.98 (m), 72.76, 67.39, 20.22, 10.01. HRMS (ESI) calculated for $C_{17}H_{19}NO_4SNa$ $[M^+Na]^+$: 356.0933 found 356.0931.

Benzyl (2-methyl-1-(phenylsulfonyl)propyl)carbamate (1g)



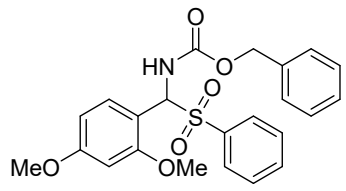
White solid; 1.99g, 61% yield; mp: 116-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.24 (m, 3H), 7.21 – 6.96 (m, 2H), 5.40 (d, *J* = 11.2 Hz, 1H), 4.92 – 4.73 (m, 3H), 2.81 – 2.71 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.25, 137.74, 135.69, 133.97, 132.01, 129.09, 128.94, 128.66, 128.48, 128.28, 127.96, 126.72, 125.02, 75.00, 67.50, 26.93, 20.77, 16.98. HRMS (ESI) calculated for $C_{18}H_{21}NO_4SNa$ $[M^+Na]^+$: 370.1089 found 370.1095.

Benzyl (3-methyl-1-(phenylsulfonyl)butyl)carbamate (1i)



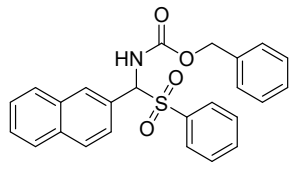
White solid; 1.94g; 57% yield; mp: 138-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.24 (m, 3H), 7.20 – 7.03 (m, 2H), 5.30 (d, *J* = 10.8 Hz, 1H), 4.99 – 4.75 (m, 3H), 2.04 – 1.96 (m, 1H), 1.81 – 1.69 (m, 2H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.83, 136.59, 135.71, 134.06, 129.46, 129.32, 129.16, 129.05, 128.62, 128.43, 128.23, 128.03, 125.07, 70.24, 67.40, 34.70, 24.76, 23.34, 21.19. HRMS (ESI) calculated for $C_{19}H_{23}ClNO_4SNa$ $[M^+Na]^+$: 384.1245 found 384.1237.

Benzyl ((2,4-dimethoxyphenyl)(phenylsulfonyl)methyl)carbamate (1i)



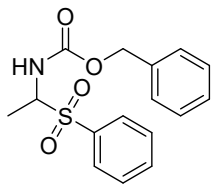
White solid; 2.40g, 58% yield; mp:130-132 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 9.09 (d, *J* = 10.5 Hz, 1H), 7.823– 7.71 (m, 3H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.29-7.18 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.01 (d, *J* = 10.5 Hz, 1H), 4.99 – 4.77 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6), δ: **^{13}C NMR** (101 MHz, DMSO-d_6) δ:157.13, 155.72, 154.71, 150.12, 148.77, 137.89, 134.53, 131.91, 129.51, 128.86, 128.23,126.69, 126.01, 125.01, 122.73, 111.79, 109.89, 75.52, 66.60, 65.39, 56.41, 56.03.

Benzyl (naphthalen-2-yl(phenylsulfonyl)methyl)carbamate (1j)



White solid; 2.52g; 62% yield; mp:152-154 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 9.26 (d, *J* = 10.7 Hz, 1H), 8.16 (s, 1H), 7.95 – 7.79 (m, 5H), 7.77 – 7.63 (m, 2H), 7.60 – 7.50 (m, 2H), 7.29 (dd, *J* = 8.7, 6.4 Hz, 3H), 7.16 (d, *J* = 6.6 Hz, 2H), 6.24 (d, *J* = 10.7 Hz, 1H), 4.95 – 4.77 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6), δ:157.14, 155.78, 137.91, 137.19, 136.3, 135.11, 134.36, 133.59, 132.77, 130.11, 129.81, 129.52, 128.84, 128.53, 128.22, 127.79, 127.57, 127.16, 125.02, 122.83, 75.59, 66.62, 65.39.

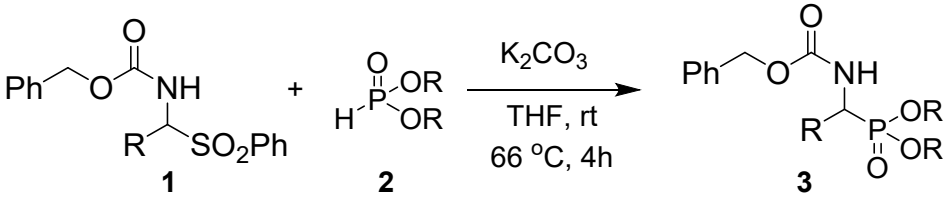
Benzyl (1-(phenylsulfonyl)ethyl)carbamate (1k)



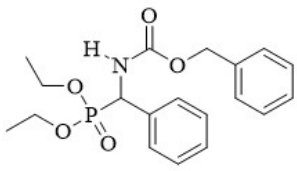
White solid; 1.35g, 45% yield; mp: 102-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.24 (m, 3H), 7.22 – 7.06 (m, 2H), 5.36 (d, *J* = 10.5 Hz, 1H), 5.11 – 4.95 (m, 1H), 4.85 (s, 2H), 1.61 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 154.63, 136.32, 135.74, 134.16, 129.39, 129.12, 128.63, 128.44, 128.25, 67.44 (d, *J* = 15.9 Hz), 13.15. HRMS (ESI) calculated for $C_{16}H_{17}NO_4SNa$ $[M^+Na]^+$: 342.0776 found 342.0785

4. General procedure for the preparation of phosphonates with spectra characterizations

In a 50 mL flask, dialkyl phosphite (2.4mmol, 1 equiv.) was added to a solution of sulfone (2.4mmol, 1 equiv.) and K_2CO_3 (9.6 mmol, 4 equiv.) in THF (15 mL). the mixture was heated 66 °C for 4 h and then cooled and filtered. The solvent and volatile components are removed under reduced pressure using a rotatory evaporator. The crude product was crystallized from diethyl ether in the case of solids. Oily products are purified by column chromatography (eluent: Hexane/ethyl acetate = 5:1 to 3:1) to obtain the pure product **3**. Spectral data for **3a**, **3e**, **3i**, **3j**[5], **3b**[6], **3d**[7] **3p**[8], and **3**r[5] agreed with those previously reported in the literature.

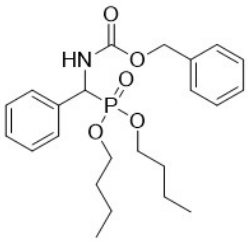


Benzyl ((diethoxyphosphoryl)(phenyl)methyl)carbamate (3a)



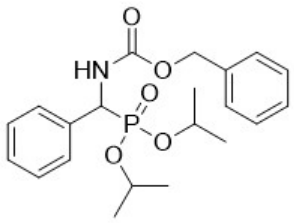
White solid; 860mg, 95% yield; mp: 112-114 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 8.43 (d, *J* = 10.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.22 (m, 8H), 5.11 – 4.96 (m, 3H), 4.02 – 3.71 (m, 4H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H**); ^{13}C NMR** (101 MHz, DMSO-d_6) δ: 156.48 (d, *J* = 8.6 Hz), 137.38 , 136.24 , 128.86, 128.74, 128.69, 128.64, 128.40, 128.31, 128.13 126.01, 66.38, 62.99 (d, *J* = 7.1 Hz), 62.77 (d, *J* = 6.8 Hz), 52.72 (d, *J* = 153.6 Hz), 16.72 (d, *J* = 5.4 Hz), 16.58 (d, *J* = 5.6 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6) δ: 21.97. HRMS (ESI) calculated for $C_{19}H_{24}NO_5PNa$ $[M^+Na]^+$: 400.1290 found 400.1289

Benzyl ((dibutoxyphosphoryl)(phenyl)methyl)carbamate (3b)



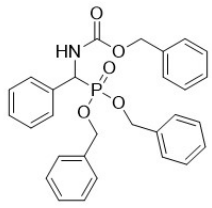
White solid; 905mg, 87% yield; mp: 104-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.23 (m, 8H), 5.89 (s, 1H, NH), 5.20 – 5.00 (m, 3H), 4.07 – 3.93 (m, 2H), 3.90 – 3.80 (m, 1H), 3.67 – 3.57 (m, 1H), 1.63 – 1.51 (m, 2H), 1.44 – 1.27 (m, 4H), 1.24 – 1.13 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.74 (d, *J* = 12.1 Hz), 136.19, 135.41, 128.70 (d, *J* = 2.0 Hz), 128.59, 128.33 – 128.14 (m), 127.97 (d, *J* = 5.8 Hz), 67.35, 67.05 (d, *J* = 7.1 Hz), 66.85 (d, *J* = 7.3 Hz), 52.51 (d, *J* = 153.3 Hz), 32.56 (d, *J* = 5.8 Hz), 32.35 (d, *J* = 5.9 Hz), 18.62 (d, *J* = 13.1 Hz), 13.61 (d, *J* = 7.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 21.94. HRMS (ESI) calculated for $C_{23}H_{32}NO_5PNa$ $[M^+Na]^+$: 456.1916 found 456.1819.

Benzyl ((diisopropoxyphosphoryl)(phenyl)methyl)carbamate (3c)



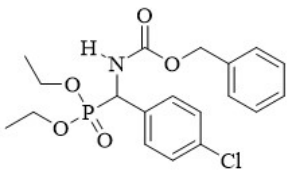
White solid; 919mg, 94% yield; mp: 102-103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.24 (m, 8H), 5.85 (s, 1H NH), 5.17 – 4.99 (m, 3H), 4.70 – 4.59 (m, 1H), 4.47 – 4.37 (m, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.89 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.80 (d, *J* = 9.5 Hz), 128.27 (d, *J* = 3.8 Hz), 128.18 – 128.05 (m), 72.31 (d, *J* = 7.2 Hz), 71.87 (d, *J* = 7.4 Hz), 67.31, 53.12 (d, *J* = 154.1 Hz), 24.28 (d, *J* = 3.1 Hz), 24.19 (d, *J* = 3.5 Hz), 23.79 (d, *J* = 5.2 Hz), 23.21 (d, *J* = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 20.18. HRMS (ESI) calculated for $C_{21}H_{28}NO_5PNa$ $[M^+Na]^+$: 428.1603 found 428.1613.

Benzyl ((bis(benzyloxy)phosphoryl)(phenyl)methyl)carbamate (3d)



White solid; 1101mg, 91% yield; mp: 124-125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.49 -7.20 (m, 18H), 7.09 (dd, *J* = 6.3, 2.8 Hz, 2H), 6.02 (s, 1H, NH), 5.27 (dd, *J* = 21.8, 9.6 Hz, 1H), 5.12 – 4.92 (m, 4H), 4.83 (dd, *J* = 11.7, 7.2 Hz, 1H), 4.60 (dd, *J* = 11.6, 8.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.73 (d, *J* = 11.3 Hz), 136.14, 135.78, 135.03, 128.81 (d, *J* = 2.1 Hz), 128.68 – 128.00 (m), 127.95, 68.67 (d, *J* = 6.7 Hz), 68.52 (d, *J* = 7.1 Hz), 67.40, 52.77 (d, *J* = 154.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 22.89. HRMS (ESI) calculated for $C_{29}H_{28}NO_5PNa$ $[M^+Na]^+$: 524.1603 found 524.1605

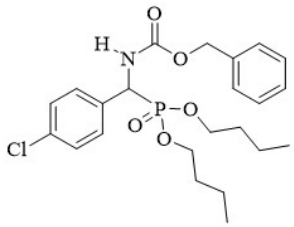
Benzyl ((4-chlorophenyl)(diethoxyphosphoryl)methyl)carbamate (3e)



White solid; 938mg, 95% yield; mp: 116-117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.24 (m, 9H), 5.98 (s, 1H, NH), 5.17 – 4.99 (m, 3H), 4.13 – 3.98 (m, 2H), 3.98 – 3.88 (m, 1H), 3.82 – 3.70 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.82 (d, *J* = 12.9 Hz), 136.09, 134.19 (d, *J* = 3.3 Hz), 134.01, 129.25 (d, J = 2.0 Hz), 128.56, 128.24, 128.02 (d, J = 6.0), 129.57 – 127.99 (m), 67.46 (s), 63.54 (d, *J* = 6.9 Hz), 63.35 (d, *J* = 7.2 Hz), 52.02

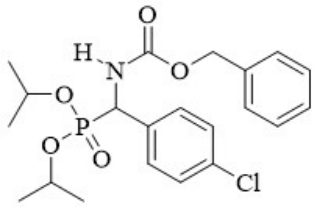
(d, J = 156.0 Hz), 16.44 (d, J = 5.7 Hz), 16.27 (d, J = 5.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 21.38 (s); HRMS (ESI) calculated for $C_{19}H_{23}ClNO_5PNa$ $[M^+Na]^+$: 434.0900 found 434.0899.

Benzyl ((4-chlorophenyl)(dibutoxyphosphoryl)methyl)carbamate (3f)



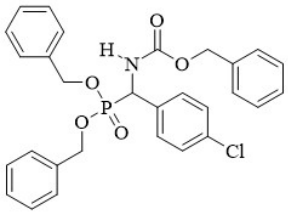
White solid; 921mg; 82% yield; mp: 95-96 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.23 (m 9H), 5.89 (brs, 1H), 5.16 – 5.01 (m, 3H), 4.06 – 3.94 (m, 2H), 3.92 – 3.83 (m, 1H), 3.73 – 3.64 (m, 1H), 1.61 – 1.52 (m, 2H), 1.47 – 1.39 (m, 2H), 1.37 – 1.27 (m, 2H), 1.26 – 1.16 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.74 (d, J = 12.4 Hz), 136.06, 134.20 , 129.32, 128.87, 128.62, 128.37, 128.22, 67.48, 67. 13 (d, J = 7.1 Hz), 67.03 (d, J = 7.5 Hz), 51.98 (d, J = 156.2 Hz), 32.54 (d, J = 5.8 Hz), 32.37 (d, J = 5.8 Hz), 18.68, 18.58, 13.63, 13.56; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 21.35. HRMS (ESI) calculated for $C_{23}H_{31}ClNO_5PNa$ $[M^+Na]^+$: 490.1526 found 490.1534.

Benzyl ((4-chlorophenyl)(diisopropoxyphosphoryl)methyl)carbamate (3g)



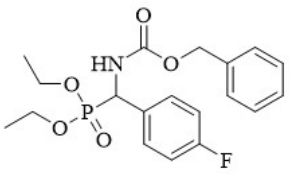
white solid; 938mg; 95% yield; mp:132-134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.45 – 7.14 (m, 9H), 5.91 (brs, 1H), 5.16 – 4.97 (m, 3H, CHP and CH2Ph), 4.69 – 4.59 (m, 1H), 4.52 – 4.42 (m, 1H), 1.28 (d, J = 6.2 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H), 1.18 (d, J = 6.2 Hz, 3H), 0.96 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.83 (d, J = 9.6 Hz), 136.15, 134.46, 134.02, 129.47, 128.71, 128.60, 128.35, 128.27, 72.39 (d, J = 7.2 Hz), 72.12 (d, J = 7.4 Hz), 67.42, 52.58 (d, J = 157.0 Hz), 24.21 (d, J = 3.3 Hz), 24.16 (d, J = 3.5 Hz), 23.78 (d, J = 5.2 Hz), 23.36 (d, J = 5.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 19.47; HRMS (ESI) calculated for $C_{21}H_{27}ClNO_5PNa$ $[M^+Na]^+$: 462.1213 found 462.1208.

Benzyl ((bis(benzyloxy)phosphoryl)(4-chlorophenyl)methyl)carbamate (3h)



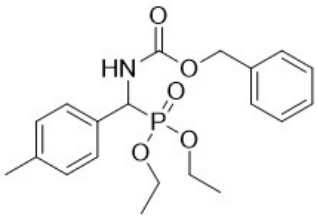
White solid; 1.221mg; 95% yield; mp: 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.20 (m, 17H), 7.10 (dd, J = 7.3, 1.9 Hz, 2H), 5.94 (brs, 1H), 5.18 (dd, J = 22.2, 9.4 Hz, 1H), 5.09 – 4.91 (m, 4H), 4.83 (dd, J = 11.7, 7.7 Hz, 1H), 4.70 (dd, J = 11.6, 9.1 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO), δ: 156.48 (d, J = 8.5 Hz), 137.21, 136.78 (d, J = 14.4 Hz), 135.08, 133.10, 130.65, 129.13 – 127.82 (m, aromatic carbon atoms), 68.17 (d, J = 6.9 Hz), 67.91 (d, J = 6.6 Hz), 66.56, 52.23 (d, J = 154.0 Hz,); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 22.38. HRMS (ESI) calculated for $C_{29}H_{27}ClNO_5PNa$ $[M^+Na]^+$: 558.1213 found 538.1221

Benzyl ((diethoxyphosphoryl)(4-fluorophenyl)methyl)carbamate (3i)



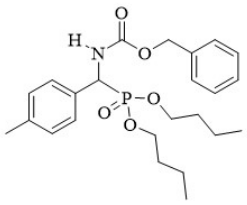
White solid; 808mg; 82% yield; mp: 124-126 ^{0}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.40 (brs, 2H), 7.31 (brs, 5H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.05 (brs, 1H), 5.17 – 5.01 (m, 3H), 4.14 – 3.99 (m, 2H), 3.98 – 3.87 (m, 1H), 3.79 – 3.68 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.82 (d, *J* = 11.1 Hz), 136.13, 131.30, 129.77, 128.59, 128.33, 128.22, 115.74 (d, *J* = 2.0 Hz), 115.53 (d, *J* = 2.0 Hz), 67.42, 63.48 (d, *J* = 6.9 Hz), 63.26 (d, *J* = 7.1 Hz), 51.90 (d, *J* = 155.6 Hz), 16.43 (d, *J* = 5.7 Hz), 16.25 (d, *J* = 5.7 Hz).; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 21.66. HRMS (ESI) calculated for $C_{19}H_{23}FNO_5PNa$ $[M^+Na]^+$: 418.1196 found 418.1190

Benzyl ((diethoxyphosphoryl)(p-tolyl)methyl)carbamate (3j)



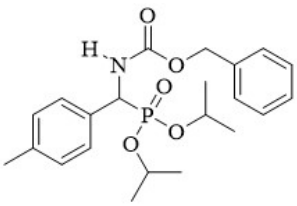
White solid; 771mg, 83% yield; mp: 115-117 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36 – 7.24 (m, 7H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.74 (brs, 1H), 5.16 – 5.00 (m, 3H), 4.13 – 4.00 (m, 2H), 3.97 – 3.87 (m, 1H), 3.78 – 3.65 (m, 1H), 2.32 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.75 (d, *J* = 11.0 Hz), 138.08, 136.22, 132.20, 129.43, 128.58, 128.28, 127.89, 67.33, 63.45 (d, *J* = 6.9 Hz), 63.16 (d, *J* = 7.1 Hz), 52.25 (d, *J* = 154.7 Hz), 21.25 (s), 16.45 (d, *J* = 5.8 Hz), 16.26 (d, *J* = 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 22.14. HRMS (ESI) calculated for $C_{20}H_{26}NO_5PNa$ $[M^+Na]^+$: 414.1446 found 414.1448

Benzyl ((dibutoxyphosphoryl)(p-tolyl)methyl)carbamate (3k)



White solid; 835mg; 74% yield; mp: 108-110 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 – 7.22 (m, 7H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.77 (brs, 1H), 5.20 – 4.96 (m, 3H), 4.06 – 3.95 (m, 2H), 3.86 (1H), 3.69 – 3.58 (m, 1H), 2.32 (s, 3H), 1.64 – 1.53 (m, 2H), 1.46 – 1.28 (m, 4H), 1.26 – 1.14 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 155.70 (d, *J* = 10.7 Hz), 138.03, 136.23, 132.33, 129.97 – 127.77 (m), 67.31, 67.04 (d, *J* = 7.1 Hz), 66.81 (d, *J* = 7.4 Hz), 52.20 (d, *J* = 154.7 Hz), 32.57 (d, *J* = 5.8 Hz), 32.37 (d, *J* = 5.8 Hz), 21.22, 18.64 (d, *J* = 11.8 Hz), 13.62 (d, *J* = 7.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$), δ: 22.13. HRMS (ESI) calculated for $C_{24}H_{34}NO_5PNa$ $[M^+Na]^+$: 470.2072 found 470.2079

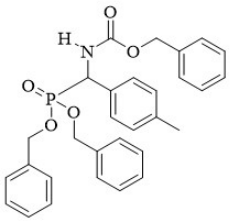
Benzyl ((diisopropoxyphosphoryl)(p-tolyl)methyl)carbamate (3l)



White solid; 812mg; 77% yield; mp: 126-128 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 – 7.22 (m, 7H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.77 (brs, 1H), 5.20 – 4.95 (m, 3H), 4.71 – 4.59 (m, 1H), 4.51 – 4.36 (m, 1H), 2.31 (s, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 0.92 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 155.78 (d, *J* = 11.0 Hz), 137.85, 136.30, 132.68, 130.19 – 127.62 (m), 72.21 (d, *J* = 7.2 Hz), 71.80 (d, *J* = 7.5 Hz), 67.24, 52.82

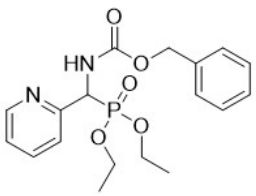
(d, *J* = 156.8 Hz), 24.29 (d, *J* = 3.1 Hz), 24.19 (d, *J* = 3.4 Hz), 23.80 (d, *J* = 5.3 Hz), 23.27 (d, *J* = 5.7 Hz), 21.23; **^{31}P NMR** (162 MHz, $CDCl_3$), δ: 20.35. HRMS (ESI) calculated for $C_{22}H_{30}NO_5PNa$ $[M^+Na]^+$: 442.1759 found 442.1758

Benzyl ((bis(benzyloxy)phosphoryl)(p-tolyl)methyl)carbamate (3m)



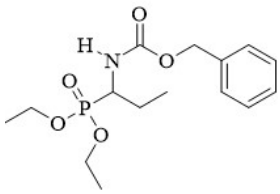
white solid; 1115mg; 91% yield; mp: 128-138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.22 (m, 15H), 7.15 – 7.07 (m, 4H), 5.84 (brs, 1H), 5.21 (dd, *J* = 21.5, 9.6 Hz, 1H), 5.11 – 4.92 (m, 4H), 4.83 (dd, *J* = 11.7, 7.3 Hz, 1H), 4.62 (dd, *J* = 11.7, 8.5 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.75 (d, *J* = 10.8 Hz), 138.15, 136.33 – 135.70 (m), 132.00, 129.52, 128.84 – 127.69 (m, aromatic carbon atom), 68.64 (d, *J* = 6.9 Hz), 68.47 (d, *J* = 7.2 Hz), 52.50 (d, *J* = 155.7 Hz), 21.27; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 23.08. HRMS (ESI) calculated for $C_{30}H_{30}NO_5PNa$ $[M^+Na]^+$: 538.1759 found 538.1765

Benzyl ((diethoxyphosphoryl)(pyridin-2-yl)methyl)carbamate (3n)



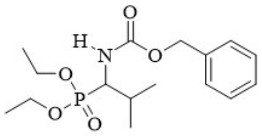
white solid; 790mg, 87% yield, mp: 110-112 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.48 (d, *J* = 4.7 Hz, 1H), 8.21 (d, *J* = 9.8 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.24 (m, 5H), 5.25 (dd, *J* = 21.7, 10.0 Hz, 1H), 5.10-4.98 (m, 2H), 4.02 – 3.79 (m, 4H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.86, 167.53, 156.42 (d, *J* = 8.0 Hz), 155.71, 149.18, 137.33, 132.26, 128.85, 128.39, 128.28, 123.47 (d, *J* = 2.4 Hz), 123.33 (d, *J* = 3.9 Hz), 66.48, 63.07 (d, *J* = 6.8 Hz), 62.91 (d, *J* = 6.7 Hz), 54.91 (d, *J* = 148.0 Hz), 16.69 (d, *J* = 5.5 Hz), 16.56 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ: 20.97. HRMS (ESI) calculated for $C_{19}H_{24}NO_5PNa$ $[M^+Na]^+$: 401.1294 found 401.1291

Benzyl (1-(diethoxyphosphoryl)propyl)carbamate (3o).



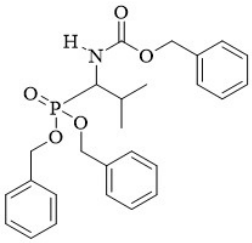
Colourless oil; 585mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.06 (m, 5H), 5.17 – 5.02 (m, 3H), 4.14 – 3.91 (m, 4H), 1.94 – 1.84 (m, 1H), 1.63 – 1.51 (m, 1H), 1.25 (dt, *J* = 17.9, 7.1 Hz, 6H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.29 (d, *J* = 6.2 Hz), 136.41 (s), 128.64 – 128.10 (m), 67.16 (s), 62.67 (d, *J* = 7.1 Hz), 62.49 (d, *J* = 6.7 Hz), 49.11 (d, *J* = 155.8 Hz), 23.35 (s), 16.41 (s), 10.49 (s); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.41 (s). HRMS (ESI) calculated for $C_{15}H_{24}NO_5PNa$ $[M^+Na]^+$: 352.1290 found 352.1286

Benzyl (1-(diethoxyphosphoryl)-2-methylpropyl)carbamate (3p)



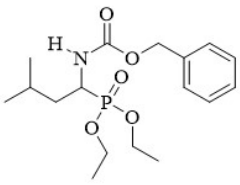
Yellowish oil; 588mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 5.19 – 5.04 (m, 3H), 4.13 – 3.94 (m, 4H), 2.23 – 2.13 (m, 1H), 1.32 – 1.19 (m, 6H), 1.02 – 0.95 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.46 (d, *J* = 6.5 Hz), 136.39 (s), 129.44 – 127.29 (m), 67.23 (s), 62.42 (m), 52.68 (d, *J* = 152.9 Hz), 29.03 (d, *J* = 4.5 Hz), 20.51 (d, *J* = 12.7 Hz), 17.78 (d, *J* = 4.2 Hz), 16.42 (d, *J* = 6.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.83 (s). HRMS (ESI) calculated for $C_{16}H_{26}NO_5PNa$ $[M^+Na]^+$: 366.1446 found 366.1450

Benzyl (1-(bis(benzyloxy)phosphoryl)-2-methylpropyl)carbamate (3q)



White solid; 728mg, 62% yield; mp: 82-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 – 7.21 (m, 15H), 5.13 – 5.03 (m, 3H), 5.02 – 4.92 (m, 4H), 4.19 – 4.06 (m, 1H), 2.26 – 2.15 (m, 1H), 1.04 – 0.93 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 156.40 (d, *J* = 6.5 Hz), 136.35 – 136.05 (m), 128.74 – 128.02 (m), 67.85 (t, *J* = 6.8 Hz), 67.29, 53.00 (d, *J* = 152.4 Hz), 29.07 (d, *J* = 4.6 Hz), 20.51 (d, *J* = 12.8 Hz), 17.87 (d, *J* = 4.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 25.77. HRMS (ESI) calculated for $C_{25}H_{30}NO_5PNa$ $[M^+Na]^+$: 490.1759 found 490.1760.

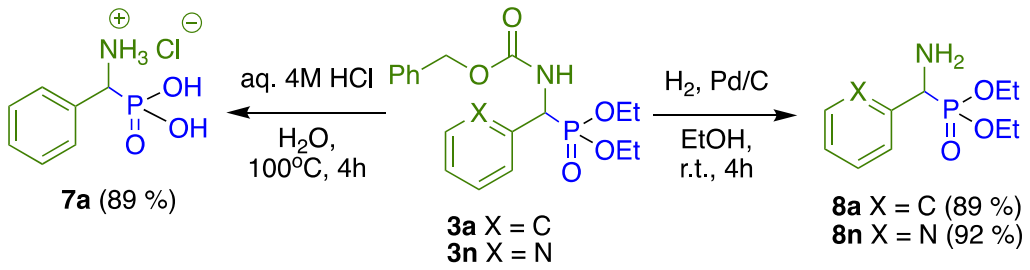
Benzyl (1-(diethoxyphosphoryl)-3-methylbutyl)carbamate (3r)



White solid; 497mg, 58% yield; 88-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 5.17 – 4.93 (m, 3H), 4.17 – 3.99 (m, 4H), 1.72 (m, 1H), 1.58 – 1.51 (m, 2H), 1.24 (dt, *J* = 19.6, 7.1 Hz, 6H), 0.91 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.04 (d, *J* = 5.0 Hz), 136.43 (s), 128.56 (s), 128.24 (s), 128.14 (s), 62.67 (d, *J* = 7.1 Hz), 62.49 (d, *J* = 6.6 Hz), 46.00 (d, *J* = 156.4 Hz), 38.61 (s), 24.47 (d, *J* = 13.3 Hz), 23.40 (s), 21.20 (s), 16.45 (dd, *J* = 5.8, 3.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.00 (s). HRMS (ESI) calculated for $C_{17}H_{28}NO_5PNa$ $[M^+Na]^+$: 380.1603 found 380.1603

5. Deprotection

The 20 mL of 4M aqueous HCl was added to a flask containing 0.5 g of **3a** or (*R,R,R*)-**6** and stirred at 100 °C for 4 h. The resulting mixture was then allowed to cool to room temperature and evaporated to dryness. The obtained crude product was purified by crystallization from $CHCl_3$ to afford the free α-aminophosphonic acids **7.**



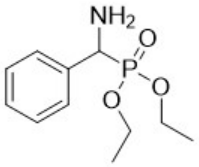
7a (89 %)

3a X = C
3n X = N

8a X = C (89 %)
8n X = N (92 %)

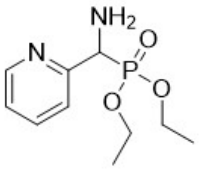
To obtain pure compound **8n**, a solution was prepared by dissolving 0.5 g of α-aminophosphonate **3n** in 20 mL of ethanol, and then Pd/C was added to the solution. The mixture was stirred at room temperature under hydrogen gas for 4 hours, and then filtered through celite and concentrated. The resulting crude product was subjected to crystallization from Et_2O.

Diethyl (amino(phenyl)methyl)phosphonate (8a)



white solid; 264mg, 89% yield; mp: 226-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.38 (d, *J* = 8.9 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.19 (m, 1H), 4.17 (d, *J* = 18.1 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.88 – 3.71 (m, 2H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 139.77 (d, *J* = 2.3 Hz), 128.38 (dd, *J* = 6.5, 4.2 Hz), 127.60 (d, *J* = 3.1 Hz), 62.54 (d, *J* = 7.0 Hz), 62.28 (d, *J* = 7.0 Hz), 53.70 (d, *J* = 147.8 Hz), 16.84 (d, *J* = 5.4 Hz), 16.68 (d, *J* = 5.4 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ: 26.08.

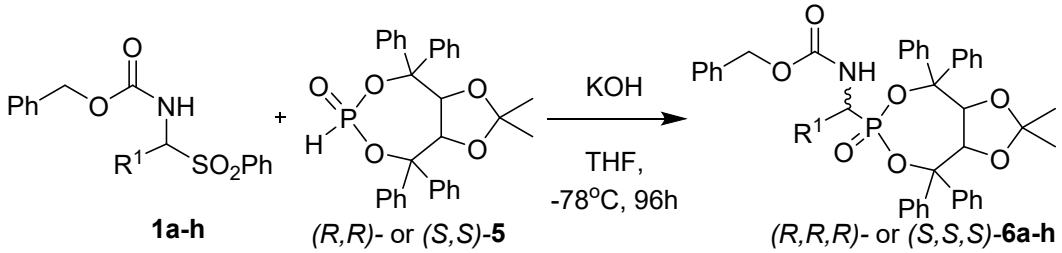
Diethyl (amino(pyridin-2-yl)methyl)phosphonate (8n)



White solid, 178mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 4.1 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.17 (t, *J* = 5.3 Hz, 1H), 4.38 (d, *J* = 17.5 Hz, 1H), 4.08 – 3.93 (m, 4H), 1.24-1.19 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 156.32, 149.13, 136.40, 123.28 (d, *J* = 4.7 Hz), 122.70 (d, *J* = 3.1 Hz), 62.95 (d, *J* = 7.0 Hz), 62.80 (d, *J* = 7.1 Hz), 55.51 (d, *J* = 143.9 Hz), 16.47 (d, *J* = 3.0 Hz), 16.41 (d, *J* = 3.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 24.51.

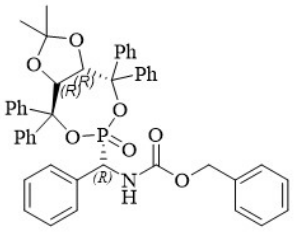
6. General procedure of the asymmetric hydrophosphonylation of α-amido sulphones.

In a 50 mL flask, TADDOL derived *H*-phosphonate (1 equiv.) was added to a solution of sulfone (1 equiv.) in THF (15 mL). After the resulting mixture had been cooled to -78°C, finely ground KOH (3 equiv.) was added in one portion to the mixture. The reaction mixture was stirred vigorously at the same temperature without any precaution to exclude air or moisture. After 4 days, saturated NH_4Cl (ca. 15 mL) was added, and then the mixture was allowed to warm to room temperature. The organic layer was separated, and the aqueous layer was extracted thrice with toluene (ca. 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated to give the crude product. The concentrated crude product was then purified by column chromatography using CH_2Cl_2 (100%) to CH_2Cl_2/MeOH 97:3 to afford the desired products **6**.



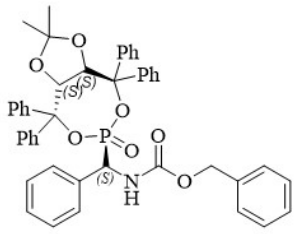
1a-h + *(R,R)*- or *(S,S)*-**5** → *(R,R,R)*- or *(S,S,S)*-**6a-h**

Benzyl (((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(phenyl)methyl)carbamate (*R,R,R*)-6a



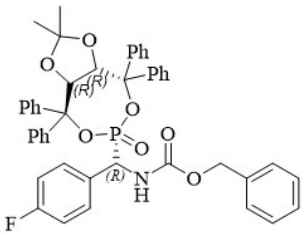
White solid; 187 mg, 85% yield; mp: 123-125°C; $[\alpha]_D^{20}$ = -145.8 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.15 (m, 24H), 7.02 – 6.97 (m, 2H), 5.73(br, s, 1H), 5.51 (d, *J* = 7.9 Hz, 1H), 5.36 – 4.96 (m, 4H) 0.81 (s, 3H), 0.53 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$), δ: 155.70 (d, $^1J_{CO}$ = 14.0 Hz), 144.14, 143.31, 139.33 (d, *J* = 9.9 Hz), 135.15, 129.82, 129.62, 128.63, 128.57, 128.54, 128.24, 128.12, 127.97, 127.91, 127.78, 127.40, 127.30, 126.62, 114.10, 90.93 (d, *J* = 12.6 Hz), 87.39 (d, *J* = 8.2 Hz), 79.94, 79.08, 67.40, 53.91 (d, $^1J_{CP}$ = 161.2 Hz), 27.02, 26.53; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 15.07; **HRMS (ESI)** calculated for $C_{46}H_{42}NO_7PNa$ $[M^+Na]^+$: 774.2596 found 774.2600

Benzyl (((3aS,8aS)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(phenyl)methyl)carbamate (*S,S,S*)-6a



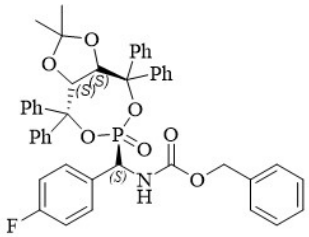
White solid; 194mg, 88% yield; mp: 124-126 °C ; $[\alpha]_D^{20}$ = +171.0 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.58 – 7.53 (m, 2H), 7.52 – 7.44 (m, 2H), 7.42 – 7.13 (m, 24H), 7.03 – 6.96 (m, 2H), 5.70 (br, s, 1H), 5.51 (d, *J* = 7.9 Hz), 5.36 – 4.96 (m, 4H), 0.80 (s, 3H), 0.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 155.69 (d, $^1J_{CO}$ = 12.6 Hz), 144.22, 143.31, 139.34 (d, $^2J_{CP}$ = 9.9 Hz), 135.17, 129.63, 128.64, 128.62, 128.56, 128.54, 128.23, 128.12 , 128.09, 127.90, 127.77, 127.39, 127.29, 126.61, 114.10, 90.94 (d, $^2J_{CP}$ = 13.0 Hz), 87.37 (d, $^2J_{CP}$ = 9.7 Hz), 79.91, 79.05, 67.39, 53.92 (d, $^1J_{CP}$ = 161.9 Hz), 27.01, 26.54; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 15.05 **HRMS (ESI)** calculated for $C_{46}H_{42}NO_7PNa$ $[M^+Na]^+$: 774.2596 found 774.2594

Benzyl(((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(4-fluorophenyl)methyl)-carbamate (*R,R,R*)-6b



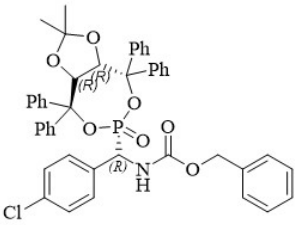
White solid; 210mg, 93% yield; mp: 174-176°C; $[\alpha]_D^{20}$ = -139.2 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.54 – 7.48 (m, 2H), 7.47-7.41 (m, 2H), 7.38 – 7.12 (m, 21H), 7.03 – 6.88 (m, 4H), 5.64 (br, s, 1H), 5.49 (d, *J* = 7.6), 5.33 – 4.89 (m, 4H), 0.76 (s, 3H), 0.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 163.87 (d, J_{CF} = 3.1 Hz), 161.41 (d, $^1J_{CO}$ = 3.3 Hz), 144.05 (d, $^2J_{CP}$ = 6.2 Hz), 143.14, 139.21 (d, $^3J_{CF}$= 9.9 Hz), 131.11, 129.78, 129.57, 128.68, 128.64, 128, 56, 128.48, 128.36, 128.26, 128.17, 127.95, 127.87, 127.39, 127.30, 127.25, 126.60, 115.51 (d, $^2J_{CF}$ = 21.7 Hz), 114.22, 91.14 (d, $^2J_{CP}$ = 11.7 Hz), 87.57 (d, $^2J_{CP}$ = 10.4 Hz), 79.68, 78.93, 67.45, 53.21 (d, J_{CP} = 161.4 Hz), 26.96, 26.52; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.69; **HRMS (ESI)** calculated for $C_{46}H_{41}FNO_7PNa$ $[M^+Na]^+$: 792.2502 found 792.2498

Benzyl (((3aS,8aS)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e] [1,3,2] dioxaphosphepin-6-yl)(4-fluorophenyl)methyl)carbamate (*S,S,S*)-6b



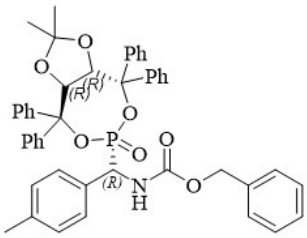
White solid; 205mg, 91% yield; mp:208-210 °C; $[\alpha]_D^{20}$ = +169.2 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.15 (m, 21H), 7.01 – 6.91 (m, 2H), 5.70 (br, s 1H), 5.49 (d, *J* = 7.8 Hz, 1H), 5.31 – 4.94 (m, 4H), 78, 0.52; **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 163.87 (d, $^1J_{CF}$ = 3.1 Hz), 161.42 (d, $^1J_{CO}$ = 3.1 Hz), 155.68, 144.10 (d, $^2J_{CP}$ = 6.2 Hz), 143.16, 139.25 (d, $^3J_{CF}$ = 9.9 Hz), 131.12, 129.59, 128.68, 128.64, 128.57, 128.50, 128.36, 128.25, 127.94, 127.88, 127.40, 127.31, 127.26, 126.62, 115.50 (d, $^2J_{CF}$ = 19.5 Hz), 114.22, 91.15 (d, $^2J_{CP}$ = 13.5 Hz), 87.54 (d, $^2J_{CP}$ = 9.0 Hz), 79.77, 78.95, 67.45, 53.24 (d, $^1J_{CP}$ = 167.8 Hz), 26.98, 26.54; ; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.65; **HRMS (ESI)** calculated for $C_{46}H_{42}NO_7PNa$ $[M^+Na]^+$: 792.2502 found 792.2498

Benzyl((4-chlorophenyl)((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8tetraphenyltetrahydro[1,3] dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)methyl)carbamate (*R,R,R*)- 6c



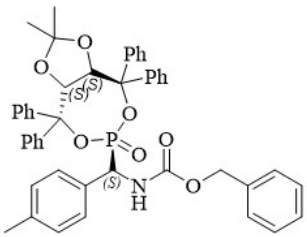
White solid; 219 mg, 95% yield; mp: 236-238 °C; $[\alpha]_D^{20}$ = -135.5 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.56 – 7.49 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.14 (m, 23H), 6.94 – 6.89 (m, 2H), 5.70 (s, br, 1H), 5.48 (d, *J* = 7.9 Hz, 1H), 5.29 – 4.94 (m, 4H), 0.77 (s, 3H), 0.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 155.71 (d, $^1J_{CO}$ = 14.1 Hz), 144.06 (d, J_{CCl} = 6.2 Hz), 143.11, 139.19 (d, $^2J_{CCl}$ = 9.9 Hz), 136.08, 134.03 (d, $^2J_{CP}$ = 3.6 Hz), 129.84, 129.62, 129.13, 128.73, 128.59, 128.50, 128.40, 128.28, 127.93 (d, $^3J_{CP}$ = 6.2 Hz), 127.40, 127.32, 126.61, 114.26, 92.02 (d, $^1J_{CP}$ = 13.5 Hz), 91.33 (d, $^1J_{CP}$ = 12.7 Hz), 79.66, 78.90, 67.49, 53.46 (d, J_{CP} = 161.5 Hz), 26.98, 26.55; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 14.51; **HRMS (ESI)** calculated for $C_{46}H_{41}ClNO_7PNa$ $[M^+Na]^+$: 808.2207 found 808.2220

Benzyl (((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(p-tolyl)methyl)carbamate (*R,R,R*)-6d



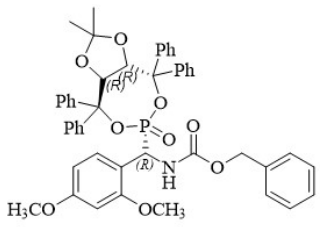
White solid; yield = 91%; mp; 128-130 °C; $[\alpha]_D^{20}$ = -122.7 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.58 – 7.52 (m, 2H), 7.50-7.45 (m, 2H), 7.40 – 7.14 (m, 21H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 6.9 Hz, 2H), 5.65 (br, s, 1H), 5.50 (d, *J* = 7.9 Hz, 1H), 5.37 – 4.97 (m, 4H), 2.35 (s, 3H), 0.80 (s, 3H), 0.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.62 (d, $^1J_{CO}$ = 12.3 Hz), 144.18 143.36, 139.38 (d, *J* = 9.9 Hz), 137.80 132.12, 129.62, 129.31, 128.59, 128.51, 128.21, 127.88, 127.75, 127.37, 127.27 (d, $^3J_{CP}$ = 4.5 Hz), 126.63, 114.06, 90.80 (d, $^2J_{CP}$ = 14.2 Hz), 87.29 (d, $^3J_{CP}$ = 9.2 Hz), 79.96, 79.09, 67.33, 53.64 (d, $^1J_{CP}$ = 165.6 Hz), 27.01, 26.53, 21.28; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 15.23; **HRMS (ESI)** calculated for $C_{47}H_{44}NO_7PNa$ $[M^+Na]^+$: 788.2753 found 788.2749

Benzyl (((3aS,8aS)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(p-tolyl)methyl)carbamate (*S,S,S*)-6d



White solid; 208 mg, 93% yield; mp: 154-156 °C; $[\alpha]_D^{20}$ = +142.2 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57 – 7.51 (m, 2H), 7.50-7.45 (m, 2H), 7.40 – 7.12 (m, 21H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 5.61 (br, s, 1H), 5.48 (d, *J* = 7.9 Hz, 1H), 5.50 – 4.99, (m, 4H), 2.34 (s, 3H), 0.79 (s, 3H), 0.52 (s, 3H);); **^{13}C NMR** (101 MHz, $CDCl_3$) δ:155.62 (d, $^1J_{CO}$ = 12.4 Hz), 144.16, 143.38, 139.37 (d, $^2J_{CP}$ = 9.9 Hz), 137.85, 132.11, 129.62 , 129.28, 128.58, 128.50, 128.21, 127.87, 127.73, 127.36 127.26, 127.24, 126.61, 114.05, 90.82 (d, $^2J_{CP}$ = 9.9 Hz), 87.27 (d, $^2J_{CP}$ = 7.9 Hz), 79.93, 79.07, 67.33, 53.61 (d, $^1J_{CP}$ = 162.8 Hz), 27.00, 26.52, 21.26; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 15.21; **HRMS (ESI)** calculated for $C_{47}H_{44}NO_7PNa$ $[M^+Na]^+$: 788.2753 found 788.2757

