Supporting Information for:

Chiral Biphenylamide Derivative: An Efficient Organocatalyst for the Enantioselective Synthesis of α-Hydroxy Phosphonates

Jun Jiang, Xiaohong Chen, Jun Wang, Yonghai Hui, Xiaohua Liu, Lili Lin and Xiaoming Feng*

†Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

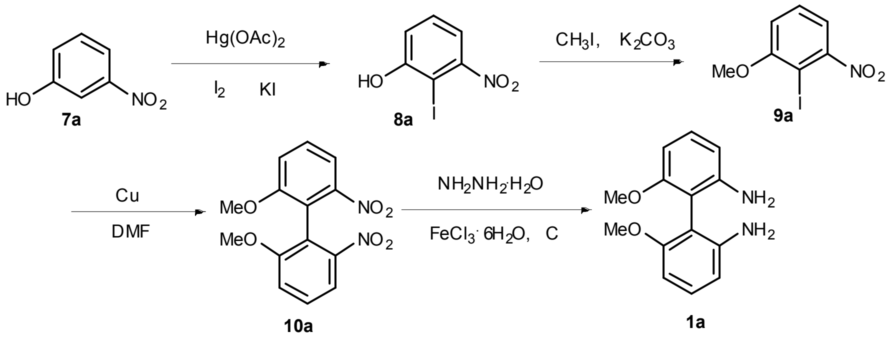
CONTENTS:

(A) General information:

^{1}H NMR spectra were recorded at 400 MHz on commercial instruments. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz on commercial instruments with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. All experiments were monitored by analytical thin layer chromatography (TLC). Enantiomeric excesses of products were determined by chiral HPLC analysis on Daicel Chiralcel OJ-H/AD-H/AS-H in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus. α-keto phosphonates were prepared according to the literature procedures.[1] Acetone, tetrahydrofuran, ethyl acetate were commercially available and purified by usual methods before use. All kinds of additives and aldehydes also were commercially available and directly used without further purification. Catalysts **2a-2d** were synthesized according to the literatures.[2] The spectra and other data were consistent with the reported values.

(B) General procedure for catalysts 2a-2d preparation

Synthesis of compound **1a**:



2-Iodo-3-nitrophenol (8a).

A solution of 13.91 g (0.1mol) 3-nitrophenol and 3.0 g (0.075mol) sodium hydroxide in 150 mL of water was stirred, while a solution of 31.87 g (0.1mol) mercuric acetate and 3 mL acetic acid in 150 mL of water was added slowly. After 1 hour at 100 °C the solution was cooled and filtered to obtain yellow solid, which were washed with 300 mL water and 150 mL ether. The 38 g (≈100 % yield) crude acetoxymercury compound was not purified, then suspended in 200 mL 10 % aqueous potassium iodide. To the suspension 200 mL 20 % aqueous potassium triiodide was added dropwise with stirring during 3 hours. After 3 h more of stirring, the reaction mixture was extracted with three 200 mL portions of dichloromethane. The combined extracts were washed with 40 mL 10 % aqueous sodium bisulfite and concentrated in vacuum to give 18.7 g of crude solid. The crude solid was purified by flash chromatography on silica gel, and eluted with 1:6 dichloromethane/petroleum ether to give yellow solid **8a** (12.5 g, 47.2 % yield), after crystallization from dichloromethane, obtained yellow acicular crystals **8a** (10.7 g, 40.4 % yield).

2-Iodo-3-nitroanisole (9a).

Methyl iodide (2.8 mL, 45 mmol)was added dropwise over a period of 0.5 h at room temperature to a suspension of 2-iodo-3-nitrophenol (8.0 g, 30 mmol), K_2CO_3 (8.3 g, 60 mmol) in dry acetone (60 mL). After 6 h of stirring, the colour of reaction mixture was from yellow to orange. When **8a** was methylated completely through monitoring by TLC, removal of solvent from the reaction mixture and the residue were washed with 50 mL dichloromethane. The washing solution was concentrated in vacuum to get bright yellow lamellar crystals **9a** (7.8 g, 93.2% yield).

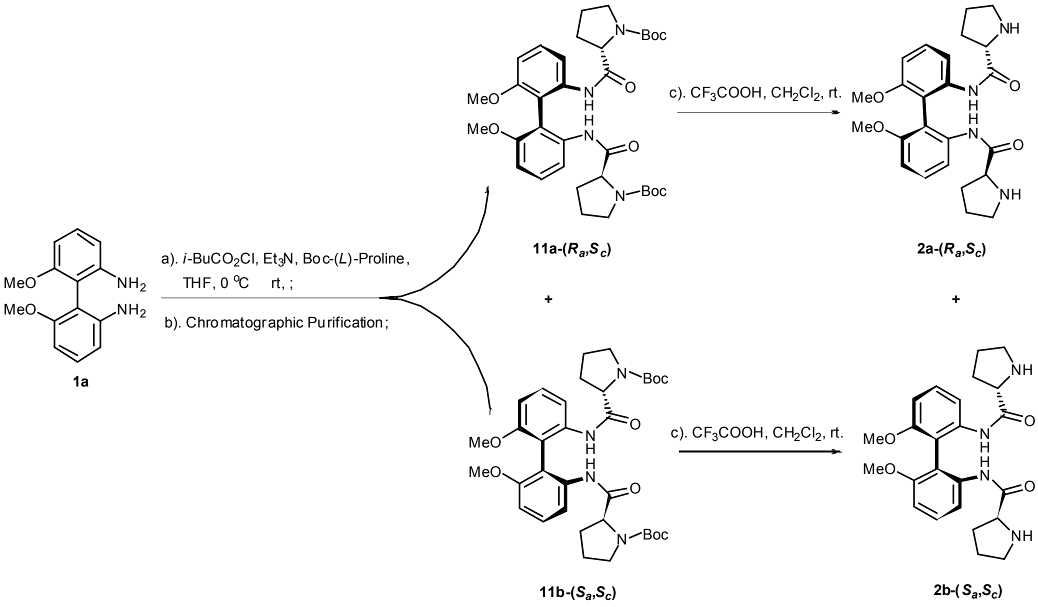
2,2'-Dimethoxy-6,6'-dinitrobiphenyl (10a).

To a stirred solution of 2-Iodo-3-nitroanisole (7.0g, 25 mmol) in 50 mL dimethylformamide was added 5.0 g activated copper[3]. After the mixture was stirred 3 h at 165 °C, another 5.0 g of activated copper was added. When the mixture had been stirred for 3 h more, it was cooled and poured into 200 mL water, then the resulting precipitate was extracted with ethyl acetate (750 mL). Removal of ethyl acetate gave yellow green granular crystals **10a** (2.8 g, 73.7% yield).

2,2'-Dimethoxy-6,6'-diaminobiphenyl (1a).

A mixture of 2,2'-Dimethoxy-6,6'-dinitrobiphenyl (2.7g, 7 mmol), ferric chloride hexahydrate (40 mg, 15 mmol), and 0.50 g activated carbon in 30 mL methanol was refluxed for 10 min. The 3.0 mL hydrazine hydrate was added dropwise over 0.5 h, while reflux continued at 70 °C. After 5 h more refluxing, the reaction mixture was filtered at reduced pressure to remove the residue. The filtrate was concentrated in vacuum and got colorless viscous liquid. The concentrated liquid was poured into 150 mL water, then the resulting precipitate **1a** was collected by filtering at reduced pressure. Pure product **1a(** 1.65g, 96.5% yield) is white lamellar crystal.

Synthesis of catalysts **2a** and **2b**



N-Boc-(*L*)-Proline (750 mg, 3.5 mmol) and Et_3N (0.58 mL, 3.5 mmol) were dissolved in THF (10 mL), while the solution was cooled to 0°C. To the solution was added dropwise isobutylchloroformate (0.45 mL, 3.5 mmol) for 15 min. After the solution was stirred for 30 min, the mixture of 2,2'-Dimethoxy-6,6'- diaminobiphenyl **1a** (366 mg, 1.5 mmol) in dry THF (20 mL) was added dropwise for 15 min. The resulting solution was stirred at 0°C for 1 h and then at room temperature for another 20 h, the solution was diluted with ethyl acetate. After filtration and removal of solvent under reduced pressure, the residue was purified through longer column chromatography on silica gel (eluent: petroleum ether /ethyl acetate/ methanol = 3/1/0.15) to respectively give **11a** (442 mg, 92.3% yield) and **11b** (413 mg, 86.2% yield).

To **11a** (320 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was added TFA (2 mL) and stirred until the reaction was finished. Then, the solution was diluted with CH_2Cl_2 (10 mL), and the pH value was brought into the range of 8–10 by the addition of 1 N NaOH. The aqueous phase was extracted with CH_2Cl_2 (5×20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuum. The ivory white powder solid **2a** (208 mg, 94.9% yield) was obtained.

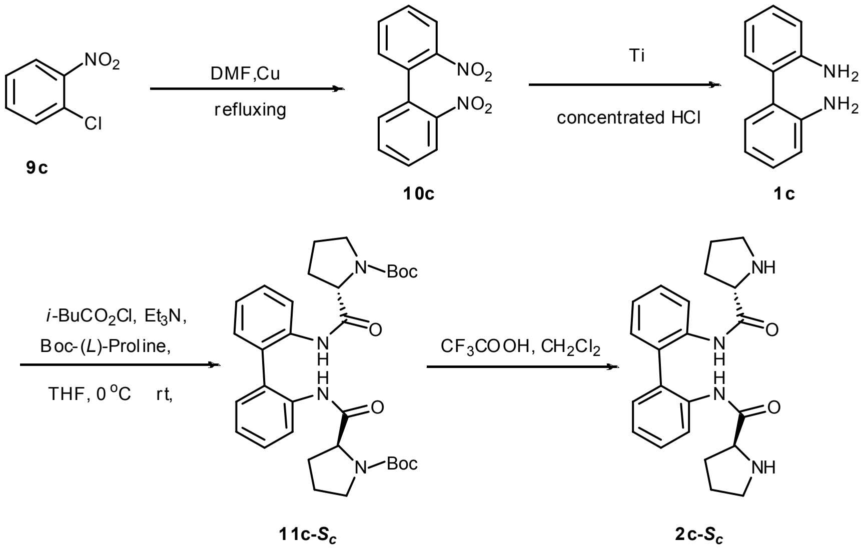
Same method got ivory white powder solid **2b** (210 mg, 95.8% yield).

Synthesis of catalysts **2d** and **2e**

According to pp5, N-Boc-(*D*)-Proline (750 mg, 3.5 mmol) was amidated by 2,2'-Dimethoxy-6,6'-

diaminobiphenyl **1a** (366 mg, 1.5 mmol), through 3 steps process, obtained catalysts **2d** (210 mg, 95.8% yield) and **2e** (203 mg, 92.6% yield)

Synthesis of catalysts **2c**



To a refluxing solution of o-chloronitrobenzene (6.3g, 40 mmol) in 40 mL dimethylformamide was added 5.0 g activated copper. After the mixture was stirred 3 h at 165 °C, another 5.0 g of activated copper was added, and continued refluxing for 3 h. When the mixture was cooled, poured it into 400 mL water, and filtered with the solution at reduced pressure. Extract the solid with 3×50mL portions of boiling ethanol. Removaled of ethanol in vacuum and gave brown acicular crystals **10c** (3.7 g, 75.8% yield).

2,2'-dinitrobiphenyl **10c** (2.9g, 12 mmol) was heated on a water bath with powdered tin and concentrated hydrochloric acid until a clear solution resulted. The mixture was made alkaline with sodium hydroxide, and ether extraction and recrystallization gave the 2,2'-diaminebiphenyl **1c** (1.8g, 83.2%).

According to pp5, N-Boc-(*L*)-Proline (3.2g, 15 mmol) was amidated by 2,2' diaminobiphenyl **1c** (1.3g, 7 mmol), purified through column chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 4/1),and obtained compound **11c** (3.26 g, 80.6% yield)**,** deprotection of Boc-group to get **2c** (2.04g, 95.6% yield).

(C) General procedure for the asymmetric aldol reaction of α-keto phosphonates[a] and aldehydes[b] with acetone

a) The aldol reaction of α-keto phosphanates with acetone

To the α-keto phosphanate (0.1 mmol) and catalyst **2a** (4.4 mg, 0.01mmol, 10 mol%) was added anhydrous acetone (0.2 mL), ethyl acetate (0.3 mL) and TFA (0.78 μL, 20 mol%), the resulting mixture was stirred at -20 °C for 2-5 d. The mixture was directly purified through flash column chromatography on a silica gel (eluent: petroleum ether /ethyl acetate = 1/1) to give the pure product.

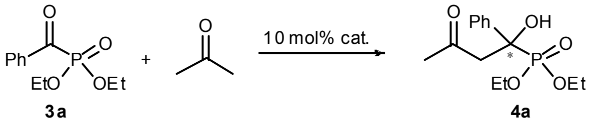
b) The aldol reaction of aldehyde with acetone

To the aldehyde (0.1 mmol) and catalyst **2a** (4.4mg, 0.01 mmol, 10 mol%) was added anhydrous acetone (0.2 mL), (0.3 mL) tetrahydrofuran and TFA (0.20 μL, 5mol%), the resulting mixture was stirred at -20 °C for 2-3 d. The mixture was directly purified through flash column chromatography on a silica gel (eluent: petroleum ether /ethyl acetate = 3/1) to give the pure product.

(D) Optimization of conditions

a) Optimization of conditions for the aldol reaction of α-keto phosphanates with acetone.

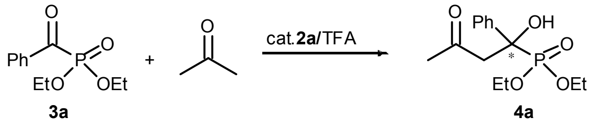
1) Screening of catalysts and additives:



Entry[a]	Cat.	Yield[b] (%)	Ee[c] (%)
1	**2a**	93	69
2	**2b**	94	35
3	**2c**	49	50
4[d]	**2d**	75	-67
5	**2e**	92	-7
6	**2a**/TFA	95	78
7	**2a**/CH_3COOH	93	65
8	**2a**/HCOOH	97	70
9	**2a**/PhCOOH	87	58
10	**2a**/CCl_3COOH	78	74
11	**2a**/TsOH	85	70
13	**2a**/PhOH	88	45

[a] Unless otherwise noted, the reaction was carried out with the diethyl benzoyl phosphonate (0.1 mmol), 0.5 mL of acetone at -20 °C for 2.5 d, using 10 mol% catalyst loading, **2a** /additive = 2/1. [b] Isolated yield. [c] Determined by chiral HPLC. [d] The absolute configuration was opposite to entry 1.

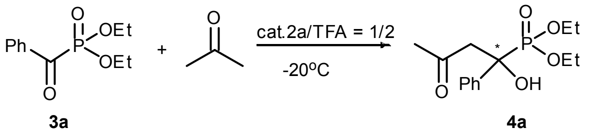
2) Screening of the ratio with catalyst, catalyst loading, temperature:



Entry[a]	Catalyst/TFA	Catalyst loading(mol%)	Temperature(°C)	Yield[b] (%)	Ee[c] (%)
1	2 / 1	10	-20	95	78
2	1 / 1	10	-20	95	86
3	1 / 1.5	10	-20	93	90
4	1 / 2	10	-20	92	92
5	1 / 2.5	10	-20	53	93
6	1 / 3	10	-20	24	93
7	1 / 2	5	-20	78	92
8	1 / 2	2.5	-20	52	91
9	1 / 2	10	0	96	87
10	1 / 2	10	20	98	85

[a]Unless otherwise noted, the reaction was carried out with the diethyl benzoyl phosphonate (0.1 mmol), 0.5 mL of acetone for 2.5 d. [b]Isolated yield. [c]Determined by chiral HPLC..

3) Screening of the solvent and ratio with acetone:

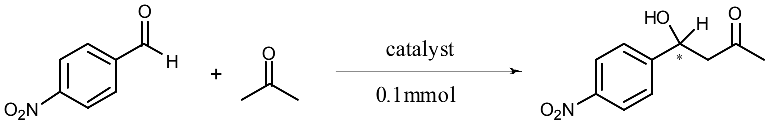


Entry[a]	solvent	Solvent (mL) / Acetone (mL)	Yield[b] (%)	Ee[c] (%)
1	Acetone	—	92	92
2	THF	0.3 / 0.2	78	93
2	THF	0.25 / 0.25	84	93
2	THF	0.125 / 0.125	67	92
2	THF	0.1 / 0.4	89	92
3	DMF	0.3 / 0.2	Trace	—
4	CH_3OH	0.3 / 0.2	45	31
5	toluene	0.3 / 0.2	43	93
6	EA	0.3 / 0.2	89	94
7	EA	0.25 / 0.25	94	93
8	EA	0.4 / 0.1	68	94
9	EA	0.125 / 0.125	82	93
10	EA	0.5 / 0.5	98	92

[a]Unless otherwise noted, the reaction was carried out with the diethyl benzoyl phosphonate (0.1 mmol), at -20 °C for 2.5 d, using 10 mol% catalyst loading, **2a** /additive = 1/2. [b]Isolated yield. [c]Determined by chiral HPLC.

b) Optimization of conditions for the aldol reaction of aldehydes with acetone.

1) Screening conditions:

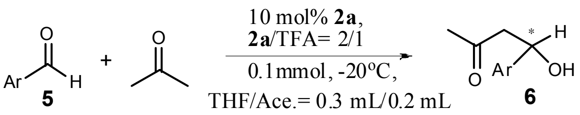


Entry[a]	Catalyst	Cat./additive	Temp. (°C)	Cat. Loading (mol%)	Sov. (mL)	Yield[b] (%)	Ee[c] (%)
1	**2a**	—	0	10	Ace.0.5	61	68
2	**2b**	—	0	10	Ace.0.5	66	54
3	**2c**	—	0	10	Ace.0.5	55	39
4	**2d**	—	0	10	Ace.0.5	29	-69
5	**2e**	—	0	10	Ace.0.5	20	-55
6	**2a**/TFA	1 / 1	0	10	Ace.0.5	60	90
7	**2a**/PhCOOH	1 / 1	0	10	Ace.0.5	97	60
8	**2a**/TsOH	1 / 1	0	10	Ace.0.5	43	92
9	**2a**/TFA	2 / 1	0	10	Ace.0.5	86	91
10	**2a**/TFA	1 / 2	0	10	Ace.0.5	41	89
11	**2a**/TFA	2 / 1	-20	10	Ace.0.5	95	93
12	**2a**/TFA	1 / 2	-20	10	Ace.0.5	41	89
13	**2a**/TFA	2 / 1	-20	5	Ace.0.5	61	78
14	**2a**/TFA	2 / 1	-20	10	Ace.(0.1)/EA(0.4)	81	94
15	**2a**/TFA	2 / 1	-20	10	Ace.(0.1)/DMF(0.4)	31	98
16	**2a**/TFA	2 / 1	-20	10	Ace.(0.1)/Toluene(0.4)	86	92
17	**2a**/TFA	2 / 1	-20	10	Ace.(0.1)/THF(0.4)	77	96
18	**2a**/TFA	2 / 1	-20	10	Ace.(0.25)/ THF(0.25)	86	94
19	**2a**/TFA	2 / 1	-20	10	Ace.(0.2)/ THF (0.3)	84	95

[a] Unless otherwise noted, the reaction was carried out with the aldehydes (0.1 mmol), for 2-3 d. [b] Isolated yield.

[c] Determined by chiral HPLC.

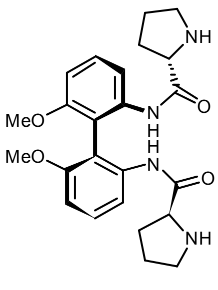
2) Asymmetric Aldol Reaction of Substrate aldehydes **5**:



Entry	Aldehydes **5**	Ar	Products **6**	Time (d)	Yield[b](%)	Ee[c] (%)
1	**5d**	4-NO2C6H4	**6d**	2	84	95
2	**5a**	3-NO2C6H4	**6a**	2	88	97
3	**5e**	2-NO2C6H4	**6e**	2	87	95
4	**5f**	4-CNC6H4	**6f**	2	79	93
5	**5b**	4-CF3C6H4	**6b**	2	86	99
6	**5g**	3-CF3C6H4	**6g**	2	73	91
7	**5h**	2.6-2ClC6H3	**6h**	2	94	93
8	**5i**	2.4-2ClC6H3	**6i**	2	97	93
9	**5c**	3.4-2ClC6H3	**6c**	2	87	97
10	**5j**	4-BrC6H4	**6j**	4	69	91

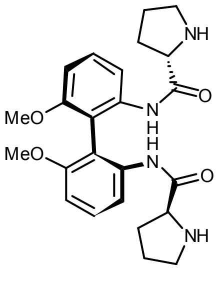
[a] Unless otherwise noted, the reaction was carried out with 0.1 mmol aldehydes, using 10 mol % catalyst loading at -20 °C, **2a**/TFA= 2/1, solvent: THF/Acetone = 0.3mL/0.2mL. [b] Isolated yield. [c] Determined by chiral HPLC.

(E) Spectral characterization data for catalysts 2a-2d



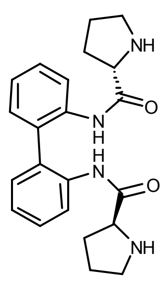
2a-(R_a,S_c)

2a: ^{1}H NMR (400 MHz, CDCl$_3$) 1.52-1.66 (m, 4H, proline-H), 1.87-1.94 (m, 4H, proline-H), 2.02-2.11 (m, 2H, proline-NH), 2.56-2.62 (m, 2H, proline-H), 2.77-2.83 (m, 2H, proline-H), 3.59-3.63 (m, J_a = 4.8 Hz, J_b = 9.2 Hz, 2H, O=C-CH), 3.72 (s, 6H, CH$_3$-O), 6.77-6.79 (d, J = 8.4 Hz, 2H, Ar-H), 7.37-7.41 (t, J ≈ 8.0 Hz, 2H, Ar-H), 8.02-8.04 (d, J = 8.4 Hz, 2H, Ar-H), 9.56 (s, 2H, Ar-NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) 25.9, 30.7, 46.9, 55.8, 60.8, 106.5, 112.5, 113.4, 129.8, 137.5, 157.4, 173.7 ppm; HRMS (ESI-TOF) calcd for C$_{24}$H$_{30}$N$_4$O$_4$ ([M+H$^+$]) = 439.2345, Found: 439.2341.



