Supporting Information for

Unprecedented *E*-stereoselectivity on sigmatropic Hurd-Claisen rearrangement of Morita-Baylis-Hillman adducts: A Joint Experimental–Theoretical Study.

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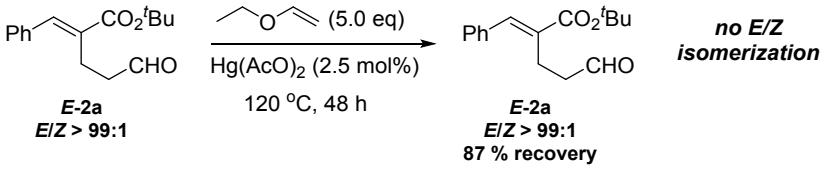
1. General procedure for evaluate of the hypothetical isomerization of the Hurd-Claisen rearrangement product 2a.



***E*-2a**
***E*/*Z* > 99:1**

***E*-2a**
***E*/*Z* > 99:1**
87 % recovery

In a Schlenk flask were added the rearrangement product ***E*-2a** (2.5 mmol), ethyl vinyl ether (13 mmol) and mercury acetate (2.5 mol%). The mixture was kept at 120 ºC under stirring for 48 h. The crude aliquot reaction was analyzed by ^{1}H NMR. The reaction was then treated with 7.5 mL of ethyl ether and washed with brine (3 x 5 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The rearrangement product ***E*-2a** was recovered in 87 % with no detectable isomerization.

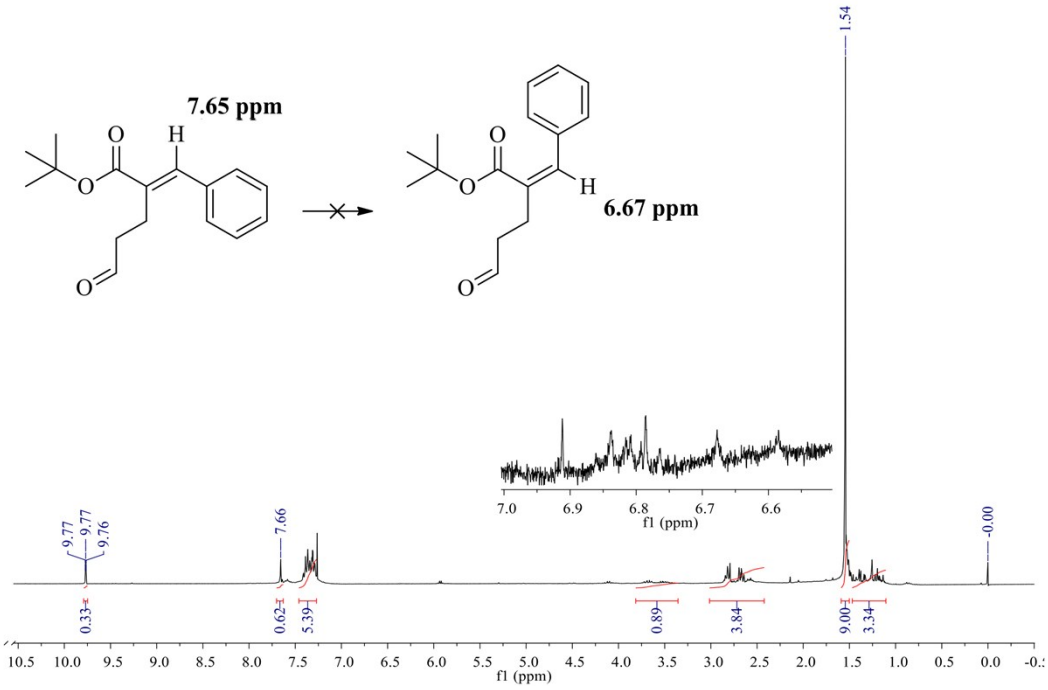
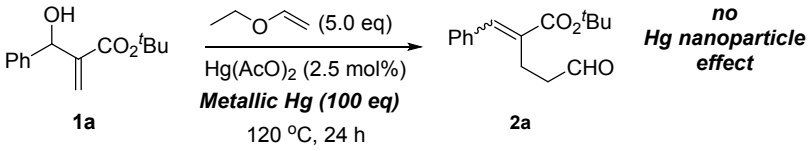


Figure S1. Evaluation of the hypothetical isomerization of the Hurd-Claisen rearrangement products **2a**.

2. General procedure for probe the Hg nanoparticle effect on the Hurd-Claisen rearrangement of MBH adducts.



In a Schlenk flask were added the MBH adduct **1a** (5.0 mmol), ethyl vinyl ether (26 mmol) and mercury acetate (0,0062 mmol). The mixture was kept at 120 ºC under stirring for 1 h. The temperature was reduced to 20°C, and half of the reaction mass was transferred to another Schlenk flak containing metallic mercury (0,62 mmol). Both Schlenk flasks were was kept at 110 ºC under stirring for 23 h. Crude aliquot reactions were analyzed by ^{1}H NMR for conversion calculation.

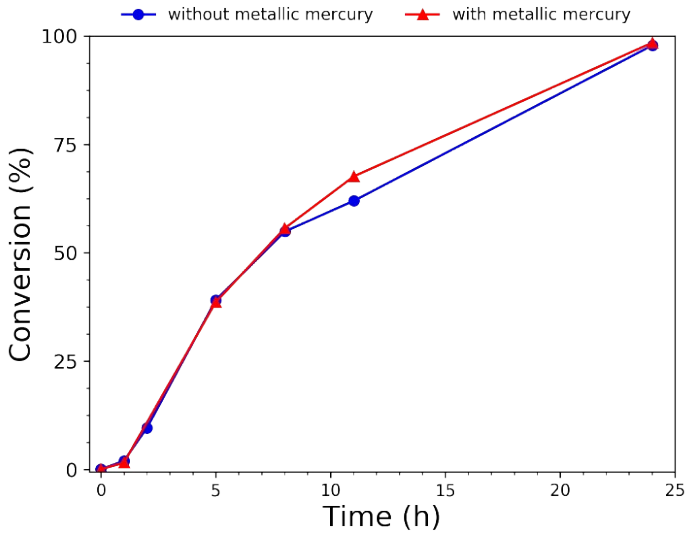


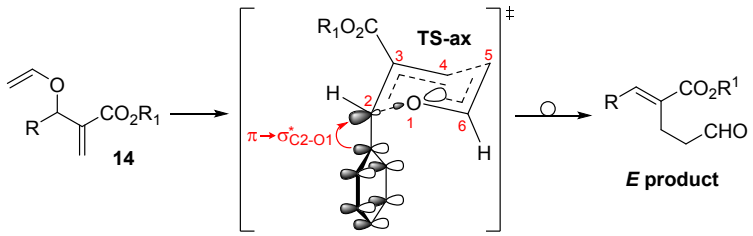
Figure S2. Influence of metallic mercury on the progress of the Hurd-Claisen rearrangement of MBH adduct **1a**.

3. Computational Results.

Text S1. Additional discussion on the hyperconjugative effects on the transition state geometries.

As discussed in the main text, the Basavaiah TS model seemed inaccurate in two cases: (1) aryl groups have *E*:*Z* ratio three-fold higher than the isopropyl group and seven-fold higher than any other alkyl group evaluated by us; (2) Aryl groups with electron withdrawing groups (EWG) have almost the same *E*:*Z* ratio observed for the isopropyl group, *e.g.* three-fold lower than aryl groups with electron donating groups (EDG) or phenyl.

The progress of the concerted [3,3] sigmatropic rearrangements reveals an asynchronous break in the O1-C2 bond and formation of the C4-C5 bond. As a consequence, the development of partial positive charge at C2 can be expected. The presence of EDG at this carbon could stabilize the development of partial positive charge, facilitating the C2-O1 bond breaking and consequently increasing the reaction rate of the rearrangement. The pseudo-axial orientation of the EDG better matches the orbital overlap between the π aromatic electron density of the aryl groups and the $\sigma^*_{C2\text{-}O1}$, increasing the rate of the reaction passing through the TS-ax (Scheme S1).



Scheme S1: Contribution of the Stereoelectronic Effect for Basavaiah TS Model for Claisen Rearrangements of MBH Adducts.

To shed some light on the stereoelectronic effects that might be controlling the *E* preference of the synthesized products, we performed a theoretical investigation with NBO theory (a method for quantifying stereoelectronic interactions) to revisit the Basavaiah TS-model. As for the NCI study, we selected the same substituents (CH_3, Ph, and *p*-NO_2Ph). NBO analysis (Table S1) provided significant inklings of the feasibility of the TS model proposed in Scheme S1, resulting from hyperconjugative stabilizing effects. The most striking evidence of hyperconjugative stabilization of the TS-ax bearing aryl substituents is observed from the π C23/C25 → $\boldsymbol{\sigma}^*$C2/O1 interaction, which is much stronger than any other electron delocalization taking place in the alkyl fragment instead. This interaction is not significant when the aryl group is in its pseudo-equatorial orientation due to small orbital overlapping as anticipated before. Interestingly, the π C23/C25 → $\boldsymbol{\sigma}^*$C2/O1 delocalization energy does not mitigate appreciably in the presence of the strong EWG NO_2 (nearly 7% lower) and therefore hyperconjugative effects do not dominate the decrease in the *E:Z* ratio in the case of aryl substituent bearing an EWG.

Inspection of Table S1 also shows a much less significant endo-hyperconjugation between the lone pair of O1 and the antibonding $\boldsymbol{\sigma}^*$ C2/R (R= CH_3, Ph, pNO_2Ph) which is present in the pseudo-axial orientation (resembling the endo-anomeric effect).[27] For aryl-bearing substituents, this electron delocalization energy does not reach 1 kcal/mol.

For the alkyl-bearing compound, this effect is also not so important, since (LP O1 → $\boldsymbol{\sigma}^*$ C2/CH_3) = 1.20 kcal/mol. This becomes even more evident when we confront the C2/O1 interatomic distance across the different substituents and conformations as presented in Figure S2, which did not surpass 0.1 Å when going from TS-*eq* to TS-*ax* conformation, regardless of the R substituent. These results indicate that the *E:Z* ratio is not importantly affected by the anomeric carbon-heteroatom distance but, instead, that the nature of the stereoselectivity has its roots in other effects such as steric and/or electrostatic, as discussed in the main text.

The possible explanation that the partial positive charge on C2 is stabilized by the aryl substituent as the driving force for the *E* preference in the MBH adducts was also investigated. Fig. S2 also portrays the NBO atomic charges on the C2 atom for every TS theoretically studied here. As anticipated in Scheme S1 we note that the atomic charges *q*(C2) are indeed more positive in the systems bearing the alkyl group than those containing aryl groups. However, it is noteworthy that the relative magnitude of the *q*(C2) values of *E*:*Z* for a given R is in sharp contrast with the experimental *E:Z* relative proportions. In the case of R = CH_3, the C2 atomic charge is nearly 19% lower when R assumes the axial position for the equatorial position. The same reasoning gives *q*(C2) values 31% and 45% lower in the TS-ax for R = Ph and *p*NO_2Ph, respectively. Thus, the hypothetical orbital overlap between the π aromatic electron density of the aryl groups and the $\sigma^*_{C2\text{-}O1}$ *does not* explain the reaction path passing preferentially through the TS-ax (Scheme S1), hence it cannot account for the experimental dramatic drop in the *E*:*Z* ratio when the EWG is present in terms of electron delocalization/charge stabilization. This is because the *q*(C2) values are much lower than they should be, due to the presence of an EWG in the aryl segment, which presumably would drain the π-electrons, inhibiting the stabilization of the partial *q*(C2) charge.

Table S1. Most Relevant Delocalization Energies, *E*(2), for the TS Stage in the Hurd-Claisen Rearrangement for the R = CH_3, Ph and *p*NO_2Ph Substituents Considering both Pseudo-axial and Equatorial Positions.

Substituent – R	Interaction	*E*(2) / kcal.mol^{-1}
Ph axial	π C23/C25 → $\boldsymbol{\sigma}$*C2/O1	12.69
	LP O1 → $\boldsymbol{\sigma}$* C2/R	0.99
Ph equatorial	$\boldsymbol{\sigma}$ C2/H → $\boldsymbol{\sigma}$*C2/O1	2.16
	LP O1 → $\boldsymbol{\sigma}$* C2/H	0.60
pNO_2Ph axial	π C23/C25 → $\boldsymbol{\sigma}$*C2/O1	11.85
	LP O1 → $\boldsymbol{\sigma}$* C2/R	0.63
pNO_2Ph equatorial	$\boldsymbol{\sigma}$ C2/H → $\boldsymbol{\sigma}$*C2/O1	2.08
	LP O1 → $\boldsymbol{\sigma}$* C2/H	0.96
CH_3 axial	$\boldsymbol{\sigma}$ C25/H18 → $\boldsymbol{\sigma}$*C2/O1	1.56
	LP O1 → $\boldsymbol{\sigma}$* C2/R	1.20
CH_3 equatorial	$\boldsymbol{\sigma}$ C25/H20 → $\boldsymbol{\sigma}$*C2/O1	5.94
	$\boldsymbol{\sigma}$ C2/H → $\boldsymbol{\sigma}$*C2/O1	2.19
	LP O1 → $\boldsymbol{\sigma}$* C2/H	2.10

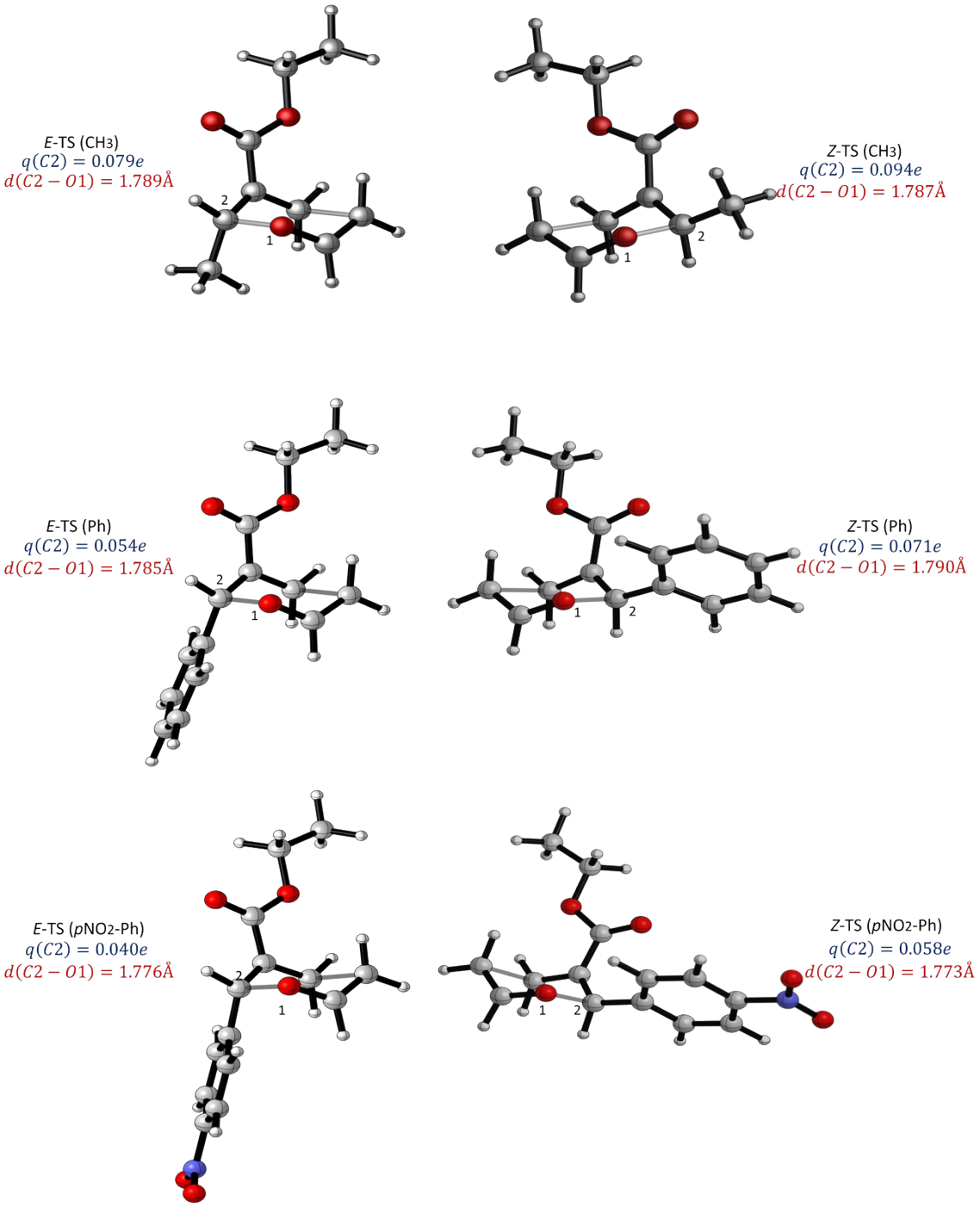


Figure S2. M06-2X/6-311+G(d,p) optimized transition state geometries of the *E* and *Z* conformers in the Hurd-Claisen rearrangement. NBO atomic charges (blue) and the interatomic distance between the C2 and O1 atoms (red) are shown to assess the hyperconjugative TS-model.

Table S2. Imaginary Frequencies for all TS calculated with thermal corrections from scaled (0.970) M06-2X/6-311+G(d,p) level of theory at the experimental temperature T=373K.

Substituent	Imaginary frequency (cm-1)
TS-ax-CH_3	-539.28
TS-eq-CH_3	-527.10
TS-ax-Ph	-520.16
TS-eq-Ph	-529.14
TS-ax-*p*NO_2Ph	-530.56
TS-eq-*p*NO_2Ph	-538.78

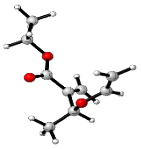
Table S3. The total s-F-SAPT/jun-cc-pVDZ energy decomposition in each transition state of the Hurd-Claisen rearrangement between the substituents and the ester fragment for both *E* and *Z* isomers. All values in kcal/mol.

Substituent	E_{lst}	E_{xch}	E_{ind}	E_{disp}	E_{tot}
TS-ax					
CH_3	1.96174	0.42886	-0.35384	-0.25342	1.178334
Ph	2.75701	0.51316	-0.52022	-0.51157	2.23837
pNO_2Ph	3.97455	0.53942	-0.63226	-0.51625	3.36546
TS-eq					
CH_3	4.97668	4.91444	-1.13465	-1.47342	7.28305
Ph	7.93321	5.87504	-1.57184	-2.59502	9.64139
pNO_2Ph	8.47053	6.0713	-1.67611	-2.68935	10.17636

Table S4. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*Z*-isomer) of the Hurd-Claisen rearrangement reaction with R = CH_3 as calculated at the M06-2X/6-311+G(d,p) level of theory.

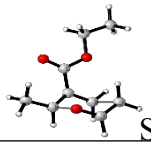
(*Z*)-Reactant

Sum of electronic and thermal free energies: -576.841575 a.u.



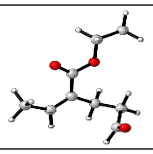
Atom	X	Y	Z
C	-1.79004	-0.8539	0.19135
O	-2.18135	0.37475	-0.41376
C	-2.22072	1.44855	0.41656
H	-2.30575	1.2156	1.47689
C	-2.19081	2.69428	-0.03823
H	-2.27731	3.52007	0.65295
H	-2.09428	2.89576	-1.09711
C	-0.36158	-0.77989	0.69202
C	-0.04064	-1.06086	1.95258
H	-0.80532	-1.3487	2.6667
C	0.69176	-0.39092	-0.30077
O	1.85547	-0.07152	0.28435
C	2.91814	0.29958	-0.60816
H	2.58983	1.1542	-1.20301
O	0.52714	-0.37079	-1.49138
H	0.98454	-1.01689	2.29666
H	3.10749	-0.53058	-1.29195
C	4.12493	0.62576	0.24157
H	4.95934	0.91787	-0.39831
H	3.9045	1.44969	0.92157
H	4.4278	-0.24125	0.83047
C	-2.03007	-1.94955	-0.83313
H	-1.4472	-1.75261	-1.73089
H	-1.74177	-2.91684	-0.41782
H	-3.08969	-1.97504	-1.0911
H	-2.42795	-1.02917	1.06856

TS-eq



Sum of electronic and thermal free energies: -576.798495 a.u.			
Atom	X	Y	Z
C	1.85401	0.74424	0.44739
O	2.27775	-0.31648	-0.92715
C	2.23076	-1.55139	-0.57167
H	3.14834	-2.00546	-0.17595
C	1.03634	-2.22175	-0.40998
H	1.05309	-3.26178	-0.10218
H	0.14719	-1.87361	-0.92038
C	0.58288	0.21734	0.81212
C	0.5705	-1.07092	1.33235
H	1.40766	-1.39961	1.93627
C	-0.64891	0.78232	0.21986
O	-1.66474	-0.10864	0.20211
C	-2.91171	0.38068	-0.31121
H	-2.75846	0.73109	-1.33388
O	-0.77769	1.90773	-0.19406
H	-0.37078	-1.56672	1.53333
H	-3.22704	1.23669	0.28918
C	-3.90418	-0.75805	-0.24317
H	-4.87086	-0.43092	-0.63002
H	-3.56134	-1.60387	-0.84119
H	-4.03886	-1.09157	0.78688
C	2.07897	2.09254	-0.16753
H	1.4646	2.22039	-1.05544
H	1.80059	2.87244	0.54441
H	3.13099	2.19896	-0.4299
H	2.66038	0.42303	1.10267

(*Z*)-Product



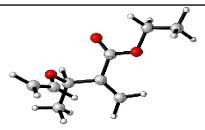
Sum of electronic and thermal free energies: -576.867461 a.u.

Atom	X	Y	Z

C	1.7061	1.48966	0.50698
O	2.1519	-2.13198	-1.52907
C	2.14034	-1.85313	-0.36193
H	3.07832	-1.53835	0.14571
C	0.92133	-1.90233	0.52313
H	1.01672	-2.79556	1.15247
H	0.03241	-2.01876	-0.09729
C	0.693	0.62022	0.62951
C	0.83152	-0.65892	1.42227
H	1.73336	-0.59065	2.0375
C	-0.60724	0.89588	-0.0451
O	-1.52496	-0.04644	0.24058
C	-2.81097	0.12495	-0.3755
H	-2.67556	0.17344	-1.45782
O	-0.84602	1.83819	-0.75724
H	-0.01537	-0.77592	2.10021
H	-3.23076	1.07861	-0.04886
C	-3.66805	-1.04892	0.04029
H	-4.65937	-0.96000	-0.40727
H	-3.22238	-1.98777	-0.29195
H	-3.77955	-1.08025	1.12509
C	1.73588	2.77741	-0.26125
H	1.57406	2.59887	-1.32616
H	0.93288	3.44455	0.05656
H	2.69412	3.27733	-0.12555
H	2.62244	1.22739	1.03277

Table S5. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*E*-isomer) of the Hurd-Claisen rearrangement reaction with R = CH_3 as calculated at the M06-2X/6-311+G(d,p) level of theory.

(*E*)-Reactant

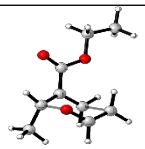


Sum of electronic and thermal free energies: -576.840386 a.u.

Atom	X	Y	Z
C	-1.56962	-0.79342	-0.54826
O	-1.92527	0.58996	-0.67188
C	-2.17868	1.25911	0.48275
H	-1.75653	0.82417	1.38595
C	-2.85635	2.40003	0.498
H	-2.99282	2.92946	1.4298
H	-3.26091	2.82012	-0.41362
C	-0.25765	-0.92786	0.19553
C	-0.0932	-1.54851	1.36041
H	-0.92289	-2.02634	1.86841
C	0.91356	-0.33312	-0.52777
O	1.95824	-0.09438	0.27543
C	3.12719	0.44016	-0.36838
H	2.85346	1.37279	-0.86544
O	0.92009	-0.11392	-1.70962
H	-1.38837	-1.09319	-1.58147
C	-2.72039	-1.6002	0.02891
H	-3.61048	-1.42807	-0.57697
H	-2.94992	-1.30357	1.05505
H	-2.48692	-2.66625	0.01641
H	0.88235	-1.60085	1.82712
H	3.45601	-0.26387	-1.13567
C	4.17389	0.64912	0.70168
H	5.08128	1.05932	0.25519
H	3.81466	1.34659	1.45948
H	4.4239	-0.29537	1.18712

TS-ax

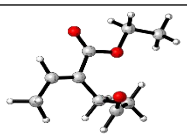
Sum of electronic and thermal free energies: -576.798817 a.u.



Atom	X	Y	Z
C	-1.67875	-1.01441	0.02359
O	-2.0454	0.19257	-1.24578
C	-2.17044	1.35808	-0.72027

H	-3.16874	1.67247	-0.39049
C	-1.0706	2.09375	-0.31987
H	-1.2239	3.07328	0.12048
H	-0.10992	1.91195	-0.78574
C	-0.52001	-0.4305	0.59903
C	-0.62528	0.77741	1.27784
H	-1.50343	0.98807	1.87368
C	0.76681	-0.8302	-0.01471
O	1.76885	0.02567	0.27421
C	3.05417	-0.31818	-0.26294
H	2.97547	-0.38175	-1.3501
O	0.93028	-1.81038	-0.69769
H	-1.47447	-1.85055	-0.63641
C	-2.98552	-1.10423	0.76012
H	-3.79475	-1.32482	0.06426
H	-3.22675	-0.18507	1.2956
H	-2.92462	-1.91357	1.4921
H	0.27725	1.28263	1.59913
H	3.3361	-1.30582	0.10791
C	4.02685	0.75301	0.17587
H	5.02214	0.53205	-0.21362
H	3.71876	1.73034	-0.19899
H	4.08373	0.79958	1.2644

(*E*)-Product



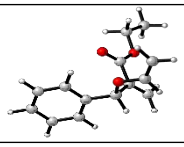
Sum of electronic and thermal free energies: -576.870160 a.u.

Atom	X	Y	Z
C	1.46217	-1.60598	-0.01362
O	2.32076	1.6582	1.50447
C	2.22797	1.67094	0.3078
H	3.14181	1.59945	-0.32196
C	0.93397	1.74579	-0.45697

H	0.98741	2.60429	-1.13521
H	0.10769	1.89115	0.23982
C	0.51645	-0.74602	-0.40579
C	0.73506	0.45931	-1.28535
H	1.60334	0.30164	-1.92938
C	-0.85534	-0.98334	0.14418
O	-1.70704	0.00008	-0.19982
C	-3.04626	-0.12976	0.30245
H	-3.00585	-0.18754	1.39199
O	-1.18745	-1.92394	0.81725
H	1.14016	-2.40224	0.65239
C	2.91481	-1.58075	-0.36248
H	3.49967	-1.32295	0.52641
H	3.15997	-0.86691	-1.14785
H	3.24377	-2.5725	-0.68176
H	-0.12567	0.599	-1.93909
H	-3.46779	-1.06745	-0.0653
C	-3.82536	1.0738	-0.1769
H	-4.85362	1.01665	0.1842
H	-3.37859	1.99605	0.1976
H	-3.84329	1.11263	-1.26707

Table S6. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*Z*-isomer) of the Hurd-Claisen rearrangement reaction with R = Ph as calculated at the M06-2X/6-311+G(d,p) level of theory.

(*Z*)-Reactant

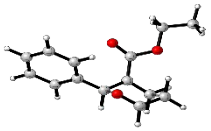


Sum of electronic and thermal free energies: -768.52363 a.u.

Atom	X	Y	Z
C	-0.68824	1.03027	0.71028
O	-0.51027	2.02046	-0.28847
C	0.30401	3.05217	0.06019
H	0.36936	3.25345	1.12831

C	0.93949	3.78227	-0.84553
H	1.52849	4.63227	-0.53272
H	0.8648	3.54647	-1.89908
C	0.61514	0.32257	1.02947
C	1.11423	0.28697	2.26232
H	0.60397	0.78445	3.08071
C	1.30921	-0.34697	-0.11704
O	2.47324	-0.90858	0.24276
C	3.19606	-1.56504	-0.81084
H	3.40061	-0.83748	-1.59891
O	0.8785	-0.37894	-1.23767
H	2.03423	-0.23934	2.48119
H	2.5627	-2.34732	-1.23411
C	4.46428	-2.1225	-0.20615
H	5.04737	-2.63195	-0.97524
H	5.07311	-1.32217	0.21673
H	4.23201	-2.83887	0.58315
H	-1.02443	1.51801	1.63601
C	-1.76927	0.06716	0.26376
C	-2.34123	-0.77959	1.21139
C	-2.18906	0.00239	-1.06105
C	-3.3308	-1.68303	0.8424
H	-2.00892	-0.73255	2.24437
C	-3.18271	-0.89936	-1.42814
H	-1.72528	0.64969	-1.79288
C	-3.75502	-1.74268	-0.4815
H	-3.772	-2.33532	1.58665
H	-3.5066	-0.94663	-2.46115
H	-4.52772	-2.44406	-0.77334

TS-eq

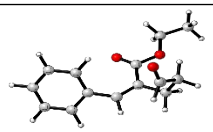


Sum of electronic and thermal free energies: -768477106 a.u.

Atom	X	Y	Z
C	-0.66114	1.1072	0.56957
O	-0.33089	1.98251	-0.95716
C	0.59858	2.85494	-0.78006
H	0.29845	3.86555	-0.4762
C	1.92697	2.50005	-0.69291
H	2.67152	3.27324	-0.53657
H	2.26806	1.56325	-1.11507

C	0.63896	0.62041	0.88421
C	1.58955	1.57299	1.22145
H	1.27346	2.46933	1.74115
C	1.07395	-0.73148	0.45196
O	2.40699	-0.77961	0.22645
C	2.92772	-2.06748	-0.13309
H	2.42969	-2.40608	-1.04389
O	0.36681	-1.69618	0.3308
H	2.62053	1.28144	1.37695
H	2.6862	-2.77776	0.66044
C	4.41957	-1.91264	-0.32461
H	4.85918	-2.87205	-0.60275
H	4.63399	-1.19243	-1.11578
H	4.89341	-1.56969	0.59642
H	-0.95579	1.97447	1.15675
C	-1.82621	0.2553	0.20234
C	-1.92978	-0.35593	-1.04541
C	-2.84236	0.08255	1.13925
C	-3.03249	-1.14404	-1.34229
H	-1.14687	-0.201	-1.77654
C	-3.94168	-0.71772	0.84521
H	-2.76917	0.56754	2.10722
C	-4.03814	-1.33229	-0.39724
H	-3.10827	-1.6161	-2.31462
H	-4.72276	-0.8535	1.5837
H	-4.89603	-1.9511	-0.63221

(*Z*)-Product



Sum of electronic and thermal free energies: -768.549277 a.u.

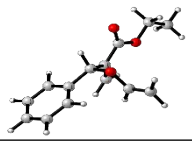
Atom	X	Y	Z
C	0.80168	0.81562	-0.87645
O	-1.5699	2.90528	1.79892
C	-1.5414	2.86775	0.59967
H	-0.84625	3.52823	0.03705
C	-2.4053	1.97259	-0.25169
H	-3.17027	2.60635	-0.71638
H	-2.90718	1.24686	0.38815
C	-0.47895	0.4184	-0.79192

C	-1.58314	1.2864	-1.35574
H	-1.1327	2.04967	-1.99636
C	-0.87265	-0.8965	-0.19487
O	-2.20511	-1.0792	-0.27299
C	-2.69667	-2.32146	0.25422
H	-2.39083	-2.40222	1.29928
O	-0.13601	-1.72482	0.26951
H	-2.25568	0.6933	-1.97648
H	-2.22988	-3.14242	-0.2938
C	-4.2004	-2.3115	0.09878
H	-4.61848	-3.24096	0.48889
H	-4.63916	-1.47788	0.64926
H	-4.4792	-2.22119	-0.9521
H	0.96521	1.73548	-1.43794
C	2.05046	0.2271	-0.35464
C	3.17098	0.21626	-1.19134
C	2.18502	-0.22595	0.96002
C	4.38747	-0.28372	-0.74346
H	3.08179	0.59261	-2.20518
C	3.40615	-0.70404	1.41432
H	1.33187	-0.19751	1.62465
C	4.50705	-0.74505	0.56292
H	5.24186	-0.30244	-1.40936
H	3.49879	-1.04773	2.43753
H	5.45652	-1.12567	0.9203

Table S7. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*E*-isomer) of the Hurd-Claisen rearrangement reaction with R = Ph as calculated at the M06-2X/6-311+G(d,p) level of theory.

(*E*)-Reactant

Sum of electronic and thermal free energies: -768.522787 a.u.

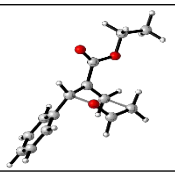


Atom	X	Y	Z
C	0.49524	0.19782	0.69225
O	0.37149	1.61995	0.71762
C	0.36611	2.27056	-0.47784
H	0.53692	1.65676	-1.35716
C	0.17756	3.58195	-0.55203
H	0.19403	4.06973	-1.51568

H	0.00662	4.17241	0.33871
C	-0.62805	-0.40113	-0.1367
C	-0.49195	-0.93471	-1.34743
H	0.48316	-1.02107	-1.81433
C	-1.96879	-0.32617	0.52905
O	-2.98506	-0.55634	-0.31083
C	-4.29715	-0.52304	0.27582
H	-4.44635	0.45535	0.73655
O	-2.11512	-0.09945	1.7012
H	0.31338	-0.08153	1.73231
H	-1.35452	-1.30342	-1.88791
H	-4.34618	-1.27594	1.06518
C	-5.29071	-0.79034	-0.83123
H	-6.3051	-0.77049	-0.42926
H	-5.21156	-0.03084	-1.61013
H	-5.11535	-1.76953	-1.27914
C	1.89063	-0.26244	0.30785
C	2.16939	-1.63107	0.25248
C	2.92333	0.64474	0.08398
C	3.44906	-2.08269	-0.04007
H	1.37659	-2.34699	0.44264
C	4.20641	0.19062	-0.21596
H	2.73374	1.70842	0.1549
C	4.4731	-1.17025	-0.28306
H	3.64836	-3.14717	-0.07722
H	4.9989	0.90858	-0.39114
H	5.47171	-1.52063	-0.51491

TS-ax

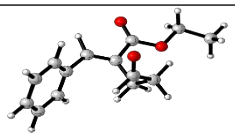
Sum of electronic and thermal free energies: -768483651 a.u.



Atom	X	Y	Z
C	-0.51905	-0.12164	-0.77391
O	-0.3821	1.63937	-1.01225
C	-0.43416	2.23037	0.13048
H	-1.42185	2.48671	0.53238
C	0.66701	2.27709	0.961
H	0.58798	2.78218	1.9177
H	1.65872	2.17644	0.53728
C	0.57872	-0.34013	0.10134
C	0.53541	0.19864	1.3817

H	-0.40936	0.23912	1.90892
C	1.87513	-0.61582	-0.55743
O	2.92874	-0.38681	0.25245
C	4.21846	-0.66052	-0.31448
H	4.3413	-0.05702	-1.21597
O	2.0018	-1.0069	-1.69081
H	-0.33556	-0.39704	-1.80806
H	1.41922	0.15562	2.00646
H	4.25512	-1.71107	-0.61038
C	5.25247	-0.32976	0.73784
H	6.25286	-0.52887	0.34963
H	5.1942	0.72317	1.01807
H	5.10093	-0.93705	1.63146
C	-1.93229	-0.31539	-0.31853
C	-2.97026	0.43946	-0.87163
C	-2.23986	-1.30543	0.61644
C	-4.28557	0.21604	-0.4861
H	-2.72999	1.20853	-1.59604
C	-3.55907	-1.53076	0.99902
H	-1.44159	-1.90932	1.03273
C	-4.58439	-0.76884	0.45199
H	-5.08062	0.81096	-0.91991
H	-3.78292	-2.30488	1.72341
H	-5.61125	-0.94262	0.75084

(*E*)-Product



Sum of electronic and thermal free energies: -768.555105 a.u.

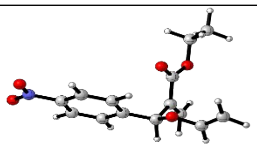
Atom	X	Y	Z
C	0.4614	-1.07191	0.48547
O	0.54613	2.51716	1.29301
C	0.58668	2.22321	0.12906
H	1.5628	2.1497	-0.39663
C	-0.62219	1.90058	-0.71209
H	-0.65161	2.60669	-1.54927
H	-1.52432	2.02366	-0.11144
C	-0.58865	-0.55401	-0.16326
C	-0.51133	0.46703	-1.27166
H	0.43338	0.36912	-1.80758
C	-1.93772	-0.93783	0.36438

O	-2.92226	-0.2501	-0.23823
C	-4.25398	-0.53425	0.22056
H	-4.30091	-0.34034	1.29398
O	-2.14241	-1.7548	1.22341
H	0.24862	-1.71213	1.33827
H	-1.31641	0.30397	-1.98765
H	-4.45731	-1.59557	0.06428
C	-5.19766	0.35039	-0.5616
H	-6.2252	0.16749	-0.24281
H	-4.96621	1.40333	-0.39417
H	-5.12486	0.14277	-1.63015
C	1.8831	-0.80023	0.18306
C	2.70012	-0.25305	1.17692
C	2.43434	-1.0768	-1.07093
C	4.03069	0.04483	0.90957
H	2.27712	-0.03218	2.15062
C	3.7696	-0.79089	-1.3332
H	1.81465	-1.5336	-1.83482
C	4.56836	-0.22158	-0.34644
H	4.64784	0.48601	1.68299
H	4.18687	-1.01631	-2.30749
H	5.60723	0.0064	-0.55276

Table S8. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*Z*-isomer) of the Hurd-Claisen rearrangement reaction with R = *p*NO_2Ph as calculated at the M06-2X/6-311+G(d,p) level of theory.

(*Z*)-Reactant

Sum of electronic and thermal free energies: -973.042329 a.u.

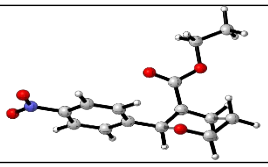


Atom	X	Y	Z
C	0.66355	1.39159	0.74145
O	1.07302	2.20283	-0.34311
C	2.21412	2.9181	-0.1334
H	2.43254	3.15048	0.90734
C	2.97362	3.3316	-1.13685
H	3.83711	3.94928	-0.93689
H	2.73269	3.07139	-2.15932
C	1.66712	0.28994	1.02288
C	2.26353	0.16081	2.20484
H	2.05296	0.85449	3.01237

C	1.94504	-0.65116	-0.10949
O	2.91465	-1.52819	0.17553
C	3.23136	-2.46655	-0.86792
H	3.52937	-1.90802	-1.75734
O	1.35906	-0.62228	-1.15818
H	2.96992	-0.6378	2.39145
H	2.32981	-3.03155	-1.11284
C	4.34019	-3.35432	-0.35222
H	4.61358	-4.08378	-1.11638
H	5.22344	-2.76353	-0.10582
H	4.01939	-3.89299	0.54049
H	0.59711	2.0113	1.64679
C	-0.71821	0.84407	0.44649
C	-1.41576	0.20966	1.47425
C	-1.29033	0.95688	-0.81754
C	-2.68287	-0.3084	1.25353
H	-0.9632	0.11648	2.45599
C	-2.55912	0.44587	-1.05429
H	-0.7308	1.43138	-1.61125
C	-3.23056	-0.1764	-0.01346
H	-3.24436	-0.80206	2.03453
H	-3.02691	0.51655	-2.02667
N	-4.58041	-0.7229	-0.26133
O	-5.04441	-0.59081	-1.37282
O	-5.14229	-1.27049	0.66322

TS-eq

Sum of electronic and thermal free energies: -972.996505 a.u.

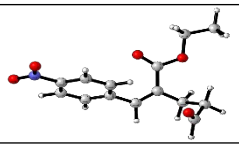


Atom	X	Y	Z
C	-0.59712	1.42149	-0.59785
O	-1.03891	2.17748	0.94342
C	-2.1789	2.76773	0.8349
H	-2.17986	3.82023	0.52791
C	-3.36347	2.06214	0.81488
H	-4.29766	2.60455	0.71705
H	-3.41276	1.07466	1.25616
C	-1.73236	0.60439	-0.85164
C	-2.92524	1.27109	-1.10723
H	-2.8961	2.21321	-1.64119
C	-1.75211	-0.80311	-0.38369
O	-3.01014	-1.25776	-0.20801
C	-3.12237	-2.63221	0.19576

H	-2.59276	-2.76364	1.14136
O	-0.78305	-1.48985	-0.18935
H	-3.84623	0.71007	-1.20468
H	-2.62884	-3.25682	-0.55142
C	-4.59578	-2.94679	0.31903
H	-4.72708	-3.98536	0.62728
H	-5.06709	-2.3039	1.06408
H	-5.1025	-2.80356	-0.63646
H	-0.56695	2.33439	-1.18926
C	0.77091	0.87981	-0.33753
C	1.62536	0.72217	-1.42868
C	1.20632	0.54165	0.94196
C	2.90247	0.20972	-1.25645
H	1.2851	0.98845	-2.42307
C	2.48273	0.03516	1.13102
H	0.54008	0.67494	1.78265
C	3.30542	-0.12494	0.02635
H	3.57959	0.07037	-2.08772
H	2.84462	-0.23918	2.11229
N	4.6649	-0.66665	0.22339
O	5.36664	-0.79312	-0.7574
O	4.99783	-0.95195	1.35337

(*Z*)-Product

Sum of electronic and thermal free energies: -973.067314 a.u.



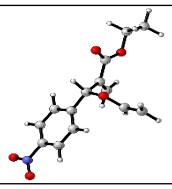
Atom	X	Y	Z
C	0.42227	-1.20969	-0.96839
O	2.30451	-2.41426	2.04526
C	2.74271	-2.64628	0.95201
H	2.49266	-3.60187	0.44231
C	3.61167	-1.70407	0.16124
H	4.54087	-2.2237	-0.09568
H	3.84649	-0.83269	0.77158
C	1.5953	-0.57265	-0.86353
C	2.89527	-1.29075	-1.14162
H	2.68272	-2.18237	-1.7382
C	1.65832	0.87279	-0.46621
O	2.92308	1.25483	-0.22676
C	3.1011	2.63291	0.14639
H	2.49898	2.8321	1.03488

O	0.7238	1.6245	-0.39618
H	3.56667	-0.65791	-1.72282
H	2.72319	3.26237	-0.66165
C	4.57667	2.84344	0.39616
H	4.75765	3.8808	0.68215
H	4.9274	2.19742	1.20236
H	5.1556	2.62701	-0.50281
H	0.45063	-2.22974	-1.35026
C	-0.92975	-0.7308	-0.60716
C	-1.95826	-0.80494	-1.54884
C	-1.21099	-0.28412	0.68667
C	-3.24535	-0.40068	-1.22444
H	-1.74653	-1.16693	-2.54827
C	-2.4933	0.10902	1.03159
H	-0.4171	-0.25043	1.42292
C	-3.48569	0.04935	0.06355
H	-4.05324	-0.43422	-1.94224
H	-2.73394	0.45734	2.02652
N	-4.85509	0.47194	0.42266
O	-5.70478	0.41171	-0.43991
O	-5.0449	0.85296	1.55709

Table S9. Cartesian coordinates (in Å) for the optimized structures of the reactant, transition state and product (*E*-isomer) of the Hurd-Claisen rearrangement reaction with R = *p*NO_2Ph as calculated at the M06-2X/6-311+G(d,p) level of theory.

(*E*)-Reactant

Sum of electronic and thermal free energies: -973.040191 a.u.

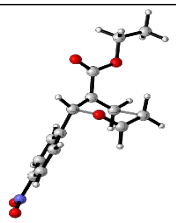


Atom	X	Y	Z
C	-0.53968	0.44601	0.74078
O	-0.8437	1.83654	0.69477
C	-0.88204	2.43535	-0.52986
H	-0.65105	1.80132	-1.38045
C	-1.17786	3.72155	-0.65947
H	-1.1924	4.16907	-1.64246
H	-1.41011	4.33088	0.20428
C	-1.5265	-0.33893	-0.10592
C	-1.26218	-0.89245	-1.286
H	-0.26704	-0.85506	-1.71597
C	-2.89208	-0.43169	0.50717

O	-3.82521	-0.84424	-0.3553
C	-5.1544	-0.97914	0.18039
H	-5.4638	-0.01311	0.5836
O	-3.11479	-0.17614	1.6611
H	-0.73204	0.18517	1.7844
H	-2.03904	-1.40256	-1.84131
H	-5.12598	-1.69393	1.0052
C	-6.04787	-1.44117	-0.9472
H	-7.07071	-1.55336	-0.58393
H	-6.04712	-0.71481	-1.76089
H	-5.71212	-2.40324	-1.33674
C	0.92179	0.15931	0.44657
C	1.37802	-1.16312	0.47589
C	1.83267	1.19027	0.22283
C	2.71439	-1.45956	0.26519
H	0.67802	-1.96859	0.66704
C	3.17703	0.90942	0.00272
H	1.49899	2.21965	0.22848
C	3.59072	-0.41048	0.02361
H	3.08454	-2.47545	0.28499
H	3.8979	1.69527	-0.17741
N	5.01703	-0.71575	-0.2131
O	5.35077	-1.88055	-0.18867
O	5.76300	0.2165	-0.4178

TS-ax

Sum of electronic and thermal free energies: -973.000639 a.u.

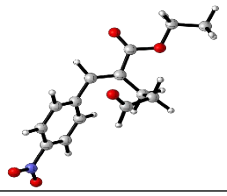


Atom	X	Y	Z
C	-0.49959	0.26302	0.84062
O	-0.75631	2.00092	0.58271
C	-0.69879	2.2674	-0.67677
H	0.28247	2.49695	-1.10938
C	-1.75987	1.99245	-1.51488
H	-1.67608	2.2295	-2.56998
H	-2.75947	1.92164	-1.10409
C	-1.51823	-0.28001	0.0142
C	-1.4387	-0.09814	-1.36153
H	-0.4706	-0.11004	-1.84678
C	-2.82842	-0.48619	0.67503
O	-3.83746	-0.61765	-0.20581
C	-5.13584	-0.84704	0.36554

H	-5.37663	-0.01616	1.03152
O	-2.99231	-0.53766	1.86802
H	-0.72688	0.25712	1.90279
H	-2.27598	-0.38828	-1.98457
H	-5.09537	-1.7563	0.96861
C	-6.11716	-0.96498	-0.77812
H	-7.12122	-1.13745	-0.38692
H	-6.13087	-0.04921	-1.37112
H	-5.85225	-1.79884	-1.42979
C	0.95183	0.07248	0.52459
C	1.89278	1.03531	0.90417
C	1.38695	-1.10398	-0.09009
C	3.24328	0.83768	0.6624
H	1.55097	1.94576	1.38019
C	2.73694	-1.31796	-0.33806
H	0.66241	-1.86086	-0.36464
C	3.63878	-0.3382	0.04116
H	3.98592	1.57114	0.94542
H	3.09274	-2.22241	-0.81223
N	5.07707	-0.55381	-0.22577
O	5.84645	0.31574	0.11992
O	5.39557	-1.58597	-0.77462

(*E*)-Product

Sum of electronic and thermal free energies: -973.071586 a.u.

