Catalyst selective and regiodivergent *O*- to *C*- or *N*-carboxyl transfer of pyrazolyl carbonates: synthetic and computational studies

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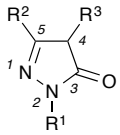
Compound numbering

The following numbering schemes have been used throughout for the pyrazoline derivatives below:



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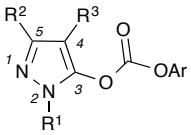
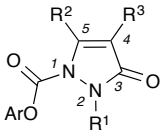
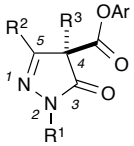


***O*-isomer**



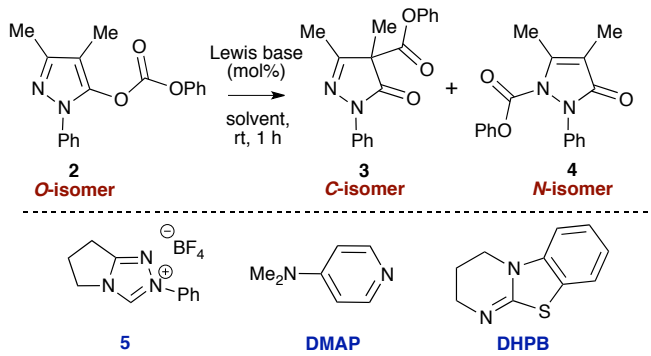
***N*-isomer**



***C*-isomer**

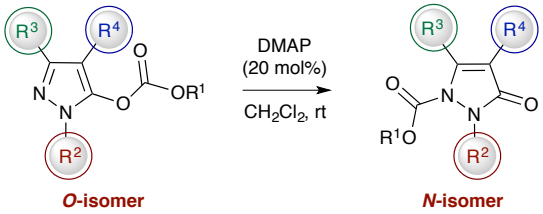
Full results breakdown for catalysed Steglich rearrangements

As determined by ^{1}H NMR spectroscopic analysis of crude reaction mixtures or direct reaction samples.

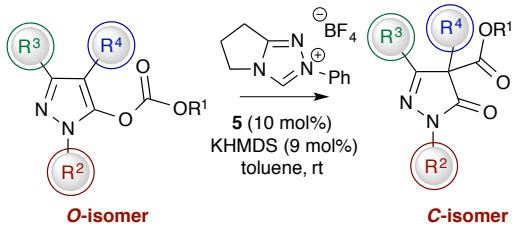


Entry	Lewis base	Solvent	% Ratio[a]				Yield (%)
			2	**3**	**4**	**S1**	
1	Precat **5** (20)[b]	THF	0	83	0	17	44 (**3**)
2	Precat **5** (10)	toluene	0	88	1	11	49 (**3**)
3	Precat **5** (5)	toluene	0	96	0	4	-
4	Precat **5** (2)	toluene	0	99	1	0	-
5	DMAP (20)	CH_2Cl_2	27	5	65	3	56 (**4**)
6	DMAP (20)[c]	CH_2Cl_2	2	62	11	25	42 (**3**)
7[a]	DHPB (20)	CH_2Cl_2	34	6	58	2	-
8	DMAP (20)	toluene	75	5	17	3	-
9	DMAP (20)	THF	75	5	16	4	-

[a] Established by ^{1}H NMR spectroscopic analysis of crude reaction mixture; [b] NHC generated by deprotonation with KHMDS; [c] overnight reaction

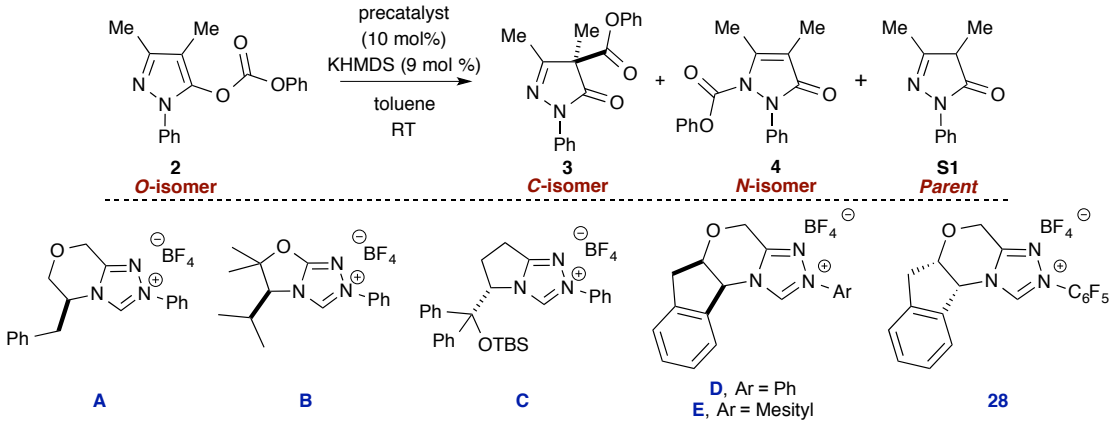


Entry	Time (h)	R^1	R^2	R^3	R^4	% Ratio				Yield (%)	C:N
						O	C	N	PAR		
1	1	Ph	Ph	Me	Me	27	5	65	3	56	7:93
2	18	Bn	Ph	Me	Me	12	0	87	1	10	<1:>99
3	1	CH_2CCl_3	Ph	Me	Me	14	14	71	1	64	16:84
4	1	4-F-C_6H_4	Ph	Me	Me	3	6	90	1	66	6:94
5	1	4-OMe-C_6H_4	Ph	Me	Me	55	3	41	1	32	7:93
6	18	Ph	Me	Ph	Me	62	2	31	6	14	6:94
7	1	4-FC_6H_4	Me	Me	Me	22	0	78	0	60	<1:>99
8	18	Ph	Me	Me	Me	3	0	92	5	77	<1:>99
9	1	4-FC_6H_4	Ph	Me	Et	12	3	85	0	74	3:97
10	18	Ph	Ph	Me	Et	12	0	77	11	40	<1:>99
11	1	4-FC_6H_4	Ph	Me	Bn	12	3	85	0	80	3:97
12	1	Ph	Ph	Me	Bn	14	4	81	1	75	5:95
13	1	4-FC_6H_4	Me	Me	Et	1	0	95	4	61	<1:>99
14	1	Ph	Me	Me	Et	3	0	92	5	81	<1:>99
15	1	4-FC_6H_4	Me	Me	Bn	15	1	82	4	50	1:99
16	1	Ph	Me	Me	Bn	64	0	35	1	35	<1:>99
17	1	4-FC_6H_4	Me	Me	*i*-Bu	0	3	86	11	77	3:97



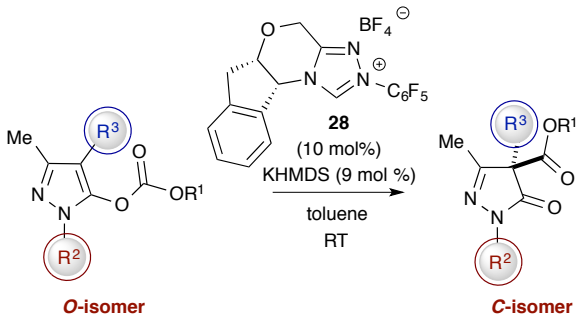
Entry	Time (h)	R^1	R^2	R^3	R^4	% Ratio				Yield (%)	C:N
						O	C	N	PAR		
1	1	Ph	Ph	Me	Me	0	88	1	11	49	>99: <1
2[a]	18	Bn	Ph	Me	Me	54	22	0	24	12	>99: <1
3	1	CH_2CCl_3	Ph	Me	Me	0	99	0	1	67	>99: <1
4	1	4-F-C_6H_4	Ph	Me	Me	0	80	0	20	49	>99: <1
5	1	4-OMe-C_6H_4	Ph	Me	Me	0	92	7	1	63	93:7
6[a]	1	Ph	Me	Ph	Me	1	83	0	16	55	>99: <1
7	1	4-FC_6H_4	Me	Me	Me	0	97	3	0	71	97:3
8[a]	1	Ph	Me	Me	Me	0	82	3	15	63	96:4
9	1	4-FC_6H_4	Ph	Me	Et	0	92	0	8	84	>99: <1
10	1	Ph	Ph	Me	Et	0	79	0	21	44	>99: <1
11	1	4-FC_6H_4	Ph	Me	Bn	0	91	1	8	73	99: 1
12	1	Ph	Ph	Me	Bn	0	98	0	2	73	>99: <1
13	1	4-FC_6H_4	Me	Me	Et	0	88	3	9	68	97:3
14	3	Ph	Me	Me	Et	0	91	0	9	77	>99: <1
15	1	4-FC_6H_4	Me	Me	Bn	1	76	12	12	31	86:14
16	1	Ph	Me	Me	Bn	0	85	6	8	47	93:7
17	1	4-FC_6H_4	Me	Me	*i*-Bu	2	62	20	16	45	76:24

a) 20 mol%



Entry	Catalyst	% Ratio				Yield (%)	% ee
		2	3	4	S1		
1	**A**	2	87	11	0	71	56
2 [a]	**A**	2	87	10	1	61	46
3	**B**	2	89	8	1	74	46
4	**C**	86	3	10	1	–	-
5	**D**	1	92	6	1	–	46[b]
6	**E**	8	30	57	5	–	40 (*ent*)
7	**28**	3	95	1	1	77	62

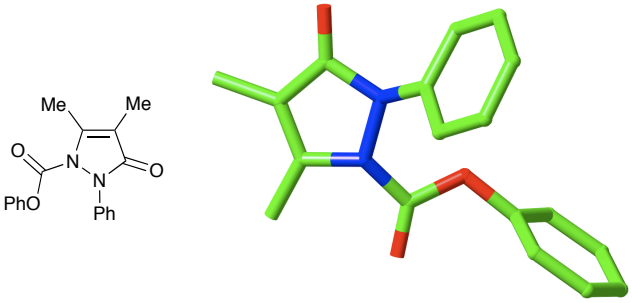
a) solvent THF; b) ee determined on crude reaction mixture.



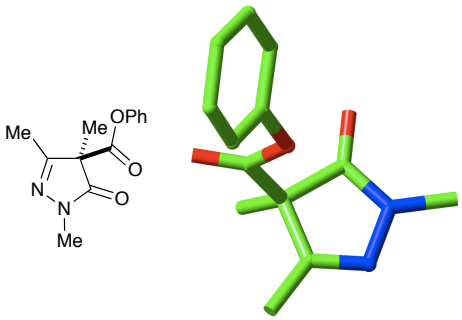
Entry	Time (h)	R^1	R^2	R^3	% Ratio				Yield (%)	C:N	% ee
					O	C	N	PAR			
1	1	Ph	Ph	Me	3	95	1	1	77	99:1	62
2	3	CH_2CCl_3	Ph	Me	9	83	1	7	75	>99: <1	10
3	3	4-FC_6H_4	Ph	Me	0	93	0	7	54	>99: <1	60
4	18	4-OMe-C_6H_4	Ph	Me	0	99	0	1	57	>99: <1	68
5	1	4-FC_6H_4	Ph	Et	0	88	0	12	74	>99: <1	69
6	1	Ph	Ph	Et	0	71	1	28	39	99: 1	66
7	1	4-FC_6H_4	Ph	Bn	2	86	1	10	67	99: 1	60
8	3	Ph	Ph	Bn	7	89	1	9	51	99:1	49
9	1	4-FC_6H_4	Me	Me	0	76	23	1	65	77:23	88
10	18	Ph	Me	Me	0	72	13	15	61	85:15	86
11	1	4-FC_6H_4	Me	Et	0	74	15	11	54	83:17	90
12	3	Ph	Me	Et	13	67	13	7	54	84:16	87
13	18	4-FC_6H_4	Me	*i*-Bu	15	37	30	18	23	55:45	92

Crystal structure information for compounds **4**, **29**, **S13** and **S22**

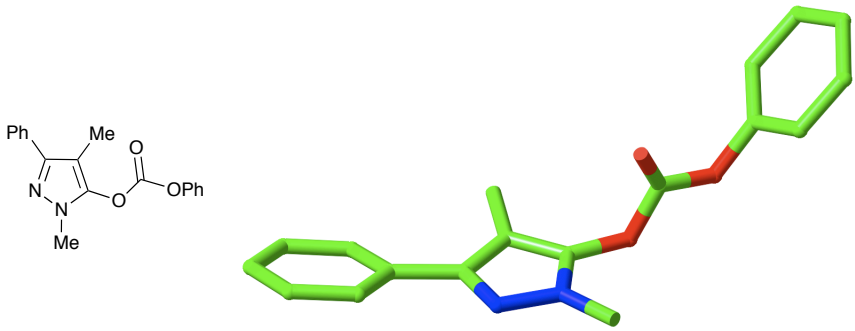
Crystallographic data (excluding structure factors) for compounds **4**, **27**, **29**, **S13** and **S22** have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 987861, CCDC 987862, CCDC 987863and CCDC 987864, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).



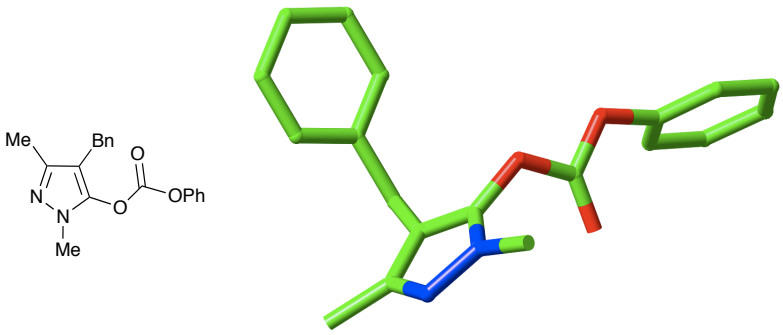
Crystal structure of compound **4** (CCDC 987861)



Crystal structure of compound **29** (absolute configuration confirmed as *R*, CCDC 987862)

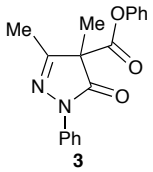


Crystal structure of compound **S13** (CCDC 987863)



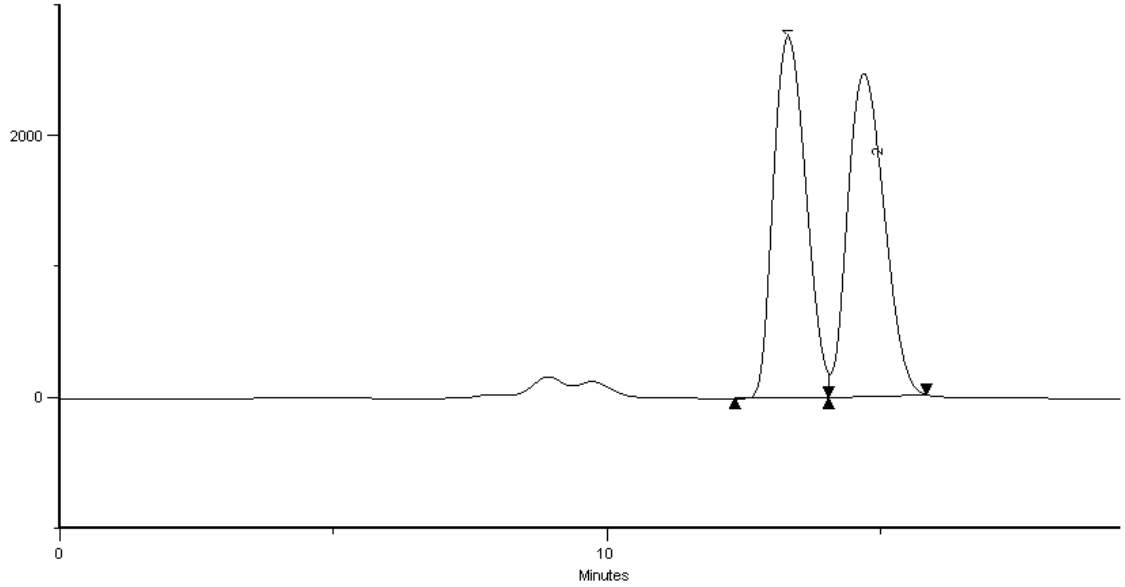
Crystal structure of compound **S22** (CCDC 987864)

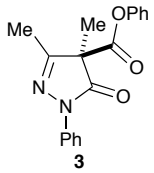
HPLC data for chiral compounds



3

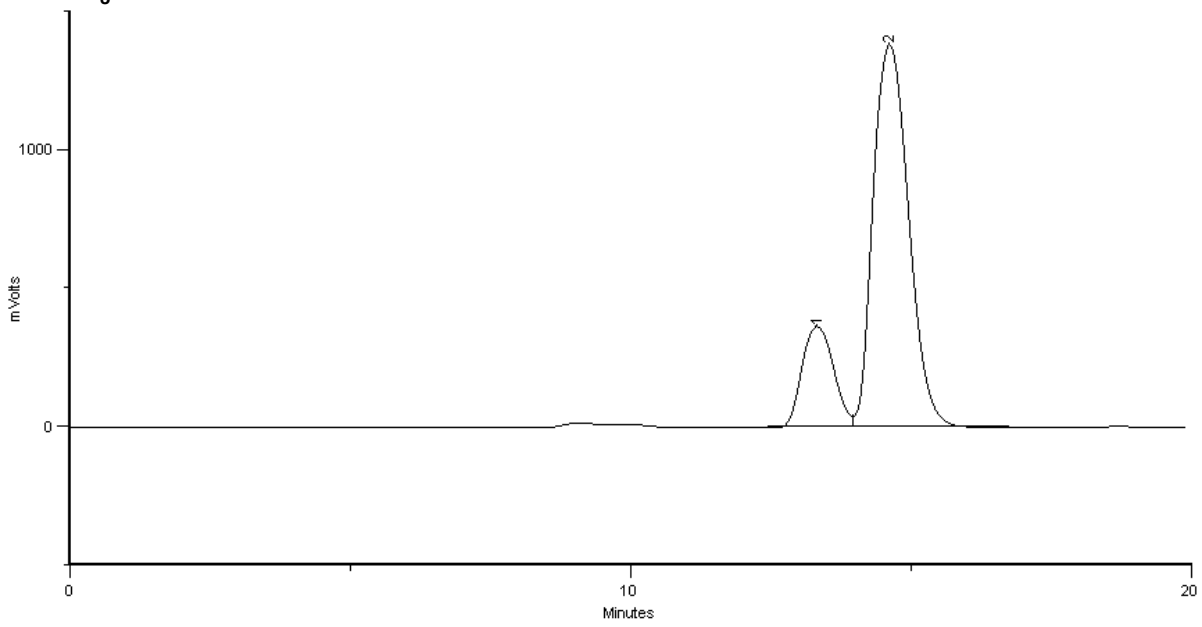
	Peak Name	R. Time	Area %
1	*1	13.32	49.71
	*2	14.70	50.29

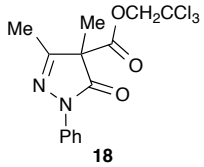




3

	Peak Name	R. Time	Area %
1	*1	13.33	19.13
	2	14.62	80.87

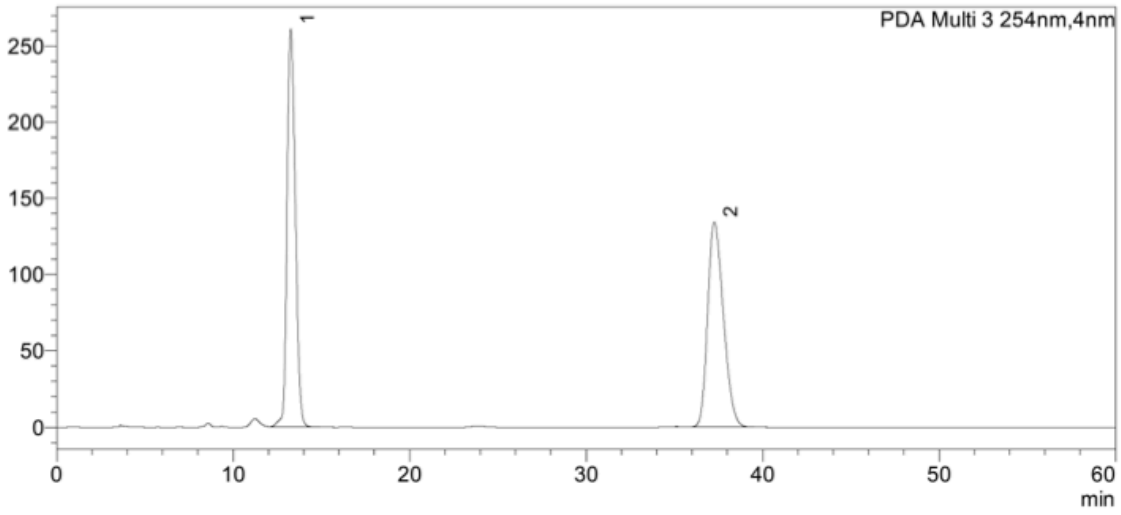


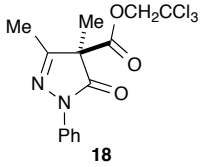


18

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	13.264	50.640
2	37.268	49.360
Total		100.000





18

PDA Ch3 254nm

Peak#	Ret. Time	Area%
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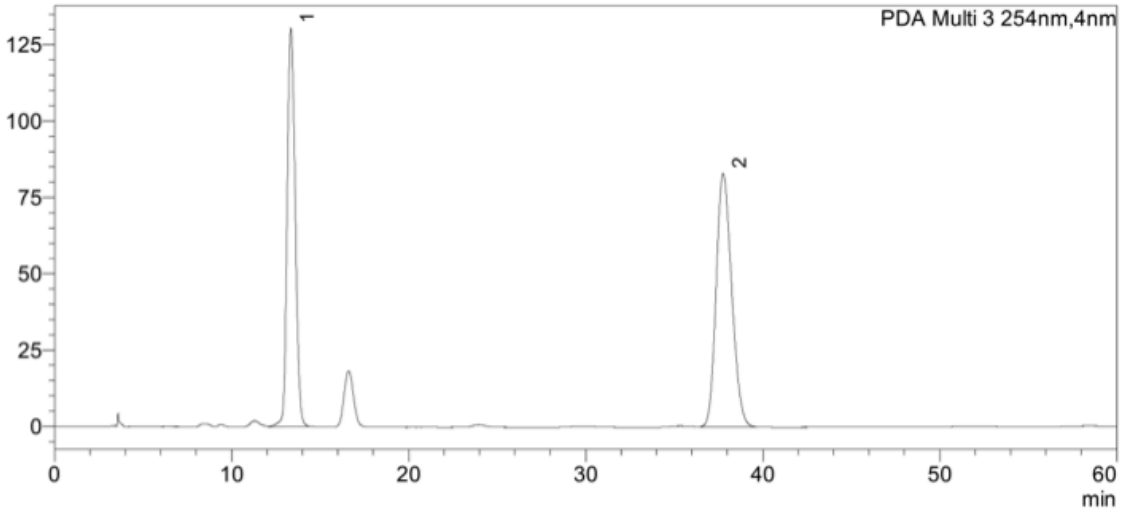
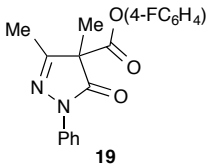
2	37.765	54.994
Total		100.000

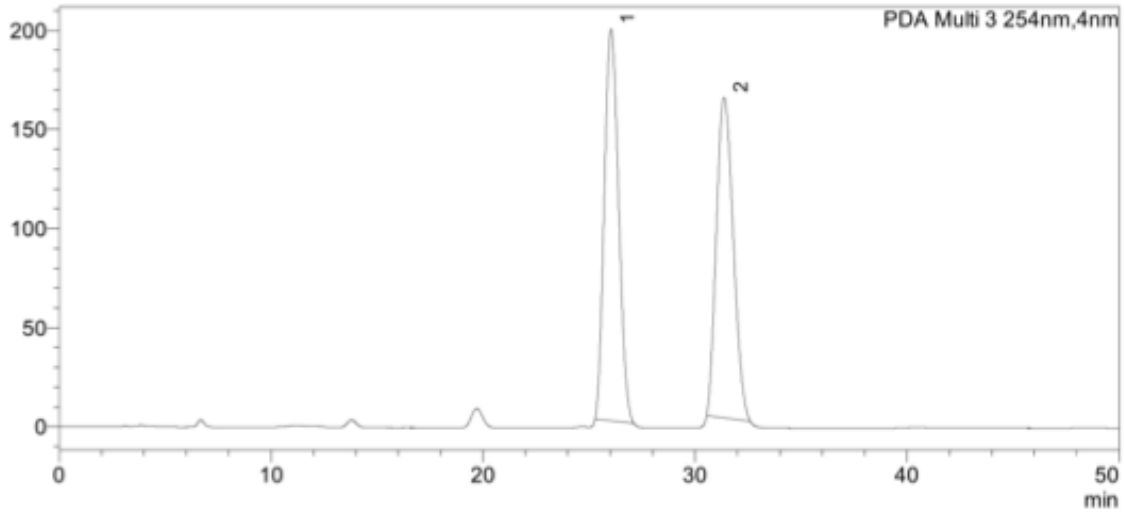


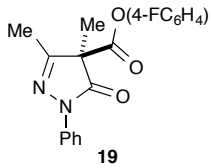


19

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	26.043	50.687
2	31.375	49.313
Total		100.000

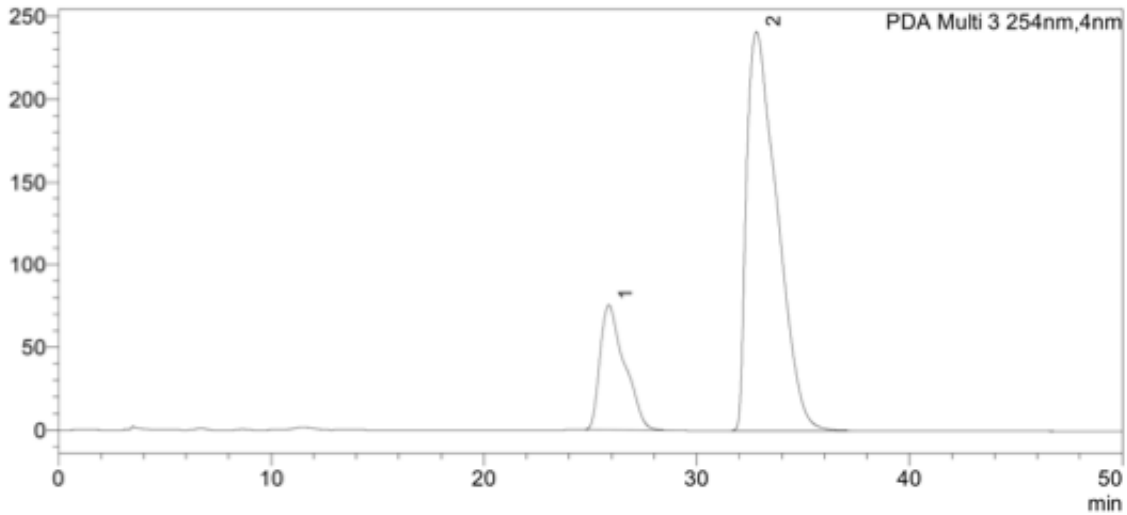


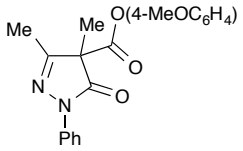


19

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	25.868	20.093
2	32.812	79.907
Total		100.000

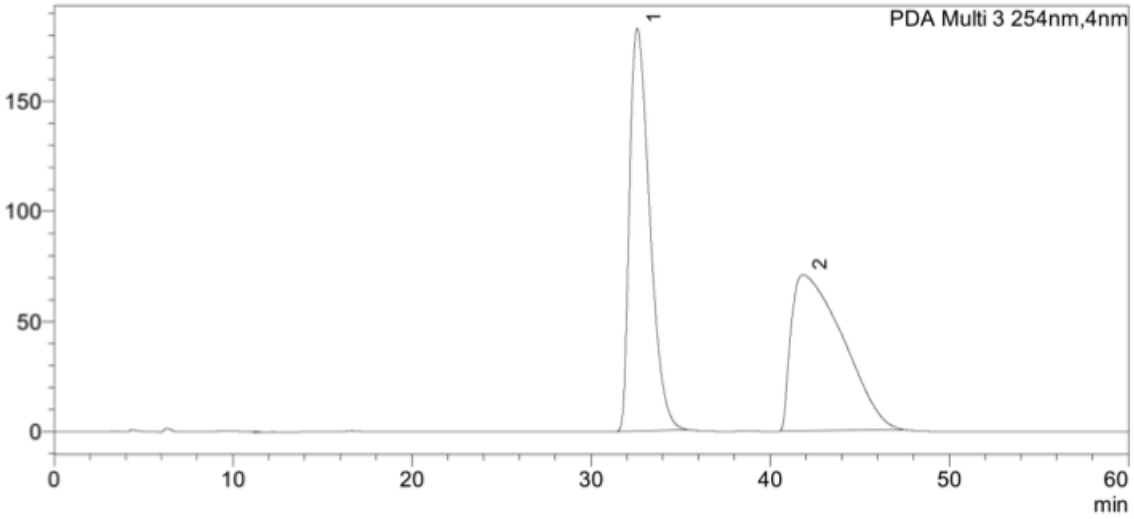


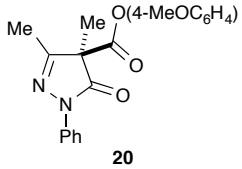


20

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	32.583	50.170
2	41.845	49.830
Total		100.000

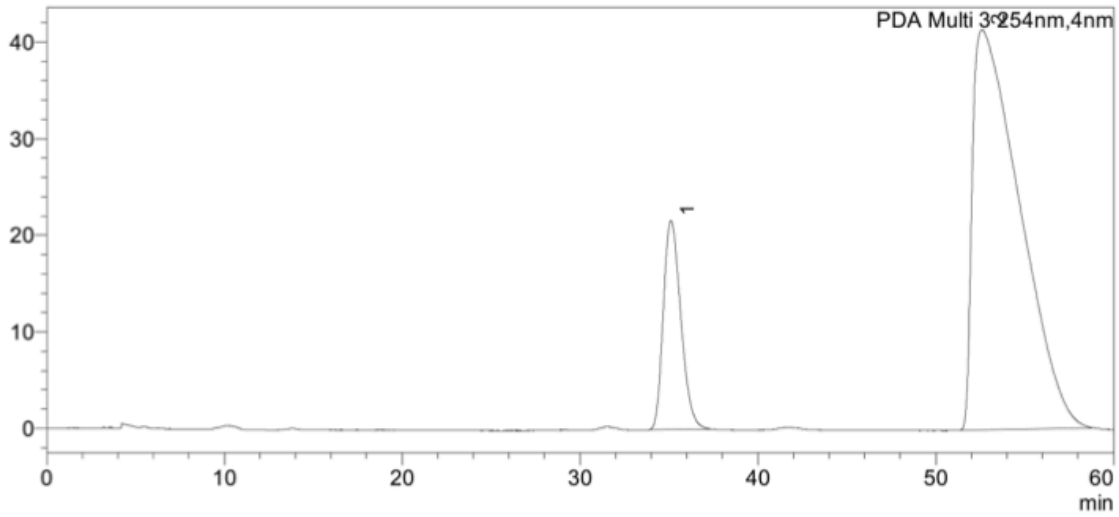


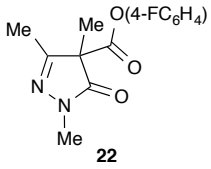


20

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	35.112	16.231
2	52.591	83.769
Total		100.000

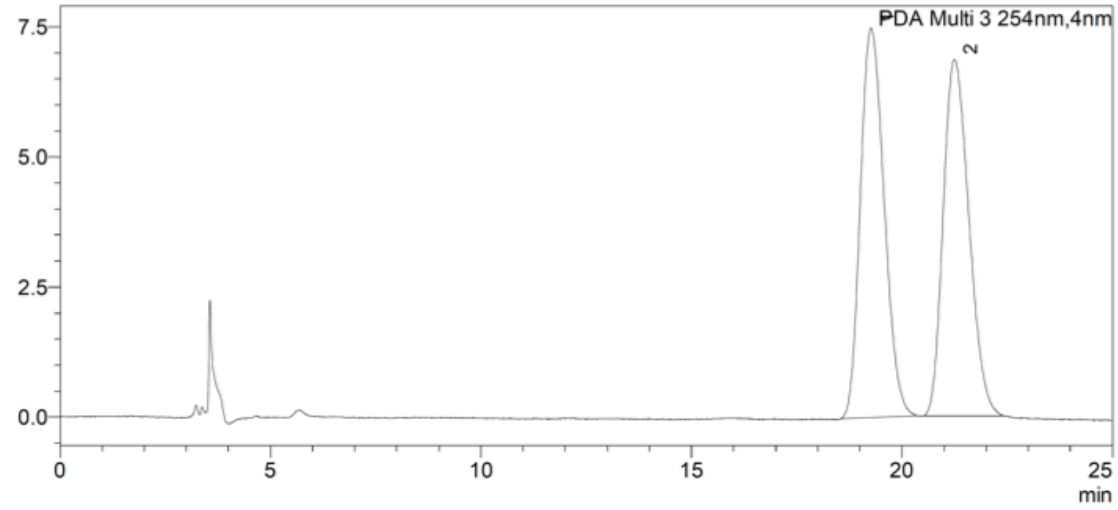


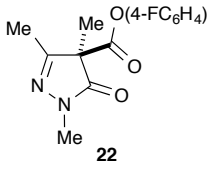


22

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	19.267	50.253
2	21.242	49.747
Total		100.000

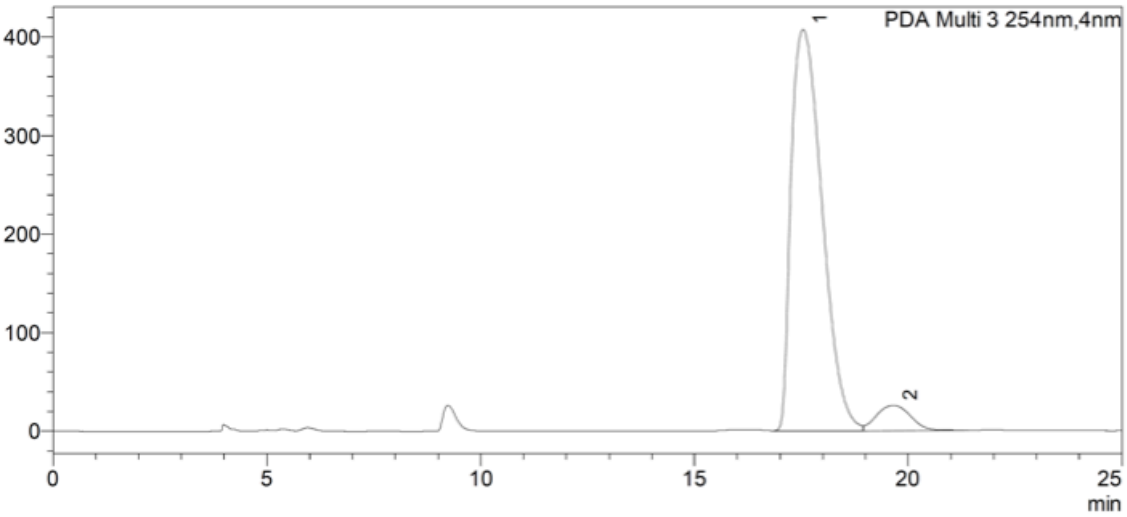


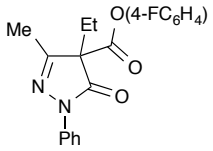


22

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	17.540	93.357
2	19.657	6.643
Total		100.000

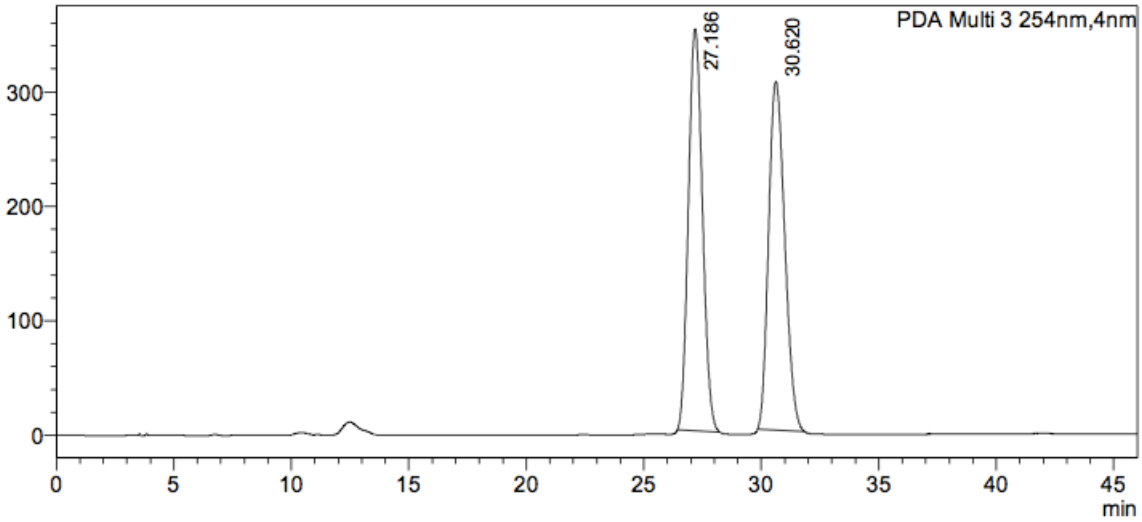


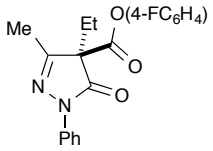


23

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	27.186	50.083
2	30.620	49.917
Total		100.000

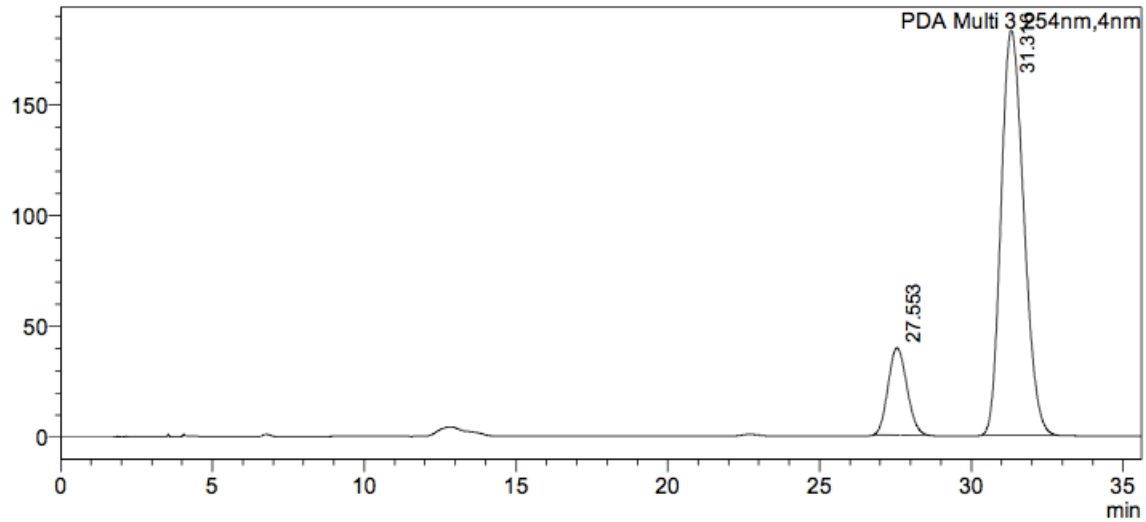


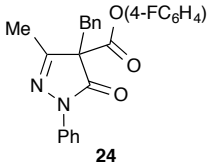


23

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	27.553	1709117	15.265
2	31.316	9487424	84.735
Total		11196541	100.000

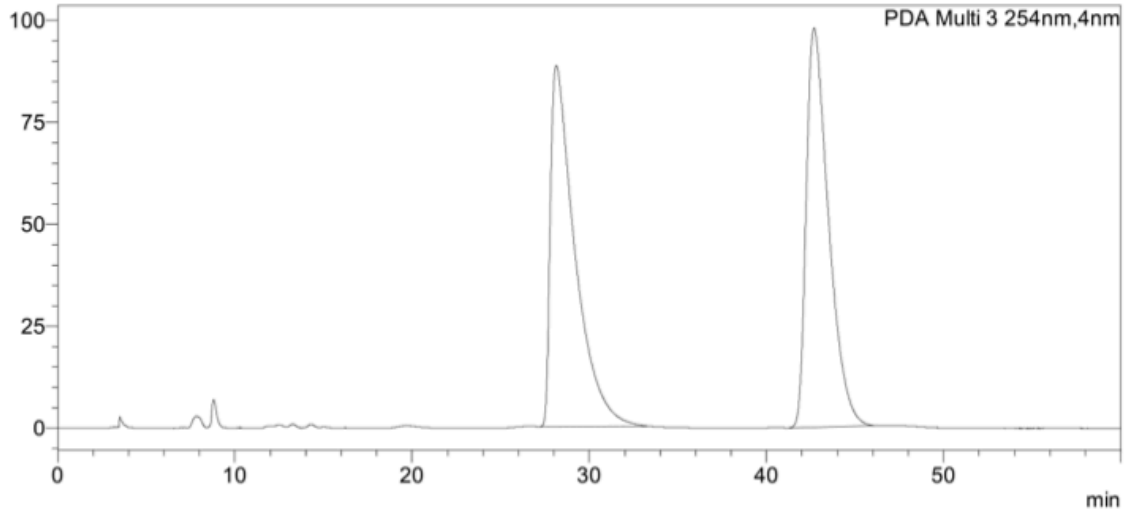


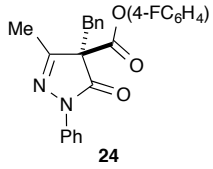


24

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	28.141	49.865
2	42.683	50.135
Total		100.000

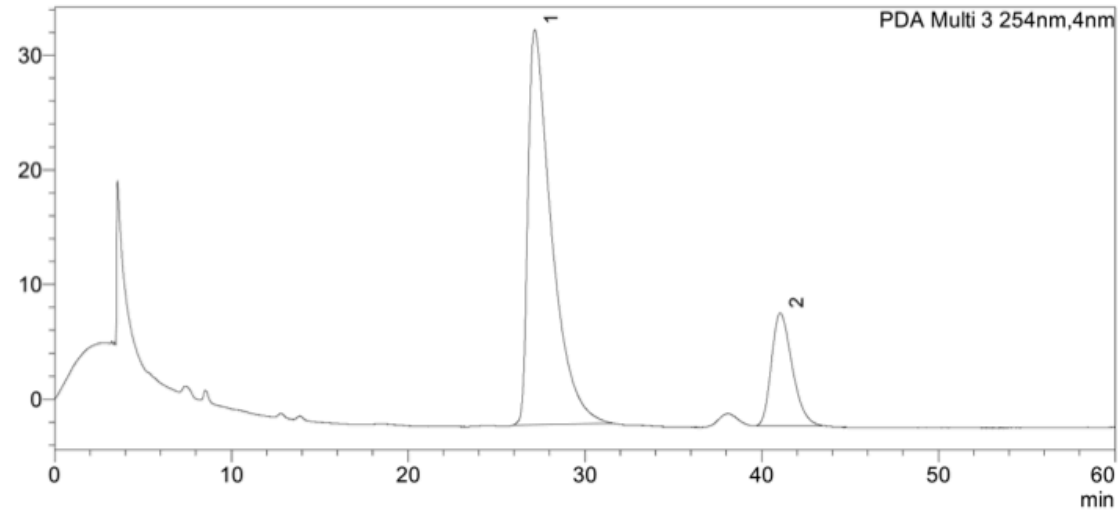


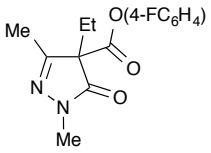


24

PDA Ch3 254nm

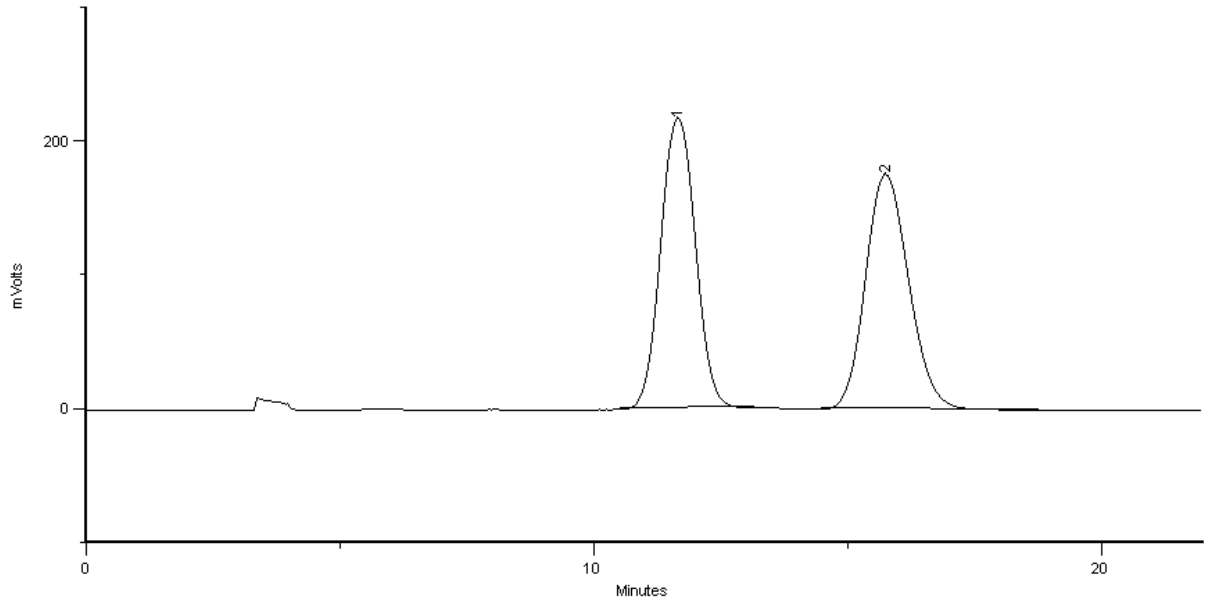
Peak#	Ret. Time	Area%
1	27.176	79.975
2	41.057	20.025
Total		100.000

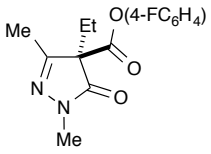




25

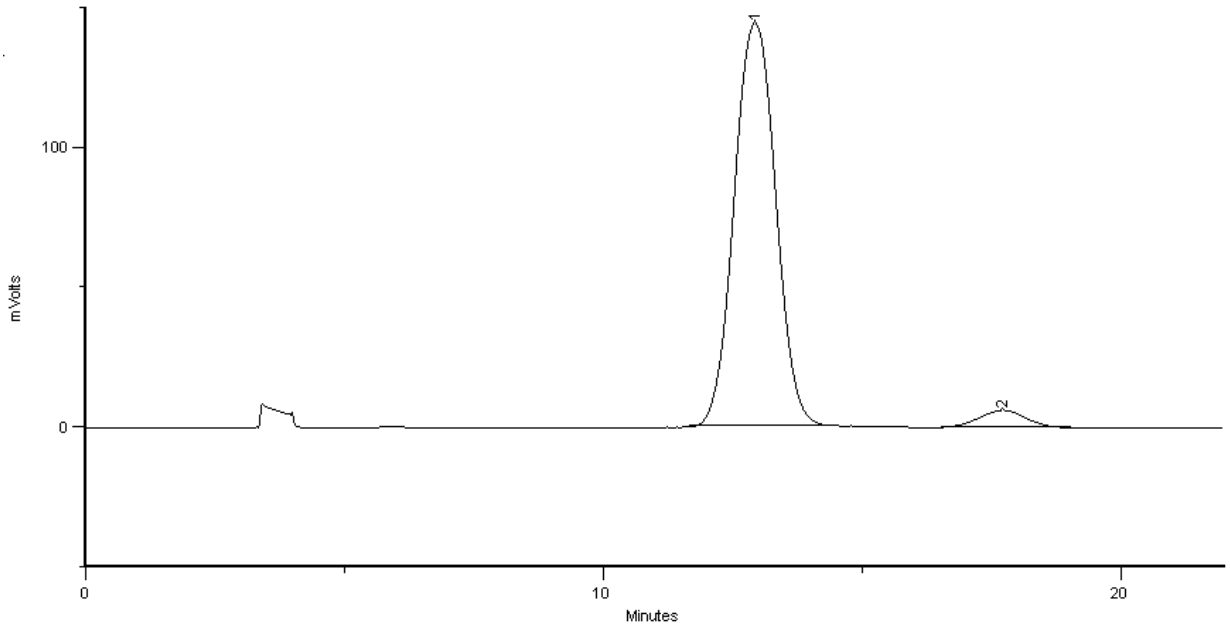
	Peak Name	R. Time	Area %
1	*1	11.66	49.79
	2	15.75	50.21

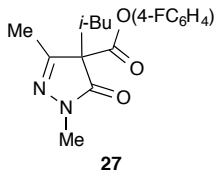




25

	Peak Name	R. Time	Area %
1	*1	12.93	95.35
	2	17.72	4.65

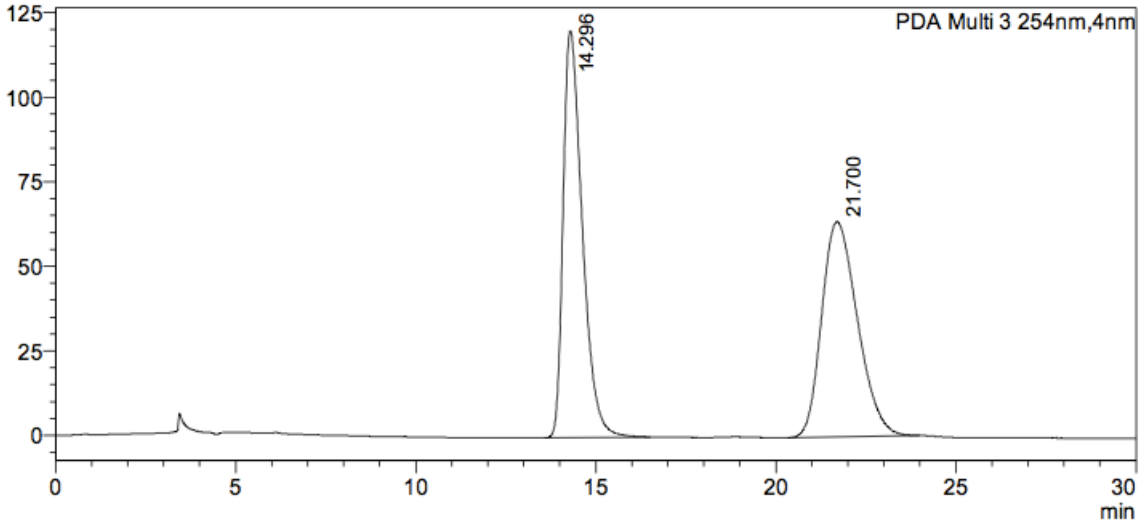


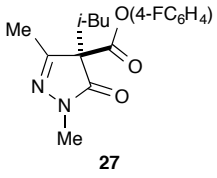


27

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	14.296	50.376
2	21.700	49.624
Total		100.000

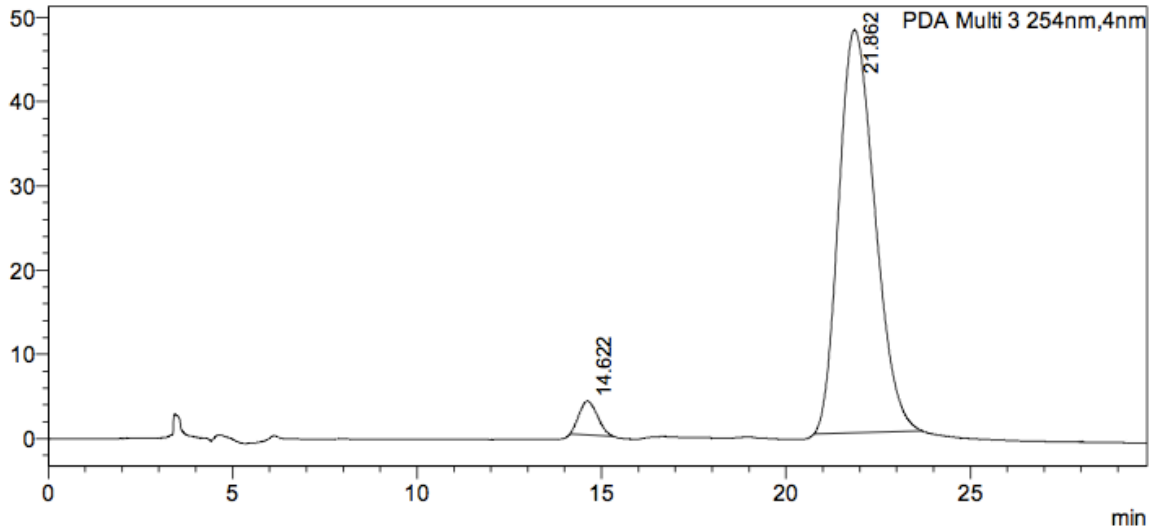


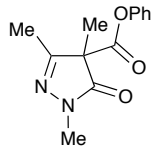


27

PDA Ch3 254nm

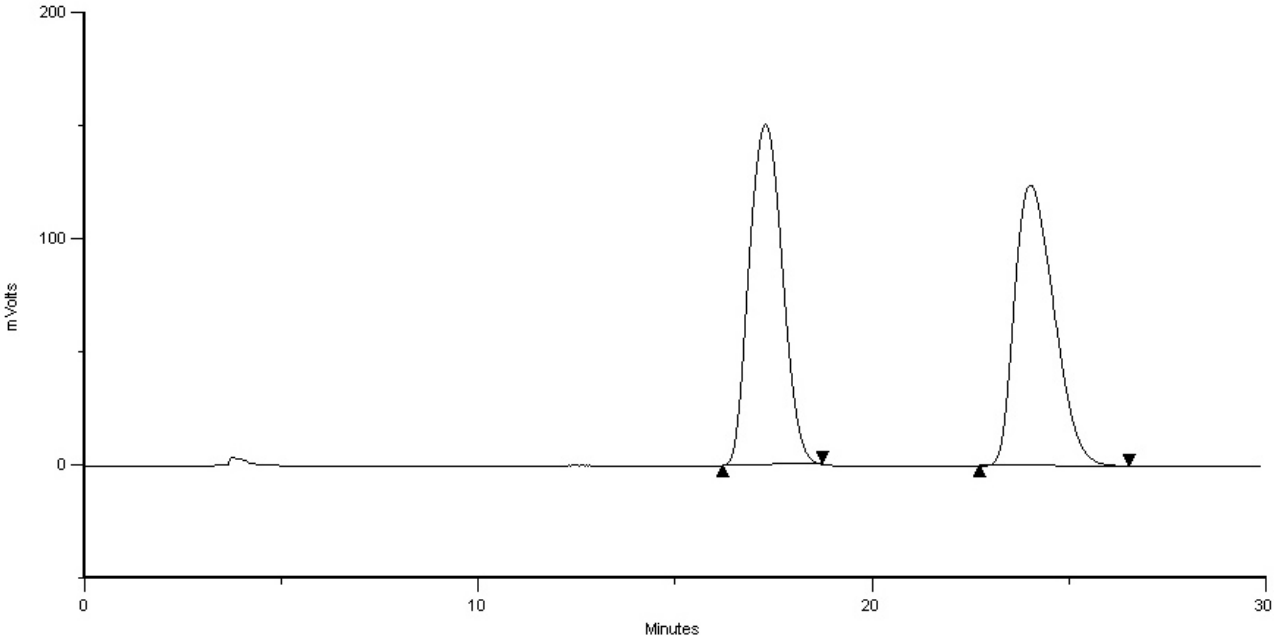
Peak#	Ret. Time	Area%
1	14.622	4.087
2	21.862	95.913
Total		100.000

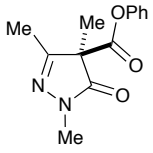




29

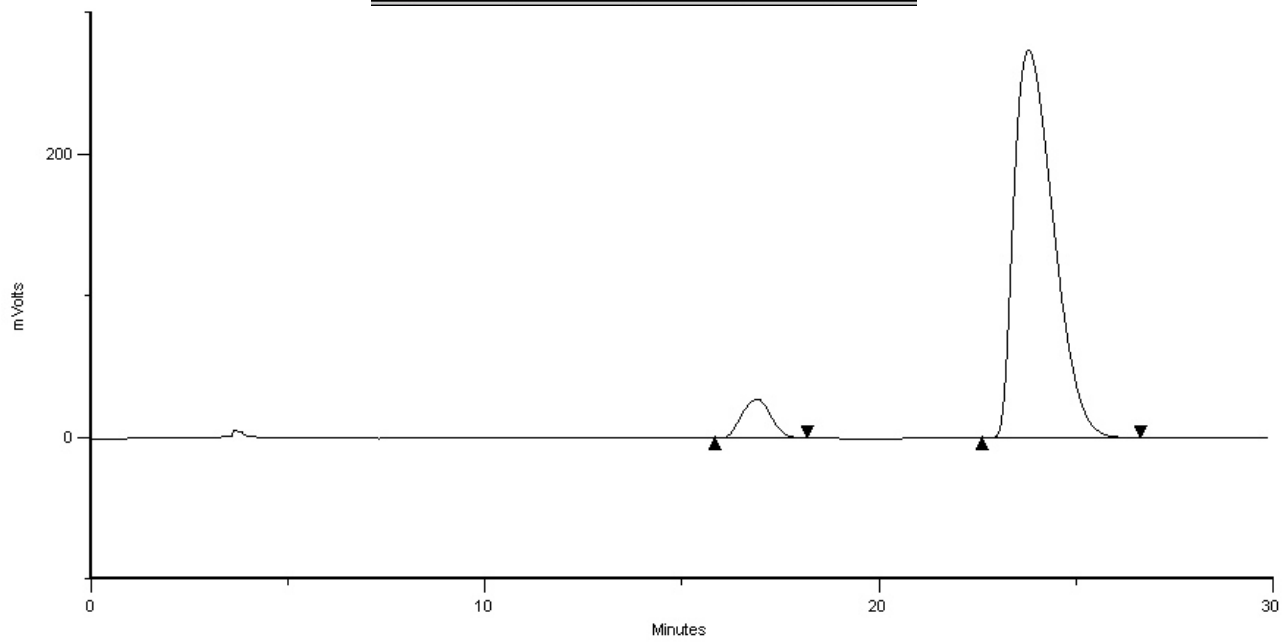
	Inj. Number	Peak Name	R. Time	Area	Area %
1	1.00	*1	17.29	4858476.00	50.43
2	1.00	*2	24.02	4607563.00	49.57

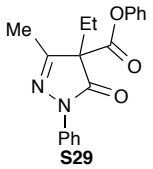




29

	Inj. Number	Peak Name	R. Time	Area	Area %
1	3.00	*1	16.90	2508109.75	7.20
	3.00	*2	23.80	32322304.00	92.80

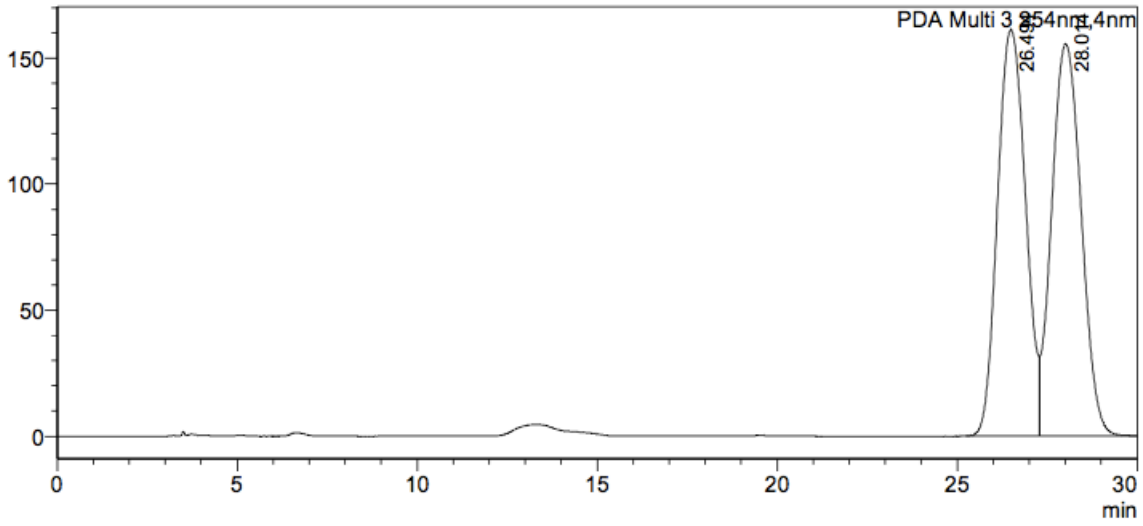


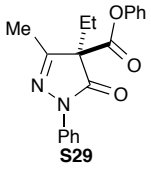


S29

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	26.494	49.453
2	28.014	50.547
Total		100.000

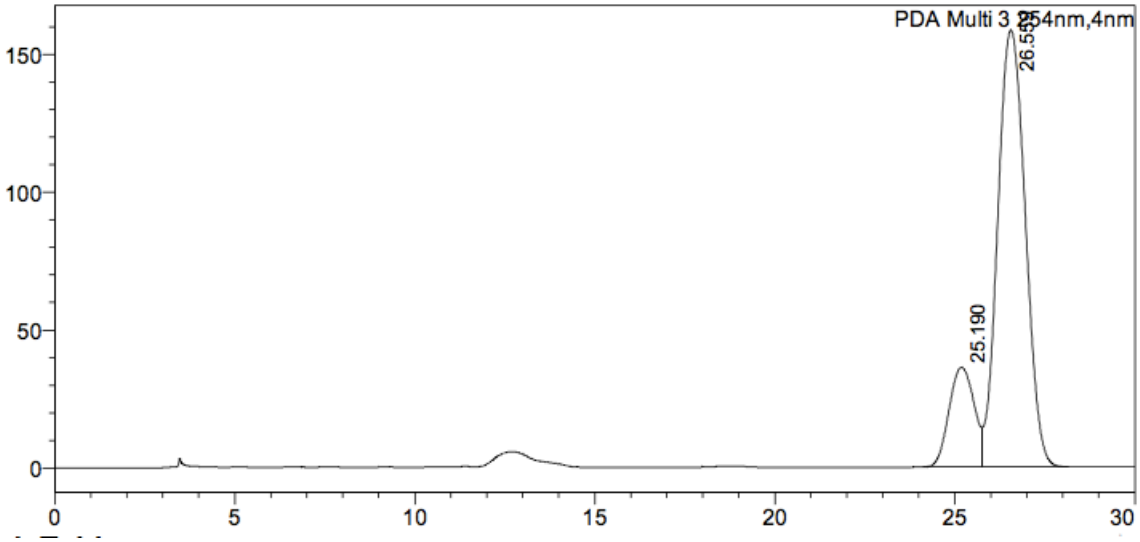


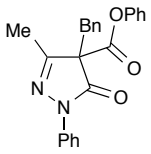


S29

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	25.190	17.205
2	26.559	82.795
Total		100.000

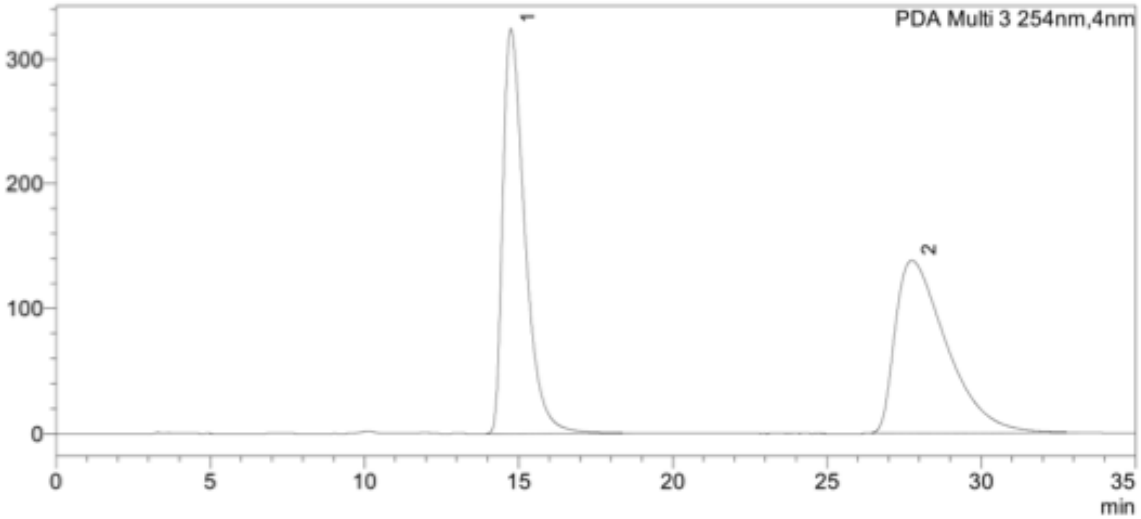


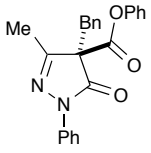


S30

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	14.757	50.070
2	27.761	49.930
Total		100.000

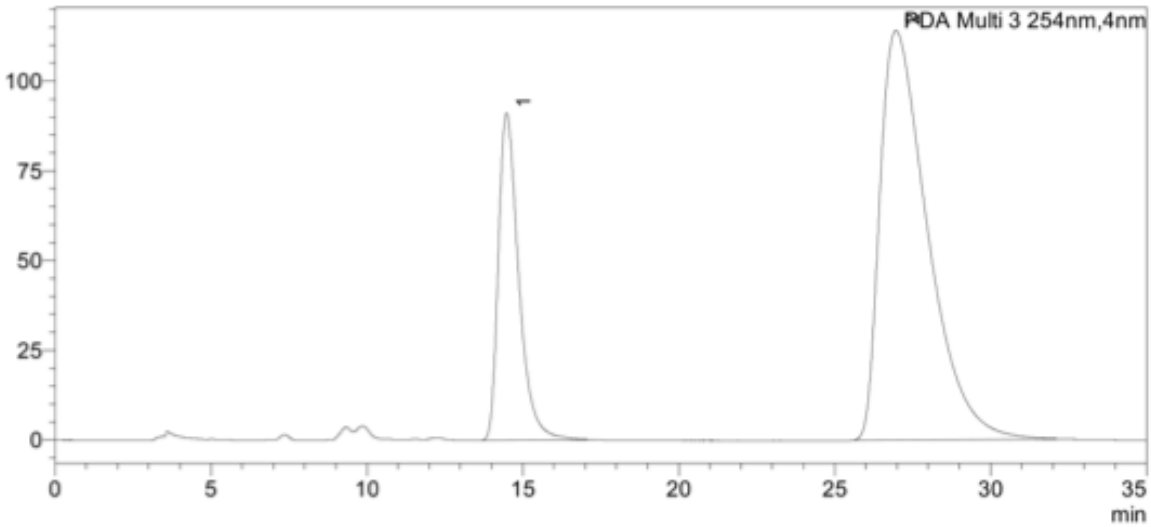


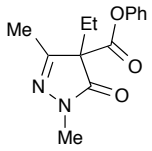


S30

PDA Ch3 254nm

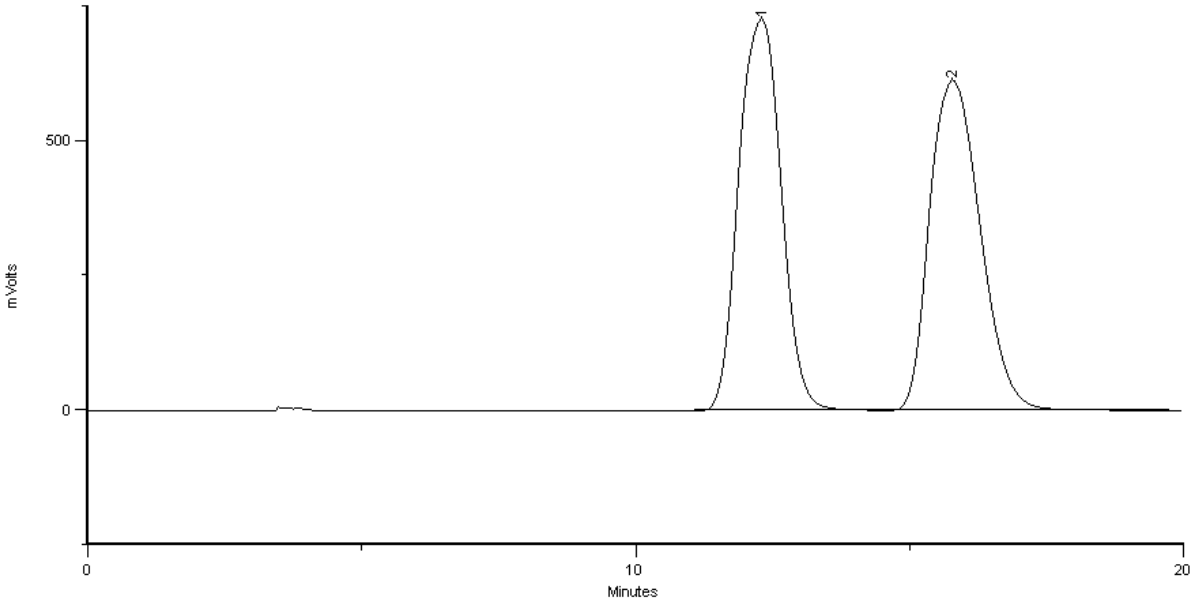
Peak#	Ret. Time	Area%
1	14.483	25.455
2	26.969	74.545
Total		100.000

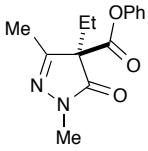




S31

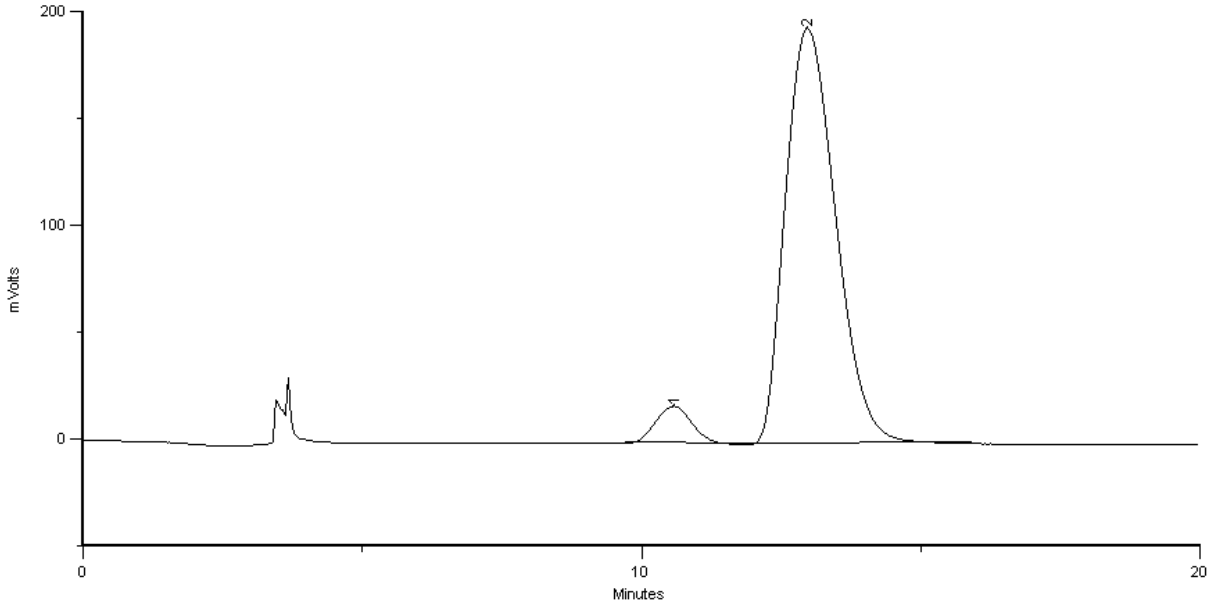
	Peak Name	R. Time	Area %
1	*1	12.30	49.91
	2	15.79	50.09





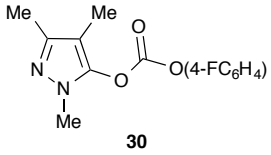
S31

	Peak Name	R. Time	Area %
1	*1	10.58	6.24
	2	12.97	93.76



Monitoring experiment

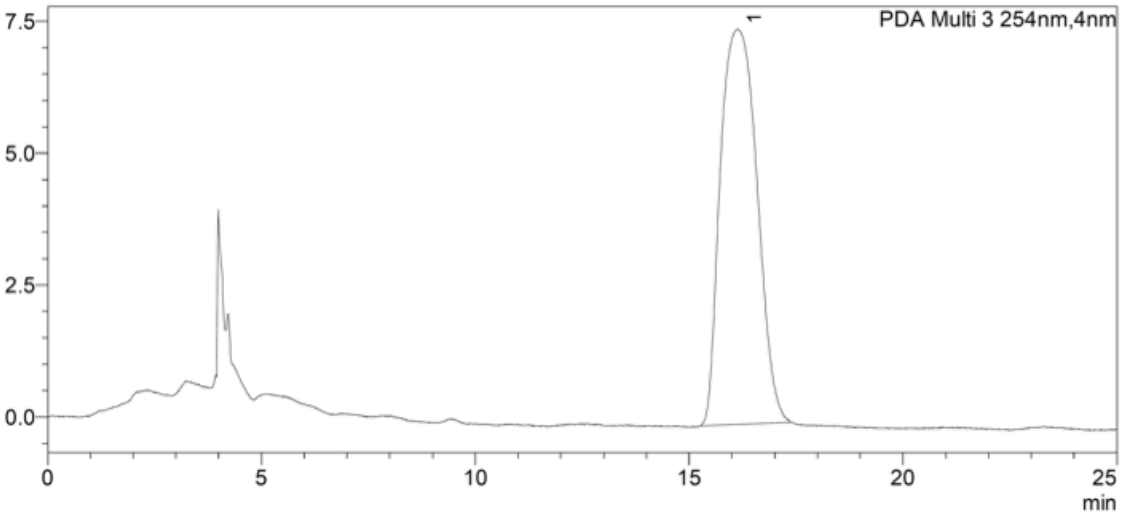
Traces run on Daicel Chiralpak OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) unless other wise stated.

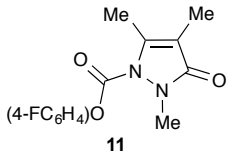


30

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	16.128	100.000
Total		100.000



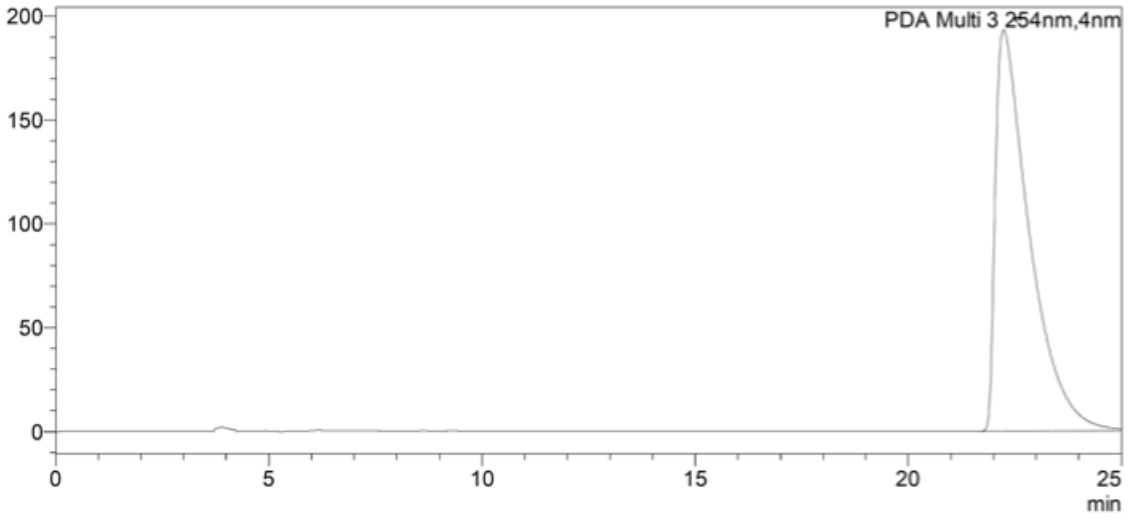


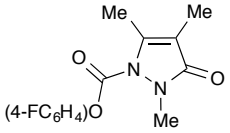
11

*i*PrOH 10:90 hexane

PDA Ch3 254nm

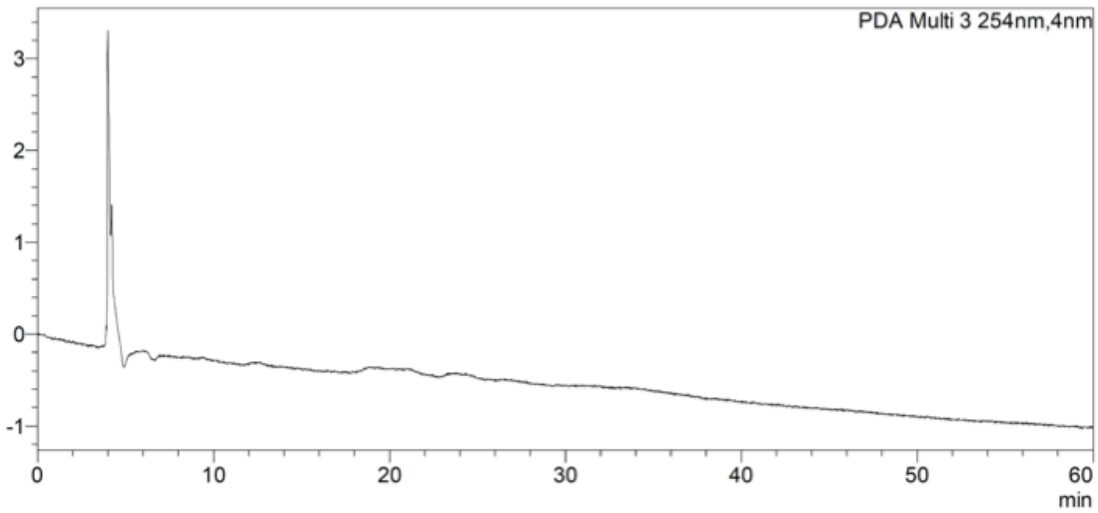
Peak#	Ret. Time	Area%
1	22.240	100.000
Total		100.000

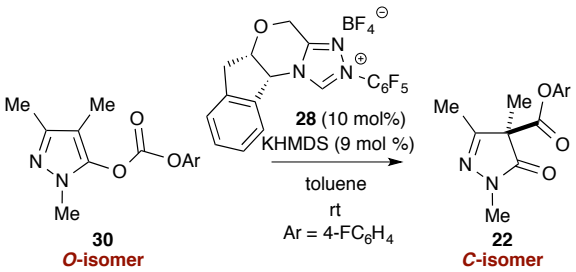




11

No peak observed within 60 min

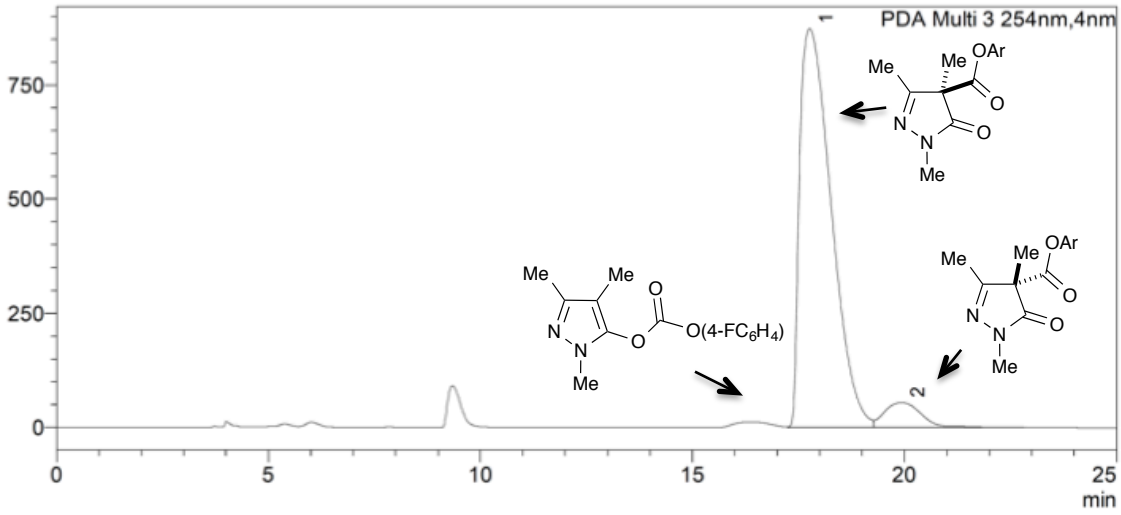




10 min timepoint

PDA Ch3 254nm

Peak#	Ret. Time	Area%
1	17.767	93.059
2	19.926	6.941
Total		100.000



Experimental details

General experimental

All reactions involving moisture sensitive reagents were performed under an atmosphere of argon or nitrogen using standard vacuum line techniques and with freshly distilled solvents. All glassware was flame dried and allowed to cool under vacuum. Temperatures of 0 ºC were obtained using an ice/water bath and –78 ºC was obtained using a dry ice/acetone bath. Room temperature refers to 20–25 ºC. For compounds synthesised by multiple routes, only experimental details for the highest yielding asymmetric route are included.

All dried and purified solvents were obtained from a solvent purification system (MBraun, SPS-800) except for dry *N*,*N*′-dimethylformamide (DMF) which was purchased directly from Aldrich. Petrol refers to the fraction of petroleum ether boiling between 40 ºC and 60 ºC, dioxane refers to 1,4-dioxane, pH 7 phosphate buffer refers to a solution of sodium dihydrogen phosphate and di-sodium hydrogen orthophosphate and brine refers to a saturated aqueous solution of sodium chloride. KHMDS solution refers to a 0.5 M solution in toluene purchased from Aldrich. All other reagents were used directly as supplied without further purification.

Flash column chromatography was carried out according to the method of Still[1] with silica gel 60 (0.043-0.060 mm) (Merck) in the solvent system stated. Analytical thin layer chromatography was performed on commercially available pre-coated aluminium-backed plates (Merck silica Kieselgel 60 F_{254}). TLCs were visualised either by UV fluorescence (254 nm), or by staining with basic $KMnO_4$ solution.

Optical rotations were determined using a PerkinElmer Model 341 Polarimeter, at 20.0 ºC using a Na/Hal lamp tuned to 589 nm and with a 100 mm path length.

Melting points were recorded on an Electrothermal apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR Spectrometer and analysed either as thin films between NaCl plates (thin film) or KBr discs (KBr disc) as stated or a Shimadzu IRAffinity-1 fourier transform IR spectrophotometer using either thin film (thin film) or solid (solid) using Pike MIRacle ATR accessory. Analysis was carried out using Shimadzu IRsolution v1.50, Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}) and only structurally significant peaks are quoted.

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz ^{1}H, 75 MHz ^{13}C, 282 MHz ^{19}F), a Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376 MHz ^{19}F) or a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C, 470 MHz ^{19}F) spectrometer in the deuterated solvent stated. The resulting spectra were processed using either iNMR (Version 3.6.3) or MestReNova (Version 8.0.1) processing software. ^{13}C NMR spectra were recorded with proton

decoupling. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to residual solvent peaks. Coupling constants, J, are quoted in. The abbreviations s, d, dd, t, dt, tt, q, dq, dqd and m denote singlet, doublet, doublet of doublets, triplet, doublet of triplets, triplet of triplets, quartet, doublet of quartets, doublet of quartet of doublets and multiplet respectively. *app* stands for apparent and *br* for broad. The abbreviation Ar is used to denote aromatic. For compounds displaying tautomers in δ_H spectroscopy, the integral ratio of the two species is given with the more abundant designated A and the less abundant designated B.

Mass spectrometric (m/z) data was acquired by electrospray ionisation (ESI) or chemical ionisation (CI), either at the University of St Andrews Mass Spectrometry facility or at the EPSRC National Mass Spectrometry Service Centre, Swansea. At the University of St Andrews, low and high resolution ESI MS was carried out on a Micromass LCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, CI MS was carried out on a Micromass Quattro II spectrometer. High resolution ESI was carried out on a Finnigan MAT 900 XLT; a Thermofisher LTQ Orbitrap XL spectrometer was used to obtain high resolution ESI MS for accurate mass determination but also provided fragmentation data for the characterisation of samples. Values are quoted as a ratio of mass to charge in Daltons.

HPLC analyses were obtained on two different machines: a Gilson HPLC consisting of a Gilson 305 pump, Gilson 401C dilutor, Gilson 213XL sample injector and sample detection was performed with a Gilson 118UV/Vis detector; secondly a Shimadzu HPLC consisting of a DGU-20A5 degasser, LX-20AT liquid chromatograph, SIL-20AHT autosampler, CMB-20A column oven with variable temperature setting (25–40 °C). Separation was achieved using Chiralcel OD-H and OJ-H columns or Chiralpak AD-H, AS-H and IA columns.

General experimental procedures

Procedure A: *Condensation of monosubstituted hydrazine with β-ketoester to give 5-pyrazolin-3-ones*

To a solution of the required β-ketoester (1 eq) in absolute ethanol (1–1.4 M) was added the required monosubstituted hydrazine (1.1–1.2 eq) dropwise and the resulting solution stirred at reflux overnight. The suspension was then concentrated *in vacuo*.

Procedure B: *Neat condensation of hydrazine with acetoacetate to give 5-pyrazolin-3-ones*

To the appropriate stirred acetoacetate (1 eq) was added 1.1–1.2 equivalents of hydrazine dropwise. After stirring for 20 min at r.t. (exothermic reaction!) the mixture was heated at 140°C for 6 h. The crude was triturated and recrystallized from ethanol.

Procedure C: *O-Carboxylation of 5-pyrazolin-3-ones*

Based upon a procedure by Fu and co-workers,[2] triethylamine (1.1 eq) was added to a stirred solution of the required 5-pyrazolin-3-one (1 eq) in THF (0.5-0.8 M) at 0 ºC, followed by addition of the required chloroformate (1.05 eq) after 15 min. The mixture was stirred at ambient temperature overnight. The resulting solution was poured into water and the aqueous phase extracted with diethyl ether (x 3). The combined organic layers were washed with 1 M hydrochloric acid solution, sodium hydrogen carbonate solution, brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*.

Procedure D: *Treatment of a pyrazolyl carbonate with DMAP*

To a solution of the appropriate pyrazolyl carbonate (1 eq) in dichloromethane (0.1 M) was added either DMAP (20 mol%) and the mixture left to stir at rt. Reaction was quenched by the addition of 0.1 M hydrochloric acid solution and extracted with dichloromethane (x 3). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, concentrated *in vacuo*.

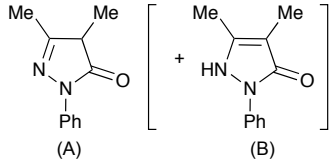
Procedure E: *Treatment of a pyrazolyl carbonate with an NHC*

To a mixture of the required triazolium salt (10 mol%) and the appropriate pyrazolyl carbonate (1 eq) in toluene (0.2 M) was added KHMDS (9 mol%) and the mixture left to stir at rt. Reaction was quenched by the addition of 0.1 M hydrochloric acid solution and extracted with dichloromethane (x 3). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, concentrated *in vacuo* and analysed by ^{1}H NMR spectroscopy.

Experimental details

Parent Pyrazolinones

4,5-Dimethyl-2-phenylpyrazolin-3-one S1

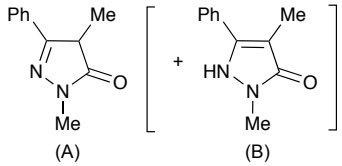


Ethyl 2-methylacetoacetate (4.00 mL, 28.3 mmol) and phenylhydrazine (3.00 mL, 31.1 mmol) were combined according to general procedure A. The resultant yellow oil was solidified upon trituration in petrol and a small volume of diethyl ether to give the title compound as an off-white solid, with spectroscopic data in accordance with the literature (4.95 g, 93%).[3]

mp 122–127 ˚C; δ_H (300 MHz, $CDCl_3$, 5:1 A:B) 7.91–7.86 (A, 2H, m, Ph*H*), 7.71–7.69 (B, 2H, m, Ph*H*), 7.43–7.34 (A, 2H, m, Ph*H* & B, 2H, m, Ph*H*), 7.21–7.13 (A, 1H, m, Ph*H* & B, 1H, m, Ph*H*), 3.24 (A, 1H, q, *J* 7.9, C*H*), 2.16 (A, 3H, s, C(3)CH_3 & B, 3H, s, C(3)CH_3), 1.83 (B, 3H, s, C(4)CH_3),

1.44 (A, 3H, d, *J* 7.9, C(4)CH_3).

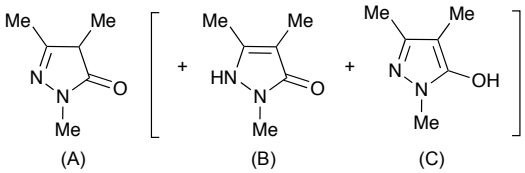
2,4-Dimethyl-5-phenylpyrazolin-3-one S2



Ethyl 2-methyl-3-oxo-3-phenylpropanoate[4] (2.00 g, 9.70 mmol) and methylhydrazine (0.560 mL, 10.7 mmol) were combined according to general procedure A. The resultant yellow oil was solidified upon trituration in a mixture of petrol, diethyl ether and a small volume of dichloromethane to give the title compound as a colourless solid, with spectroscopic data in accordance with the literature (1.17 g, 64%).[5]

mp 101–105 °C; δ_H (300 MHz, $CDCl_3$, 9:1 A:B) 7.68–7.65 (A, 2H, m, Ph*H*), 7.57–7.54 (B, 1H, m, Ph*H*), 7.50–7.47 (B, 2H, m, Ph*H*), 7.48–7.41 (A, 3H, m, Ph*H*), 7.34–7.31 (B, 2H, m, Ph*H*), 3.61 (B, 3H, s, NCH_3), 3.63 (A, 1H, q, *J* 7.9, C*H*CH_3), 3.41 (A, 3H, s, NCH_3), 1.92 (B, 3H, s, CCH_3), 1.48 (A, 3H, s, CHCH_3).

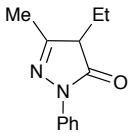
2,4,5-Trimethylpyrazolin-3-one S3



Ethyl 2-methylacetoacetate (2.00 mL, 14.2 mmol) and methylhydrazine (0.820 mL, 15.6 mmol) were combined according to general procedure A. The resultant yellow oil was solidified upon trituration in diethyl ether to give the title compound as a colourless solid (1.52 g, 85%).

mp 128–131 °C; ν_{max} (KBr disc)/cm^{-1} (C only) 3150–2000 (O-H), 2917 (CH), 2723 (CH), 2576 (CH), 1614 (C=N) and 1587 (C=C); δ_H (300 MHz, $CDCl_3$, 1.1:1 A:B) 3.34 (B, 3H, s, NCH_3), 3.26 (A, 3H, s, NCH_3), 2.97 (A, 1H, q, *J* 8.0, C*H*), 2.07 (B, 3H, s, C(3)CH_3), 2.04 (A, 3H, s, C(3)CH_3), 1.75 (B, 3H, s, C(4)CH_3), 1.32 (A, 3H, d, *J* 8.0, CHCH_3); δ_C (75 MHz, $CDCl_3$) 175.7 (A, *C*(O)), 163.1 (B, *C*(O)), 160.4 (A, *C*CH_3), 144.1 (B, *C*(3)CH_3), 100.0 (B, *C*(4)CH_3), 45.8 (A, *C*H), 31.2 (A, N*C*H_3), 31.0 (B, N*C*H_3), 15.3 (A, C*C*H_3), 12.1 (A, CH*C*H_3), 11.1 (B, C(3)*C*H_3), 6.8 (B, C(4)*C*H_3); *m/z* HRMS (ESI^+) $C_6H_{10}N_2O$: 126.0788 $[M]^+$, found 126.0787 (–0.5 ppm).

