Supporting Information for

Enantioselective synthesis of α-aryl α-hydrazino phosphonates

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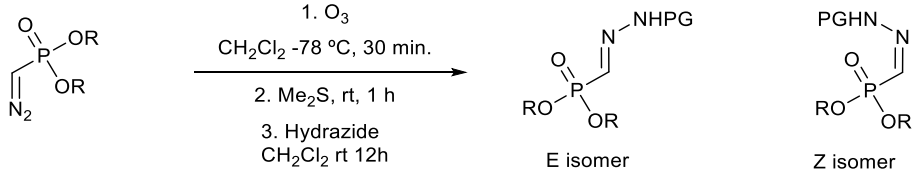
1. General information

^{1}H NMR spectra were recorded at 300 MHz or 500 MHz (internal reference; $CDCl_3$ = 7.26; DMSO-d^6 = 2.50). ^{13}C NMR spectra were recorded at 75.5 MHz or 126 MHz (internal reference; $CDCl_3$ = 77.0; DMSO-d^6 = 39.5); ^{19}F NMR spectra were recorded at 282 MHz. ^{31}P NMR spectra were recorded at 122 MHz. Multiplicities were given as: s (singlet), br s (broad singlet), d (doublet), dd (double doublet), ddd (double doublet of doublet), t (triplet), dt, (double triplet), td (triple doublet), q (quartet), dq (double quartet) and m (multiplet). Column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminum backed plates (1.5 × 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were visualized by exposure to UV light or/and by dipping the plates in solutions of vainilline or phosphomolibdic acid stains followed by heating. Optical rotations were measured on a JASCO P-2000 polarimeter. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak IA/IB/IC/ID and Chiralcel OD). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. All commercial arylboronic acids were purified by filtration trough a short silica gel pad (50 x 40 mm) and eluted with CH_2Cl_2/Et_2O (2/1). $Pd(TFA)_2$ was purchased from TCI Europe and pyridine-oxazolines (**L1**, **L2**) from Aldrich. Not-commercially available pyridine-hydrazone ligands (**L3**, **L5**),[1] (**L4**, **L6**),[2] methyl 6-formylnicotinate,[3] (2*R*,5*R*)-1-amino-2,5-diphenylpyrrolidine,[4] diethyl and dimethyl (diazomethyl)phosphonate,[5] bromoacetic anhydride,[6] and *N*-Boc protected phenylalanine anhydride [**(*N*-Boc-Phe)$_2$O**][7] were synthesized according to literature procedures.

2. General procedure for the synthesis of α-hydrazono phosphonates 1A-E



To a solution of diazomethylphosphonate (1.25 equiv.) in CH_2Cl_2 (1.0 M) was bubbled ozone at –78 °C for 30 min. After this time, Me_2S (1.5 equiv.) was added and the reaction mixture was stirred for 1 hour at room temperature. Then, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (0.5 M) and the corresponding hydrazide was added (1 equiv.). The resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (*n*-hexane/EtOAc 2/1 to EtOAc) to afford the α-hydrazono phosphonate **1A-E**.

Benzyl (*E*)-2-[(diethoxyphosphoryl)methylene]hydrazine-1-carboxylate. 1A: Following the general procedure **2**, starting from diethyl (diazomethyl)phosphonate (1.11 g, 6.25 mmol) and benzyl carbazate (830 mg, 5 mmol), the α-hydrazono phosphonates (*E*)-**1A** and (*Z*)-**1A** were obtained as a colorless oil (800 mg, 51% and 126 mg, 8%, respectively; E/Z ratio: 6/1). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 10.03 (br s, 1H), 7.58 (d, $^{2}J_{P,H}$ = 47.6 Hz, 1H), 7.40 – 7.27 (m, 5H), 5.20 (s, 2H), 4.22 – 4.04 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 153.0, 137.0 (d, $^{1}J_{P,C}$ = 232.2 Hz), 135.5, 128.5, 128.4, 128.3, 67.53, 63.3 (d, $^{2}J_{P,C}$ = 6.1 Hz), 16.1 (d, $^{3}J_{P,C}$ = 6.3 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 8.73. **HRMS** (ESI) *m/z* calcd. for $C_{13}H_{19}O_5N_2PNa$ [M^++Na] 337.0924, found 337.0922.

Spectroscopy data of (*Z*)-**1A**: **^{1}H NMR** (300 MHz, $CDCl_3$): δ 11.54 (br s, 1H), 7.38 (m, 5H), 6.86 (d, $^{2}J_{P,H}$ = 44.9 Hz, 1H), 5.27 (s, 2H), 4.24 – 4.03 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 153.3, 136.5 (d, $^{1}J_{P,C}$ = 234.0 Hz), 135.5, 128.6, 128.5, 128.4, 67.7, 63.5 (d, $^{2}J_{P,C}$ = 6.3 Hz), 16.2 (d, $^{3}J_{P,C}$ = 6.3 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 4.86.

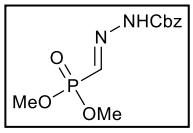
(9*H*-Fluoren-9-yl)methyl (*E*)-2-[(diethoxyphosphoryl)methylene]hydrazine-1-carboxylate. 1B: Following the general procedure **2**, starting from diethyl (diazomethyl)phosphonate (445 mg, 2.5 mmol) and (9*H*-fluoren-9-yl)methyl carbazate (508 mg, 2 mmol), the α-hydrazono phosphonates (*E*)-**1B** and (*Z*)-**1B** were obtained as a white solid (612 mg, 76% and 80 mg, 10%, respectively; E/Z ratio: 8/1). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 10.48 (br s, 1H), 7.80 – 7.56 (m, 5H), 7.42 – 7.34 (m, 2H), 7.28 (td, *J* = 7.5, 1.2 Hz, 2H), 4.45 (d, *J* = 7.4 Hz, 2H), 4.30 – 4.14 (m, 5H), 1.35 (td, $J_{H,H}$ = 7.2, $^{4}J_{P,H}$ = 0.4 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 153.3, 143.4, 141.2, 136.9 (d, $^{1}J_{P,C}$ = 232.1 Hz), 127.7, 127.0, 125.1, 119.9, 67.8, 63.3 (d, $^{2}J_{P,C}$ = 6.2 Hz), 46.7, 16.2 (d, $^{3}J_{P,C}$ = 6.2 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 8.69. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{23}O_5N_2PNa$ [M^++Na] 425.1237, found 425.1225.

Diethyl (*E*)-[(2-benzoylhydrazineylidene)methyl]phosphonate 1C: Following the general procedure **2**, starting from diethyl (diazomethyl)phosphonate (445 mg, 2.5 mmol) and benzohydrazide (272 mg, 2 mmol), the α-hydrazono phosphonate (*E*)-**1C** was obtained as a colorless solid (216 mg, 38%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 11.74 (br s, 1H), 8.29 (d, $^{2}J_{P,H}$ = 44.0 Hz, 1H) 7.56 – 7.30 (m, 5H), 4.25 – 4.04 (m, 4H), 1.29 (t, *J* = 7.0, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 164.9, 141.2 (d, $^{1}J_{P,C}$ = 225.3 Hz), 132.2, 131.7, 128.6, 128.4, 63.3 (d, $^{2}J_{P,C}$ = 6.1 Hz), 16.2 (d, $^{3}J_{P,C}$ = 6.1 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 8.95. **HRMS** (ESI) *m/z* calcd. for $C_{12}H_{17}O_4N_2PNa$ [M^++Na] 307.0818, found 307.0814.

***tert*-Butyl (*E*)-2-[(diethoxyphosphoryl)methylene]hydrazine-1-carboxylate. 1D:** Following the general procedure **2**, starting from diethyl (diazomethyl)phosphonate (445 mg, 2.5 mmol) and *tert*-butyl carbazate (264 mg, 2 mmol), the α-hydrazono phosphonates (*E*)-**1D** and (*Z*)-**1D** were obtained as a colorless oil (348 mg, 62% and 50 mg, 9%, respectively; E/Z ratio: 7/1). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.79 (br s, 1H), 7.53 (d, $^{2}J_{P,H}$ = 46.4 Hz, 1H), 4.14 (dq, $^{3}J_{P,H}$ = 14.2, $J_{H,H}$ = 7.1 Hz, 4H), 1.44 (s, 9H), 1.30 (td, $J_{H,H}$ = 7.1, $^{4}J_{P,H}$ = 0.5 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 152.0, 135.4 (d, $^{1}J_{P,C}$ = 229.7 Hz), 81.7, 63.1 (d, $^{2}J_{P,C}$ = 6.2 Hz), 28.0, 16.2 (d, $^{3}J_{P,C}$ = 6.3 Hz). **^{31}P NMR** (122

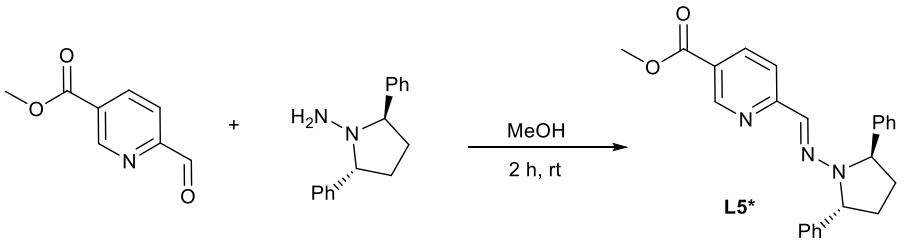
MHz, $CDCl_3$): δ 9.12. **HRMS** (ESI) *m/z* calcd. for $C_{10}H_{21}O_5N_2PNa$ [M^++Na] 303.1080, found 310.1078.

Benzyl (*E*)-2-[(dimethoxyphosphoryl)methylene]hydrazine-1-carboxylate. 1E: Following



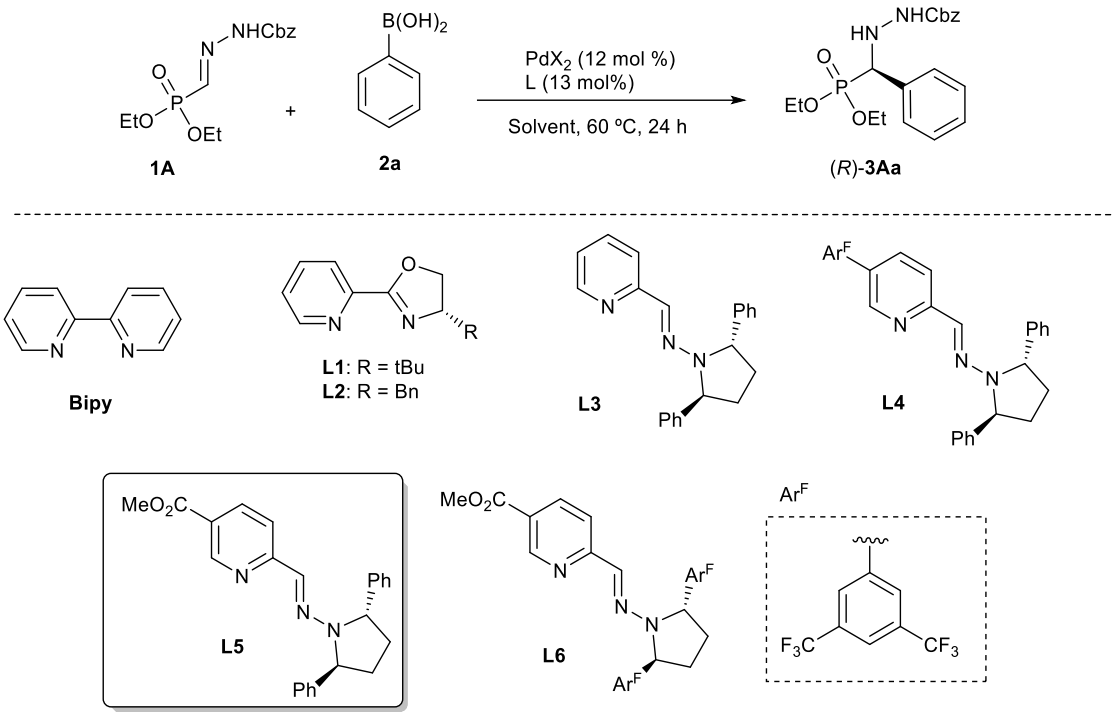
the general procedure **2**, starting from dimethyl (diazomethyl)phosphonate (0.19 g, 1.25 mmol) and benzyl carbazate (166 mg, 1 mmol), the α-hydrazono phosphonate (*E*)-**1E** was obtained as a colorless oil (210 mg, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 10.46 (br s, 1H), 7.52 (d, $^2J_{P,H}$ = 46.4 Hz, 1H), 7.37 – 7.25 (m, 5H), 5.18 (s, 2H), 3.71 (d, *J* = 11.1 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 153.1, 135.8 (d, $^1J_{P,C}$ = 232.1 Hz), 135.4, 128.4, 128.3, 128.2, 67.5, 53.5 (d, $^2J_{P,C}$ = 6.3 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 10.52. **HRMS** (ESI) *m/z* calcd. for $C_{11}H_{15}O_5N_2PNa$ [M^++Na] 309.0611, found 309.0613.

3. Synthesis of pyridine-hydrazone ligand *ent*-L5*



To a solution of methyl 6-formylnicotinate (181 mg, 1.1 mmol) in MeOH (0.3 M) was added dropwise a solution of (2*R*,5*R*)-1-amino-2,5-diphenylpyrrolidine (262 mg, 1.1 mmol) in MeOH (0.3 M). The resulting mixture was stirred at room temperature for 2 h. After this time, the resulting solid was washed with cold MeOH to afford ***ent*-L5*** as a crystalline white solid. (179 mg, 42%). Mp: 127-129 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 2.0, 0.6 Hz, 1H), 8.02 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.33 – 7.20 (s, 6H), 7.03 (s, 1H), 5.25 (d, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 2.68 – 2.50 (m, 2H), 2.01 – 1.82 (m, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 166.0, 159.8, 150.4, 142.2, 136.5, 130.7, 128.7, 127.1, 126.1, 122.6, 117.6, 65.6, 52.0, 31.5. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{24}O_2N_3$ [M^++H] 386.1857, found 386.1851. **$[\alpha]_D^{25}$** = +404.2 (*c* 1.0, $CHCl_3$).

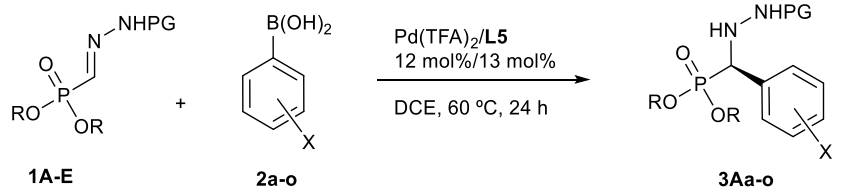
4. Table S1. Optimization of reaction conditions



Entry	PdX_2	L	Solvent	Conv. [%][b]	ee [%][c]
1	$PdCl_2$	**Bipy**	DCE	9	--
2	$Pd(OAc)_2$	**Bipy**	DCE	33	--
3	$Pd(TFA)_2$	**Bipy**	DCE	58	--
4	$Pd(TFA)_2$	**L1**	DCE	20	33*
5	$Pd(TFA)_2$	**L2**	DCE	46	4*
6	$Pd(TFA)_2$	**L3**	DCE	70	94
7	$Pd(TFA)_2$	**L4**	DCE	52	97
8	$Pd(TFA)_2$	**L5**	DCE	84	99
9[d]	$Pd(TFA)_2$	**L5**	DCE	86	98
10	$Pd(TFA)_2$	**L6**	DCE	85	93
11	$Pd(TFA)_2$	**L5**	1,4-Dioxane	nr	--
12	$Pd(TFA)_2$	**L5**	Toluene	35	86
13	$Pd(TFA)_2$	**L5**	TFE	62	90
14	$Pd(TFA)_2$	**L5**	DCE[e]	64	97
15	$Pd(TFA)_2$	**L5**	DCE/H_2O[f]	74	95
16[g]	$Pd(TFA)_2$	**L5**	DCE	68	98
17[h]	$Pd(TFA)_2$	**L5**	DCE	73	96

[a] Reaction conditions: **1A** (0.1 mmol), **2a** (0.15 mmol), **L** (13 mol%), PdX_2 (12 mol%), solvent (0.25 mL), 60 °C, 24 h. [b] Estimated by ^{31}P-NMR. [c] Determined by HPLC on chiral stationary phases. [d] Starting from (*Z*)-**1A**. [e] Dry DCE and 12 mg of M.S. (4 Å). [f] Dry DCE and 2 μL of H_2O (0.55 equiv.). [g]Performed with 2,4,6-triphenylboroxine (0.05 mmol). [h]Performed at 80 °C. TFE = trifluoroethanol. DCE = 1,2-Dichloroethane. nr = not reaction. *(*S*)-**3Aa**.

5. General procedure for the palladium catalyzed enantioselective synthesis of α-aryl α-hydrazino phosphonates 3



1A-E **2a-o** **3Aa-o**

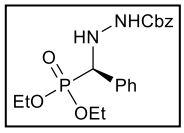
PG: Cbz, Fmoc, Boc, Bz
R: Et, Me

General procedure 5A: To a sealed tube charged with $Pd(TFA)_2$ (8 mg, 0.024 mmol), **L5** (10 mg, 0.026 mmol), and arylboronic acid **2** (0.3 mmol) was added a solution of α-hydrazono phosphonate **(*E*)-1A-E** (0.2 mmol) in DCE (0.5 mL). The resulting mixture was stirred at 60 ºC for 36 h. After this time, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (*n*-hexane/EtOAc 2/1 to EtOAc).

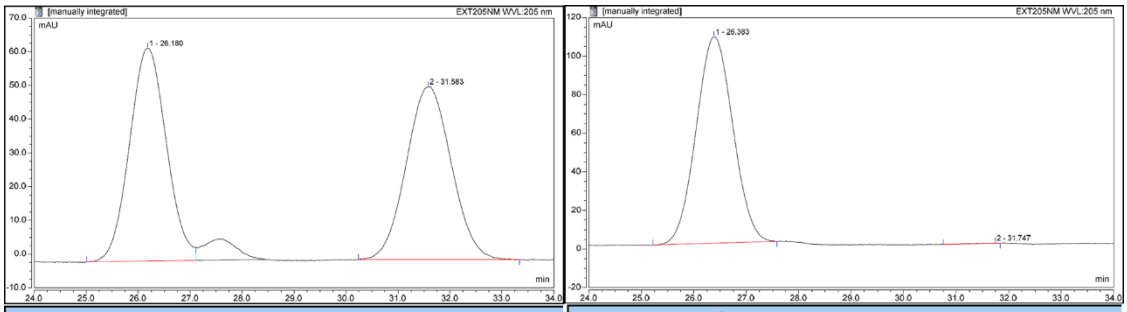
General procedure 5B: To a sealed tube charged with $Pd(TFA)_2$ (8 mg, 0.024 mmol), **L5** (10 mg, 0.026 mmol), and arylboronic acid **2** (0.15 mmol) was added a solution of α-hydrazono phosphonate (*E*)-**1A-E** (0.2 mmol) in DCE (0.5 mL). The resulting mixture was stirred at 60 ºC for 8 h. Then, the reaction mixture was allowed to cold to rt and more arylboronic acid **2** (0.15 mmol) was added and the mixture was stirred at 60 ºC for 28 h. After this time, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (*n*-hexane/EtOAc 2/1 to EtOAc).

Racemic products were synthesized using an analogous procedure with bipyridine instead of **L5**.

Benzyl (*R*)-2-[(diethoxyphosphoryl)(phenyl)methyl]hydrazine-1-carboxylate. 3Aa:



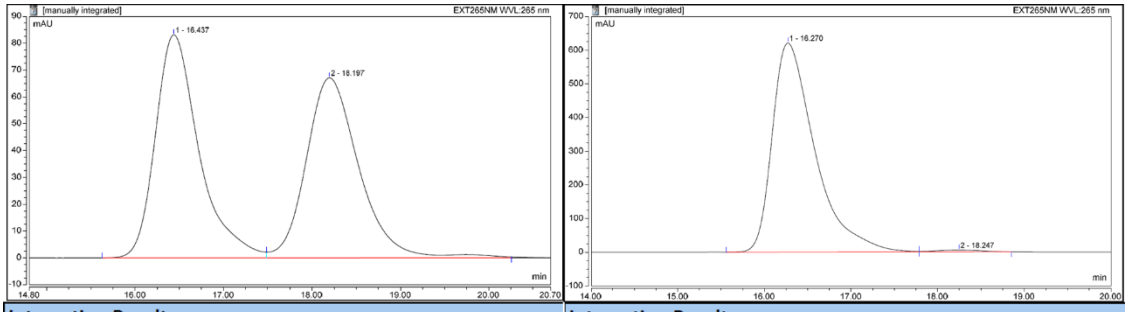
Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and phenylboronic acid **2a** (37 mg, 0.3 mmol), the compound (*R*)-**3Aa** was obtained as a yellow oil (52 mg, 66%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.50 – 7.39 (m, 2H), 7.37 – 7.23 (m, 8H), 6.45 (br s, 1H), 5.15 – 5.02 (m, 2H), 4.73 (br s, 1H), 4.61 (d, $^2J_{P,H}$ = 13.9, 1H), 4.10 – 3.85 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 135.8, 133.5 (d, $^2J_{P,C}$ = 7.2 Hz), 129.0 (d, $^3J_{P,C}$ = 6.0 Hz), 128.48 (d, $^4J_{P,C}$ = 3.1 Hz), 128,46, 128.3 (d, $^5J_{P,C}$ = 3.1 Hz), 128.2, 128.0, 67.1, 63.1 (d, $^2J_{P,C}$ = 6.8 Hz), 62.8 (d, $^2J_{P,C}$ = 7.1 Hz), 62.1 (d, $^1J_{P,C}$ = 146.5 Hz), 16.3 (d, $^3J_{P,C}$ = 5.5 Hz), 16.2 (d, $^3J_{P,C}$ = 5.4 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.66. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{25}O_5N_2PNa$ [M^+ + Na] 415.1393, found 415.1395. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 75:25, flow rate 1 mL/min, 30 ºC); τ_{major} = 26.2 min, τ_{minor} = 31.6 min. **$[\alpha]_D^{25}$** = +72.9 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	26.180	51.844	50.25
2	31.583	51.328	49.75

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	26.383	86.828	99.91
2	31.747	0.076	0.09

(9*H*-Fluoren-9-yl)methyl (*R*)-2-[(diethoxyphosphoryl)(phenyl)methyl]hydrazine-1-carboxylate. 3Ba: Following the general procedure **5A**, starting from α-hydrazono phosphonate **(*E*)-1B** (80 mg, 0.2 mmol) and phenylboronic acid **2a** (37 mg, 0.3 mmol) the compound (*R*)-**3Ba** was obtained as a yellow oil (66 mg, 69%, 98% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.75 (d, J = 7.5 Hz, 2H), 7.56 – 7.32 (m, 9H), 7.30 – 7.24 (m, 2H), 6.40 (br s, 1H), 4.74 (br s, 1H), 4.62 (d, $^{2}J_{P,H}$ = 12.2, 1H) 4.49 – 4.29 (m, 2H), 4.25 – 4.13 (m, 1H), 4.12 – 3.86 (m, 4H), 1.35 – 1.16 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 143.6, 143.5, 141.2, 133.6 (d, $^{2}J_{P,C}$ = 7.0 Hz) 129.0 (d, $^{3}J_{P,C}$ = 5.8 Hz), 128.6 (d, $^{4}J_{P,C}$ = 1.9 Hz), 128.4 (d, $^{5}J_{P,C}$ = 2.9 Hz), 127.7, 127.0, 125.0, 124.9, 120.0, 67.1, 63.2 (d, $^{2}J_{P,C}$ = 6.8 Hz), 62.9 (d, $^{2}J_{P,C}$ = 7.0 Hz), 62.2 (d, $^{1}J_{P,C}$ = 143.5 Hz), 47.0, 16.4 (d, $^{3}J_{P,C}$ = 5.8 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.8 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.68. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{29}O_5N_2Na$ [M^+ + Na] 503.1706, found 503.1694. **HPLC** (Chiralpak ID, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{major} = 16.4 min, τ_{minor} = 18.2 min. **$[\alpha]_D^{25}$** = +60.4 (*c* 1.0, $CHCl_3$).

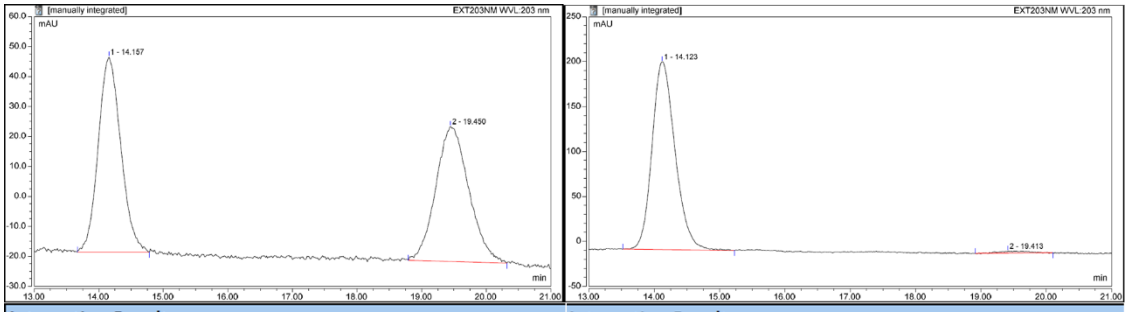


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.437	47.499	50.62
2	18.197	46.340	49.38

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.270	353.742	99.05
2	18.247	3.401	0.95

Diethyl (*R*)-[(2-benzoylhydrazineyl)(phenyl)methyl]phosphonate. 3Ca: Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1C** (57 mg, 0.2 mmol) and phenylboronic acid **2a** (37 mg, 0.3 mmol), the compound (*R*)-**3Ca** was obtained as a colorless oil (49 mg, 68%, 98% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.13 (d, J = 7.0 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.54 – 7.43 (m, 3H), 7.42 – 7.30 (m, 5H), 5.54 (ddd, $^{2}J_{P,H}$ = 17.7, $J_{H,H}$ = 7.1, 2.0 Hz, 1H), 4.59 (dd, $^{1}J_{P,H}$ = 13.1, $J_{H,H}$ = 2.0 Hz, 1H), 4.16 – 3.96 (m, 4H), 1.31 – 1.20 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 166.7, 133.7 (d, $^{2}J_{P,C}$ = 7.2 Hz), 132.5, 131.8, 128.9 (d, $^{4}J_{P,C}$ = 6.0 Hz), 128.6, 128.5 (d, $^{3}J_{P,C}$ = 2.5 Hz), 128.4 (d, $^{5}J_{P,C}$ = 3.0 Hz), 126.9, 63.4 (d, $^{2}J_{P,C}$ = 6.9 Hz), 62,84 (d, $^{1}J_{P,C}$ = 154.8 Hz), 62.76 (d, $^{2}J_{P,C}$

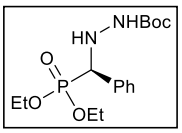
= 7.1 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.8 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.04. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{23}O_4N_2PNa$ [M^+ + Na] 385.1288, found 385.1281. **HPLC** (Chiralpak ID, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{major} = 14.1 min, τ_{minor} = 19.4 min. **$[\alpha]_D^{25}$** = +52.9 (*c* 1.0, $CHCl_3$).



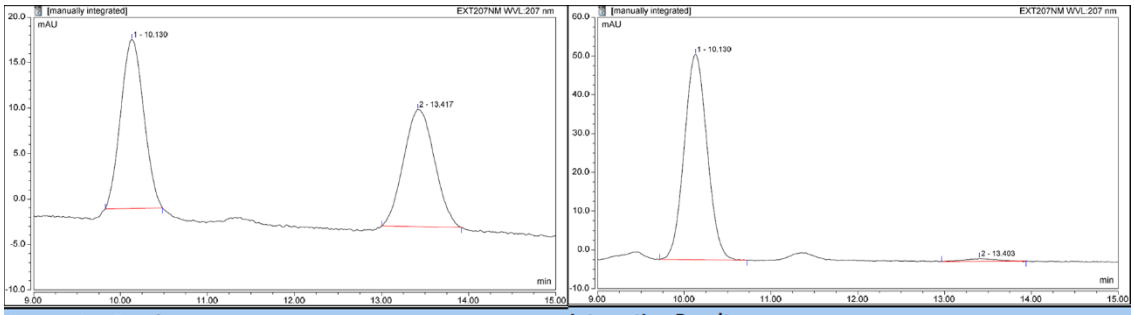
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	14.157	26.396	49.70
2	19.450	26.713	50.30

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	14.123	85.538	98.76
2	19.413	1.072	1.24

***tert*-Butyl (*R*)-2-[(diethoxyphosphoryl)(phenyl)methyl]hydrazine-1-carboxylate. 3Da:**



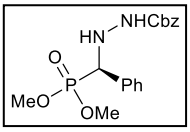
Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1D** (56 mg, 0.2 mmol) and phenylboronic acid **2a** (37 mg, 0.3 mmol) the compound (*R*)-**3Da** was obtained as a yellow oil (12 mg, 17%, 97% ee). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 2H), 7.39 – 7.28 (m, 3H), 6.05 (br s, 1H), 4.80 – 4.47 (m, 2H), 4.13 – 3.89 (m, 4H), 1.41 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 156.1, 133.9 (d, $^{2}J_{P,C}$ = 7.3 Hz), 129.1 (d, $^{4}J_{P,C}$ = 5.9 Hz), 128.5 (d, $^{3}J_{P,C}$ = 1.5 Hz), 128.3 (d, $^{5}J_{P,C}$ = 2.1 Hz), 80.7, 63.0 (d, $^{2}J_{P,C}$ = 6.9 Hz), 62.8 (d, $^{2}J_{P,C}$ = 7.1 Hz), 62.2 (d, $^{1}J_{P,C}$ = 150.5 Hz), 28.2, 16.4 (d, $^{3}J_{P,C}$ = 5.7 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.7 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.60. **HRMS** (ESI) *m/z* calcd. for $C_{16}H_{28}O_5N_2PNa$ [M^+ + Na] 415.1393, found 415.1395. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{major} = 10.1 min, τ_{minor} = 13.4 min. **$[\alpha]_D^{25}$** = +72.9 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.130	5.702	51.76
2	13.417	5.314	48.24

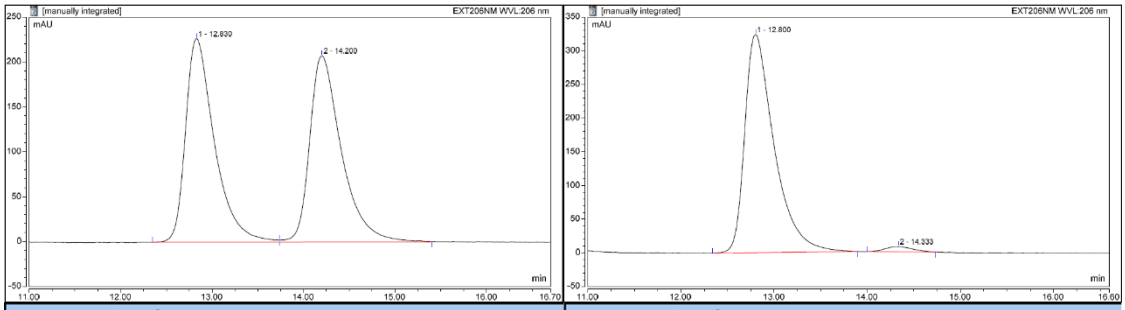
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.130	16.137	98.28
2	13.403	0.282	1.72

Benzyl (*R*)-2-[(dimethoxyphosphoryl)(phenyl)methyl]hydrazine-1-carboxylate. 3Ea:



Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1E** (57 mg, 0.2 mmol) and phenylboronic acid **2a** (37 mg, 0.3 mmol), the compound (*R*)-**3Ea** was obtained as a yellow oil (45 mg, 62%, 96% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.23 (m, 10H), 6.44 (br s, 1H), 5.16 – 4.99 (m, 2H), 4.89 – 4.48 (m, 2H), 3.67 (d, $^{3}J_{P,H}$ = 10.7 Hz, 3H), 3.62 (d, $^{3}J_{P,H}$ = 10.6 Hz, 3H). **^{13}C**

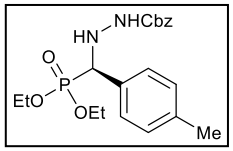
NMR (75.5 MHz, $CDCl_3$): δ 156.7, 135.8, 133.3 (d, $^2J_{P,C}$ = 7.2 Hz), 128.9 (d, $^3J_{P,C}$ = 6.0 Hz), 128.6 (d, $^4J_{P,C}$ = 2.4 Hz), 128.49, 128.47 (d, $^5J_{P,C}$ = 2.9 Hz), 128.3, 128.0, 67.2, 61.7 (d, $^1J_{P,C}$ = 148.9 Hz), 53.6 (d, $^2J_{P,C}$ = 6.9 Hz), 53.4 (d, $^2J_{P,C}$ = 7.0 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 23.04. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{21}O_5N_2PNa$ [M^+ + Na] 387.1091, found 387.1078. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 12.8 min, τ_{minor} = 14.2 min. **$[\alpha]_D^{25}$** = +81.4 (*c* 1.0, $CHCl_3$).



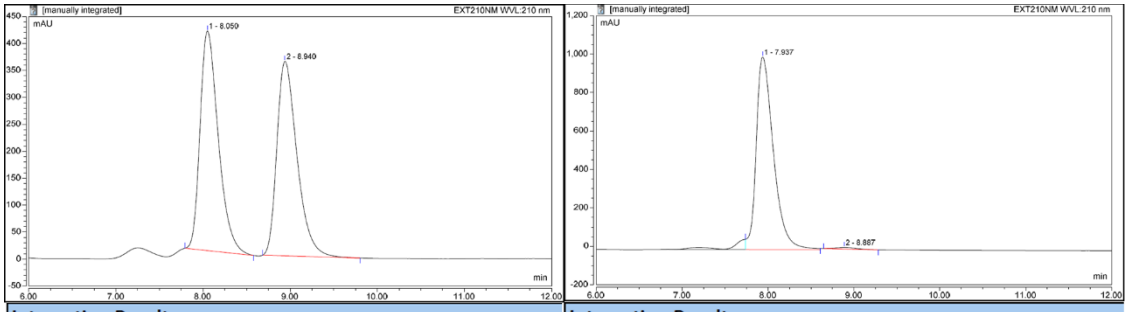
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.830	82.866	49.86
2	14.200	83.339	50.14

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.800	118.518	97.90
2	14.333	2.545	2.10

Benzyl (*R*)-2-[(diethoxyphosphoryl)(*p*-tolyl)methyl]hydrazine-1-carboxylate. 3Ab:



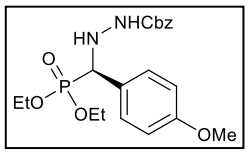
Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and *p*-tolylboronic acid **2b** (46 mg, 0.3 mmol), the compound (*R*)-**3Ab** was obtained as a yellow oil (59 mg, 73%, 98% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40 – 7.19 (m, 7H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.41 (br s, 1H), 5.21 – 4.97 (m, 2H), 4.70 (br s, 1H), 4.58 (d, $^2J_{P,H}$ = 14.2 Hz, 1H), 4.15 – 3.83 (m, 4H), 2.33 (d, $^6J_{P,H}$ = 1.7 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 138.1 (d, $^5J_{P,C}$ = 3.2 Hz), 135.9, 130.3 (d, $^2J_{P,C}$ = 7.1 Hz), 129.2 (d, $^3J_{P,C}$ = 2.4 Hz), 128.8 (d, $^4J_{P,C}$ = 6.0 Hz), 128.4, 128.2, 128.0, 67.0, 63.1 (d, $^2J_{P,C}$ = 6.8 Hz), 62.8 (d, $^2J_{P,C}$ = 7.2 Hz), 61.8 (d, $^1J_{P,C}$ = 148.9 Hz), 21.1, 16.3 (d, $^3J_{P,C}$ = 5.3 Hz), 16.2 (d, $^3J_{P,C}$ = 5.0 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.97. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{27}O_5N_2PNa$ [M^+ + Na] 429.1549, found 429.1538. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 8.0 min, τ_{minor} = 8.9 min. **$[\alpha]_D^{25}$** = +85.9 (*c* 1.0, $CHCl_3$).



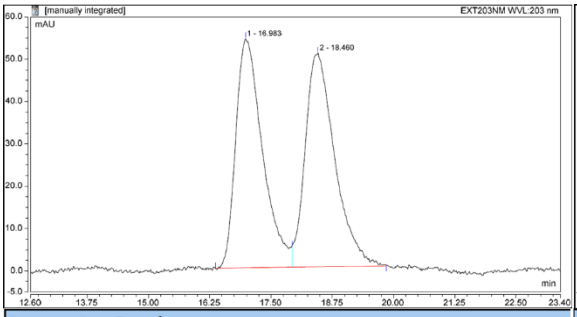
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.050	98.805	50.55
2	8.940	96.663	49.45

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.937	232.483	99.06
2	8.887	2.199	0.94

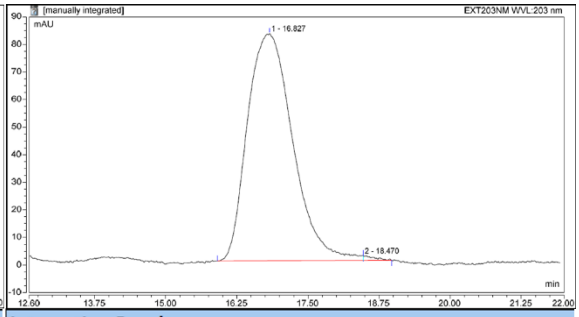
Benzyl (*R*)-2-[(diethoxyphosphoryl)(4-methoxyphenyl)methyl]hydrazine-1-carboxylate.



3Ac: Following the general procedure **5A**, starting from α-hydrazono phosphonate **(*E*)-1A** (63 mg, 0.2 mmol) and 4-methoxyphenylboronic acid **2c** (46 mg, 0.3 mmol), the compound (*R*)-**3Ac** was obtained as a yellow oil (72 mg, 85%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 7H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.35 (br s, 1H), 5.09 (br s, 2H), 4.67 (br s, 1H), 4.55 (d, $^{2}J_{P,H}$ = 11.3 Hz, 1H), 4.10 – 3.87 (m, 4H), 3.79 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 159.6 (d, $^{5}J_{P,C}$ = 2.9 Hz), 156.7, 135.9, 130.2 (d, $^{3}J_{P,C}$ = 6.2 Hz), 128.5, 128.2, 128.0, 125.3 (d, $^{2}J_{P,C}$ = 7.2 Hz), 114.0 (d, $^{4}J_{P,C}$ = 2.3 Hz), 67.1, 63.0 (d, $^{2}J_{P,C}$ = 7.1 Hz), 62.8 (d, $^{2}J_{P,C}$ = 6.9 Hz), 61.3 (d, $^{1}J_{P,C}$ = 155.1 Hz), 55.0, 16.34 (d, $^{3}J_{P,C}$ = 5.5 Hz), 16.27 (d, $^{3}J_{P,C}$ = 4.8 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.70. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{27}O_6N_2PNa$ [M^+ + Na] 445.1499, found 445.1488. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 90:10, flow rate 1 mL/min, 30 ºC); τ_{major} = 17.0 min, τ_{minor} = 18.5 min. **$[\alpha]_D^{20}$** = +99.8 (*c* 1.0, $CHCl_3$).

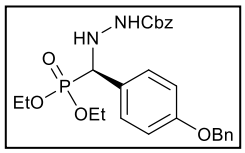


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.983	34.107	49.18
2	18.460	35.239	50.82

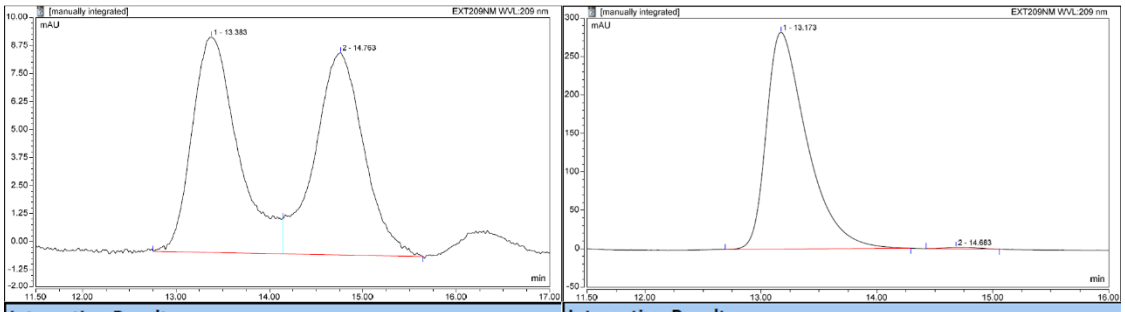


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.827	75.932	99.50
2	18.470	0.383	0.50

Benzyl (*R*)-2-{[4-(benzyloxy)phenyl](diethoxyphosphoryl)methyl}hydrazine-1-carboxylate.



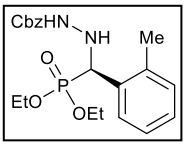
3Ad: Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 4-benzyloxyphenylboronic acid **2d** (68 mg, 0.3 mmol), the compound (*R*)-**3Ad** was obtained as a yellow oil (88 mg, 88%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.24 (m, 12H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.53 (br s, 1H), 5.14 – 5.03 (m, 2H), 5.04 (s, 2H), 4.69 (br s, 1H), 4.58 (d, $^{2}J_{P,H}$ = 13.2 Hz, 1H), 4.11 – 3.84 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 158.8 (d, $^{5}J_{P,C}$ = 2.9 Hz), 156.6, 136.7, 135.9, 130.2 (d, $^{3}J_{P,C}$ = 6.1 Hz), 128.5, 128.4, 128.1, 127.93, 127.87, 127.4, 125.5 (d, $^{2}J_{P,C}$ = 7.2 Hz), 114.8 (d, $^{4}J_{P,C}$ = 2.1 Hz), 69.9, 66.9, 63.0 (d, $^{2}J_{P,C}$ = 7.0 Hz), 62.7 (d, $^{2}J_{P,C}$ = 7.0 Hz), 61.3 (d, $^{1}J_{P,C}$ = 154.6 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.5 Hz), 16.2 (d, $^{2}J_{P,C}$ = 5.5 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.11. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{31}O_6N_2PNa$ [M^+ + Na] 521.1812, found 521.1802. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 13.4 min, τ_{minor} = 14.8 min. **$[\alpha]_D^{20}$** = +77.8 (*c* 1.0, $CHCl_3$).



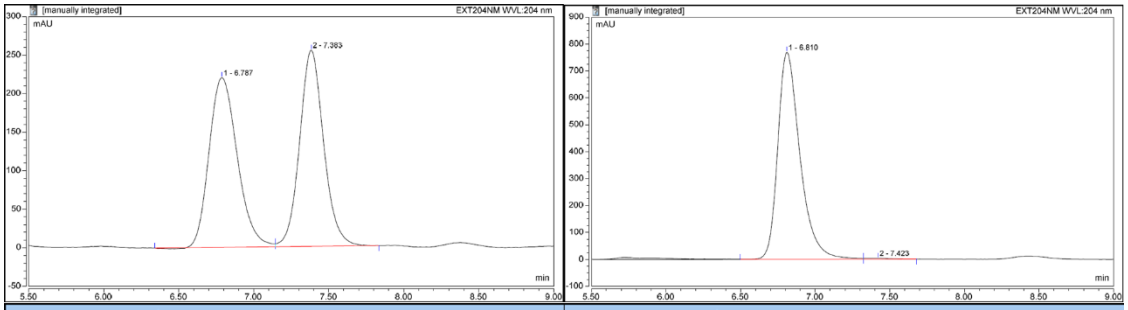
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.383	5.495	49.99
2	14.763	5.497	50.01

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.173	114.355	99.48
2	14.683	0.594	0.52

Benzyl (*R*)-2-[(diethoxyphosphoryl)(*o*-tolyl)methyl]hydrazine-1-carboxylate. 3Ae:



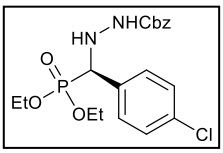
Following the general procedure **7A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and *o*-tolylboronic acid **2e** (46 mg, 0.3 mmol), the compound (*R*)-**3Ae** was obtained as a yellow oil (54 mg, 66%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.58 – 7.49 (m, 1H), 7.30 – 7.17 (m, 5H), 7.16 – 7.03 (m, 3H), 6.37 (br s, 1H), 5.09 – 4.97 (m, 2H), 4.87 (d, $^{2}J_{P,H}$ = 13.4 Hz, 1H), 4.60 (br s, 1H), 4.03 – 3.72 (m, 4H), 2.24 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 137.8 (d, $^{3}J_{P,C}$ = 7.0 Hz), 135.9, 131.7 (d, $^{2}J_{P,C}$ = 6.9 Hz), 130.6 (d, $^{4}J_{P,C}$ = 2.4 Hz), 128.5, 128.2, 128.1 (d, $^{3}J_{P,C}$ = 4.3 Hz), 127.98, (d, $^{5}J_{P,C}$ = 1.4 Hz) 127.96, 126.1 (d, $^{4}J_{P,C}$ = 2.9 Hz), 67.0, 63.0 (d, $^{2}J_{P,C}$ = 7.0 Hz), 62.80 (d, $^{2}J_{P,C}$ = 7.2 Hz), 57.5 (d, $^{1}J_{P,C}$ = 155.3 Hz), 19.6, 16.3 (d, $^{3}J_{P,C}$ = 6.0 Hz), 16.2 (d, $^{3}J_{P,C}$ = 5.8 Hz,). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.60. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{27}O_5N_2PNa$ [M^+ + Na] 429.1549, found 429.1549. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 6.8 min, τ_{minor} = 7.4 min. **$[\alpha]_D^{25}$** = +64.6 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.787	47.824	50.27
2	7.383	47.307	49.73

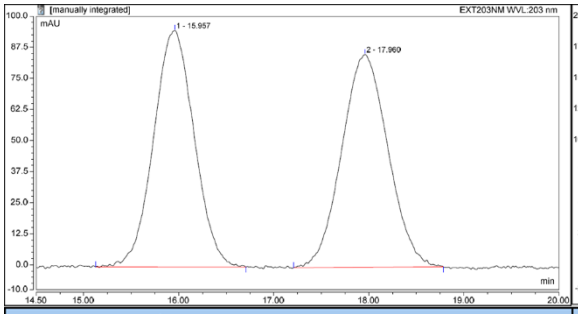
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.810	132.764	99.50
2	7.423	0.668	0.50

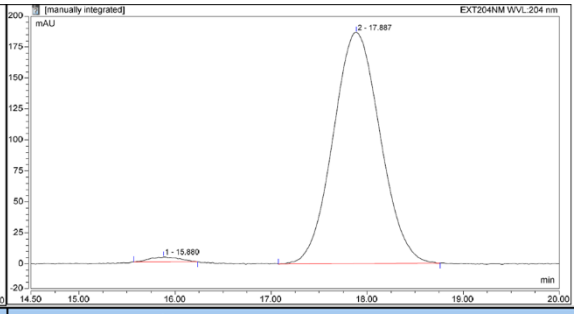
Benzyl (*R*)-2-[(4-chlorophenyl)(diethoxyphosphoryl)methyl]hydrazine-1-carboxylate. 3Af:



Following the general procedure **5B**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 4-chlorophenylboronic acid **2f** (46 mg, 0.3 mmol), the compound (*R*)-**3Af** was obtained as a yellow oil (49 mg, 57%, 97% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.28 (m, 9H), 6.30 (br s, 1H), 5.16 – 5.03 (m, 2H), 4.73 (br s, 1H), 4.61 (d, $^{2}J_{P,H}$ = 16.4 Hz, 1H), 4.13 – 3.91 (m, 4H), 1.31 – 1.17 (m, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 135.8, 134.2 (d, $^{5}J_{P,C}$ = 3.6 Hz), 132.3 (d, $^{2}J_{P,C}$ = 7.4 Hz), 130.3 (d, $^{4}J_{P,C}$ = 5.9 Hz), 128.7 (d, $^{3}J_{P,C}$ = 2.6 Hz), 128.5, 128.3, 128.1, 67.2, 63.2 (d, $^{2}J_{P,C}$ = 6.8 Hz), 63.0 (d, $^{2}J_{P,C}$ = 7.2 Hz), 61.5 (d, $^{1}J_{P,C}$ = 146.9 Hz), 16.4 (d, $^{3}J_{P,C}$ = 2.3 Hz), 16.3

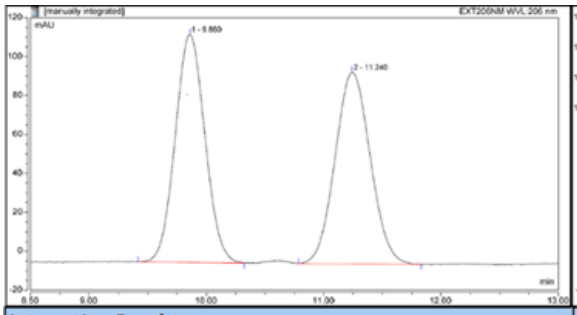
(d, $^{3}J_{P,C}$ = 2.3 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.01. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{24}O_5N_2PClNa$ [M^+ + Na] 449.1003, found 449.0998. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 75:25, flow rate 1 mL/min, 30 ºC); τ_{minor} = 15.9 min, τ_{major} = 17.9 min. **$[\alpha]_D^{20}$** = +99.8 (*c* 1.0, $CHCl_3$).

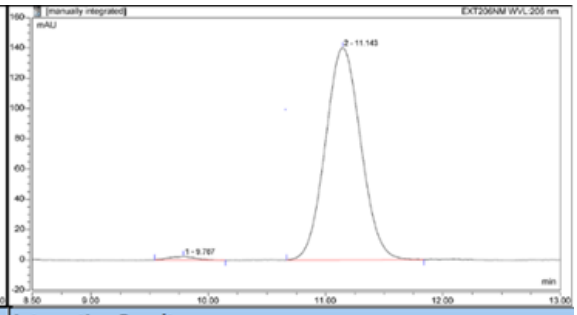




Integration Results				Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %	No.	Retention Time min	Area mAU*min	Relative Area %
1	15.957	47.208	49.45	1	15.880	1.397	1.30
2	17.960	48.256	50.55	2	17.887	106.019	98.70

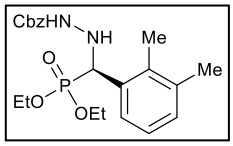
Benzyl (*R*)-2-{(diethoxyphosphoryl)[4-(trifluoromethyl)phenyl]methyl}hydrazine-1-carboxylate. 3Ag: Following the general procedure **5B**, starting from α-hydrazono phosphonate **(*E*)-1A** (63 mg, 0.2 mmol) and (4-trifluoromethyl)phenylboronic acid **2g** (57 mg, 0.3 mmol), the compound (*R*)-**3Ag** was obtained as a yellow oil (28 mg, 30%, 98% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.66 – 7.49 (m, 4H), 7.39 – 7.26 (m, 5H), 6.33 (s, 1H), 5.16 – 5.00 (m, 2H), 4.88 – 4.57 (m, 2H), 4.15 – 3.93 (m, 4H), 1.31 – 1.16 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 138.1 (d, $^{2}J_{P,C}$ = 7.2 Hz), 135.7, 130.4 (dd, $J_{F,C}$ = 33.4 Hz, $^{5}J_{P,C}$ = 3.2 Hz,), 129.3 (d, $^{3}J_{P,C}$ = 5.6 Hz), 128.5, 128.4, 128.1, 125.5 – 125.2 (m), 124.0 (c, $J_{F,C}$ = 271.5 Hz) 67.3, 63.3 (d, $^{2}J_{P,C}$ = 6.9 Hz), 63.0 (d, $^{2}J_{P,C}$ = 7.1 Hz), 61.8 (d, $^{1}J_{P,C}$ = 149.3 Hz), 16.3 (d, $^{3}J_{P,C}$ = 1.8 Hz), 16.2 (d, $^{3}J_{P,C}$ = 1.7 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 19.50. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –62.63 (s, $C\underline{F}_3$). **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{24}O_5N_2PF_3Na$ [M^+ + Na] 483.1267, found 483.1261. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 75:25, flow rate 1 mL/min, 30 ºC); τ_{minor} = 9.8 min, τ_{major} = 11.2 min. **$[\alpha]_D^{20}$** = +97.1 (*c* 1.0, $CHCl_3$).



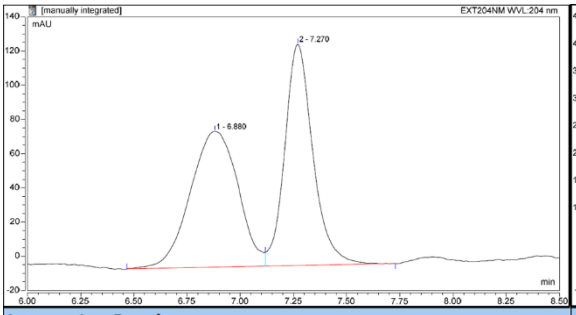


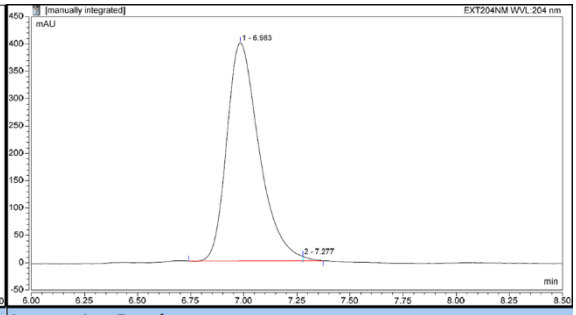
Integration Results				Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %	No.	Retention Time min	Area mAU*min	Relative Area %
1	9.860	34.405	50.14	1	9.787	0.556	1.12
2	11.240	34.214	49.86	2	11.143	49.100	98.88

Benzyl (*R*)-2-[(diethoxyphosphoryl)(2,3-dimethylphenyl)methyl]hydrazine-1-carboxylate.



3Ah: Following the general procedure **5A**, starting from α-hydrazono phosphonate **(*E*)-1A** (63 mg, 0.2 mmol) and 2,3-dimethylphenylboronic acid **2h** (45 mg, 0.3 mmol), the compound **(*R*)-3Ah** was obtained as a yellow oil (43 mg, 51%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.42 (m, 1H), 7.37 – 7.25 (m, 5H), 7.15 – 7.05 (m, 2H), 6.34 (br s, 1H), 5.21 – 5.06 (m, 2H), 5.01 (d, $^{2}J_{P,H}$ = 15.8 Hz, 1H), 4.67 (br s, 1H), 4.10 – 3.81 (m, 4H), 2.28 (s, 3H), 2.21 (br s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 137.0 (d, $^{4}J_{P,C}$ = 2.6 Hz), 136.4 (d, $^{3}J_{P,C}$ = 7.0 Hz), 135.9, 131.6 (d, $^{2}J_{P,C}$ = 6.7 Hz), 129.7 (d, $^{4}J_{P,C}$ = 3.1 Hz), 128.5, 128.2, 128.0, 125.8 (d, $^{3}J_{P,C}$ = 4.1 Hz), 125.0 (d, $^{5}J_{P,C}$ = 2.9 Hz), 67.1, 62.9 (d, $^{2}J_{P,C}$ = 7.5 Hz), 62.8 (d, $^{2}J_{P,C}$ = 7.7 Hz), 57.8 (d, $^{1}J_{P,C}$ = 151.4 Hz), 21.0, 16.3 (d, $^{3}J_{P,C}$ = 5.9 Hz), 16.2 (d, $^{3}J_{P,C}$ = 5.8 Hz), 15.1. **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.63. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{29}O_5N_2PNa$ [M^+ + Na] 443.1703, found 443.1695. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 6.9 min, τ_{minor} = 7.3 min. **$[\alpha]_D^{20}$** = +92.6 (*c* 1.0, $CHCl_3$).





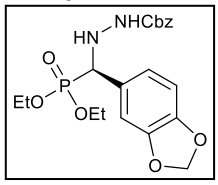
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	6.880	20.633	50.98
2	7.270	19.836	49.02

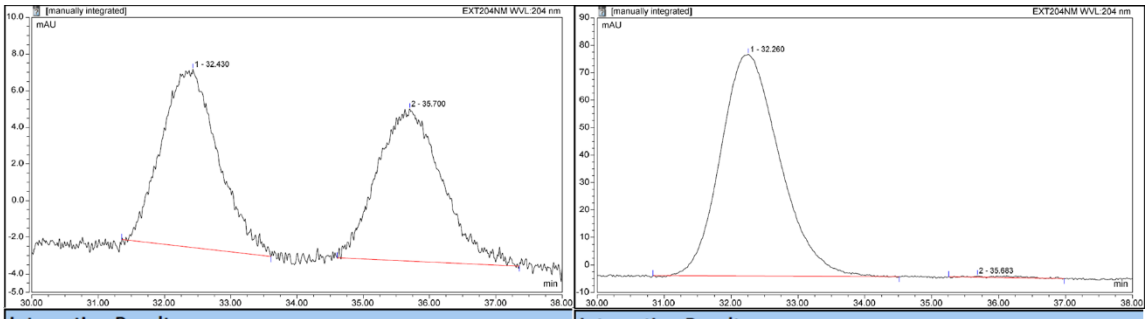
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	6.983	70.325	99.57
2	7.277	0.302	0.43

Benzyl



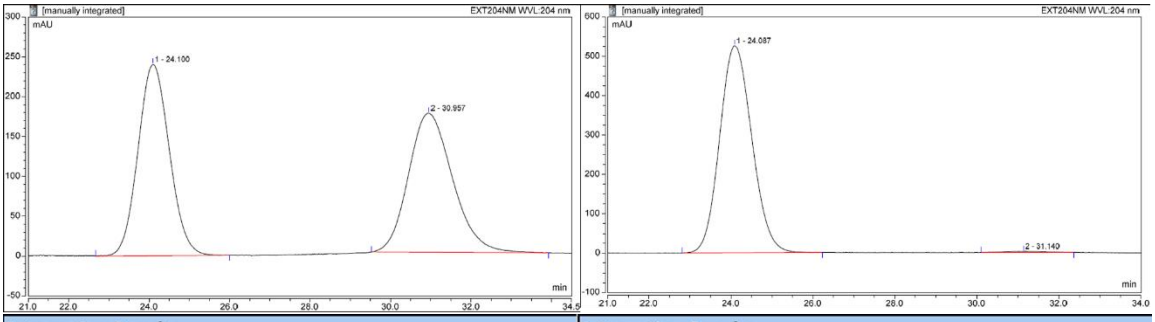
(*R*)-2-[benzo(*d*)(1,3)dioxol-5-yl(diethoxyphosphoryl)methyl]hydrazine-1-carboxylate. 3Ai: Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 3,4-(methylendioxy)phenylboronic acid **2i** (50 mg, 0.3 mmol), the compound (*R*)-**3Ai** was obtained as a yellow oil (80 mg, 92%, 99% ee, reaction run for 24 h), reaction performed at 1 mmol scale (36 h): 370 mg, 85%, 99% ee. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38 – 7.26 (m, 5H), 6.97 (br s, 1H), 6.89 – 6.80 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.36 (br s, 1H) 5.94 (s, 2H), 5.14 – 5.03 (m, 2H), 4.67 (br s, 1H), 4.53 (d, *J* = 16.2 Hz, 1H), 4.13 – 3.94 (m, 4H), 1.31 – 1.18 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 147.8 (d, $^{4}J_{P,C}$ = 2.8 Hz), 147.7 (d, $^{5}J_{P,C}$ = 3.1 Hz), 135.9, 128.5, 128.2, 128.0, 127.1 (d, $^{2}J_{P,C}$ = 7.5 Hz) 122.8 (d, $^{3}J_{P,C}$ = 7.3 Hz), 109.1 (d, $^{3}J_{P,C}$ = 5.3 Hz), 108.2 (d, $^{4}J_{P,C}$ = 2.5 Hz), 101.1, 67.1, 63.1 (d, $^{2}J_{P,C}$ = 6.9 Hz), 62.8 (d, $^{2}J_{P,C}$ = 7.2 Hz), 61.6 (d, $^{1}J_{P,C}$ = 153.5 Hz), 16.4 (d, $^{3}J_{P,C}$ = 5.7 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.7 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.70. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{25}O_7N_2PNa$ [M^+ + Na] 459.1292, found 449.1288. **HPLC** (Chiralpak ID, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{major} = 32.4 min, τ_{minor} = 35.7 min. **$[\alpha]_D^{20}$** = +92.6 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	32.430	9.645	50.53
2	35.700	9.444	49.47

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	32.260	82.416	99.59
2	35.683	0.341	0.41

Benzyl (*R*)-2-[(3-chloro-4-ethoxyphenyl)(diethoxyphosphoryl)methyl]hydrazine-1-carboxylate. 3Aj: Following the general procedure **5B**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 3-chloro-4-ethoxyphenylboronic acid **2j** (60 mg, 0.3 mmol), the compound (*R*)-**3Aj** was obtained as a yellow oil (59 mg, 63%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46 (br s, 1H), 7.38 – 7.23 (m, 6H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.28 (br s, 1H), 5.10 (br s, 2H), 4.69 (br s, 1H), 4.54 (d, $^{2}J_{P,H}$ = 14.1 Hz, 1H), 4.14 – 3.95 (m, 6H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.31 – 1.19 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 154.5 (d, $^{5}J_{P,C}$ = 2.9 Hz), 135.8, 130.6 (d, $^{3}J_{P,C}$ = 5.9 Hz), 128.55, 128.49 (d, $^{3}J_{P,C}$ = 5.9 Hz), 128.3, 128.1, 126.4 (d, $^{2}J_{P,C}$ = 7.9 Hz), 122.92 (d, $^{4}J_{P,C}$ = 2.5 Hz), 113.1 (d, $^{4}J_{P,C}$ = 2.4 Hz), 67.2, 64.7, 63.2 (d, $^{2}J_{P,C}$ = 6.9 Hz), 63.0 (d, $^{2}J_{P,C}$ = 7.2 Hz), 61.0 (d, $^{1}J_{P,C}$ = 149.4 Hz), 16.4 (d, $^{3}J_{P,C}$ = 2.3 Hz), 16.3 (d, $^{3}J_{P,C}$ = 2.3 Hz), 14.7. **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.31. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{28}O_6N_2PClNa$ [M^+ + Na] 493.1266, found 493.1256. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{major} = 24.1 min, τ_{minor} = 31.0 min. **$[\alpha]_D^{25}$** = +72.9 (*c* 1.0, $CHCl_3$).