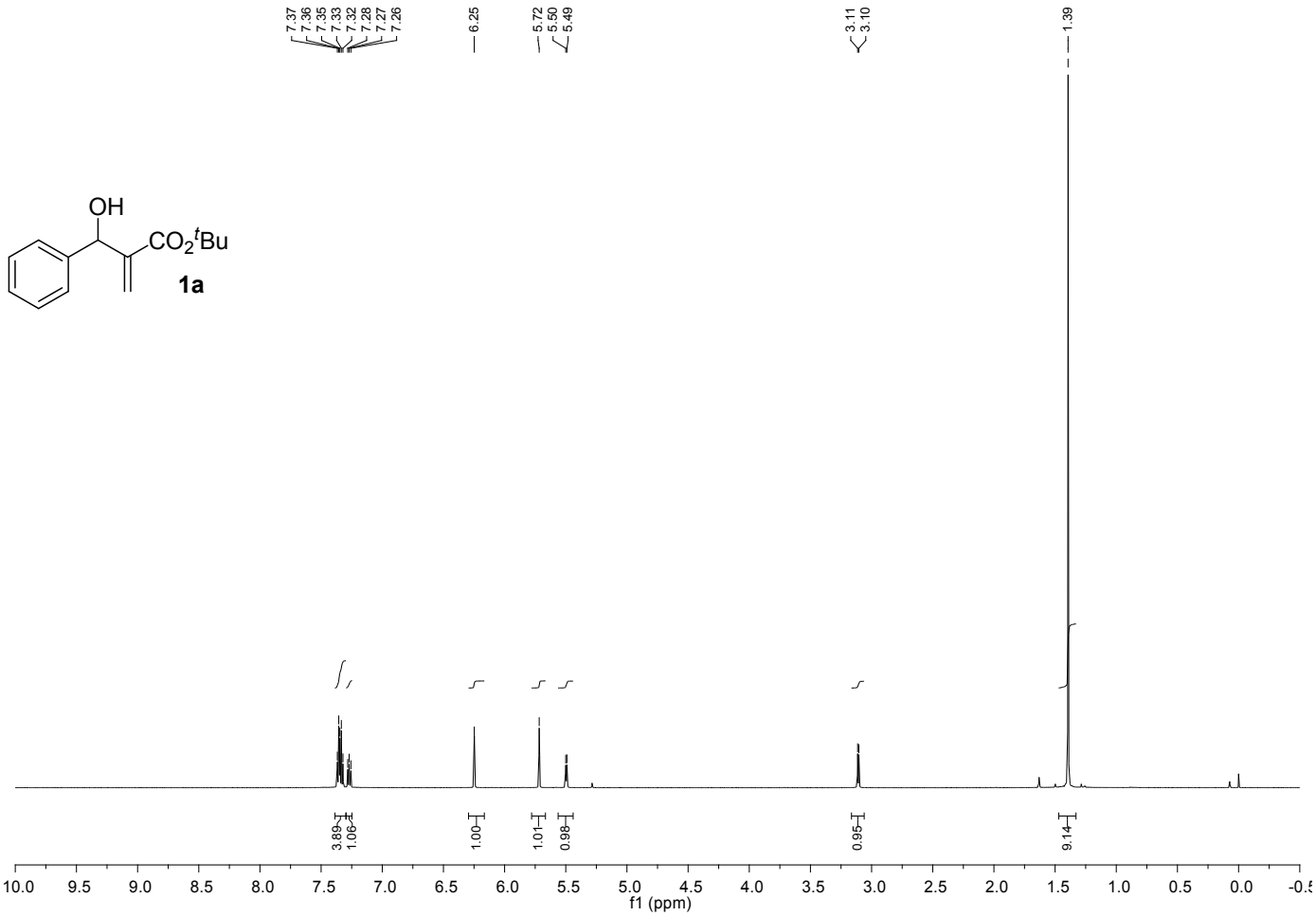


Atom	X	Y	Z
C	-0.53853	-1.0192	0.66941
O	-0.43364	2.4997	1.17682
C	-0.3555	2.21844	0.01187
H	0.63538	2.18477	-0.49056
C	-1.52824	1.8387	-0.85415
H	-1.51587	2.46224	-1.7537
H	-2.45587	2.01227	-0.30757
C	-1.5449	-0.55423	-0.07844
C	-1.39924	0.35661	-1.27155
H	-0.42936	0.20463	-1.7476
C	-2.92603	-0.87857	0.41339
O	-3.86862	-0.2513	-0.30501
C	-5.2276	-0.48468	0.10611
H	-5.3287	-0.18713	1.15157

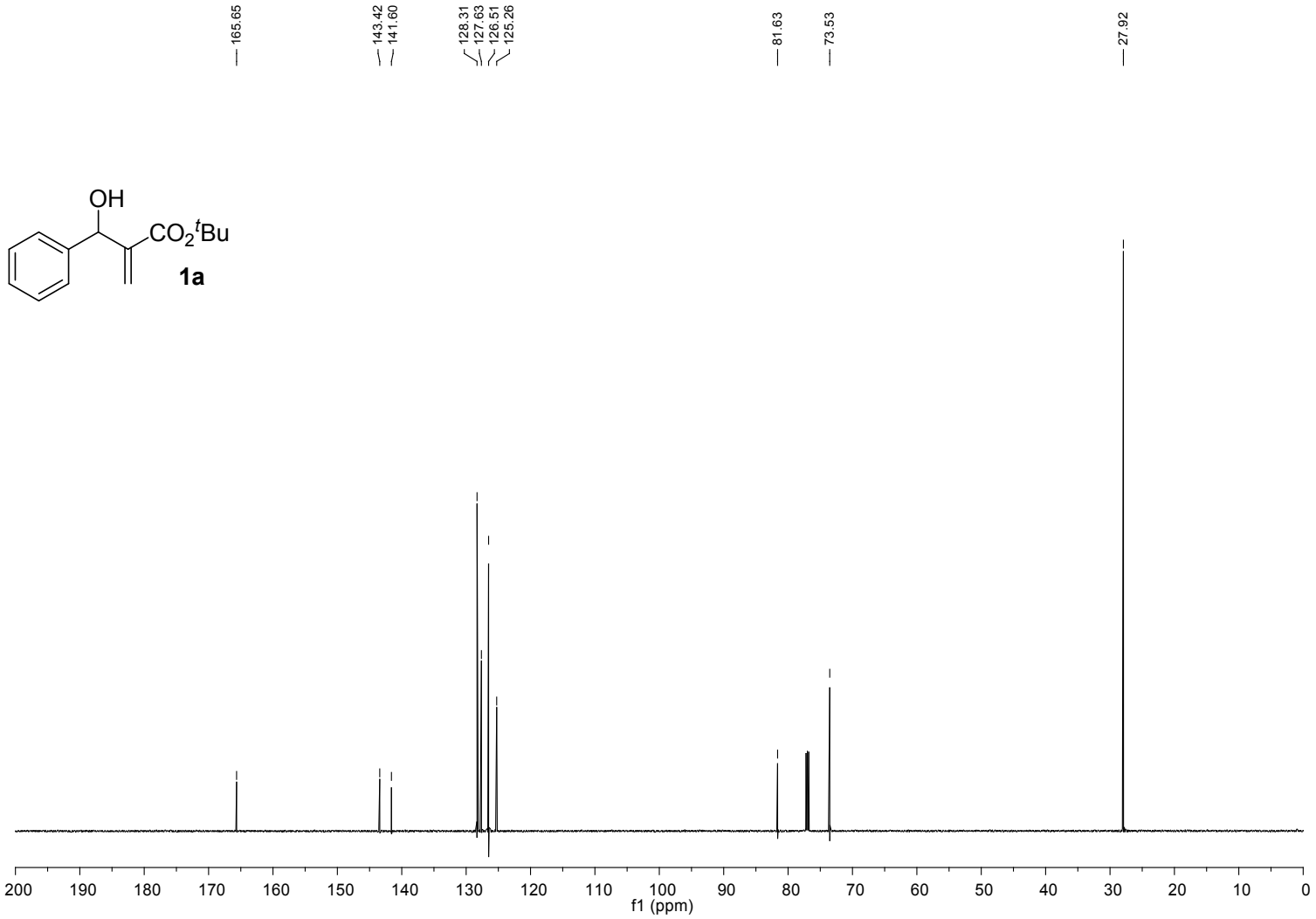
O	-3.1765	-1.60646	1.33687
H	-0.79893	-1.57704	1.56566
H	-2.16853	0.13096	-2.00937
H	-5.42998	-1.55554	0.04187
C	-6.1194	0.32323	-0.8081
H	-7.16386	0.17526	-0.52895
H	-5.88888	1.38674	-0.73066
H	-5.99184	0.01249	-1.84601
C	0.89928	-0.78653	0.41373
C	1.50829	-1.21977	-0.76825
C	1.66741	-0.12581	1.37868
C	2.85564	-0.98186	-0.99977
H	0.92287	-1.76012	-1.50293
C	3.01295	0.12833	1.15833
H	1.19579	0.22006	2.29087
C	3.57979	-0.30435	-0.03124
H	3.34682	-1.31175	-1.90502
H	3.61939	0.6531	1.88384
N	5.01346	-0.03811	-0.27512
O	5.62914	0.54427	0.59004
O	5.48133	-0.41698	-1.32694