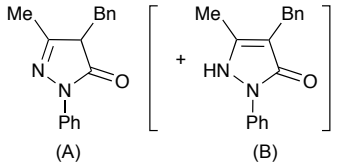
4-Ethyl-5-methyl-2-phenylpyrazolin-3-one S4



Ethyl 2-ethylacetoacetate (prepared by the method of Rapport *et al.*)[6] (2.81 g, 17.8 mmol) and phenylhydrazine (1.92 mL, 19.5 mmol) were combined according to general procedure A to give the title compound as a colourless solid, with spectroscopic data in accordance with the literature (3.59 g, 99%).[7]

mp 91–94 °C; δ_H (300 MHz, $CDCl_3$) 7.94–7.91 (2H, m, Ph*H*), 7.45–7.39 (2H, m, Ph*H*), 7.29–7.18 (1H, m, Ph*H*), 3.26 (1H, t, *J* 5.3, C*H*), 2.16 (3H, s, C(3)CH_3), 2.10 (1H, dqd, *J* 14.1, 7.5, 5.3, CHCH_AH$_B$), 1.91 (1H, dqd, *J* 14.1, 7.5, 5.3, CHCH$_A$$H_B$), 0.95 (3H, t, *J* 7.5, CH$_2$CH_3).

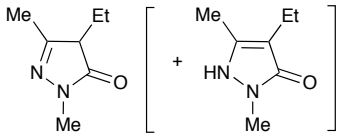
4-Benzyl-5-methyl-2-phenylpyrazolin-3-one S5



Ethyl 2-benzylacetoacetate (prepared by the method of Gellman *et al.*)[8] (5.59 g, 25.4 mmol) and phenylhydrazine (3.0 ml, 3.29 g, 30.5 mmol) were combined following general procedure B. Trituration from petrol ether and recrystallisation from ethyl acetate and ethanol gave the title compound as an off-white solid (4.79 g, 71%).

mp 135 °C; ν_{max} (film)/cm^{-1} 3061, 3022 (ArH), 2978, 2918, 2895 (CH), 1595, 1576, 1526, 1499 (Ar C=N, C=C); δ_H (500 MHz, $CDCl_3$), A:B 1:2) 8.04–8.00 (A, 2H, m, NPh(2,6)*H*), 7.73–7.69 (B, 2H, m, NPh(2,6)*H*), 7.63–7.58 (A, 2H, m, NPh(3,5)*H*), 7.53–7.48 (A, 2H, m, CH$_2$Ph(2,6)*H*), 7.47–7.31 (B, 11H, m, NPh(3,5)*H* and CH$_2$Ph(2,3,4,5,6)*H*, A, NPh(4)*H* and CH$_2$Ph(3,4,5)*H*), 7.28–7.25 (B, 1H, m, NPh(4)*H*), 3.76 (A, 1H, dd, *J* 7.0, 5.3, C(4)*H*), 3.66 (B, 2H, s, PhCH_2), 3.52 (A, 1H, dd, *J* 14.4, *J* 5.3, PhCH$_A$$H_B$), 3.46 (A, 1H, dd, *J* 14.4, *J* 7.0, PhCH_AH$_B$), 2.27 (A, 3H, s, C(3)CH_3), 2.10 (B, 3H, s, C(3)CH_3); δ_C (125 MHz, $CDCl_3$) 172.9 (A, *C*(5)), 162.7 (B, *C*(5)), 159.7 (A, *C*(3)), 147.4 (B, *C*(3)), 140.4 (B, CH$_2$Ph(1)*C*), 137.9 (A, NPh(1)*C*), 136.8 (B, NPh(1)*C*), 136.4 (A, CH$_2$Ph(1)*C*), 128.9 (A, NPh(3,5)*C*), 128.8 (A, CH$_2$Ph(2,4,6)*C*), 128.8 (B, NPh(3,5)*C*), 128.4 (B, CH$_2$Ph(3,5)*C*), 128.2 (B, CH$_2$Ph(2,6)*C*), 127.3 (A, CH$_2$Ph(3,5)*C*), 125.9 (B, CH$_2$Ph(4)*C*), 125.4 (B, NPh(4)*C*), 125.3 (A, NPh(4)*C*), 120.3 (B, NPh(2,6)*C*), 119.2 (A, NPh(2,6)*C*), 105.6 (B, *C*(4)), 53.8 (A, *C*(4)H), 30.8 (A, Ph*C*H$_2$), 27.9 (B, Ph*C*H$_2$), 16.5 (A, C(3)*C*H$_3$), 11.2 (B, C(3)*C*H$_3$); *m/z* (NSI$^+$) 551 ([2M+Na]$^+$ 23%), 529 ([2M+H]$^+$ 15%), 287 ([M+Na]$^+$ 14%), 265 ([M+H]$^+$ 100%), 187 ([M-PhH]$^+$ 3%); HRMS (NSI$^+$) $C_{17}H_{17}N_2O$ [M+H]$^+$: found 265.1340, requires 265.1335 (1.7 ppm).

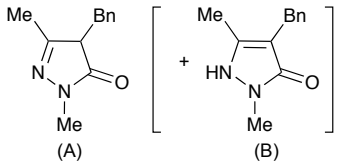
4-Ethyl-2,5-dimethylpyrazolin-3-one S6



Ethyl 2-ethylacetoacetate (2.00 g, 12.6 mmol) and methylhydrazine (0.740 mL, 13.9 mmol) were combined according to general procedure A. The resultant yellow oil was solidified by stirring in diethyl ether to give the title compound as a colourless solid (1.62 g, 92%).

mp 29–30 °C; ν_{max} (KBr disc)/cm^{-1} 3366–3173 (NH), 2968 (CH), 2936 (CH), 2880 (CH), 1693 (C=O), 1578 (C=C); δ_H (300 MHz, CD_3CN, 1.1:1 A:B) 3.27 (B, 3H, s, NCH_3), 3.15 (A, 3H, s, NCH_3), 3.04 (A, 1H, t, *J* 5.4, C*H*), 2.20 (B, 2H, d, *J* 7.5, C(4)CH_2), 2.04 (B, 3H, s, C(3)CH_3), 1.98 (A, 3H, s, C(3)CH_3), 1.81 (A, 2H, m, CH_2), 1.00 (B, 3H, t, *J* 7.5, CH_2CH_3), 0.78 (A, 3H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 175.6 (B, *C*(O)), 163.3 (A, *C*(O)), 160.0 (B, *C*(3)CH_3), 146.3 (A, *C*(3)CH_3), 107.6 (A, *C*(4)CH_2), 52.2 (B, *C*H), 31.5 (A, N*C*H_3), 31.0 (B, N*C*H_3), 21.0 (B, C(4)H*C*H_2), 16.1 (A, C(4)*C*H_2), 15.8 (B, C(3)*C*H_3), 14.7 (A, CH_2CH_3), 11.4 (A, C(3)*C*H_3), 9.9 (B, CH_2CH_3); *m/z* HRMS (ESI$^+$) $C_7H_{13}N_2O$: 141.1022 $[M+H]^+$, found 141.1023 (+0.4 ppm).

4-Benzyl-2,5-dimethylpyrazolin-3-one S7

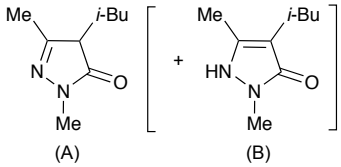


Ethyl 2-benzylacetoacetate (5.57 g, 25.27 mmol) and methylhydrazine (1.6 ml, 1.41 g, 30.6 mmol) were combined following general procedure B. Trituration from petrol ether and recrystallisation from ethyl acetate and ethanol gave 4 the title compound as a red solid (**86** 3 : 20 **86'**, 3.48 g, 68%).

mp 134–136 °C; ν_{max} (film)/cm^{-1} 3082, 3065, 3028, 3001 (ArH), 2922, 2882 (CH), 3200–2000 (broad, OH, NH), 1603, 1587, 1568, 1549 (Ar C=N, C=C); δ_H (500 MHz, $CDCl_3$) 7.30–7.25 (A, 2H, m, CH_2Ph(2,6)*H*, A), 7.25–7.20 (A, 1H, m, CH_2Ph(4)*H*), 7.19–7.13 (B, 4H, m, CH_2Ph(3,5)*H*, and A, CH_2Ph(3,5)*H*), 7.11–7.05 (B, 3H, m, CH_2Ph(2,4,6)*H*), 3.55 (B, 2H, s, PhCH_2), 3.29 (A, 1H, dd, *J* 6.6, 5.7, C(4)*H*), 3.27 (B, 3H, s, NCH_3), 3.21 (A, 1H, dd, *J* 14.5, *J* 5.2, PhC$H_A$$H_B$), 3.19 (A, 3H, s, NC$H_3$), 3.10 (A, 1H, dd, *J* 14.5, *J* 7.3, PhC$H_A$$H_B$), 1.93 (A, 3H, s, C(3)C$H_3$), 1.90 (B, 3H, s, C(3)C$H_3$); δ_C (125 MHz, $CDCl_3$) 174.3 (A, *C*(5)), 162.1 (B, *C*(5)), 159.0 (A, *C*(3)), 143.7 (B, *C*(3)), 140.9 (B, CH_2Ph(1)*C*), 136.6 (A, CH_2Ph(1)*C*), 128.8 and 128.7 (A, CH_2Ph(2,3,4,5)*C*), 128.3 (B, CH_2Ph(3,5)*C*), 128.0 (B, CH_2Ph(2,6)*C*), 127.2 (A, CH2Ph(4)*C*), 125.9 (B, CH_2Ph(4)*C*), 102.2 (B, C(4)), 52.3 (A, *C*(4)H), 33.6 (A, Ph*C*H_2), 31.1 (A, N*C*H_3), 30.5 (B, N*C*H_3), 28.0 (B, Ph*C*H_2), 16.4 (A, C(4)*C*H_3), 11.0

(B, C(4)*C*H$_3$); *m/z* (NSI$^+$) 427 ([2M+Na]$^+$ 26%), 405 ([2M+H]$^+$ 9%), 241 ([M+K]$^+$ 2%), 221 ([M+Na]$^+$ 21%), 203 ([M+H]$^+$ 100%); HRMS (NSI$^+$) $C_{12}H_{15}N_2O$ [M+H]$^+$: found 203.1179, requires 203.1179 (0.1 ppm).

4-iso-Butyl-2,5-dimethylpyrazolin-3-one S8

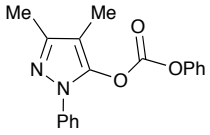


Ethyl 2-*iso*-butylacetoacetate (prepared by the method of Rapport *et al*.)[6] (1.60 g, 8.60 mmol) and methylhydrazine (0.510 mL, 9.46 mmol) were combined according to general procedure A. The resultant brown solid was solidified upon trituration in diethyl ether to give the title compound as a yellow solid (1.28 g, 88%).

mp 84–87 °C; ν_{max} (KBr disc)/cm^{-1} 3347–3055 (NH), 2955 (CH), 2926 (CH), 2866 (CH), 1700 (C=O), 1576 (C=C); δ_H (300 MHz, $CDCl_3$, 1.7:1 A:B) 3.32 (A, 3H, s, NC*H*$_3$), 3.26 (B, 3H, s, NC*H*$_3$), 3.00 (B, 1H, t, *J* 6.6, C*H*), 2.09 (A, 3H, s, C(3)C*H*$_3$), 2.07 (A, 2H, d, *J* 6.8, C(4)C*H*$_2$), 2.06 (B, 3H, s, C(3)C*H*$_3$), 1.95 (B, 1H, app nonet, *J* 6.8, C*H*(CH$_3$)$_2$), 1.80 (A, 1H, app nonet, *J* 7.0, C*H*(CH$_3$)$_2$), 1.65 (B, 2H, t, J 7.0, C(4)HC*H*$_2$), 0.92 (B, 3H, t, *J* 6.6, CH(C*H*$_3$)$_2$), 0.84 (A, 3H, d, *J* 7.5, CH(C*H*$_3$)$_2$); δ_C (75 MHz, $CDCl_3$) 175.3 (A, *C*(O)), 163.9 (B, *C*(O)), 160.0 (A, *C*(3)CH$_3$), 145.1 (B, *C*(3)CH$_3$), 105.4 (B, *C*(4)CH$_2$), 49.3 (A, *C*H), 36.5 (A, C(4)H*C*H$_2$), 31.6 (B, C(4)*C*H$_2$), 31.1 (N*C*H$_3$), 30.8 (N*C*H$_3$), 28.7 (B, *C*H(CH$_3$)$_2$), 25.4 (A, *C*H(CH$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$), 16.0 (A, C(3)*C*H$_3$), 11.4 (B, C(3)*C*H$_3$); *m/z* HRMS (ESI$^+$) $C_9H_{17}N_2O$: 169.1335 [M+H]$^+$, found 169.1333 (–1.4 ppm).

O-Carboxylates

Phenyl 4,5-Dimethyl-2-phenylpyrazol-3-yl carbonate 2

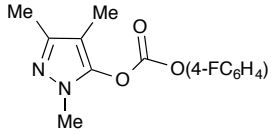


4,5-Dimethyl-2-phenylpyrazolin-3-one **S1** (1.00 g, 5.31 mmol), triethylamine (0.810 mL, 5.84 mmol) and phenyl chloroformate (0.790 mL, 5.58 mmol) were combined according to general procedure C to give the title compound as a colourless solid (1.60 g, 97%).

mp 57–59 °C; ν_{max} (KBr disc)/cm^{-1} 3061 (ArH), 2944 (CH), 2918 (CH), 1787 (C=O), 1620 (C=N), 1595 (C=C); δ_H (300 MHz, $CDCl_3$) 7.60–7.56 (2H, m, Ph*H*), 7.50–7.44 (2H, m, Ph*H*), 7.40–7.33 (2H, m, Ph*H*), 7.31–7.23 (2H, m, Ph*H*), 7.17–7.10 (2H, m, Ph*H*), 2.28 (3H, s, C(3)C*H*$_3$), 2.00 (3H, s, C(4)C*H*$_3$); δ_C (75 MHz, $CDCl_3$) 150.8 (OPh(1)*C*), 149.9 (*C*(O)O), 148.5 (*C*(3)CH$_3$), 141.6 (*C(5)*O),

138.1 (NPh(1)*C*), 129.8 (Ph*C*), 129.4 (Ph*C*), 127.2 (Ph*C*), 126.8 (Ph*C*), 122.6 (Ph*C*), 120.6 (Ph*C*), 104.3 (*C*(4)CH_3), 12.9 (C(3)*C*H_3), 7.14 (C(4)*C*H_3); *m/z* HRMS (ESI^+) $C_{18}H_{17}N_2O_3$: 309.1234 $[M+H]^+$, found 309.1229 (–1.5 ppm).

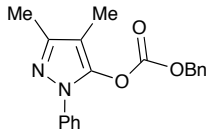
para-Fluorophenyl 2,4,5-trimethylpyrazol-3-yl carbonate 30



2,4,5-Trimethylpyrazolin-3-one **S3** (500 mg, 3.96 mmol), triethylamine (610 μl, 4.38 mmol) and *para*-fluorophenyl chloroformate (550 μl, 4.19 mmol) were combined following general procedure C. Purification by silica column chromatography with 45% diethyl ether in petrol ether gave the title compound as a white solid (570 mg, 42%).

mp 94–97 °C; ν_{max} (film)/cm^{-1} 3082 (ArH), 2949, 2924 (CH), 1784 (C=O), 1605, 1504 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.28–7.23 (2H, OPh(2,6)*H*), 7.15–7.09 (2H, m, OPh(3,5)*H*), 3.69 (3H, s, NCH_3), 2.17 (3H, m, C(3)CH_3), OPh(4)*C*); δ_C (75 MHz, $CDCl_3$) 160.8 (d, *J* 245.9, OPh(4)*C*), 156.3 (*C*=O), 146.7 (d, *J* 3.3, OPh(1)*C*), 146.4 (*C*(3)), 142.2 (*C*(5)), 122.2 (d, *J* 8.6, OPh(2,6)*C*), 116.6 (d, *J* 23.7, OPh(3,5)*C*), 102.1 (*C*(4)), 34.6 (N*C*H_3), 12.6 (C(3)*C*H_3), 7.1 (C(4)*C*H_3); *m/z* (NSI^+) 537 ($[2(M+4H)+H]^+$ 9%), 303 ($[M+K]^+$ 5%), 287 ($[M+Na]^+$ 6%), 265 ($[M+H]^+$ 74%), 215 ($[M–FPh+7H+K]^+$ 4%), 199 ($[M–FPh+7H+Na]^+$ 9%), 149 ($[M–FPhOCOO+Na]^+$ 19%), 127 ($[M–FPhOCOO+H]^+$ 100%); HRMS (NSI^+) $C_{13}H_{14}FN_2O_3$ $[M+H]^+$: found 265.0987, requires 265.0983 (1.5 ppm); *Chiral HPLC* (for doping experiments) Daicel Chiralpak OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R = 16.1 min.

Benzyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate S9

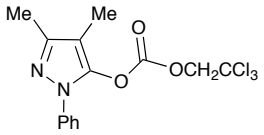


3,4-Dimethyl-2-phenylpyrazolin-3-one **S1** (500 mg, 2.66 mmol), triethylamine (405 μl, 2.91 mmol) and benzyl chloroformate (400 μl, 2.80 mmol) were combined following general procedure C. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a yellow oil (535 mg, 62%).

ν_{max} (film)/cm^{-1} 3065, 3036 (ArH), 2953, 2922, 2864 (CH), 1775 (C=O, carbonate), 1694, 1616, 1597, 1506 (Ar C=N, C=C); δ_H (400 MHz, $CDCl_3$) 7.41–7.38 (2H, m, NPh(2,6)*H*), 7.30-7.25 (5H, m, NPh(3,5)*H*, CH_2Ph(3,4,5)*H*), 7.25–7.21 (2H, m, CH_2Ph(2,6)*H*), 7.20–7.15 (1H, m, NPh(4)*H*), 5.12 (2H, s, PhCH_2), 2.17 (3H, s, C(3)CH_3), 1.83 (3H, s, C(4)CH_3); δ_C (100 MHz, $CDCl_3$) 151.5 (*C*=O), 148.3 (*C*(5)), 141.8 (*C*(3)), 122.4 (NPh(2,6)*C*), 127.0 (NPh(4)*C*), 128.5 (CH_2Ph(2,6)*C*),

128.8 ($CH_2Ph(3,5)C$), 129.0 ($CH_2Ph(4)C$), 129.3 (NPh(3,5)*C*), 134.2 ($CH_2Ph(1)C$), 138.1 (NPh(1)*C*), 104.2 (*C*(4)), 71.4 (PhCH_2), 12.8 (C(3)CH_3), 7.0 (C(4)CH_3); *m/z* (NSI$^+$) 345 ([M+Na]$^+$ 3%), 323 ([M+H]$^+$ 100%), 279 ([M+H–CO_2]$^+$ 89%), 189 ([M+H–BnCO_2]$^+$ 51%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_3$ [M+H]$^+$: found 323.1388, requires 323.1390 (0.7 ppm).

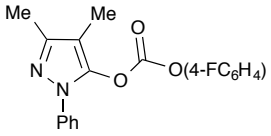
2',2',2'-Trichloroethyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate S10



4,5-Dimethyl-2-phenylpyrazolin-3-one **S1** (500 mg, 2.66 mmol), triethylamine (405 μl, 2.91 mmol) and 1,1,1-trichloroethyl chloroformate (385 μl, 2.80 mmol) were combined following general procedure C. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a yellow solid (759 mg, 79%).

mp 63–64 °C; ν_{max} (film)/cm^{-1} 2999 (ArH), 2955, 2926 (CH), 1784, 1732 (C=O carbonate), 1612, 1597, 1504 (Ar C=N, C=C); δ_H (400 MHz, $CDCl_3$) 7.54–7.51 (2H, m, NPh(2,6)*H*), 7.43–7.39 (2H, m, NPh(3,5)*H*), 7.31–7.27 (1H, m, NPh(1)*H*), 4.80 (2H, s, CH_2CCl_3), 2.27 (3H, s, C(3)CH_3), 1.95 (3H, s, C(4)CH_3); δ_C (100 MHz, $CDCl_3$) 150.8 (*C*=O), 148.5 (*C*(5)), 141.3 (*C*(3)), 137.9 (NPh(1)*C*), 129.4 (NPh(3,5)*C*), 127.3 (NPh(4)*C*), 122.7 (NPh(2,6)*C*), 104.4 (*C*(4)), 93.9 (*C*Cl_3), 77.7 (CH_2CCl_3), 12.9 (C(3)CH_3), 7.0 (C(4)CH_3); *m/z* (ESI$^+$) 749 ([M($^{35}Cl_2{}^{37}Cl$)+M($^{35}Cl_3$)+Na]$^+$ 8%), 403 ([M($^{35}Cl^{37}Cl_2$)+K]$^+$ 39%), 401 ([M($^{35}Cl_3$)+K]$^+$ 41%), 389 ([M($^{35}Cl^{37}Cl_2$)+Na]$^+$ 29%), 387 ([M($^{35}Cl_2{}^{37}Cl$)+Na]$^+$ 94%), 385 ([M($^{35}Cl_3$)+Na]$^+$ 100%), 211 ([M–Cl_3CCH_2OCOO+Na]$^+$ 40%); HRMS (ESI$^+$) $C_{14}H_{13}N_2O_3NaCl_3$ [M+Na]$^+$: found 384.9889, requires 384.9889 (0.2 ppm); *Chiral HPLC* Daicel Chiralpak IB (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R = 9.5 min (for mixtures with (-)**77d**).

para-Fluorophenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate S11

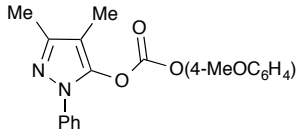


4,5-Dimethyl-2-phenylpyrazolin-3-one **2** (501 mg, 2.66 mmol), triethylamine (405 μl, 2.91 mmol) and *para*-fluorophenyl chloroformate (365 μl, 2.78 mmol) were combined following general procedure C. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a white solid (535 mg, 62%).

mp 78–79 °C; (film)/cm^{-1} 3074, 3044, 3001 (ArH), 2922, 2855 (CH, Me), 1778 (C=O), 1610, 1601 (Ar C=N), 1508 (C=C); δ_H (500 MHz, $CDCl_3$) 7.57–7.56 (2H, m, N Ph(2,6)*H*), 7.48–7.45 (2H, m, NPh(3,5)*H*), 7.35–7.32 (1H, m, NPh(4)*H*), 7.05–7.04 (4H, m, OPh(2,3,5,6)*H*), 2.28 (3H, s, C(3)CH_3),

2.00 (3H, s, C(4)CH_3); δ_C (125 MHz, $CDCl_3$) 160.7 (d, *J* 245.5, OPh(1)*C*), 150.0 (*C*=O), 148.5 (*C*(5)), 146.6 (d, *J* 2.1, OPh(1)*C*), 141.5 (*C*(3)), 138.1 (NPh(1)*C*), 129.5 (NPh(3,5)*C*), 127.3 (NPh(4)*C*), 122.7 (NPh(2,6)*C*), 122.2 (d, *J* 8.4, OPh(2,6)*C*), 116.5 (d, *J* 23.8, OPh(3,5)*C*), 12.9 (C(3)*C*H_3), 104.3 (*C*(4)), 7.1 (C(4)*C*H_3); *m/z* (ESI$^+$) 675 ([2M+Na]$^+$ 9%), 365 ([M+K]$^+$ 3%), 349 ([M+Na]$^+$ 100%), 327 ([M+H]$^+$ 10%), 211 ([M–FPhOCOO+Na]$^+$ 39%); HRMS (ESI$^+$) $C_{18}H_{16}N_2O_3F$ ([M+Na]$^+$) requires 349.0964, found 349.0959 (-1.6 ppm).

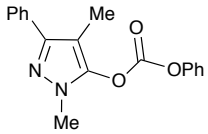
para-Methoxyphenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate S12



4,5-Dimethyl-2-phenylpyrazolin-3-one **S1** (500 mg, 2.66 mmol), triethylamine (405 μl, 2.91 mmol) and *para*-methoxyphenyl chloroformate (415 μl, 2.79 mmol) were combined following general procedure C. Purification by silica column chromatography 50% diethyl ether in petrol gave the title compound as a white solid (638 mg, 71%).

mp 57–58 °C; ν_{max} (film)/cm^{-1} 3474, 3426 (MeOPh), 3075, 3063, 3007 (ArH), 2978, 2920, 2903, 2839 (CH, Me), 1778 (C=O), 1609, 1597, 1508 (Ar C=N, C=C); δ_H (500 MHz, $CDCl_3$) 7.62–7.60 (2H, m, NPh(2,6)*H*), 7.51–7.48 (2H, m, NPh(3,5)*H*), 7.37–7.34 (1H, m, NPh(4)*H*), 7.02 (2H, d, *J* 9.1, OPh(3,5)*H*), 6.89 (2H, d, *J* 9.1, OPh(2,6)*H*), 3.81 (3H, s, OCH_3), 2.31 (3H, s, C(3)CH_3), 2.03 (3H, s, C(4)CH_3); δ_C (125 MHz, $CDCl_3$) 157.9 (OPh(4)*C*), 150.2 (*C*=O), 148.5 (*C*(5)), 144.4 (OPh(1)*C*), 141.6 (*C*(3)), 138.1 (NPh(1)*C*), 129.4 (NPh(3,5)*C*), 127.2 (NPh(4)*C*), 122.6 (NPh(2,6)*C*), 121.5 (OPh(2,6)*C*), 114.7 (OPh(3,5)*C*), 104.3 (*C*(4)), 55.7 (O*C*H_3), 12.9 (C(3)*C*H_3), 7.1 (C(4)*C*H_3); *m/z* (NSI$^+$) 399 (100%), 377 ([M+K]$^+$ 22%), 339 ([M+H]$^+$ 100%), 211 ([M+Na–H_3COPhCO_2] 67%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_4$ [M+H]$^+$: found 339.1348, requires 339.1339 (2.6 ppm).

Phenyl 2,4-Dimethyl-5-phenylpyrazol-3-yl carbonate S13

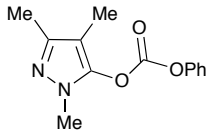


2,4-Dimethyl-5-phenylpyrazolin-3-one **S2** (500 mg, 2.67 mmol), triethylamine (0.400 mL, 2.89 mmol) and phenyl chloroformate (0.350 mL, 2.80 mmol) were combined according to general procedure C. The crude material was purified by column chromatography on silica gel, eluting with 25% diethyl ether in petrol to give the title compound as a colourless solid (740 mg, 90%).

mp 57–58 °C; ν_{max} (KBr disc)/cm^{-1} 3094 (ArH), 3066 (ArH), 2945 (CH), 2875 (CH), 1783 (C=O), 1600 (C=N), 1572 (C=C); δ_H (500 MHz, $CDCl_3$) 7.67–7.66 (2H, m, Ph*H*), 7.47–7.41 (4H, m, Ph*H*),

7.35–7.30 (4H, m, Ph*H*), 3.83 (3H, s, NCH_3), 2.16 (3H, s, CCH_3); δ_C (125 MHz, $CDCl_3$) 150.9 (OPh(1)*C*), 150.2 (*C*(O)O), 148.8 (*C*Ph), 142.9 (*C*(5)O), 134.0 (CPh(1)*C*), 129.9 (Ph*C*), 128.6 (Ph*C*), 127.7 (Ph*C*), 127.4 (Ph*C*), 126.9 (Ph*C*), 120.6 (Ph*C*), 102.0 (*C*CH_3), 35.1 (N*C*H_3), 8.59 (C*C*H_3); *m/z* HRMS (ESI^+) $C_{18}H_{17}N_2O_3$: 309.1234 $[M+H]^+$, found 309.1237 (+1.1 ppm).

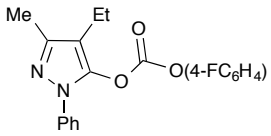
Phenyl 2,4,5-Trimethylpyrazol-3-yl carbonate S14



2,4,5-Trimethylpyrazolin-3-one **S3** (500 mg, 3.96 mmol), triethylamine (0.600 mL, 4.33 mmol) and phenyl chloroformate (0.520 mL, 4.15 mmol) were combined according to general procedure C. The crude material was purified by column chromatography on silica gel, eluting with 50% diethyl ether in petrol to give the title compound as a colourless solid (571 mg, 59%).

mp 38–40 °C; ν_{max} (KBr disc)/cm^{-1} 2948 (CH), 2925 (CH), 1793 (C=O), 1607 (C=N), 1593 (C=C); δ_H (500 MHz, $CDCl_3$) 7.38–7.35 (2H, m, Ph*H*), 7.25–7.19 (3H, m, Ph*H*), 3.62 (3H, s, NCH_3), 2.10 (3H, s, C(3)CH_3), 1.84 (3H, s, C(4)CH_3); δ_C (125 MHz, $CDCl_3$) 150.9 (OPh(1)*C*), 150.1 (*C*(O)O), 146.4 (*C*(3)CH_3), 142.2 (*C*(5)O), 129.9 (Ph*C*), 126.9 (Ph*C*), 120.6 (Ph*C*), 101.9 (*C*(4)CH_3), 34.6 (N*C*H_3), 12.7 (C(3)*C*H_3), 7.15 (C(4)*C*H_3); *m/z* HRMS (ESI^+) $C_{13}H_{15}N_2O_3$: 247.1077 $[M+H]^+$, found 247.1080 (+1.1 ppm).

***para*-Fluorophenyl 4-ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate S15**

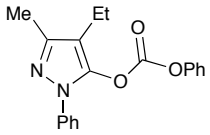


4-Ethyl-5-methyl-2-phenylpyrazolin-3-one **S4** (250 mg, 1.25 mmol), triethylamine (0.200 mL, 1.40 mmol) and *para*-fluorophenyl chloroformate (0.180 mL, 1.30 mmol) were combined according to general procedure C although reaction time was reduced to 3 h. The crude product was purified by column chromatography, eluting with 20% diethyl ether in petrol to give the title compound as a clear orange oil (315 mg, 74%).

ν_{max} (thin film)/cm^{-1} 2970 (CH), 2932 (CH), 2875 (CH), 1789 (C=O), 1717 (C=N), 1503 (C=C); δ_F (282 MHz, $CDCl_3$) –115.9 (Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.59–7.55 (2H, m, Ph*H*), 7.49–7.44 (2H, m, Ph*H*), 7.36–7.26 (1H, m, Ph*H*), 7.07–6.97 (4H, m, Ar*H*), 2.45 (2H, q, *J* 7.6, C(4)CH_2), 2.30 (3H, s, CH_3), 1.20 (3H, t, *J* 7.6, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 160.7 (d, *J* 245.9, OPh*C*(4)), 150.2 (*C*(O)O), 148.0 (*C*(3)CH_3), 146.6 (d, *J* 2.8, OPh*C*(1)), 141.1 (*C*(5)O), 138.1 (NPh*C*(1)), 129.4 (Ph*C*), 127.3 (Ph*C*), 122.7, (Ph*C*), 122.2 (d, *J* 8.7, Ph*C*(2,6)), 116.5 (d, *J* 23.7, Ph*C*(3,5)), 110.4 (*C*(4)CH_2), 15.9

(CH_2CH_3), 14.0 (C(3)CH_3), 13.1 (CH_2CH_3); *m/z* HRMS (ESI^+) $C_{19}H_{18}N_2O_3F$: 341.1296 $[M+H]^+$, found 341.1298 (+0.6 ppm).

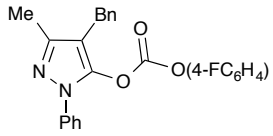
Phenyl 4-ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate S16



4-Ethyl-5-methyl-2-phenylpyrazolin-3-one **S4** (1.00 g, 5.00 mmol), triethylamine (0.770 mL, 5.50 mmol) and phenyl chloroformate (0.660 mL, 5.25 mmol) were combined according to general procedure C to give the title compound as a colourless solid (1.42 g, 88%).

mp 45–46 °C; ν_{max} (thin film)/cm^{-1} 3061 (PhH), 2970 (CH), 2930 (CH), 2874 (CH), 1782 (C=O), 1720 (C=N), 1597 (C=C); ν_{max} (thin film) cm^{-1} 964 (PhH), 2932 (PhH), 1751 (C=O), 1683 (C=O), 1645, 1587 (C=C); δ_H (300 MHz, $CDCl_3$) 7.53–7.49 (2H, m, Ph*H*), 7.42–7.36 (2H, m, Ph*H*), 7.31–7.26 (2H, m, Ph*H*), 7.20–7.17 (2H, m, Ph*H*), 6.98–6.95 (2H, m, Ph*H*), 2.39 (2H, q, *J* 7.5, C(4)CH_2), 2.23 (3H, s, CH_3), 1.13 (3H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 150.8 (OPh*C*(1)), 150.1 (*C*(O)O), 148.0 (*C*(5)O), 141.2 (*C*(3)CH_3), 138.1 (NPh*C*(1)), 129.8 (Ph*C*), 129.4 (Ph*C*), 127.3 (Ph*C*), 126.8 (Ph*C*), 122.7 (Ph*C*), 120.6 (Ph*C*), 110.4 (*C*(4)CH_2), 15.9 (CH_2CH_3), 14.0 (CH_2CH_3), 13.1 (C(3)CH_3); *m/z* HRMS (ESI^+) $C_{19}H_{19}N_2O_3$: 323.1390 $[M+H]^+$, found 323.1394 (+1.2 ppm).

para-Fluorophenyl 4-benzyl-5-methyl-2-phenylpyrazol-3-yl carbonate S17

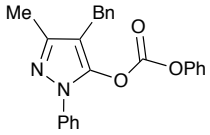


4-Benzyl-5-methyl-2-phenylpyrazolin-3-one **S5** (1.00 g, 3.78 mmol), triethylamine (580 μl, 4.16 mmol) and phenyl chloroformate (522 μl, 3.97 mmol) were combined following general procedure C. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a white solid (1.49 g, 98%).

mp 58–59 °C; ν_{max} (film)/cm^{-1} 3082, 3026 (ArH), 2976, 2934, 2903 (CH), 1790, 1720 (C=O), 1610, 1597, 1501 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.61–7.57 (2H, m, NPh(2,6)*H*), 7.50–7.44 (2H, m, NPh(3,5)*H*), 7.38–7.32 (1H, m, NPh(4)*H*), 7.33–7.20 (5H, CH_2Bn(2,3,4,5,6)*H*), 7.03–6.96 (2H, m, OPh(2,6)*H*), 6.89–6.83 (2H, m, OPh(3,5)*H*), 3.82 (2H, s, PhCH_2) 2.22 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 160.7 (d, *J* 245.9 , OPh(1)*C*), 149.7 (*C*=O), 148.5 (*C*(5)), 146.5 (d, *J* 2.6, OPh(2,6)*C*), 141.8 (*C*(3)), 139.1 (CH_2Ph(1)*C*), 138.0 (NPh(1)*C*), 129.5 (NPh(3,5)*C*), 128.7 (CH_2Ph(2,6)*C*), 128.6 (CH_2Ph(3,5)*C*), 127.5 (NPh(4)*C*), 126.5 (CH_2Ph(4)*C*), 122.7 (NPh(2,6)*C*), 122.1 (d, *J* 8.7, OPh(2,6)*C*), 116.4 (d, *J* 23.9, OPh(3,5)*C*), 107.7 (*C*(4)), 28.8 (PhCH_2), 13.2 (C(3)CH_3); *m/z* (NSI^+) = 871

([2M+HCN+K]$^+$ 93%), 827 ([2M+Na]$^+$ 39%), 447 ([M+HCN+NH_4]$^+$ 100%), 425 ([M+Na]$^+$ 23%), 403 ([M+H] 16%), 235 ([M–OPhF–Ph+4H]$^+$ 4%); HRMS (NSI$^+$) $C_{24}H_{20}FN_2O_3$ [M+H]$^+$: found 403.1449, requires 403.1452 (-0.9 ppm).

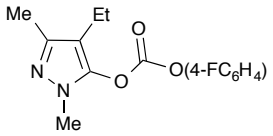
Phenyl 4-benzyl-5-methyl-2-phenylpyrazol-3-yl carbonate S18



4-Benzyl-5-methyl-2-phenylpyrazolin-3-one **S5** (1.00 g, 3.78 mmol), triethylamine (580 μl, 4.16 mmol) and phenyl chloroformate (543 μl, 3.97 mmol) were combined following general procedure C. Purification by silica column chromatography with 45% diethyl ether in petrol gave gave the title compound as a white solid (1.38 g, 95%).

mp 86 °C; ν_{max} (film)/cm^{-1} 3063, 3032 (ArH), 2976, 2908, 2843 (CH), 1788 (C=O), 1616, 1595, 1502, 1495 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.62–7.58 (2H, m, NPh(2,6)*H*), 7.49–7.44 (2H, m, NPh(3,5)*H*), 7.37–7.20 (9H, CH_2Ph(2,3,4,5,6,)*H*, OPh(3,4,5)*C*, NPh(4)*H*), 6.92–6.89 (2H, m, OPh(2,6)*H*), 3.82 (2H, s, PhCH_2), 2.21 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 150.7 (OPh(1)*C*), 149.7 (*C*=O), 148.5 (*C*(5)), 141.9 (*C*(3)), 139.2 (CH_2Ph(1)*C*), 138.0 (NPh(1)*C*), 129.7 (OPh(3,5)*C*), 129.5 (NPh(3,5)*C*), 128.7 (CH_2Ph(2,6)*C*), 128.6 (CH_2(3,5)*C*), 127.4 (NPh(4)*C*), 126.8 (OPh(4)*C*), 126.4 (CH_2Ph(4)*C*), 122.8 (NPh(2,6)*C*), 120.6 (OPh(2,6)*C*), 107.7 (*C*(4)), 28.8 (Ph*C*H$_2$), 13.2 (C(3)*C*H$_3$); *m/z* (NSI$^+$) 529 ([2(M–PhOCOO)+H]$^+$ 9%), 371 ([M–CH_2+H]$^+$ 3%), 287 ([M–PhOCOO+Na]$^+$ 2%), 265 ([M–PhOCOO+H]$^+$ 100%), 187 ([M–PhOCOO–Ph]$^+$ 5%); HRMS (NSI$^+$) $C_{24}H_{21}N_2O_3$ [M+H]$^+$: found 385.1551, requires 385.1547(1.1 ppm).

para-Fluorophenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate S19

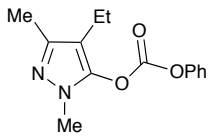


4-Ethyl-2,5-dimethylpyrazolin-3-one **S6** (100 mg, 0.710 mmol), triethylamine (0.110 mL, 0.780 mmol) and *para*-fluorophenyl chloroformate (0.100 mL, 0.750 mmol) were combined according to general procedure C. Reaction was stirred for 2.5 h then concentrated *in vacuo* and purified by column chromatography, eluting with 75% diethyl ether in petrol. The subsequent material was re-columned with 60% diethyl ether in petrol to give to give the title compound as a colourless solid (162 mg, 81%).

mp 77–78 °C; ν_{max} (thin film)/cm^{-1} 2974 (CH), 2943 (CH), 1788 (C=O), 1505 (C=C); δ_F (282 MHz, $CDCl_3$) –115.8 (tt, *J* 8.0, 4.4, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.27–7.21 (2H, m, Ar*H*), 7.14–7.09 (2H, m, Ar*H*), 3.68 (3H, s, NCH_3), 2.36 (2H, q, *J* 7.6, C(4)CH_2), 2.19 (3H, s, C(3)CH_3), 1.12 (3H, t, *J* 7.6,

CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 160.8 (d, *J* 246.2, OPh*C*(4)), 150.5 (*C*(O)O), 146.7 (d, *J* 2.9, OPh*C*(1)), 145.9 (*C*(3)CH_3), 141.8 (*C*(5)O), 122.2 (d, *J* 8.7, Ph*C*(2,6)), 116.6 (d, *J* 23.7, Ph*C*(3,5)), 108.3 (*C*(4)CH_2), 34.5 (N*C*H_3), 15.9 (*C*H_2CH_3), 14.1 (CH_2CH_3), 12.9 (C(3)*C*H_3); *m/z* HRMS (ESI^+) $C_{14}H_{16}N_2O_3F$: 279.1139 $[M+H]^+$, found 279.1142 (+0.9 ppm).

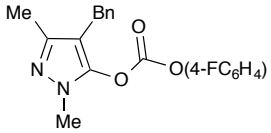
Phenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate S20



4-Ethyl-2,5-dimethylpyrazolin-3-one **S6** (0.500 g, 3.57 mmol), triethylamine (0.540 mL, 3.92 mmol) and phenyl chloroformate (0.470 mL, 3.75 mmol) were combined according to general procedure C to directly give the title compound as a colourless solid (903 mg, 51%).

mp 57–58 °C; ν_{max} (thin film)/cm^{-1} 2972 (CH), 2930 (CH), 1784 (C=O), 1558 (C=C); δ_H (300 MHz, $CDCl_3$) 7.47–7.41 (2H, m, Ph*H*), 7.34–7.25 (2H, m, Ph*H*), 3.67 (3H, s, NCH_3), 2.37 (2H, q, *J* 7.6, C(4)CH_2), 2.20 (3H, s, C(3)CH_3), 1.13 (3H, t, *J* 7.6, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 150.9 (OPh*C*(1)), 150.4 (*C*(O)O), 145.9 (*C*(3)CH_3), 141.9 (*C*(5)O), 129.9 (Ph*C*), 126.9 (Ph*C*), 120.6 (Ph*C*), 108.3 (*C*(4)CH_2), 34.5 (N*C*H_3), 15.9 (*C*H_2CH_3), 14.1 (CH_2CH_3), 12.8 (C(3)*C*H_3); *m/z* HRMS (ESI^+) $C_{14}H_{17}N_2O_3$: 261.1234 $[M+H]^+$, found 261.1230 (–1.4 ppm).

para-Fluorophenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate S21

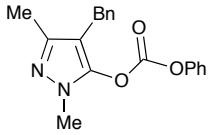


4-Benzyl-2,5-dimethylpyrazolin-3-one **S7** (800 mg, 3.96 mmol), triethylamine (610 μl, 4.38 mmol) and phenyl chloroformate (545 μl, 4.15 mmol) were combined following general procedure C. Purification by silica column chromatography with 55% diethyl ether in petrol gave, after several weeks standing, the title compound as a white solid (298 mg, 22%).

mp 78 °C, ν_{max} (film)/cm^{-1} 3082, 3063, 3028 (ArH), 2945 (CH), 1786 (C=O), 1599, 1503 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.31–7.17 (5H, CH_2Ph(2,3,4,5,6)*H*), 7.08–7.06 (4H, m, OPh(2,3,5,6)*H*), 3.73 (2H, s, PhCH_2), 3.70 (3H, s, NCH_3); δ_C (75 MHz, $CDCl_3$) 160.7 (d, *J* 245.9, OPh(4)*C*), 150.0 (*C*=O), 146.5 (OPh(1)*C*, *C*(5)), 139.4 (CH_2Ph(1)*C*), 142.4 (*C*(3)), 128.5 (CH_2Ph(2,6)*C*), 128.6 (CH2Ph(3,5)*C*), 126.3 (CH_2Ph(4)*C*), 122.2 (d, *J* 8.7, OPh(2,6)*C*), 116.5 (d, *J* 23.8, OPh(3,5)*C*), 105.6 (*C*(4)), 34.7 (N*C*H_3), 28.8 (Ph*C*H_2), 12.9 (C(3)*C*H_3); *m/z* (NSI^+) 703 ($[2M+Na]^+$ 4%), 681 ($[2M+H]^+$ 3%), 565 ($[2M–FPhOCOO+Na]^+$ 5%), 403 ($[M-M$ (- 2H)–FPhOCOO + $H]^+$ 10%), 341 ($[M + H]^+$

100%), 241 ([M–FPhOCOO + K]$^+$ 2%), 219 ([M–FPhOCOO + NH_3]$^+$ 9%), 203 ([M–FPhOCOO + H]$^+$ 33%); HRMS (NSI$^+$) $C_{19}H_{18}FN_2O_3$ [M+H]$^+$: found 341.1301, requires 341.1296 (1.5 ppm).

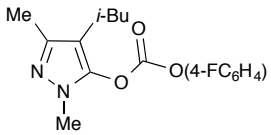
Phenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate S22



4-Benzyl-2,5-dimethylpyrazolin-3-one **S7** (800 mg, 3.96 mmol), triethylamine (610 μl, 4.38 mmol) and phenyl chloroformate (570 μl, 4.17 mmol) were combined following general procedure C. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a white solid (620 mg, 49%).

mp 58 °C; ν_{max} (film)/cm^{-1} 3059, 3022 (ArH), 2951, 2911 (CH), 1788 (C=O), 1597, 1492 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.44–7.37 (2H, m, OPh(3,5)*C*), 7.31–7.25 (3H, m, CH_2Ph(3,5)*H*, OPh(4)*C*), 7.22–7.18 (3H, m, CH_2Ph(2,4,6)*H*), 7.15–7.10 (2H, m, OPh(2,6)*H*), 3.74 (2H, s, PhCH_2), 3.71 (3H, s, NCH_3), 2.13 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 150.8 (OPh(1)*C*), 150.0 (*C*=O), 146.4 (*C*(5)), 142.5 (*C*(3)), 129.8 (OPh(3,5)*C*), 128.5 (CH_2Ph(2,6)*C*), 126.8 (OPh(4)*C*), 126.3 (CH_2Ph(4)*C*), 120.6 (OPh(2,6)*C*), 105.6 (*C*(4)), 34.7 (N*C*H_3), 28.8 (Ph*C*H_2), 13.0 (C(3)*C*H_3); *m/z* (NSI$^+$) 427 ([2(M–PhOCOO)+Na]$^+$ 11%), 405 ([2(M–PhOCOO)+H]$^+$ 8%), 323 ([M+H]$^+$ 11%), 225 ([M–PhOCOO+Na]$^+$ 6%), 203 ([M–PhOCOO+H]$^+$ 100%), 125 ([M–PhOCOO–Ph] 10%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_3$ [M+H]$^+$: found 323.1395, requires 323.1390 (1.5 ppm).

para-Fluorophenyl 4-iso-butyl-2,5-dimethylpyrazol-3-yl carbonate S23



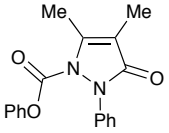
4-*iso*-Butyl-2,5-dimethylpyrazolin-3-one **S8** (250 mg, 1.49 mmol), triethylamine (0.230 mL, 1.64 mmol) and *para*-fluorophenyl chloroformate (0.210 mL, 1.56 mmol) were combined according to general procedure C. Reaction was stirred overnight then concentrated *in vacuo* and purified by column chromatography, eluting with 40% diethyl ether in petrol to give the title compound as a colourless oil (130 mg, 29%).

ν_{max} (thin film)/cm^{-1} 2965 (CH), 2920 (CH), 2868 (CH), 1773 (C=O), 1506 (C=C); δ_F (282 MHz, $CDCl_3$) –115.7 (1F, tt, *J* 8.1, 4.1, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.25–7.19 (2H, m, Ar*H*), 7.15–7.07 (2H, m, Ar*H*), 3.68 (3H, s, NCH_3), 2.21 (2H, d, *J* 7.2, C(4)CH_2), 2.17 (3H, s, C(3)CH_3), 1.77 (1H, app nonet, *J* 6.8, C*H*(CH_3)$_2$), 0.90 (6H, d, *J* 6.6, CH(CH_3)$_2$); δ_C (75 MHz, $CDCl_3$) 160.8 (d, *J* 246, OPh*C*(4)), 150.4 (*C*(O)O), 146.7 (d, *J* 3.0, OPh*C*(1)), 146.5 (*C*(3)CH_3), 142.3 (*C*(5)O), 122.1 (d, *J* 8.6,

Ph*C*(2,6)), 116.6 (d, *J* 23.8, Ph*C*(3,5)), 106.0 (*C*(4)CH_2), 34.7 (N*C*H_3), 31.8 (C(4)*C*H_2), 29.0 (*C*H$(CH_3)_2$), 22.5 (CH(*C*H_3)$_2$), 13.1 (C(3)*C*H_3); *m/z* HRMS (ESI$^+$) $C_{16}H_{20}N_2O_3F$: 307.1452 $[M+H]^+$, found 307.1456 (+1.1 ppm).

N-Carboxylates

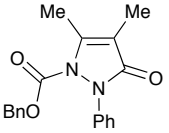
Phenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-1-yl carboxylate 4



Phenyl 4,5-Dimethyl-2-phenylpyrazol-3-yl carbonate **2** (200 mg, 0.650 mmol) and DMAP (15.9 mg, 0.130 mmol) were combined according to general procedure D. The crude material was purified by column chromatography on silica gel, eluting with 50% diethyl ether in petrol to give the title compound as a colourless solid (112 mg, 56%).

mp 140–141 °C; ν_{max} (KBr disc)/cm^{-1} 3074 (ArH), 3045 (ArH), 2924 (CH), 1753 (C=O), 1686 (C=O), 1649 and 1589 (C=C); δ_H (300 MHz, $CDCl_3$) 7.47–7.40 (4H, m, Ph*H*), 7.32–7.26 (3H, m, Ph*H*), 7.19 (1H, tt, *J* 7.4, 1.2, Ph*H*), 6.83–6.79 (2H, m, Ph*H*), 2.58 (3H, d, *J* 0.8, C(3)CH_3) and 1.93 (3H, d, *J* 0.8, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 167.9 (*C*(5)O), 149.9 (*C*(3)CH_3), 149.4 (OPh(1)*C*), 148.6 (*C*(O)O), 139.2 (NPh(1)*C*), 129.6 (Ph*C*), 129.1 (Ph*C*), 126.8 (Ph*C*), 126.6 (Ph*C*), 123.2 (Ph*C*), 120.9 (Ph*C*), 111.0 (*C*(4)CH_3), 13.9 (C(3)*C*H_3) and 7.3 (C(4)*C*H_3); *m/z* HRMS (ESI$^+$) $C_{18}H_{17}N_2O_3$: 309.1234 $[M+H]^+$, found 309.1235 (+0.4 ppm).

Benzyl 4,5-dimethyl-2-phenylpyrazolin-3-on-1-yl carboxylate 6

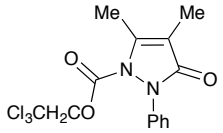


Benzyl 4,5-dimethyl-2-phenyl-3-pyrazolyl carbonate **S9** (65.2 mg, 0.20 mmol) and DMAP (4.8 mg, 0.04 mmol) were combined following the general procedure D. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a yellow oil (7.8 mg, 10%).

ν_{max} (film)/cm^{-1} 3065, 3034 (ArH), 2955, 2926 (CH), 1744 (C=O, carbonate), 1688 (C=O, lactam), 1654 (C=C), 1593, 1492 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.32–7.24 (NPh(3,5)*H*), 7.24–7.11 (6H, m, CH_2Ph(3,4,5)*H*, NPh(2,4,6)*H*), 6.84–6.80 (2H, m, CH_2Ph(2,6)*H*), 4.99 (2H, s, PhCH_2), 2.40 (3H, m, C(3)CH_3), 1.78 (3H, m, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 167.7 (*C*(5)), 150.4 (*C*(O)O), 139.1 (NPh(1)*C*), 134.0 (CH_2Ph(1)*C*), 128.9 (NPh(3,5)*C*), 128.7 (CH_2Ph(4)*C*), 128.6 (CH_2Ph(3,5)*C*), 128.4 (CH_2Ph(2,6)*C*), 126.4 (NPh(4)*C*), 123.0 (NPh(2,6)*C*), 110.4 (*C*(4)), 69.5 (CH_2Ph), 14.0 (C(3)*C*H_3), 7.2 (C(4)*C*H_3); *m/z* (NSI$^+$) = 990 ($[3M+Na]^+$ 2%), 667 ($[2M+Na]^+$ 52%), 645 ($[2M+H]^+$ 34%), 345

([M+Na]$^+$ 34%), 323 ([M+H]$^+$ 100%), 279 ([M+H–CO_2]$^+$ 62%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_3$ [M+H]$^+$: found 323.1398, requires 323.1390 (1.2 ppm).

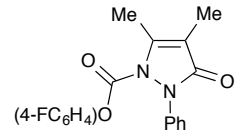
2',2',2'-Trichloroethyl 4,5-dimethyl-2-phenylpyrazolin-3-on-1-yl carboxylate 7



2',2',2'-Trichloroethyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S10** (72.9 mg , 0.20 mmol) and DMAP (4.9 mg, 0.04 mmol) were combined following the general procedure D. Purification by silica column chromatography with 25% diethyl ether in petrol gave the title compound as a white solid (46.3 mg, 64%).

mp 98–99 °C; ν_{max} (film)/cm^{-1} 3734 (CCl), 3049, 3011 (ArH), 2957, 2930 (CH), 1738, 1688 (C=O, lactam), 1636 (C=C), 1593, 1491 (Ar C=C); δ_H (400 MHz, $CDCl_3$) 7.42–7.31 (4H, m, NPh(3,5)*C*, NPh(2,6)*C*), 7.25–7.20 (1H, m, NPh(1)*C*), 4.71 (2H, s, CH_2CCl_3), 2.56 (3H, s, C(3)CH_3), 1.89 (3H, s, C(4)CH_3); δ_C (100 MHz, $CDCl_3$) 168.1 (*C*(5)), 149.0 (*C*(O)O), 149.3 (*C*(3)), 138.8 (NPh(1)*C*), 129.0 (NPh(3,5)*C*), 126.8 (NPh(4)*C*), 123.2 (NPh(2,6)*C*), 111.5 (*C*(4)), 93.5 (*C*Cl_3), 76.2 (*C*H_2CCl_3), 14.3 (C(3)*C*H_3), 7.3 (C(4)*C*H_3); *m/z* (ES$^+$) in progress; HRMS in progress; *Chiral HPLC* Daicel Chiralpak IB (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R = 9.5 min.

para-Fluorophenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-1-yl carboxylate 8

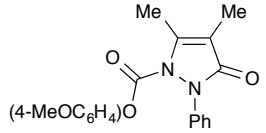


para-Fluorophenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S11** (65.2 mg, 0.20 mmol) and DMAP (4.9 mg, 0.04 mmol) were combined following the general procedure D. Purification by silica column chromatography with 17% diethyl ether in petrol gave the title compound as a white solid (47.9 mg, 66%).

mp 137–138 °C; ν_{max} (film)/cm^{-1} 3121, 3076 (ArH), 2926 (CH), 1755 (C=O, carboxylate), 1688 (C=O, lactam), 1649 (C=C) 1589, 1503 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.47–7.41 (2H, m, NPh(3,5)*C*), 7.42–7.38 (2H, m, NPh(2,6)*C*), 7.32–7.26 (1H, m,NPh(4)*C*), 7.00–6.92 (2H, m, OPh(3,5)*H*), 6.79–6.71 (2H, m, OPh(2, 6)*H*), 2.57 (3H, s, C(3)CH_3), 1.92 (3H, m, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 167.9 (*C*(5)), 160.6 (d, *J* 245.8, OPh(1)*C*), 149.4 (*C*(3)), 148.5 (*C*(O)O), 145.7 (d, *J* 2.8, OPh(1)*C*), 139.2 (NPh(1)*C*), 129.1 (NPh(3,5)*C*), 126.9 (NPh(4)*C*), 123.2 (NPh(2,6)*C*), 122.4 (d, *J* 8.6, OPh(2,6)*C*), 116.3 (d, *J* 23.8, OPh(3,5)*C*), 111.1 (*C*(4)), 13.9 (C(3)*C*H_3), 7.3 (C(4)*C*H_3); *m/z* (NSI$^+$) = 675

([2M+Na]$^+$ 25%), 653 ([2M+H]$^+$ 14%), ([M+Na]$^+$ 15%), 327 ([M+H]$^+$ 100%), 189 ([M–FPhCO$_2$+H]$^+$ 14%); HRMS (NSI$^+$) $C_{18}H_{16}FN_2O_3$ [M+H]$^+$: found 327.1144, requires 327.1139 (1.4 ppm)

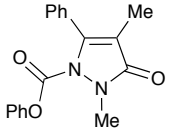
para-Methoxyphenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-1-yl carboxylate 9



para-Methoxyphenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S12** (67.3 mg, 0.20 mmol) and DMAP (4.9 mg, 0.04 mmol) were combined following the general procedure D. Purification by silica column chromatography with 17% diethyl ether in petrol gave the title compound as a white solid (22.8 mg, 32%).

mp 143–144 °C; ν_{max} (film)/cm^{-1} 3078, 3067, 3042 (ArH), 2994, 2967, 2934, 2837 (CH, Me), 1746, 1690 (C=O, lactam), 1651 (C=C) 1595, 1503 (Ar C=C); δ_H (500 MHz, $CDCl_3$) 7.45–7.41 (2H, m, NPh(3,5)*H*), 7.42–7.39 (2H, m, NPh(2,6)*H*), 7.31–7.25 (1H, m, NPh(4)*H*), 6.88–6.71 (2H, m, OPh(2,6)*H*), 6.81–6.76 (2H, m, OPh(3,5)*H*), 3.74 (3H, s, OCH_3), 2.56 (3H, s, C(3)CH_3), 1.92 (3H, s, C(4)CH_3); δ_C (125 MHz, $CDCl_3$) 167.9 (*C*(5)), 157.8 (OPh(4)*C*), 149.4 (*C*(3)), 149.0 (*C*(O)O), 143.5 (OPh(1)*C*), 139.2 (NPh(1)*C*), 129.2 (NPh(3,5)*C*), 126.8 (NPh(4)*C*), 123.2 (NPh(2,6)*C*), 121.7 (OPh(2,6)*C*), 114.6 (OPh(3,5)*C*), 110.9 (*C*(4)), 55.7 (O*C*H$_3$), 7.3 (C(4)*C*H$_3$); *m/z* (NSI$^+$) = 699 ([2M+Na]$^+$ 15%), 677 ([2M+H]$^+$ 12%), 361 ([M+Na]$^+$ 22%), 339 ([M+H]$^+$ 100%), 263 (11%), 189 ([M–CH$_3$OPhCO$_2$+H] 4%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_4$ [M+H]$^+$: found 339.1347, requires 339.1339 (2.3 ppm).

Phenyl 2,4-dimethyl-5-phenylpyrazolin-3-on-1-yl carboxylate 10

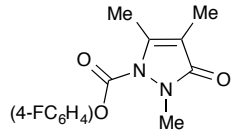


Phenyl 2,4-dimethyl-5-phenylpyrazolyl-3-yl carbonate **S13** (31.0 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. The crude material was purified by column chromatography on silica gel, eluting with 20% diethyl ether in petrol then 50% diethyl ether in petrol to give the title compound as a colourless solid (4.4 mg, 14%) and residual starting material (10 mg).

mp 83–85 °C; ν_{max} (KBr disc)/cm^{-1} 3054 (ArH), 3020 (ArH), 2961 (CH), 2921 (CH), 1754 (C=O), 1680 (C=O), 1646, 1597 (C=C); δ_H (300 MHz, $CDCl_3$) 7.44 (5H, app s, Ph*H*), 7.30–7.25 (2H, m, Ph*H*), 7.17 (1H, tt, *J* 6.4, 1.2, Ph*H*), 6.86–6.82 (2H, m, Ph*H*), 3.67 (3H, s, NCH_3), 1.87 (3H, s, CCH_3); δ_C (75 MHz, $CDCl_3$) 168.4 (*C*(5)O), 149.8 (OPh(1)*C*), 149.7 (*C*Ph), 149.1 (*C*(O)O), 130.4 (CPh(1)*C*), 129.8 (Ph*C*), 129.6 (Ph*C*), 129.4 (Ph*C*), 128.4 (Ph*C*), 126.5 (Ph*C*), 120.7 (Ph*C*), 113.9 (*C*CH$_3$), 34.8

(N*C*H$_3$), 8.0 (C*C*H$_3$ *m/z* HRMS (ESI$^+$) $C_{18}H_{17}N_2O_3$: 309.1234 [M+H]$^+$, found 309.1236 (+0.7 ppm).

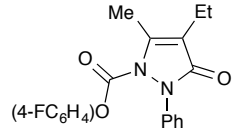
***para*-Fluorophenyl 2,4,5-trimethylpyrazolin-3-on-1-yl carbonate 11**



para-Fluorophenyl 2,4,5-trimethylpyrazol-3-yl carbonate **30** (200.0 mg, 0.757 mmol) and DMAP (18.5 mg, 0.151 mmol) were combined following the general procedure D. Purification by silica column chromatography with 17% diethyl ether in petrol gave the title compound as a white solid (120.8 mg, 60%).

ν_{max} (film)/cm^{-1} 3125, 3082, 3057 (ArH), 2951, 2928, 2855 (CH), 1740, 1682 (C=O, lactam), 1645 (C=C), 1597, 1506 (PhO); δ_H (300 MHz, $CDCl_3$) 7.20–7.06 (4H, m, OPh(2,3,5,6)*H*), 3.53 (3H, s, NCH_3), 2.45 (3H, m, C(3)CH_3), 1.87 (3H, m, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 162.4 (*C*(5)), 160.8 (d, *J* 245.9, OPh(4)*C*), 148.5 (*C*O$_2$), 147.4 (*C*(3)), 145.7 (d, *J* 2.8, OPh(1)*C*), 122.8 (d, *J* 8.6, OPh(2,6)*C*), 116.6 (d, *J* 23.8, OPh(3,5)*C*), 111.7 (*C*(4)), 35.1 (N*C*H$_3$), 14.1 (C(3)*C*H$_3$), 7.2 (C(4)*C*H$_3$); *m/z* (NSI$^+$) 287 ([M+Na]$^+$ 38%), 265 ([M+H]$^+$ 100%); HRMS (NSI$^+$) $C_{13}H_{14}FN_2O_3$ [M+H]$^+$: found 265.0986, requires 265.0983 (1.1 ppm); *Chiral HPLC* (for doping experiments) Daicel Chiralpak OD-H (*i*PrOH 10:90 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R = 22.2 min.

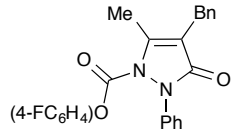
***para*-Fluorophenyl 4-ethyl-5-methyl-2-phenylpyrazolin-3-on-1-yl carboxylate 12**



Phenyl 4-Ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S15** (34.0 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. The crude material was purified by column chromatography on silica gel, eluting with 35% diethyl ether in petrol to give the title compound as a colourless solid (25 mg, 74%).

mp 112–114 °C; ν_{max} (thin film)/cm^{-1} 2971 (CH), 2932 (CH), 1754 (C=O), 1687 (C=O), 1654, 1595 (C=C); δ_F (282 MHz, $CDCl_3$) –116.1 (1F, tt, *J* 8.2, 4.2, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.47–7.38 (4H, m, Ph*H*), 7.32–7.27 (1H, m, Ph*H*), 6.99–6.93 (2H, m, Ar*H*), 6.77–6.73 (2H, m, Ar*H*), 2.57 (3H, s, C(3)CH_3), 2.38 (2H, q, *J* 7.5, C(4)CH_2CH$_3$), 1.16 (3H, t, *J* 7.5, CH$_2$CH_3); δ_C (125 MHz, $CDCl_3$) 167.5 (*C*(5)O), 160.6 (d, *J* 246, OPh*C*(4)), 149.2 (*C*(3)CH$_3$), 148.6 (*C*(O)O), 145.7 (d, *J* 2.6, OPh*C*(1)), 139.2 (NPh*C*(1)), 129.1 (Ph*C*), 126.9 (Ph*C*), 123.2 (Ph*C*), 122.4 (d, *J* 8.5, Ph*C*(2,6)), 116.7 (*C*(4)CH$_2$), 116.3 (d, *J* 23.7, Ph*C*(3,5)), 15.9 (*C*H$_2$CH$_3$), 13.7 (C(3)*C*H$_3$), 13.5 (CH$_2$*C*H$_3$); *m/z* HRMS (ESI$^+$) $C_{19}H_{18}N_2O_3F$: 341.1296 [M+H]$^+$, found 341.1295 (–0.3 ppm).

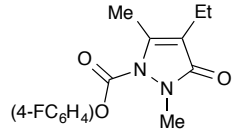
para-Fluorophenyl 4-benzyl-5-methyl-2-phenylpyrazolin-3-on-1-yl carboxylate 13



para-Fluorophenyl 4-benzyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S17** (40.0 mg, 0.10 mmol) and DMAP (2.4 mg, 0.02 mmol) were combined following the general procedure D. Purification by silica column chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (32 mg, 80%).

ν_{max} (film)/cm^{-1} 3063, 3028 (ArH), 2922, 2849 (CH), 1755, 1688 (C=O, lactam), 1639 (C=C), 1595, 1503, 1495 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.46–7.38 (4H, m, NPh(2,6)*H*, CH_2Ph(3,5)*H*), 7.36–7.19 (6H, CH_2Bn(2, 4, 6)*C*, NPh(3,4,5)*H*), 6.77–6.70 (2H, m, OPh(3,5)*H*), 6.92–7.00 (2H, m, OPh(2,6)*H*), 3.71 (2H, s, PhCH_2), 2.59 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 167.4 (*C*(5)), 160.7 (d, *J* 245.9, OPh(4)*C*), 150.2 (*C*(3)), 148.4 (CO_2), 145.6 (OPh(1)*C*), 139.1 (CH_2Ph(1)*C*), 139.0 (NPh(1)*C*), 129.2 (CH_2Ph(3,5)*C*), 128.8 (NPh(3,5)*C*), 128.6 (CH_2Ph(2,6)*C*), 127.0 (CH_2Ph(4)*C*), 126.6 (NPh(4)*C*), 123.3 (NPh(2,6)*C*), 122.4 (d, *J* 8.6, OPh(2,6)*C*), 116.3 (d, *J* 23.7, OPh(3,5)*C*), 114.7 (*C*(4)), 28.4 (PhCH_2), 14.1 (C(3)CH_3); *m/z* (NSI$^+$) 805 ([2M+H]$^+$ 6%), 425 ([M+Na]$^+$ 6%), 403 ([M+H]$^+$ 100%), 265 ([M-COOPhF+2H]$^+$ 6%); HRMS (NSI$^+$) $C_{24}H_{20}FN_2O_3$ [M+H]$^+$: found 403.1452, requires 403.1452 (-0.1 ppm).

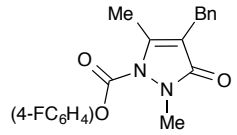
para-Fluorophenyl 4-ethyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate 14



para-Fluorophenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate **S19** (27.8 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. Reaction was stirred for 1 h then concentrated *in vacuo* and purified and purified by column chromatography on silica gel, eluting with 75% diethyl ether in petrol to give the title compound as a colourless solid (17 mg, 61%).

mp 35–36 °C; ν_{max} (thin film)/cm^{-1} 2974 (CH), 2934 (CH), 2878 (CH), 1738 (C=O), 1668 (C=O), 1595 (C=C), 1504; δ_F (282 MHz, $CDCl_3$) –115.8 (1F, tt, *J* 8.0, 4.5, Ar*F*); δ_H (400 MHz, $CDCl_3$) 7.20–7.10 (4H, m, Ar*H*), 3.54 (3H, s, NCH_3), 2.46 (3H, s, C(3)CH_3), 2.35 (2H, q, *J* 7.5, C(4)CH_2CH_3), 1.12 (3H, t, *J* 7.5, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 168.9 (*C*(5)O), 160.7 (d, *J* 245.9, OPh*C*(4)), 148.5 (*C*(3)CH_3), 147.1 (*C*(O)O), 145.7 (d, *J* 2.8, OPh*C*(1)), 122.8 (d, *J* 8.7, Ph*C*(2,6)), 117.4 (*C*(4)CH_2), 116.7 (d, *J* 23.7, Ph*C*(3,5)), 35.1 (NCH_3), 15.8 (CH_2CH_3), 13.8 (C(3)CH_3), 13.6 (CH_2CH_3); *m/z* HRMS (ESI$^+$) $C_{14}H_{16}N_2O_3F$: 279.1139 [M+H]$^+$, found 279.1142 (+0.9 ppm).

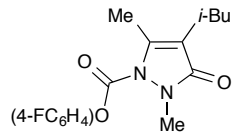
para-Fluorophenyl 4-benzyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate 15



para-Fluorophenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate **S21** (34.0 mg, 0.10 mmol) and DMAP (2.4 mg, 0.02 mmol) were combined following the general procedure D. Purification by silica column chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (16.8 mg, 50%).

ν_{max} (film)/cm^{-1} 3123, 3063, 3026 (ArH), 3001, 2922 (CH), 1751, 1674 (C=O, lactam), 1637 (C=C), 1599, 1504 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.30–7.28 (4H, m, Bn(2,3,5,6)*H*), 7.23–7.09 (4H, m, OPh(2,3,5,6)*H*, Bn(4)*H*), 3.68 (2H, s, PhCH_2), 3.56 (3H, s, NCH_3), 2.47 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 168.8 (*C*(5)), 160.7 (d, *J* 246.0, OPh(4)*C*), 148.2 (*C*O_2), 148.1 (*C*(3)), 145.5 (d, *J* 2.8, OPh(1)*C*), 139.0 (Bn(1)*C*), 128.6 (Bn(3,5)*C*), 128.4 (CH_2Ph(2,6)*C*), 126.4 (CH_2Ph(4)*C*), 122.7 (2H, d, *J* 8.6, OPh(2,6)*C*), 115.0 (*C*(4)), 35.0 (N*C*H_3), 28.1 (Ph*C*H_2), 14.1 (C(3)*C*H_3); *m/z* (NSI$^+$) 703 ([2M+Na]$^+$ 8%), 681 ([2M+H]$^+$ 4%), 363 ([M+Na]$^+$ 17%), 341 ([M+H]$^+$ 100%), 203 ([M-COOPhF+2H]$^+$ 10%); HRMS (NSI$^+$) $C_{19}H_{18}FN_2O_3$ [M+H]$^+$: found 341.1301, requires 341.1296 (1.5 ppm).

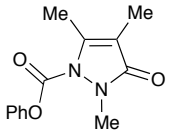
para-Fluorophenyl 4-iso-butyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate 16



para-Fluorophenyl 4-*iso*-butyl-2,5-dimethylpyrazol-3-yl carbonate **S23** (31.0 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. Reaction was stirred for 1 h then concentrated *in vacuo* and purified by column chromatography on silica gel, eluting with 60% diethyl ether in petrol to give the title compound as a colourless oil (24 mg, 77%).

ν_{max} (thin film)/cm^{-1} 2957 (CH), 2928 (CH), 2870 (CH), 1751 (C=O), 1678 (C=O), 1636 (C=C), 1505; δ_F (282 MHz, $CDCl_3$) –115.8 (1F, tt, *J* 7.8, 4.5, Ar*F*); δ_H (400 MHz, $CDCl_3$) 7.21–7.09 (4H, m, Ar*H*), 3.53 (3H, s, NCH_3), 2.44 (3H, s, C(3)CH_3), 2.18 (2H, d, *J* 7.2, C(4)CH_2), 1.91 (1H, app nonet, *J* 6.8, C*H*(CH_3)$_2$), 0.92 (6H, d, *J* 6.6, CH(CH_3)$_2$); δ_C (75 MHz, $CDCl_3$) 169.2 (*C*(5)O), 160.8 (d, *J* 246.0, OPh*C*(4)), 148.4 (*C*(3)CH_3), 147.9 (*C*(O)O), 145.7 (d, *J* 2.9, OPh*C*(1)), 122.8 (d, *J* 8.6, Ph*C*(2,6)), 116.6 (d, *J* 23.7, Ph*C*(3,5)), 115.2 (*C*(4)CH_2), 35.1 (N*C*H_3), 31.4 (C(4)*C*H_2), 28.3 (*C*H(CH_3)$_2$), 22.5 (CH(*C*H_3)$_2$), 14.2 (C(3)*C*H_3); *m/z* HRMS (ESI$^+$) $C_{16}H_{20}N_2O_3F$: 307.1452 [M+H]$^+$, found 307.1455 (+0.8 ppm).

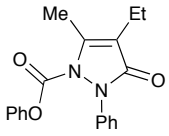
Phenyl 2,4,5-Trimethylpyrazolin-3-on-1-yl carboxylate S24



Phenyl 2,4,5-trimethylpyrazol-3-yl carbonate **S14** (24.6 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. The crude material was purified by trituration in diethyl ether give the title compound as a colourless solid (19 mg, 77%).

mp 90–91 °C; ν_{max} (KBr disc)/cm^{-1} 068 (ArH), 2927 (CH), 1748 (C=O), 1677 (C=O), 1646, 1590 (C=C); δ_H (300 MHz, $CDCl_3$) 7.44 (2H, app t, *J* 7.8, Ph(3,5)*H*), 7.31 (1H, t, *J* 7.5, Ph(4)*H*), 7.20 (2H, d, *J* 8.0, Ph(2,6)*H*), 3.55 (3H, s, NCH_3), 2.46 (3H, s, C(3)CH_3), 1.88 (3H, s, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 169.3 (*C*(5)O), 149.9 (OPh(1)*C*), 148.5 (*C*(O)O), 147.4 (*C*(3)CH_3), 129.9 (Ph*C*), 126.9 (Ph*C*), 121.3 (Ph*C*), 111.5 (*C*(4)CH_3), 35.1 (NCH_3), 14.1 (C(3)CH_3), 7.3 (C(4)CH_3); *m/z* HRMS (ESI$^+$) $C_{13}H_{15}N_2O_3$: 247.1077 $[M+H]^+$, found 247.1080 (+0.4 ppm).

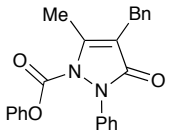
Phenyl 4-ethyl-5-methyl-2-phenylpyrazolin-3-on-1-yl carboxylate S25



Phenyl 4-ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S16** (64.0 mg, 0.200 mmol) and DMAP (4.90 mg, 40.0 μmol) were combined according to general procedure D. The crude material was purified by column chromatography on silica gel, eluting with 50% diethyl ether in petrol to give the title compound as a colourless solid (26 mg, 40%).

mp 134–135 °C; ν_{max} (thin film)/ cm^{-1} 2964 (Ph-H), 2932 (Ph-H), 1751 (C=O), 1683 (C=O), 1645, 1587 (C=C); δ_H (300 MHz, $CDCl_3$) 7.47–7.40 (4H, m, Ph*H*), 7.32–7.17 (4H, m, Ph*H*), 6.83–6.80 (2H, m, Ph*H*), 2.58 (3H, s, C(3)CH_3), 2.39 (2H, q, *J* 7.5, C(4)CH_2CH$_3$), 1.17 (3H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 162.2 (*C*(5)O) 150.0 (*C*(3)CH_3), 149.2 (OPh*C*(1)), 148.7 (*C*(O)O), 139.1 (NPh*C*(1)), 129.6 (Ph*C*), 129.1 (Ph*C*), 126.8 (Ph*C*), 126.6 (Ph*C*), 123.2 (Ph*C*), 120.9 (Ph*C*), 116.6 (*C*(4)CH_2), 15.9 (CH_2CH_3), 13.7 (C(3)CH_3), 13.5 (CH_2CH_3); *m/z* HRMS (ESI$^+$) $C_{19}H_{19}N_2O_3$: 323.1390 $[M+H]^+$, found 323.1394 (+1.2 ppm).

Phenyl 4-benzyl-5-methyl-2-phenylpyrazolin-3-on-1-yl carboxylate S26

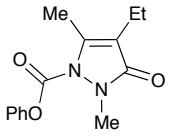


Phenyl 4-benzyl-5-methyl-2-phenylpyrazolyl carbonate **S18** (38.3 mg, 0.10 mmol) and DMAP (2.5 mg, 0.02 mmol) were combined following the general procedure D. Purification by silica column

chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (29 mg, 75%).

ν_{max} (film)/cm^{-1} 3061, 3028 (ArH), 2922, 2853 (CH), 1753, 1688 (C=O, lactam), 1639 (C=C), 1593, 1492 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.46–7.39 (4H, m, OPh(2,6)*H*, Bn(3,5)*H*), 7.37–7.16 (9H, CH_2Ph(2,4,6,)*H*, NPh(3,4,5)*H*, OPh(3,4,5)*H*), 6.81–6.77 (2H, m, NPh(2,6)*H*), 3.71 (2H, s, PhCH_2), 2.60 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 167.4 (*C*(5)), 150.3 (*C*(3)), 149.9 (NPh(1)*C*), 148.5 (*C*O_2), 139.1 (CH_2Ph(1)*C*, OPh(1)*C*), 129.7 (NPh(3,5)*C*), 129.1 (OPh(3,5)*C*), 128.8 (CH_2Ph(3,5)*C*), 128.6 (CH_2(2,6)*C*), 127.0 (OPh(4)*C*), 126.7 (CH_2Ph(4)*C*), 126.6 (NPh(4)*C*), 123.8 (OPh(2,6)*C*), 120.9 (NPh(2,6)*C*), 114.5 (*C*(4)), 28.4 (Ph*C*H_2), 14.1 (C(3)*C*H_3); *m/z* (NSI$^+$) 769 ([2M+H]$^+$ 2%), 407 ([M+Na]$^+$ 3%), 285 ([M+H]$^+$ 100%), 265 ([M-COOPh+2H] 7%); HRMS (NSI$^+$) $C_{24}H_{21}N_2O_3$ [M+H]$^+$: found 385.1550, requires 385.1547 (0.9 ppm).

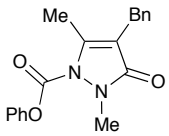
Phenyl 4-ethyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate S27



Phenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate **S20** (26.0 mg, 0.100 mmol) and DMAP (2.40 mg, 20.0 μmol) were combined according to general procedure D. Reaction was stirred for 1 h then concentrated *in vacuo* and purified by column chromatography on silica gel, eluting with 75% diethyl ether in petrol to give the title compound as a colourless oil (21 mg, 81%).

ν_{max} (thin film)/cm^{-1} 2968 (CH), 2934 (CH), 2874 (CH), 1748 (C=O), 1674 (C=O), 1639, 1591 (C=C); δ_H (400 MHz, $CDCl_3$) 7.47–7.40 (2H, m, Ph*H*), 7.34–7.28 (1H, m, Ph*H*), 7.22–7.18 (2H, m, Ph*H*), 3.54 (3H, s, NCH_3), 2.46 (3H, s, C(3)CH_3), 2.34 (2H, q, *J* 7.5, C(4)CH_2CH$_3$), 1.12 (3H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 168.8 (*C*(5)O), 150.0 (OPh*C*(1)), 148.5 (*C*(3)CH$_3$), 147.1 (*C*(O)O), 129.9 (Ph*C*), 126.9 (Ph*C*), 121.3 (Ph*C*), 117.1 (*C*(4)CH_2), 35.0 (N*C*H$_3$), 15.8 (*C*H_2CH$_3$), 13.8 (C(3)*C*H$_3$), 13.6 (CH_2*C*H$_3$); *m/z* HRMS (ESI$^+$) $C_{14}H_{17}N_2O_3$: 261.1234 [M+H]$^+$, found 261.1229 (–1.8 ppm).

Phenyl 4-benzyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate S28

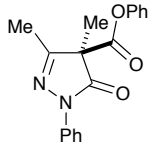


Phenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate **S22** (32.1 mg, 0.10 mmol) and DMAP (2.3 mg, 0.02 mmol) were combined following the general procedure D. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a colourless oil (11 mg, 35%).

ν_{max} (film)/cm^{-1} 3061, 3026 (ArH), 2922, 2851 (CH), 1749, 1678 (C=O, lactam), 1639 (C=C), 1601, 1595, 1493 (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.46–7.42 (2H, m, OPh(3,5)*C*), 7.33–7.27 (5H, m, CH_2Ph(2,3,5,6)*H*, OPh(4)*C*), 7.22–7.18 (3H, m, OPh(2,6)*H*, Bn(4)*H*), 3.68 (2H, s, PhCH_2), 3.57 (3H, s, NCH_3), 2.48 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 168.6 (*C*(5)), 149.8 (OPh(1)*C*), 148.4 (*C*O_2), 148.2 (*C*(3)), 139.2 (CH_2Ph(1)*C*), 130.0 (OPh(3,5)*C*), 128.8 (CH_2Ph(3,5)*C*), 128.5 (CH_2Ph(2,6)*C*), 126.9 (OPh(4)*C*), 126.5 (CH_2Ph(4)*C*), 121.3 (OPh(2,6)*C*), 115.0 (*C*(4)), 35.1 (N*C*H_3), 28.3 (Ph*C*H_2), 14.2 (C(3)*C*H_3); *m/z* (NSI$^+$) 345 ([M+Na]$^+$ 11%), 323 ([M+H]$^+$ 100%), 263 ([M-Me-CO_2]$^+$ 9%), 245 ([M-PhH]$^+$ 2%), 203 ([M-COOPh+2H]$^+$ 8%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_3$ [M+H]$^+$: found 323.1395, requires 363.1390 (1.5 ppm).

C-Carboxylates

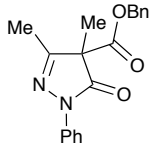
(R)-Phenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-4-yl carboxylate 3



Phenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **2** (31.0 mg, 0.100 mmol), triazolium salt **28** (3.50 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. The crude material was purified by column chromatography on silica gel, eluting with 15% diethyl ether in petrol to give the title compound as a colourless oil (24 mg, 77%).

$[\alpha]_D^{20}$ –10.8 (*c* 0.3, chloroform); ν_{max} (KBr disc)/cm^{-1} 3065 (ArH), 2988 (CH), 2936 (CH), 1764 (C=O), 1713 (C=O), 1621 (Ar C=C), 1596 (C=N); δ_H (300 MHz, $CDCl_3$) 7.96–7.93 (2H, m, Ph*H*), 7.45–7.35 (4H, m, Ph*H*), 7.27–7.19 (2H, m, Ph*H*), 7.09–7.05 (2H, m, Ph*H*), 2.26 (3H, s, C(3)CH_3), 1.73 (3H, s, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 170.4 (*C*(5)O), 164.9 (*C*(O)O), 158.3 (*C*(3)CH_3), 150.3 (OPh(1)*C*), 137.8 (NPh(1)*C*), 129.7 (Ph*C*), 129.1 (Ph*C*), 126.7 (Ph*C*), 125.6 (Ph*C*), 121.2 (Ph*C*), 119.0 (Ph*C*), 61.6 (*C*(4)CH_3), 17.3 (C(4)*C*H_3), 14.4 (C(3)*C*H_3; *m/z* HRMS (ESI$^+$) $C_{18}H_{17}N_2O_3$: 309.1234 [M+H]$^+$, found 309.1233 (–0.2 ppm). *Chiral HPLC* Chiralpak AS-H column (1:99 *i*PrOH:hexane, flow rate=1.0 mL/min, 254 nm), t_R minor = 13.3 min and t_R major = 14.7 min, 62% ee.

Benzyl 4,5-dimethyl-2-phenylpyrazolin-3-on-4-yl carboxylate 17

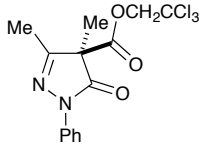


Benzyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S9** (64.9 mg, 0.20 mmol), triazolium salt **5** (5.6 mg, 0.02 mmol) and KHMDS solution (36 μl, 0.018 mmol) were combined following the general

procedure E. Purification by silica column chromatography with 20% diethyl ether in petrol gave the title compound as a colourless oil (7.8 mg, 12%).

ν_{max} (film)/cm^{-1} 3065, 3034 (ArH), 2957, 2934, 2857 (CH), 1753 (C=O, carboxylate), 1711 (C=O, lactam), 1622, 1595, 1499 (Ar C=N, C=C); δ_H (400 MHz, $CDCl_3$) 7.90–7.86 (2H, m, NPh(2,6)*C*), 7.44-7.37 (2H, m, NPh(3,5)*H*), 7.36–7.27 (5H, m, CH_2Ph(2,3,4,5,6)*H*), 7.23–7.17 (1H, m, NPh(4)*H*), 5.12 (2H, s, PhCH_2), 2.02 (3H, s, C(3)CH_3), 1.63 (3H, s, C(4)CH_3); δ_C (100 MHz, $CDCl_3$) 170.7 (*C*(5)), 158.7 (*C*(3)), 166.0 (*C*O_2), 137.9 (NPh(1)*C*), 135.1 (CH_2Ph(1)*C*), 129.0 (NPh(3,5)*C*), 128.8 (CH_2Ph(3,5)*C*), 128.7 (CH_2Ph(4)*C*), 128.1 (CH_2Ph(2,6)*C*), 125.5 (NPh(4)*C*), 119.1 (NPh(3,5)*C*), 68.1 (*C*H_2Ph), 61.6 (*C*(4)), 17.2 (C(4)*C*H_3), 14.2 (C(3)*C*H_3); *m/z* (NSI$^+$) 667 ([2M+Na]$^+$ 19%), 345 ([M+Na]$^+$ 34%), 323 ([M+H]$^+$ 100%), 279 ([M–CO_2+H]$^+$ 48%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_3$ [M+H]$^+$: found 323.1399, requires 323.1390 (2.7 ppm).

(R)-2',2',2'-Trichloroethyl 4,5-dimethyl-2-phenylpyrazolin-3-on-4-yl carboxylate 18

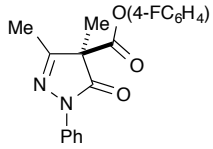


2',2',2'-Trichloroethyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S10** (36.4 mg, 0.10 mmol), triazolium salt **28** (4.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 25% diethyl ether in petrol gave the title compound as a colourless oil (28.0 mg, 55%).

$[\alpha]_D^{20}$ = –11.9 (*c* 1.4, chloroform); ν_{max} (film)/cm^{-1} 3065 (ArH), 2992, 2959 (CH), 1767 (C=O, carboxylate), 1713 (C=O, lactam), 1622, 1595, 1499 (Ar C=N, C=C); δ_H (400 MHz, $CDCl_3$) 7.88–7.85 (2H, m, NPh(2,6)*H*), 7.43–7.38 (2H, m, NPh(3,5)*H*), 7.24–7.19 (1H, m,NPh(4)*H*), 4.96 (1H, d, *J* 11.9, $CH_AH_BCCl_3$), 4.65 (1H, d, *J* 11.9, $CH_AH_BCCl_3$), 2.20 (3H, s, C(3)CH_3), 1.69 (3H, s, C(4)CH_3); δ_C (100 MHz, $CDCl_3$) 169.8 (*C*(5)), 164.6 (*C*O_2), 159.0 (*C*(3)), 137.6 (NPh(1)*C*), 129.1 (NPh(3,5)*C*), 125.7 (NPh(4)*C*), 119.3 (NPh(2,6)*C*), 94.3 (*C*Cl_3), 74.7 (*C*H_2CCl_3), 61.2 (*C*(4)), 17.0 (C(4)*C*H_3), 14.4 (C(3)*C*H_3); *m/z* (NSI$^+$) 765 ([2M($^{35}Cl_5{}^{37}Cl$)+K]$^+$ 0.4%), 755 ([2M($^{35}Cl_2{}^{37}Cl_4$)+Na]$^+$ 0.3%), 754 ([2M($^{37}Cl_6$)+NH_4]$^+$ 0.6%), 753 ([2M($^{35}Cl_3{}^{37}Cl_3$)+Na]$^+$ 2.4%), 752 ([2M($^{35}Cl_1{}^{37}Cl_5$)+NH_4]$^+$ 1.5%), 751 ([2M($^{35}Cl_4{}^{37}Cl_2$)+Na]$^+$ 8.5%), 750 ([2M($^{35}Cl_2{}^{37}Cl_4$)+NH_4]$^+$ 2.2%), 749 ([2M($^{35}Cl_5{}^{37}Cl_1$)+Na]$^+$ 11.0%), 748 ([2M($^{35}Cl_3{}^{37}Cl_3$)+NH_4]$^+$ 0.9%), 747 ([2M($^{35}Cl_6$)+Na]$^+$ 5.0%), 746 ([2M($^{35}Cl_4{}^{37}Cl_2$)+NH_4]$^+$ 2.0%), 744 ([2M($^{35}Cl_5{}^{37}Cl$)+NH_4]$^+$ 3.0%), 742 ([2M($^{35}Cl_6$)+NH_4]$^+$ 1.1%), 403 ([M($^{35}Cl_2{}^{37}Cl$)+K]$^+$ 3.2%), 401 ([M($^{35}Cl_3$)+K]$^+$ 3.1%), 387 ([M($^{35}Cl_2{}^{37}Cl$)+Na]$^+$ 5.0%), 385 ([M($^{35}Cl_3$)+Na]$^+$ 5.0%), 384 ([M($^{35}Cl^{37}Cl_2$)+NH_4]$^+$ 10.0%), 382 ([M($^{35}Cl_2{}^{37}Cl$)+NH_4]$^+$ 31.5%), 380 ([M($^{35}Cl_3$)+NH_4]$^+$ 32.1%), 369 ([M($^{37}Cl_3$)+H]$^+$ 1.3%), 367 ([M($^{35}Cl^{37}Cl_2$)+H]$^+$ 2.0%), 365 ([M($^{35}Cl_2{}^{37}Cl$)+H]$^+$ 60.5%), 363 ([M($^{35}Cl_3$)+H]$^+$ 63.0%), 247 ([M–OCH_2CCl_3+MeO + H]$^+$ 100%), 187 ([M–$OCOOCH_2CCl_z$–H_2+H]$^+$

15%); HRMS $C_{14}H_{14}N_2O_3Cl_3$ $[M+H]^+$: found 363.0073, requires 363.0065, (2.3 ppm). *Chiral HPLC* Daicel Chiralcel OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 13.4 min, t_R major = 37.8 min, 10% ee.

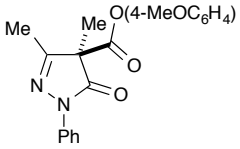
(R)-para-Fluorophenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-4-yl carboxylate 19



para-Fluorophenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S11** (32.5 mg, 0.10 mmol), triazolium salt **28** (4.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 15% diethyl ether in petrol gave the title compound as a colourless oil (17.5 mg, 54%).

$[\alpha]_D^{20}$ = –11.7 (*c* 1.4, chloroform); ν_{max} (film)/cm^{-1} 3078 (ArH), 2990, 2918 (CH), 1771 (C=O, carboxylate), 1713 (C=O, lactam), 1622, 1595, 1501 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.95–7.91 (2H, m, NPh(2,6)*H*), 7.46–7.39 (2H, m, NPh(3,5)*H*), 7.26–7.19 (1H, m, NPh(4)*H*), 7.06–7.03 (4H, m, OPh(2,3,5,6)*H*), 2.25 (3H, s, C(3)CH_3), 1.72 (3H, s, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 170.3 (*C*(5)), 165.0 (*C*O_2), 160.7 (d, *J* 245.5, OPh(4)*C*), 158.2 (*C*(3)), 146.1 (d, *J* 2.8, OPh(1)*C*), 137.8 (NPh(1)*C*), 129.1 (NPh(3,5)*C*), 125.7 (NPh(4)*C*), 122.8 (d, *J* 8.6, OPh(2,6)*C*), 119.0 (NPh(2,6)*C*), 116.4 (d, *J* 23.7, OPh(3,5)*C*), 61.5 (*C*(4)), 17.3 (C(4)*C*H_3), 14.4 (C(3)*C*H_3); *m/z* (NSI$^+$) 675 ($[2M+Na]^+$ 20%), 349 ($[M+Na]^+$ 14%), 344 ($[M+NH_4]^+$ 35%), 327 ($[M+H]^+$ 100%), 247 ($[M+CH_4\text{-FPh}]^+$ 61%), 187 ([M-FPhCC=O]$^+$ 13%); HRMS $C_{18}H_{16}FN_2O_3$ $[M+H]^+$: found 327.1138, requires 327.1139, (0.4 ppm). *Chiral HPLC* Daicel Chiralpak AD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 25.9 min, t_R major = 32.8 min, 60% ee.