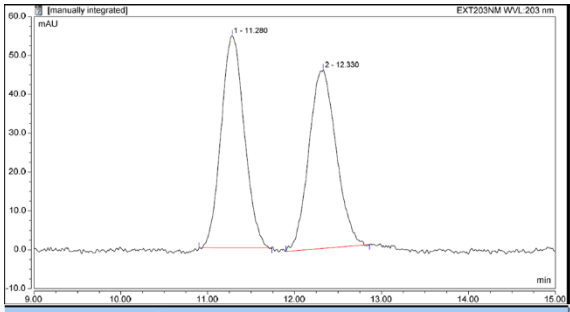


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	24.100	216.898	49.59
2	30.957	220.517	50.41

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	24.087	478.882	99.40
2	31.140	2.887	0.60

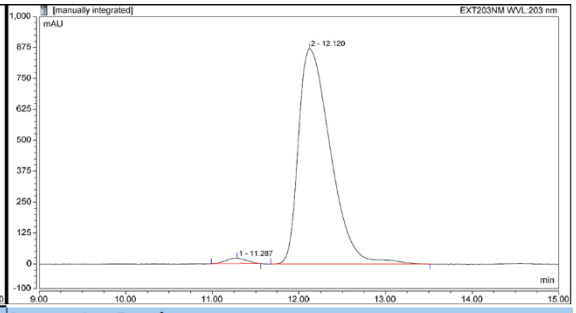
Benzyl (*R*)-2-[(diethoxyphosphoryl)(3,5-dimethylphenyl)methyl]hydrazine-1-carboxylate. 3Ak: Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 3,5-dimethylphenylboronic acid **2k** (45 mg, 0.3 mmol), the compound (*R*)-**3Ak** was obtained as a yellow oil (60 mg, 71%, 97% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40 – 7.26 (m, 5H), 7.10 – 6.99 (m, 2H), 6.97 – 6.89 (m, 1H), 6.33 (br s, 1H), 5.17 – 5.03 (m, 2H), 4.69 (br s, 1H), 4.53 (d, *J* = 13.9 Hz, 1H), 4.11 – 3.88 (m, 4H), 2.29 (s, 6H), 1.31 – 1.13 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 138.0 (d, $^{4}J_{P,C}$ = 2.6 Hz), 135.9, 133.2 (d, $^{2}J_{P,C}$

= 6.9 Hz), 130.1 (d, $^{5}J_{P,C}$ = 3.1 Hz), 128.5, 128.2, 128.0, 126.7 (d, $^{3}J_{P,C}$ = 6.0 Hz), 67.1, 63.0 (d, $^{2}J_{P,C}$ = 6.8 Hz), 62.9 (d, $^{2}J_{P,C}$ = 7.0 Hz), 62.0 (d, $^{1}J_{P,C}$ = 148.2 Hz) , 21.2, 16.3 (d, $^{3}J_{P,C}$ = 5.6 Hz), 16.2 (d, $^{3}J_{P,C}$ = 5.5 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.92. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{29}O_5N_2PNa$ [M^+ + Na] 443.1703, found 443.1697. **HPLC** (Chiralpak ID, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC); τ_{minor} = 11.3 min, τ_{major} = 12.3 min. **$[\alpha]_D^{20}$** = +86.5 (*c* 1.0, $CHCl_3$).



Integration Results

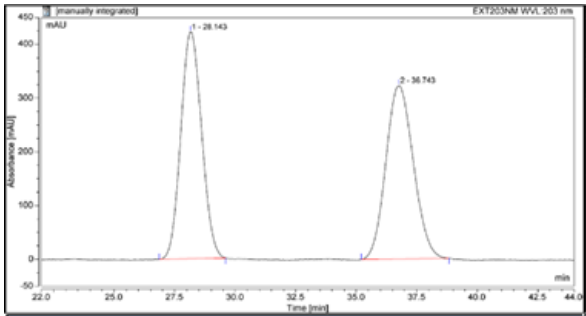
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.280	16.909	50.22
2	12.330	16.760	49.78



Integration Results

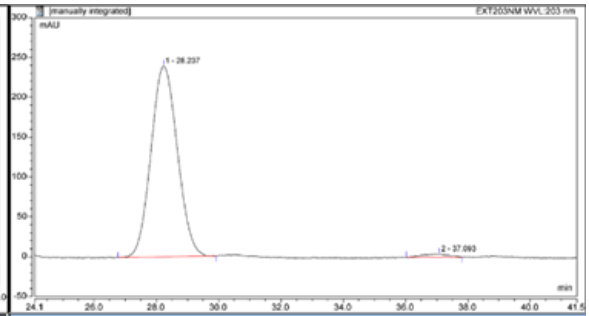
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.287	6.056	1.60
2	12.120	372.192	98.40

Benzyl (*R*)-2-[(diethoxyphosphoryl)(4-methoxy-3,5-dimethylphenyl)methyl]hydrazine-1-carboxylate. 3Al: Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and (4-methoxy-3,5-dimethyl)phenylboronic acid **2l** (54 mg, 0.3 mmol), the compound (*R*)-**3Al** was obtained as a yellow oil (76 mg, 85%, 97% ee, reaction run for 24 h). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38 – 7.26 (m, 5H), 7.05 (br s, 2H), 6.35 (br s, 1H), 5.17 – 5.01 (m, 2H), 4.65 (s, 1H), 4.48 (d, $^{2}J_{P,H}$ = 13.5 Hz, 1H), 4.13 – 3.88 (m, 4H), 3.70 (br s, 3H), 2.25 (s, 6H), 1.31 – 1.18 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 157.1 (d, $^{5}J_{P,C}$ = 3.4 Hz), 156.7, 135.9, 131.0 (d, $^{4}J_{P,C}$ = 2.5 Hz), 129.3 (d, $^{3}J_{P,C}$ = 6.1 Hz), 128.5, 128.4 (d, $^{2}J_{P,C}$ = 67.2 Hz), 128.3, 128.0, 67.1, 63.0 (d, $^{2}J_{P,C}$ = 6.9 Hz), 62.9 (d, $^{2}J_{P,C}$ = 7.1 Hz), 61.6 (d, $^{1}J_{P,C}$ = 151.4 Hz), 59.6 (d, $^{7}J_{P,C}$ = 1.8 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.6 Hz), 16.2 (d, $^{3}J_{P,C}$ = 5.5 Hz) 16.1. **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.05. **HRMS** (ESI) *m/z* calcd. for $C_{22}H_{31}O_6N_2PNa$ [M^+ + Na] 473.1812, found 473.1809. **HPLC** (Chiralpak ID, *n*-hexane/2-propanol 65:35, flow rate 1 mL/min, 30 ºC); τ_{minor} = 28.1 min, τ_{major} = 36.7 min. **$[\alpha]_D^{20}$** = +88.8 (*c* 1.0, $CHCl_3$).



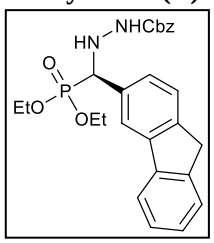
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	28.143	420.814	49.74
2	36.743	425.248	50.26

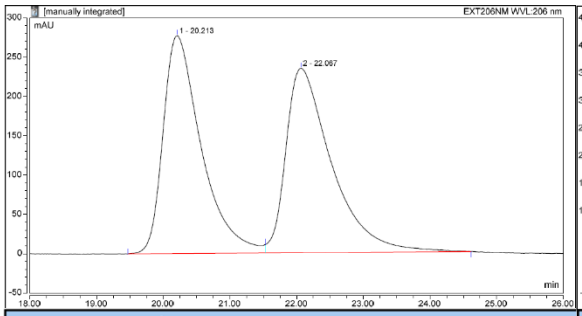


Integration Results

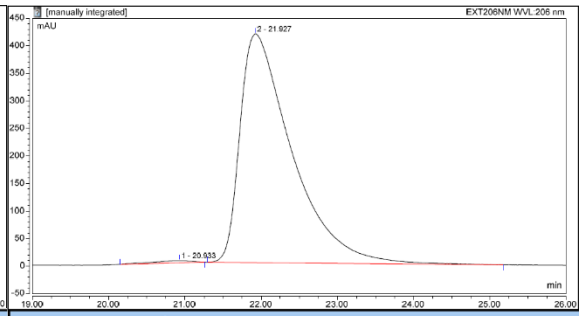
No.	Retention Time min	Area mAU*min	Relative Area %
1	28.237	235.004	98.50
2	37.093	3.574	1.50

Benzyl (*R*)-2-[(diethoxyphosphoryl)(9*H*-fluoren-3-yl)methyl]hydrazine-1-carboxylate. 3Am: 

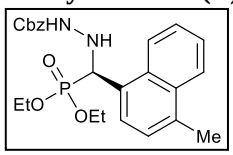
Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and (9*H*-fluoren-3-yl)boronic acid **2m** (63 mg, 0.3 mmol), the compound (*R*)-**3Am** was obtained as a yellow pale solid (72 mg, 75%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 (td, *J* = 7.5, 3.8 Hz, 1H), 7.34 – 7.24 (m, 6H), 6.43 (br s, 1H), 5.17 – 5.02 (m, 2H), 4.88 – 4.61 (m, 2H), 4.12 – 3.92 (m, 4H), 3.88 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 143.5 (d, $^4J_{P,C}$ = 2.2 Hz), 143.4, 142.0 (d, $^5J_{P,C}$ = 3.0 Hz), 141.2, 135.9, 131.9 (d, $^2J_{P,C}$ = 7.2 Hz), 128.4, 128.2, 128.0, 127.7 (d, $^3J_{P,C}$ = 6.1 Hz), 126.9, 126.8, 125.7 (d, $^3J_{P,C}$ = 6.0 Hz), 125.0, 119.9, 119.8 (d, $^4J_{P,C}$ = 2.1 Hz), 67.1, 63.1 (d, $^2J_{P,C}$ = 6.9 Hz), 62.9 (d, $^2J_{P,C}$ = 7.0 Hz), 62.3 (d, $^1J_{P,C}$ = 152.3 Hz), 36.8, 16.3 (d, $^3J_{P,C}$ = 5.5 Hz), 16.2 (d, $^3J_{P,C}$ = 5.5 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.84. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{29}O_5N_2PNa$ [M^+ + Na] 503.1700, found 503.1706. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 90:10, flow rate 1 mL/min, 30 ºC); τ_{minor} = 20.2 min, τ_{major} = 22.1 min. **$[\alpha]_D^{25}$** = +142.3 (*c* 1.0, $CHCl_3$).



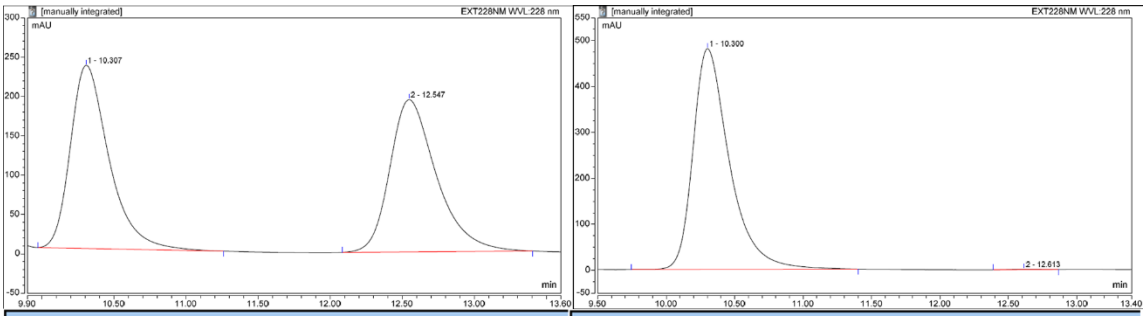
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.213	183.396	49.62
2	22.067	186.214	50.38



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.933	2.484	0.75
2	21.927	327.711	99.25

Benzyl (*R*)-2-[(diethoxyphosphoryl)(4-methylnaphthalen-1-yl)methyl]hydrazine-1-carboxylate. 3An: 

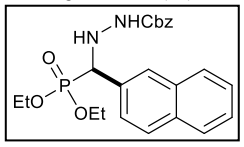
Following the general procedure **5A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and (4-methylnaphthalen-1-yl)boronic acid **2n** (56 mg, 0.3 mmol), the compound (*R*)-**3An** was obtained as a yellow oil (57 mg, 63%, >99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.22 (br s, 1H), 8.10 – 8.00 (m, 1H), 7.82 – 7.71 (m, 1H), 7.62 – 7.49 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.17 (m, 5H), 6.46 (br s, 1H), 5.55 (d, $^2J_{P,H}$ = 14.4 Hz, 1H), 5.16 – 5.01 (m, 2H), 4.89 (br s, 1H), 4.15 – 3.69 (s, 4H), 2.71 (d, *J* = 1.5 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 135.8, 135.0 (d, $^5J_{P,C}$ = 3.6 Hz), 132.9 (d, $^4J_{P,C}$ = 2.1 Hz), 132.2 (d, $^3J_{P,C}$ = 5.7 Hz), 128.4, 128.1, 127.9, 127.6 (d, $^2J_{P,C}$ = 7.0 Hz), 126.5, 126.2 (d, $^3J_{P,C}$ = 3.5 Hz), 125.9, 125.5, 124.7, 124.1, 67.0, 63.1 (d, $^2J_{P,C}$ = 6.9 Hz), 62.8 (d, $^2J_{P,C}$ = 7.1 Hz), 57.4 (d, $^1J_{P,C}$ = 154.9 Hz), 19.6 (d, $^6J_{P,C}$ = 0.9 Hz), 16.3 (d, $^3J_{P,C}$ = 5.9 Hz), 16.1 (d, $^3J_{P,C}$ = 5.7 Hz). **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{29}O_5N_2PNa$ [M^+ + Na] 479.1706, found 479.1699. **^{31}P NMR** (122 MHz, $CDCl_3$): δ 21.16. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min, 30 ºC); τ_{major} = 10.3 min, τ_{minor} = 12.6 min. **$[\alpha]_D^{25}$** = +81.1 (*c* 1.0, $CHCl_3$).



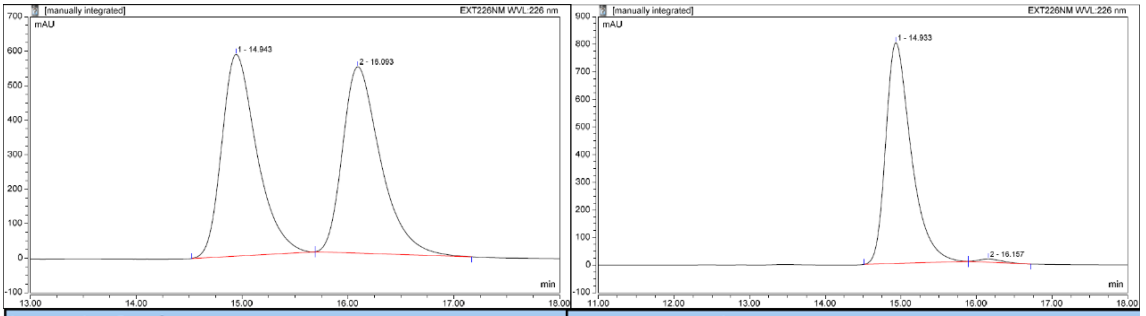
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.307	72.483	49.93
2	12.547	72.693	50.07

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.300	148.219	99.86
2	12.613	0.206	0.14

Benzyl (*R*)-2-[(diethoxyphosphoryl)(naphthalen-2-yl)methyl]hydrazine-1-carboxylate.



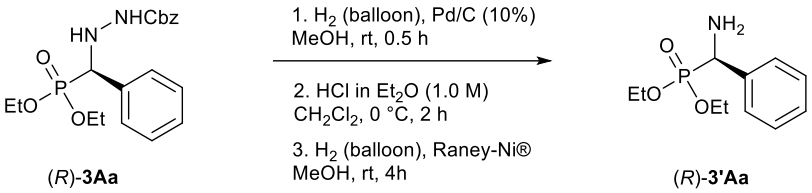
3Ao: Following the general procedure **7A**, starting from α-hydrazono phosphonate (*E*)-**1A** (63 mg, 0.2 mmol) and 2-naphthylboronic acid **2o** (52 mg, 0.3 mmol), the compound (*R*)- **3Ao** was obtained as a yellow oil (63 mg, 71%, 98% ee), reaction performed at 1 mmol scale: 287 mg, 65%, 98% ee. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.96 – 7.76 (m, 4H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.38 – 7.19 (m, 5H), 6.35 (br s, 1H), 5.16 – 5.01 (m, 2H), 4.95 – 4.66 (m, 2H), 4.14 – 3.89 (m, 4H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 156.7, 135.8, 133.3 (d, $^{4}J_{P,C}$ = 2.3 Hz), 133.2 (d, $^{5}J_{P,C}$ = 2.6 Hz) , 131.1 (d, $^{2}J_{P,C}$ = 7.7 Hz), 128.51 (d, $^{3}J_{P,C}$ = 4.7 Hz), 128.48, 128.3, 128.2 (d, $J_{P,C}$ = 2.3 Hz), 127.99, 127.97 (d, $J_{P,C}$ = 1.3 Hz), 127.7 (d, $J_{P,C}$ = 1.3 Hz), 126.33 (d, $^{3}J_{P,C}$ = 4.7 Hz), 126.25 (d, $J_{P,C}$ = 1.9 Hz), 126.2 (d, $J_{P,C}$ = 1.3 Hz), 67.1, 63.2 (d, $^{2}J_{P,C}$ = 6.9 Hz) , 63.0 (d, $^{2}J_{P,C}$ = 7.1 Hz), 62.2 (d, $^{1}J_{P,C}$ = 149.5 Hz), 16.4 (d, $^{3}J_{P,C}$ = 5.2 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.2 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 20.50. **HRMS** (ESI) *m/z* calcd. for $C_{23}H_{27}O_5N_2PNa$ [M^+ + Na] 465.1550, found 465.1537. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 85:15, flow rate 0.7 mL/min, 30 ºC); τ_{major} = 14.9 min, τ_{minor} = 16.1 min. **$[\alpha]_D^{25}$**= +79.1 (*c* 1.0, $CHCl_3$). Reaction performed with the opposite enantiopure ligand **L5*** afforded (*S*)- **3Ao** as a yellow oil (64 mg, 72%, 97% ee) **$[\alpha]_D^{25}$** = –73.5 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	14.943	224.195	49.90
2	16.093	225.123	50.10

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	14.933	312.841	98.76
2	16.157	3.932	1.24

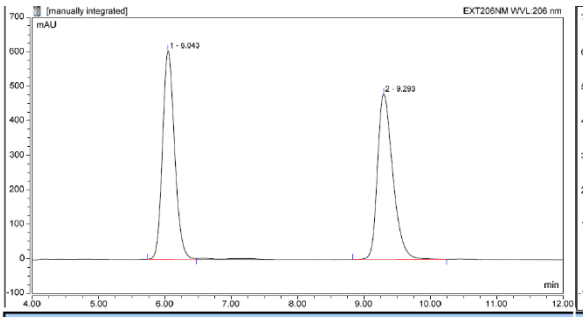
6. Determination of absolute configuration (*R*) by chemical correlation.



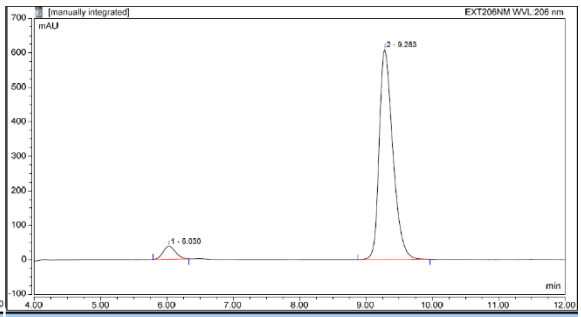
(*R*)-**3Aa** (*R*)-**3'Aa**

A round bottomed flask was charged with Pd/C (10% w/w) (8 mg, 0.008 mmol), methanol (2.5 mL), **(*R*)-3Aa** (65 mg, 0.166 mmol, 98% ee) and sealed with a rubber septum. The head-space was evacuated and back-filled with hydrogen three times and then stirred under a balloon of hydrogen at room temperature for 0.5 h. After this time, the mixture was filtered through a celite pad and the solvent was eliminated under reduced pressure. The crude was dissolved in dry CH_2Cl_2 (1 mL) and cooled at 0 °C. Then, HCl (1.0 M in Et_2O, 0.5 mL, 0.5 mmol) was added drop-wise and the mixture was stirred at 0 °C for 2 h. After that, the solvent was eliminated under reduced pressure and the residue obtained was solved in EtOH/AcOH 5/1 (2 mL) (47 mg, 0.160 mmol) and Raney-Ni® (0.25 g, 50% in H_2O) was added. The reaction was stirred under hydrogen atmosphere (1 atm) at room temperature for 4 h. After this time, the mixture was purified by flash chromatography (*n*-hexane/EtOAc 2/1) to afford the corresponding aminophosphonate (*R*)-**3'Aa** as a yellow oil (29 mg, 72%, 90% ee). Spectroscopic and physical data matched those reported in the literature.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.40 (m, 2H), 7.38 – 7.24 (m, 3H), 4.24 (d, *J* = 17.2 Hz, 1H), 4.11 – 3.77 (m, 4H), 2.02 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{31}P NMR** (122 MHz, $CDCl_3$): δ 24.85. **$[\alpha]_D^{25}$** = +14.8 (*c* 1.0, $CHCl_3$). Literature: **$[\alpha]_D^{20}$** = –15.0 (*c* 0.3, $CHCl_3$), 98% ee (*S*).

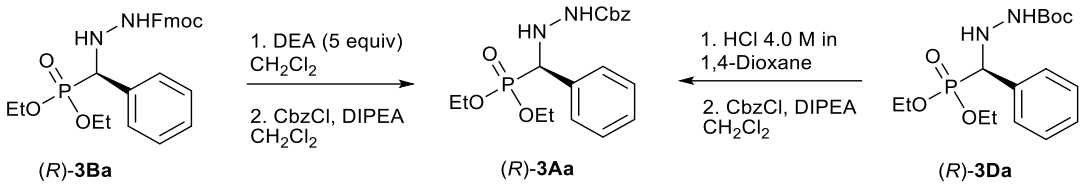
*The enantiomeric excess was determined after protection of the aminophosphonate **(*R*)-3'Aa** (16 mg, 0.066 mmol), with benzyl chloroformate (1.1 equiv.), diisopropylethylamine (1 equiv.) in dry CH_2Cl_2 (1.0 M). The product **(*R*)-Cbz-3'Aa** was purified by flash chromatography (n-hexane /EtOAc 1/3) to afford the compound as a white solid (15 mg, 87%, 90% ee). The enantiomeric excess (ee) was determined by HPLC analysis (Chiralcel OD, *n*-hexane/2-propanol 90:10, flow rate 1 mL/min, 30 ºC) τ_{minor} = 6.0 min, τ_{major} = 9.3 min). Literature: HPLC analysis of **(*R*)-Cbz-3'Aa** (Chiralcel OD-H, *n*-hexane/2-propanol 95:5, flow rate 1,1 mL/min 20 °C) τ_{minor} = 11.9 min, τ_{major} 32.6 min.[9]



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.043	127.482	49.82
2	9.293	128.408	50.18



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.030	8.226	5.38
2	9.283	144.711	94.62



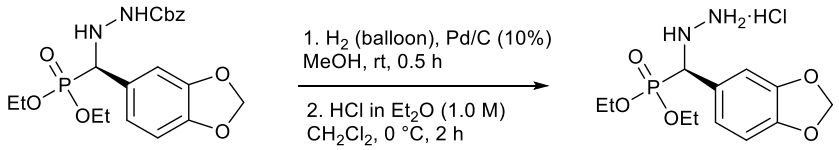
(*R*)-**3Ba** (*R*)-**3Aa** (*R*)-**3Da**

Transformations of (*R*)-**3Ba** and (*R*)-**3Da** in (*R*)-**3Aa** were carried out, in order to check if the stereochemical pathway is maintained employing different α-hydrazono phosphonates. In both experiments, the product (*R*)-**3Aa** was purified by preparative TLC (n-hexane /EtOAc 1/3) and analyzed by HPLC: (Chiralpak IC, *n*-hexane/2-propanol 75:25, flow rate 1 mL/min, 30 ºC); τ_{major} = 26.2 min, τ_{minor} = 31.6 min.

(*R*)-**3Ba** → (*R*)-**3Aa**: First, deprotection of (*R*)-**3Ba** was carried out by addition of diethylamine (5 equiv.) to a solution of (*R*)-**3Ba** in CH_2Cl_2 (0.1 M). The resulting mixture was stirred at room temperature for 1 h. After that, the solvent was eliminated under reduced pressure and the residue obtained was employed to introduce the Cbz protecting group, with benzyl chloroformate (1.1 equiv.), diisopropylethylamine (1 equiv.) in dry CH_2Cl_2 (1.0 M).

(*R*)-**3Da** → (*R*)-**3Aa**: First, deprotection of (*R*)-**3Da** was carried out by addition of HCl (4.0 M in 1,4-dioxane, 20 equiv.) to a solution of (*R*)-**3Da** in CH_2Cl_2 (0.2 M). The mixture was stirred at room temperature for 1 h. After that, the solvent and excess of HCl were eliminated under reduced pressure and the residue obtained was employed to introduce the Cbz protecting group, with benzyl chloroformate (1.1 equiv.), diisopropylethylamine (2 equiv.) in dry CH_2Cl_2 (1.0 M).

7. Synthesis of diethyl (*R*)-[benzo[d][1,3]dioxol-5-yl(hydrazineyl)methyl]phosphonate hydrochloride (4i)



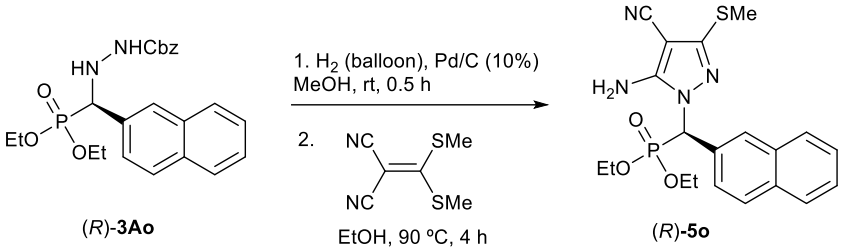
(*R*)-**3Ai** (*R*)-**4i**

A round bottomed flask was charged with Pd/C (10% w/w) (17 mg, 0.016 mmol), methanol (4 mL), (*R*)-**3Ai** (175 mg, 0.4 mmol, 99% ee) and sealed with a rubber septum. The head-space was evacuated and back-filled with hydrogen three times and then stirred under a balloon of hydrogen at room temperature for 0.5 h. After this time, the mixture was filtered through a celite pad and the solvent was eliminated under reduced pressure. The crude was dissolved in dry CH_2Cl_2 (1 mL) and cooled at 0 °C. Then, HCl (1.0 M in Et_2O, 1 mL, 1 mmol) was added drop-wise. After the mixture was stirred at 0 °C for 2 h, the solid was washed with pentane/Et_2O 2:1 (5 mL x 2) and dried under vacuum to obtain the pure hydrochloride salt **4i** as a yellow solid (130 mg, 90%, 99% ee). **^{1}H NMR** (300 MHz, DMSO-d^6): δ 9.30 (br s, 3H), 7.06 (s, 1H), 7.00 – 6.86 (m, 2H), 6.04 (br s, 3H), 4.63 (d, $^2J_{P,H}$ = 21.7 Hz, 1H), 4.13 – 3.98 (m, 2H),

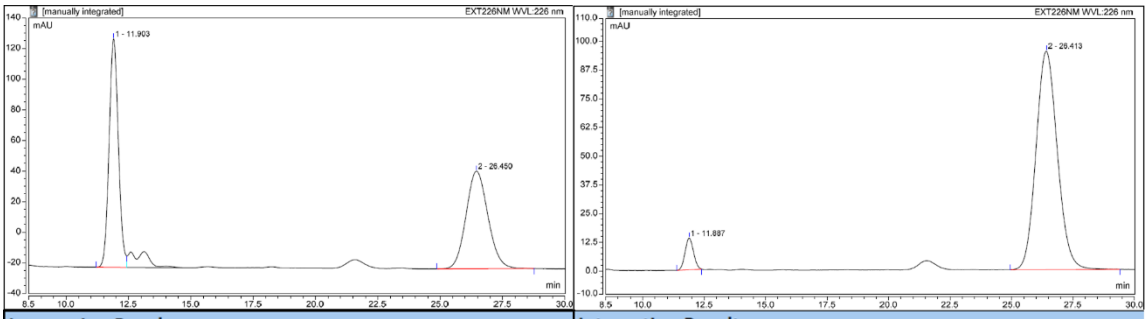
3.94 – 3.71 (m, 2H), 1.24 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^6): δ 147.5 (d, $^5J_{P,C}$ = 2.8 Hz), 147.3(d, $^4J_{P,C}$ = 2.2 Hz), 126.6 (d, $^3J_{P,C}$ = 4.2 Hz) 123.3(d, $^2J_{P,C}$ = 7.3 Hz), 109.0 (d, $^3J_{P,C}$ = 4.8 Hz), 108.2 (d, $^4J_{P,C}$ = 1.8 Hz), 101.2, 62.7 (d, $^2J_{P,C}$ = 6.8 Hz), 62.6 (d, $^2J_{P,C}$ = 6.7 Hz), 59.5 (d, $^1J_{P,C}$ = 154.1 Hz), 16.3 (d, $^3J_{P,C}$ = 5.6 Hz), 16.1 (d, $^3J_{P,C}$ = 5.5 Hz). **^{31}P NMR** (122 MHz, DMSO-d^6): δ 19.39. **HRMS** (ESI) *m/z* calcd. for $C_{12}H_{20}O_5N_2PNa$ [M^+] 303.1104, found 303.1099. **$[\alpha]_D^{25}$** = +22.6 (*c* 1.0, $CHCl_3$).

*The enantiomeric excess was determined after protection of the hydrochloride salt (*R*)-**4i** (34 mg, 0.1 mmol, 99% ee), with benzyl chloroformate (1.1 equiv.), diisopropylethylamine (2 equiv.) in dry CH_2Cl_2 (1.0 M). The resulting product (*R*)-**3Ai** was purified by preparative TLC (n-hexane /EtOAc 1/3) and the enantiomeric excess (ee) was determined by HPLC analysis (Chiralpak ID, *n*-hexane/2-propanol 70:30, flow rate 1 mL/min, 30 ºC) τ_{major} = 32.4 min, τ_{minor} = 35.7 min).

8. Synthesis of diethyl (*R*)-{[5-amino-4-cyano-3-(methylthio)-1*H*-pyrazol-1-yl](naphthalen-2-yl)methyl}phosphonate (5o)



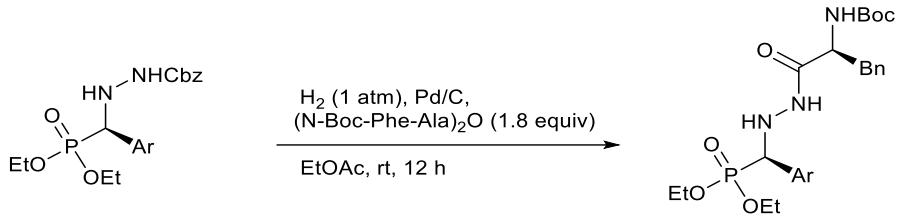
A round bottomed flask was charged with Pd/C (10% w/w) (12 mg, 0.011 mmol), methanol (3 mL), (*R*)-**3Ao** (110 mg, 0.25 mmol, 98% ee) and sealed with a rubber septum. The head-space was evacuated and back-filled with hydrogen three times and then stirred under a balloon of hydrogen at room temperature for 0.5 h. After this time, the mixture was filtered through a celite pad and the solvent was eliminated under reduced pressure. The crude was dissolved in dry EtOH (3 mL) and 2-[bis(methylthio)methylene]malononitrile (43 mg, 0.25 mmol) was added. Then, the reaction was refluxed at 90 ºC for 4h. After this time, the reaction mixture was cooled to room temperature and the solvent was eliminated under reduced pressure. Finally, the residue was purified by flash chromatography (*n*-hexane/EtOAc 1/1 to EtOAc) to afford (*R*)-**5o** as an amorphous white solid (70 mg, 65%, 90% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.04 (br s, 1H), 7.89 – 7.79 (m, 3H), 7.61 – 7.47 (m, 3H), 5.90 (d, $^2J_{P,H}$ = 24.4 Hz, 1H), 5.51 (br s, 2H), 4.25 – 3.97 (m, 4H), 2.53 (s, 3H), 1.26 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 152.8 (d, $^3J_{P,C}$ = 2.1 Hz), 149.2 (d, $^4J_{P,C}$ = 2.0 Hz), 133.2 (d, $^5J_{P,C}$ = 0.9 Hz), 132.9, 129.1 (d, $^3J_{P,C}$ = 1.5 Hz), 128.7, 128.4 (d, $^2J_{P,C}$ = 7.0 Hz), 128.3, 127.6, 126.9, 126.6, 126.0 (d, $^3J_{P,C}$ = 6.7 Hz), 113.5, 77.3, 64.2 (d, $^2J_{P,C}$ = 7.2 Hz), 64.1 (d, $^2J_{P,C}$ = 7.3 Hz), 62.3 (d, $^1J_{P,C}$ = 155.1 Hz), 16.25 (d, $^3J_{P,C}$ = 5.6 Hz), 14.5. **^{31}P NMR** (122 MHz, $CDCl_3$): δ 17.63. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{23}O_3N_4PSNa$ [M^+ + Na] 453.1121, found 453.1107. **HPLC** (Chiralpak IC, *n*-hexane/2-propanol 80:20, flow rate 1.0 mL/min) τ_{minor} = 11.9 min, τ_{major} = 26.4 min. **$[\alpha]_D^{25}$** = +14.0 (*c* 1.0, $CHCl_3$).



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.903	64.575	49.89
2	26.450	64.853	50.11

Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.887	5.492	5.43
2	26.413	95.724	94.57

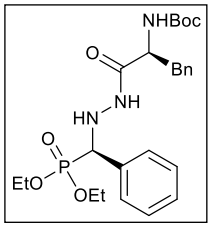
9. One-pot protocol for the synthesis of aminoacid derived hydrazides 6



(*R*)-**3Aa**: Ar = Ph
(*R*)-**3Ai**: Ar = 3,4-dioxymethylen-Ph

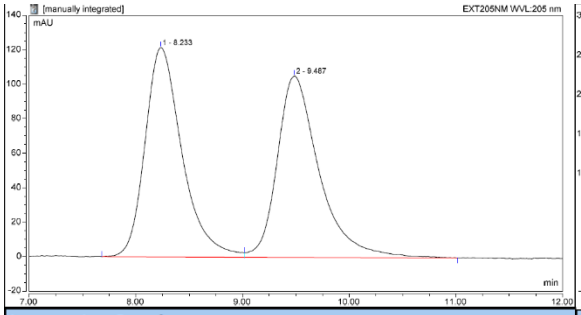
(*S,R*)-**6a**: Ar = Ph
(*S,R*)-**6i**: Ar = 3,4-dioxymethylen-Ph

To a solution of hydrazide adduct **3** (1 equiv.) in EtOAc (0.2 M) at 0 ºC was added dropwise a solution of symmetric anhydride of *N*-Boc protected L-phenyl alanine **(*N*-Boc-Phe-Ala)$_2$O** (1.8 equiv.) in EtOAc (0.2 M). While the reaction mixture was allowed to reach room temperature, Pd/C (10% w/w) (0.03 equiv.) was added, and the headspace was purged with hydrogen. Then, the reaction was stirred under a balloon of hydrogen at room temperature for 3 h. After this time, more Pd/C (10% w/w) (0.06 equiv.) was added and the reaction was stirred under a balloon of hydrogen at room temperature for 12 h. Finally, the resulting mixture was filtered through a celite pad and the solvent was removed under reduced pressure. The residue was purified by flash chromatography.

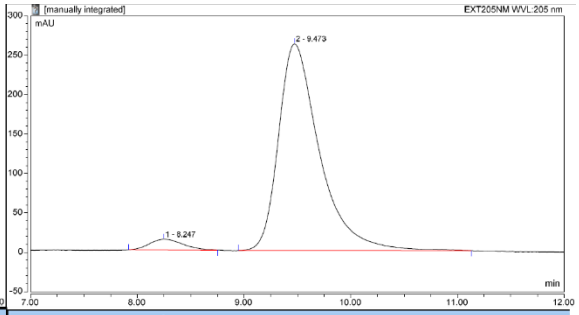


***tert*-Butyl {(*S*)-1-[2-((*R*)-(diethoxyphosphoryl)(phenyl)methyl)hydrazineyl]-1-oxo-3-phenylpropan-2-yl}carbamate. 6a:** Following the general procedure **9**, starting from hydrazide adduct **(*R*)-3Aa** (157 mg, 0.4 mmol, 98% ee), symmetric anhydride **(*N*-Boc-Phe-Ala)$_2$O** (369 mg, 0.72 mmol) and Pd/C (10% w/w) (38 mg, 0.036 mmol), the compound (*S,R*)-**6a** was obtained as white foam after purification by flash chromatography (*n*-hexane/EtOAc 2/1 to EtOAc) (113 mg, 56%, d.r. = 96:4). **^{1}H NMR** (300 MHz, DMSO-d^6): δ 9.49 (d, *J* = 6.1 Hz, 1H), 7.45 – 7.10 (m, 10H), 6.82 (d, *J* = 8.7 Hz, 1H), 5.46 – 5.34 (m, 1H), 4.37 (dd, $^2J_{P,H}$ = 17.6, 4.5 Hz, 1H), 4.07 – 3.79 (m, 5H), 2.68 – 2.52 (m, 2H), 1.26 (s, 9H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^6) δ 170.67, 155.1, 138.0, 134.7 (d, $^2J_{P,C}$ = 6.1 Hz), 129.2 (d, $^4J_{P,C}$ = 1.9 Hz), 129.1, 129.0 (d, $^3J_{P,C}$ = 5.9 Hz), 127.96, 127.82 (d, $^5J_{P,C}$ = 2.6 Hz), 126.2, 78.0, 62.8, 62.36 (d, $^2J_{P,C}$ = 6.6 Hz), 62.35 (d, $^2J_{P,C}$ = 6.6 Hz), 61.9 (d, $^1J_{P,C}$ = 147.0 Hz), 54.3, 37.5, 28.1, 16.2 (d, $^3J_{P,C}$ = 5.6 Hz), 16.1 (d, $^3J_{P,C}$ = 5.6 Hz). **^{31}P NMR** (122 MHz, DMSO-d^6): δ 20.97. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{36}O_6N_3Na$ [M^+ + Na] 528.2234, found

528.2229. **HPLC** (Chiralpak IA, *n*-hexane/2-propanol 85:15, flow rate 1 mL/min) τ_{minor} = 8.2 min, τ_{major} = 9.5 min. **$[\alpha]_D^{25}$** = +67.2 (*c* 1.0, DMSO).

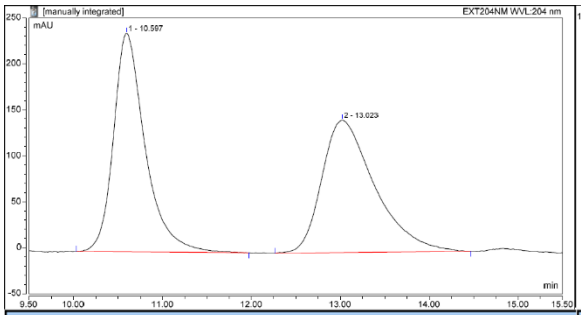


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.233	48.746	50.41
2	9.487	47.956	49.59

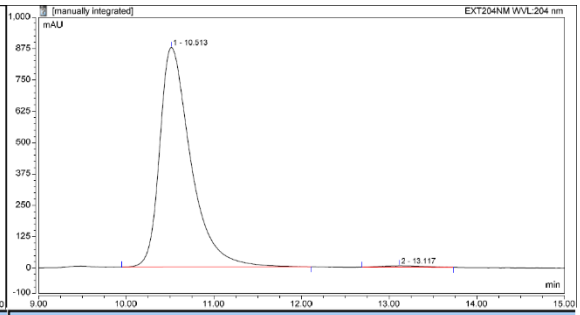


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.247	4.898	4.03
2	9.473	116.584	95.97

***tert*-Butyl {(*S*)-1-[2-((*R*)-(diethoxyphosphoryl)(phenyl)methyl)hydrazineyl]-1-oxo-3-phenylpropan-2-yl}carbamate. 6i:** Following the general procedure **9**, starting from hydrazine adduct **(*R*)-3Ai** (157 mg, 0.4 mmol, 98% ee), symmetric anhydride **(*N*-Boc-Phe-Ala)$_2$O** (369 mg, 0.72 mmol) and Pd/C (10% w/w) (38 mg, 0.036 mmol), the compound (*S*,*R*)-**6i** was obtained as white foam after purification by flash chromatography (*n*-hexane/EtOAc 2/1 to EtOAc) (148 mg, 69%, d.r. = 99:1). **^{1}H NMR** (300 MHz, DMSO-d^6: δ 9.46 (d, *J* = 5.0 Hz, 1H), 7.30 – 7.09 (m, 5H), 6.98 (s, 1H), 6.93 – 6.75 (m, 3H), 6.00 (s, 2H), 5.33 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.30 (dd, , $^2J_{P,H}$ = 17.2, 4.9 Hz, 1H), 4.10 – 3.80 (m, 5H), 2.77 – 2.51 (m, 2H), 1.27 (s, 9H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^6): δ 170.7, 155.1, 147.0 (d, $^4J_{P,C}$ = 2.6 Hz), 146.9 (d, $^5J_{P,C}$ = 3.1 Hz), 138.0, 129.1, 128.3 (d, $^3J_{P,C}$ = 6.2 Hz), 127.9, 126.2, 122.8 (d, $^2J_{P,C}$ = 7.3 Hz), 109.0 (d, $^3J_{P,C}$ = 5.0 Hz), 107.8, 101.0, 77.9, 62.3 (d, $^2J_{P,C}$ = 6.5 Hz), 61.3 (d, $^1J_{P,C}$ = 149.0 Hz) 54.3, 37.5, 28.1 16.2 (d, $^3J_{P,C}$ = 5.6 Hz), 16.1 (d, $^3J_{P,C}$ = 5.6 Hz). **^{31}P NMR** (122 MHz, DMSO-d^6): δ 20.73. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{36}O_8N_3PNa$ [M^+ + Na] 572.2132, found 572.2128. **HPLC** (Chiralpak IB, *n*-hexane/2-propanol 90:10, flow rate 1 mL/min) τ_{major} = 10.6 min, τ_{minor} = 13.0 min. **$[\alpha]_D^{25}$** = +74.4 (*c* 1.0, DMSO).

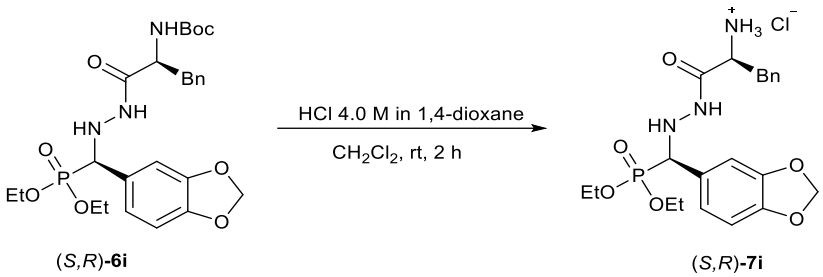


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.597	98.122	49.71
2	13.023	99.260	50.29



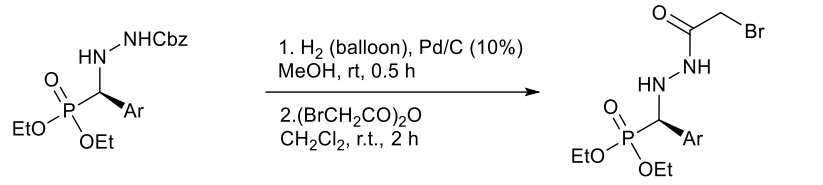
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.513	360.679	99.11
2	13.117	3.236	0.89

(*S*)-1-{2-[(*R*)-benzo[d][1,3]dioxol-5-yl(diethoxyphosphoryl)methyl]hydrazineyl]-1-oxo-3-phenylpropan-2-aminium chloride. 7i



To a solution of (*S*,*R*)-**6i** (126 mg, 0.25 mmol) in CH_2Cl_2 (1 mL) was added drop-wise HCl (4.0 M in 1,4-dioxane, 0.75 mL, 3 mmol) at 0 ºC. Then, the mixture was stirred from 0 ºC to room temperature for 2 h. After this time, the solvent and the excess of HCl were removed under reduced pressure to afford the salt (*S*,*R*)-**7i** as a white solid (109 mg, 90%). **^{1}H NMR** (300 MHz, DMSO-d^6) δ 10.17 (br s, 1H), 8.52 (br s, 3H), 7.37 – 7.20 (m, 5H), 7.17 – 7.08 (m, 1H), 6.99 (br s, 1H), 6.87 (br s, 1H), 6.01 (br s, 2H), 5.38 (br s, 1H), 4.29 (d, $^2J_{P,H}$ = 18.5 Hz, 1H), 4.11 – 3.98 (m, 2H), 3.95 – 3.80 (m, 2H), 3.23 – 3.11 (m, 1H), 3.03 – 2.79 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^6): δ 170.2, 166.7, 146.99 (d, $^5J_{P,C}$ = 2.5 Hz), 146.97 (d, $^4J_{P,C}$ = 1.6 Hz), 135.2, 134.9, 129.6, 129.4, 128.5, 128.4, 128.3 (d, $^3J_{P,C}$ = 5.6 Hz), 127.11, 127.01, 122.84, 122.74, 108.95, 107.85, 101.05, 62.5 (d, $^2J_{P,C}$ = 6.6 Hz), 62.4 (d, $^2J_{P,C}$ = 6.4 Hz), 61.4 (d, $^1J_{P,C}$ = 148.6 Hz), 52.7 (d, *J* = 90.2 Hz), 36.2 (d, *J* = 74.0 Hz), 16.3 (d, $^3J_{P,C}$ = 5.6 Hz), 16.2 (d, $^3J_{P,C}$ = 5.5 Hz). **^{31}P NMR** (122 MHz, DMSO-d^6): δ 20.77. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{29}O_6N_3P$ [M$^+$] 450.1788, found 450.1782. **$[\alpha]_D^{25}$** = +30.3 (*c* 1.0, MeOH).

10. Synthesis of 2-bromoacetyl derivatives 8



(*R*)-**3Ai**: Ar = 3,4-dioxymethylen-Ph
(*R*)-**3Ao** and (*S*)-**3Ao** Ar = 2-naphthyl

(*R*)-**8i**: Ar = 3,4-dioxymethylen-Ph
(*R*)-**8o** and (*S*)-**8o** Ar = 2-naphthy

A round bottomed flask was charged with Pd/C (10% w/w) (0.05 equiv.) and a solution of **(*R*)-3** (1 equiv.) in methanol (0.1 M) was added, then the whole system was sealed with a rubber septum. The head-space was evacuated and back-filled with hydrogen three times and then stirred under a balloon of hydrogen at room temperature for 0.5 h. After this time, the mixture was filtered through a celite pad and the solvent was removed under reduced pressure. Then, the crude was dissolved in dry CH_2Cl_2 (0.1 M), bromoacetic anhydride (1.5 equiv.) was added and the mixture of reaction was stirred at room temperature for 1 h. After this time, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (*n*-hexane/EtOAc 1/1 to EtOAc).

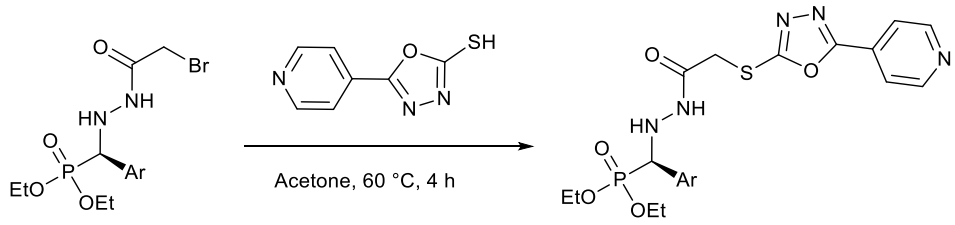
Diethyl (*R*)-{benzo[d][1,3]dioxol-5-yl[2-(2-bromoacetyl)hydrazineyl]methyl}phosphonate. 8i: Following the general procedure **10**, starting from **(*R*)-3Ai** (140 mg, 0.325 mmol, 99% ee),

Pd/C (10% w/w) (16 mg, 0.016 mmol) and bromoacetic anhydride (60 μL, 0.488 mmol), the compound **(*R*)-8i** was obtained as colorless oil (89 mg, 77%, 99% ee). **^{1}H NMR** (300 MHz, $CDCl_3$): (*R*)-**8i** exists as ≈ 9:1 rotamers) s*ignals corresponding to the major rotamer*: δ 8.28 (br s, 1H), 6.99 (dd, $^{2}J_{P,H}$ = 1.7 Hz, $J_{H,H}$ = 1.7 Hz 1H), 6.94 – 6.82 (m, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.96 (s, 1H), 4.38 (d, $^{2}J_{P,H}$ = 13.6 Hz, 1H), 4.16 – 3.95 (m, 5H), 3.76 (s, 2H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). *Representative signals corresponding to the minor rotamer*: δ 5.98 (s, 1H), 3.85 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): s*ignals corresponding to the major rotamer*: δ 164.9, 147.9 (d, $^{5}J_{P,C}$ = 2.6 Hz), 147.8 (d, $^{4}J_{P,C}$ = 1.7 Hz), 126.7 (d, $^{3}J_{P,C}$ = 7.1 Hz), 122.8 (d, $^{3}J_{P,C}$ = 7.3 Hz), 109.0 (d, $^{3}J_{P,C}$ = 5.4 Hz), 108.3 (d, $^{4}J_{P,C}$ = 2.2 Hz), 101.2, 63.5 (d, $^{2}J_{P,C}$ = 7.0 Hz), 62.9 (d, $^{2}J_{P,C}$ = 7.1 Hz), 62.0 (d, $^{1}J_{P,C}$ = 156.0 Hz), 26.7, 16.4 (d, $^{3}J_{P,C}$ = 5.6 Hz). *Representative signals corresponding to the minor rotamer*: δ 170.7, 126.4 (d, $^{3}J_{P,C}$ = 6.8 Hz), 122.6 (d, $^{2}J_{P,C}$ = 7.4 Hz), 108.7 (d, $^{4}J_{P,C}$ = 5.2 Hz), 108.6 (d, $^{3}J_{P,C}$ = 5.9 Hz), 101.4, 25.3. **^{31}P NMR** (122 MHz, $CDCl_3$) s*ignal corresponding to the major rotamer*: δ 20.56. S*ignal corresponding to the minor rotamer*: 20.12. **HRMS** (ESI) *m/z* calcd. for $C_{14}H_{20}O_6N_3BrPNa$ [M^+ + Na] 445.0135, found 445.0126. **$[\alpha]_D^{25}$** = +68.9 (*c* 1.0, $CHCl_3$).

Diethyl (*R*)-{[2-(2-bromoacetyl)hydrazineyl](naphthalen-2-yl)methyl}phosphonate. 8o: Following the general procedure **10**, starting from (*R*)-**3Ao** (121 mg, 0.275 mmol, 98% ee), Pd/C (10% w/w) (14 mg, 0.014 mmol) and bromoacetic anhydride (50 μL, 0.413 mmol), the compound **(*R*)-8o** was obtained as colorless oil (81 mg, 70%, 98% ee). Reaction performed with (*S*)-**3Ao** (121 mg, 0.275 mmol, 97% ee): 79 mg, 69%, 97% ee. **^{1}H NMR** (300 MHz, $CDCl_3$): (*R*)-**8o** exists as ≈ 10:1 rotamers) s*ignals corresponding to the major rotamer*: δ 8.16 (d, *J* = 4.3 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.89 – 7.80 (m, 3H), 7.60 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.56 – 7.46 (m, 2H), 5.49 – 5.28 (m, 1H), 4.65 (d, $^{2}J_{P,H}$ = 14.1 Hz, 1H), 4.27 – 3.90 (m, 4H), 3.74 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). *Representative signals corresponding to the minor rotamer*: δ 6.79 (br s, 1H), 4.85 – 4.77 (m, 1H), 4.41 (d, $^{2}J_{P,H}$ = 10.6 Hz, 1H) 3.79 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) s*ignals corresponding to the major rotamer*: δ 164.8, 133.3 (d, $^{4}J_{P,C}$ = 2.1 Hz), 133.2 (d, $^{5}J_{P,C}$ = 2.5 Hz), 130.8 (d, $^{2}J_{P,C}$ = 7.3 Hz), 128.40 (d, $^{4}J_{P,C}$ = 1.7 Hz), 128.39, 128.3, 128.0 (d, $^{6}J_{P,C}$ = 0.8 Hz), 127.7 (d, $^{5}J_{P,C}$ = 1.2 Hz), 126.4 (d, $^{3}J_{P,C}$ = 4.9 Hz), 126.2 (d, $^{3}J_{P,C}$ = 4.7 Hz), 63.5 (d, $^{2}J_{P,C}$ = 7.0 Hz), 63.0 (d, $^{2}J_{P,C}$ = 7.1 Hz), 62.7 (d, $^{1}J_{P,C}$ = 154.2 Hz), 26.7, 16.4 (d, $^{3}J_{P,C}$ = 5.8 Hz), 16.3 (d, $^{3}J_{P,C}$ = 5.8 Hz). **^{31}P NMR** (122 MHz, $CDCl_3$) s*ignal corresponding to the major rotamer*: δ 20.43. S*ignal corresponding to the minor rotamer*: 20.07. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{22}O_4N_2BrPNa$ [M^+ + Na] 451.0404, found 451.0389. **$[\alpha]_D^{25}$** = +77.2 (*c* 1.0, $CHCl_3$). For (*S*)-**8b $[\alpha]_D^{25}$** = –74.4 (*c* 1.0, $CHCl_3$).

The enantiomeric excesses of **8i** and **8o** were determined in products **9i** and **9o**, respectively.

11. Synthesis of compounds 9

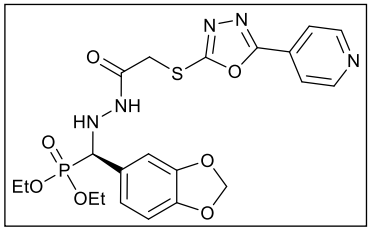


(*R*)-**3Ai**: Ar = 3,4-dioxymethylen-Ph
(*R*)-**3Ao** and (*S*)-**3Ao** Ar = 2-naphthyl

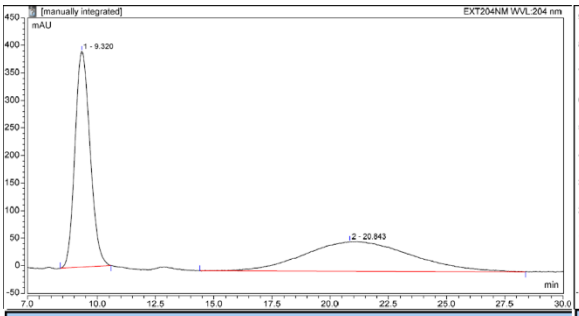
(*R*)-**9i**: Ar = 3,4-dioxymethylen-Ph
(*R*)-**9o** and (*S*)-**9o** Ar = 2-naphthyl ⟹ **HCT116 antitumor**

A solution of (*R*)-**8** (1 equiv.) in acetone (0.2 M) was added to 5-(Pyridin-4-yl)-1,3,4-oxadiazole-2-thiol (1 equiv.). The reaction was heated at 60 ºC for 4 h. After this time, K_2CO_3 (0.5 equiv.) was added and the mixture was purified by flash chromatography (EtOAc to EtOAc/MeOH 10:1) to afford (*R*)-**9**.

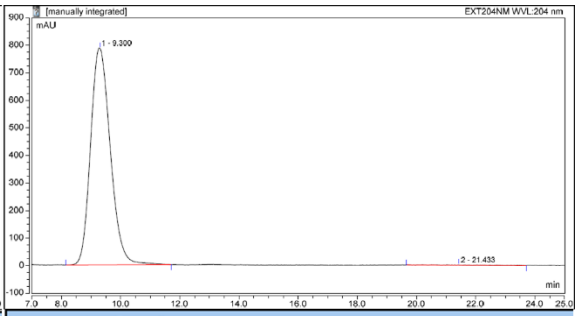
Diethyl (*R*)-{benzo[d][1,3]dioxol-5-yl[2-(2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)acetyl)hydrazineyl]methyl}phosphonate (*R*)-9i:



Following the general procedure **11**, starting from **(*R*)-8i** (80 mg, 0.189 mmol, 99% ee), and 5-(pyridin-4-yl)-1,3,4-oxadiazole-2-thiol (34 mg, 0.189 mmol), the compound **(*R*)-9i** was obtained as an amorphous yellow solid (79 mg, 80%, 99% ee). **^{1}H NMR** (500 MHz, DMSO-d^6, **(*R*)-9i** exists as ≈ 4:1 rotamers) s*ignals corresponding to the major rotamer*: δ 9.75 (d, *J* = 5.1 Hz, 1H), 8.84 – 8.78 (m, 2H), 7.89 – 7.86 (m, 2H), 6.95 (br s, 1H), 6.79 (br s, 2H), 5.97 (d, *J* = 0.9 Hz, 1H), 5.96 (d, *J* = 0.9 Hz, 1H), 5.50 – 5.42 (m, 1H), 4.36 (dd, $^2J_{P,H}$ = 17.1, 3.4 Hz, 1H), 4.11 – 3.72 (m, 6H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). *Representative signals corresponding to the minor rotamer*: δ 8.88 (br s, 1H), 7.92 – 7.89 (m, 2H), 7.04 (br s, 1H), 6.90 (br s, 2H), 6.01 (d, *J* = 0.9 Hz, 1H), 6.00 (d, *J* = 0.9 Hz, 1H), 5.84 (dd, $^2J_{P,H}$ = 10.3, 6.2 Hz, 1H), 4.57 (dd, *J* = 55.7, 16.0 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^6) s*ignals corresponding to the major rotamer*: δ 169.6, 165.5, 164.5, 163.6, 150.9, 147.0 (d, $^4J_{P,C}$ = 2.6 Hz), 146.9 (d, $^5J_{P,C}$ = 3.1 Hz), 130.0, 128.0 (d, $^3J_{P,C}$ = 6.8 Hz), 122.6 (d, $^2J_{P,C}$ = 7.1 Hz), 119.9, 108.8 (d, $^3J_{P,C}$ = 5.0 Hz), 107.7 (d, $^4J_{P,C}$ = 2.2 Hz), 101.0, 62.4 (d, $^2J_{P,C}$ = 6.7 Hz), 62.3 (d, $^2J_{P,C}$ = 6.7 Hz), 60.9 (d, $^1J_{P,C}$ = 148.4 Hz), 33.8, 16.2 (d, $^3J_{P,C}$ = 5.6 Hz), 16.1 (d, $^3J_{P,C}$ = 5.6 Hz). *Representative signals corresponding to the minor rotamer*: δ 165.4, 163.4, 147.2 (d, $^4J_{P,C}$ = 2.0 Hz), 147.1 (d, $^5J_{P,C}$ = 2.8 Hz), 131.0, 128.2 (d, $^3J_{P,C}$ = 4.1 Hz), 123.0 (d, $^2J_{P,C}$ = 7.4 Hz), 109.1 (d, $^3J_{P,C}$ = 5.5 Hz), 108.0 (d, $^4J_{P,C}$ = 15 Hz), 101.1, 62.2, 62.1, 61.8 (d, $^1J_{P,C}$ = 152.0 Hz), 35.9. **^{31}P NMR** (122 MHz, DMSO-d^6) s*ignal corresponding to the major rotamer*: δ 20.62. S*ignal corresponding to the minor rotamer*: 21.41. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{25}O_7N_5PS$ [M$^+$ + H] 522.1194, found 522.1201. **HPLC** (Chiralcel OD, *n*-hexane/2-propanol 30:70, flow rate 1 mL/min) τ_{major} = 9.3 min, τ_{minor} = 20.8 min. **$[\alpha]_D^{25}$** = +132.9 (*c* 1.0, acetone).

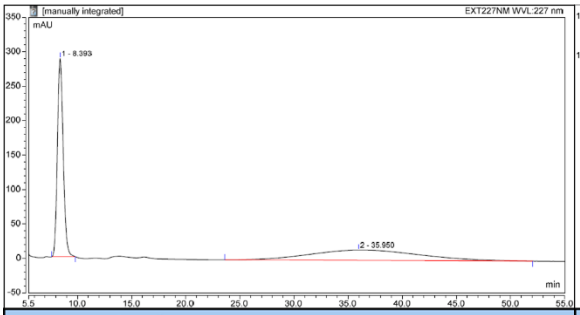


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.320	294.930	50.56
2	20.843	288.354	49.44



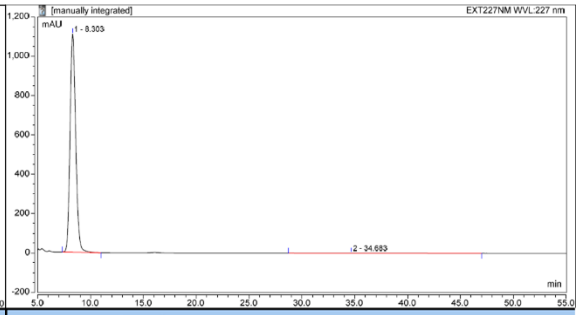
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.300	607.466	99.72
2	21.433	1.722	0.28

Diethyl (*R*)-(naphthalen-2-yl(2-(2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)acetyl)hydrazineyl)methyl)phosphonate (*R*)-9o: Following the general procedure **11**, starting from (*R*)-**8o** (81 mg, 0.189 mmol, 98% ee), and and 5-(pyridin-4-yl)-1,3,4-oxadiazole-2-thiol (34 mg, 0.189 mmol), the compound **(*R*)-9o** was obtained as an amorphous yellow solid (71 mg, 71%, 98% ee). Reaction performed with (*S*)-**8o** (121 mg, 0.275 mmol, 97% ee): 70 mg, 70%, 97% ee. **^{1}H NMR** (300 MHz, DMSO-d^{6}, (*R*)-**9o** exists as ≈ 4:1 rotamers) s*ignals corresponding to the major rotamer*: δ 9.83 (br s, 1H), 8.86 – 8.73 (m, 2H), 8.00 – 7.76 (m, 6H), 7.67 – 7.41 (m, 3H), 5.64 (br s, 1H), 4.64 (d, *J* = 17.6 Hz, 1H), 4.20 – 3.73 (m, 6H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). *Representative signals corresponding to the minor rotamer*: δ 8.98 (br s, 1H), 6.02 (dd, $^{2}J_{P,H}$ = 10.6, 5.8 Hz, 1H) 4.64 (dd, *J* = 24.0, 16.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75.5 MHz, DMSO-d^{6}) s*ignals corresponding to the major rotamer*: δ 169.6, 165.6, 164.5, 163.5, 150.94, 150.87, 132.7 (d, $^{4}J_{P,C}$ = 2.5 Hz), 132.6 (d, $^{5}J_{P,C}$ = 3.0 Hz), 132.1 (d, $^{3}J_{P,C}$ = 7.0 Hz), 129.9, 128.0 (d, $^{2}J_{P,C}$ = 7.6 Hz), 127.8, 127.45 (d, $^{4}J_{P,C}$ = 2.1 Hz), 127.42 (d, $^{6}J_{P,C}$ = 1.8 Hz), 126.6 (d, $^{3}J_{P,C}$ = 4.2 Hz), 126.1 (d, $^{5}J_{P,C}$ = 2.9 Hz), 119.9, 62.5, (d, $^{2}J_{P,C}$ = 6.5 Hz), 62.4 (d, $^{2}J_{P,C}$ = 6.4 Hz), 61.6 (d, $^{1}J_{P,C}$ = 147.3 Hz), 33.8, 16.2 (d, $^{3}J_{P,C}$ = 5.6 Hz), 16.1 (d, $^{3}J_{P,C}$ = 5.6 Hz). *Representative signals corresponding to the minor rotamer*: δ 165.4, 163.4, 151.0, 132.7 (d, $J_{P,C}$ = 3.7 Hz), 130.1, 128.3 (d, $^{2}J_{P,C}$ = 8.0 Hz), 127.7 (d, $^{6}J_{P,C}$ = 0.9 Hz), 127.6, 126.8 (d, $^{4}J_{P,C}$ = 4.0 Hz), 126.3 (d, $^{4}J_{P,C}$ = 3.4z Hz), 119.5, 36.0, 16.3 (d, $^{3}J_{P,C}$ = 5.2 Hz), 16.1 (d, $^{3}J_{P,C}$ = 5.6 Hz). **^{31}P NMR** (122 MHz, DMSO-d^{6}) s*ignal corresponding to the major rotamer*: δ 20.44. S*ignal corresponding to the minor rotamer*: 21.19. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{26}O_5N_5PSNa$ [M^{+} + Na] 550.1295, found 550.1280. **HPLC** (Chiralcel OD, *n*-hexane/2-propanol 20:80, flow rate 1 mL/min) τ_{major} = 8.4 min, τ_{minor} = 36.0 min. **$[\alpha]_D^{25}$** = +147.3 (*c* 1.0, acetone). For (*S*)-**9o $[\alpha]_D^{25}$** = –144.4 (*c* 1.0, acetone).



