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Article

1-(*N*-Acylamino)alkyltriarylphosphonium salts with modulated C_{α}-P^{+} bond strength—synthetic application

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Supporting information

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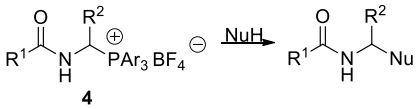
Table S1. Comparison of conditions and yields for reactions of 1-(*N*-acylamino)alkyltriphenylphosphonium salts (former studies) and 1-(*N*-acylamino)alkyltriarylphosphonium salts (the current work) with selected nucleophiles



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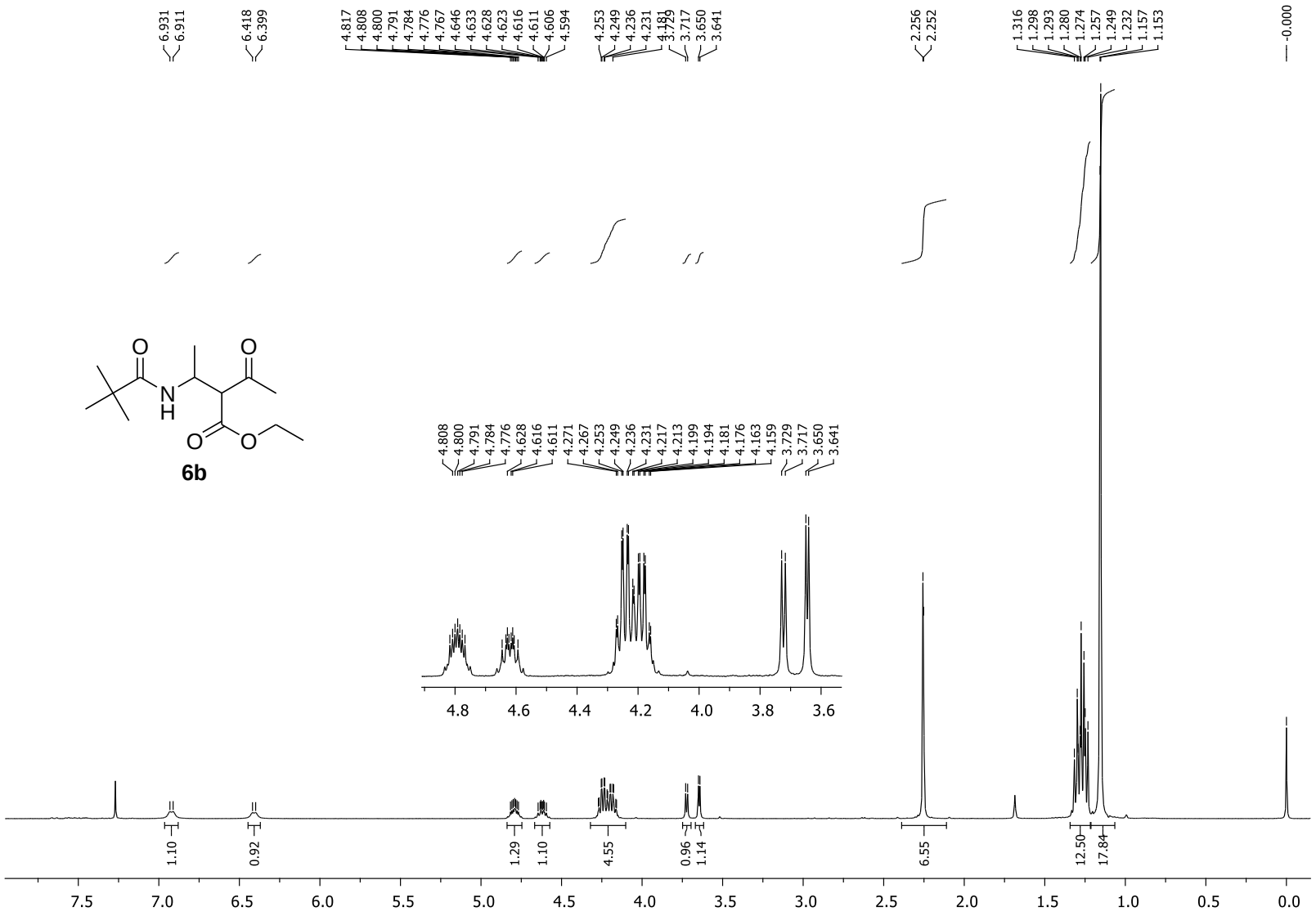
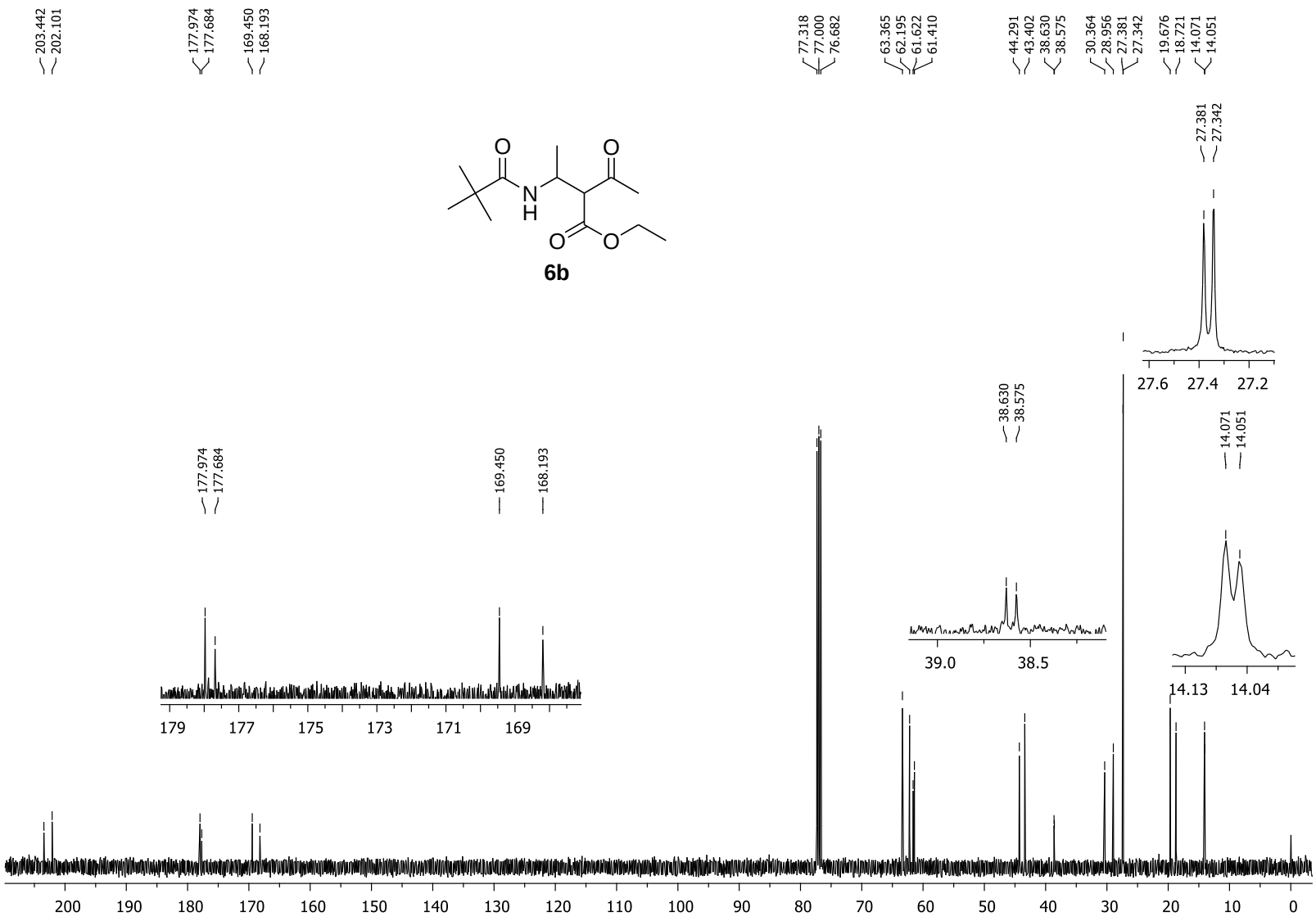
Ar = Ph, *m*-C_6H_4Cl, *p*-$C_6H_4CF_3$

Entry	Phosphonium salt 4				Nucleophile	Solvent	Catalyst	Temp., °C	MW	Time, min	Product	Yield, %	References[a]
	R^1	R^2	Ar	X									
1	*t*-Bu	Me	*m*-C_6H_4Cl	BF_4	diethyl malonate	THF	LDA	20	-	15	**6a**	65	this work
2	*t*-Bu	Me	*p*-$C_6H_4CF_3$	BF_4	diethyl malonate	THF	LDA	20	-	15	**6a**	67	this work
3	*t*-Bu	Me	Ph	BF_4	diethyl malonate	THF	LDA	20	-	15	**6a**	21	this work
4	*t*-Bu	Me	Ph	I	diethyl malonate	CH_3CN	DBU	60	10-12 W[b]	90	**6a**	61	[8]
5[c]	*t*-Bu	Me	*m*-C_6H_4Cl	BF_4	1-morpholinocyclohexene	CH_3CN		20	-	60	**8a**	63	this work
6[c]	Ph	Me	Ph	I	1-morpholinocyclohexene	CH_3CN	(*i*-Pr)$_2$EtN	60	8W[b]	60	**8f**	76	[8]
7	*t*-Bu	Me	*p*-$C_6H_4CF_3$	BF_4	Bt^-Na^+	$CHCl_3$	-	20	-	15	**10a**	99	this work
8	*t*-Bu	Me	Ph	BF_4	Bt^-Na^+	$CHCl_3$	-	20	-	120	**10a**	90	[6]
9	BnO	Bn	*m*-C_6H_4Cl	BF_4	Bt^-Na^+	$CHCl_3$	-	20	-	15	**10b**	70	this work
10	BnO	Bn	Ph	BF_4	Bt^-Na^+	$CHCl_3$	-	20	-	120	**10b**	74	[6]
11	*t*-Bu	Me	*p*-$C_6H_4CF_3$	BF_4	$TolSO_2^-Na^+$	$CHCl_3$	-	20	-	15	**10c**	88	this work
12	*t*-Bu	Me	Ph	BF_4	$TolSO_2^-Na^+$	$CHCl_3$	-	20	-	120	**10c**	90	[5]
13	*t*-Bu	Me	*m*-C_6H_4Cl	BF_4	$P(OMe)_3$	$CHCl_3$	-	20	-	180	**12a**	85	this work
14	*t*-Bu	Me	Ph	BF_4	$P(OMe)_3$	CH_2Cl_2	(*i*-Pr)$_2$EtN	60	-	120	**12a**	89	[7]
15	Bn	*i*-Bu	*m*-C_6H_4Cl	BF_4	$P(OMe)_3$	$CHCl_3$	-	20	-	180	**12b**	77	this work
16	Bn	*i*-Bu	Ph	BF_4	$P(OMe)_3$	CH_2Cl_2	(*i*-Pr)$_2$EtN	60	-	240	**12b**	83	[4]
17	BnO	*i*-Bu	*p*-$C_6H_4CF_3$	BF_4	Ph_2POMe	$CHCl_3$	-	20	-	180	**12e**	**83**	this work
18	BnO	*i*-Bu	Ph	BF_4	Ph_2POMe	CH_2Cl_2	(*i*-Pr)$_2$EtN	60	-	120	**12e**	56	[8]

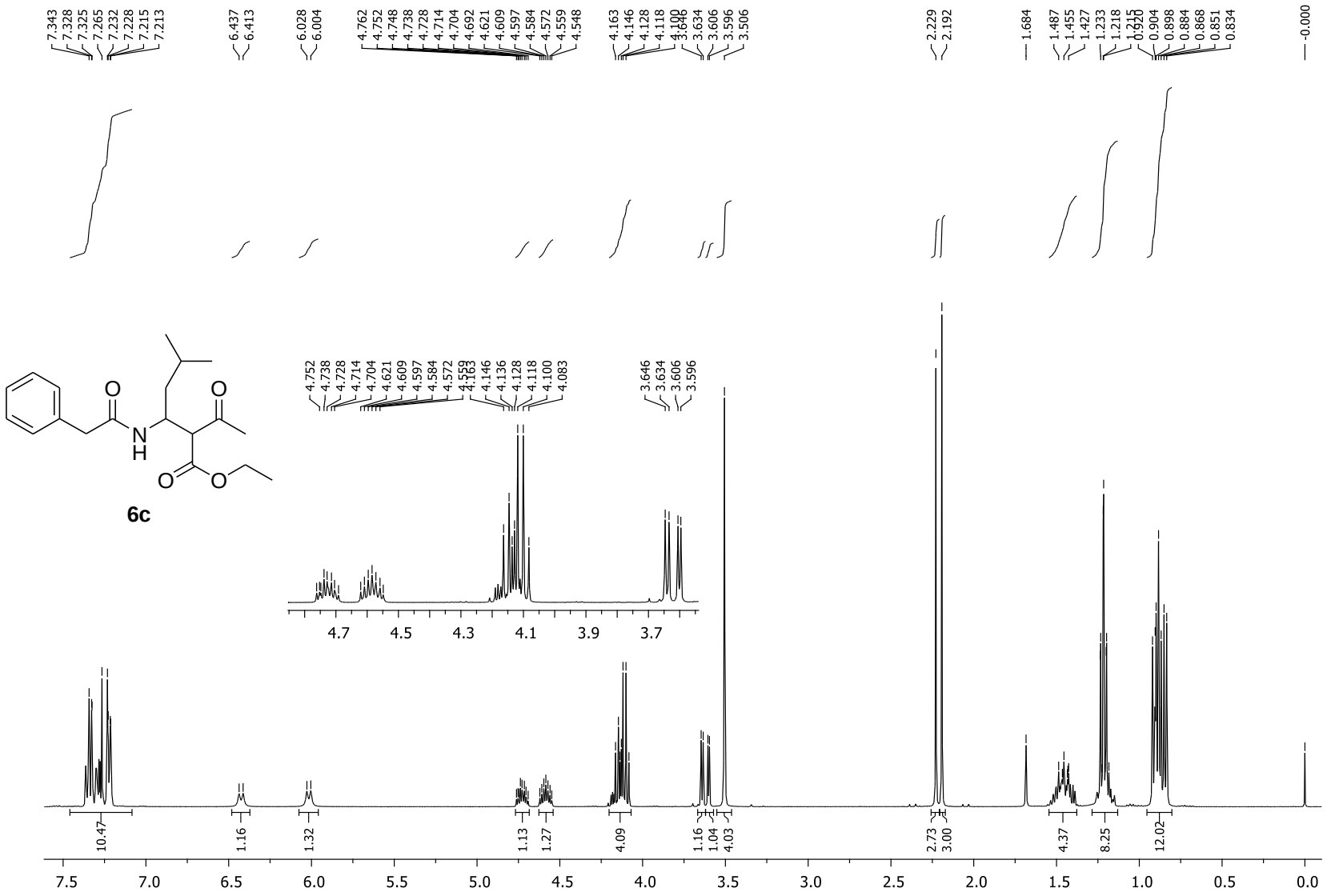
[a]See *References* in the main text of the publication. [b]The average microwave power that provides the desired reaction temperature. [c]Substrates differ slightly in structure. More accurate data are not available.



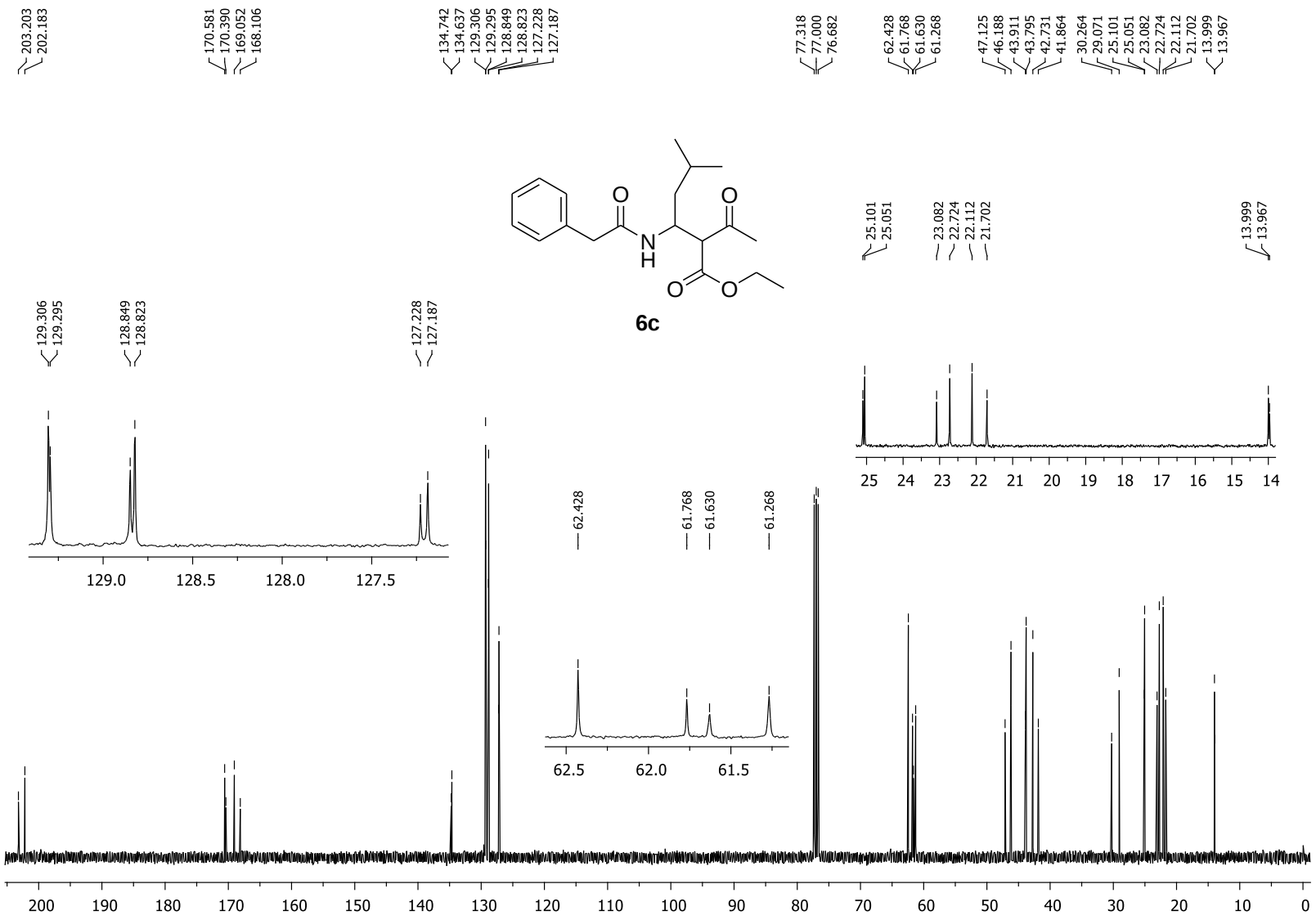
^{1}H NMR spectrum of ethyl 2-acetyl-3-(pivaloylamino)butanoate (**6b**) – the mixture of two diastereoisomers; 400 MHz/$CDCl_3$/TMS; δ (ppm).



