Cobalt-Catalyzed Oxidative Phosphonylation of α-Amino Acid Derivatives and α-Amino Ketones for α-Aminophosphonates

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Supporting Information

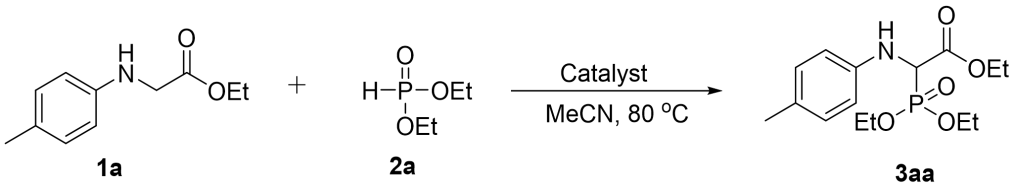
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1. Optimization of the Reaction Conditions

Table S1. Screening of Catalysts[a]

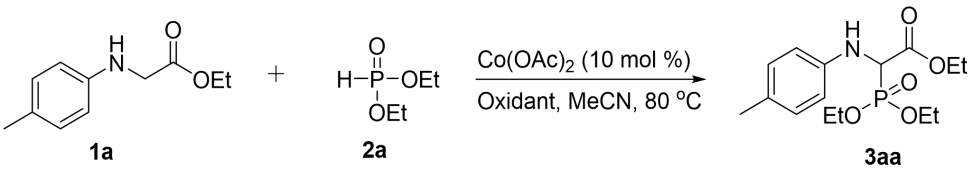


1a **2a** **3aa**

Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]
1	CuO	Air	MeCN	22
2	CuCl	Air	MeCN	trace
3	$CuBr_2$	Air	MeCN	trace
4	$CuCl_2$	Air	MeCN	10
5	$Cu(OAc)_2$	Air	MeCN	trace
6	$Cu(OTf)_2$	Air	MeCN	36
7	CoO	Air	MeCN	8
8	$CoCl_2$	Air	MeCN	12
9	$Co(ClO_4)_2·6H_2O$	Air	MeCN	23
10	**$Co(OAc)_2$**	**Air**	**MeCN**	**38**
11	$CoSO_4·6H_2O$	Air	MeCN	trace
12	$FeCl_2$	Air	MeCN	trace
13	$Pd(OAc)_2$	Air	MeCN	0
14[c]	--	Air	MeCN	0

(a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (10 mol %), MeCN (2 mL) in air at 80 °C for 12 h. (b) Isolated yields. (c) In the absence of a catalyst.

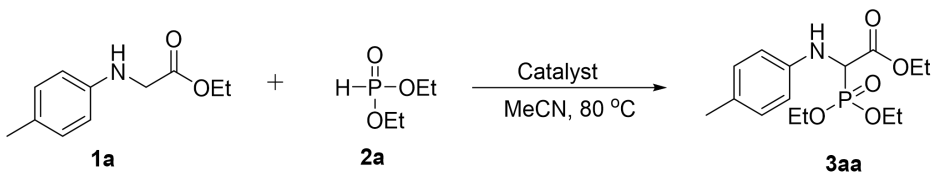
Table S2. Screening of Oxidant.[a]



Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]
1	$Co(OAc)_2$	DTBP	MeCN	32
2	$Co(OAc)_2$	TBHP	MeCN	33
3	$Co(OAc)_2$	TBPB	MeCN	trace
4	$Co(OAc)_2$	DCP	MeCN	35
5	$Co(OAc)_2$	BPO	MeCN	trace
6	$Co(OAc)_2$	$K_2S_2O_8$	MeCN	30
7	$Co(OAc)_2$	$PhI(OAc)_2$	MeCN	0
8	$Co(OAc)_2$	O_2	MeCN	37
9	**$Co(OAc)_2$**	**Air**	**MeCN**	**38**
10[c]	$Co(OAc)_2$	--	MeCN	0

(a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Co(OAc)_2$ (10 mol %), MeCN (2 mL) in air at 80 °C for 12 h. (b) Isolated yields. (c) Under N_2 atmosphere.

Table S3. Screening of Substrate Molar Ratio.[a]

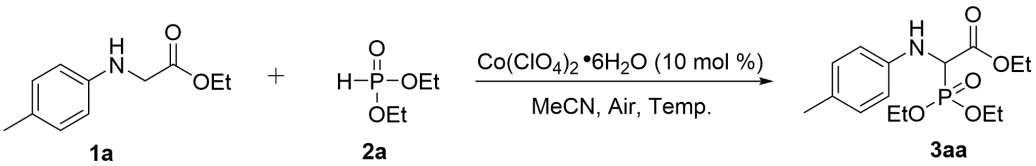


Entry	Catalyst	**1a** / **2a**	Solvent	Yield(%)[b]
1	$Co(OAc)_2$	1:1	MeCN	38
2	$Co(ClO_4)_2·6H_2O$	1:1	MeCN	23
3	$Co(OAc)_2$	1:5	MeCN	70
4	$Co(ClO_4)_2·6H_2O$	1:5	MeCN	72
5	$Co(OAc)_2$	1:7	MeCN	73

6	**$Co(ClO_4)_2·6H_2O$**	**1:7**	**MeCN**	**83**
7	$Co(ClO_4)_2·6H_2O$	1:8	MeCN	82
8	$Co(OAc)_2$	1:8	MeCN	75

(a) Reaction conditions: **1a** (0.2 mmol), **2a**, Catalyst (10 mol %), MeCN (2 mL) in air at 80 °C for 12 h. (b) Isolated yields.

Table S4. Screening of Solvent and Temperature.[a]



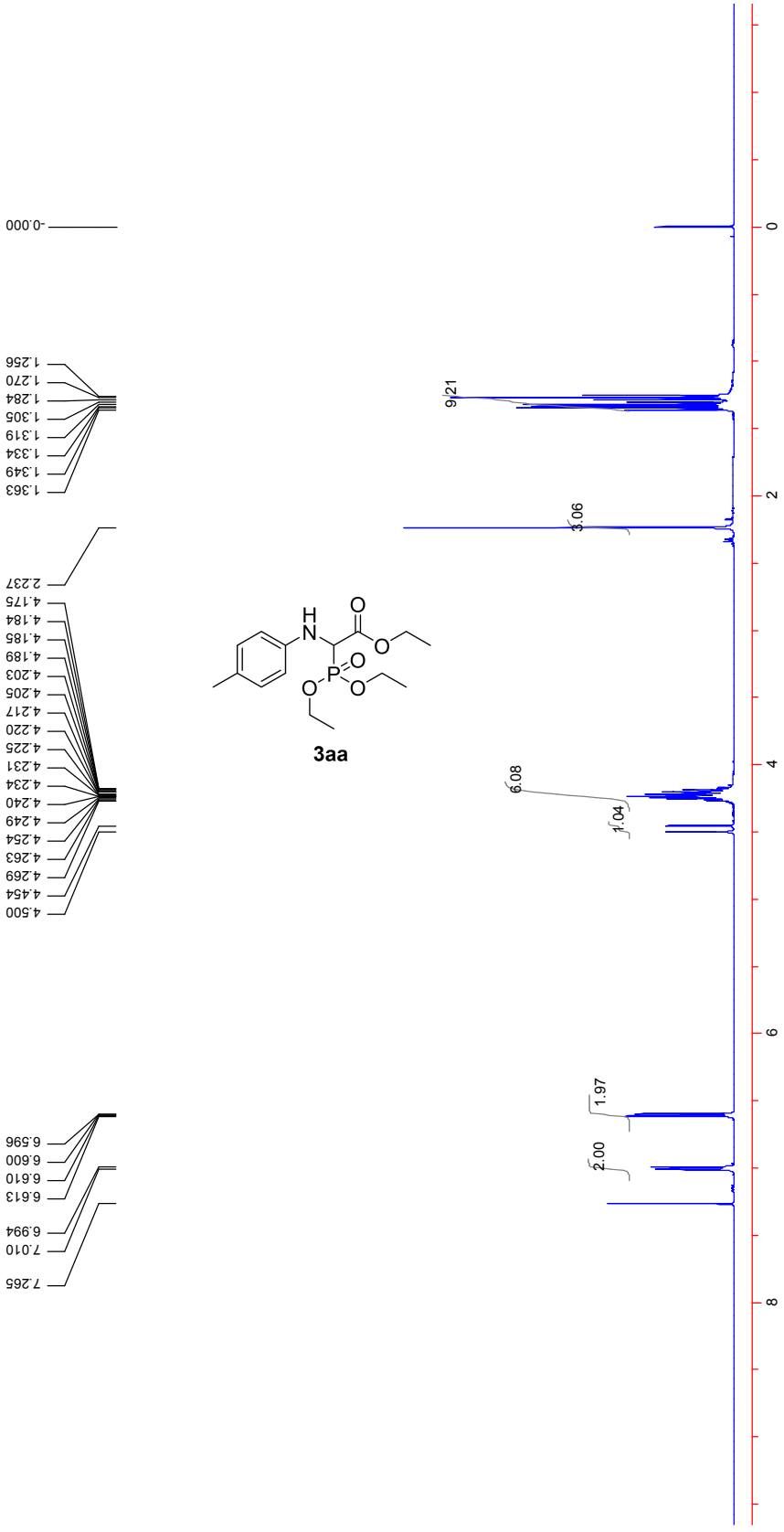
1a **2a** **3aa**

Entry	Catalyst	Temperature	Solvent	Yield(%)[b]
1	$Co(ClO_4)_2·6H_2O$	80	DCE	52
2	$Co(ClO_4)_2·6H_2O$	80	EtOH	34
3	$Co(ClO_4)_2·6H_2O$	80	Toluene	68
4	$Co(ClO_4)_2·6H_2O$	80	DMSO	trace
5	$Co(ClO_4)_2·6H_2O$	80	Dioxane	32
6	**$Co(ClO_4)_2·6H_2O$**	**80**	**MeCN**	**83**
7	$Co(ClO_4)_2·6H_2O$	60	MeCN	63
8	$Co(ClO_4)_2·6H_2O$	100	MeCN	80

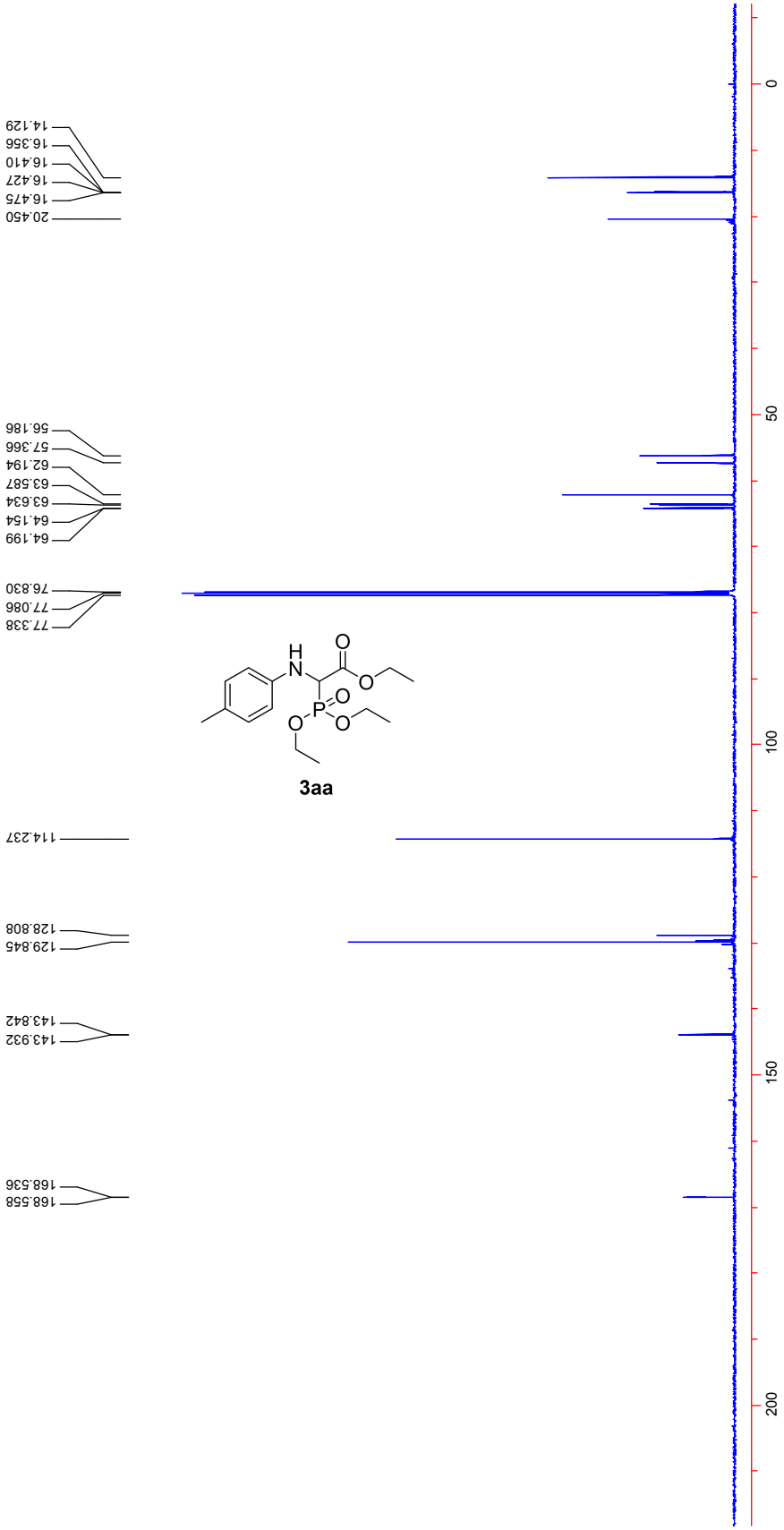
(a) Reaction conditions: **1a** (0.2 mmol), **2a** (1.4 mmol), $Co(ClO_4)_2·6H_2O$ (10 mol %), Solvent (2 mL) in air for 12 h. (b) Isolated yields.

2. ^{1}H NMR and ^{13}C NMR Spectra of Products

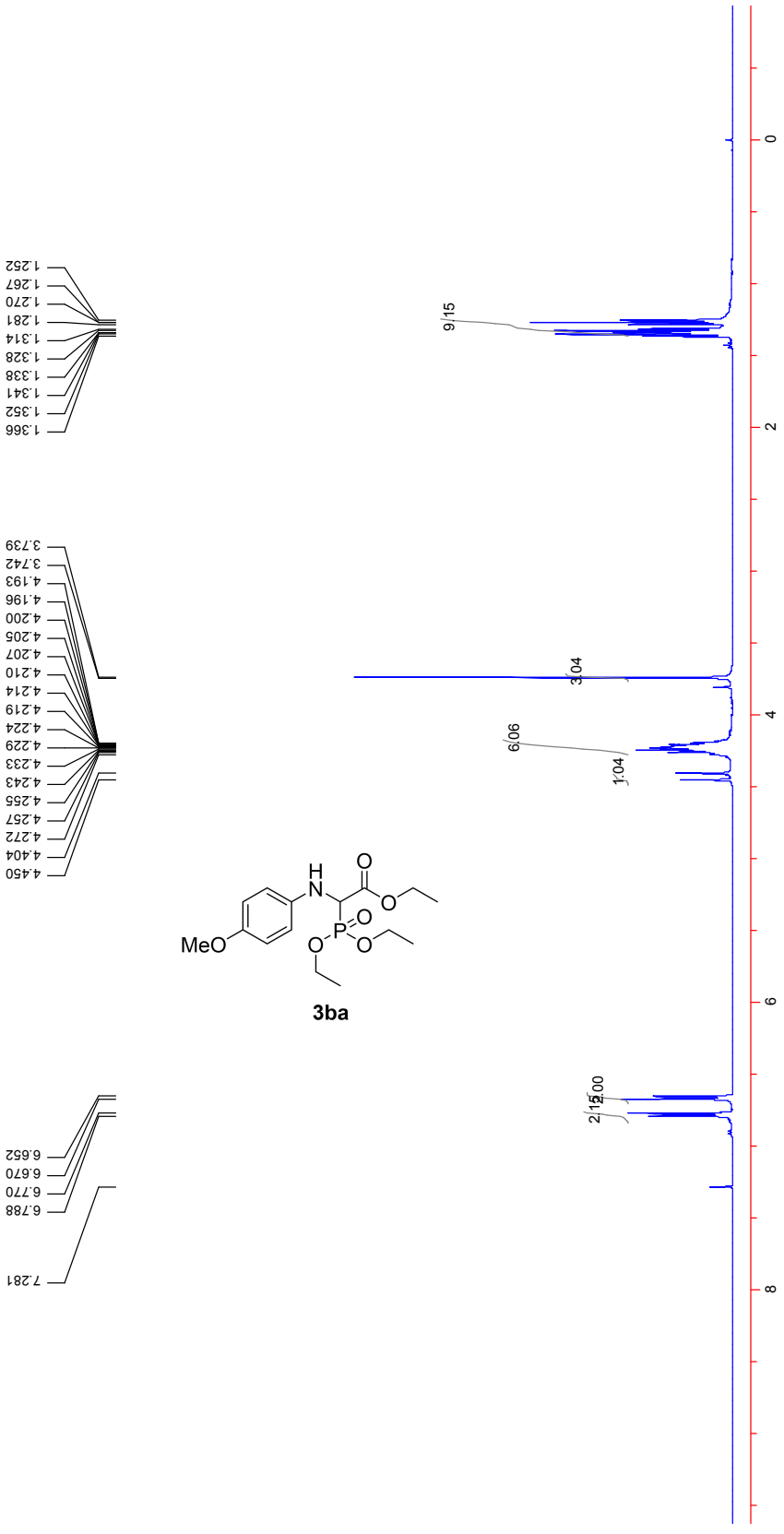
^{1}H NMR Spectra of ethyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3aa**



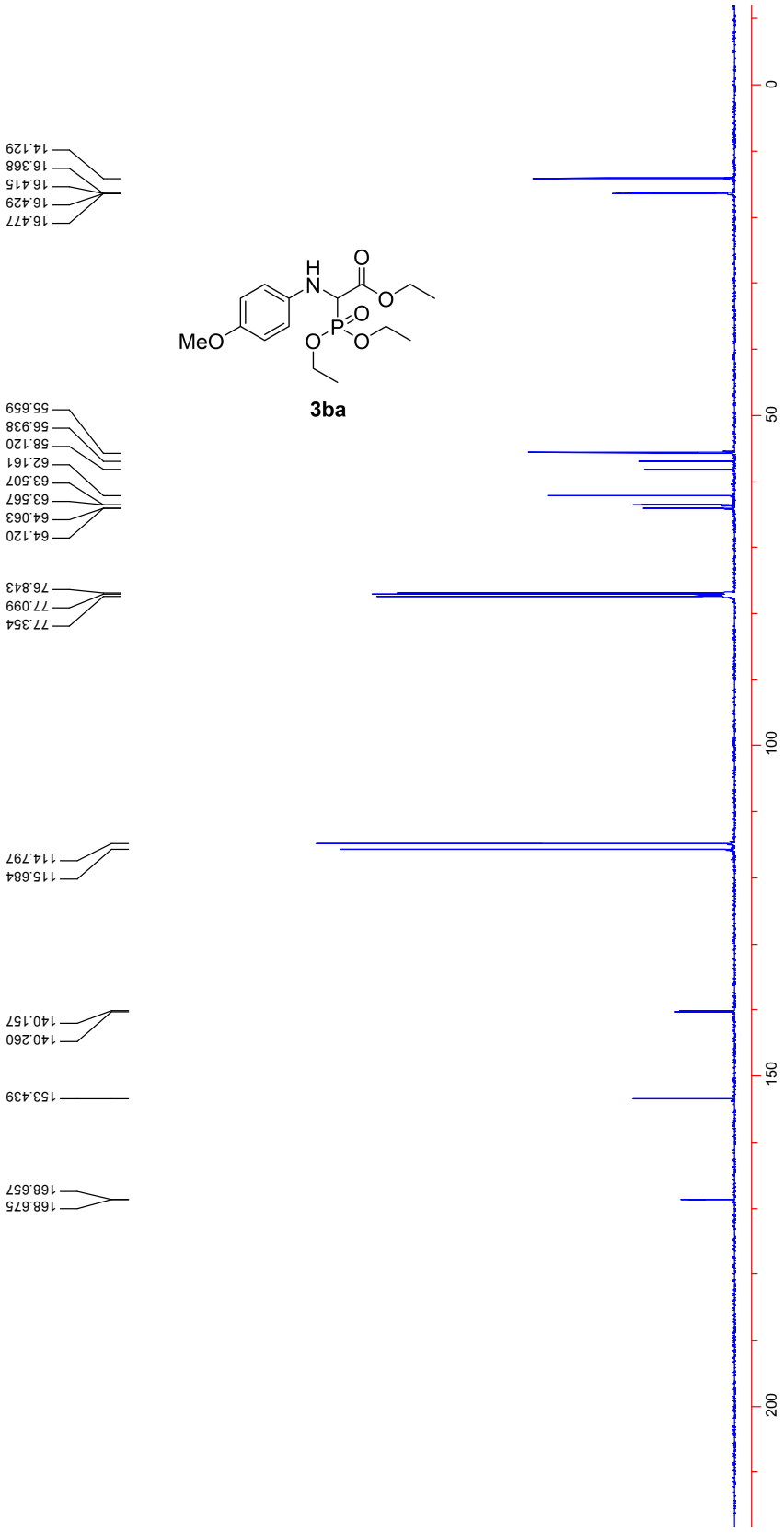
^{13}C NMR Spectra of ethyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3aa**