4. Copy of spectra for Morita-Baylis-Hillman Adducts

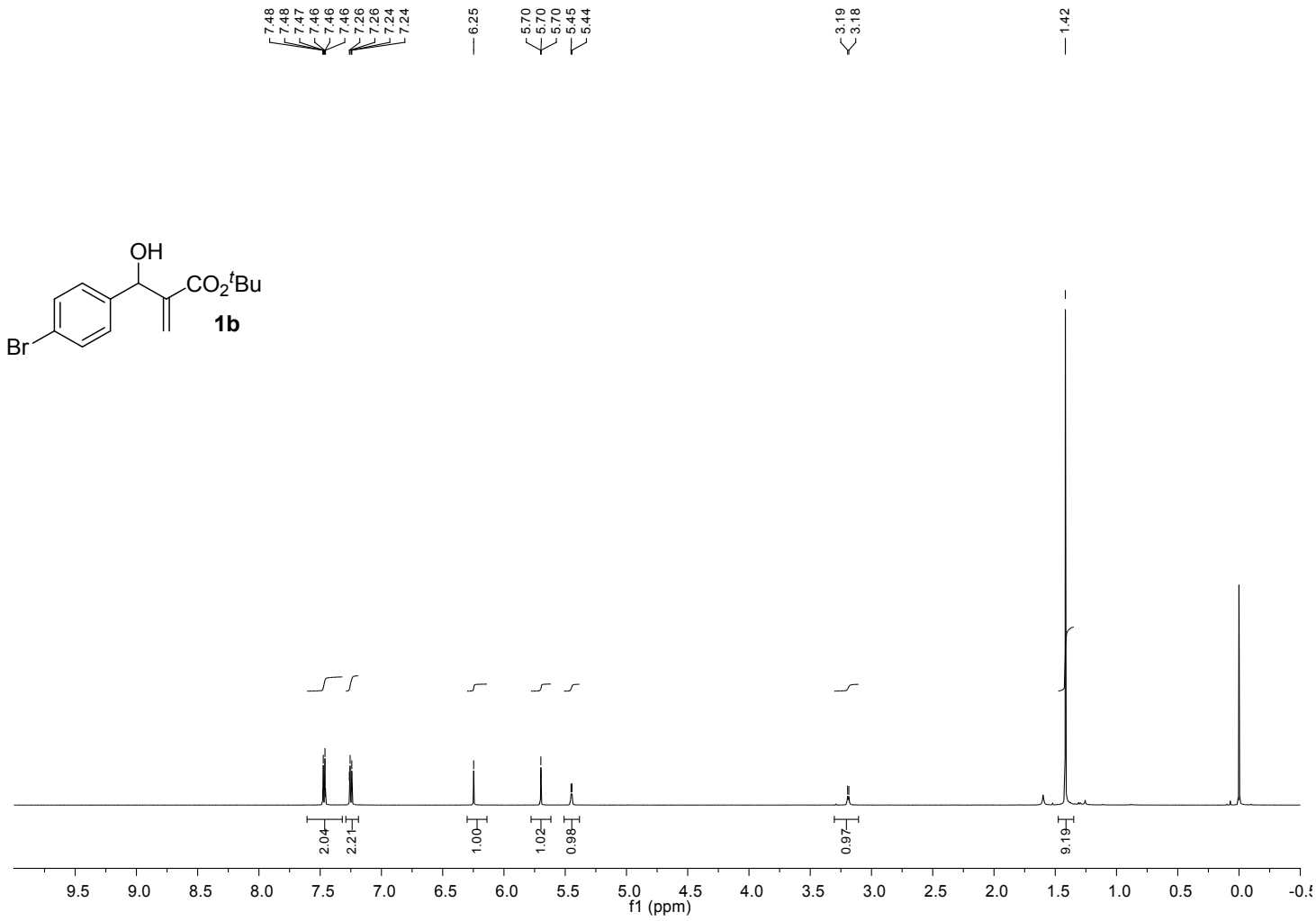
^{1}H NMR Spectra of **1a**



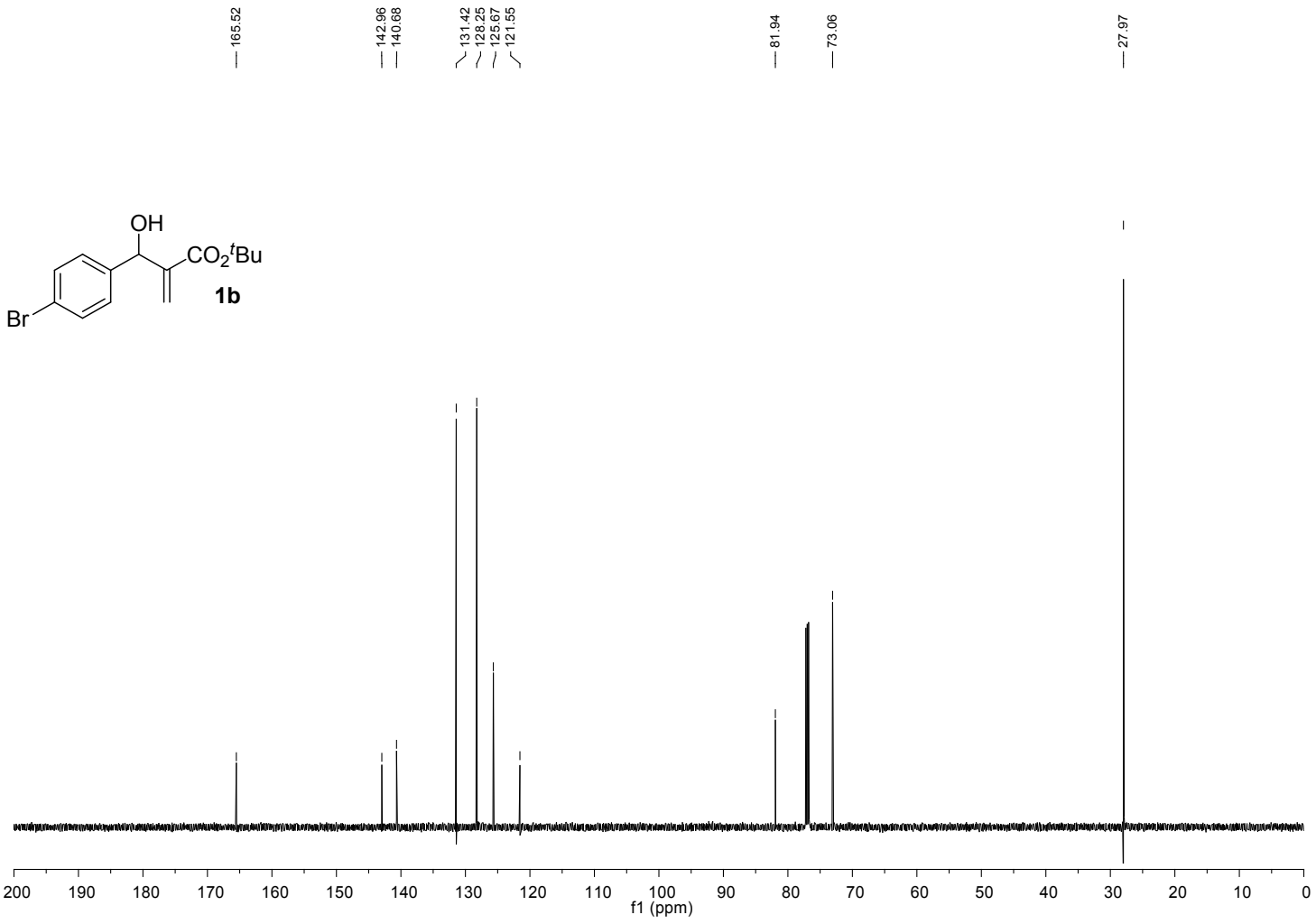
^{13}C NMR Spectra of **1a**



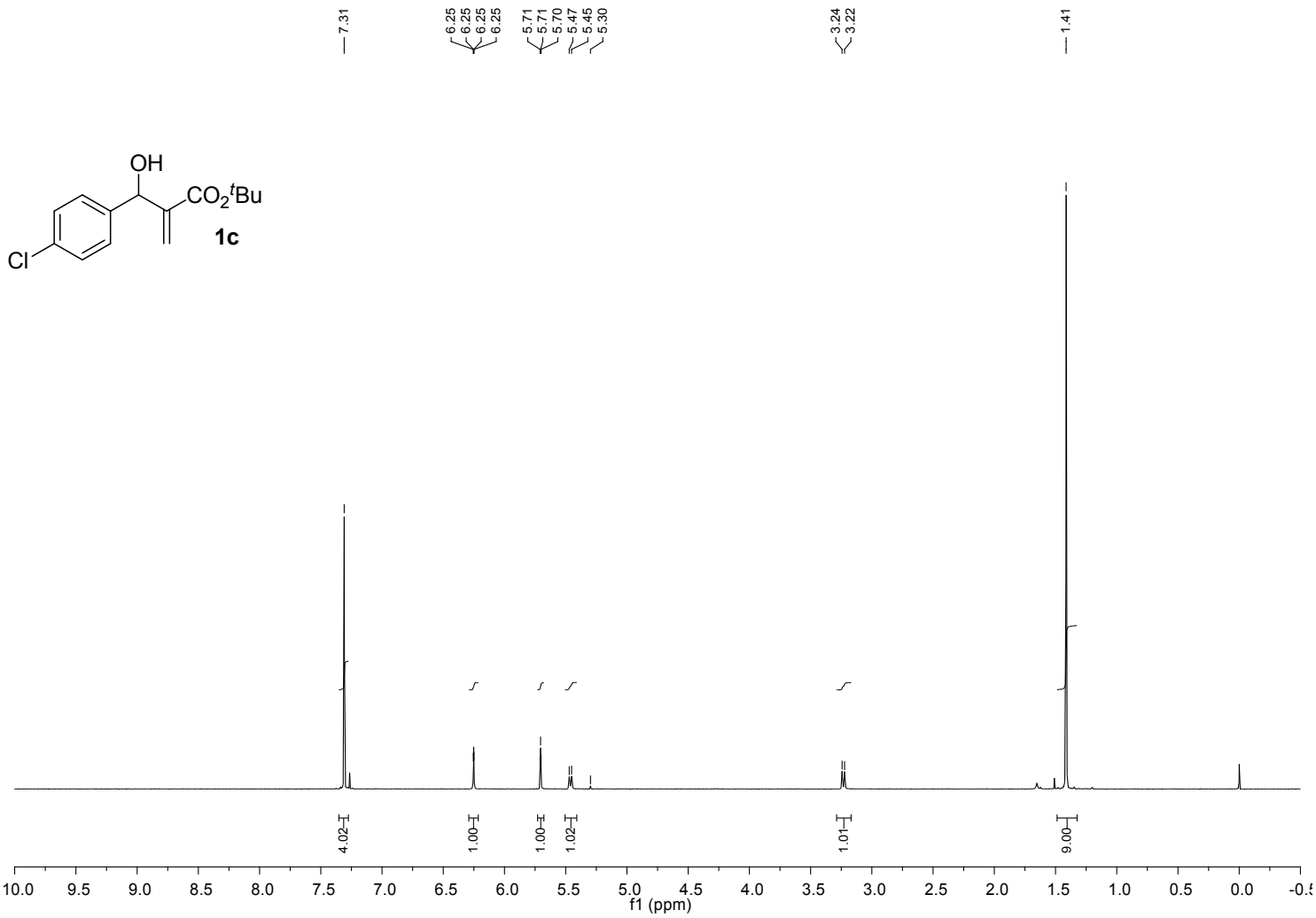
^{1}H NMR Spectra of **1b**



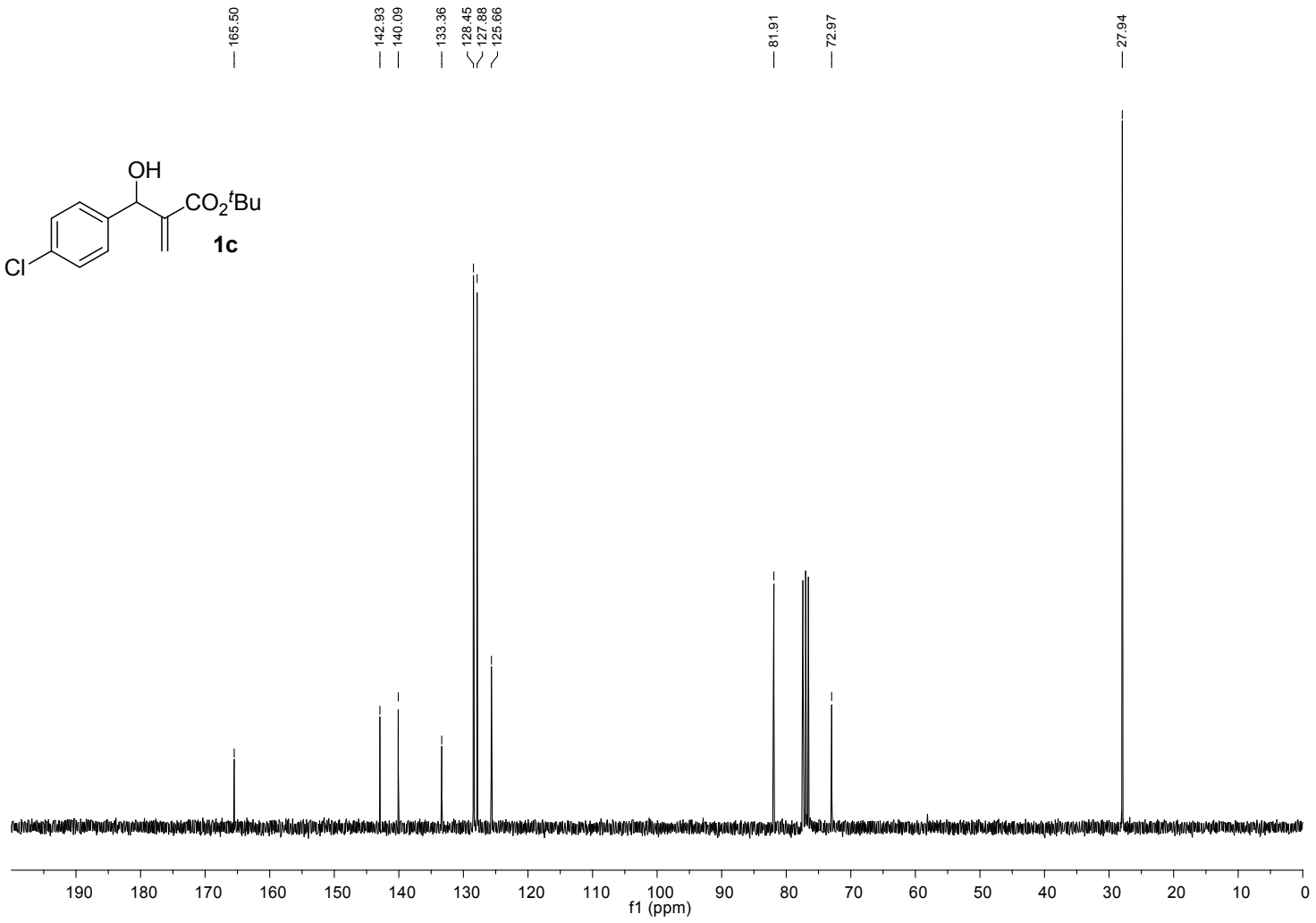
^{13}C NMR Spectra of **1b**



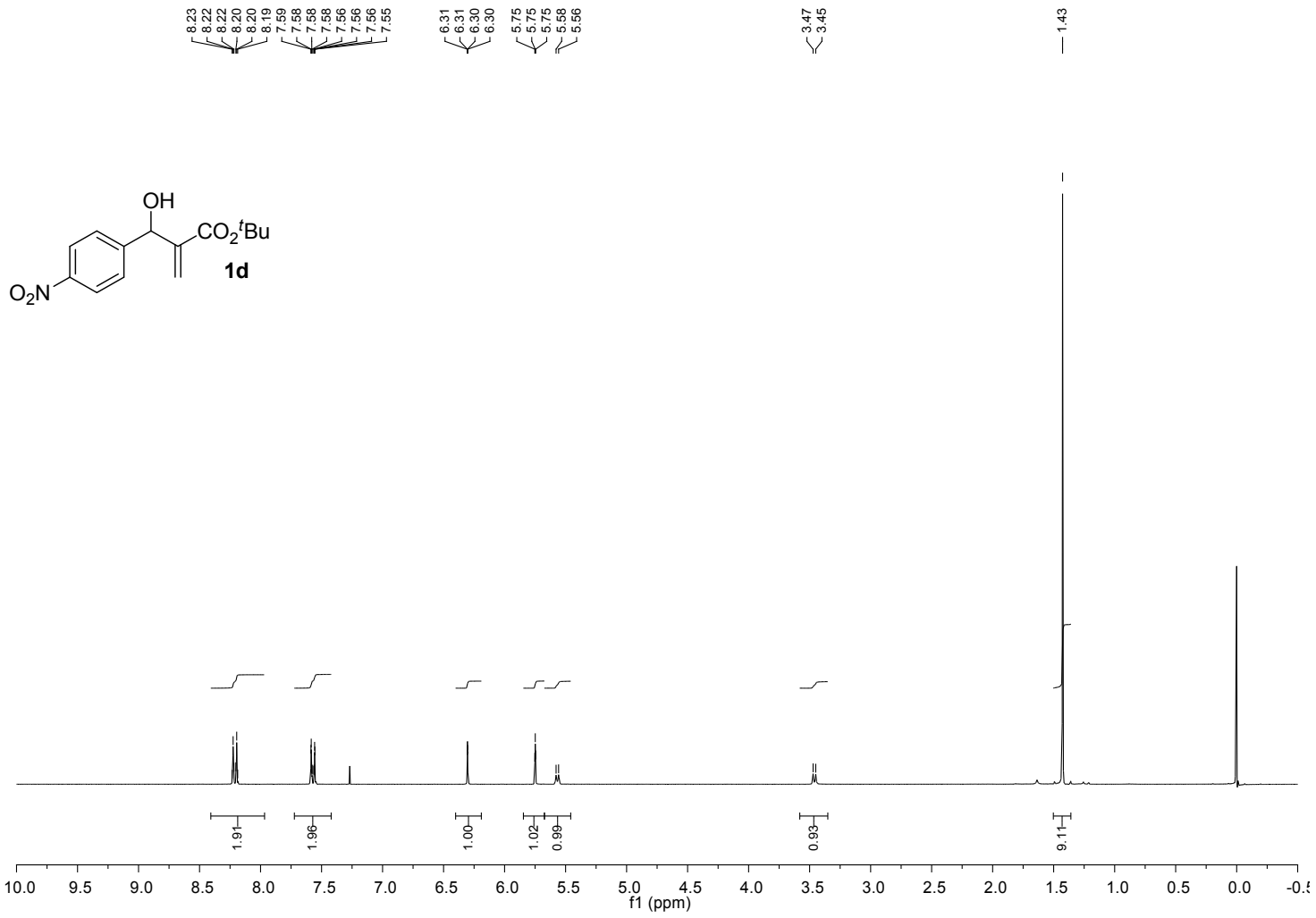
^{1}H NMR Spectra of **1c**



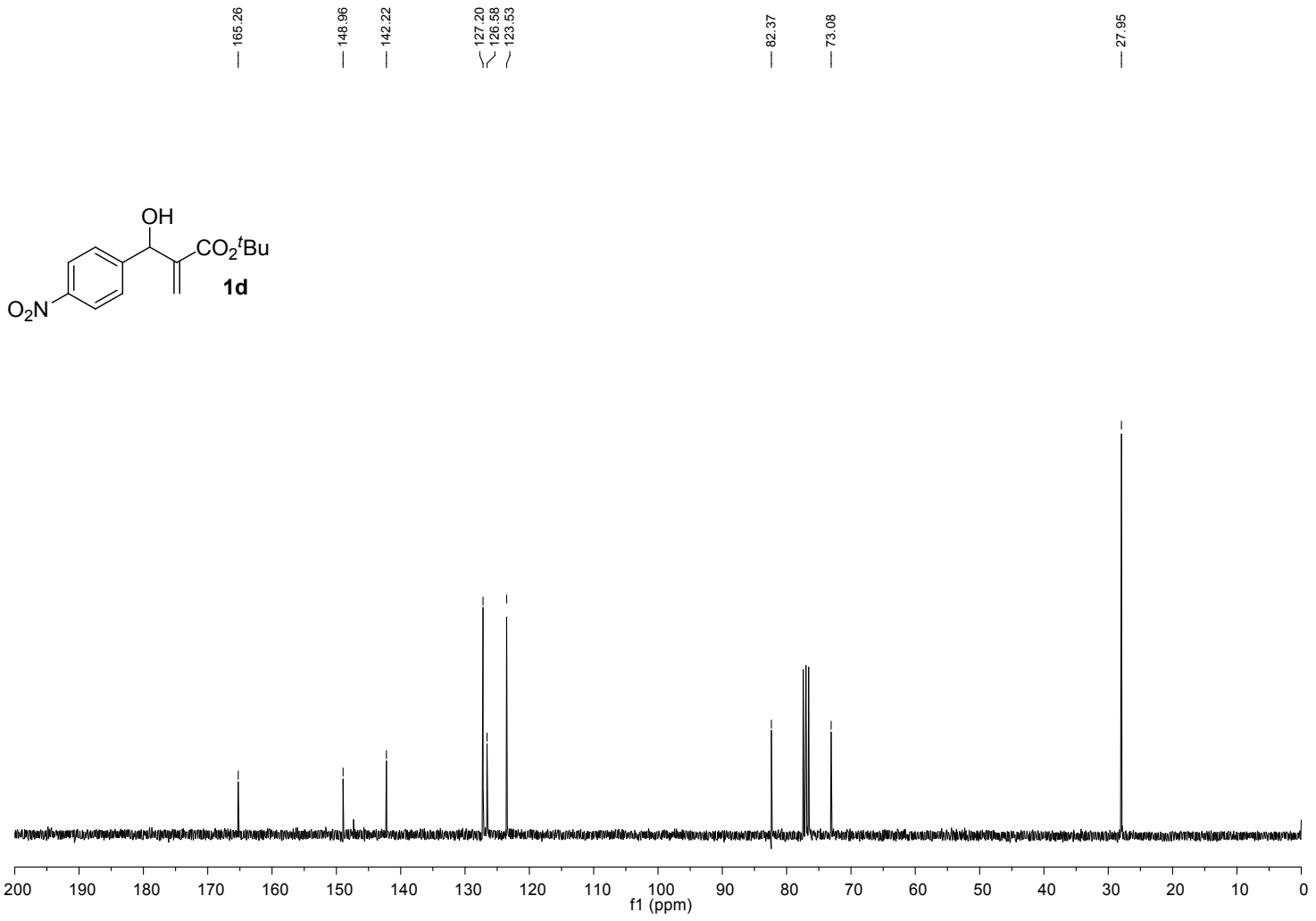
^{13}C NMR Spectra of **1c**



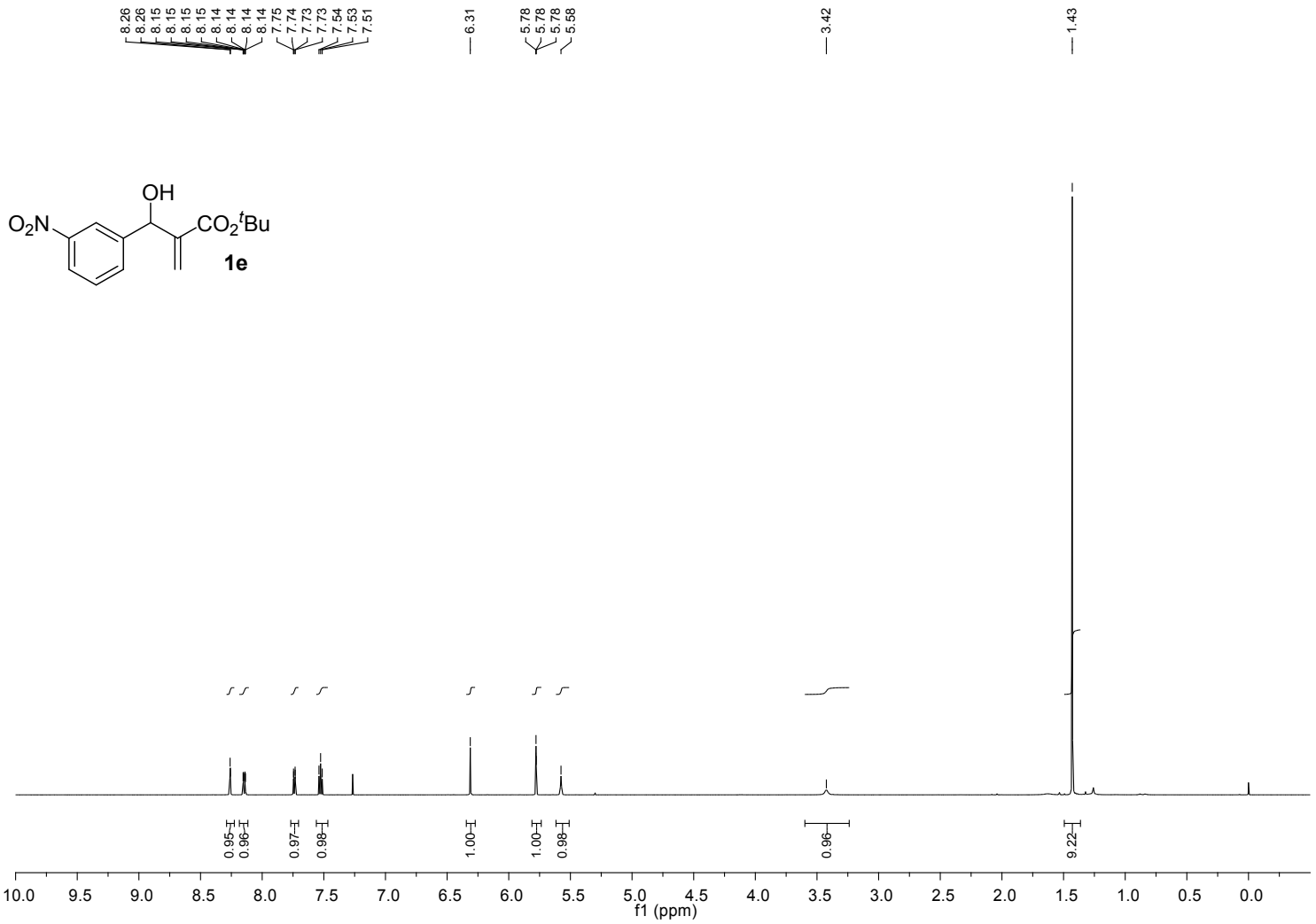
^{1}H NMR Spectra of **1d**



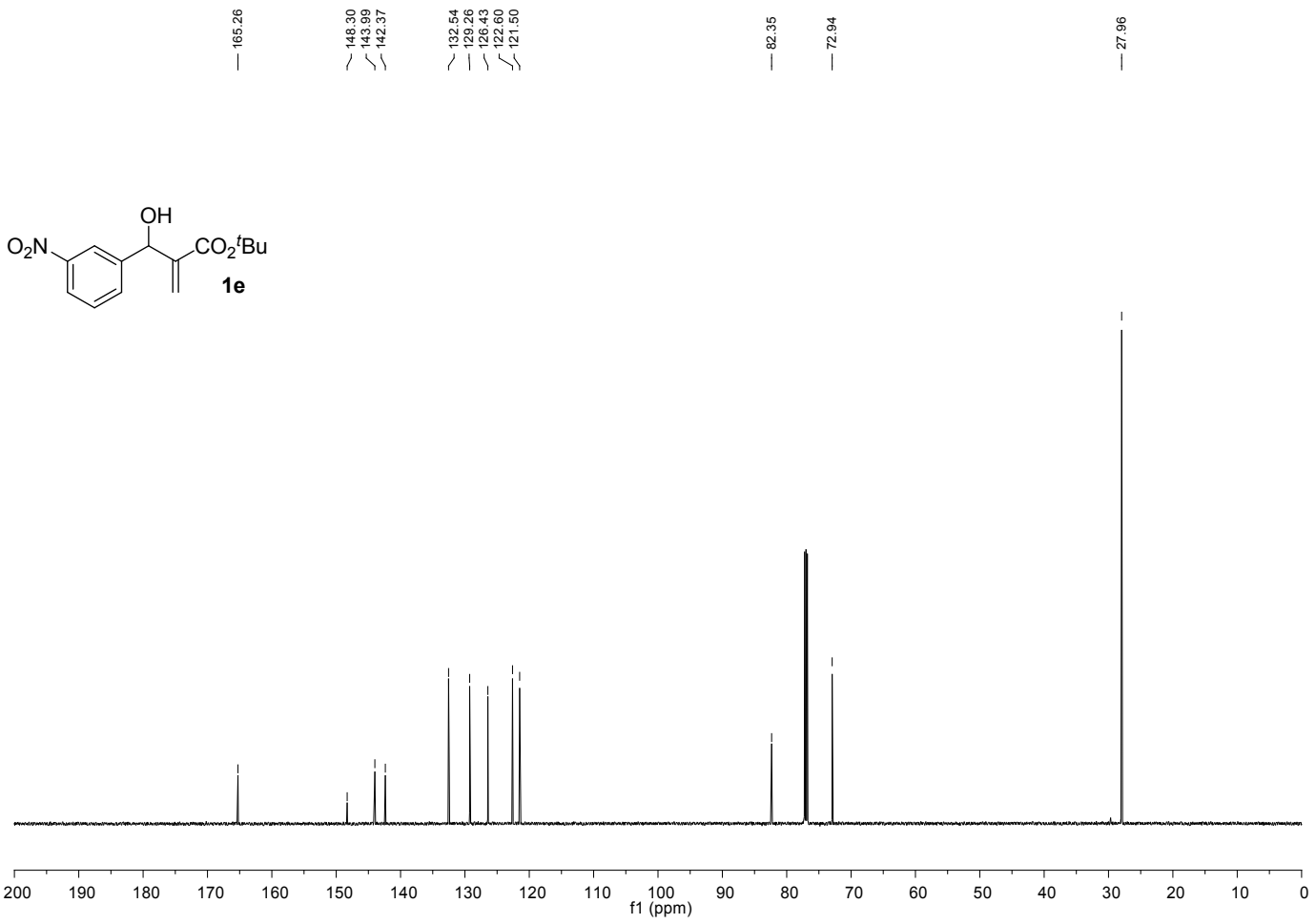
^{13}C NMR Spectra of **1d**



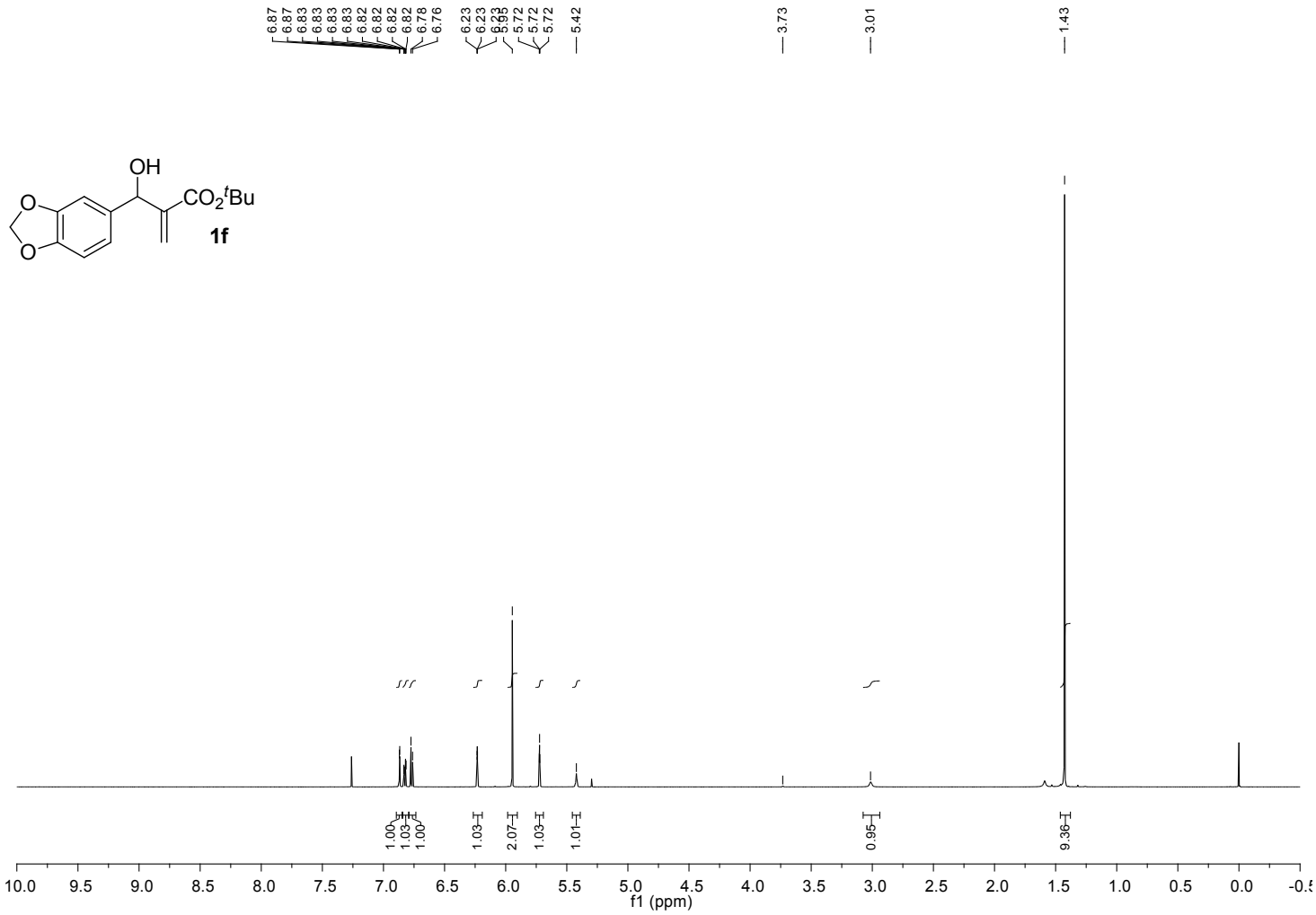
^{1}H NMR Spectra of **1e**



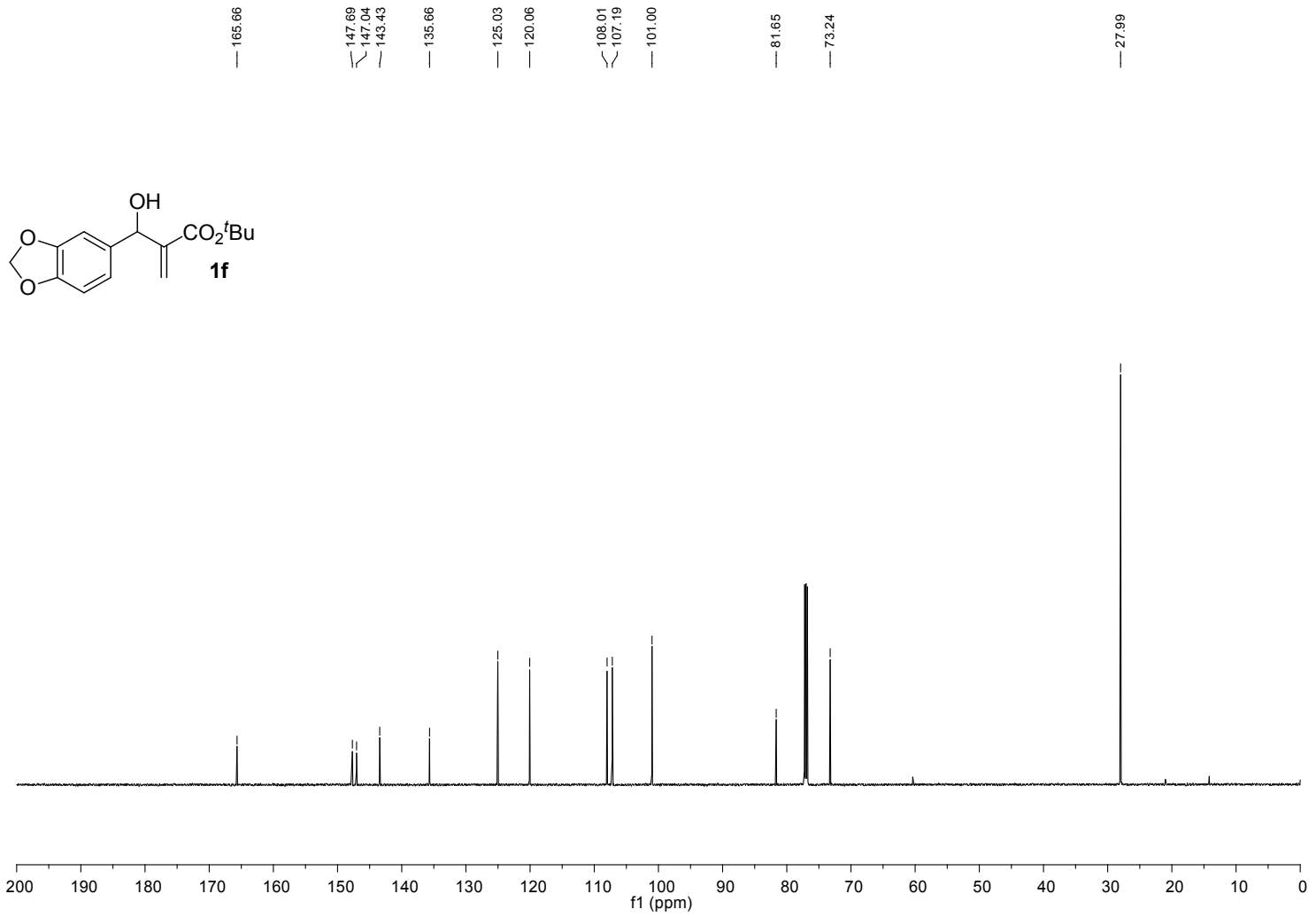
^{13}C NMR Spectra of **1e**



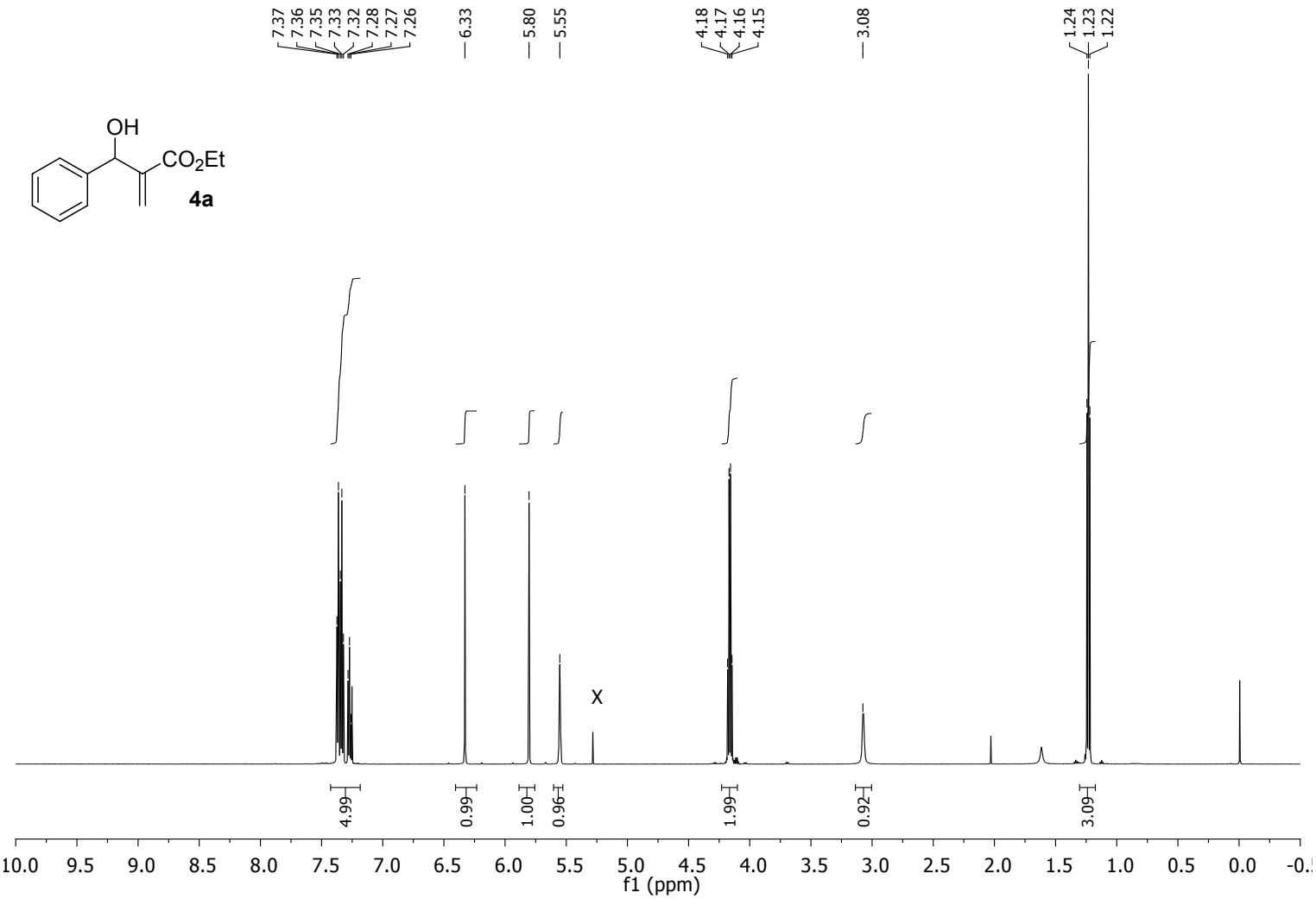
^{1}H NMR Spectra of **1f**



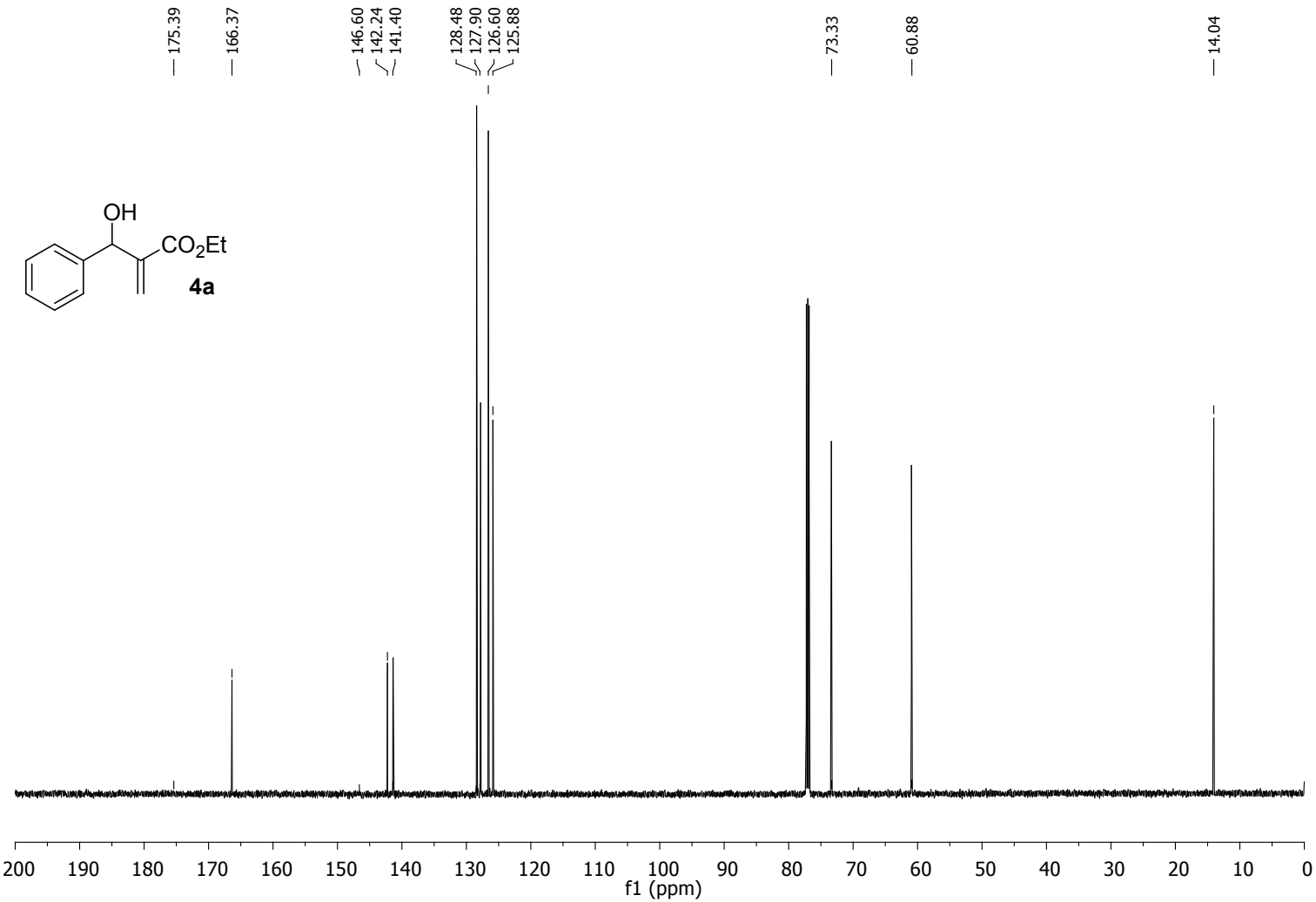
^{13}C NMR Spectra of **1f**



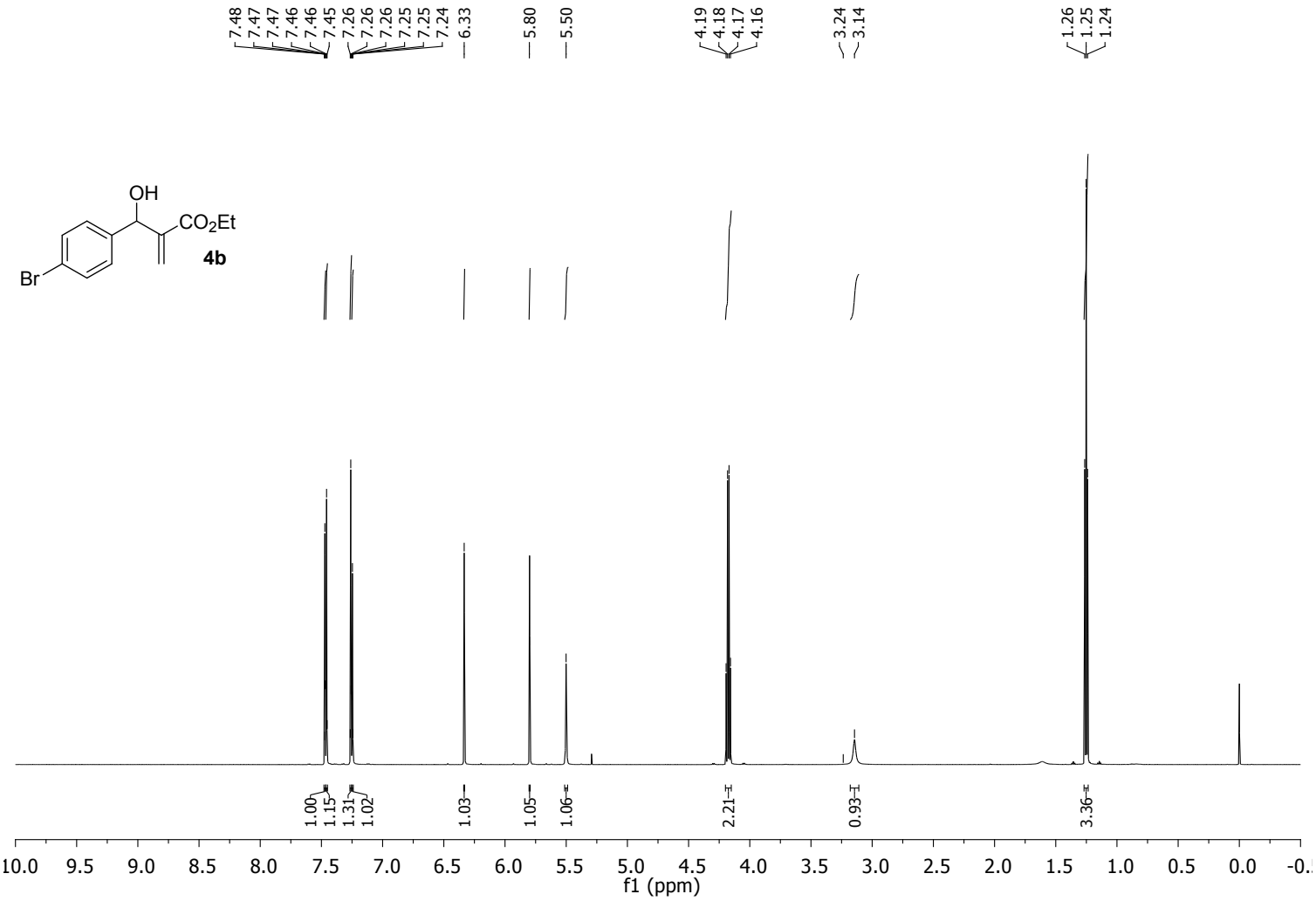
^{1}H NMR Spectra of **4a**



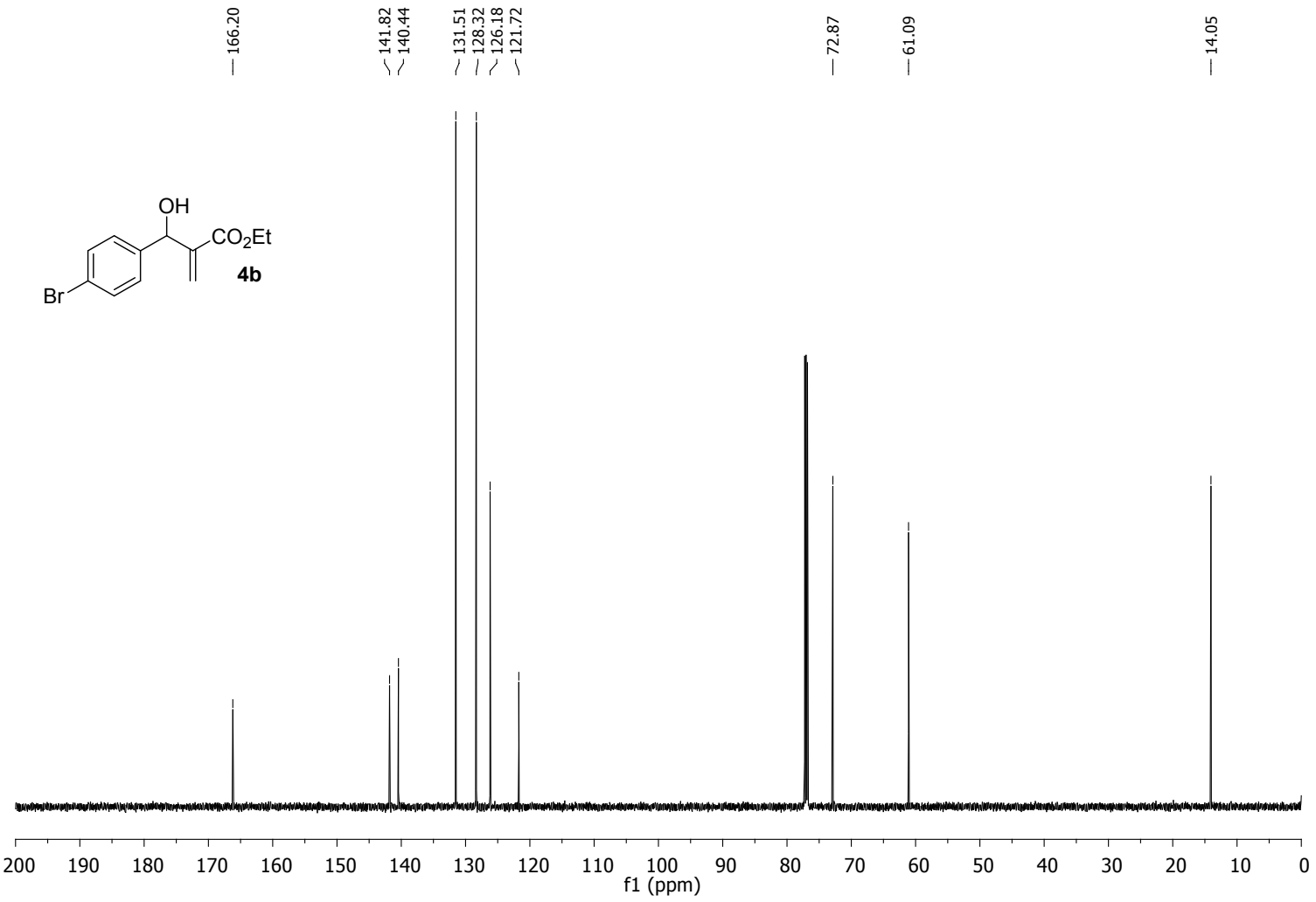
^{13}C NMR Spectra of **4a**



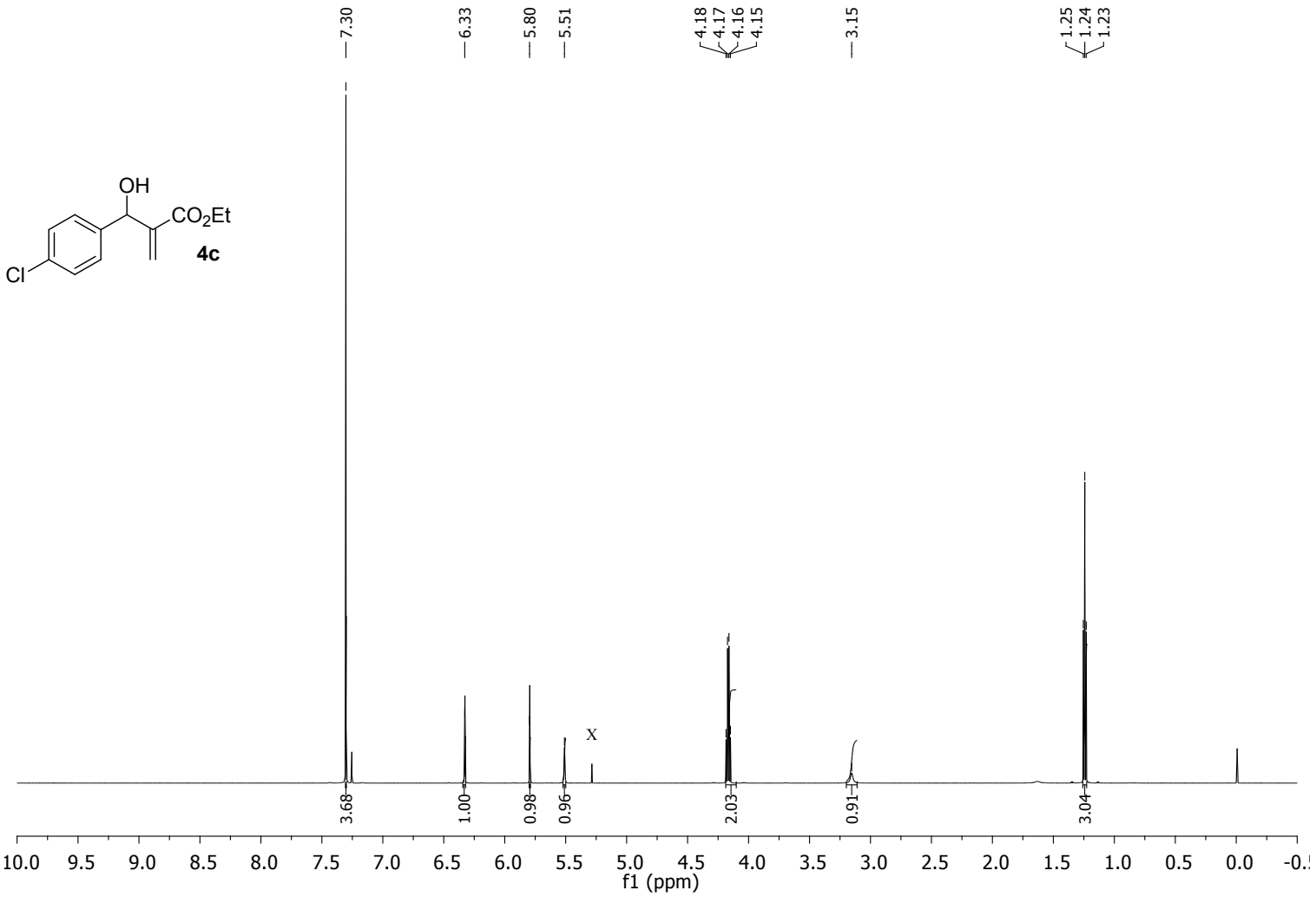
^{1}H NMR Spectra of **4b**



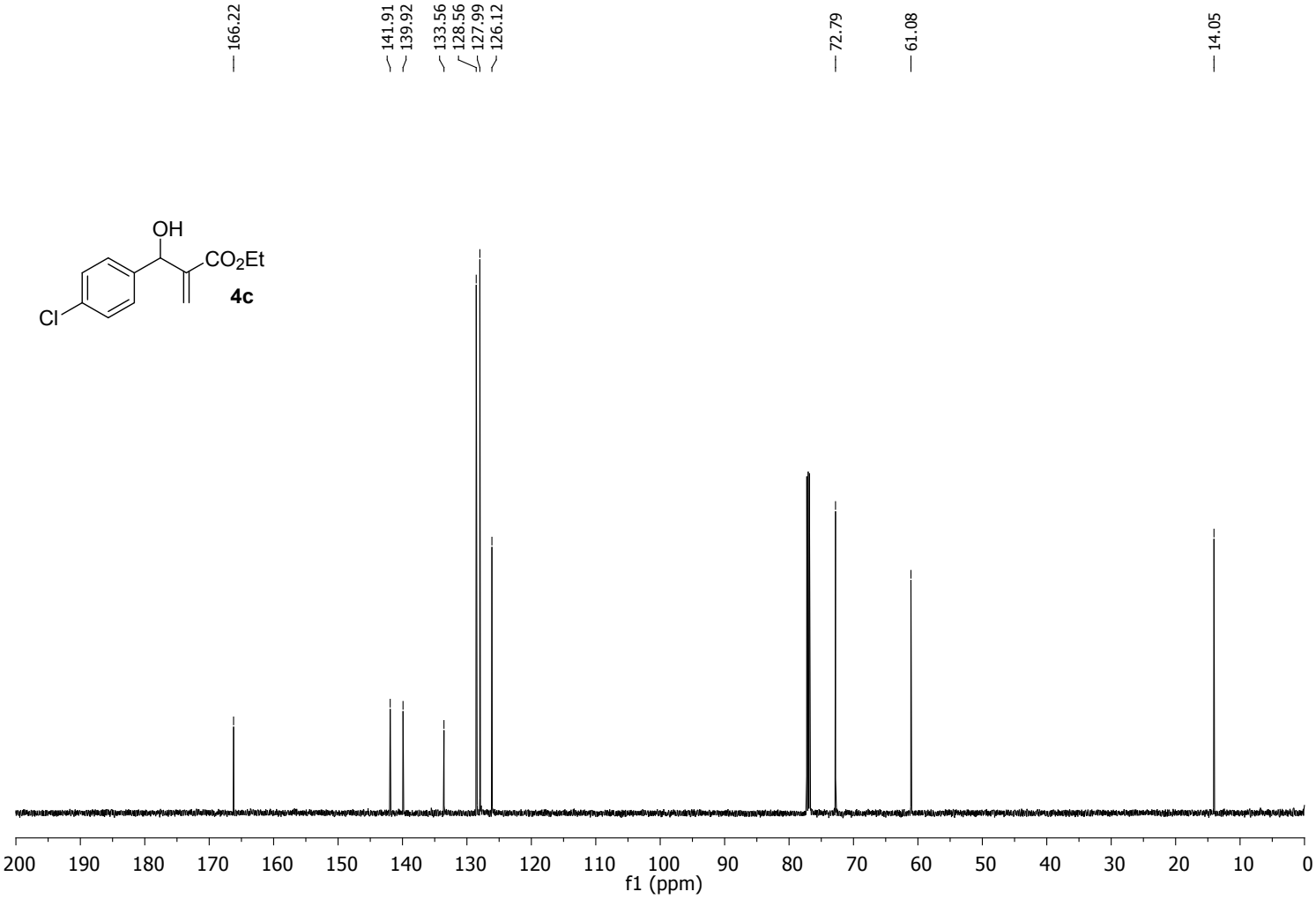
^{13}C NMR Spectra of **4b**



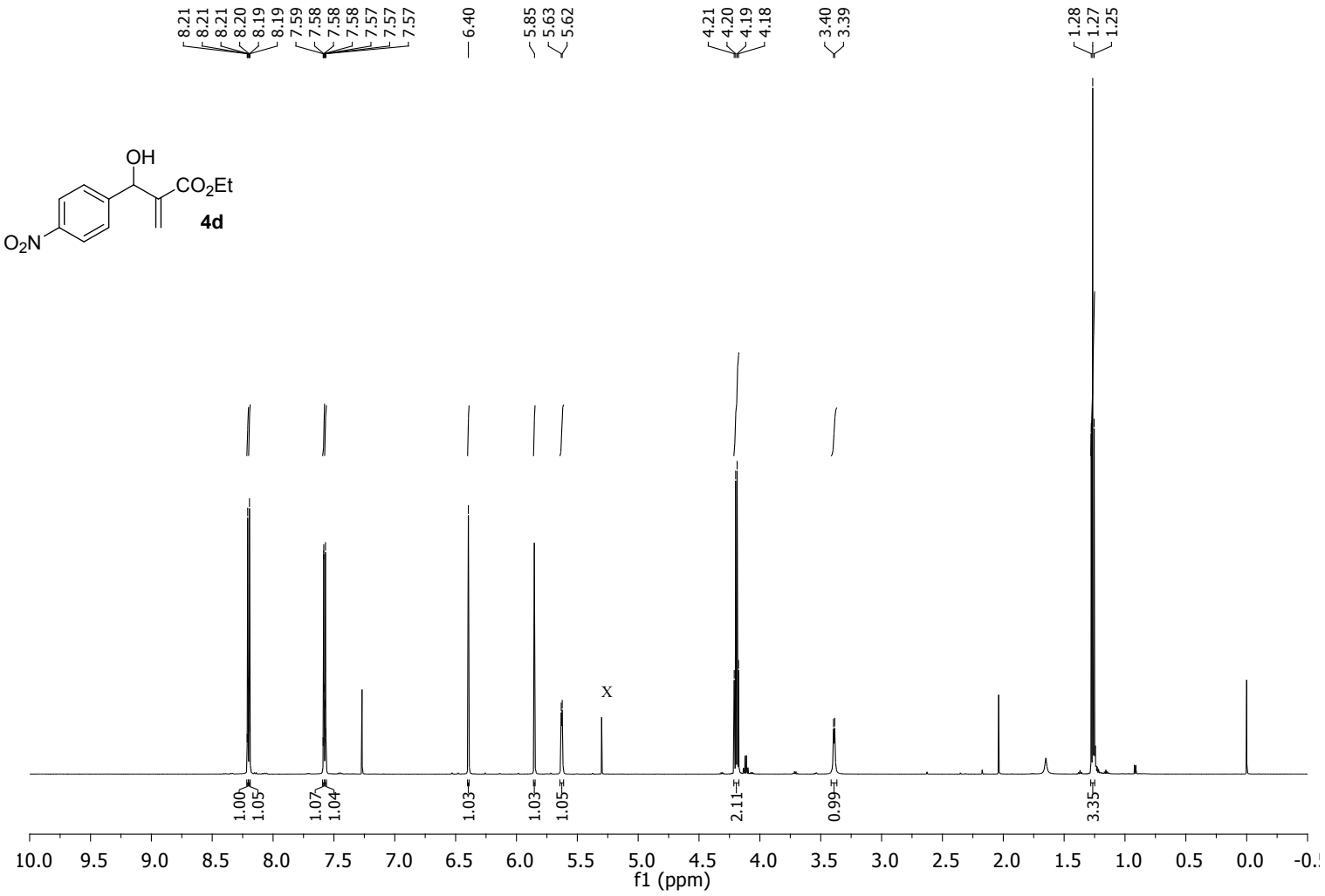
^{1}H NMR Spectra of **4c**



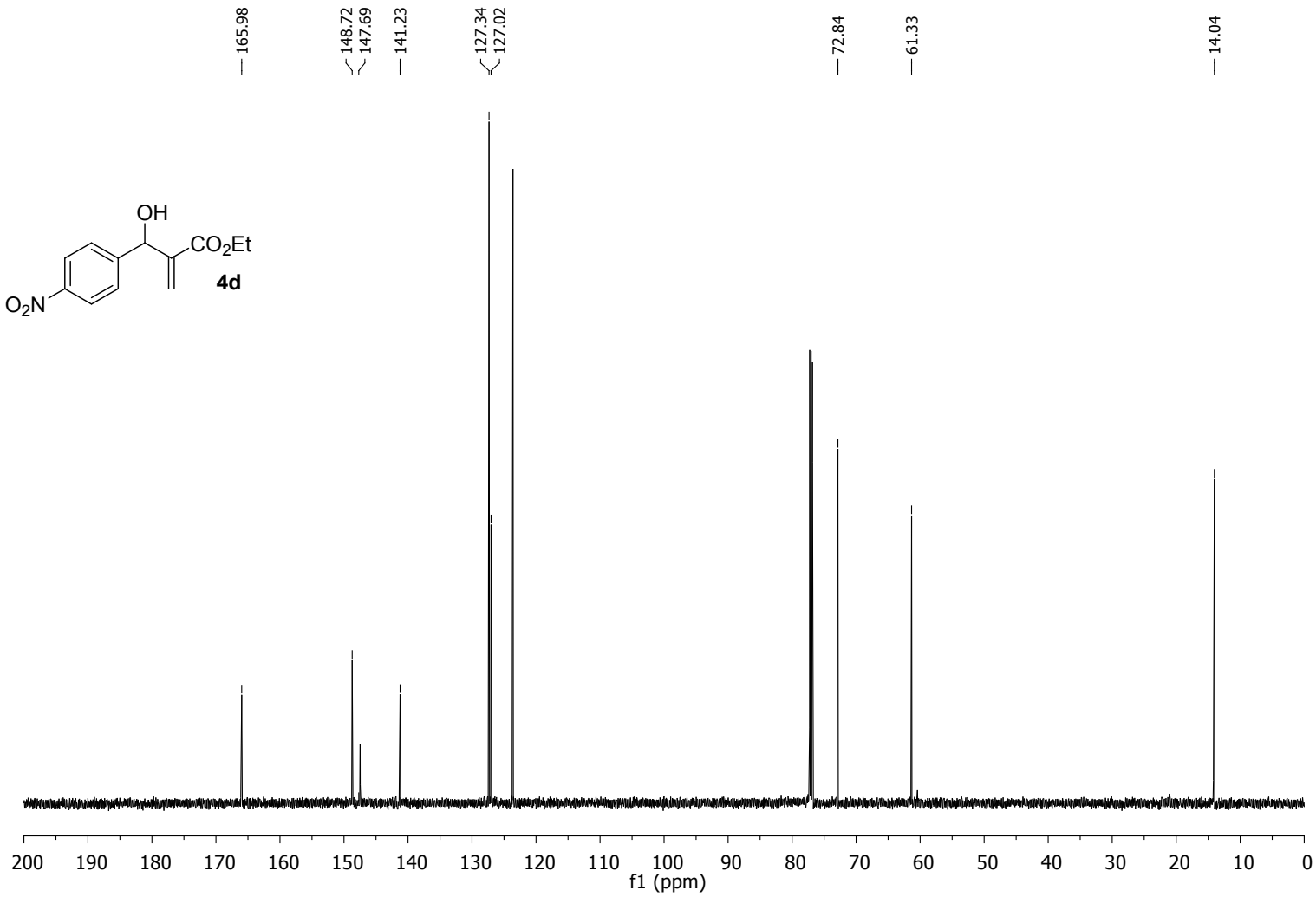
^{13}C NMR Spectra of **4c**



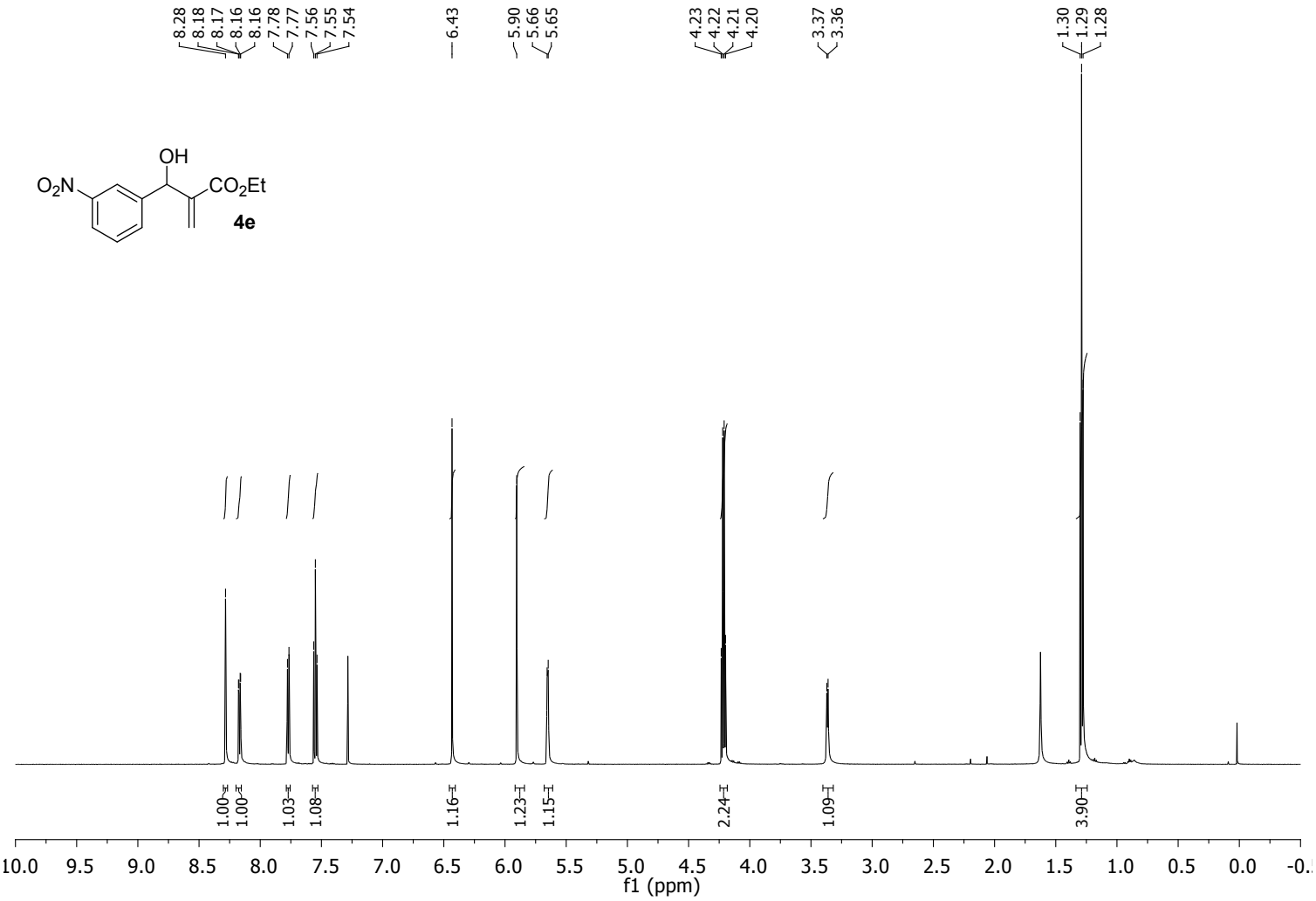
^{1}H NMR Spectra of **4d**



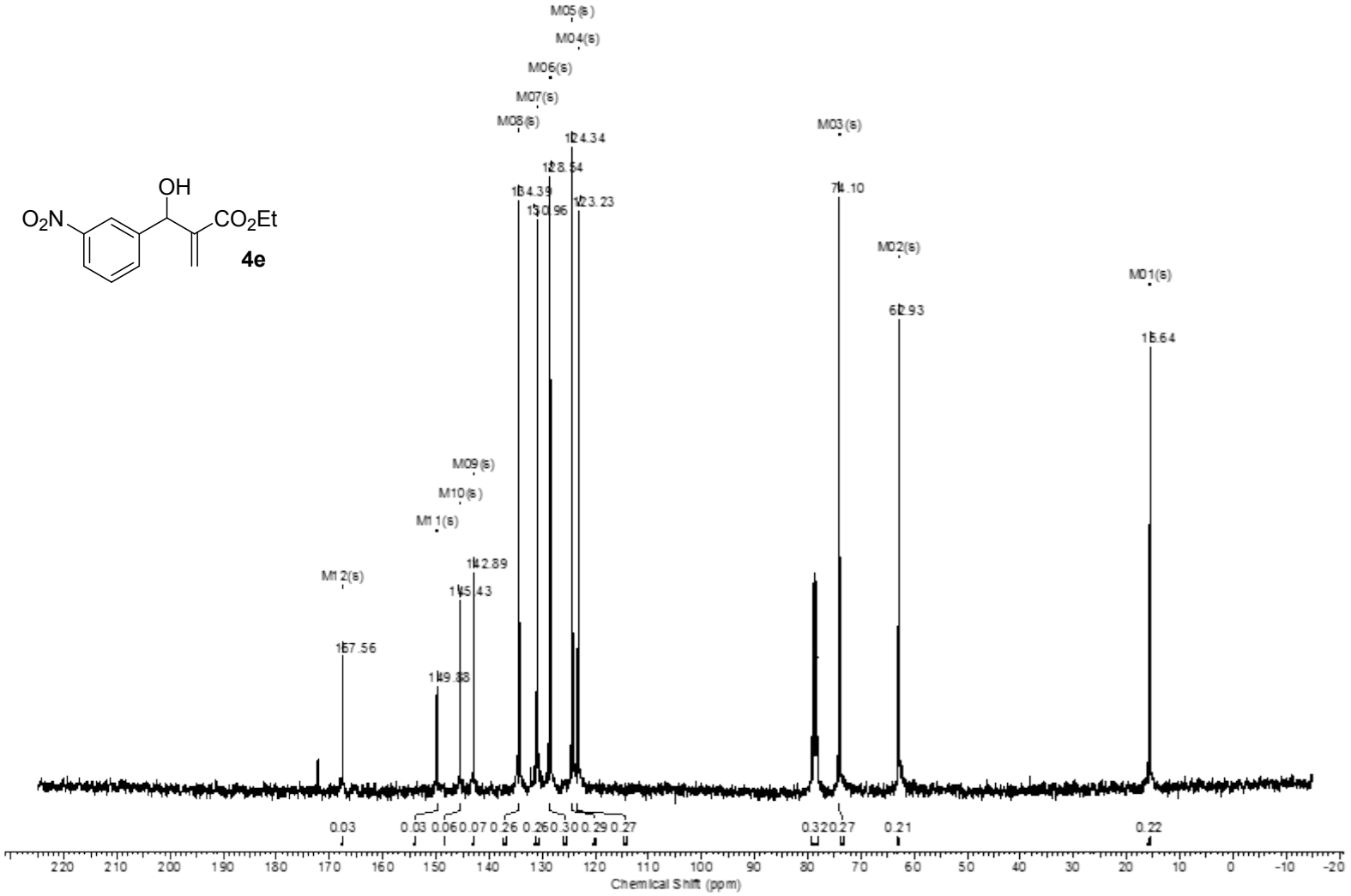
^{13}C NMR Spectra of **4d**



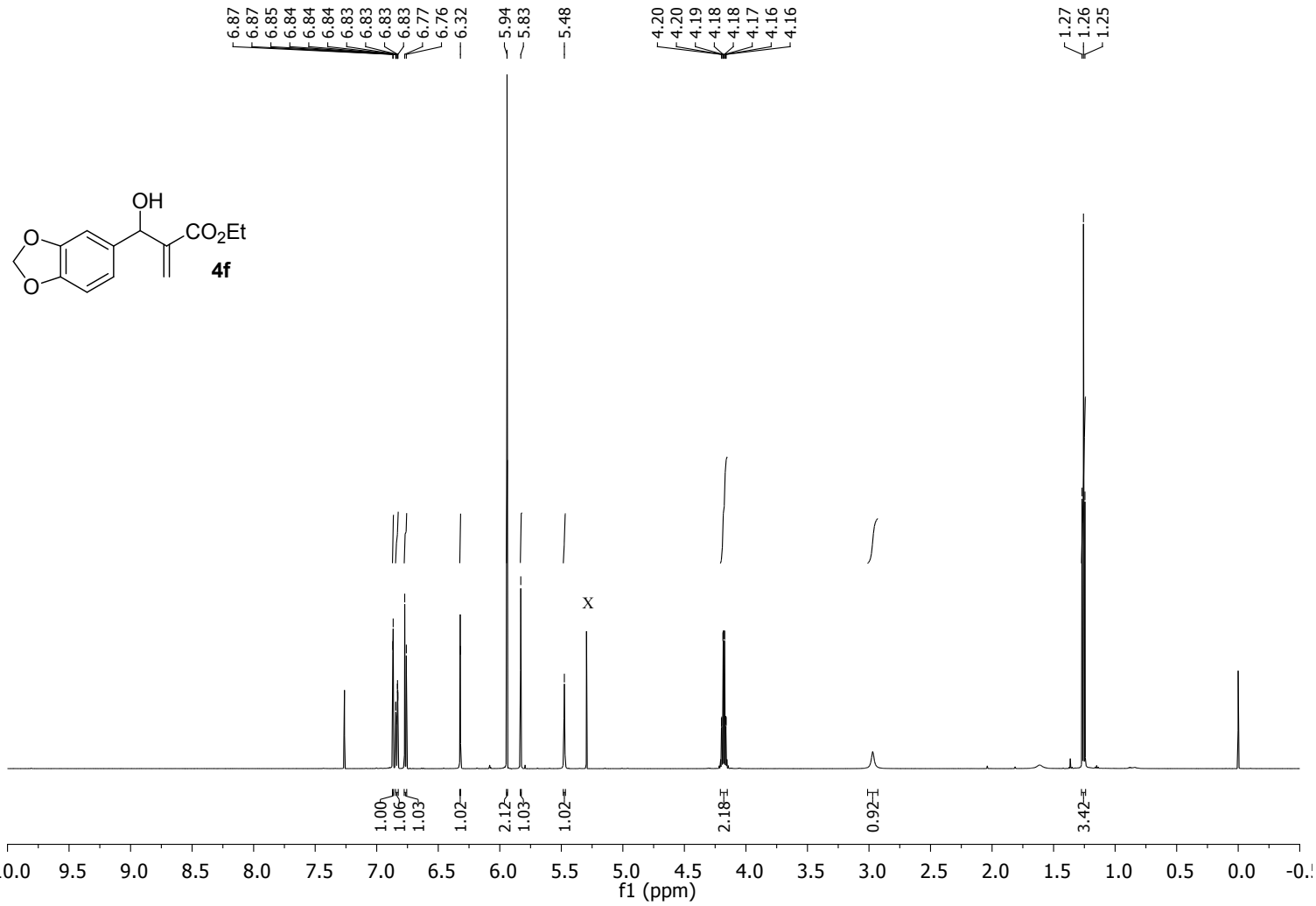
^{1}H Spectra of **4e**



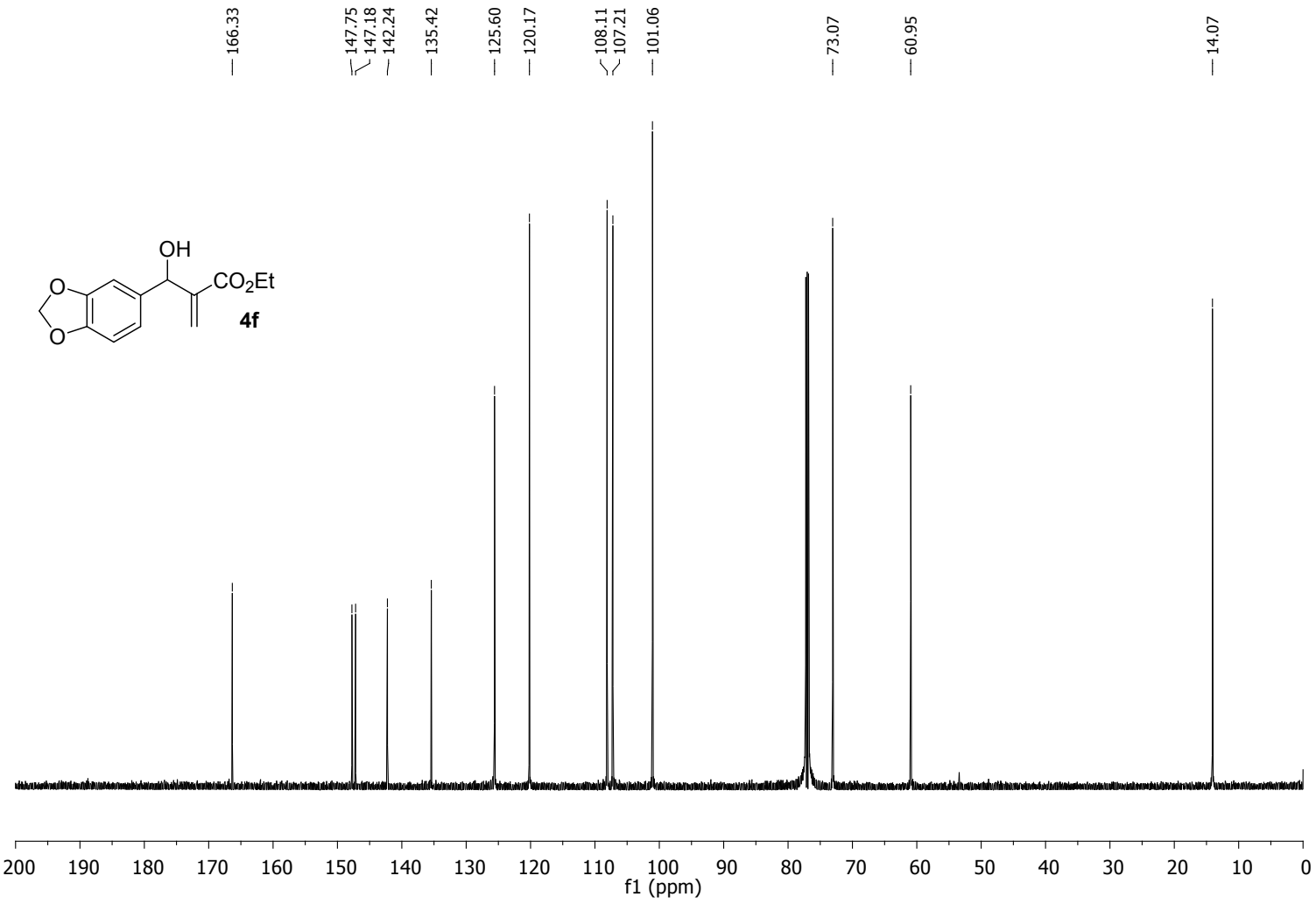
^{13}C NMR Spectra of **4e**



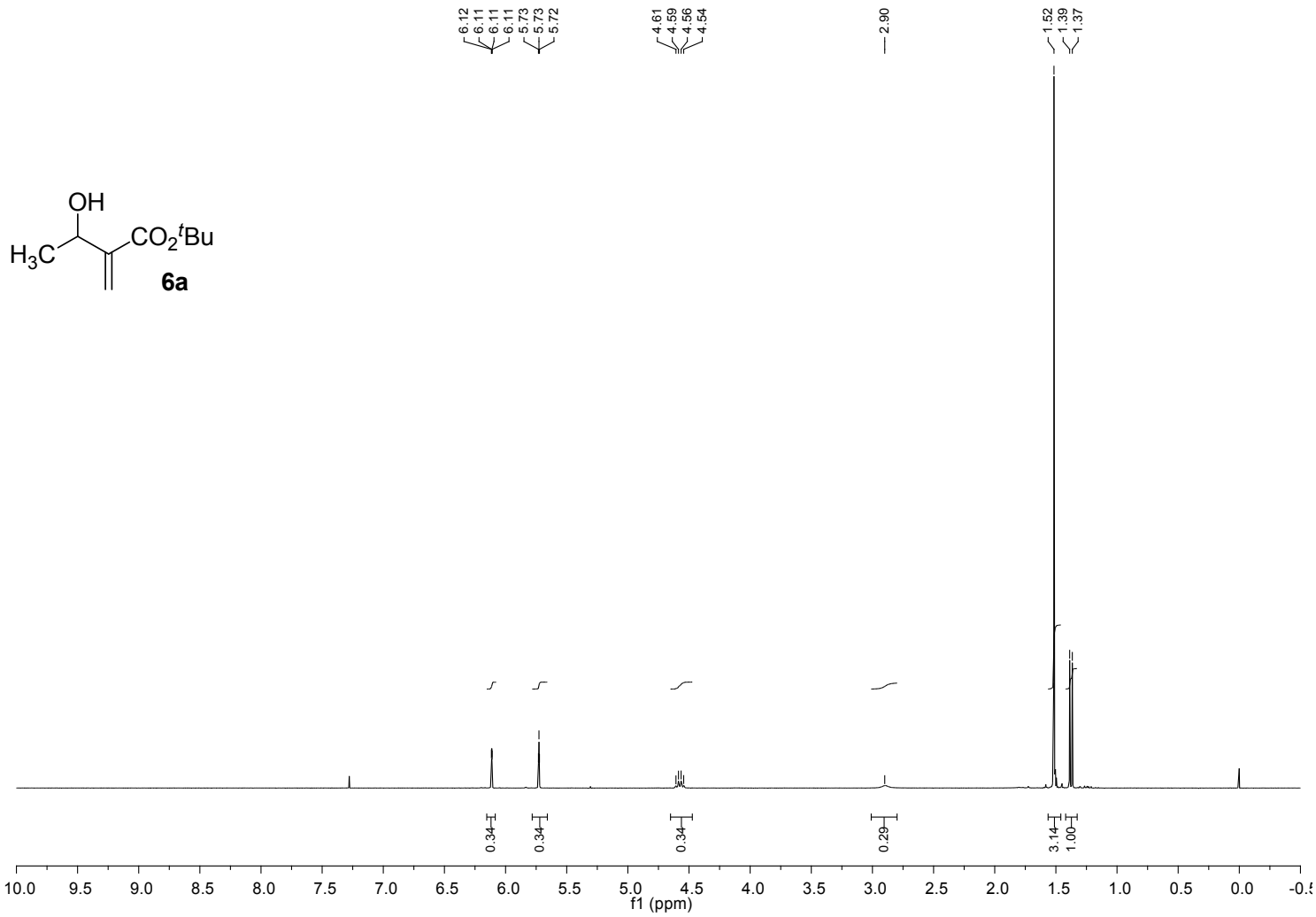
^{1}H NMR Spectra of **4f**



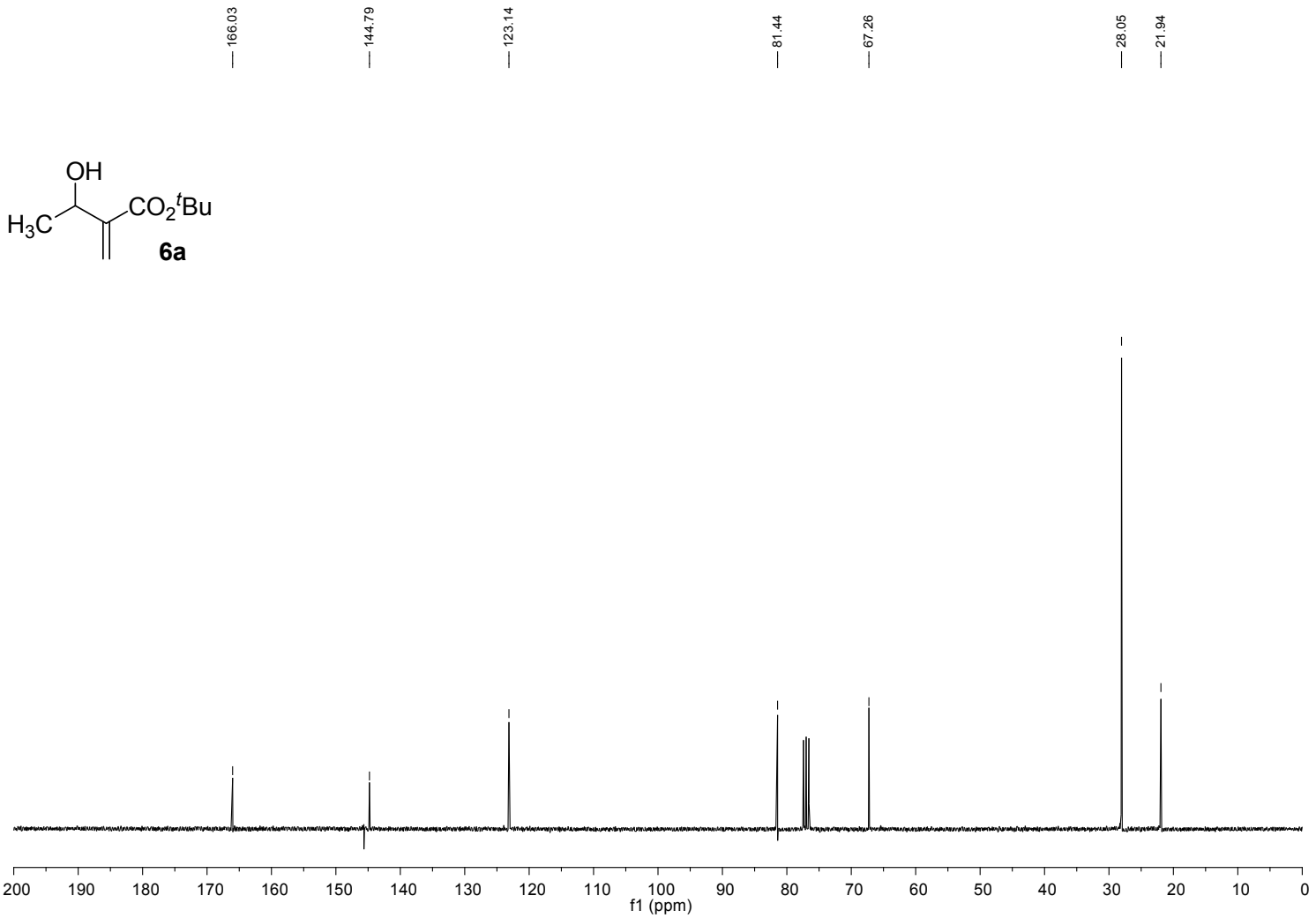
^{13}C NMR Spectra of **4f**



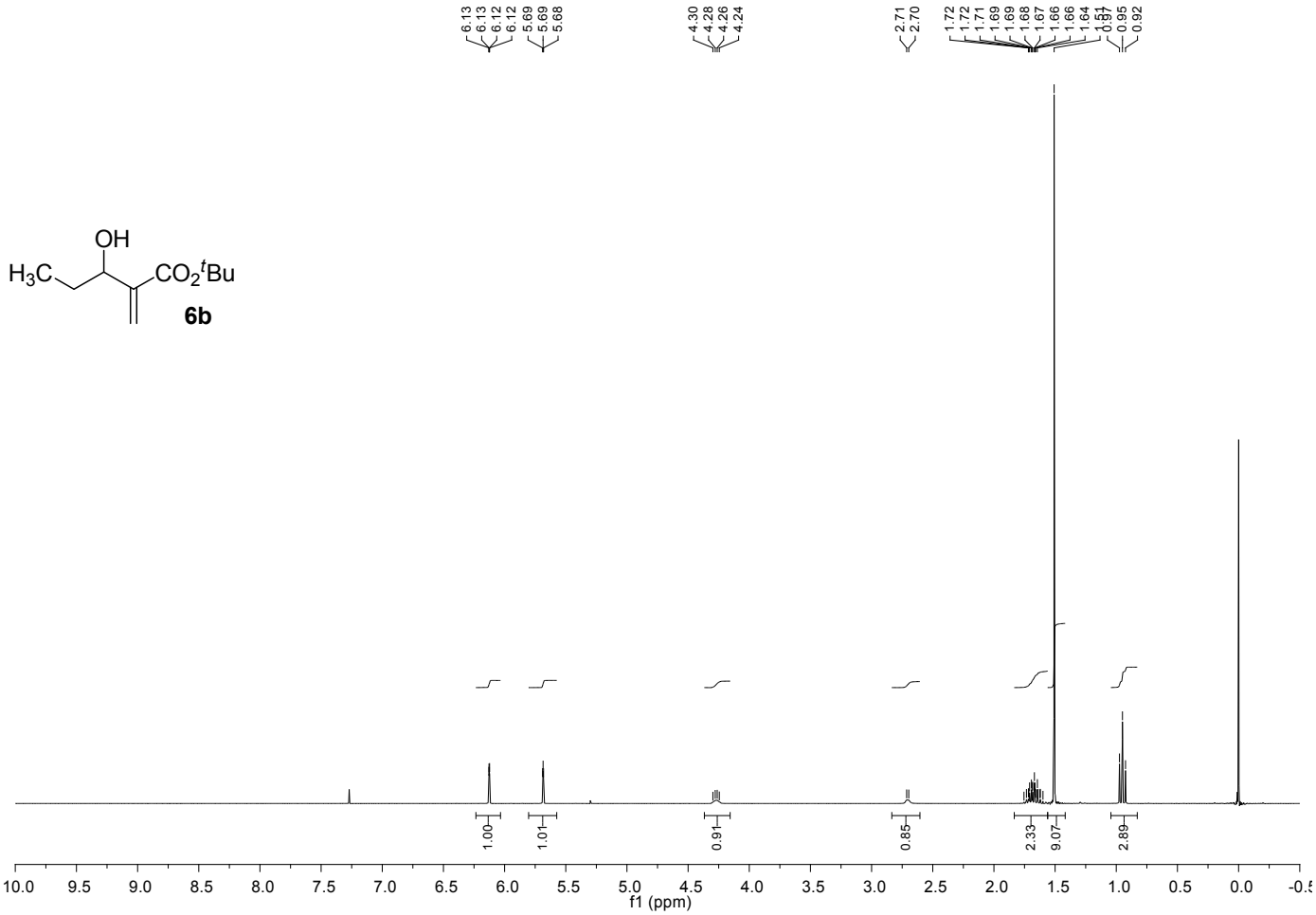
^{1}H NMR Spectra of **6a**



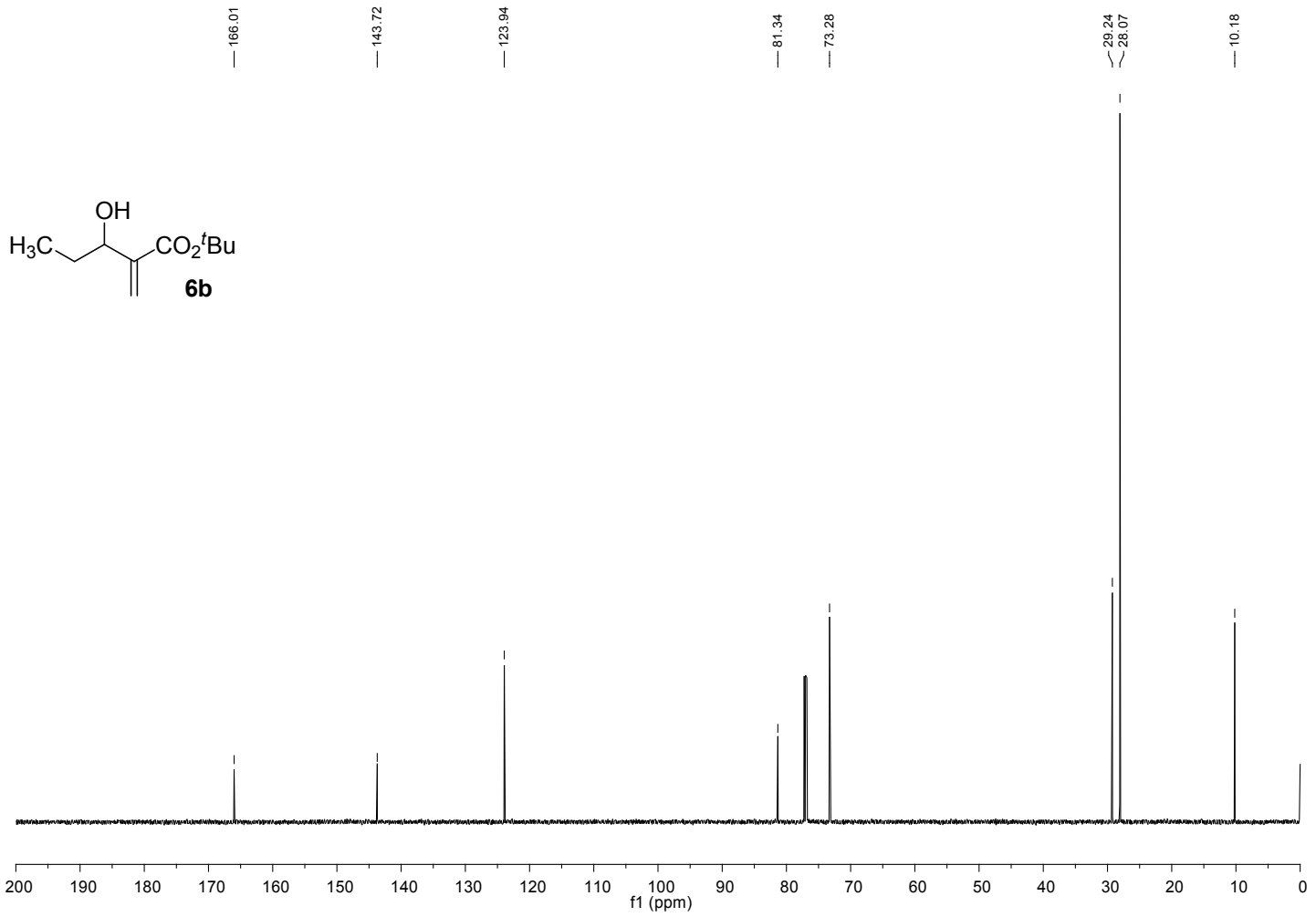
^{13}C NMR Spectra of **6a**



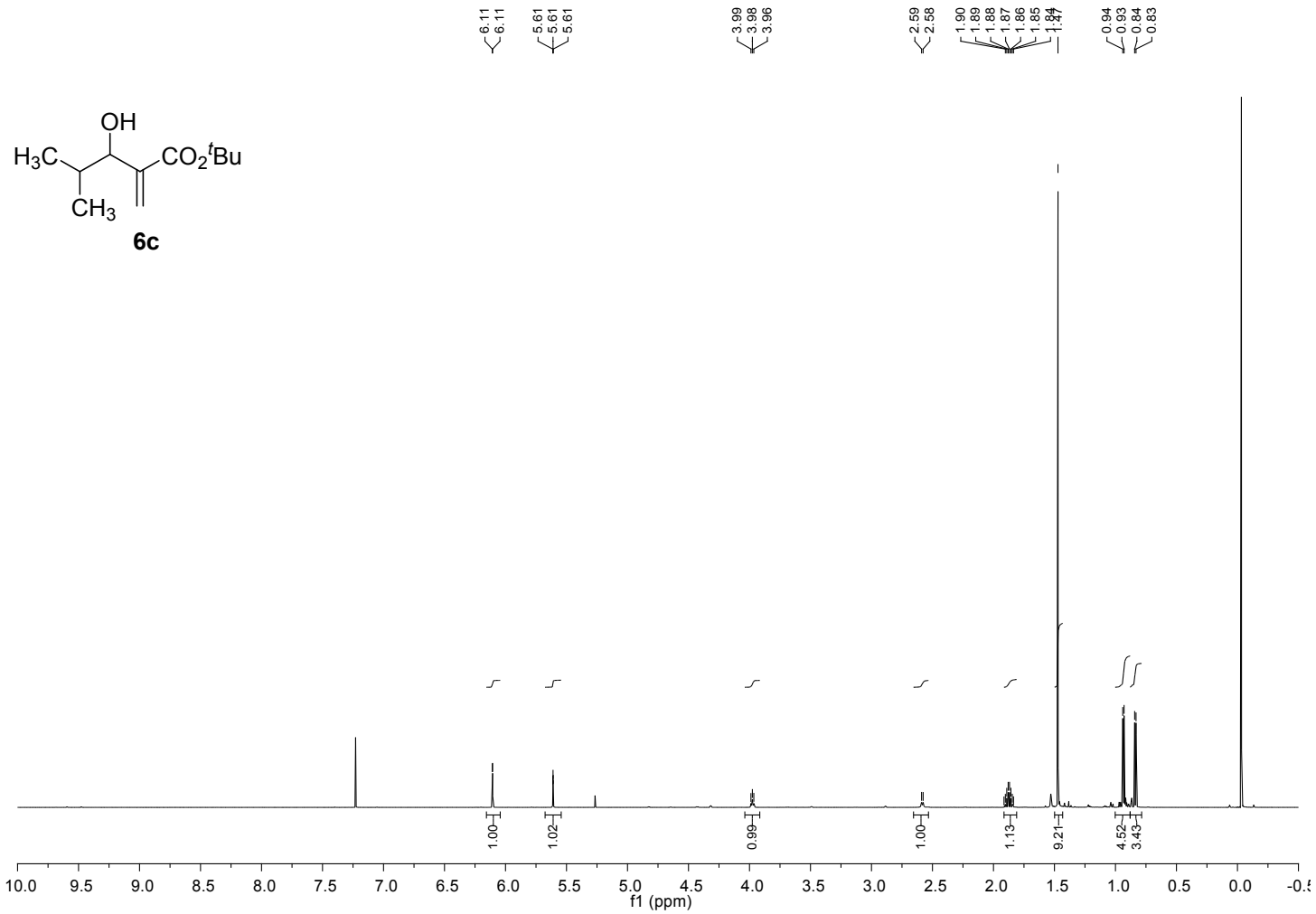
^{1}H NMR Spectra of **6b**



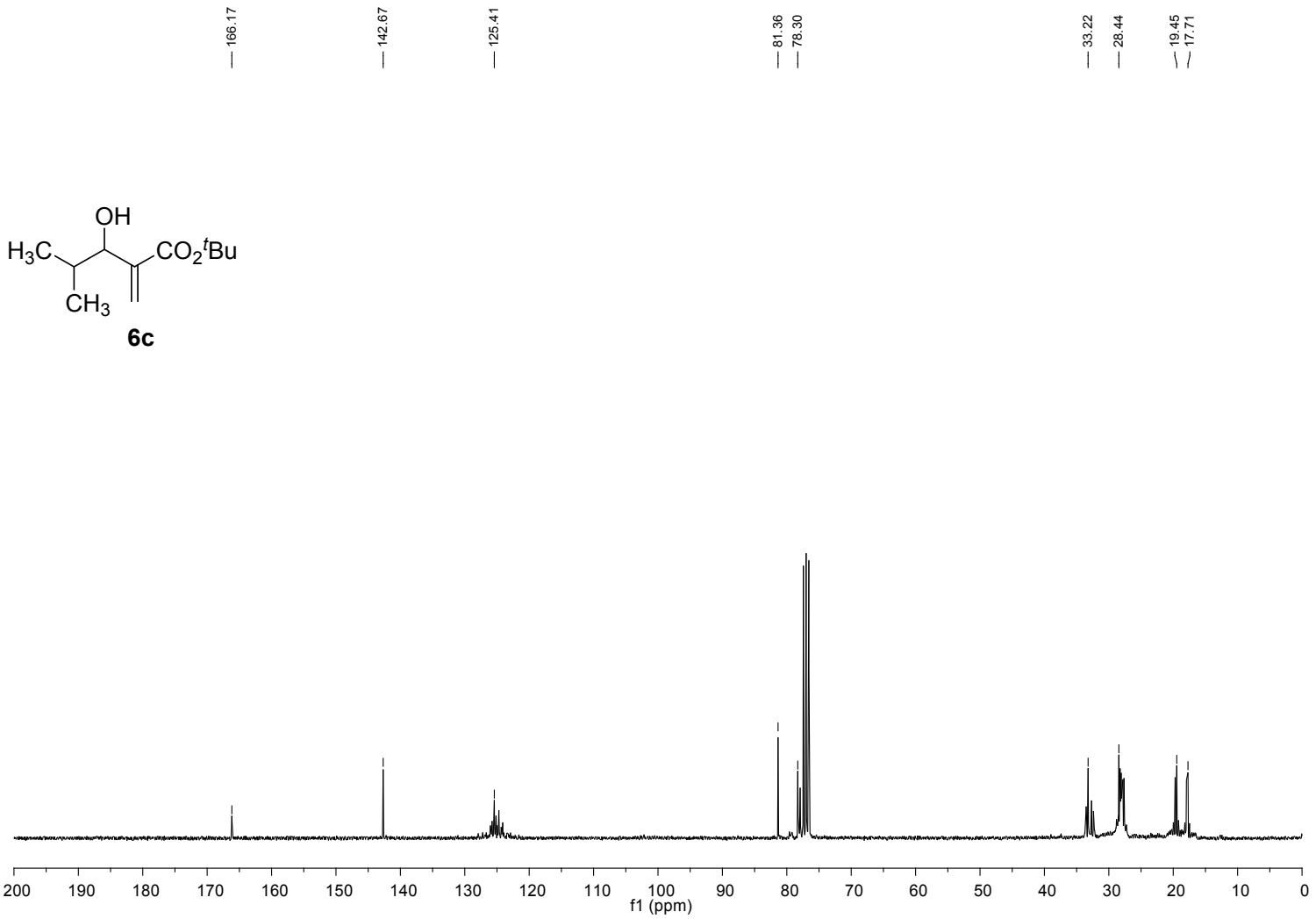
^{13}C NMR Spectra of **6b**



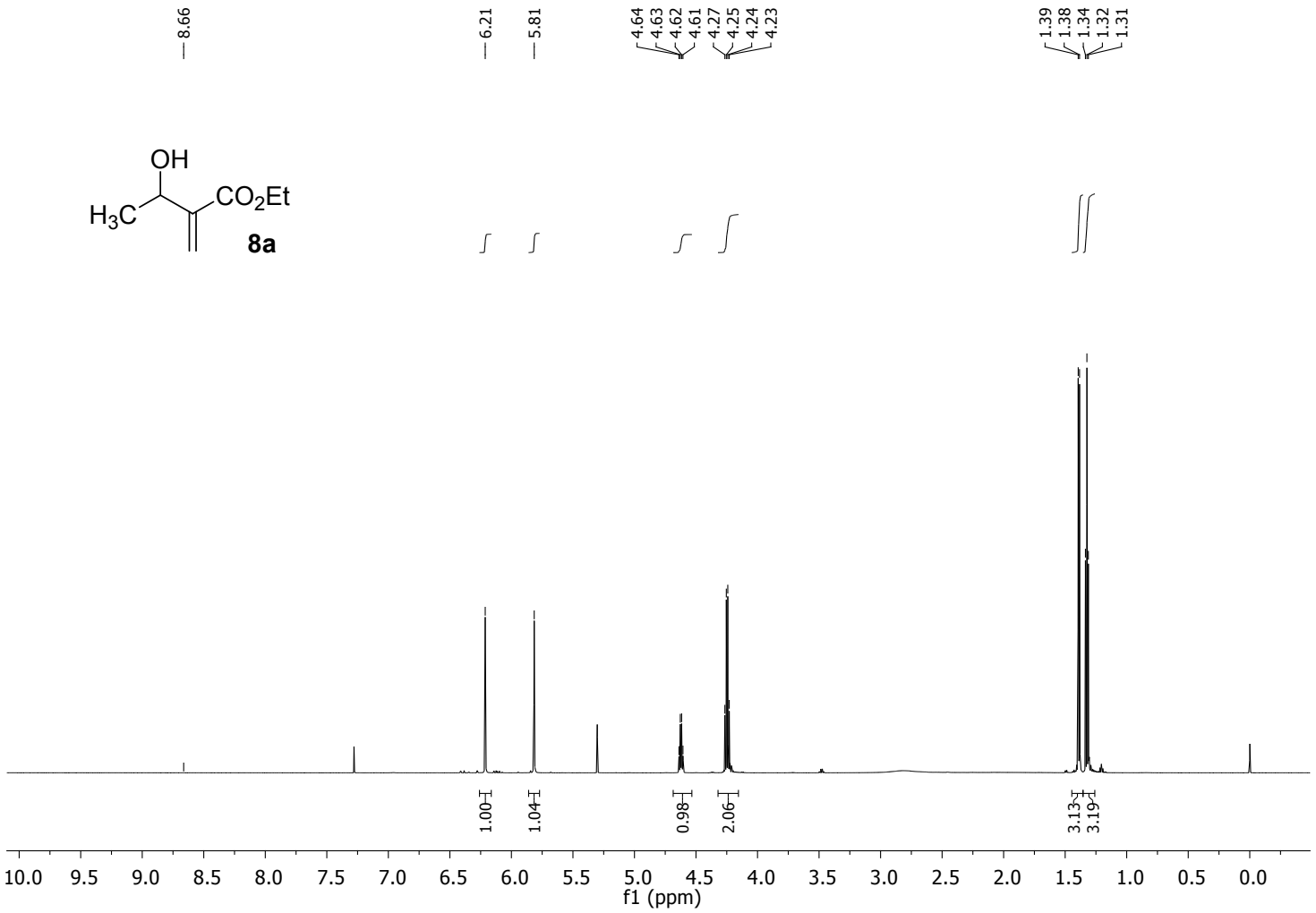
^{1}H NMR Spectra of **6c**



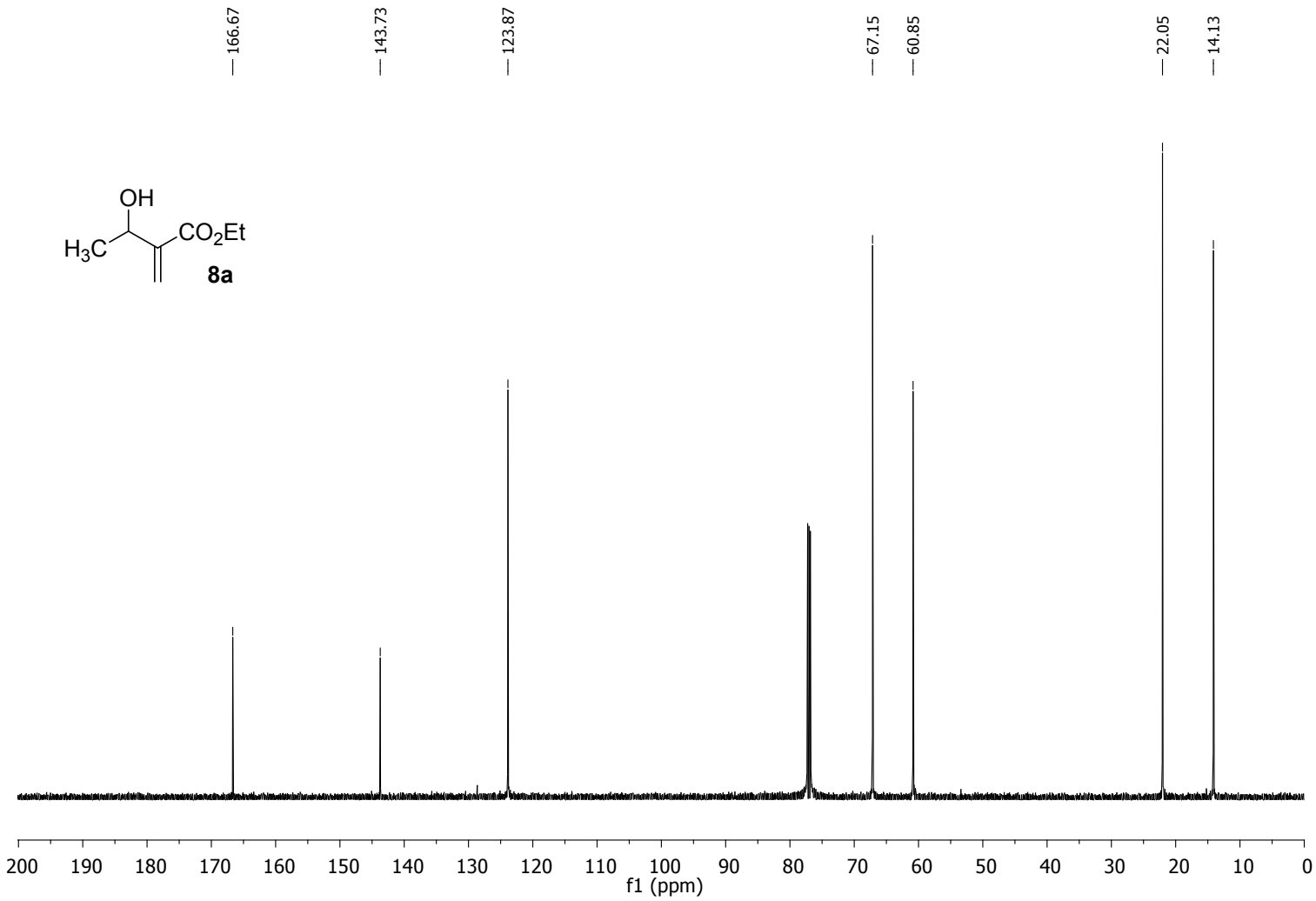
^{13}C NMR Spectra of **6c**



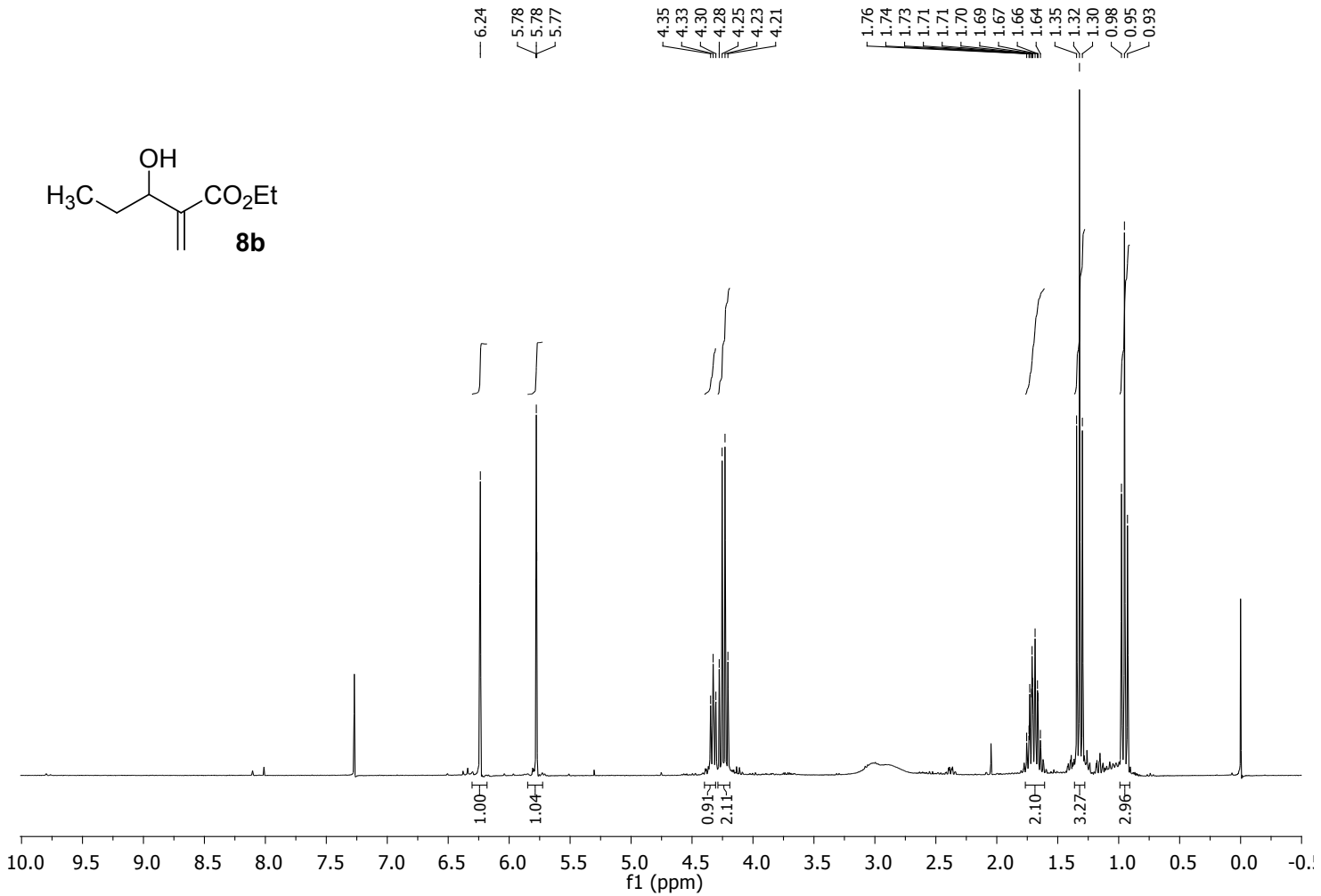
^{1}H NMR Spectra of **8a**



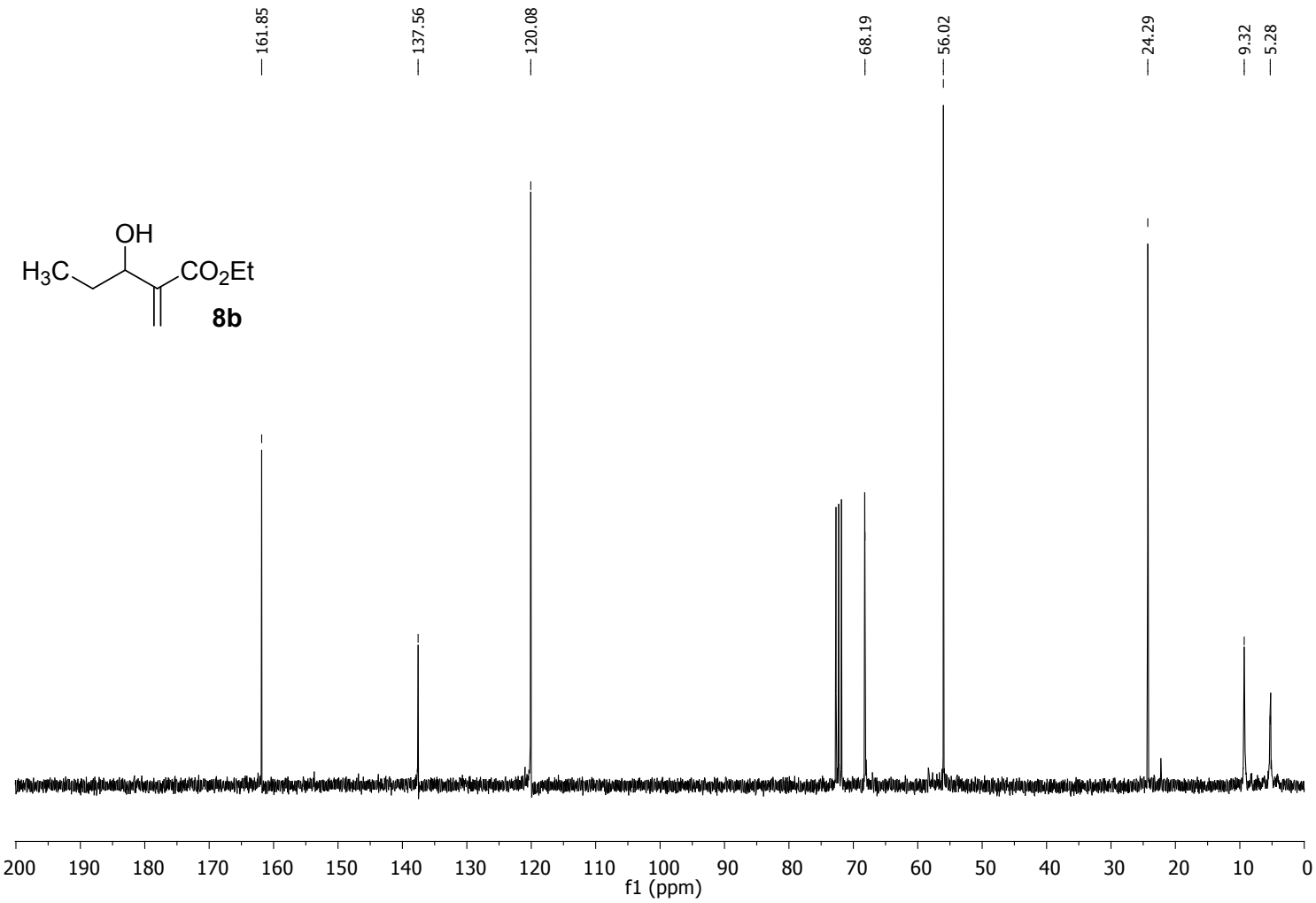
