

Supporting Information

Can a Biaryl-Like Architecture Compete with its Biaryl Counterpart in Asymmetric Catalysis?

Enantiopure Me-CATPHOS, A Remarkably Efficient Ligand for Asymmetric Hydrogenation

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General Considerations. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane was distilled from calcium hydride, THF from sodium/benzophenone and isopropanol from sodium. 9-Methylanthracene and methyl-2-acetamido acrylate were purchased from Lancaster and used without further purification. 1,4-Bis(diphenylphosphino)buta-1,3-diyne,¹ (Z)-methyl-2-acetamidocinnamate,² β -N-acetylamino-vinylphosphonates³ [emim][NTf₂],⁴ [RhCl(1,5-COD)]₂,⁵ and [Rh(1,5-COD)₂][BF₄]⁶ were prepared as previously described. ¹H, ¹³C{¹H} and ³¹P NMR spectra were recorded on a JEOL LAMBDA 500 or a Bruker AMX 300 instrument. Optical rotations were measured on a Optical Activity PolAAR 2001 digital polarimeter with a sodium lamp and are reported as follows: [α]_D²⁰ (c g/100 mL, solvent). Thin-layer chromatography (TLC) was carried out on aluminum sheets pre-coated with silica gel 60F 254 and column chromatography was performed using Merck Kieselgel 60. Gas chromatography was performed on a Shimadzu 2010 series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detection using a Supelco Beta DEX column. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable wavelength detector using a Daicel Chiralcel OD-H or Chiralpak AD-H column. Enantiomeric excesses were calculated from the HPLC and GC profiles.

(E)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (8a). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, δ): 22.7; ¹H NMR (300.0 MHz, CDCl₃, δ): 7.90 (s, 1H, NH), 7.38 (m, 5H, C₆H₅), 6.74 (d, *J* = 12.0 Hz, 1H, =CH), 3.33 (d, *J* = 11.2 Hz, 6H, OCH₃), 2.01 (s, 3H, CH₃); ¹³C{¹H} NMR (75.8 MHz, CDCl₃, δ): 169.6 (C=O), 151.2 (d, *J* = 16.7 Hz, C=CP), 136.3 (d, *J* = 6.2 Hz, C₆H₅ *Q*), 129.5 (C₆H₅), 128.5 (C₆H₅), 128.1 (C₆H₅), 97.8 (d, *J* = 202 Hz, C=CP), 51.7 (d, *J* = 6.1 Hz, OCH₃), 24.6 (CH₃); LRMS (ESI⁺) *m/z* 292 [M+Na]⁺; HRMS (ESI⁺) exact mass calcd for C₁₂H₁₆NO₄PNa [M+Na]⁺ requires *m/z* 292.0715, found *m/z* 292.0721.

¹ Corriu, R. J. P.; Guerin, C.; Henner, J. L.; Jolivet, A. *J. Organomet. Chem.* **1997**, 530, 39.

² Riordan, J. M.; Sato, M.; Stammer, C. H. *J. Org. Chem.* **1977**, 42, 236.

³ Kadyrov, R.; Holz, J.; Schaffner, B.; Zayas, O.; Almena, J.; Borner, A. *Tetrahedron: Asymmetry* **2008**, 19, 1189.

⁴ P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.* **1996**, 35, 1168.

⁵ Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, 28, 88.

⁶ Schenk, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, T. G.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, 24, 2334.

(Z)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (8a). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3 , δ): 22.6; ^1H NMR (300.0 MHz, CDCl_3 , δ): 10.1 (s, 1H, NH), 7.35 (m, 5H, C_6H_5), 4.81 (d, $J = 11.6$ Hz, 1H, =CH), 3.73 (d, $J = 11.4$ Hz, 6H, OCH_3), 2.12 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3 , δ): 168.3 (C=O), 157.8 (d, $J = 3.1$ Hz, C_6H_5 Q), 137.1 (d, $J = 18.9$ Hz, C=CP), 129.4 (C_6H_5), 128.0 (C_6H_5), 126.7 (C_6H_5), 94.7 (d, $J = 184$ Hz, C=CP), 52.2 (d, $J = 5.3$ Hz, OCH_3), 24.2 (CH_3); LRMS (ESI^+) m/z 292 [$\text{M}+\text{Na}$] $^+$; HRMS (ESI^+) exact mass calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_4\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ requires m/z 292.0715, found m/z 292.0689.

(E)-Dimethyl-2-acetylamino-2-p-tolylvinylphosphonate (8b). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3 , δ): 22.3; ^1H NMR (300.0 MHz, CDCl_3 , δ): 8.03 (s, 1H, NH), 7.27 (d, $J = 7.9$ Hz, 2H, C_6H_4), 7.13 (d, $J = 7.9$ Hz, 2H, C_6H_4), 6.66 (d, $J = 12.1$ Hz, 1H, =CH), 3.33 (d, $J = 11.2$ Hz, 6H, OCH_3), 2.32 (s, 3H, CH_3), 1.98 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3 , δ): 169.5 (C=O), 151.3 (d, $J = 16.7$ Hz, C=CP), 139.7 (C_6H_4), 133.5 (d, $J = 6.2$ Hz, C_6H_4 Q), 128.7 (C_6H_4), 128.4 (C_6H_4), 97.4 (d, $J = 202$ Hz, C=CP), 51.6 (m, OCH_3), 24.5 (CH_3), 21.1 ($\text{C}_6\text{H}_4\text{CH}_3$); LRMS (ESI^+) m/z 306 [$\text{M}+\text{Na}$] $^+$; HRMS (ESI^+) exact mass calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_4\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ requires m/z 306.0871, found m/z 306.0858.

(Z)-Dimethyl-2-acetylamino-2-p-tolylvinylphosphonate (8b). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3 , δ): 22.1; ^1H NMR (300.0 MHz, CDCl_3 , δ): 9.89 (s, 1H, NH), 7.16 (d, $J = 7.9$ Hz, 2H, C_6H_4), 7.01 (d, $J = 7.6$ Hz, 2H, C_6H_4), 4.75 (d, $J = 11.7$ Hz, 1H, =CH), 3.58 (d, $J = 11.4$ Hz, 6H, OCH_3), 2.22 (s, 3H, CH_3), 1.98 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3 , δ): 168.1 (C=O), 157.3 (d, $J = 3.0$ Hz, C_6H_4 Q), 139.4 (C_6H_4), 133.9 (d, $J = 18.9$ Hz, C=CP), 128.4 (C_6H_4), 126.5 (C_6H_4), 94.1 (d, $J = 185$ Hz, C=CP), 51.9 (d, $J = 5.4$ Hz, OCH_3), 23.9 (CH_3), 20.8 ($\text{C}_6\text{H}_4\text{CH}_3$); LRMS (ESI^+) m/z 306 [$\text{M}+\text{Na}$] $^+$; HRMS (ESI^+) exact mass calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_4\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ requires m/z 306.0871, found m/z 306.0851.

General Procedure for the Rhodium-Catalyzed Hydrogenation of Dehydroamino Acid Derivatives. A flame-dried Schlenk flask was charged with $[\text{Rh}(\text{COD})_2][\text{BF}_4]$ (2.0 mg, 0.005 mmol), (*S*)-**2** (4.4 mg, 0.0055 mmol) and CH_2Cl_2 (3.0 mL), and the resulting orange solution stirred for 15 min. The olefin substrate (0.50 mmol) was added followed by additional CH_2Cl_2 (2.0 mL). The flask was purged five times with hydrogen and

the reaction left to stir under an atmosphere of hydrogen for 1h, after which time the solution was passed through a silica plug and the solvent removed *in vacuo* to leave a pale orange oil. The pure product was isolated after purification by column chromatography, eluting with hexane/CH₂Cl₂. The known products were characterized by ¹H NMR spectroscopy and either chiral GC or HPLC and the absolute configuration assigned by comparison of the sign of the optical rotation with that reported in the literature.⁷

Determination of Enantiomeric Excess

***N*-Acetylalanine methyl ester:**

Chiral GC. Column: Supelco Beta DEX column. Dimension 25 m, x 0.25 mm (i.d) Carrier gas : He (1 mL/min). The racemic products were obtained by hydrogenation of substrate with an achiral catalyst. Retention times for the racemic product: *N*-acetylalanine methyl ester (capillary GC, 95 °C, hold 15 min, ramp to 100 °C (0.5 °C/min), hold 3 min, ramp to 180 °C (20 °C/min) hold 30 min): (*S*) *t*₁ = 25.81 min, (*R*) *t*₂ = 26.2 min;

***N*-Acetylphenylalanine methyl ester:**

Chiral GC. Column: Supelco Beta DEX column. Dimension 25 m, x 0.25 mm (i.d) Carrier gas : He (1 mL/min). The racemic products were obtained by hydrogenation of substrate with an achiral catalyst: Retention times for the racemic product (capillary GC, 90 °C, hold 21 min, ramp to 100 °C (0.5 °C/min), hold 40 min, ramp to 150 °C (1 °C/min) hold 20 min, ramp to 180 °C (20 °C/min) hold 40 min): (*R*) *t*₁ = 156.07 min, (*S*) *t*₂ = 156.30 min.

***N*-acetyl-4-chlorophenylalanine methyl ester:**

Chiral HPLC, Column Daicel Chiralpak AD-H, (flow rate: 0.6 mL/min flow rate, hexane:2-propanol = 90:10). Retention times: (*R*) *t*₁ = 18.6 min; (*S*) *t*₂ = 22.9 min.

***N*-acetyl-4-methylphenylalanine methyl ester:**

Chiral HPLC, Column Daicel Chiralpak AD-H, (flow rate: 0.8 mL/min flow rate, hexane:2-propanol = 90:10). Retention times: (*R*) *t*₁ = 18.9 min; (*S*) *t*₂ = 26.9 min.

⁷ (a) Boaz, N. W.; Debenham, S. D.; Mackenzie, E. B.; Large, S. E. *Org. Lett.* **2002**, *4*, 2421. (b) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125. (c) Navarre, L.; Martinez, R.; Genet, J.-P.; Darses, S. *J. Am. Chem. Soc.* **2008**, *130*, 6159. (d) Wu, S.; He, M.; Zhang, X. *Tetrahedron: Asymmetry* **2004**, *15*, 2177.

***N*-acetyl-4-methoxyphenylalanine methyl ester:**

Chiral HPLC, Column Daicel Chiralpak AD-H, (flow rate: 0.6 mL/min flow rate, hexane:2-propanol = 90:10). Retention times: (*R*) t_1 = 20.9 min; (*S*) t_2 = 27.8 min.

***N*-acetyl-4-nitrophenylalanine methyl ester:**

Chiral HPLC, Column Daicel Chiralpak AD-H, (flow rate: 0.6 mL/min flow rate, hexane:2-propanol = 90:10). Retention times: (*R*) t_1 = 20.9 min; (*S*) t_2 = 27.8 min.

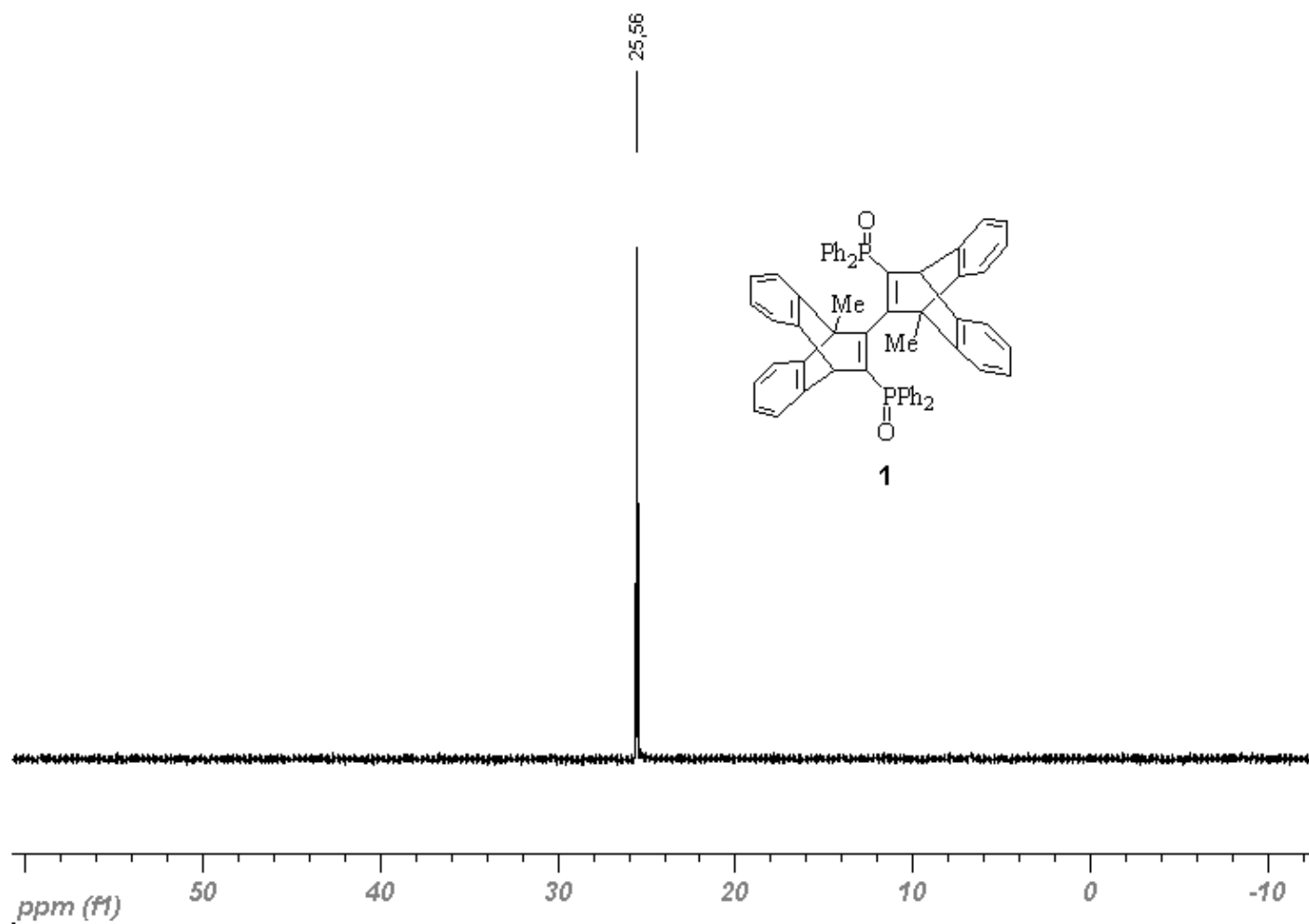
General Procedure for the Rhodium-Catalyzed Hydrogenation of (*E*)- and (*Z*)- β -*N*-acetylamino-vinylphosphonates. A flame-dried Schlenk flask was charged with [Rh(COD)₂][BF₄] (0.72 mg, 0.00176 mmol), (*S*)-**2** (1.48 mg, 0.00176 mmol) and CH₂Cl₂ (5.0 mL), and the resulting orange solution stirred for 15 min. The substrate (0.1765 mmol) was added followed additional CH₂Cl₂ (3.0 mL) and the resulting solution transferred to a 50 mL Parr stainless steel bench top reactor. The vessel was pressurized to 5 atm with hydrogen and left to stand for 10 s before releasing the gas through an outlet valve. After this sequence had been repeated six times the reactor was pressurized to *ca.* 5 atm and the solution stirred vigorously at 20-22 °C for 32 h. After releasing the pressure the mixture was diluted with dichloromethane, extracted from the reactor and the solvent removed to leave a pale orange oil. The pure product was isolated after purification by column chromatography eluting with CHCl₃/MeOH (96:4).

Dimethyl-2-acetylamino-2-phenylethylphosphonate (9a). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, δ): 30.1; ¹H NMR (300.0 MHz, CDCl₃, δ): 7.31-7.24 (m, 5H, C₆H₅), 7.09 (br d, J = 6.7 Hz, 1H, *NH*), 5.39 (ddd, J = 23.9, 13.3, 7.2 Hz, 1H, *CH*), 3.67 (d, J = 11.0 Hz, 3H, OCH₃), 3.37 (d, J = 11.0 Hz, 3H, OCH₃), 2.34 (m, 2H, CH₂), 2.02 (s, 3H, CH₃); ¹³C{¹H} NMR (75.8 MHz, CDCl₃, δ): 169.2 (C=O), 141.4 (d, J = 8.2 Hz, C₆H₅ *Q*), 128.6 (C₆H₅), 127.5 (C₆H₅), 126.2 (C₆H₅), 52.3 (d, J = 6.8 Hz, OCH₃), 52.1 (d, J = 6.7 Hz, OCH₃), 48.5 (d, J = 4.3 Hz, CHCH₂), 31.7 (d, J = 139 Hz, CHCH₂), 23.2 (CH₃); LRMS (ESI⁺) m/z 294 [M+Na]⁺; HRMS (ESI⁺) exact mass calcd for C₁₂H₁₈NO₄PNa [M+Na]⁺ requires m/z 294.0871, found m/z 294.0868. Anal. Calcd for C₁₂H₁₈NO₄P: C, 53.14; H, 6.69; N, 5.16. Found: C, 53.27; H, 6.39; N, 5.29. [α]_D = -38.3 (c = 1.0, CH₂Cl₂). The enantiomeric

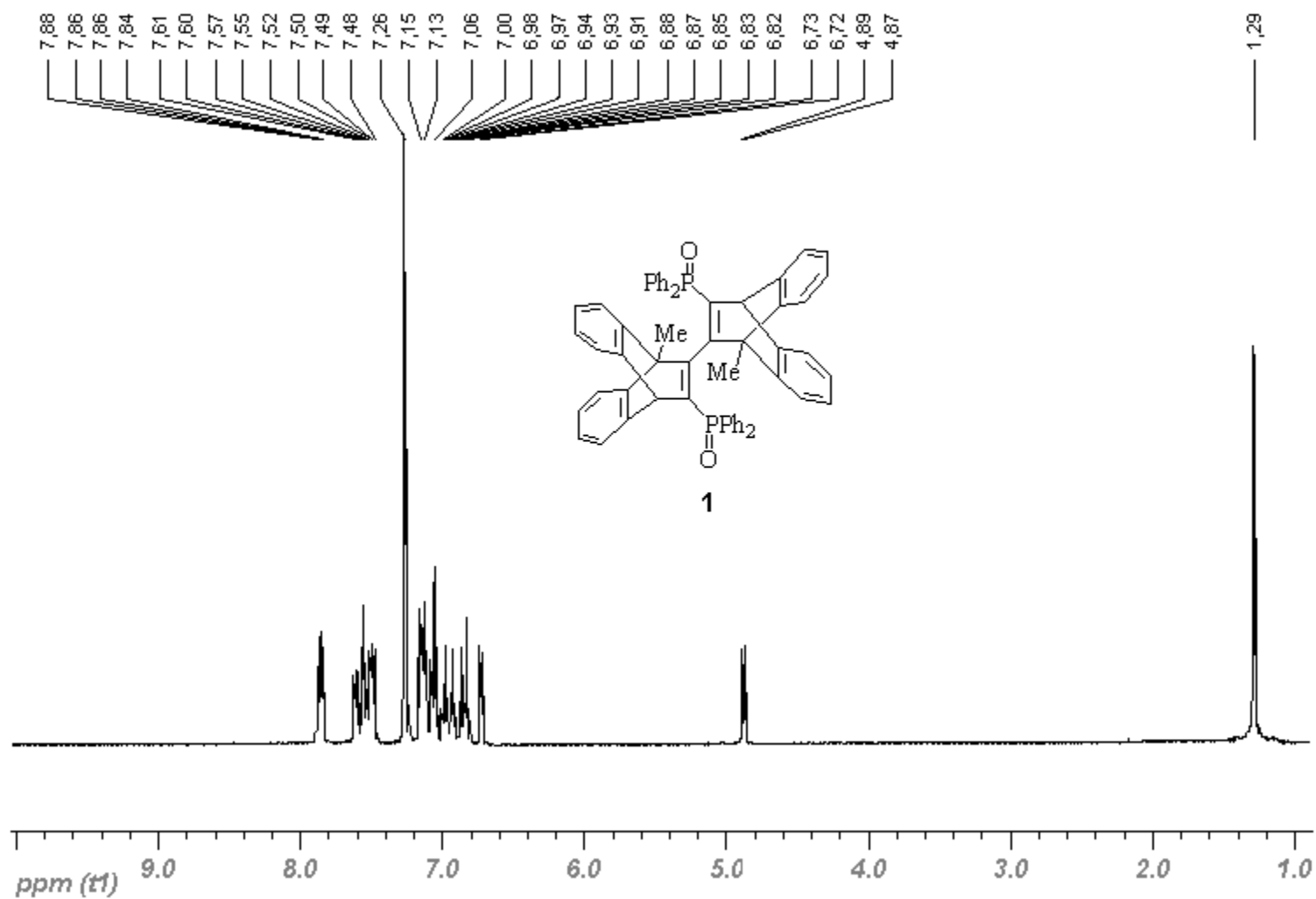
excess was calculated from the HPLC profile (Daicel Chiracel OD-H, flow rate: 0.5 mL/min flow rate, hexane:2-propanol = 85:15). Retention times: t_R of (+)-enantiomer 22.0 min; t_R of (–)-enantiomer 26.6 min.

Dimethyl-2-acetylamino-2-*p*-tolylethylphosphonate (9b). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3 , δ): 30.0; ^1H NMR (300.0 MHz, CDCl_3 , δ): 7.83 (d, $J = 7.8$ Hz, 2H, C_6H_4), 7.10 (d, $J = 8.0$ Hz, 2H, C_6H_4), 7.05 (s, 1H, NH), 5.32 (m, 1H, =CH), 3.65 (d, $J = 10.9$ Hz, 3H, OCH_3), 3.39 (d, $J = 11.0$ Hz, 3H, OCH_3), 2.43-2.20 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.98 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3 , δ): 169.1 (C=O), 138.4 (d, $J = 8.5$ Hz, C_6H_4 *Q*), 137.1 (C_6H_4), 129.2 (C_6H_4), 126.1 (C_6H_4), 52.2 (d, $J = 6.6$ Hz, OCH_3), 52.0 (d, $J = 6.7$ Hz, OCH_3), 48.2 (d, $J = 4.1$ Hz, CHCH_2), 31.7 (d, $J = 139$ Hz, CHCH_2), 23.2 (CH_3), 20.8 ($\text{C}_6\text{H}_4\text{CH}_3$); LRMS (ESI^+) m/z 308 $[\text{M}+\text{Na}]^+$; HRMS (ESI^+) exact mass calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_4\text{PNa}$ $[\text{M}+\text{Na}]^+$ requires m/z 308.1028, found m/z 308.1032. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_4\text{P}$: C, 54.73; H, 7.07; N, 4.91. Found: C, 54.97; H, 7.03; N, 5.08. $[\alpha]_D = -45.2$ ($c = 1.0$, CH_2Cl_2). The enantiomeric excess was calculated from the HPLC profile (Daicel Chiracel OD-H, flow rate: 0.5 mL/min flow rate, hexane:2-propanol = 85:15). Retention times: t_R (+)-enantiomer 19.7 min; t_R of (–)-enantiomer 37.9 min.

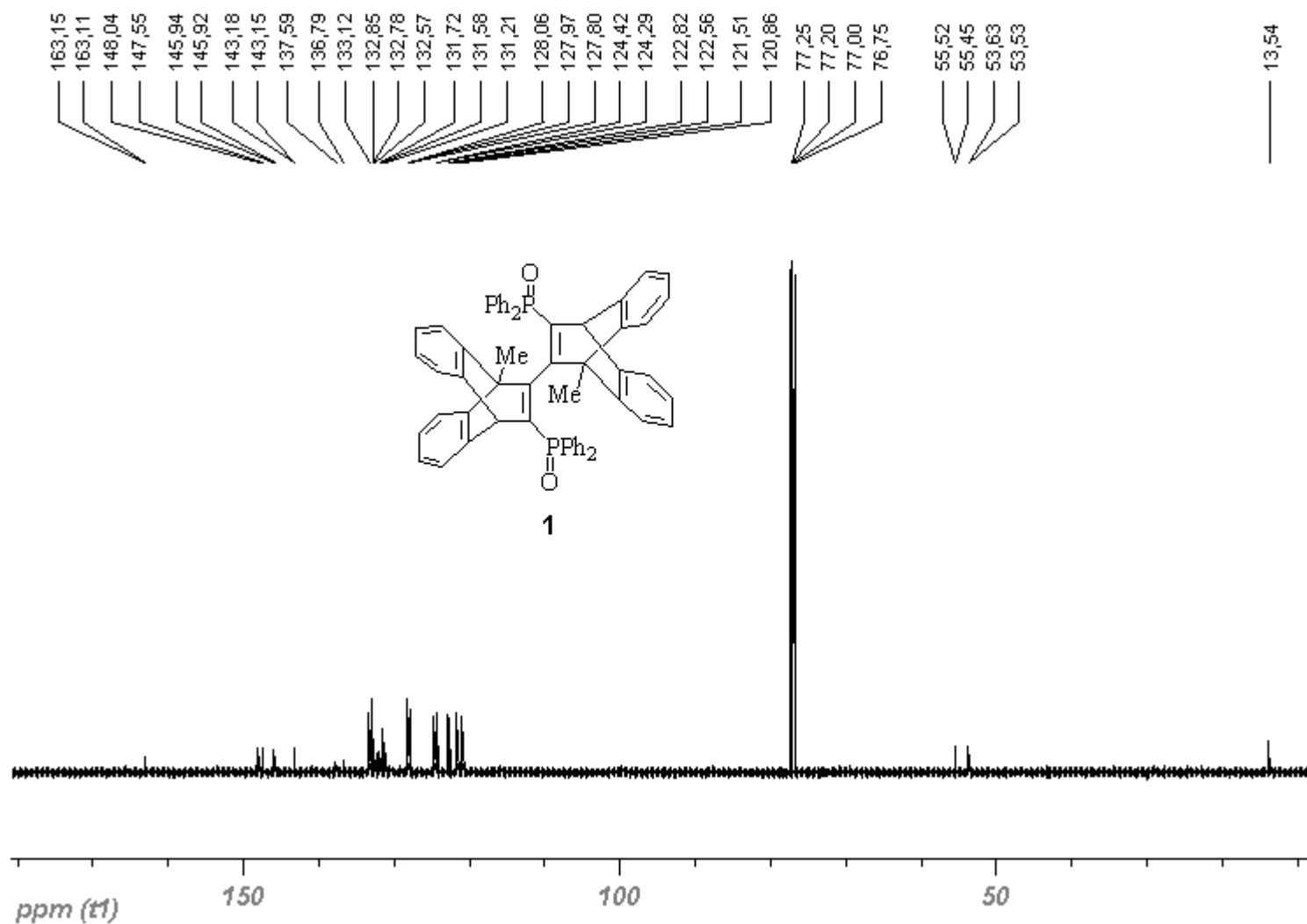
³¹P NMR Spectrum of rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (1)