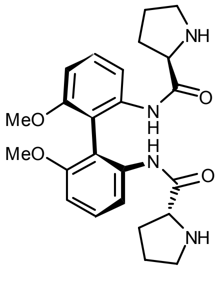
2b-(S_a,S_c)

2b: ^{1}H NMR (400 MHz, CDCl$_3$) 1.56-1.60 (m, 4H, proline-H), 1.75-1.81 (m, 4H, proline-H), 1.91-2.01 (m, 2H, proline-NH), 2.41-2.42 (d, 2H, J_a = 4.0 Hz, proline-H), 2.72-2.78 (m, J_a ≈ 7.2 Hz, J_b ≈ 16.8 Hz, 2H, proline-H), 3.69-3.73 (m, J_a = 4.4 Hz, J_b = 9.2 Hz, 2H, O=C-CH), 3.76 (s, 6H, CH$_3$-O), 6.76-6.82 (m, J_a = 8.4 Hz, J_b = 16.8 Hz, 2H, Ar-H), 7.37-7.41 (t, J ≈ 8.0 Hz, 2H, Ar-H), 7.95 (s, 2H, Ar-H), 9.50 (s, 2H, Ar-NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) 25.7, 30.5, 46.8, 56.0, 60.8, 107.1, 113.2, 113.8, 129.7, 137.2, 157.5, 173.1 ppm; HRMS (ESI-TOF) calcd for C$_{16}$H$_{24}$N$_3$O ([M+H$^+$]) = 439.2345, Found: 439.2342.



2c-S_c

2c: ^{1}H NMR (400 MHz, CDCl$_3$) 1.52-1.62 (m, 4H, proline-H), 1.80-1.89 (m, 4H, proline-H), 2.03-2.10 (m, 2H, proline-NH), 2.44-2.79 (m, 4H, proline-H), 3.60-3.68 (m, 2H, O=C-CH), 7.19-7.27 (m, 4H, Ar-H), 7.41-7.45 (m, 2H, Ar-H),8.25-8.50 (m, J_a ≈ 7.8 Hz, J_b ≈ 13.8 Hz, 2H, Ar-H), 9.66 (s, 2H, Ar-NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) 25.9 (d, J = 9.0 Hz), 30.7 (d, J = 2.0 Hz), 25.9, 30.8, 46.9, 55.0, 60.8, 114.3, 121.4, 124.3, 129.9, 136.2, 173.5, ppm; HRMS (ESI-TOF) calcd for C$_{16}$H$_{24}$N$_3$O ([M+H$^+$]) = 379.2134, Found: 379.2132.

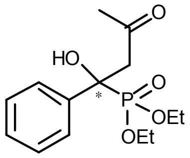


2d-(S_a,R_c)

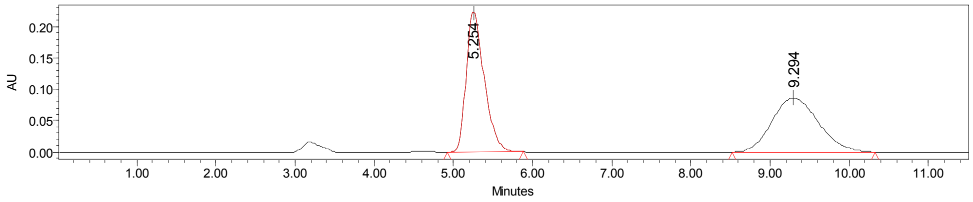
2d: ^{1}H NMR (400 MHz, CDCl$_3$) 1.52-1.62 (m, 4H, proline-H), 1.76-1.94 (m, 4H, proline-H), 2.01-2.11 (m, 2H, proline-NH), 2.55-2.61 (m, 2H, proline-H), 2.76-2.82 (m, 2H, proline-H), 3.58-3.62 (m, J_a = 4.8 Hz, J_b = 9.2 Hz, 2H, O=C-CH), 3.72 (s, 6H, CH$_3$-O), 6.76-6.78 (d, J = 8.4 Hz, 2H, Ar-H), 7.37-7.41 (t, J = 8.4 Hz, 2H, Ar-H), 8.03-8.05 (d, J = 8.0 Hz, 2H, Ar-H), 9.58 (s, 2H, Ar-NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) 25.9, 30.7, 46.9, 55.8, 60.8, 106.5, 112.3, 113.4, 129.8, 137.5, 157.4, 173.7 ppm; HRMS (ESI-TOF) calcd for C$_{24}$H$_{30}$N$_4$O$_4$ ([M+H$^+$]) = 439.2345, Found: 439.2340.

(H) The analytical and spectral characterization data of reaction products

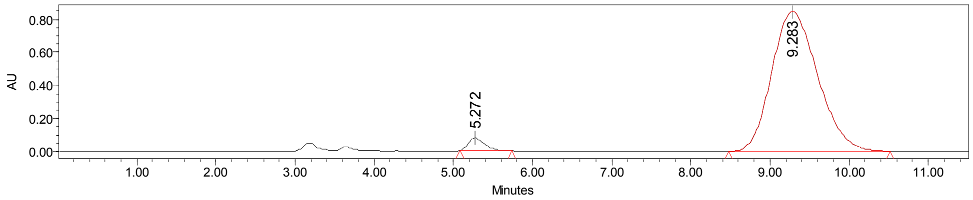
Diethyl (1-hydroxy-3-oxo-1-phenylbutyl) phosphonate (4a)



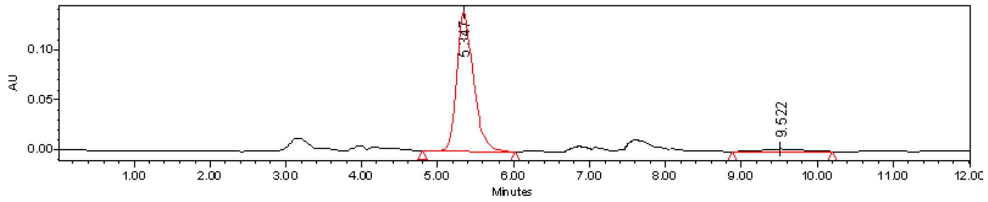
(Entry 1) solid; 89% yield, 94% *ee*. $[\alpha]_D^{21} = 41.2$ (c 0.398 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 5.3 min (minor) and 9.3 min (major); (Entry 2)solid;71% yield, -92% *ee*. $[\alpha]_D^{21} = -38.8$ (c 0.422 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 5.3 min (major) and 9.5 min (minor); ^1H NMR (400 MHz, $CDCl_3$) 1.09 (t, J = 7.2 Hz, 3H, Me-H), 1.32 (t, J = 7.2 Hz, 3H, Me-H), 2.15 (s, 3H, $O{=}CCH_3$), 3.30-3.43 (m, 2H, $O{=}CCH_2$-C), 3.64-4.20 (m, 4H, $O{=}PCH_2$-Me), 5.07 (d, J = 18.4 Hz, 1H, $O{=}PCH_2$-Me), 7.27-7.63 (m, 5H, Ar-H) ppm.



	Retention Time	Peak Type	Area	% Area	Height	% Height
1	5.254	Unknown	3534485	50.21	223041	72.03
2	9.294	Unknown	3505096	49.79	86589	27.97

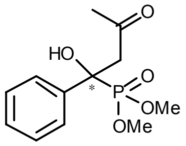


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	5.272	Unknown	1082681	3.08	75938	8.26
2	9.283	Unknown	34120692	96.92	843641	91.74



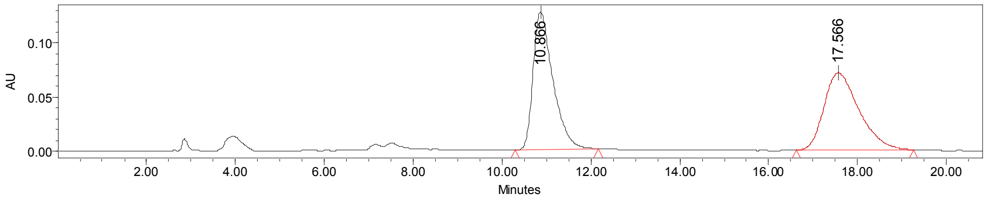
	Retention Time	Peak Type	Area	% Area	Height	% Height
1	5.347	Unknown	2109700	96.07	138563	98.29
2	9.522	Unknown	86223	3.93	2410	1.71

Dimethyl (1-hydroxy-3-oxo-1-phenylbutyl) phosphonate (4b)

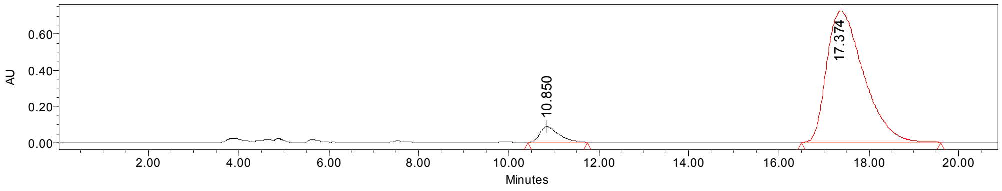


solid; 91% yield, 89% *ee*. $[\alpha]_D^{23} = 33.9$ (c 0.260 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OJH, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 10.9 min (minor) and 17.4 min (major); ^1H NMR

(400 MHz, $CDCl_3$) 2.15 (s, 3H, O=CCH_3), 3.30-3.41 (m, 2H, O=CCH_2-C), 3.45 (d, *J* = 10.0 Hz, 3H, O=PCH_3), 3.81 (d, *J* = 10.4 Hz, 3H, O=PCH_3), 5.12 (d, *J* = 19.6 Hz, 1H, C-OH), 7.30-7.63 (m, 5H, Ar-H) ppm.

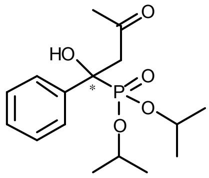


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	10.866	Unknown	3956374	50.42	127505	64.11
2	17.566	Unknown	3890521	49.58	71388	35.89

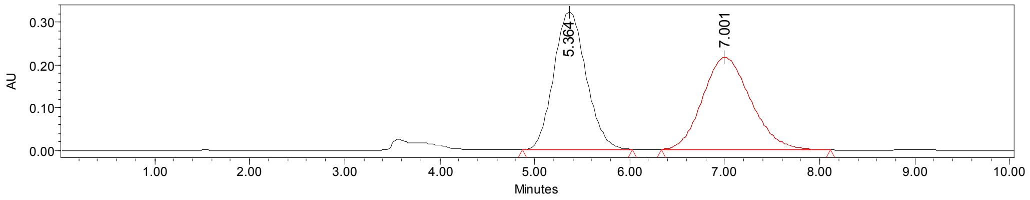


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	10.850	Unknown	2593481	5.70	86397	10.65
2	17.374	Unknown	41337146	94.30	724902	89.35

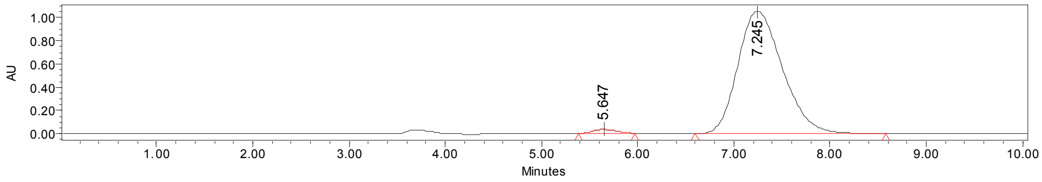
Diisopropyl (1-hydroxy-3-oxo-1-phenylbutyl) phosphonate (4c)



solid; 74% yield, 97% *ee*. $[\alpha]_D^{23}$ = 33.2 (*c* 0.458 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/*n*-hexane = 8/92, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 5.6 min (minor) and 7.2 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) 0.93-1.34 (m, 12H, Me-H), 2.12 (s, 3H, O=CCH_3), 3.26-3.39 (m, 2H, O=CCH_2-C), 4.30-4.78 (m, 2H, O-CH-$(Me)_2$), 4.96 (d, *J* = 18.0 Hz, 1H, C-OH), 7.27-7.62 (m, 5H Ar-H) ppm.

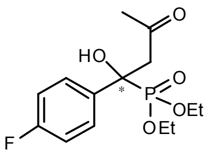


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	5.364	Unknown	7621180	50.06	322035	59.92
2	7.001	Unknown	7602533	49.94	215397	40.08

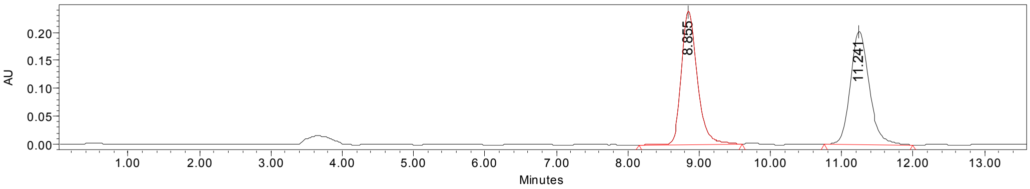


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	5.647	Unknown	589116	1.70	34025	3.12
2	7.245	Unknown	34087778	98.30	1055961	96.88

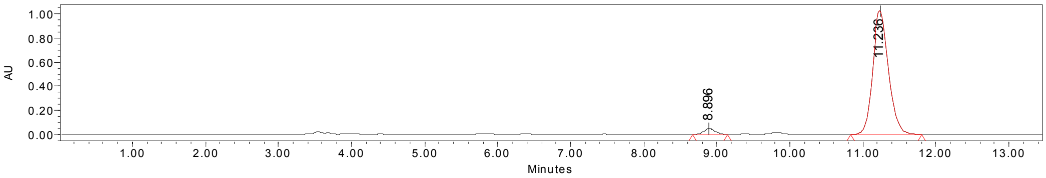
Diethyl [1-(4- fluorophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4d)



solid; 89% yield, 93% *ee*. $[\alpha]_D^{23} = 36.5$ (c 0.318 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 8.9 min (minor) and 11.2 min (major); ^1H NMR (400 MHz, $CDCl_3$) 1.10-1.13 (t, J = 7.0 Hz, 3H, Me-H), 1.31-1.34 (t, J = 7.0 Hz, 3H, Me-H), 2.16 (s, 3H,O=CCH_3), 3.32-3.34 (d, J = 9.2 Hz, 2H, O=CCH_2-C), 3.71-4.19 (m, 4H, O=PCH_2-Me), 5.10-5.15 (d, J = 18.8 Hz, 1H, C-OH), 7.04-7.08 (m, 2H, Ar-H), 7.57-7.61 (m, 2H, Ar-H) ppm.

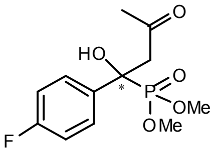


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	8.855	Unknown	3598056	49.71	238051	54.05
2	11.241	Unknown	3639494	50.29	202404	45.95

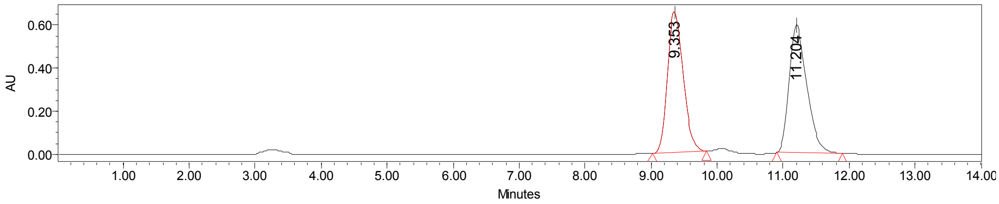


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	8.896	Unknown	564364	3.47	48547	4.53
2	11.236	Unknown	15693270	96.53	1023046	95.47

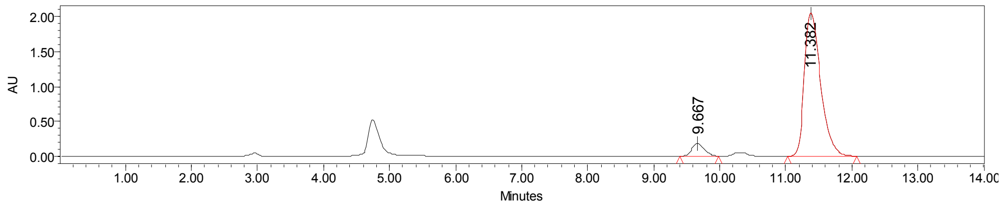
Dimethyl [1-(4- fluorophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4e)



solid; 68% yield, 87% *ee*. $[\alpha]_D^{20} = 33.6$ (c 0.286 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.7 min (minor) and 11.4 min (major); ^1H NMR (400 MHz, $CDCl_3$) 2.16 (s, 3H,O=CCH_3), 3.33-3.35 (d, J = 9.6 Hz, 2H, O=CCH_2-C), 3.48-3.51 (d, J = 9.6 Hz, 3H, O=PCH_3), 3.80-3.82 (d, J = 10.4 Hz, 3H, O=PCH_3), 5.17-5.22 (d, J = 19.2 Hz, 1H, C-OH), 7.05-7.09 (m, 2H, Ar-H), 7.57-7.60 (m, 2H, Ar-H) ppm.

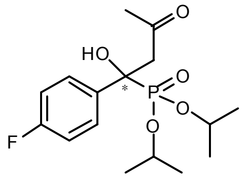


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.353	Unknown	10881941	49.53	654596	52.42
2	11.204	Unknown	11089477	50.47	594210	47.58

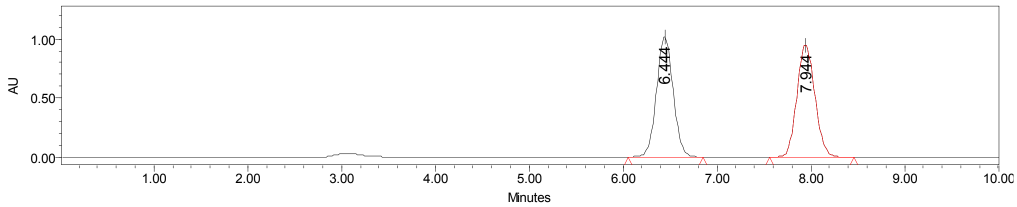


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.667	Unknown	2389425	6.39	181323	8.14
2	11.382	Unknown	35001830	93.61	2047127	91.86

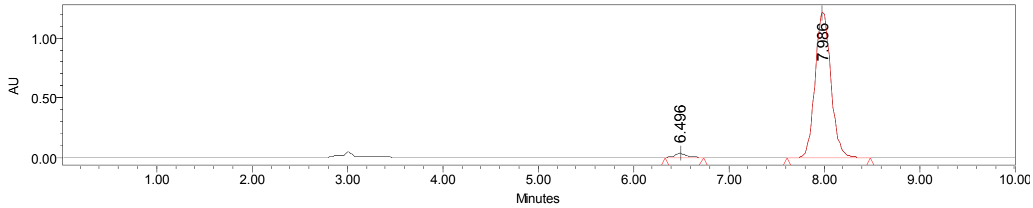
Diethyl [1-(4- fluorophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4f)



solid; 86% yield, 96% *ee*. $[\alpha]_D^{21}$ = 31.7 (*c* 0.322 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 6.5 min (minor) and 8.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) 0.97-1.34 (m, 12H, Me-H), 2.14 (s, 3H,O=CCH_3), 3.28-3.31 (d, *J* = 9.2 Hz, 2H, O=CCH_2-C), 4.35-4.76 (m, 2H, O-CH-$(Me)_2$), 5.00-5.04 (d, *J* = 18.0 Hz, 1H, C-OH), 7.02-7.06 (m, 2H, Ar-H), 7.57-7.62 (m, 2H, Ar-H) ppm.

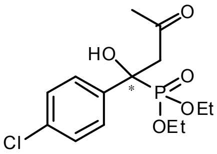


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	6.444	Unknown	12633382	50.10	1019608	51.87
2	7.944	Unknown	12583415	49.90	946183	48.13

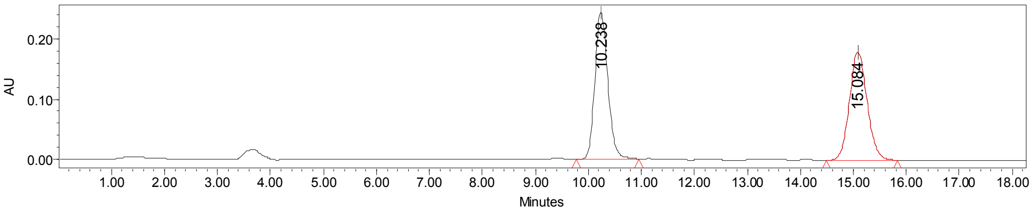


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	6.496	Unknown	288560	2.04	33188	2.66
2	7.986	Unknown	13869960	97.96	1214046	97.34

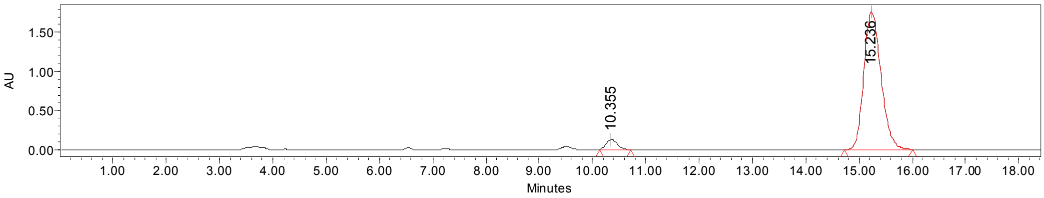
Diethyl [1-(4-chlorophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4g)



solid; 92% yield, 91% *ee*. $[\alpha]_D^{23}$ = 41.4 (*c* 0.584 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.4 min (major) and 13.5 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 1.12 (t, *J* = 7.2 Hz, 3H, Me-H), 1.32 (t, *J* = 7.2 Hz, 3H, Me-H), 2.16 (s, 3H, O=CCH_3), 3.31-3.33 (m, 2H, O=CCH_2-C), 3.71-4.20 (m, 4H, O=PCH_2-Me), 5.11 (d, *J* = 18.4 Hz, 1H, C-OH), 7.34-7.56 (m, 2H, Ar-H) ppm.

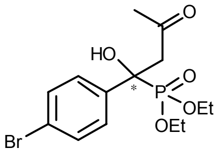


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	10.238	Unknown	4136167	49.91	244429	57.57
2	15.084	Unknown	4151268	50.09	180152	42.43

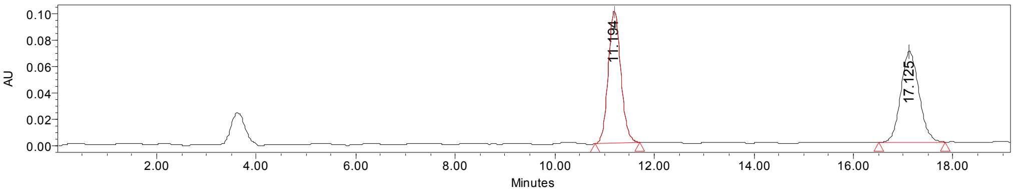


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	10.355	Unknown	1793593	4.33	127598	6.75
2	15.236	Unknown	39625403	95.67	1763254	93.25

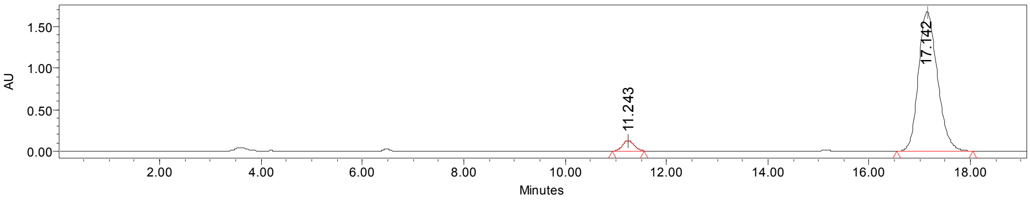
Diethyl [1-(4-bromophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4h)



solid; 86% yield, 92% *ee*. $[\alpha]_D^{23}$ = 39.5 (*c* 0.440 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 11.2 min (minor) and 17.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) 1.11-1.15 (t, *J* = 7.2 Hz, 3H, Me-H), 1.31-1.34 (t, *J* = 7.0 Hz, 3H, Me-H), 2.16 (s, 3H,O=CCH_3), 3.12-3.33 (d, *J* = 8.4 Hz, 2H, O=CCH_2-C), 3.72-4.19 (m, 4H, O=PCH_2-Me), 5.09-5.14 (d, *J* = 18.8 Hz, 1H, C-OH), 7.49 (d, 4H, Ar-H) ppm.