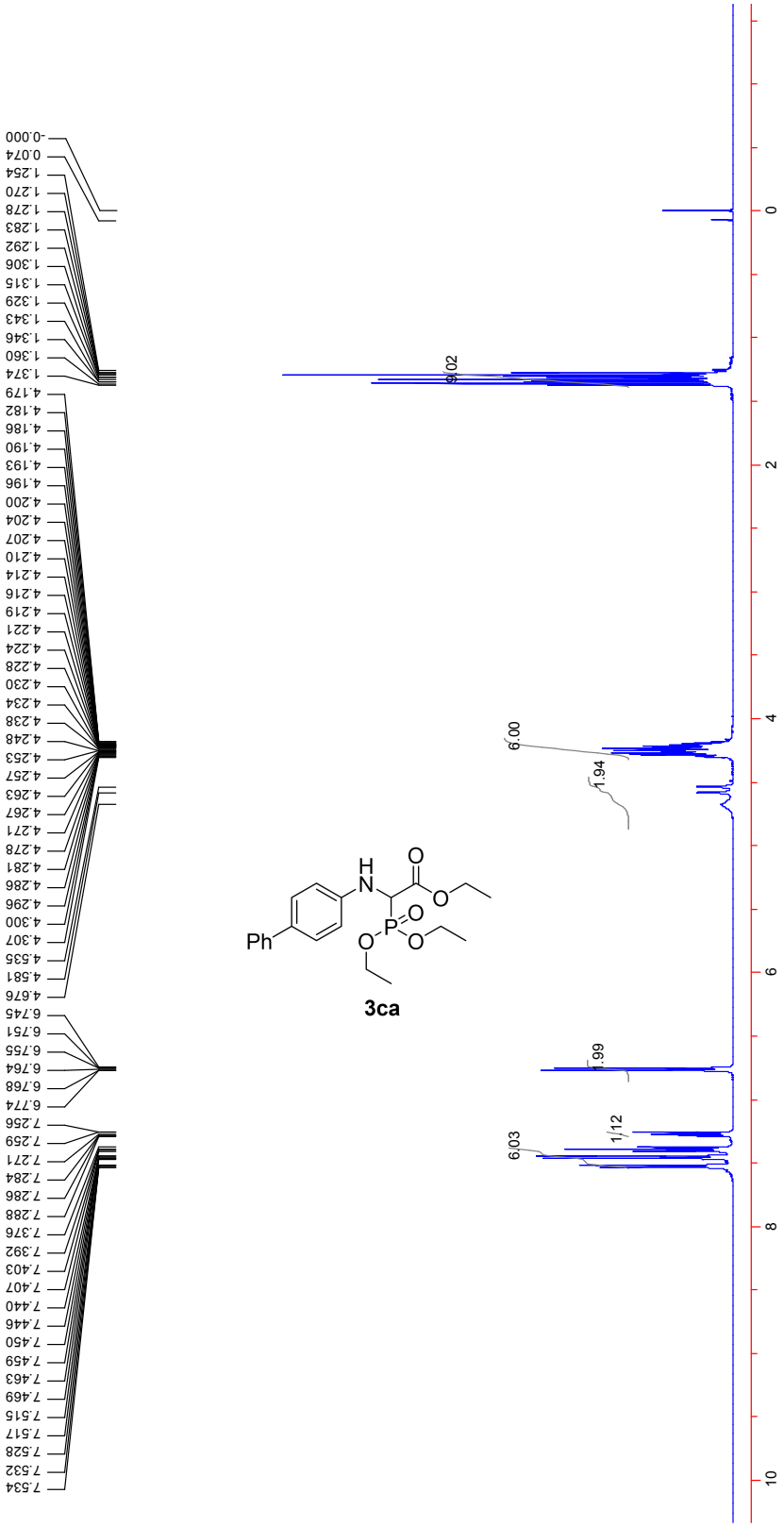
^{1}H NMR Spectra of ethyl 2-(diethoxyphosphoryl)-2-((4-methoxyphenyl)amino)-acetate **3ba**



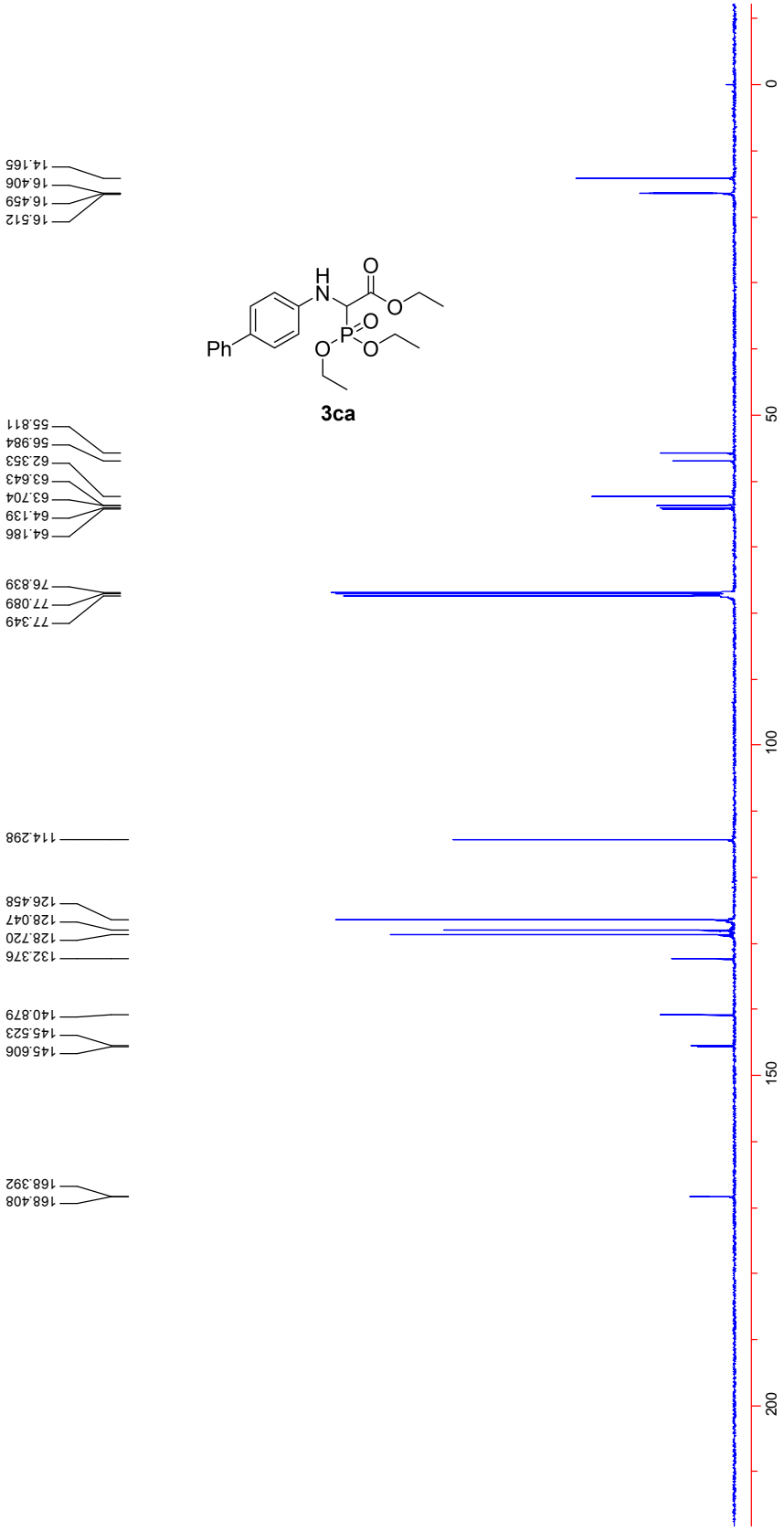
^{13}C NMR Spectra of ethyl 2-(diethoxyphosphoryl)-2-((4-methoxyphenyl)amino)-acetate **3ba**



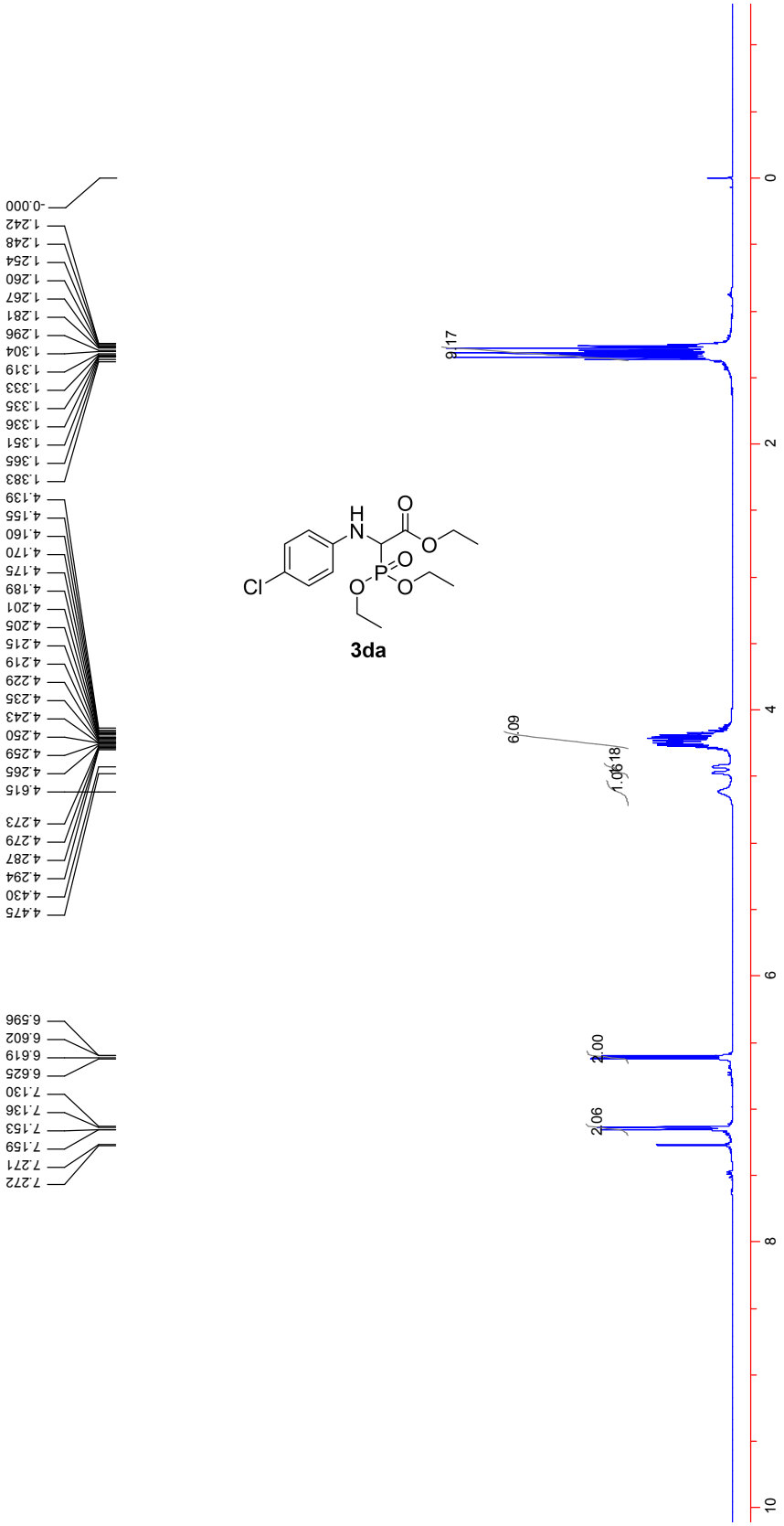
^{1}H NMR Spectra of ethyl 2-([1,1'-biphenyl]-4-ylamino)-2-(diethoxyphosphoryl)-acetate **3ca**



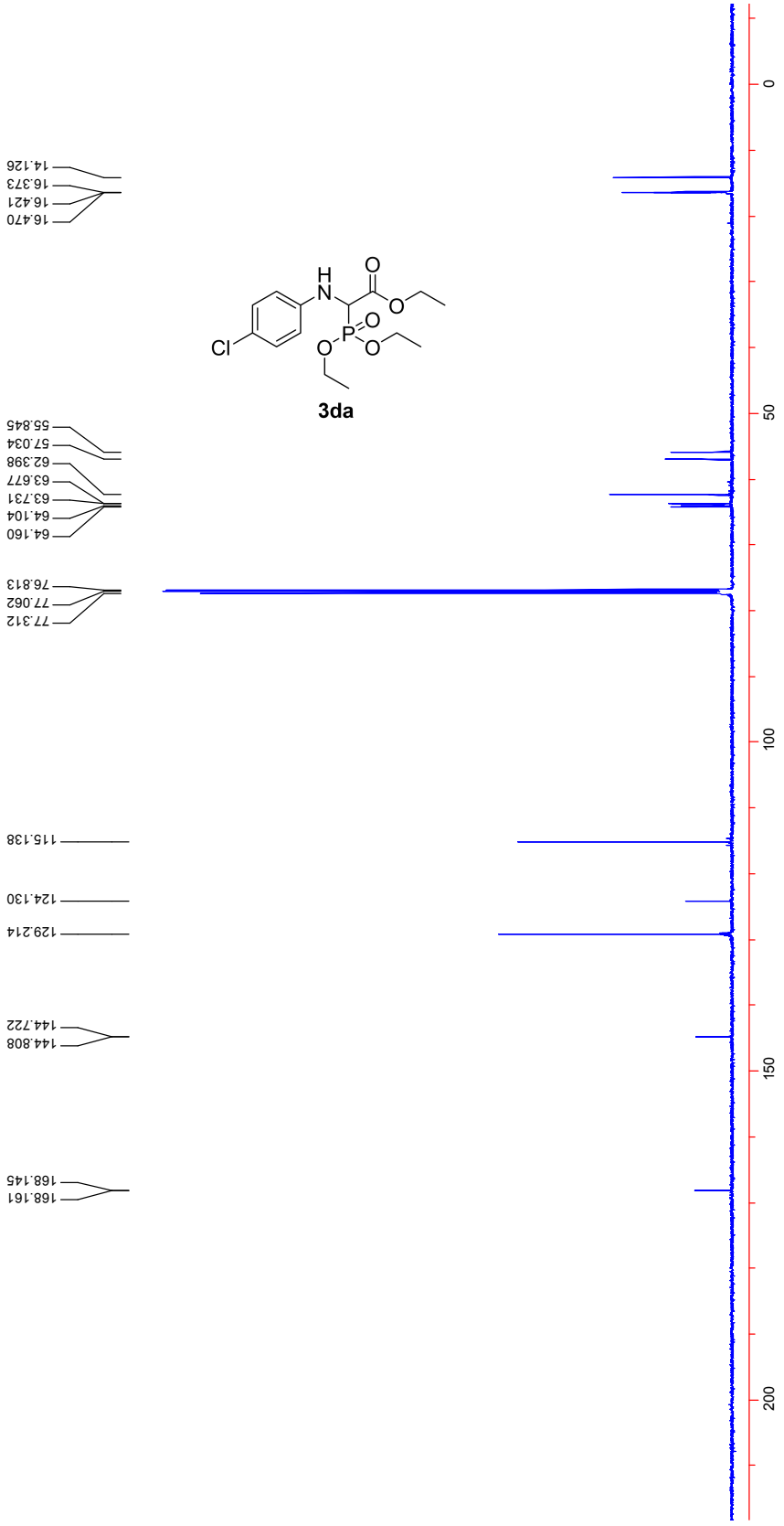
^{13}C NMR Spectra of ethyl 2-([1,1'-biphenyl]-4-ylamino)-2-(diethoxyphosphoryl)-acetate **3ca**



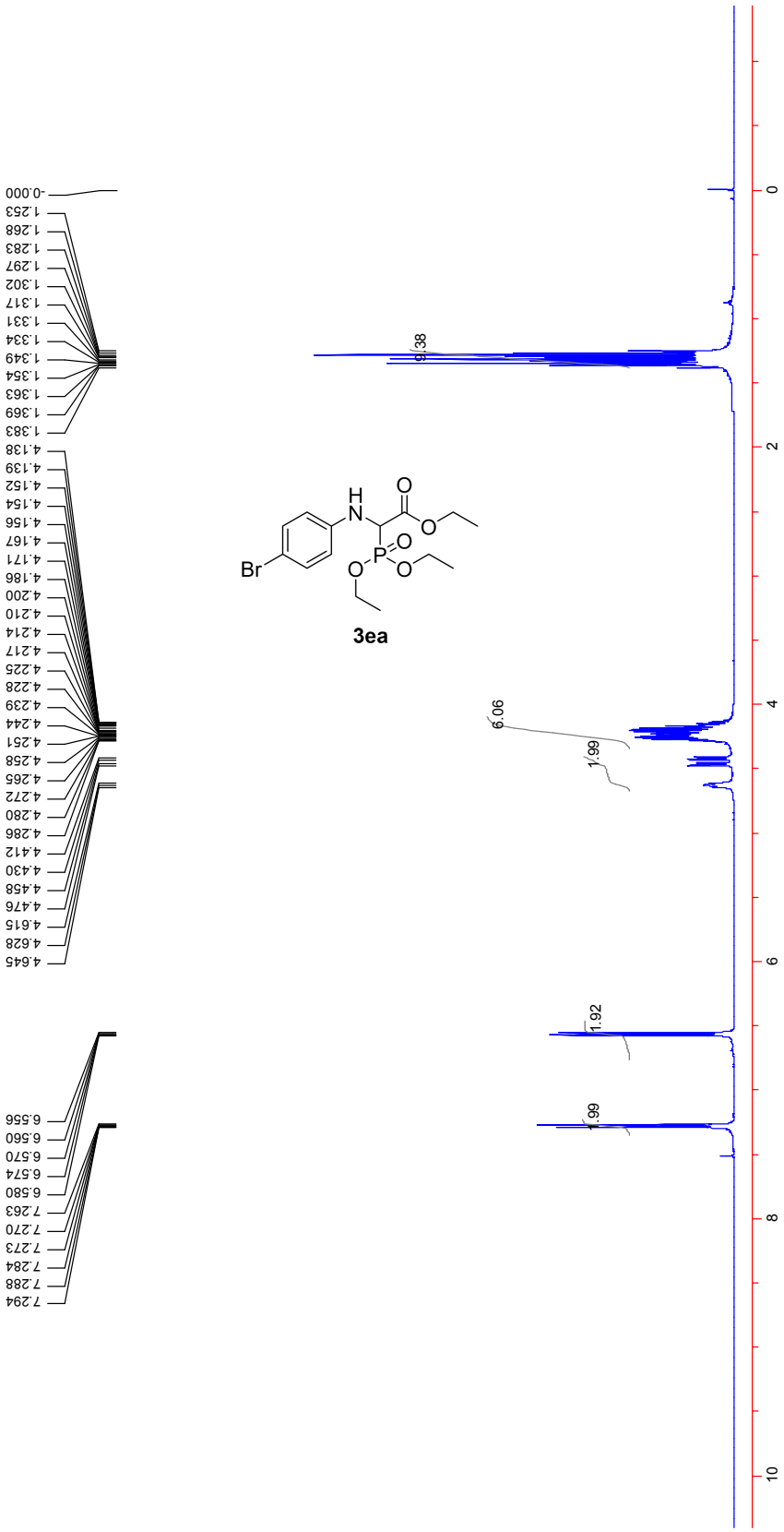
^{1}H NMR Spectra of ethyl 2-((4-chlorophenyl)amino)-2-(diethoxyphosphoryl)acetate **3da**



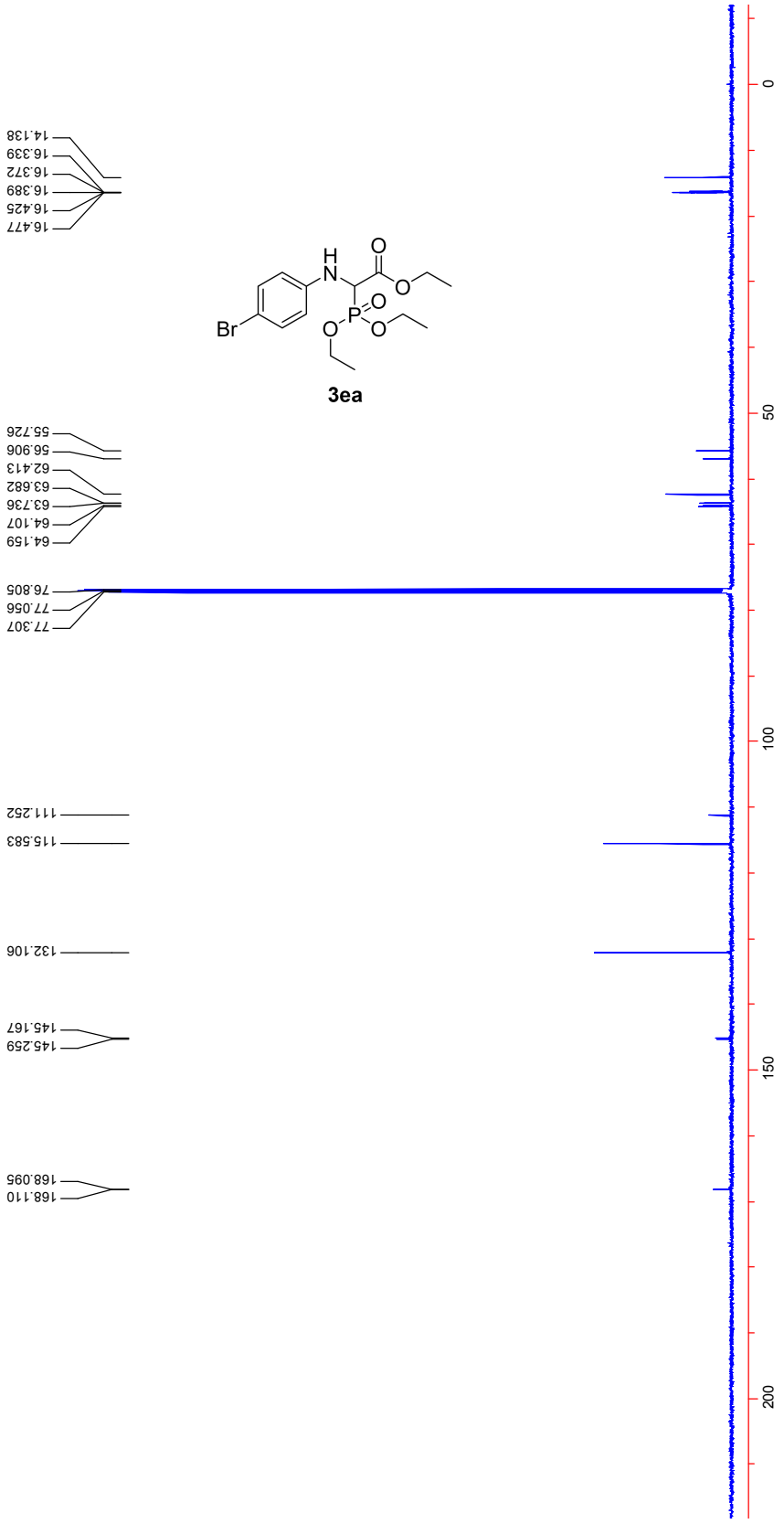
^{13}C NMR Spectra of ethyl 2-((4-chlorophenyl)amino)-2-(diethoxyphosphoryl)acetate **3da**