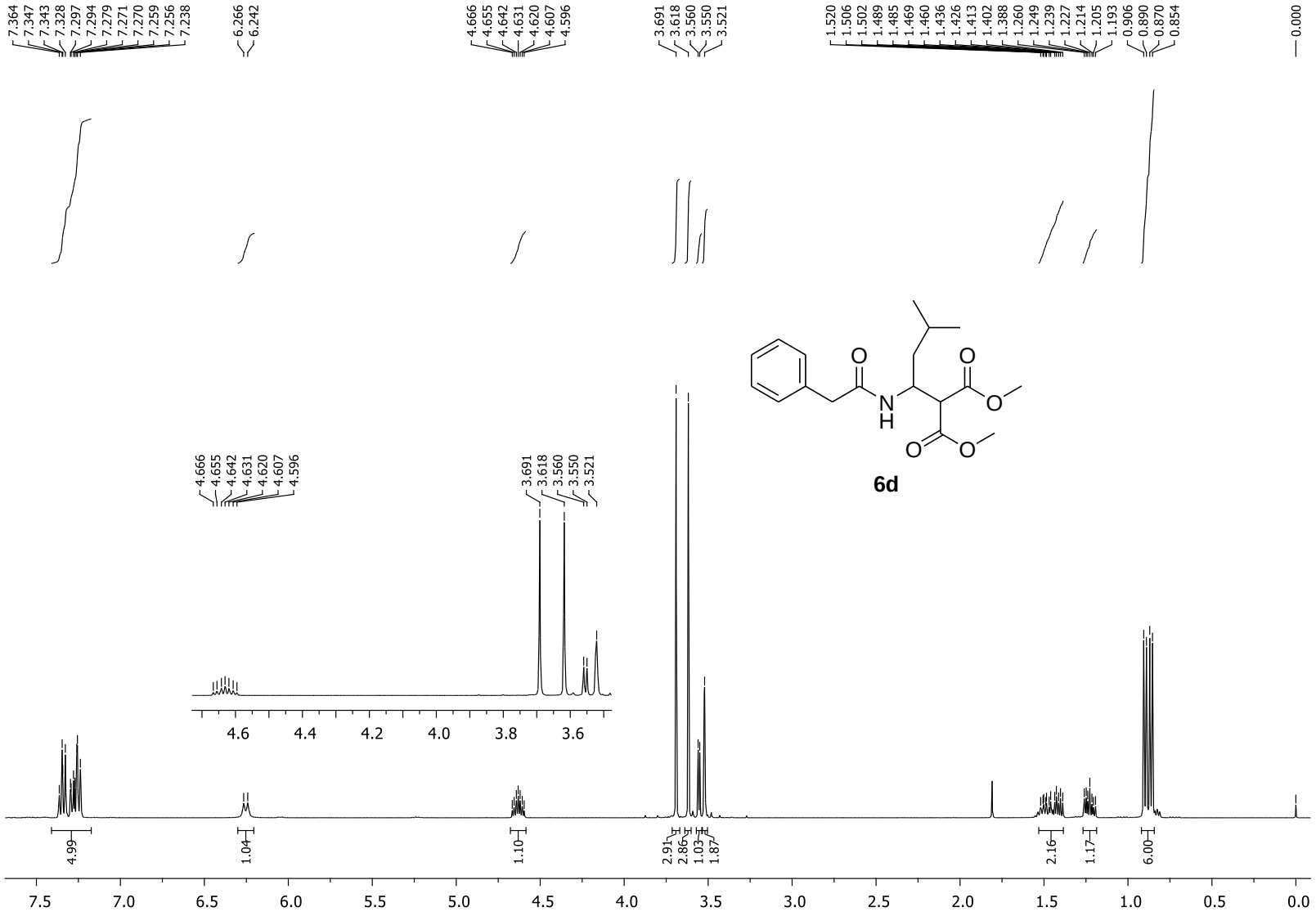
^{13}C NMR spectrum of ethyl 2-acetyl-3-(pivaloylamino)butanoate (**6b**) - the mixture of two diastereoisomers; 100 MHz/$CDCl_3$/TMS; δ (ppm).



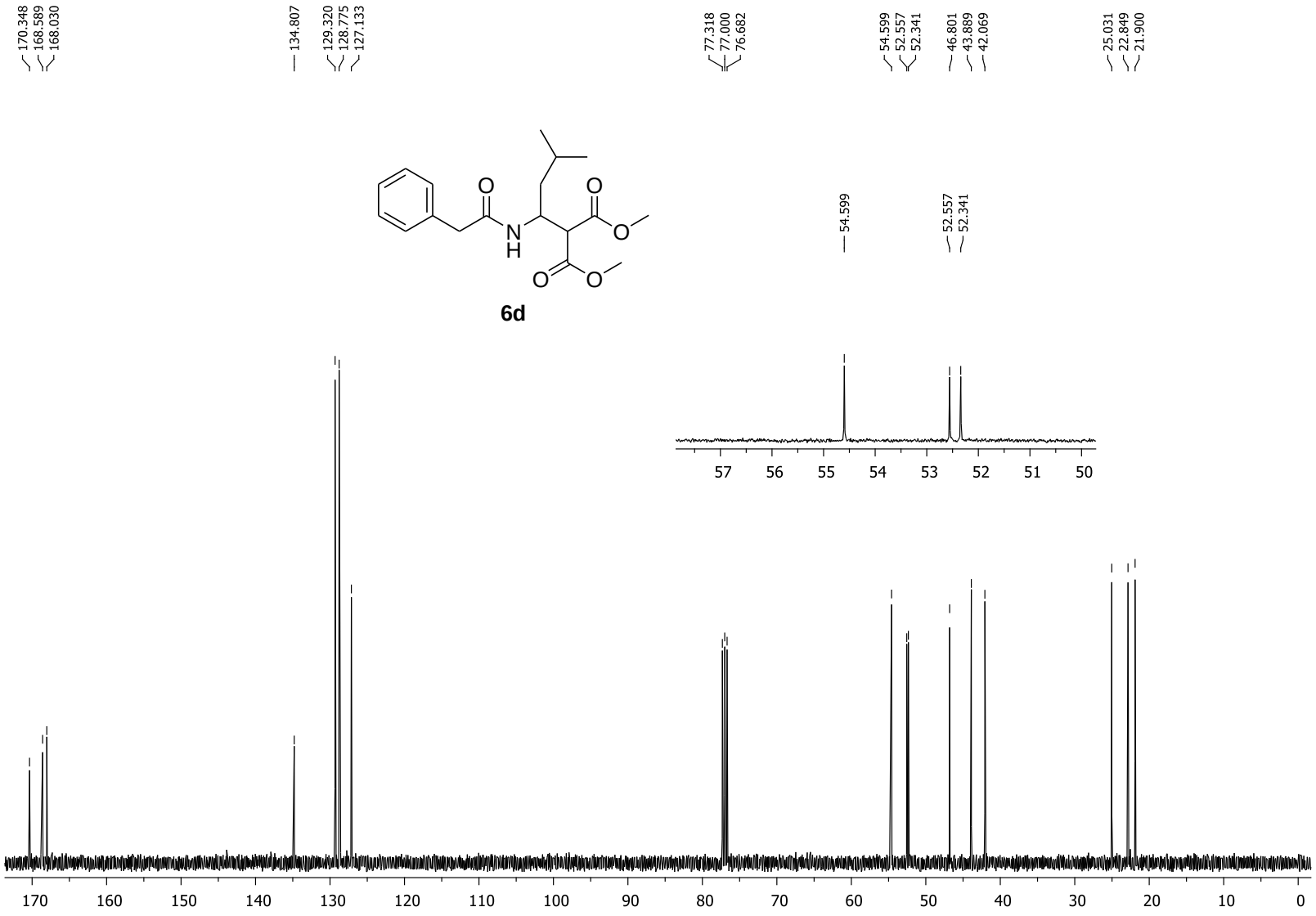
^{1}H NMR spectrum of ethyl 2-acetyl-5-methyl-3-(phenylacetylamino)hexanoate (**6c**) - the mixture of two diastereoisomers; 400 MHz/$CDCl_3$/TMS; δ (ppm).



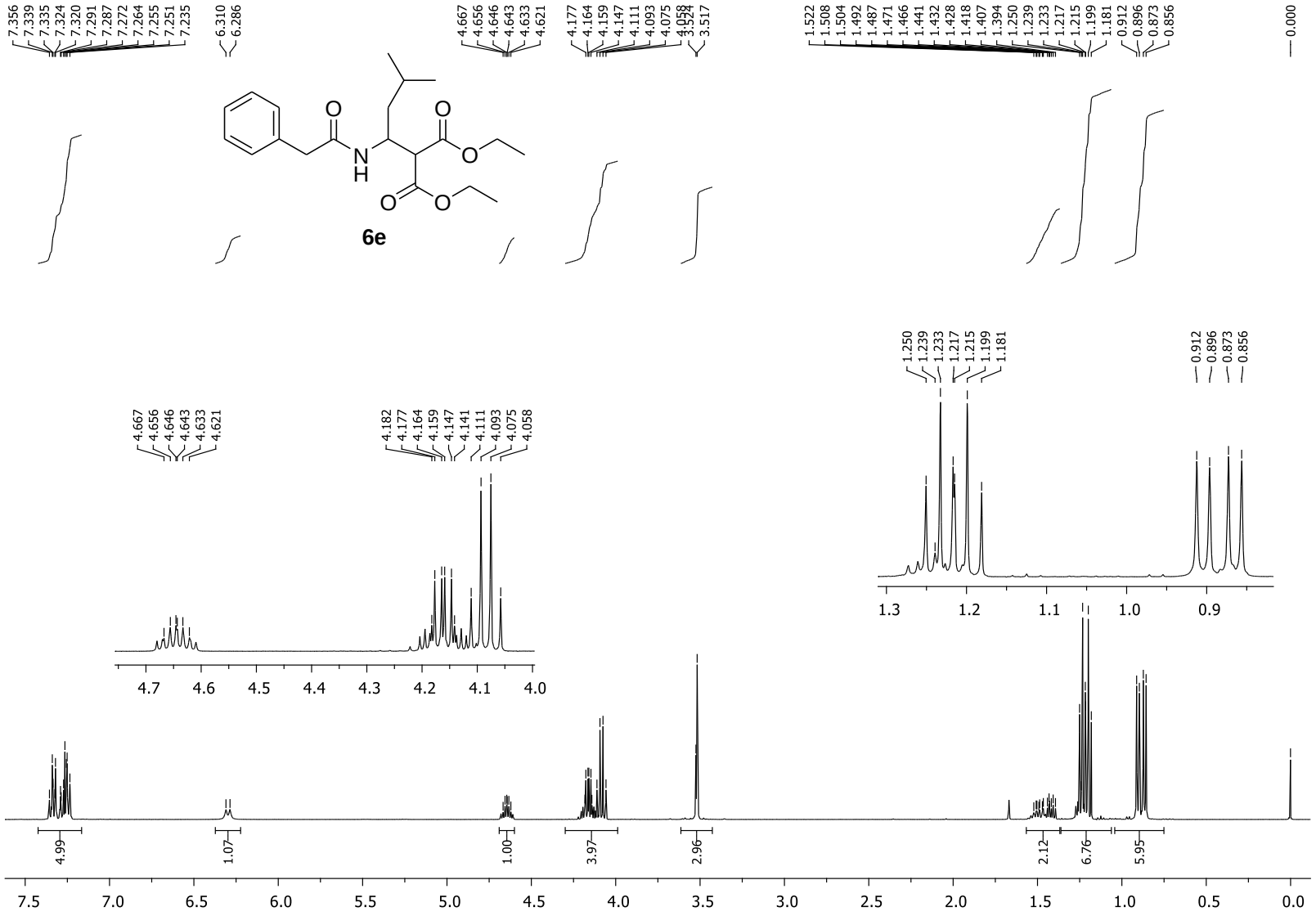
^{13}C NMR spectrum of ethyl 2-acetyl-5-methyl-3-(phenylacetylamino)hexanoate (**6c**) - the mixture of two diastereoisomers; 100 MHz/$CDCl_3$/TMS; δ (ppm).



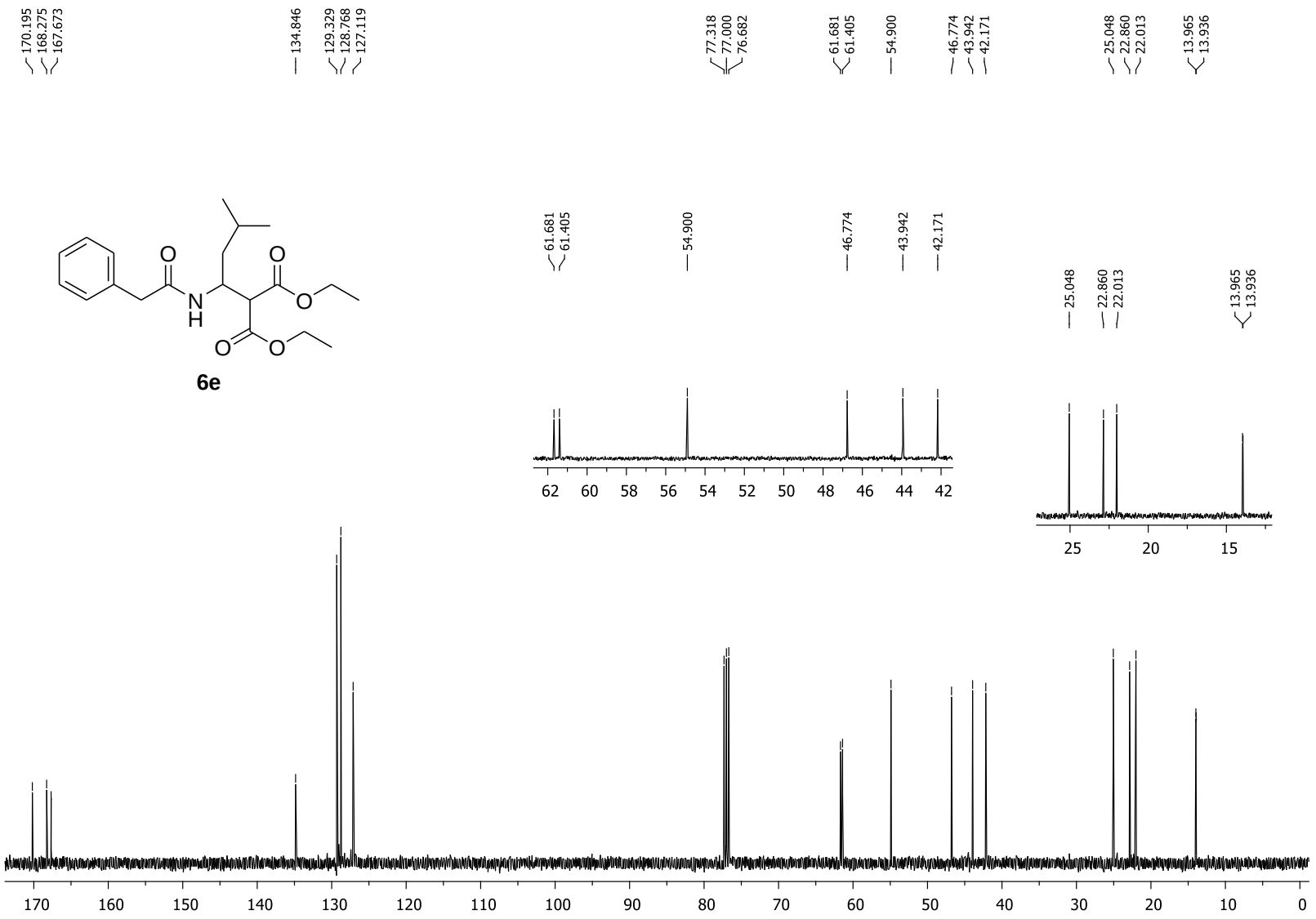
^{1}H NMR spectrum of dimethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6d**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



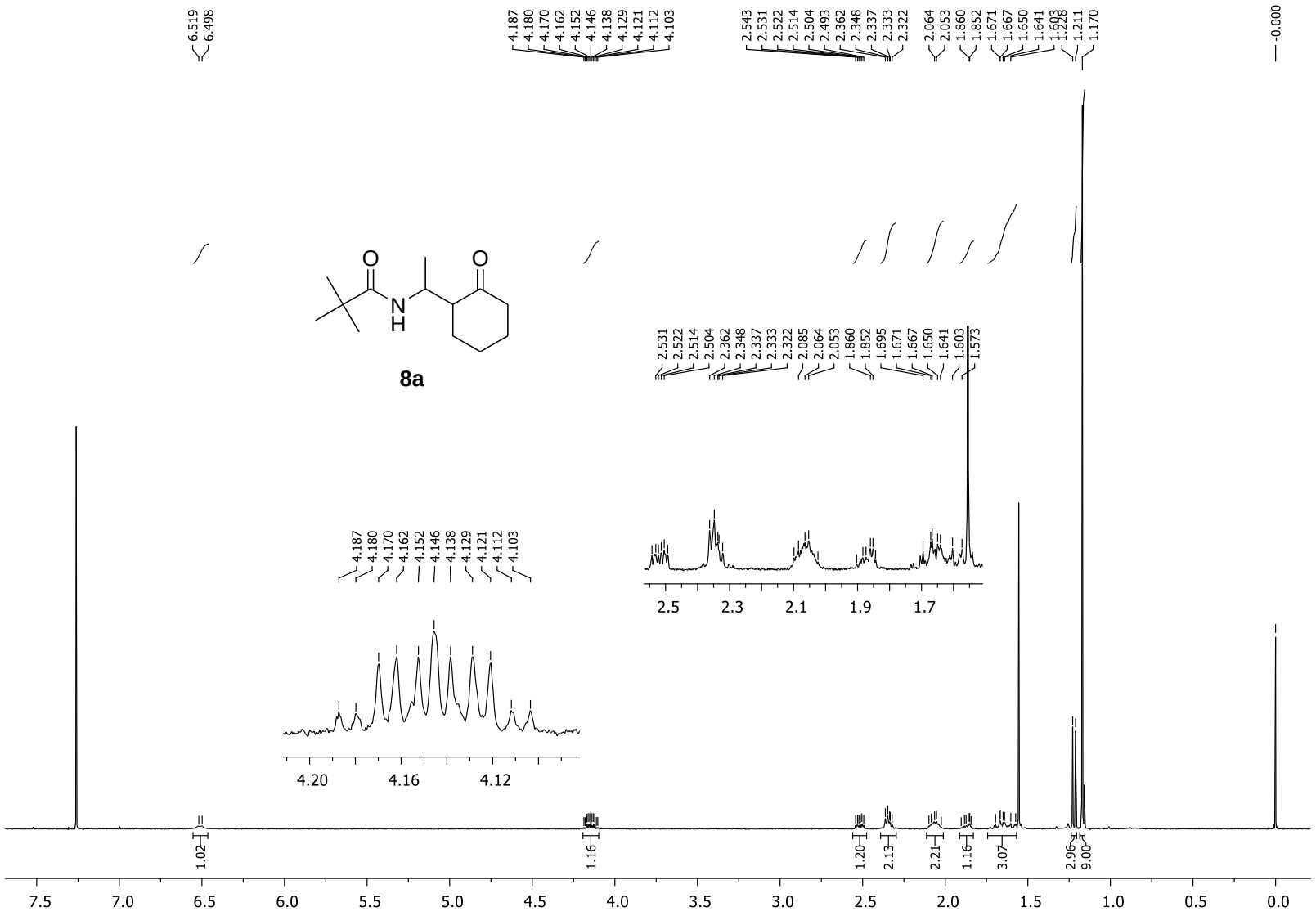
^{13}C NMR spectrum of dimethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6d**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