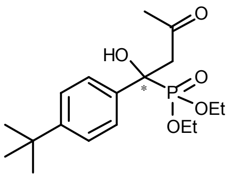


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	11.194	Unknown	1765136	50.25	100235	59.19
2	17.125	Unknown	1747537	49.75	69096	40.81

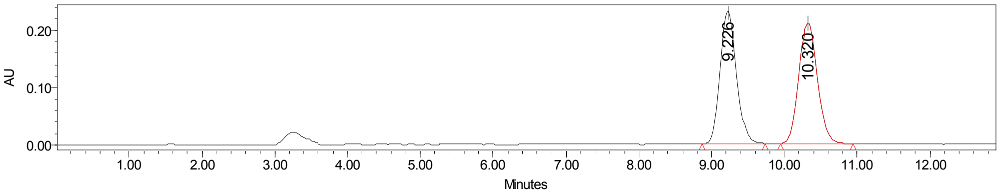


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	11.243	Unknown	1938666	4.26	125068	6.94
2	17.142	Unknown	43621286	95.74	1676593	93.06

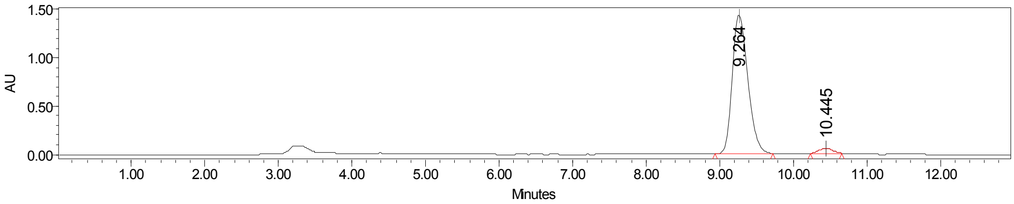
Diethyl [1-(4-tert-butylphenyl)-1-hydroxy-3-oxobutyl] phosphonate (4i)



solid; 60% yield, 94% *ee*. $[\alpha]_D^{23}$ = 38.3 (*c* 0.308 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.3 min (major) and 10.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 1.05-1.09 (t, *J* = 7.0 Hz, 3H, Me-H), 1.30-1.34 (t, *J* = 7.2 Hz, 3H, Me-H), 1.30 (s, 9H,Ar-$C(CH_3)_3$), 2.16 (s, 3H, O=CCH_3), 3.33-3.37 (m, 2H, O=CCH_2-C), 3.62-4.17 (m, 4H, O=PCH_2-Me), 5.02-5.06 (d, *J* = 18.8 Hz, 1H, C-OH), 7.36-7.52 (d, 4H, Ar-H) ppm.

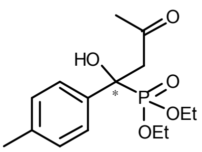


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.226	Unknown	3647130	50.06	231161	52.29
2	10.320	Unknown	3638317	49.94	210916	47.71

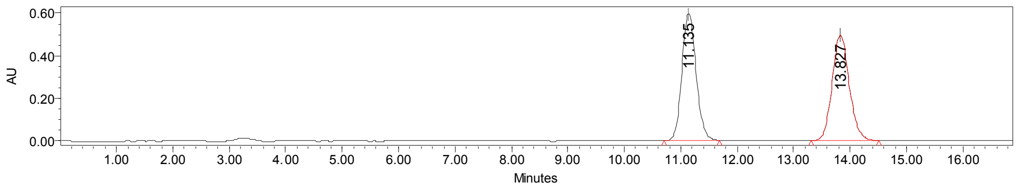


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.264	Unknown	21577023	96.79	1441440	96.45
2	10.445	Unknown	716538	3.21	53006	3.55

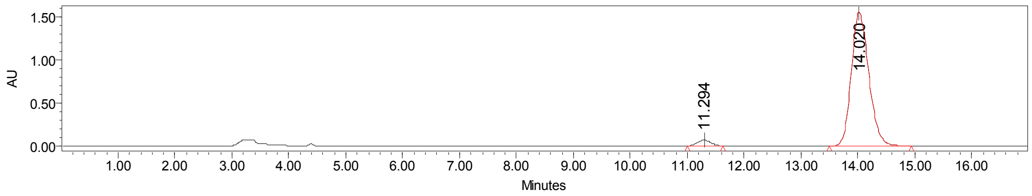
Diethyl [1-(4-methylphenyl)-1-hydroxy-3-oxobutyl] phosphonate (4j)



solid; 69% yield, 94% *ee*. $[\alpha]_D^{18}$ = 48.9 (*c* 0.176 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 11.3 min (minor) and 14.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) 1.11 (t, *J* = 7.2 Hz, 3H, Me-H), 1.32 (t, *J* = 6.8 Hz, 3H, Me-H), 2.14 (s, 3H, O=CCH_3), 2.33 (s, 3H, Ar-CH_3), 3.27-3.41 (m, 2H, O=CCH_2-C), 3.66-4.19 (m, 4H, O=PCH_2-Me), 4.99 (d, *J* = 19.6 Hz, 1H, C-OH), 7.17-7.49 (m, 4H, Ar-H)ppm.

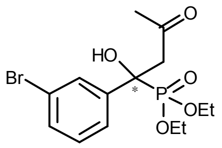


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	11.135	Unknown	10444324	50.05	598075	54.62
2	13.827	Unknown	10425171	49.95	496926	45.38

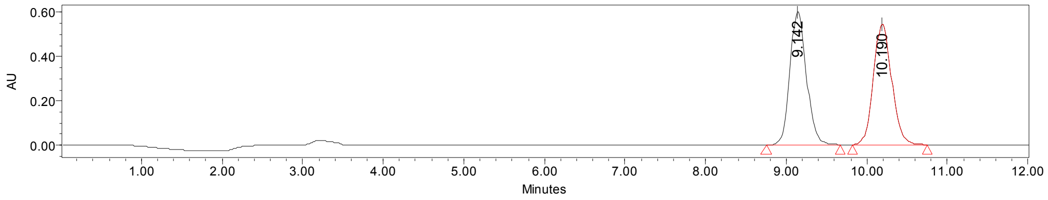


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	11.294	Unknown	1113884	3.25	67771	4.20
2	14.020	Unknown	33152462	96.75	1545345	95.80

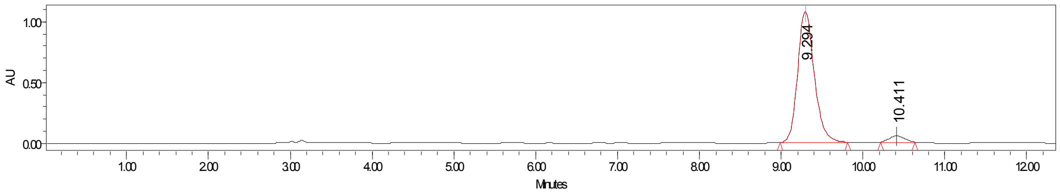
Diethyl [1-(3-bromophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4k)



solid; 87% yield, 92% *ee*. $[\alpha]_D^{18}$ = 35.9 (*c* 0.640 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.3 min (major) and 10.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 1.14 (t, J = 6.8 Hz, 3H, Me-H), 1.33 (t, J = 6.8 Hz, 3H, Me-H), 2.18 (s, 3H, $O{=}CCH_3$), 3.31-3.35 (m, 2H, $O{=}CCH_2$-C), 3.75-4.20 (m, 4H, $O{=}PCH_2$-Me), 5.23 (d, J = 18.4 Hz, 1H, C-OH), 7.22-7.79 (m, 4H, Ar-H) ppm.



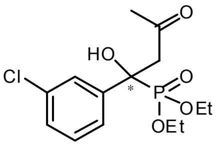
	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.142	Unknown	8604927	50.06	601889	52.47
2	10.190	Unknown	8584844	49.94	545254	47.53



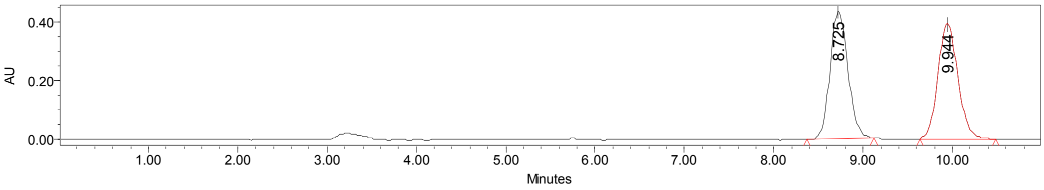
	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.294	Unknown	15265484	95.93	1079670	95.52

2	10.411	Unknown	648432	4.07	50682	4.48

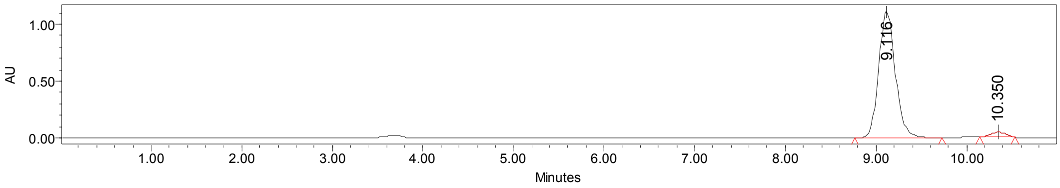
Diethyl [1-(3-chlorophenyl)-1-hydroxy-3-oxobutyl] phosphonate (4l)



solid; 95% yield, 94% *ee*. $[\alpha]_D^{17}$ = 42.9 (*c* 0.756 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.1 min (major) and 10.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 1.11-1.15 (t, *J* = 7.0 Hz, 3H, Me-H), 1.31-1.35 (t, *J* = 6.8 Hz, 3H, Me-H), 2.18 (s, 3H, $O{=}CCH_3$), 3.31-3.35 (m, 2H, $O{=}CCH_2$-C), 3.74-4.21 (m, 4H, $O{=}PCH_2$-Me), 5.13-5.18 (d, *J* = 18.4 Hz, 1H, C-OH), 7.25-7.64 (m, 4H, Ar-H) ppm.

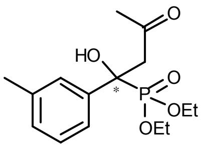


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	8.725	Unknown	6009822	49.93	433062	52.59
2	9.944	Unknown	6025680	50.07	390428	47.41

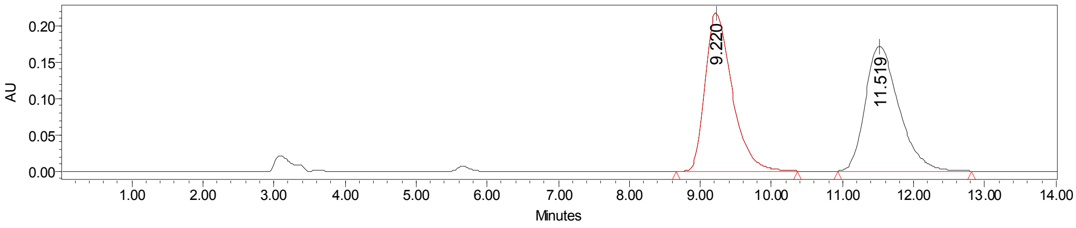


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.116	Unknown	14277763	96.79	1113649	96.30
2	10.350	Unknown	488733	3.21	42813	3.70

Diethyl [1-(3-methylphenyl)-1-hydroxy-3-oxobutyl] phosphonate (4m)

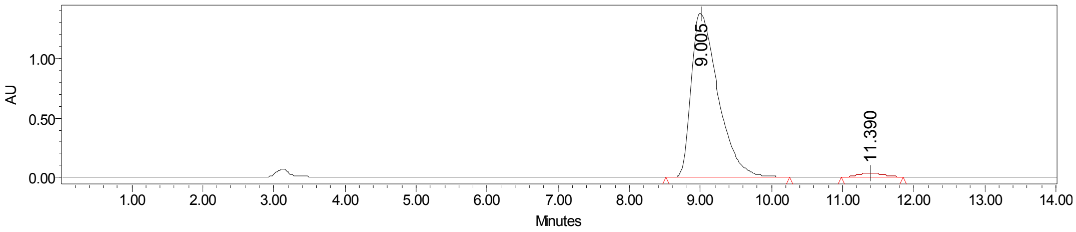


solid; 96% yield, 96% *ee*. $[\alpha]_D^{18}$ = 38.7 (*c* 0.630 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 8.7 min (major) and 10.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 1.10 (t, *J* = 7.2 Hz, 3H, Me-H), 1.33 (t, *J* = 7.2 Hz, 3H, Me-H), 2.15 (s, 3H, $O{=}CCH_3$), 2.37 (s, 3H,Ar-CH_3), 3.29-3.41 (m, 2H, $O{=}CCH_2$-C), 3.64-4.19 (m, 4H, $O{=}PCH_2$-Me), 5.04 (d, *J* = 18.8 Hz, 1H, C-OH), 7.09-7.44 (m, 4H, Ar-H) ppm.



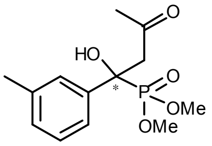
	Retention Time	Peak Type	Area	% Area	Height	% Height

1	9.220	Unknown	5712006	50.57	216987	55.97
2	11.519	Unknown	5582762	49.43	170697	44.03

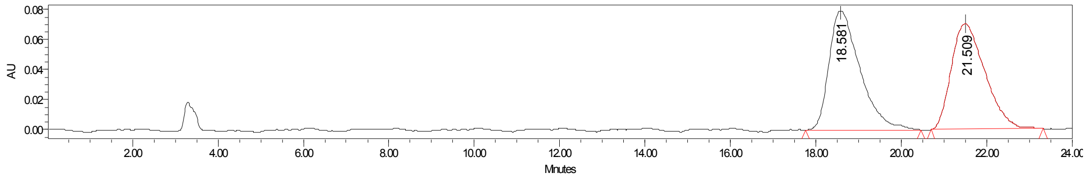


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.005	Unknown	36176385	97.82	1378028	97.66
2	11.390	Unknown	806844	2.18	33024	2.34

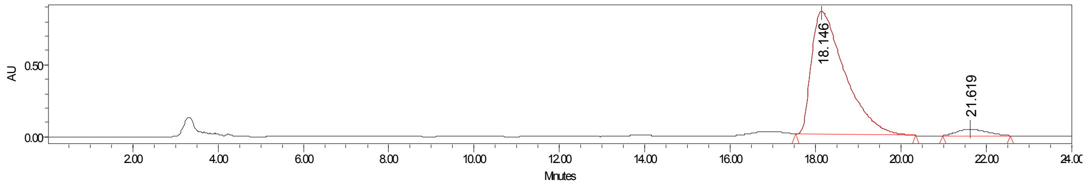
Dimethyl [1-(3-methylphenyl)-1-hydroxy-3-oxobutyl] phosphonate (4n)



solid; 75% yield, 91% *ee*. $[\alpha]_D^{21} = 36.9$ (*c* 0.412 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 220$ nm, retention time: 8.7 min (minor) and 10.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) 2.15 (s, 3H,O=CCH_3), 2.37 (s, 3H,Ar-CH_3),3.29-3.43 (m, 2H, O=CCH_2-C), 3.45-3.47 (d, *J* = 10.4 Hz, 3H, O=PCH_3), 3.79-3.82 (d, *J* = 10.4 Hz, 3H, O=PCH_3), 5.08-5.13 (d, *J* = 19.6 Hz, 1H, C-OH), 7.10-7.45 (m, 4H, Ar-H) ppm.

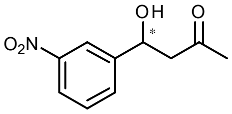


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	18.581	Unknown	4001648	50.88	79207	52.92
2	21.509	Unknown	3863927	49.12	70472	47.08

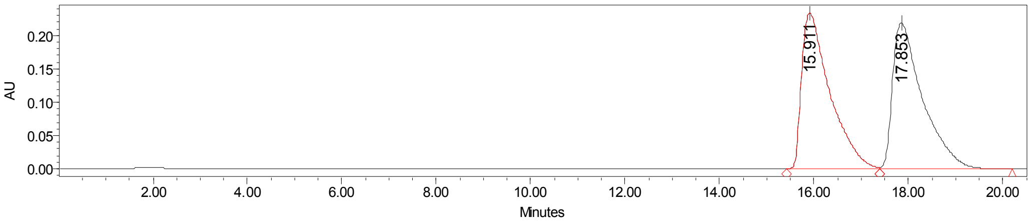


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	18.146	Unknown	46656521	95.59	856025	95.07
2	21.619	Unknown	2151415	4.41	44414	4.93

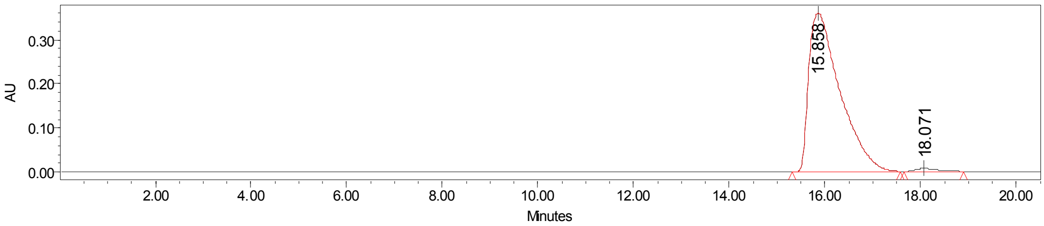
4-Hydroxy-4-(3'-nitrophenyl)-butan-2-one (6a)



88% yield, 97% *ee*. $[\alpha]_D^{22} = 53.8$ (*c* 0.176 in CH_2Cl_2) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 15.86 min (major) and 18.07 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 2.24 (s, 3H, O=C-CH_3), 2.88-2.90 (m, 2H, O=C-CH_2-), 3.63 (d, *J* = 3.2 Hz, 1H, Ar-CH-), 5.25-5.29 (m, 1H, -OH), 7.52-8.25 (m, 4H, Ar-H) ppm.

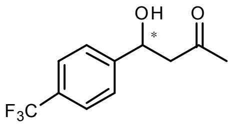


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	15.911	Unknown	9677383	50.01	233819	51.59
2	17.853	Unknown	9672411	49.99	219401	48.41

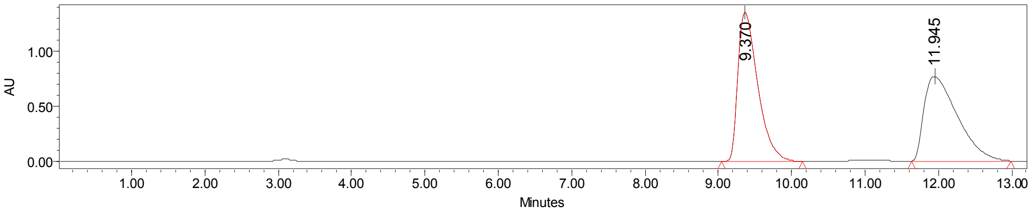


	Retention Time	Peak Type	Area	% Area	Height	% Height
1	15.858	Unknown	16269892	98.63	359282	98.12
2	18.071	Unknown	225856	1.37	6882	1.88

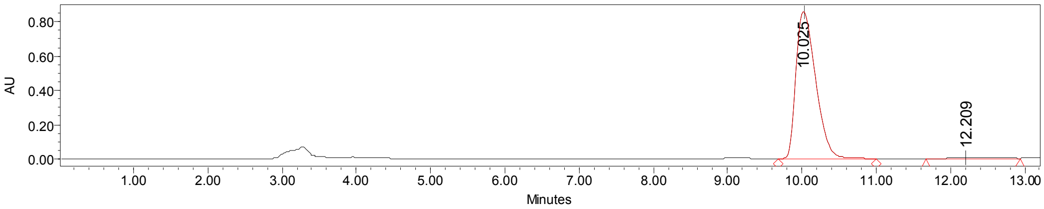
4-Hydroxy-4-(4'-trifluoromethyl)-butan-2-one (6b)



86% yield, 99% *ee*. $[\alpha]_D^{22}$ = 61.3 (*c* 0.166 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AS-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.0 min (major) and 12.2 min (minor); ^1H NMR (400 MHz, $CDCl_3$) 2.21 (s, 3H, O=C-CH_3), 2.84-2.86 (m, 2H, O=C-CH_2-), 3.22 (s, Ar-CH-), 5.20-5.22 (t, *J* = 5.2 Hz, 1H, -OH), 7.47-7.62 (m, 4H, Ar-H) ppm.



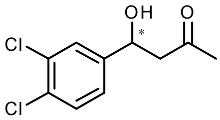
	Retention Time	Peak Type	Area	% Area	Height	% Height
1	9.370	Unknown	25409304	51.26	1355579	63.80
2	11.945	Unknown	24163067	48.74	769102	36.20



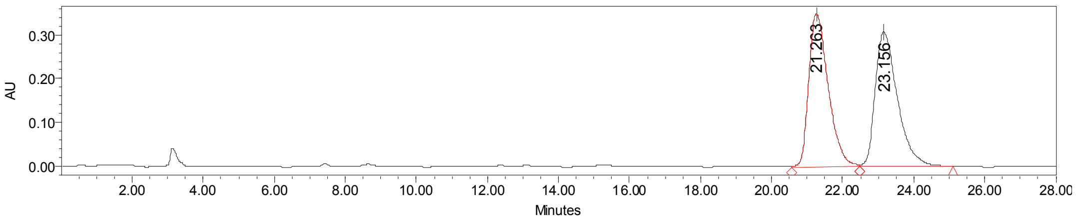
	Retention Time	Peak Type	Area	% Area	Height	% Height
1	10.025	Unknown	15662353	99.62	854898	99.80

2	12.209	Unknown	59226	0.38	1750	0.20

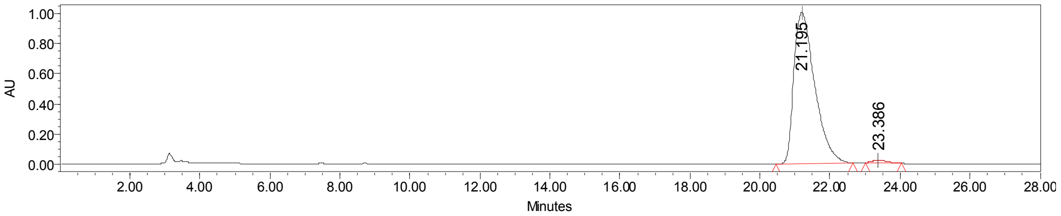
4-Hydroxy-4-(3’,4’-dichlorophenyl)-butan-2-one (6c)



87% yield, 97% *ee*. $[\alpha]_D^{22}$ = 56.4 (*c* 0.192 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AS-H, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 21.2 min (major) and 23.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) 2.20 (s, 3H, O=C-CH_3), 2.88-2.82 (t, *J* =5.4 Hz 2H, O=C-CH_2-), 3.54-3.55 (d, *J* = 3.2 Hz, 1H, Ar-CH-), 5.10-5.12 (m, 1H, -OH), 7.16-7.47 (m, 4H, Ar-H) ppm.