(R)-para-Methoxyphenyl 4,5-dimethyl-2-phenylpyrazolin-3-on-4-yl carboxylate 20

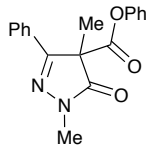


para-Methoxyphenyl 4,5-dimethyl-2-phenylpyrazol-3-yl carbonate **S12** (67.6 mg, 0.20 mmol), triazolium salt **28** (9.4 mg, 0.02 mmol) and KHMDS solution (36 μl, 0.018 mmol) were combined following the general procedure E. Purification by silica column chromatography with 1% acetone in DCM gave the title compound as a colourless oil (38.9 mg, 57%).

$[\alpha]_D^{20}$ = -108.8 (*c* 0.5, chloroform); ν_{max} (film)/cm^{-1} 3064 (ArH), 2995, 2951, 2936, 2916, 2837 (CH), 1765 (C=O, carboxylate), 1711 (C=O, lactam), 1622, 1595, 1503 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.96–7.92 (2H, m, NPh(2,6)*H*), 7.46–7.39 (2H, m, NPh(3,5)*H*), 7.26–7.19 (1H, m, NPh(4)*H*),

6.99 (2H, ddd, *J* 9.2, *J* 3.5, *J* 2.4, OPh(3,5)*H*), 6.86 (2H, ddd, *J* 9.2, *J* 3.5, *J* 2.4, OPh(2,6)*H*), 3.78 (3H, s, OCH_3), 2.24 (3H, s, C(3)CH_3), 1.72 (3H, s, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 170.5 (*C*(5)), 165.3 (*C*O_2), 158.4 (*C*(3)), 157.8 (OPh(4)*C*), 143.8 (OPh(1)*C*), 137.9 (NPh(1)*C*), 129.1 (NPh(3,5)*C*), 125.6 (NPh(4)*C*), 122.0 (OPh(2,6)*C*), 119.0 (NPh(2,6)*C*), 114.6 (OPh(3,5)*C*), 61.6 (*C*(4)), 55.7 (O*C*H_3), 17.3 (C(4)*C*H_3), 14.4 (C(3)*C*H_3); *m/z* (NSI$^+$) 715 ([2M+K]$^+$ 1%), 699 ([2M+Na]$^+$ 22%), 694 ([2M+NH_4]$^+$ 30%), 677 ([2M+H]$^+$ 1%), 377 ([M+K]$^+$ 3%), 361 ([M+Na]$^+$ 15%), 356 ([M+NH4]$^+$ 36%), 339 ([M+H]$^+$ 100%), 247 ([M+H–H_3COPh]$^+$ 5%), 211 ([M–H_3COPhCO_2]$^+$ 8%), 135 ([M+Na–Ph–H_3COPhOC=O]$^+$ 2%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_4$ [M+H]$^+$: found 339.1336, requires 339.1339 (1.0 ppm). *Chiral HPLC* Daicel Chiralpak IA (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 35.1 min, t_R major = 52.6 min, 68% ee.

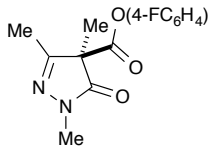
Phenyl 2,4-dimethyl-5-phenylpyrazolin-3-on-4-yl carboxylate 21



Phenyl 2,4-dimethyl-5-phenylpyrazol-3-yl carbonate **S13** (31.0 mg, 0.100 mmol), triazolium salt **5** (5.50 mg, 20.0 μmol) and KHMDS (36.0 μL, 9.00 μmol) were combined according to general procedure E. The crude material was purified by column chromatography on silica gel, eluting with 10% diethyl ether in petrol to give the title compound as a colourless solid (17 mg, 55%).

mp 92 ºC; ν_{max} (KBr disc)/cm^{-1} 2921 (CH), 2852 (CH), 1759 (C=O), 1710 (C=O), 1596 (C=N); δ_H (300 MHz, $CDCl_3$) 7.78–7.75 (2H, m, Ph*H*), 7.45–7.44 (3H, m, Ph*H*), 7.34–7.18 (3H, m, Ph*H*), 6.94–6.90 (2H, m, Ph*H*), 3.51 (3H, s, NCH_3), 1.79 (3H, s, CCH_3); δ_C (75 MHz, $CDCl_3$) 172.4 (*C*(5)O), 166.2 (*C*(O)O), 156.5 (*C*Ph), 150.3 (OPh(1)*C*), 130.8 (Ph*C*), 129.8 (CPh(1)*C*), 129.6 (Ph*C*), 129.3 (Ph*C*), 126.6 (Ph*C*), 126.0 (Ph*C*), 121.3 (Ph*C*), 58.4 (*C*CH_3), 32.0 (NCH_3), 18.8 (CCH_3); *m/z* HRMS (ESI$^+$) $C_{18}H_{17}N_2O_3$: 309.1234 [M+H]$^+$, found 309.1238 (+1.4 ppm).

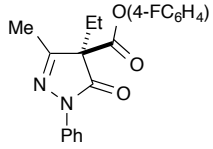
(R)-para-Fluorophenyl 2,4,5-trimethylpyrazolin-3-on-4-yl carboxylate 22



para-Fluorophenyl 2,4,5-trimethylpyrazol-3-yl carbonate **S13** (26.4 mg, 0.10 mmol), triazolium salt **28** (4.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 3% acetone in DCM gave the title compound as a white solid (17.2 mg, 65%).

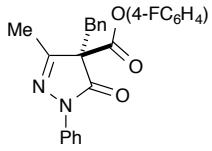
$[\alpha]_D^{20}$ = -148.5 (*c* 0.8, chloroform); ν_{max} (film)/cm^{-1} 3074 (ArH), 2988, 2951, 2922, 2853 (CH), 2361, 1759 (C=O, carboxylate), 1701 (C=O, lactam), 1607, 1599, 1504 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.07–7.01 (4H, m, OPh(2,3,5,6)*H*), 3.36 (3H, s, NCH_3), 2.13 (3H, m, C(3)CH_3), 1.61 (3H, m, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 172.1 (*C*(5)), 165.3 (*C*O_2), 160.7 (d, *J* 245.4, OPh(4)*C*), 146.1 (d, *J* 2.8, OPh(1)*C*), 122.8 (d, *J* 8.5, OPh(2,6)*C*), 116.3 (d, *J* 23.6, OPh(3,5)*C*), 59.8 (*C*(4)), 32.6 (NCH_3), 17.0 (C(4)*C*H_3), 14.2 (C(3)*C*H_3); *m/z* (NSI$^+$) 537 ([2(M+4H) + H]$^+$ 6%), 287 ([M+Na]$^+$ 13%), 282 ([M+NH_4]$^+$ 15%), 265 ([M+H]$^+$ 100%), 149 ([M–FPhOCOO+2H]$^+$ 11%); HRMS (NSI$^+$) $C_{19}H_{14}FN_2O_3$ [M+H]$^+$: found 265.0987, requires 265.0983 (1.5 ppm). *Chiral HPLC* Daicel Chiralcel OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 19.7 min, t_R major = 17.5 min, 87% ee.

(R)-para-Fluorophenyl 4-ethyl-5-methyl-2-phenylpyrazolin-3-on-4-yl carboxylate 23



para-Fluorophenyl 4-ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S15** (34.0 mg, 0.100 mmol), triazolium salt **28** (4.70 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. The crude material was purified by column chromatography on silica gel, eluting with 15% diethyl ether in petrol to give the title compound as a colourless oil (25.0 mg, 74%). $[\alpha]_D^{20}$ –55.3 (*c* 0.6, chloroform); ν_{max} (thin film)/cm^{-1} 2974 (CH), 2938 (CH), 2880, (CH), 1769 (C=O), 1713 (C=O), 1595 (C=N); δ_F (282 MHz, $CDCl_3$) –116.2 (1F, tt, *J* 8.2, 6.3, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.96–7.92 (2H, m, Ph*H*), 7.46–7.40 (2H, m, Ph*H*), 7.25–7.20 (1H, m, Ph*H*), 7.06–7.03 (4H, m, Ar*H*), 2.44 (1H, dq, ABX_3 system, J_{AB} 14.1, J_{AX} 7.6, C(4)CH_AH_B), 2.24 (3H, s, C(3)CH_3), 2.22 (1H, dq, ABX_3 system, J_{BA} 14.1, J_{BX} 7.5, C(4)CH_AH_B), 0.89 (3H, app t, J 7.6, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 169.4 (*C*(5)O), 164.7 (*C*(O)O), 160.8 (d, *J* 245.4, OPh*C*(4)), 156.8 (*C*(3)CH_3), 146.0 (d, *J* 2.9, OPh*C*(1)), 137.7 (NPh*C*(1)), 129.1 (Ph*C*), 125.7 (Ph*C*), 122.8 (d, *J* 8.6, Ph*C*(2,6)), 119.1 (Ph*C*), 116.4 (d, *J* 23.6, Ph*C*(3,5)), 66.7 (*C*(4)CH_2), 25.1 (*C*H_2CH$_3$), 14.7 (C(3)*C*H_3), 7.9 (CH_2*C*H_3); *m/z* HRMS (ESI$^+$) $C_{19}H_{18}N_2O_3F$: 341.1296 [M+H]$^+$, found 341.1299 (+0.9 ppm). *Chiral HPLC* Daicel Chiralpak AD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 27.6 min, t_R major = 31.3 min, 69% ee.

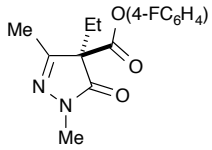
(R)-para-Fluorophenyl 4-benzyl-5-methyl-2-phenylpyrazolin-3-on-4-yl carboxylate 24



para-Fluorophenyl 4-benzyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S17** (40.2 mg, 0.10 mmol), triazolium salt **28** (4.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (27.0 mg, 67%).

$[\alpha]_D^{20}$ = -24.4 (*c* 1.7, chloroform); ν_{max} (film)/cm^{-1} 3109, 3065 (ArH), 2926 (CH), 1767 (C=O, carboxylate), 1709 (C=O, lactam), 1595, 1501 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.65–7.61 (2H, m, NPh(2,6)*H*), 7.38–7.32 (2H, m, NPh(3,5)*H*), 7.24–7.15 (6H, CH_2Bn(2,3,4,5,6)*H*, NPh(4)*H*), 7.10–7.03 (4H, m, OPh(3,5), OPh(2,6)*H*), 3.73 (1H, d, *J* 13.9, PhC$H_A$$H_B$), 3.49 (1H, d, *J* 13.9, PhC$H_A$$H_B$), 2.28 (3H, s, C(3)C$H_3$); δ_C (75 MHz, $CDCl_3$) 169.4 + 164.6 (*C*(5), *C*=O), 160.7 (d, *J* 245.9 , OPh(1)*C*), 156.2 (*C*(3)), 146.0 (d, *J* 2.8, OPh(2,6)*C*), 137.3 (NPh(1)*C*), 133.1 (CH_2Ph(1)*C*), 129.4 (CH_2Ph(2,6)*C*), 129.0 (NPh(3,5)*C*), 128.8 (CH_2Ph(3,5)*C*), 128.0 (CH_2Ph(4)*C*), 125.9 (NPh(4)*C*), 122.8 (d, *J* 8.6, OPh(2,6)*C*), 119.6 (NPh(2,6)*C*), 116.5 (d, *J* 23.7, OPh(3,5)*C*), 67.3 (*C*(4)), 37.7 (Ph*C*H_2), 15.6 (C(3)*C*H_3); *m/z* (NSI$^+$) 822 ([2M+NH4]$^+$ 10%), 420 ([M+NH_4]$^+$ 57%), 403 ([M+H]$^+$ 100%), 340 ([M–FPh+Me+NH_4]$^+$ 10%), 323 ([M–FPh+Me+NH_4]$^+$ 37%), 309 ([M–FPh+2H]$^+$ 20%), 291 ([M–FPhOCOO+4H+Na]$^+$ 9%), 212 ([M–FPhOCOO–Ph+8H+NH_4]$^+$ 4%); HRMS (NSI$^+$) $C_{24}H_{20}FN_2O_2$ [M+H]$^+$: found 403.1452, requires 403.1452 (-0.1 ppm). *Chiral HPLC* Daicel Chiralpak OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 41.1 min, t_R major = 27.2 min, 60% ee.

(R)-para-Fluorophenyl 4-ethyl-2,5-dimethylpyrazolin-3-on-4-yl carboxylate 25

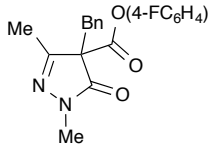


para-Fluorophenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate **S19** (27.8 mg, 0.100 mmol), triazolium salt **28** (4.70 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. After 1 h, the reaction mixture was concentrated *in vacuo* then purified by column chromatography on silica gel, eluting with 35% diethyl ether in petrol to give the title compound as a colourless solid (15 mg, 54%).

$[\alpha]_D^{20}$ –113 (*c* 0.3, chloroform); *mp* 54-56 °C (racemic 67-69 °C); ν_{max} (thin film)/cm^{-1} 3074 (CH), 3055 (CH), 2968, (CH), 1761 (C=O), 1701 (C=O), 1500 (C=C); δ_F (282 MHz, $CDCl_3$) –116.3 (1F, tt, *J* 7.5, 5.2, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.08–6.98 (4H, m, Ar*H*), 3.36 (3H, s, NCH_3), 2.33 (1H, dq, ABX_3 system, J_{AB} 14.0, J_{AX} 7.6, C(4)C$H_A$$H_B$), 2.14 (3H, s, C(3)C$H_3$), 2.10 (1H, dq, ABX_3 system, J_{BA} 14.1,

J_{BX} 7.4, C(4)CH_AH_B), 0.81 (3H, app t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 171.0 (*C*(5)O), 165.0 (*C*(O)O), 160.6 (d, *J* 245.4, OPh*C*(4)), 156.0 (*C*(3)CH_3), 146.0 (d, *J* 2.7, OPh*C*(1)), 122.8 (d, *J* 8.6, Ph*C*(2,6)), 116.3 (d, *J* 23.7, Ph*C*(3,5)), 65.0 (*C*(4)CH_2), 31.5 (NCH_3), 24.7 (CH_2CH_3), 14.5 (C(3)CH_3), 7.8 (CH_2CH_3); *m/z* HRMS (ESI$^+$) $C_{14}H_{16}N_2O_3F$: 279.1139 $[M+H]^+$, found 279.1138 (–0.5 ppm). *Chiral HPLC* Daicel Chiralcel OD-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm) t_R minor = 12.9 min, t_R major = 17.7 min, 90% ee.

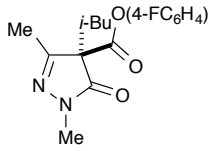
***para*-Fluorophenyl 4-benzyl-2,5-dimethylpyrazolin-3-on-4-yl carboxylate 26**



para-Fluorophenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate **S21** (34.0 mg, 0.10 mmol), triazolium salt **28** (2.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 50% diethyl ether in petrol gave the title compound as a colourless oil (10.4 mg, 31%).

ν_{max} (film)/cm^{-1} 3067, 3032 (ArH), 2924 (CH), 1765 (C=O, carboxylate), 1705 (C=O, lactam), 1603, 1584, 1503 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.28–7.23 (3H, m, CH_2Ph(3,4,5)*H*), 7.16–7.13 (2H, m, CH_2Ph(2,6)*H*), 7.07–7.05 (4H, m, OPh(2,3,5,6)*H*), 3.61 (1H, d, *J* 13.8, PhCH_AH_B), 3.39 (1H, d, *J* 13.8, PhCH_AH_B), 3.10 (3H, s, NCH_3), 2.18 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 170.7 (*C*(5)), 164.8 (*C*O_2), 160.7 (d, *J* 245.5, OPh(4)*C*), 155.5 (*C*(3)), 146.0 (d, *J* 2.4, OPh(1)*C*), 133.2 (CH_2Ph(1)*C*), 129.4 (CH2Ph(2,6)*C*), 128.6 (CH_2Ph(3,5)*C*), 127.9 (CH_2Ph(4)*C*), 122.8 (2H, d, *J* 8.7, OPh(2,6)*C*), 116.4 (2H, d, *J* 23.7, OPh(3,5)*C*), 66.0 (*C*(4)), 37.4 (Ph*C*H_2), 31.3 (N*C*H_3), 15.2 (C(3)*C*H_3); *m/z* (NSI$^+$) 703 ($[2M+Na]^+$ 11%), 379 ($[M+K]^+$ 7%), 363 ($[M+Na]^+$ 31%), 358 ($[M+NH_4]^+$ 38%), 341 ($[M+H]^+$ 100%); HRMS (NSI$^+$) $C_{19}H_{18}FN_2O_3$ $[M+H]^+$: found 341.1301, requires 341.1296 (1.5 ppm).

***(R)-para*-Fluorophenyl 4-iso-butyl-2,5-dimethylpyrazolin-3-on-4-yl carboxylate 27**

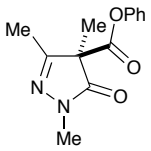


para-Fluorophenyl 4-*iso*-butyl-2,5-dimethylpyrazol-3-yl carbonate **S23** (31.0 mg, 0.100 mmol), triazolium salt **28** (4.70 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. After overnight reaction, the reaction mixture was concentrated *in vacuo* then purified by column chromatography on silica gel, eluting with 20% diethyl ether in petrol to give the title compound as a colourless solid (7.0 mg, 23%).

mp 103-105 °C; $[\alpha]_D^{20}$ –89.7 (*c* 0.3, dichloromethane); ν_{max} (thin film)/cm^{-1} 2957 (CH), 2920 (CH),

1765 (C=O), 1705 (C=O), 1501 (C=C); δ_F (282 MHz, $CDCl_3$) –116.4 (1F, tt, *J* 7.6, 4.9, Ar*F*); δ_H (300 MHz, $CDCl_3$) 7.08–6.98 (4H, m, Ar*H*), 3.37 (3H, s, NCH_3), 2.25 (1H, dd, ABX system, J_{AB} 14.4, J_{AX} 7.7, C(4)CH_AH$_B$), 2.14 (3H, s, C(3)CH_3), 2.08 (1H, dd, ABX system, J_{BA} 14.4, J_{BX} 5.7, C(4)CH$_A$$H_B$), 1.64–1.50 (1H, m, C*H*$(CH_3)_2$), 0.92 (3H, d, *J* 6.7, CH(CH_3)$_A$$(CH_3)_B$), 0.87 (3H, d, *J* 6.6, CH$(CH_3)_A$(CH_3)$_B$); δ_C (75 MHz, $CDCl_3$) 171.5 (*C*(5)O), 165.2 (*C*(O)O), 160.1 (d, *J* 227.1, OPh*C*(4)), 156.8 (*C*(3)CH_3), 146.1 (d, *J* 2.9, OPh*C*(1)), 122.8 (d, *J* 8.6, Ph*C*(2,6)), 116.4 (d, *J* 23.6, Ph*C*(3,5)), 39.8 (*C*(4)CH_2), 39.8 (C(4)*C*H_2), 31.6 (N*C*H_3), 25.0 (*C*H$(CH_3)_2$), 23.8 (CH(*C*H_3)$_A$$(CH_3)_B$), 23.1 (CH$(CH_3)_A$(*C*$H_3$)$_B$), 15.0 (C(3)*C*$H_3$); *m/z* HRMS (ESI$^+$) $C_{16}H_{20}N_2O_3F$: 307.1452 $[M+H]^+$, found 307.1455 (+0.8 ppm). *Chiral HPLC* Daicel Chiralcel OJ-H (*i*PrOH 2:98 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 14.6 min, t_R major = 21.9 min, 92% ee.

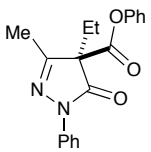
(R)-Phenyl 2,4,5-trimethylpyrazolin-3-on-4-yl carboxylate 29



Phenyl 2,4,5-trimethylpyrazol-3-yl carbonate **S14** (24.6 mg, 0.100 mmol), triazolium salt **28** (4.70 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. The crude material was purified by column chromatography on silica gel, eluting with 40% diethyl ether in petrol to give the title compound as a colourless solid (15 mg, 61%).

$[\alpha]_D^{20}$ –116.9 (*c* 0.1, chloroform); *mp* 94–95 °C; ν_{max} (KBr disc)/cm^{-1} 3059 (ArH), 2985 (CH), 2941 (CH), 1762 (C=O), 1708 (C=O), 1607 (Ar C=C), 1592 (C=N); δ_H (300 MHz, $CDCl_3$) 7.40–7.34 (2H, m, Ph*H*), 7.24 (1H, tt, *J* 7.4, 1.2, Ph*H*), 7.07–7.03 (2H, m, Ph*H*), 3.36 (3H, s, NCH_3), 2.14 (3H, s, C(3)CH_3), 1.61 (3H, s, C(4)CH_3); δ_C (75 MHz, $CDCl_3$) 172.1 (*C*(5)O), 165.2 (*C*(O)O), 157.6 (*C*(3)CH_3), 150.3 (Ph(1)*C*), 129.7 (Ph*C*), 126.6 (Ph*C*), 121.3 (Ph*C*), 59.9 (*C*(4)CH_3), 31.6 (N*C*H_3), 19.9 (C(4)*C*H_3), 14.2 (C(3)*C*H_3); *m/z* HRMS (ESI$^+$) $C_{13}H_{15}N_2O_3$: 247.1077 $[M+H]^+$, found 247.1082 (+1.9 ppm). *Chiral HPLC* Chiralpak AS-H column (1:99 *i*PrOH:hexane, flow rate = 1.0 mL/min, 254 nm), t_R minor = 16.9 min and t_R major = 23.8 min, 86% ee.

(R)-Phenyl 4-ethyl-5-methyl-2-phenylpyrazolin-3-on-4-yl carboxylate S29

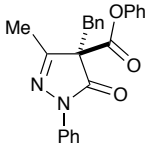


Phenyl 4-ethyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S16** (64.5 mg, 0.200 mmol), triazolium salt **28** (9.30 mg, 20.0 μmol) and KHMDS (36.0 μL, 9.00 μmol) were combined according to general procedure E. The crude material was purified by column chromatography on silica gel, eluting with

15% diethyl ether in petrol to give the title compound as a colourless oil (25 mg, 39%).

$[\alpha]_D^{20}$ –79.6 (*c* 1.3, chloroform); ν_{max} (thin film)/cm^{-1} 3066 (PhH), 2972 (CH), 2934 (CH), 1795 (C=O), 1713 (C=O), 1647, 1622 (Ph C=C), 1595 (C=N); δ_H (300 MHz, $CDCl_3$) 8.00–7.97 (2H, m, Ph*H*), 7.50–7.38 (4H, m, Ph*H*), 7.30–7.26 (2H, m, Ph*H*), 7.13–7.10 (2H, m, Ph*H*), 2.50 (1H, dq, ABX_3 system, J_{AB} 14.0, J_{AX} 7.6, C(4)CH_AH$_B$), 2.29 (3H, s, C(3)CH_3), 2.26 (1H, dq, ABX_3 system, J_{BA} 14.0, J_{BX} 7.5, C(4)CH$_A$$H_B$), 0.93 (3H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 169.6 (*C*(5)O), 164.7 (*C*(O)O), 157.0 (*C*(3)CH_3), 150.3 (OPh*C*(1)), 137.8 (NPh*C*(1)), 129.7 (Ph*C*), 129.1 (Ph*C*), 126.6 (Ph*C*), 125.6 (Ph*C*), 121.3 (Ph*C*), 119.1 (Ph*C*), 66.8 (*C*(4)CH_2), 25.1 (C(4)*C*H_2), 14.7 (C(3)*C*H_3), 8.00 (CH_2CH_3); *m/z* HRMS (ESI$^+$) $C_{19}H_{19}N_2O_3$: 323.1390 $[M+H]^+$, found 323.1395 (+1.5 ppm). *Chiral HPLC* Chiralpak AD-H column (1:99 *i*PrOH:hexane, flow rate = 1.0 mL/min, 254 nm), t_R minor = 25.2 min and t_R major = 26.7 min, 66% ee.

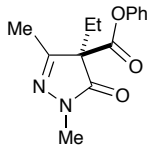
(R)-Phenyl 4-benzyl-5-methyl-2-phenylpyrazolin-3-on-4-yl carboxylate S30



Phenyl 4-benzyl-5-methyl-2-phenylpyrazol-3-yl carbonate **S18** (38.4 mg, 0.10 mmol), triazolium salt **28** (4.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (28.7 mg, 75%).

$[\alpha]_D^{20}$ = 28.1 (*c* 1.5, chloroform); ν_{max} (film)/cm^{-1} 3063, 3032 (ArH), 2957, 2924 (CH), 1763 (C=O,carboxylate), 1707 (C=O, lactam), 1618, 1593, 1491 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.66–7.63 (2H, m, NPh(2,6)*H*), 7.42–7.37 (2H, m, OPh(3,5)*H*), 7.37–7.32 (2H, m, NPh(3,5)*H*), 7.29–7.25 (1H, m, OPh(4)*H*), 7.24–7.16 (6H, CH_2Ph(2,3,4,5,6)*H*, NPh(4)*H*), 7.12–7.09 (2H, m, OPh(2,6)*H*), 3.75 (1H, d, *J* 13.9, PhCH$_A$CH_B), 3.50 (1H, d, *J* 14, PhCH_AH$_B$), 2.29 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 169.4 (*C*(5)), 164.5 (*C*=O), 156.2 (*C*(3)), 150.3 (OPh(1)*C*), 137.3 (NPh(1)*C*), 133.2 (CH_2Ph(1)*C*), 129.7 (OPh(3,5)*C*), 129.4 (CH_2Ph(2,6)C), 128.9 (NPh(3,5)*C*), 128.7 (CH_2Ph(3,5)*C*), 127.9 (CH_2Ph(4)*C*), 126.8 (OPh(4)*C*), 125.8 (NPh(4)*C*), 121.3 (NPh(2,6)*C*), 119.7 (NPh(2,6)*C*), 67.3 (*C*(4)), 37.7 (Ph*C*H$_2$), 15.3 (C(3)*C*H_3); *m/z* (NSI$^+$) 786 ($[(2M)+NH_4]^+$ 21%), 402 ($[M+NH_4]^+$ 47%), 385 ($[M+H]^+$ 100%), 309 ($[M–H_3COPhO+H]^+$ 17%), 291 ($[M–H_3COPhOCOO–4H+Na]^+$ 7%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_4$ $[M+H]^+$: found 339.1348, requires 339.1339 (2.6 ppm). *Chiral HPLC* Daicel Chiralpak AS-H (*i*PrOH 1:99 hexane, flow rate 1 mL/min, 254 nm, 30 °C) t_R minor = 14.5 min, t_R major = 27.0 min, 49% ee.

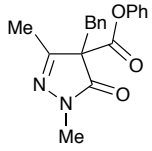
(R)-Phenyl 4-ethyl-2,5-dimethylpyrazolin-3-on-4-yl carboxylate S31



Phenyl 4-ethyl-2,5-dimethylpyrazol-3-yl carbonate **S20** (26.0 mg, 0.100 mmol), triazolium salt **28** (4.70 mg, 10.0 μmol) and KHMDS (18.0 μL, 9.00 μmol) were combined according to general procedure E. After 3 h reaction, the reaction mixture was concentrated *in vacuo* then purified by column chromatography on silica gel, eluting with 35% diethyl ether in petrol to give the title compound as a colourless solid (14.0 mg, 54%).

mp 72-75 °C (racemic 72-73 °C); $[\alpha]_D^{20}$ –101 (*c* 0.4, chloroform); ν_{max} (thin film)/cm^{-1} 3062 (CH), 2968, (CH), 1755 (C=O), 1707 (C=O), 1506 (C=C); δ_H (300 MHz, $CDCl_3$) 7.39–7.34 (2H, m, Ar*H*), 7.27–7.21 (1H, m, Ar*H*), 7.07–7.03 (2H, m, Ar*H*), 3.36 (3H, s, NCH_3), 2.34 (1H, dq, ABX_3 system, J_{AB} 14.1, J_{AX} 7.4, C(4)CH_AH$_B$), 2.13 (3H, s, C(3)CH_3), 2.12 (1H, dq, ABX_3 system, J_{BA} 14.1, J_{BX} 7.4, C(4)CH$_A$$H_B$), 0.81 (3H, app t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 171.1 (*C*(5)O), 164.9 (*C*(O)O), 156.2 (*C*(3)CH_3), 150.2 (OPh*C*(1)), 129.6 (Ph*C*), 126.7 (Ph*C*), 121.3 (Ph*C*), 65.1 (*C*(4)CH_2), 31.4 (NCH_3), 24.7 (*C*H_2CH$_3$), 14.5 (C(3)*C*H_3), 7.9 (CH_2*C*H_3); *m/z* HRMS (ESI$^+$) $C_{14}H_{17}N_2O_3$: 261.1234 [M+H]$^+$, found 261.1233 (–0.3 ppm). *Chiral HPLC* Daicel Chiralpak AS-H (*i*PrOH 2:98 hexane, flow rate 1 mL/min, 254 nm) t_R minor = 10.6 min, t_R major = 13.0 min, 87% ee.

Phenyl 4-benzyl-2,5-dimethylpyrazolin-3-on-4-yl carboxylate S32

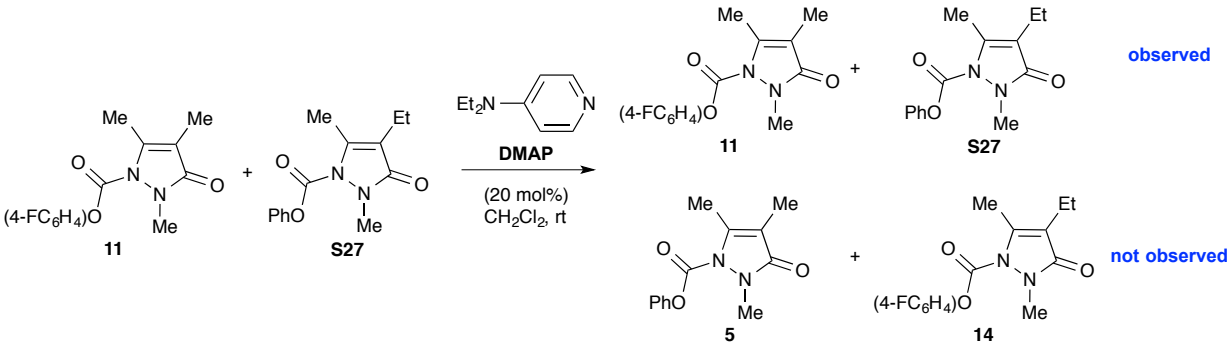


Phenyl 4-benzyl-2,5-dimethylpyrazol-3-yl carbonate **S22** (32.2 mg, 0.10 mmol), triazolium salt **5** (2.7 mg, 0.01 mmol) and KHMDS solution (18 μl, 0.009 mmol) were combined following the general procedure E. Purification by silica column chromatography with 33% diethyl ether in petrol gave the title compound as a colourless oil (15.1 mg, 47%).

ν_{max} (film)/cm^{-1} 3063, 3032 (ArH), 2920, 2653 (CH), 1761 (C=O, carboxylate), 1703 (C=O, lactam), 1591, 1493 (Ar C=N, C=C); δ_H (300 MHz, $CDCl_3$) 7.42–7.36 (2H, m, OPh(3,5)*C*), 7.29–7.24 (4H, m, CH_2Ph(3,4,5)*H*, OPh(4)*C*), 7.18–7.14 (2H, m, CH_2Ph(2,6)*H*), 7.11–7.06 (2H, m, OPh(2,6)*H*), 3.62 (1H, d, *J* 13.8, PhCH$_A$$H_B$), 3.40 (1H, d, *J* 13.8, PhCH_AH$_B$), 3.10 (3H, s, NCH_3), 2.19 (3H, s, C(3)CH_3); δ_C (75 MHz, $CDCl_3$) 171.2 (*C*(5)), 164.7 (*C*O_2), 155.6 (*C*(3)), 150.3 (OPh(1)*C*), 133.4 (CH_2Ph(1)*C*), 129.7 (OPh(3,5)*C*), 129.4 (CH_2Ph(2,6)*C*), 128.6 (CH_2Ph(3,5)*C*), 127.8 (CH_2Ph(4)*C*), 126.7 (OPh(4)*C*), 121.3 (OPh(2,6)*C*), 66.9 (*C*(4)), 37.3 (Ph*C*H_2), 31.3 (NCH_3), 15.2 (C(3)*C*H_3); *m/z* (NSI$^+$) 399 (100%),

377 ([M+K]$^+$ 22%), 339 ([M+H]$^+$ 100%), 211 ([M–$H_3COPhCO_2$+Na] 67%); HRMS (NSI$^+$) $C_{19}H_{19}N_2O_4$ [M+H]$^+$: found 339.1348, requires 339.1339 (2.6 ppm).

Crossover experiment with substrates 11 and S27



To a stirred solution of *p*-fluorophenyl 1,3,4-trimethylpyrazolin-5-on-2-yl carboxylate **11** (14.0 mg, 0.053 mmol) and phenyl 4-ethyl-2,5-dimethylpyrazolin-3-on-1-yl carboxylate **S27** (13.8 mg, 0.053 mmol) in CH_2Cl_2 (1.1 ml) was added DMAP (2.6 mg, 0.021 mmol, 20 mol% based on total substrate). The reaction was stirred overnight and was quenched by the addition of solid ammonium chloride. The suspension was filtered through a plug of silica with diethyl ether as eluent and concentrated *in vacuo*. The subsequent residue was analysed by both ^{1}H and ^{19}F NMR spectroscopy with starting material **11** and **S27** only observed and no crossover products **5** and **14**.

Computational Details

Full Gaussian 09 Reference

Gaussian 09, Revision **C.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Computed structures, energies, and thermal corrections

DMAP-I

Supporting Information: 000-DMAP.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
=====================================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H10N2   C1[X(C7H10N2)]  #Atoms= 19
 Charge = 0        Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -382.089704878      Predicted Change= -8.417504D-09
=====================================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00002 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00104 ||  0.00180   [ YES ]      0.00104 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic      Coordinates (Angstroms)
      Type     X          Y      Z
---------------------------------------------------------------------
      C        0.564001     -1.197520     -0.000102
      H        0.082178     -2.167226     -0.000147
      C       -0.185755     -0.000019     -0.000197
      N       -1.548348     -0.000006     -0.000512
      C       -2.269626     -1.258822      0.000218
      H       -3.339821     -1.055518     -0.000317
      H       -2.033126     -1.855457      0.889582
      H       -2.032554     -1.856696     -0.888145
      C       -2.269561      1.258844      0.000159
```

H	-2.032354	1.856709	-0.888173
H	-2.033122	1.855460	0.889554
H	-3.339768	1.055600	-0.000500
C	0.563974	1.197494	-0.000068
H	0.082123	2.167189	-0.000077
C	1.947705	1.130264	0.000071
H	2.518638	2.057254	0.000152
N	2.665249	0.000010	0.000122
C	1.947732	-1.130260	0.000035
H	2.518686	-2.057237	0.000095

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -382.089704878 Predicted Change= -8.417504D-09
Zero-point correction (ZPE)= -381.9252 0.16442
Internal Energy (U)= -381.9168 0.17286
Enthalpy (H)= -381.9158 0.17381
Gibbs Free Energy (G)= -381.9587 0.13096

Frequencies -- 64.2746 98.1133 164.9872

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C7H10N2 C1[X(C7H10N2)] #Atoms= 19
Charge = 0 Multiplicity = 1

SCF Energy= -382.112788667

==========

Supporting Information: 000-pyrcarbonate.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.651864305 Predicted Change= -3.891676D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00165	0.00180	[YES]	0.00165	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	-2.708515	-1.025075	0.074074
C	-4.031226	-1.667999	0.339165
H	-3.892067	-2.726147	0.569088
H	-4.690959	-1.582777	-0.530560
H	-4.537354	-1.188913	1.183518
C	-3.460714	1.455564	-0.364882
H	-4.205189	1.241884	-1.138625
H	-2.955571	2.387817	-0.629615
H	-3.998127	1.615370	0.575374
O	-0.327530	1.457494	-0.728611
C	0.761615	-1.257544	-0.185374
C	-2.473439	0.340758	-0.239997
C	-1.114151	0.390838	-0.392074
N	-0.597744	-0.853231	-0.192026
N	-1.584869	-1.727061	0.110195
C	1.166999	-2.238374	0.719285
H	0.437955	-2.665111	1.398336
C	2.495843	-2.646872	0.731302
H	2.812121	-3.411582	1.433701
C	3.420277	-2.072135	-0.139822
H	4.458024	-2.388691	-0.120298
C	3.004022	-1.094389	-1.039539
H	3.713176	-0.652743	-1.732306
C	1.672299	-0.689470	-1.078027
H	1.341643	0.045277	-1.803994
C	0.484338	1.933902	0.256624
O	0.495176	1.548344	1.393031
O	1.239320	2.872850	-0.282914
C	2.172102	3.480287	0.623317
H	2.703672	4.224285	0.034666
H	2.860575	2.726031	1.007278
H	1.637963	3.950892	1.449899

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.651864305 Predicted Change= -3.891676D-09
Zero-point correction (ZPE)= -838.3932 0.25861
Internal Energy (U)= -838.3762 0.27556
Enthalpy (H)= -838.3753 0.27651
Gibbs Free Energy (G)= -838.4393 0.21255

Frequencies -- 29.0399 48.0758 63.9209

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.691348233

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DMAP-TS-II

Supporting Information: 005-DMAP-Attack.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73614558 Predicted Change= -4.023409D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00164	0.00180	[YES]	0.00164	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.358957	-0.717899	-0.678065
C	5.790269	-1.129616	-0.808253
H	6.438680	-0.252560	-0.754776
H	5.968165	-1.637762	-1.761865
H	6.073409	-1.823913	-0.010122
C	3.222163	-1.567467	-0.708078
C	3.170163	-3.053343	-0.866145
H	3.647228	-3.562317	-0.021509
H	3.688911	-3.371920	-1.776821
H	2.132413	-3.390703	-0.913891
C	2.168857	-0.696842	-0.562787
O	0.832402	-0.930010	-0.524128
C	0.392417	-1.507069	0.698818
O	0.680524	-0.620438	1.686030
C	0.368694	-1.103069	2.987748
H	0.630656	-0.301456	3.677123
H	0.942639	-2.004511	3.211839
H	-0.701166	-1.325901	3.058800
O	0.351078	-2.712602	0.841527
N	2.672079	0.569316	-0.461044
C	1.978337	1.788085	-0.266152
N	4.024755	0.556179	-0.530227
C	0.721834	1.991747	-0.838754
H	0.266613	1.211772	-1.437815
C	0.063579	3.200636	-0.627539

H	-0.917276	3.352593	-1.068610
C	0.657795	4.209505	0.126723
H	0.143091	5.152221	0.281872
C	1.922656	4.002702	0.675554
H	2.396801	4.783939	1.261490
C	2.584006	2.794004	0.488145
H	3.564586	2.616309	0.914566
N	-1.464213	-0.966244	0.393449
C	-1.897547	0.289233	0.536470
H	-1.160436	1.004322	0.893138
C	-3.192689	0.670845	0.253715
H	-3.478235	1.705309	0.393982
C	-4.118109	-0.298915	-0.209431
N	-5.399813	0.025578	-0.509368
C	-5.852430	1.399076	-0.366540
H	-5.764594	1.741351	0.671000
H	-6.899553	1.459169	-0.659341
H	-5.275286	2.075825	-1.007084
C	-6.314550	-0.999123	-0.984266
H	-6.446189	-1.791185	-0.238263
H	-5.954314	-1.452374	-1.914895
H	-7.285473	-0.545166	-1.176628
C	-3.634943	-1.624885	-0.339896
H	-4.275423	-2.428668	-0.678177
C	-2.318562	-1.898275	-0.029363
H	-1.902343	-2.899757	-0.112548

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73614558 Predicted Change= -4.023409D-09
Zero-point correction (ZPE)= -1220.3122 0.42384
Internal Energy (U)= -1220.2863 0.44983
Enthalpy (H)= -1220.2853 0.45078
Gibbs Free Energy (G)= -1220.3708 0.36530

Frequencies -- -129.9967 12.0116 22.3105

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79564184

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DMAP-III

Supporting Information: 010-DMAP-TI.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

```
================================================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C20H24N4O3   C1[X(C20H24N4O3)]  #Atoms= 51
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -1220.73932849      Predicted Change= -4.025534D-08
================================================================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00003 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00502 ||  0.00180   [ NO ]       0.00502 ||  0.00180   [ YES ]
--------------------------------------------------------------------------------
      Atomic      Coordinates (Angstroms)
       Type     X          Y       Z
--------------------------------------------------------------------------------
      C         4.174164   -1.170739   -0.591624
      C         5.522346   -1.814240   -0.657305
      H         6.303458   -1.061802   -0.528894
      H         5.674564   -2.313506   -1.620255
      H         5.634833   -2.572885    0.124365
      C         2.915708   -1.818062   -0.692683
      C         2.635086   -3.274194   -0.878989
      H         2.936641   -3.856523   -0.001546
      H         3.175849   -3.674729   -1.743938
      H         1.564338   -3.430364   -1.020418
      C         2.009047   -0.788234   -0.584707
      O         0.661469   -0.791589   -0.604037
      C         0.067767   -1.273051    0.660484
      O         0.479569   -0.302389    1.588011
      C         0.208428   -0.675180    2.927194
      H         0.573525    0.139353    3.554008
      H         0.717363   -1.607221    3.182801
      H        -0.870164   -0.802278    3.089336
      O         0.164053   -2.478602    0.928942
      N         2.716639    0.375477   -0.437343
      C         2.224722    1.690116   -0.271753
      N         4.051145    0.140097   -0.437458
      C         1.075291    2.107458   -0.945680
      H         0.558281    1.418405   -1.603562
      C         0.612186    3.408566   -0.768310
      H        -0.283185    3.729112   -1.292981
      C         1.298969    4.299462    0.053840
      H         0.936970    5.314506    0.181879
      C         2.458627    3.879619    0.703031
      H         3.005130    4.566806    1.341632
      C         2.921862    2.577036    0.549167
      H         3.819025    2.234497    1.052329
      N        -1.461047   -0.852362    0.340224
      C        -1.821474    0.436247    0.212741
```

H	-1.024436	1.160217	0.343170
C	-3.116029	0.800130	-0.054736
H	-3.349884	1.852349	-0.143737
C	-4.115829	-0.201145	-0.204110
N	-5.399736	0.114034	-0.461050
C	-5.798069	1.509040	-0.588875
H	-5.593928	2.062384	0.333991
H	-6.867416	1.554084	-0.786974
H	-5.271981	1.995635	-1.417040
C	-6.391477	-0.942088	-0.610796
H	-6.464225	-1.544741	0.300758
H	-6.142056	-1.599247	-1.450756
H	-7.362563	-0.489659	-0.802565
C	-3.690794	-1.549221	-0.063533
H	-4.384753	-2.372776	-0.159892
C	-2.373167	-1.824102	0.206550
H	-1.979304	-2.826201	0.334908

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73932849 Predicted Change= -4.025534D-08
Zero-point correction (ZPE)= -1220.3147 0.42455
Internal Energy (U)= -1220.2885 0.45073
Enthalpy (H)= -1220.2876 0.45168
Gibbs Free Energy (G)= -1220.3727 0.36656

Frequencies -- 12.5417 27.3553 36.8048

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.80064994

==========

DMAP-TS-IV

Supporting Information: 015-DMAP.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73294594 Predicted Change= -2.310756D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.00297 ‖	0.00180	[NO]	0.00297 ‖	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.901032	-1.341876	-0.688778
C	5.206610	-2.073910	-0.683387
H	6.027642	-1.379559	-0.489748
H	5.387489	-2.567263	-1.644804
H	5.218985	-2.853253	0.086714
C	2.615961	-1.899597	-0.870648
C	2.226295	-3.330187	-1.059633
H	2.523526	-3.955632	-0.209123
H	2.673039	-3.770754	-1.959890
H	1.137904	-3.394568	-1.147817
C	1.736574	-0.819627	-0.801023
O	0.445862	-0.774357	-0.797989
C	-0.089655	-1.138967	1.104260
O	0.488625	-0.064811	1.664333
C	1.713319	-0.334994	2.355753
H	2.161563	0.641117	2.538623
H	2.376337	-0.948001	1.743177
H	1.499146	-0.843957	3.299038
O	0.188238	-2.292890	1.339437
N	2.542948	0.301063	-0.600576
C	2.137209	1.628883	-0.390792
N	3.867960	-0.027046	-0.516038
C	0.941548	2.110535	-0.938943
H	0.327423	1.444274	-1.532292
C	0.558778	3.428622	-0.707330
H	-0.371645	3.792406	-1.135135
C	1.359918	4.284431	0.047416
H	1.056750	5.312259	0.219747
C	2.559355	3.805200	0.570503
H	3.198082	4.460174	1.155922
C	2.949272	2.486627	0.359433
H	3.879453	2.103607	0.762841
N	-1.478468	-0.779077	0.745857
C	-1.816879	0.494871	0.439103
H	-1.021150	1.224328	0.521853
C	-3.083785	0.814388	0.044137
H	-3.302635	1.847989	-0.185652
C	-4.078111	-0.201114	-0.069634
N	-5.329746	0.078917	-0.454129
C	-5.706141	1.450032	-0.782095
H	-5.563330	2.110053	0.079276
H	-6.757370	1.468544	-1.061904

H	-5.115073	1.825918	-1.623310
C	-6.318661	-0.988715	-0.561335
H	-6.468275	-1.478449	0.405942
H	-6.007806	-1.736710	-1.297485
H	-7.265541	-0.559693	-0.882388
C	-3.668773	-1.529448	0.241754
H	-4.353123	-2.363405	0.174123
C	-2.382853	-1.774795	0.631306
H	-2.008133	-2.762125	0.869825

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1220.73294594 Predicted Change= -2.310756D-08
Zero-point correction (ZPE)= -1220.3086 0.42431
Internal Energy (U)= -1220.2827 0.45019
Enthalpy (H)= -1220.2818 0.45114
Gibbs Free Energy (G)= -1220.3656 0.36729

Frequencies -- -213.4219 18.1866 25.5297

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79546757

==========

DMAP-V

Supporting Information: 020-AcDMAP-Enolate-Complex.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73725609 Predicted Change= -5.842790D-08

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00390	0.00180	[NO]	0.00390	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	3.775074	-1.283281	-0.760451
C	5.072917	-2.028369	-0.699048
H	5.888725	-1.347770	-0.443181
H	5.303436	-2.502869	-1.659582
H	5.034868	-2.825947	0.051810
C	2.505603	-1.826799	-1.036762
C	2.118417	-3.248297	-1.289693
H	2.414694	-3.916788	-0.470785
H	2.554925	-3.656630	-2.211065
H	1.029141	-3.306767	-1.382511
C	1.605657	-0.745080	-0.986324
O	0.344606	-0.692132	-1.092584
C	-0.100904	-1.262187	1.420820
O	0.599764	-0.209784	1.772896
C	1.943595	-0.482280	2.218786
H	2.433989	0.489044	2.242091
H	2.437764	-1.147389	1.509085
H	1.902773	-0.929273	3.213958
O	0.197303	-2.418964	1.527230
N	2.423350	0.368900	-0.696259
C	2.013460	1.675014	-0.418271
N	3.749209	0.024601	-0.539793
C	0.780462	2.163755	-0.880767
H	0.148901	1.511513	-1.470034
C	0.390257	3.463629	-0.570556
H	-0.566346	3.827766	-0.936890
C	1.211847	4.302685	0.180834
H	0.900585	5.315746	0.415100
C	2.445487	3.822227	0.616507
H	3.103970	4.462882	1.196483
C	2.847952	2.523176	0.325340
H	3.805601	2.143903	0.661613
N	-1.418184	-0.862984	0.978772
C	-1.694654	0.425175	0.639738
H	-0.886785	1.133796	0.762686
C	-2.916733	0.777307	0.154302
H	-3.083520	1.815498	-0.097131
C	-3.931196	-0.209136	-0.035461
N	-5.134789	0.103154	-0.517749
C	-5.446257	1.483003	-0.883966
H	-5.378495	2.141029	-0.012541
H	-6.462094	1.521973	-1.270603
H	-4.763818	1.840541	-1.660488
C	-6.144140	-0.936806	-0.705223
H	-6.375218	-1.426260	0.245420
H	-5.799541	-1.686592	-1.423666
H	-7.053107	-0.478894	-1.088843
C	-3.586972	-1.551889	0.309282
H	-4.288190	-2.365122	0.187885
C	-2.347444	-1.836144	0.792902
H	-2.027306	-2.836266	1.054142

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1220.73725609 Predicted Change= -5.842790D-08
Zero-point correction (ZPE)= -1220.3123 0.42490
Internal Energy (U)= -1220.2857 0.45152
Enthalpy (H)= -1220.2847 0.45246
Gibbs Free Energy (G)= -1220.3698 0.36739

Frequencies -- 22.7984 28.3541 44.8077
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.80221403
==========

DMAP-TS-VI-C

Supporting Information: 025-C-attack.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.72521348 Predicted Change= -1.910201D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.00094 ‖	0.00180	[YES]	0.00094 ‖	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-0.174509	-1.741999	0.829565
O	0.715224	-1.023621	1.571743
C	1.545481	-1.804793	2.427682
H	2.085046	-2.565668	1.861777
H	0.946819	-2.281221	3.208471
H	2.252515	-1.100475	2.864806
O	-0.414600	-2.933165	1.006380

N	-1.365681	-0.844442	0.614454
C	-1.309602	0.500364	0.761140
H	-0.350002	0.907153	1.048078
C	-2.417735	1.284803	0.587740
H	-2.312305	2.351177	0.730175
C	-3.655306	0.703321	0.205114
N	-4.755655	1.445403	0.003513
C	-6.004156	0.809347	-0.398640
H	-6.763793	1.577207	-0.530556
H	-6.351193	0.105535	0.364960
H	-5.882727	0.275985	-1.346927
C	-4.701401	2.891905	0.176889
H	-5.683739	3.309382	-0.035206
H	-3.976546	3.340719	-0.509807
H	-4.427754	3.152871	1.204386
C	-3.670513	-0.713065	0.053419
H	-4.572785	-1.244415	-0.215661
C	-2.532964	-1.436702	0.270310
H	-2.491203	-2.516106	0.202444
C	1.933053	-2.133528	-0.765157
C	2.272967	-3.582278	-0.660440
H	3.287319	-3.712023	-0.275443
H	2.202144	-4.067371	-1.640745
H	1.557760	-4.078277	0.004784
C	0.632690	-1.602420	-1.098411
C	-0.388961	-2.309032	-1.936958
H	-0.773860	-3.191293	-1.411634
H	0.024513	-2.642546	-2.895710
H	-1.222610	-1.632266	-2.153092
C	0.861701	-0.175744	-1.211055
O	0.083184	0.718962	-1.570420
N	2.160339	0.007113	-0.730764
C	2.803108	1.203805	-0.377438
N	2.798342	-1.201866	-0.482124
C	4.042705	1.151411	0.276479
H	4.481501	0.186040	0.494029
C	4.691444	2.327544	0.633840
H	5.651721	2.267318	1.138114
C	4.124638	3.569895	0.355480
H	4.635929	4.484788	0.637261
C	2.892840	3.616649	-0.291818
H	2.435631	4.575521	-0.519367
C	2.227990	2.451344	-0.662961
H	1.274921	2.492129	-1.170991

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.72521348 Predicted Change= -1.910201D-09
Zero-point correction (ZPE)= -1220.3006 0.42451
Internal Energy (U)= -1220.2755 0.44961
Enthalpy (H)= -1220.2746 0.45056

Gibbs Free Energy (G)= -1220.3555 0.36962

Frequencies -- -334.5779 16.3858 26.8661

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.78787598

==========

DMAP-TS-VI-N

Supporting Information: 025-N-attack.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73081640 Predicted Change= -8.287531D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00068	0.00180	[YES]	0.00068	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.670471	1.658801	-1.174637
O	-1.617107	0.896168	-1.789959
C	-2.803673	1.623217	-2.087619
H	-3.531110	0.885032	-2.423728
H	-2.609177	2.360792	-2.869798
H	-3.172033	2.130636	-1.192089
O	-0.554139	2.865190	-1.352745
N	0.594492	0.833368	-1.201207
C	1.755792	1.477757	-0.948462
H	1.671648	2.556825	-0.894266
C	2.934185	0.806602	-0.783365
H	3.829860	1.379851	-0.588333
C	2.955793	-0.616785	-0.840538
N	4.081093	-1.314716	-0.625619
C	5.322125	-0.620676	-0.304834

H	6.111145	-1.356863	-0.165249
H	5.218733	-0.040436	0.618642
H	5.615650	0.051229	-1.117502
C	4.048261	-2.772350	-0.644409
H	3.339647	-3.154459	0.097515
H	5.039857	-3.150669	-0.404051
H	3.764442	-3.144919	-1.633985
C	1.722287	-1.257313	-1.139013
H	1.647681	-2.332121	-1.229434
C	0.582402	-0.516349	-1.299559
H	-0.376349	-0.966599	-1.521479
C	-0.094774	1.757054	1.447258
C	0.206313	3.219758	1.538244
H	1.277396	3.386193	1.686315
H	-0.319807	3.654951	2.395557
H	-0.122197	3.736965	0.636376
C	0.550654	0.733214	2.087193
C	1.724752	0.760945	3.008444
H	2.654459	0.506382	2.480917
H	1.599187	0.027167	3.810950
H	1.858488	1.746908	3.462264
C	-0.129843	-0.484721	1.714936
O	0.062179	-1.651492	2.070556
N	-1.142938	-0.060687	0.839116
C	-2.285056	-0.810919	0.502757
N	-1.125959	1.318225	0.644860
C	-3.542556	-0.200332	0.463540
H	-3.621247	0.852631	0.708967
C	-4.664243	-0.945765	0.119024
H	-5.636101	-0.461700	0.087381
C	-4.550342	-2.305163	-0.171506
H	-5.429017	-2.884585	-0.436214
C	-3.298359	-2.912126	-0.113860
H	-3.196850	-3.970841	-0.333689
C	-2.163312	-2.175010	0.215062
H	-1.188210	-2.643655	0.270137

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73081640 Predicted Change= -8.287531D-10
Zero-point correction (ZPE)= -1220.3067 0.42411
Internal Energy (U)= -1220.2813 0.44951
Enthalpy (H)= -1220.2803 0.45045
Gibbs Free Energy (G)= -1220.3616 0.36920

Frequencies -- -234.3560 25.3596 29.1696

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51

Charge = 0 Multiplicity = 1

SCF Energy= -1220.79488856

==========

DMAP-VII-N

Supporting Information: 030-N-attack-TI-from-IRC.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73557171 Predicted Change= -8.043056D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ǁ	0.00045	[YES]	0.00000 ǁ	0.00030	[YES]
Displ	0.00243 ǁ	0.00180	[NO]	0.00243 ǁ	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.562444	1.139435	-1.459627
O	-1.290686	0.098925	-2.052659
C	-2.328283	0.576574	-2.892103
H	-2.942927	-0.289976	-3.140148
H	-1.917871	1.023338	-3.801462
H	-2.941663	1.323258	-2.377169
O	-0.362214	2.201201	-2.073908
N	0.824120	0.354958	-1.131469
C	1.936207	1.103622	-1.081459
H	1.789879	2.142566	-1.355724
C	3.157251	0.580443	-0.739611
H	4.016180	1.236840	-0.722096
C	3.269618	-0.800864	-0.427885
N	4.445876	-1.356268	-0.080058
C	5.648178	-0.536703	-0.017886
H	6.489468	-1.164953	0.268517
H	5.542657	0.261002	0.725152
H	5.868412	-0.086549	-0.991753
C	4.517802	-2.777138	0.231602
H	3.859197	-3.028714	1.069416
H	5.540012	-3.025442	0.511151
H	4.237583	-3.386179	-0.634514
C	2.075860	-1.567586	-0.512551
H	2.070376	-2.630256	-0.311817

C	0.894134	-0.961836	-0.859591
H	-0.034310	-1.513400	-0.946314
C	-0.513610	2.257845	0.765951
C	-0.277558	3.662415	0.312931
H	-0.181188	4.308738	1.189436
H	-1.103806	4.006804	-0.308714
H	0.633284	3.749642	-0.283752
C	-0.187995	1.712476	1.964335
C	0.463069	2.324628	3.160306
H	1.539139	2.119530	3.180496
H	0.033275	1.902207	4.073317
H	0.330257	3.409492	3.182151
C	-0.668429	0.338393	1.963965
O	-0.655662	-0.496368	2.861178
N	-1.246355	0.150448	0.700926
C	-2.307063	-0.765450	0.487619
N	-1.183905	1.334527	-0.050420
C	-3.538610	-0.334544	-0.009695
H	-3.677222	0.716038	-0.240111
C	-4.562751	-1.254650	-0.200680
H	-5.516968	-0.915432	-0.592499
C	-4.375014	-2.599554	0.119323
H	-5.178317	-3.314256	-0.027986
C	-3.150057	-3.017961	0.631642
H	-2.993599	-4.061700	0.886543
C	-2.110145	-2.108404	0.811605
H	-1.152466	-2.425142	1.208995

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73557171 Predicted Change= -8.043056D-09
Zero-point correction (ZPE)= -1220.3111 0.42441
Internal Energy (U)= -1220.2849 0.45057
Enthalpy (H)= -1220.2840 0.45151
Gibbs Free Energy (G)= -1220.3687 0.36681

Frequencies -- 15.4470 21.8914 43.0393

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup=C1 Stoichiometry=C20H24N4O3 C1[X(C20H24N4O3)]
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79935337

==========

DMAP-TS-VIII-N

Supporting Information: 035-N-attack-TI-from-IRC-endo-175.log

---

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73457219 Predicted Change= -4.388434D-08

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.05144	0.00180	[NO]	0.05144	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-0.559988	1.070887	-1.442097
O	-1.256824	-0.007745	-1.975035
C	-1.823160	0.241065	-3.251229
H	-2.395209	-0.653791	-3.498807
H	-1.048862	0.410747	-4.004025
H	-2.488147	1.109041	-3.224038
O	-0.324231	2.085796	-2.107988
N	0.919159	0.274841	-1.050528
C	2.036327	1.003190	-1.158175
H	1.885936	2.002214	-1.555355
C	3.275306	0.512094	-0.821772
H	4.139204	1.153164	-0.935211
C	3.394544	-0.817784	-0.340839
N	4.586424	-1.341089	0.014885
C	5.795589	-0.540135	-0.102402
H	6.647572	-1.137180	0.218042
H	5.741329	0.353376	0.529141
H	5.963455	-0.228301	-1.139215
C	4.663198	-2.706581	0.512699
H	4.046298	-2.833045	1.408967
H	5.696550	-2.929694	0.772347
H	4.333700	-3.425218	-0.245944
C	2.194634	-1.573638	-0.267725
H	2.194384	-2.604625	0.059450
C	0.999561	-0.997894	-0.629591
H	0.067679	-1.551482	-0.609621
C	-0.448484	2.198458	0.761431
C	-0.055559	3.559526	0.287851
H	-0.823941	3.976348	-0.363032
H	0.875548	3.537078	-0.282724
H	0.088453	4.209121	1.155007
C	-0.248050	1.663135	1.989876

C	0.377719	2.255444	3.209655
H	1.453449	2.052944	3.250701
H	-0.074288	1.814954	4.102811
H	0.240754	3.339574	3.249346
C	-0.845769	0.335831	1.991807
O	-0.964259	-0.466994	2.909246
N	-1.354454	0.153068	0.695931
C	-2.493650	-0.656097	0.445422
N	-1.150775	1.312844	-0.067098
C	-3.606417	-0.143943	-0.226169
H	-3.587266	0.881977	-0.577396
C	-4.709443	-0.959318	-0.445676
H	-5.571112	-0.558680	-0.971333
C	-4.718804	-2.278699	0.009171
H	-5.584422	-2.910170	-0.164385
C	-3.608110	-2.778580	0.681588
H	-3.601892	-3.804560	1.036834
C	-2.489347	-1.975858	0.897316
H	-1.619723	-2.356514	1.419480

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73457219 Predicted Change= -4.388434D-08
Zero-point correction (ZPE)= -1220.3108 0.42372
Internal Energy (U)= -1220.2851 0.44941
Enthalpy (H)= -1220.2842 0.45035
Gibbs Free Energy (G)= -1220.3686 0.36592

Frequencies -- -93.6821 12.7985 19.0047

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79729475

==========

DMAP-IX-C

Supporting Information: 030-C-isomer.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.653706219 Predicted Change= -1.663813D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00071	0.00180	[YES]	0.00071	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.279978	-0.557818	-0.775343
O	0.113662	-1.679710	-1.208433
N	-0.655254	0.299084	-0.239493
C	-2.040442	0.084254	-0.041434
N	-0.097710	1.513452	0.165302
C	1.156615	1.494754	-0.087232
C	2.058474	2.636639	0.227593
H	2.847969	2.317196	0.916876
H	1.490469	3.446933	0.686802
H	2.543227	3.006051	-0.681993
C	1.603827	0.212216	-0.744192
C	2.599593	-0.543418	0.131168
O	2.114894	-0.703470	1.363386
C	2.962445	-1.418210	2.273806
H	3.912254	-0.893523	2.389884
H	3.143993	-2.426653	1.898553
H	2.420300	-1.448907	3.216097
O	3.674933	-0.940085	-0.238848
C	2.156767	0.395395	-2.157298
H	1.461690	0.980677	-2.764277
H	2.293923	-0.586975	-2.614636
H	3.122860	0.903371	-2.121793
C	-2.663447	-1.069675	-0.530046
H	-2.089228	-1.812320	-1.065498
C	-4.027291	-1.248657	-0.316844
H	-4.502920	-2.146647	-0.699129
C	-4.778004	-0.298811	0.369813
H	-5.840746	-0.448886	0.529550
C	-4.147435	0.846926	0.849034
H	-4.716058	1.599473	1.386603
C	-2.785813	1.045214	0.649520
H	-2.296492	1.935719	1.022180

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.653706219 Predicted Change= -1.663813D-09

Zero-point correction (ZPE)= -838.3958 0.25786

Internal Energy (U)= -838.3789 0.27475

Enthalpy (H)= -838.3780 0.27570

Gibbs Free Energy (G)= -838.4418 0.21184

Frequencies -- 21.9332 33.8075 44.3001
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.694745843
==========

DMAP-IX-N

Supporting Information: 040-N-isomer-1.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.650666144 Predicted Change= -4.568405D-05
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00017	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.21643	0.00180	[NO]	0.21643	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	0.863280	-1.693972	-0.424226
O	0.403736	-2.772112	-0.759680
N	0.110622	-0.502405	-0.340866
C	-1.269730	-0.532140	0.016845
N	0.930235	0.490000	0.207564
C	0.715234	1.836839	-0.124030
O	-0.385984	1.989422	-0.847322
C	-0.752368	3.352792	-1.102015
H	-1.668962	3.299913	-1.684820
H	0.036586	3.853971	-1.664078
H	-0.922791	3.874598	-0.158952
O	1.433184	2.728032	0.262269
C	2.221785	-0.048221	0.363438
C	3.360713	0.779783	0.851664
H	3.095614	1.308627	1.768931
H	3.644654	1.532597	0.111881
H	4.215411	0.128084	1.038898

C	2.214723	-1.350416	0.002053
C	3.312131	-2.362177	0.027381
H	3.771404	-2.474113	-0.960108
H	2.904376	-3.336389	0.311229
H	4.096404	-2.093068	0.738325
C	-1.736229	0.111241	1.163288
H	-1.046502	0.652964	1.802576
C	-3.089237	0.045840	1.479543
H	-3.451337	0.550025	2.370155
C	-3.971561	-0.667500	0.670408
H	-5.025383	-0.717785	0.924497
C	-3.492427	-1.311109	-0.467818
H	-4.171411	-1.866325	-1.107366
C	-2.144276	-1.238623	-0.806933
H	-1.763770	-1.723023	-1.697777

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.650666144 Predicted Change= -4.568405D-05
Zero-point correction (ZPE)= -838.3925 0.25807
Internal Energy (U)= -838.3757 0.27494
Enthalpy (H)= -838.3747 0.27589
Gibbs Free Energy (G)= -838.4380 0.21264

Frequencies -- 38.3459 50.9531 57.6435

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.691508220

==========

NHC-I

Supporting Information: 000-NHC-cat.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C11H11N3 C1[X(C11H11N3)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -589.753872741 Predicted Change= -4.235514D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ǁ	0.00045	[YES]	0.00000 ǁ	0.00030	[YES]
Displ	0.00714 ǁ	0.00180	[NO]	0.00714 ǁ	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.111191	0.036836	0.304743
H	5.096354	0.041549	-0.163657
H	4.250480	0.041789	1.389085
C	3.284312	-1.208263	-0.094217
H	3.398239	-2.042485	0.598684
H	3.515484	-1.552490	-1.106646
N	1.922802	-0.687989	-0.052317
C	1.876265	0.680559	-0.061318
C	3.252238	1.263525	-0.104277
H	3.376025	2.114051	0.567560
H	3.484053	1.596784	-1.121456
C	0.679720	-1.238404	-0.039836
N	-0.058317	-0.092157	-0.035911
C	-1.479329	-0.036714	-0.007659
N	0.652853	1.099458	-0.048687
C	-2.209276	-1.226232	0.002667
H	-1.674560	-2.168496	-0.009430
C	-3.597681	-1.173483	0.027800
H	-4.163597	-2.099987	0.035619
C	-4.262097	0.051750	0.042751
H	-5.346660	0.086203	0.062508
C	-3.521979	1.230379	0.032440
H	-4.027316	2.191313	0.044414
C	-2.130533	1.195000	0.007290
H	-1.546851	2.106871	-0.000585

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -589.753872741 Predicted Change= -4.235514D-08
Zero-point correction (ZPE)= -589.5465 0.20728
Internal Energy (U)= -589.5361 0.21773
Enthalpy (H)= -589.5351 0.21868
Gibbs Free Energy (G)= -589.5839 0.16994

Frequencies -- 31.4259 67.0624 138.4079

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C11H11N3 C1[X(C11H11N3)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -589.785363133

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.647696431 Predicted Change= -1.168422D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00390	0.00180	[NO]	0.00390	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-2.718564	-1.003421	0.072020
C	-4.042883	-1.642792	0.337267
H	-3.904239	-2.702399	0.560065
H	-4.705488	-1.551432	-0.529824
H	-4.544967	-1.168115	1.186714
C	-3.458312	1.482996	-0.360394
H	-4.209395	1.273443	-1.129072
H	-2.948456	2.410967	-0.631403
H	-3.988430	1.650089	0.582899
O	-0.325297	1.470003	-0.723581
C	0.747596	-1.252901	-0.187690
C	-2.477570	0.362302	-0.239106
C	-1.118474	0.406655	-0.390603
N	-0.608693	-0.840750	-0.194124
N	-1.599102	-1.710296	0.106511
C	1.140981	-2.251710	0.702020
H	0.402967	-2.684431	1.367202
C	2.466435	-2.669231	0.714722
H	2.772874	-3.448352	1.405664
C	3.400248	-2.086977	-0.140794
H	4.435571	-2.411645	-0.120863
C	2.995840	-1.092154	-1.026331
H	3.711653	-0.645113	-1.708982
C	1.667480	-0.677090	-1.065641
H	1.346111	0.071183	-1.781886
C	0.497592	1.927475	0.261290
O	0.495617	1.553497	1.400113
O	1.284636	2.840363	-0.284325
C	2.237736	3.411083	0.620935

H 2.797133 4.135564 0.032997
H 2.897495 2.631498 1.005972
H 1.723455 3.899750 1.449979

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.647696431 Predicted Change= -1.168422D-08
Zero-point correction (ZPE)= -838.3891 0.25857
Internal Energy (U)= -838.3720 0.27560
Enthalpy (H)= -838.3711 0.27654
Gibbs Free Energy (G)= -838.4354 0.21221

Frequencies -- 25.9437 47.5863 61.1320

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.686703482

NHC-TS-II

Supporting Information: 005-NHC-attack-8.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.41171074 Predicted Change= -9.448146D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00201	0.00180	[NO]	0.00201	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	0.190154	-1.227704	-0.576382
O	0.986150	-0.873243	-1.432274
O	-0.505564	-2.396840	-0.612167
C	-0.890674	-2.766948	-1.924874
H	-1.580751	-2.020034	-2.338583

H	-1.399718	-3.725993	-1.834055
H	-0.017159	-2.851899	-2.574953
O	0.476095	-1.066155	0.815176
C	1.140382	0.072100	1.117754
C	0.643137	1.228988	1.675380
C	-0.758817	1.512183	2.111419
H	-1.350667	0.592403	2.130223
H	-1.263430	2.220065	1.440354
H	-0.779160	1.946894	3.116312
C	1.774266	2.081260	1.737950
C	1.830691	3.471486	2.286342
H	1.590965	3.480977	3.355048
H	1.110910	4.129405	1.787136
H	2.832874	3.883595	2.152655
N	2.861838	1.493094	1.260721
N	2.475326	0.251960	0.886275
C	3.434458	-0.651384	0.356816
C	4.570347	-0.128731	-0.259283
H	4.682544	0.946378	-0.332419
C	5.539028	-0.992908	-0.757821
H	6.423061	-0.581514	-1.235321
C	5.377536	-2.371966	-0.652125
H	6.132845	-3.044308	-1.046295
C	4.238713	-2.882012	-0.033787
H	4.103920	-3.955236	0.059782
C	3.265838	-2.031001	0.479581
H	2.384440	-2.432251	0.964676
C	-1.869984	2.202538	-1.296996
C	-1.435321	3.522313	-1.847359
H	-1.878193	4.366670	-1.317816
H	-1.715581	3.594576	-2.903660
C	0.101700	3.418866	-1.668412
H	0.376126	3.805449	-0.681692
H	0.650442	3.985176	-2.421825
C	0.437138	1.912518	-1.719479
H	1.264272	1.624002	-1.072372
H	0.635261	1.545772	-2.728775
N	-0.821898	1.328043	-1.240909
C	-1.232862	0.151645	-0.730645
N	-2.540013	0.393100	-0.498904
C	-3.473263	-0.507359	0.094398
N	-2.959921	1.659587	-0.846411
C	-3.008227	-1.513832	0.937716
H	-1.945752	-1.610798	1.133434
C	-3.928504	-2.388864	1.507115
H	-3.573851	-3.176766	2.163695
C	-5.290543	-2.250006	1.251219
H	-6.002100	-2.933390	1.703410
C	-5.737605	-1.228660	0.415817
H	-6.797712	-1.112692	0.214176
C	-4.831421	-0.351789	-0.171200
H	-5.161368	0.448533	-0.823299

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1428.41171074 Predicted Change= -9.448146D-09
Zero-point correction (ZPE)= -1427.9442 0.46743
Internal Energy (U)= -1427.9167 0.49494
Enthalpy (H)= -1427.9158 0.49588
Gibbs Free Energy (G)= -1428.0032 0.40847

Frequencies -- -176.1697 20.4366 27.1623
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.47706311

NHC-III

Supporting Information: 010-Initial-TI-1.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.41408446 Predicted Change= -7.413850D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00114	0.00180	[YES]	0.00114	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-4.115687	0.624981	0.167818
C	-5.541176	0.184411	0.086074
H	-6.207569	0.981894	-0.243793
H	-5.876375	-0.158459	1.070019
C	-5.439405	-0.984160	-0.930436
H	-5.623601	-0.602222	-1.937409
H	-6.164673	-1.772558	-0.728029
C	-3.987500	-1.513208	-0.848557
H	-3.572165	-1.807507	-1.811217

H	-3.856638	-2.330638	-0.137264
N	-3.285394	-0.330343	-0.339429
C	-2.025115	0.094943	-0.206196
C	-0.802522	-0.655999	-0.811953
O	-0.506745	-0.233921	-1.961288
O	-1.189441	-2.018116	-0.678608
C	-0.684986	-2.862838	-1.702588
H	-0.919541	-2.460528	-2.690911
H	-1.171743	-3.829708	-1.558367
H	0.399917	-2.986261	-1.614506
O	0.226436	-0.403994	0.267012
C	1.181113	-1.322396	0.473853
N	-2.136858	1.307213	0.352964
C	-1.106302	2.249986	0.685847
N	-3.444658	1.648293	0.602254
C	-1.250593	2.992931	1.852761
H	-2.120504	2.845384	2.483201
C	-0.261556	3.913171	2.182624
H	-0.357187	4.498731	3.091231
C	0.850852	4.070459	1.358419
H	1.626977	4.780180	1.627251
C	0.971687	3.317690	0.192617
H	1.841920	3.428335	-0.447212
C	-0.018169	2.408161	-0.164632
H	0.054120	1.809037	-1.067813
C	1.145044	-2.518162	1.163918
C	-0.040050	-3.170097	1.798904
H	-0.468397	-3.954313	1.163507
H	-0.827586	-2.432181	1.973495
H	0.231481	-3.624838	2.757719
C	2.492607	-2.952588	1.166460
C	3.040427	-4.202804	1.778455
H	4.123104	-4.238790	1.639338
H	2.600299	-5.095905	1.322179
H	2.825546	-4.244798	2.851936
N	3.293668	-2.097584	0.546671
N	2.484207	-1.104696	0.106142
C	3.053760	0.035125	-0.517716
C	4.239826	0.556601	-0.000422
H	4.686621	0.085579	0.868106
C	4.826360	1.660037	-0.610093
H	5.750161	2.065300	-0.208521
C	4.232366	2.244678	-1.727789
H	4.693784	3.105056	-2.203087
C	3.049382	1.711743	-2.236971
H	2.585933	2.154800	-3.114016
C	2.455321	0.600252	-1.642495
H	1.533254	0.174965	-2.030390

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.41408446 Predicted Change= -7.413850D-09
Zero-point correction (ZPE)= -1427.9455 0.46850
Internal Energy (U)= -1427.9177 0.49638
Enthalpy (H)= -1427.9167 0.49732
Gibbs Free Energy (G)= -1428.0040 0.41003

Frequencies -- 20.1118 32.1394 38.4996

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48038659

NHC-TS-IV

Supporting Information: 015-NHC-collapse.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.40956376 Predicted Change= -4.504589D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00110	0.00180	[YES]	0.00110	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.835799	0.818188	-0.640891
C	5.184777	0.299144	-1.019834
H	5.957437	1.067056	-0.970862
H	5.151464	-0.090525	-2.042049
C	5.383867	-0.830994	0.025233
H	5.923160	-0.434020	0.888680
H	5.955057	-1.667920	-0.376891
C	3.970382	-1.275317	0.470529
H	3.894572	-1.518331	1.528546
H	3.566055	-2.103625	-0.114937
N	3.188063	-0.068021	0.174026
C	1.980254	0.433937	0.438054

C	0.851193	-0.212636	1.225576
O	0.222908	0.435885	2.057517
O	1.249556	-1.510177	1.454207
C	0.451212	-2.186130	2.425215
H	0.606735	-1.752021	3.415794
H	0.780582	-3.225355	2.404383
H	-0.608297	-2.127420	2.165463
O	-0.077661	-0.360485	-0.313245
C	-0.783580	-1.459165	-0.413899
N	1.944688	1.608721	-0.190427
C	0.848228	2.533459	-0.273158
N	3.099300	1.860891	-0.885204
C	0.323810	2.808723	-1.529881
H	0.723780	2.302939	-2.402004
C	-0.721478	3.719277	-1.631528
H	-1.151269	3.936620	-2.603495
C	-1.222514	4.336772	-0.487191
H	-2.043338	5.042224	-0.570062
C	-0.681207	4.046018	0.762931
H	-1.074309	4.524874	1.653939
C	0.366983	3.138067	0.880709
H	0.787076	2.878548	1.844558
C	-0.392649	-2.751128	-0.735186
C	0.994237	-3.187021	-1.075735
H	1.498095	-3.692238	-0.241084
H	1.592937	-2.306867	-1.337366
H	1.004990	-3.870742	-1.932200
C	-1.584402	-3.509934	-0.685464
C	-1.736998	-4.977488	-0.934157
H	-2.789905	-5.259004	-0.862216
H	-1.168592	-5.566788	-0.205935
H	-1.370574	-5.250031	-1.930146
N	-2.636155	-2.768964	-0.374432
N	-2.149368	-1.509491	-0.192356
C	-3.056562	-0.436018	-0.023778
C	-4.380682	-0.611739	-0.439336
H	-4.668499	-1.559573	-0.877512
C	-5.299954	0.418526	-0.282152
H	-6.325748	0.269220	-0.606829
C	-4.911595	1.633418	0.277810
H	-5.631513	2.437089	0.398944
C	-3.591382	1.799521	0.687490
H	-3.275211	2.736530	1.137054
C	-2.657571	0.775784	0.549966
H	-1.639830	0.906046	0.899226

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.40956376 Predicted Change= -4.504589D-09
Zero-point correction (ZPE)= -1427.9427 0.46679
Internal Energy (U)= -1427.9149 0.49460

Enthalpy (H)= -1427.9140 0.49554
Gibbs Free Energy (G)= -1428.0019 0.40757

Frequencies -- -93.5221 14.9813 24.0944

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.47747004

NHC-V

Supporting Information: 020-Complex-attempt-3.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.42905764 Predicted Change= -2.123346D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00292	0.00180	[NO]	0.00292	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.082079	2.187568	1.198772
C	0.342532	3.452905	1.475335
H	0.023579	3.873287	0.514495
H	0.940795	4.195080	2.004274
C	-0.869046	2.932312	2.289548
H	-1.769753	3.516437	2.097459
H	-0.642863	2.988300	3.357440
C	-1.073781	1.456913	1.875077
H	-1.783312	1.346871	1.051397
H	-1.354707	0.797363	2.693990
N	0.275444	1.108202	1.395599
C	0.953073	0.026234	1.006767
C	0.366411	-1.338666	1.140218
O	-0.711134	-1.474077	1.664629
O	1.178584	-2.298916	0.740864
C	0.594709	-3.608821	0.766171

H	1.337129	-4.266152	0.319108
H	-0.330788	-3.601445	0.187478
H	0.381635	-3.903705	1.795410
O	-0.049733	-0.619436	-1.203104
C	-0.858300	0.362637	-1.289997
N	2.157648	0.474917	0.627103
C	3.258640	-0.241953	0.047890
N	2.248425	1.835309	0.741276
C	3.047455	-0.993682	-1.103084
H	2.045555	-1.049212	-1.522163
C	4.143094	-1.638465	-1.669833
H	4.005502	-2.230341	-2.569003
C	5.409873	-1.515861	-1.101542
H	6.257232	-2.018951	-1.556596
C	5.596272	-0.742337	0.042642
H	6.583551	-0.640736	0.480819
C	4.513094	-0.095571	0.628192
H	4.630057	0.518314	1.515372
C	-0.643327	1.722473	-1.584970
C	0.647615	2.302732	-2.067737
H	0.581426	2.659908	-3.103184
H	1.428178	1.533853	-2.032002
H	0.999811	3.149980	-1.462683
C	-1.894516	2.347663	-1.401090
C	-2.224984	3.792784	-1.612259
H	-2.050374	4.086566	-2.653203
H	-1.605202	4.448801	-0.988753
H	-3.274639	3.975041	-1.370948
N	-2.842640	1.500501	-1.018898
N	-2.217651	0.279627	-0.973203
C	-2.935345	-0.857592	-0.564184
C	-2.523412	-2.139477	-0.948600
H	-1.639942	-2.244126	-1.566022
C	-3.247110	-3.248579	-0.523971
H	-2.923476	-4.240117	-0.829770
C	-4.384522	-3.101851	0.267655
H	-4.945542	-3.973169	0.590876
C	-4.799291	-1.822227	0.627955
H	-5.690025	-1.690022	1.235772
C	-4.083178	-0.702557	0.218226
H	-4.402358	0.298247	0.485093

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.42905764 Predicted Change= -2.123346D-08
Zero-point correction (ZPE)= -1427.9615 0.46751
Internal Energy (U)= -1427.9329 0.49613
Enthalpy (H)= -1427.9319 0.49708
Gibbs Free Energy (G)= -1428.0209 0.40806

Frequencies -- 17.6440 34.6827 49.8607

```
=====================================================================
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)
---------------------------------------------------------------------
Pointgroup= C1   Stoichiometry= C24H25N5O3   C1[X(C24H25N5O3)]  #Atoms= 57
Charge = 0        Multiplicity = 1
---------------------------------------------------------------------
SCF Energy= -1428.49699961
=====================================================================
```

NHC-TS-VI-C

```
        Supporting Information: 025-C-Diastereomer.log
---------------------------------------------------------------------
Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
=====================================================================
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
Pointgroup= C1   Stoichiometry= C24H25N5O3   C1[X(C24H25N5O3)]  #Atoms= 57
Charge = 0        Multiplicity = 1
---------------------------------------------------------------------
SCF Energy= -1428.41706811      Predicted Change= -1.435567D-10
=====================================================================
Optimization completed.          {Found       2       times}
Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
Displ      0.00020 ||  0.00180   [ YES ]      0.00020 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic      Coordinates (Angstroms)
      Type     X          Y       Z
---------------------------------------------------------------------
       C       -2.899148       1.118610      -2.136751
       H       -3.441708       1.573475      -2.966243
       H       -3.539859       1.136870      -1.253777
       C       -1.601458       1.901433      -1.827768
       H       -1.683474       2.572699      -0.976907
       H       -1.203344       2.433887      -2.694555
       N       -0.667825       0.807257      -1.502229
       C       -1.113043      -0.418316      -1.892275
       C       -2.497869      -0.352418      -2.442280
       H       -3.149154      -1.073047      -1.938356
       H       -2.493784      -0.576333      -3.512733
       C        0.563613       0.653438      -0.989569
       C        1.364775       1.723436      -0.247114
       C        0.646746       1.457245       1.574907
       C        1.217205       2.673686       2.252689
       H        1.151545       2.593086       3.343307
       H        0.655537       3.558784       1.941088
       H        2.270531       2.795037       1.977131
       O        2.604028       1.654334      -0.196255
```

O	0.732647	2.926397	-0.592128
C	1.618223	4.021599	-0.781537
H	2.374940	3.786772	-1.534695
H	0.991391	4.848012	-1.119032
H	2.121596	4.297615	0.147568
N	0.829846	-0.652302	-1.129967
C	2.024734	-1.388222	-0.824468
N	-0.215977	-1.338489	-1.689138
C	1.886869	-2.611901	-0.177093
H	0.901553	-2.948637	0.122305
C	3.026039	-3.363684	0.084576
H	2.932253	-4.317194	0.593785
C	4.280545	-2.889543	-0.296278
H	5.168664	-3.475643	-0.082305
C	4.395470	-1.668199	-0.955245
H	5.369486	-1.301938	-1.262020
C	3.262767	-0.910213	-1.237396
H	3.335150	0.047528	-1.735989
C	1.069844	0.106308	1.927346
C	2.455973	-0.279742	2.314596
H	2.726200	0.186319	3.269375
H	3.155731	0.087330	1.555723
H	2.540458	-1.364724	2.407718
N	0.118226	-0.770390	1.809485
N	-1.036478	-0.057038	1.484204
C	-2.213761	-0.754940	1.168571
C	-0.807450	1.321757	1.430532
O	-1.661778	2.180453	1.214505
C	-3.447814	-0.096103	1.079047
H	-3.503059	0.962253	1.294114
C	-4.585415	-0.813497	0.713119
H	-5.535609	-0.290924	0.647376
C	-4.521346	-2.178454	0.447281
H	-5.413805	-2.728583	0.166868
C	-3.294417	-2.831967	0.562885
H	-3.224787	-3.898580	0.371069
C	-2.148533	-2.133415	0.920328
H	-1.195462	-2.638194	1.015115

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.41706811 Predicted Change= -1.435567D-10
Zero-point correction (ZPE)= -1427.9495 0.46746
Internal Energy (U)= -1427.9225 0.49451
Enthalpy (H)= -1427.9216 0.49545
Gibbs Free Energy (G)= -1428.0050 0.41201

Frequencies -- -259.8921 28.6820 36.6552

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48333606

NHC-TS-VI-N

Supporting Information: 025-N.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.41334638 Predicted Change= -6.643926D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00058	0.00180	[YES]	0.00058	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.029525	-1.121731	-1.728996
C	3.444325	-1.549982	-1.926527
H	3.643483	-1.702268	-2.991115
H	3.654559	-2.483840	-1.402174
C	4.232285	-0.346721	-1.340031
H	5.102326	-0.096648	-1.947684
H	4.574176	-0.594459	-0.333439
C	3.254639	0.850818	-1.251296
H	3.347644	1.555487	-2.080151
H	3.311670	1.386908	-0.306423
N	1.947927	0.183623	-1.352578
C	0.650989	0.488690	-1.215652
C	0.096103	1.845785	-0.790133
N	-0.678076	1.264579	0.922849
O	-0.774069	2.397141	-1.456014
O	1.185173	2.530326	-0.301719
C	0.866117	3.835921	0.158190
H	0.191107	3.759882	1.017378
H	0.394866	4.420952	-0.634379
H	1.809344	4.291197	0.460870
N	-0.003283	-0.633705	-1.533446
C	-1.412109	-0.915048	-1.476165

N	0.848739	-1.654285	-1.847379
C	-1.803078	-2.089281	-0.842049
H	-1.060151	-2.741817	-0.398002
C	-3.158797	-2.374370	-0.746314
H	-3.477959	-3.270133	-0.224367
C	-4.097718	-1.500639	-1.291217
H	-5.156912	-1.722415	-1.203470
C	-3.682331	-0.340877	-1.940641
H	-4.412688	0.337036	-2.370685
C	-2.327726	-0.038825	-2.046882
H	-1.984932	0.869510	-2.525825
N	-0.353013	-0.013335	1.372786
C	0.975926	-0.359219	1.644051
C	-1.489232	-0.720279	1.823535
O	-1.455596	-1.867604	2.284209
C	-2.575416	0.187021	1.592435
C	-3.999795	-0.125434	1.920147
H	-4.328856	0.335502	2.860257
H	-4.108787	-1.209211	2.029514
H	-4.682478	0.204546	1.129738
C	-2.035103	1.321921	1.030649
C	-2.793387	2.519223	0.553520
H	-2.187556	3.425660	0.608533
H	-3.694751	2.651446	1.158695
H	-3.088751	2.391521	-0.493402
C	1.373029	-1.701630	1.560539
H	0.626777	-2.456451	1.345918
C	2.701054	-2.043495	1.795082
H	2.997896	-3.086894	1.736841
C	3.644614	-1.066370	2.111198
H	4.677942	-1.340751	2.302019
C	3.242246	0.266292	2.200524
H	3.963218	1.035454	2.465103
C	1.916918	0.624457	1.973253
H	1.590234	1.655357	2.045492

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.41334638 Predicted Change= -6.643926D-10
Zero-point correction (ZPE)= -1427.9462 0.46709
Internal Energy (U)= -1427.9188 0.49445
Enthalpy (H)= -1427.9179 0.49539
Gibbs Free Energy (G)= -1428.0023 0.41096

Frequencies -- -136.4525 19.5964 46.8608

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48152947

NHC-VII-C

Supporting Information: 030-C-TI-NHC-Diastereomer-1.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.42009307 Predicted Change= -5.565088D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00330	0.00180	[NO]	0.00330	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.963511	-1.076995	-2.085369
H	3.521646	-1.577160	-2.877542
H	3.617158	-0.972482	-1.217765
C	1.718032	-1.900051	-1.679056
H	1.852738	-2.495972	-0.779943
H	1.339986	-2.529680	-2.489032
N	0.726141	-0.837417	-1.432660
C	1.094241	0.369659	-1.946030
C	2.468905	0.329843	-2.523266
H	3.087413	1.133500	-2.114129
H	2.428158	0.443132	-3.610341
C	-0.509581	-0.716623	-0.915857
C	-1.238476	-1.781781	0.021134
C	-0.664325	-1.472493	1.545503
C	-1.134094	-2.619621	2.425291
H	-2.189728	-2.810634	2.215530
H	-1.008417	-2.381608	3.485851
H	-0.554379	-3.513294	2.187320
O	-2.504577	-1.787516	-0.050399
O	-0.546047	-3.000852	-0.324366
C	-1.160783	-3.655906	-1.413557
H	-2.204043	-3.891857	-1.193114
H	-1.134850	-3.033201	-2.323830
H	-0.590951	-4.570277	-1.591660
N	-0.847718	0.555150	-1.175028
C	-2.067481	1.254624	-0.884131

N	0.147348	1.250728	-1.812303
C	-1.968222	2.538248	-0.356263
H	-0.989827	2.958982	-0.153668
C	-3.134127	3.249564	-0.097741
H	-3.070044	4.249041	0.319625
C	-4.376103	2.676542	-0.367766
H	-5.285117	3.231723	-0.158810
C	-4.452381	1.395430	-0.908357
H	-5.418437	0.950667	-1.123350
C	-3.294198	0.673272	-1.182813
H	-3.330114	-0.337536	-1.568268
C	-1.133817	-0.100945	1.915930
C	-2.537605	0.242535	2.270302
H	-3.204717	-0.206223	1.528478
H	-2.668823	1.326392	2.305459
H	-2.787848	-0.183984	3.249104
N	-0.198807	0.783316	1.868324
N	0.999122	0.115009	1.580278
C	2.138267	0.860422	1.224182
C	0.827546	-1.262422	1.510886
O	1.715983	-2.087606	1.381419
C	1.994437	2.216300	0.902084
H	1.016880	2.674886	0.983852
C	3.097901	2.951554	0.488065
H	2.970592	4.000725	0.239113
C	4.354709	2.354972	0.388567
H	5.213969	2.933393	0.064819
C	4.494479	1.012315	0.727529
H	5.469625	0.536729	0.673800
C	3.401638	0.259184	1.152423
H	3.518805	-0.780746	1.424858

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.42009307 Predicted Change= -5.565088D-08
Zero-point correction (ZPE)= -1427.9519 0.46810
Internal Energy (U)= -1427.9247 0.49537
Enthalpy (H)= -1427.9237 0.49631
Gibbs Free Energy (G)= -1428.0077 0.41232

Frequencies -- 28.6403 37.5865 50.2886

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48655266

==========

NHC-VII-N

Supporting Information: 030-N-TI.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.41709564 Predicted Change= -5.450924D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004 ll	0.00045	[YES]	0.00000 ll	0.00030	[YES]
Displ	0.00743 ll	0.00180	[NO]	0.00743 ll	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	1.837822	2.389800	0.144207
C	3.228596	2.906842	-0.018416
H	3.397960	3.734599	0.677322
H	3.419239	3.266547	-1.030290
C	4.066399	1.654481	0.351229
H	4.991431	1.917084	0.865526
H	4.321027	1.105722	-0.558498
C	3.166208	0.755468	1.231876
H	3.307023	0.905441	2.303842
H	3.248192	-0.304556	0.999756
N	1.824363	1.230036	0.863928
C	0.554510	0.826039	0.972671
C	0.005960	-0.421025	1.750735
N	-0.615525	-1.365212	0.634106
O	-0.785068	-0.139213	2.688511
O	1.239663	-1.059280	2.098705
C	1.038898	-2.147427	2.976426
H	0.389871	-2.902279	2.512178
H	0.586410	-1.815062	3.914298
H	2.022319	-2.582899	3.165157
N	-0.152594	1.762288	0.330902
C	-1.555605	1.752455	0.028346
N	0.637651	2.745044	-0.205332
C	-1.924387	1.807020	-1.311326
H	-1.162887	1.849317	-2.083062
C	-3.275182	1.768075	-1.633814
H	-3.576953	1.786912	-2.675739
C	-4.231483	1.684439	-0.622971
H	-5.285837	1.646920	-0.879470

C	-3.840134	1.640744	0.713077
H	-4.586261	1.574408	1.498667
C	-2.490212	1.679027	1.054250
H	-2.152922	1.601316	2.081223
N	-0.216451	-1.093457	-0.682266
C	1.129134	-1.244323	-1.082111
C	-1.305720	-1.211806	-1.567158
O	-1.220916	-1.073825	-2.783350
C	-2.435110	-1.524022	-0.717993
C	-3.809197	-1.763604	-1.255311
H	-4.011139	-2.829472	-1.415087
H	-3.905274	-1.262721	-2.223273
H	-4.580654	-1.367653	-0.588295
C	-1.985662	-1.564221	0.567855
C	-2.795519	-1.827640	1.794625
H	-2.224760	-2.406000	2.523203
H	-3.698622	-2.378244	1.518474
H	-3.072295	-0.889062	2.279808
C	1.622368	-0.391017	-2.073395
H	0.956559	0.343752	-2.513455
C	2.944956	-0.509922	-2.489484
H	3.322826	0.150462	-3.264568
C	3.781790	-1.465123	-1.914010
H	4.814114	-1.553502	-2.238201
C	3.280799	-2.316164	-0.928549
H	3.922865	-3.072052	-0.486103
C	1.956423	-2.215142	-0.513251
H	1.552315	-2.869047	0.251246

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.41709564 Predicted Change= -5.450924D-08
Zero-point correction (ZPE)= -1427.9492 0.46788
Internal Energy (U)= -1427.9215 0.49550
Enthalpy (H)= -1427.9206 0.49645
Gibbs Free Energy (G)= -1428.0059 0.41112

Frequencies -- 12.9097 46.7813 58.0531

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48644464

==========

NHC-TS-VIII-C

Supporting Information: 035-C-Diastereomer.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.41645940 Predicted Change= -1.095547D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00170	0.00180	[YES]	0.00170	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.870968	1.389254	-1.984501
H	-3.492431	1.925980	-2.702448
H	-3.393251	1.362290	-1.025354
C	-1.508724	2.086565	-1.777727
H	-1.488016	2.765249	-0.928564
H	-1.153809	2.598639	-2.677741
N	-0.628877	0.937311	-1.527872
C	-1.166590	-0.244567	-1.952263
C	-2.566786	-0.064550	-2.439406
H	-3.241162	-0.795649	-1.984696
H	-2.611545	-0.179878	-3.526694
C	0.617491	0.722778	-1.055368
C	1.454265	1.888595	0.210716
C	0.740493	1.402396	1.544403
C	1.090180	2.418151	2.635137
H	0.756642	2.066915	3.615953
H	0.596694	3.365840	2.408978
H	2.172065	2.569139	2.651974
O	2.690973	1.831042	0.176586
O	0.796077	3.056873	-0.189167
C	1.443621	3.687776	-1.275915
H	1.488229	3.005267	-2.139075
H	0.845367	4.563925	-1.530413
H	2.462339	3.980285	-1.012182
N	0.773193	-0.597967	-1.262372
C	1.938614	-1.368920	-0.975528
N	-0.322984	-1.222246	-1.809986
C	1.792507	-2.696550	-0.582300
H	0.799586	-3.123893	-0.501900
C	2.931013	-3.442538	-0.300873
H	2.829066	-4.477690	0.008694

C	4.195150	-2.862669	-0.406042
H	5.080643	-3.447908	-0.179279
C	4.320471	-1.534458	-0.804682
H	5.302307	-1.080726	-0.892736
C	3.190910	-0.777450	-1.104407
H	3.267574	0.264738	-1.393501
C	1.151634	-0.011513	1.855712
C	2.525826	-0.434835	2.242990
H	2.740844	-0.106654	3.267266
H	3.248459	0.042336	1.577425
H	2.613123	-1.522849	2.190389
N	0.180972	-0.848430	1.771857
N	-0.982193	-0.133841	1.464228
C	-2.166033	-0.839357	1.166244
C	-0.761978	1.229897	1.393206
O	-1.610443	2.088197	1.231526
C	-3.408682	-0.195391	1.161576
H	-3.474084	0.849594	1.432580
C	-4.549093	-0.912639	0.804139
H	-5.509073	-0.404793	0.801765
C	-4.471459	-2.261163	0.468895
H	-5.365371	-2.812434	0.195665
C	-3.231830	-2.899216	0.500790
H	-3.154663	-3.952707	0.249751
C	-2.082868	-2.199635	0.845919
H	-1.116135	-2.687467	0.867319

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.41645940 Predicted Change= -1.095547D-08
Zero-point correction (ZPE)= -1427.9489 0.46746
Internal Energy (U)= -1427.9221 0.49430
Enthalpy (H)= -1427.9212 0.49524
Gibbs Free Energy (G)= -1428.0041 0.41226

Frequencies -- -183.7683 27.3373 42.8450

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.48198985

==========

NHC-TS-VIII-N

Supporting Information: 035-N-NHC.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