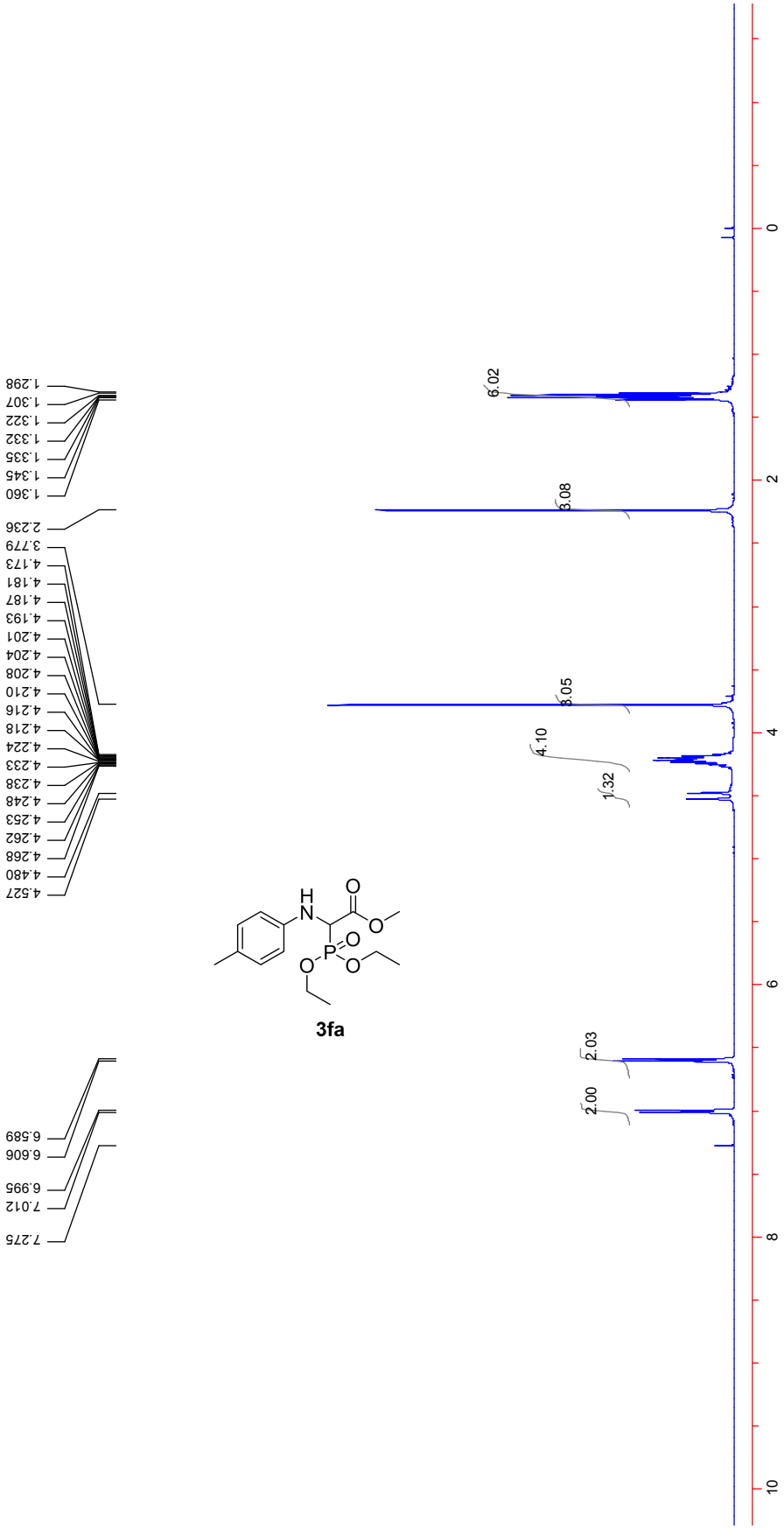
^{1}H NMR Spectra of ethyl 2-((4-bromophenyl)amino)-2-(diethoxyphosphoryl)acetate **3ea**



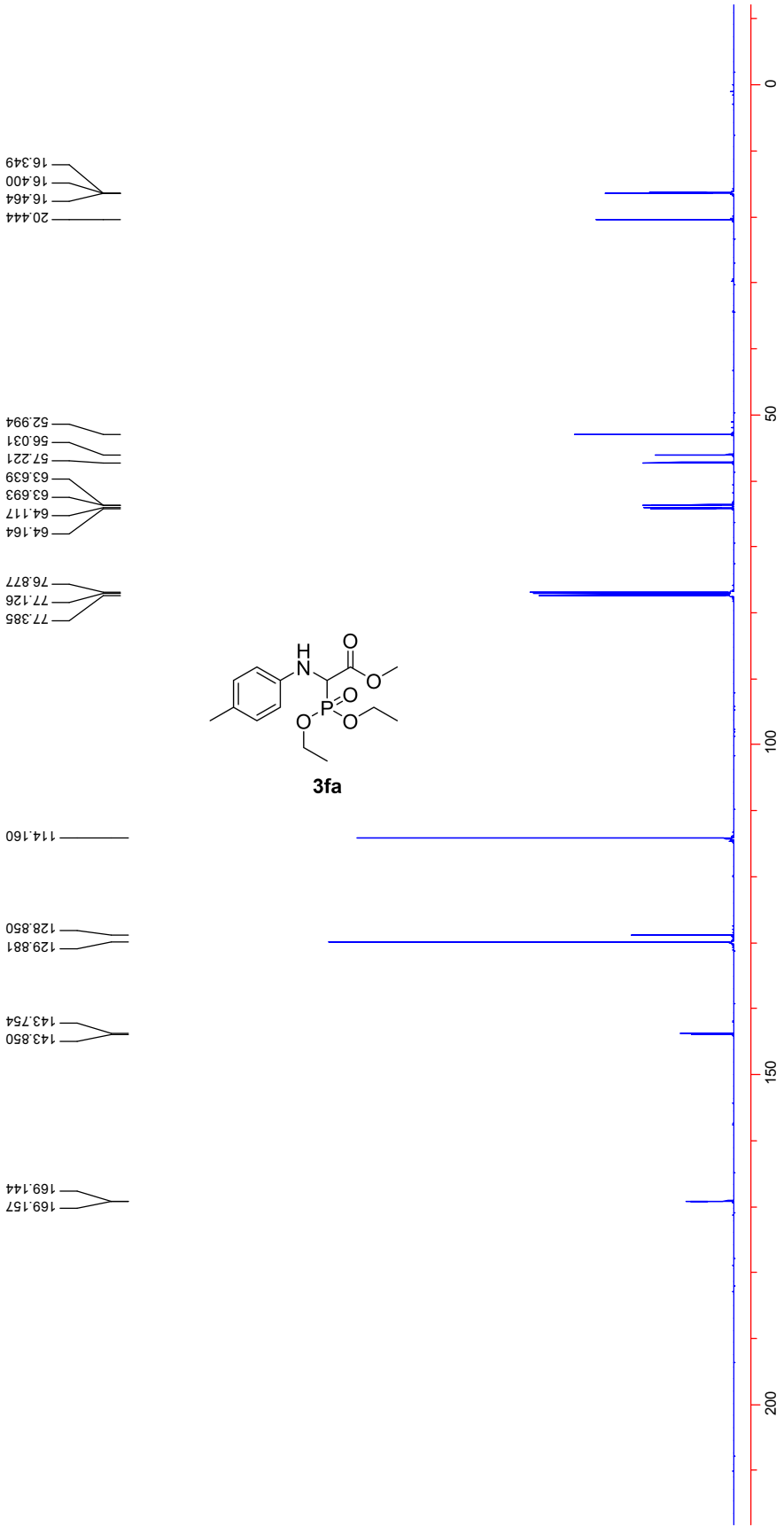
^{13}C NMR Spectra of ethyl 2-((4-bromophenyl)amino)-2-(diethoxyphosphoryl)acetate **3ea**



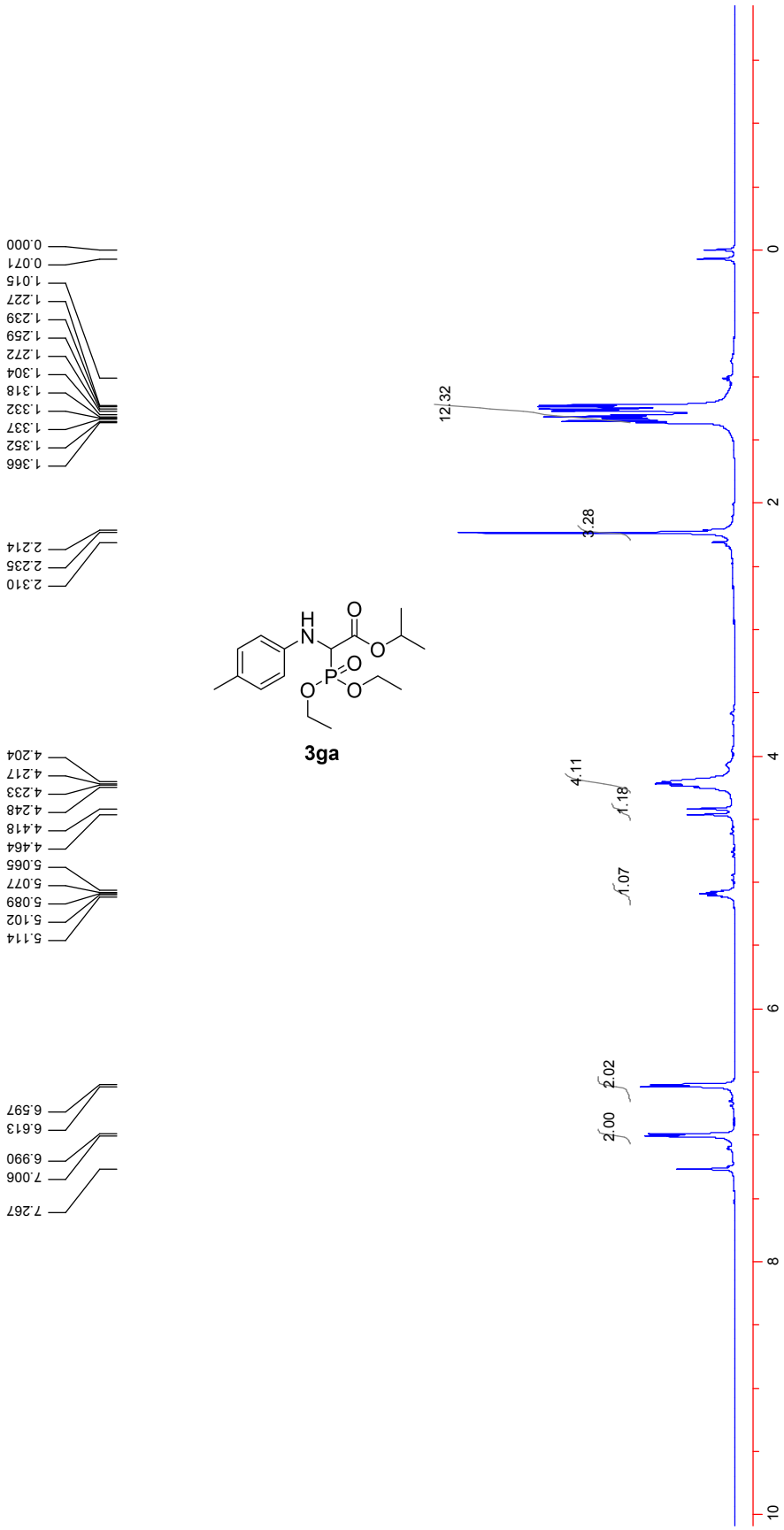
[1]H NMR Spectra of methyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3fa**



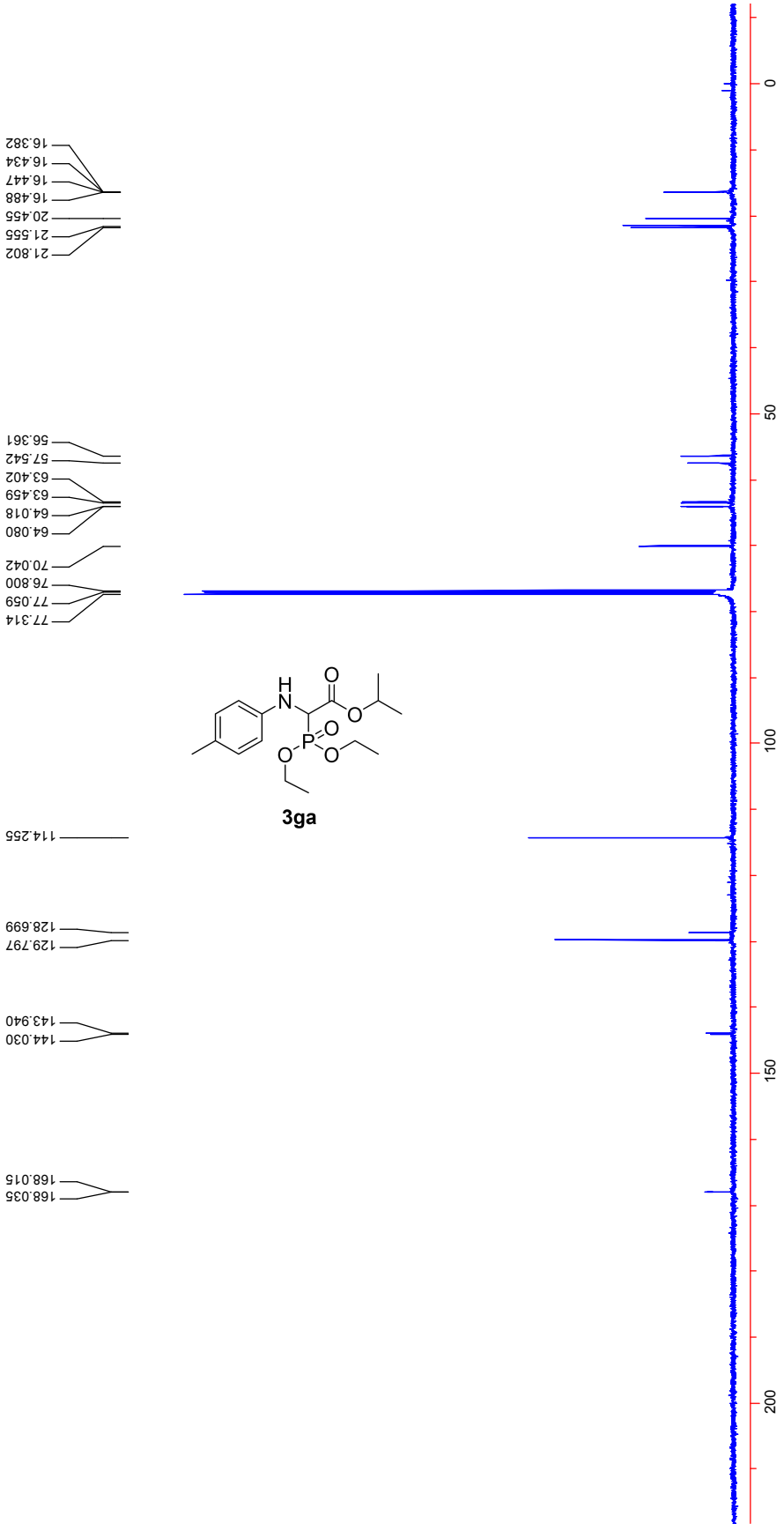
^{13}C NMR Spectra of methyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3fa**



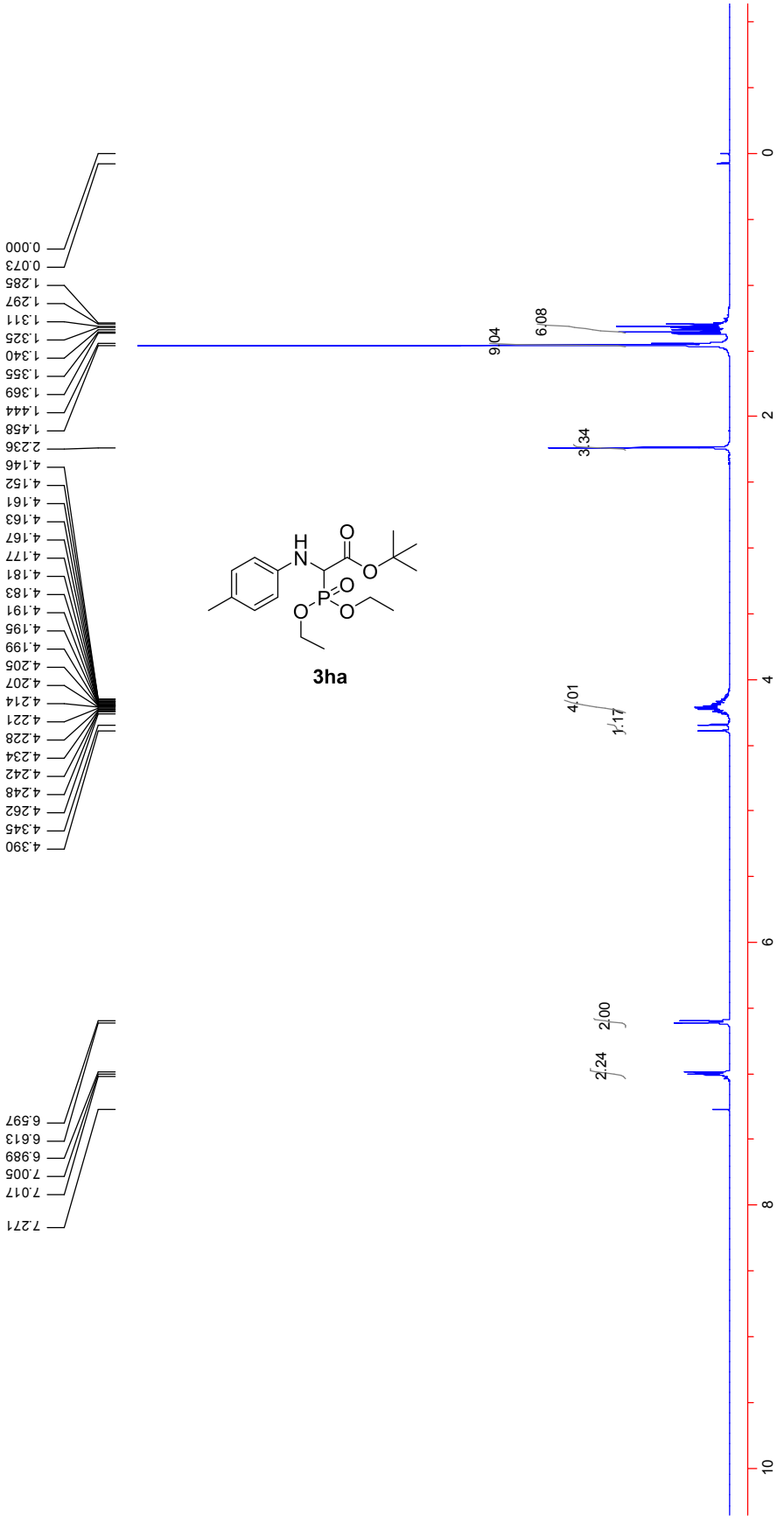
[1]H NMR Spectra of isopropyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ga**



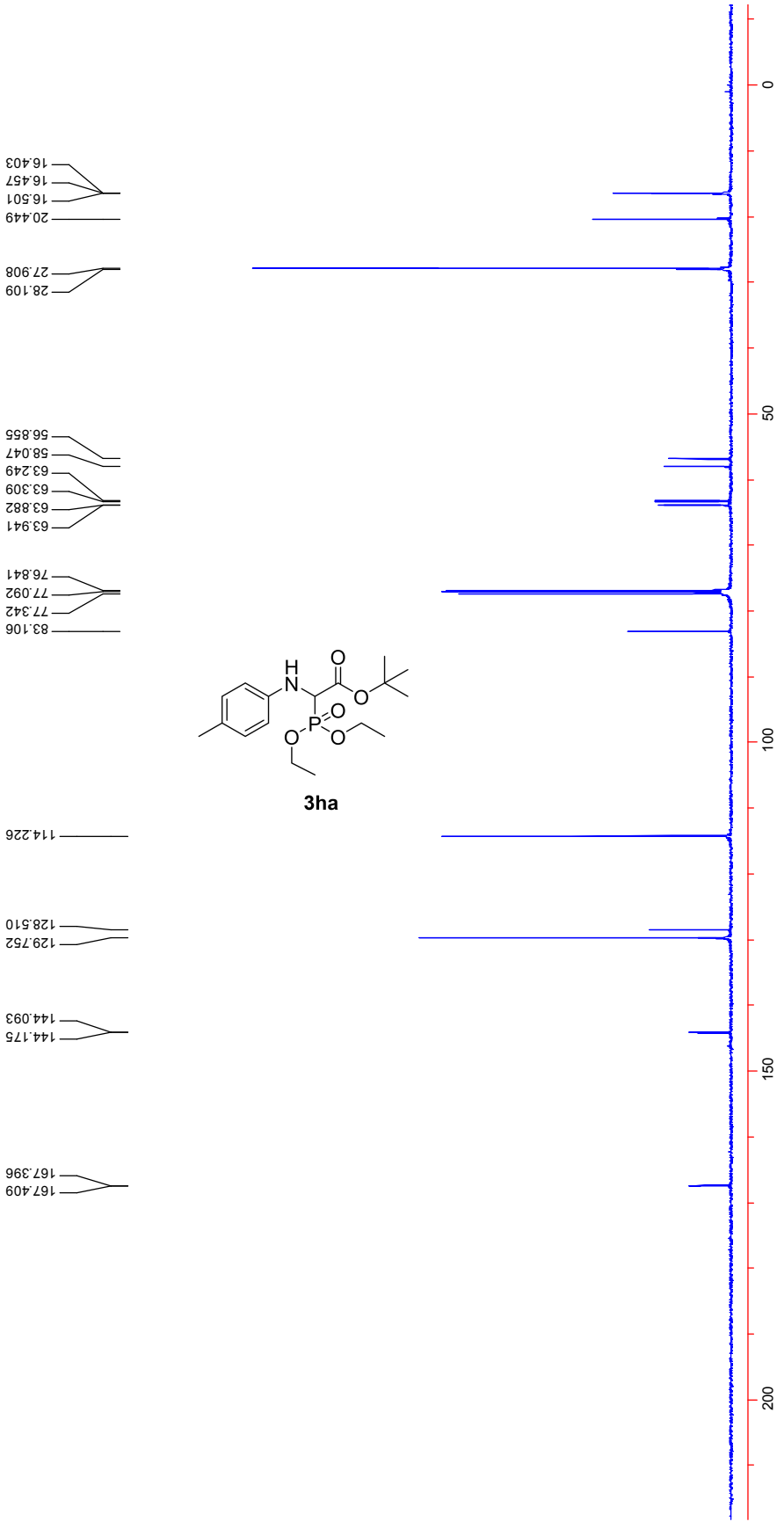
^{13}C NMR Spectra of isopropyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ga**



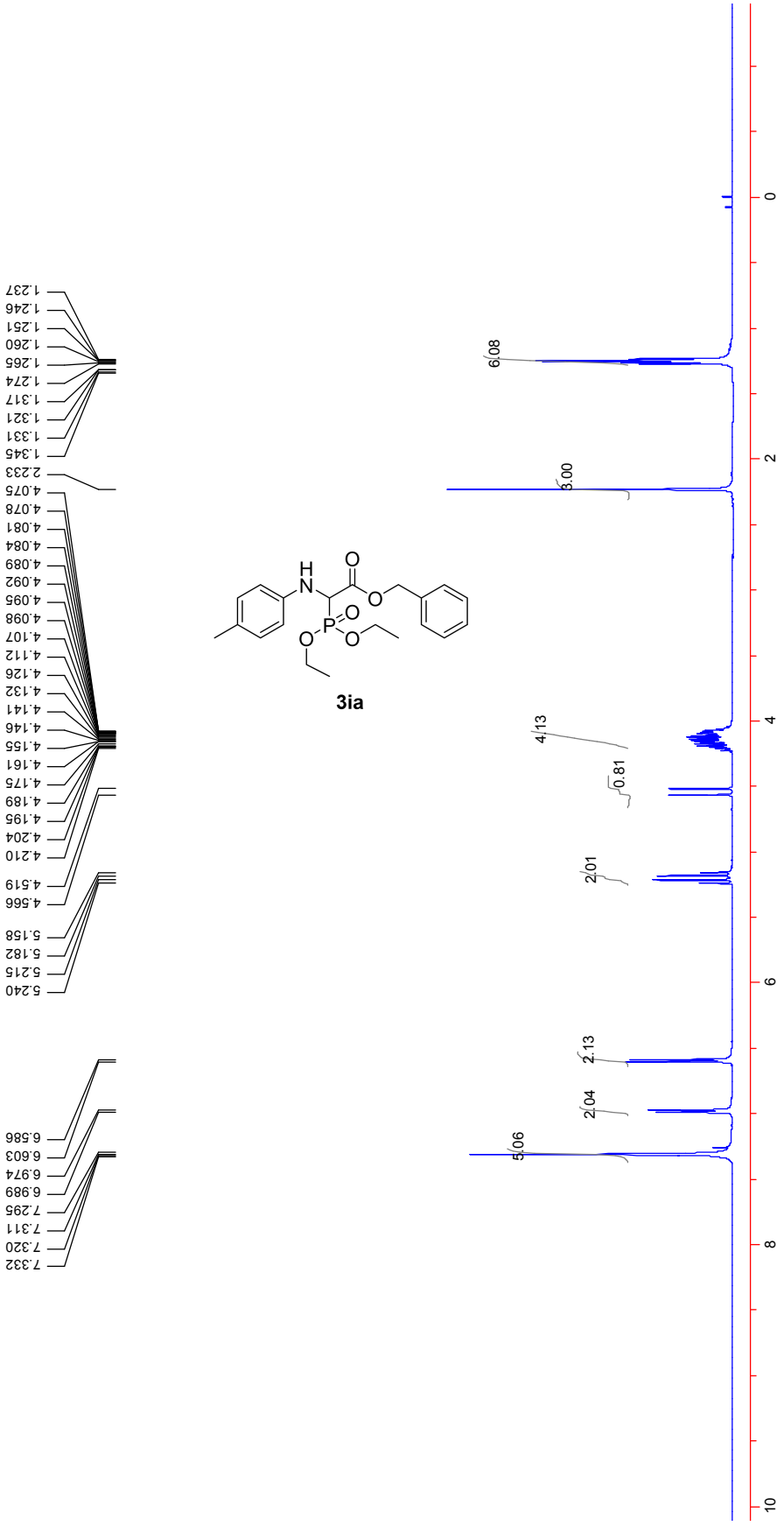
[1]H NMR Spectra of *tert*-butyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ha**