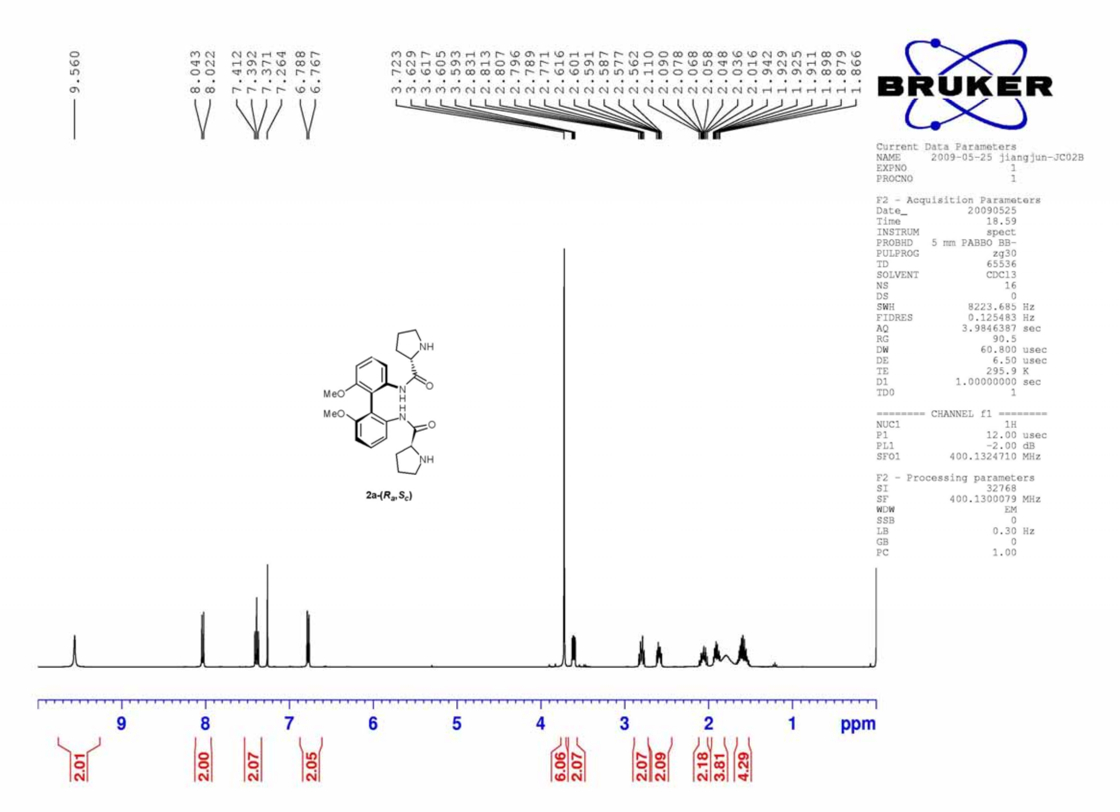
	Name	Retention Time	Peak Type	Area	% Area	Height	% Height
1		21.263	Unknown	13313206	50.02	348840	53.20
2		23.156	Unknown	13300809	49.98	306828	46.80

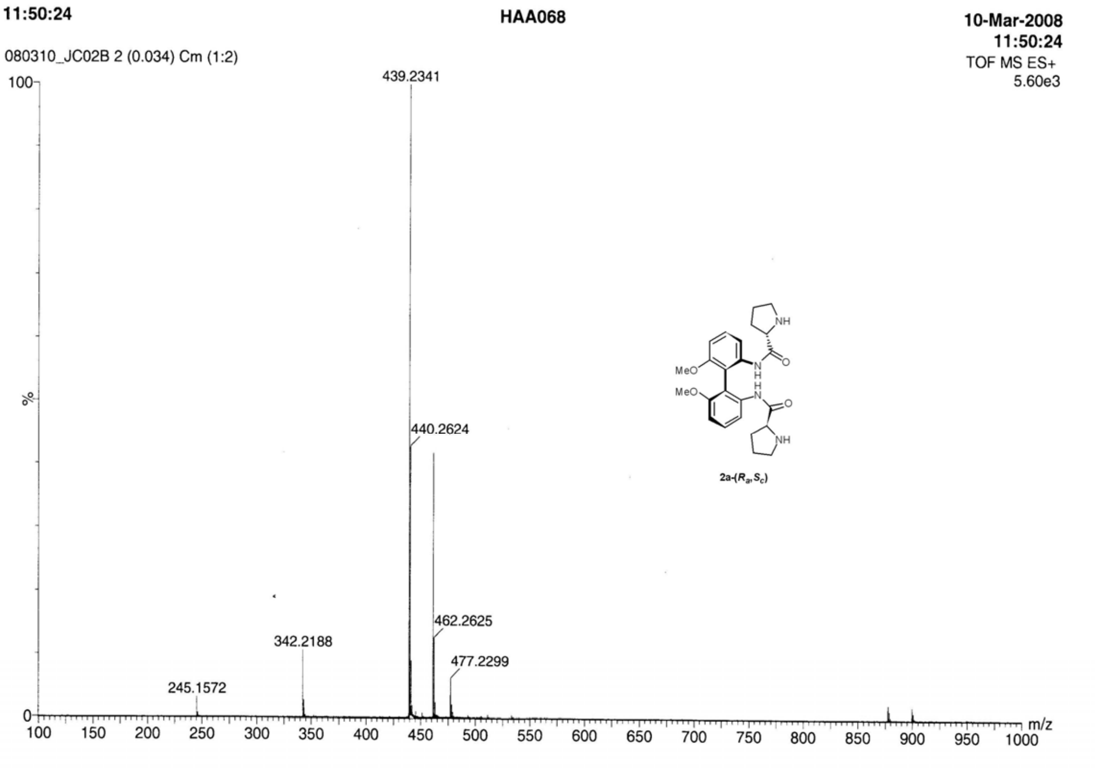


	Name	Retention Time	Peak Type	Area	% Area	Height	% Height
1		21.195	Unknown	41836529	98.74	1007093	98.30
2		23.386	Unknown	532063	1.26	17434	1.70

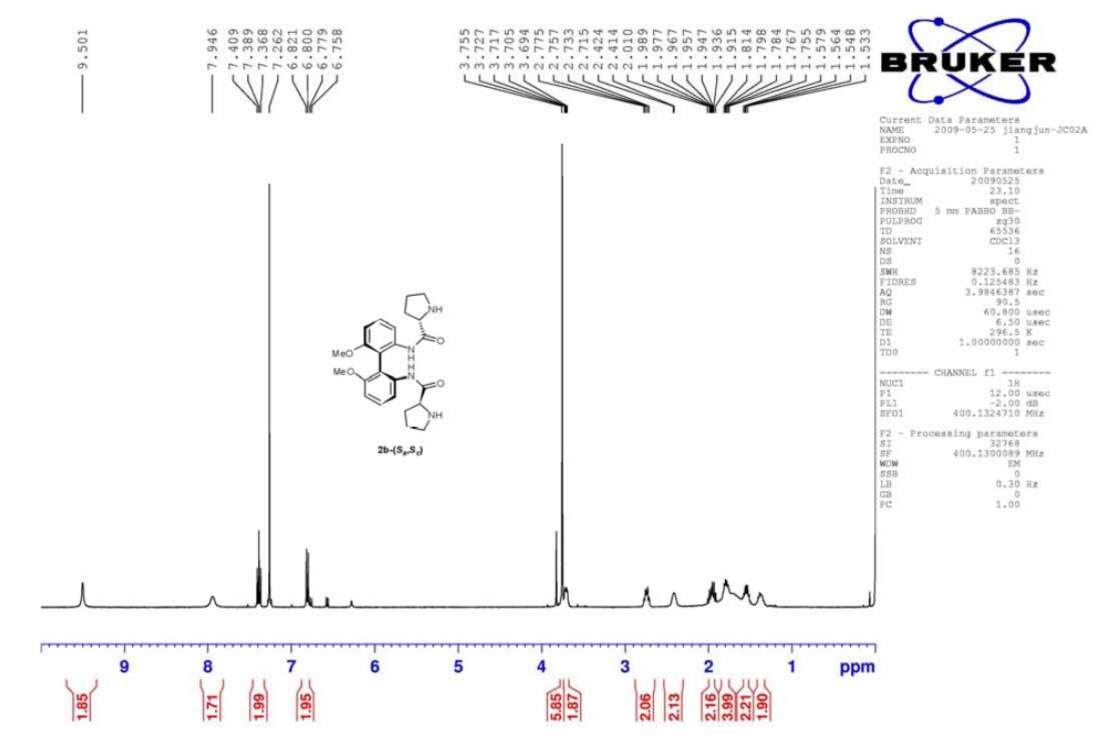
(G) Copies of NMR spectra for 2a-2d and products

Catalyst **2a:**




11:50:24
HAA068
10-Mar-2008
11:50:24
TOF MS ES+
5.60e3
080310_JC02B 2 (0.034) Cm (1:2)
100
%
0
439.2341
440.2624
462.2625
477.2299
342.2188
245.1572
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z
MeO
MeO
NH
NH
N
H
N
H
O
O
2a-(Ra,Sc)

Catalyst **2b:**


9.501
7.946
7.409
7.389
7.368
7.262
6.821
6.800
6.779
6.758
3.755
3.727
3.717
3.705
3.694
2.775
2.757
2.733
2.715
2.424
2.414
2.010
1.989
1.977
1.967
1.957
1.947
1.936
1.915
1.814
1.798
1.784
1.767
1.755
1.579
1.564
1.548
1.533
BRUKER
Current Data Parameters
NAME 2009-05-25 jiangjun-JC02A
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090525
Time 23.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
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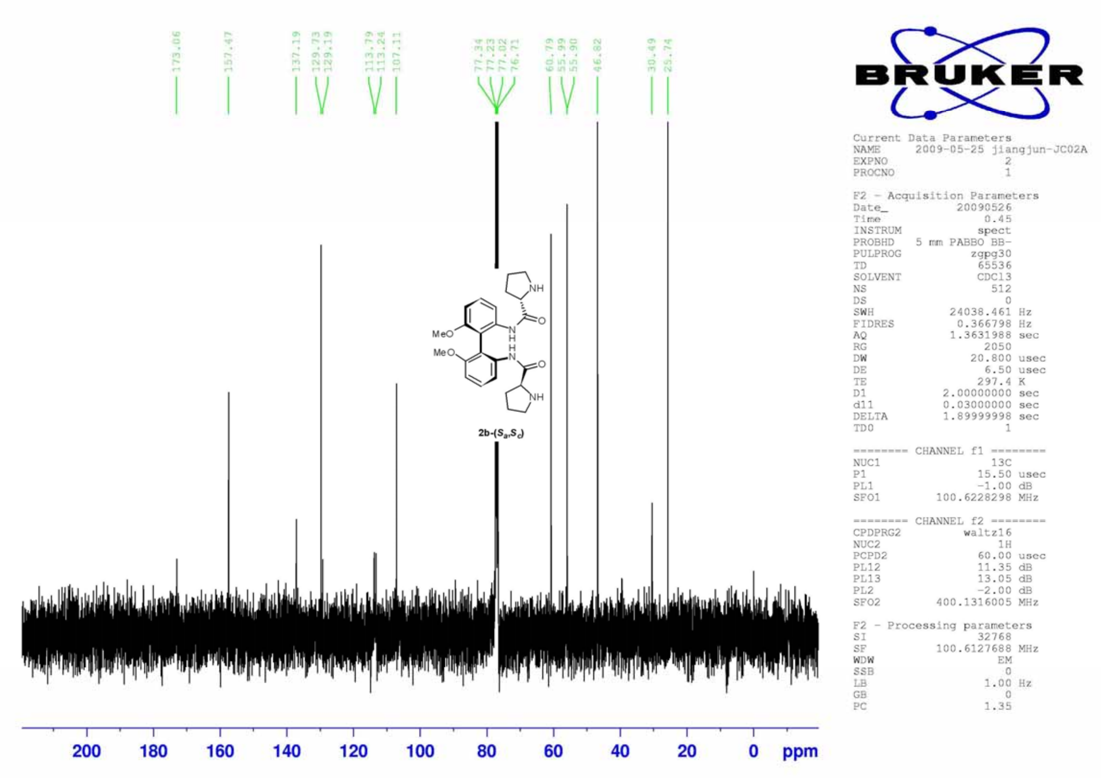
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO
MeO
NH
NH
N
H
N
H
O
O
2b-(Sa,Sc)
9
8
7
6
5
4
3
2
1
ppm
1.85
1.71
1.99
1.95
5.85
1.87
2.06
2.13
2.16
3.99
2.21
1.90



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EXPNO                     2
PROCNO                    1

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PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                     6.50 usec
TE                    297.4 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    15.50 usec
PL1                   -1.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 60.00 usec
PL12                  11.35 dB
PL13                  13.05 dB
PL2                   -2.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
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SF              100.6127688 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
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PC                     1.35
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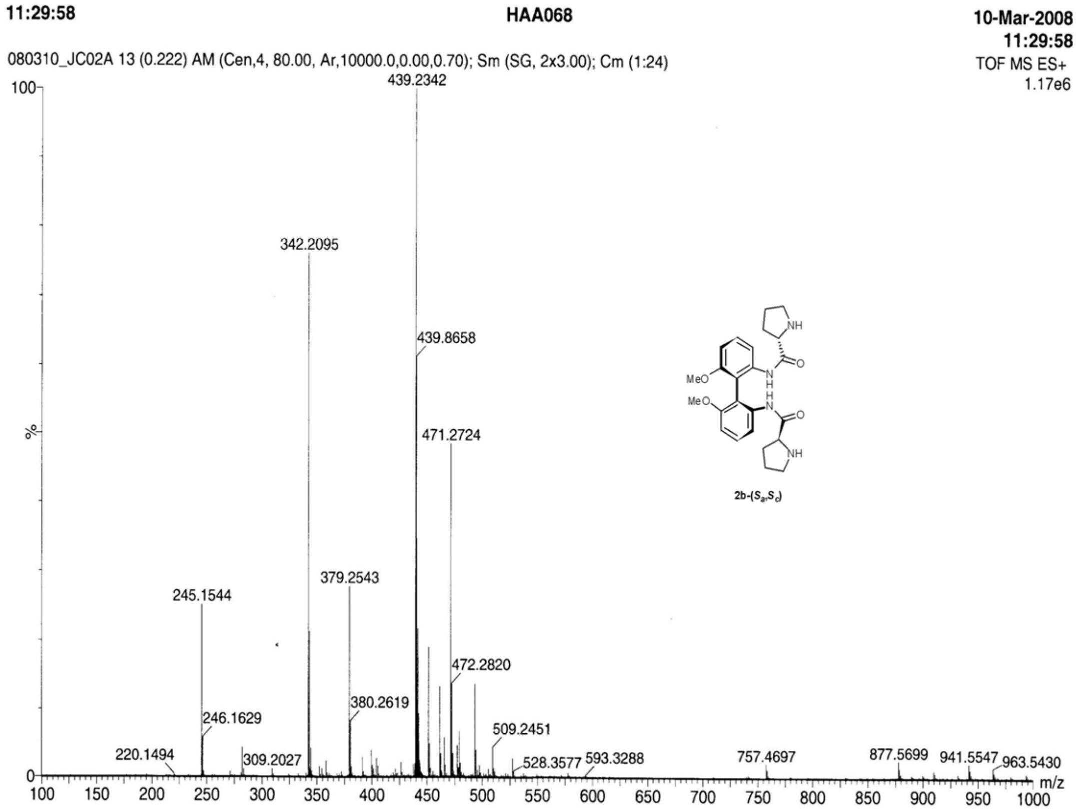

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                                                                   11:29:58
080310_JC02A 13 (0.222) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (1:24)
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                                                                    1.17e6
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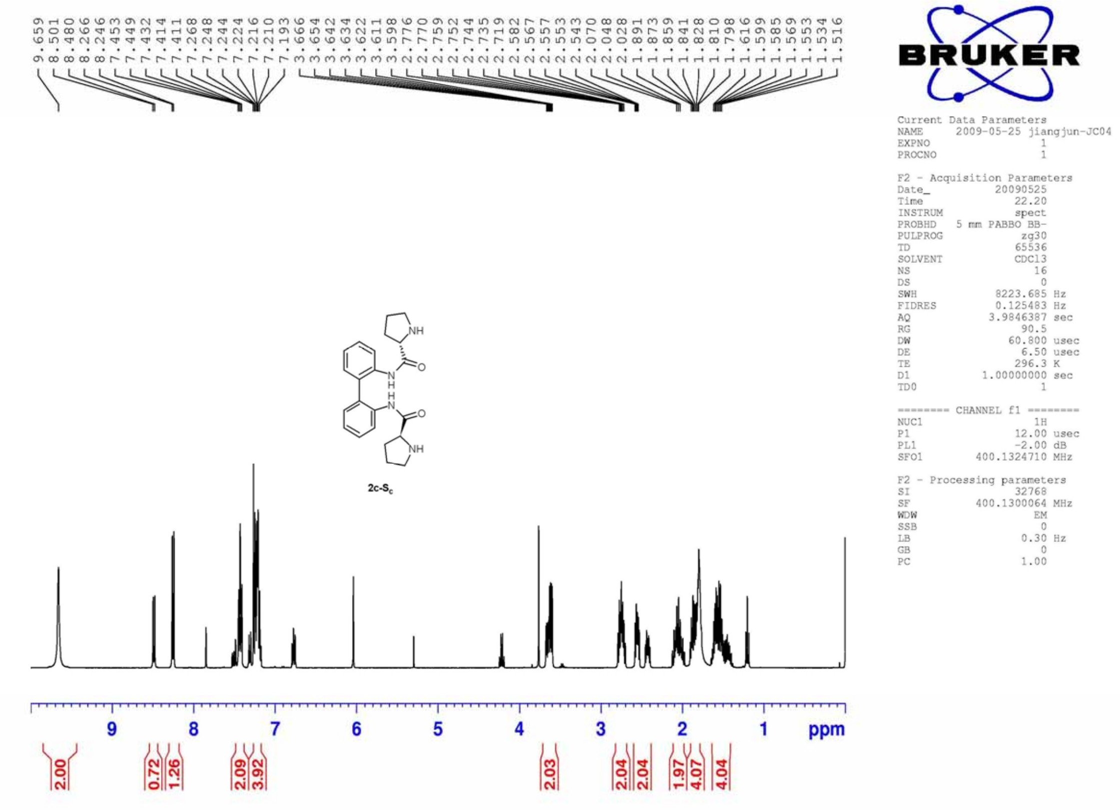
Catalyst **2c:**



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EXPNO                   1
PROCNO                  1

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Date_            20090525
Time                22.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                   90.5
DW                 60.800 usec
DE                   6.50 usec
TE                  296.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300064 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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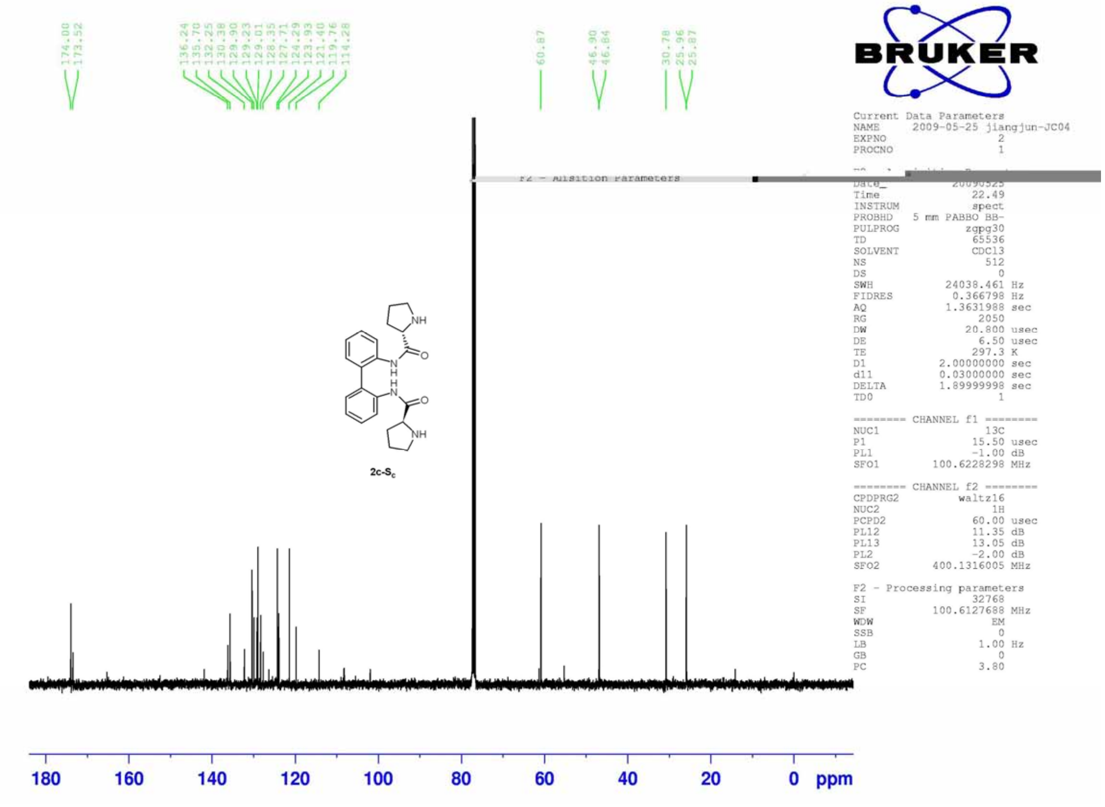