Integration Results

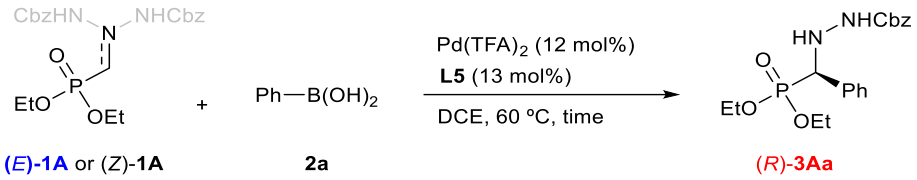
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.393	179.110	50.74
2	35.950	173.860	49.26



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	8.303	689.090	99.03
2	34.683	6.778	0.97

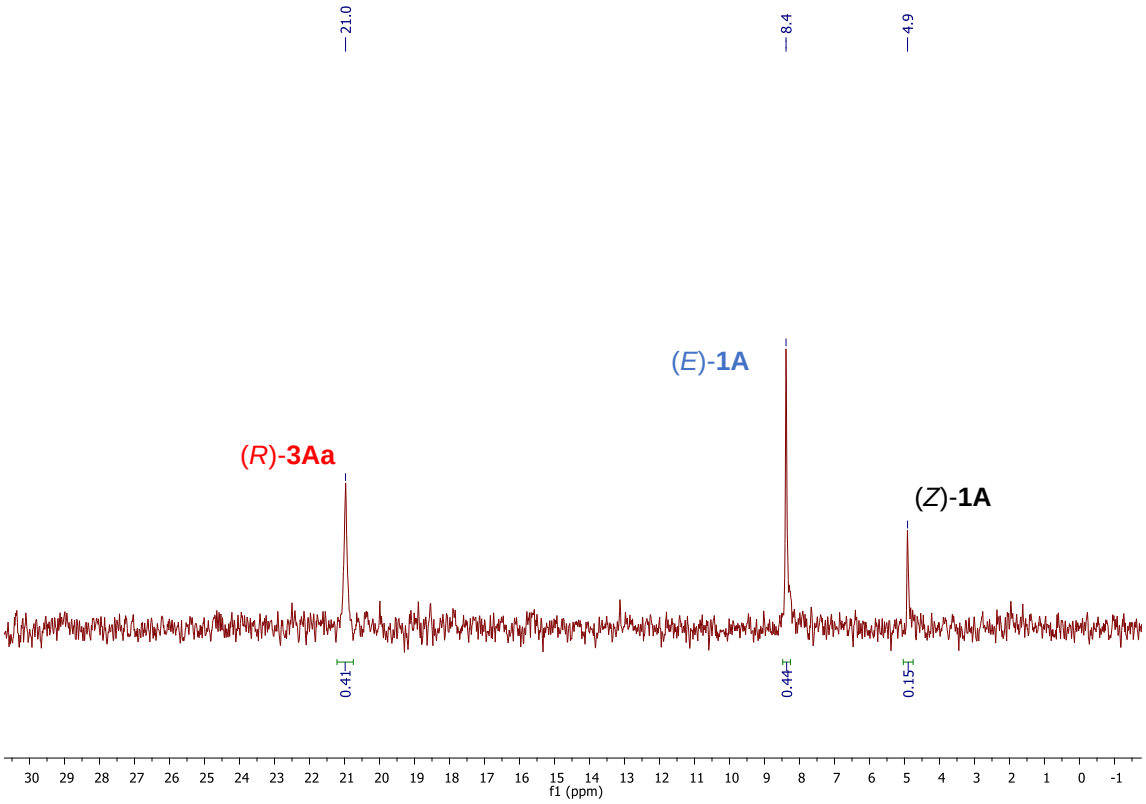
12. Protocol for kinetic experiments



To a sealed tube charged with $Pd(TFA)_2$ (8 mg, 0.024 mmol), **L5** (10 mg, 0.026 mmol), (0.2 mmol), and phenylboronic acid (0.3 mmol) was added a solution of α-hydrazono phosphonate **(*E*)-1A** or **(Z)-1A** (0.2 mmol) in DCE (0.5 mL). The reaction mixture was stirred at 60 ºC and monitored by ^{31}P-NMR at different times: 2, 4, 8, 12, 24 and 36 h.

Sample aliquot: The reaction is allowed to cool to room temperature, the sealed tube is uncovered, and a 0.025 mL aliquot is taken. Then, the reaction is sealed and heated back to 60 °C. The aliquot is eliminated under reduced pressure and dissolved in 0.45 mL of $CDCl_3$ for analysis by ^{31}P-NMR.

All phosphorus peaks were integrated and adjusted so that the total sum of integrals equaled 1.0. See the next example, which corresponds to an aliquot taken at 4 hours when **(*E*)-1A** was used as the starting material.



13. Computational Details.

All the calculations reported in this paper were obtained with the Gaussian 16 suite of programs.[10] All species were optimized using the meta-hybrid functional M06L[11] in conjunction with standard double-ζ quality def2-SVP[12] basis sets for all atoms which includes the corresponding effective core potential for palladium.[13] Solvents effects (solvent = dichloroethane) were taken into account during the geometry optimizations using the polarizable continuum model (PCM).[14] All stationary points were characterized by frequency calculations.[15] Reactants and products have positive definite Hessian matrices, whereas transition structures show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.[16] This level is denoted PCM(dichloroethane)-M06L/def2-SVP.

Activation Strain Model (ASM) of Reactivity and Energy Decomposition Analysis (EDA):

Within the ASM method,[17] also known as the distortion/interaction model,[17c] the potential energy surface $\Delta E(\zeta)$ is decomposed along the reaction coordinate, ζ, into two contributions, namely the strain $\Delta Estrain(\zeta)$ associated with the deformation (or distortion) required by the individual reactants during the process and the interaction $\Delta Eint(\zeta)$ between these increasingly deformed reactants:

$$\Delta E(\zeta) = \Delta Estrain(\zeta) + \Delta Eint(\zeta)$$

Within the EDA method,[18] the interaction energy can be further decomposed into the following chemically meaningful terms:

$$\Delta Eint(\zeta) = \Delta Velstat(\zeta) + \Delta EPauli(\zeta) + \Delta Eorb(\zeta)$$

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction ΔE_{orb} accounts for bond pair formation, charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals on the other, including HOMO-LUMO interactions), and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment).

The program package ADF[19] was used for EDA calculations using the optimized PCM(dichloroethane)-M06L/def2-SVP geometries at the same M06L level in conjunction with a triple-ζ-quality basis set using uncontracted Slater-type orbitals (STOs) augmented by polarization functions.[20] Auxiliary sets of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[21] Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA).[22] This level of theory is denoted ZORA-M06L/DZP//PCM(dichloroethane)-M06L/def2-SVP.

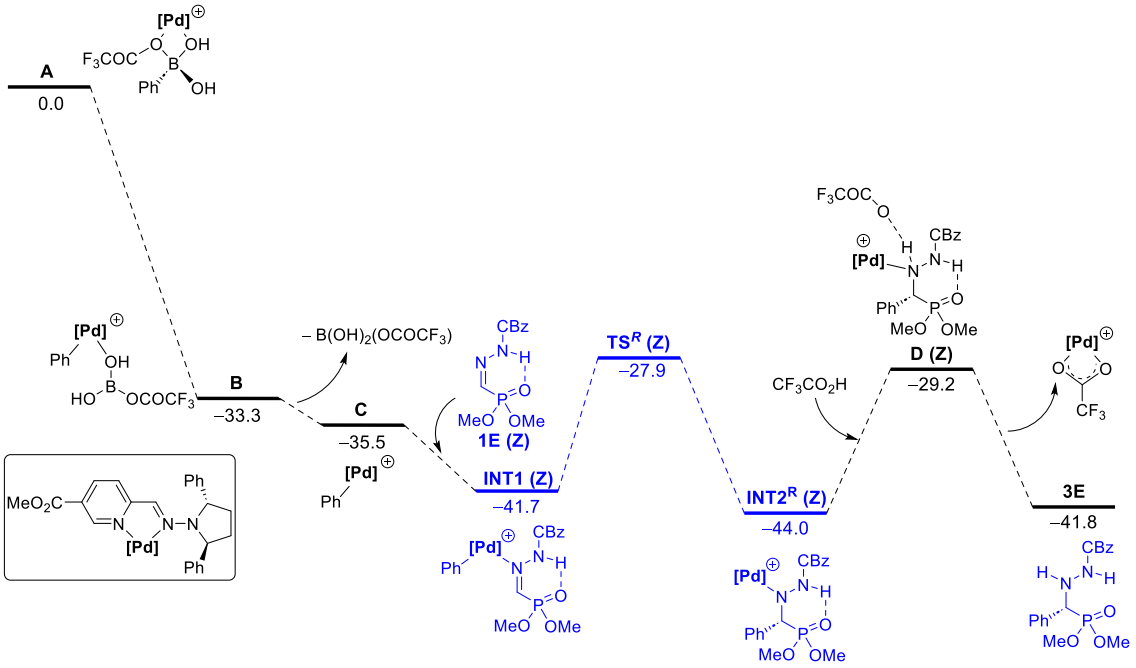


Figure S1. Computed reaction profile for the formation of **3E**. Relative free energies (ΔG, at 333 K) a are given in kcal·mol^{-1}.

As commented in the main text, the transformation follows a rather similar profile than that computed for the related PdII-catalyzed asymmetric addition of arylboronic acids to cyclic N-sulfonyl ketimine esters (see reference 20e in the main text). Thus, it involves the initial phenyl transfer from the boronic acid to the active palladium(II) catalyst (we were not able to locate the corresponding transition state associated with the formation of B, which can be ascribed to the highly exergonicitiy of the transformation), coordination of the hydrazone followed by intramolecular C–C bond formation, protonation (mediated by TFA or H_2O)* and concomitant regeneration of the catalyst.

*In this process, water assists the catalytic turnover and accelerate the reaction as confirmed comparing with the reaction performed under anhydrous conditions. On small scale, the moisture in the air, on the glassware and DCE provided sufficient water to drive the reaction to completion. Stoichiometric arylboronic acid might form variable amounts of boroxine and water which might hydrolyze $B(OH)_2OCOCF_3$ (included in reaction profile, Figure S1), giving $B(OH)_3$ and TFA. In fact, a control experiment revealed that reactivity dropped when 2,4,6-triphenylboroxine (**2a'**) was used instead of phenyl boronic acid **2a** (Table 1, entry 8 in the manuscript), in agreement with less amount of water in the reaction media.

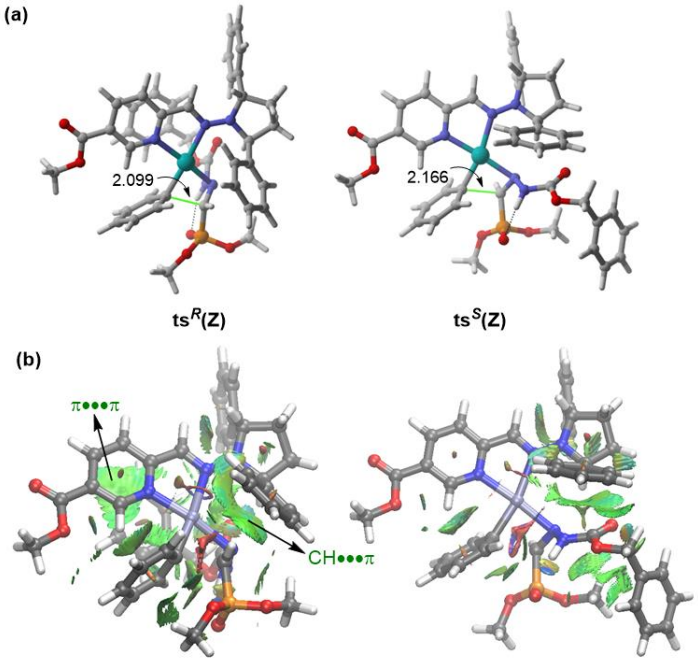


Figure S2. Optimized geometries (a) and NCI-plots (b) of transition states **ts^{R}(Z)** and **ts^{S}(Z)**.

Cartesian coordinates (in Å) and electronic energies (in a.u., ZPVE included) and free energies (in a.u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM(dichloroethane)-M06L/def2-SVP level.

INT1 (E): E = -2854.948588; G = -2855.05392

C	1.171630000	1.347652000	-2.132374000
C	2.080087000	1.928557000	-3.035490000
C	3.324909000	1.357300000	-3.224829000
C	3.660765000	0.207125000	-2.499852000
C	2.707516000	-0.332387000	-1.636723000
N	1.497556000	0.204238000	-1.463141000
H	4.052091000	1.790759000	-3.913989000
H	1.790047000	2.835787000	-3.566985000
H	2.942818000	-1.229282000	-1.064976000
C	-0.095261000	1.964990000	-1.855747000
H	-0.326418000	2.906899000	-2.360839000
N	-0.905746000	1.423616000	-0.978114000
Pd	0.021164000	-0.487122000	-0.153182000
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C	-3.720704000	3.588168000	-0.308782000
H	-2.483161000	3.458980000	-2.106168000
H	-4.579436000	2.470522000	1.378858000
H	-2.955681000	3.128537000	1.669842000
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C	-0.485580000	4.236972000	0.507820000
C	-1.294102000	5.664603000	-1.260427000
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C	3.547608000	0.327820000	3.753937000
C	2.659059000	1.735239000	2.004272000
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C	3.735622000	1.391851000	1.187026000
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H	3.809377000	1.821641000	0.184359000
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O	5.162603000	-1.445995000	-1.820245000
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H	7.233583000	-1.399878000	-1.604751000
H	6.382372000	-2.912092000	-1.141924000
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H	-0.994675000	-5.031971000	-1.855342000
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H	0.627714000	-3.120191000	-1.494336000
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H	3.710131000	-4.914200000	0.933155000

TS^R (E): E = -2854.918765; G = -2855.030244 (i = -330 cm-1)

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C	-1.404920000	4.769691000	-1.754078000
C	-0.186773000	4.614044000	-1.079215000

C	0.127214000	3.351330000	-0.572874000
N	-0.682559000	2.302706000	-0.707832000
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H	1.064429000	3.185475000	-0.036862000
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H	-3.675327000	1.388869000	-1.975016000
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Pd	-0.253611000	0.330713000	-0.075828000
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H	-5.444403000	1.162155000	2.581457000
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C	-1.248937000	-2.581726000	-2.649627000
C	-0.148702000	-4.908649000	-1.575778000
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C	-0.325168000	-3.328558000	-3.389591000
H	-1.673040000	-1.670324000	-3.079844000
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C	5.460181000	-1.896879000	-1.228738000
C	5.516896000	-0.836963000	-2.143617000
C	6.206496000	-1.815463000	-0.048544000

C	6.312874000	0.277482000	-1.884981000
C	7.007296000	-0.704247000	0.209385000
C	7.063039000	0.343602000	-0.709018000
H	4.933146000	-0.890209000	-3.067491000
H	6.148837000	-2.631421000	0.676383000
H	6.354958000	1.095858000	-2.607736000
H	7.587998000	-0.655074000	1.133356000
H	7.690672000	1.215237000	-0.508576000
C	0.717343000	5.776025000	-0.919043000
O	0.475751000	6.884555000	-1.341735000
O	1.832461000	5.453946000	-0.252873000
C	2.763879000	6.511645000	-0.046179000
H	3.107522000	6.921093000	-1.004509000
H	2.309391000	7.320524000	0.539610000
H	3.605267000	6.078892000	0.500909000
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O	-1.609480000	-0.258371000	2.551748000
O	-0.866256000	-2.655946000	2.930532000
C	0.083828000	-3.694988000	3.157775000
H	0.712909000	-3.859265000	2.269173000
H	0.727145000	-3.468710000	4.019694000
H	-0.481480000	-4.609527000	3.362445000
O	0.483785000	-0.777752000	4.095289000
C	-0.140533000	-0.537910000	5.358466000
H	0.657778000	-0.309220000	6.070049000
H	-0.831977000	0.313079000	5.296310000
H	-0.688143000	-1.426811000	5.701966000
C	1.409626000	0.806134000	1.045226000
C	1.239577000	1.673213000	2.141467000
C	2.605824000	0.849627000	0.302568000
C	2.246199000	2.575863000	2.474654000
C	3.604990000	1.758553000	0.643857000
C	3.427866000	2.619150000	1.729478000
H	0.311255000	1.650353000	2.719269000
H	2.747575000	0.201187000	-0.566304000
H	2.105993000	3.253168000	3.320172000
H	4.522404000	1.795875000	0.051356000
H	4.212894000	3.330848000	1.994190000

TS^{S} (E): E = -2854.920299; G = -2855.023117 (i = -345 cm-1)

C	0.916731000	1.537084000	-2.019631000
C	1.730171000	2.330591000	-2.847739000
C	3.053649000	1.983140000	-3.039532000
C	3.563773000	0.848098000	-2.395352000
C	2.693358000	0.089455000	-1.609626000
N	1.410295000	0.407306000	-1.441123000
H	3.715809000	2.583177000	-3.666232000
H	1.306951000	3.223015000	-3.310556000
H	3.054728000	-0.806459000	-1.101483000
C	-0.439573000	1.909571000	-1.738687000
H	-0.834925000	2.811908000	-2.213141000
N	-1.163358000	1.176096000	-0.926420000
Pd	0.074358000	-0.524659000	-0.075972000
C	-0.387070000	-2.576877000	1.327807000

H	0.017260000	-1.385219000	3.377686000
N	-0.986494000	-1.392059000	1.573537000
H	0.043947000	-3.138117000	2.175019000
C	-3.296361000	0.586705000	0.044421000
C	-3.065906000	2.720276000	-1.148769000
C	-4.389139000	1.552443000	0.498487000
H	-2.757496000	0.144510000	0.892246000
C	-4.514775000	2.498242000	-0.685770000
H	-3.011361000	2.723871000	-2.254151000
H	-5.327004000	1.040385000	0.747647000
H	-4.045473000	2.087113000	1.397896000
H	-5.092070000	2.022581000	-1.492942000
H	-5.012322000	3.445554000	-0.443336000
N	-2.395266000	1.514440000	-0.639659000
C	-2.447278000	4.004866000	-0.639245000
C	-1.830375000	4.078807000	0.614091000
C	-2.535982000	5.160586000	-1.424289000
C	-1.316531000	5.292419000	1.073407000
H	-1.739210000	3.178108000	1.227030000
C	-2.028863000	6.373187000	-0.960791000
H	-3.008290000	5.108667000	-2.410328000
C	-1.416110000	6.442465000	0.291043000
H	-0.830014000	5.337855000	2.051791000
H	-2.105439000	7.266876000	-1.584419000
H	-1.012623000	7.390785000	0.653067000
C	-3.808807000	-0.513553000	-0.858971000
C	-4.448248000	-1.609022000	-0.269312000
C	-3.709221000	-0.462639000	-2.254056000
C	-4.986664000	-2.625709000	-1.052088000
H	-4.507453000	-1.670961000	0.821971000
C	-4.248487000	-1.481002000	-3.040303000
H	-3.201283000	0.374743000	-2.741424000
C	-4.891541000	-2.563474000	-2.442084000
H	-5.468175000	-3.481013000	-0.571673000
H	-4.162695000	-1.427275000	-4.128076000
H	-5.310687000	-3.362124000	-3.058552000
N	-0.608029000	-0.855443000	2.768213000
C	-0.688777000	0.506739000	2.964494000
O	-1.255345000	1.270227000	2.219170000
O	-0.002468000	0.833434000	4.064098000
C	0.568624000	2.171324000	4.036836000
H	0.835808000	2.374117000	5.079133000
H	-0.201218000	2.885522000	3.715617000
C	1.759957000	2.157684000	3.127223000
C	2.978422000	1.636916000	3.586580000
C	1.654688000	2.558651000	1.788084000
C	4.065721000	1.508853000	2.725832000
C	2.748359000	2.437837000	0.929481000
C	3.949808000	1.901524000	1.391074000
H	3.068207000	1.324441000	4.631080000
H	0.711281000	2.969173000	1.415232000
H	5.009010000	1.101187000	3.097007000
H	2.660917000	2.772480000	-0.107848000
H	4.799732000	1.795530000	0.711539000
C	4.993624000	0.500405000	-2.554777000
O	5.758455000	1.097946000	-3.278903000

O	5.344778000	-0.543488000	-1.793577000
C	6.707878000	-0.947842000	-1.883862000
H	6.954226000	-1.258603000	-2.907105000
H	7.376897000	-0.127490000	-1.594939000
H	6.826227000	-1.789254000	-1.196856000
P	-1.183480000	-3.651550000	0.089881000
O	-1.235665000	-3.163073000	-1.310917000
O	-0.298658000	-4.969821000	0.380233000
C	-0.348948000	-6.073626000	-0.524065000
H	-1.327604000	-6.571842000	-0.480693000
H	-0.155589000	-5.745350000	-1.554608000
H	0.427648000	-6.779273000	-0.213925000
O	-2.653141000	-3.967056000	0.662312000
C	-2.878388000	-4.434817000	1.988523000
H	-2.219776000	-5.279291000	2.236458000
H	-2.731502000	-3.626958000	2.720974000
H	-3.920177000	-4.767741000	2.038748000
C	1.404765000	-1.976163000	0.533611000
C	2.274141000	-1.498452000	1.536256000
C	1.876303000	-2.934157000	-0.387897000
C	3.585292000	-1.965382000	1.606776000
C	3.183229000	-3.403336000	-0.298172000
C	4.037311000	-2.925174000	0.699414000
H	1.948023000	-0.727874000	2.241919000
H	1.220733000	-3.296555000	-1.183330000
H	4.256529000	-1.571825000	2.373604000
H	3.541066000	-4.143263000	-1.017918000
H	5.062902000	-3.295150000	0.762661000

INT2^{R} (E): E= -2854.946607; G = -2855.049866

C	0.787730000	2.818495000	-0.989389000
C	1.381837000	4.052056000	-1.316464000
C	2.713191000	4.273351000	-1.016525000
C	3.451533000	3.255758000	-0.397292000
C	2.796242000	2.059639000	-0.105300000
N	1.510497000	1.845192000	-0.374703000
H	3.201309000	5.220819000	-1.253289000
H	0.780033000	4.819199000	-1.805488000
H	3.340459000	1.242109000	0.365705000
C	-0.589513000	2.555978000	-1.299147000
H	-1.167245000	3.365030000	-1.754556000
N	-1.121977000	1.383387000	-1.048695000
Pd	0.452157000	0.026198000	0.063635000
C	-0.506496000	-1.894195000	1.807924000
H	-0.558576000	-2.502002000	-1.436150000
N	-0.645572000	-1.660226000	0.364503000
H	-0.289215000	-2.942882000	2.069240000
C	-3.028696000	-0.127568000	-1.052196000
C	-3.304379000	2.174537000	-1.864470000
C	-4.508307000	0.248491000	-1.120768000
H	-2.754134000	-0.442340000	-0.036936000
C	-4.541172000	1.330492000	-2.184349000
H	-2.872756000	2.602812000	-2.786698000
H	-5.148165000	-0.611961000	-1.352213000

H	-4.830546000	0.645164000	-0.145563000
H	-4.437336000	0.887917000	-3.186974000
H	-5.457724000	1.933196000	-2.179719000
N	-2.385277000	1.160395000	-1.327453000
C	-3.579359000	3.291101000	-0.877210000
C	-3.467012000	3.097905000	0.504633000
C	-4.005580000	4.534271000	-1.359333000
C	-3.782867000	4.132861000	1.385565000
H	-3.124578000	2.136274000	0.900824000
C	-4.324729000	5.564907000	-0.478116000
H	-4.089017000	4.693716000	-2.438852000
C	-4.213575000	5.366432000	0.898849000
H	-3.690013000	3.971559000	2.462105000
H	-4.657941000	6.529423000	-0.868309000
H	-4.458878000	6.174800000	1.591347000
C	-2.631395000	-1.221960000	-2.015113000
C	-3.178020000	-2.499260000	-1.821572000
C	-1.721626000	-1.032125000	-3.061349000
C	-2.817208000	-3.562471000	-2.644547000
H	-3.879126000	-2.659053000	-0.997694000
C	-1.356778000	-2.100979000	-3.886987000
H	-1.285132000	-0.045431000	-3.238119000
C	-1.899524000	-3.367865000	-3.680079000
H	-3.246952000	-4.552250000	-2.472919000
H	-0.640324000	-1.937933000	-4.695673000
H	-1.607141000	-4.202576000	-4.320604000
N	-0.248720000	-2.650457000	-0.475254000
C	0.731597000	-3.609601000	-0.318013000
O	1.291823000	-3.900741000	0.713947000
O	0.991080000	-4.152681000	-1.523909000
C	2.384940000	-4.469633000	-1.705631000
H	2.438351000	-4.886121000	-2.719724000
H	2.694860000	-5.251775000	-0.998588000
C	3.214263000	-3.224050000	-1.547041000
C	2.739141000	-2.000883000	-2.042751000
C	4.435916000	-3.247851000	-0.866668000
C	3.472373000	-0.829319000	-1.864484000
C	5.174230000	-2.076431000	-0.695239000
C	4.693577000	-0.862824000	-1.189075000
H	1.783191000	-1.967911000	-2.574449000
H	4.807675000	-4.191272000	-0.457708000
H	3.086507000	0.113937000	-2.261334000
H	6.125404000	-2.110126000	-0.158628000
H	5.265699000	0.057563000	-1.042912000
C	4.876346000	3.465868000	-0.059014000
O	5.490927000	4.481533000	-0.294729000
O	5.407083000	2.391979000	0.545521000
C	6.780079000	2.492618000	0.912428000
H	7.407096000	2.679416000	0.031530000
H	6.930802000	3.306867000	1.632474000
H	7.047735000	1.535475000	1.368174000
P	-2.176465000	-1.467627000	2.428823000
O	-2.600124000	-0.050038000	2.264748000
O	-3.186849000	-2.448912000	1.637047000
C	-3.036770000	-3.866202000	1.675245000
H	-2.256377000	-4.197263000	0.973317000

H	-2.790347000	-4.218366000	2.687089000
H	-3.992224000	-4.305353000	1.369293000
O	-2.080441000	-2.036229000	3.937217000
C	-3.145069000	-1.788820000	4.859047000
H	-2.793138000	-2.094739000	5.848661000
H	-3.407634000	-0.722703000	4.877235000
H	-4.034902000	-2.377145000	4.593827000
C	0.607188000	-0.981945000	2.296048000
C	0.469814000	-0.089011000	3.378201000
C	1.867642000	-1.064728000	1.640122000
C	1.554631000	0.655404000	3.819185000
C	2.958558000	-0.313275000	2.117844000
C	2.805363000	0.545090000	3.193008000
H	-0.491489000	0.015600000	3.883624000
H	2.062725000	-1.862471000	0.919878000
H	1.430982000	1.328355000	4.670044000
H	3.932423000	-0.429259000	1.634489000
H	3.654052000	1.128132000	3.557316000

INT2^{S} (E): E = -2854.940759; G = -2855.045728

C	-0.788169000	-1.877139000	-1.852617000
C	-1.411373000	-2.897416000	-2.594047000
C	-2.778535000	-2.857346000	-2.796166000
C	-3.516790000	-1.785976000	-2.274933000
C	-2.829698000	-0.812875000	-1.546227000
N	-1.520591000	-0.863109000	-1.322023000
H	-3.293313000	-3.636385000	-3.361826000
H	-0.804116000	-3.707026000	-3.001276000
H	-3.366337000	0.042672000	-1.135961000
C	0.635872000	-1.847442000	-1.673289000
H	1.228571000	-2.630332000	-2.155642000
N	1.194782000	-0.852358000	-1.026826000
Pd	-0.468243000	0.378650000	0.090819000
C	-0.478243000	2.606907000	1.506670000
H	0.067281000	1.309630000	3.450891000
N	0.550775000	1.568953000	1.446958000
H	-0.565818000	3.053048000	2.517384000
C	3.134144000	0.493012000	-0.509684000
C	3.439482000	-1.685993000	-1.596816000
C	4.558798000	0.000046000	-0.275618000
H	2.648948000	0.821808000	0.419128000
C	4.779620000	-0.948563000	-1.444287000
H	3.168572000	-1.781490000	-2.666240000
H	5.287977000	0.819196000	-0.240925000
H	4.606833000	-0.534527000	0.685740000
H	4.992569000	-0.377542000	-2.360459000
H	5.611402000	-1.648092000	-1.294290000
N	2.497699000	-0.748652000	-0.955682000
C	3.427051000	-3.067647000	-0.980099000
C	3.248672000	-3.246786000	0.395288000
C	3.650348000	-4.188256000	-1.788925000
C	3.288102000	-4.526239000	0.949859000
H	3.052316000	-2.379472000	1.029899000
C	3.697705000	-5.465540000	-1.232300000

H	3.784772000	-4.058616000	-2.867361000
C	3.514326000	-5.638540000	0.140085000
H	3.135694000	-4.654115000	2.025040000
H	3.871453000	-6.331089000	-1.875824000
H	3.543392000	-6.639912000	0.575680000
C	3.059595000	1.601690000	-1.538954000
C	3.498208000	2.877480000	-1.165801000
C	2.617544000	1.400680000	-2.851018000
C	3.502762000	3.925835000	-2.080063000
H	3.831652000	3.049741000	-0.138433000
C	2.620114000	2.452162000	-3.769705000
H	2.265456000	0.416185000	-3.171053000
C	3.065323000	3.716128000	-3.388634000
H	3.840057000	4.916853000	-1.766121000
H	2.272035000	2.278088000	-4.790622000
H	3.066762000	4.538553000	-4.107689000
N	0.699009000	1.027368000	2.700146000
C	1.316171000	-0.193570000	2.850859000
O	1.974830000	-0.735831000	1.995358000
O	1.012209000	-0.699846000	4.054770000
C	0.986604000	-2.151837000	4.099969000
H	0.951576000	-2.388610000	5.168513000
H	1.920845000	-2.545246000	3.676026000
C	-0.225974000	-2.642091000	3.364593000
C	-1.473170000	-2.665636000	4.004229000
C	-0.154057000	-2.998699000	2.010202000
C	-2.621800000	-3.038679000	3.308536000
C	-1.304310000	-3.371244000	1.314590000
C	-2.540231000	-3.387910000	1.958915000
H	-1.540336000	-2.391786000	5.061121000
H	0.811410000	-2.983438000	1.498352000
H	-3.586030000	-3.058462000	3.822302000
H	-1.231631000	-3.664323000	0.264357000
H	-3.440131000	-3.679370000	1.410916000
C	-4.976508000	-1.709617000	-2.503687000
O	-5.612413000	-2.533454000	-3.122096000
O	-5.512983000	-0.616572000	-1.942952000
C	-6.916751000	-0.449640000	-2.116369000
H	-7.170865000	-0.373484000	-3.181124000
H	-7.466706000	-1.294262000	-1.682221000
H	-7.182025000	0.477236000	-1.600474000
P	0.036770000	3.974966000	0.397264000
O	-0.055139000	3.725704000	-1.063322000
O	-0.929306000	5.127000000	0.997871000
C	-0.999157000	6.397100000	0.347641000
H	-0.074327000	6.968658000	0.509973000
H	-1.165080000	6.277993000	-0.731621000
H	-1.839940000	6.941295000	0.788013000
O	1.529367000	4.369557000	0.846210000
C	1.866724000	4.664570000	2.197550000
H	1.126545000	5.331322000	2.663210000
H	1.954260000	3.741261000	2.789266000
H	2.839595000	5.166880000	2.187369000
C	-1.806463000	1.937167000	1.119220000
C	-2.203070000	0.749586000	1.799561000
C	-2.757226000	2.564459000	0.271782000

C	-3.516768000	0.264412000	1.682910000
C	-4.050737000	2.080657000	0.183516000
C	-4.440632000	0.936947000	0.901509000
H	-1.554283000	0.270123000	2.533842000
H	-2.477173000	3.454573000	-0.292647000
H	-3.802461000	-0.630545000	2.238538000
H	-4.774160000	2.595940000	-0.452022000
H	-5.466853000	0.571873000	0.827443000

INT1(Z): E = -2854.950921; G = -2855.056763

C	-2.605856000	0.332592000	-1.465472000
C	-3.869861000	0.806480000	-1.857039000
C	-4.103509000	2.166990000	-1.918813000
C	-3.073399000	3.052966000	-1.579126000
C	-1.833877000	2.521723000	-1.223535000
N	-1.598188000	1.208065000	-1.179766000
H	-5.077563000	2.566189000	-2.208452000
H	-4.654010000	0.086516000	-2.094858000
H	-1.003449000	3.181352000	-0.968176000
C	-2.335363000	-1.074615000	-1.363554000
H	-3.120993000	-1.777029000	-1.656080000
N	-1.159093000	-1.466580000	-0.938298000
Pd	0.145414000	0.309427000	-0.486400000
C	3.064440000	-0.239913000	0.020849000
O	4.416417000	0.637457000	2.237668000
H	2.567444000	0.259202000	2.449676000
N	1.914855000	-0.342740000	0.602884000
H	3.051886000	-0.316570000	-1.072745000
P	4.618235000	0.194425000	0.823504000
C	0.495613000	-3.163661000	-0.443014000
C	-1.710572000	-3.828260000	-1.309937000
C	0.259891000	-4.659230000	-0.227447000
H	0.713663000	-2.647783000	0.508035000
C	-0.740588000	-5.014210000	-1.314216000
H	-2.075102000	-3.615583000	-2.331987000
H	1.185502000	-5.244568000	-0.282029000
H	-0.175844000	-4.825455000	0.769553000
H	-0.238257000	-5.074449000	-2.291748000
H	-1.256762000	-5.967609000	-1.147233000
N	-0.832496000	-2.732488000	-0.888458000
C	-2.902982000	-4.006611000	-0.392472000
C	-2.874805000	-3.595629000	0.945012000
C	-4.053869000	-4.629398000	-0.889332000
C	-3.976538000	-3.820427000	1.771937000
H	-1.992983000	-3.082395000	1.342210000
C	-5.152861000	-4.852721000	-0.062769000
H	-4.087157000	-4.942195000	-1.937381000
C	-5.115870000	-4.449773000	1.272733000
H	-3.943628000	-3.501123000	2.816383000
H	-6.044207000	-5.339842000	-0.464933000
H	-5.976814000	-4.622463000	1.922243000
C	1.603161000	-2.840447000	-1.427174000
C	2.905532000	-3.265316000	-1.125762000
C	1.398810000	-2.083752000	-2.585538000

C	3.977406000	-2.934196000	-1.951414000
H	3.082093000	-3.856506000	-0.221592000
C	2.474658000	-1.746007000	-3.412244000
H	0.395130000	-1.750824000	-2.860126000
C	3.765720000	-2.164544000	-3.097006000
H	4.985268000	-3.267428000	-1.692584000
H	2.295303000	-1.152808000	-4.311992000
H	4.604666000	-1.896304000	-3.742604000
N	1.789731000	-0.181240000	1.935053000
O	5.604862000	-1.056893000	0.607792000
O	5.195423000	1.249856000	-0.223840000
C	5.480562000	-2.190523000	1.470706000
H	6.141043000	-2.968194000	1.075762000
H	5.783194000	-1.936457000	2.494520000
H	4.447880000	-2.572041000	1.484002000
C	6.001948000	2.356318000	0.194942000
H	7.061532000	2.072013000	0.191937000
H	5.835074000	3.164695000	-0.523004000
H	5.713214000	2.692129000	1.199078000
C	0.560079000	-0.462858000	2.508329000
O	-0.267704000	-1.191098000	2.010370000
O	0.430951000	0.195563000	3.656435000
C	-0.895190000	0.124996000	4.240867000
H	-0.776311000	0.630057000	5.206535000
H	-1.152362000	-0.927460000	4.422354000
C	-1.912291000	0.795393000	3.364352000
C	-1.785690000	2.153446000	3.044579000
C	-2.972852000	0.065625000	2.817449000
C	-2.702527000	2.768799000	2.192938000
C	-3.901311000	0.681564000	1.980157000
C	-3.766689000	2.034791000	1.666663000
H	-0.961875000	2.733196000	3.471401000
H	-3.057674000	-1.000784000	3.041783000
H	-2.589614000	3.827560000	1.942321000
H	-4.725954000	0.099314000	1.559783000
H	-4.496077000	2.520551000	1.013229000
C	-3.331388000	4.510831000	-1.574668000
O	-4.380702000	5.013224000	-1.910681000
O	-2.274172000	5.205364000	-1.136772000
C	-2.430760000	6.621052000	-1.092298000
H	-2.620693000	7.022425000	-2.095785000
H	-3.266311000	6.898773000	-0.437680000
H	-1.493686000	7.021938000	-0.698235000
C	1.115135000	2.040449000	-0.398084000
C	1.149609000	2.815779000	0.763385000
C	1.810414000	2.450854000	-1.539338000
C	1.868743000	4.015822000	0.773318000
C	2.530685000	3.648454000	-1.518970000
C	2.560393000	4.431511000	-0.364531000
H	0.617356000	2.496843000	1.664915000
H	1.803186000	1.839708000	-2.448186000
H	1.889750000	4.623392000	1.682024000
H	3.075338000	3.965481000	-2.412453000
H	3.127072000	5.365552000	-0.350515000

TS^R (Z): E = -2854.930379; G = -2855.034792 (i = -367 cm-1)

C	-1.396525000	2.080768000	-1.381958000
C	-1.817982000	3.360161000	-1.783889000
C	-0.900598000	4.393011000	-1.843678000
C	0.432697000	4.149971000	-1.485888000
C	0.788438000	2.850863000	-1.119998000
N	-0.087191000	1.848487000	-1.089094000
H	-1.196096000	5.400269000	-2.144229000
H	-2.867730000	3.521374000	-2.033372000
H	1.819636000	2.616713000	-0.846372000
C	-2.308622000	0.973076000	-1.295944000
H	-3.344738000	1.125971000	-1.610590000
N	-1.861450000	-0.190498000	-0.884318000
Pd	0.306392000	-0.093304000	-0.355935000
C	1.953405000	-1.912931000	0.054560000
O	3.665114000	-1.968904000	2.229239000
H	1.773503000	-1.464600000	2.494302000
N	0.781030000	-1.860216000	0.715708000
H	1.840424000	-2.238370000	-0.989538000
P	3.499325000	-2.479389000	0.834547000
C	-2.061100000	-2.588713000	-0.601509000
C	-3.959017000	-1.294850000	-1.489342000
C	-3.331563000	-3.440776000	-0.616444000
H	-1.621482000	-2.545977000	0.406762000
C	-4.179251000	-2.796549000	-1.700493000
H	-3.938419000	-0.765355000	-2.461124000
H	-3.120093000	-4.501381000	-0.799883000
H	-3.831810000	-3.366911000	0.361395000
H	-3.810123000	-3.084486000	-2.696605000
H	-5.241159000	-3.067515000	-1.651115000
N	-2.609060000	-1.265538000	-0.920103000
C	-4.981686000	-0.623503000	-0.595721000
C	-4.758616000	-0.429304000	0.771894000
C	-6.194320000	-0.201498000	-1.154773000
C	-5.738393000	0.171704000	1.564260000
H	-3.809534000	-0.738945000	1.221224000
C	-7.170516000	0.397944000	-0.362603000
H	-6.371857000	-0.343587000	-2.225165000
C	-6.944325000	0.586816000	1.001554000
H	-5.557598000	0.316034000	2.632337000
H	-8.110732000	0.724093000	-0.813248000
H	-7.706905000	1.059930000	1.624212000
C	-0.985560000	-3.041894000	-1.567642000
C	-0.261096000	-4.200875000	-1.253756000
C	-0.654032000	-2.342988000	-2.733554000
C	0.774938000	-4.642584000	-2.071974000
H	-0.509097000	-4.754319000	-0.342312000
C	0.389831000	-2.780897000	-3.553570000
H	-1.206407000	-1.442359000	-3.015770000
C	1.111140000	-3.926208000	-3.223657000
H	1.334014000	-5.542467000	-1.802806000
H	0.636430000	-2.218922000	-4.457556000
H	1.929979000	-4.264492000	-3.862376000
N	0.855636000	-1.584457000	2.044820000
O	3.408042000	-4.080745000	0.671978000

O	4.609902000	-2.125704000	-0.247777000
C	2.522319000	-4.819709000	1.514757000
H	2.713631000	-5.880908000	1.329924000
H	2.704717000	-4.594619000	2.574169000
H	1.471722000	-4.599861000	1.269417000
C	5.900301000	-1.621780000	0.116973000
H	6.626728000	-2.443209000	0.126114000
H	6.187028000	-0.884533000	-0.639966000
H	5.872269000	-1.143468000	1.104511000
C	-0.293185000	-1.151402000	2.675426000
O	-1.401632000	-1.184288000	2.194641000
O	0.031985000	-0.639572000	3.868768000
C	-0.935213000	0.300239000	4.389474000
H	-0.544308000	0.556949000	5.381342000
H	-1.907114000	-0.196550000	4.513564000
C	-1.034572000	1.492311000	3.481897000
C	0.116227000	2.224853000	3.158464000
C	-2.251256000	1.843857000	2.889545000
C	0.048407000	3.291872000	2.264516000
C	-2.324404000	2.917733000	2.003379000
C	-1.175117000	3.644496000	1.692129000
H	1.072758000	1.954736000	3.616420000
H	-3.145438000	1.258279000	3.118543000
H	0.952883000	3.854525000	2.013554000
H	-3.281832000	3.179765000	1.544041000
H	-1.232473000	4.493397000	1.006509000
C	2.345732000	0.128211000	-0.243755000
C	3.021835000	0.258822000	-1.471207000
C	2.828163000	0.799130000	0.895048000
C	4.126960000	1.099769000	-1.568538000
C	3.938010000	1.636893000	0.787432000
C	4.580681000	1.793562000	-0.442609000
H	2.673832000	-0.296715000	-2.347589000
H	2.323332000	0.694349000	1.858983000
H	4.640298000	1.212558000	-2.526367000
H	4.295427000	2.176751000	1.667637000
H	5.445734000	2.455850000	-0.523385000
C	1.411702000	5.260072000	-1.490188000
O	1.155156000	6.390510000	-1.839803000
O	2.613420000	4.866116000	-1.049134000
C	3.627752000	5.865659000	-1.021946000
H	3.800016000	6.272286000	-2.026495000
H	3.345797000	6.687907000	-0.352270000
H	4.532687000	5.374878000	-0.654465000

TS^{S} (Z): E= -2854.910500; G = -2855.015699 (i = -298 cm-1)

C	-3.711033000	1.018364000	0.315927000
C	-5.105046000	1.147808000	0.439742000
C	-5.876214000	0.024082000	0.667014000
C	-5.251422000	-1.225281000	0.780730000
C	-3.865843000	-1.286161000	0.622400000
N	-3.120935000	-0.207799000	0.375037000
H	-6.960847000	0.089451000	0.771357000
H	-5.555809000	2.138276000	0.366989000

H	-3.346216000	-2.241763000	0.707209000
C	-2.859536000	2.166200000	0.195935000
H	-3.318837000	3.158117000	0.189329000
N	-1.557347000	1.999468000	0.211036000
Pd	-1.045221000	-0.192102000	-0.074446000
C	0.699985000	-1.417763000	-1.344074000
O	2.228819000	-3.346676000	-0.029567000
H	2.032277000	-1.496356000	0.766583000
N	1.044806000	-0.335386000	-0.640687000
H	0.157380000	-1.200342000	-2.271154000
P	1.750889000	-2.910743000	-1.375389000
C	0.699714000	2.867604000	0.407216000
C	-1.185032000	4.425372000	0.119390000
C	1.191291000	4.212845000	-0.117296000
H	1.027003000	2.040926000	-0.243378000
C	0.125237000	5.179976000	0.370022000
H	-1.923799000	4.646049000	0.910883000
H	2.200593000	4.472568000	0.217892000
H	1.219042000	4.187268000	-1.217010000
H	0.243862000	5.367611000	1.447912000
H	0.139763000	6.151216000	-0.139599000
N	-0.748430000	3.028246000	0.236286000
C	-1.805391000	4.718313000	-1.231868000
C	-1.461525000	3.988852000	-2.375650000
C	-2.708692000	5.780493000	-1.351828000
C	-2.003827000	4.322478000	-3.616554000
H	-0.771033000	3.143419000	-2.298025000
C	-3.248275000	6.116035000	-2.591858000
H	-2.988086000	6.352915000	-0.462153000
C	-2.897043000	5.386839000	-3.728702000
H	-1.728015000	3.743064000	-4.500600000
H	-3.951084000	6.948570000	-2.670103000
H	-3.322753000	5.646338000	-4.700576000
C	1.096551000	2.549584000	1.845231000
C	2.371374000	2.895737000	2.314263000
C	0.248059000	1.846522000	2.712165000
C	2.787034000	2.547250000	3.597574000
H	3.066871000	3.426126000	1.661014000
C	0.665540000	1.490583000	3.995135000
H	-0.759187000	1.564786000	2.398615000
C	1.938019000	1.836664000	4.444018000
H	3.788500000	2.828390000	3.933376000
H	-0.016484000	0.941350000	4.648380000
H	2.264116000	1.559050000	5.448856000
N	1.913835000	-0.543691000	0.400626000
O	2.918214000	-2.501306000	-2.410250000
O	0.865779000	-3.908028000	-2.241090000
C	1.165879000	-5.307911000	-2.292433000
H	0.223282000	-5.833192000	-2.475869000
H	1.868044000	-5.510687000	-3.110713000
H	1.595630000	-5.650790000	-1.342617000
C	2.987834000	0.314869000	0.549927000
O	3.227936000	1.271375000	-0.149631000
O	3.723032000	-0.121509000	1.578704000
C	5.011720000	0.513135000	1.746420000
H	5.281594000	0.289533000	2.785302000

H	4.892719000	1.599637000	1.638173000
C	6.012609000	-0.034150000	0.775434000
C	6.549113000	-1.314779000	0.965800000
C	6.394396000	0.702195000	-0.352071000
C	7.451699000	-1.847710000	0.047756000
C	7.300060000	0.171028000	-1.270032000
C	7.829028000	-1.104350000	-1.072182000
H	6.253531000	-1.896545000	1.843792000
H	5.970761000	1.697421000	-0.508953000
H	7.866430000	-2.845663000	0.207757000
H	7.593631000	0.756299000	-2.144614000
H	8.539329000	-1.520074000	-1.790721000
C	-1.036467000	-2.225817000	-0.331633000
C	-0.725623000	-2.967345000	0.817676000
C	-1.839149000	-2.787009000	-1.339008000
C	-1.264584000	-4.245036000	0.978463000
C	-2.371125000	-4.061872000	-1.168902000
C	-2.086035000	-4.789064000	-0.010187000
H	-0.079197000	-2.552599000	1.596094000
H	-2.053950000	-2.222748000	-2.250968000
H	-1.036740000	-4.816781000	1.880881000
H	-3.007808000	-4.491965000	-1.945674000
H	-2.503405000	-5.790154000	0.120387000
C	4.016018000	-1.692484000	-1.978221000
H	3.760592000	-0.624808000	-2.054380000
H	4.306077000	-1.932409000	-0.943840000
H	4.860962000	-1.902210000	-2.641900000
C	-6.069186000	-2.430728000	1.047067000
O	-7.271997000	-2.414878000	1.184964000
O	-5.322036000	-3.538788000	1.109636000
C	-6.023183000	-4.755245000	1.348073000
H	-6.566598000	-4.711506000	2.300331000
H	-6.741171000	-4.954045000	0.542213000
H	-5.267199000	-5.544027000	1.381372000

INT2^{R} (Z): E = -2854.955148; G = -2855.060461

C	-2.440640000	0.923320000	-1.363942000
C	-3.613422000	1.593855000	-1.756970000
C	-3.650182000	2.975881000	-1.735245000
C	-2.518190000	3.682357000	-1.307295000
C	-1.387070000	2.947839000	-0.945575000
N	-1.338080000	1.620010000	-0.983286000
H	-4.545351000	3.527811000	-2.028945000
H	-4.481016000	1.010415000	-2.068388000
H	-0.483880000	3.460908000	-0.613306000
C	-2.366935000	-0.510729000	-1.375359000
H	-3.236786000	-1.063199000	-1.740779000
N	-1.272360000	-1.120710000	-0.987019000
Pd	0.293191000	0.389277000	-0.255428000
C	2.870286000	-0.211791000	0.014070000
O	4.210602000	0.490961000	2.328382000
H	2.283712000	0.011783000	2.448211000
N	1.693999000	-0.836836000	0.623667000
H	3.097638000	-0.797570000	-0.892340000

P	4.411776000	-0.182162000	1.006296000
C	0.061364000	-3.136830000	-0.708345000
C	-2.202148000	-3.286488000	-1.661579000
C	-0.421391000	-4.587759000	-0.739393000
H	0.333507000	-2.825883000	0.311301000
C	-1.438307000	-4.596836000	-1.866501000
H	-2.520807000	-2.862111000	-2.631458000
H	0.400443000	-5.298867000	-0.887140000
H	-0.904137000	-4.836550000	0.218449000
H	-0.930616000	-4.578325000	-2.843078000
H	-2.107057000	-5.466308000	-1.855523000
N	-1.161178000	-2.422868000	-1.090456000
C	-3.412304000	-3.419518000	-0.758600000
C	-3.335975000	-3.187609000	0.619369000
C	-4.629715000	-3.832862000	-1.313681000
C	-4.458590000	-3.380472000	1.426149000
H	-2.397188000	-2.847111000	1.068263000
C	-5.748820000	-4.024085000	-0.506533000
H	-4.697940000	-4.009545000	-2.391507000
C	-5.665258000	-3.799856000	0.868311000
H	-4.388095000	-3.204823000	2.502228000
H	-6.691693000	-4.348115000	-0.953246000
H	-6.541310000	-3.949280000	1.503341000
C	1.240550000	-2.860280000	-1.616456000
C	2.469414000	-3.449457000	-1.286286000
C	1.180245000	-2.022458000	-2.734158000
C	3.610952000	-3.201809000	-2.042894000
H	2.529146000	-4.109074000	-0.414958000
C	2.325437000	-1.774207000	-3.497614000
H	0.234580000	-1.555533000	-3.022836000
C	3.544037000	-2.355127000	-3.152884000
H	4.560447000	-3.662105000	-1.758662000
H	2.259550000	-1.117522000	-4.368593000
H	4.438122000	-2.154126000	-3.747113000
N	1.604005000	-0.589601000	1.963014000
O	4.956461000	-1.692632000	1.022360000
O	5.473967000	0.465650000	0.001220000
C	4.360014000	-2.649365000	1.900634000
H	4.981872000	-3.548853000	1.863153000
H	4.329828000	-2.273007000	2.932181000
H	3.340298000	-2.904855000	1.574930000
C	5.929661000	1.814042000	0.155495000
H	6.999751000	1.830580000	-0.074792000
H	5.395783000	2.467920000	-0.547004000
H	5.772207000	2.169343000	1.181608000
C	0.483670000	-1.035104000	2.634248000
O	-0.360151000	-1.765478000	2.168837000
O	0.449595000	-0.474361000	3.850925000
C	-0.880873000	-0.367985000	4.400864000
H	-0.723418000	0.065877000	5.395833000
H	-1.316682000	-1.369270000	4.521570000
C	-1.734306000	0.500216000	3.520957000
C	-1.296942000	1.782418000	3.158494000
C	-2.942693000	0.024373000	3.004044000
C	-2.069847000	2.579852000	2.316035000
C	-3.720649000	0.822892000	2.165895000

C	-3.287187000	2.103503000	1.824703000
H	-0.345091000	2.157643000	3.547205000
H	-3.269715000	-0.987331000	3.258370000
H	-1.724022000	3.581357000	2.041534000
H	-4.664331000	0.437891000	1.770024000
H	-3.899867000	2.733283000	1.174540000
C	2.475584000	1.194157000	-0.424139000
C	2.702451000	1.604120000	-1.757897000
C	1.988025000	2.145486000	0.508556000
C	2.501607000	2.923625000	-2.132493000
C	1.794119000	3.478041000	0.114017000
C	2.052257000	3.865158000	-1.194332000
H	3.071066000	0.869610000	-2.479375000
H	1.879823000	1.891240000	1.563724000
H	2.702257000	3.231144000	-3.160533000
H	1.436468000	4.206534000	0.845582000
H	1.898499000	4.903867000	-1.495675000
C	-2.548414000	5.159170000	-1.232347000
O	-3.489253000	5.840077000	-1.574029000
O	-1.409243000	5.655689000	-0.728441000
C	-1.342375000	7.074560000	-0.616963000
H	-1.427130000	7.546794000	-1.603865000
H	-2.147917000	7.452930000	0.024794000
H	-0.369536000	7.303486000	-0.174087000

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C	-6.016899000	0.170303000	-0.088737000
C	-5.489100000	-1.085388000	0.238452000
C	-4.106900000	-1.191158000	0.410085000
N	-3.278307000	-0.160877000	0.271452000
H	-7.094037000	0.275118000	-0.231636000
H	-5.541275000	2.243928000	-0.460731000
H	-3.660246000	-2.149079000	0.675855000
C	-2.860040000	2.162523000	-0.075876000
H	-3.248106000	3.173364000	-0.227733000
N	-1.590303000	1.937229000	0.165935000
Pd	-1.114391000	-0.277378000	0.129703000
C	0.544163000	-1.715116000	-1.164205000
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H	2.022170000	-1.553628000	0.875787000
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H	0.179196000	-1.461465000	-2.173053000
P	1.934900000	-2.893748000	-1.410036000
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C	-1.073966000	4.338557000	0.084156000
C	1.292793000	4.010348000	0.351061000
H	1.037881000	1.864976000	0.106675000
C	0.192036000	5.027308000	0.608868000
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H	2.205695000	4.202060000	0.927238000
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H	0.088479000	5.212023000	1.688985000

H	0.360713000	5.996270000	0.122953000
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C	-0.949833000	3.864723000	-2.417203000
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C	-1.237748000	4.213531000	-3.737084000
H	-0.371159000	2.958684000	-2.210818000
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H	-0.879501000	3.581758000	-4.553046000
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H	-2.205385000	5.631740000	-5.048121000
C	0.730349000	2.311018000	2.185950000
C	1.999451000	2.246327000	2.778207000
C	-0.384971000	2.002617000	2.974470000
C	2.154665000	1.863431000	4.107954000
H	2.879339000	2.506614000	2.184902000
C	-0.231269000	1.624320000	4.310015000
H	-1.393583000	2.065324000	2.561803000
C	1.037296000	1.545496000	4.880228000
H	3.155797000	1.817392000	4.544059000
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O	1.196946000	-3.925610000	-2.388911000
C	1.853161000	-5.127861000	-2.800710000
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H	2.674853000	-4.901101000	-3.493196000
H	2.243583000	-5.678349000	-1.934793000
C	2.940321000	0.231886000	0.550170000
O	3.125118000	1.232580000	-0.104193000
O	3.748539000	-0.245354000	1.508471000
C	5.000503000	0.448630000	1.705762000
H	5.259416000	0.234587000	2.749712000
H	4.834966000	1.528825000	1.596394000
C	6.053824000	-0.040563000	0.760384000
C	6.656155000	-1.288880000	0.966881000
C	6.426570000	0.718682000	-0.354768000
C	7.612564000	-1.769060000	0.075375000
C	7.387971000	0.241166000	-1.245346000
C	7.980620000	-1.003364000	-1.032688000
H	6.369041000	-1.887396000	1.836338000
H	5.954397000	1.690229000	-0.523792000
H	8.077706000	-2.742558000	0.247013000
H	7.674634000	0.843884000	-2.110288000
H	8.733701000	-1.377571000	-1.730174000
C	-0.596632000	-2.398126000	-0.407372000
C	-0.567006000	-2.498750000	1.009637000
C	-1.553603000	-3.164055000	-1.123329000
C	-1.456842000	-3.359652000	1.673778000
C	-2.393115000	-4.034751000	-0.456806000
C	-2.339827000	-4.141214000	0.946247000
H	0.205628000	-2.002839000	1.599546000
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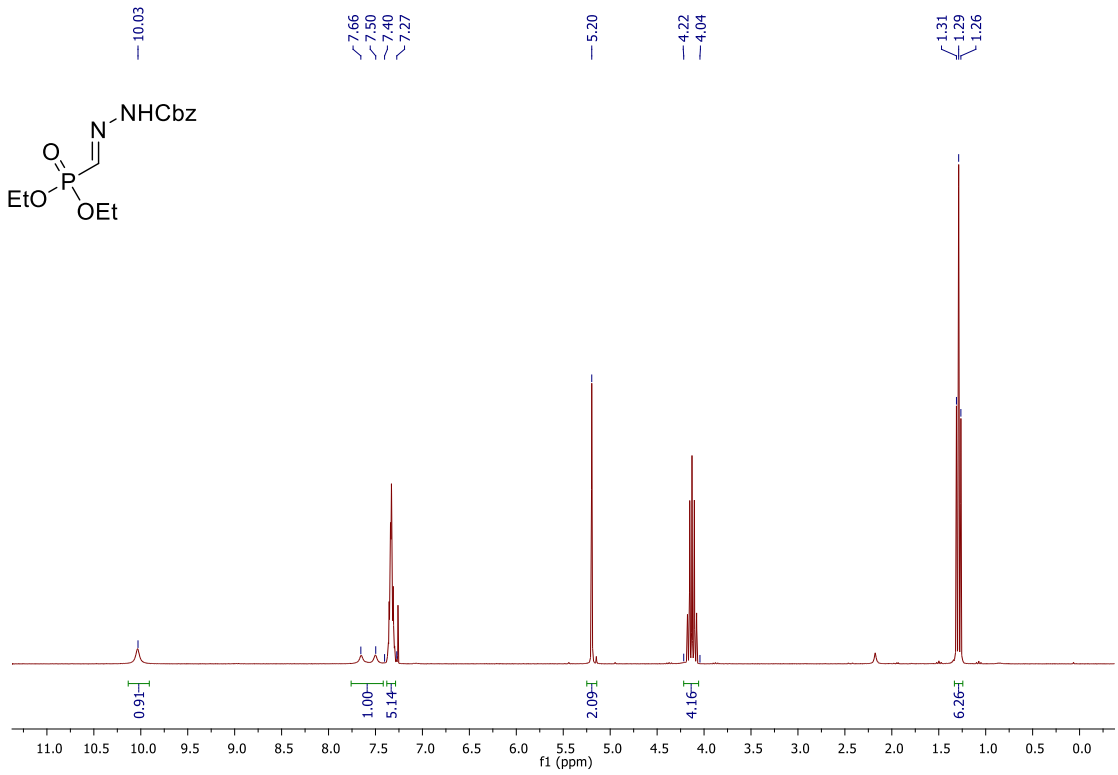
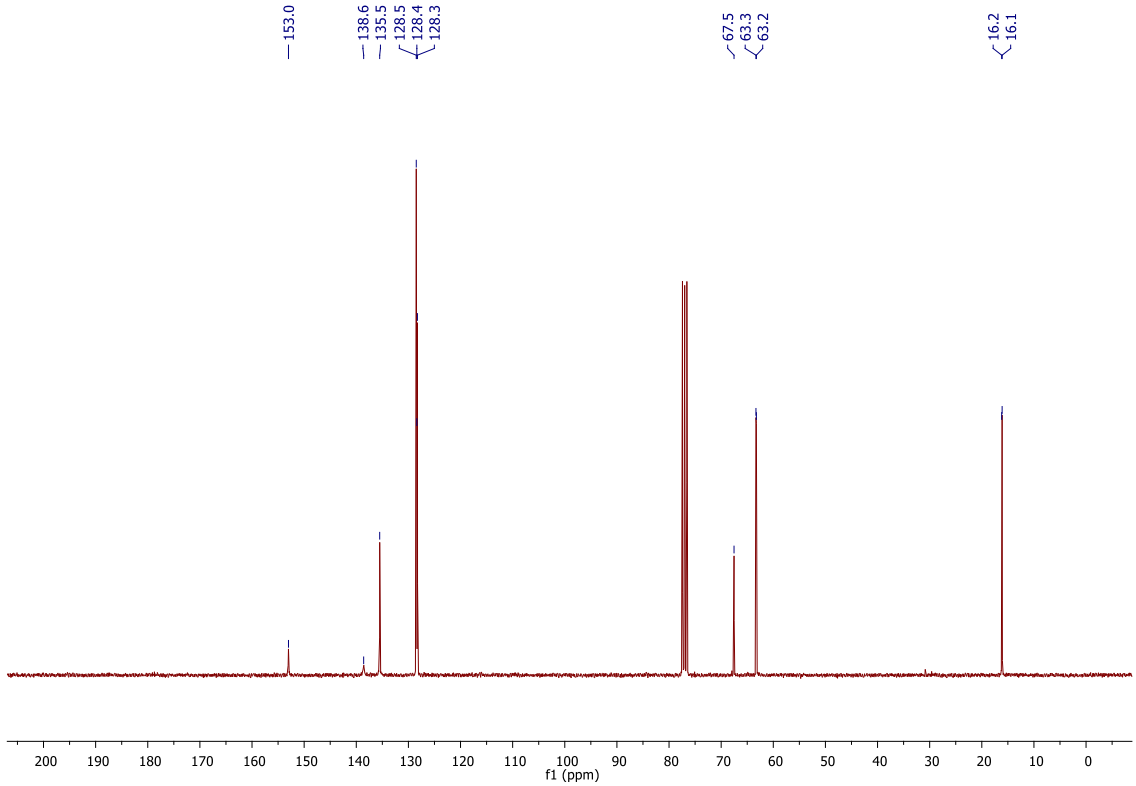
C	4.147549000	-1.509841000	-1.916555000
H	3.983923000	-0.423331000	-1.915050000
H	4.404047000	-1.848735000	-0.902041000
H	4.978023000	-1.747595000	-2.590623000
C	-6.393917000	-2.248067000	0.381400000
O	-7.596834000	-2.188702000	0.259741000
O	-5.723277000	-3.375481000	0.652964000
C	-6.514807000	-4.551285000	0.799895000
H	-7.210162000	-4.449482000	1.642611000
H	-7.092758000	-4.747550000	-0.111807000
H	-5.817160000	-5.371751000	0.986955000