^{13}C NMR Spectra of **8a**



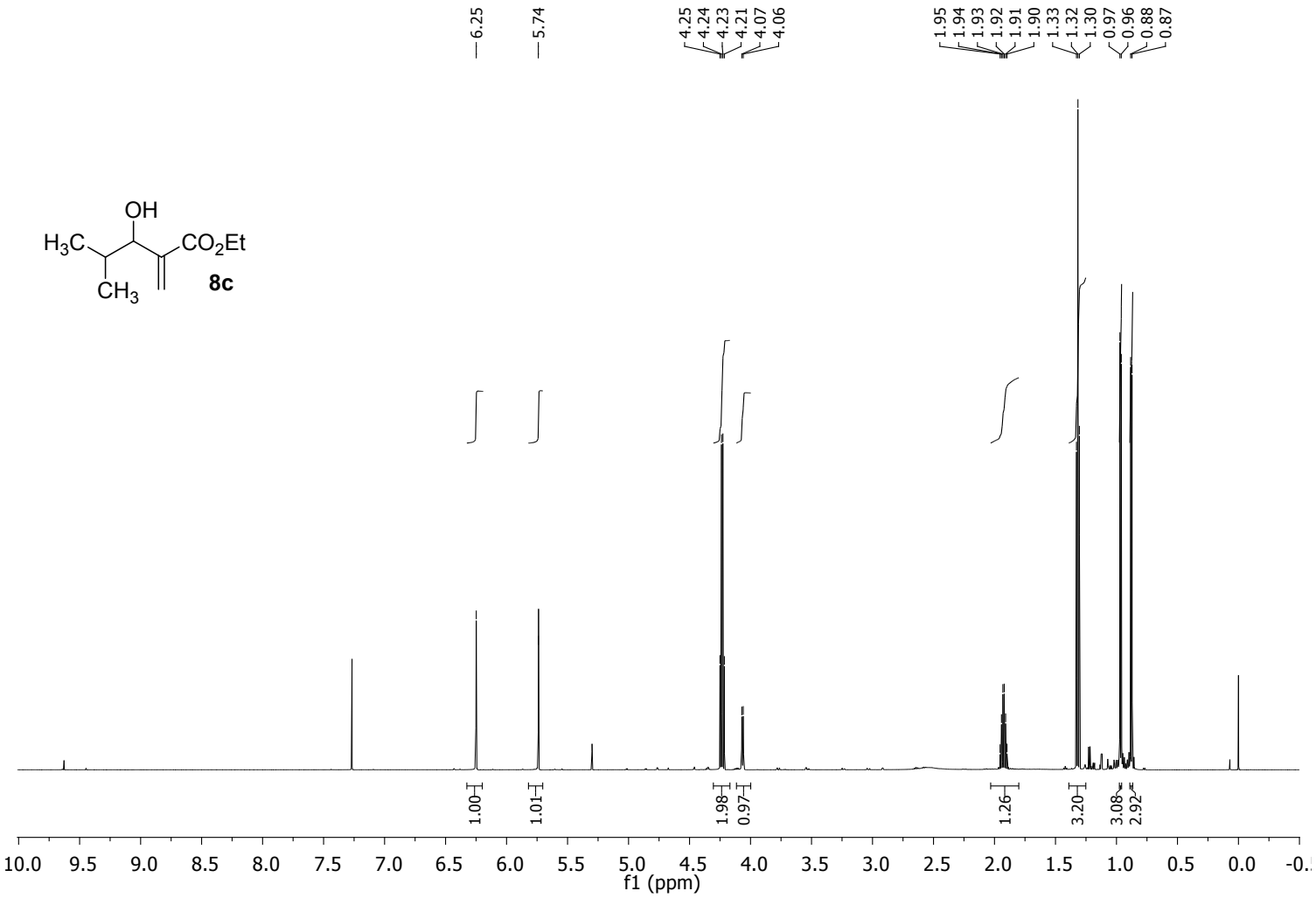
^{1}H NMR Spectra of **8b**



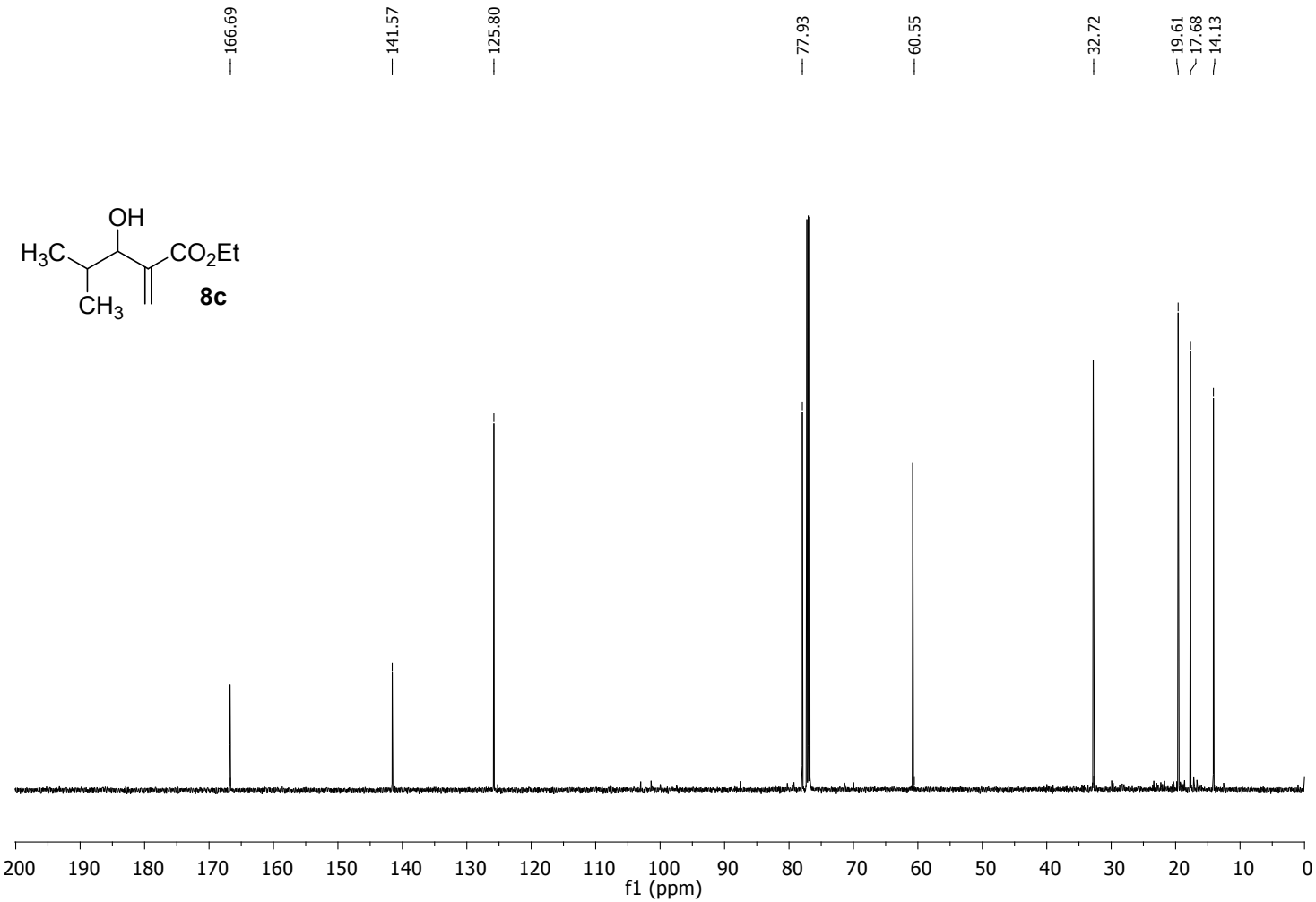
^{13}C NMR Spectra of **8b**



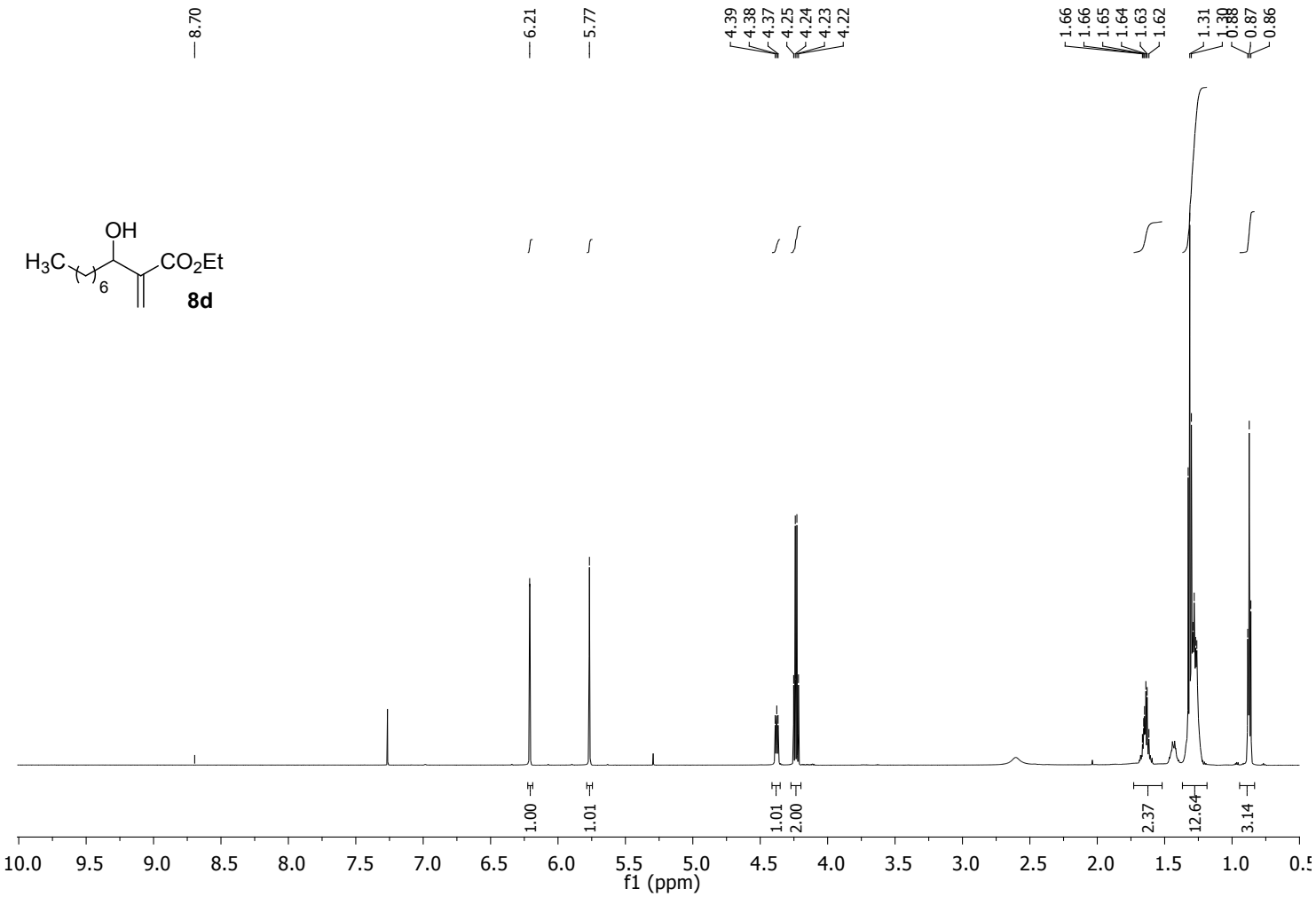
^{1}H NMR Spectra of **8c**



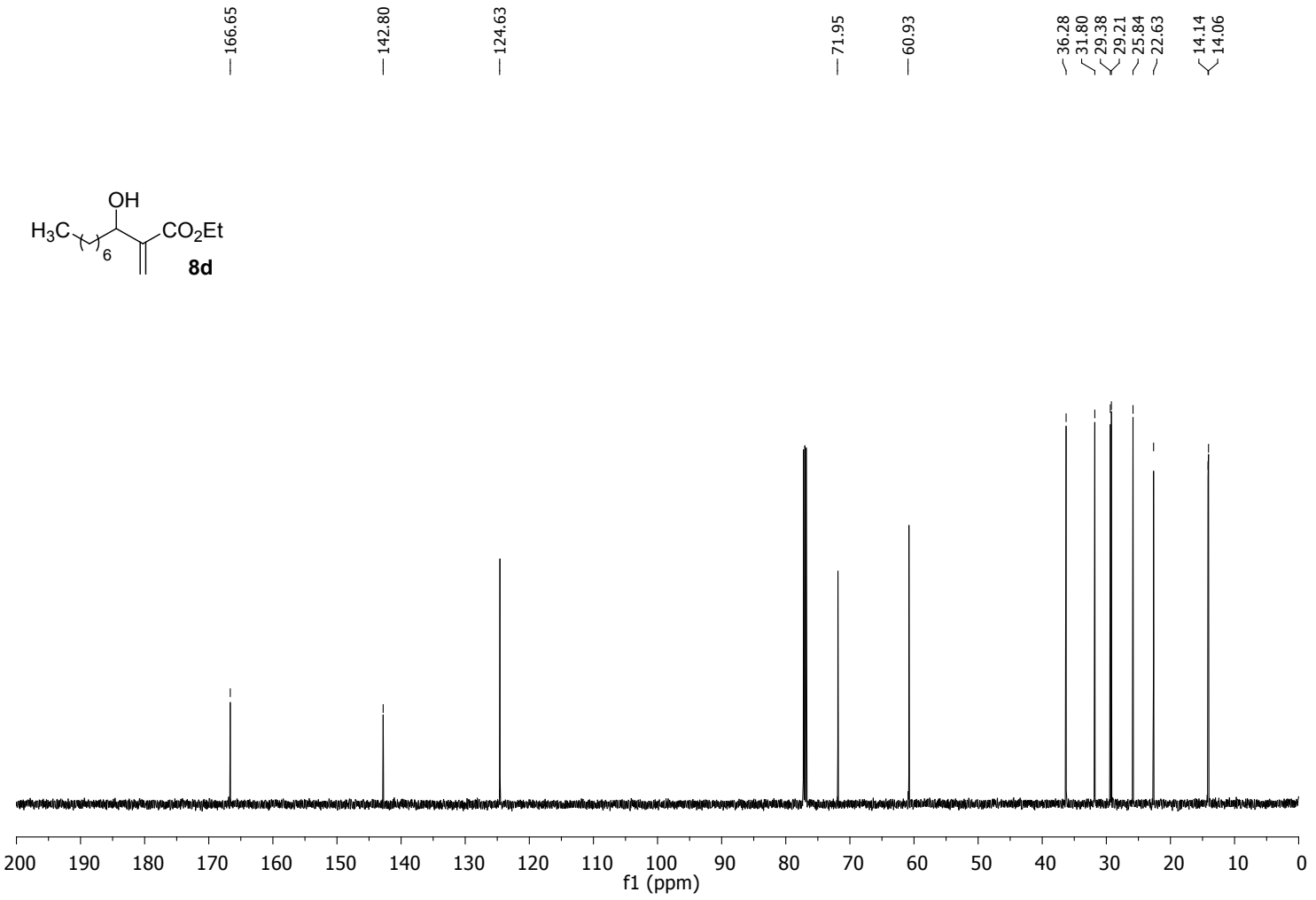
^{13}C NMR Spectra of **8c**



^{1}H NMR Spectra of **8d**



^{13}C NMR Spectra of **8d**



5. Copy of spectra for the crude Hurd-Claisen rearrangement reaction for calculation of the conversion, selectivity, and *E*/*Z* ratio.

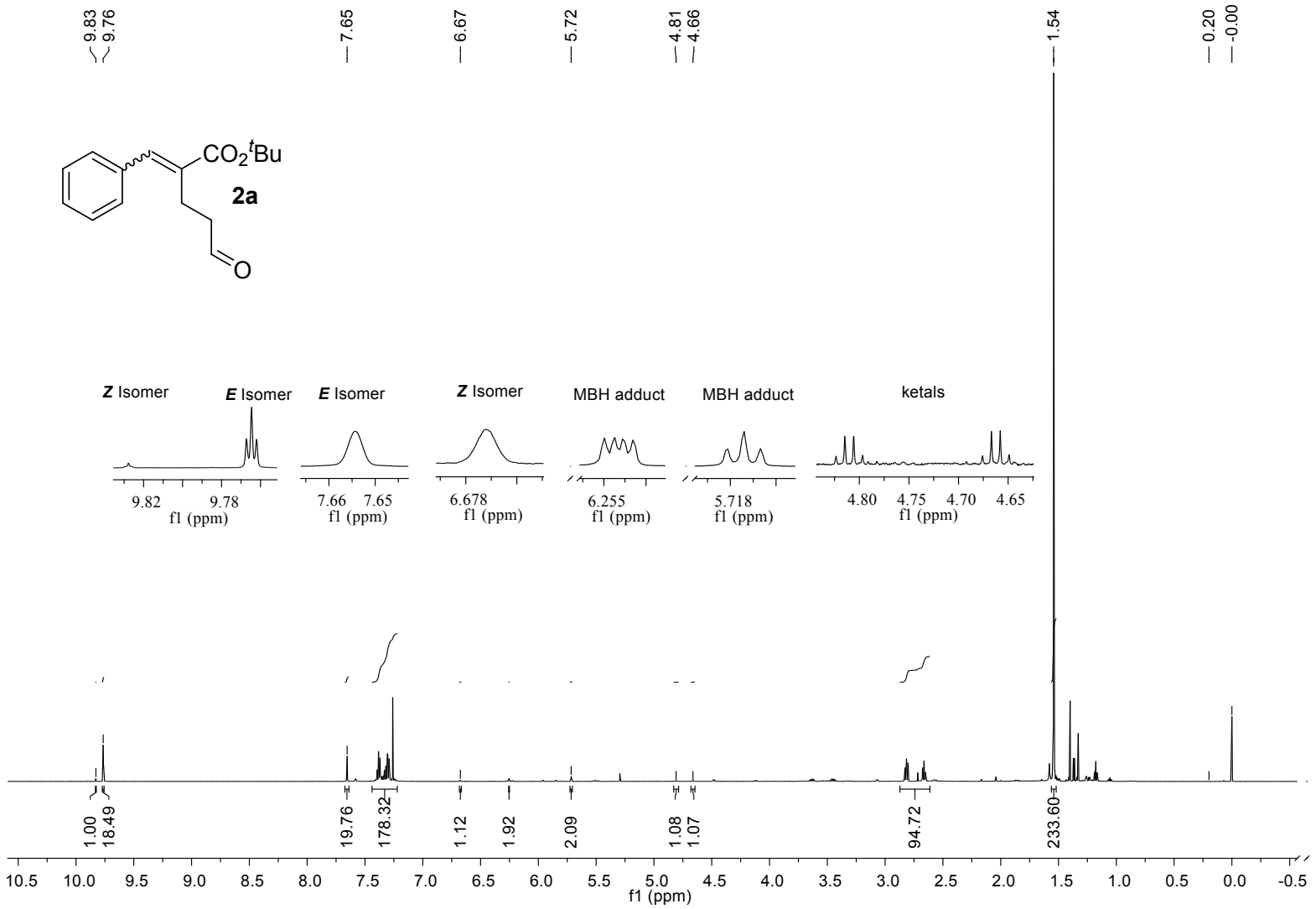
Conversion, selectivity and *E*/*Z* ratio were calculated according to the equations below:

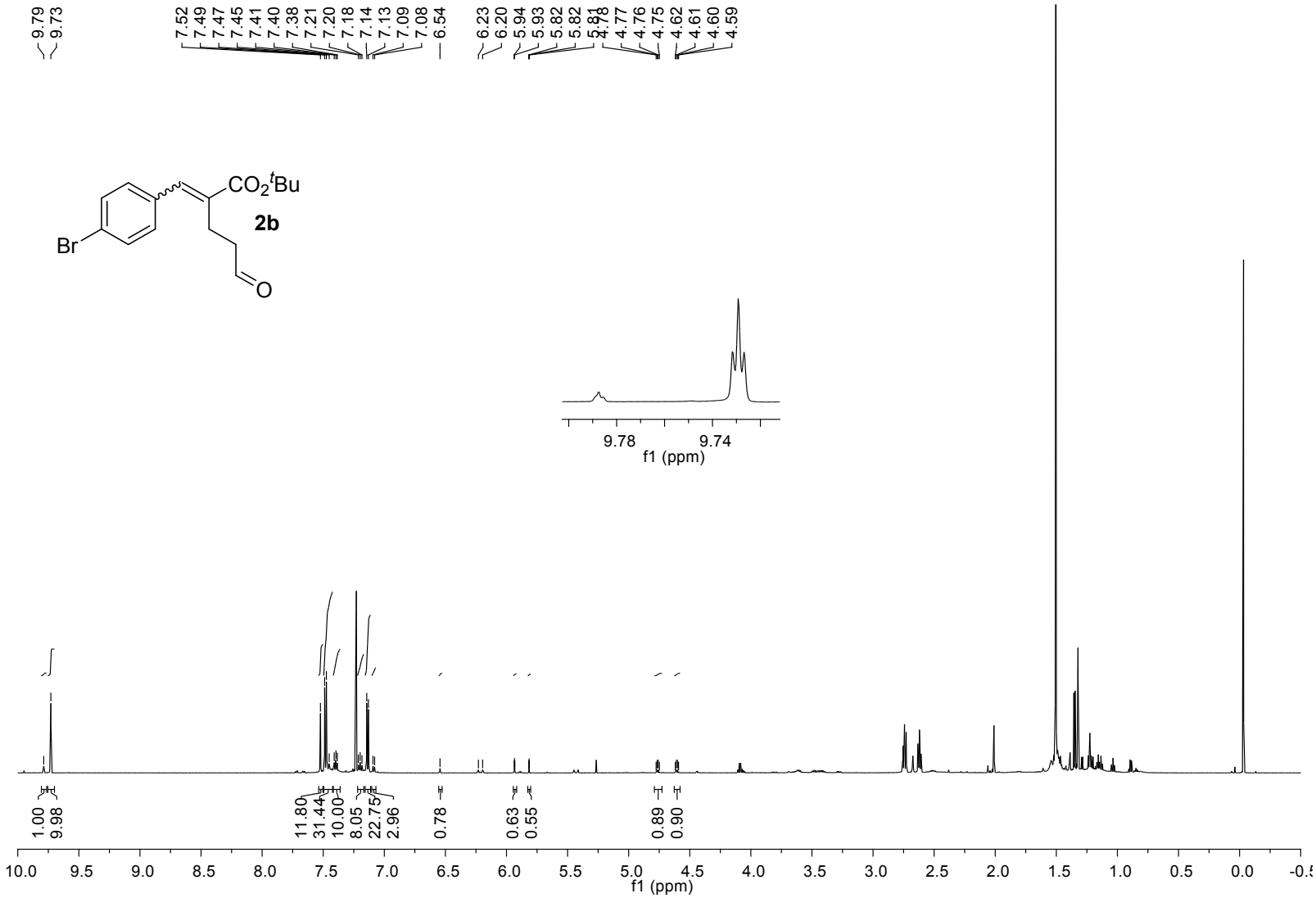
$$\textbf{Conversion} = [(x_{\boldsymbol{E}}) + (x_{\boldsymbol{Z}}) + (x_{\textbf{ketals}})] \,/\, [(x_{\textbf{MBH}}) + (x_{\textbf{E}}) + (x_{\boldsymbol{Z}}) + (x_{\textbf{ketals}})]$$

$$\textbf{Selectivity} = [(x_{\boldsymbol{E}}) + (x_{\boldsymbol{Z}})] \,/\, [(x_{\boldsymbol{E}}) + (x_{\boldsymbol{Z}}) + (x_{\textbf{ketals}})]$$

$$\boldsymbol{E/Z} = (x_{\boldsymbol{E}}) \,/\, (x_{\boldsymbol{Z}})$$

where $x_{\mathbf{i}}$ = molar fraction of the component i determined by ^{1}H NMR


9.83
9.76
7.65
6.67
5.72
4.81
4.66
1.54
0.20
-0.00
CO2tBu
2a
O
Z Isomer
E Isomer
E Isomer
Z Isomer
MBH adduct
MBH adduct
ketals
9.82
9.78
f1 (ppm)
7.66
7.65
f1 (ppm)
6.678
f1 (ppm)
6.255
f1 (ppm)
5.718
f1 (ppm)
4.80
4.75
4.70
4.65
f1 (ppm)
1.00
18.49
19.76
178.32
1.12
1.92
2.09
1.08
1.07
94.72
233.60
10.5
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
-0.5
f1 (ppm)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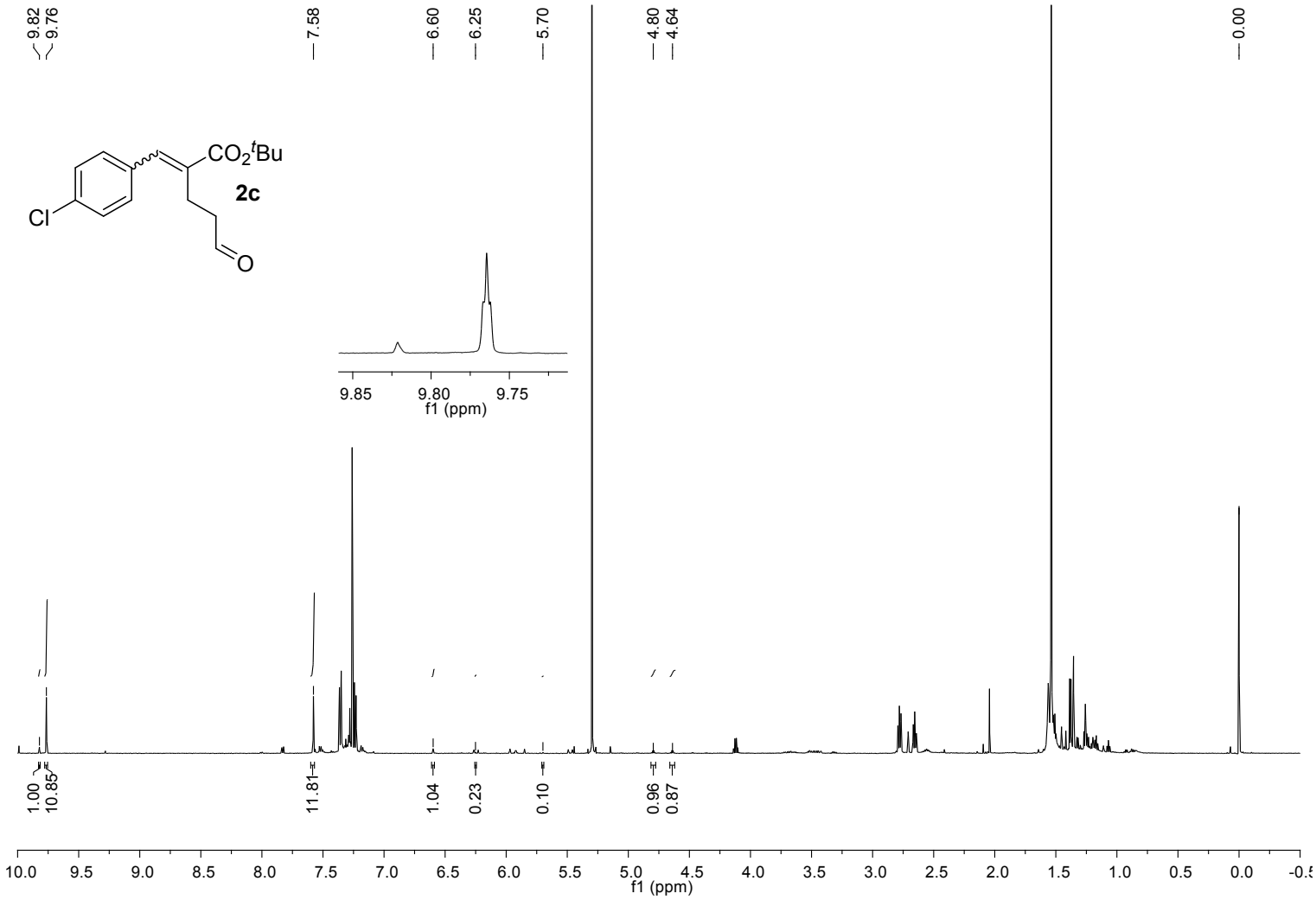
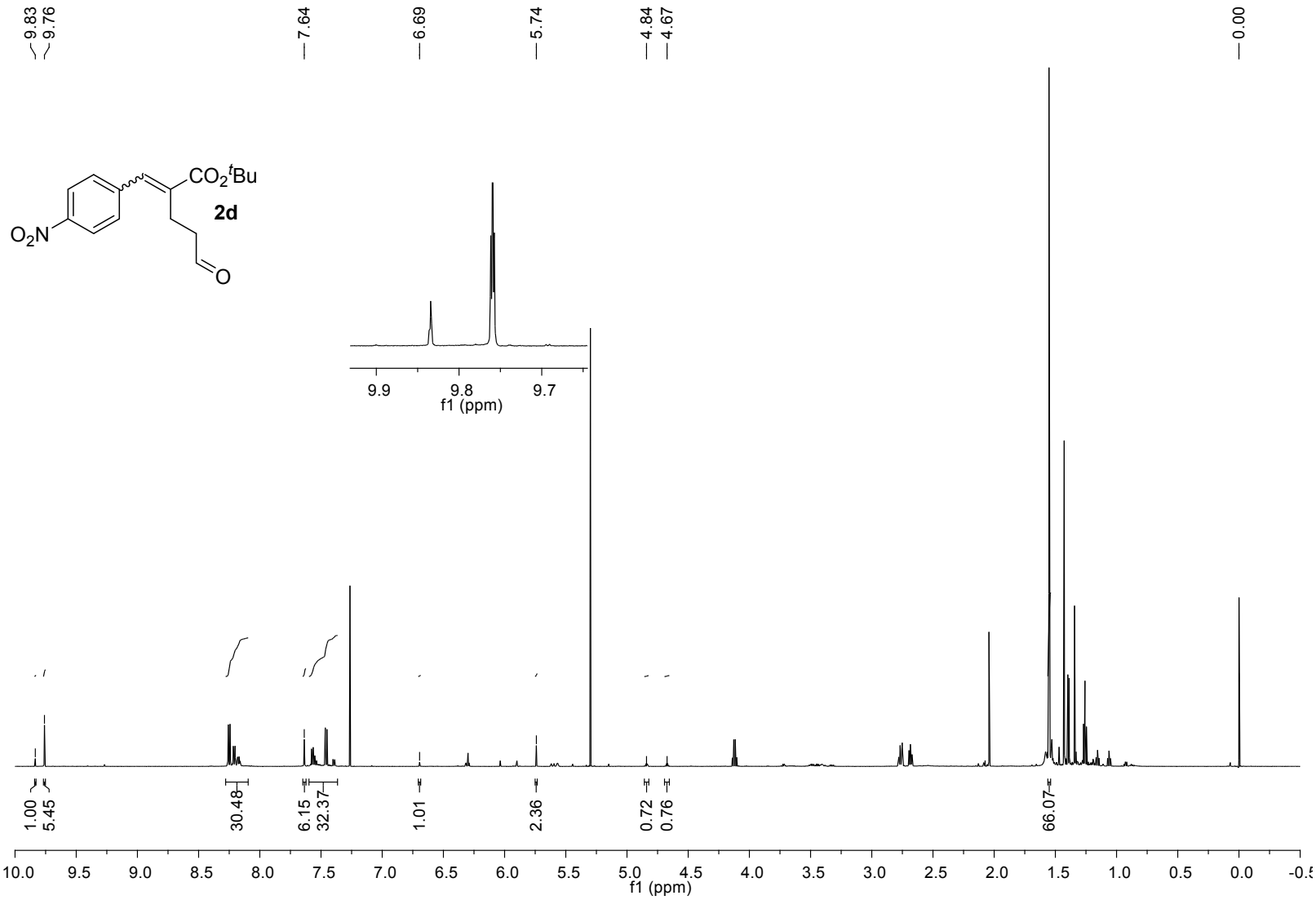
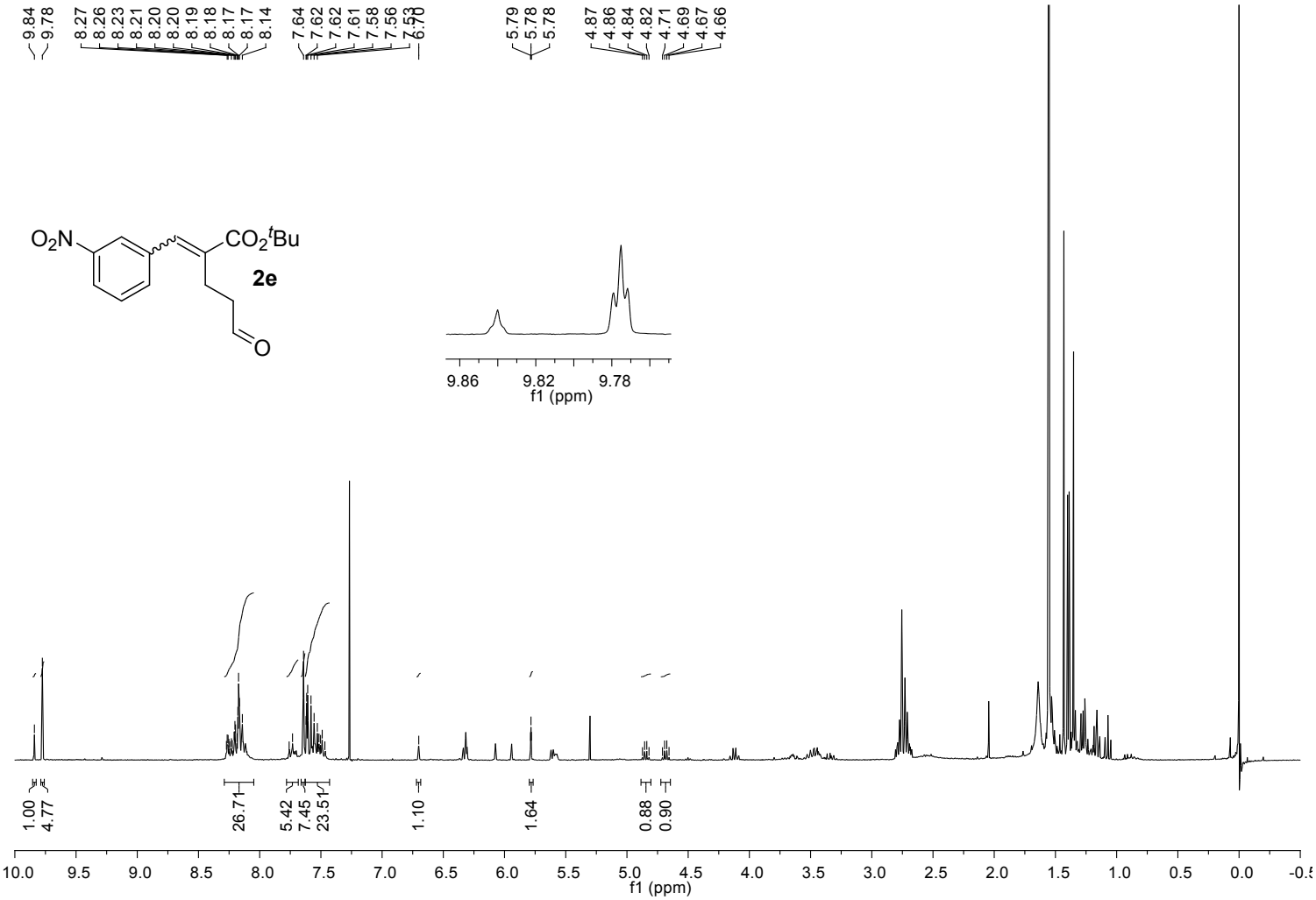
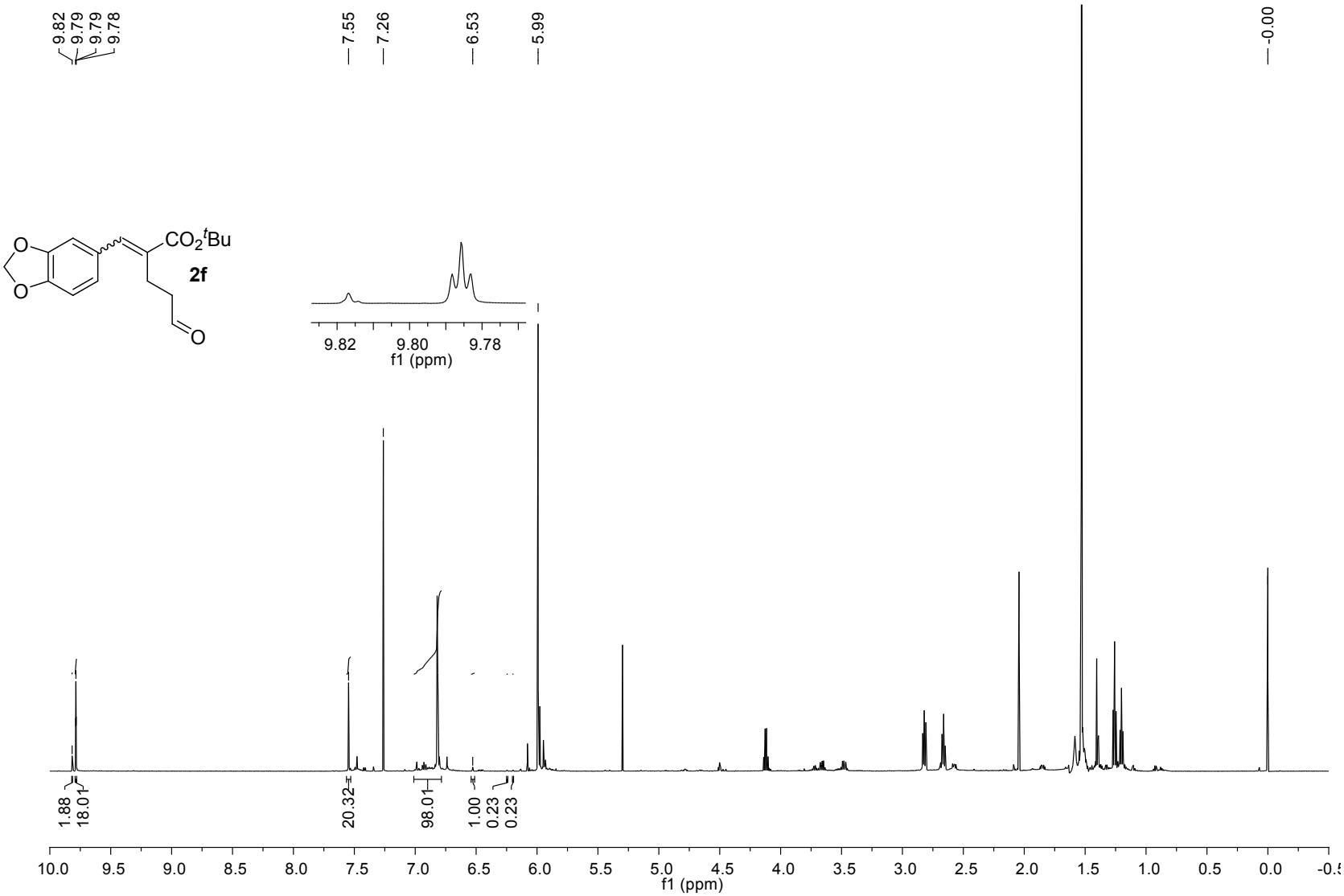
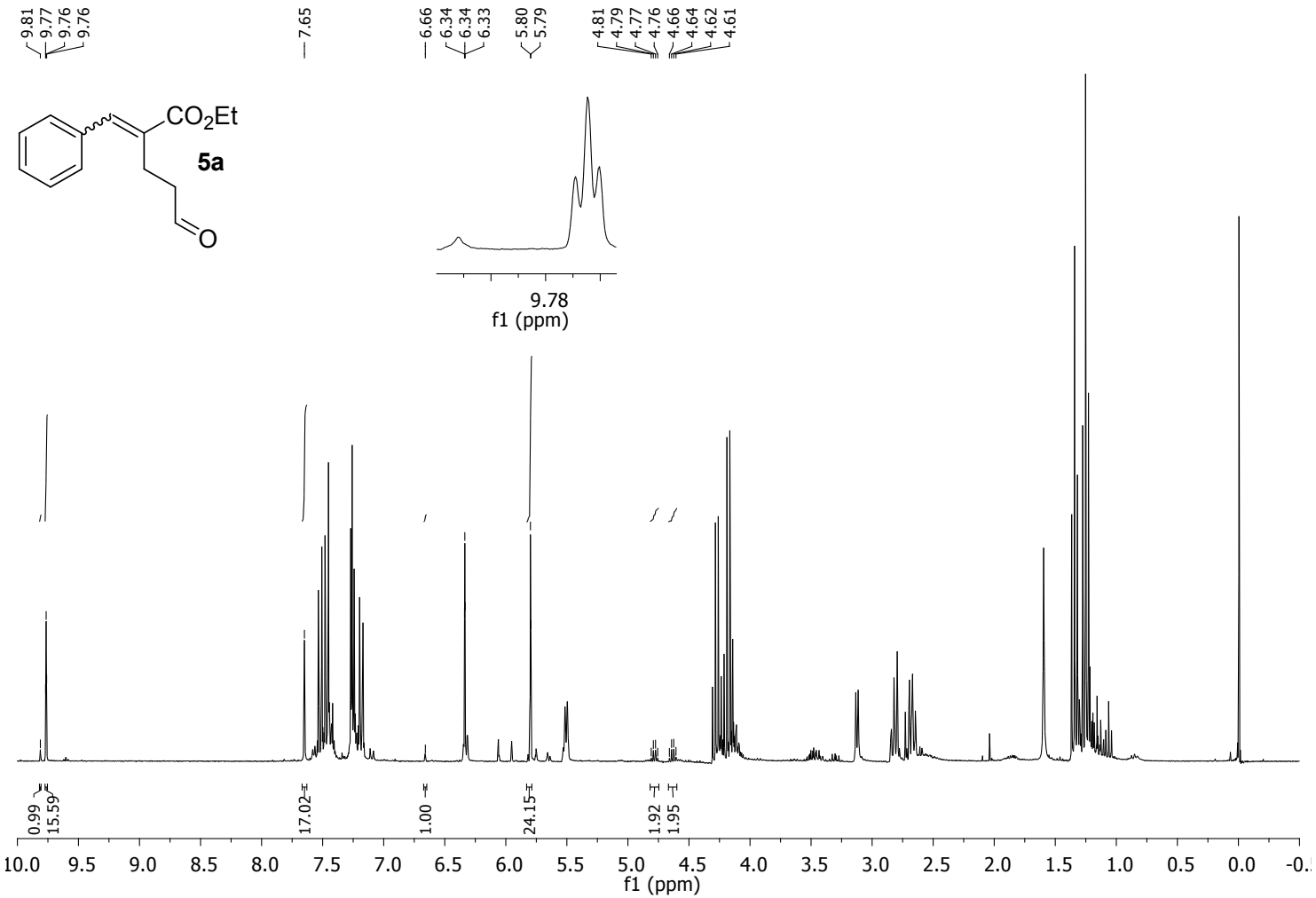
9.73
7.52
7.49
7.47
7.45
7.41
7.40
7.38
7.21
7.20
7.18
7.14
7.13
7.09
7.08
6.54
6.23
6.20
5.94
5.93
5.82
5.82
5.81
5.78
4.77
4.76
4.75
4.62
4.61
4.60
4.59
CO2tBu
2b
Br
O
9.78
9.74
f1 (ppm)
1.00
9.98
11.80
31.44
10.00
8.05
22.75
2.96
0.78
0.63
0.55
0.89
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.82
9.76
7.58
6.60
6.25
5.70
4.80
4.64
0.00
CO2tBu
2c
Cl
O
9.85
9.80
9.75
f1 (ppm)
1.00
10.85
11.81
1.04
0.23
0.10
0.96
0.87
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)