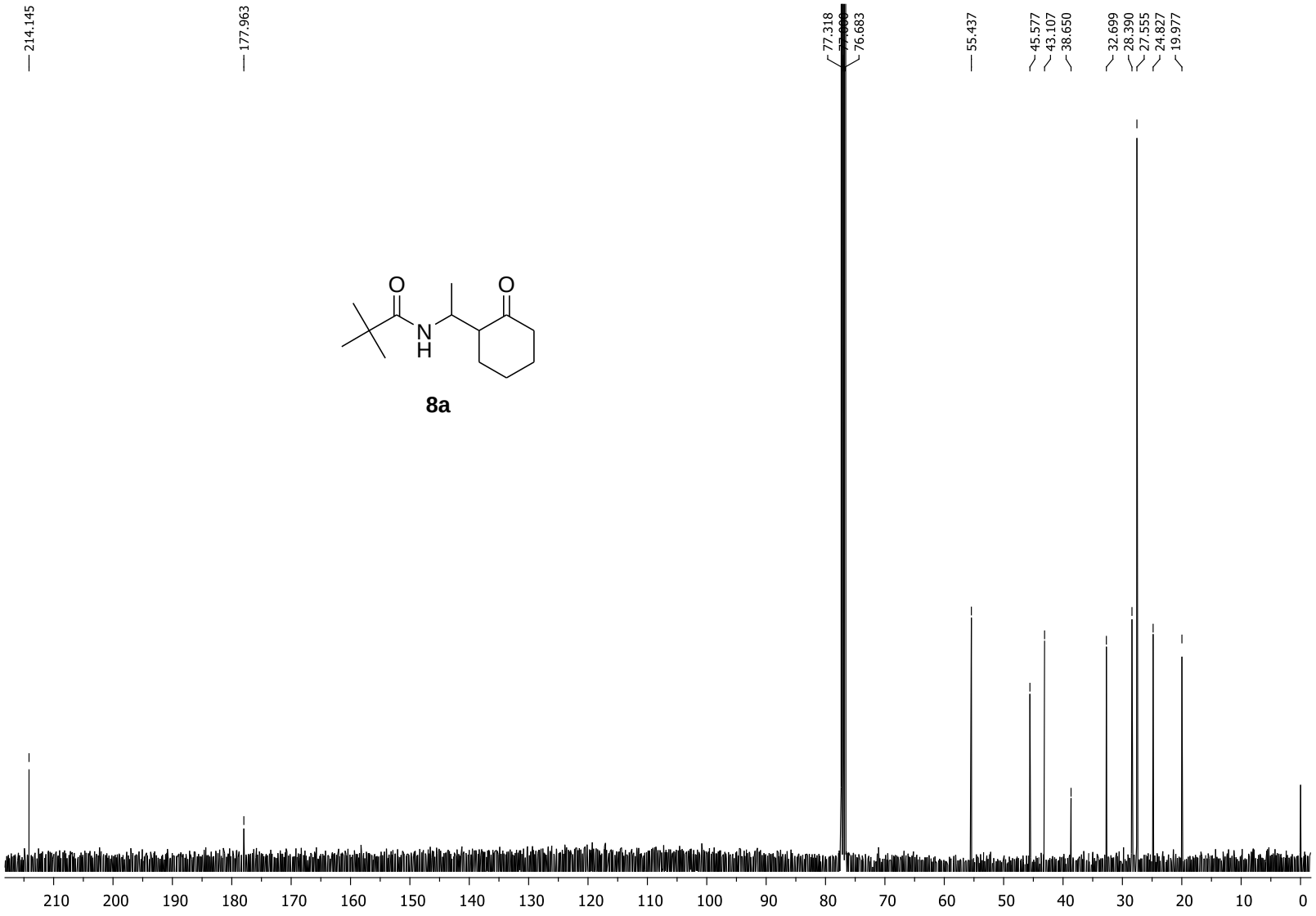
^{1}H NMR spectrum of diethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6e**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



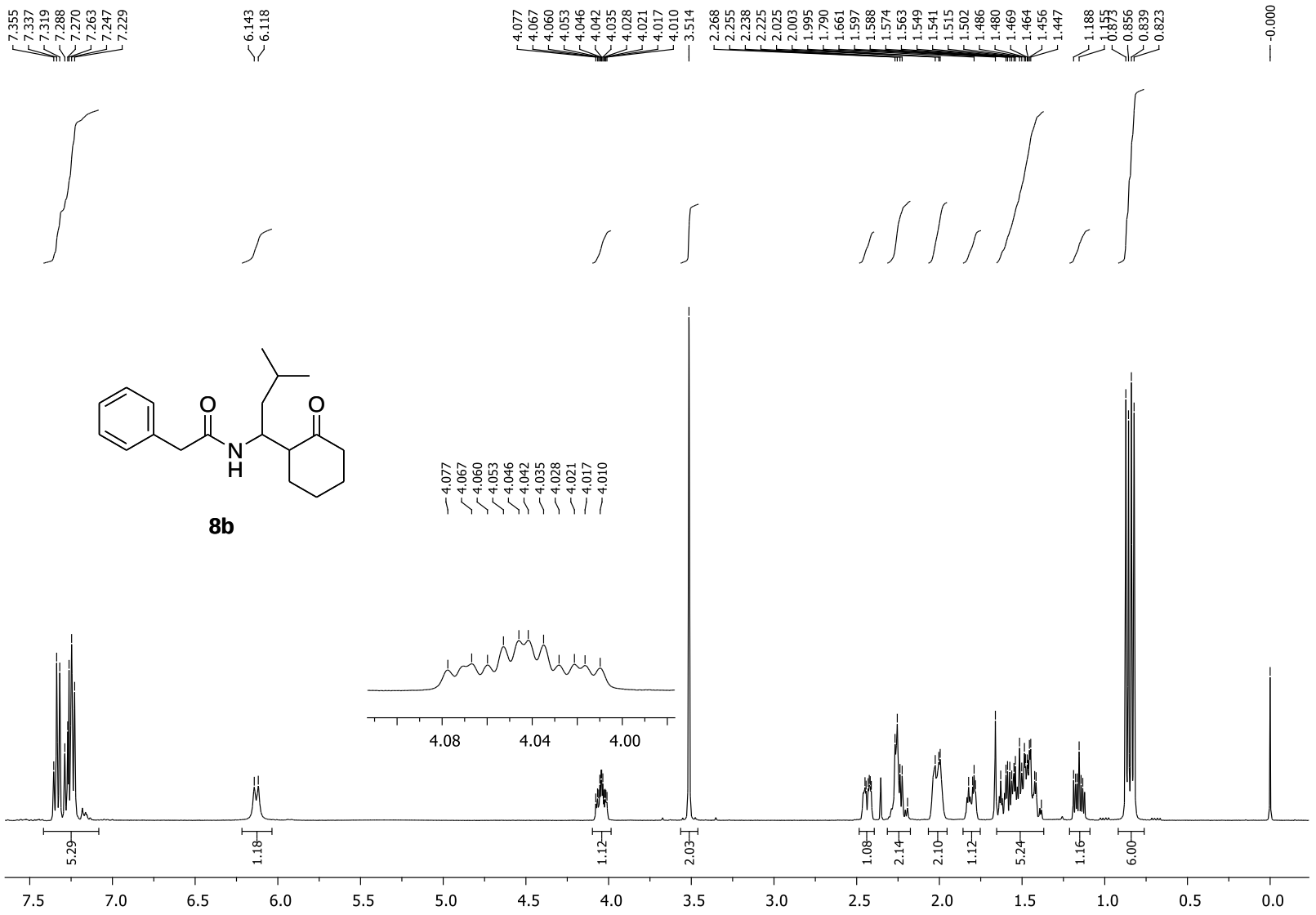
^{13}C NMR spectrum of diethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6e**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



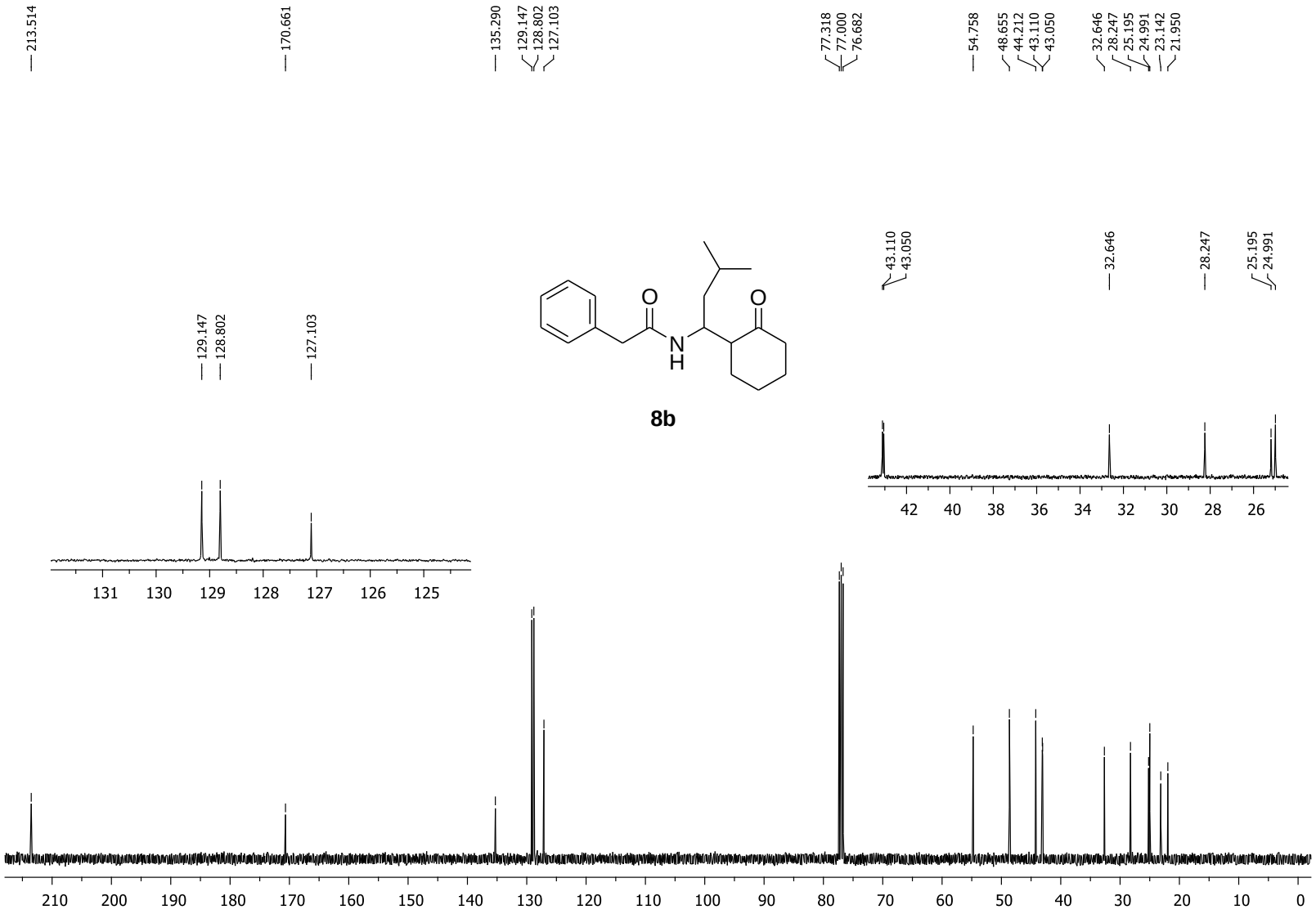
^{1}H NMR spectrum of *N*-[1-(2-oxocyclohexyl)ethyl]pivalamide (**8a**) – the major disatereoisomer; 400 MHz/$CDCl_3$/TMS; δ (ppm).



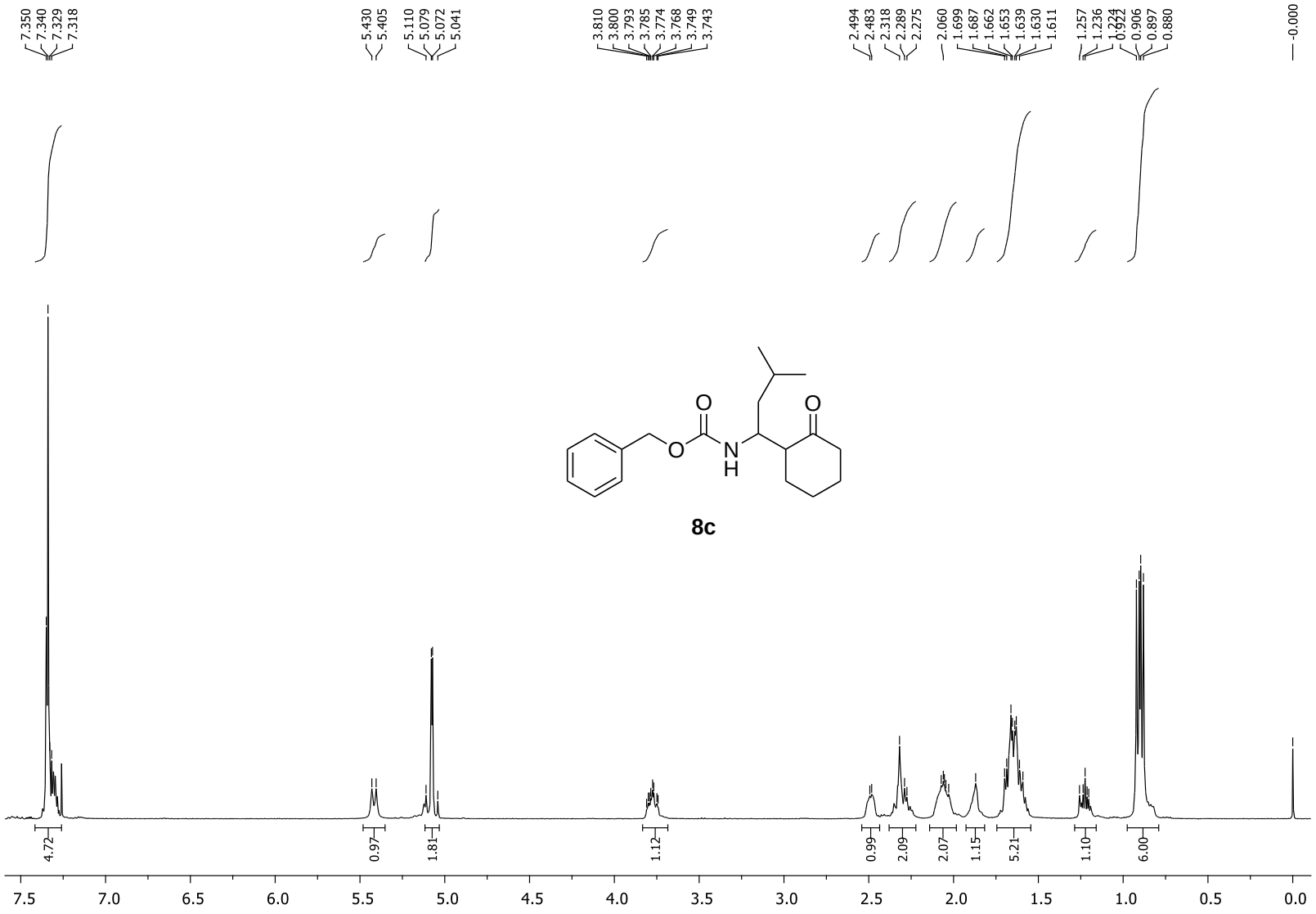
^{13}C NMR spectrum of *N*-[1-(2-oxocyclohexyl)ethyl]pivalamide (**8a**) - the major disatereoisomer; 100 MHz/$CDCl_3$/TMS; δ (ppm).



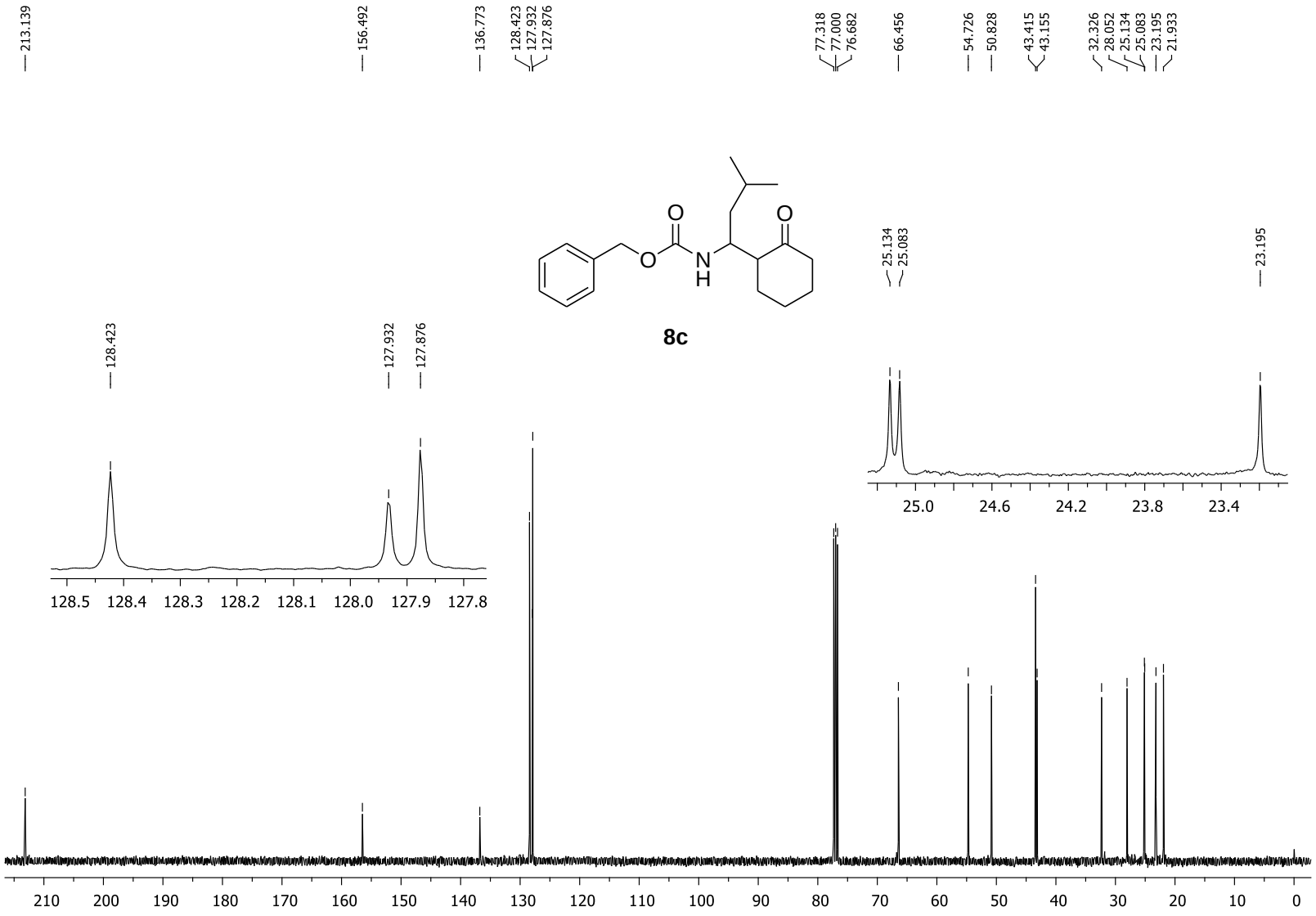
^{1}H NMR spectrum of *N*-[1-(2-oxocyclohexyl)-3-methylbutyl]phenylacetamide (**8b**) – the major disatereoisomer; 400 MHz/$CDCl_3$/TMS; δ (ppm).