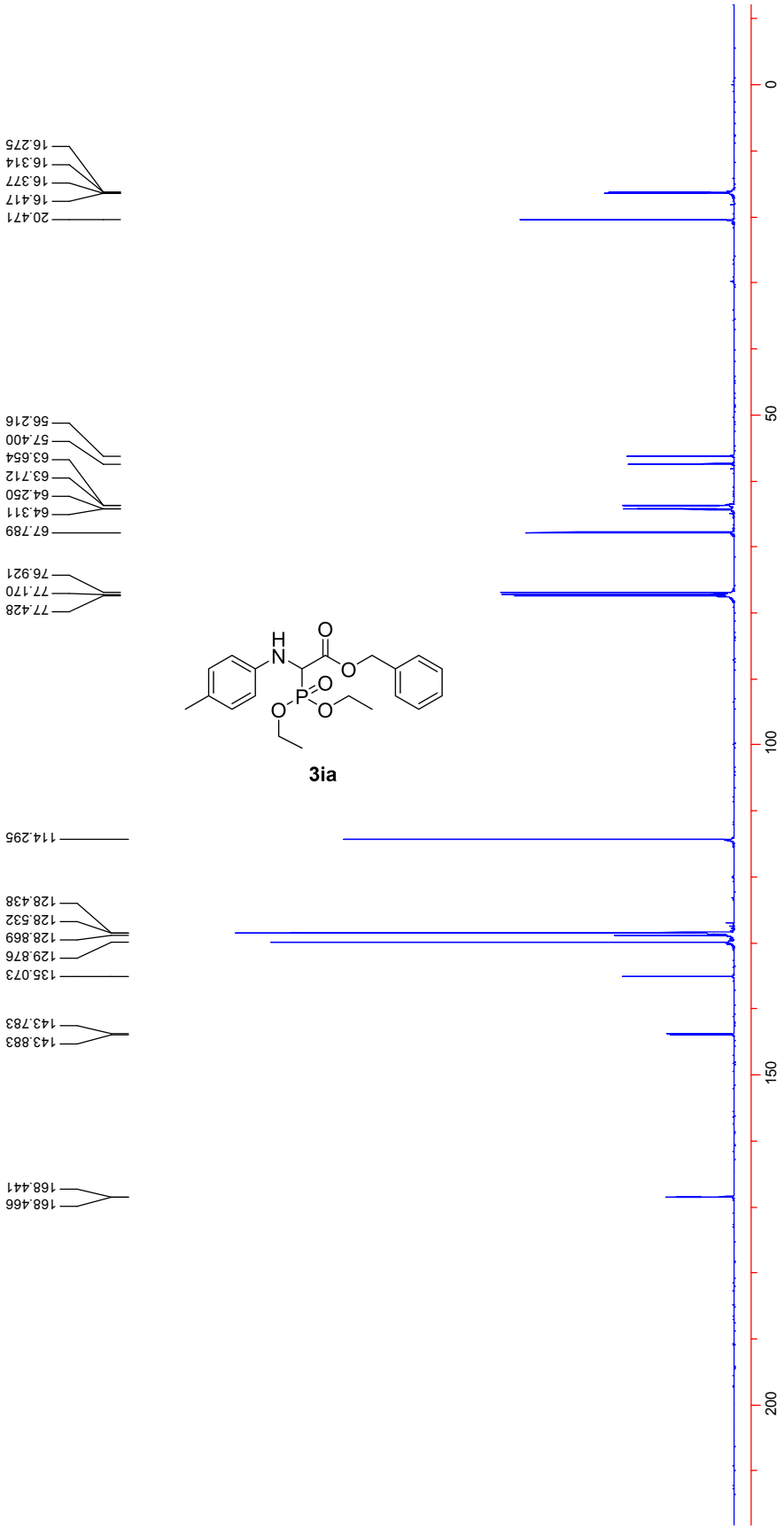
^{13}C NMR Spectra of *tert*-butyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ha**



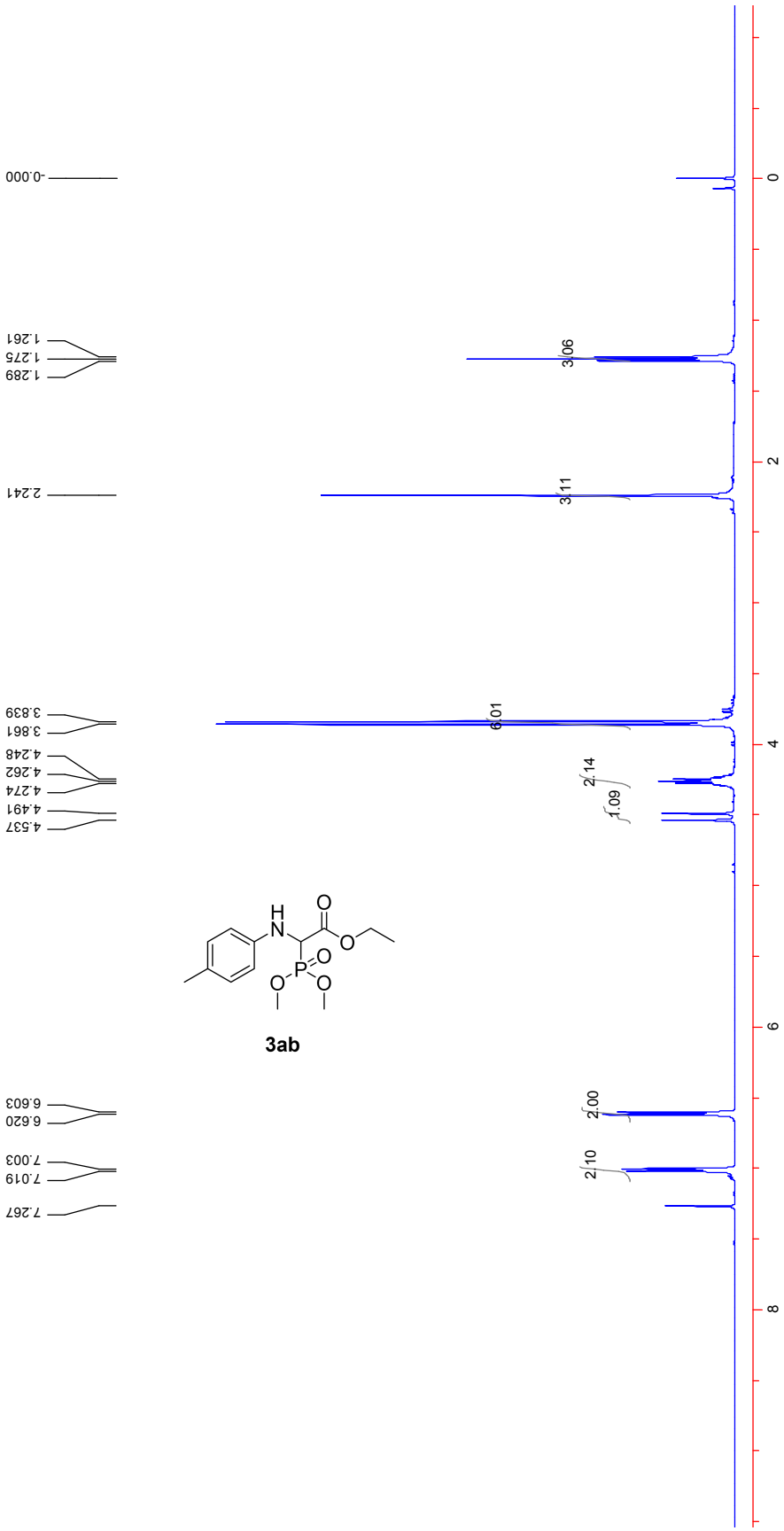
[1]H NMR Spectra of benzyl 2-(diethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ia**



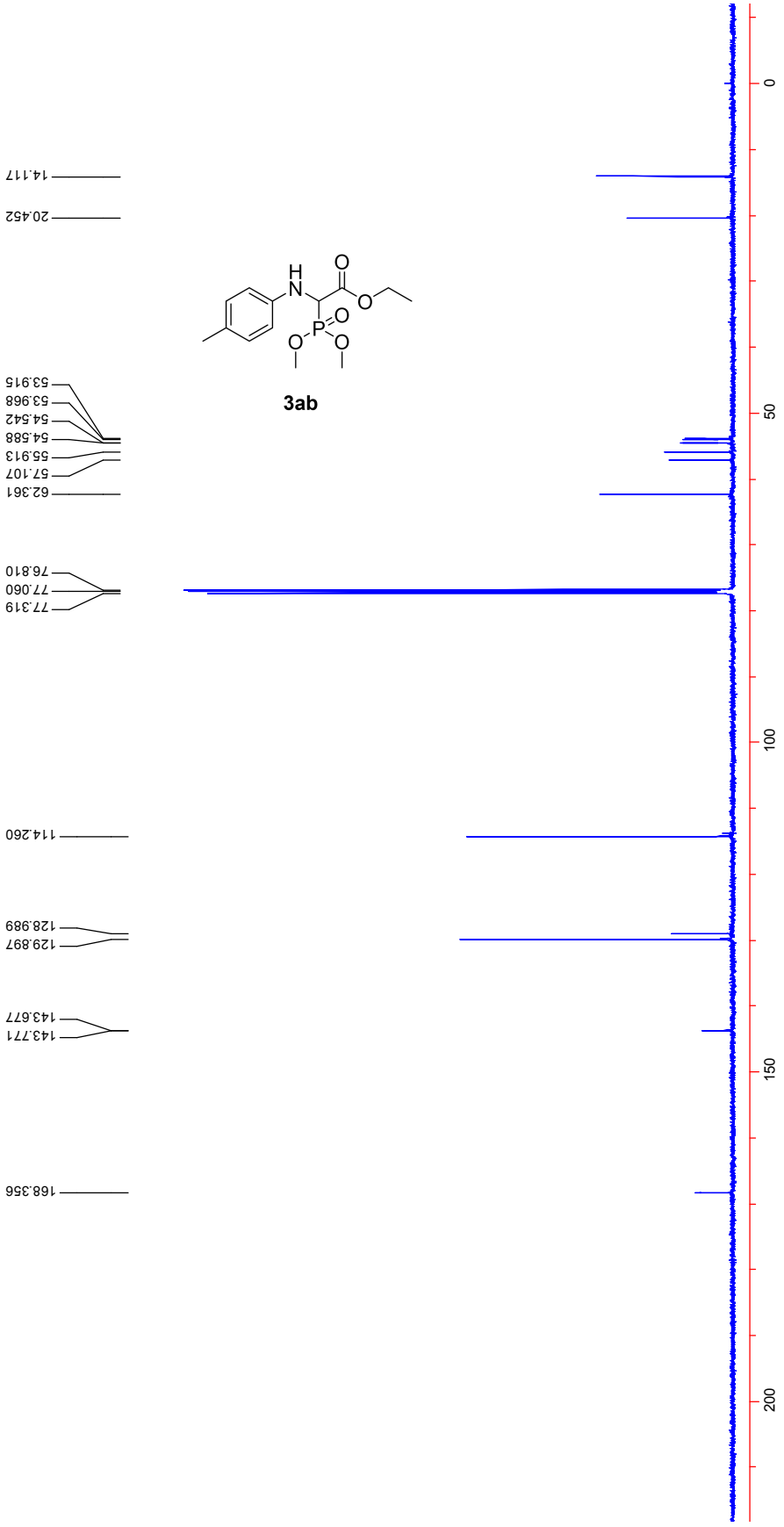
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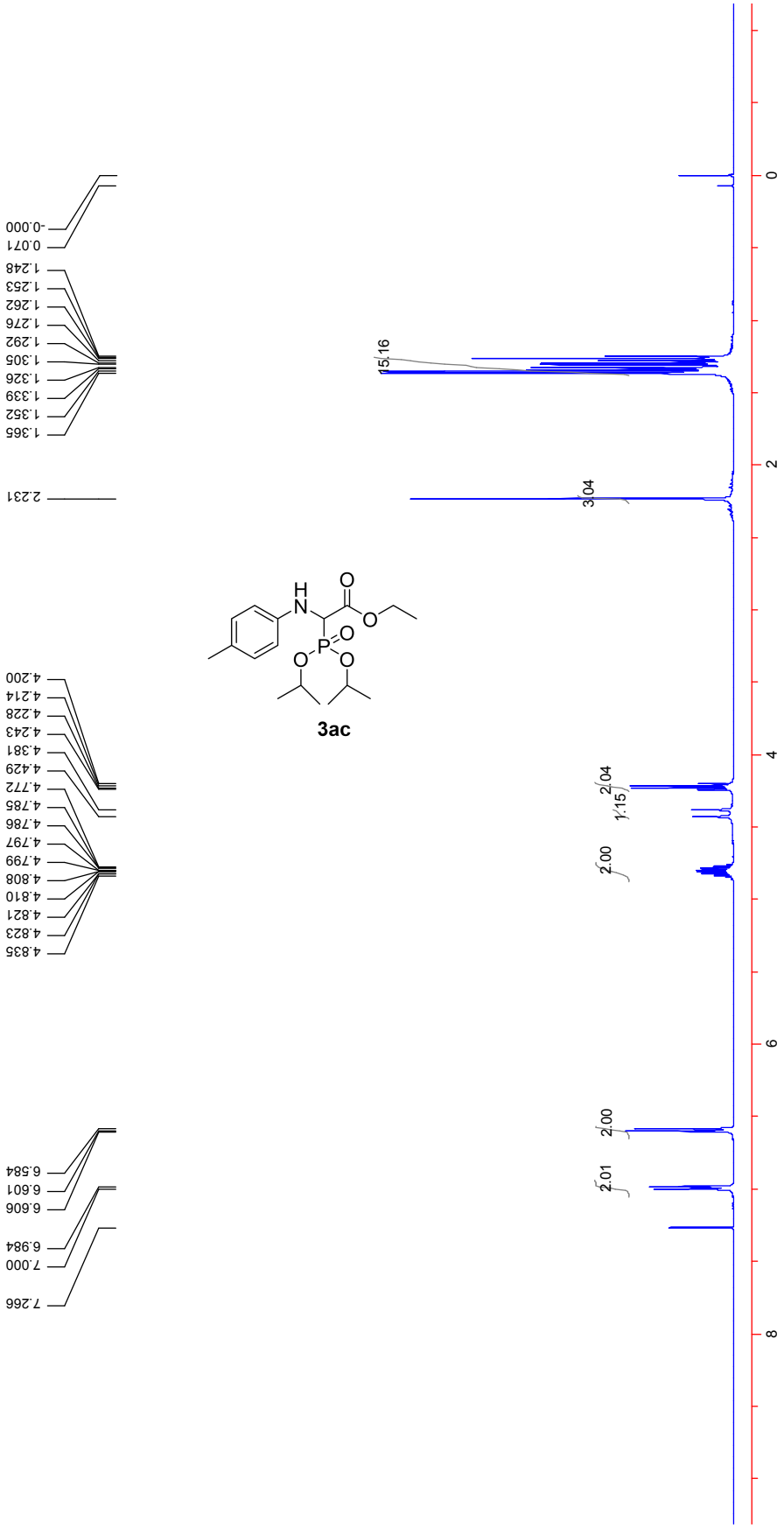
[1]H NMR Spectra of ethyl 2-(dimethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ab**



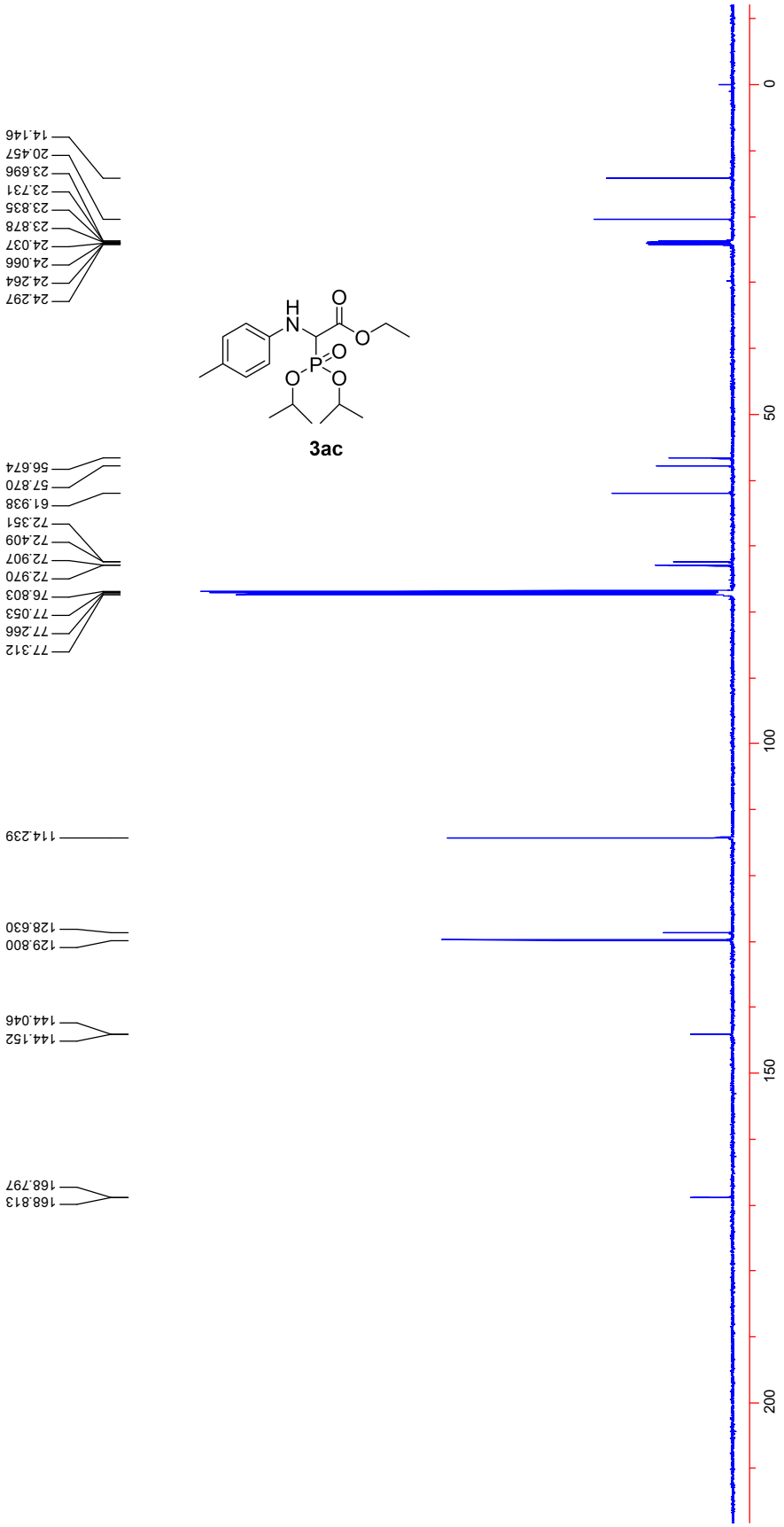
^{13}C NMR Spectra of ethyl 2-(dimethoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ab**



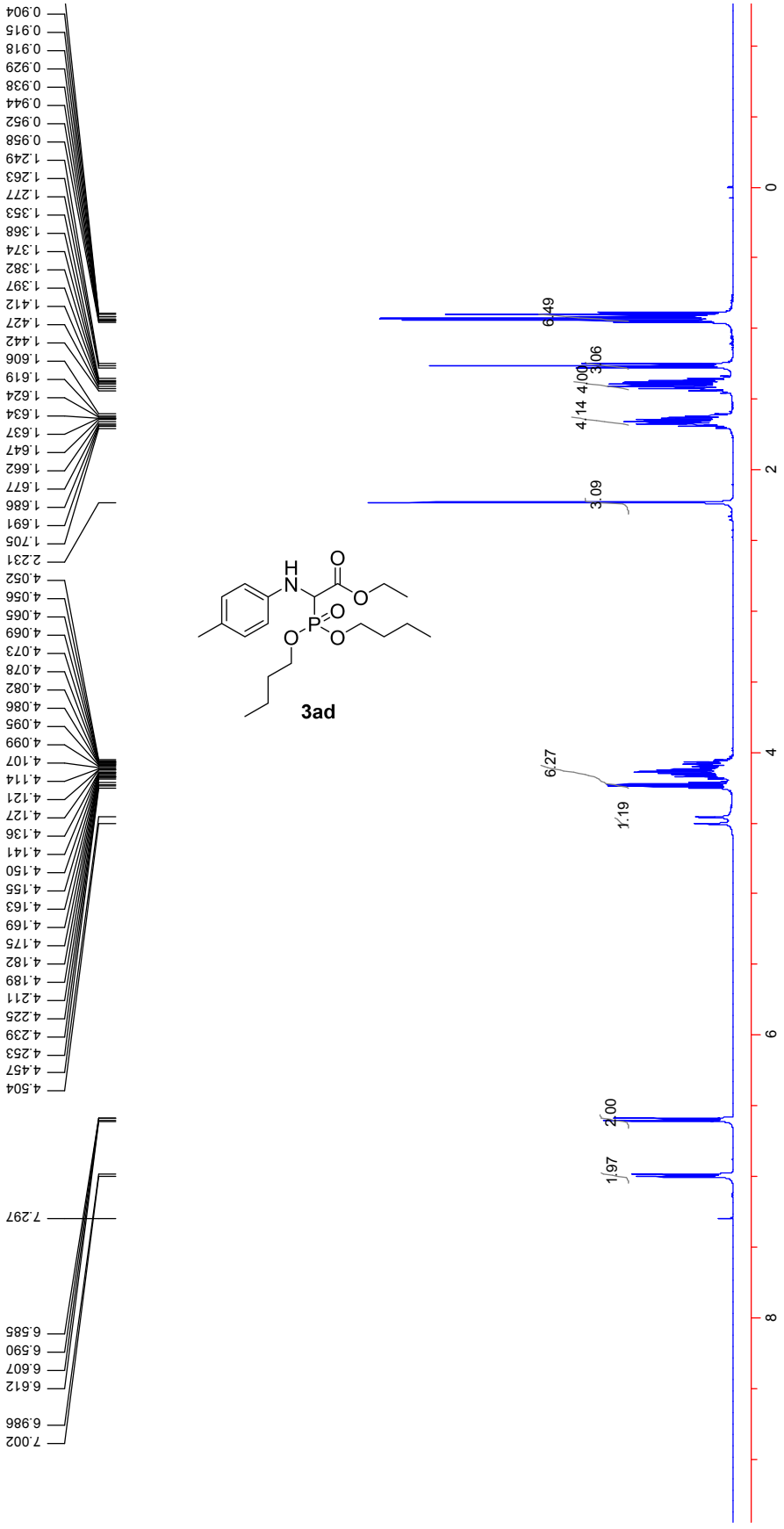
[1]H NMR Spectra of ethyl 2-(diisopropoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ac**