9.83
9.76
7.64
6.69
5.74
4.84
4.67
0.00
CO2tBu
2d
O2N
O
9.9
9.8
9.7
f1 (ppm)
1.00
5.45
30.48
6.15
32.37
1.01
2.36
0.72
0.76
66.07
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)


9.84
9.78
8.27
8.26
8.23
8.21
8.20
8.20
8.19
8.18
8.17
8.17
8.14
7.64
7.62
7.62
7.61
7.58
7.56
7.53
5.79
5.78
5.78
4.87
4.86
4.84
4.82
4.71
4.69
4.67
4.66
O2N
CO2tBu
2e
O
9.86
9.82
9.78
f1 (ppm)
1.00
4.77
26.71
5.42
7.45
23.51
1.10
1.64
0.88
0.90
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)


9.82
9.79
9.79
9.78
7.55
7.26
6.53
5.99
0.00
CO2tBu
2f
O
O
O
9.82
9.80
9.78
f1 (ppm)
1.88
18.01
20.32
98.01
1.00
0.23
0.23
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)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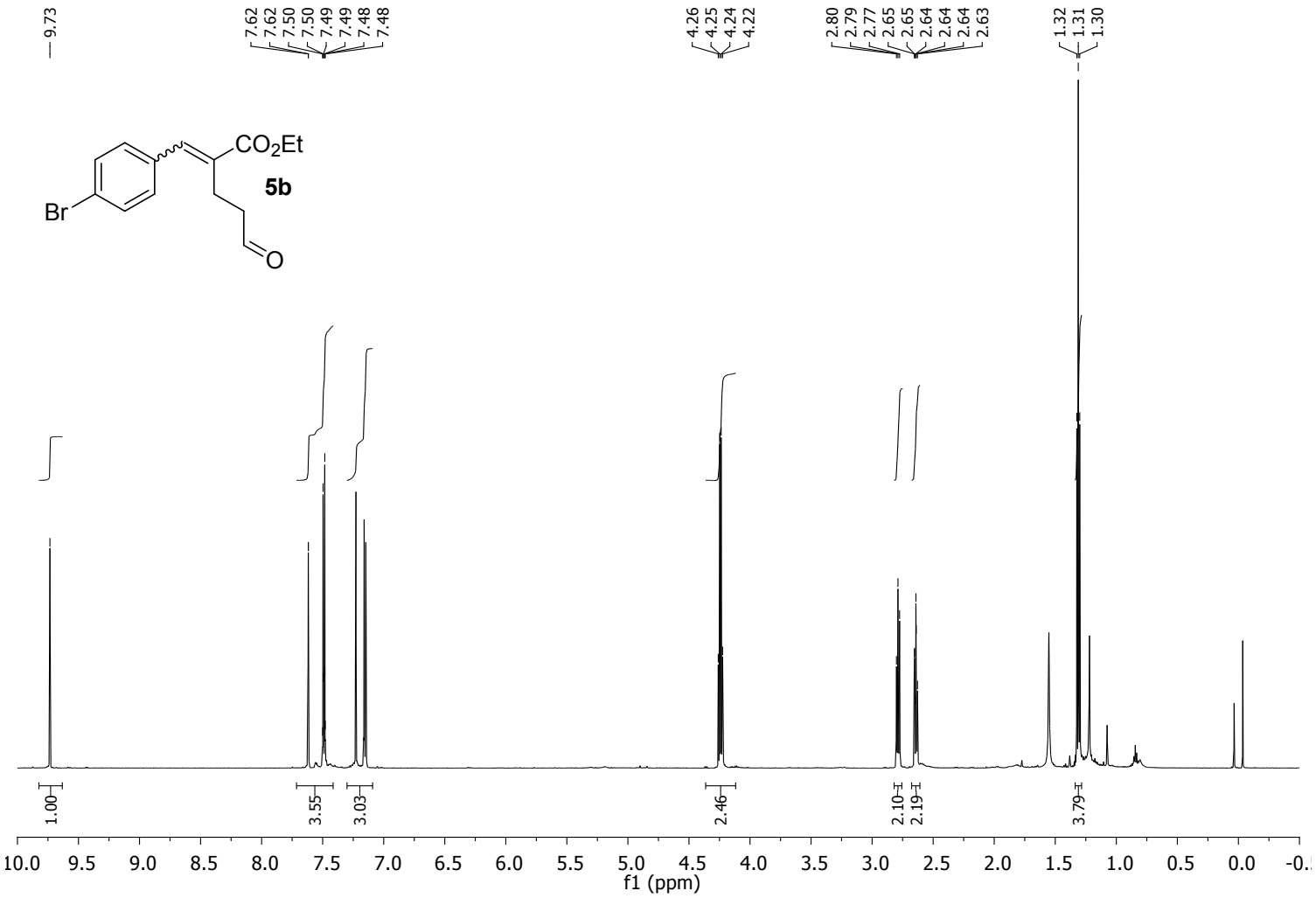
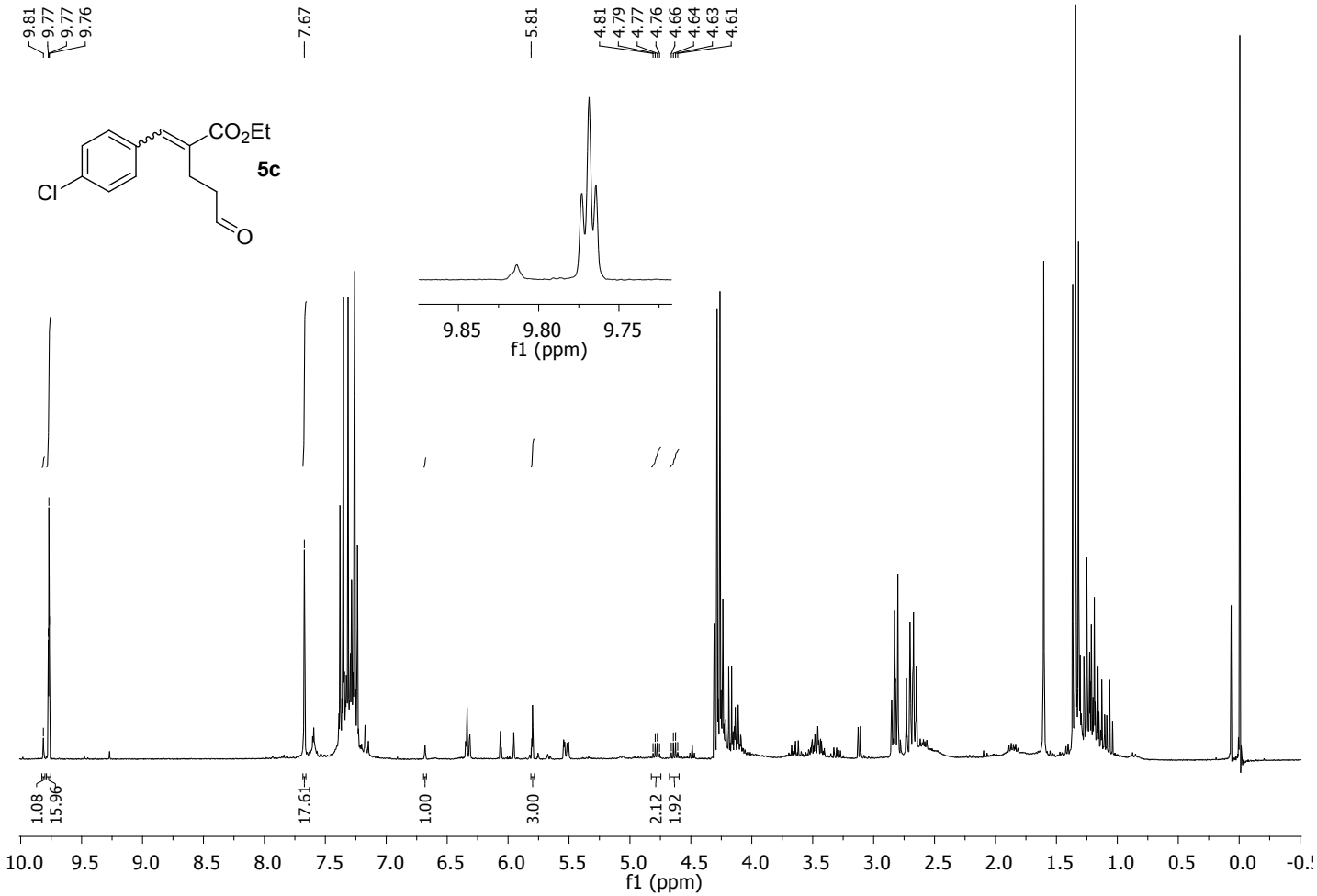
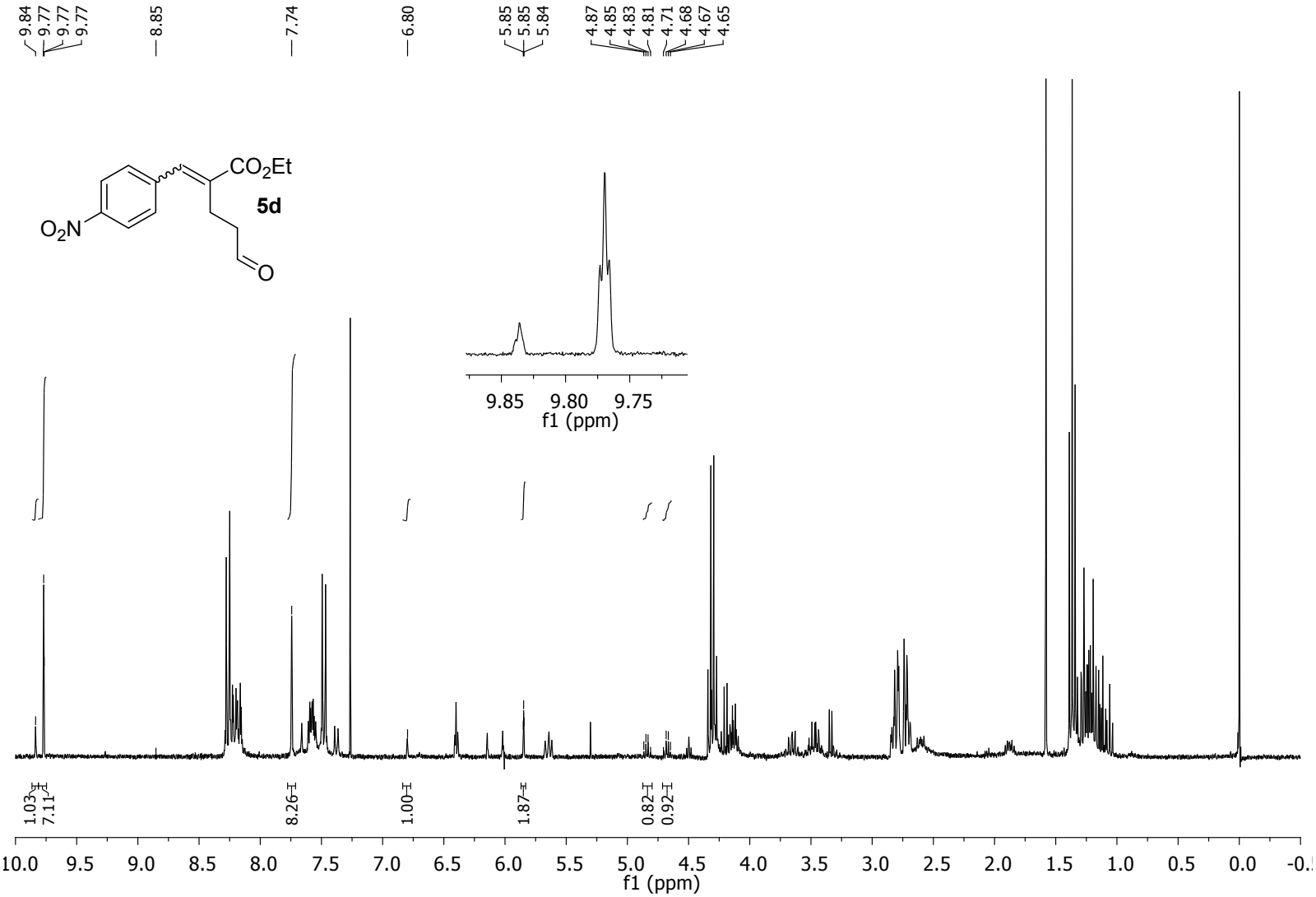
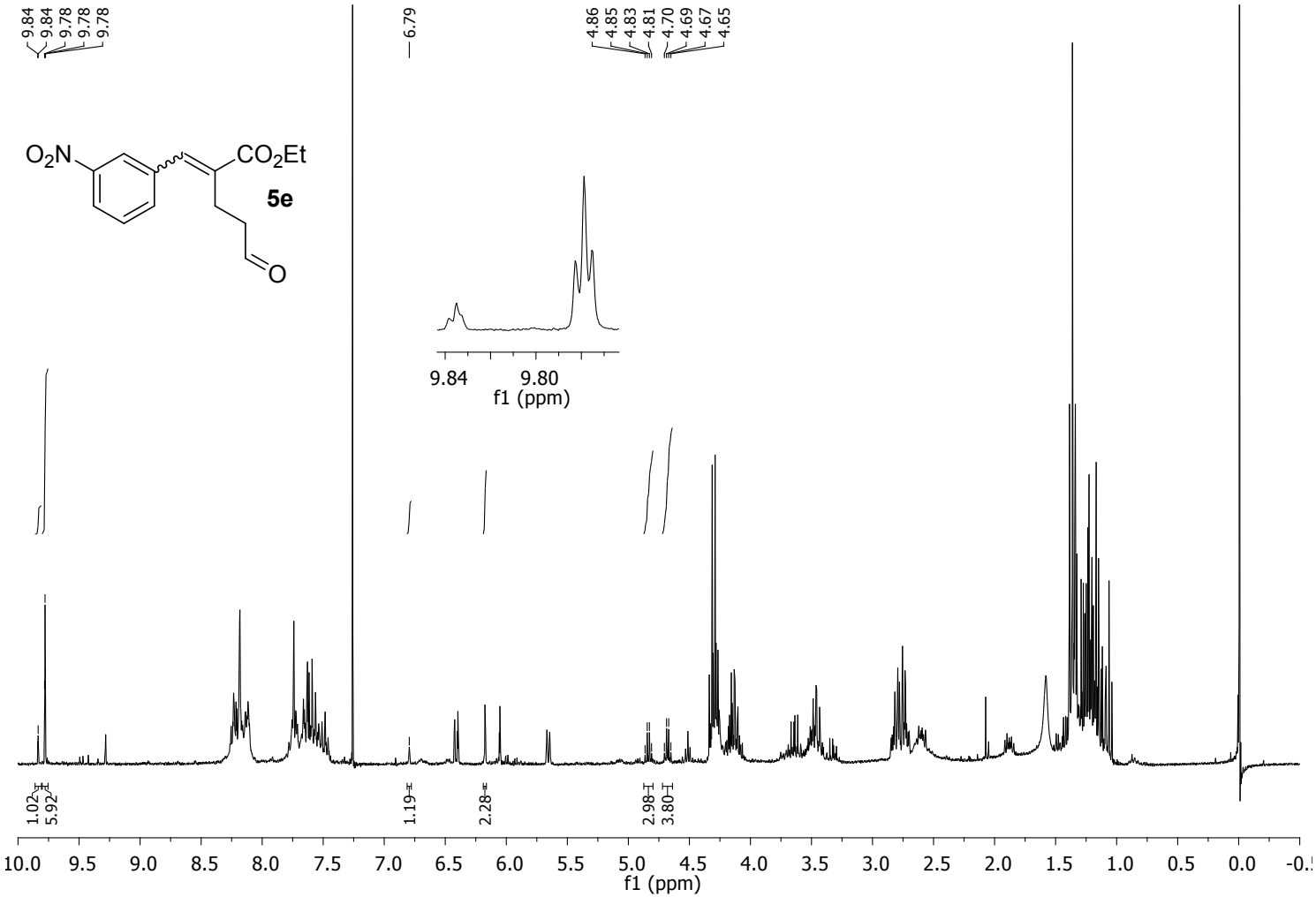
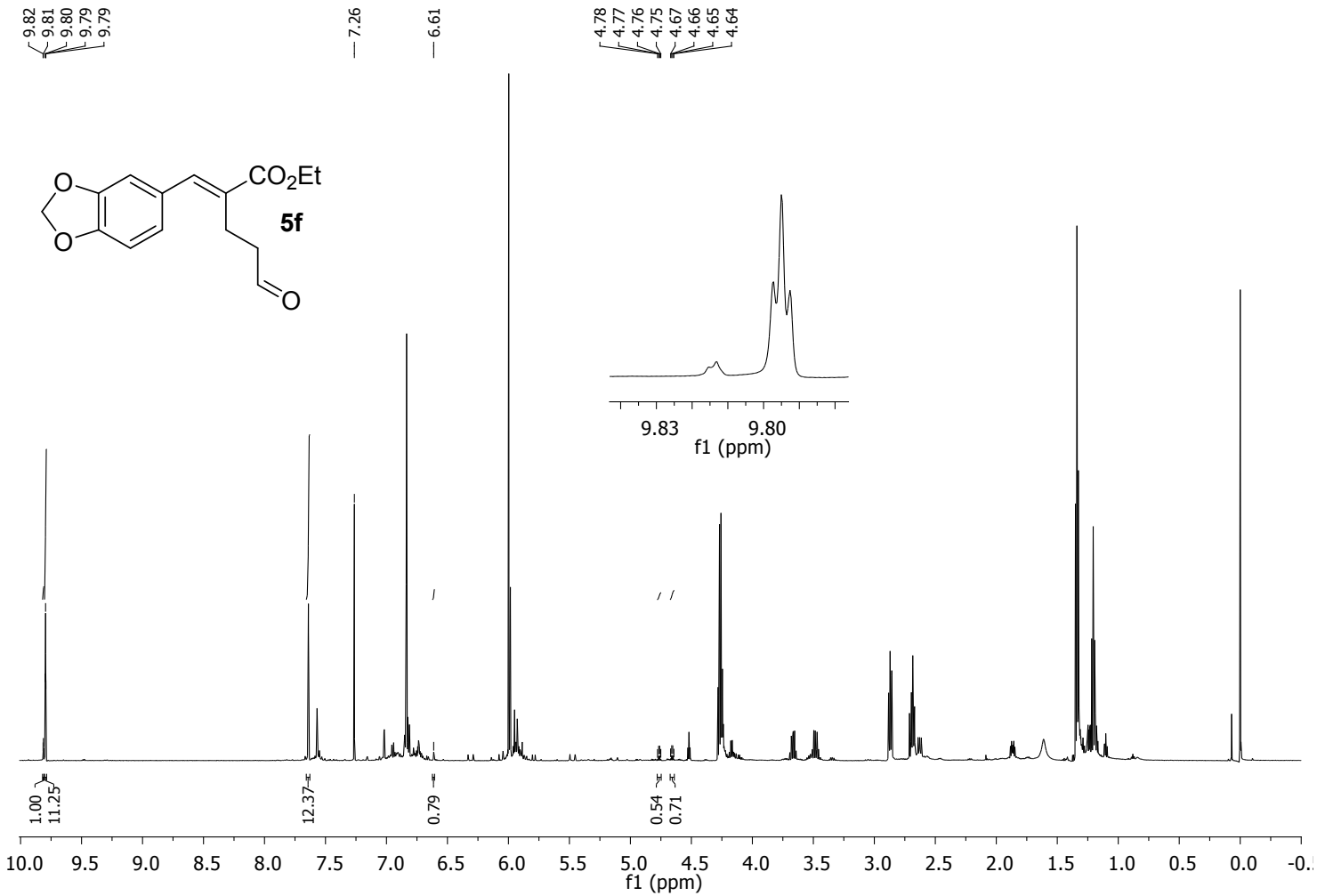
9.77
9.76
9.76
7.65
6.66
6.34
6.34
6.33
5.80
5.79
4.81
4.79
4.77
4.76
4.66
4.64
4.62
4.61
CO2Et
5a
O
9.78
f1 (ppm)
0.99
15.59
17.02
1.00
24.15
1.92
1.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

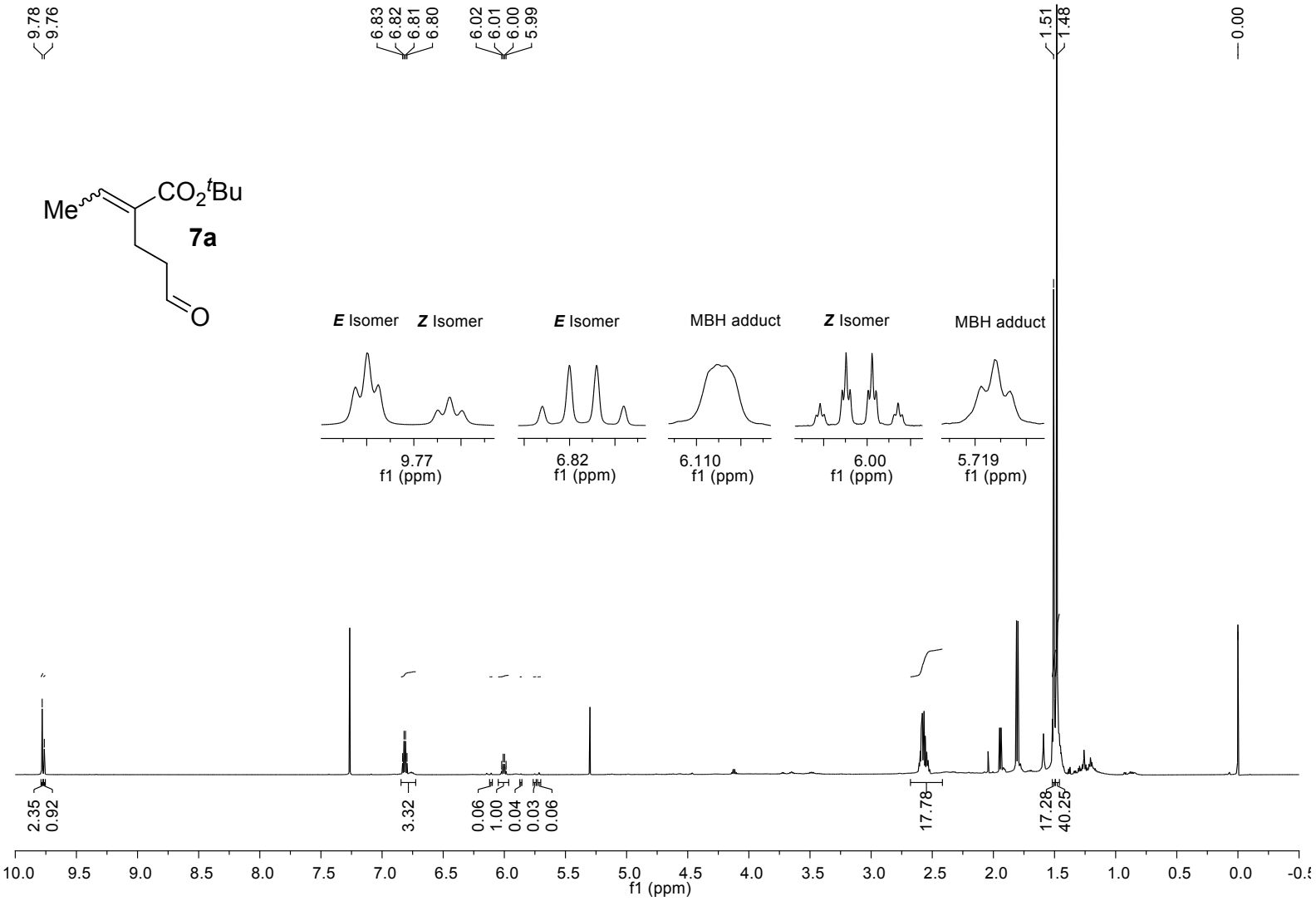

9.73
7.62
7.62
7.50
7.50
7.49
7.49
7.48
7.48
4.26
4.25
4.24
4.22
2.80
2.79
2.77
2.65
2.65
2.64
2.64
2.64
2.63
1.32
1.31
1.30
CO2Et
5b
Br
O
1.00
3.55
3.03
2.46
2.10
2.19
3.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

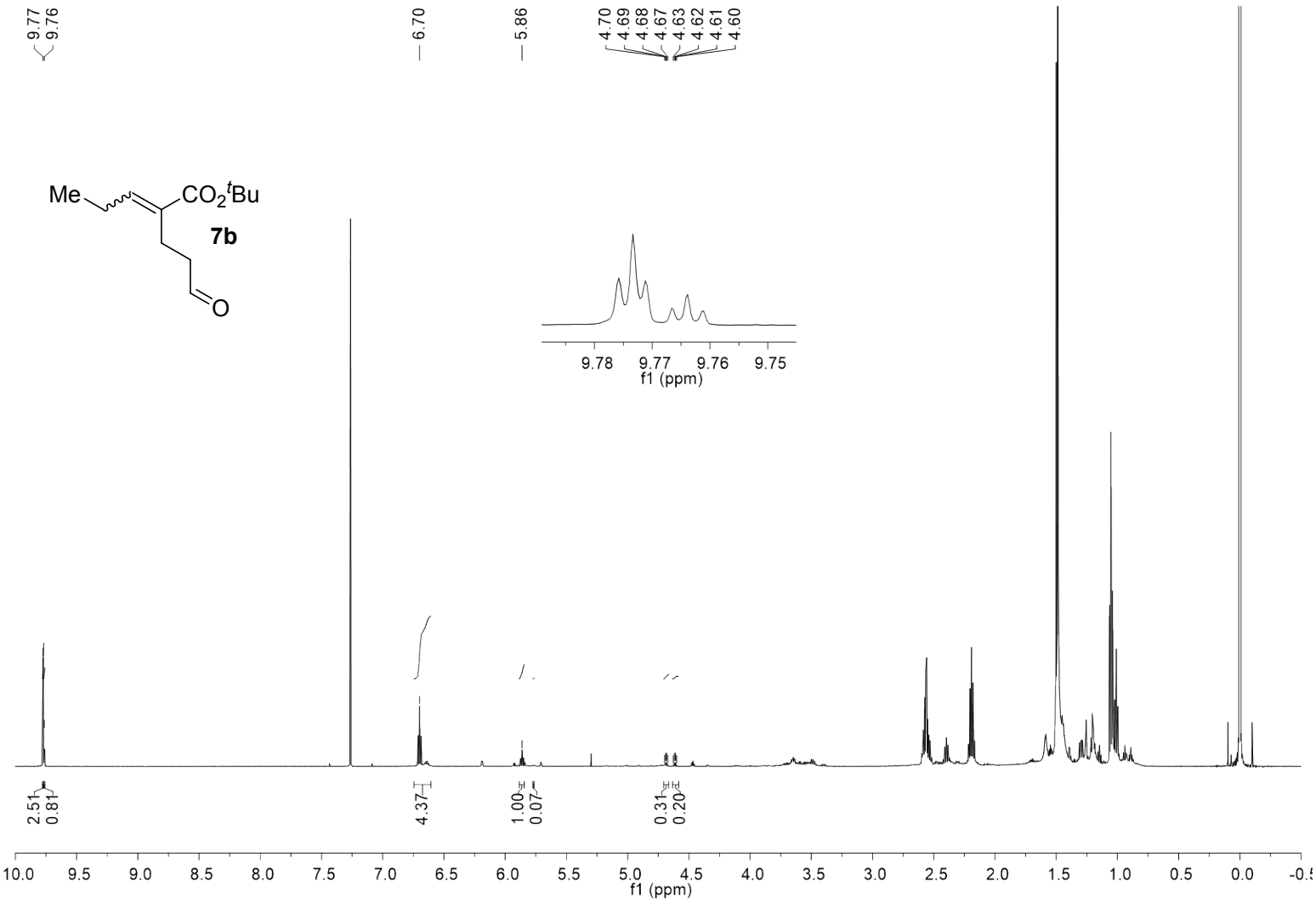

9.81
9.77
9.77
9.76
7.67
5.81
4.81
4.79
4.77
4.76
4.66
4.64
4.63
4.61
CO2Et
5c
Cl
O
9.85
9.80
9.75
f1 (ppm)
1.08
15.96
17.61
1.00
3.00
2.12
1.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

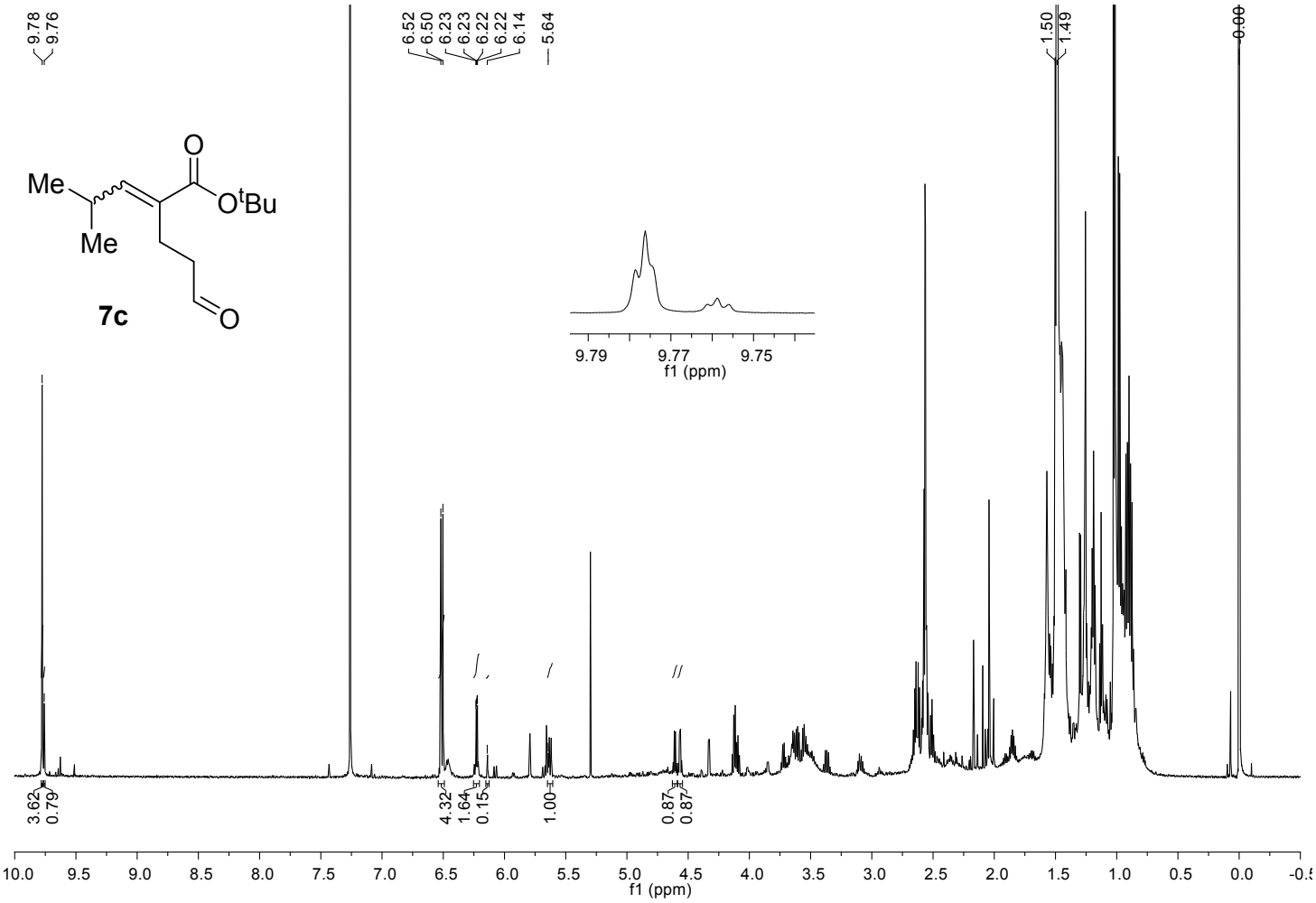

9.84
9.77
9.77
9.77
8.85
7.74
6.80
5.85
5.85
5.84
4.87
4.85
4.83
4.81
4.71
4.68
4.67
4.65
CO2Et
5d
O2N
O
9.85
9.80
9.75
f1 (ppm)
1.03
7.11
8.26
1.00
1.87
0.82
0.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

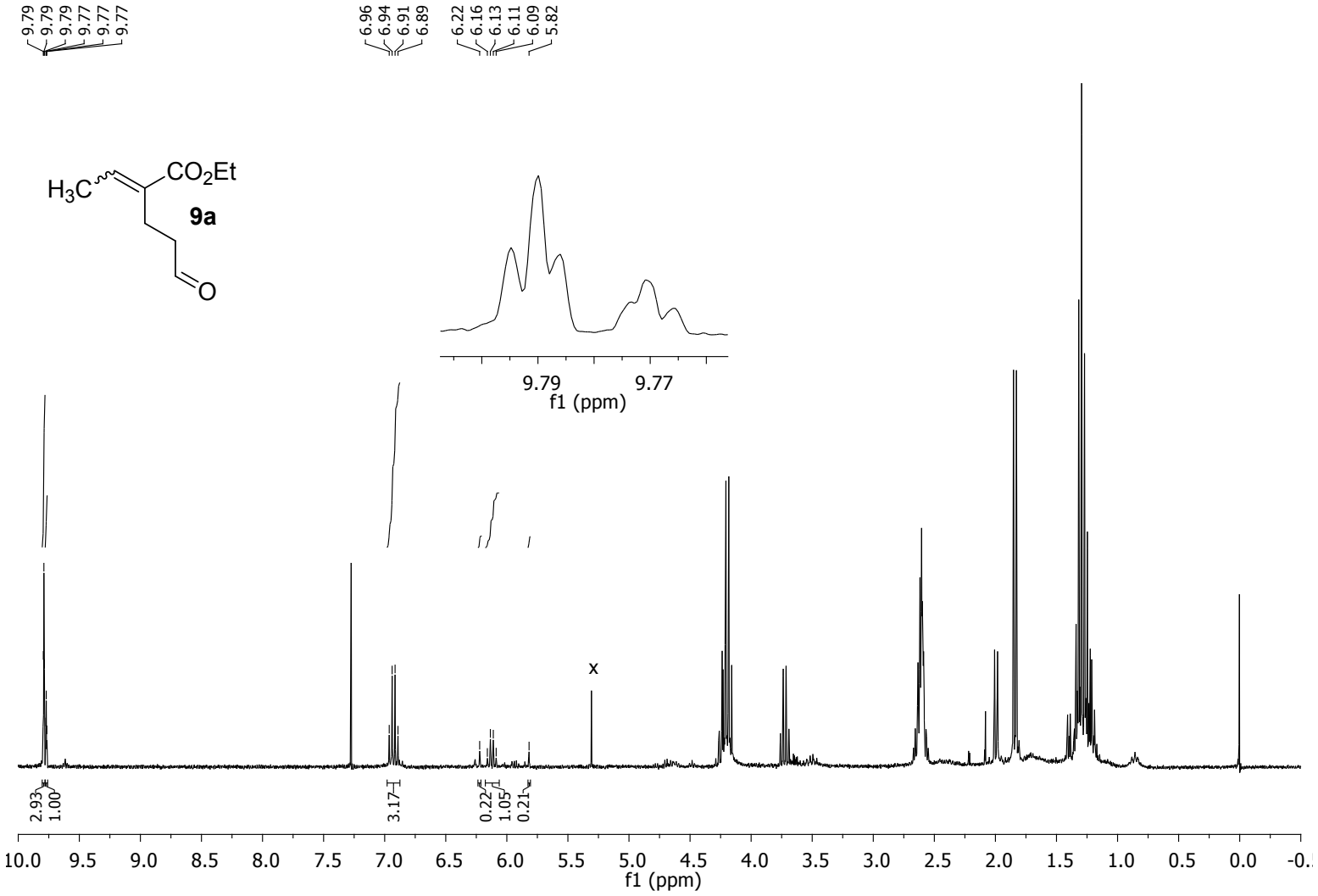

9.84
9.84
9.78
9.78
9.78
6.79
4.86
4.85
4.83
4.81
4.70
4.69
4.67
4.65
O2N
CO2Et
5e
O
9.84
9.80
f1 (ppm)
1.02
5.92
1.19
2.28
2.98
3.80
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

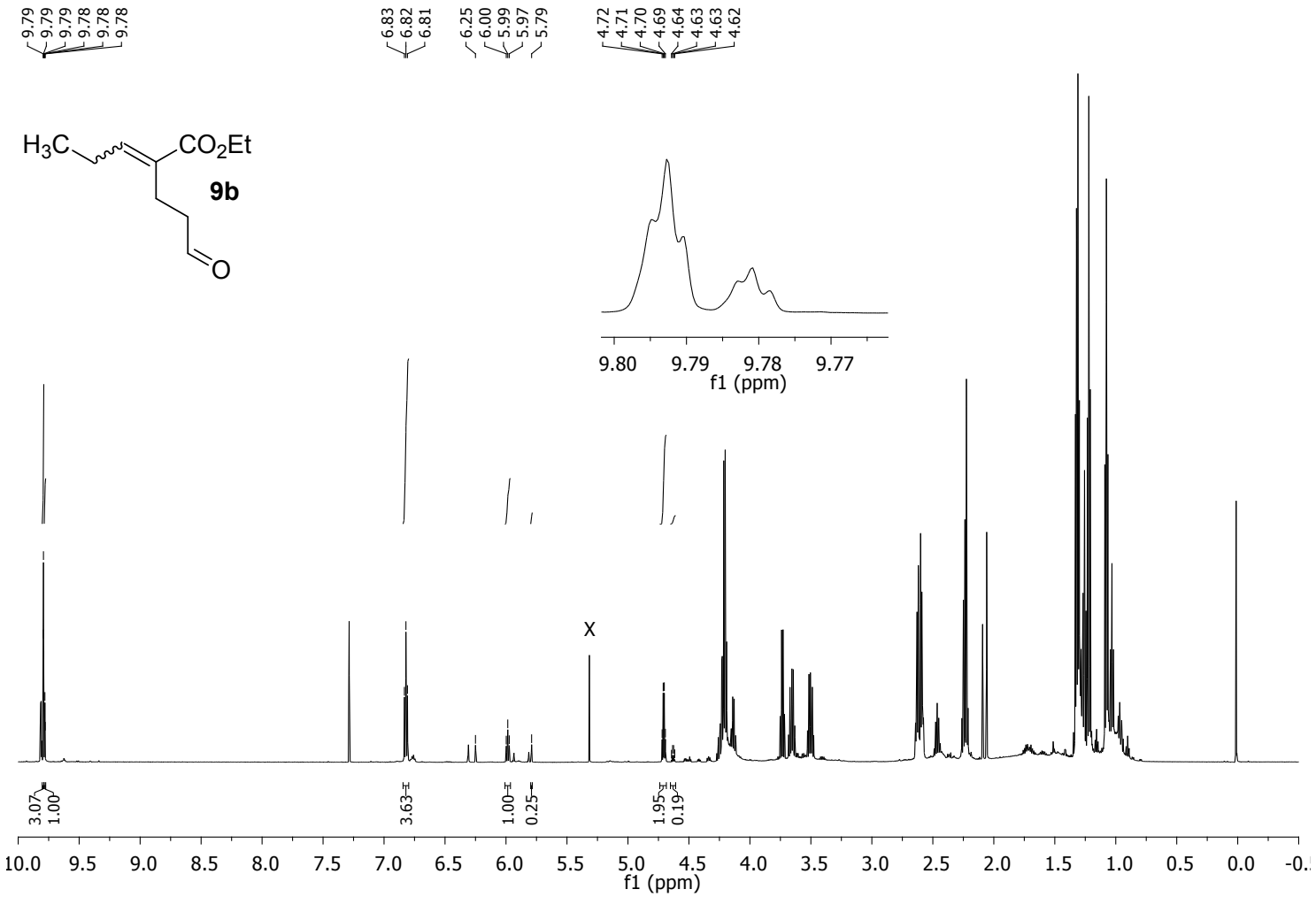

9.82
9.81
9.80
9.79
9.79
7.26
6.61
4.78
4.77
4.76
4.75
4.67
4.66
4.65
4.64
O
O
CO2Et
5f
O
9.83
9.80
f1 (ppm)
1.00
11.25
12.37
0.79
0.54
0.71
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

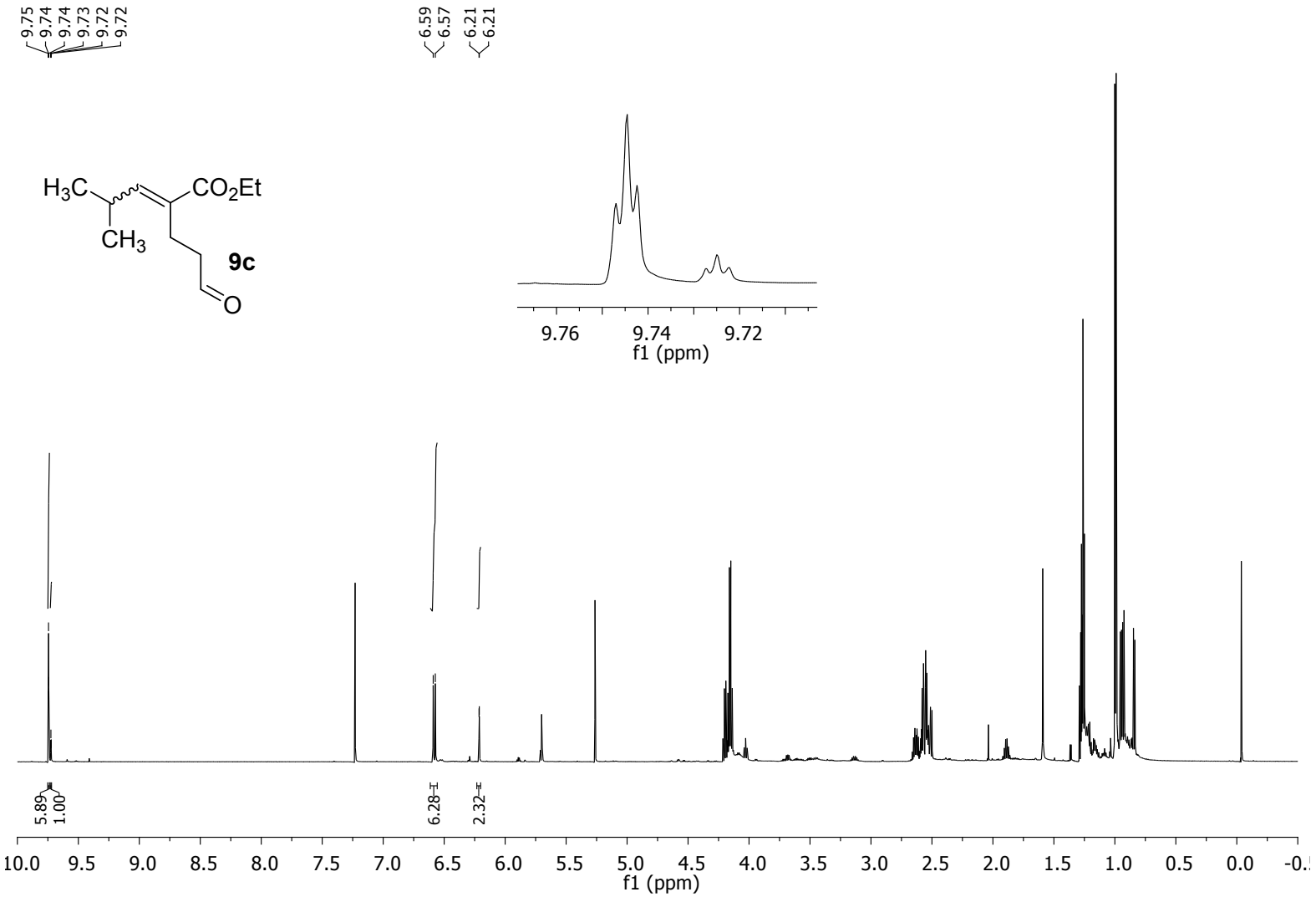

9.78
9.76
6.83
6.82
6.81
6.80
6.02
6.01
6.00
5.99
1.51
1.48
0.00
Me
CO2tBu
7a
O
E Isomer
Z Isomer
E Isomer
MBH adduct
Z Isomer
MBH adduct
9.77
f1 (ppm)
6.82
f1 (ppm)
6.110
f1 (ppm)
6.00
f1 (ppm)
5.719
f1 (ppm)
2.35
0.92
3.32
0.06
1.00
0.04
0.03
0.06
17.78
17.28
40.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)

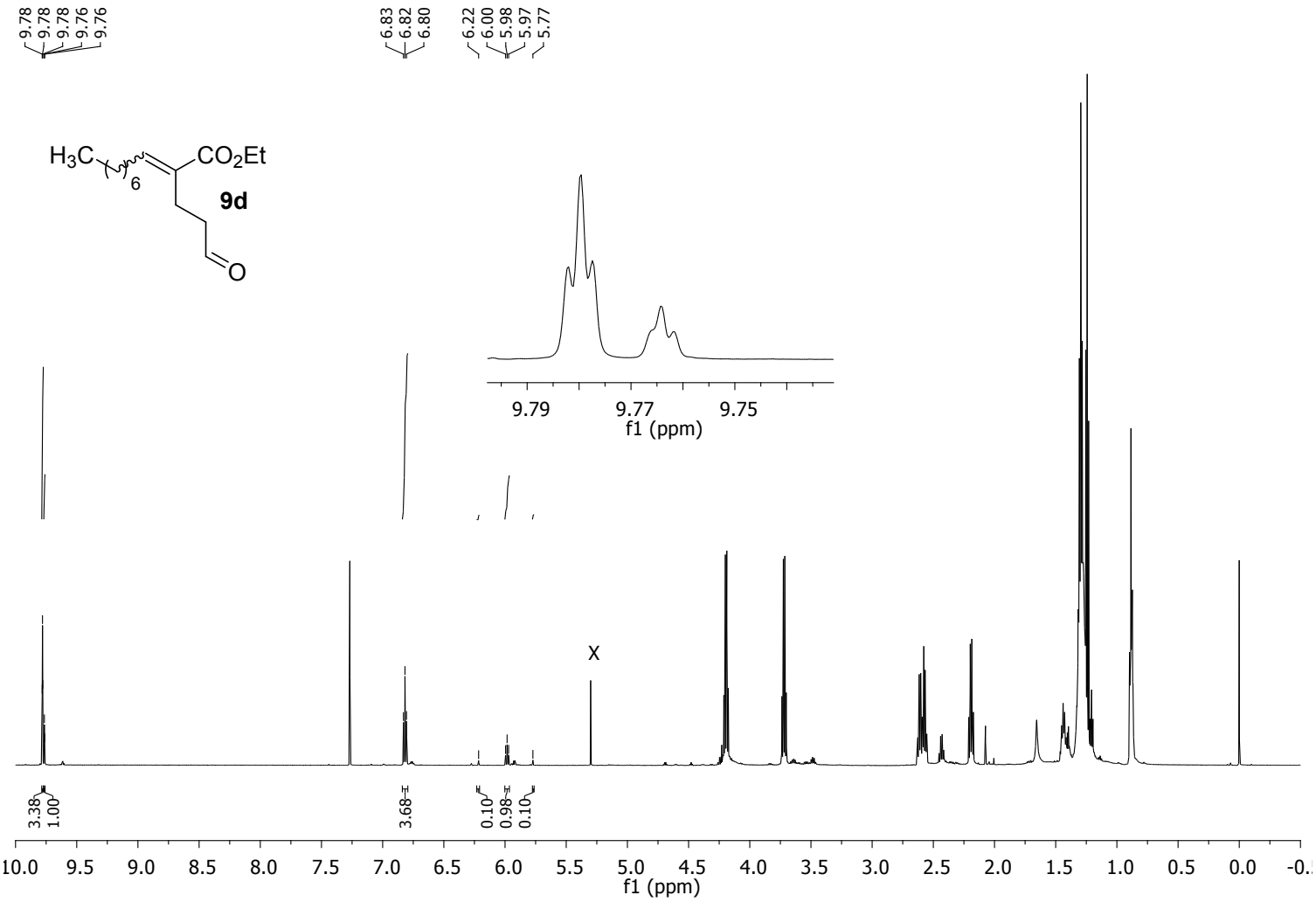

9.77
9.76
6.70
5.86
4.70
4.69
4.68
4.67
4.63
4.62
4.61
4.60
Me
CO2tBu
7b
O
9.78
9.77
9.76
9.75
f1 (ppm)
2.51
0.81
4.37
1.00
0.07
0.31
0.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.78
9.76
6.52
6.50
6.23
6.23
6.22
6.22
6.14
5.64
1.50
1.49
0.00
Me
Me
O
O
tBu
O
7c
9.79
9.77
9.75
f1 (ppm)
3.62
0.79
4.32
1.64
0.15
1.00
0.87
0.87
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)


9.79
9.79
9.79
9.77
9.77
9.77
6.96
6.94
6.91
6.89
6.22
6.16
6.13
6.11
6.09
5.82
H3C
CO2Et
9a
O
9.79
9.77
f1 (ppm)
x
2.93
1.00
3.17
0.22
1.05
0.21
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)

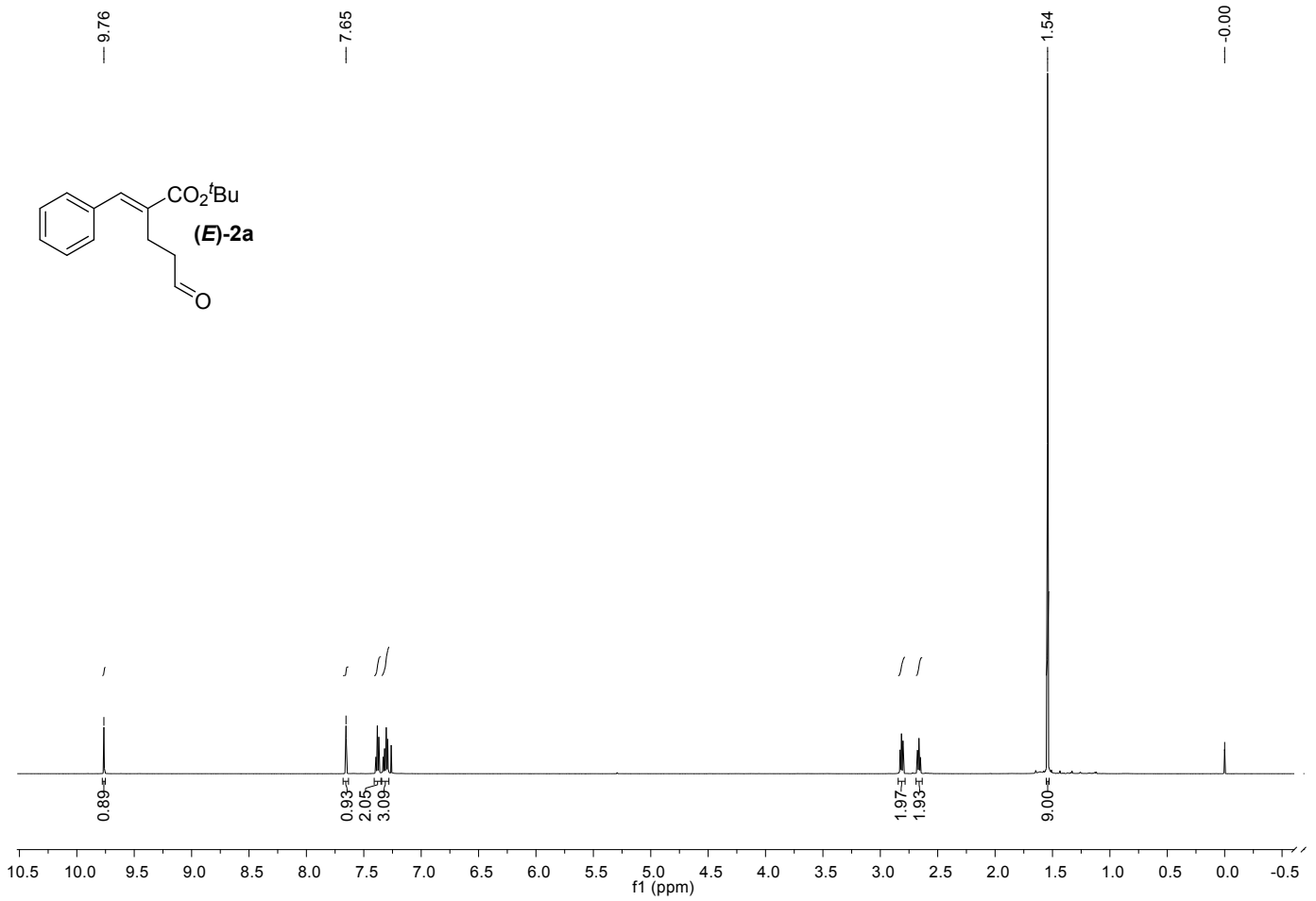

9.79
9.79
9.79
9.78
9.78
9.78
6.83
6.82
6.81
6.25
6.00
5.99
5.97
5.79
4.72
4.71
4.70
4.69
4.64
4.63
4.63
4.62
H3C
CO2Et
9b
O
9.80
9.79
9.78
9.77
f1 (ppm)
X
3.07
1.00
3.63
1.00
0.25
1.95
0.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.75
9.74
9.74
9.73
9.72
9.72
6.59
6.57
6.21
6.21
H3C
CH3
CO2Et
9c
O
9.76
9.74
9.72
f1 (ppm)
5.89
1.00
6.28
2.32
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)