```
================================================================================
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
--------------------------------------------------------------------------------
Pointgroup= C1   Stoichiometry= C24H25N5O3   C1[X(C24H25N5O3)]  #Atoms= 57
Charge = 0        Multiplicity = 1
--------------------------------------------------------------------------------
SCF Energy= -1428.40694584      Predicted Change= -1.391629D-09
================================================================================
Optimization completed.          {Found       2       times}
Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
Displ      0.00118 ||  0.00180   [ YES ]      0.00118 ||  0.00180   [ YES ]
--------------------------------------------------------------------------------
     Atomic      Coordinates (Angstroms)
      Type     X          Y      Z
--------------------------------------------------------------------------------
      C        0.759854      2.744495     -0.403963
      C        1.947194      3.586891     -0.734420
      H        1.892542      4.531823     -0.184224
      H        2.013452      3.816783     -1.798647
      C        3.106514      2.689066     -0.231835
      H        3.941308      3.270395      0.161786
      H        3.475649      2.075504     -1.056938
      C        2.505908      1.757439      0.845524
      H        2.612548      2.165221      1.854594
      H        2.910740      0.745322      0.814590
      N        1.081851      1.752393      0.482194
      C       -0.025897      1.039958      0.784916
      C       -0.022525     -0.634852      1.810315
      N       -0.108018     -1.597214      0.672309
      O       -0.899595     -0.660240      2.668527
      O        1.315560     -0.570114      2.173407
      C        1.501948      0.106870      3.404324
      H        1.024721     -0.434780      4.223053
      H        1.074842      1.118193      3.360650
      H        2.580428      0.164853      3.558918
      N       -0.966872      1.661228      0.049174
      C       -2.345391      1.306741     -0.060693
      N       -0.500700      2.718575     -0.703079
      C       -2.960825      1.395593     -1.306246
      H       -2.385381      1.722156     -2.165634
      C       -4.301896      1.045926     -1.418777
      H       -4.790507      1.108110     -2.386030
      C       -5.009911      0.605587     -0.301454
      H       -6.055615      0.329948     -0.394880
      C       -4.374264      0.521980      0.935146
      H       -4.923017      0.182879      1.808566
      C       -3.035533      0.882369      1.068909
      H       -2.518272      0.802839      2.019822
```

N	0.518869	-1.190171	-0.516452
C	1.923459	-1.265642	-0.655949
C	-0.363331	-1.343694	-1.602802
O	-0.082540	-1.115432	-2.769268
C	-1.597139	-1.861480	-1.028644
C	-2.778126	-2.205183	-1.874163
H	-3.705198	-2.186297	-1.296056
H	-2.670727	-3.193704	-2.334698
H	-2.865184	-1.475191	-2.684117
C	-1.411285	-1.988738	0.303426
C	-2.367464	-2.539960	1.309313
H	-1.831208	-3.111772	2.068417
H	-3.082726	-3.191492	0.801029
H	-2.904887	-1.740951	1.822375
C	2.535779	-0.517437	-1.666116
H	1.923778	0.088678	-2.323475
C	3.918975	-0.578372	-1.820565
H	4.390115	-0.003236	-2.612763
C	4.695297	-1.357682	-0.967205
H	5.773602	-1.392286	-1.085746
C	4.073563	-2.101354	0.035419
H	4.667976	-2.720147	0.700810
C	2.692739	-2.069575	0.189742
H	2.201841	-2.633907	0.973037

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1428.40694584 Predicted Change= -1.391629D-09
Zero-point correction (ZPE)= -1427.9394 0.46745
Internal Energy (U)= -1427.9122 0.49473
Enthalpy (H)= -1427.9112 0.49568
Gibbs Free Energy (G)= -1427.9971 0.40982

Frequencies -- -166.5457 14.0692 37.1638

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C24H25N5O3 C1[X(C24H25N5O3)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1428.47390609

==========

NHC-IX-C

Supporting Information: 040-C-isomer.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.649422241 Predicted Change= -3.753503D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00263	0.00180	[NO]	0.00263	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.282857	-0.499833	0.814081
O	-0.116880	-1.581046	1.336658
N	0.654375	0.313826	0.211762
C	2.040400	0.086738	0.034181
N	0.098916	1.494257	-0.279346
C	-1.154705	1.498124	-0.024906
C	-2.053546	2.616544	-0.423864
H	-2.848826	2.250740	-1.082997
H	-1.483006	3.385669	-0.946365
H	-2.532981	3.059036	0.455573
C	-1.605504	0.267468	0.723401
C	-2.608855	-0.530807	-0.103491
O	-2.074472	-0.891537	-1.272876
C	-2.933091	-1.652636	-2.130854
H	-3.811332	-1.062959	-2.400358
H	-3.250272	-2.566410	-1.625488
H	-2.338057	-1.884720	-3.011375
O	-3.733845	-0.785356	0.240847
C	-2.164152	0.553610	2.116577
H	-1.471717	1.182462	2.681823
H	-2.300356	-0.392941	2.644814
H	-3.131827	1.053532	2.040275
C	2.646553	-1.070576	0.535182
H	2.058046	-1.806357	1.064719
C	4.011615	-1.260300	0.341857
H	4.474511	-2.160855	0.733688
C	4.779213	-0.320047	-0.338427
H	5.842864	-0.479202	-0.483060
C	4.164352	0.827751	-0.831755
H	4.746252	1.572838	-1.365698
C	2.802430	1.038323	-0.651068
H	2.324138	1.929938	-1.034982

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.649422241 Predicted Change= -3.753503D-08
Zero-point correction (ZPE)= -838.3914 0.25799
Internal Energy (U)= -838.3745 0.27487
Enthalpy (H)= -838.3736 0.27582
Gibbs Free Energy (G)= -838.4374 0.21196

Frequencies -- 23.1978 32.0843 38.2600
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.689944539
==========

NHC-IX-N

Supporting Information: 040-N-isomer.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.644087176 Predicted Change= -1.678087D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00013	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00490	0.00180	[NO]	0.00490	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.213231	-1.918445	-0.303182
O	-0.517676	-2.860382	-0.546432
N	-0.183287	-0.569400	-0.319904
C	-1.517267	-0.168936	-0.028684
N	0.878996	0.215497	0.138191
C	0.941347	1.510017	-0.410487
O	2.017032	2.157032	0.042487
C	2.137799	3.504376	-0.430421
H	3.053539	3.886317	0.016262
H	1.275748	4.091952	-0.111128
H	2.203919	3.517252	-1.519489
O	0.095697	1.978737	-1.125347

C	1.986022	-0.641455	0.346434
C	3.314238	-0.129054	0.794344
H	3.936026	-0.975770	1.088162
H	3.205267	0.549673	1.642366
H	3.822255	0.417887	-0.003627
C	1.618953	-1.916194	0.098431
C	2.382385	-3.191992	0.218257
H	3.355910	-3.046092	0.690188
H	2.542221	-3.638470	-0.768277
H	1.810585	-3.913764	0.809129
C	-2.549913	-0.715716	-0.788806
H	-2.315565	-1.408073	-1.587632
C	-3.865271	-0.365809	-0.500478
H	-4.669185	-0.795712	-1.089833
C	-4.152366	0.534088	0.522504
H	-5.180190	0.809341	0.736065
C	-3.111004	1.080763	1.268457
H	-3.322511	1.782526	2.069335
C	-1.792517	0.728057	1.003314
H	-0.982230	1.138966	1.596706

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.644087176 Predicted Change= -1.678087D-07
Zero-point correction (ZPE)= -838.3851 0.25890
Internal Energy (U)= -838.3685 0.27554
Enthalpy (H)= -838.3676 0.27648
Gibbs Free Energy (G)= -838.4297 0.21431

Frequencies -- 46.9666 55.8823 63.0678

==========

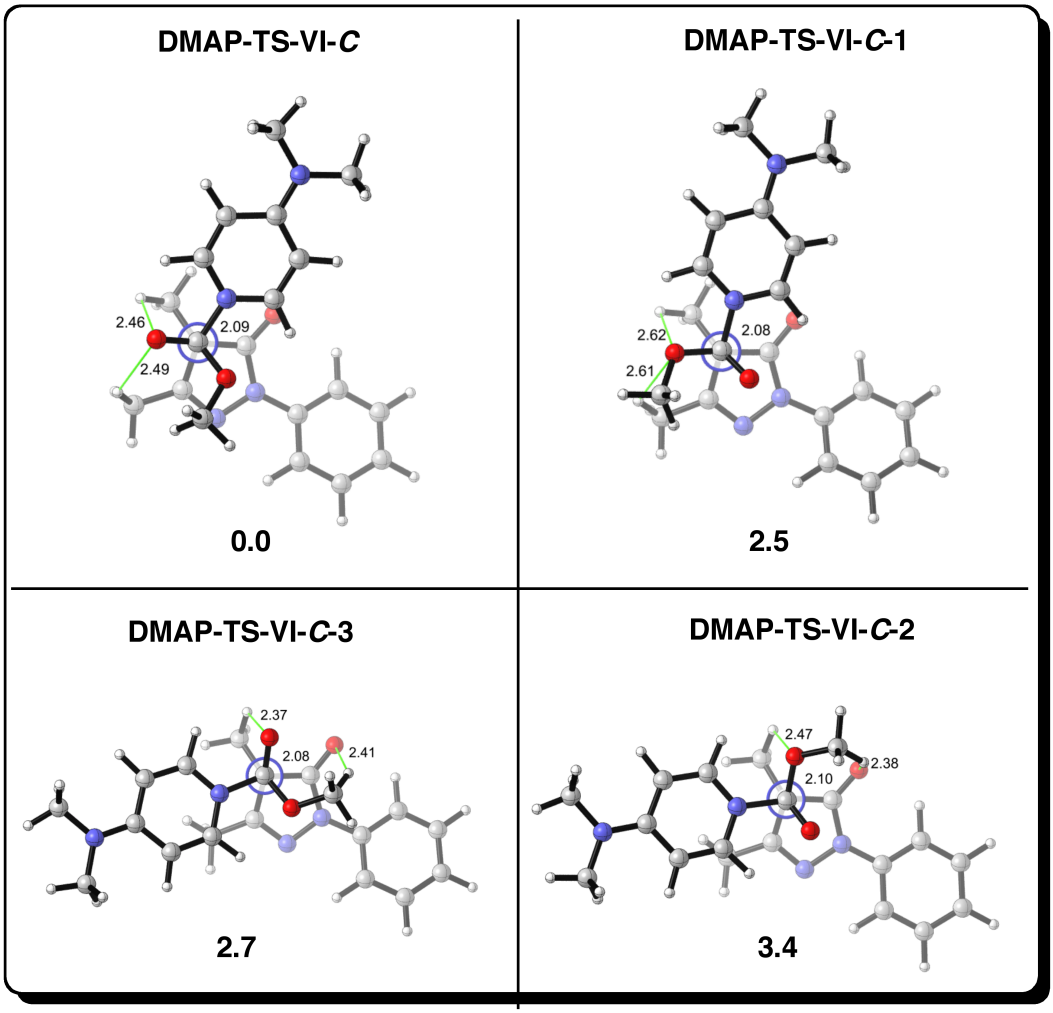
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.684259209

==========

DMAP-TS-VI-*C* Rotamers



Transition state rotamer geometries and their relative Gibb's free energy (ΔΔG) given in kcal/mol for DMAP-TS-VI-*C*. Geometries and energies calculated with M06-2X/6-31G*/PCM, dichloromethane and M06-2X/6-31G**/PCM, dichloromethane thermal corrections.

DMAP-TS-VI-C-1

Supporting Information: 025-C-DMAP-rotamer-1.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.72030931 Predicted Change= -8.650885D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00169	0.00180	[YES]	0.00169	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.380424	0.708506	-0.774831
N	1.383538	-0.635330	-0.623936
C	0.082695	-1.359877	-0.870759
O	0.402215	-2.691338	-1.011295
C	-0.422931	-3.365656	-1.960514
O	-0.734046	-0.790000	-1.582684
C	2.529169	-1.272708	-0.281532
C	3.690423	-0.588225	-0.058541
C	3.723630	0.829724	-0.191261
N	4.846969	1.531429	0.028138
C	6.070708	0.849215	0.430493