14. NMR spectra of compounds

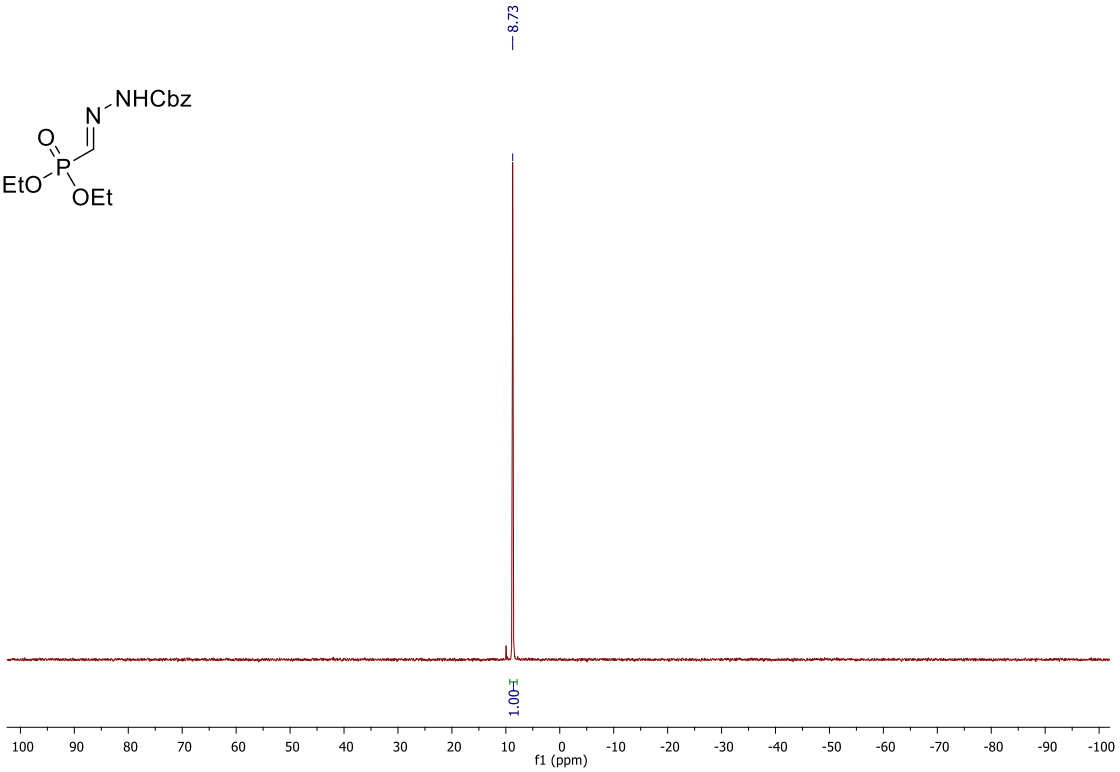
^{1}H NMR (300 MHz, $CDCl_3$) of ***(E)*-1A**



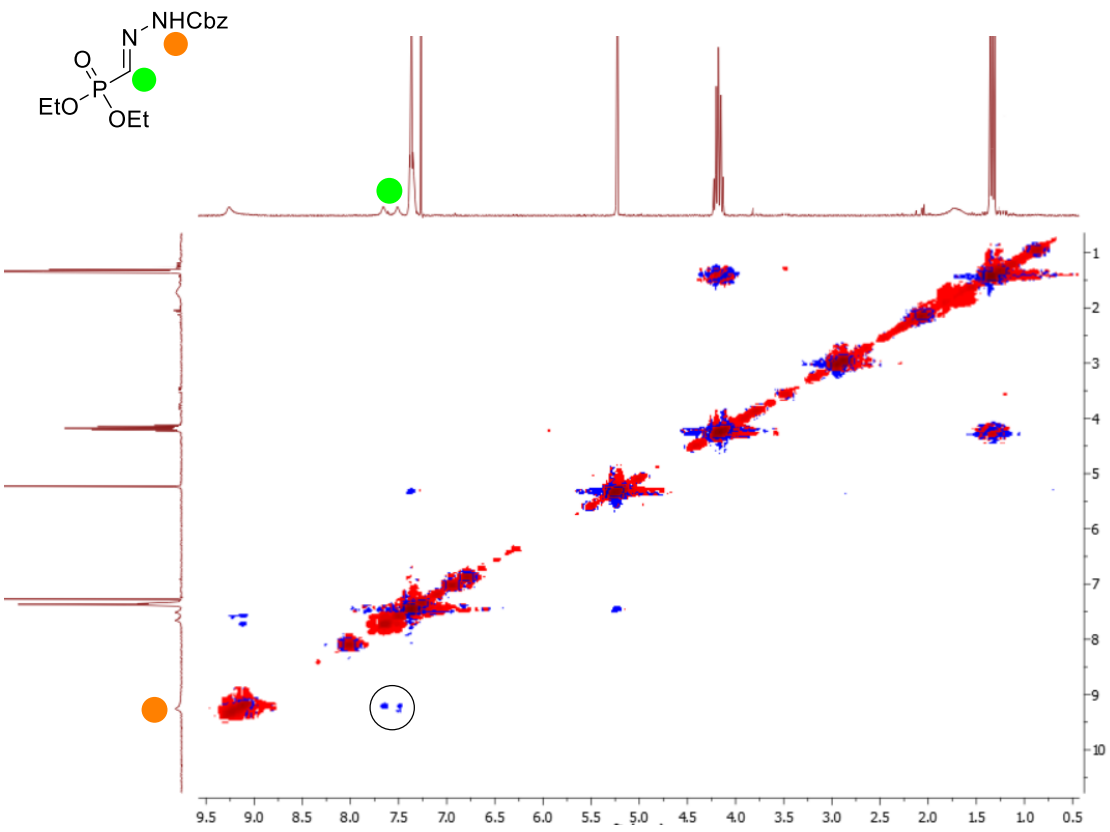
^{13}C NMR (75.5 MHz, $CDCl_3$) of **(*E*)-1A**



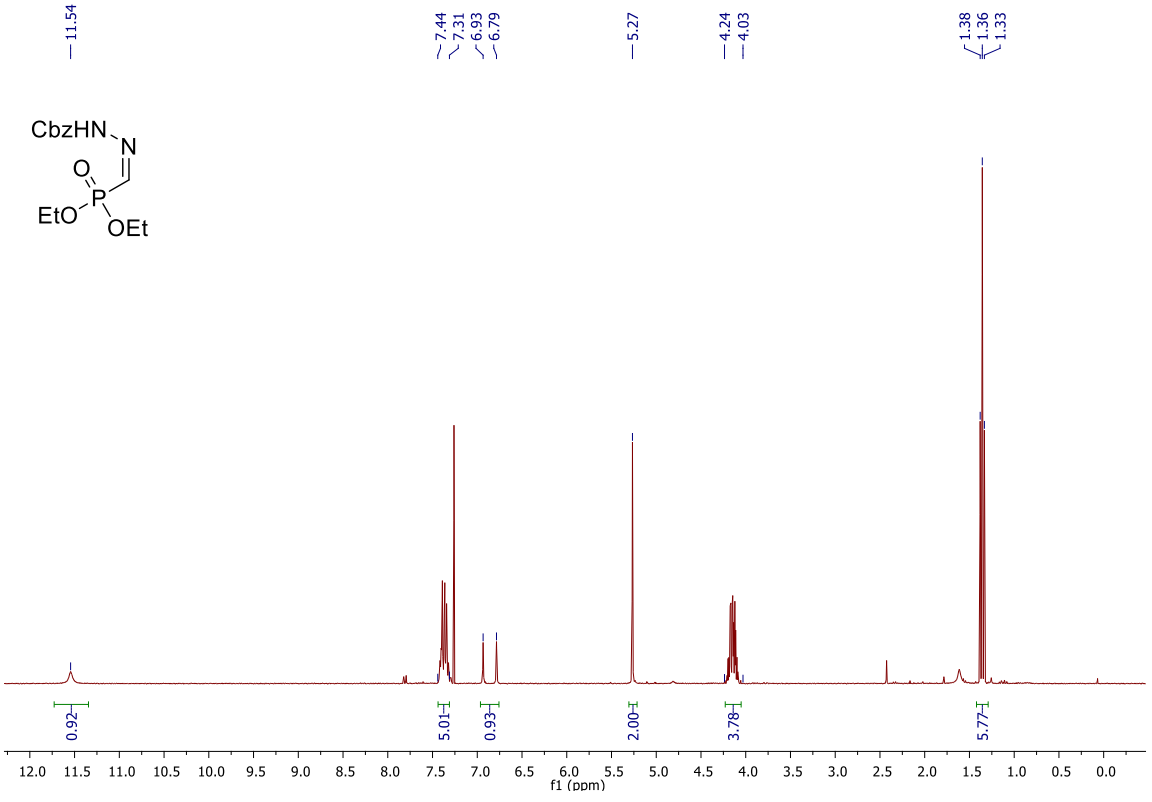
^{31}P NMR (122 MHz, $CDCl_3$) of **(*E*)-1A**



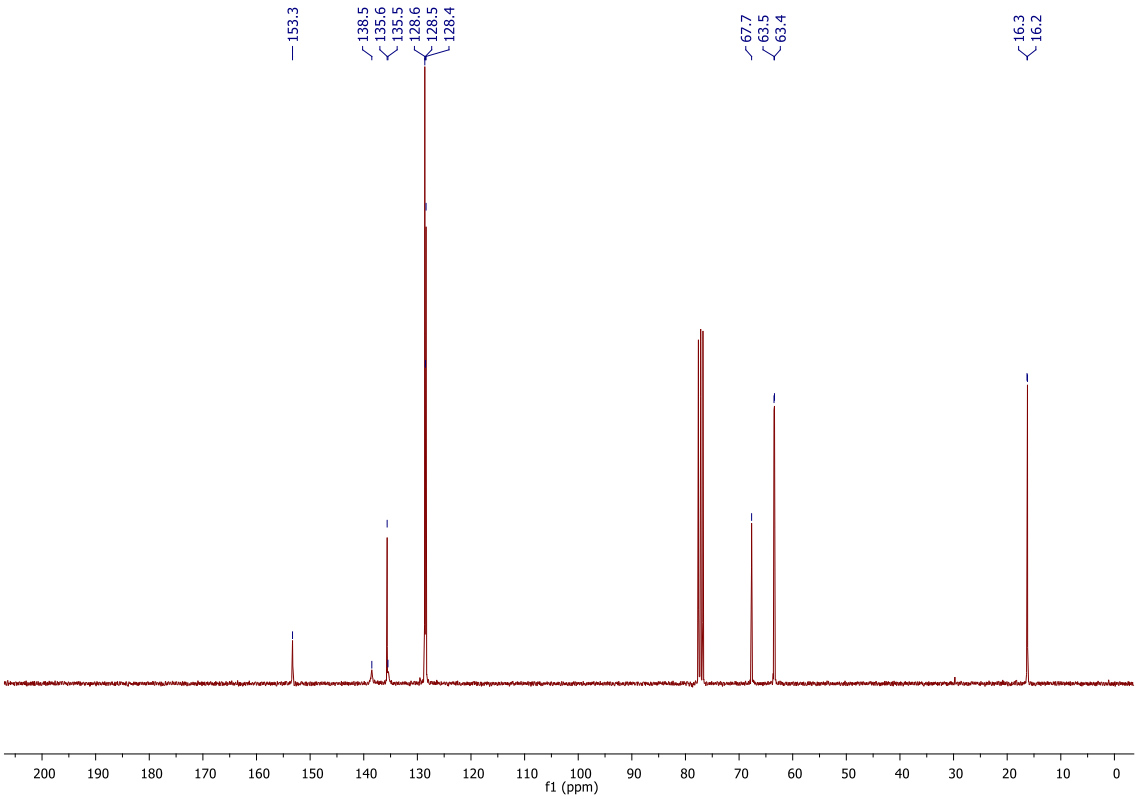
NOESY of ***(E)*-1A**



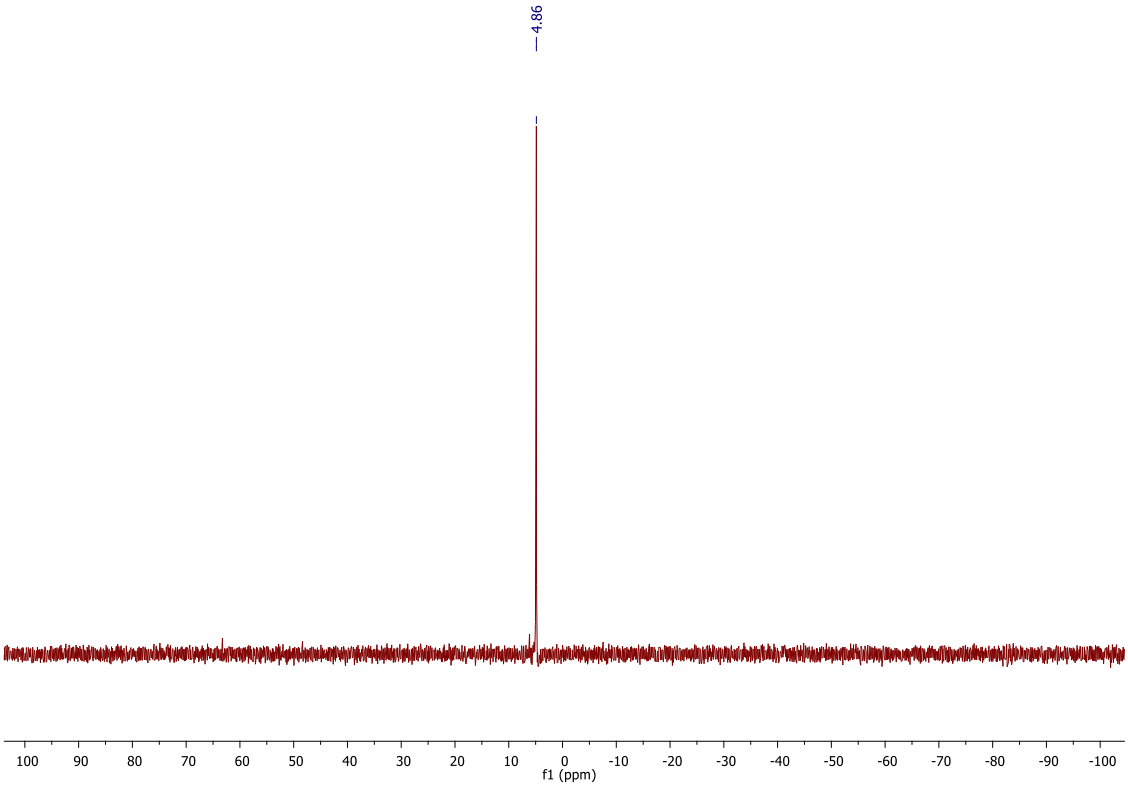
^{1}H NMR (300 MHz, $CDCl_3$) of **(*Z*)-1A**



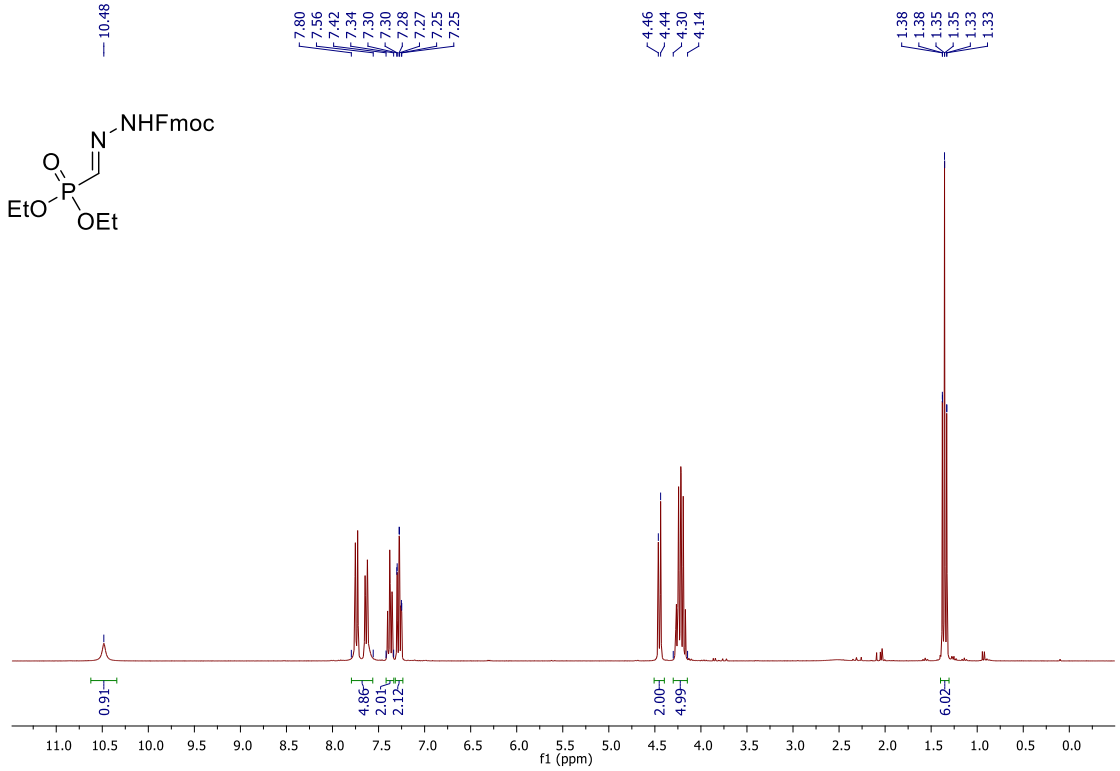
^{13}C NMR (75.5 MHz, $CDCl_3$) of **(*Z*)-1A**



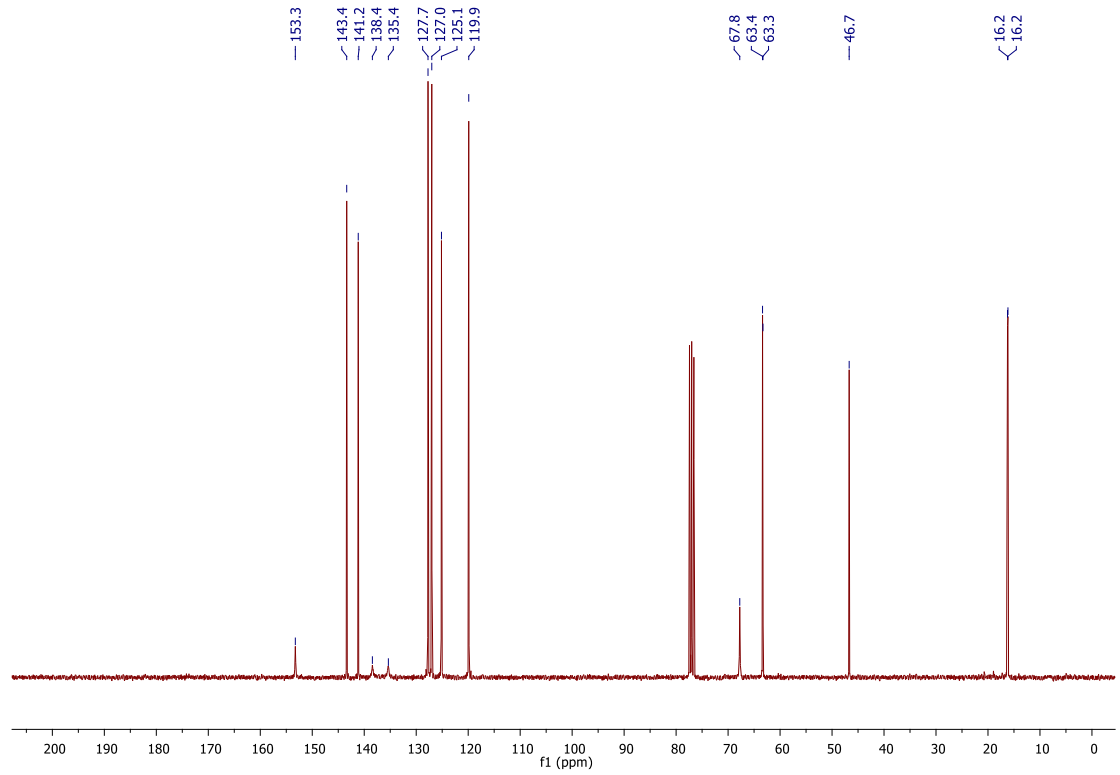
^{31}P NMR (122 MHz, $CDCl_3$) of **(*Z*)-1A**



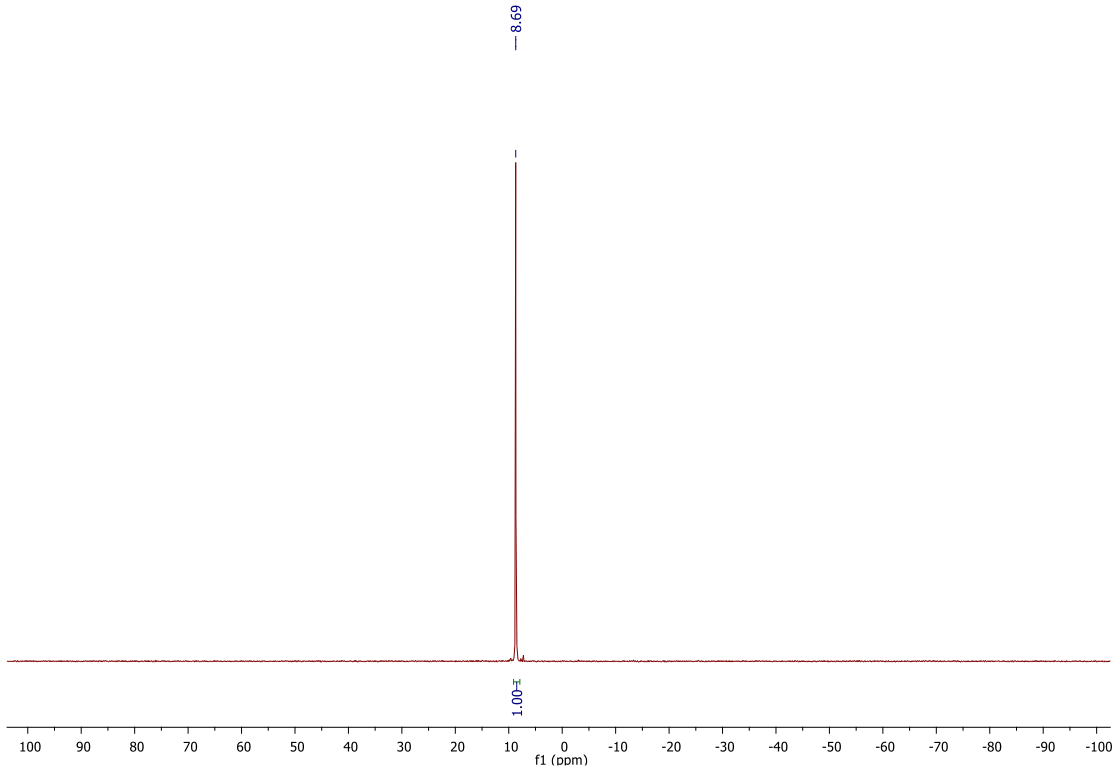
^{1}H NMR (300 MHz, $CDCl_3$) of ***(E)*-1B**



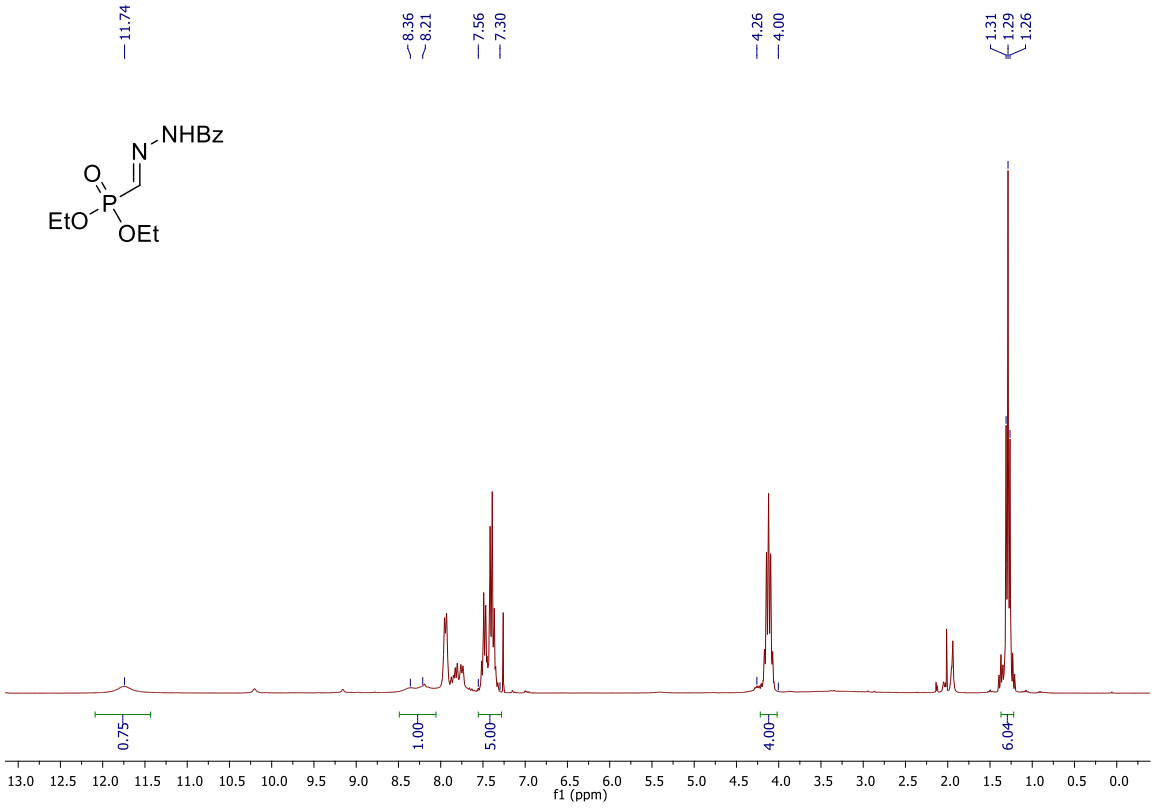
^{13}C NMR (75.5 MHz, $CDCl_3$) of ***(E)*-1B**



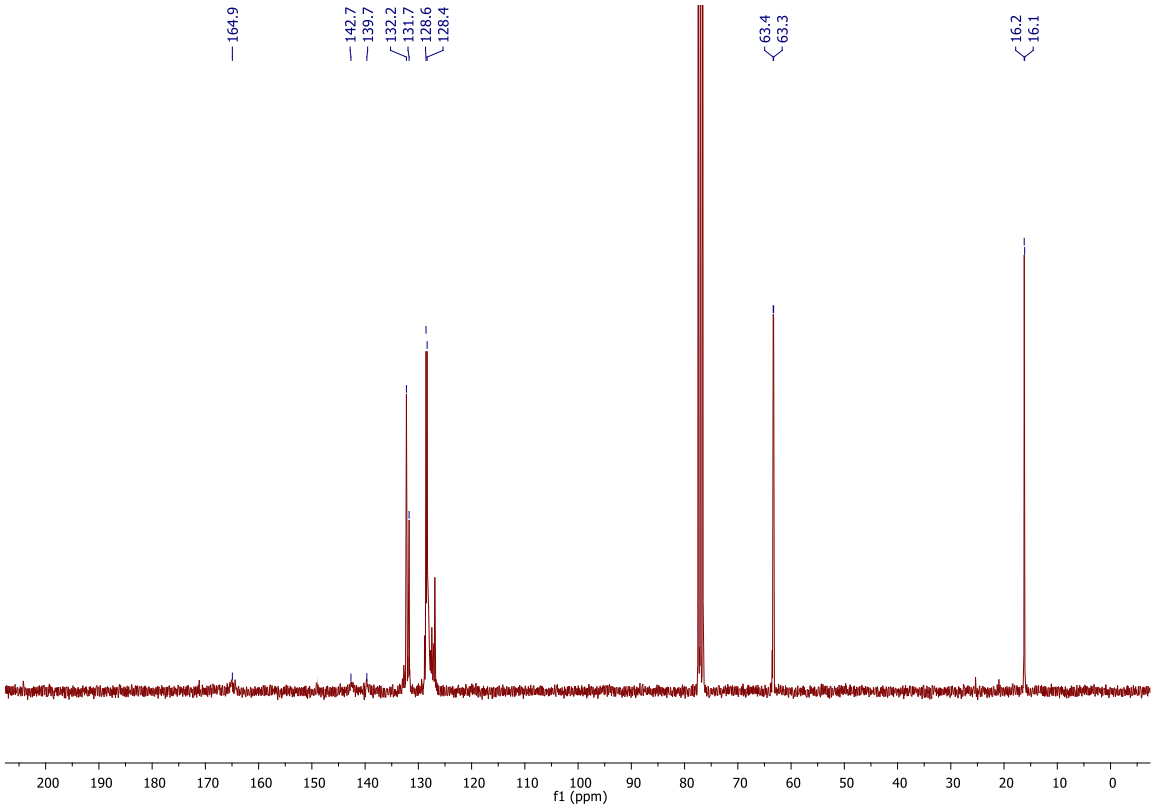
^{31}P NMR (122 MHz, $CDCl_3$) of **(*E*)-1B**



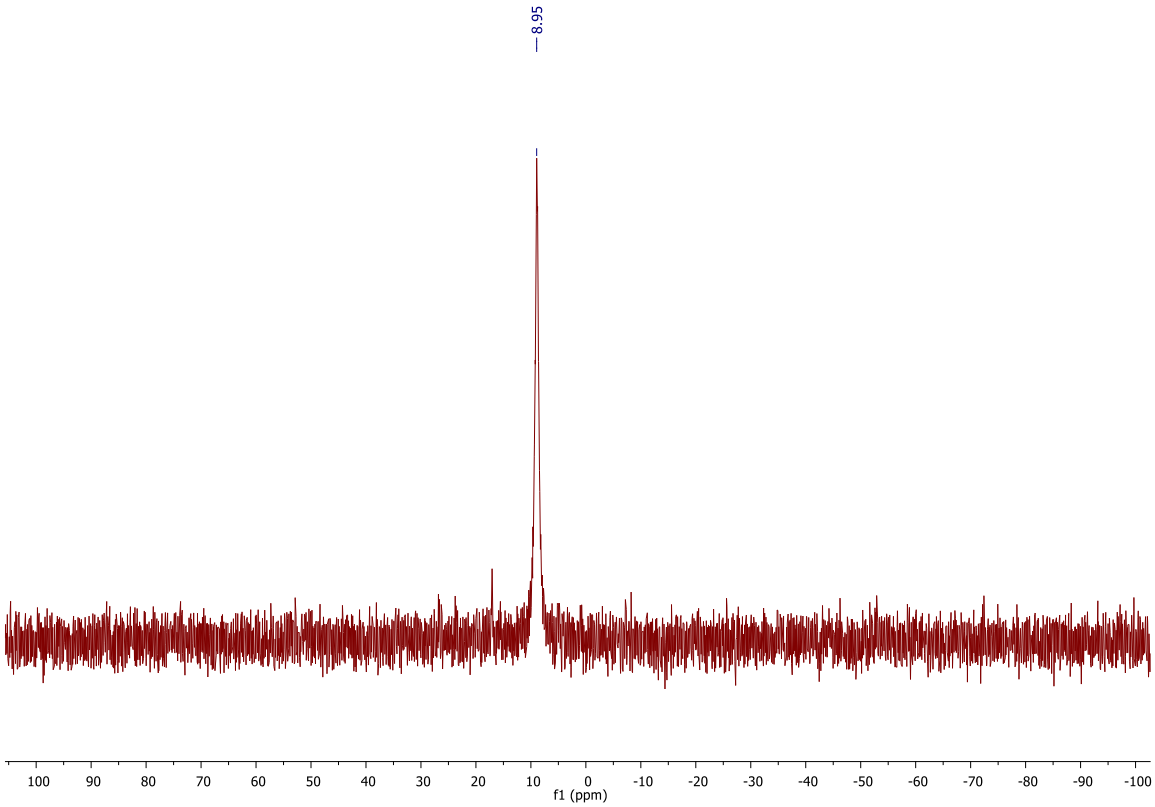
^{1}H NMR (300 MHz, $CDCl_3$) of **(*E*)-1C**



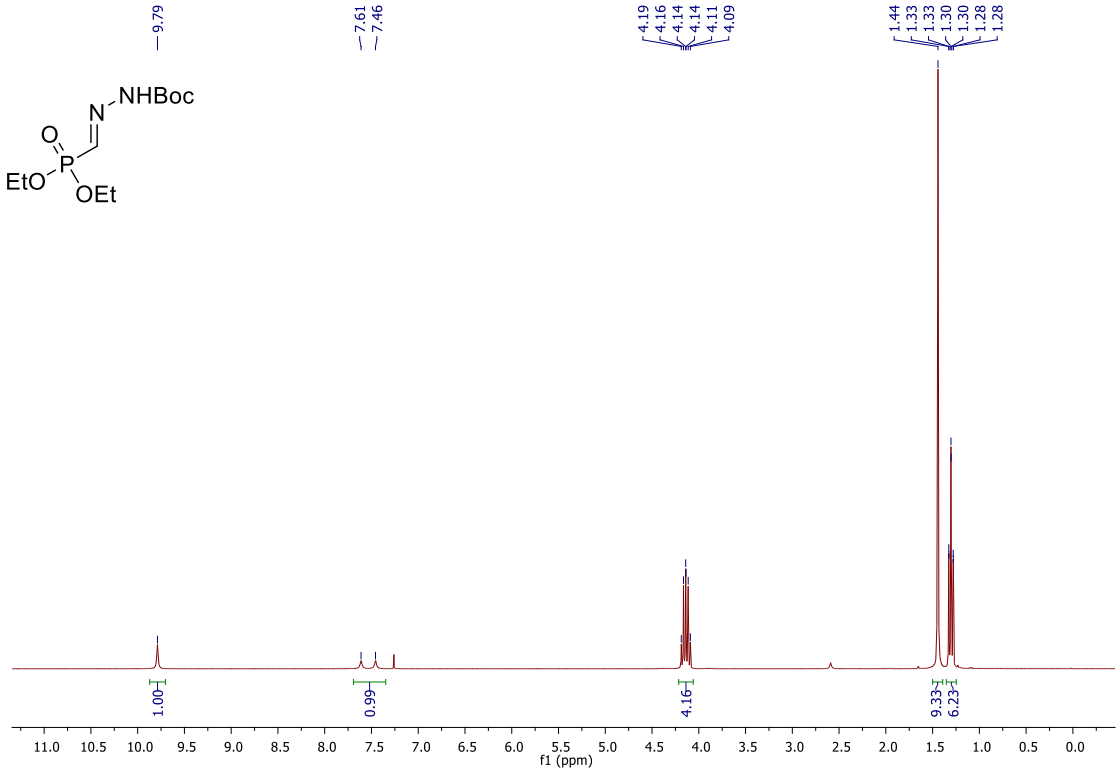
^{13}C NMR (75.5 MHz, $CDCl_3$) of **(*E*)-1C**



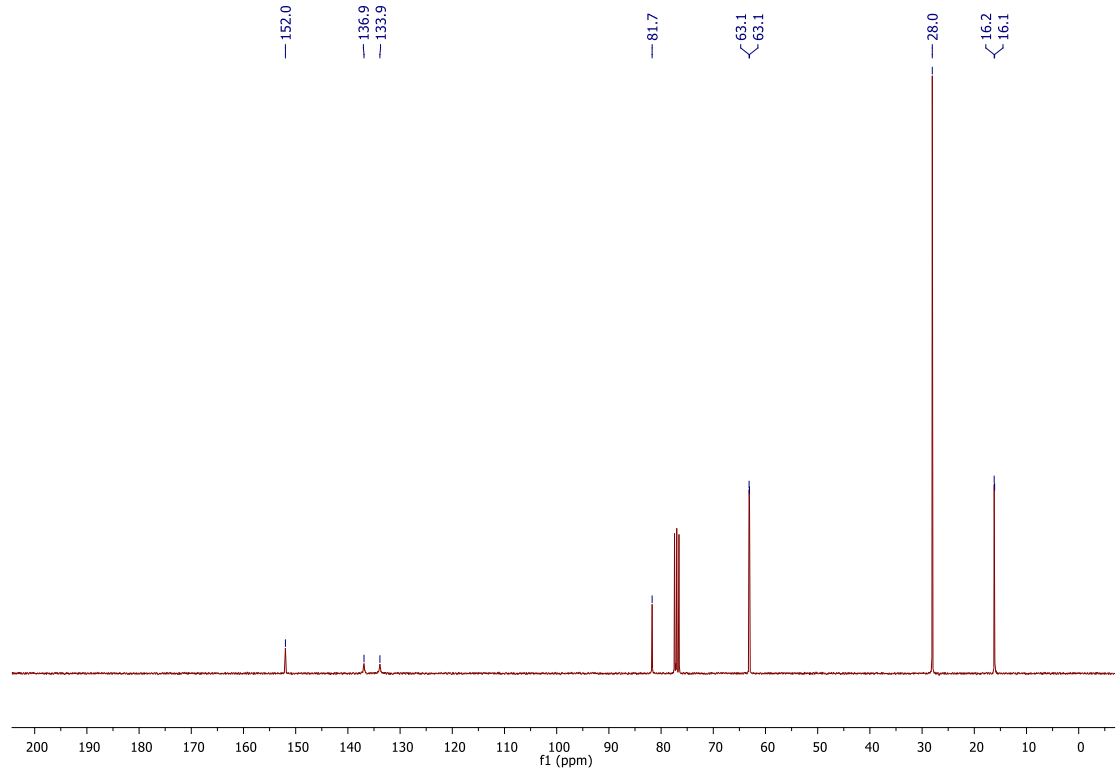
^{31}P NMR (122 MHz, $CDCl_3$) of **(*E*)-1C**



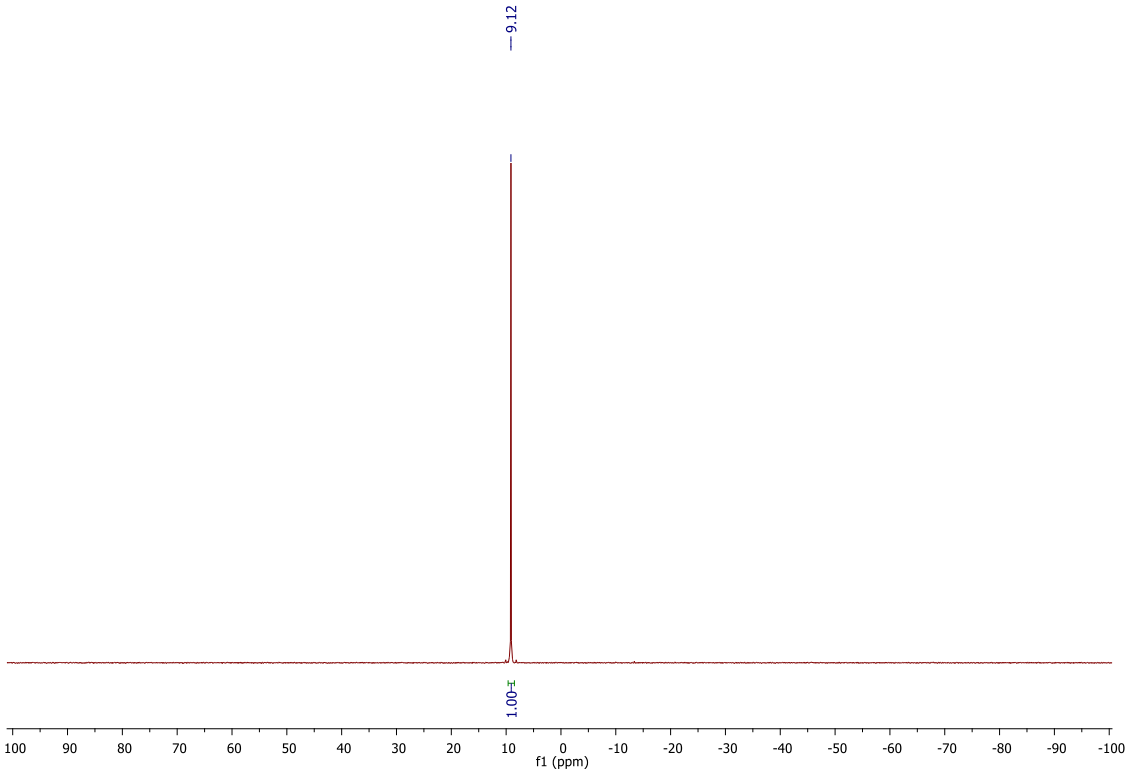
^{1}H NMR (300 MHz, $CDCl_3$) of **(*E*)-1D**



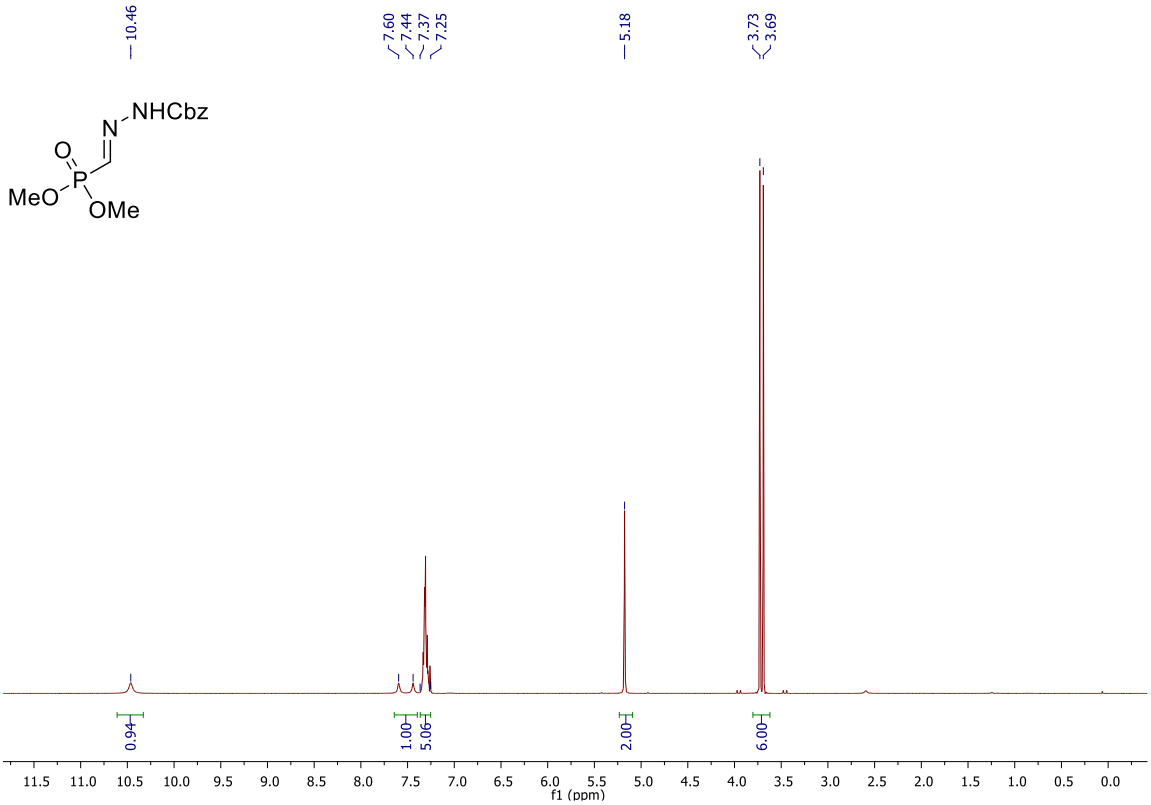
^{13}C NMR (75.5 MHz, $CDCl_3$) of **(*E*)-1D**



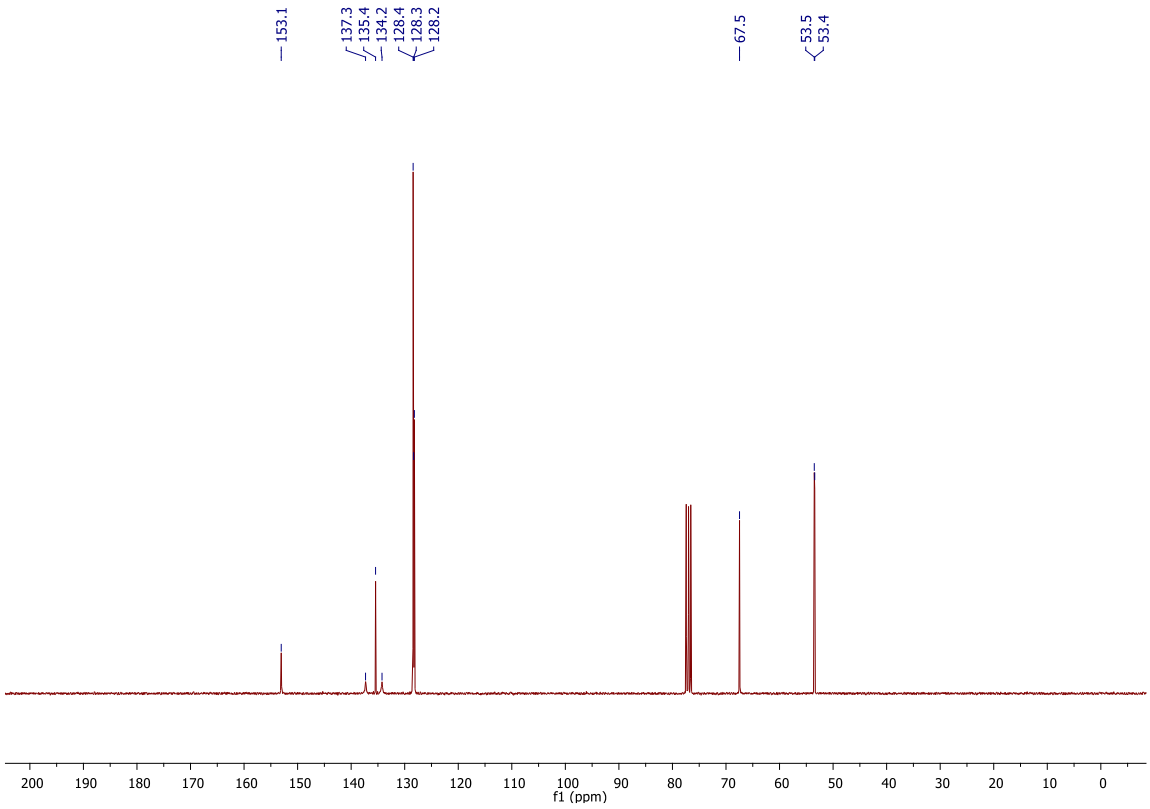
^{31}P NMR (122 MHz, $CDCl_3$) of **(*E*)-1D**



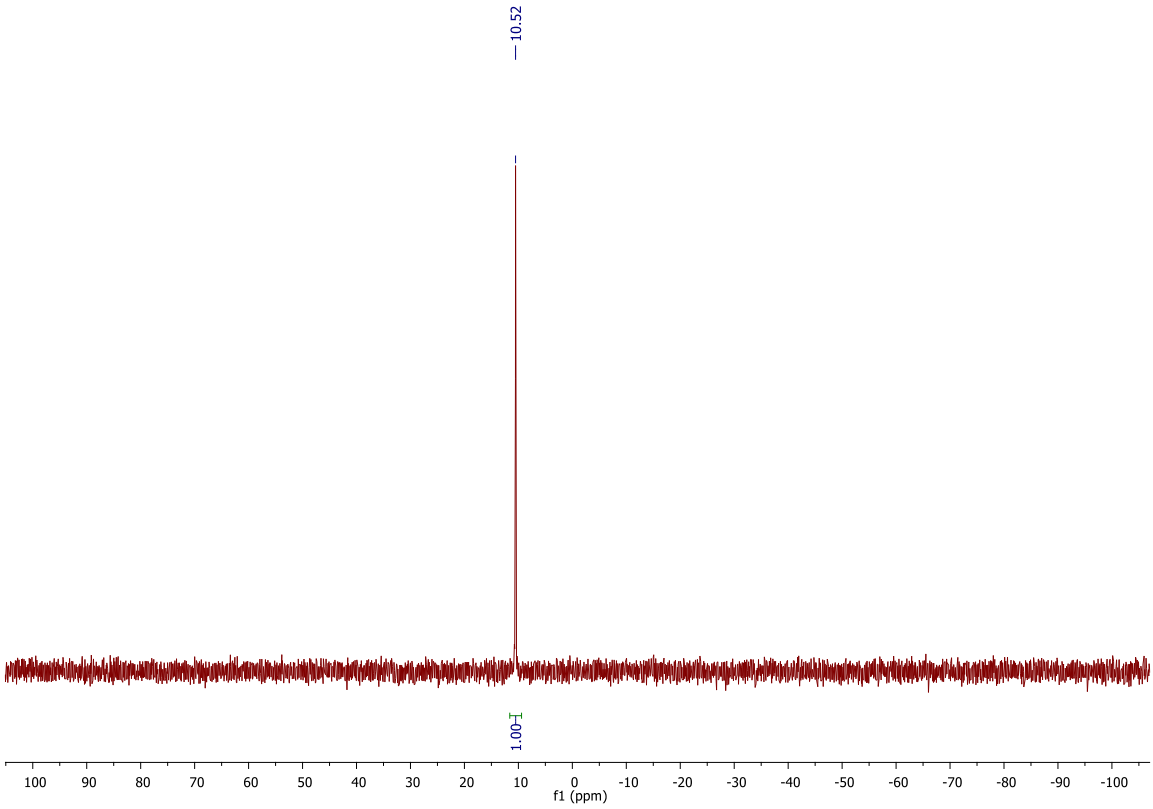
^{1}H NMR (300 MHz, $CDCl_3$) of **(*E*)-1E**



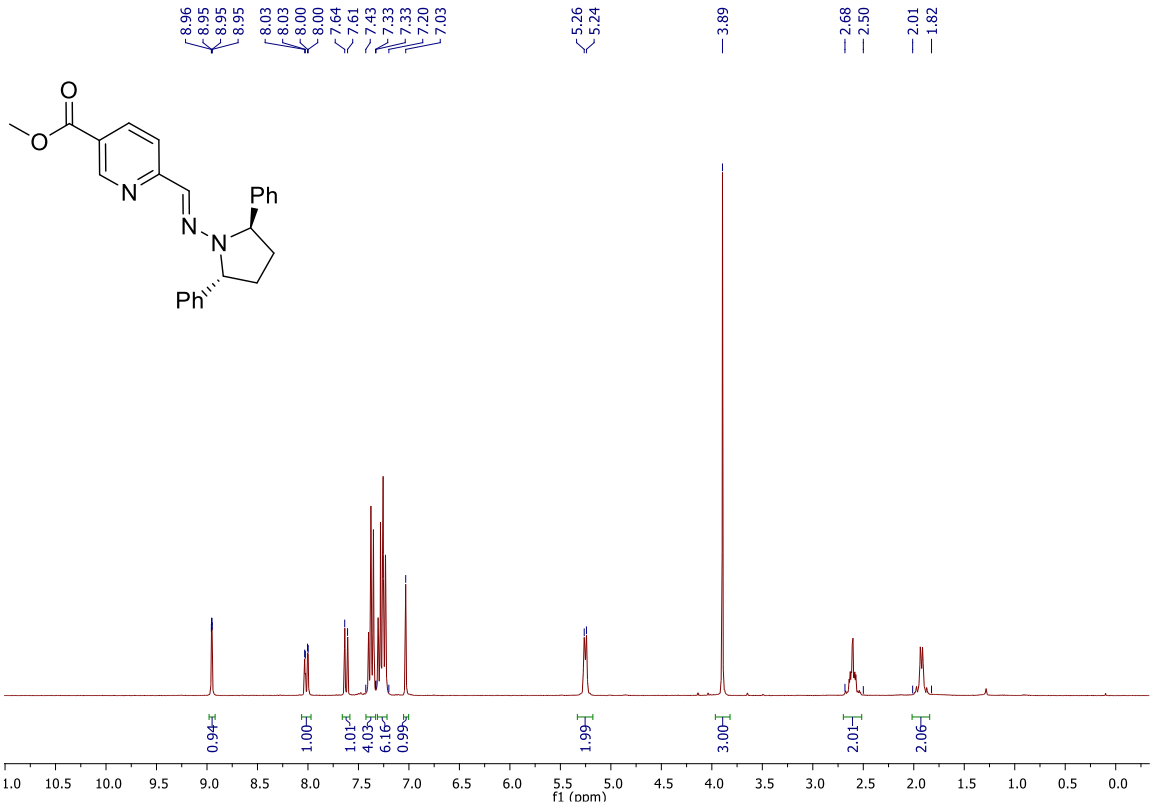
^{13}C NMR (75.5 MHz, $CDCl_3$) of **(*E*)-1E**



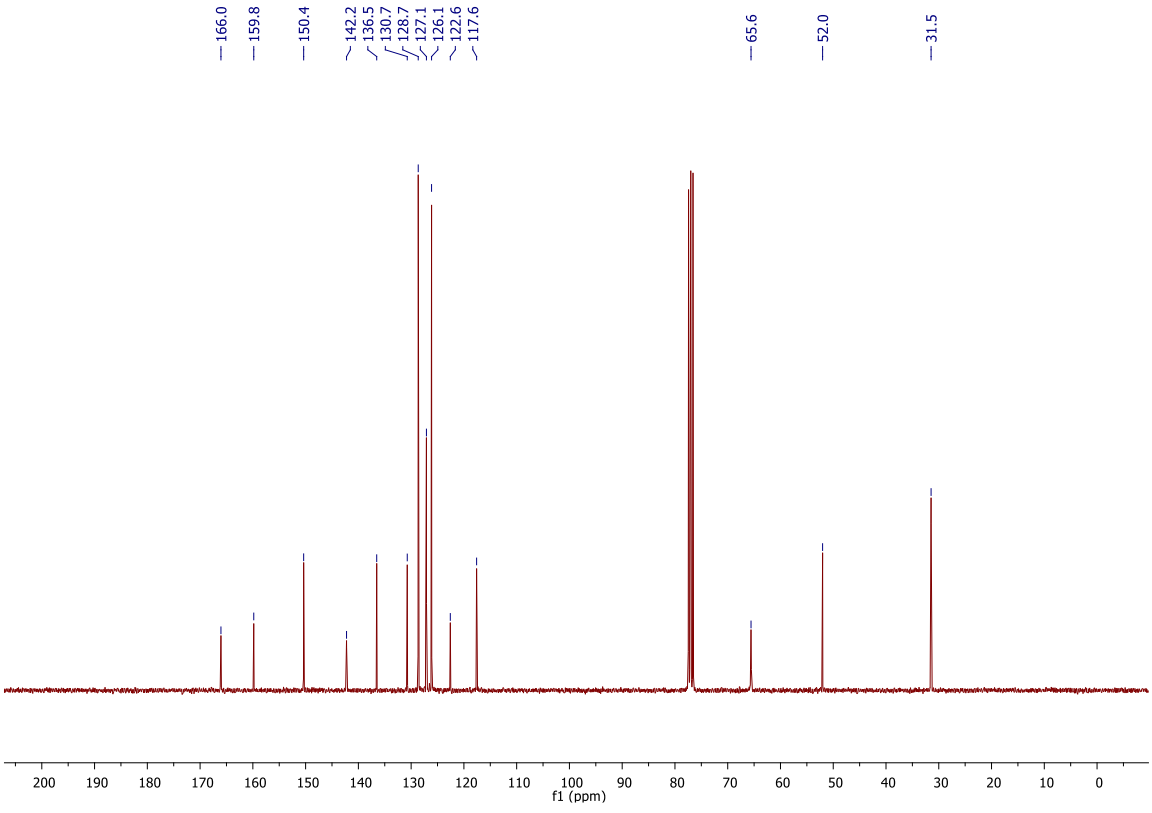
^{31}P NMR (122 MHz, $CDCl_3$) of **(*E*)-1E**



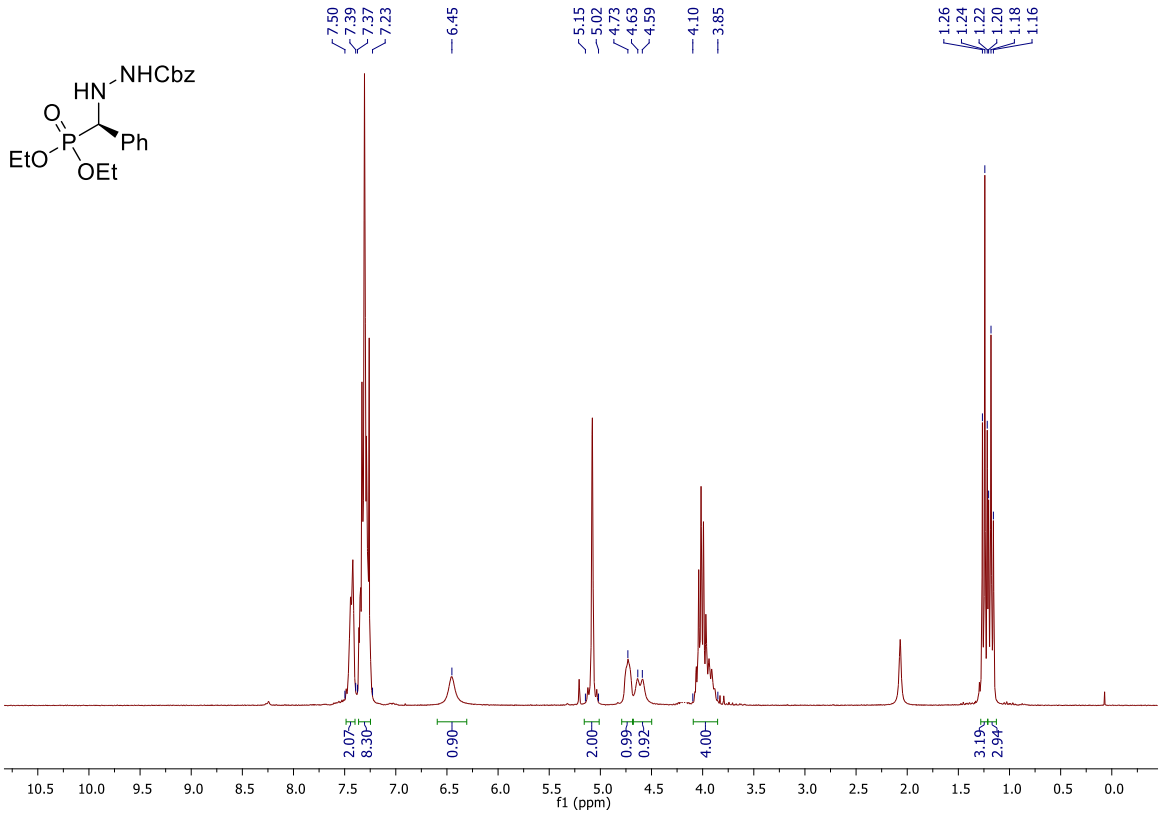
^{1}H NMR (300 MHz, $CDCl_3$) of **L5***



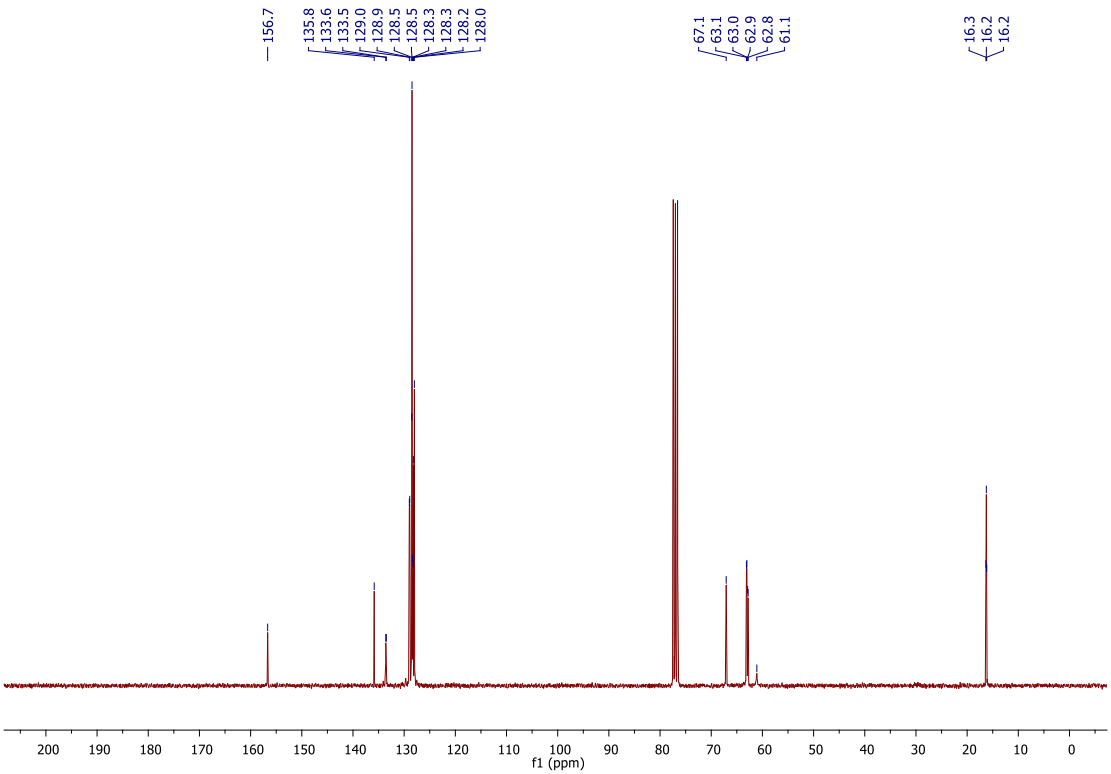
^{13}C NMR (75.5 MHz, $CDCl_3$) of **L5***