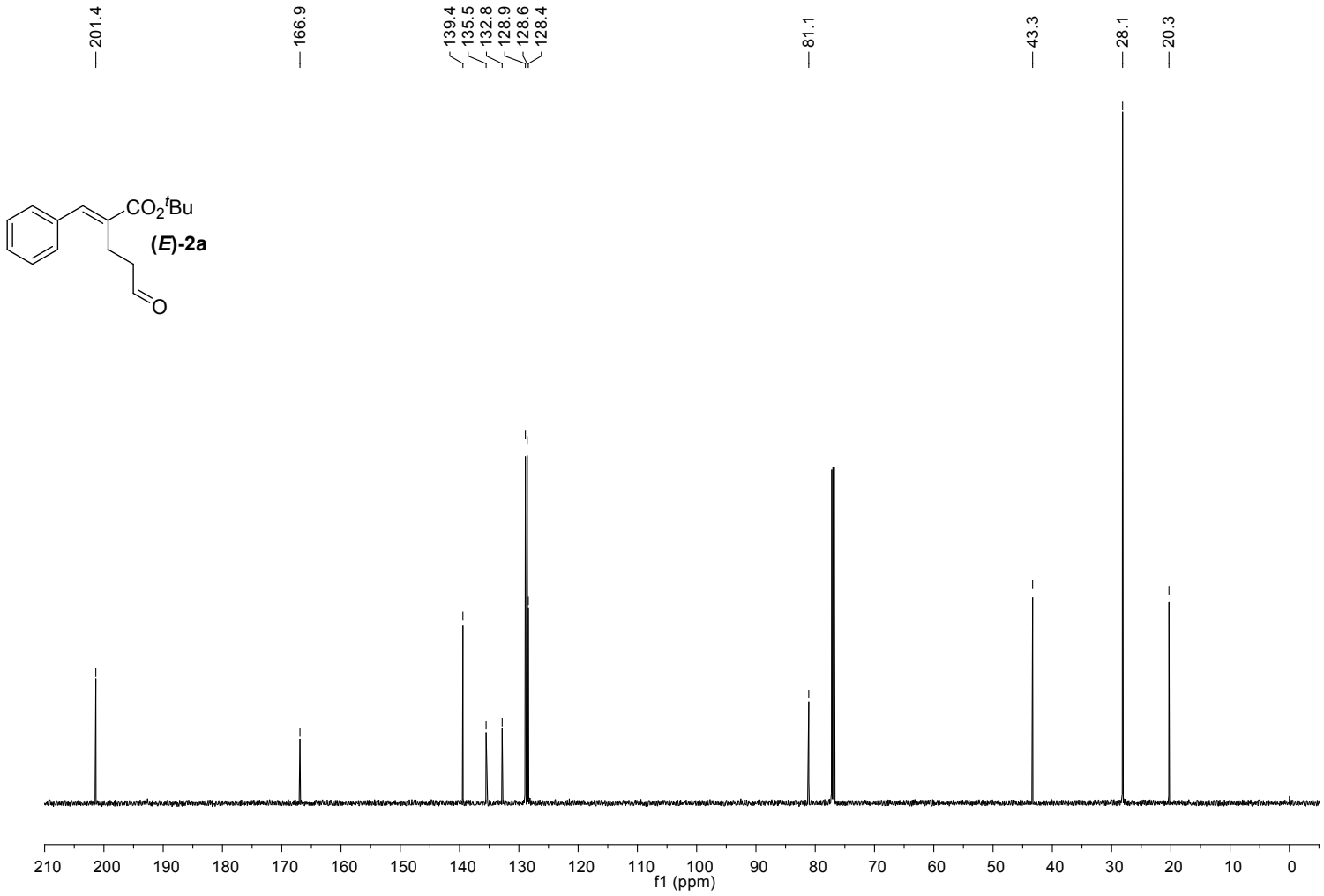

9.78
9.78
9.78
9.76
9.76
6.83
6.82
6.80
6.22
6.00
5.98
5.97
5.77
H3C
6
CO2Et
9d
O
9.79
9.77
9.75
f1 (ppm)
X
3.38
1.00
3.68
0.10
0.98
0.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