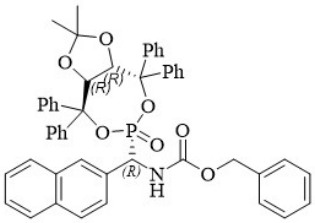
Benzyl ((2,5-dimethoxyphenyl)((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)methyl)carbamate (*R,R,R*)-6e



White solid; 212 mg, 89% yield; mp: 120-122 °C $[\alpha]_D^{20}$ = -133.5 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57 – 7.52 (m, 2H), 7.50 – 7.46 (m, 2H), 7.38 – 7.15 (m, 19H), 7.07 – 7.03 (m, 2H), 6.95 – 6.84 (m, 2H), 6.79 (d, *J* = 6.7 Hz, 1H), 5.68-5.58 (br, s, 1H), 5.51 (d, *J* = 8.0 Hz), 5.30 – 4.93 (m, 4H), 3.86 (s, 3H), 3.69 (s, 3H), 0.82 (s, 3H), 0.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.63 (d, $^1J_{CO}$ = 13.6 Hz), 149.09 (d, $^3J_{CP}$ = 2.0 Hz), 149.03 (d, $^3J_{CP}$ = 2.7 Hz), 129.47, 128.63, 128.53, 128.47, 128.17, 127.90, 127.82, 127.42, 127.29, 127.14, 126.61, 120.57 (d, $^2J_{CP}$ = 7.2 Hz), 113.92, 111.08, 90.60 (d, $^1J_{CP}$ = 11.7 Hz), 87.21 (d,$^1J_{CP}$ = 11.5 Hz), 80.35, 79.09, 67.39, 56.01,, 55.90, 53.50 (d, $^1J_{CP}$ = 164.1 Hz),

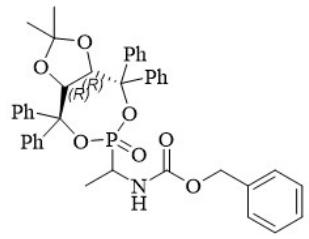
26.99, 26.47; **^{31}P NMR** (162 MHz, $CDCl_3$) δ:15.29; **HRMS (ESI)** calculated for $C_{48}H_{46}NO_9PNa$ $[M^+Na]^+$: 834.2808 found 834.2809

Benzyl (((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2] dioxaphosphepin-6-yl)(naphthalen-2-yl)methyl)carbamate (*R,R,R*)-6f



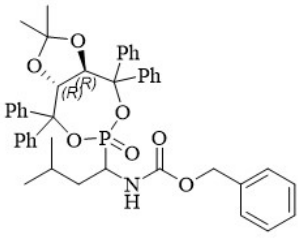
White solid; 211 mg, 90% yield; mp: 126-128 ^oC ; $[\alpha]_D^{20}$ = -119.0 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 5.7 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.58 – 7.07 (m, 24H), 7.06 – 6.91 (m, 2H), 6.82 (d, *J* = 7.9 Hz, 2H), 5.77(s, br, 1H), 5.49 (d, *J* = 7.7 Hz, 1H), 5.41 – 4.94 (m, 4H), 0.77 (s, 3H), 0.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ:155.76 (d, $^1J_{CO}$ = 14.0 Hz), 144.18, 143.23, 139.25, 133.20 (d, $^2J_{CP}$ = 10.6 Hz), 129.65, 128.61, 128.47, 128.24, 127.92, 127.70, 127.39, 127.16, 126.83, 126.60, 126.32, 125.58, 114.14, 91.15 (d, $^2J_{CP}$ = 13.6 Hz), 87.43 (d, $^2J_{CP}$ = 8.9 Hz), 79.77, 78.98, 67.46 , 54.21 (d, $^1J_{CP}$ = 162.9 Hz), 26.98, 26.54; **^{31}P NMR** (162 MHz, $CDCl_3$) δ:15.05; **HRMS (ESI)** calculated for $C_{50}H_{44}NO_7PNa$ $[M^+Na]^+$: 824.2753 found 824.2769

Benzyl (1-((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e] [1,3,2]dioxaphosphepin-6-yl)ethyl)carbamate (6g)



White solid; 131 mg, 65% yield; mp: 156-158 ^oC ;dr = 9:1; $[\alpha]_D^{20}$ = -163.7 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.60 – 7.46 (m, 4H), 7.45 – 7.13 (m, 21H), 5.54 (d, *J* = 7.9 Hz, 1H), 5.35 – 4.93 (m, 4H), 4.34 – 4.18 (m, 1H), 1.38 (dd, *J* = 17.7, 7.3 Hz, 3H), 0.77 (s, 3H), 0.58 (s, 3H);); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 155.64 (d, $^1J_{CO}$ = 6.4 Hz), *155.41 (d, $^1J_{CO}$ = 8.8 Hz), 144.44, 143.73, 143.38, 139.55, 136.24, 129.75, 128.84, 128.76, 128.64, 128.58, 128.39, 128.36, 128.28, 128.22, 128.12, 127.92, 127.83, 127.39, 127.33, 127.20, 127.08, 126.87, 126.65, *114.4, 114.12, 90.87 (d, $^2J_{CP}$ = 13.5 Hz), 86.87 (d, $^2J_{CP}$ = 8.8 Hz), 79.68, 78.99, 67.19, *67.02, 45.04 (d, ^1JCP = 167.66 Hz), *44.44 (d, $^1J_{CP}$ = 166.65 Hz), 26.94 (d, $^2J_{CP}$ = 6.3 Hz), *26.66 (d, $^2J_{CP}$ = 7.9 Hz), 16.20, 15.71; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 19.38, *18.88; **HRMS (ESI)** calculated for $C_{41}H_{40}NO_7PNa$ $[M^+Na]^+$: 712.2440 found 721.2435

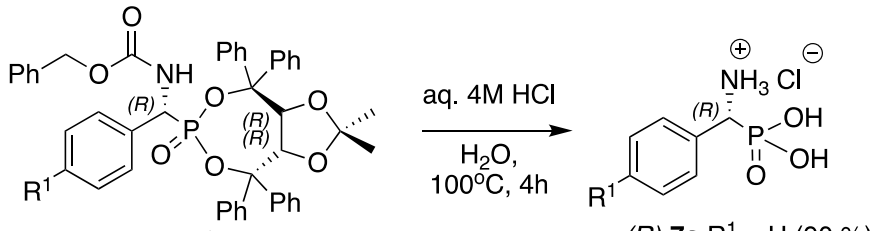
Benzyl (1-((3aR,8aR)-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e] [1,3,2] dioxaphosphepin-6-yl)-3-methylbutyl)carbamate (6h)



White solid; 161mg, 75% yield; mp: 114-116 ^oC ;dr = 1:9; $[\alpha]_D^{20}$ = -153.8 (c = 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ:δ 7.61 – 7.48 (m, 4H), 7.42 – 7.06 (m, 21H), 5.54 (d, *J* = 7.9 Hz, 1H), 5.27 – 5.07 (m, 2H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.94 (d, *J* = 12.1 Hz, 1H), 4.30 – 4.16 (m, 1H), 1.77 – 1.56 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H), 0.74 (s, 3H), 0.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 156.03 (d, $^1J_{CO}$ = 4.3 Hz), *155.73 (d, $^1J_{CO}$ = 5.1 Hz), 144.69 (d, $^3J_{CP}$= 7.2 Hz), *144.52 (d, $^3J_{CP}$ = 5.8 Hz), 143.78, 139.56, 136.26, 129.82, 128.94, 128.73, 128.65, 128.60, 128.54, 128.44, 128.39, 128.35, 128.26, 128.17, 128.06, 127.77, 127.36, 127.32 , 127.23, 126.95, 126.67, *114.33, 114.16, 91.10 (d, $^2J_{CP}$ = 13.8 Hz), *90.61 (d, $^2J_{CP}$ = 14.1 Hz), *87.07 (d, $^2J_{CP}$ = 9.1 Hz), 86.80 (d, $^2J_{CP}$ = 8.9 Hz), *80.21, 79.79, *79.49, 78.93, 67.23, *67.06, 47.97 (d, $^1J_{CP}$ = 165.64 Hz, *47.31 (d, $^1J_{CP}$ = 165.64 Hz), *38.36 (d, $^2J_{CP}$ = 4.1 Hz), 37.82 (d, $^2J_{CP}$ = 3.4 Hz), 26.94, *26.72, 24.63, *24.46, *24.32, *23.52, 23.48, *21.27, 21.18; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: *19.21, 18.90; **HRMS (ESI)** calculated for $C_{44}H_{46}NO_7PNa$ $[M^+Na]^+$: 754.2910 found 754.2913

7. General protocol for the cleavage of the chiral auxiliary and the iminic substituent

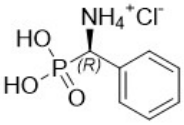
See section 5 for the procedure.



(R,R,R)-**6a** R^1 = H
(R,R,R)-**6b** R^1 = F

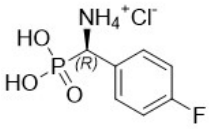
(R)-**7a** R^1 = H (90 %)
(R)-**7b** R^1 = F (87 %)

(Amino(phenyl)methyl)phosphonic acid (7a)



White solid; 90% yield; mp: 224-226 °C; $[\alpha]_D^{20}$ = +19.0 (c = 1.0, 1M NaOH); **^{1}H NMR** (400 MHz, D_2O) δ: 7.25 (s, 5H), 4.29 (d, *J* = 16.4 Hz); **^{13}C NMR** (101 MHz, D_2O) δ 132.00 (d, $^2J_{CP}$ = 3.7 Hz), 129.07, 129.05, 129.03, 53.01 (d, $^1J_{CP}$ = 141.5 Hz); **^{31}P NMR** (162 MHz, D_2O) δ: 12.02

(Amino(4-fluorophenyl)methyl)phosphonic acid (7b)



White solid; 87% yield; mp: 295-397 °C; $[\alpha]_D^{20}$ = +10.4 (c = 1.0, 1M NaOH); **^{1}H NMR** (400 MHz, D_2O) δ: 7.32 (s, 2H), 7.12 – 7.01 (m, 2H), 4.33 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR** (151 MHz, D_2O) δ 162.72 (d, $^1J_{CF}$ = 245.4 Hz), 129.84, 129.10, 128.48, 127.09, 115.88 (d, $^2J_{CP}$ = 21.9 Hz), 52.69 (d, $^1J_{CP}$ = 139.8 Hz); **^{31}P NMR** (162 MHz, D_2O) δ: 11.33.

8. X-Ray Analysis

Structures (*R,R,R*)-**6a** was measured on a Rigaku Oxford Diffraction XtaLAB Synergy-R DW diffractometer equipped with a HyPix ARC 150° Hybrid Photon Counting (HPC) detector using CuK_α (λ = 1.54184 Å). For structure (*S,S,S*)-**6d** an Xcalibur Gemini diffractometer equipped with Ruby CCD detector using CuK_α (λ = 1.54184 Å) was used. Data were processed using the CrystAlisPro software. The structures were solved by intrinsic phasing with SHELXT (2015 release) and refined by full-matrix least-squares methods based F^2 using SHELXL. For all structures, H atoms bound to C atoms were placed in the geometrically idealized positions and treated in riding mode, with C-H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for C-H groups, and C-H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 groups.

CCDC 2248672 for **(***R,R,R*)-**6a** and 2248673 for (*S,S,S*)-**6d** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table SI1: Crystal data and structure refinement details

Compound reference	(*S,S,S*)-**6d**	(*R,R,R*)-**6a**
Chemical formula	$C_{47}H_{44}NO_7P$	$C_{46}H_{42}NO_7P$
Formula Mass	765.80	751.77
Crystal system	orthorhombic	monoclinic
a[Å]	9.466(4)	10.768(3)
b[Å]	16.073(6)	11.588(3)
c[Å]	26.339(9)	31.149(7)
β[°]		98.37(2)
Unit cell volume/Å ^{3}	4007(3)	3845.4(17)
Temperature/K	100(2)	100(2)
Space group	$P2_12_12_1$	$P2$
No. of formula units per unit cell, *Z*	4	4
Radiation type	CuK_α	CuK_α
Absorption coefficient, μ/mm^{-1}	1.042	1.076
No. of reflections measured	16956	19844
No. of independent reflections	7164	19844
R_{int}	0.0591	
Final R_1 values ($I > 2\sigma(I)$)	0.0527	0.0463
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1346	0.1197
Final R_1 values (all data)	0.0634	0.0478
Final $wR(F^2)$ values (all data)	0.1463	0.1206
Goodness of fit on F^2	1.058	1.112
Flack parameter	-0.12(2)	0.044(18)

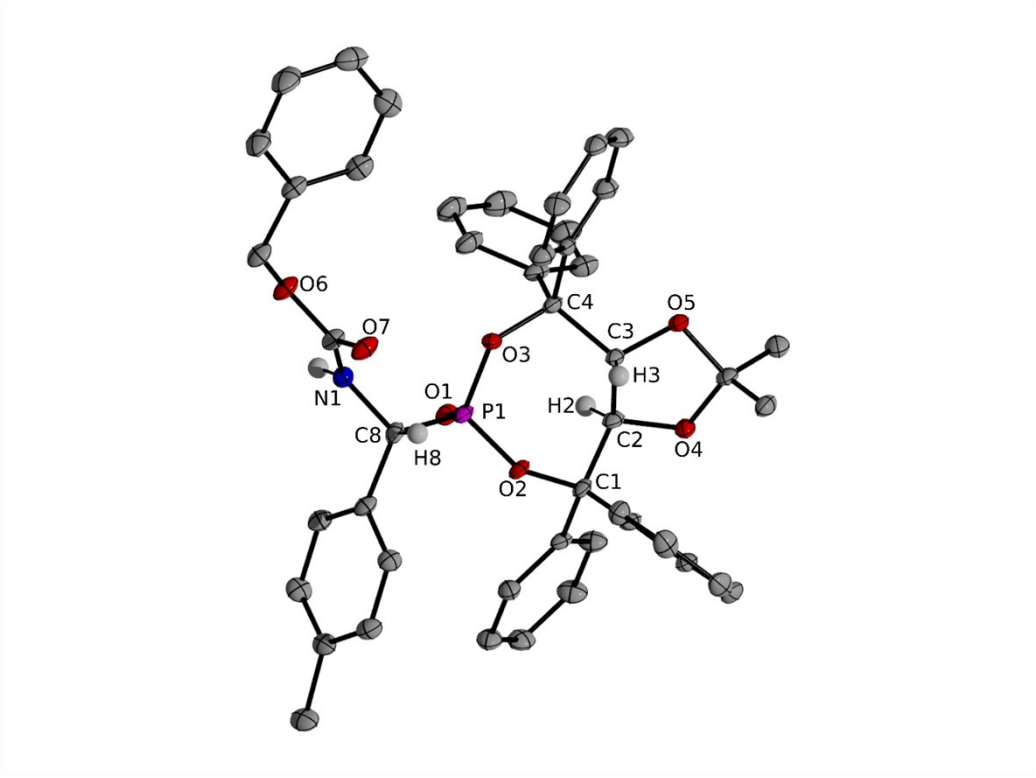


Figure SI1. The molecular structure of compound (*S,S,S*)-**6d**, showing 30% probability displacement ellipsoids. The hydrogen atoms except H1, H2, H3 and H8 were omitted for clarity.

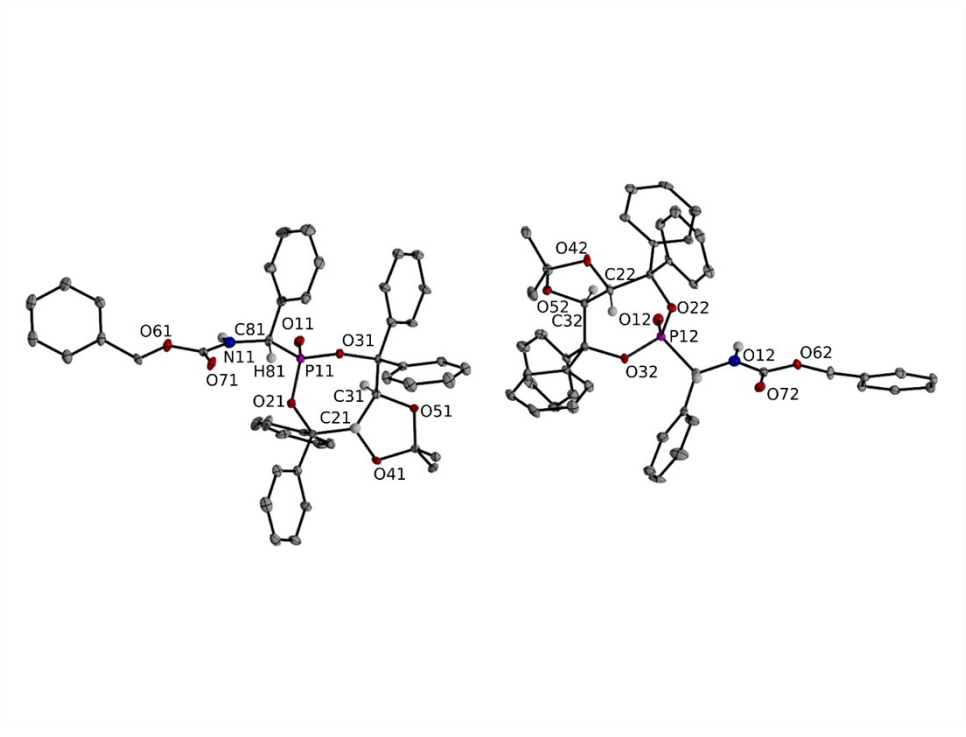


Figure SI2. The molecular structure of compound (*R,R,R*)-**6a**, showing 30% probability displacement ellipsoids. The hydrogen atoms except H11,H12 H21,H22, H31, H32, H81 and H82 were omitted for clarity.

Table SI2. Selected bond distances and angles (Å, °) for (*S,S,S*)-**6d.**

P1—O1	1.459 (4)	C24—C14	1.385 (8)
P1—O2	1.578 (3)	C24—C34	1.388 (8)
P1—O3	1.595 (3)	C21—C31	1.411 (8)
P1—C8	1.817 (5)	C55—C65	1.394 (7)
O4—C2	1.431 (6)	C55—C45	1.399 (8)
O4—C5	1.433 (6)	C32—C42	1.384 (8)
O3—C4	1.443 (6)	C45—C35	1.374 (8)
O5—C3	1.413 (6)	C210—C310	1.400 (9)
O5—C5	1.439 (5)	C14—C64	1.413 (8)
O2—C1	1.457 (5)	C34—C44	1.388 (9)
O6—C9	1.353 (6)	C62—C52	1.407 (8)
O6—C10	1.448 (5)	C12—C62	1.389 (7)
O7—C9	1.225 (6)	C12—C22	1.395 (7)
N1—C9	1.344 (6)	C0AA—C25	1.380 (8)
N1—C8	1.453 (6)	C0AA—C65	1.397 (8)
C18—C28	1.370 (7)	C22—C32	1.390 (7)
C18—C68	1.392 (7)	C110—C210	1.381 (8)
C18—C8	1.527 (7)	C110—C610	1.401 (7)
C1—C11	1.519 (6)	C110—C10	1.490 (8)
C1—C12	1.529 (6)	C25—C35	1.391 (7)
C1—C2	1.552 (7)	C28—C38	1.408 (8)
C4—C14	1.535 (7)	C68—C58	1.385 (8)
C4—C0AA	1.542 (6)	C11—C61	1.388 (7)
C4—C3	1.559 (6)	C11—C21	1.400 (7)
C3—C2	1.551 (6)	C61—C51	1.378 (8)
C5—C7	1.514 (8)	C48—C38	1.387 (8)
C5—C6	1.518 (7)	C48—C58	1.394 (8)
C48—C78	1.520 (7)	C42—C52	1.372 (9)
C41—C51	1.370 (10)	C610—C510	1.362 (9)
C41—C31	1.383 (10)	C44—C54	1.391 (11)
C64—C54	1.389 (9)	C310—C410	1.382 (10)

C410—C510	1.394 (11)	C11—C21—C31	119.9 (5)
O1—P1—O2	115.46 (18)	N1—C8—C18	115.1 (4)
O1—P1—O3	115.6 (2)	N1—C8—P1	110.6 (4)
O2—P1—O3	104.41 (18)	C18—C8—P1	110.3 (3)
O1—P1—C8	119.3 (2)	C65—C55—C45	120.2 (5)
O2—P1—C8	98.9 (2)	C42—C32—C22	120.2 (6)
O3—P1—C8	100.6 (2)	O7—C9—N1	125.4 (4)
C2—O4—C5	109.8 (3)	O7—C9—O6	124.0 (4)
C4—O3—P1	125.1 (3)	N1—C9—O6	110.6 (4)
C3—O5—C5	106.6 (3)	C28—C18—C68	119.3 (5)
C1—O2—P1	125.0 (3)	C28—C18—C8	122.3 (4)
C9—O6—C10	115.3 (4)	C68—C18—C8	118.3 (4)
C9—N1—C8	119.9 (4)	C35—C45—C55	119.2 (5)
O2—C1—C11	105.3 (4)	C110—C210—C310	120.4 (5)
O2—C1—C12	107.8 (4)	C24—C14—C64	118.3 (5)
C11—C1—C12	110.8 (4)	C24—C14—C4	125.1 (5)
O2—C1—C2	107.6 (3)	C64—C14—C4	116.6 (5)
C11—C1—C2	112.0 (4)	C0AA—C4—C3	107.7 (4)
C12—C1—C2	112.8 (4)	O5—C3—C2	103.6 (4)
O3—C4—C14	110.0 (4)	O5—C3—C4	110.5 (4)
O3—C4—C0AA	104.9 (4)	C2—C3—C4	117.3 (4)
C14—C4—C0AA	110.1 (4)	O3—C4—C3	107.0 (4)
C14—C4—C3	116.4 (4)	C44—C34—C24	120.6 (6)
O4—C5—O5	105.0 (4)	C12—C62—C52	119.8 (5)
O4—C5—C7	108.3 (4)	C52—C42—C32	119.6 (5)
O5—C5—C7	109.0 (4)	C51—C41—C31	121.1 (5)
O4—C5—C6	111.9 (4)	C54—C64—C14	119.9 (7)
O5—C5—C6	110.9 (4)	C55—C65—C0AA	120.0 (5)
C7—C5—C6	111.5 (5)	C45—C35—C25	120.9 (6)
C58—C68—C18	120.8 (5)	C41—C51—C61	119.7 (6)
C61—C11—C21	118.5 (5)	C41—C31—C21	119.1 (6)
C61—C11—C1	120.4 (4)	C42—C52—C62	120.8 (5)

C21—C11—C1	121.1 (4)	C510—C610—C110	121.0 (6)
C51—C61—C11	121.5 (5)	C34—C44—C54	118.7 (6)
C38—C48—C58	118.9 (5)	C64—C54—C44	121.2 (6)
C38—C48—C78	121.0 (5)	C410—C310—C210	120.3 (6)
C58—C48—C78	120.1 (5)	C310—C410—C510	119.0 (6)
C62—C12—C22	118.8 (5)	C62—C12—C1	122.0 (5)
C18—C28—C38	120.4 (4)	C22—C12—C1	119.3 (4)
O6—C10—C110	114.2 (4)	C25—C0AA—C65	119.4 (5)
C14—C24—C34	121.3 (6)	C25—C0AA—C4	120.8 (5)
C610—C510—C410	120.7 (6)	C65—C0AA—C4	119.7 (5)
C48—C38—C28	120.4 (5)	O4—C2—C3	103.6 (4)
O1—P1—O3—C4	−57.1 (4)	O4—C2—C1	111.6 (4)
O2—P1—O3—C4	70.8 (4)	C3—C2—C1	114.7 (4)
C8—P1—O3—C4	173.0 (3)	C68—C58—C48	120.3 (5)
O1—P1—O2—C1	40.2 (4)	C32—C22—C12	120.9 (5)
O3—P1—O2—C1	−87.8 (4)	C210—C110—C610	118.6 (5)
C8—P1—O2—C1	168.7 (4)	C210—C110—C10	124.9 (5)
C8—N1—C9—O7	−0.7 (8)	C610—C110—C10	116.5 (5)
C78—C48—C58—C68	177.6 (5)	C0AA—C25—C35	120.3 (5)
C62—C12—C22—C32	0.5 (7)	C4—C0AA—C25—C35	−178.5 (5)
C1—C12—C22—C32	−179.2 (5)	C68—C18—C28—C38	−0.2 (8)
C65—C0AA—C25—C35	−0.4 (7)	C8—C18—C28—C38	174.7 (5)
C8—N1—C9—O6	177.1 (5)	C9—O6—C10—C110	97.8 (5)
C10—O6—C9—O7	−15.7 (8)	C210—C110—C10—O6	−20.4 (7)
C10—O6—C9—N1	166.5 (4)	C610—C110—C10—O6	161.1 (5)
P1—O2—C1—C11	160.3 (3)	C58—C48—C38—C28	2.7 (8)
P1—O2—C1—C12	−81.3 (4)	C78—C48—C38—C28	−177.0 (5)
P1—O2—C1—C2	40.6 (5)	C18—C28—C38—C48	−1.6 (8)
P1—O3—C4—C14	72.9 (4)	C61—C11—C21—C31	1.3 (8)
P1—O3—C4—C0AA	−168.6 (3)	C1—C11—C21—C31	−179.5 (5)
P1—O3—C4—C3	−54.4 (5)	C9—N1—C8—C18	117.0 (5)
C5—O5—C3—C2	−33.2 (4)	C9—N1—C8—P1	−117.3 (5)

C5—O5—C3—C4	−159.8 (4)	C28—C18—C8—N1	49.8 (6)
O3—C4—C3—O5	−172.9 (3)	C68—C18—C8—N1	−135.2 (5)
C14—C4—C3—O5	63.6 (5)	C28—C18—C8—P1	−76.0 (5)
C0AA—C4—C3—O5	−60.5 (5)	C68—C18—C8—P1	98.9 (5)
O3—C4—C3—C2	68.7 (5)	O1—P1—C8—N1	−68.5 (4)
C14—C4—C3—C2	−54.8 (6)	O2—P1—C8—N1	165.5 (3)
C0AA—C4—C3—C2	−179.0 (4)	O3—P1—C8—N1	58.9 (4)
O2—C1—C12—C62	144.4 (4)	O1—P1—C8—C18	59.8 (4)
C2—O4—C5—O5	−18.7 (5)	O2—P1—C8—C18	−66.1 (3)
C2—O4—C5—C7	−135.0 (4)	O3—P1—C8—C18	−172.7 (3)
C2—O4—C5—C6	101.7 (4)	C12—C22—C32—C42	−0.4 (8)
C3—O5—C5—O4	33.0 (5)	C65—C55—C45—C35	−0.2 (8)
C3—O5—C5—C7	148.9 (4)	C610—C110—C210—C310	−1.1 (7)
C3—O5—C5—C6	−88.1 (5)	C10—C110—C210—C310	−179.6 (5)
C28—C18—C68—C58	0.7 (8)	C34—C24—C14—C64	−0.2 (8)
C8—C18—C68—C58	−174.4 (4)	C34—C24—C14—C4	−177.0 (5)
O2—C1—C11—C61	162.3 (5)	O3—C4—C14—C24	−144.4 (5)
C12—C1—C11—C61	45.9 (7)	C0AA—C4—C14—C24	100.4 (6)
C2—C1—C11—C61	−81.0 (6)	C3—C4—C14—C24	−22.4 (7)
O2—C1—C11—C21	−16.8 (6)	O3—C4—C14—C64	38.8 (6)
C12—C1—C11—C21	−133.2 (5)	C0AA—C4—C14—C64	−76.4 (6)
C2—C1—C11—C21	99.9 (6)	C3—C4—C14—C64	160.7 (5)
C21—C11—C61—C51	−1.8 (8)	C14—C24—C34—C44	0.1 (10)
C1—C11—C61—C51	179.0 (5)	C22—C12—C62—C52	−0.5 (7)
C11—C1—C12—C62	−100.8 (5)	C1—C12—C62—C52	179.2 (5)
C2—C1—C12—C62	25.8 (6)	C22—C32—C42—C52	0.2 (9)
O2—C1—C12—C22	−35.9 (5)	C24—C14—C64—C54	0.2 (8)
C11—C1—C12—C22	78.9 (5)	C4—C14—C64—C54	177.3 (5)
C2—C1—C12—C22	−154.5 (4)	C45—C55—C65—C0AA	0.8 (8)
O3—C4—C0AA—C25	−158.6 (4)	C25—C0AA—C65—C55	−0.5 (7)
C14—C4—C0AA—C25	−40.2 (6)	C4—C0AA—C65—C55	177.6 (5)
C3—C4—C0AA—C25	87.6 (5)	C55—C45—C35—C25	−0.8 (8)

O3—C4—C0AA—C65	23.3 (5)	C0AA—C25—C35—C45	1.1 (8)
C14—C4—C0AA—C65	141.7 (5)	C31—C41—C51—C61	−2.7 (10)
C3—C4—C0AA—C65	−90.5 (5)	C11—C61—C51—C41	2.5 (9)
C5—O4—C2—C3	−1.4 (5)	C51—C41—C31—C21	2.2 (9)
C5—O4—C2—C1	−125.3 (4)	C11—C21—C31—C41	−1.5 (9)
O5—C3—C2—O4	21.1 (4)	C32—C42—C52—C62	−0.1 (9)
C4—C3—C2—O4	143.2 (4)	C12—C62—C52—C42	0.3 (9)
O5—C3—C2—C1	143.0 (4)	C210—C110—C610—C510	1.0 (9)
C4—C3—C2—C1	−94.9 (5)	C10—C110—C610—C510	179.6 (6)
O2—C1—C2—O4	161.6 (3)	C24—C34—C44—C54	−0.1 (10)
C11—C1—C2—O4	46.3 (5)	C14—C64—C54—C44	−0.2 (10)
C12—C1—C2—O4	−79.6 (5)	C34—C44—C54—C64	0.1 (10)
O2—C1—C2—C3	44.2 (5)	C110—C210—C310—C410	−0.2 (8)
C11—C1—C2—C3	−71.1 (5)	C210—C310—C410—C510	1.5 (9)
C12—C1—C2—C3	163.0 (4)	C110—C610—C510—C410	0.3 (10)
C18—C68—C58—C48	0.4 (8)	C310—C410—C510—C610	−1.6 (10)
C38—C48—C58—C68	−2.1 (8)		

Table SI2. Selected bond distances and angles (Å, ˚) for (*R,R,R*)-**6a.**

P11—O11	1.457 (4)	P12—O12	1.451 (4)
P11—O31	1.585 (4)	P12—O32	1.576 (4)
P11—O21	1.597 (4)	P12—O22	1.597 (4)
P11—C81	1.823 (5)	P12—C82	1.810 (5)
O21—C11	1.459 (6)	O22—C12	1.458 (6)
O31—C41	1.462 (6)	O32—C42	1.458 (6)
O41—C51	1.427 (6)	O42—C52	1.431 (6)
O41—C21	1.437 (6)	O42—C22	1.432 (6)
O51—C51	1.437 (7)	O52—C32	1.432 (5)
O51—C31	1.438 (6)	O52—C52	1.449 (6)
O61—C91	1.357 (6)	O62—C92	1.362 (6)
O61—C101	1.445 (6)	O62—C102	1.438 (6)
O71—C91	1.195 (7)	O72—C92	1.190 (6)

N11—C91	1.362 (7)	N12—C92	1.357 (7)
N11—C81	1.448 (7)	N12—C82	1.471 (6)
C11—C111	1.529 (7)	C12—C112	1.526 (7)
C11—C121	1.530 (7)	C12—C122	1.547 (7)
C11—C21	1.536 (7)	C12—C22	1.550 (7)
C21—C31	1.539 (7)	C22—C32	1.555 (7)
C31—C41	1.545 (8)	C32—C42	1.537 (7)
C41—C141	1.539 (7)	C42—C142	1.524 (7)
C41—C151	1.541 (7)	C42—C152	1.540 (7)
C51—C71	1.513 (8)	C52—C72	1.510 (8)
C51—C61	1.515 (8)	C52—C62	1.521 (8)
C81—C181	1.528 (8)	C82—C182	1.516 (8)
C101—C110	1.496 (7)	C102—C192	1.492 (7)
C111—C611	1.394 (7)	C112—C612	1.388 (7)
C111—C211	1.402 (8)	C112—C212	1.397 (7)
C211—C311	1.375 (9)	C212—C312	1.372 (8)
C311—C411	1.361 (9)	C312—C412	1.396 (8)
C411—C511	1.363 (9)	C412—C512	1.378 (8)
C511—C611	1.409 (8)	C512—C612	1.393 (7)
C121—C621	1.404 (8)	C122—C222	1.388 (7)
C121—C221	1.406 (7)	C122—C622	1.394 (8)
C221—C321	1.382 (9)	C222—C322	1.410 (7)
C321—C421	1.395 (10)	C322—C422	1.370 (8)
C421—C521	1.382 (9)	C422—C522	1.383 (8)
C521—C621	1.387 (8)	C522—C622	1.405 (8)
C141—C641	1.390 (8)	C142—C642	1.388 (8)
C141—C241	1.395 (7)	C142—C242	1.398 (7)
C241—C341	1.388 (7)	C242—C342	1.396 (8)
C341—C441	1.378 (8)	C342—C442	1.370 (9)
C441—C541	1.404 (8)	C442—C542	1.382 (8)
C541—C641	1.387 (8)	C542—C642	1.385 (8)
C151—C251	1.377 (7)	C152—C652	1.378 (7)

C151—C651	1.388 (7)	C152—C252	1.394 (7)
C251—C351	1.400 (8)	C252—C352	1.381 (7)
C351—C451	1.398 (8)	C352—C452	1.401 (8)
C451—C551	1.383 (9)	C452—C552	1.375 (8)
C551—C651	1.384 (8)	C552—C652	1.382 (8)
C181—C281	1.375 (8)	C182—C682	1.392 (9)
C181—C681	1.388 (8)	C182—C282	1.397 (8)
C281—C381	1.387 (9)	C282—C382	1.380 (9)
C381—C481	1.382 (10)	C382—C482	1.365 (9)
C481—C581	1.360 (10)	C482—C582	1.398 (9)
C581—C681	1.395 (9)	C582—C682	1.382 (9)
C110—C610	1.378 (8)	C192—C692	1.390 (8)
C110—C210	1.389 (9)	C192—C292	1.398 (8)
C210—C310	1.377 (8)	C292—C392	1.378 (8)
C310—C410	1.396 (9)	C392—C492	1.383 (8)
C410—C510	1.366 (10)	C492—C592	1.390 (8)
C510—C610	1.385 (8)	C592—C692	1.382 (8)
O11—P11—O31	115.9 (2)	O12—P12—O32	115.2 (2)
O11—P11—O21	115.8 (2)	O12—P12—O22	116.0 (2)
O31—P11—O21	105.3 (2)	O32—P12—O22	105.7 (2)
O11—P11—C81	118.6 (2)	O12—P12—C82	118.4 (2)
O31—P11—C81	97.8 (2)	O32—P12—C82	98.6 (2)
O21—P11—C81	100.9 (2)	O22—P12—C82	100.5 (2)
C11—O21—P11	126.6 (3)	C12—O22—P12	126.4 (3)
C41—O31—P11	127.5 (3)	C42—O32—P12	130.0 (3)
C51—O41—C21	107.7 (4)	C52—O42—C22	108.5 (4)
C51—O51—C31	110.1 (4)	C32—O52—C52	110.4 (4)
C91—O61—C101	114.0 (4)	C92—O62—C102	114.0 (4)
C91—N11—C81	116.2 (4)	C92—N12—C82	116.4 (4)
O21—C11—C111	108.4 (4)	O22—C12—C112	109.0 (4)
O21—C11—C121	105.7 (4)	O22—C12—C122	105.6 (4)
C111—C11—C121	110.0 (5)	C112—C12—C122	109.8 (5)

O21—C11—C21	105.9 (4)	O22—C12—C22	105.1 (4)
C111—C11—C21	117.3 (4)	C112—C12—C22	118.7 (4)
C121—C11—C21	108.8 (4)	C122—C12—C22	107.8 (4)
O41—C21—C11	108.9 (5)	O42—C22—C12	110.5 (4)
O41—C21—C31	103.4 (4)	O42—C22—C32	102.9 (4)
C11—C21—C31	118.0 (4)	C12—C22—C32	116.7 (4)
O51—C31—C21	104.1 (4)	O52—C32—C42	110.8 (4)
O51—C31—C41	110.2 (4)	O52—C32—C22	104.2 (4)
C21—C31—C41	115.1 (4)	C42—C32—C22	114.8 (4)
O31—C41—C141	108.3 (4)	O32—C42—C142	107.9 (4)
O31—C41—C151	104.8 (4)	O32—C42—C32	106.8 (4)
C141—C41—C151	109.0 (4)	C142—C42—C32	113.8 (4)
O31—C41—C31	106.6 (4)	O32—C42—C152	104.3 (4)
C141—C41—C31	113.6 (4)	C142—C42—C152	109.1 (4)
C151—C41—C31	114.0 (4)	C32—C42—C152	114.3 (4)
O41—C51—O51	105.4 (4)	O42—C52—O52	104.4 (4)
O41—C51—C71	107.8 (5)	O42—C52—C72	108.0 (5)
O51—C51—C71	108.5 (5)	O52—C52—C72	109.0 (4)
O41—C51—C61	110.3 (5)	O42—C52—C62	110.9 (5)
O51—C51—C61	110.3 (5)	O52—C52—C62	111.4 (5)
C71—C51—C61	114.1 (5)	C72—C52—C62	112.8 (5)
N11—C81—C181	114.5 (4)	N12—C82—C182	114.3 (5)
N11—C81—P11	110.8 (4)	N12—C82—P12	111.2 (4)
C181—C81—P11	111.0 (4)	C182—C82—P12	112.0 (4)
O71—C91—O61	125.8 (5)	O72—C92—N12	124.9 (5)
O71—C91—N11	124.0 (5)	O72—C92—O62	126.2 (5)
O61—C91—N11	110.2 (5)	N12—C92—O62	108.8 (4)
O61—C101—C110	110.2 (4)	O62—C102—C192	110.4 (5)
C611—C111—C211	116.9 (5)	C612—C112—C212	118.3 (5)
C611—C111—C11	123.7 (5)	C612—C112—C12	123.9 (5)
C211—C111—C11	119.2 (5)	C212—C112—C12	117.8 (5)
C311—C211—C111	122.4 (6)	C312—C212—C112	121.5 (5)

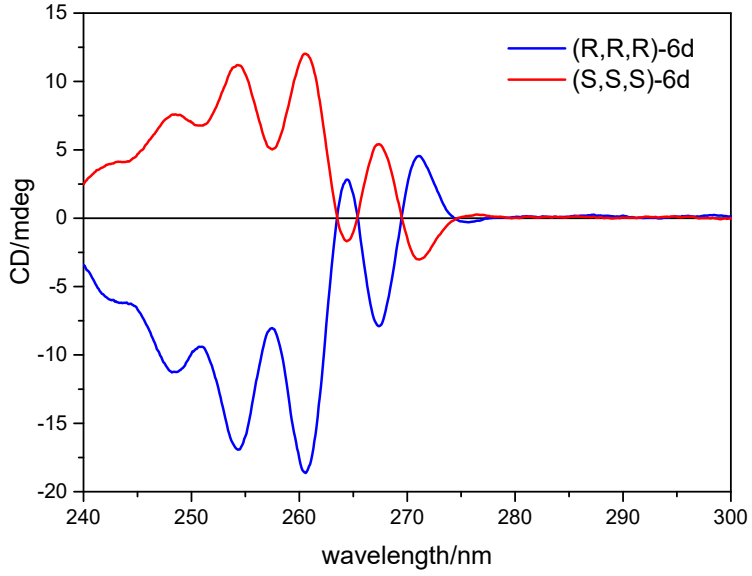
C411—C311—C211	119.4 (6)	C212—C312—C412	120.1 (5)
C311—C411—C511	121.1 (6)	C512—C412—C312	118.6 (5)
C411—C511—C611	120.0 (5)	C412—C512—C612	121.4 (5)
C111—C611—C511	120.3 (5)	C112—C612—C512	119.9 (5)
C621—C121—C221	118.5 (5)	C222—C122—C622	120.1 (5)
C621—C121—C11	120.5 (5)	C222—C122—C12	120.6 (5)
C221—C121—C11	120.8 (5)	C622—C122—C12	119.3 (5)
C321—C221—C121	120.4 (6)	C122—C222—C322	118.8 (5)
C221—C321—C421	120.4 (6)	C422—C322—C222	120.9 (6)
C521—C421—C321	119.8 (6)	C322—C422—C522	120.6 (5)
C421—C521—C621	120.3 (6)	C422—C522—C622	119.2 (6)
C521—C621—C121	120.6 (6)	C122—C622—C522	120.3 (5)
C641—C141—C241	120.3 (5)	C642—C142—C242	118.8 (5)
C641—C141—C41	118.8 (5)	C642—C142—C42	119.5 (5)
C241—C141—C41	120.8 (5)	C242—C142—C42	121.6 (5)
C341—C241—C141	119.8 (5)	C342—C242—C142	120.2 (5)
C441—C341—C241	119.9 (5)	C442—C342—C242	120.0 (6)
C341—C441—C541	120.6 (6)	C342—C442—C542	120.2 (6)
C641—C541—C441	119.4 (6)	C442—C542—C642	120.2 (6)
C541—C641—C141	119.9 (5)	C542—C642—C142	120.5 (5)
C251—C151—C651	119.6 (5)	C652—C152—C252	119.0 (5)
C251—C151—C41	118.9 (5)	C652—C152—C42	121.8 (5)
C651—C151—C41	121.4 (5)	C252—C152—C42	119.1 (5)
C151—C251—C351	120.7 (5)	C352—C252—C152	120.2 (5)
C451—C351—C251	119.4 (6)	C252—C352—C452	119.7 (5)
C551—C451—C351	119.3 (6)	C552—C452—C352	120.3 (5)
C451—C551—C651	120.9 (6)	C452—C552—C652	119.2 (6)
C551—C651—C151	120.1 (5)	C152—C652—C552	121.6 (5)
C281—C181—C681	119.0 (6)	C682—C182—C282	117.8 (6)
C281—C181—C81	119.5 (5)	C682—C182—C82	122.4 (5)
C681—C181—C81	121.4 (5)	C282—C182—C82	119.8 (6)
C181—C281—C381	121.0 (6)	C382—C282—C182	121.3 (6)

C481—C381—C281	119.4 (6)	C482—C382—C282	119.9 (6)
C581—C481—C381	120.5 (7)	C382—C482—C582	120.6 (6)
C481—C581—C681	120.1 (7)	C682—C582—C482	118.9 (6)
C181—C681—C581	120.0 (6)	C582—C682—C182	121.5 (6)
C610—C110—C210	118.4 (5)	C692—C192—C292	118.9 (5)
C610—C110—C101	118.9 (6)	C692—C192—C102	118.5 (5)
C210—C110—C101	122.7 (5)	C292—C192—C102	122.5 (5)
C310—C210—C110	120.7 (6)	C392—C292—C192	119.8 (5)
C210—C310—C410	120.4 (7)	C292—C392—C492	121.3 (6)
C510—C410—C310	118.8 (6)	C392—C492—C592	119.1 (5)
C410—C510—C610	120.8 (6)	C692—C592—C492	120.1 (5)
C110—C610—C510	120.9 (7)	C592—C692—C192	120.8 (5)

9. Chiroptical analysis - ECD Measurements.

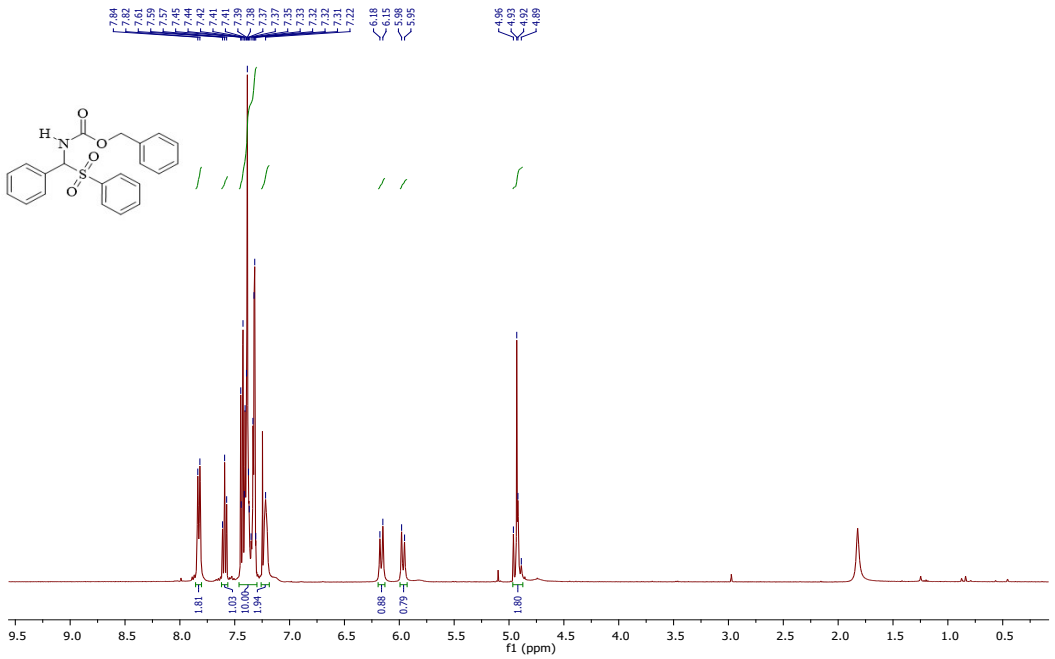
ECD spectra were recorded in the 240–300 nm range with a Jasco J-1500 1500spectropolarimeter (Jasco Inc, USA). Before use, the optical chamber of the CD spectrometer was deoxygenated with dry nitrogen and was held under a nitrogen atmosphere during the measurements. All optical measurements were performed in quartz cell cuvettes with conventional path lengths of 10 mm. The sample solutions in CH_2Cl_2 were of concentration $1 \cdot 10^{-5}$ M.