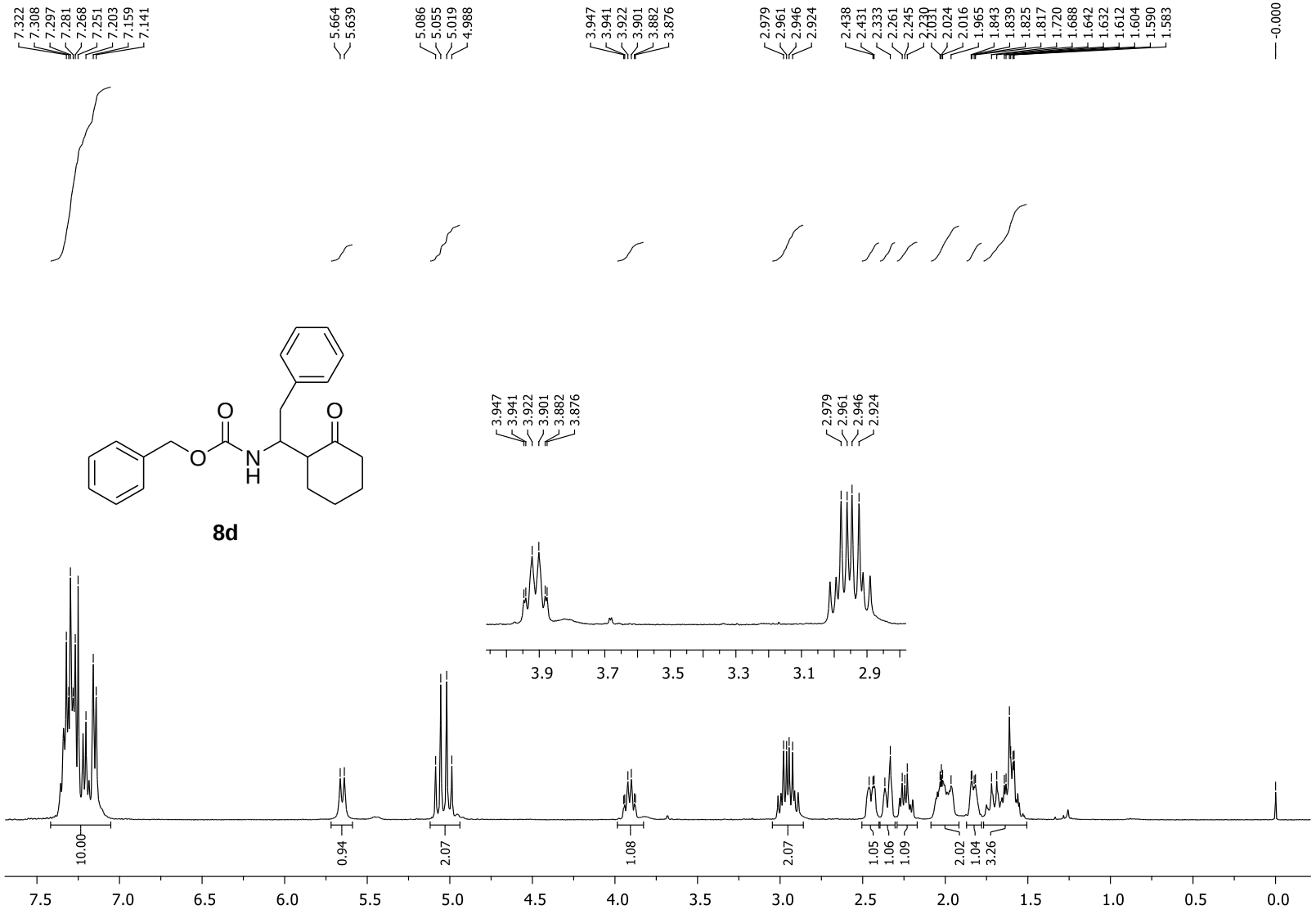
^{13}C NMR spectrum of *N*-[1-(2-oxocyclohexyl)-3-methylbutyl]phenylacetamide (**8b**) – the major disatereoisomer; 100 MHz/$CDCl_3$/TMS; δ (ppm).



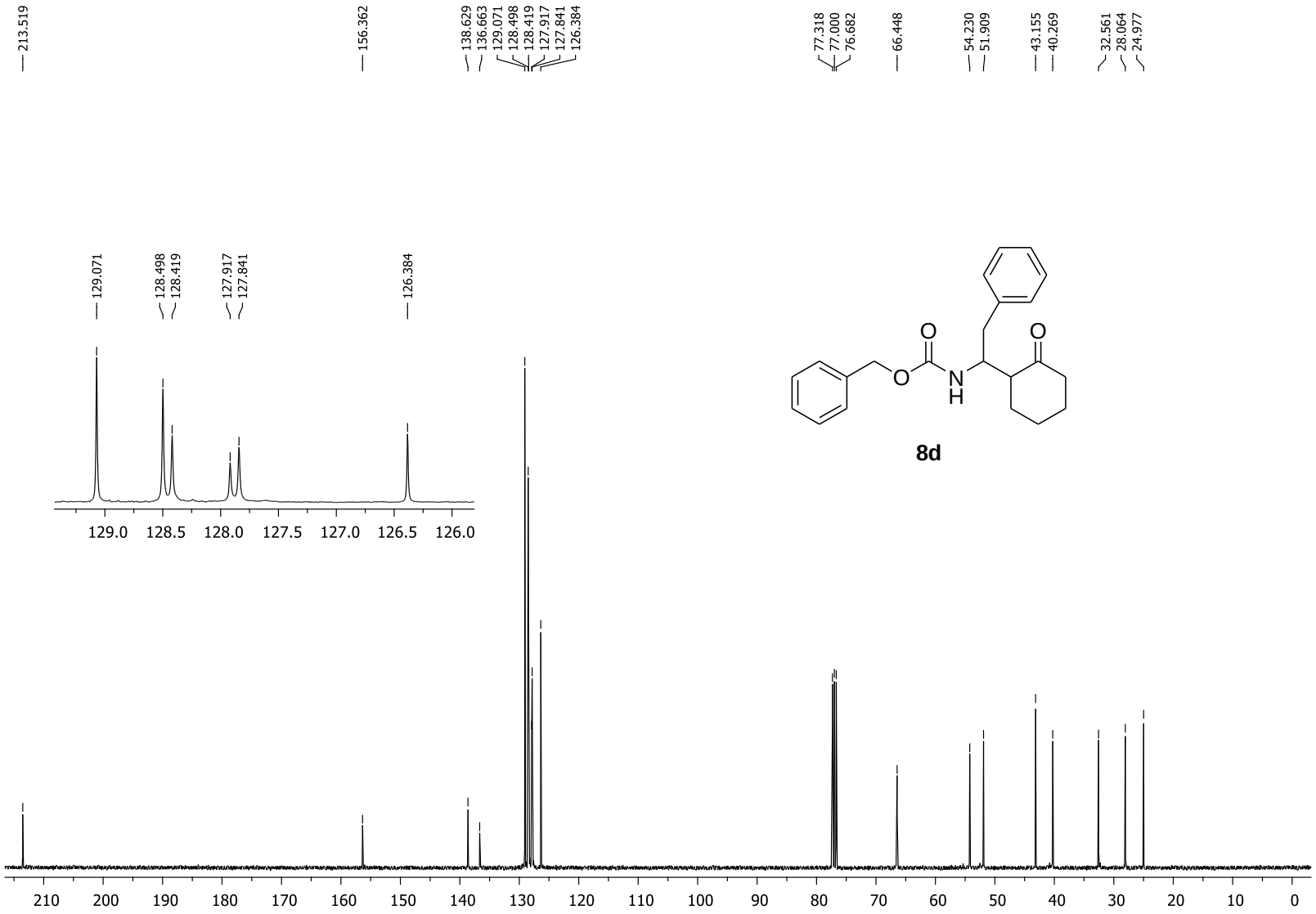
^{1}H NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-3-methylbutyl]carbamate (**8c**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



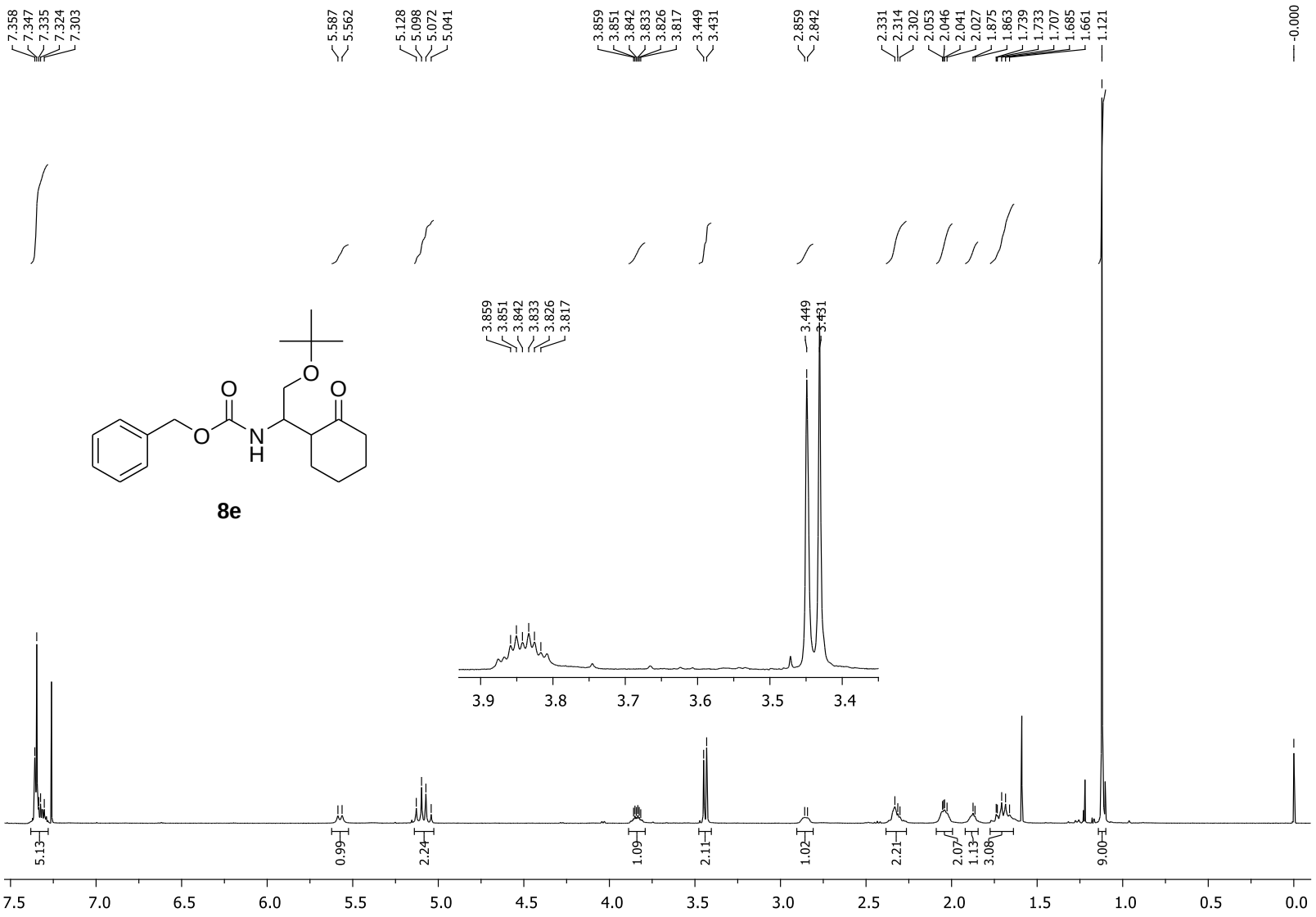
^{13}C NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-3-methylbutyl]carbamate (**8c**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



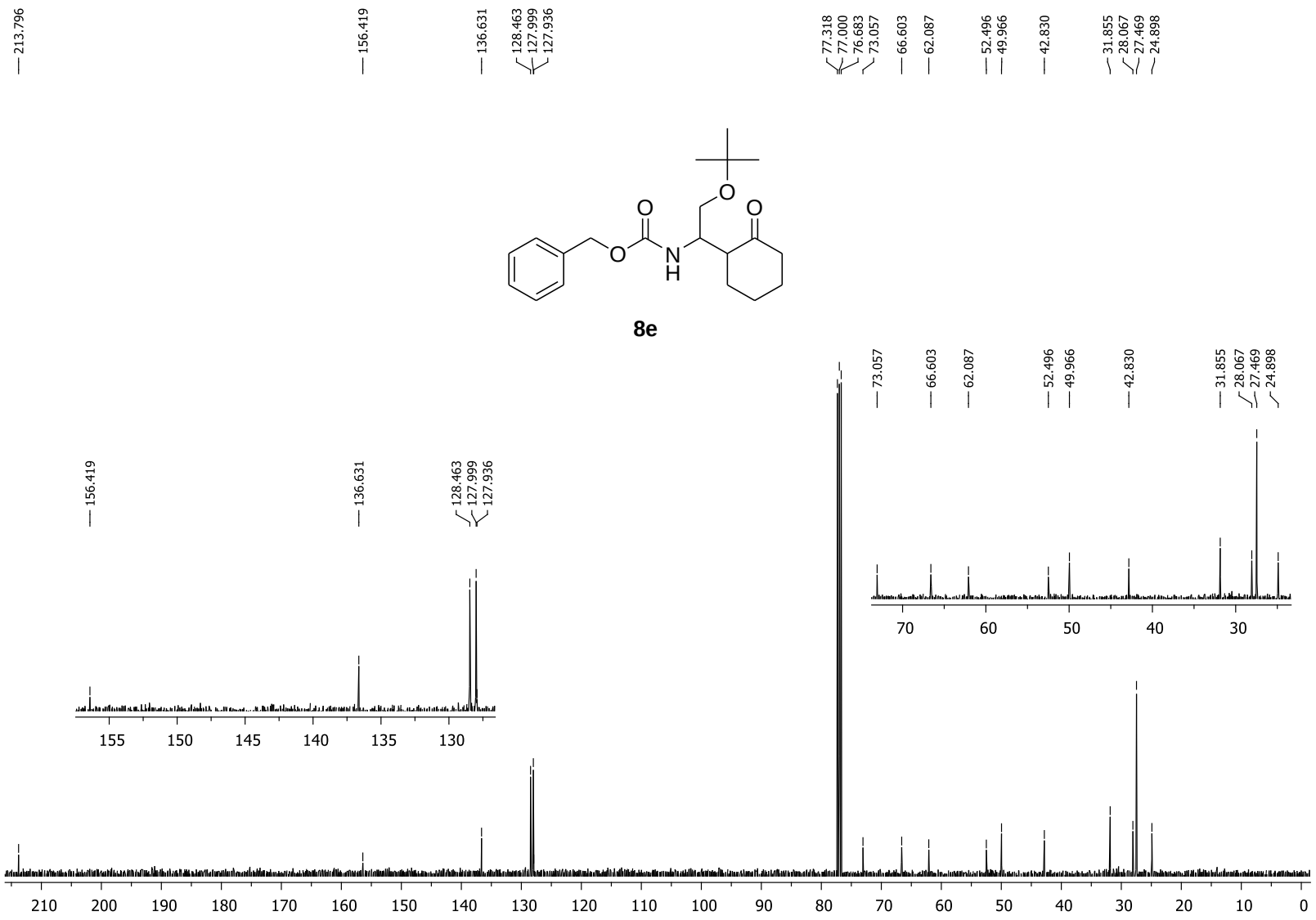
^{1}H NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-2-phenylethyl]carbamate (**8d**) – the major disatereoisomer; 400 MHz/$CDCl_3$/TMS; δ (ppm).



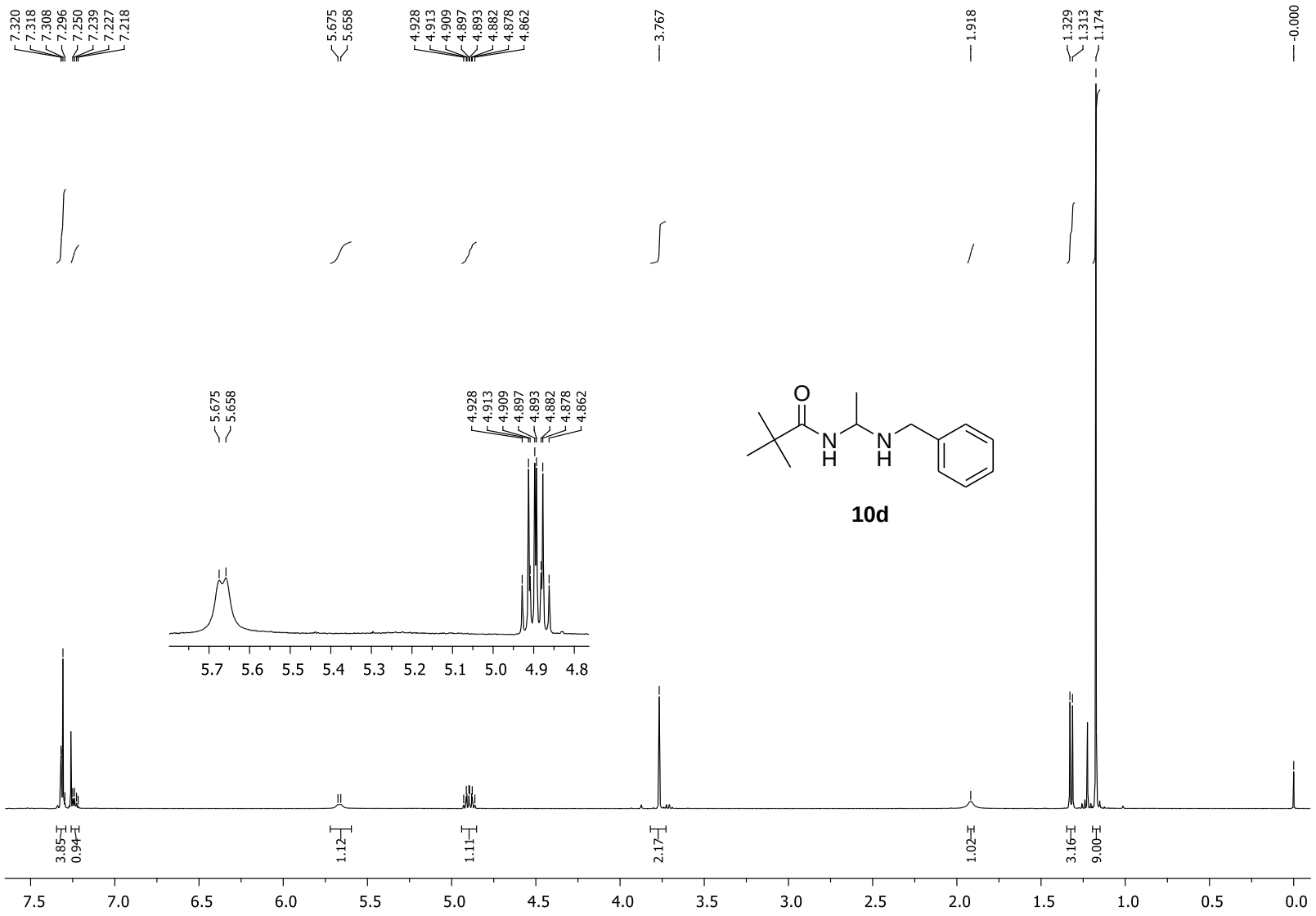
^{13}C NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-2-phenylethyl]carbamate (**8d**) – the major disatereoisomer; 100 MHz/$CDCl_3$/TMS; δ (ppm).