C	4.845362	2.979629	-0.139481
C	2.510083	1.456140	-0.579626
H	0.433257	1.130631	-1.081399
H	-0.241201	-2.978490	-2.966073
H	-1.479740	-3.238828	-1.715223
H	-0.142041	-4.417061	-1.901510
H	2.468937	-2.349720	-0.215549
H	4.574044	-1.153387	0.203361
H	6.408663	0.154082	-0.345311
H	5.919894	0.296701	1.363432
H	6.849863	1.591384	0.592373
H	4.127929	3.450410	0.540274
H	4.593638	3.254459	-1.169021
H	5.838978	3.361357	0.086880
H	2.444562	2.525563	-0.722912
N	-2.274351	0.010860	0.695536
C	-3.046460	1.103865	0.273755
C	-0.956862	0.006070	1.145744
O	-0.272152	1.003003	1.412855
C	-0.570081	-1.393182	1.108132
C	0.527272	-1.932206	1.978408
C	-1.814108	-2.085125	0.860323
C	-2.024869	-3.560840	0.957431
N	-2.779958	-1.275944	0.538506
C	-2.674773	2.420669	0.581269
C	-3.469497	3.477986	0.146655
C	-4.634195	3.252649	-0.582259
C	-4.999872	1.941198	-0.880124
C	-4.217274	0.871890	-0.460932
H	1.305492	-1.174586	2.115509
H	0.981184	-2.828379	1.539824
H	0.155814	-2.206685	2.973035
H	-2.055733	-3.866870	2.009967

H	-1.199622	-4.104671	0.488337
H	-2.968118	-3.847989	0.486671
H	-1.773612	2.599902	1.150511
H	-3.170996	4.493418	0.391603
H	-5.247814	4.085026	-0.911874
H	-5.903670	1.742640	-1.449001
H	-4.494293	-0.147682	-0.696730

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.72030931 Predicted Change= -8.650885D-09
Zero-point correction (ZPE)= -1220.2960 0.42429
Internal Energy (U)= -1220.2707 0.44958
Enthalpy (H)= -1220.2697 0.45052
Gibbs Free Energy (G)= -1220.3509 0.36931

Frequencies -- -317.2503 19.4183 27.0812

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.78362377

DMAP-TS-VI-C-2

Supporting Information: 025-C-DMAP-rotamer-2.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.71666562 Predicted Change= -2.497593D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00318	0.00180	[NO]	0.00318	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	0.084658	0.964136	-0.750266
O	0.105882	2.326500	-0.827090
C	-0.899057	2.876706	-1.684877
H	-1.886560	2.530700	-1.384217
H	-0.697447	2.600642	-2.723209
H	-0.822668	3.956495	-1.560429
O	-0.617546	0.244929	-1.447347
N	1.534102	0.524096	-0.611126
C	2.519732	1.347232	-0.190006
H	2.226406	2.366169	0.023479
C	3.809784	0.909649	-0.057221
H	4.554492	1.614167	0.286370
C	4.147898	-0.435417	-0.381635
N	5.400284	-0.898565	-0.258317
C	6.461535	-0.019371	0.218827
H	6.581693	0.842542	-0.445155
H	7.397299	-0.574193	0.235932
H	6.248887	0.336903	1.232107
C	5.701447	-2.287343	-0.587250
H	5.115187	-2.970783	0.035314
H	6.757698	-2.471968	-0.402495
H	5.490856	-2.495119	-1.641164
C	3.084508	-1.259596	-0.847198
H	3.248799	-2.290741	-1.127904
C	1.817327	-0.754276	-0.944081
H	0.963479	-1.331130	-1.278103
C	-0.341779	-0.646201	1.432313
C	0.828026	-1.391344	1.994104
H	1.777666	-0.925950	1.711879
H	0.824459	-2.430622	1.656239
H	0.780974	-1.385314	3.089416
C	-0.446162	0.782594	1.276616
C	0.317381	1.795912	2.078960
H	1.372869	1.519538	2.180571
H	-0.089530	1.895447	3.092443
H	0.257482	2.777670	1.600051
C	-1.852962	0.994184	0.972738
O	-2.479058	2.055177	0.870438
N	-2.351359	-0.286944	0.745261
C	-3.587568	-0.662155	0.199237
N	-1.410483	-1.273096	1.032475
C	-3.829004	-2.012252	-0.093422
H	-3.050675	-2.739506	0.098385
C	-5.052429	-2.401420	-0.625873
H	-5.222086	-3.451621	-0.845904
C	-6.052515	-1.464716	-0.879526
H	-7.006081	-1.775067	-1.294848
C	-5.807284	-0.125027	-0.589724
H	-6.574465	0.620759	-0.778005
C	-4.590820	0.285972	-0.052297
H	-4.407057	1.326099	0.176689

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1220.71666562 Predicted Change= -2.497593D-08
Zero-point correction (ZPE)= -1220.2928 0.42383
Internal Energy (U)= -1220.2672 0.44942
Enthalpy (H)= -1220.2662 0.45036
Gibbs Free Energy (G)= -1220.3494 0.36726

Frequencies -- -307.8298 14.7970 26.2099

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.78016805

DMAP-TS-VI-C-3

Supporting Information: 025-C-DMAP-rotamer-3.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.71993434 Predicted Change= -2.110242D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.00136 ‖	0.00180	[YES]	0.00136 ‖	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.151199	1.086550	-0.964537
O	0.133052	2.215432	-1.439242
O	-0.612211	0.049177	-1.418129
C	-1.691611	0.438342	-2.270323
N	1.525799	0.481741	-0.725138
C	2.565184	1.333554	-0.601983
C	3.838584	0.888597	-0.372337
C	4.101667	-0.508296	-0.289916

N	5.337894	-0.983848	-0.080710
C	6.455051	-0.063716	0.097810
C	5.572905	-2.423038	-0.048718
C	2.981574	-1.372829	-0.446965
C	1.732683	-0.853792	-0.652487
H	-1.299856	0.865284	-3.197160
H	-2.336865	1.164378	-1.773156
H	-2.245057	-0.478253	-2.474149
H	2.309295	2.380229	-0.712340
H	4.628971	1.620925	-0.283451
H	6.625092	0.529041	-0.807099
H	7.353872	-0.638754	0.310769
H	6.270879	0.612246	0.938498
H	5.032629	-2.891289	0.780432
H	6.637654	-2.602253	0.086408
H	5.259232	-2.889252	-0.988121
H	3.085667	-2.447952	-0.397912
H	0.851517	-1.472931	-0.753574
C	-0.253585	-0.022899	1.589089
C	0.944616	-0.520609	2.334991
C	-0.419152	1.295575	1.025995
C	0.313526	2.525344	1.473033
C	-1.841015	1.358086	0.717965
O	-2.521541	2.313086	0.334933
N	-2.285194	0.040791	0.879249
C	-3.480025	-0.532956	0.419669
N	-1.301046	-0.779486	1.421326
C	-3.567147	-1.925860	0.288462
C	-4.740013	-2.508597	-0.177955
C	-5.837321	-1.722684	-0.525631
C	-5.745480	-0.339334	-0.393017
C	-4.583632	0.263666	0.080066
H	1.874879	-0.117501	1.922787
H	0.987775	-1.612488	2.316562
H	0.889880	-0.195929	3.380627
H	1.362703	2.304836	1.701474
H	-0.134096	2.961536	2.373339
H	0.280549	3.278541	0.679032
H	-2.709814	-2.531719	0.553525
H	-4.791609	-3.589331	-0.274693
H	-6.749729	-2.181295	-0.893243
H	-6.592709	0.287707	-0.655496
H	-4.515484	1.337658	0.184084

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.71993434 Predicted Change= -2.110242D-09
Zero-point correction (ZPE)= -1220.2955 0.42434
Internal Energy (U)= -1220.2703 0.44954
Enthalpy (H)= -1220.2694 0.45049
Gibbs Free Energy (G)= -1220.3504 0.36953

Frequencies -- -331.1968 17.5003 31.1143
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.78354042
==========

References

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

[2] Suarez, A.; Downey, C. W.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 11244–11245.

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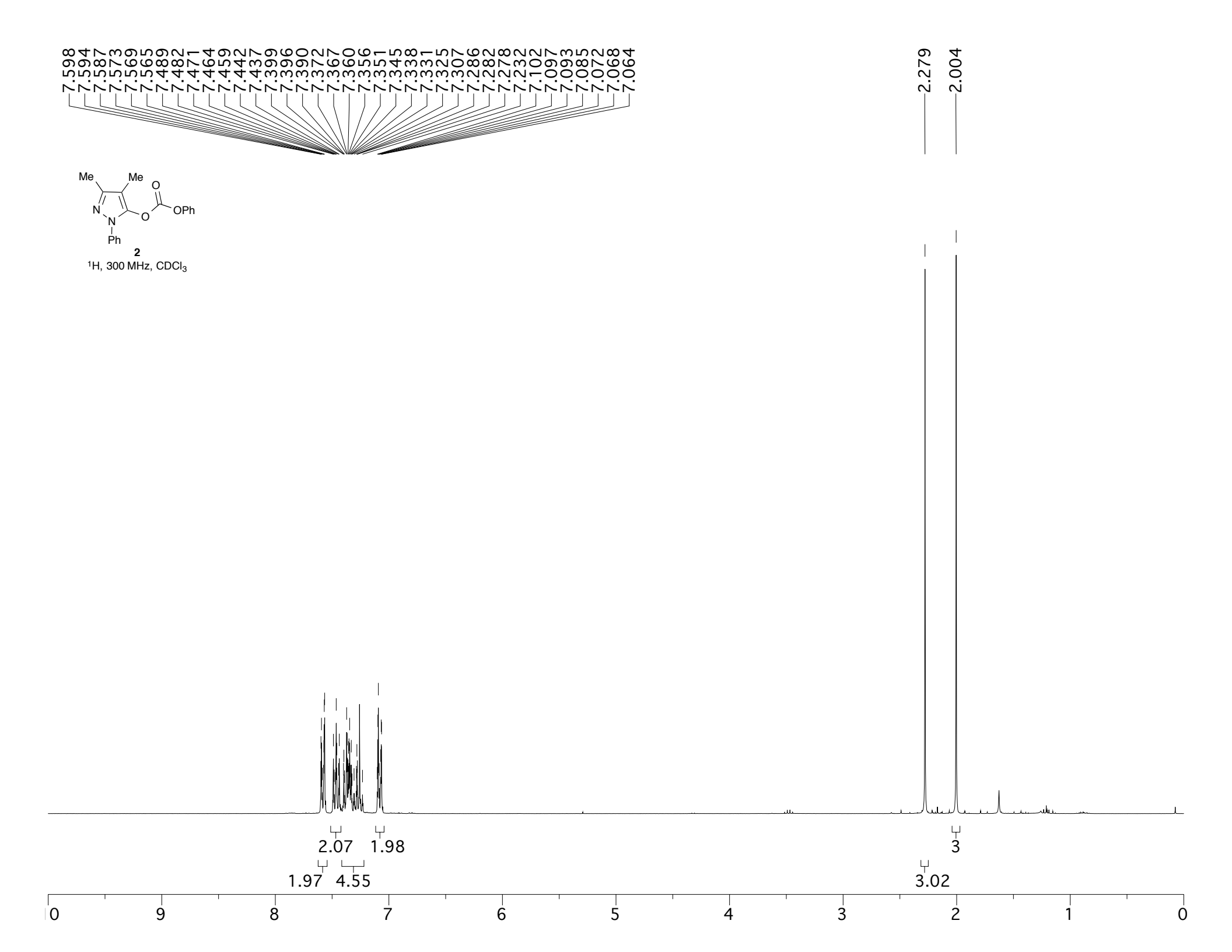
Appendix

^{1}H and ^{13}C NMR spectra for novel compounds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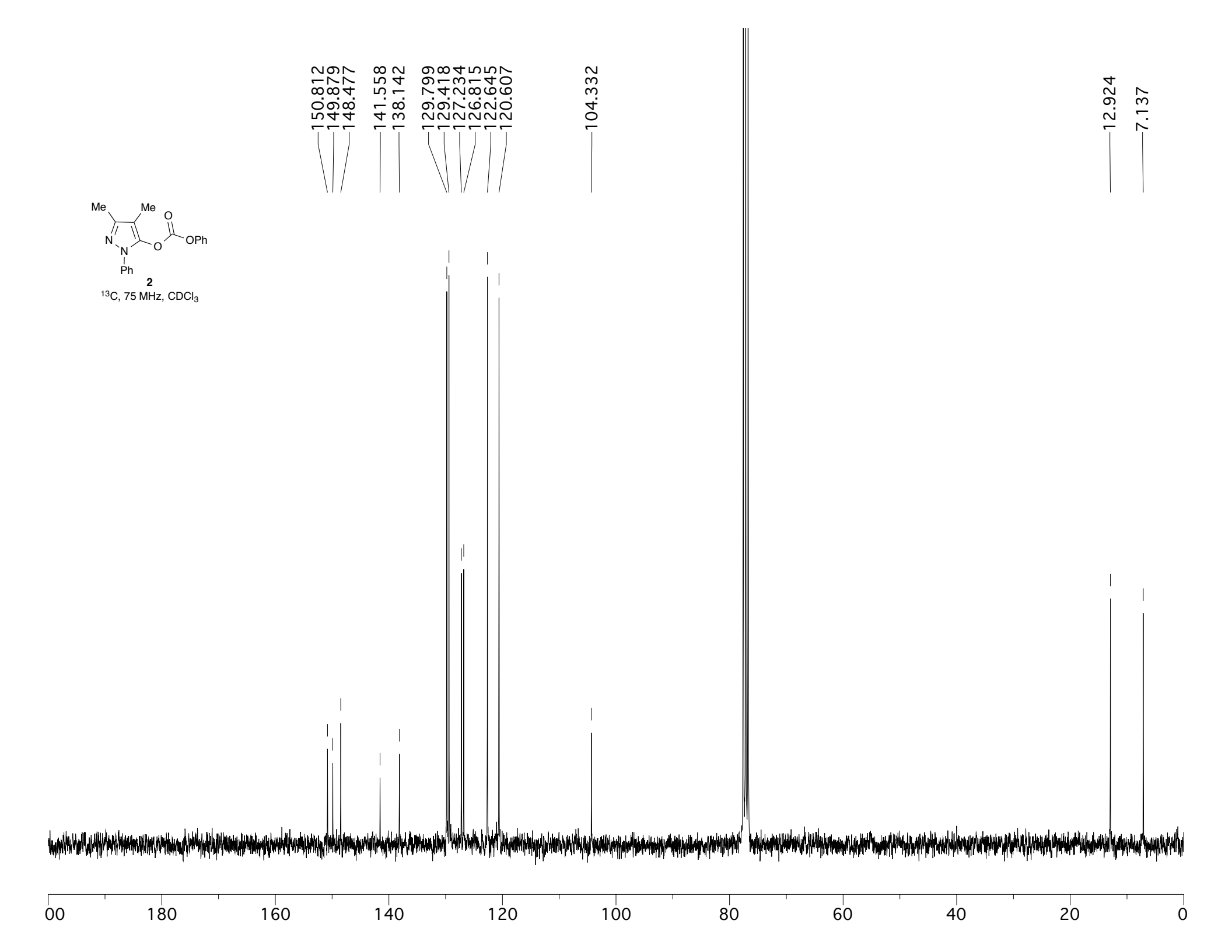
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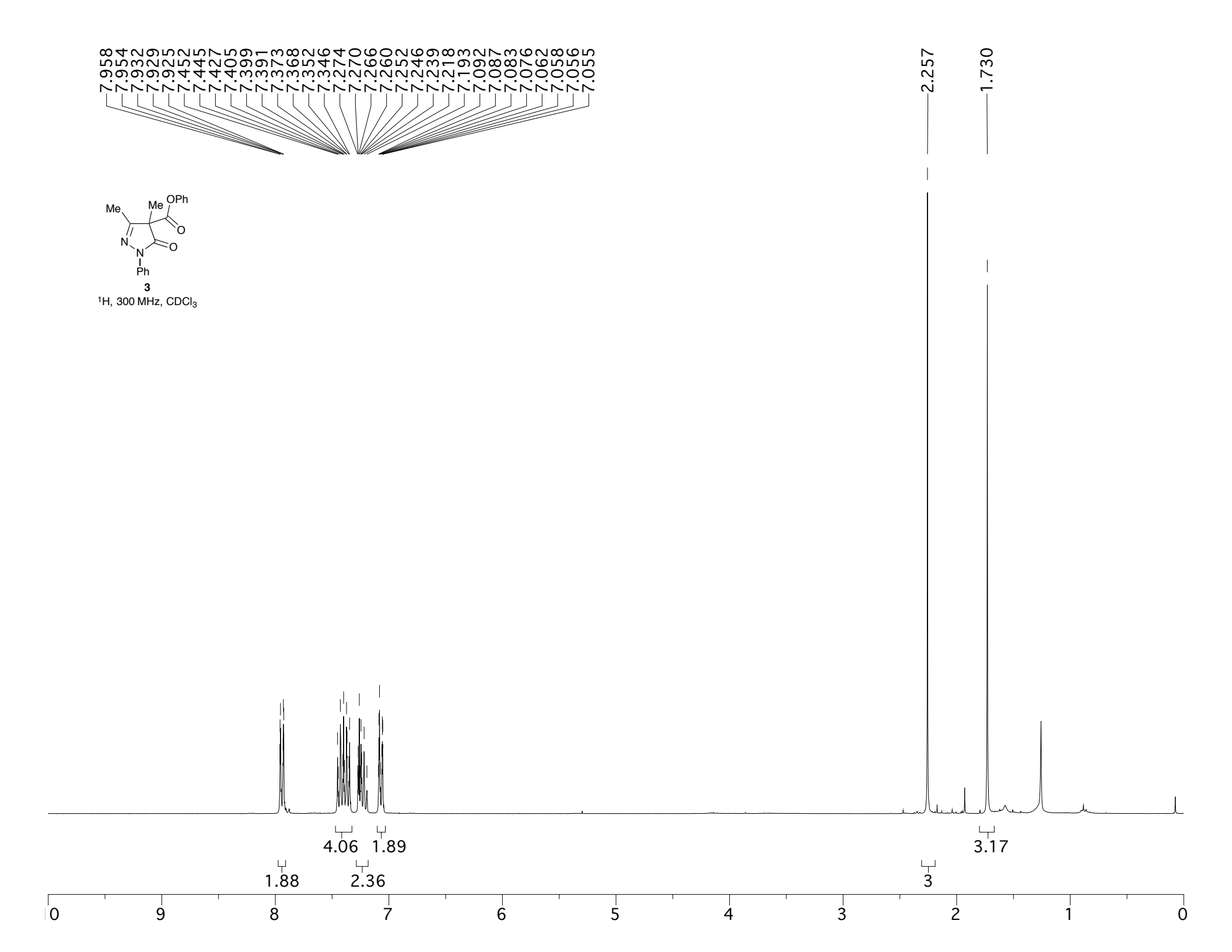
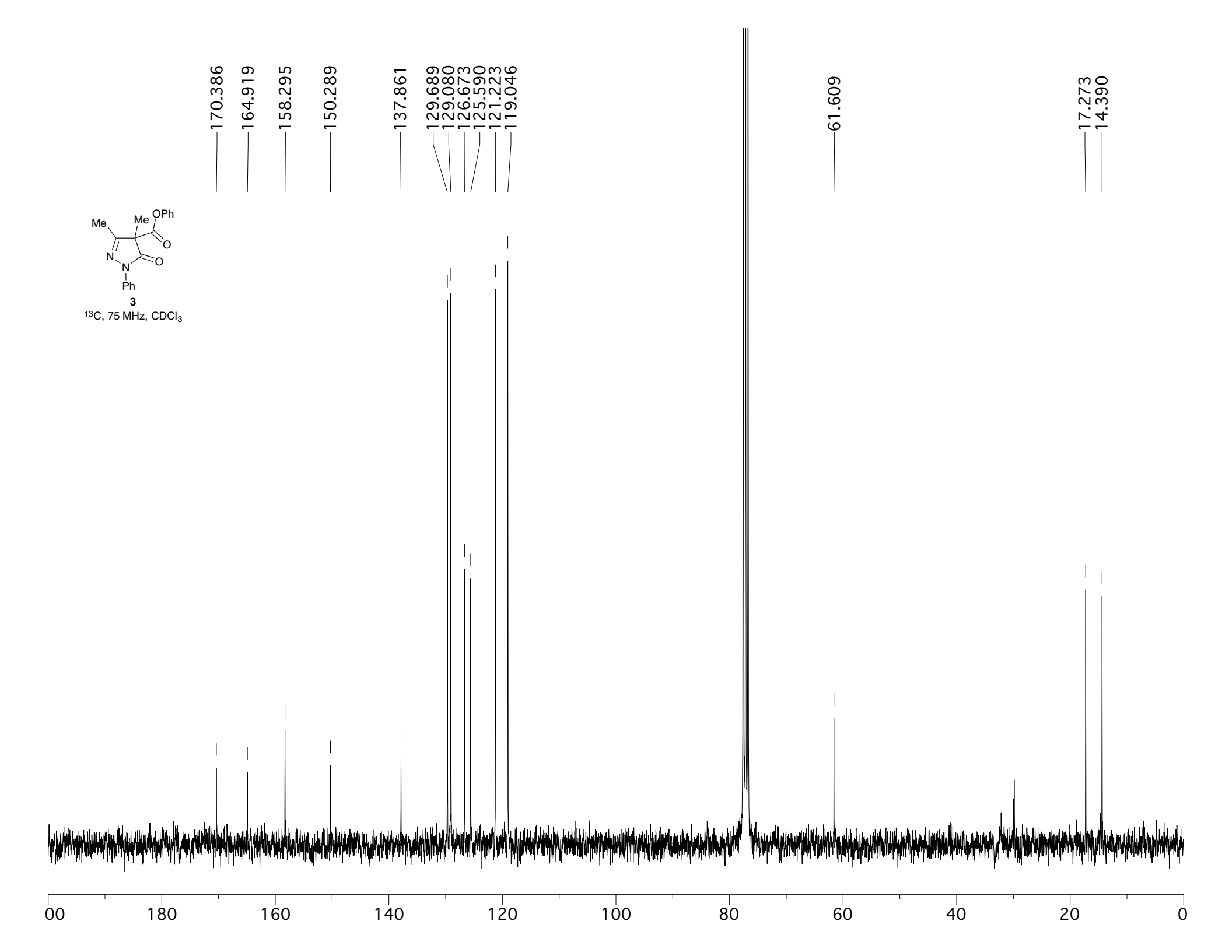
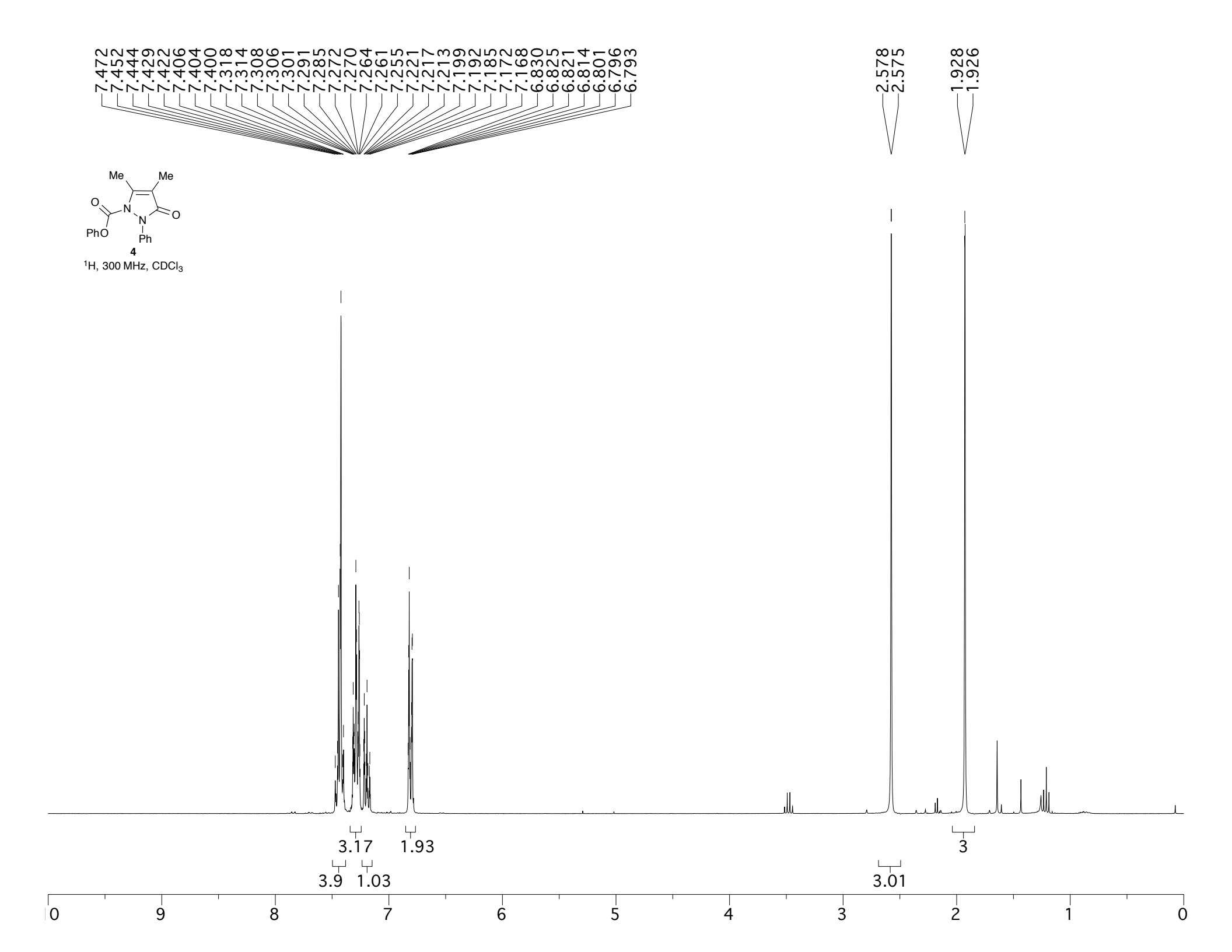
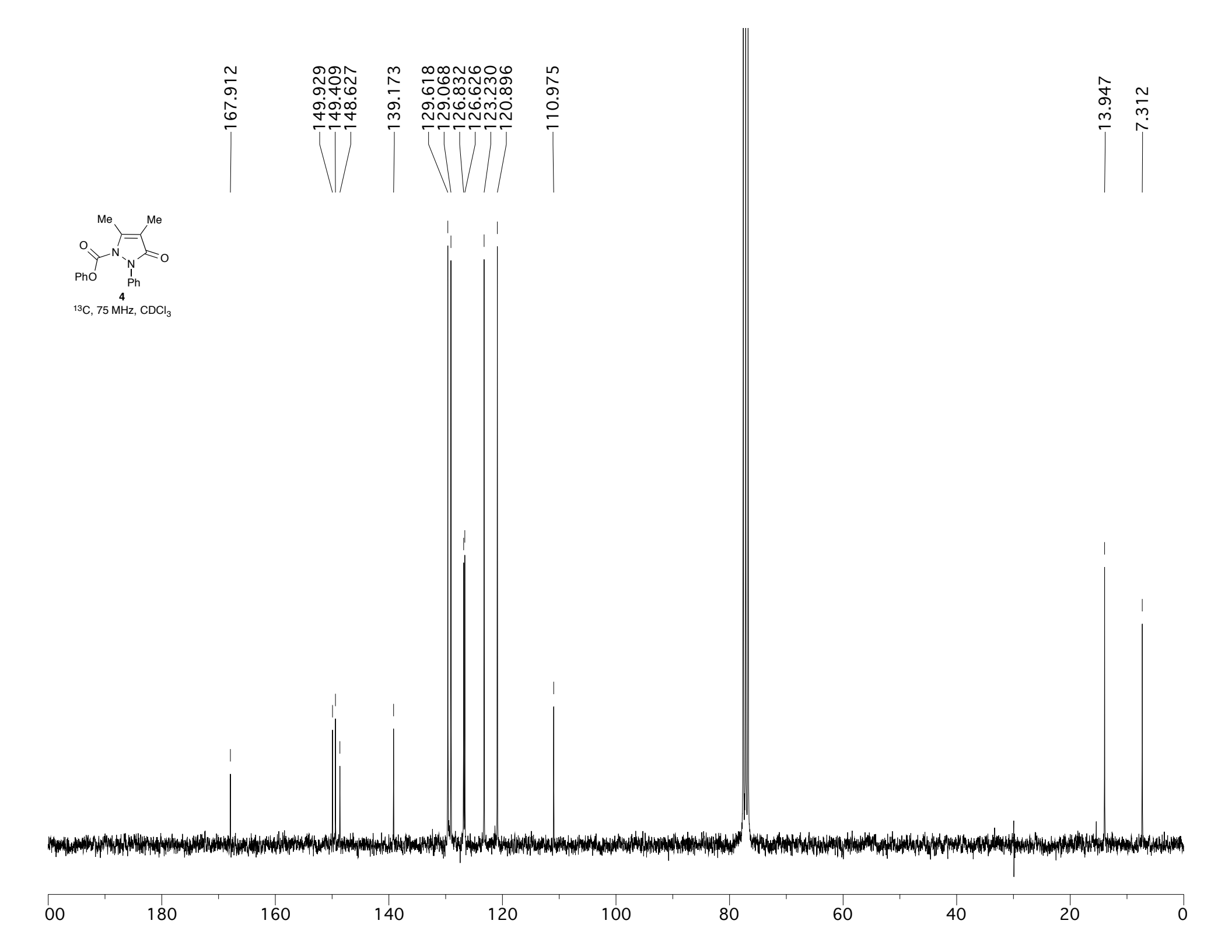
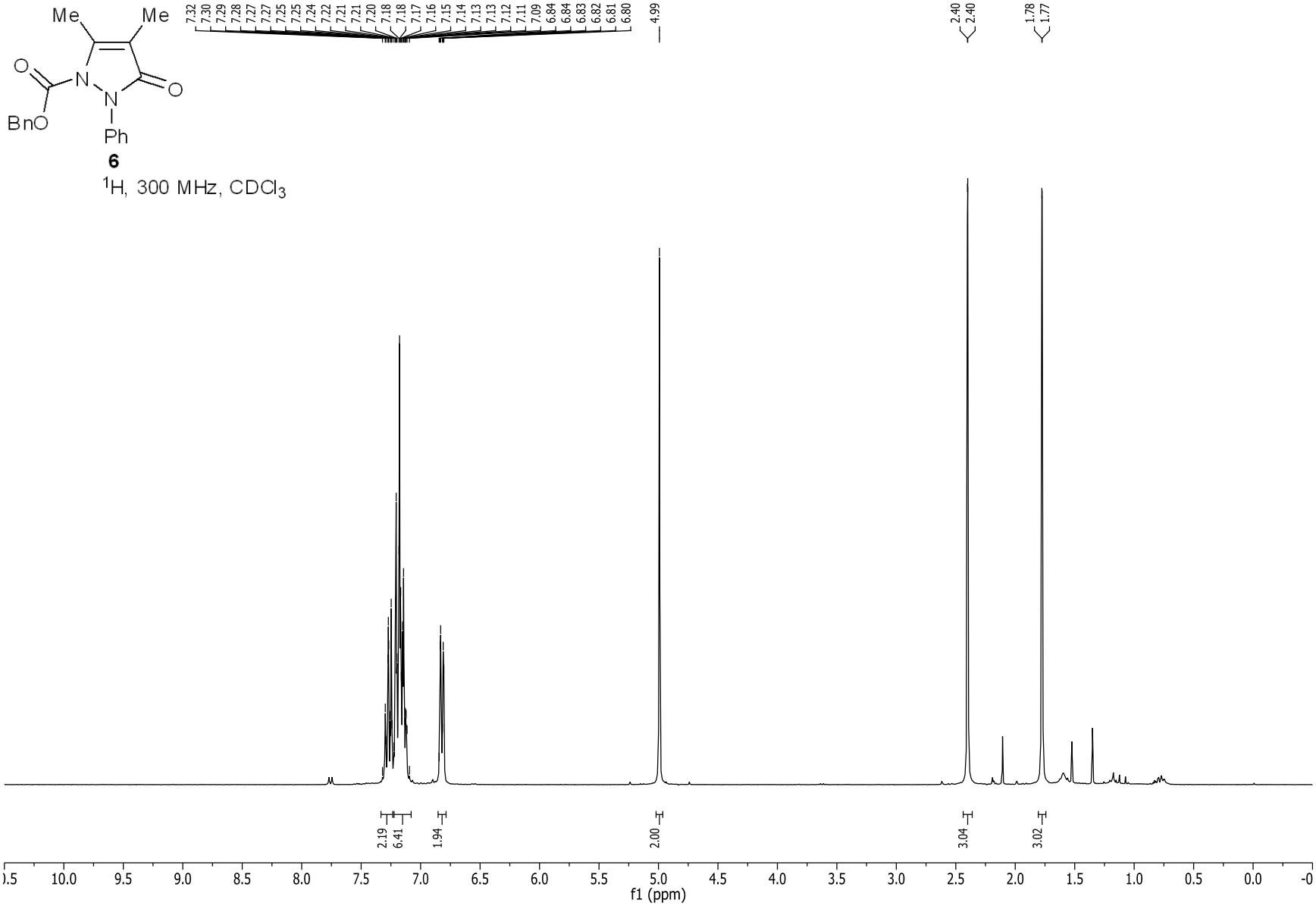
138.142
129.799
129.418
127.234
126.815
122.645
120.607
104.332
12.924
7.137
Me
Me
O
N
N
O
OPh
Ph
2
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

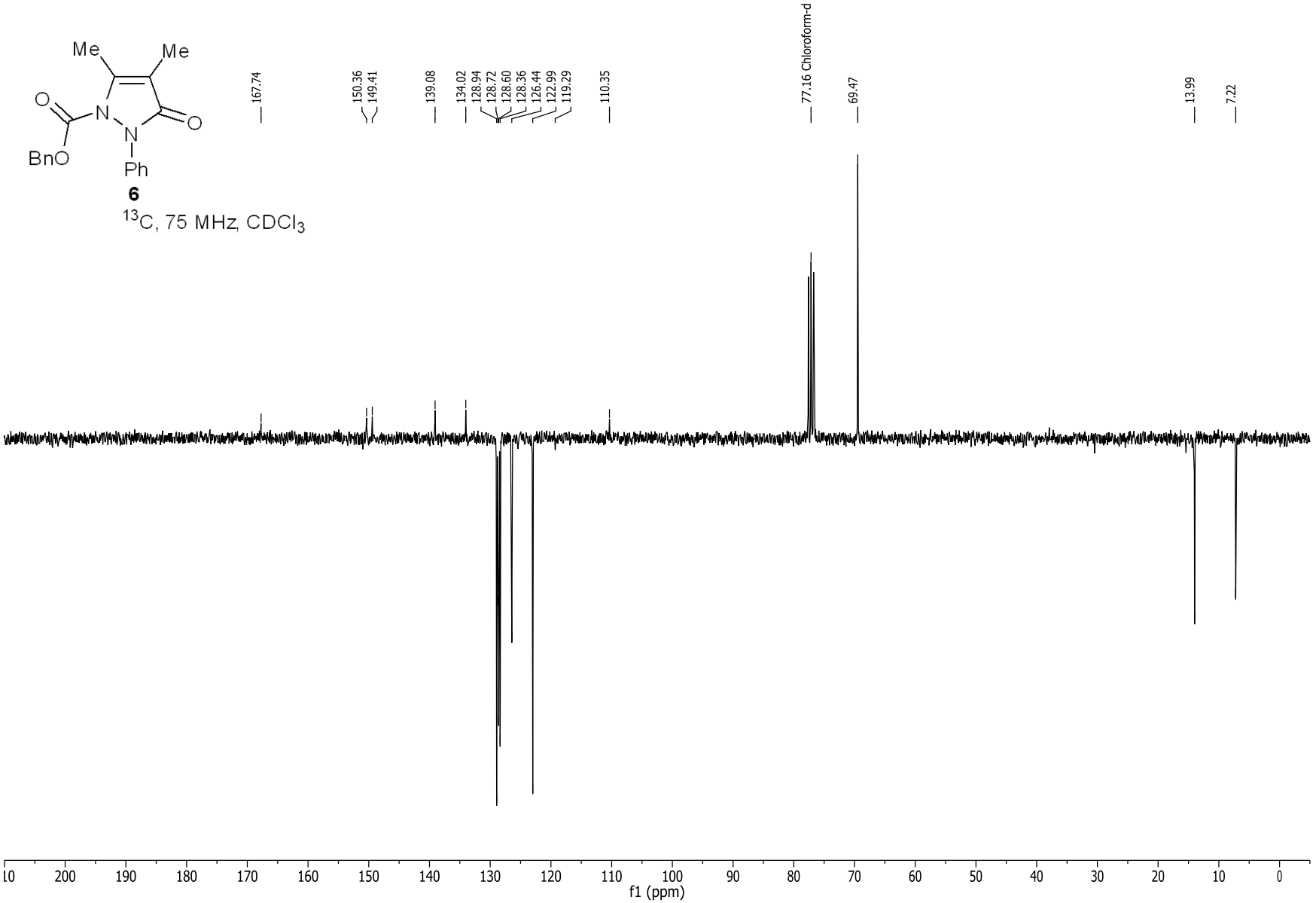

7.958
7.954
7.932
7.929
7.925
7.452
7.445
7.427
7.405
7.399
7.391
7.373
7.368
7.352
7.346
7.274
7.270
7.266
7.260
7.252
7.246
7.239
7.218
7.193
7.092
7.087
7.083
7.076
7.062
7.058
7.056
7.055
2.257
1.730
Me
Me
OPh
O
O
N
N
Ph
3
1H, 300 MHz, CDCl3
4.06
1.89
1.88
2.36
3
3.17
0
9
8
7
6
5
4
3
2
1
0

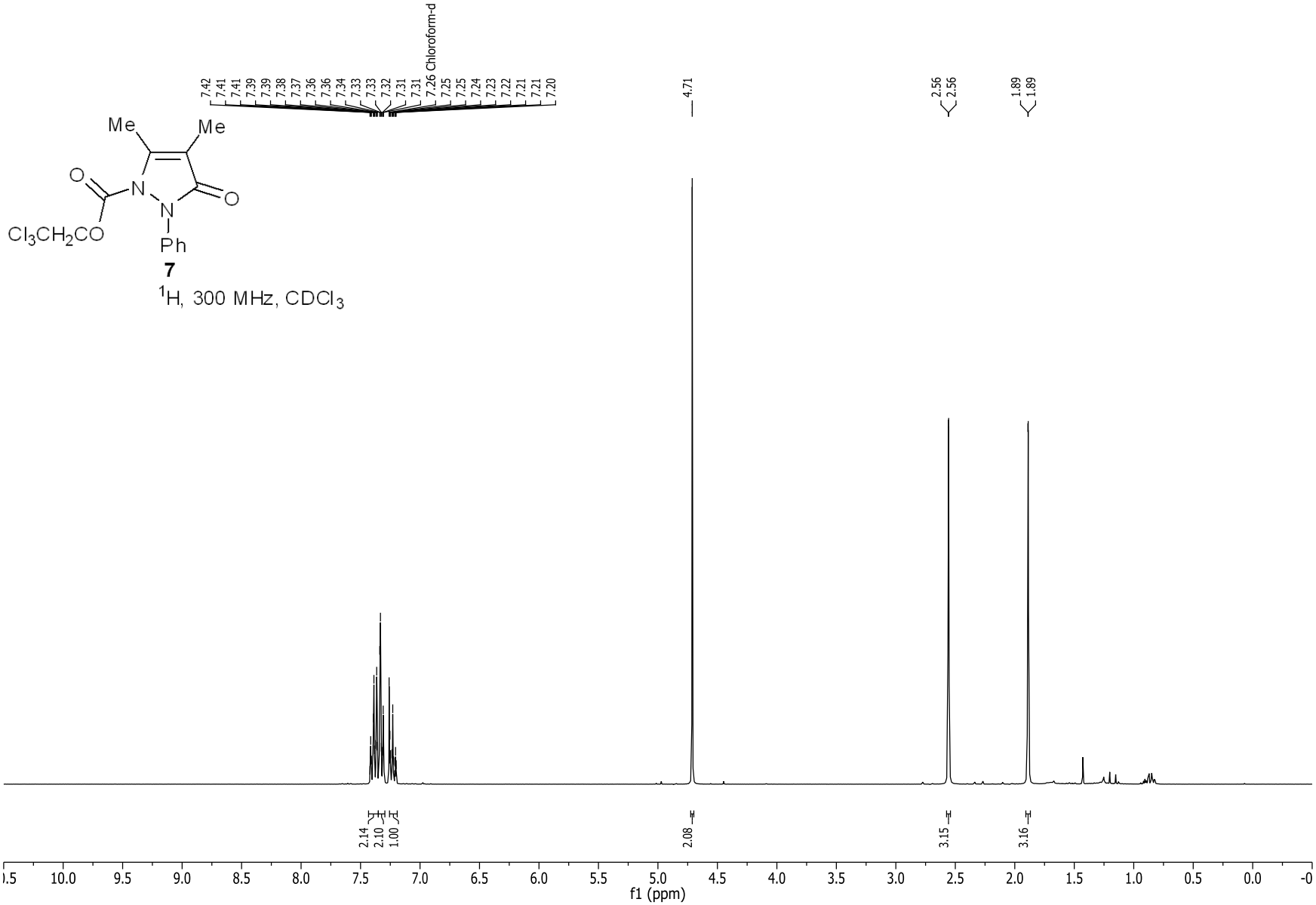

170.386
164.919
158.295
150.289
137.861
129.689
129.080
126.673
125.590
121.223
119.046
61.609
17.273
14.390
Me
Me
OPh
O
N
O
N
Ph
3
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

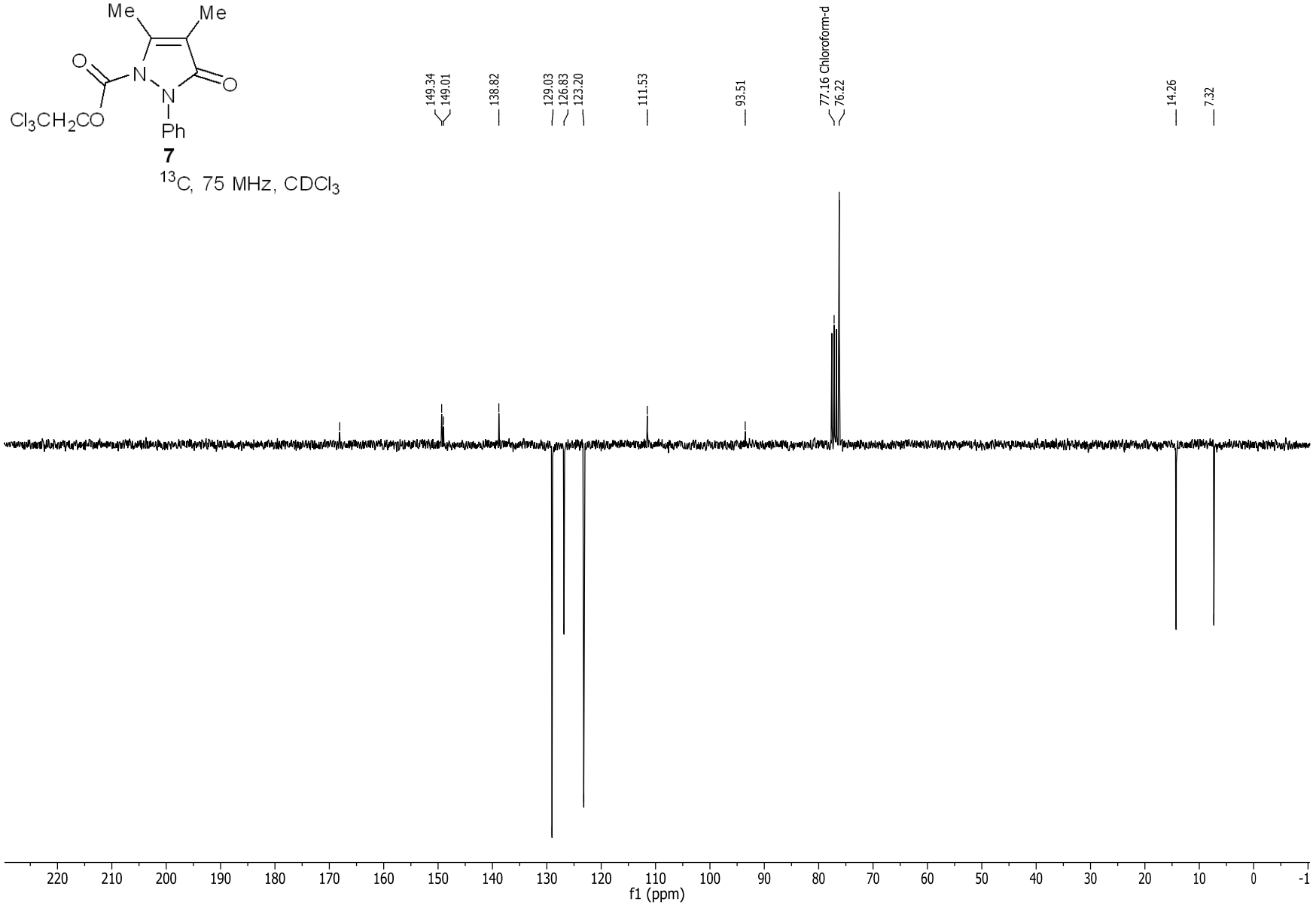

7.472
7.452
7.444
7.429
7.422
7.406
7.404
7.400
7.318
7.314
7.308
7.306
7.301
7.291
7.285
7.272
7.270
7.264
7.261
7.255
7.221
7.217
7.213
7.199
7.192
7.185
7.172
7.168
6.830
6.825
6.821
6.814
6.801
6.796
6.793
2.578
2.575
1.928
1.926
Me
Me
O
N
N
O
PhO
Ph
4
1H, 300 MHz, CDCl3
3.17
1.93
3
3.9
1.03
3.01
0
9
8
7
6
5
4
3
2
1
0

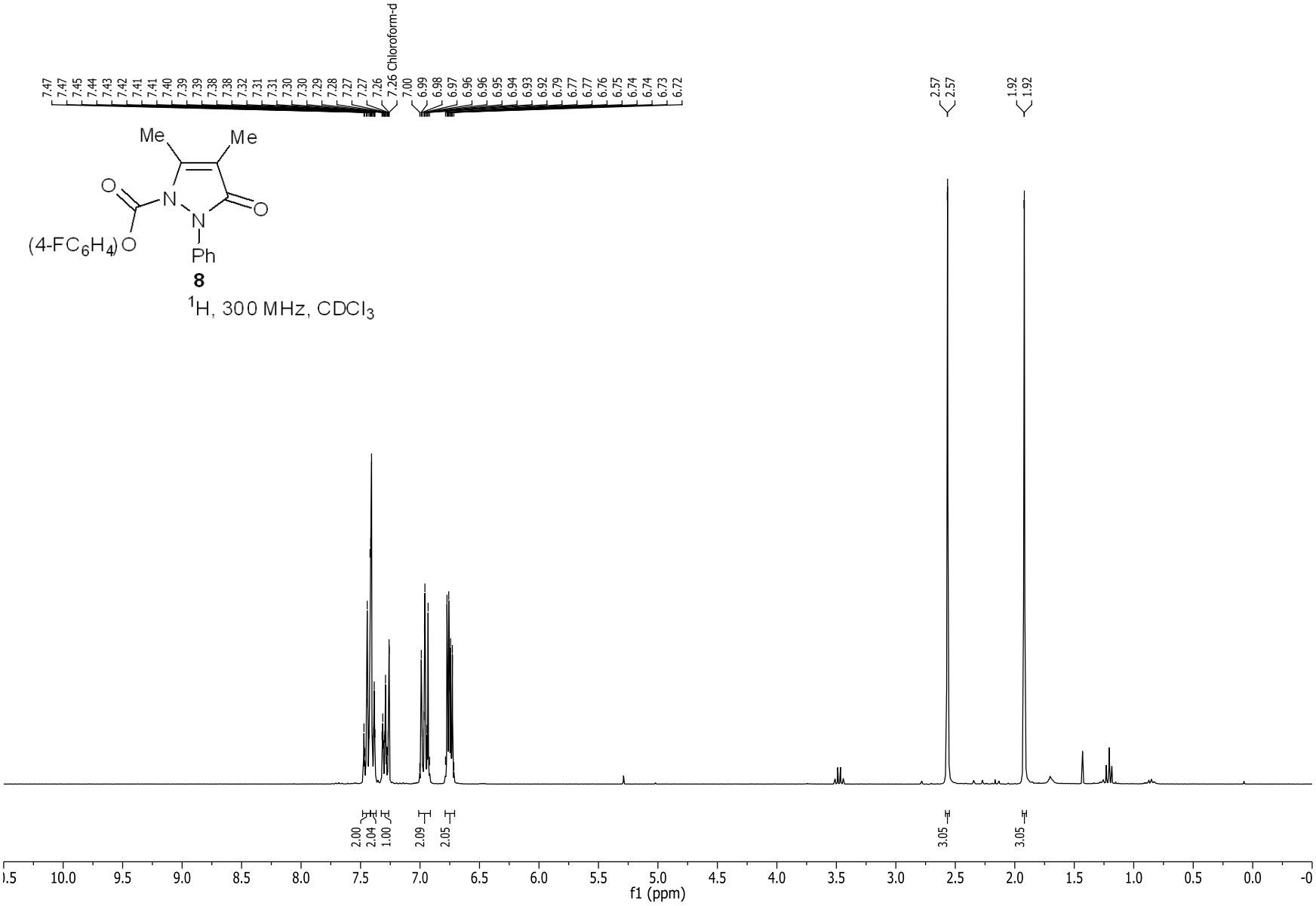

167.912
149.929
149.409
148.627
139.173
129.618
129.068
126.832
126.626
123.230
120.896
110.975
13.947
7.312
Me
Me
O
N
N
O
PhO
Ph
4
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

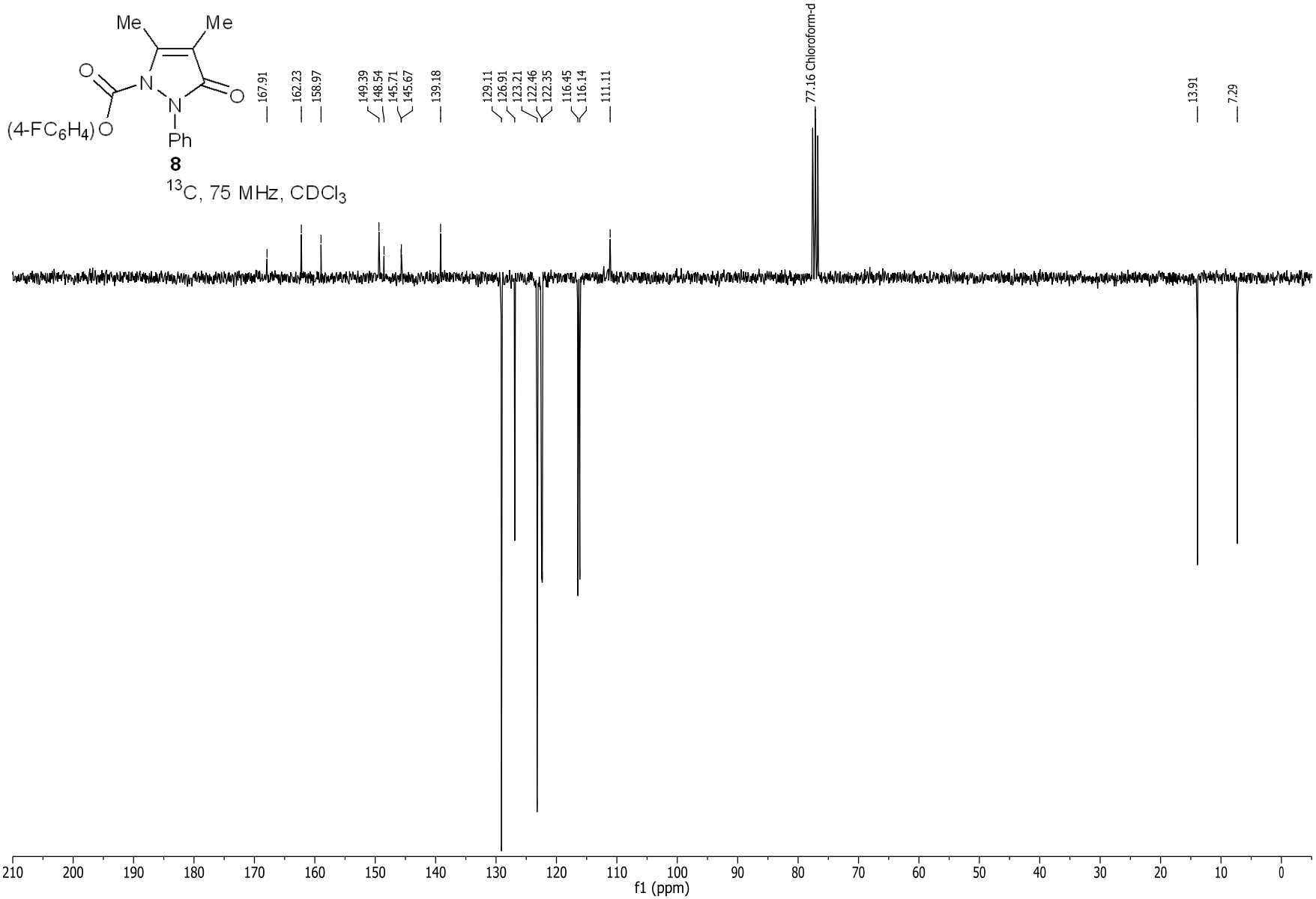

Me
Me
O
N
N
O
BnO
Ph
6
1H, 300 MHz, CDCl3
7.32
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.24
7.22
7.21
7.21
7.20
7.18
7.18
7.17
7.16
7.15
7.14