Figure SI3. ECD spectra of measured for individual (*R,R,R*)-**6d** and (*S,S,S*)-**6d**.

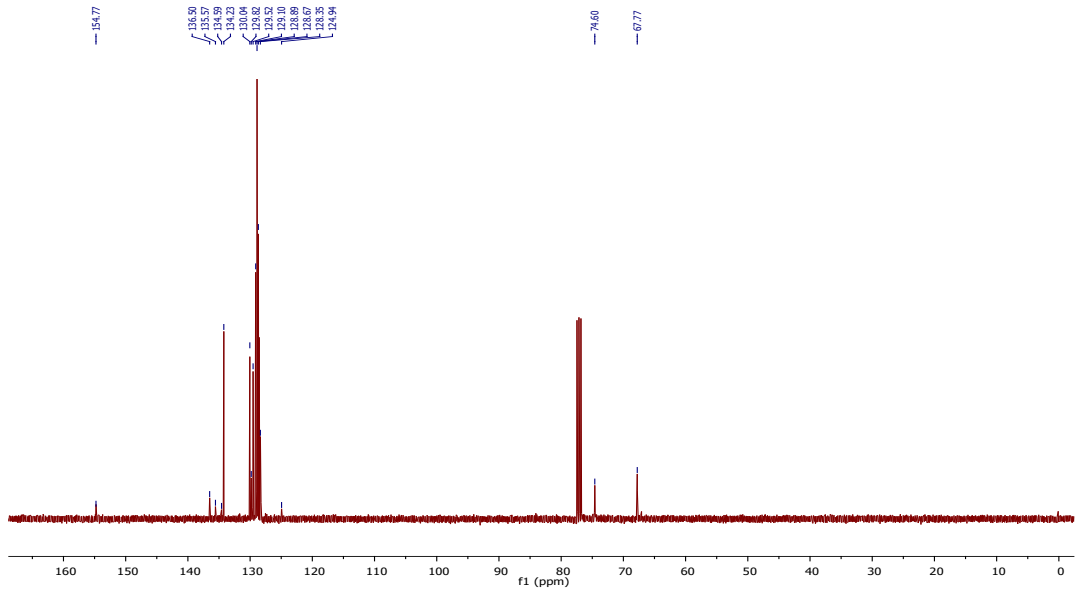


10. NMR spectra

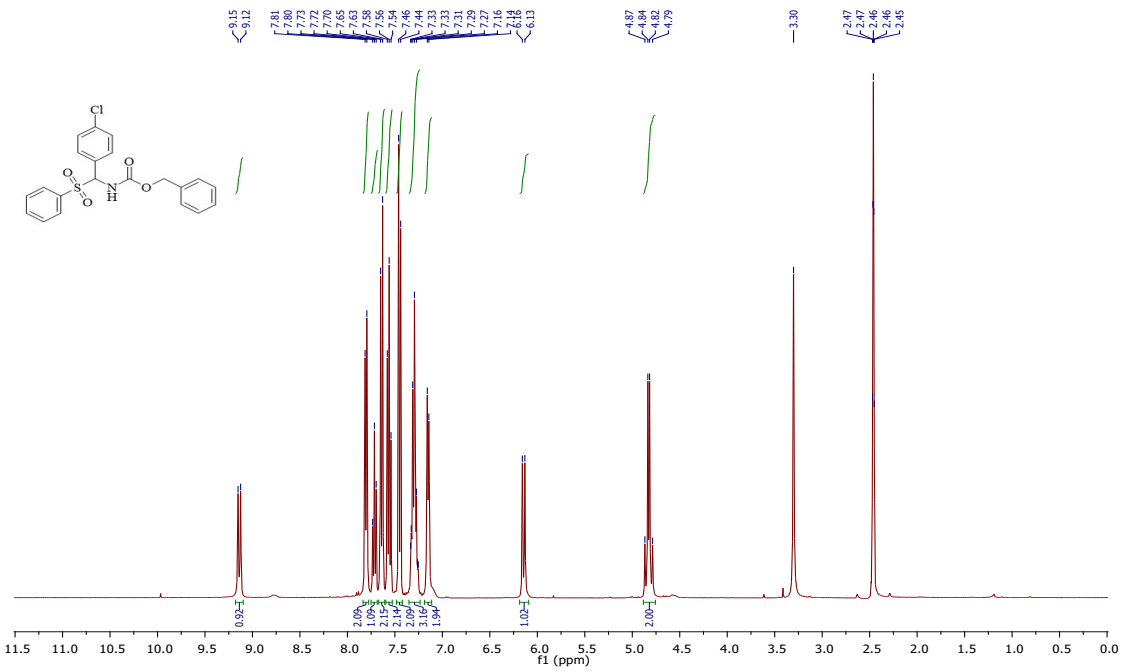
^{1}H NMR spectrum **1a**



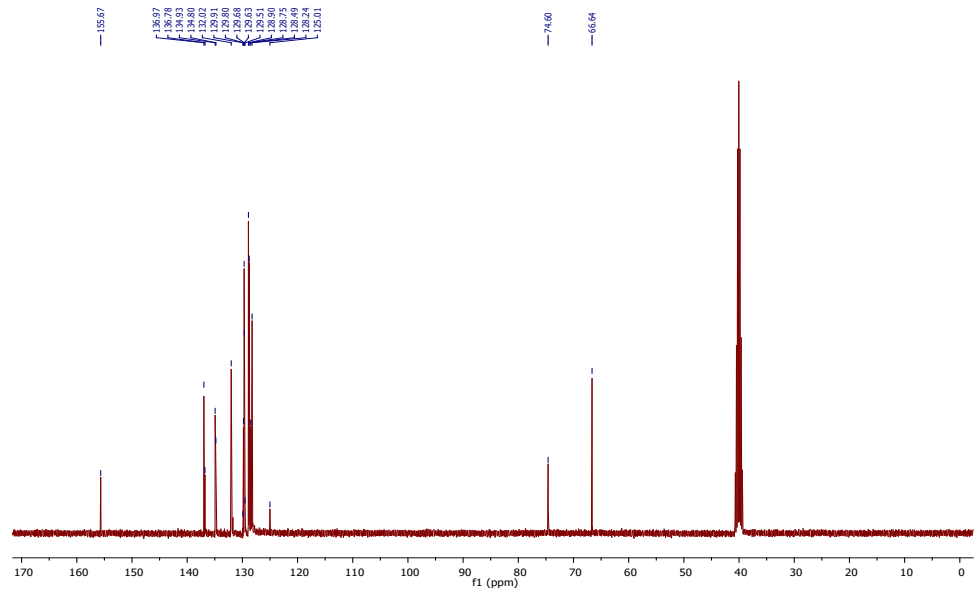
^{13}C NMR spectrum **1a**



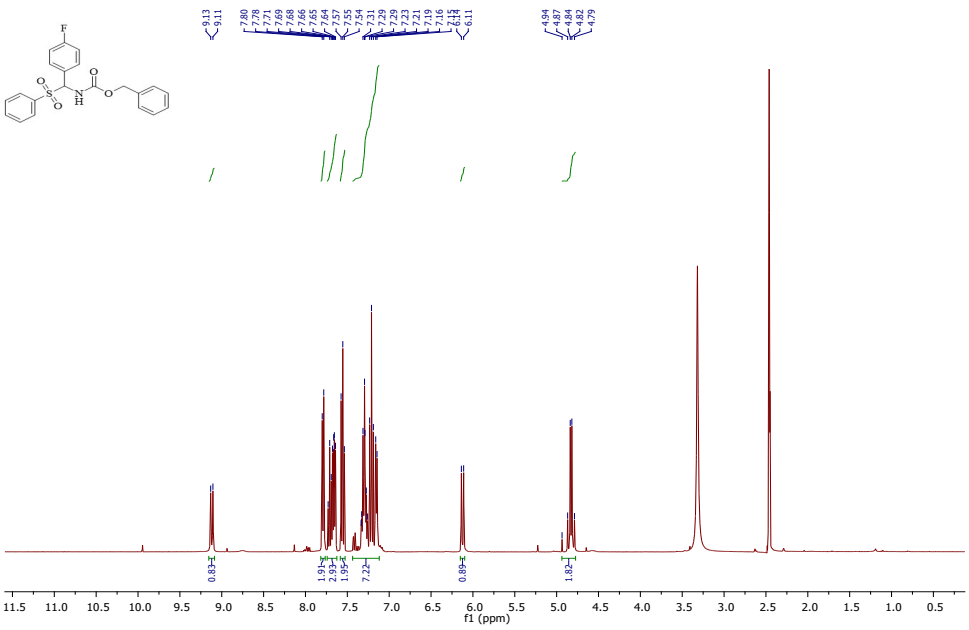
^{1}H NMR spectrum of **1b**



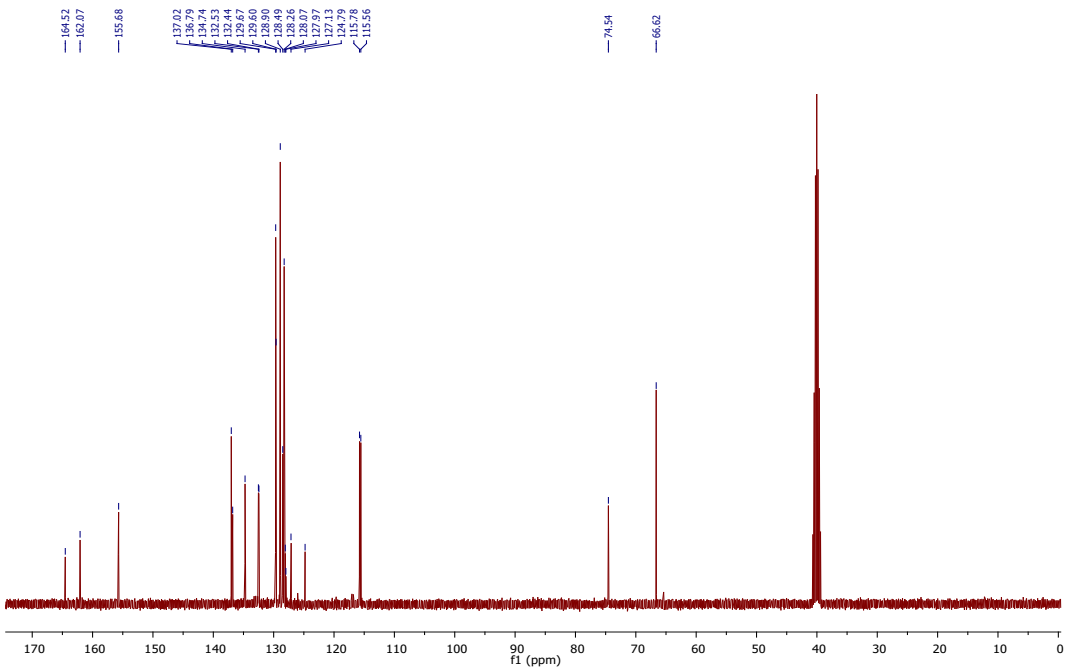
^{13}C NMR spectrum of 1**b**



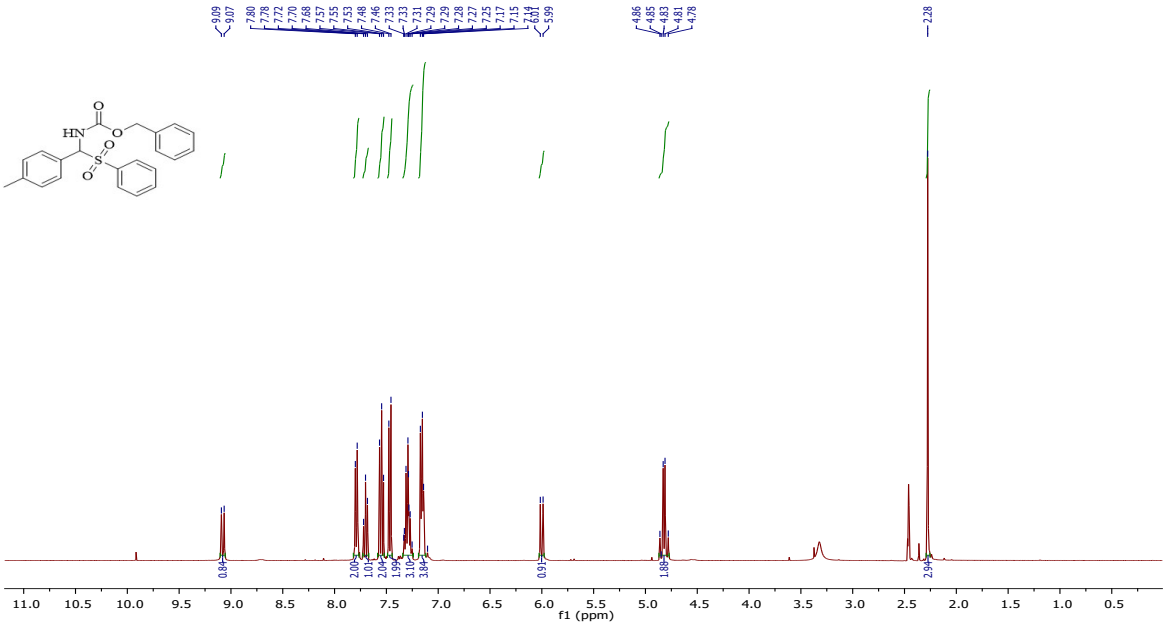
^{1}H NMR spectrum **1c**



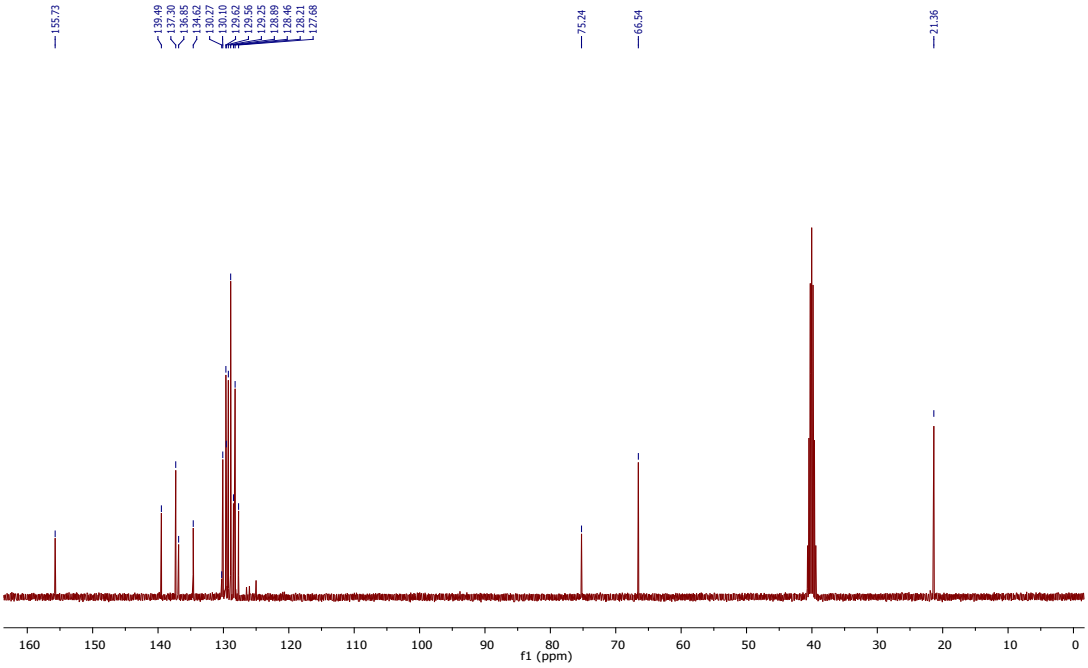
^{13}C NMR spectrum of **1c**



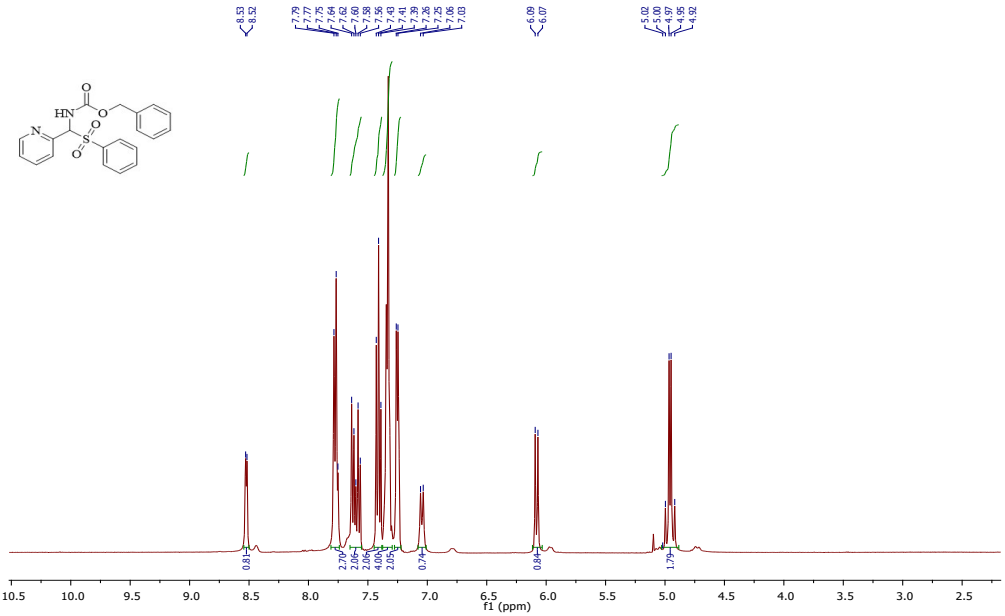
^{1}H NMR spectrum **1d**



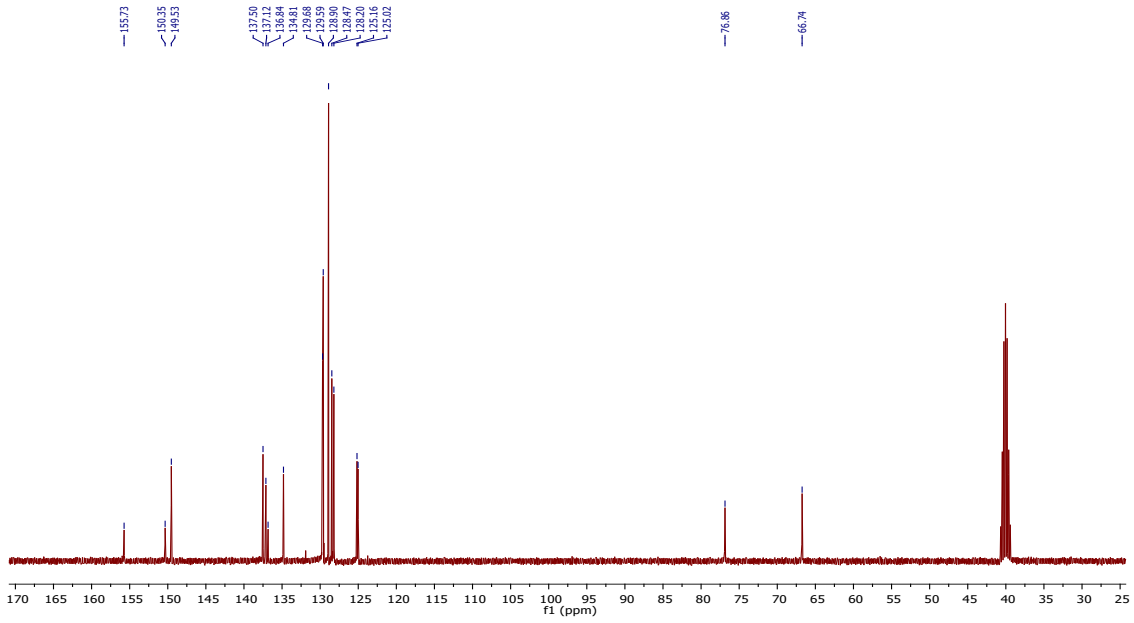
^{13}C NMR spectrum of **1d**



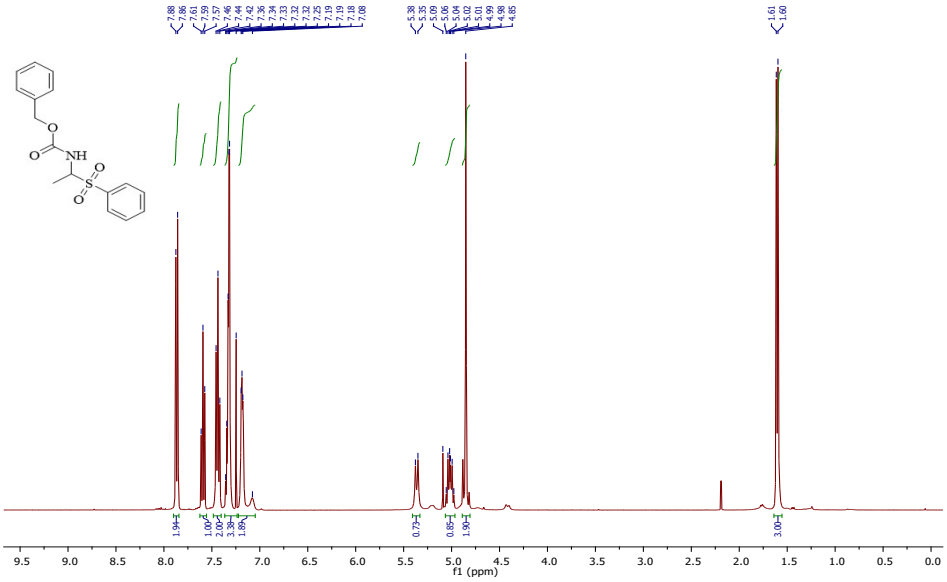
^{1}H NMR spectrum of **1e**



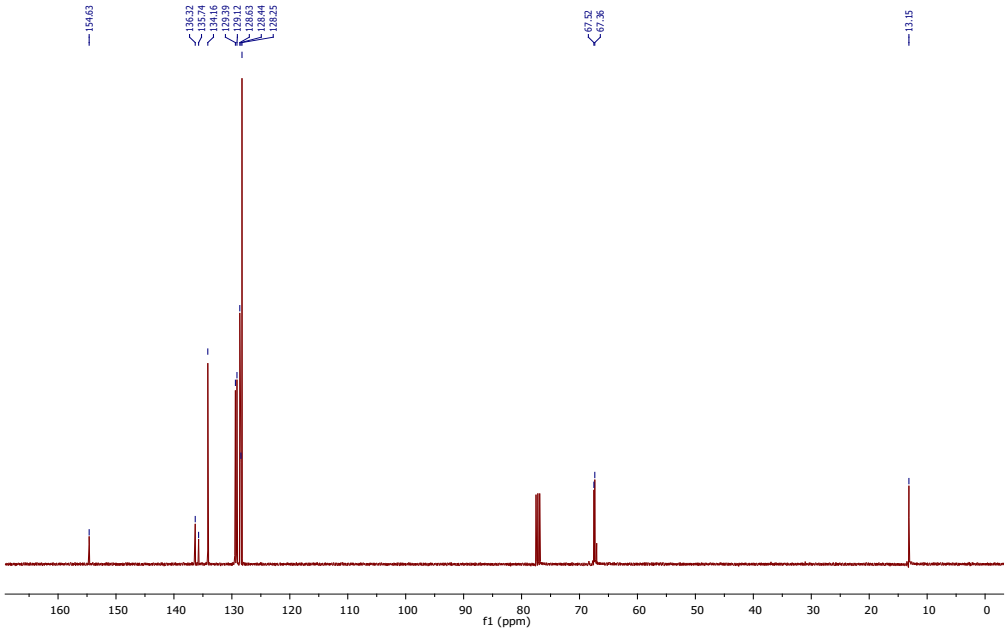
^{13}C NMR spectrum of **2e**



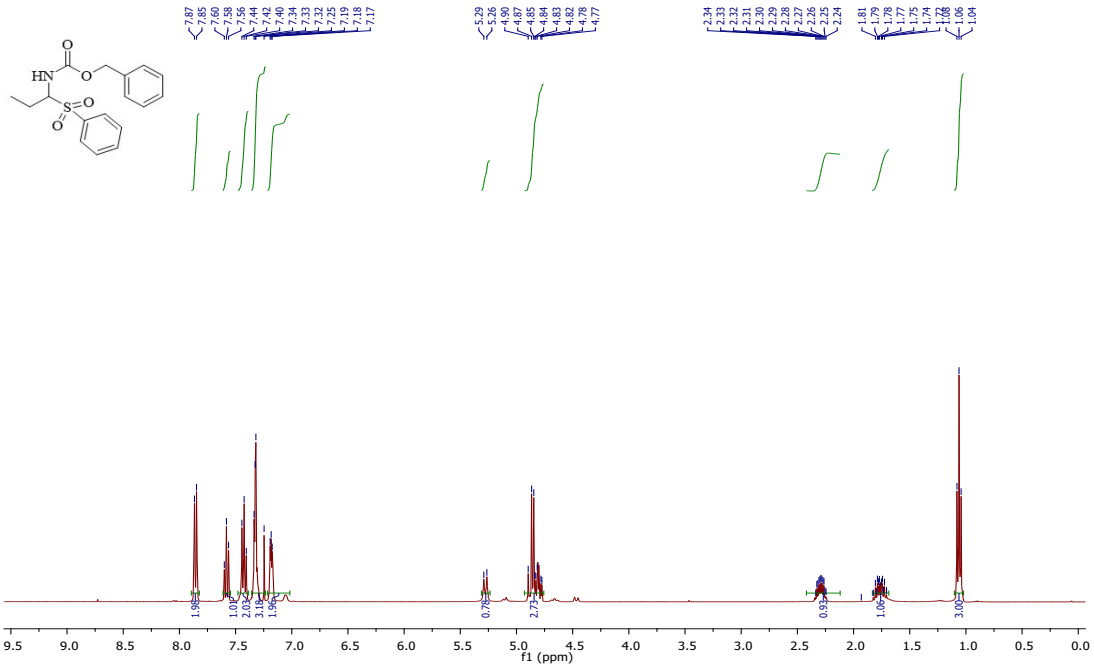
^{1}H NMR spectrum of **1k**



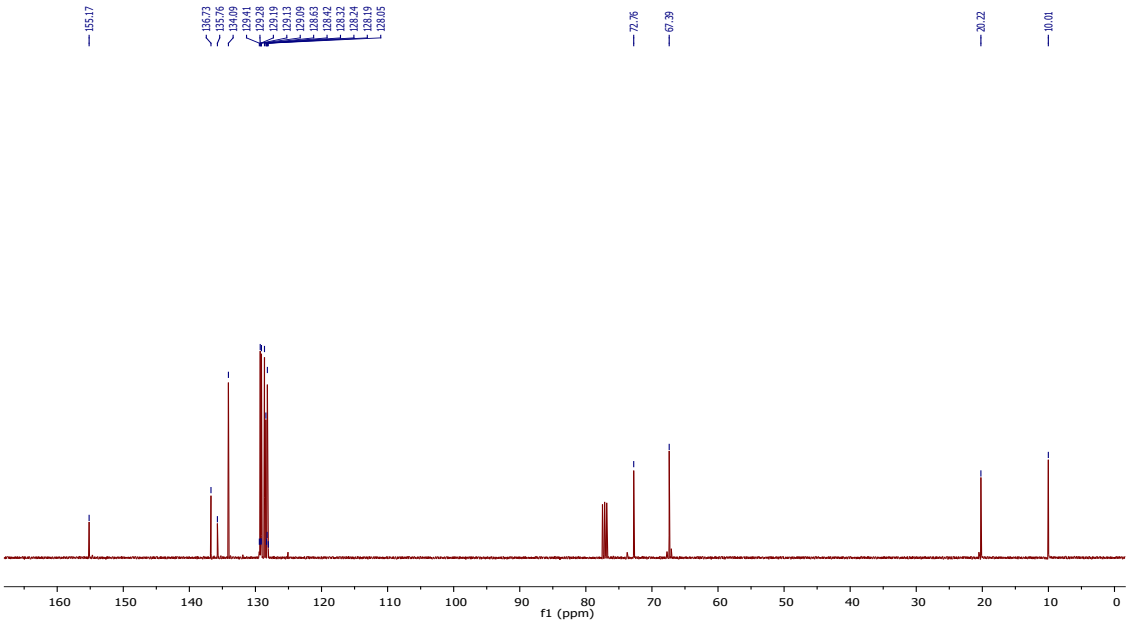
^{13}C NMR spectrum of **1k**



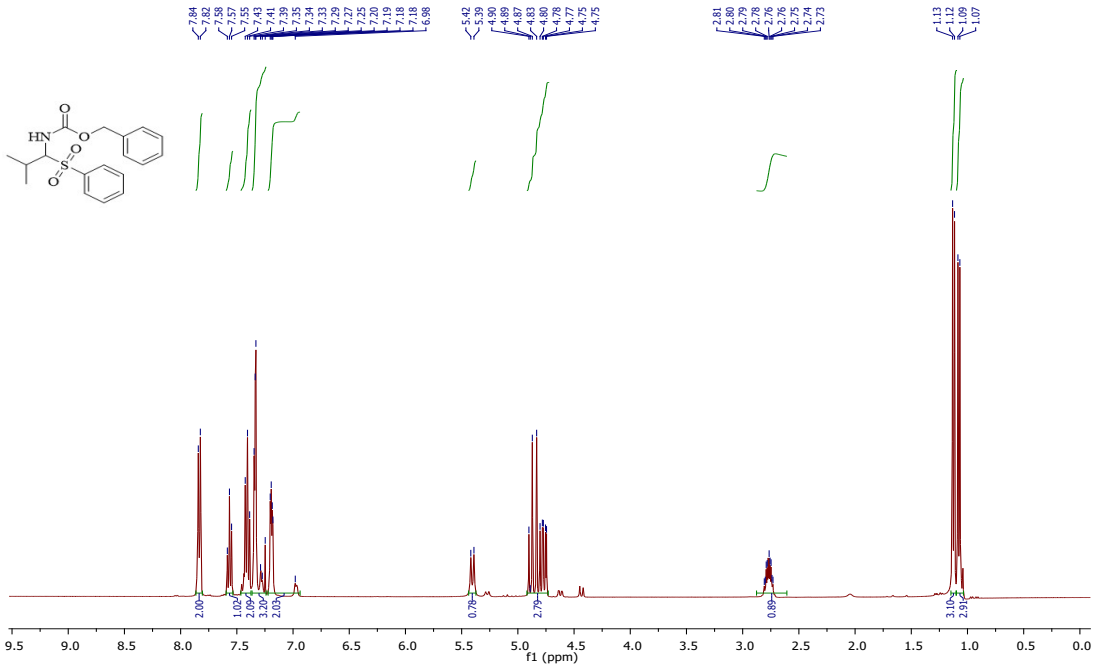
^{1}H NMR spectrum of **1f**



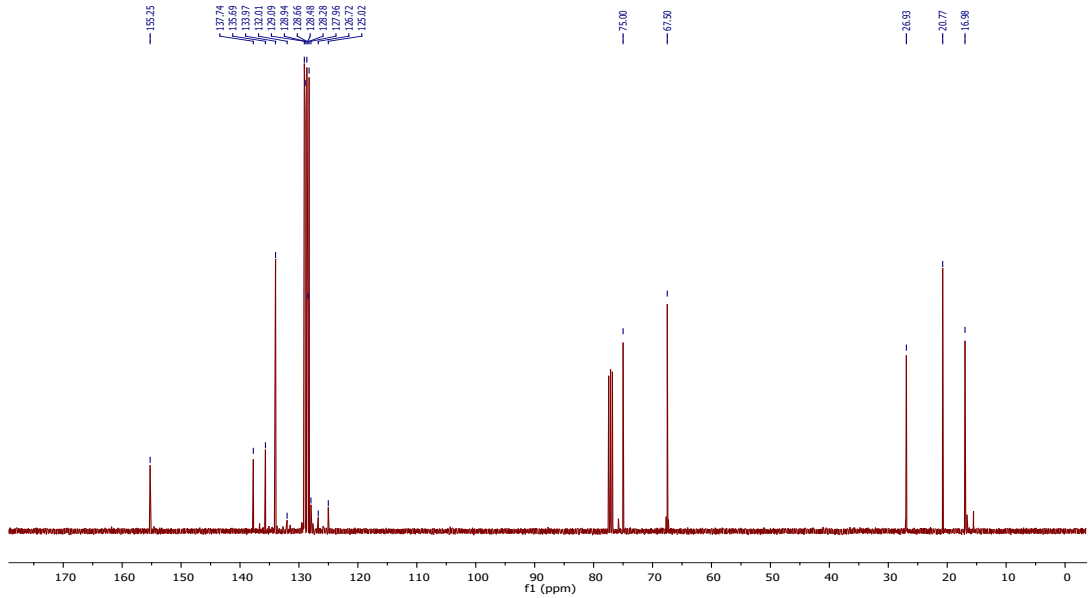
^{13}C NMR spectrum of **1f**



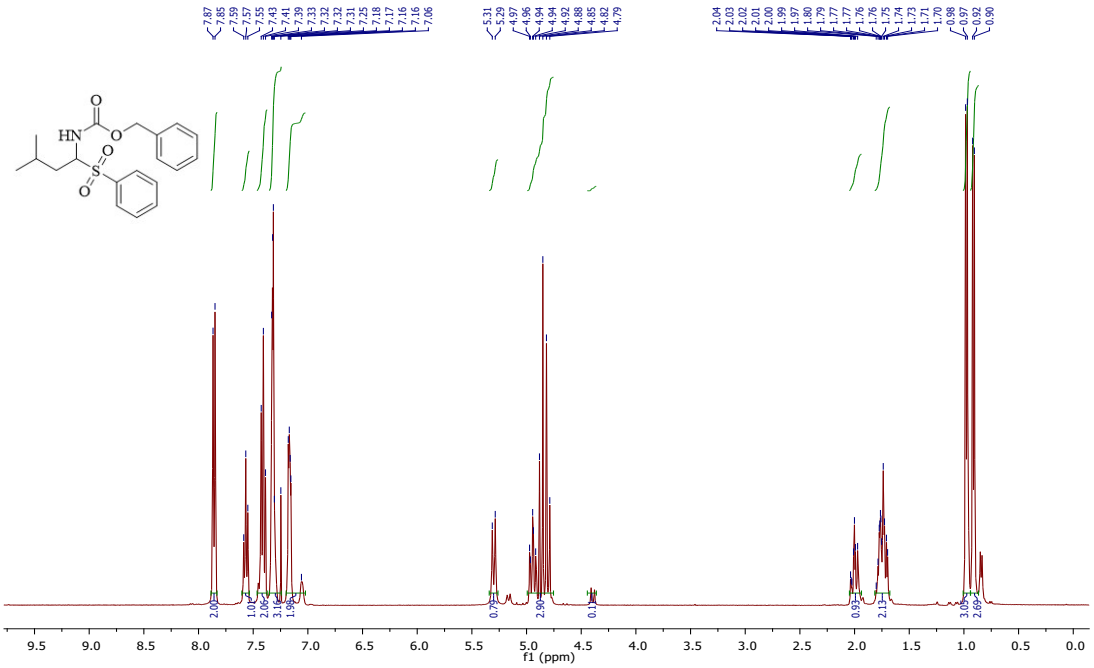
^{1}H NMR spectrum of **1g**



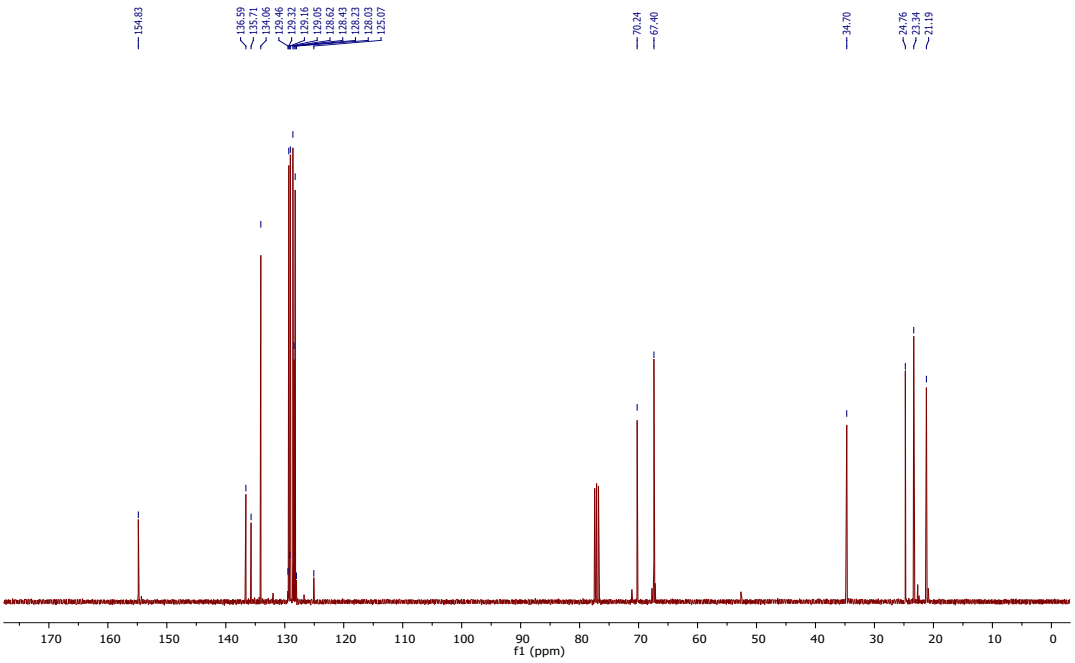
^{13}C NMR spectrum of **1g**



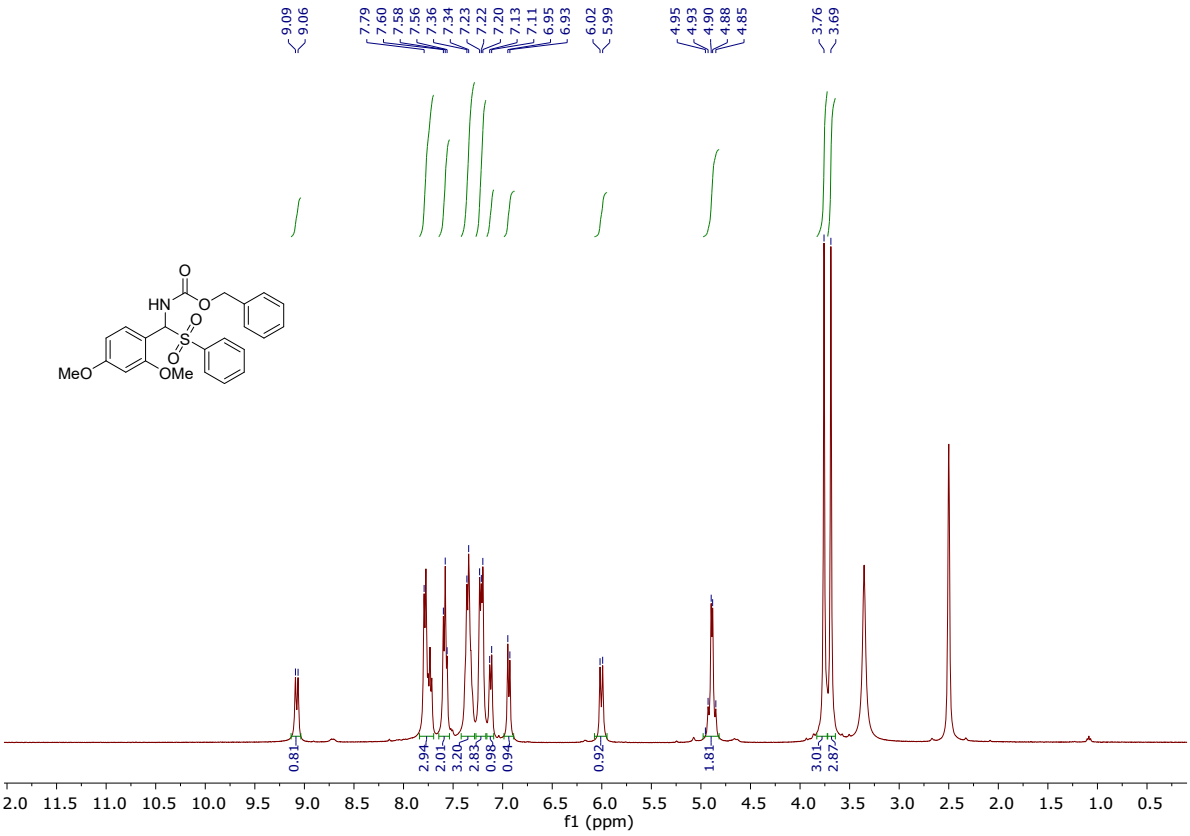
^{1}H NMR spectrum of **1h**



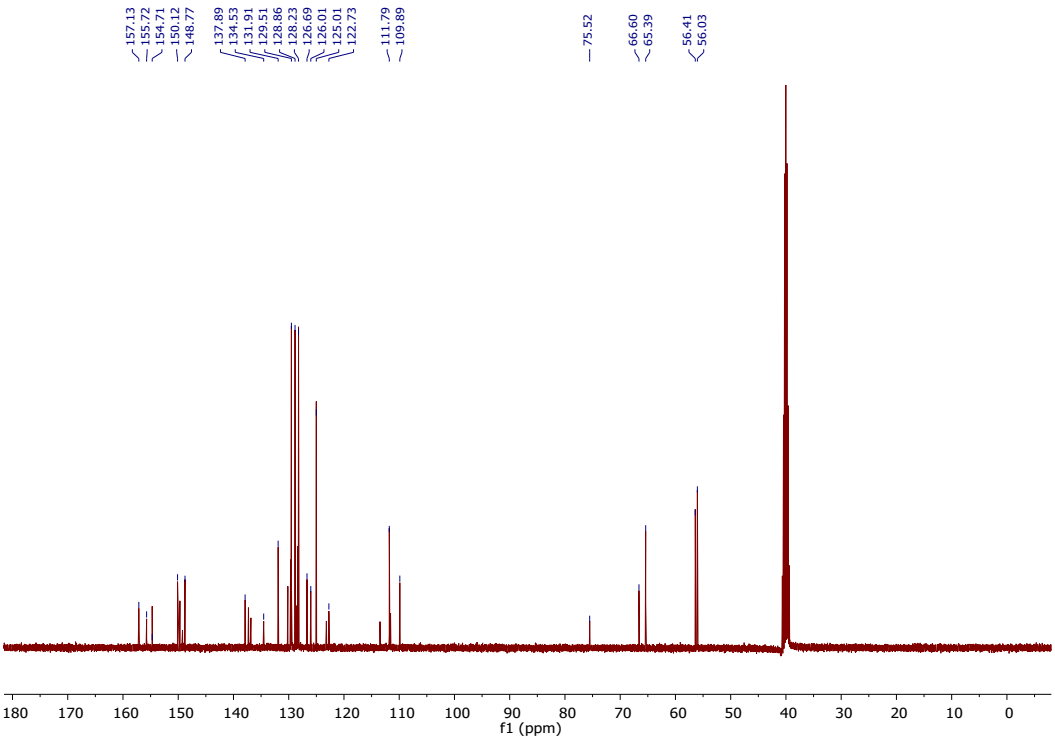
^{13}C NMR spectrum of **1h**



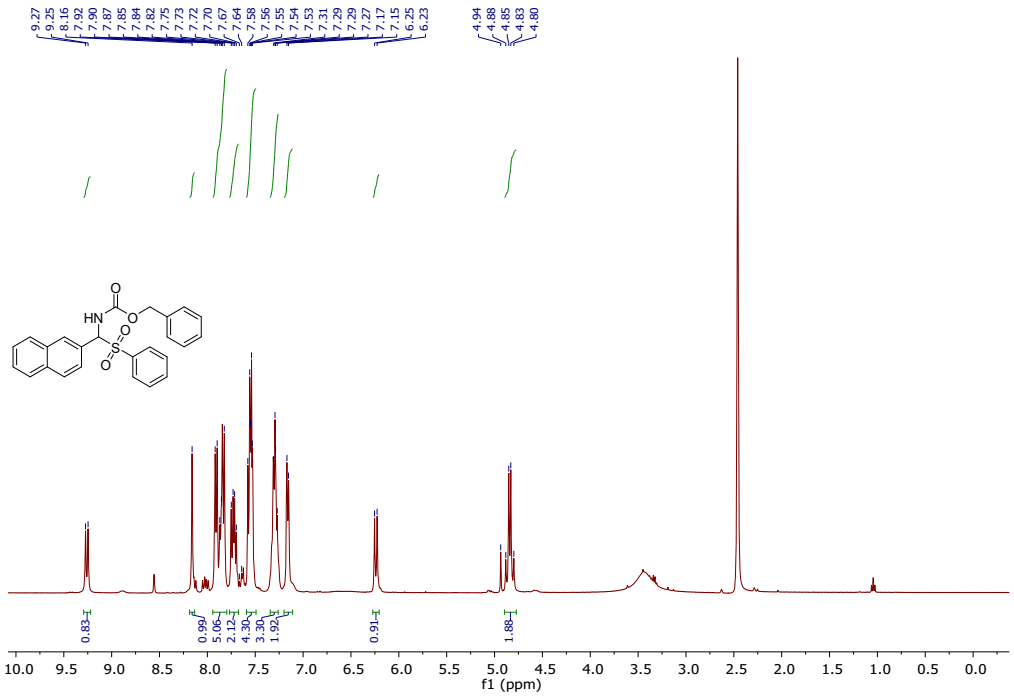
^{1}H NMR spectrum of **1i**