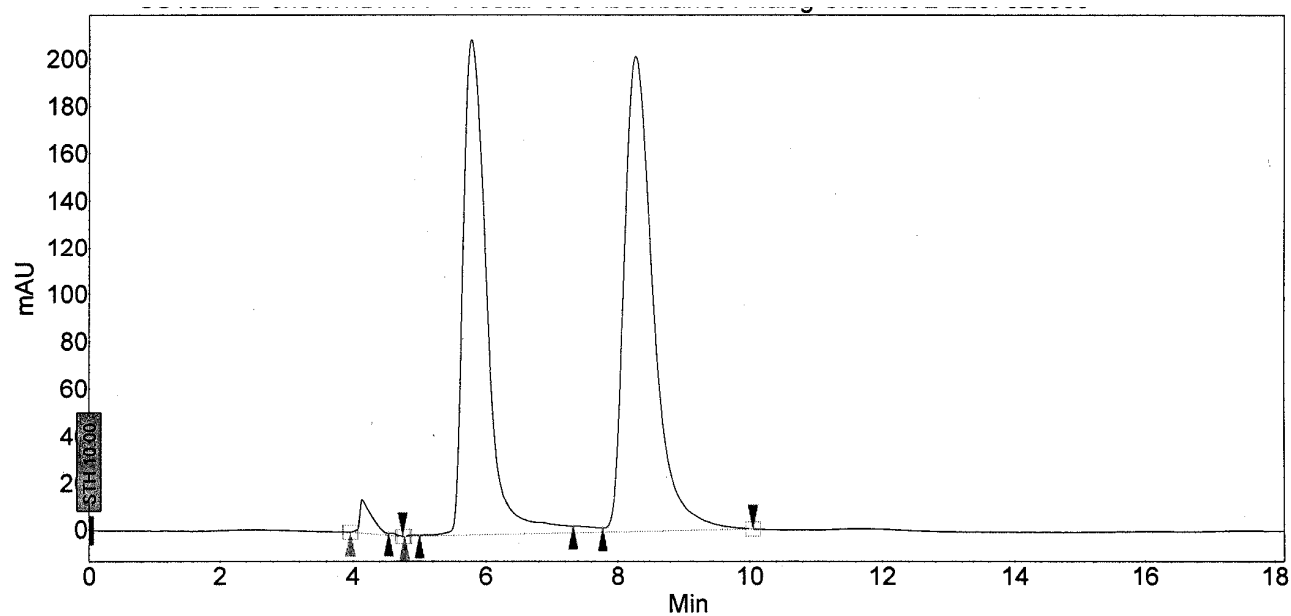
^1H NMR Spectrum of rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (1)



^{13}C NMR Spectrum of rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (1)



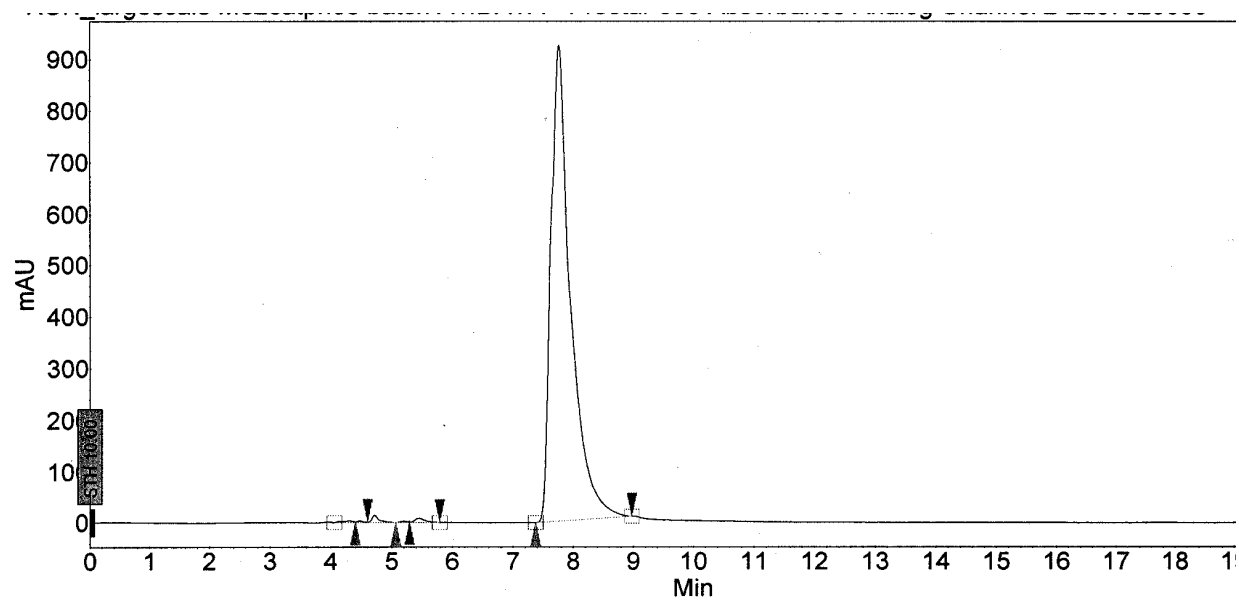
HPLC trace of Rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (rac-1)



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.13	1.52	14.1	3.0	1.517
2	UNKNOWN	4.57	0.06	1.0	0.1	0.061
3	UNKNOWN	4.88	0.04	0.5	0.1	0.042
4	UNKNOWN	5.77	44.76	210.5	87.1	44.762
5	UNKNOWN	7.35	0.55	2.8	1.1	0.547
6	UNKNOWN	8.27	53.07	202.1	103.3	53.071
Total			100.00	431.1	194.6	100.000

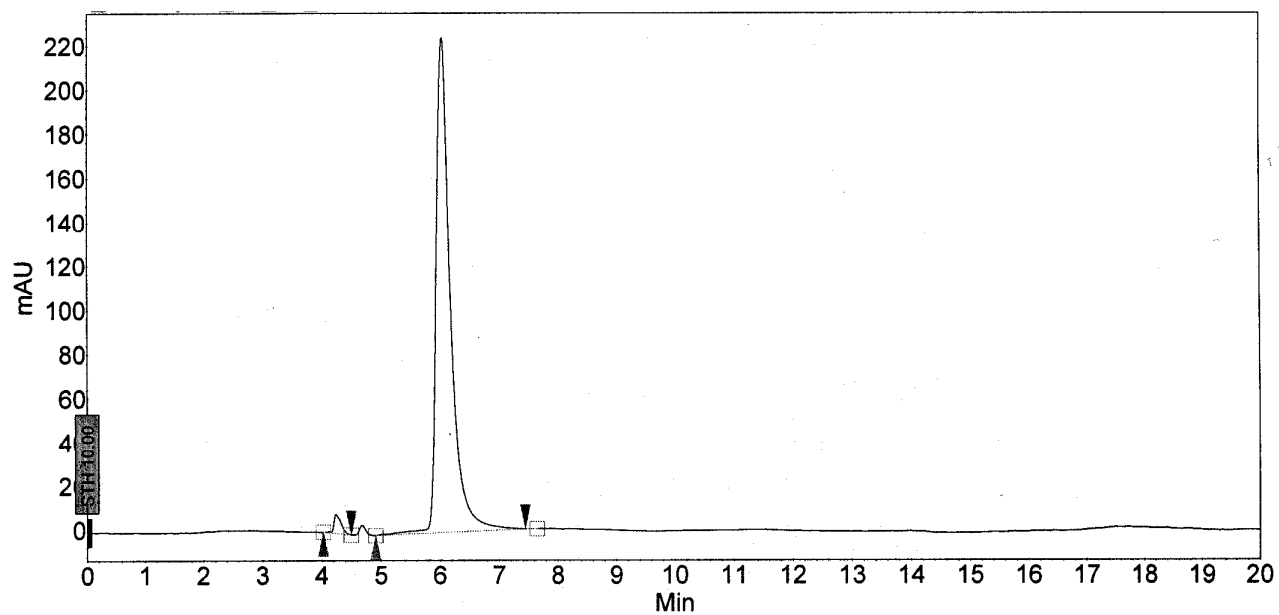
HPLC trace of (S)-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (S-1)



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.48	0.11	3.3	0.4	0.114
2	UNKNOWN	5.19	0.09	2.3	0.3	0.089
3	UNKNOWN	5.44	0.43	8.0	1.5	0.429
4	UNKNOWN	7.77	99.37	924.3	350.5	99.368
Total			100.00	937.9	352.7	100.000

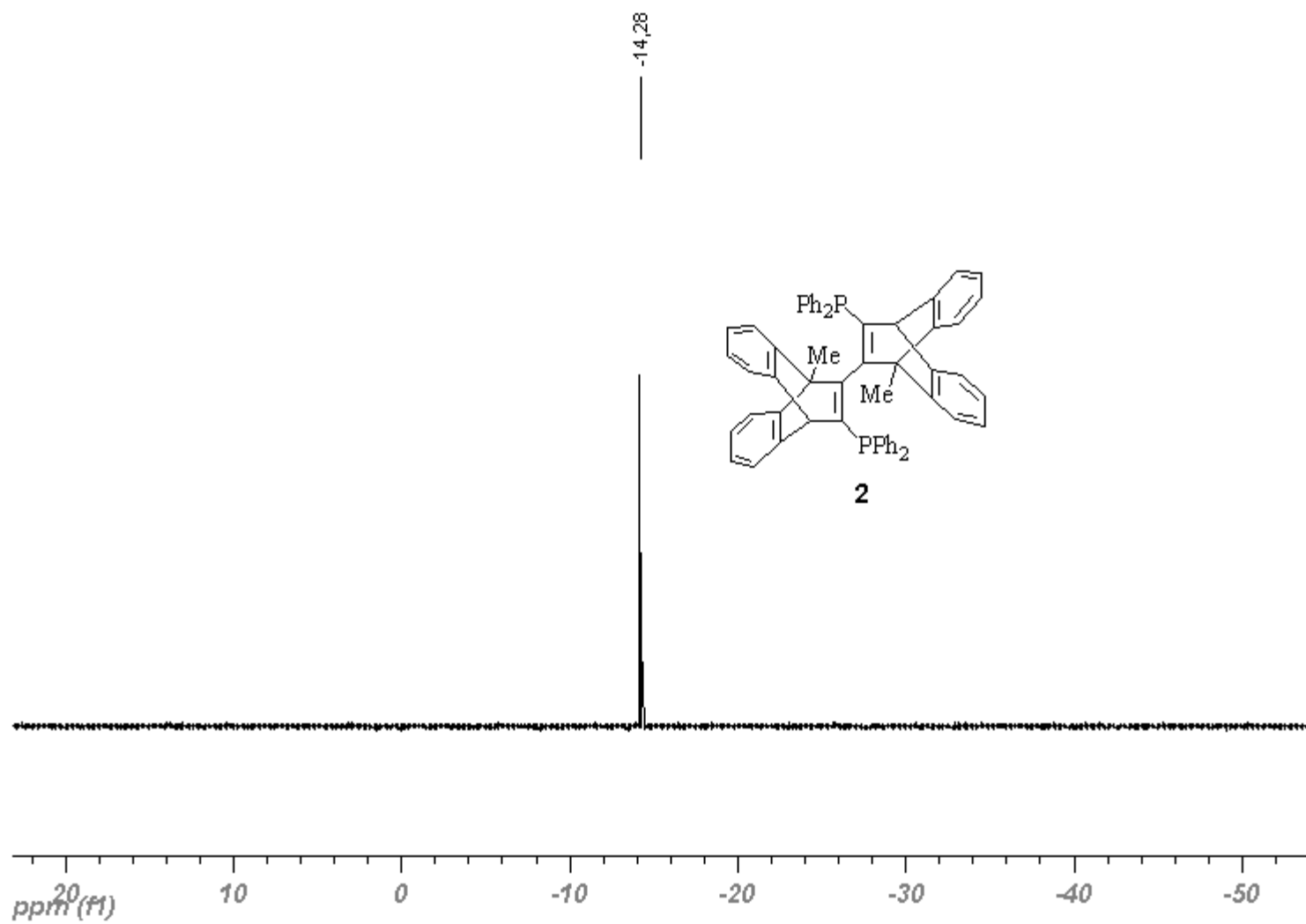
HPLC trace of (R)-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphinoyl)-12,12'-diyl (R-1)



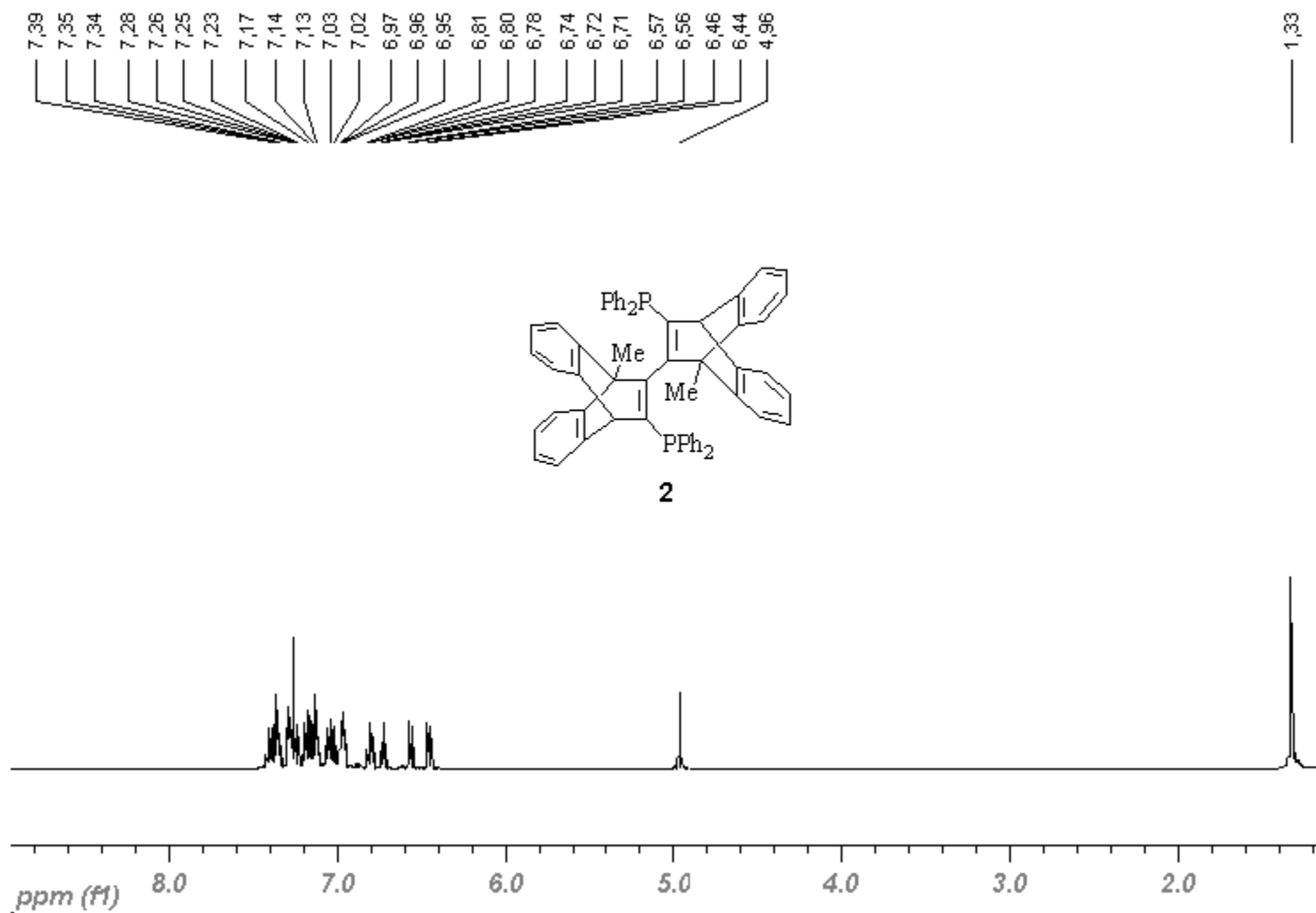
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.24	1.90	8.6	1.2	1.901
2	UNKNOWN	6.04	98.10	224.7	63.2	98.099
Total			100.00	233.3	64.4	100.000

³¹P NMR Spectrum of rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphanyl)-12,12'-diyl (2)



¹H NMR Spectrum of rac-9,9'-dimethyl-9,9',10,10'-tetrahydro-9,10,9',10'-biethenobianthracene-11,11'-bis-(diphenylphosphanyl)-12,12'-diyl (2)

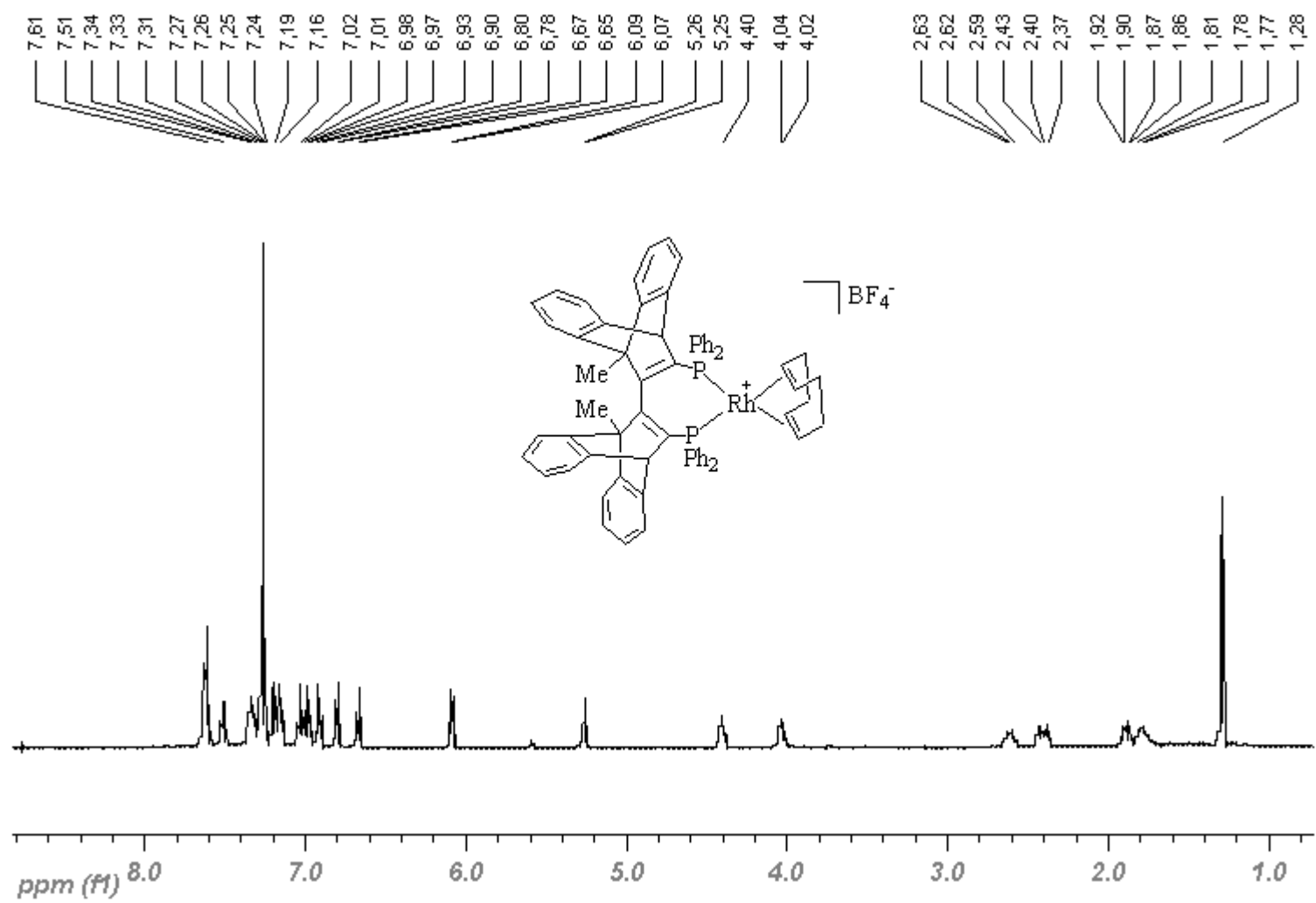


Chemical structure of compound **2** is shown above the spectrum. The structure is a [1,1'-biphenyl]-2,2'-diylidenebis(phosphine) derivative with two phenyl groups on each phosphorus and two methyl groups on the central carbon atoms.

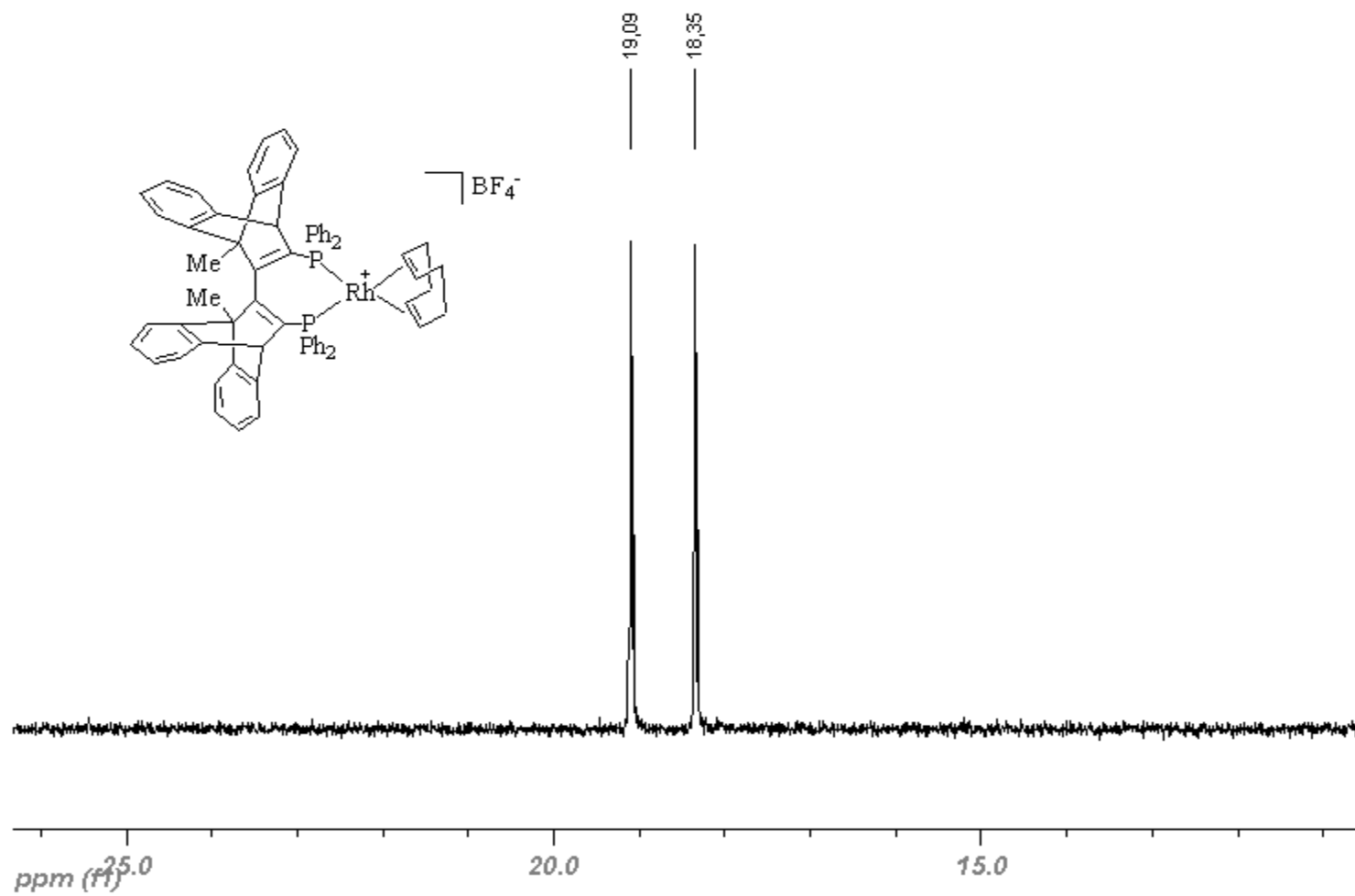
13C NMR spectrum (CDCl₃) peaks (ppm):

Peak (ppm)
164.18
163.88
148.07
146.56
146.48
146.38
143.04
142.88
138.07
138.04
138.00
137.97
136.97
136.90
136.86
134.66
134.58
134.50
132.65
132.56
132.48
128.57
128.15
127.94
127.43
124.36
124.26
123.79
123.75
123.12
122.70
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120.63
77.25
77.00
76.75
55.02
54.88
54.85
54.81
14.03

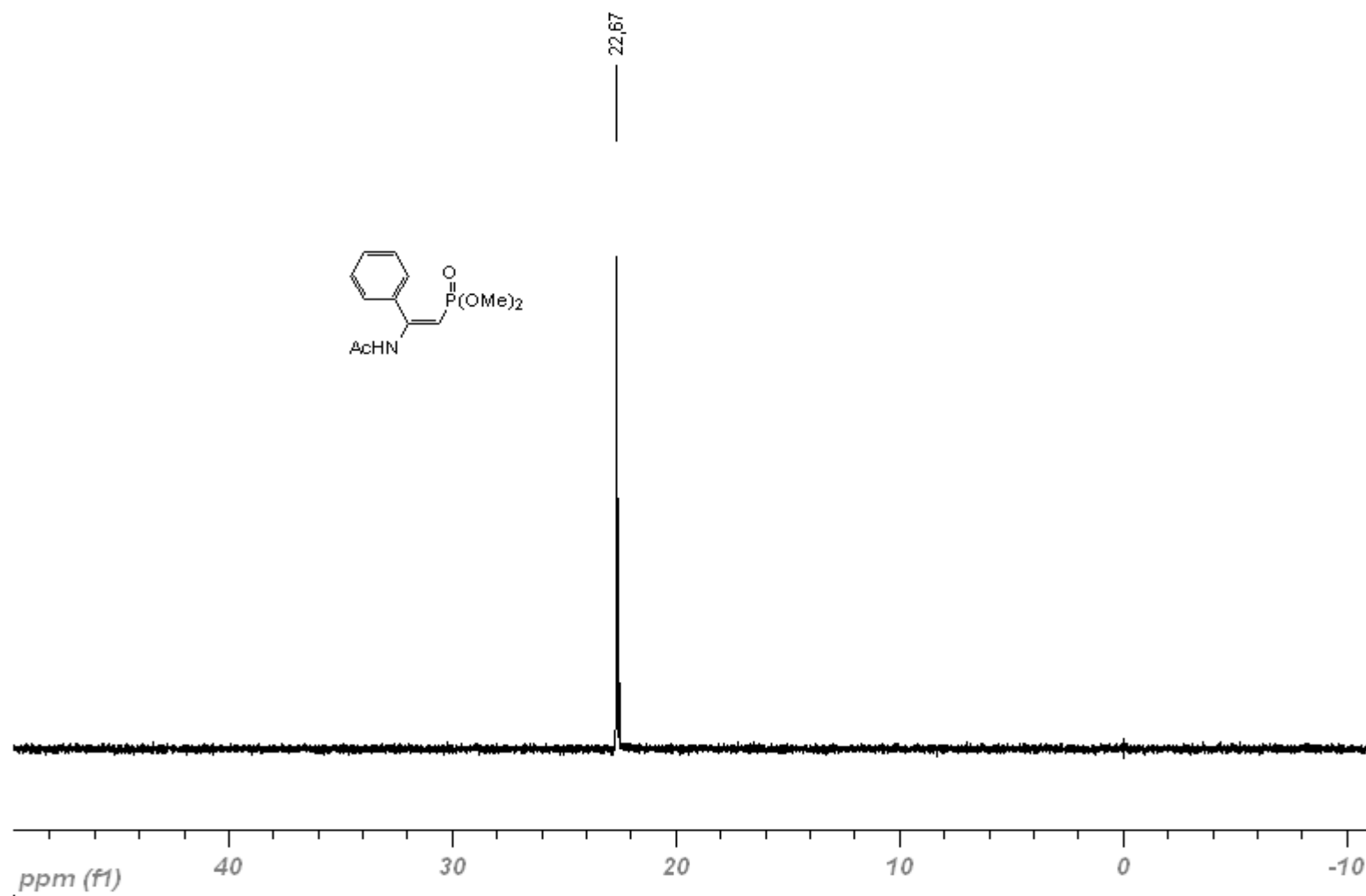
¹H NMR Spectrum of [{(S)-2}Rh(1,5-COD)][BF₄] (3)