7.13
7.13
7.12
7.11
7.09
6.84
6.84
6.83
6.82
6.81
6.80
4.99
2.40
2.40
1.78
1.77
2.19
6.41
1.94
2.00
3.04
3.02
f1 (ppm)

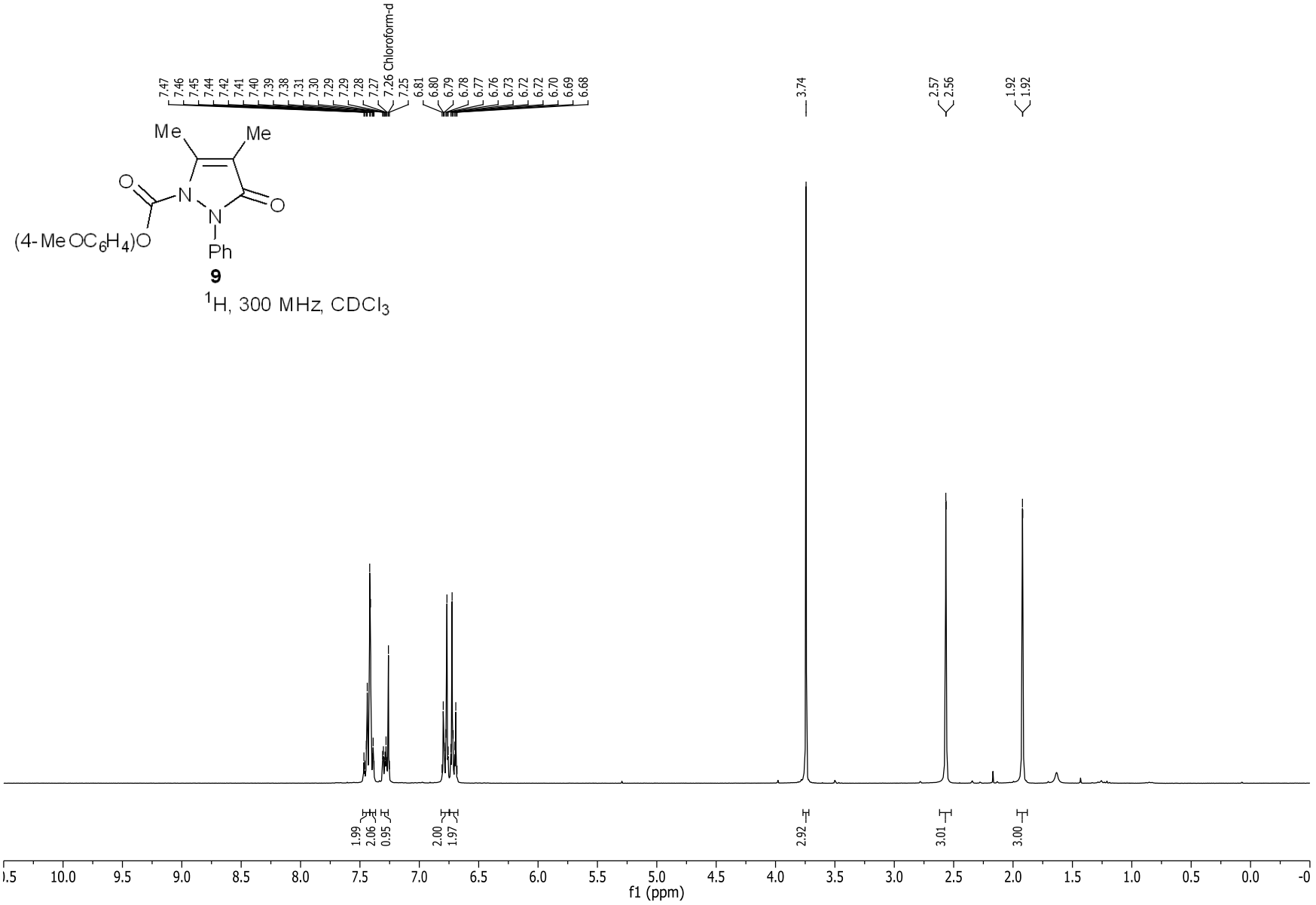

Me
Me
O
N
N
O
BnO
Ph
6
^{13}C, 75 MHz, $CDCl_3$
167.74
150.36
149.41
139.08
134.02
128.94
128.72
128.60
128.36
126.44
122.99
119.29
110.35
77.16 Chloroform-d
69.47
13.99
7.22
f1 (ppm)

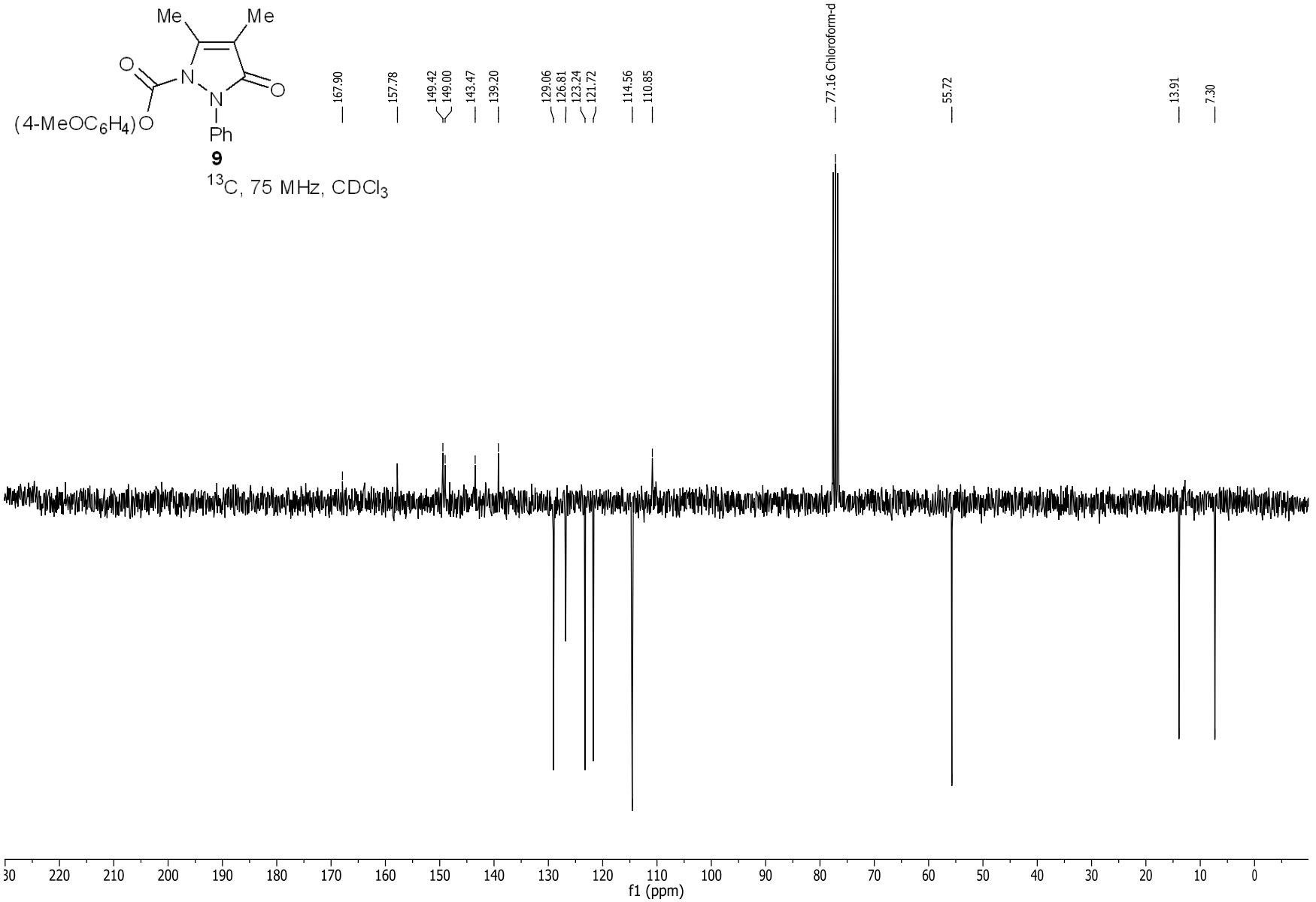

Me
Me
O
N
N
O
Cl3CH2CO
Ph
7
1H, 300 MHz, CDCl3
Chloroform-d
7.42
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.33
7.33
7.32
7.31
7.31
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.20
4.71
2.56
2.56
1.89
1.89
2.14
2.10
1.00
2.08
3.15
3.16
f1 (ppm)

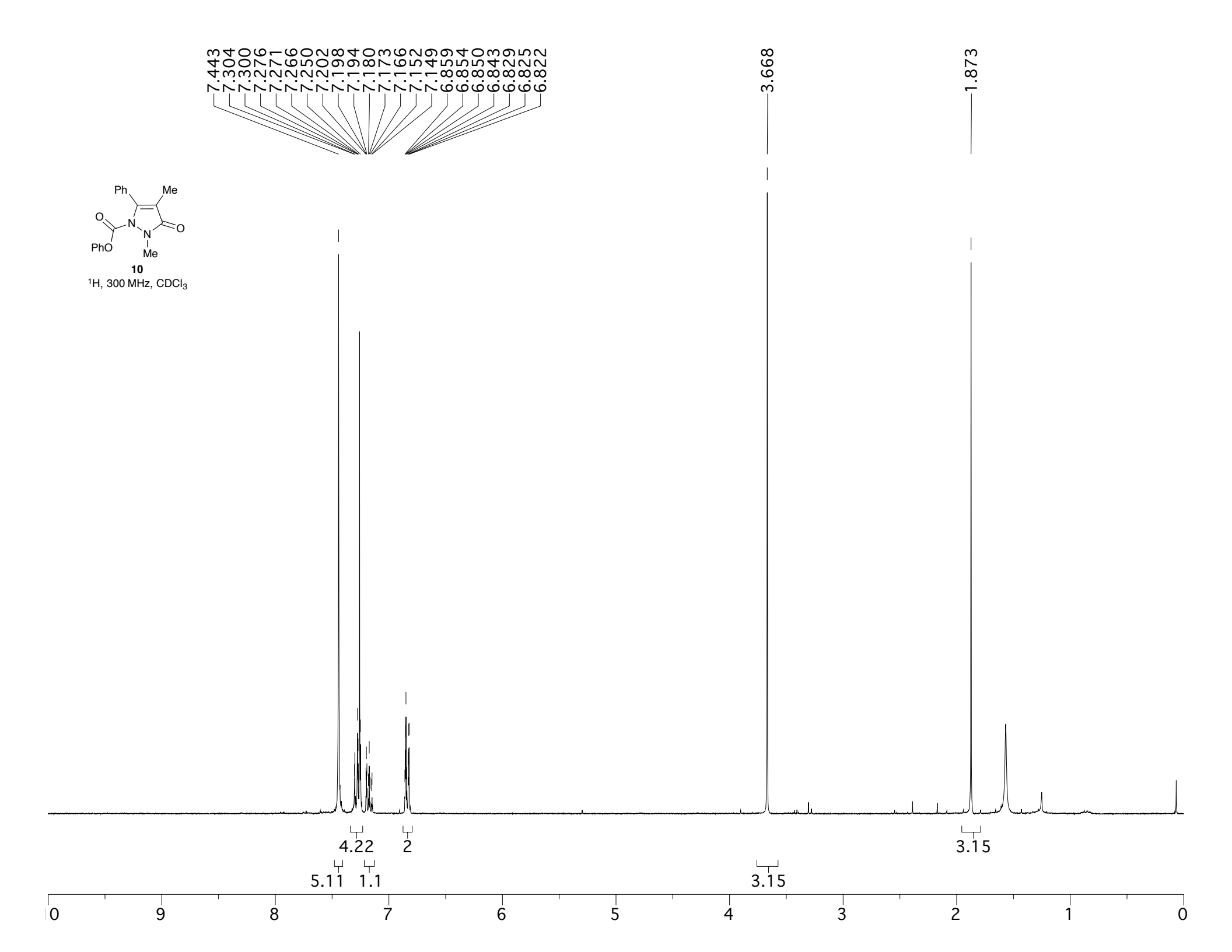

Me
Me
O
N
N
O
Cl3CH2CO
Ph
7
13C, 75 MHz, CDCl3
149.34
149.01
138.82
129.03
126.83
123.20
111.53
93.51
77.16 Chloroform-d
76.22
14.26
7.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

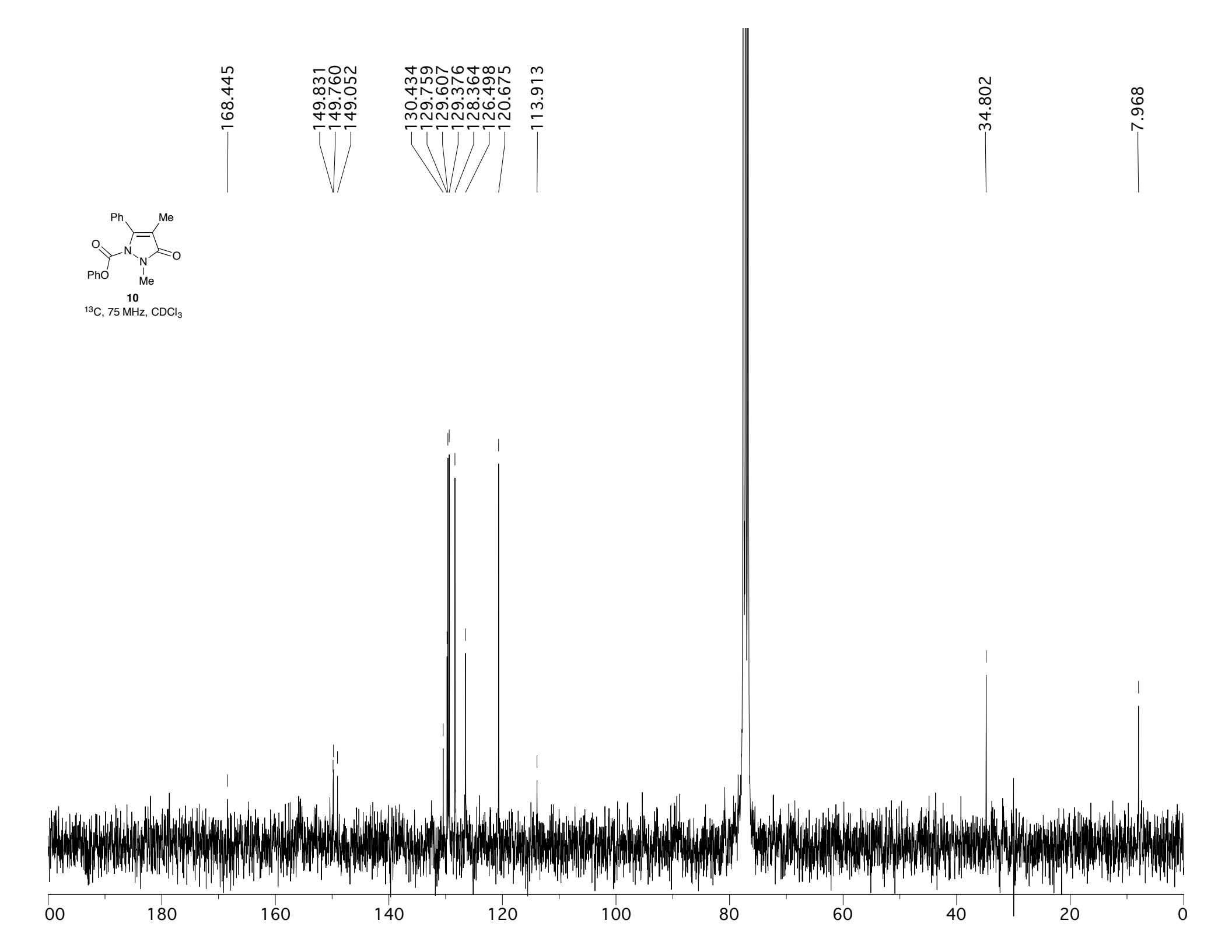

Chloroform-d
Me
Me
O
N
N
O
(4-FC6H4)O
Ph
8
1H, 300 MHz, CDCl3
2.00
2.04
1.00
2.09
2.05
3.05
3.05
f1 (ppm)

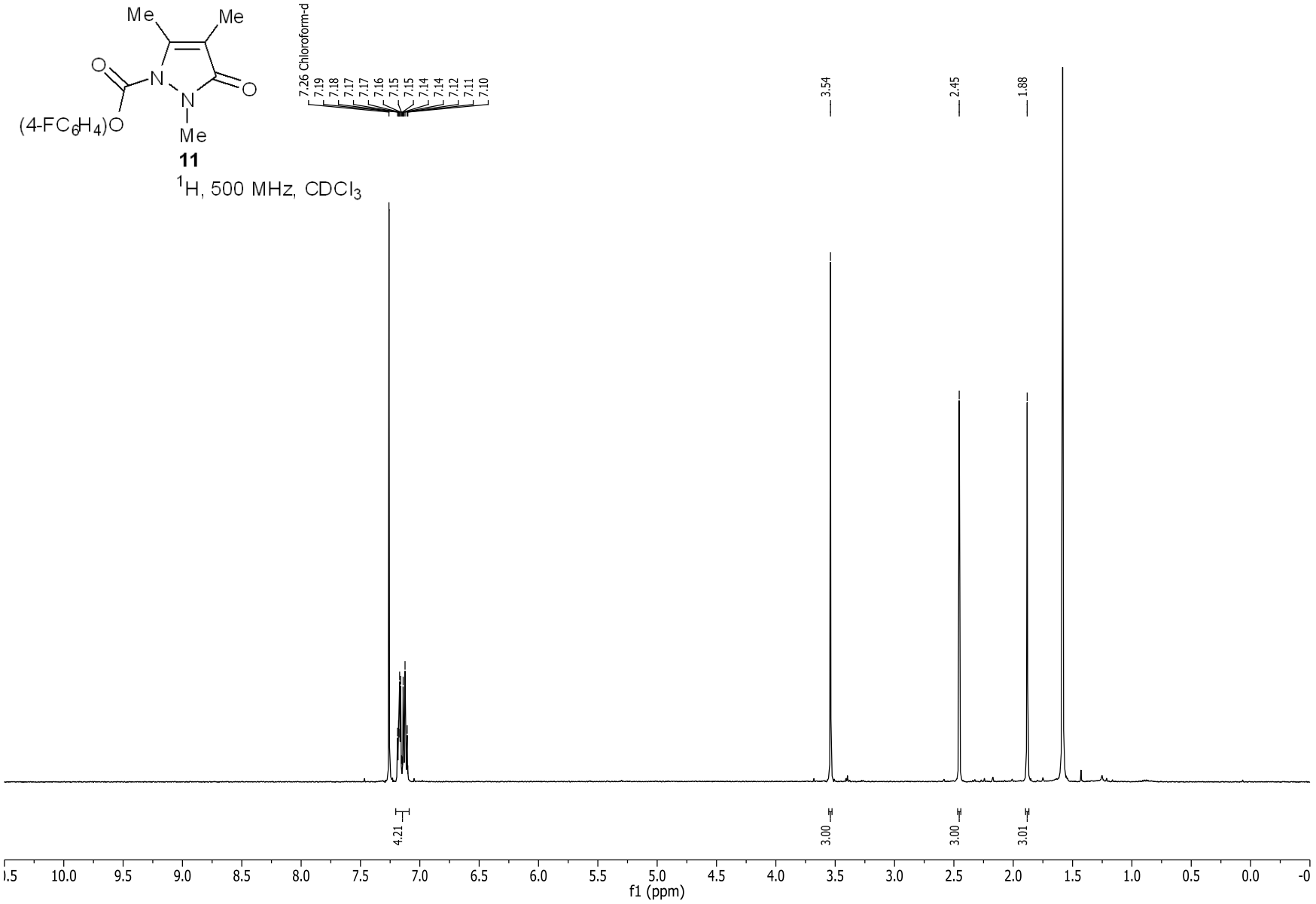

Me
Me
O
N
N
O
(4-FC6H4)O
Ph
8
13C, 75 MHz, CDCl3
167.91
162.23
158.97
149.39
148.54
145.71
145.67
139.18
129.11
126.91
123.21
122.46
122.35
116.45
116.14
111.11
77.16 Chloroform-d
13.91
7.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

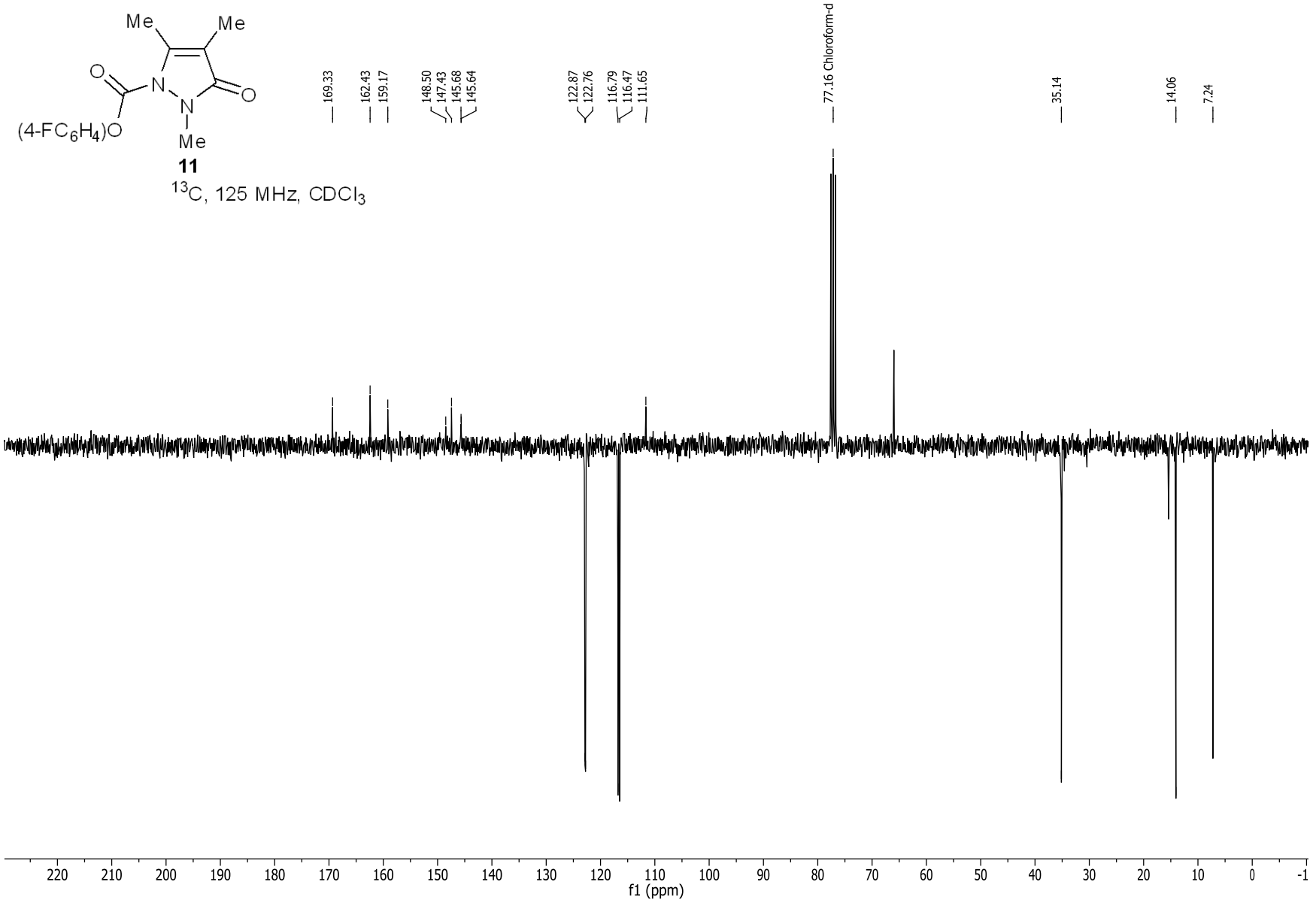

Chloroform-d
Me
Me
O
N
N
O
(4-MeOC6H4)O
Ph
9
1H, 300 MHz, CDCl3
f1 (ppm)

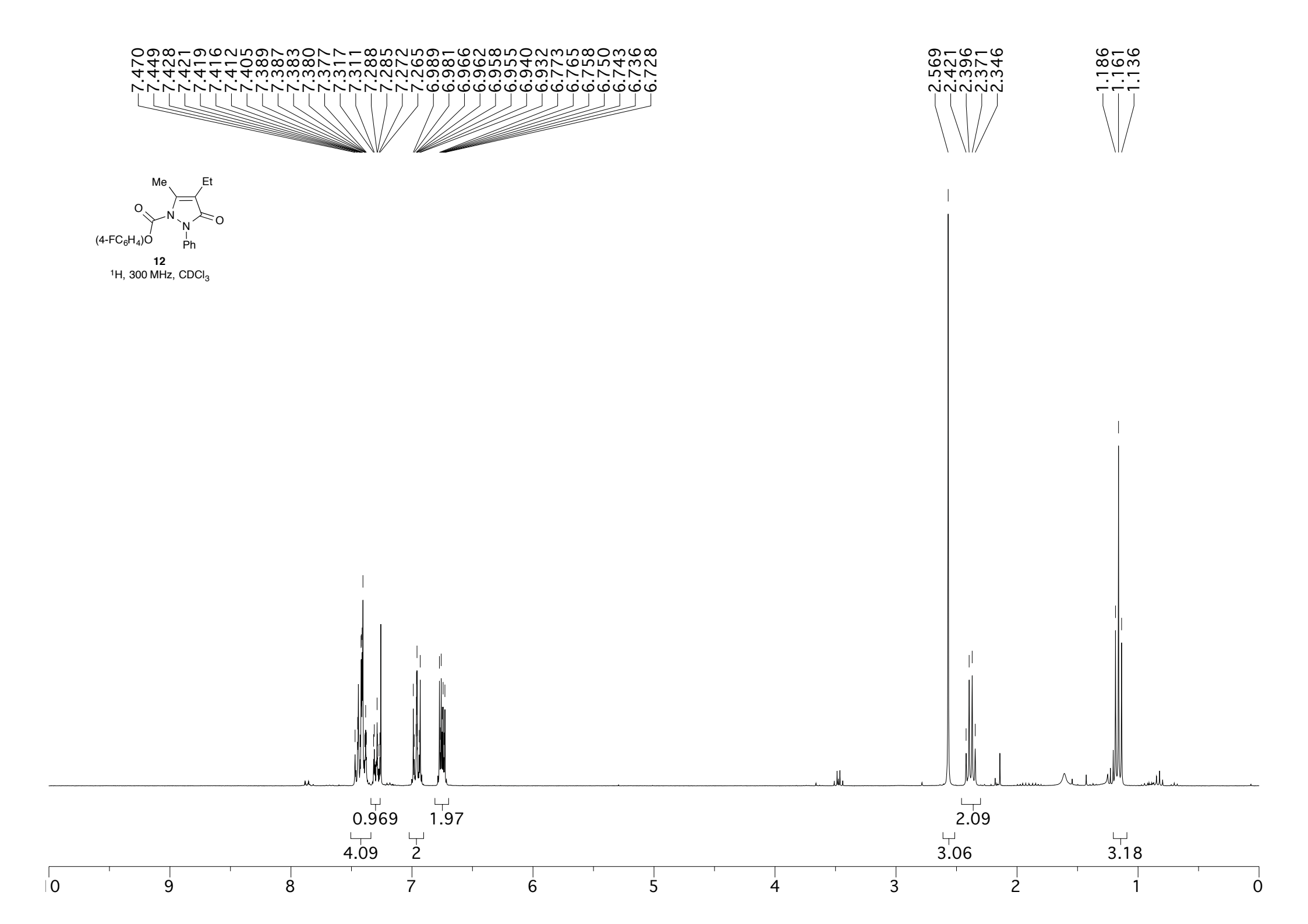

Me
Me
O
N
N
O
(4-MeOC6H4)O
Ph
9
13C, 75 MHz, CDCl3
167.90
157.78
149.42
149.00
143.47
139.20
129.06
126.81
123.24
121.72
114.56
110.85
77.16 Chloroform-d
55.72
13.91
7.30
f1 (ppm)

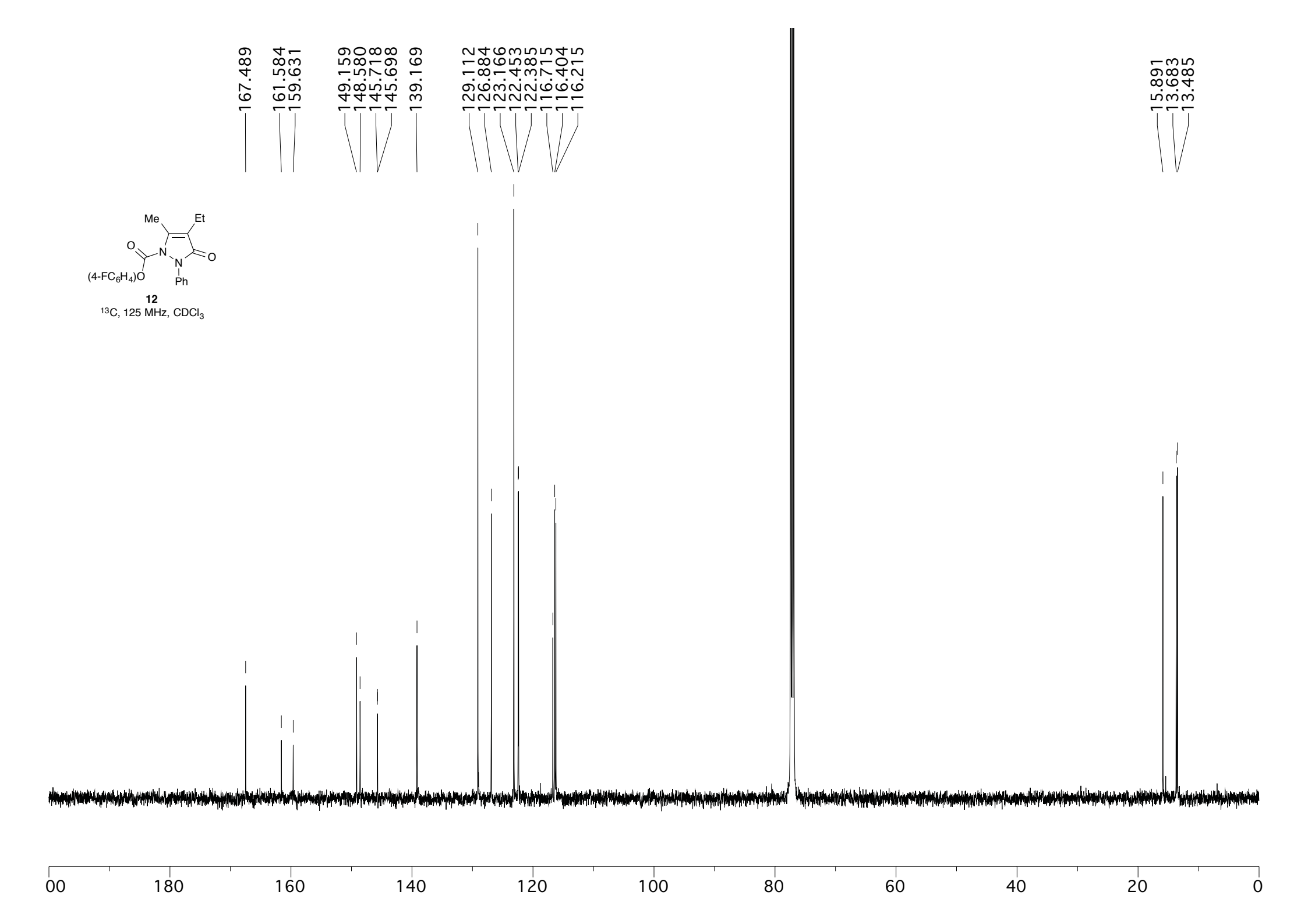

7.443
7.304
7.300
7.276
7.271
7.266
7.250
7.202
7.198
7.194
7.180
7.173
7.166
7.152
7.149
6.859
6.854
6.850
6.843
6.829
6.825
6.822
3.668
1.873
Ph
Me
O
N
N
O
PhO
Me
10
1H, 300 MHz, CDCl3
4.22
2
3.15
5.11
1.1
3.15
0
9
8
7
6
5
4
3
2
1
0

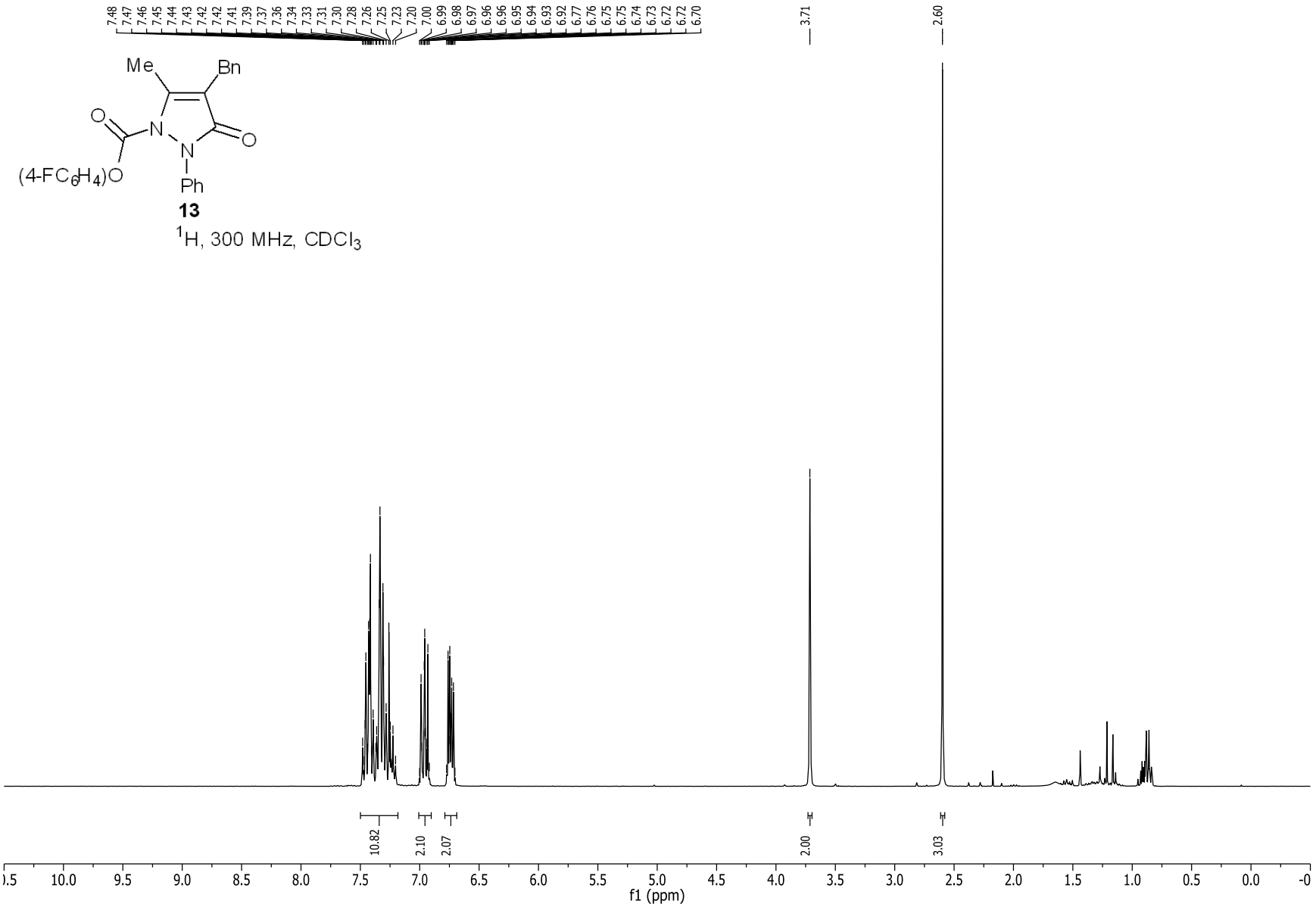

168.445
149.831
149.760
149.052
130.434
129.759
129.607
129.376
128.364
126.498
120.675
113.913
34.802
7.968
Ph
Me
O
N
N
O
PhO
Me
10
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

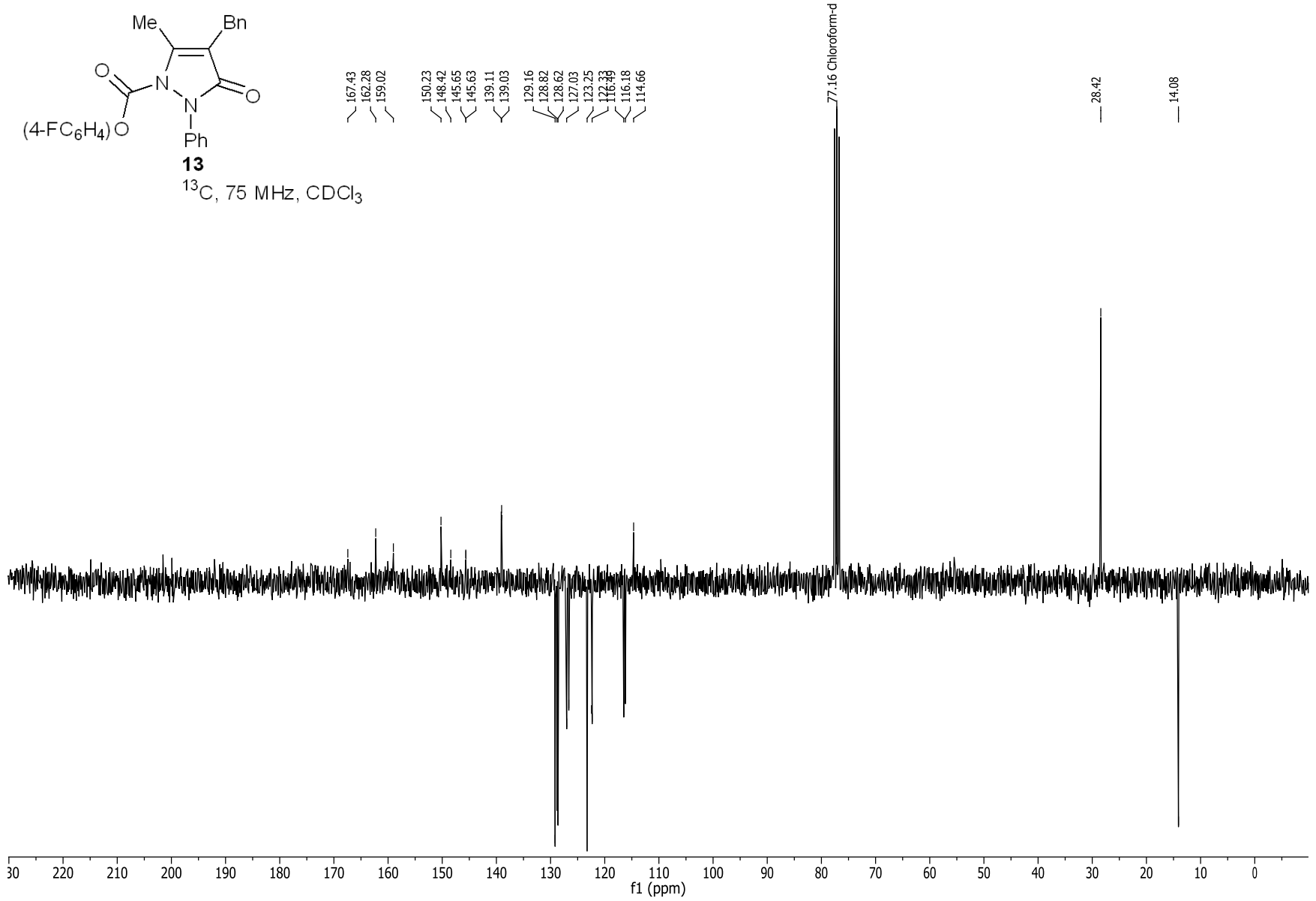

Me
Me
O
N
N
O
(4-FC6H4)O
Me
11
1H, 500 MHz, CDCl3
7.26 Chloroform-d
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.12
7.11
7.10
3.54
2.45
1.88
4.21
3.00
3.00
3.01
f1 (ppm)

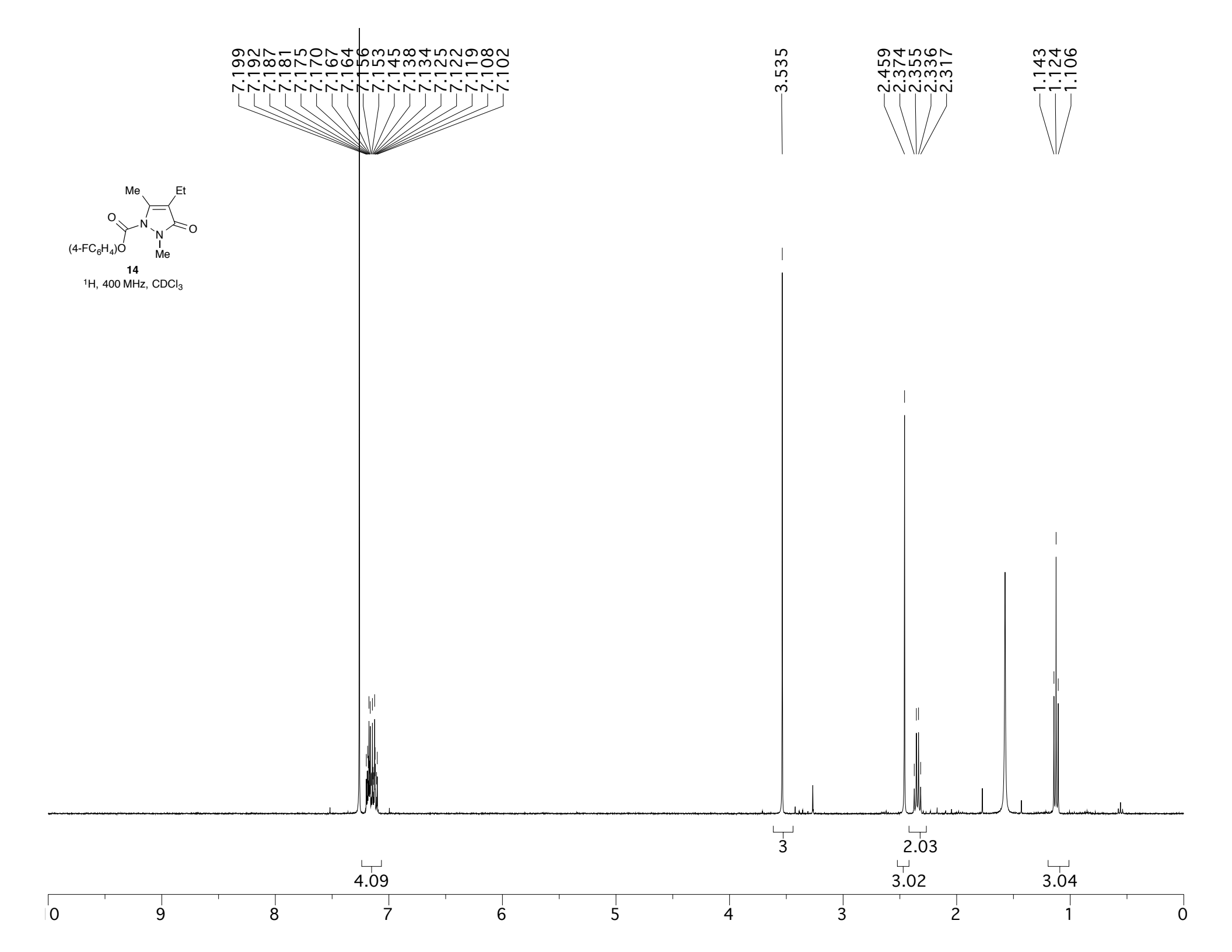

Me
Me
O
N
N
O
(4-FC6H4)O
Me
11
13C, 125 MHz, CDCl3
169.33
162.43
159.17
148.50
147.43
145.68
145.64
122.87
122.76
116.79
116.47
111.65
77.16 Chloroform-d
35.14
14.06
7.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

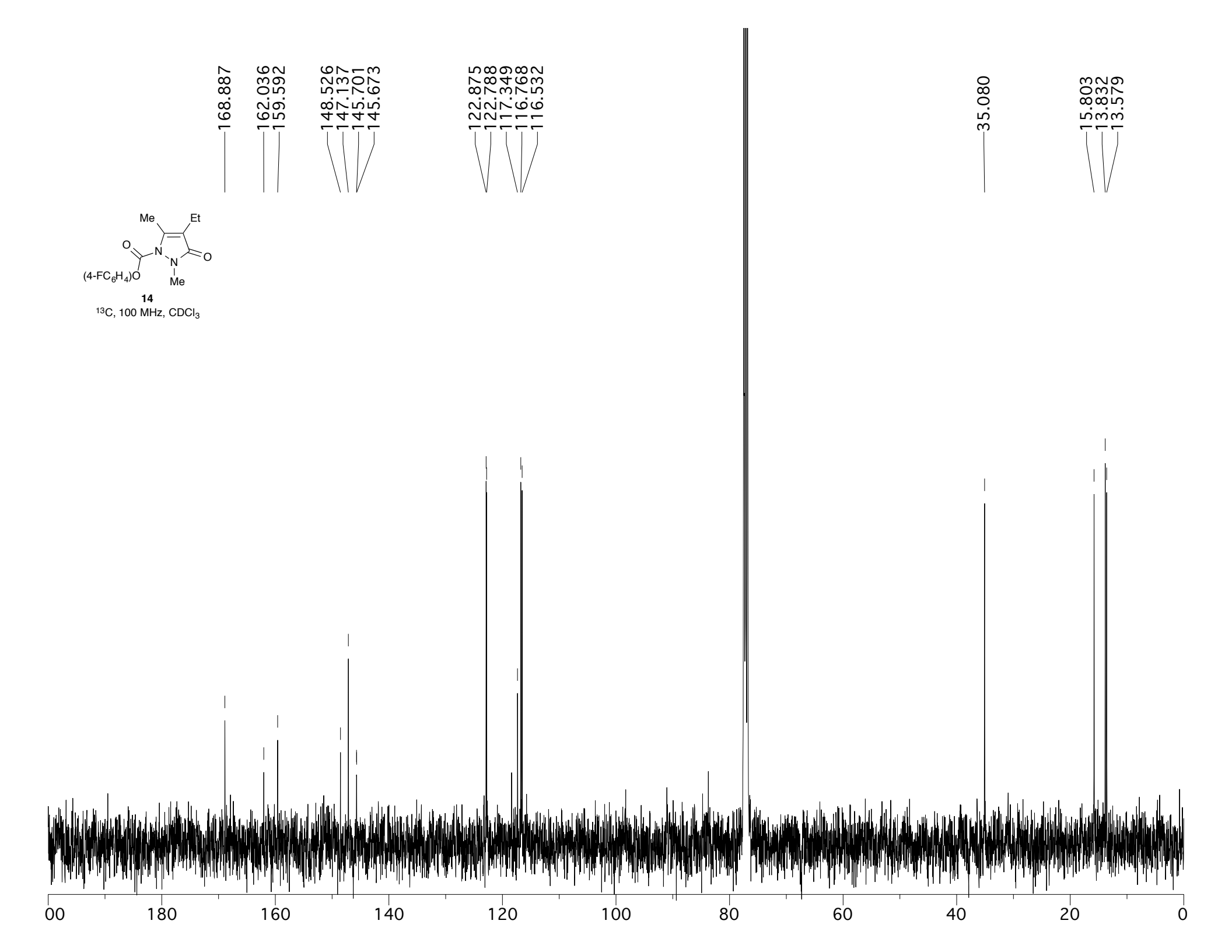

7.470
7.449
7.428
7.421
7.419
7.416
7.412
7.405
7.389
7.387
7.383
7.380
7.377
7.317
7.311
7.288
7.285
7.272
7.265
6.989
6.981
6.966
6.962
6.958
6.955
6.940
6.932
6.773
6.765
6.758
6.750
6.743
6.736
6.728
2.569
2.421
2.396
2.371
2.346
1.186
1.161
1.136
Me
Et
O
N
N
O
(4-FC6H4)O
Ph
12
1H, 300 MHz, CDCl3
0.969
1.97
2.09
4.09
2
3.06
3.18
0
9
8
7
6
5
4
3
2
1
0

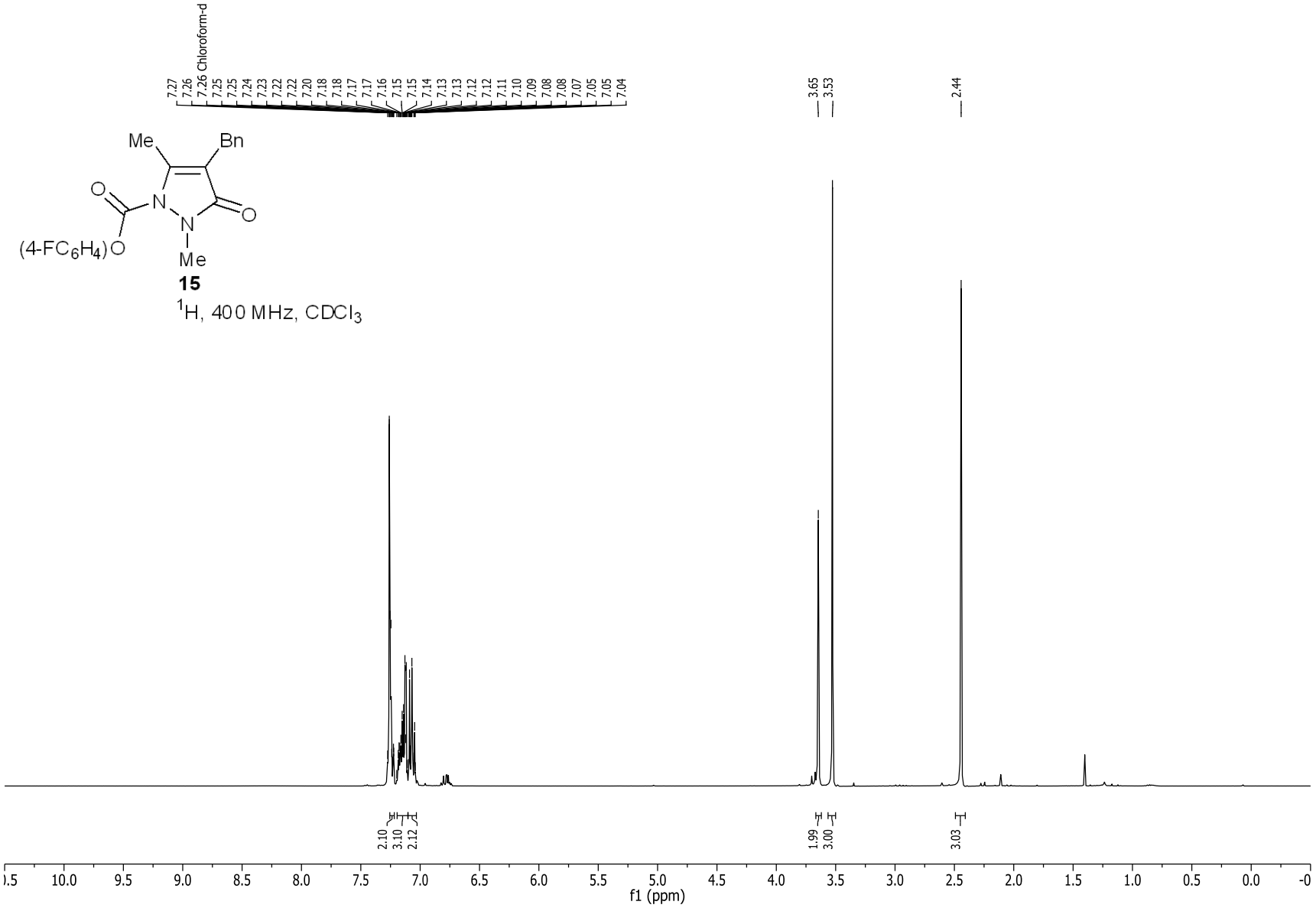

167.489
161.584
159.631
149.159
148.580
145.718
145.698
139.169
129.112
126.884
123.166
122.453
122.385
116.715
116.404
116.215
15.891
13.683
13.485
Me
Et
O
N
N
O
(4-FC6H4)O
Ph
12
13C, 125 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

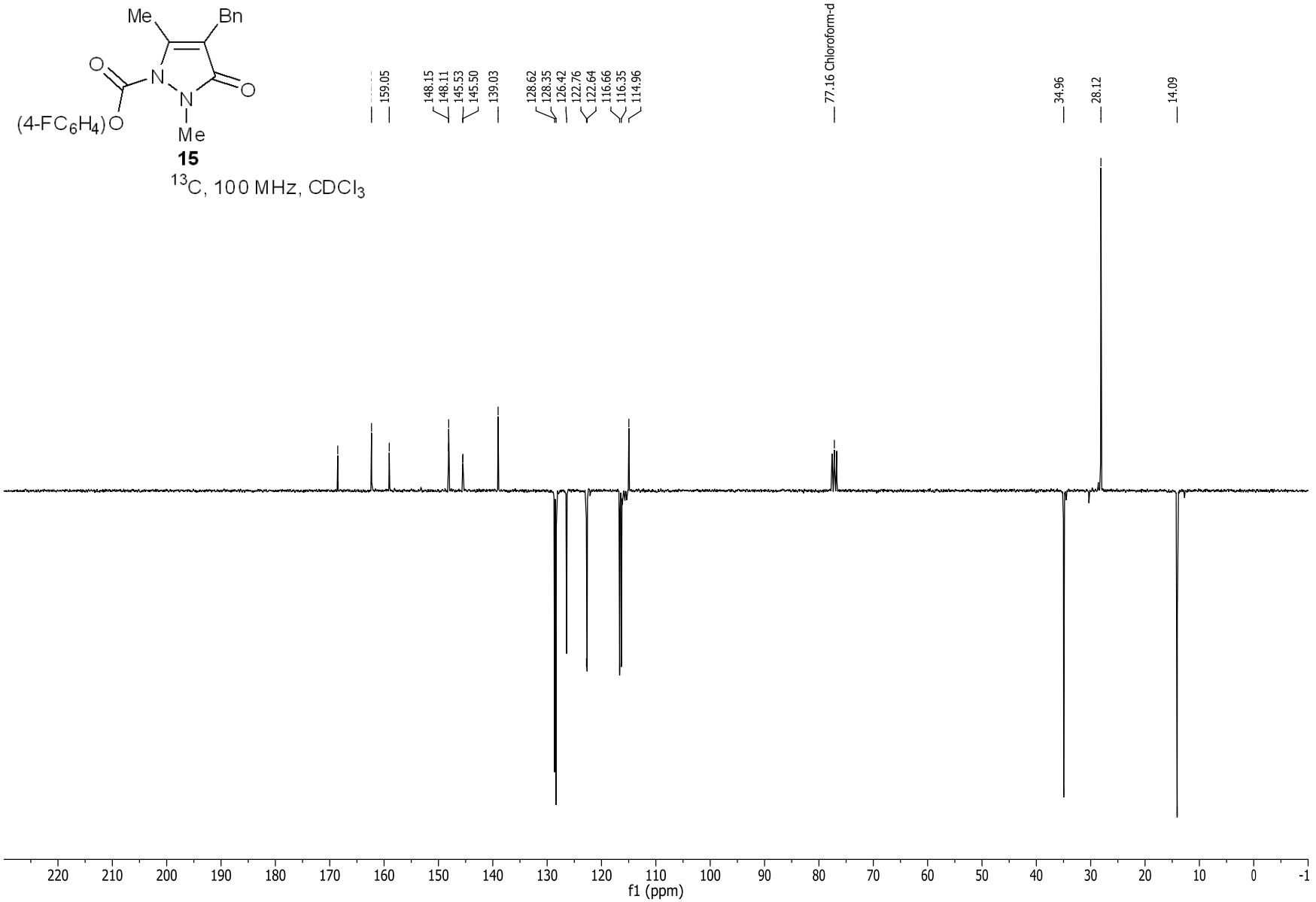

Me
Bn
O
N
N
O
(4-FC6H4)O
Ph
13
1H, 300 MHz, CDCl3
7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.42 7.41 7.39 7.37 7.36 7.34 7.33 7.31 7.30 7.28 7.26 7.25 7.23 7.20 7.00 6.99 6.98 6.97 6.96 6.96 6.96 6.95 6.94 6.93 6.92 6.77 6.76 6.75 6.75 6.74 6.73 6.72 6.72 6.70
3.71
2.60
10.82
2.10
2.07
2.00
3.03
f1 (ppm)

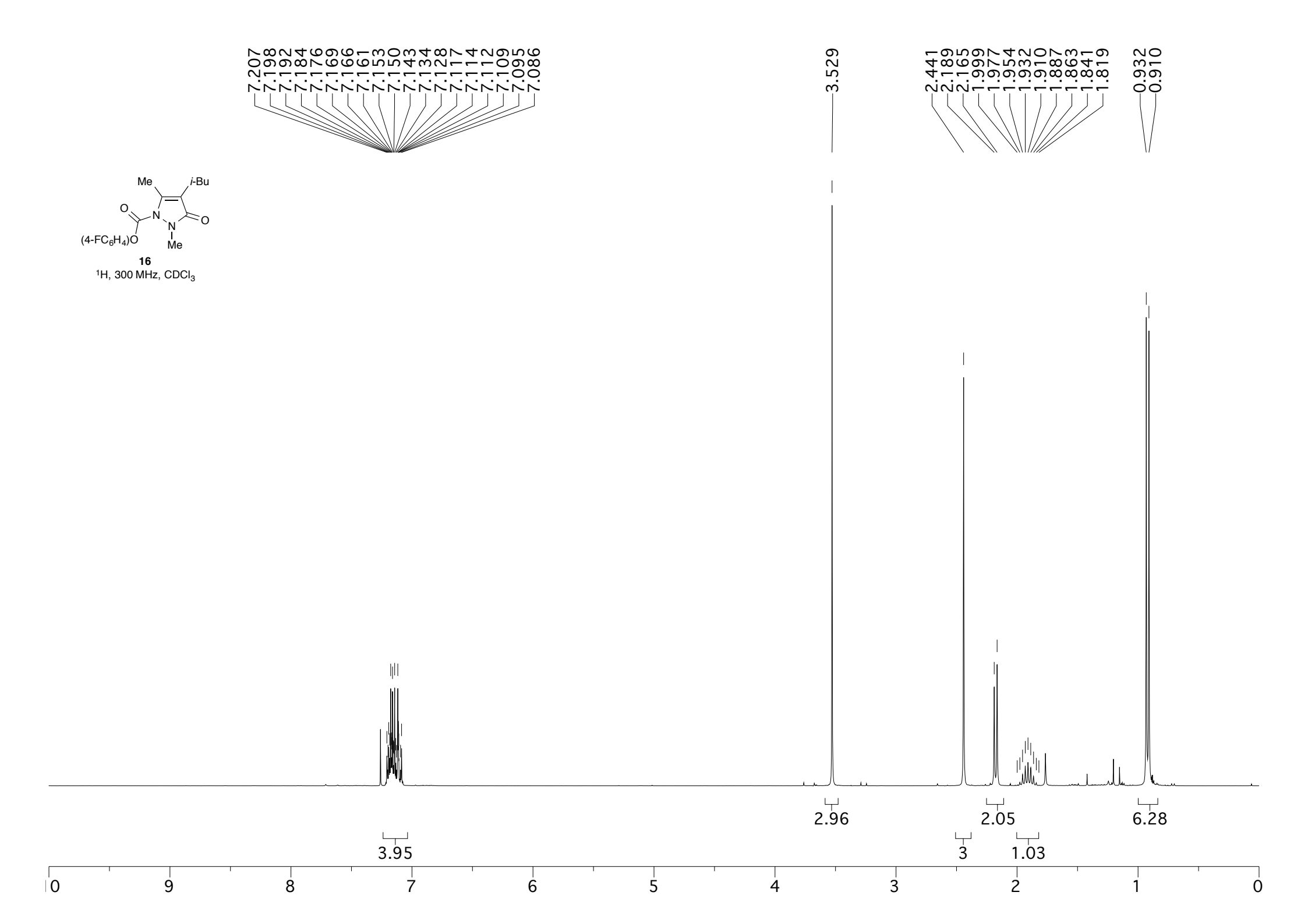

Me
Bn
O
N
N
O
(4-FC6H4)O
Ph
13
13C, 75 MHz, CDCl3
167.43
162.28
159.02
150.23
148.42
145.65
145.63
139.11
139.03
129.16
128.82
128.62
127.03
123.25
122.33
116.49
116.18
114.66
77.16 Chloroform-d
28.42
14.08
f1 (ppm)

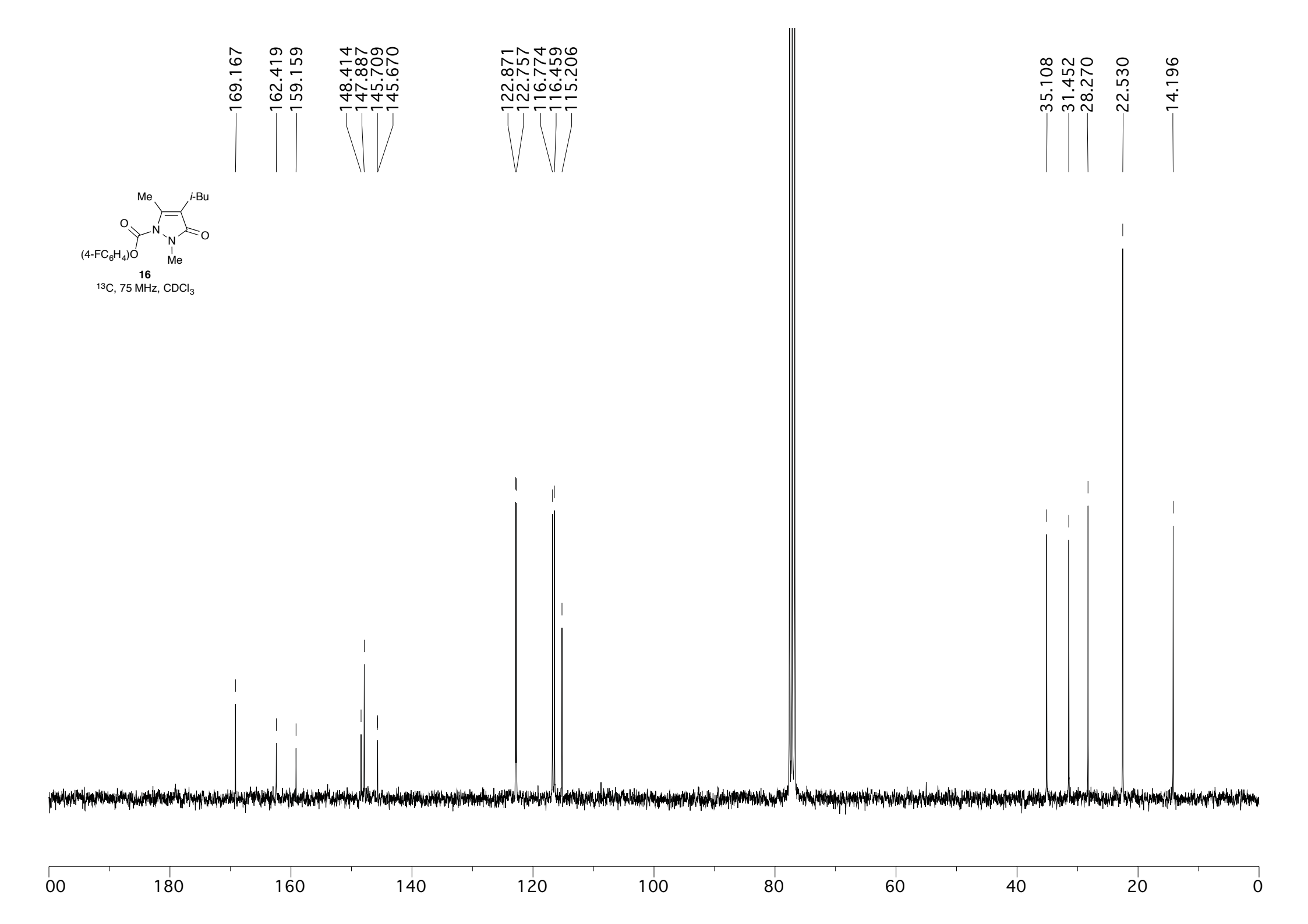

7.199
7.192
7.187
7.181
7.175
7.170
7.167
7.164
7.156
7.153
7.145
7.138
7.134
7.125
7.122
7.119
7.108
7.102
3.535
2.459
2.374
2.355
2.336
2.317
1.143
1.124
1.106
Me
Et
O
N
N
O
(4-FC6H4)O
Me
14
1H, 400 MHz, CDCl3
3
2.03
4.09
3.02
3.04
0
9
8
7
6
5
4
3
2
1
0

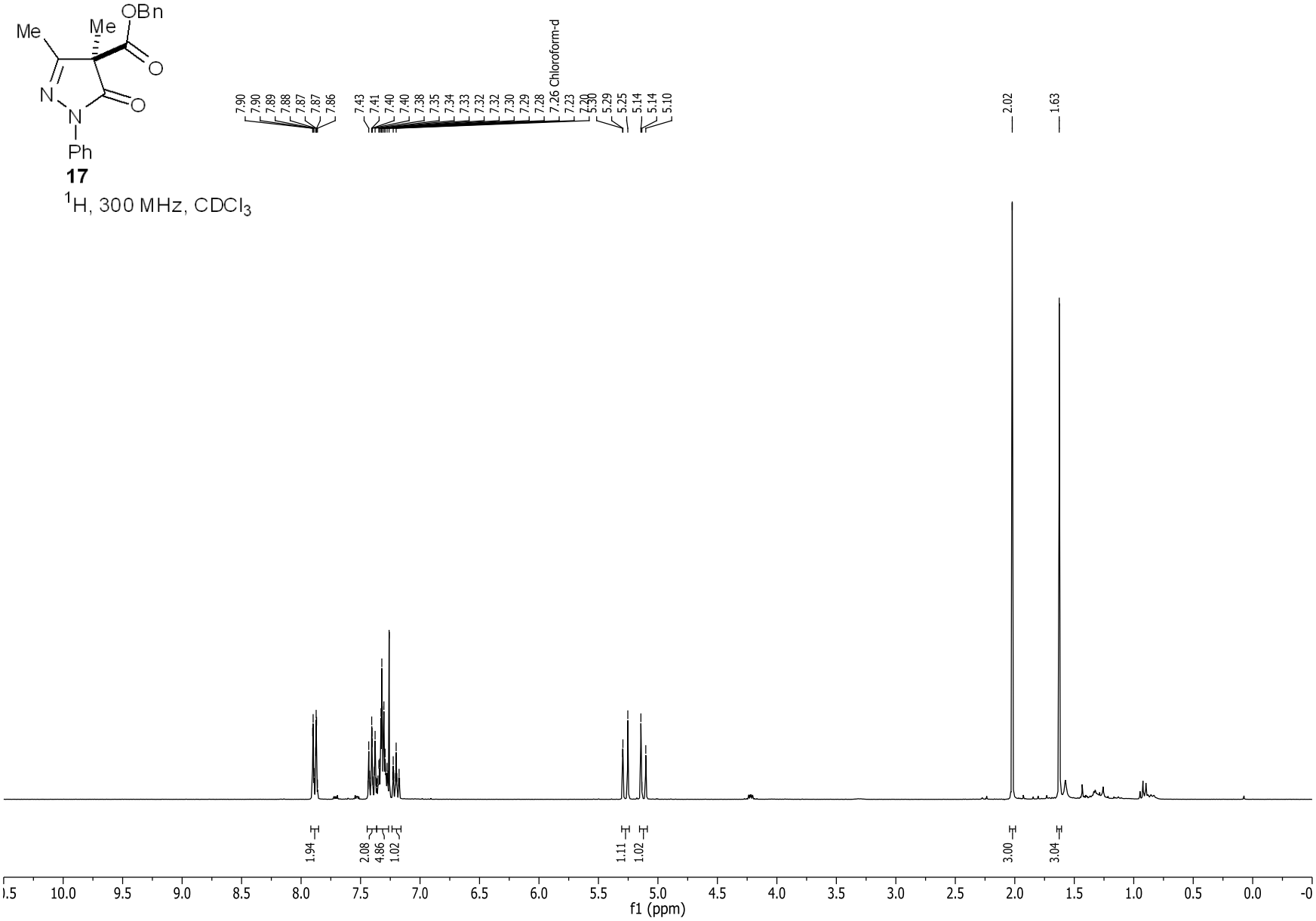

168.887
162.036
159.592
148.526
147.137
145.701
145.673
122.875
122.788
117.349
116.768
116.532
35.080
15.803
13.832
13.579
Me
Et
O
N
N
O
(4-FC6H4)O
Me
14
13C, 100 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

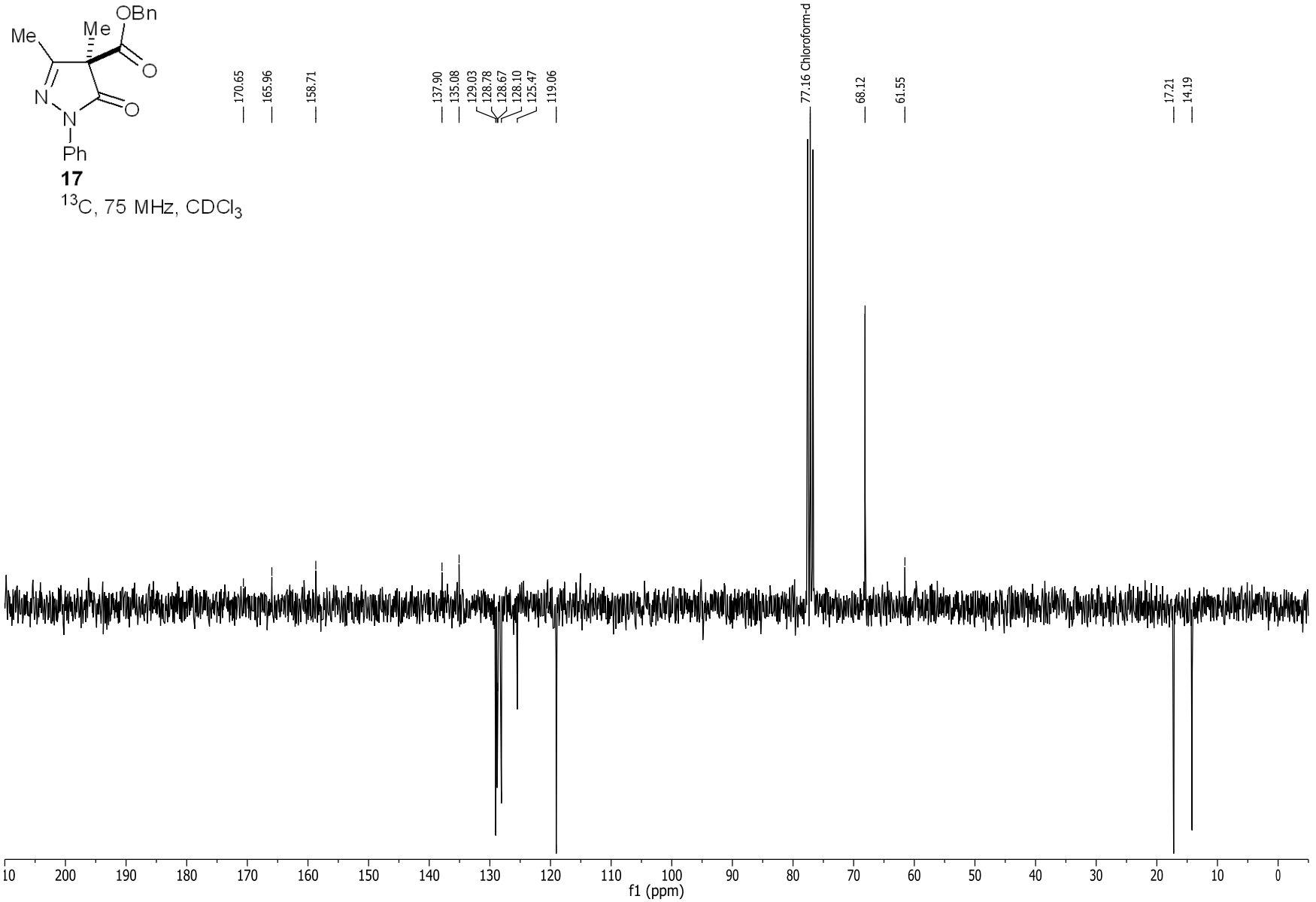

Chloroform-d
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.20
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.11
7.10
7.09
7.08
7.08
7.07
7.05
7.05
7.04
3.65
3.53
2.44
Me
Bn
O
N
N
O
(4-FC6H4)O
Me
15
1H, 400 MHz, CDCl3
2.10
3.10
2.12
1.99
3.00
3.03
f1 (ppm)

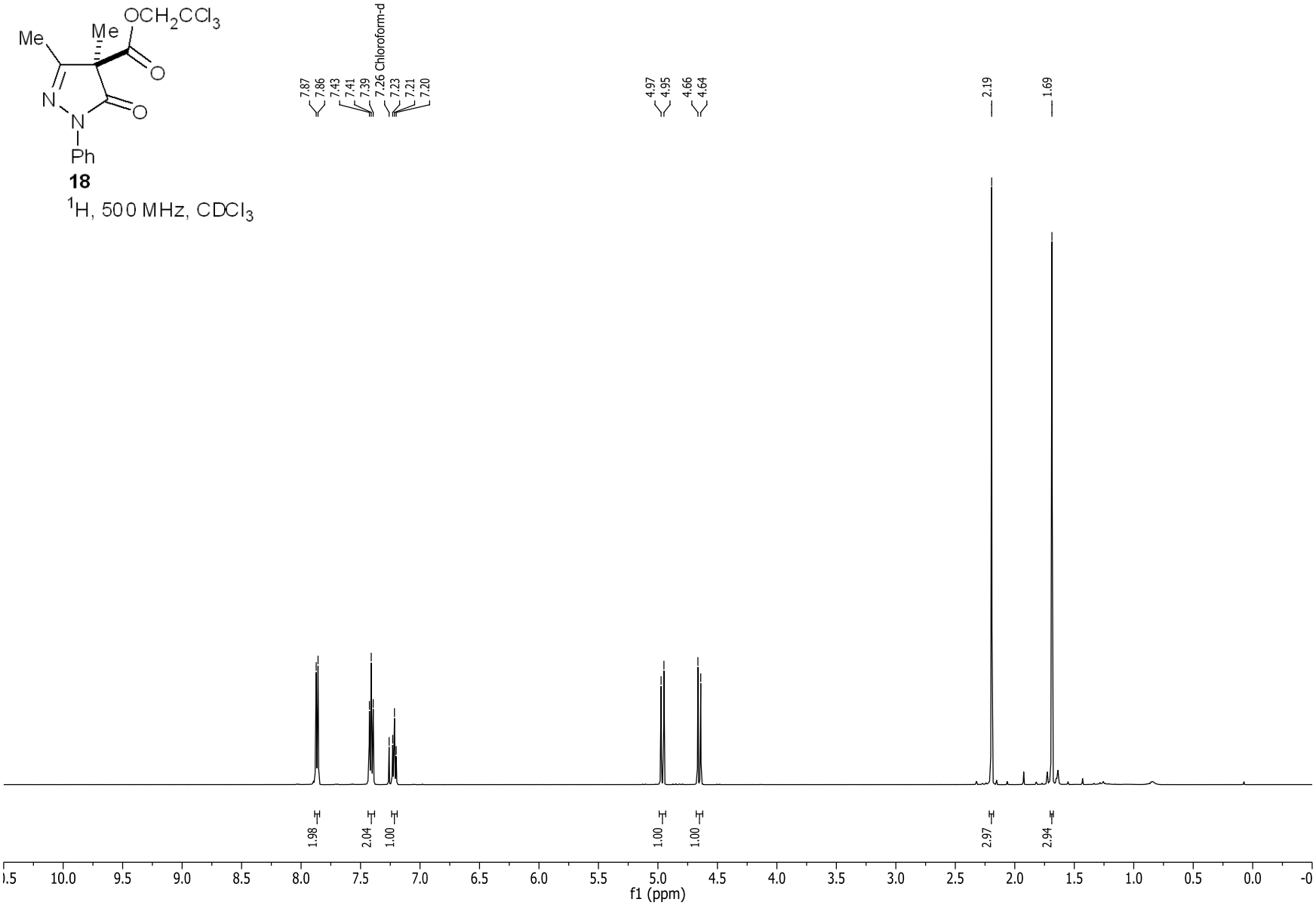

Me
Bn
O
N
N
O
(4-FC6H4)O
Me
15
13C, 100 MHz, CDCl3
159.05
148.15
148.11
145.53
145.50
139.03
128.62
128.35
126.42
122.76
122.64
116.66
116.35
114.96
77.16 Chloroform-d
34.96
28.12
14.09
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

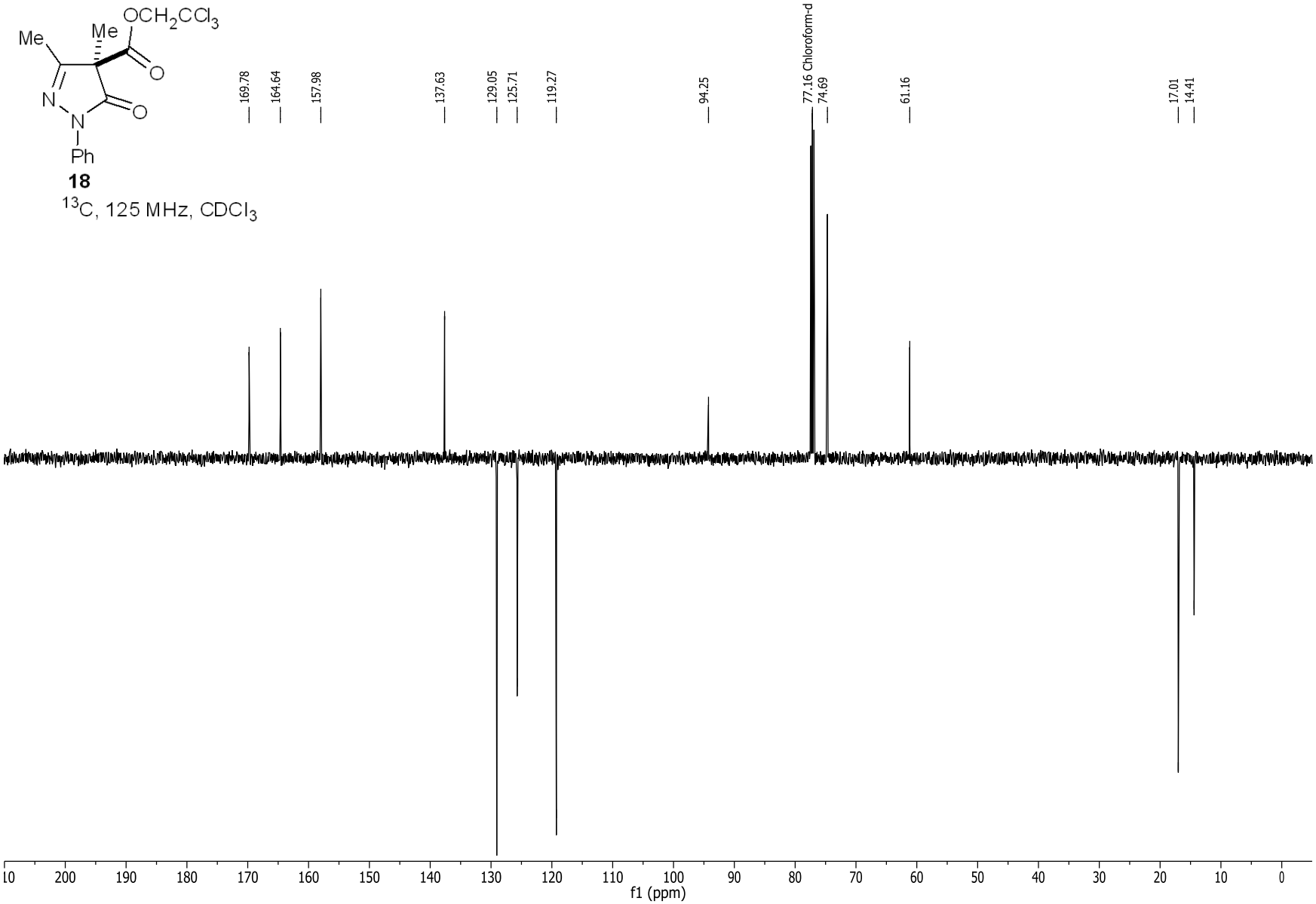

7.207
7.198
7.192
7.184
7.176
7.169
7.166
7.161
7.153
7.150
7.143
7.134
7.128
7.117
7.114
7.112
7.109
7.095
7.086
3.529
2.441
2.189
2.165
1.999
1.977
1.954
1.932
1.910
1.887
1.863
1.841
1.819
0.932
0.910
Me
i-Bu
O
N
N
O
(4-FC6H4)O
Me
16
1H, 300 MHz, CDCl3
2.96
2.05
6.28
3.95
3
1.03
0
9
8
7
6
5
4
3
2
1
0

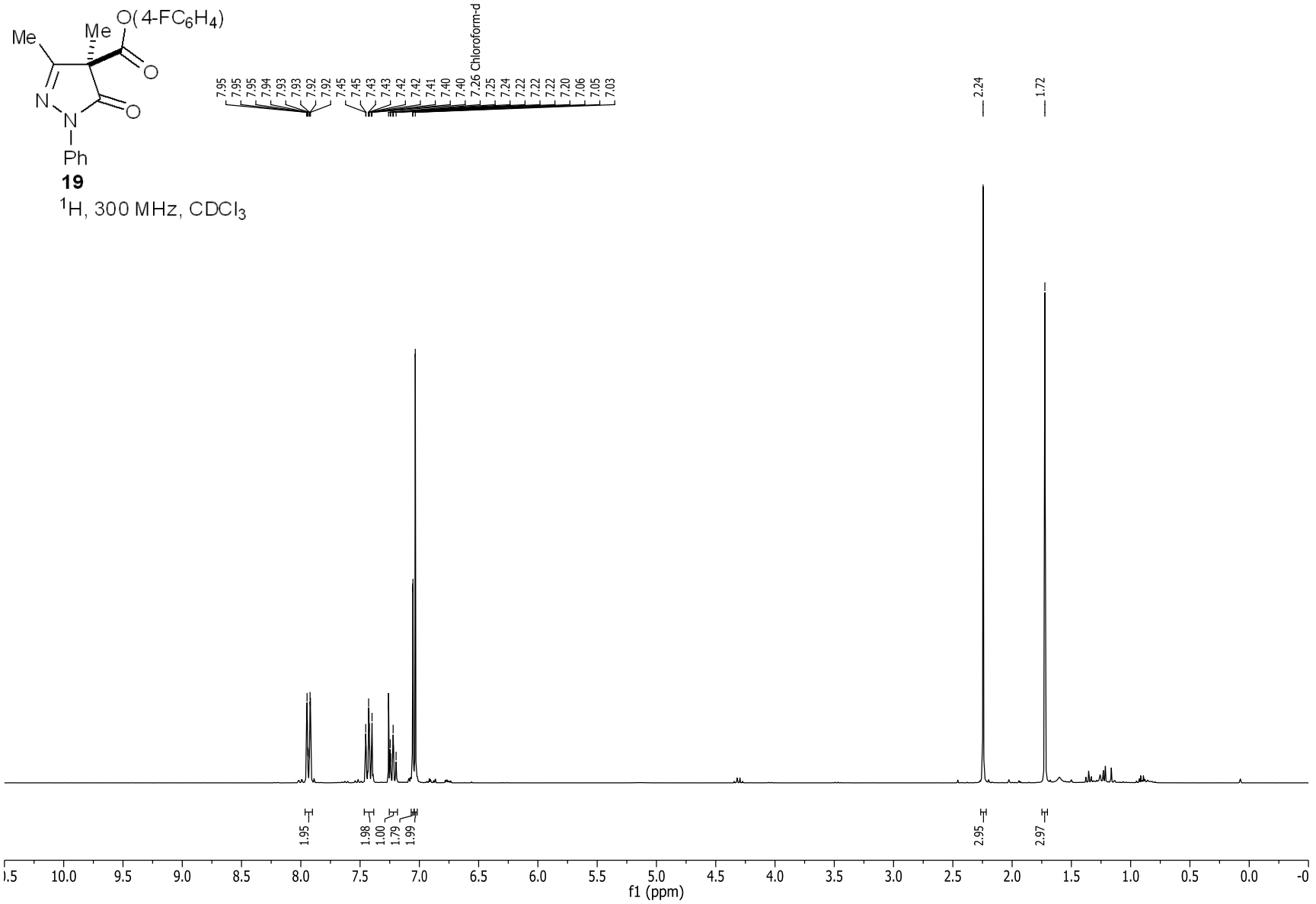

169.167
162.419
159.159
148.414
147.887
145.709
145.670
122.871
122.757
116.774
116.459
115.206
35.108
31.452
28.270
22.530
14.196
Me
i-Bu
O
N
N
O
(4-FC6H4)O
Me
16
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

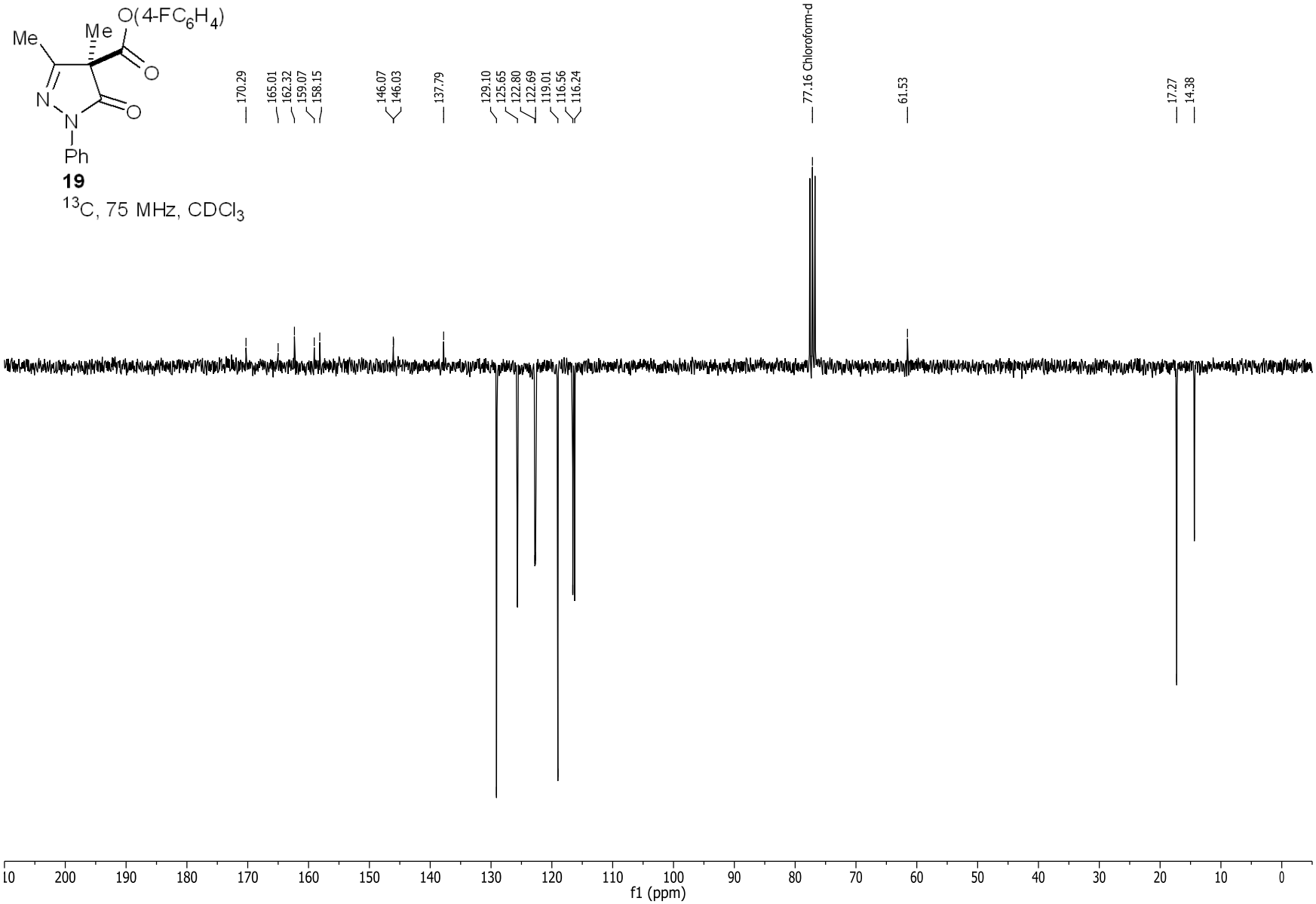

Me
Me
OBn
O
N
N
O
Ph
17
1H, 300 MHz, CDCl3
7.90
7.90
7.89
7.88
7.87
7.87
7.86
7.43
7.41
7.40
7.40
7.38
7.35
7.34
7.33
7.32
7.32
7.30
7.29
7.28
7.26 Chloroform-d
7.23
7.20
5.30
5.29
5.25
5.14
5.14
5.10
2.02
1.63
1.94
2.08
4.86
1.02
1.11
1.02
3.00
3.04
f1 (ppm)

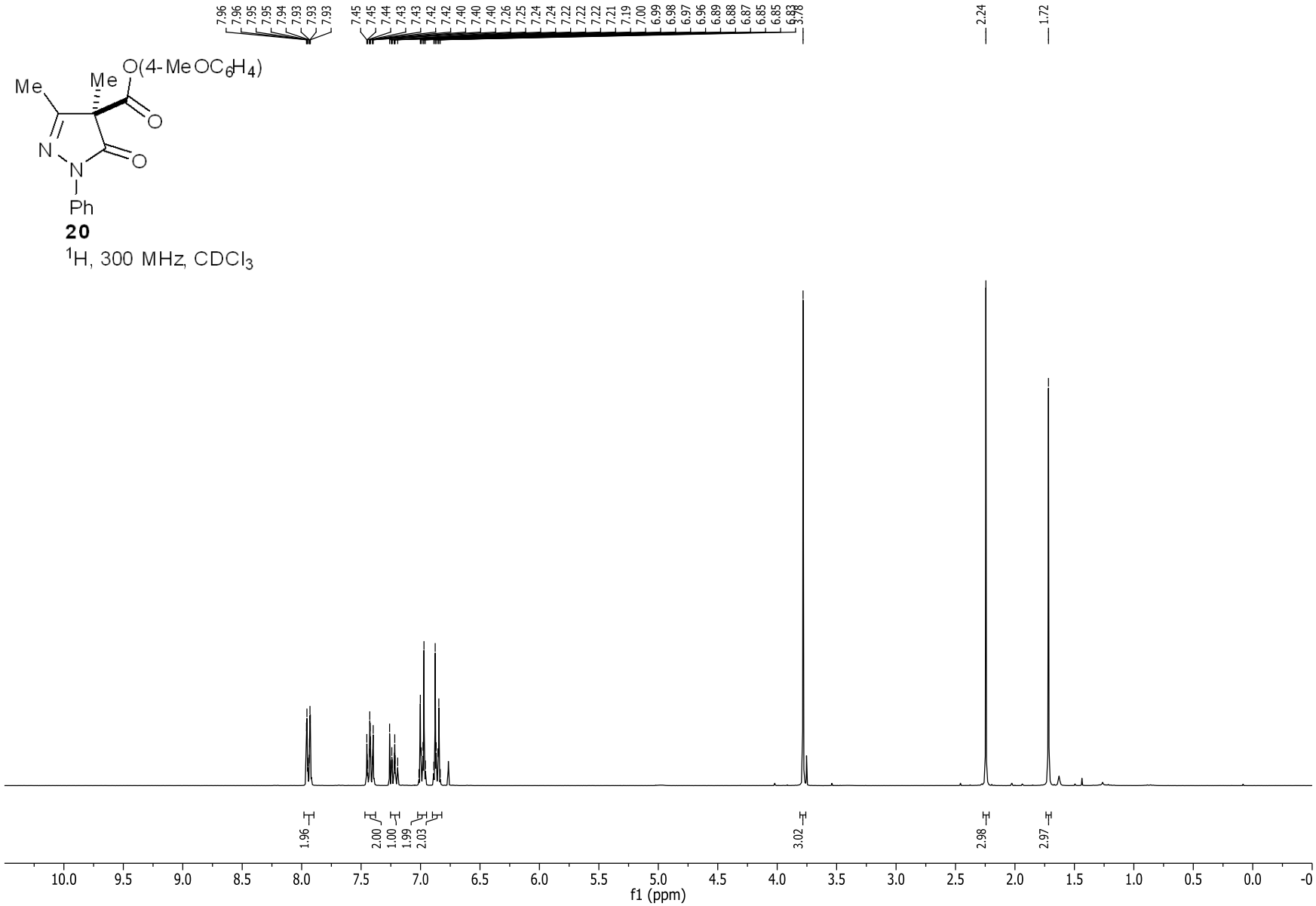

OBn
Me
Me
O
N
O
N
Ph
17
13C, 75 MHz, CDCl3
170.65
165.96
158.71
137.90
135.08
129.03
128.78
128.67
128.10
125.47
119.06
77.16 Chloroform-d
68.12
61.55
17.21
14.19
f1 (ppm)

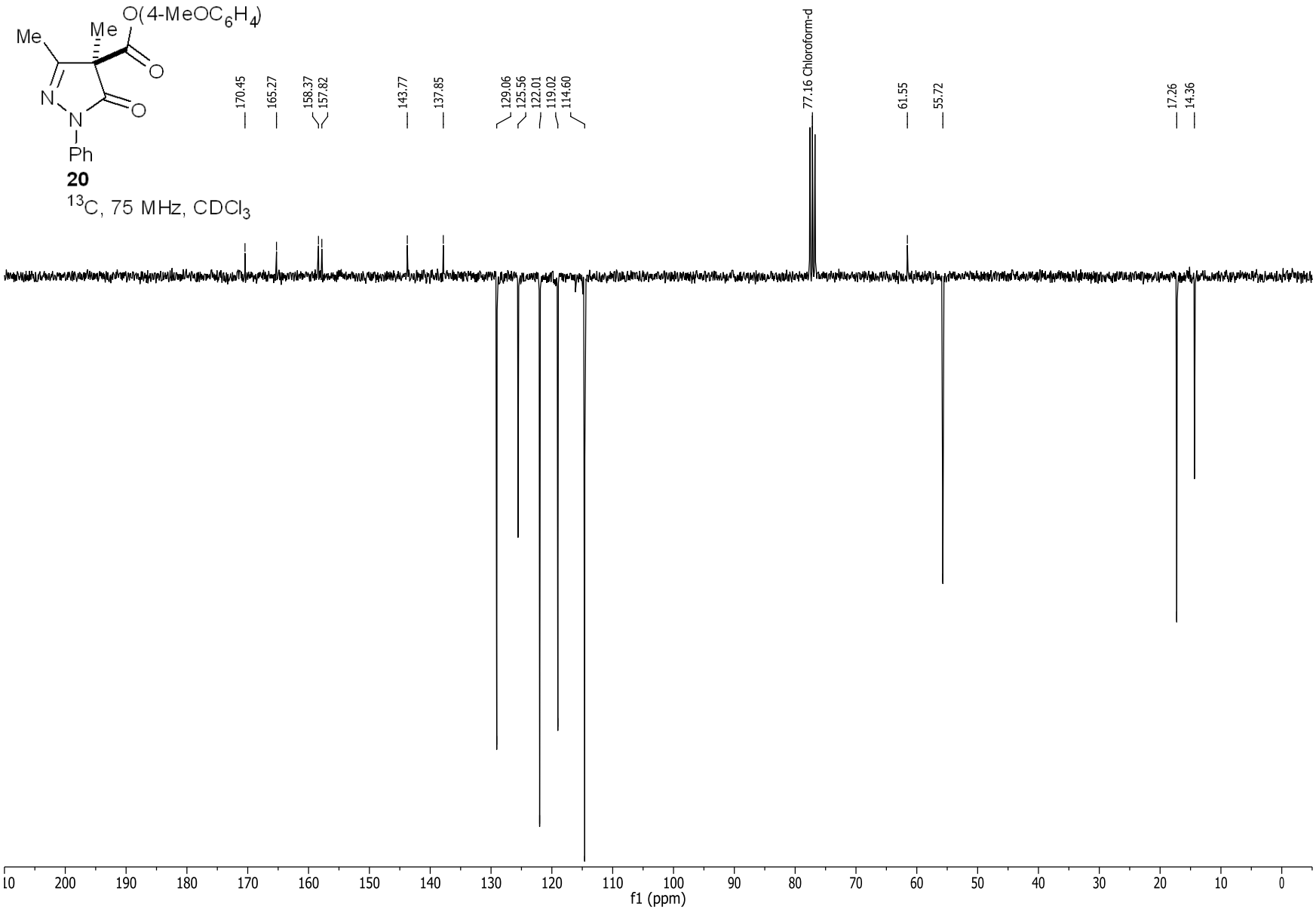

OCH2CCl3
Me
Me
O
N
N
O
Ph
18
1H, 500 MHz, CDCl3
7.87
7.86
7.43
7.41
7.39
7.26 Chloroform-d
7.23
7.21
7.20
4.97
4.95
4.66
4.64
2.19
1.69
1.98
2.04
1.00
1.00
1.00
2.97
2.94
f1 (ppm)

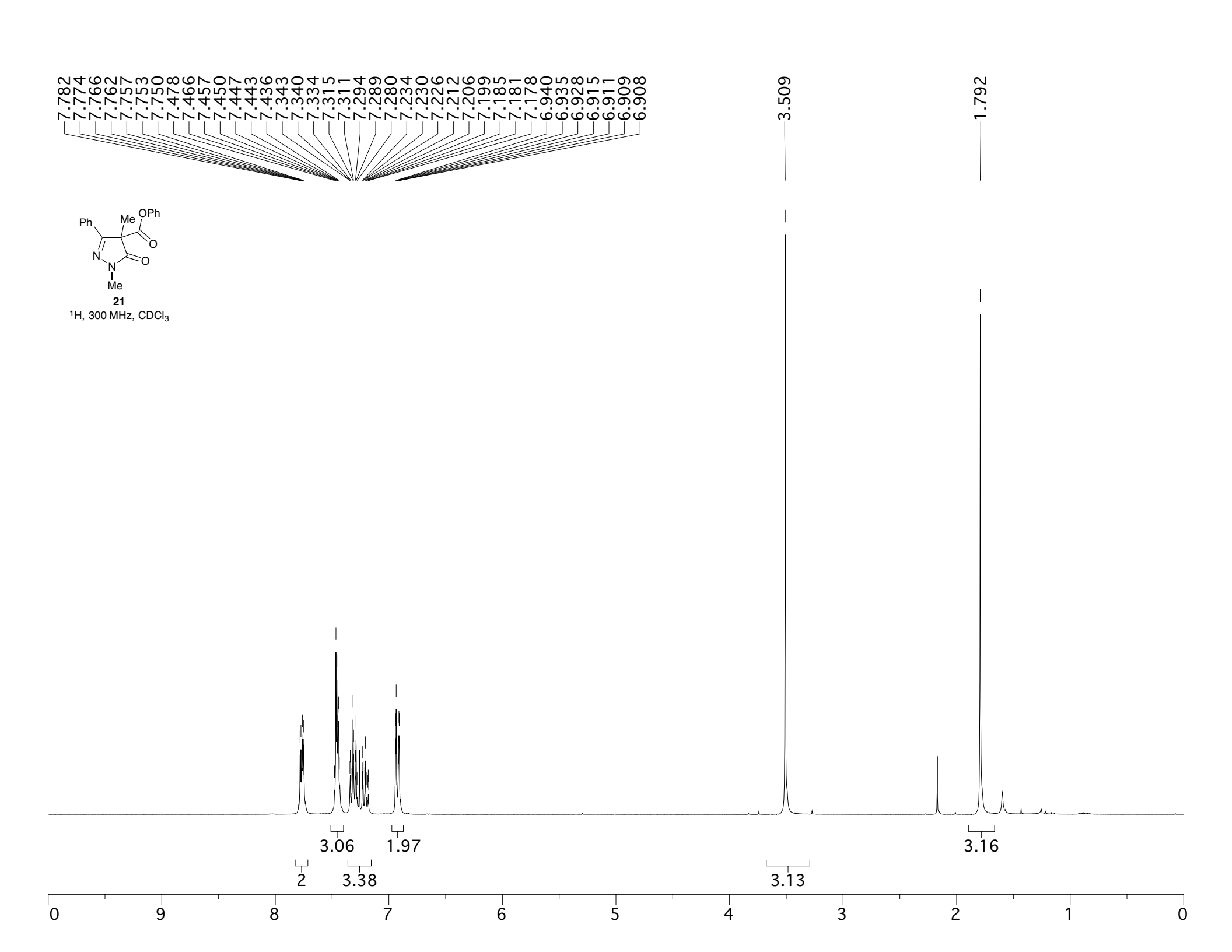

OCH2CCl3
Me
Me
O
N
N
O
Ph
18
13C, 125 MHz, CDCl3
169.78
164.64
157.98
137.63
129.05
125.71
119.27
94.25
77.16 Chloroform-d
74.69
61.16
17.01
14.41
f1 (ppm)

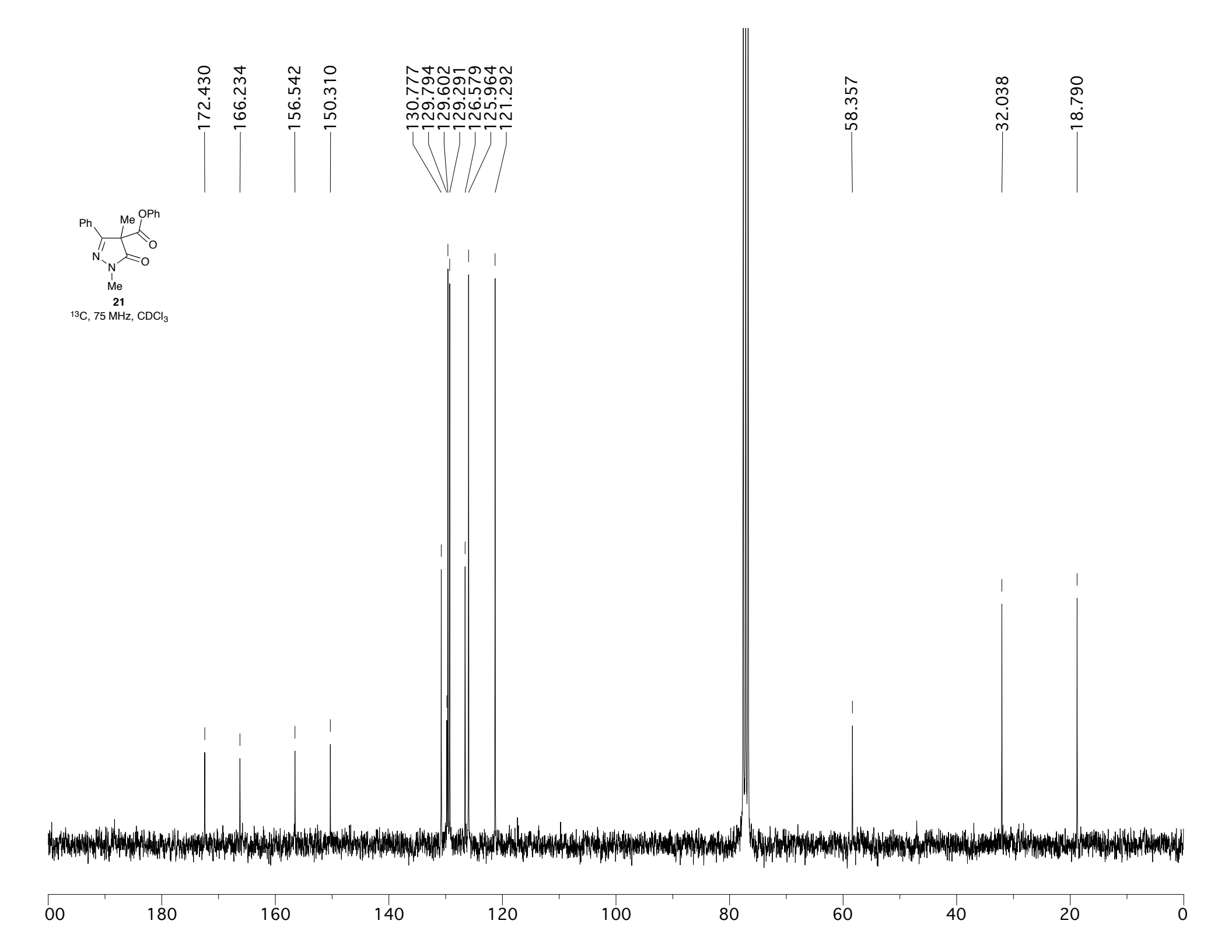

Me
Me
O(4-FC6H4)
O
N
N
O
Ph
19
1H, 300 MHz, CDCl3
7.95
7.95
7.95
7.94
7.93
7.93
7.92
7.92
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.26 Chloroform-d
7.25
7.24
7.22
7.22
7.22
7.20
7.06
7.05
7.03
2.24
1.72
1.95
1.98
1.00
1.79
1.99
2.95
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

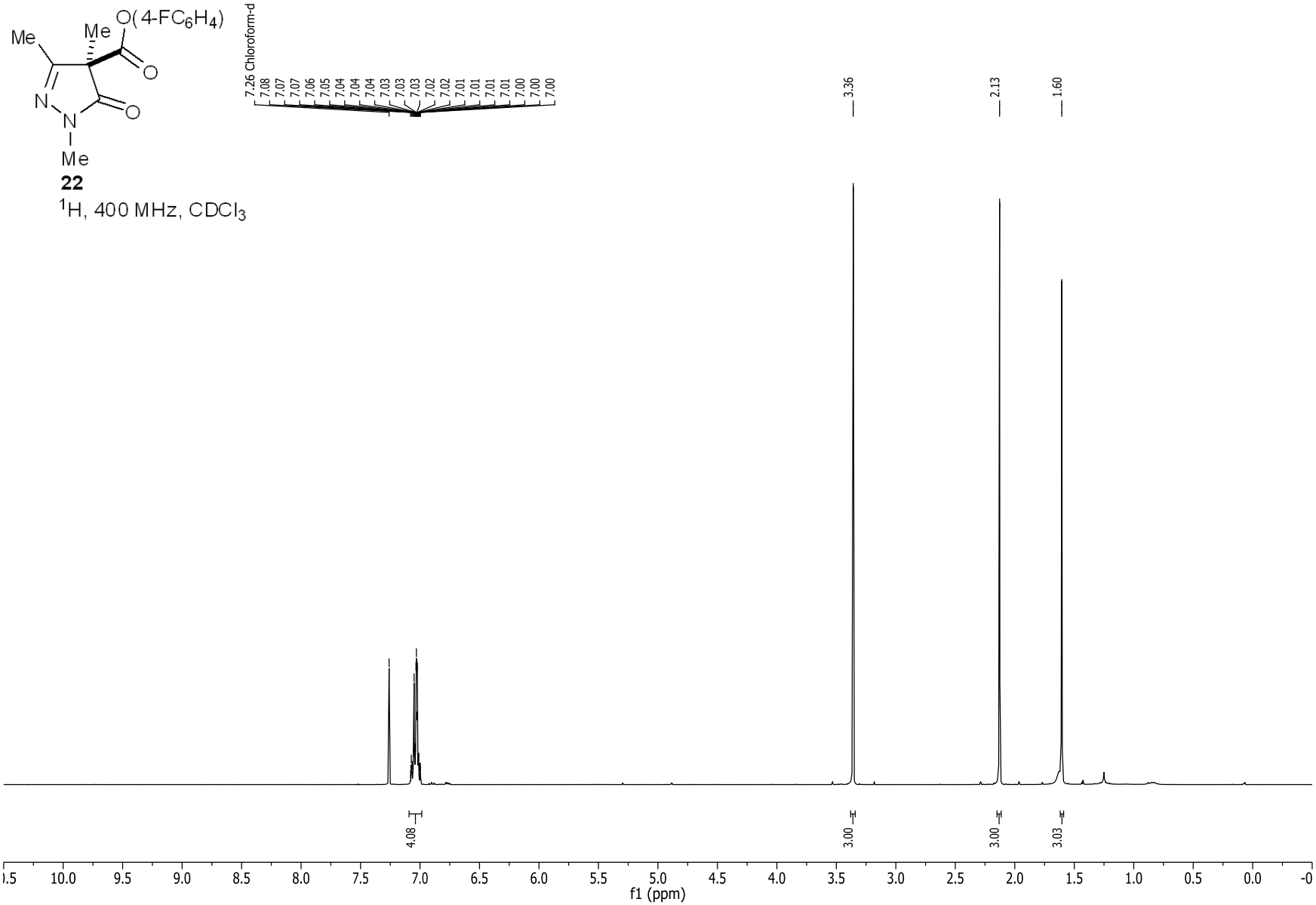

Me
Me
O(4-FC6H4)
O
N
N
O
Ph
19
13C, 75 MHz, CDCl3
170.29
165.01
162.32
159.07
158.15
146.07
146.03
137.79
129.10
125.65
122.80
122.69
119.01
116.56
116.24
77.16 Chloroform-d
61.53
17.27
14.38
f1 (ppm)

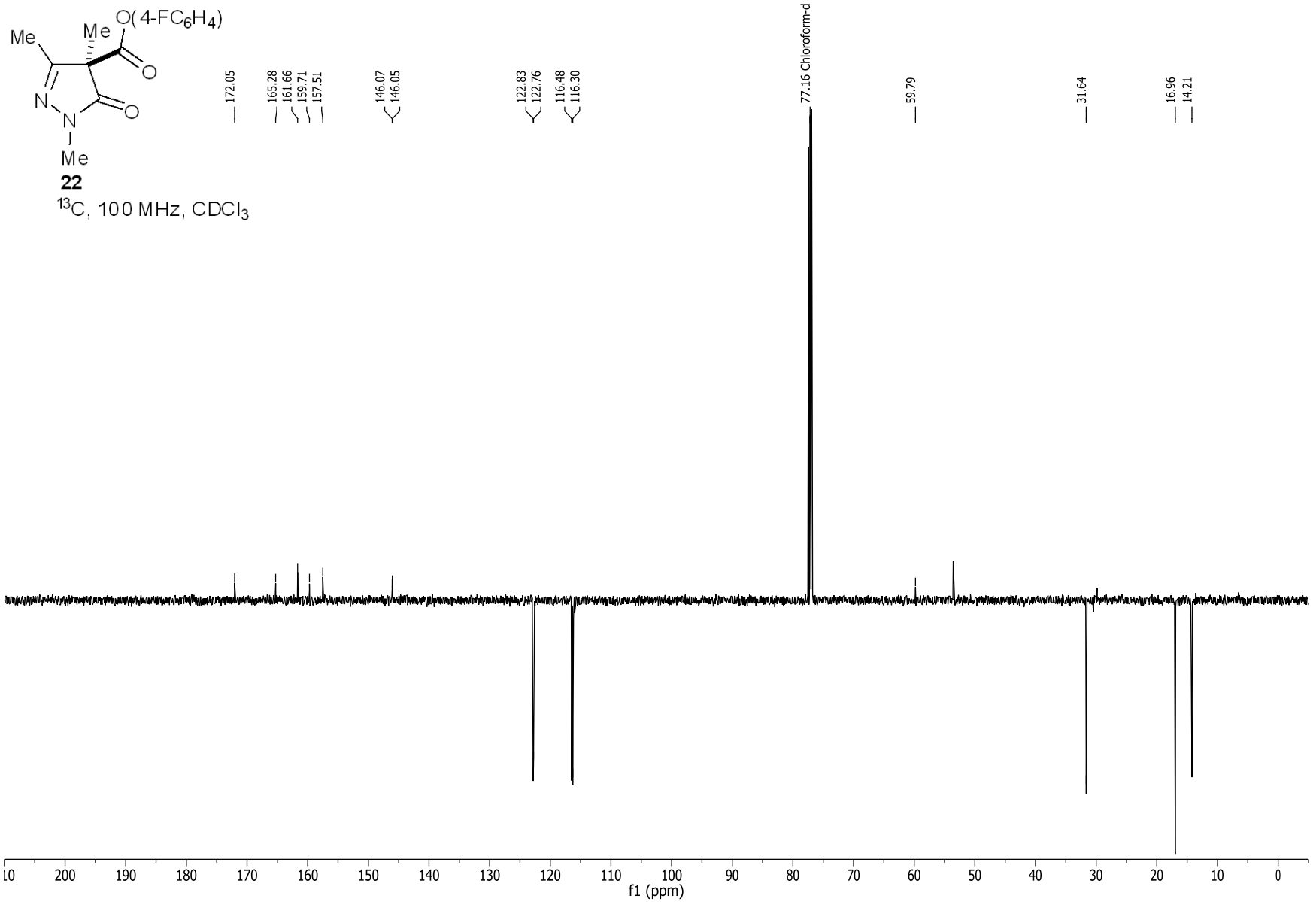

7.96
7.96
7.95
7.95
7.94
7.93
7.93
7.93
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.40
7.40
7.40
7.26
7.25
7.24
7.24
7.22
7.22
7.22
7.21
7.19
7.00
6.99
6.98
6.97
6.96
6.89
6.88
6.87
6.85
6.85
6.83
3.78
2.24
1.72
Me
Me
O(4-MeOC6H4)
O
N
N
O
Ph
20
1H, 300 MHz, CDCl3
1.96
2.00
1.00
1.99
2.03
3.02
2.98
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

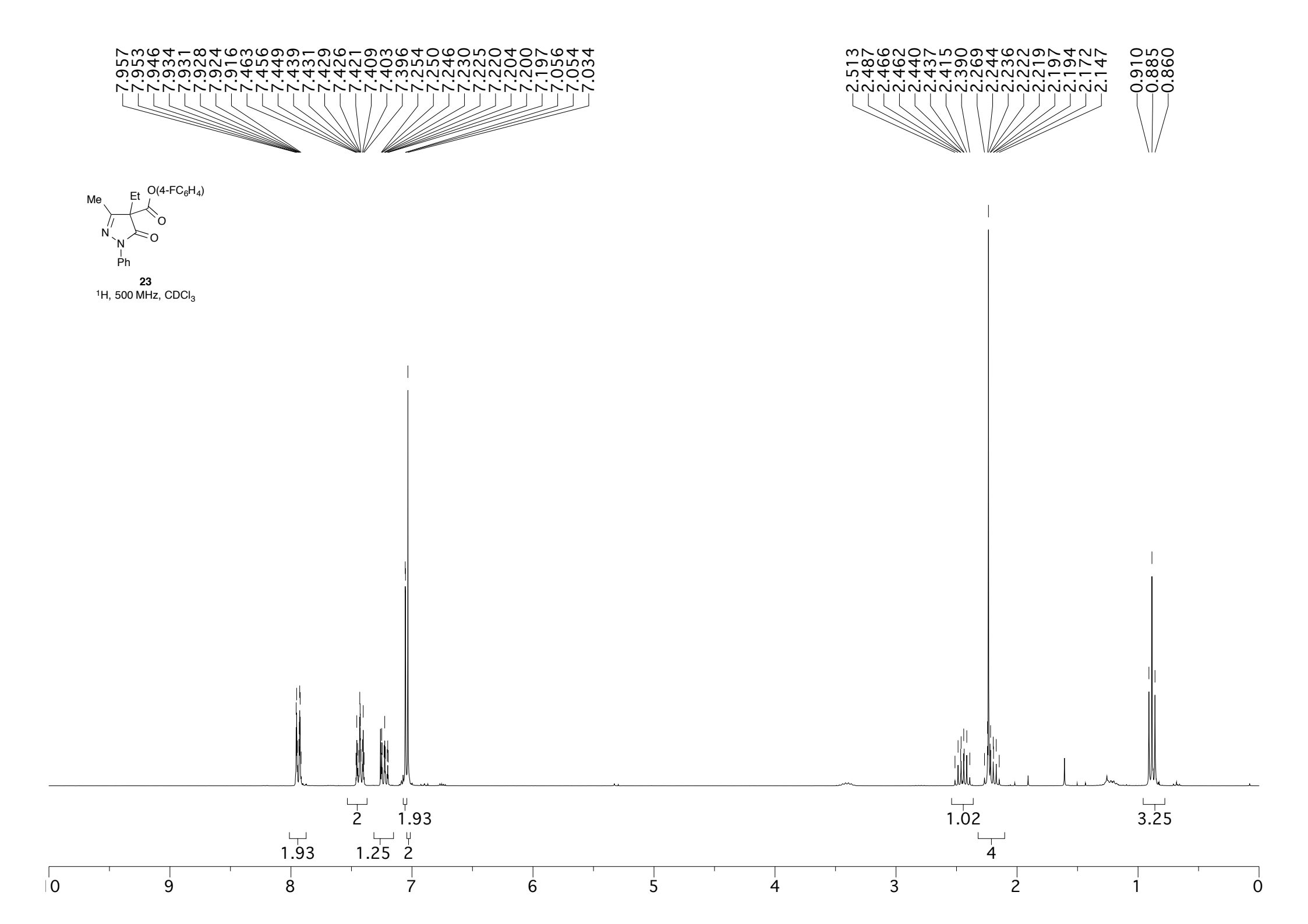

O(4-MeOC6H4)
Me
Me
O
O
N
N
Ph
20
13C, 75 MHz, CDCl3
170.45
165.27
158.37
157.82
143.77
137.85
129.06
125.56
122.01
119.02
114.60
77.16 Chloroform-d
61.55
55.72
17.26
14.36
f1 (ppm)

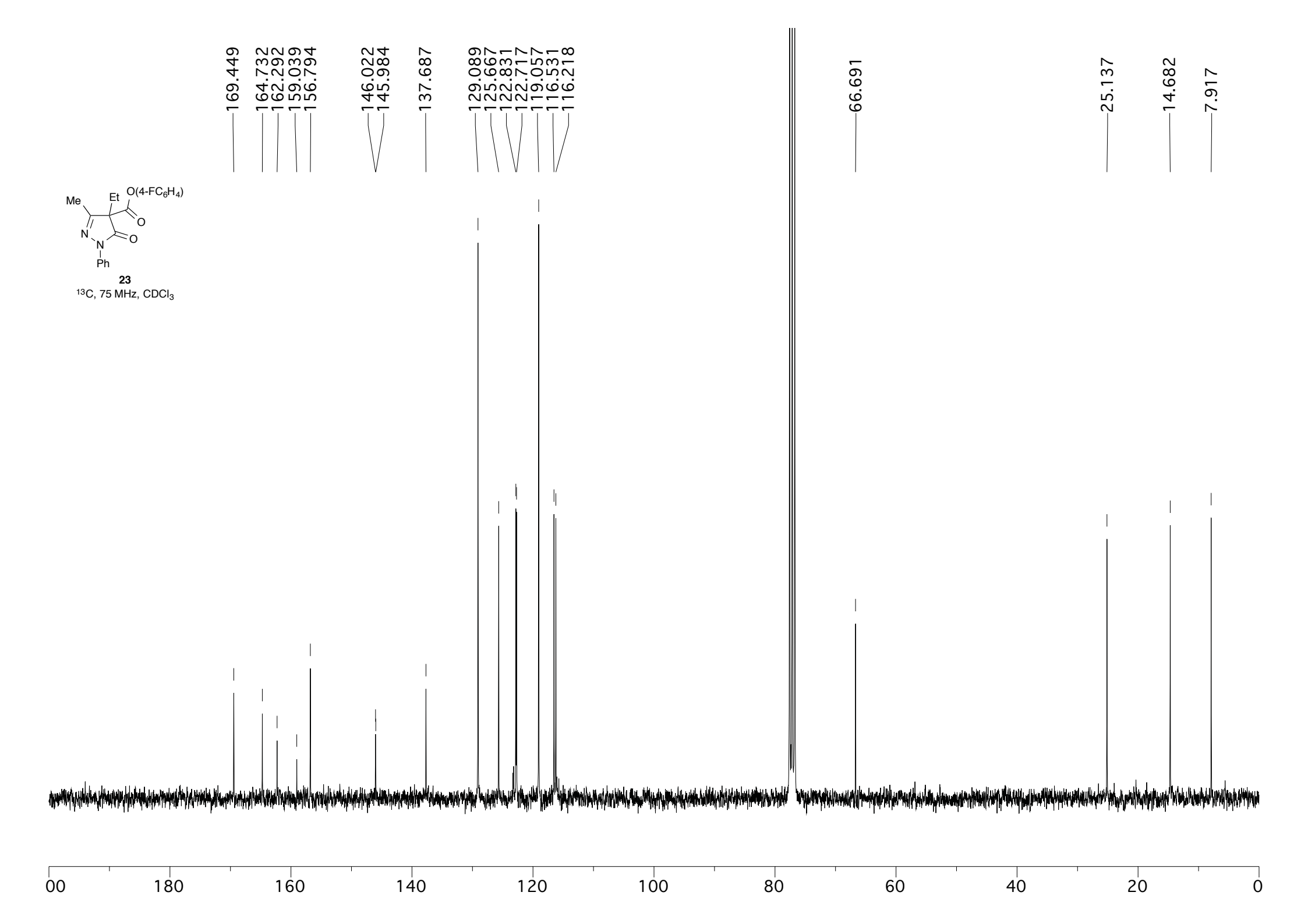

7.782
7.774
7.766
7.762
7.757
7.753
7.750
7.478
7.466
7.457
7.450
7.447
7.443
7.436
7.343
7.340
7.334
7.315
7.311
7.294
7.289
7.280
7.234
7.230
7.226
7.212
7.206
7.199
7.185
7.181
7.178
6.940
6.935
6.928
6.915
6.911
6.909
6.908
3.509
1.792
Ph
Me
OPh
O
N
N
O