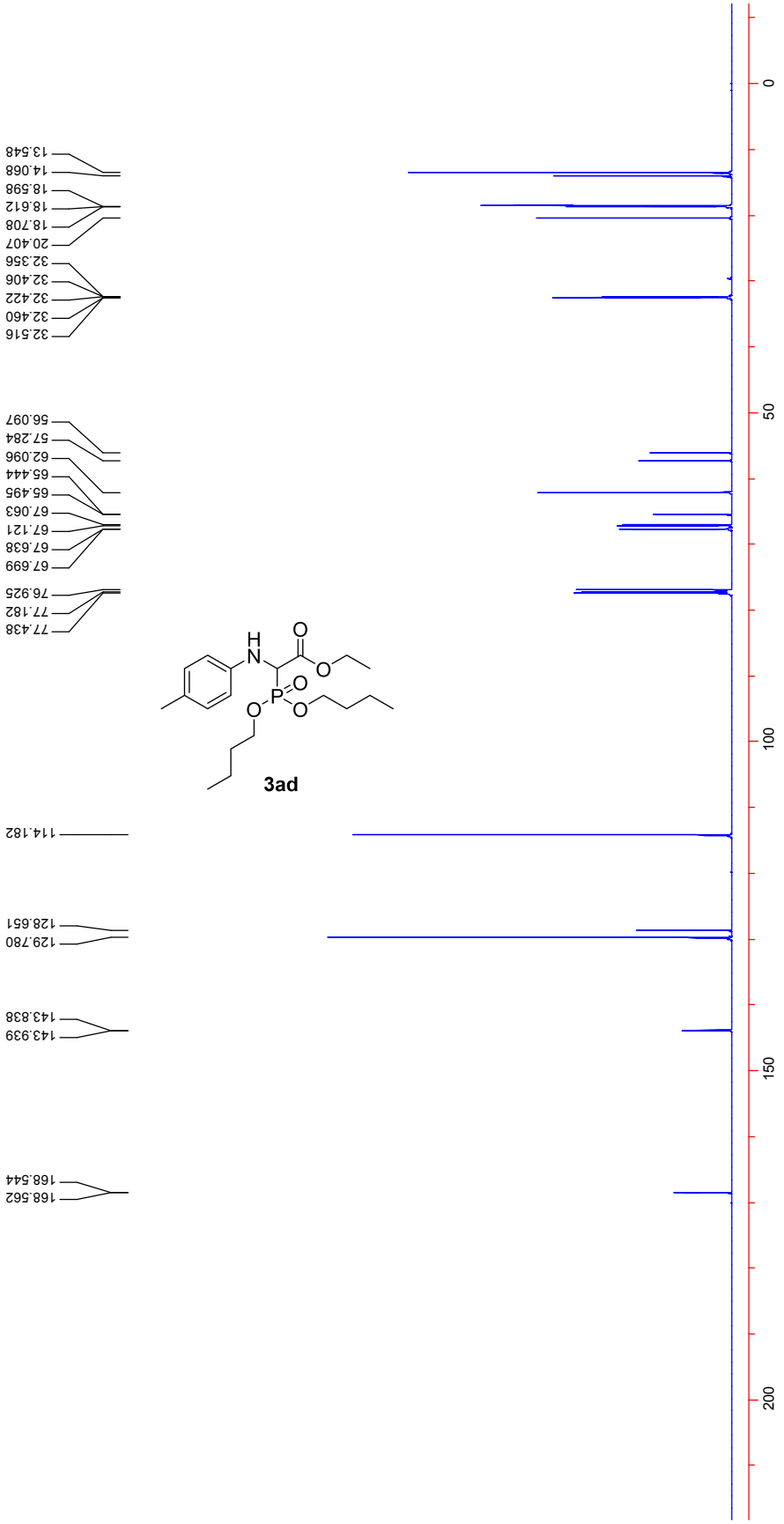
^{13}C NMR Spectra of ethyl 2-(diisopropoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ac**



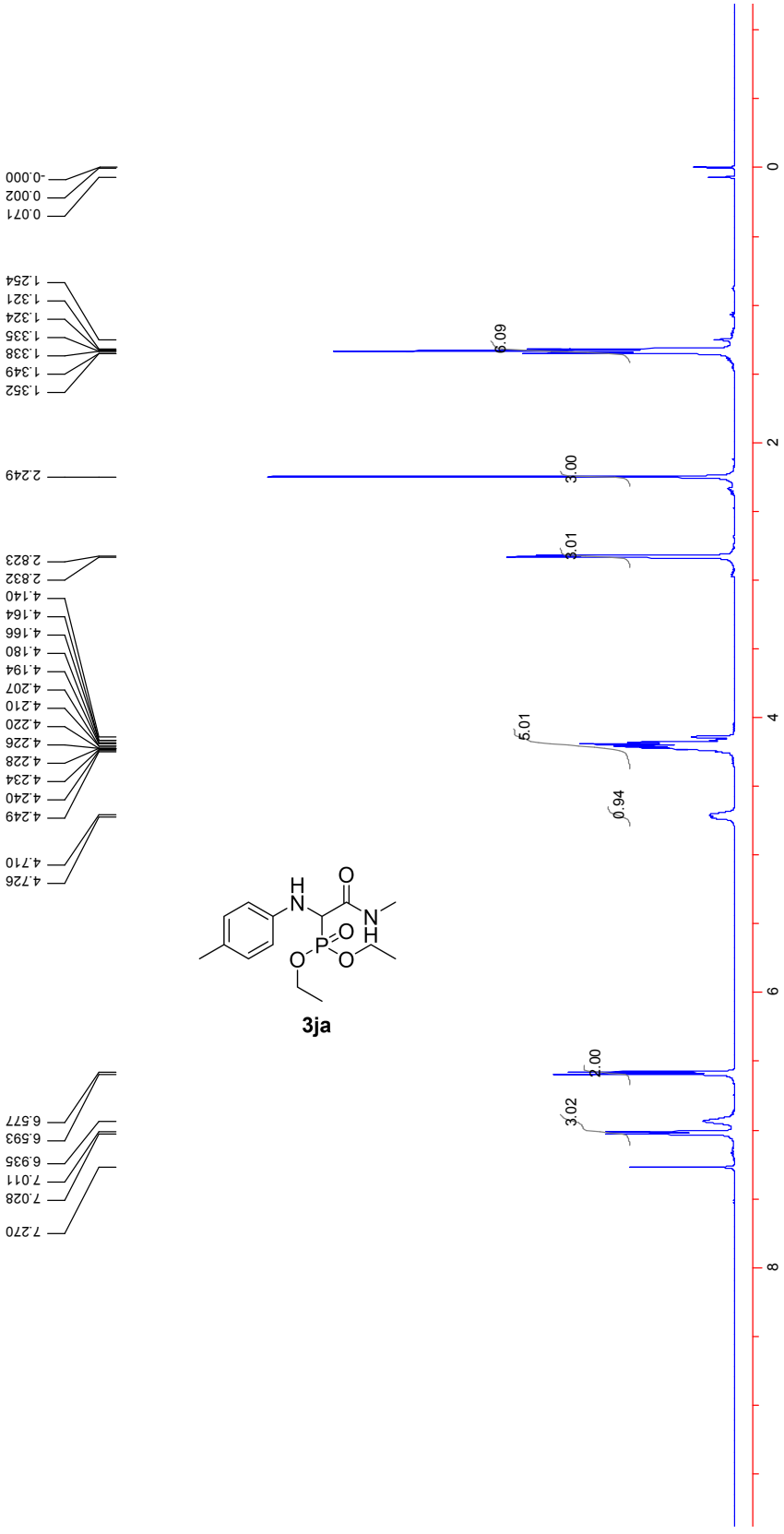
[1]H NMR Spectra of ethyl 2-(dibutoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ad**



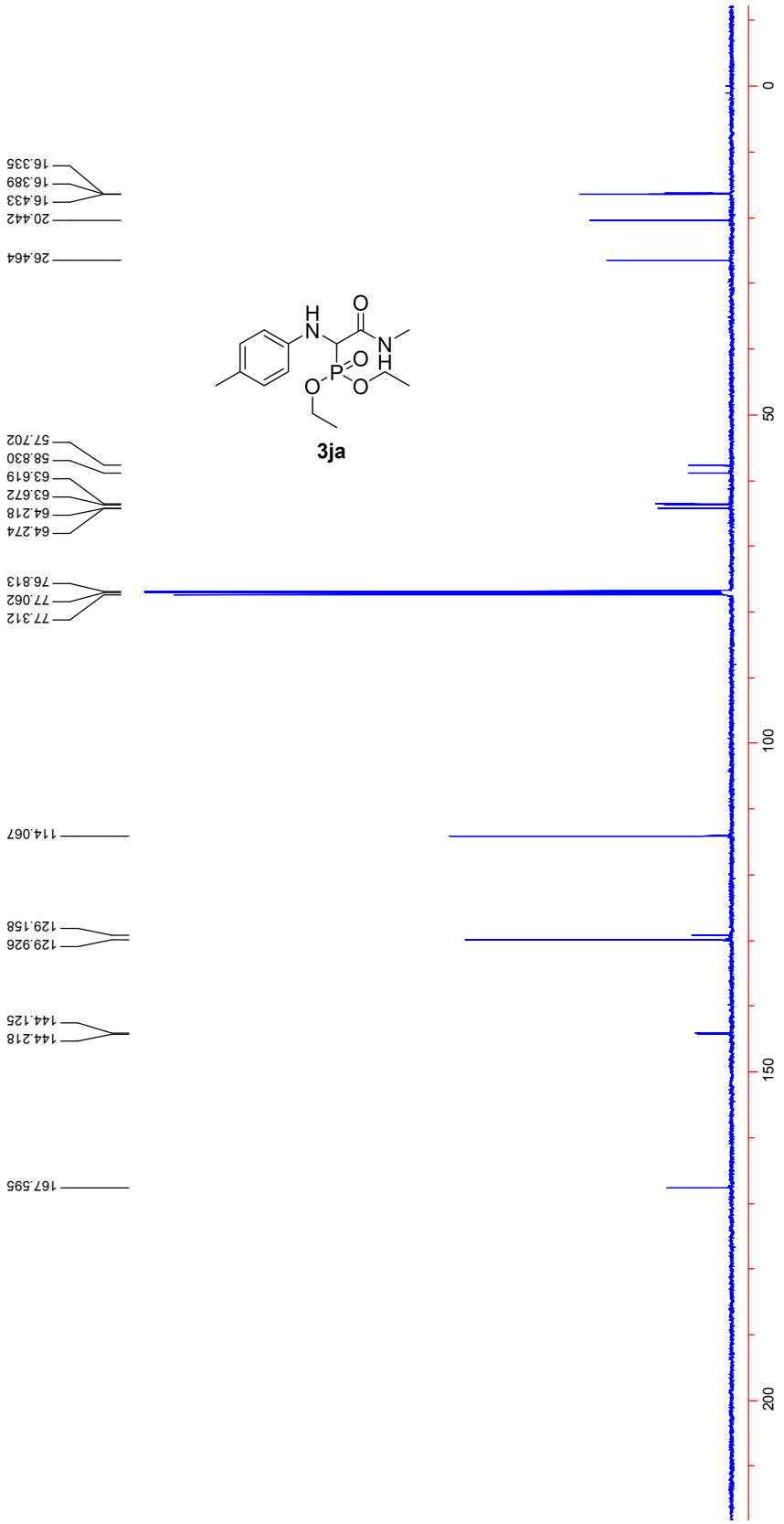
^{13}C NMR Spectra of ethyl 2-(dibutoxyphosphoryl)-2-(*p*-tolylamino)acetate **3ad**



^{1}H NMR Spectra of diethyl (2-(methylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ja**

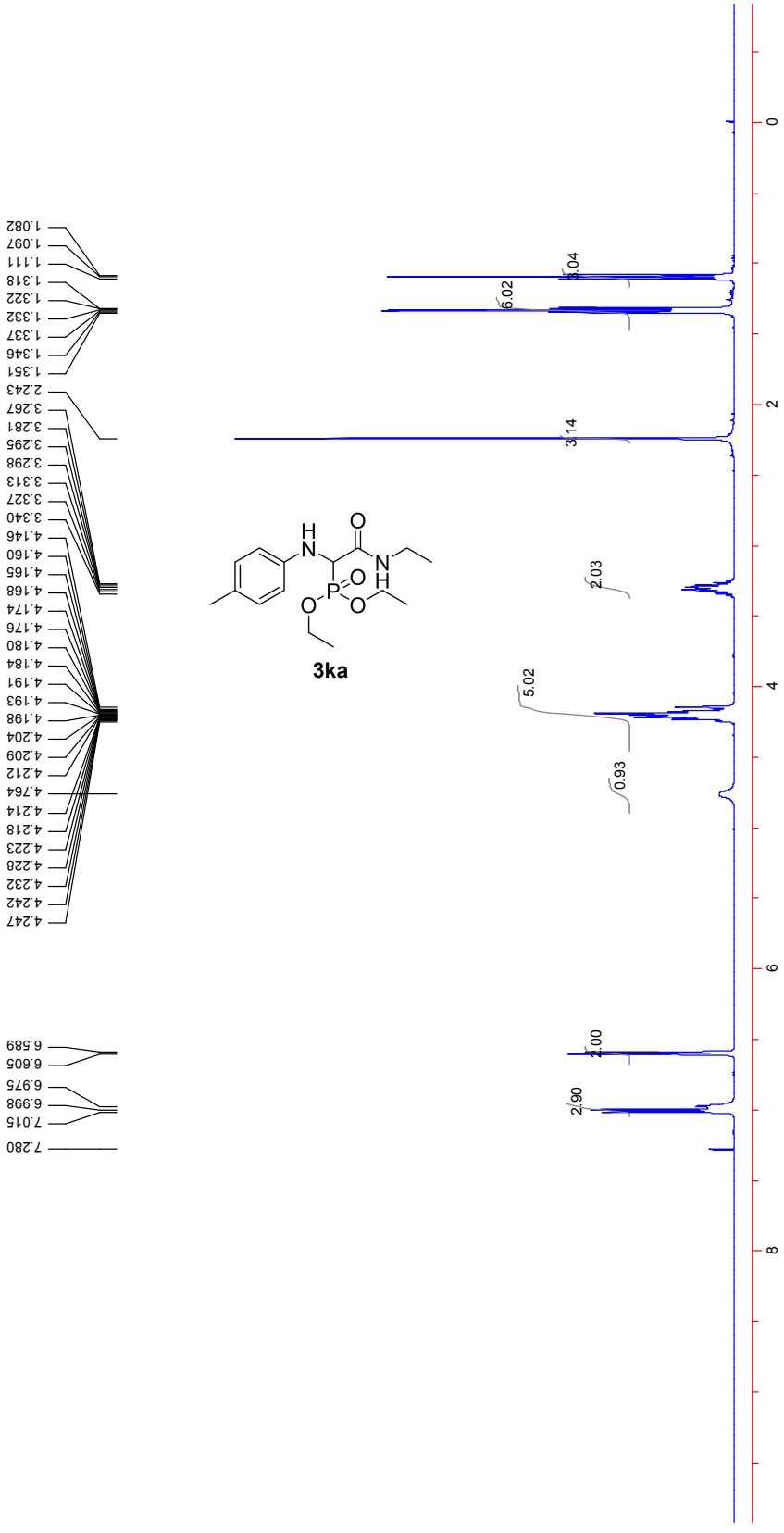


^{13}C NMR Spectra of diethyl (2-(methylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ja**

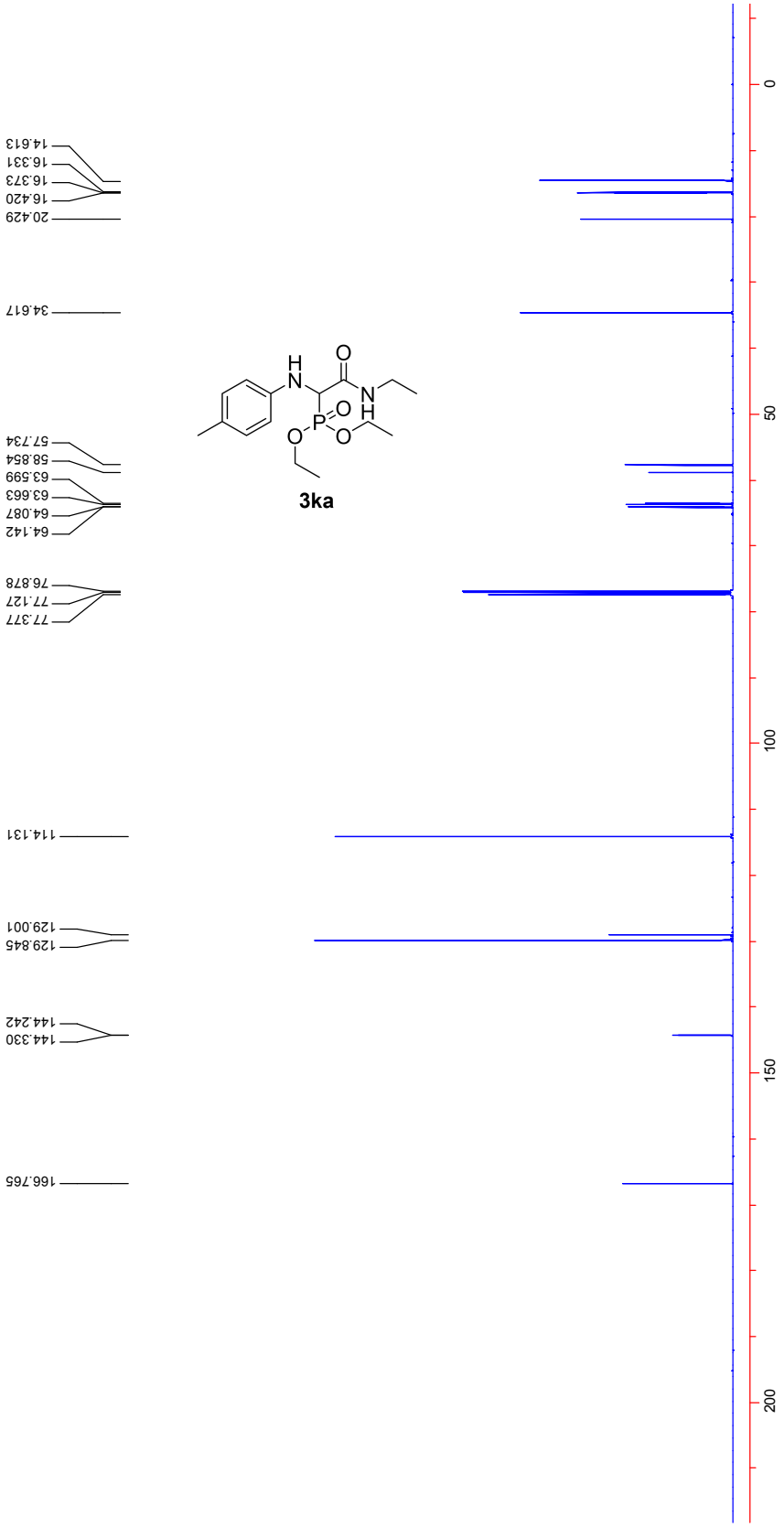


^{1}H NMR Spectra of diethyl (2-(ethylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate

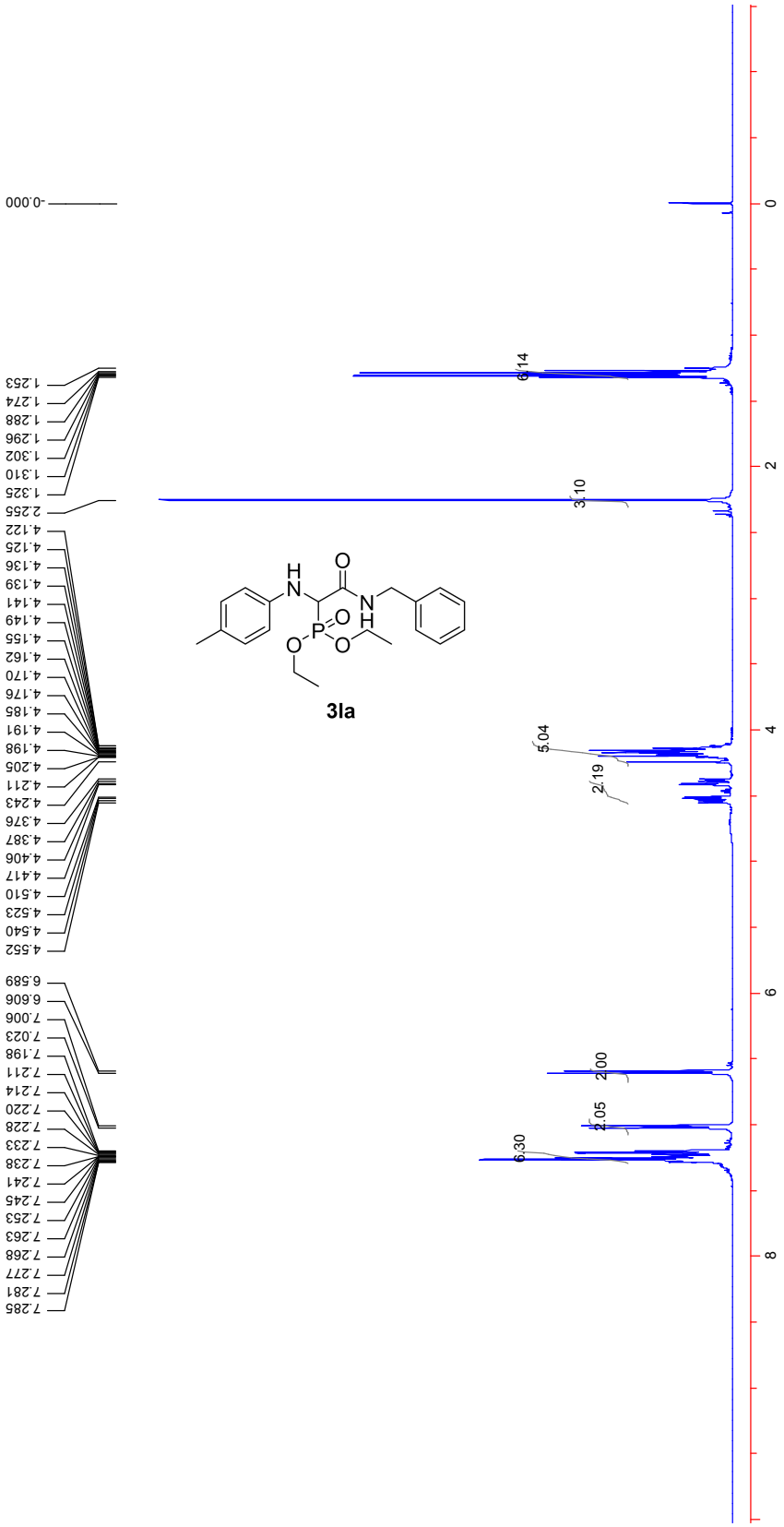
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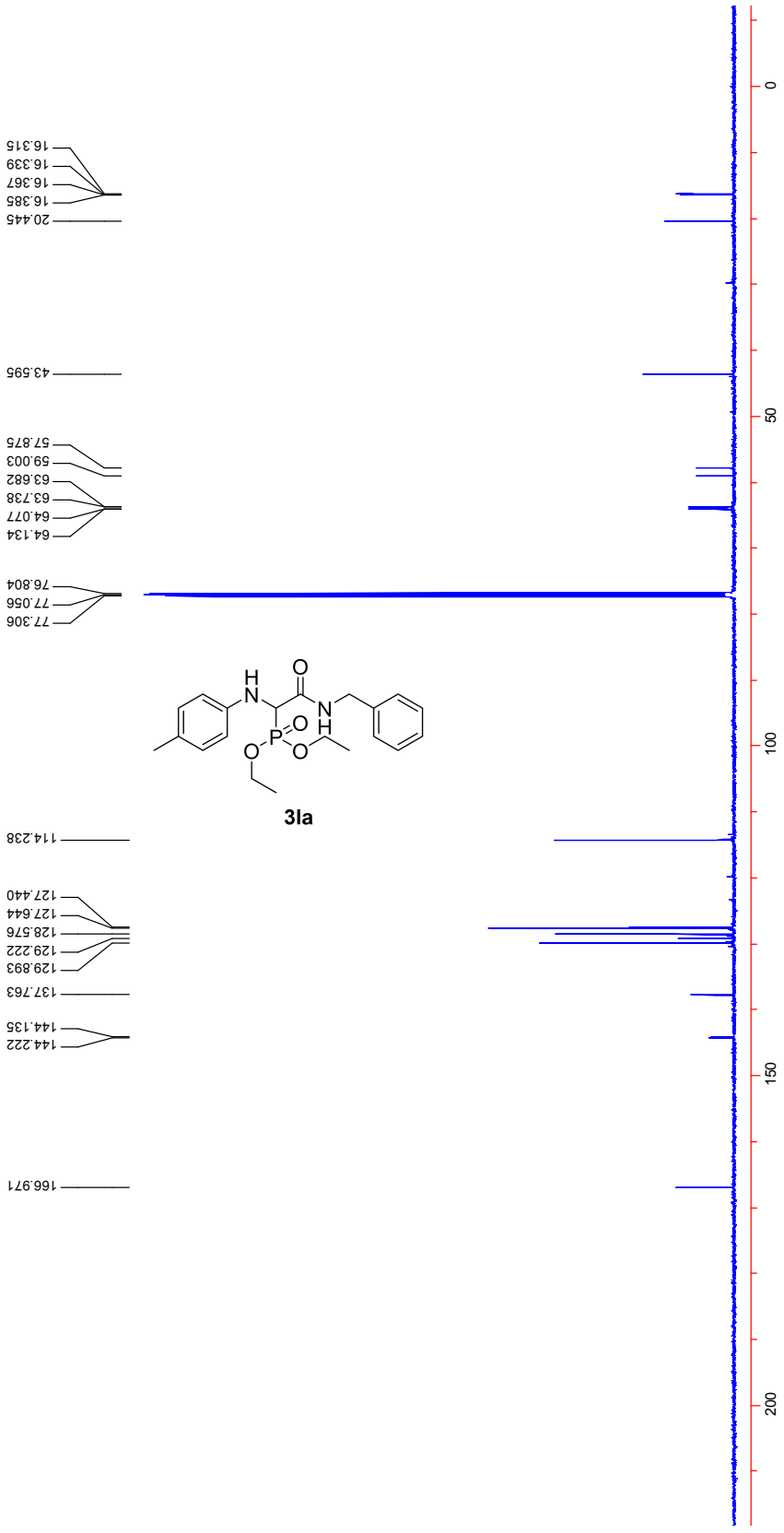
^{13}C NMR Spectra of diethyl (2-(ethylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ka**



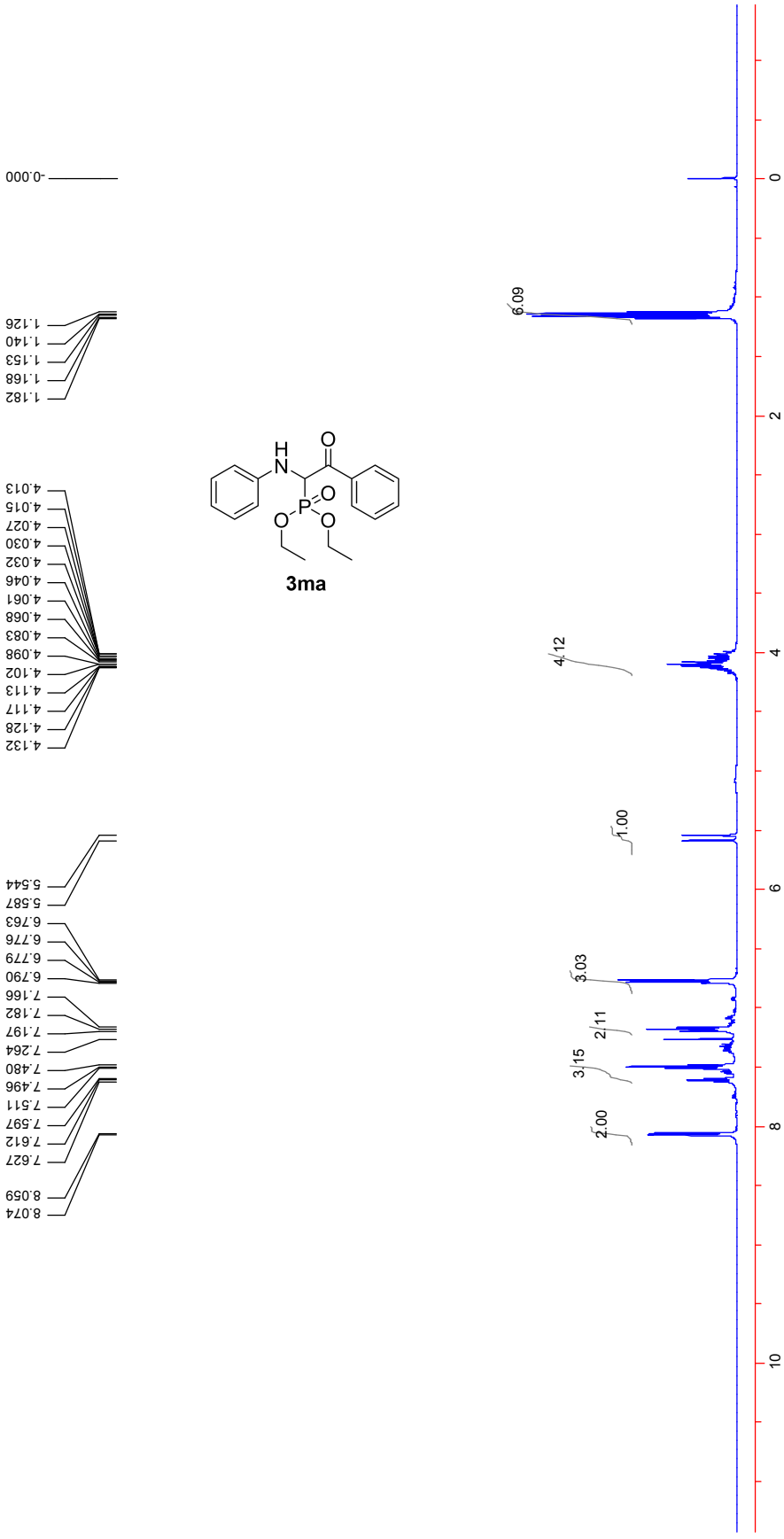
^{1}H NMR Spectra of diethyl (2-(benzylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3la**



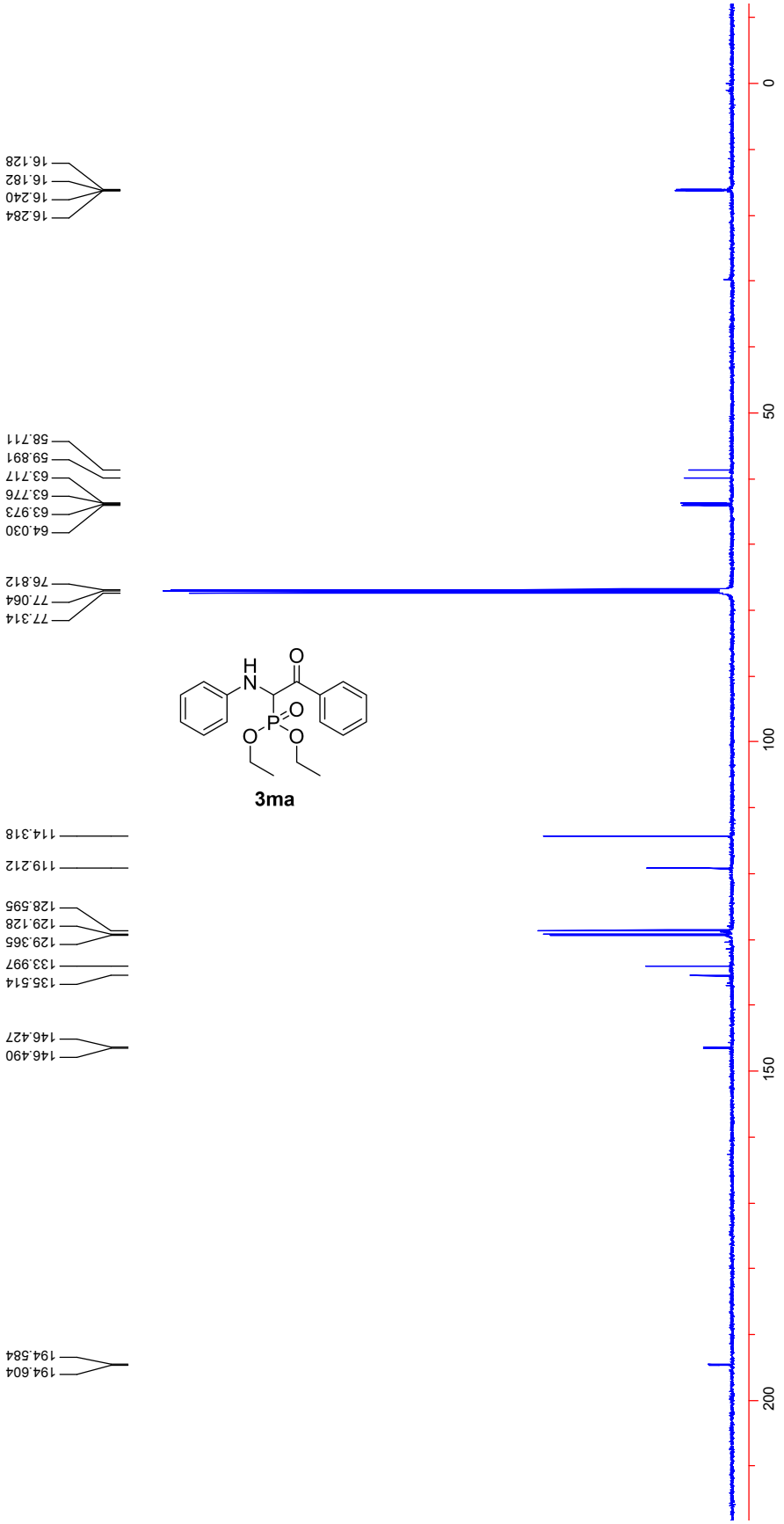
^{13}C NMR Spectra of diethyl (2-(benzylamino)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3la**



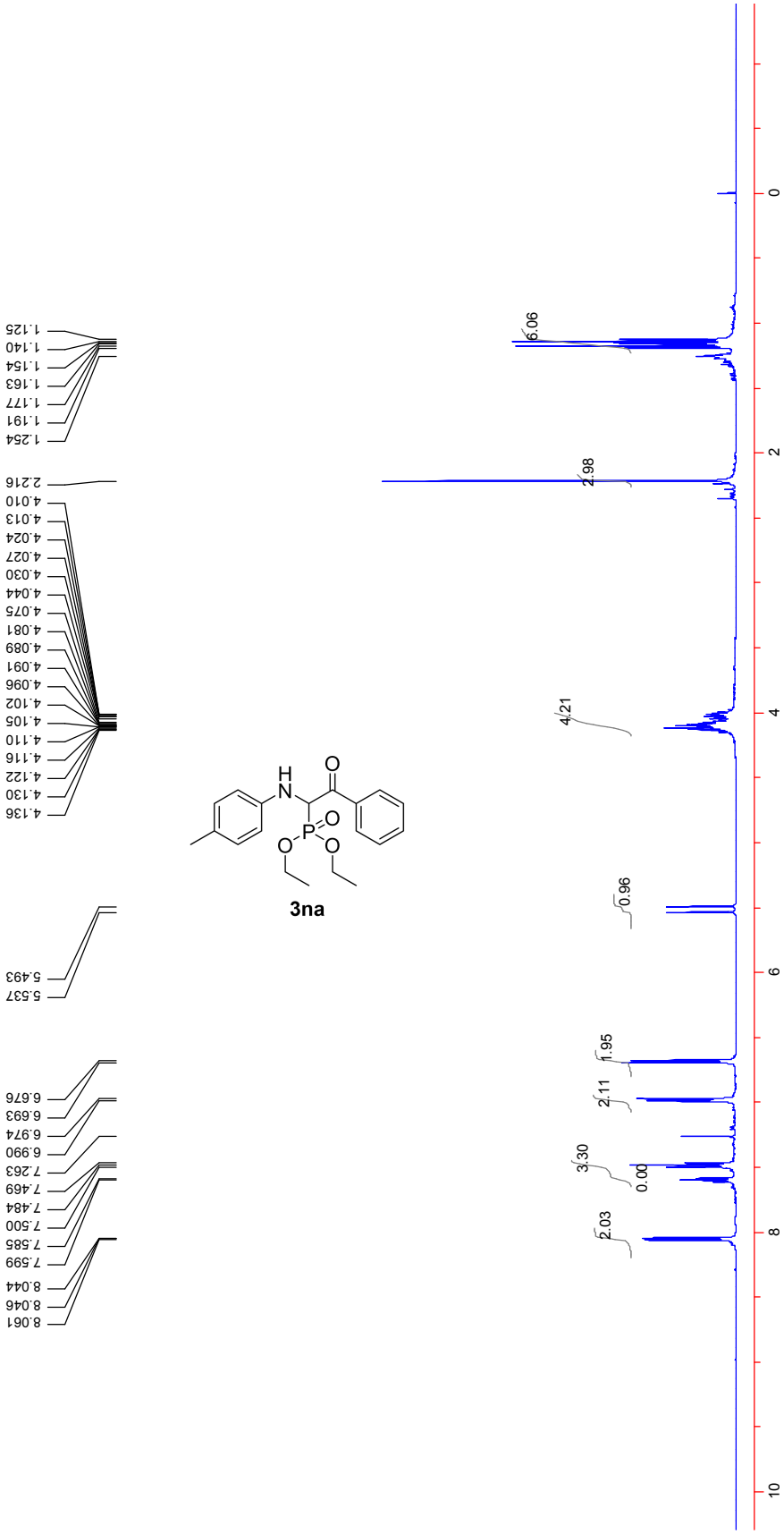
[1]H NMR Spectra of diethyl (2-oxo-2-phenyl-1-(phenylamino)ethyl)phosphonate **3ma**



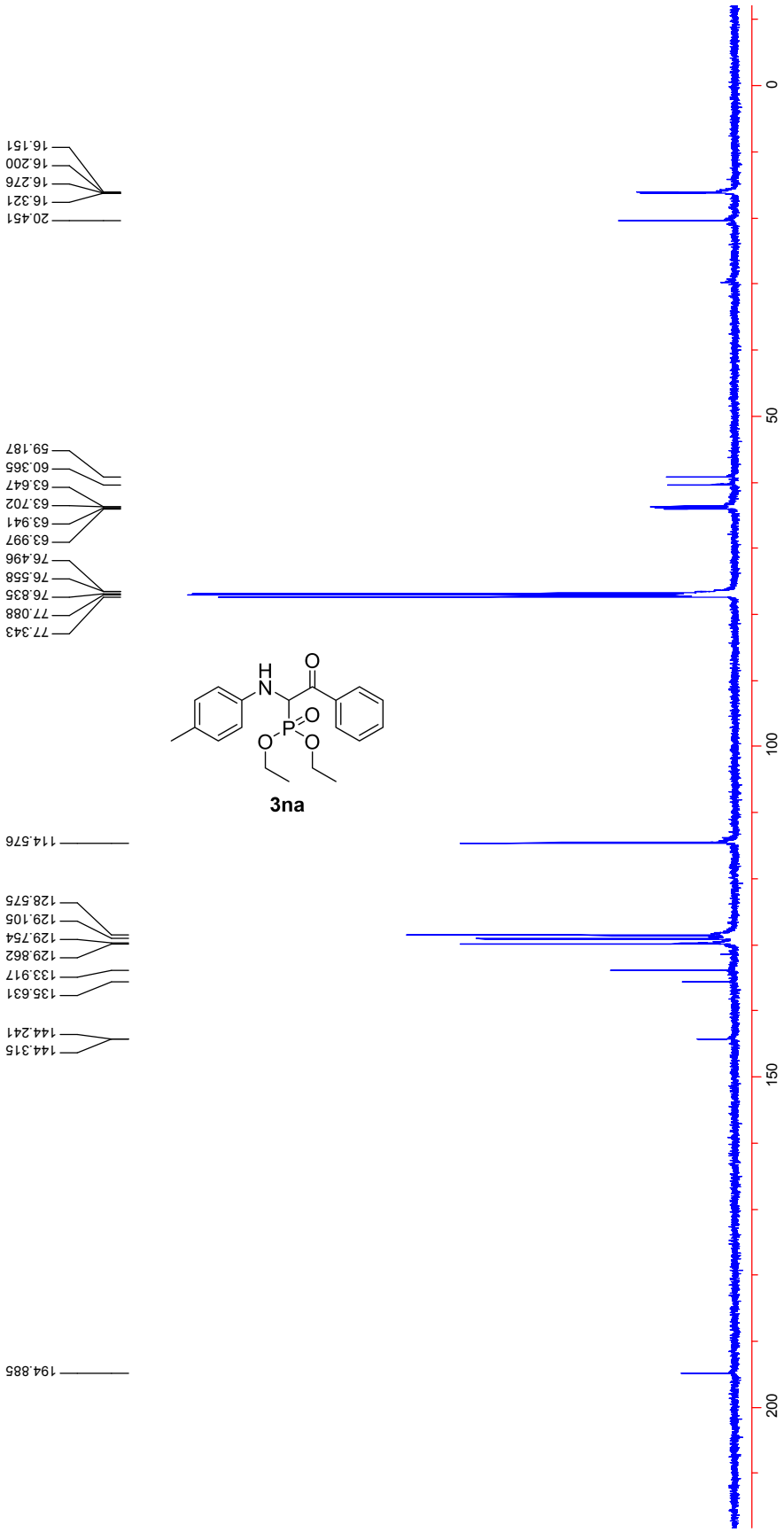
^{13}C NMR Spectra of diethyl (2-oxo-2-phenyl-1-(phenylamino)ethyl)phosphonate **3ma**



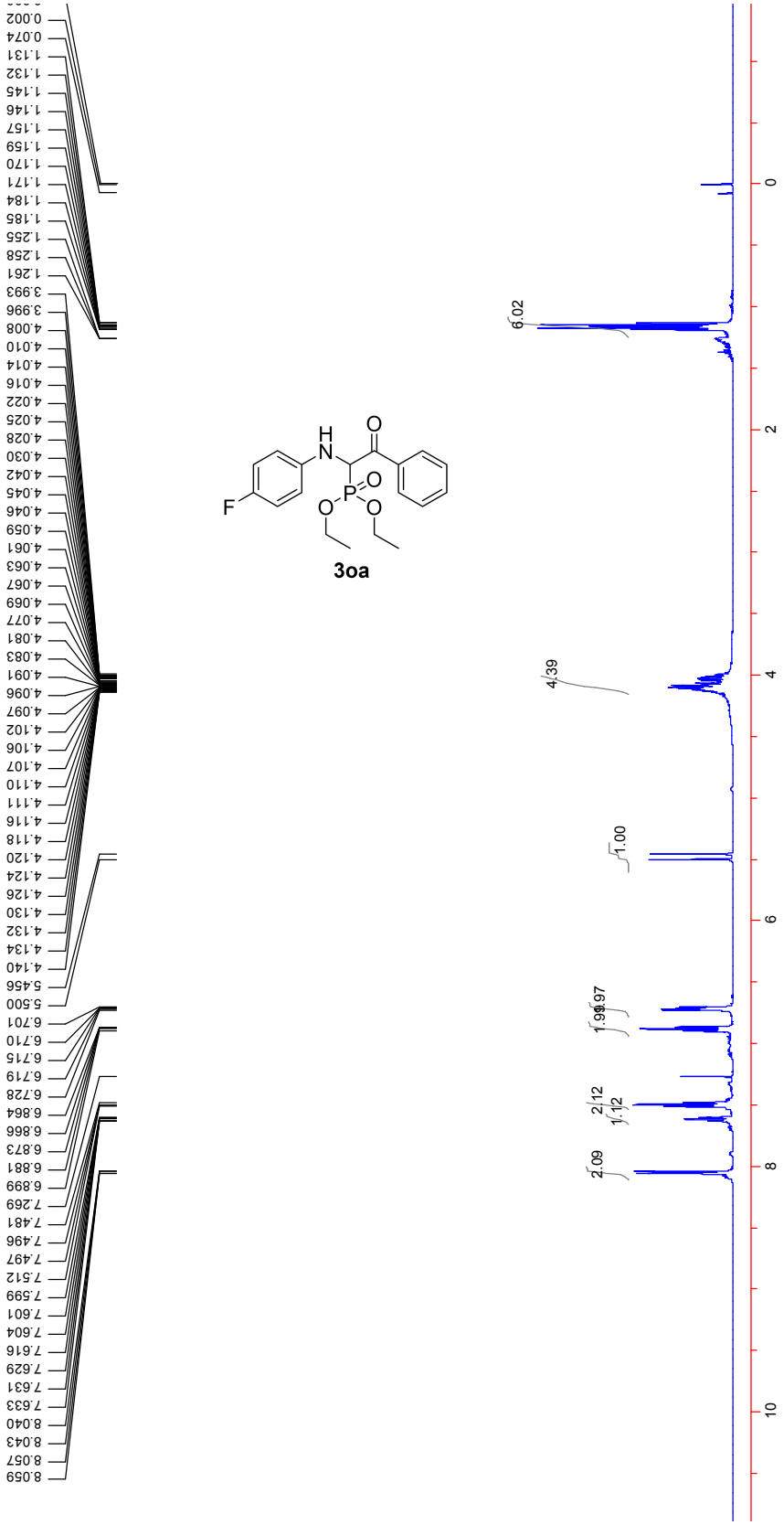
[1]H NMR Spectra of diethyl (2-oxo-2-phenyl-1-(*p*-tolylamino)ethyl)phosphonate **3na**