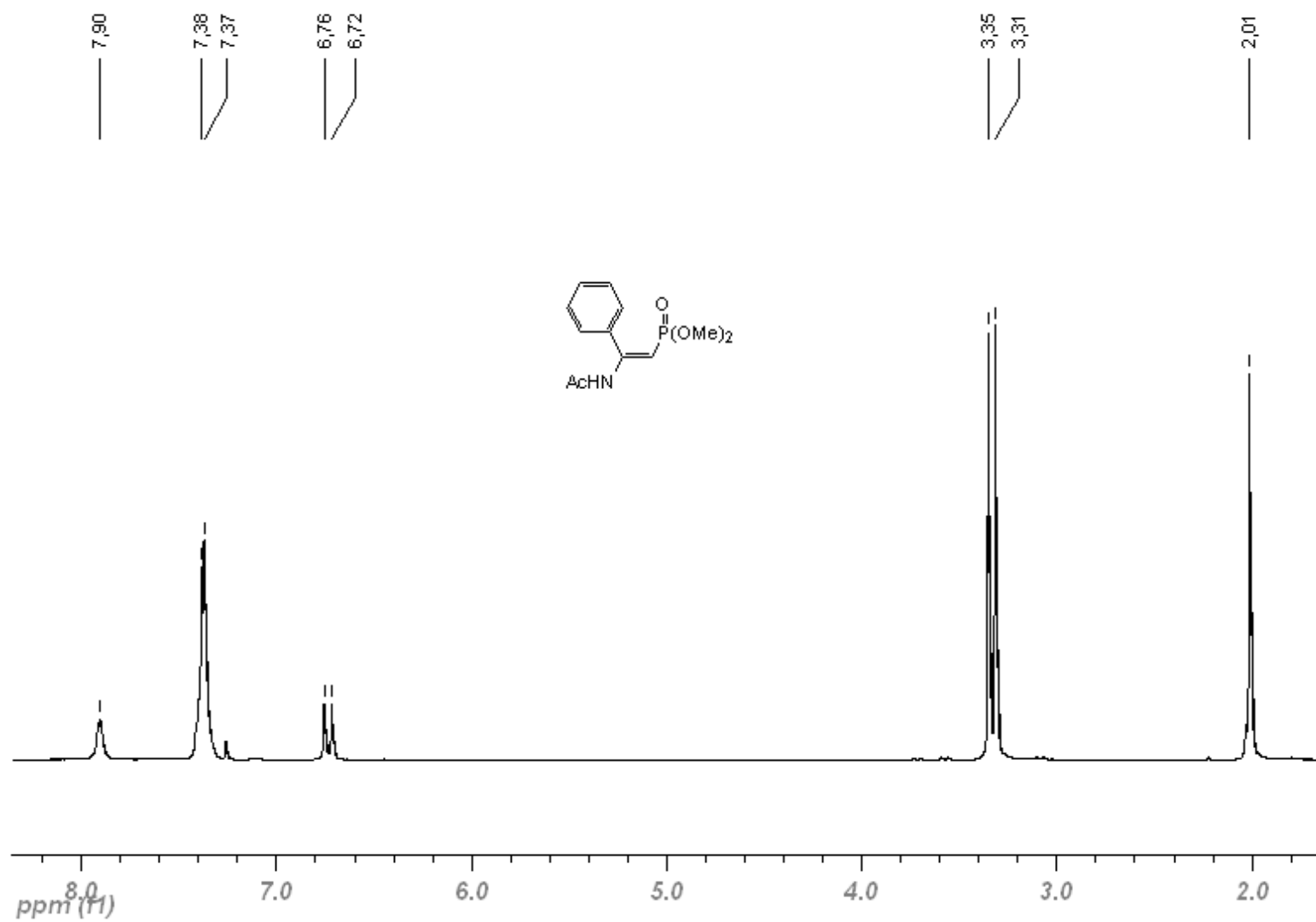
³¹P NMR Spectrum of [{(S)-2}Rh(1,5-COD)][BF₄] (3)



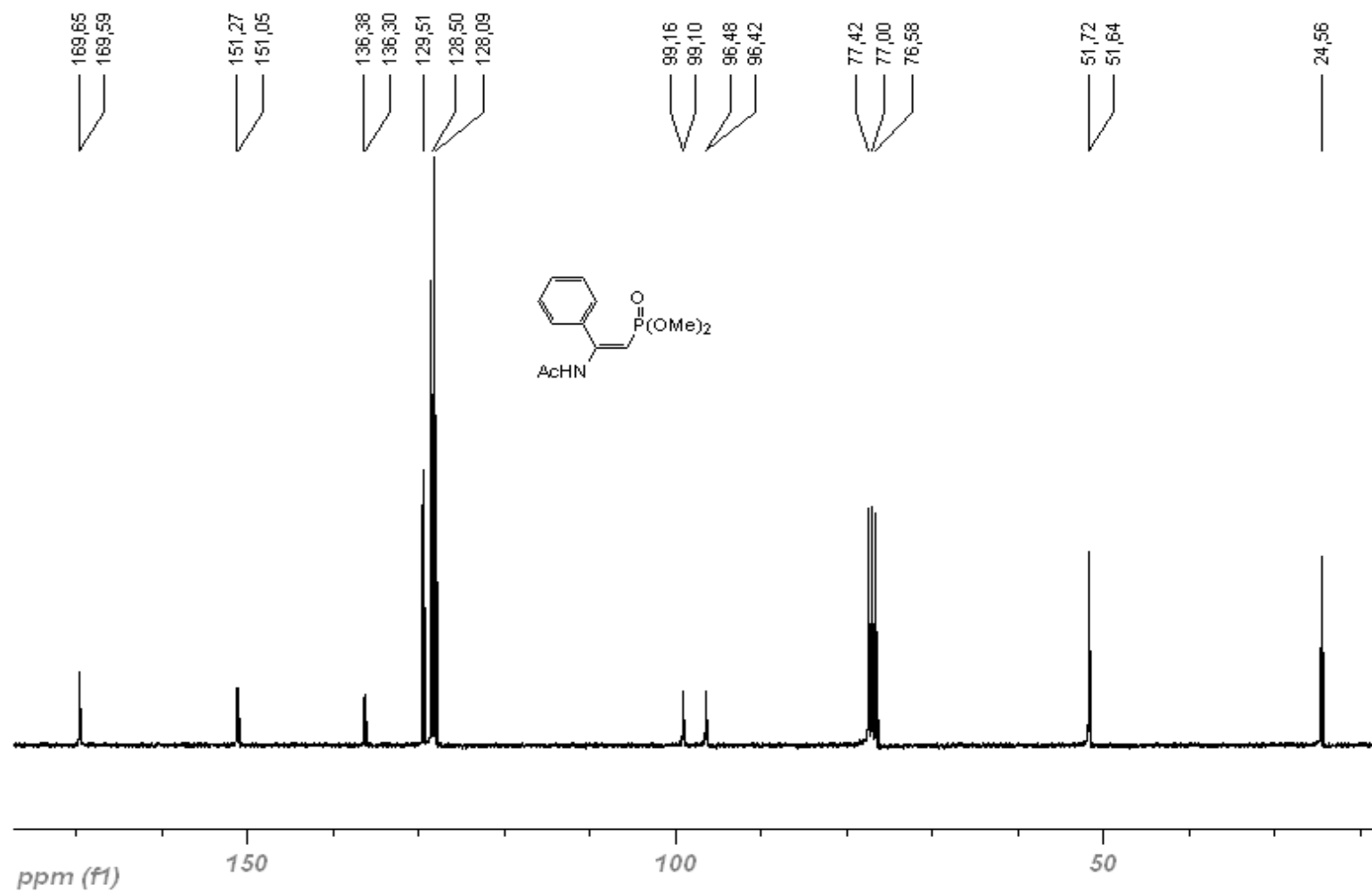
³¹P NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (*E*-8a)



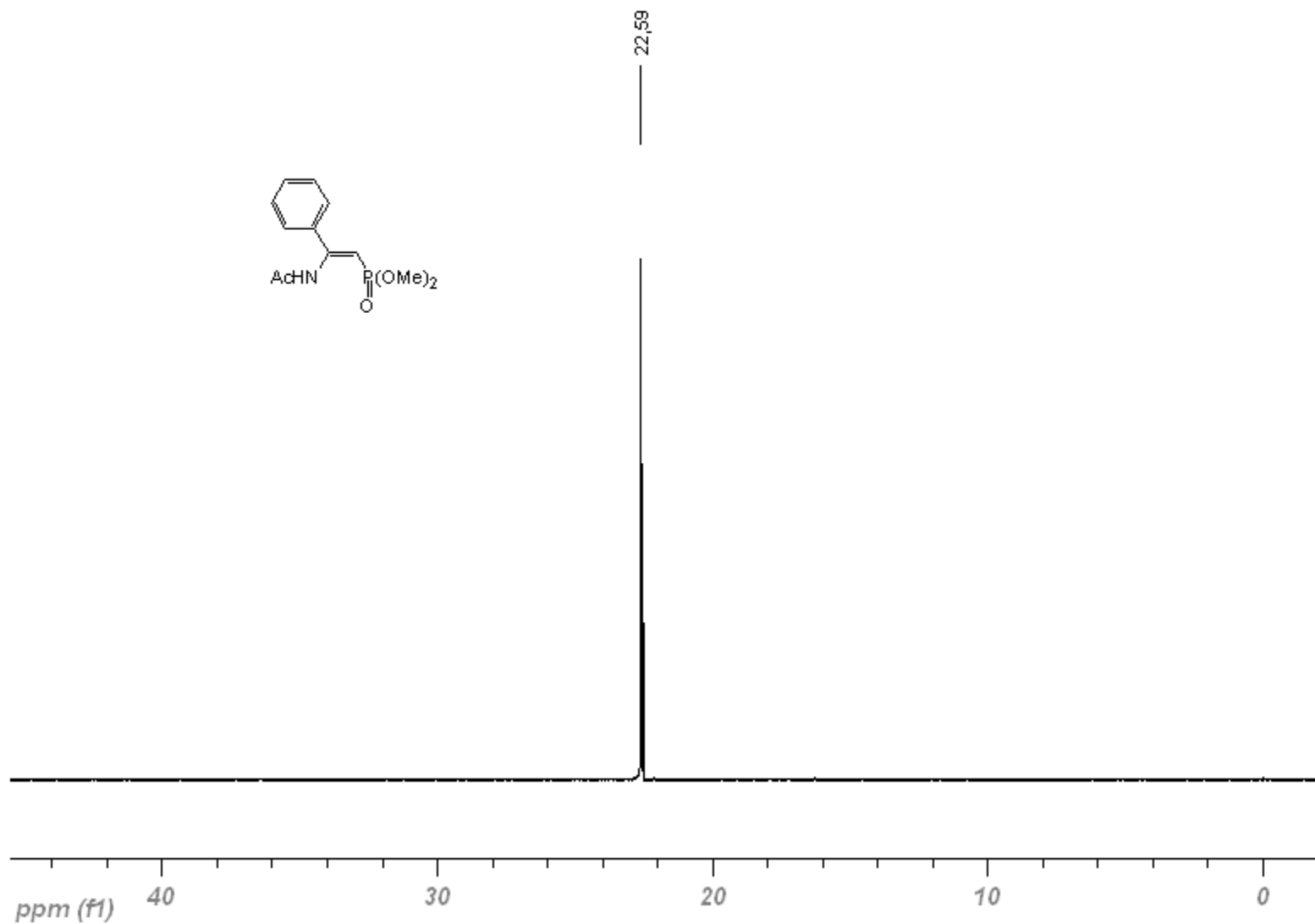
¹H NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (*E*-8a)



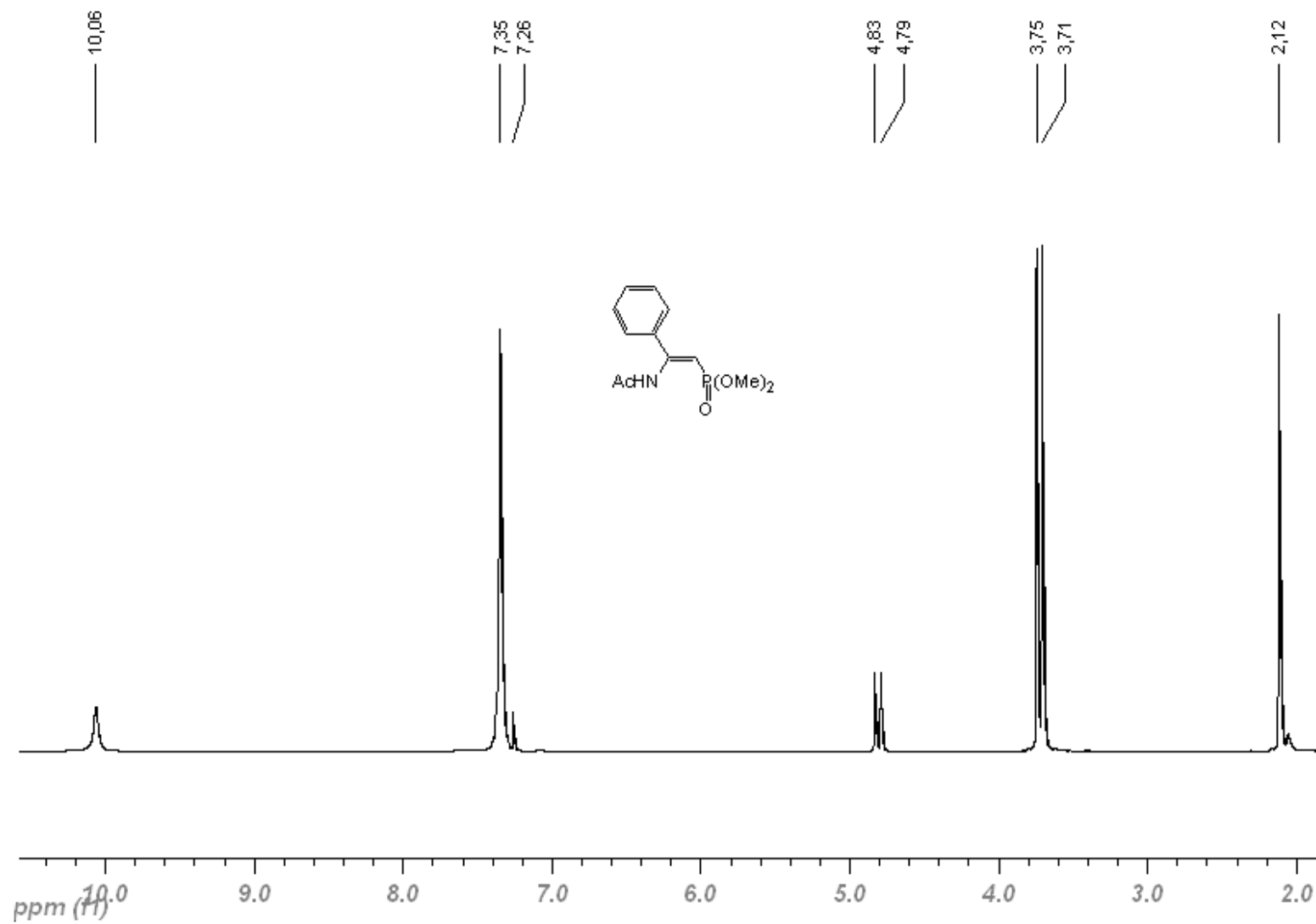
¹³C NMR Spectrum of (*E*)-Dimethyl-2-acetyl-2-phenylvinylphosphonate (*E*-8a)



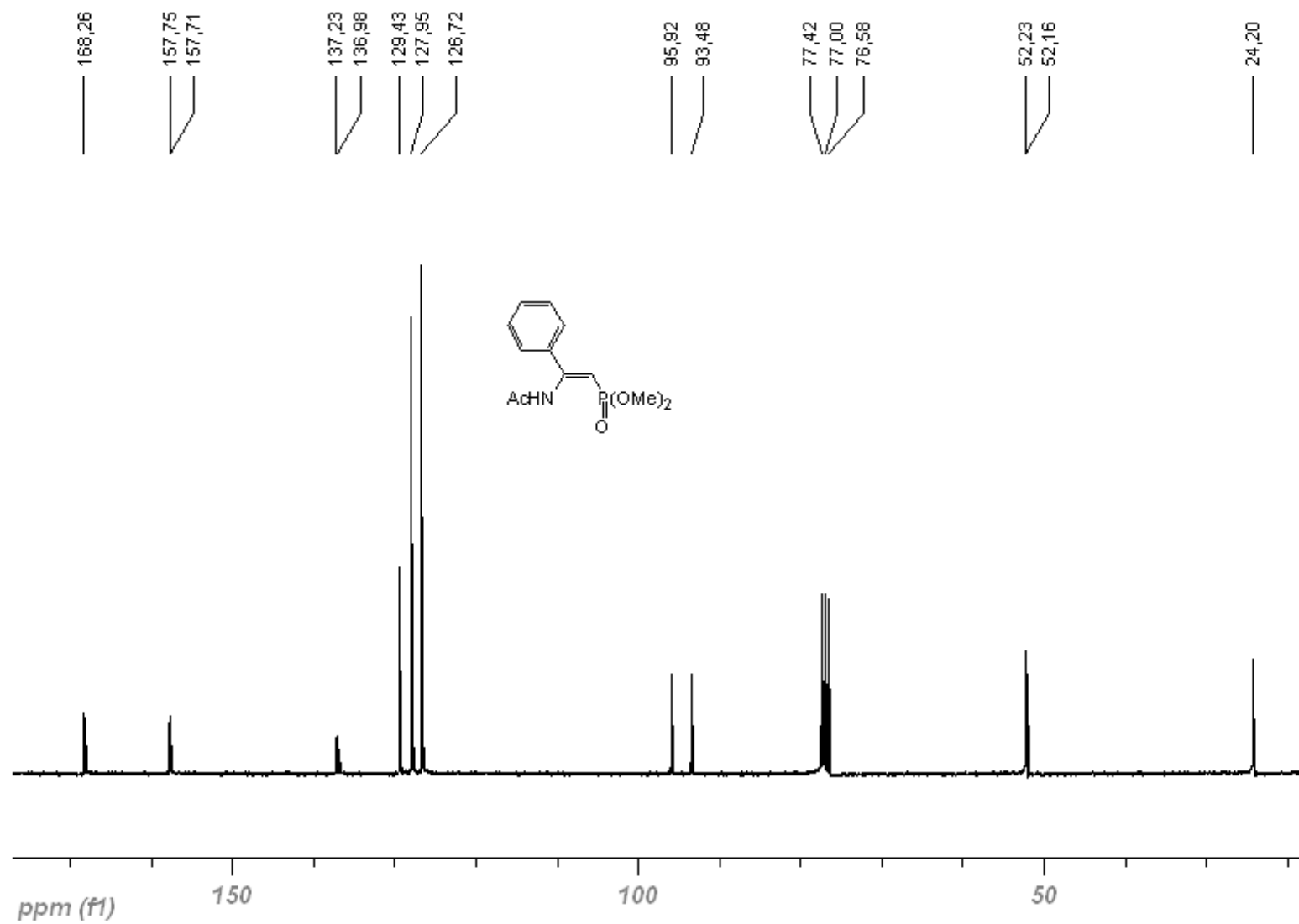
³¹P NMR Spectrum of (Z)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (Z-8a)



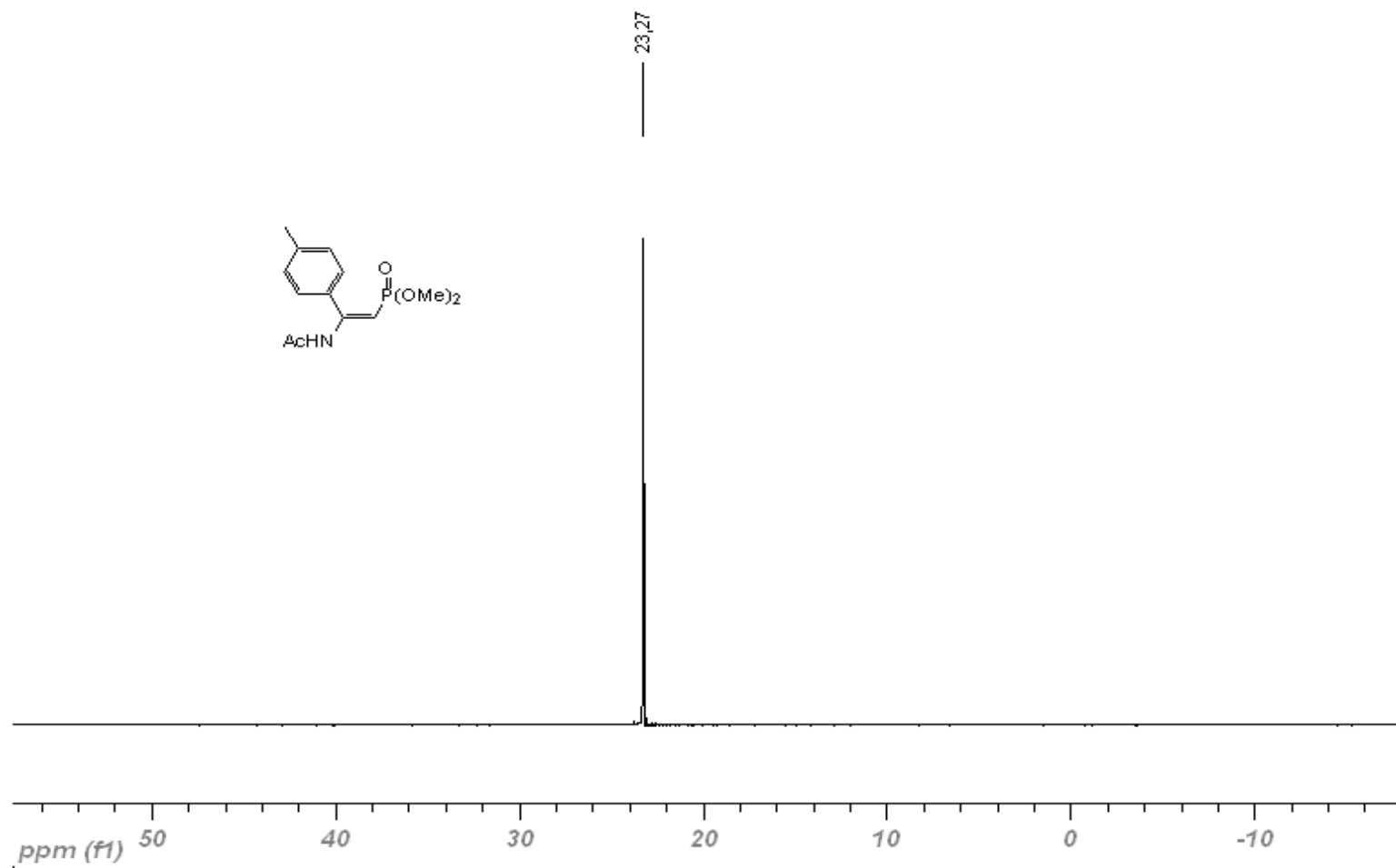
¹H NMR Spectrum of (Z)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (Z-8a)



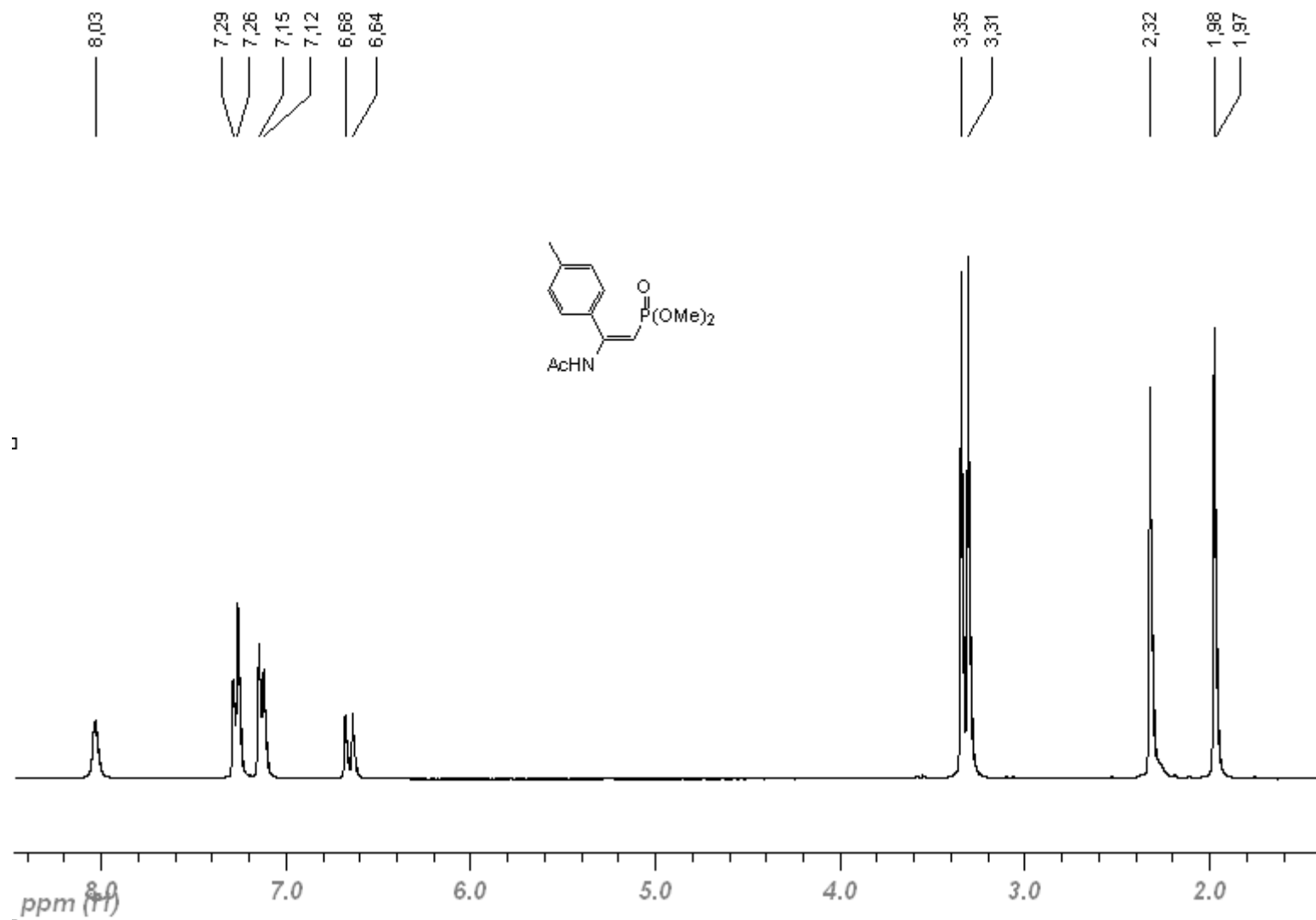
¹³C NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-phenylvinylphosphonate (Z-8a)