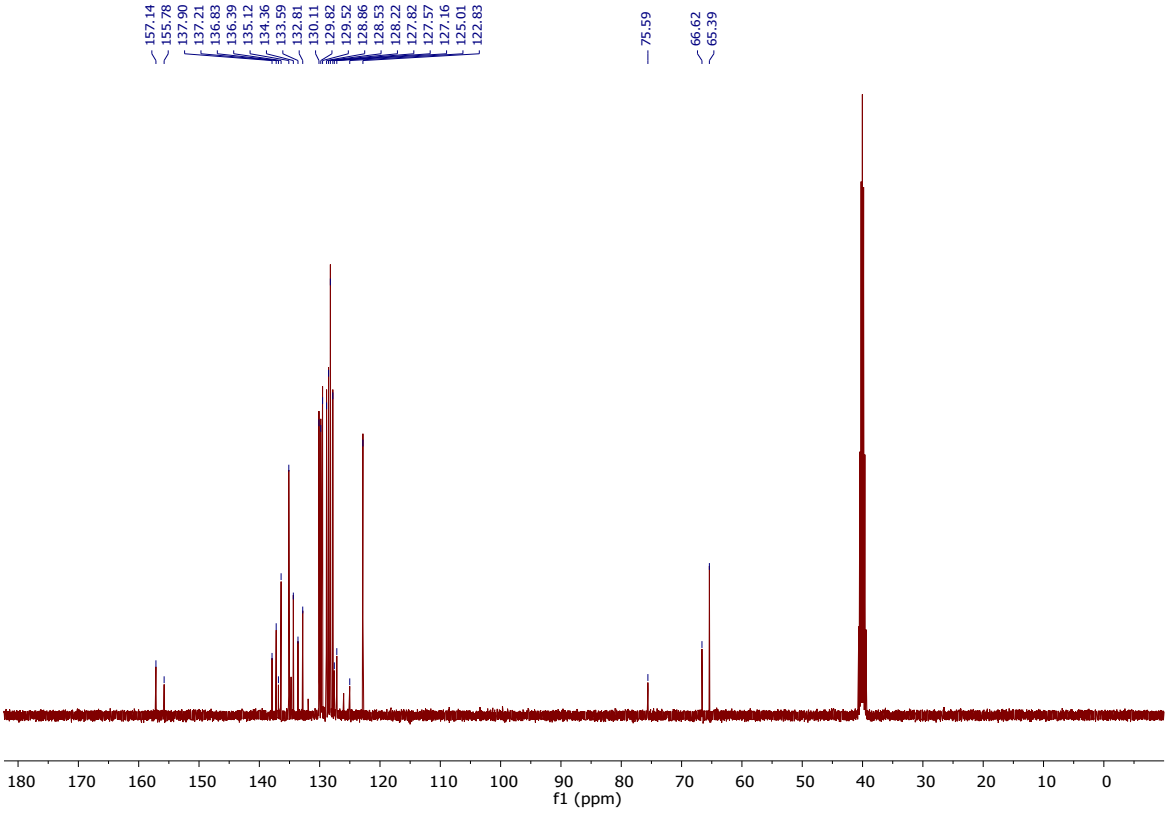
^{13}C NMR spectrum of **1i**



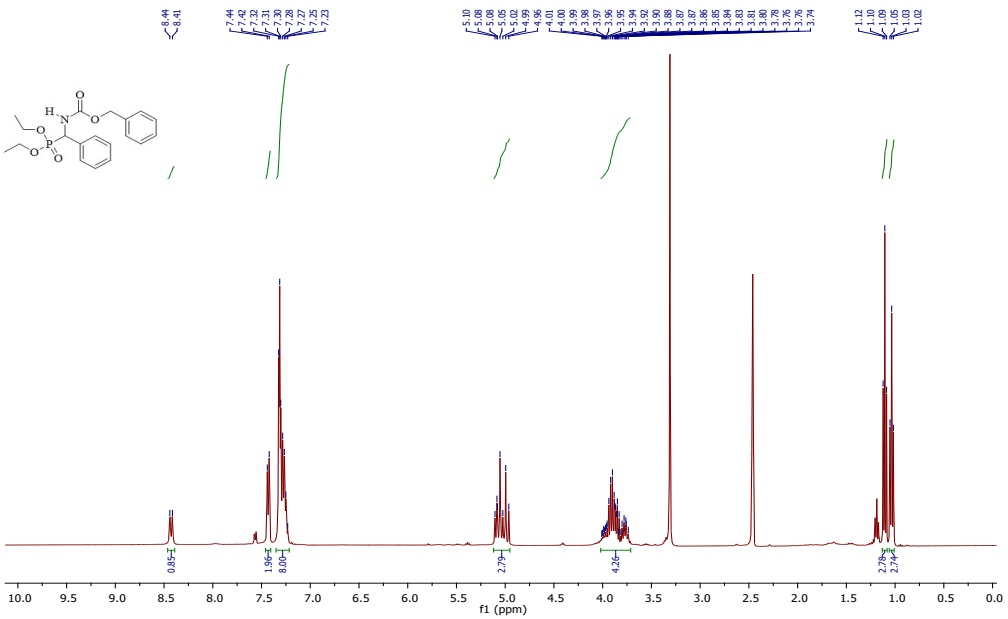
^{1}H NMR spectrum of **1j**



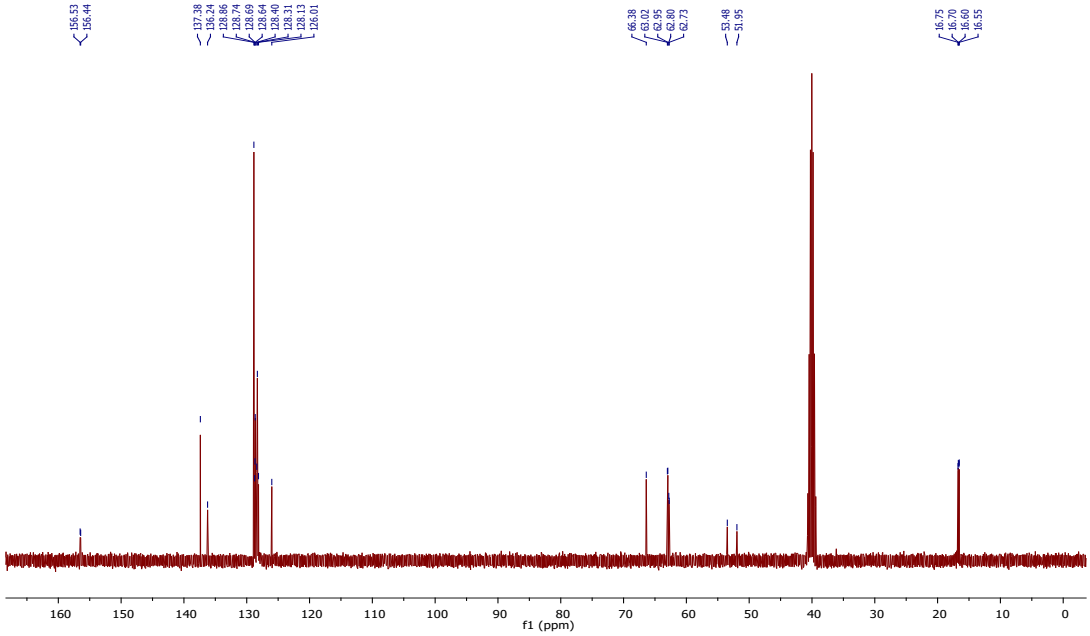
^{13}C NMR spectrum of **1j**



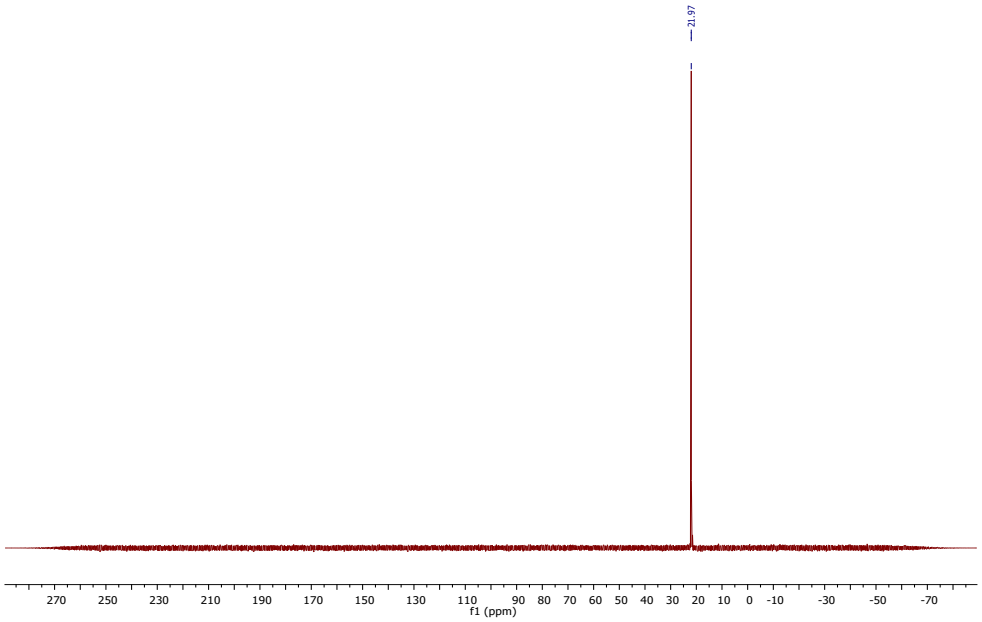
^{1}H NMR spectrum of **3a**



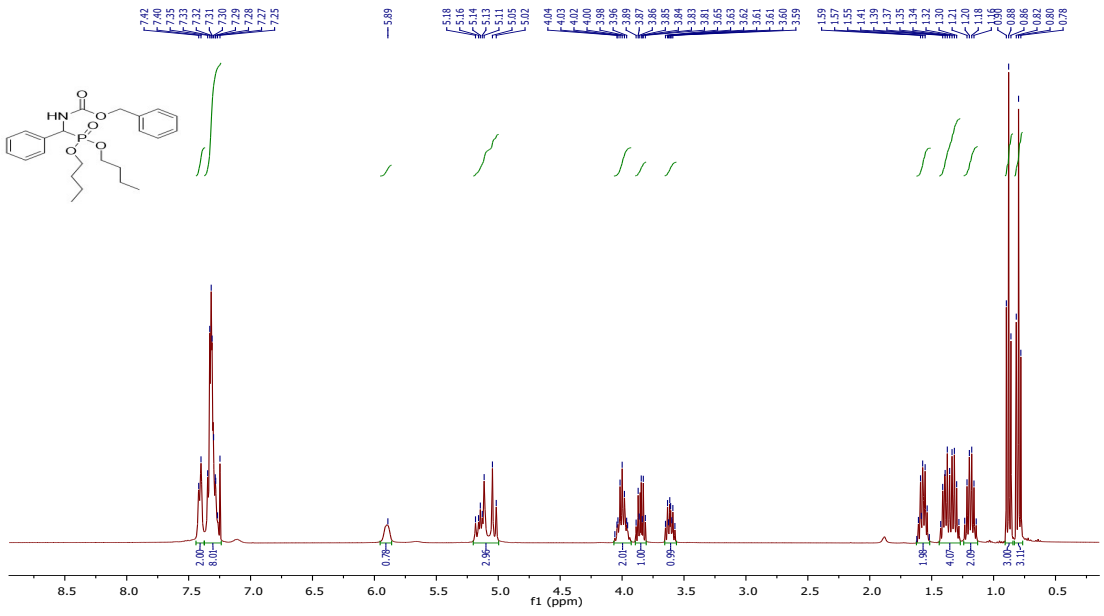
^{13}C NMR spectrum of **3a**



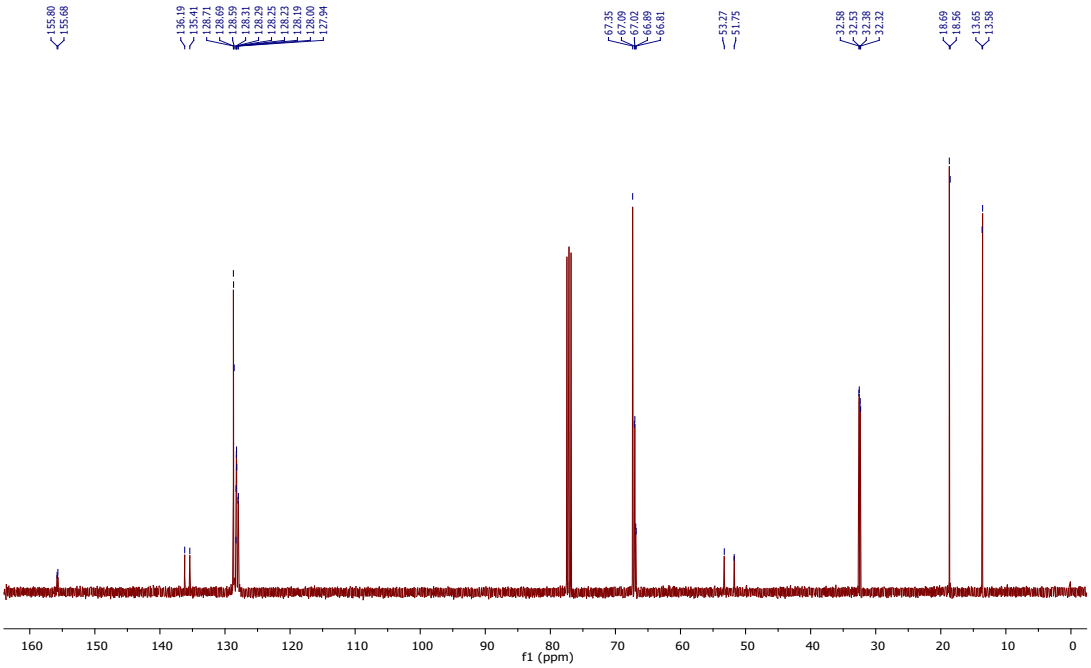
^{31}P NMR spectrum of **3a**



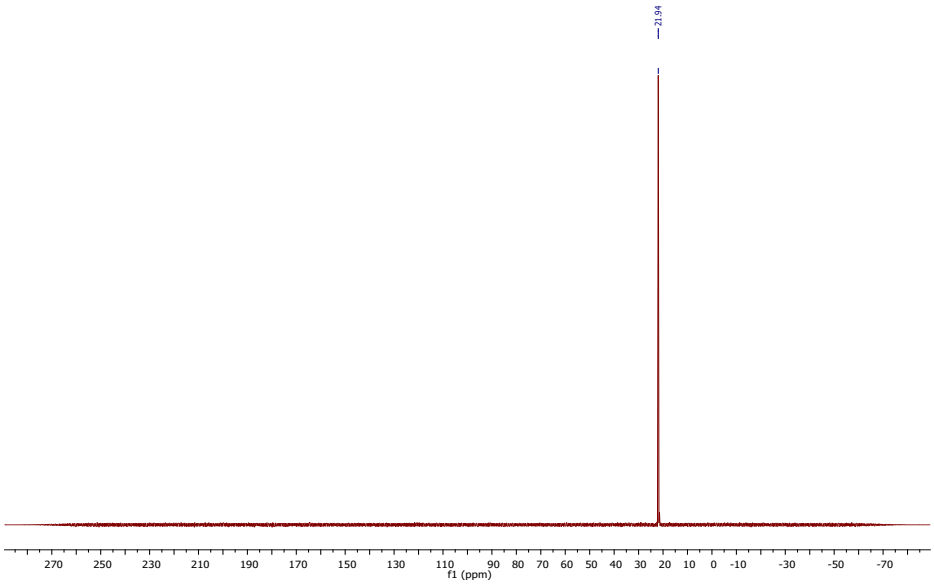
^{1}H NMR spectrum of **3b**



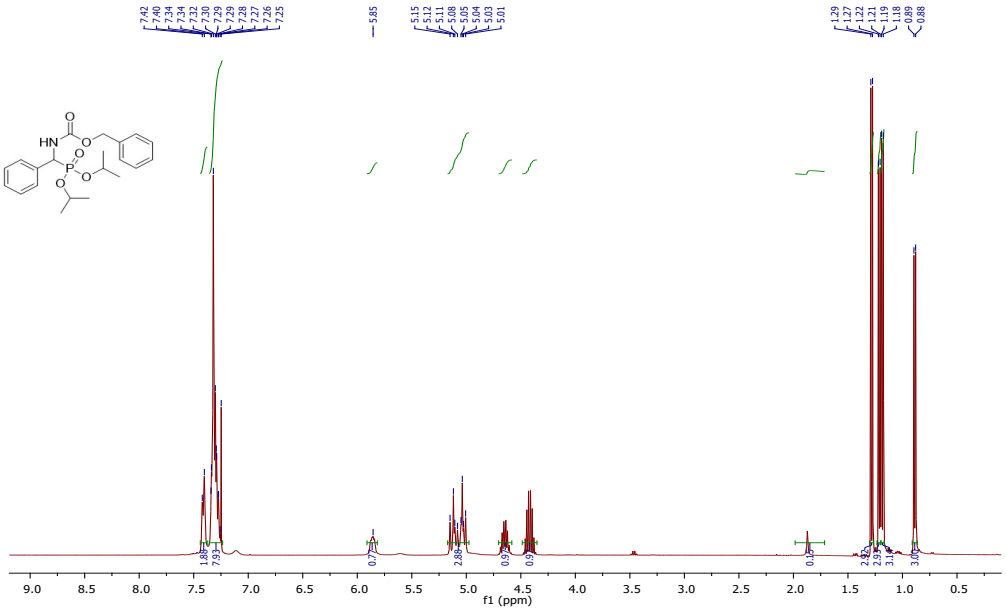
^{13}C NMR spectrum of **3b**



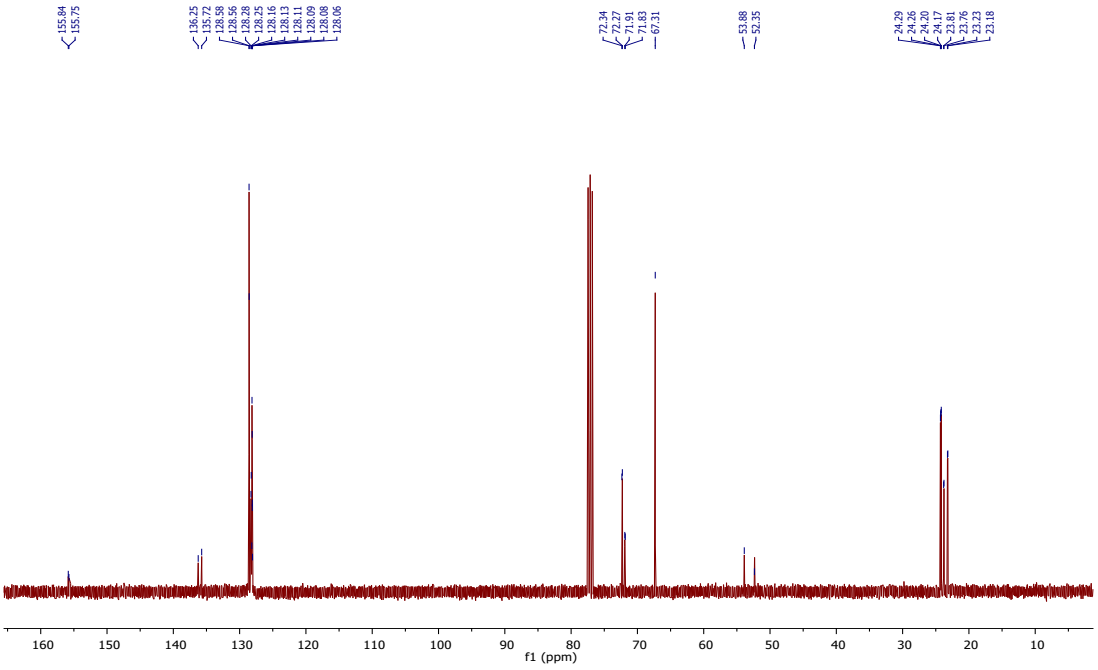
^{31}P NMR spectrum of **3b**



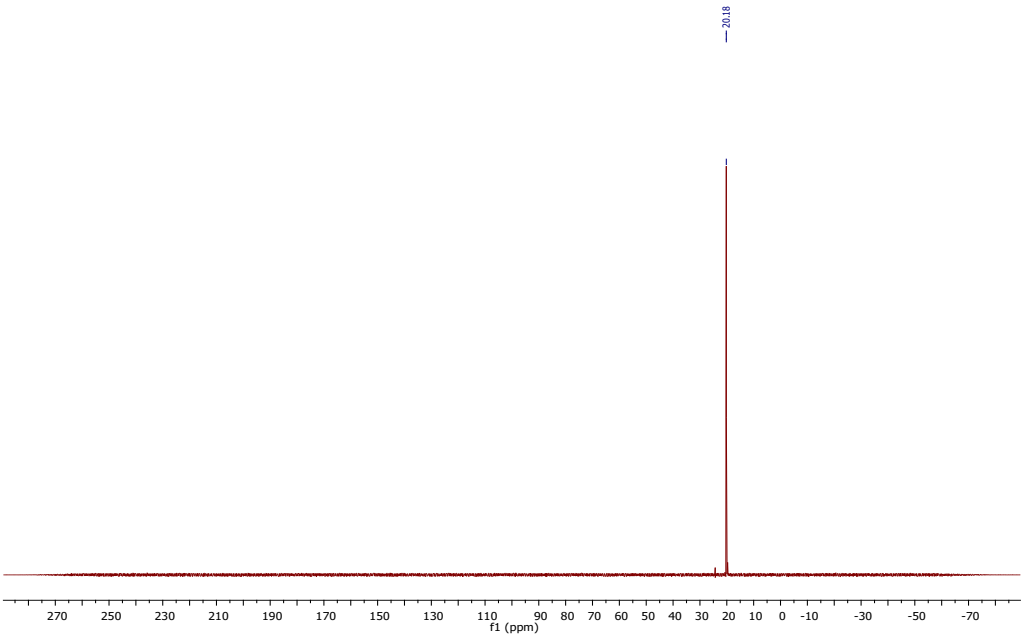
^{1}H NMR spectrum of **3c**



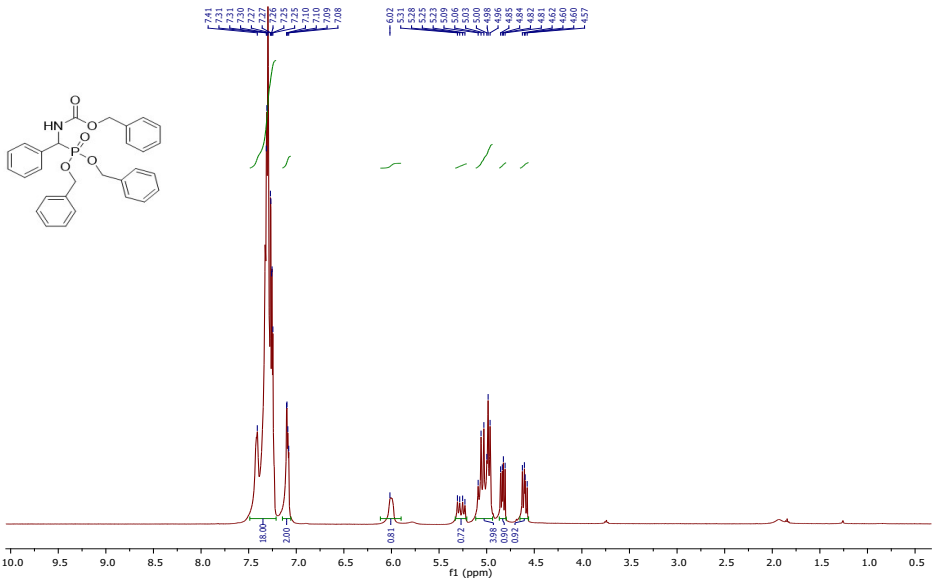
^{13}C NMR spectrum of **3c**



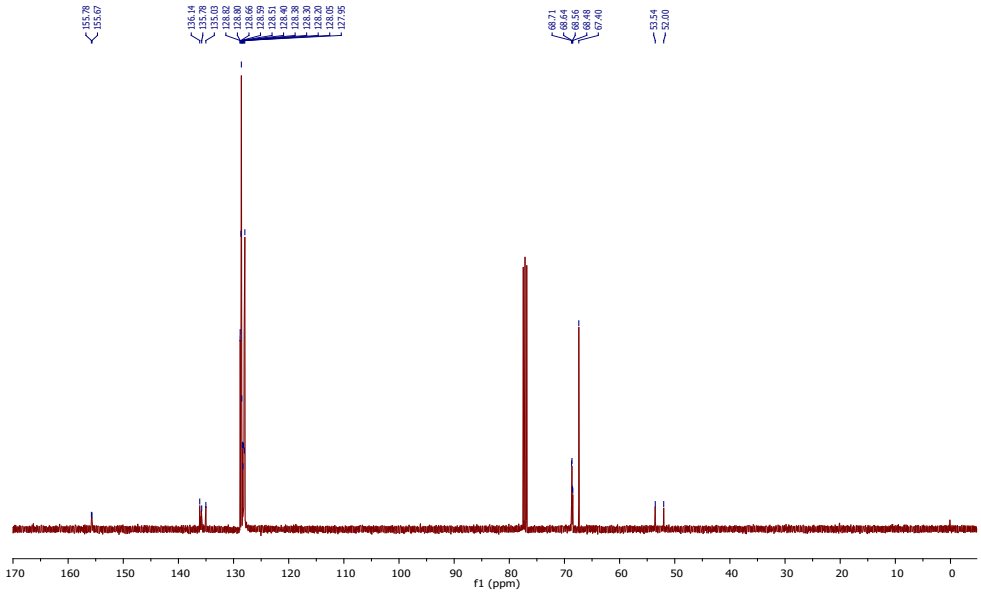
^{31}P NMR spectrum of **3c**



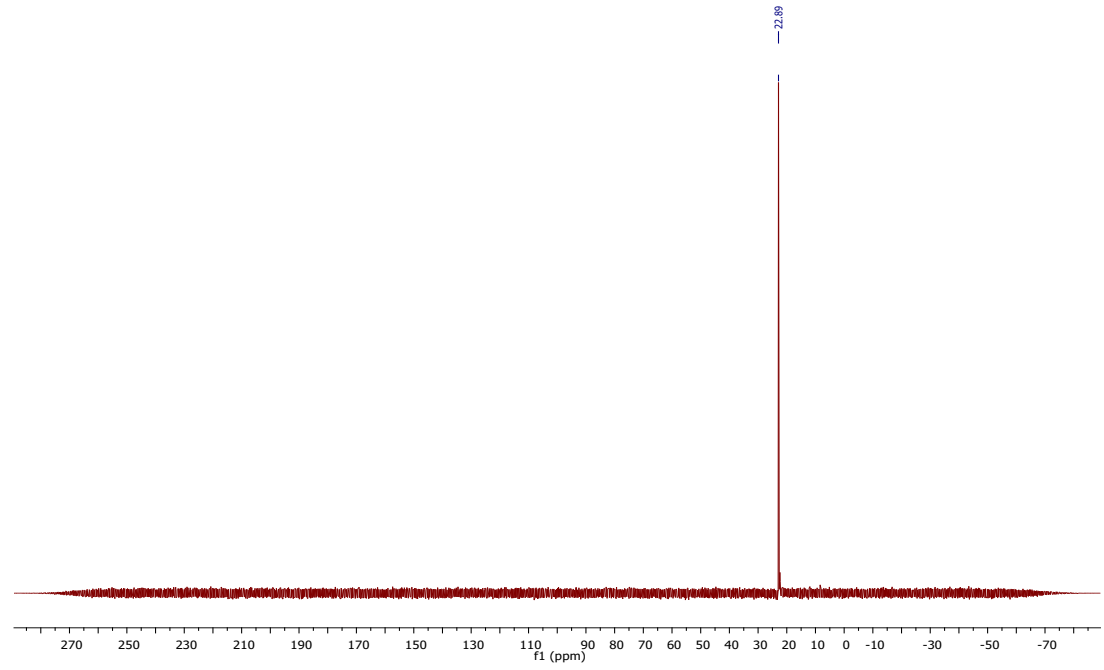
^{1}H NMR spectrum of **3d**



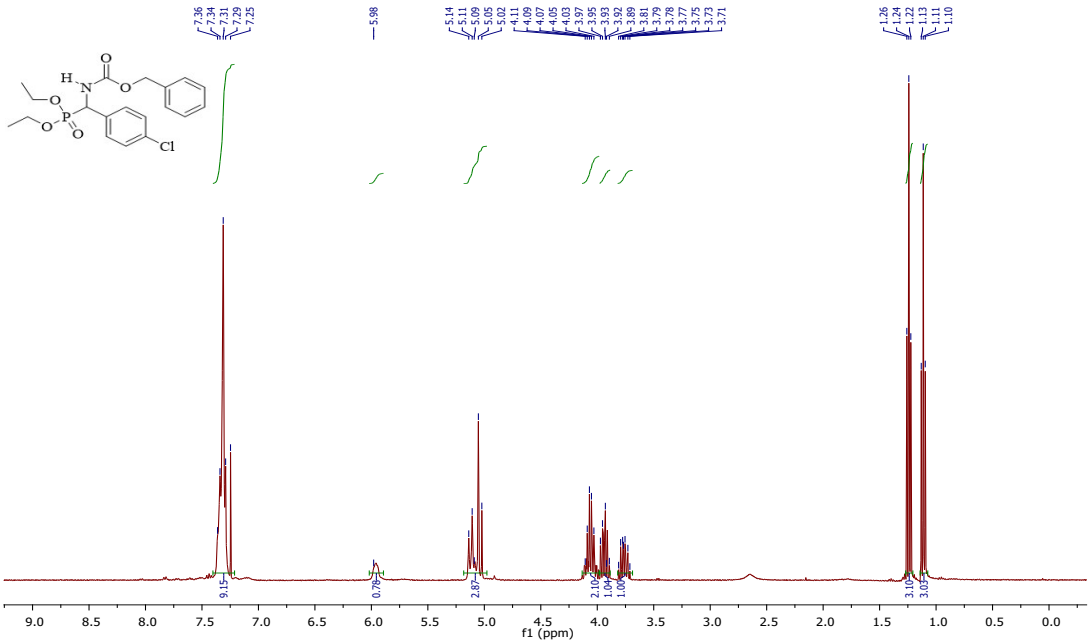
^{13}C NMR spectrum of **3d**



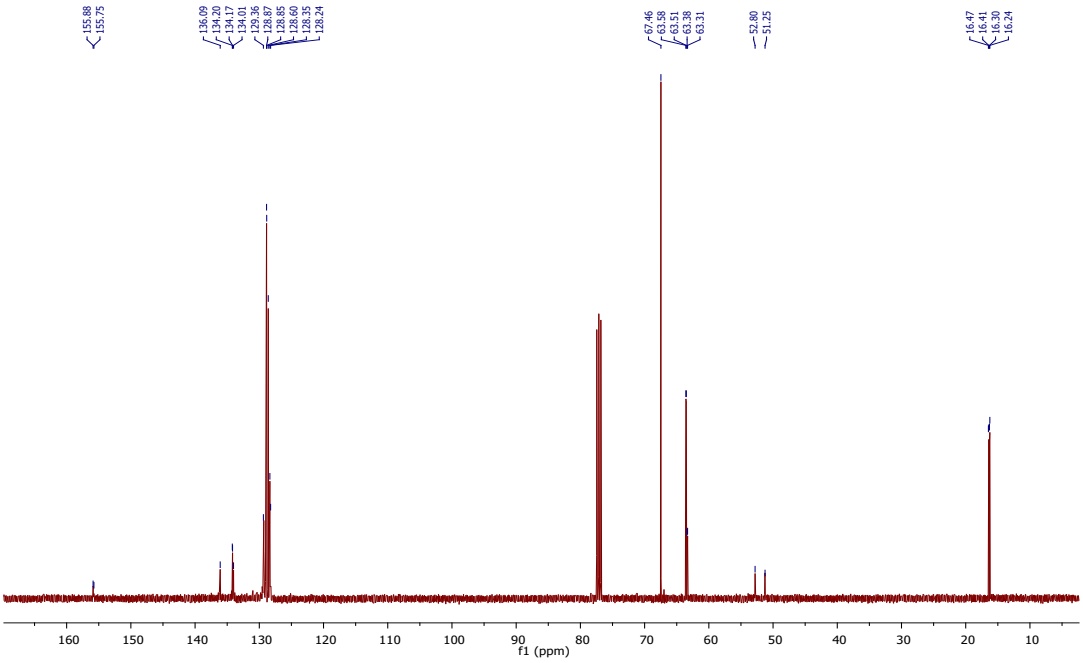
^{31}P NMR spectrum of **3d**



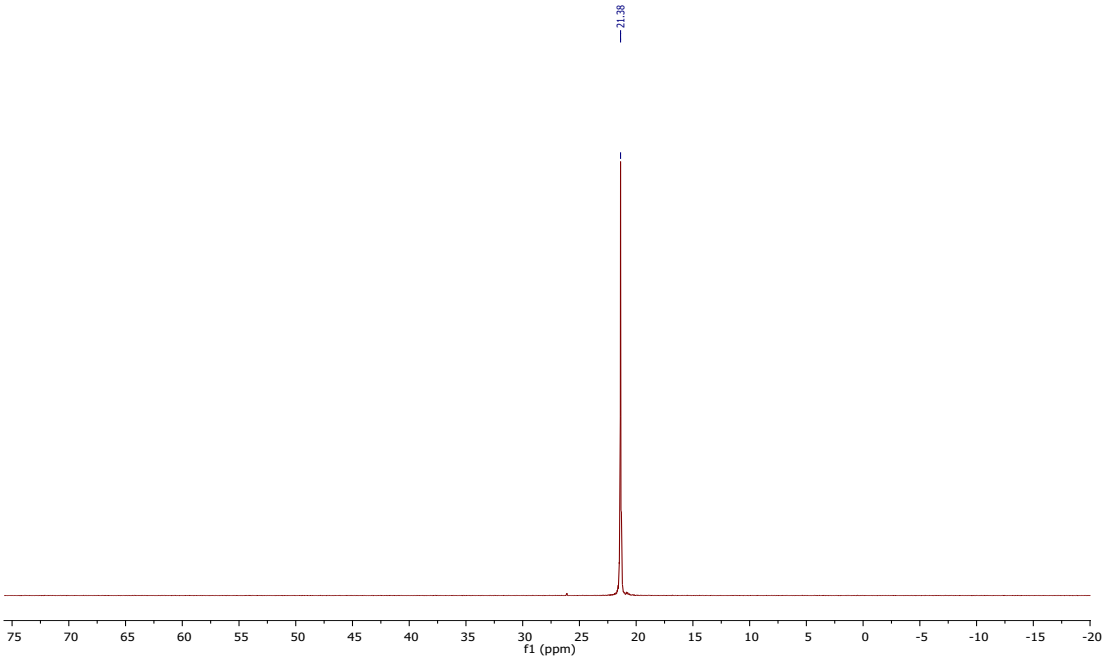
^{1}H NMR spectrum of **3e**



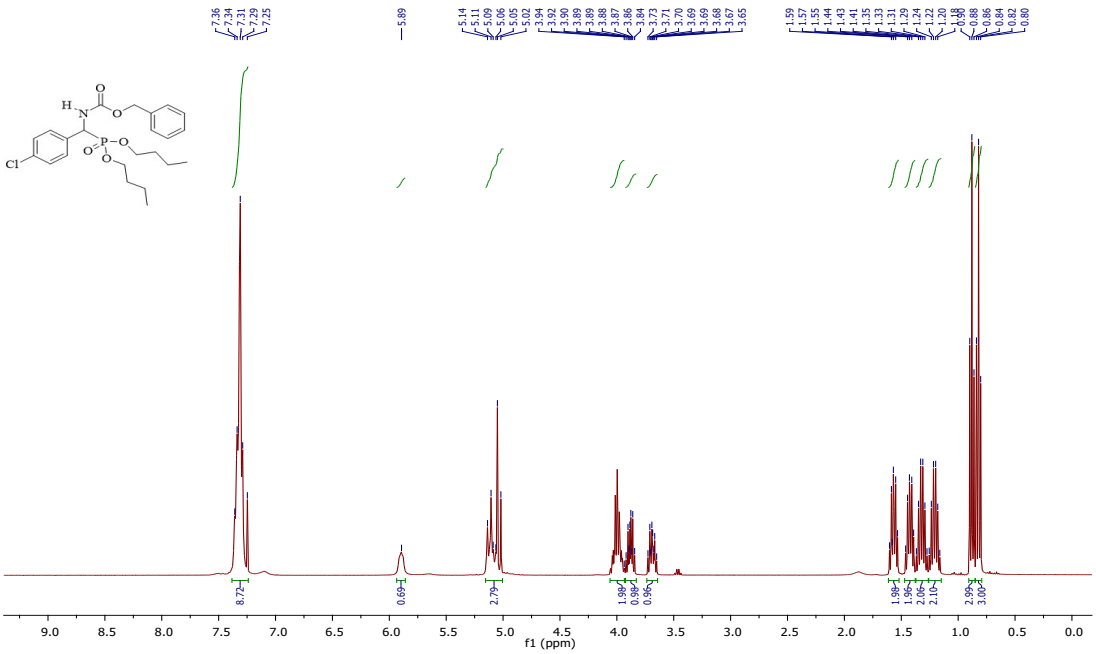
^{13}C NMR spectrum of **3e**



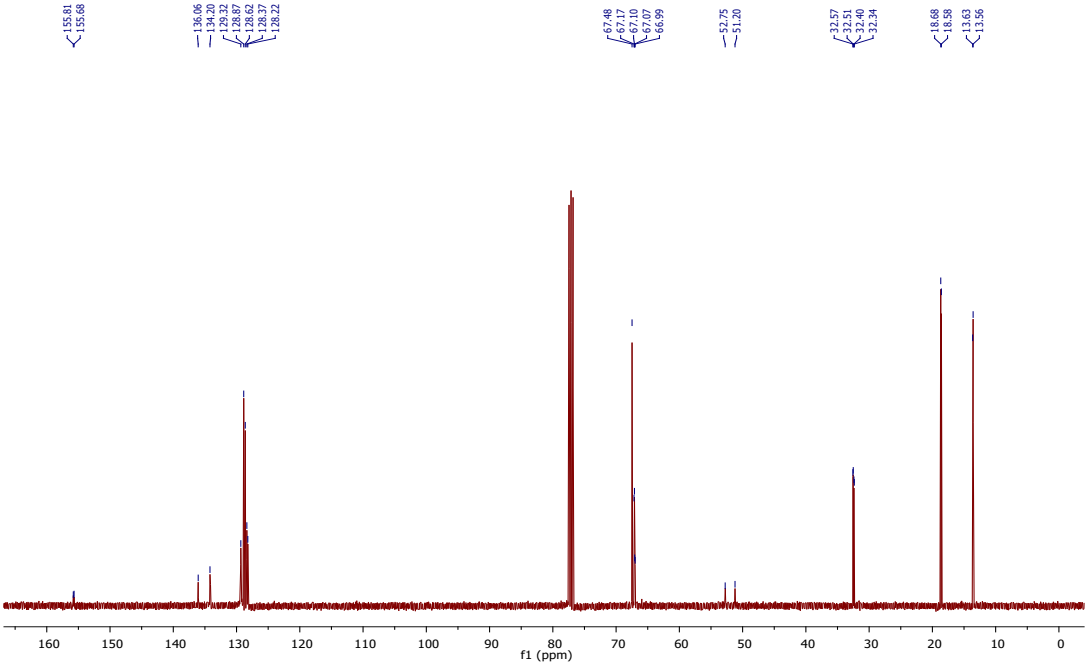
^{31}P NMR spectrum of **3e**



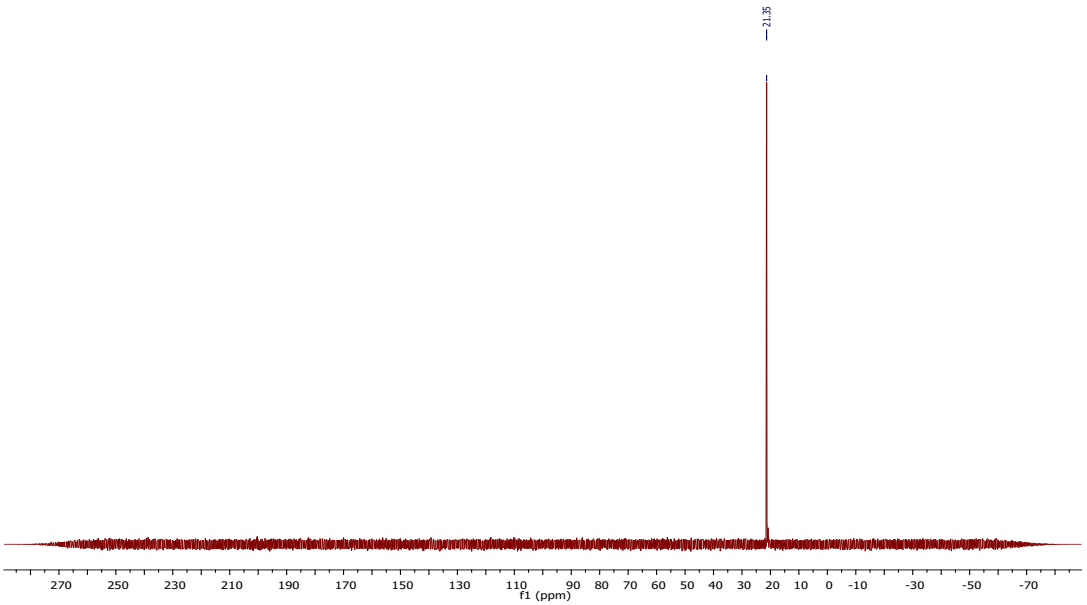
^{1}H NMR spectrum of **3f**



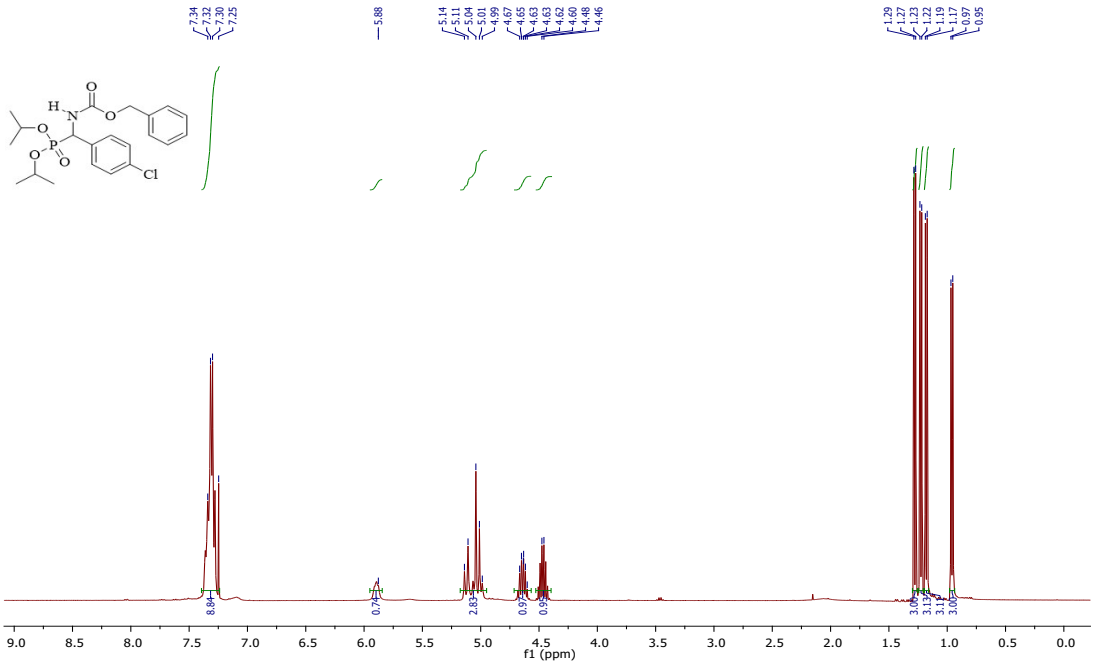
^{13}C NMR spectrum of **3f**



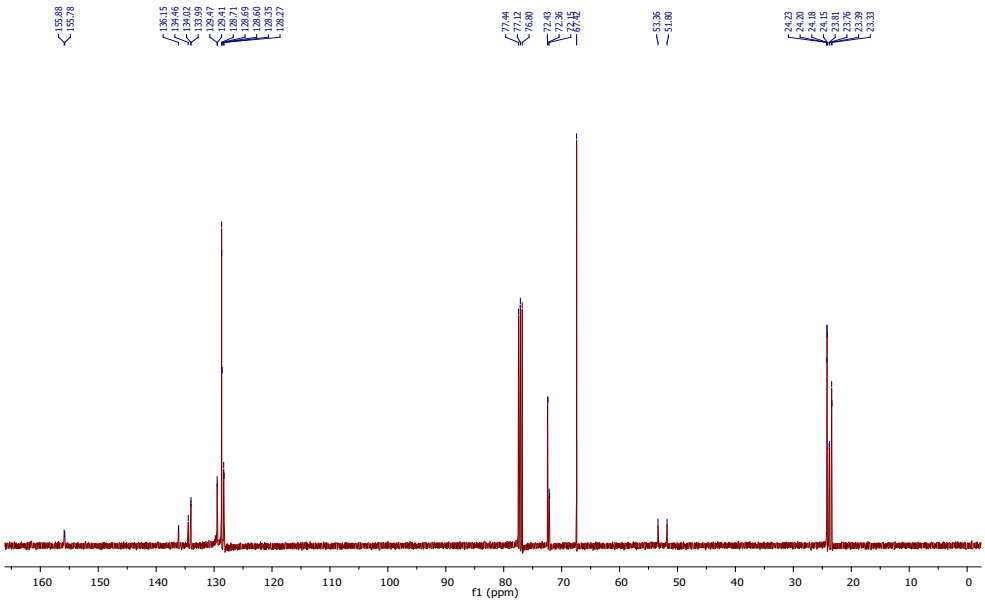