6. Copy of Spectra for pure Hurd-Claisen rearrangement products.

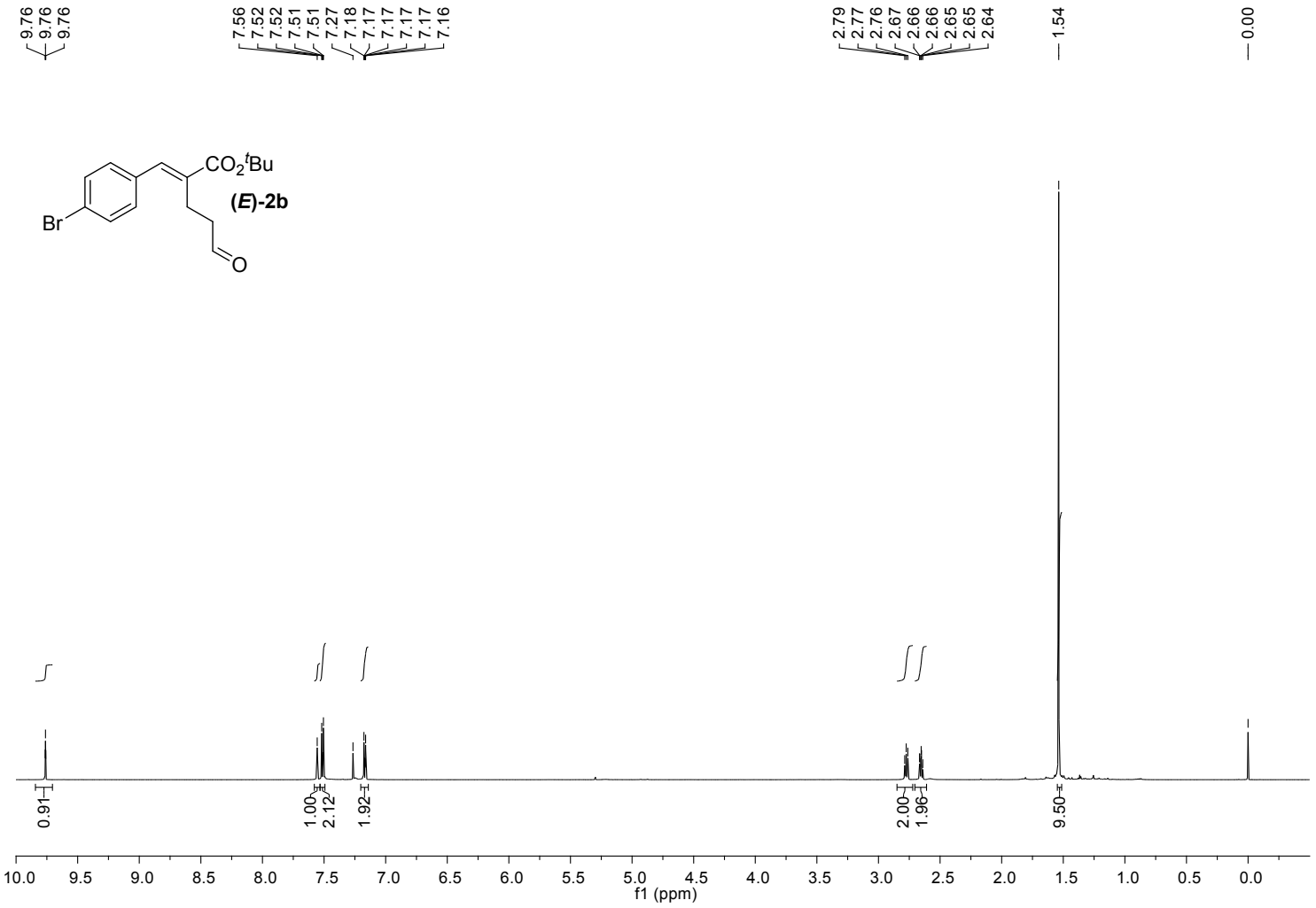
^{1}H NMR Spectra of **(*E*)-2a**



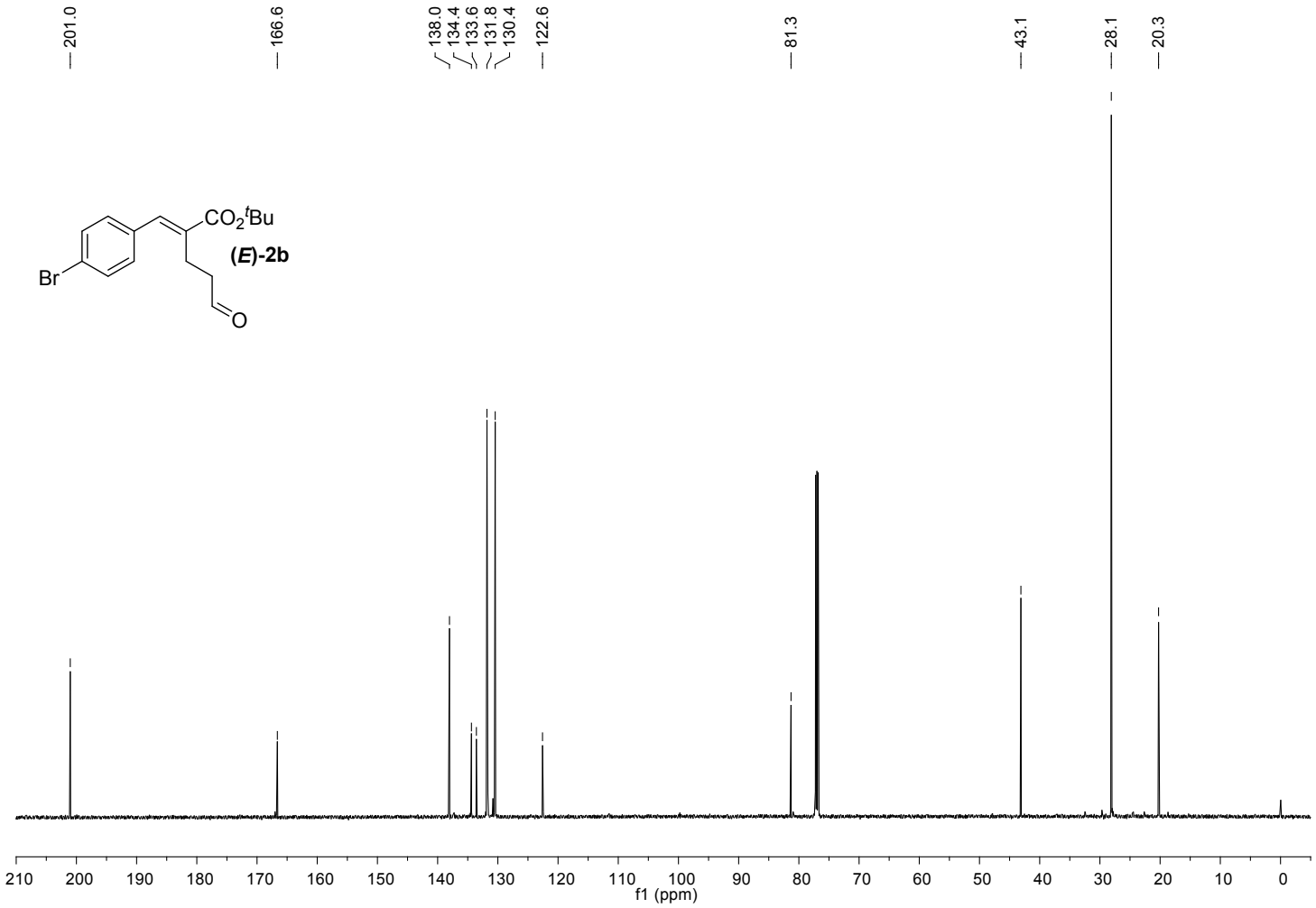
^{13}C NMR Spectra of **(*E*)-2a**



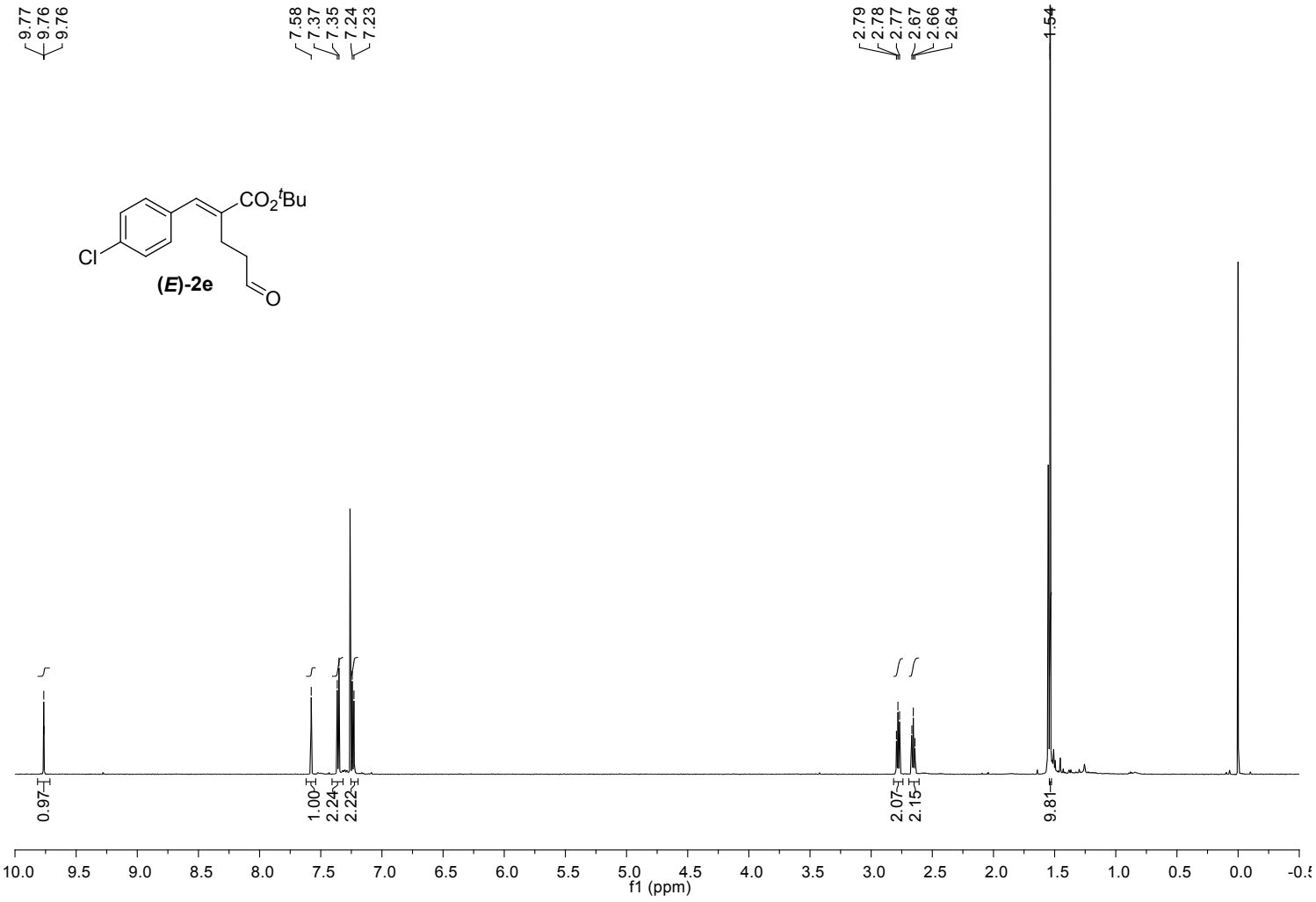
^{1}H NMR Spectra of **(*E*)-2b**



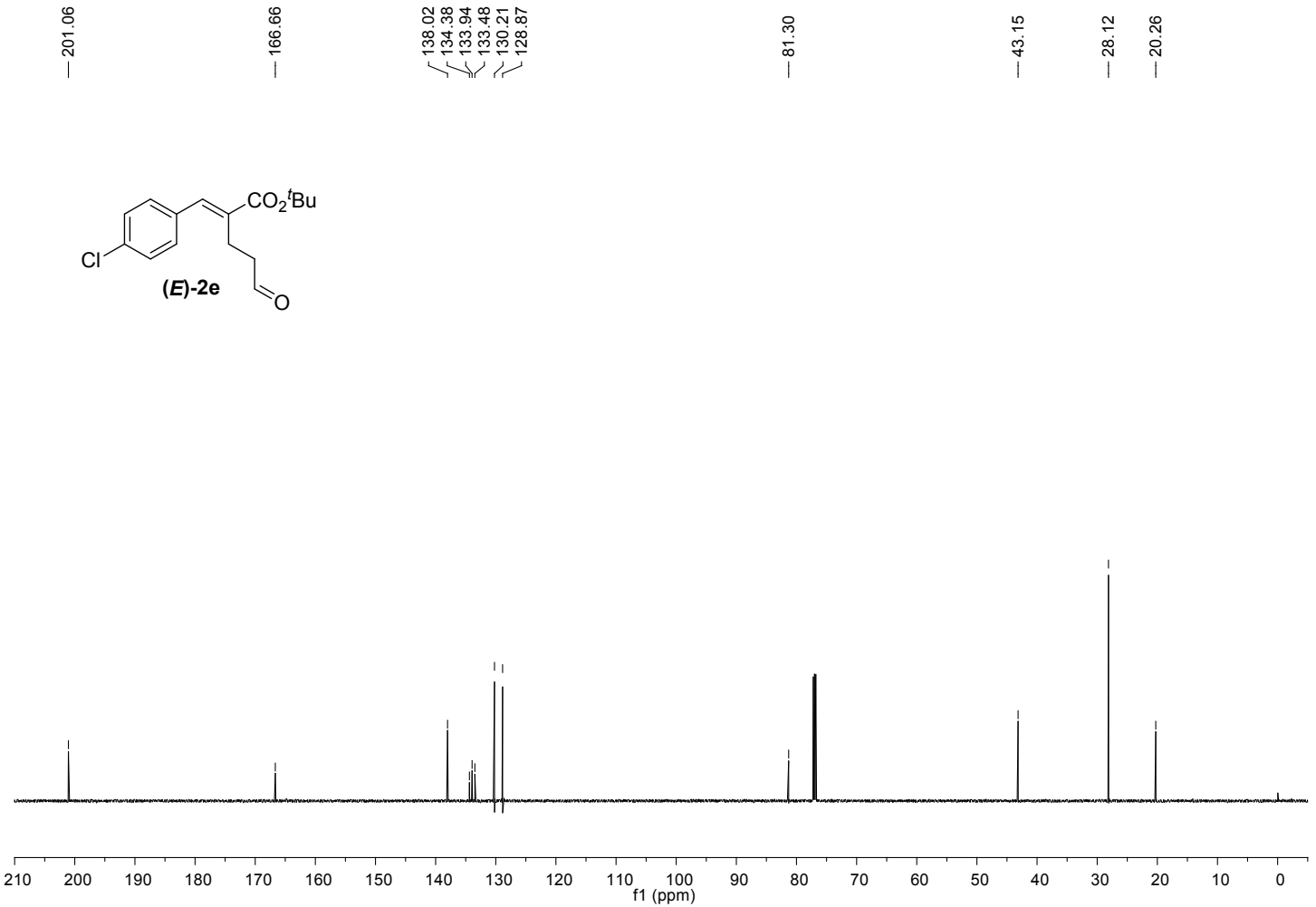
^{13}C NMR Spectra of **(*E*)-2b**



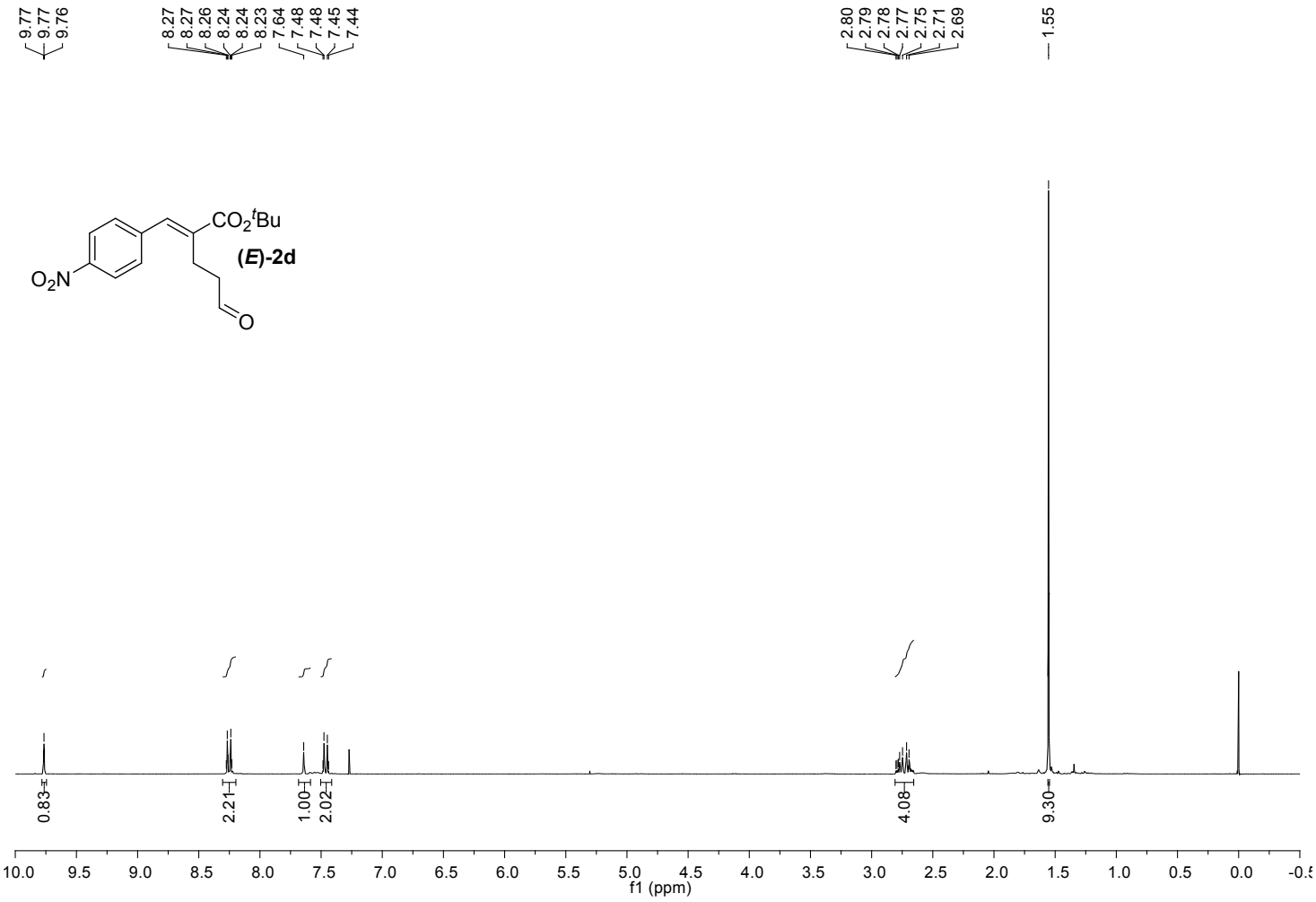
^{1}H NMR Spectra of (*E*)-2c



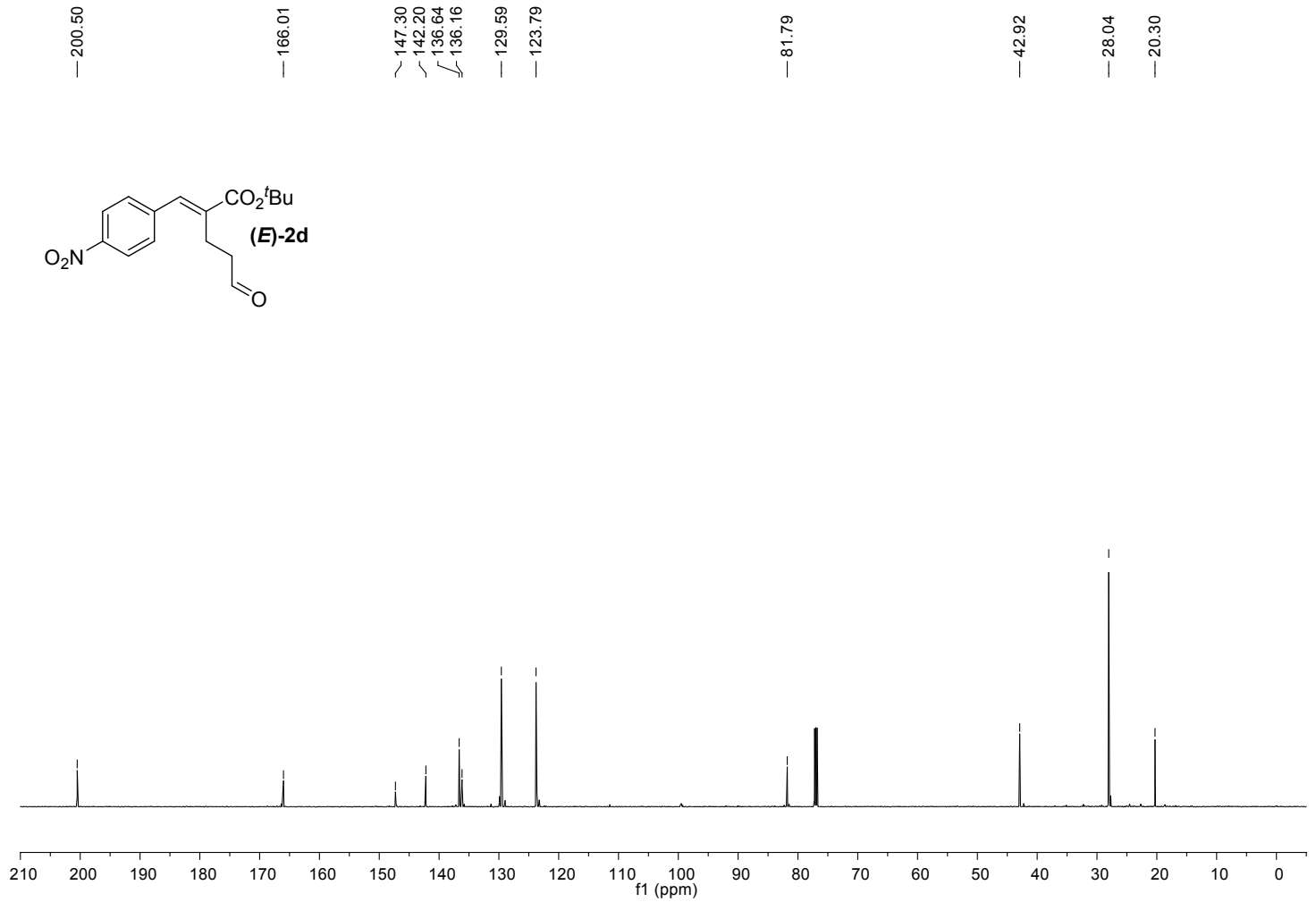
^{13}C NMR Spectra of **(*E*)-2c**



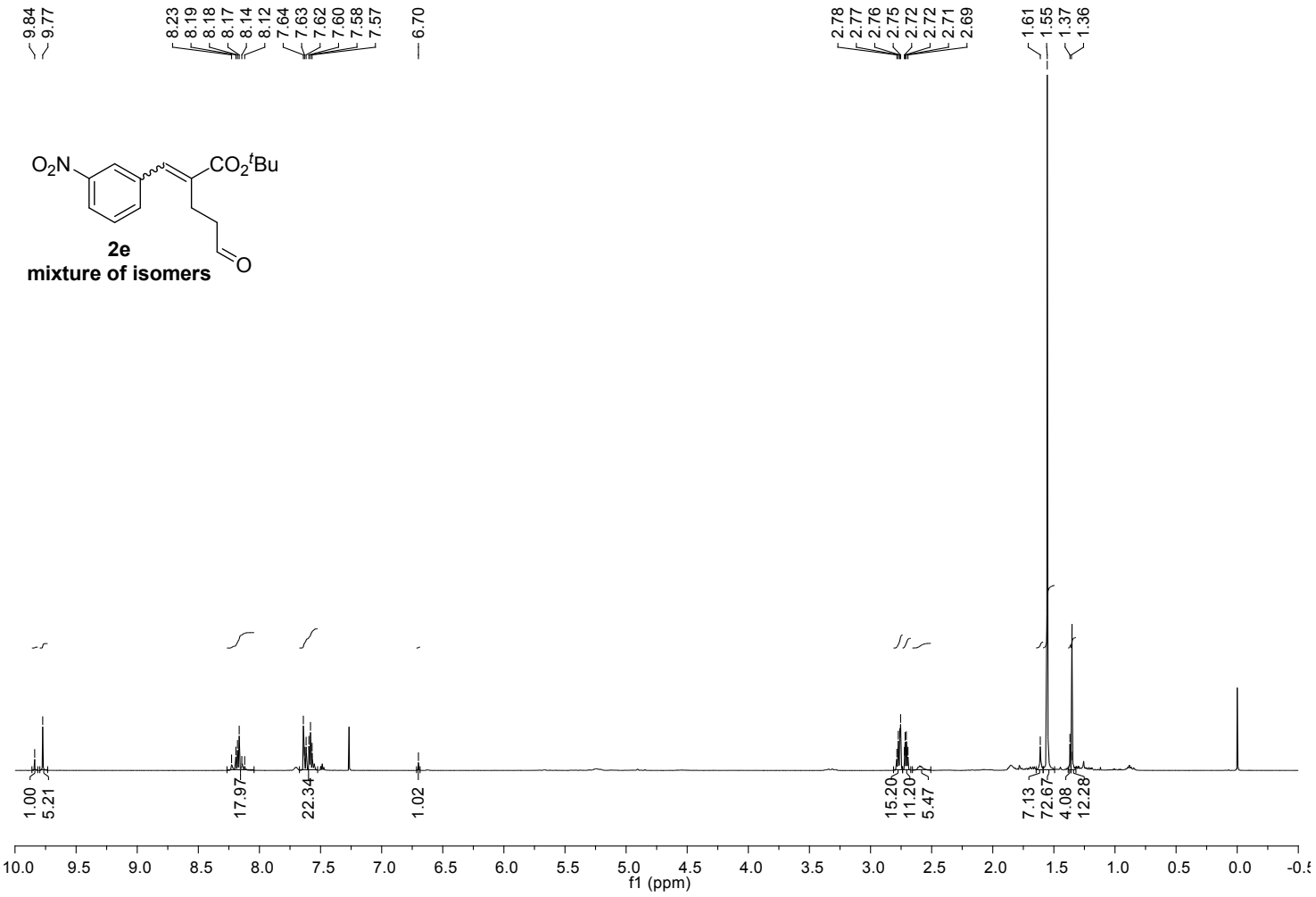
^{1}H NMR Spectra of **(*E*)-2d**



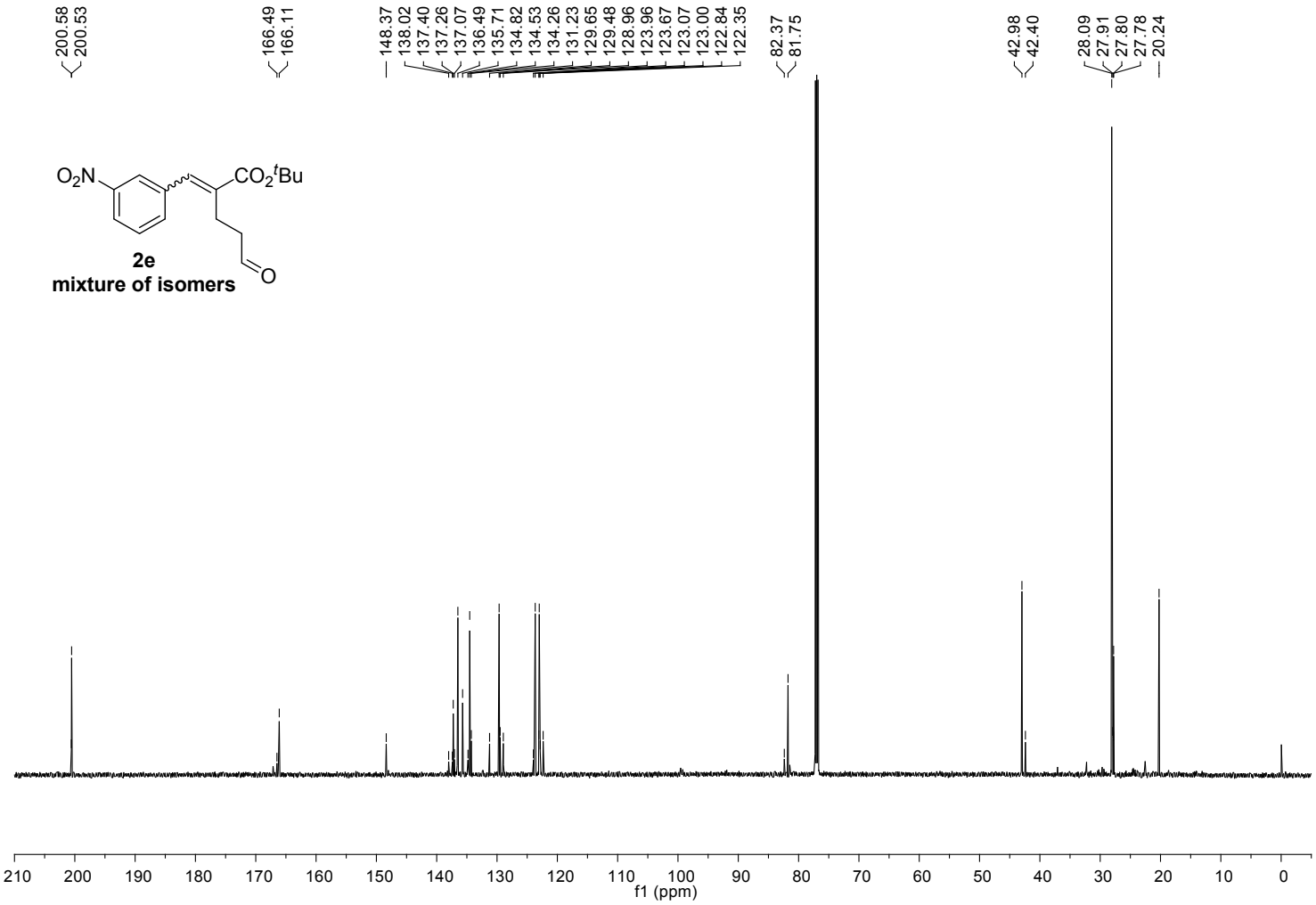
^{13}C NMR Spectra of **(*E*)-2d**



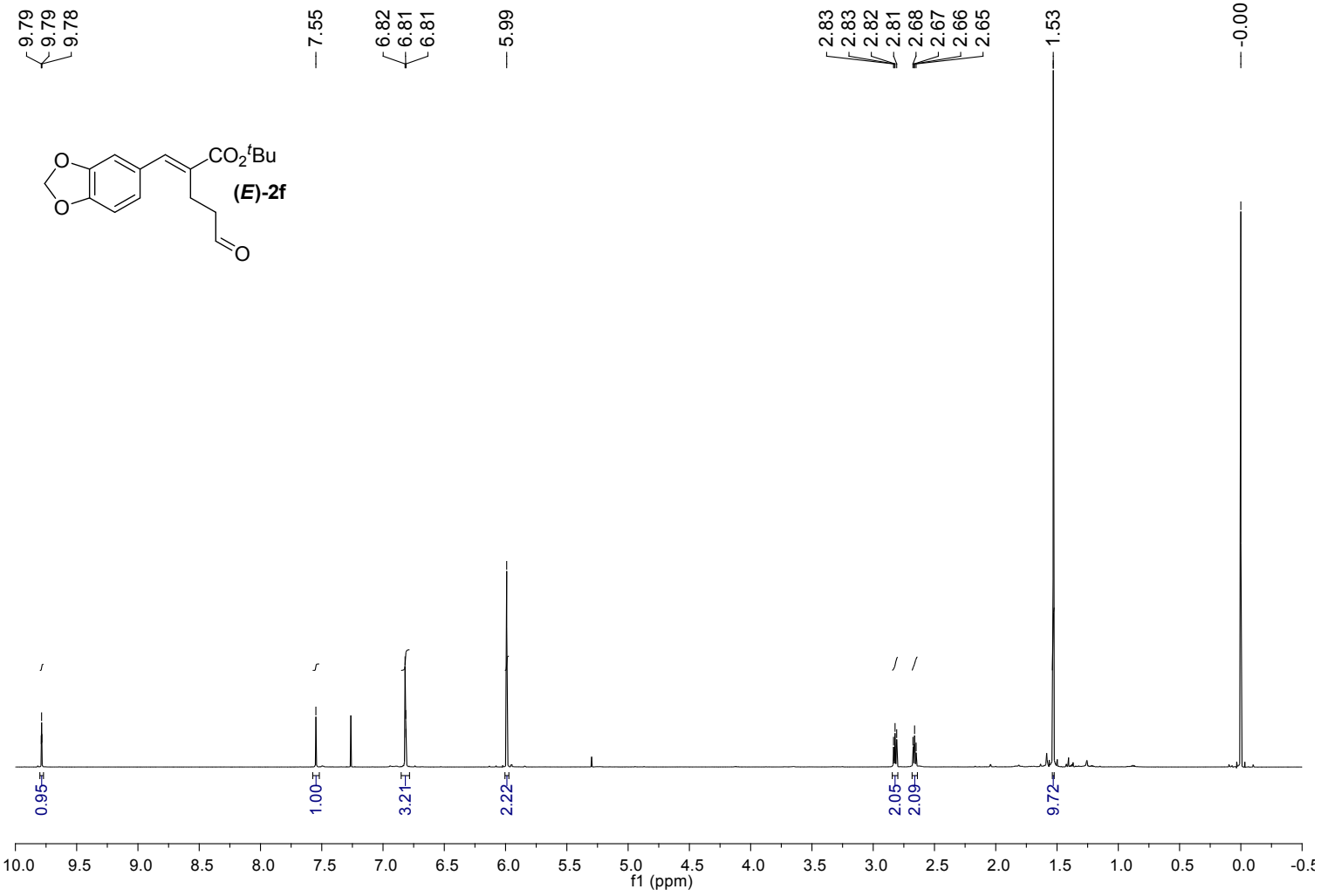
^{1}H NMR Spectra of **(*E*/*Z*)-2e**



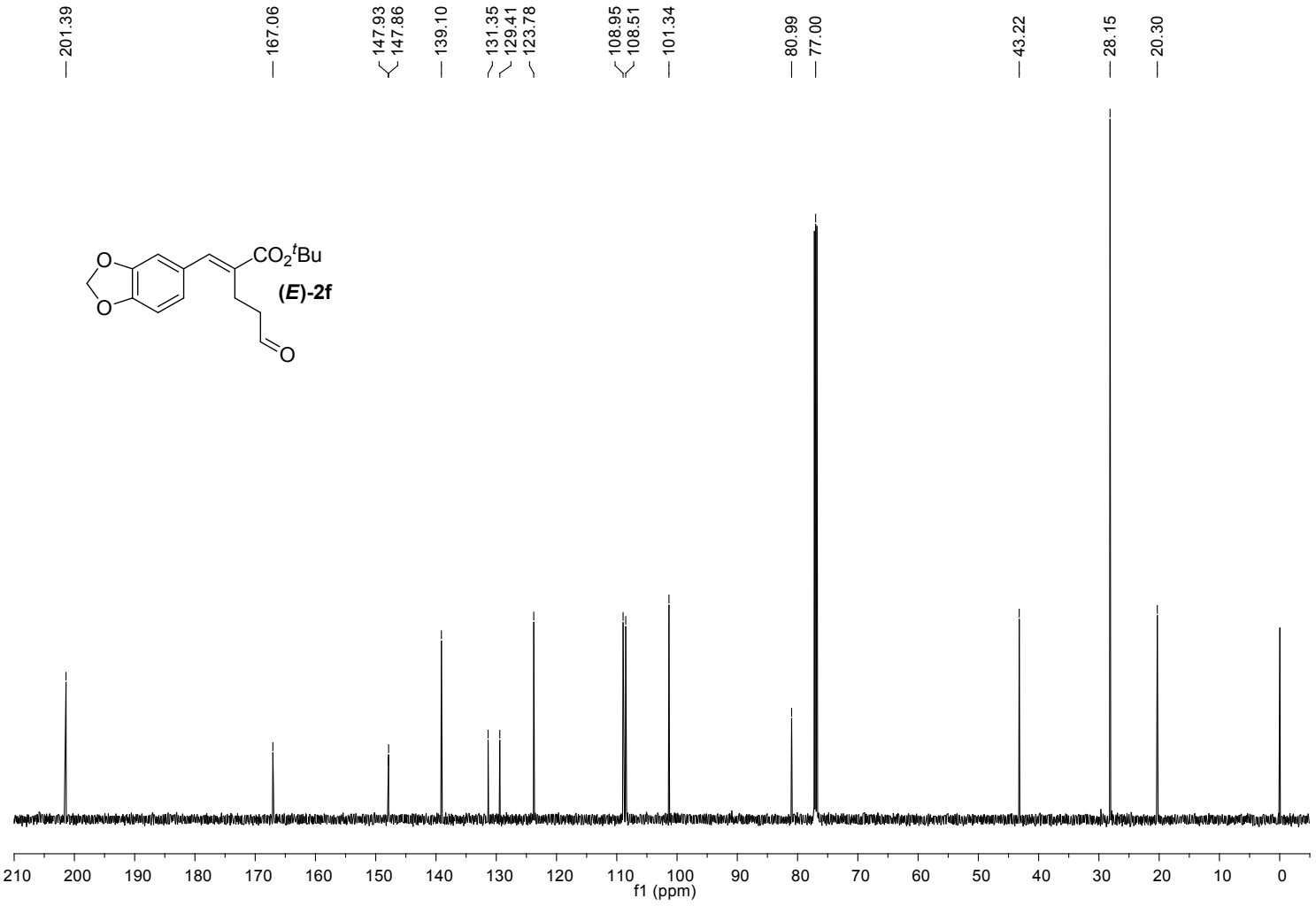
^{13}C NMR Spectra of **(*E*/*Z*)-2e**



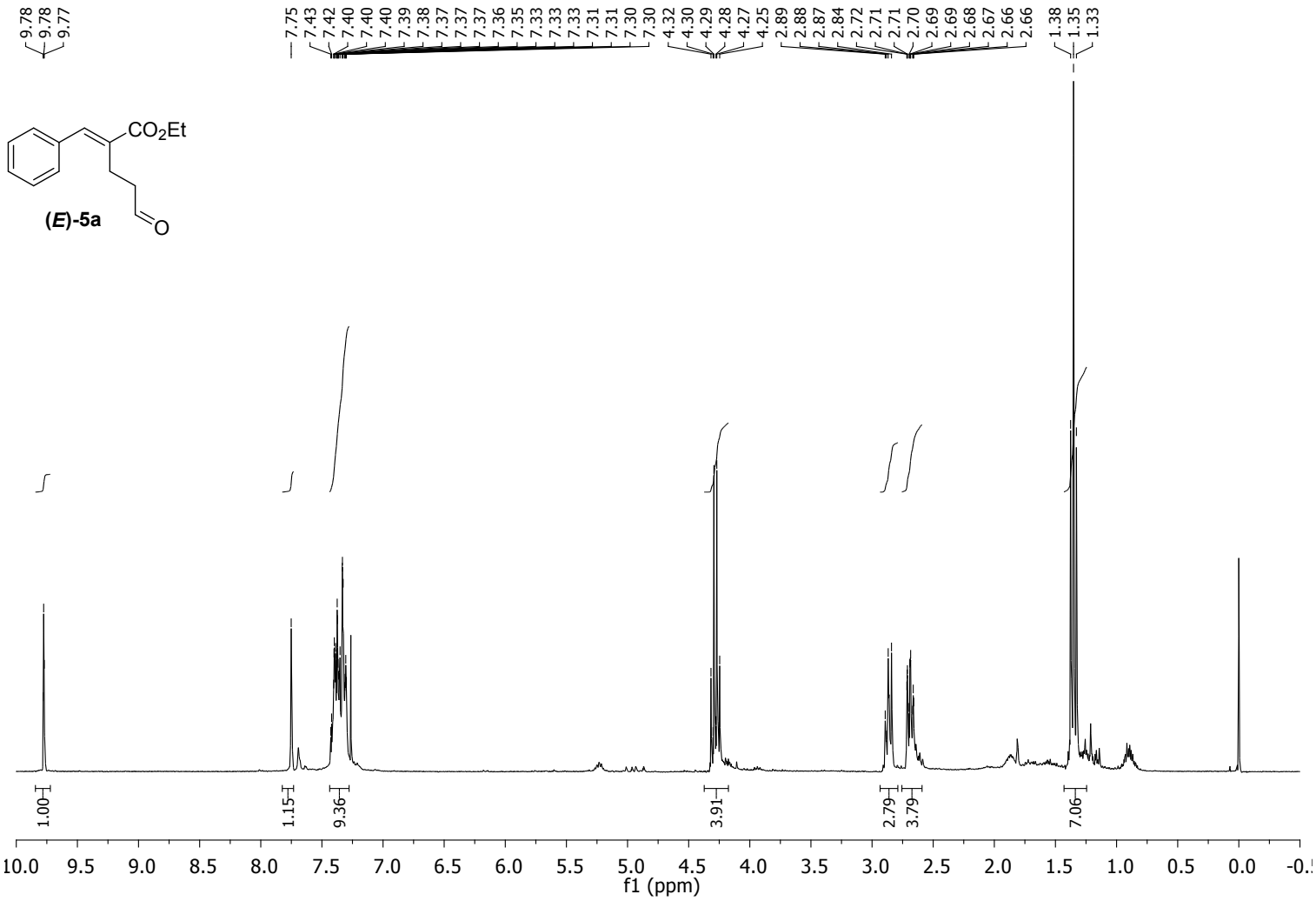
^{1}H NMR Spectra of **(*E*)-2f**



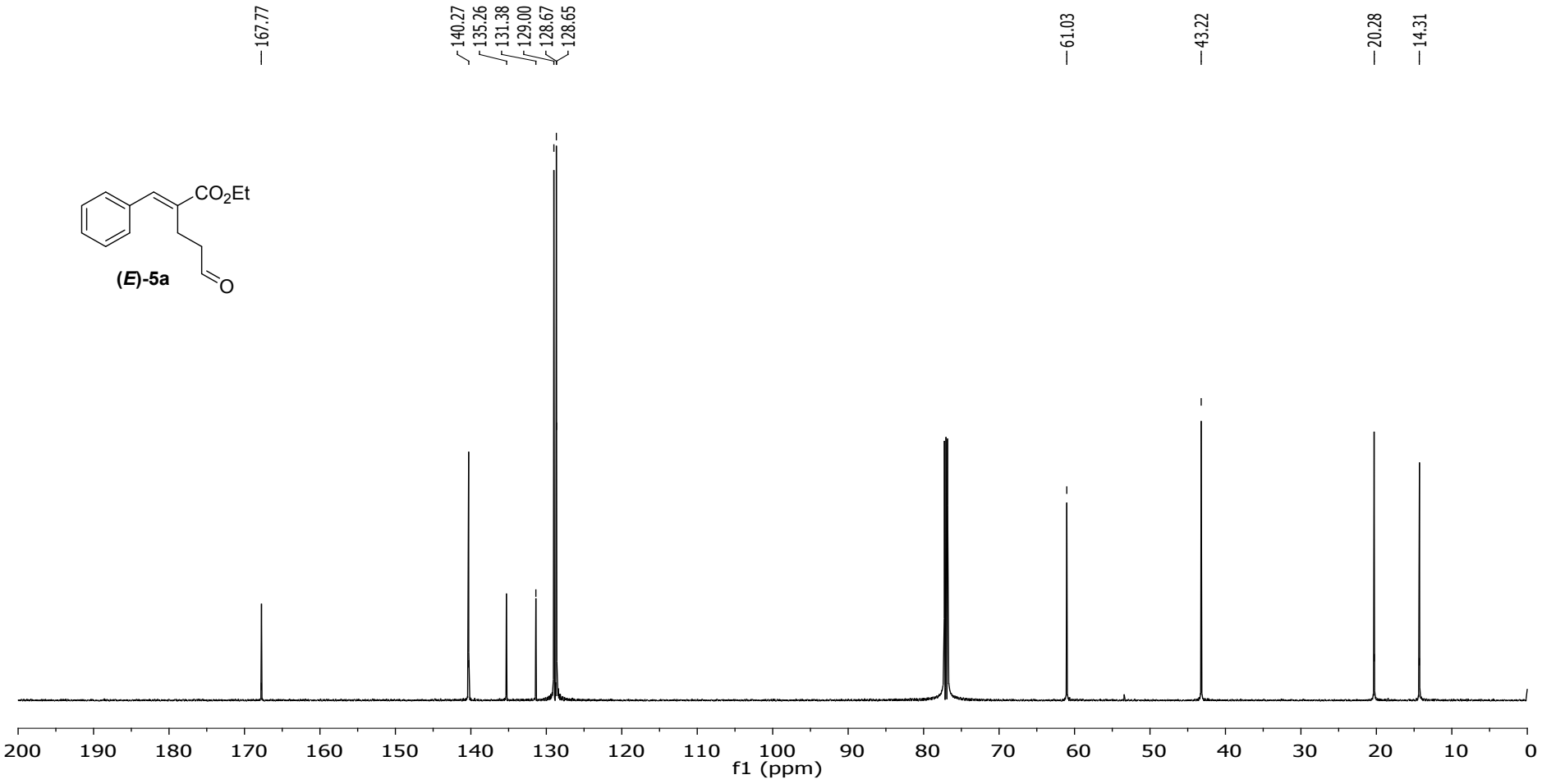
^{13}C NMR Spectra of **(*E*)-2f**



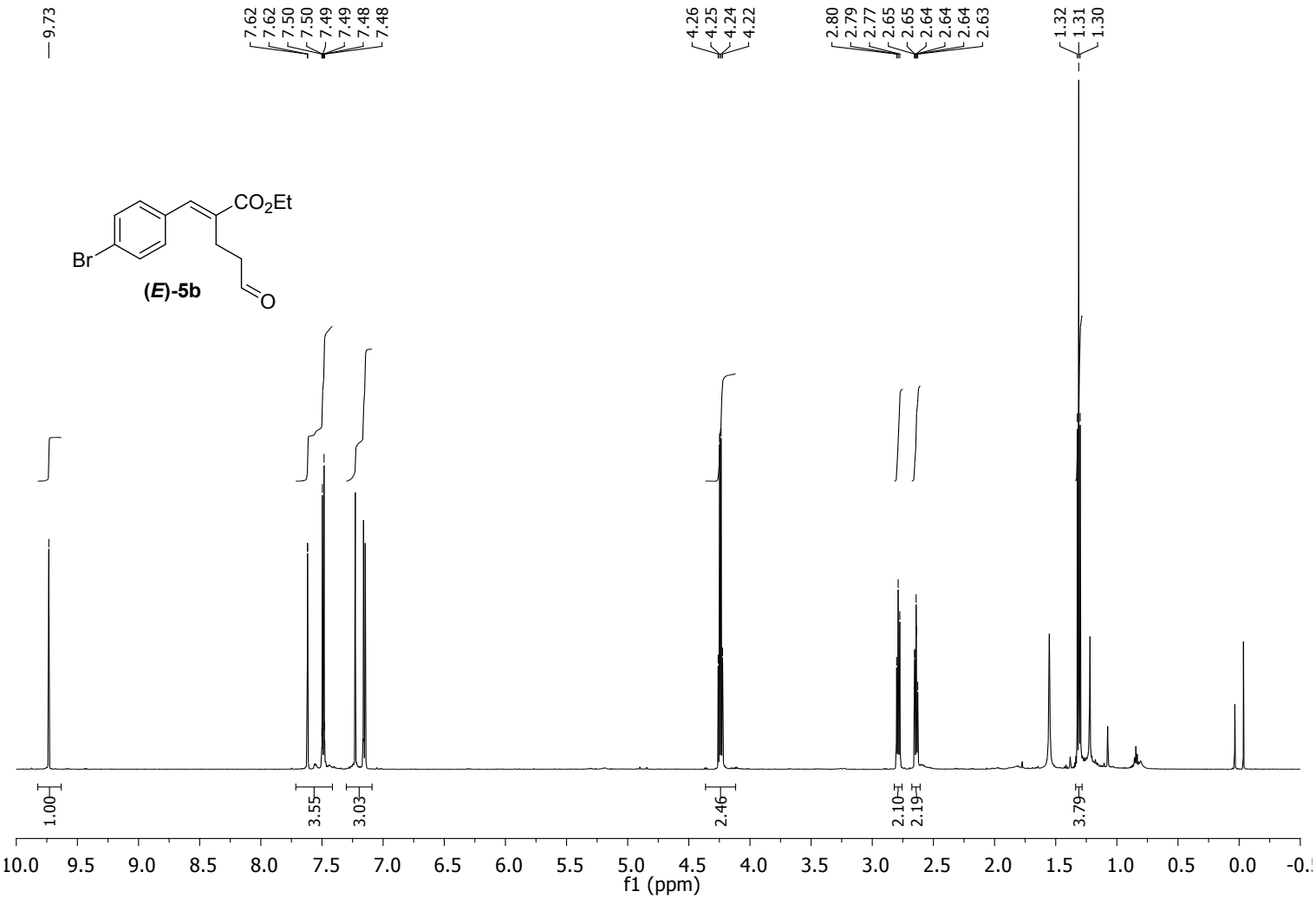
^{1}H NMR Spectra of **(*E*)-5a**



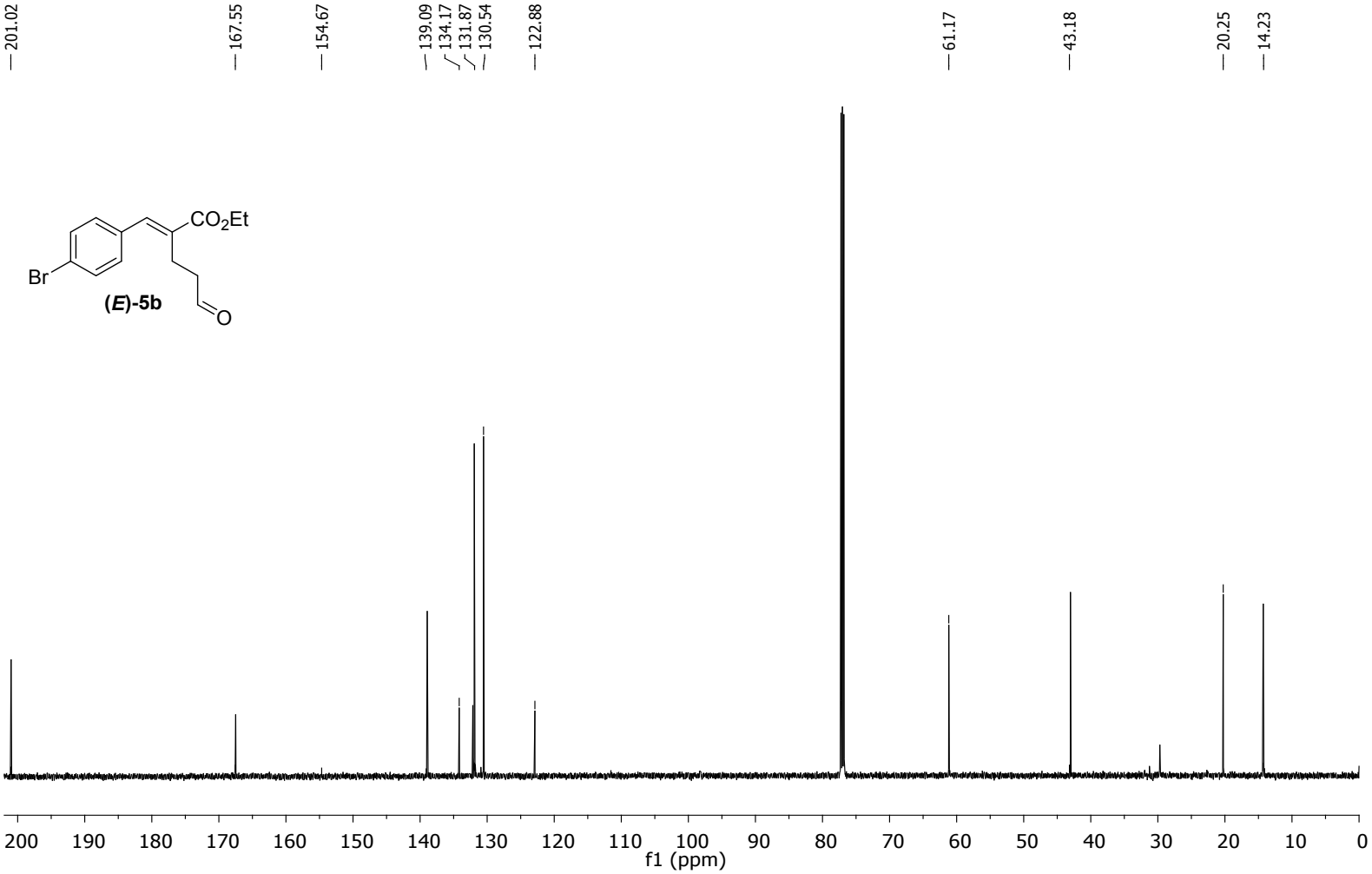
^{13}C NMR Spectra of **(*E*)-5a**



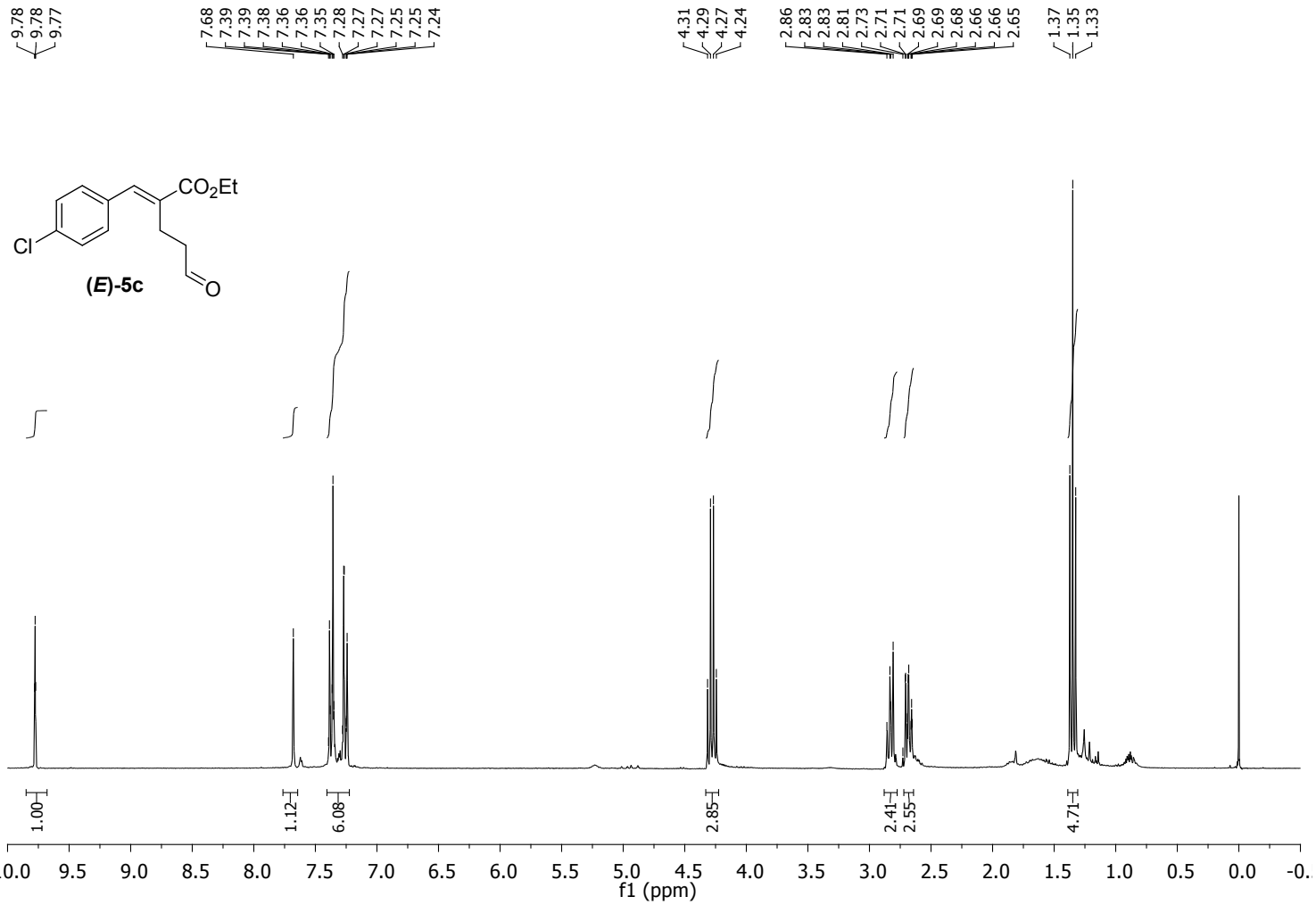
^{1}H NMR Spectra of **(*E*)-5b**



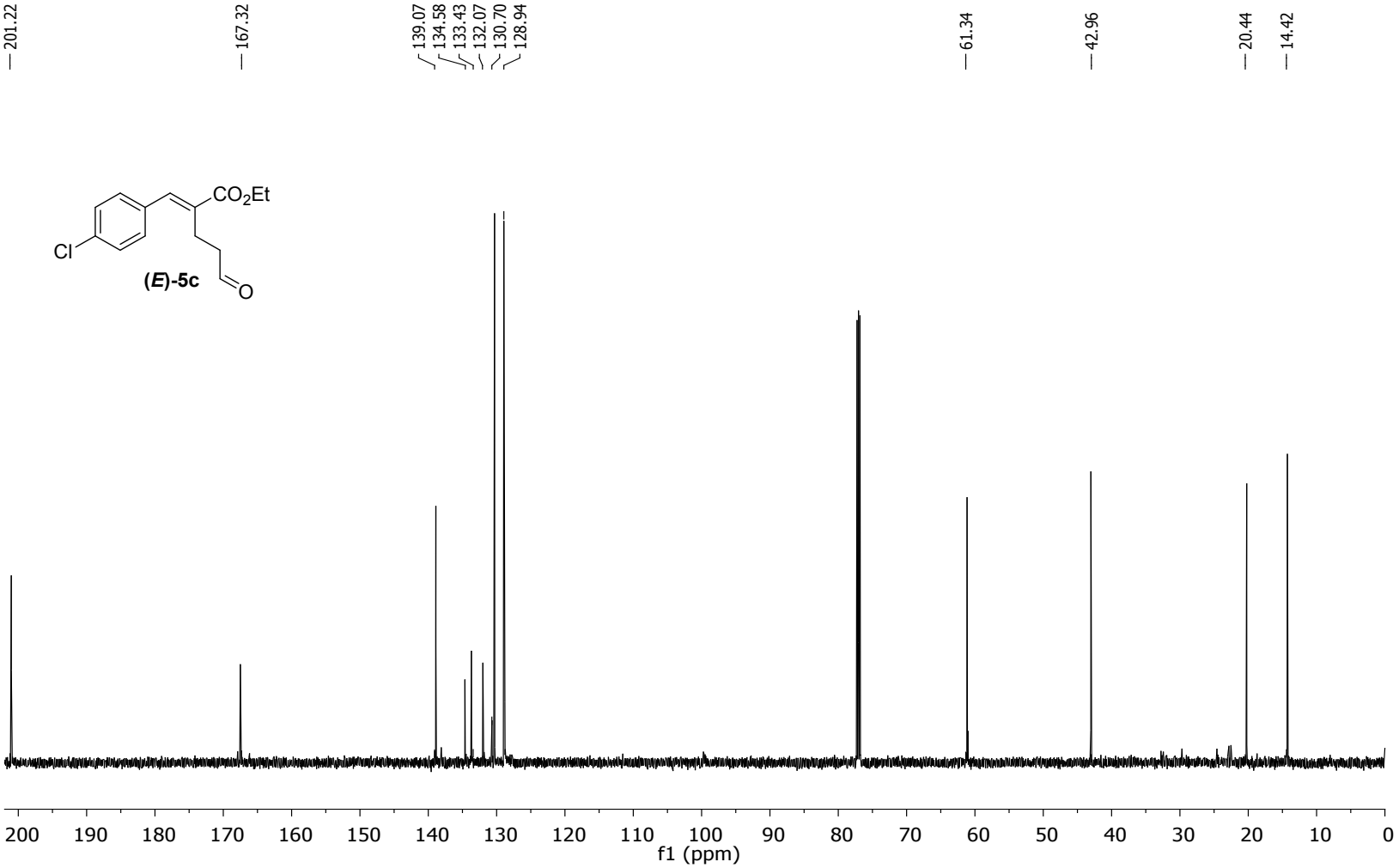
^{13}C NMR Spectra of **(*E*)-5b**



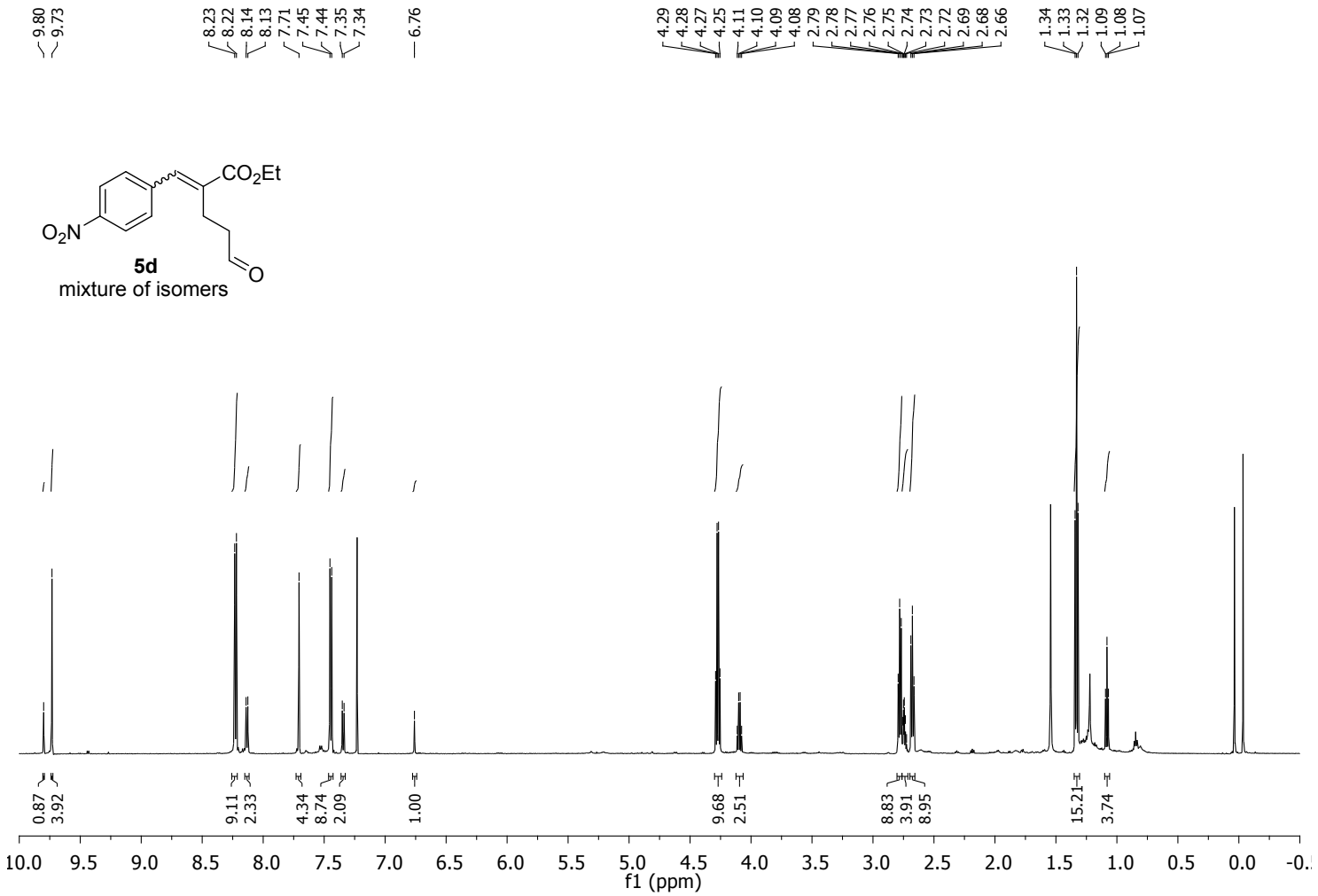
^{1}H NMR Spectra of **(*E*)-5c**



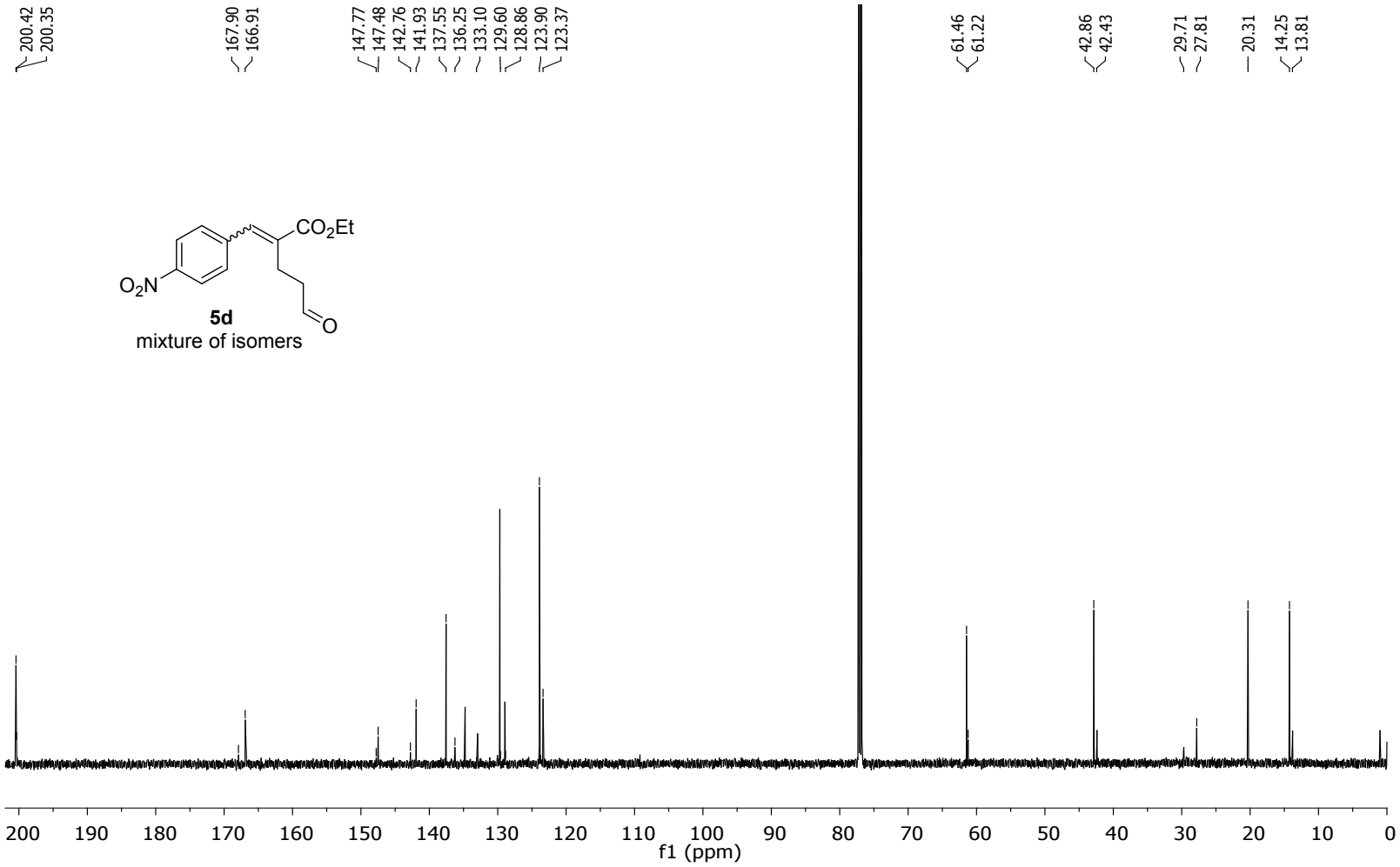
^{13}C NMR Spectra of **(*E*)-5c**



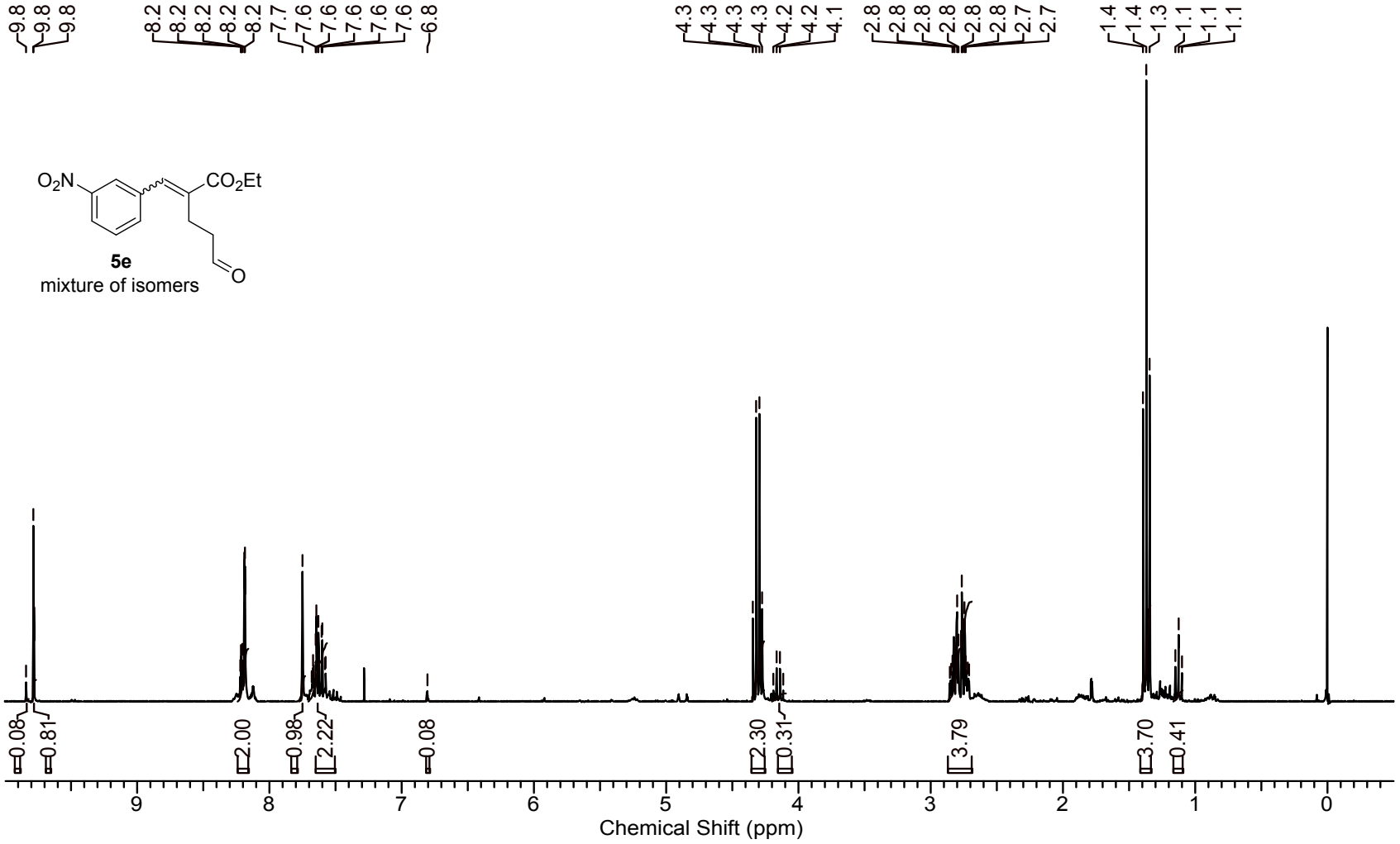
^{1}H NMR Spectra of **(*E*/*Z*)-5d**



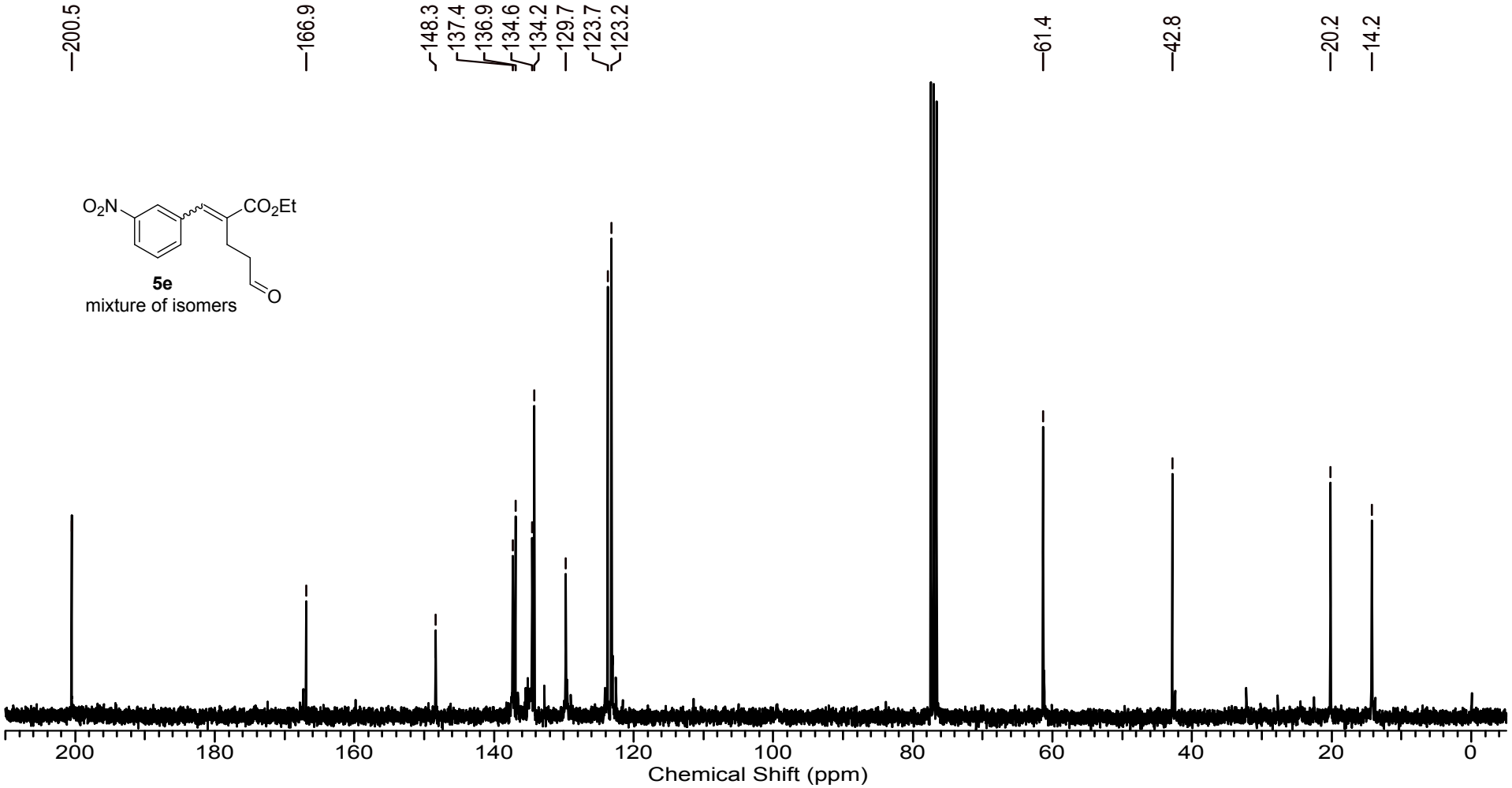
^{13}C NMR Spectra of **(*E*/*Z*)-5d**



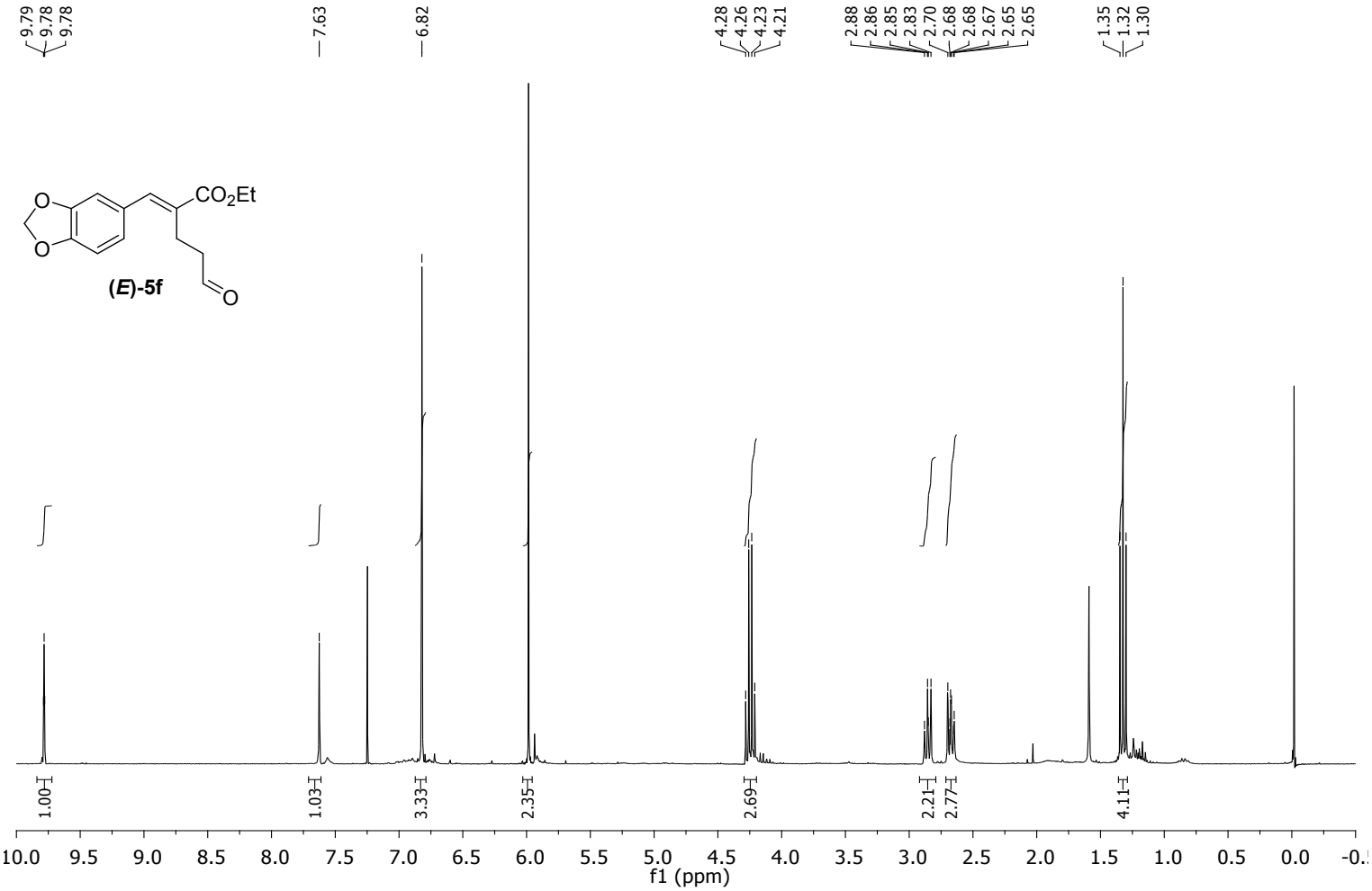
^{1}H NMR Spectra of **(*E*/*Z*)-5e**



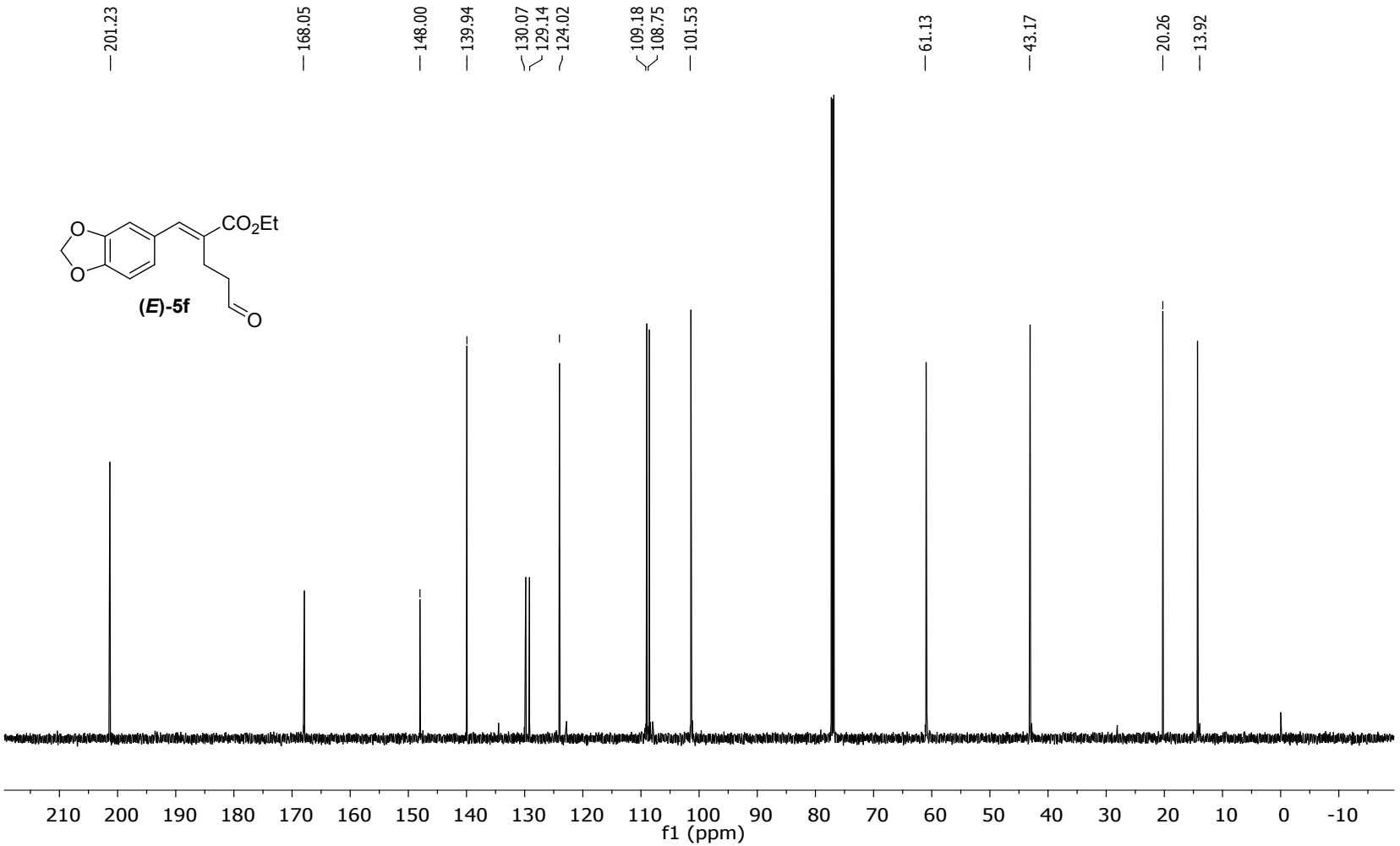
^{13}C NMR Spectra of **(*E*/*Z*)-5e**