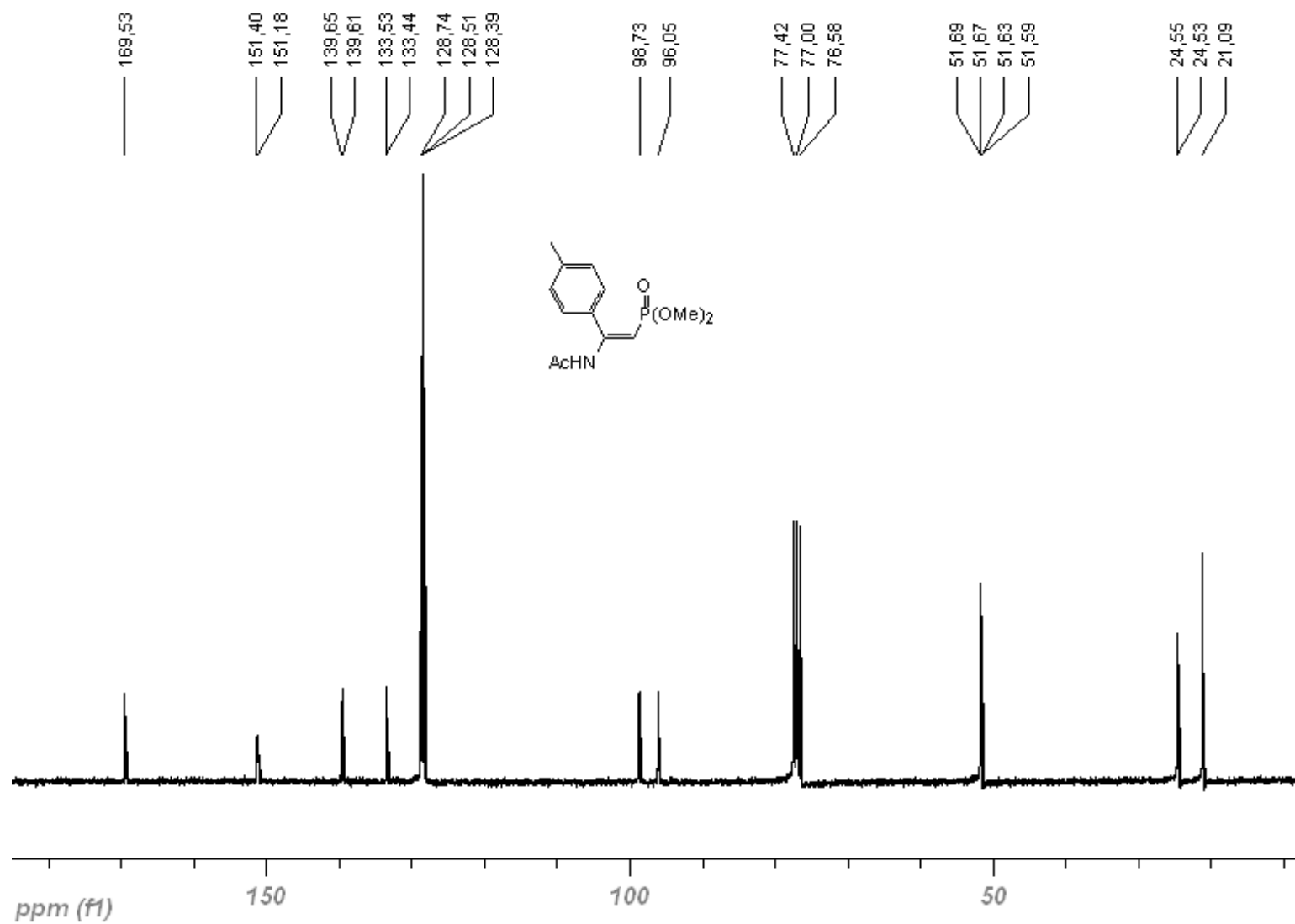
³¹P NMR Spectrum of (Z)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (*E*-8b)



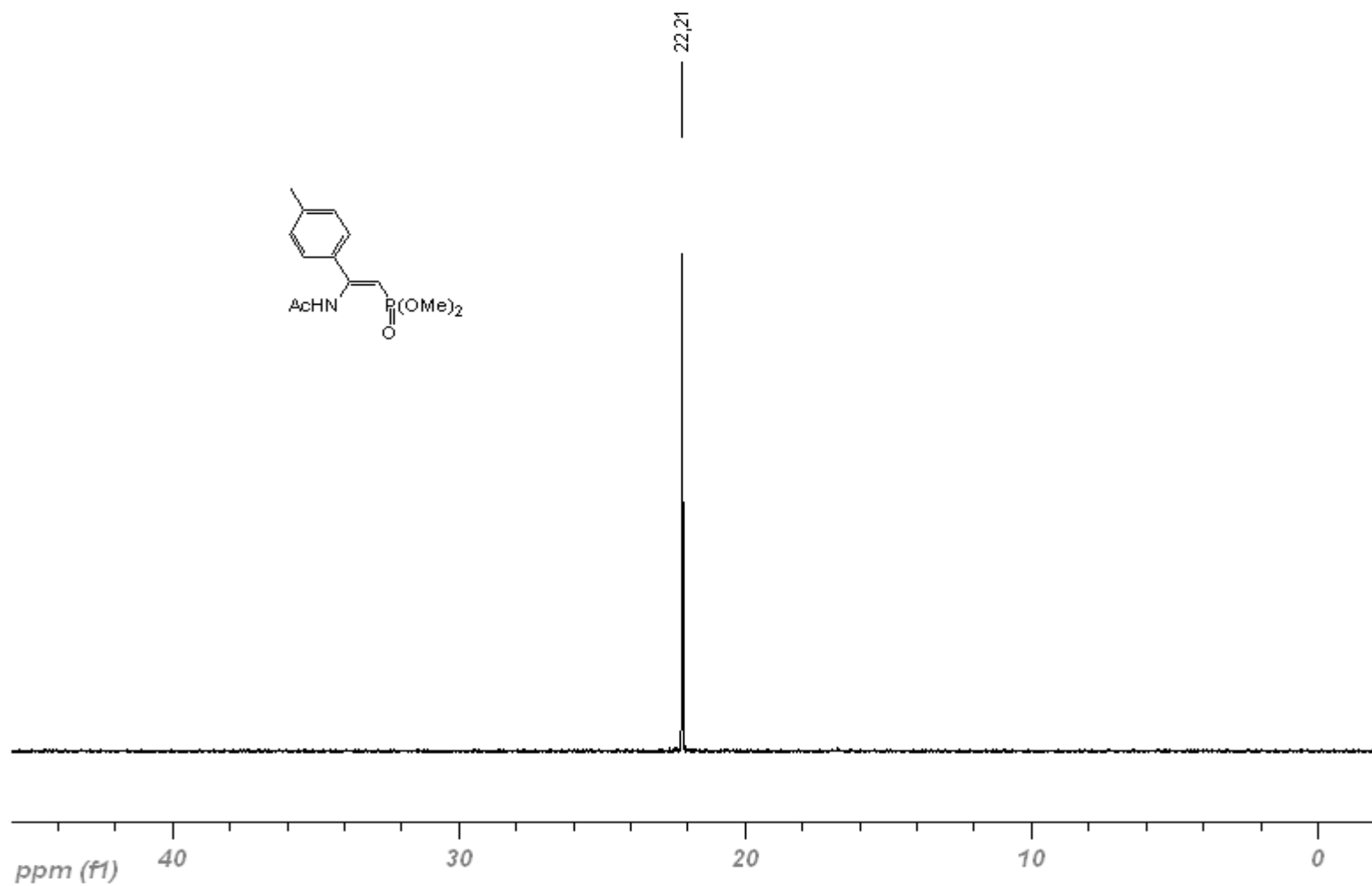
¹H NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (*E*-8b)



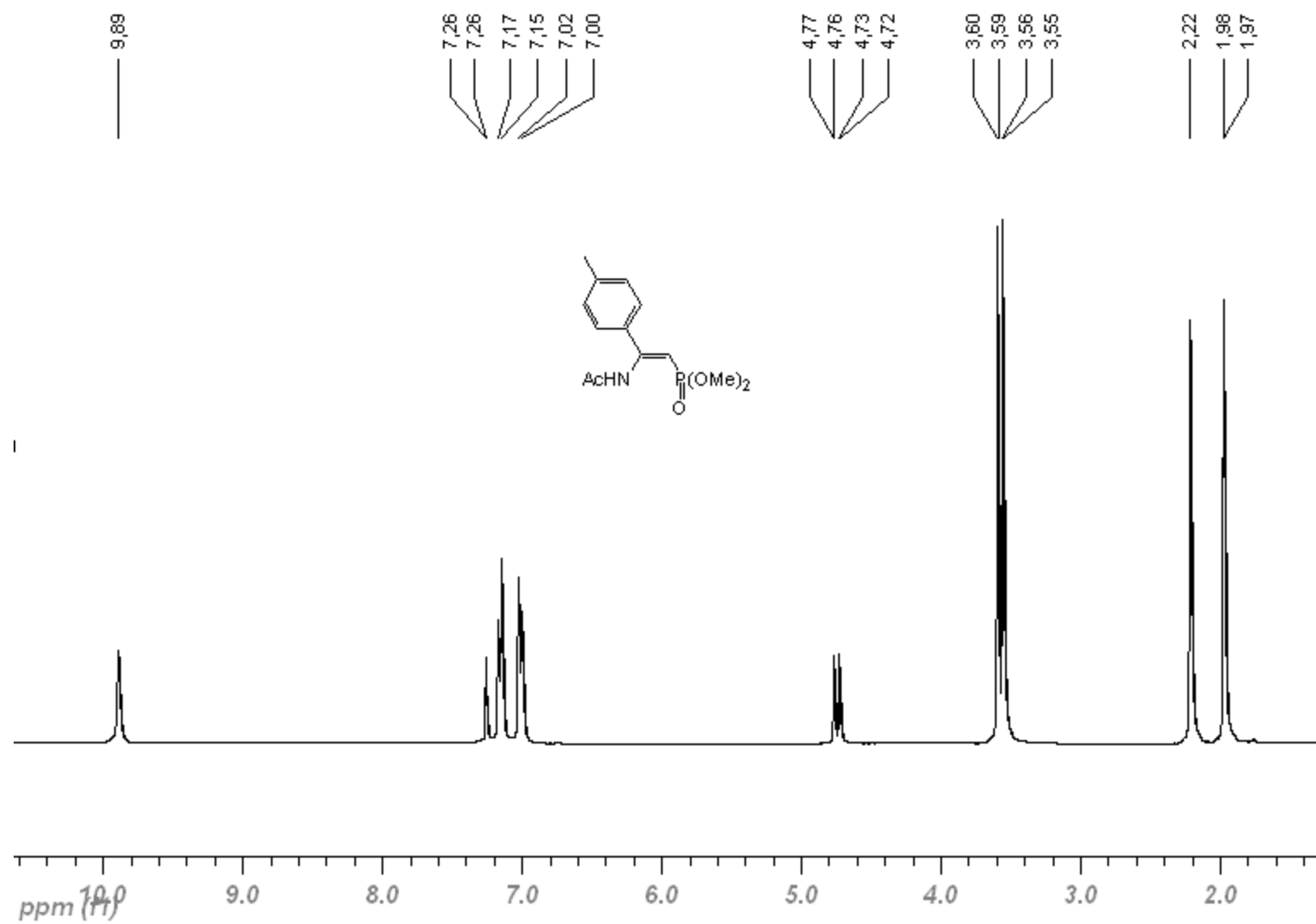
¹³C NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (*E*-8b)



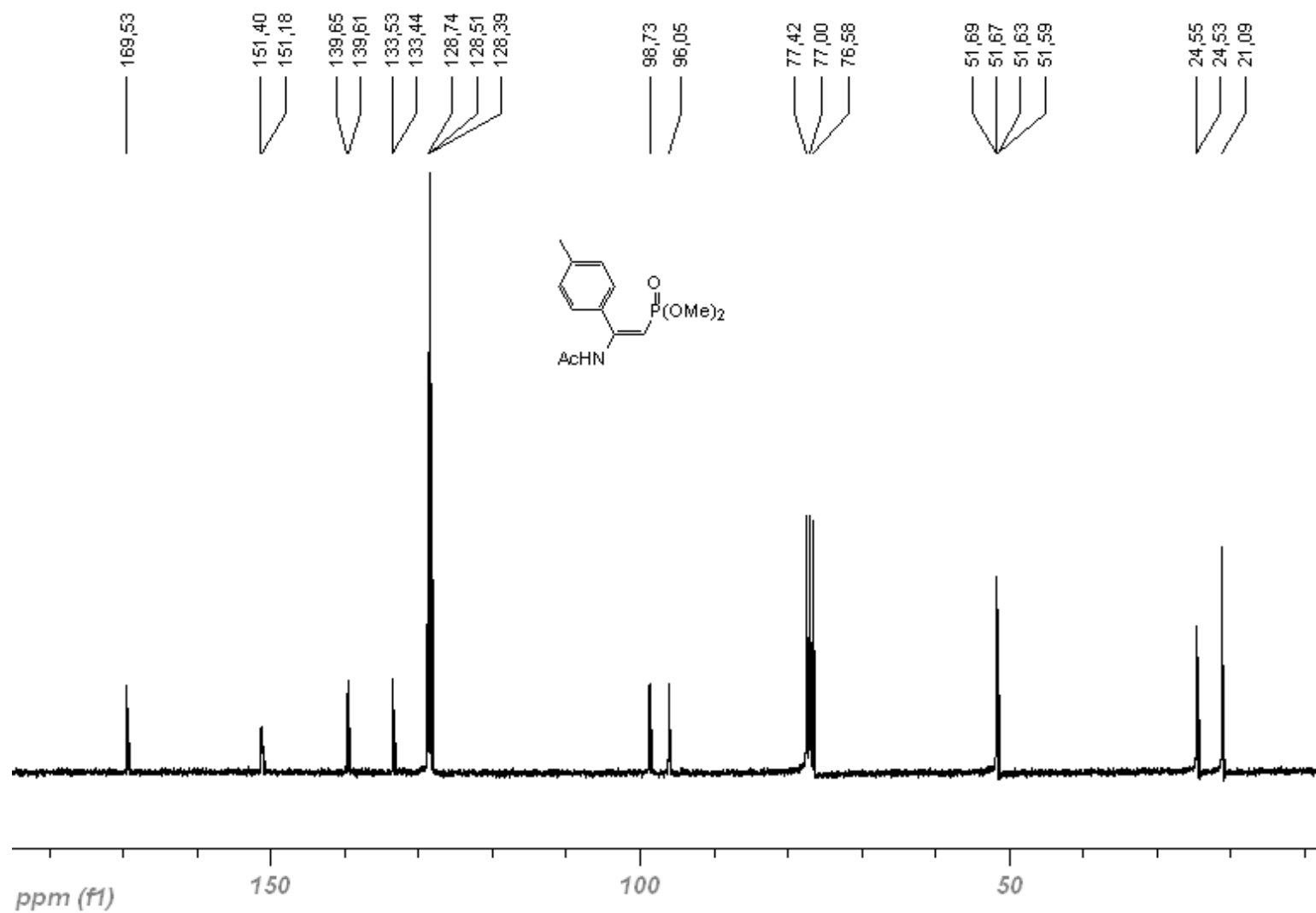
³¹P NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (Z-8b)



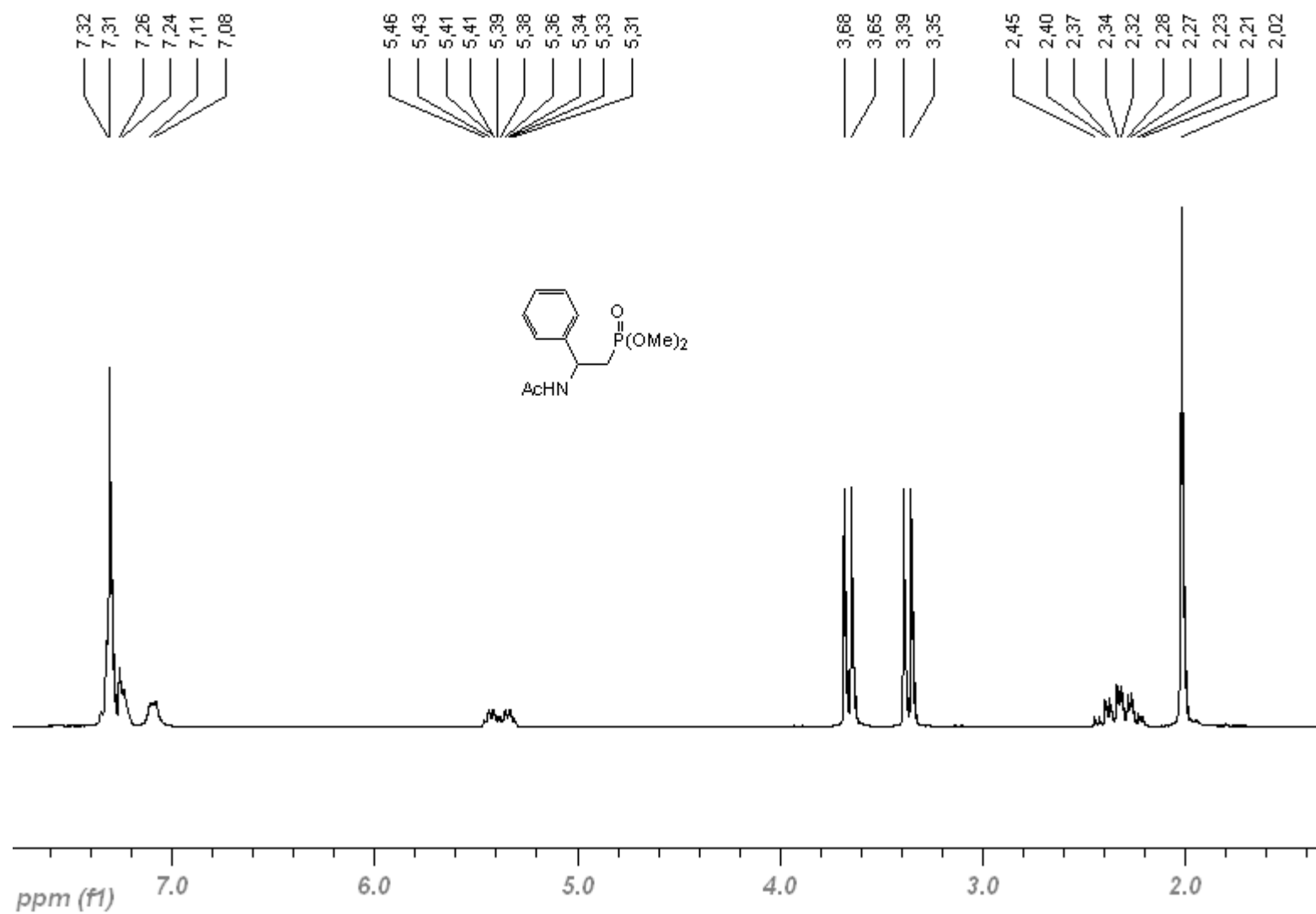
¹H NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (Z-8b)



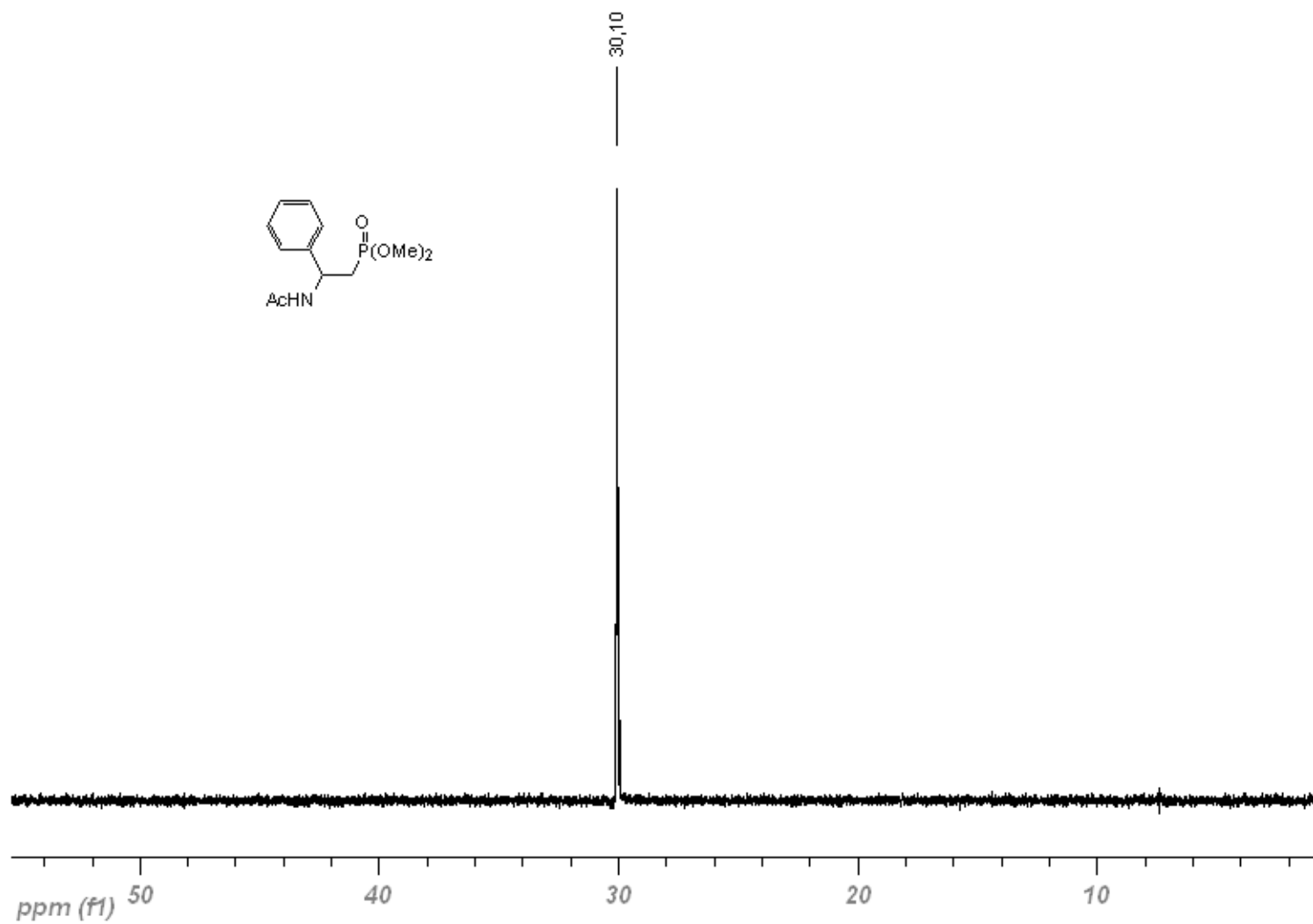
¹H NMR Spectrum of (*E*)-Dimethyl-2-acetylamino-2-*p*-tolylvinylphosphonate (Z-8b)



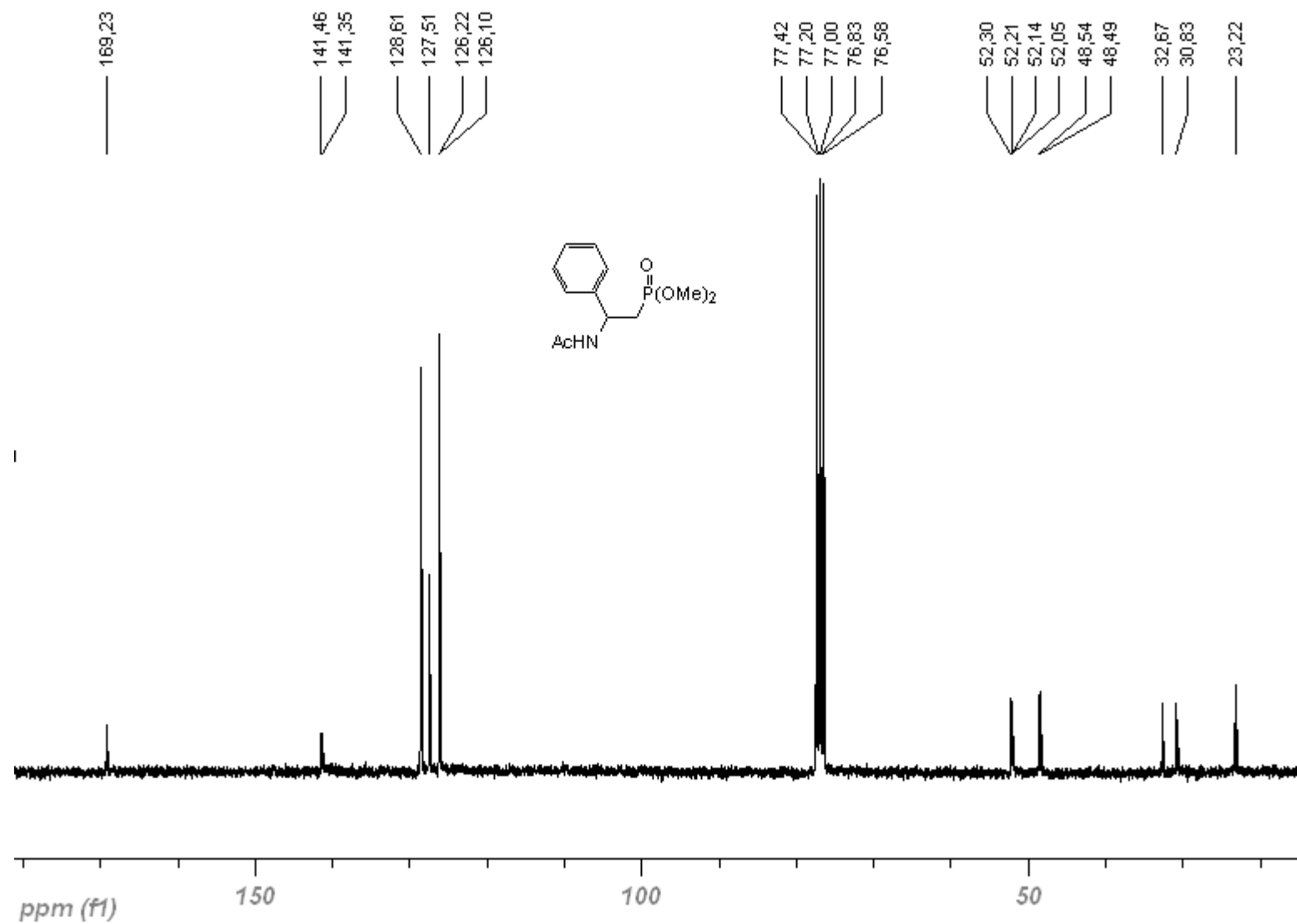
¹H NMR Spectrum of Dimethyl-2-acetylamino-2-phenylethylphosphonate (9a)