Me
21
1H, 300 MHz, CDCl3
3.06
1.97
3.16
2
3.38
3.13
0
9
8
7
6
5
4
3
2
1
0

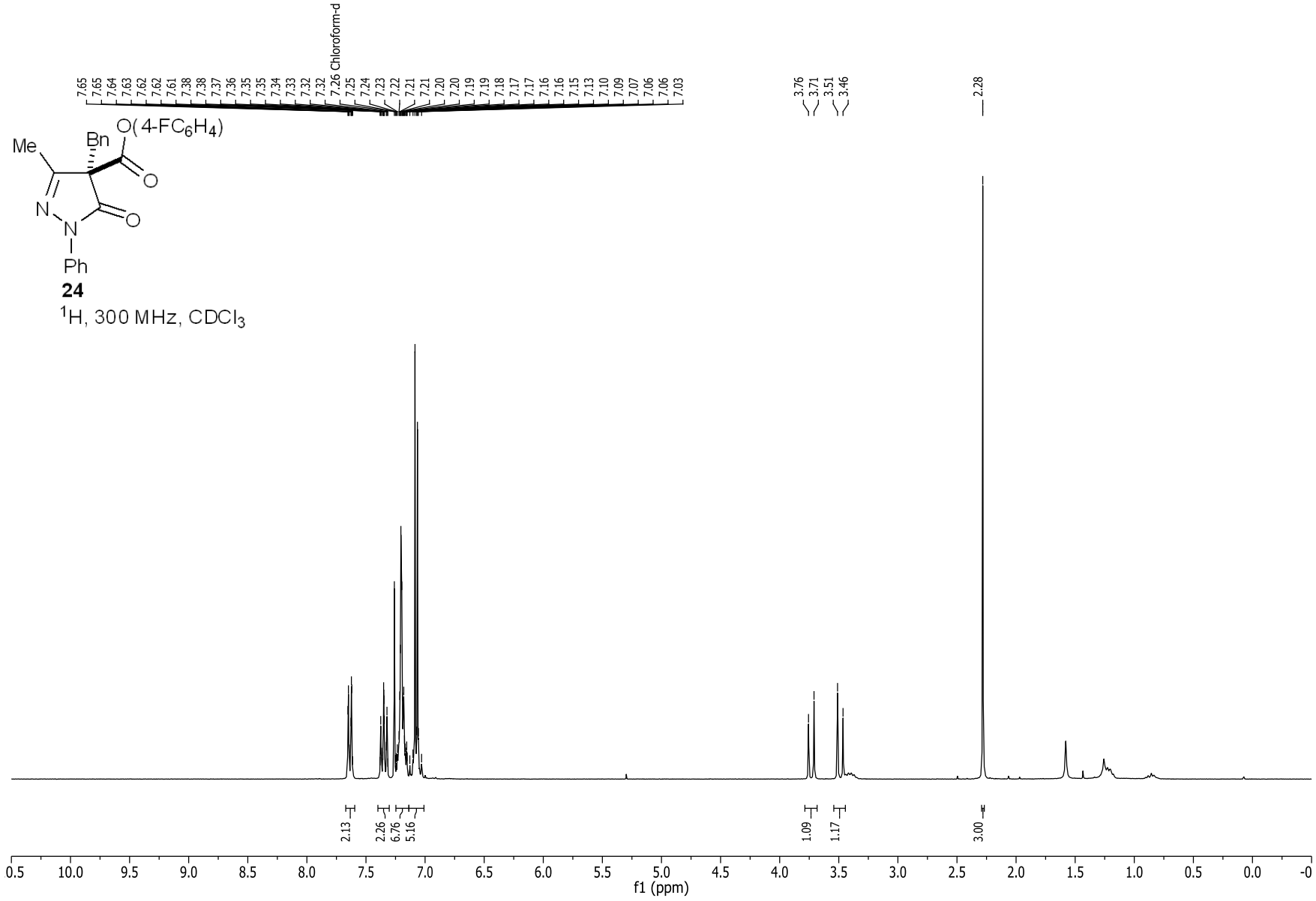

172.430
166.234
156.542
150.310
130.777
129.794
129.602
129.291
126.579
125.964
121.292
58.357
32.038
18.790
Ph
Me
OPh
O
N
N
O
Me
21
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

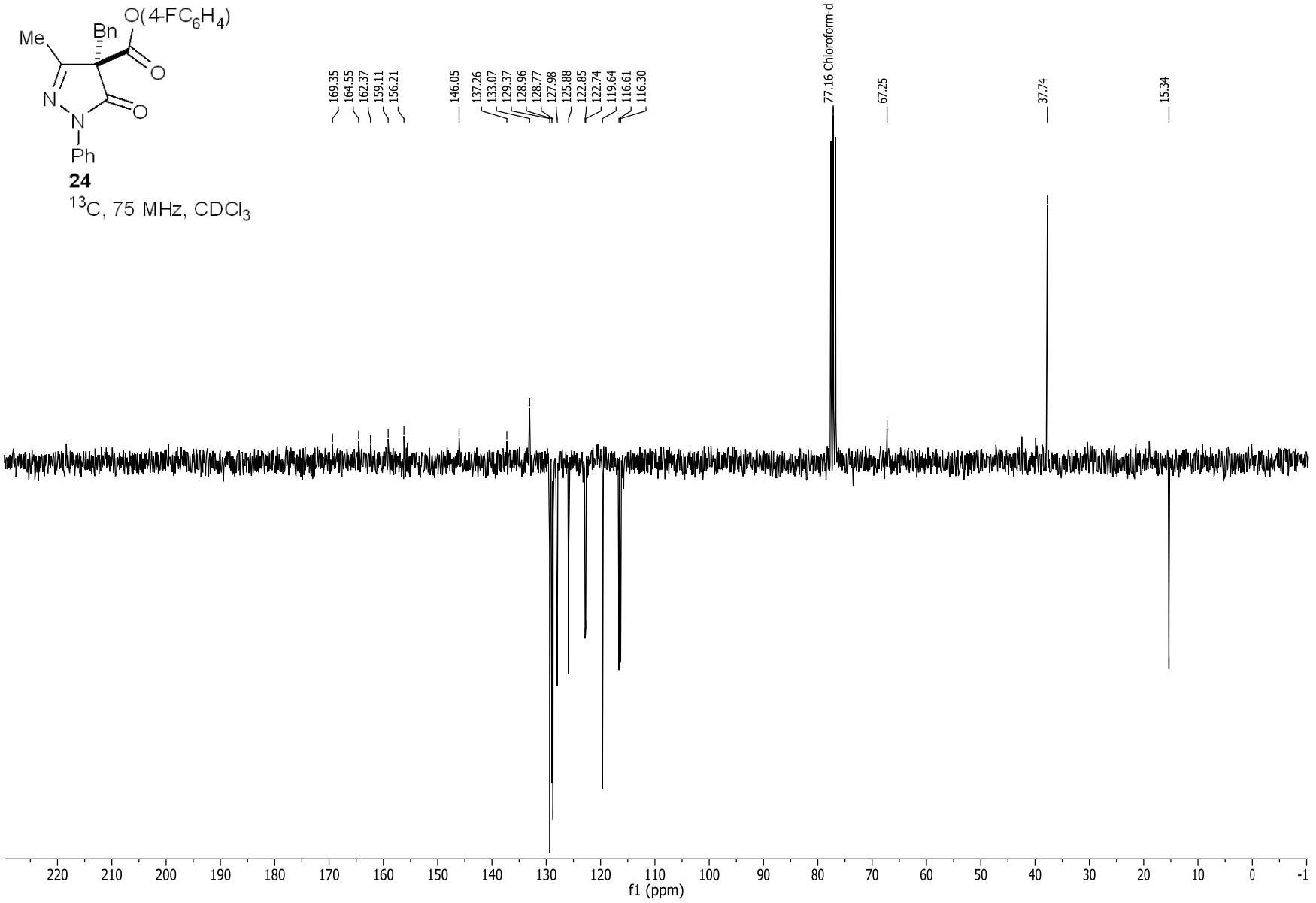

Me
Me
O(4-FC6H4)
O
N
N
O
Me
22
1H, 400 MHz, CDCl3
7.26 Chloroform-d
7.08
7.07
7.07
7.06
7.05
7.04
7.04
7.04
7.03
7.03
7.03
7.02
7.02
7.01
7.01
7.01
7.01
7.00
7.00
7.00
3.36
2.13
1.60
4.08
3.00
3.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

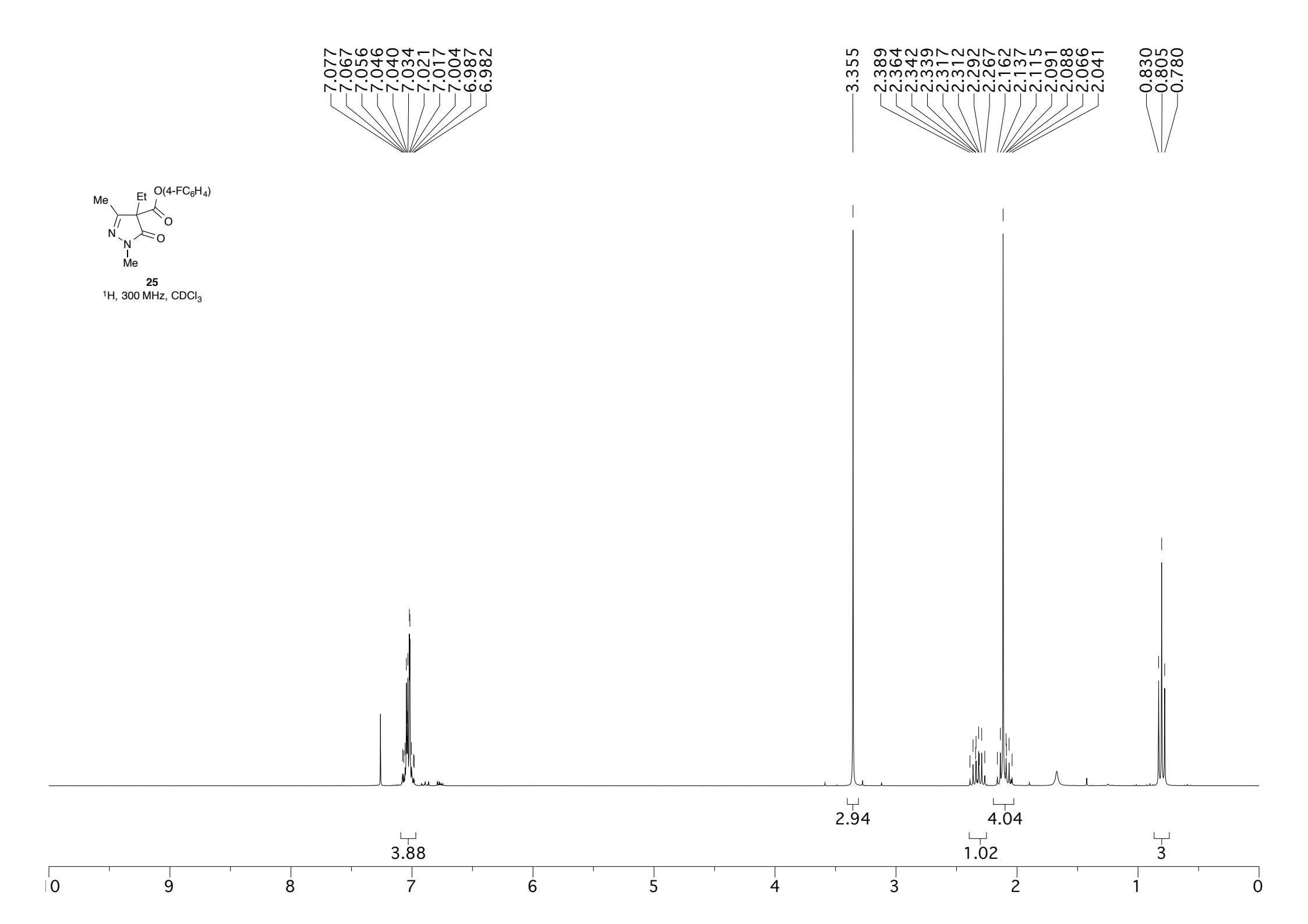

Me
Me
O(4-FC6H4)
O
O
N
N
Me
22
13C, 100 MHz, CDCl3
172.05
165.28
161.66
159.71
157.51
146.07
146.05
122.83
122.76
116.48
116.30
77.16 Chloroform-d
59.79
31.64
16.96
14.21
f1 (ppm)

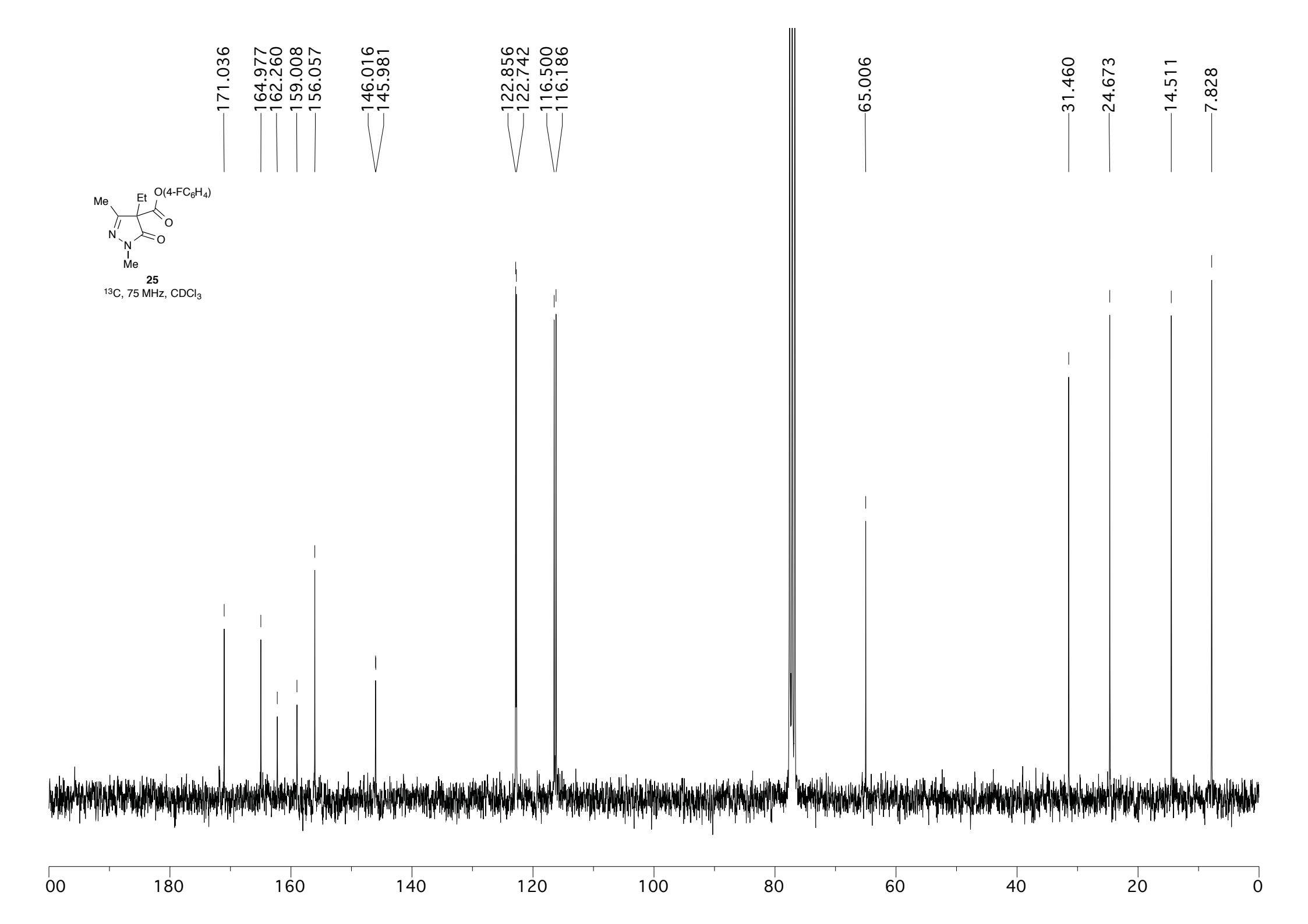

7.957
7.953
7.946
7.934
7.931
7.928
7.924
7.916
7.463
7.456
7.449
7.439
7.431
7.429
7.426
7.421
7.409
7.403
7.396
7.254
7.250
7.246
7.230
7.225
7.220
7.204
7.200
7.197
7.056
7.054
7.034
2.513
2.487
2.466
2.462
2.440
2.437
2.415
2.390
2.269
2.244
2.236
2.222
2.219
2.197
2.194
2.172
2.147
0.910
0.885
0.860
Me
Et
O(4-FC6H4)
O
O
N
N
Ph
23
1H, 500 MHz, CDCl3
2
1.93
1.02
3.25
1.93
1.25
2
4
0
9
8
7
6
5
4
3
2
1
0

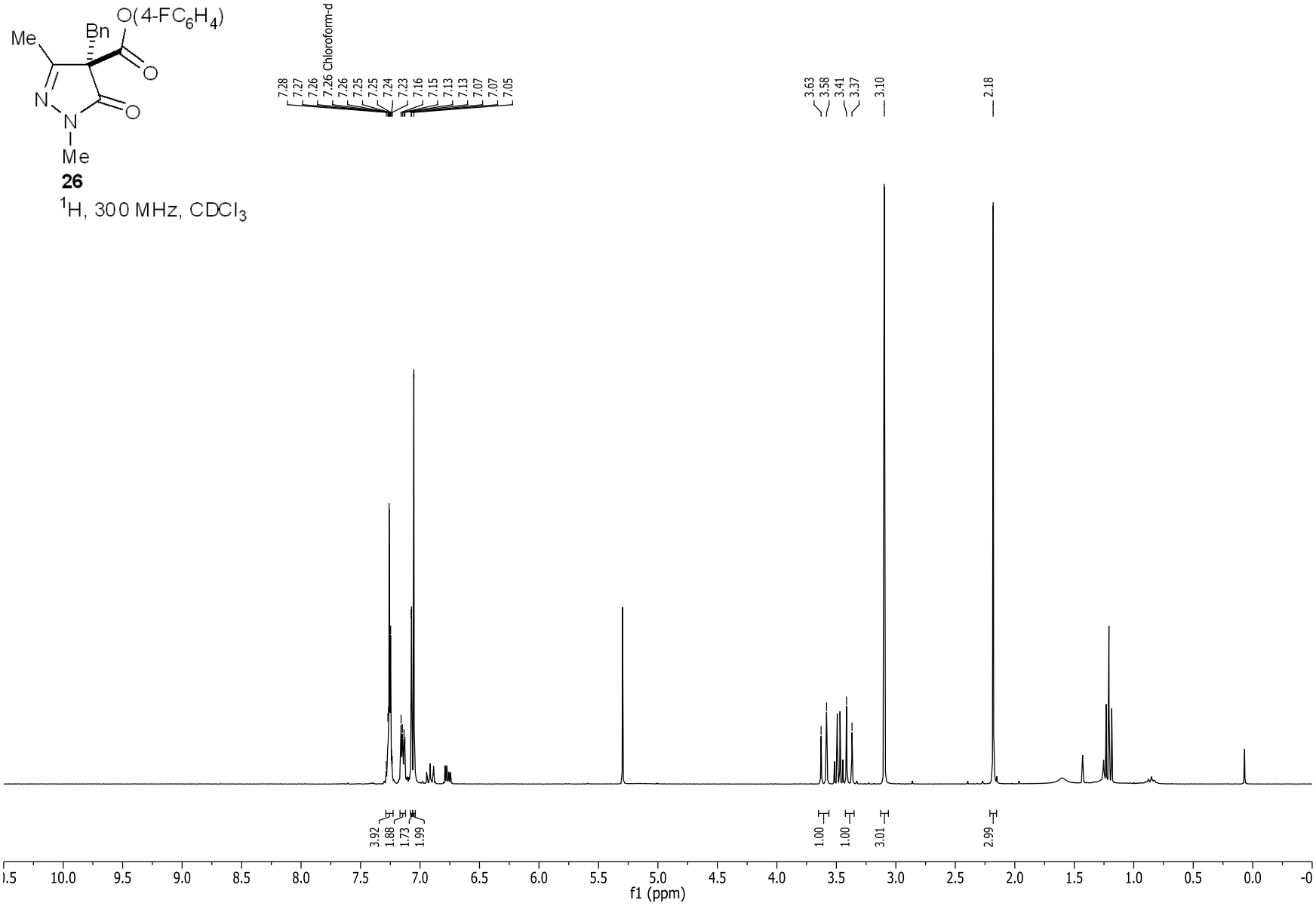

169.449
164.732
162.292
159.039
156.794
146.022
145.984
137.687
129.089
125.667
122.831
122.717
119.057
116.531
116.218
66.691
25.137
14.682
7.917
Me
Et
O(4-FC6H4)
O
O
N
N
Ph
23
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

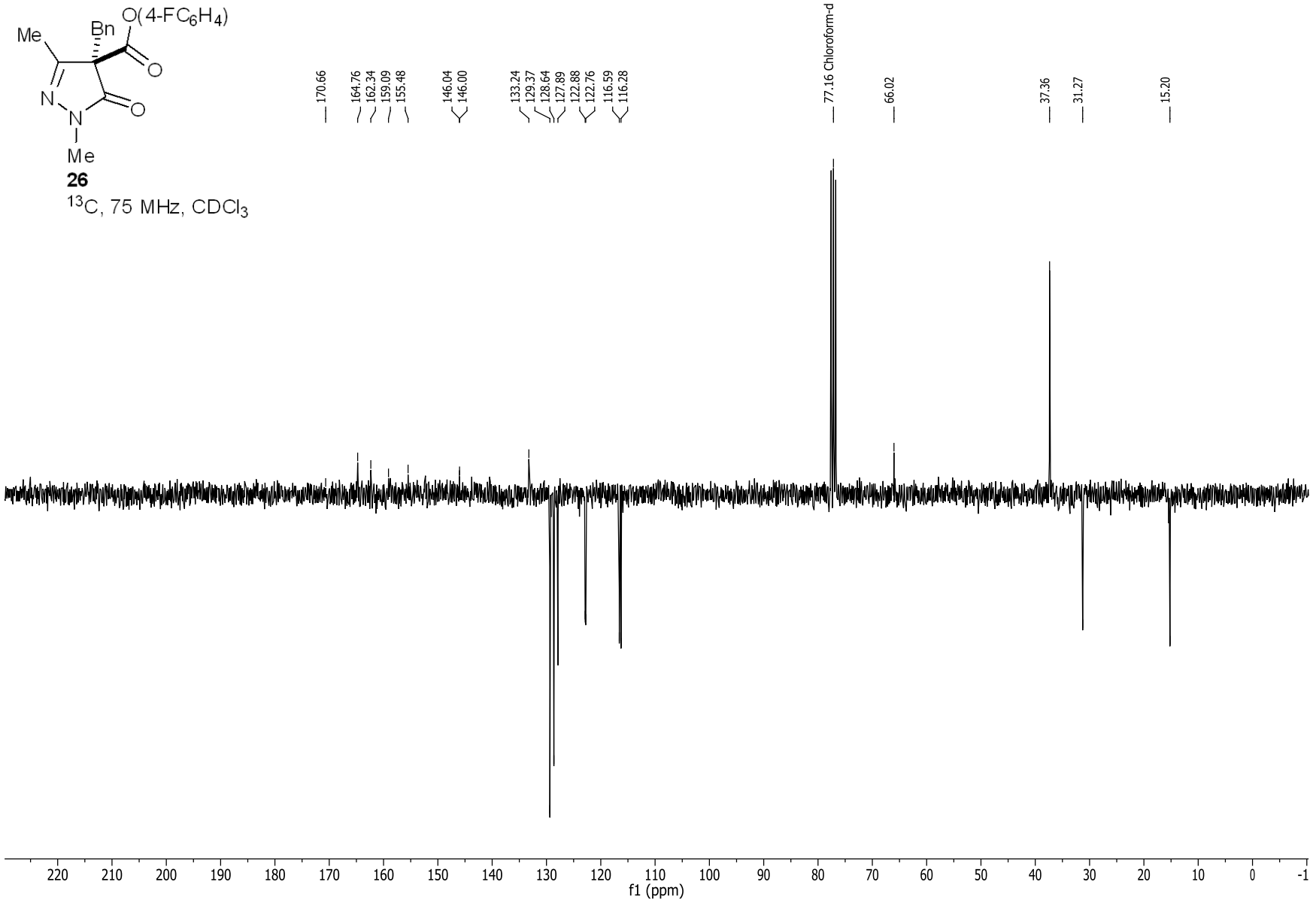

Chloroform-d
7.65 7.65 7.64 7.63 7.62 7.62 7.61 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.13 7.10 7.09 7.07 7.06 7.06 7.03
3.76 3.71 3.51 3.46
2.28
O(4-FC6H4)
Bn
Me
O
O
N
N
Ph
24
1H, 300 MHz, CDCl3
2.13 2.26 6.76 5.16 1.09 1.17 3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

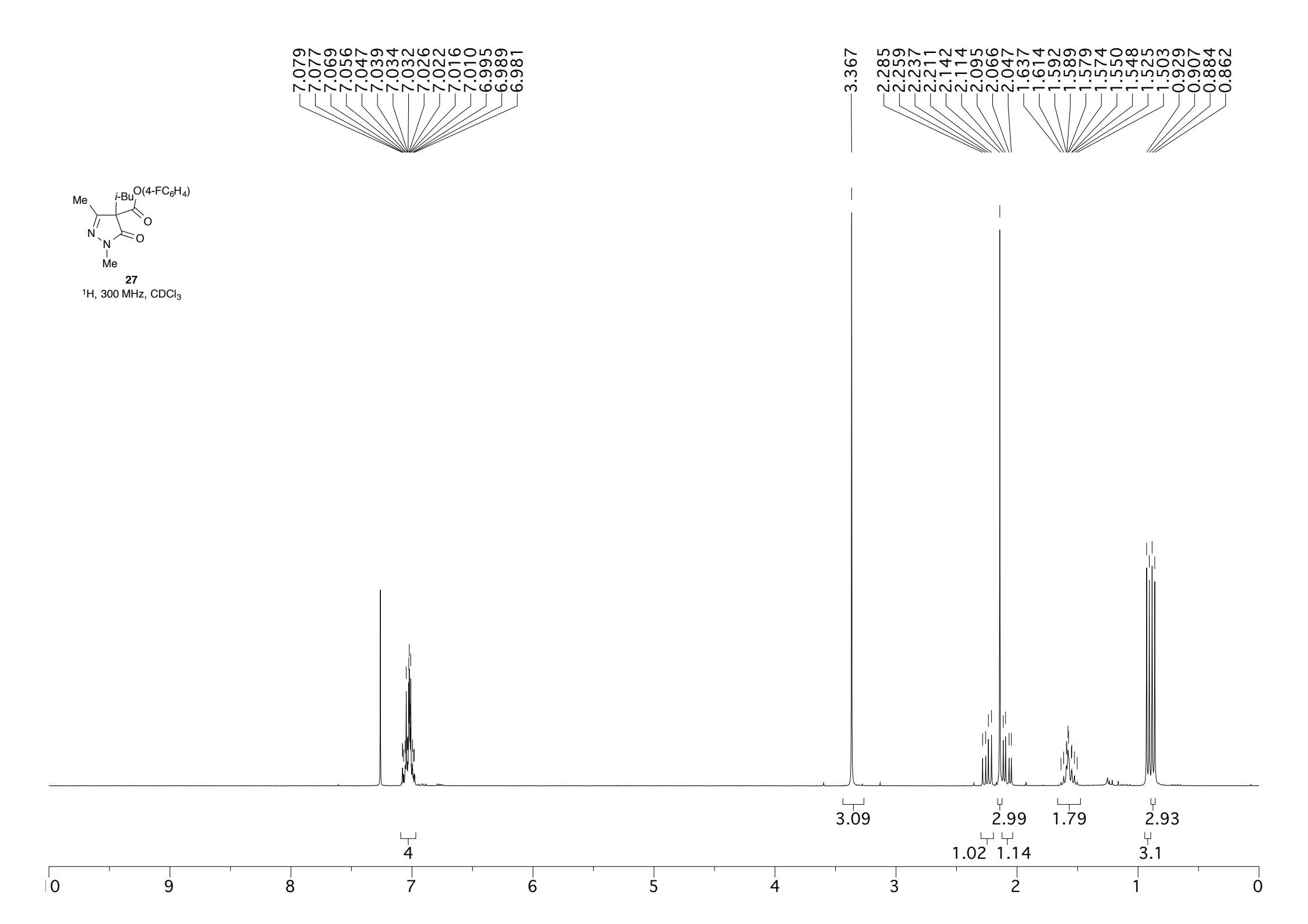

O(4-FC6H4)
Bn
Me
O
N
N
O
Ph
24
13C, 75 MHz, CDCl3
169.35
164.55
162.37
159.11
156.21
146.05
137.26
133.07
129.37
128.96
128.77
127.98
125.88
122.85
122.74
119.64
116.61
116.30
77.16 Chloroform-d
67.25
37.74
15.34
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

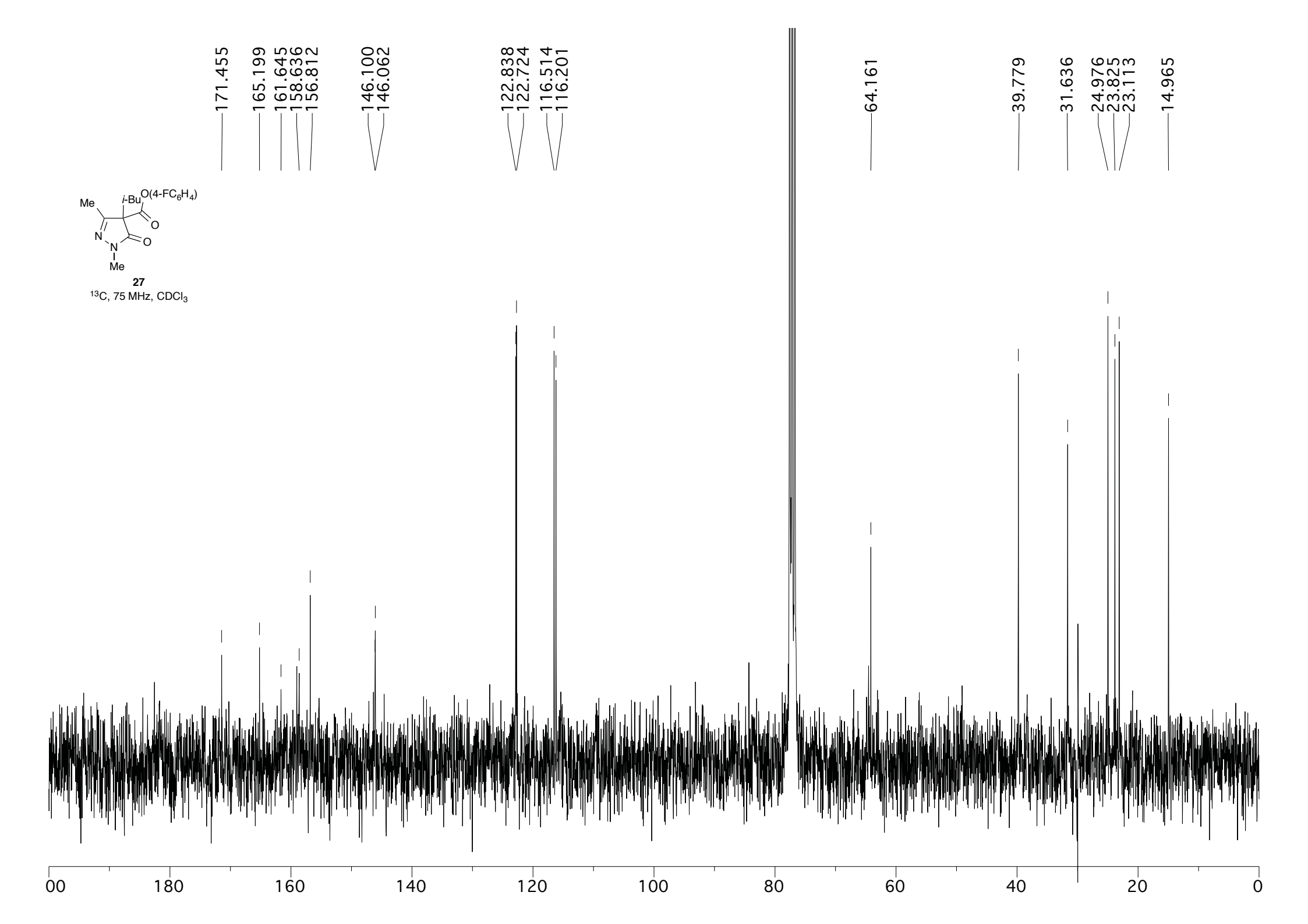

7.077
7.067
7.056
7.046
7.040
7.034
7.021
7.017
7.004
6.987
6.982
3.355
2.389
2.364
2.342
2.339
2.317
2.312
2.292
2.267
2.162
2.137
2.115
2.091
2.088
2.066
2.041
0.830
0.805
0.780
Me
Et
O(4-FC6H4)
O
O
N
N
Me
25
1H, 300 MHz, CDCl3
2.94
4.04
3.88
1.02
3
0
9
8
7
6
5
4
3
2
1
0

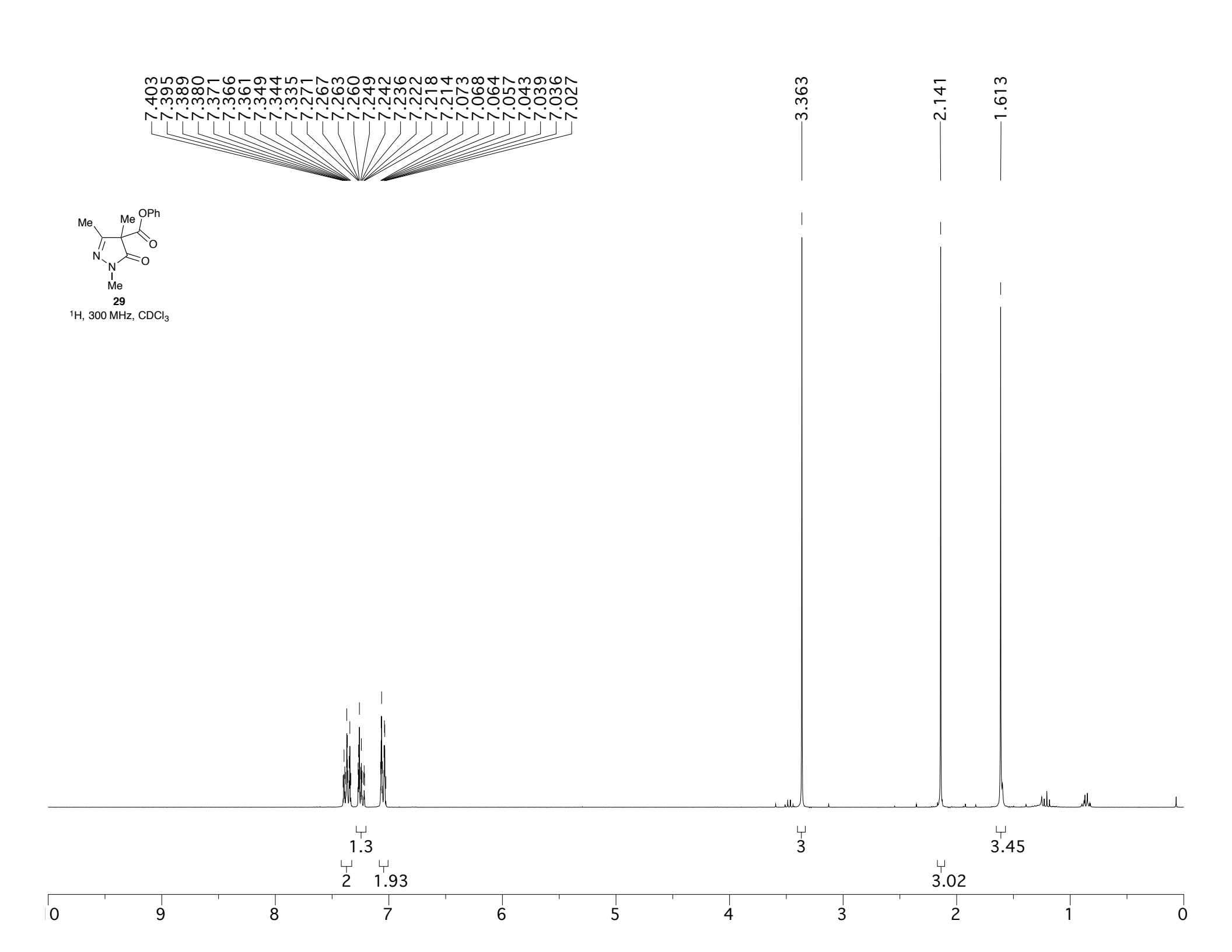

171.036
164.977
162.260
159.008
156.057
146.016
145.981
122.856
122.742
116.500
116.186
65.006
31.460
24.673
14.511
7.828
Me
Et
O(4-FC6H4)
O
O
N
N
Me
25
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

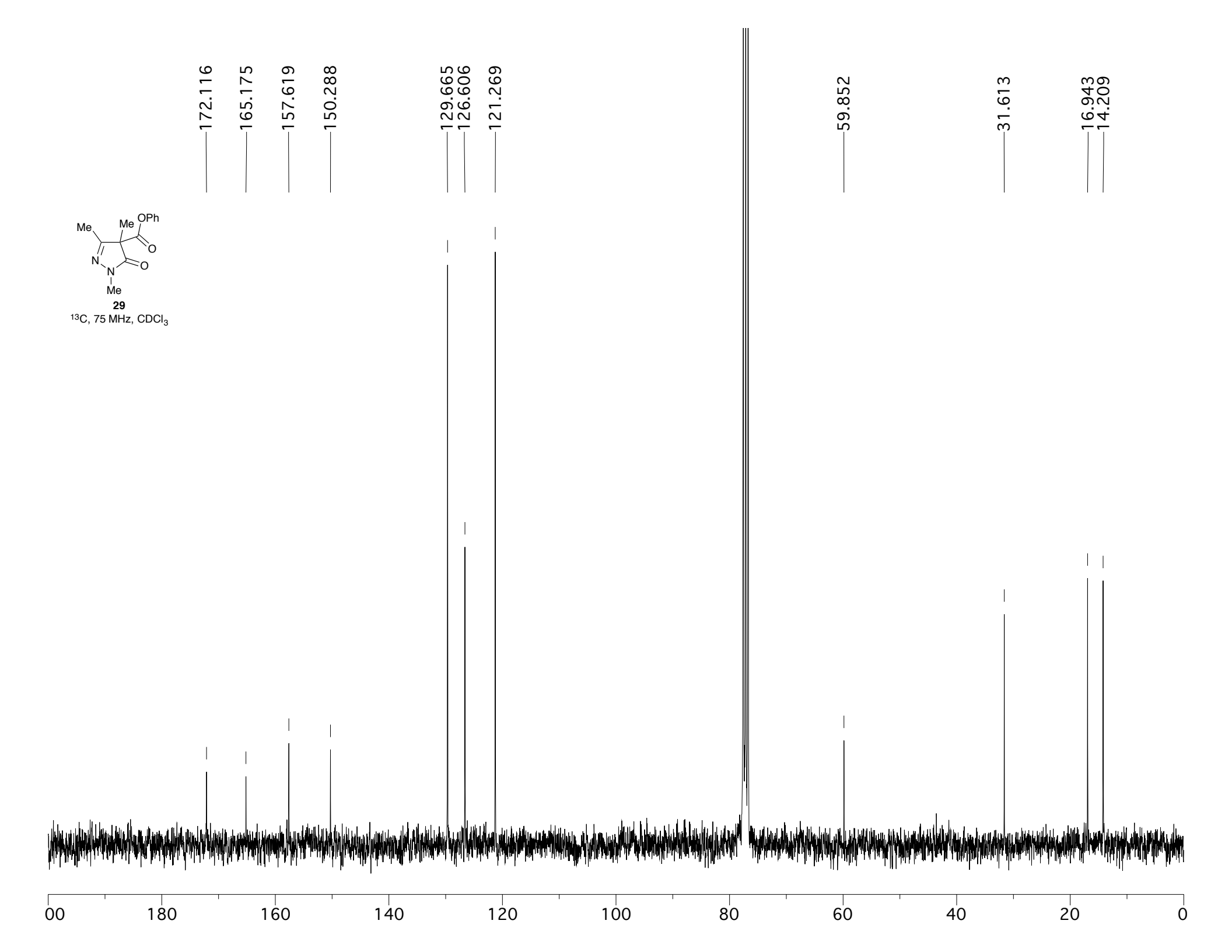

Me
Bn
O(4-FC6H4)
O
N
N
O
Me
26
1H, 300 MHz, CDCl3
Chloroform-d
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.16
7.15
7.13
7.07
7.07
7.05
3.63
3.58
3.41
3.37
3.10
2.18
3.92
1.88
1.73
1.99
1.00
1.00
3.01
2.99
f1 (ppm)

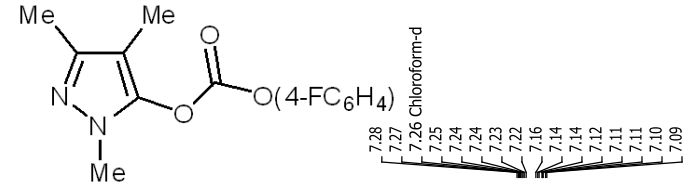

Me
Bn
O(4-FC6H4)
O
N
N
O
Me
26
13C, 75 MHz, CDCl3
170.66
164.76
162.34
159.09
155.48
146.04
146.00
133.24
129.37
128.64
127.89
122.88
122.76
116.59
116.28
77.16 Chloroform-d
66.02
37.36
31.27
15.20
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.079
7.077
7.069
7.056
7.047
7.039
7.034
7.032
7.026
7.022
7.016
7.010
6.995
6.989
6.981
3.367
2.285
2.259
2.237
2.211
2.142
2.114
2.095
2.066
2.047
1.637
1.614
1.592
1.589
1.579
1.574
1.550
1.548
1.525
1.503
0.929
0.907
0.884
0.862
Me
i-Bu
O(4-FC6H4)
O
O
N
N
Me
27
1H, 300 MHz, CDCl3
3.09
2.99
1.79
2.93
4
1.02
1.14
3.1
0
9
8
7
6
5
4
3
2
1
0


171.455
165.199
161.645
158.636
156.812
146.100
146.062
122.838
122.724
116.514
116.201
64.161
39.779
31.636
24.976
23.825
23.113
14.965
Me
i-Bu
O(4-FC6H4)
O
O
N
N
Me
27
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

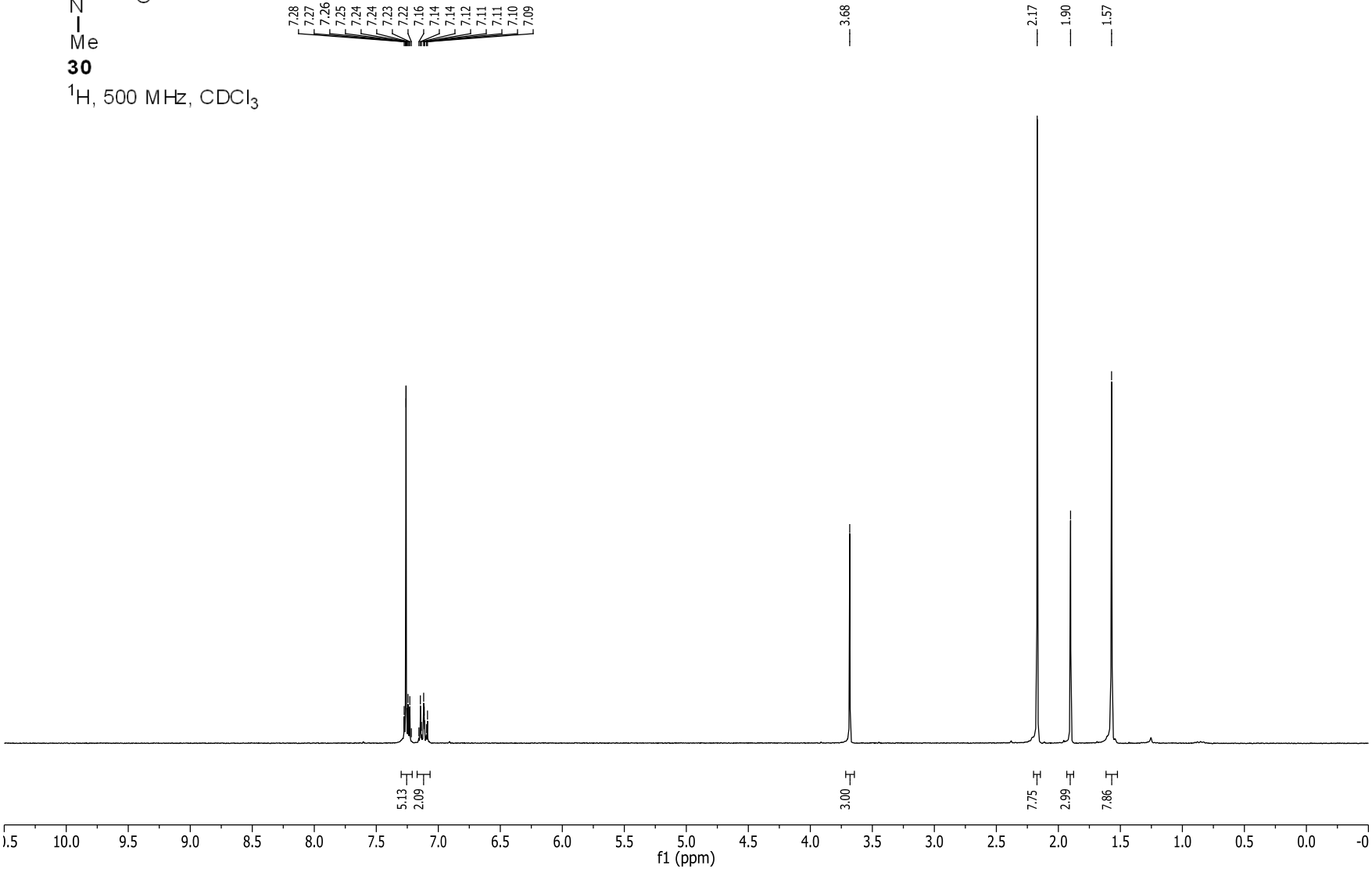

7.403
7.395
7.389
7.380
7.371
7.366
7.361
7.349
7.344
7.335
7.271
7.267
7.263
7.260
7.249
7.242
7.236
7.222
7.218
7.214
7.073
7.068
7.064
7.057
7.043
7.039
7.036
7.027
3.363
2.141
1.613
Me
Me
OPh
O
N
O
N
Me
29
1H, 300 MHz, CDCl3
1.3
3
3.45
2
1.93
3.02
0
9
8
7
6
5
4
3
2
1
0

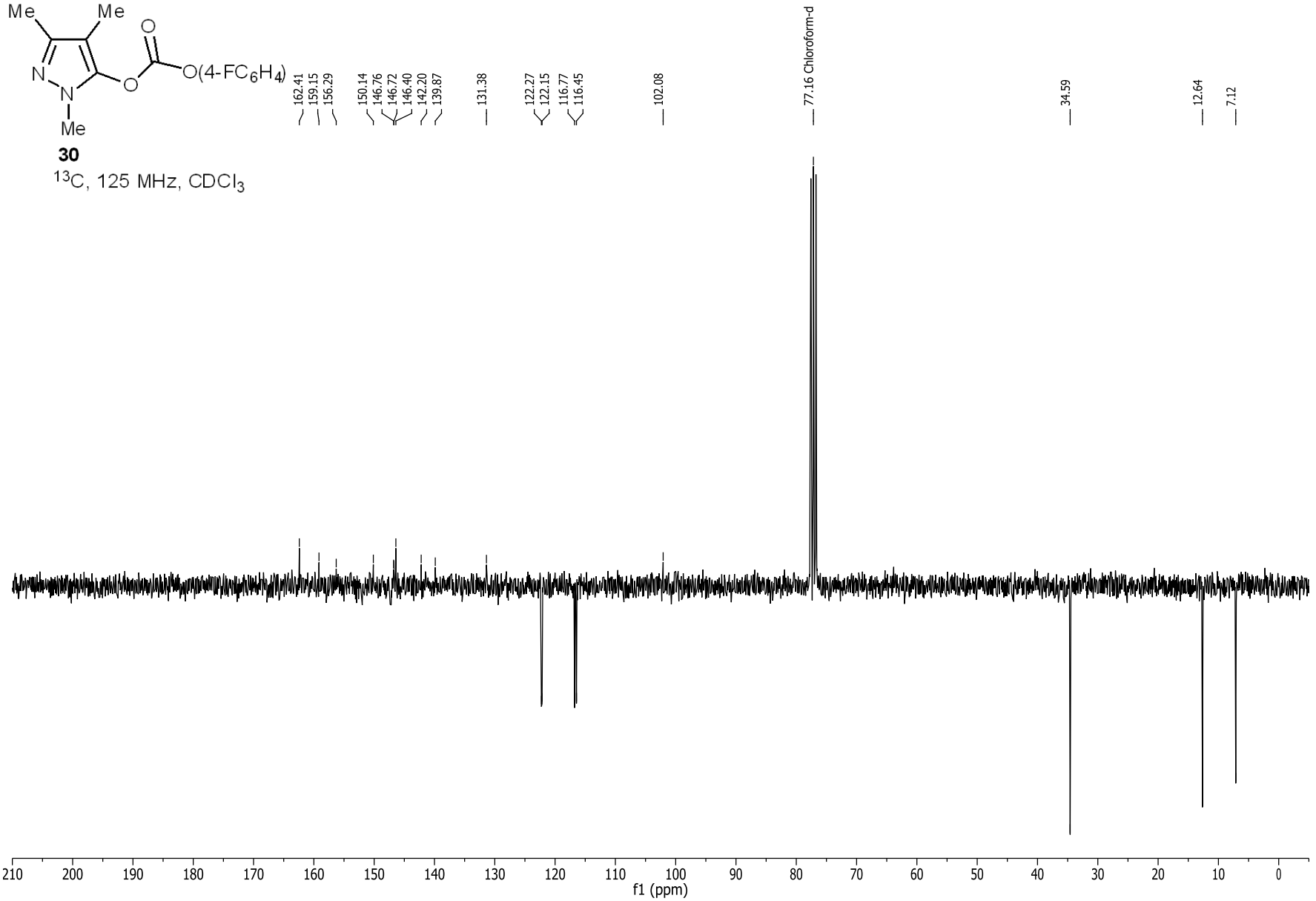

172.116
165.175
157.619
150.288
129.665
126.606
121.269
59.852
31.613
16.943
14.209
Me
Me
OPh
O
O
N
N
Me
29
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

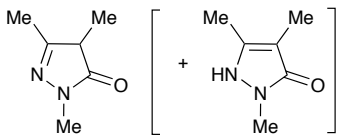


30

^{1}H, 500 MHz, $CDCl_3$

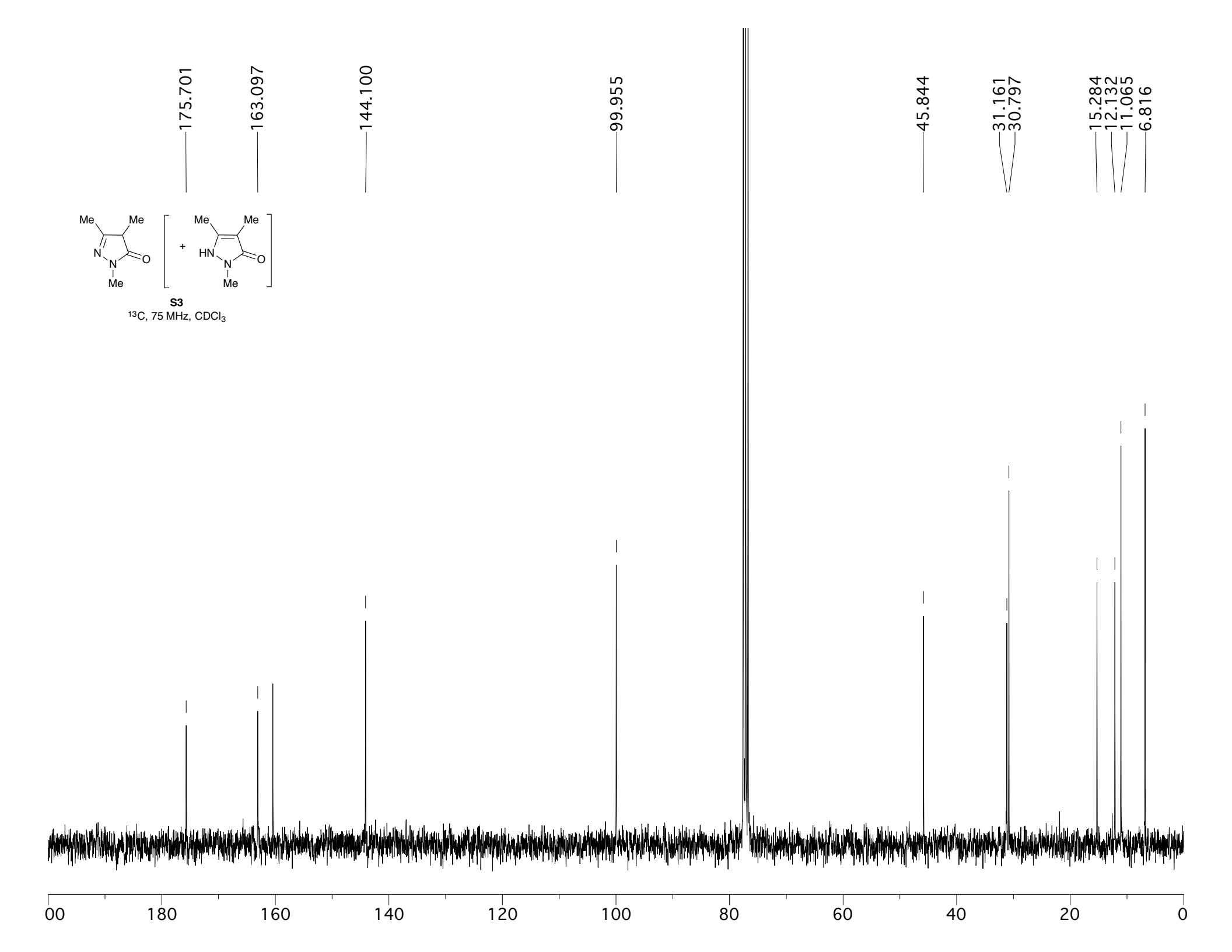



Me
Me
O
N
N
O
O(4-FC6H4)
Me
30
13C, 125 MHz, CDCl3
162.41
159.15
156.29
150.14
146.76
146.72
146.40
142.20
139.87
131.38
122.27
122.15
116.77
116.45
102.08
77.16 Chloroform-d
34.59
12.64
7.12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



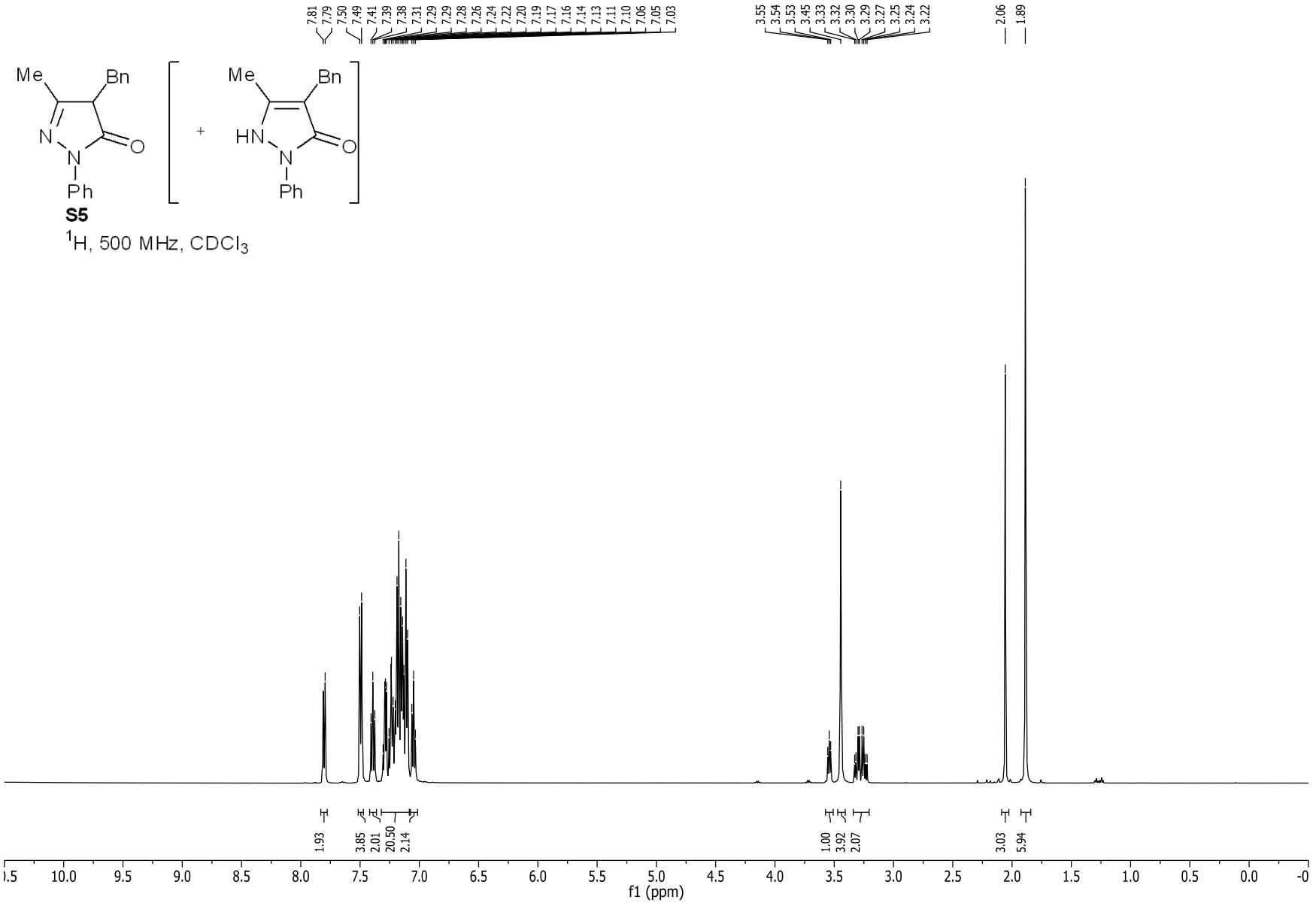
S3

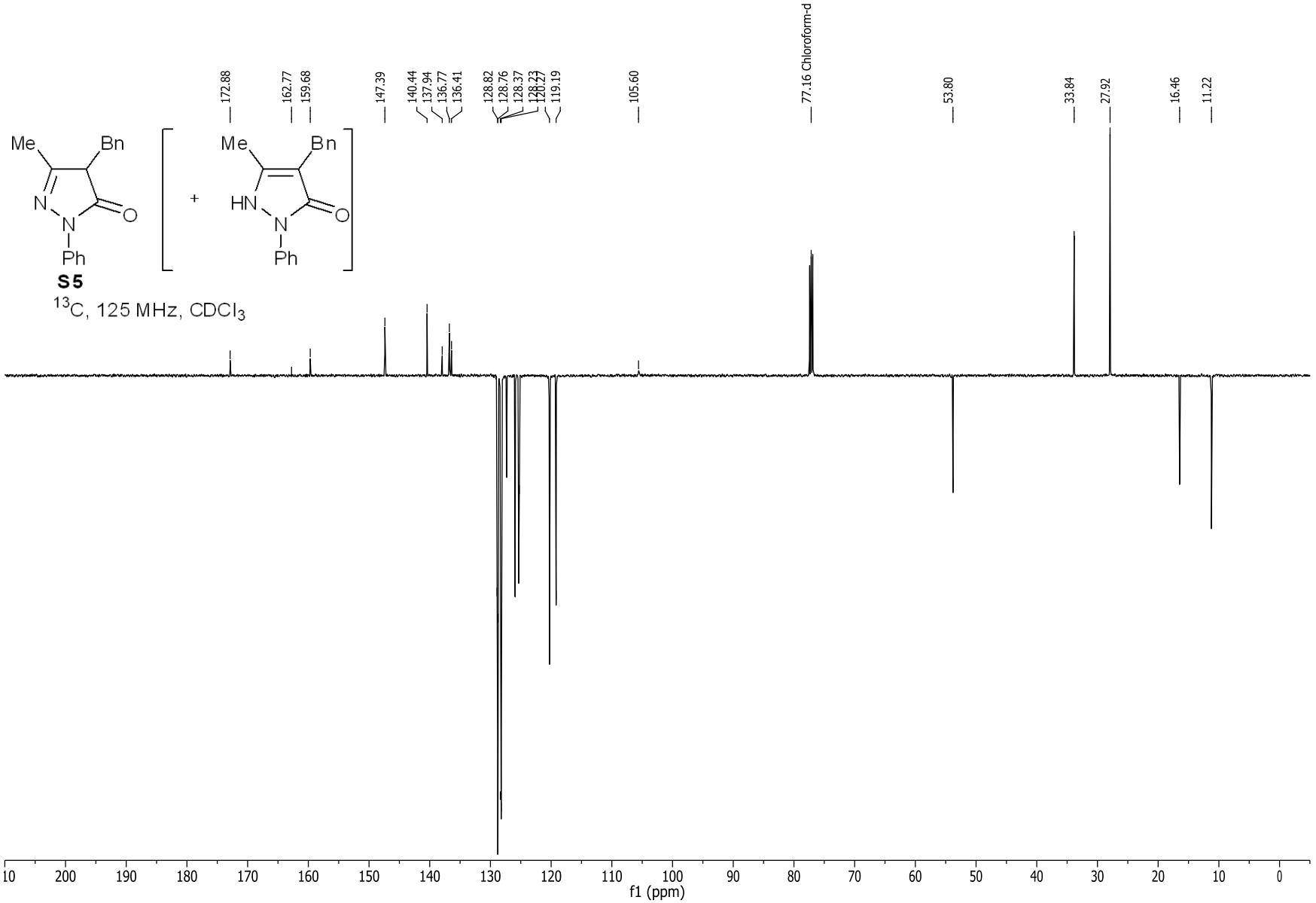
^{1}H, 300 MHz, $CDCl_3$

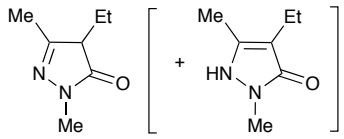


S3

^{13}C, 75 MHz, $CDCl_3$

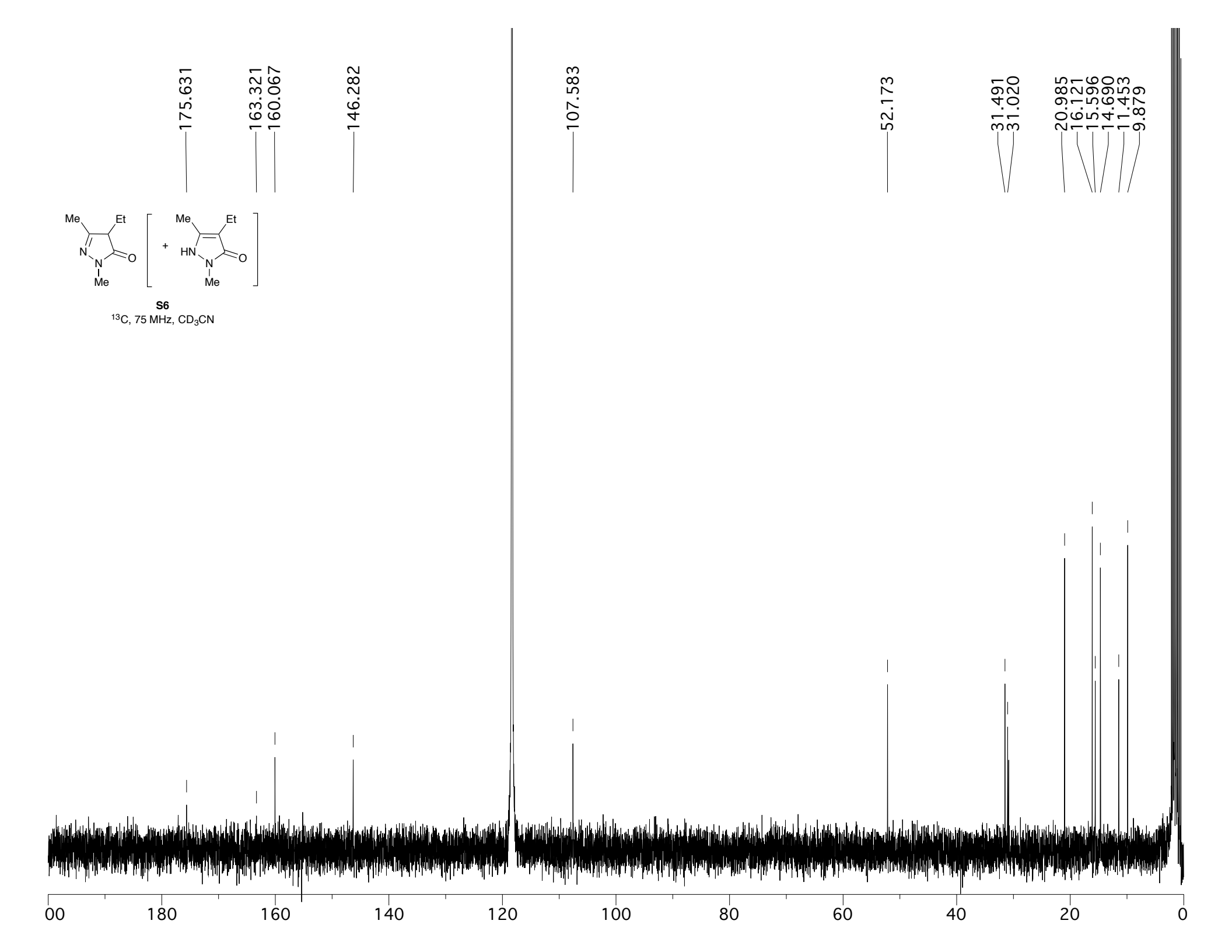

Me
Bn
N
N
O
Ph
+
Me
Bn
HN
N
O
Ph
S5
1H, 500 MHz, CDCl3
7.81
7.79
7.50
7.49
7.41
7.39
7.38
7.31
7.29
7.29
7.28
7.26
7.24
7.22
7.20
7.19
7.17
7.16
7.14
7.13
7.11
7.10
7.06
7.05
7.03
3.55
3.54
3.53
3.45
3.33
3.32
3.30
3.29
3.27
3.25
3.24
3.22
2.06
1.89
1.93
3.85
2.01
20.50
2.14
1.00
3.92
2.07
3.03
5.94
f1 (ppm)


172.88
162.77
159.68
147.39
140.44
137.94
136.77
136.41
128.82
128.76
128.37
128.23
128.17
119.19
105.60
77.16 Chloroform-d
53.80
33.84
27.92
16.46
11.22
Me
Bn
N
N
O
Ph
+
Me
Bn
HN
N
O
Ph
S5
13C, 125 MHz, CDCl3
f1 (ppm)



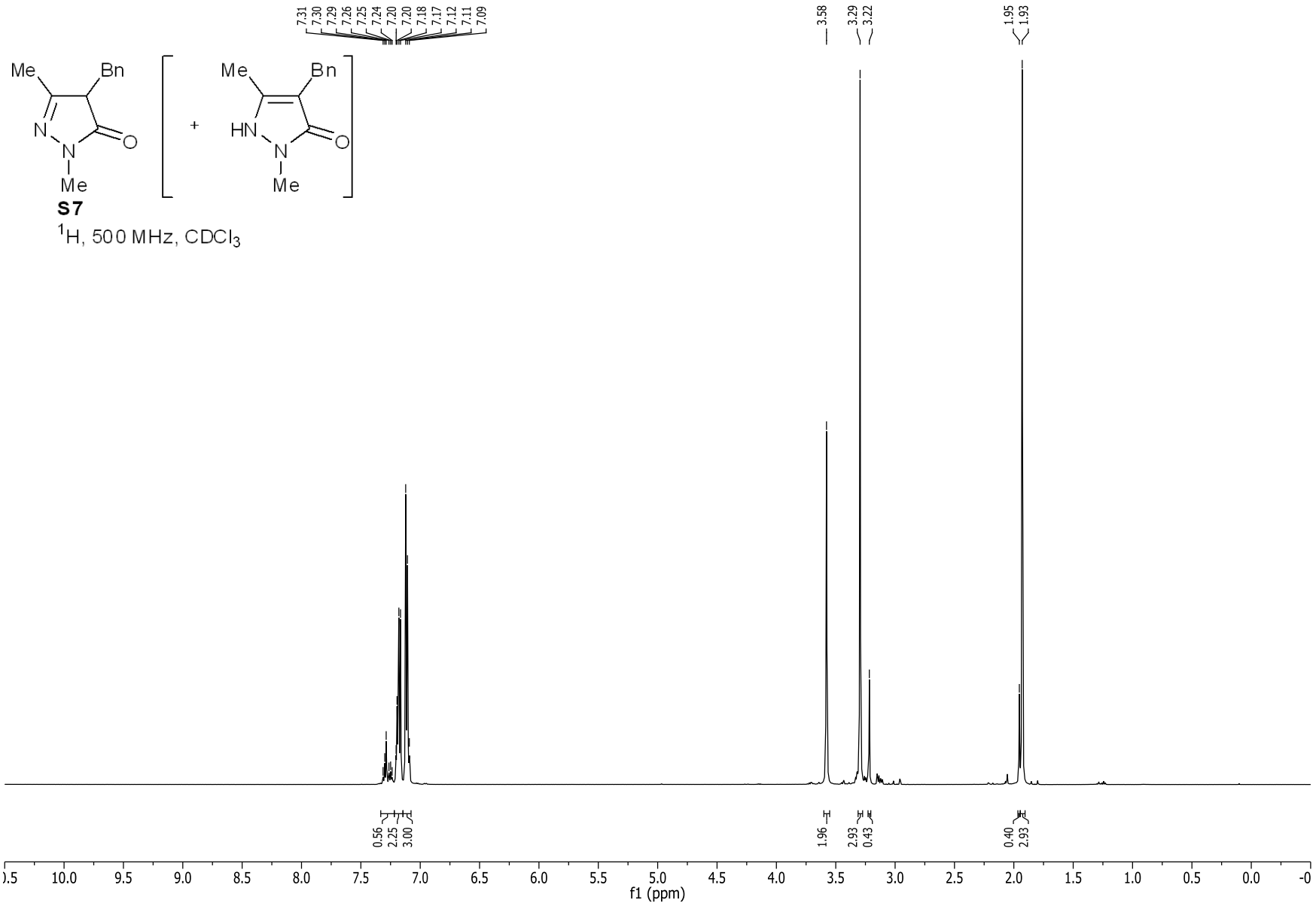
S6

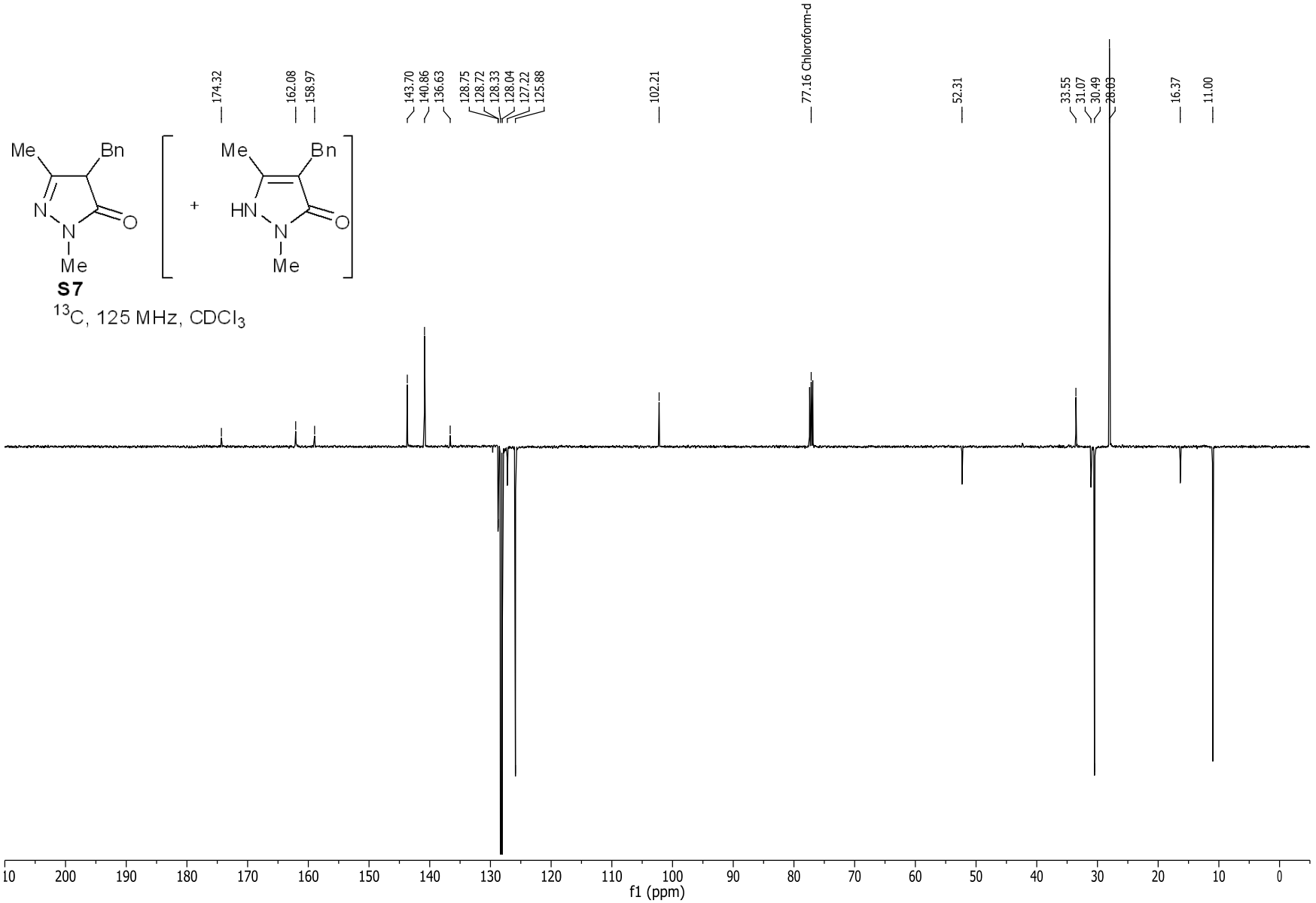
^{1}H, 100 MHz, CD_3CN

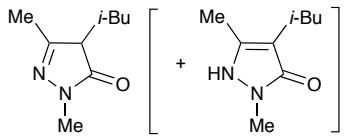


S6

^{13}C, 75 MHz, CD_3CN

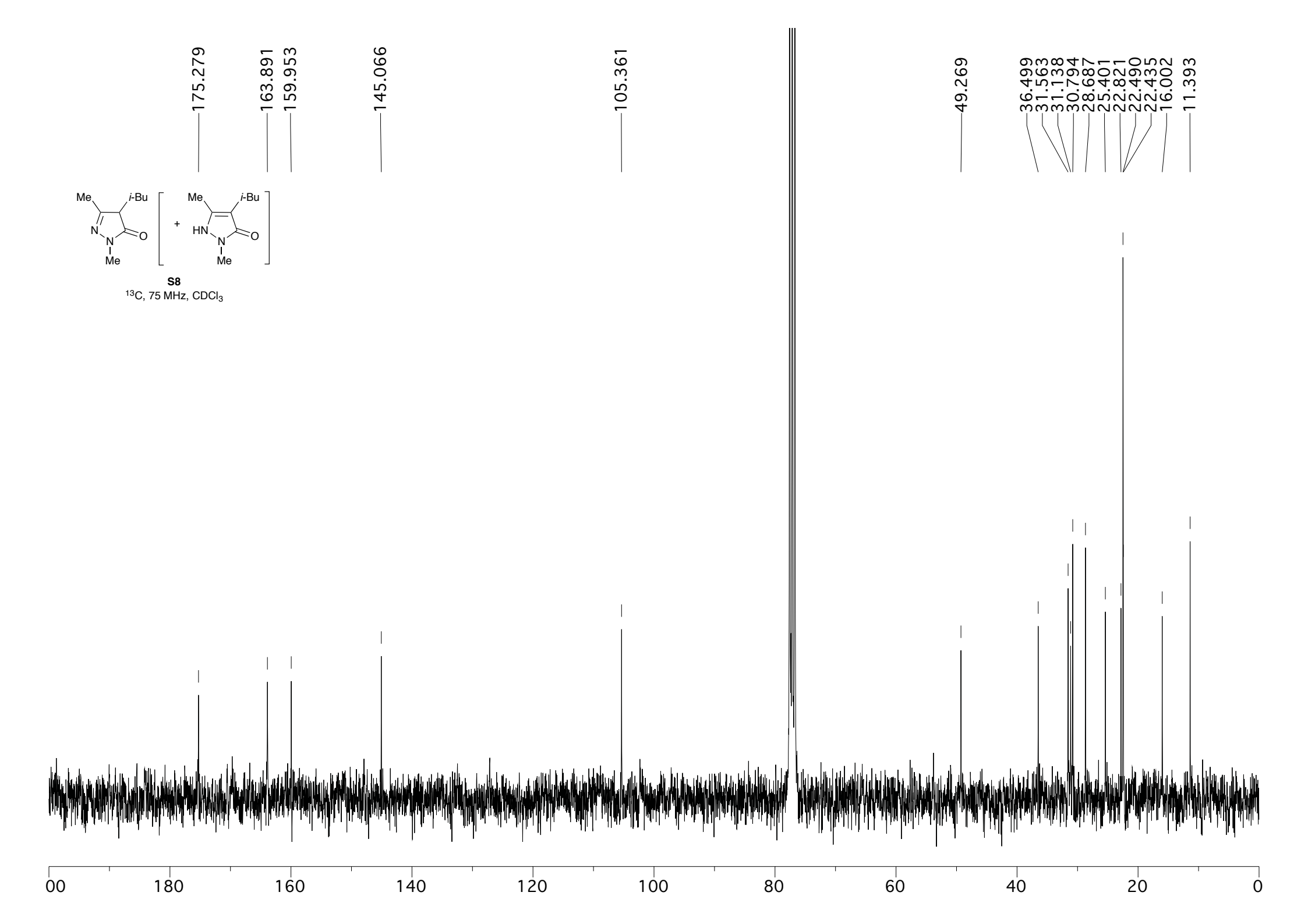

Me
Bn
N
N
O
Me
+
Me
Bn
HN
N
O
Me
S7
1H, 500 MHz, CDCl3
7.31
7.30
7.29
7.26
7.25
7.24
7.20
7.20
7.18
7.17
7.12
7.11
7.09
3.58
3.29
3.22
1.95
1.93
0.56
2.25
3.00
1.96
2.93
0.43
0.40
2.93
f1 (ppm)

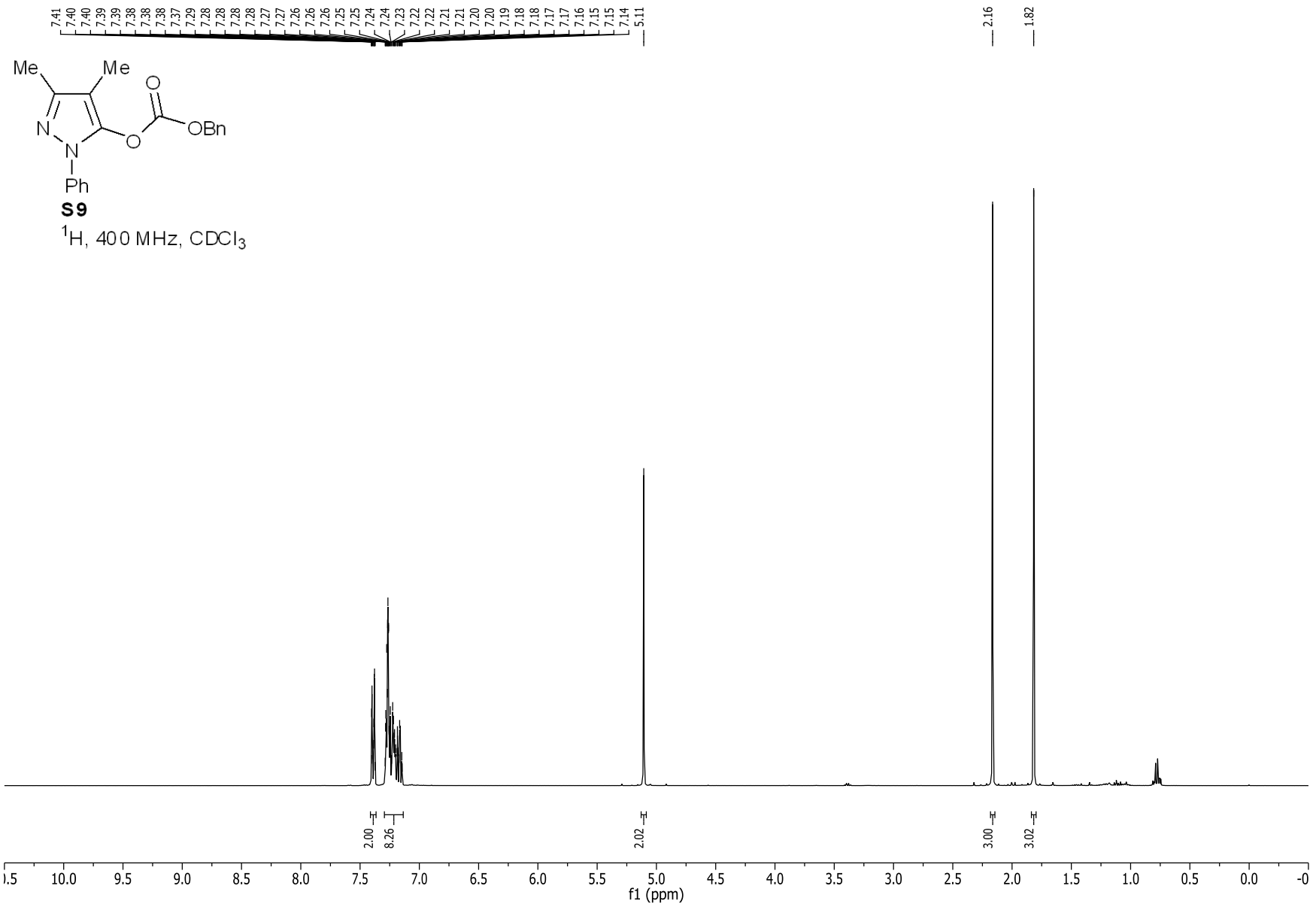

174.32
162.08
158.97
143.70
140.86
136.63
128.75
128.72
128.33
128.04
127.22
125.88
102.21
77.16 Chloroform-d
52.31
33.55
31.07
30.49
28.03
16.37
11.00
Me
Bn
N
N
O
Me
+
Me
Bn
HN
N
O
Me
S7
13C, 125 MHz, CDCl3
f1 (ppm)

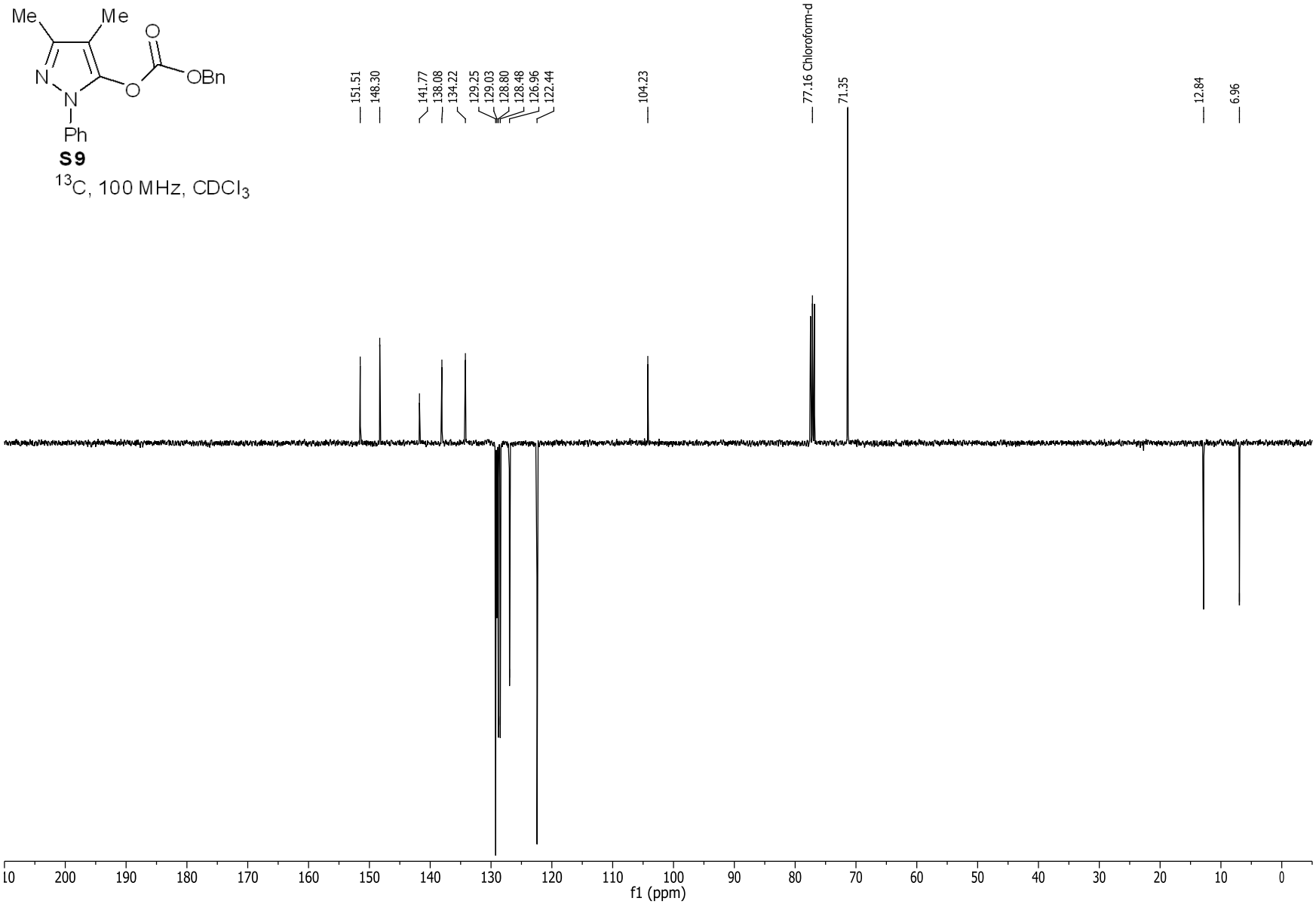


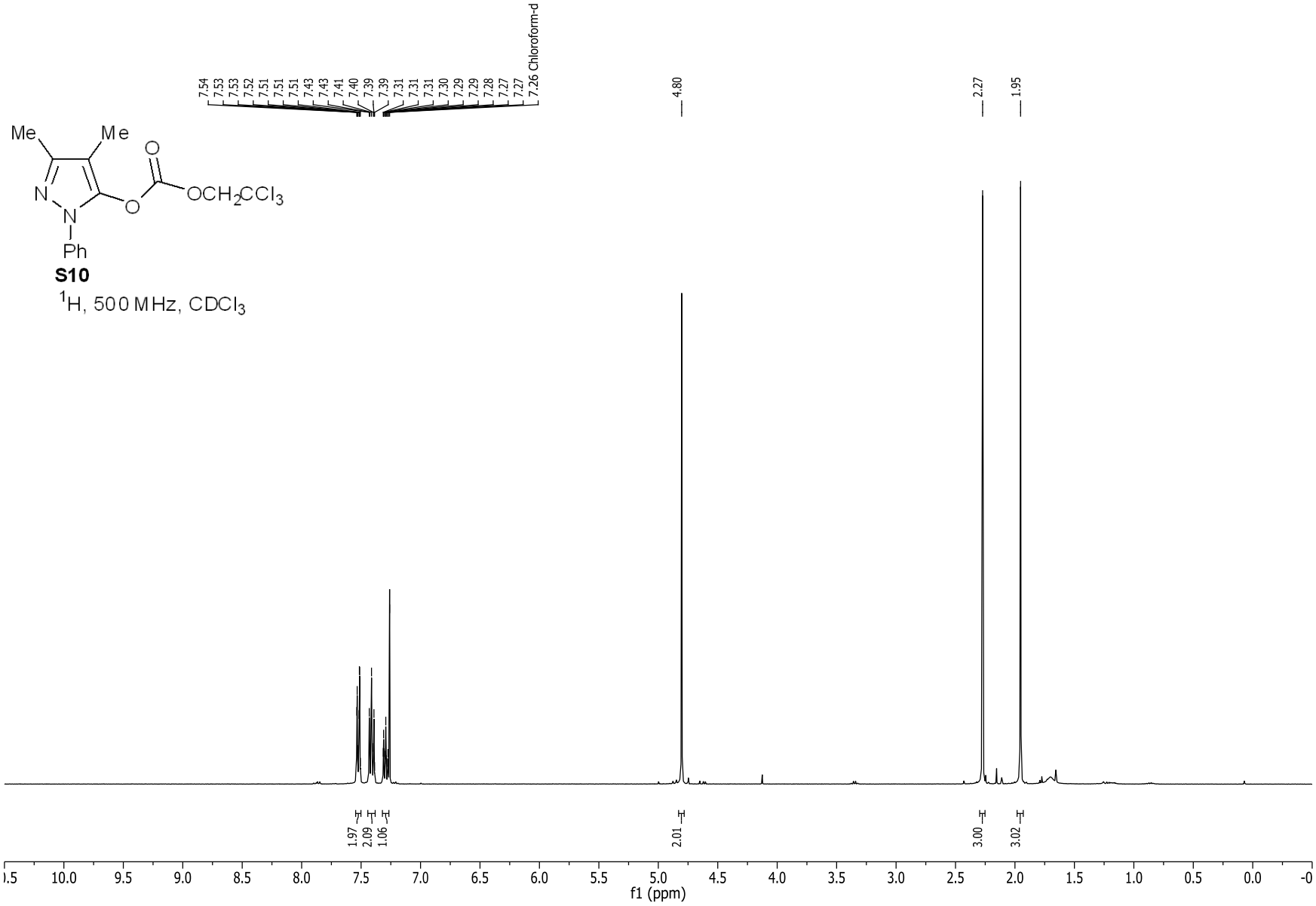
S8

^{1}H, 300 MHz, $CDCl_3$


175.279
163.891
159.953
145.066
105.361
49.269
36.499
31.563
31.138
30.794
28.687
25.401
22.821
22.490
22.435
16.002
11.393
Me
i-Bu
N
N
Me
O
+
HN
S8
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

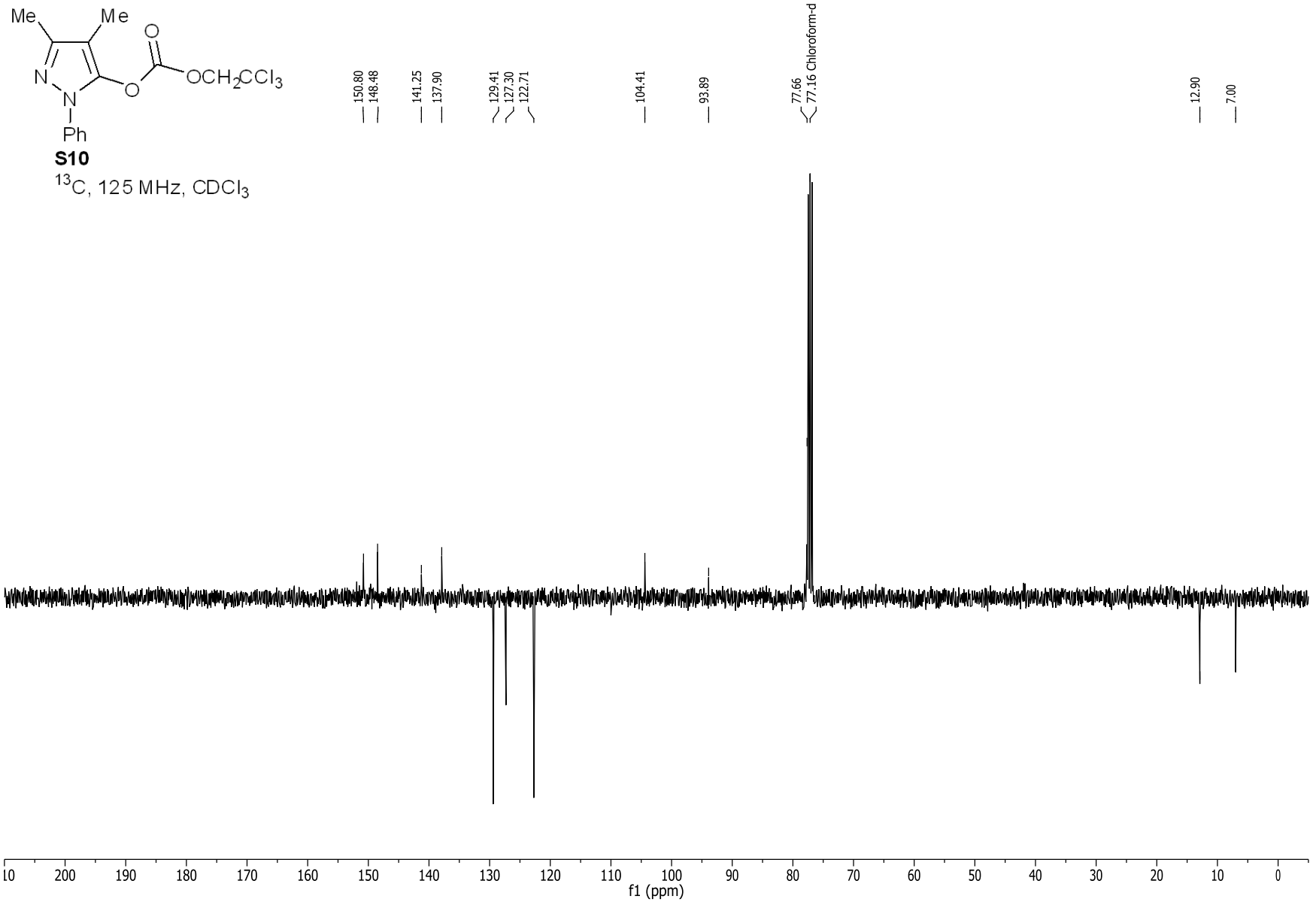

Me
Me
O
N
N
O
OBn
Ph
S9
1H, 400 MHz, CDCl3
7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.29 7.28 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.14 5.11
2.16
1.82
2.00
8.26
2.02
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
Me
O
N
N
O
OBn
Ph
S9
13C, 100 MHz, CDCl3
151.51
148.30
141.77
138.08
134.22
129.25
129.03
128.80
128.48
126.96
122.44
104.23
77.16 Chloroform-d
71.35
12.84
6.96
f1 (ppm)



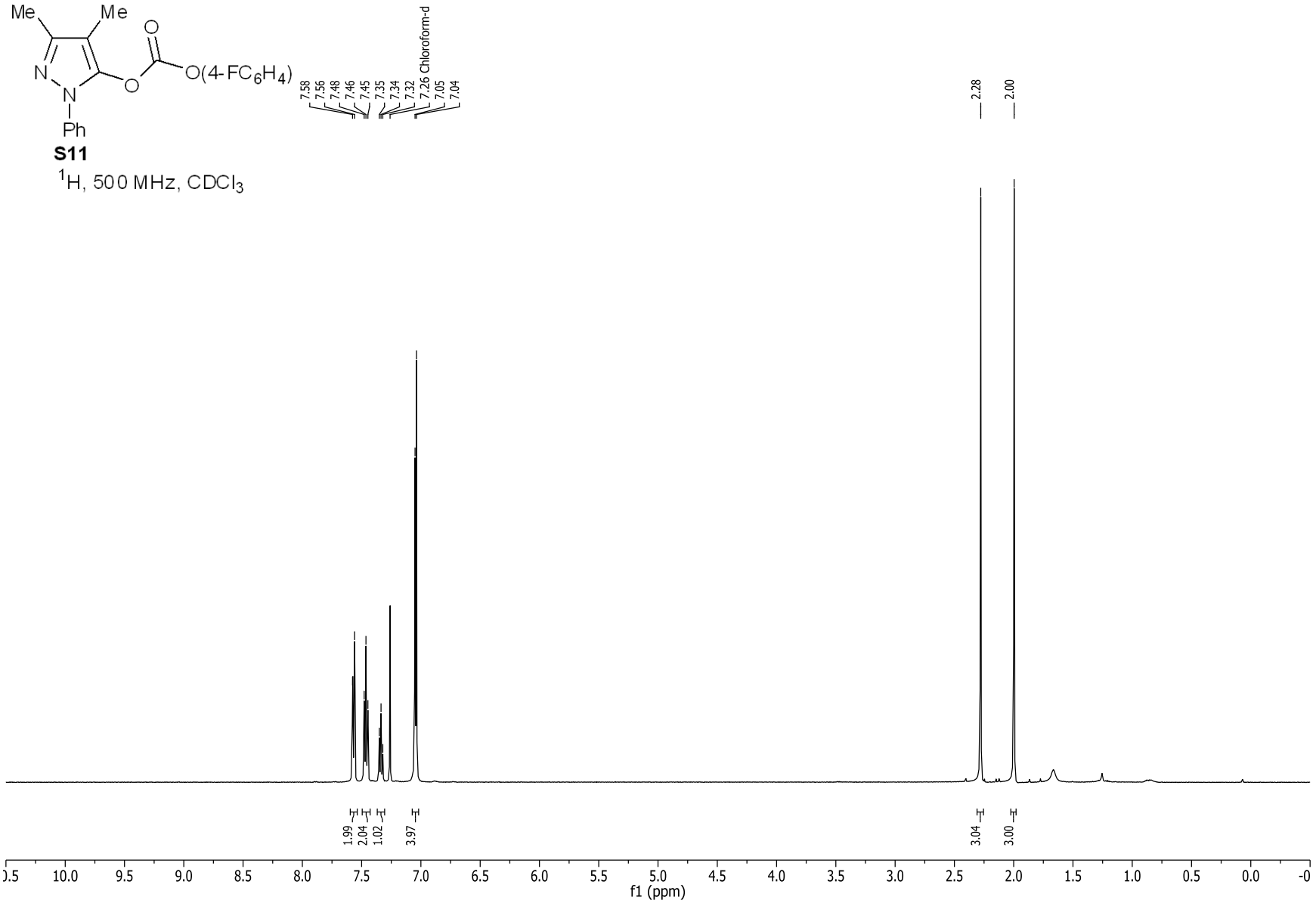
S10

^{1}H, 500 MHz, $CDCl_3$



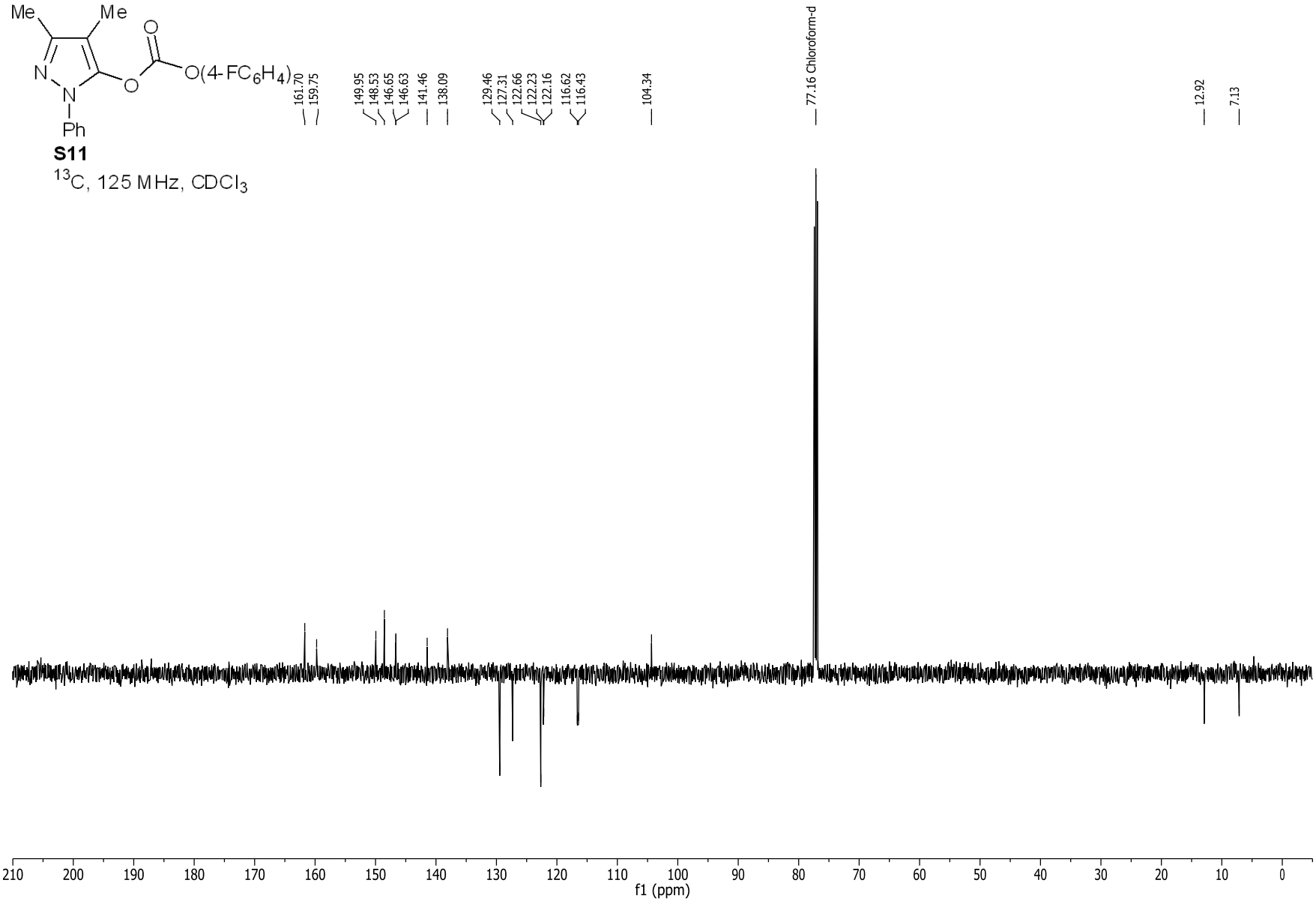
S10

^{13}C, 125 MHz, $CDCl_3$



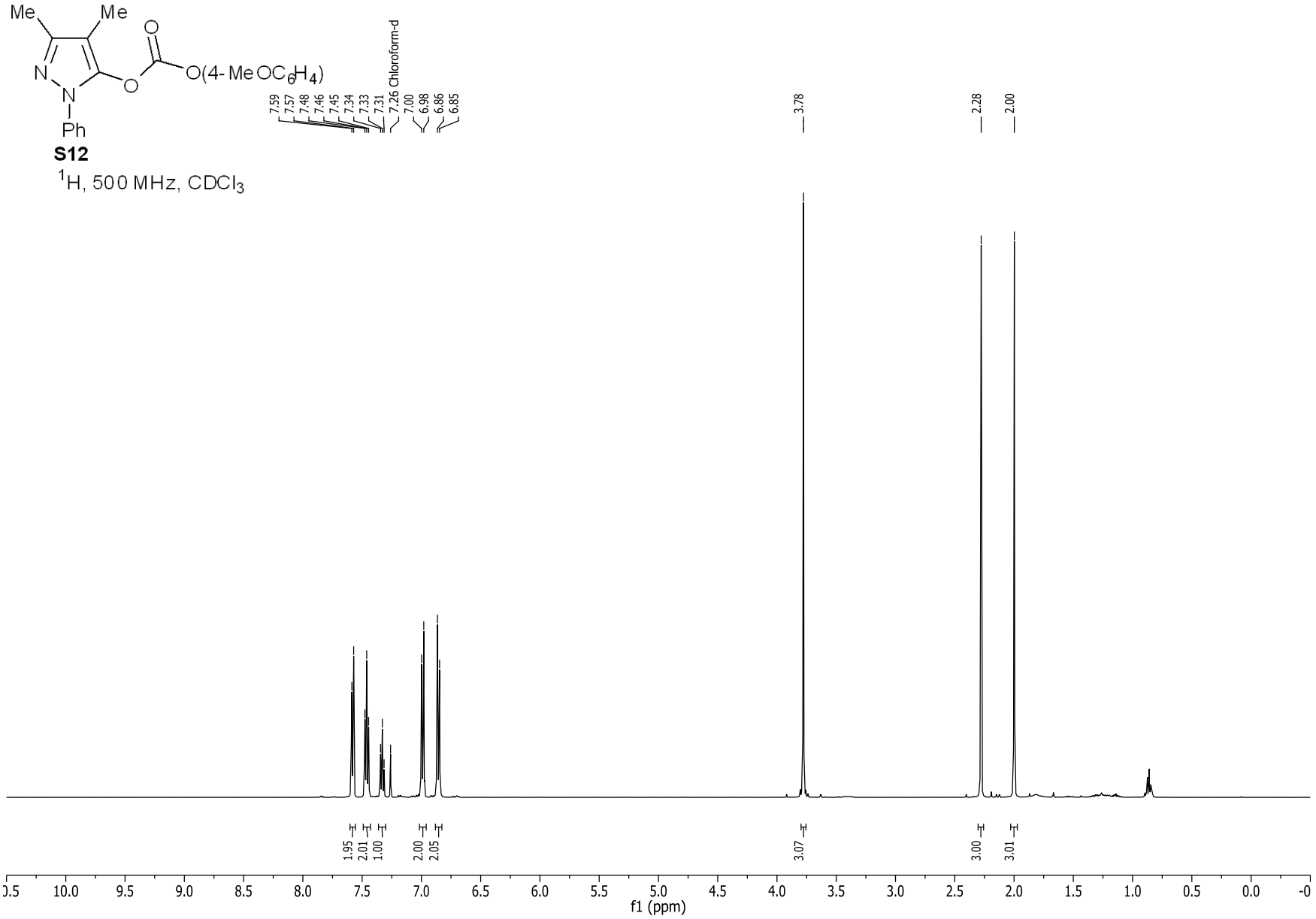
S11

^{1}H, 500 MHz, $CDCl_3$



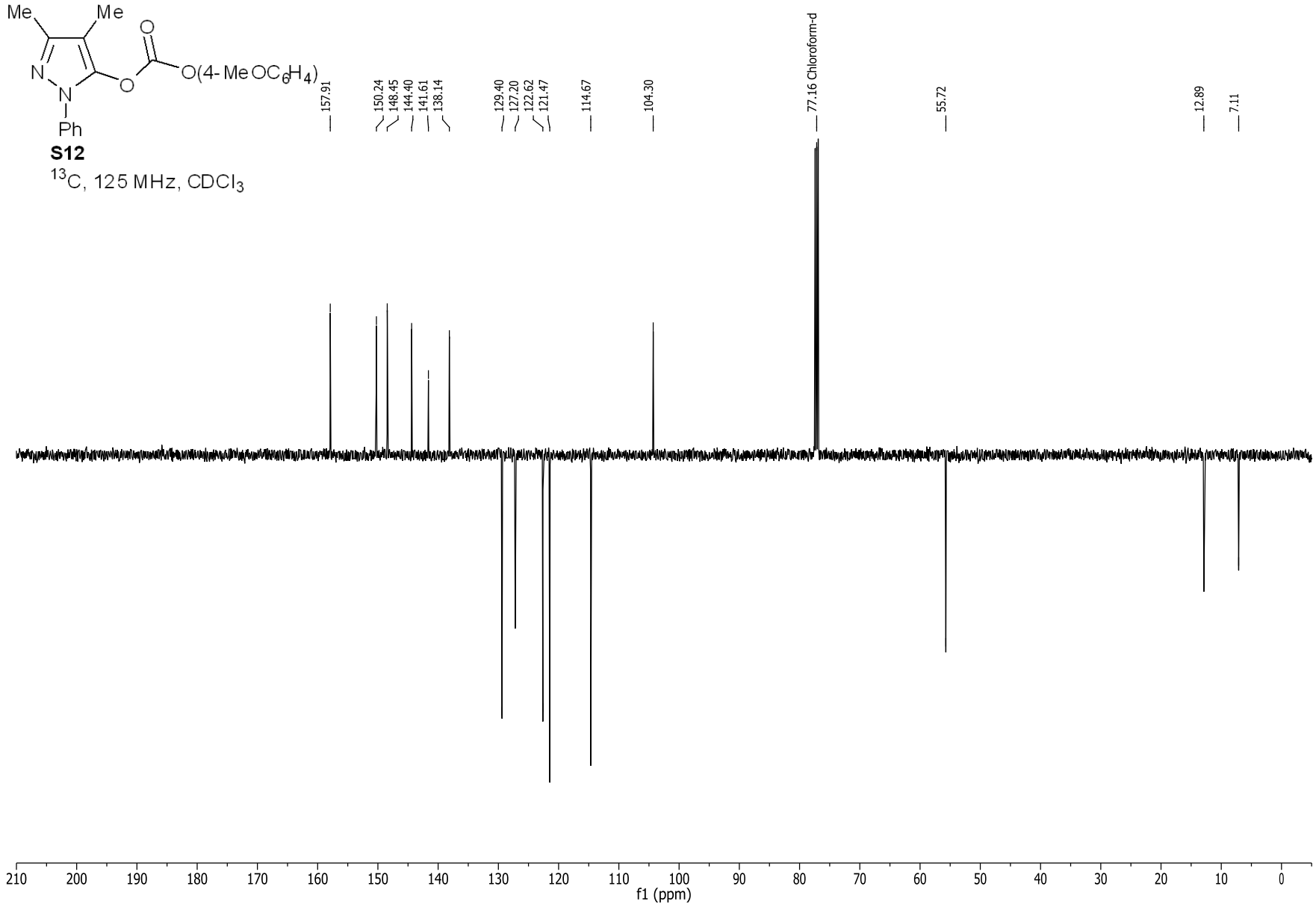
S11

^{13}C, 125 MHz, $CDCl_3$



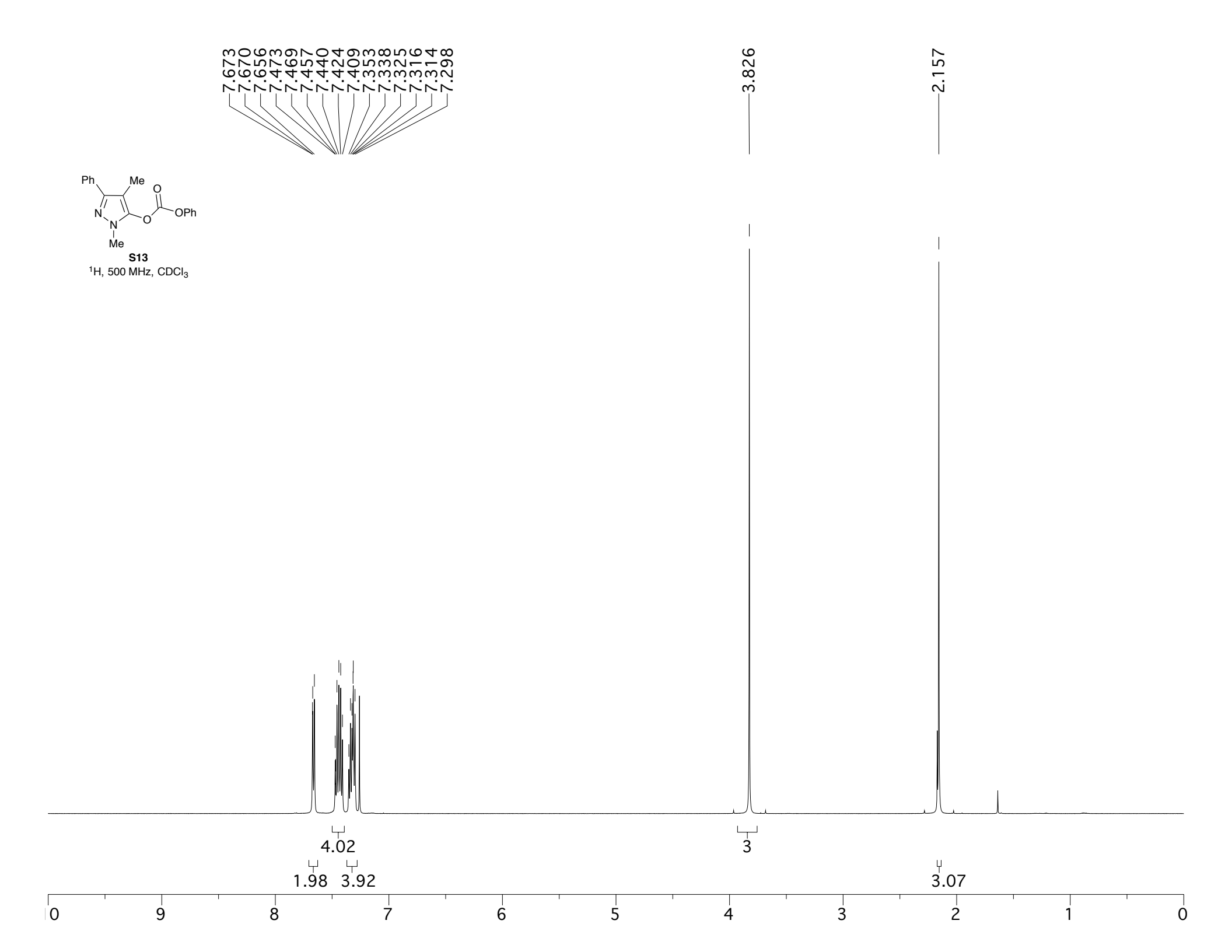
S12

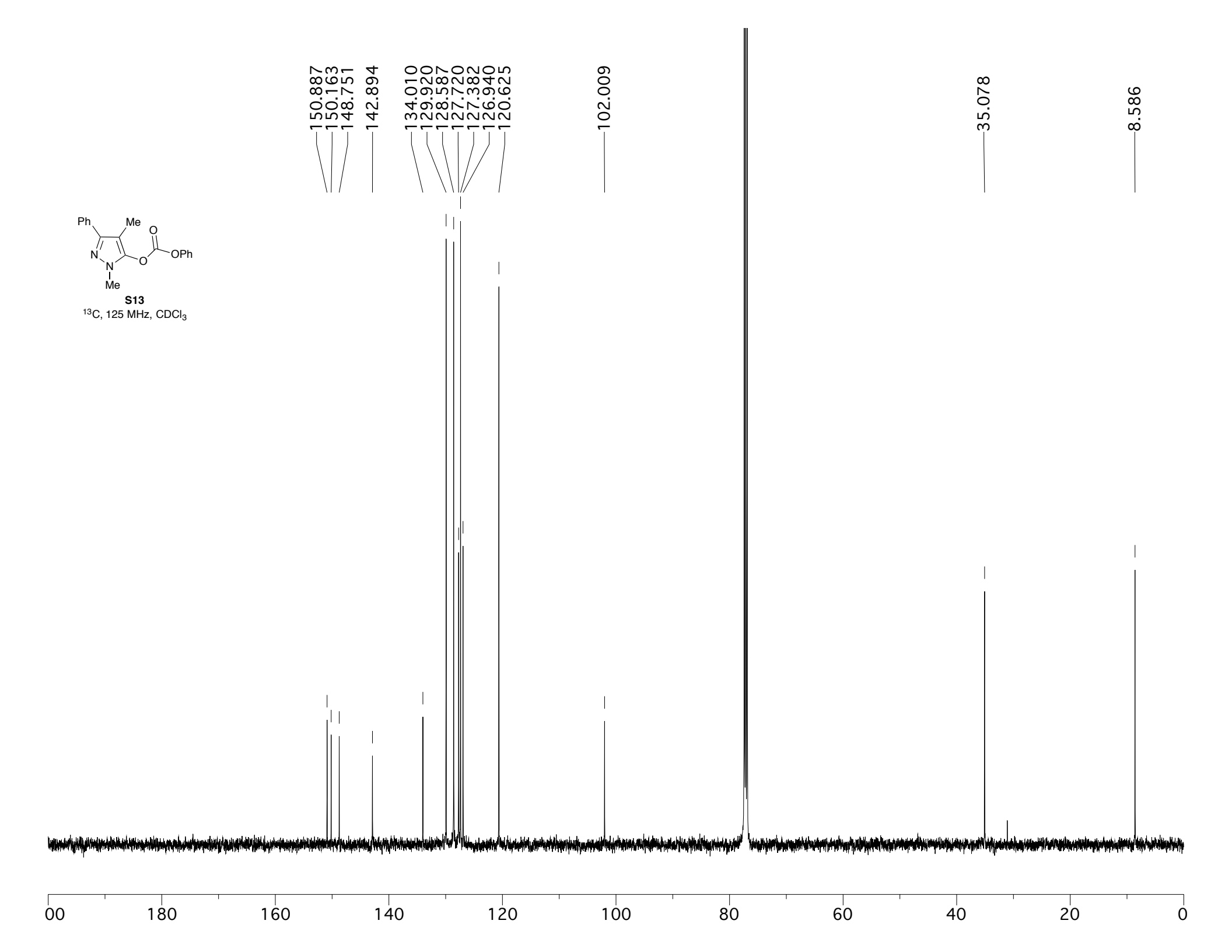
^{1}H, 500 MHz, $CDCl_3$

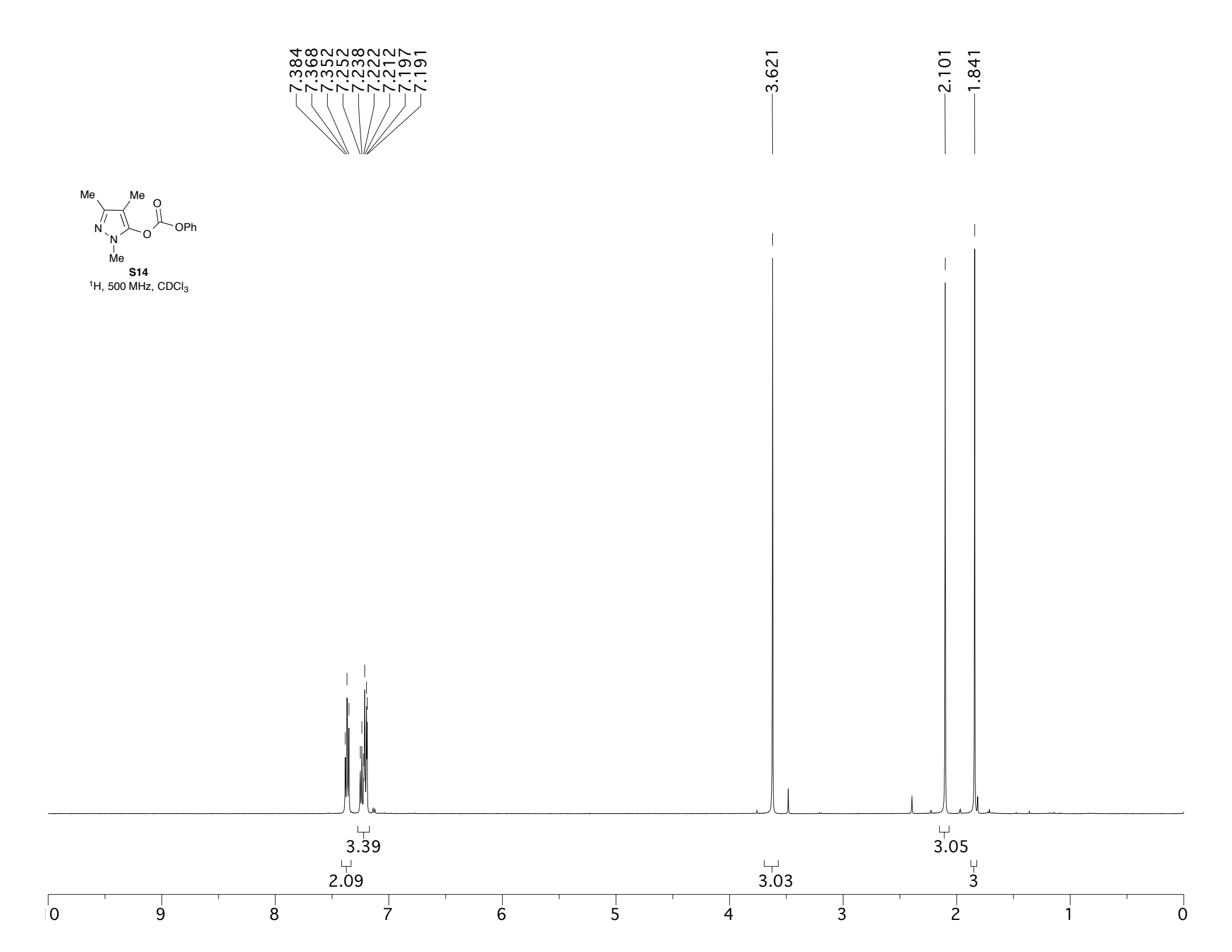


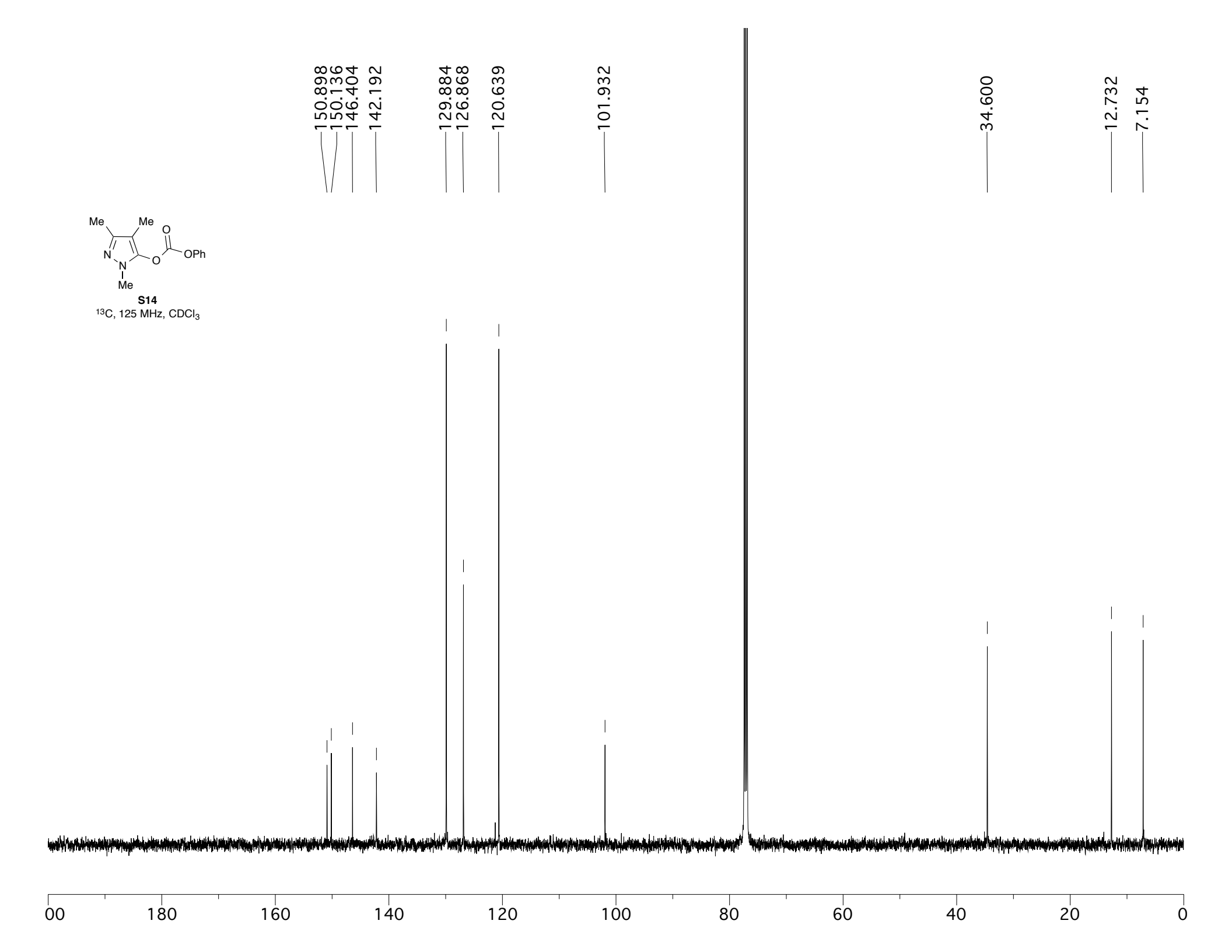
S12

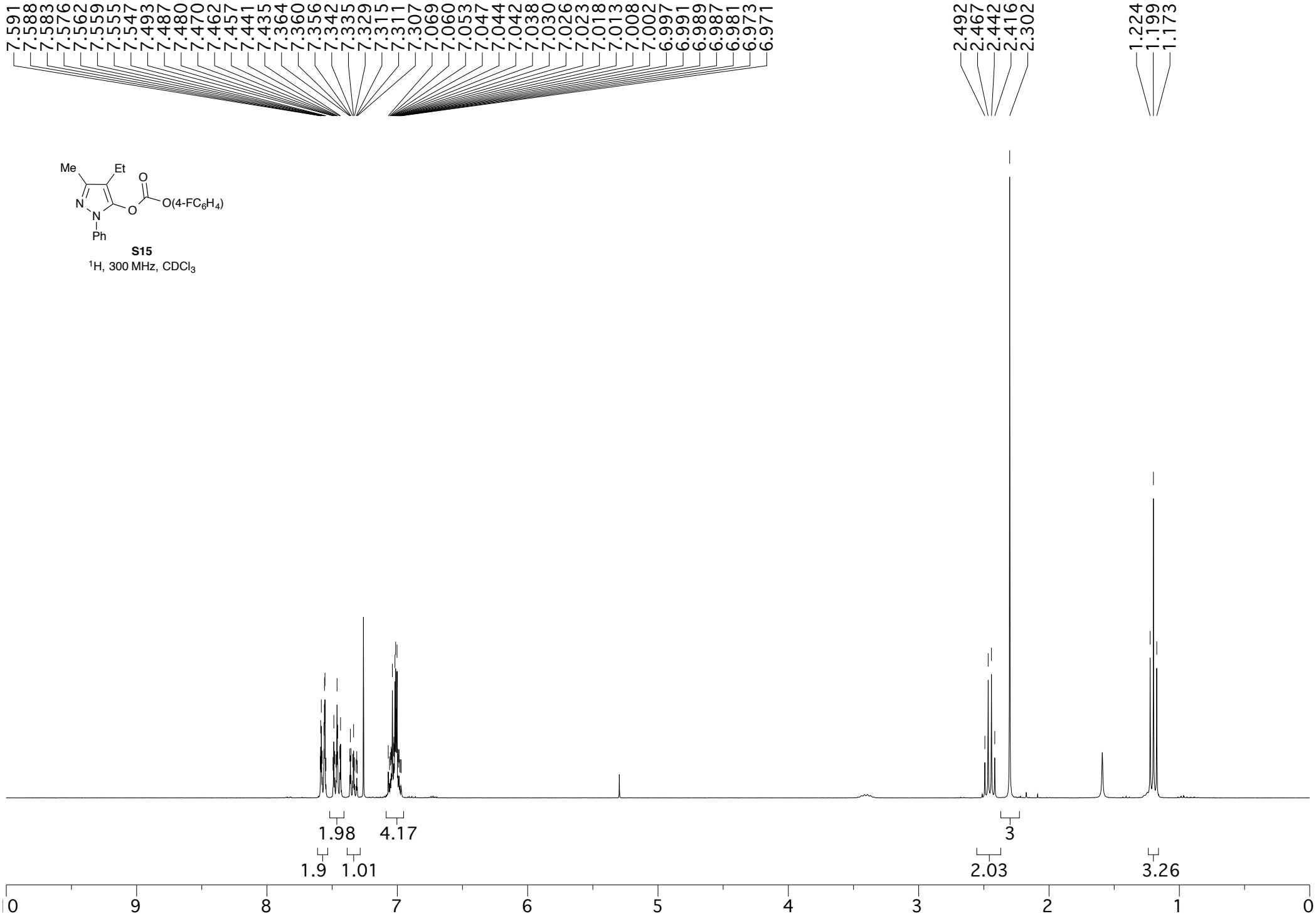
^{13}C, 125 MHz, $CDCl_3$

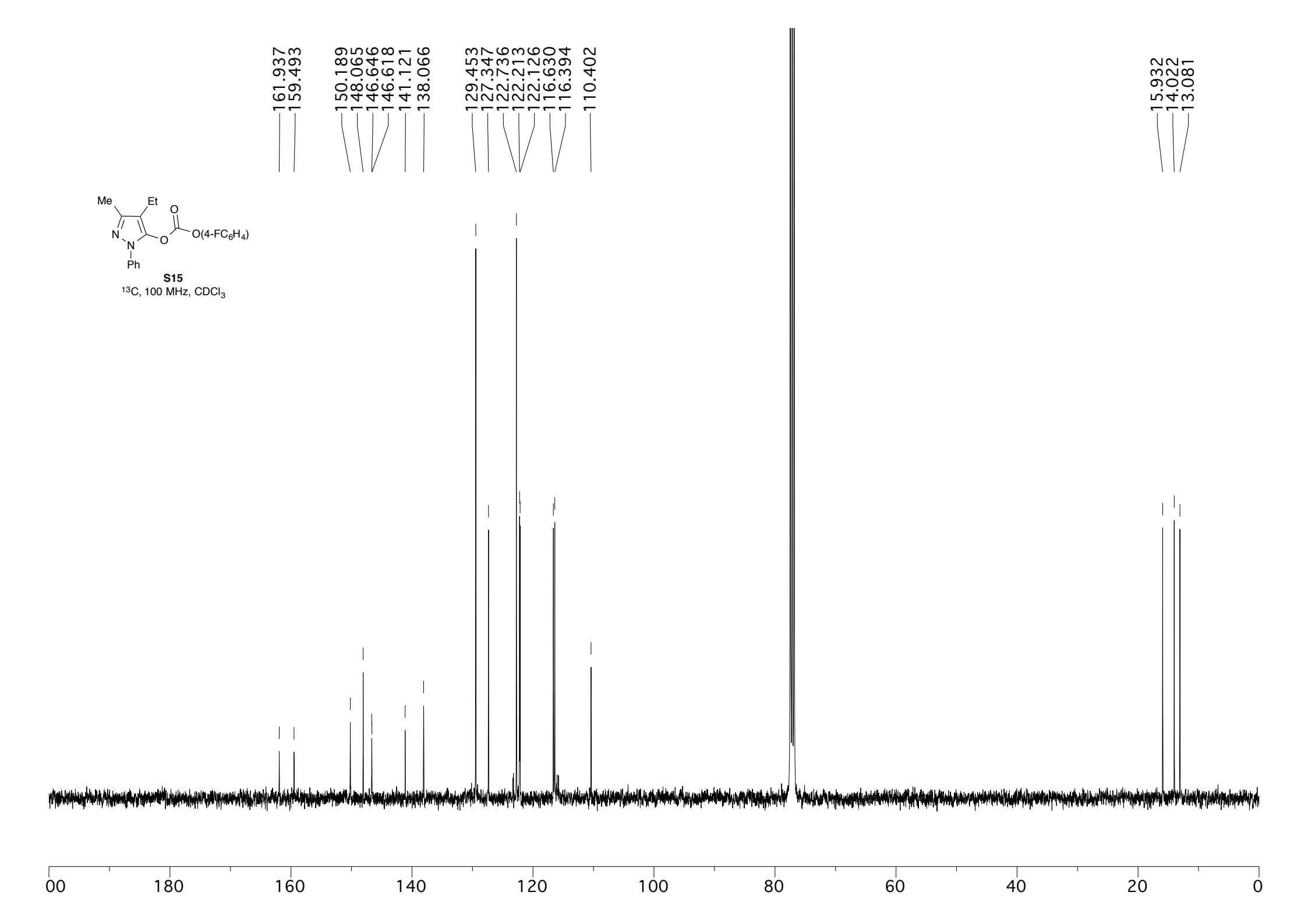

7.673
7.670
7.656
7.473
7.469
7.457
7.440
7.424
7.409
7.353
7.338
7.325
7.316
7.314
7.298
3.826
2.157
Ph
Me
O
N
N
O
OPh
Me
S13
1H, 500 MHz, CDCl3
4.02
3
1.98
3.92
3.07
0
9
8
7
6
5
4
3
2
1
0

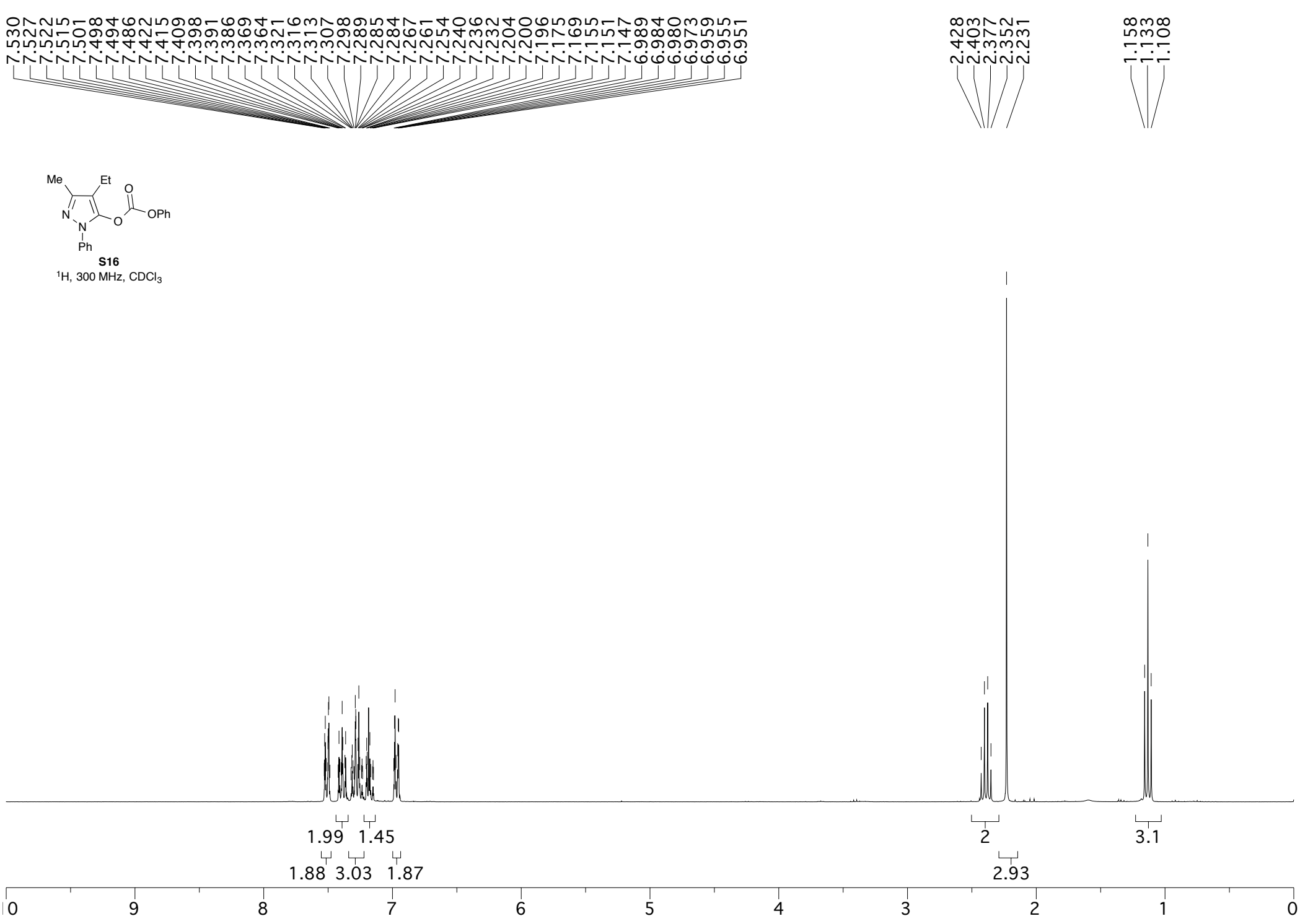

150.887
150.163
148.751
142.894
134.010
129.920
128.587
127.720
127.382
126.940
120.625
102.009
35.078
8.586
Ph
Me
O
N
O
OPh
N
Me
S13
13C, 125 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

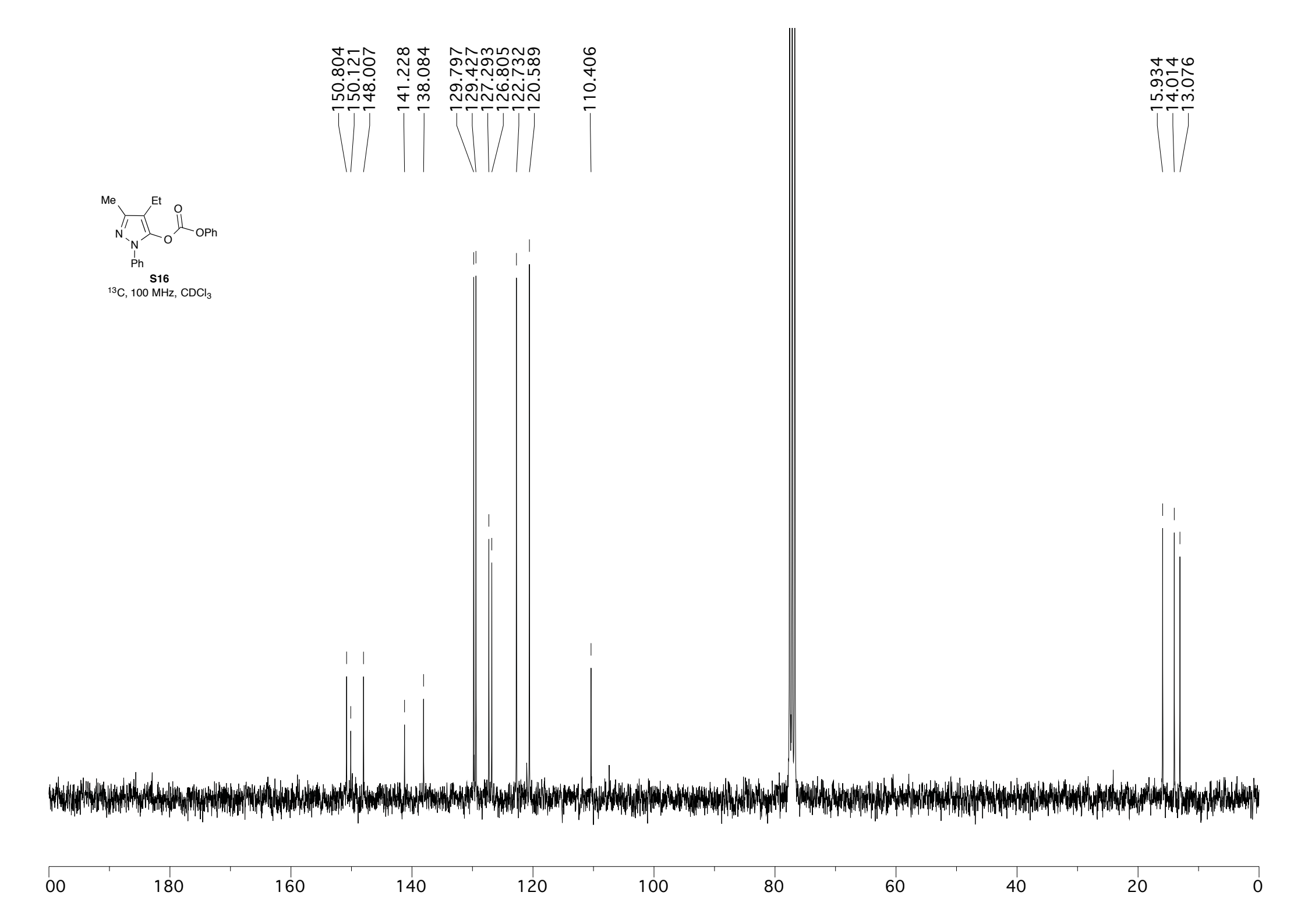

7.384
7.368
7.352
7.252
7.238
7.222
7.212
7.197
7.191
3.621
2.101
1.841
Me
Me
O
N
N
O
OPh
Me
S14