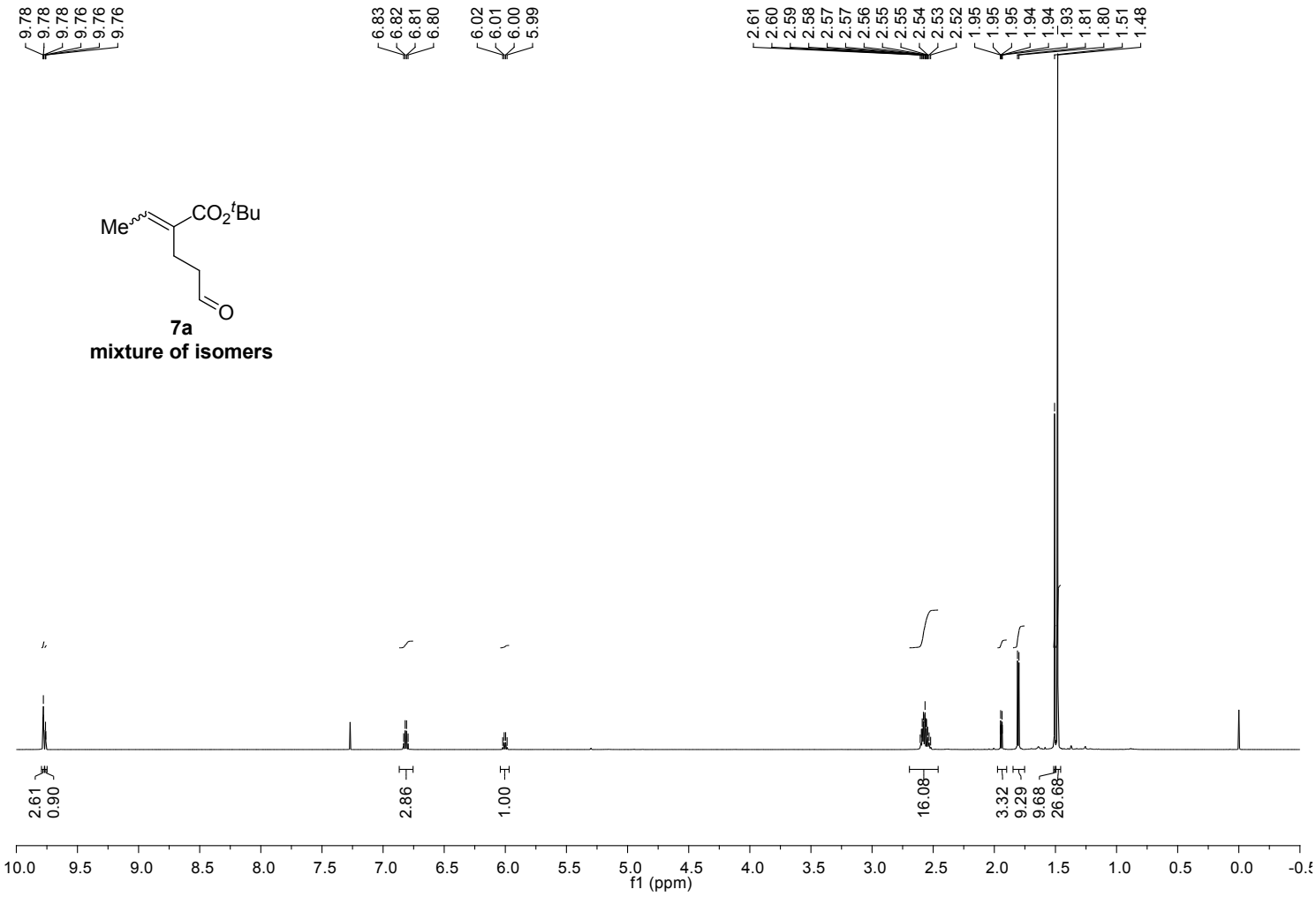
^{1}H NMR Spectra of **(*E*)-5f**



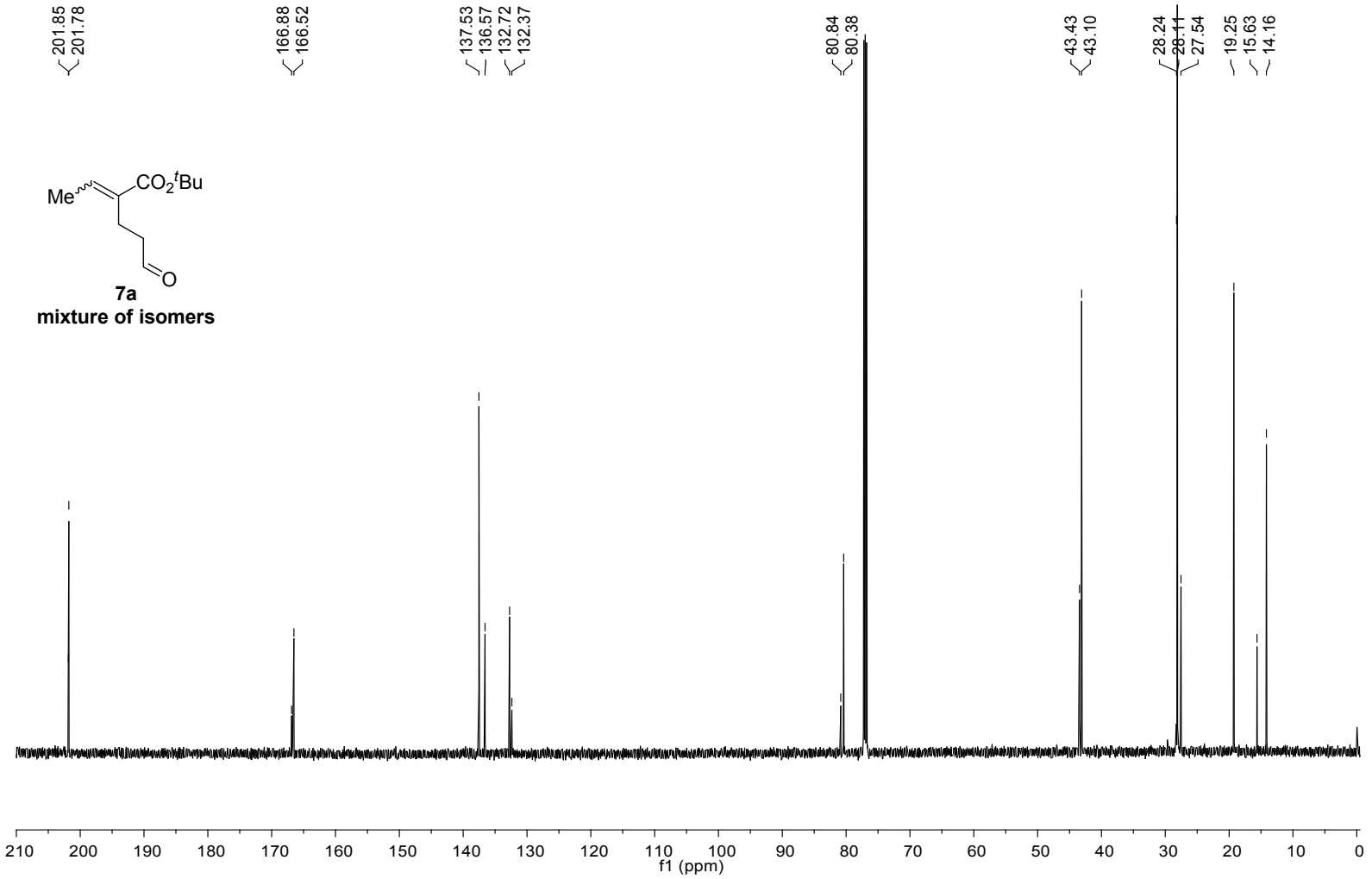
^{13}C NMR Spectra of **(*E*)-5f**



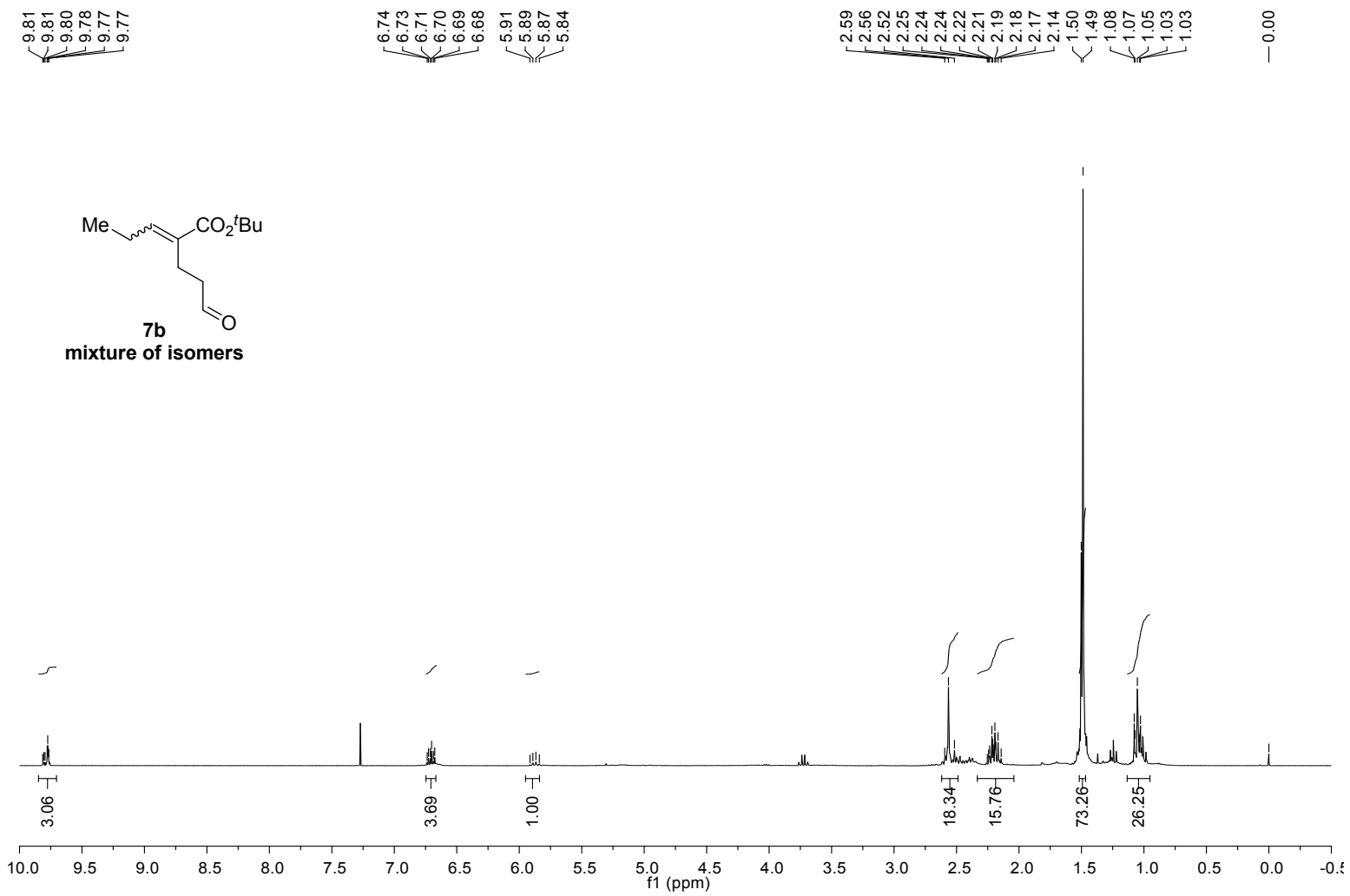
^{1}H NMR Spectra of **(*E*/*Z*)-7a**



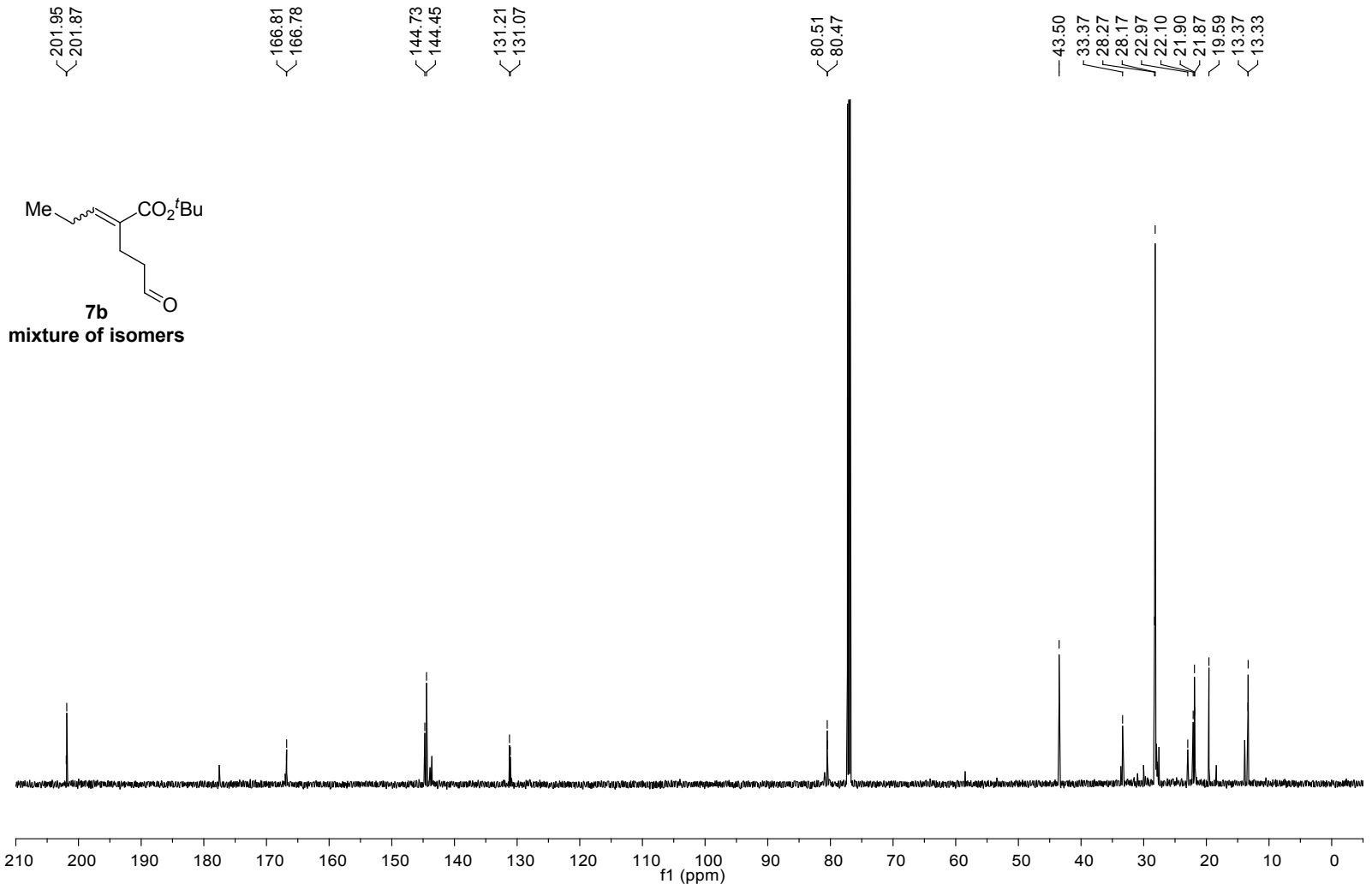
^{13}C NMR Spectra of **(*E*/*Z*)-7a**



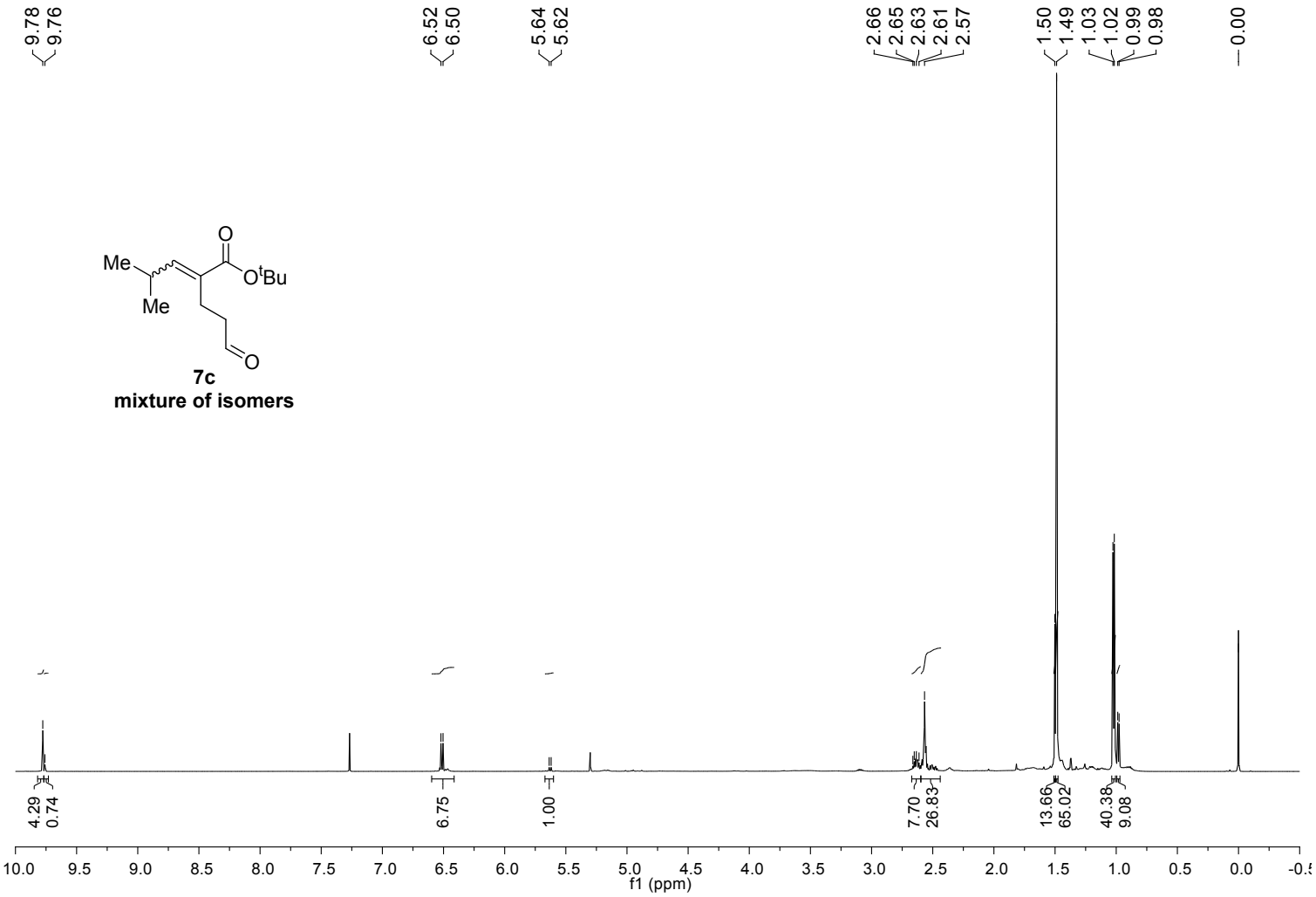
^{1}H NMR Spectra of **(*E*/*Z*)-7b**



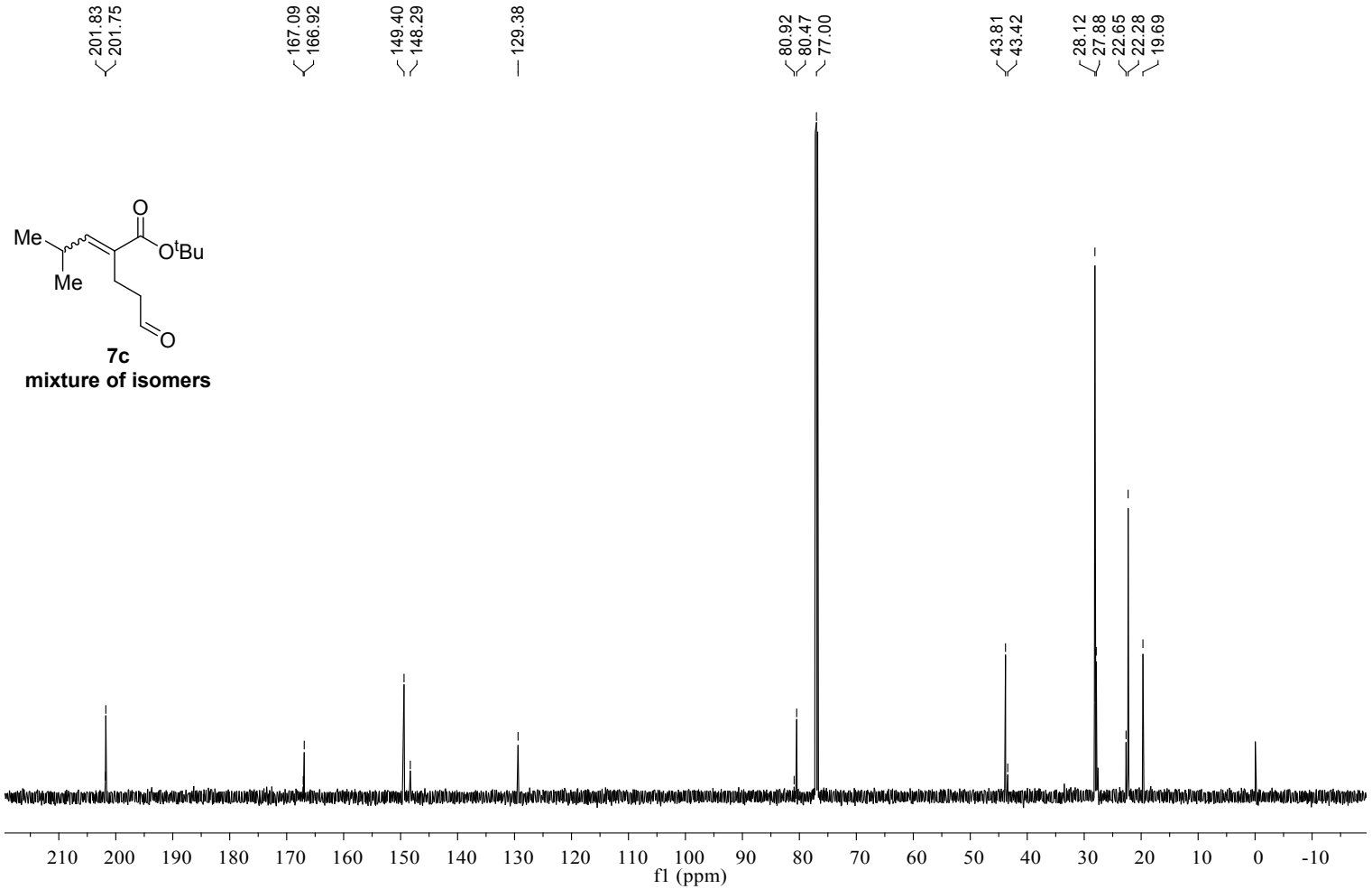
^{13}C NMR Spectra of **(*E*/*Z*)-7b**



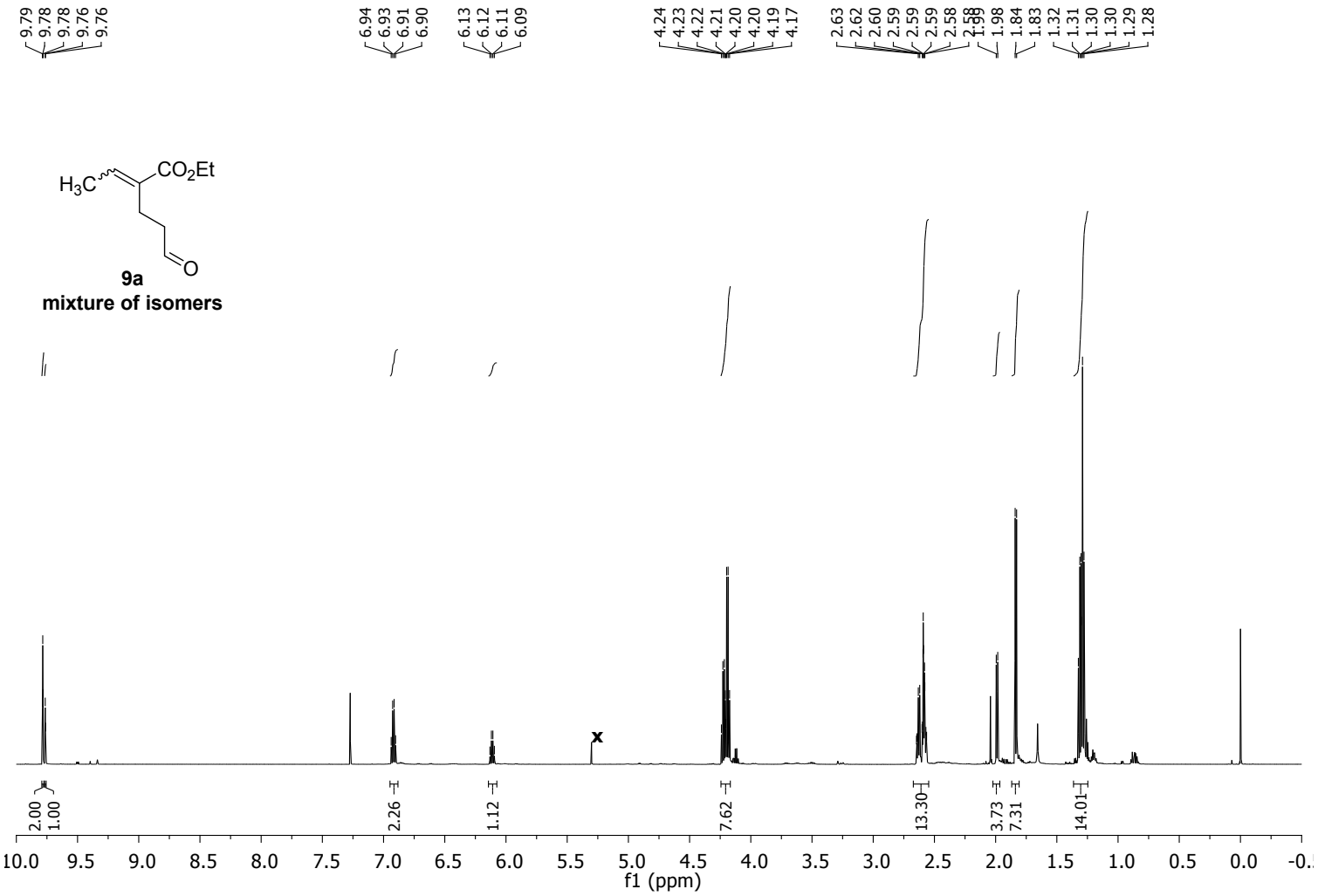
^{1}H NMR Spectra of **(*E*/*Z*)-7c**



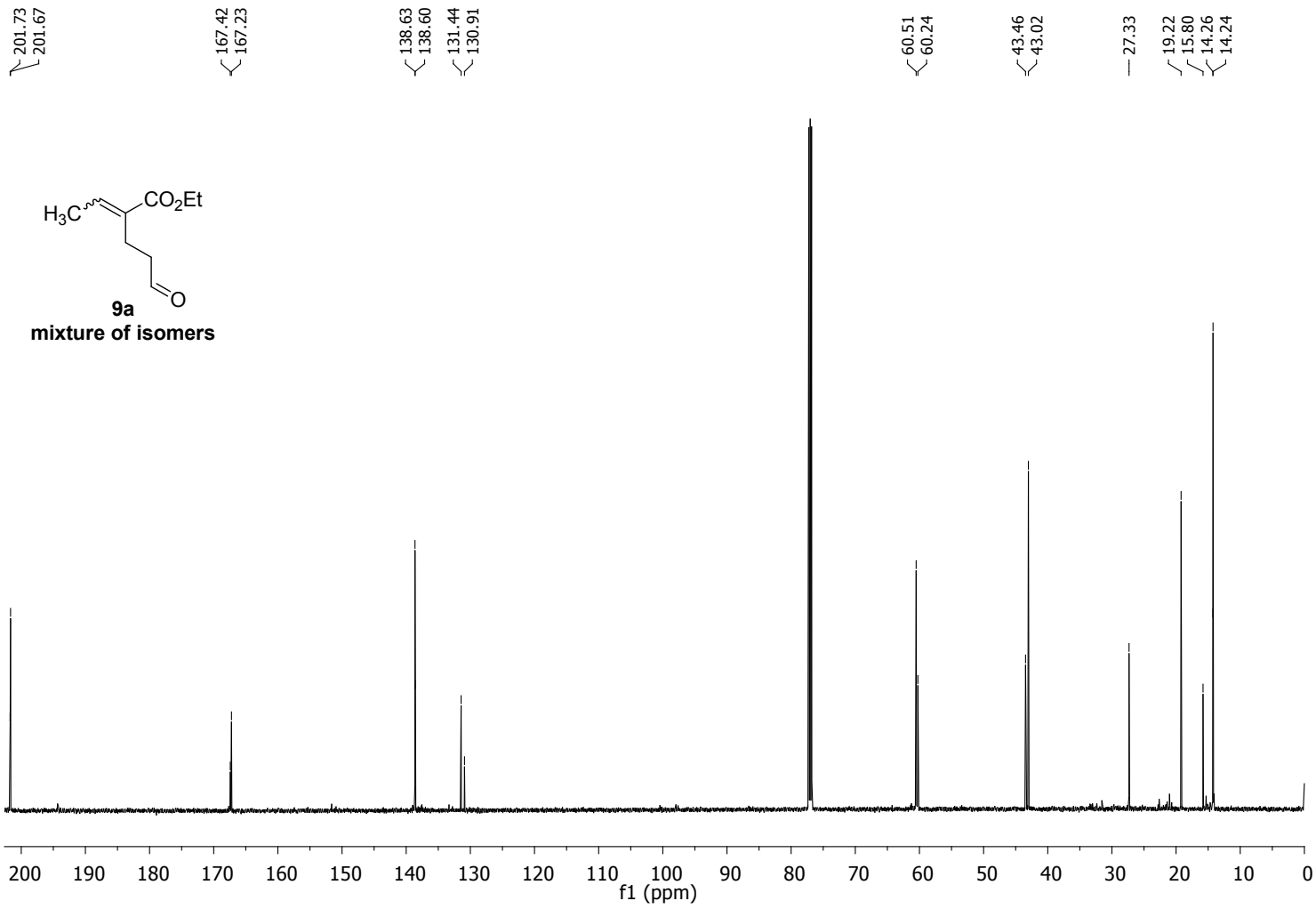
^{13}C NMR Spectra of **(*E*/*Z*)-7c**



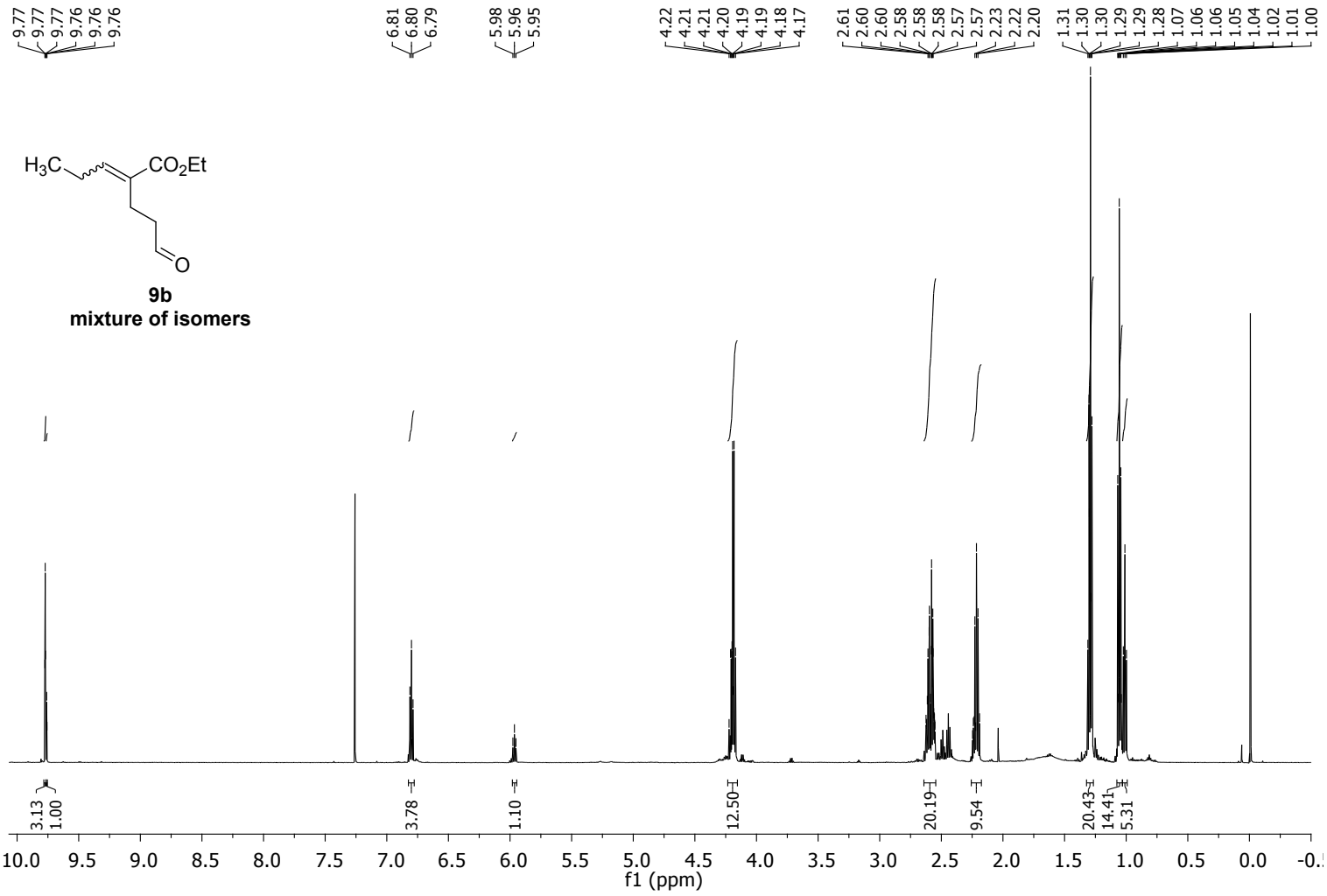
^{1}H NMR Spectra of**(*E*/*Z*)- 9a**



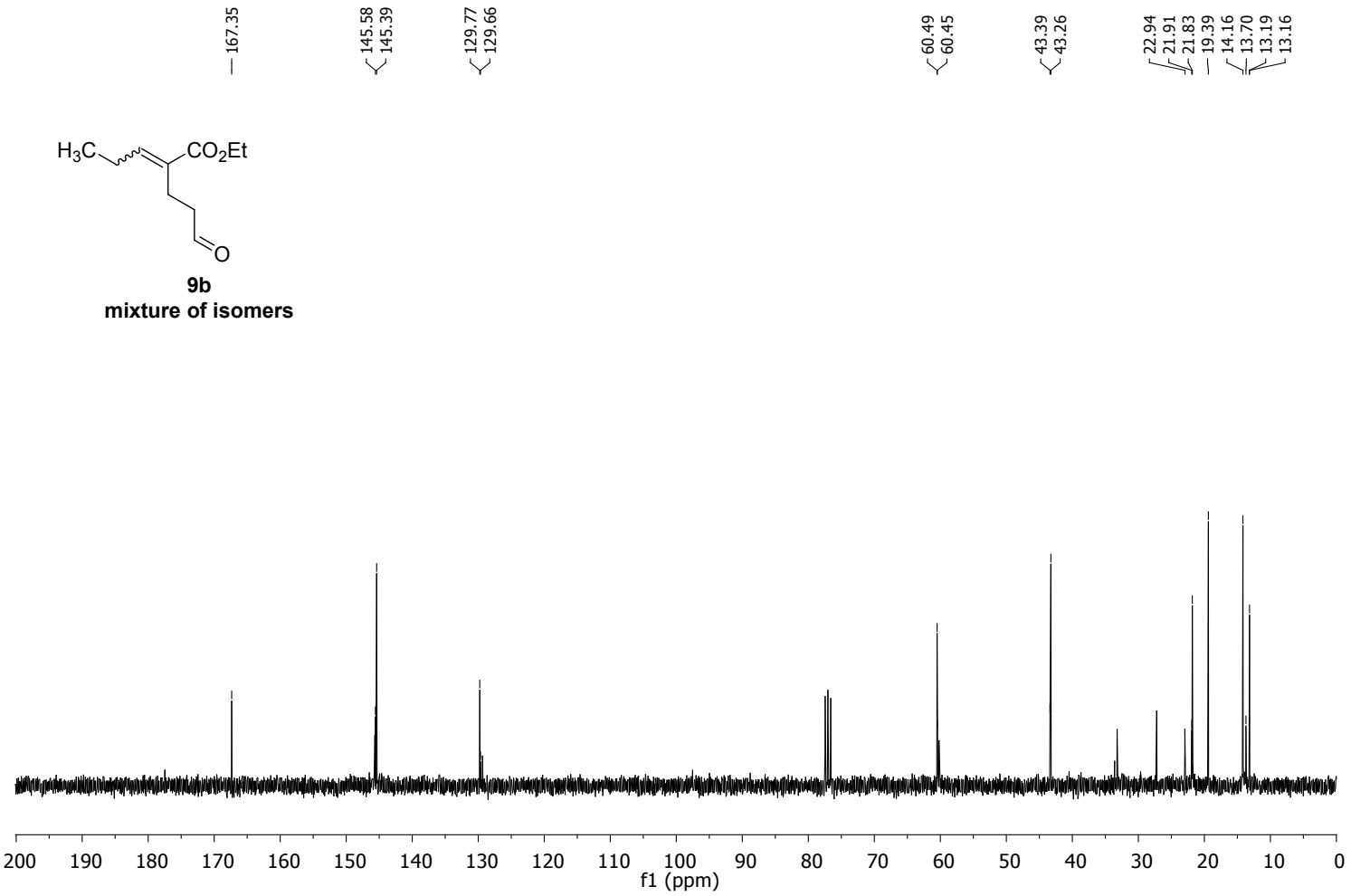
^{13}C NMR Spectra of**(*E*/*Z*)- 9a**



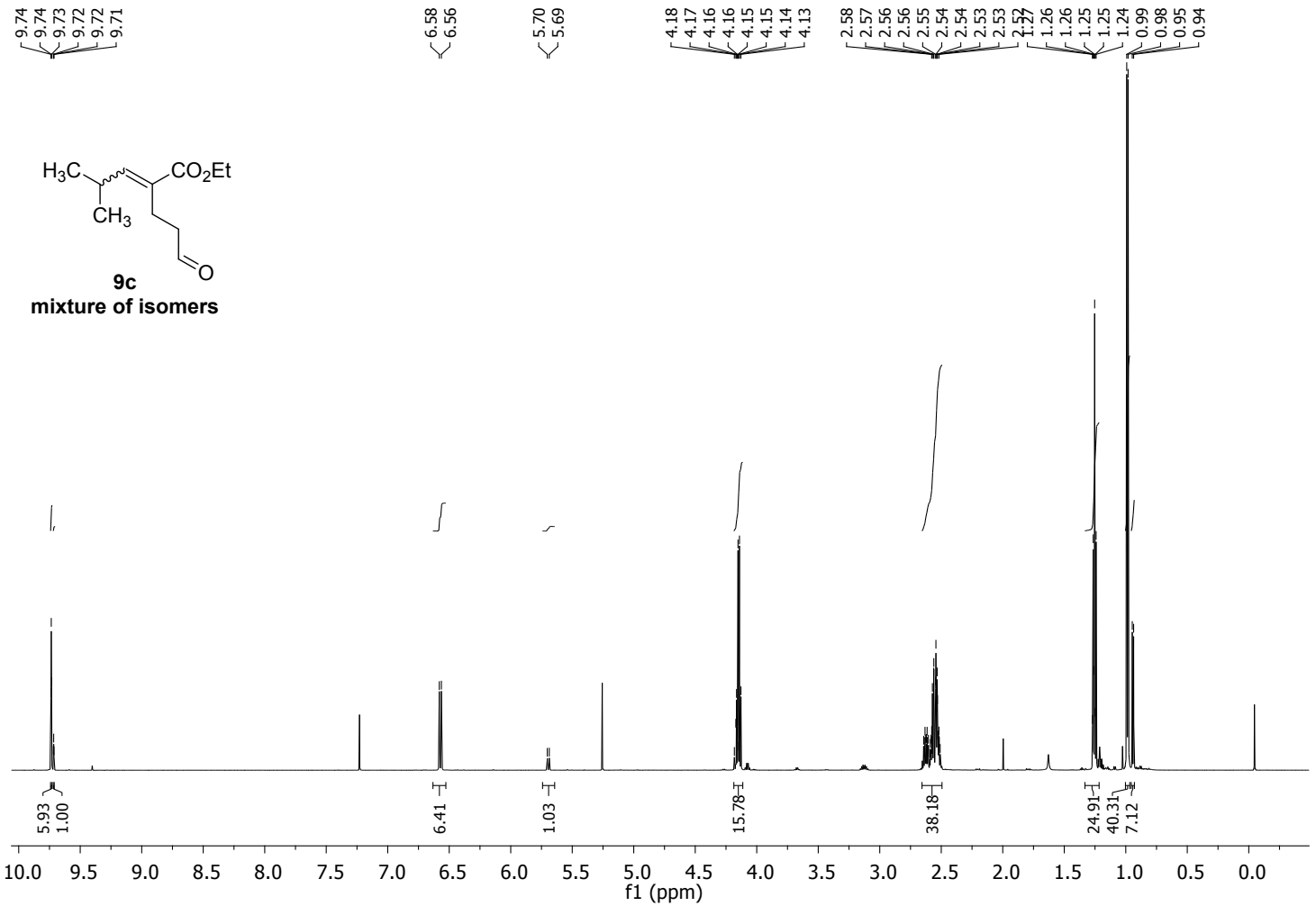
^{1}H NMR Spectra of **(*E*/*Z*)-9b**



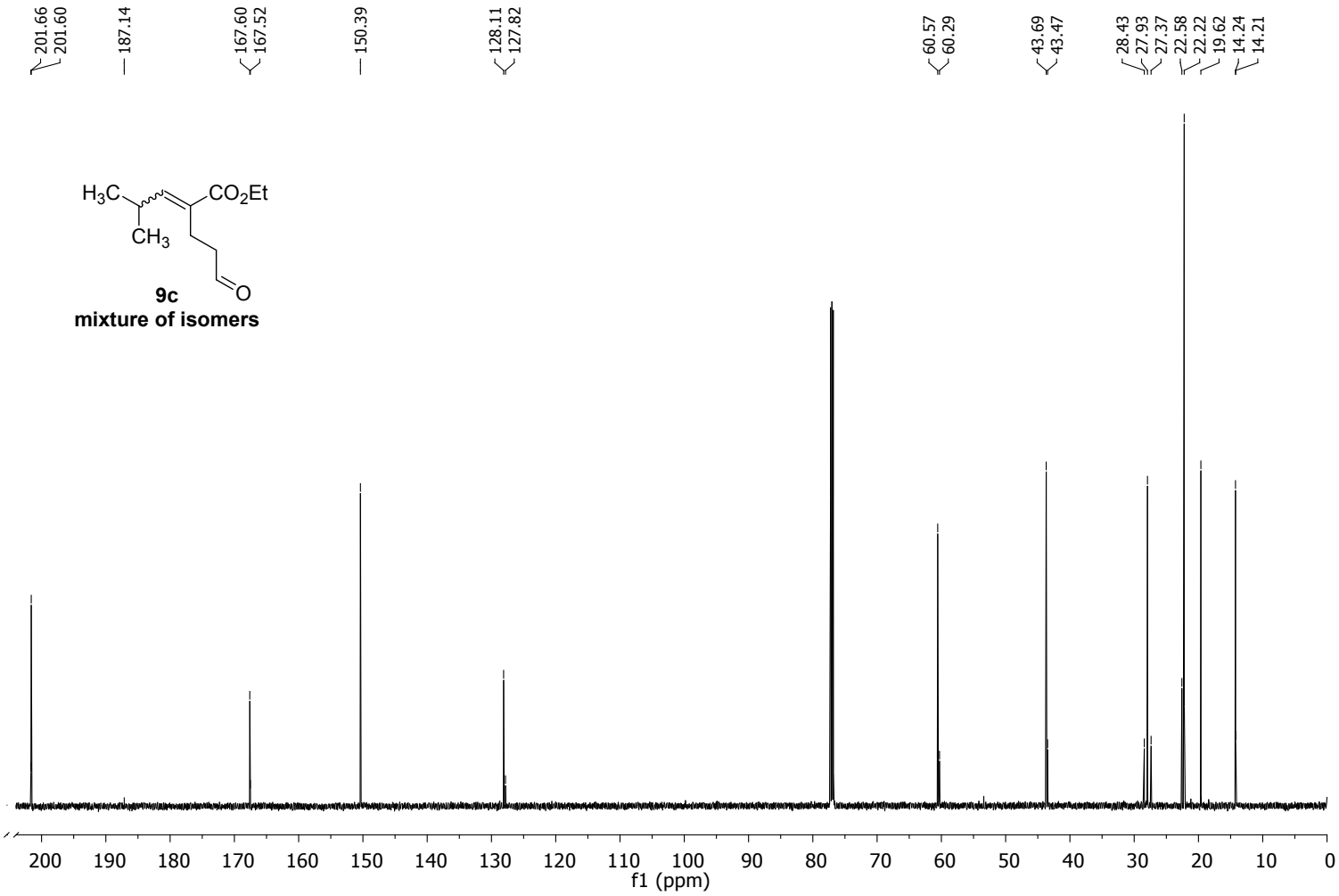
^{13}C NMR Spectra of **(*E*/*Z*)-9b**



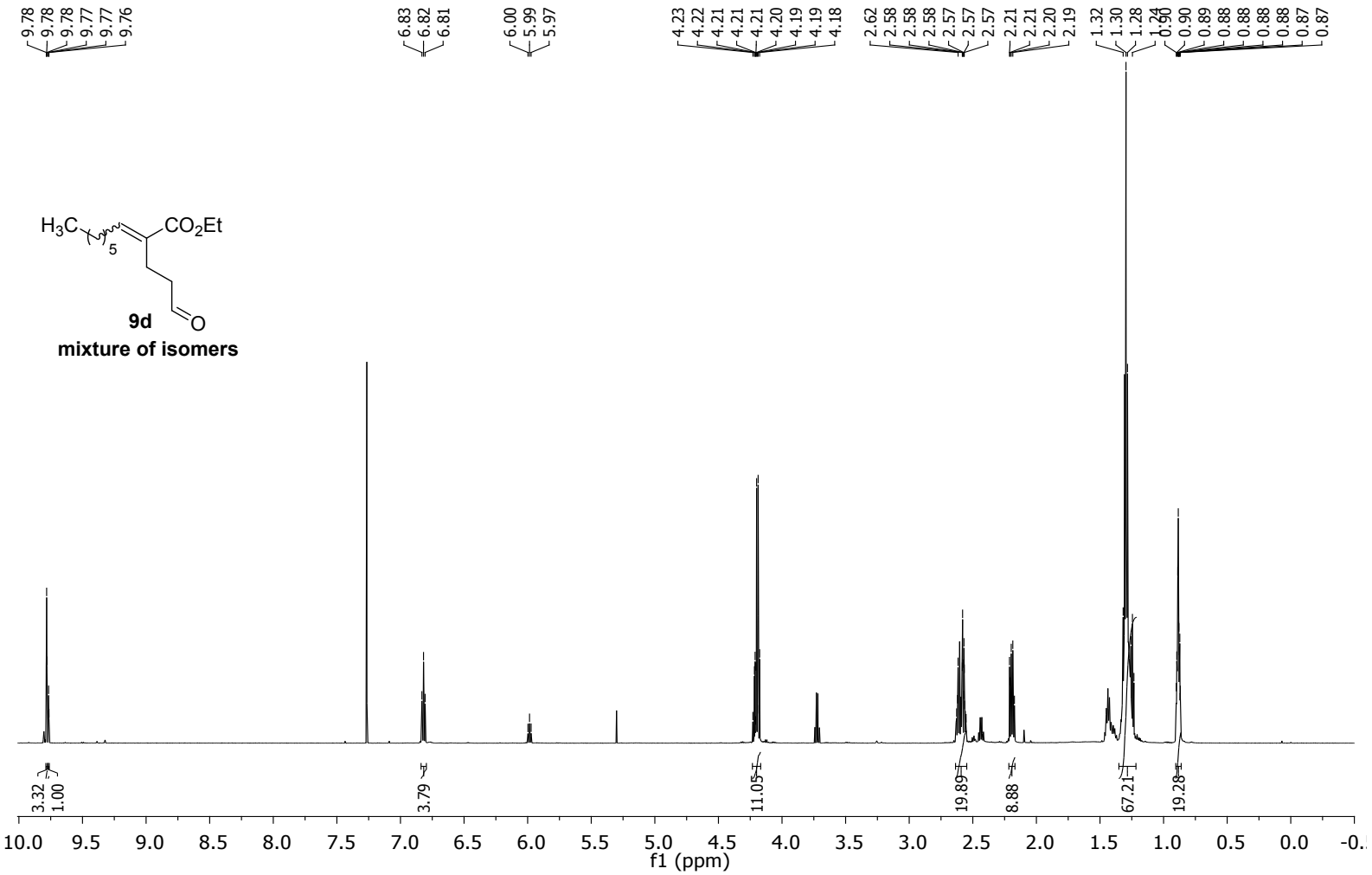
^{1}H NMR Spectra of **(*E*/*Z*)-9c**



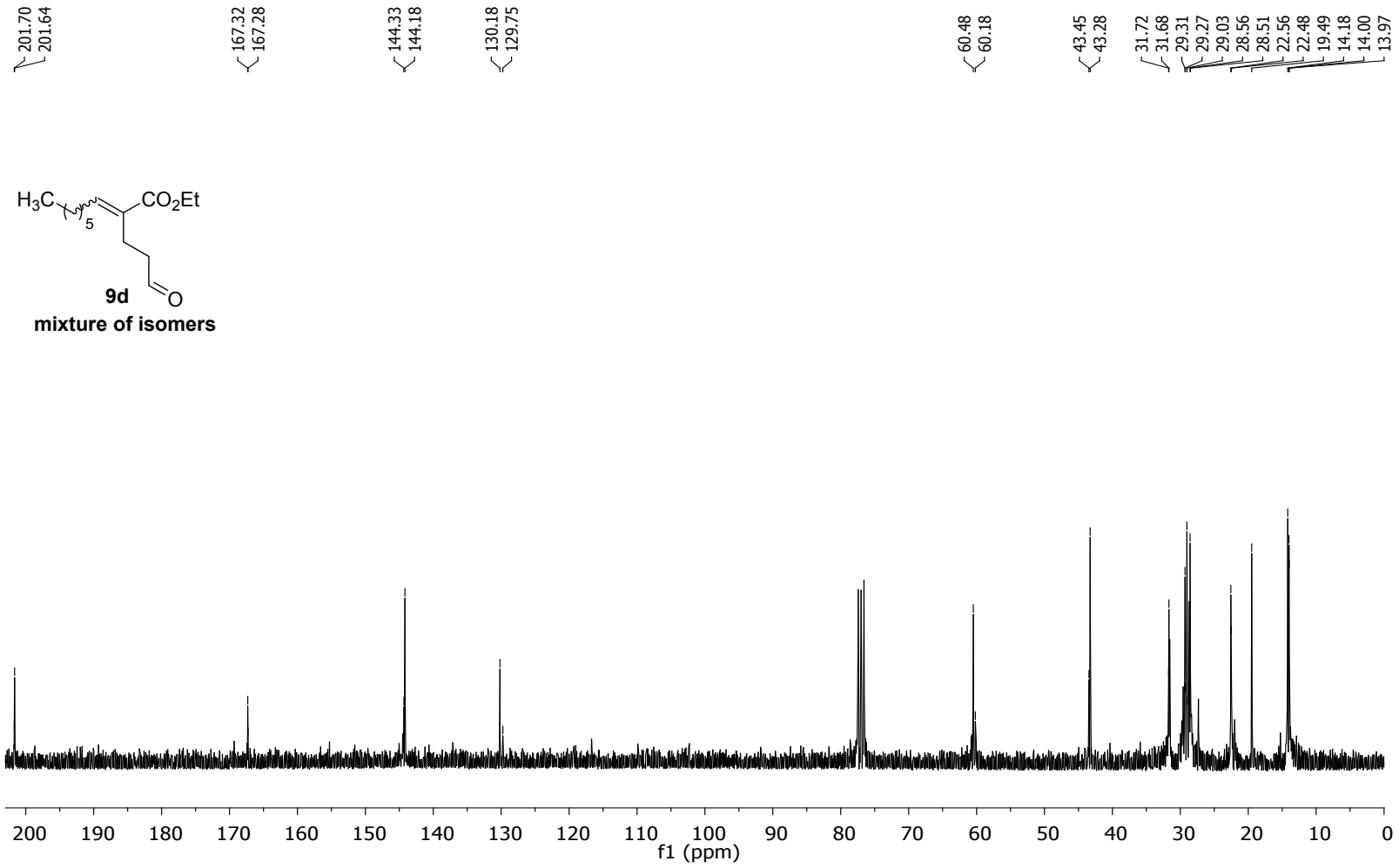
^{13}C NMR Spectra of **(*E*/*Z*)-9c**



^{1}H NMR Spectra of **(*E*/*Z*)-9d**

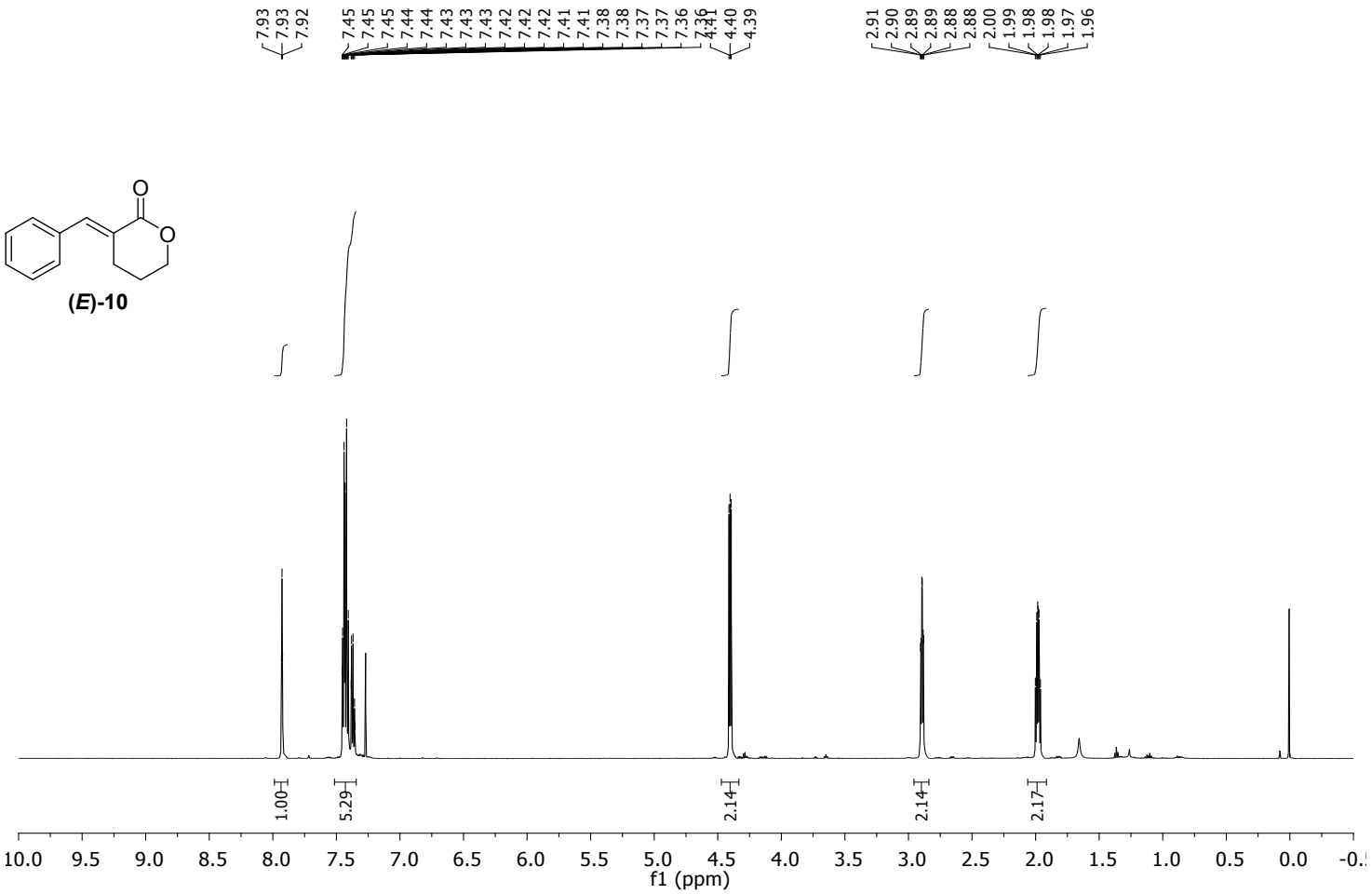


^{13}C NMR Spectra of **(*E*/*Z*)-9d**

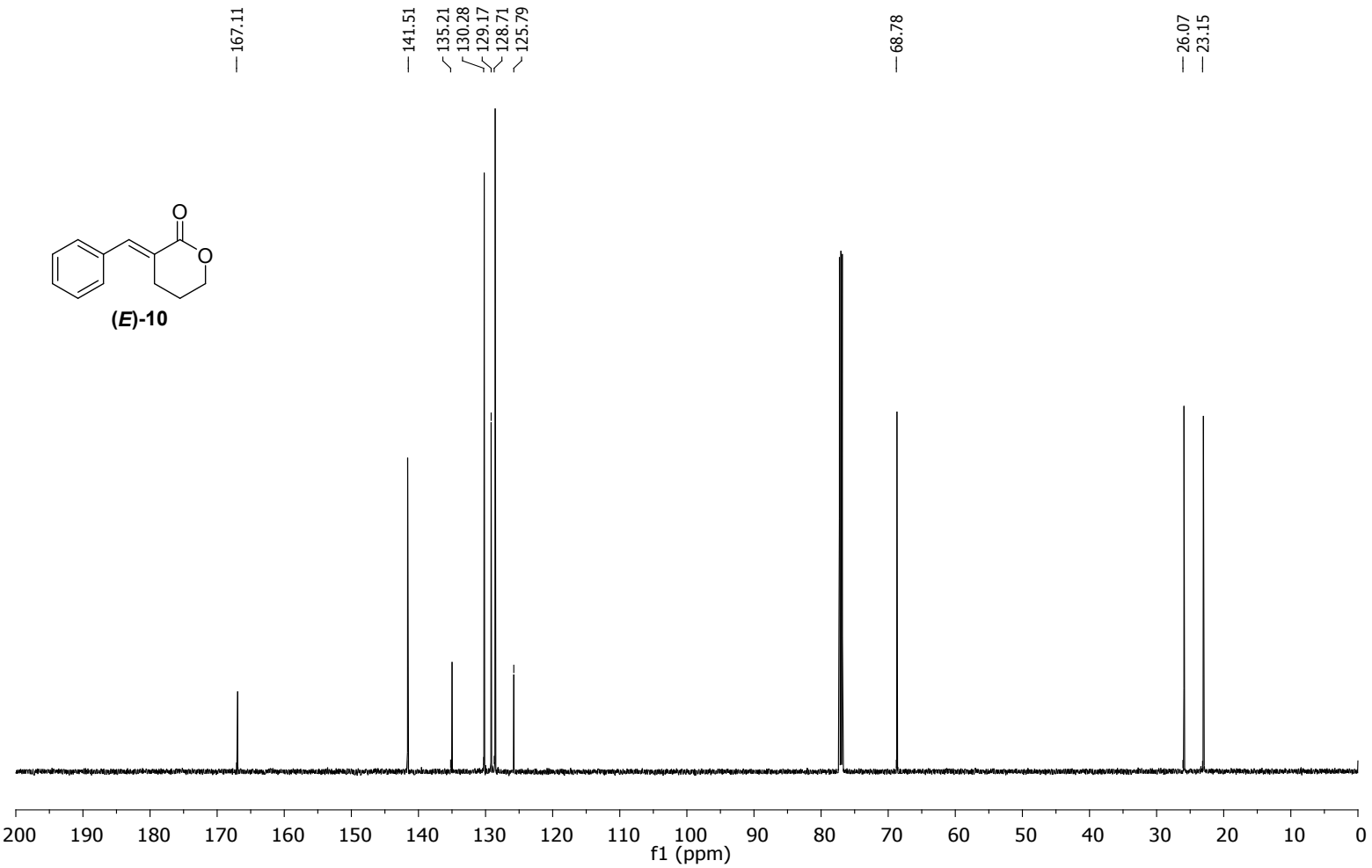


7. Copy of spectra for the 2-alkenyl δ-valerolactones.

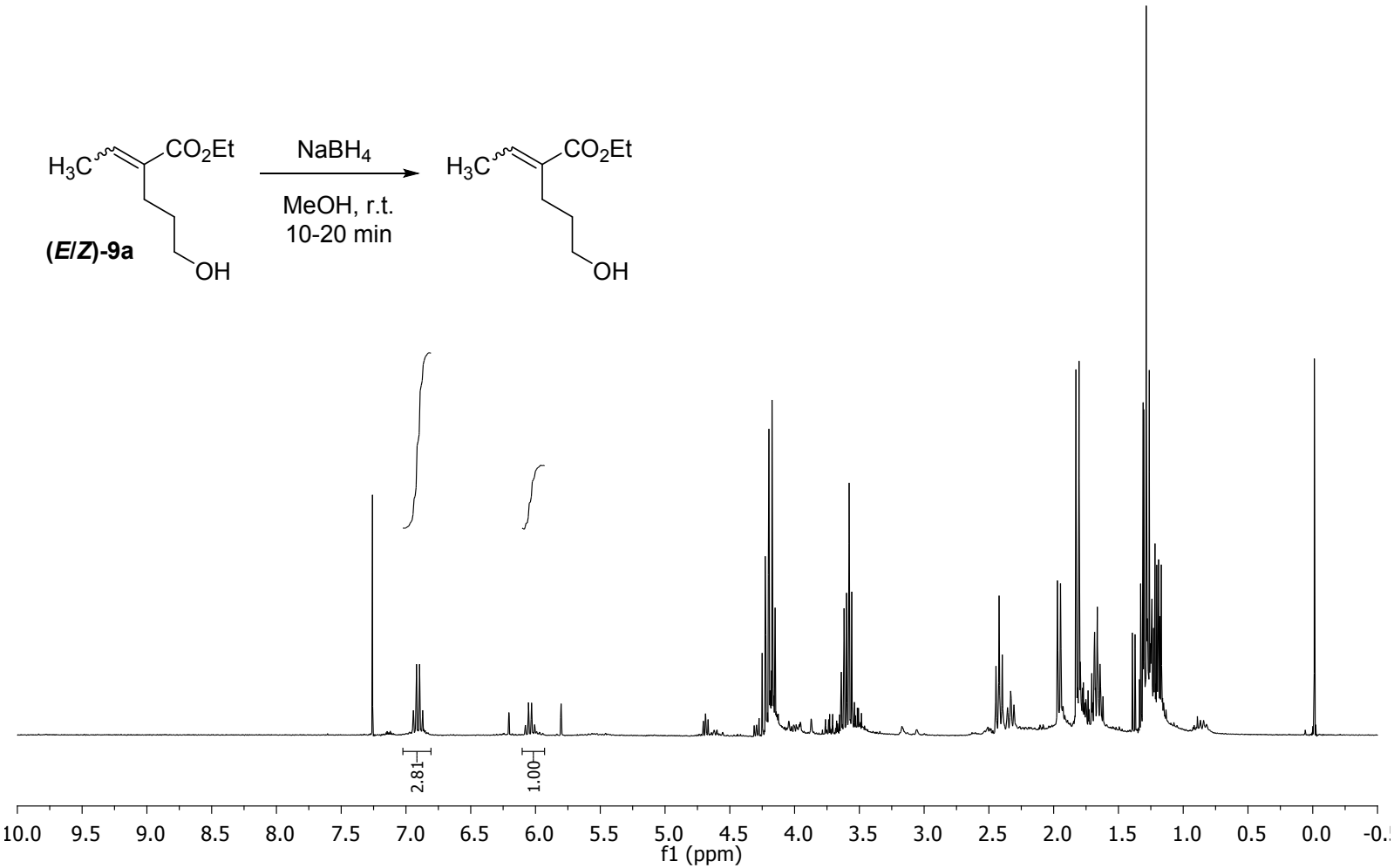
^{1}H NMR Spectra of **(*E*)-10**



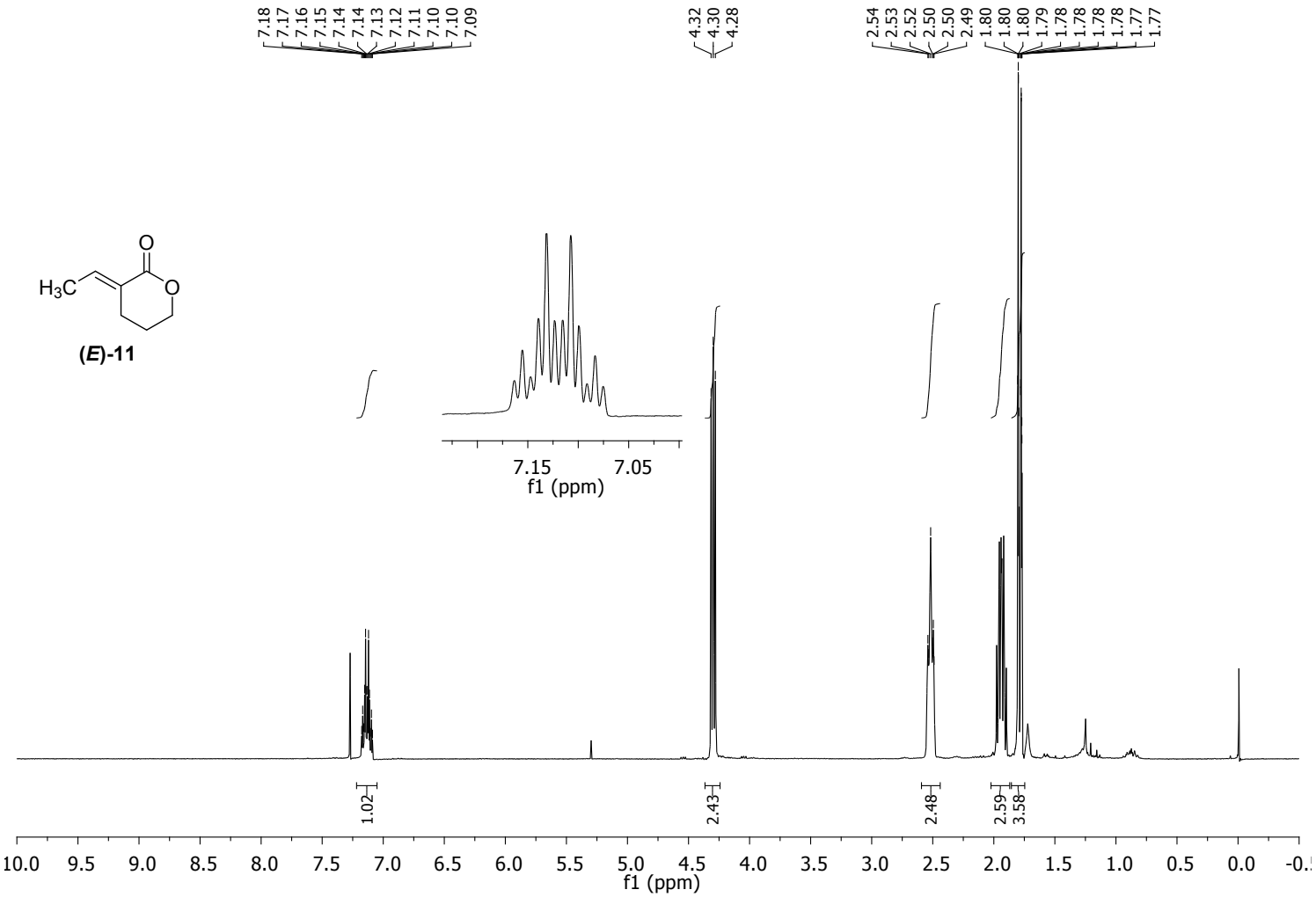
^{13}C NMR Spectra of **(*E*)-10**



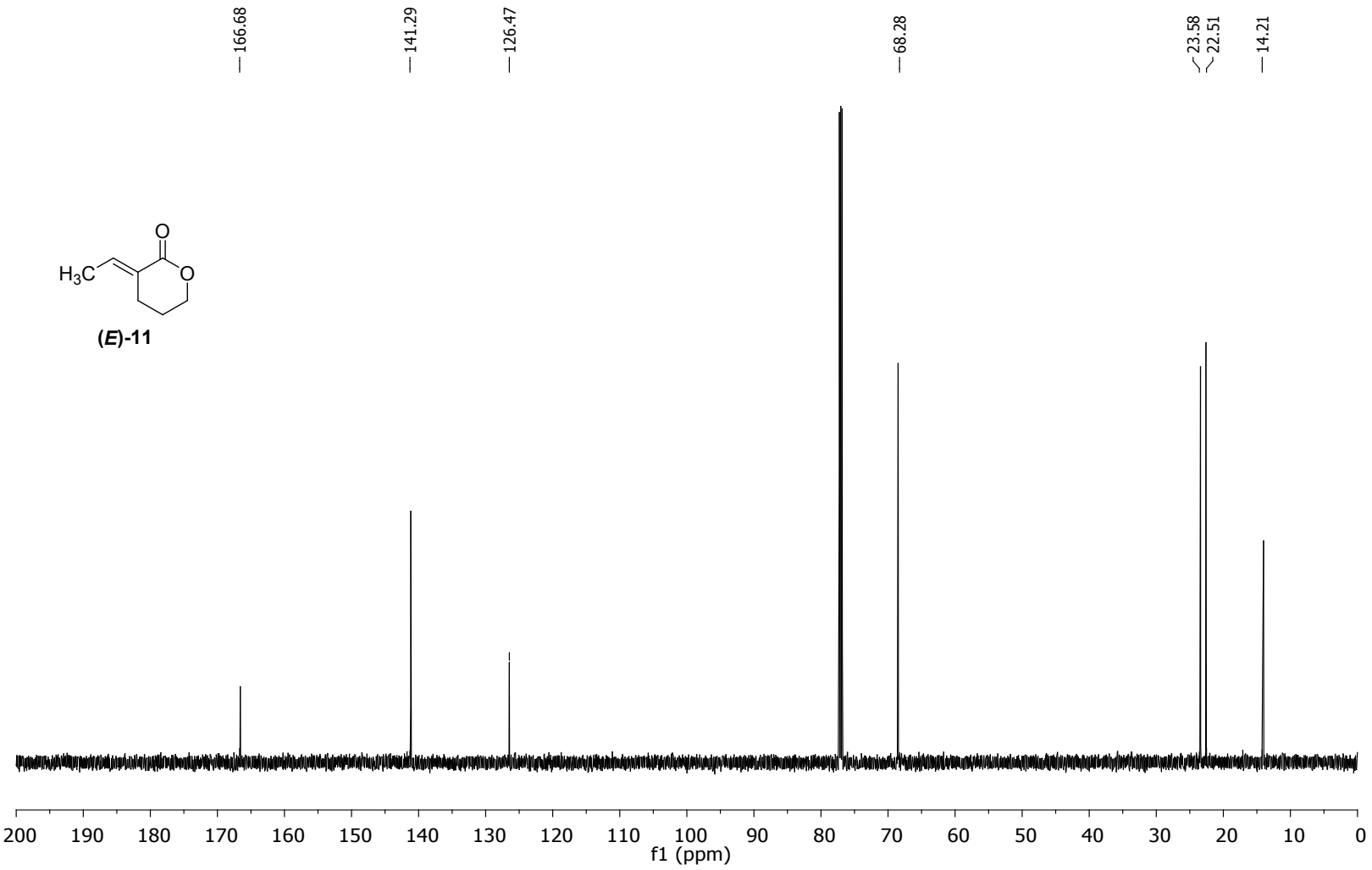
^{1}H NMR spectrum of the crude product for the reduction of **9a**.



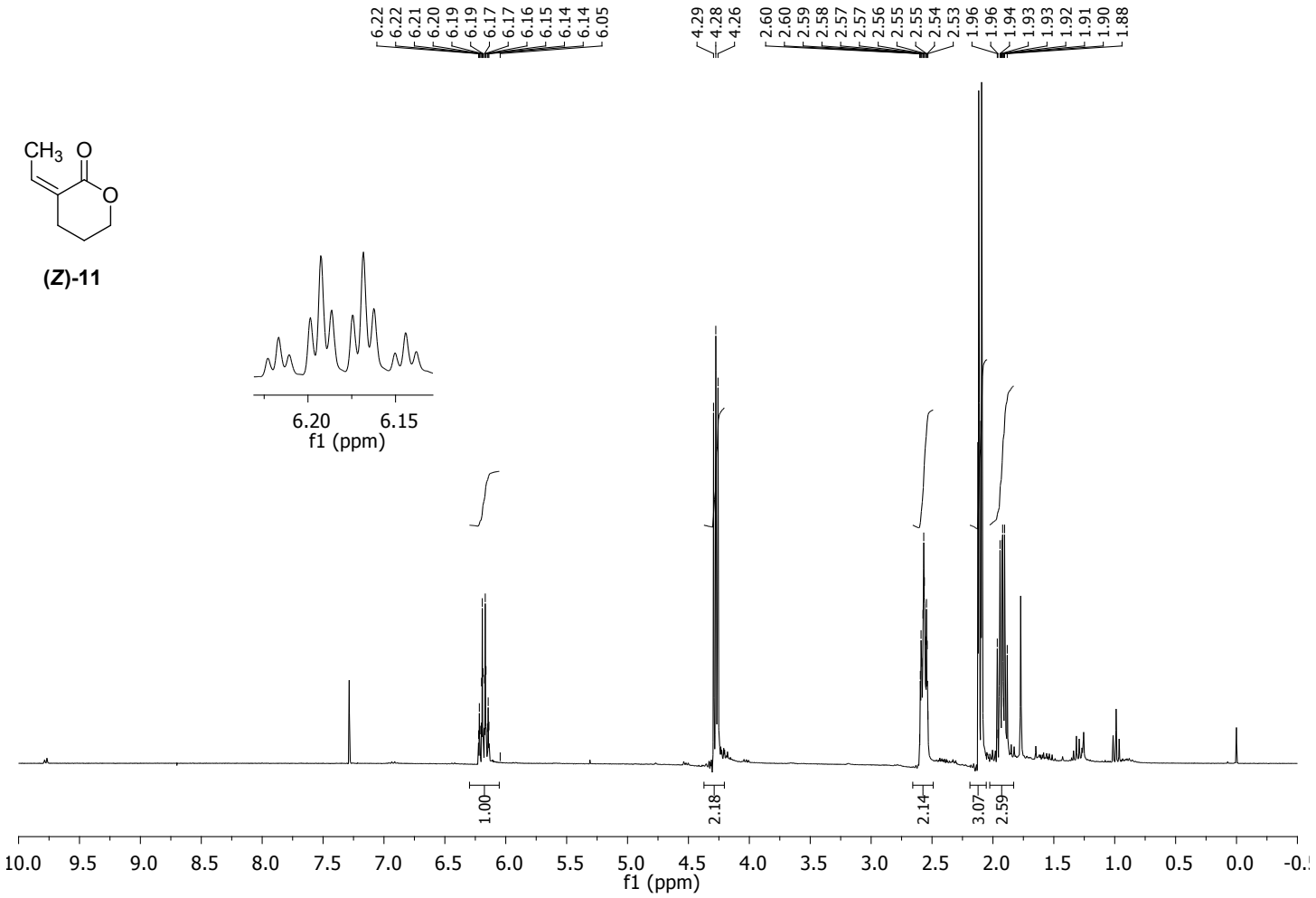
^{1}H NMR Spectra of **(*E*)-11**



^{13}C NMR Spectra of **(*E*)-11**



^{1}H NMR Spectra of **(*Z*)-11**



^{13}C NMR Spectra of **(*Z*)-11**