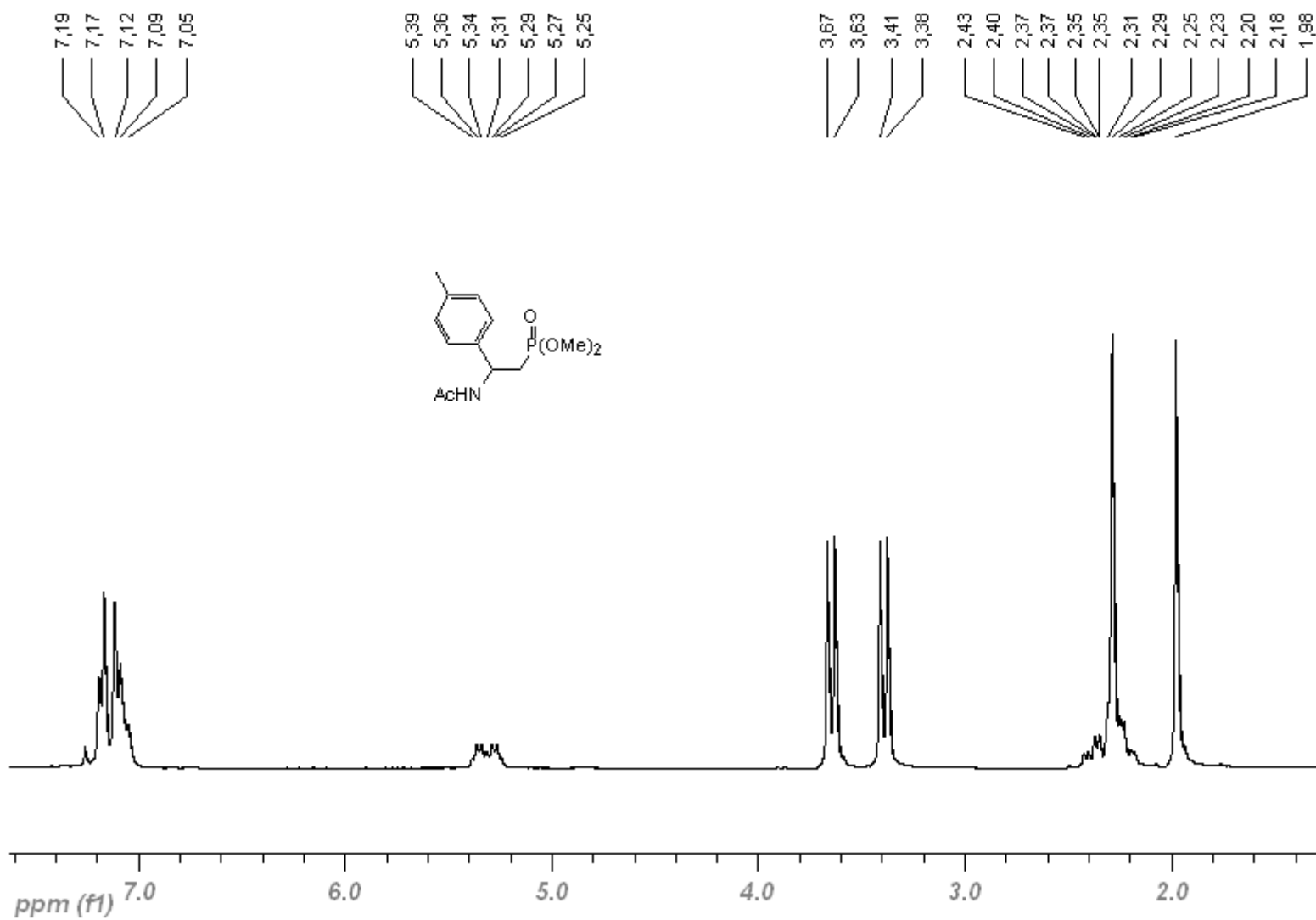
³¹P NMR Spectrum of Dimethyl-2-acetylamino-2-phenylethylphosphonate (9a)



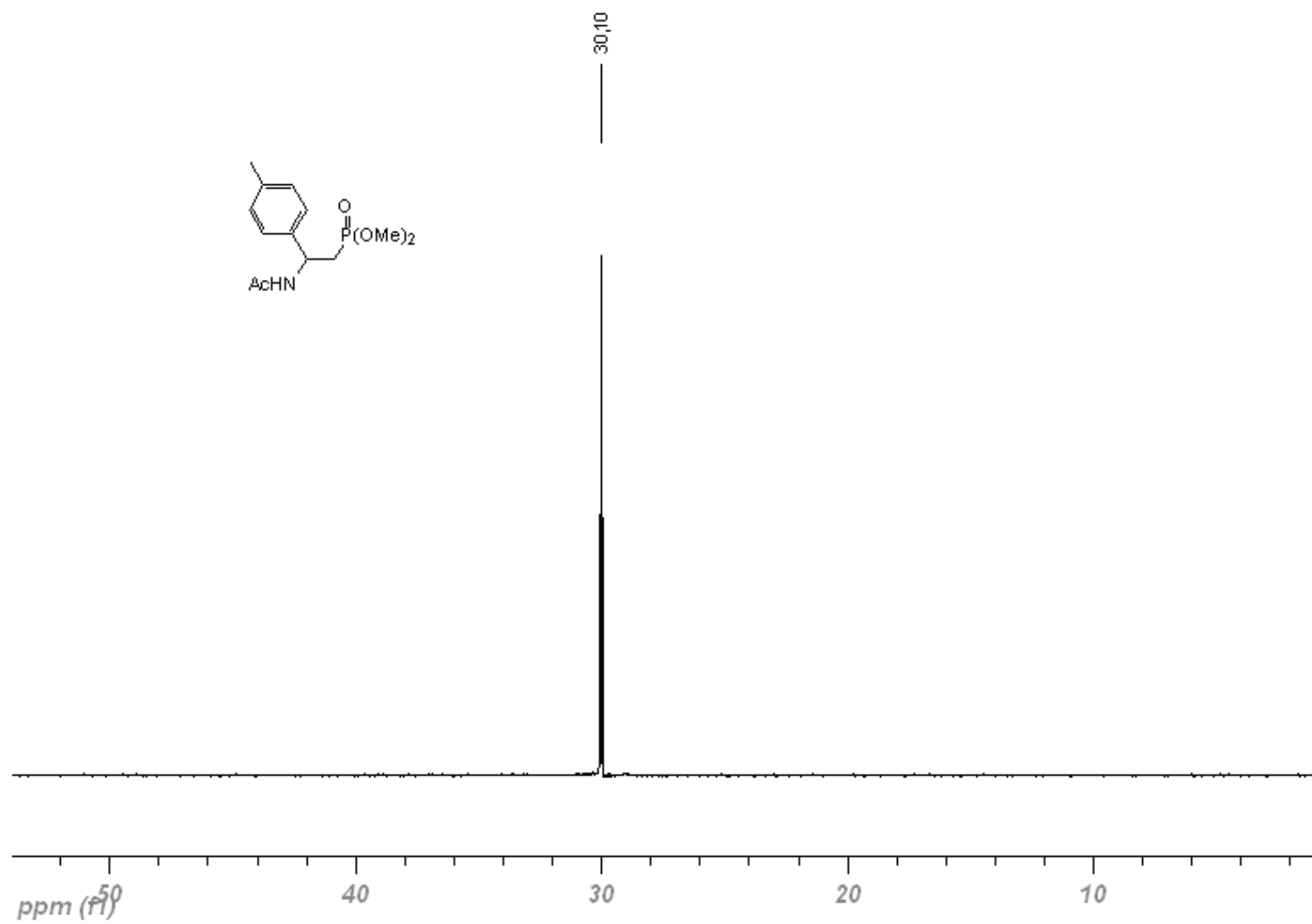
¹³C NMR Spectrum of Dimethyl-2-acetylamino-2-phenylethylphosphonate (9a)



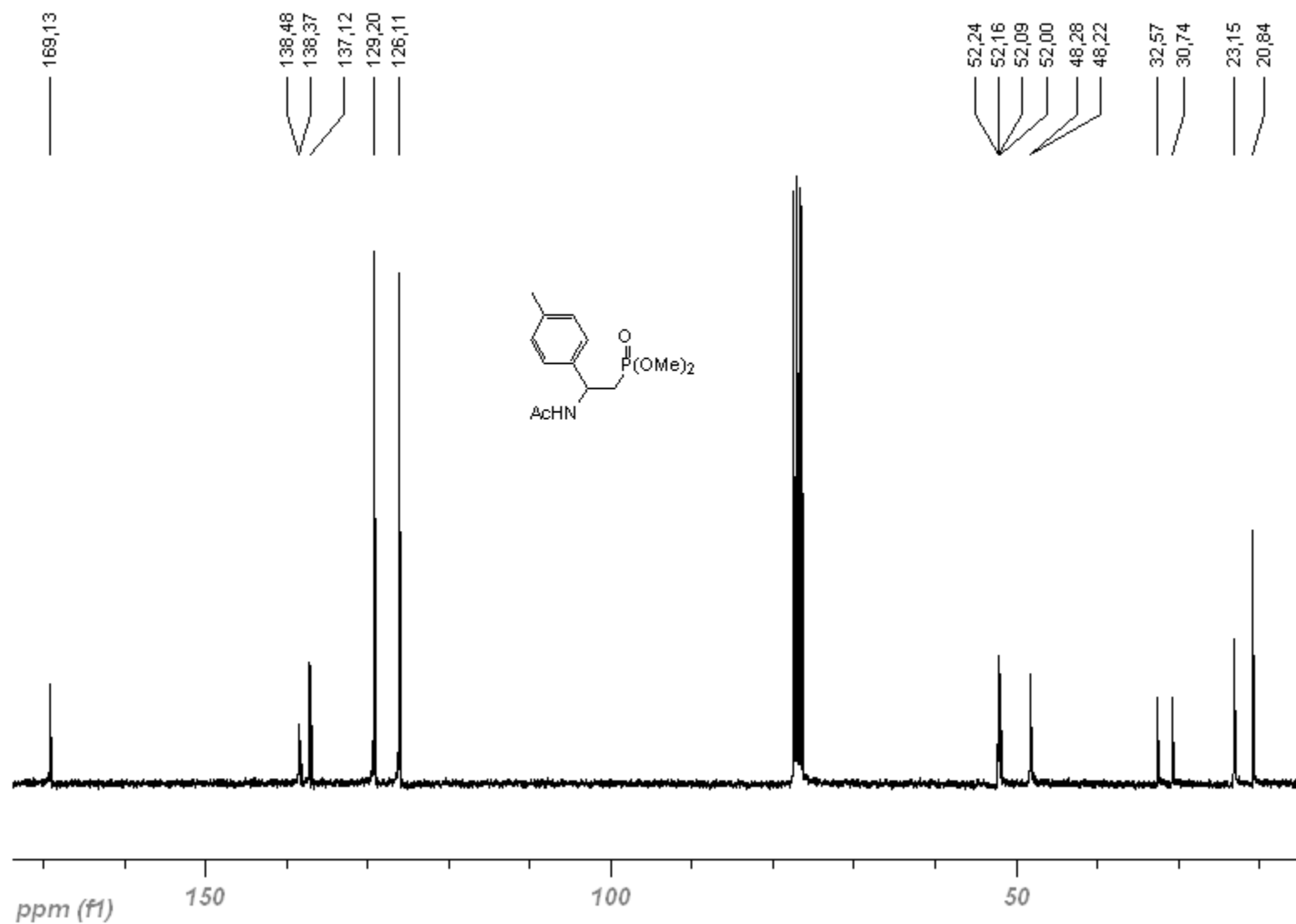
¹H NMR Spectrum of Dimethyl-2-acetylamino-2-*p*-tolylethylphosphonate (9b)



³¹P NMR Spectrum of Dimethyl-2-acetylamino-2-*p*-tolylethylphosphonate (9b)



¹³C NMR Spectrum of Dimethyl-2-acetylamino-2-*p*-tolylethylphosphonate (9b).