1H, 500 MHz, CDCl3
3.39
3.05
2.09
3.03
3
0
9
8
7
6
5
4
3
2
1
0

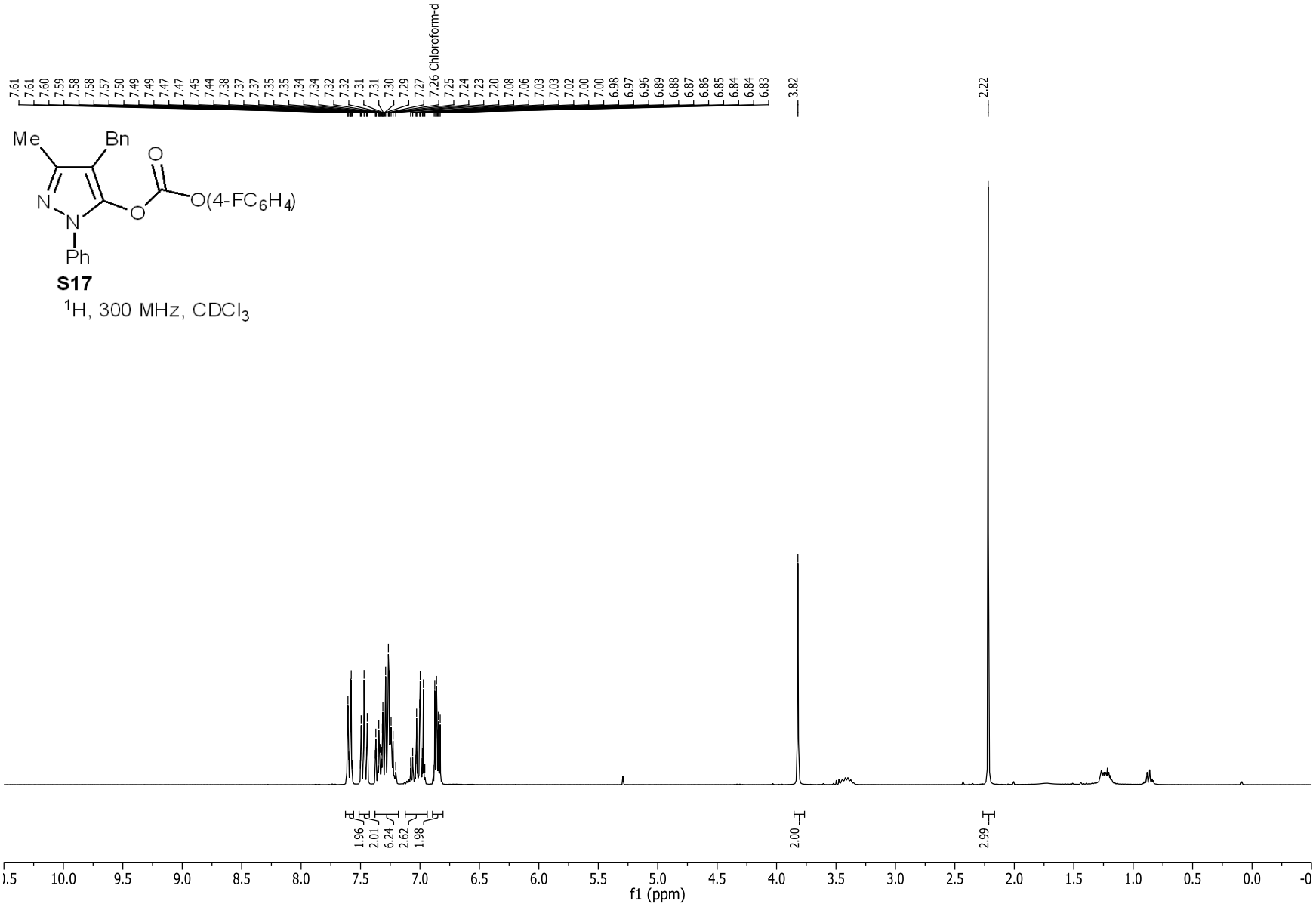

150.898
150.136
146.404
142.192
129.884
126.868
120.639
101.932
34.600
12.732
7.154
Me
Me
O
N
N
O
OPh
Me
S14
13C, 125 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

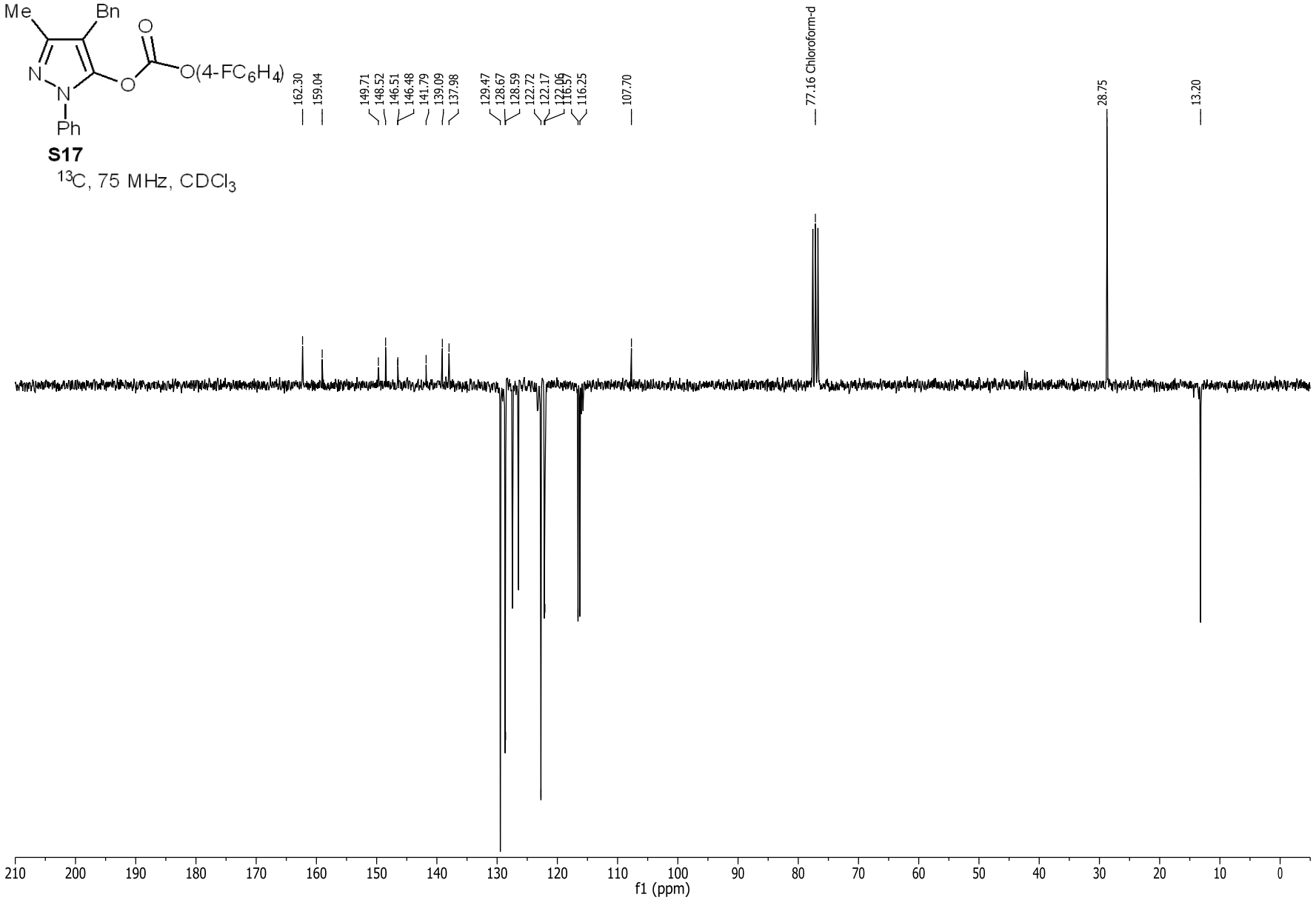

7.591
7.588
7.583
7.576
7.562
7.559
7.555
7.547
7.493
7.487
7.480
7.470
7.462
7.457
7.441
7.435
7.364
7.360
7.356
7.342
7.335
7.329
7.315
7.311
7.307
7.069
7.060
7.053
7.047
7.044
7.042
7.038
7.030
7.026
7.023
7.018
7.013
7.008
7.002
6.997
6.991
6.989
6.987
6.981
6.973
6.971
2.492
2.467
2.442
2.416
2.302
1.224
1.199
1.173
Me
Et
O
N
N
O
O(4-FC6H4)
Ph
S15
1H, 300 MHz, CDCl3
1.98
4.17
3
1.9
1.01
2.03
3.26
0
9
8
7
6
5
4
3
2
1
0


161.937
159.493
150.189
148.065
146.646
146.618
141.121
138.066
129.453
127.347
122.736
122.213
122.126
116.630
116.394
110.402
15.932
14.022
13.081
Me
Et
O
N
N
O
O(4-FC6H4)
Ph
S15
13C, 100 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0


7.530
7.527
7.522
7.515
7.501
7.498
7.494
7.486
7.422
7.415
7.409
7.398
7.391
7.386
7.369
7.364
7.321
7.316
7.313
7.307
7.298
7.289
7.285
7.284
7.267
7.261
7.254
7.240
7.236
7.232
7.204
7.200
7.196
7.175
7.169
7.155
7.151
7.147
6.989
6.984
6.980
6.973
6.959
6.955
6.951
2.428
2.403
2.377
2.352
2.231
1.158
1.133
1.108
Me
Et
O
N
N
O
OPh
Ph
S16
1H, 300 MHz, CDCl3
1.99
1.45
1.88
3.03
1.87
2
3.1
2.93
0
9
8
7
6
5
4
3
2
1
0

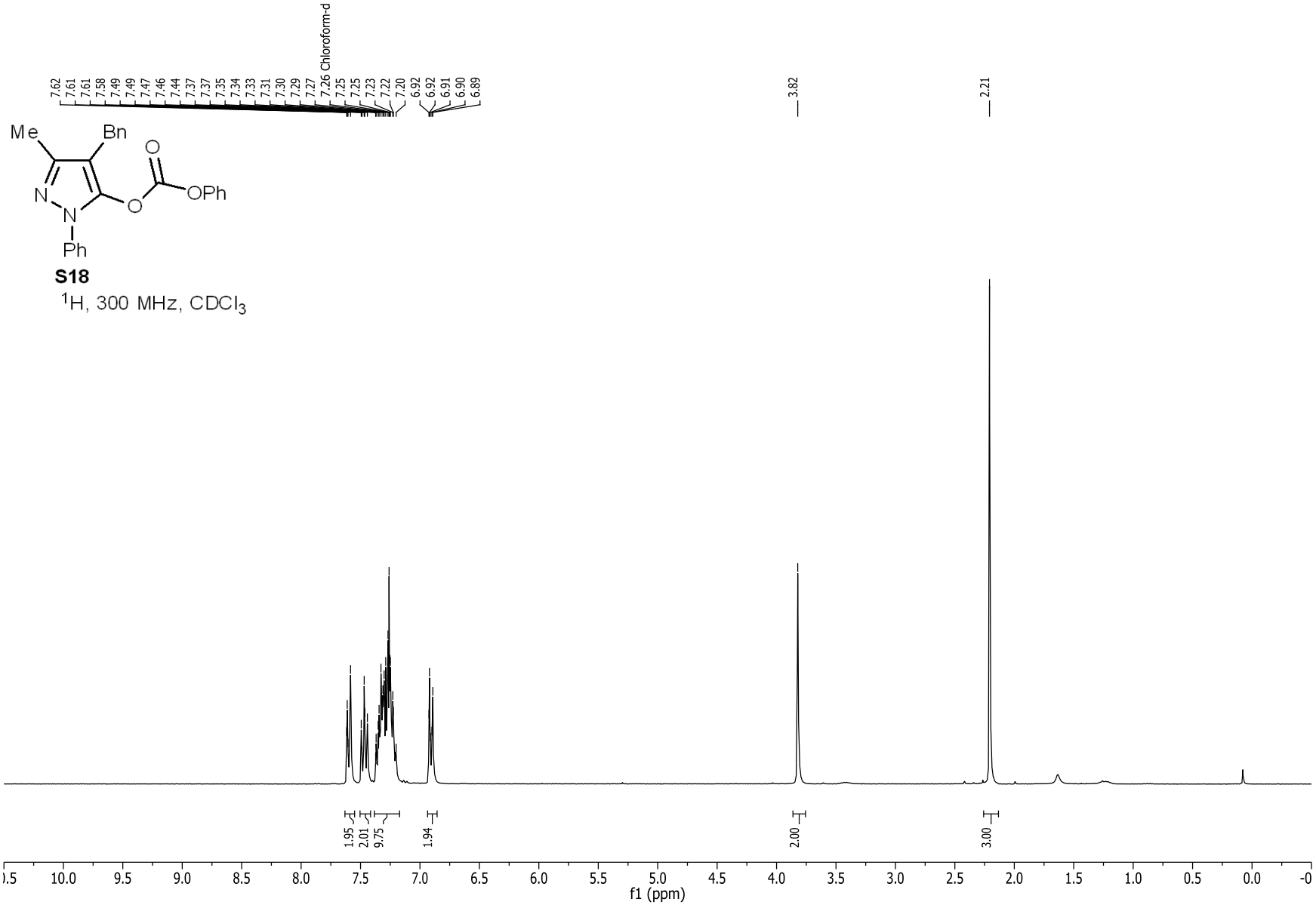

150.804
150.121
148.007
141.228
138.084
129.797
129.427
127.293
126.805
122.732
120.589
110.406
15.934
14.014
13.076
Me
Et
O
N
N
O
OPh
Ph
S16
13C, 100 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0


Chloroform-d
3.82
2.22
Me
Bn
O
N
N
O
O(4-FC6H4)
Ph
S17
1H, 300 MHz, CDCl3
1.96
2.01
6.24
2.62
1.98
2.00
2.99
f1 (ppm)



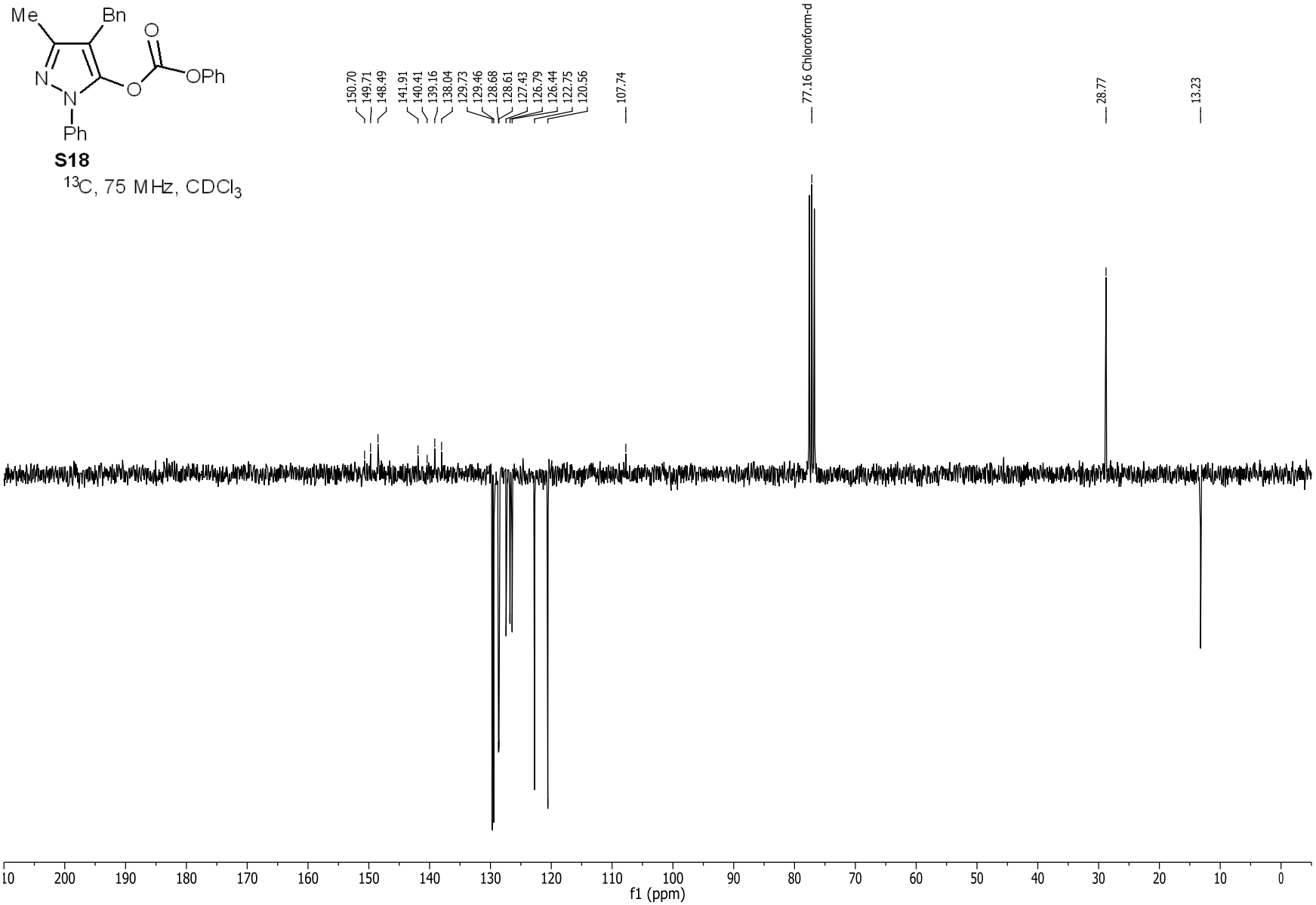
S17

^{13}C, 75 MHz, $CDCl_3$



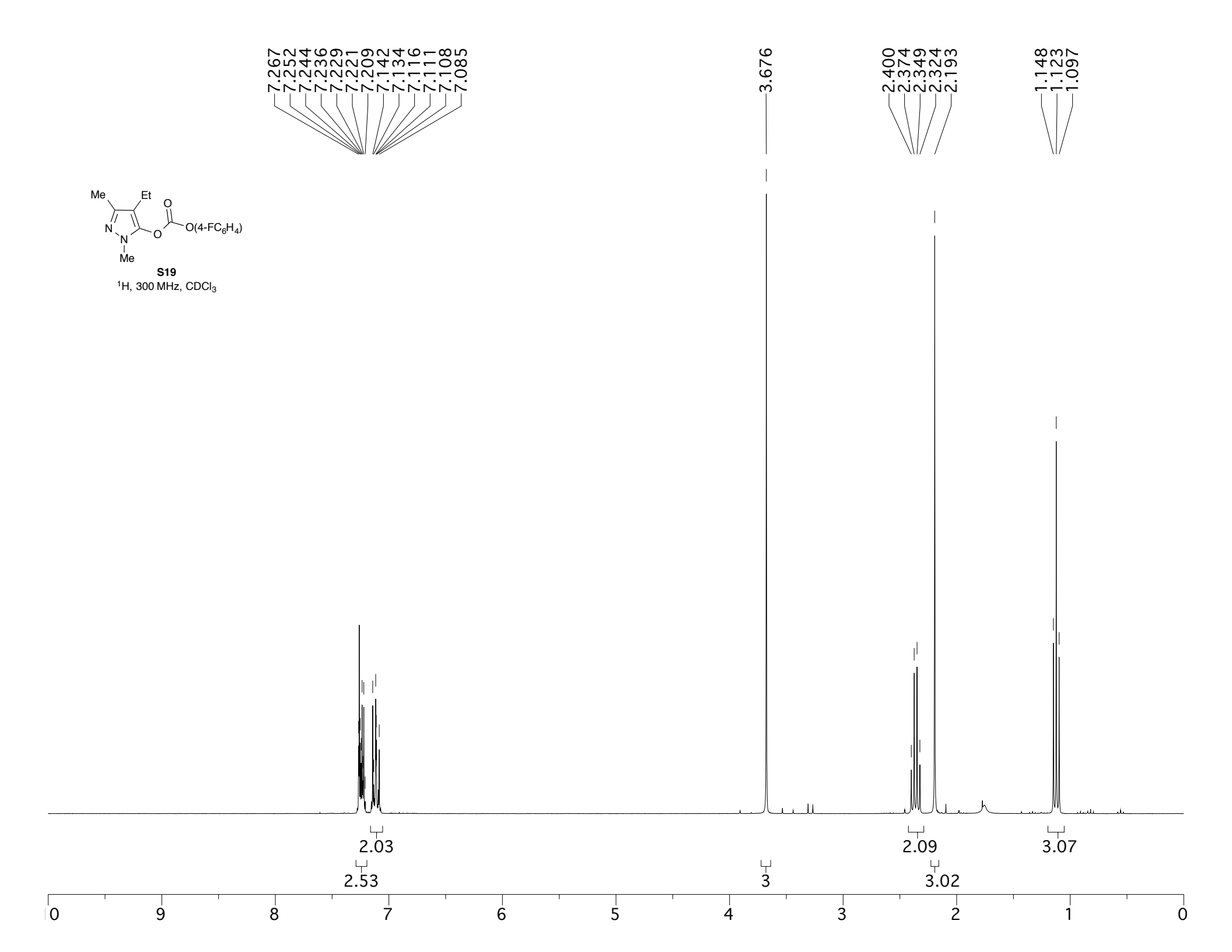
S18

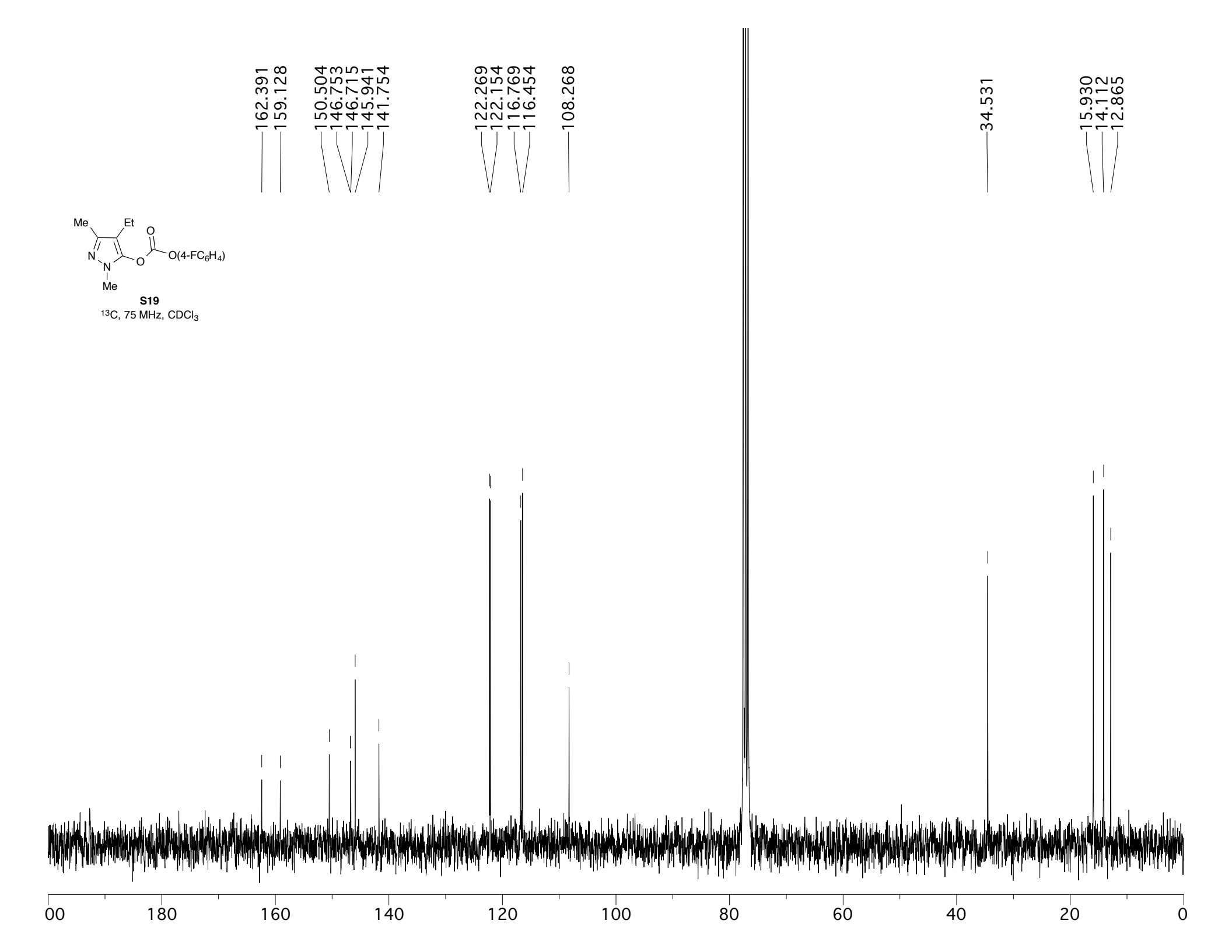
^{1}H, 300 MHz, $CDCl_3$

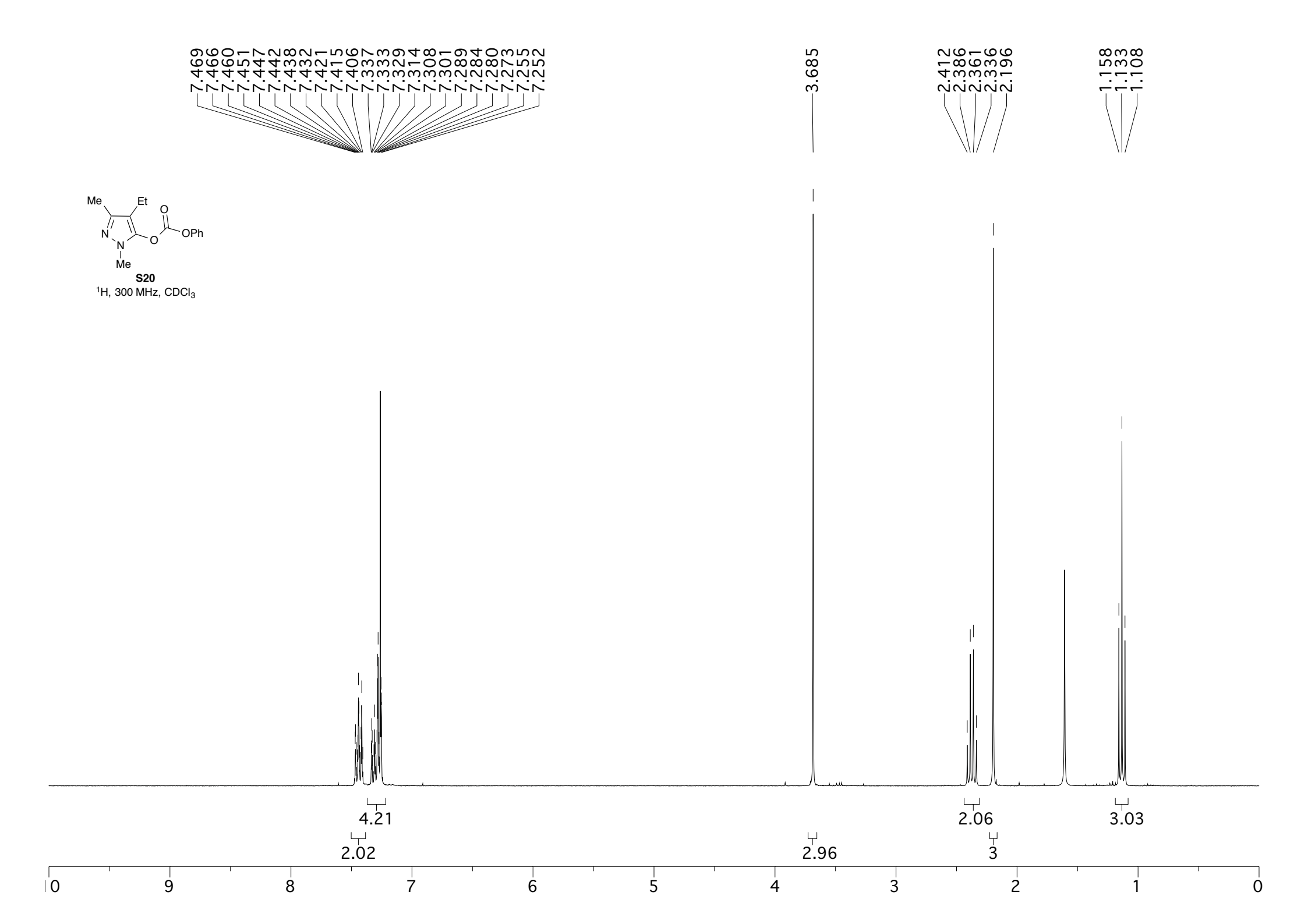


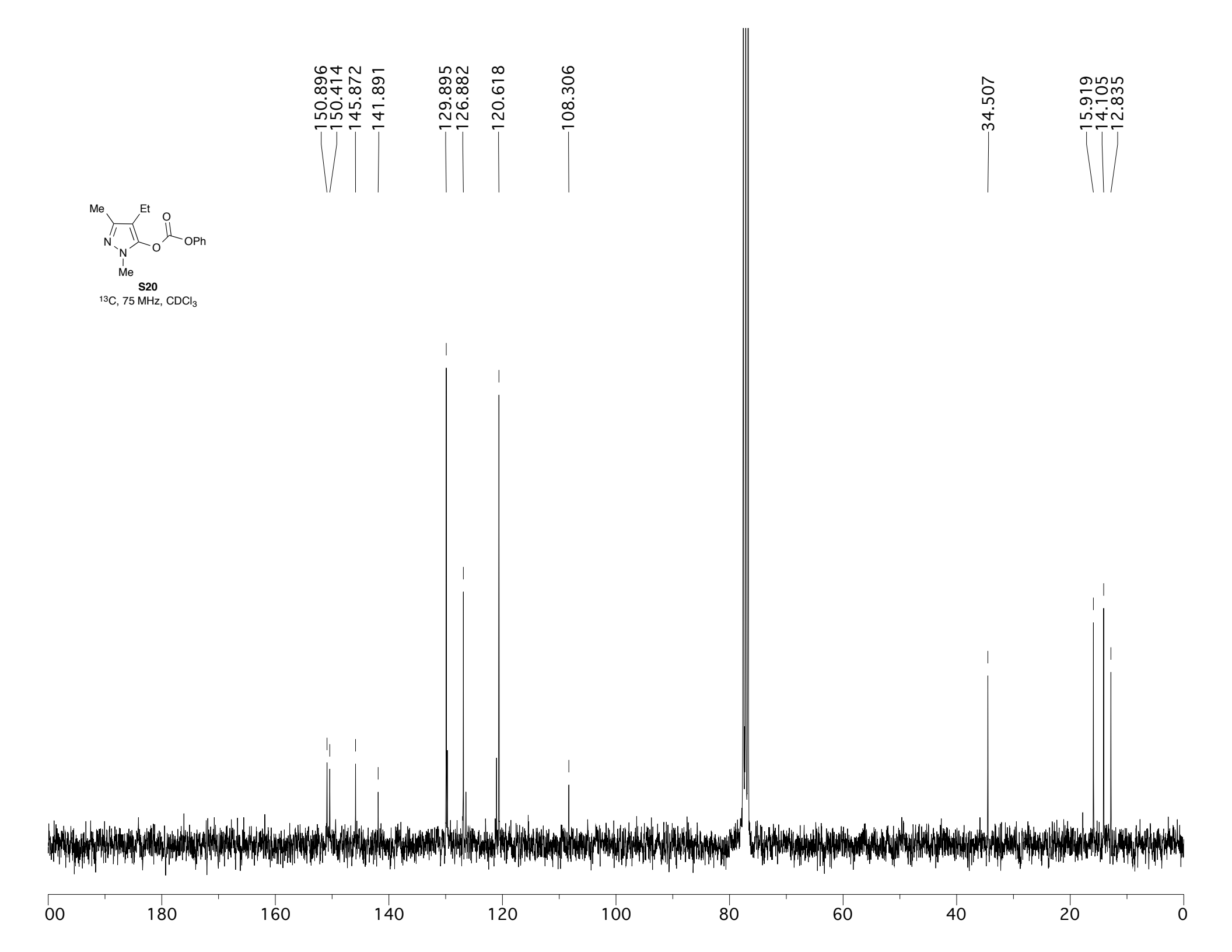
S18

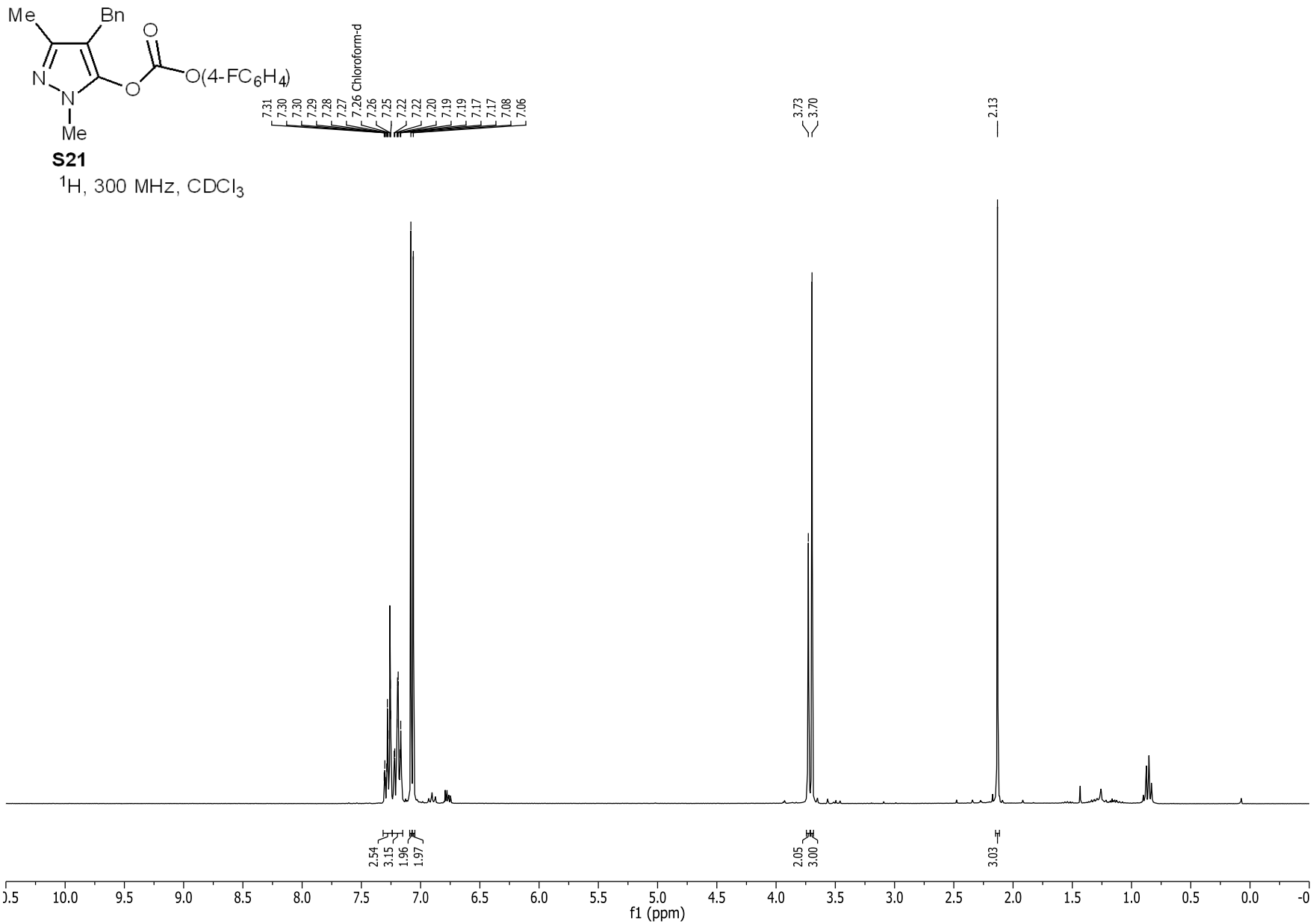
^{13}C, 75 MHz, $CDCl_3$

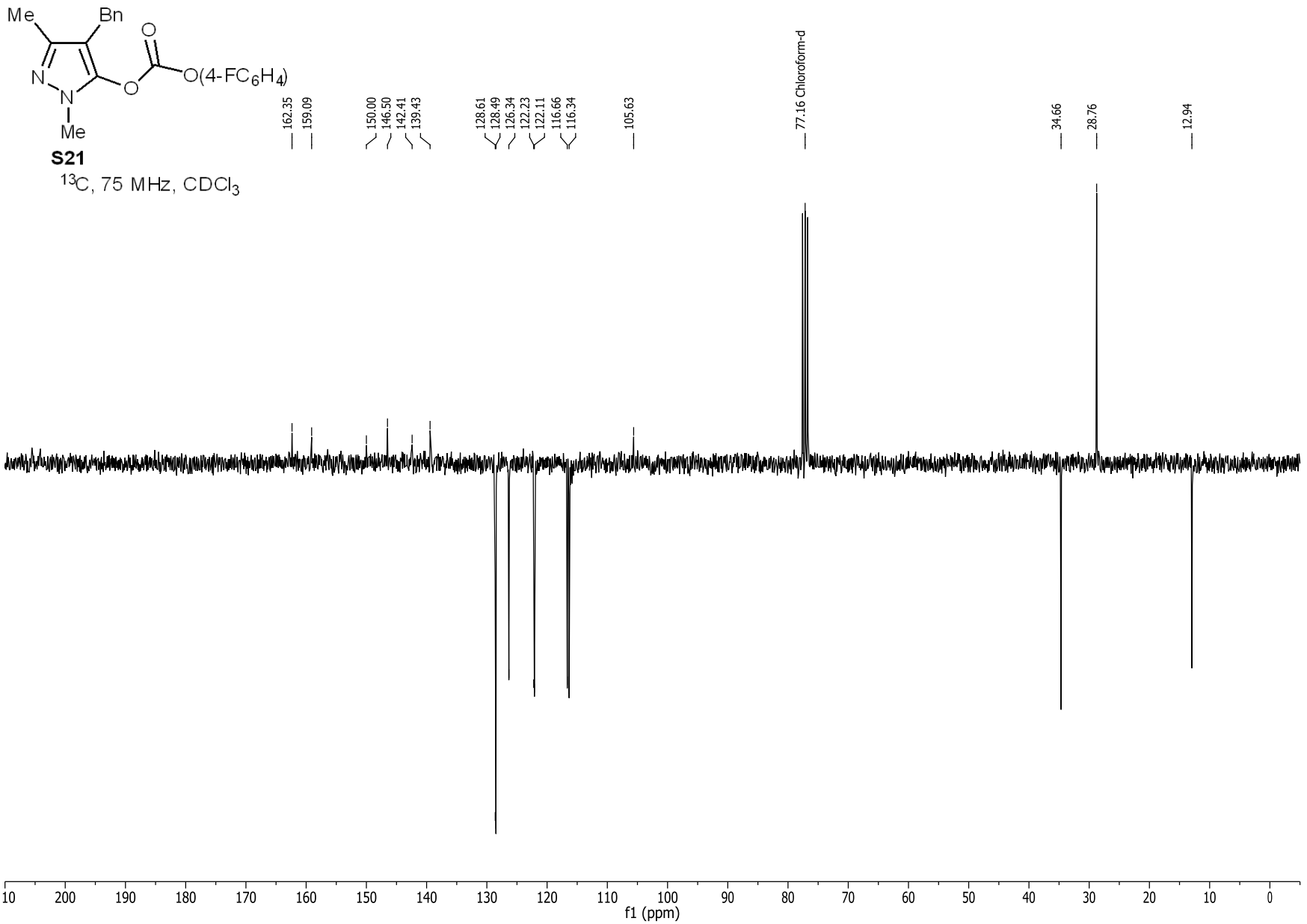

7.267
7.252
7.244
7.236
7.229
7.221
7.209
7.142
7.134
7.116
7.111
7.108
7.085
3.676
2.400
2.374
2.349
2.324
2.193
1.148
1.123
1.097
Me
Et
O
N
N
O
O(4-FC6H4)
Me
S19
1H, 300 MHz, CDCl3
2.03
2.09
3.07
2.53
3
3.02
0
9
8
7
6
5
4
3
2
1
0

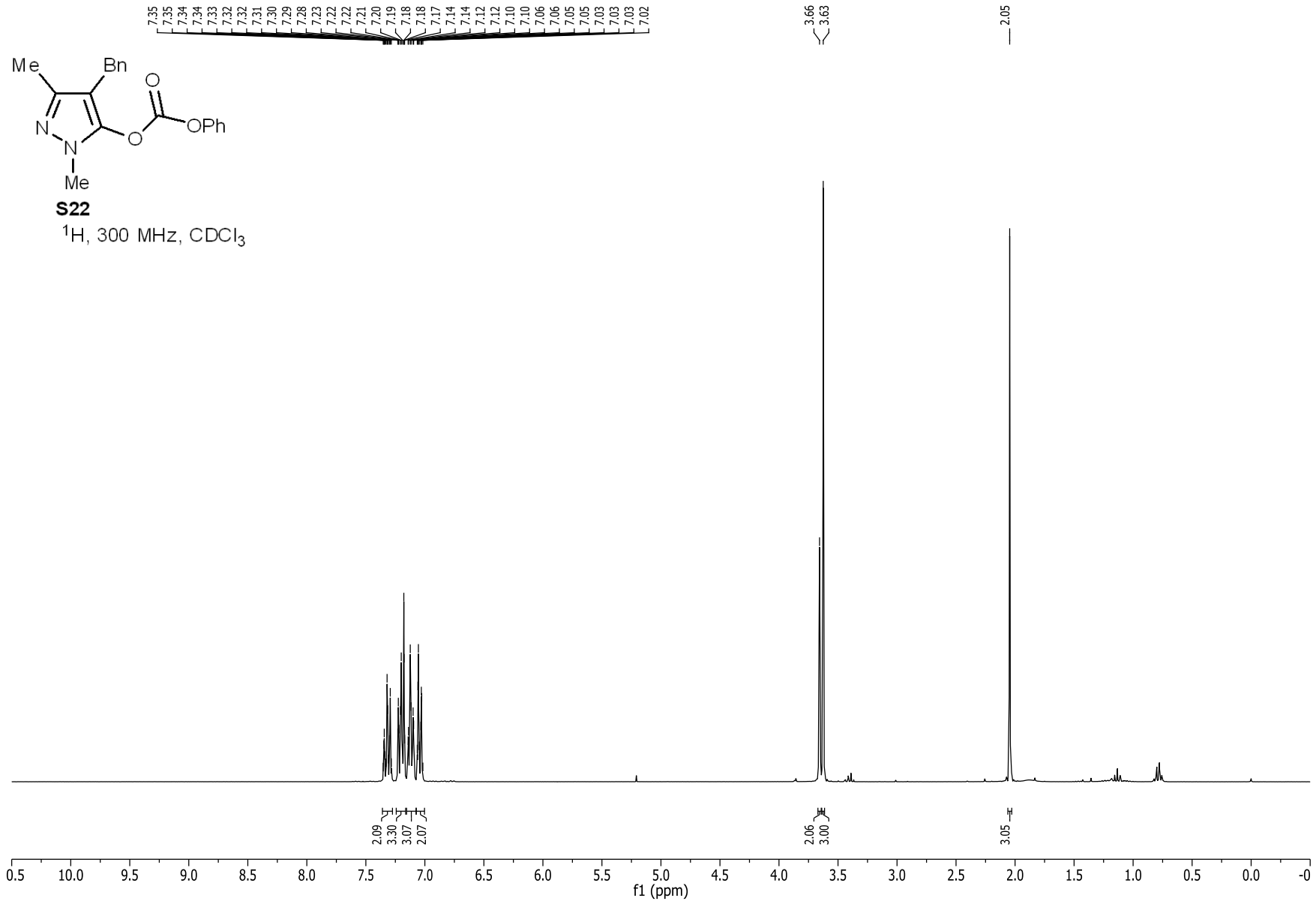

162.391
159.128
150.504
146.753
146.715
145.941
141.754
122.269
122.154
116.769
116.454
108.268
34.531
15.930
14.112
12.865
Me
Et
O
N
N
O
O(4-FC6H4)
Me
S19
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

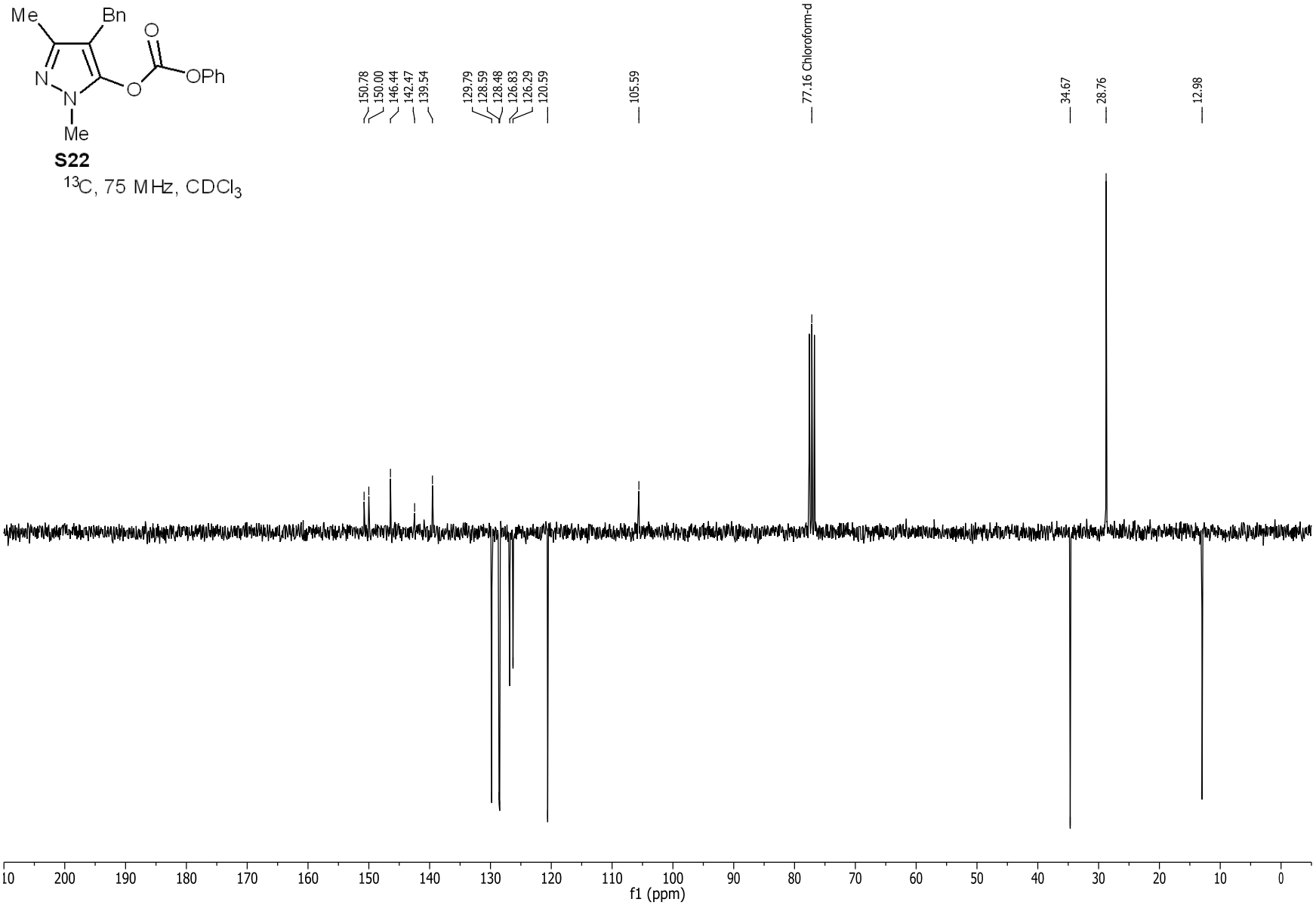

7.469
7.466
7.460
7.451
7.447
7.442
7.438
7.432
7.421
7.415
7.406
7.337
7.333
7.329
7.314
7.308
7.301
7.289
7.284
7.280
7.273
7.255
7.252
3.685
2.412
2.386
2.361
2.336
2.196
1.158
1.133
1.108
Me
Et
O
N
N
O
OPh
Me
S20
1H, 300 MHz, CDCl3
4.21
2.02
2.96
2.06
3
3.03
0
9
8
7
6
5
4
3
2
1
0


150.896
150.414
145.872
141.891
129.895
126.882
120.618
108.306
34.507
15.919
14.105
12.835
Me
Et
O
N
N
O
OPh
Me
S20
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0


Me
Bn
O
N
N
O
O(4-FC6H4)
Me
S21
1H, 300 MHz, CDCl3
Chloroform-d
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.22
7.22
7.20
7.19
7.19
7.17
7.17
7.08
7.06
3.73
3.70
2.13
2.54
3.15
1.96
1.97
2.05
3.00
3.03
f1 (ppm)

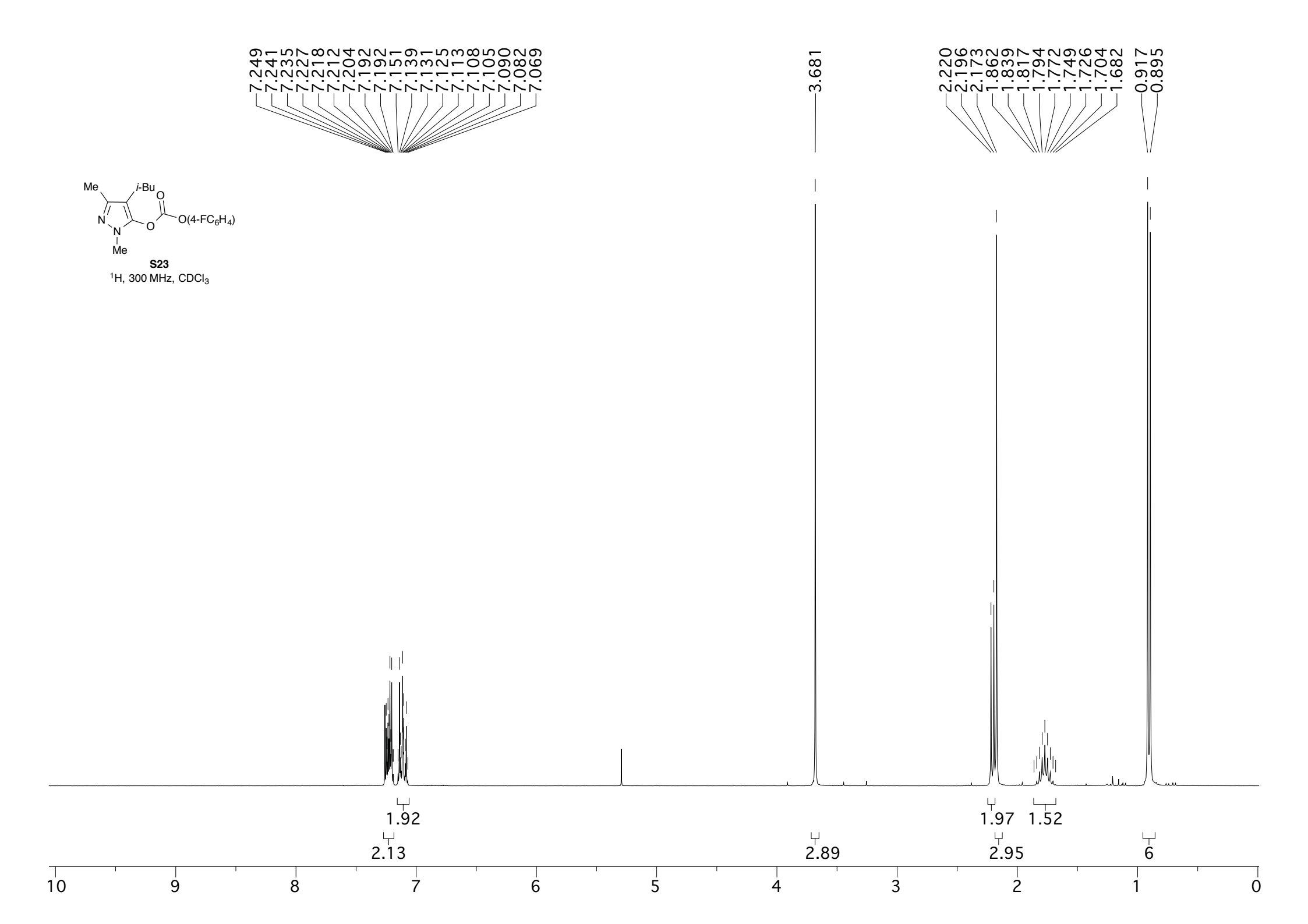

Me
Bn
O
N
N
O
O(4-FC6H4)
Me
S21
13C, 75 MHz, CDCl3
162.35
159.09
150.00
146.50
142.41
139.43
128.61
128.49
126.34
122.23
122.11
116.66
116.34
105.63
77.16 Chloroform-d
34.66
28.76
12.94
f1 (ppm)

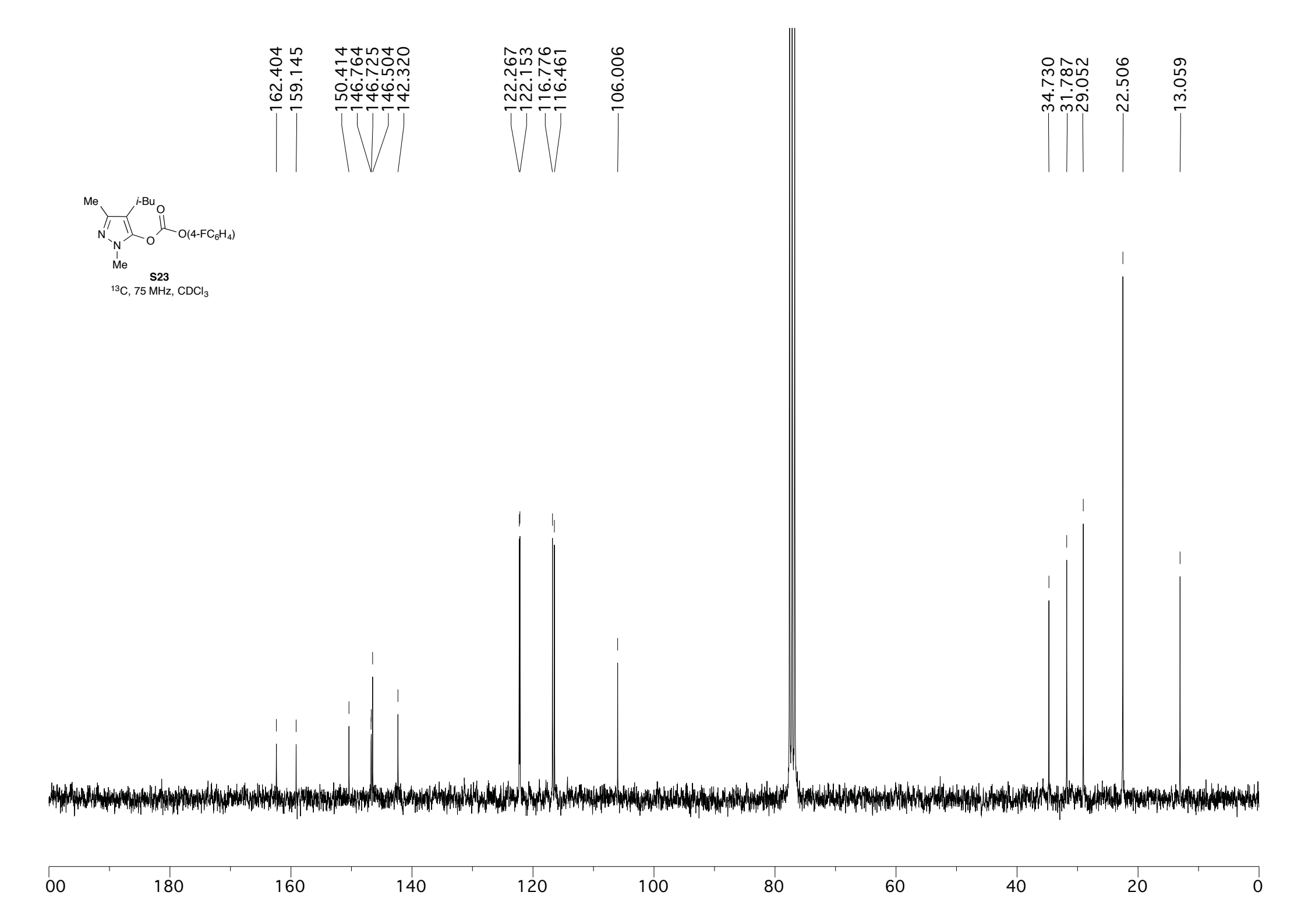

Me
Bn
O
N
N
O
OPh
Me
S22
1H, 300 MHz, CDCl3
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.14
7.14
7.12
7.12
7.10
7.10
7.06
7.06
7.05
7.05
7.03
7.03
7.03
7.02
3.66
3.63
2.05
2.09
3.30
3.07
2.07
2.06
3.00
3.05
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

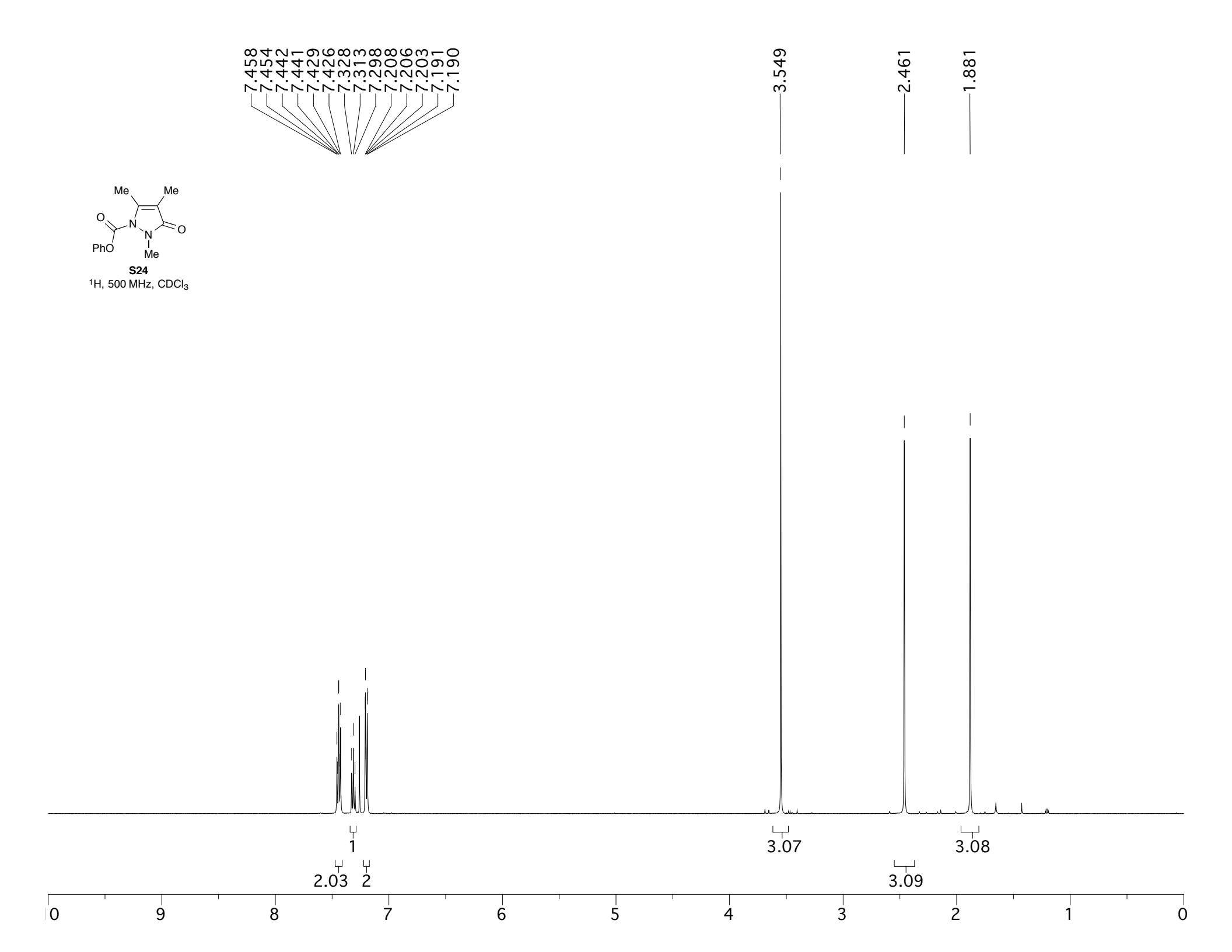


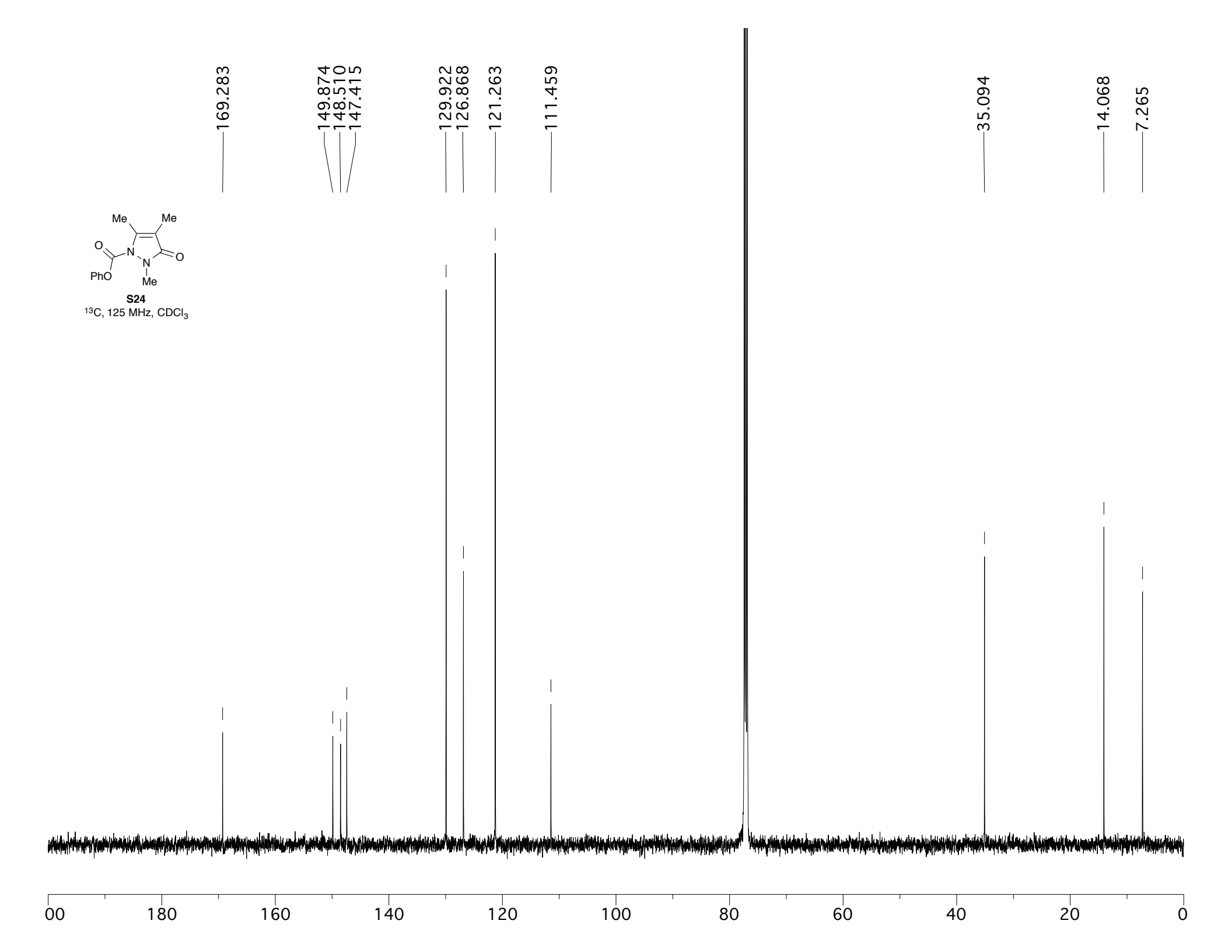
S22

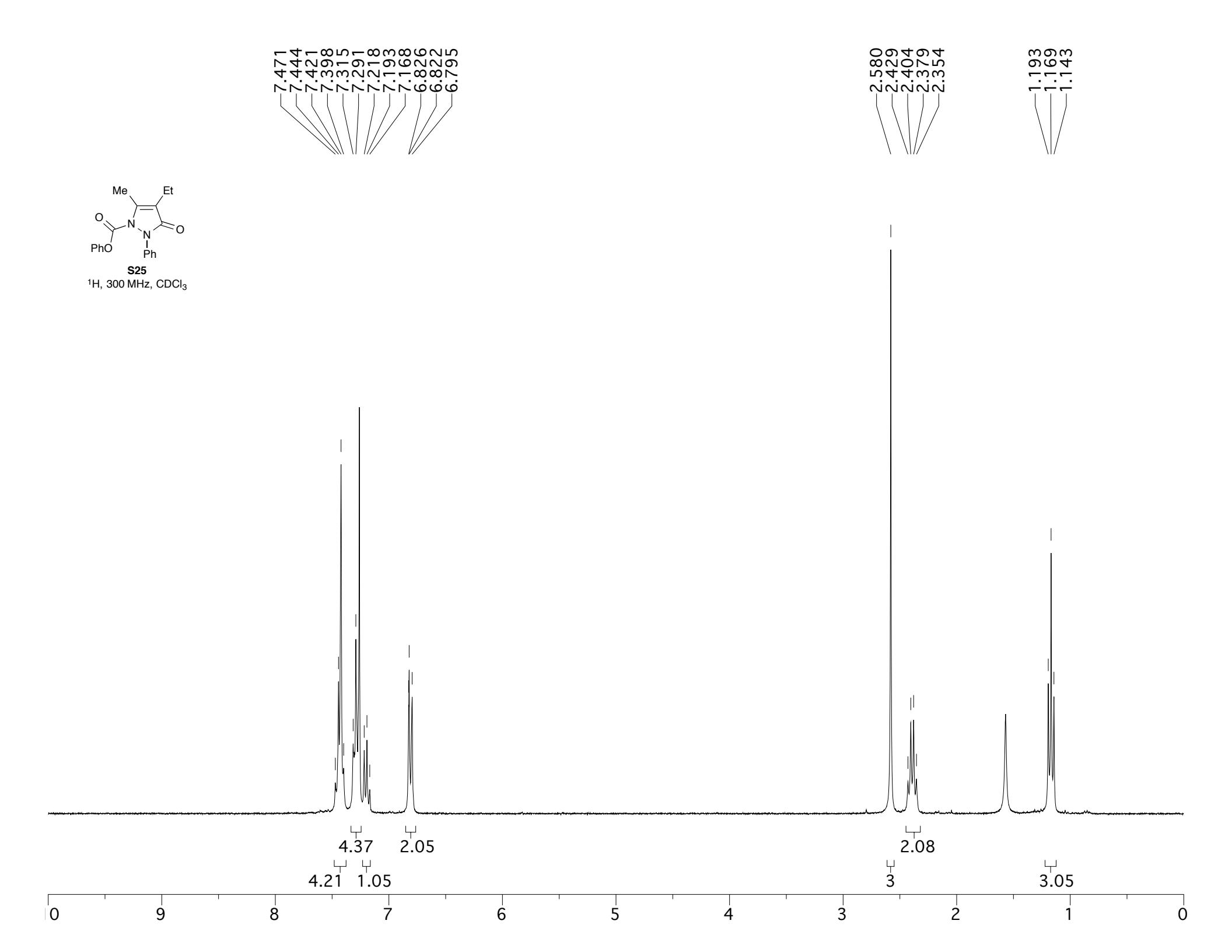
^{13}C, 75 MHz, $CDCl_3$

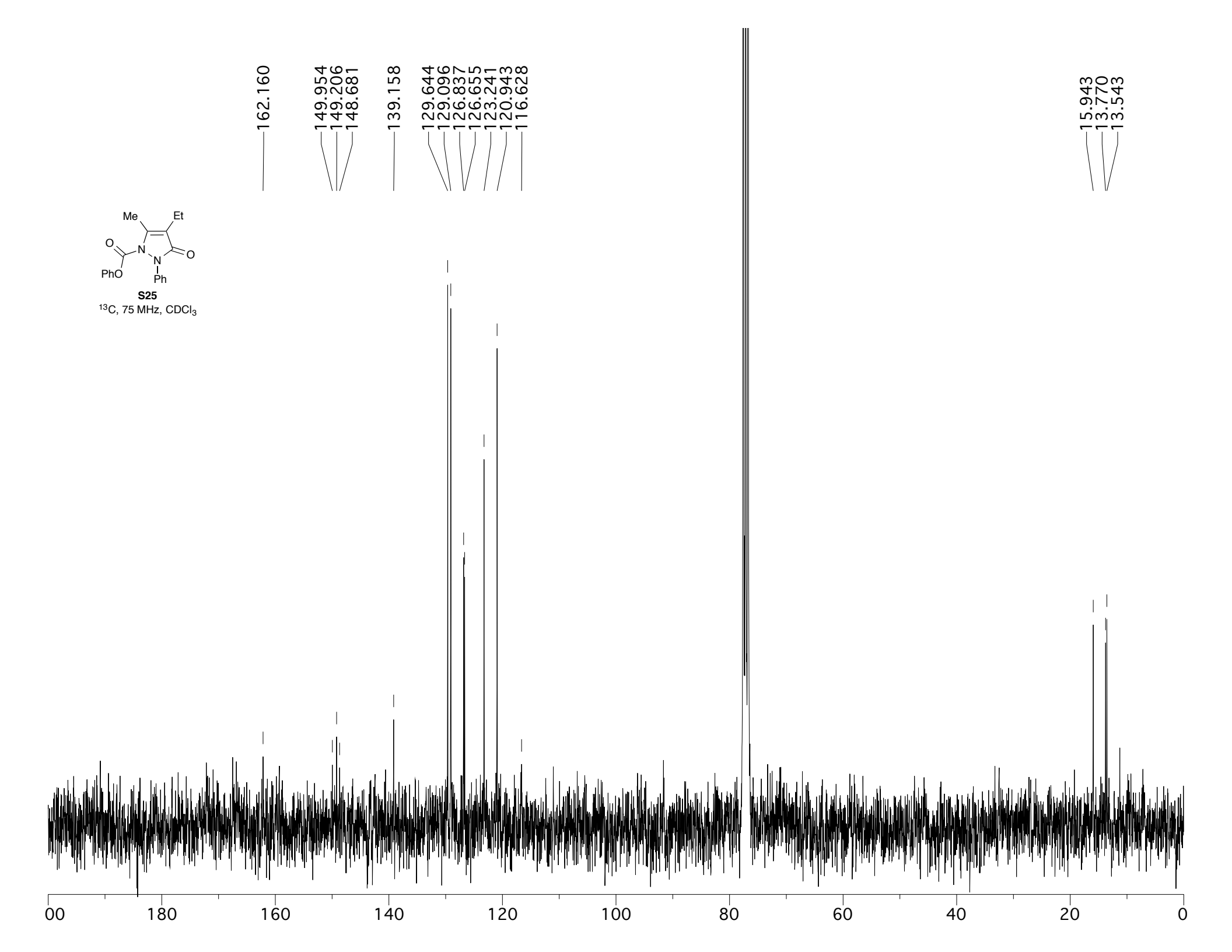

7.249
7.241
7.235
7.227
7.218
7.212
7.204
7.192
7.192
7.151
7.139
7.131
7.125
7.113
7.108
7.105
7.090
7.082
7.069
3.681
2.220
2.196
2.173
1.862
1.839
1.817
1.794
1.772
1.749
1.726
1.704
1.682
0.917
0.895
Me
i-Bu
O
N
N
O
O(4-FC6H4)
Me
S23
1H, 300 MHz, CDCl3
1.92
2.13
2.89
1.97
1.52
2.95
6
10
9
8
7
6
5
4
3
2
1
0

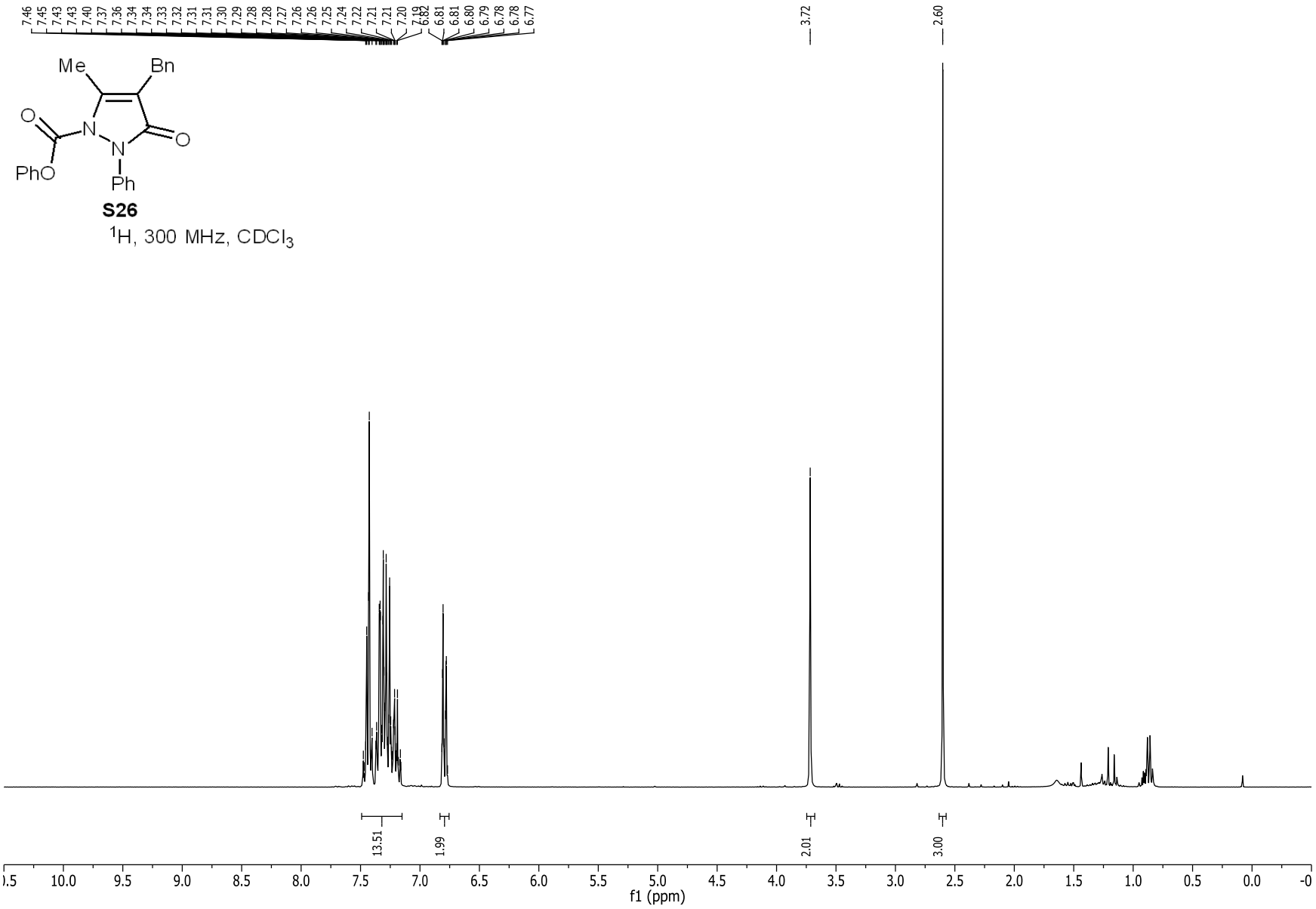

162.404
159.145
150.414
146.764
146.725
146.504
142.320
122.267
122.153
116.776
116.461
106.006
34.730
31.787
29.052
22.506
13.059
Me
i-Bu
O
N
N
Me
O
O(4-FC6H4)
S23
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

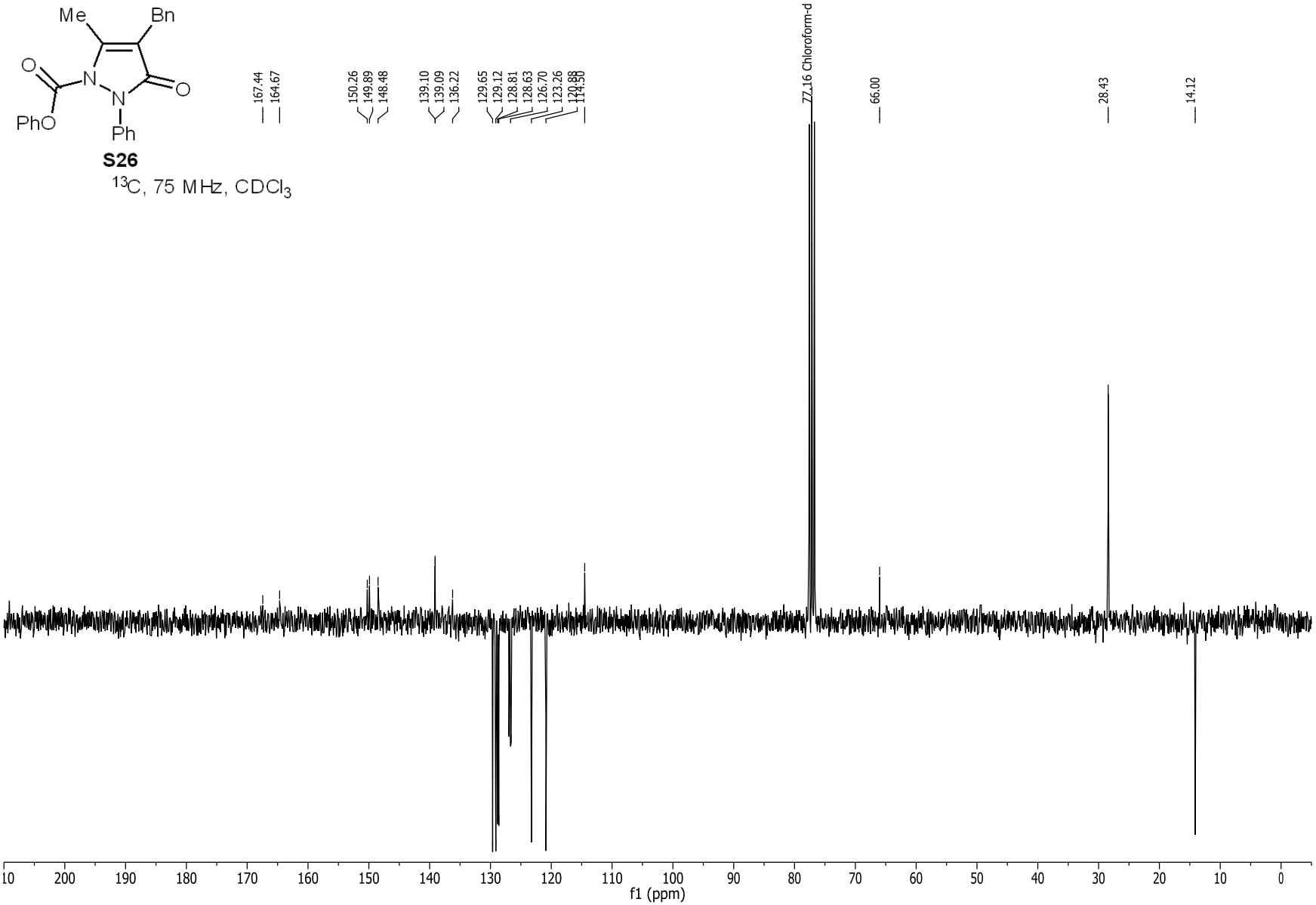

7.458
7.454
7.442
7.441
7.429
7.426
7.328
7.313
7.298
7.208
7.206
7.203
7.191
7.190
3.549
2.461
1.881
Me
Me
O
N
N
O
PhO
Me
S24
1H, 500 MHz, CDCl3
1
3.07
3.08
2.03
2
3.09
0
9
8
7
6
5
4
3
2
1
0


169.283
149.874
148.510
147.415
129.922
126.868
121.263
111.459
35.094
14.068
7.265
Me
Me
O
N
N
O
PhO
Me
S24
13C, 125 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0


7.471
7.444
7.421
7.398
7.315
7.291
7.218
7.193
7.168
6.826
6.822
6.795
2.580
2.429
2.404
2.379
2.354
1.193
1.169
1.143
Me
Et
O
N
N
O
PhO
Ph
S25
1H, 300 MHz, CDCl3
4.37
2.05
2.08
4.21
1.05
3
3.05
0
9
8
7
6
5
4
3
2
1
0

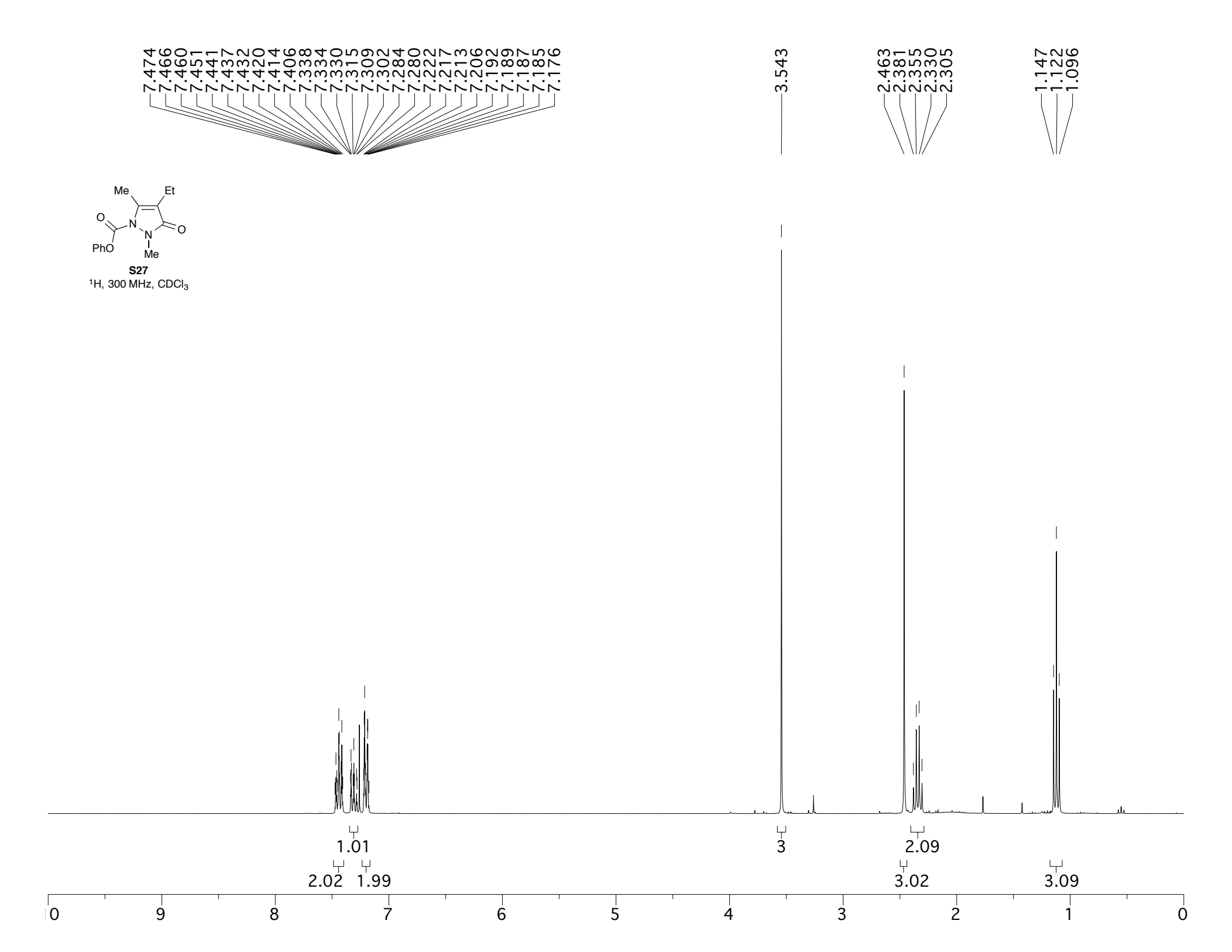

162.160
149.954
149.206
148.681
139.158
129.644
129.096
126.837
126.655
123.241
120.943
116.628
15.943
13.770
13.543
Me
Et
O
N
N
O
PhO
Ph
S25
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

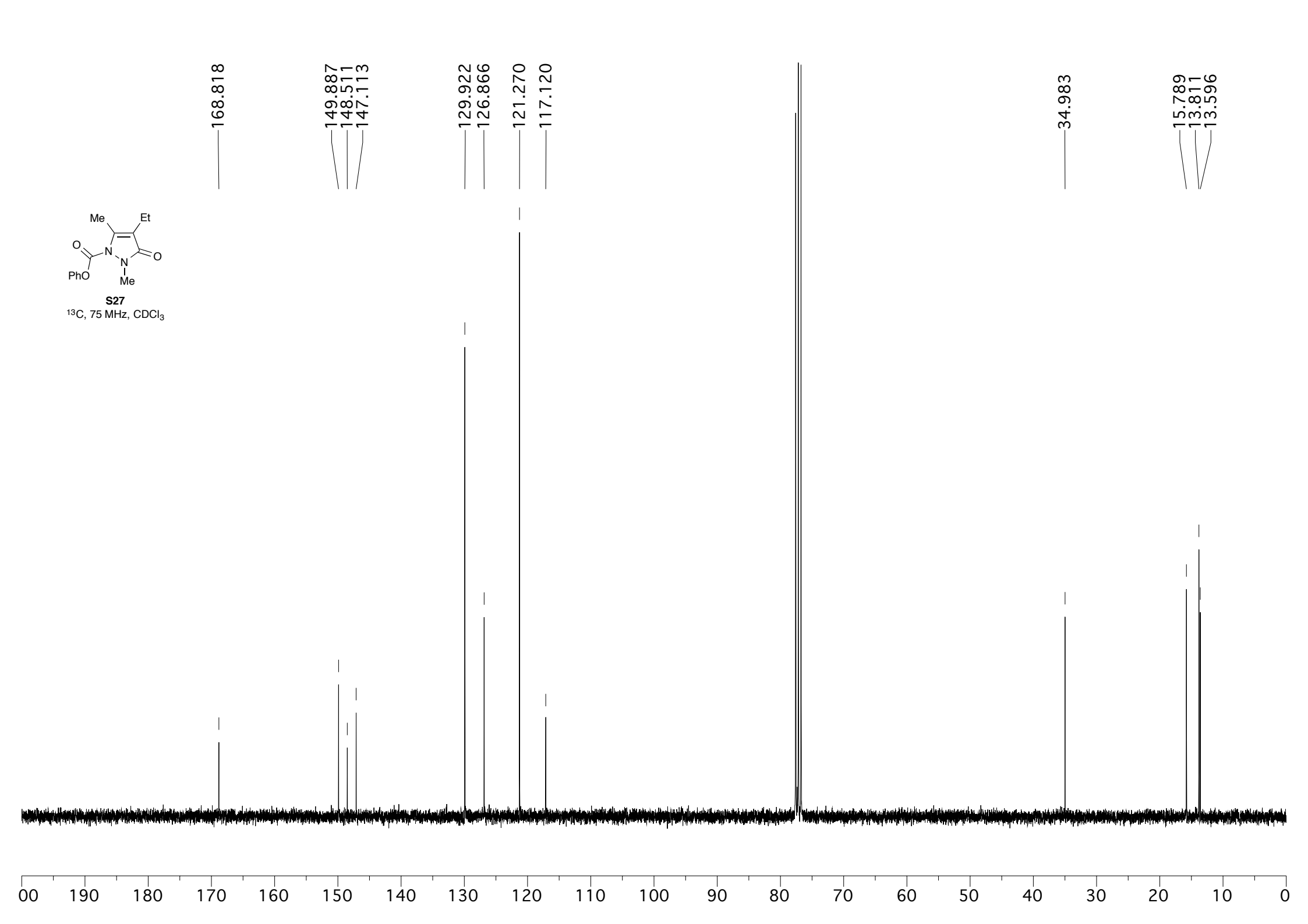

7.46
7.45
7.43
7.43
7.40
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.22
7.21
7.21
7.20
7.19
6.82
6.81
6.81
6.80
6.79
6.78
6.78
6.77
3.72
2.60
Me
Bn
O
N
N
O
PhO
Ph
S26
1H, 300 MHz, CDCl3
13.51
1.99
2.01
3.00
f1 (ppm)

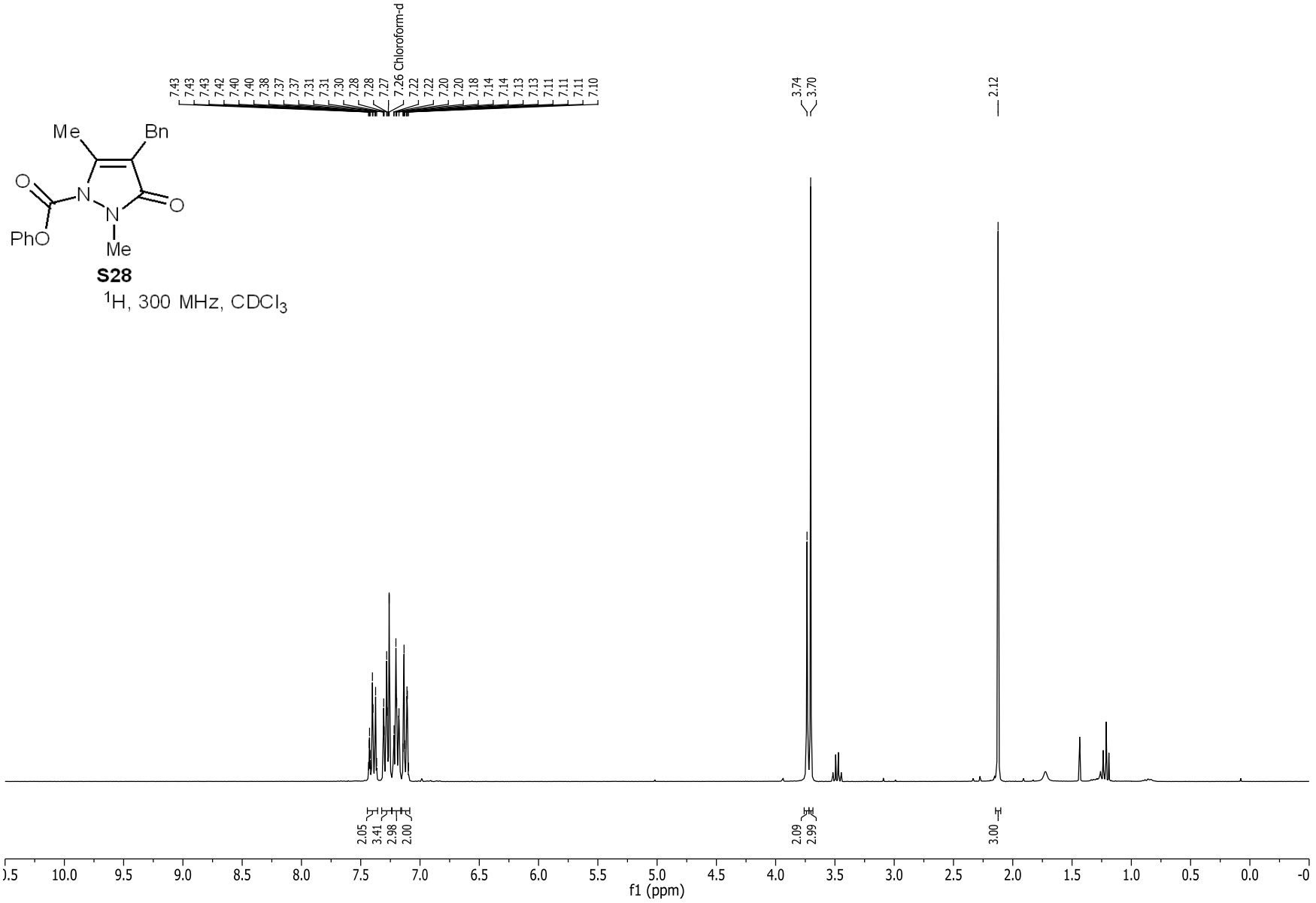


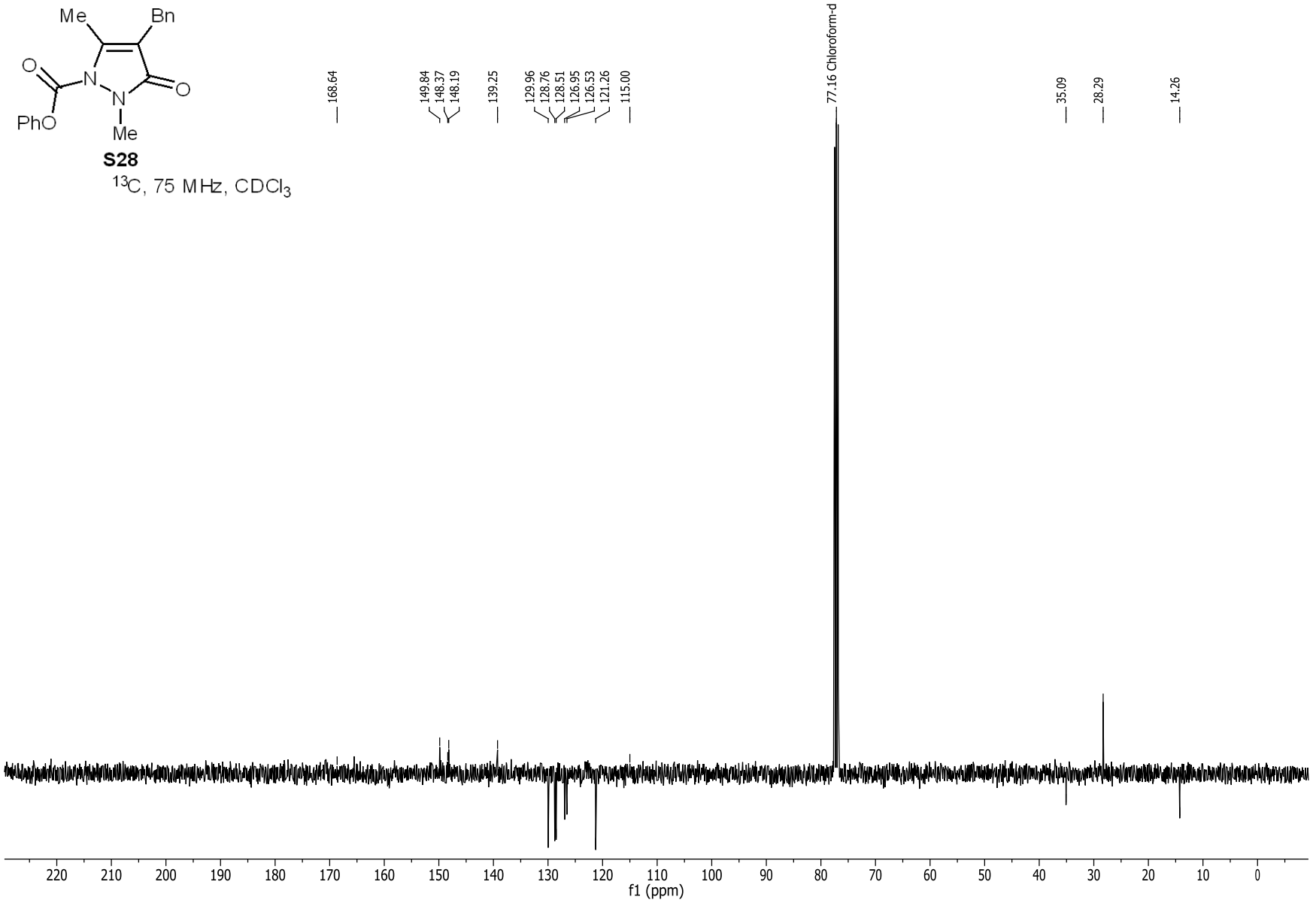
S26

^{13}C, 75 MHz, $CDCl_3$


7.474
7.466
7.460
7.451
7.441
7.437
7.432
7.420
7.414
7.406
7.338
7.334
7.330
7.315
7.309
7.302
7.284
7.280
7.222
7.217
7.213
7.206
7.192
7.189
7.187
7.185
7.176
3.543
2.463
2.381
2.355
2.330
2.305
1.147
1.122
1.096
Me
Et
O
N
N
O
PhO
Me
S27
1H, 300 MHz, CDCl3
1.01
3
2.09
2.02
1.99
3.02
3.09
0
9
8
7
6
5
4
3
2
1
0

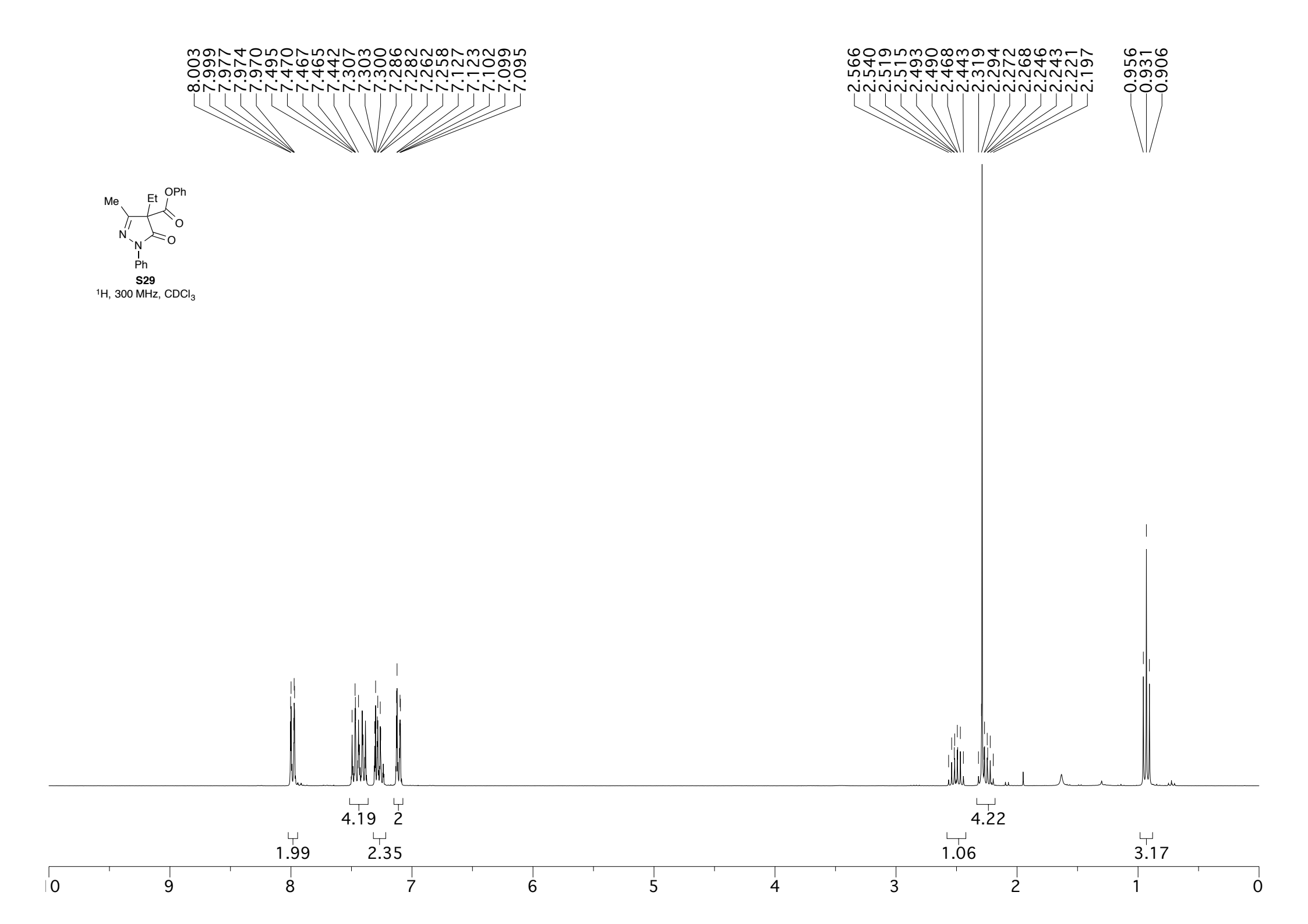

168.818
149.887
148.511
147.113
129.922
126.866
121.270
117.120
34.983
15.789
13.811
13.596
Me
Et
O
N
N
O
PhO
Me
S27
13C, 75 MHz, CDCl3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
Bn
O
N
N
O
PhO
Me
S28
1H, 300 MHz, CDCl3
Chloroform-d
7.43
7.43
7.43
7.42
7.40
7.40
7.38
7.37
7.37
7.31
7.31
7.30
7.28
7.28
7.27
7.26
7.22
7.22
7.20
7.20
7.18
7.14
7.14
7.13
7.13
7.11
7.11
7.11
7.10
3.74
3.70
2.12
2.05
3.41
2.98
2.00
2.09
2.99
3.00
f1 (ppm)



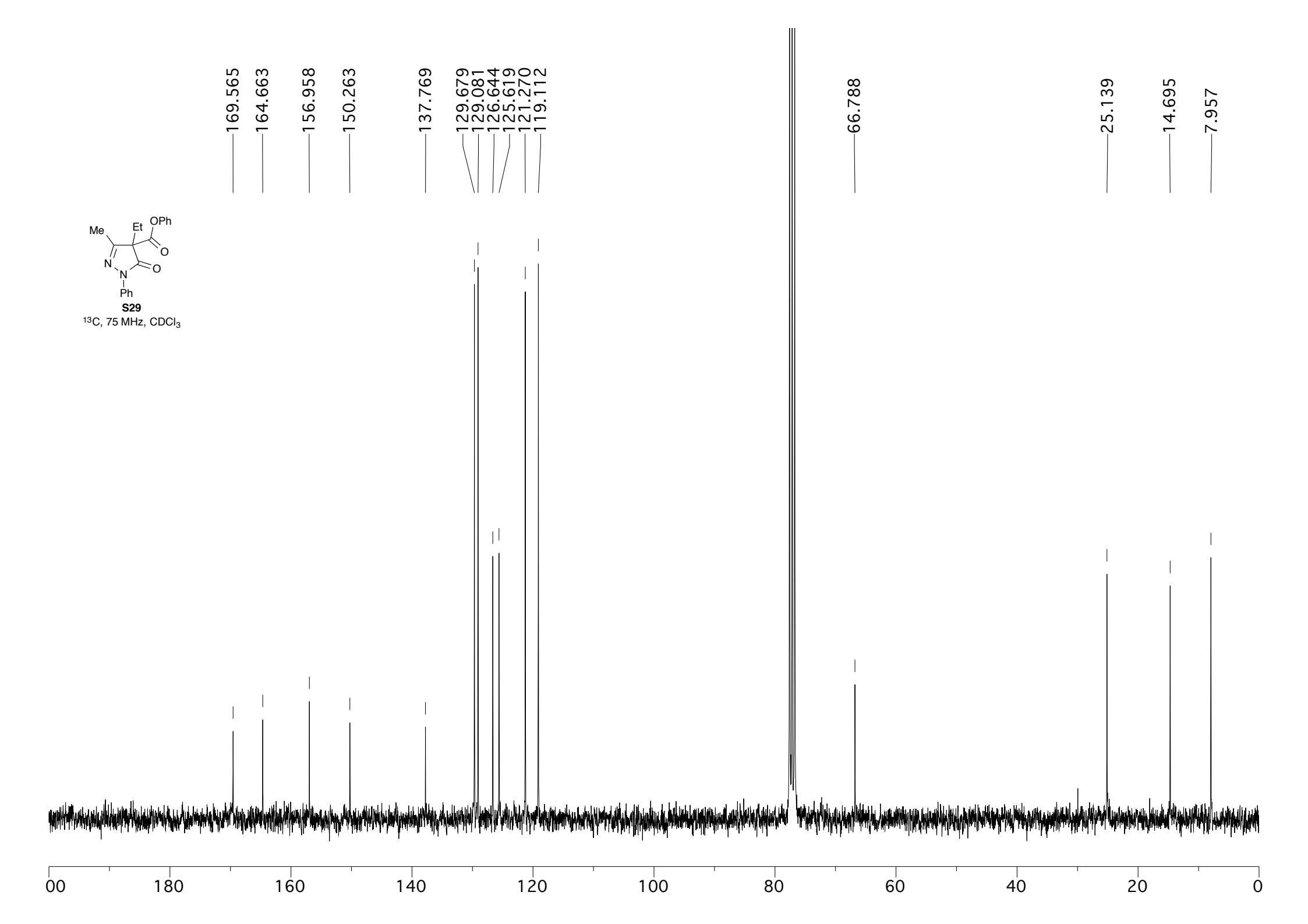
S28

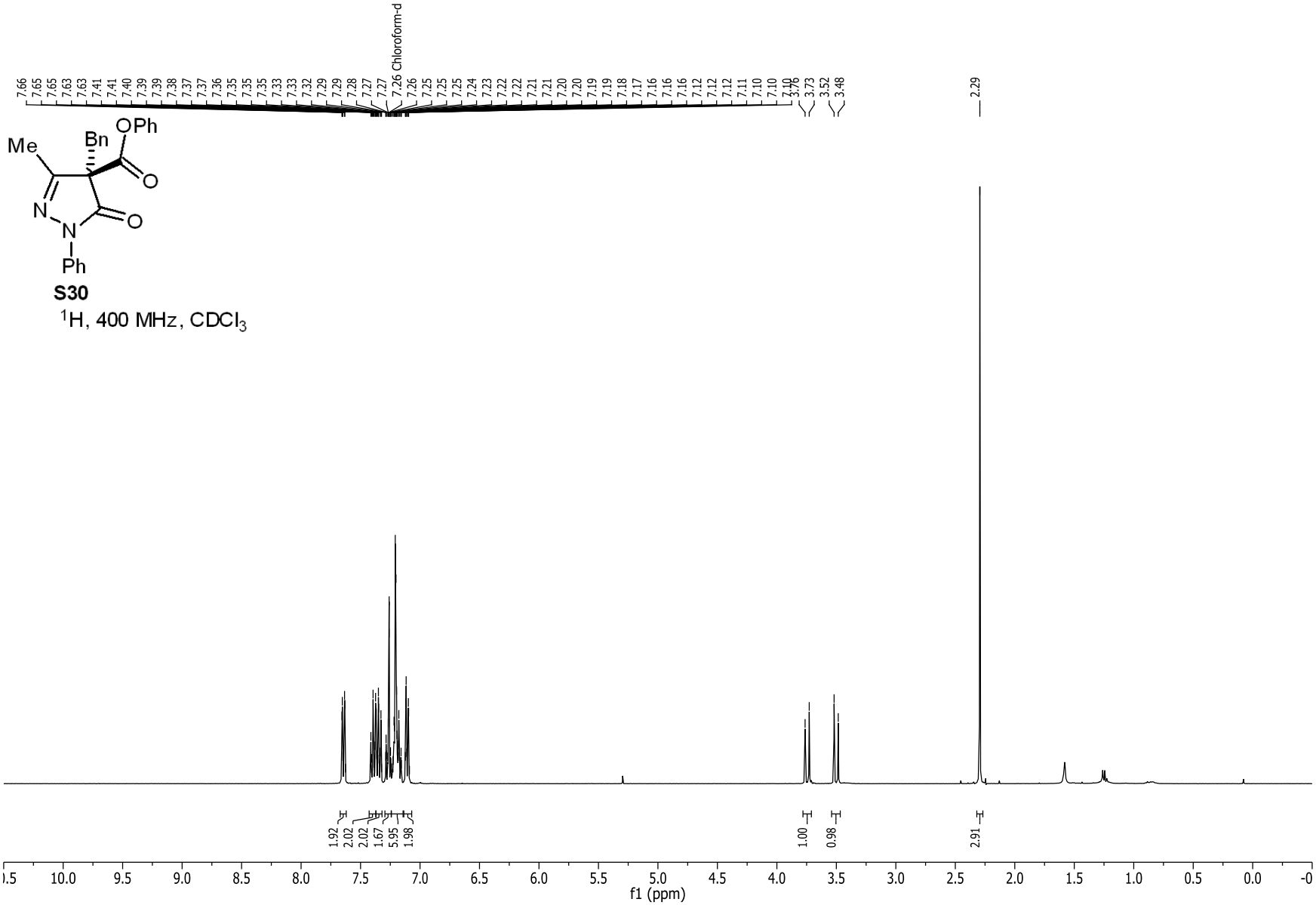
^{13}C, 75 MHz, $CDCl_3$

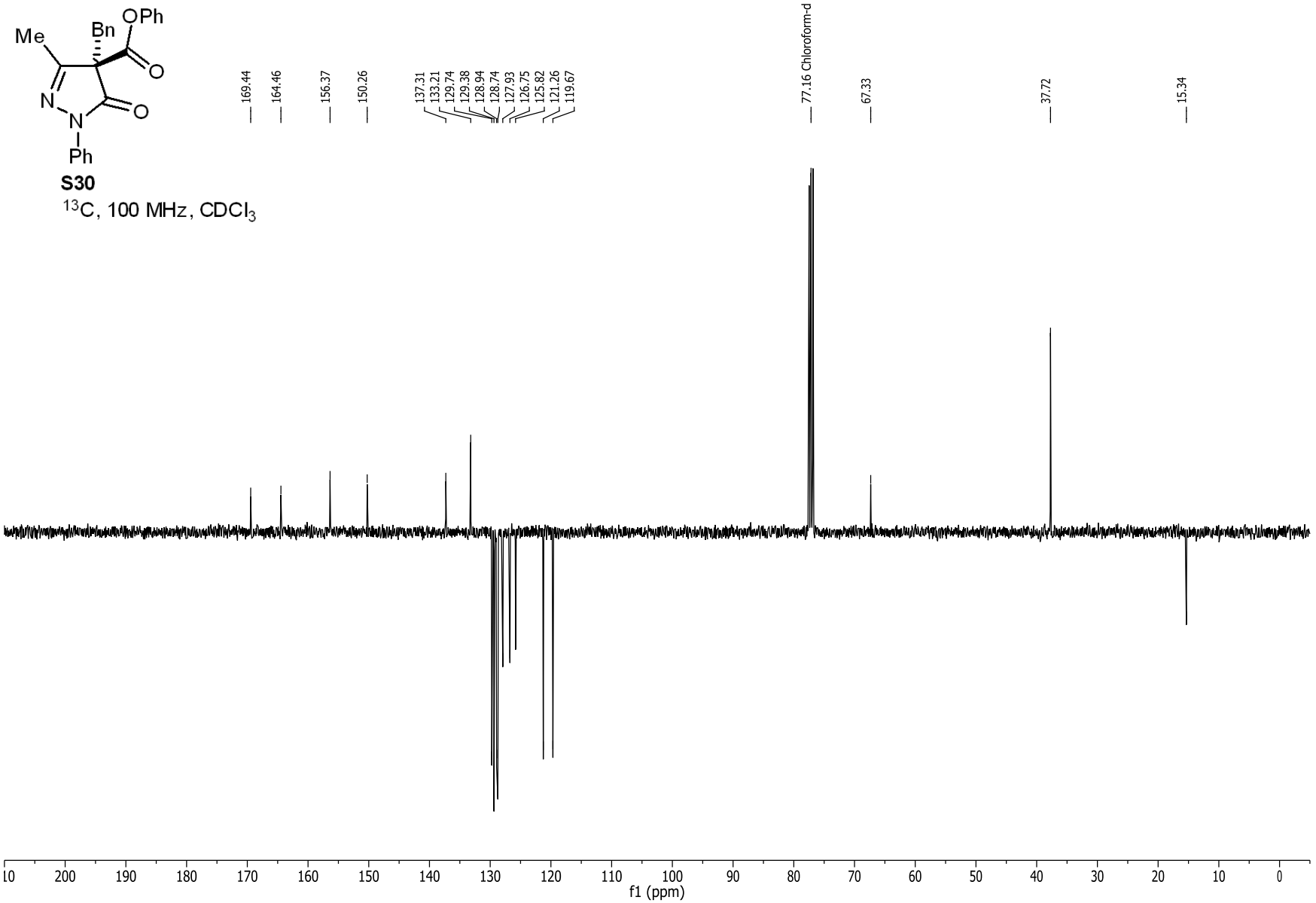


S29

^{1}H, 300 MHz, $CDCl_3$

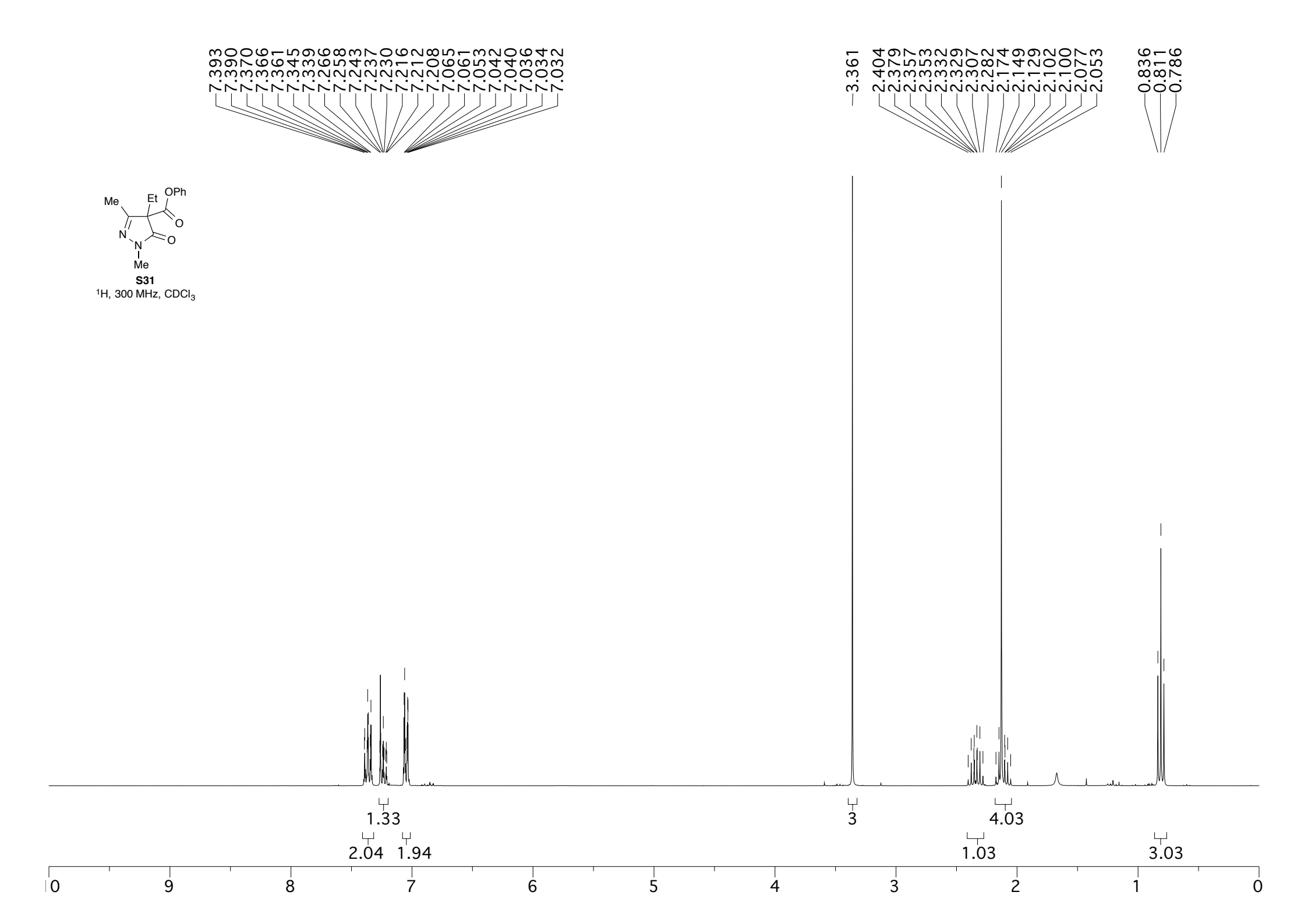

169.565
164.663
156.958
150.263
137.769
129.679
129.081
126.644
125.619
121.270
119.112
66.788
25.139
14.695
7.957
Me
Et
OPh
O
O
N
N
Ph
S29
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0

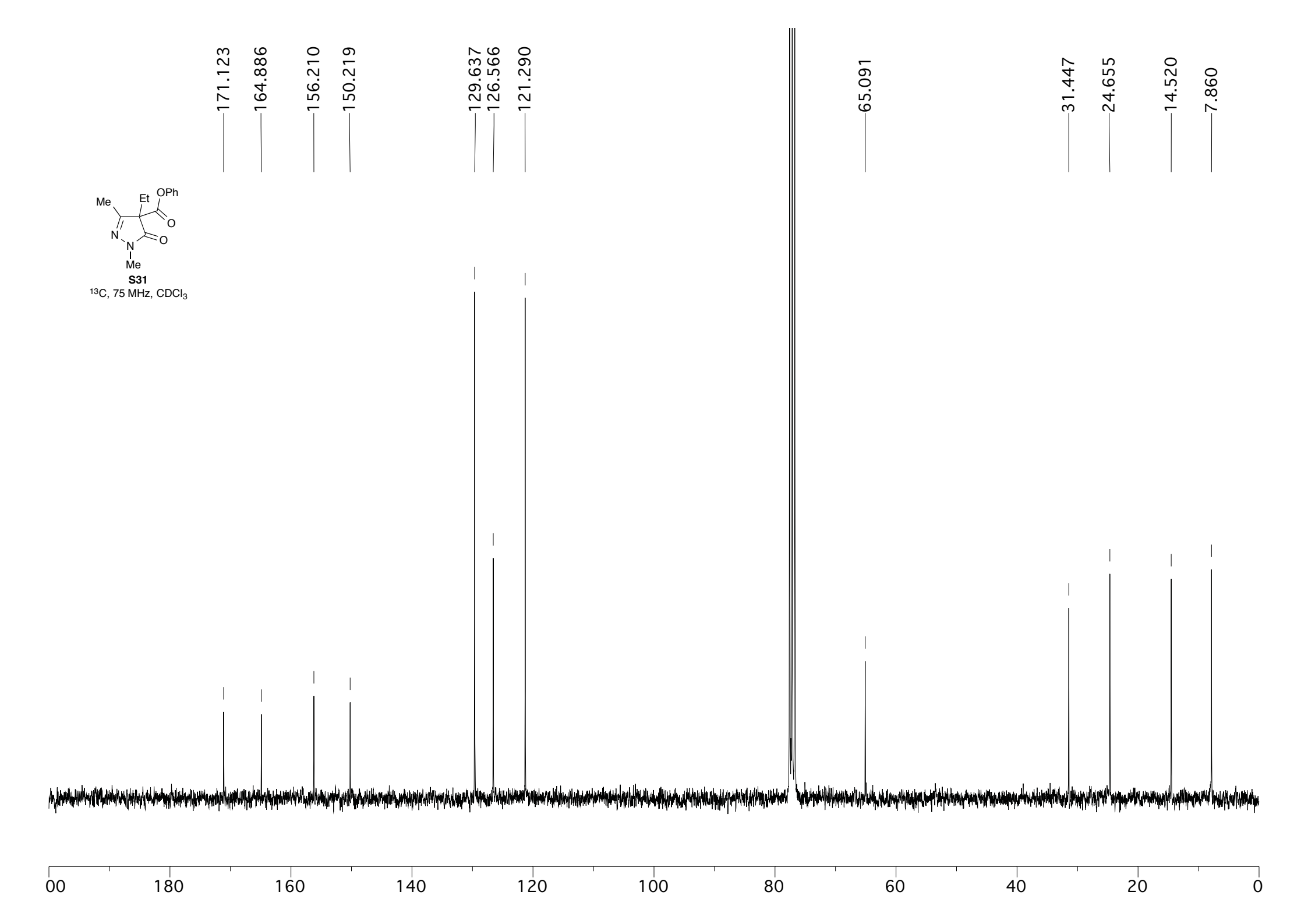

Chloroform-d
Me
Bn
OPh
O
O
N
N
Ph
S30
^{1}H, 400 MHz, $CDCl_3$
f1 (ppm)

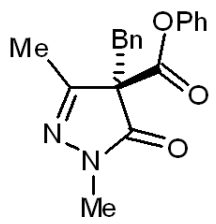


S30

^{13}C, 100 MHz, $CDCl_3$

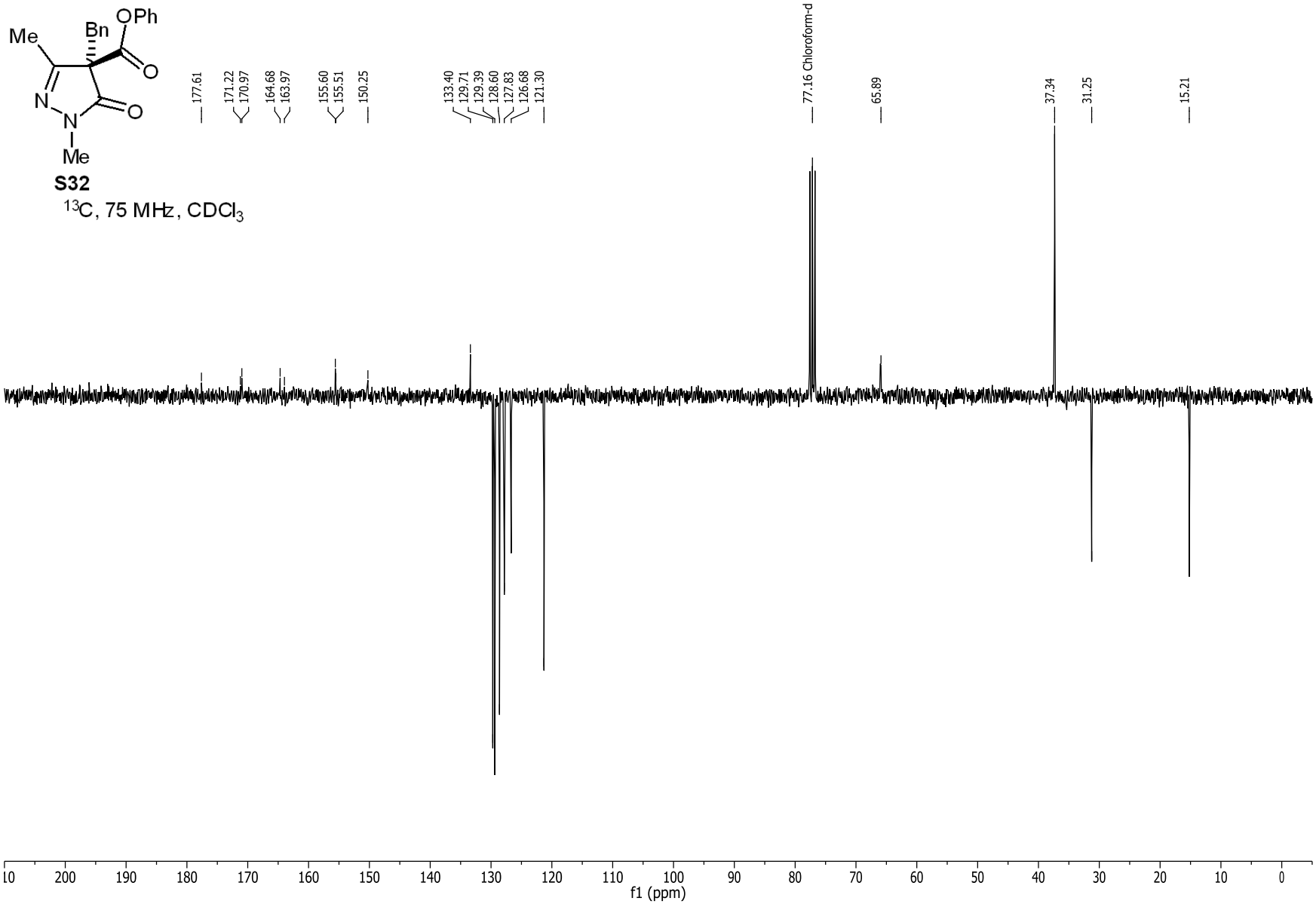

7.393
7.390
7.370
7.366
7.361
7.345
7.339
7.266
7.258
7.243
7.237
7.230
7.216
7.212
7.208
7.065
7.061
7.053
7.042
7.040
7.036
7.034
7.032
3.361
2.404
2.379
2.357
2.353
2.332
2.329
2.307
2.282
2.174
2.149
2.129
2.102
2.100
2.077
2.053
0.836
0.811
0.786
Me
Et
OPh
O
N
O
N
Me
S31
1H, 300 MHz, CDCl3
1.33
3
4.03
2.04
1.94
1.03
3.03
0
9
8
7
6
5
4
3
2
1
0


171.123
164.886
156.210
150.219
129.637
126.566
121.290
65.091
31.447
24.655
14.520
7.860
Me
Et
OPh
O
N
O
N
Me
S31
13C, 75 MHz, CDCl3
00
180
160
140
120
100
80
60
40
20
0



S32

^{1}H, 300 MHz, $CDCl_3$


Me
Bn
OPh
O
N
N
O
Me
177.61
171.22
170.97
164.68
163.97
155.60
155.51
150.25
133.40
129.71
129.39
128.60
127.83
126.68
121.30
77.16 Chloroform-d
65.89
37.34
31.25
15.21
S32
13C, 75 MHz, CDCl3
f1 (ppm)