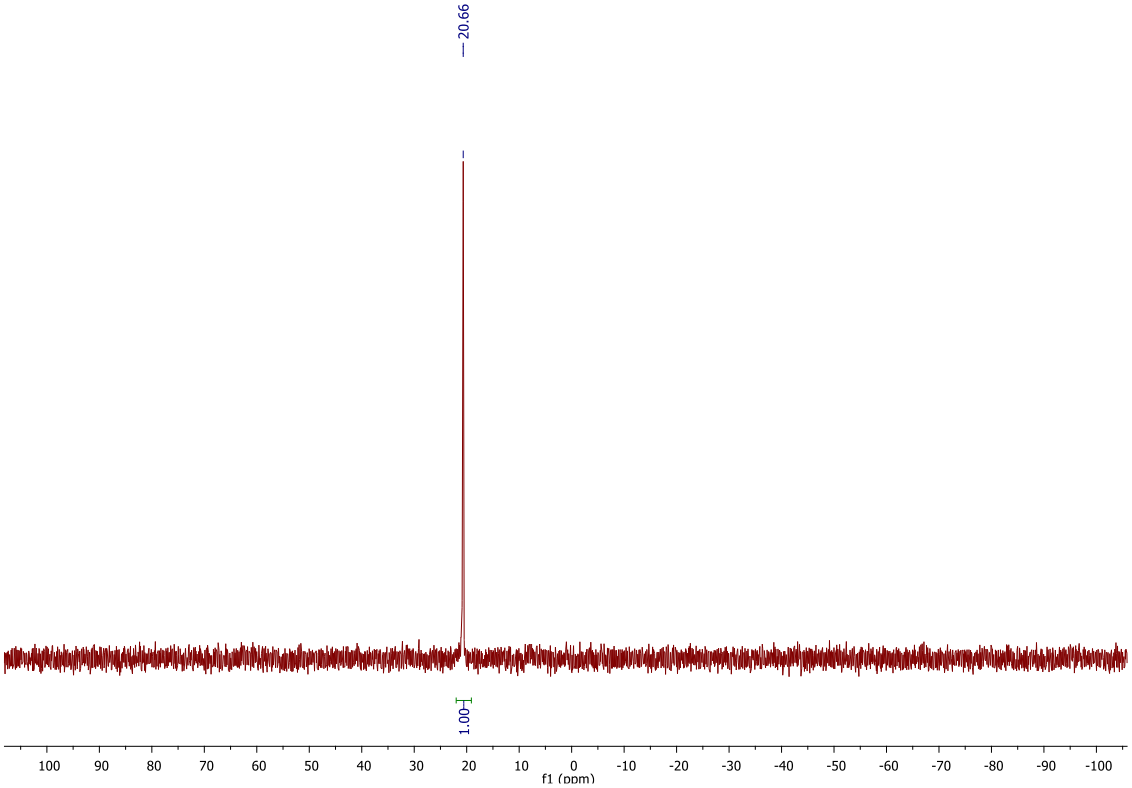
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Aa**



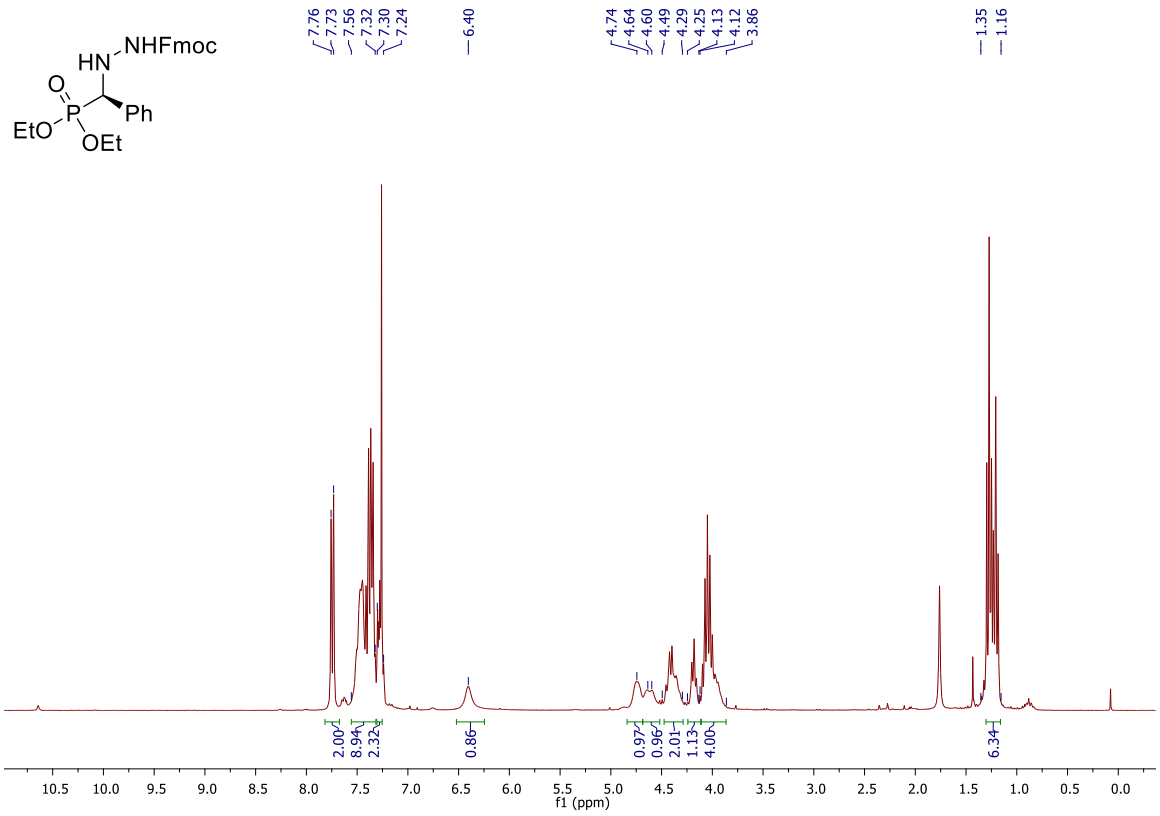
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Aa**



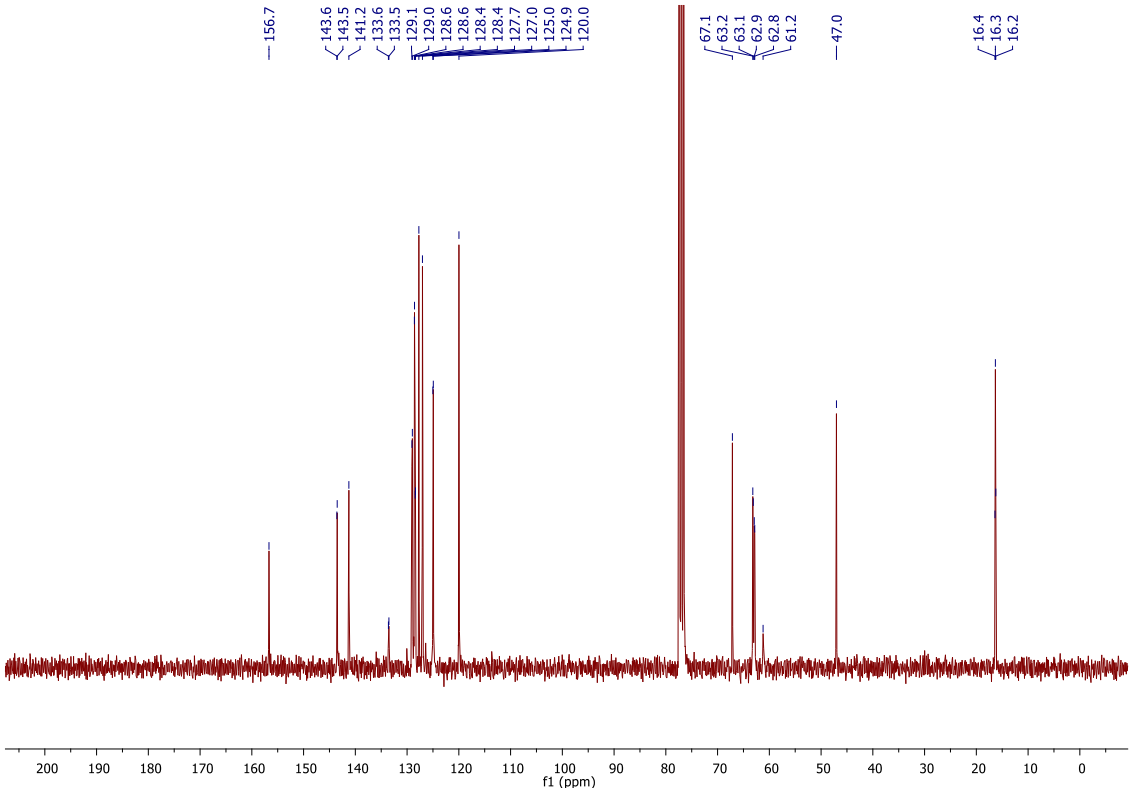
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Aa**



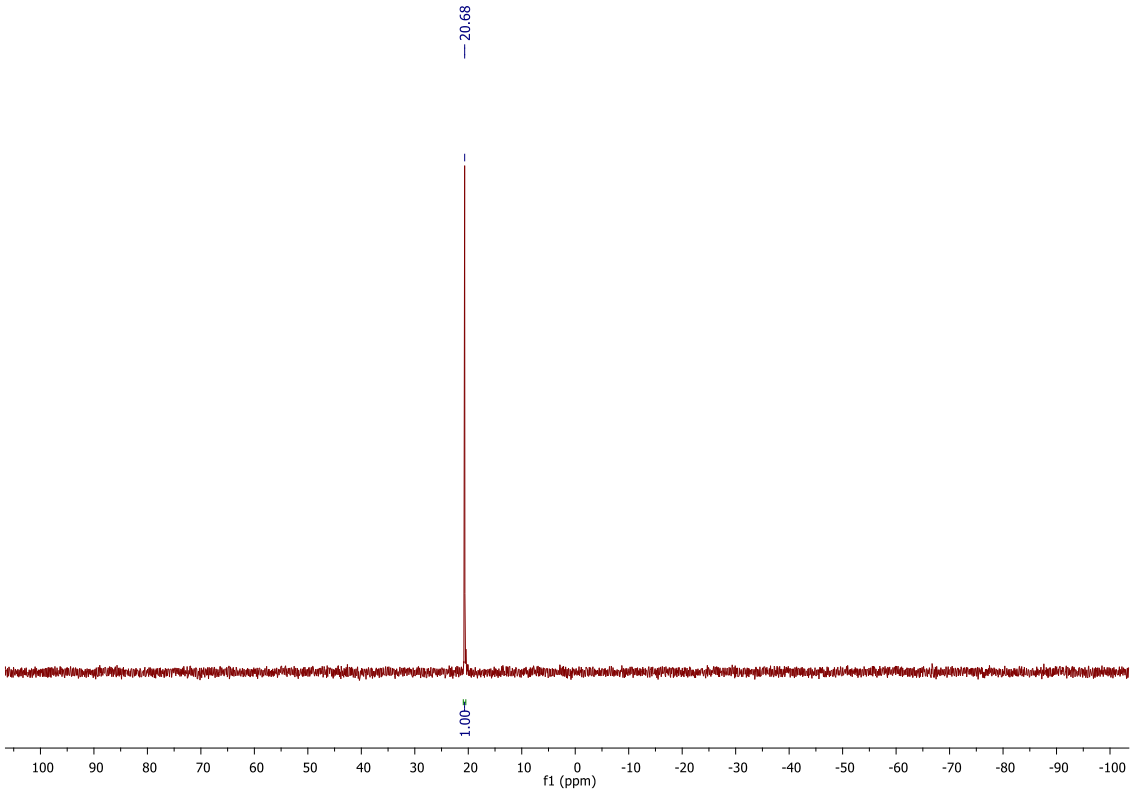
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ba**



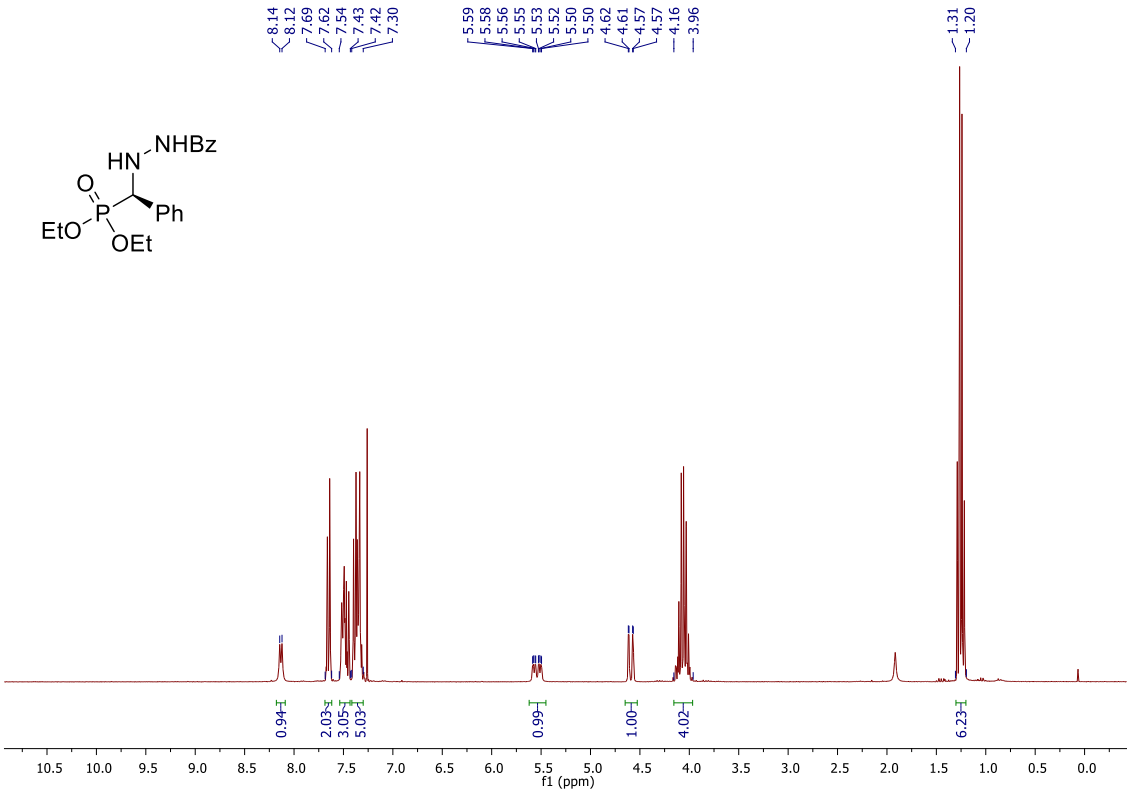
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ba**



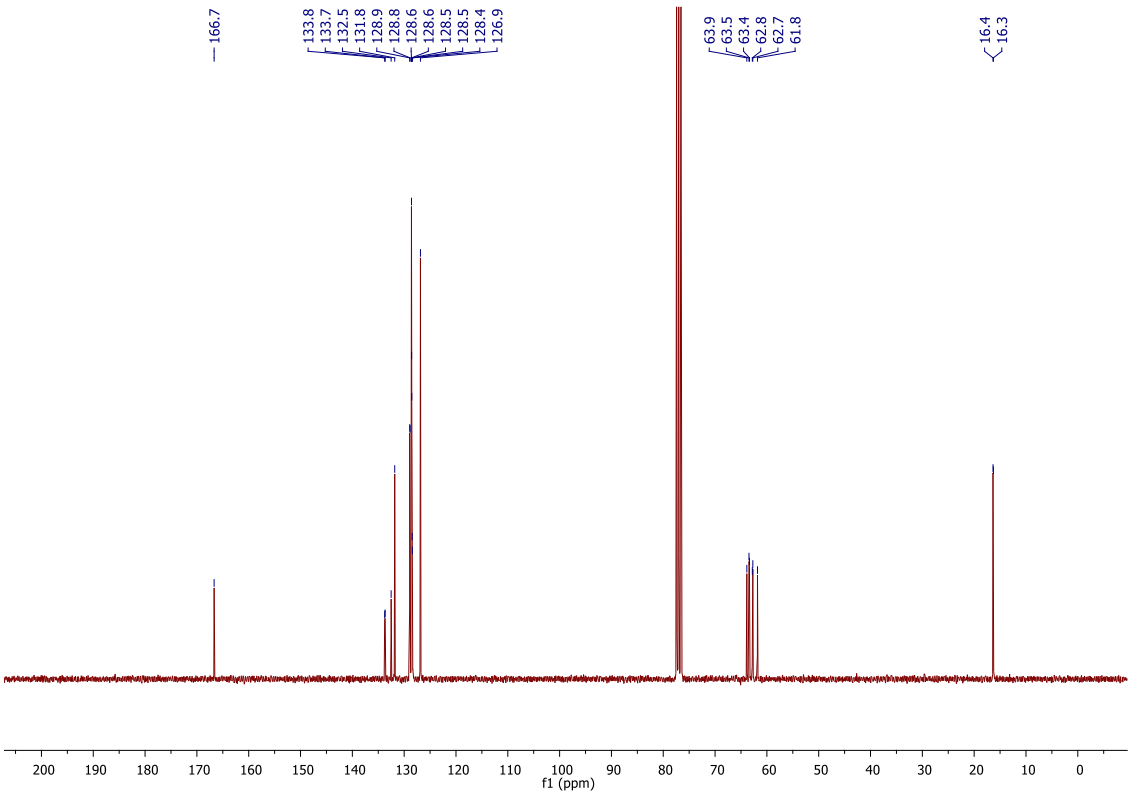
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ba**



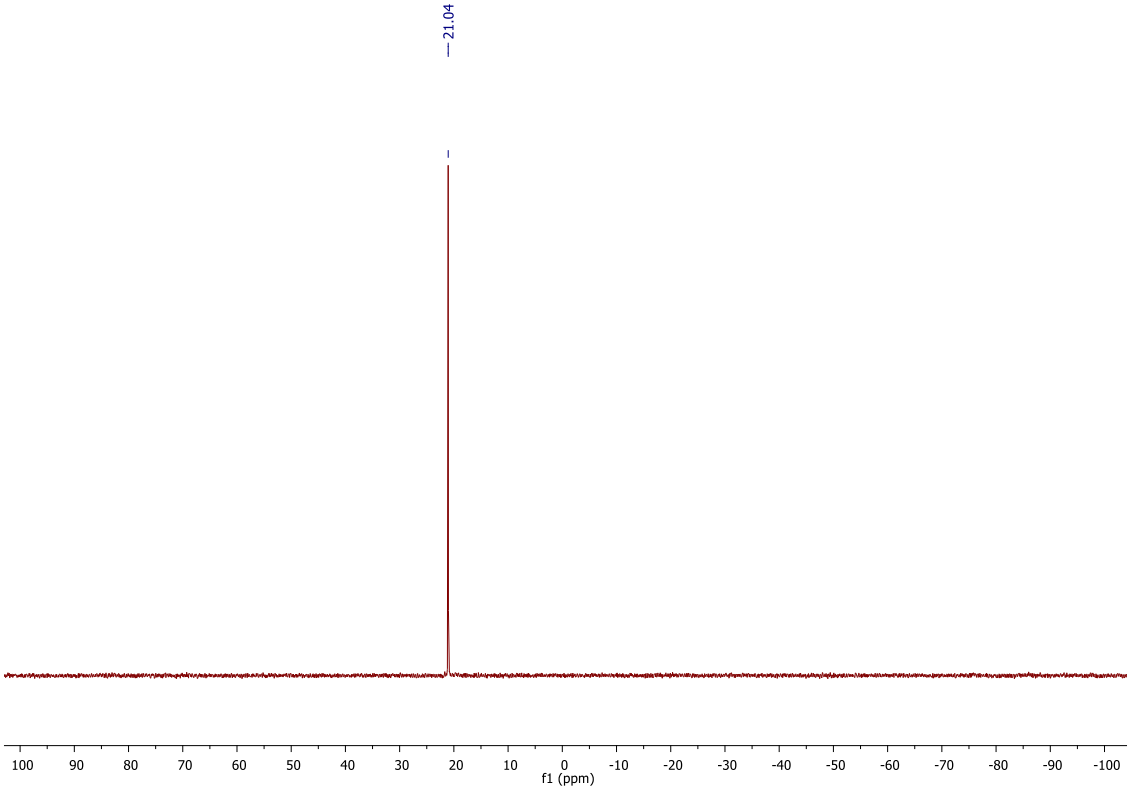
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ca**



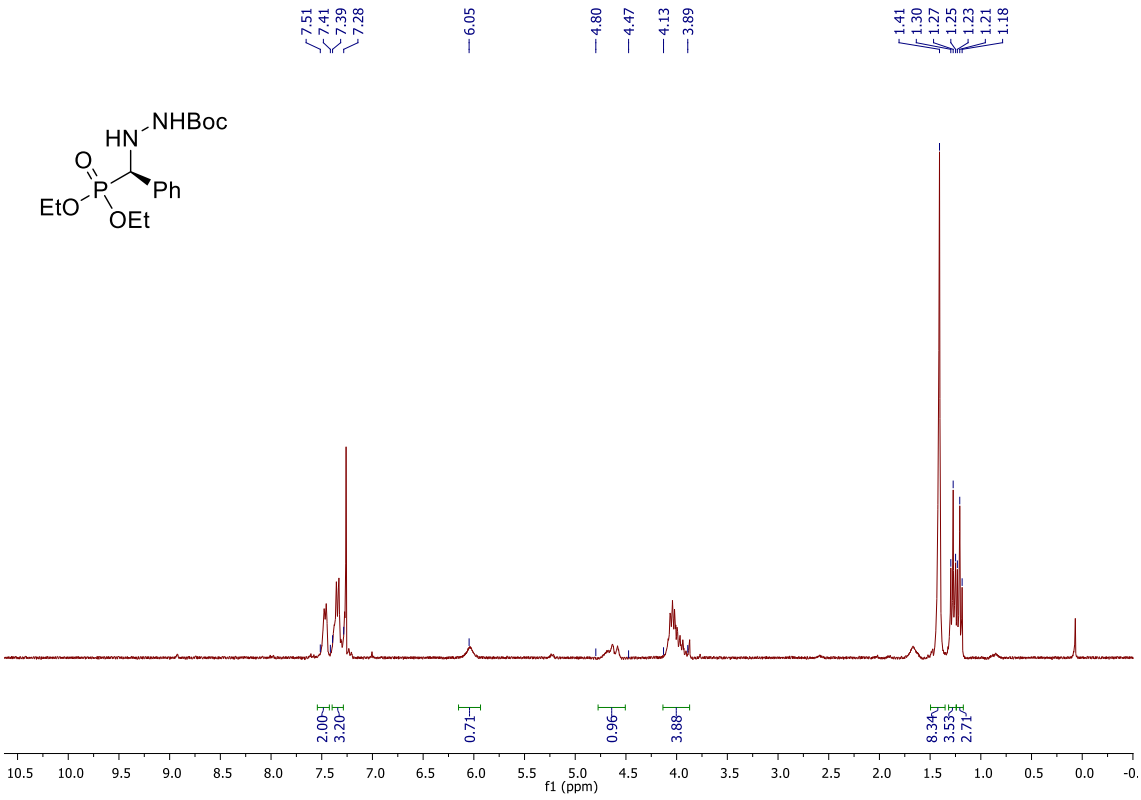
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ca**



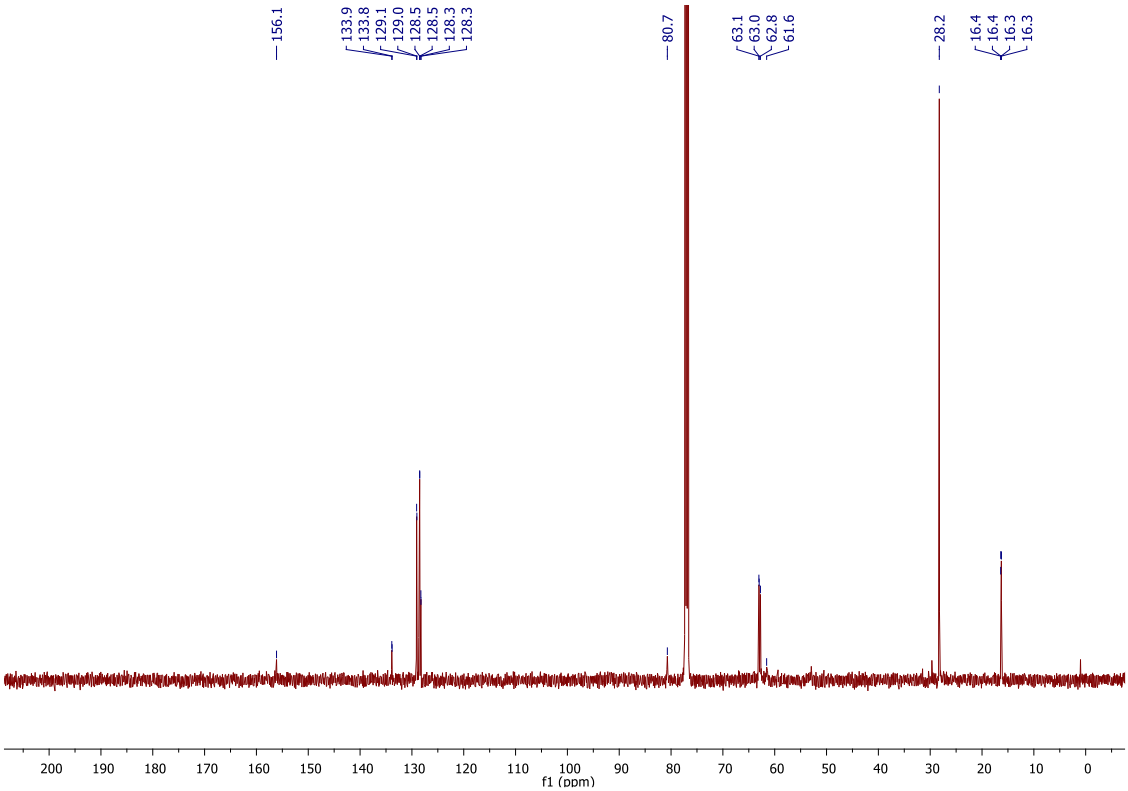
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ca**



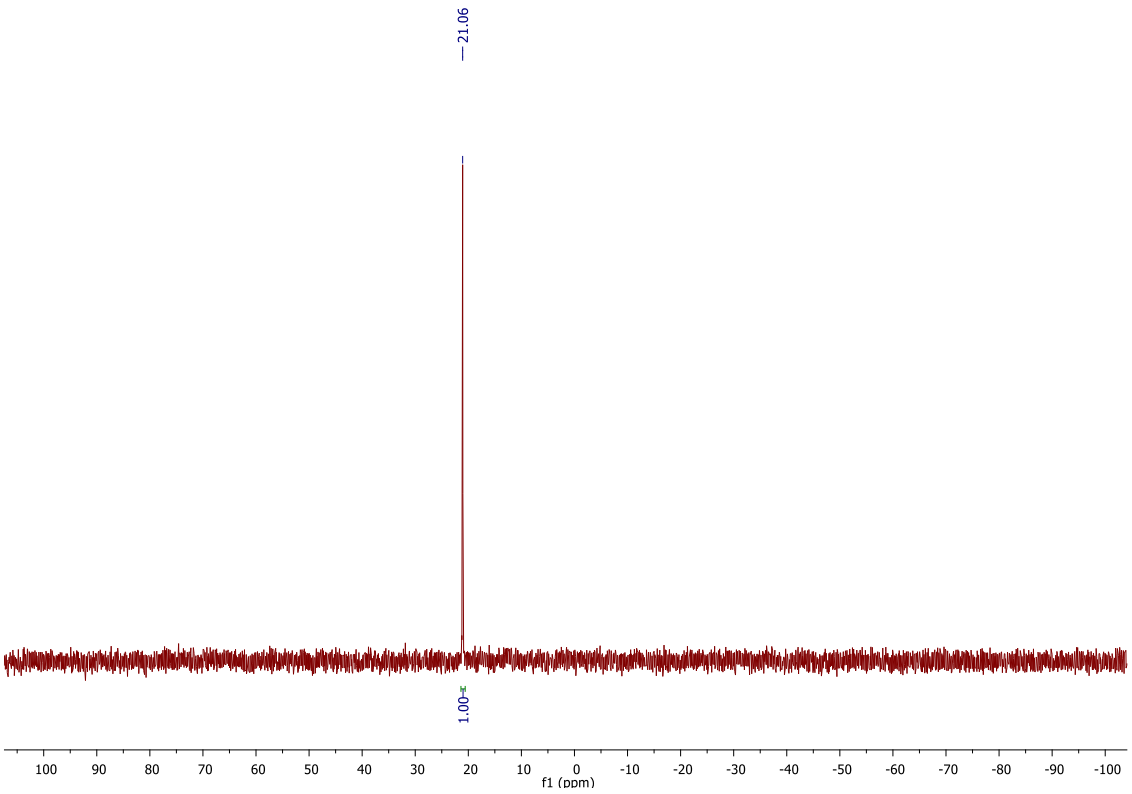
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Da**



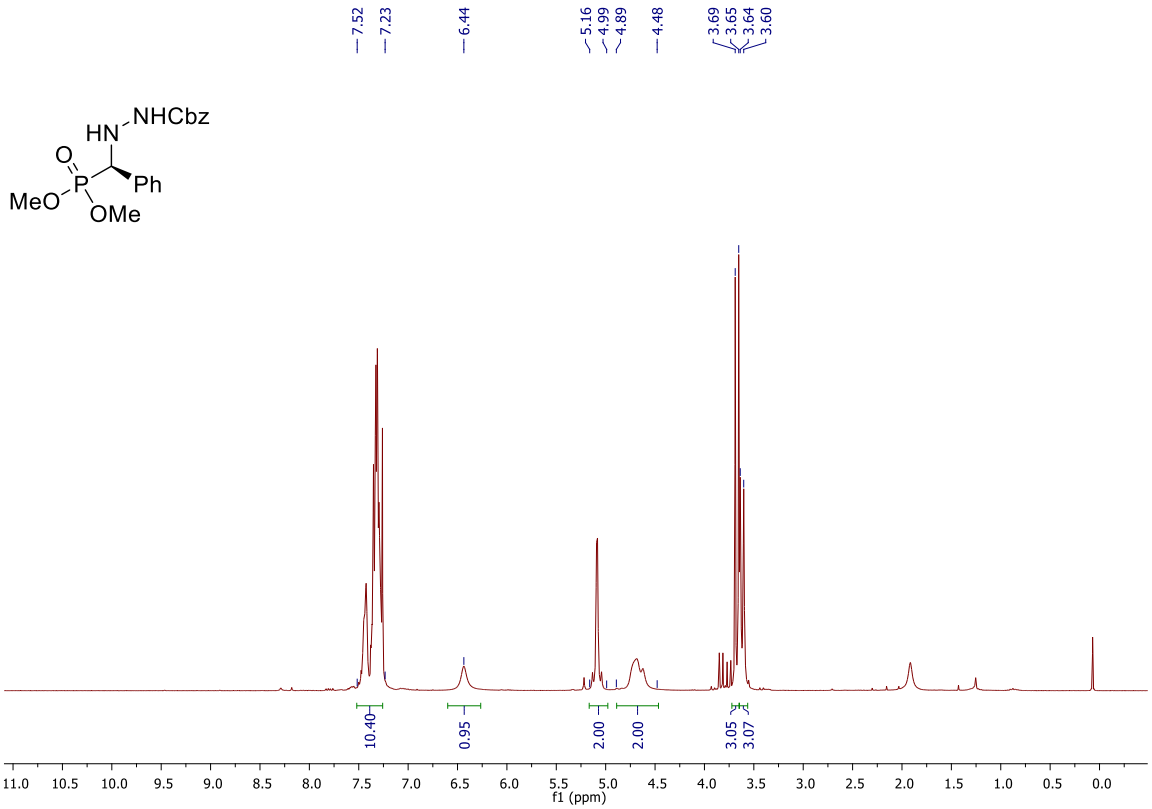
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Da**



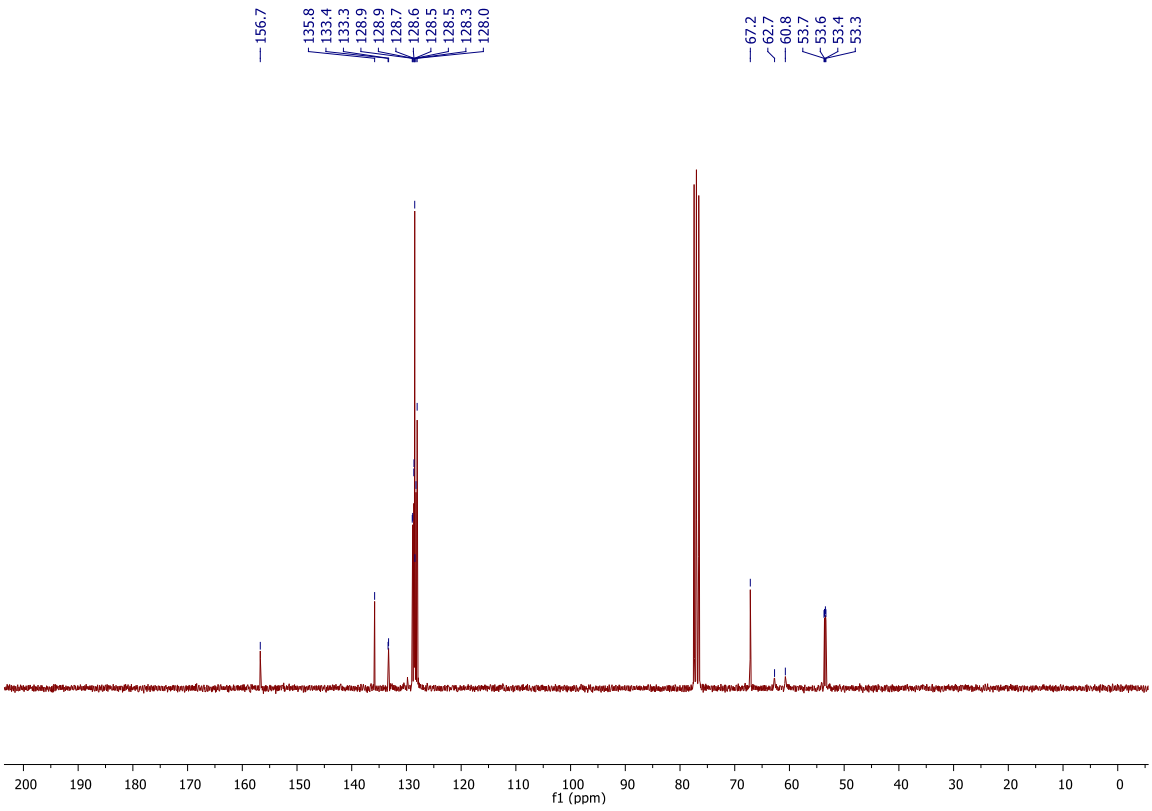
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Da**



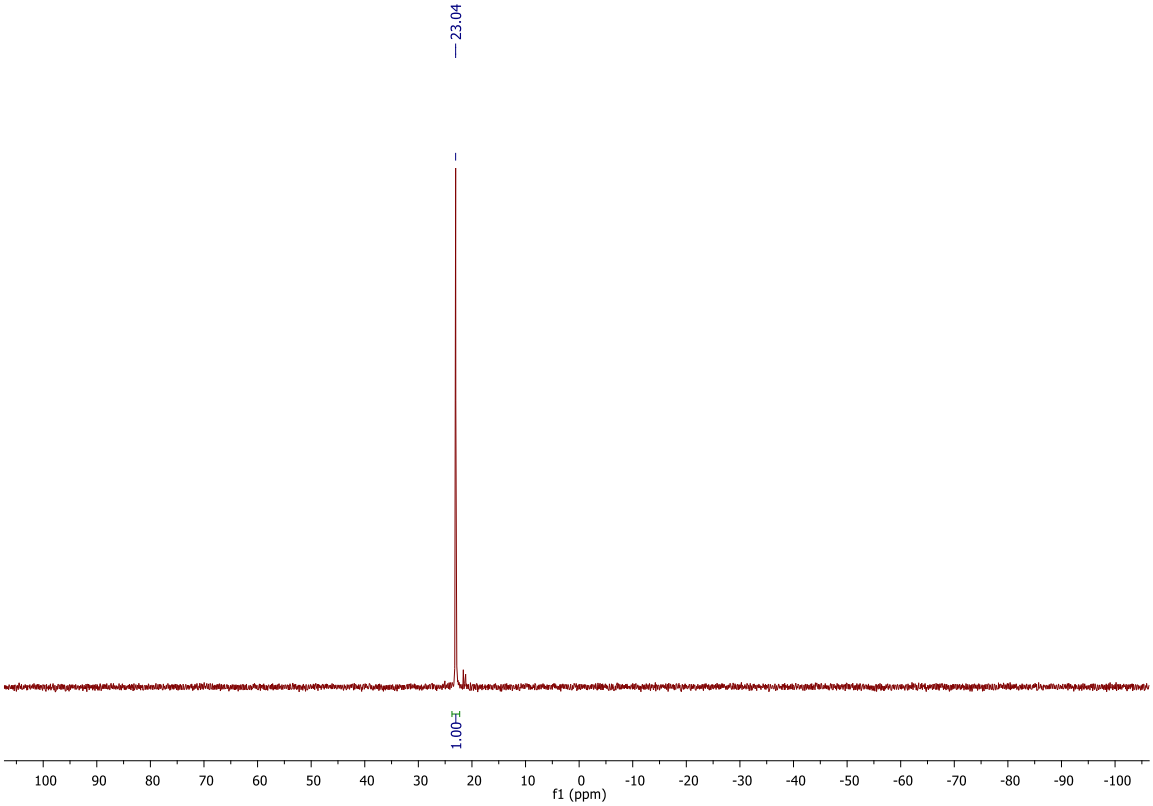
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ea**



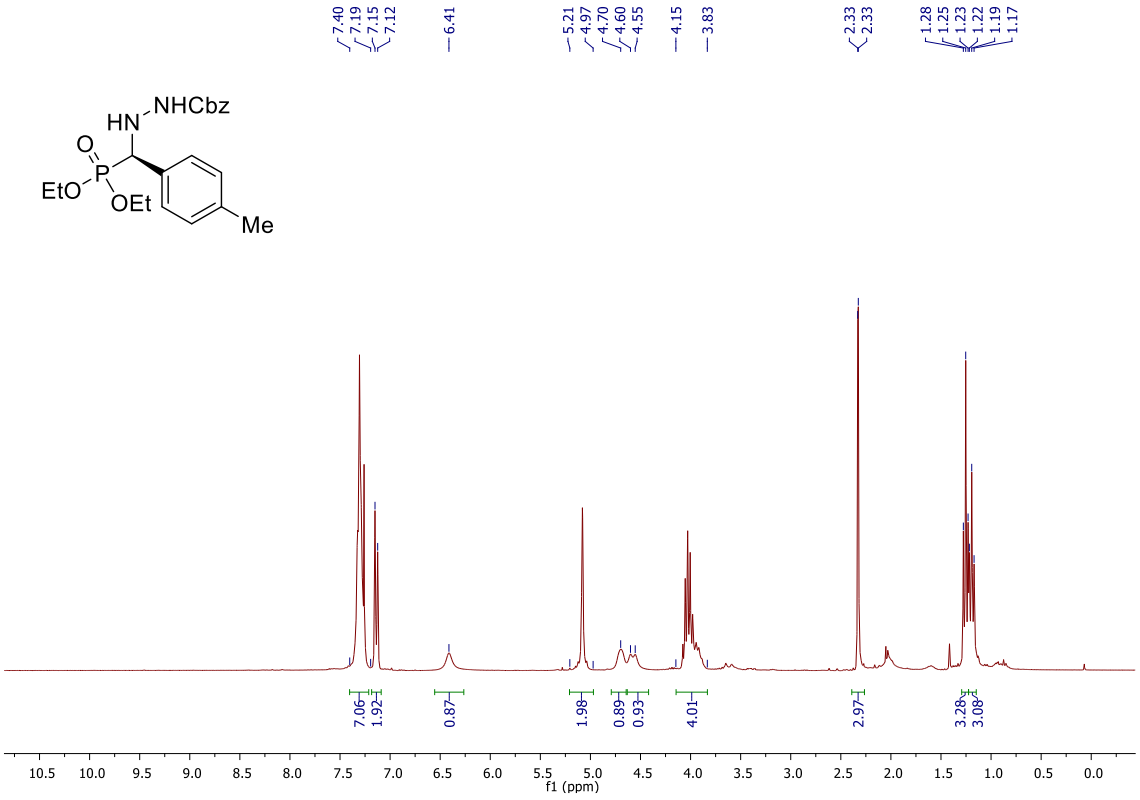
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ea**



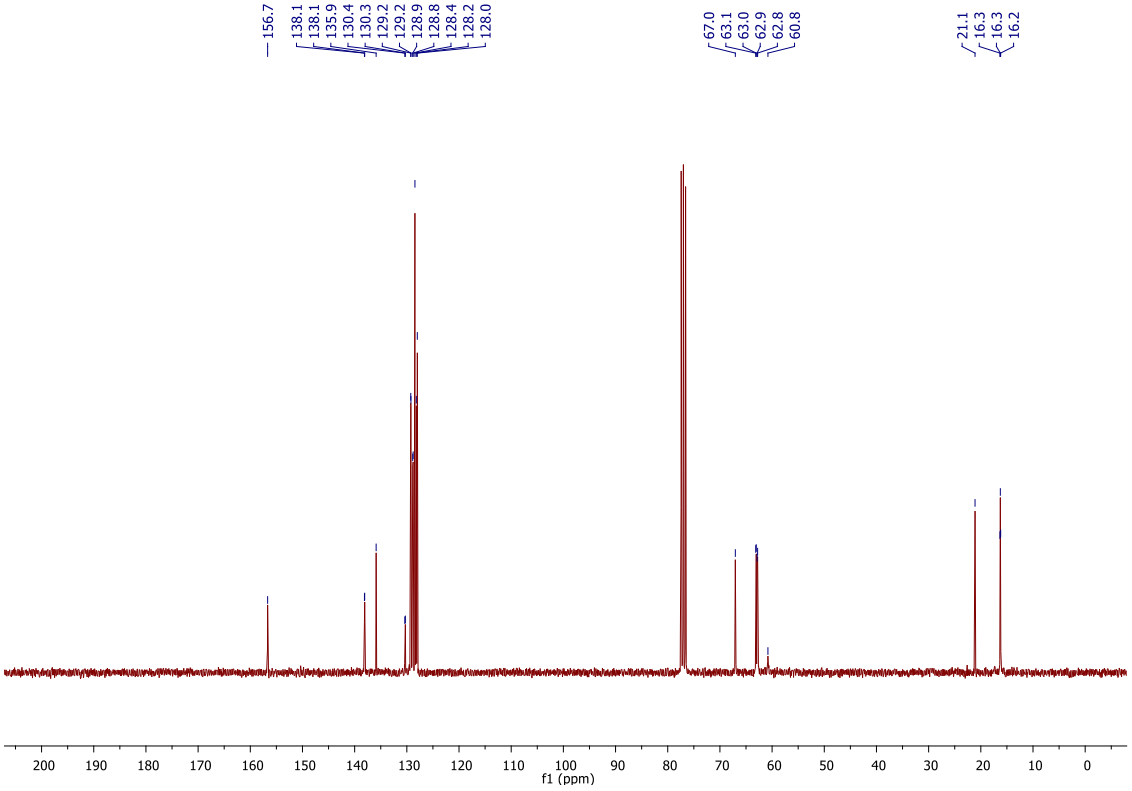
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ea**



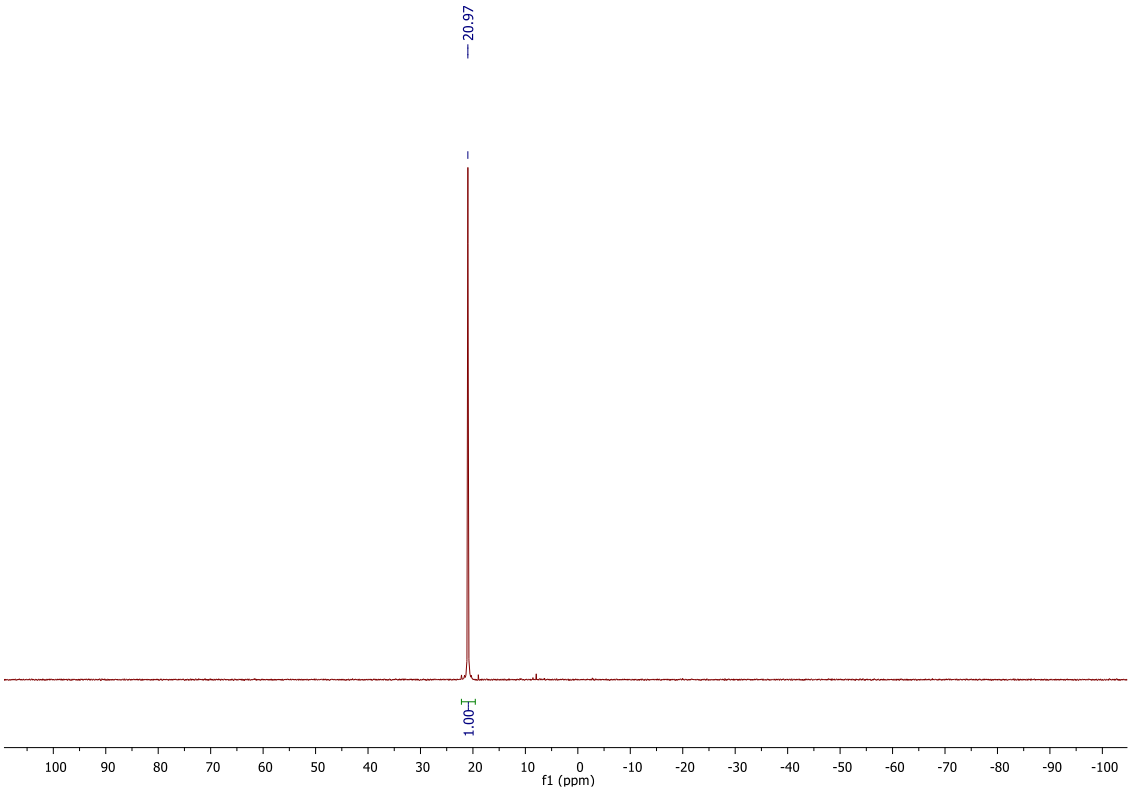
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ab**



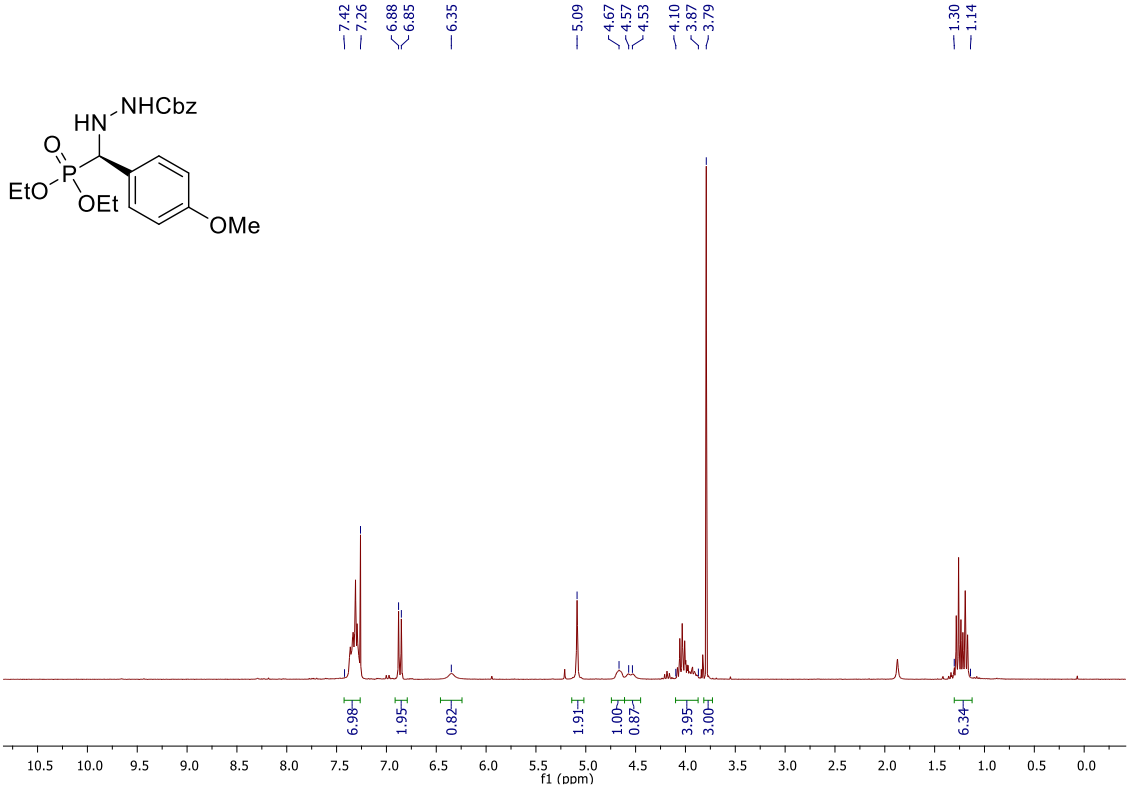
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ab**



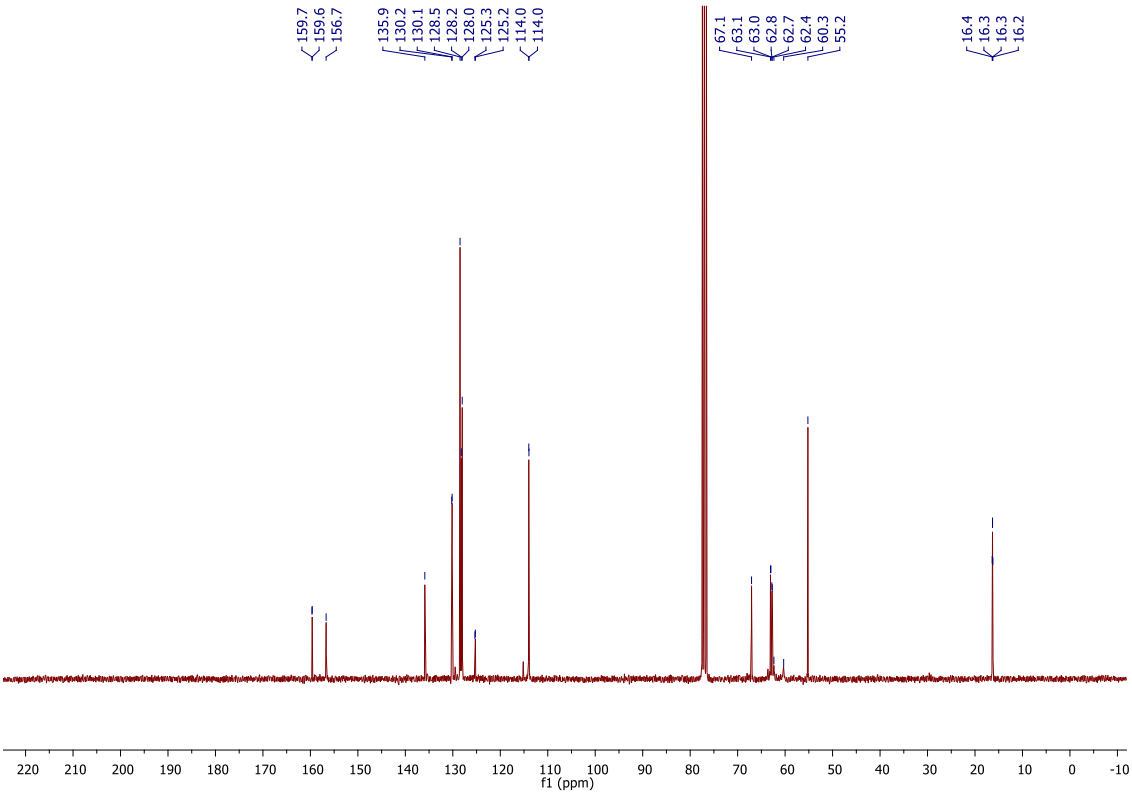
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ab**



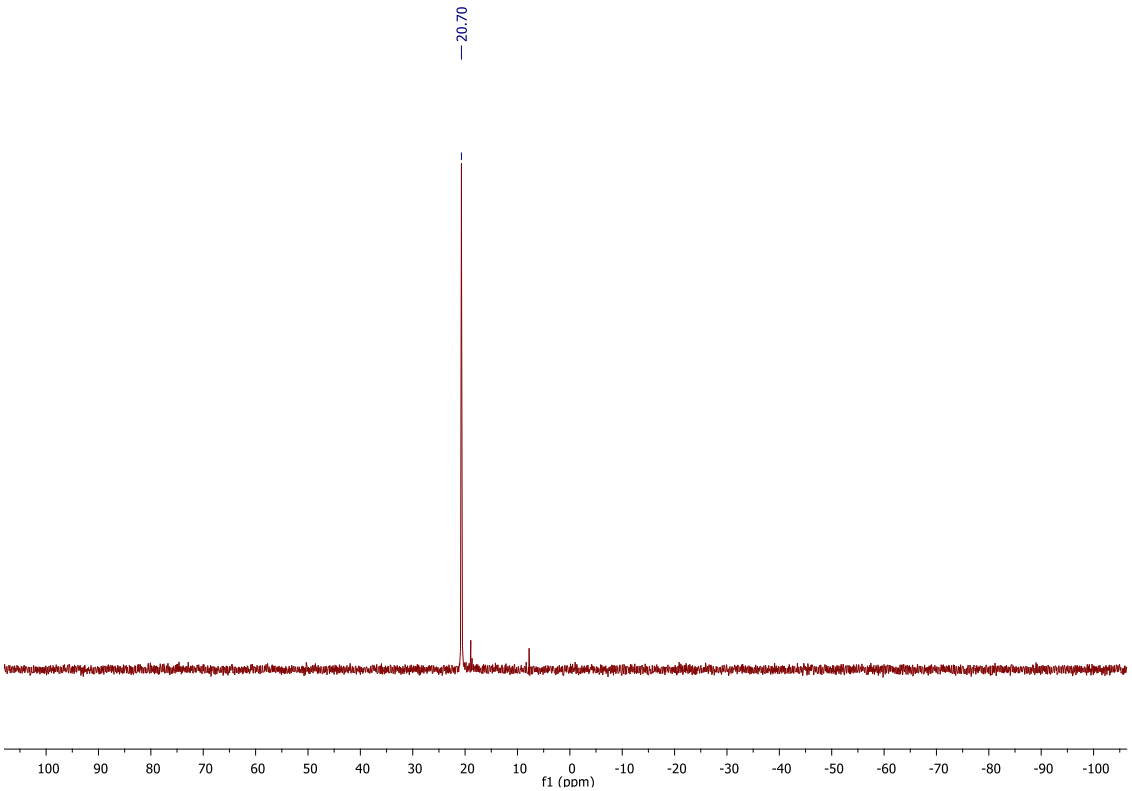
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ac**



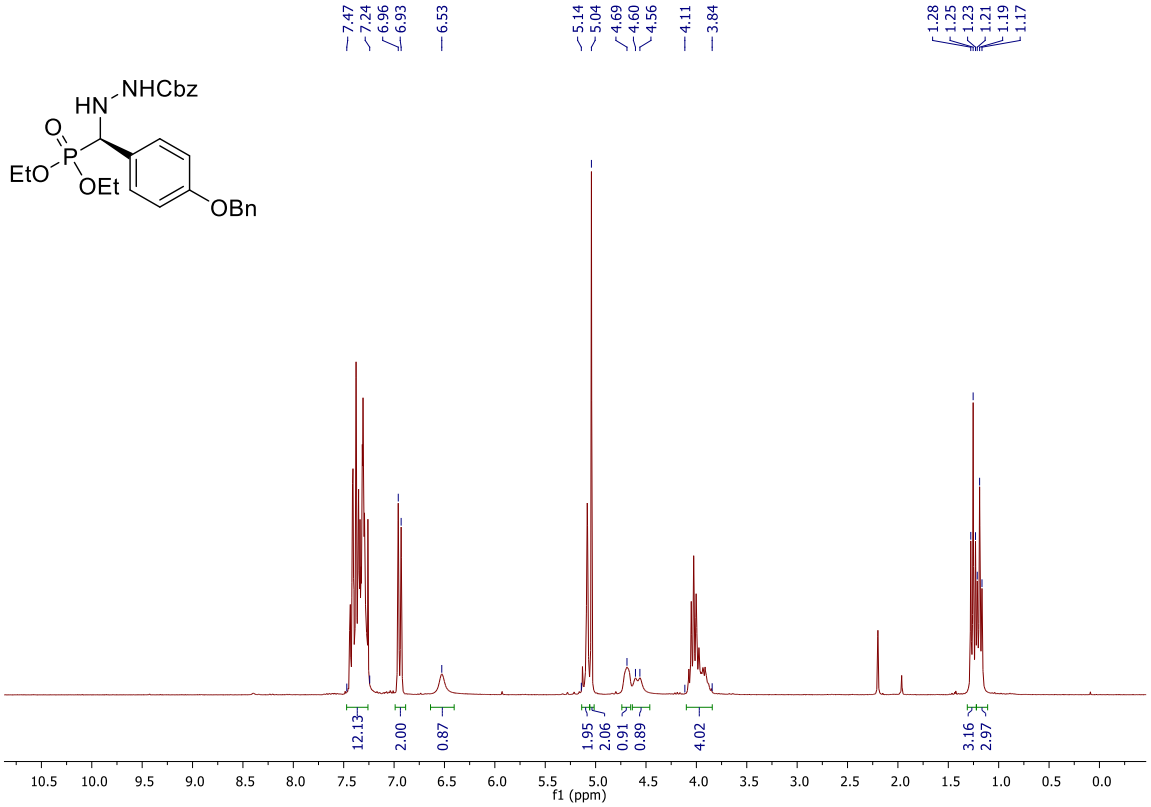
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ac**



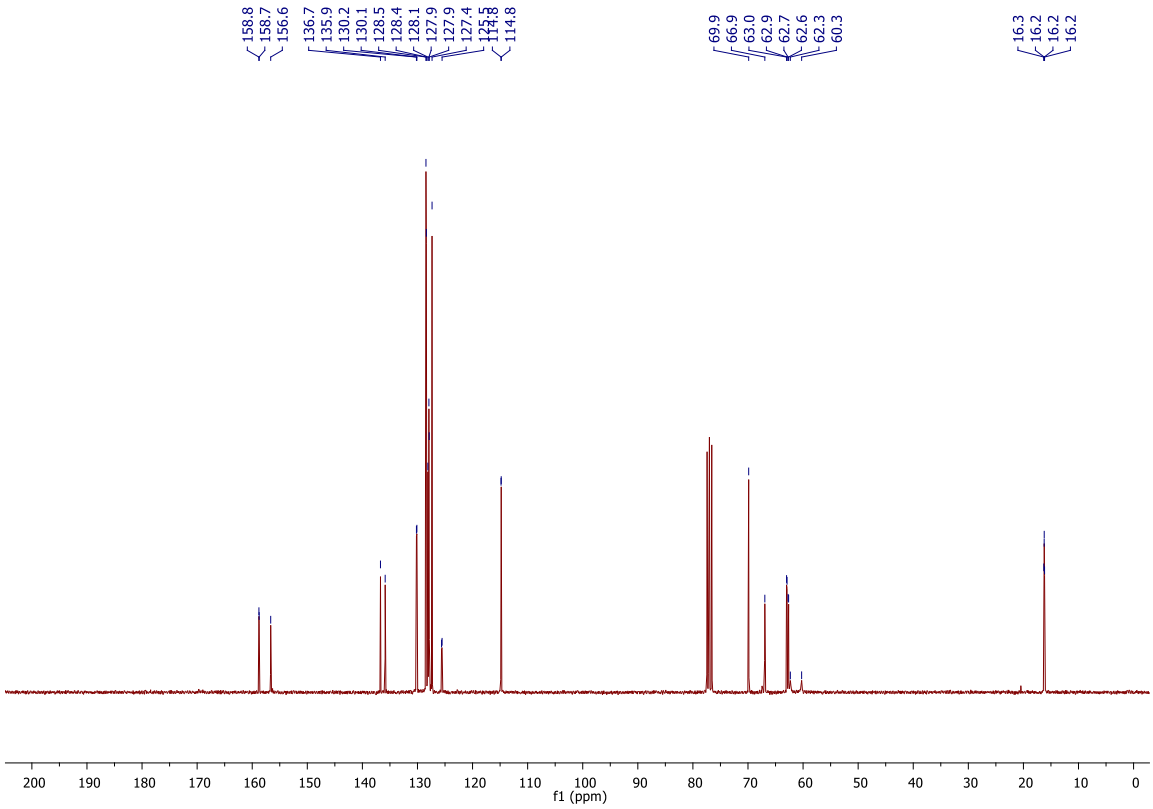
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ac**



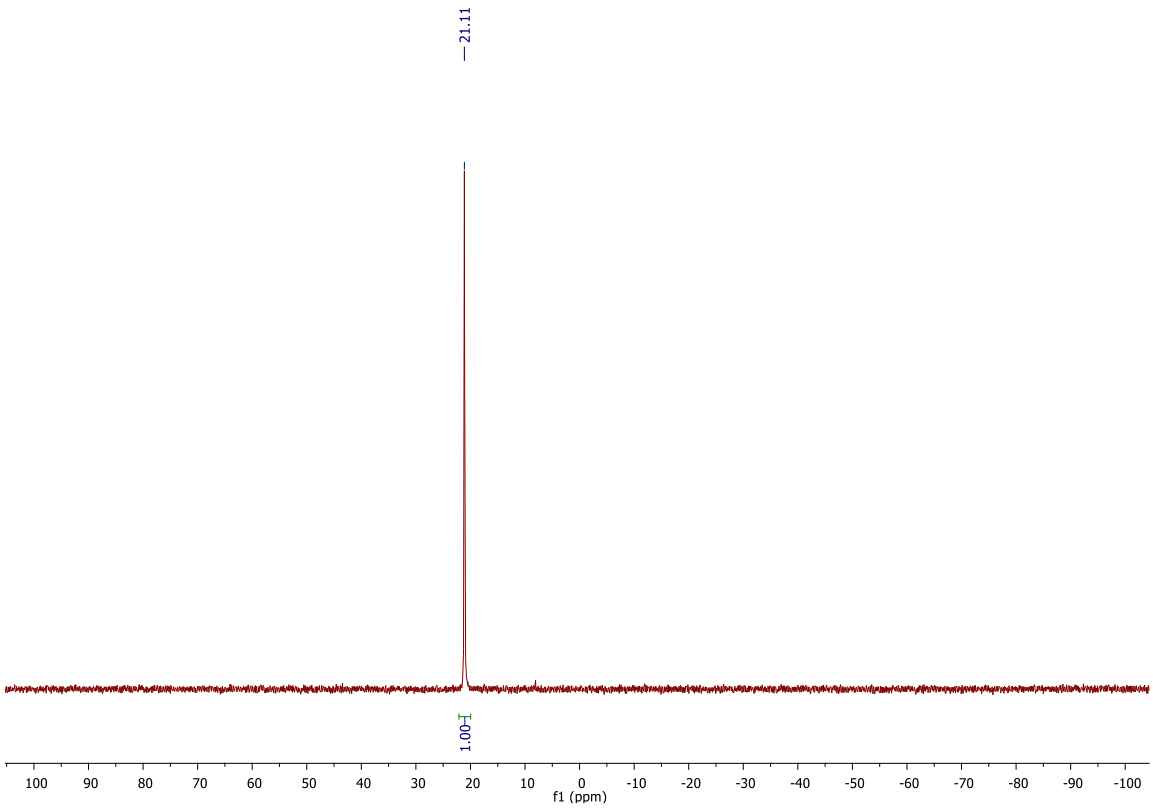
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ad**