^{31}P NMR spectrum of **3f**



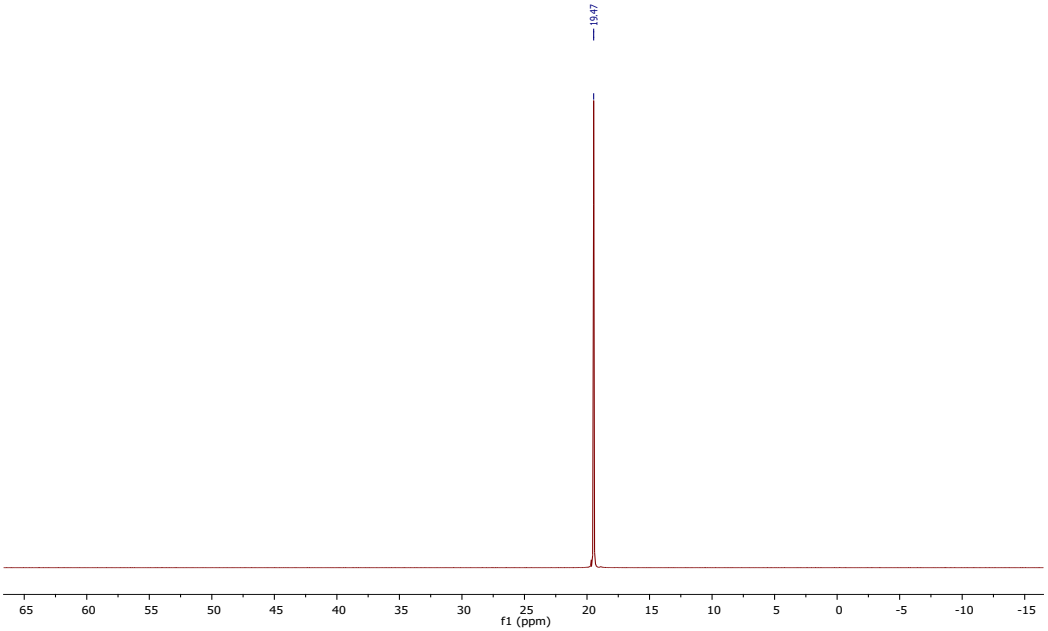
^{1}H NMR spectrum of **3g**



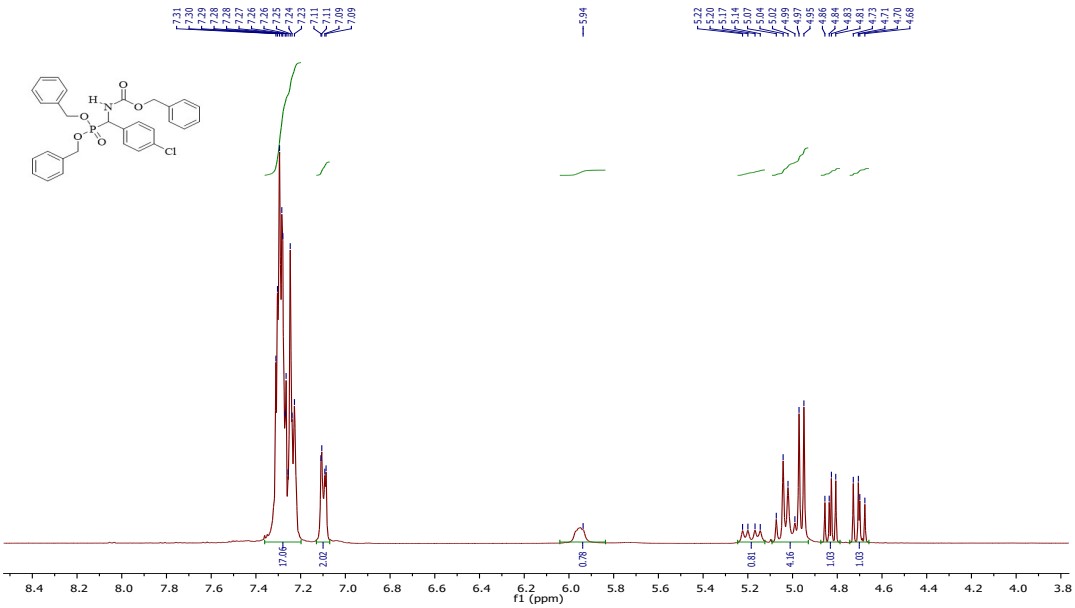
^{13}C NMR spectrum of **3g**



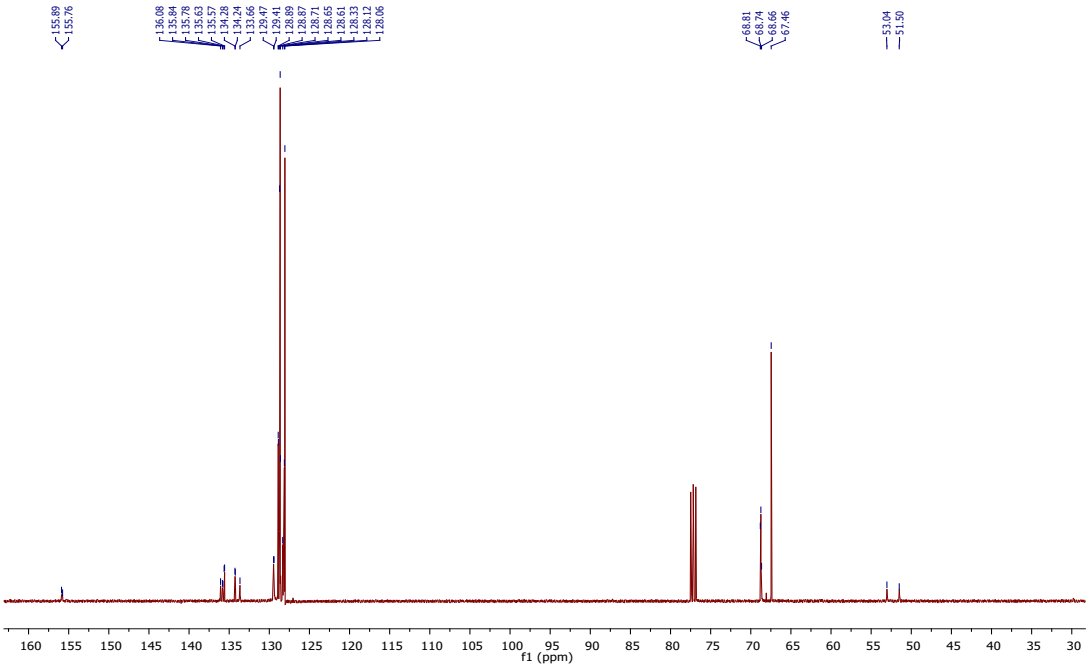
^{31}P NMR spectrum of **3g**



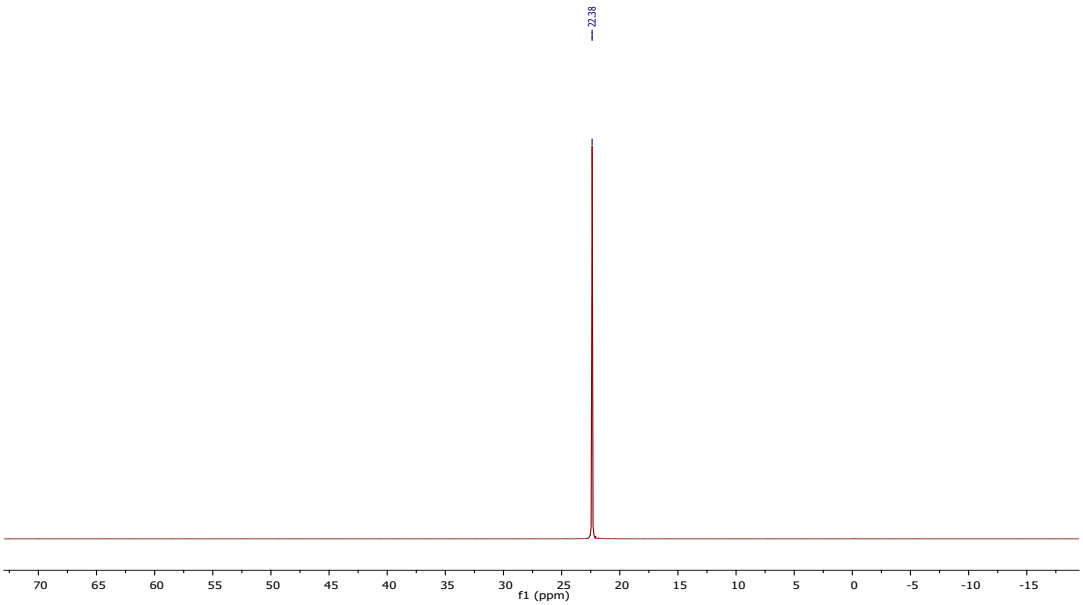
^{1}H NMR spectrum of **3h**



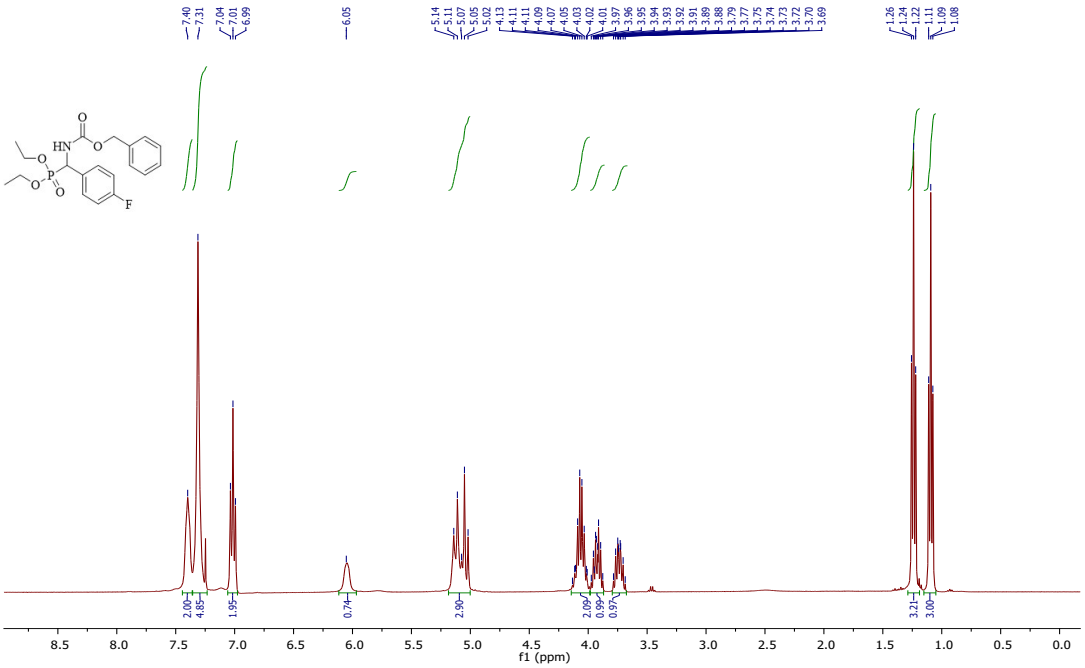
^{13}C NMR spectrum of **3h**



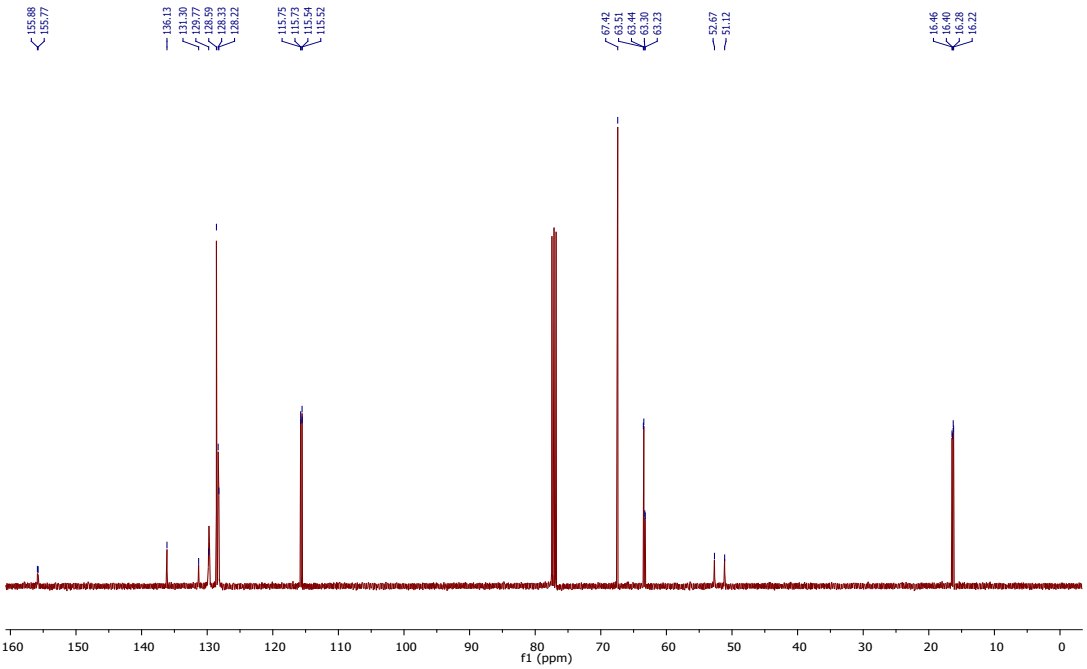
^{31}P NMR spectrum of **3h**



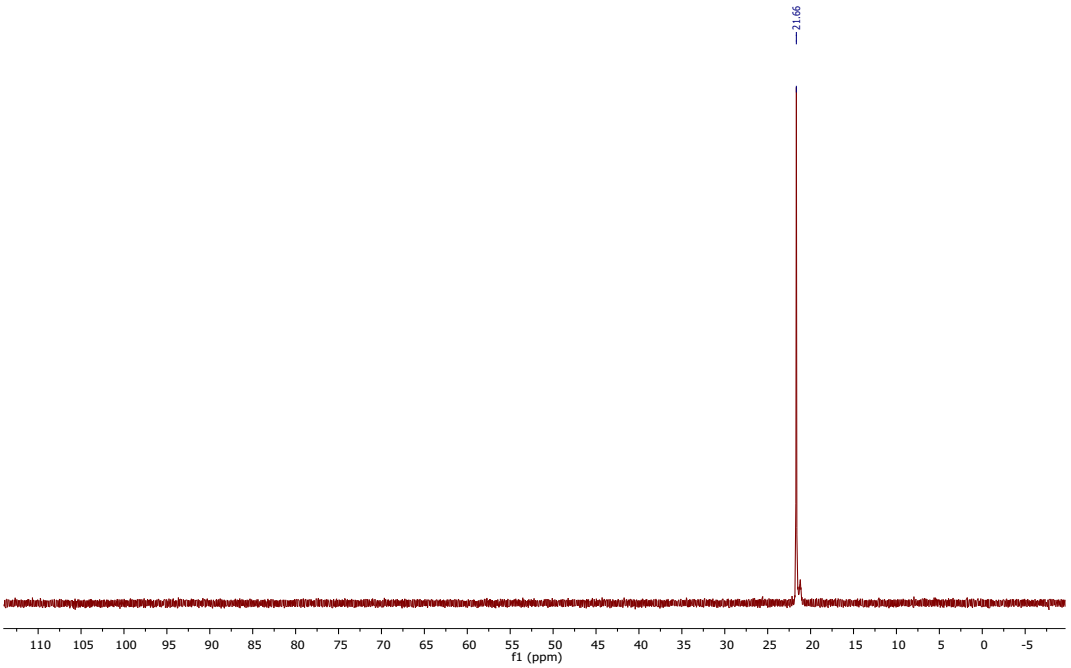
^{1}H NMR spectrum of **3i**



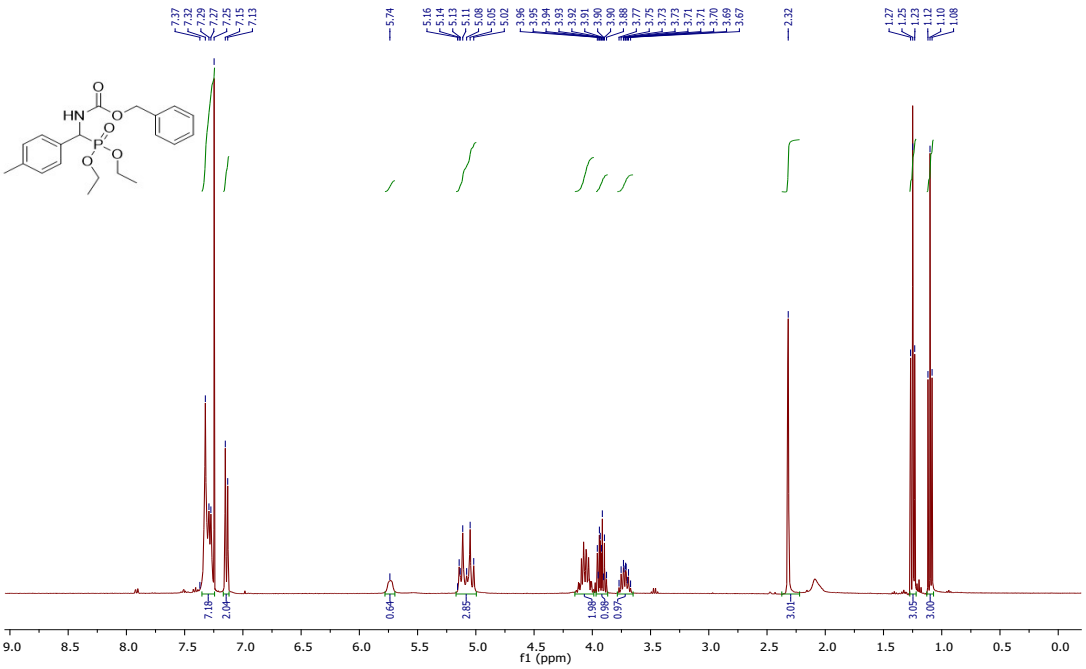
^{13}C NMR spectrum of **3i**



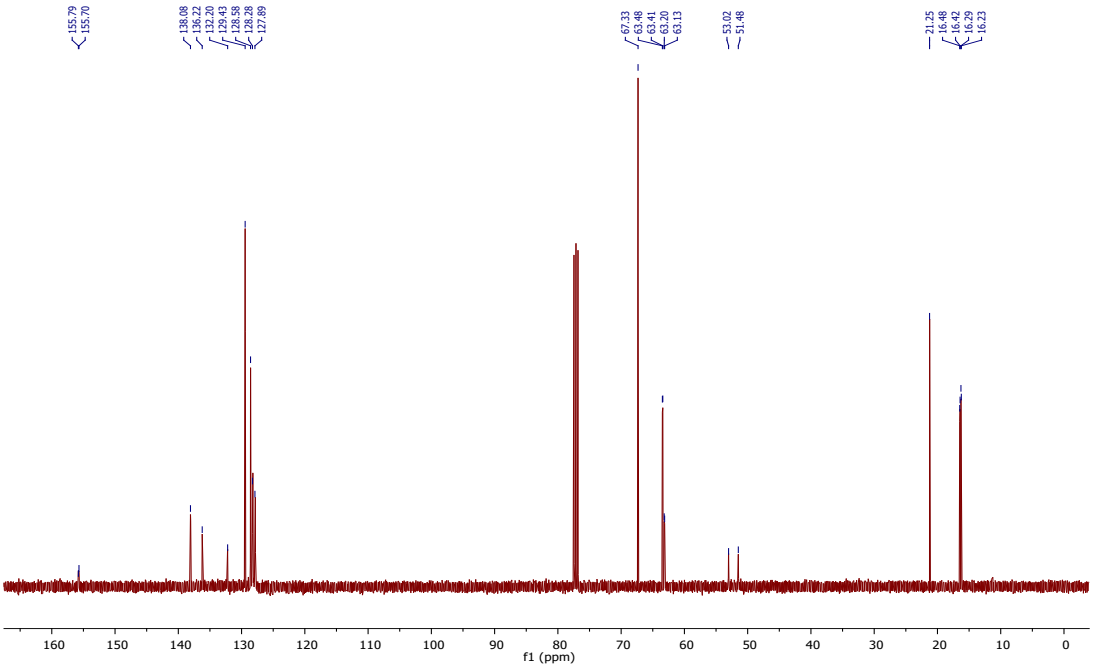
^{31}P NMR spectrum of **3i**



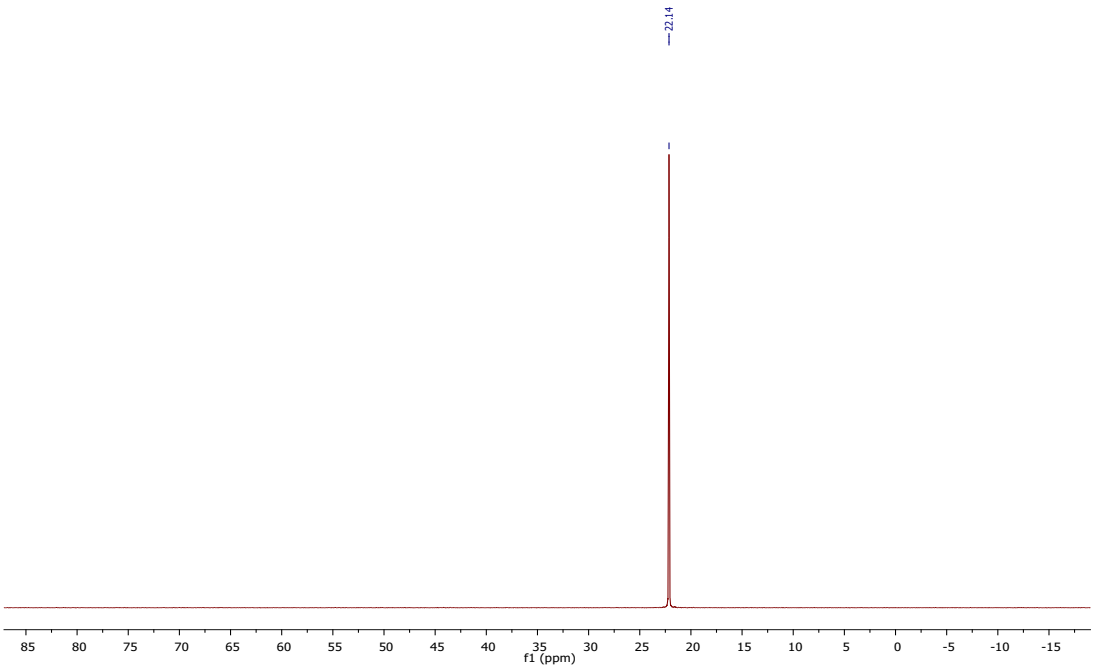
^{1}H NMR spectrum of **3j**



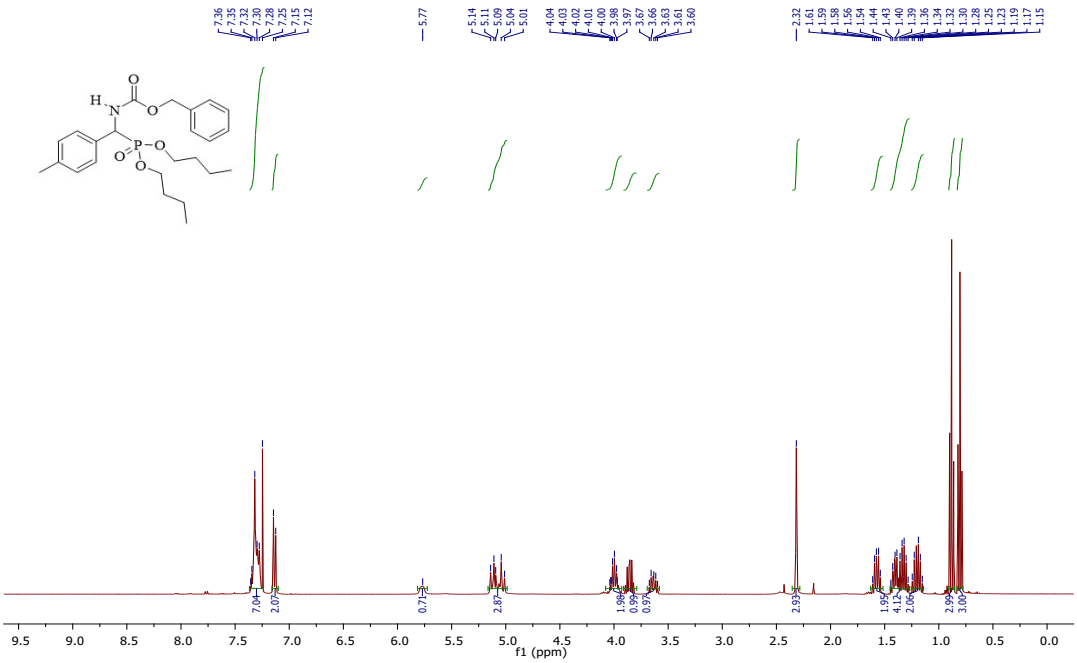
^{13}C NMR spectrum of **3j**



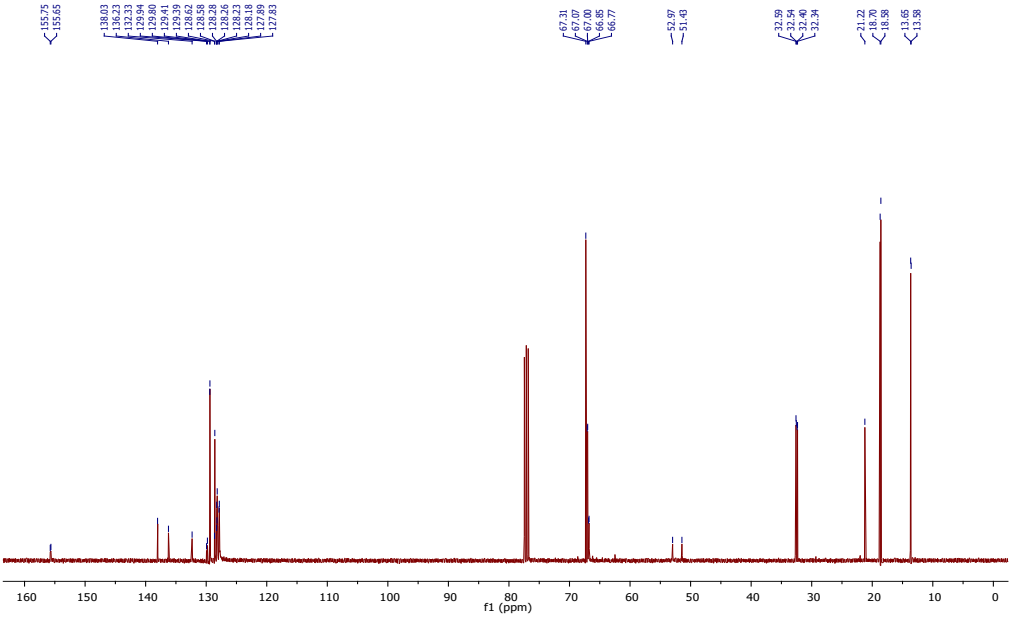
^{31}P NMR spectrum of **3j**



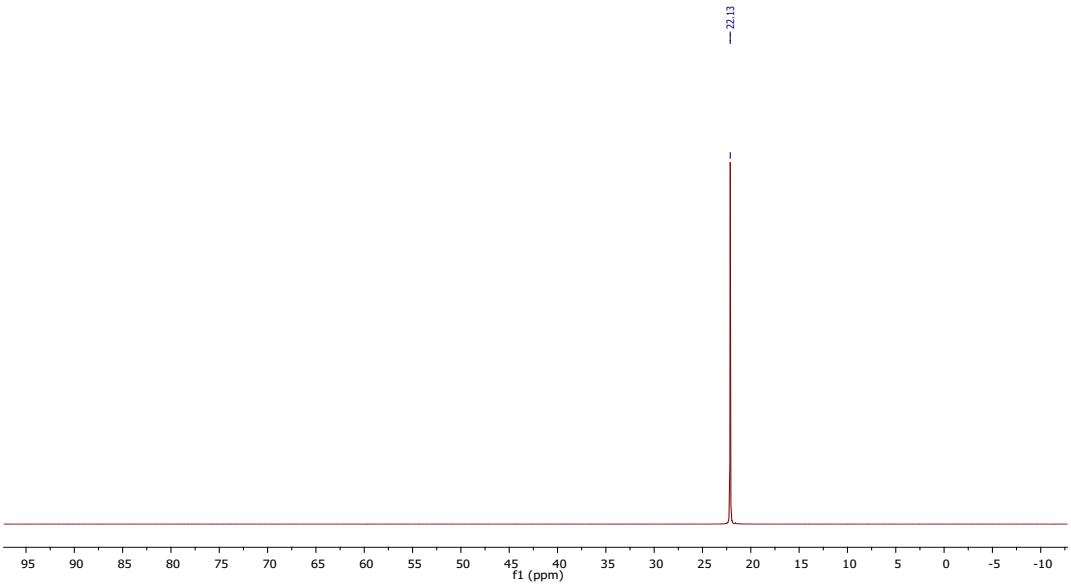
^{1}H NMR spectrum of **3k**



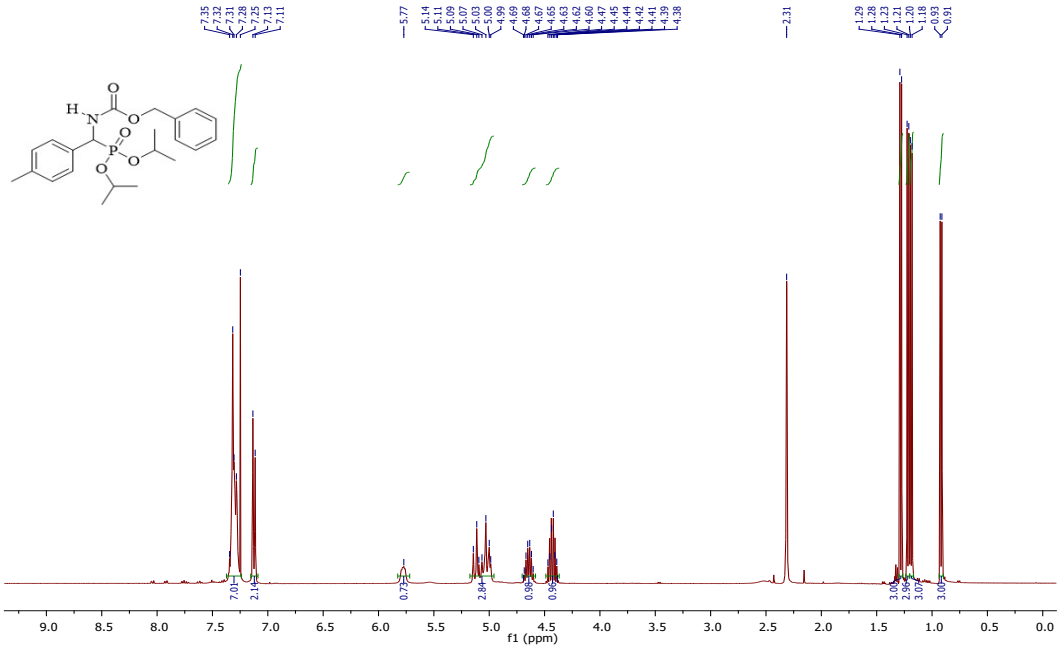
^{13}C NMR spectrum of **3k**



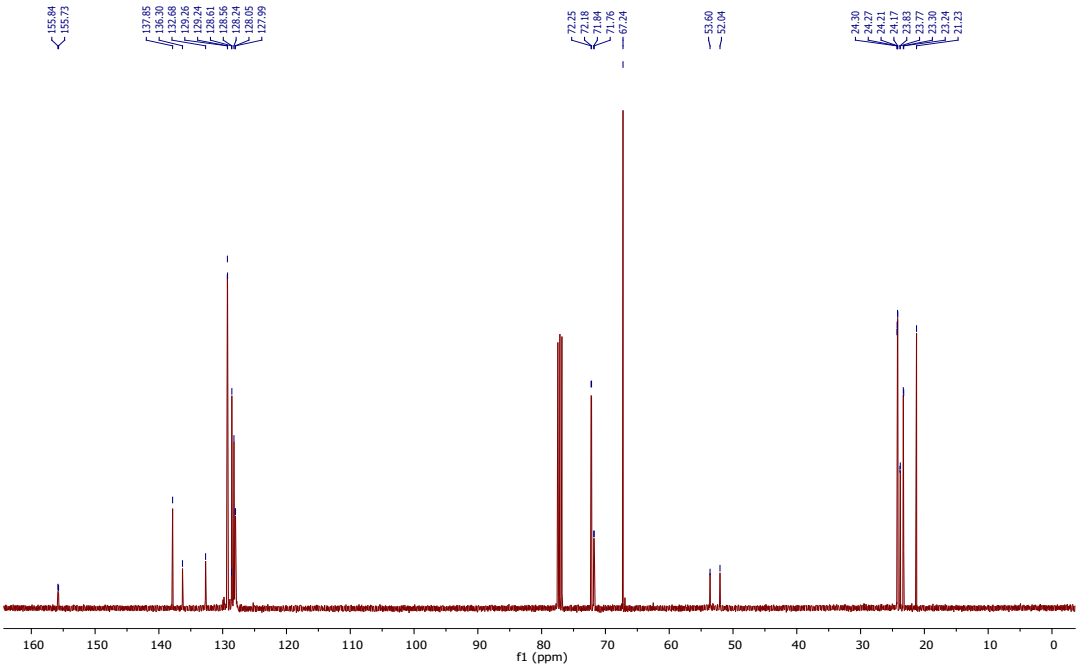
^{31}P NMR spectrum of **3k**



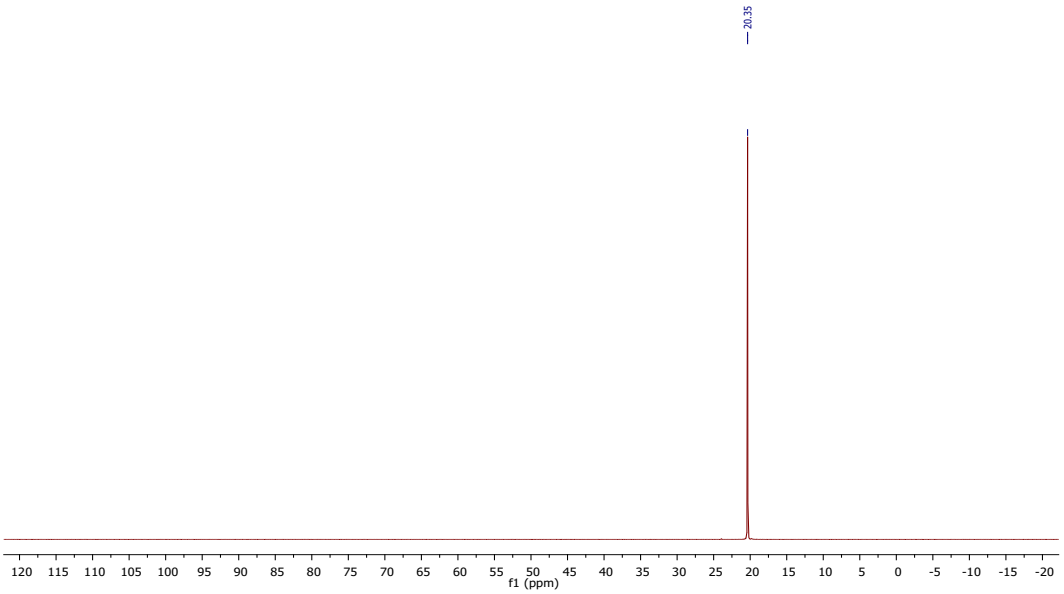
^{1}H NMR spectrum of **3l**



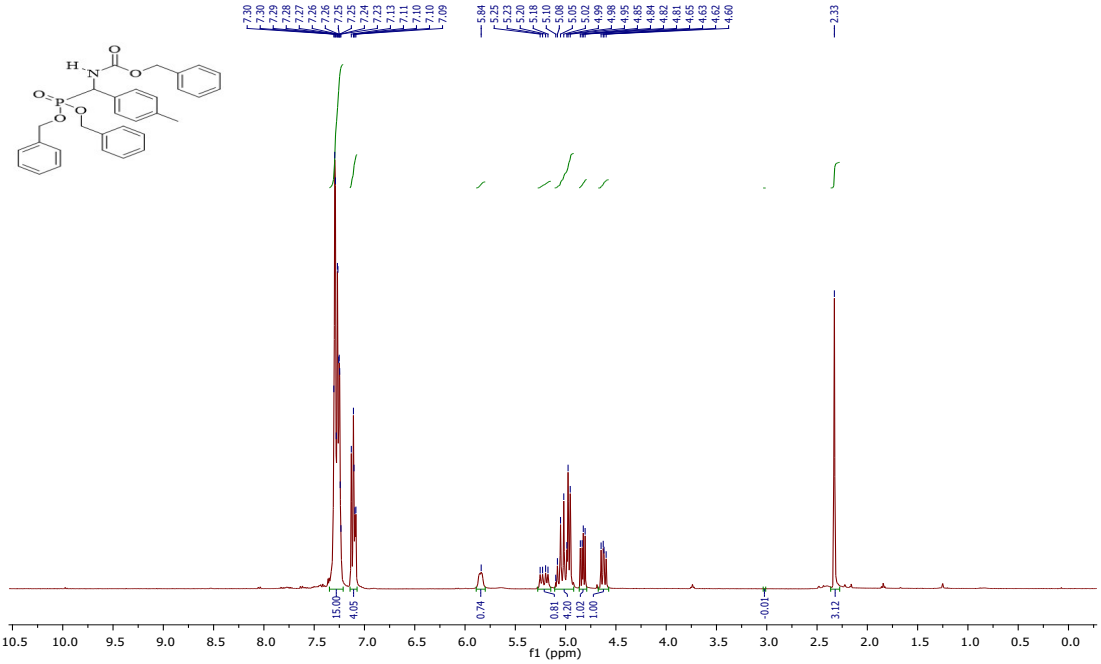
^{13}C NMR spectrum of **3l**



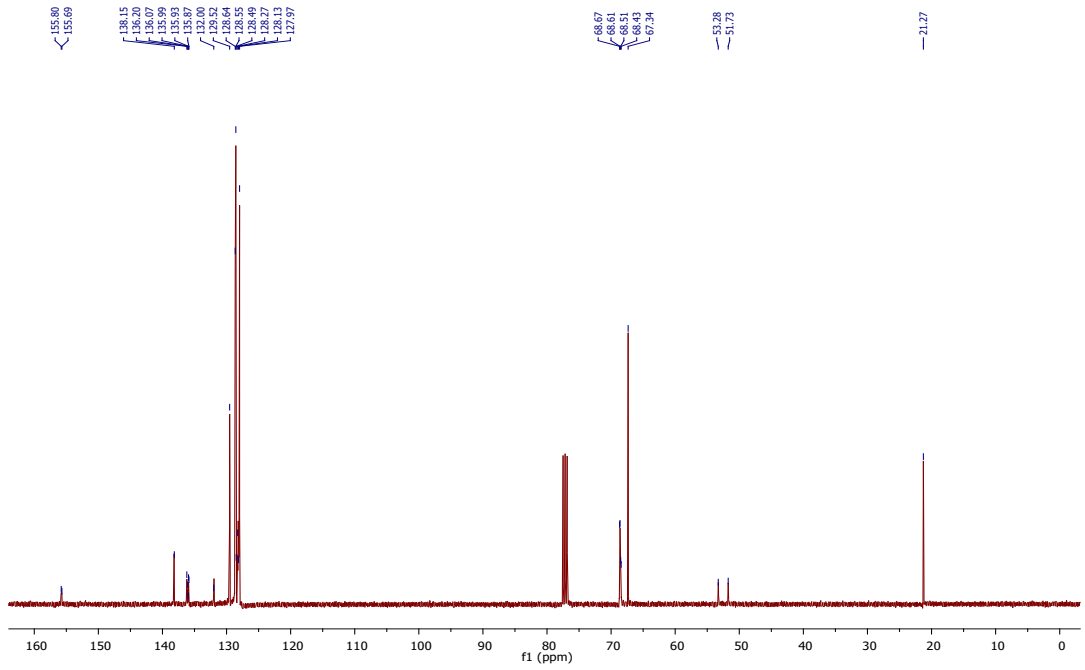
^{31}P NMR spectrum of **3l**



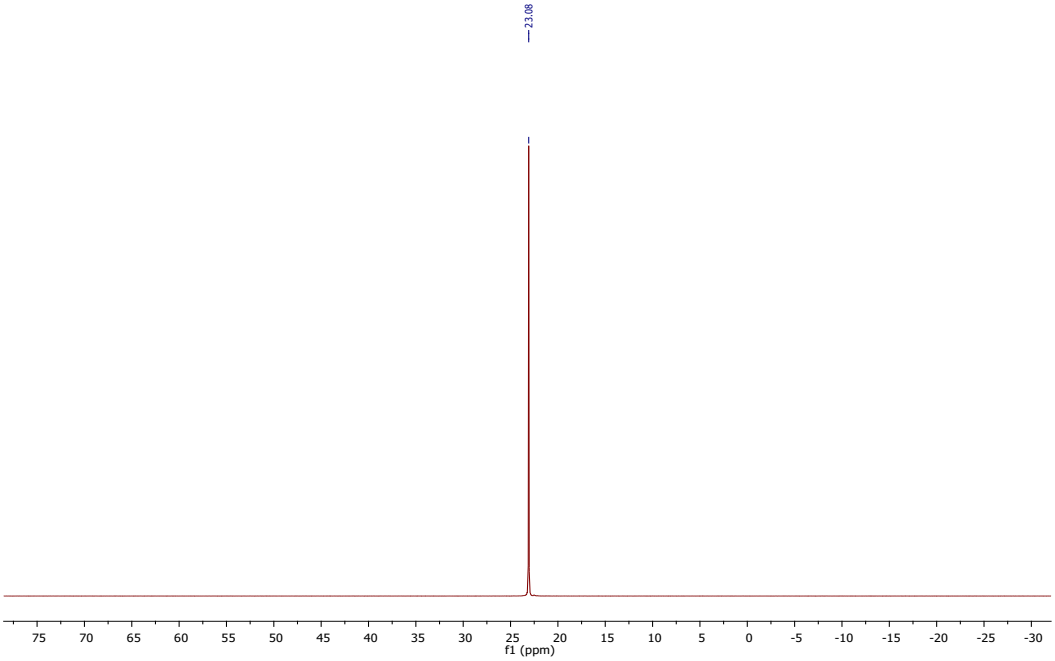
^{1}H NMR spectrum of **3m**



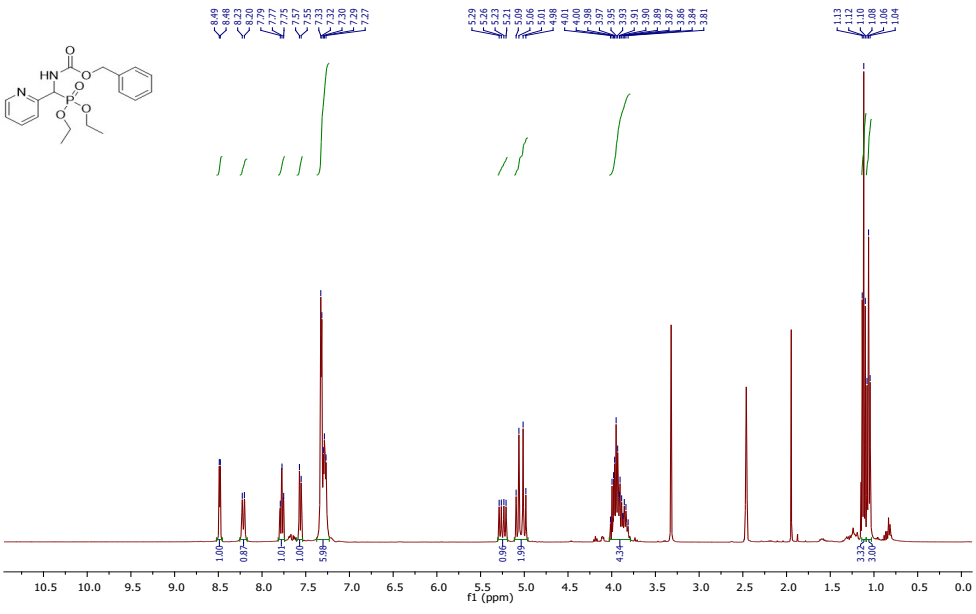
^{13}C NMR spectrum of **3m**