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EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
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Time                22.49
INSTRUM             spect
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PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                   2050
DW                 20.800 usec
DE                   6.50 usec
TE                  297.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.50 usec
PL1                 -1.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               60.00 usec
PL12                11.35 dB
PL13                13.05 dB
PL2                 -2.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
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SF            100.6127688 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   3.80
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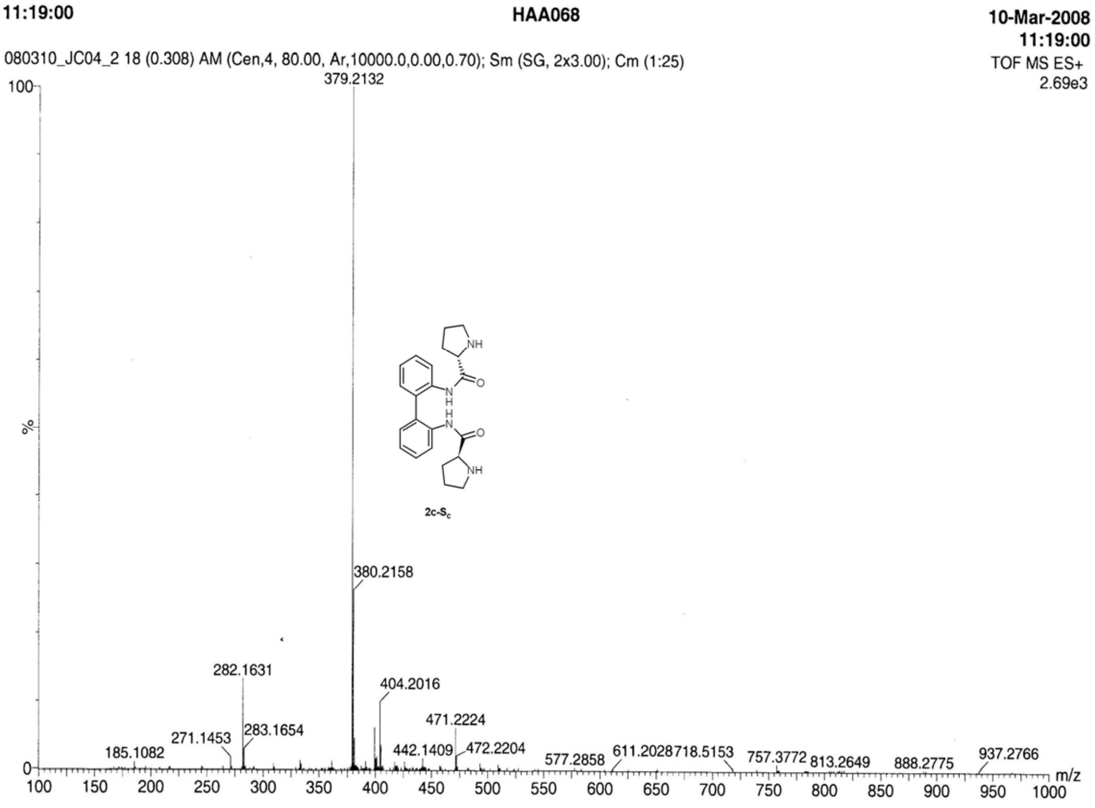
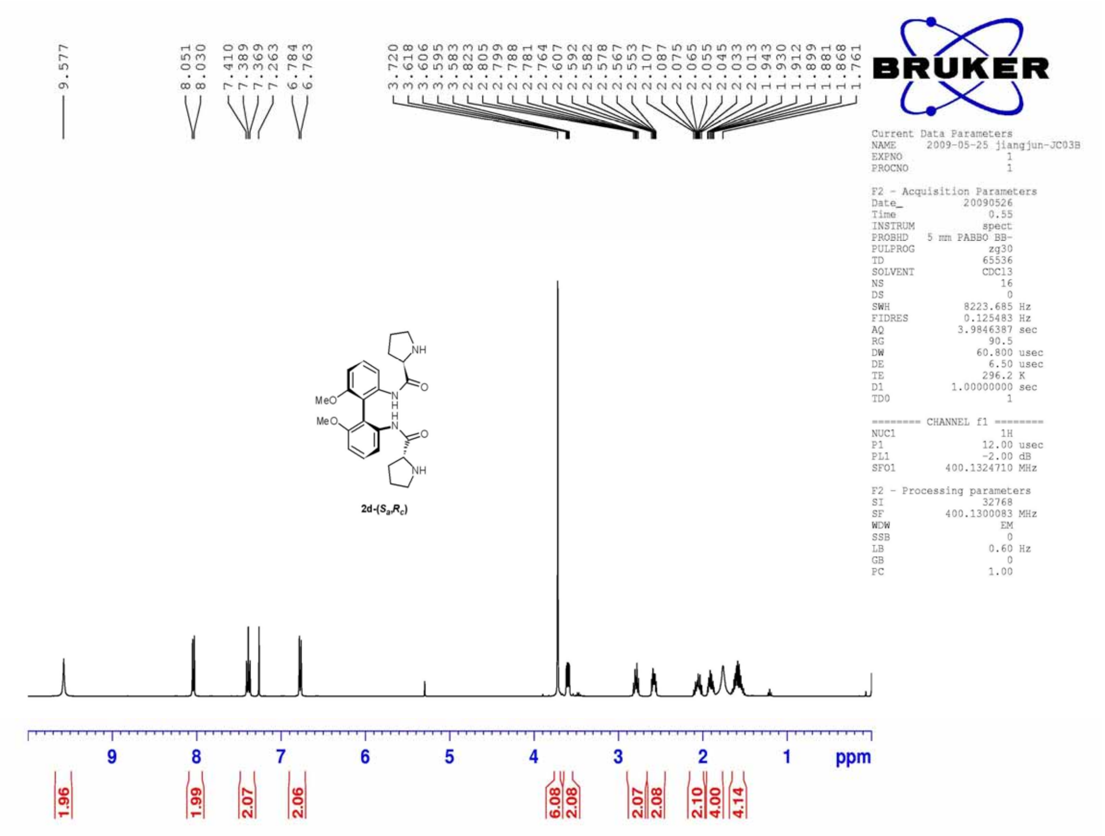


Catalyst **2d:**



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Current Data Parameters
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EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090526
Time                   0.55
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                     90.5
DW                   60.800 usec
DE                     6.50 usec
TE                    296.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.00 usec
PL1                   -2.00 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF              400.1300083 MHz
WDW                      EM
SSB                       0
LB                     0.60 Hz
GB                        0
PC                     1.00
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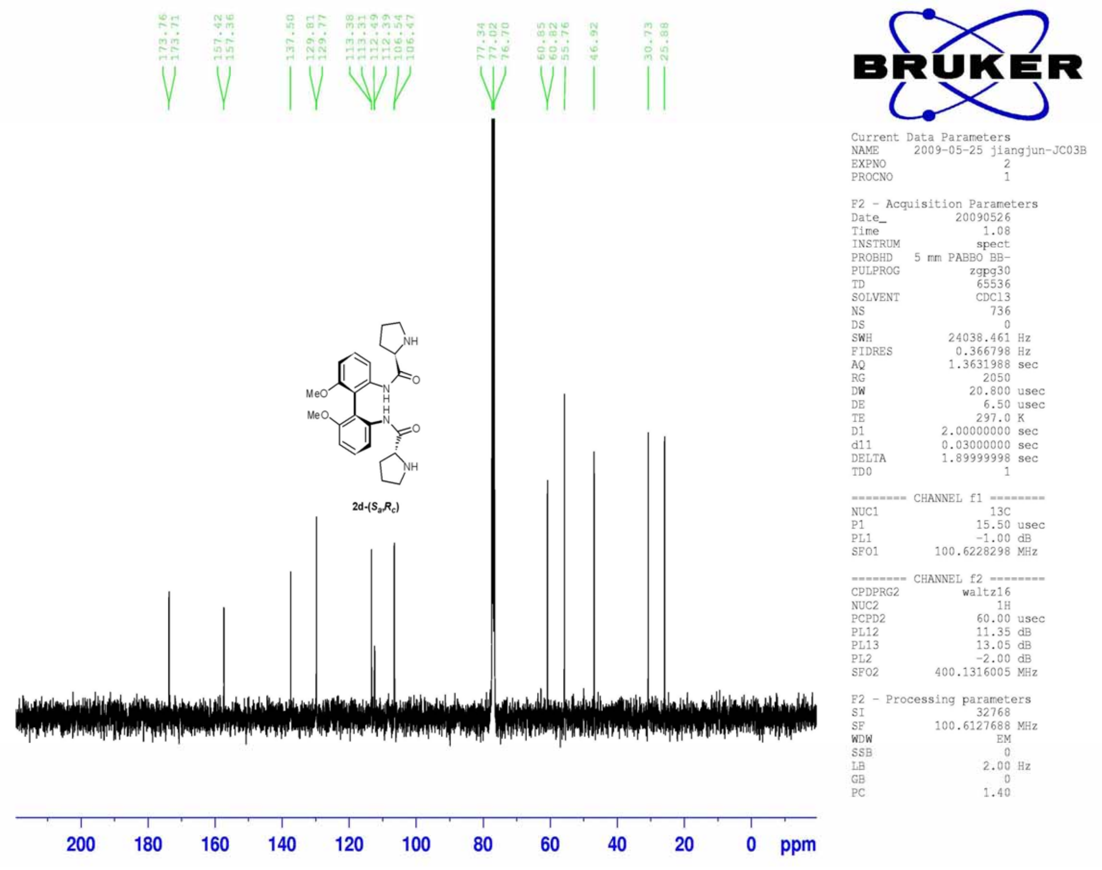

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EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
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Time                  1.08
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PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     736
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   297.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
PL1                  -1.00 dB
SFO1          100.6228298 MHz

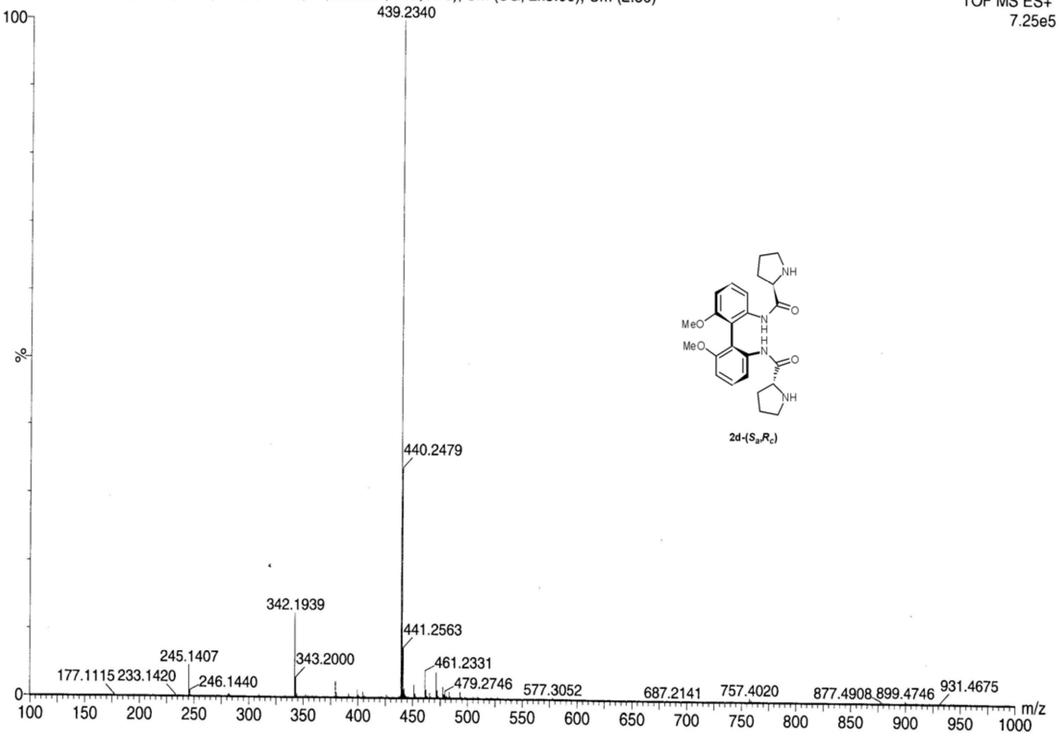
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 11.35 dB
PL13                 13.05 dB
PL2                  -2.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127688 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

11:42:55 **HAA068** **10-Mar-2008**
11:42:55

080310_JC03B 17 (0.291) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (2:30)

TOF MS ES+
7.25e5



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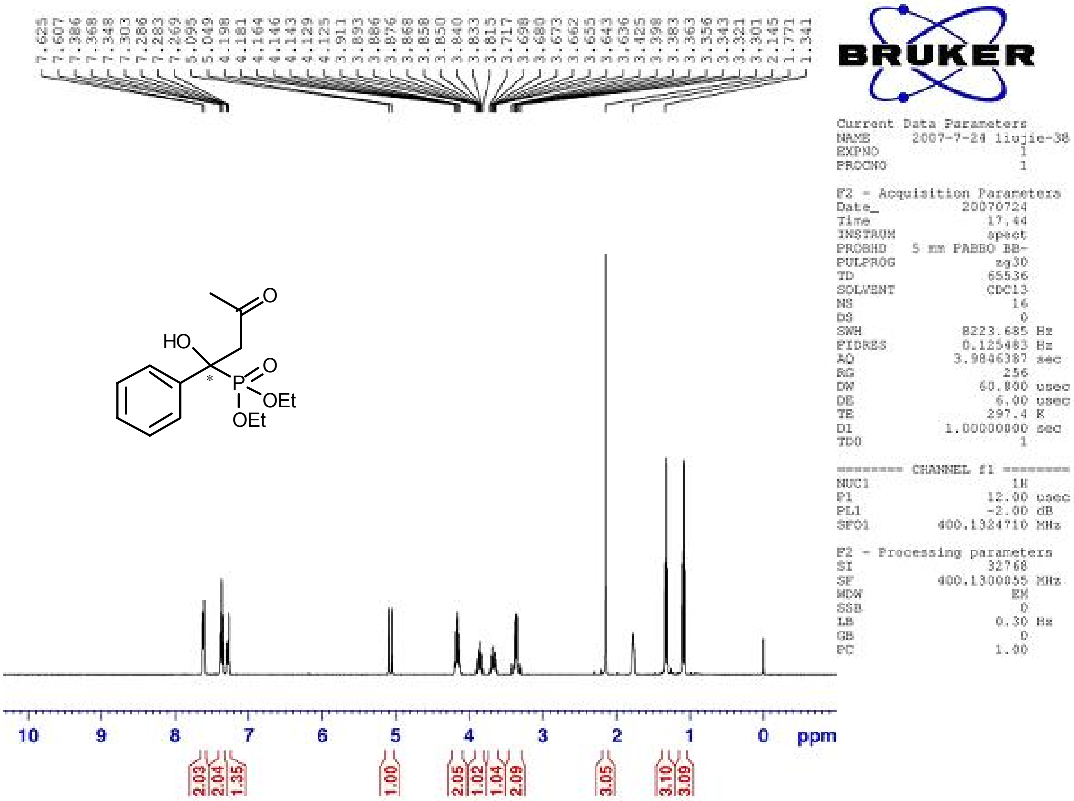

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Current Data Parameters
NAME       2007-7-24 liujie-38
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070724
Time                 17.44
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                     256
DW                  60.800 usec
DE                    6.00 usec
TE                   297.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -2.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300055 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```
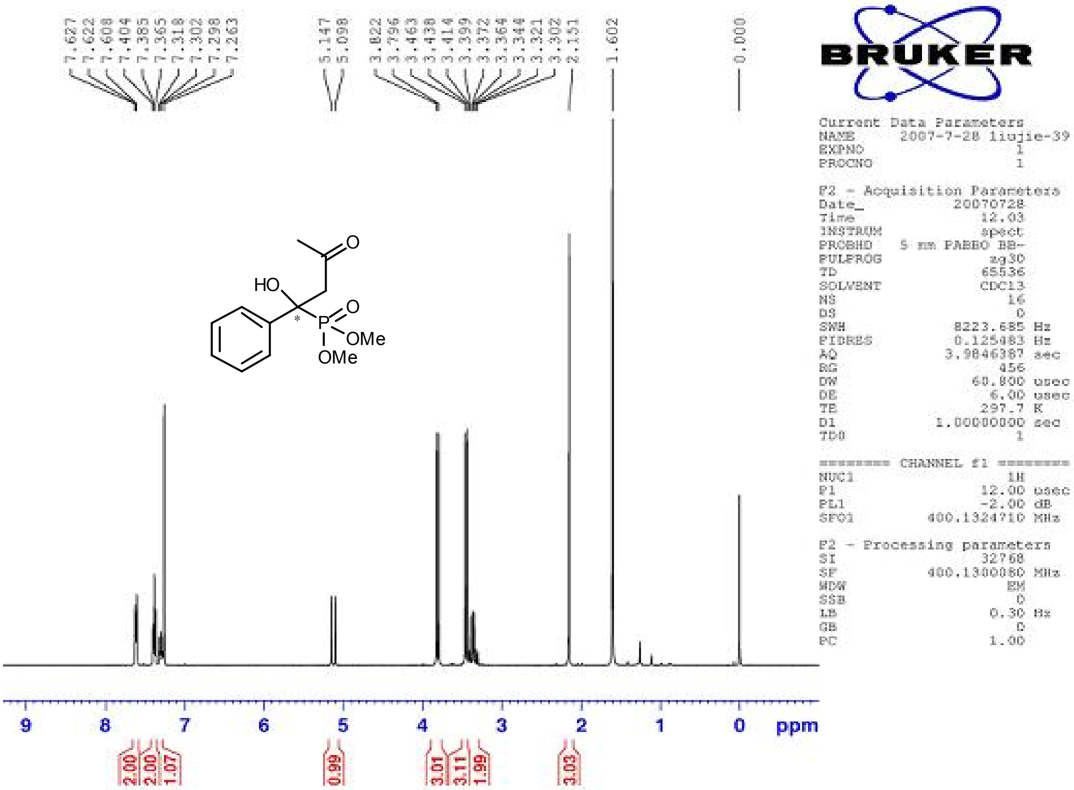

Product **4b:**



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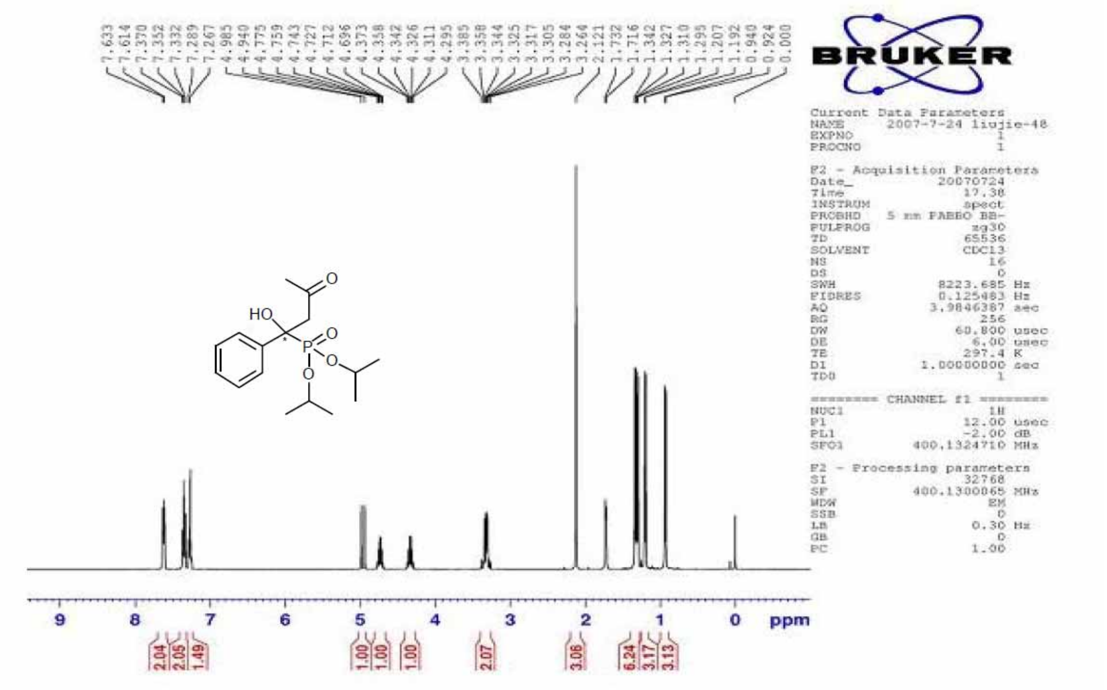
Current Data Parameters
NAME       2007-7-28 liujie-39
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070728
Time                 12.03
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                     456
DW                  60.800 usec
DE                    6.00 usec
TE                   297.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -2.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300080 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Product **4c:**



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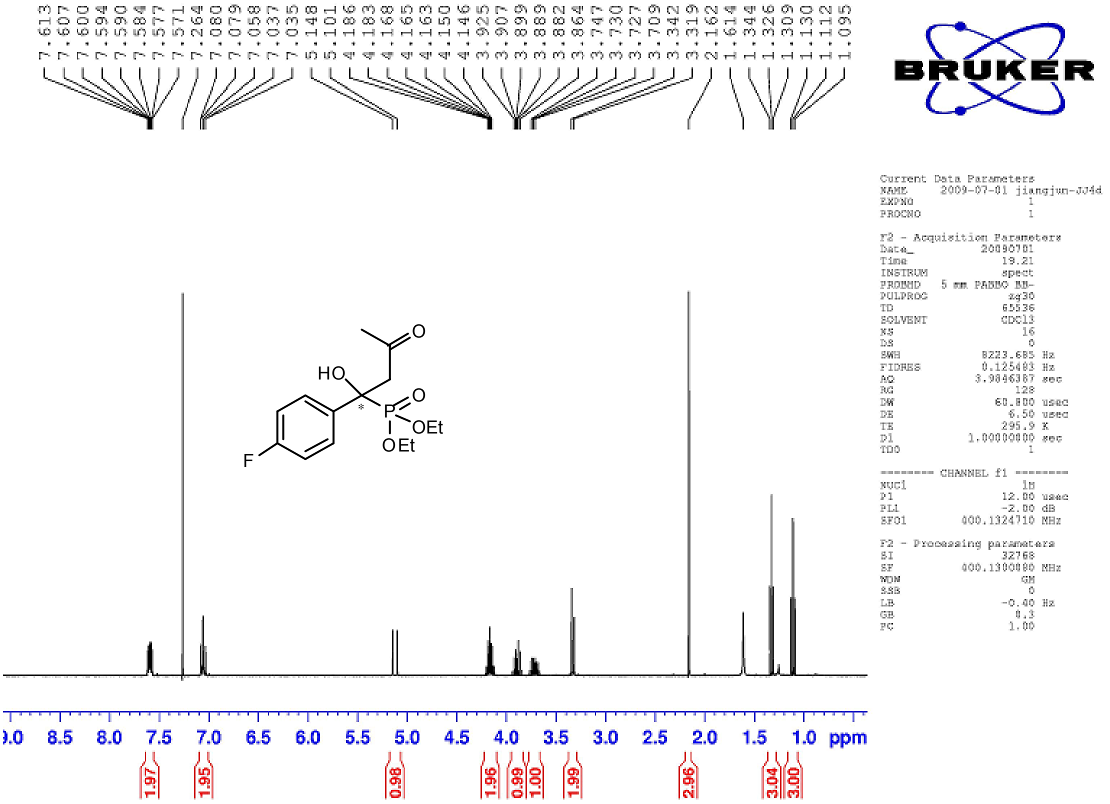