Benchmark racemic sample of *N*-acetylalanine methyl ester **5**

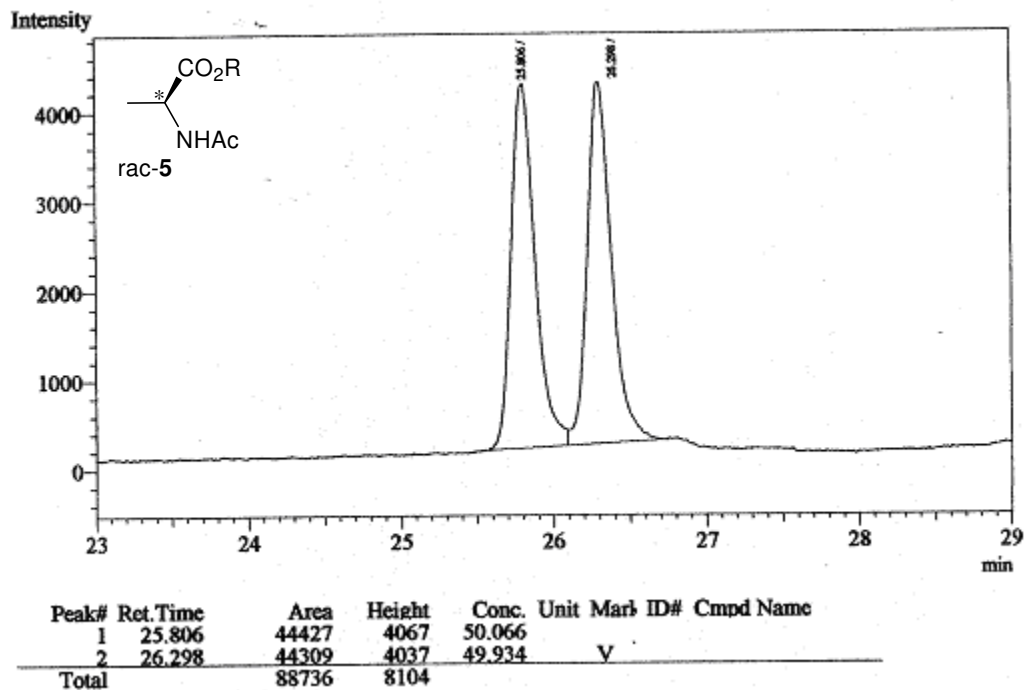


Table 1, Entry 1

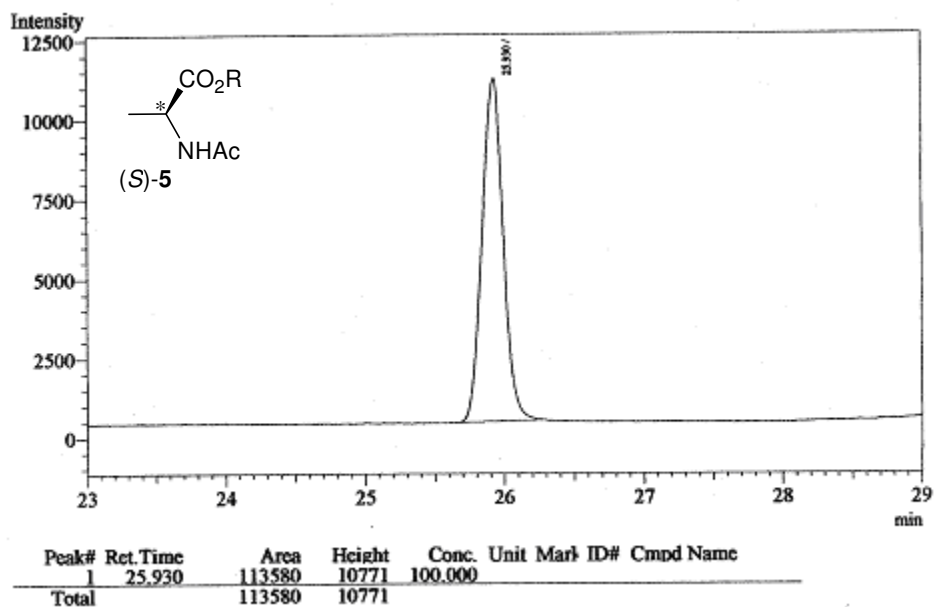


Table 1, Entry 2

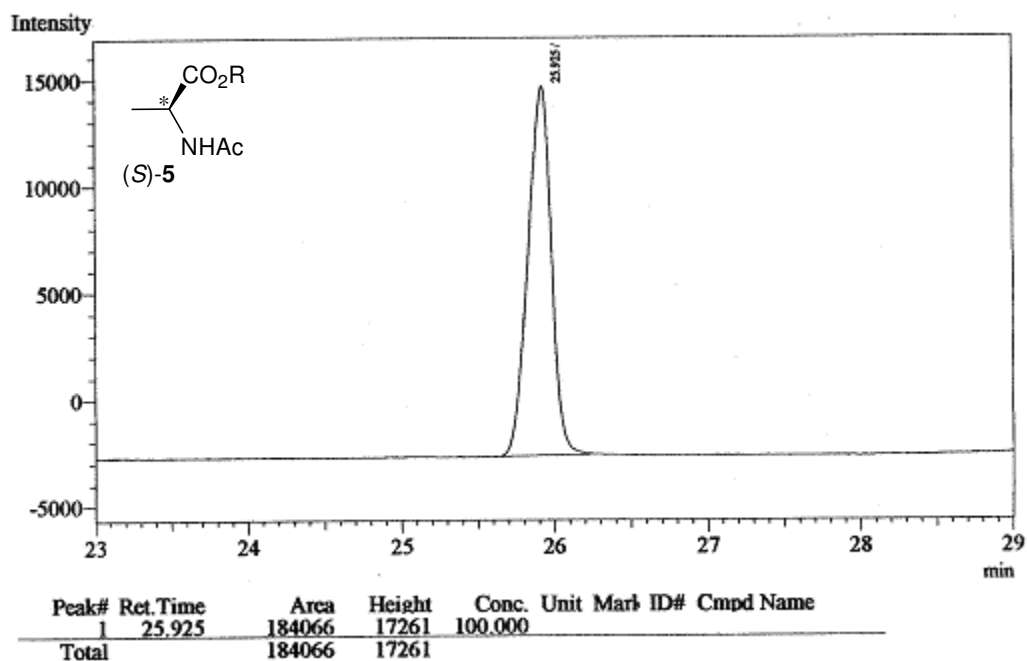


Table 1, Entry 3

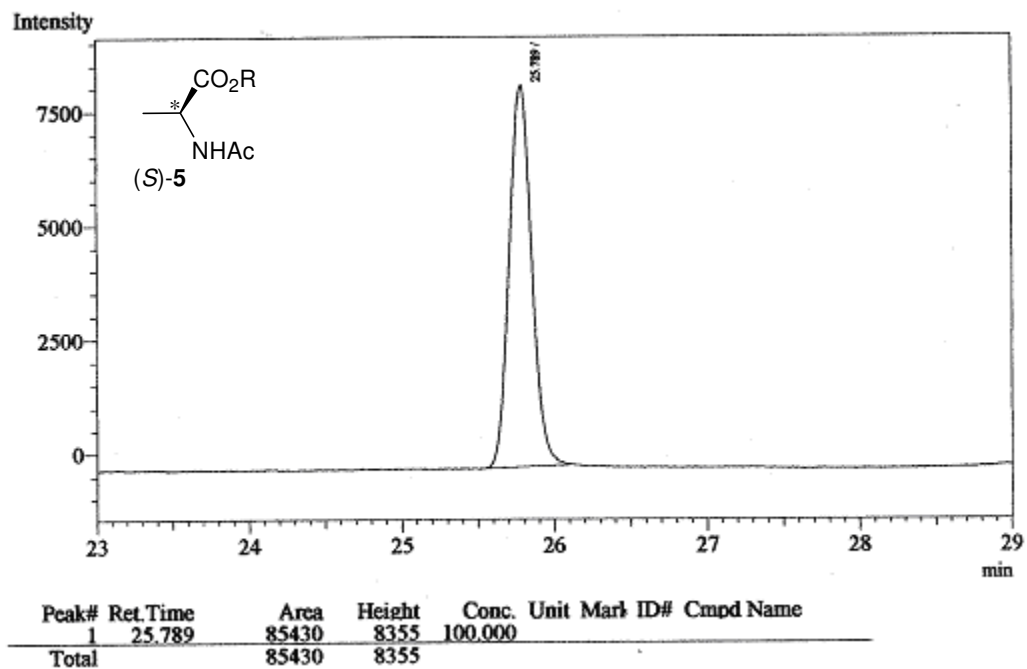


Table 1, Entry 4

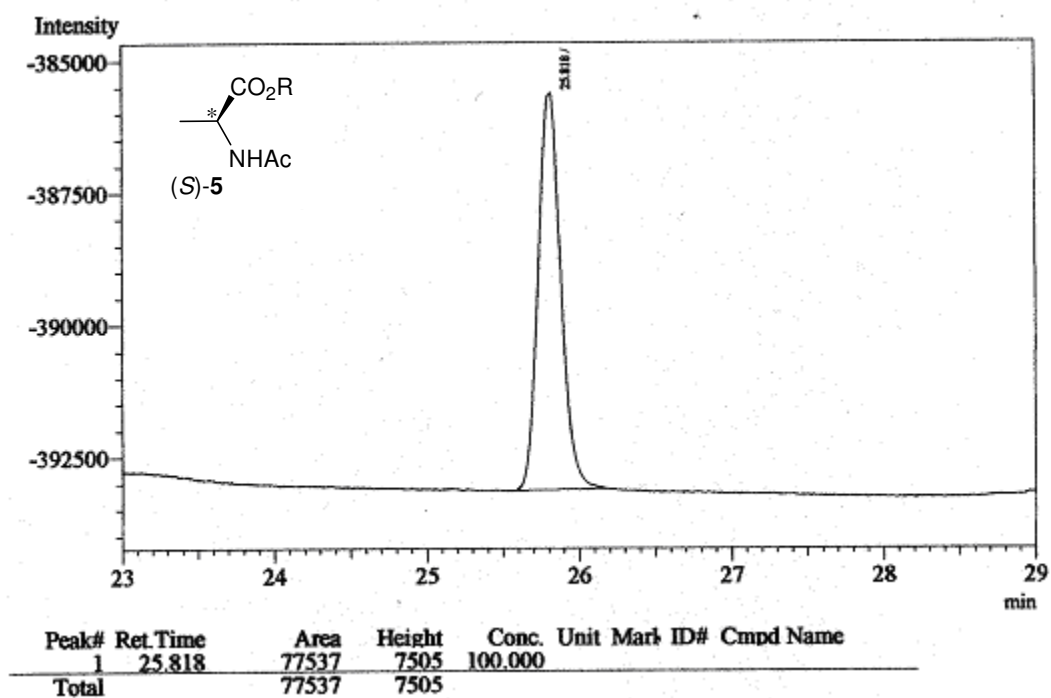


Table 1, Entry 5

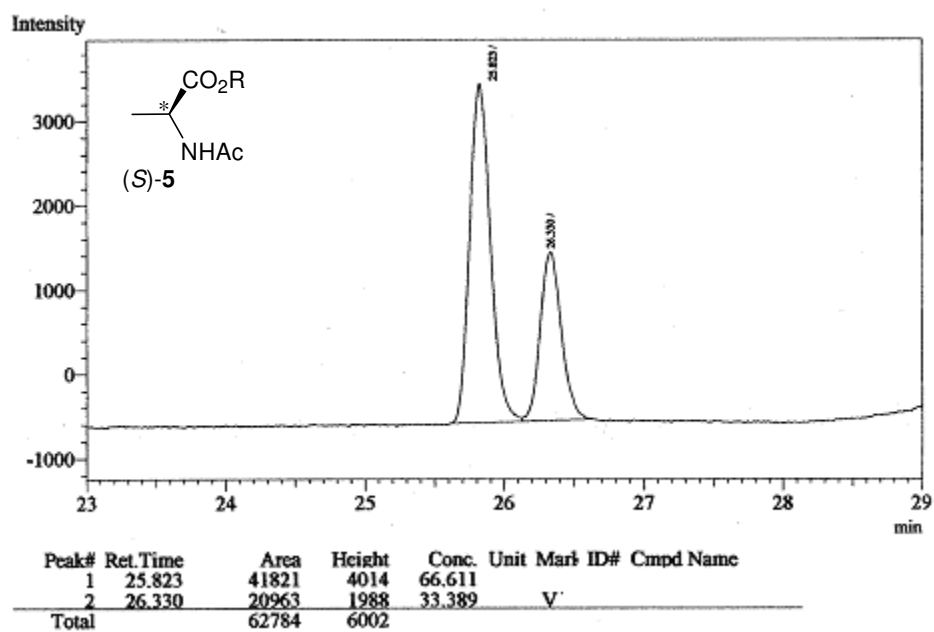


Table 1, Entry 6

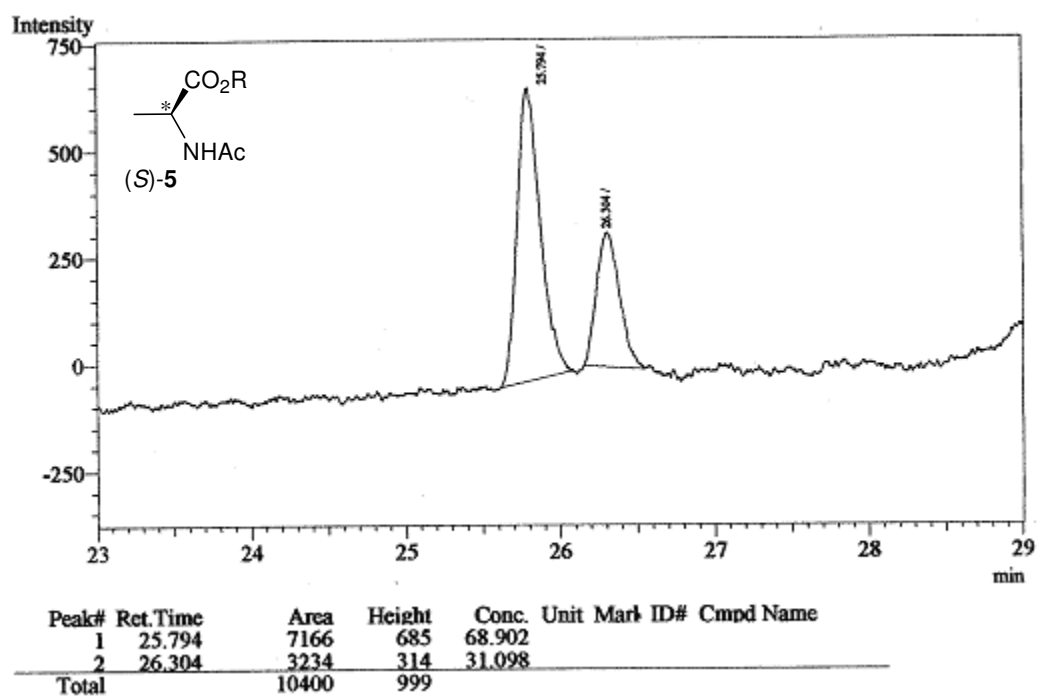


Table 1, Entry 8

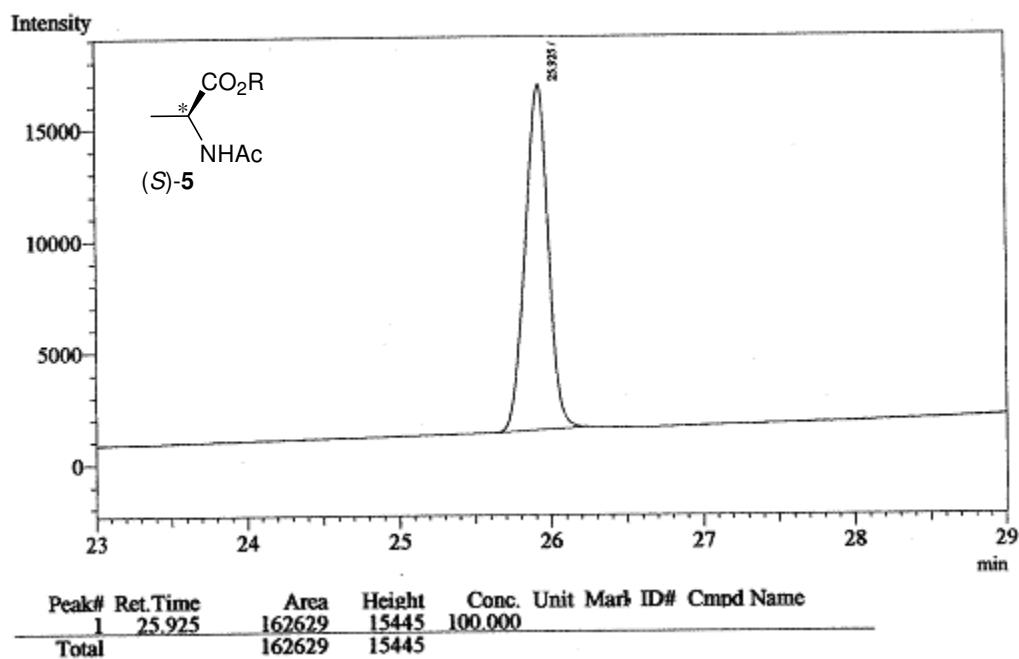


Table 1, Entry 9

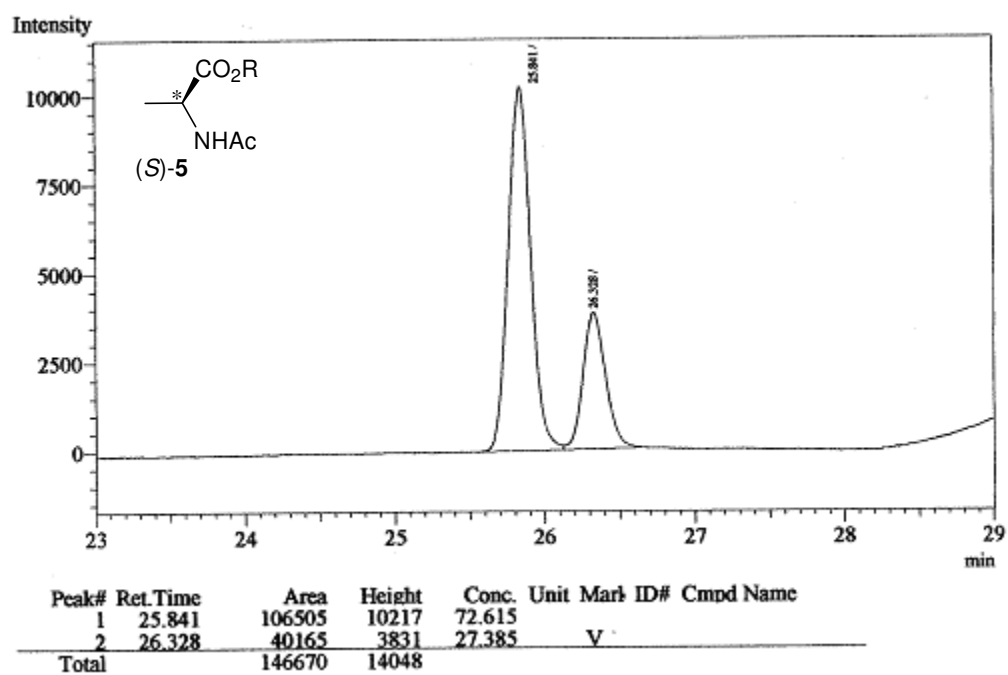


Table 1, Entry 10

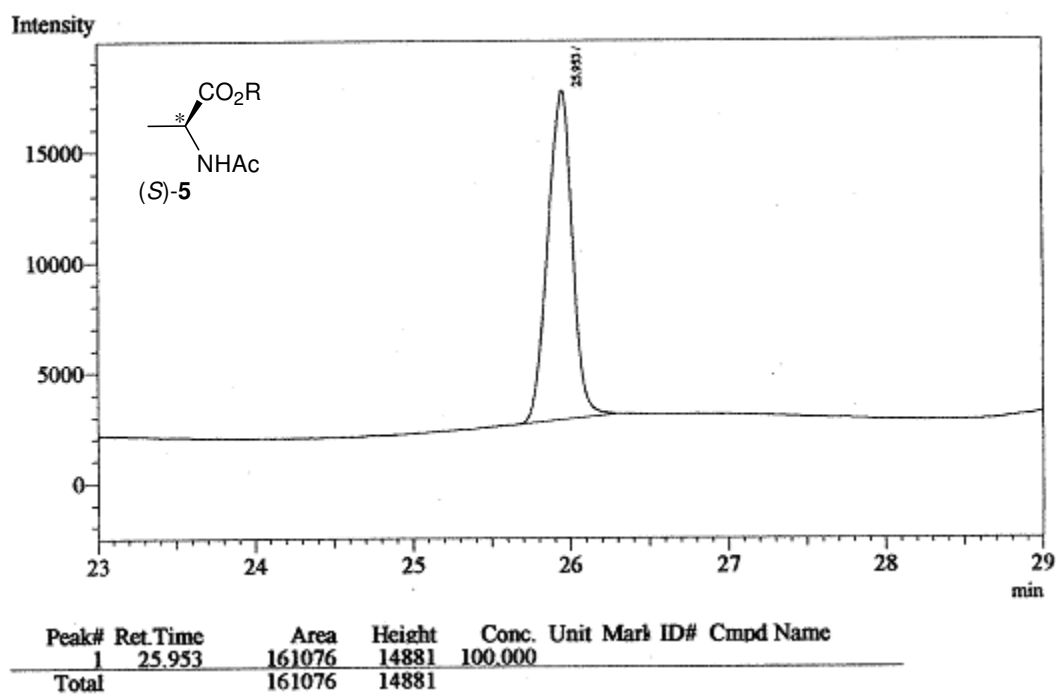


Table 1, Entry 11

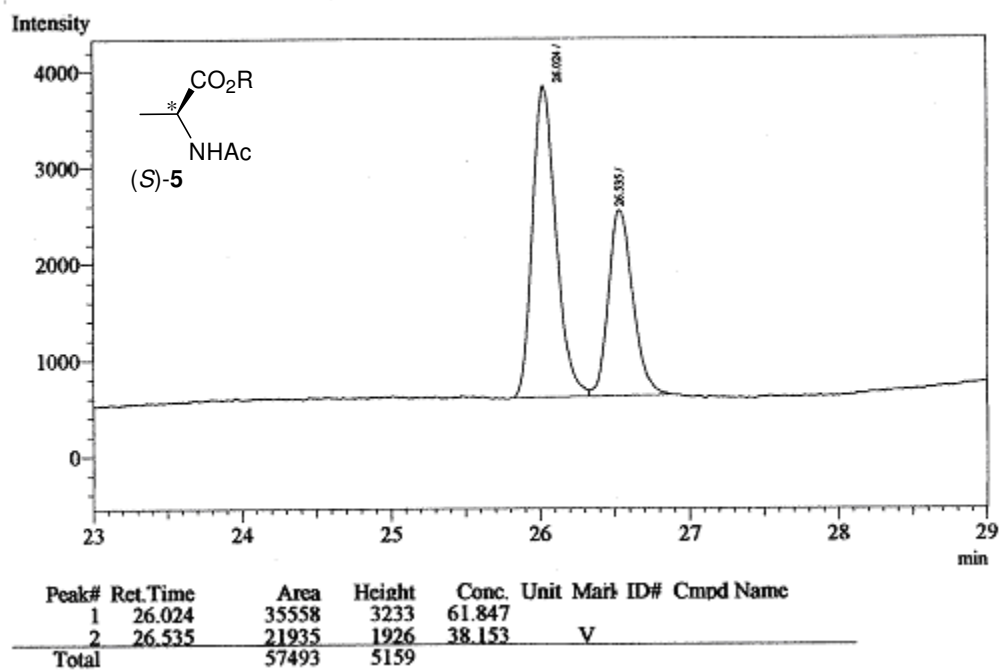
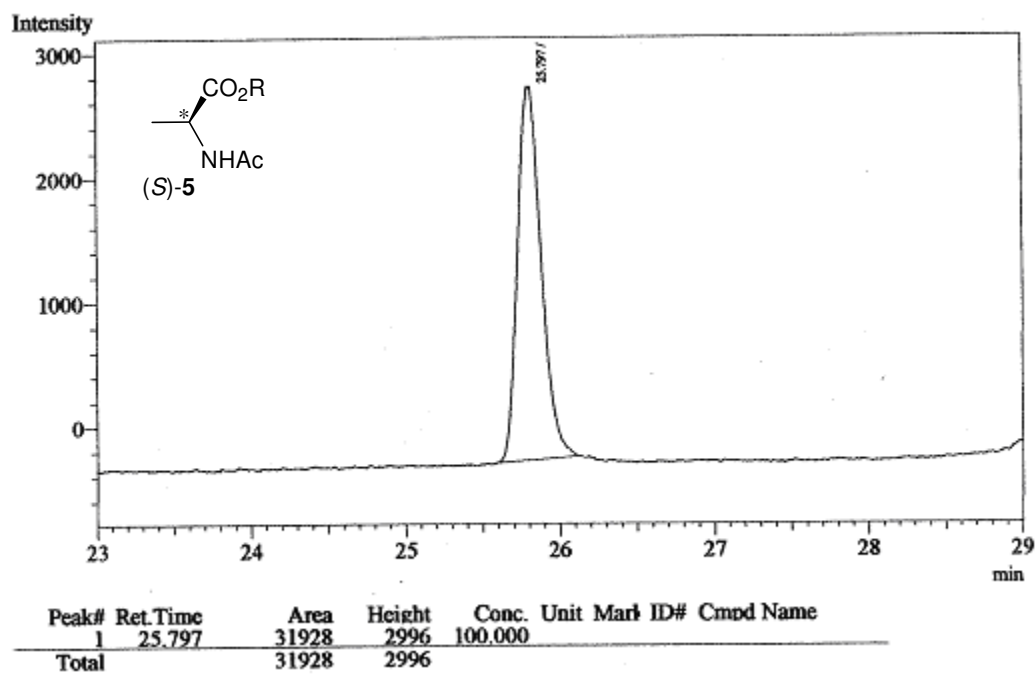


Table 1, Entry 12



Benchmark racemic sample of *N*-acetylphenylalanine methyl ester **7a**

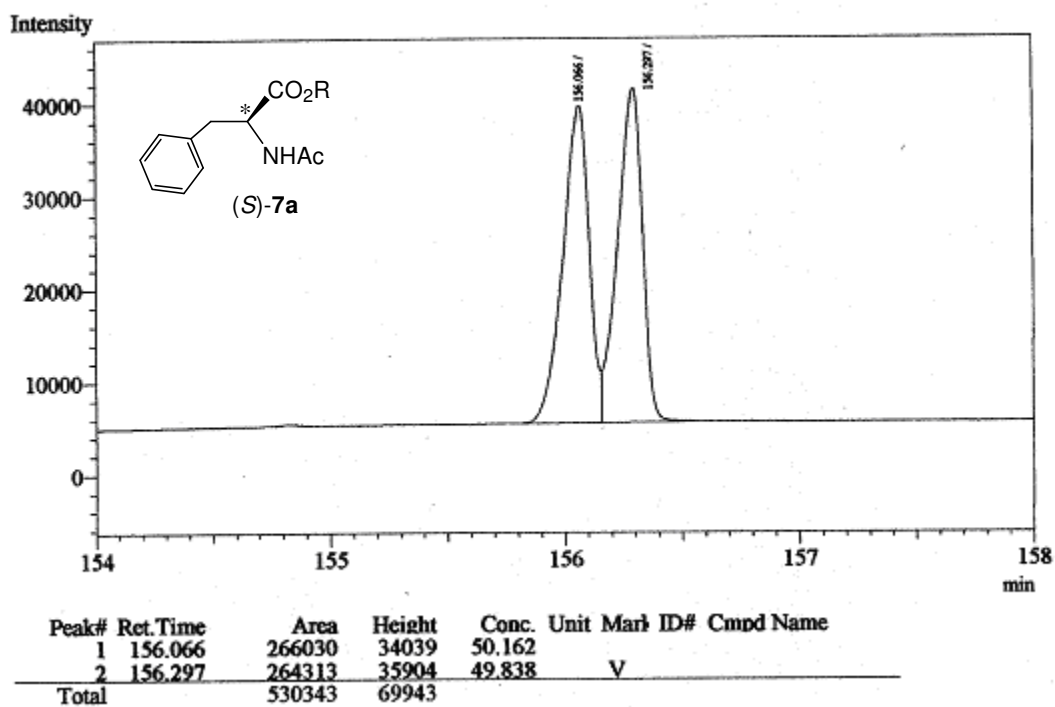


Table 2, Entry 1

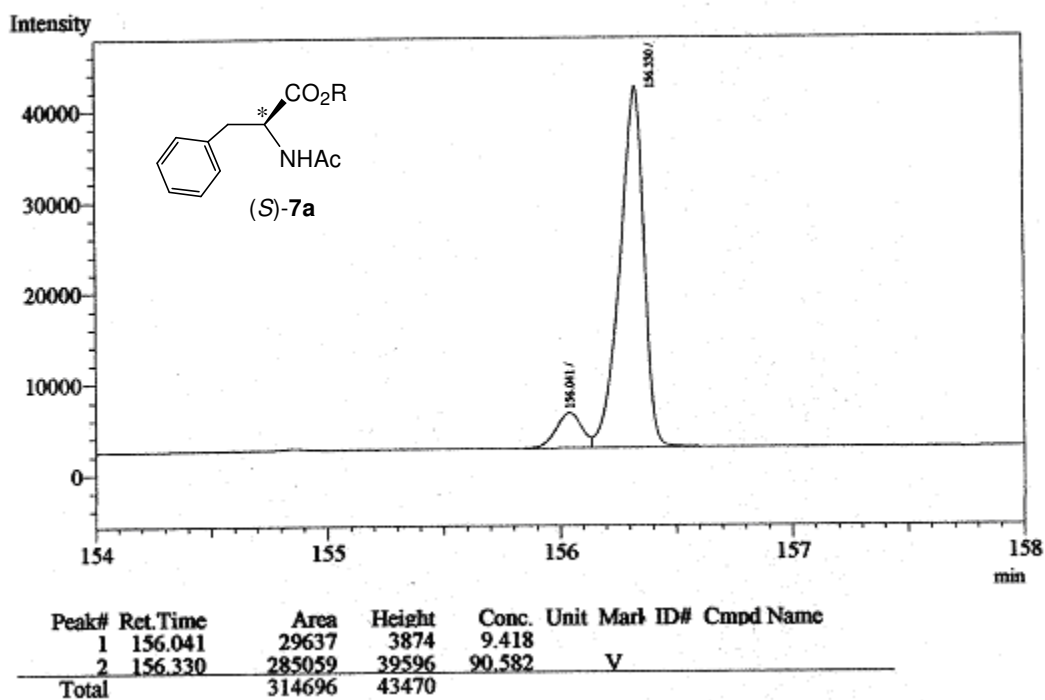


Table 2, Entry 2

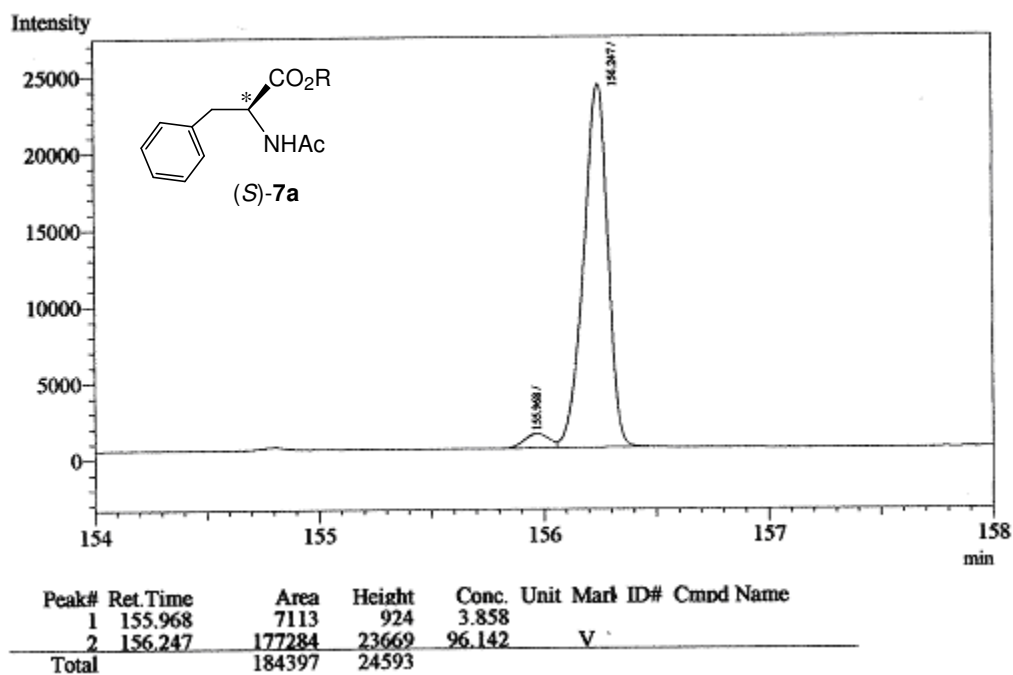
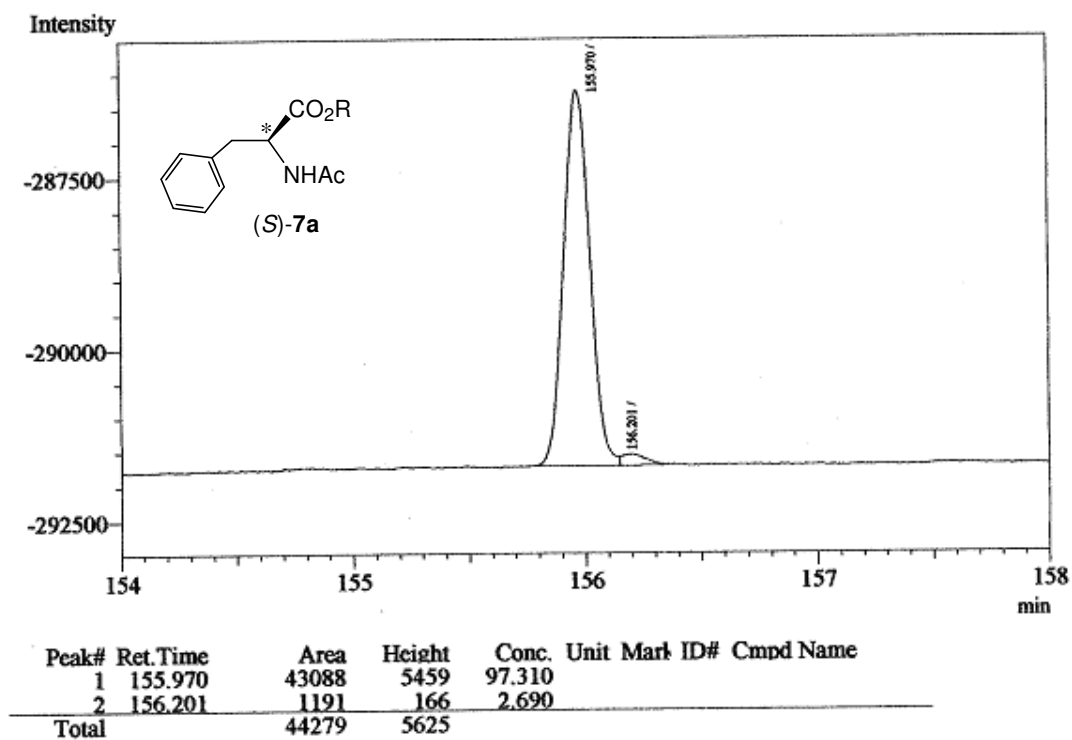
Table 2, Entry 3, Product of *R*-absolute configuration using catalyst generated from [Rh{(*R*)-2}(cod)][BF₄]