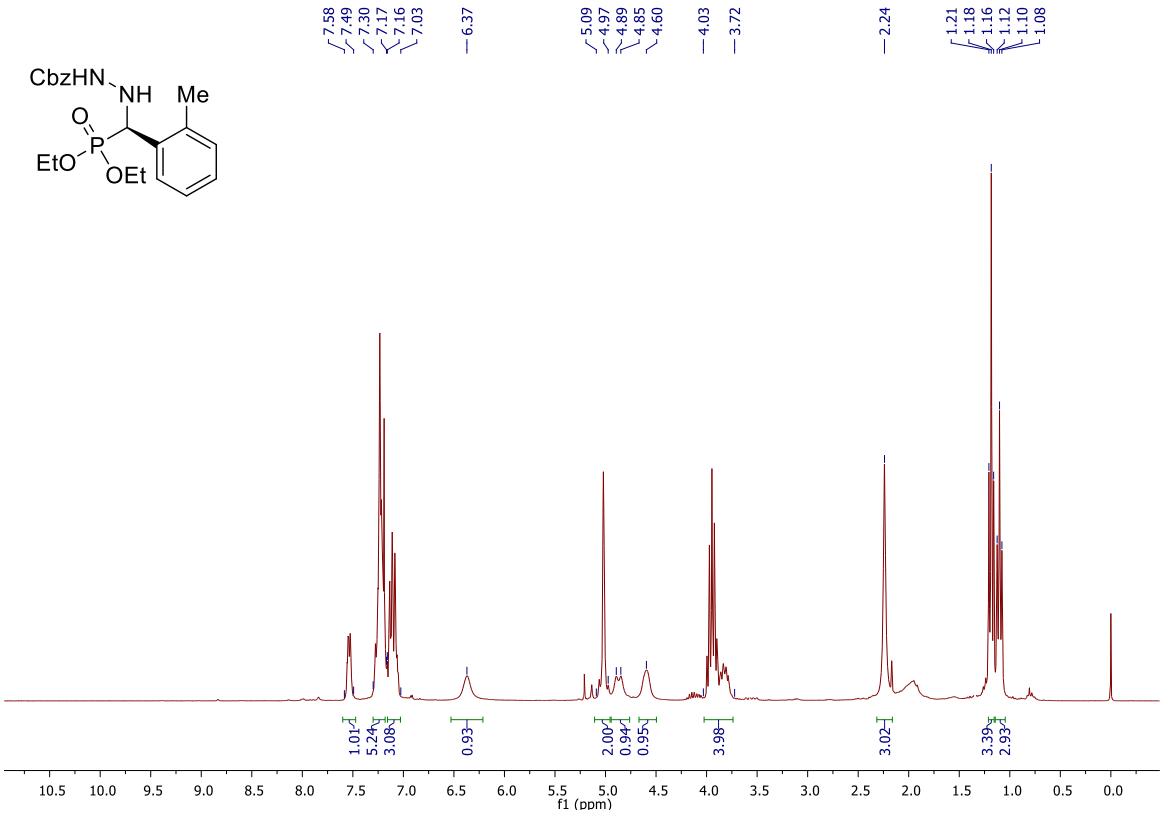
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ad**



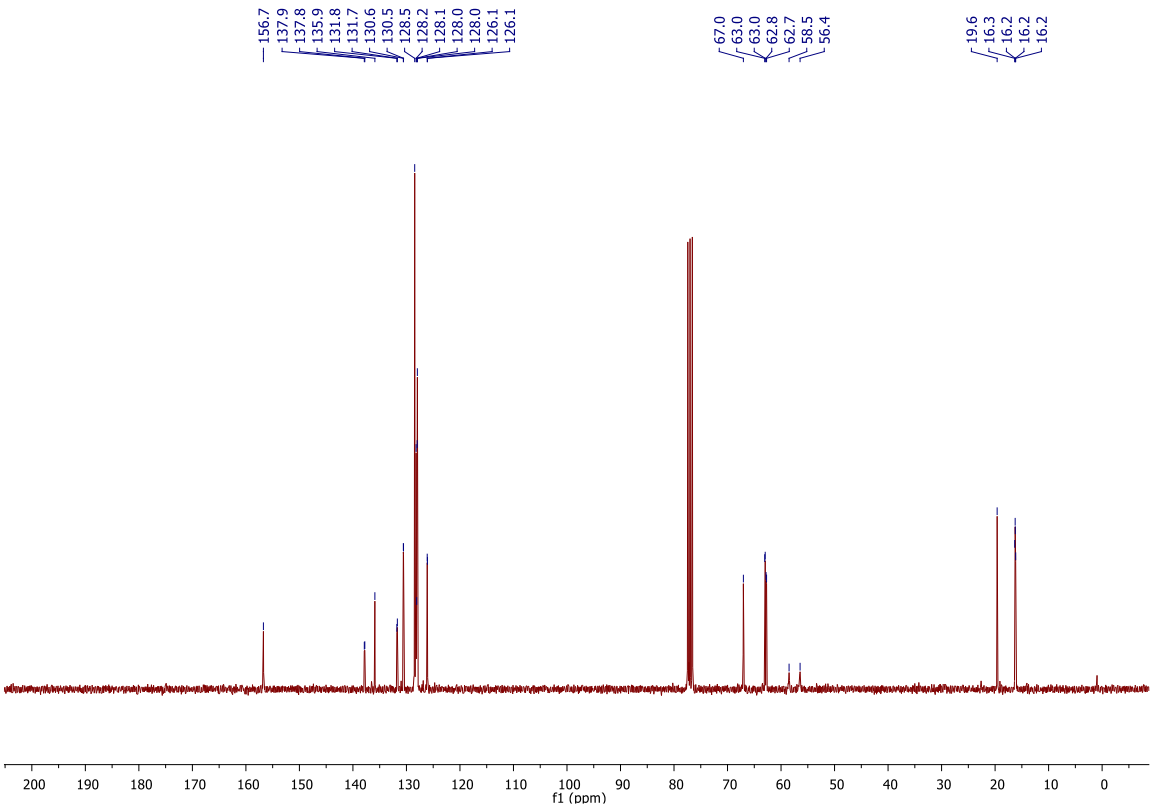
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ad**



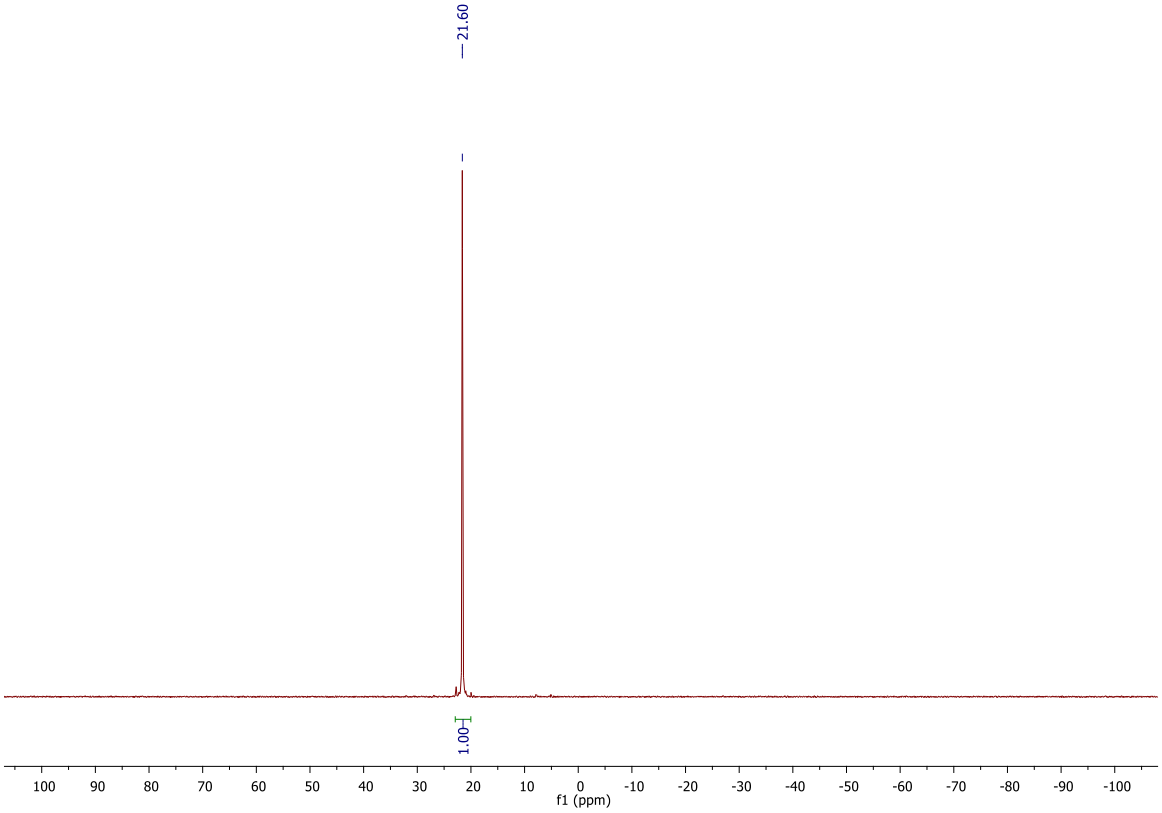
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ae**



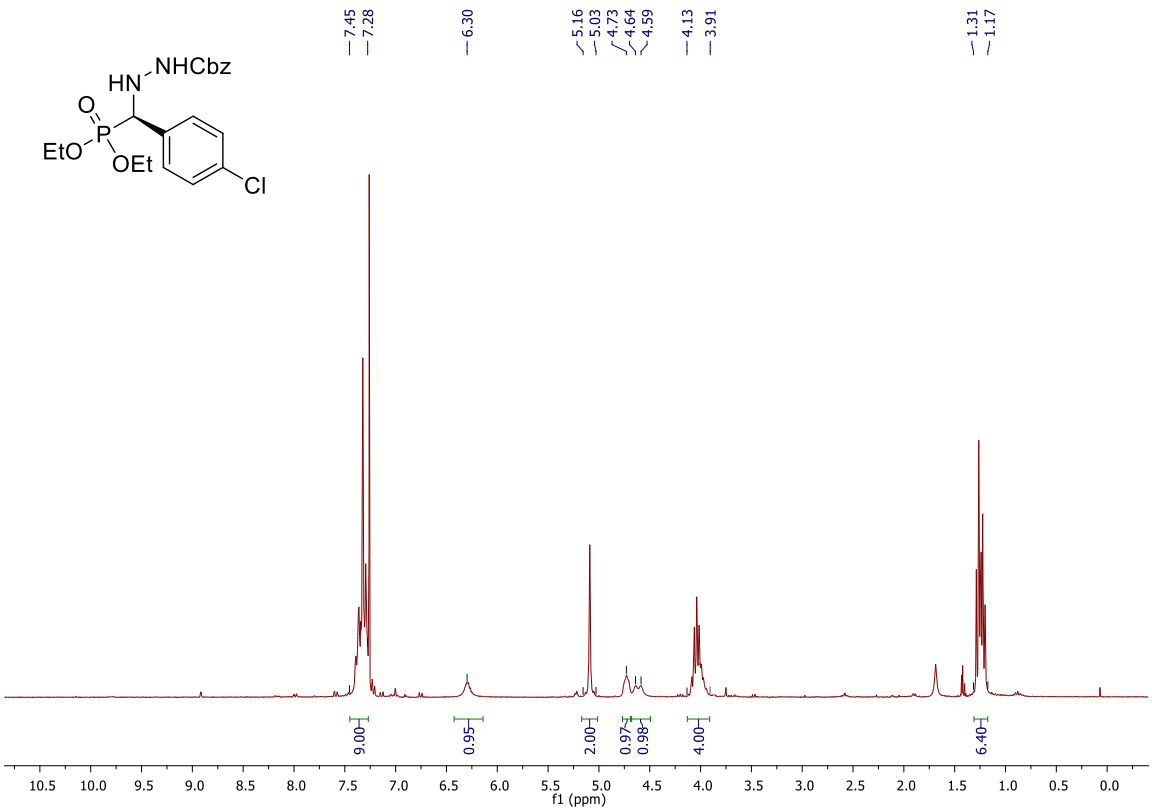
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ae**



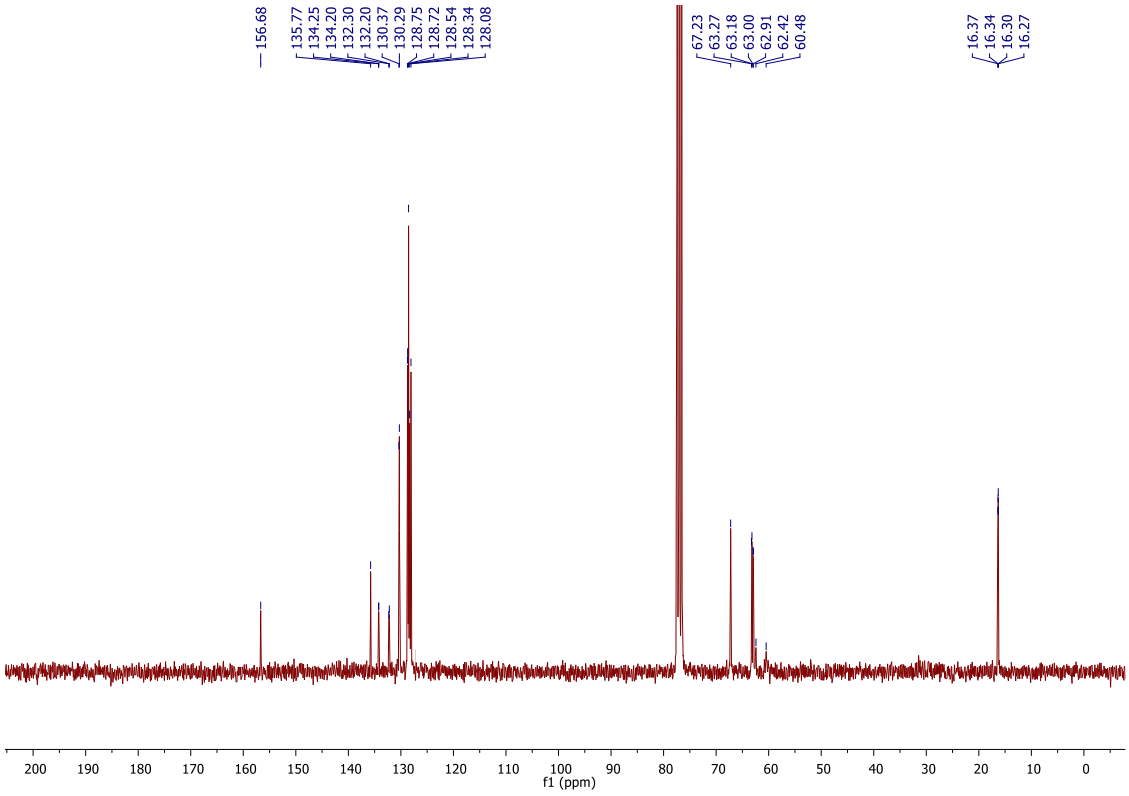
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ae**



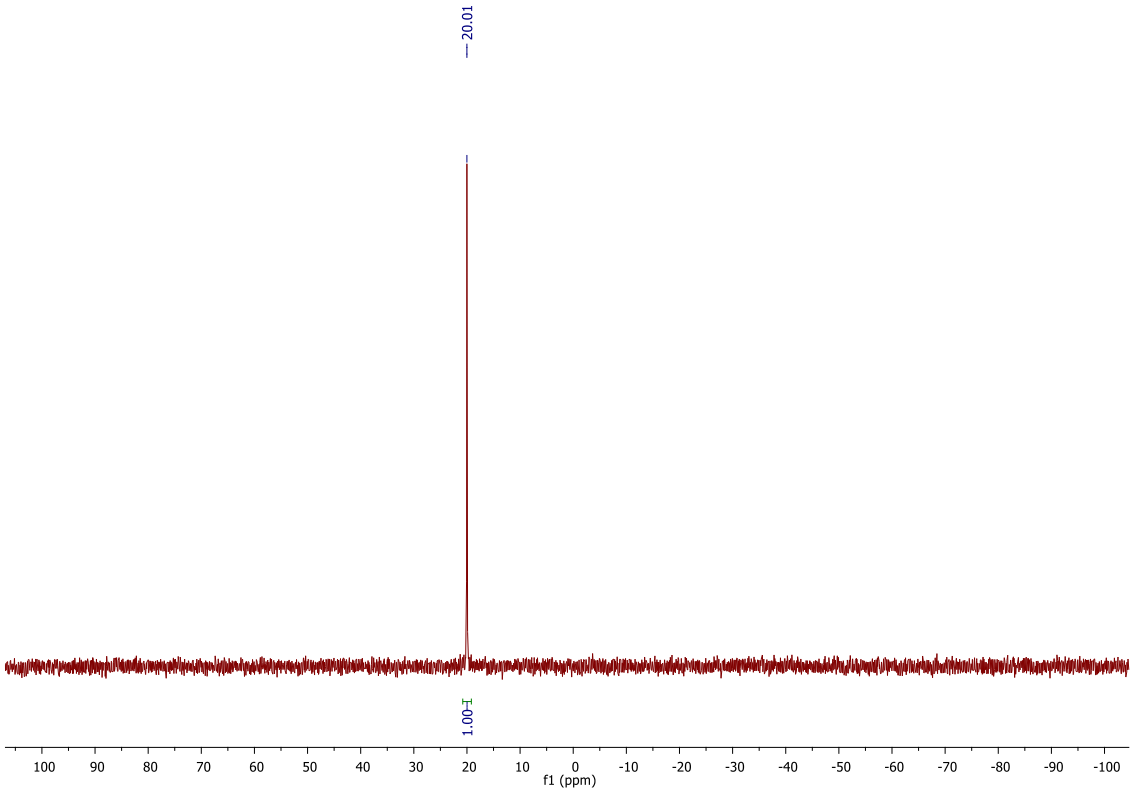
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Af**



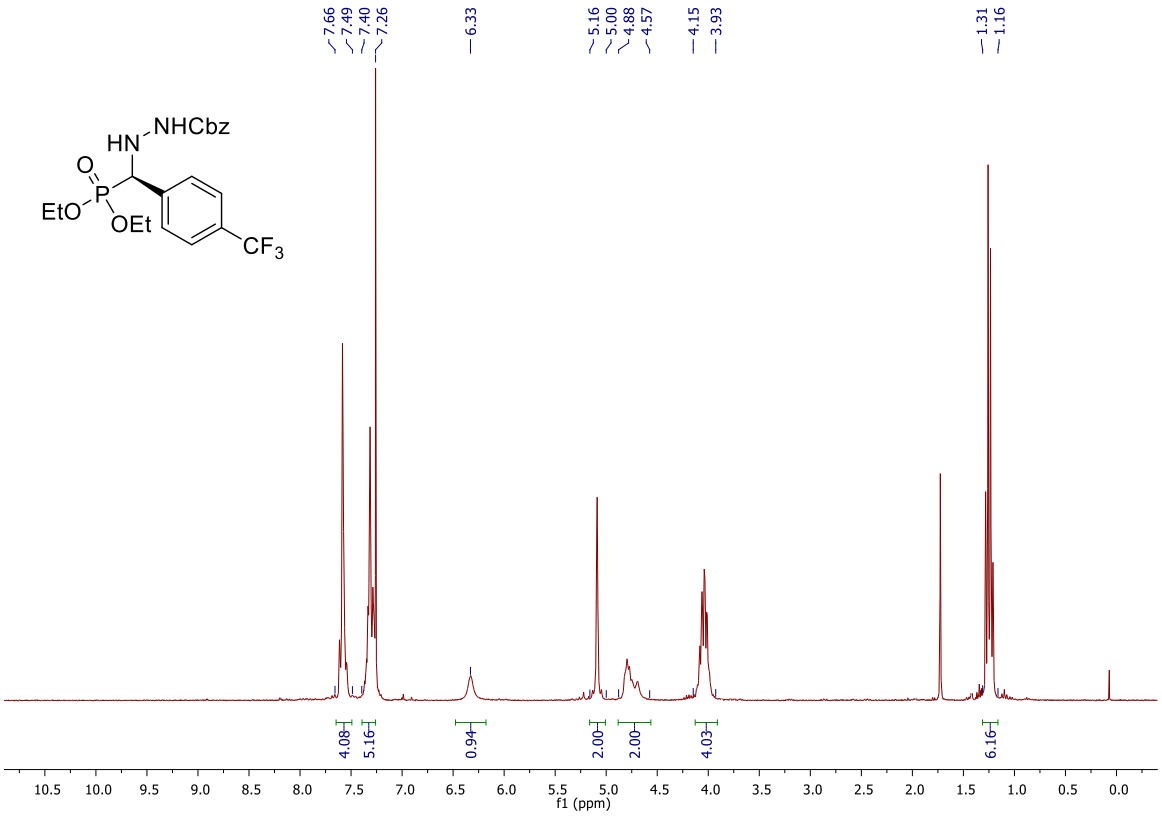
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Af**



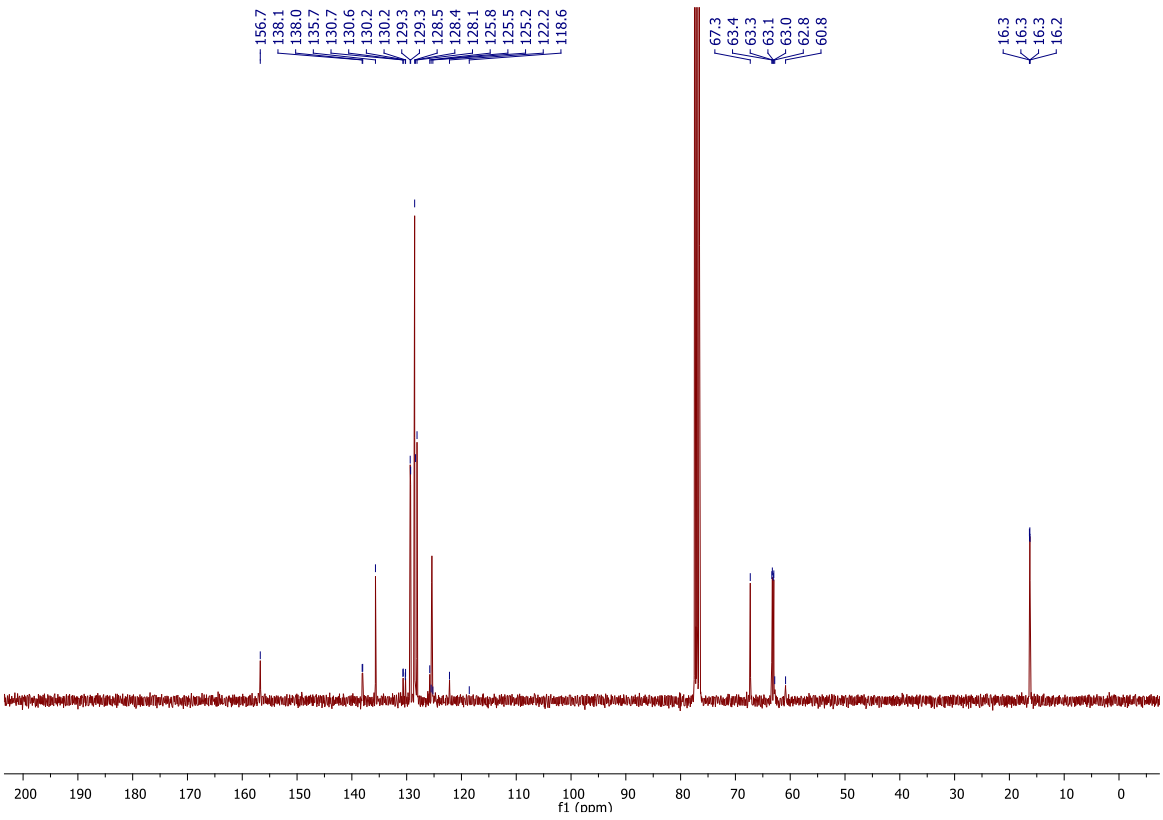
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Af**



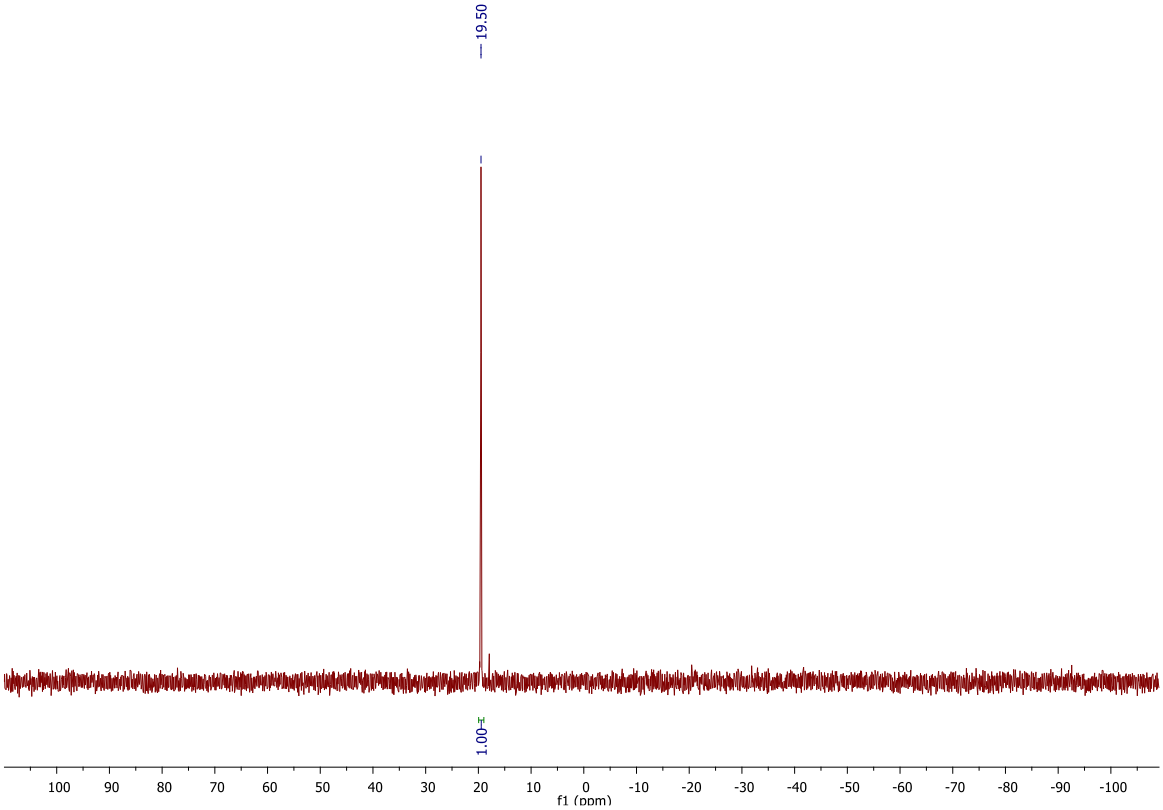
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ag**



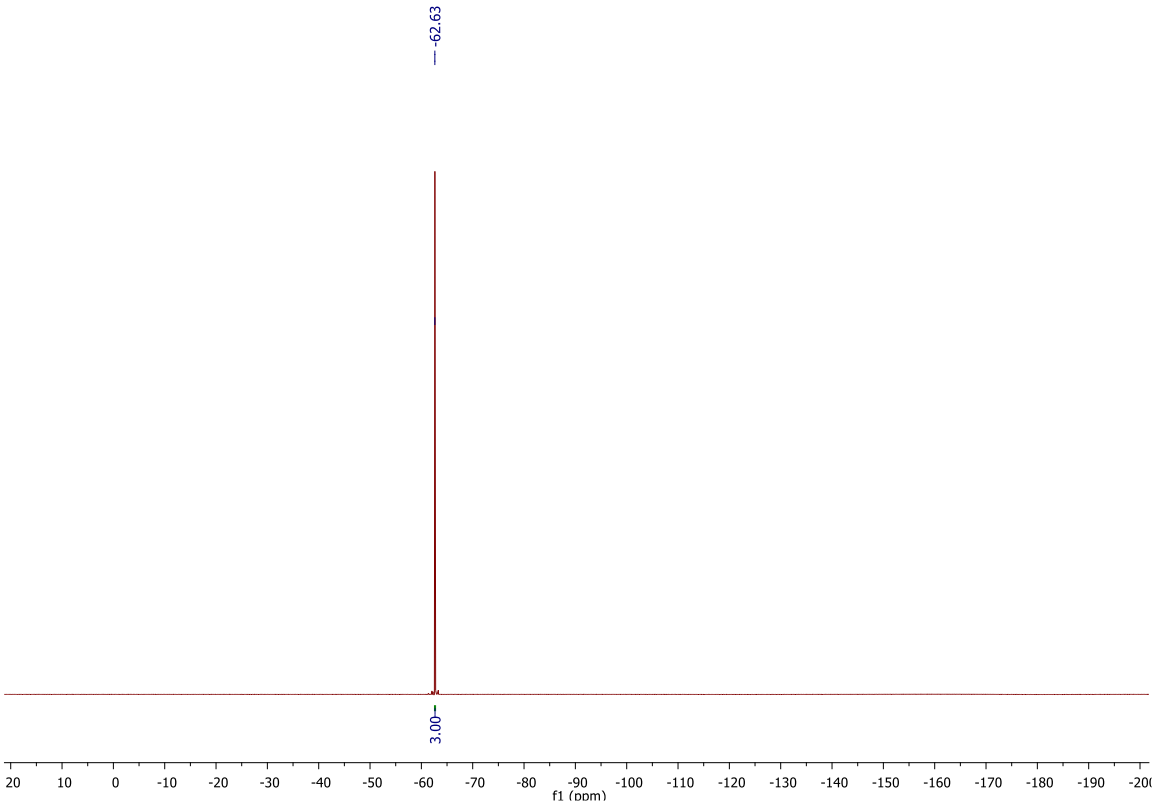
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ag**



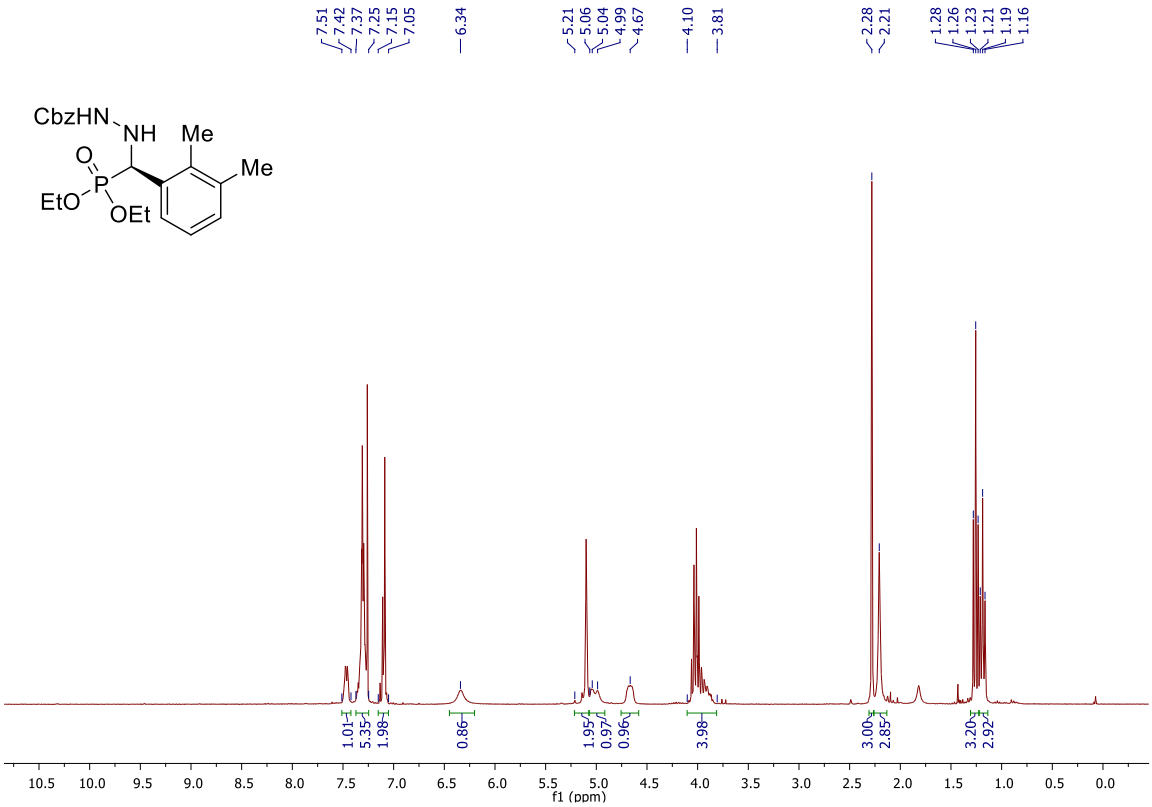
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ag**



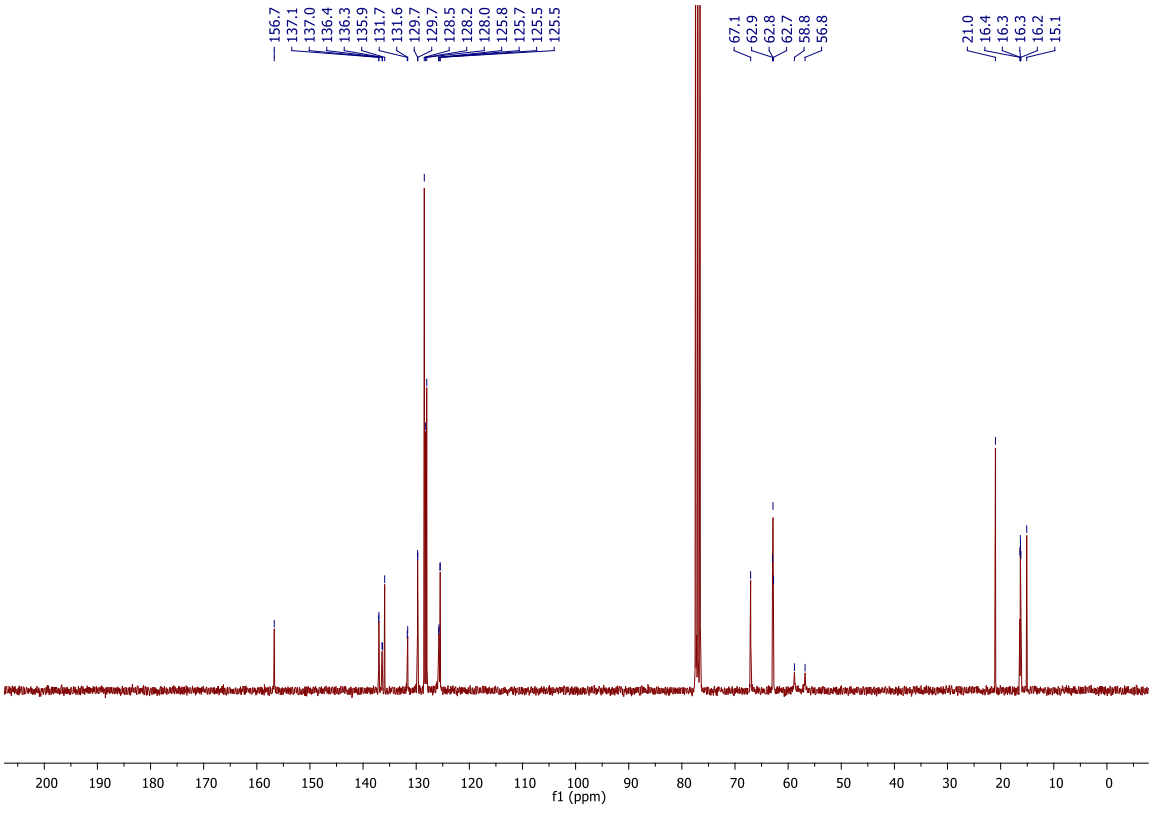
^{19}F NMR (471 MHz, $CDCl_3$) of (*R*)-**3Ag**



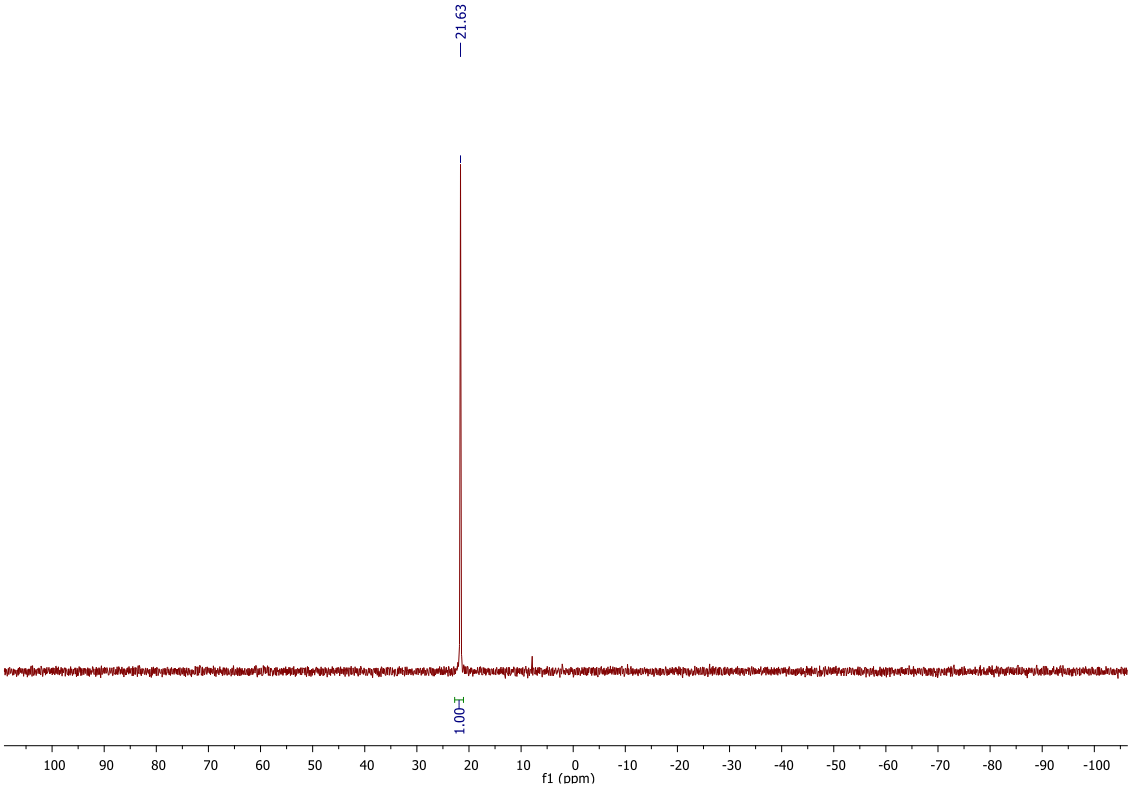
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ah**



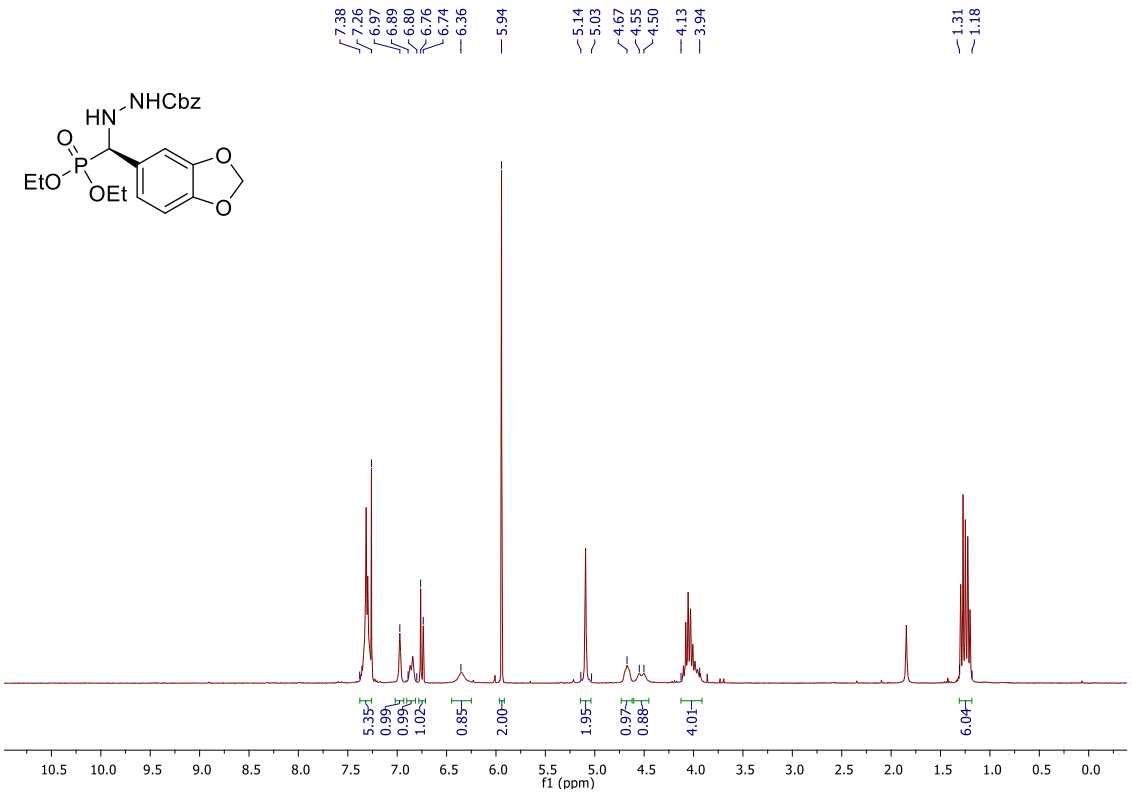
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ah**



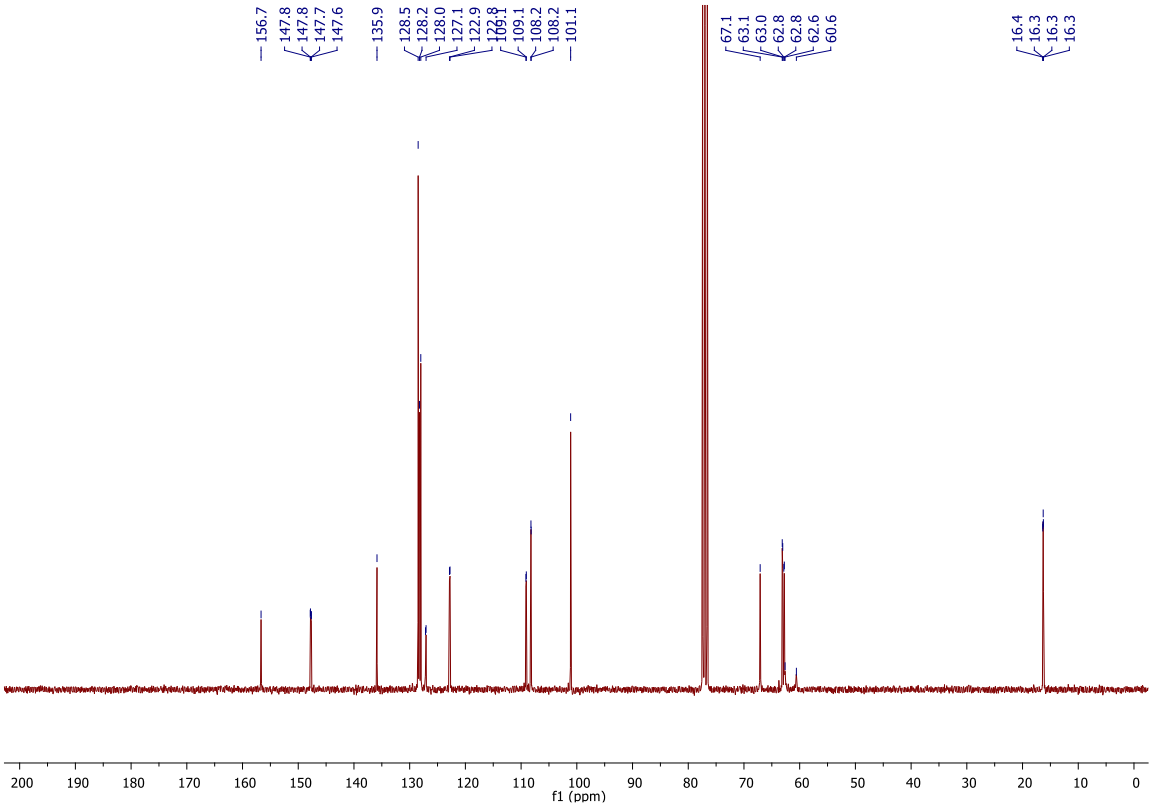
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ah**



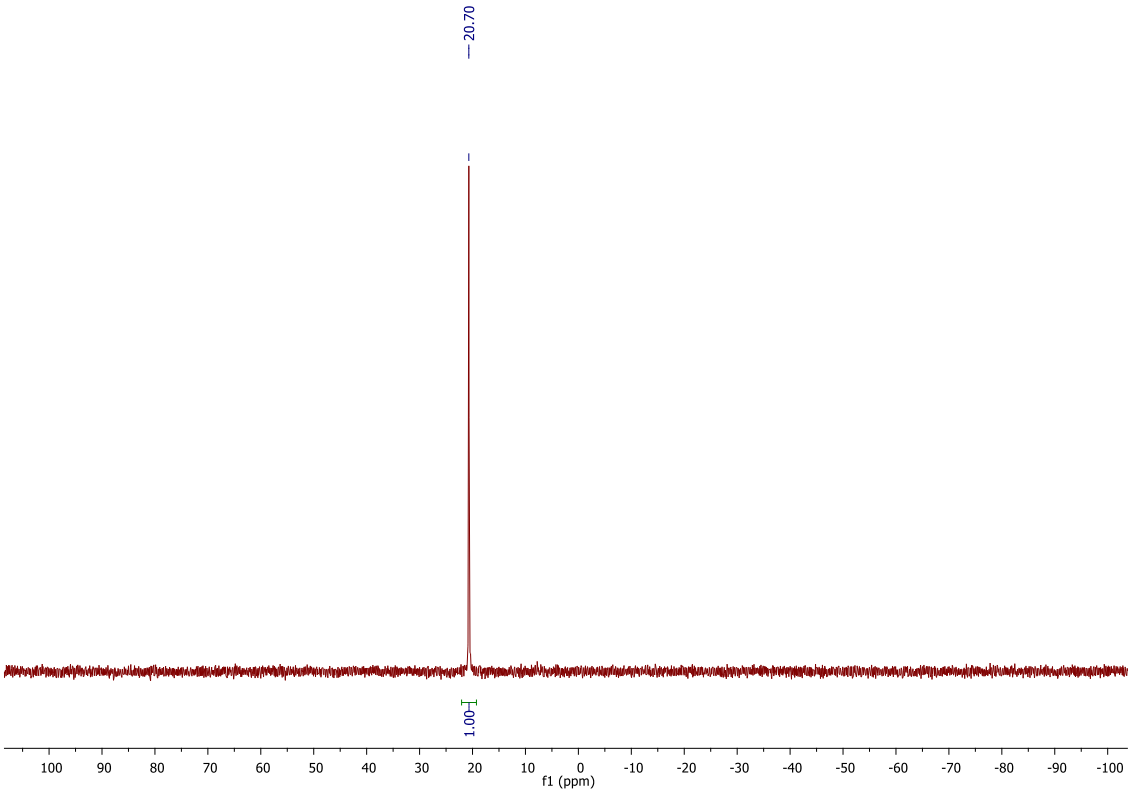
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ai**



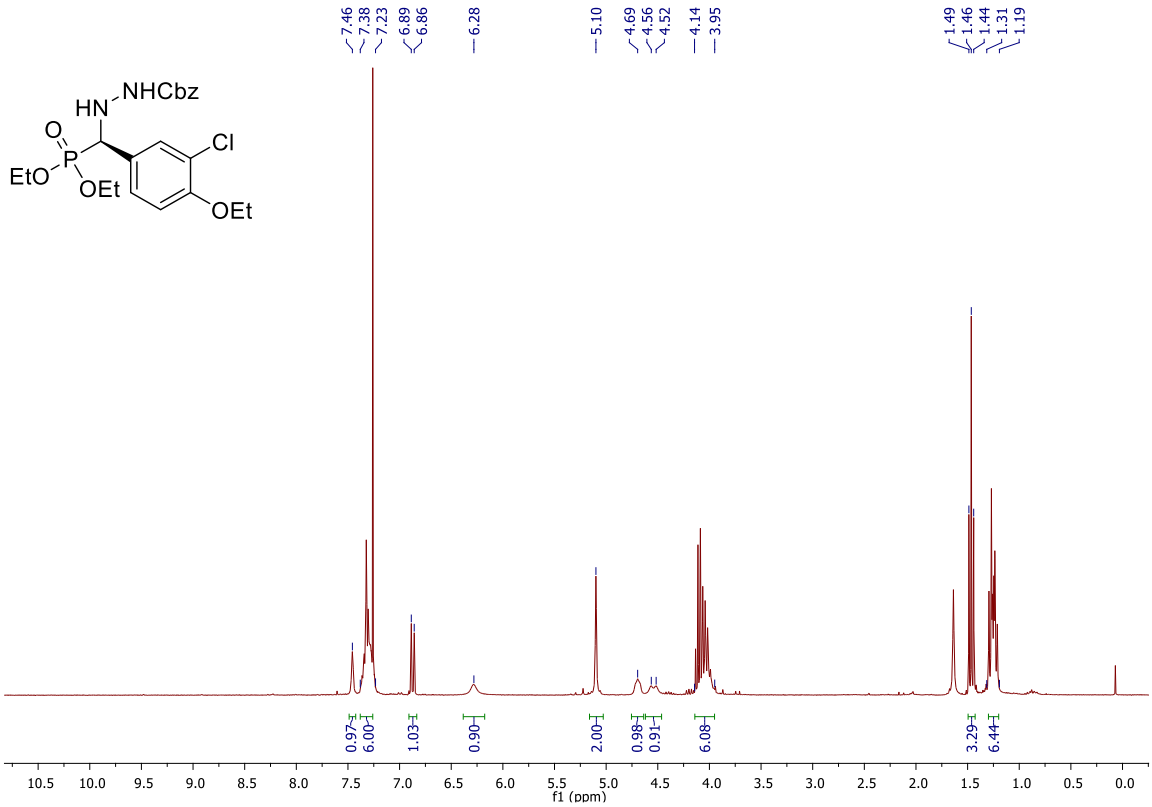
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ai**



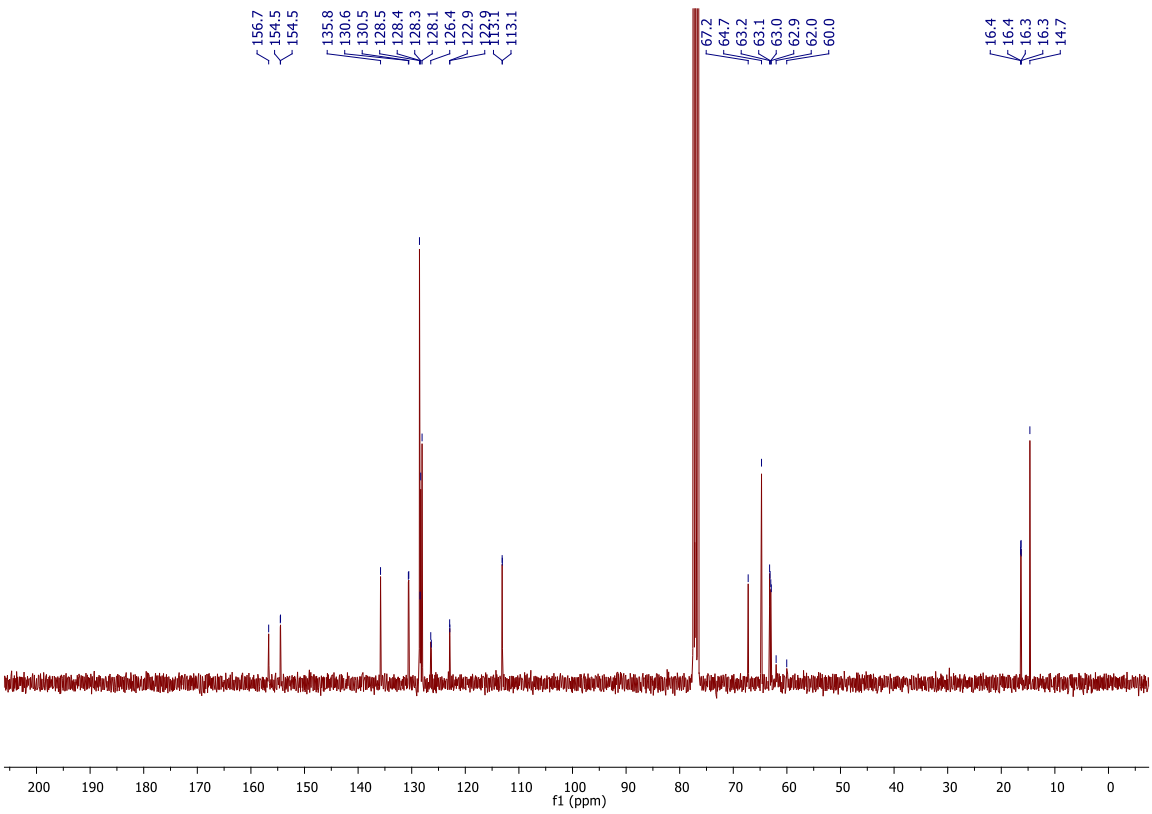
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ai**



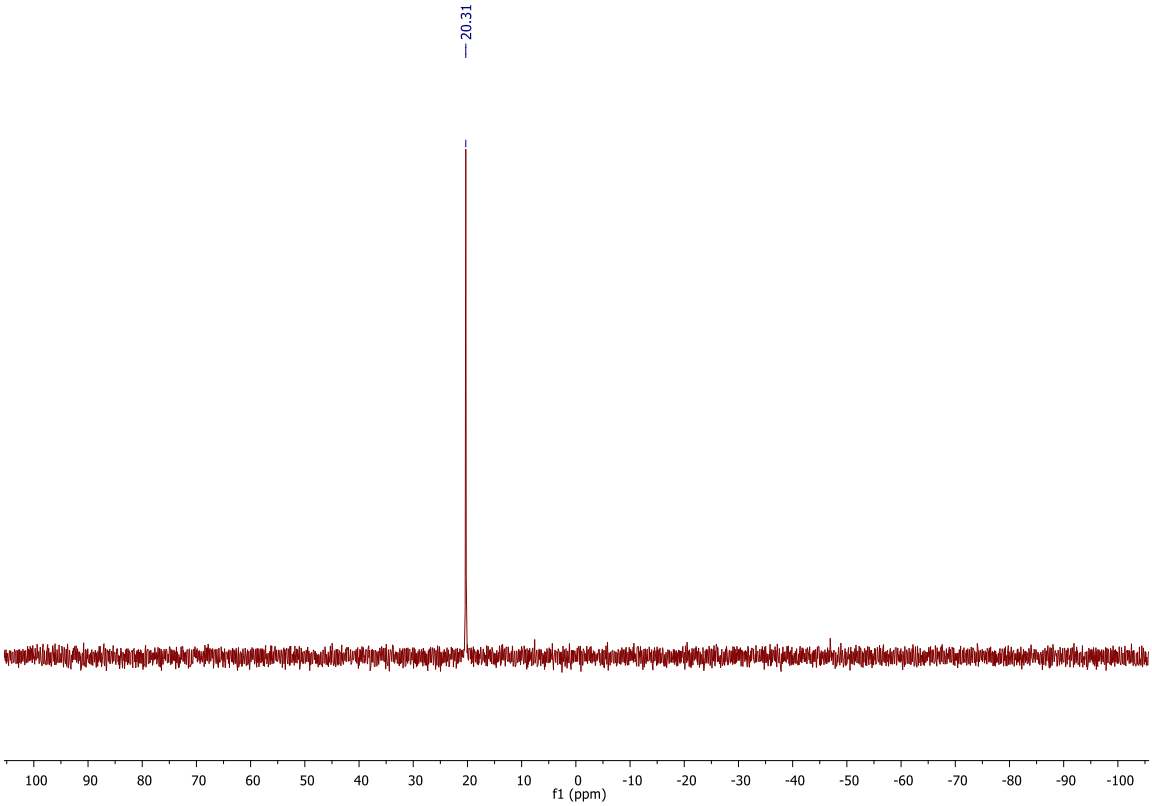
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Aj**



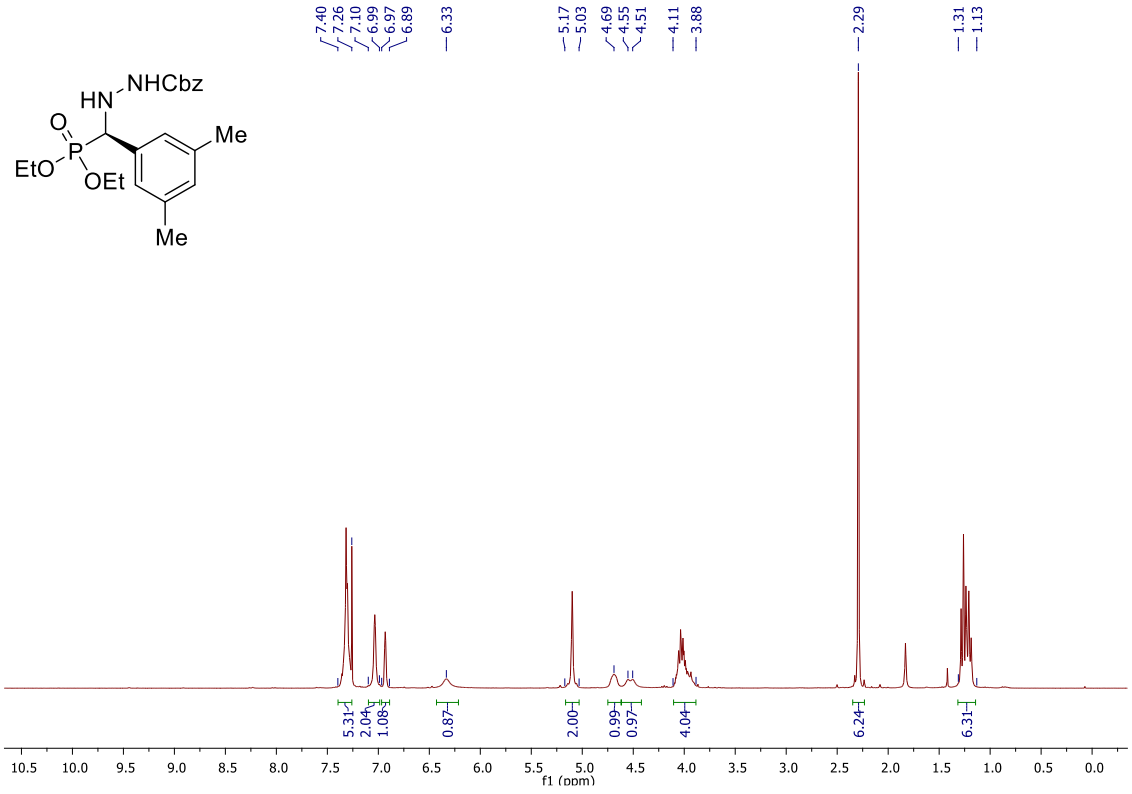
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Aj**



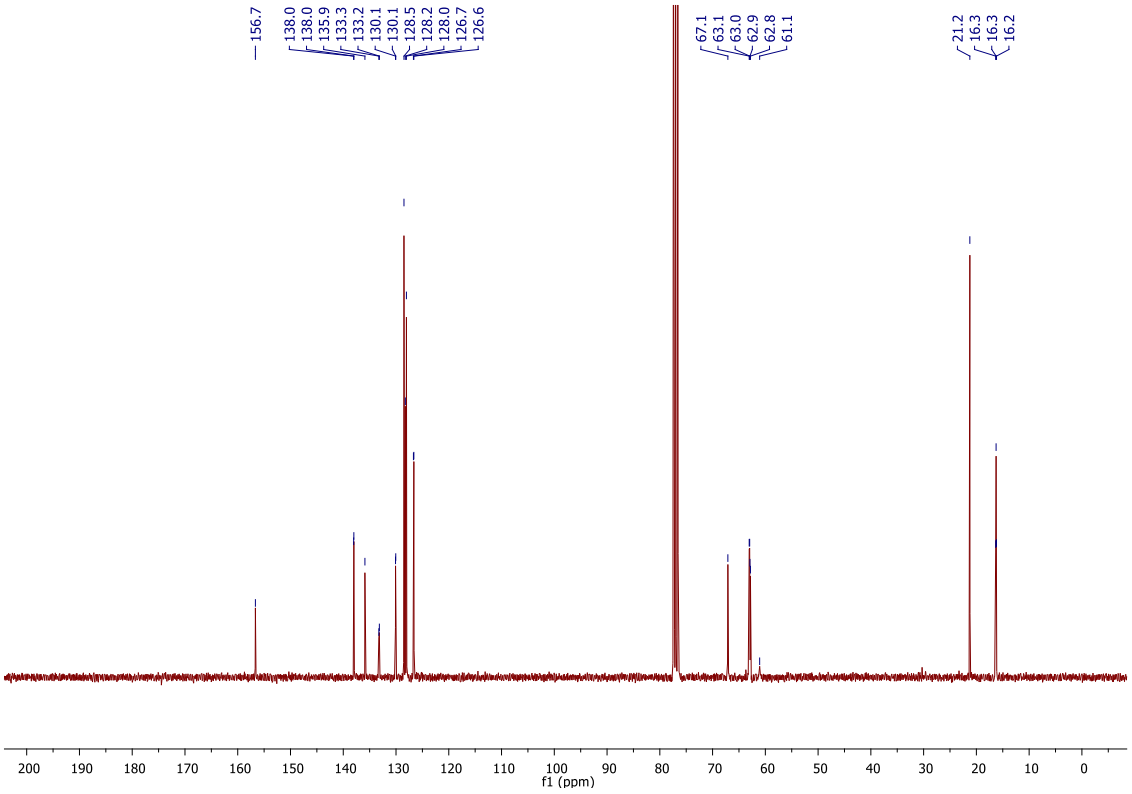
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Aj**