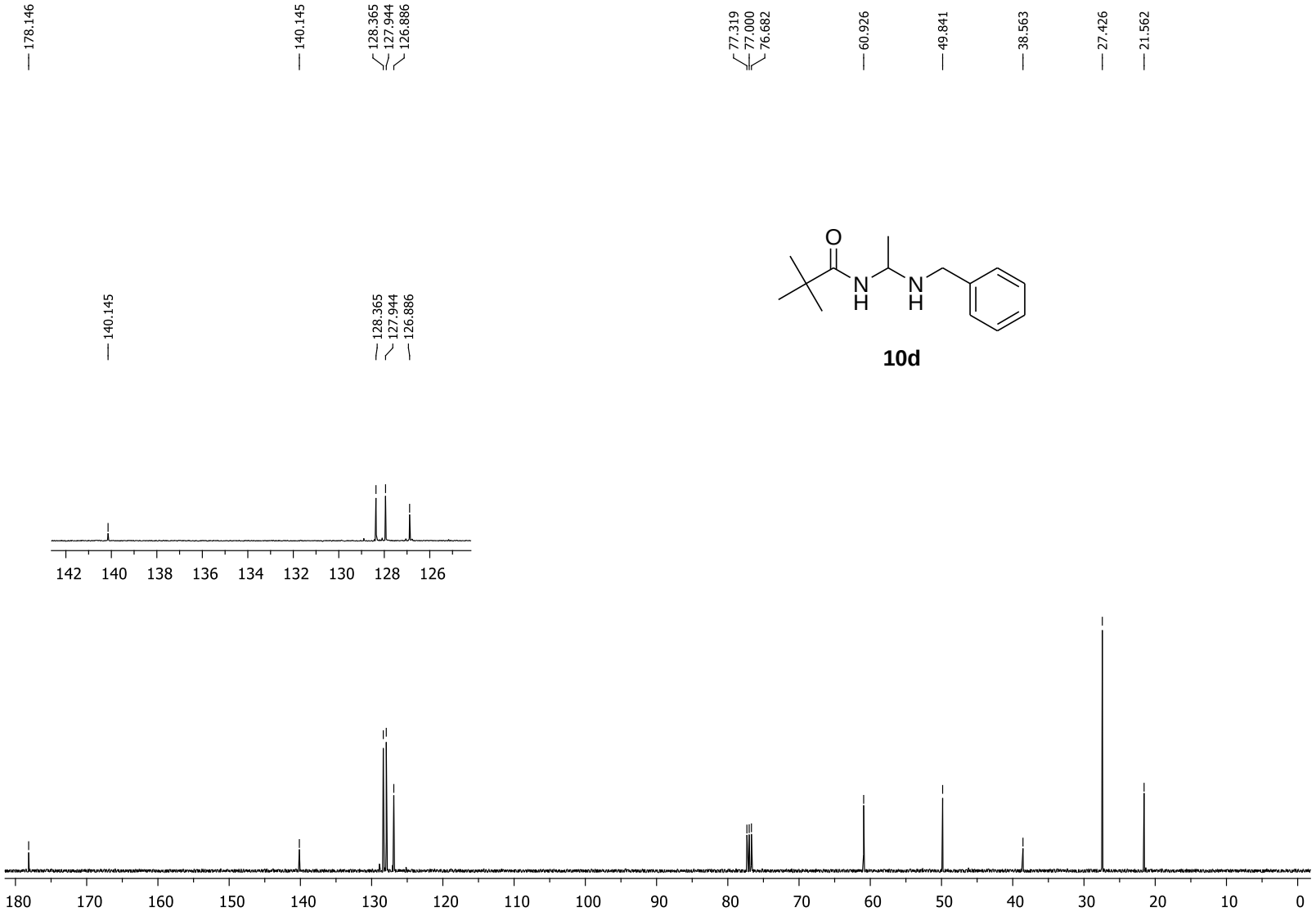
^{1}H NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-2-*tert*-butoxyethyl]carbamate (**8e**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



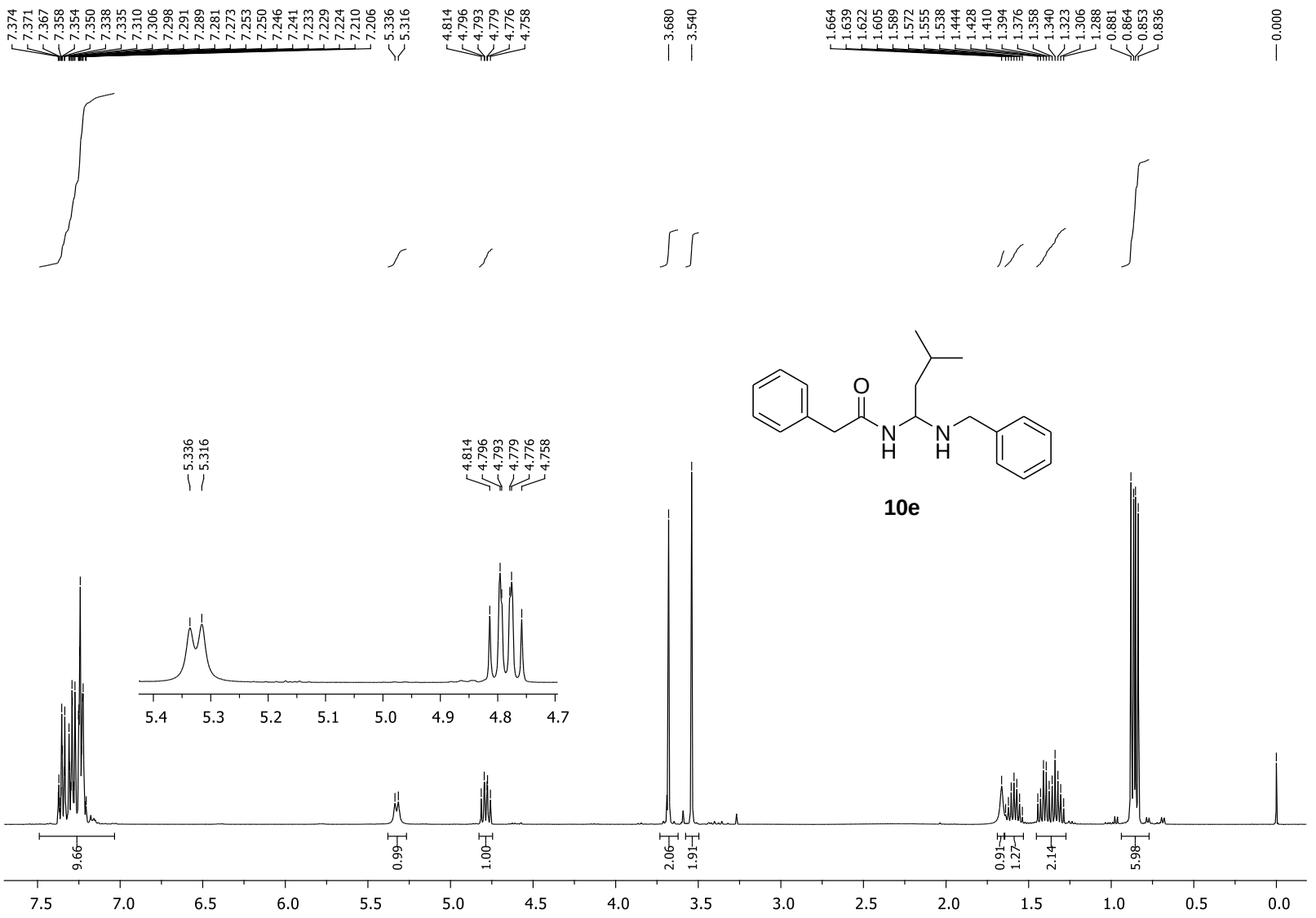
^{13}C NMR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-2-*tert*-butoxyethyl]carbamate (**8e**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



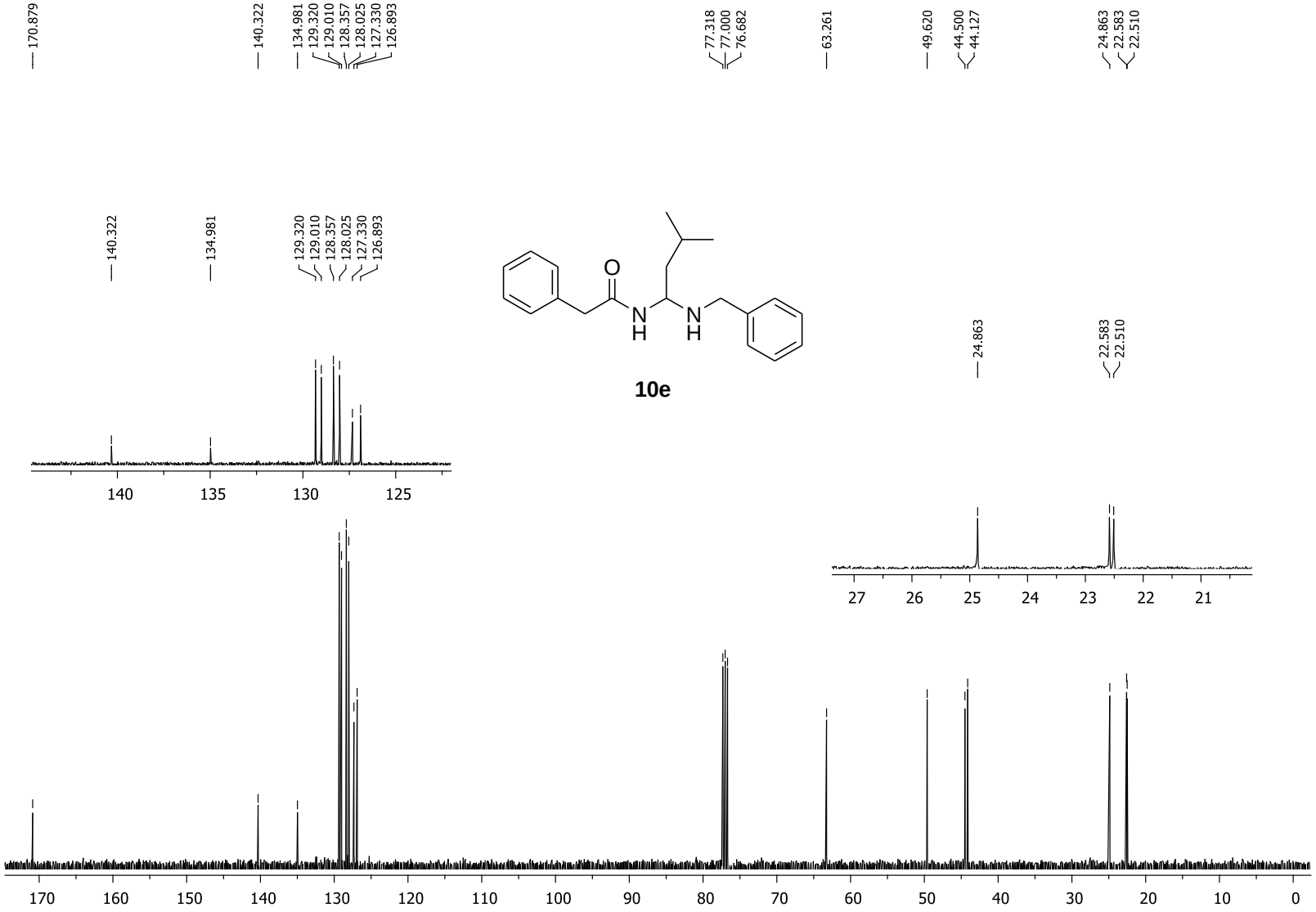
^{1}H NMR spectrum of *N*-[1-(benzylamino)ethyl]pivalamide (**10d**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



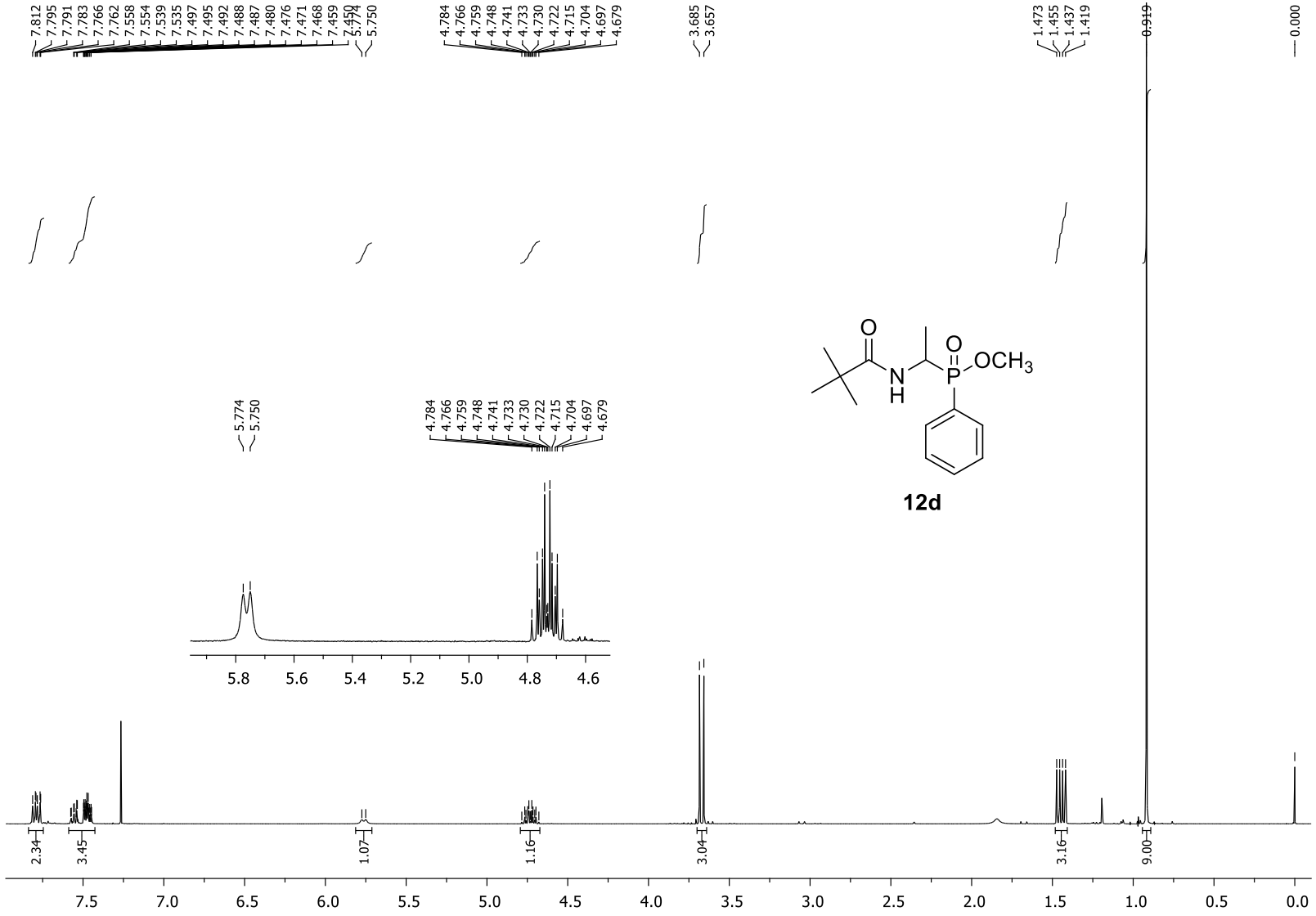
^{13}C NMR spectrum of *N*-[1-(benzylamino)ethyl]pivalamide (**10d**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



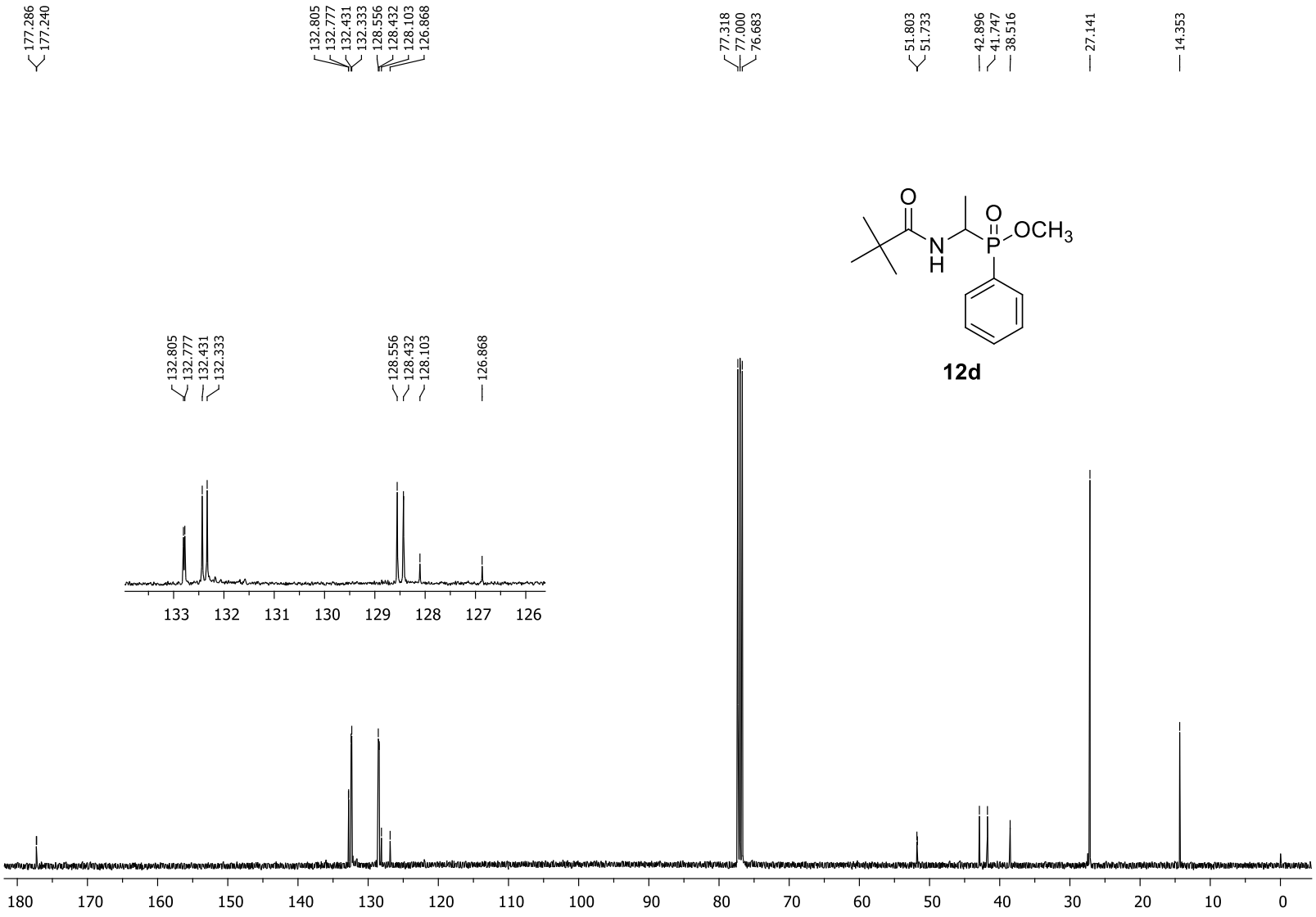
^{1}H NMR spectrum of *N*-[1-(benzylamino)-3-methylbutyl]phenylacetamide (**10e**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