Table 2, Entry 4

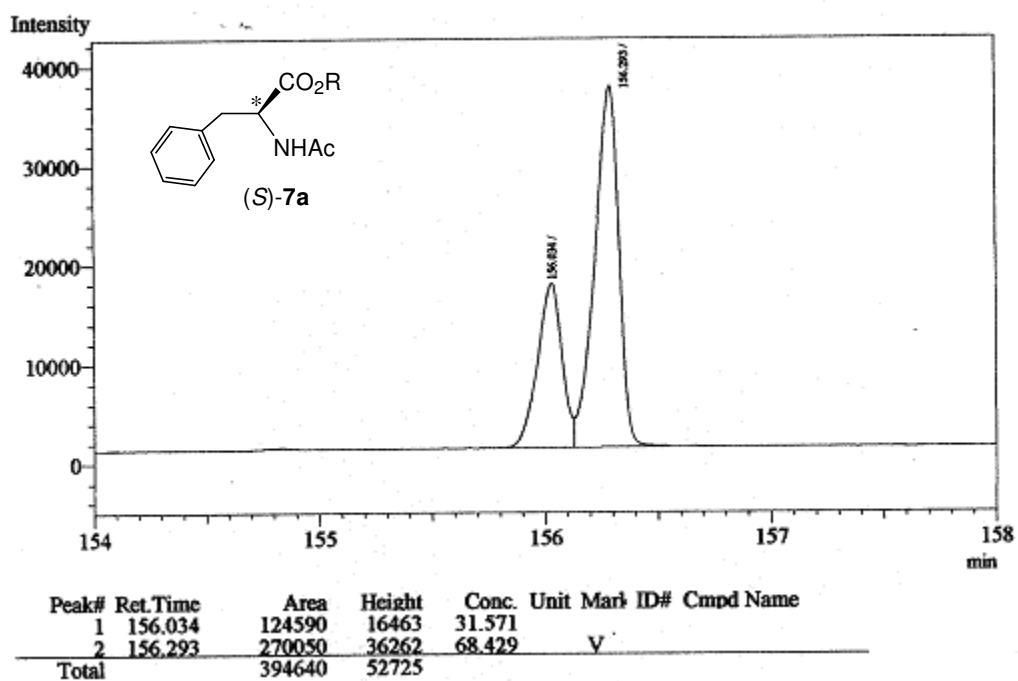


Table 2, Entry 5

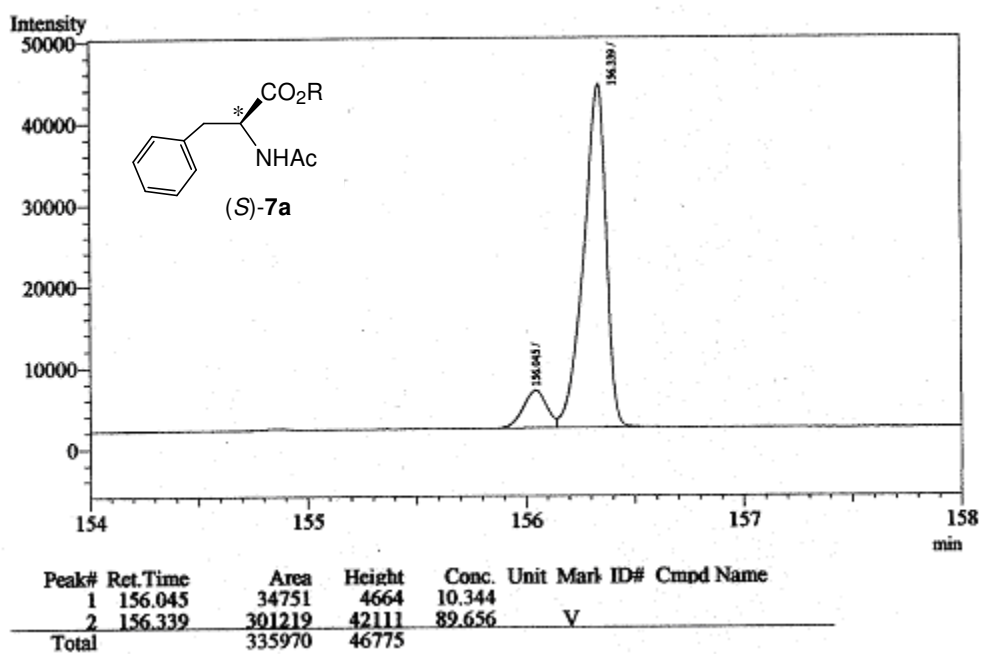


Table 2, Entry 6

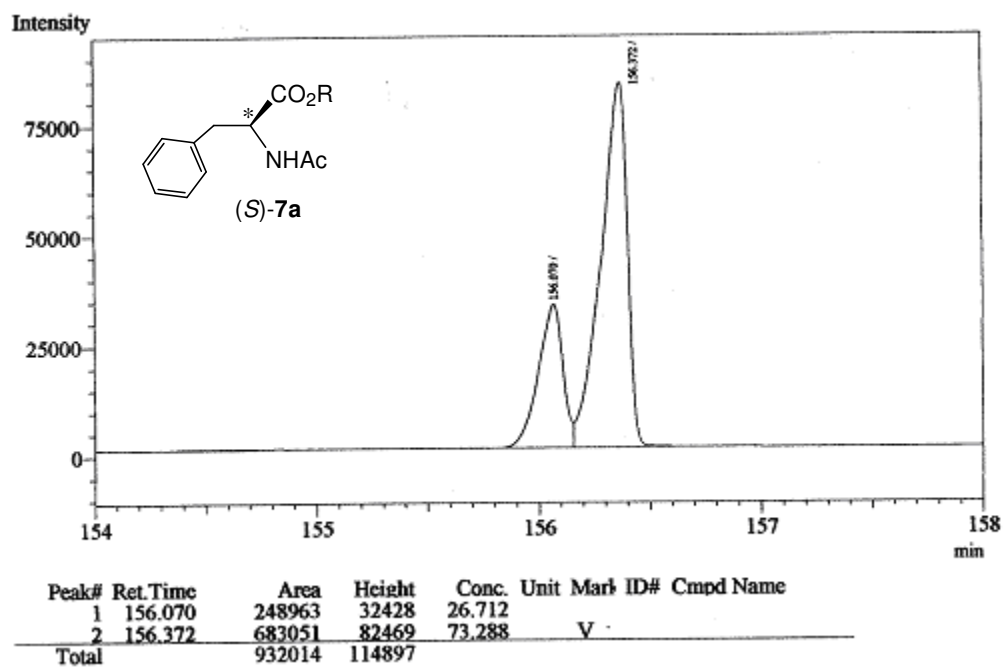


Table 2, Entry 7

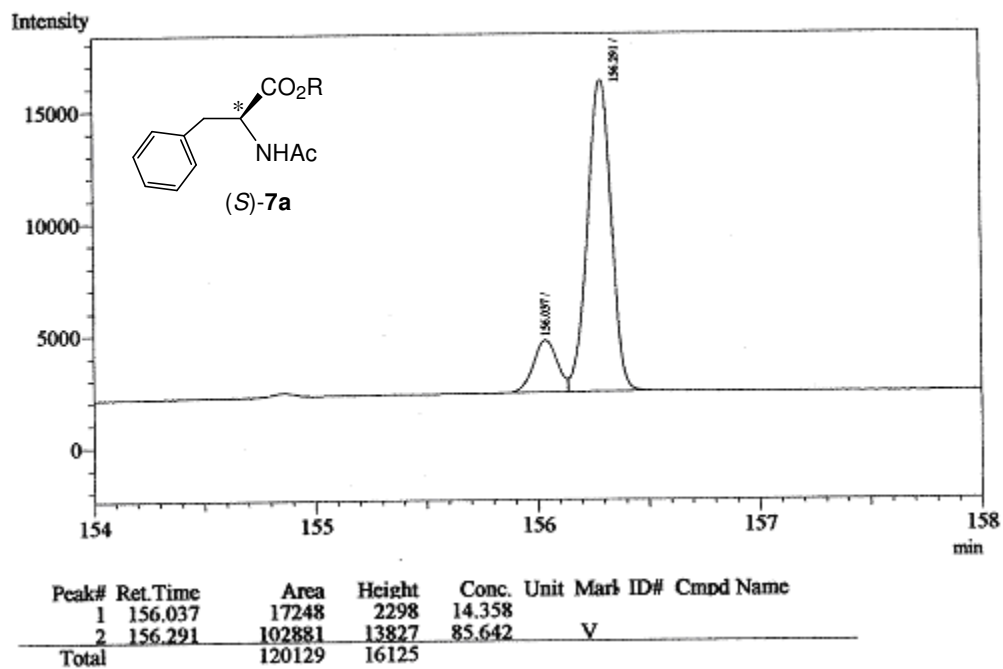


Table 2, Entry 8

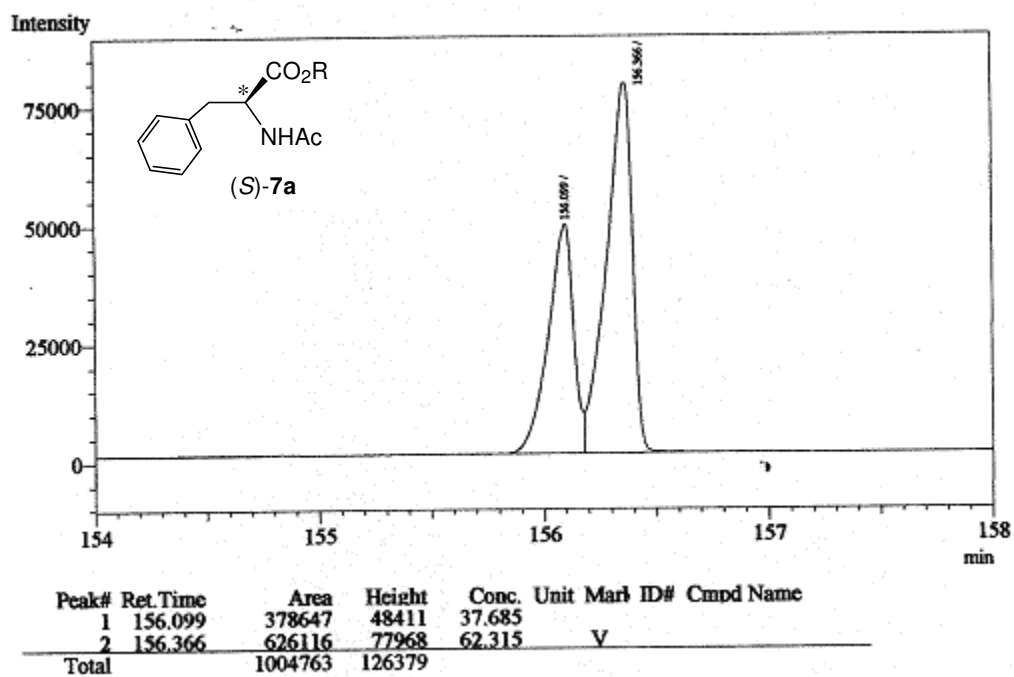


Table 2, Entry 9

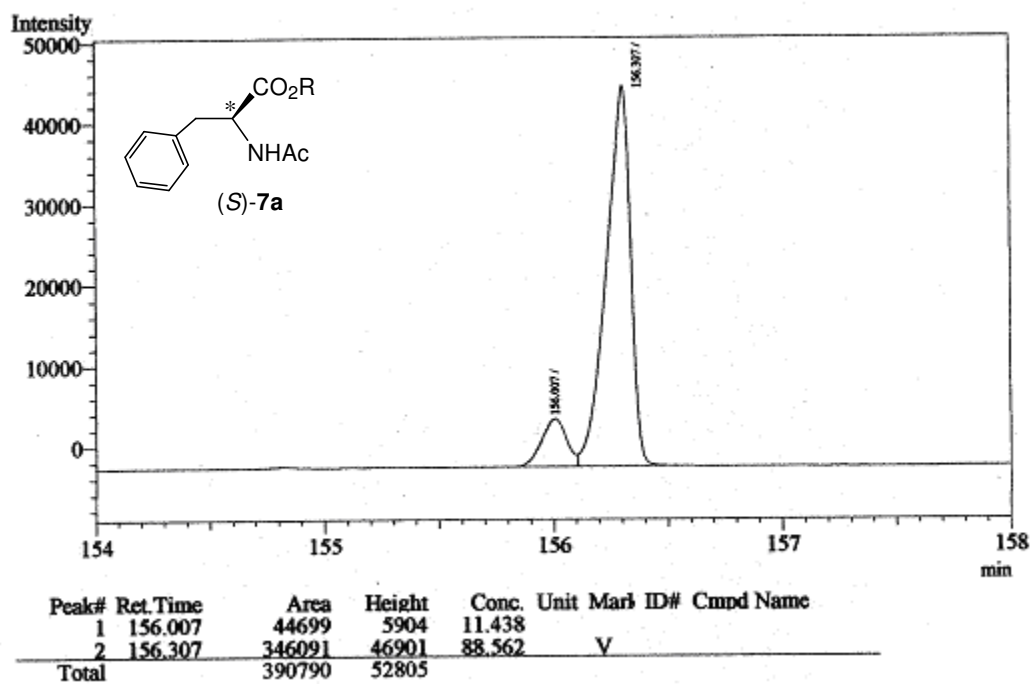
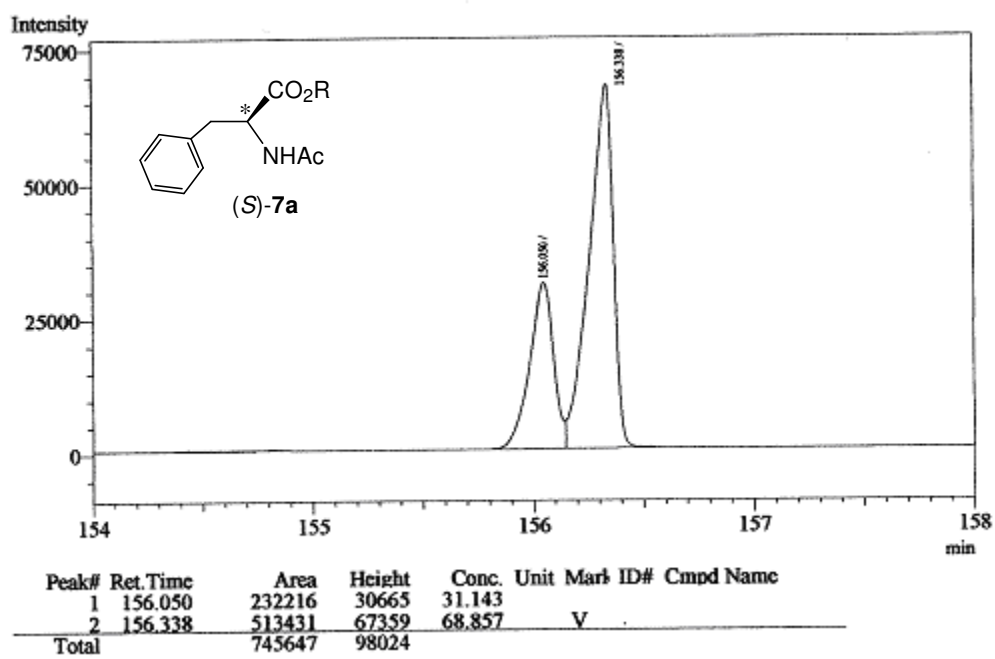
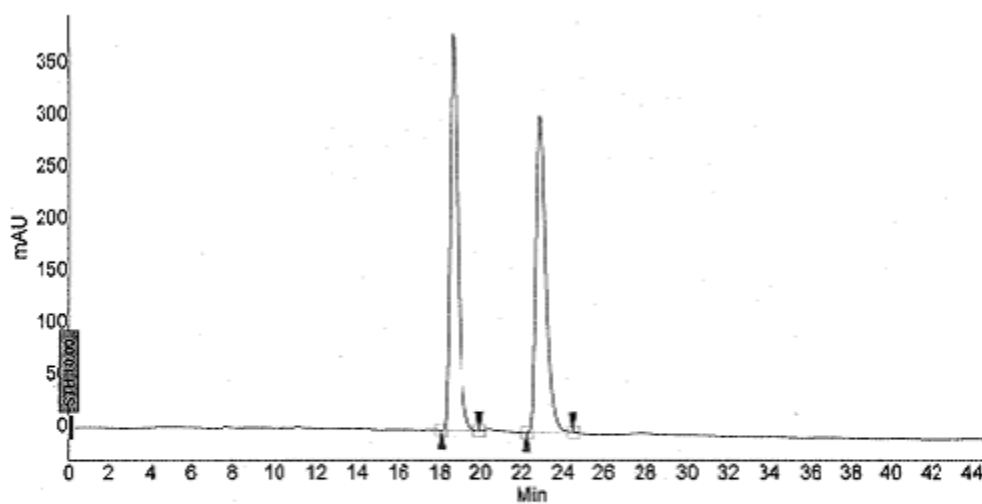


Table 2, Entry 10



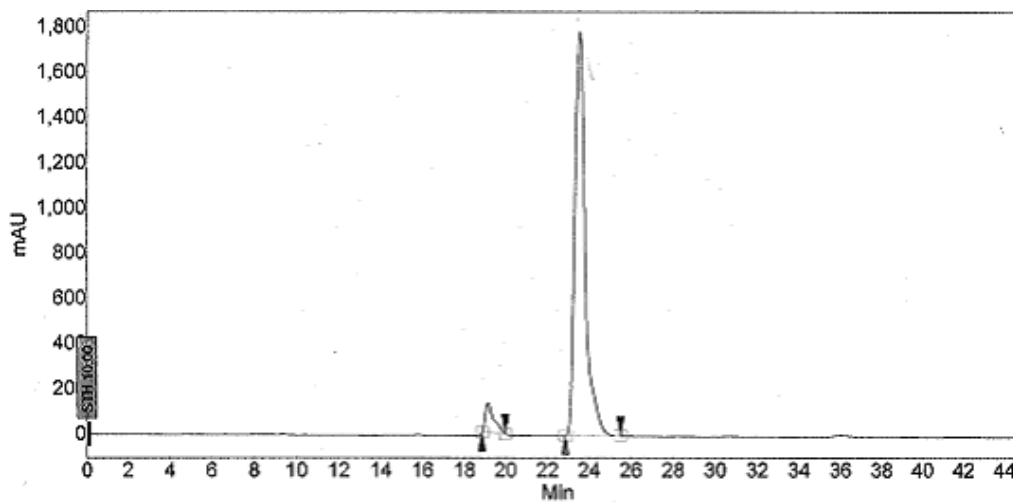
Benchmark racemic sample of *N*-acetyl-4-chlorophenylalanine methyl ester **7b**



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	18.64	50.10	381.5	184.9	50.100
2	UNKNOWN	22.89	49.90	304.2	184.2	49.900
Total			100.00	685.8	329.2	100.000

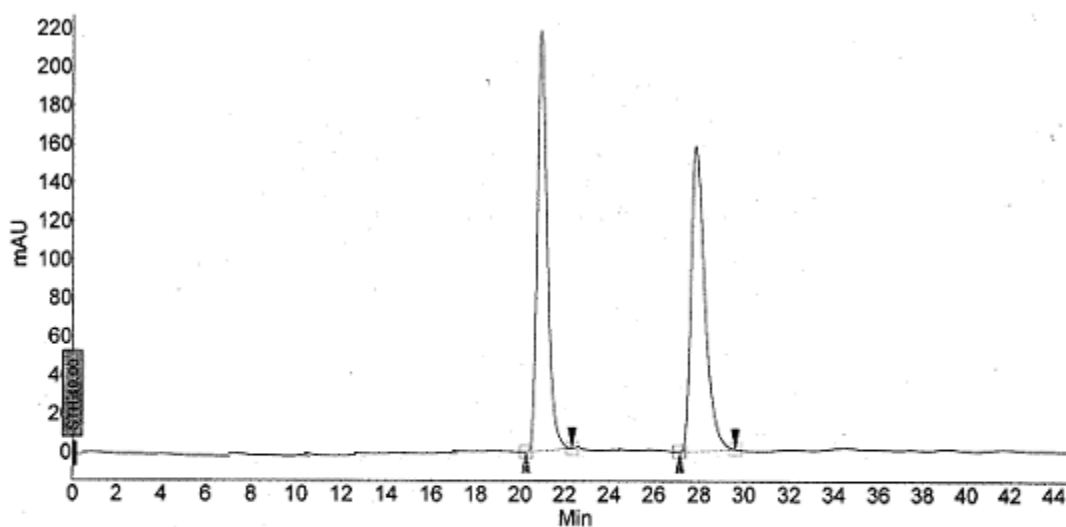
Table 3, Entry 2



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	19.15	5.60	129.3	61.6	5.600
2	UNKNOWN	23.59	94.40	1786.3	1037.0	94.400
Total			100.00	1915.6	1098.6	100.000

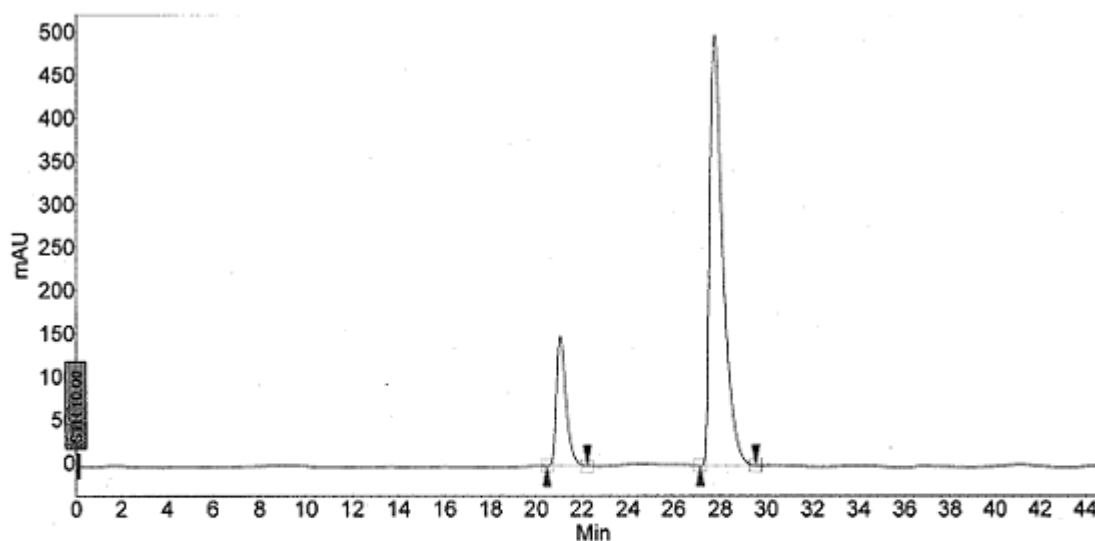
Benchmark racemic sample of *N*-acetyl-4-methoxyphenylalanine methyl ester **7c**



Peak results :

Index	Name	Time (Min)	Quantity [% Area]	Height (mAU)	Area (mAU.Min)	Area % [%]
1	UNKNOWN	20.91	50.20	218.2	113.2	50.201
2	UNKNOWN	27.83	49.80	158.3	112.3	49.799
Total			100.00	376.6	225.5	100.000

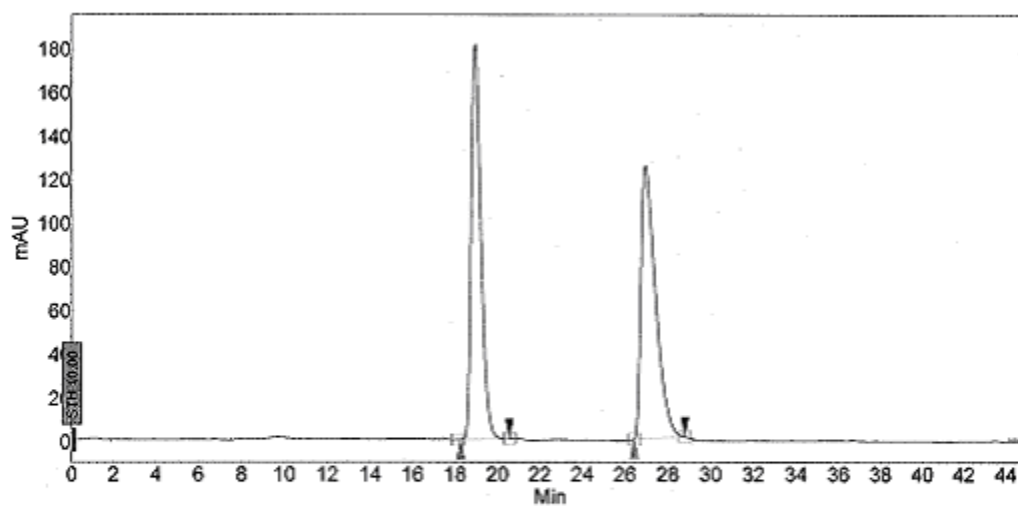
Table 3, Entry 3



Peak results :

Index	Name	Time (Min)	Quantity [% Area]	Height (mAU)	Area (mAU.Min)	Area % [%]
1	UNKNOWN	21.08	18.04	150.6	72.4	18.043
2	UNKNOWN	27.79	81.96	498.6	328.6	81.957
Total			100.00	649.2	401.0	100.000

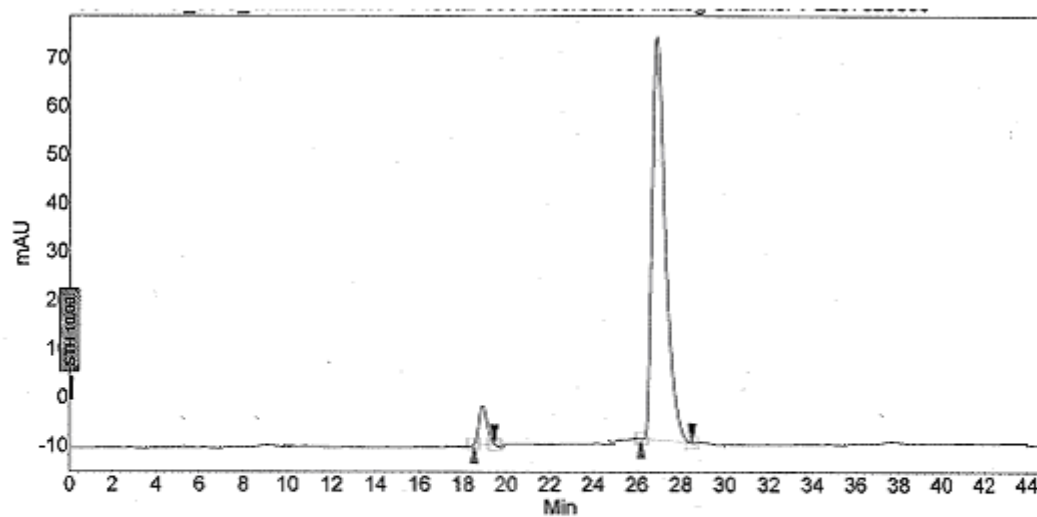
Benchmark racemic sample of *N*-acetyl-4-methylphenyllalanine methyl ester 7d



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.93	49.12	181.2	95.2	49.116
2	UNKNOWN	26.95	50.88	125.1	98.7	50.884
Total			100.00	306.4	193.9	100.000

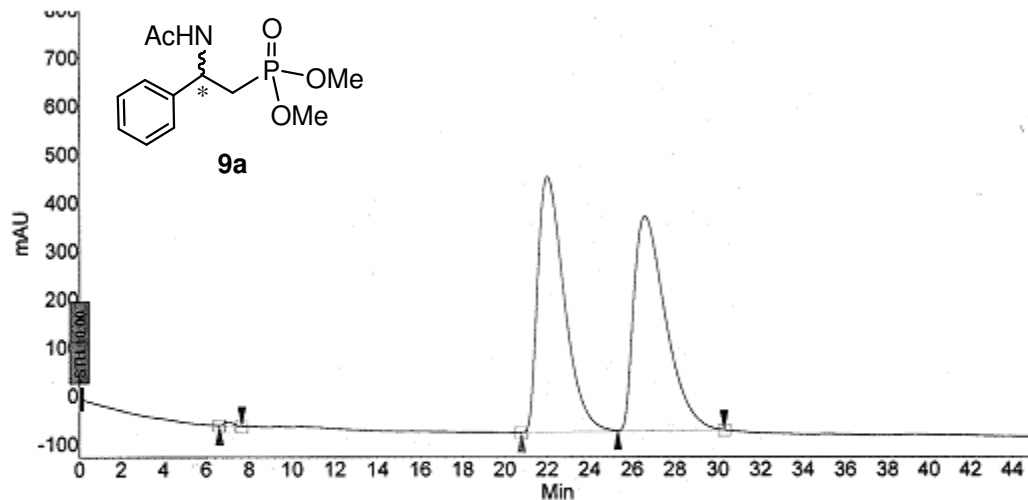
Table 3, Entry 4



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	18.91	5.53	7.9	3.4	5.532
1	UNKNOWN	26.87	94.47	83.1	58.0	94.468
Total			100.00	90.9	61.4	100.000

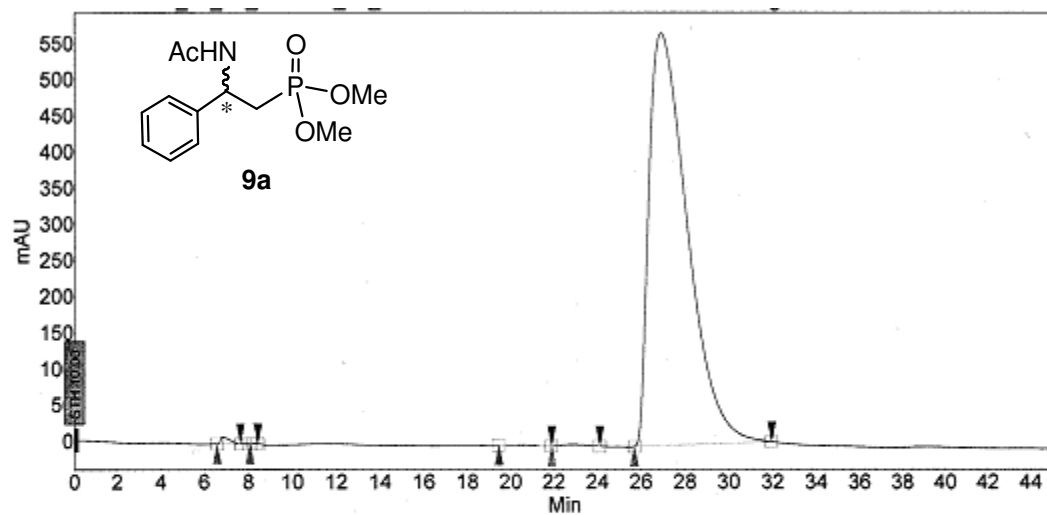
Benchmark sample of rac-9a prepared using catalyst generated with rac-BINAP



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.96	0.28	7.9	4.3	0.278
2	UNKNOWN	22.01	49.90	529.2	768.2	49.898
3	UNKNOWN	26.57	49.83	444.6	767.1	49.828
Total			100.00	981.7	1539.5	100.000

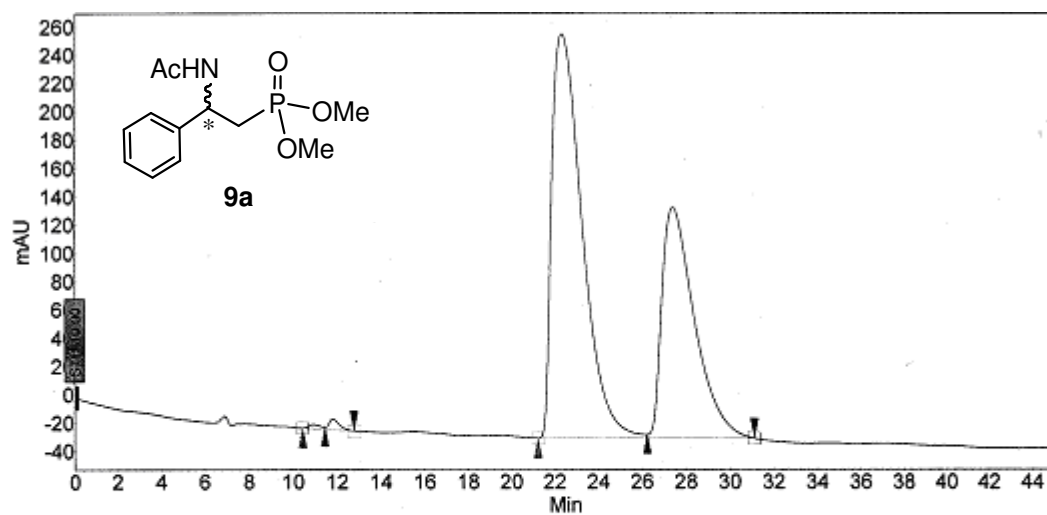
Table 4, Entry 1



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.81	0.37	9.3	4.4	0.375
2	UNKNOWN	8.28	0.01	0.5	0.1	0.009
4	UNKNOWN	20.60	0.08	1.1	0.9	0.079
5	UNKNOWN	22.81	0.26	2.5	3.0	0.260
3	UNKNOWN	26.92	99.28	570.9	1158.2	99.278
Total			100.00	584.2	1166.6	100.000