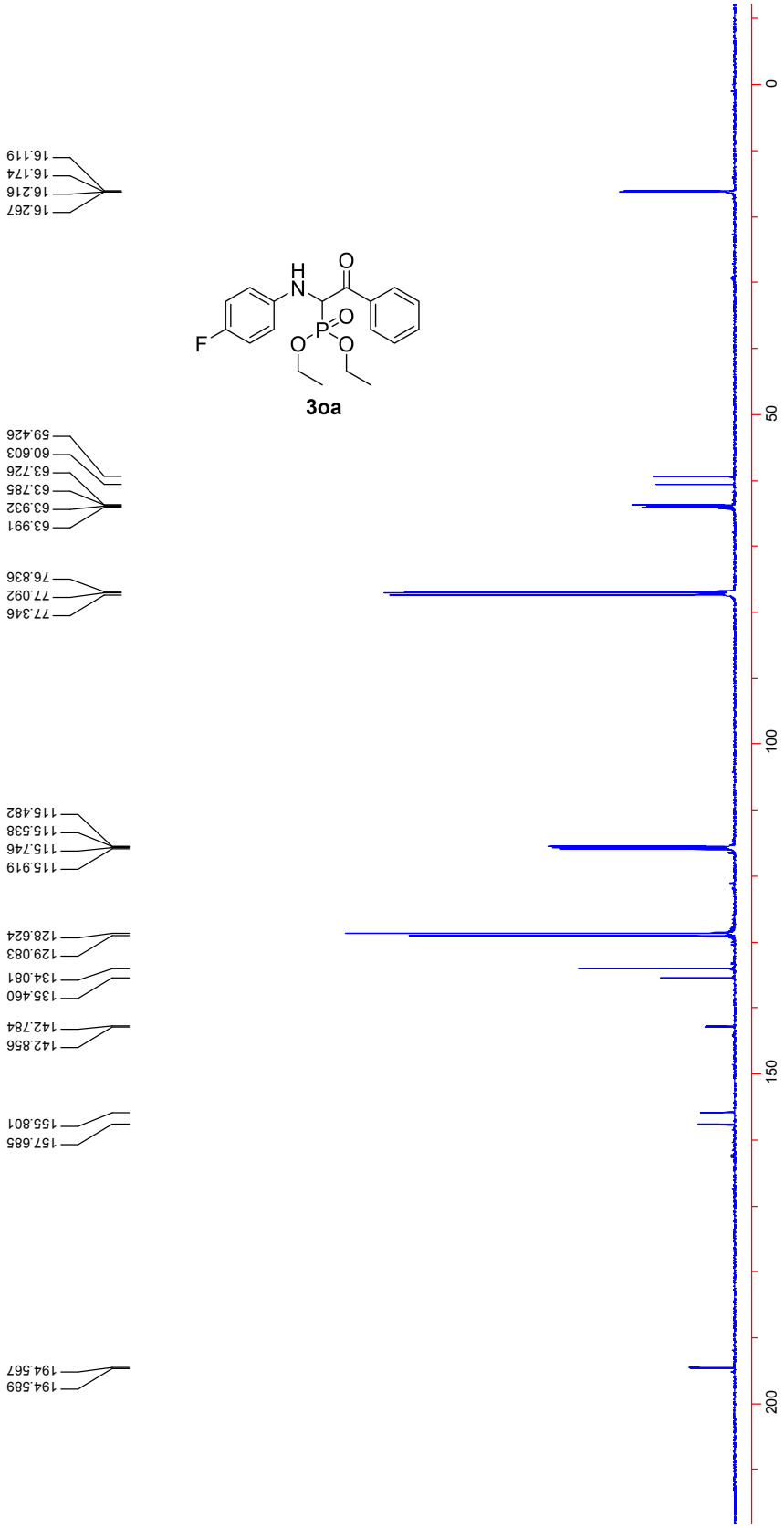
^{13}C NMR Spectra of diethyl (2-oxo-2-phenyl-1-(*p*-tolylamino)ethyl)phosphonate **3na**



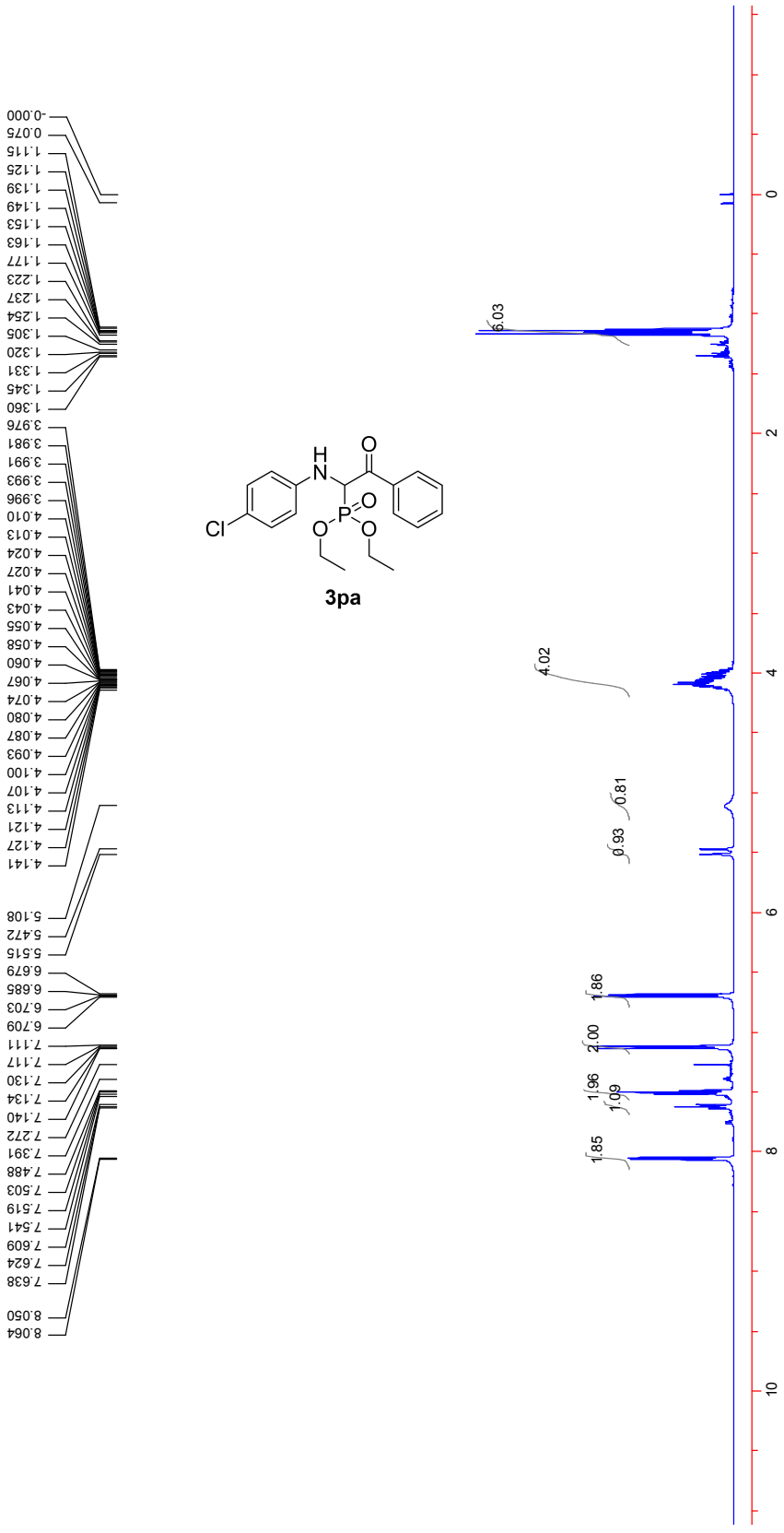
^{1}H NMR Spectra of diethyl (1-((4-fluorophenyl)amino)-2-oxo-2-phenylethyl)phosphonate **3oa**



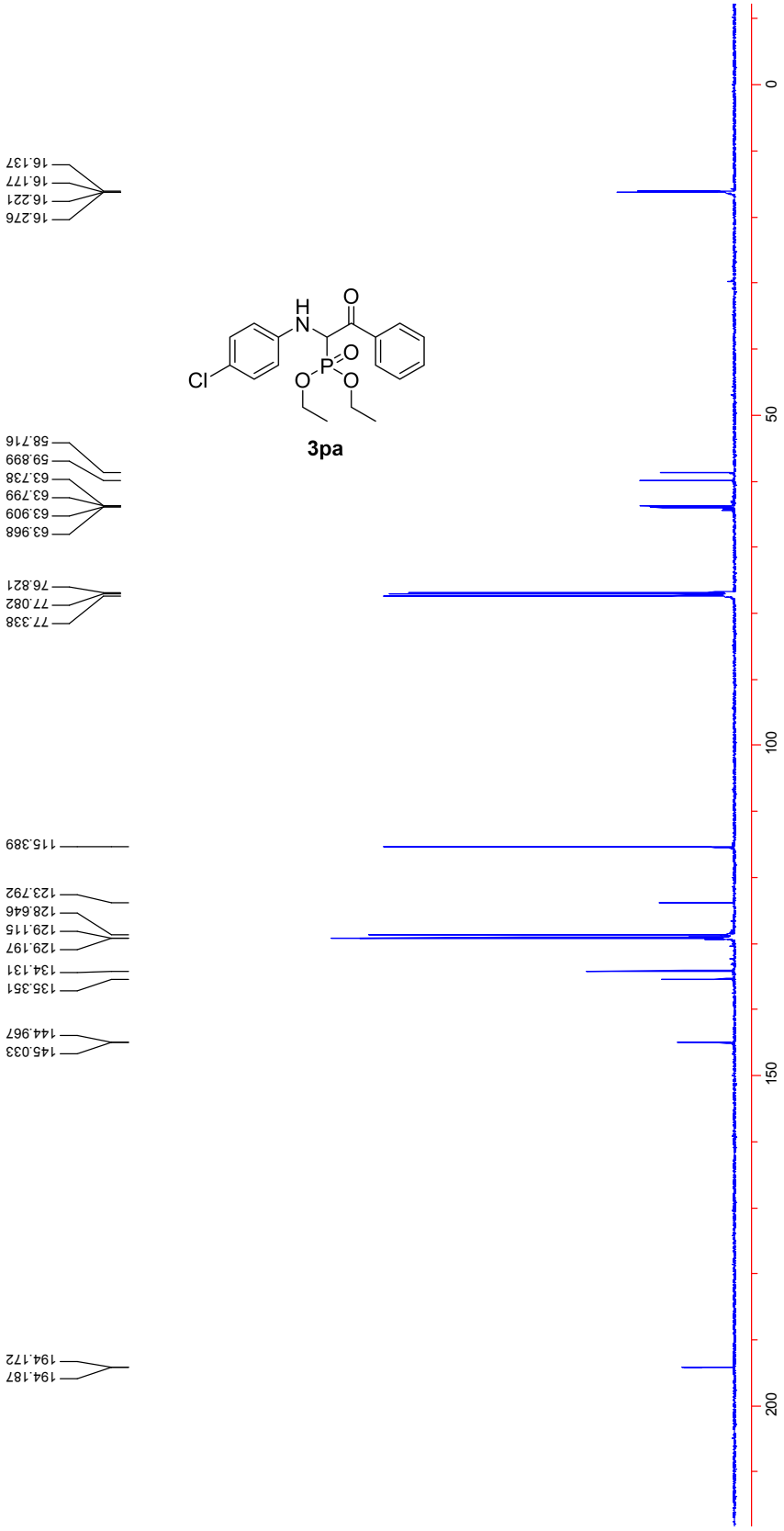
^{13}C NMR Spectra of diethyl (1-((4-fluorophenyl)amino)-2-oxo-2-phenylethyl)phosphonate **3oa**



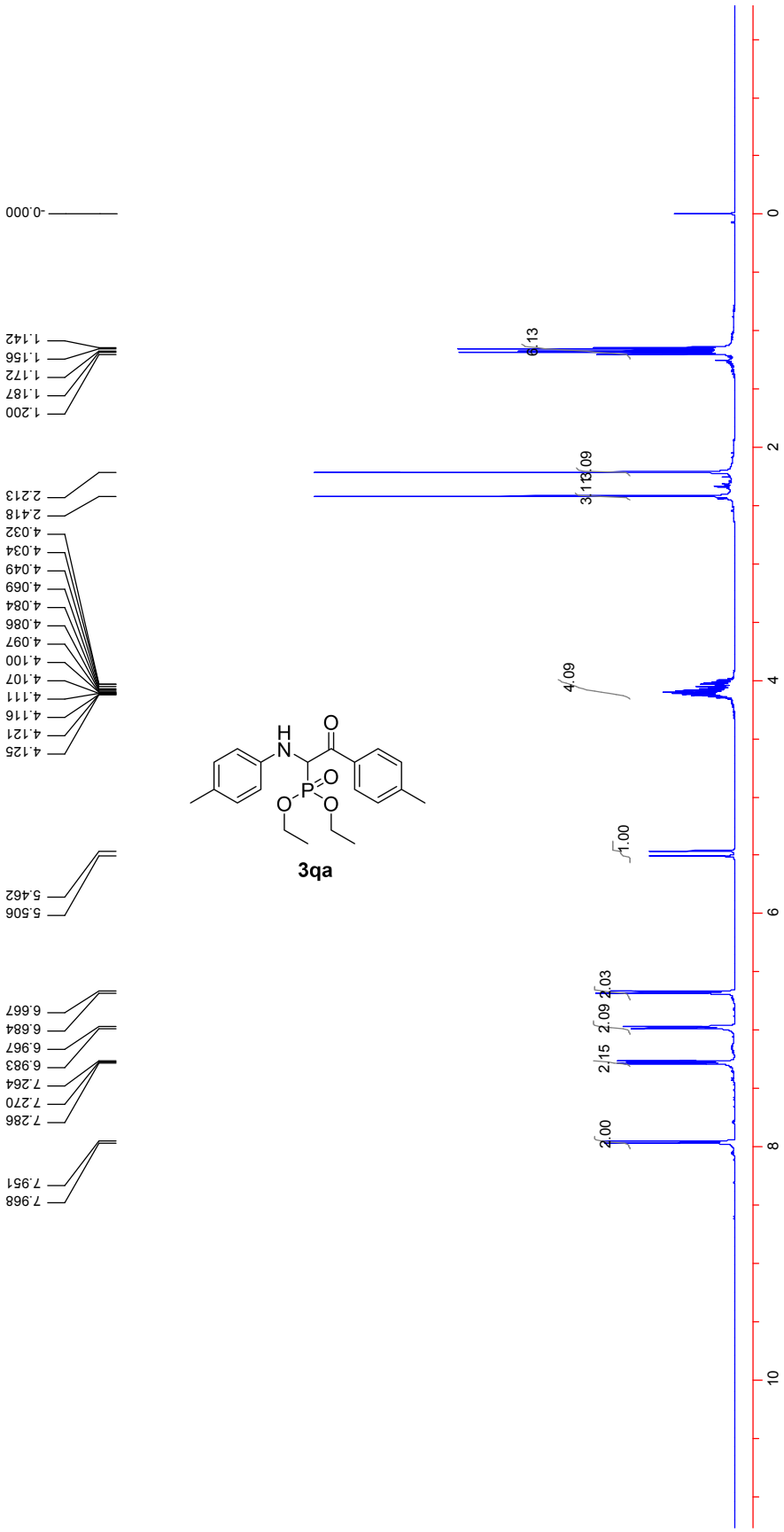
^{1}H NMR Spectra of diethyl (1-((4-chlorophenyl)amino)-2-oxo-2-phenylethyl)phosphonate **3pa**



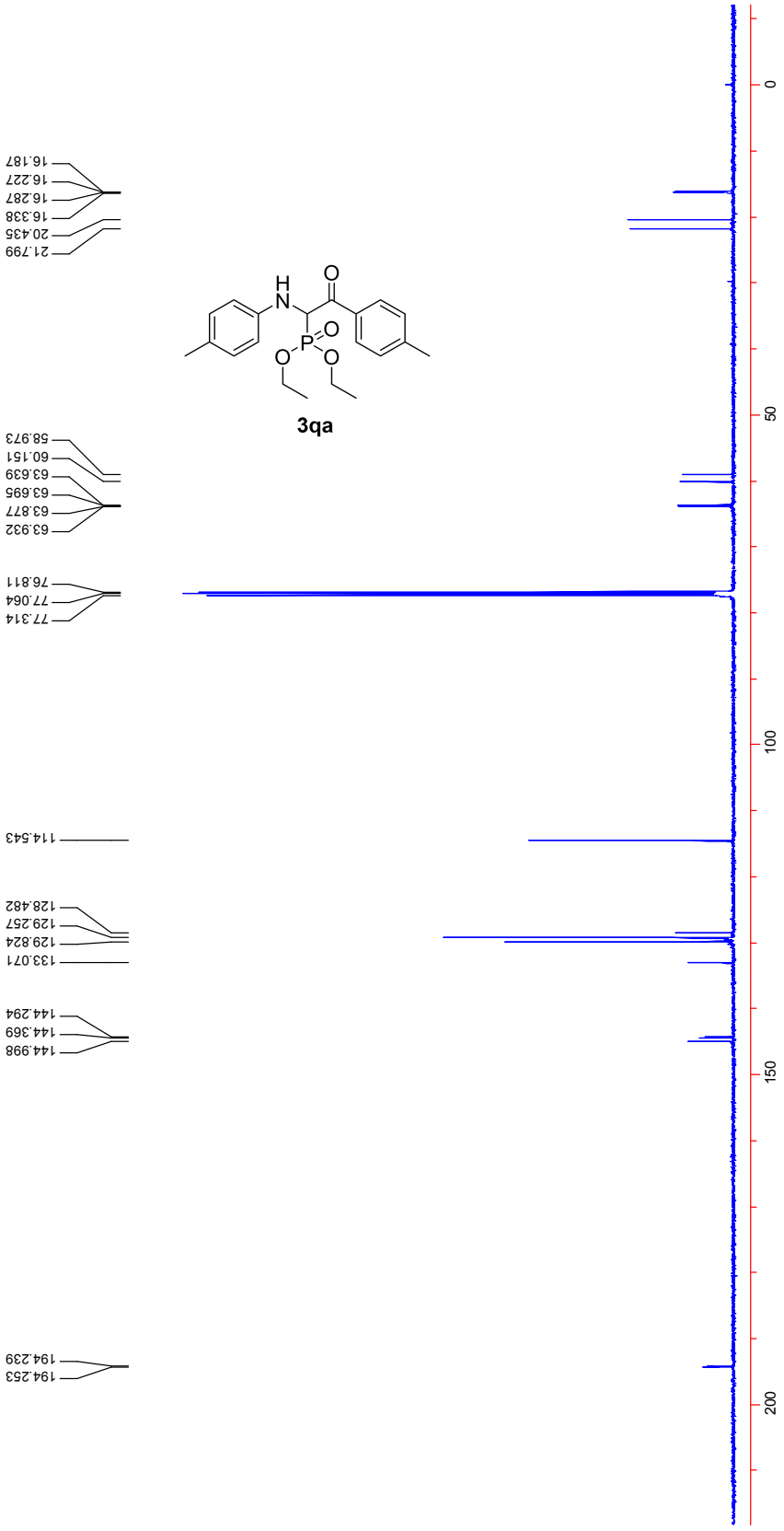
^{13}C NMR Spectra of diethyl (1-((4-chlorophenyl)amino)-2-oxo-2-phenylethyl)phosphonate **3pa**



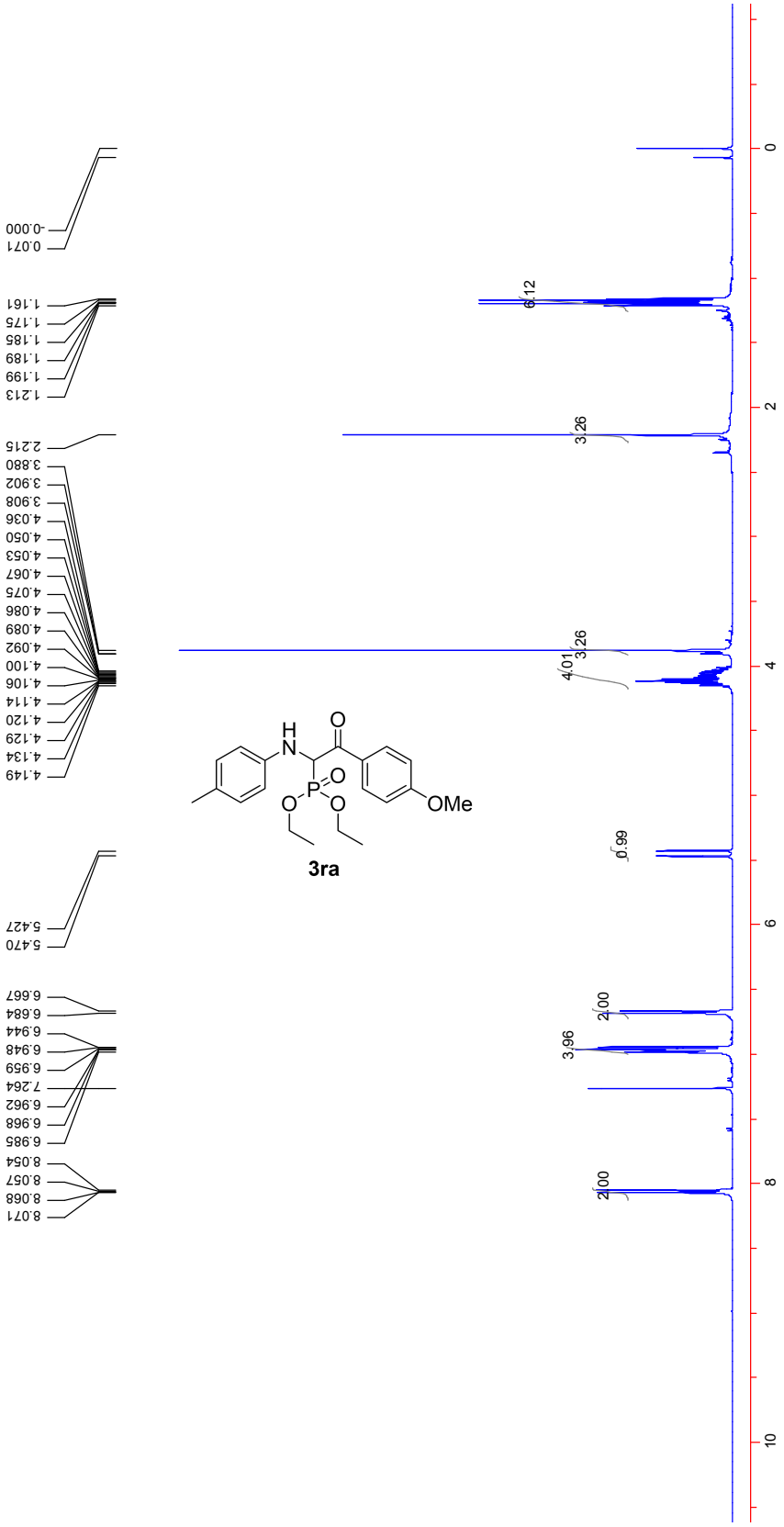
[1]H NMR Spectra of diethyl (2-oxo-2-(*p*-tolyl)-1-(*p*-tolylamino)ethyl)phosphonate **3qa**