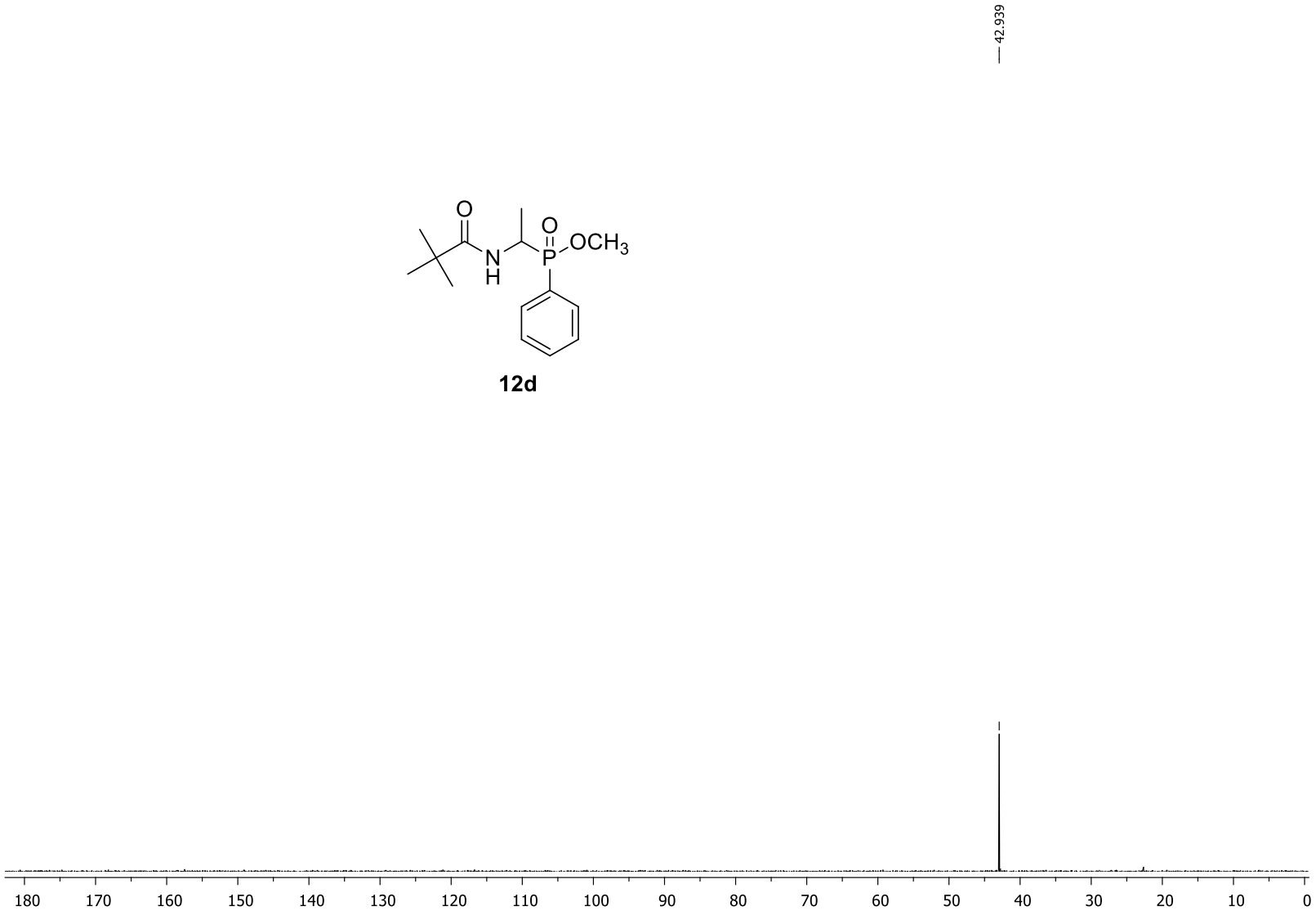
^{13}C NMR spectrum of *N*-[1-(benzylamino)-3-methylbutyl]phenylacetamide (**10e**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



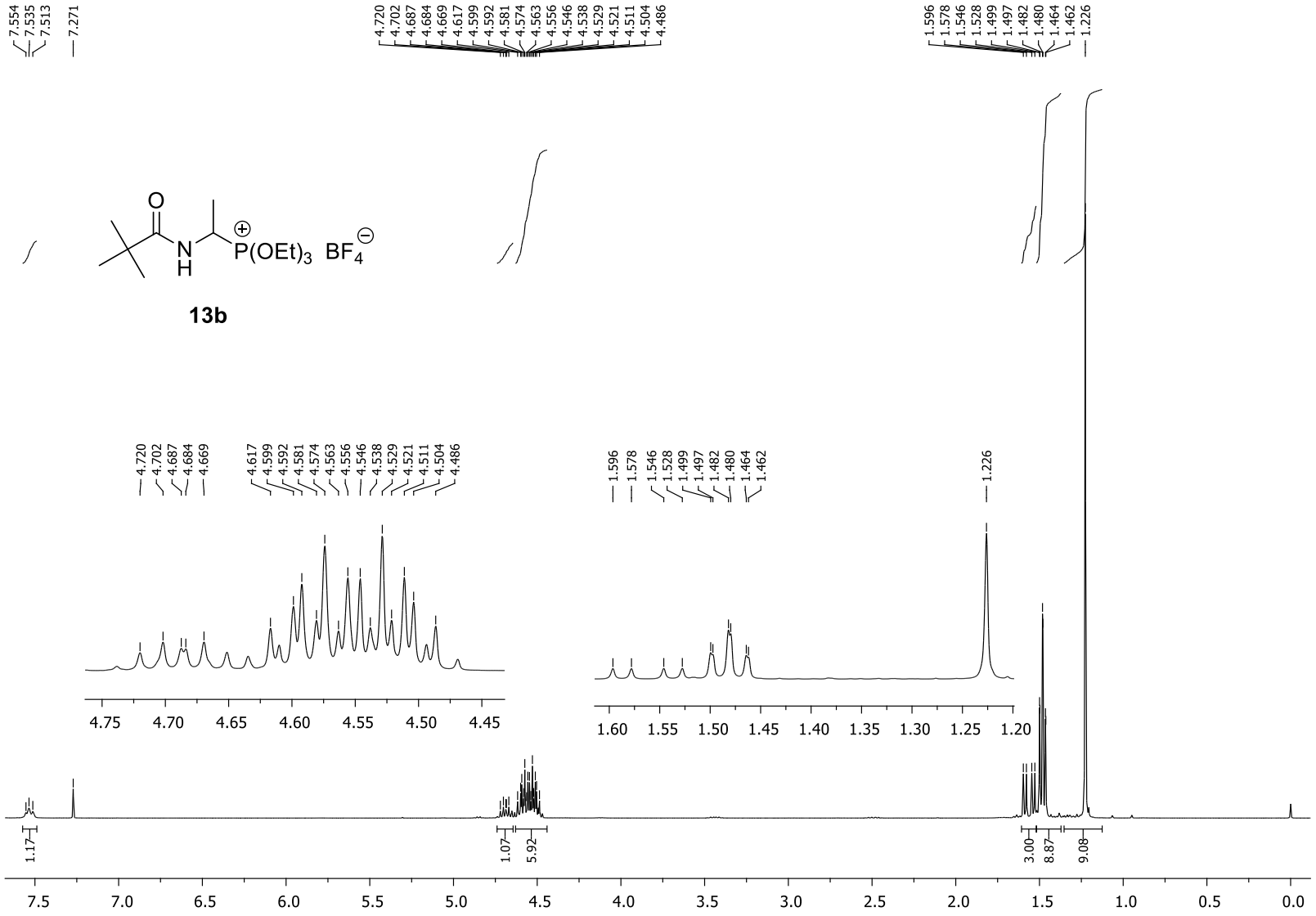
^{1}H NMR spectrum of methyl phenyl(1-pivaloylaminoethyl)phosphinate (**12d**); 400 MHz/$CDCl_3$/TMS; δ (ppm).



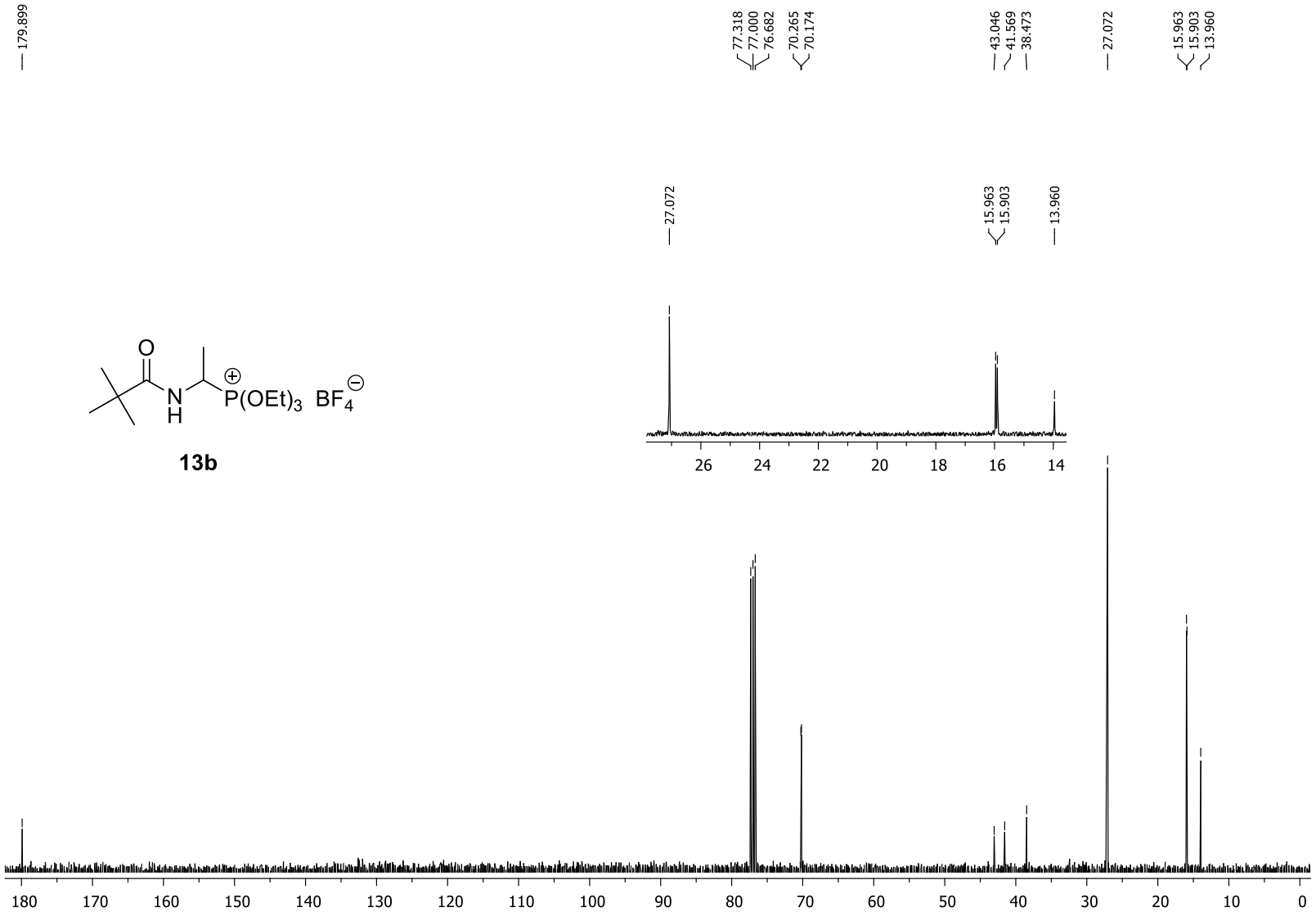
^{13}C NMR spectrum of methyl phenyl(1-pivaloylaminoethyl)phosphinate (**12d**); 100 MHz/$CDCl_3$/TMS; δ (ppm).



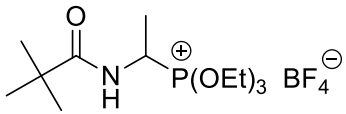
^{31}P NMR spectrum of methyl phenyl(1-pivaloylaminoethyl)phosphinate (**12d**); 161.9 MHz/$CDCl_3$; δ (ppm).



^{1}H NMR spectrum of 1-(*N*-pivaloylamino)ethyltriethoxyphosphonium tetrafluoroborate (**13b**); 400 MHz/$CDCl_3$/TMS; δ (ppm).

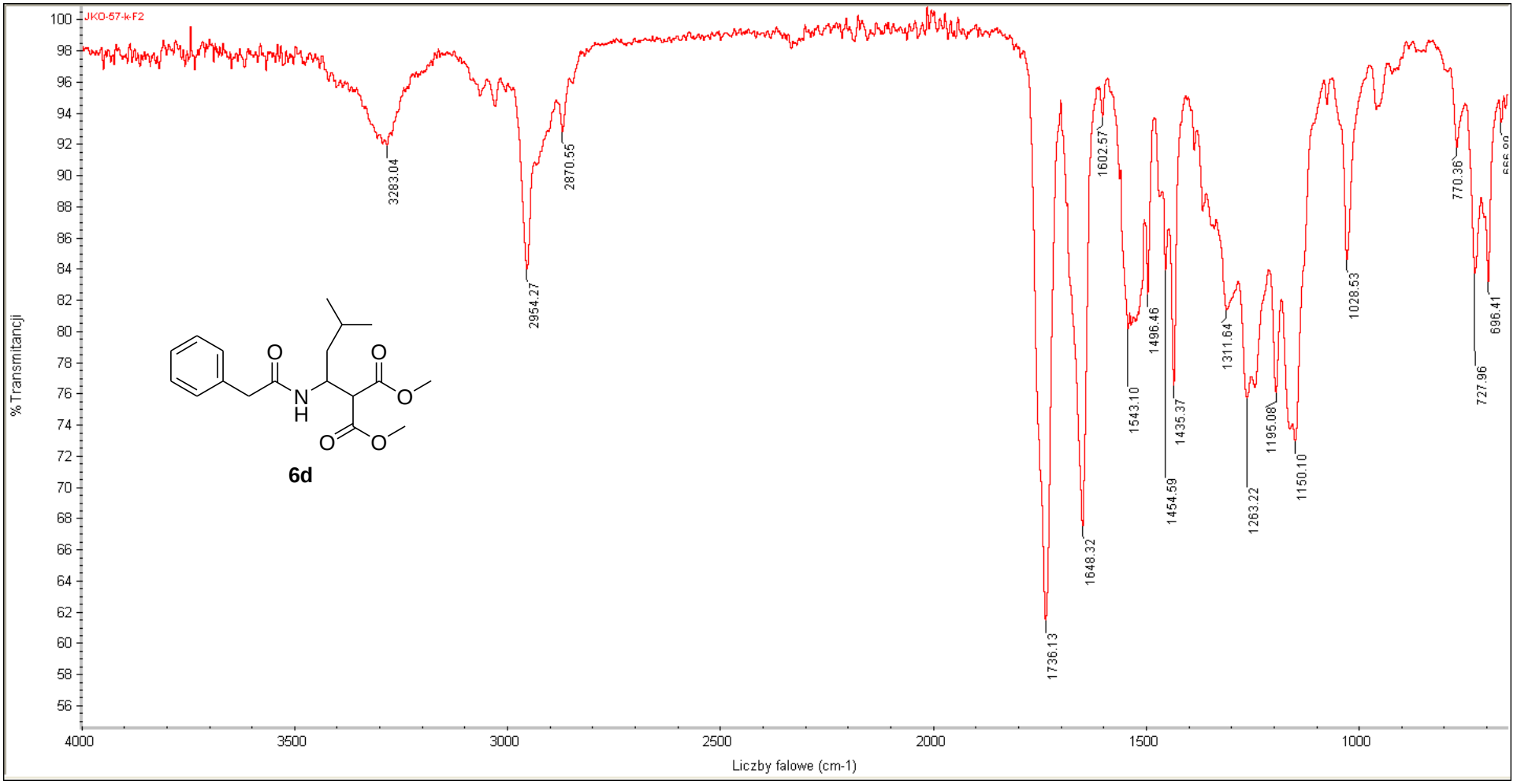


^{13}C NMR spectrum of 1-(*N*-pivaloylamino)ethyltriethoxyphosphonium tetrafluoroborate (**13b**); 100 MHz/$CDCl_3$/TMS; δ (ppm).