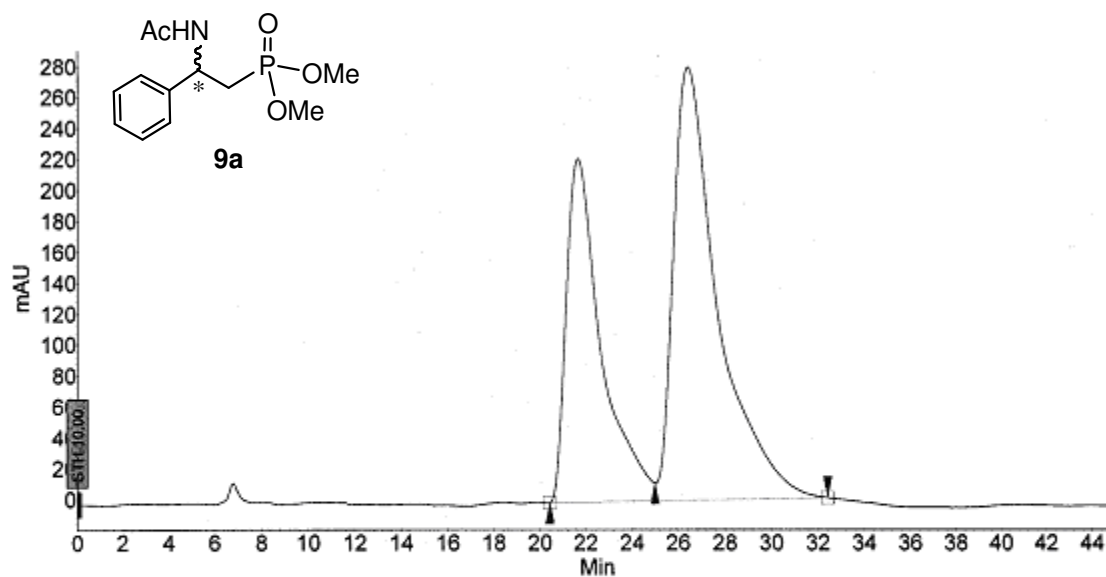
Table 4, Entry 2



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	10.97	0.25	2.9	1.9	0.254
2	UNKNOWN	11.83	0.55	7.7	4.2	0.554
3	UNKNOWN	22.33	61.67	285.7	462.6	61.673
4	UNKNOWN	27.43	37.52	163.3	281.5	37.520
Total			100.00	459.6	750.1	100.000

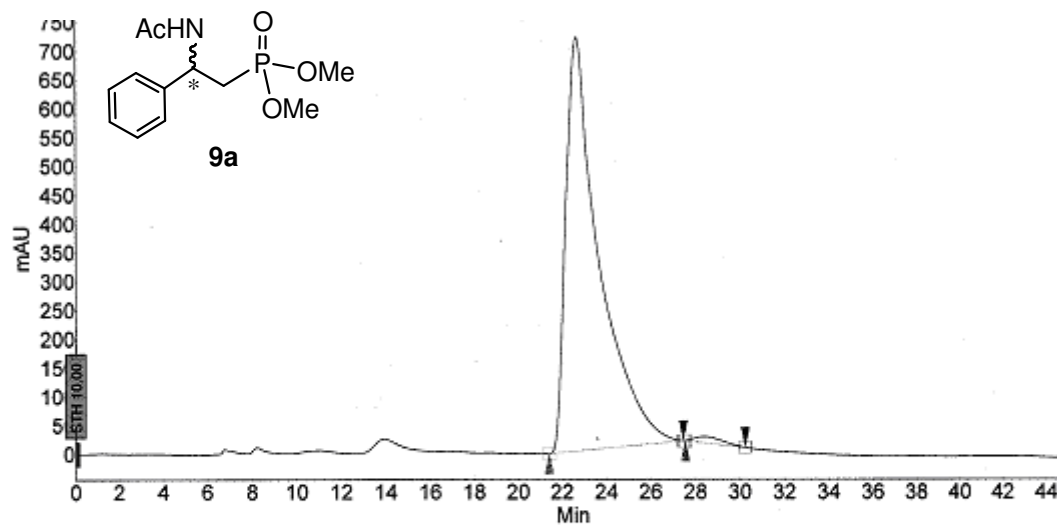
Table 4, Entry 3



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	21.64	38.57	221.7	388.0	38.565
2	UNKNOWN	26.40	61.43	279.9	618.2	61.435
Total			100.00	501.6	1006.2	100.000

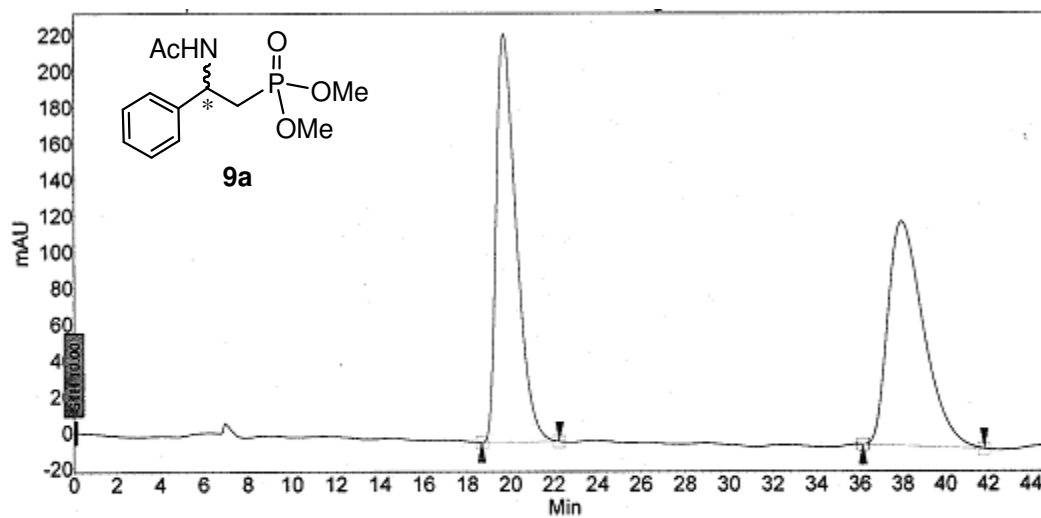
Table 4, Entry 4



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	22.64	98.76	718.9	1259.2	98.761
2	UNKNOWN	28.49	1.24	11.1	15.8	1.239
Total			100.00	730.0	1275.0	100.000

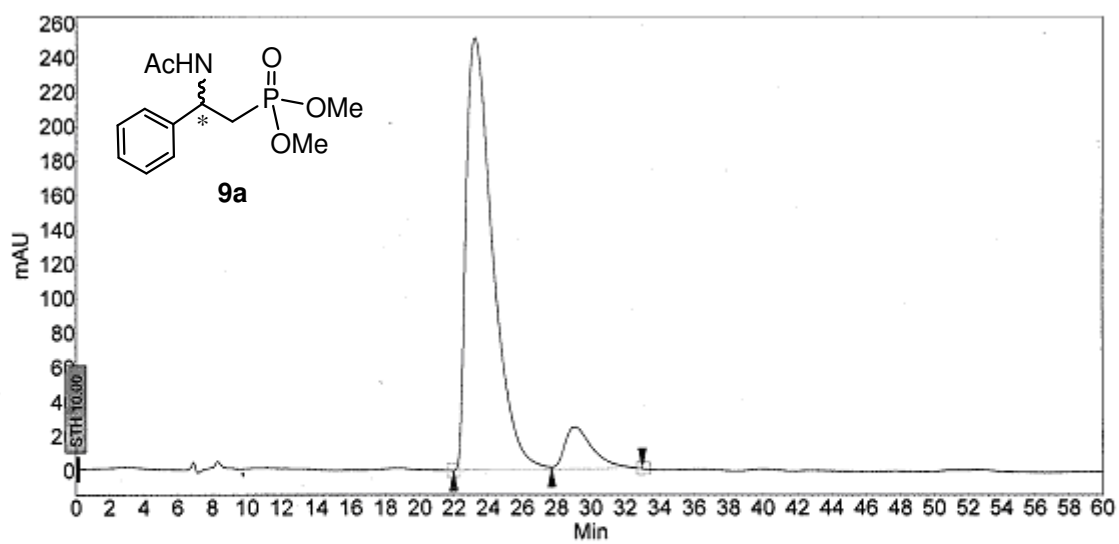
Benchmark sample of rac-8b prepared using catalyst generated with rac-BINAP



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.71	50.01	226.2	241.1	50.012
2	UNKNOWN	37.95	49.99	124.3	241.0	49.988
Total			100.00	350.4	482.2	100.000

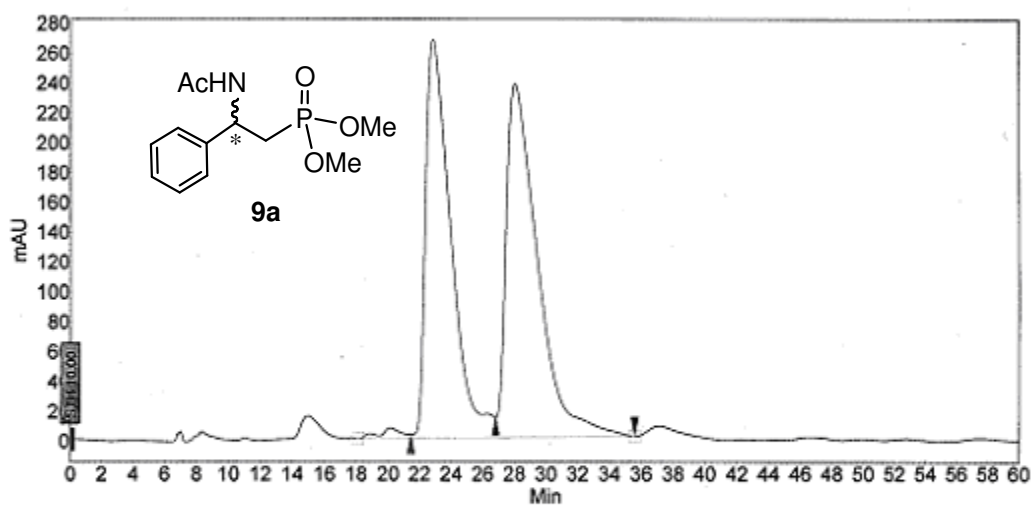
Table 4, Entry 5



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % [%]
1	UNKNOWN	23.21	90.70	251.3	450.6	90.703
2	UNKNOWN	29.08	9.30	24.5	46.2	9.297
Total			100.00	275.8	496.8	100.000

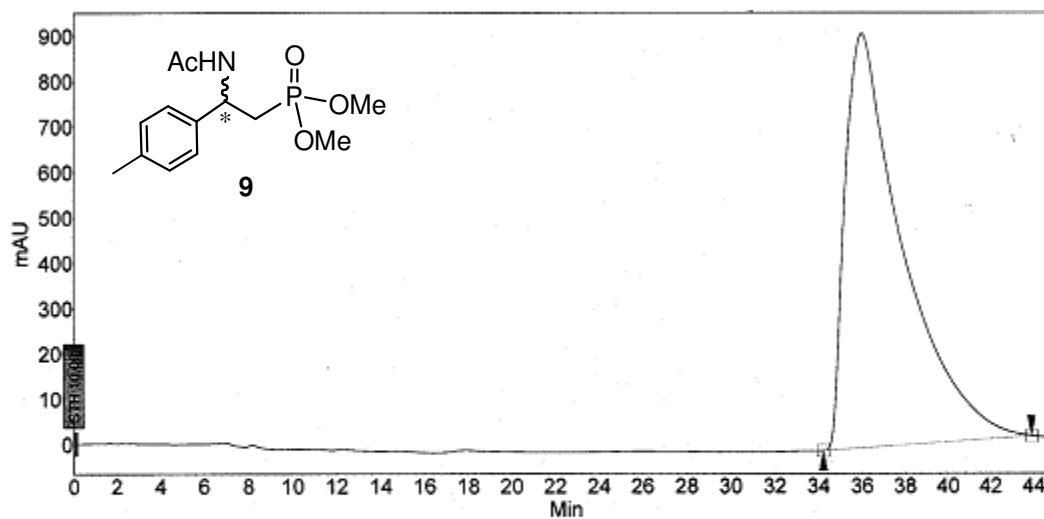
Table 4, Entry 6



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % [%]
1	UNKNOWN	22.84	47.51	267.4	491.6	47.505
2	UNKNOWN	28.03	52.49	237.1	543.3	52.495
Total			100.00	504.5	1034.9	100.000

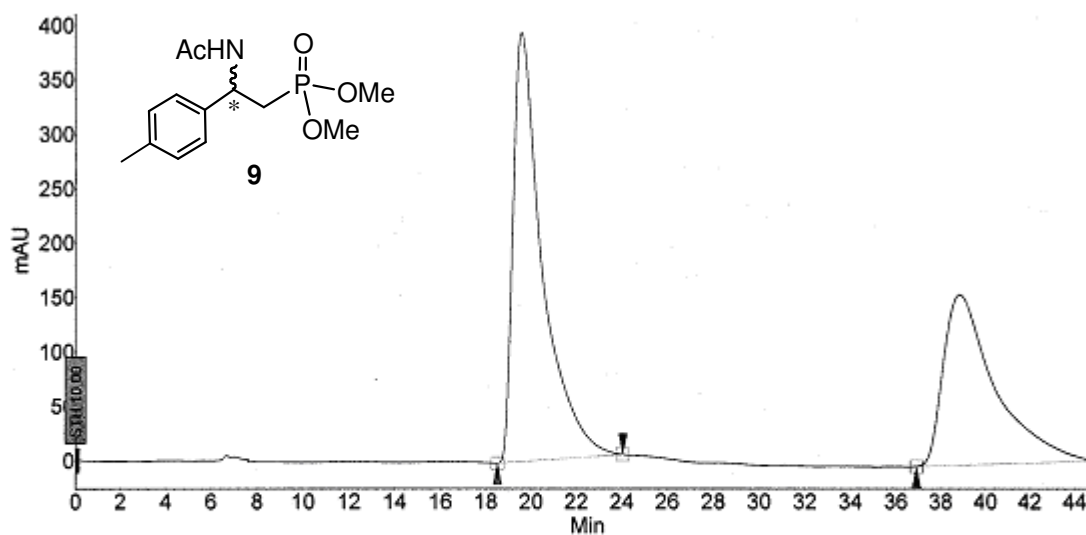
Table 4, Entry 7



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU Min)	Area % (%)
1	UNKNOWN	36.00	100.00	813.8	2837.8	100.000
Total			100.00	813.8	2837.8	100.000

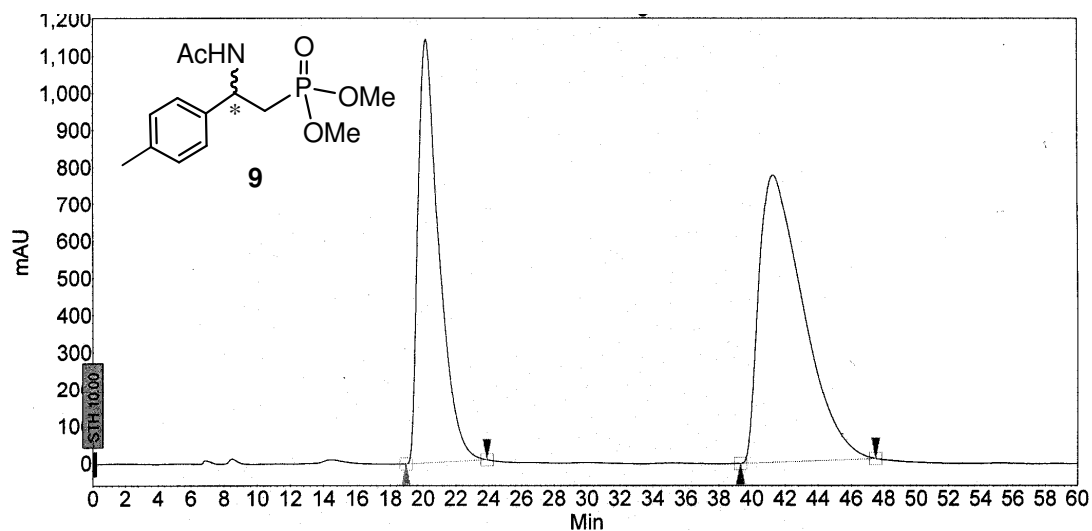
Table 4, Entry 8



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU Min)	Area % (%)
1	UNKNOWN	19.59	58.55	393.9	590.9	58.547
2	UNKNOWN	38.84	41.45	156.4	418.4	41.453
Total			100.00	550.2	1009.3	100.000

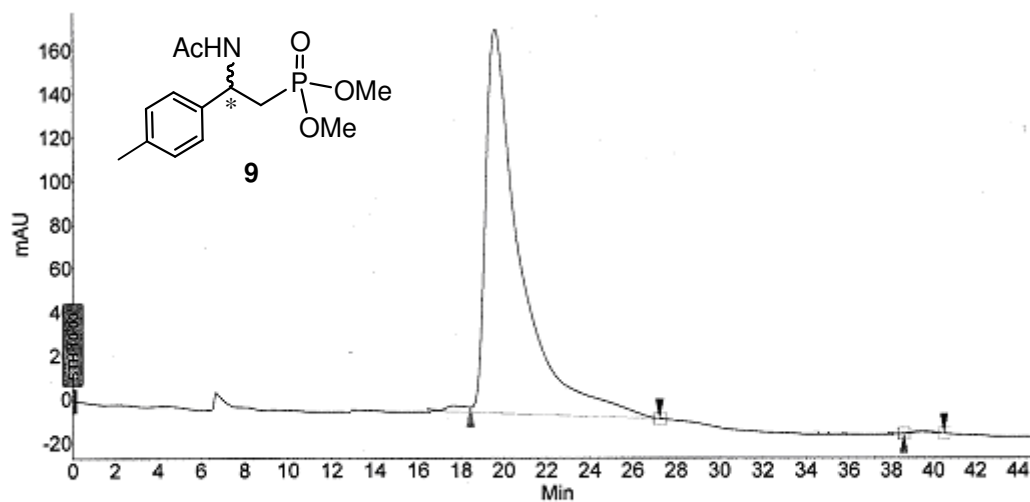
Table 4, Entry 9



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.17	41.23	1144.4	1694.6	41.226
2	UNKNOWN	41.28	58.77	777.9	2415.9	58.774
Total			100.00	1922.3	4110.5	100.000

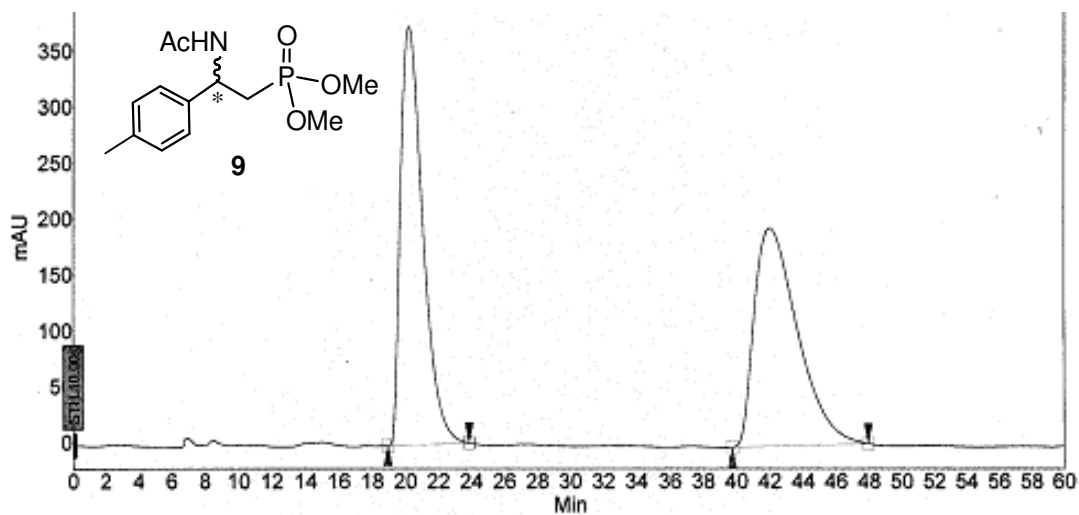
Table 4, Entry 10



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.60	99.67	176.4	326.2	99.671
2	UNKNOWN	39.48	0.33	1.0	1.1	0.328
Total			100.00	177.4	327.2	100.000

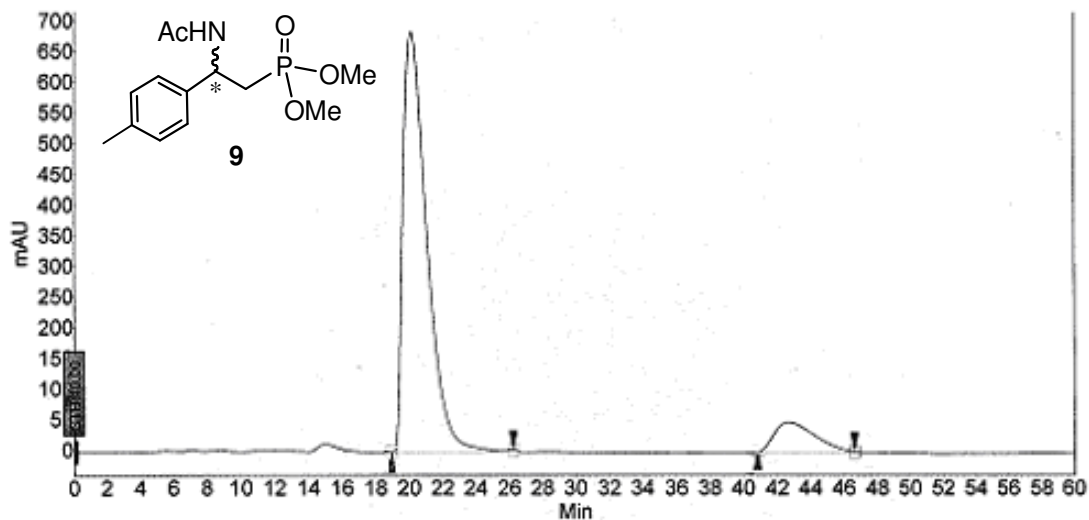
Second benchmark sample of rac-8b prepared using catalyst generated with rac-BINAP



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	20.20	49.85	374.4	584.9	49.850
2	UNKNOWN	42.01	50.15	195.1	588.5	50.150
Total			100.00	569.5	1173.4	100.000

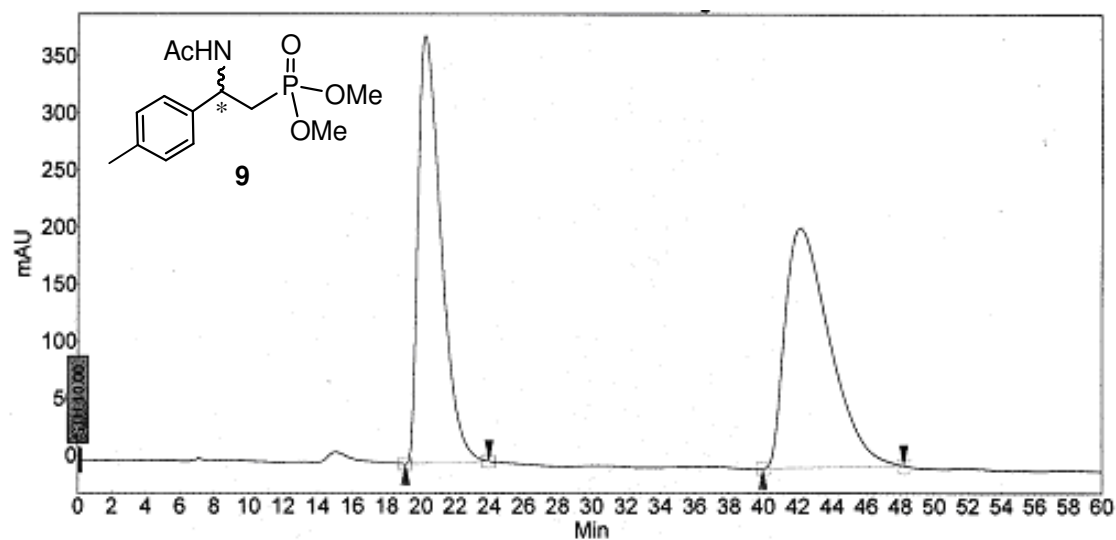
Table 4, Entry 11



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU.Min)	Area % (%)
1	UNKNOWN	20.09	88.58	684.9	1119.2	88.579
2	UNKNOWN	42.65	11.42	50.2	144.3	11.421
Total			100.00	735.1	1263.5	100.000

Table 4, Entry 12



Peak results :

Index	Name	Time (Min)	Quantity (% Area)	Height (mAU)	Area (mAU Min)	Area % (%)
1	UNKNOWN	20.24	47.85	374.6	580.0	47.846
2	UNKNOWN	42.13	52.15	210.0	632.2	52.154
Total			100.00	584.7	1212.3	100.000

X-ray Crystallography. A summary of crystal data and information on the data collections and structure determinations is given in Table S1. Data were measured on an Oxford Diffraction Gemini A Ultra diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$) for **2** and MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) for **3**, both at 150 K.¹ Further details are in the deposited CIF. The structures were solved by direct methods and refined on all unique F^2 values,² including unambiguous determination of the absolute configuration through the refined Flack parameter.³ Disorder was modeled for chloroform solvent molecules in the structure of **3**.

- (1) CrysAlisPro (Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2008).
- (2) SHELXTL (Sheldrick, G. M., *Acta Crystallogr. Sect. A*, **2008**, *64*, 112).
- (3) Flack, H. D., *Acta Crystallogr. Sect. A*, **1983**, *39*, 876.

Table S1. Crystallographic data for compounds (*R*)-**2** and **3**

compound	(<i>R</i>)- 2	3
formula	C ₅₈ H ₄₄ P ₂	C ₆₆ H ₅₆ P ₂ Rh ⁺ ·BF ₄ [−] ·2CHCl ₃
form wt	802.9	1339.5
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> (Å)	10.2668(2)	11.6252(3)
<i>b</i> (Å)	39.5599(6)	22.6983(4)
<i>c</i> (Å)	10.3939(2)	11.7098(3)
β (deg)	92.417(2)	104.729(2)
<i>V</i> (Å ³)	4127.76(13)	2988.35(12)
<i>Z</i>	4	2
<i>D</i> _c (g cm ^{−3})	1.264	1.489
μ (mm ^{−1})	1.233	0.663
transmission	0.773–0.791	0.733–0.937
cryst size (mm)	0.22 × 0.20 × 0.20	0.50 × 0.35 × 0.10
θ _{max}	62.5	29.6
reflns measd	31603	30809
unique reflns	12761	13733
<i>R</i> _{int}	0.0561	0.0282
refined params	1085	777
<i>R</i> (<i>F</i> , <i>F</i> ² > 2σ)	0.0511	0.0387
<i>R</i> _w (<i>F</i> ² , all data)	0.1296	0.0936
<i>S</i> (<i>F</i> ² , all data)	1.039	1.031
Absolute structure parameter ³	0.069(17)	−0.014(17)
diff map extremes (e Å ^{−3})	0.41, −0.30	1.03, −1.03