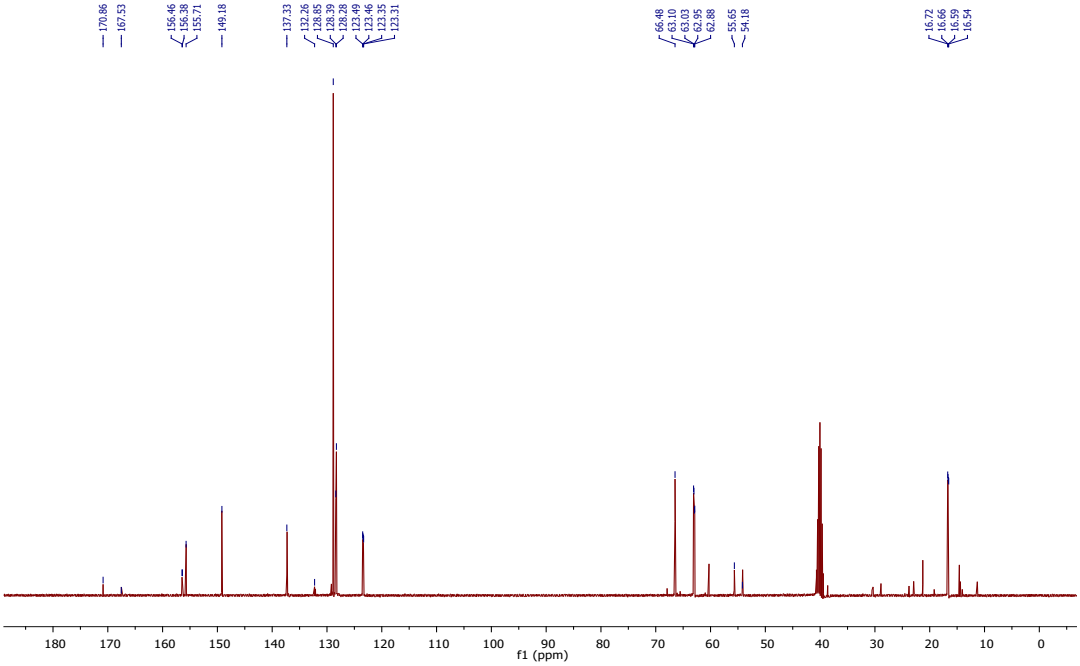
^{31}P NMR spectrum of **3m**



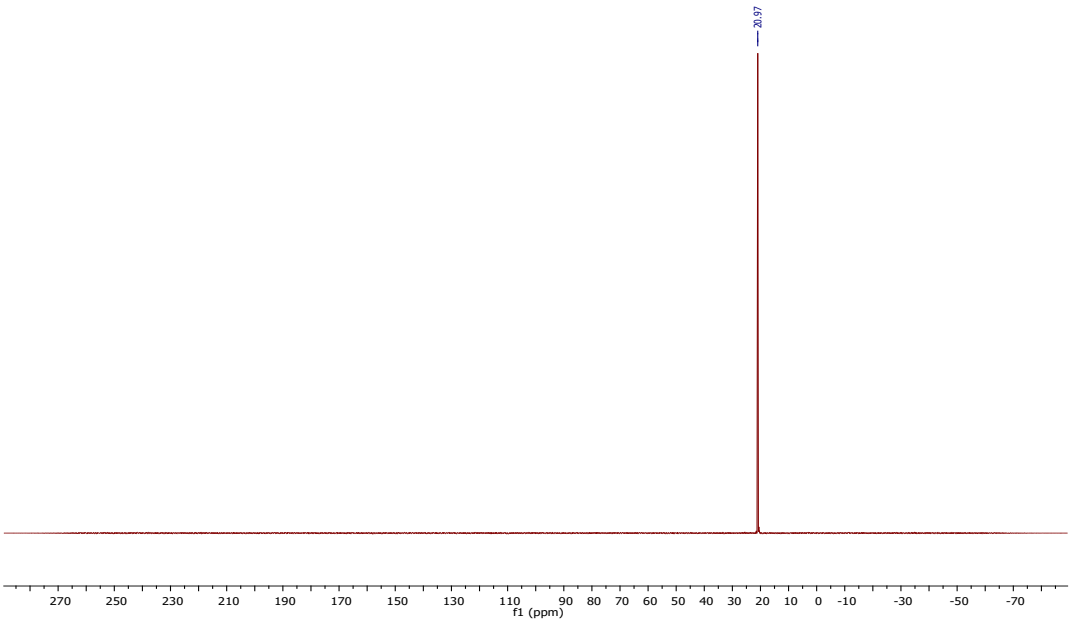
^{1}H NMR spectrum of **3n**



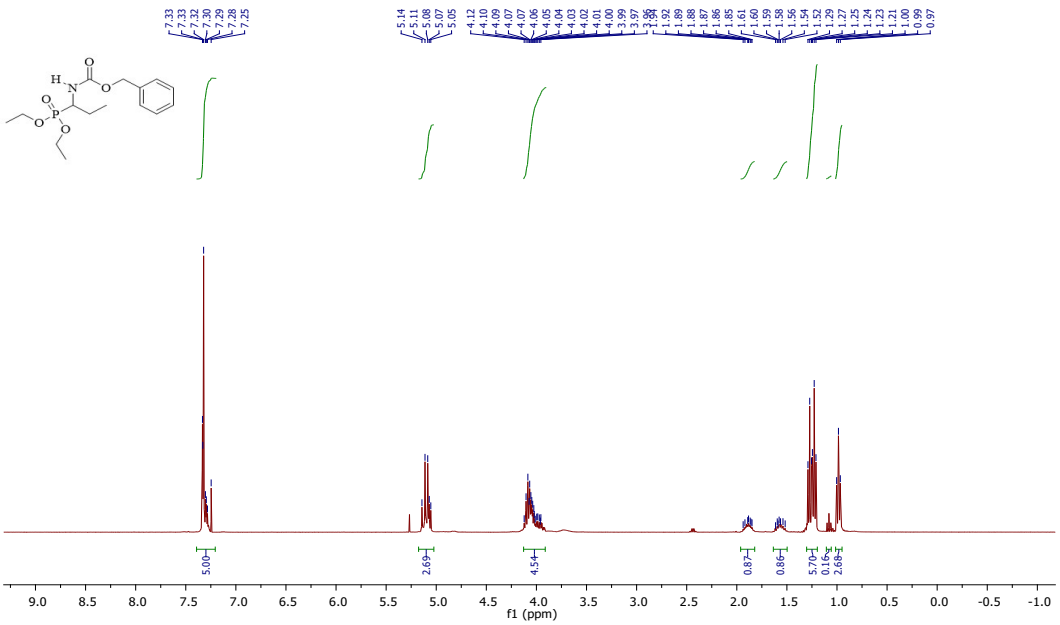
^{13}C NMR spectrum of **3n**



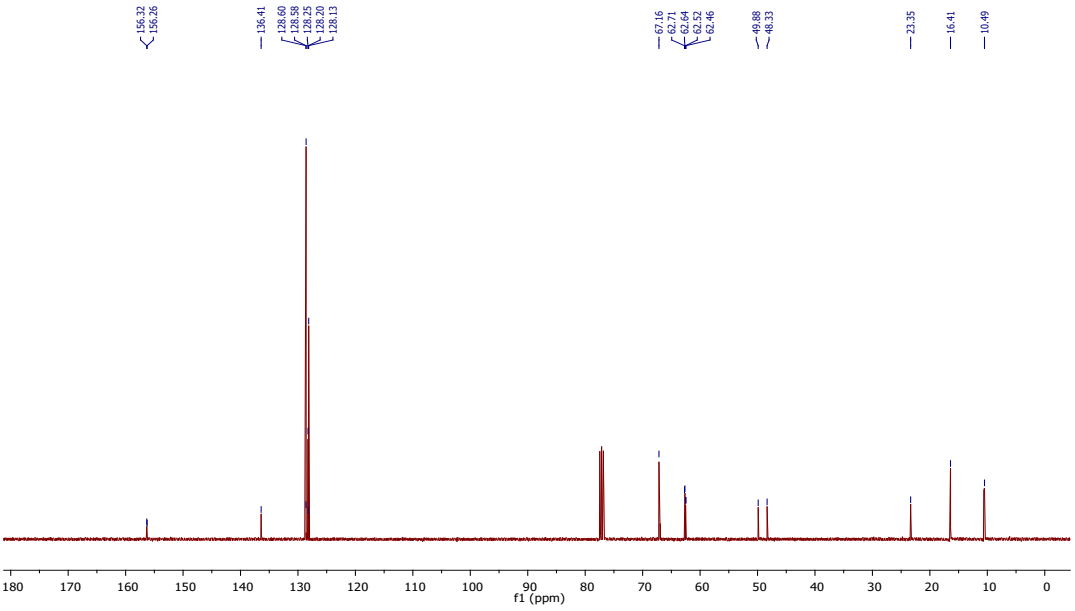
^{31}P NMR spectrum of **3n**



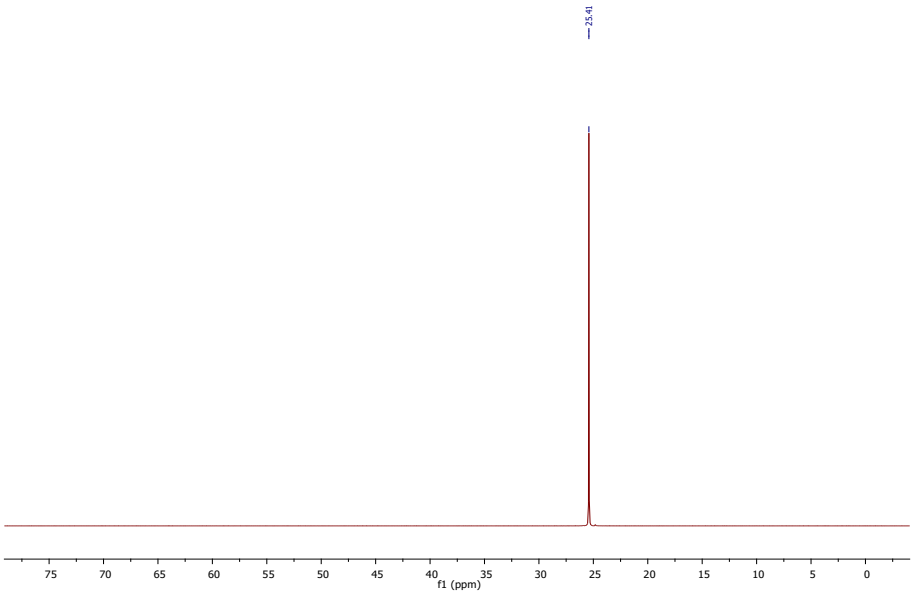
^{1}H NMR spectrum of **3o**



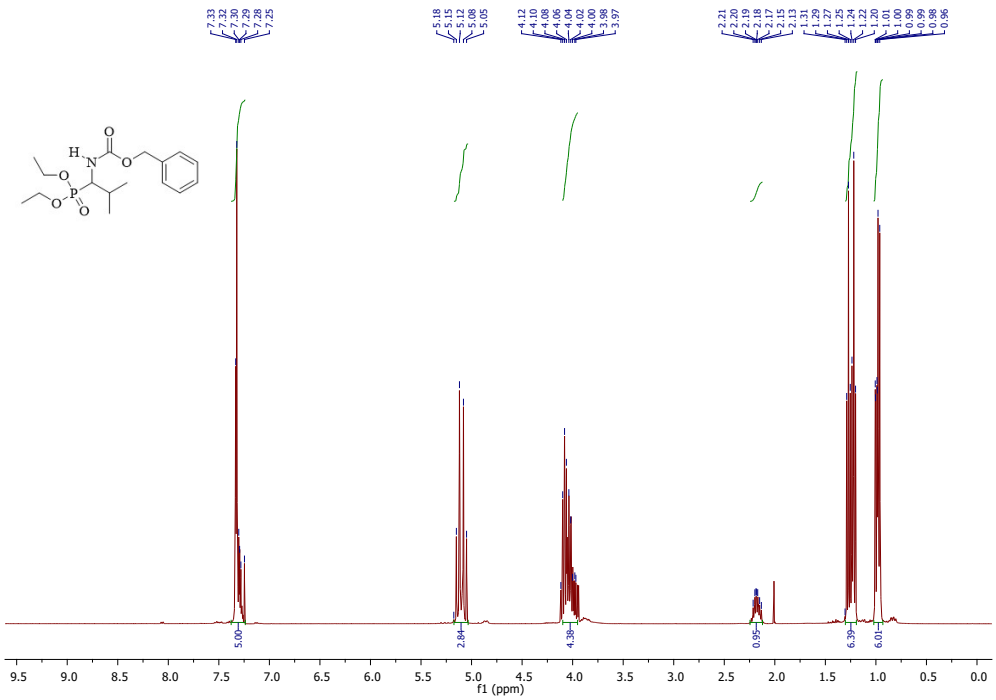
^{13}C NMR spectrum of **3o**



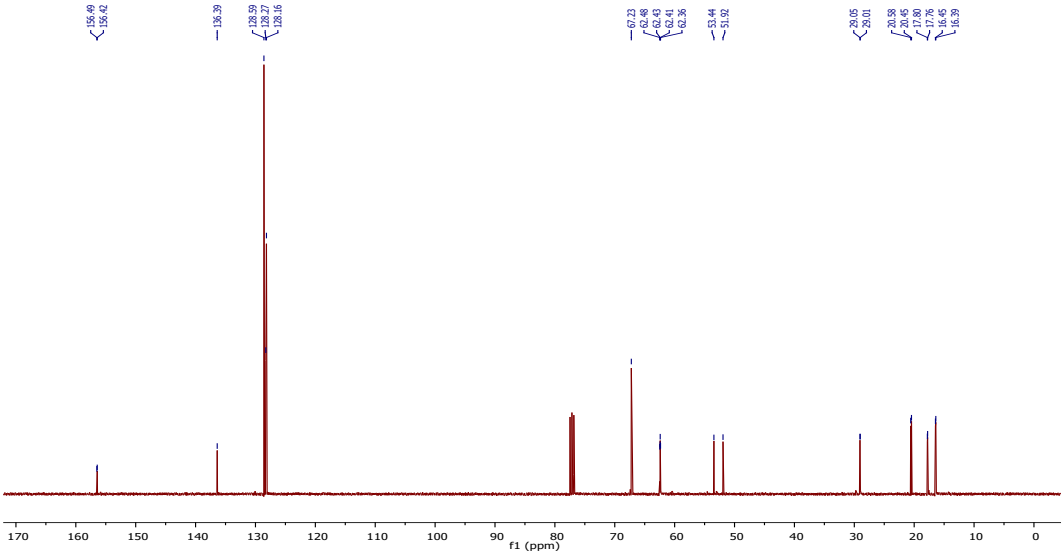
^{31}P NMR spectrum of **3o**



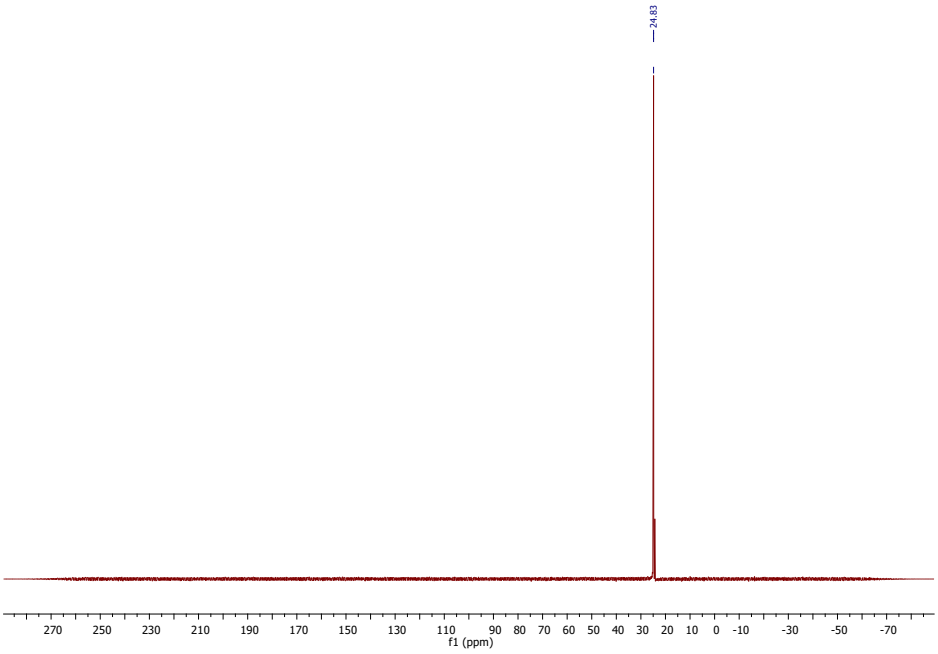
^{1}H NMR spectrum of **3p**



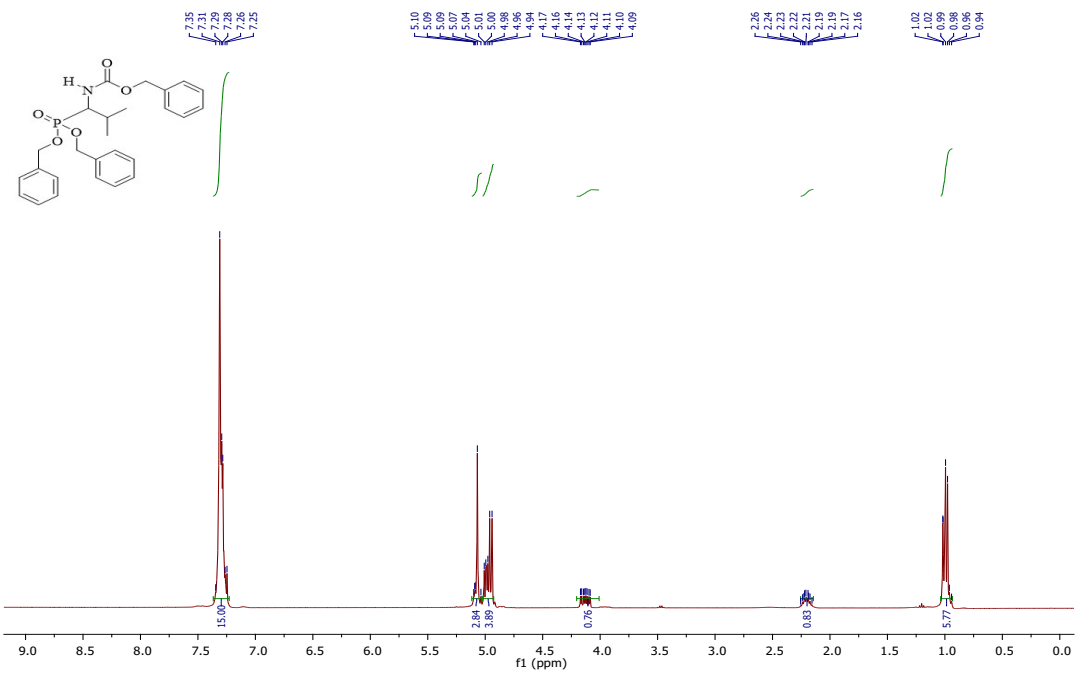
^{13}C NMR spectrum of **3p**



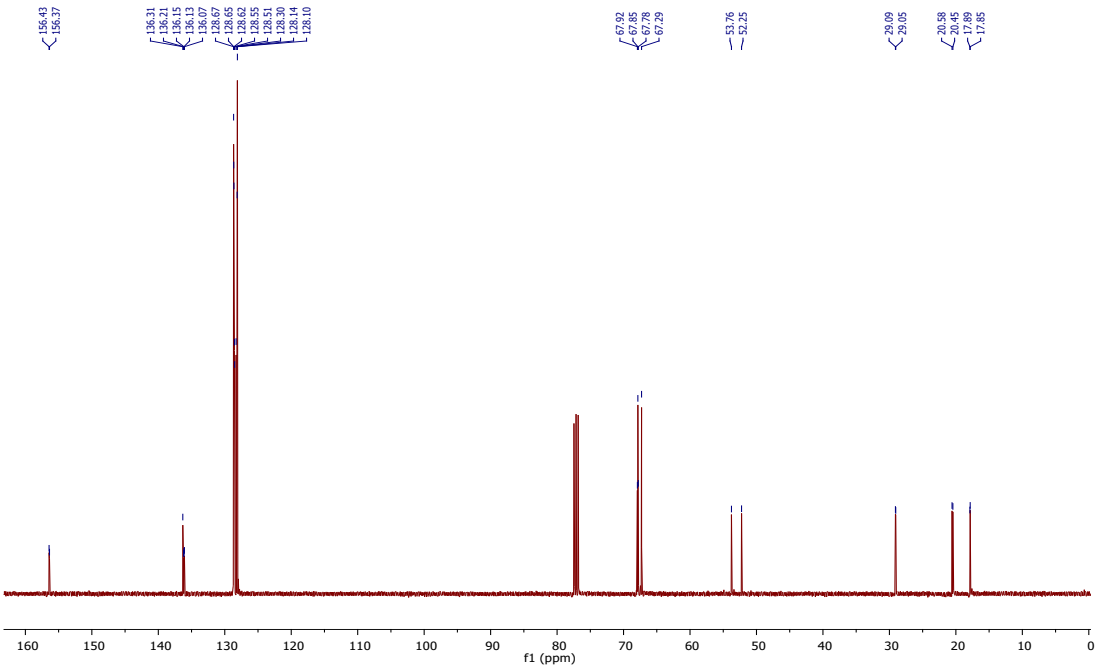
^{31}P NMR spectrum of **3p**



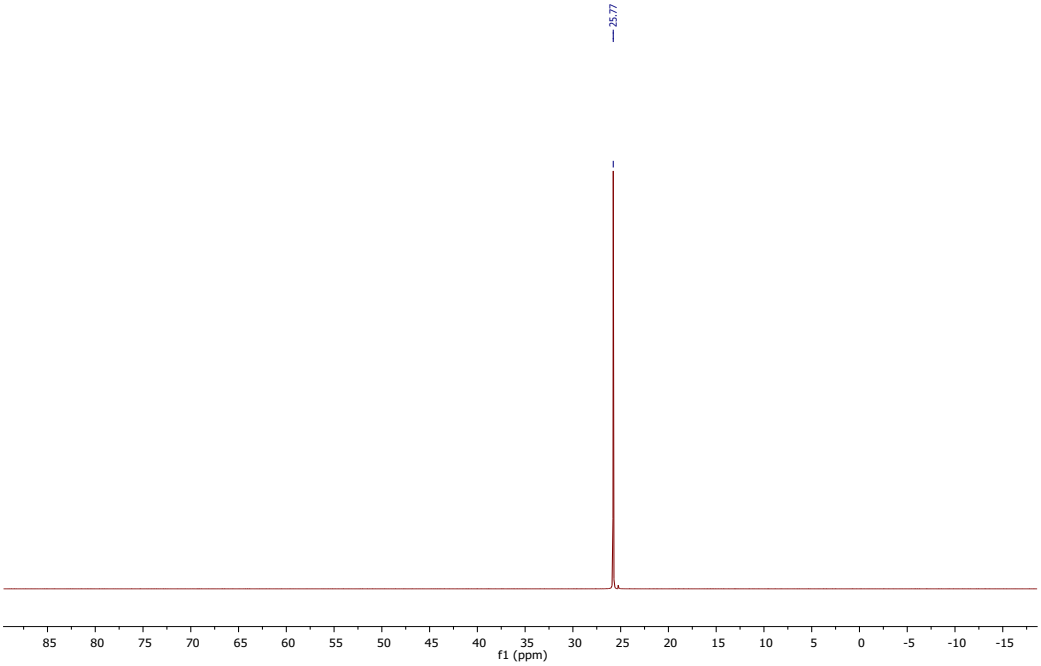
^{1}H NMR spectrum of **3q**



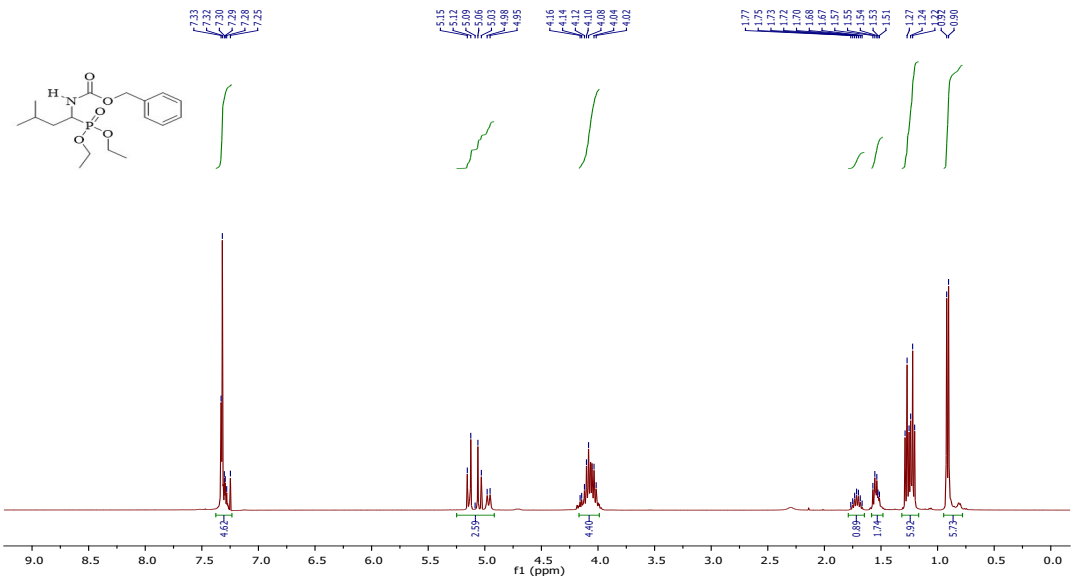
^{13}C NMR spectrum of **3q**



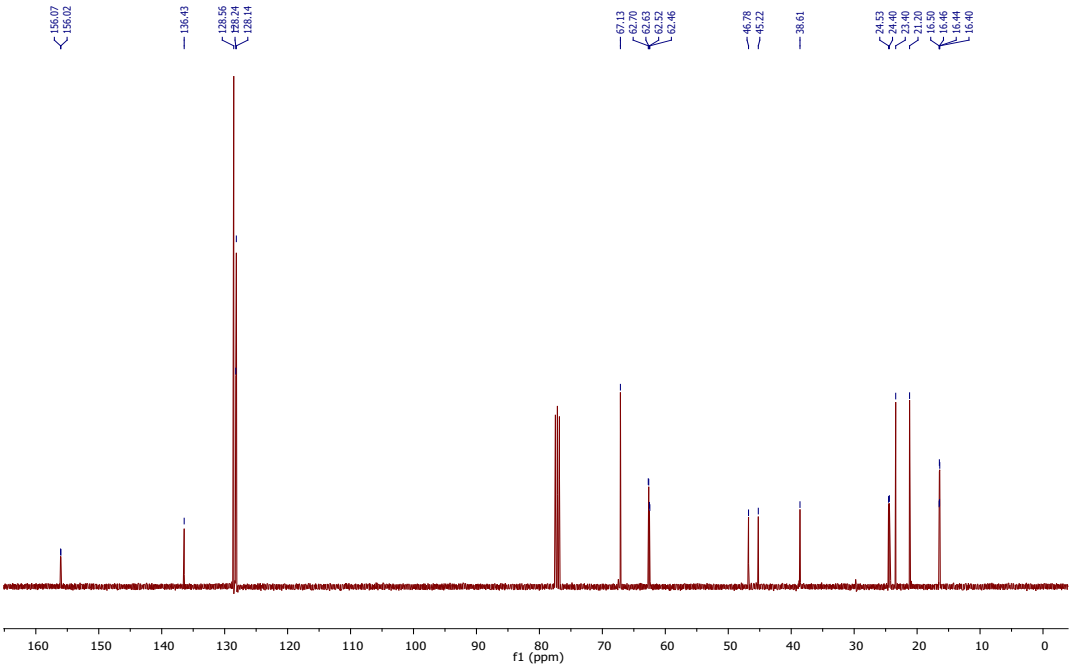
^{31}P NMR spectrum of **3q**



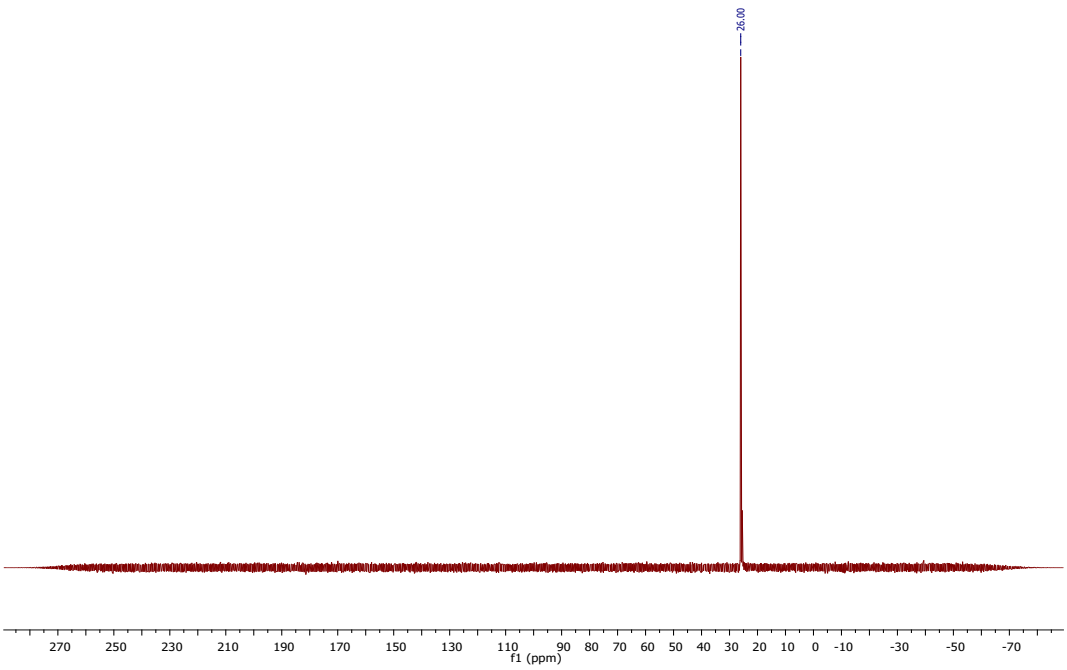
^{1}H NMR spectrum of **3r**



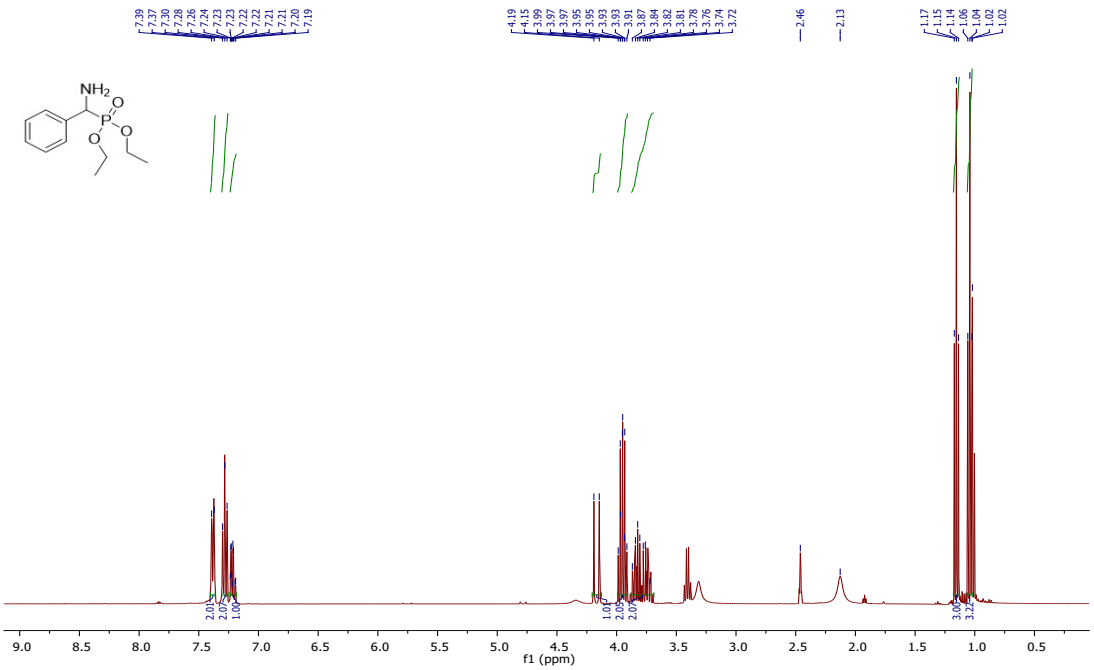
^{13}C NMR spectrum of **3r**



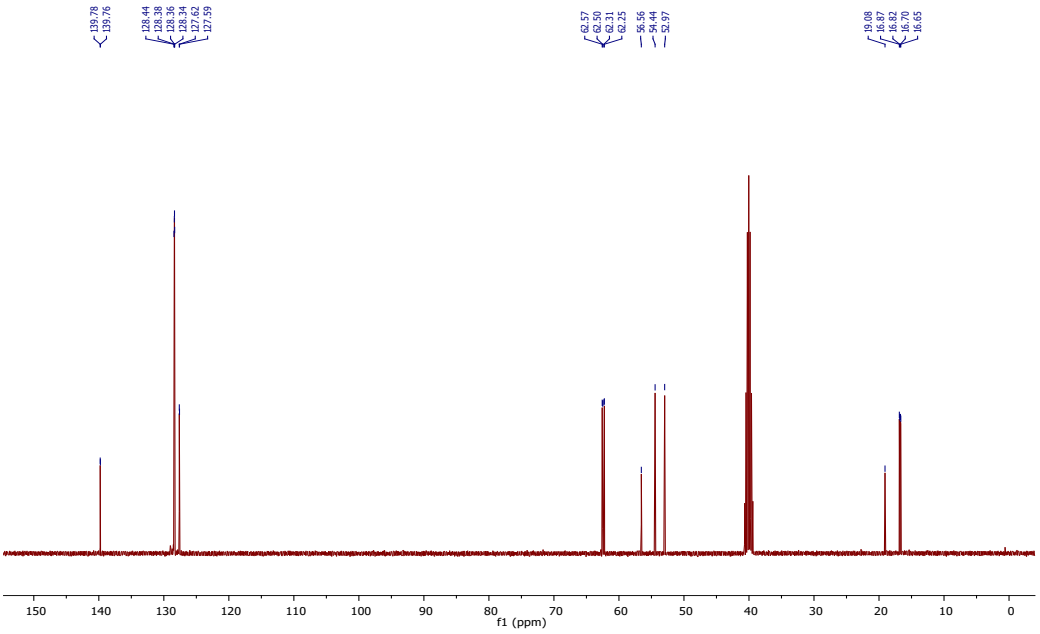
^{31}P NMR spectrum of **3r**



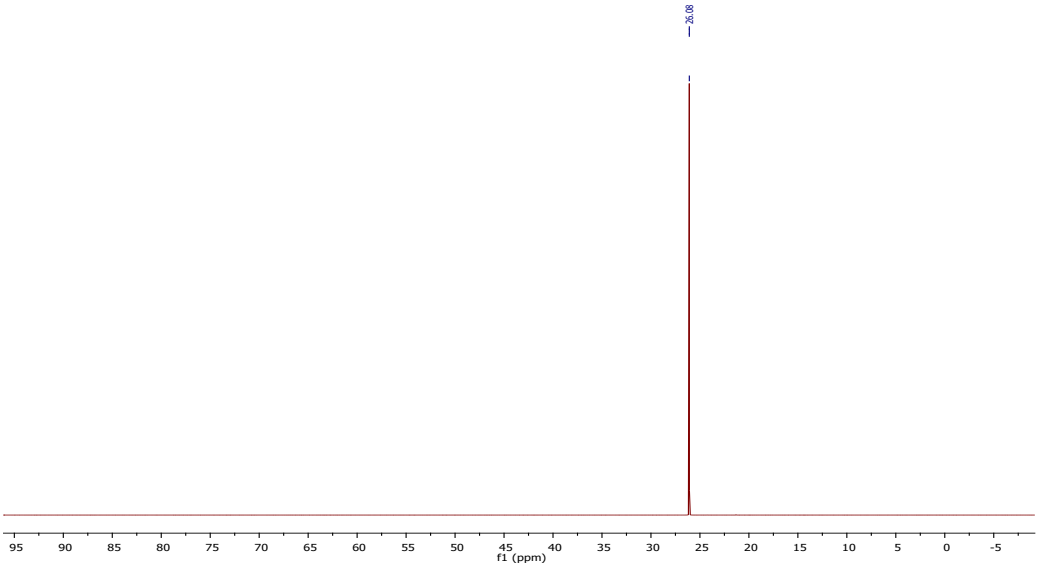
^{1}H NMR spectrum of **8a**



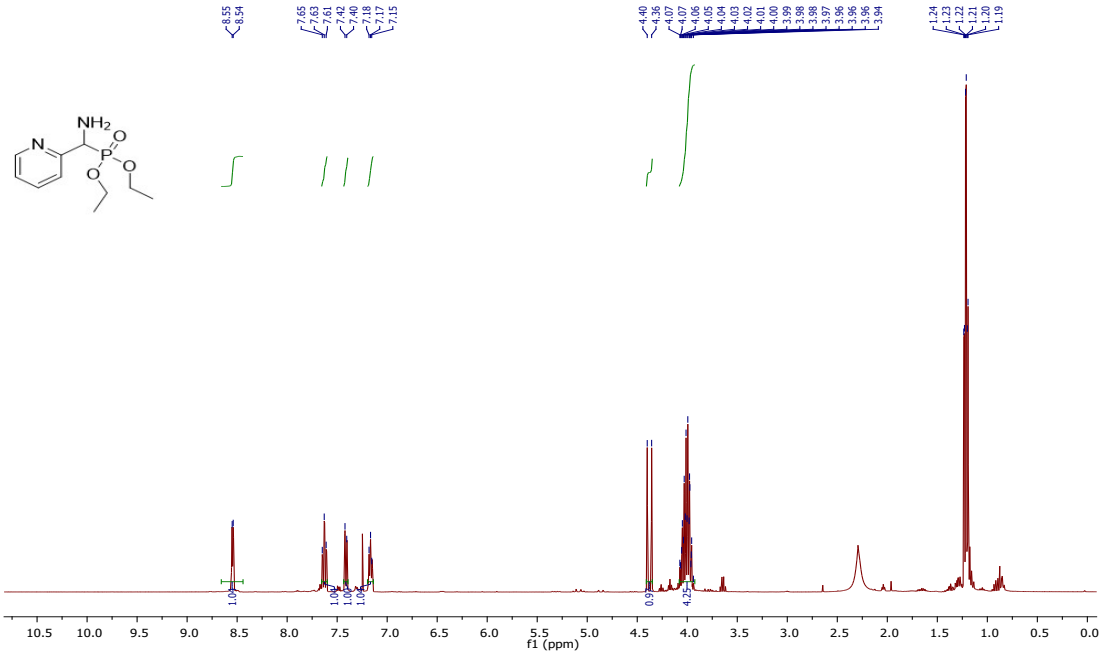
^{13}C NMR spectrum of **8a**



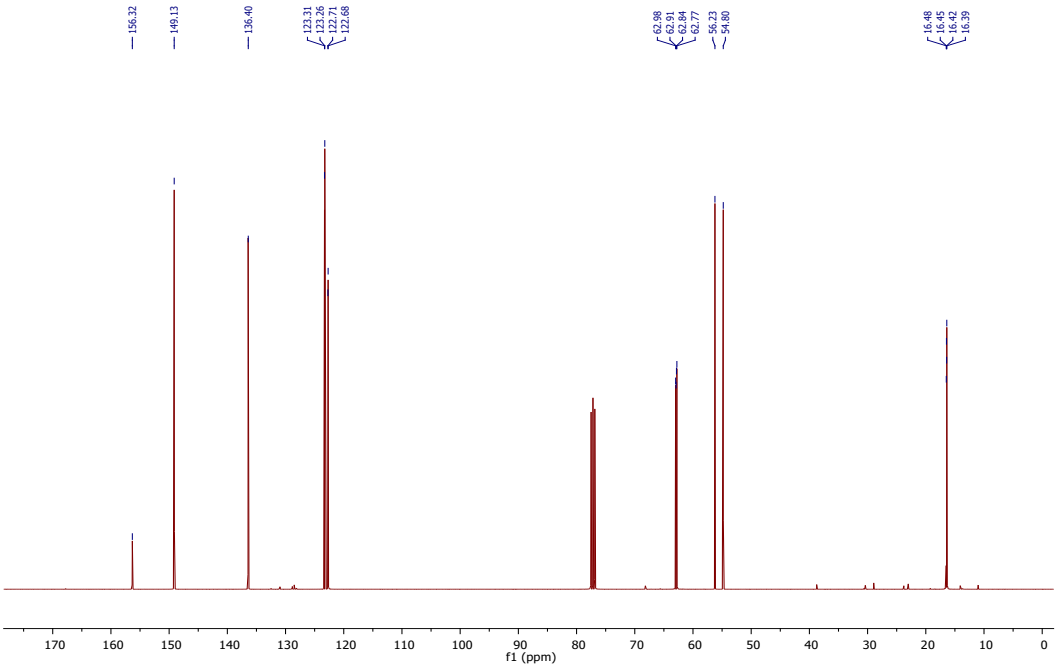
^{31}P NMR spectrum of **8a**



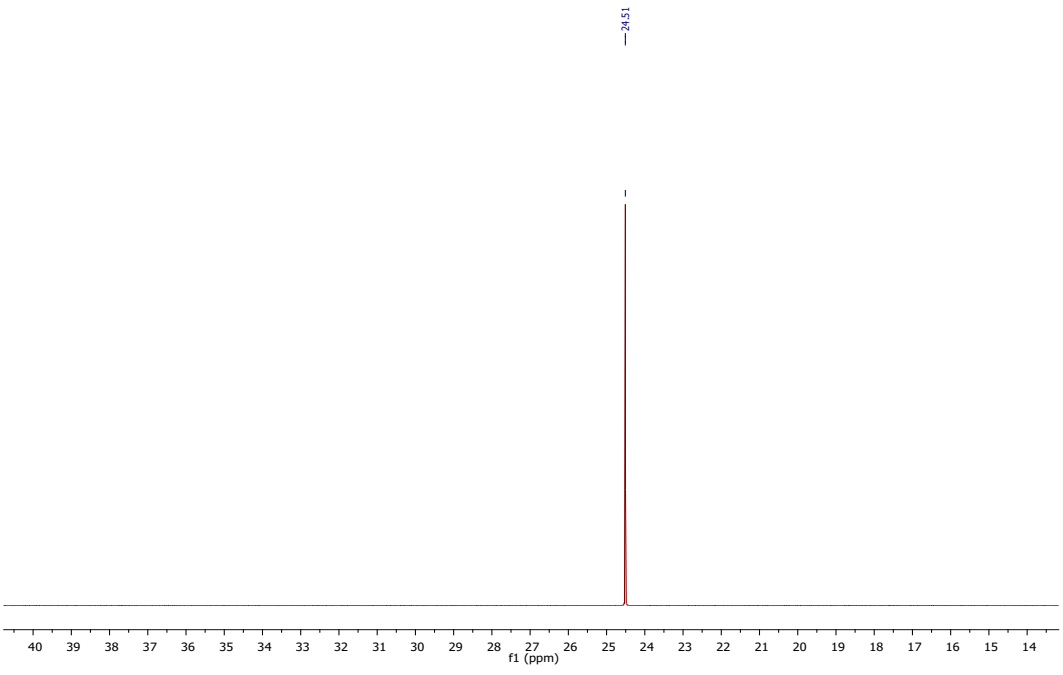
^{1}H NMR spectrum of **8n**



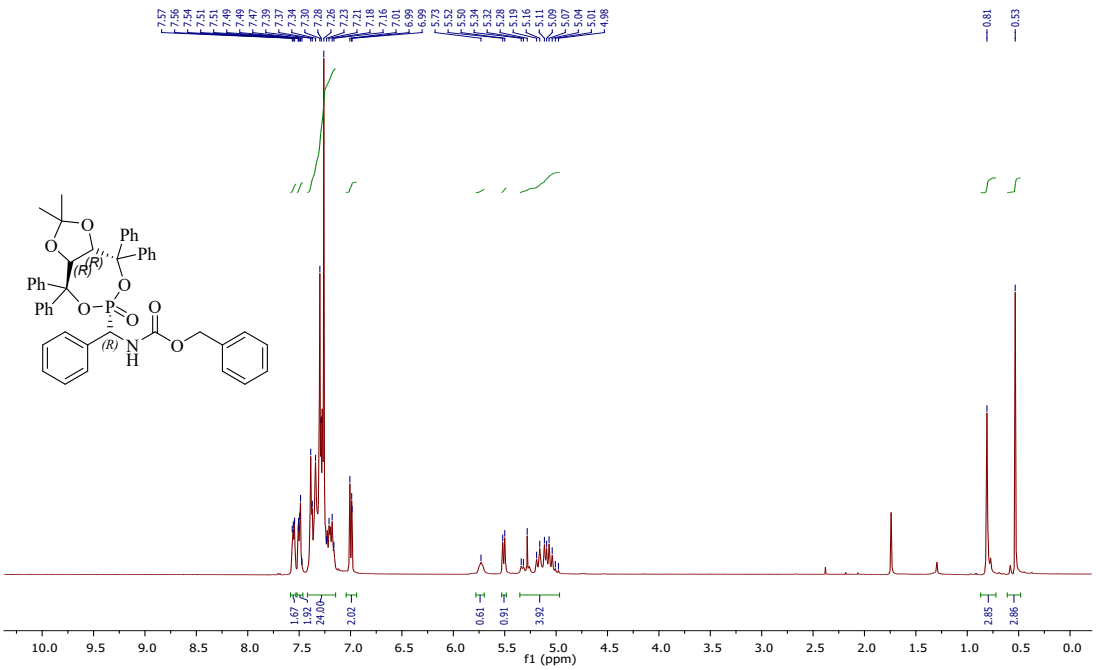