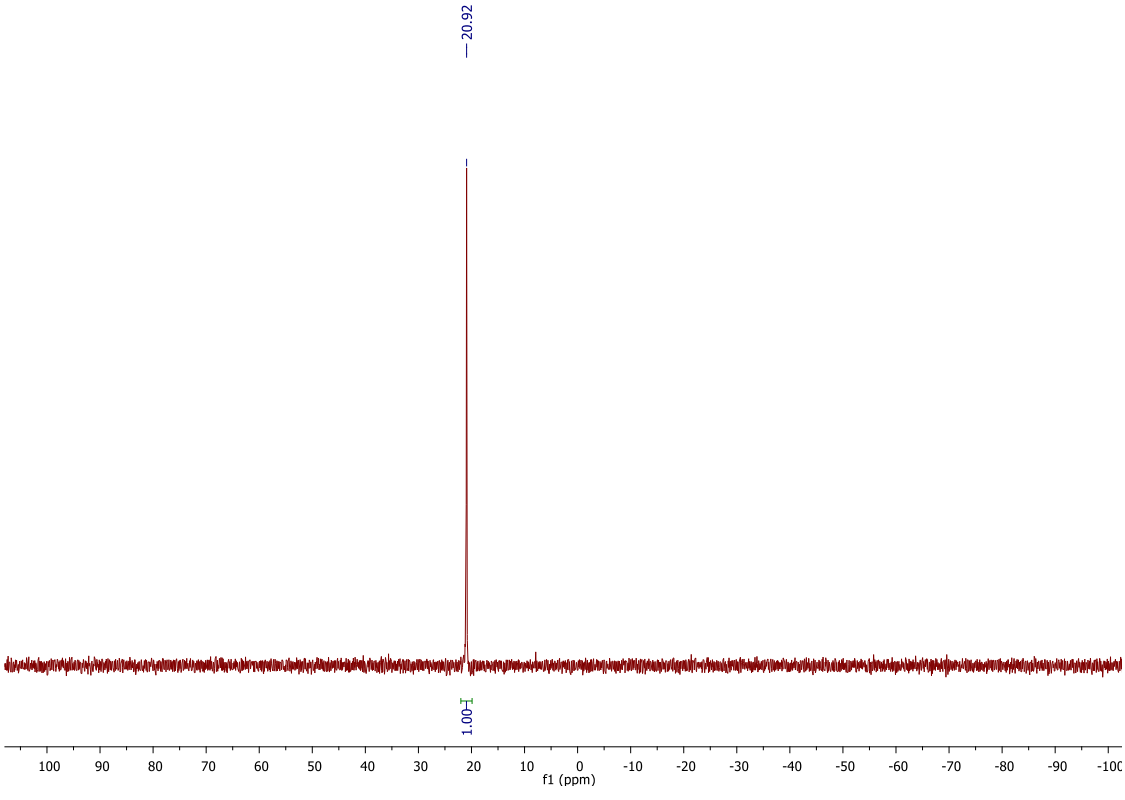
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ak**



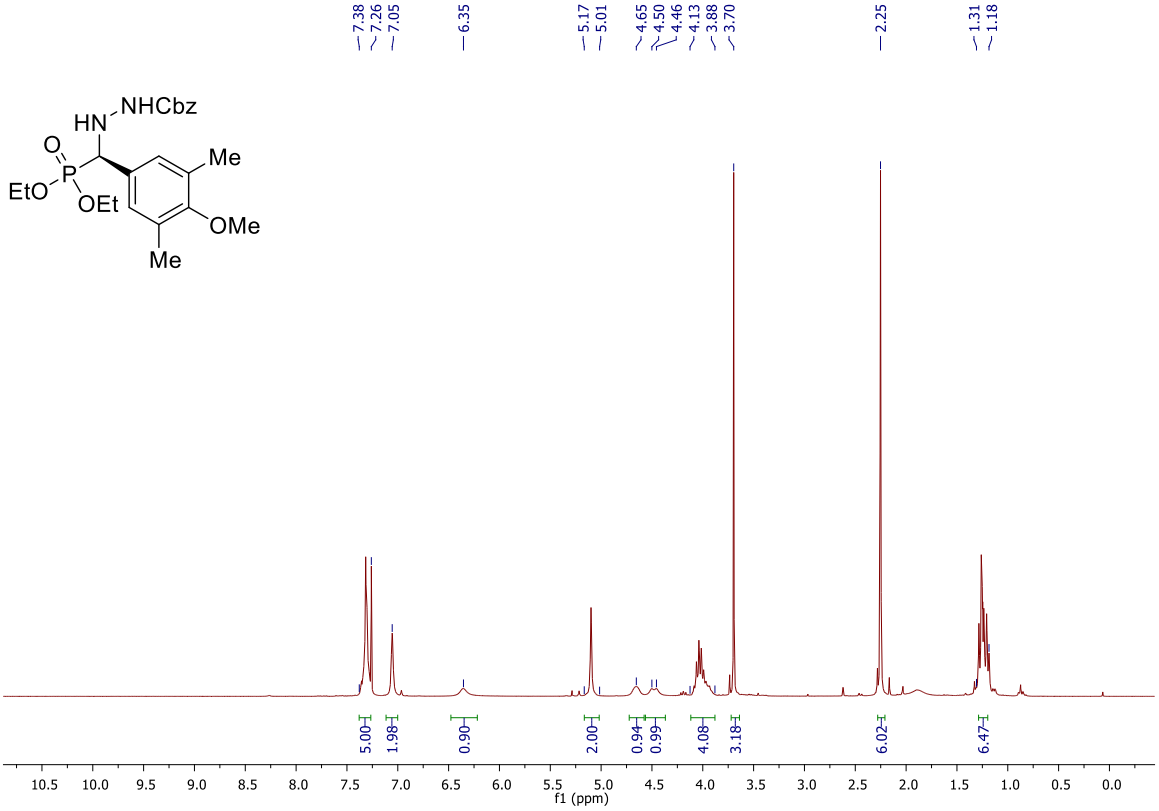
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ak**



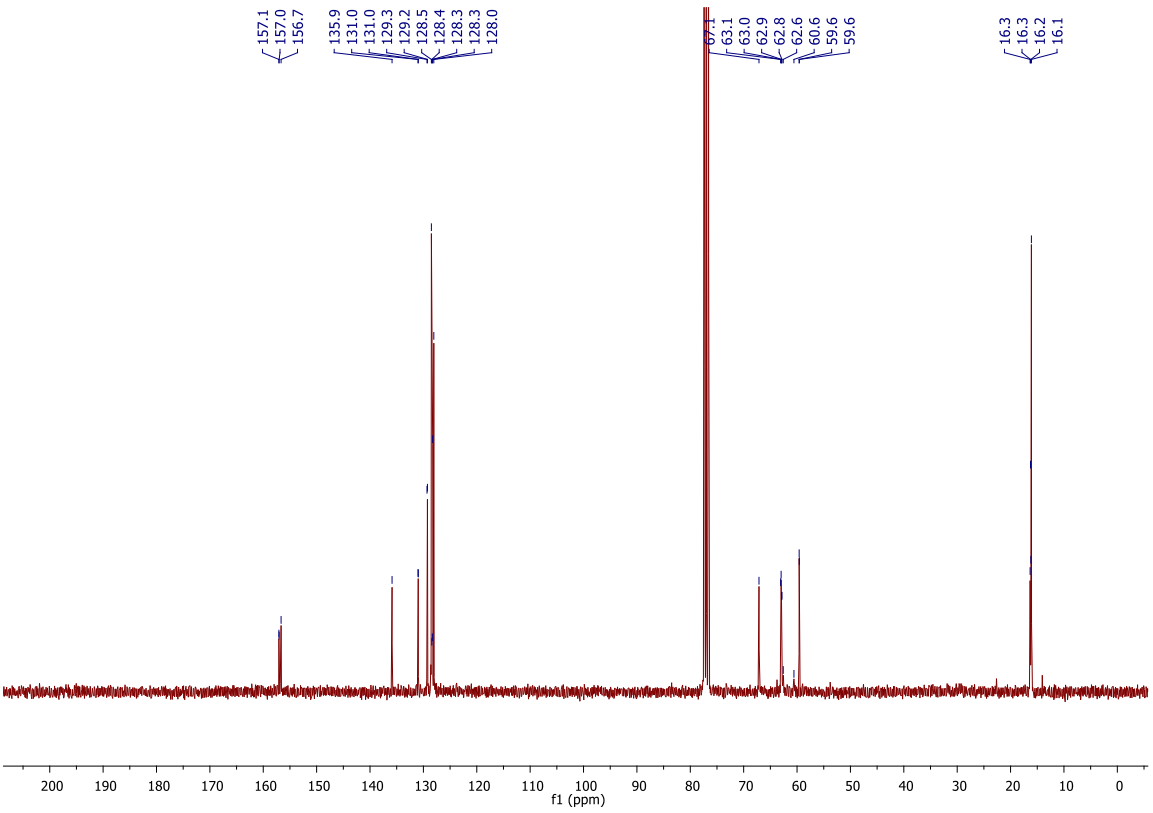
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ak**



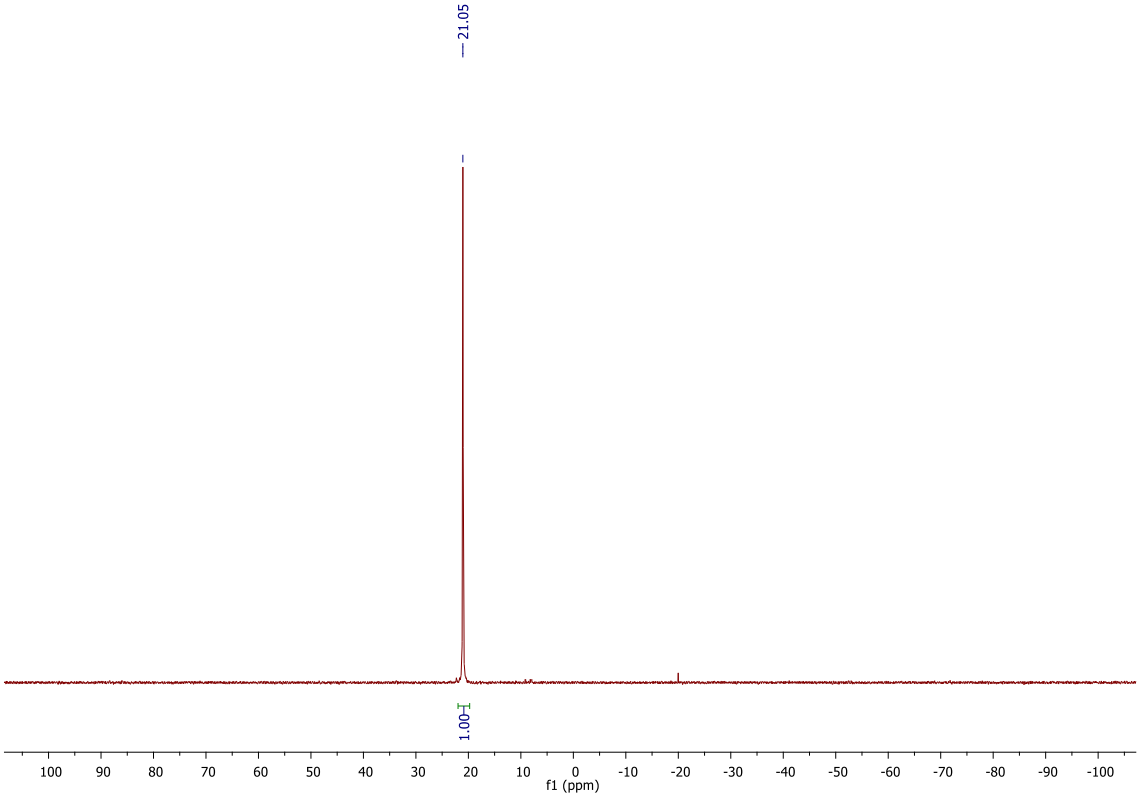
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Al**



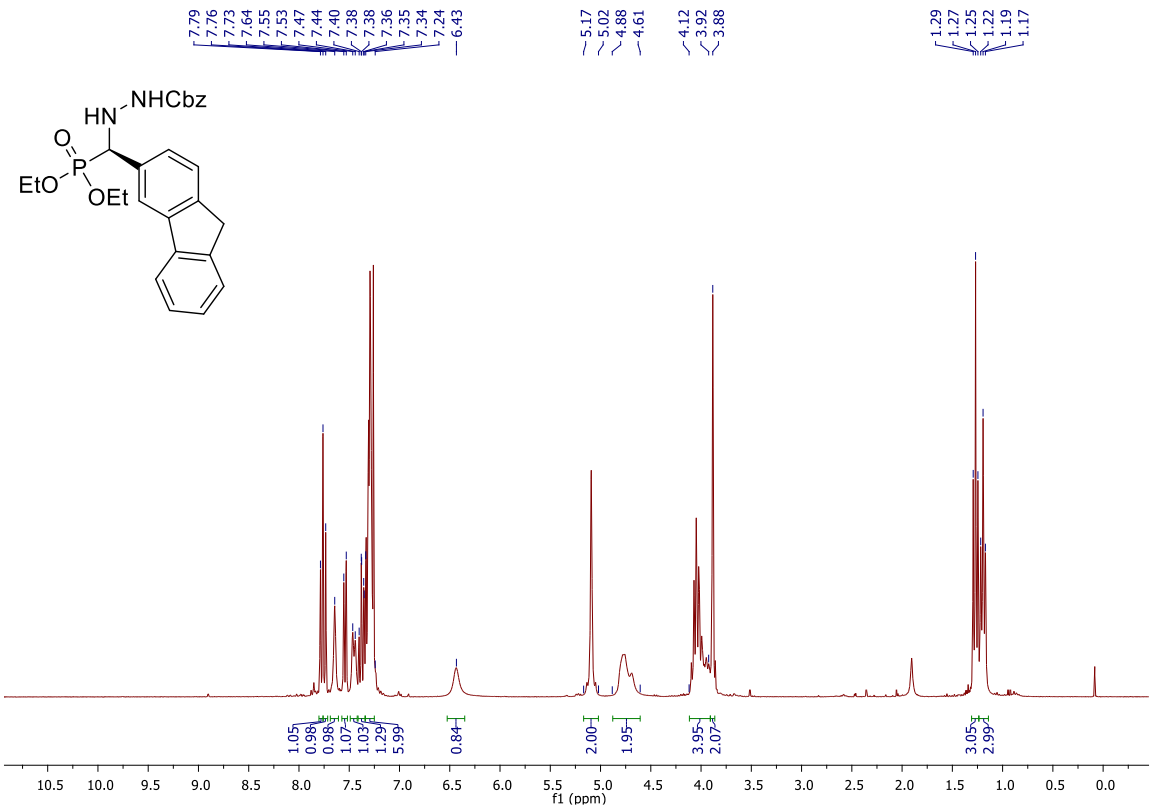
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Al**



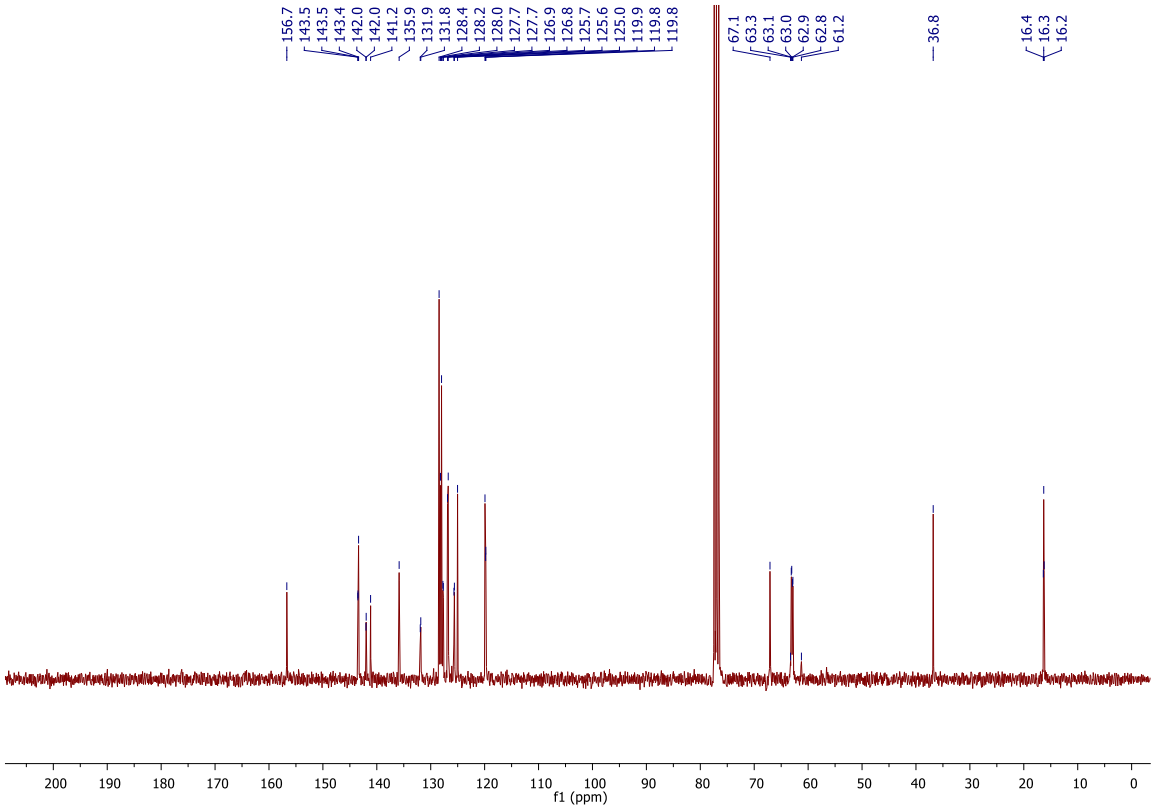
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Al**



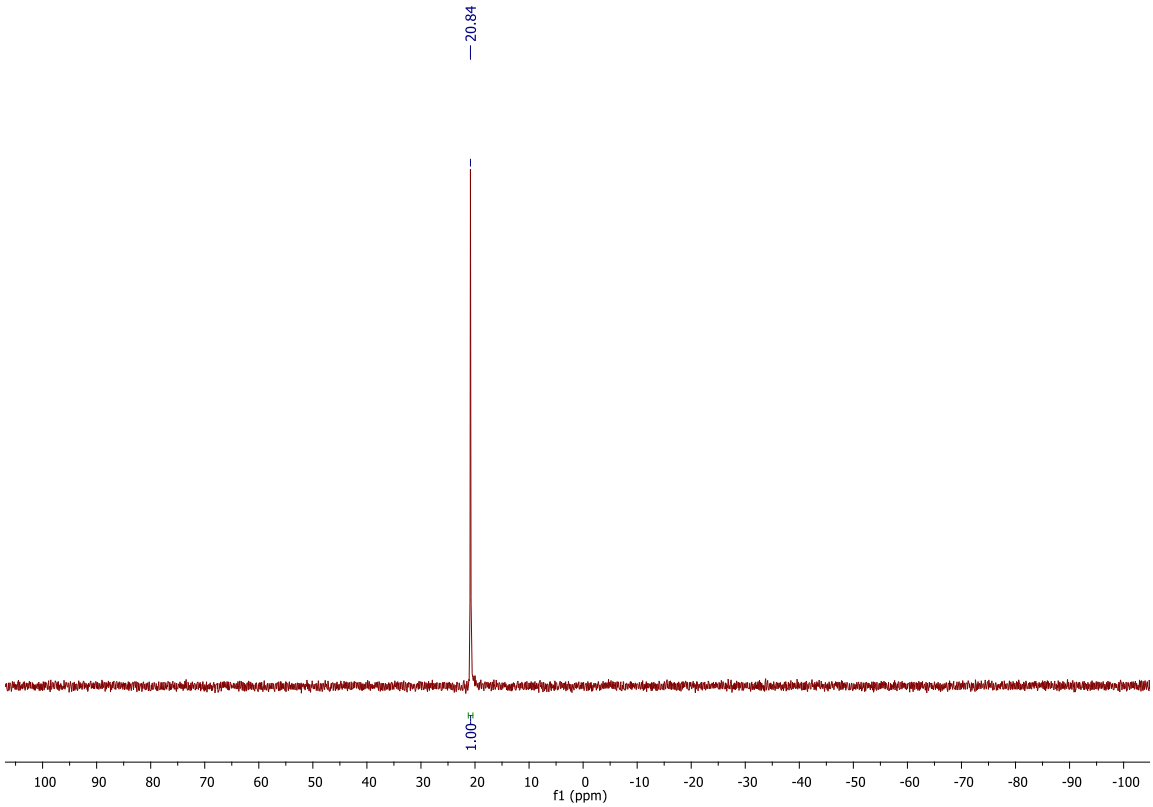
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Am**



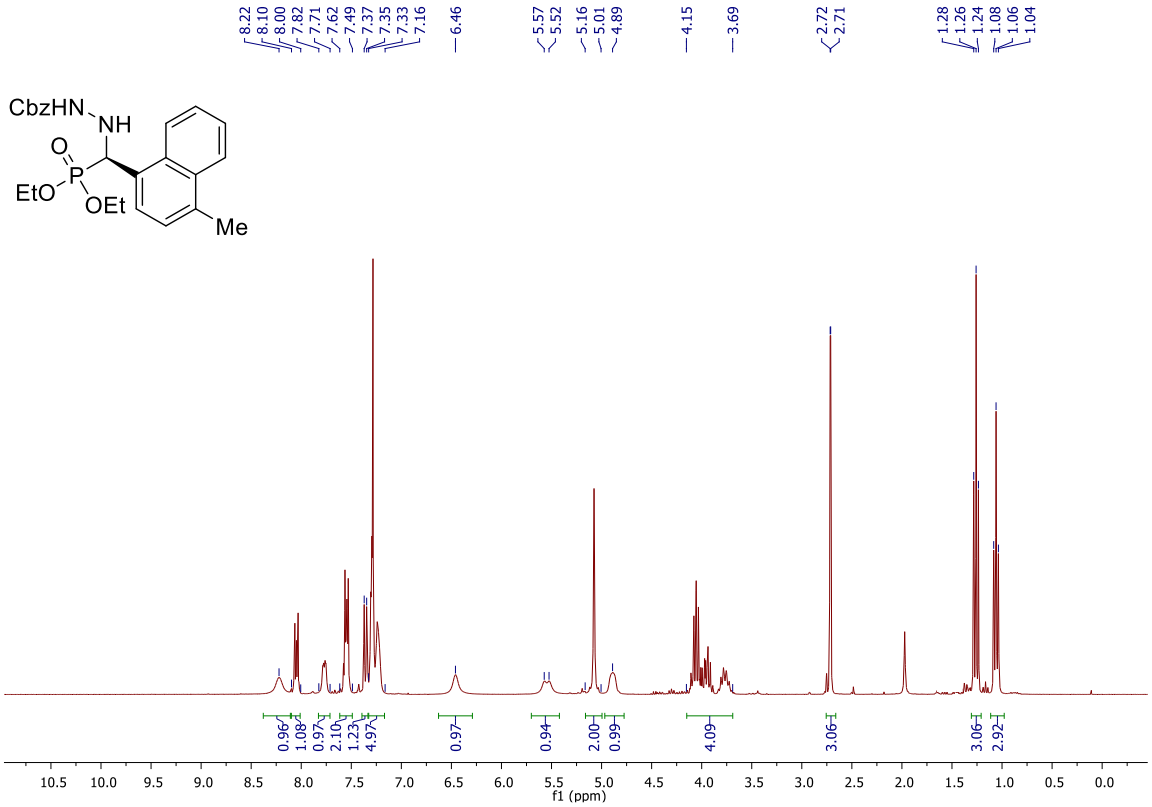
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Am**



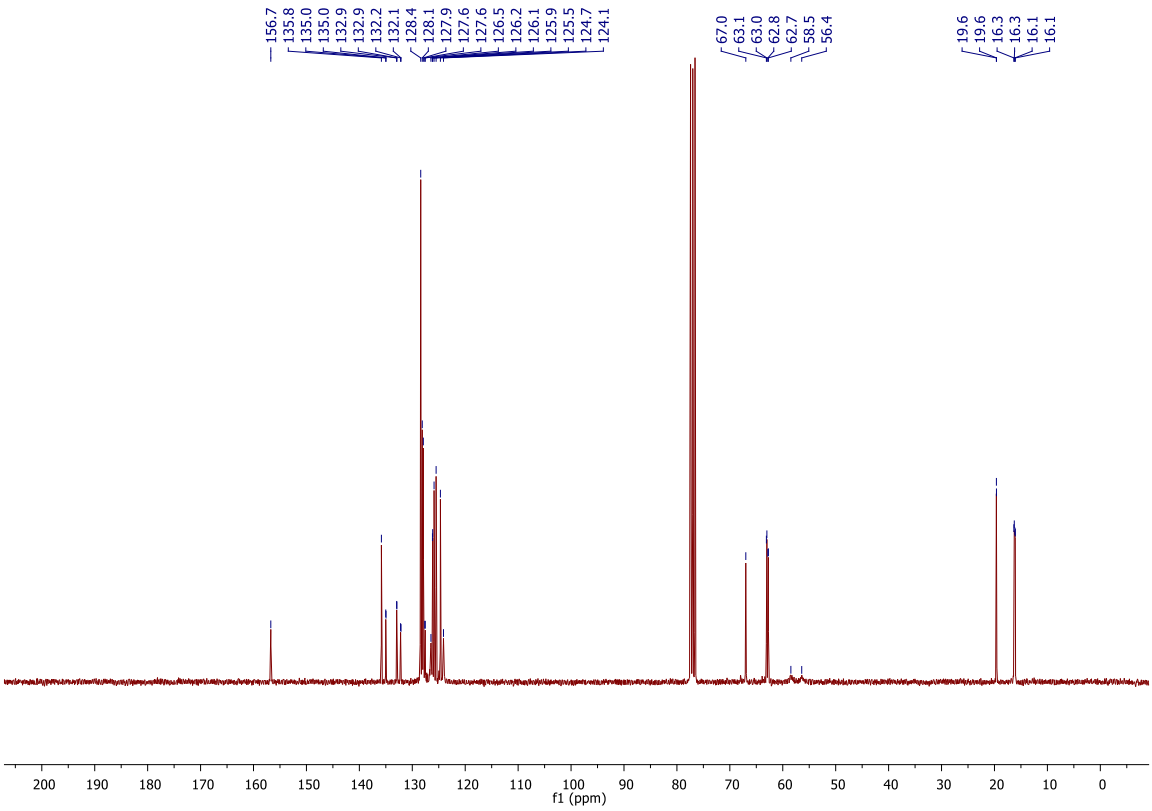
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Am**



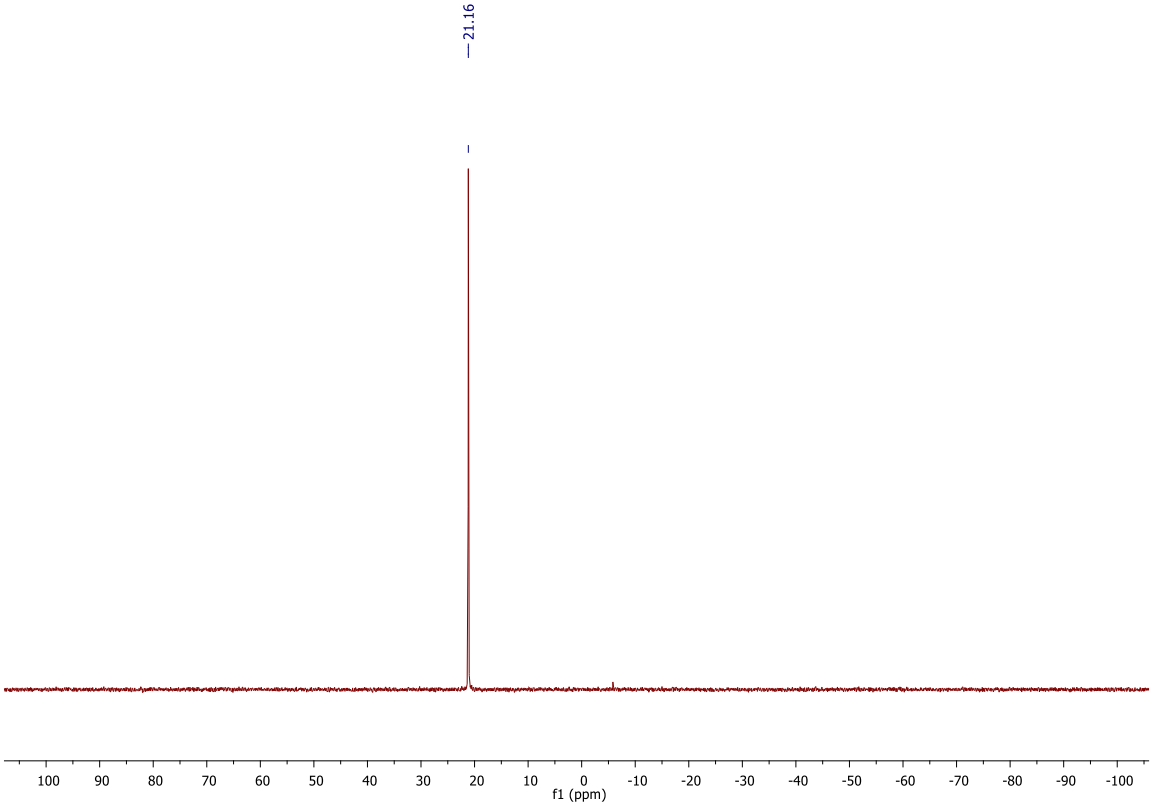
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3An**



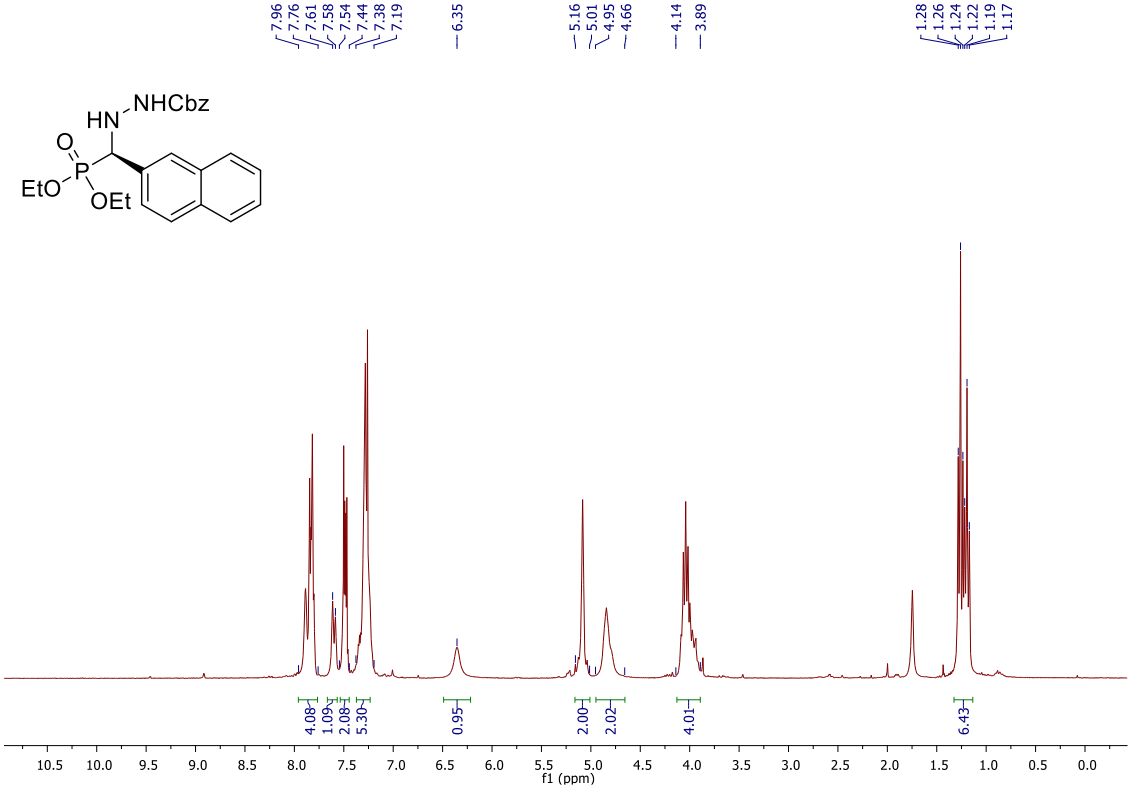
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3An**



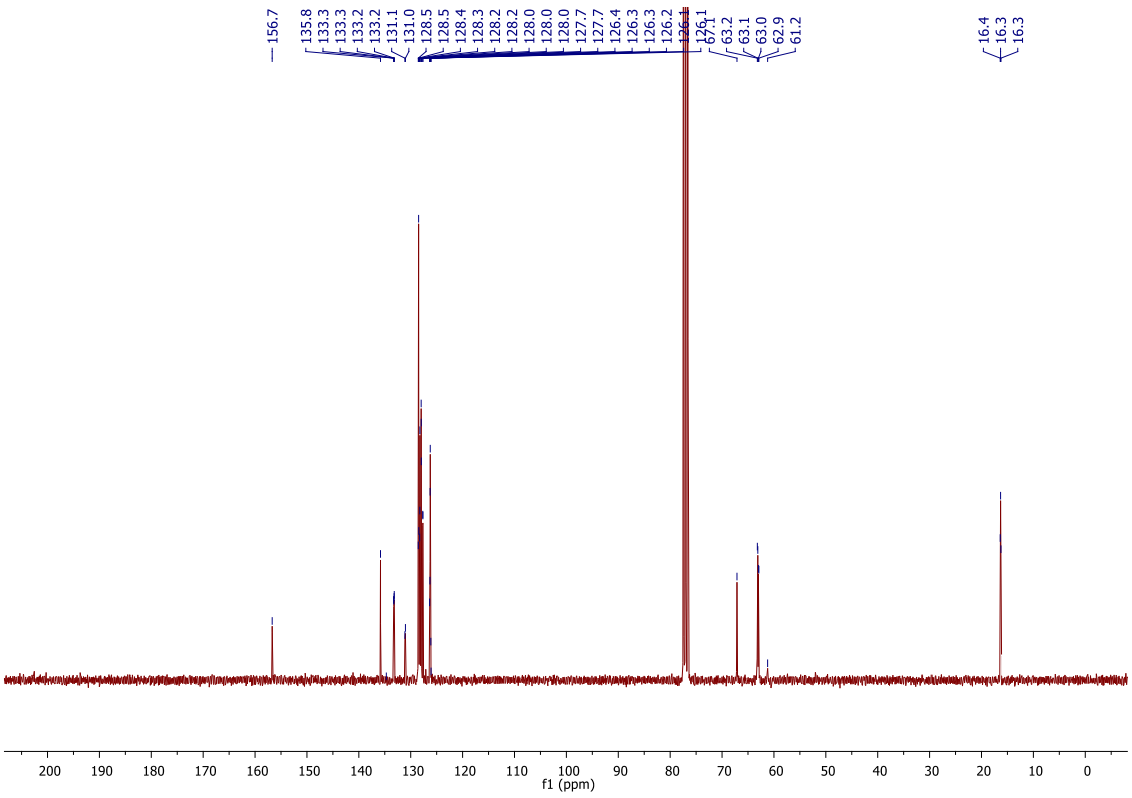
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3An**



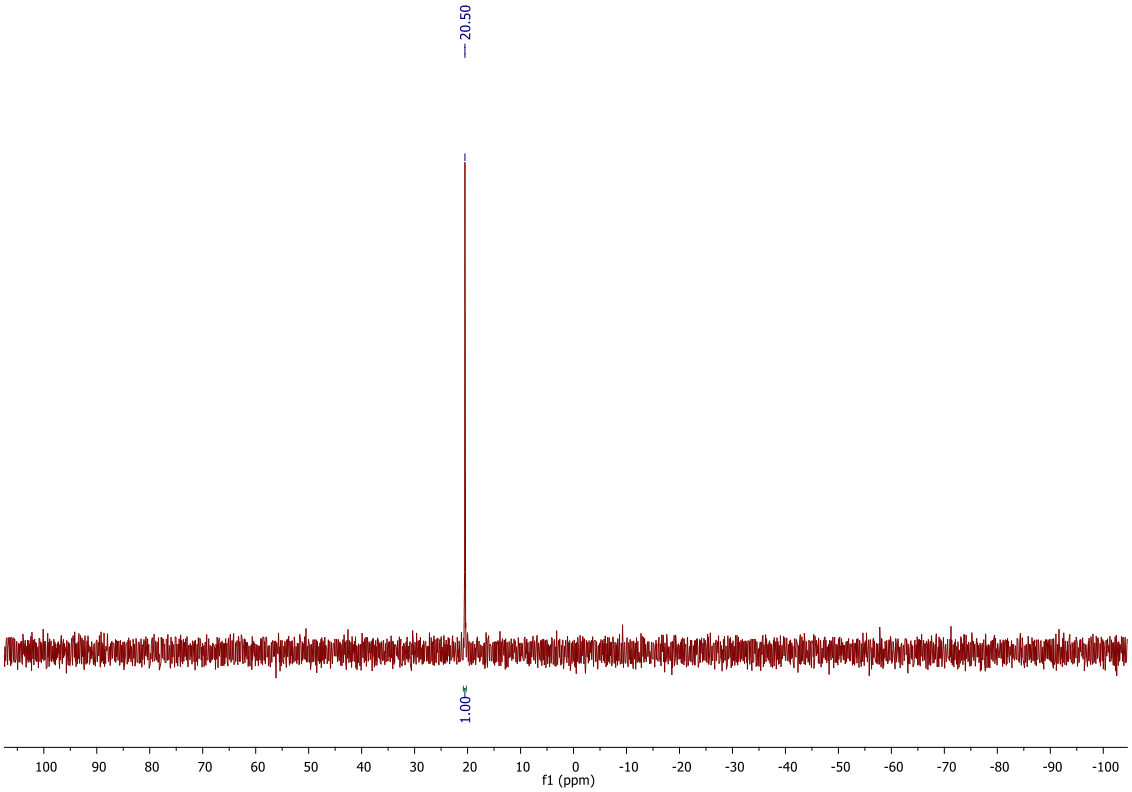
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Ao**



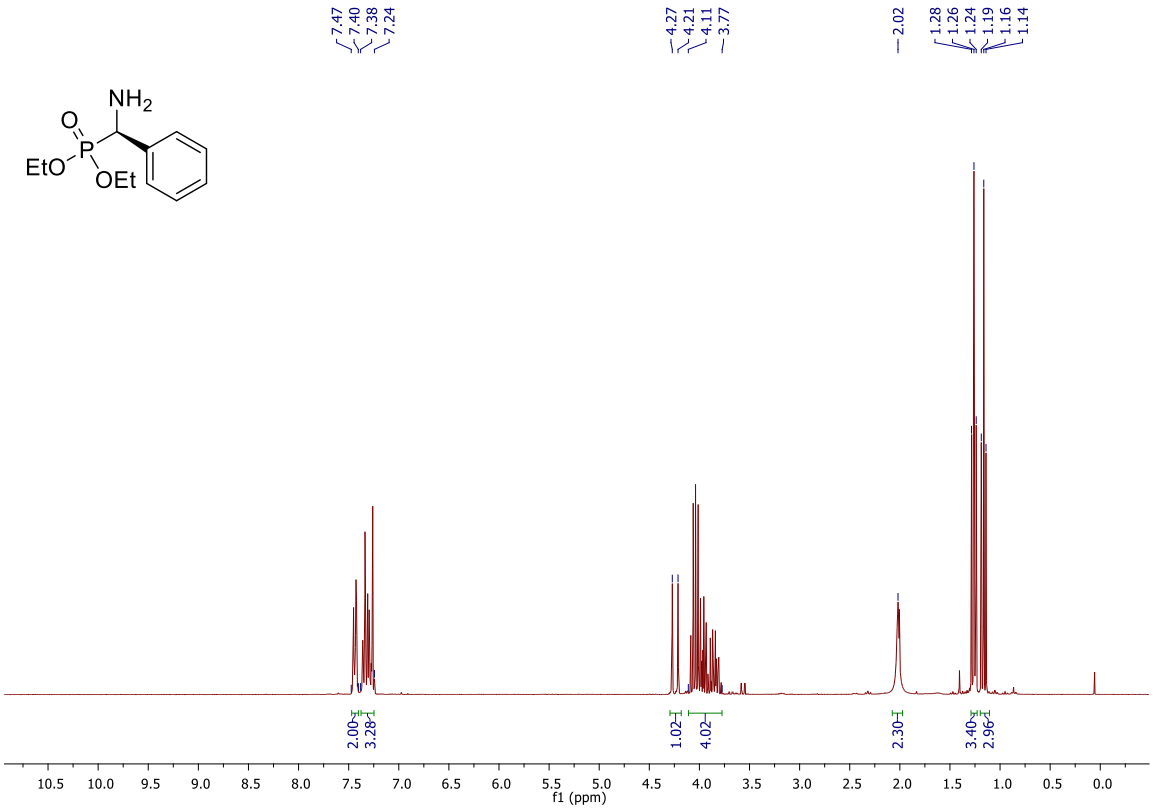
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Ao**



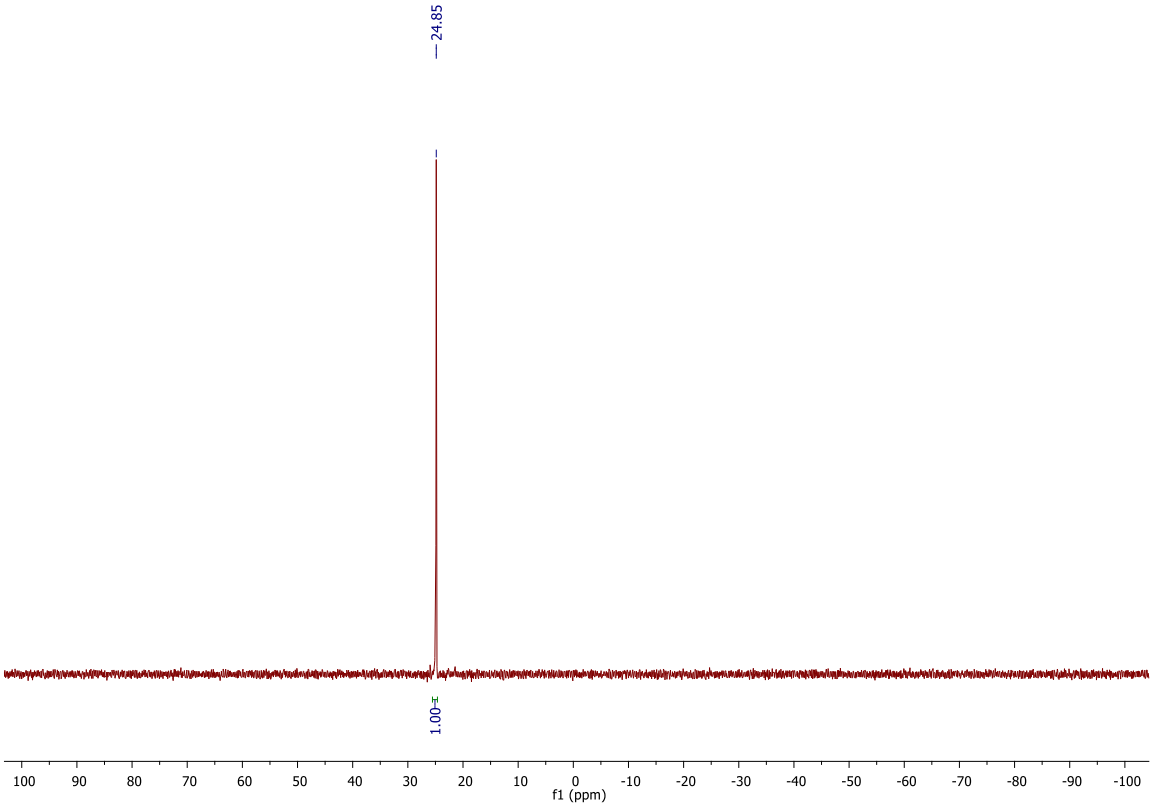
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3Ao**



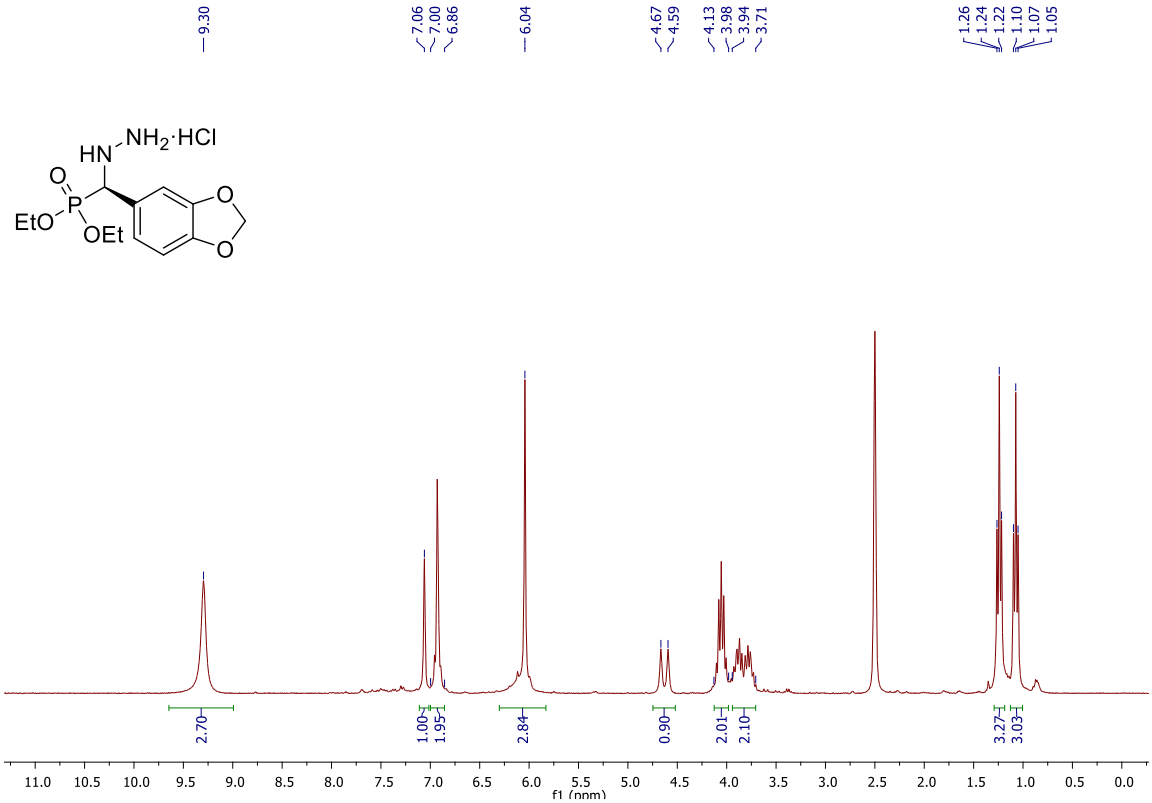
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3'Aa**



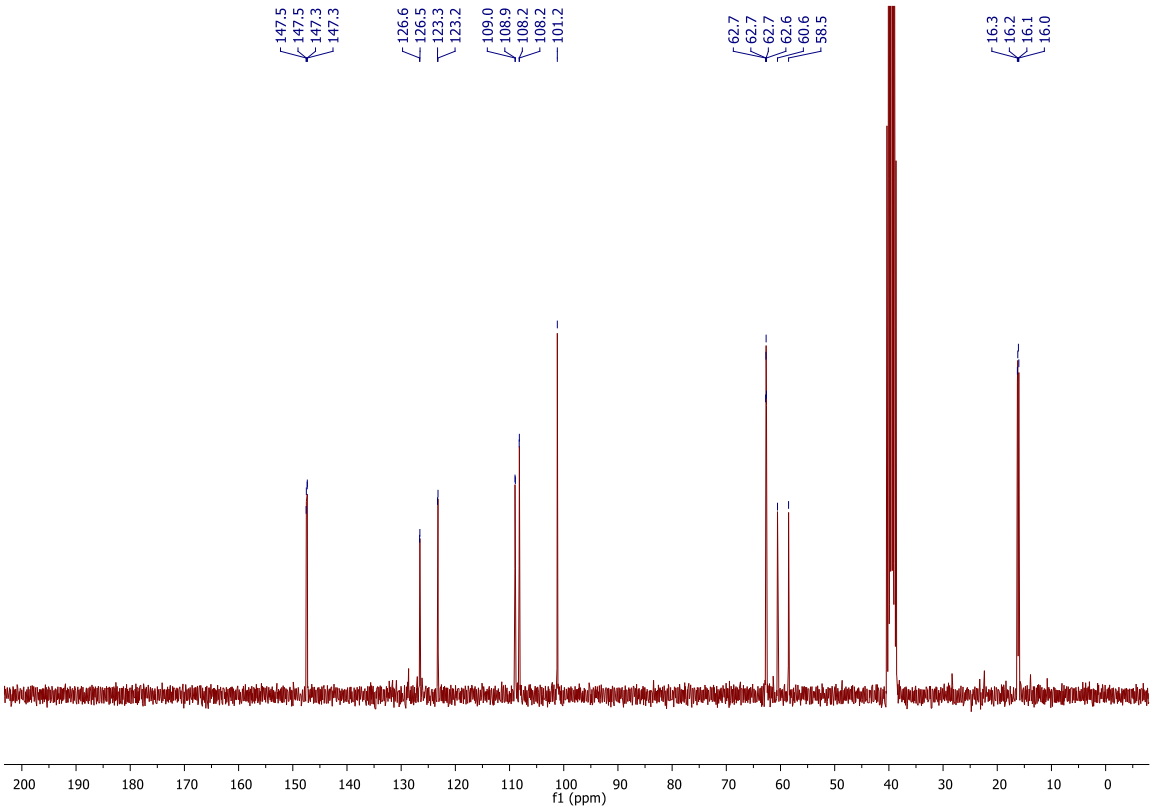
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**3'Aa**



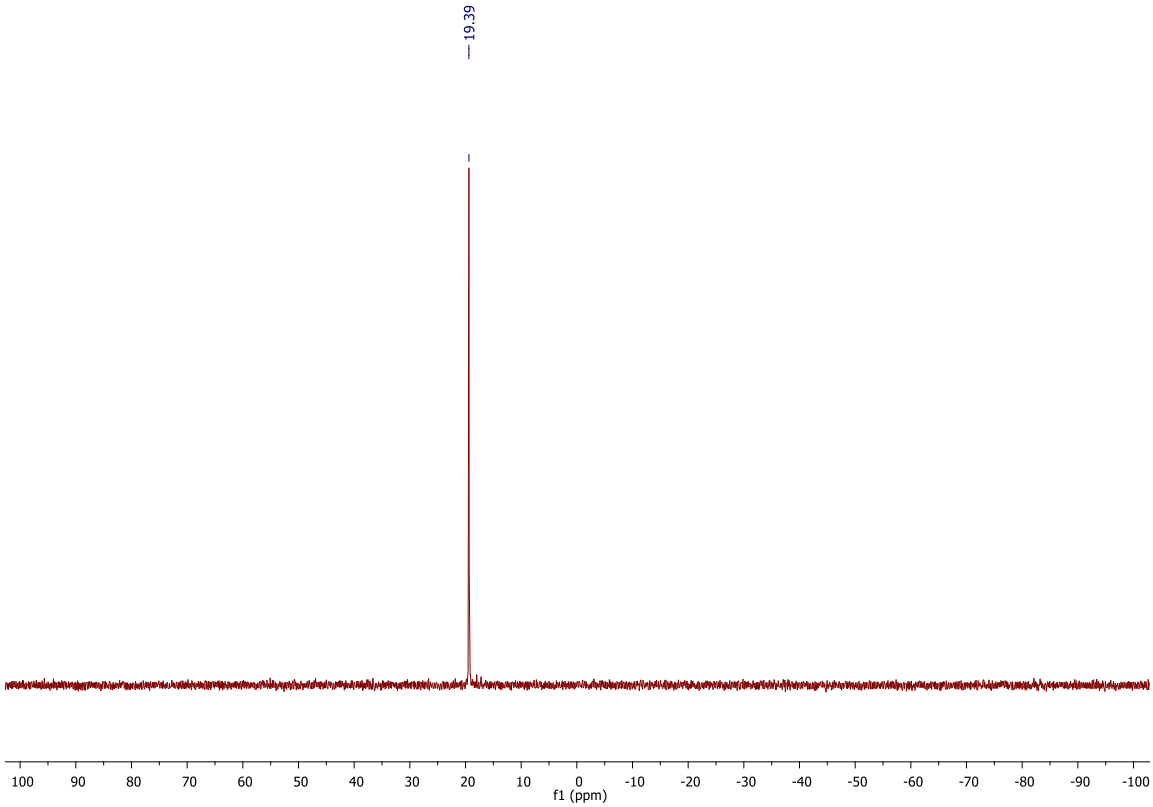
^{1}H NMR (300 MHz, DMSO-d^{6}) of (*R*)-**4i**



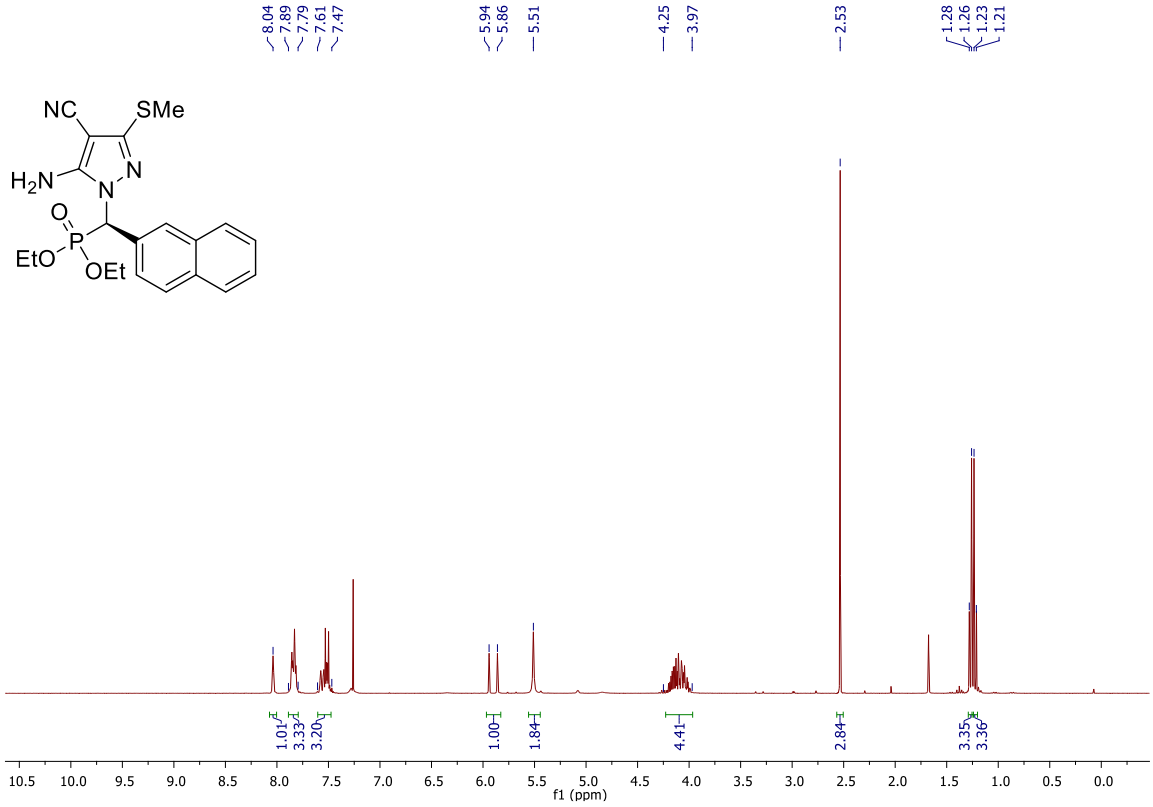
^{13}C NMR (75.5 MHz, DMSO-d^{6}) of (*R*)-**4i**



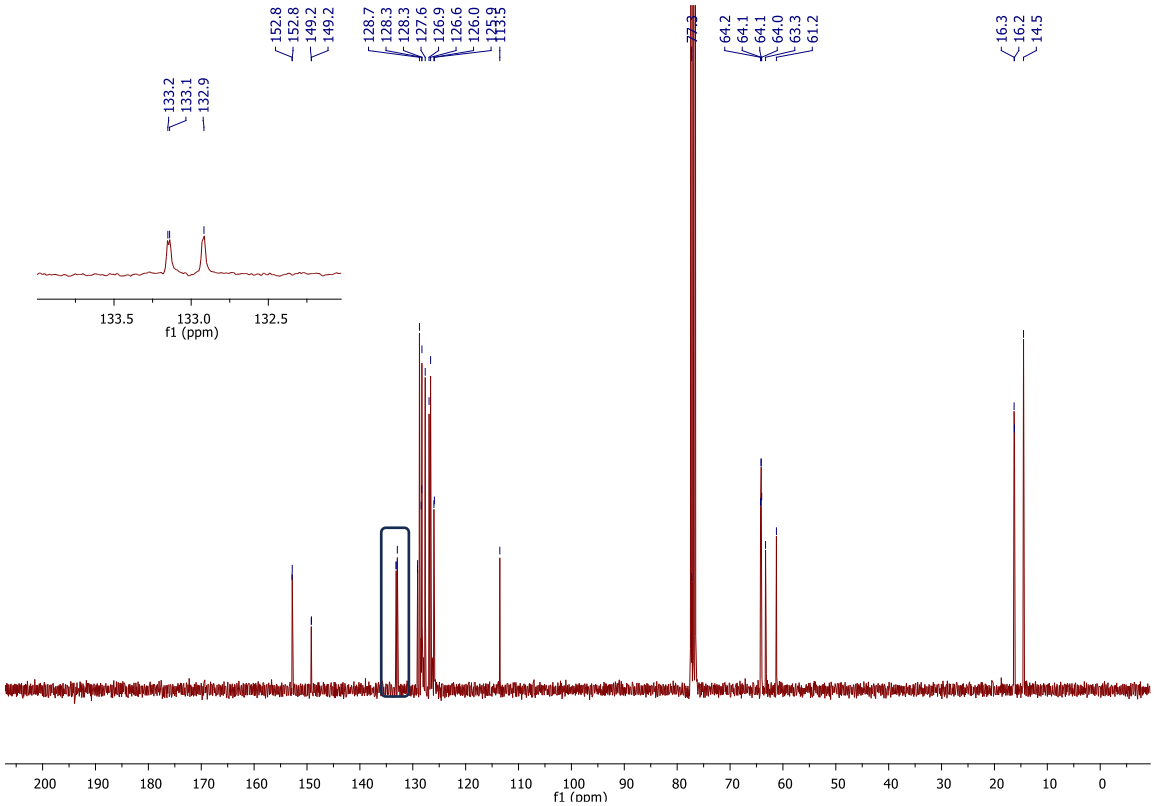
^{31}P NMR (122 MHz, DMSO-d^{6}) of (*R*)-**4i**



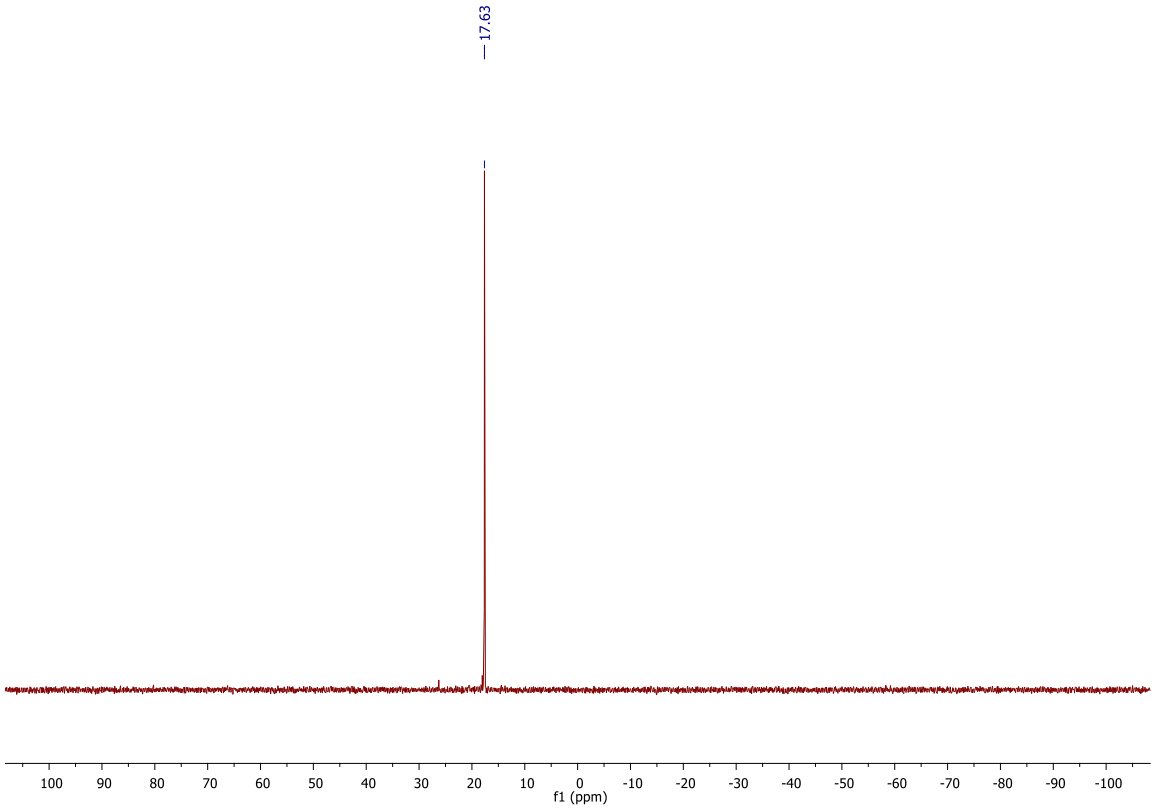
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**5o**