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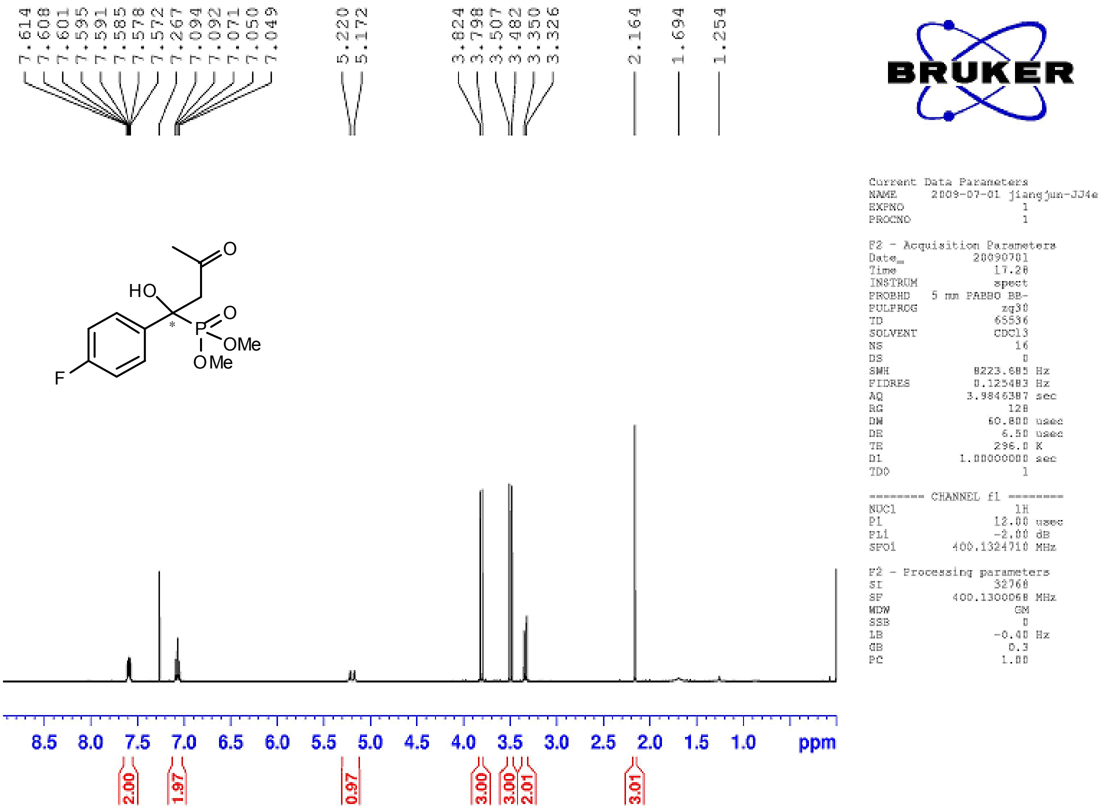

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Current Data Parameters
NAME     2009-07-01 jiangjun-JJ4e
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090701
Time                17.28
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ           3.9846387 sec
RG                    128
DW             60.800 usec
DE               6.50 usec
TE               296.0 K
D1         1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1               12.00 usec
PL1              -2.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF          400.1300068 MHz
WDW                    EM
SSB                     0
LB               -0.40 Hz
GB                    0.3
PC                   1.00
```
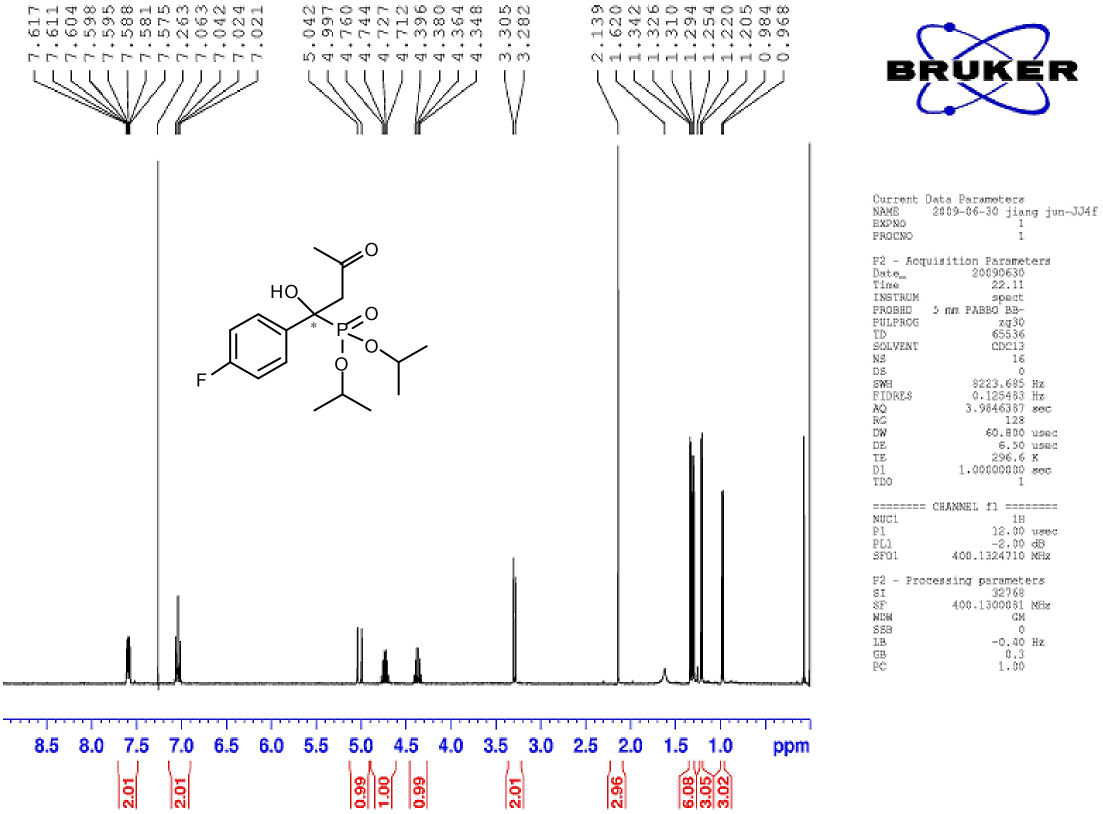

Product **4f:**



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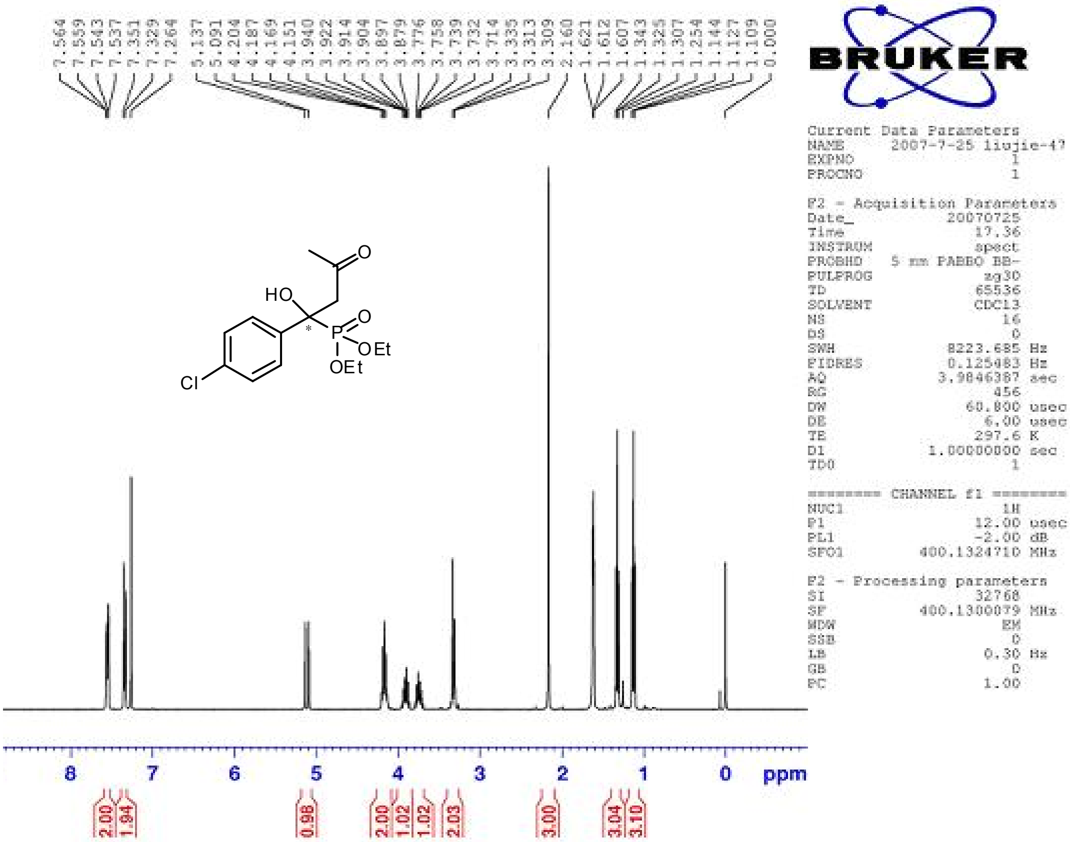
Current Data Parameters
NAME     2009-06-30 jiang jun-JJ4f
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090630
Time                22.11
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ           3.9846387 sec
RG                    128
DW             60.800 usec
DE               6.50 usec
TE               296.6 K
D1         1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1               12.00 usec
PL1              -2.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF          400.1300081 MHz
WDW                    EM
SSB                     0
LB               -0.40 Hz
GB                    0.3
PC                   1.00
```

Product **4g:**



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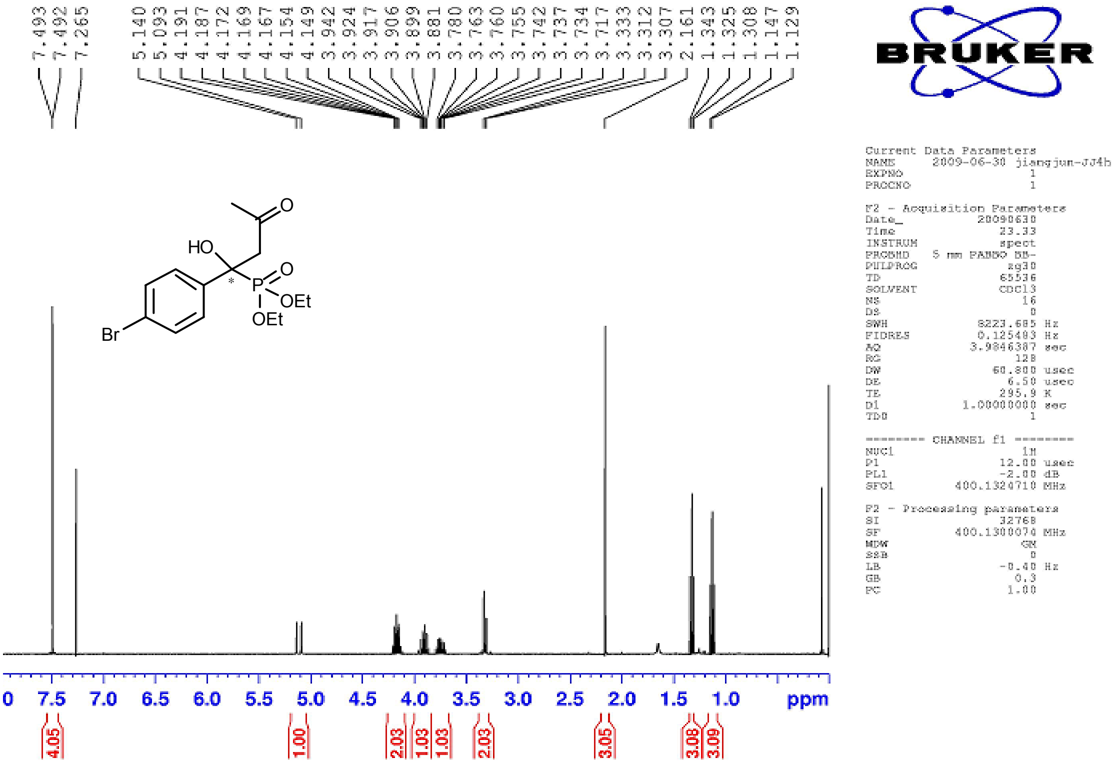
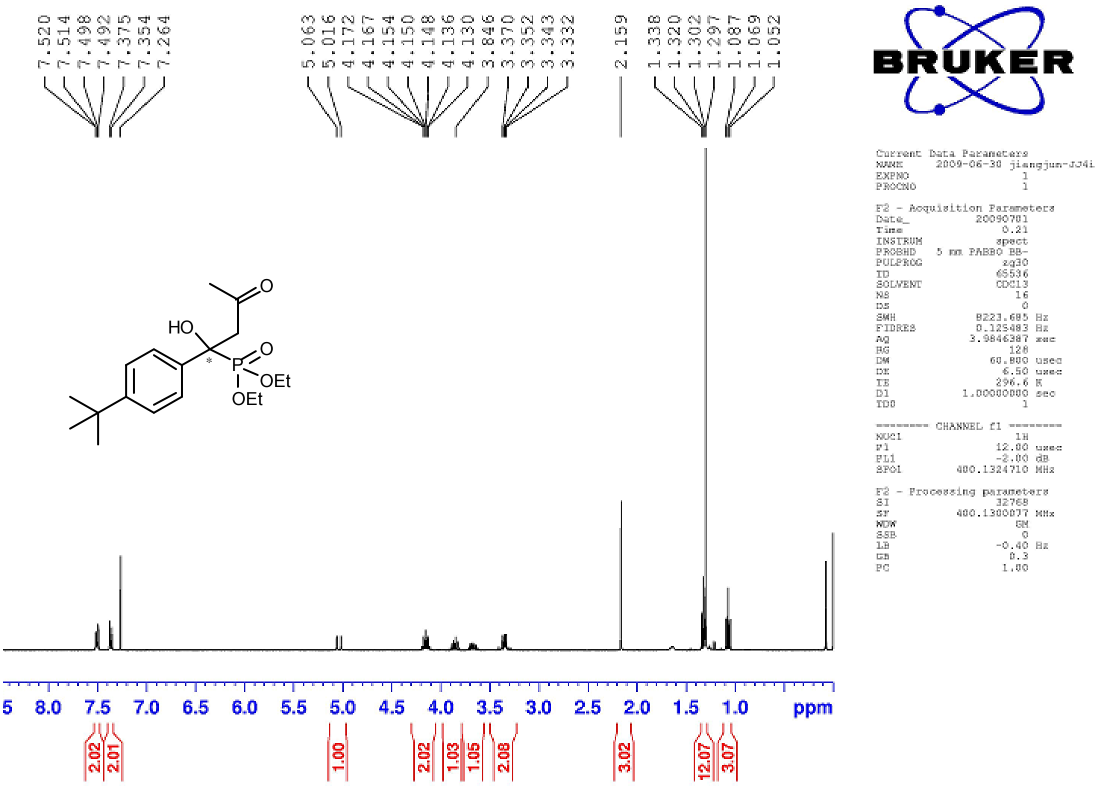


Product **4i:**



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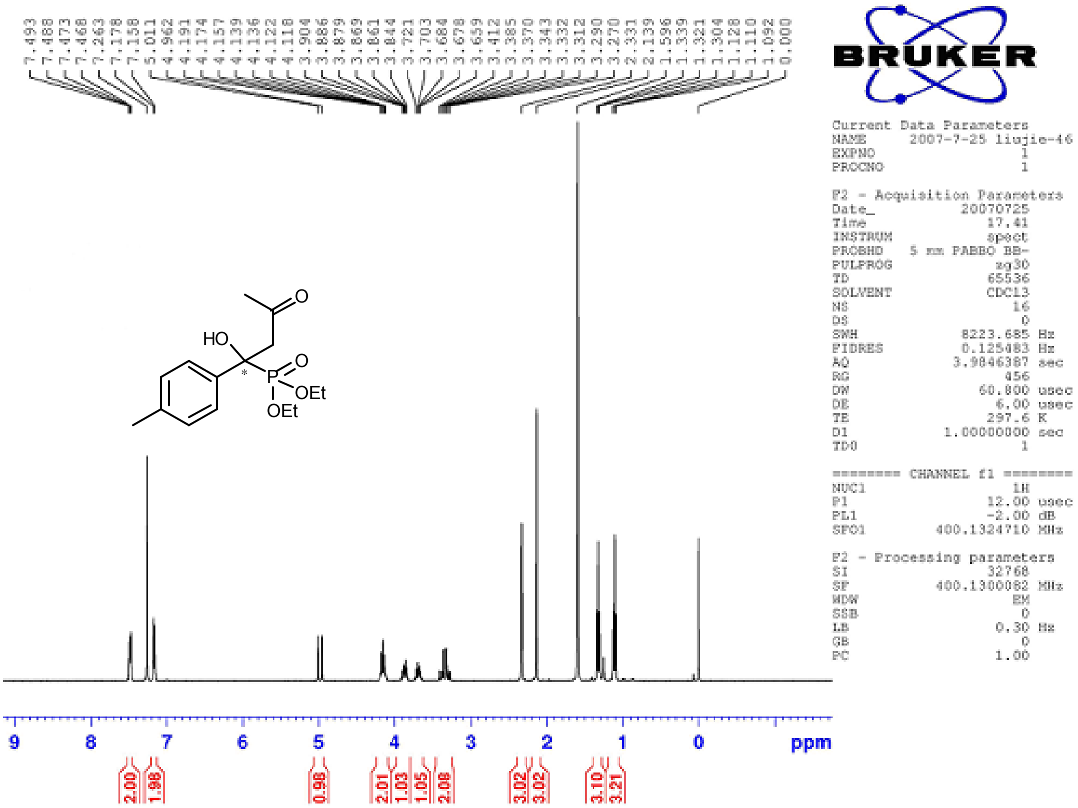

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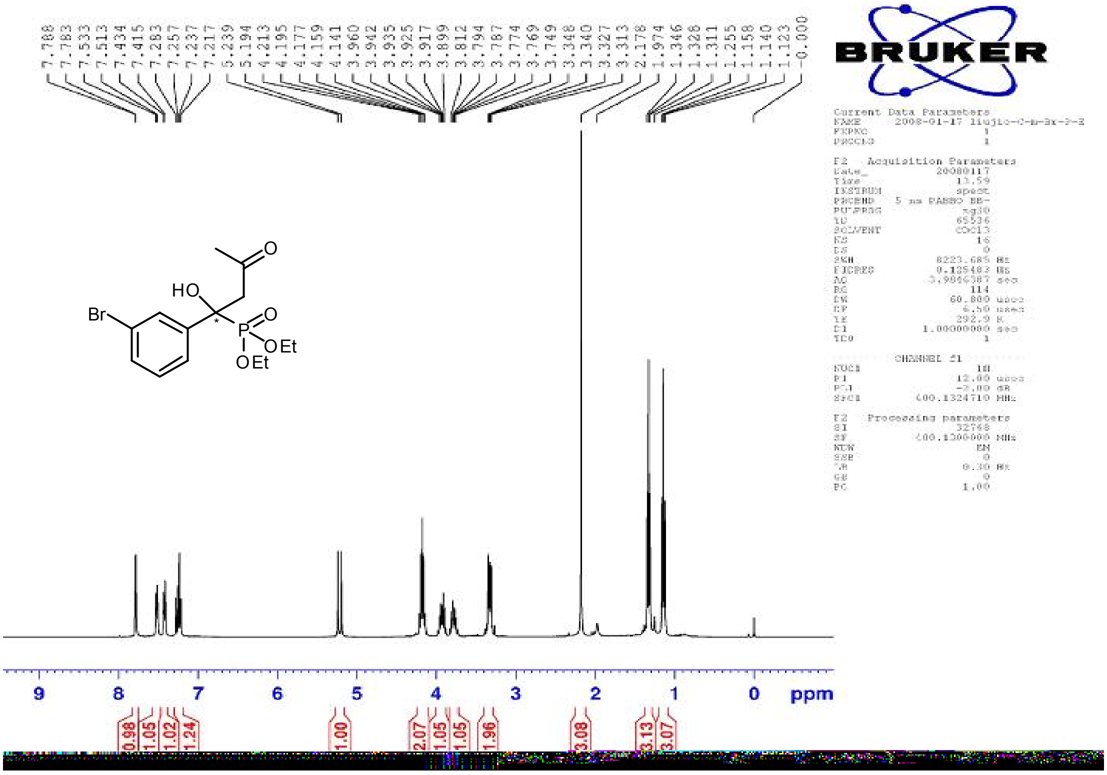

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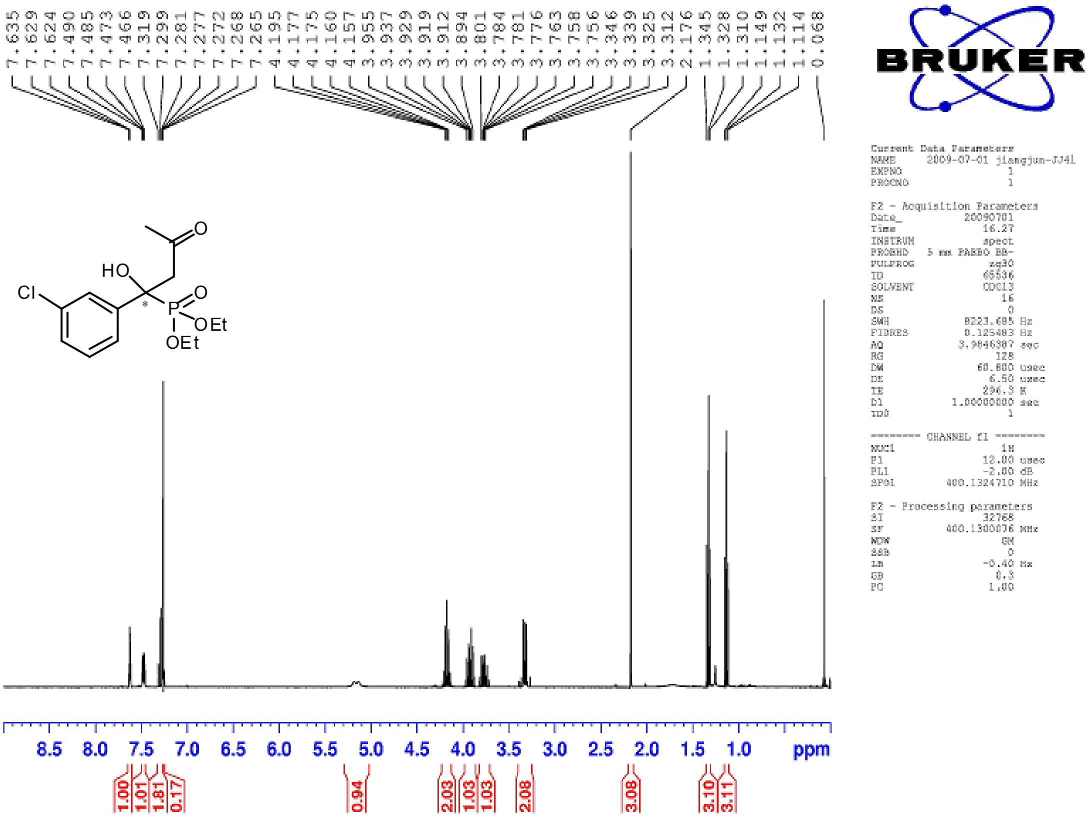