^{13}C NMR spectrum of **8n**



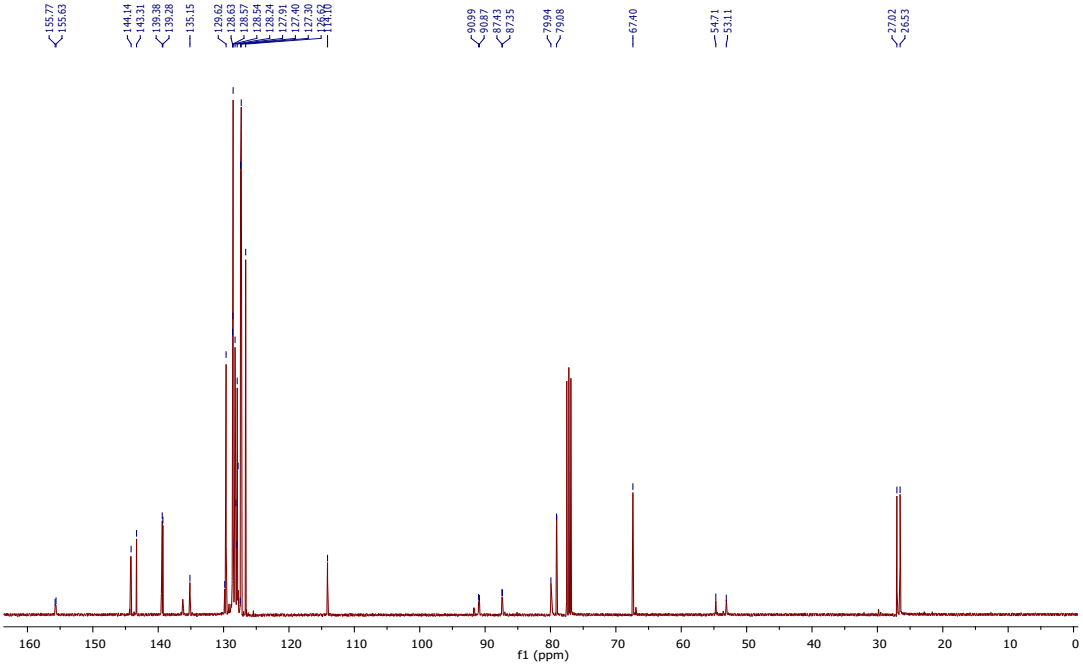
^{31}P NMR spectrum of **8n**



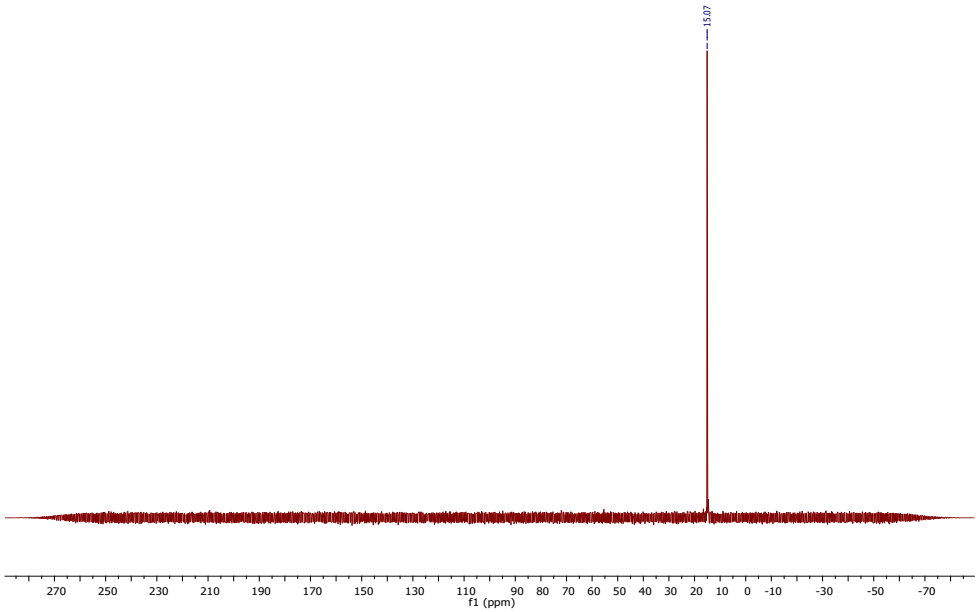
[1]H NMR Spectrum **(*R*,*R*,*R*)-6a**



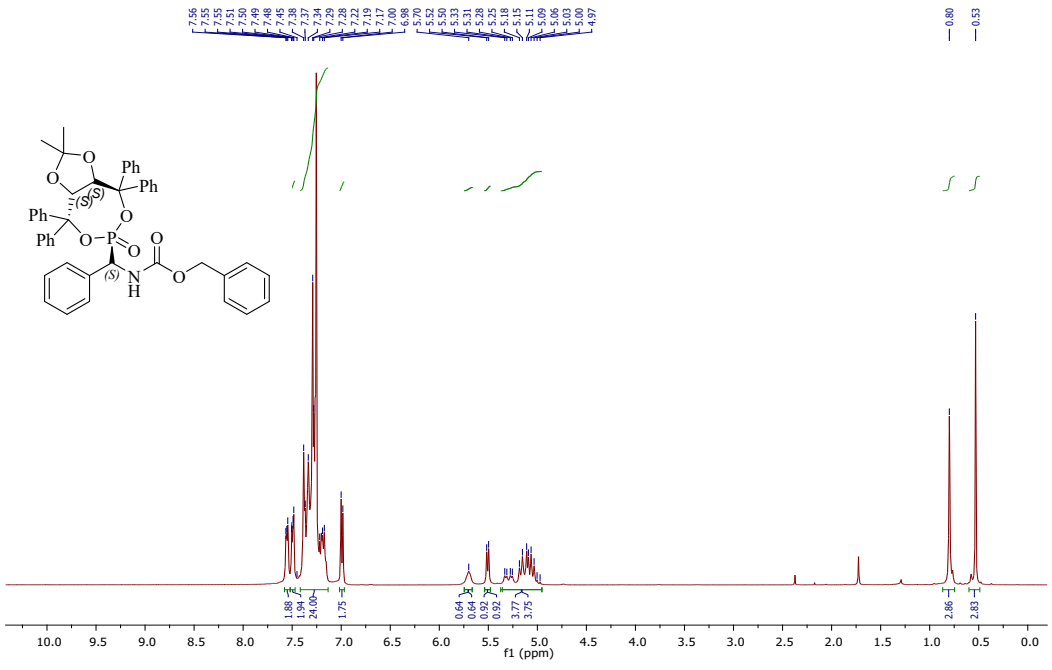
[13]C NMR Spectrum **(*R*,*R*,*R*)-6a**



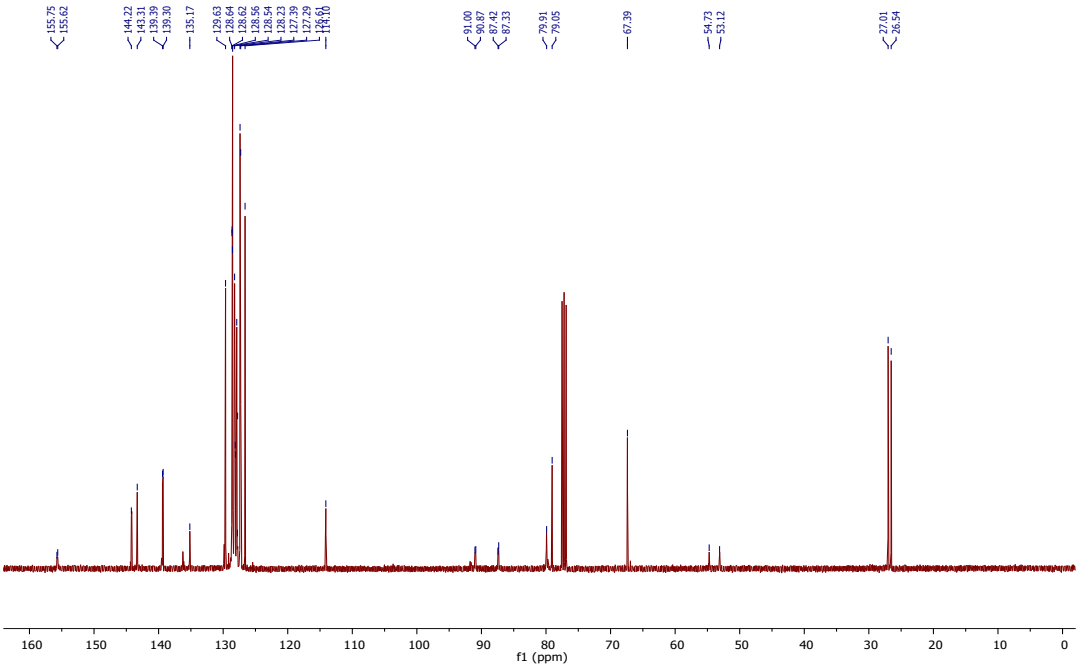
^{31}P NMR Spectrum ***(R,R,R)*- 6a**



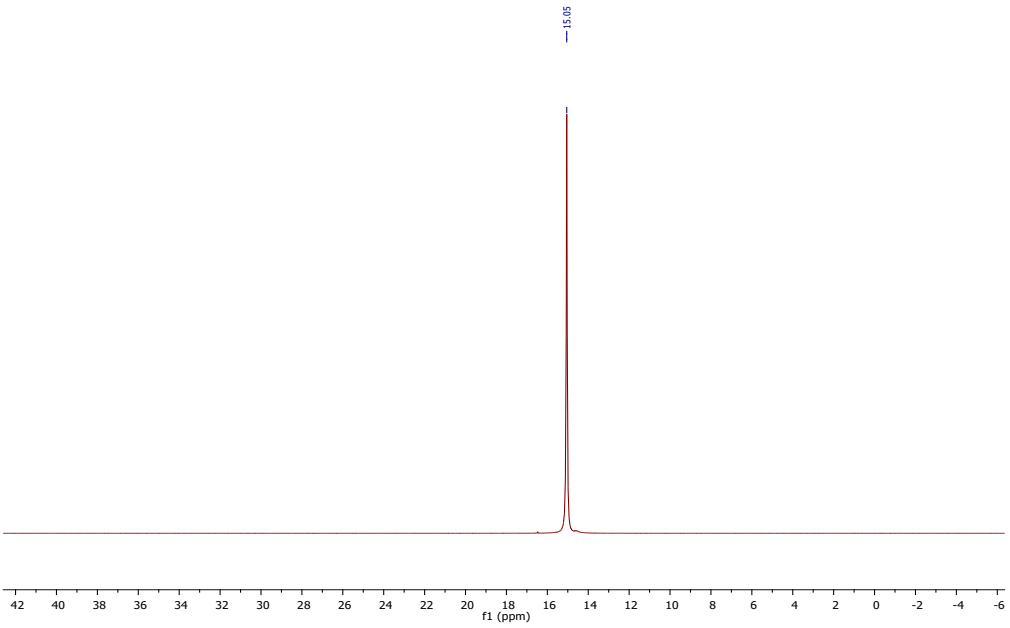
^{1}H NMR Spectrum ***(S,S,S)*-6a**



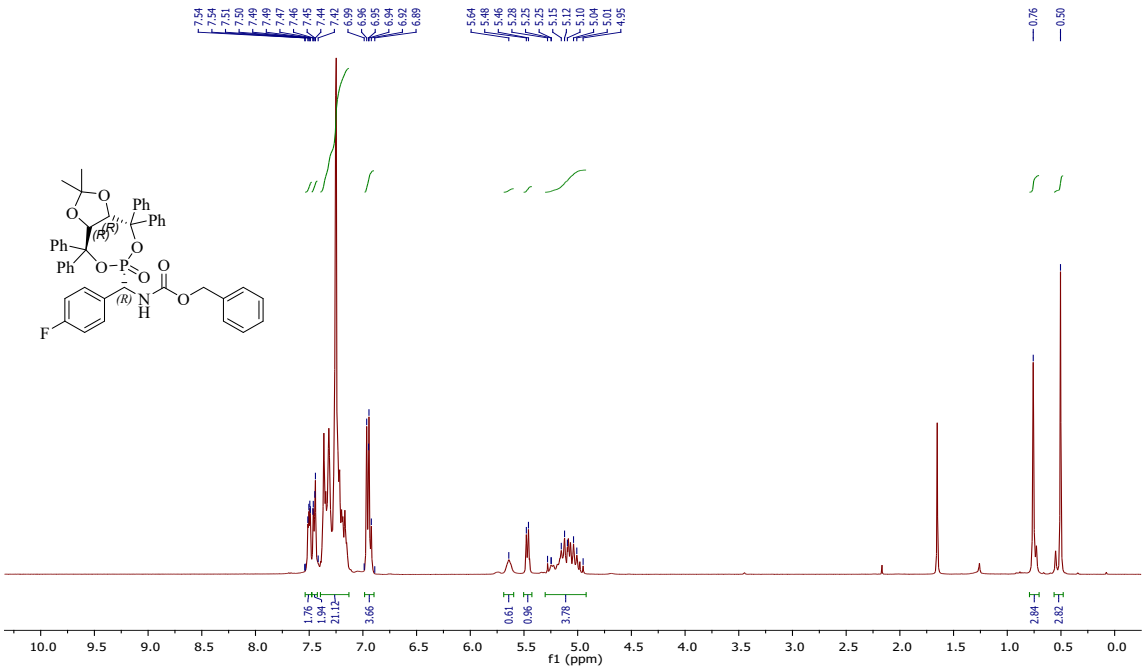
^{13}C NMR Spectrum **(*S*,*S*,*S*)-6a**



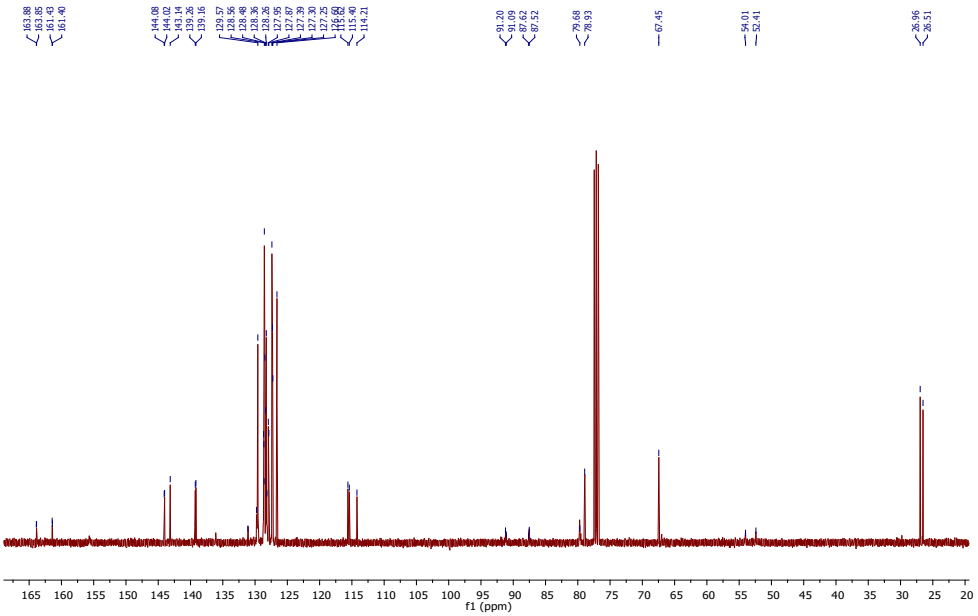
^{31}P NMR Spectrum **(*S*,*S*,*S*)-6a**



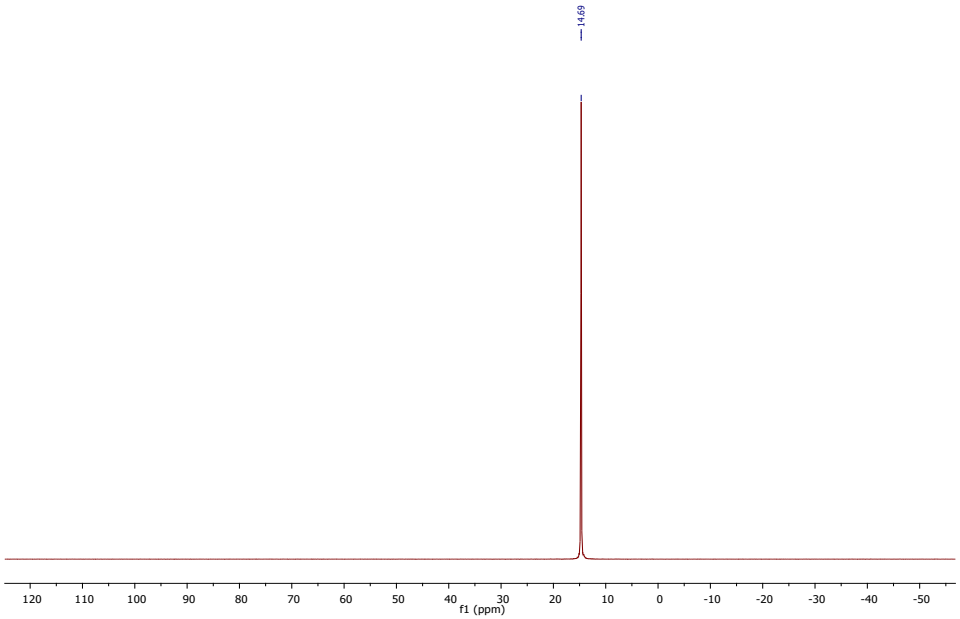
[1]H NMR Spectrum **(*R*,*R*,*R*)-6b**



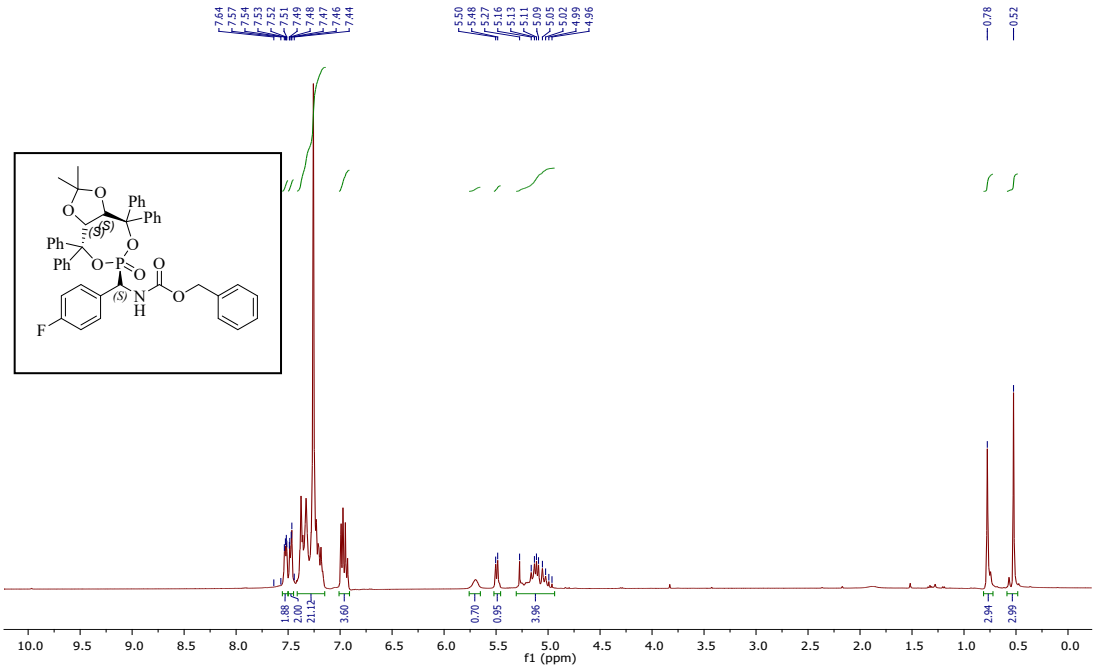
[13]C NMR Spectrum **(*R*,*R*,*R*)-6b**



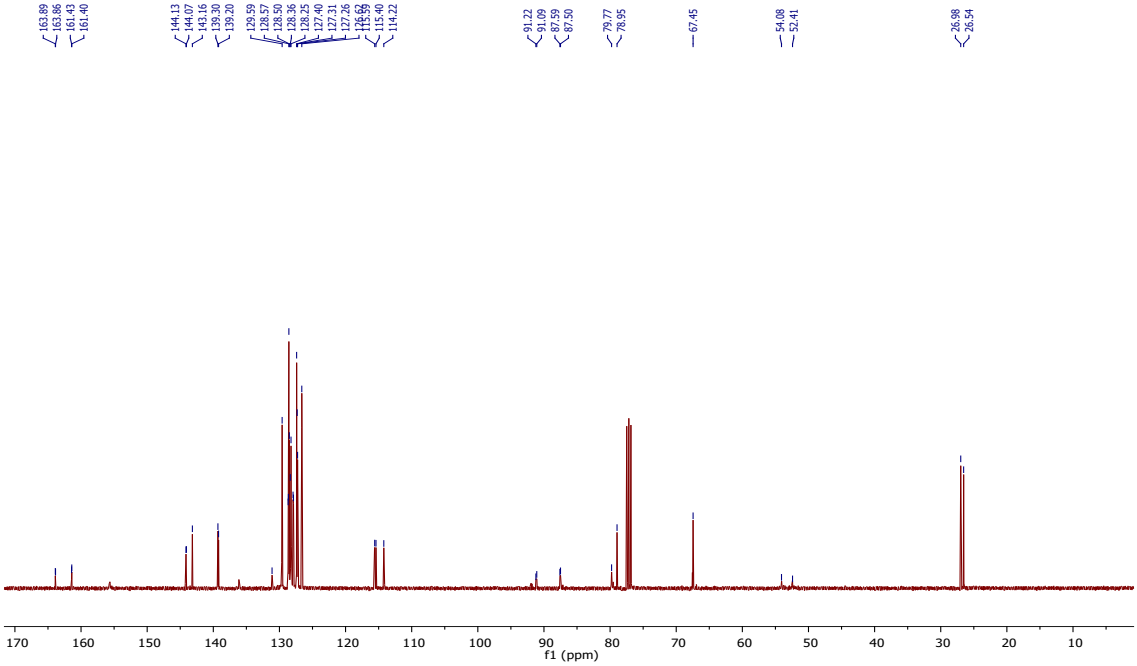
^{31}P NMR Spectrum **(*R*,*R*,*R*)-6b**



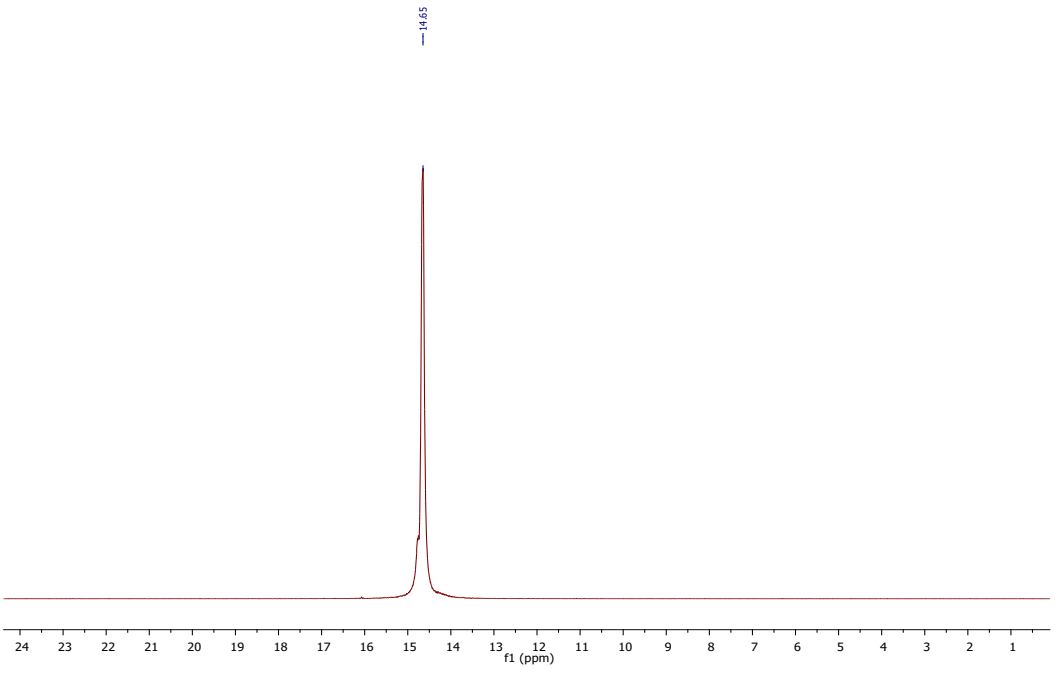
^{1}H NMR Spectrum **(*S*,*S*,*S*)-6b**



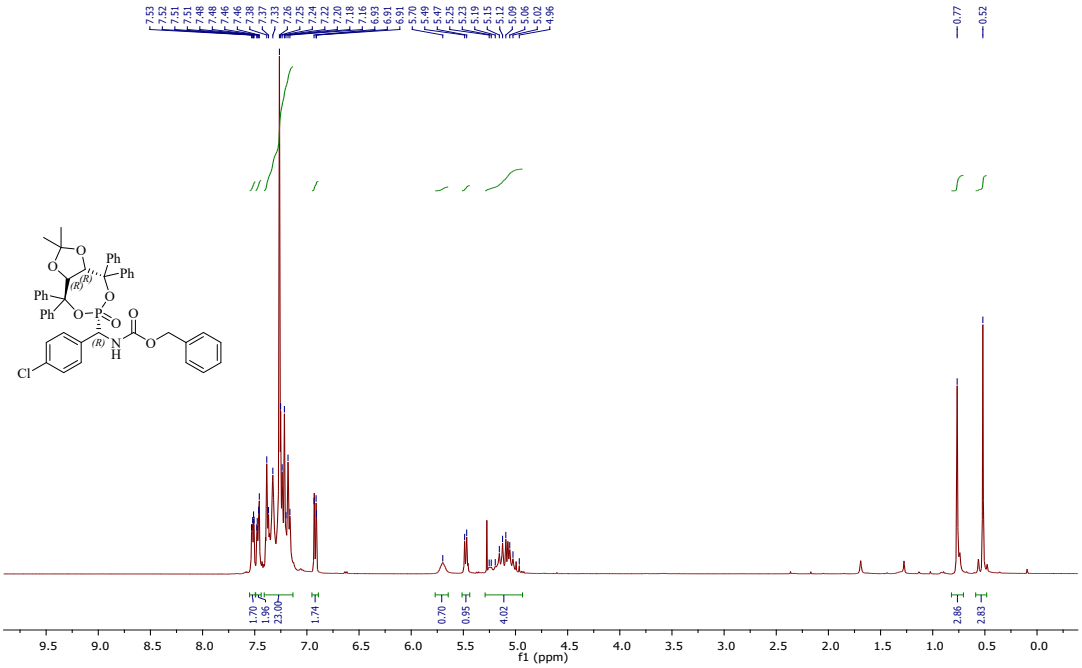
^{13}C NMR Spectrum **(*S*,*S*,*S*)-6b**



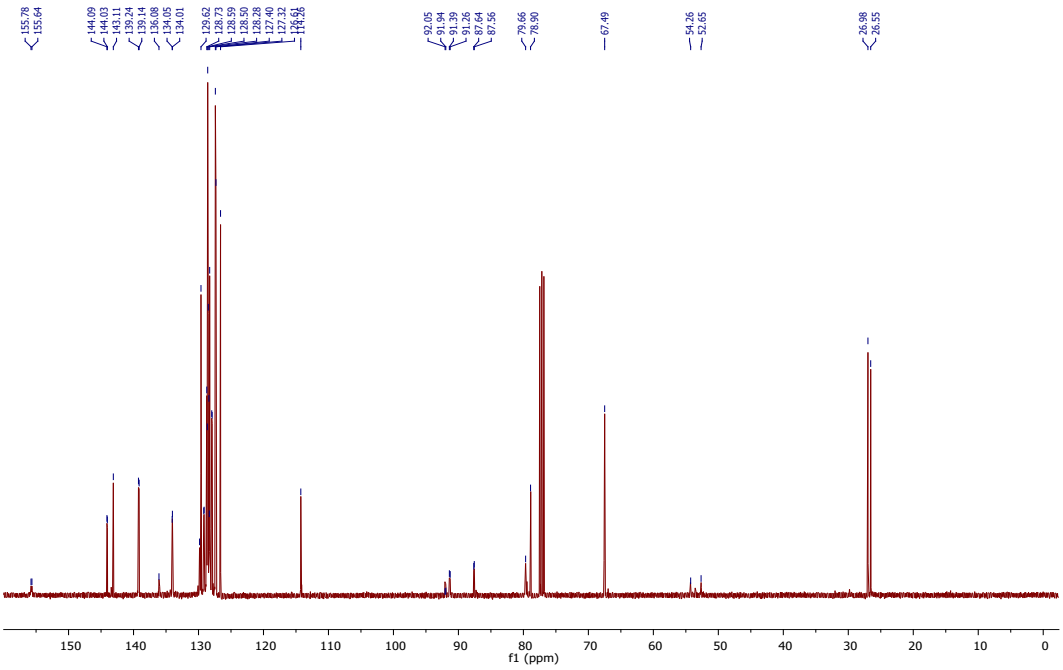
^{31}P NMR Spectrum **(*S*,*S*,*S*)-6b**



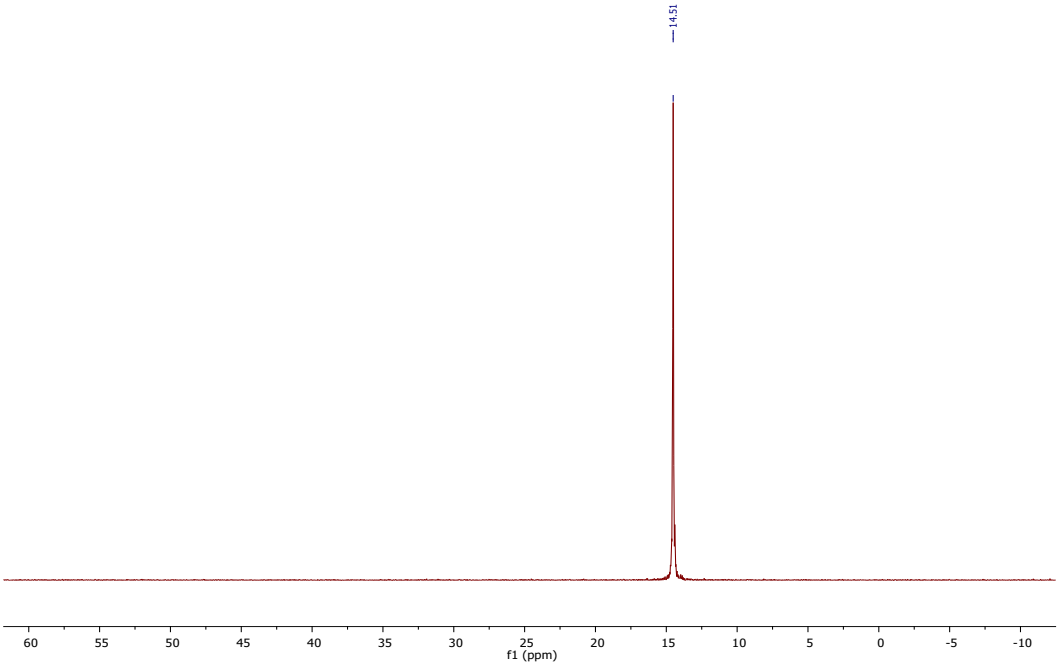
[1]H NMR Spectrum **(*R*,*R*,*R*)-6c**



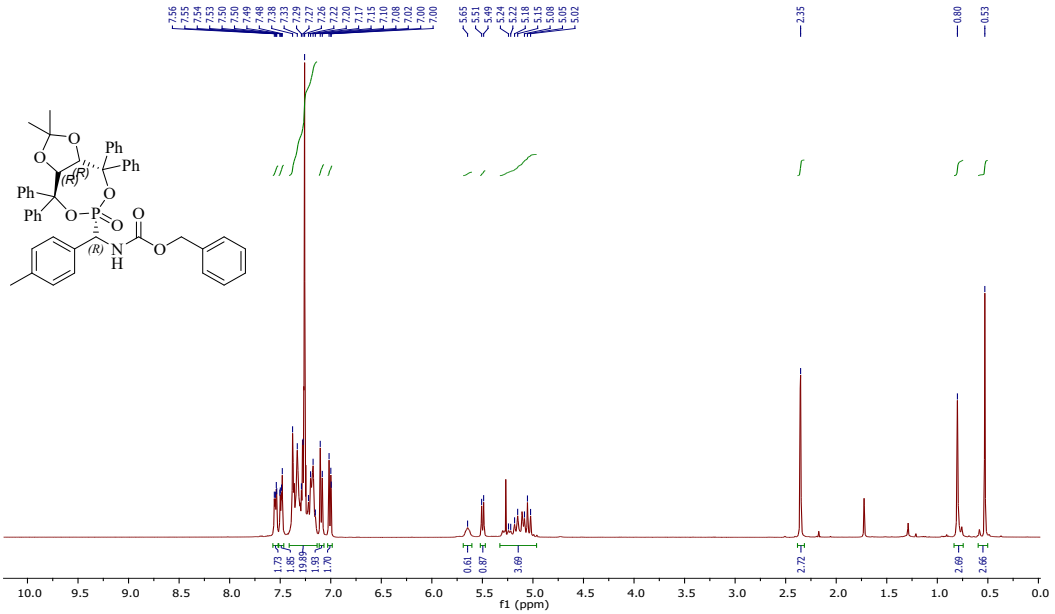
[13]C NMR Spectrum **(*R*,*R*,*R*)-6c**



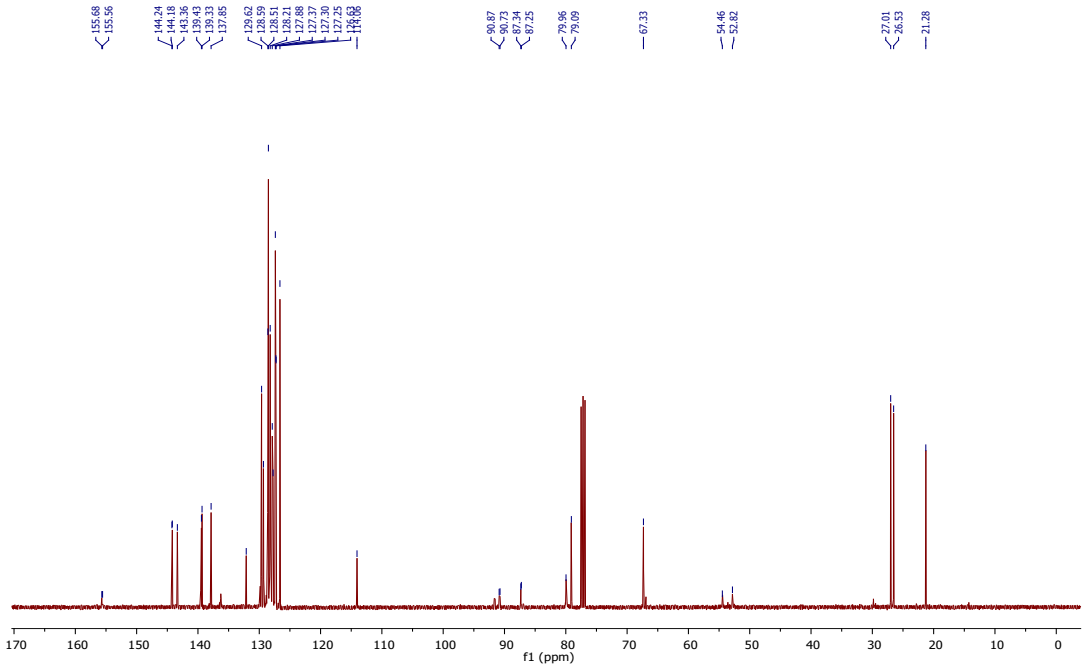
^{31}P NMR Spectrum **(*R*,*R*,*R*)-6c**



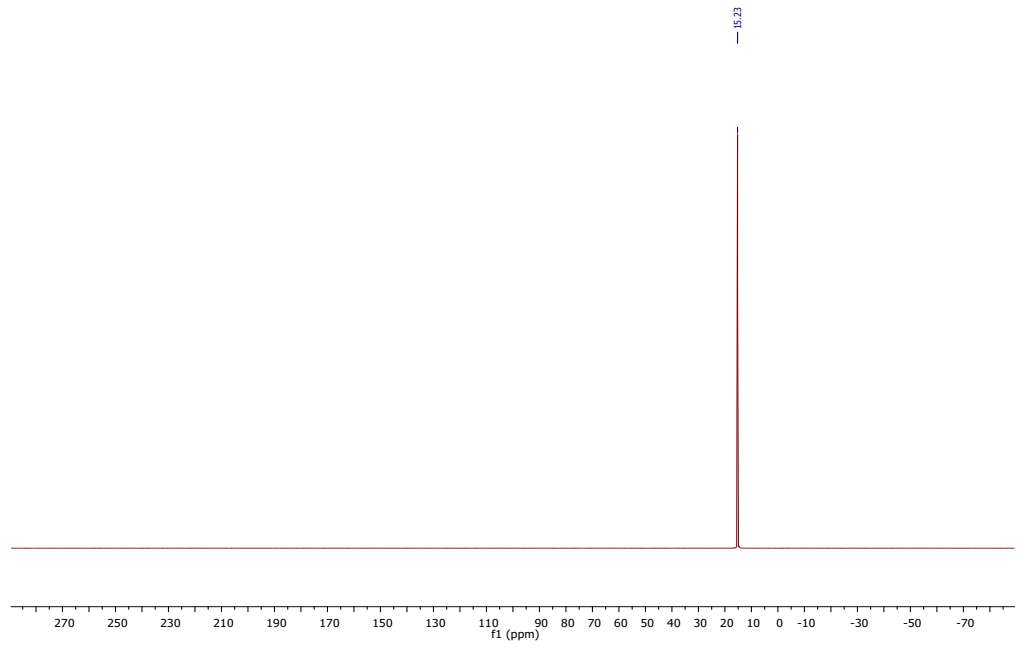
^{1}H NMR Spectrum **(*R*,*R*,*R*)-6d**



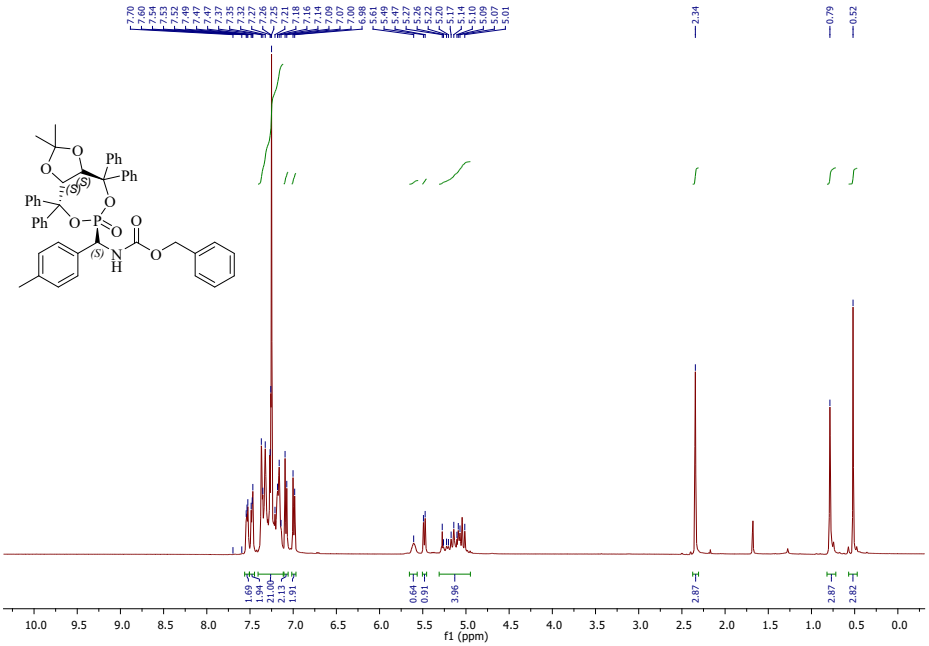
^{13}C NMR Spectrum **(*R*,*R*,*R*)-6d**