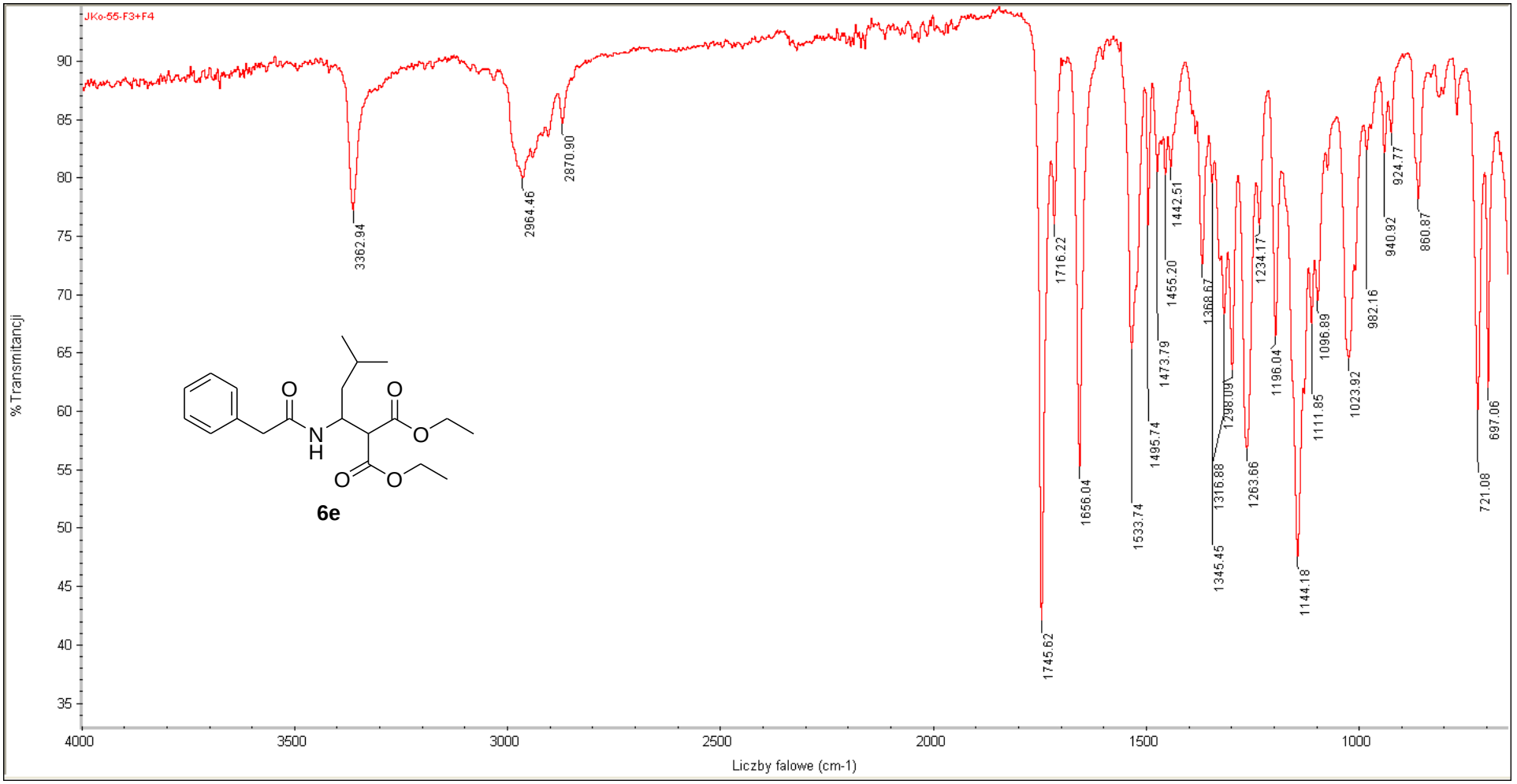


13b

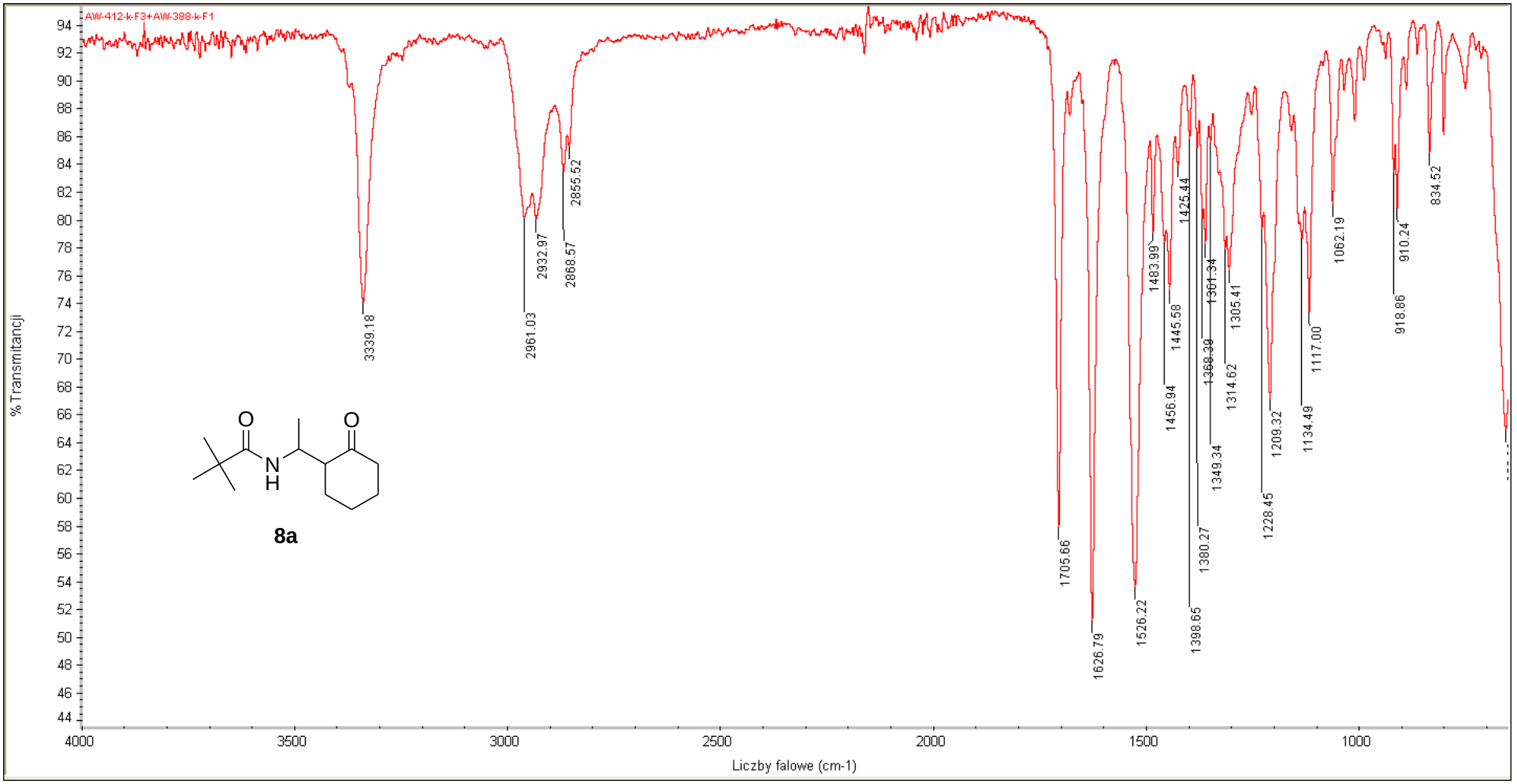
^{31}P NMR spectrum of 1-(*N*-pivaloylamino)ethyltriethoxyphosphonium tetrafluoroborate (**13b**); 161.9 MHz/$CDCl_3$; δ (ppm).



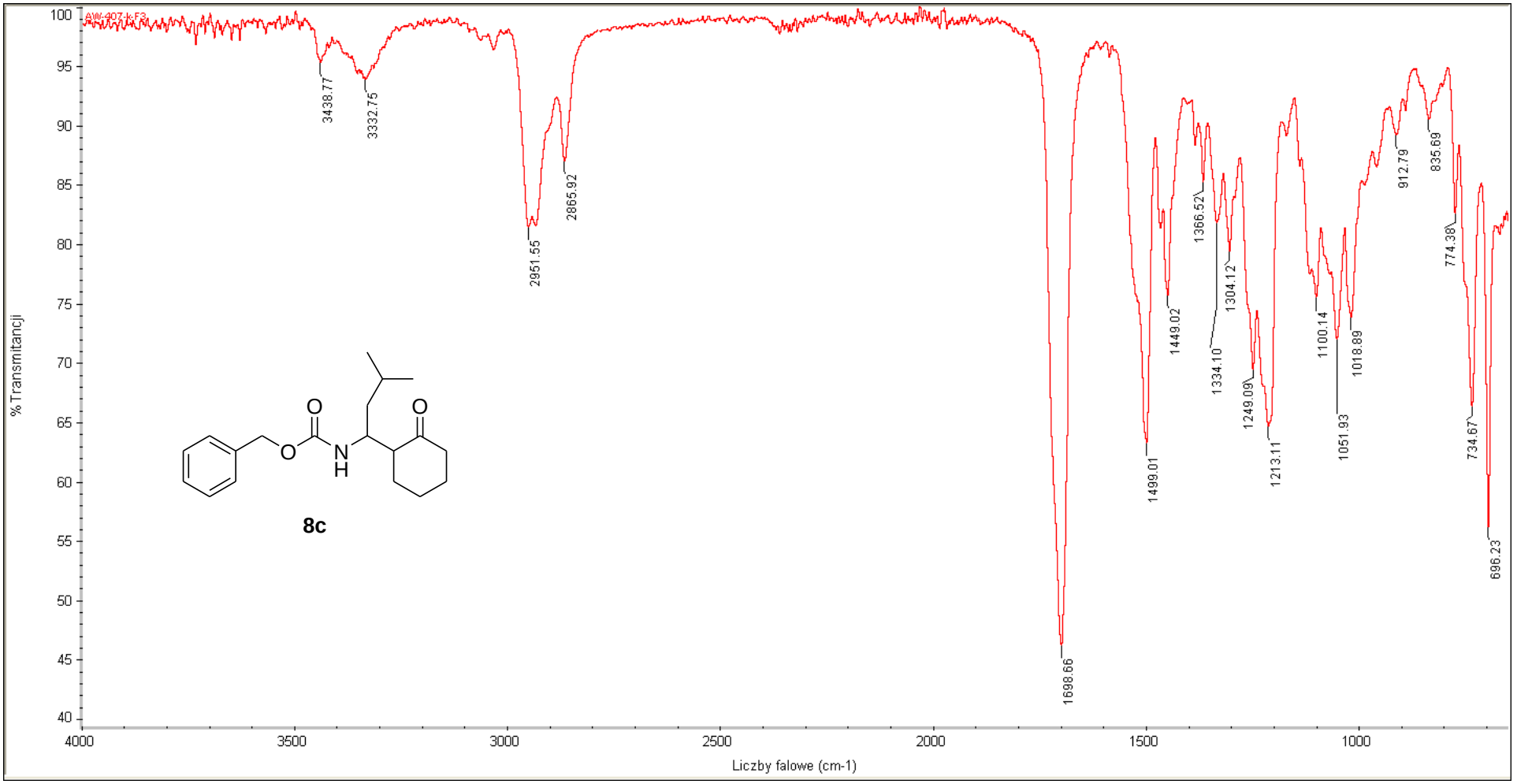
IR spectrum of dimethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6d**); ATR (cm^{-1}).



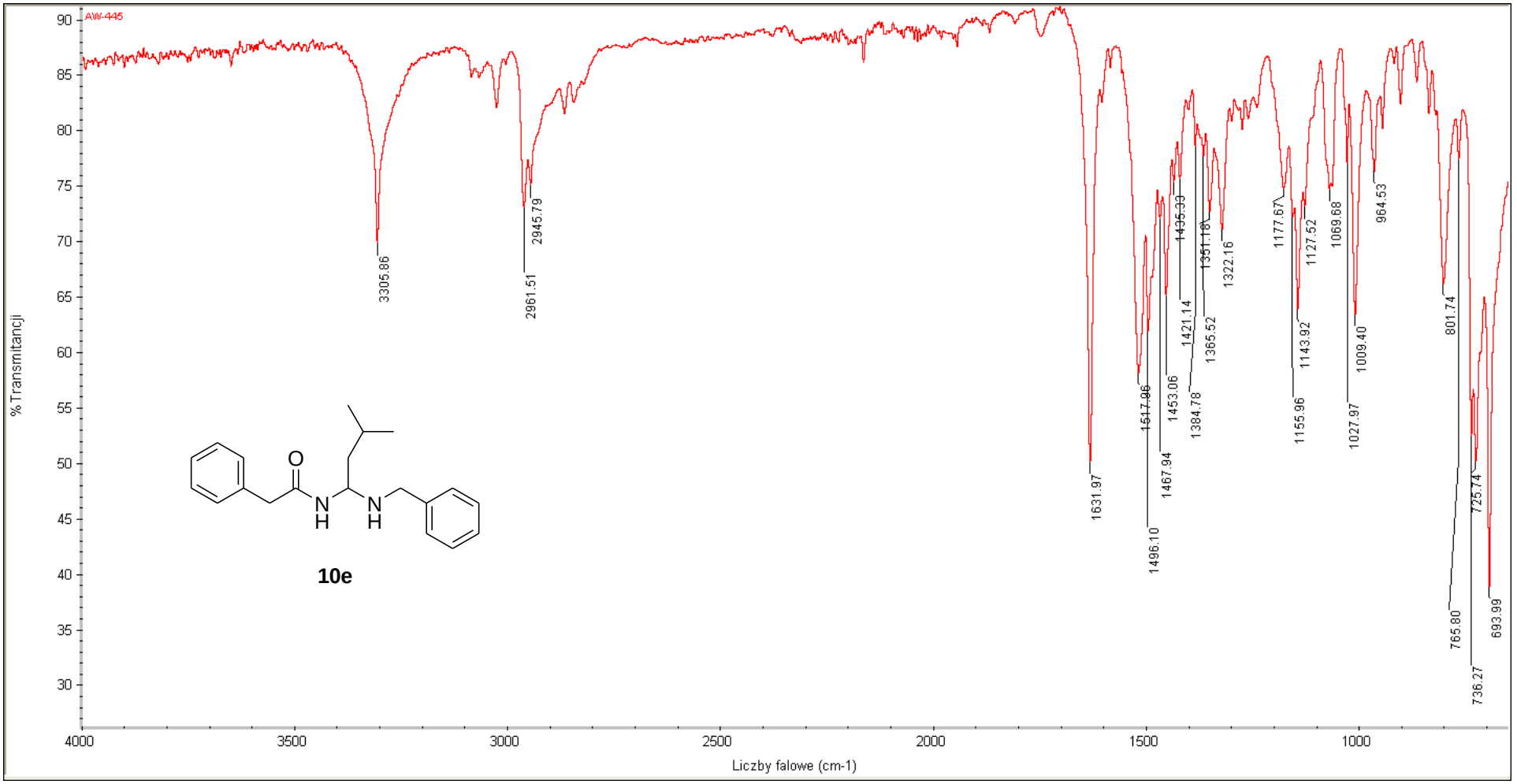
IR spectrum of diethyl 3-methyl-1-(phenylacetylamino)butylpropanedioate (**6e**); ATR (cm^{-1}).



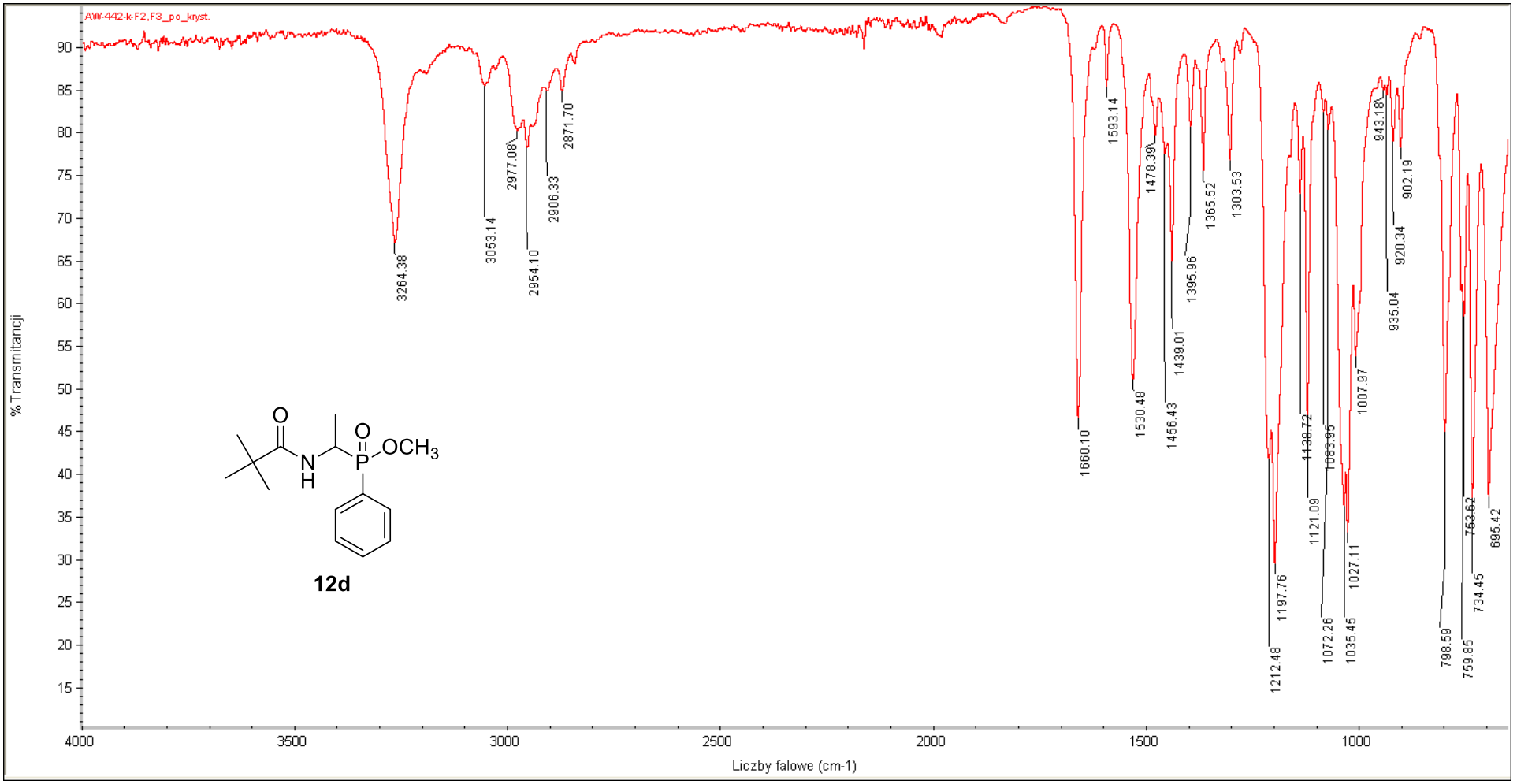
IR spectrum of *N*-[1-(2-oxocyclohexyl)ethyl]pivalamide (**8a**); ATR (cm^{-1}).



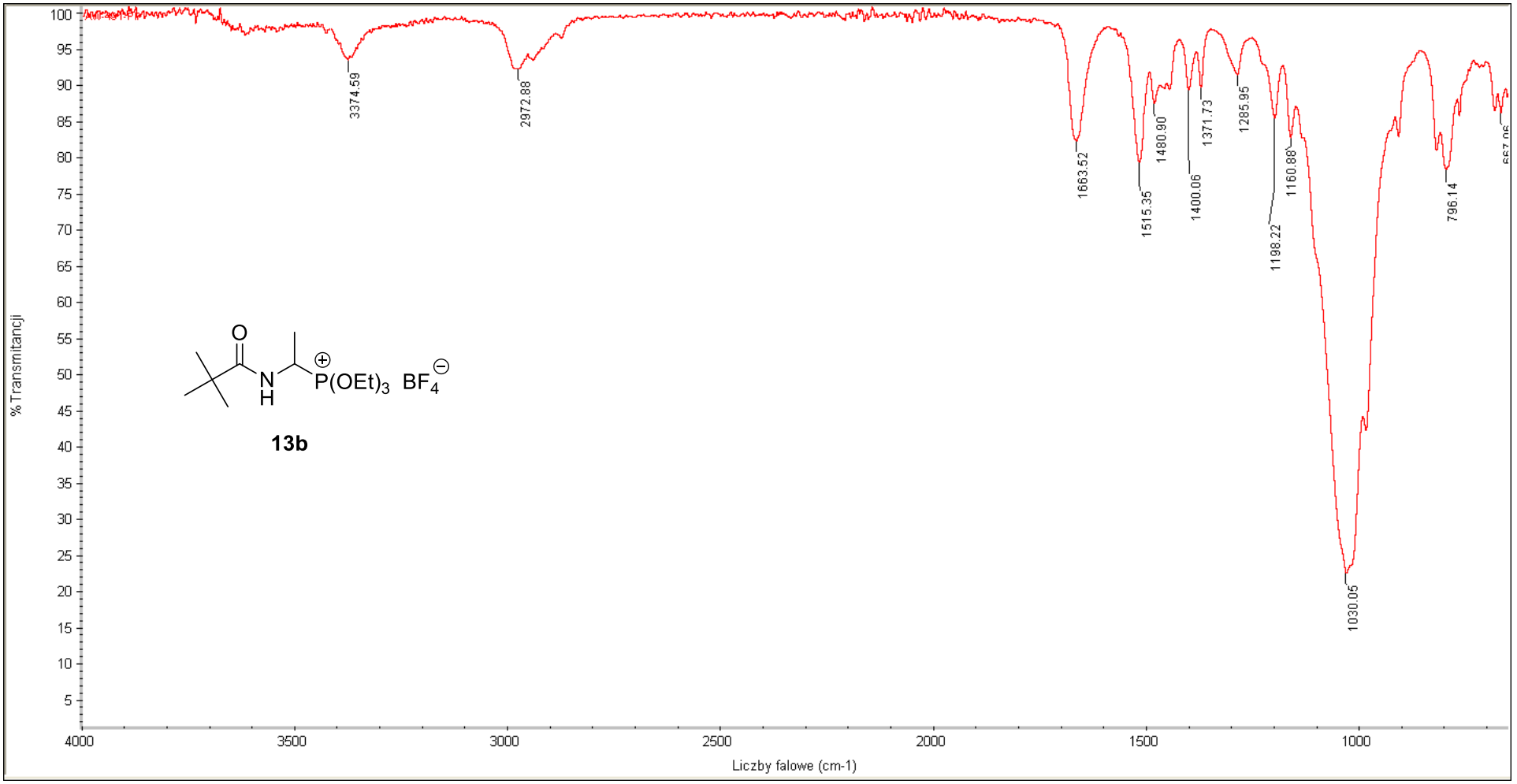
IR spectrum of benzyl *N*-[1-(2-oxocyclohexyl)-3-methylbutyl]carbamate (**8c**); ATR (cm^{-1}).