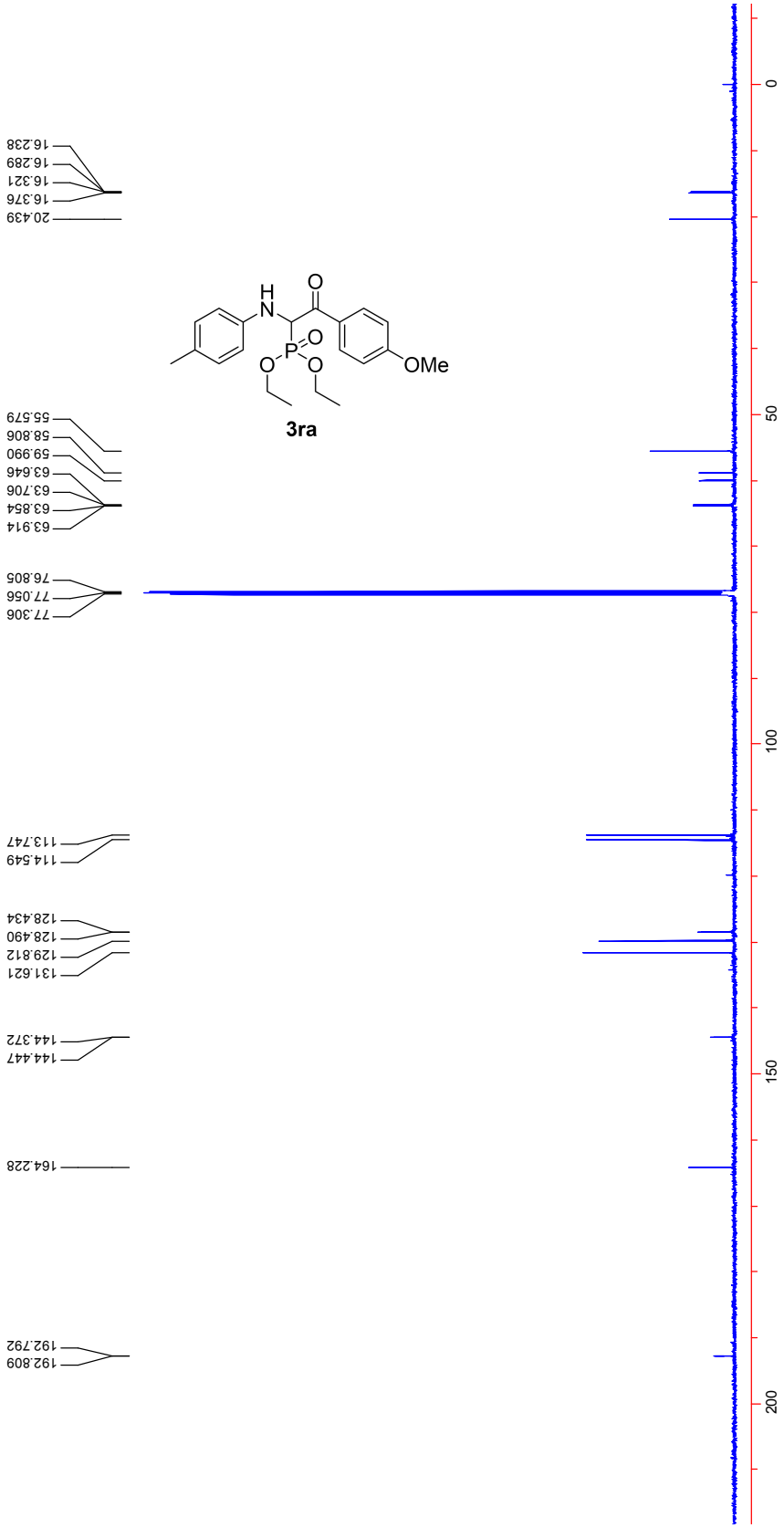
^{13}C NMR Spectra of diethyl (2-oxo-2-(*p*-tolyl)-1-(*p*-tolylamino)ethyl)phosphonate **3qa**



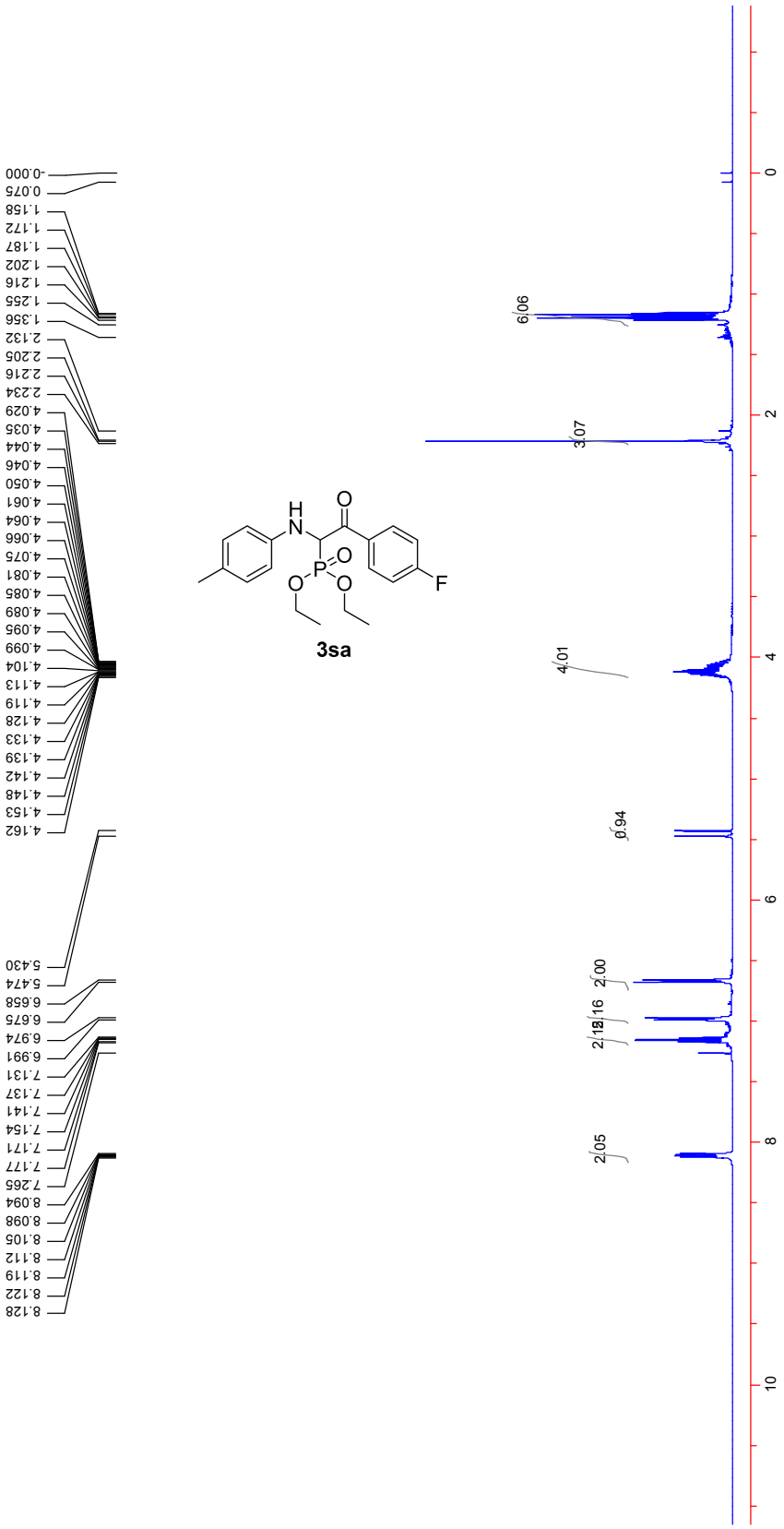
^{1}H NMR Spectra of diethyl (2-(4-methoxyphenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ra**



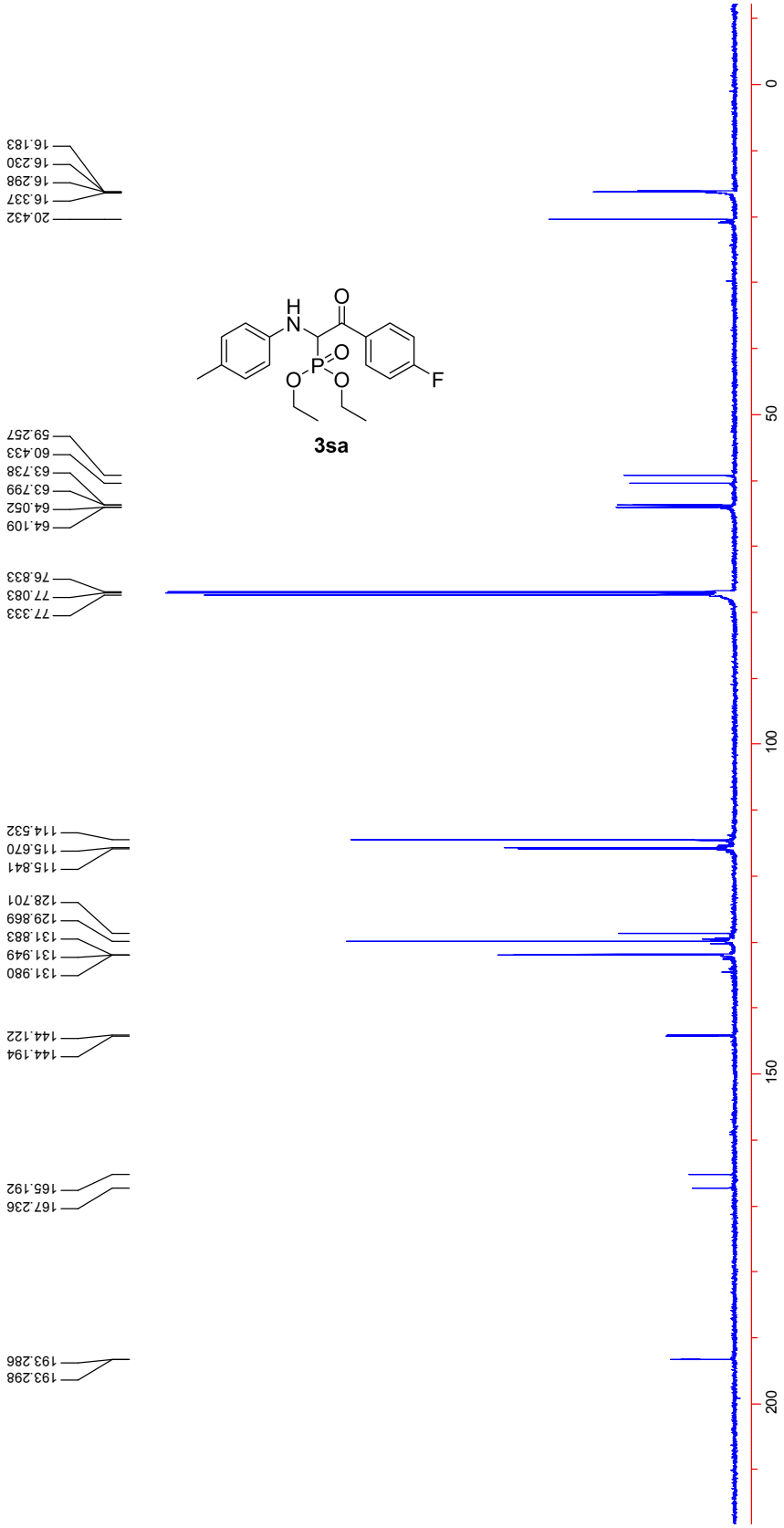
^{13}C NMR Spectra of diethyl (2-(4-methoxyphenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ra**



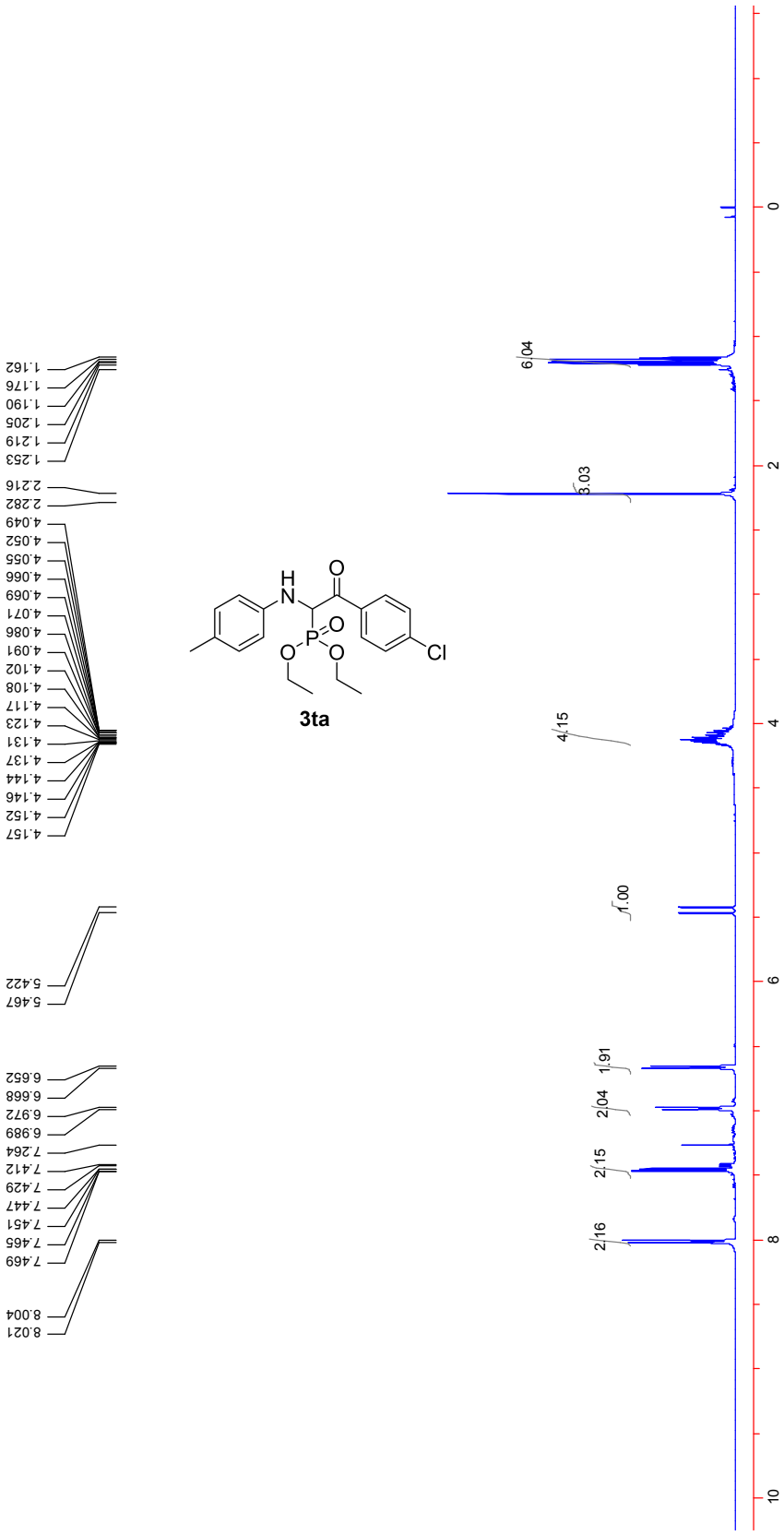
^{1}H NMR Spectra of diethyl (2-(4-fluorophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3sa**



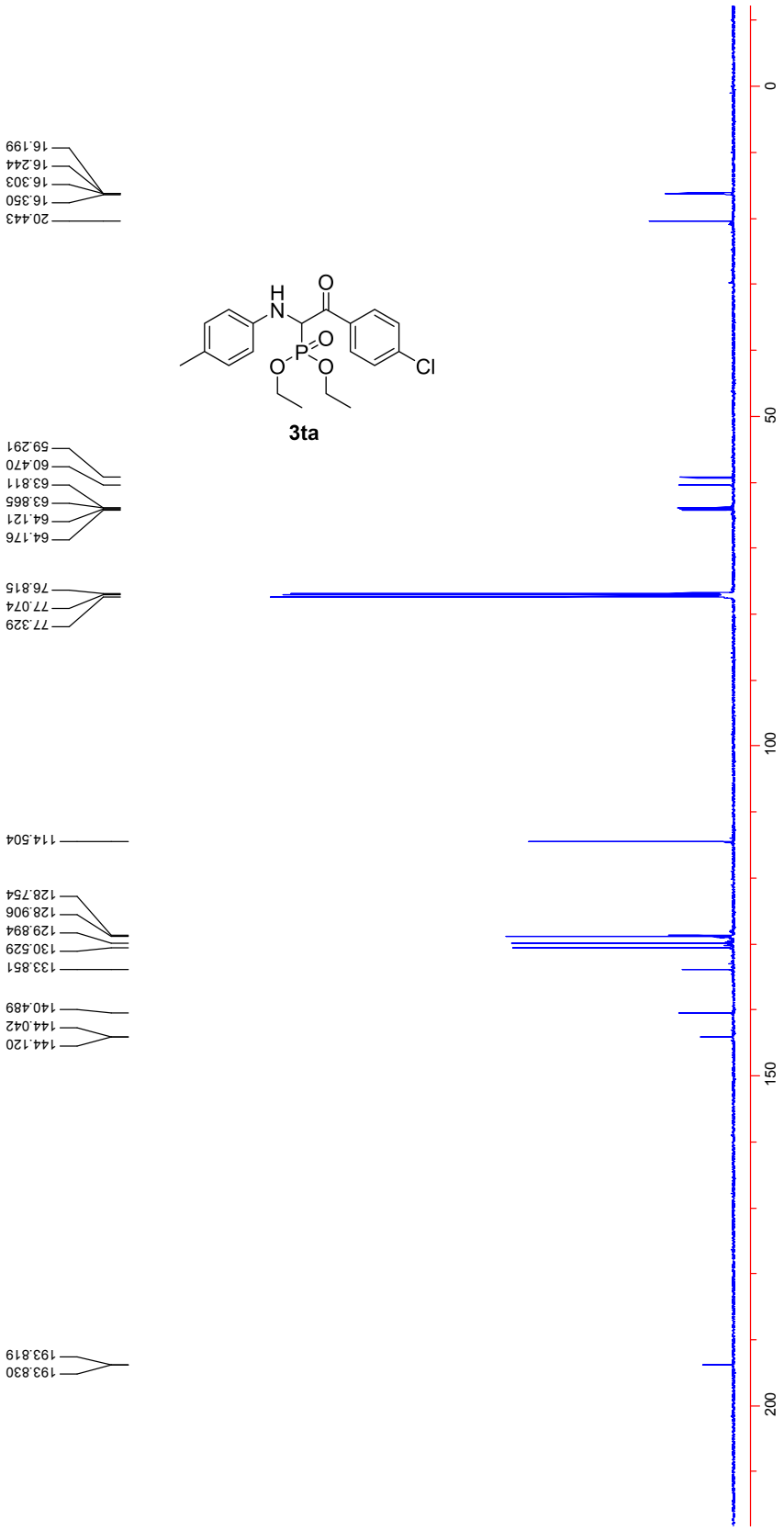
^{13}C NMR Spectra of diethyl (2-(4-fluorophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3sa**



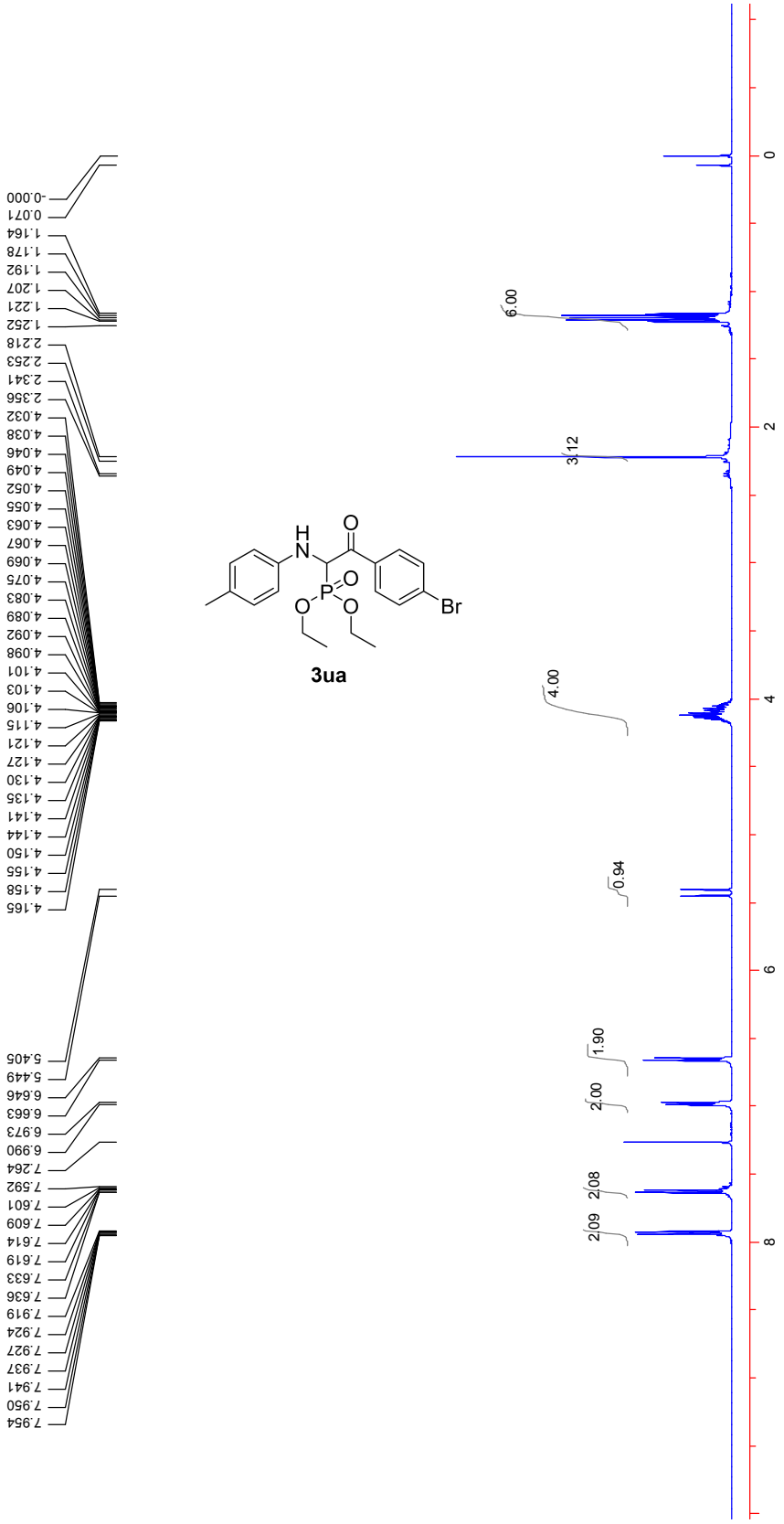
^{1}H NMR Spectra of diethyl (2-(4-chlorophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ta**



^{13}C NMR Spectra of diethyl (2-(4-chlorophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ta**



^{13}C NMR Spectra of diethyl (2-(4-bromophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ua**



^{1}H NMR Spectra of diethyl (2-(4-bromophenyl)-2-oxo-1-(*p*-tolylamino)ethyl)phosphonate **3ua**