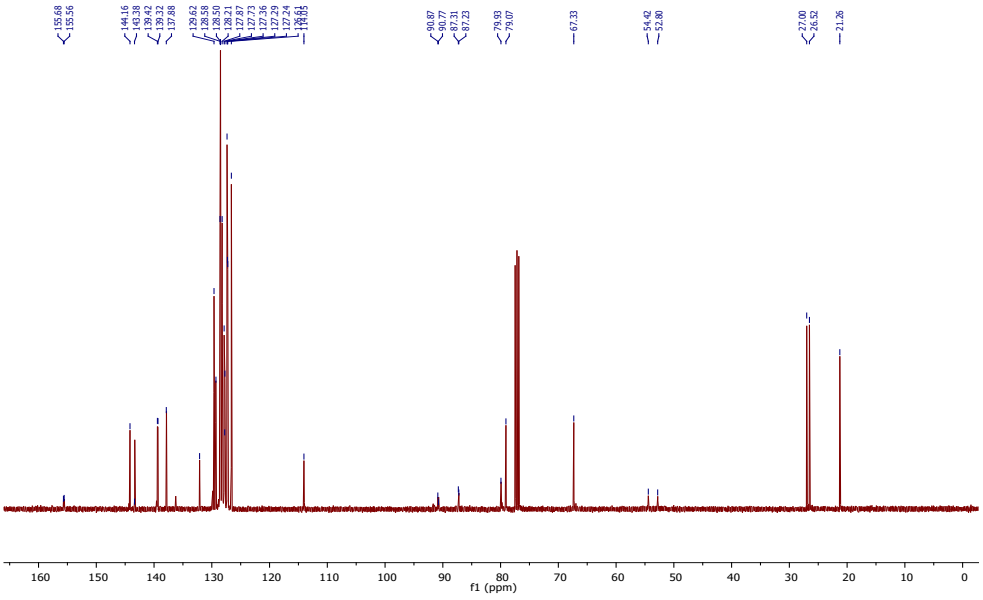
^{31}P NMR Spectrum **(*R*,*R*,*R*)-6d**



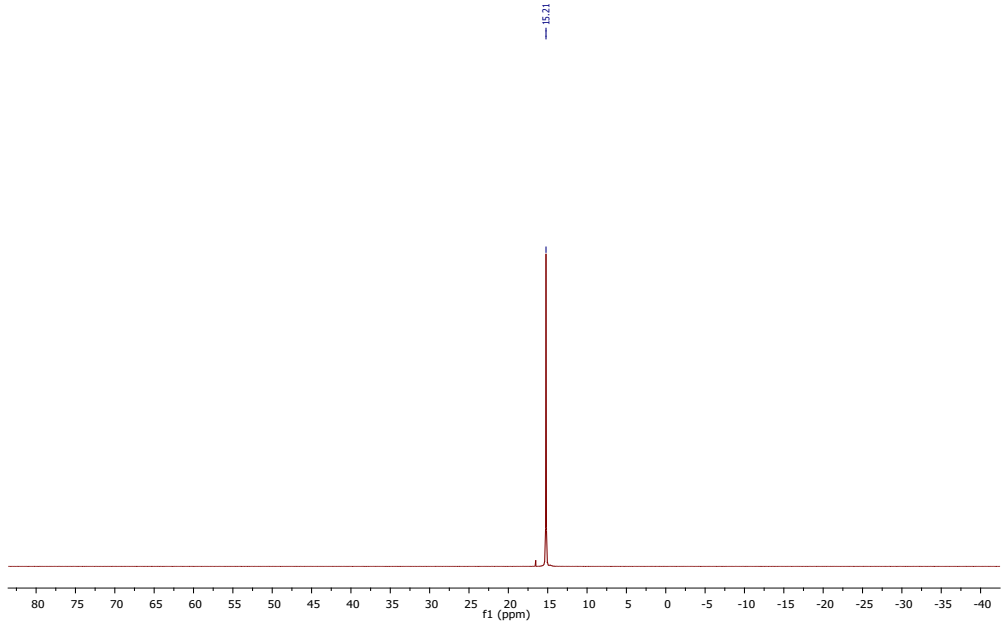
^{1}H NMR Spectrum **(*S*,*S*,*S*)-6d**



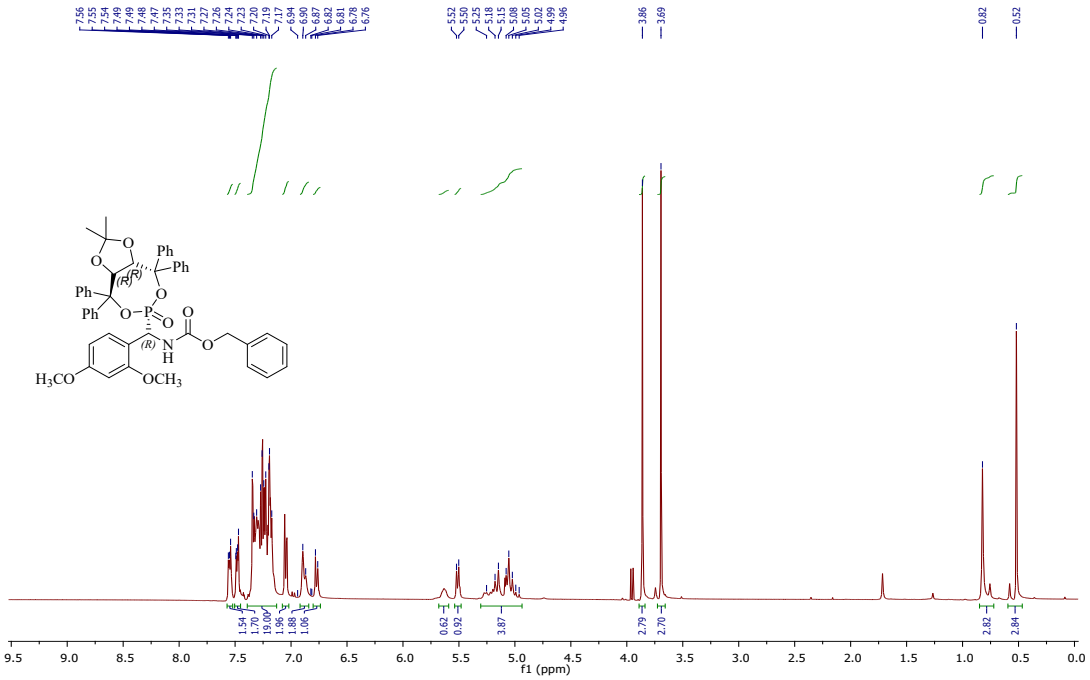
^{13}C NMR Spectrum **(*S*,*S*,*S*)-6d**



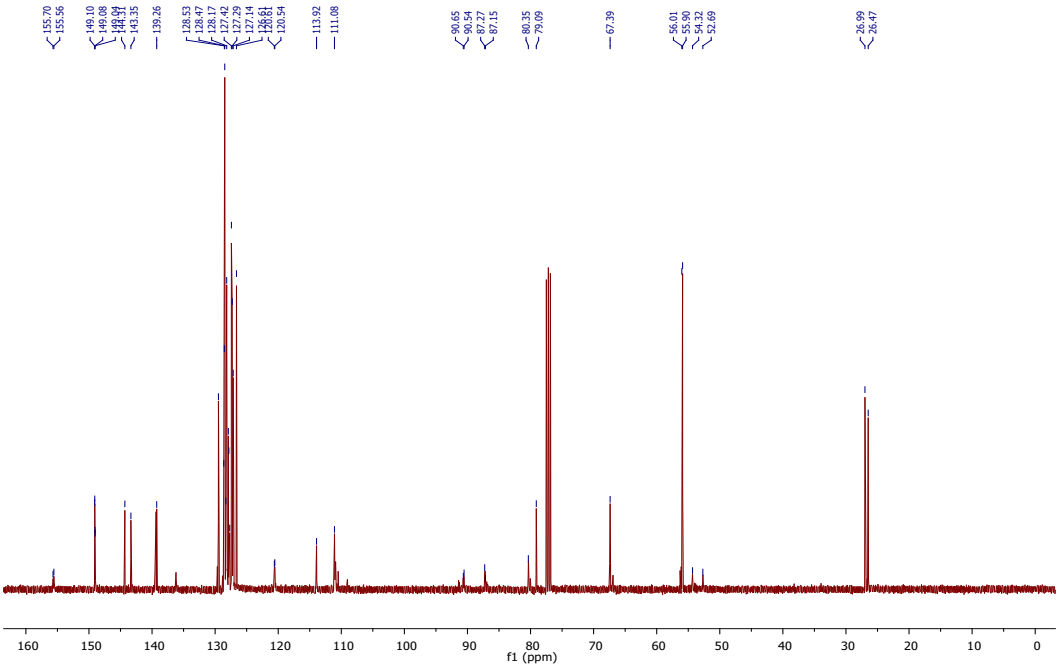
^{31}P NMR Spectrum **(*S*,*S*,*S*)-6d**



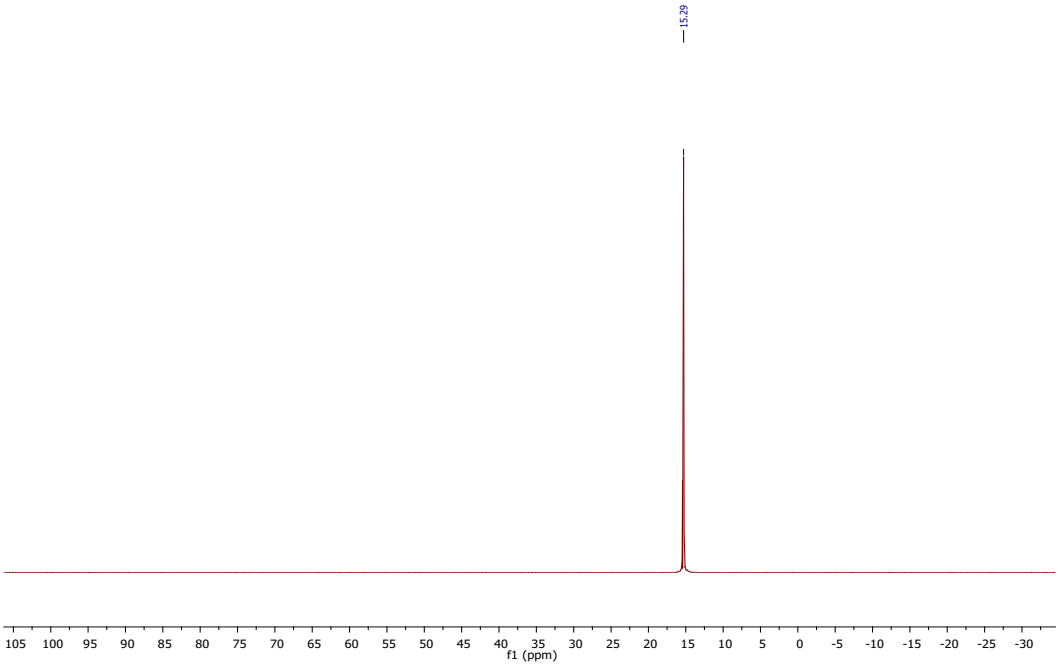
^{1}H NMR Spectrum **(*R*,*R*,*R*)-6e**



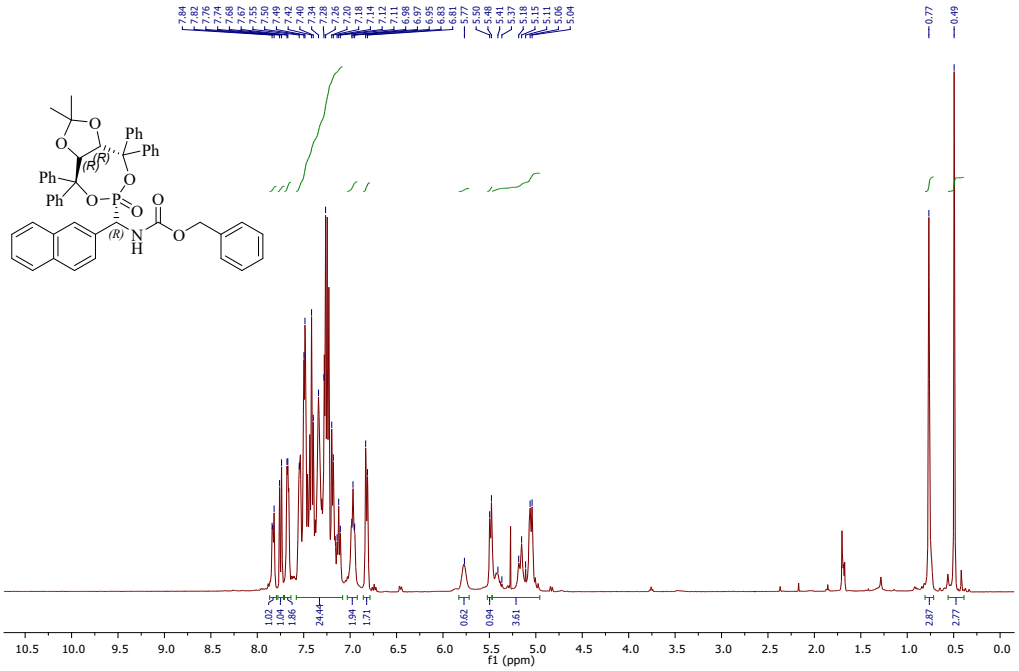
^{13}C NMR Spectrum **(*R*,*R*,*R*)-6e**



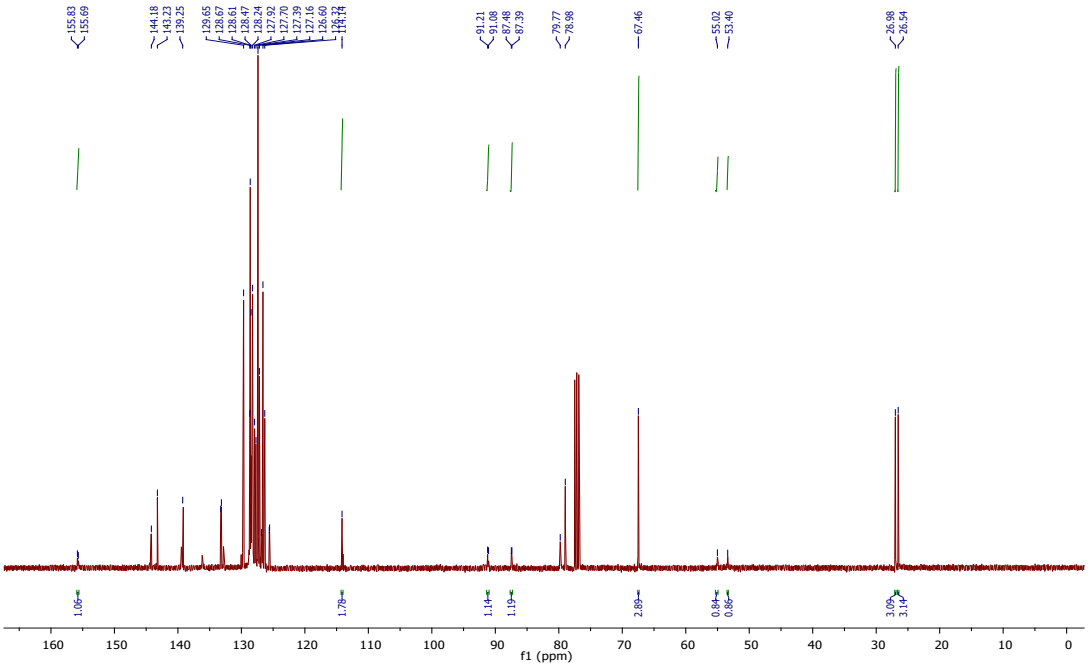
^{31}P NMR Spectrum **(*R*,*R*,*R*)-6e**



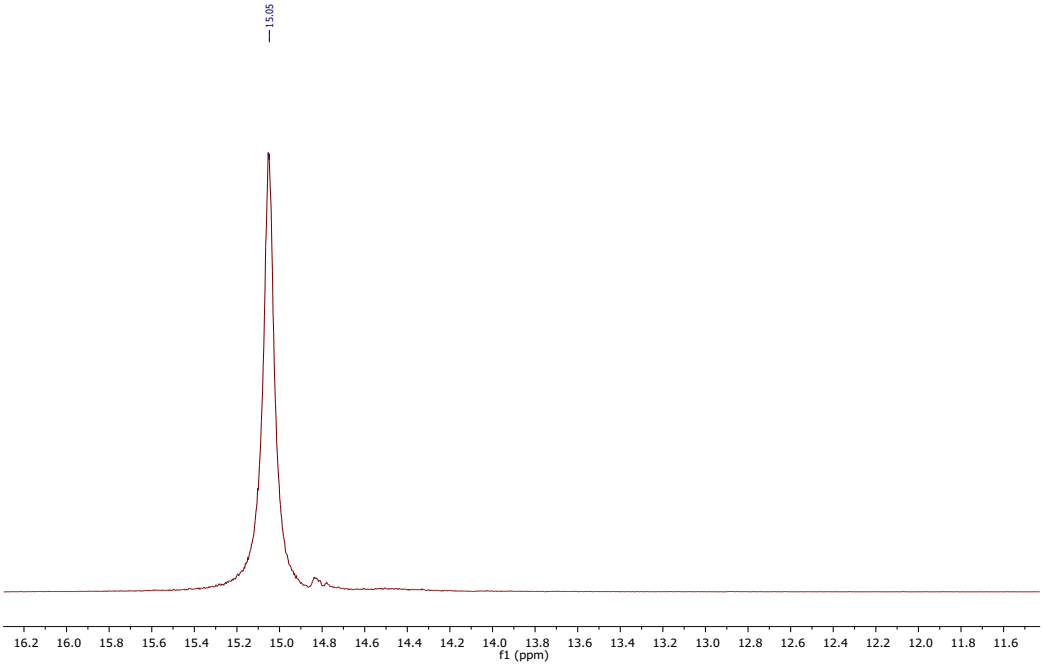
[1]H NMR Spectrum **(*R*,*R*,*R*)-6f**



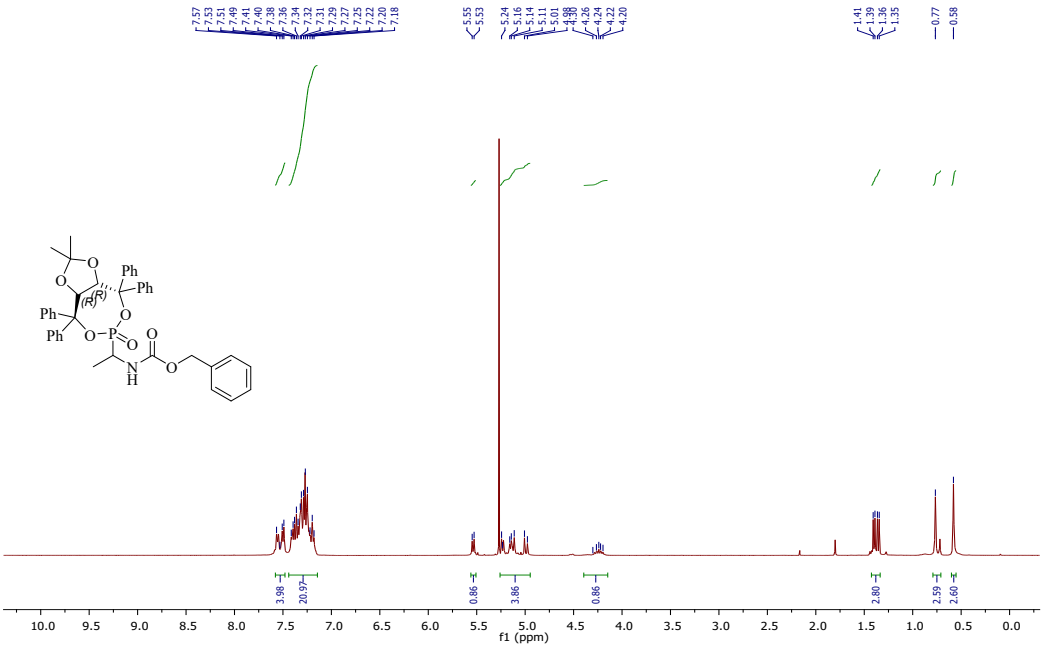
[13]C NMR Spectrum **(*R*,*R*,*R*)-6f**



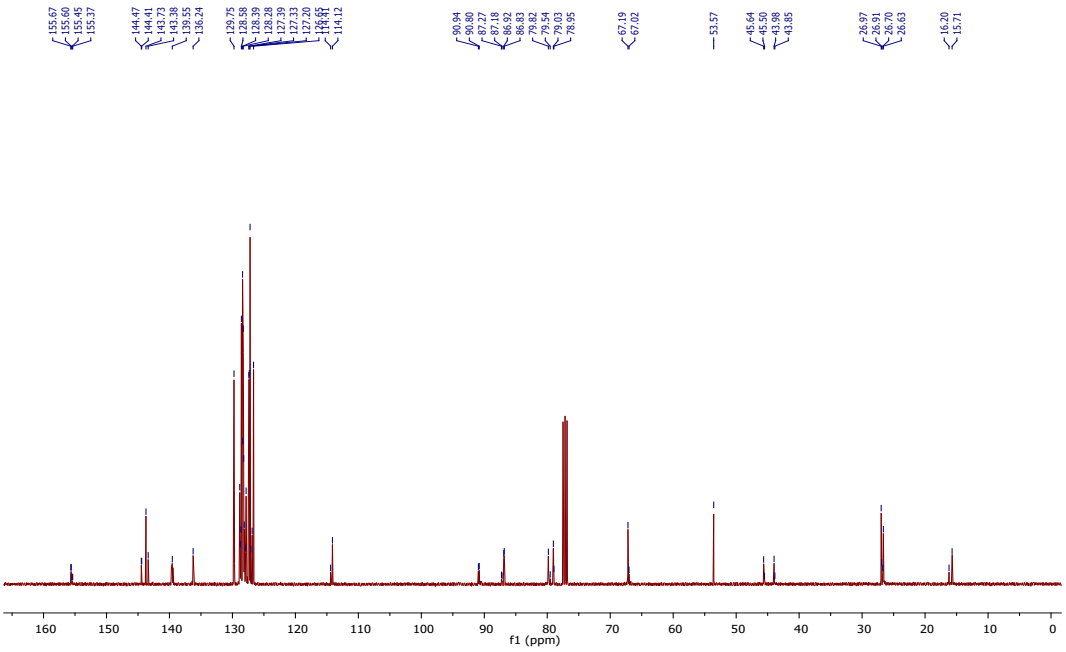
^{31}P NMR Spectrum **(*R,R,R*)-6f**



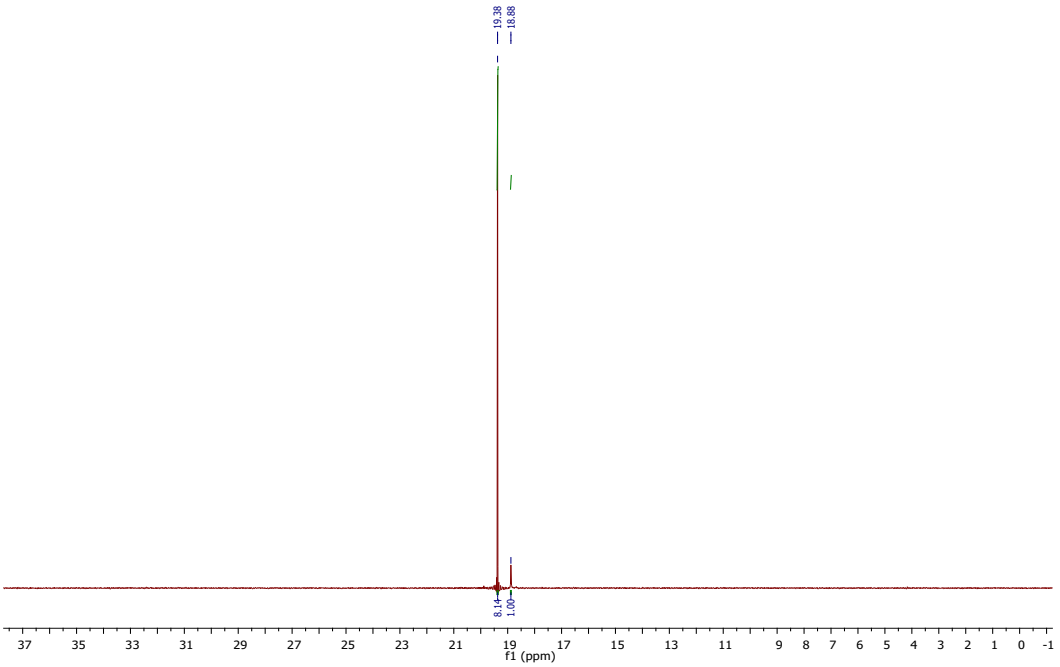
^{1}H NMR Spectrum **6g**



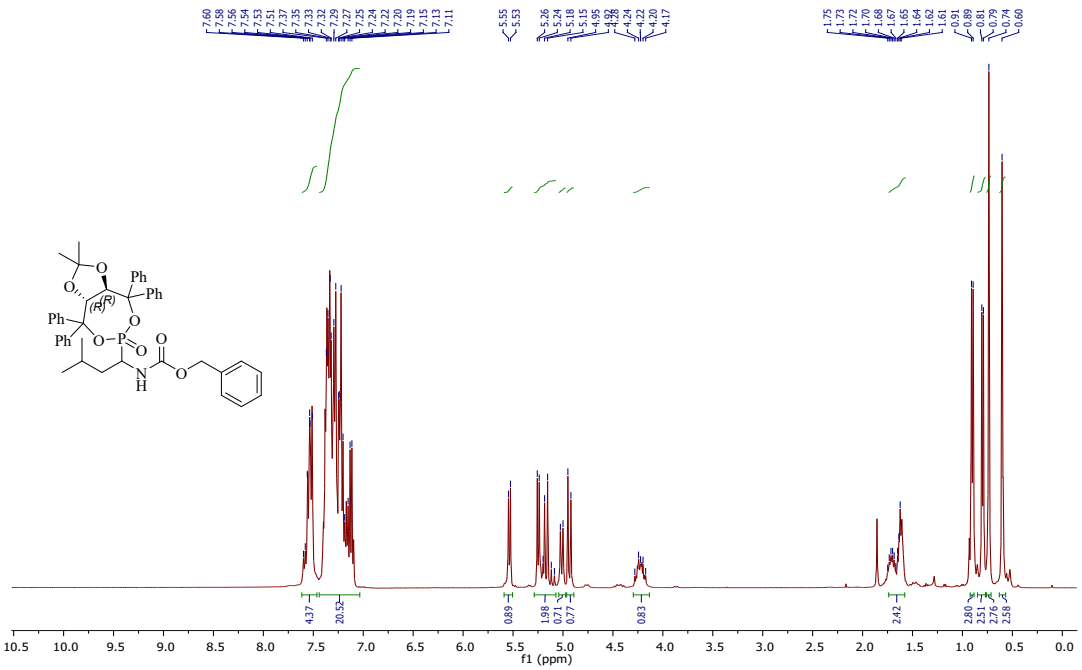
^{13}C NMR Spectrum **6g**



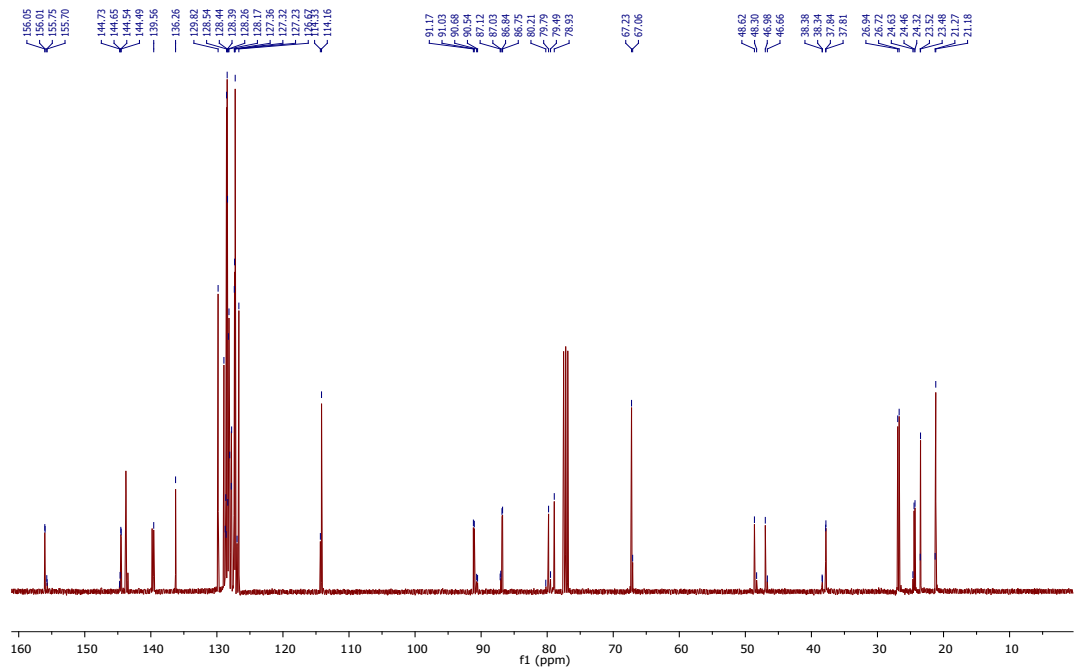
^{31}P NMR Spectrum **6g**



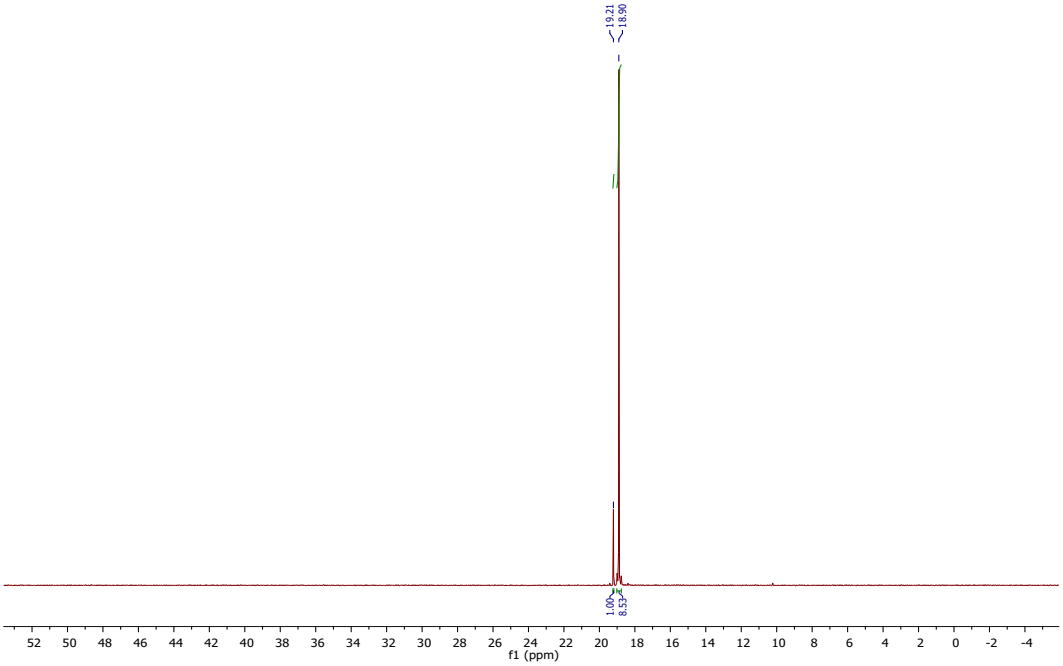
^{1}H NMR Spectrum **6h**



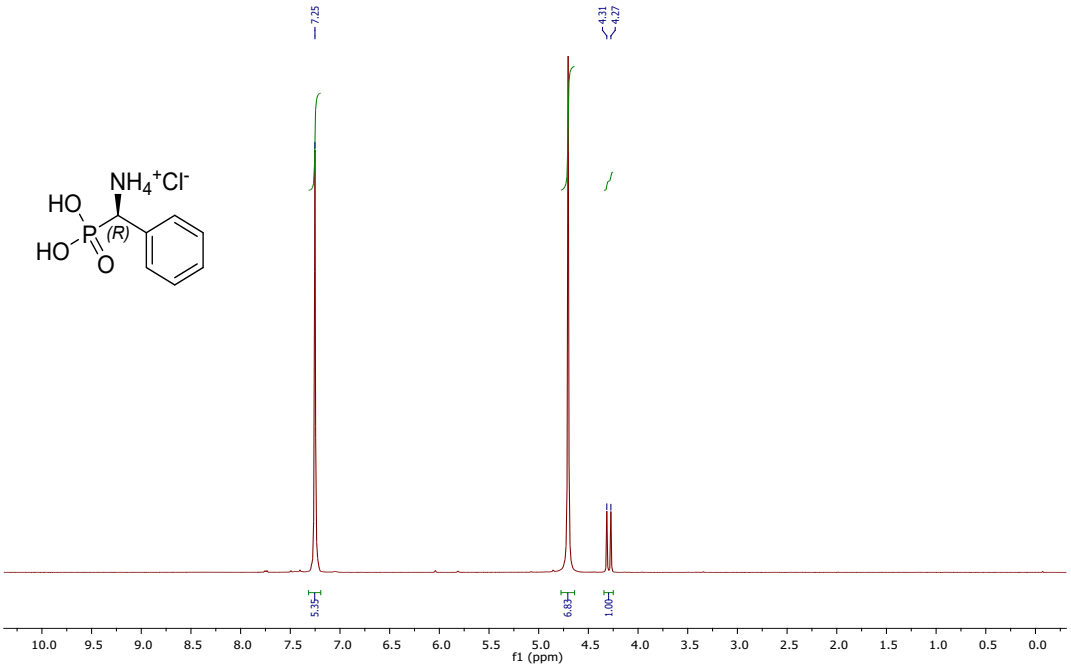
^{13}C NMR Spectrum **6h**



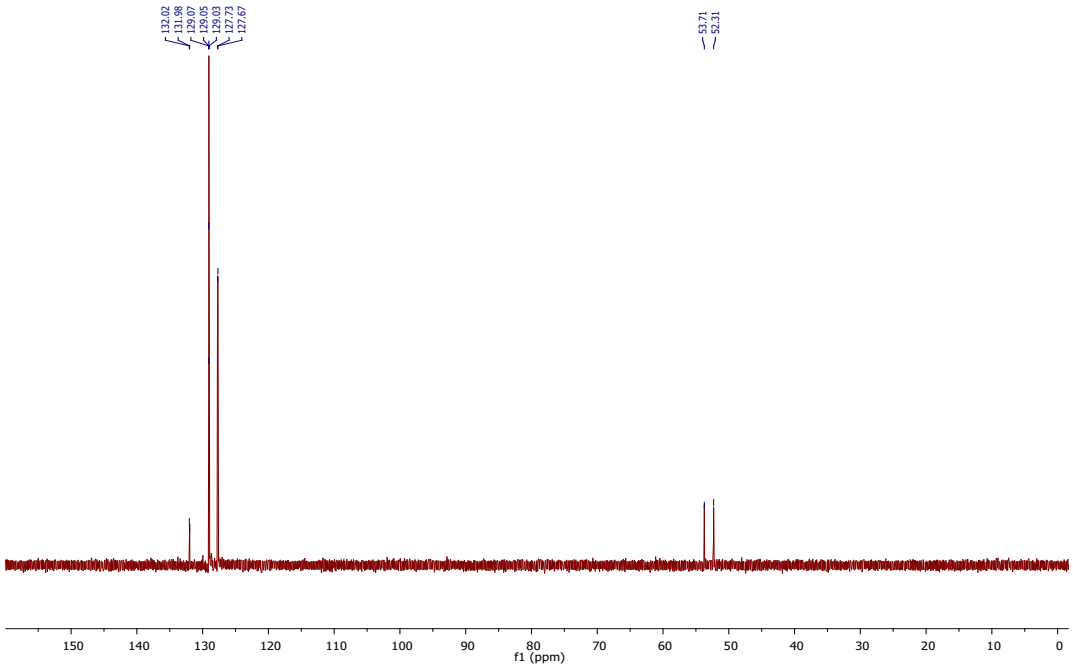
^{31}P NMR Spectrum **6h**



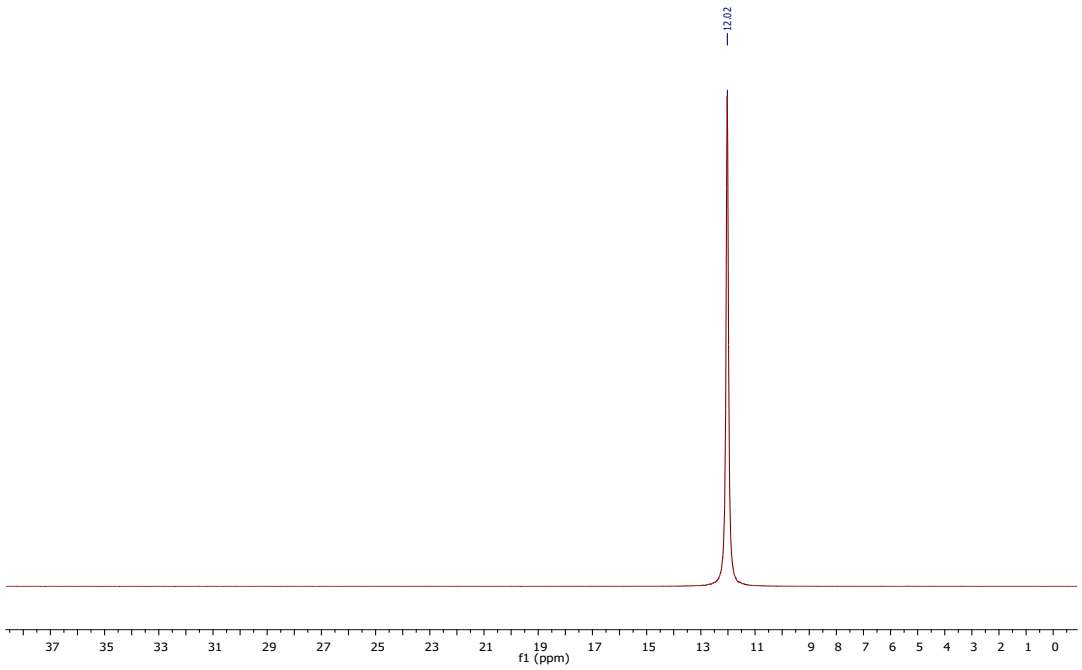
^{1}H NMR Spectrum **(*R*)-7a**



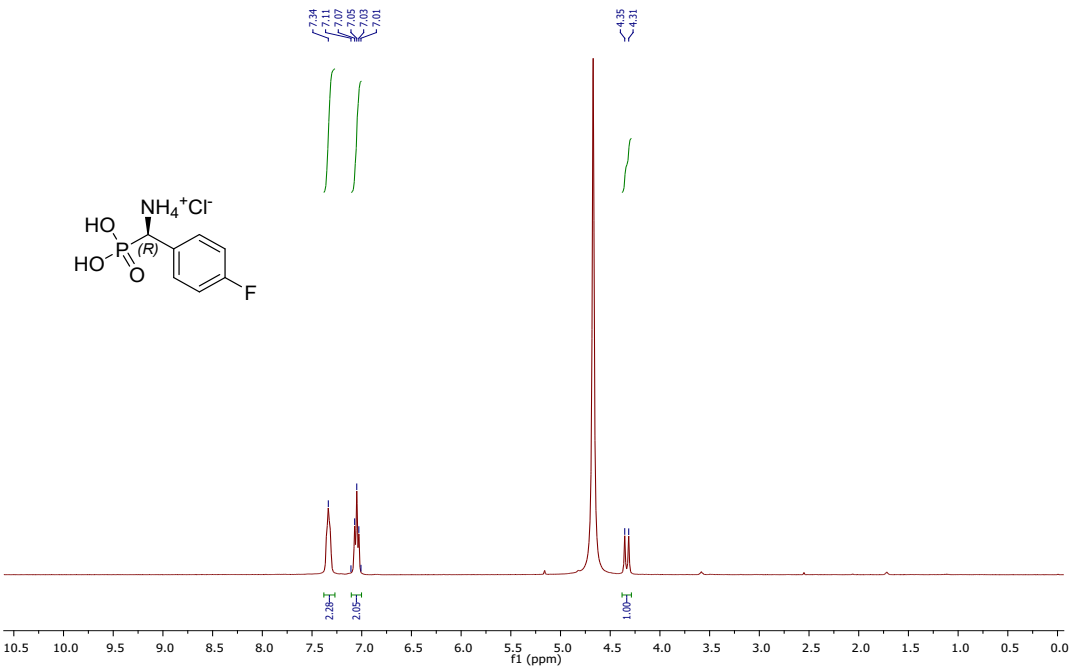
^{13}C NMR Spectrum **(*R*)-7a**



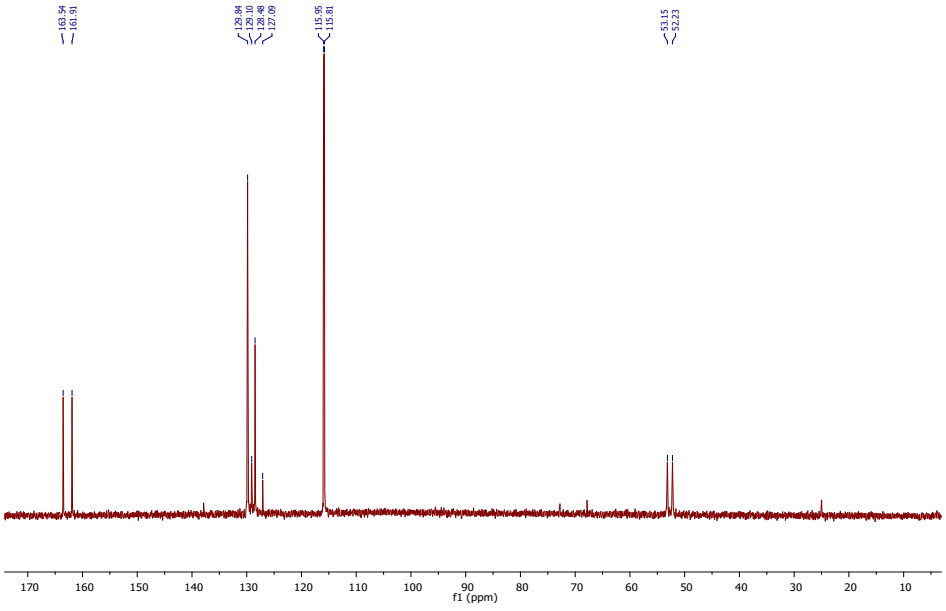
^{31}P NMR Spectrum **(*R*)-7a**



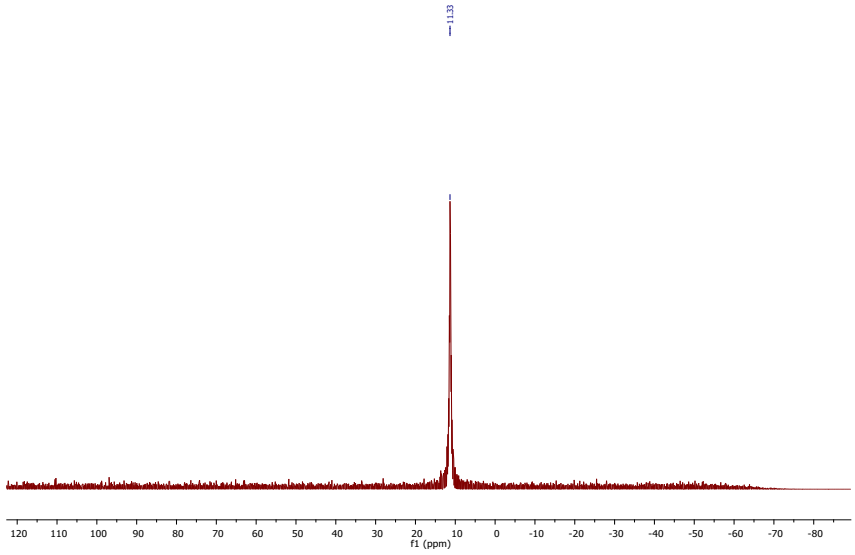
[1]H NMR Spectrum **(*R*)-7b**



[13]C NMR Spectrum **(*R*)-7b**



^{31}P NMR Spectrum **(*R*)-7b**



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