IR spectrum of *N*-[1-(benzylamino)-3-methylbutyl]phenylacetamide (**10e**); ATR (cm^{-1}).



IR spectrum of methyl phenyl(1-pivaloylaminoethyl)phosphinate (**12d**); ATR (cm^{-1}).



IR spectrum of 1-(*N*-pivaloylamino)ethyltriethoxyphosphonium tetrafluoroborate (**13b**); ATR (cm^{-1}).

Examples of the measurements of the changes in concentrations for the reaction of 1-(*N* pivaloylamino)ethyltris(3-chlorophenyl)phosphonium tetrafluoroborate **4c** with trimethylphosphite at 26°C

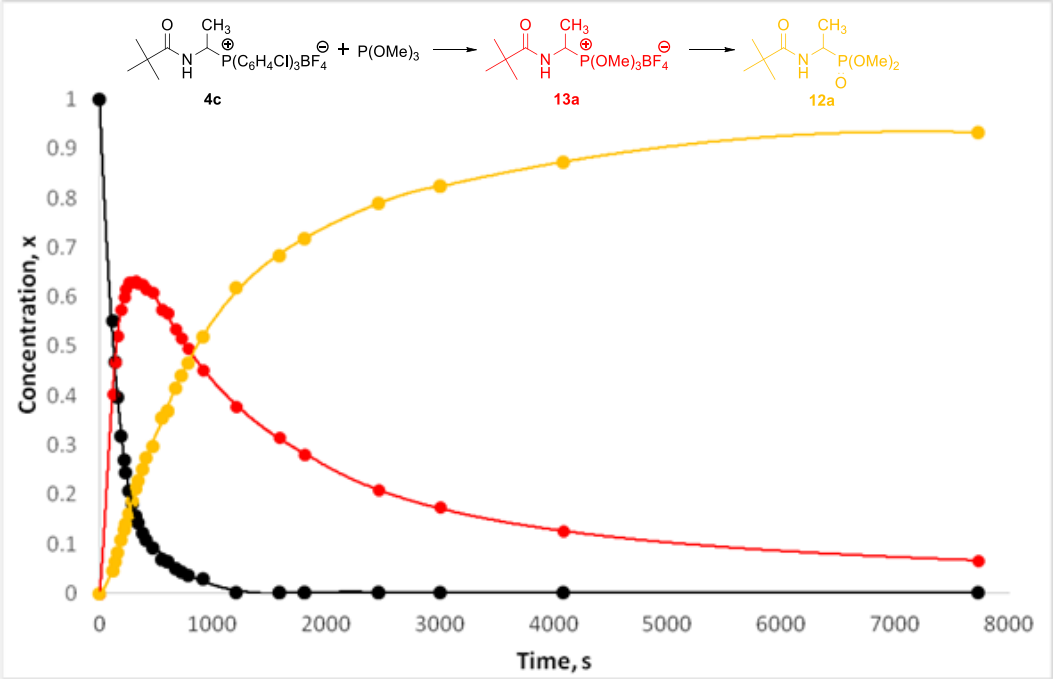
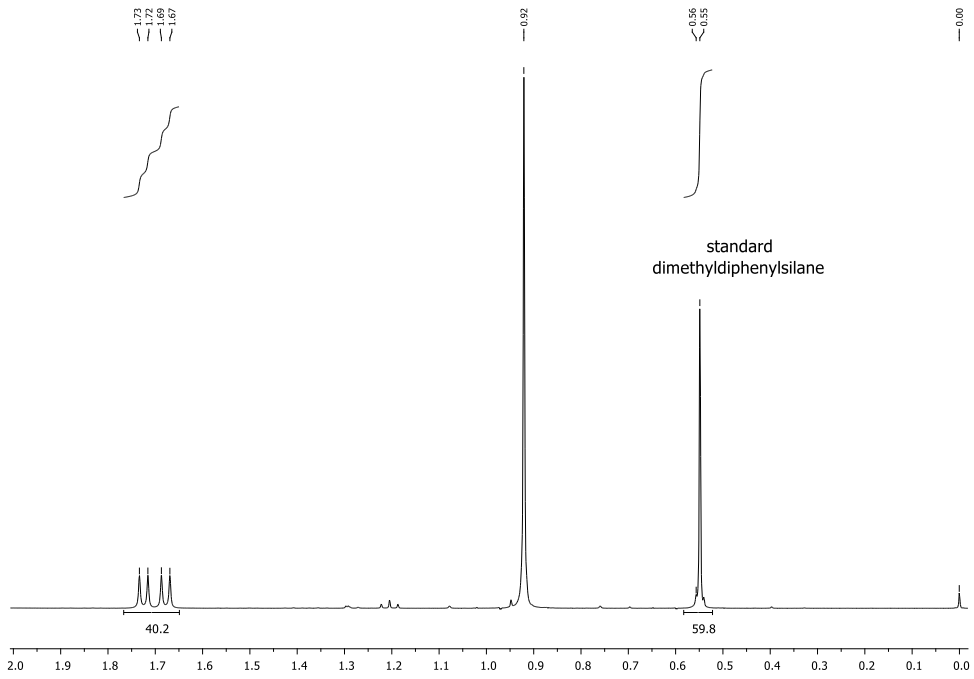


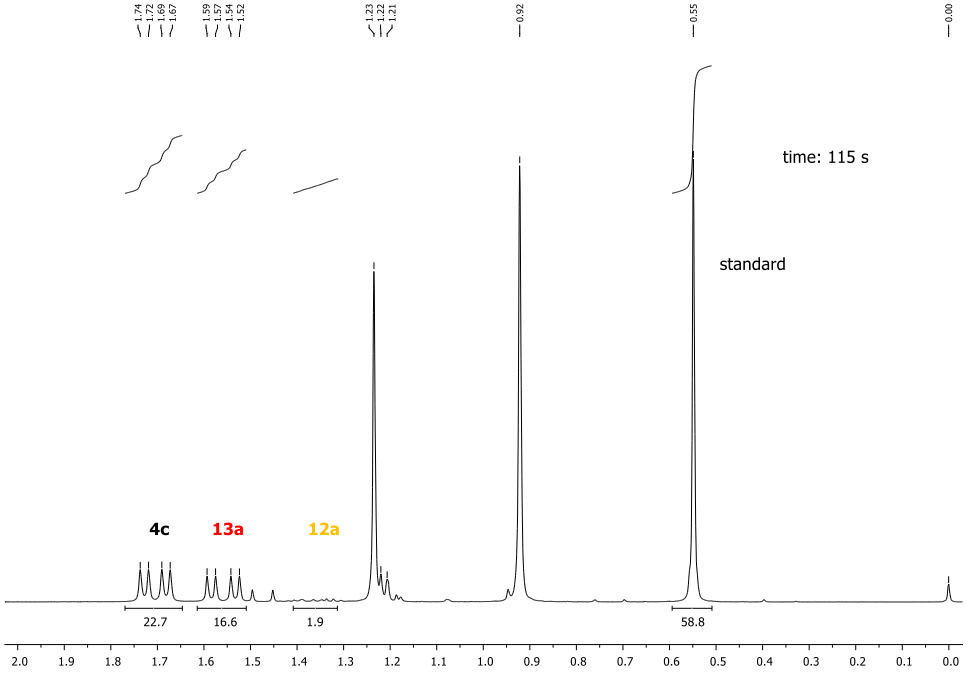
Figure 1. Concentration of the substrate **4c**, intermediate **13a** and product **12a** as a function of time for the reaction of 1-(*N*-pivaloylamino)ethyltris(3-chlorophenyl)phosphonium tetrafluoroborate **4c** with trimethylphosphite at 26°C. [1]

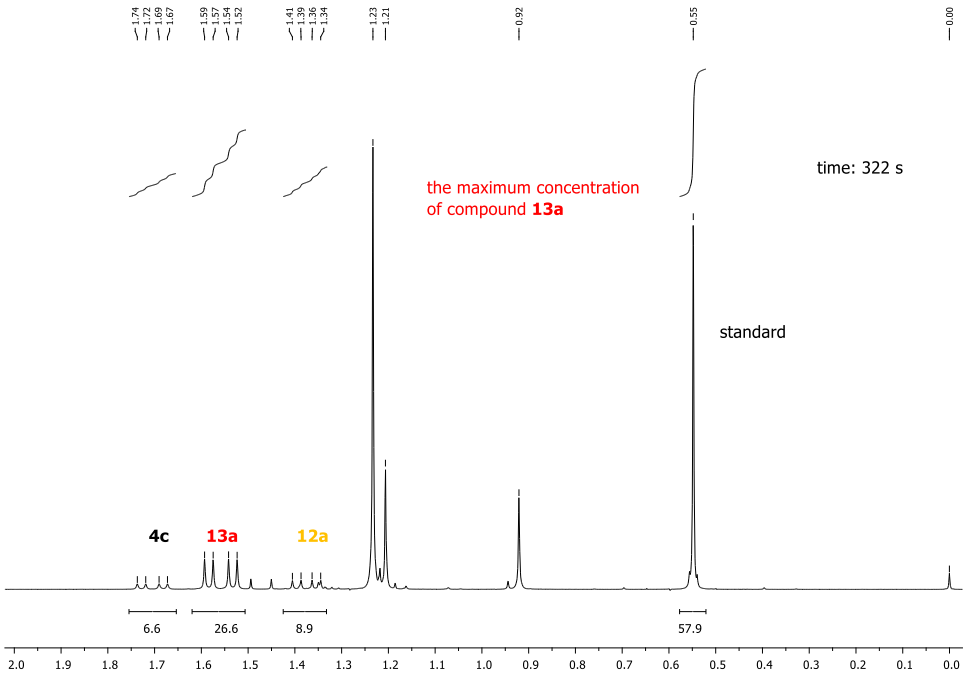
H NMR spectrum of 1-(*N*-pivaloylamino)ethyltris(3-chlorophenyl)phosphonium tetrafluoroborate before adding trimethylphosphite (the characteristic range: 2.0-0.0 ppm); 400 MHz/$CDCl_3$/TMS; δ (ppm).

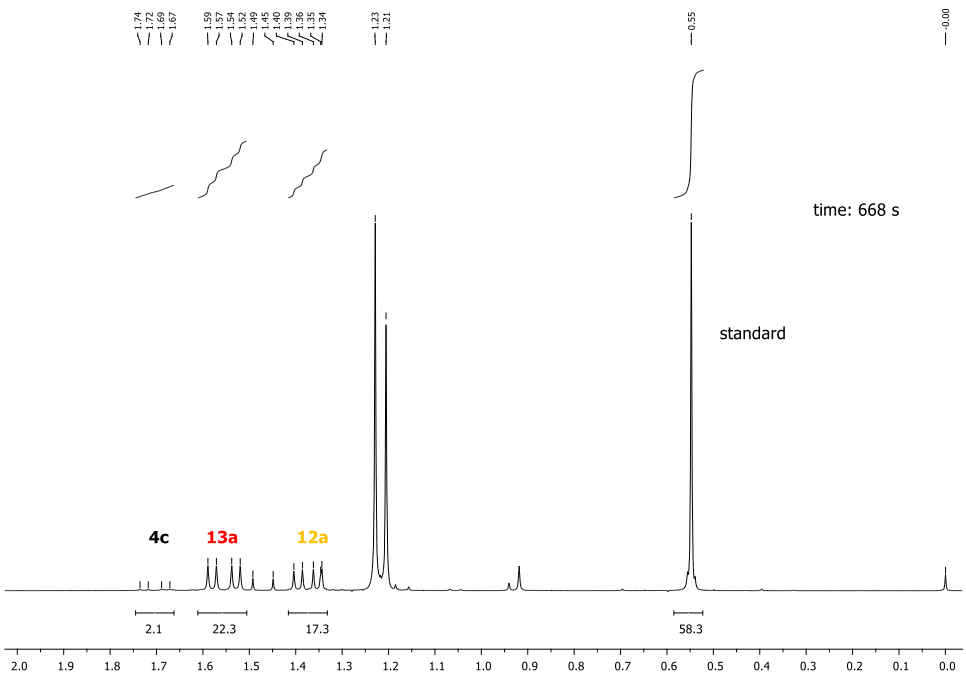


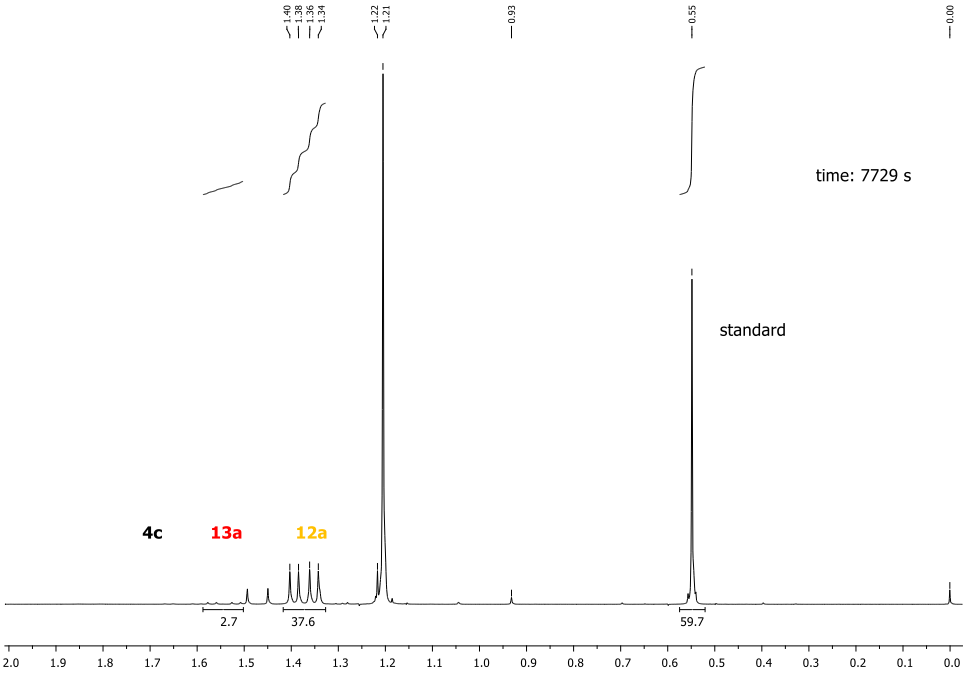
[1]H NMR spectra of the reaction mixture after 115, 322, 668 and 7729 seconds

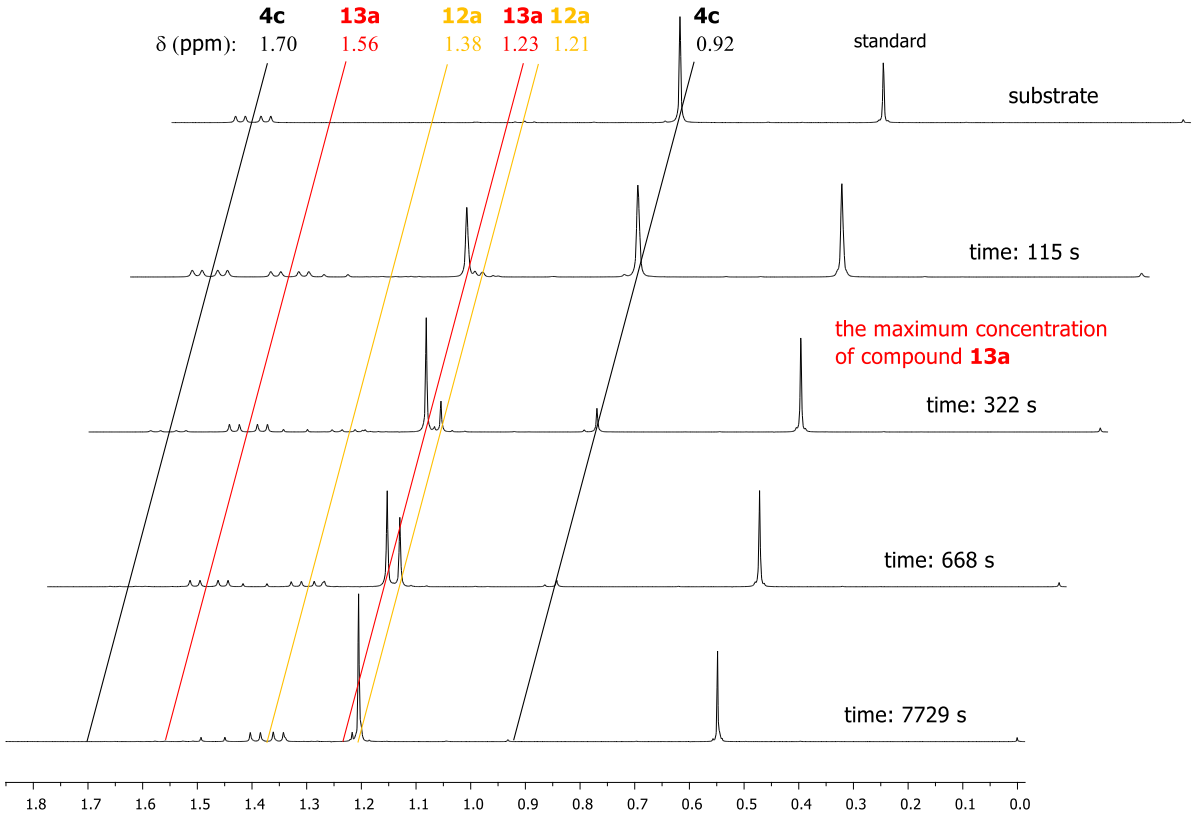
(the characteristic range: 2.0-0.0 ppm); 400 MHz/$CDCl_3$/TMS; δ (ppm).






1.74
1.72
1.69
1.67
1.59
1.57
1.54
1.52
1.49
1.45
1.40
1.39
1.36
1.35
1.34
1.23
1.21
0.55
0.00
time: 668 s
standard
4c
13a
12a
2.1
22.3
17.3
58.3
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0


1.40
1.38
1.36
1.34
1.22
1.21
0.93
0.55
0.00
time: 7729 s
standard
4c
13a
12a
2.7
37.6
59.7
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0


4c
13a
12a
13a 12a
4c
δ (ppm):
1.70
1.56
1.38
1.23
1.21
0.92
standard
substrate
time: 115 s
the maximum concentration
of compound 13a
time: 322 s
time: 668 s
time: 7729 s
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0