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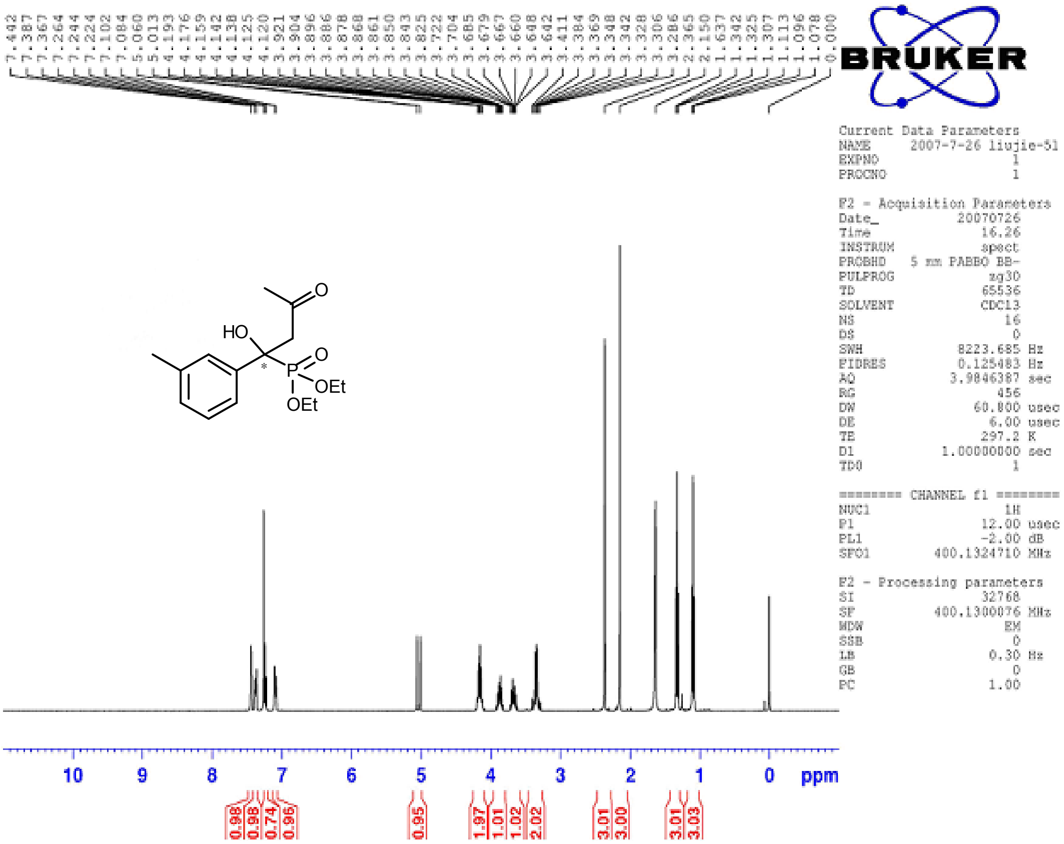

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Current Data Parameters
NAME     2007-7-26 liujie-51
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070726
Time                16.26
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                    456
DW                 60.800 usec
DE                   6.00 usec
TE                  297.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300076 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```
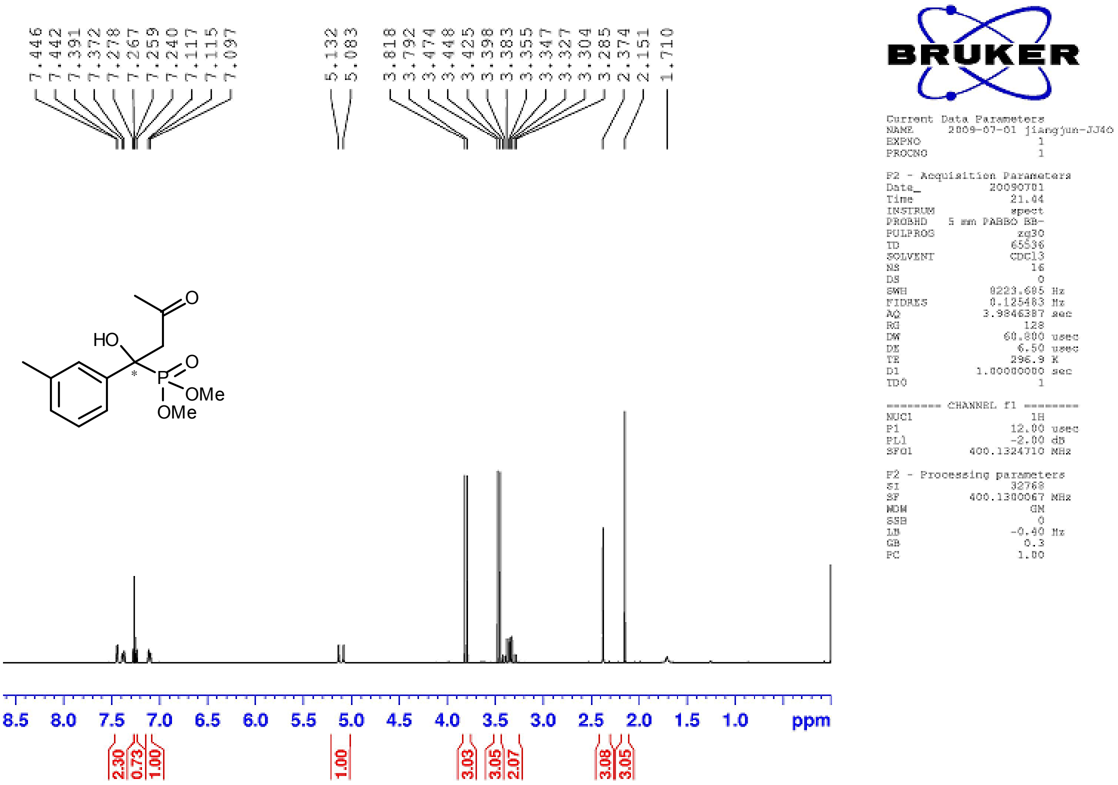
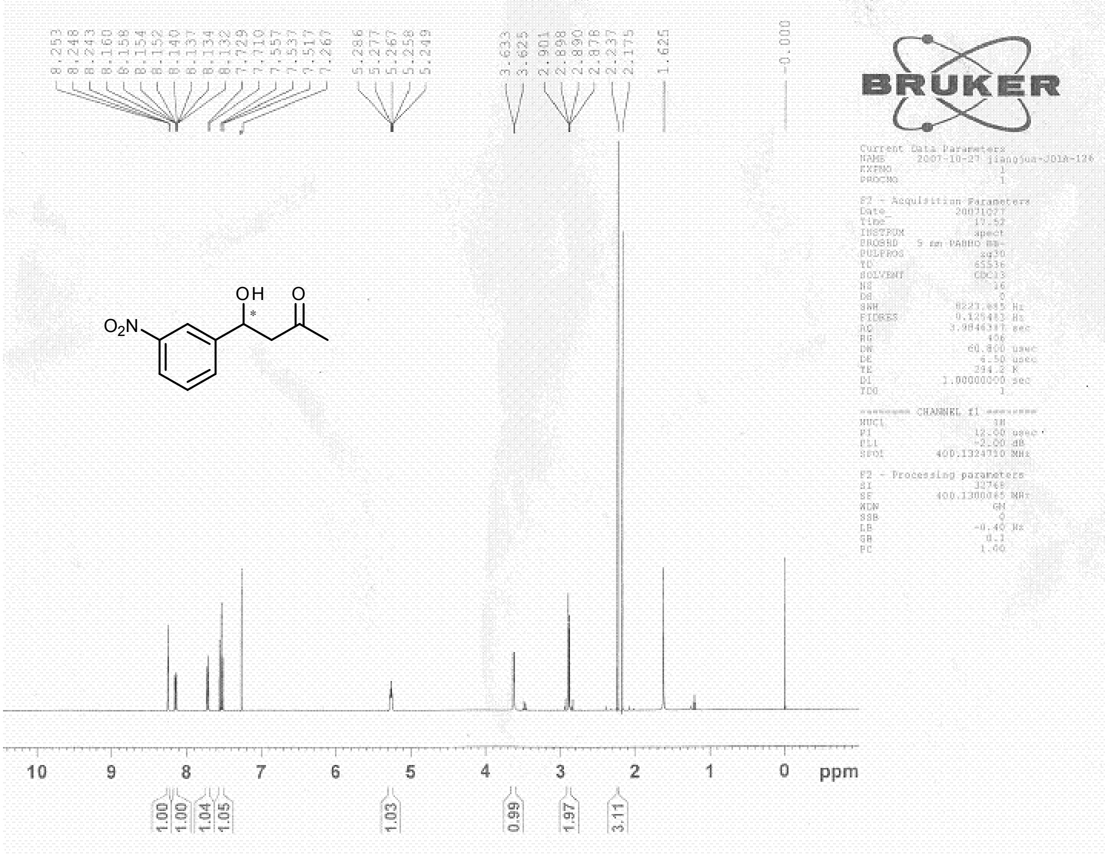

Product **4n:**

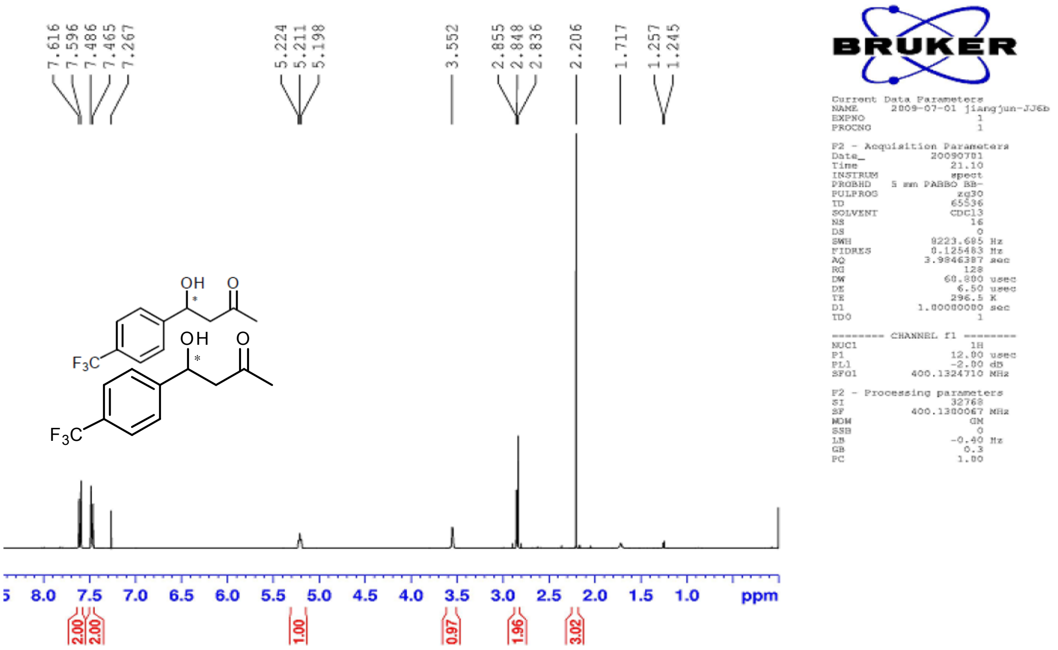


```
Current Data Parameters
NAME     2009-07-01 jiangjun-JJ40
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090701
Time                21.44
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                    128
DW                 60.800 usec
DE                   6.50 usec
TE                  296.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300067 MHz
WDW                    GM
SSB                     0
LB                  -0.40 Hz
GB                    0.3
PC                   1.00
```

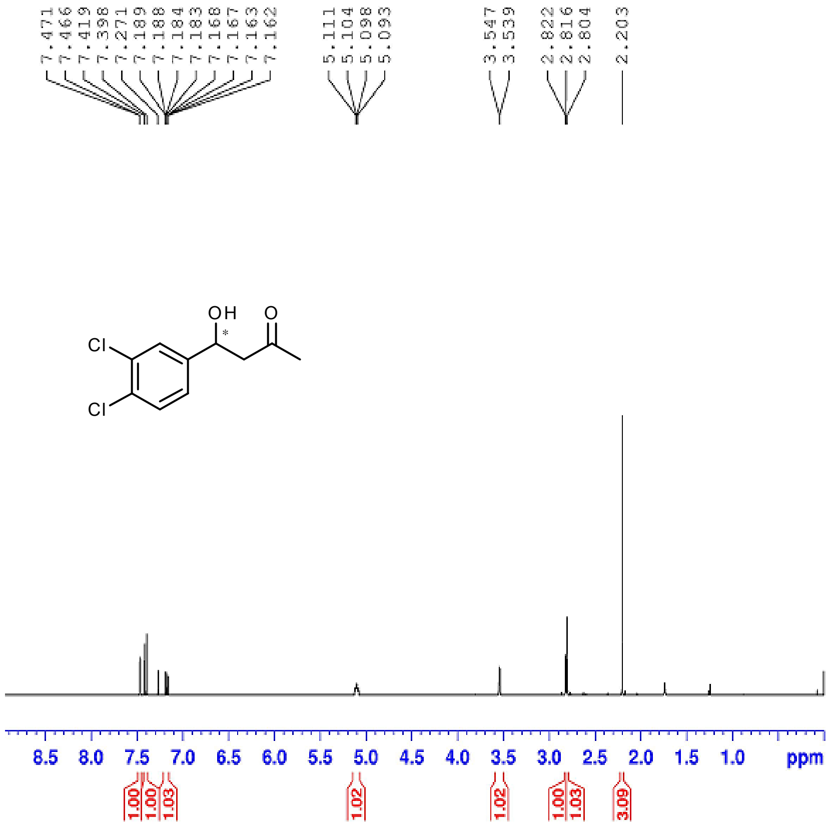
Product **6a:**



Product **6b:**



Product **6c:**



BRUKER

```
Current Data Parameters
NAME     2009-07-01 jiangjun-JJ6c
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090701
Time                22.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                    128
DW                 60.800 usec
DE                   6.50 usec
TE                  296.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300051 MHz
WDW                    GM
SSB                     0
LB                  -0.40 Hz
GB                    0.3
PC                   1.00
```

(H) References

(1) (a) K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, 1964, **86**, 3862.

(2) (a) J. Hine; S. M. Linden and V. M. Kanagasabapathy, *J. Org. Chem.*, 1985**, 50**, 5092; (b) L. Q. Qiu; J. Wu; S. S. Chan; T. T. L. Au-Yeung; J. X. Ji; R. W. Guo; C. C. Pai; Z. Y. Zhou; X. S. Li; Q. H. Fan and A. S. C. Chan, *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 5815; (c) Y. B. Sun; X. B. Wang; M, J. Guo; D. H. Wang; X, C. Dong; Y. Pan and Z. G. Zhang, *Tetrahedron. Asymmetry*, 2004, **15***,* 2185; (d) X. B. Wan; Y. H. Sun; Y. F. Luo; D. Li and Z. G. Zhang, *J. Org. Chem.*, 2005, **70**, 1070

(3) A. I. Vogel, “Textbook of Practical Organic Chemistry”, 4th ed.; Longman: New York, 1978; pp 285-286.

(I) The information of single crystal X-ray diffraction analysis

CCDC 738508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac./conts/retrieving.html

Check CIF/PLATON report

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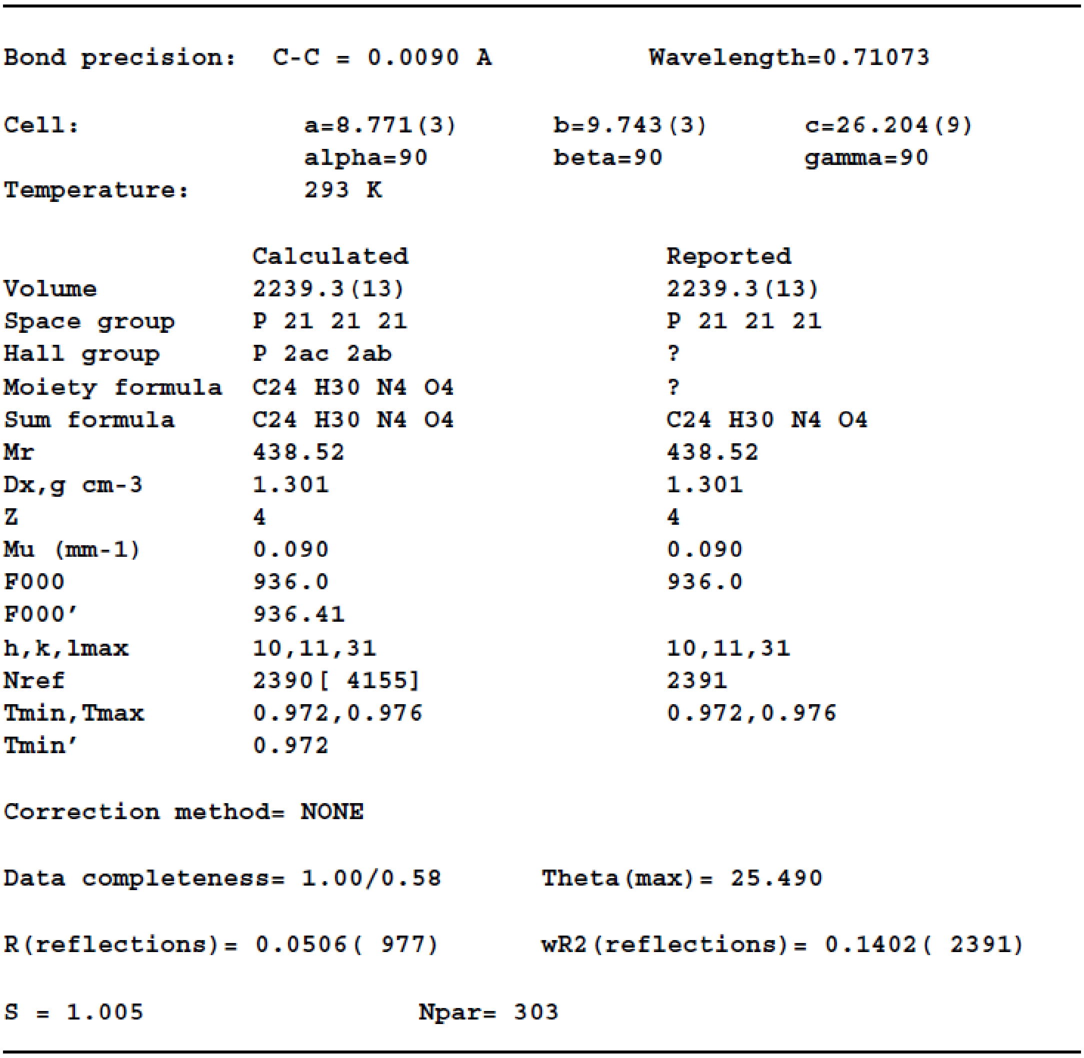

```
Bond precision:   C-C = 0.0090 A          Wavelength=0.71073

Cell:                a=8.771(3)      b=9.743(3)      c=26.204(9)
                     alpha=90        beta=90         gamma=90
Temperature:         293 K

                  Calculated                  Reported
Volume            2239.3(13)                  2239.3(13)
Space group       P 21 21 21                  P 21 21 21
Hall group        P 2ac 2ab                   ?
Moiety formula    C24 H30 N4 O4               ?
Sum formula       C24 H30 N4 O4               C24 H30 N4 O4
Mr                438.52                      438.52
Dx,g cm-3         1.301                       1.301
Z                 4                           4
Mu (mm-1)         0.090                       0.090
F000              936.0                       936.0
F000'             936.41
h,k,lmax          10,11,31                    10,11,31
Nref              2390[ 4155]                 2391
Tmin,Tmax         0.972,0.976                 0.972,0.976
Tmin'             0.972

Correction method= NONE

Data completeness= 1.00/0.58       Theta(max)= 25.490

R(reflections)= 0.0506( 977)       wR2(reflections)= 0.1402( 2391)

S = 1.005                   Npar= 303
```

PLATON version of 13/08/2009; check.def file version of 12/08/2009

Datablock cd4 - ellipsoid plot

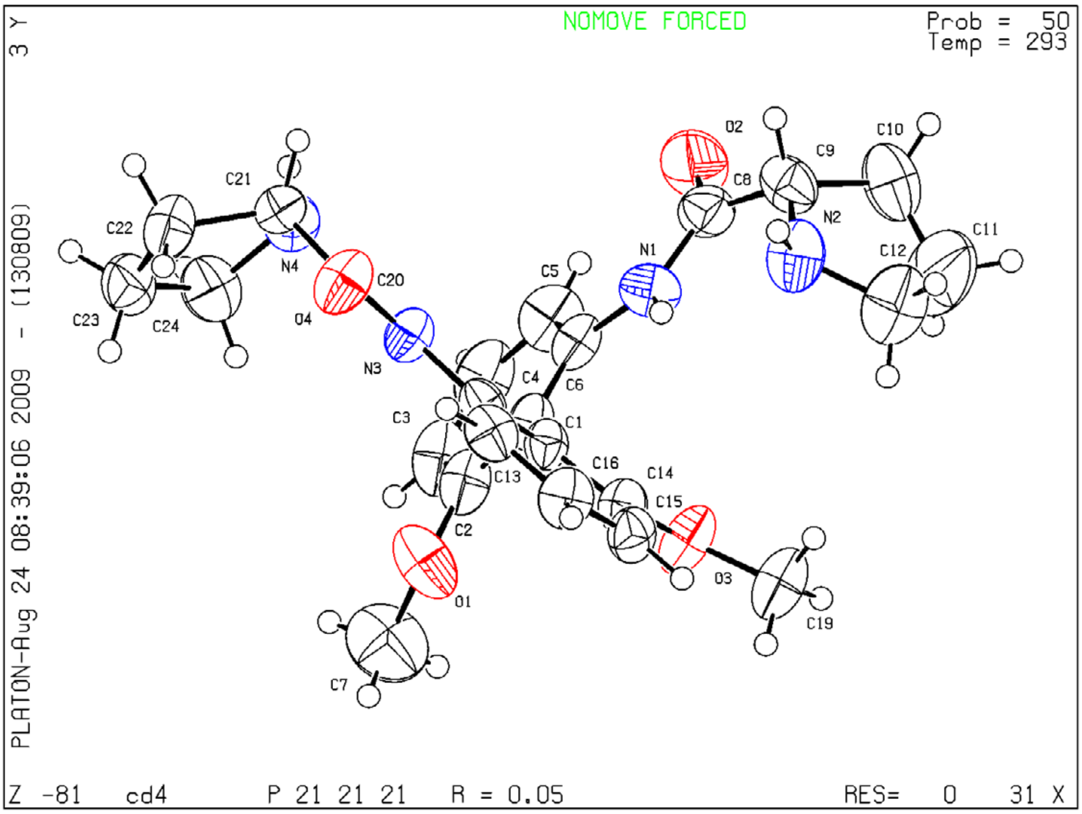

Table 1. Crystal data and structure refinement for 2a.