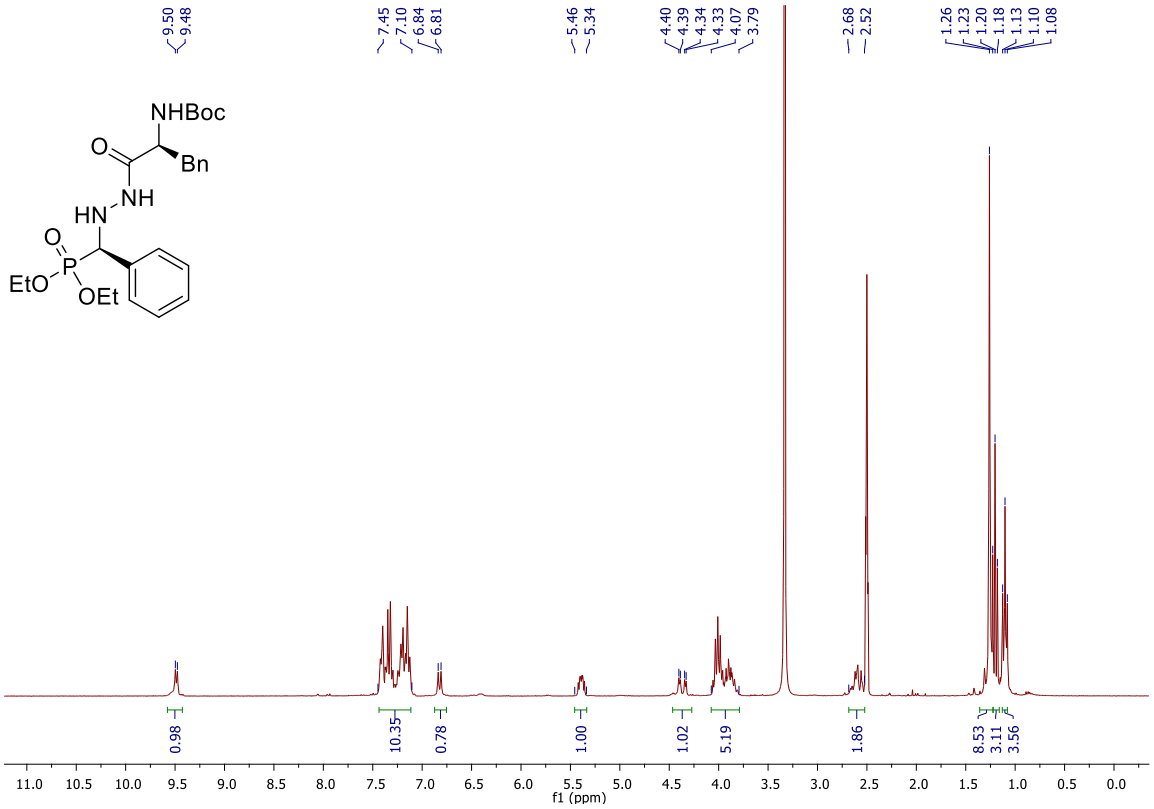
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**5o**



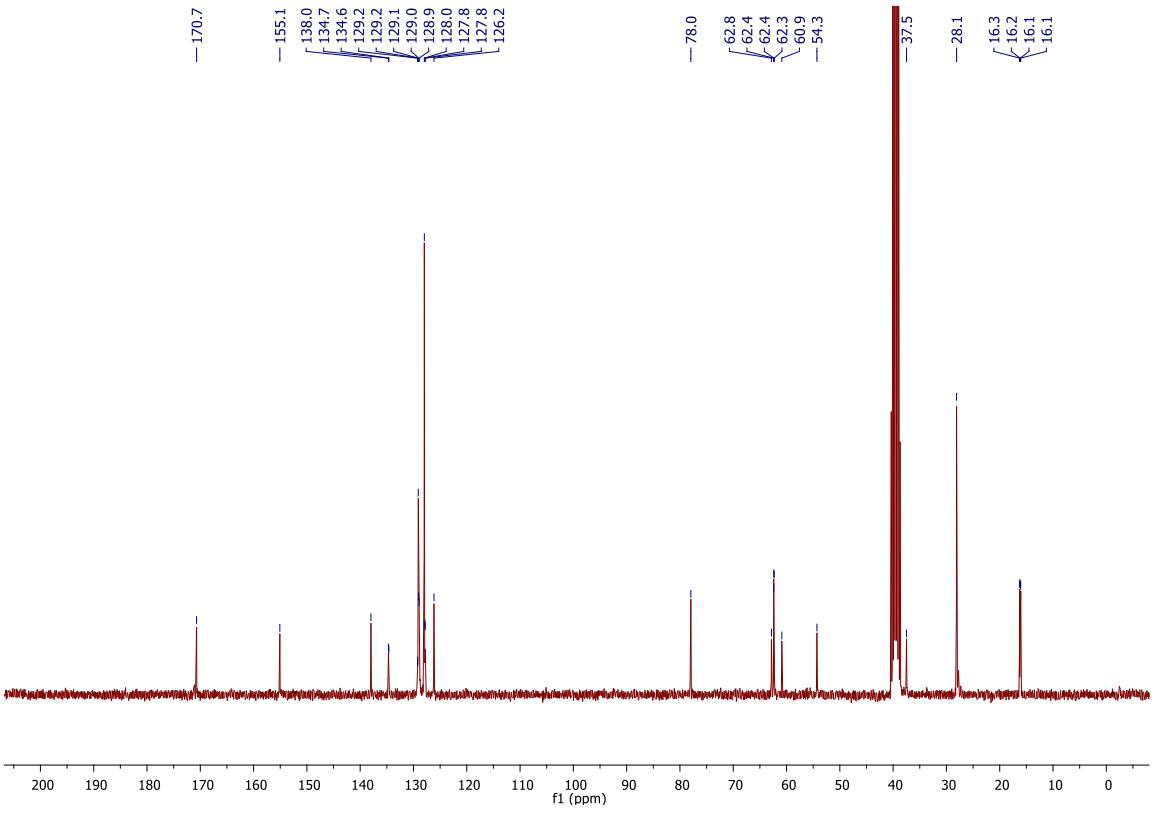
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**5o**



^{1}H NMR (300 MHz, DMSO-d^{6}) of (*R*)-**6a**



^{13}C NMR (75.5 MHz, DMSO-d^{6}) of (*R*)-**6a**



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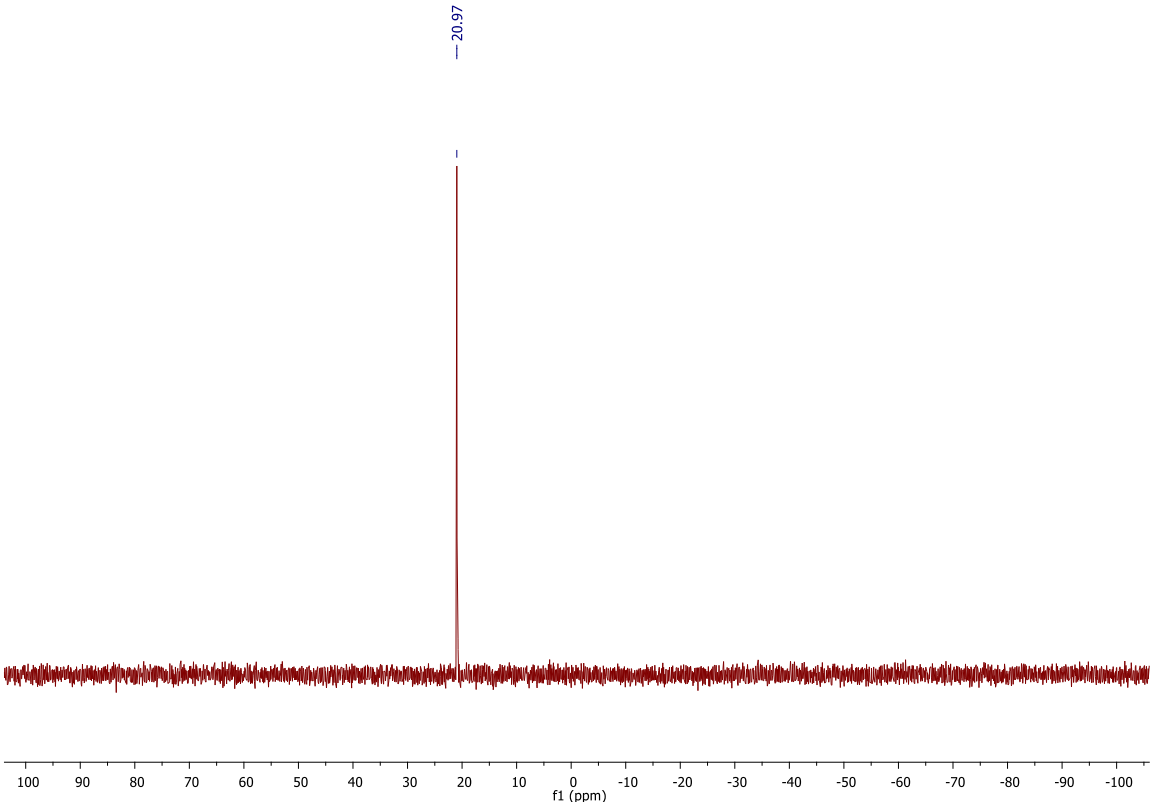

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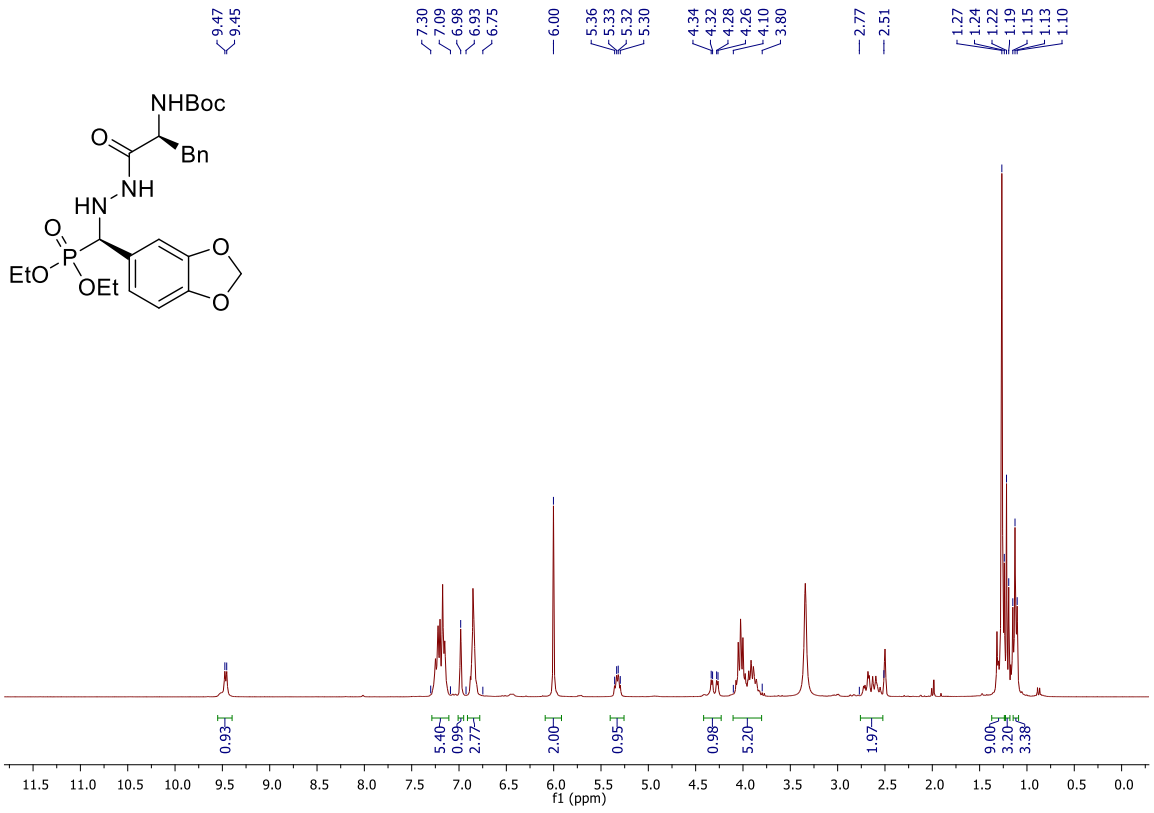
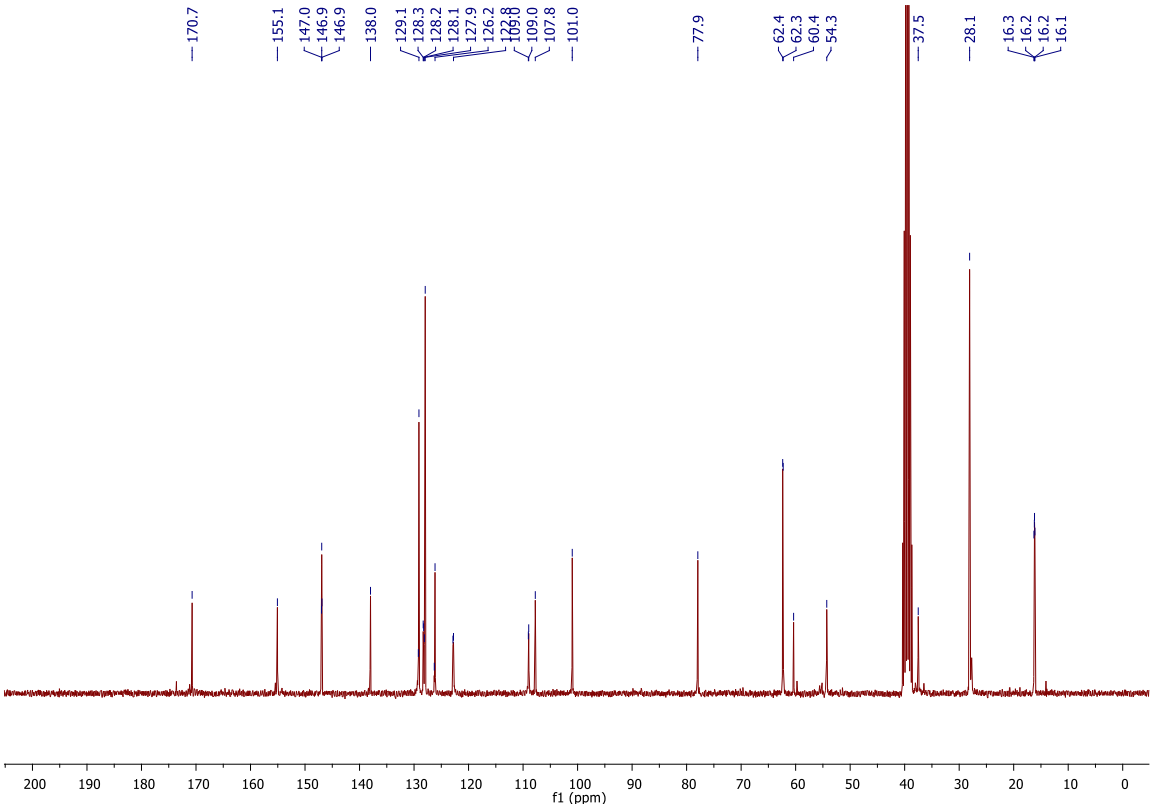
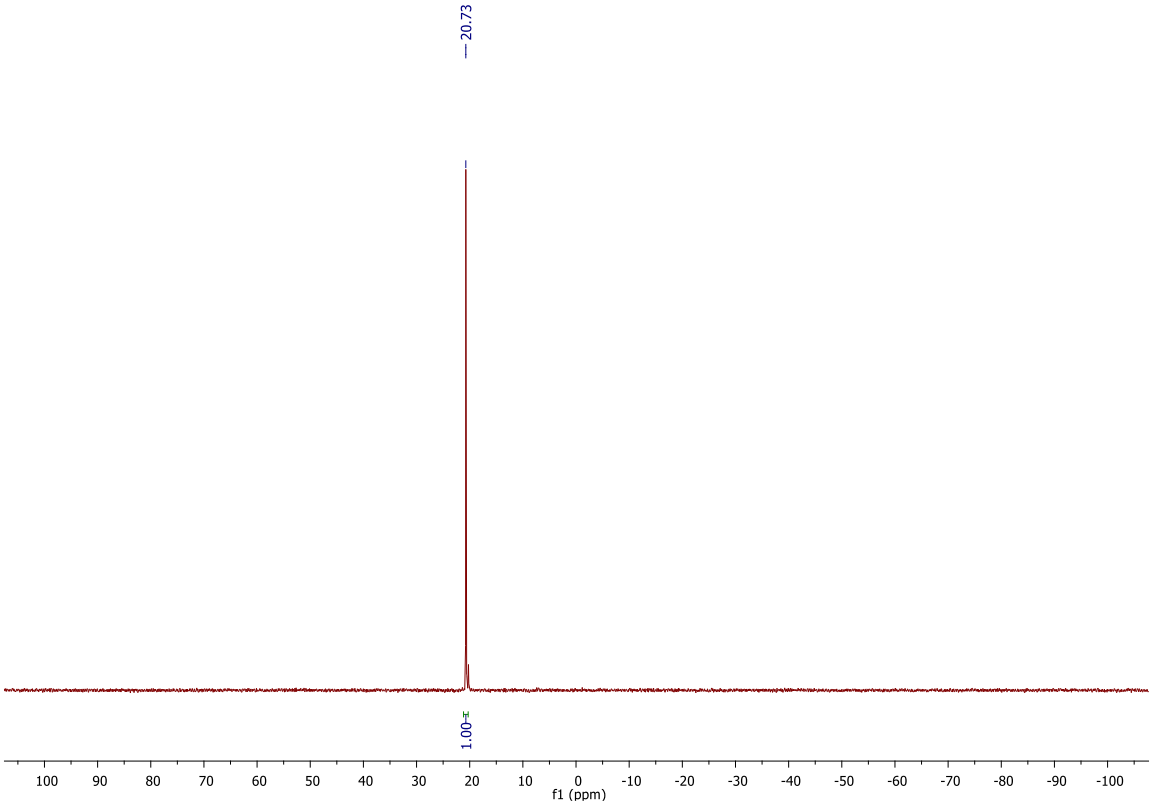


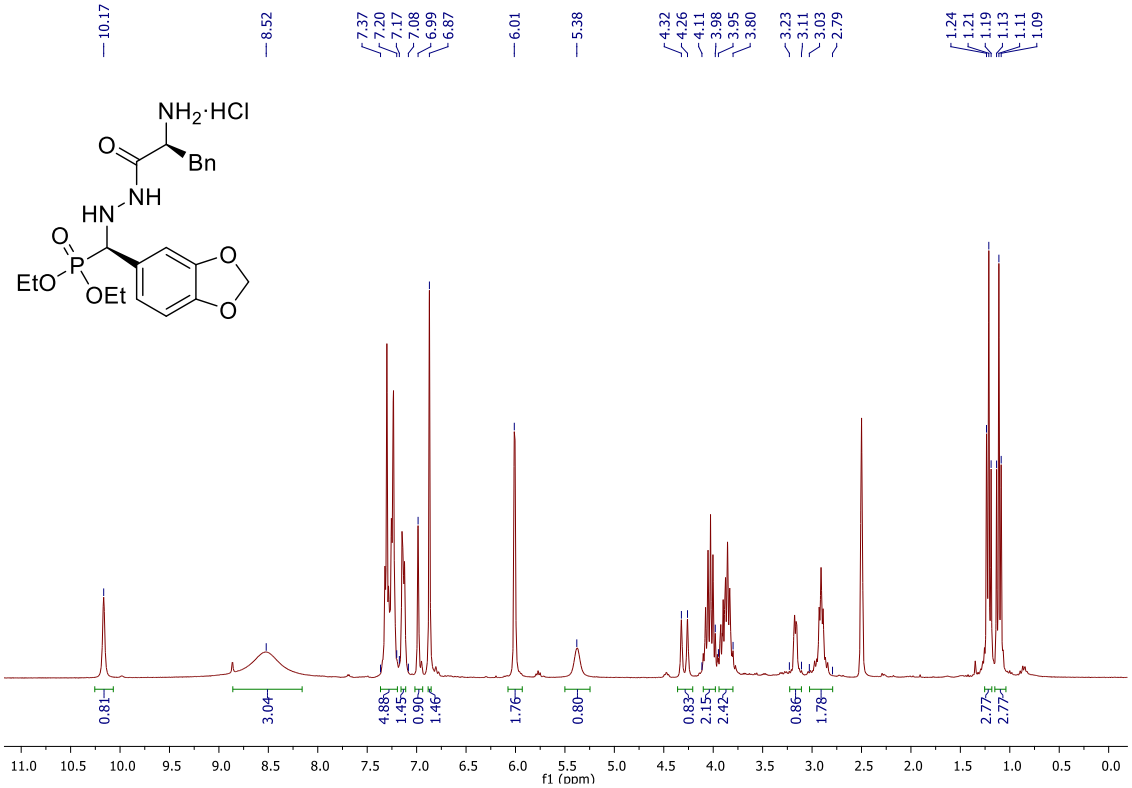
^{13}C NMR (75.5 MHz, DMSO-d^{6}) of (*R*)-**6i**



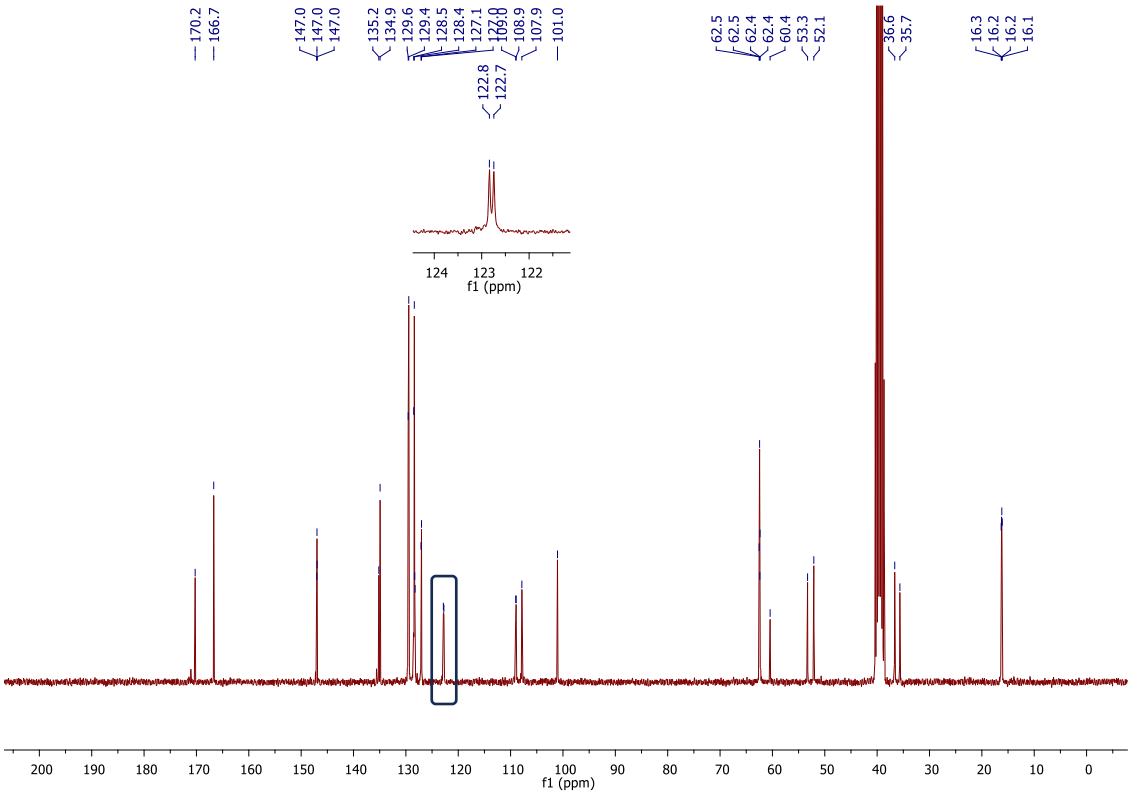
^{31}P NMR (122 MHz, DMSO-d^{6}) of (*R*)-**6i**



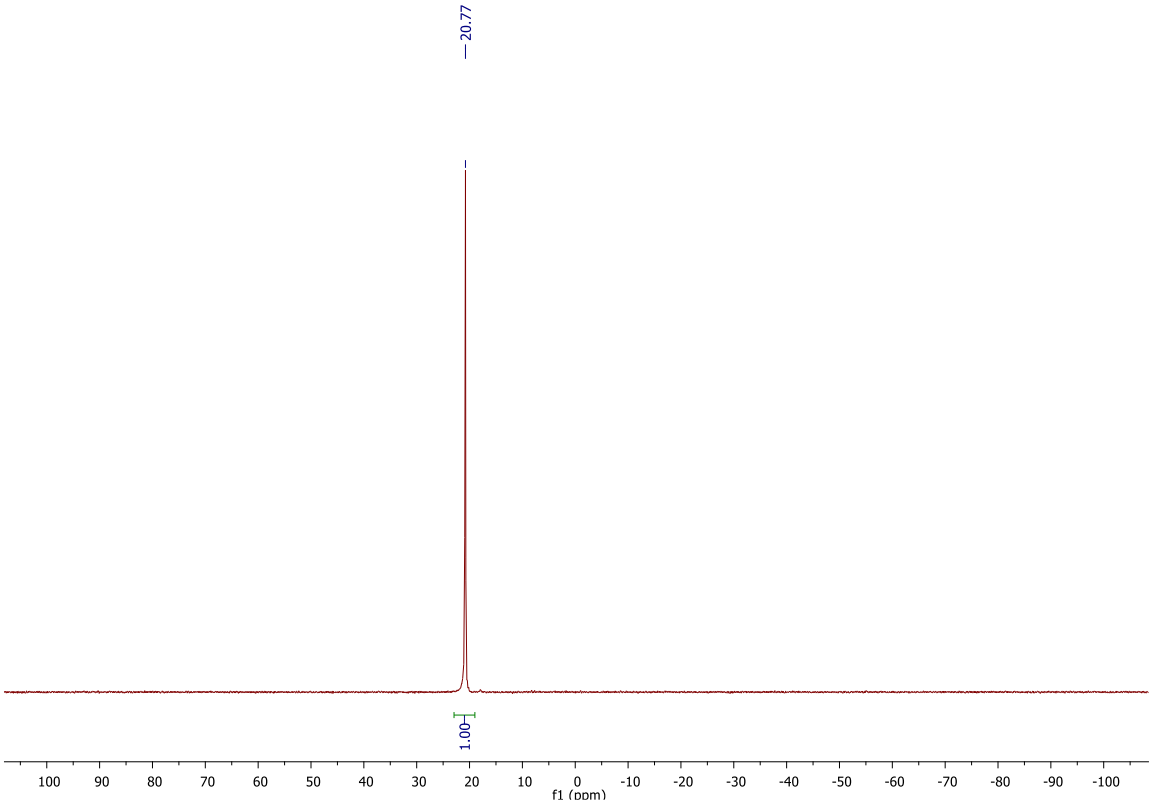
^{1}H NMR (300 MHz, DMSO-d^{6}) of (*R*)-**7i**



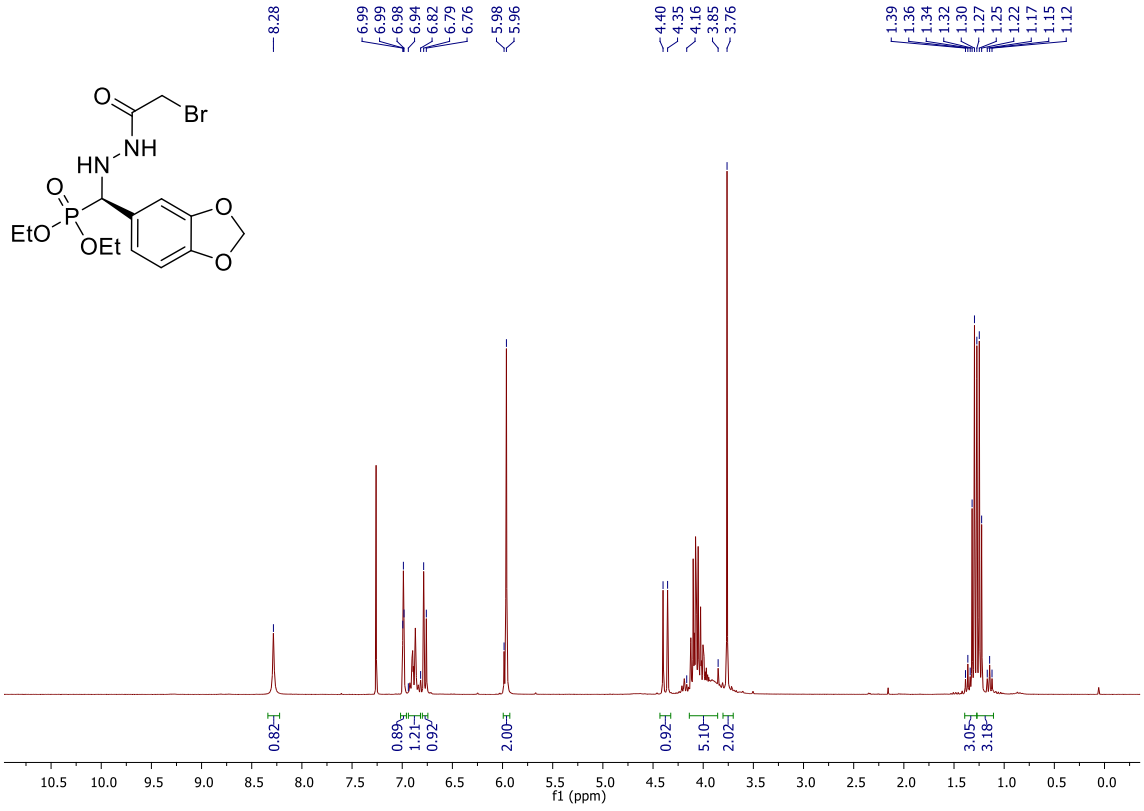
^{13}C NMR (75.5 MHz, DMSO-d^{6}) of (*R*)-**7i**



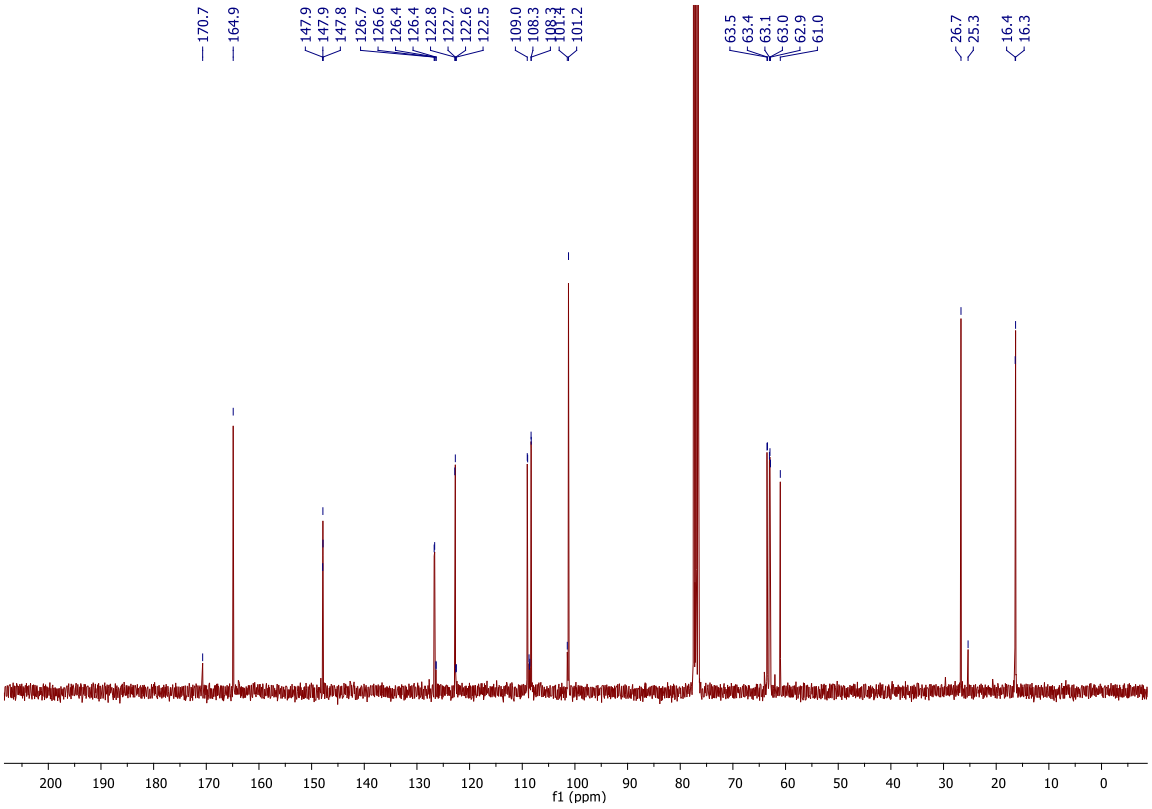
^{31}P NMR (122 MHz, DMSO-d^{6}) of (*R*)-**7i**



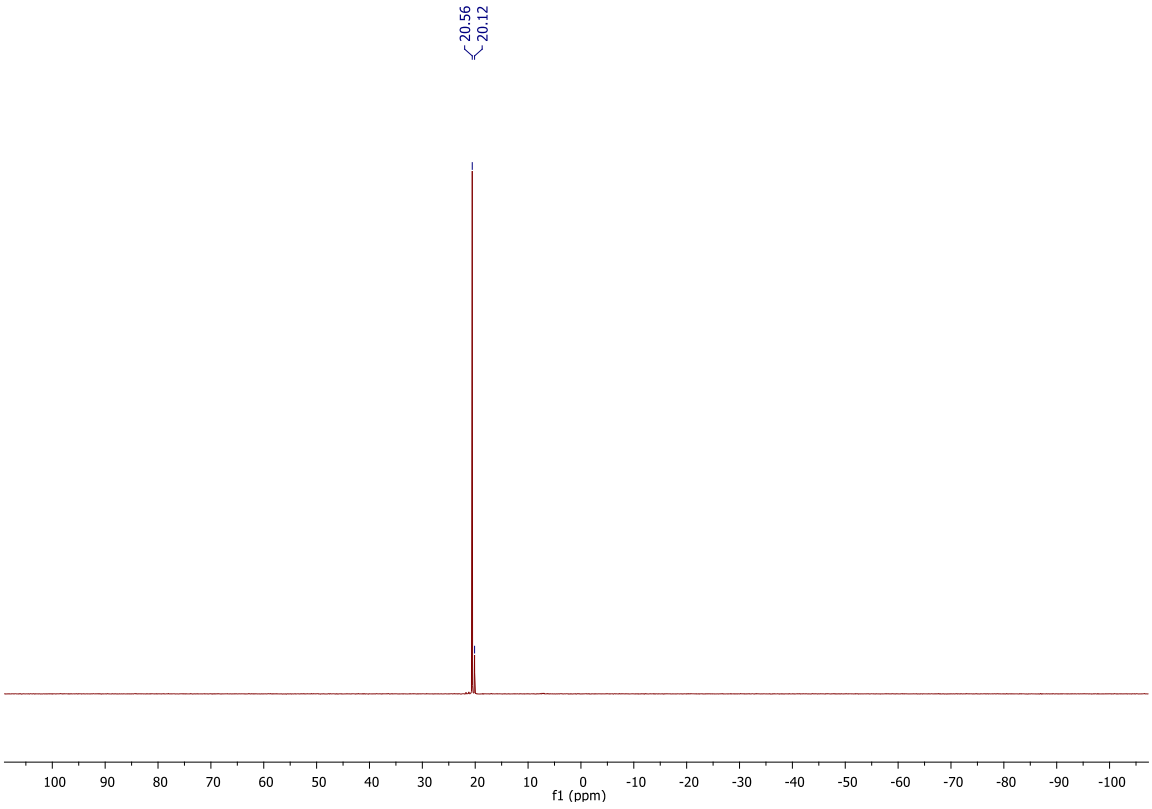
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**8i**



^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**8i**



^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**8i**



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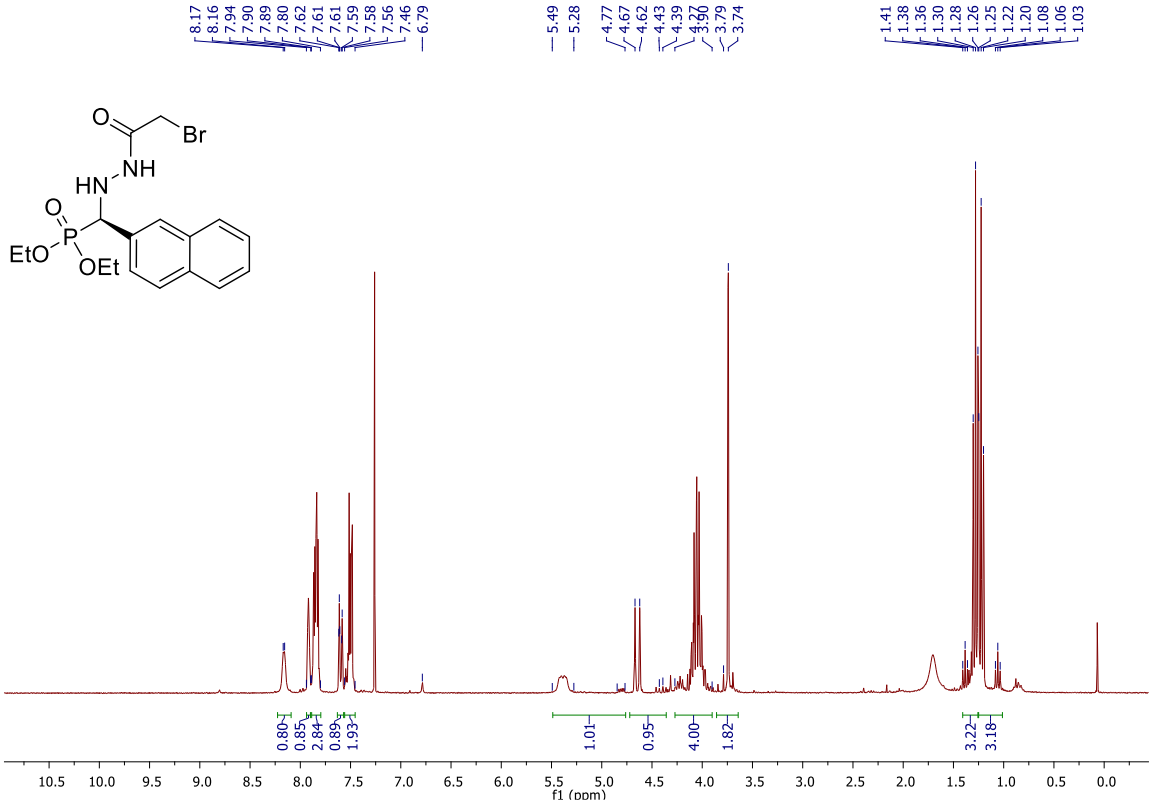
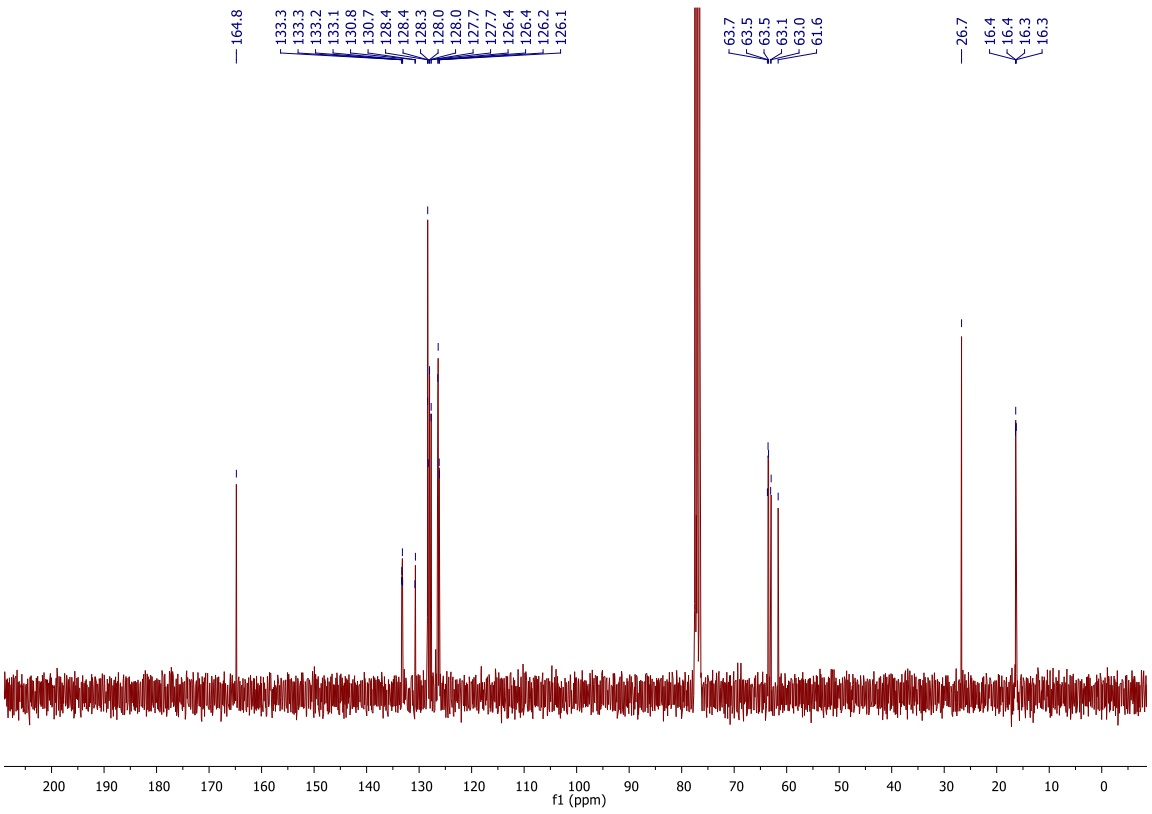
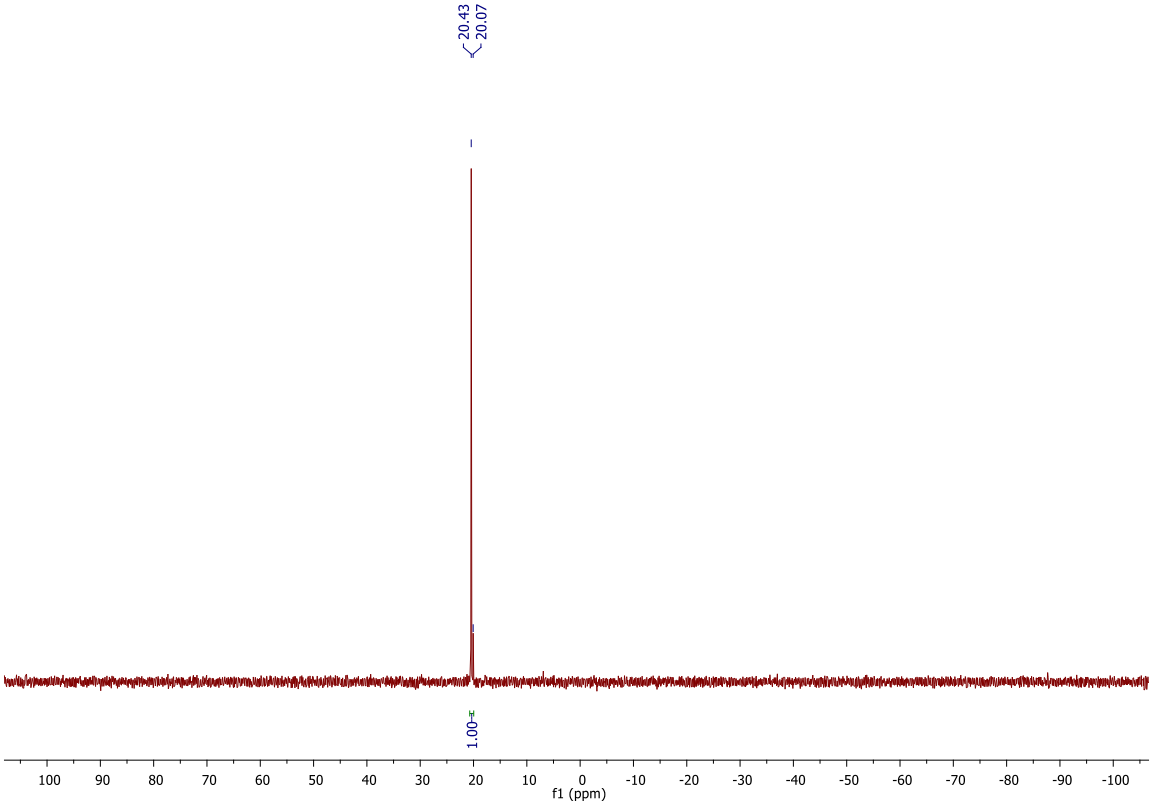


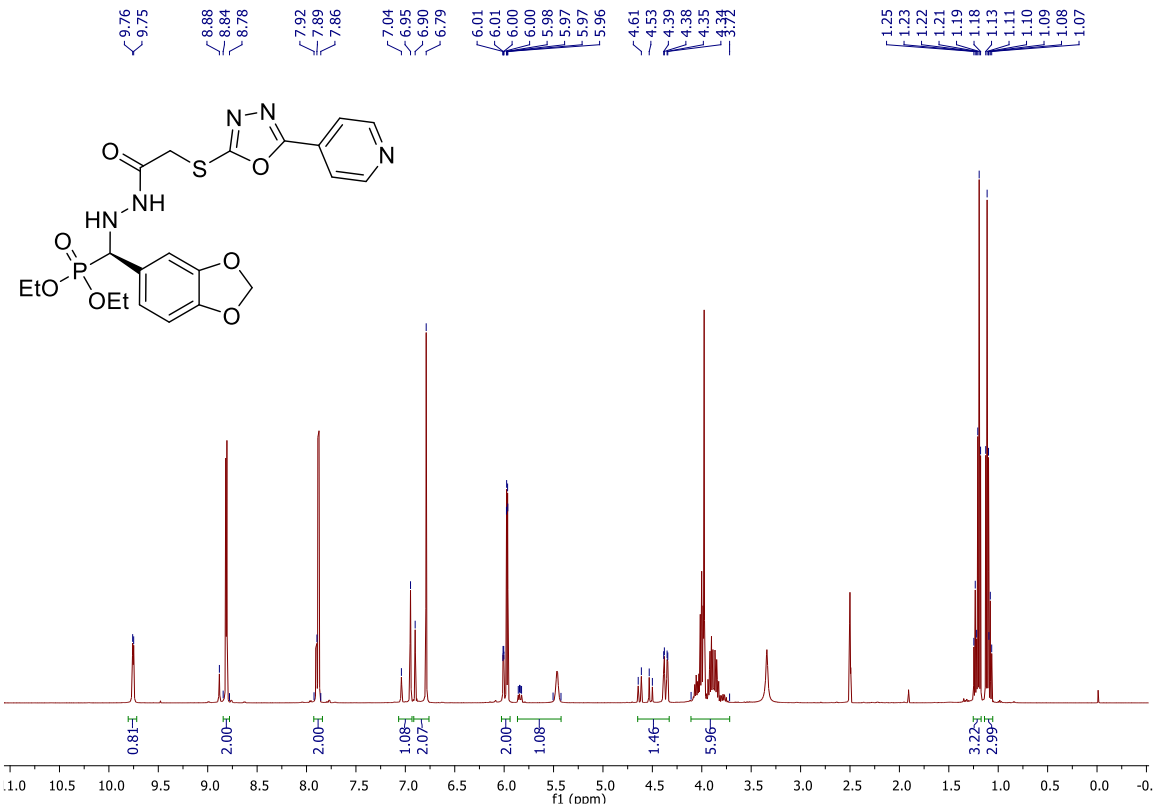
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**8o**



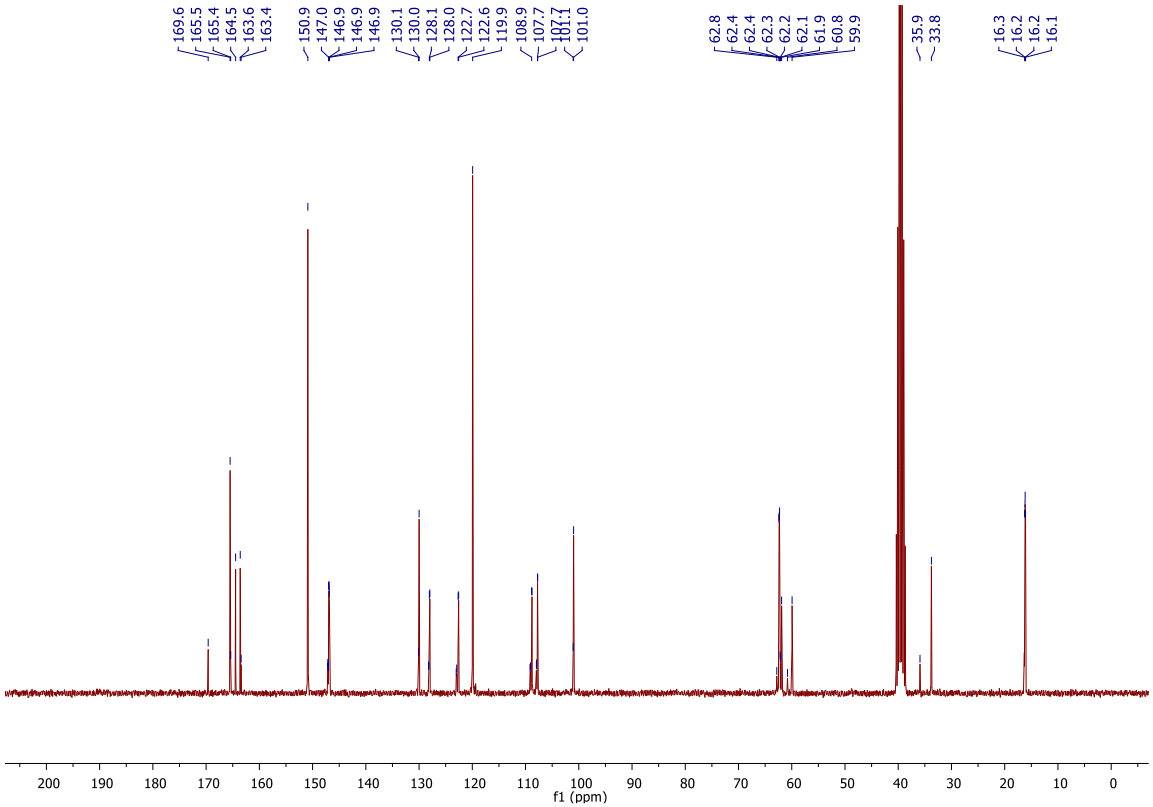
^{31}P NMR (122 MHz, $CDCl_3$) of (*R*)-**8o**



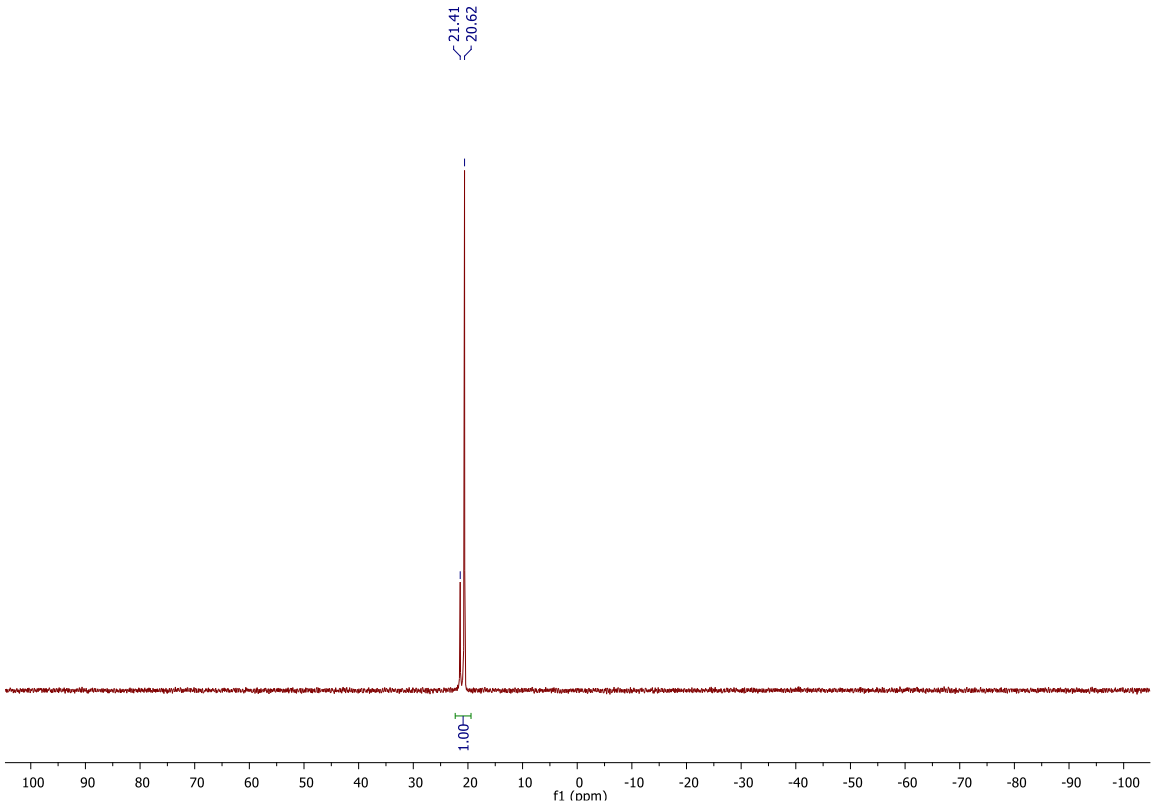
^{1}H NMR (500 MHz, DMSO-d^6) of (*R*)-**9i**



^{13}C NMR (75.5 MHz, DMSO-d^6) of (*R*)-**9i**



^{31}P NMR (122 MHz, DMSO-d^6) of (*R*)-**9i**



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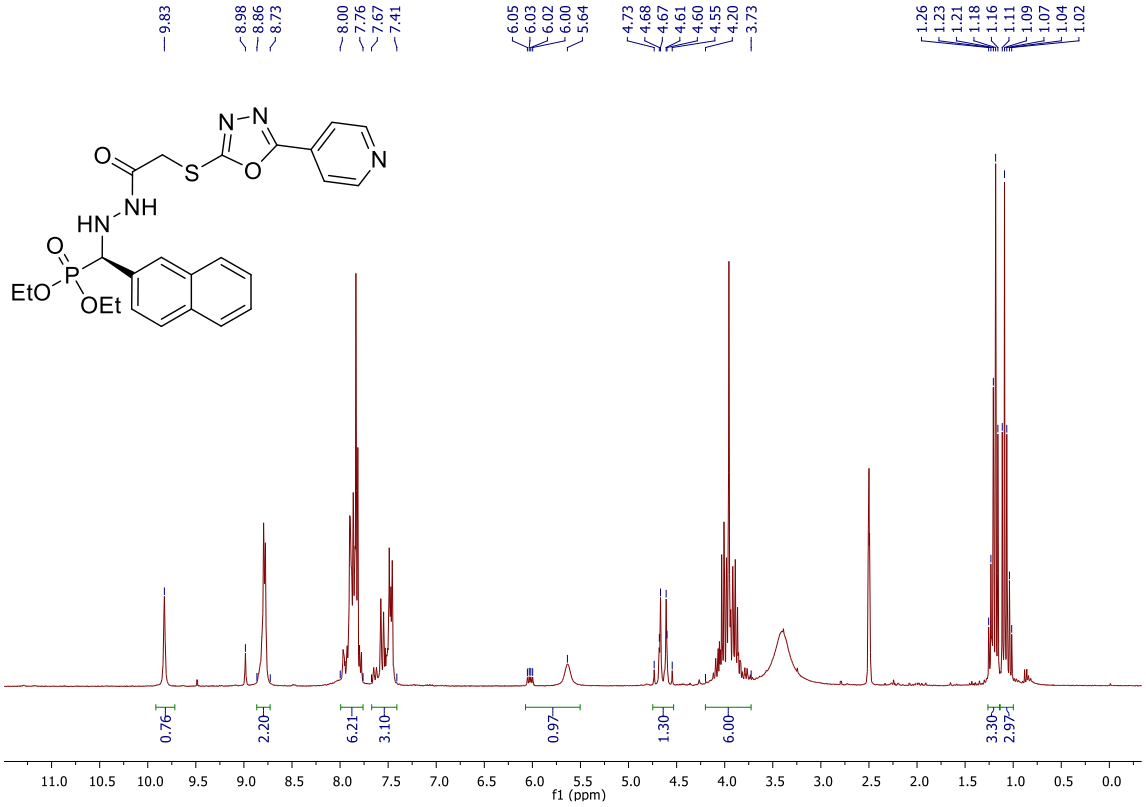
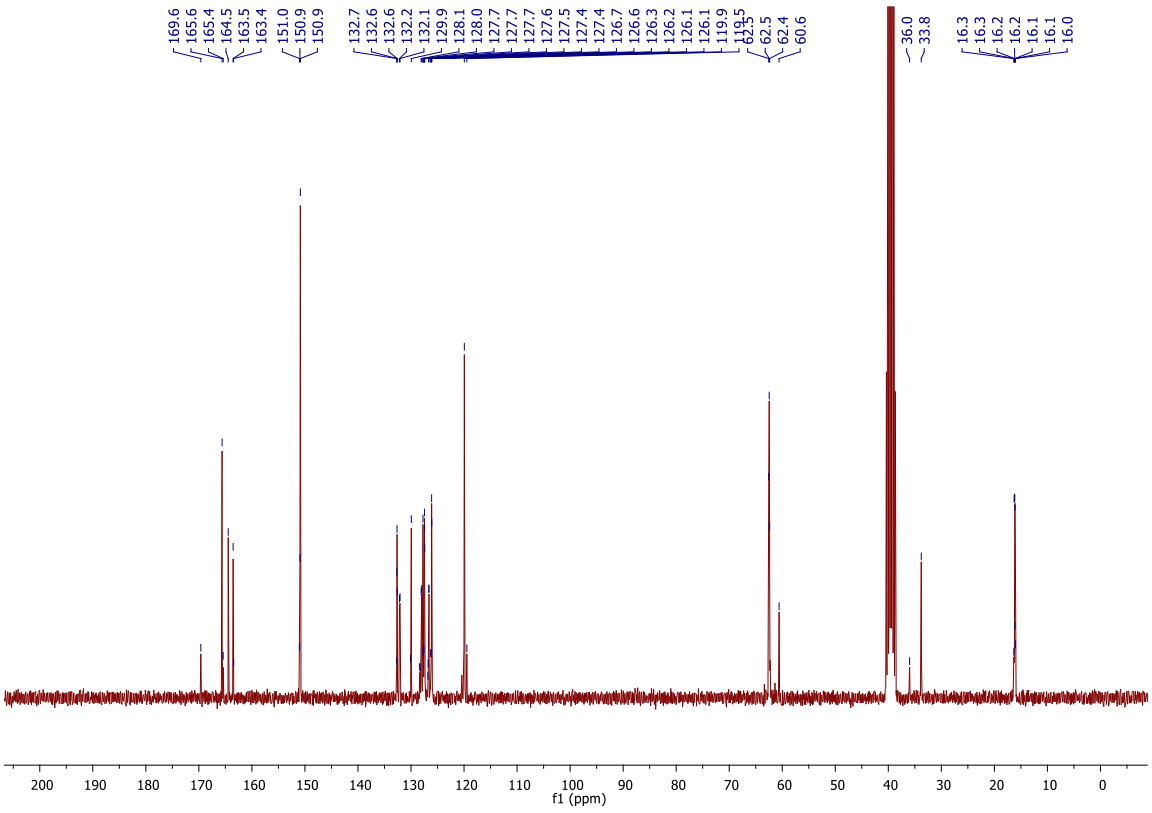
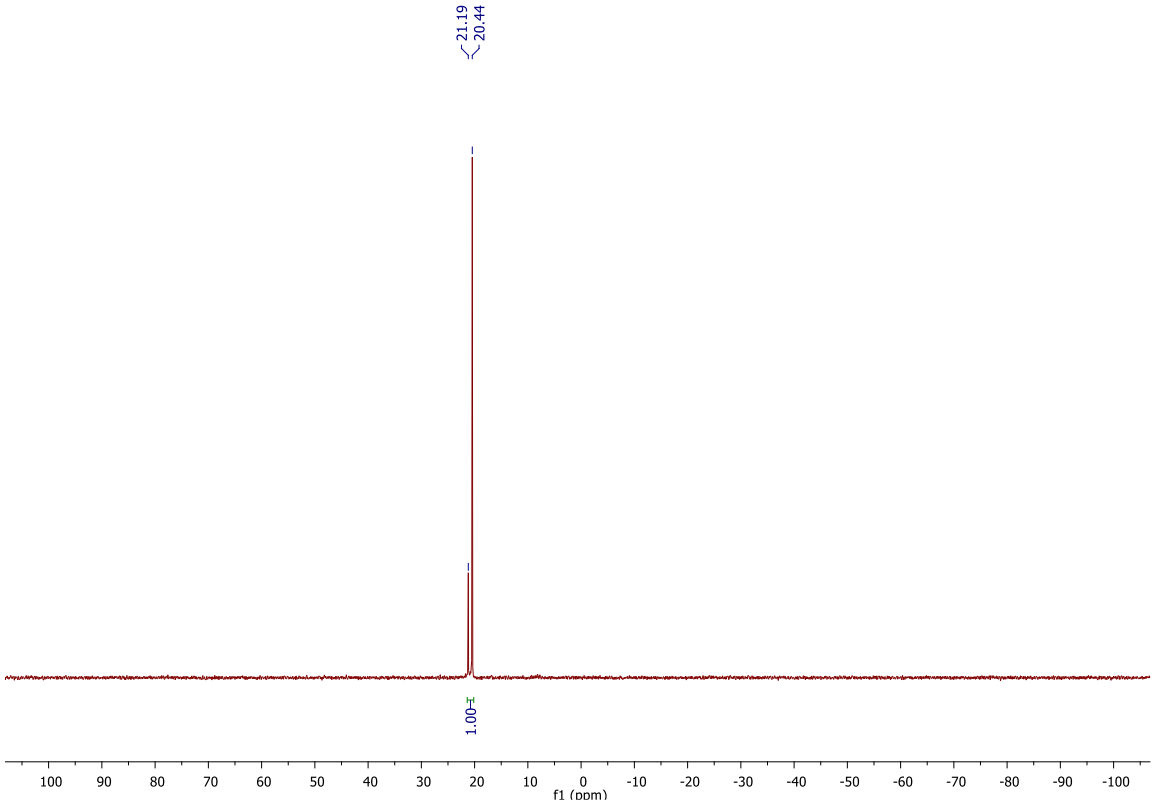


^{13}C NMR (75.5 MHz, DMSO-d^{6}) of (*R*)-**9o**



^{31}P NMR (122 MHz, DMSO-d^{6}) of (*R*)-**9o**



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