Identification code	2a	
Empirical formula	$C_{24} H_{30} N_4 O_4$	
Formula weight	438.52	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.771(3) Å	α = 90 deg.
	b = 9.743(3) Å	β = 90 deg.
	c = 26.204(9) Å	γ = 90 deg.
Volume	2239.3(13) Å ^{3}	
Z	4	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	936	
Crystal size	0.32 x 0.30 x 0.27 mm	
θ range for data collection	1.55 to 25.49 deg.	
Index ranges	0<=h<=10, 0<=k<=11, 0<=l<=31	
Reflections collected	2417	

Independent reflections	2391 [R(int) = 0.0070]
Absorption correction	None
Max. and min. transmission	0.9761 and 0.9718
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2391 / 0 / 303
Goodness-of-fit on F^2	1.005
Final R indices [$I>2\sigma(I)$]	R1 = 0.0506, wR2 = 0.1054
R indices (all data)	R1 = 0.1969, wR2 = 0.1402
Absolute structure parameter	0(4)
Largest diff. peak and hole	0.307 and -0.282 eÅ^{-3}

Note: The crystal diffraction ability for **2a** was weak, and result in more weak diffraction data for collection, which was the cause for a poor ratio of observed to unique reflections and also a poor data/parameter ratio.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 2a.

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-10828(6)	-8775(5)	-8618(2)	76(2)
O(2)	-4248(6)	-10307(5)	-9672(2)	85(2)
O(3)	-9797(6)	-12276(4)	-8981(1)	68(2)
O(4)	-6551(5)	-9333(4)	-7028(2)	62(1)
N(1)	-6176(6)	-10828(5)	-9119(2)	54(2)
N(2)	-5196(7)	-13340(6)	-8937(2)	69(2)
N(3)	-7316(6)	-9175(4)	-7853(2)	46(1)
N(4)	-5984(8)	-6780(6)	-8004(2)	62(2)
C(1)	-8457(8)	-9717(6)	-8848(2)	45(2)
C(2)	-9574(10)	-8709(7)	-8924(2)	61(2)
C(3)	-9355(10)	-7666(7)	-9284(2)	70(2)
C(4)	-8058(10)	-7683(7)	-9575(2)	71(2)
C(5)	-6967(9)	-8683(7)	-9522(2)	66(2)
C(6)	-7182(8)	-9712(6)	-9170(2)	50(2)
C(7)	-12195(9)	-8124(9)	-8776(3)	107(3)
C(8)	-4871(8)	-11107(7)	-9371(2)	59(2)
C(9)	-4202(8)	-12515(7)	-9266(2)	61(2)
C(10)	-3963(11)	-13351(7)	-9748(3)	89(3)
C(11)	-5182(12)	-14355(11)	-9748(3)	155(5)
C(12)	-5690(11)	-14563(7)	-9224(3)	95(3)
C(13)	-8668(7)	-10708(5)	-8421(2)	41(2)
C(14)	-9385(7)	-11964(6)	-8491(2)	49(2)
C(15)	-9712(7)	-12841(6)	-8083(2)	51(2)
C(16)	-9261(7)	-12470(6)	-7609(2)	54(2)

C(17)	-8484(7)	-11271(6)	-7517(2)	51(2)
C(18)	-8154(7)	-10404(6)	-7925(2)	46(2)
C(19)	-10206(9)	-13683(7)	-9088(3)	84(2)
C(20)	-6585(7)	-8723(6)	-7440(2)	46(2)
C(21)	-5732(7)	-7378(6)	-7505(2)	53(2)
C(22)	-6261(8)	-6317(6)	-7105(2)	65(2)
C(23)	-7288(8)	-5364(6)	-7385(2)	67(2)
C(24)	-7222(9)	-5773(7)	-7945(2)	71(2)

Table 3. Bond lengths [Å] for 2a.

O(1)-C(2)	1.363(8)	O(1)-C(7)	1.418(8)
O(2)-C(8)	1.235(7)	O(3)-C(14)	1.368(6)
O(3)-C(19)	1.444(7)	O(4)-C(20)	1.231(6)
N(1)-C(8)	1.350(7)	N(1)-C(6)	1.407(7)
N(1)-H(1)	0.8600	N(2)-C(9)	1.466(8)
N(2)-C(12)	1.474(8)	N(2)-HN2	0.97(7)
N(3)-C(20)	1.332(7)	N(3)-C(18)	1.417(7)
N(3)-H(3)	0.8600	N(4)-C(21)	1.448(8)
N(4)-C(24)	1.472(8)	N(4)-HN4	0.81(7)
C(1)-C(6)	1.401(8)	C(1)-C(2)	1.401(9)
C(1)-C(13)	1.489(7)	C(2)-C(3)	1.399(8)
C(3)-C(4)	1.370(9)	C(3)-H(3A)	0.9300
C(4)-C(5)	1.372(9)	C(4)-H(4)	0.9300
C(5)-C(6)	1.375(8)	C(5)-H(5)	0.9300
C(7)-H(7A)	0.9600	C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600	C(8)-C(9)	1.517(9)
C(9)-C(10)	1.519(8)	C(9)-H(9)	0.9800
C(10)-C(11)	1.449(10)	C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700	C(11)-C(12)	1.458(10)
C(11)-H(11A)	0.9700	C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700	C(12)-H(12B)	0.9700
C(13)-C(14)	1.388(7)	C(13)-C(18)	1.407(7)
C(14)-C(15)	1.398(7)	C(15)-C(16)	1.354(7)
C(15)-H(15)	0.9300	C(16)-C(17)	1.374(8)
C(16)-H(16)	0.9300	C(17)-C(18)	1.393(7)
C(17)-H(17)	0.9300	C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600	C(19)-H(19C)	0.9600
C(20)-C(21)	1.518(8)	C(21)-C(22)	1.545(8)
C(21)-H(21)	0.9800	C(22)-C(23)	1.488(8)
C(22)-H(22A)	0.9700	C(22)-H(22B)	0.9700
C(23)-C(24)	1.519(8)	C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700	C(24)-H(24A)	0.9700

C(24)-H(24B)	0.9700

Table 4. Angles [deg] for 2a.

C(2)-O(1)-C(7)	119.2(5)	C(14)-O(3)-C(19)	117.2(5)
C(8)-N(1)-C(6)	129.9(6)	C(8)-N(1)-H(1)	115.1
C(6)-N(1)-H(1)	115.1	C(9)-N(2)-C(12)	108.5(5)
C(9)-N(2)-HN2	116(4)	C(12)-N(2)-HN2	114(4)
C(20)-N(3)-C(18)	129.6(5)	C(20)-N(3)-H(3)	115.2
C(18)-N(3)-H(3)	115.2	C(21)-N(4)-C(24)	106.5(5)
C(21)-N(4)-HN4	109(5)	C(24)-N(4)-HN4	113(6)
C(6)-C(1)-C(2)	118.1(6)	C(6)-C(1)-C(13)	123.6(6)
C(2)-C(1)-C(13)	118.3(6)	O(1)-C(2)-C(3)	122.8(7)
O(1)-C(2)-C(1)	116.6(6)	C(3)-C(2)-C(1)	120.6(7)
C(4)-C(3)-C(2)	118.7(7)	C(4)-C(3)-H(3A)	120.6
C(2)-C(3)-H(3A)	120.6	C(3)-C(4)-C(5)	122.1(7)
C(3)-C(4)-H(4)	118.9	C(5)-C(4)-H(4)	118.9
C(4)-C(5)-C(6)	119.3(7)	C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3	C(5)-C(6)-C(1)	121.0(7)
C(5)-C(6)-N(1)	122.8(6)	C(1)-C(6)-N(1)	116.2(5)
O(1)-C(7)-H(7A)	109.5	O(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	O(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
O(2)-C(8)-N(1)	124.0(7)	O(2)-C(8)-C(9)	121.0(6)
N(1)-C(8)-C(9)	114.9(6)	N(2)-C(9)-C(8)	111.9(6)
N(2)-C(9)-C(10)	106.1(6)	C(8)-C(9)-C(10)	112.7(6)
N(2)-C(9)-H(9)	108.7	C(8)-C(9)-H(9)	108.7
C(10)-C(9)-H(9)	108.7	C(11)-C(10)-C(9)	105.0(7)
C(11)-C(10)-H(10A)	110.7	C(9)-C(10)-H(10A)	110.7
C(11)-C(10)-H(10B)	110.7	C(9)-C(10)-H(10B)	110.7
H(10A)-C(10)-H(10B)	108.8	C(10)-C(11)-C(12)	108.7(7)
C(10)-C(11)-H(11A)	109.9	C(12)-C(11)-H(11A)	109.9
C(10)-C(11)-H(11B)	109.9	C(12)-C(11)-H(11B)	109.9
H(11A)-C(11)-H(11B)	108.3	C(11)-C(12)-N(2)	106.2(7)
C(11)-C(12)-H(12A)	110.5	N(2)-C(12)-H(12A)	110.5
C(11)-C(12)-H(12B)	110.5	N(2)-C(12)-H(12B)	110.5
H(12A)-C(12)-H(12B)	108.7	C(14)-C(13)-C(18)	116.9(5)
C(14)-C(13)-C(1)	121.9(5)	C(18)-C(13)-C(1)	121.2(5)
O(3)-C(14)-C(13)	116.0(5)	O(3)-C(14)-C(15)	121.8(5)
C(13)-C(14)-C(15)	122.1(5)	C(16)-C(15)-C(14)	118.5(5)
C(16)-C(15)-H(15)	120.7	C(14)-C(15)-H(15)	120.7
C(15)-C(16)-C(17)	122.3(6)	C(15)-C(16)-H(16)	118.9
C(17)-C(16)-H(16)	118.9	C(16)-C(17)-C(18)	118.9(6)

C(16)-C(17)-H(17)	120.5	C(18)-C(17)-H(17)	120.5
C(17)-C(18)-C(13)	121.0(6)	C(17)-C(18)-N(3)	121.1(5)
C(13)-C(18)-N(3)	117.9(5)	O(3)-C(19)-H(19A)	109.5
O(3)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
O(3)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	O(4)-C(20)-N(3)	124.3(6)
O(4)-C(20)-C(21)	120.2(5)	N(3)-C(20)-C(21)	115.5(5)
N(4)-C(21)-C(20)	112.0(5)	N(4)-C(21)-C(22)	107.4(5)
C(20)-C(21)-C(22)	110.7(5)	N(4)-C(21)-H(21)	108.9
C(20)-C(21)-H(21)	108.9	C(22)-C(21)-H(21)	108.9
C(23)-C(22)-C(21)	105.3(5)	C(23)-C(22)-H(22A)	110.7
C(21)-C(22)-H(22A)	110.7	C(23)-C(22)-H(22B)	110.7
C(21)-C(22)-H(22B)	110.7	H(22A)-C(22)-H(22B)	108.8
C(22)-C(23)-C(24)	106.9(6)	C(22)-C(23)-H(23A)	110.3
C(24)-C(23)-H(23A)	110.3	C(22)-C(23)-H(23B)	110.3
C(24)-C(23)-H(23B)	110.3	H(23A)-C(23)-H(23B)	108.6
N(4)-C(24)-C(23)	107.8(6)	N(4)-C(24)-H(24A)	110.1
C(23)-C(24)-H(24A)	110.1	N(4)-C(24)-H(24B)	110.1
C(23)-C(24)-H(24B)	110.1	H(24A)-C(24)-H(24B)	108.5

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 2a.
The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U^{11} + ... + 2hka^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	89(4)	89(4)	51(3)	12(2)	11(3)	37(3)
O(2)	88(4)	78(3)	89(4)	8(3)	37(3)	-13(3)
O(3)	100(4)	54(3)	50(3)	-2(2)	-11(3)	-24(3)
O(4)	83(3)	53(2)	50(3)	8(2)	-27(2)	-4(3)
N(1)	54(4)	62(4)	46(3)	16(3)	6(3)	-3(3)
N(2)	101(5)	73(4)	33(3)	0(3)	-5(3)	1(4)
N(3)	58(4)	36(3)	43(3)	7(2)	-6(3)	-4(3)
N(4)	70(5)	56(4)	61(4)	2(3)	17(4)	-10(4)
C(1)	65(5)	34(3)	37(3)	3(3)	-3(3)	-2(4)
C(2)	84(6)	47(4)	53(4)	-2(4)	-12(4)	2(5)
C(3)	111(7)	50(4)	47(4)	8(4)	-18(4)	11(5)
C(4)	112(7)	45(4)	55(4)	17(4)	-9(4)	-12(5)
C(5)	87(6)	65(4)	47(4)	21(4)	0(4)	-6(5)
C(6)	64(5)	41(4)	43(4)	0(3)	-10(4)	-9(4)
C(7)	106(7)	133(8)	83(6)	16(6)	-20(5)	31(7)
C(8)	54(5)	67(5)	55(4)	-4(4)	10(4)	-10(5)

C(9)	61(5)	78(5)	42(3)	-1(4)	8(4)	9(5)
C(10)	109(7)	93(6)	66(5)	-16(4)	20(5)	19(6)
C(11)	157(11)	199(11)	109(7)	-94(8)	66(8)	-69(11)
C(12)	128(8)	80(5)	76(5)	1(5)	1(6)	-14(6)
C(13)	49(4)	33(3)	42(3)	1(3)	-4(3)	5(3)
C(14)	59(4)	47(4)	42(3)	0(3)	-4(3)	1(4)
C(15)	60(5)	35(3)	57(4)	3(3)	3(3)	0(4)
C(16)	72(5)	42(4)	48(4)	16(3)	-2(4)	1(4)
C(17)	58(5)	52(4)	43(4)	9(3)	-4(3)	13(4)
C(18)	48(4)	40(4)	52(4)	2(3)	2(3)	12(4)
C(19)	106(7)	59(4)	87(5)	-17(4)	-12(5)	-16(5)
C(20)	47(4)	45(4)	46(4)	-7(3)	-6(3)	9(4)
C(21)	46(4)	51(4)	62(4)	-7(4)	-5(3)	-4(4)
C(22)	85(6)	47(4)	64(4)	-6(4)	-17(4)	2(4)
C(23)	72(5)	43(4)	87(5)	3(4)	17(4)	-2(4)
C(24)	80(6)	67(4)	67(4)	7(4)	4(4)	10(5)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2a.

	x	y	z	U(eq)
H(1)	-6432	-11424	-8893	65
H(3)	-7273	-8642	-8114	55
H(3A)	-10076	-6975	-9325	84
H(4)	-7911	-6995	-9816	85
H(5)	-6092	-8665	-9722	80
H(7A)	-12047	-7147	-8782	161
H(7B)	-13000	-8347	-8542	161
H(7C)	-12463	-8436	-9112	161
H(9)	-3216	-12399	-9095	73
H(10A)	-4025	-12770	-10048	107
H(10B)	-2976	-13800	-9744	107
H(11A)	-4820	-15214	-9890	186
H(11B)	-6024	-14031	-9956	186
H(12A)	-5233	-15385	-9082	114
H(12B)	-6790	-14656	-9211	114
H(15)	-10229	-13662	-8137	61
H(16)	-9484	-13046	-7336	65
H(17)	-8183	-11041	-7188	61
H(19A)	-9395	-14279	-8980	126
H(19B)	-10374	-13793	-9447	126
H(19C)	-11121	-13913	-8906	126

H(21)	-4639	-7547	-7461	64
H(22A)	-6803	-6764	-6828	78
H(22B)	-5395	-5825	-6964	78
H(23A)	-6950	-4423	-7343	80
H(23B)	-8323	-5440	-7258	80
H(24A)	-8185	-6173	-8049	86
H(24B)	-7026	-4973	-8155	86
HN2	-4810(8)	-13540(7)	-8600(3)	120(3)
HN4	-5190(8)	-6440(8)	-8100(3)	90(3)

Table 7. Selected torsion angles for 2a.

23.90 (0.96)	C7 - O1 - C2 - C3	-158.75 (0.59)	C7 - O1 - C2 - C1
177.51 (0.50)	C6 - C1 - C2 - O1	-4.20 (0.83)	C13 - C1 - C2 - O1
-5.07 (0.87)	C6 - C1 - C2 - C3	173.22 (0.53)	C13 - C1 - C2 - C3
179.92 (0.60)	O1 - C2 - C3 - C4	2.67 (0.94)	C1 - C2 - C3 - C4
-0.39 (1.00)	C2 - C3 - C4 - C5	0.64 (0.99)	C3 - C4 - C5 - C6
-3.19 (0.89)	C4 - C5 - C6 - C1	175.16 (0.53)	C4 - C5 - C6 - N1
5.36 (0.84)	C2 - C1 - C6 - C5	-172.84 (0.55)	C13 - C1 - C6 - C5
-173.10 (0.49)	C2 - C1 - C6 - N1	8.71 (0.79)	C13 - C1 - C6 - N1
1.60 (0.91)	C8 - N1 - C6 - C5	-179.98 (0.55)	C8 - N1 - C6 - C1
7.49 (1.00)	C6 - N1 - C8 - O2	-171.70 (0.53)	C6 - N1 - C8 - C9
117.44 (0.60)	C12 - N2 - C9 - C8	-5.88 (0.83)	C12 - N2 - C9 - C10
-174.55 (0.58)	O2 - C8 - C9 - N2	4.66 (0.75)	N1 - C8 - C9 - N2
-55.06 (0.93)	O2 - C8 - C9 - C10	124.16 (0.68)	N1 - C8 - C9 - C10
18.16 (0.88)	N2 - C9 - C10 - C11	-104.64 (0.79)	C8 - C9 - C10 - C11
-24.10 (1.00)	C9 - C10 - C11 - C12	20.70 (1.04)	C10 - C11 - C12 - N2
-8.62 (0.95)	C9 - N2 - C12 - C11	-89.39 (0.76)	C6 - C1 - C13- C14
92.42 (0.72)	C2 - C1 - C13 - C14	91.06 (0.71)	C6 - C1 - C13 - C18
-87.13 (0.72)	C2 - C1 - C13 - C18	165.66 (0.60)	C19 - O3 - C14 - C13
-16.26 (0.89)	C19 - O3 - C14 - C15	-176.29 (0.51)	C18 - C13 - C14 - O3
4.14 (0.88)	C1 - C13 - C14 - O3	5.64 (0.87)	C18 - C13 - C14 - C15
-173.92 (0.59)	C1 - C13 - C14 - C15	179.54 (0.57)	O3 - C14 - C15 - C16
-2.50 (0.92)	C13 - C14 - C15 - C16	-0.60 (0.92)	C14 - C15 - C16 - C17
0.26 (0.90)	C15 - C16 - C17 - C18	3.13 (0.86)	C16 - C17 - C18 - C13
-178.12 (0.52)	C16 - C17 - C18 - N3	-5.93 (0.84)	C14 - C13 - C18 - C17
173.64 (0.57)	C1 - C13 - C18 - C17	175.28 (0.53)	C14 - C13 - C18 - N3
-5.15 (0.81)	C1 - C13 - C18 - N3	8.51 (0.89)	C20 - N3 - C18 - C17
-172.71 (0.58)	C20 - N3 - C18 - C13	-1.64 (0.99)	C18 - N3 - C20 - O4
177.11 (0.52)	C18 - N3 - C20 - C21	96.02 (0.58)	C24 - N4 - C21 - C20
-25.66 (0.71)	C24 - N4 - C21 - C22	-176.58 (0.57)	O4 - C20 - C21 - N4
4.62 (0.74)	N3 - C20 - C21 - N4	-56.82 (0.75)	O4 - C20 - C21 - C22
124.37 (0.57)	N3 - C20 - C21 - C22	19.49 (0.72)	N4 - C21 - C22 - C23

-103.01 (0.58)	C20 - C21 - C22 - C23	-5.73 (0.70)	C21 - C22 - C23 - C24
22.07 (0.70)	C21 - N4 - C24 - C23	-9.62 (0.72)	C22 - C23 - C24 - N4

Table 8. Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane) for 2a.

- 4.1200 (0.0189) x - 5.4716 (0.0184) y - 17.8490 (0.0475) z = 24.6211 (0.0261)

*	-0.0268 (0.0041)	C1
*	0.0175 (0.0044)	C2
*	-0.0008 (0.0045)	C3
*	-0.0067 (0.0047)	C4
*	-0.0032 (0.0044)	C5
*	0.0200 (0.0040)	C6

Rms deviation of fitted atoms = 0.0157

7.6407 (0.0109) x - 4.5415 (0.0207) y - 4.0467 (0.0606) z = 1.6792 (0.0609)

Angle to previous plane (with approximate esd) = 87.58 (0.17)

*	-0.0315 (0.0040)	C13
*	0.0193 (0.0042)	C14
*	0.0030 (0.0043)	C15
*	-0.0126 (0.0042)	C16
*	-0.0009 (0.0041)	C17
*	0.0227 (0.0041)	C18

Rms deviation of fitted atoms = 0.0185

Reference(Program):

(1). Data collection and Cell reduction:

DIFRAC, A Fortran 77 Control Routine for 4-Circle Diffractometers

E. J. Gabe, P. S. White and G. D. Enright, (1993) DIFRAC *American Crystallographic Association*, Pittsburgh Meeting Abstract, PA 104.

(2). Structure solution:

(a).Data reduction

NRCVAX

E. J. Gabe, Y. Le Page, J. P. Charland, F. L Lee & P. S White, *J.Appl.Cryst.*,1989, **22**, 384-387.

(b).Structure Solution and refinement

SHELXS-97 and SHELXL-97

G. M. Sheldrick, *Acta Cryst.* 1990, **A46** 467-473;

G. M. Sheldrick, (1997), SHELXL97 Program for the Refinement of Crystal Structure, University of Gottingen, Germany.

(3). Graphics:

Ortep-3 for Windoms 1.076

L. J. Frarrugia, *J. Appl. Cryst.* 1997, **30**, 565.